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Copper Catalyzed Sequential Arylation-Oxidative Dimerization of *o*-Haloanilides: Synthesis of Dimeric HPI Alkaloids

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Supporting Information

Experimental details and Copies of ^{1}H and ^{13}C spectra of new compounds

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Supporting information for

Copper Catalyzed Sequential Arylation-Oxidative Dimerization of *o*-Haloanilides: Synthesis of Dimeric HPI Alkaloids

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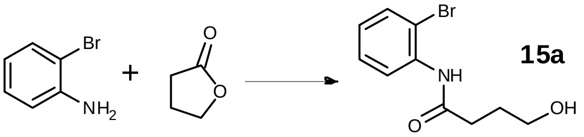
General Experimental: Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance 300 or 400 spectrometer at 300 or 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on Bruker Avance 300 or 400 spectrometer at 75 or 100 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer or Agilent G6230 TOF MS spectrometer. Chiral HPLC analyses were performed on Agilent 1100 series with a tunable UV detector at wavelength $\lambda = 254$ nm. Melting points were determined on a capillary melting point apparatus and are uncorrected. Optical rotations were obtained on a UV-210A spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, J&K and were used without purification, unless otherwise indicated. THF and toluene used in the reactions were dried by distillation over metallic sodium; dichloromethane were distilled over P_2O_5. Unless otherwise stated, all reactions were conducted in dried glassware under a positive pressure of dry nitrogen. Silica gel (Qingdao, 200-300 mesh) was used for column chromatography.



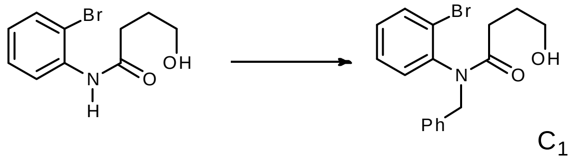
15a

N-(2-bromophenyl)-4-hydroxybutanamide

$C_{10}H_{12}BrNO_2$ Mol. Wt.: 257.01, 258.11

2-Bromoaniline (12.04 g, 70.0 mmol) was dissolved in toluene (200 mL) under nitrogen. To this mixture, a solution of trimethylaluminum in toluene (2.0 M, 49 mL, 98.0 mmol, 1.4 eq.) was added dropwise at 0 ºC. The resulting mixture was then stirred at room temperature for 45 minutes. γ-Butyrolactone (7.5 mL, 98 mmol, 1.4 eq.) was added via syringe and the reaction mixture was stirred at room temperature overnight. The solidified mixture was then cooled to 0 ºC, and HCl (1N, 150 mL) was added slowly. After 30 minutes, the resulting mixture was extracted with ethyl acetate (4 × 80 mL). The combined organic phases were washed with brine (50 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude products were chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) to provide amide **15a** (17.34 g, 96%) as a white solid.

m.p.: 65-67 ºC. R_f: 0.55 (Petroleum ether: ethyl acetate = 1:2). **FTIR** (KBr, thin film) cm^{-1}: 3271, 2943, 2875, 1660, 1527, 1430, 1285, 1051, 755, 673. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 8.27 (1H, *d*, *J* = 7.8 Hz), 7.81 (1H, *brs*), 7.53 (1H, *d*, *J* = 7.8 Hz), 7.30 (1H, *t*, *J* = 7.8 Hz), 6.98 (1H, *t*, *J* = 7.8 Hz), 3.75 (2H, *t*, *J* = 5.7 Hz), 2.59 (3H, *t*, *J* = 6.9 Hz), 2.05-1.91 (2H, *m*). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 171.73, 135.72, 132.41, 128.48, 125.48, 122.42, 113.71, 62.06, 34.80, 28.04. +TOF-MS *m/z* (%) : 282 (M^++1+Na, 100%), 281 (M^++Na, 8%), 280 (M^++Na, 96%), 260 (42), 258 (40), 240 (20), 200 (9), 174 (29), 172 (30). **HRMS** *m/z* Found: 258.0124, Calcd. for $C_{10}H_{13}NO_2Br$ $(M+1)^+$: 258.0129.

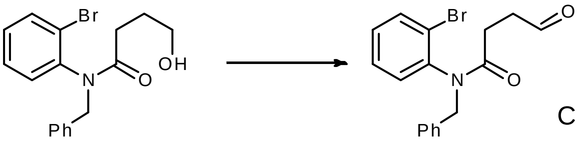


16a *N*-benzyl-*N*-(2-bromophenyl)-4-hydroxybutanamide

$C_{17}H_{18}BrNO_2$ Mol. Wt.: 347.05, 348.23

To a mixture of cesium carbonate (17.43 g, 53.5 mmol, 1.5 eq.) in acetonitrile (90 mL) and *N,N*-dimethylformamide (DMF, 45 mL) at 0 ºC was added dropwise a solution of amide **15a** (9.20 g, 35.7 mmol) in acetonitrile (10 mL) and DMF (5 mL). Benzyl bromide (6.4 mL, 53.5 mmol, 1.5 eq.) was then added. The resulting mixture was allowed to stir at room temperature for 8 h. After filtration through a short column of silica gel and washed with ethyl acetate (180 mL), the combined organic phases were concentrated under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to afford alcohol **16a** (11.86 g , 96%) as a colorless oil.

R_f: 0.60 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3417, 2963, 1651, 1402, 1270, 1203, 1050, 728. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.68 (1H, *dd*, *J* = 2.7, 7.8 Hz), 7.37-7.12 (7H, *m*), 6.77 (1H, *dd*, *J* = 3.3, 7.8 Hz), 5.64 (1H, *d*, *J* = 14.4 Hz), 4.01 (1H, *d*, *J* = 14.4 Hz), 3.71-3.55 (2H, *m*), 2.89-2.68 (1H, *m*), 2.14 (2H, *t*, *J* = 6.6 Hz), 1.98-1.78 (2H, *m*). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ (ppm): 173.43, 140.71, 136.99, 134.07, 131.52, 130.03, 129.46, 128.55, 127.72, 123.86, 62.78, 51.77, 32.06, 27.85. +TOF-MS *m/z* (%) : 372 (M^++1+Na, 99%), 371 (M^++Na, 9%), 370 (M^++Na,100%), 350 (32), 348 (34), 330 (2), 264 (3). **HRMS** *m/z* Found: 370.0410, Calcd. for $C_{17}H_{18}NO_2NaBr$ $(M+23)^+$: 370.0418.

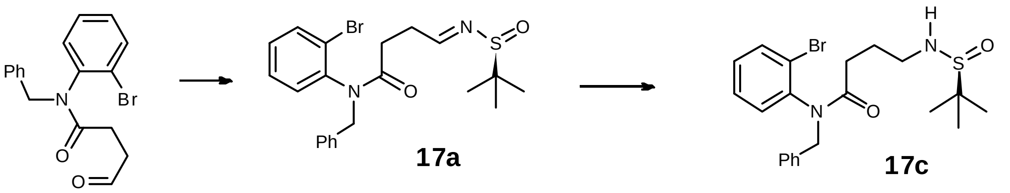


10a *N*-benzyl-*N*-(2-bromophenyl)-4-oxobutanamide

$C_{17}H_{16}BrNO_2$ Mol. Wt.: 345.04, 346.22

Alcohol **16a** (11.86 g, 34.1 mmol) was dissolved in dichloromethane (120 mL). To this solution, a powder of Dess-Martin periodinane (21.67 g, 51.1 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at room temperature for 6 h. After filtration through a short column of silica gel and washed with ethyl acetate (150 mL), the combined organic phases were concentrated under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 3:1) to afford aldehyde **10a** (10.85 g , 92%) as white plates.

m.p.: 52-54 ºC. R_f: 0.53 (Petroleum ether: ethyl acetate = 3:1). **FTIR** (KBr, thin film) cm^{-1}: 3419, 3060, 2921, 2827, 2730, 1657, 1400, 1265, 1196, 1020, 727. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 9.81 (1H, *s*), 7.72-7.62 (1H, *m*), 7.38-7.12 (7H, *m*), 6.92-6.82 (1H, *m*), 5.62 (1H, *d*, J = 14.4 Hz), 4.03 (1H, *d*, J = 14.4 Hz), 2.91 (1H, *ddd*, J = 6.9, 7.8, 18.6 Hz), 2.68 (1H, *dt*, J = 6.3, 18.6 Hz), 2.42-2.16 (2H, *m*). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 200.99, 171.12, 140.45, 136.88, 133.99, 131.60, 130.08, 129.29, 128.62, 128.50, 127.64, 123.87, 51.75, 38.98, 27.18. +TOF-MS *m*/*z* (%) : 370 (M^++1+Na, 98%), 369 (M^++Na, 13%), 368 (M^++Na, 100%), 348 (81), 346 (90), 332 (30), 330 (31), 262 (3). **HRMS** *m*/*z* Found: 368.0266, Calcd. for $C_{17}H_{16}NO_2NaBr$ $(M+Na)^+$: 368.0262.



17a

(*S*,*E*)-*N*-benzyl-*N*-(2-bromophenyl)-4-((*tert*-butylsulfinyl)imino)butanamide

$C_{21}H_{25}BrN_2O_2S$ Mol. Wt.: 448.08, 448.40

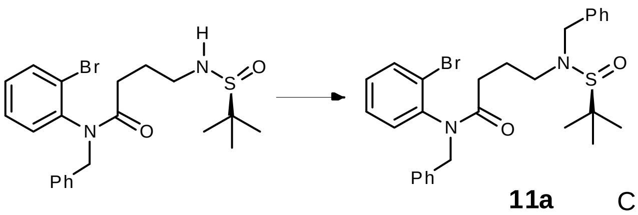
17c

(*S*)-*N*-benzyl-*N*-(2-bromophenyl)-4-(1,1-dimethylethylsulfinamido)butanamide

$C_{21}H_{27}BrN_2O_2S$ Mol. Wt.: 450.10, 451.42

To a solution of aldehyde **10a** (5.85 g, 16.8 mmol) in toluene (60 mL) was added a powder of (*S*)-(–)-*tert*-butanesulfinamide (4.1 g, 33.7 mmol, 2.0 eq.) and $KHSO_4$ (4.56 g, 33.7 mmol, 2.0 eq.). The resulting mixture was stirred at 45 °C for 3 h. After filtration through a short column of silica gel and washed with ethyl acetate (80 mL), the combined organic phases were concentrated under reduced pressure and the residue was flash chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 3:1) to afford the sulfinyl imine (**17a**: 7.36 g , 97%) as colorless syrup. The sulfinyl imine was re-dissolved in anhydrous methanol (60 mL) and the resulting solution was cooled to 0 °C. A powder of sodium borohydride (1.87 g, 49.2 mmol, 3.0 eq.) was added in small portion over a period of 30 minutes. The resulting mixture was then allowed to stir at 0 °C for 4 h. After which, a saturated solution of NH_4Cl (20 mL) was introduced and the resulting mixture was concentrated (ca. 20-30 mL). The mixture was diluted with water (100 mL) and extracted with ethyl acetate (4 × 50 mL). The combined organic phases were washed with brine (60 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude products were chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) to provide sulfinamide **17c** (6.6 g, 89%) as a white solid.

m.p.: 102-103 ºC. $[\alpha]^{20}_{D}$ +71 (c 0.90, $CHCl_3$). R_f: 0.45 (Petroleum ether: ethyl acetate = 1:2). **FTIR** (KBr, thin film) cm^{-1}: 3244, 3063, 2950, 2868, 1662, 1559, 1468, 1398, 1266, 1203, 1063, 947, 767, 732, 628. **^{1}H-NMR** (as a mixture of rotamers, 300 MHz, $CDCl_3$), δ (ppm): 7.71-7.61 (1H, *m*), 7.31-7.12 (7H, *m*), 6.81-6.70 (1H, *m*), 5.58 (1H, *d*, J = 14.1 Hz), 4.00 (0.5H, *d*, J = 14.1 Hz)[3.99 (0.5H, *d*, J = 14.1 Hz)], 3.42-3.23 (1H, *m*), 3.22-3.10 (1H, *m*), 3.10-2.94 (1H, *m*), 2.11-1.97 (2H, *m*), 1.93-1.78 (2H, *m*), 1.13 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 75 MHz, $CDCl_3$), δ (ppm): 172.16, 140.67, 137.02, 134.00 (133.94), 131.57 (131.50), 129.94, 129.41, 128.47, 127.63, 123.85, 55.64, 51.58, 45.07 (44.99), 31.62, 26.15, 22.71. +TOF-MS *m/z* (%) : 475 (M^++1+Na, 60%), 474 (M^++Na, 8%), 473 (M^++Na, 65%), 453 (98), 452 (12), 451 (100), 435 (25), 433 (23), 402 (4), 400 (4), 294 (2), 282 (6), 280 (5), 262 (2). **HRMS** *m/z* Found: 473.0878, Calcd. for $C_{21}H_{27}N_2O_2NaSBr$ $(M+Na)^+$: 473.0874.

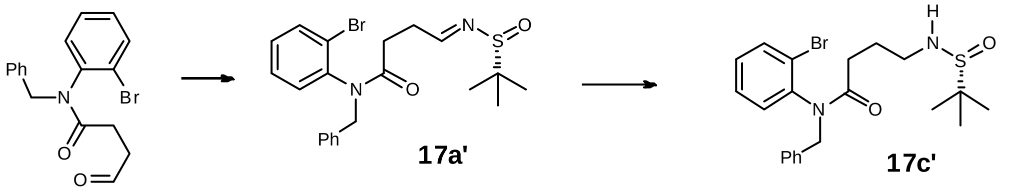


(*S*)-*N*-benzyl-4-(*N*-benzyl-2-methylpropan-2-ylsulfinamido)-*N*-(2-bromophenyl)butanamide

11a $C_{28}H_{33}BrN_2O_2S$ Mol. Wt.: 540.14, 541.54

To a mixture of sodium hydride (60% in mineral oil, 1.32 g, 33 mmol, 1.5 eq., freshly washed with anhydrous hexane 3 times under nitrogen) in anhydrous THF (30 mL) at 0 °C was added a solution of sulfonamide **17c** (9.9 g, 22 mmol) in THF (80 mL) via syringe. After stirring at 0 °C for 30 min, benzyl bromide (3.9 mL, 33 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at 0 °C for 2h, then at room temperature for 12 h under nitrogen. A powder of NH_4Cl (1.62 g, 30.0 mmol) was added and the mixture was stirred for 10 min. After concentrated under reduced pressure, the residue was diluted with water (60 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the product (**11a**: 11.2 g, 94%) as an off-yellow oil.

$[\alpha]^{20}_{D}$ -3.9 (c 0.40, $CHCl_3$). R_f: 0.51 (Petroleum ether: ethyl acetate = 2:1). **FTIR** (KBr, thin film) cm^{-1}: 3421, 2960, 1665, 1467, 1396, 1278, 1204, 1070, 1024, 928, 700. **^{1}H-NMR** (as a mixture of rotamers, 300 MHz, $CDCl_3$), δ (ppm): 7.71-7.61 (1H, *m*), 7.37-7.11 (12H, *m*), 6.77-6.67 (1H, *m*), 5.59 (0.5H, *d*, J = 14.4 Hz)[5.59 (0.5H, *d*, J = 14.1 Hz)], 4.26 (1H, *d*, J = 15.6 Hz), 4.10 (0.5H, *d*, J = 15.6 Hz)[4.08 (0.5H, *d*, J = 15.3 Hz)], 3.98 (0.5H, *d*, J = 14.1 Hz)[3.97 (0.5H, *d*, J = 14.4 Hz)], 3.03-2.85 (1H, *m*), 2.84-2.68 (1H, *m*), 1.97-1.76 (4H, *m*), 1.16 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 75 MHz, $CDCl_3$), δ (ppm): 171.69, 140.56, 137.24, 137.02, 133.92, 131.52, 131.45, 129.88, 129.32, 128.54, 128.44, 127.57, 127.35, 123.85, 58.22, 51.47 (51.07), 48.23 (47.92), 31.79 (31.71), 23.93 (23.81), 23.39. EI-MS *m/z* (%) : 543 (M^++2, 6%), 541 (M^++1, 6%), 486 (10), 486 (34), 484 (30), 430 (25), 395 (26), 330 (16), 263 (31), 261 (30), 212 (17), 174 (16), 147 (11), 91 (48), 90 (100), 85 (4), 76 (12), 57 (29). **HRMS** *m*/*z* Found: 540.1448, Calcd. for $C_{28}H_{33}N_2O_2SBr$ $(M)^+$: 540.1446.



17a'

(*R*,*E*)-*N*-benzyl-*N*-(2-bromophenyl)-4-((*tert*-butylsulfinyl)imino)butanamide

$C_{21}H_{25}BrN_2O_2S$ Mol. Wt.: 448.08, 448.40

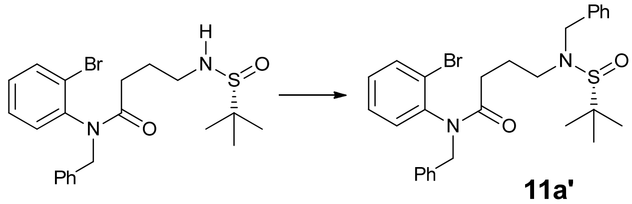
17c'

(*R*)-*N*-benzyl-*N*-(2-bromophenyl)-4-(1,1-dimethylethylsulfinamido)butanamide

$C_{21}H_{27}BrN_2O_2S$ Mol. Wt.: 450.10, 451.42

To a solution of aldehyde **10a** (17.3 g, 50 mmol) in THF (60 mL) was added a powder of (*R*)-(–)-*tert*-butanesulfinamide (12.1 g, 100 mmol, 2.0 eq.) and $Ti(OEt)_4$ (22.8 g, 100 mmol, 2.0 eq.). The resulting mixture was stirred at 60 °C for 12 h. The reaction mixture was then cooled to room temperature and treated with saturated NaCl aqueous solution (100 mL) for 1h. After filtration through a short column of celite and washed with ethyl acetate (80 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was flash chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 3:1) to afford the sulfinyl imine (**17a'**: 20.8 g, 93%) as pale yellow syrup. The sulfinyl imine was re-dissolved in anhydrous methanol (200 mL) and the resulting solution was cooled to 0 °C. A powder of sodium borohydride (5.27 g, 139.2 mmol, 3.0 eq.) was added in small portion over a period of 30 minutes. The resulting mixture was then stirred at 0 °C for 4 h. A saturated solution of NH_4Cl (80 mL) was introduced and the resulting mixture was concentrated (ca. 80-90 mL). The mixture was diluted with water (150 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic phases were washed with brine (100 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude products were chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) to provide sulfinamide **17c'** (19.8 g, 88% over two steps) as a white solid.

17c': m.p.: 102-104 ºC. $[\alpha]^{20}_{D}$ -70 (c 0.95, $CHCl_3$). R_f: 0.45 (Petroleum ether: ethyl acetate = 1:2). **FTIR** (KBr, thin film) cm^{-1}: 3371, 2971, 1654, 1402, 1278, 1046, 881, 731. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.72-7.64 (1H, *m*), 7.30-7.14 (7H, *m*), 6.81-6.74 (1H, *m*), 5.62 (0.5H, *d*, *J* = 14.4 Hz)[5.61 (0.5H, *d*, *J* = 14.4 Hz)], 4.03 (0.5H, *d*, *J* = 14.4 Hz)[4.03 (0.5H, *d*, *J* = 14.4 Hz)], 3.42 (0.5H, *t*, *J* = 6.0 Hz) [3.34 (0.5H, *t*, *J* = 6.0 Hz)], 3.24-3.14 (1H, *m*), 3.12-2.98 (1H, *m*), 2.13-1.97 (2H, *m*), 1.94-1.84 (2H, *m*), 1.16 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 172.19 (172.10), 140.67, 137.03 (136.99), 134.02 (133.96), 131.58 (131.51), 129.97, 129.42, 128.56 (128.49), 127.65, 123.92 (123.85), 55.66, 51.60, 45.09 (45.01), 31.63 (31.57), 26.19 (26.16), 22.73. +TOF-MS *m*/*z* (%) : 475 (M^++1+Na, 60%), 474 (M^++Na, 8%), 473 (M^++Na, 65%), 453 (98), 452 (12), 451 (100), 435 (25), 433 (23), 402 (4), 400 (4), 294 (2), 282 (6), 280 (5), 262 (2). **HRMS** *m*/*z* Found: 473.0878, Calcd. for $C_{21}H_{27}N_2O_2NaSBr$ $(M+Na)^+$: 473.0874.



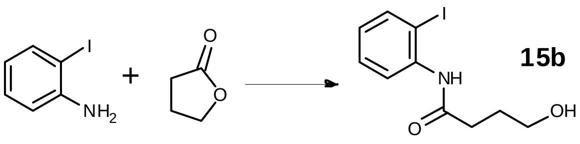
11a'

(*R*)-*N*-benzyl-4-(*N*-benzyl-2-methylpropan-2-ylsulfinamido)-*N*-(2-bromophenyl)butanamide

$C_{28}H_{33}BrN_2O_2S$ Mol. Wt.: 540.14, 541.54

To a mixture of sodium hydride (60% in mineral oil, 2.64 g, 66 mmol, 1.5 eq., freshly washed with anhydrous hexane 3 times under nitrogen) in anhydrous THF (50 mL) at 0 °C was added a solution of sulfonamide **17c'** (19.8 g, 44 mmol) in THF (150 mL) via syringe. After stirring at 0 °C for 30 min, benzyl bromide (7.8 mL, 66 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at 0 °C for 2h, then at room temperature for 12 h under nitrogen. A powder of NH_4Cl (3.24 g, 60.0 mmol) was added and the mixture was stirred for 10 min. After concentrated under reduced pressure, the residue was diluted with water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the product (**11a'**: 23.1 g, 97%) as an off-yellow oil.

11a': $[\alpha]^{20}_{D}$ +4.1 (c 0.51, $CHCl_3$). R_f: 0.51 (Petroleum ether: ethyl acetate = 2:1). **FTIR** (KBr, thin film) cm^{-1}: 3431, 2968, 1660, 1471, 1400, 1054. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.68-7.62 (1H, *m*), 7.32-7.11 (12H, *m*), 6.74-6.67 (1H, *m*), 5.60 (0.5H, *d*, *J* = 14.4 Hz)[5.58 (0.5H, *d*, *J* = 14.4 Hz)], 4.27 (0.5H, *d*, *J* = 15.6 Hz)[4.26 (0.5H, *d*, *J* = 15.6 Hz)], 4.10 (0.5H, *d*, *J* = 15.6 Hz)[4.08 (0.5H, *d*, *J* = 15.6 Hz)], 3.98 (0.5H, *d*, *J* = 14.4 Hz)[3.97 (0.5H, *d*, *J* = 14.4 Hz)], 3.01-2.88 (1H, *m*), 2.83-2.72 (1H, *m*), 1.97-1.77 (4H, *m*), 1.16 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 171.76, 140.60, 137.27, 137.05, 133.95, 131.56, 131.49, 129.92, 129.39, 129.36, 128.58, 128.47, 127.61, 127.40, 123.86, 58.28, 51.51 (51.14), 48.26 (47.97), 31.84 (31.75), 23.97 (23.85), 23.44 (23.41). EI-MS *m/z* (%) : 543 (M^++2, 9%), 541 (M^+, 9%), 486 (7%), 484 (6), 395 (3), 393 (3), 263 (5), 261 (5), 174 (6), 106 (7), 91 (100), 57 (52). **HRMS** *m/z* Found: 540.1461, Calcd. for $C_{28}H_{33}N_2O_2SBr$ $(M)^+$: 540.1456; Found: 541.1513, Calcd. for $C_{28}H_{34}N_2O_2SBr$ $(M+H)^+$: 541.1524.



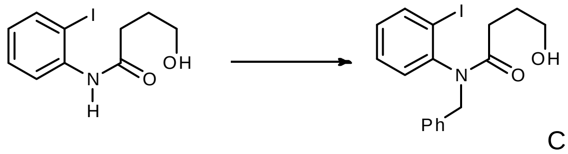
15b

4-hydroxy-*N*-(2-iodophenyl)butanamide

$C_{10}H_{12}INO_2$ Mol. Wt.: 304.99, 305.11

2-Iodoaniline (21.9 g, 100.0 mmol) was dissolved in toluene (300 mL) under nitrogen. To this mixture, a solution of trimethylaluminum in toluene (2.0 M, 60 mL, 120 mmol, 1.2 eq.) was added dropwise at 0 ºC. The resulting mixture was then stirred at room temperature for 45 minutes, after which, γ-butyrolactone (9.2 mL, 120 mmol, 1.2 eq.) was added via syringe and the reaction mixture was stirred at room temperature overnight. The solidified mixture was then cooled to 0 ºC and HCl (1N, 360 mL) was added slowly. After 1 hour, the resulting mixture was extracted with ethyl acetate (4 ×150 mL). The combined organic phases were washed with brine (100 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude products were chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) to provide amide **15b** (29.30 g, 96%) as a white solid.

m.p.: 65-66 ºC. *R*f: 0.59 (Petroleum ether: ethyl acetate = 1:2). **FTIR** (KBr, thin film) cm^{-1}: 3268, 2935, 1658, 1528, 1430, 1287, 1059, 749, 664. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 8.02 (1H, *d*, *J* = 8.0 Hz), 7.76 (1H, *s*), 7.75 (1H, *d*, *J* = 8.0 Hz), 7.30 (1H, *t*, *J* = 7.6 Hz), 6.83 (1H, *t*, *J* = 7.6 Hz), 3.72 (2H, *t*, *J* = 6.0 Hz), 3.32 (1H, *brs*), 2.56 (3H, *t*, *J* = 6.9 Hz), 2.05-1.91 (2H, *m*). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 171.92, 138.90, 138.16, 129.16, 126.43, 123.11, 91.14, 61.76, 34.52, 28.06. EI-MS *m/z* (%) : 304 (M$^+$, 28%), 268 (89%), 224 (12%), 182 (30), 180 (40), 152 (10), 128 (6), 104 (12), 91 (100). **HRMS** *m/z* Found: 304.9969, Calcd. for $C_{10}H_{12}NO_2I$ (M)$^+$: 304.9913.

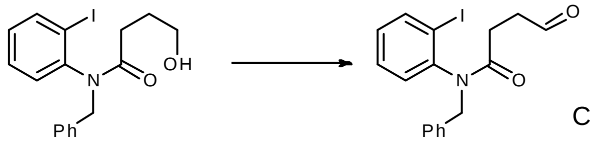


16b *N*-benzyl-4-hydroxy-*N*-(2-iodophenyl)butanamide

$C_{17}H_{18}INO_2$ Mol. Wt.: 395.04, 395.23

To a mixture of amide **15b** (29.3 g, 96 mmol), cesium carbonate (46.9 g, 144 mmol, 1.5 eq.) in acetonitrile (200 mL) and *N,N*-dimethylformamide (DMF, 100 mL) at 0 ºC was added dropwise a solution of benzyl bromide (17.1 mL, 144 mmol, 1.5 eq.) was then added. The resulting mixture was then stirred at room temperature for 12 h. After filtration through a short column of silica gel and washed with ethyl acetate (200 mL), the combined organic phases were concentrated under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to afford alcohol **16b** (36.03 g , 95%) as a white powder.

m.p.: 72-74 ºC. *R*f: 0.55 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3500, 2940, 2871, 1631, 1405, 1322, 1051, 1008, 731, 616, 491. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.93 (1H, *dd*, *J* = 1.2, 8.0 Hz), 7.28-7.15 (6H, *m*), 7.03 (1H, *ddd*, *J* = 1.2, 7.8, 8.0 Hz), 6.71 (1H, *dd*, *J* = 1.2, 7.8 Hz), 5.67 (1H, *d*, *J* = 14.4 Hz), 3.91 (1H, *d*, *J* = 14.4 Hz), 3.70-3.53 (2H, *m*), 3.12-3.04 (1H, *m*), 2.10 (2H, *t*, *J* = 6.6 Hz), 1.92-1.78 (2H, *m*). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 173.18, 143.80, 140.31, 136.83, 130.83, 130.00, 129.43, 129.35, 128.47, 127.65, 100.36, 62.51, 51.81, 32.23, 27.79. EI-MS *m/z* (%) : 395 (M$^+$, 10%), 351 (3%), 309 (20%), 224 (4), 203 (5), 182 (15), 180 (30), 152 (6), 134 (9), 119 (17), 104 (7), 91 (100), 77 (14). **HRMS** *m/z* Found: 395.0378, Calcd. for $C_{17}H_{18}NO_2I$ (M)$^+$: 395.0382.

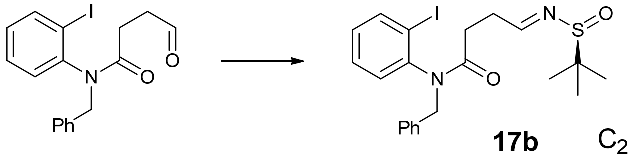


10b *N*-benzyl-*N*-(2-iodophenyl)-4-oxobutanamide

$C_{17}H_{16}INO_2$ Mol. Wt.: 393.02, 393.22

Alcohol **16b** (36.0 g, 91.1 mmol) was dissolved in dichloromethane (300 mL). To this solution, a powder of Dess-Martin periodinane (46.4 g, 109.3 mmol, 1.2 eq.) was added. The resulting mixture was then stirred at room temperature for 3 h. After filtration through a short column of silica gel and washed with ethyl acetate (150 mL), the combined organic phases were concentrated and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 3:1) to afford aldehyde **10b** (32.94 g , 92%) as pale yellow plates.

m.p.: 76-78 ºC. R_f: 0.53 (Petroleum ether: ethyl acetate = 3:1). **FTIR** (KBr, thin film) cm^{-1}: 3433, 3056, 2826, 1713, 1651, 1400, 1268, 1017, 771, 724. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 9.77 (1H, *s*), 7.93 (1H, *dd*, *J* = 1.2, 8.0 Hz), 7.29-7.13 (6H, *m*), 7.01 (1H, *ddd*, *J* = 1.2, 7.8, 8.0 Hz), 6.83 (1H, *dd*, *J* = 1.2, 7.8 Hz), 5.65 (1H, *d*, *J* = 14.4 Hz), 3.92 (1H, *d*, *J* = 14.4 Hz), 2.86 (1H, *ddd*, *J* = 6.0, 7.6, 18.7 Hz), 2.65 (1H, *dt*, *J* = 6.0, 18.7 Hz), 2.32 (1H, *ddd*, *J* = 6.0, 7.6, 17.1 Hz), 2.18 (1H, *dt*, *J* = 6.0, 17.1 Hz). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 200.64, 170.60, 143.34, 139.98, 136.49, 130.65, 129.86, 129.21, 128.99, 128.18, 127.33, 100.11, 51.54, 38.57, 27.26. EI-MS *m*/*z* (%) : 393 (M^+, 12%), 369 (3%), 351 (3%), 309 (28), 282 (5), 268 (70), 230 (4), 224 (4), 203 (9), 182 (23), 180 (63), 152 (12), 104 (7), 91 (100), 77 (13). **HRMS** *m*/*z* Found: 393.0265, Calcd. for $C_{17}H_{16}NO_2I$ $(M)^+$: 393.0226.

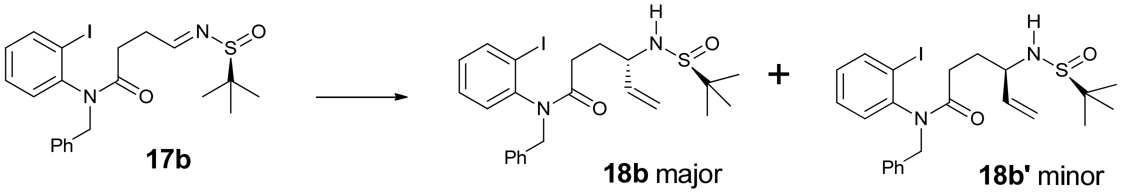


(*S*,*E*)-*N*-benzyl-4-((*tert*-butylsulfinyl)imino)-*N*-(2-iodophenyl)butanamide

17b $C_{21}H_{25}IN_2O_2S$ Mol. Wt.: 496.07, 496.40

To a solution of aldehyde **10b** (19.7 g, 50 mmol) in THF (200 mL) was added a powder of (*S*)-(–)-*tert*-butanesulfinamide (12.1 g, 100 mmol, 2.0 eq.) and $Ti(OEt)_4$ (22.8 g, 100 mmol, 2.0 eq.). The resulting mixture was stirred at 60 °C under nitrogen for 12 h. The reaction mixture was then cooled to room temperature and treated with saturated NaCl aqueous solution (100 mL) for 1h. After filtration through a short column of celite and washed with ethyl acetate (80 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was flash chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 3:1) to afford the sulfinyl imine (**17b**: 22.85 g, 92%) as a pale yellow syrup.

$[\alpha]^{20}_{D}$ +52 (c 0.19, $CHCl_3$). R_f: 0.51 (Petroleum ether: ethyl acetate = 3:1). **FTIR** (KBr, thin film) cm^{-1}: 3445, 2964, 1663, 1466, 1400, 1079. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 8.09 (1H, *brs*), 7.93 (1H, *d*, *J* = 8.0 Hz), 7.28-7.14 (6H, *m*), 7.08-7.01 (1H, *m*), 6.75 (0.5H, *d*, *J* = 7.6 Hz)[6.74 (0.5H, *d*, *J* = 7.6 Hz)], 5.67 (0.5H, *d*, *J* = 14.4 Hz)[5.59 (0.5H, *d*, *J* = 14.0 Hz)], 3.97 (0.5H, *d*, *J* = 14.0 Hz)[3.92 (0.5H, *d*, *J* = 14.4 Hz)], 3.00-2.87 (1H, *m*), 2.81-2.68 (1H, *m*), 2.46-2.18 (2H, *m*), 1.14 (4.5H, *s*)[1.12 (4.5H, *s*)]. **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 170.51 (170.39), 168.11 (168.06), 143.54, 140.20 (140.13), 136.69 (136.60), 130.76 (130.65), 129.89, 129.45 (129.24), 129.13, 128.24, 127.45 (127.42), 100.24, 56.57 (56.53), 51.71 (51.55), 31.13 (30.99), 29.88 (29.83), 22.25 (22.22). EI-MS *m*/*z* (%) : 496 (M^+, 10%), 395 (3), 378 (16), 309 (10), 298 (15), 268 (20), 253 (4), 224 (2), 201 (7), 182 (11), 180 (20), 152 (5), 133 (21), 119 (46), 103 (6), 91 (100), 77 (14). **HRMS** *m*/*z* Found: 496.0663, Calcd. for $C_{21}H_{25}N_2O_2SI$ $(M)^+$: 496.0682.



17b

18b major
(*S*)-*N*-benzyl-4-((*S*)-1,1-dimethylethylsulfinamido)-*N*-(2-iodophenyl)hex-5-enamide

18b' minor
(*R*)-*N*-benzyl-4-((*S*)-1,1-dimethylethylsulfinamido)-*N*-(2-iodophenyl)hex-5-enamide

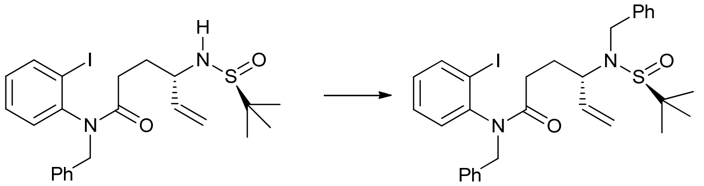
$C_{23}H_{29}IN_2O_2S$ Mol. Wt.: 524.10, 524.46

A solution of imine **17b** (19.8 g, 40 mmol) in dichloromethane (200 mL) was stirred at −78 °C for 10 minutes. To this mixture was added slowly a solution of vinyl magnesium bromide in THF (1.0 M, 60 mL, 60 mmol, 1.5 eq.). The reaction mixture was then stirred at −78 °C for 5 h before warming up to room temperature. Saturated NH_4Cl aqueous solution (80 mL) was introduced and the resulting mixture was stirred at room temperature for 1h. The mixture was diluted with water (150 mL) and extracted with dichloromethane (3 x 100 mL) and the combined organic phases were dried over anhydrous Na_2SO_4. After filtration and concentrated, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the major amide (**18b**: 16.35 g, 78%) as a yellow syrup. Further elution with solvents (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) provided the minor sulfinamide **18b'** (1.64 g, 7.8%) as a pale yellow oil.

Major: 18b: $[\alpha]^{20}_{D}$ +20 (c 0.50, $CHCl_3$). R_f: 0.56 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3223, 2963, 1640, 1462, 1397, 1269, 1199, 1061. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.92 (1H, *d*, *J* = 8.0 Hz), 7.30-7.13 (6H, *m*), 7.03 (1H, *t*, *J* = 7.6 Hz), 6.68 (1H, *d*, *J* = 8.0 Hz), 5.78 (1H, *ddd*, *J* = 6.4, 10.8, 17.2 Hz), 5.65 (1H, *d*, *J* = 14.4 Hz), 5.18 (1H, *dd*, *J* = 10.8, 17.2 Hz), 5.09 (1H, *d*, *J* = 10.4 Hz), 3.91 (1H, *d*, *J* = 14.4 Hz), 3.73-3.63 (1H, *m*), 3.37 (1H, *t*, *J* = 8.4 Hz), 2.12-1.88 (4H, *m*), 1.11 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 171.89, 143.84, 140.27, 139.42, 136.90, 130.84 (130.81), 129.92, 129.45 (129.43), 129.29, 128.42, 127.60, 116.67 (116.56), 100.44, 58.62 (58.39), 55.97, 51.69, 31.07 (30.93), 30.68 (30.46), 22.65. EI-MS *m*/*z* (%) :

524 (M^+, 36%), 467 (100), 419 (6), 404 (47), 351 (14), 309 (77), 278 (12), 238 (13), 224 (17), 182 (21), 180 (30), 146 (5), 140 (9), 110 (8), 91 (88), 77 (9). **HRMS** *m/z* Found: 524.1001, Calcd. for $C_{23}H_{29}N_2O_2SI$ $(M)^+$: 524.0995.

Minor: 18b': $[\alpha]^{20}_{D}$ +41 (c 0.20, $CHCl_3$). R_f: 0.53 (Petroleum ether: ethyl acetate = 1:1). **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.37-7.13 (7H, *m*), 6.99-6.90 (2H, *m*), 5.76 (1H, *ddd*, *J* = 6.0, 9.0, 18.0 Hz), 5.17 (1H, *d*, *J* = 18.0 Hz), 5.08 (1H, *d*, *J* = 9.0 Hz), 4.87 (2H, *s*), 3.66 (1H, *dt*, *J* = 6.0, 15.0 Hz), 3.50 (1H, *d*, *J* = 9.0 Hz), 2.20-2.05 (2H, *m*), 1.96-1.84 (2H, *m*), 1.11 (9H, *s*). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 172.35, 142.19, 139.47, 137.42, 129.68, 128.91, 128.43, 128.14, 127.46, 116.62, 58.79, 56.07, 53.13, 30.92, 30.75, 22.65. EI-MS *m/z* (%) : 525 (M^++1, 10%), 511 (5), 467 (30), 404 (10), 341 (100), 309 (21), 278 (37), 250 (4), 238 (6), 225 (36), 183 (79), 180 (15), 140 (11), 112 (6), 110 (9), 91 (78), 77 (12). **HRMS** *m/z* Found: 524.0996, Calcd. for $C_{23}H_{29}N_2O_2SI$ $(M)^+$: 524.0995.

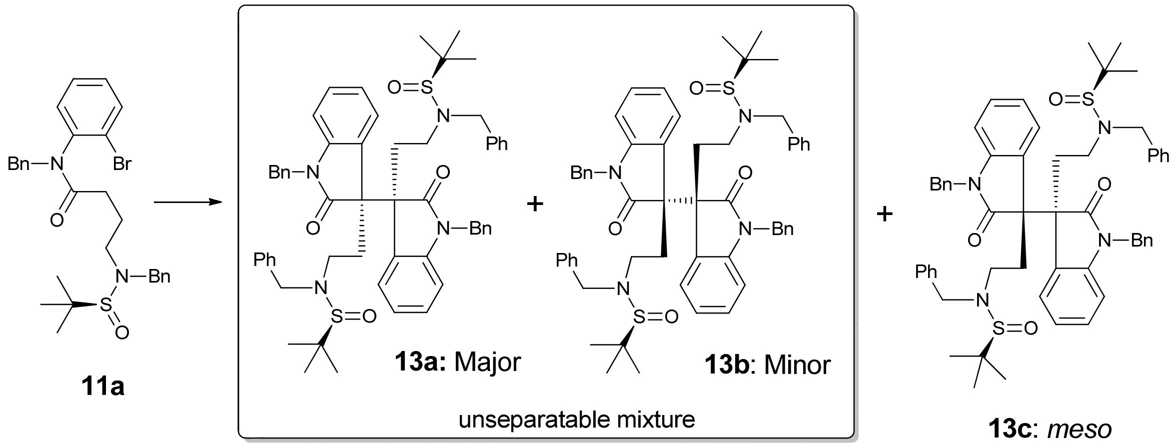


(*S*)-*N*-benzyl-4-((*S*)-*N*-benzyl-2-methylpropan-2-ylsulfinamido)-*N*-(2-iodophenyl)hex-5-enamide

11b $C_{30}H_{35}IN_2O_2S$ Mol. Wt.: 614.15, 614.58

To a mixture of sodium hydride (60% in mineral oil, 1.87 g, 46.7 mmol, 1.5 eq., freshly washed with anhydrous hexane 3 times under nitrogen) in anhydrous THF (50 mL) at 0 °C was added a solution of sulfonamide **18b** (16.3 g, 31.1 mmol) in THF (150 mL) via syringe. After stirring at 0 °C for 10 min, benzyl bromide (5.5 mL, 46.7 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at 0 °C for 2h, then at room temperature for 12 h under nitrogen. A powder of NH_4Cl (2.7 g, 50.0 mmol) was added and the mixture was stirred for 10 min. After concentrated under reduced pressure, the residue was diluted with water (150 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the product (**11b**: 18.1 g, 95%) as a pale yellow oil.

$[\alpha]^{20}_{D}$ −37 (c 0.12, $CHCl_3$). R_f: 0.54 (Petroleum ether: ethyl acetate = 2:1). **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.90 (1H, *d*, *J* = 8.0 Hz), 7.34-7.06 (11H, *m*), 7.00 (1H, *t*, *J* = 7.6 Hz), 6.64 (0.5H, *dd*, *J* = 1.2, 7.6 Hz), 6.60 (0.5H, *dd*, *J* = 1.2, 7.6 Hz), 5.74-5.59 (2H, *m*), 5.06 (1H, *dd*, *J* = 6.8, 10.0 Hz), 4.97 (1H, *t*, *J* = 18.0 Hz), 4.41 (1H, *dd*, *J* = 10.0, 16.4 Hz), 4.02 (1H, *d*, *J* = 16.4 Hz), 3.85 (1H, *t*, *J* = 14.0 Hz), 3.59-3.38 (1H, *m*), 2.35-2.17 (1H, *m*), 2.03-1.80 (3H, *m*), 1.12 (9H, *s*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 171.61 (171.44), 143.81, 140.21 (140.19), 138.64 (138.54), 137.54, 137.08 (137.02), 131.00, 130.87, 129.83, 129.38, 129.35, 129.21, 128.44 (128.39), 128.11 (128.08), 127.51, 127.00, 117.75 (117.69), 100.49 (100.45), 63.29 (63.08), 58.14 (58.09), 51.56, 46.27, 31.72 (31.59), 26.94 (26.88), 23.57. EI-MS *m/z* (%) : 614 (M^+, 4%), 509 (7), 482 (3), 458 (1), 420 (4), 405 (5), 309 (5), 278 (4), 236 (2), 182 (8), 180 (13), 146 (7), 128 (5), 106 (12), 91 (100). **HRMS** *m/z* Found: 614.1480, Calcd. for $C_{30}H_{35}N_2O_2SI$ $(M)^+$: 614.1464.



(*S*,*S*)-*N*,*N*'-(((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

(*S*,*S*)-*N*,*N*'-(((3*R*,3'*R*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

$C_{56}H_{62}N_4O_4S_2$ Mol. Wt.: 919.25

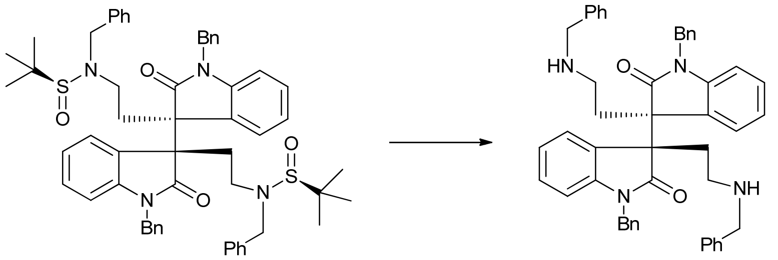
A mixture of copper iodide [CuI, 133.3 mg, 0.7 mmol, 0.1 eq.] and bromoanilide **11a** (3.78 g, 7.0 mmol) in anhydrous toluene (140 mL) was degassed and purged with argon (3 times). A solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 14 mL, 14 mmol, 2.0 eq.) was added and the resulting mixture was stirred at 80 °C (oil bath) under argon for 5 h. After cooling to room temperature then to 0 °C, a solution of anhydrous *t*-BuOOH (degassed and purged with argon, ~3.0 M in toluene, 3.5 mL, 10.5 mmol, 1.5 eq.) was added. The reaction mixture was allowed to stir at 0 °C under argon for 3 h. Saturated aqueous solution of NH_4Cl (8 mL) was added. After 30 min, the mixture was diluted with water (100 mL). The aqueous phase was extracted with ethyl acetate (3 × 60 mL). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1→1:1→1:2) to afford the major product (**13a**+**13b**, as a mixture of C3-C3a diasteromers, 2.51 g, 78.1%) as pale yellow syrup. Further elution afforded the minor product (**13c**: *meso*-isomer, 0.23 g, 7.2%) as a pale yellow oil, which was characterized after removal of the *tert*-butylsulfinyl group (**13d**).

* The anhydrous *tert*-butylhydroperoxide (*t*-BuOOH) in toluene (ca. ~3.0M) was prepared by the following procedure: 70% aqueous solution of *t*-BuOOH (40.6 mL, density = 0.93 g/mL) was added to toluene (46 mL) and the resulting water (ca. 10 mL) was separated and back-extracted with toluene (2 × 10 mL). The combined organic phases were then dried over anhydrous sodium sulfate. After filtration, the resulting solution was kept with 4Å molecular sieve and could be used for this reaction without further purification.

13a + **13b**: An 83:17 mixture of diastereomers at C3-C3' position: R_f: 0.45 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3396, 3057, 2957, 1705, 1609, 1460, 1360, 1176, 1072, 982, 929, 746, 703. **^{1}H-NMR**

(400 MHz, $CDCl_3$, major C3*S*-C3'*S*-isomer reported), δ (ppm): 7.34-7.18 (2×8H, *m*), 7.11-7.03 (2×2H, *m*), 6.81 (2×1H, *t*, *J* = 7.6 Hz), 6.68 (2×1H, *d*, *J* = 7.2 Hz), 6.49 (2×1H, *t*, *J* = 7.6 Hz), 6.27 (2×1H, *d*, *J* = 7.6 Hz), 4.92 (2×1H, *d*, *J* = 15.6 Hz), 4.36 (2×1H, *d*, *J* = 15.6 Hz), 4.21 (2×2H, *s*), 3.10 (2×1H, *ddd*, *J* = 4.8, 12.4, 12.8 Hz), 2.51 (2×1H, *ddd*, *J* = 3.6, 12.4, 12.8 Hz), 2.37 (2×1H, *ddd*, *J* = 4.0, 13.2, 13.6 Hz), 2.21-2.11 (2×1H, *m*), 1.17 (2×9H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$, major C3*S*-C3'*S*-isomer reported), δ (ppm): 176.69, 142.50, 137.07, 135.38, 129.02, 128.87, 128.54, 128.39, 127.75, 127.69, 127.50, 126.79, 123.58, 122.17, 108.69, 58.37, 54.28, 52.40, 44.02, 43.58, 27.78, 23.45. EI-MS *m/z* (%) : 919 (M^+, 1%), 862 (5), 813 (3), 756 (50), 709 (12), 662 (25), 647 (24), 629 (12), 601 (16), 575 (49), 551 (51), 537 (39), 523 (56), 404 (18), 354 (28), 313 (22), 261 (18), 236 (25), 195 (17), 118 (27), 106 (27), 91 (100), 65 (18). **HRMS** *m/z* Found: 941.4114, Calcd. for $C_{56}H_{62}N_4O_4NaS_2$ $(M+Na)^+$: 941.4110.

13c: R_f: 0.48 (Petroleum ether: ethyl acetate = 1:3). **HRMS** *m/z* Found: 941.4113, Calcd. for $C_{56}H_{62}N_4O_4NaS_2$ $(M+Na)^+$: 941.4110.



13c: *meso*

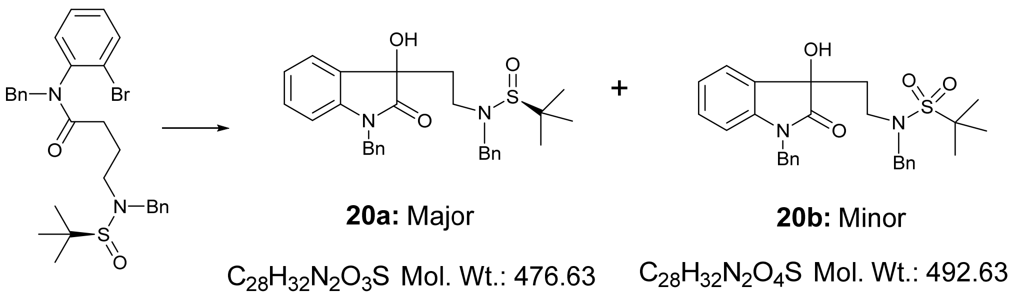
13d

$C_{48}H_{46}N_4O_2$ Mol. Wt.: 710.90

(3*R*,3'*S*)-1,1'-dibenzyl-3,3'-bis(2-(benzylamino)ethyl)-[3,3'-biindoline]-2,2'-dione

13c→13d: *meso*-isomer: Sulfinamide (**13c**: 257 mg, 0.28 mmol) was dissolved in methanol (6 mL). To this mixture was added an aqueous solution of HCl (4N, 0.21 mL, 0.84 mmol, 3 eq.). The resulting mixture was allowed to stir at room temperature under nitrogen for 1 h. The reaction mixture was then treated with saturated aqueous solution of sodium bicarbonate (~3 mL) and concentrated under reduced pressure. The mixture was diluted with water (10 mL) and extracted with dichloromethane (3 × 5 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (Dichloromethane : Methanol = 20 : 1) to afford the amine (**13d**) (175mg, 88%) as pale yellow syrup.

R_f: 0.35 (CH_2Cl_2: MeOH: Et_3N= 20: 1 : 0.01). **FTIR** (KBr, thin film) cm^{-1}: 3475, 2921, 1704, 1614, 1454, 1362, 1102, 745. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.32-6.29 (2×14H, *m*), 5.00-4.89 (2×1H, *m*), 4.76 (2×0.17H, *d*, *J* = 16.0 Hz), 4.72 (2×0.17H, *d*, *J* = 16.0 Hz), 4.43 (2×0.17H, *d*, *J* = 15.2 Hz), 4.33 (2×0.34H, *d*, *J* = 15.2 Hz), 4.19 (2×0.17H, *d*, *J* = 15.2 Hz), 3.62-3.45 (2×2H, *m*), 3.24-3.12 (2×0.66H, *m*), 2.63-2.10 (2×3.34H, *m*), 1.18 (2×1H, *brs*). **^{13}C-NMR** (as a mixture of rotamers, 100 MHz, $CDCl_3$), δ (ppm): 178.20 (177.90), 143.07 (142.89), 140.82 (140.61), 140.33 (140.21), 136.12 (136.03), 135.78 (135.62), 131.83 (131.45), 128.87 (128.84), 128.65 (128.46), 128.31 (128.19), 128.15 (128.02), 127.91, 127.86 (127.72), 127.52 (127.45), 127.32, 127.00, 126.73, 124.85 (124.80), 123.92, 122.62 (122.56), 121.71 (121.59), 120.06 (119.86), 109.40, 108.50 (108.31), 107.32 (107.01), 55.19, 53.97 (53.64), 45.44, 44.19 (44.02), 29.10 (28.96). **HRMS** *m/z* Found: 711.3658, Calcd. for $C_{48}H_{47}N_4O_2$ $(M+H)^+$: 711.3699.



20a: Major

$C_{28}H_{32}N_2O_3S$ Mol. Wt.: 476.63

20b: Minor

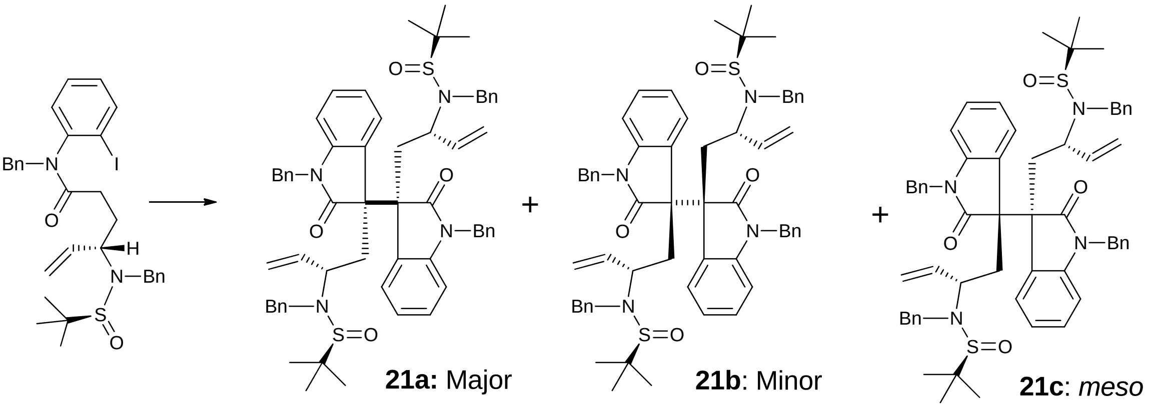
$C_{28}H_{32}N_2O_4S$ Mol. Wt.: 492.63

A mixture of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$, FW 915.72, 46.0 mg, 0.05 mmol, 0.025 eq.] and triphenylphosphine (FW 262.29, 52 mg, 0.2 mmol, 0.1 eq.) and bromoanilide **11a** (1.08 g, 2.0 mmol) in anhydrous toluene (40 mL) was degassed and purged with argon (3 times). A solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 4 mL, 4 mmol, 2.0 eq.) was added and the resulting mixture was stirred at 80 °C (oil bath) under argon for 6 h. After cooling to room temperature then 0 °C, a solution of anhydrous *t*-BuOOH (~3.0 M in toluene, 1.0 mL, 3 mmol, 1.5 eq.) was added and the reaction mixture was stirred at 0 °C (ca. 5 h). Saturated aqueous solution of NH_4Cl (0.5 mL) was added. After 10 min, anhydrous sodium sulfate (ca. 2-3 g) was added. The resulting mixture was then filtered and washed with ethyl acetate (3 × 5 mL). After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1→1:1) to afford the minor product (**20b**, 276 mg, 28%) as white plates. Further elution afforded the major product (**20a**, 489 mg, 51%) as a yellow solid.

20a: m.p.: 125-127 ºC. R_f: 0.54 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3321, 3057, 2958, 2866, 1722, 1611, 1460, 1359, 1273, 1174, 1068, 928, 743, 704, 633, 596, 464. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.30-7.11 (12H, *m*), 7.08 (0.5H, *t*, *J* = 7.6 Hz), 7.07 (0.5H, *t*, *J* = 7.6 Hz), 6.92 (0.5H, *t*, *J* = 7.6 Hz), 6.91 (0.5H, *t*, *J* = 7.6 Hz), 6.61 (0.5H, *d*, *J* = 7.6 Hz), 6.60 (0.5H, *d*, *J* = 7.6 Hz), 5.07 (0.5H, *s*), 5.04 (0.5H, *s*), 4.86 (0.5H, *d*, *J* = 15.6 Hz), 4.83 (0.5H, *d*, *J* = 15.6 Hz), 4.61 (0.5H, *d*, *J* = 15.6 Hz), 4.59 (0.5H, *d*, *J* = 15.6 Hz), 4.19 (0.5H, *d*, *J* = 15.2 Hz), 4.17 (0.5H, *d*, *J* = 15.2 Hz), 4.02 (0.5H, *d*, *J* = 15.2 Hz), 4.01 (0.5H, *d*, *J* = 15.2 Hz), 3.10-2.95 (1H, *m*), 2.93-2.70 (1H, *m*), 2.38-2.18 (2H, *m*), 1.10 (4.5H, *s*), 1.09 (4.5H, *s*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 177.54, 141.86, 136.62 (136.56), 135.29, 129.86 (129.80), 129.21, 128.60, 128.36 (128.30), 127.41 (127.20), 127.03 (127.00), 123.73 (123.68), 122.88, 109.24, 74.75 (74.71), 57.97, 51.24, 43.46, 42.72, 36.55 (36.43), 23.09. **HRMS** *m/z* Found: 499.2028, Calcd. for $C_{28}H_{32}N_2NaO_3S$ $(M+Na)^+$: 499.2031.

20b: m.p.: 113-115 ºC. R_f: 0.52 (Petroleum ether: ethyl acetate = 2:1). **FTIR** (KBr, thin film) cm^{-1}: 3415, 3059, 2980, 2930, 1718, 1612, 1462, 1360, 1310, 1172, 1124, 996, 934, 743, 702, 645, 521. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.39-7.10 (12H, *m*), 6.95 (1H, *t*, *J* = 7.6 Hz), 6.63 (1H, *t*, *J* = 7.6 Hz), 4.90

(0.4H, *d*, *J* = 16.0 Hz), 4.89 (0.6H, *d*, *J* = 16.0 Hz), 4.62 (0.4H, *d*, *J* = 15.6 Hz), 4.61 (0.6H, *d*, *J* = 15.6 Hz), 4.51-4.37 (1H, *brs*), 4.05 (0.4H, *s*), 3.99 (0.6H, *s*), 3.32-3.11 (2H, *m*), 2.27-2.15 (2H, *m*), 1.40 (4.5H, *s*), 1.39 (4.5H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 177.44, 141.95, 136.04, 135.31, 129.61, 129.37, 128.82, 128.57, 127.79, 127.66, 127.15, 123.77, 123.18, 109.52, 74.81, 61.62, 52.20, 43.69, 42.52, 36.79, 24.79. **HRMS** *m*/*z* Found: 515.1974, Calcd. for $C_{28}H_{32}N_2NaO_4S$ $(M+Na)^+$: 515.1975.



21a: Major

21b: Minor

21c: *meso*

$C_{60}H_{66}N_4O_4S_2$ Mol. Wt.: 970.45

21a: (*S*,*S*)-*N*,*N*'-((2*S*,2'*S*)-((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(but-3-ene-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

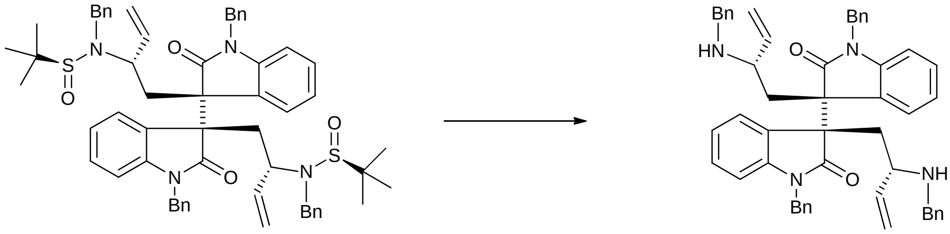
21b: (*S*,*S*)-*N*,*N*'-((2*S*,2'*S*)-((3*R*,3'*R*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(but-3-ene-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

To a mixture of copper iodide [CuI, 190 mg, 1.0 mmol, 0.1 eq.] and *o*-iodoanilide **11b** (6.14 g, 10.0 mmol) in anhydrous toluene (200 mL) was added a solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 20 mL, 20 mmol, 2.0 eq.). The resulting mixture was degassed and purged with argon (3 times). The reaction mixture was then allowed to stir at 60 °C (oil bath) under argon for 5 h. After cooling to room temperature then to 0 °C, a solution of anhydrous *t*-BuOOH (degassed and purged with argon, ~3.0 M in toluene, 5.0 mL, 15 mmol, 1.5 eq.) was added. The reaction mixture was then stirred at 0 °C under argon for 3 h. Saturated aqueous solution of $Na_2S_2O_3$ (10 mL) was added followed by saturated aqueous solution of NH_4Cl (10 mL). After 30 min, the resulting mixture was diluted with water (200 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1→1:1→1:2) to afford the major product (**21a**, 2.42 g, 50%) as a pale yellow syrup. Further elution afforded the *meso*-isomer (**21c**, characterized after removal of *tert*-butylsulfinyl group, 0.205 g, 4.2%), followed by minor product (**21b**, characterized after removal of the *tert*-butylsulfinyl group, 0.40g, 8.2%) as a pale yellow oil.

21a (major isomer): $[\alpha]^{20}_D$ −211 (c 0.14, $CHCl_3$). R_f: 0.55 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3440, 2960, 1702, 1609, 1465, 1361, 1177, 1071, 924, 745, 701. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.45 (2×2H, *d*, *J* = 8.0 Hz), 7.42 (2×2H, *d*, *J* = 8.0 Hz), 7.32-7.25 (2×1H, *m*), 7.21-7.11 (2×3H, *m*), 7.01 (2×2H, *d*, *J* = 7.2 Hz), 6.85 (2×1H, *d*, *J* = 7.6 Hz), 6.79 (2×1H, *t*, *J* = 7.6 Hz), 6.52 (2×1H, *t*, *J* = 7.6 Hz), 6.21 (2×1H, *d*, *J* = 8.0

Hz), 5.21 (2×1H, *ddd*, *J* = 9.6, 10.4, 16.8 Hz), 4.80 (2×1H, *d*, *J* = 15.2 Hz), 4.58 (2×1H, *d*, *J* = 16.8 Hz), 4.14 (2×1H, *d*, *J* = 15.2 Hz), 4.13 (2×1H, *d*, *J* = 10.4 Hz), 3.90 (2×1H, *d*, *J* = 17.2 Hz), 3.84 (2×1H, *d*, *J* = 17.2 Hz), 3.29 (2×1H, *dd*, *J* = 11.2, 13.0 Hz), 3.02-2.89 (2×2H, *m*), 1.18 (2×9H, *s*). **^{13}C-NMR** (100 MHz, CDCl$_3$), δ (ppm): 176.36, 142.92, 138.63, 137.51, 135.60, 128.65, 128.57, 128.24, 128.11, 127.93, 127.59, 127.29, 126.97, 125.34, 121.21, 115.89, 108.09, 62.93, 58.10, 54.96, 45.28, 43.83, 33.08, 23.35. **HRMS** *m*/*z* Found: 971.4619, Calcd. for $C_{60}H_{67}N_4O_4S_2$ $(M+H)^+$: 971.4604.

21b (minor-isomer): **HRMS** *m*/*z* Found: 993.4416, Calcd. for $C_{60}H_{66}N_4O_4S_2Na$ $(M+Na)^+$: 993.4423.
21c (*meso*-isomer): **HRMS** *m*/*z* Found: 993.4426, Calcd. for $C_{60}H_{66}N_4O_4S_2Na$ $(M+Na)^+$: 993.4423.



21b: minor isomer

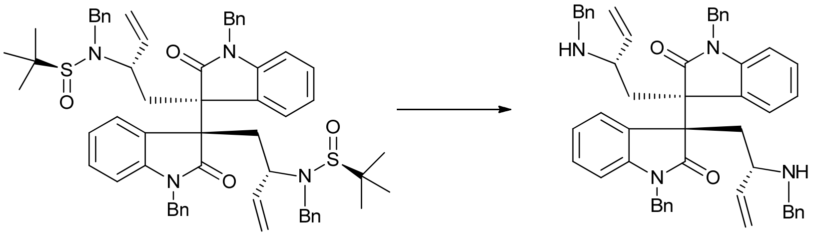
(3*R*,3'*R*)-1,1'-dibenzyl-3,3'-bis((*S*)-2-(benzylamino)but-3-en-1-yl)-[3,3'-biindoline]-2,2'-dione

21d $C_{52}H_{50}N_4O_2$ Mol. Wt.: 762.98

21b→21d (minor-isomer): Sulfinamide (**21b**: 400 mg, 0.41 mmol) was dissolved in methanol (6 mL). To this mixture was added an aqueous solution of HCl (4N, 0.31 mL, 1.23 mmol, 3 eq.). The resulting mixture was allowed to stir at room temperature under nitrogen for 1 h. The reaction mixture was then treated with saturated aqueous solution of sodium bicarbonate (~8 mL) and concentrated under reduced pressure. The mixture was diluted with water (10 mL) and extracted with dichloromethane (3 × 10 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the diamine (**21d**) (290 mg, 92%) as yellow oil.

21d (minor isomer): $[\alpha]^{20}_{D}$ −153 (c 0.18, CHCl$_3$). *R*$_f$: 0.42 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3420, 3061, 2925, 2843, 2357, 1712, 1608, 1482, 1460, 1358, 1175, 1110, 991, 921, 743, 701. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, CDCl$_3$), δ (ppm): 7.50-6.31 (2×14H, *m*), 5.62-5.46 (2×1H, *m*), 5.10-4.72 (2×2.35H, *m*), 4.56 (2×0.33H, *d*, *J* = 16.0 Hz), 4.44 (2×0.33H, *d*, *J* = 15.6 Hz), 4.33 (2×0.67H, *dd*, *J* = 11.6, 15.6 Hz), 4.03 (2×0.33H, *d*, *J* = 15.6 Hz), 3.66 (2×0.33H, *d*, *J* = 13.2 Hz), 3.55 (2×0.33H, *d*, *J* = 13.2 Hz), 3.49 (2×0.33H, *d*, *J* = 12.8 Hz), 3.43-3.31 (2×0.67H, *m*), 3.14 (2×0.33H, *d*, *J* = 13.2 Hz), 3.02 (2×0.33H, *d*, *J* = 13.2 Hz), 2.91-2.80 (2×0.33H, *m*), 2.77 (2×0.33H, *d*, *J* = 12.8 Hz), 2.67-2.50 (2×1H, *m*), 2.50-2.38 (2×0.67H, *m*), 2.22-2.14 (2×0.33H, *m*), 0.97 (2×1H, *brs*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, CDCl$_3$), δ (ppm): 179.54 (179.21), 143.82 (143.70), 141.22, 140.53 (140.42), 140.35, 140.14 (140.09), 136.39, 136.06 (135.86), 130.91, 128.87 (128.61), 128.49

(128.45), 128.36, 128.21 (128.13), 128.04, 127.86 (127.83), 127.52, 127.39 (127.34), 127.24, 126.76 (126.59), 126.42 (126.35), 125.26, 124.76, 121.94 (121.29), 119.45, 115.73, 115.44 (115.21), 109.33, 108.16 (107.18), 58.37, 58.09 (57.68), 54.81, 54.74 (54.59), 50.81, 50.75 (50.42), 44.57 (44.42), 44.11 (44.06), 34.89. **HRMS** *m/z* Found: 763.4008, Calcd. for $C_{52}H_{51}N_4O_2$ $(M+H)^+$: 763.4012.



21c: *meso*-isomer

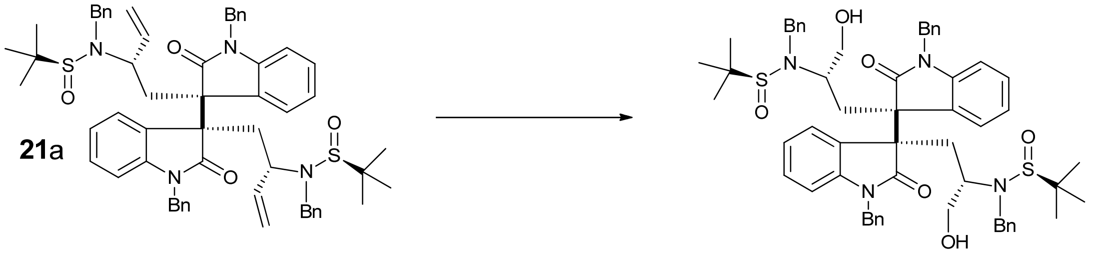
21e

$C_{52}H_{50}N_4O_2$ Mol. Wt.: 762.98

(3*R*,3'*S*)-1,1'-dibenzyl-3,3'-bis((*S*)-2-(benzylamino)but-3-en-1-yl)-[3,3'-biindoline]-2,2'-dione

21c→21e (*meso*-isomer): Sulfinamide (**21c**: 205 mg, 0.21 mmol) was dissolved in methanol (6 mL). To this mixture was added an aqueous solution of HCl (4N, 0.16 mL, 0.63 mmol, 3 eq.). The resulting mixture was allowed to stir at room temperature under nitrogen for 1 h. The reaction mixture was then treated with saturated aqueous solution of sodium bicarbonate (~4 mL) and concentrated under reduced pressure. The mixture was diluted with water (10 mL) and extracted with dichloromethane (3 × 5 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel ((Petroleum ether 60-90 ºC: ethyl acetate = 1:2)) to afford the diamine (**21e**) (145mg, 91%) as yellow syrup.

21e (*meso*-isomer): $[\alpha]^{20}_{D}$ −29 (c 0.18, $CHCl_3$). R_f: 0.41 (Petroleum ether: ethyl acetate = 1:3). **FTIR** (KBr, thin film) cm^{-1}: 3311, 3062, 2975, 2924, 2846, 1704, 1613, 1492, 1455, 1354, 1257, 1182, 1113, 995, 921, 742, 703, 634. **^{1}H-NMR** (as a mixture of rotamers, 400 MHz, $CDCl_3$), δ (ppm): 7.23-7.01 (2×9H, *m*), 6.96-6.60 (2×4H, *m*), 6.48 (2×0.5H, *d*, *J* = 8.0 Hz), 6.45 (2×0.5H, *d*, *J* = 8.0 Hz), 5.56-5.35 (2×1H, *m*), 4.98 (2×0.5H, *d*, *J* = 16.0 Hz), 4.87 (2×0.5H, *d*, *J* = 10.0 Hz), 4.87 (2×0.5H, *d*, *J* = 10.0 Hz), 4.76 (2×0.5H, *d*, *J* = 15.6 Hz), 4.68 (2×0.5H, *d*, *J* = 16.8 Hz), 4.54 (2×0.5H, *d*, *J* = 16.8 Hz), 4.32 (2×0.5H, *brs*), 3.88 (2×0.5H, *brs*), 3.55 (2×0.5H, *d*, *J* = 13.2 Hz), 3.49 (2×0.5H, *d*, *J* = 13.2 Hz), 3.13 (2×0.5H, *d*, *J* = 13.2 Hz), 3.01 (2×0.5H, *d*, *J* = 13.2 Hz), 3.00 (2×0.5H, *brs*), 2.92 (2×1H, *brs*), 2.68-2.50 (2×2H, *m*), 0.97 (2×1H, *brs*). **^{13}C-NMR** (rotamer in brackets, 100 MHz, $CDCl_3$), δ (ppm): 178.05 (176.96), 145.05 (144.20), 140.49 (140.39), 140.31 (140.19), 136.17 (135.85), 128.56 (128.44), 128.22 (128.00), 127.55, 127.25 (127.21), 126.95, 126.69 (126.56), 125.10, 124.54, 121.74 (121.45), 115.99 (115.44), 109.41 (109.30), 58.75 (58.56), 55.83 (55.34), 50.92 (50.85), 44.37, 37.69 (36.62). **HRMS** *m/z* Found: 763.4003, Calcd. for $C_{52}H_{51}N_4O_2$ $(M+H)^+$: 763.4012.



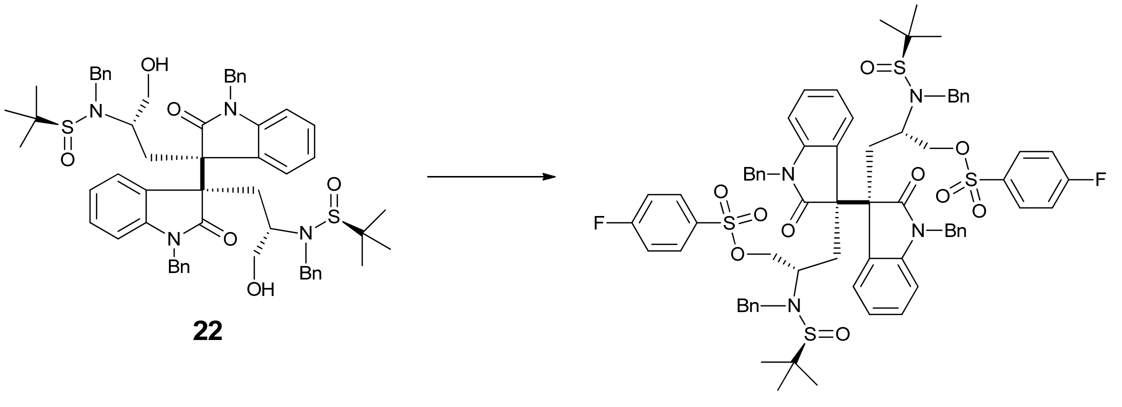
21a

(*S*,*S*)-*N*,*N*'-((2*S*,2'*S*)-((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(1-hydroxypropane-3,2-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

22: $C_{58}H_{66}N_4O_6S_2$ Mol. Wt.: 979.30

A solution of **21a** (485 mg, 0.5 mmol) in dichloromethane and methanol (20 mL, 1:1 mixture) was cooled to -78 °C (dry ice-acetone bath). Ozone was then passed through the solution for 10 minutes. The reaction progress was monitored by TLC. Sodium borohydride (189 mg, 5 mmol, 10 eq.) was added. The reaction mixture was then gradurally warmed up to room termperature under argon at stirration overnight. Saturated aqueous solution of NH_4Cl (10 mL) was added. The resulting mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:2) to afford the product (**22**, 401 mg, 82%) as a pale yellow syrup.

22: $[\alpha]^{20}_{D}$ −332 (c 0.14, $CHCl_3$). R_f: 0.45 (Petroleum ether: ethyl acetate = 1:2). **FTIR** (KBr, thin film) cm^{-1}: 3730, 3436, 2921, 2351, 1703, 1609, 1460, 1364, 1174, 1046, 745. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.51 (2×2H, *d*, *J* = 7.6 Hz), 7.35 (2×2H, *t*, *J* = 7.6 Hz), 7.25-7.16 (2×4H, *m*), 7.04 (2×2H, *dd*, *J* = 1.6, 7.6 Hz), 6.92 (2×1H, *d*, *J* = 6.8 Hz), 6.88 (2×1H, *d*, *J* = 8.0 Hz), 6.63 (2×1H, *t*, *J* = 7.6 Hz), 6.32 (2×1H, *d*, *J* = 8.0 Hz), 4.84 (2×1H, *d*, *J* = 15.6 Hz), 4.52 (2×1H, *d*, *J* = 16.8 Hz), 4.35 (2×1H, *d*, *J* = 15.6 Hz), 3.90 (2×1H, *d*, *J* = 16.8 Hz), 3.12 (2×1H, *ddd*, *J* = 3.6, 11.0, 12.8 Hz), 3.03 (2×1H, *dd*, *J* = 9.2, 14.0 Hz), 2.92 (2×1H, *d*, *J* = 14.0 Hz), 2.59 (2×1H, *ddd*, *J* = 3.2, 9.2, 12.8 Hz), 2.05-1.97 (2×1H, *m*), 1.20 (2×9H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 176.31, 142.80, 138.33, 135.12, 129.09, 128.92, 128.78, 128.38, 127.78, 127.63, 127.35, 124.16, 122.28, 109.11, 63.92, 63.28, 58.37, 55.42, 45.36, 44.02, 30.25, 23.75. **HRMS** *m*/*z* Found: 979.4513, Calcd. for $C_{58}H_{67}N_4O_6S_2$ $(M+H)^+$: 979.4502.



22

(*S*,2*S*,2'*S*)-((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(2-((*S*)-*N*-benzyl-2-methylpropan-2-ylsulfinamido)propane-3,1-diyl) bis(4-fluorobenzenesulfonate)

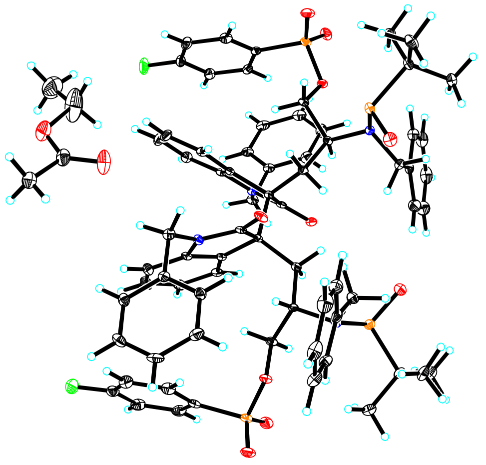
23: $C_{70}H_{72}F_2N_4O_{10}S_4$ Mol. Wt.: 1295.60

To a mixture of diol **22** (49 mg, 0.05 mmol), trimethylamine (20 mg, 0.027 mL, 0.2 mmol) and DMAP (3 mg, 0.025 mmol) in dichloromethane (5 mL) was added 4-fluorobenzene-1-sulfonyl chloride (39 mg, 0.2 mmol, 4.0 eq.). The resulting mixture was then allowed to stir at room termperature for 6 h. A solution of saturated aqueous solution of $NaHCO_3$ (2 mL) was added and diluted with water (5 mL). The mixture was extracted with dichloromethane (3 × 4 mL). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to afford the product (**23**, 60 mg, 92%) as a plate. An X-ray crystallography analysis of compound **23** was conducted to determine the absolute configuration.*

23: m.p.: 127-129 ºC. $[\alpha]^{20}_{D}$ −160 (c 0.72, $CHCl_3$). R_f: 0.55 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3730, 3456, 2921, 2351, 1703, 1459, 1368, 1016, 752. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.46 (2×2H, *d*, *J* = 7.6 Hz), 7.42-7.31 (2×4H, *m*), 7.28-7.20 (2×2H, *m*), 7.16 (2×2H, *t*, *J* = 7.6 Hz), 6.96-6.76 (2×6H, *m*), 6.52 (2×1H, *m*), 6.23 (2×1H, *d*, *J* = 7.2 Hz), 4.64 (2×1H, *d*, *J* = 15.6 Hz), 4.63 (2×1H, *d*, *J* = 17.2 Hz), 4.13 (2×1H, *d*, *J* = 15.6 Hz), 3.83 (2×1H, *d*, *J* = 17.2 Hz), 3.82 (2×1H, *d*, *J* = 10.8 Hz), 3.20-3.01 (2×2H, *m*), 2.84 (2×1H, *dd*, *J* = 2.8, 10.8 Hz), 2.71-2.61 (2×1H, *m*), 1.27 (2×9H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 176.36, 166.80, 164.25, 142.70, 137.16, 135.09, 131.64, 130.51, 130.41, 129.61, 129.14, 128.95, 128.70, 128.61, 128.33, 127.75, 127.53, 127.32, 126.55, 124.09, 122.18, 116.52, 116.29, 109.37, 70.58, 58.80, 58.48, 55.14, 46.39, 44.03, 30.62, 23.60. **HRMS** *m*/*z* Found: 1317.3994, Calcd. for $C_{70}H_{72}N_4O_{10}S_4F_2Na$ $(M+Na)^+$: 1317.3997.

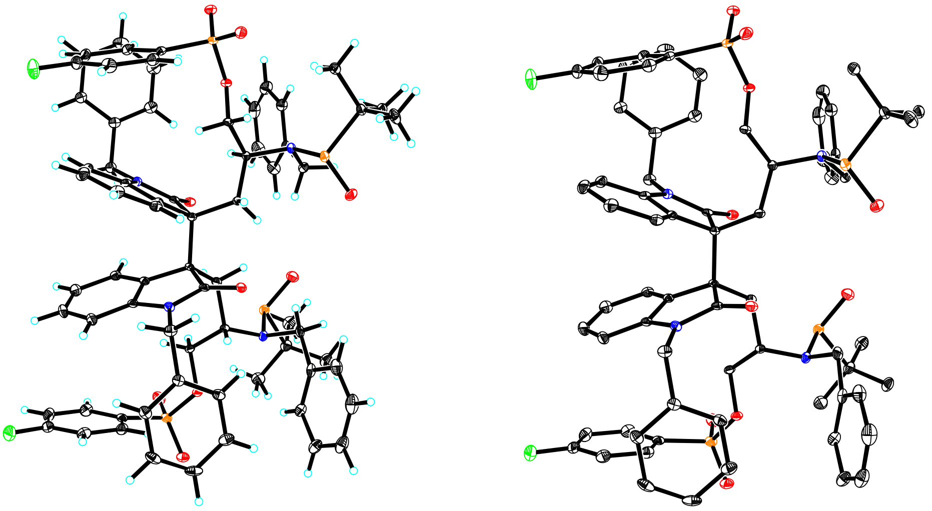
*Dr. Xiaonian Li in Kunming Institute of Botany is gratefully acknowledged for X-ray crystallography analysis of compound **23**.

Crystal data for mo_zhb_s3_0m: $C_{70}H_{72}F_2N_4O_{10}S_4 \cdot C_4H_8O_2$, *M* = 1383.66, orthorhombic, *a* = 10.1404(9) Å, *b* = 25.087(2) Å, *c* = 27.663(3) Å, *α* = 90.00°, *β* = 90.00°, *γ* = 90.00°, *V* = 7037.4(11) $Å^3$, *T* = 100(2) K, space group *P*212121, *Z* = 4, $\mu(\mathrm{MoK}\alpha) = 0.205\ \mathrm{mm}^{-1}$, 70275 reflections measured, 17497 independent reflections ($R_{int} = 0.0645$). The final R_1 values were 0.0434 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0969 ($I > 2\sigma(I)$). The final R_1 values were 0.0596 (all data). The final $wR(F^2)$ values were 0.1063 (all data). The goodness of fit on F^2 was 1.030. Flack parameter = 0.03(4).



View of the molecules in an asymmetric unit.

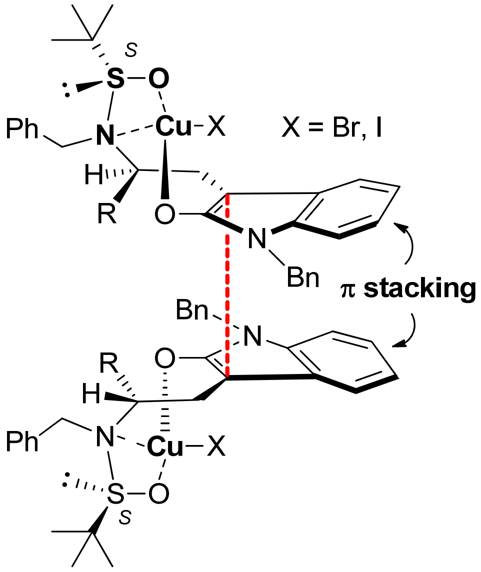
Displacement ellipsoids are drawn at the 30% probability level.



View of a molecule of zhb_s3 with the atom-labelling scheme.

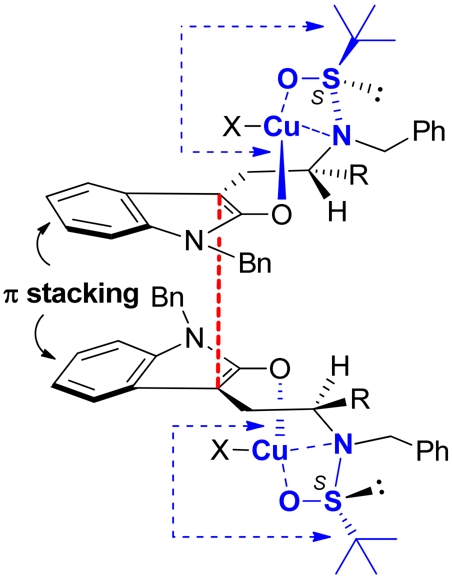
Displacement ellipsoids are drawn at the 30% probability level.

Prediction of stereochemistry for copper catalyzed arylation-oxidative dimerization of *o*-bromoanilides.



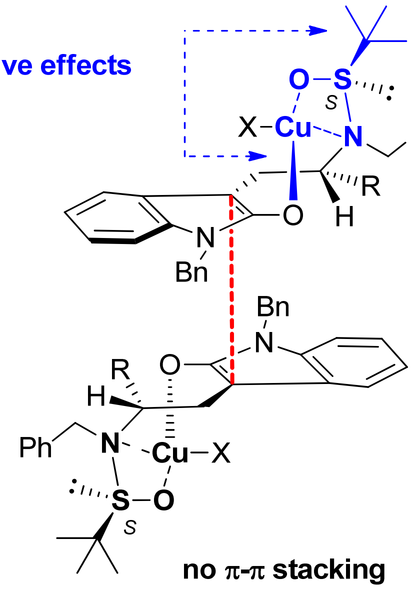
Favored approach, resulting in the major dimeric diastereoisomer (C3*S*-C3'*S*)

+

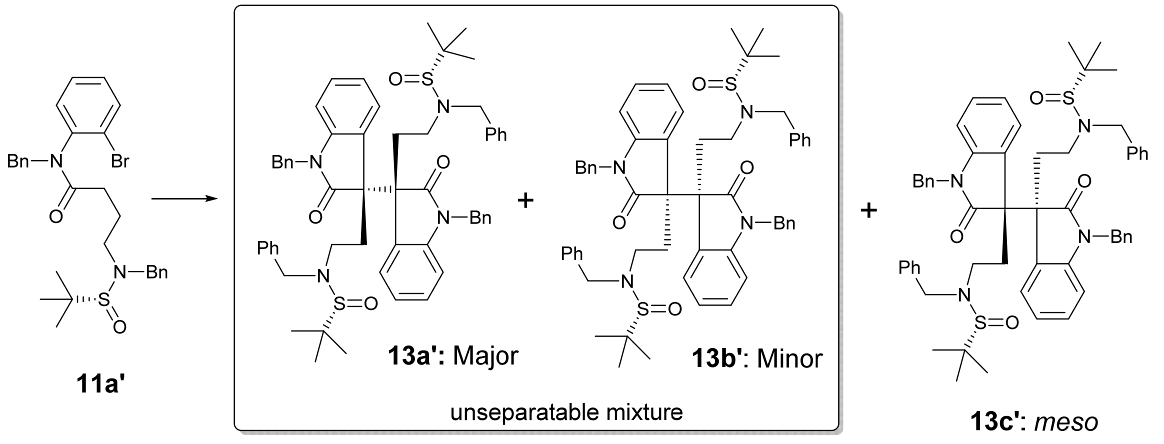


Unfavored approach, resulting in the minor dimeric diastereoisomer (C3*R*-C3'*R*)

+



resulting in the *meso*-form



13a': (*R*,*R*)-*N*,*N*'-(((3*R*,3'*R*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

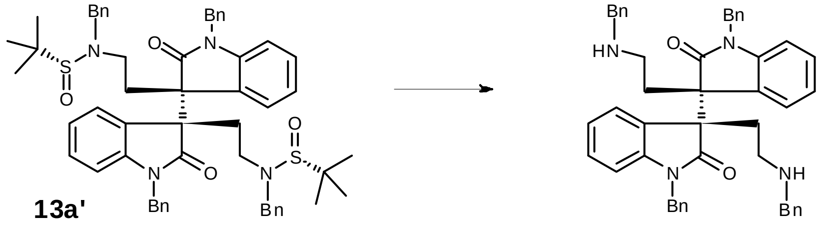
13b': (*R*,*R*)-*N*,*N*'-(((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))bis(*N*-benzyl-2-methylpropane-2-sulfinamide)

$C_{56}H_{62}N_4O_4S_2$ Mol. Wt.: 919.25

To a mixture of copper iodide [CuI, 190.4 mg, 1.0 mmol, 0.1 eq.] and bromoanilide **11a'** (5.41 g, 10 mmol) in anhydrous toluene (200 mL) was added a solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 20 mL, 20 mmol, 2.0 eq.). The resulting mixture was degassed and purged with argon (3 times). After which, the reaction mixture was stirred at 80 °C (oil bath) under argon for 5 h. After cooling to room temperature then to 0 °C, a solution of anhydrous *t*-BuOOH (~3 M in toluene, 5.0 mL, 15 mmol, 1.5 eq.) was added. The reaction mixture was allowed to stir at 0 °C under argon for 3 h. Saturated aqueous solution of NH_4Cl (10 mL) was added. After 30 min, the mixture was diluted with water (200 mL). The resulting mixture was then extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1→1:2→1:3) to afford the major product (**13a'** + **13b'**, 3.59 g, 78%) as a pale yellow syrup. Further elution afforded the minor product (**13c'**, 0.32 g, 7%) as a pale yellow oil, which was characterized after removal of *tert*-butylsulfinyl group (see **13d**).

13a' + **13b'**: An 84:16 mixture of diastereomers at C3-C3' position: R_f: 0.45 (Petroleum ether: ethyl acetate = 1:1). **FTIR** (KBr, thin film) cm^{-1}: 3429, 2969, 2352, 1702, 1612, 1456, 1365, 1052. **^{1}H-NMR** (400 MHz, $CDCl_3$, major C3*R*-C3'*R*-isomer reported), δ (ppm): 7.37-7.19 (2×8H, *m*), 7.10-7.03 (2×2H, *m*), 6.81 (2×1H, *t*, *J* = 7.6 Hz), 6.68 (2×1H, *d*, *J* = 7.6 Hz), 6.49 (2×1H, *t*, *J* = 7.6 Hz), 6.26 (2×1H, *d*, *J* = 8.0 Hz), 4.91 (2×1H, *d*, *J* = 15.6 Hz), 4.36 (2×1H, *d*, *J* = 15.6 Hz), 4.21 (2×2H, *s*), 3.11 (2×1H, *ddd*, *J* = 4.4, 12.4, 12.8 Hz), 2.48 (2×1H, *ddd*, *J* = 3.6, 12.4, 12.8 Hz), 2.37 (2×1H, *ddd*, *J* = 3.6, 13.2, 13.6 Hz), 2.22-2.10 (2×1H, *m*), 1.17 (2×9H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$, major C3*R*-C3'*R*-isomer reported), δ (ppm): 176.63, 142.44, 137.01, 135.32, 128.96, 128.81, 128.49, 128.34, 127.70, 127.64, 127.45, 126.80, 126.72, 123.52, 122.11, 108.63, 58.31, 54.22, 52.40, 43.96, 43.51, 27.70, 23.40. EI-MS *m*/*z* (%) : 919 (M^+, 1%), 918 (1%), 706 (2), 588 (3), 575 (1), 354 (3), 249 (2), 236 (4), 223 (4), 132

(10), 118 (19), 106 (7), 91 (100), 65 (5). **HRMS** *m/z* Found: 918.4224, Calcd. for $C_{56}H_{62}N_4O_4S_2$ $(M)^+$: 918.4213; Found: 919.4307, Calcd. for $C_{56}H_{63}N_4O_4S_2$ $(M+H)^+$: 919.4291.



13a'

24 $C_{48}H_{46}N_4O_2$
Mol. Wt.: 710.90

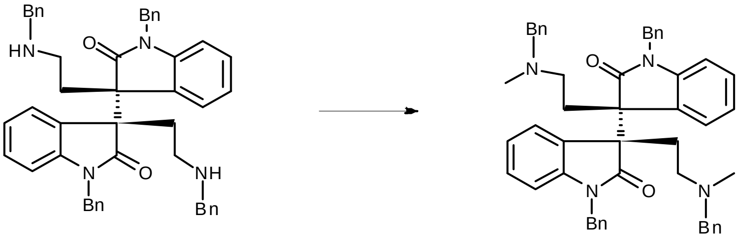
24: (3R,3'R)-1,1'-dibenzyl-3,3'-bis(2-(benzylamino)ethyl)-[3,3'-biindoline]-2,2(3R,3'R)-1,1'-dibenzyl-3,3'-bis(2-(benzylamino)ethyl)-[3,3'-biindoline]-2,2'-dione

Sulfinamide (**13a'** + **13b'**: 3.59g, 3.9 mmol) was dissolved in methanol (60 mL). To this mixture was added an aqueous solution of HCl (4N, 2.9 mL, 11.7 mmol, 3 eq.). The resulting mixture was allowed to stir at room temperature under nitrogen for 1 h. The reaction mixture was then treated with saturated aqueous solution of sodium bicarbonate (~50 mL) and concentrated under reduced pressure. The mixture was diluted with water (100 mL) and extracted with dichloromethane (3 × 50 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (Dichloromethane : Methanol = 20 : 1) to afford the amine (**24**) (2.63g, 95%) as white foam.*[1] The diamine was dissolved in methanol (20 mL) and HCl (2N, 5.6 mL, 11.1 mmol, 3.0 eq.) was added. This solution was allowed to crystallize at room temperature. The needle-like crystals were collected and subjected to HPLC analysis (a 1:1 mixture of C3*R*-C3'*R* and C3*S*-C3'*S* enantiomers). The mother liquid was then treated with saturated aqueous solution of sodium bicarbonate to pH = 8, and extracted with dichloromethane (3). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvents, the enantiomeric pure product **24** was obtained (1.60 g, 61%) as a pale yellow syrup.*[2]

24: $[\alpha]^{20}_D$ +171 (c 0.12, MeOH). *ee* = 99.1%. R_f: 0.40 (CH_2Cl_2: MeOH: Et_3N= 20: 1 : 0.01). **FTIR** (KBr, thin film) cm^{-1}: 3426, 2967, 1701, 1611, 1456, 1365, 1174, 1047, 746, 700. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.32-7.16 (2×9H, *m*), 7.10 (2×2H, *d*, *J* = 7.2 Hz), 7.04 (2×1H, *d*, *J* = 7.2 Hz), 6.97 (2×1H, *t*, *J* = 7.6 Hz), 6.71 (2×1H, *t*, *J* = 7.6 Hz), 6.39 (2×1H, *d*, *J* = 7.6 Hz), 5.03 (2×1H, *d*, *J* = 15.6 Hz), 4.45 (2×1H, *d*, *J* = 15.6 Hz), 3.60 (2×1H, *d*, *J* = 13.6 Hz), 3.53 (2×1H, *d*, *J* = 13.6 Hz), 3.26 (2×1H, *ddd*, *J* = 5.6, 6.0, 13.2 Hz), 2.64 (2×1H, *ddd*, *J* = 7.6, 8.0, 13.2 Hz), 2.27-2.17 (2×2H, *m*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 178.03, 143.09, 140.31, 135.85, 128.68, 128.32, 128.06, 128.01, 127.85, 127.58, 126.74, 124.12, 121.76, 108.52, 55.14, 53.65, 45.41, 44.12, 29.22. EI-MS *m/z* (%) : 710 (M^+, 2%), 577 (1), 356 (4), 344 (2), 262 (3), 236 (4), 223 (4), 134 (8), 118 (12), 106 (21), 91 (100). **HRMS** *m/z* Found: 710.3622, Calcd. for $C_{48}H_{46}N_4O_2$ $(M)^+$: 710.3621.

(**24** racemic)*[1] Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel OD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / *iso*-propanol 85 / 15; flow rate: 0.500 mL/min; detection, UV 254 nm; tR_1 = 48.247 min, Area = 39.4094; tR_2 = 53.887 min, Area = 60.5906.

(**24**)[*2] Chiral HPLC analysis: 25 ºC; column: DAICEL Chiralcel OD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / *iso*-propanol 85/ 15; flow rate: 0.500 mL/min; detection, UV 254 nm; tR_1 = 50.183 min, Area = 0.4883; tR_2 = 52.932 min, Area = 99.5117.

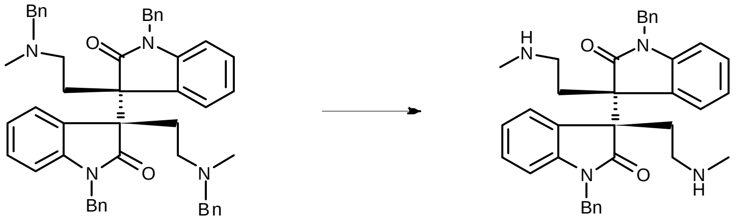


25 $C_{50}H_{50}N_4O_2$
Mol. Wt.: 738.96

(3*R*,3'*R*)-1,1'-dibenzyl-3,3'-bis(2-(benzyl(methyl)amino)ethyl)-[3,3'-biindoline]-2,2'-dione

To diamine **24** (0.82 g, 1.15 mmol) in acetonitrile (10 mL) was added a solution of formaldehyde (37% aqueous solution, 0.44 mL, 5.75 mmol, 5.0 eq.). Sodium triacetoxyborohydride (1.22 g, 5.75 mmol, 5.0 eq.) was added and the resulting mixture was stirred at room temperature under argon for 2 h. A solution of methanol in dichloromethane (MeOH : CH_2Cl_2 = 5:95, 10 mL) saturated with ammonia was added. The mixture was then allowed to stir at room temperature for 5 min. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (Dichloromethane: MeOH : NH_3-H_2O = 300 : 10 : 1) to afford the product (**25**, 0.82 g, 96% yield) as a pale yellow syrup.

$[\alpha]^{20}_{D}$ +171 (c 0.10, MeOH). R_f: 0.45 (CH_2Cl_2: MeOH = 30 : 1). **FTIR** (KBr, thin film) cm^{-1}: 3436, 2930, 2789, 1702, 1608, 1462, 1361, 1177, 1036, 744, 700. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.18-7.01 (2×10H, *m*), 6.89 (2×1H, *d*, *J* = 7.5 Hz), 6.79 (2×1H, *t*, *J* = 7.5 Hz), 6.55 (2×1H, *t*, *J* = 7.5 Hz), 6.25 (2×1H, *d*, *J* = 7.5 Hz), 4.92 (2×1H, *d*, *J* = 15.0 Hz), 4.32 (2×1H, *d*, *J* = 15.0 Hz), 3.26 (2×1H, *d*, *J* = 12.9 Hz), 3.15 (2×1H, *d*, *J* = 12.9 Hz), 3.18-3.07 (2×1H, *m*), 2.67-2.53 (2×1H, *m*), 1.94 (2×3H, *s*), 1.98-1.86 (2×1H, *m*), 1.79-1.67 (2×1H, *m*). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 177.53, 142.97, 138.34, 135.84, 129.27, 128.62, 128.05, 128.01, 127.86, 127.56, 126.83, 124.02, 121.75, 108.35, 61.81, 55.00, 53.04, 43.99, 41.80, 26.11. EI-MS *m*/*z* (%) : 738 (M^+, 9%), 647 (21), 591 (43), 444 (4), 370 (23), 293 (2), 277 (13), 235 (12), 148 (17), 134 (93), 120 (25), 91 (100), 65 (10). **HRMS** *m*/*z* Found: 738.3931, Calcd. for $C_{50}H_{50}N_4O_2$ $(M)^+$: 738.3934.

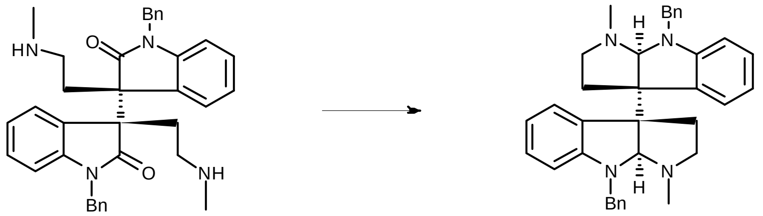


26 $C_{36}H_{38}N_4O_2$
Mol. Wt.: 558.71

(3*R*,3'*R*)-1,1'-dibenzyl-3,3'-bis(2-(methylamino)ethyl)-[3,3'-biindoline]-2,2'-dione

Diamine **25** (369 mg, 0.5 mmol) in anhydrous 1,2-dichloroethane (15 mL) was stirred with a solution of α-chloroethyl chloroformate (ACE-Cl, 0.54 mL, 5 mmol, 10.0 eq.) at 0 °C for 2h, then at room temperature for 1 h. After which, the reaction mixture was allowed to stir at 80 °C (oil bath) for 12 h. After removal of the solvents, the residue was diluted with methanol (15 mL) and stirred at 70 °C (oil bath) for 3 h. The resulting mixture was concentrated under reduced pressure and diluted with dichloromethane (5 mL), ice (~10 g) and saturated aqueous solution of $NaHCO_3$ (10 mL). The mixture was then extracted with dichloromethane (3 × 15 mL), and the combined organic phases was dried over anhydrous sodium sulfate. After filtration and removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (Dichloromethane: MeOH: NH_3-H_2O = 100 :100 :1) to afford the product (**26**, 265 mg, 95% yield) as a pale yellowish syrup.

$[\alpha]^{20}_{D}$ +203 (c 0.10, MeOH). R_f: 0.44 (CH_2Cl_2: MeOH = 1 : 1). **FTIR** (KBr, thin film) cm^{-1}: 3431, 2970, 2352, 1628, 1397, 1089. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.32-7.11 (2×5H, *m*), 7.03 (2×1H, *d*, *J* = 7.2 Hz), 6.92 (2×1H, *dt*, *J* = 0.8, 7.6 Hz), 6.70 (2×1H, *t*, *J* = 7.6 Hz), 6.35 (2×1H, *d*, *J* = 7.6 Hz), 5.10 (2×1H, *d*, *J* = 15.6 Hz), 4.40 (2×1H, *d*, *J* = 15.6 Hz), 3.25-3.13 (2×1H, *m*), 2.58-2.49 (2×1H, *m*), 2.21 (2×3H, *s*), 2.12-2.03 (2×3H, *m*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 177.73, 142.98, 135.88, 128.74, 128.20, 128.00, 127.86, 127.66, 124.02, 121.84, 108.54, 55.04, 47.81, 44.05, 36.12, 29.00. EI-MS *m/z* (%) : 558 (M^+, 21%), 526 (5), 501 (100), 470 (12), 444 (43), 280 (52), 248 (7), 236 (38), 223 (28), 187 (7), 158 (13), 91 (56). **HRMS** *m/z* Found: 558.2989, Calcd. for $C_{36}H_{38}N_4O_2$ $(M)^+$: 558.2995.



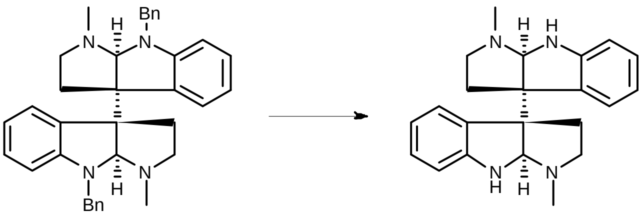
27

(3a*R*,8a*S*,8'a*S*)-8,8'-dibenzyl-1,1'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1*H*,1'*H*-3a,3'a-bipyrrolo[2,3-*b*]indole

$C_{36}H_{38}N_4$ Mol. Wt.: 526.71

Diamine **26** (558 mg, 1.0 mmol) in THF (25 mL) was degassed and purged with argon (3 times). A solution of diisobutylaminium hydride (DIBAL-H, 1.1 M in THF, 10 mL, 10 mmol, 10.0 eq.) was added and the resulting mixture was stirred at 0 °C for 1 h, then at room temperature for 2 h and finally at 80 °C (oil bath) under argon for 15 h. After cooling to room temperature, a saturated aqueous solution of potassium sodium tartrate (10 mL) was added and the resulting mixture was stirred at room temperature for 2 h. The mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over anhydrous sodium sulfate. After filtration and removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:4) to afford the product (**27**, 284 mg, 54% yield) as white foam.

$[\alpha]^{20}_{D}$ +248 (c 0.11, $CHCl_3$). R_f: 0.54 (Petroleum ether: ethyl acetate = 1:4). **FTIR** (KBr, thin film) cm^{-1}: 3419, 3029, 2919, 2791, 1598, 1488, 1350, 1258, 1147, 1039, 736. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.31-7.21 (2×4H, *m*), 7.20-7.13 (2×1H, *m*), 6.90 (2×1H, *d*, *J* = 6.8 Hz), 6.82 (2×1H, *t*, *J* = 7.6 Hz), 6.46 (2×1H, *t*, *J* = 7.6 Hz), 6.10 (2×1H, *d*, *J* = 7.6 Hz), 4.49 (2×1H, *brs*), 4.42 (2×1H, *d*, *J* = 16.4 Hz), 4.36 (2×1H, *d*, *J* = 16.4 Hz), 2.57-2.50 (2×2H, *m*), 2.42-2.33 (2×1H, *m*), 2.18 (2×3H, *s*), 1.94-1.87 (2×1H, *m*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 152.69, 139.44, 133.08, 128.54, 128.09, 127.39, 126.87, 126.73, 124.13, 117.29, 106.80, 92.96, 63.27, 53.21, 52.61, 38.99, 35.74. EI-MS *m*/*z* (%) : 526 (M^+, 10%), 482 (6), 439 (26), 392 (3), 309 (12), 263 (49), 262 (100), 220 (15), 172 (26), 171 (19), 130 (8), 91 (42). **HRMS** *m*/*z* Found: 526.3099, Calcd. for $C_{36}H_{38}N_4$ $(M)^+$: 526.3096.



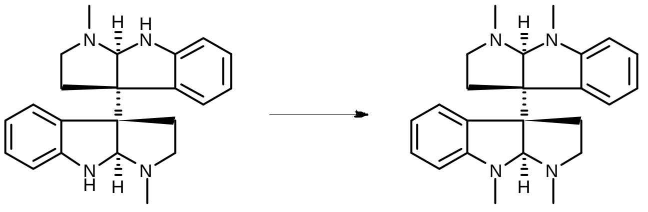
(3a*R*,8a*R*,8'a*R*)-1,1'-dimethyl-
2,2',3,3',8,8a,8',8'a-octahydro-
1*H*,1'*H*-3a,3'a-bipyrrolo[2,3-*b*]indole

$C_{22}H_{26}N_4$ Mol. Wt.: 346.47

1: (+)-Chimonanthine

To a solution of liquid ammonia (freshly distilled and collected by Birch condenser, acetone-dry ice, 50-60 ml) at -78 ºC was added sodium metal (ca. 124 mg, 5.4 mmol, 10 eq.). A solution of chimonanthine precursor (**27**, 284 mg, 0.54 mmol) in anhydrous THF (10 mL) was added to this dark blue solution of liquid ammonia. After stirring at -78 ºC for 15 min, a powder of NH_4Cl (433 mg, 8.1 mmol) was added in one portion followed by saturated aqueous solution of NH_4Cl (5 mL). The resulting mixture was allowed to evaporate in fume hood. The residue was then diluted with water (20 ml) and extracted with dichloromethane (3 × 20 ml). The organic phases were combined and dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure and the crude product was chromatographed on silica gel (CH_2Cl_2 : MeOH: NH_3-H_2O = 200: 10: 1) to afford the product (**1**, 177 mg, 95%) as white plates.

m.p.: 170-172 ºC, $[\alpha]^{20}_{D}$ +285 (c 0.12, EtOH). R_f: 0.48 (CH_2Cl_2 : MeOH: NH_3-H_2O = 200: 10: 1). **FTIR** (KBr, thin film) cm^{-1}: 3404, 3219, 2930, 2856, 2797, 1601, 1480, 1252, 1161, 1031, 739, 648. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.19 (2×1H, *d*, *J* = 7.2 Hz), 6.99 (2×1H, *t*, *J* = 7.2 Hz), 6.67 (2×1H, *t*, *J* = 7.2 Hz), 6.54 (2×1H, *d*, *J* = 7.2 Hz), 4.34 (2×1H, *brs*), 4.12 (2×1H, *brs*), 2.63-2.48 (2×3H, *m*), 2.30 (2×3H, *s*), 2.18-2.01 (2×1H, *m*). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 150.74, 133.27, 128.27, 124.58, 118.78, 109.41, 85.40, 63.41, 52.83, 37.38, 35.66. EI-MS *m*/*z* (%) : 346 (M^+, 7%), 302 (2), 259 (2), 245 (3), 231 (3), 190 (11), 173 (37), 172 (100), 157 (6), 143 (8), 130 (30), 117 (6), 103 (5), 85 (24), 83 (28). **HRMS** *m*/*z* Found: 346.2151, Calcd. for $C_{22}H_{26}N_4$ $(M)^+$: 346.2157.
($[\alpha]^{20}_{D}$ = +285, *c* 0.12, EtOH, lit.[6p] $[\alpha]^{20}_{D}$ = +279, *c* 0.1, EtOH; lit.[4a] $[\alpha]^{20}_{D}$ = +254, *c* 1.0, EtOH)



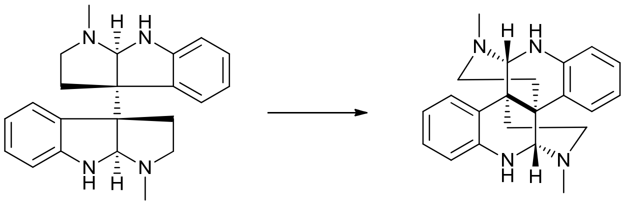
(3a*R*,8a*S*,8'a*S*)-1,1',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-1*H*,1'*H*-3a,3'a-bipyrrolo[2,3-*b*]indole

$C_{24}H_{30}N_4$ Mol. Wt.: 374.52

2: (+)-Folicanthine

To a solution of amine **1** (35 mg, 0.1 mmol) in acetonitrile (3 ml) was added a solution of formalin (37% HCHO in water, 39 μL, 0.52 mmol, 5.2 eq.) and sodium triacetoxyborohydride [$NaBH(OAc)_3$, 110 mg, 0.52 mmol]. The resulting mixture was then stirred at room temperature under argon for 1 h. The mixture was then treated with a solution of methanol in dichloromethane saturated with ammonia (ca. 5 mL, CH_2Cl_2: MeOH = 95 : 5). After stirring for 5 minutes, the mixture was concentrated and the residue was chromatographed on silica gel (Dichloromethane : Methanol : NH_3-H_2O = 500 :10 : 1) to afford the product (**2**, 35.5 mg, 95%) as white plates.

m.p.: 183-185 ºC, $[\alpha]^{20}_{D}$ +315 (c 0.10, MeOH). R_f: 0.48 (CH_2Cl_2 : MeOH: NH_3-H_2O = 200: 10: 1). **FTIR** (KBr, thin film) cm^{-1}: 3434, 2944, 2784, 1601, 1488， 1345, 1156, 1034, 730. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.02-6.88 (2×2H, *m*), 6.50 (2×1H, *t*, *J* = 7.5 Hz), 6.26 (2×1H, *d*, *J* = 7.5 Hz), 4.38 (2×1H, *brs*), 3.00 (2×3H, *s*), 2.70-2.58 (2×1H, *m*), 2.51-2.33 (2×2H, *m*), 2.41 (2×3H, *s*), 2.04-1.91 (2×1H, *m*). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 153.00, 132.95, 128.14, 123.70, 116.71, 105.90, 92.03, 62.74, 52.72, 38.03, 35.52, 35.39. EI-MS *m*/*z* (%) : 374 (M^+, 11%), 273 (2), 187 (45), 186 (100), 172 (9), 157 (8), 145 (14), 144 (31), 130 (7), 115 (5), 85 (19), 83 (22). **HRMS** *m*/*z* Found: 374.2480, Calcd. for $C_{24}H_{30}N_4$ $(M)^+$: 374.2470.
($[\alpha]^{20}_{D}$ = +315, *c* 0.10, MeOH, lit.[6o] $[\alpha]^{20}_{D}$ = +318, *c* 0.11, MeOH; lit.[6p] $[\alpha]^{20}_{D}$ = +314, *c* 0.25, MeOH)



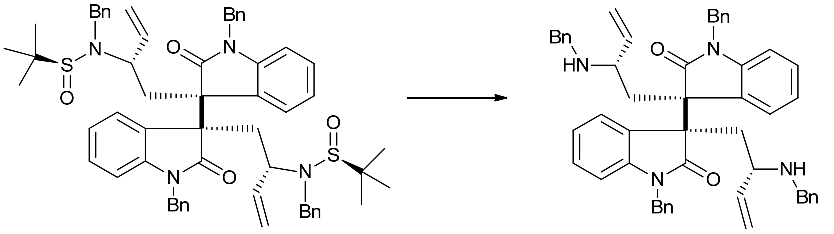
(4b*R*,5*S*,10b*R*,11*S*)-13,18-dimethyl-5,6,11,12-tetrahydro-5,10b:11,4b-bis(epiminoethano)dibenzo[*c*,*h*][2,6]naphthyridine

$C_{22}H_{26}N_4$ Mol. Wt.: 346.47

4: (-)-Calycanthine

To a solution of acetic acid in D_2O (0.43 M, 4 mL) was added chimonanthine **1** (35 mg, 0.1 mmol). The resulting mixture was then stirred at 95 °C for 18 h under an atmosphere of argon. After cooling down to room temperature, the mixture was diluted with dichloromethane (10 mL) and treated with a saturated aqueous solution of sodium bicarbonate (until pH = 8). The combined aqueous phases were back-extracted with dichloromethane (3 × 8 mL). The organic phases were combined and dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the residue was chromatographed on silica gel (Dichloromethane : Methanol : NH_3-H_2O = 500 :10 : 1) to afford the product (**4**, 18 mg, 52%) as a white solid.

m.p.: 232-235 ºC, $[\alpha]^{20}_{D}$ –615 (c 0.15, EtOH). **FTIR** (KBr, thin film) cm^{-1}: 3435, 2968, 1627, 1451, 1047, 744, 608. **^{1}H-NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.01 (2×1H, *d*, *J* = 7.5 Hz), 6.82 (2×1H, *t*, *J* = 7.5 Hz), 6.55 (2×1H, *t*, *J* = 7.5 Hz), 6.28 (2×1H, *d*, *J* = 7.5 Hz), 4.69 (2×1H, *brs*), 4.44 (2×1H, *s*), 3.17 (2×1H, *ddd*, *J* = 5.4, 13.2, 13.2 Hz), 2.70 (2×1H, *dd*, *J* = 4.6, 11.4 Hz), 2.46 (2×3H, *s*), 2.29 (2×1H, *ddd*, *J* = 3.6, 11.4, 11.4 Hz), 1.33 (2×1H, *dd*, *J* = 3.6, 13.2 Hz). **^{13}C-NMR** (75 MHz, $CDCl_3$), δ (ppm): 145.00, 126.88, 124.58, 116.90, 112.36, 71.37, 46.63, 42.50, 35.96, 31.55. EI-MS *m/z* (%) : 347 (M^++H, 31%), 346 (M^+, 100%), 314 (5), 302 (18), 288 (29), 270 (23), 259 (13), 245 (28), 231 (59), 219 (11), 199 (9), 185 (13), 172 (21), 149 (30), 143 (27), 130 (27), 115 (14), 87 (69), 83 (72), 74 (91). **HRMS** *m/z* Found: 346.2149, Calcd. for $C_{22}H_{26}N_4$ $(M)^+$: 346.2157.
($[\alpha]^{20}_{D}$ = –615, *c* 0.15, EtOH, lit.[4a] $[\alpha]^{20}_{D}$ = –612, *c* 0.18, EtOH)



28 $C_{52}H_{50}N_4O_2$
Mol. Wt.: 762.98

21a

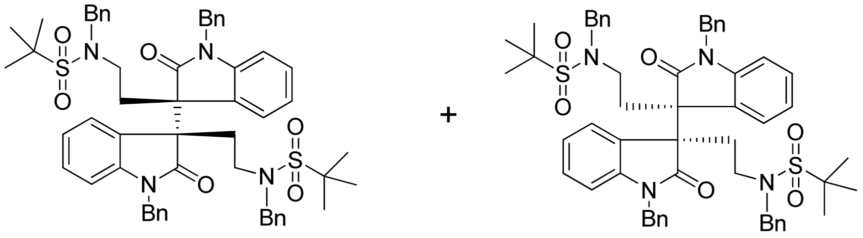
28: (3*S*,3'*S*)-1,1'-dibenzyl-3,3'-bis((*S*)-2-(benzylamino)but-3-en-1-yl)-[3,3'-biindoline]-2,2'-dione

To a solution of sulfinamide **21a** (2.42 g, 2.5 mmol) in methanol (50 mL) was added an aqueous solution of HCl (4N, 1.88 mL, 7.5 mmol, 3 eq.). The resulting mixture was allowed to stir at room temperature for 1 h. The reaction mixture was then treated with saturated aqueous solution of sodium bicarbonate (until pH = 8) and concentrated under reduced pressure. The mixture was diluted with water (80 mL) and extracted with dichloromethane (3 × 50 mL), the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the amine (**28**) (1.81 g, 95%) as a pale yellow syrup.

$[\alpha]^{20}_{D}$ –241 (c 0.18, $CHCl_3$). *ee* = 99.8%, R_f: 0.65 (Petroleum ether: ethyl acetate = 2:1). **FTIR** (KBr, thin film) cm^{-1}: 3454, 3061, 2921, 1699, 1609, 1485, 1361, 742. **^{1}H-NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.23-7.15 (2×5H, *m*), 7.11-7.04 (2×3H, *m*), 6.98 (2×1H, *t*, *J* = 6.8 Hz), 6.97 (2×1H, *d*, *J* = 7.2 Hz), 6.72-6.66 (2×2H, *m*), 6.61 (2×1H, *t*, *J* = 7.2 Hz), 6.35 (2×1H, *t*, *J* = 8.0 Hz), 5.52 (2×1H, *ddd*, *J* = 8.4, 10.0, 17.2 Hz), 5.00 (2×1H, *d*, *J* = 10.0 Hz), 4.75 (2×1H, *d*, *J* = 17.2 Hz), 4.48 (2×1H, *d*, *J* = 15.6 Hz), 4.42 (2×1H, *d*, *J* = 15.6 Hz), 3.50 (2×1H, *d*, *J* = 13.2 Hz), 3.33 (2×1H, *dd*, *J* = 4.0, 13.6 Hz), 3.01 (2×1H, *d*, *J* = 13.2 Hz), 2.54 (2×1H, *ddd*, *J* = 4.0, 8.6, 10.8 Hz), 2.40 (2×1H, *dd*, *J* = 10.8, 13.6 Hz), 0.91 (2×1H, *brs*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 179.28, 143.86, 140.53, 140.01, 136.12, 128.44, 128.07, 128.02, 127.87, 127.70, 127.31, 126.32, 124.88, 121.36, 115.53, 108.44, 57.58, 54.78, 50.31, 44.45, 34.85. +TOF-MS *m/z* (%) : 763 (M^++1, 100%), 382 (15), 275 (2), 236 (20). **HRMS** *m/z* Found: 763.4015, Calcd. for $C_{52}H_{51}N_4O_2$ $(M+H)^+$: 763.4012.

(**28** racemic) Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel AD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / iso-propanol 90 / 10; flow rate: 0.600 mL/min; detection, UV 254 nm; $tR_1 = 11.693$ min, Area = 49.2003; $tR_2 = 24.015$ min, Area = 50.7997.

(**28**) Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel AD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / iso-propanol 90 / 10; flow rate: 0.600 mL/min; detection, UV 254 nm; $tR_1 = 11.769$ min, Area = 0.1004; $tR_2 = 24.349$ min, Area = 99.8996.

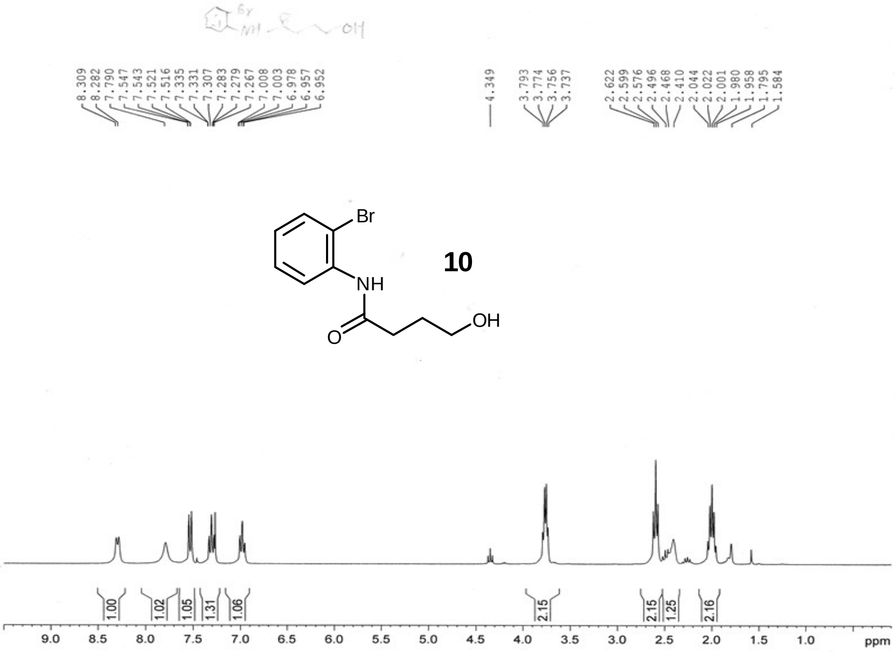


^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.45 (2×2H, *d*, *J* = 7.2 Hz), 7.36 (2×2H, *t*, *J* = 7.2 Hz), 7.33-7.24 (2×4H, *m*), 7.14-7.08 (2×2H, *m*), 6.81 (2×1H, *t*, *J* = 7.6 Hz), 6.59 (2×1H, *d*, *J* = 7.2 Hz), 6.49 (2×1H, *t*, *J* = 7.6 Hz), 6.25 (2×1H, *d*, *J* = 8.0 Hz), 5.02 (2×1H, *d*, *J* = 15.6 Hz), 4.72-4.55 (2×1H, *m*), 4.48-4.32 (2×1H, *m*), 4.27 (2×1H, *d*, *J* = 15.6 Hz), 3.27-3.14 (2×1H, *m*), 2.69-2.54 (2×1H, *m*), 2.46-2.31 (2×2H, *m*), 1.41 (2×9H, *s*). **^{13}C-NMR** (100 MHz, $CDCl_3$), δ (ppm): 176.32, 142.37, 136.18, 135.44, 129.09, 128.91, 128.65, 128.49, 127.87, 127.78, 127.65, 126.38, 123.56, 122.11, 108.57, 61.60, 54.13, 51.89, 43.90, 43.43, 27.04, 24.96. **HRMS** *m*/*z* Found: 951.4199, Calcd. for $C_{42}H_{41}N_6O_4$ $(M+H)^+$: 951.4189.

(Racemic sample) Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel AD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / iso-propanol 85 / 15; flow rate: 0.800 mL/min; detection, UV 254 nm; $tR_1 = 9.824$ min, Area = 49.9388; $tR_2 = 16.856$ min, Area = 50.0612.

Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel AD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / iso-propanol 85 / 15; flow rate: 0.800 mL/min; detection, UV 254 nm; $tR_1 = 9.840$ min, Area = 83.8872; $tR_2 = 16.982$ min, Area = 16.1128. ee = 67.8%.

Chiral HPLC analysis: 25 °C; column: DAICEL Chiralcel AD-H (0.46 cm Φ × 25 cm); mobile phase: hexane / iso-propanol 85 / 15; flow rate: 0.800 mL/min; detection, UV 254 nm; $tR_1 = 9.813$ min, Area = 17.5101; $tR_2 = 16.763$ min, Area = 82.4899. ee = 65%.



10

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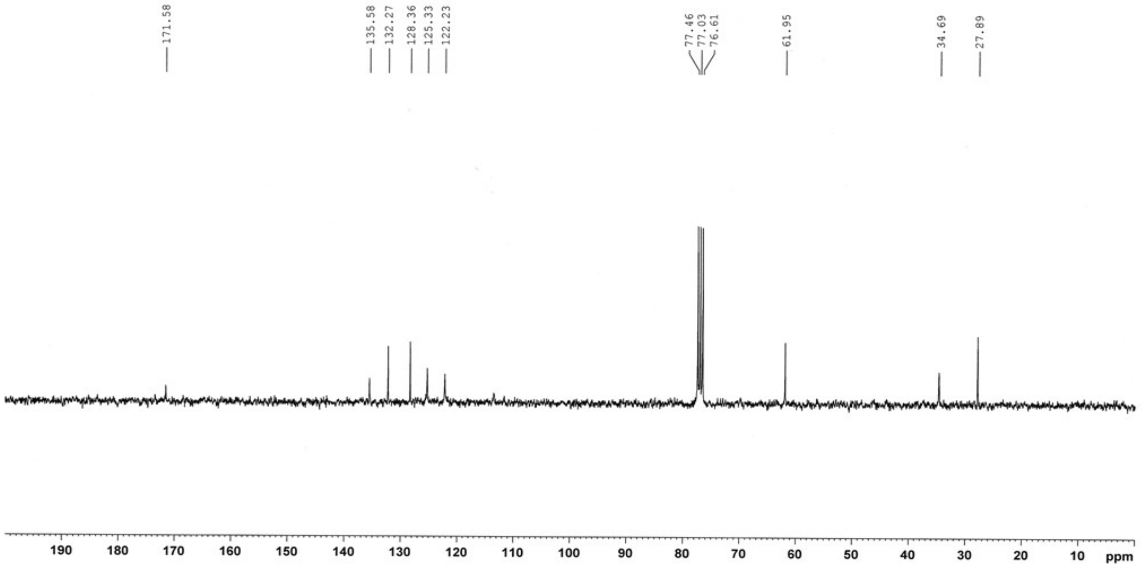

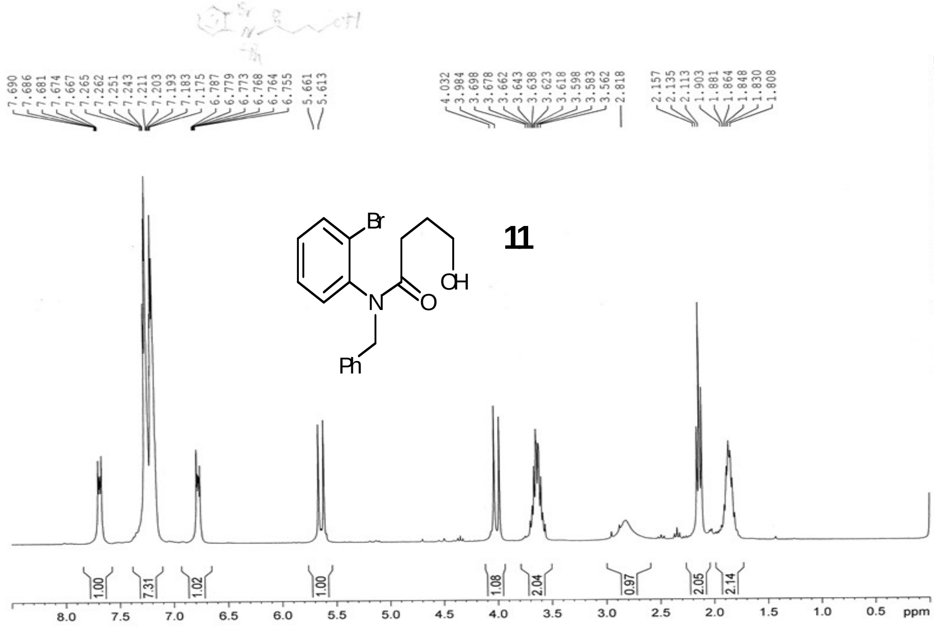

11

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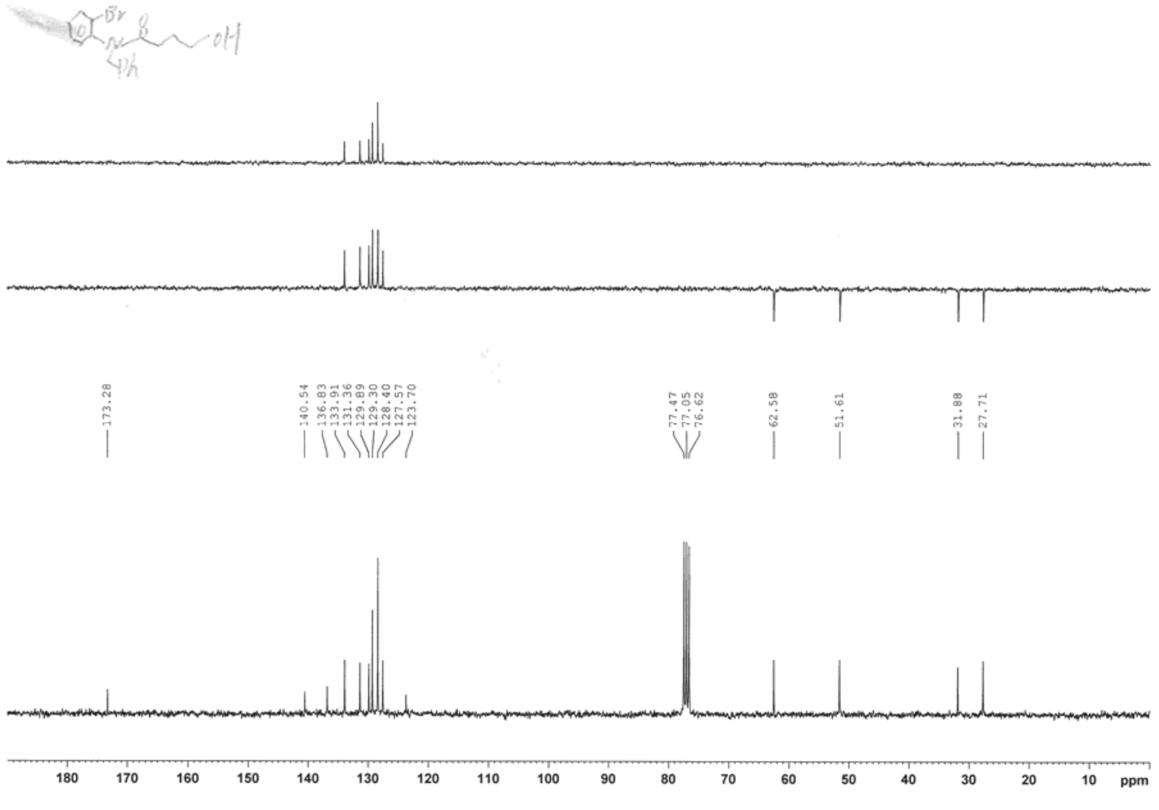

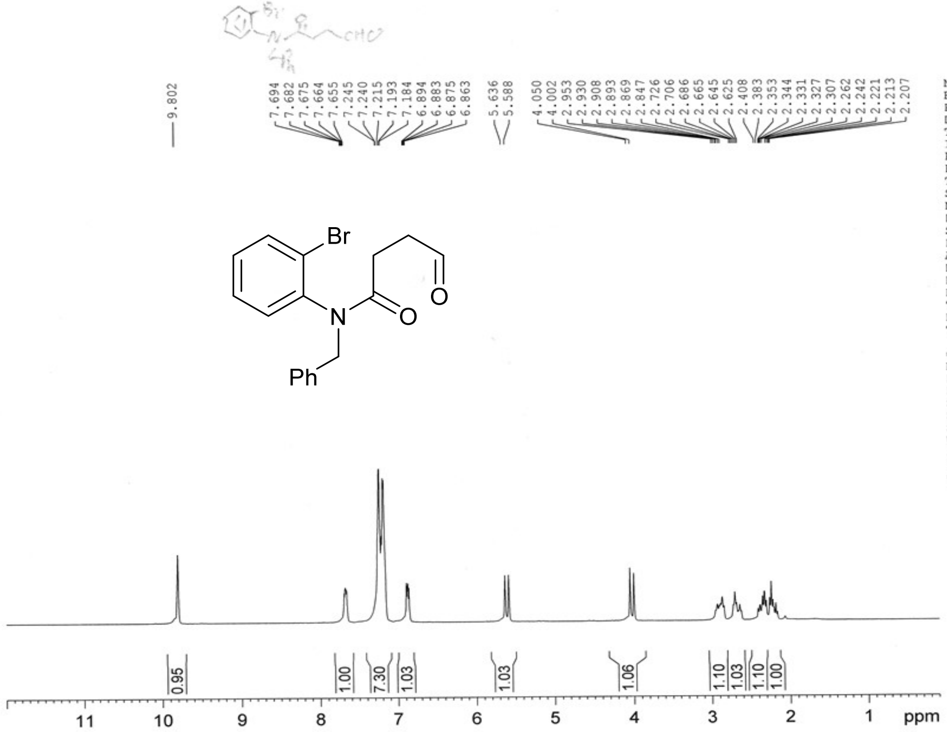

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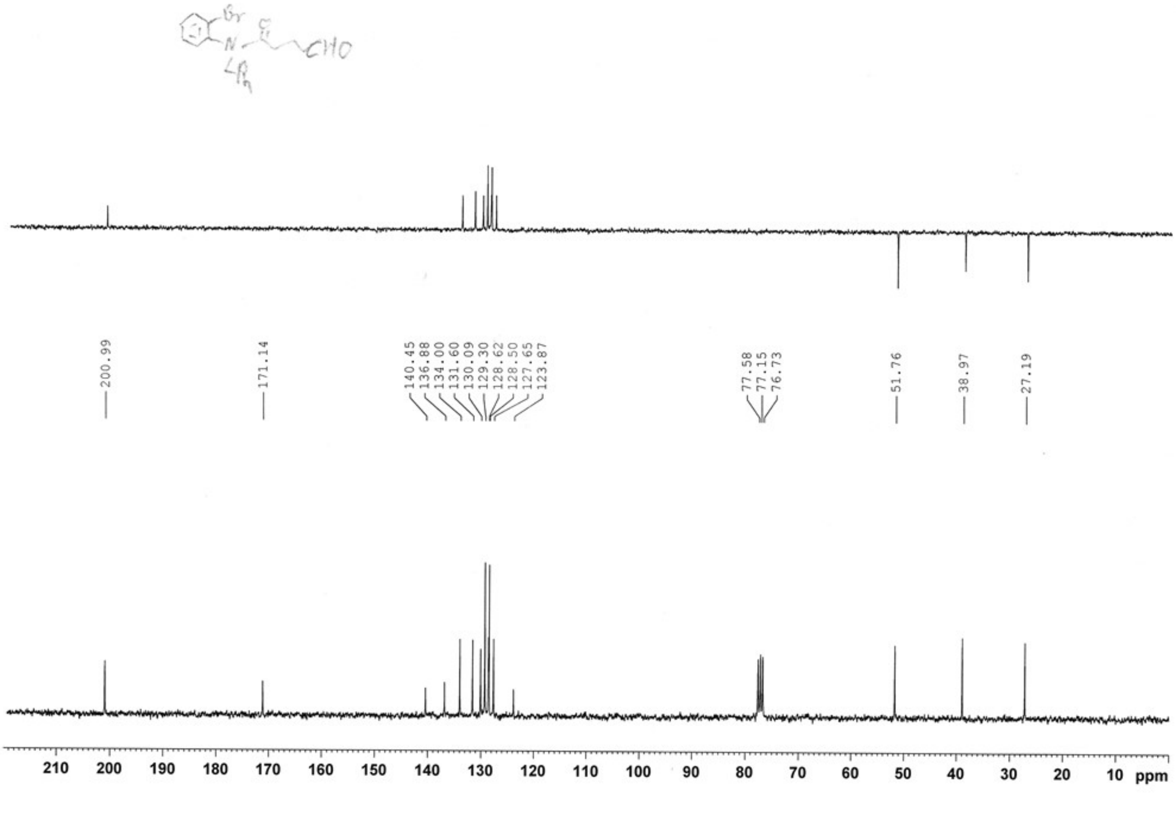

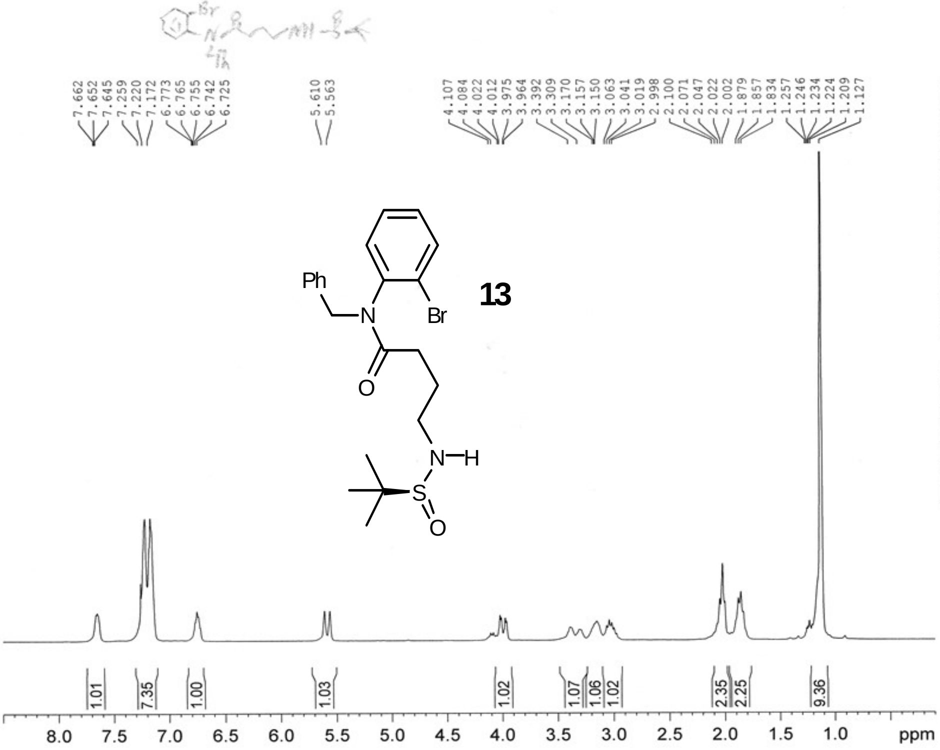

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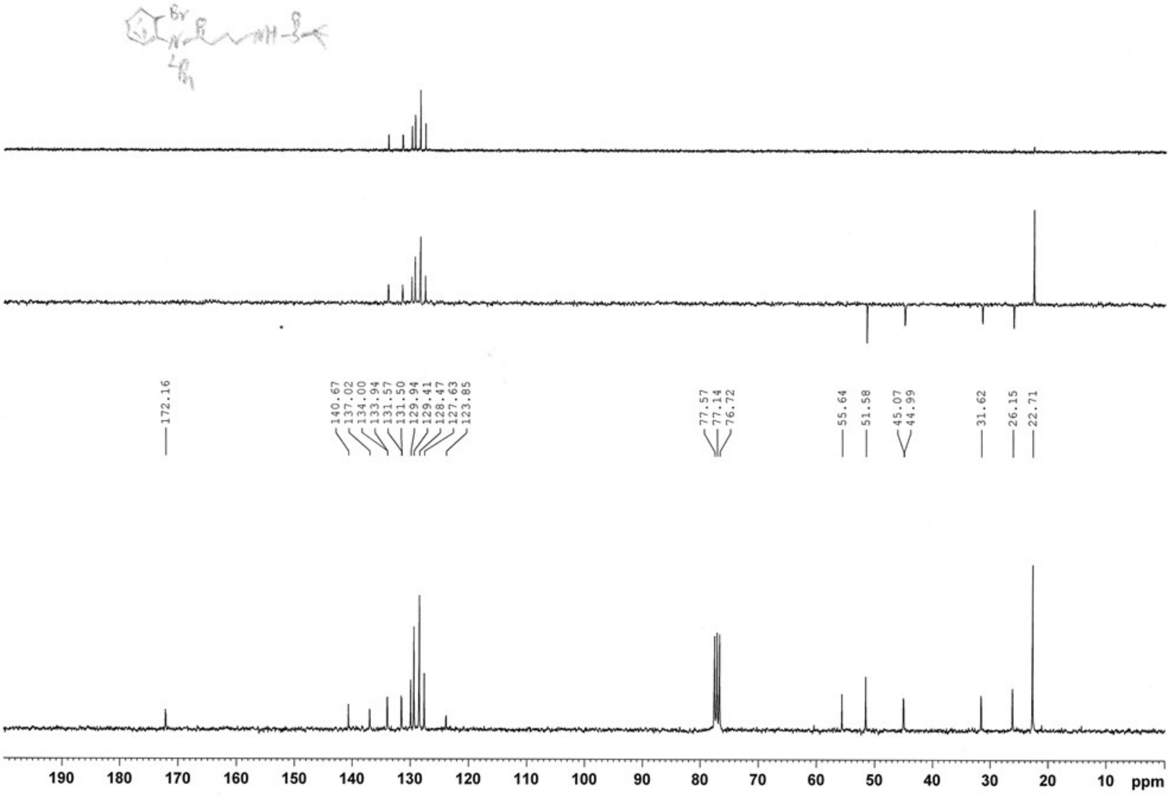

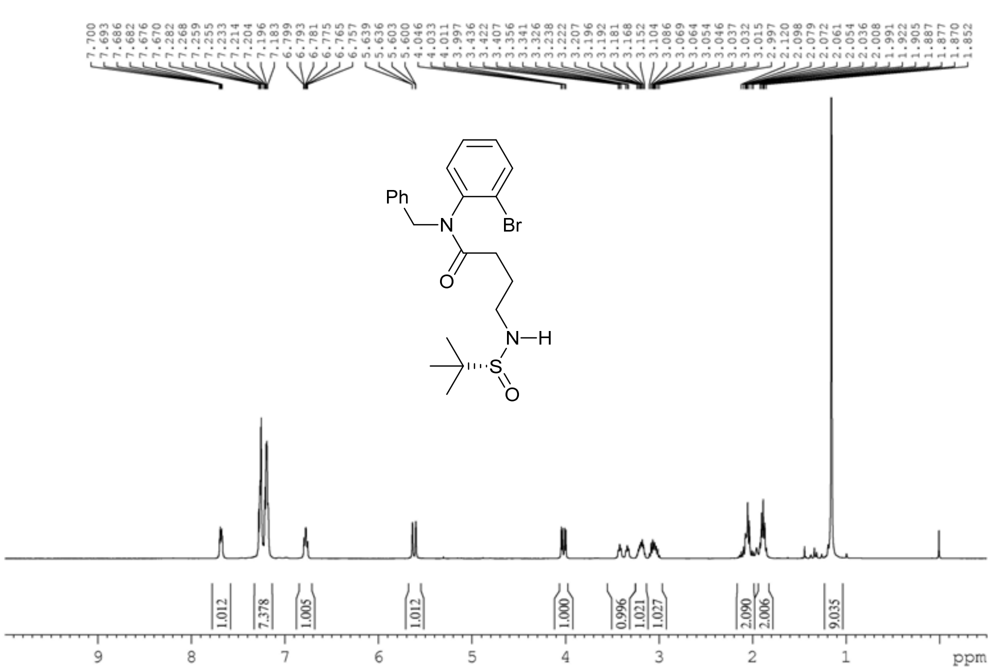

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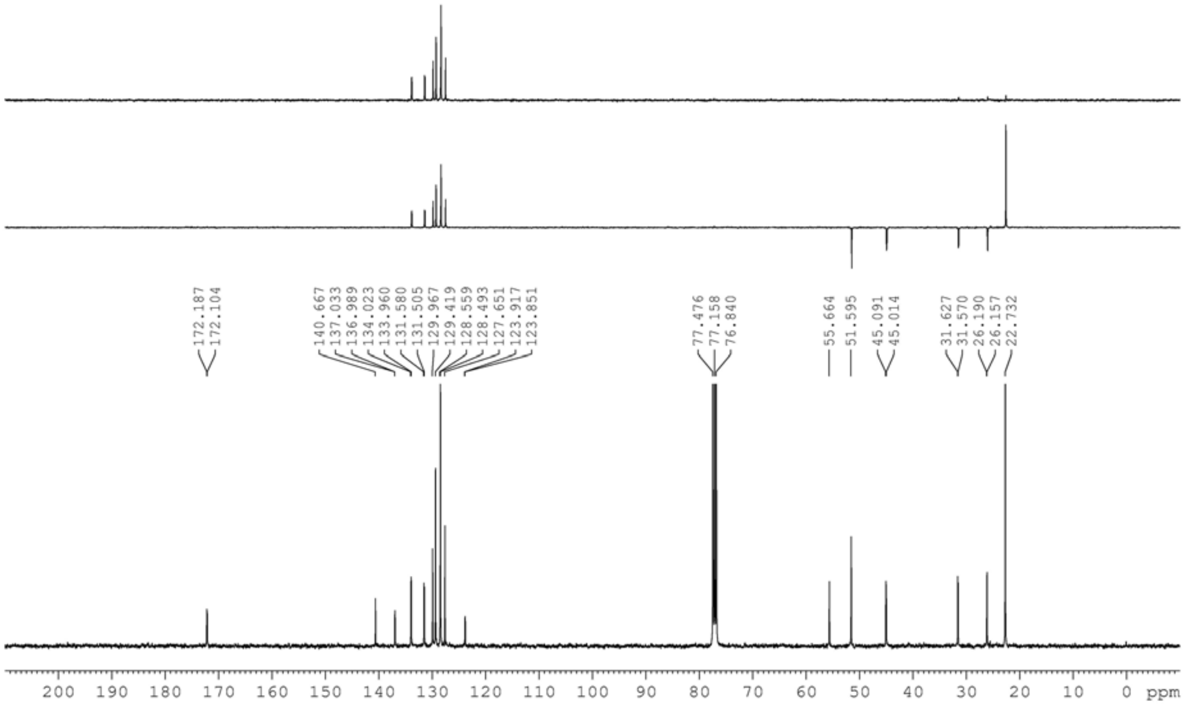

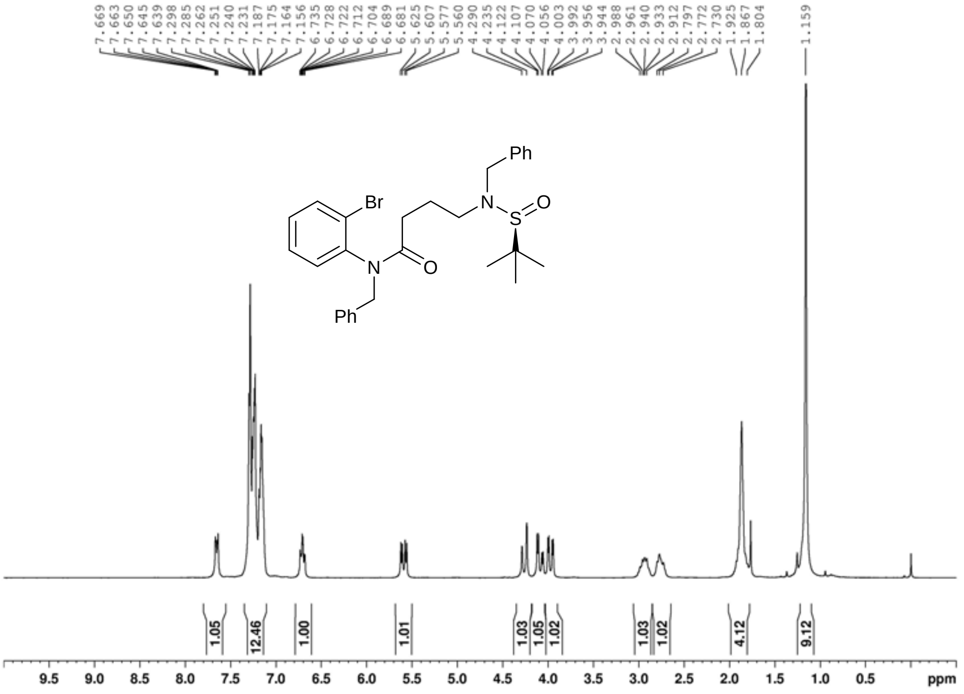

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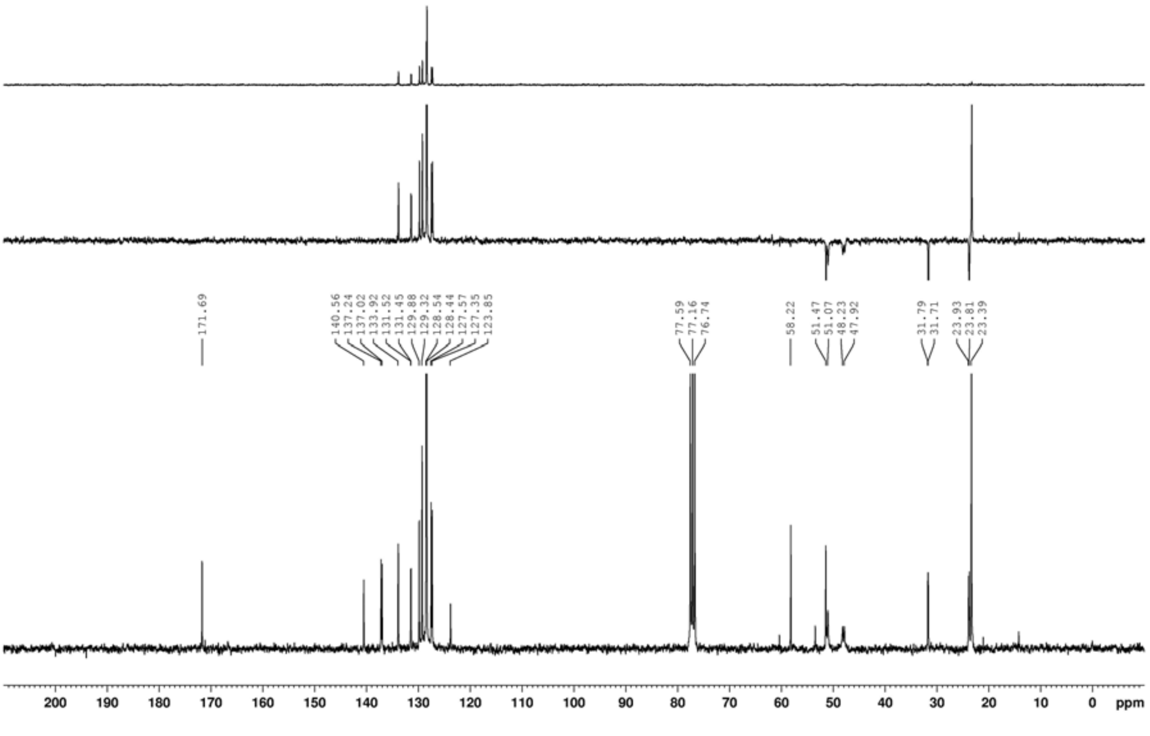

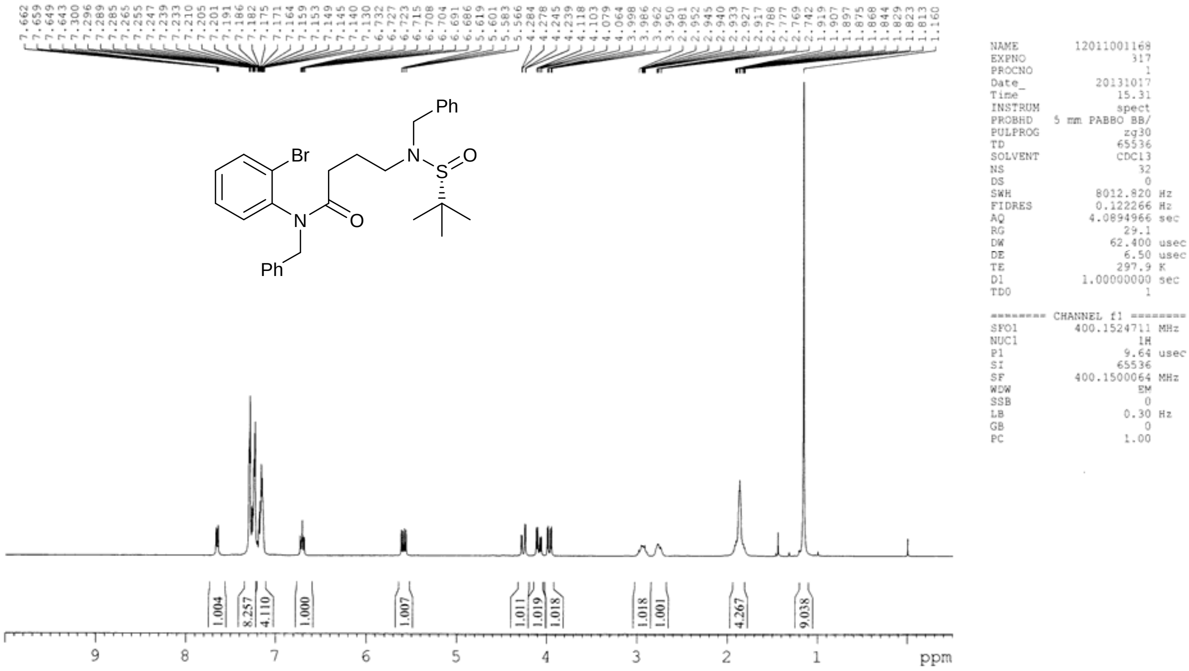

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TE                    297.9 K
D1               1.00000000 sec
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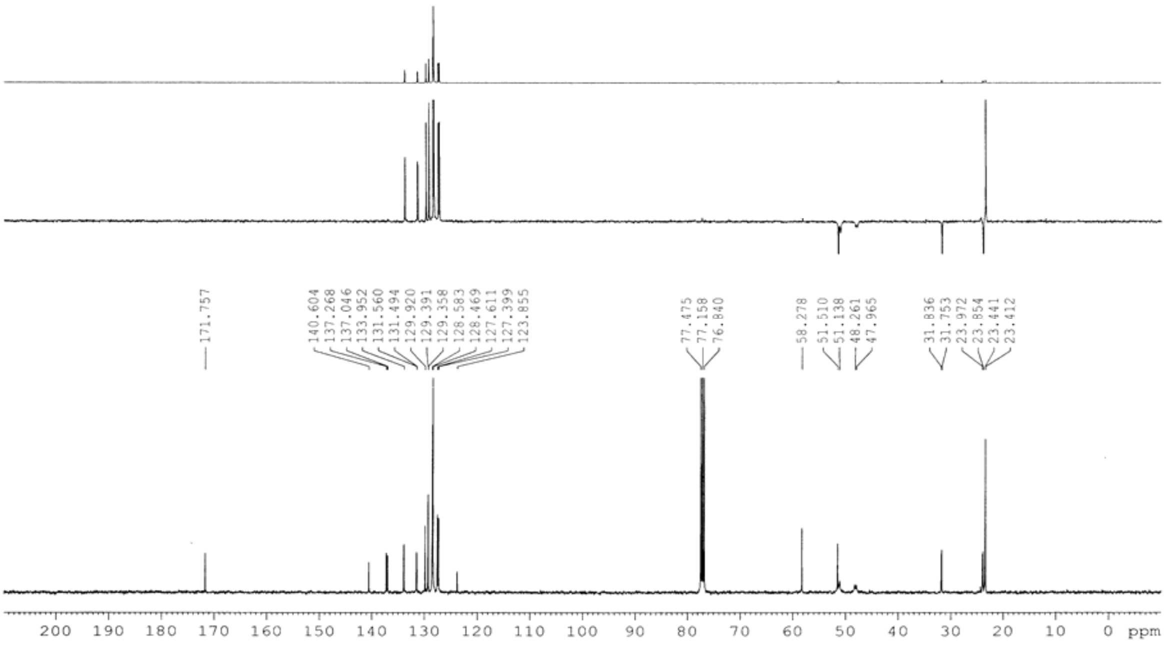
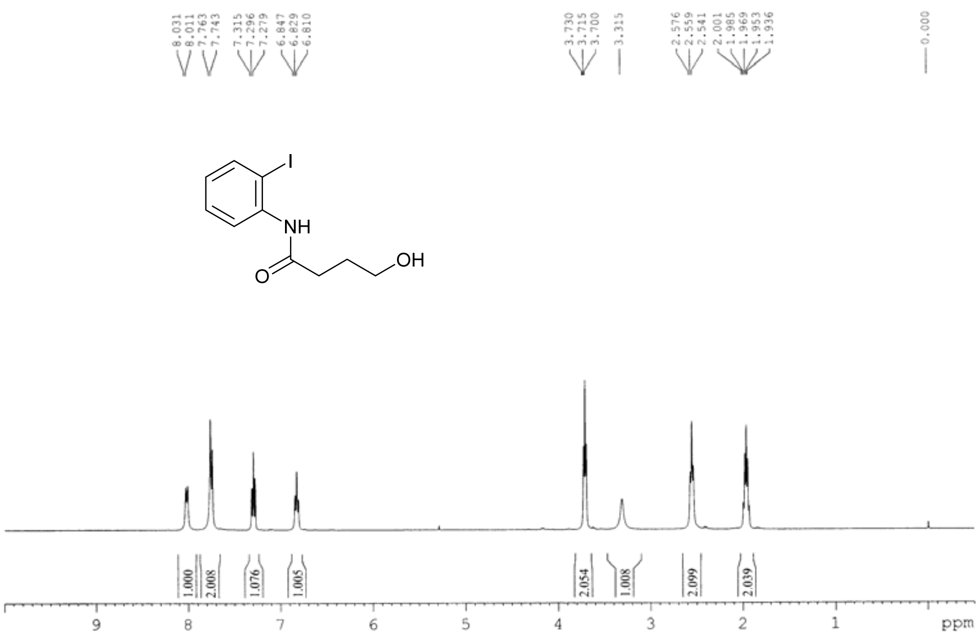
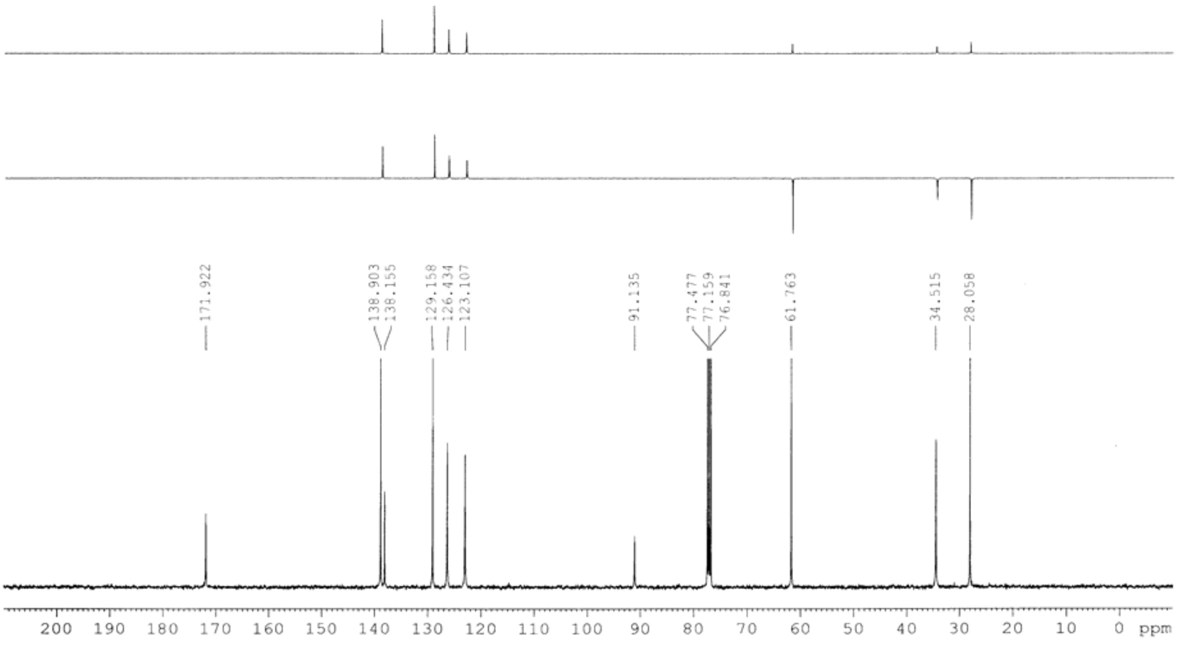
PC                     1.00
```

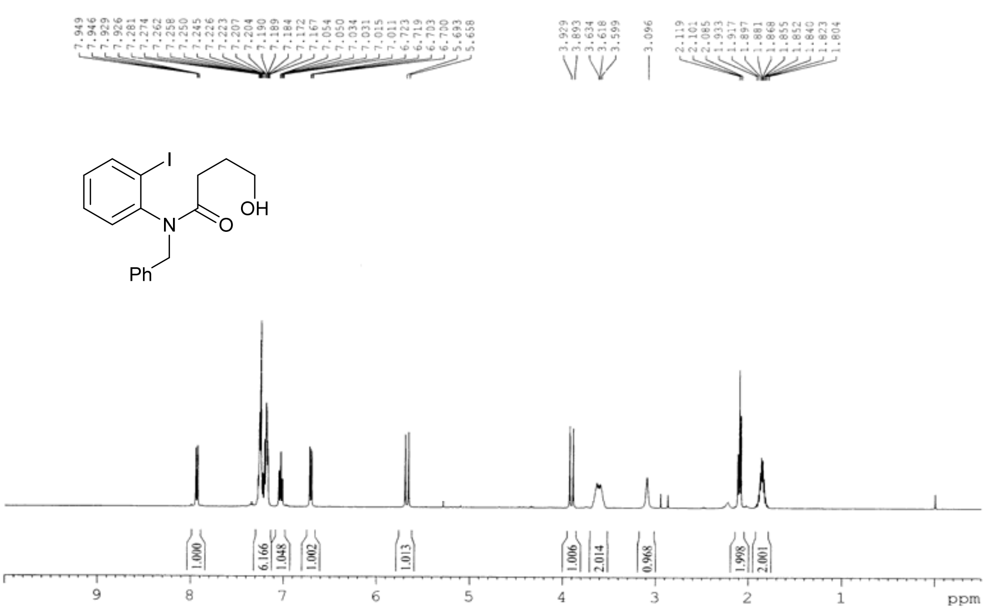




```
NAME          12011001168
EXPNO                 751
PROCNO                  1
Date_            20140401
Time                 9.56
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                   29.1
DW                 75.733 usec
DE                   6.50 usec
TE                  294.1 K
D1             1.00000000 sec
TD0                     1

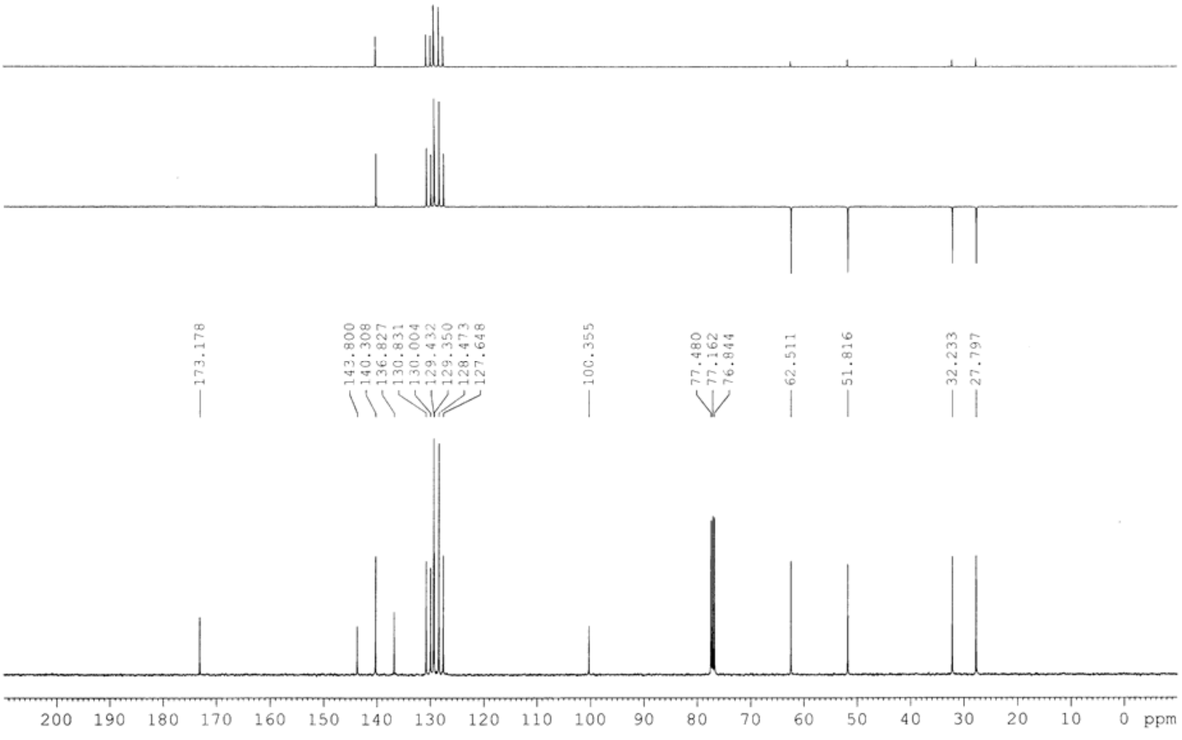
======== CHANNEL f1 ========
SFO1          400.1526964 MHz
NUC1                   1H
P1                   9.64 usec
SI                  65536
SF            400.1500011 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

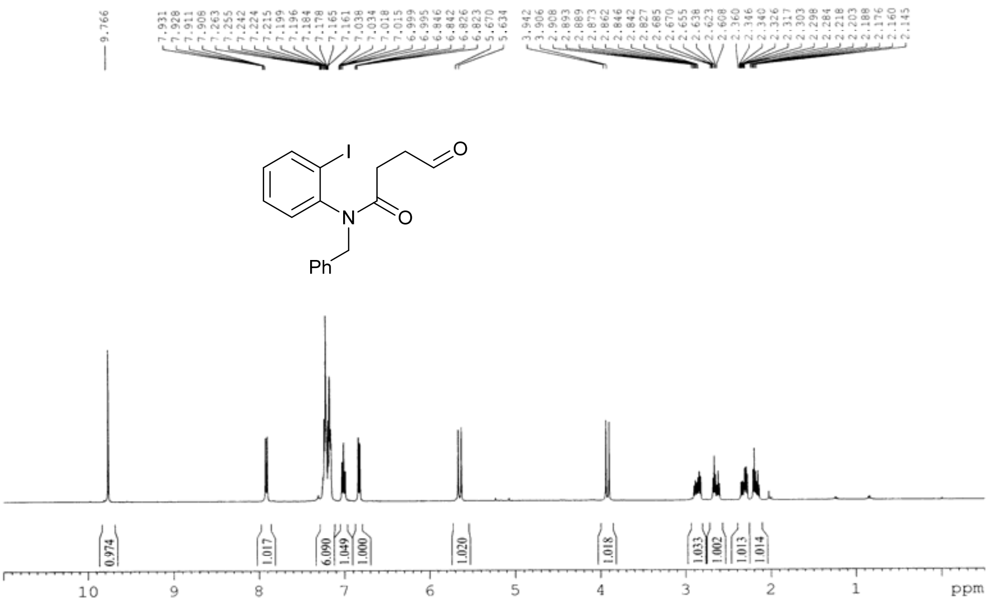




```
NAME          12011001168
EXPNO                 755
PROCNO                  1
Date_            20140401
Time                10.37
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                   29.1
DW                 75.733 usec
DE                   6.50 usec
TE                  294.2 K
D1             1.00000000 sec
TD0                     1

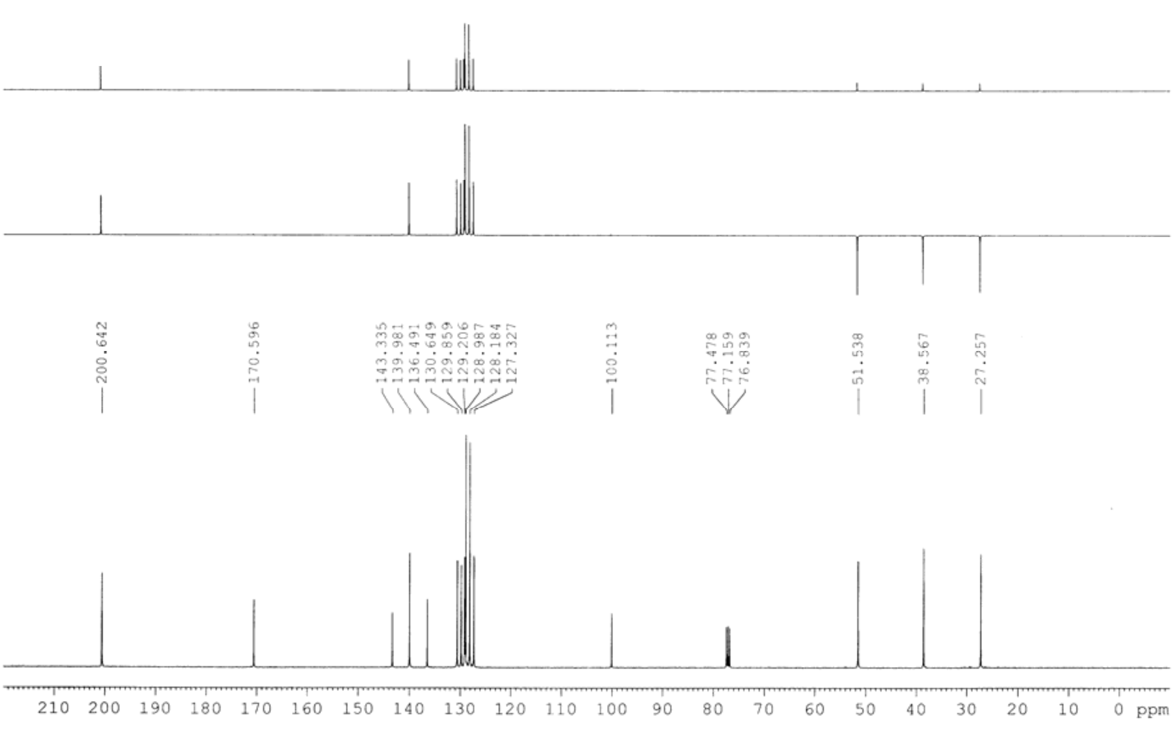
======== CHANNEL f1 ========
SFO1          400.1526964 MHz
NUC1                   1H
P1                   9.64 usec
SI                  65536
SF            400.1500030 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

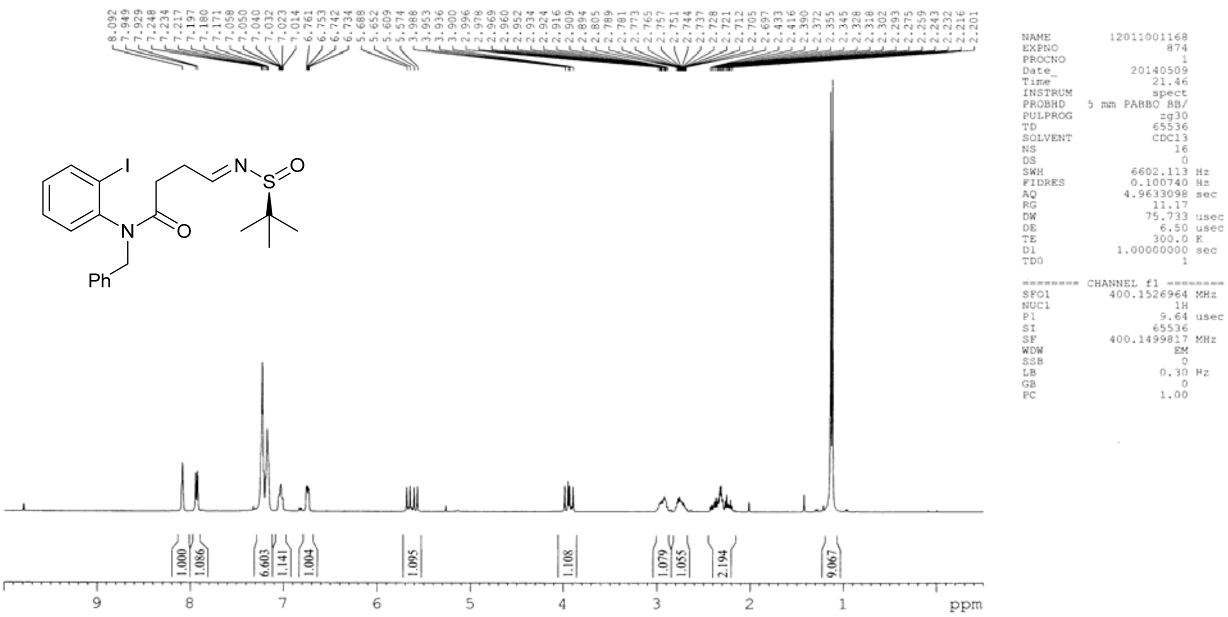


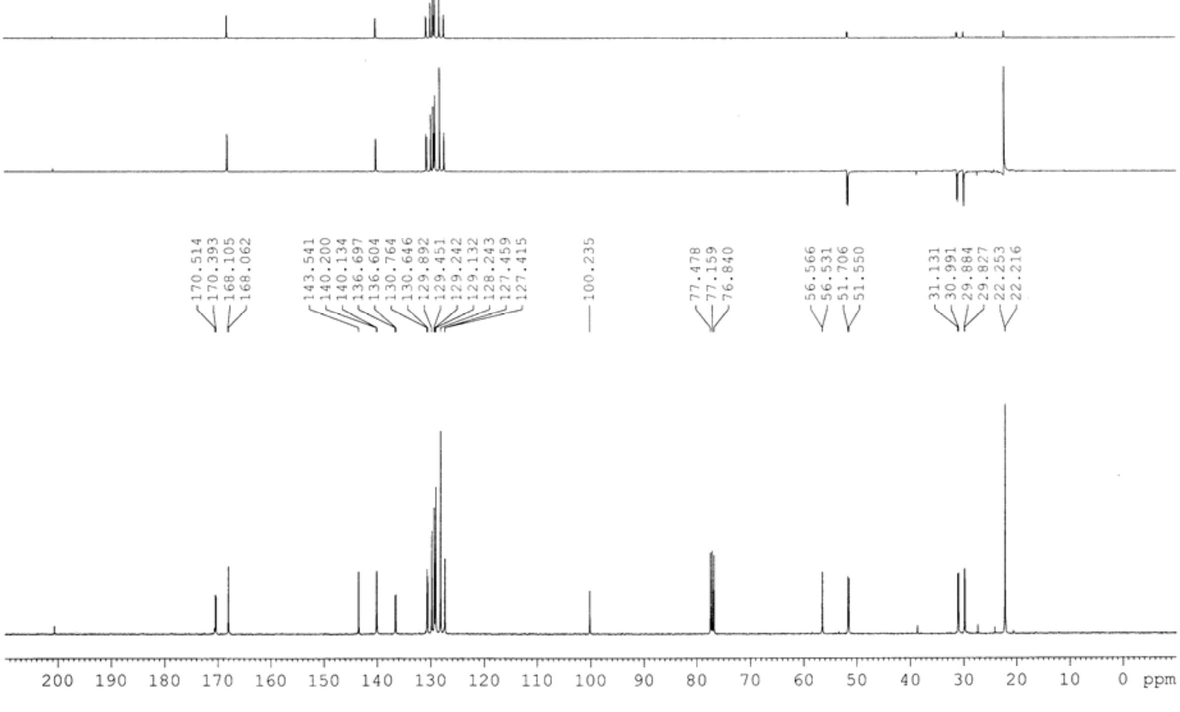


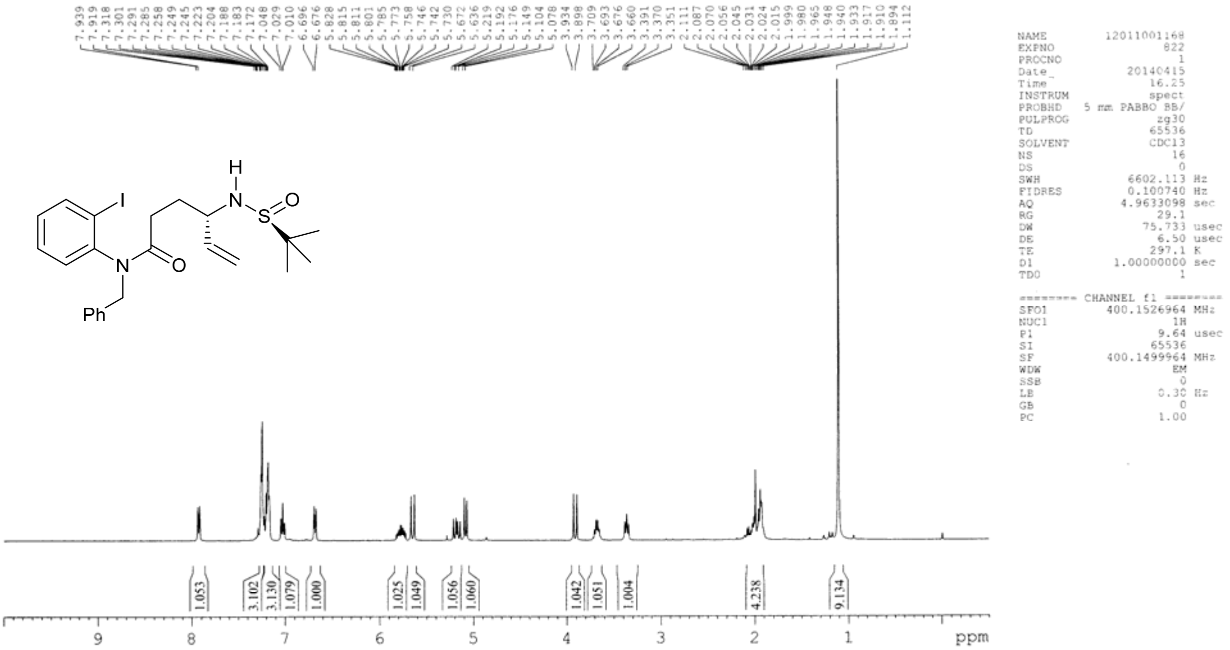
```
NAME          12011001168
EXPNO                 759
PROCNO                  1
Date_            20140401
Time                16.51
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                   9.73
DW                 75.733 usec
DE                   6.50 usec
TE                  294.4 K
D1             1.00000000 sec
TD0                     1

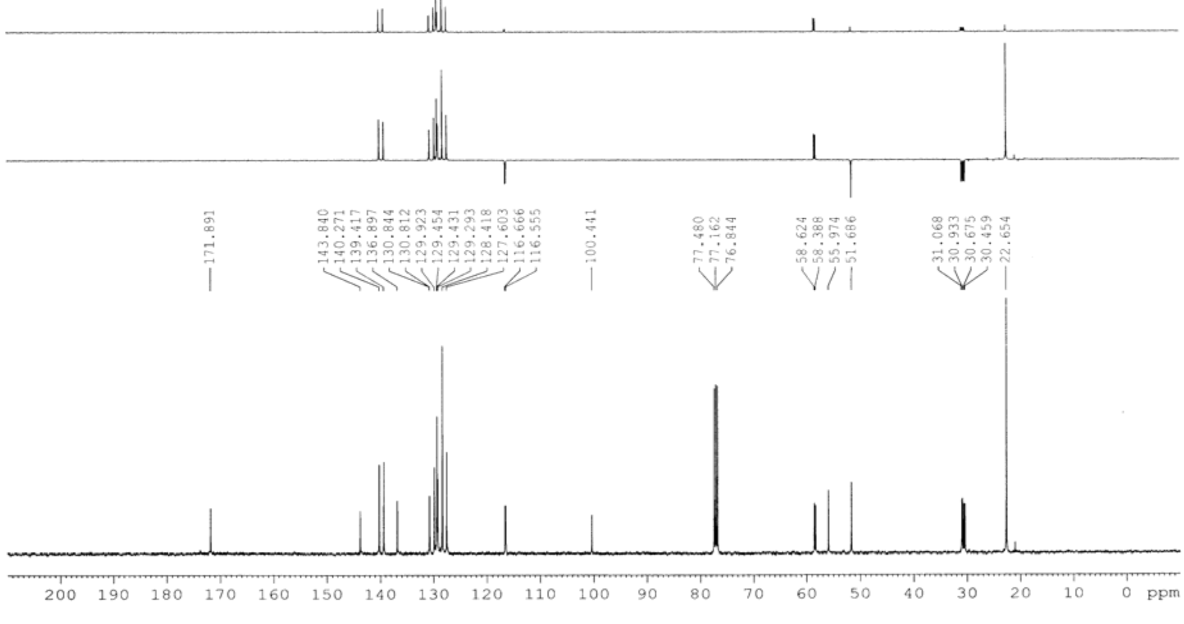
======== CHANNEL f1 ========
SFO1          400.1526964 MHz
NUC1                   1H
P1                   9.64 usec
SI                  65536
SF            400.1499883 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

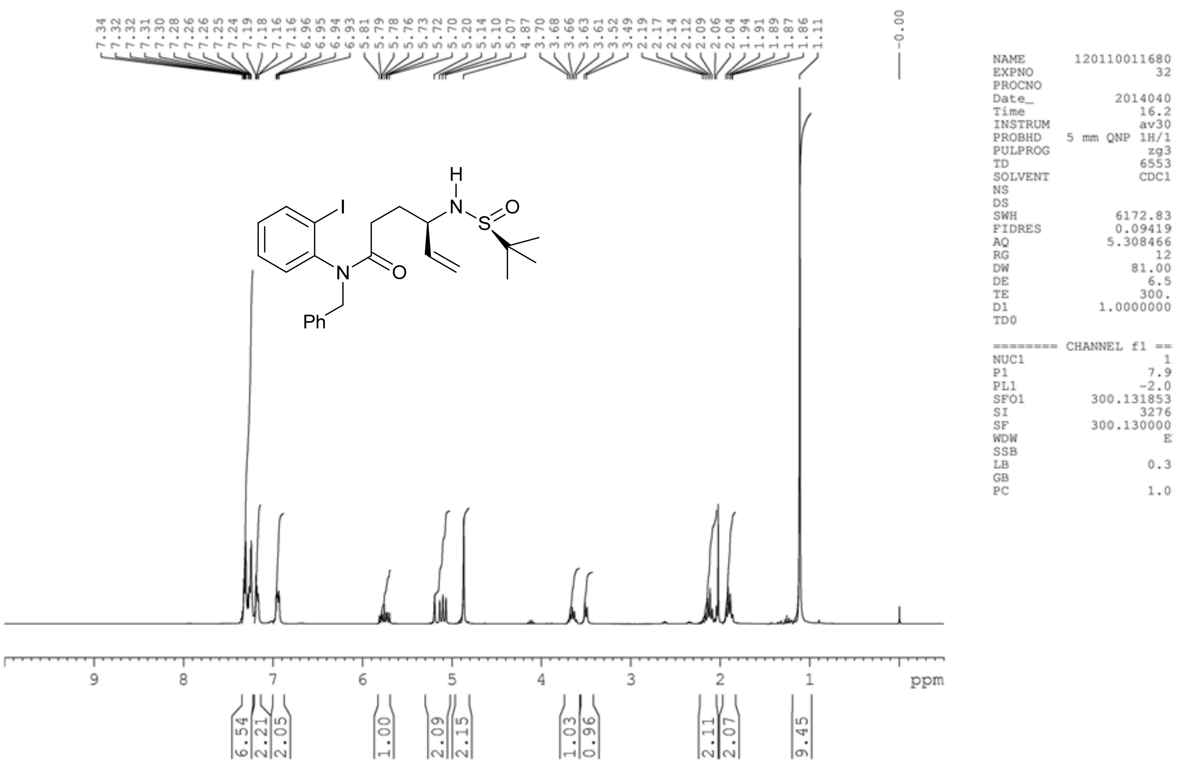



8.092
7.949
7.929
7.248
7.234
7.217
7.197
7.180
7.171
7.058
7.050
7.040
7.032
7.023
7.014
6.761
6.753
6.742
6.734
5.688
5.652
5.609
5.574
3.988
3.953
3.936
3.900
2.996
2.978
2.969
2.960
2.952
2.934
2.924
2.916
2.909
2.894
2.805
2.789
2.781
2.773
2.765
2.757
2.751
2.744
2.737
2.728
2.721
2.712
2.705
2.697
2.433
2.416
2.390
2.372
2.355
2.345
2.328
2.318
2.302
2.293
2.275
2.259
2.243
2.232
2.216
2.201
I
N
S
O
O
N
Ph
NAME 12011001168
EXPNO 874
PROCNO 1
Date_ 20140509
Time 21.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 6602.113 Hz
FIDRES 0.100740 Hz
AQ 4.9633098 sec
RG 11.17
DW 75.733 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1526964 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1499817 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.000
1.086
6.603
1.141
1.004
1.095
1.108
1.079
1.055
2.194
9.067
9
8
7
6
5
4
3
2
1
ppm


170.514
170.393
168.105
168.062
143.541
140.200
140.134
136.697
136.604
130.764
130.646
129.892
129.451
129.242
129.132
128.243
127.459
127.415
100.235
77.478
77.159
76.840
56.566
56.531
51.706
51.550
31.131
30.991
29.884
29.827
22.253
22.216
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

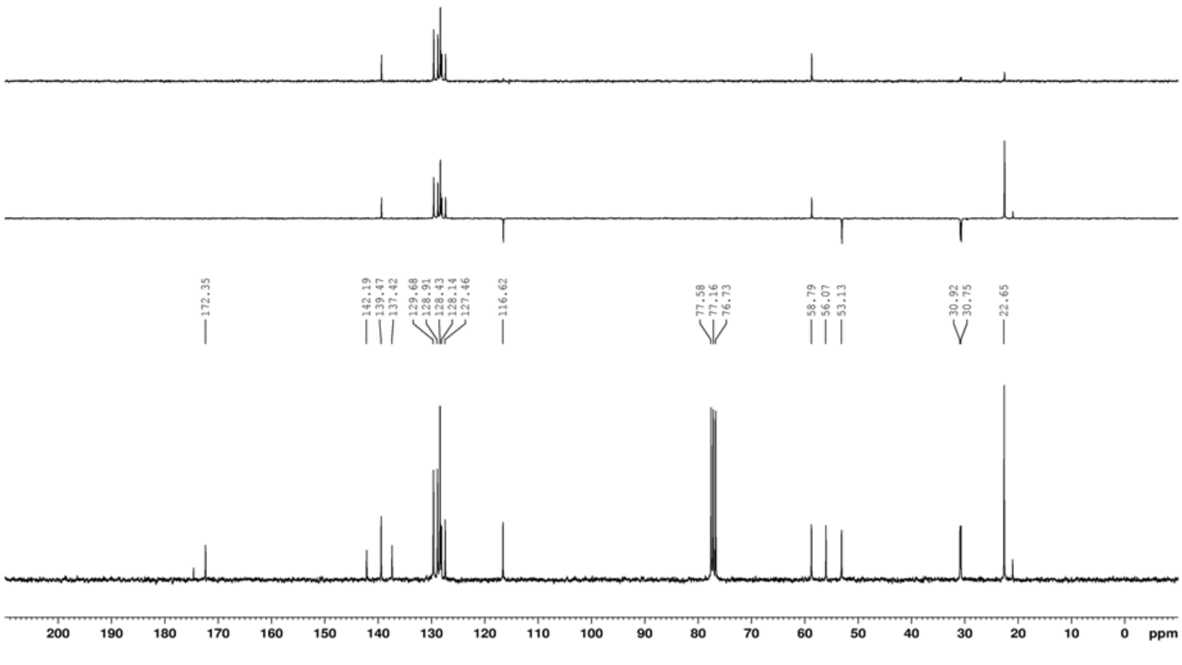

7.939
7.919
7.318
7.301
7.291
7.285
7.258
7.249
7.245
7.223
7.204
7.188
7.183
7.172
7.048
7.029
7.010
6.696
6.676
5.828
5.815
5.811
5.801
5.785
5.773
5.758
5.746
5.742
5.730
5.672
5.636
5.219
5.192
5.176
5.149
5.104
5.078
3.934
3.898
3.709
3.693
3.676
3.660
3.391
3.370
3.351
2.111
2.087
2.070
2.056
2.045
2.031
2.024
2.015
1.999
1.980
1.965
1.948
1.940
1.933
1.917
1.910
1.894
1.112
H
N
S
O
I
N
O
Ph
NAME 12011001168
EXPNO 822
PROCNO 1
Date_ 20140415
Time 16.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 6602.113 Hz
FIDRES 0.100740 Hz
AQ 4.9633098 sec
RG 29.1
DW 75.733 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1526964 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1499964 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.053
3.102
3.130
1.079
1.000
1.025
1.049
1.056
1.060
1.042
1.051
1.004
4.238
9.134
9
8
7
6
5
4
3
2
1
ppm

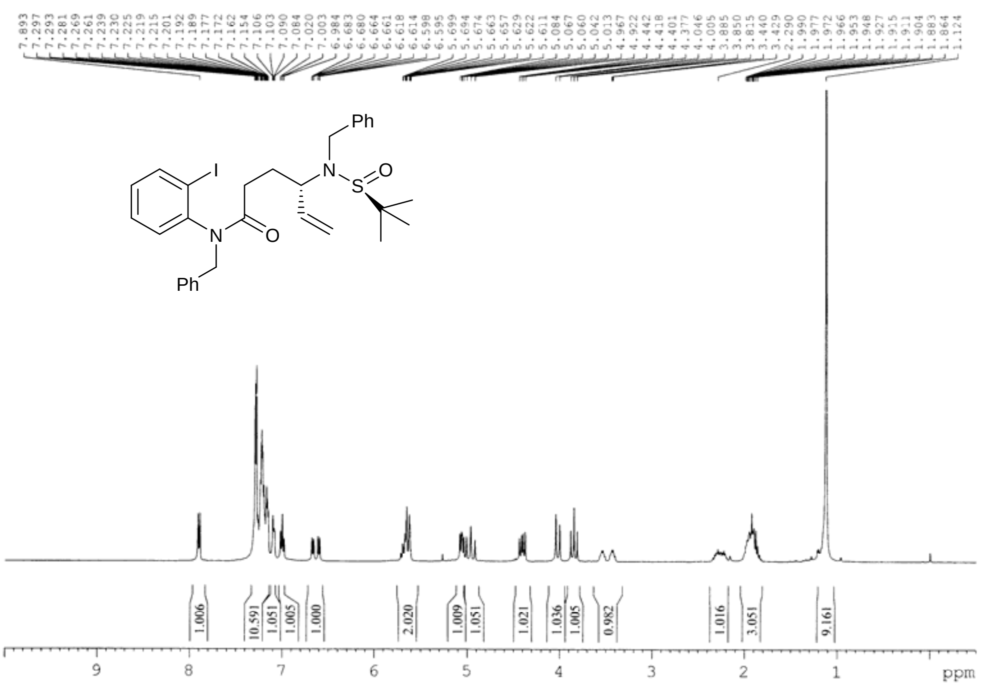

171.891
143.840
140.271
139.417
136.897
130.844
130.812
129.923
129.454
129.431
129.293
128.418
127.603
116.666
116.555
100.441
77.480
77.162
76.844
58.624
58.388
55.974
51.686
31.068
30.933
30.675
30.459
22.654
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



```
NAME         120110011680
EXPNO                  32
PROCNO
Date_             2014040
Time                 16.2
INSTRUM              av30
PROBHD    5 mm QNP 1H/1
PULPROG               zg3
TD                   6553
SOLVENT              CDCl
NS
DS
SWH               6172.83
FIDRES            0.09419
AQ               5.308466
RG                     12
DW                  81.00
DE                    6.5
TE                   300.
D1              1.0000000
TD0

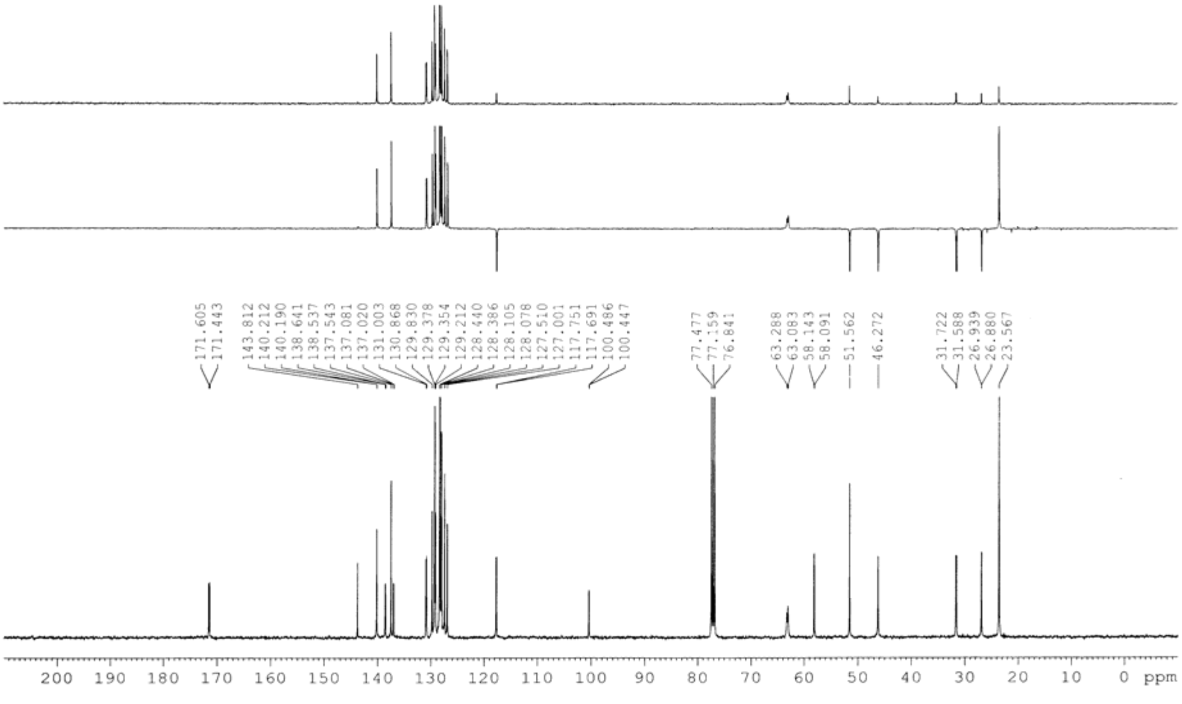
======== CHANNEL f1 ==
NUC1                    1
P1                    7.9
PL1                  -2.0
SFO1           300.131853
SI                   3276
SF             300.130000
WDW                     E
SSB
LB                    0.3
GB
PC                    1.0
```

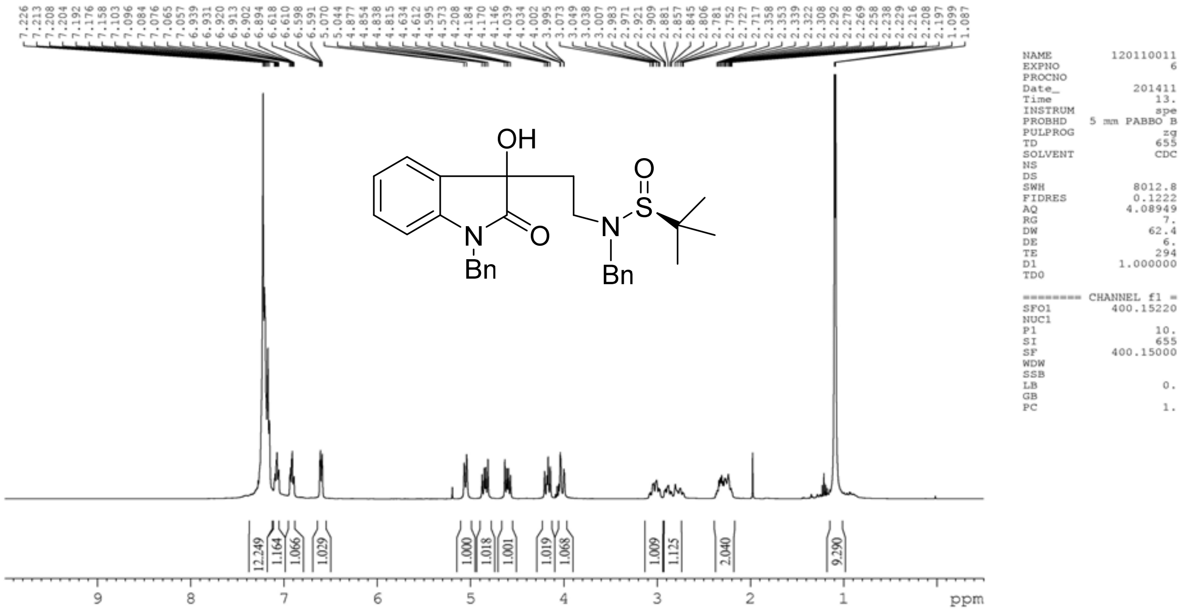


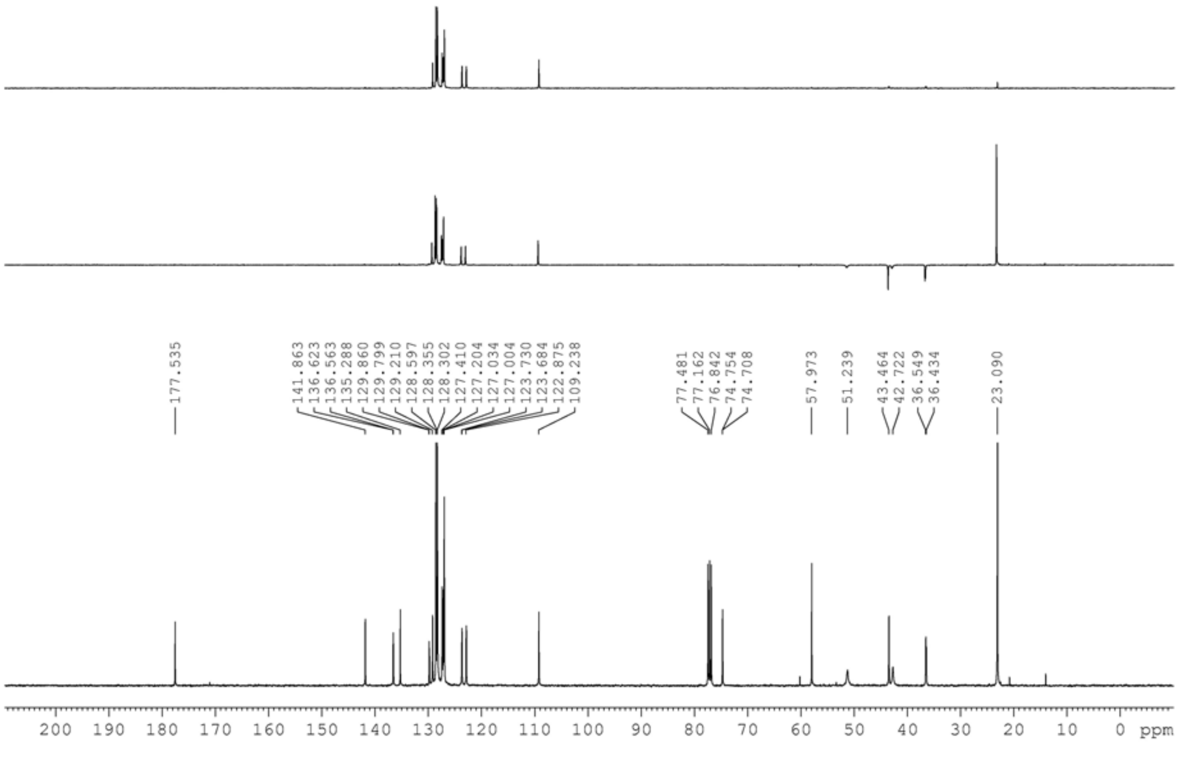


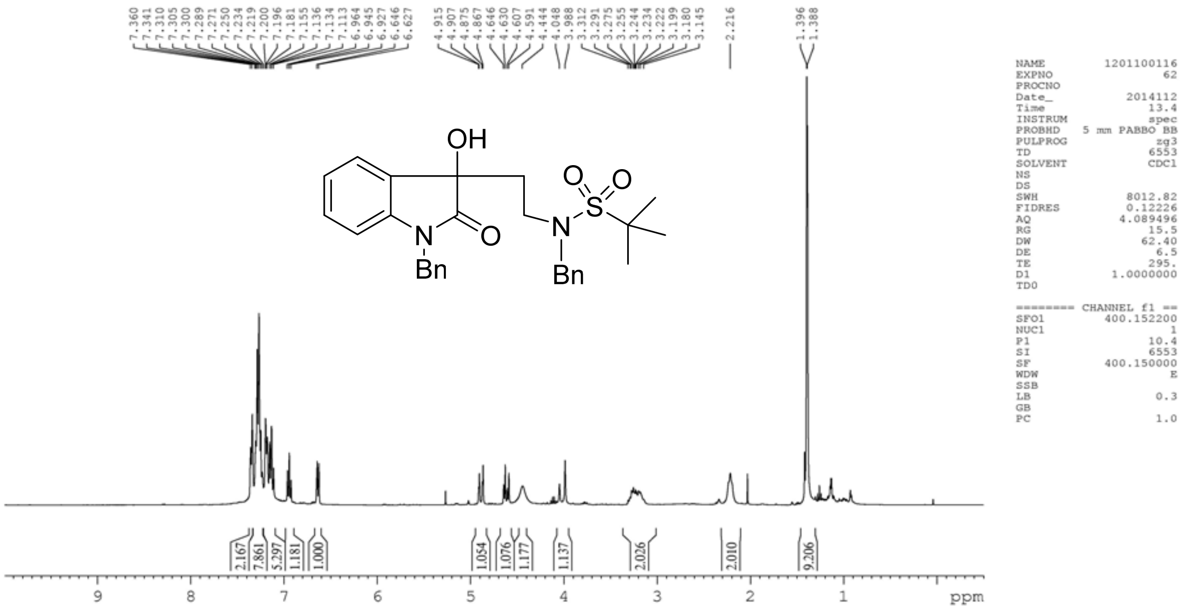
```
NAME          12011001168
EXPNO                 831
PROCNO                  1
Date_            20140418
Time                 3.13
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                     16
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                   20.4
DW                 75.733 use
DE                   6.50 use
TE                  297.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 =======
SFO1          400.1526964 MHz
NUC1                   1H
P1                   9.64 use
SI                  65536
SF            400.1500052 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



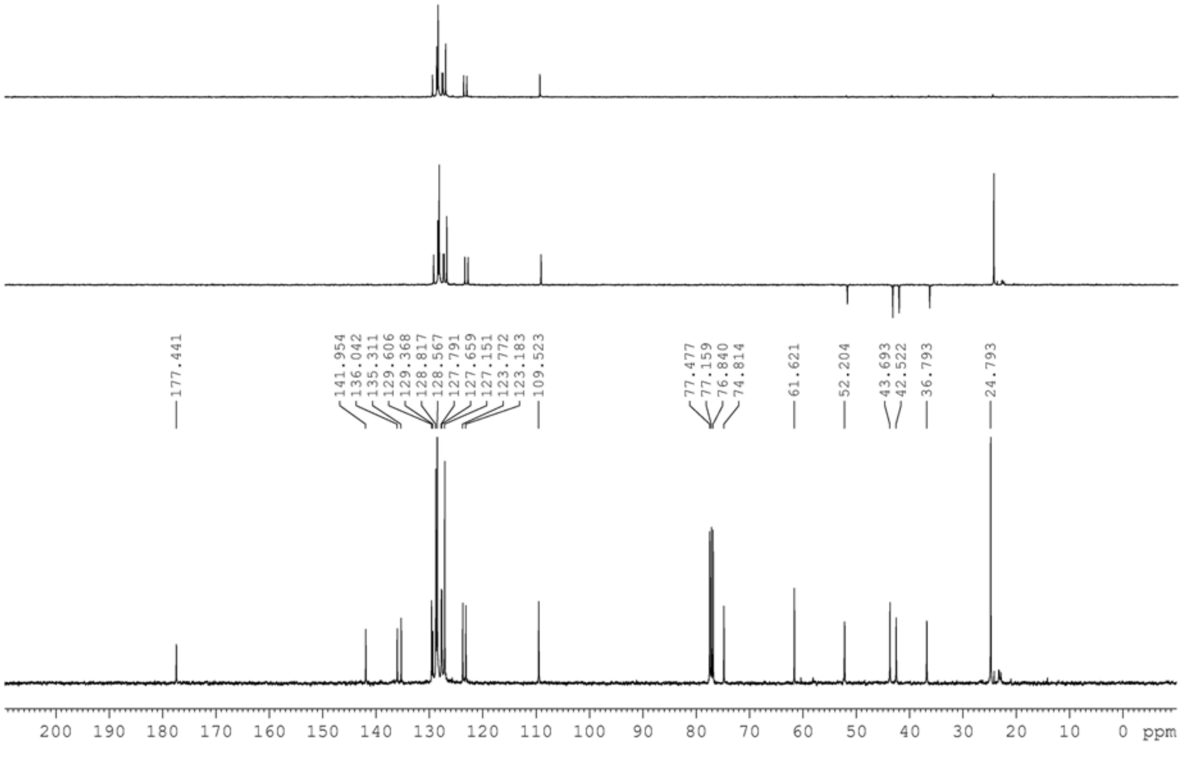

7.226
7.213
7.208
7.204
7.192
7.176
7.158
7.103
7.096
7.084
7.076
7.065
7.057
6.939
6.931
6.920
6.913
6.902
6.894
6.618
6.610
6.598
6.591
5.070
5.044
4.877
4.854
4.838
4.815
4.634
4.612
4.595
4.573
4.208
4.184
4.170
4.146
4.039
4.034
4.002
3.995
3.073
3.049
3.038
3.007
2.983
2.971
2.921
2.909
2.881
2.857
2.845
2.806
2.781
2.752
2.727
2.717
2.358
2.353
2.339
2.322
2.308
2.292
2.278
2.269
2.258
2.238
2.229
2.216
2.208
2.197
1.099
1.087
OH
O
S
N
O
N
Bn
Bn
12.249
1.164
1.066
1.029
1.000
1.018
1.001
1.019
1.068
1.009
1.125
2.040
9.290
9
8
7
6
5
4
3
2
1
ppm
NAME 120110011
EXPNO 6
PROCNO
Date_ 201411
Time 13.
INSTRUM spe
PROBHD 5 mm PABBO B
PULPROG zg
TD 655
SOLVENT CDC
NS
DS
SWH 8012.8
FIDRES 0.1222
AQ 4.08949
RG 7.
DW 62.4
DE 6.
TE 294
D1 1.000000
TD0
======== CHANNEL f1 =
SFO1 400.15220
NUC1
P1 10.
SI 655
SF 400.15000
WDW
SSB
LB 0.
GB
PC 1.

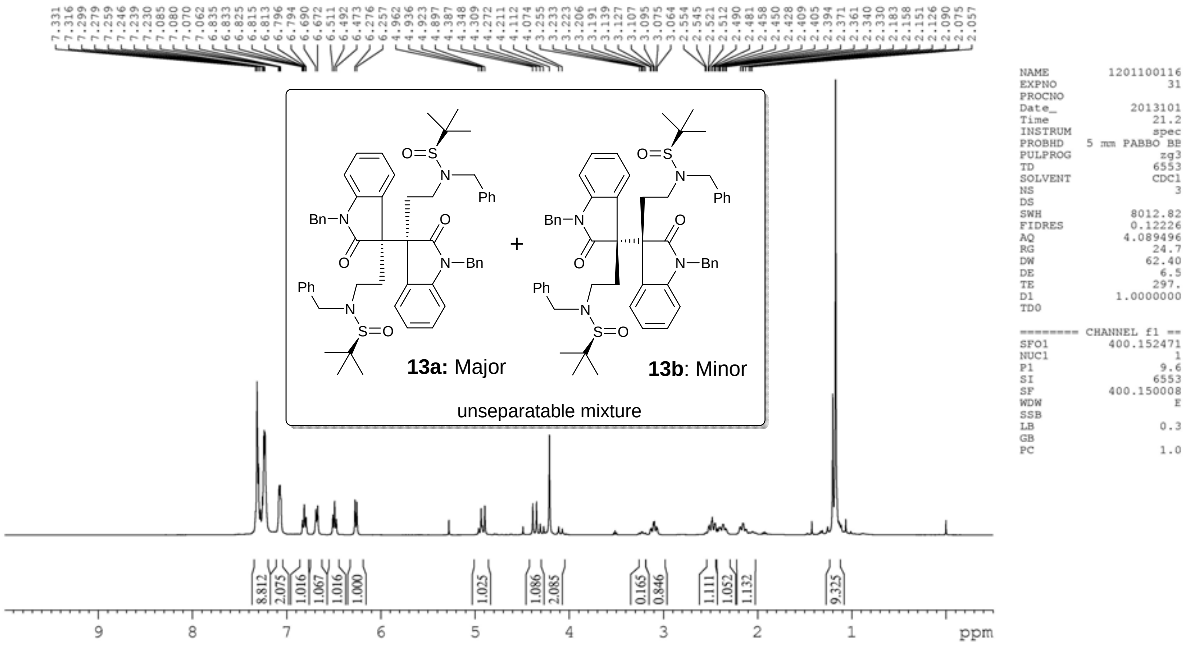

177.535
141.863
136.623
136.563
135.288
129.860
129.799
129.210
128.597
128.355
128.302
127.410
127.204
127.034
127.004
123.730
123.684
122.875
109.238
77.481
77.162
76.842
74.754
74.708
57.973
51.239
43.464
42.722
36.549
36.434
23.090
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

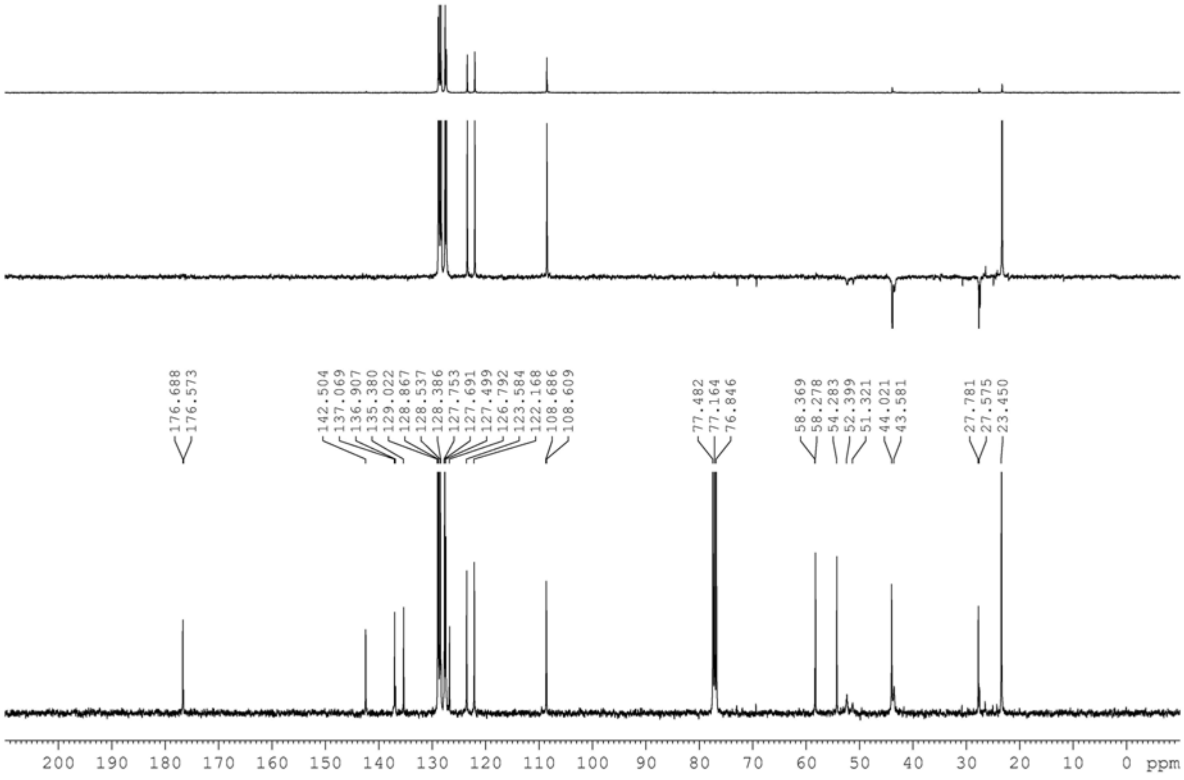


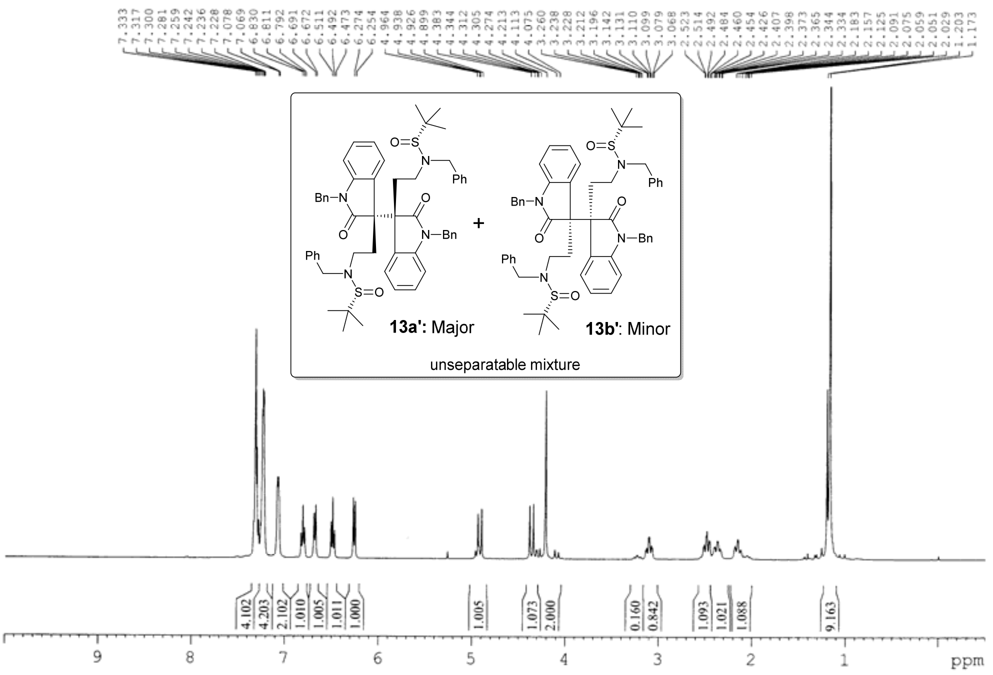
```
NAME        1201100116
EXPNO               62
PROCNO
Date_          2014112
Time              13.4
INSTRUM           spec
PROBHD   5 mm PABBO BB
PULPROG            zg3
TD                6553
SOLVENT           CDCl
NS
DS
SWH            8012.82
FIDRES         0.12226
AQ            4.089496
RG                15.5
DW               62.40
DE                 6.5
TE                295.
D1           1.0000000
TD0

======== CHANNEL f1 ==
SFO1        400.152200
NUC1                 1
P1                10.4
SI                6553
SF          400.150000
WDW                  E
SSB
LB                 0.3
GB
PC                 1.0
```



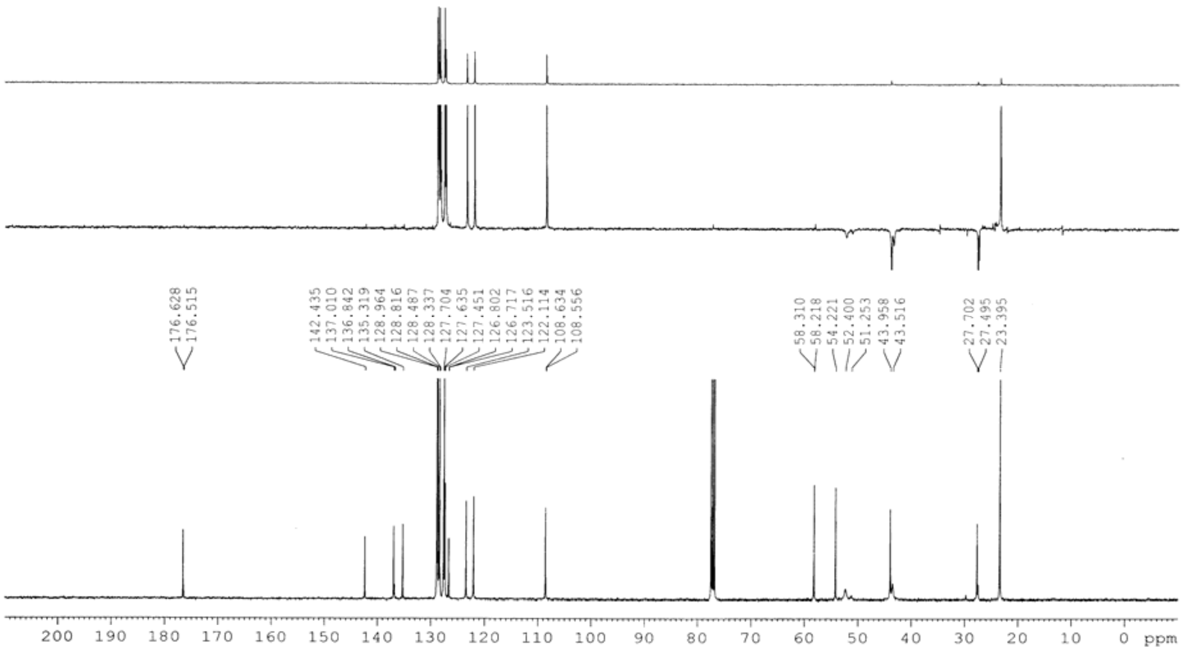

7.331
7.316
7.299
7.279
7.259
7.246
7.239
7.230
7.085
7.080
7.070
7.062
6.835
6.833
6.825
6.815
6.813
6.796
6.794
6.690
6.672
6.511
6.492
6.473
6.276
6.257
4.962
4.936
4.923
4.897
4.387
4.348
4.309
4.272
4.211
4.112
4.074
3.255
3.233
3.206
3.191
3.139
3.127
3.107
3.095
3.075
3.064
2.554
2.545
2.521
2.512
2.490
2.481
2.458
2.450
2.428
2.409
2.405
2.394
2.371
2.361
2.340
2.330
2.183
2.158
2.151
2.126
2.090
2.075
2.057
O=S
N
Ph
Bn−N
O
O
N−Bn
+
13a: Major
13b: Minor
unseparatable mixture
8.812
2.075
1.016
1.067
1.016
1.000
1.025
1.086
2.085
0.165
0.846
1.111
1.052
1.132
9.325
9
8
7
6
5
4
3
2
1
ppm
NAME 1201100116
EXPNO 31
PROCNO
Date_ 2013101
Time 21.2
INSTRUM spec
PROBHD 5 mm PABBO BB
PULPROG zg3
TD 6553
SOLVENT CDCl
NS 3
DS
SWH 8012.82
FIDRES 0.12226
AQ 4.089496
RG 24.7
DW 62.40
DE 6.5
TE 297.
D1 1.0000000
TD0
======== CHANNEL f1 ==
SFO1 400.152471
NUC1 1
P1 9.6
SI 6553
SF 400.150008
WDW E
SSB
LB 0.3
GB
PC 1.0

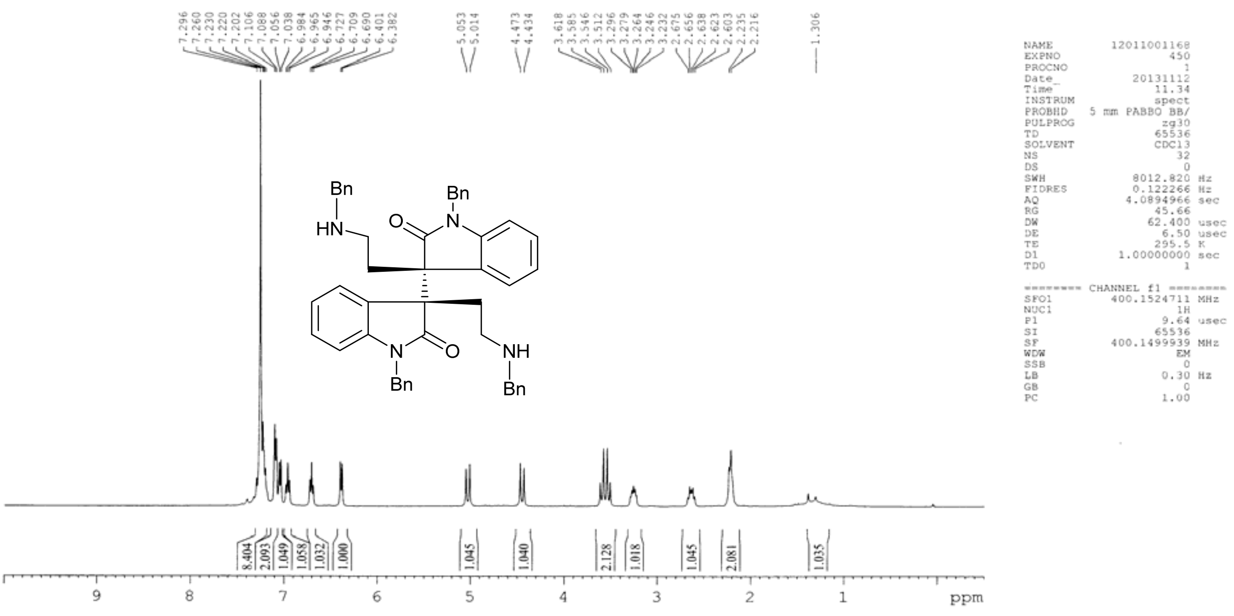

176.688
176.573
142.504
137.069
136.907
135.380
129.022
128.867
128.537
128.386
127.753
127.691
127.499
126.792
123.584
122.168
108.686
108.609
77.482
77.164
76.846
58.369
58.278
54.283
52.399
51.321
44.021
43.581
27.781
27.575
23.450
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



```
NAME          12011001168
EXPNO                 388
PROCNO                  1
Date_            20131030
Time                16.05
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  17.77
DW                 62.400 usec
DE                   6.50 usec
TE                  295.7 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1524711 MHz
NUC1                   1H
P1                   9.64 usec
SI                  65536
SF            400.1500086 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




7.296
7.260
7.230
7.220
7.202
7.106
7.088
7.056
7.038
6.984
6.965
6.946
6.727
6.709
6.690
6.401
6.382
5.053
5.014
4.473
4.434
3.618
3.585
3.546
3.512
3.296
3.279
3.264
3.246
3.232
2.675
2.656
2.638
2.623
2.603
2.235
2.216
1.306
Bn
HN
Bn
N
O
N
O
NH
Bn
Bn
NAME 12011001168
EXPNO 450
PROCNO 1
Date_ 20131112
Time 11.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 45.66
DW 62.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1499939 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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1.049
1.058
1.032
1.000
1.045
1.040
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1.045
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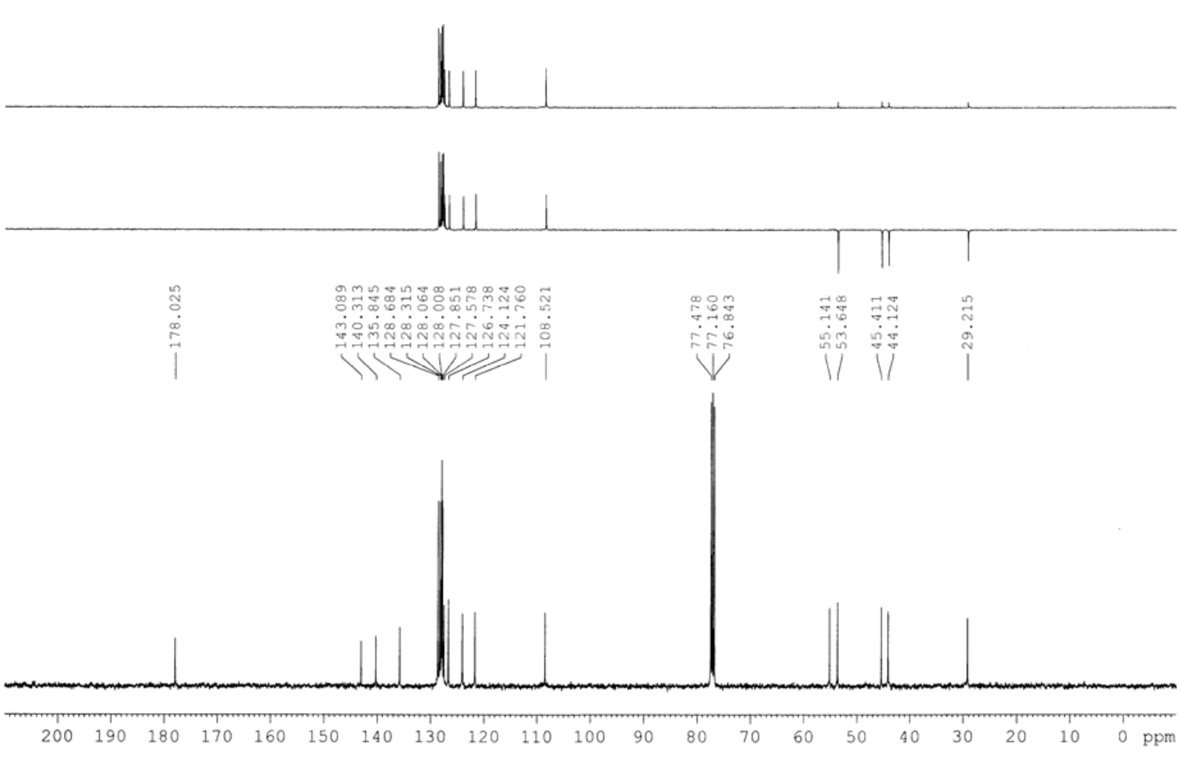
ppm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108.521
77.478
77.160
76.843
55.141
53.648
45.411
44.124
29.215
200
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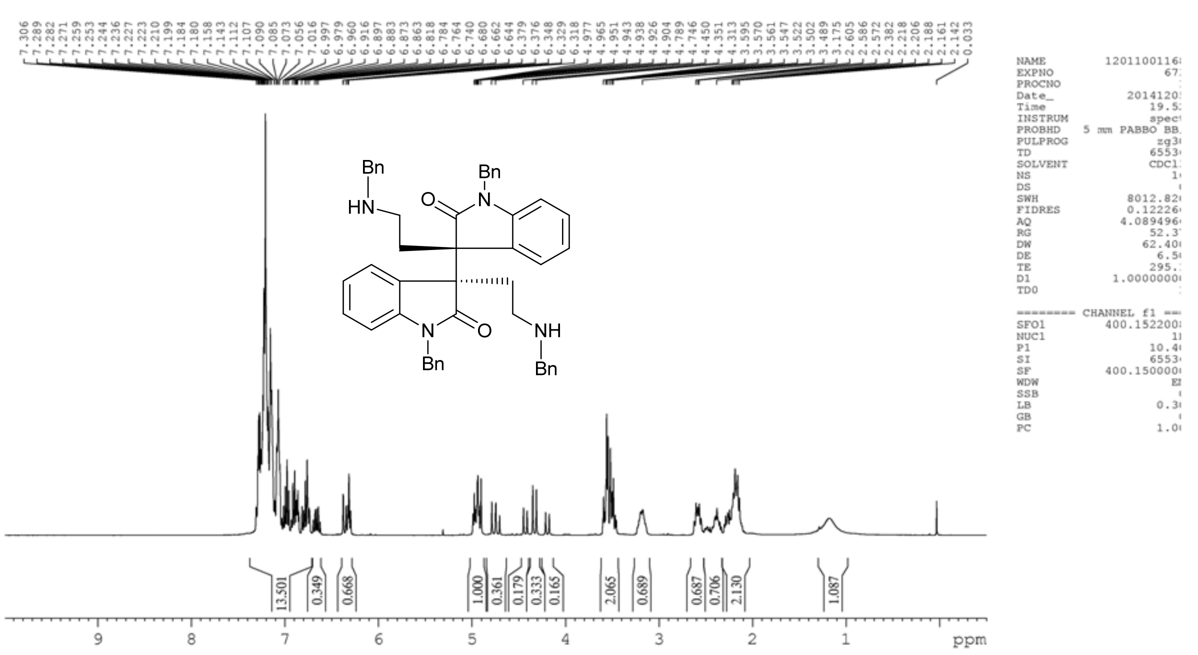
0
ppm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7.107
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6.784
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6.376
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4.450
4.351
4.313
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3.522
3.502
3.489
3.175
2.605
2.586
2.572
2.382
2.218
2.206
2.188
2.161
2.142
0.033
NAME 1201100116
EXPNO 67
PROCNO
Date_ 2014120
Time 19.5
INSTRUM spec
PROBHD 5 mm PABBO BB
PULPROG zg3
TD 6553
SOLVENT CDCl
NS 1
DS
SWH 8012.82
FIDRES 0.12226
AQ 4.089496
RG 52.3
DW 62.40
DE 6.5
TE 295.
D1 1.0000000
TD0
======== CHANNEL f1 ==
SFO1 400.152200
NUC1 1
P1 10.4
SI 6553
SF 400.150000
WDW E
SSB
LB 0.3
GB
PC 1.0
Bn
HN
O
N
Bn
Bn
N
O
NH
Bn
13.501
0.349
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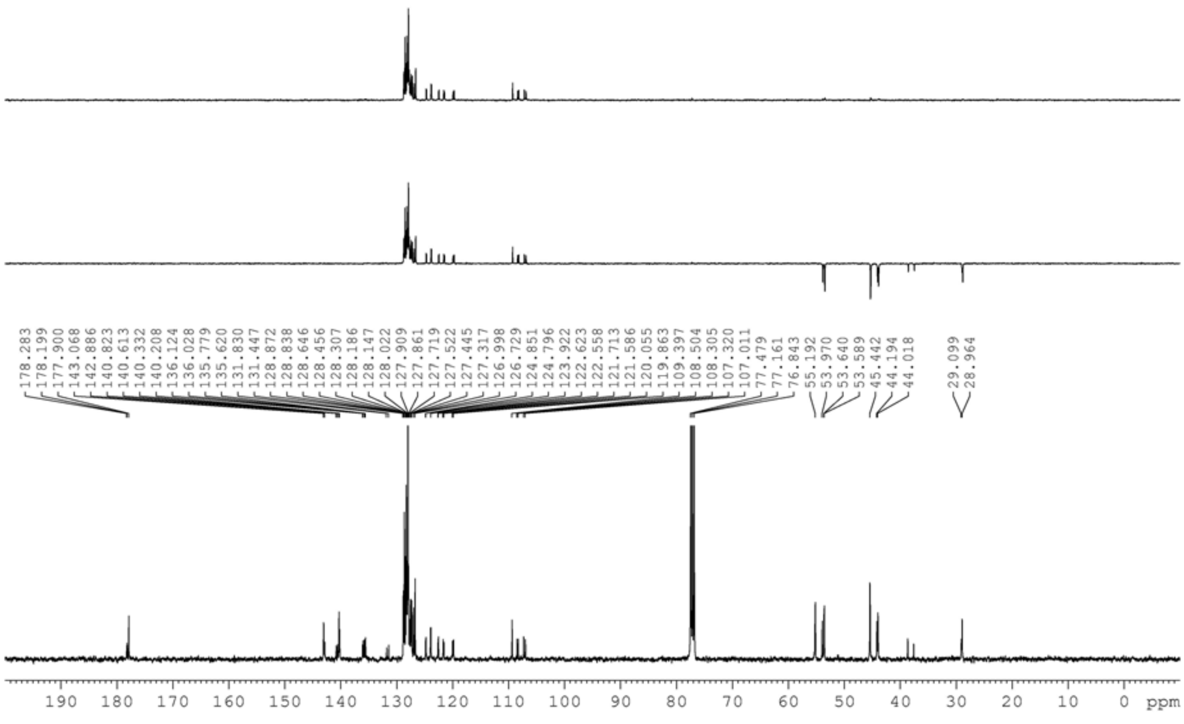
ppm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127.317
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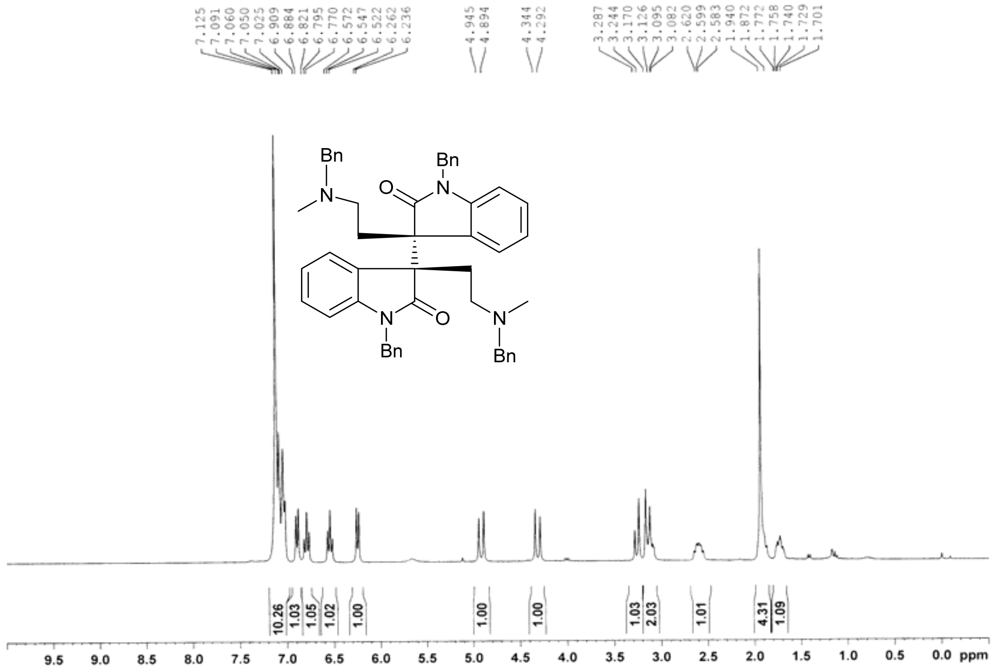
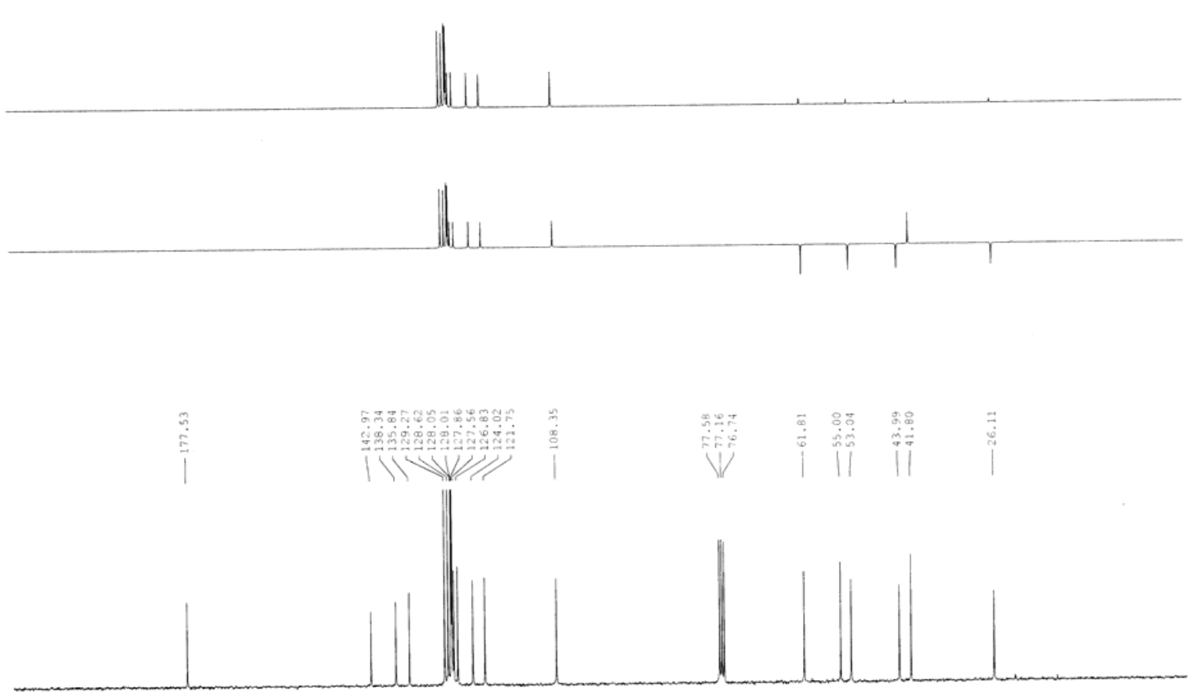
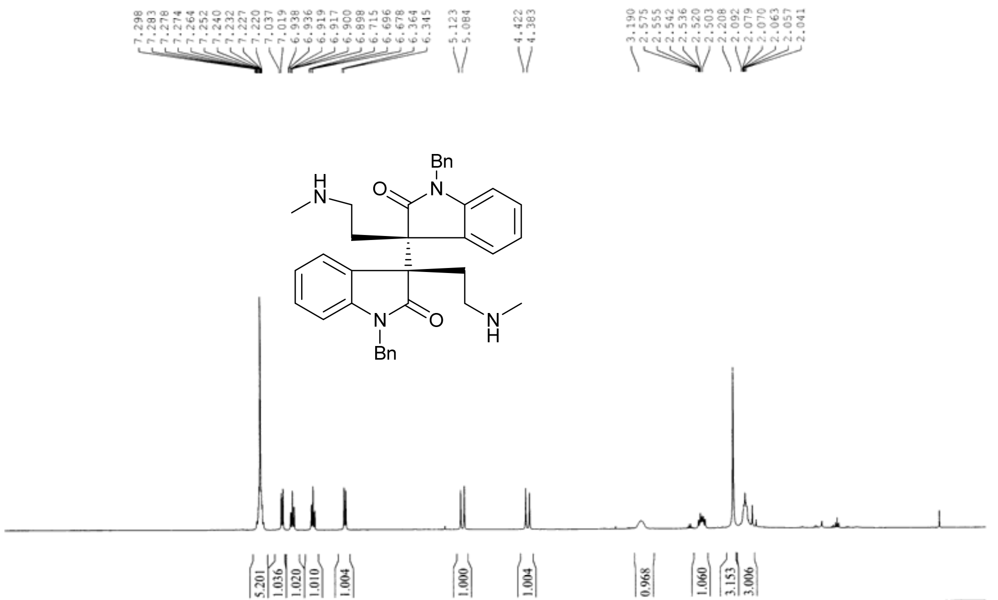
ppm



```
NAME          17011001168
EXPNO                1158
PROCNO                  1
Date_            20130904
Time                18.00
INSTRUM             av300
PROBHD    5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                   40.3
DW                 81.000 usec
DE                   6.50 usec
TE                  298.7 K
D1             1.00000000 sec
TD0                     1

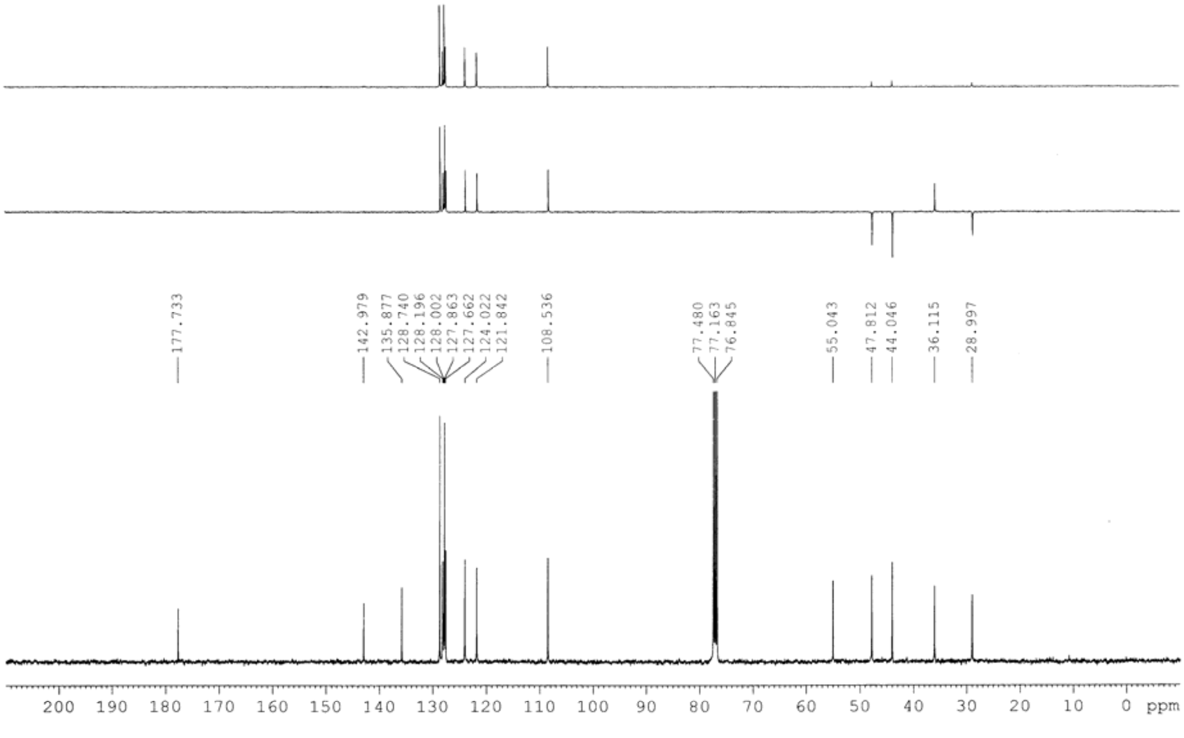
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.90 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz
SI                  32768
SF            300.1300468 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

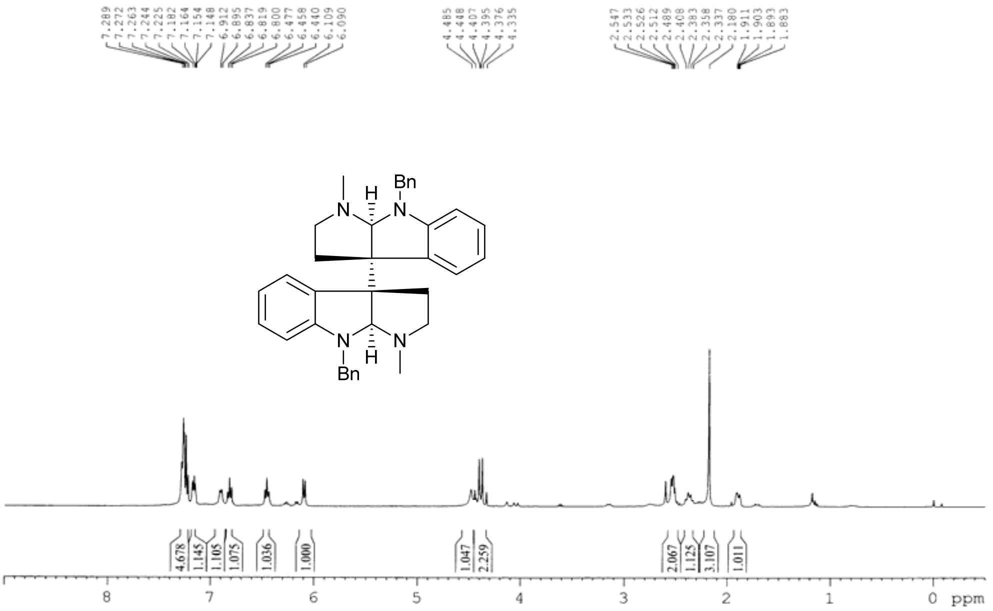




```
NAME          12011001168
EXPNO                 252
PROCNO                  1
Date_            20130828
Time                15.52
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  55.34
DW                 62.400 usec
DE                   6.50 usec
TE                  299.1 K
D1             1.00000000 sec
TD0                     1

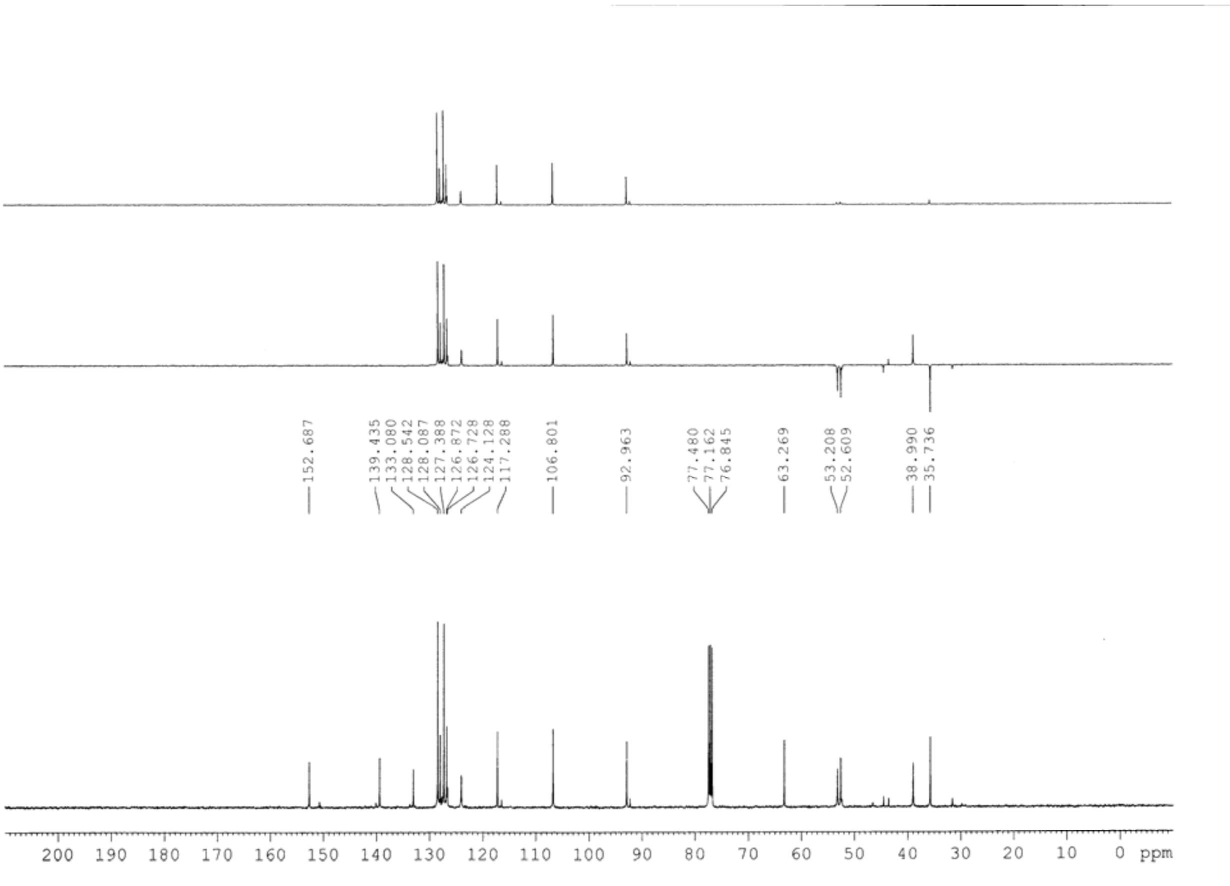
======== CHANNEL f1 ========
SFO1          400.1524711 MHz
NUC1                   1H
P1                   9.64 usec
SI                  65536
SF            400.1500068 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

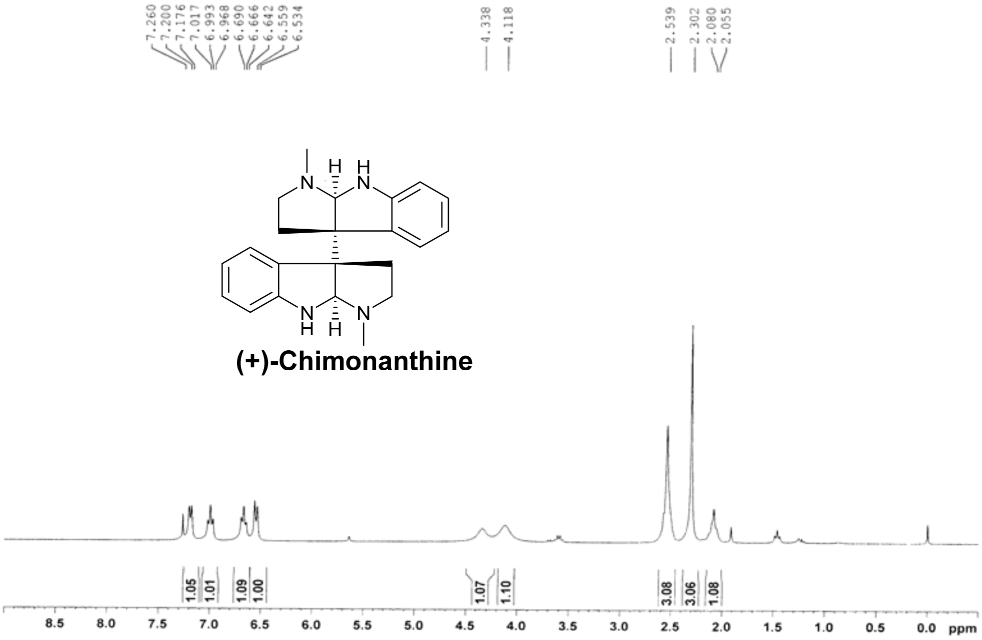




```
NAME            12011001168
EXPNO                   498
PROCNO                    1
Date_              20131122
Time                  14.37
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894966 sec
RG                    24.73
DW                   62.400 usec
DE                     6.50 usec
TE                    295.6 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1524711 MHz
NUC1                     1H
P1                     9.64 usec
SI                    65536
SF              400.1500507 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

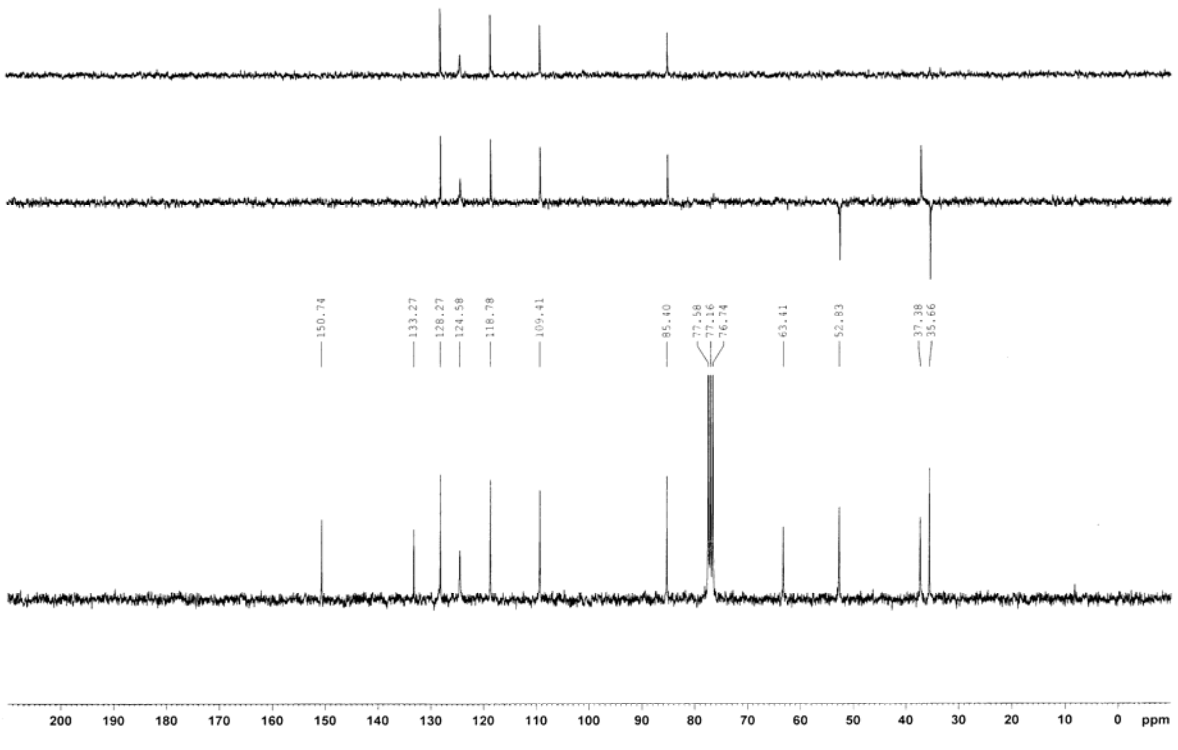


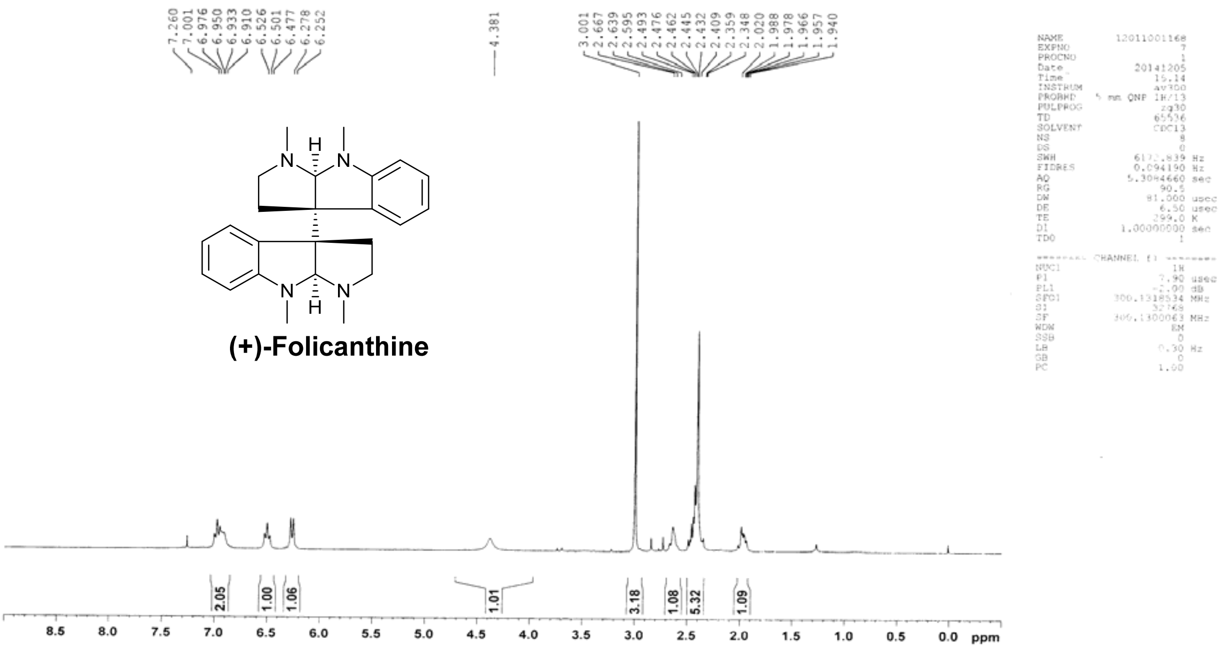


(+)-Chimonanthine

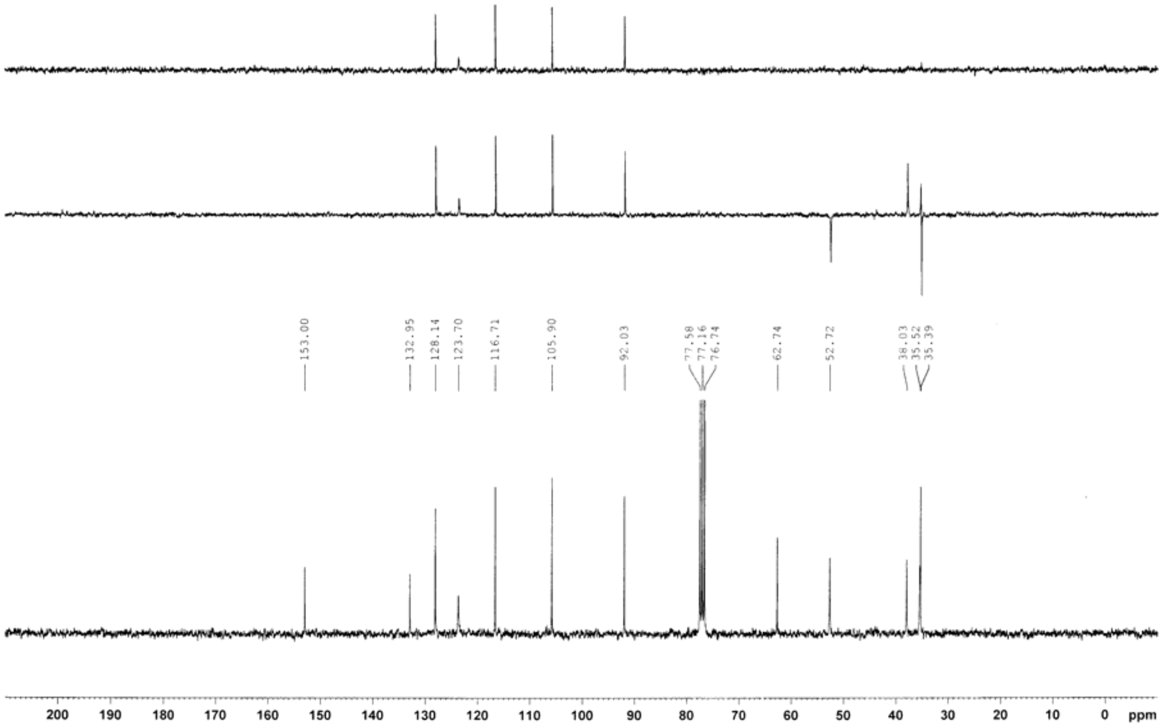
```
NAME              12011001168
EXPNO                     539
PROCNO                      1
Date_                20141125
Time                    13.24
INSTRUM                 av300
PROBHD      5 mm QNP 1H/13
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                  5.3084660 sec
RG                        256
DW                     81.000 usec
DE                       6.50 usec
TE                      297.9 K
D1                 1.00000000 sec
TD0                         1

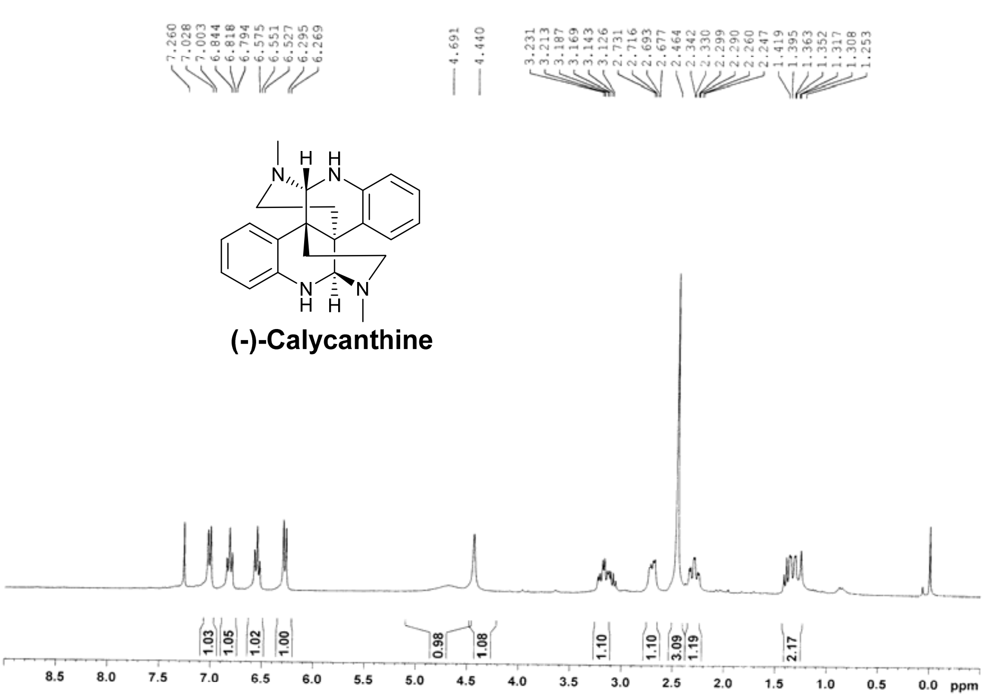
======== CHANNEL f1 ========
NUC1                       1H
P1                       7.90 usec
PL1                     -2.00 dB
SFO1              300.1318534 MHz
SI                      32768
SF                300.1300062 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```





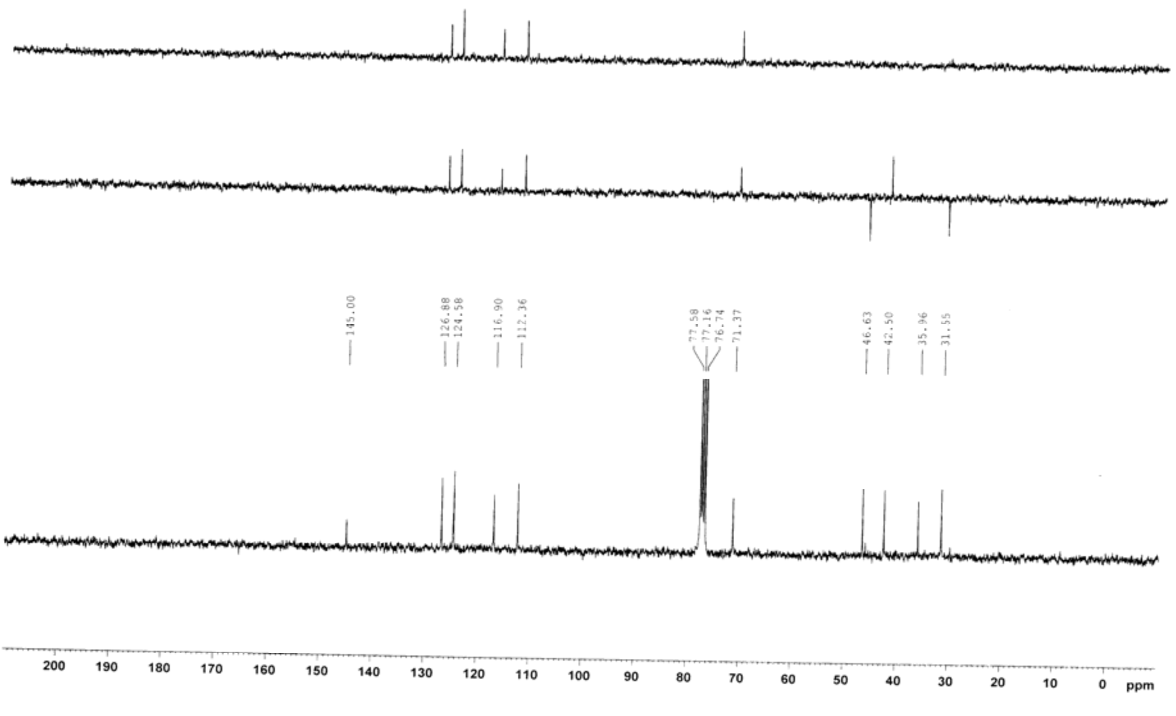
(+)-Folicanthine

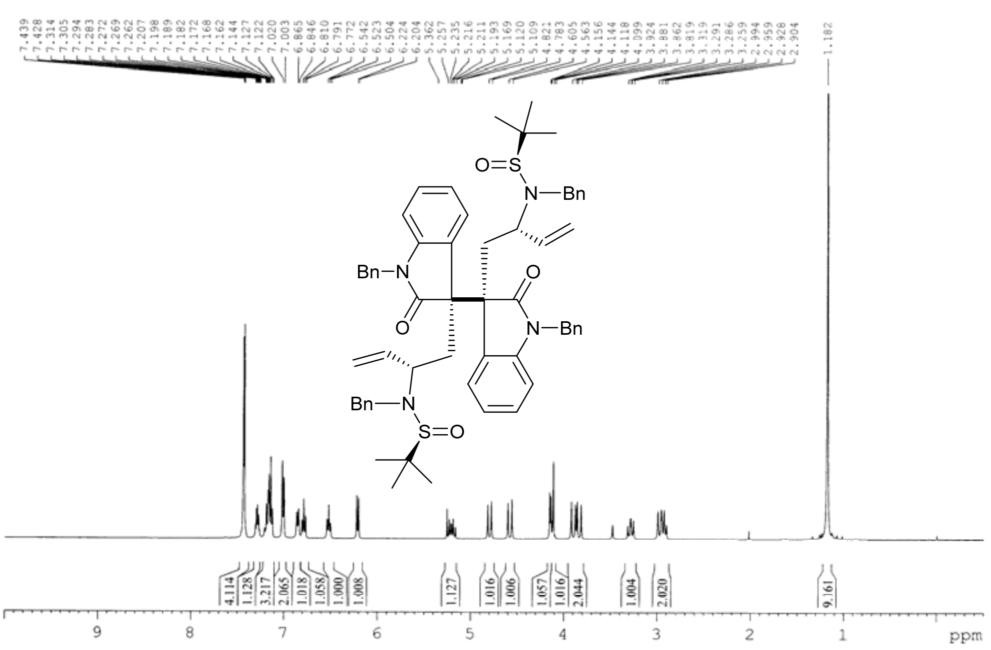




```
NAME             12011001168
EXPNO                    598
PROCNO                     1
Date_               20141210
Time                   12.22
INSTRUM                av300
PROBHD   5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                 5.3084660 sec
RG                       362
DW                    81.000 usec
DE                      6.50 usec
TE                     297.1 K
D1                1.00000000 sec
TD0                        1

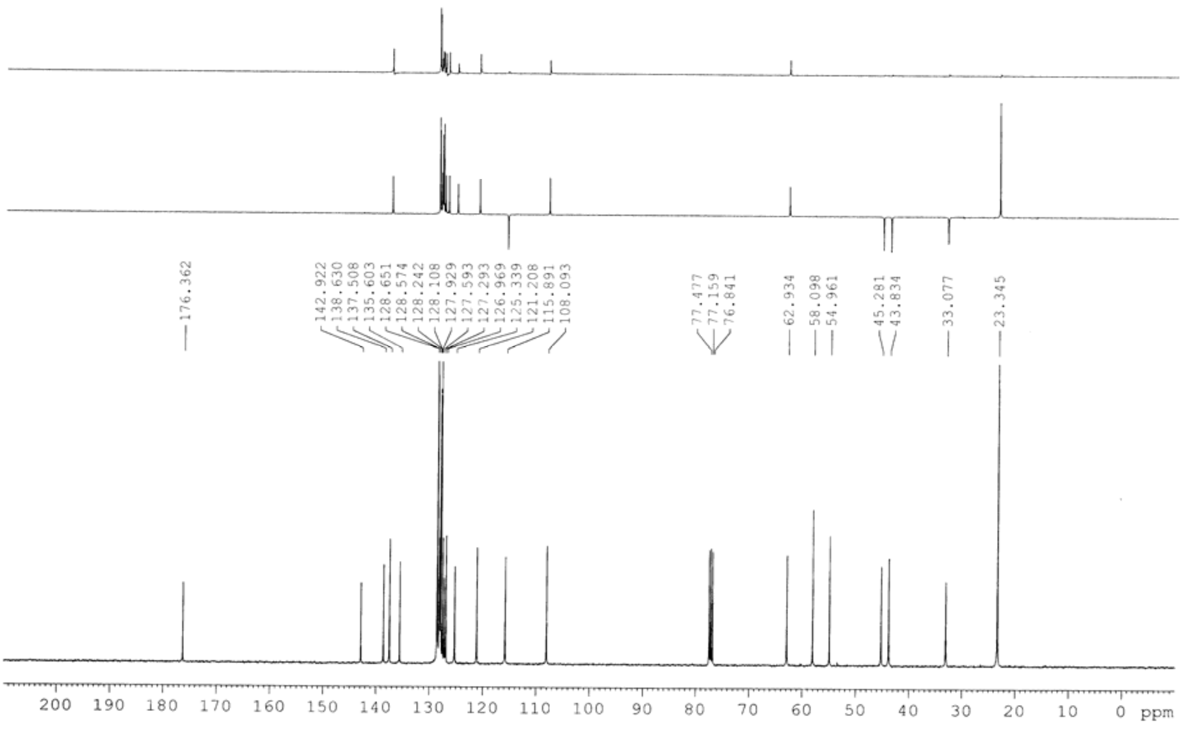
======== CHANNEL f1 ========
NUC1                      1H
P1                      7.90 usec
PL1                    -2.00 dB
SFO1             300.1319534 MHz
SI                     32768
SF               300.1300061 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

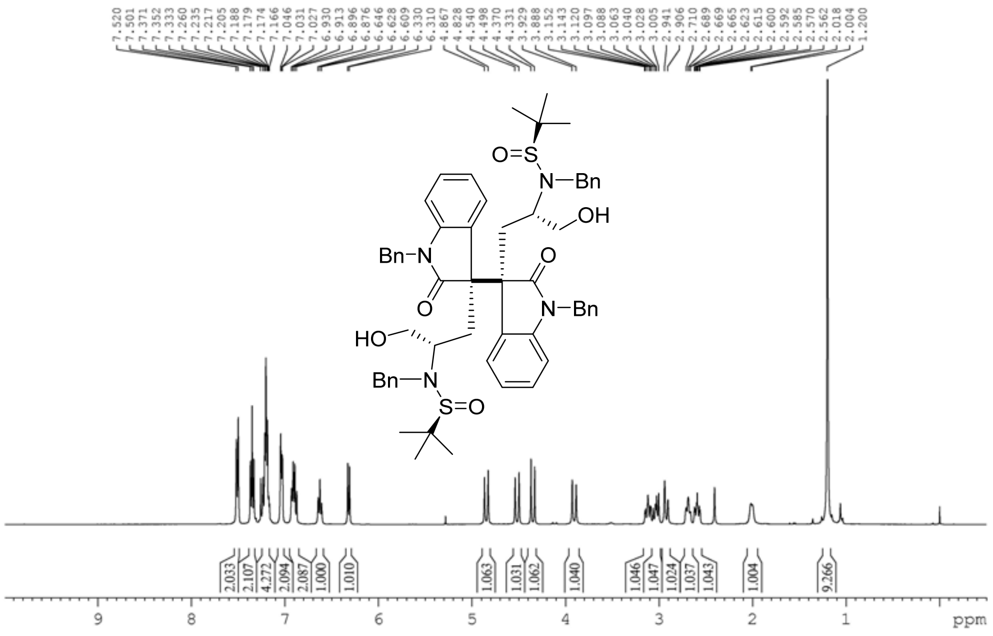




```
NAME          12011001168
EXPNO                   5
PROCNO                  1
Date_            20140614
Time                17.47
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                  14.14
DW                 75.733 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

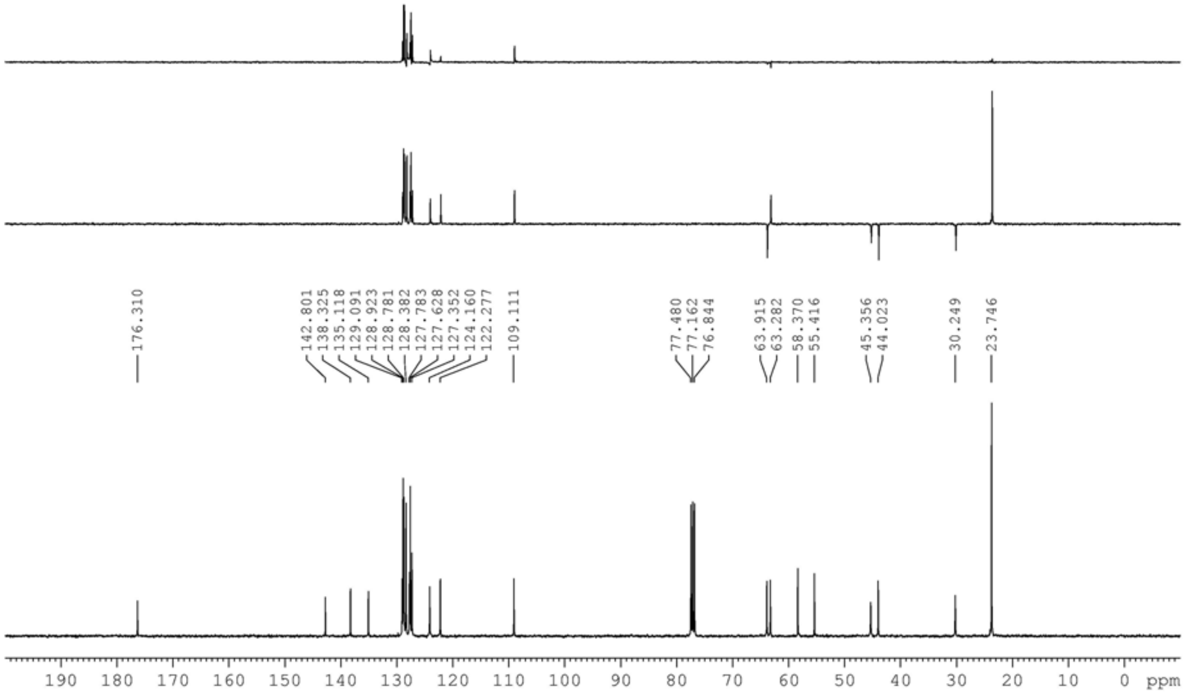
-------- CHANNEL f1 ========
SFO1          400.1526964 MHz
NUC1                   1H
P1                  10.40 usec
SI                  65536
SF            400.1500050 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

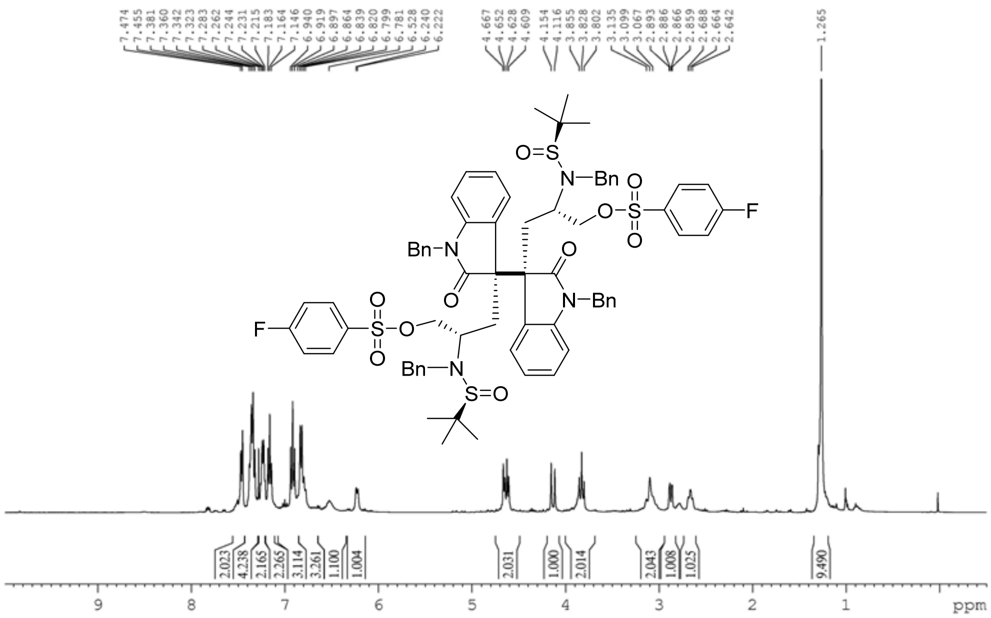




```
NAME          12011001168
EXPNO                   9
PROCNO                  1
Date_            20140615
Time                17.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              6602.113
FIDRES           0.100740
AQ              4.9633098
RG                   29.1
DW                 75.733
DE                   6.50
TE                  297.8
D1             1.00000000
TD0                     1

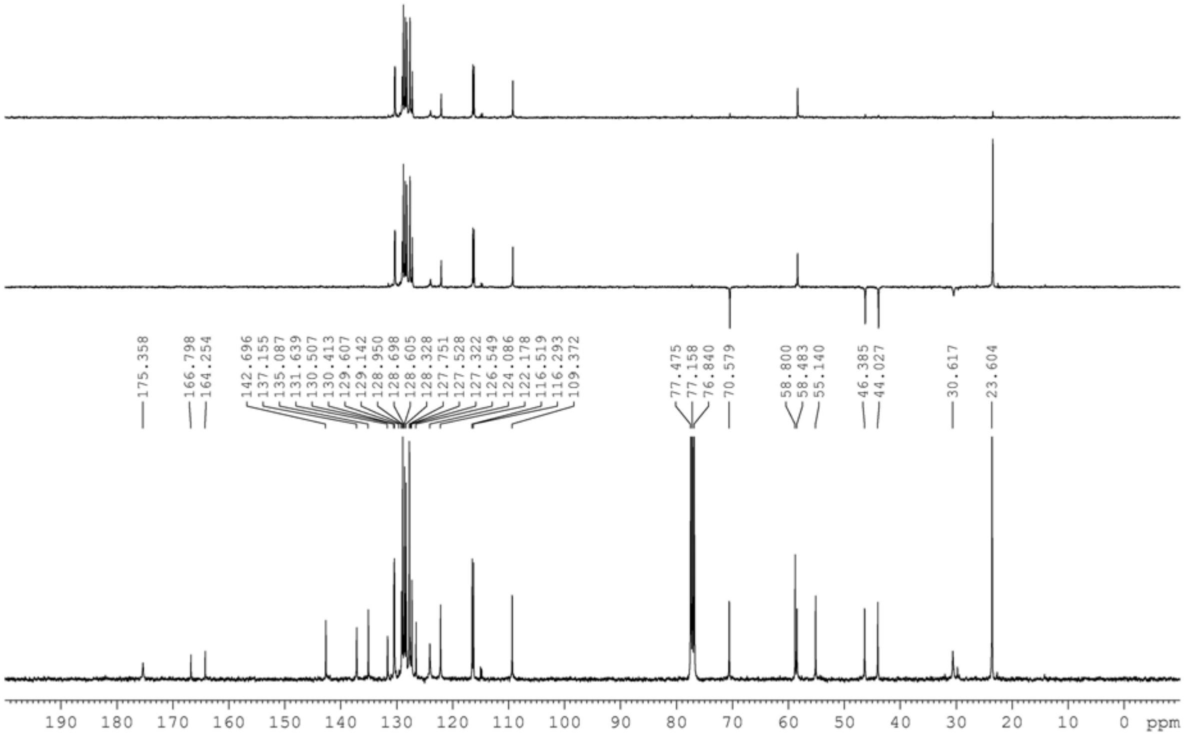
======== CHANNEL f1 ====
SFO1          400.1526964
NUC1                   1H
P1                  10.40
SI                  65536
SF            400.1500087
WDW                    EM
SSB                     0
LB                   0.30
GB                      0
PC                   1.00
```

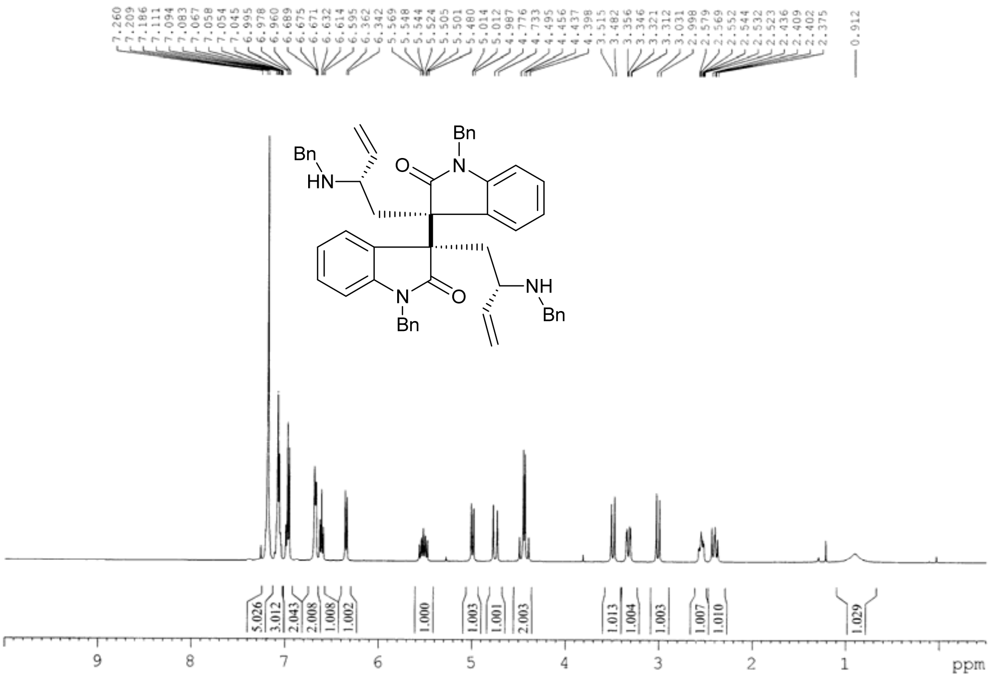




```
NAME          22014000177
EXPNO                  56
PROCNO                  1
Date_            20150518
Time                20.09
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820
FIDRES           0.122266
AQ              4.0894966
RG                  45.66
DW                 62.400
DE                   6.50
TE                  296.1
D1             1.00000000
TD0                     1

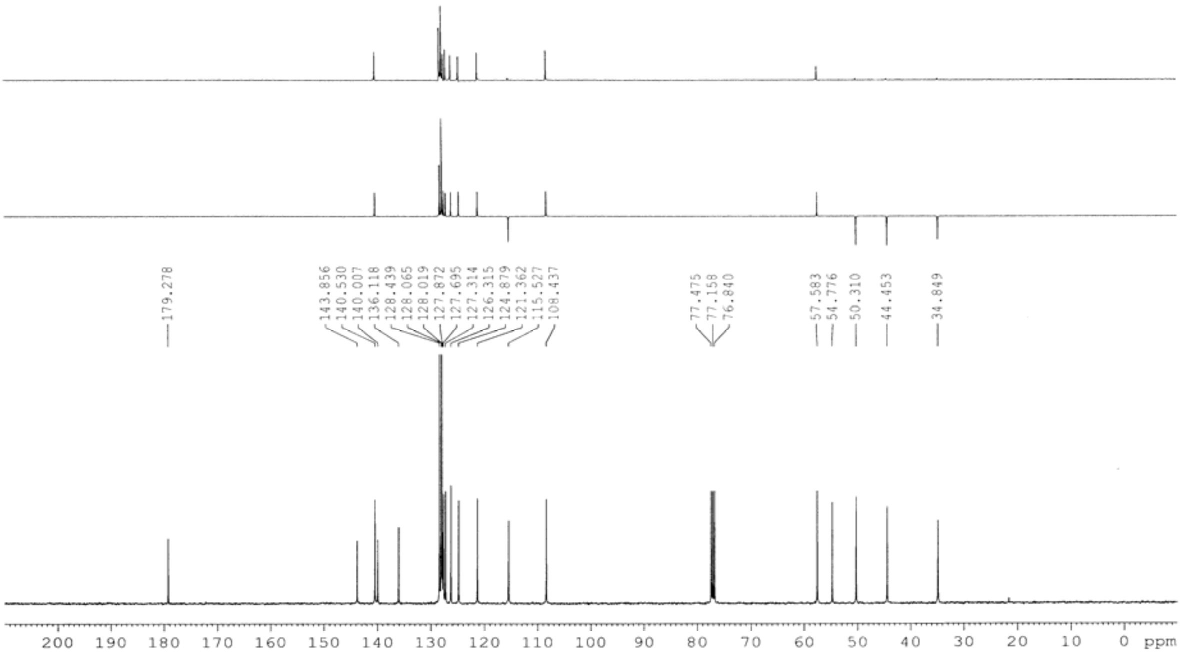
======== CHANNEL f1 ====
SFO1          400.1522008
NUC1                   1H
P1                  10.40
SI                  65536
SF            400.1500000
WDW                    EM
SSB                     0
LB                   0.30
GB                      0
PC                   1.00
```

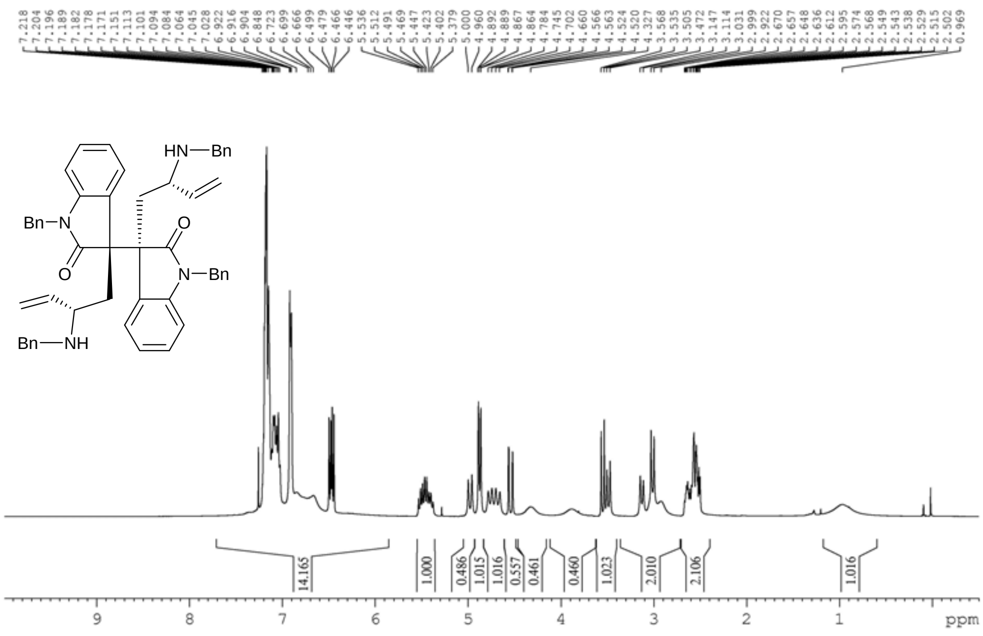




```
NAME         12011001168
EXPNO                507
PROCNO                 1
Date_           20141023
Time               15.33
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 15.56
DW                62.400 usec
DE                  6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                    1

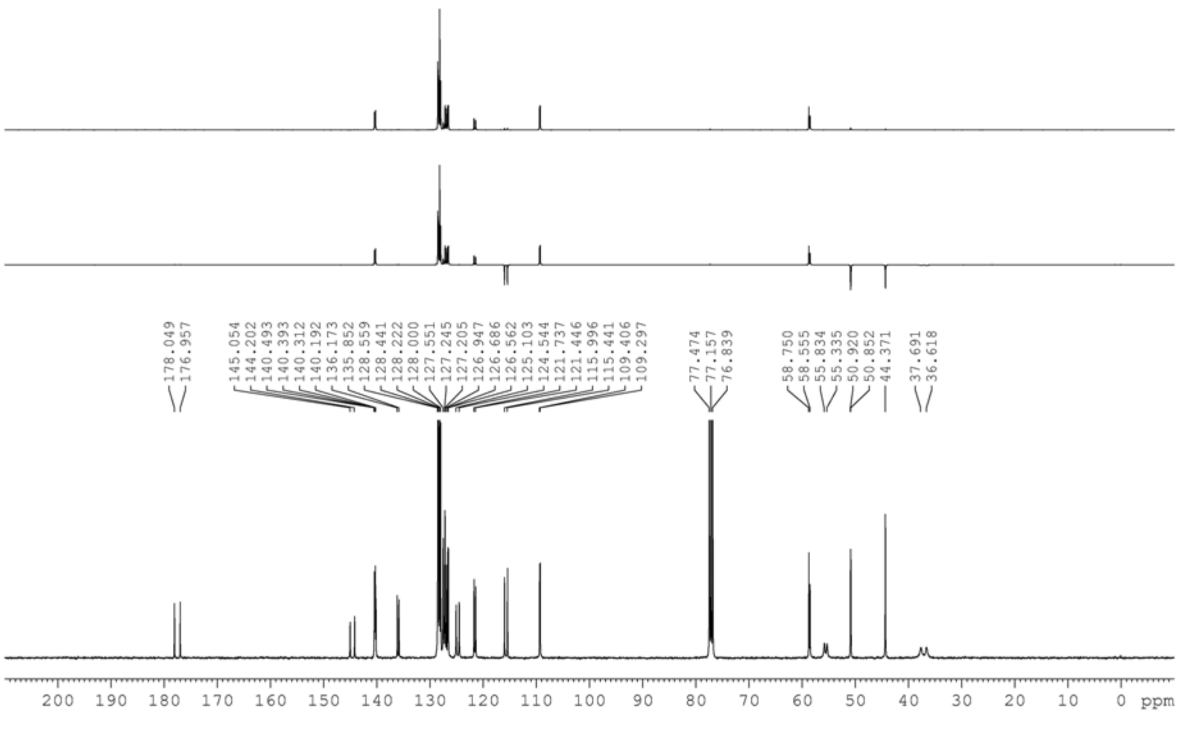
======== CHANNEL f1 ========
SFO1         400.1522008 MHz
NUC1                  1H
P1                 10.40 usec
SI                 65536
SF           400.1500085 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

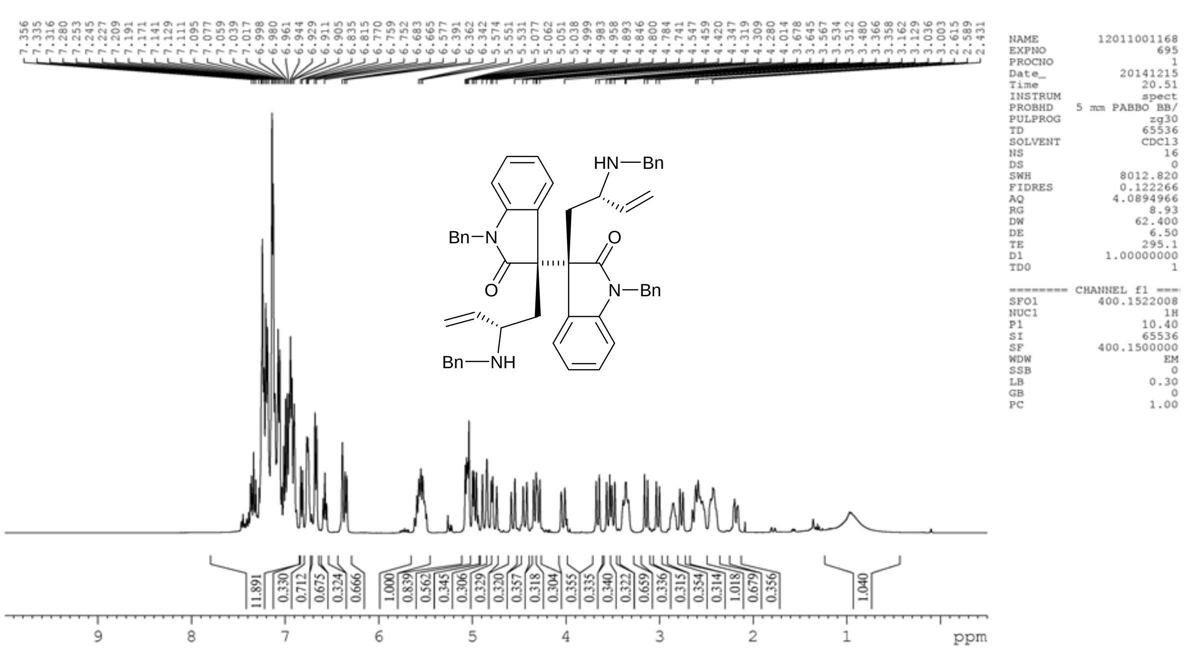




```
NAME           1201100116
EXPNO                  69
PROCNO
Date_             2014121
Time                 23.3
INSTRUM              spec
PROBHD   5 mm PABBO BB
PULPROG               zg3
TD                   6553
SOLVENT              CDCl
NS                      1
DS
SWH               8012.82
FIDRES            0.12226
AQ               4.089496
RG                   31.5
DW                  62.40
DE                    6.5
TE                   294.
D1              1.0000000
TD0

======== CHANNEL f1 ==
SFO1           400.152200
NUC1                    1
P1                   10.4
SI                   6553
SF             400.150008
WDW                     E
SSB
LB                    0.3
GB
PC                    1.0
```

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HN—Bn
Bn—N
O
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N—Bn
Bn—NH
NAME 12011001168
EXPNO 695
PROCNO 1
Date_ 20141215
Time 20.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820
FIDRES 0.122266
AQ 4.0894966
RG 8.93
DW 62.400
DE 6.50
TE 295.1
D1 1.00000000
TD0 1
======== CHANNEL f1 ===
SFO1 400.1522008
NUC1 1H
P1 10.40
SI 65536
SF 400.1500000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
11.891
0.330
0.712
0.675
0.324
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1.000
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0.562
0.345
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0.329
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0.357
0.318
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0.336
0.315
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6
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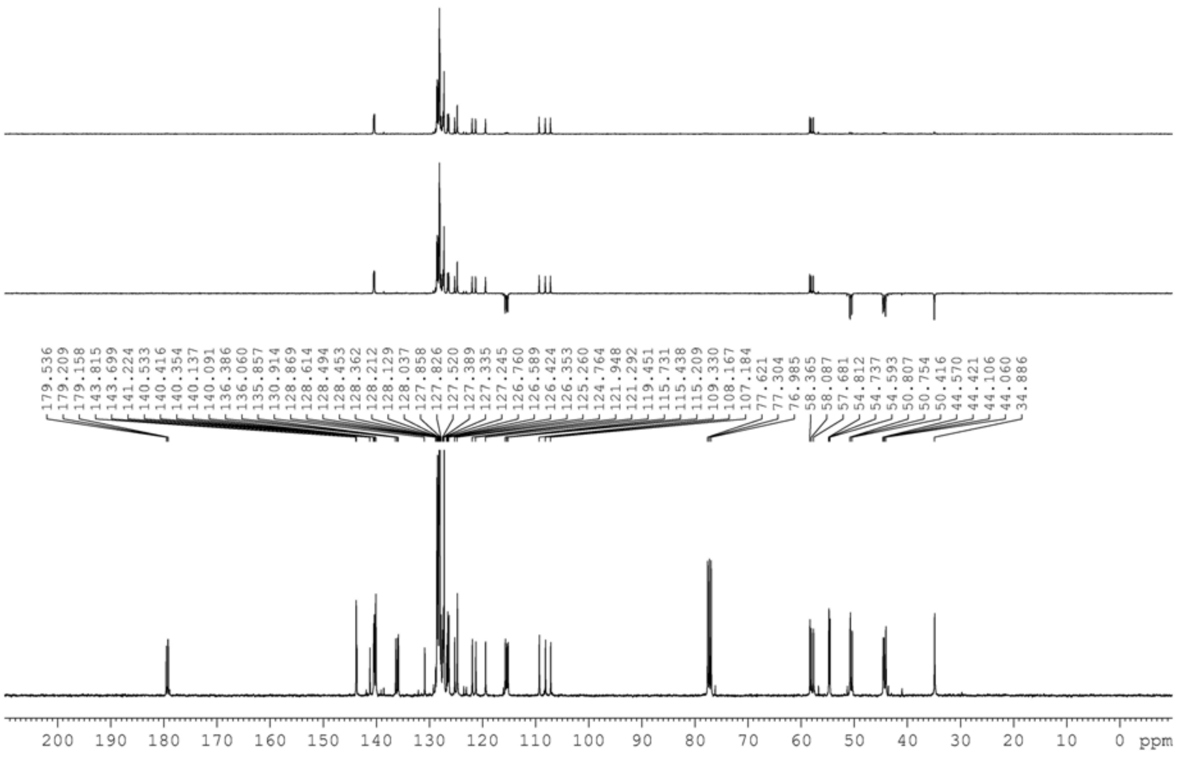
4
3
2
1
ppm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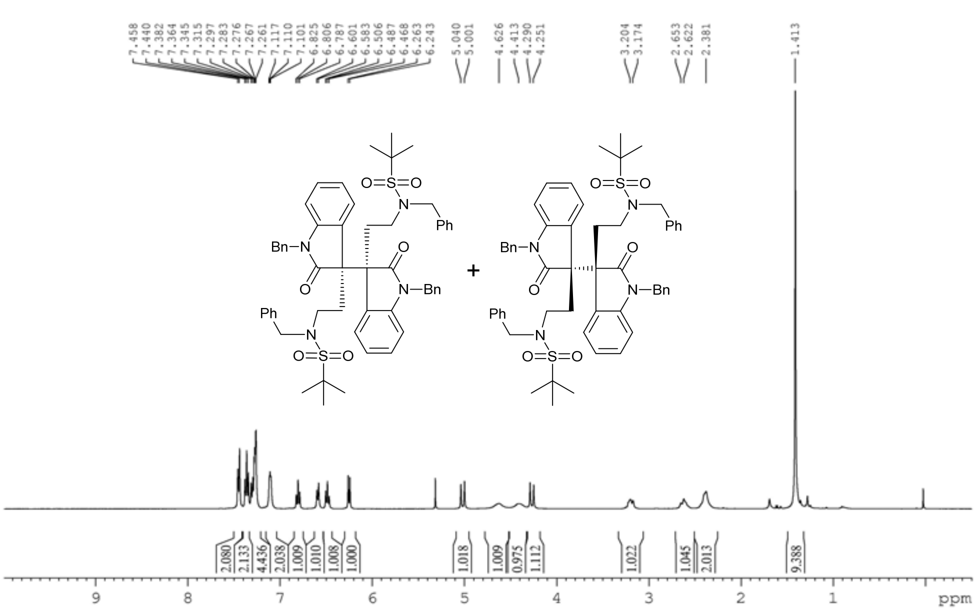
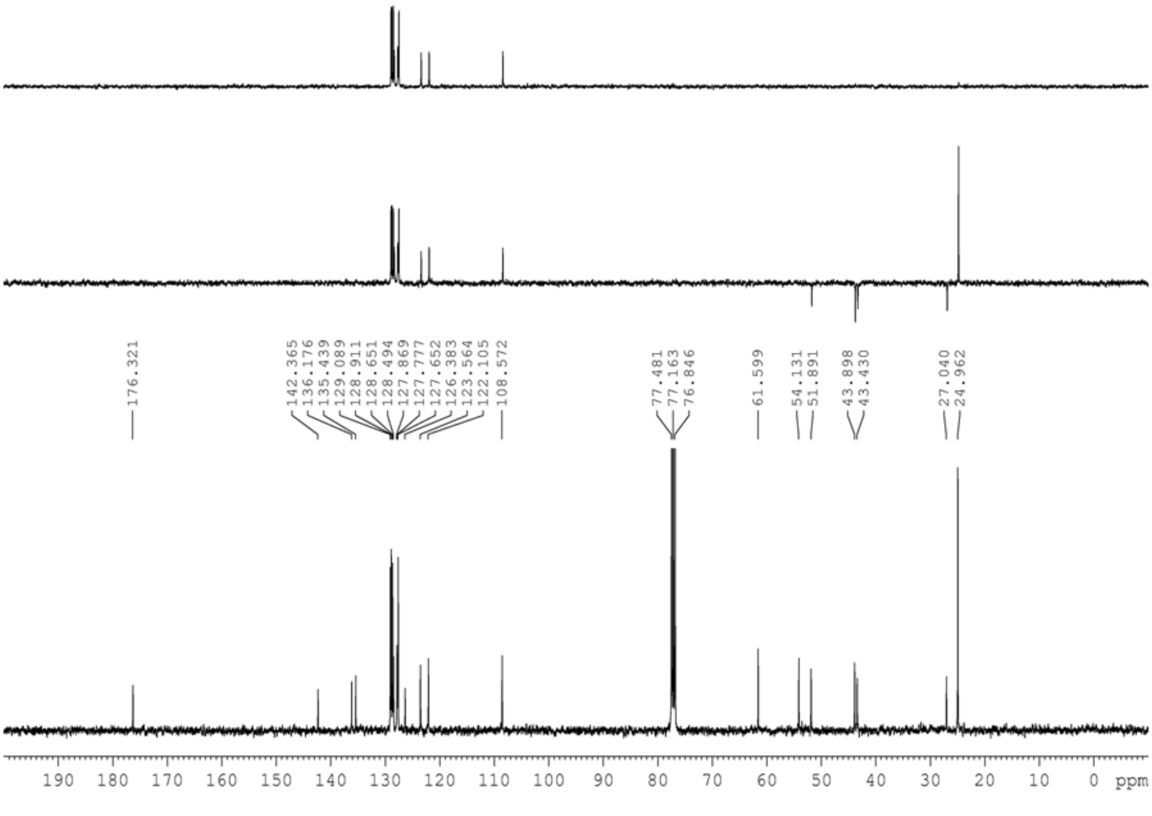
30
20
10
0 ppm



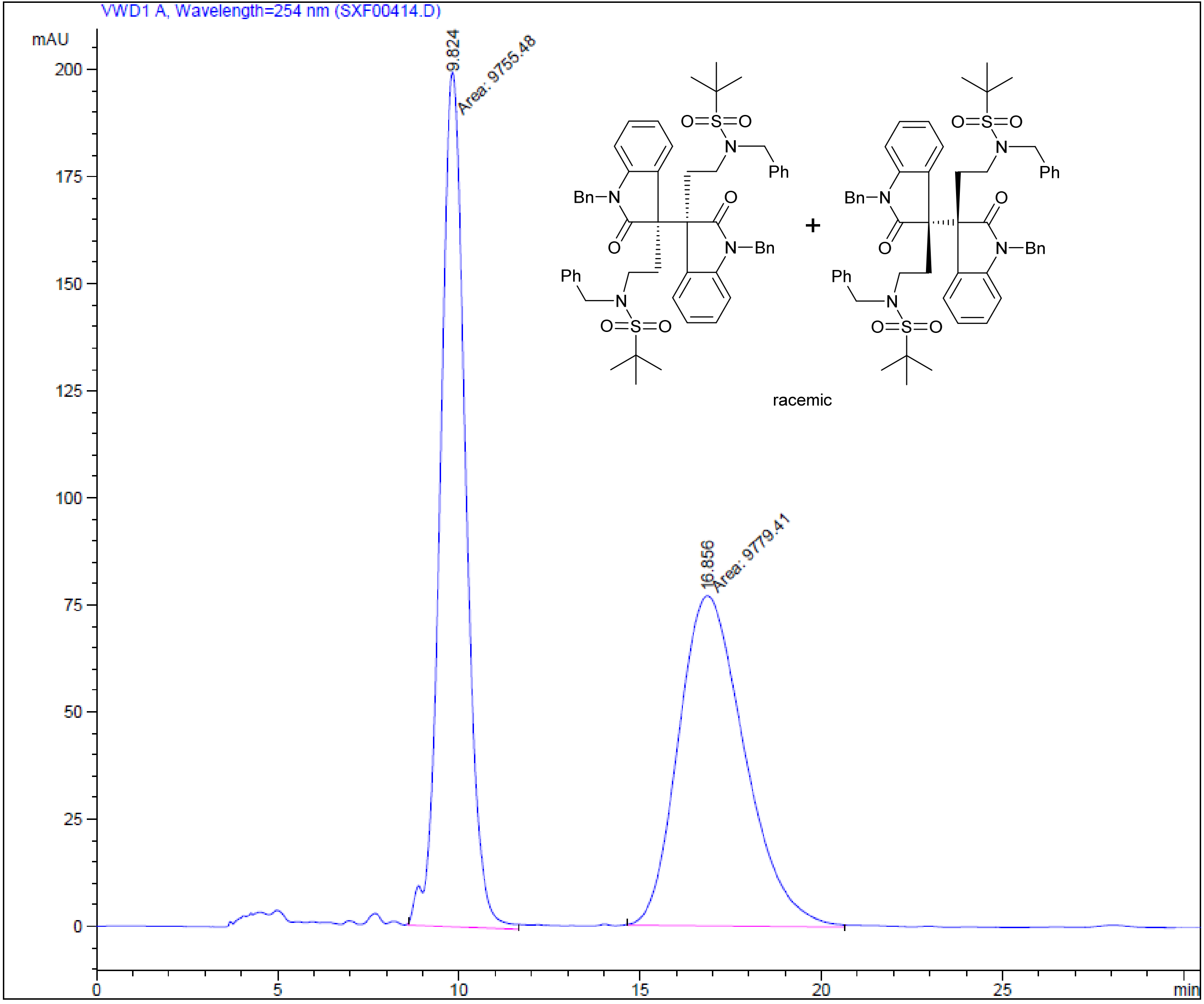
```
NAME           22014000177
EXPNO                  115
PROCNO                   1
Date_             20150603
Time                 14.55
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      10
DS                       0
SWH             8012.820 H
FIDRES          0.122266 H
AQ             4.0894966 s
RG                   55.34
DW                62.400 u
DE                  6.50 u
TE                 298.0 K
D1            1.00000000 s
TD0                      1

======== CHANNEL f1 =====
SFO1        400.1522008 M
NUC1                    1H
P1                 10.40 u
SI                   65536
SF          400.1500000 M
WDW                     EM
SSB                      0
LB                  0.30 H
GB                       0
PC                    1.00
```



```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00414.D                         Sample Name: 00011

    =====================================================================
    Injection Date  : 2015-6-3 22:11:24 下午
    Sample Name     : 00011                          Location :   -
    Acq. Operator   :
    Method          : C:\HPCHEM\1\METHODS\ZJF.M
    Last changed    : 2015-6-3 20:49:24 下午
                      (modified after loading)
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000


    Signal 1: VWD1 A, Wavelength=254 nm

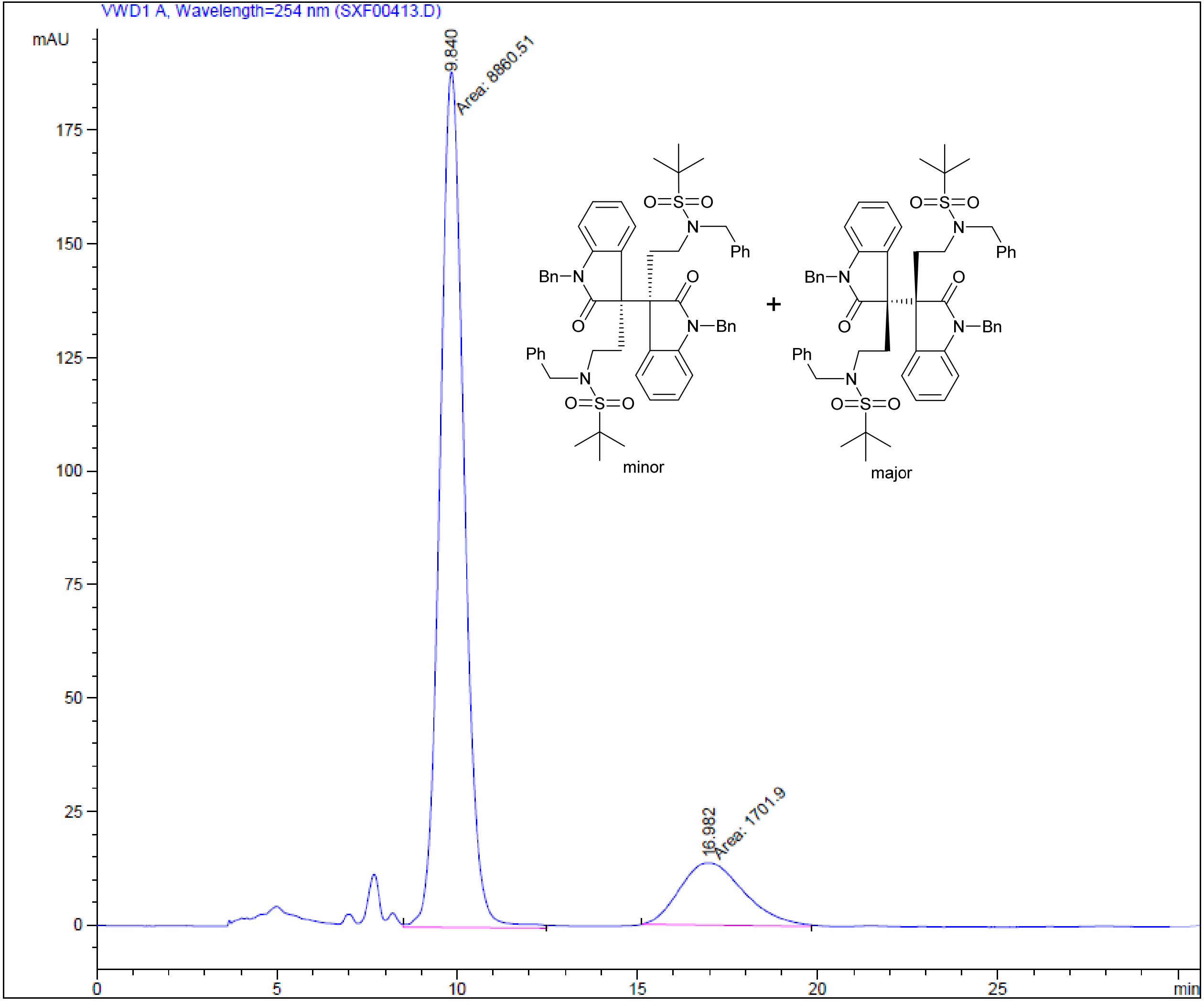
    Peak RetTime Type  Width      Area      Height     Area
      #   [min]        [min]   mAU    *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   9.824 MM    0.8150 9755.48340  199.49382  49.9388
       2  16.856 MM    2.1142 9779.41211   77.09438  50.0612

    Totals :                  1.95349e4   276.58820

     Results obtained with enhanced integrator!
    =====================================================================
Instrument 1 2015-6-3 22:41:53 下午                                          Page 1 of 1
```

```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00413.D                          Sample Name: 00011

    =====================================================================
    Injection Date  : 2015-6-3 21:37:49 下午
    Sample Name     : 00011                          Location :   -
    Acq. Operator   :
    Method          : C:\HPCHEM\1\METHODS\ZJF.M
    Last changed    : 2015-6-3 20:49:24 下午
                      (modified after loading)
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000


    Signal 1: VWD1 A, Wavelength=254 nm

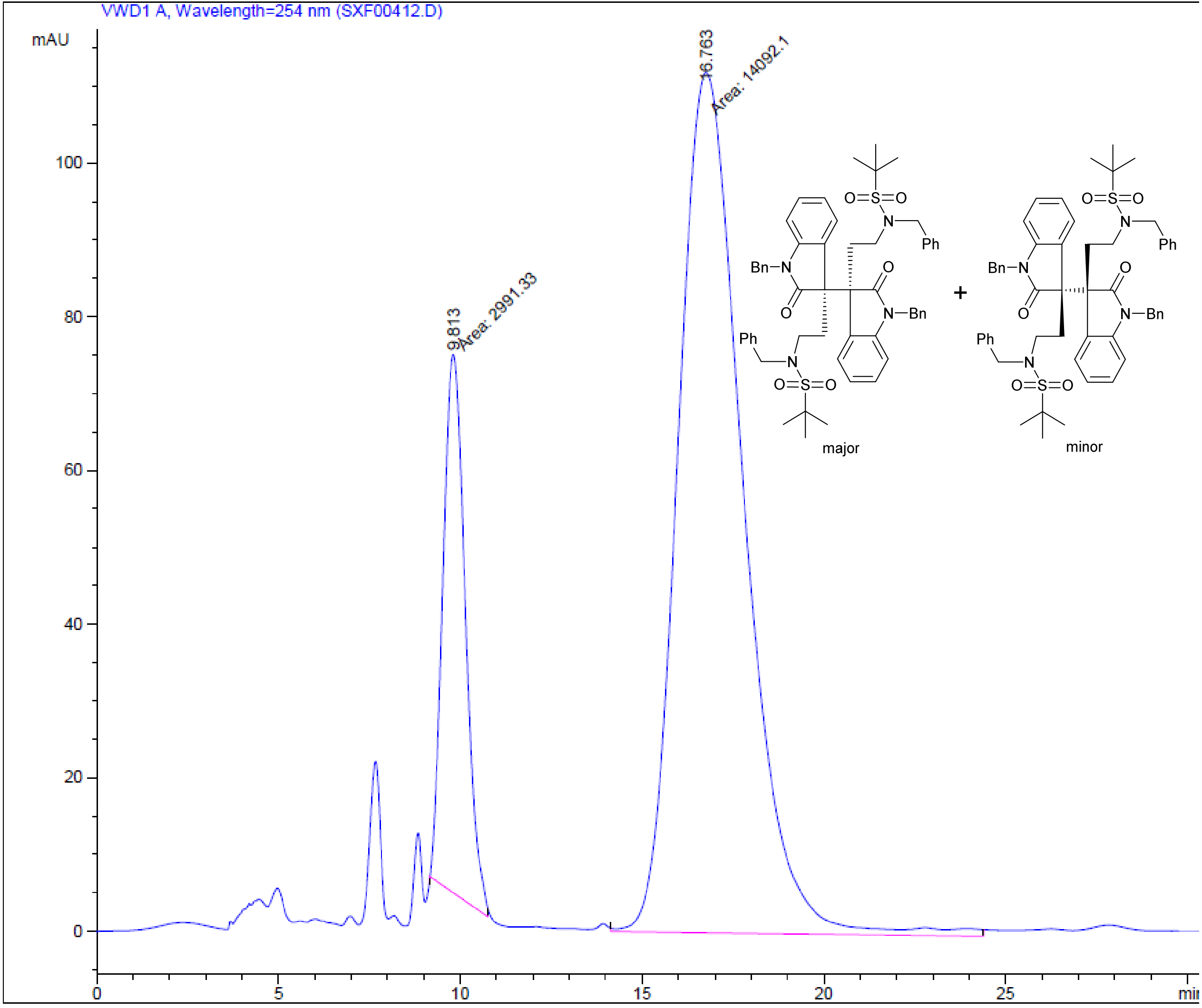
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   mAU   *s   [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1   9.840 MM    0.7843 8860.50586  188.29802 83.8872
       2  16.982 MM    2.0655 1701.90039   13.73279 16.1128

    Totals :                  1.05624e4   202.03081

     Results obtained with enhanced integrator!
    =====================================================================
Instrument 1 2015-6-3 22:08:46 下午                                        Page 1 of 1
```

```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00412.D                      Sample Name: 0001

    ===================================================================
    Injection Date  : 2015-6-3 21:04:43 下午
    Sample Name     : 00011                         Location :   -
    Acq. Operator   :
    Method          : C:\HPCHEM\1\METHODS\ZJF.M
    Last changed    : 2015-6-3 20:49:24 下午
                      (modified after loading)
```



```
    ===================================================================
                          Area Percent Report
    ===================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000


    Signal 1: VWD1 A, Wavelength=254 nm

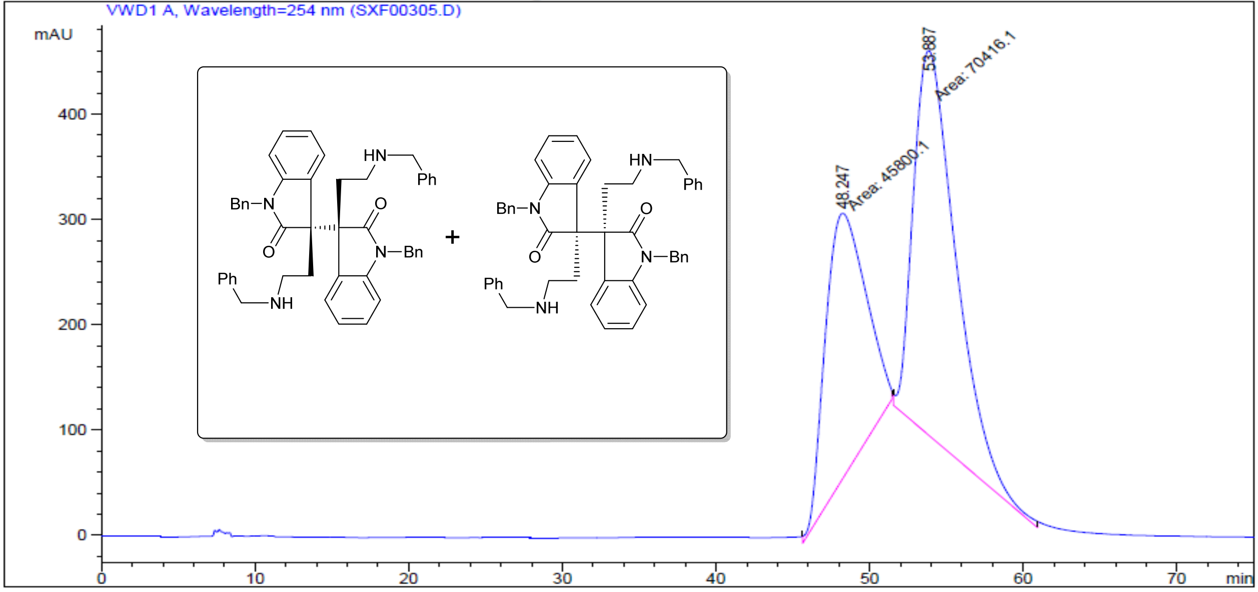
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   mAU   *s   [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1   9.813 MM     0.7120 2991.33228   70.01850  17.5101
       2  16.763 MM     2.0989 1.40921e4  111.90126  82.4899

    Totals :                   1.70835e4  181.91976

     Results obtained with enhanced integrator!
    ===================================================================
Instrument 1 2015-6-3 21:39:59 下午                                        Page 1 of 1
```

```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00305.D                        Sample Name: zero

    ======================================================================
    Injection Date  : 2013-8-26 18:46:18 下午
    Sample Name     : zero                              Location :   -
    Acq. Operator   :
    Acq. Method     : C:\HPCHEM\1\METHODS\CQ.M
    Last changed    : 2013-8-26 18:40:14 下午
                      (modified after loading)
    Analysis Method : C:\HPCHEM\1\METHODS\CQ.M
    Last changed    : 2013-8-26 20:10:32 下午
                      (modified after loading)
```



```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000


    Signal 1: VWD1 A, Wavelength=254 nm

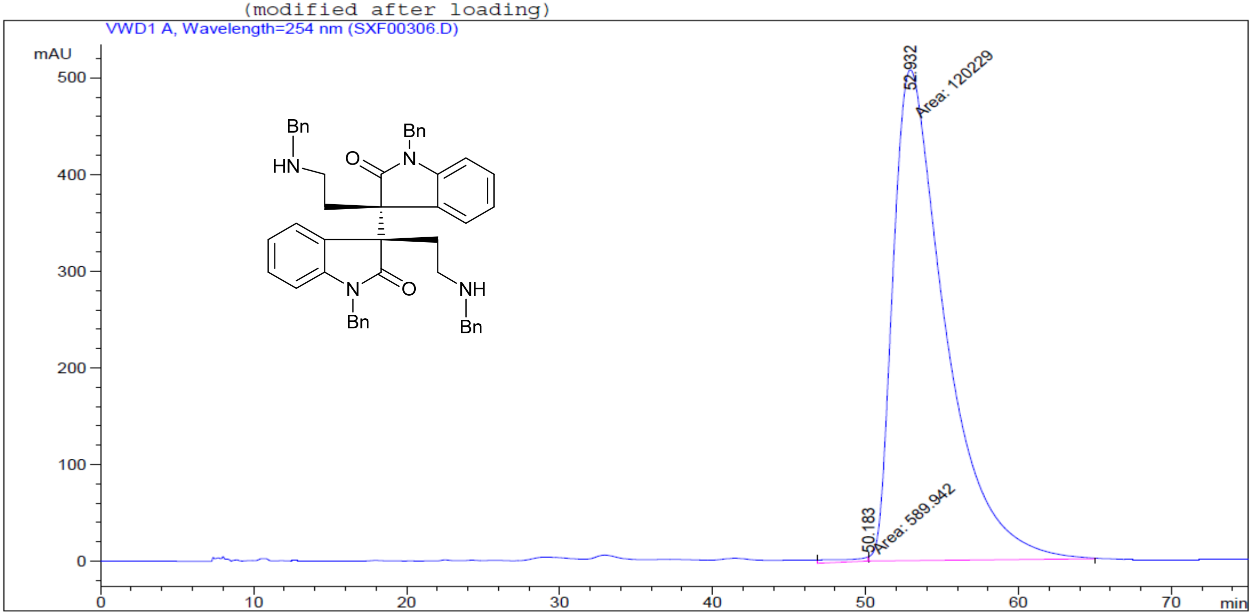
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   mAU   *s   [mAU    ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  48.247 MM    3.0300 4.58001e4  251.92842  39.4094
       2  53.887 MM    3.2118 7.04161e4  365.40591  60.5906

    Totals :                  1.16216e5  617.33434

     Results obtained with enhanced integrator!
    ======================================================================
                              *** End of Report ***
```

```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00306.D                          Sample Name: zero

    =====================================================================
    Injection Date  : 2013-8-26 20:29:40 下午
    Sample Name     : zero                          Location :   -
    Acq. Operator   :
    Method          : C:\HPCHEM\1\METHODS\CQ.M
    Last changed    : 2013-8-26 20:10:32 下午
                      (modified after loading)
```



```
    =====================================================================
                        Area Percent Report
    =====================================================================

    Sorted By            :      Signal
    Multiplier           :      1.0000
    Dilution             :      1.0000

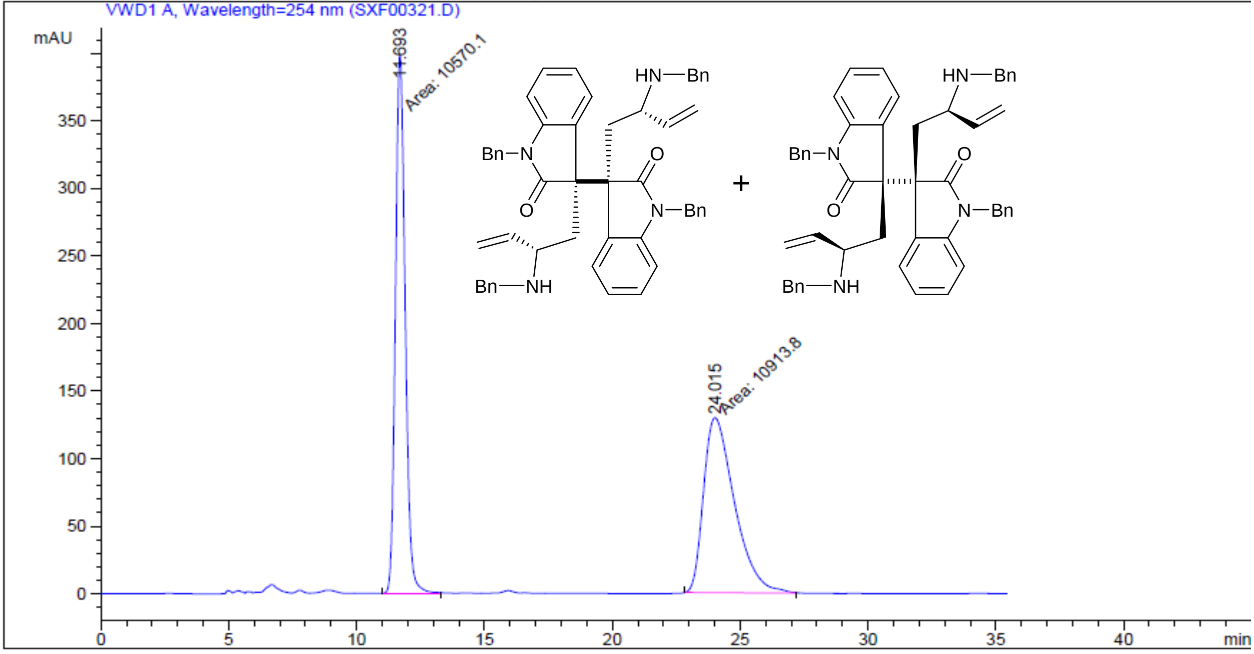

    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   mAU   *s   [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  50.183 MM    2.2697  589.94226    4.33207   0.4883
       2  52.932 MM    3.9482 1.20229e5  507.53134  99.5117

    Totals :                   1.20819e5  511.86342

     Results obtained with enhanced integrator!
    =====================================================================
                              *** End of Report ***
```

```
=====================================================================
Injection Date   : 2014-4-9 14:57:53 下午
Sample Name      : 00011                            Location :   -
Acq. Operator    :
Method           : C:\HPCHEM\1\METHODS\ZYY.M
Last changed     : 2014-4-9 11:32:11 下午
                  (modified after loading)
```



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

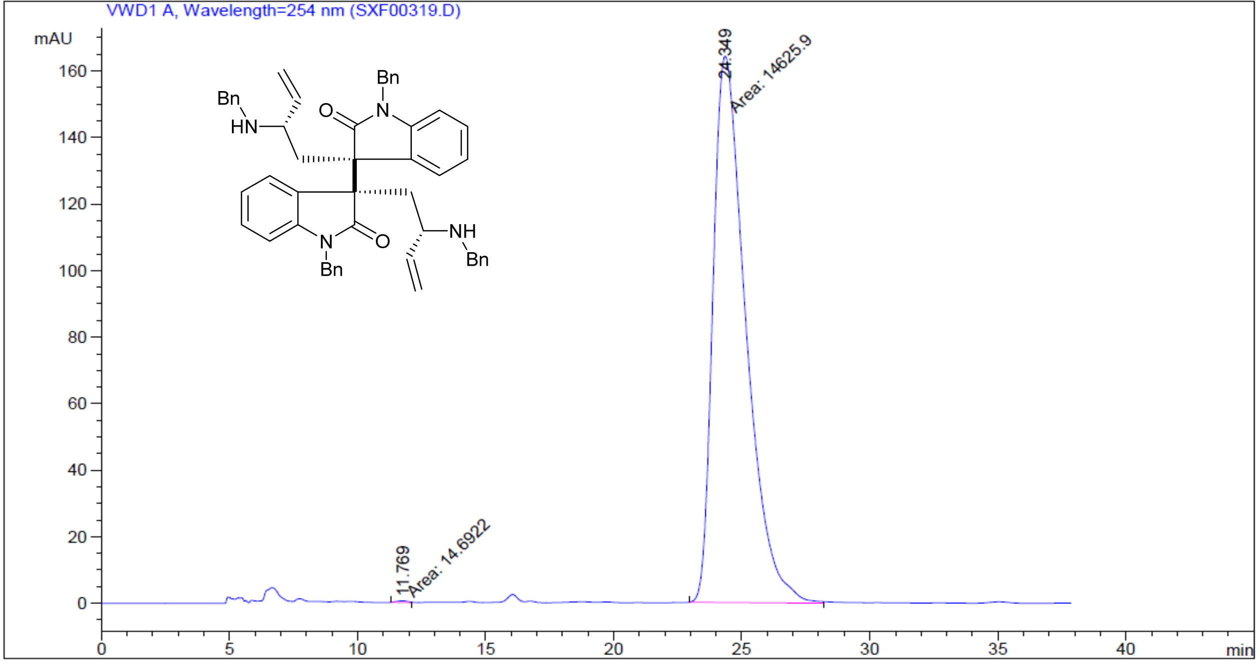
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.693 MM    0.4423 1.05701e4  398.32251  49.2003
   2  24.015 MM    1.4049 1.09138e4  129.46898  50.7997

Totals :                  2.14839e4  527.79149

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

```
Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00319.D                     Sample Name: 00011

    =====================================================================
    Injection Date  : 2014-4-9 13:37:47 下午
    Sample Name     : 00011                           Location :   -
    Acq. Operator   :
    Method          : C:\HPCHEM\1\METHODS\ZYY.M
    Last changed    : 2014-4-9 11:32:11 下午
                      (modified after loading)
```



```
    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU    *s   [mAU    ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  11.769 MM    0.5018   14.69220 4.87975e-1   0.1004
       2  24.349 MM    1.4844 1.46259e4   164.21399  99.8996

    Totals :                  1.46406e4   164.70196

     Results obtained with enhanced integrator!
    =====================================================================
                             *** End of Report ***



Instrument 1 2014-4-9 14:16:26 下午                                    Page 1 of 1
```