SUPPORTING INFORMATION

Annulated Diketopiperazines from Dipeptides or Schöllkopf Reagents via Tandem Cyclization-Intramolecular *N*-Arylation

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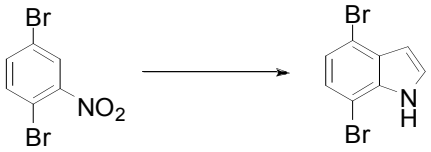
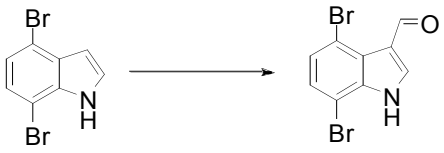
General Information. All solvents were dried by standard methods prior to use. Methylene chloride was distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl. Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen by using Schlenk techniques or a Vacuum Atmospheres glovebox. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). NMR experiments were performed using $CDCl_3$ with $CHCl_3$ (δ 7.24) as an internal standard. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter at the sodium D line in chloroform. Rhodium catalysts for asymmetric hydrogenation, CuI, and CsOAc were stored in a Vacuum Atomspheres drybox. CuI and CsOAc were purchased from Sigma-Aldrich Inc. Both Rh(COD)(*S,S*-MeDuPhos)BF_4 and ethyl analogue were either purchased from Strem Chemicals or prepared by known routes.[1] (*R*)-Schöllkopf reagent[2] and other Rh-hydrogenation catalysts (Tables 1 and 3)[3] were prepared according to procedures published before. For pressurized hydrogenation reaction, Parr Pressure Reactor was used.

Synthesis of 4,7-dibromo-1*H*-indole (5). Under N_2 atmosphere, 1 M vinyl magnesium bromide



(160.5 mL, 16.05 mmol) in anhydrous THF (320 mL) was added to a stirred solution of 2,5-dibromonitrobenzene (15 g, 5.34 mmol) at – 70 °C. The resulting mixture was stirred additional 20 min at - 50 °C, and then poured into sat. NH_4Cl. After the crude product was extracted with EtOAc (300 mL x 3), combined organics were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (10 % EtOAc in hexane.) to yield 6.95 g (47 %) of the title compound. ^1H NMR δ ($CDCl_3$): 8.39 (br s, 1H, N*H*), 7.28-7.21 (m, 3H, Ar 2, 5, and 6), 6.73-6.71 (dd, 1H, J = 3.2, 2.4 Hz, Ar 3); ^{13}C NMR δ ($CDCl_3$): 134.6, 129.5, 125.5, 125.1, 123.1, 104.4, 103.9.

Synthesis of 4,7-dibromo-1*H*-indole-3-carboxaldehyde (6). To an ice-cooled reaction vessel



containing DMF (50 mL) under N_2 atmosphere, $POCl_3$ (2.6 mL, 27.2 mmol) was added dropwise. Indole **5** (6.8 g, 24.7 mmol) in DMF (100 mL) was slowly added to the mixture. The resulting solution was stirred for 1 h at 0 °C and then for 5 h at RT. After the starting indole was consumed completely, the solution was poured into

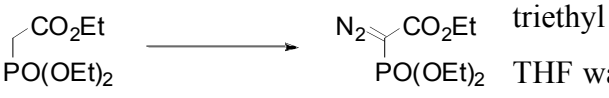
crushed ice. The mixture was treated with 1 M NaOH to adjust pH to 10 ~ 11, followed by quick heating to boil for 5 min. The mixture was cooled to 0 °C, and then acidified with 3 M HCl. The desired aldehyde was collected by filtration, and washed with water and hexane to get 5.9 g (79 %) of the title compound. ^{1}H NMR δ (DMSO-d_6): 10.67 (s, 1H, C*H*O), 8.28 (s, 1H, Ar 2), 7.40 (s, 2H, Ar 5 and 6); ^{13}C NMR δ (DMSO-d_6): 146.1, 144.3, 136.7, 135.8, 135.6, 128.5, 121.4, 114.7.

Synthesis of 4,7-dibromo-*N*-Boc-indole carboxaldehyde (7). To a stirred solution of 4,7-dibromo-1*H*-indole-3-carboxaldehyde **6** (10 g, 33.0 mmol) in THF (500 mL) was added NaH (3.4 g, 83.0 mmol) at 0 °C portionwise. After H_2 gas evolution ceased, $(BOC)_2O$ (8.8 g, 44.0 mmol) in THF (200 mL) was added slowly. The resulting mixture was stirred overnight at RT, and then the reaction was quenched by slow addition of water (500 mL). The crude product was extracted by ether (500 mL x 3) and the combined organic layers was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (10 % EtOAc in hexane.) to get 11.1 g (83 %) of the title compound. ^{1}H NMR δ ($CDCl_3$): 10.92 (s, 1H, C*H*O), 8.25 (s, 1H, Ar), 7.43-7.37 (dd, 2H, J = 12.8, 8.4 Hz, Ar), 1.65 (s, 9H, tBu); ^{13}C NMR δ ($CDCl_3$): 186.5, 147.1, 135.4, 135.3, 131.2, 129.9, 129.7, 121.0, 113.0, 107.5, 87.1, 28.0; IR cm^{-1} (KBr) : 3142, 2978, 2937, 2887, 1764, 1668, 1544, 1534, 1470, 1374, 1310, 1235, 1144, 1021.

Synthesis of *N*-Boc,*N*-Me-*L*-valine amide (9).[4] To a stirred solution of *N*-Boc,*N*-Me-*L*-valine (5 g, 21.6 mmol) and *N*-methyl morpholine (2.38 mL, 21.6 mmol) in anhydrous DME (100 mL) was added isobutyl chloroformate (2.82 mL, 21.65 mmol) dropwise at – 15 °C. After 0.5 h of stirring, NH_3 gas was bubbled into the reaction mixture for 15 min at – 15 °C and, for additional 15 min at rt. After addition of water (100 mL), the crude product was extracted by chloroform (100 mL x 3) and the combined organics were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by recrystallization (10 % EtOAc in hexane.) to yield 3.9 g (78 %) of the title compound. ^{1}H NMR δ ($CDCl_3$); 6.14 (br s, 1H, $CONH_2$), 5,35 (br s, 1H, $CONH_2$), 4.07-4.04 (d, 1H, J = 10.8 Hz, α-H), 2.78 (s, 3H, NCH_3), 2.27-2.18 (m, 1H, -C*H*$(CH_3)_2$), 1.45 (s, 9H, tBu), 0.96-0.94 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3)_2$), 0.86-0.84 (d, 3H, J = 6.8 Hz, -CH(C*H*$_3)_2$); ^{13}C NMR δ ($CDCl_3$): 173.2,

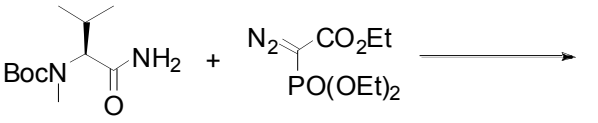
157.0, 80.3, 64.0, 30.2, 28.5, 26.1, 19.8, 18.6.

Synthesis of ethyl 2-diazo-2-(diethoxyphosphoryl)acetate (10).[5] To a stirred solution of



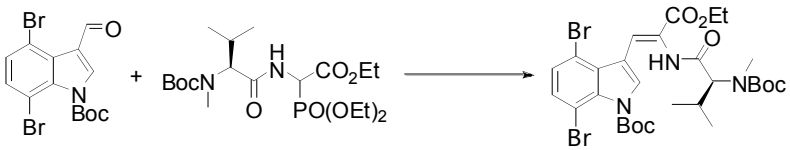
triethyl phosphonate (2.5 g, 11.15 mmol) in anhydrous THF was added a mixture of NaH (0.54 g, 13.38 mmol) and *p*-toluenesulfonyl azide (2.64 g, 13.38 mmol) in THF (5 mL) slowly at 0 °C. The resulting mixture was stirred at the same temperature for 10 min, and then stirred additional 10 min at RT. After ether (10 mL) and water (10 mL) were added, the crude product was extracted by ether (10 mL x 3). The combined organic layers was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (25 % EtOAc in hexane.) to get 2.35 g (84 %) of the title compound. ^{1}H NMR δ ($CDCl_3$): 4.24-4.10 (m, 4H, -OC*H*$_2$CH$_3$), 1.32-1.23 (m, 6H, -OCH$_2$C*H*$_3$); ^{13}C NMR δ ($CDCl_3$): 163.6, 163.4, 63.7, 61.8, 16.3, 14.5.

Synthesis of Schmidt's phosphonate 11.[5] To a single-necked rb flask, triethyl



diazophosphonate (2.2 g, 4.34 mmol), *N*-Boc,*N*-Me-*L*-valine amide (2 g, 4.34 mmol) were added. After the solution was treated with rhodium acetate (19 mg, 0.087 mmol), the mixture was heated to refluxed temperature until the starting diazo-compound was completely consumed. The solvent was evaporated, and the crude product was purified by column chromatography (10 % EtOAc in hexane) to get 11.1 g (83 %) of the title compound. ^{1}H NMR δ ($CDCl_3$): 4.30-4.05 (m, 8H, 3OC*H*$_2$CH$_3$, 2α-H), 2.76 (s, 3H, NC*H*$_3$), 2.30-2.14 (m, 1H, *i*Pr), 1.43 (s, 9H, *t*Bu), 1.35-1.20 (m, 9H, 3OCH$_2$C*H*$_3$), ^{13}C NMR δ ($CDCl_3$): 167.5, 166.3, 80.2, 68.5, 64.5, 63.6, 61.7, 51.2, 49.7, 30.0, 28.3, 19.7, 18.9, 18.4, 16.3, 14.9, 14.1; ^{31}P NMR δ ($CDCl_3$): 15.9, 14.4; IR cm^{-1} (KBr pellet): 3372, 3195, 2973, 1743, 1677, 1471, 1444, 1366, 1311, 1255, 1166, 1028.

Synthesis of enamide 12 using Horner-Emmons reaction.[6] After the aldehyde **7** (2.3 g, 5.71



mmol) and Schmidt's phosphonate **11** in anhydrous CH_2Cl_2 were treated with DBU (0.94 mL, 5.80 mmol) at 0 °C, the resulting mixture was stirred for 1 d at RT. The solvent was evaporated, and the crude product (**12**) was purified by column chromatography (20 % to 50 % EtOAc in hexane) to get 2.7 g (71 %) of the title compound. ^{1}H NMR δ ($CDCl_3$): 8.23 (s, 1H,

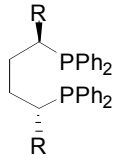
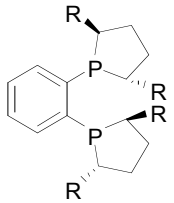
enamide), 7.76 (s, 1H, Ar2), 7.34-7.32 (d, 1H, J = 8.4 Hz, Ar), 7.28-7.26 (d, 1H, J = 8.4 Hz, Ar), 4.30-4.20 (m, 3H, -OC*H*$_2$CH$_3$ & α-H of Val.), 2.82 (s, 3H, -NC*H*$_3$), 2.29 (br s, 1H, -C*H*(CH$_3$)$_2$), 1.65 (s, 9H, tBu), 1.43 (s, 9H, *t*Bu), 1.33-1.30 (t, 3H, J = 7.2 Hz, -OCH$_2$C*H*$_3$), 1.01-0.99 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3$)$_2$), 0.87-0.85 (d, 3H, J = 6.8 Hz, -C*H*(CH$_3$)$_2$); ^{13}C NMR δ (CDCl$_3$): 169.8, 164.6, 157.3, 147.6, 134.9, 131.0, 130.7, 130.5, 129.1, 125.6, 124.0, 114.5, 113.5, 107.5, 85.9, 80.6, 61.5, 30.6, 28.4, 27.9, 25.9, 20.2, 18.6, 14.4; IR cm^{-1} (KBr pellet) : 3423, 3256, 2969, 2921, 2873, 1755, 1666, 1468, 1367, 1241, 1146; HRMS 724.1034 (M+Na$^{+\bullet}$; calcd for $C_{29}H_{39}Br_2NaN_3O_7$ 724.1029).

General procedure for Rh-catalyzed asymmetric hydrogenation (Table 1). Synthesis of 13a.[1,3] To a high-pressure Parr reactor, enamide **12**, Rh-catalyst (10 mol%) and degassed MeOH (10 mL) were added in a N_2-charged drybox. The reactor was brought out of the box, and set up in a fume hood. The reactor was evacuated and refilled with H_2-gas three times and finally pressurized to 90 psi. The mixture was stirred for 4 d at RT. After the pressure was released, the solvent was evaporated, and the crude product was purified by column chromatography. Hydrogenation of **12** was conducted using the following complexes and the results are recorded in Table 1: {[(*RR*)-2,5-diphenylphosphinohexane]Rh[NBD]}$^+$BF$_4^-$, {[(*RR*)-3,6-diphenylphosphino-2.7-dimethyloctane] Rh[NBD]}$^+$BF$_4^-$ (Table 1, entries 1, 2); [(*SS*)-Me-DuPhos]Rh[NBD]}$^+$BF$_4$ (entries 3 and 4).

Use of [(*SS*)-Et-DuPhos]Rh[COD]}$^+$BF$_4$-catalyzed asymmetric hydrogenation (entry 5, Table 1).[1] Following the general procedure, enamide **12** (0.5 g, 0.73 mmol) was hydrogenated using Rh[COD](Et-*S,S*-Duphos)$^+$BF$_4^-$ (44.0 mg, 0.073 mmol) and degassed MeOH (10 mL) under 90 psi for 4 d at RT. The crude product was purified by column chromatography (20 % EtOAc in hexane) to get 0.5 g (conv. 90 %, *S*:*R* = 8.5:1) of the title compound with 10 % of the unreacted starting enamide. ^{1}H NMR δ (CDCl$_3$): 7.41 (s, 1H, Ar), 7.34-7.32 (d, 1H, J = 8.4 Hz, Ar), 7.28-7.24 (t, 1H, J = 8.0 Hz, Ar), 4.9 (br s, α-H of Typ.), 4.18-4.09 (m, 2H, -OC*H*$_2$CH$_3$), 4.03-4.00 (d, 1H, J = 10 Hz, α-H of Val.), 3.55-3.50 (dd, 1H, J = 15.2, 5.6 Hz, -C*H*$_2$-), 3.38-3.32 (dd, 1H, J = 14.8, 8.8 Hz, -C*H*$_2$-), 2.70 (s, 3H, -NC*H*$_3$), 2.25 (br s, 1H, -C*H*(CH$_3$)$_2$), 1.64 (s, 9H, *t*Bu), 1.36 (s, 9H, *t*Bu), 1.33-1.30 (t, 3H, J = 7.0 Hz, -OCH$_2$C*H*$_3$), 0.94-0.93 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3$)$_2$), 0.85-0.84 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3$)$_2$); ^{13}C NMR δ (CDCl$_3$): 171.1, 170.5, 147.6;

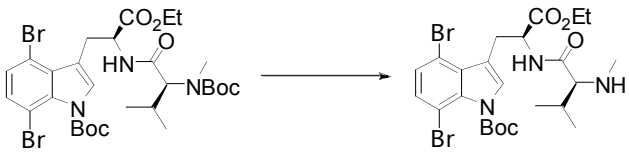
135.5, 131.2, 130.3, 129.2, 128.4, 113.3, 107.4, 84.9, 80.2, 61.4, 60.4, 28.2, 27.9, 21.0, 18.5, 14.2; IR cm^{-1} (neat) : 3322, 3119, 3057, 2976, 2873, 1746, 1693, 1530, 1469, 1392, 1315, 1242, 1153; HRMS 726.1192 ((M+$Na^{+\bullet}$); 726.1186 calcd for $C_{29}H_{41}Br_2NaN_3O_7$).

Table 1. Rh(I)-Catalyzed Hydrogenation of the Dehydro-dipeptide **12**

entry	ligand	conditions[a]	yield % (dr)[b]
1		R = Me (10 mol%), 90 psi, 3 d	> 99 (3.2:1.0)
2		R = *i*-Pr (10 mol%), 90 psi, 3 d	92 (2.9:1.0)
3		R = Me (10 mol%), 70 psi, 4 d	85 (4.6:1.0)
4		R = Me (10 mol%), 90 psi, 2 d	88 (4.6:1.0)
5		R = Et (10 mol%), 90 psi, 4 d	90 (8.5:1.0)

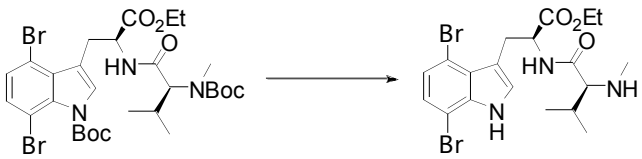
[a] Reactions done using {[Rh(ligand)(**L**)]$^+$ BF_4^- (**L** = NBD entries 1,2; or COD (entries 3-5)} in deoxygenated MeOH in a high pressure Parr hydrogenator. [b] dr = diastereomeric ratio, determined by ^{1}H NMR.

Attempts to prepare indolyl *N*-BOC protected NHMe dipeptide 13c by selective deprotection of the BOC group in Valine.



Di-BOC-protected dipeptide **13a** was treated with 3 M HCl or only formic acid at 0 ^oC, and then the reaction mixture was stirred at rt for 12 h. After, the solvent was evaporated, the residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. Only starting dipeptide compound **13a** was recovered.

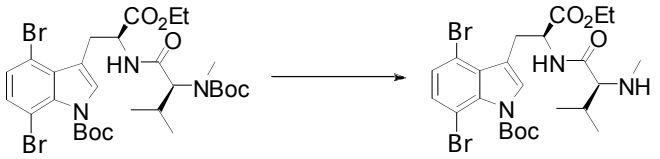
Synthesis of the dipeptide 13b by deprotection of both BOC groups.



Di-BOC-protected dipeptide **13a** (91 mg, 0.132 mmol) was treated with 30 % TFA in CH_2Cl_2 (5 mL), and then the reaction mixture was stirred for

1 h at RT. After the starting **13a** was consumed completely, the mixture was evaporated. The residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc) to get 66 mg (99 %) of the desired amine **13b**. ^{1}H NMR δ ($CDCl_3$): 8.38 (br s, 1H, N*H* of indole), 7.69-7.66 (d, 1H, J = 9.3 Hz, NH of amide), 7.22-7.21 (d, 1H, J = 1.0 Hz, Ar), 7.13 (s, 2H, Ar), 4.99-4.95 (m, 1H, α-H of Typ.), 4.20-4.12 (m, 2H, -OC*H*$_2$CH$_3$), 3.65-3.40 (m, 2H, benzylic H), 2.70-2.68 (d, 1H, J = 5.0 Hz, α-H of Val.), 2.32 (s, 3H, -NC*H*$_3$), 1.91-1.72 (m, 1H, -C*H*(CH$_3$)$_2$), 1.23-1.17 (t, 3H, J = 7.1 Hz, -OCH$_2$C*H*$_3$), 0.86-0.83 (d, 3H, J = 6.7 Hz, -CH(C*H*$_3$)$_2$), 0.63-0.60 (d, 3H, J = 6.7 Hz, -CH(C*H*$_3$)$_2$); ^{13}C NMR δ ($CDCl_3$): 173.8, 172.4, 136.0, 126.6, 125.3, 125.2, 113.9, 113.6, 104.4, 75.9, 71.1, 61.5, 53.1, 36.1, 34.3, 31.4, 29.9, 28.8, 19.5, 17.9, 14.3; IR cm^{-1} (neat) : 3323, 2959, 2922, 2852, 1737, 1659, 1517, 1478, 1371, 1335, 1247, 1170, 1070, 1029.; HRMS 526.0117 (M+Na$^{+\bullet}$); 526.0141 calcd for $C_{19}H_{25}Br_2NaN_3O_3$); $[\alpha]^{22}_D$ = -8.3 (c = 0.405, $CHCl_3$)

Synthesis of indolyl *N*-BOC protected dipeptide 13c by selective deprotection of the BOC group in valine.



Di-BOC-protected dipeptide **13a** (0.36 g, 0.52 mmol) was treated with 20 % TFA in CH_2Cl_2 (5 mL) at 0 ^{o}C, and then the reaction mixture was stirred for 12 h at the same temperature. The solvent was evaporated, and the residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc) to get the mono-protected amine **13c** (0.21 g, 67 %) along with some **13b** (71 mg, 30 %). **13c**: ^{1}H NMR δ ($CDCl_3$): 7.72-7.70 (d, 1H, J = 9.2 Hz, NH of amide), 7.47 (s, 1H, Ar), 7.35-7.33 (d, 1H, J = 8.0, Ar), 7.28-7.26 (d, 1H, J = 8.0 Hz, Ar), 5.06 (m, 1H, α-H of Typ.), 4.23-4.17 (q, 2H, J = 7.2 Hz, -OC*H*$_2$CH$_3$), 3.65-3.60 (dd, 1H, J = 14.0, 5.2 Hz, benzylic H), 3.42-3.36 (dd, 1H, J = 15.6, 9.6 Hz, benzylic H), 2.76-2.75 (d, 1H, J = 4.8 Hz, α-H of Val.), 2.39 (s, 3H, -NC*H*$_3$), 1.97-1.86 (m, 1H, -C*H*(CH$_3$)$_2$), 1.65 (s, 9H, *t*Bu), 1.25-1.22 (t, 3H, J = 7.2 Hz, -OCH$_2$C*H*$_3$), 0.85-0.83 (d, 3H, J = 6.8 Hz, -CH(C*H*$_3$)$_2$), 0.73-0.72 (d, 3H, J = 6.8 Hz, -CH(C*H*$_3$)$_2$); ^{13}C NMR δ ($CDCl_3$): 173.5, 172.0, 147.6, 131.3, 130.4, 129.3, 128.4, 115.8, 113.33, 107.3, 84.86, 70.8, 61.4, 52.1, 36.0, 31.3, 27.9, 19.4, 17.8, 14.1; IR cm^{-1} (KBr pellet) : 3326, 2971, 2794, 1737, 1659, 1515, 1459, 1376, 1315, 1238, 1143, 1088, 1016.; HRMS 604.0840 ((M+H$^{+\bullet}$); 604.0841 calcd for $C_{24}H_{33}Br_2N_3O_5$).

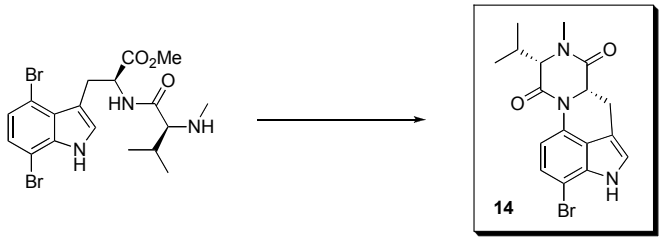
General procedure of Buchwald-Hartwig amination for macrocyclization (Table 2). To a sealable pressure tube, the Pd source (e. g., $Pd_2dba_3 \cdot CHCl_3$, 5-10 mol%), phosphine ligand (10 mol%), and a strong base like NaO*t*Bu (200 mol%) were added to a solution of the starting amine **13c** in toluene or 1,4-dioxane. The vessel was heated to 80 - 100 ^oC for 4-20 h. The mixture was cooled to RT, and then diluted with water (10 mL) and EtOAc (10 mL). The product was extracted by EtOAc (10 mL x 3), and the combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography. Results are tabulated in Table 2.

Table 2. Attempted Pd-catalyzed Intramolecular *N*-Arylation Reactions

entry	conditions	temp. (^oC) time (h)	result
1	$Pd(OAc)_2$ (5 mol%), DPPP (10 mol%), NaO^{t}Bu (200 mol%), toluene[a]	80 ^oC, 14 h	--b
2	$Pd_2dba_3.CHCl_3$(5 mol%), 3-$(tol)_3P$ (10 mol%), ^{t}BuONa (200 mol%), toluene	rt, 4 d	-- b
3	$Pd(OAc)_2$ (3.3 mol%), MOP (10 mol%), Cs_2CO_3 (200 mol%), toluene[a]	100 ^oC, 20 h	sm recovered
4	$Pd_2dba_3 \cdot CHCl_3$ (10 mol%), BINAP (10 mol%), ^{t}BuOK (200 mol%), K_2CO_3 (200 mol%), toluene[a]	90 ^oC, 14 h	-- b
5	$Pd_2dba_3 \cdot CHCl_3$ (8 mol%), BINAP (9 mol%), ^{t}BuONa (200 mol%), dioxane	100 ^oC, 5 h	-- b

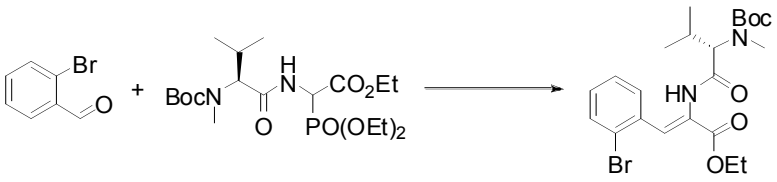
[a] Reaction was performed in sealed tube.
[b] No desired product without any starting material.

Synthesis of tetracyclic DKP 14 by the Cu-mediated tandem cyclization. CuI (62 mg, 0.123 mmol) and CsOAc (60 mg, 0.307 mmol) were added to a 1-neck flask in N_2 charged drybox, and then the vessel was taken out. To the vessel, Free amine **13b** (62 mg, 0.123 mmol) in anhydrous DMSO (1.5 mL) was added. The resulting mixture was heated to 90 ^oC for 12 h under N_2 atmosphere. After



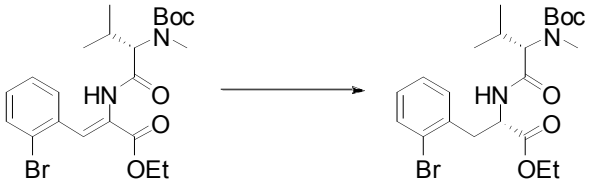
the starting material was completely consumed, the mixture was cooled to RT, and then diluted with water (10 mL) and EtOAc (10 mL). The product was extracted by EtOAc (10 mL x 3), and the combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by preparative TLC (67% EtOAc in *n*-Hex.) to get 29.3 mg (63 %) of **14** and 4.8 mg (10 %) of an unidentified compound. Pure major product **14** was crystallized under ether/EtOAc (2:1) for X-ray crystallography**. 14:** ^{1}H NMR δ ($CDCl_3$): 8.15 (br s, 1H, N*H* of indole), 7.78-7.74 (d, J = 8.0 Hz, Ar), 7.33-7.29 (d, J = 8.3 Hz, Ar), 6.97 (s, 1H, Ar), 4.50-4.44 (dd, 1H, J = 12.2, 3.0 Hz, Benzylic), 4.04-4.03 (d, 1H, J = 3.7 Hz, α-H of Typ.), 3.80-3.72 (dd, 1H, J = 15.7, 3.2 Hz, Benzylic), 3.16-3.08 (m, 4H, -NCH_3 & α-H of Val.), 2.35-2.28 (m, 1H, -C*H*$(CH_3)_2$), 1.16-1.13 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3)_2$), 0.88-0.86 (d, 3H, J = 6.2 Hz, -CH(C*H*$_3)_2$); ^{13}C NMR δ ($CDCl_3$): 165.5, 163.6, 133.6, 130.5, 125.6, 122.0, 118.7, 113.8, 110.1, 100.3, 68.4, 60.2, 34.5, 32.4, 29.1, 19.8, 18.2; IR cm^{-1} (KBr pellet): 3299, 2922, 1650, 1494, 1402, 1344, 1292, 1260, 1080.; HRMS 376.0644 ((M+H$^{+\bullet}$); 376.0661 calcd for $C_{17}H_{19}BrN_3O_2$); $[\alpha]^{22}_D$ = – 51.1 (c = 0.355, $CHCl_3$)

Synthesis of (*S*)-*N*-BOC-valinyl 2-bromophenylalanyl ethyl ester (19) using Horner-Emmons reaction followed by hydrogenation. (a) Synthesis of dehydrodipeptide substrate



18. After 2-bromobenzladehyde (0.5 g, 2.7 mmol) and Schmidt's phosphonate **11** (1.25 g, 2.7 mmol) in anhydrous CH_2Cl_2 were treated with DBU (0.41 mL, 0.54 mmol) at 0 ^{o}C, the resulting mixture was stirred for 1 d at RT. The solvent was evaporated, and the crude product was purified by column chromatography (10 % to 20 % EtOAc in hexane.) to get 0.85 g (65 %) of the dehydrodipeptide **18**. ^{1}H NMR δ ($CDCl_3$): 7.76 (br s, 1H, C*H* in enamide), 7.54-7.52 (d, 1H, J = 8.0 Hz, Ar), 7.40 (s, 1H, N*H*), 7.33-7.32 (d, 1H, J = 7.2 Hz, Ar), 7.17-7,14 (t, 1H, J = 7.2 Hz, Ar), 7.10-7.06 (m, 1H, Ar), 4.27-4.22 (q, 2H, 6.8 Hz, -OC*H*$_2$CH$_3$), 4.09-4.06 (d, 1H, J = 11.2 Hz, α-H of Val.), 2.65 (s, 3H, -NC*H*$_3$), 2.20-2.06 (m, 1H, -C*H*$(CH_3)_2$), 1.41 (s, 9H, *t*Bu), 1.30-1.27 (t, 3H, J = 7.1 Hz, -OCH$_2$C*H*$_3$), 0.85-0.83 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3)_2$), 0.79-0.77 (d, 3H, J = 6.4 Hz, -C*H*$(CH_3)_2$); ^{13}C NMR δ ($CDCl_3$): 168.6, 164.5; 157.1, 134.9, 133.0, 130.2, 130.1, 129.5, 127.1, 126.1, 124.4, 80.6, 64.5, 61.9, 30.2, 28.5, 25.9, 19.6, 18.5, 14.3; IR cm^{-1} (neat): 3277, 2973, 2932, 2874, 1725, 1666, 1480, 1392, 1368, 1296, 1256, 1153, 1100, 1026.; HRMS 483.1472 ((M+H$^{+\bullet}$); 483.1495 calcd for

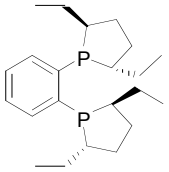
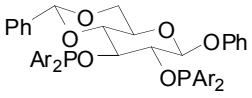
$C_{22}H_{32}BrN_2O_5$).

(b) Synthesis of dipeptide 19 using Rh-catalyzed asymmetric hydrogenation of 18 (entry 3, Table 3).[3a] 

To a high-pressure Parr reactor, enamide **18** (0.36 g, 0.74 mmol), {Rh[[2,3-**D**-gluco-1,2-diarylphosphinite][NBD]}$^{+}$ BF_4^{-}[2b] (3.9 mg, 0.037 mmol) and anhydrous THF (10 mL) were added in N_2 charged drybox. The reactor was brought out, and set up in a fume hood. The reactor was evacuated and refilled 3 times, and finally pressurized to 90 psi. The mixture was stirred for 4 d at RT. After the pressure was released, the solvent was evaporated, and the crude product was purified by column chromatography (20 % EtOAc in *n*-Hex.) to yield 0.36 g (conv. > 99 %, *SS*:*RS* = 6.8:1, based on ^{1}H NMR) of the 2-Br-Phe-Val derivative **19**. ^{1}H NMR δ ($CDCl_3$): 7.47-7.45 (d, 1H, J = 8.0 Hz, Ar), 7.15-7.10 (m, 2H, Ar), 7.04-7.00 (m, 1H, Ar), 6.58 (br s, 1H, N*H*), 4.85-4.84 (br d, 1H, 6.8 Hz, α-H of Tyr.), 4.13-3.99 (m, 3H, -OC*H*$_2$CH$_3$, & α-H of Val.), 3.29-3.24 (dd, 1H, J = 14.0, 5.6 Hz, benzylic), 3.06-2.98 (br m, 1H, Benzylic), 2.67 (s, 3H, -NC*H*$_3$, minor isomer), 2.53 (s, 3H, -NC*H*$_3$, major isomer), , 2.17-2.06 (m, 1H, -C*H*(CH$_3$)$_2$), 1.42 (s, 9H, *t*Bu), 1.19-1.14 (t, 3H, J = 7.0 Hz, -OCH$_2$C*H*$_3$), 0.85-0.83 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3$)$_2$), 0.77-0.75 (d, 3H, J = 6.4 Hz, -CH(C*H*$_3$)$_2$); ^{13}C NMR δ ($CDCl_3$): 171.1, 170.1, 156.7, 136.1, 132.9, 131.2, 128.5, 127.3, 124.9, 80.1, 64.4, 61.4, 60.3, 51.7, 38.4, 29.9, 28.4, 26.0, 21.0, 19.7, 18.4, 14.0; IR cm^{-1} (neat): 3330, 3058, 2964, 2870, 1740, 1677, 1510, 1469, 1442, 1369, 1333, 1307, 1155, 1030.; HRMS 485.1630 ((M+H$^{+\bullet}$); 485.1651 calcd for $C_{22}H_{34}BrN_2O_5$); $[\alpha]^{22}_{D\ 589nm}$ = -79.3 (c = 0.75, $CHCl_3$).

Results of hydrogenation using other catalysts are summarized in Table 3.

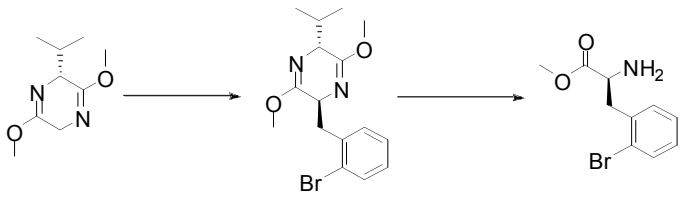
Table 3. Rh-catalyzed asymmetric hydrogenations of *Z*-dehydro-dipeptide **18**[a]

entry	ligand	condition	yield (dr) [b]
1		cat. 5 mol%, MeOH 60 psi, rt, 24 h	100 % (*SS/SR* = 3.6:1.0)
2	 Ar = 3,5 dimethylphenyl	cat. 5 mol%, THF 40 psi, rt, 24 h	38% (*SS/SR* = 10:1.0)
3		cat. 5 mol%, THF 60 psi, rt, 48 h	**100 % (*SS/SR* = 6.8:1.0)**

[a] High pressure Paar hydrogenator was used.
[b] Selectivities were determined by ^{1}H NMR.

Dipeptide *N*-Val-2-Br-Phe-OEt (20) via deprotection of the BOC group from 19. *N*-BOC-protected dipeptide **19** (0.16 g, 0.33 mmol) was treated with 30 % TFA in CH_2Cl_2 (5 mL), and then the reaction mixture was stirred overnight at RT. After the starting BOC-derivative was consumed completely, the mixture was evaporated. The residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc) to get 0.13 g (> 99 %) of the desired dipeptide (**20**). ^{1}H NMR δ ($CDCl_3$): 7.66-7.64 (d, 1H, J = 8.8 Hz, N*H*), 7.52-7.50 (d, 1H, J = 8.0 Hz, Ar), 7.28-7.26 (d, 1H, J = 8.0 Hz, Ar), 7.23-7.19 (t, 1H, J = 6.8 Hz, Ar), 7.08-7.05 (t, 1H, J = 6.8 Hz, Ar), 4.96-4.93 (m, 1H, α-H of Tyr.), 4.19-4.14 (q, 2H, J = 7.2 Hz, -OC*H*$_2$CH$_3$), 3.35-3.30 (dd, 1H, J = 14.0, 5.6 Hz, benzylic), 3.19-3.13 (dd, 1H, J = 14.4, 10.0 Hz, Benzylic), 2.73- 2.72 (d, 1H, J = 4.8 Hz, α-H of Val.), 2.34 (s, 3H, -NC*H*$_3$), 1.95-1.83 (m, 1H, -C*H*(CH$_3$)$_2$), 0.94-0.93 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3$)$_2$, minor isomer (*RS*)), 0.88-0.86 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3$)$_2$, minor isomer (*RS*)), 0.80-0.78 (d, 3H, J = 6.8 Hz, -CH(C*H*$_3$)$_2$), major isomer (*SS*)), 0.73-0.71 (d, 3H, J = 6.8 Hz, -C*H*(CH$_3$)$_2$, major isomer (*SS*)); ^{13}C NMR δ ($CDCl_3$): 173.5, 171.8, 136.4, 133.0, 131.3, 128.7, 127.6, 125.1, 70.9, 70.5, 61.6, 53.6, 51.9, 38.1, 36.1, 35.9, 31.3, 19.4, 18.1, 14.2; IR cm^{-1} (neat): 3319, 3055, 2964, 2801, 1736, 1655, 1513, 1473, 1437, 1366, 1199, 1133, 1026.

Synthesis of *2*-bromophenylalanine (23a) using Schöllkopf reagent.[7] *n*-BuLi (3.7 ml, 5.43 mmol, 1.47 M in hexane) was added dropwise to the solution of Schöllkopf reagent (1.0 g, 5.43 mmol) in anhydrous THF (5 mL) at -78 ^{o}C under N_2. The resulting solution was stirred additional 20 min. A solution of 2-bromobenzyl bromide (1.29 g, 5.43 mmol) was added to the mixture over 5 min periods, and the resulting mixture was stirred for 3 h at –78 ^{o}C. After the reaction was quenched with sat. NH_4Cl (5 mL), the reaction was warmed up to RT, and diluted with EtOAc (20 mL) and water (10 mL). The crude product was extracted with EtOAc (3 x 20 mL), and combined organic phase was dried over $MgSO_4$. After volatiles were evaporated, the crude product was purified by column chromatography (5 % EtOAc in hexane.). 1.7 g (93 %) of desired alkylated compound **22a** was obtained. ^{1}H NMR δ ($CDCl_3$): 7.51-7.50 (d, 1H, J = 7.5 Hz, Ar), 7.21-7.16 (m, 2H, Ar), 7.05-7.02 (m, 1H, Ar), 4.33-4.30 (m, 1H, α-H of Tyr.), 3.71 (s, 3H, OCH_3), 3.66-3.65 (t, 1H, J = 3.5 Hz, α-H of Val.), 3.62 (s, 3H, OCH_3), 3.47-3.43 (dd, 1H, J = 13.8, 4.8 Hz, benzylic), 2.95-2.90 (dd, 1H, J = 13.8, 8.2 Hz, benzylic), 2.21-2.18 (m, 1H, -CH(CH_3)$_2$), 1.00-0.99 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$), 0.65-0.63 (d, 3H, J = 6.5 Hz, -CH(CH_3)$_2$); ^{13}C NMR δ ($CDCl_3$): 163.8, 163.1, 137.9, 132.6, 131.9, 127.9, 126.8, 125.4, 60.5, 55.9, 52.5, 40.3, 31.4, 19.1, 16.6; IR cm^{-1} (neat): 3056, 2962, 2870, 1685, 1587, 1461, 1458, 1374, 1239, 1109, 1026.



The alkylated compound **22a** (0.5 g, 1.42 mmol) in CH_3CN (10 mL) was treated with 0.3 N HCl (10 mL), and the resulting solution was stirred at rt for 30 min. The solution was made basic with sat. $NaHCO_3$, and the product was extracted with CH_2Cl_2 (3 x 20 mL). After drying and evaporation, the product was purified by column chromatography (EtOAc) to yield 0.34 g (92 %) of 2-bromo-*L*-phenylalanine methyl ester **23a**. All spectral data were matched with reported data. ^{1}H NMR δ ($CDCl_3$): 7.58-7.56 (d, 1H, J = 8.0 Hz, Ar), 7.28-7.24 (m, 2H, Ar), 7.15-7.10 (m, 1H, Ar), 3.90 (br s, 1H, α-H of Tyr.), 3.73 (s, 3H, OCH_3), 3.30-3.26 (dd, 1H, J = 13.4, 5.4 Hz, benzylic), 2.97-2.92 (dd, 1H, J = 13.6, 8.8 Hz, benzylic).

Synthesis of *o*-iodo phenylalanine (23b) using Schöllkopf reagent.[7] Using the same procedure as in the previous experiment, but with 2-iodobenzyl bromide (0.385 g, 1.3 mmol), 0.388 g (75 %) of desired alkylated compound **22b** was obtained. ^{1}H NMR δ ($CDCl_3$): 7.80-7.79 (d, 1H, J = 7.5 Hz, Ar), 7.24-7.19 (m, 2H, Ar), 6.88-6.84 (m, 1H, Ar), 4.30-4.27 (m, 1H, α-H of Tyr.), 3.72-3.71 (4H, OC*H*$_3$ & α-H of Val.), 3.63 (s, 3H, OC*H*$_3$), 3.44-3.40 (dd, 1H, J = 13.8, 4.8 Hz, benzylic), 2.95-2.91 (dd, 1H, J = 13.8, 7.8 Hz, benzylic), 2.22-2.19 (m, 1H, -C*H*$(CH_3)_2$), 1.01-1.00 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3)_2$), 0.66-0.64 (d, 3H, J = 6.5 Hz, -CH(C*H*$_3)_2$); ^{13}C NMR δ ($CDCl_3$): 163.9, 163.2, 141.4, 139.5, 131.1, 128.2, 127.9, 102.0, 60.7, 56.3, 52.8, 52.7, 45.0, 31.6, 19.3, 16.8; IR cm^{-1} (neat): 3222, 2969, 1722, 1681, 1585, 1462, 1373, 1342, 1215, 1168, 1014.

The alkyated compound **22b** (0.24 g, 0.601 mmol) in CH_3CN (10 mL) was treated with 0.3 N HCl (5 mL), and the resulting solution was stirred at rt for 30 min. The solution was made basic with sat. $NaHCO_3$, and the product was extracted with CH_2Cl_2 (3 x 20 mL). After drying and evaporation, the product was purified by column chromatography (EtOAc) to get 0.184 g of the mixture of 2-iodo-*L*-phenylalanine methyl ester **23b** (85 %) with valine methyl ester (15 %). This mixture was used for a coupling reaction without further purification. All spectral data were matched with reported data. ^{1}H NMR δ ($CDCl_3$): 7.86-7.85 (d, 1H, J = 7.8 Hz, Ar), 7.31-7.28 (m, 1H, Ar), 7.24-7.22 (dd, 1H, J = 7.8, 1.8 Hz, Ar), 6.96-6.92 (m, 1H, Ar), 3.86-3.83 (dd, 1H, J = 8.2, 4.2 Hz, α-H of Tyr.), 3.73 (s, 3H, OC*H*$_3$), 3.27-3.23 (dd, 1H, J = 13.8, 4.2 Hz, benzylic), 2.95-2.90 (dd, 1H, J = 13.5, 8.0 Hz, benzylic); ^{13}C NMR δ ($CDCl_3$): 175.4, 140.5, 139.9, 130.9, 128.8, 128.4, 101.1, 54.8, 52.2, 45.9.

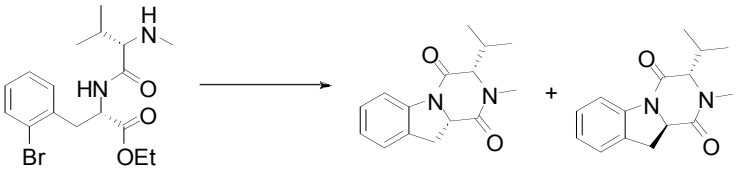
Synthesis of dipeptide 25b using a peptide coupling reaction, followed by deprotection. To a stirred solution of *N*-Boc, *N*-Me-*L*-valine (52 mg, 0.224 mmol), 2-iodo-*L*-phenylalanine methyl ester (57 mg, 0.187 mmol), and DIEA (79 μL, 0.449 mmol) in anhydrous CH_2Cl_2 (3 mL) was added HBTU (72 mg, 0.224 mmol), and the resulting solution was stirred for 12 h at RT. After the solvent was evaporated, the crude product was purified by column chromatography (10 to 20 % EtOAc in hexane) to get 95 mg (98

%) of the dipeptide **24b**. ^{1}H NMR δ ($CDCl_3$): 7.79-7.77 (d, 1H, J = 7.6 Hz, Ar), 7.49 (br s, 1H, Ar), 7.11-7.09 (d, 1H, J = 7.2 Hz, Ar), 6.90-6.86 (t, 1H, J = 7.6 Hz, Ar), 6.55 (br s, 1H, N*H*), 4.88 (br s, 1H, α-H of Tyr.), 4.10-3.99 (d, 1H, J = 10.8 Hz, α-H of Val.), 3.69 (s, 3H, -OCH_3) 3.30-3.25 (dd, 1H, J = 14.0, 5.6 Hz, benzylic), 3.06-2.98 (br d, 1H, J = 6.0 Hz, Benzylic), 2.54 (s, 3H, -NCH_3), 2.20-2.10 (m, 1H, -C*H*(CH_3)$_2$), 1.44 (s, 9H, *t*Bu), 0.87-0.85 (d, 3H, J = 6.4 Hz, -CH(CH_3)$_2$), 0.79-0.78 (d, 3H, J = 6.4 Hz, -C*H*(CH_3)$_2$); ^{13}C NMR δ ($CDCl_3$): 171.7, 170.3, 157.0, 139.9, 139.4, 130.5, 128.8, 128.4, 101.1, 80.36, 64.7, 52.6, 51.9, 43.1, 30.2, 28.6, 26.1, 19.8, 18.6; $[\alpha]^{22}_{D\ 589nm}$ = -74.4 (c = 1.285, $CHCl_3$).

The resulting compound **24b** (85 mg, 0.164 mmol) was treated with by 30 % TFA in CH_2Cl_2 (5 mL), and then the reaction mixture was stirred at RT for 8 h. After the starting BOC derivative was consumed completely, the mixture was evaporated. The residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc) to yield 67.2 mg (98 %) of the desired amine **25b**. ^{1}H NMR δ ($CDCl_3$): 7.78-7.77 (d, 1H, J = 8.0 Hz, Ar), 7.59-7.57 (d, 1H, J = 8.5 Hz, N*H*), 7.24-7.22 (m, 2H, Ar), 6.89-6.85 (m, 1H, Ar), 4.95-4.91 (m, 1H, α-H of Tyr.), 3.71 (s, 3H, -OCH_3), 3.34-3.30 (dd, 1H, J = 14.0, 6.0 Hz, benzylic), 3.14-3.09 (dd, 1H, J = 14.0, 10.0 Hz, Benzylic), 2.69-2.68 (d, 1H, J = 5.0 Hz, α-H of Val.), 2.33 (s, 3H, -NCH_3), 1.88-1.84 (m, 1H, -C*H*(CH_3)$_2$), 0.77-0.76 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$), 0.69-0.67 (d, 3H, J = 7.0 Hz, -C*H*(CH_3)$_2$); ^{13}C NMR δ ($CDCl_3$): 173.7, 172.4, 139.8, 130.4, 128.9, 128.6, 101.4, 71.1, 52.6, 52.1, 42.7, 36.1, 31.5, 19.5, 18.1.

General procedure of Cu-mediated tandem cyclizations (Table 1 in the article). Copper iodide (100 mol%) and CsOAc (250 mol%) were added to a 1-neck rb-flask in a N_2 charged drybox, and then the vessel was taken out. To the vessel, free amine (100 mol%) in anhydrous DMSO (1~1.5 mL/0.1 mmol of starting amines) was added. The resulting mixture was heated to 90 ^{o}C for 12 h under N_2 atmosphere. After the starting material was completely consumed, the mixture was cooled to RT, and then diluted with water (10 mL) and EtOAc (10 mL). The product was extracted by EtOAc (10 mL x 3), and the combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by preparative TLC or column chromatography.

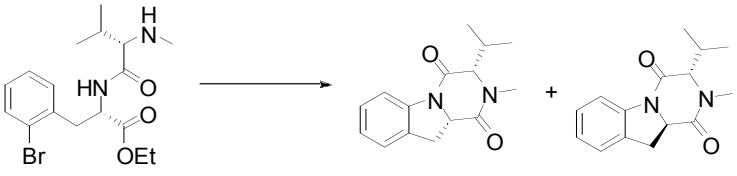
Synthesis of the tricyclic DKP 27 and 28 by Cu-mediated tandem cyclization (entry 3, Table 1 in article). Using the general procedure with 25 mg (0.065 mmol) of amine **20** and stoichiometric amount of CuI, (10.0 mg, 59 %) **27** and **28** (3.1 mg, 18 %) were obtained**.**



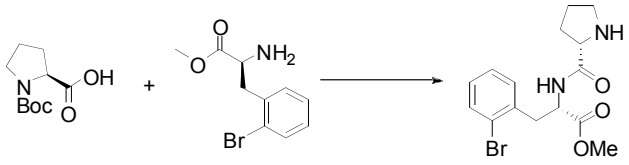
27: ^{1}H NMR: δ ($CDCl_3$): 8.01-8.00 (d, 1H, J = 8.0 Hz, Ar), 7.28-7.22 (m, 2H, Ar), 7.11-7.08 (t, 1H, J = 7.5 Hz, Ar), 4.74-4.70 (dd, 1H, J = 11.2, 9.2 Hz, α-H of Tyr.), 4.00-3.99 (d, 1H, J = 1.0 Hz, α-H of Val.), 3.40-3.28 (m, 2H, , benzylic), 3.04 (s, 3H, -NCH_3), 2.45-2.42 (m, 1H, -CH(CH_3)$_2$), 1.24-1.23 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$), 0.94-0.92 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$); ^{13}C NMR δ ($CDCl_3$): 166.7, 162.8, 141.5, 130.1, 127.9, 125.2, 124.9, 116.9, 67.5, 60.1, 32.8, 32.7, 30.7, 19.5, 16.3; IR cm^{-1} (neat): 2984, 2922, 1668, 1602, 1485, 1421, 1394, 1249, 1092.; HRMS 259.1431 ((M+H$^{+\bullet}$); 259.1447 calcd for $C_{15}H_{19}N_2O_2$); $[\alpha]^{22}_D$ = -71.9 (c = 0.42, $CHCl_3$).

28: ^{1}H NMR δ ($CDCl_3$): 8.10-8.09 (d, 1H, J = 8.0 Hz, Ar), 7.27-7.25 (s, 2H, Ar), 7.14-7.11 (t, 1H, J = 7.2 Hz, Ar), 4.91-4.87 (t, 1H, J = 10.0 Hz, α-H of Tyr.), 3.73-3.71 (d, 1H, J = 7.5 Hz, α-H of Val.), 3.59-3.54 (dd, 1H, J = 16.2, 10.2 Hz, benzylic), 3.13 (s, 3H, -NCH_3), 2.35-2.21 (m, 1H, -CH(CH_3)$_2$), 1.20-1.19 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$), 1.16-1.15 (d, 3H, J = 6.5 Hz, -CH(CH_3)$_2$); ^{13}C NMR δ ($CDCl_3$): 167.4, 164.1, 141.3, 130.0, 128.0, 125.3, 125.0, 116.70, 72.0, 59.6, 35.6, 32.4, 32.1, 20.3, 19.5; IR cm^{-1} (neat): 2962, 2924, 1713, 1672, 1601, 1483, 1464, 1390, 1242, 1149, 1049; HRMS 281.1247 ((M+Na$^{+\bullet}$); 281.1266 calcd for $C_{15}H_{18}NaN_2O_2$); $[\alpha]^{22}_D$ = +24.6 (c = 0.570, $CHCl_3$).

Synthesis of the tricyclic DKPs 27 and 28 by catalytic amount of Cu-mediated tandem cyclization (entry 4, Table 1 in article). Using the general procedure, 11 mg (0.027 mmol) of amine **20** and catalytic amount of CuI (0.43 mg, 0.0027 mmol) gave **27** (1.2 mg, 20 %) and **28** (4.0 mg, 69 %)**.**



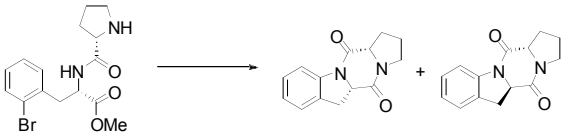
Synthesis of proline-containing dipeptide 26a by an aminoacid coupling reaction, and deprotection to 26b. To a stirred solution of *N*-Boc-*L*-proline (25 mg, 0.116 mmol), 2-bromo-phenylalanine methyl ester **23a** (20



mg, 0.0077 mmol), and DIEA (40.5 μL, 0.233 mmol) in anhydrous CH_2Cl_2 (3 mL) was added HBTU (38 mg, 0.116 mmol). The resulting solution was stirred for 12 h at RT. After the solvent was evaporated, the crude product was purified by column chromatography (20 % EtOAc in *n*-Hex.) to yield 35 mg (99 %) of the title compound **26a**. ^{1}H NMR δ ($CDCl_3$): 7.51-7.49 (d, 1H, J = 8.0 Hz, Ar), 7.20-7.18 (2H, Ar), 7.08-7.05 (t, 1H, J = 6.6 Hz, Ar), 6.59 (br s, 1H, N*H*), 4.93-4.86 (d, 1H, J = 6.0 Hz, α-H of Tyr.), 4.16 (br s, 1H, α-H of Pro.), 3.70 (s, 3H, OCH_3), 3.33-3.10 (m, 4H, benzylic & N(BOC)CH_2R in proline), 2.25-1.72 (m, 4H, CHCH_2CH_2 in proline), 1.43 (s, 9H, *t*Bu); ^{13}C NMR δ ($CDCl_3$): 171.9, 133.1, 131.4, 128.9, 125.3, 52.6, 52.3, 47.3, 28.5; $[\alpha]^{23}_D$ = -50.7 (c = 0.38, $CHCl_3$).

BOC-protected dipeptide **26a** (25 mg, 0.055 mmol) was treated with 30 % TFA in CH_2Cl_2 (5 mL), and then the reaction mixture was stirred overnight at rt. After the starting material was consumed completely, the mixture was evaporated. The residue was diluted with CH_2Cl_2 (10 mL) and washed with sat. $NaHCO_3$ (10 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (only EtOAc) to yield 19.3 mg (> 99 %) of the desired amine **26b**. ^{1}H NMR δ ($CDCl_3$): 8.06-8.05 (d, 1H, J = 8.0 Hz, N*H*), 7.51-7.50 (d, 1H, J = 7.5 Hz, Ar), 7.22-7.18 (m, 2H, Ar), 7.08-7.05 (m, 1H, Ar), 4.92-4.87 (m, 1H, α-H of Tyr.), 3.71 (s, 3H, OCH_3), 3.68-3.65 (m, 1H, α-H of Pro.), 3.35-3.31 (dd, 2H, J = 14.0, 6.0 Hz, benzylic), 3.15-3.11 (dd, 2H, J = 13.8, 8.8 Hz, benzylic), 2.95-2.91 (m, 1H, NHCH_2R in proline), 2.83-2.78 (m, 1H, NHCH_2R in proline), 2.02-1.96 (m, 1H, $CHCH_2CH_2$ in proline) 1.64-1.47 (m, 3H, CHCH_2CH_2 in proline); ^{13}C NMR δ ($CDCl_3$): 175.2, 172.4, 136.3, 133.1, 131.4, 128.8, 127.6, 125.3, 60.5, 52.6, 51.8, 47.4, 38.3, 30.8, 26.2; HRMS 379.0448 ((M+$Na^{+\bullet}$); 379.0458 calcd for $C_{15}H_{19}BrNaN_2O_3$).

Synthesis of the tetracyclic DKPs 29 and 30 by Cu-mediated tandem cyclization. The



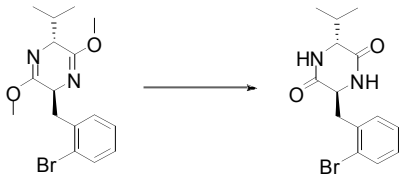
proline amine **26b** (12 mg, 0.0338 mmol) was cyclized to yield the title compounds **29** (3.9 mg, 48%) and 1.0 mg. (12 %) of isomerized product **30**, using the general procedure (stoichiometric amount of CuI). **29**: ^{1}H NMR δ ($CDCl_3$): 8.07-8.05 (d, 1H, J = 8.0 Hz, Ar), 7.22-7.20 (2H, Ar), 7.09-7.05 (m, 1H, Ar), 4.86-4.82 (t, 1H, 9.8 Hz, α-H of Tyr.), 4.32-4.29 (t, 1H, J = 6.8 Hz, α-H of Pro.), 3.71-3.66 (dd, 1H, J = 16.8, 9.2 Hz, benzylic), 3.61-3.58 (dd, 2H, J = 8.2, 5.8 Hz, NCH_2R in proline), 3.38-3.32 (dd, 1H, J = 16.5, 9.5 Hz, benzylic), 2.40-2.32 (m, 2H, CHCH_2CH_2 in proline), 2.05-1.96 (m, 2H, $CHCH_2CH_2$ in

proline); ^{13}C NMR δ ($CDCl_3$): 165.8, 165.4, 140.9, 130.2, 128.0, 125.2, 125.1, 116.0, 61.6, 61.1, 45.8, 30.5, 27.9, 23.7; IR cm^{-1} (neat) : 2959, 2925, 2855, 1666, 1601, 1485, 1462, 1410, 1245, 1215, 1131, 1087.; HRMS 265.0935 ($M+Na^{+\bullet}$; calcd for $C_{14}H_{14}NaN_2O_2$ 265.0953); $[\alpha]^{22}_D$ = -10.2 (c = 0.380, $CHCl_3$).

30: ^{1}H NMR δ ($CDCl_3$): 8.04-8.03 (d, 1H, J = 8.0 Hz, Ar), 7.28-7.20 (2H, Ar), 7.11-7.08 (t, 1H, J = 7.5 Hz, Ar), 5.15-5.10 (m, 2H, α-H of Tyr. & α-H of Pro.), 3.85-3.81 (t, 1H, J = 9.0 Hz, benzylic), 3.61-3.54 (m, 2H, NC*H*$_2$R in proline), 3.39-3.33 (m, 1H, benzylic), 2.59-2.45 (m, 1H, CHC*H*$_2$CH$_2$ in proline), 3.32-2.18 (m, 2H, CHCH$_2$C*H*$_2$ in proline).

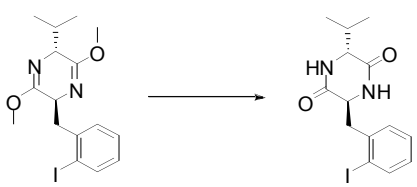
General procedure of demethylations of dimethoxy-2,5-dihydropyrazine to 2,5-diketopiperazine. To a stirred solution of alkylated dimethoxy-2,5-dihydropyrazine in $CHCl_3$ was added TMSI (300 mol%) under N_2, and the resulting solution was stirred for 1 h at RT. The reaction was quenched with few drops of MeOH, and then evaporated under reduced pressure. The crude product was purified by recrystallization.

Synthesis of (3*S*,6*R*)-3-(2-bromobenzyl)-6-isopropylpiperazine-2,5-dione (31a) Using the



general demethylation procedure with 30 mg (0.0852 mmol) of dimethyl substrate **22a**, 25 mg (90 %) of the title compound **31a** was obtained. ^{1}H NMR δ (DMSO-d_6): 8.07 (s, 1H, N*H* of Val.), 7.89-7.88 (d, 1H, J = 2.0 Hz, N*H* of Tyr.), 7.59-7.58 (d, 1H, J = 7.5 Hz, Ar), 7.33-7.29 (m, 2H, Ar), 7.20-7.17 (m, 1H, Ar), 4.14-4.11 (m, 1H, α-H of Tyr.), 3.50 (d, 1H, J = 1.5 Hz, α-H of Val.), 3.34 (s, 3H, -NC*H*$_3$), 3.25-3.21 (dd, 1H, J = 14.2, 5.2 Hz, benzylic), 3.11-3.07 (dd, 1H, J = 14.0, 7.0 Hz, benzylic), 2.23-2.2.17 (m, 1H, -C*H*(CH$_3$)$_2$), 0.94-0.93 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3$)$_2$), 0.83-0.82 (d, 3H, J = 7.0 Hz, -CH(C*H*$_3$)$_2$); ^{13}C NMR δ (DMSO-d_6): 167.9, 167.3, 136.0, 132.5, 131.8, 128.7, 127.5, 124.6, 58.9, 54.9, 53.9, 38.5, 30.6, 18.2, 16.7; IR cm^{-1} (KBr pellet): 3446, 3190, 3056, 2962, 2876, 1673, 1471, 1447, 1346, 1290, 1105, 1028.; HRMS 347.0352 (($M+Na^{+\bullet}$); 347.0371 calcd for $C_{14}H_{17}BrNaN_2O_2$); $[\alpha]^{22}_D$ = – 19.5 (c = 0.465, MeOH).

Synthesis of (3*S*,6*R*)-3-(2-iodobenzyl)-6-isopropylpiperazine-2,5-dione (31b). Using the



general demethylation procedure with 30 mg (0.0852 mmol) of dimethyl substrate **22b**, 25 mg (90 %) of the title compound **31b** was obtained. ^{1}H NMR δ (DMSO-d_6): 8.09 (s, 1H, N*H* of Val.), 7.85-7.84 (2H, N*H* of Tyr. & Ar), 7.35-7.32 (t, 1H, J =

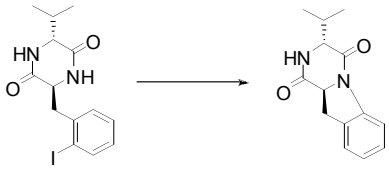
7.2 Hz, Ar), 7.29-7.27 (q, 1H, J = 6.5 Hz, Ar), 7.01-6.98 (m, 1H, Ar), 4.11-4.09 (t, 1H, J = 4.8 Hz, α-H of Tyr.), 3.55 (d, 1H, J = 2.5 Hz, α-H of Val.), 3.30 (s, 3H, -NCH_3), 3.20-3.16 (dd, 1H, J = 14.0, 5.0 Hz, benzylic), 3.09-3.04 (dd, 1H, J = 14.0, 7.0 Hz, benzylic), 2.22-2.2.18 (m, 1H, -CH(CH_3)$_2$), 0.95-0.94 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$), 0.84-0.83 (d, 3H, J = 7.0 Hz, -CH(CH_3)$_2$); ^{13}C NMR δ (DMSO-d_6): 167.9, 167.3, 139.2, 130.7, 128.6, 128.2, 60.0, 54.9, 42.8, 30.5, 18.2, 16.7; IR cm^{-1} (KBr pellet): 3444, 3190, 3055, 2961, 2874, 1665, 1448, 1384, 1344, 1288, 1105, 1010.

Synthesis of tricyclic DKP 32 using stoichiometric amount of CuI. Following the general procedure using 30 mg (0.0923 mmol) of bromide substrate **31a** 19.0 mg (84 %) of the title compound **32** and 3.0 mg of isomerized product **33** (13 %) were obtained. **32**: ^{1}H NMR δ ($CDCl_3$): 8.16-8.14 (d, 8.0 Hz, 1H, Ar), 7.29-7.26 (m, 2H, Ar), 7.15-7.20 (t, 7.5 Hz, Ar), 7.10 (br s, 1H, NH), 4.89-4.85 (t, J = 10.2 Hz, α-H of Tyr.), 3.87-3.85 (dd, J = 6.0, 2.0 Hz, 1H, α-H of Val.), 3.50-3.46 (dd, J = 16.5, 10.5 Hz, 1H, Benzylic H), 3.42-3.37 (dd, J = 16.0, 10.2 Hz, 1H, Benzylic H), 2.38-2.33 (q, J = 6.5 Hz, 1H, CH_3CHRCH_3), 1.16-1.14 (d, J = 6.5 Hz, 3H, CH_3CHRCH_3), 1.11-1.10 (d, J = 7.0 Hz, 3H, CH_3CHRCH_3); ^{13}C NMR δ ($CDCl_3$): 169.3, 164.4, 141.5, 129.5, 128.1, 125.4, 125.0, 64.2, 59.4, 33.2, 32.2, 19.4, 18.3; IR cm^{-1} (neat) : 3237, 2965, 2931, 2874, 1681, 1601, 1463, 1417, 1284.; HRMS 267.1093 (M+Na$^{+\bullet}$; calcd for $C_{14}H_{16}N_2O_2Na$ 267.1109); $[\alpha]^{22}_D$ = -14.6 (c = 0.600, $CHCl_3$).

33: ^{1}H NMR δ ($CDCl_3$): 8.12-8.11 (d, 7.5 Hz, 1H, Ar), 7.26-7.22 (m, 2H, Ar), 7.10-7.07 (m, 1H, Ar), 5.93 (br s, 1H, NH), 4.79-4.75 (t, J = 10.0 Hz, α-H of Tyr.), 4.06-4.05 (d, J = 1.5 Hz, 1H, α-H of Val.), 3.59-3.54 (dd, J = 10.0, 16.0 Hz, 1H, Benzylic H), 3.39-3.34 (dd, J = 10.0, 16.0 Hz, 1H, Benzylic H), 2.74-2.71 (m, 1H, CH_3CHRCH_3), 1.13-1.11 (d, J = 7.5 Hz, 3H, CH_3CHRCH_3), 0.99-0.97 (d, J = 7.0 Hz, 3H, CH_3CHRCH_3); ^{13}C NMR δ ($CDCl_3$): 169.9, 141.3, 129.6, 128.1, 125.2, 116.4, 60.9, 60.1, 31.1, 28.0, 19.6, 16.4.; $[\alpha]^{22}_D$ = + 88.6 (c = 0.150, $CHCl_3$).

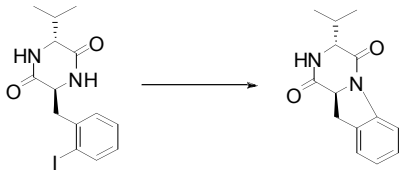
Synthesis of tricyclic DKP 32 using catalytic amount of CuI and bromo substrate 31a. Following the general procedure using 20 mg (0.0615 mmol) of bromo-substrate **31a**, 11.9 mg (79 %) of the title compound **32** and 2.4 mg (16 %) of isomerized product **33** were obtained.

Synthesis of tricyclic DKP 32 using stoichiometric amount of CuI and iodo substrate 31b.



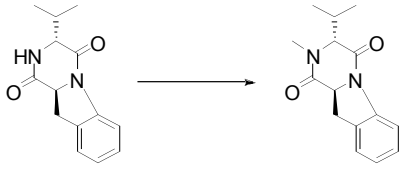
Following the general procedure using 11.8 mg (0.0317 mmol) of iodo-substrate **31b**, 7.8 mg (> 99 %) of the title compound **32** was obtained.

Synthesis of tricyclic DKP 32 using catalytic amount of CuI and iodo-substrate 31b.



Following the general procedure using 10 mg (0.0267 mmol) of iodo-substrate **31b**, 6.2 mg (95 %) of the title compound **32** and 0.1 mg (1.5 %) of isomerized product **33** were obtained.

Synthesis of tricyclic DKP *ent*-28. To a stirred solution of 3**2** (5.0 mg, 0.0205 mmol) and MeI



(6.2 μL, 0.1 mmol) in THF (2 mL), was added NaH (4.0 mg, 0.1 mmol) at 0 ^{o}C. The resulting solution was stirred at RT for 1 h, and then quenched with water. The product was extracted with EtOAc (3 x 5 mL), and combined organics were dried over $MgSO_4$. After the solvent was evaporated, the crude product was purified by prep. TLC to yield the title compound ***ent*-28** (5.3 mg, > 99 %). ^{1}H NMR δ ($CDCl_3$): 8.07-8.05 (d, 7.6 Hz, 1H, Ar), 7.22-7.21 (2H, Ar), 7.10-7.06 (t, 7.2 Hz, Ar), 4.87-4.82 (t, J = 10.0 Hz, α-H of Tyr.), 3.69-3.67 (d, 1H, J = 7.2 Hz, α-H of Val.), 3.56-3.3.50 (dd, J = 16.4, 10.0 Hz, benzylic), 3.41-3.44 (dd, J = 16.4, 10.0 Hz, 1H, Benzylic H), 3.08 (s, 3H, NCH_3), 2.32-2.25 (m, 1H, CH_3CHRCH_3), 1.16-1.14 (d, J = 7.2 Hz, 3H, CH_3CHRCH_3), 1.12-1.11 (d, J = 6.8 Hz, 3H, CH_3CHRCH_3; ^{13}C NMR δ ($CDCl_3$): 167.2, 163.8, 141.1, 129.8, 127.8, 125.1, 124.8, 116.5, 71.9, 67.1, 59.4, 35.3, 32.2, 32.0, 20.1, 19.3; IR cm^{-1} (neat) : 2930, 2922, 1667, 1601, 1483, 1402, 1241, 1110, 1050.; HRMS 281.1248 ((M+$Na^{+\bullet}$); 281.1266 calcd for $C_{15}H_{18}NaN_2O_2$); $[\alpha]^{22}_{D}$ = – 49.1 (c = 0.285, $CHCl_3$).

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RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 4137. [**D**-Glucose derived ligand]Rh^+ (Scheme 3, Supporting Information Table 3): (b) T. V. RajanBabu, T. A. Ayers, G. A. Halliday, K. K. You, J. C. Calabrese, *J. Org. Chem.* **1997**, *62*, 6012.

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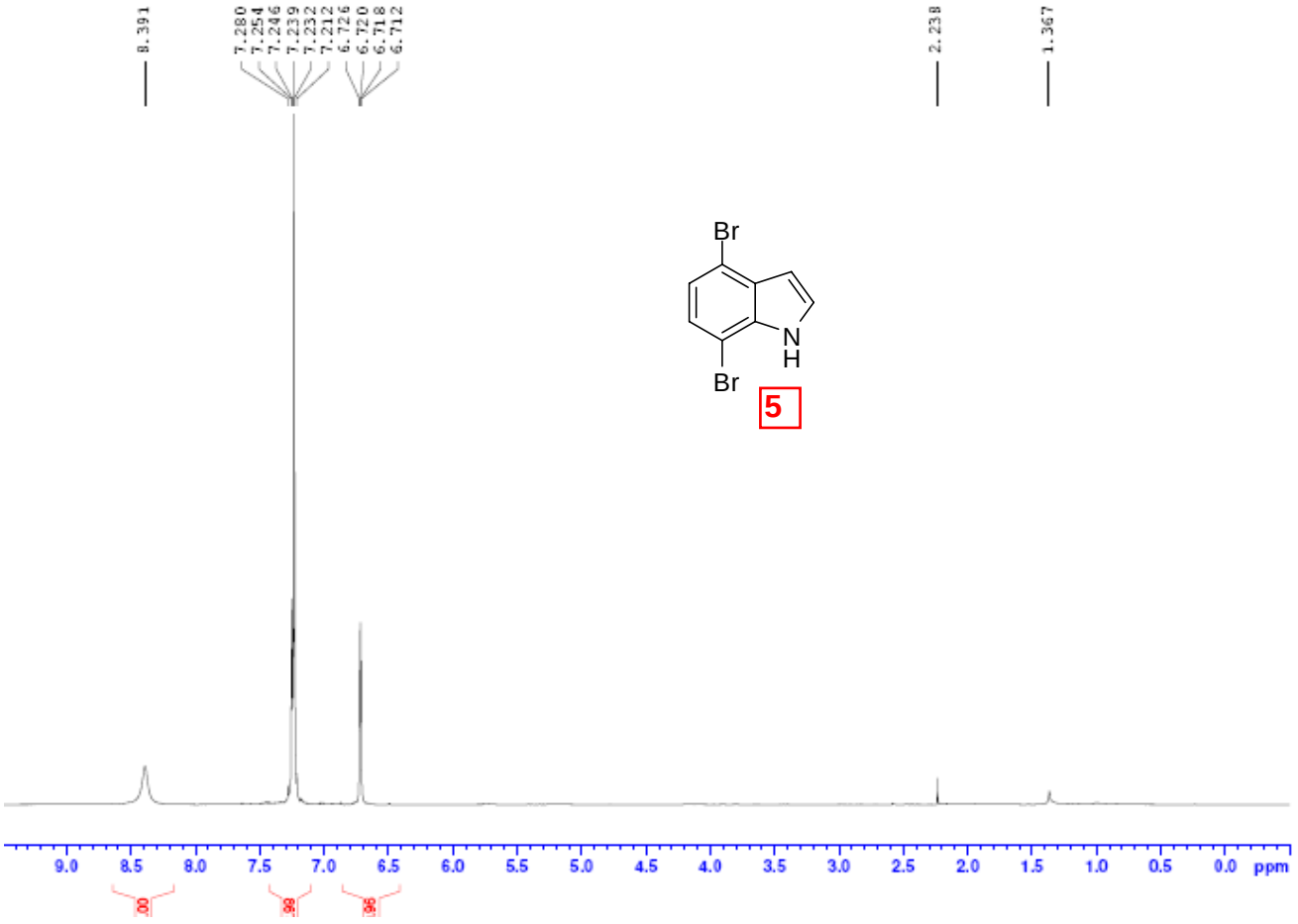


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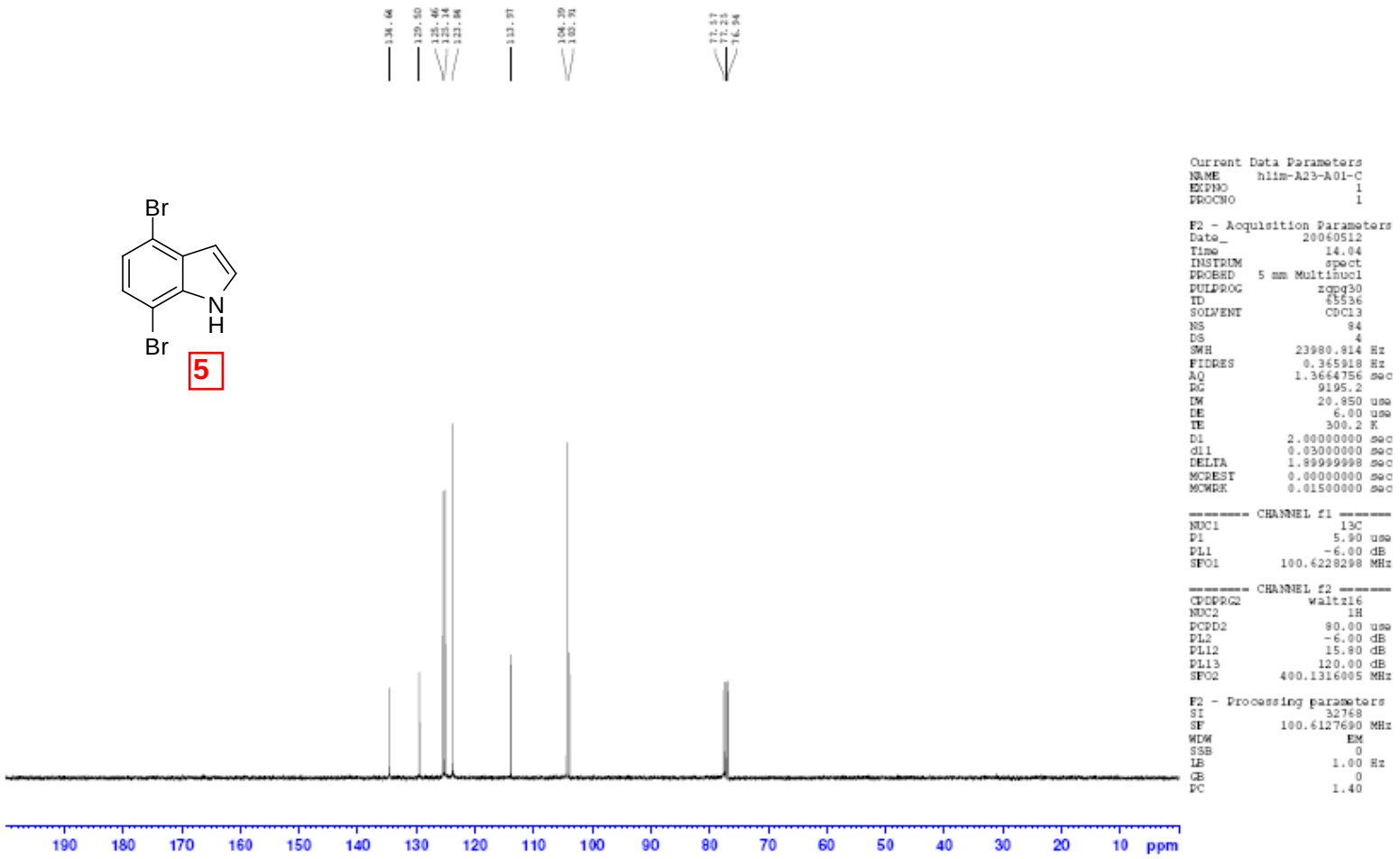
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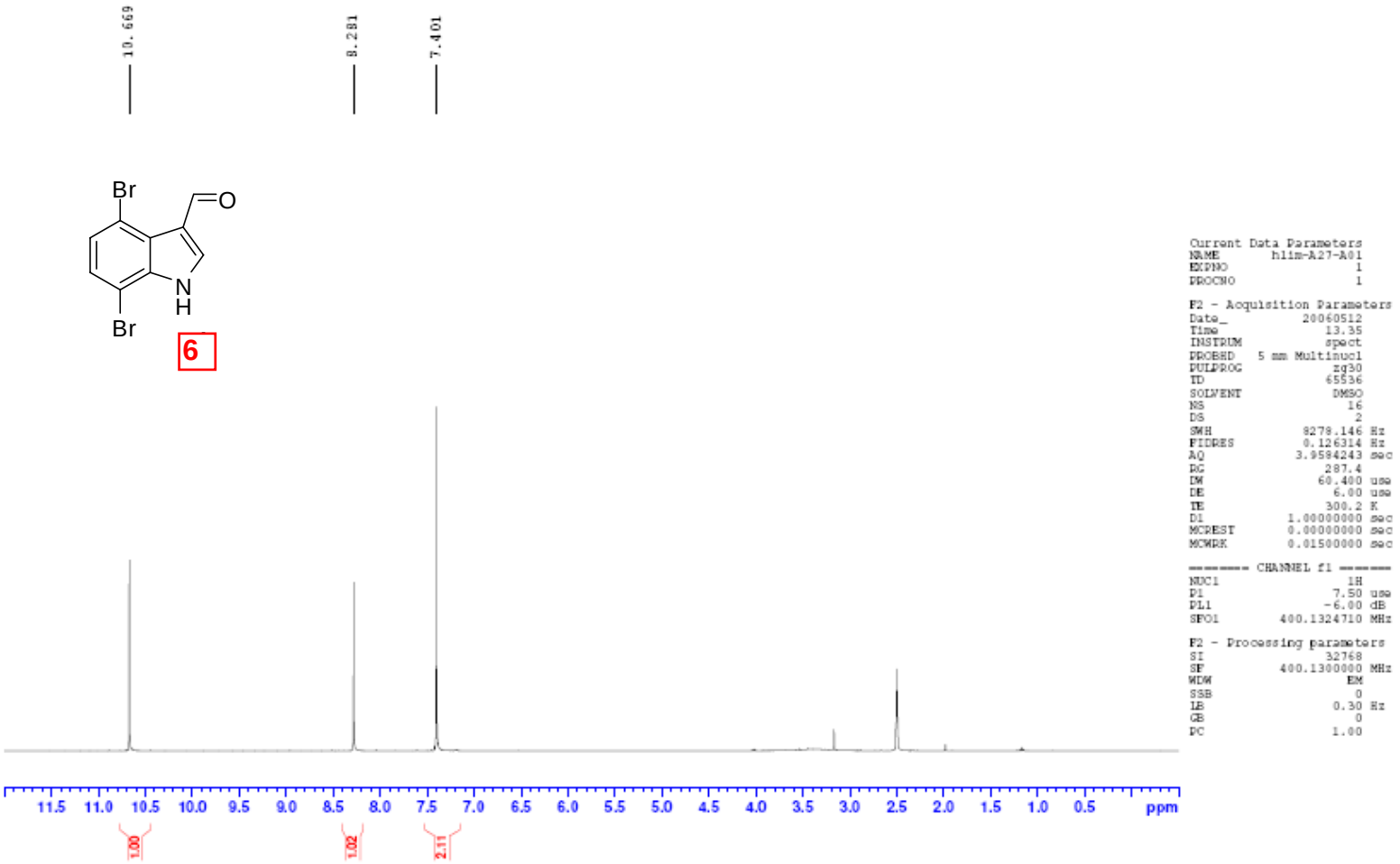
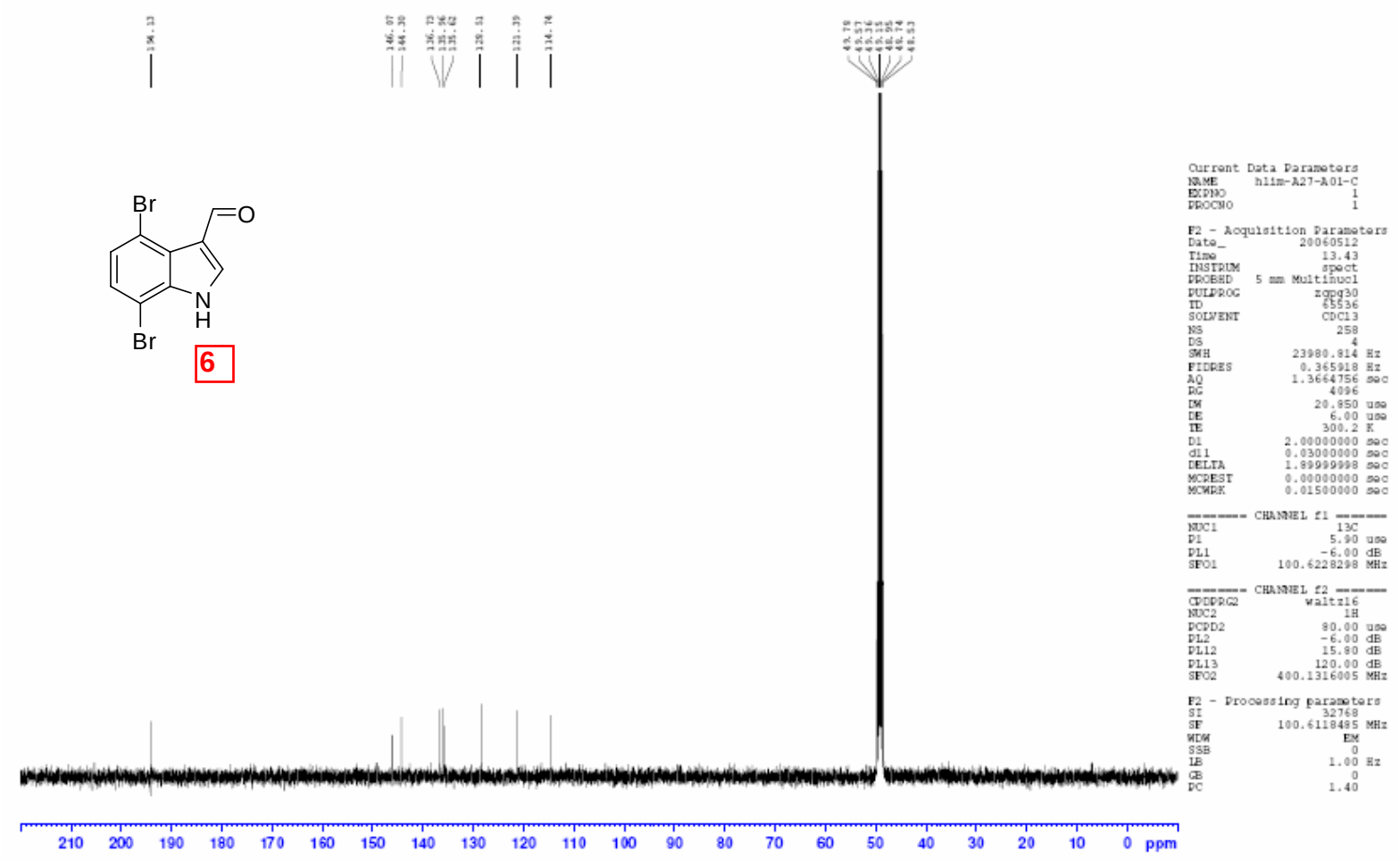
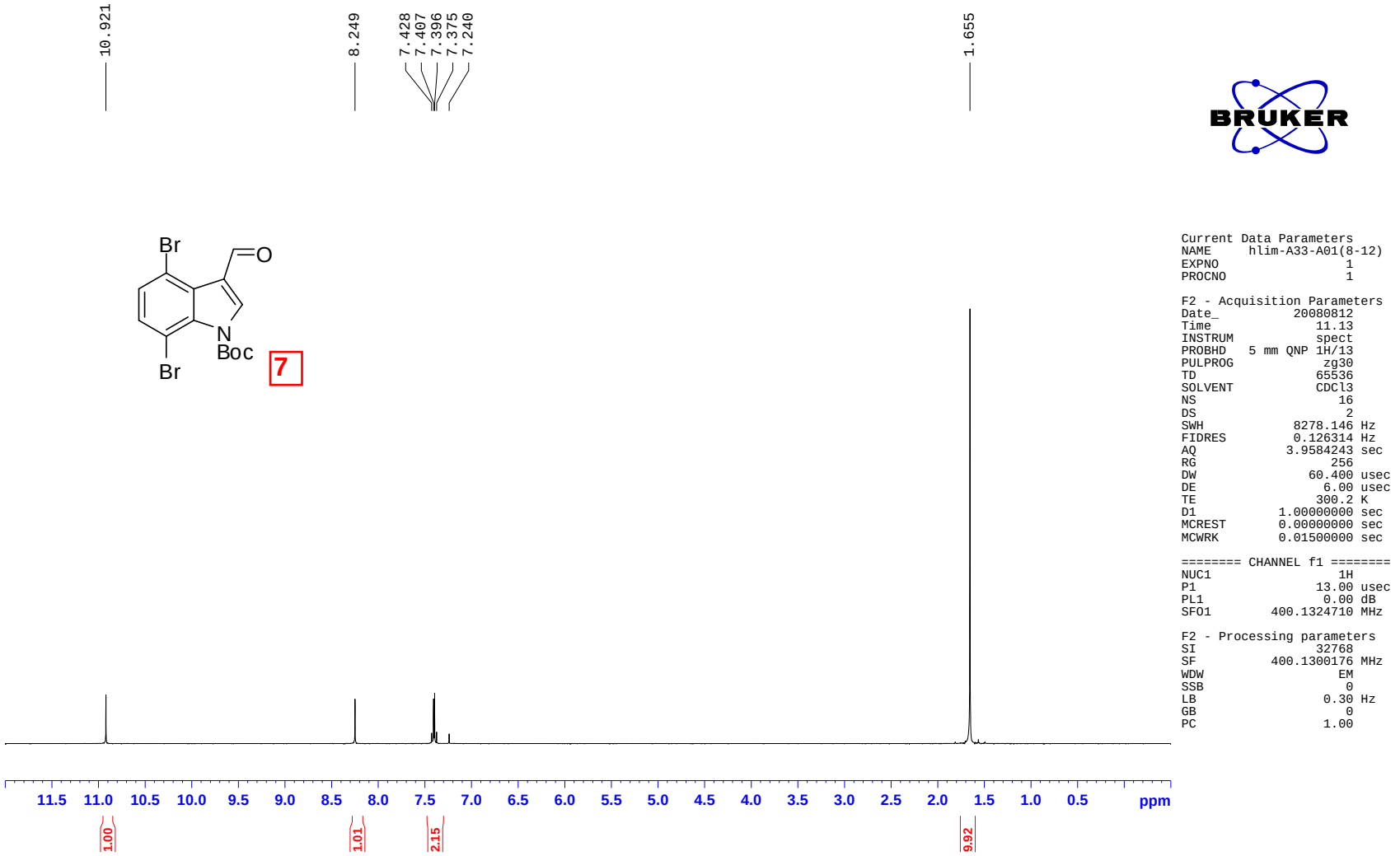
NUC1 13C
P1 5.90 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 15.80 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

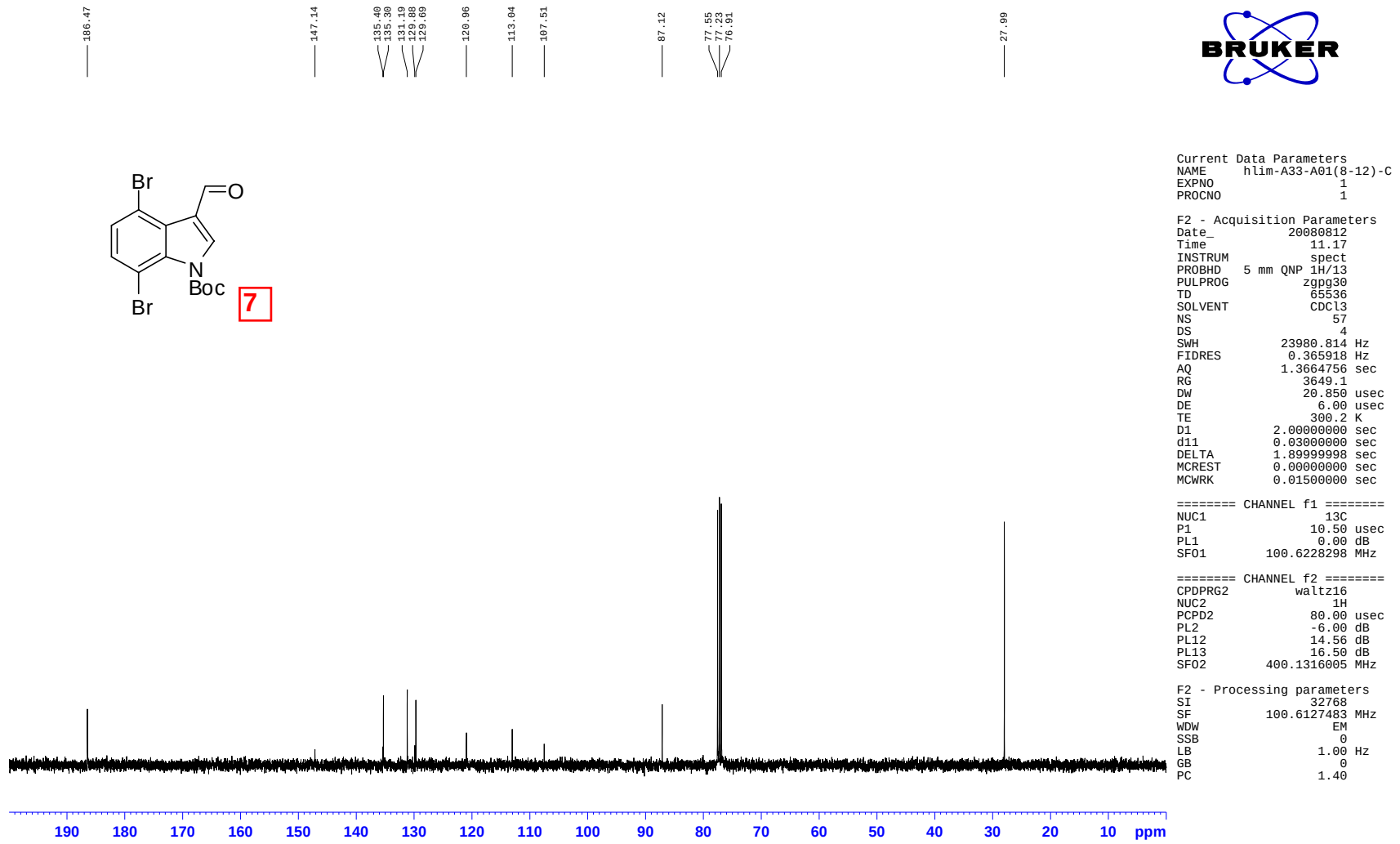



```
Current Data Parameters
NAME          hlim-A27-A01
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060512
Time                  13.35
INSTRUM                spect
PROBHD   5 mm Multinucl
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                    287.4
DW                   60.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ======
NUC1                     1H
P1                    7.50 usec
PL1                  -6.00 dB
SFO1          400.1324710 MHz

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

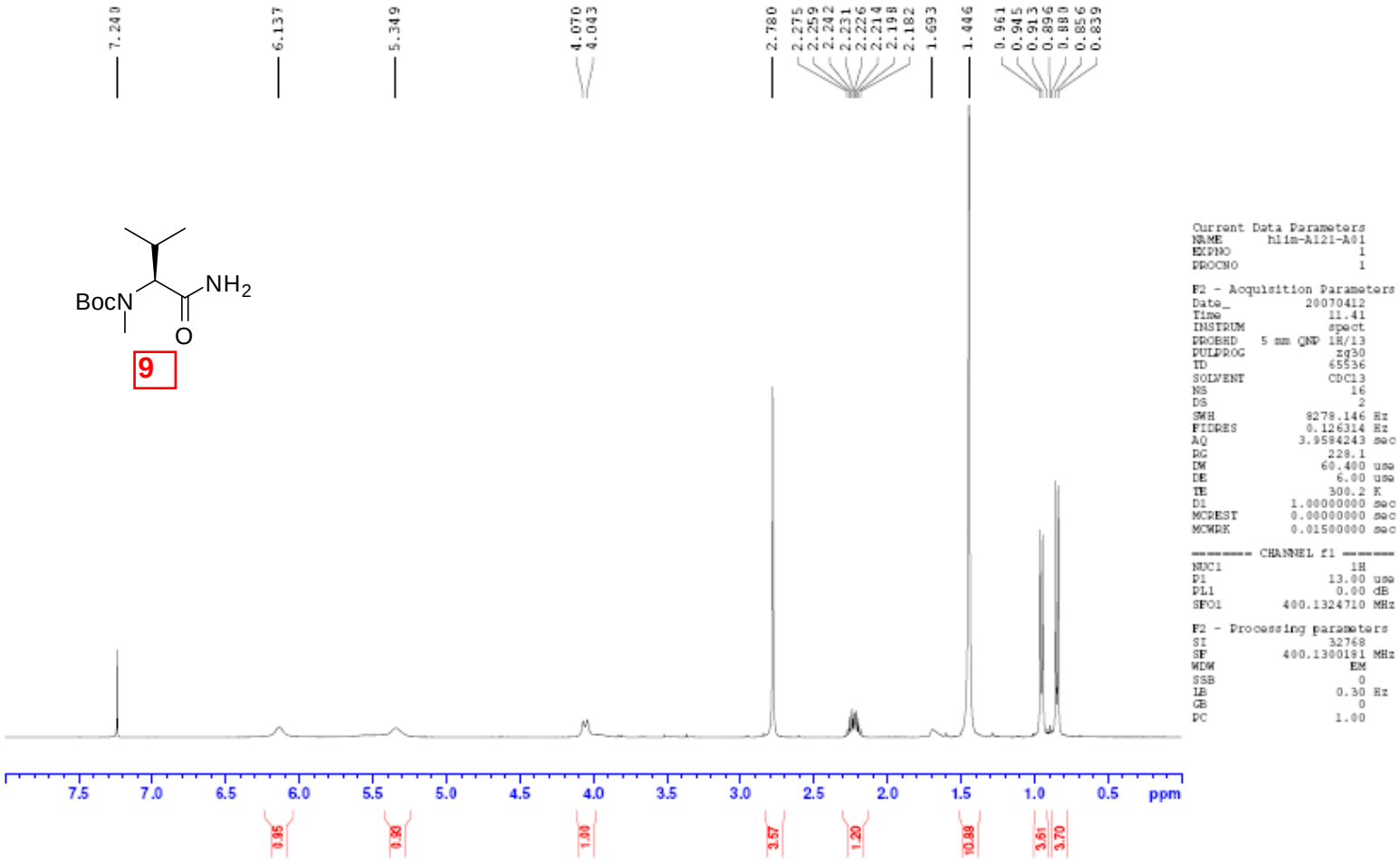

Br
O
N
H
Br
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Current Data Parameters
NAME hlim-A27-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060512
Time 13.43
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 258
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4096
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 5.90 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 15.80 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6118485 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

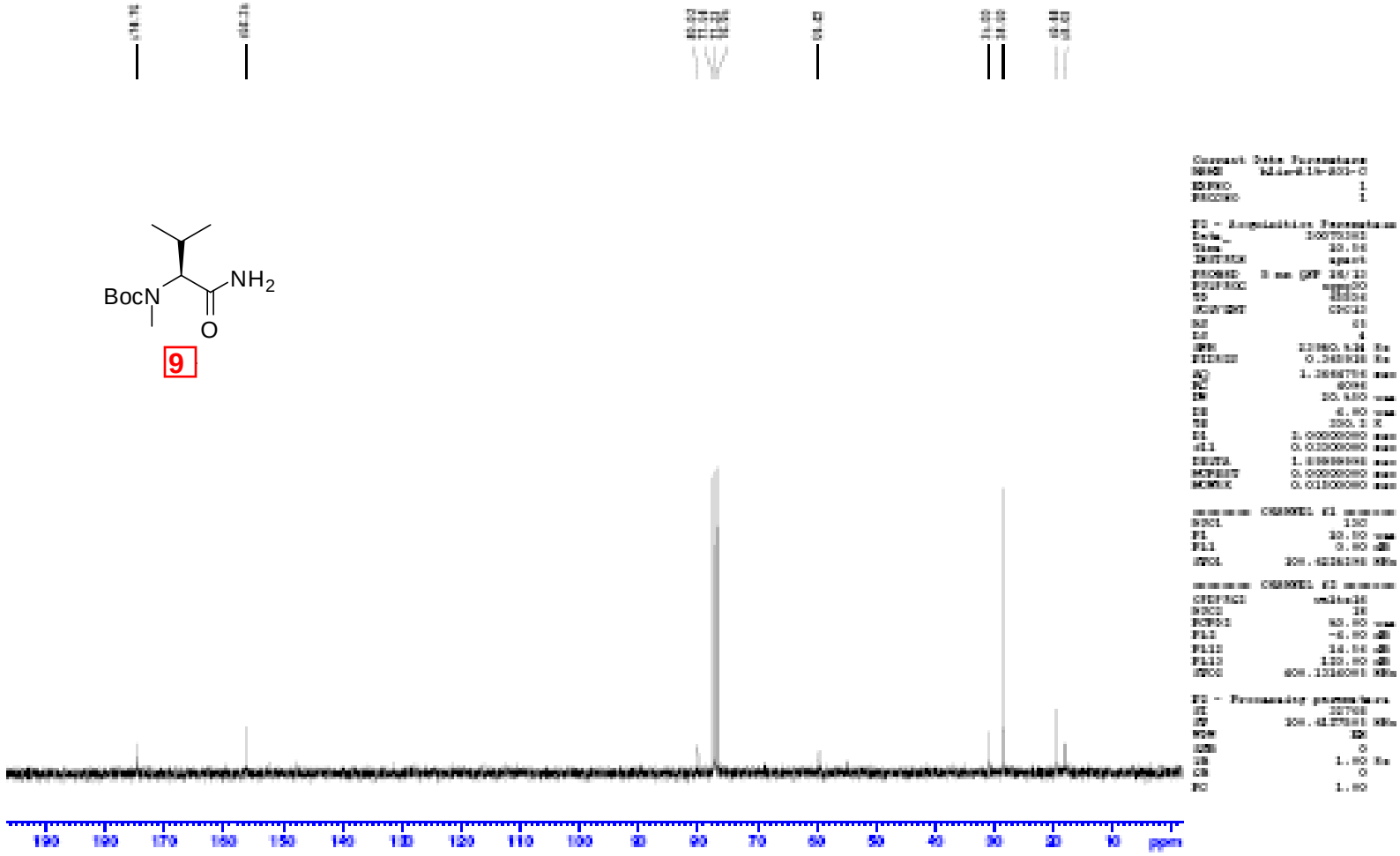


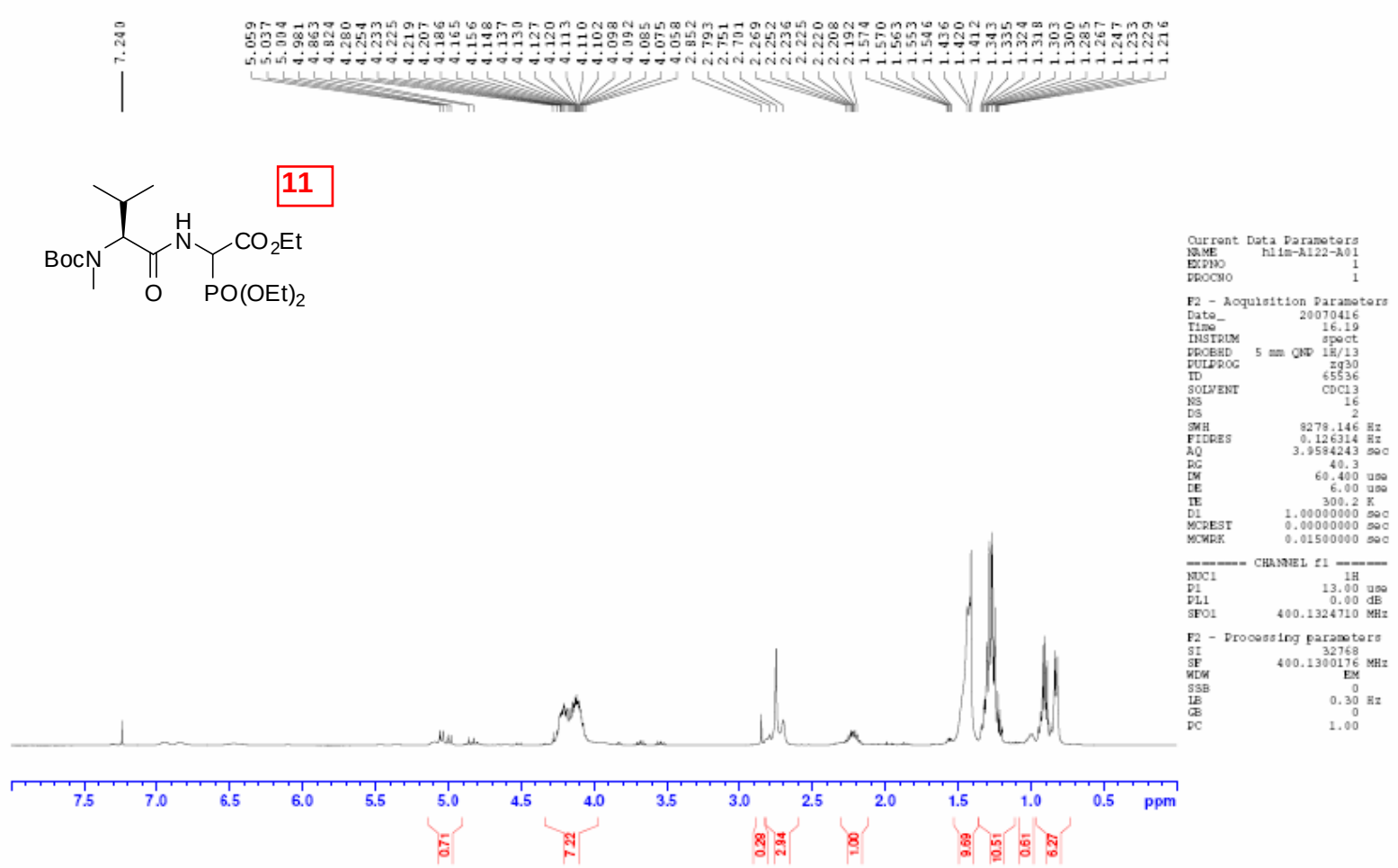

```
Current Data Parameters
NAME      hlim-A33-A01(8-12)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080812
Time                  11.13
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      256
DW                   60.400 usec
DE                    6.00 usec
TE                   300.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   13.00 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300176 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

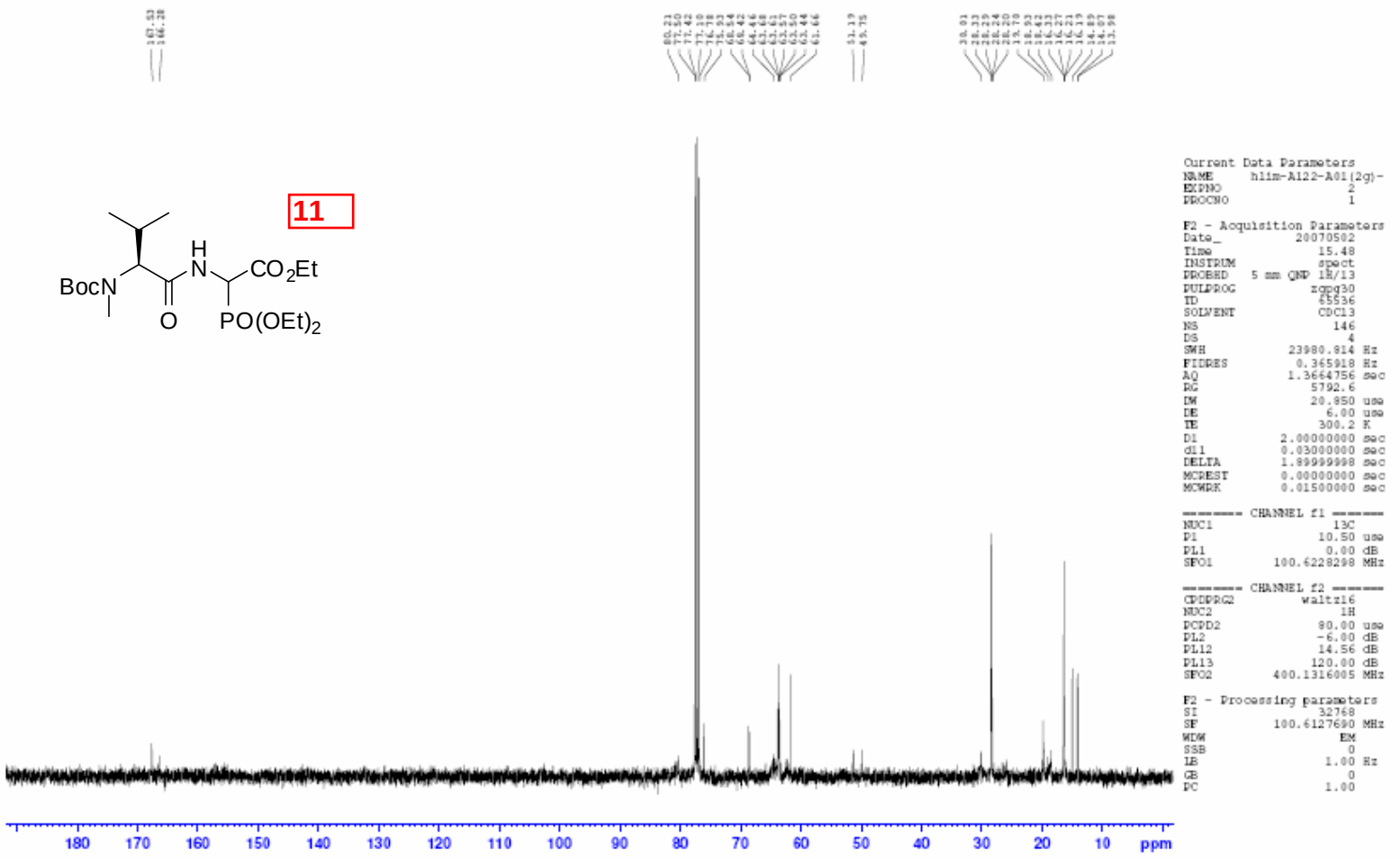


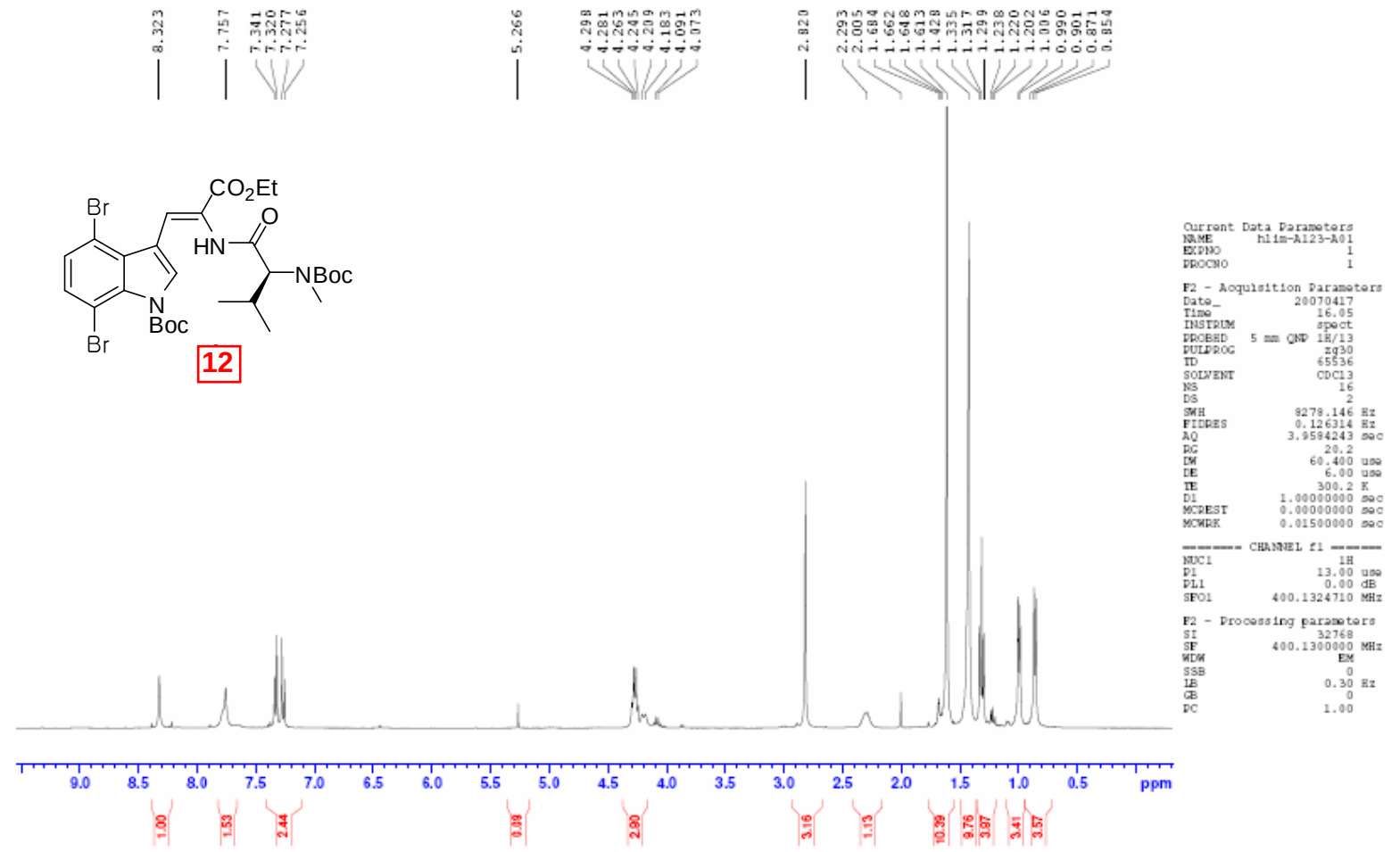

```
Current Data Parameters
NAME      hlim-A33-A01(8-12)-C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20080812
Time                  11.17
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      57
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                  3649.1
DW                 20.850 usec
DE                  6.00 usec
TE                 300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                14.56 dB
PL13                16.50 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127483 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

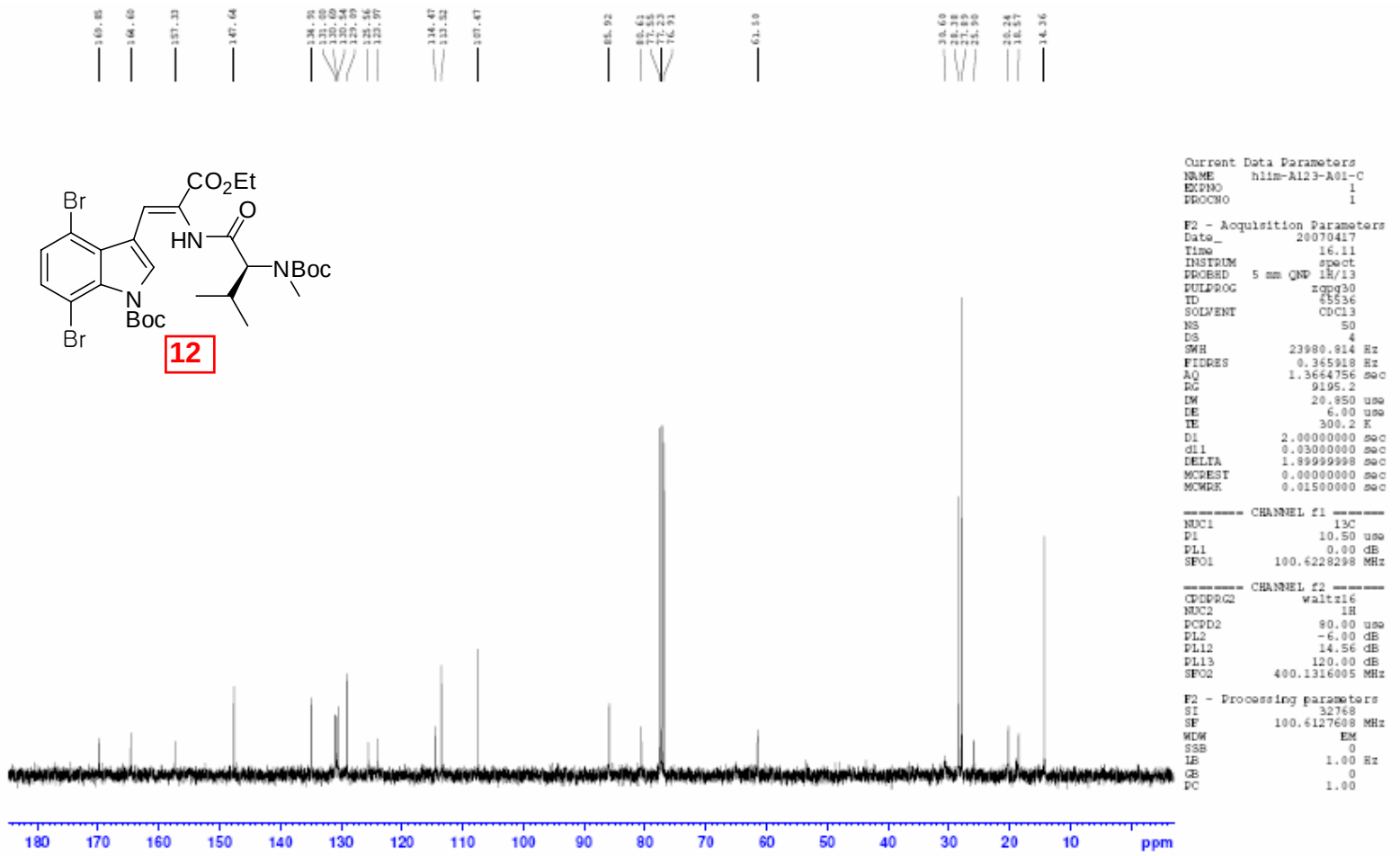

7.240
6.137
5.349
4.070
4.043
2.780
2.275
2.259
2.242
2.231
2.226
2.214
2.198
2.182
1.693
1.446
0.961
0.945
0.913
0.896
0.880
0.856
0.839
BocN
NH2
O
9
Current Data Parameters
NAME hlm-A121-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070412
Time 11.41
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300181 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
0.90
1.00
3.57
1.20
10.88
3.61
3.70

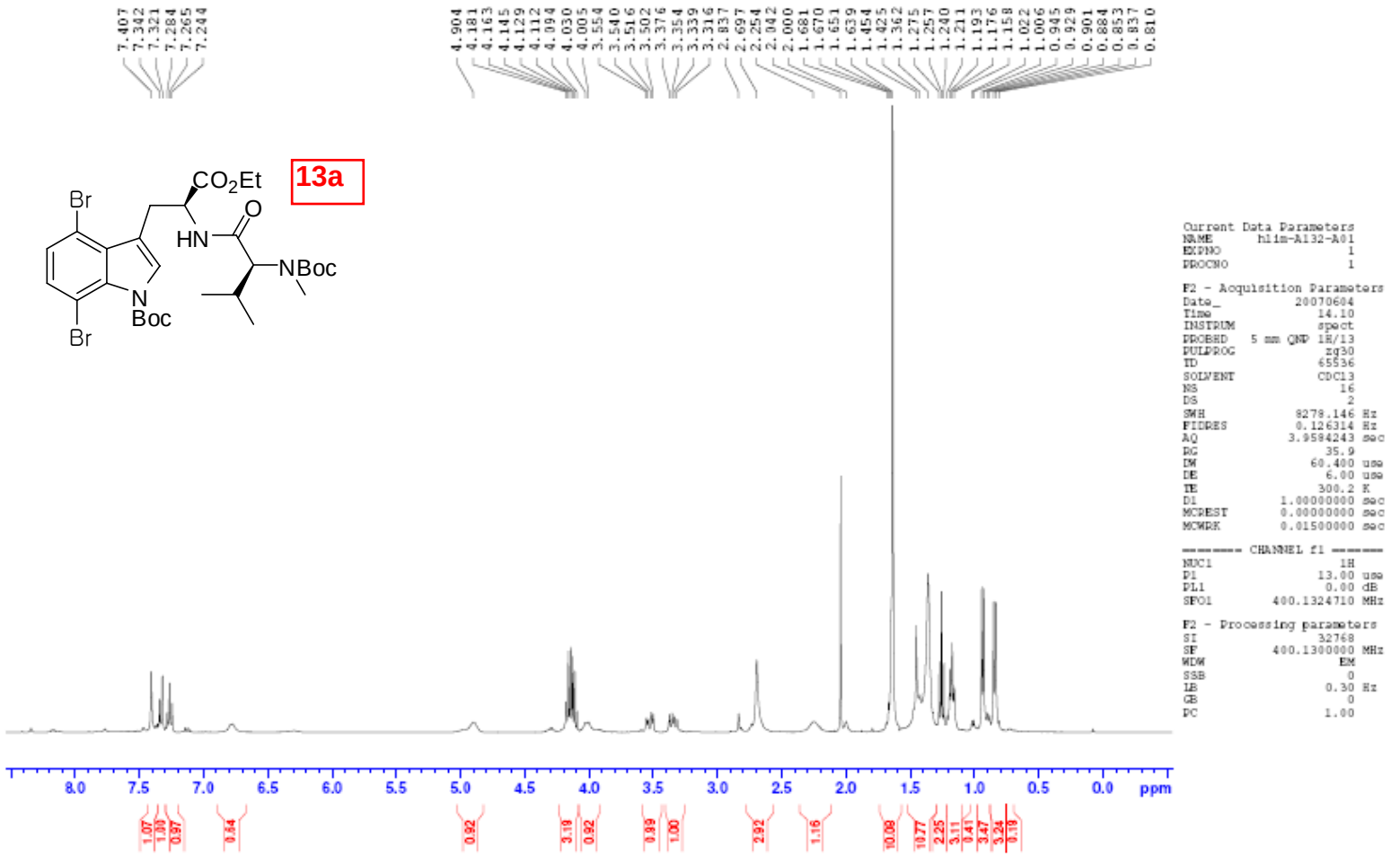

BocN
NH2
O
9
ppm

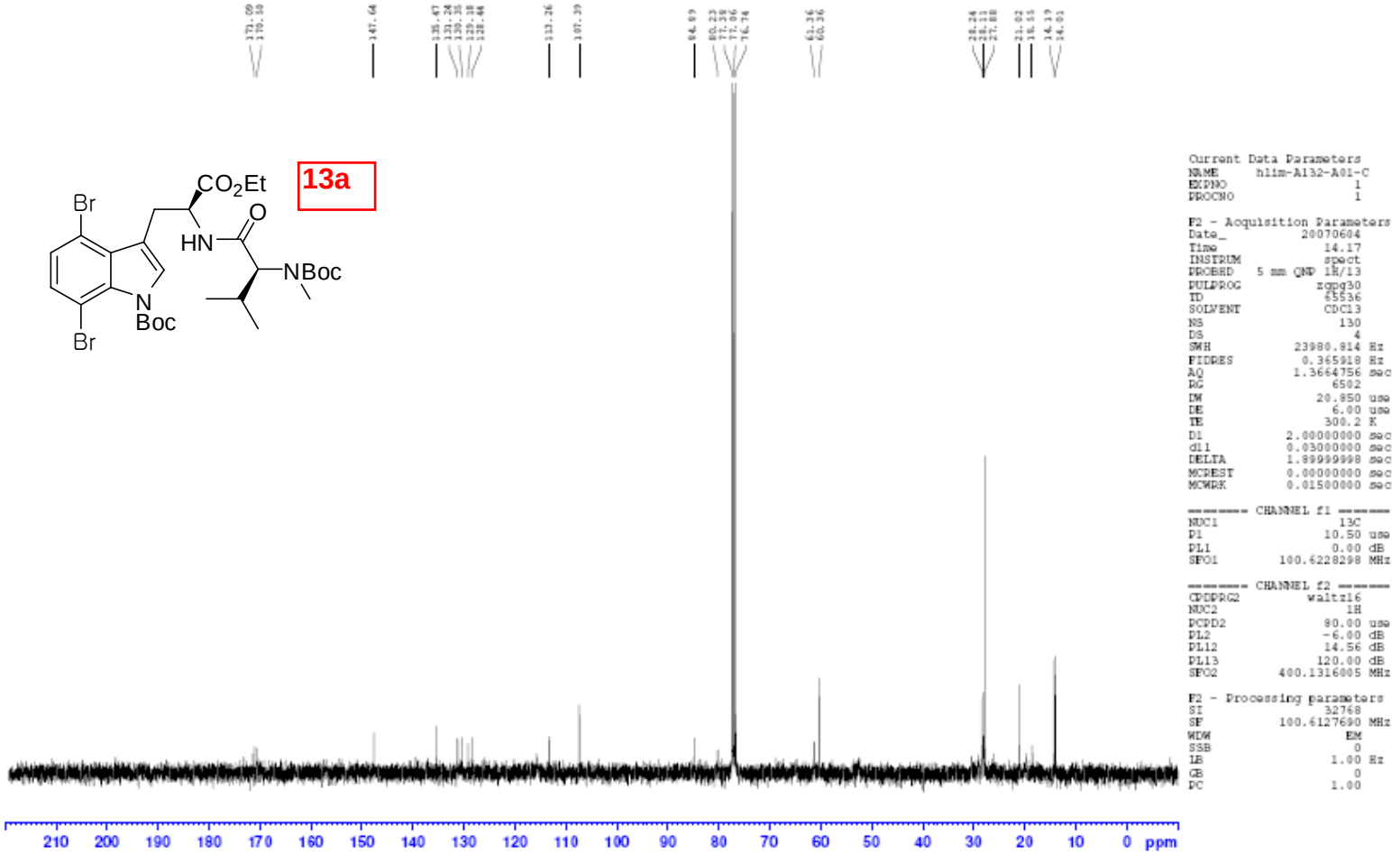

7.240
5.059
5.037
5.004
4.981
4.863
4.824
4.280
4.254
4.233
4.225
4.219
4.207
4.186
4.165
4.156
4.148
4.137
4.130
4.127
4.120
4.113
4.110
4.102
4.098
4.092
4.085
4.075
4.058
2.852
2.793
2.751
2.701
2.269
2.252
2.236
2.225
2.220
2.208
2.192
1.574
1.570
1.563
1.553
1.546
1.436
1.420
1.412
1.343
1.335
1.324
1.318
1.303
1.300
1.285
1.267
1.247
1.233
1.229
1.216
11
BocN
H
N
CO2Et
O
PO(OEt)2
Current Data Parameters
NAME hlim-A122-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070416
Time 16.19
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 40.3
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.71
7.22
0.28
2.94
1.00
9.69
10.51
0.61
6.27


11
BocN
H
N
CO2Et
O
PO(OEt)2
Current Data Parameters
NAME hlim-A122-A01(2g)-
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070502
Time 15.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 146
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

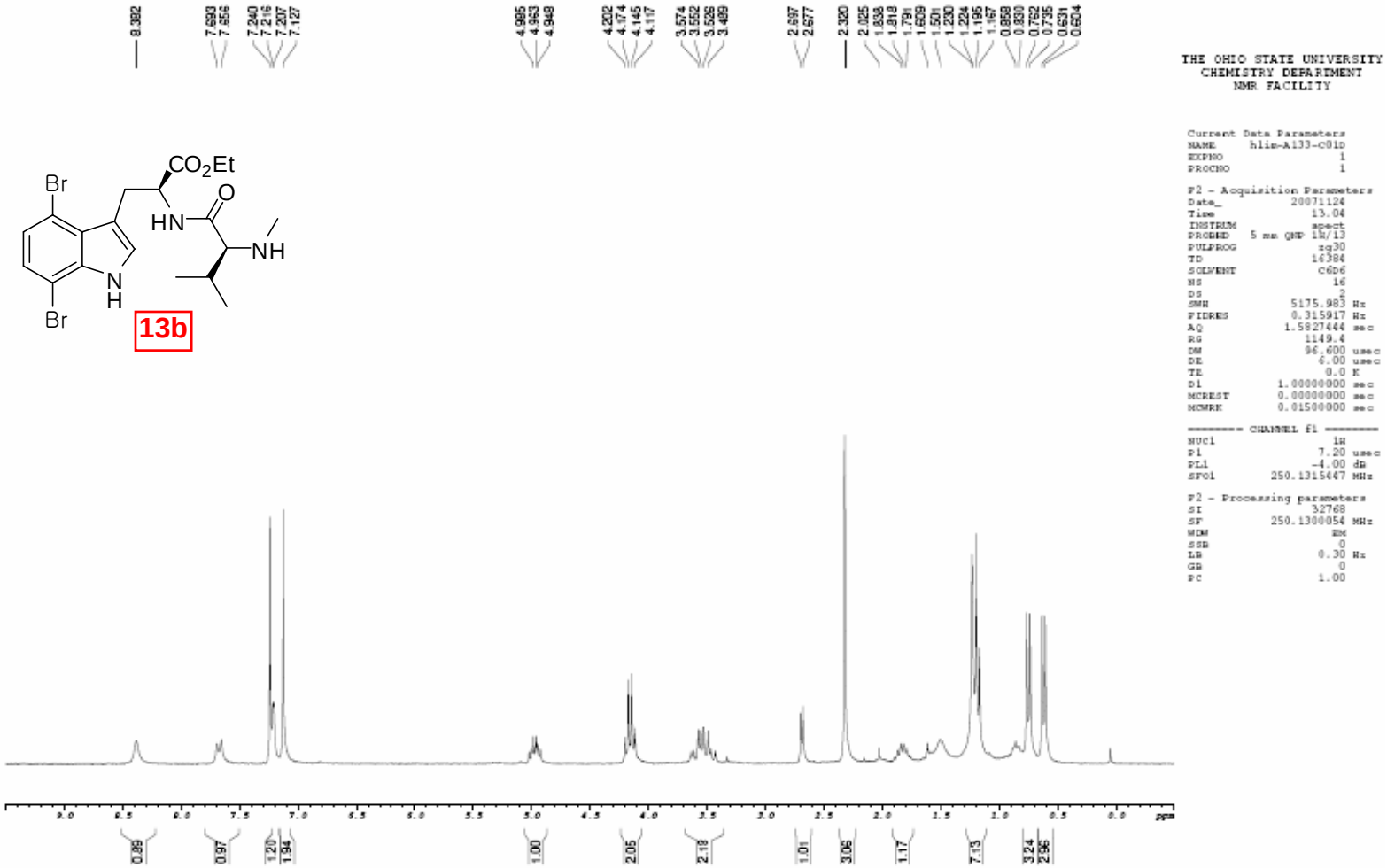

8.323
7.757
7.341
7.320
7.277
7.256
5.266
4.298
4.281
4.263
4.245
4.209
4.183
4.091
4.073
2.820
2.293
2.005
1.684
1.662
1.648
1.613
1.428
1.335
1.317
1.299
1.238
1.220
1.202
1.006
0.990
0.901
0.871
0.854
Br
CO2Et
O
HN
NBoc
N
Boc
Br
12
Current Data Parameters
NAME hlim-A123-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070417
Time 16.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 20.2
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.53
2.44
0.99
2.80
3.16
1.13
10.39
9.76
3.97
3.41
3.57

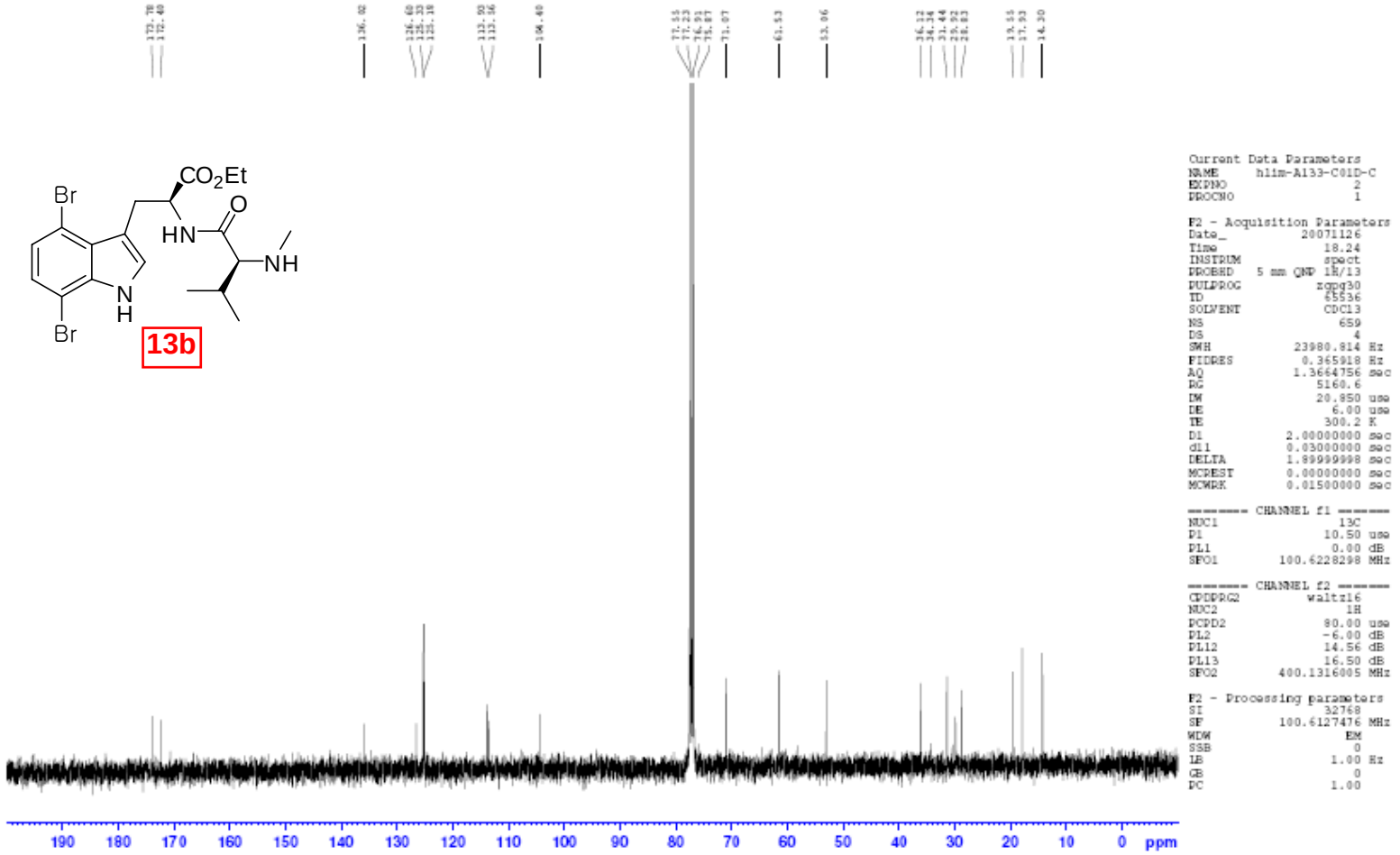

169.85
164.60
157.33
147.64
138.91
131.00
130.54
129.09
125.56
123.97
114.47
113.52
107.47
85.92
85.61
77.55
77.23
76.91
62.10
36.69
31.38
27.89
21.90
20.24
16.57
14.36
Br
CO2Et
HN
O
NBoc
N
Boc
Br
12
Current Data Parameters
NAME hlim-A123-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070417
Time 16.11
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 9195.2
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127608 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

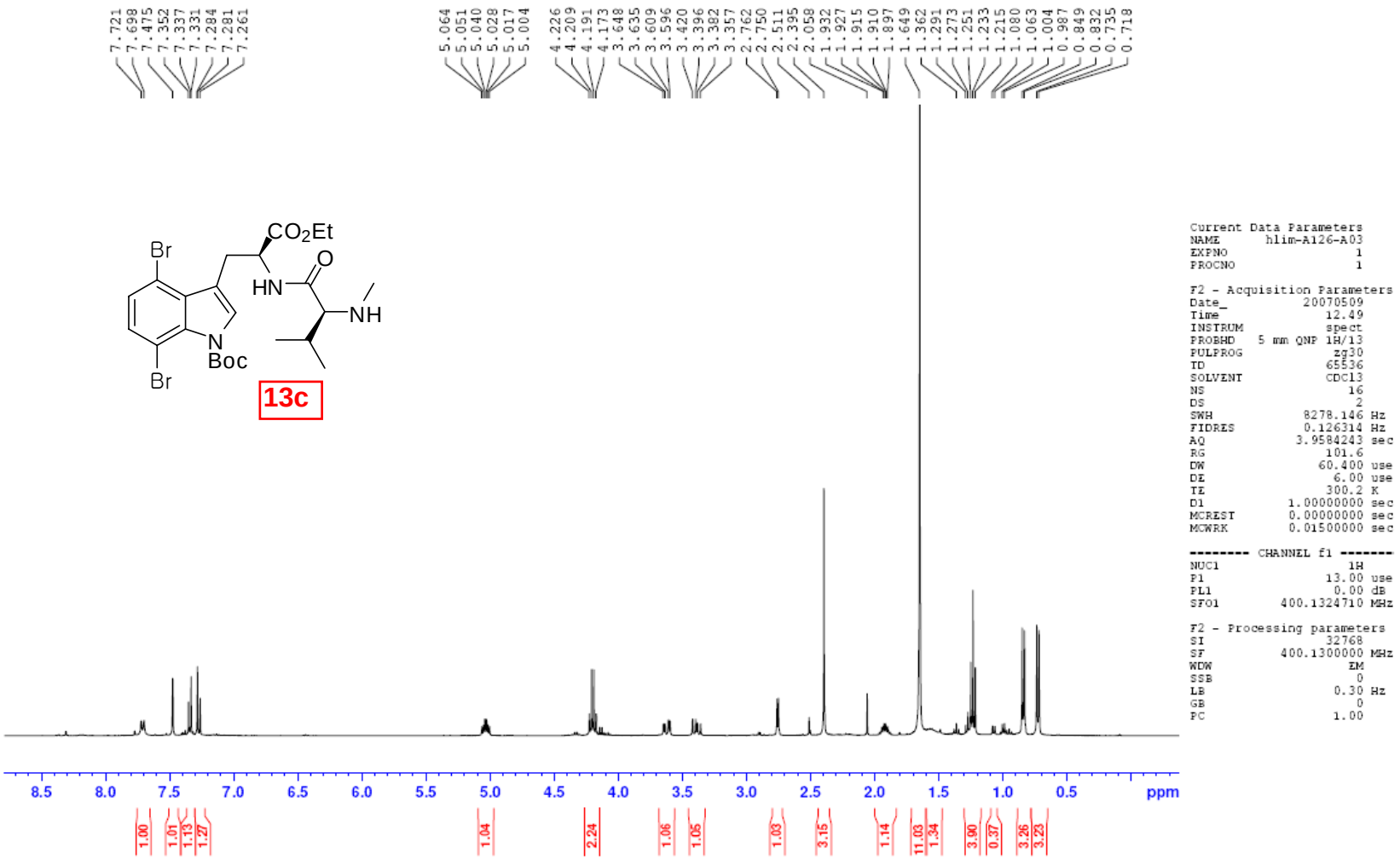

13a
Br
CO2Et
HN
O
NBoc
N
Boc
Br
7.407
7.342
7.321
7.284
7.265
7.244
4.904
4.181
4.163
4.145
4.129
4.112
4.094
4.030
4.005
3.554
3.540
3.516
3.502
3.376
3.354
3.339
3.316
2.837
2.697
2.254
2.042
2.000
1.681
1.670
1.651
1.639
1.454
1.425
1.362
1.275
1.257
1.240
1.211
1.193
1.176
1.158
1.022
1.006
0.945
0.929
0.901
0.884
0.853
0.837
0.810
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.07
1.00
0.97
0.84
0.92
3.19
0.92
0.89
1.00
2.92
1.16
10.08
10.77
2.25
3.11
0.41
3.47
3.24
0.19
Current Data Parameters
NAME hlim-A132-A01
EXPNO 1
PROCNO 1
F2 - Acqulsition Parameters
Date_ 20070604
Time 14.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



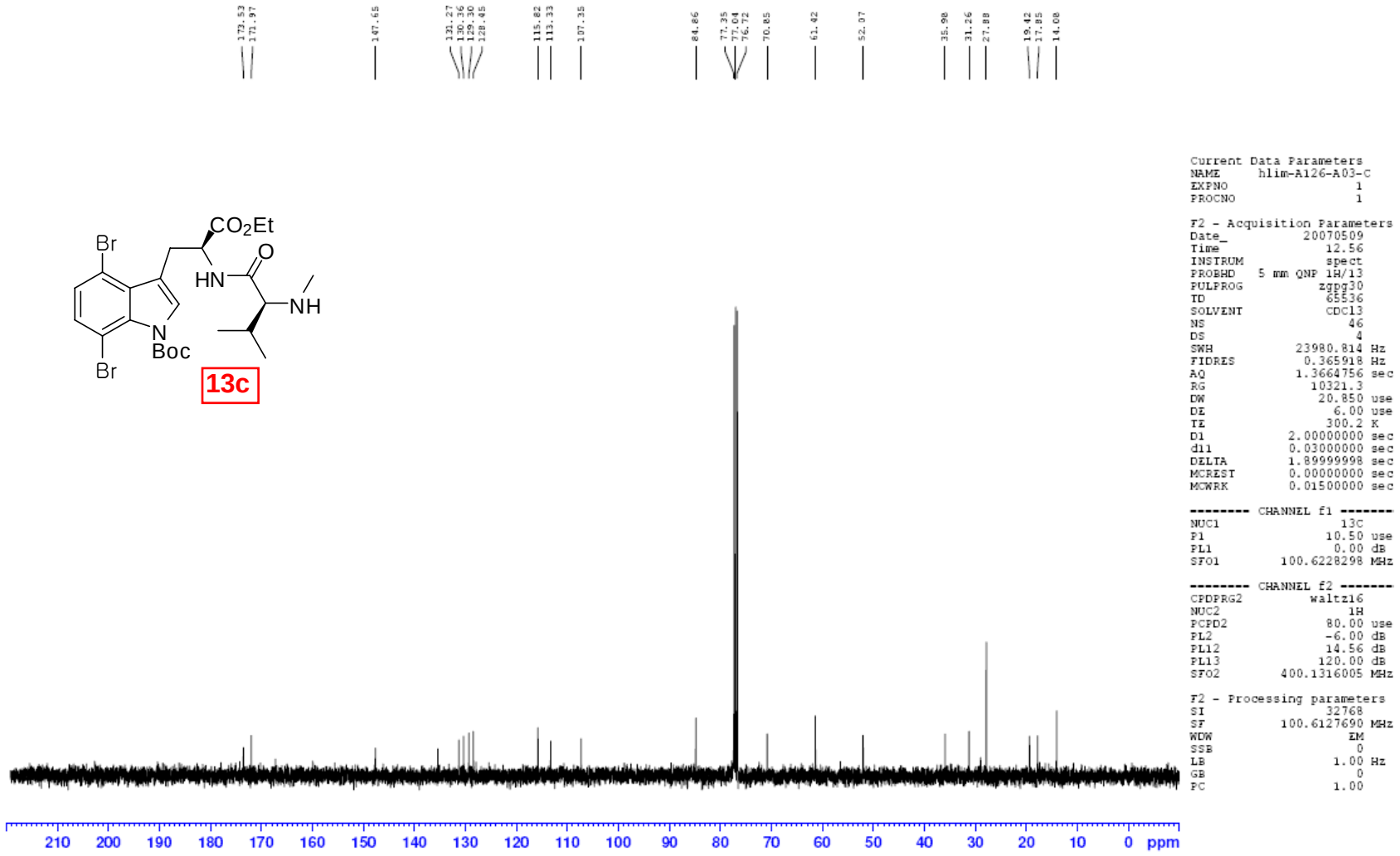

```
Current Data Parameters
NAME      hlim-A132-A01-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070604
Time              14.17
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 130
DS                   4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ           1.3664756 sec
RG                6502
DW              20.850 usec
DE               6.00 usec
TE              300.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               10.50 usec
PL1               0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2              -6.00 dB
PL12             14.56 dB
PL13            120.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00
```


8.382
7.693
7.656
7.240
7.216
7.207
7.127
4.985
4.963
4.948
4.202
4.174
4.145
4.117
3.574
3.552
3.526
3.489
2.697
2.677
2.320
2.025
1.838
1.818
1.791
1.669
1.501
1.230
1.224
1.195
1.167
0.968
0.930
0.762
0.735
0.631
0.604
Br
CO2Et
O
HN
NH
N
H
Br
13b
THE OHIO STATE UNIVERSITY
CHEMISTRY DEPARTMENT
NMR FACILITY
Current Data Parameters
NAME hlis-A133-c01d
EXPNO 1
PROCNO 1
P2 - Acquisition Parameters
Date_ 20071124
Time 13.04
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 16384
SOLVENT c6d6
NS 16
DS 2
SWH 5175.983 Hz
FIDRES 0.315917 Hz
AQ 1.5827444 sec
RG 1149.4
DW 96.600 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.20 usec
PL1 -4.00 dB
SFO1 250.1315447 MHz
F2 - Processing parameters
SI 32768
SF 250.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.89
0.97
1.20
1.94
1.00
2.05
2.18
1.01
3.06
1.17
7.13
3.24
2.36

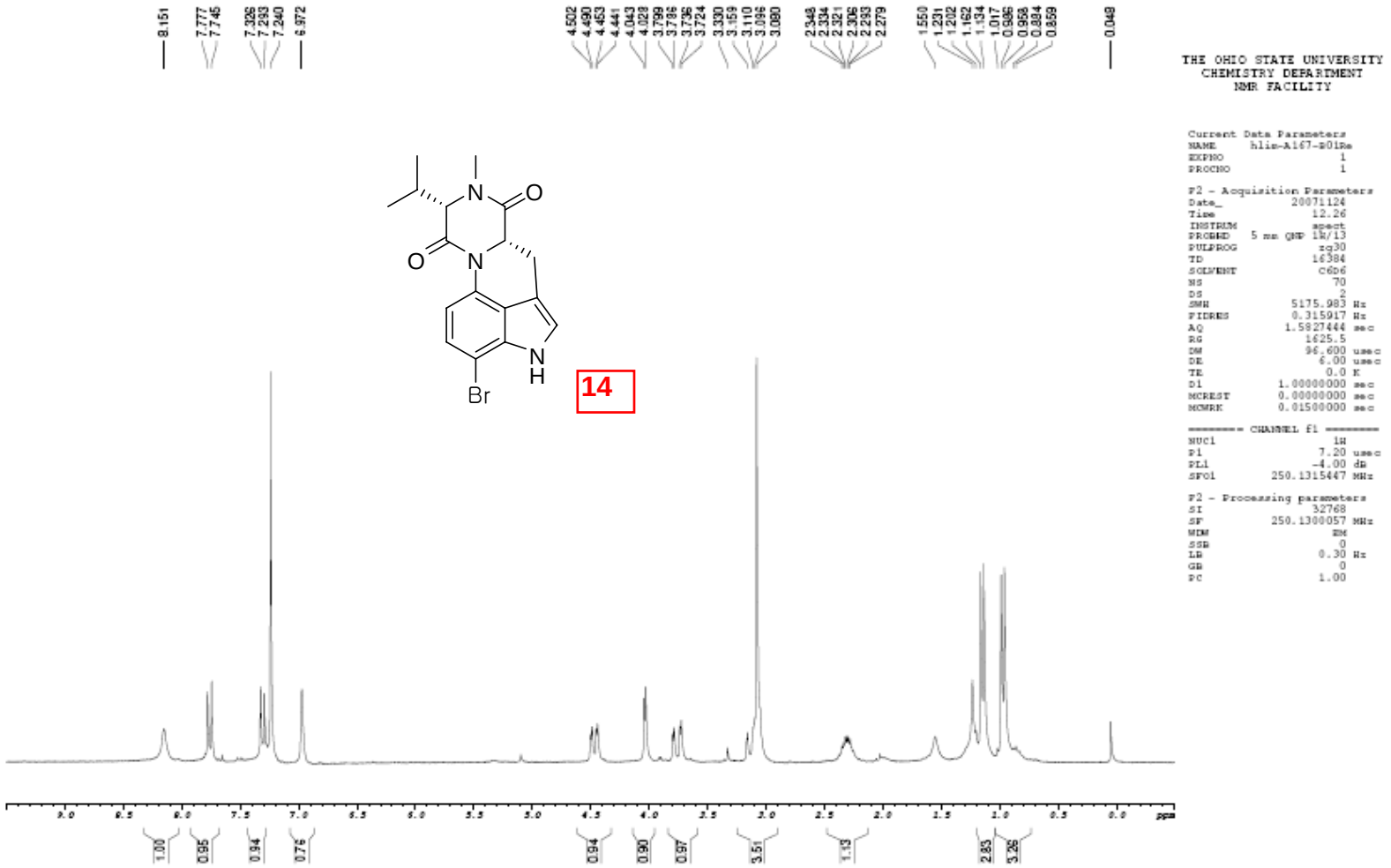

172.78
172.40
136.92
126.60
125.33
125.18
113.90
113.56
104.40
77.55
77.23
76.91
75.87
71.07
61.53
53.06
36.12
34.34
31.44
29.92
28.83
19.55
17.93
14.30
Br
CO2Et
HN
O
NH
N
H
Br
13b
Current Data Parameters
NAME hlim-A133-C01D-C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071126
Time 18.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 659
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5160.6
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127476 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm




```
Current Data Parameters
NAME        hlim-A126-A03
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070509
Time                12.49
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                 101.6
DW                60.400 use
DE                 6.00 use
TE                300.2 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

-------- CHANNEL f1 -------
NUC1                   1H
P1                 13.00 use
PL1                 0.00 dB
SFO1        400.1324710 MHz

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




```
Current Data Parameters
NAME      hlim-A126-A03-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070509
Time              12.56
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  46
DS                   4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG              10321.3
DW               20.850 use
DE                6.00 use
TE               300.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

-------- CHANNEL f1 -------
NUC1               13C
P1               10.50 use
PL1               0.00 dB
SFO1        100.6228298 MHz

-------- CHANNEL f2 -------
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 use
PL2              -6.00 dB
PL12             14.56 dB
PL13            120.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.00
```



THE OHIO STATE UNIVERSITY
CHEMISTRY DEPARTMENT
NMR FACILITY

Current Data Parameters

NAME	hlie-A167-B01Re
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

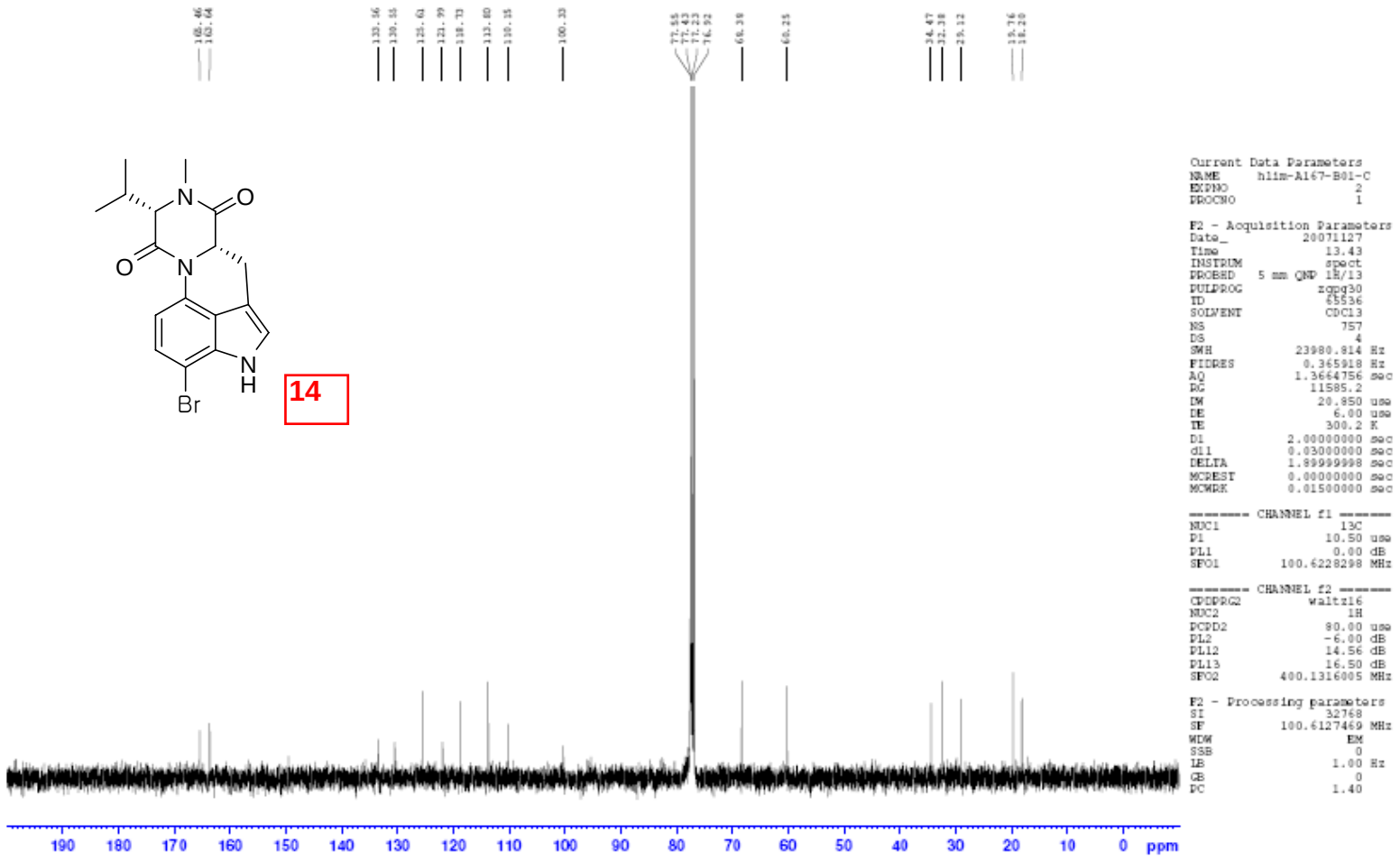
Date_	20071124
Time	12.26
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	16384
SOLVENT	C6D6
NS	70
DS	2
SWH	5175.983 Hz
FIDRES	0.315917 Hz
AQ	1.5827444 sec
RG	1625.5
DW	96.600 usec
DE	6.00 usec
TE	0.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

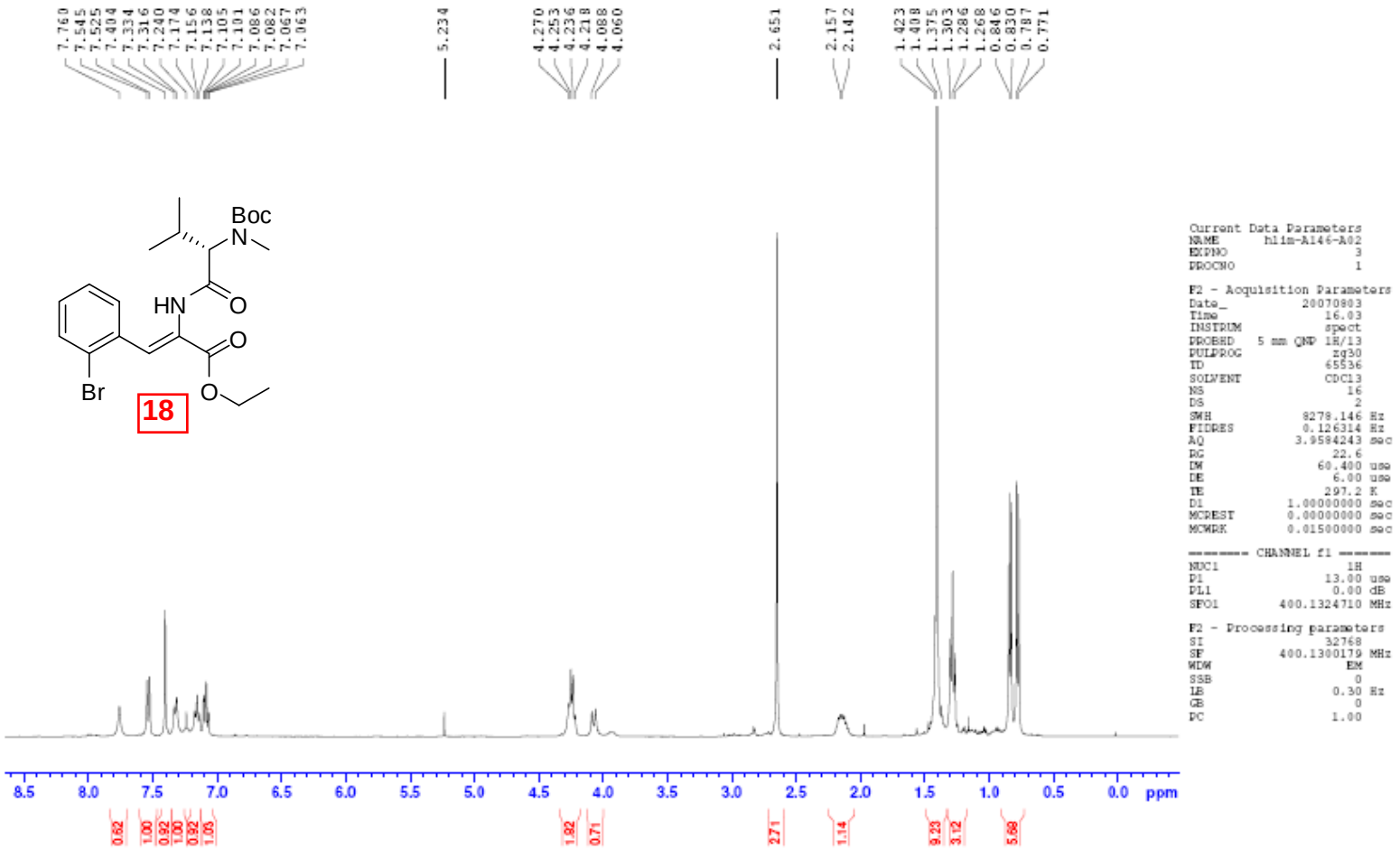
NUC1	1H
P1	7.20 usec
PL1	-4.00 dB
SFO1	250.1315447 MHz

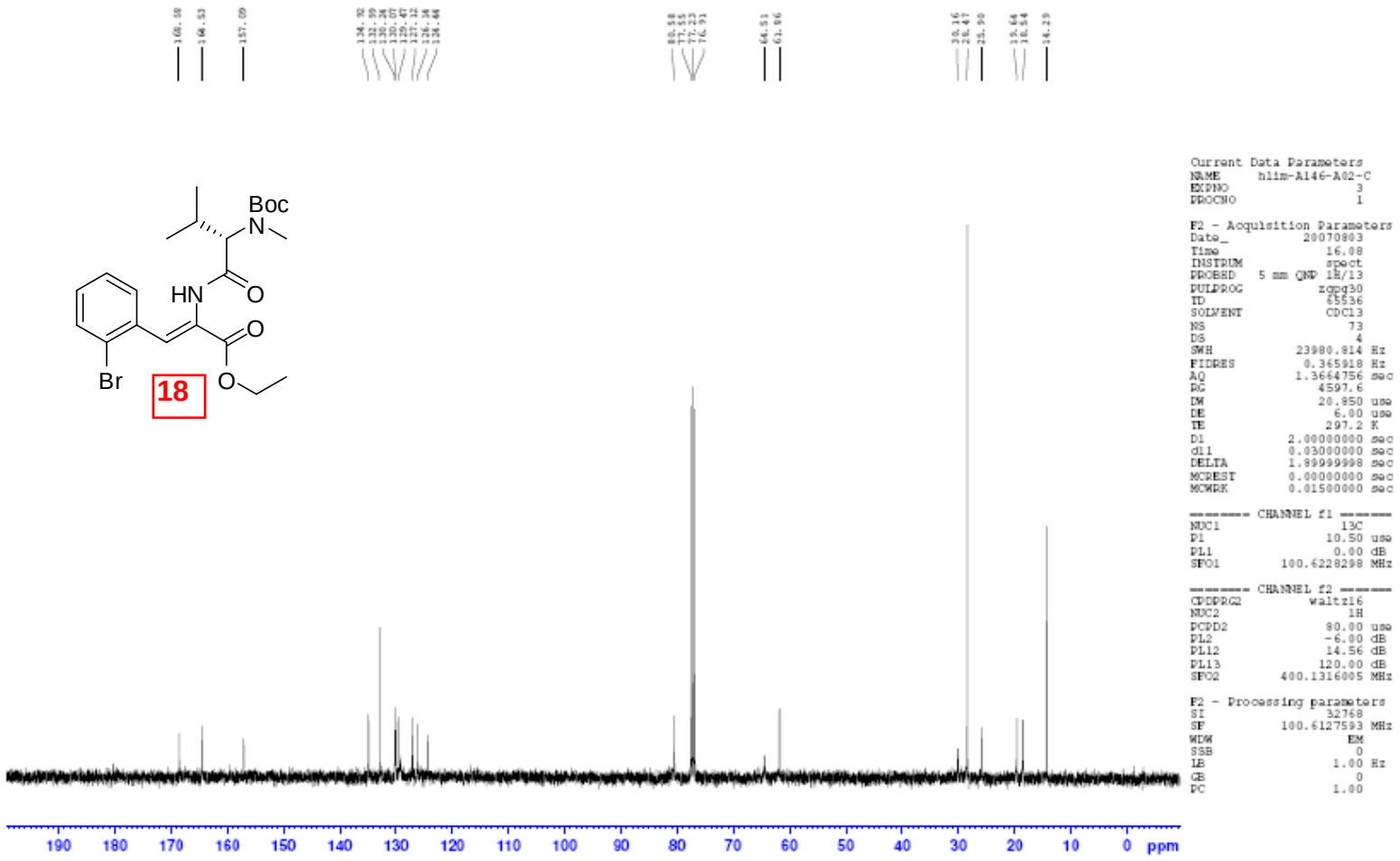
F2 - Processing parameters

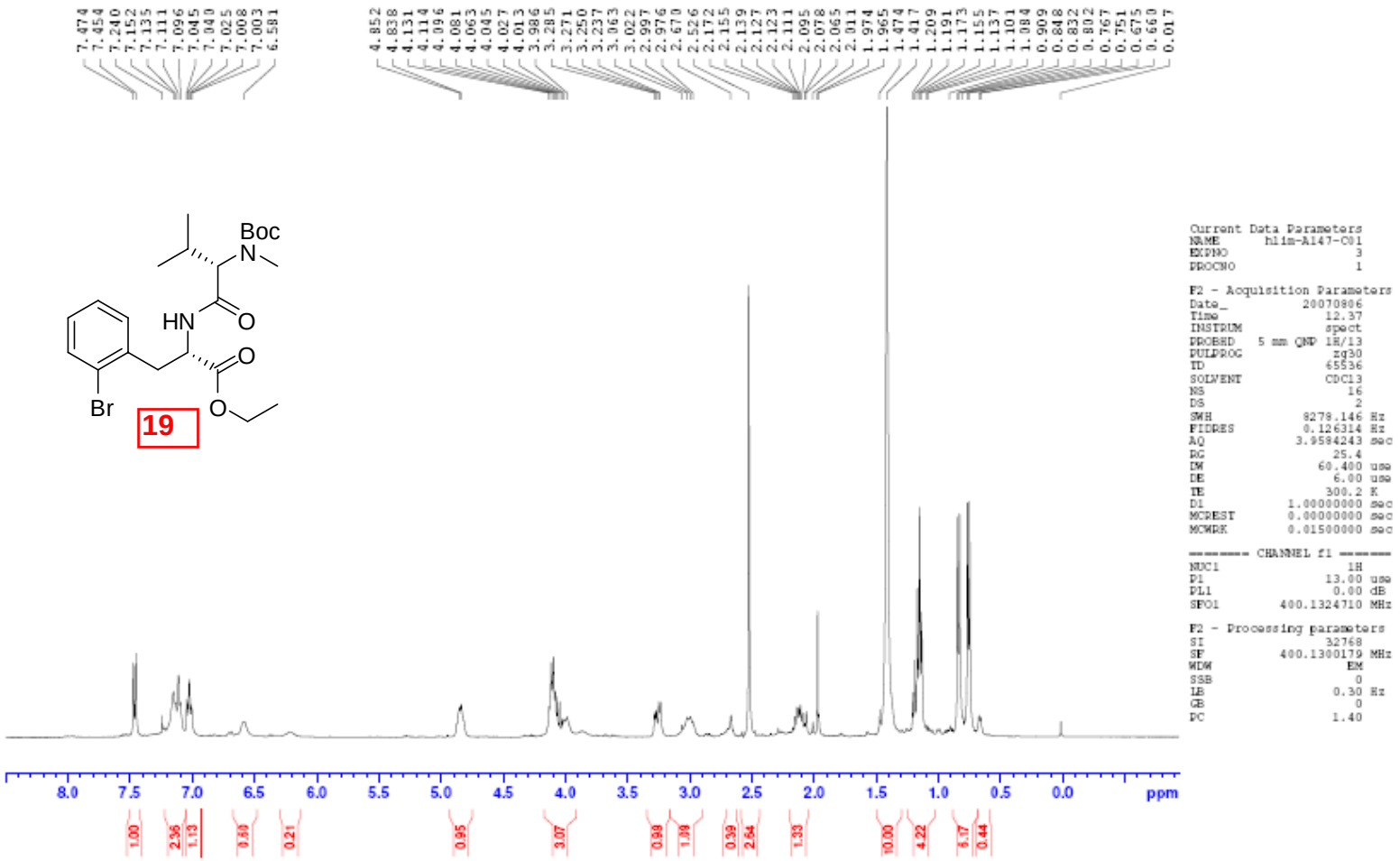
SI	32768
SF	250.1300057 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

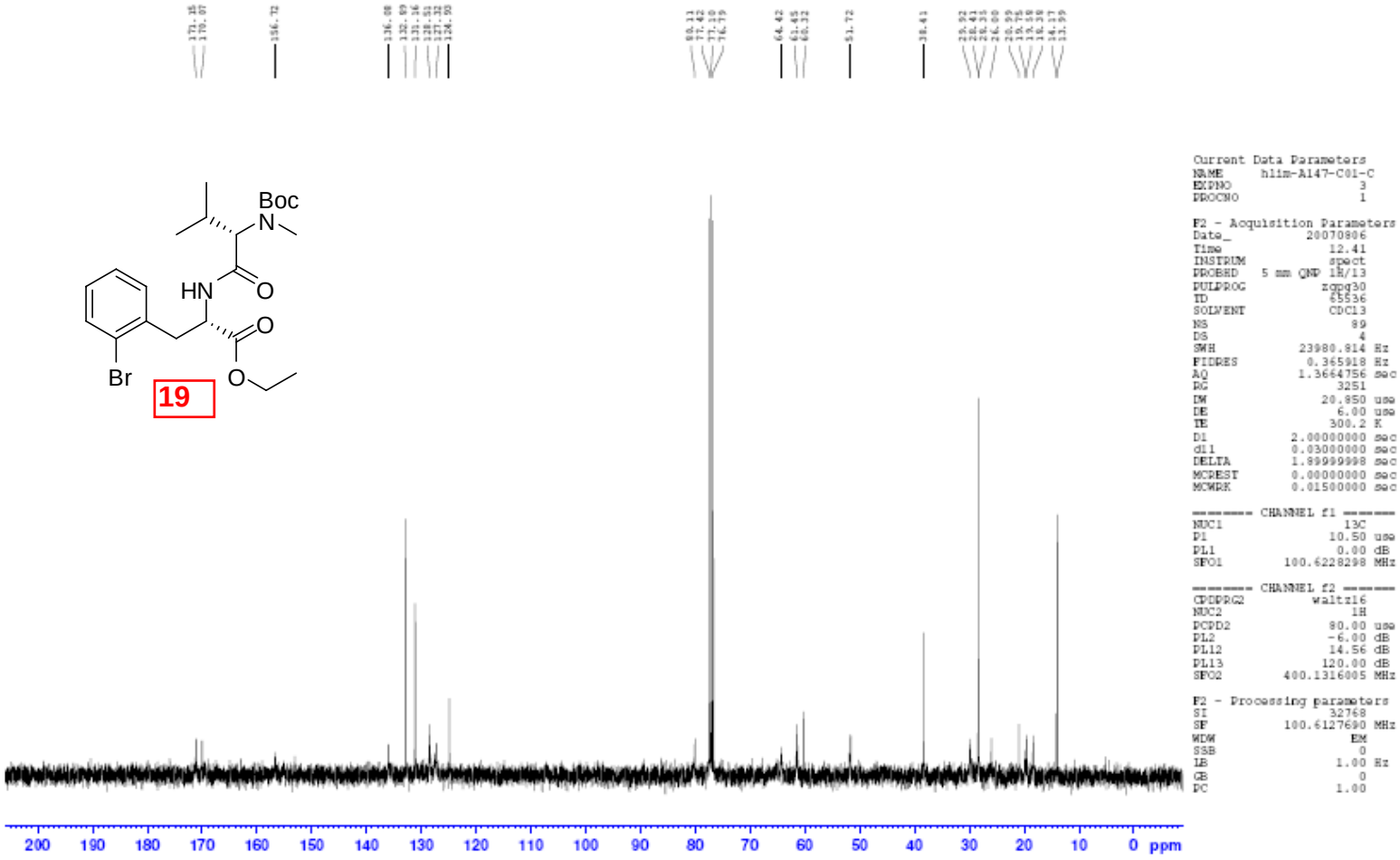


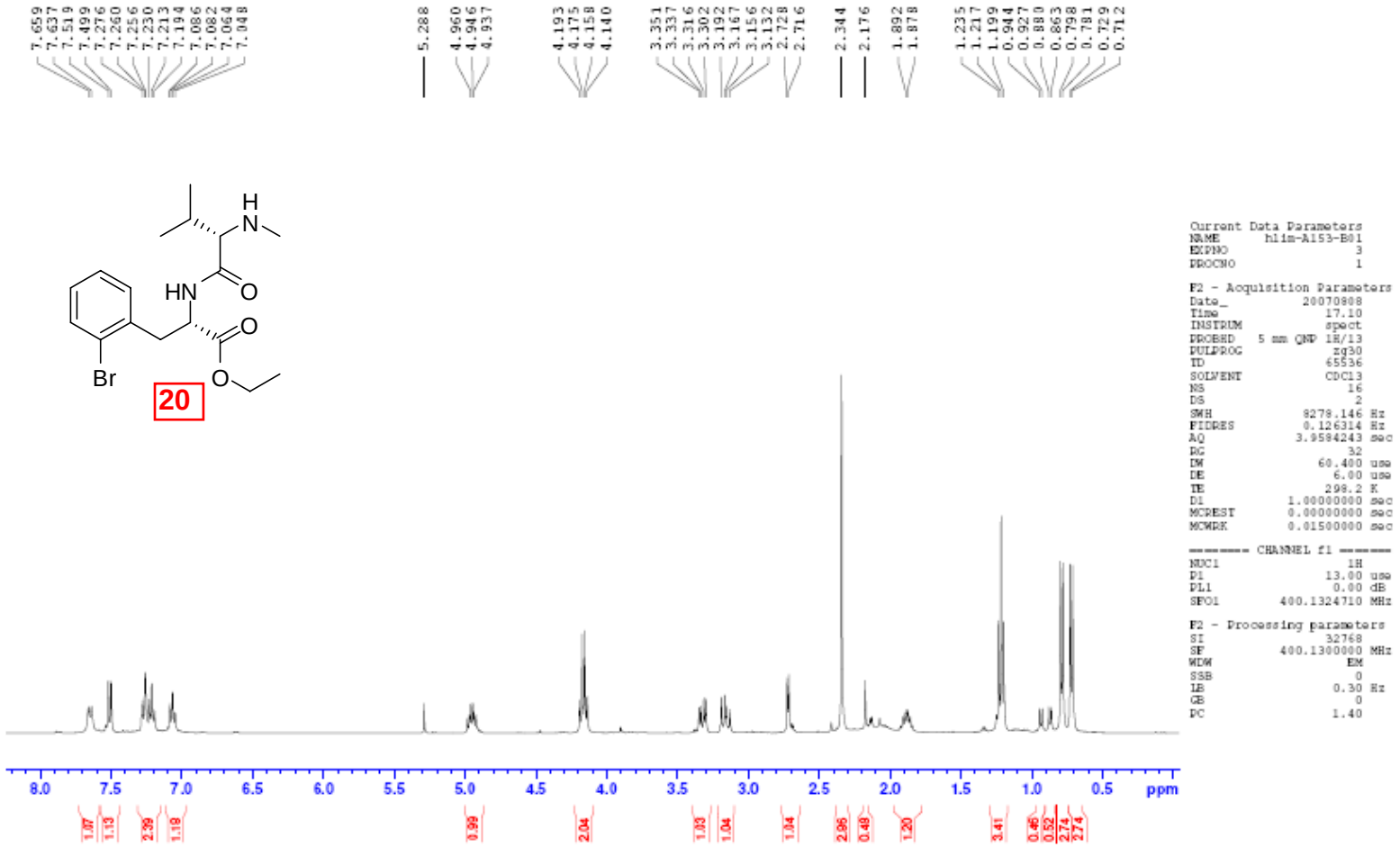

```
Current Data Parameters
NAME      hlim-A167-B01-C
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071127
Time                13.43
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     757
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                 11585.2
DW                  20.850 usec
DE                   6.00 usec
TE                  300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ======
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -6.00 dB
PL12                 14.56 dB
PL13                 16.50 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF            100.6127469 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                   1.40
```

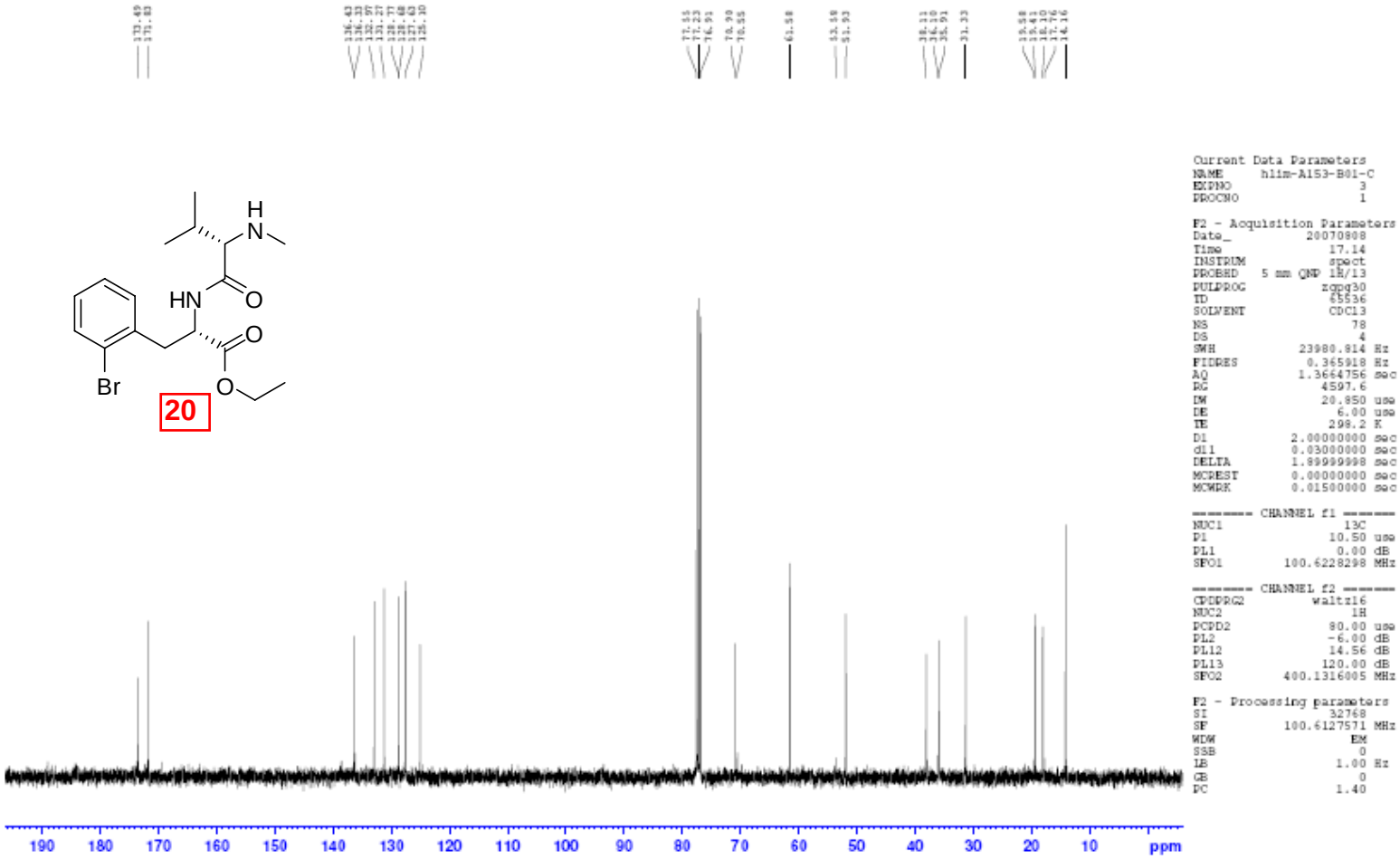

7.760
7.545
7.525
7.404
7.334
7.316
7.240
7.174
7.156
7.138
7.105
7.101
7.086
7.082
7.067
7.063
5.234
4.270
4.253
4.236
4.218
4.088
4.060
2.651
2.157
2.142
1.423
1.408
1.375
1.303
1.286
1.268
0.846
0.830
0.787
0.771
Boc
N
HN
O
O
O
Br
18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.62
1.00
0.92
1.00
0.92
1.05
1.82
0.71
2.71
1.14
9.23
3.12
5.68
Current Data Parameters
NAME hlim-A146-A02
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070803
Time 16.03
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 22.6
DW 60.400 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300179 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

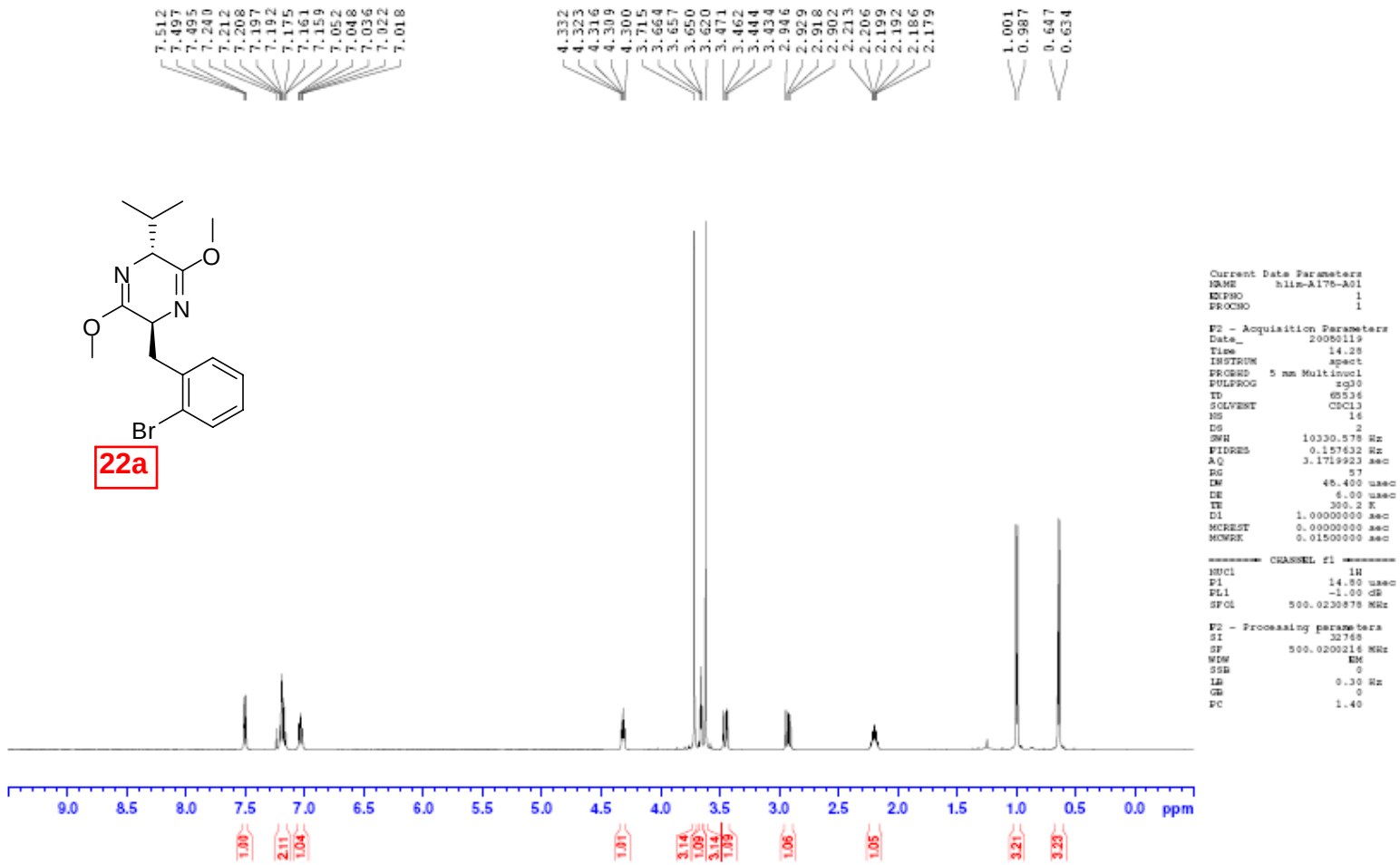

168.58
166.53
157.09
134.92
132.99
130.24
129.67
129.42
127.12
126.34
124.44
80.68
77.55
77.23
76.91
64.51
61.66
30.16
28.47
25.90
19.64
18.54
14.29
Boc
N
HN
O
O
O
Br
18
Current Data Parameters
NAME hlim-A146-A02-C
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070803
Time 16.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 73
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4597.6
DW 20.850 usec
DE 6.00 usec
TE 297.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127593 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

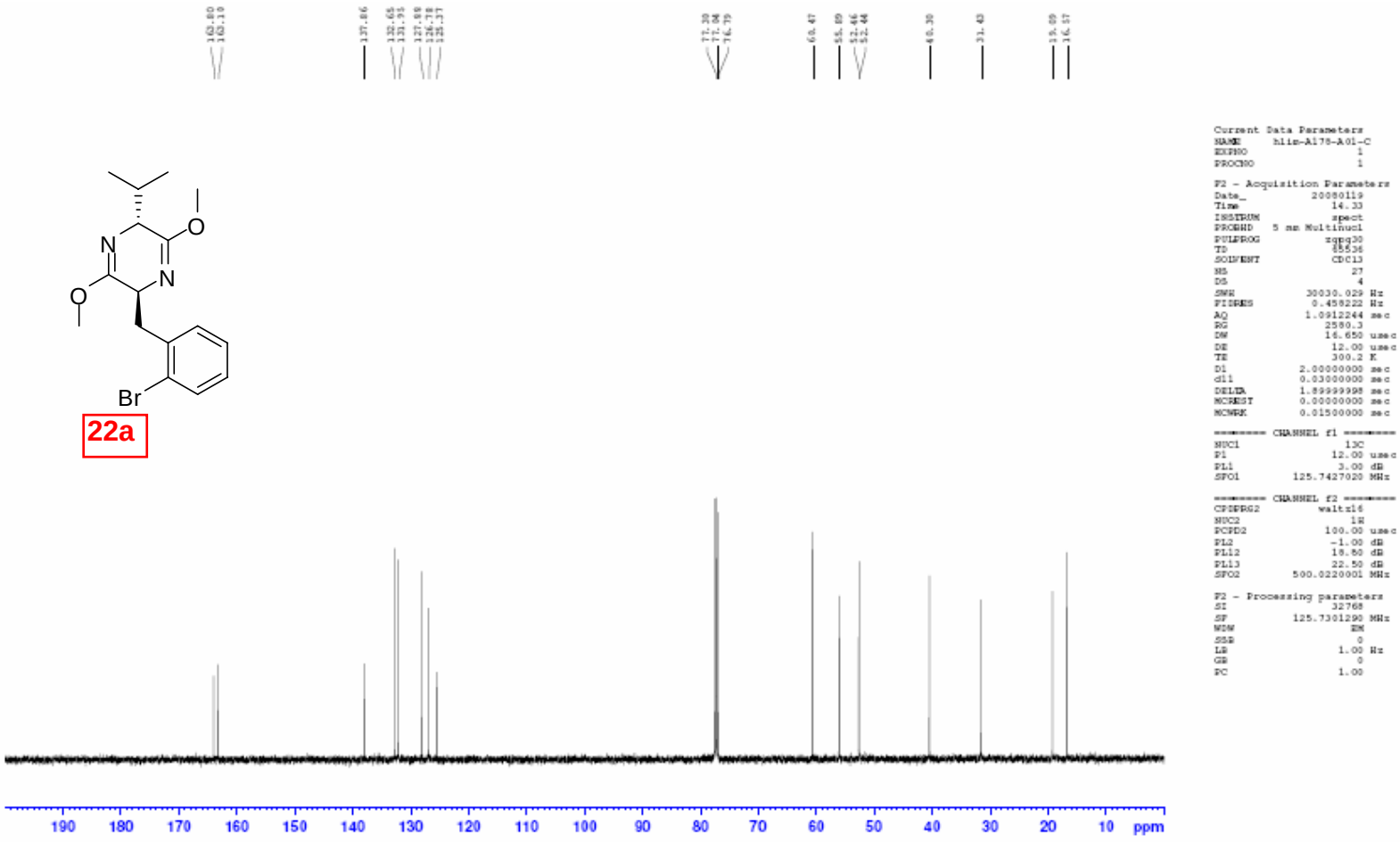

Boc
N
HN
O
O
O
Br
19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Boc
N
HN
O
O
O
Br
19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

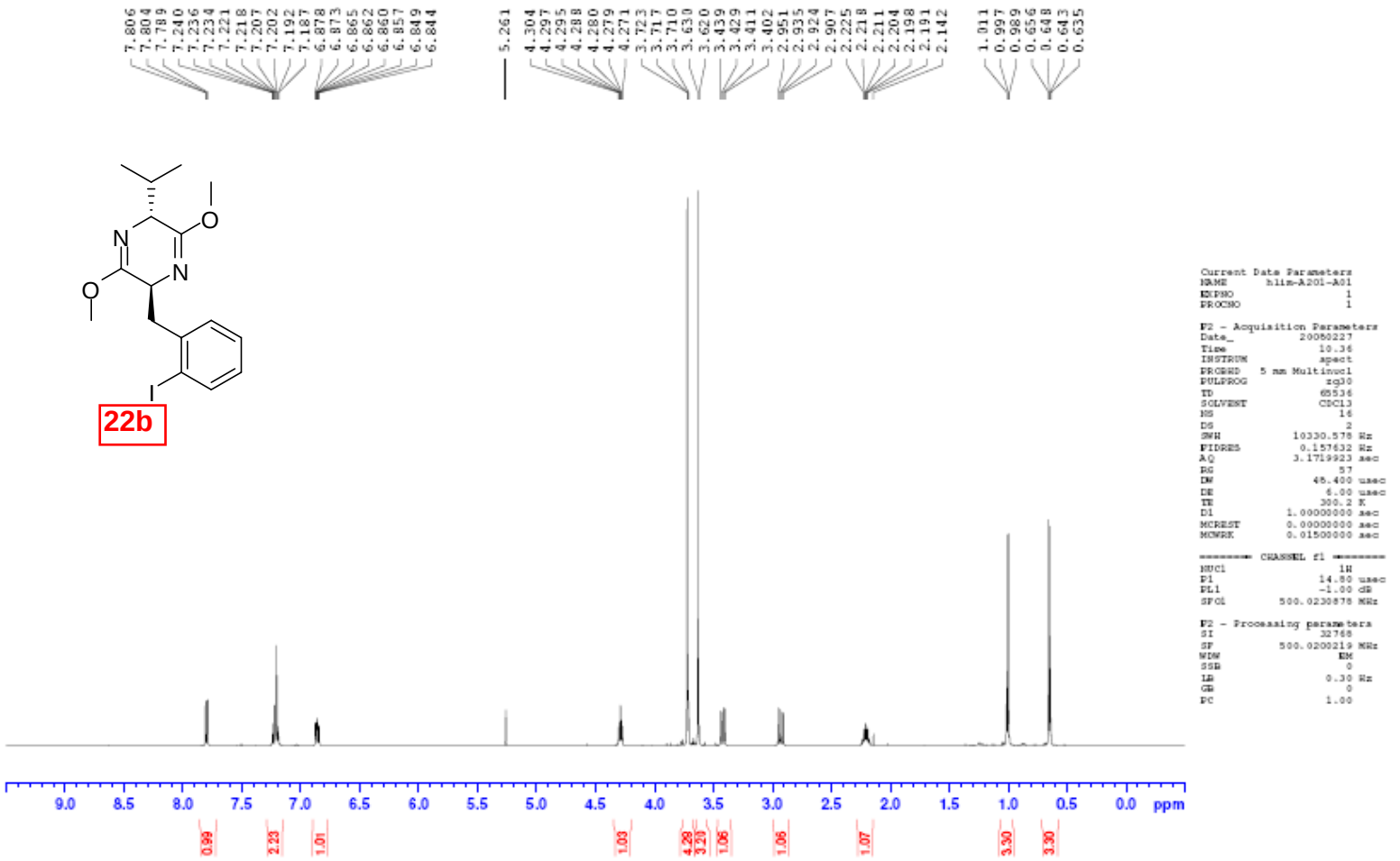

7.659
7.637
7.519
7.499
7.276
7.260
7.256
7.230
7.213
7.194
7.086
7.082
7.064
7.048
5.288
4.960
4.946
4.937
4.193
4.175
4.158
4.140
3.351
3.337
3.316
3.302
3.192
3.167
3.156
3.132
2.728
2.716
2.344
2.176
1.892
1.878
1.235
1.217
1.199
0.944
0.927
0.880
0.863
0.798
0.781
0.729
0.712
H
N
HN
O
O
O
Br
20
Current Data Parameters
NAME hlim-A153-B01
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070808
Time 17.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 32
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.07
1.13
2.39
1.18
0.99
2.04
1.03
1.04
1.04
2.96
0.49
1.20
3.41
0.46
0.52
2.74
2.74

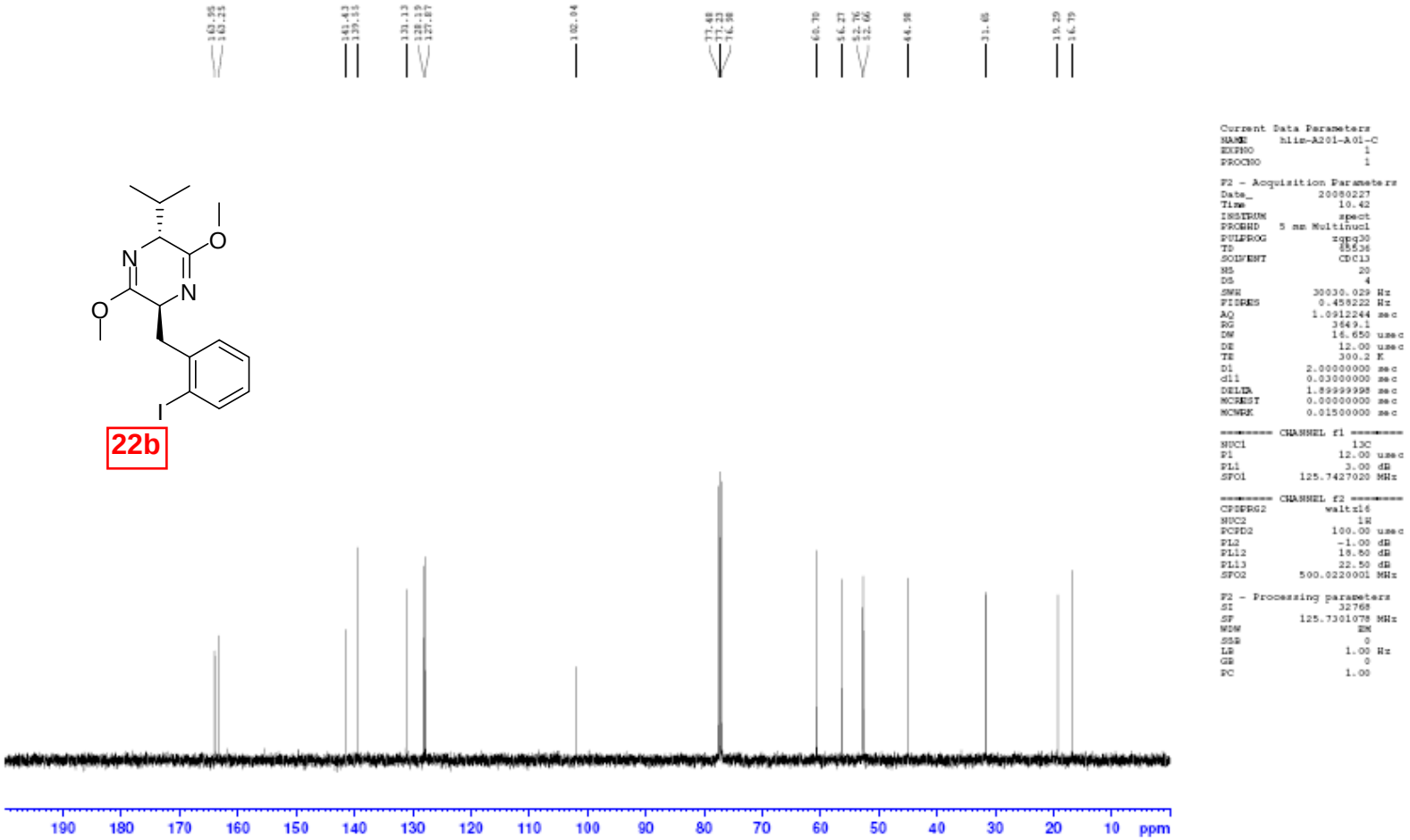

20
Br
HN
O
O
O
H
N
ppm


7.512
7.497
7.495
7.240
7.212
7.208
7.197
7.192
7.175
7.161
7.159
7.052
7.048
7.036
7.022
7.018
4.332
4.323
4.316
4.309
4.300
3.715
3.664
3.657
3.650
3.620
3.471
3.462
3.444
3.434
2.946
2.929
2.918
2.902
2.213
2.206
2.199
2.192
2.186
2.179
1.001
0.987
0.647
0.634
N
O
N
O
Br
22a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.11
1.04
1.01
3.14
1.09
3.14
1.09
1.06
1.05
3.21
3.23
Current Data Parameters
NAME hlim-A176-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050119
Time 14.28
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200216 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME      hlim-A178-A01-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080119
Time              14.33
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   27
DS                    4
SWH           30030.029 Hz
FIDRES        0.458222 Hz
AQ            1.0912244 sec
RG               2580.3
DW               16.650 usec
DE               12.00 usec
TE               300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.00 usec
PL1               3.00 dB
SFO1        125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2              -1.00 dB
PL12             18.80 dB
PL13             22.50 dB
SFO2        500.0220001 MHz

F2 - Processing parameters
SI                 32768
SF          125.7301290 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.00
```


7.806
7.804
7.789
7.240
7.236
7.234
7.221
7.218
7.207
7.202
7.192
7.187
6.878
6.873
6.865
6.862
6.860
6.857
6.849
6.844
5.261
4.304
4.297
4.295
4.288
4.280
4.279
4.271
3.723
3.717
3.710
3.630
3.620
3.439
3.429
3.411
3.402
2.951
2.935
2.924
2.907
2.225
2.218
2.211
2.204
2.198
2.191
2.142
1.011
0.997
0.989
0.656
0.648
0.643
0.635
22b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.99
2.23
1.01
1.03
4.28
3.23
1.06
1.06
1.07
5.90
3.30
Current Data Parameters
NAME hlim-A201-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060227
Time 10.36
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



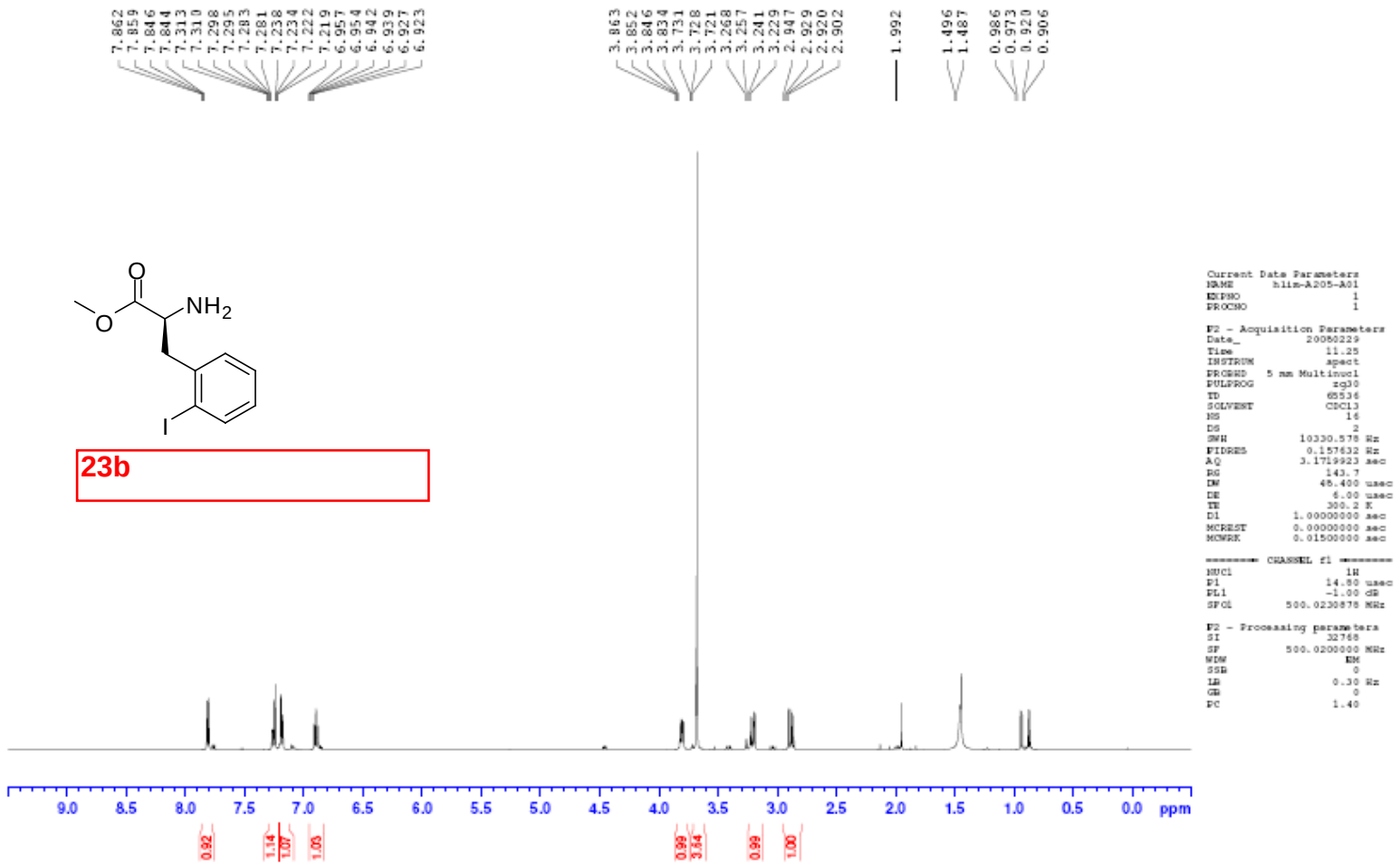
Current Data Parameters
NAME hlm-A201-A01-C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080227
Time 10.42
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 20
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 3449.1
DW 16.650 usec
DE 12.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
SFO1 125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.80 dB
PL13 22.50 dB
SFO2 500.0220001 MHz

F2 - Processing parameters
SI 32768
SF 125.7301078 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00


7.862
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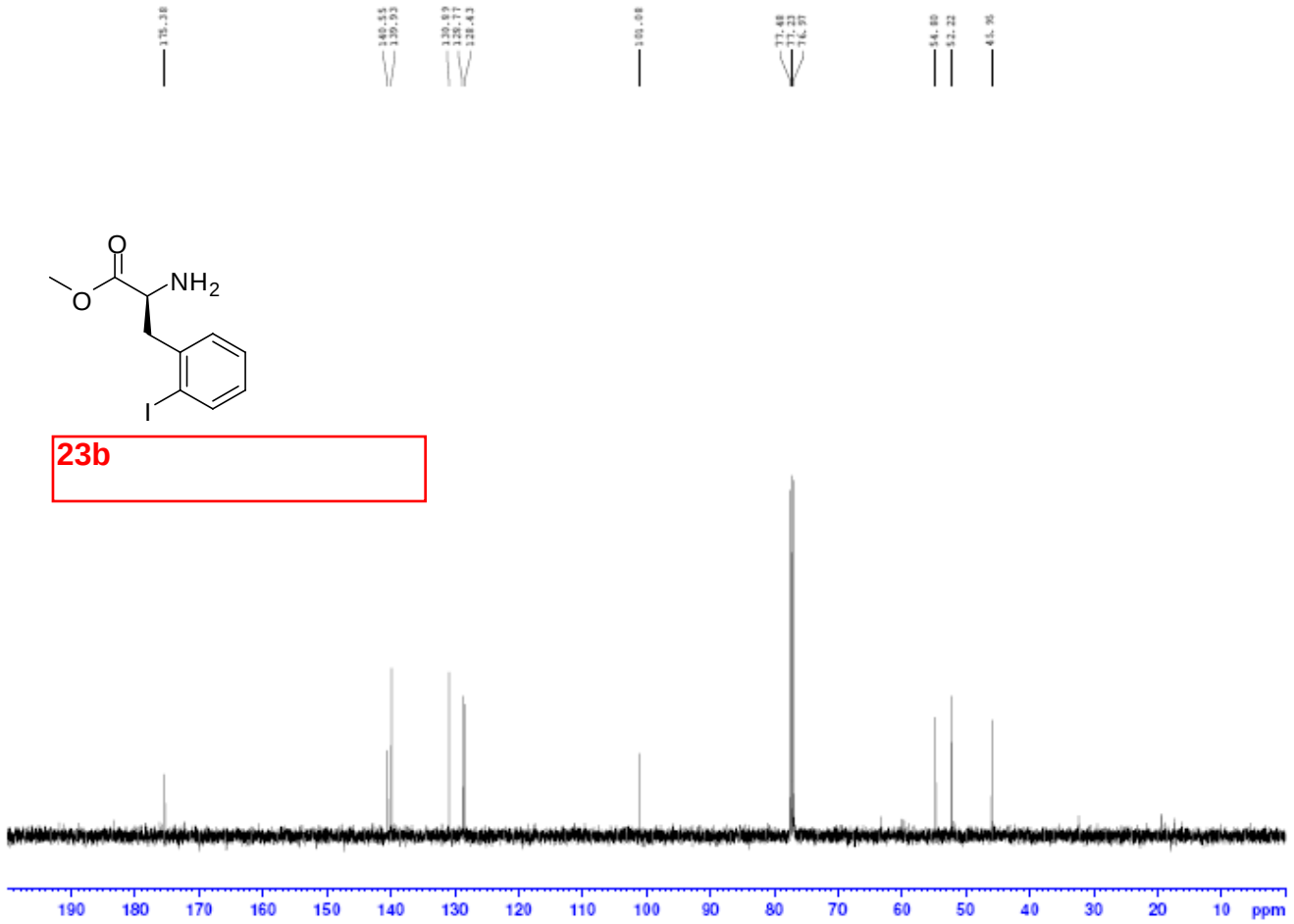
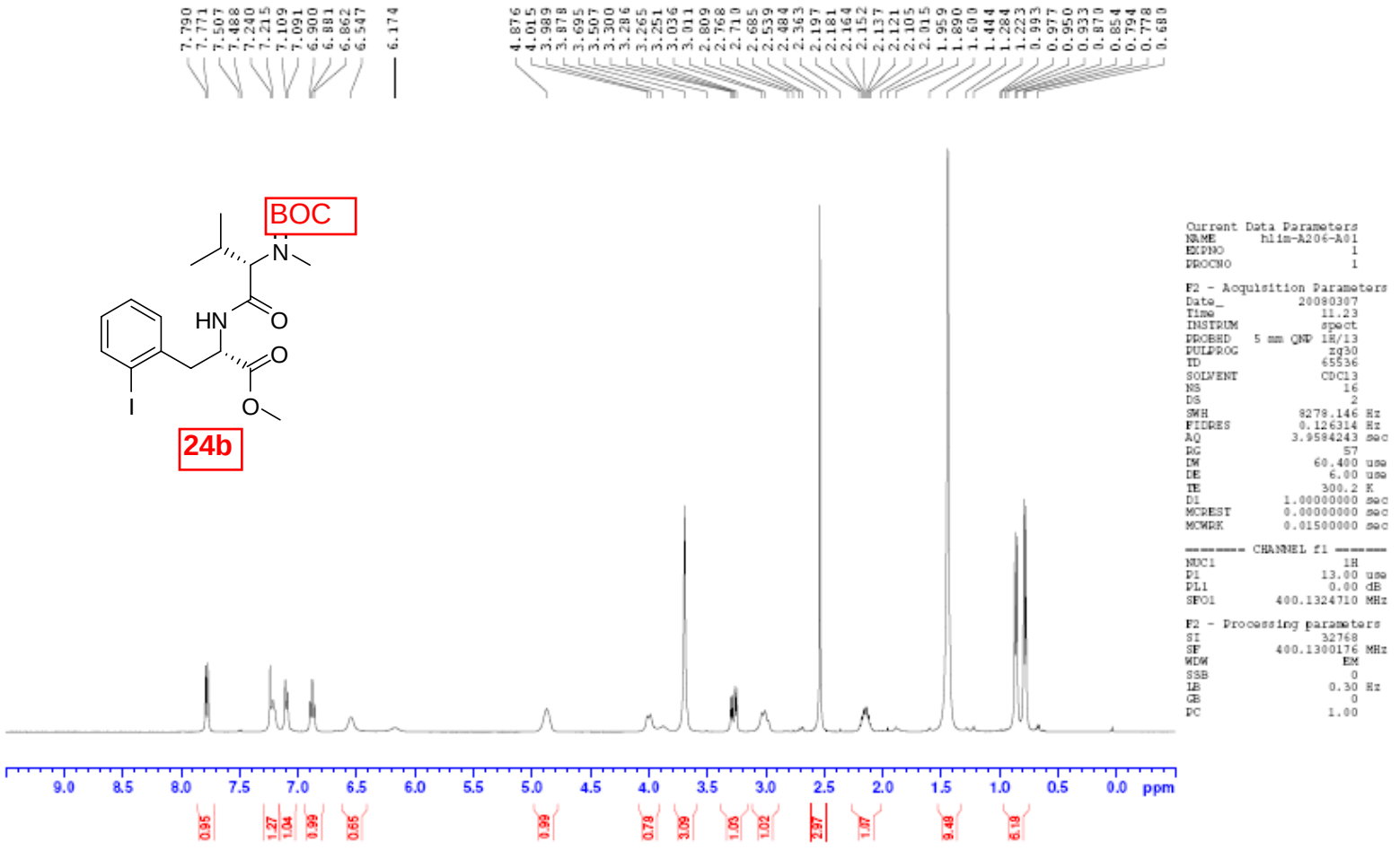
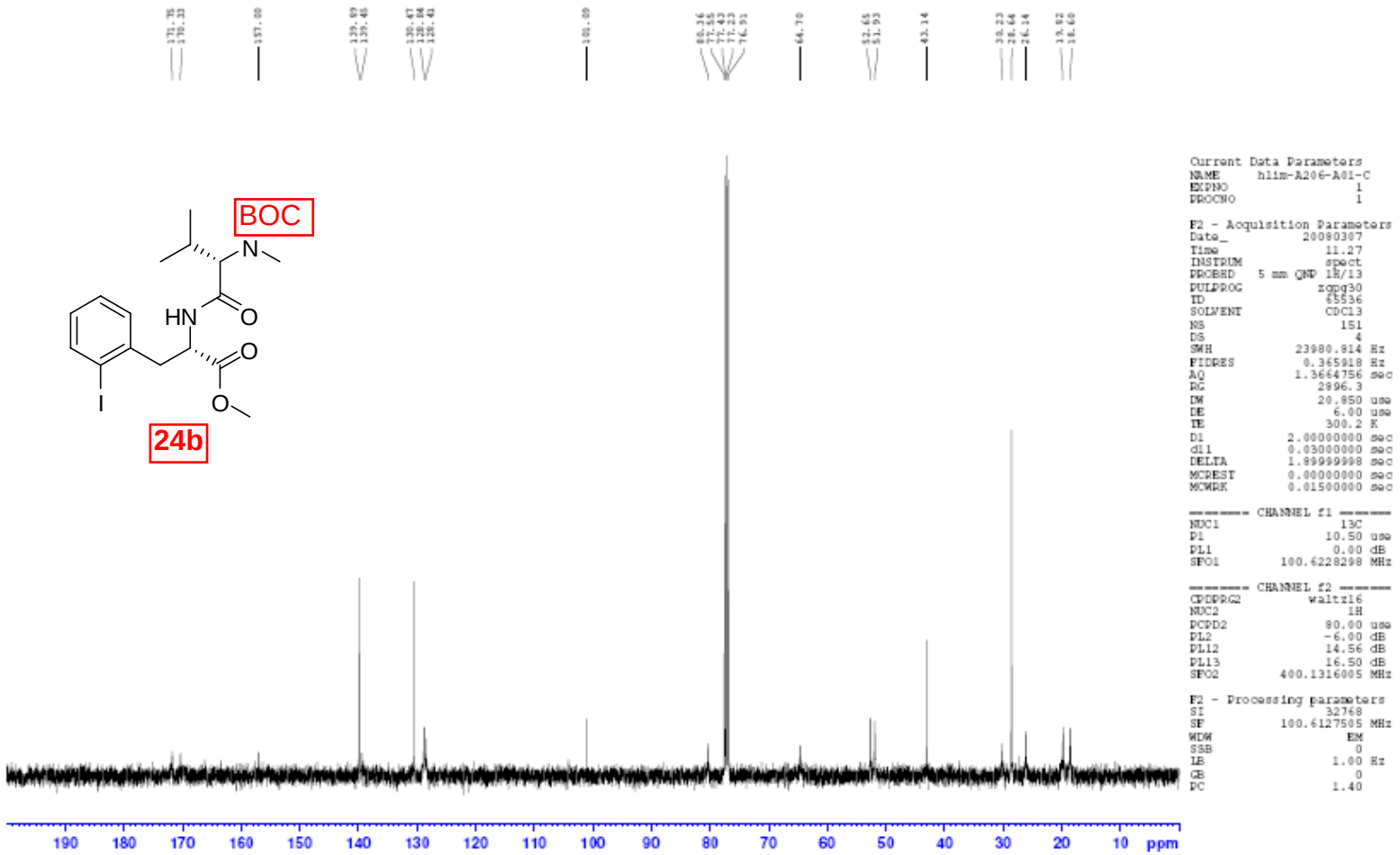
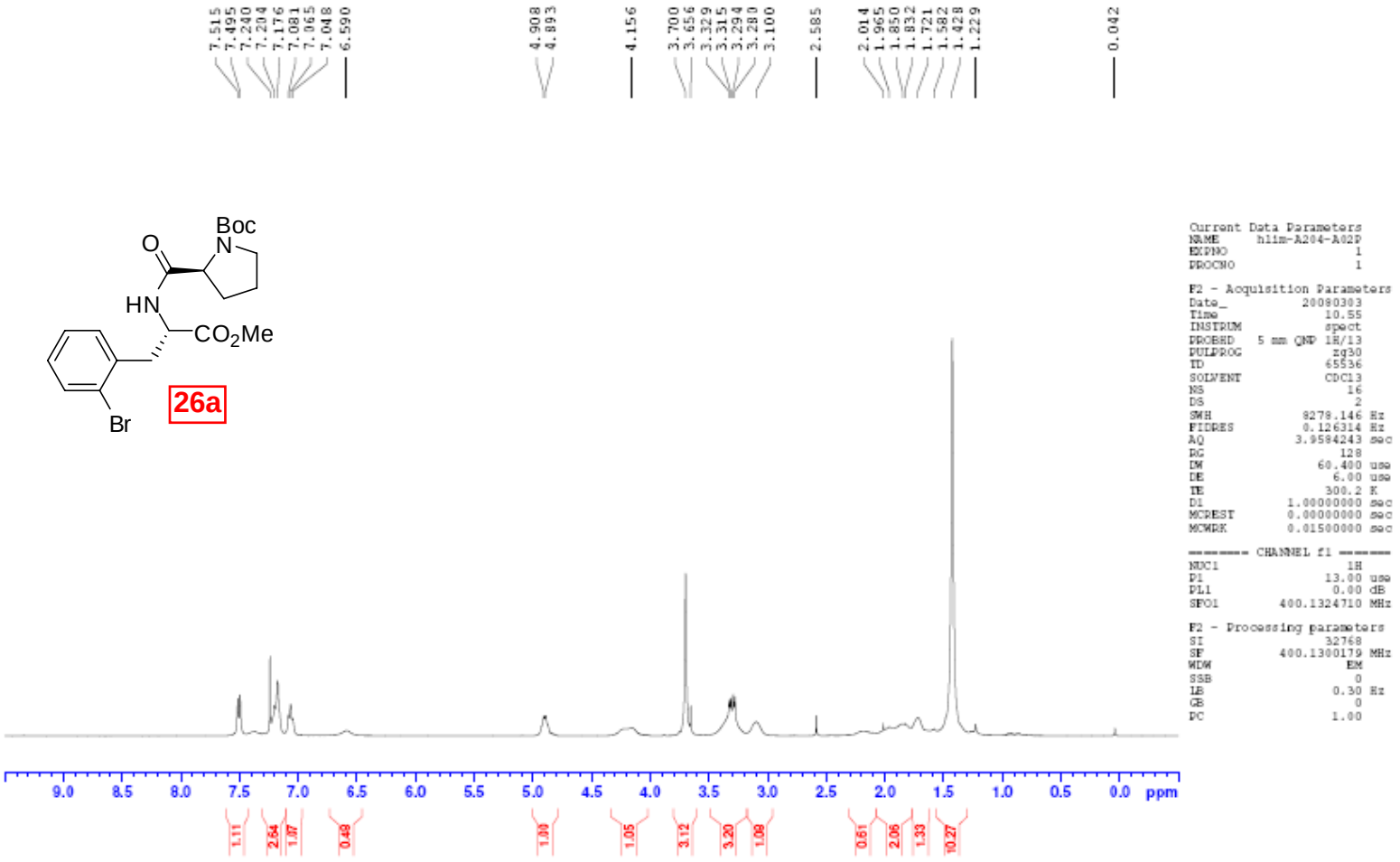
7.846
7.844
7.313
7.310
7.298
7.295
7.283
7.281
7.238
7.234
7.222
7.219
6.957
6.954
6.942
6.939
6.927
6.923
3.863
3.852
3.846
3.834
3.731
3.728
3.721
3.268
3.257
3.241
3.229
2.947
2.929
2.920
2.902
1.992
1.496
1.487
0.986
0.973
0.920
0.906
O
NH2
O
I
23b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.92
1.14
1.07
1.05
0.99
3.64
0.99
1.00
Current Data Parameters
NAME hlim-A205-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080229
Time 11.25
INSTRUM apect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 143.7
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



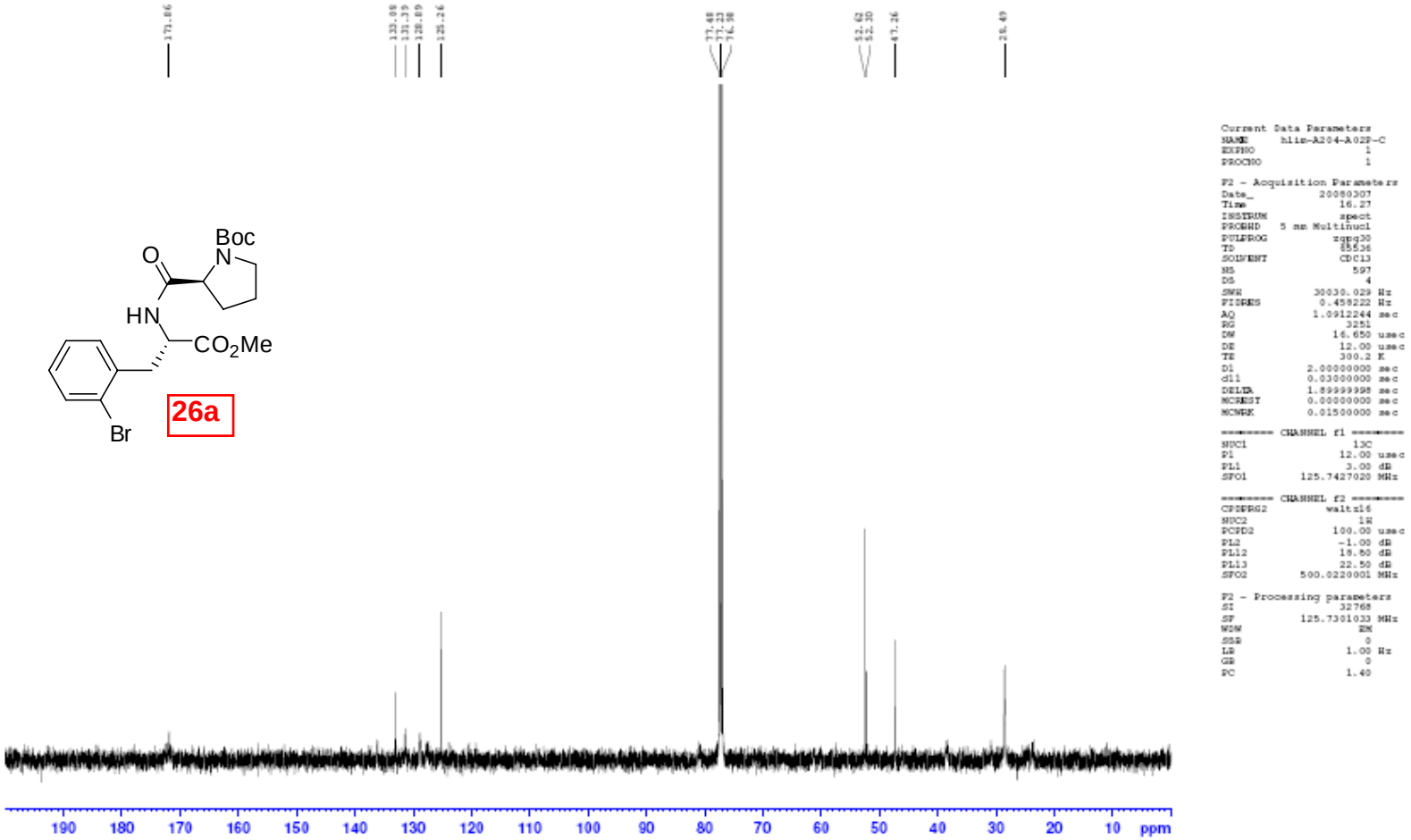

```
Current Data Parameters
NAME      hlin-A205-A01-C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20080229
Time              11.31
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   21
DS                    4
SWH           30030.029 Hz
FIDRES            0.458222 Hz
AQ            1.0912244 sec
RG                5792.6
DW               16.650 usec
DE               12.00 usec
TE                300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                12.00 usec
PL1                3.00 dB
SFO1        125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              16.60 dB
PL13              22.50 dB
SFO2        500.0220001 MHz

F2 - Processing parameters
SI                  32768
SF          125.7301097 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```


7.790
7.771
7.507
7.488
7.240
7.215
7.109
7.091
6.900
6.881
6.862
6.547
6.174
4.876
4.015
3.989
3.878
3.695
3.507
3.300
3.286
3.265
3.251
3.036
3.011
2.809
2.768
2.710
2.685
2.539
2.484
2.363
2.197
2.181
2.164
2.152
2.137
2.121
2.105
2.015
1.959
1.890
1.600
1.444
1.284
1.223
0.993
0.977
0.950
0.933
0.870
0.854
0.794
0.778
0.680
BOC
N
HN
O
O
O
I
O
24b
Current Data Parameters
NAME hlim-A206-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080307
Time 11.23
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 57
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
------- CHANNEL f1 ------
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
1.27
1.04
0.99
0.65
0.99
0.78
3.09
1.05
1.02
2.97
1.07
9.48
6.18

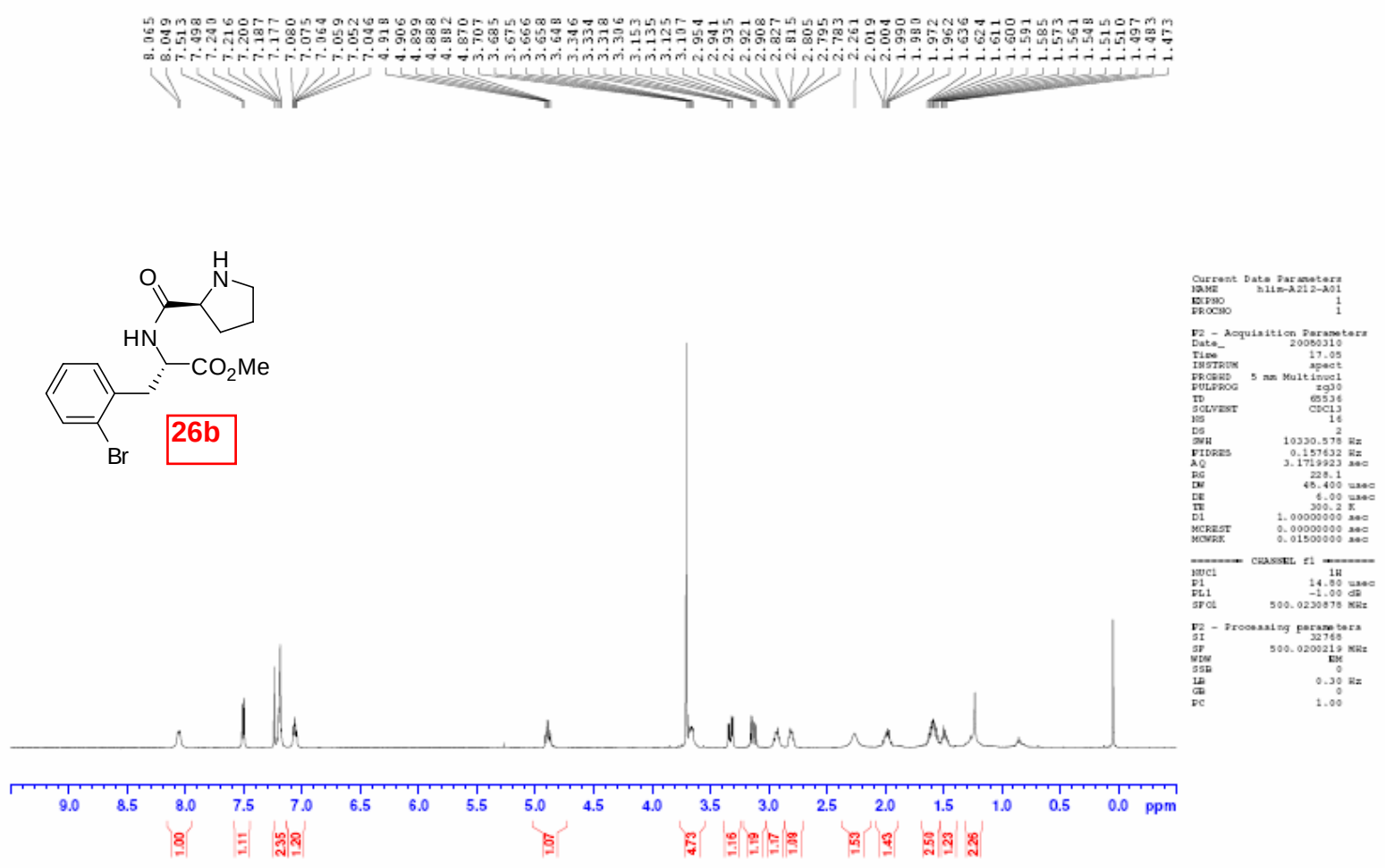

BOC
N
HN
O
O
O
I
24b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Current Data Parameters
NAME hlim-A206-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080307
Time 11.27
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 151
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2896.3
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127505 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

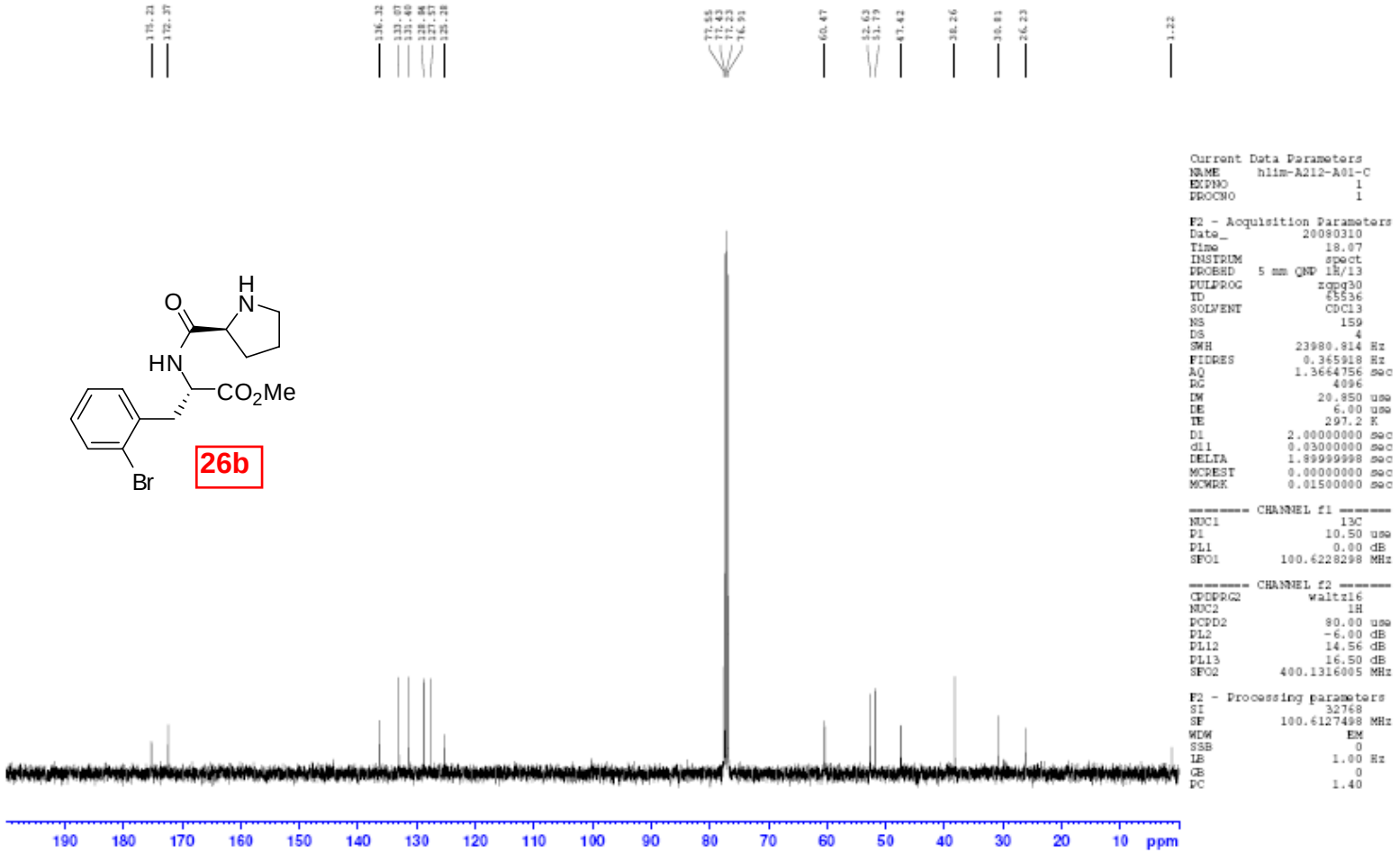


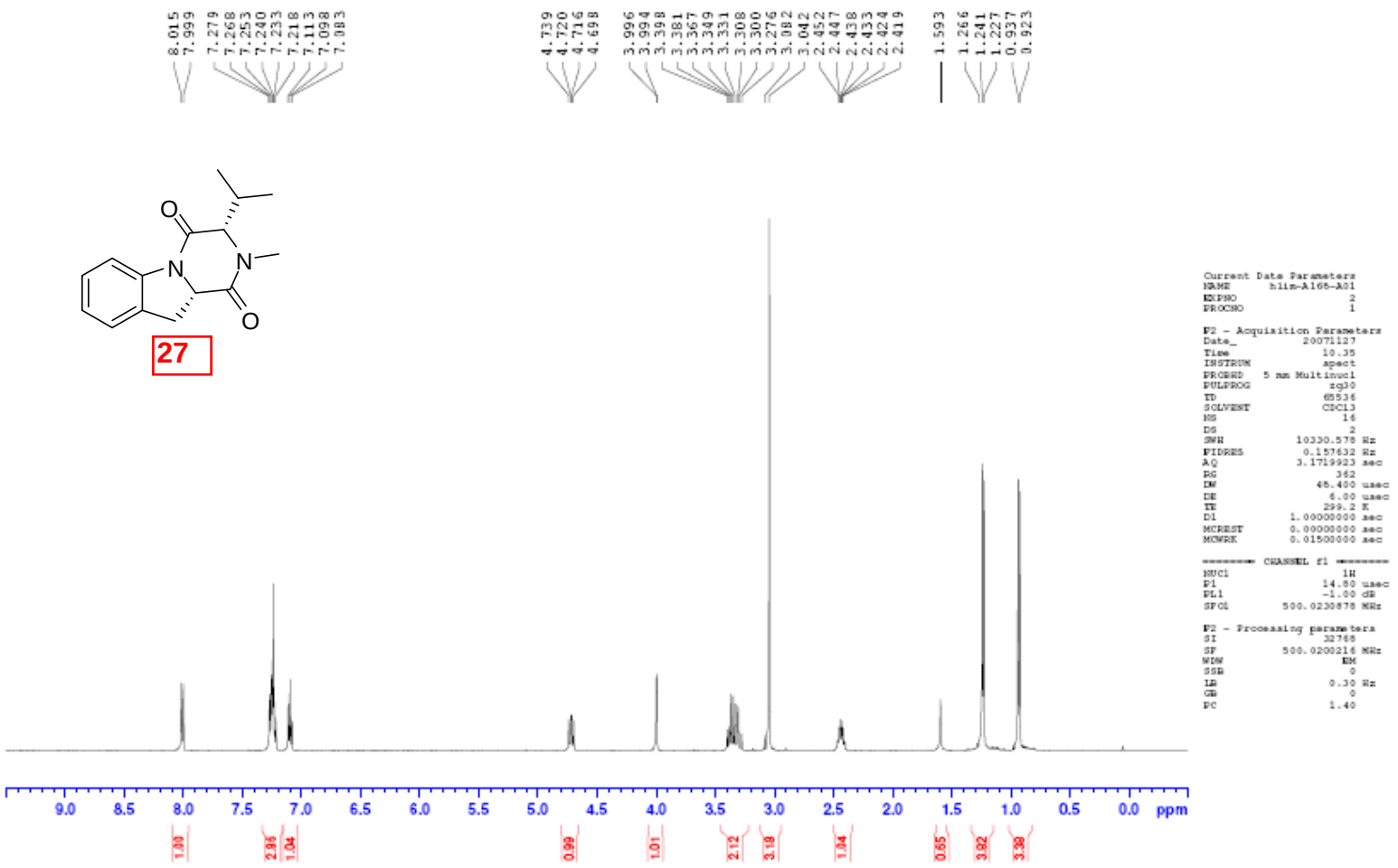

```
Current Data Parameters
NAME      hlim-A204-A02P
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080303
Time              10.55
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                   128
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ======
NUC1                  1H
P1                13.00 usec
PL1                0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF            400.1300179 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

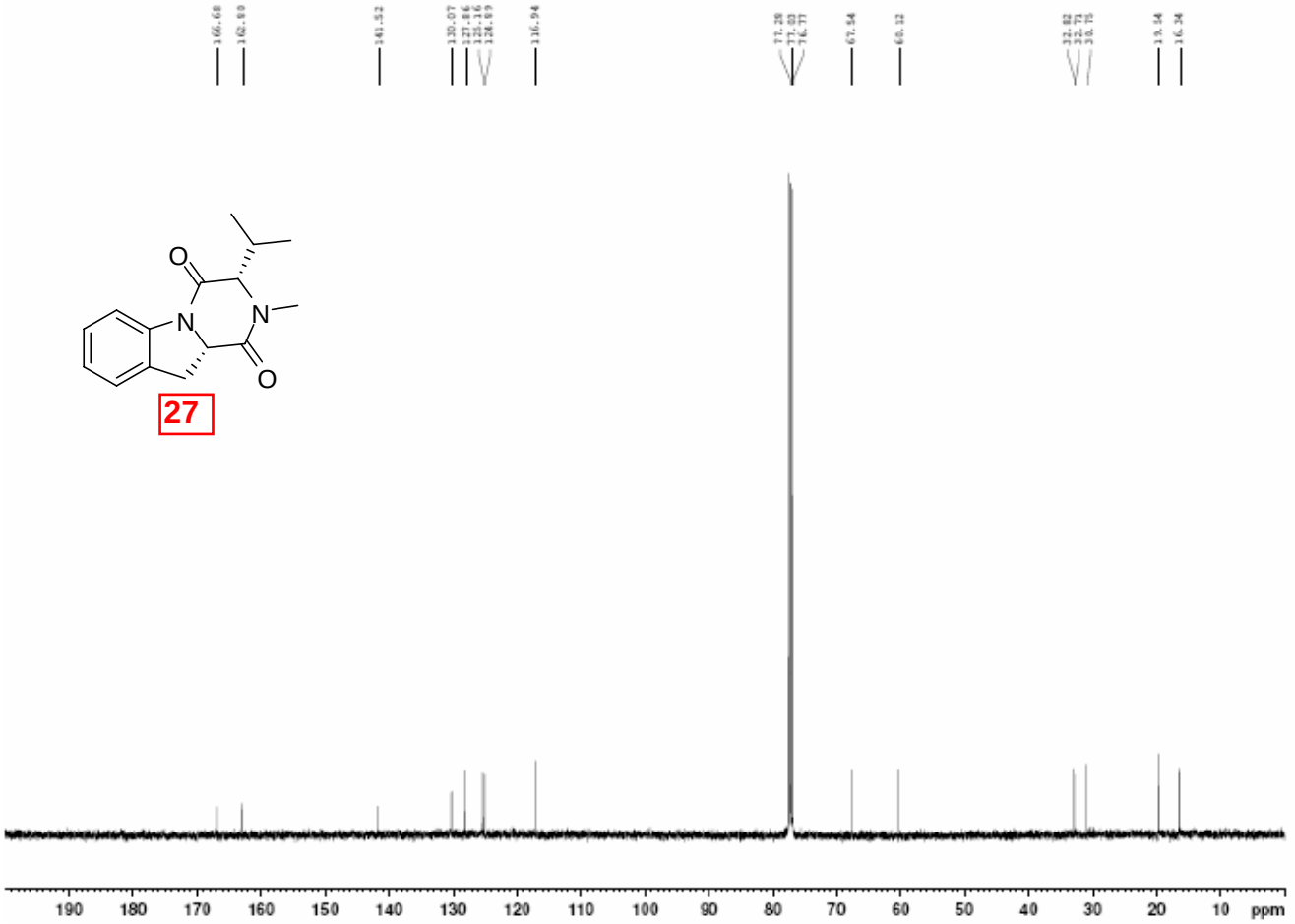



```
Current Data Parameters
NAME      hlim-A204-A02P-C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20060307
Time              16.27
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD               65536
SOLVENT            CDCl3
NS                   597
DS                     4
SWH           30030.029 Hz
FIDRES        0.458222 Hz
AQ            1.0912244 sec
RG                  3251
DW               16.650 usec
DE               12.00 usec
TE               300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               12.00 usec
PL1               3.00 dB
SFO1        125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2               1H
PCPD2           100.00 usec
PL2              -1.00 dB
PL12             18.80 dB
PL13             22.50 dB
SFO2        500.0220001 MHz

F2 - Processing parameters
SI                 32768
SF          125.7301033 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

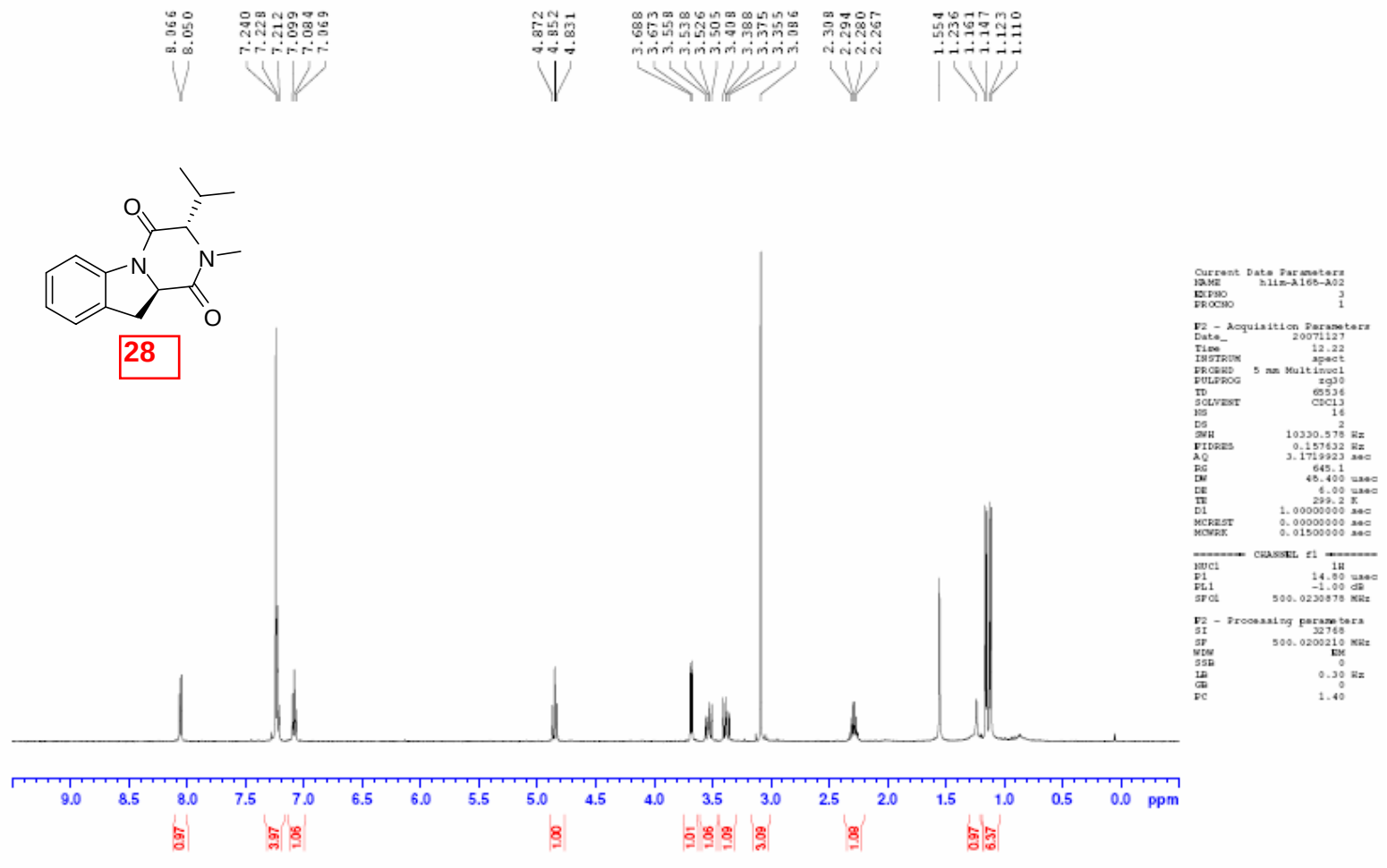

8.065
8.049
7.513
7.498
7.240
7.216
7.200
7.187
7.177
7.080
7.075
7.064
7.059
7.052
7.046
4.918
4.906
4.899
4.888
4.882
4.870
3.707
3.685
3.675
3.666
3.658
3.648
3.346
3.334
3.318
3.306
3.153
3.135
3.125
3.107
2.954
2.941
2.935
2.921
2.908
2.827
2.815
2.805
2.795
2.783
2.261
2.019
2.004
1.990
1.980
1.972
1.962
1.636
1.624
1.611
1.600
1.591
1.585
1.573
1.561
1.548
1.515
1.510
1.497
1.483
1.473
O
H
N
HN
CO2Me
Br
26b
Current Data Parameters
NAME hlim-A212-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060310
Time 17.05
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 228.1
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.50 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.11
2.35
1.20
1.07
4.73
1.16
1.19
1.17
1.09
1.53
1.43
2.50
1.20
2.26


175.23
172.37
136.32
133.07
131.40
128.84
127.57
125.28
77.55
77.43
77.23
76.91
60.47
52.63
51.79
47.42
30.26
26.81
26.23
1.22
O
H
N
HN
CO2Me
Br
26b
Current Data Parameters
NAME hlim-A212-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080310
Time 18.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 159
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4096
DW 20.850 usec
DE 6.00 usec
TE 297.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127498 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.015
7.999
7.279
7.268
7.253
7.240
7.233
7.218
7.113
7.098
7.083
4.739
4.720
4.716
4.698
3.996
3.994
3.398
3.381
3.367
3.349
3.331
3.308
3.300
3.276
3.082
3.042
2.452
2.447
2.438
2.433
2.424
2.419
1.593
1.266
1.241
1.227
0.937
0.923
27
Current Data Parameters
NAME hlim-A168-A01
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071127
Time 10.35
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200216 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.96
1.04
0.99
1.01
2.12
3.19
1.04
0.65
3.92
3.38




```
Current Data Parameters
NAME      hlin-A168-A01-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071127
Time              12.05
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH           30030.029 Hz
FIDRES            0.458222 Hz
AQ            1.0912244 sec
RG                 645.1
DW               16.650 usec
DE                 38.00 usec
TE                299.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.00 usec
PL1                3.00 dB
SFO1         125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2               -1.00 dB
PL12              18.60 dB
PL13              22.50 dB
SFO2         500.0220001 MHz

F2 - Processing parameters
SI                 32768
SF           125.7301290 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

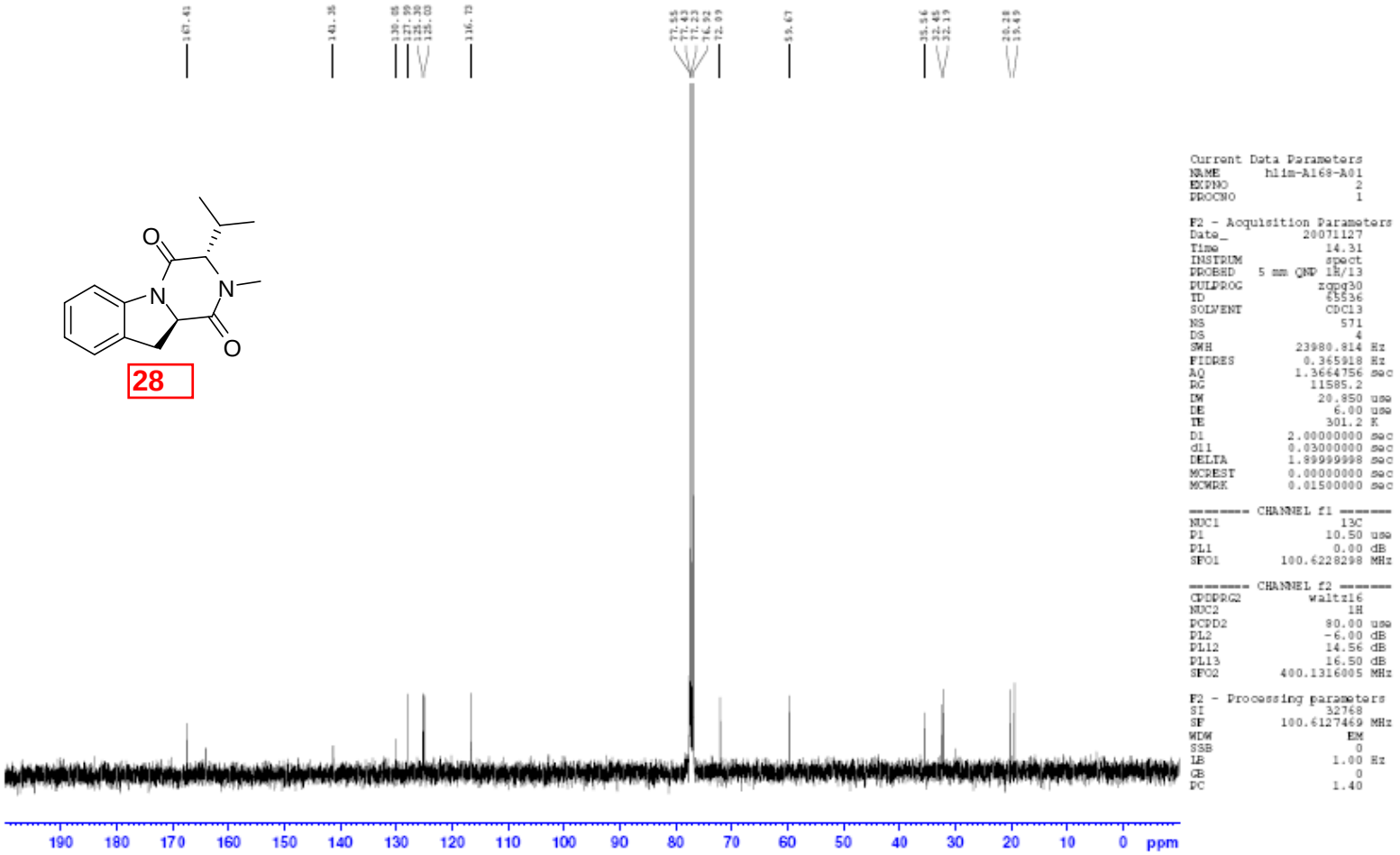


Current Data Parameters
NAME hlim-A165-A02
EXPNO 3
PROCNO 1

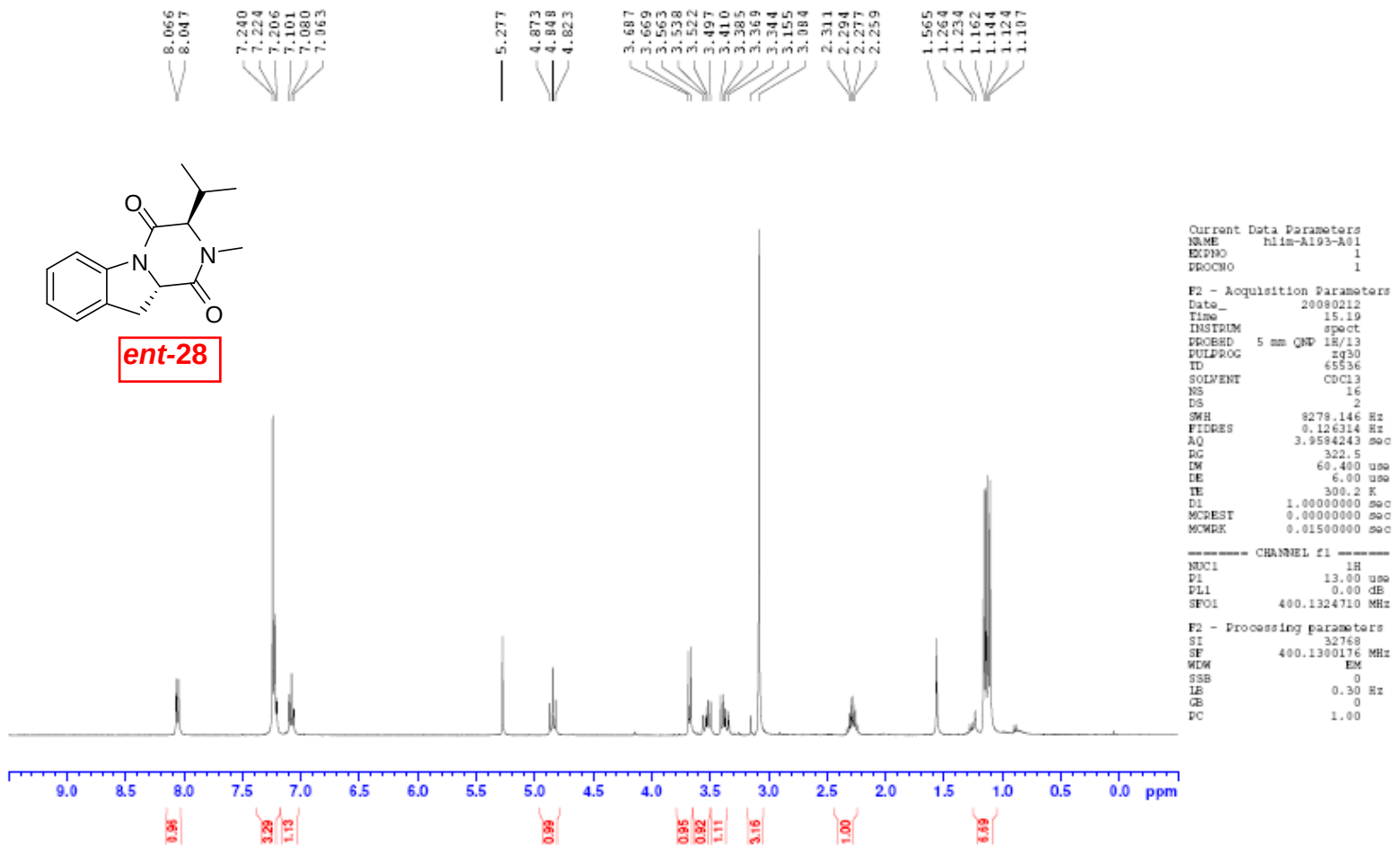
F2 - Acquisition Parameters
Date_ 20071127
Time 12.22
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 645.1
DW 48.400 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

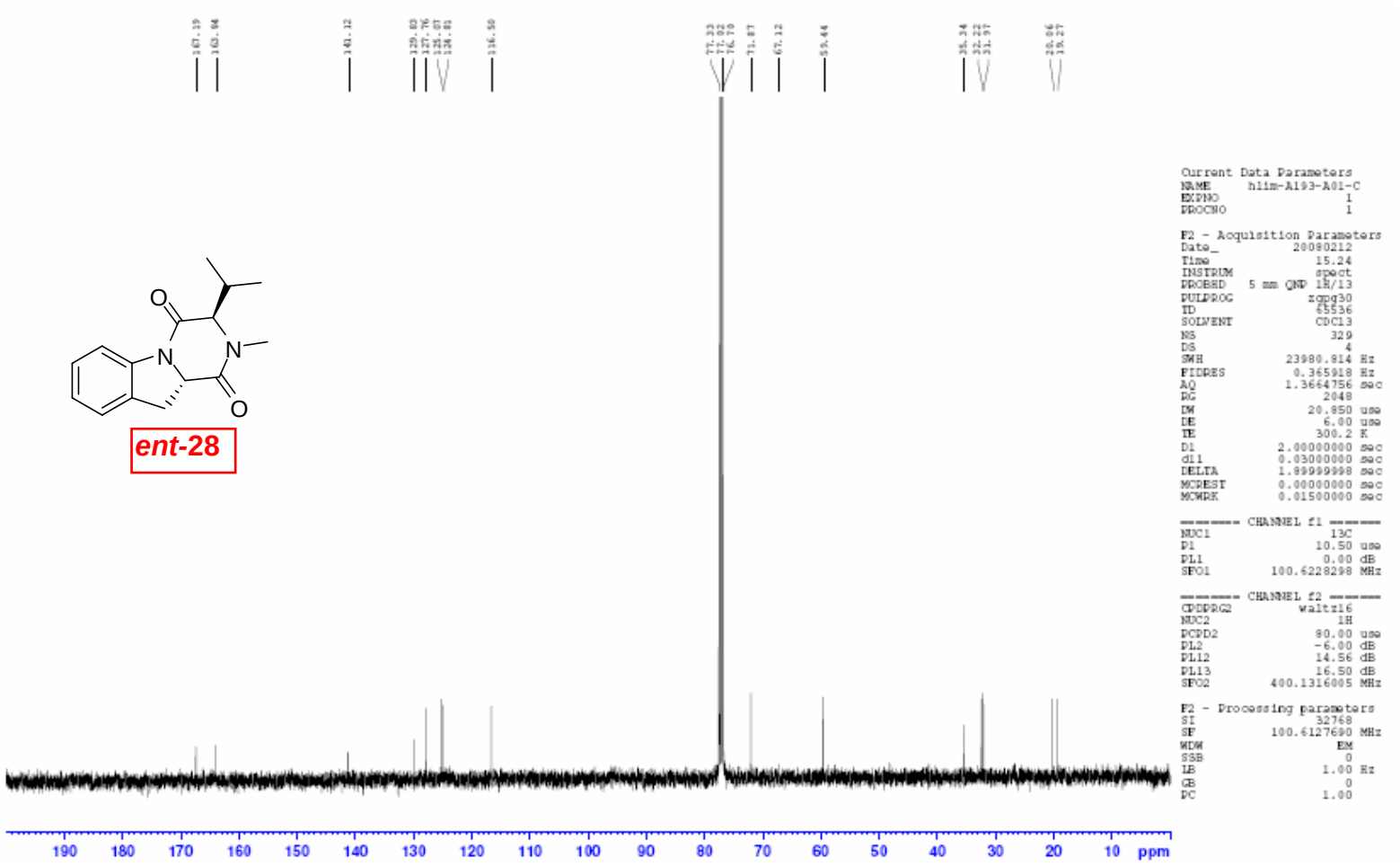
======== CHANNEL f1 ========
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz

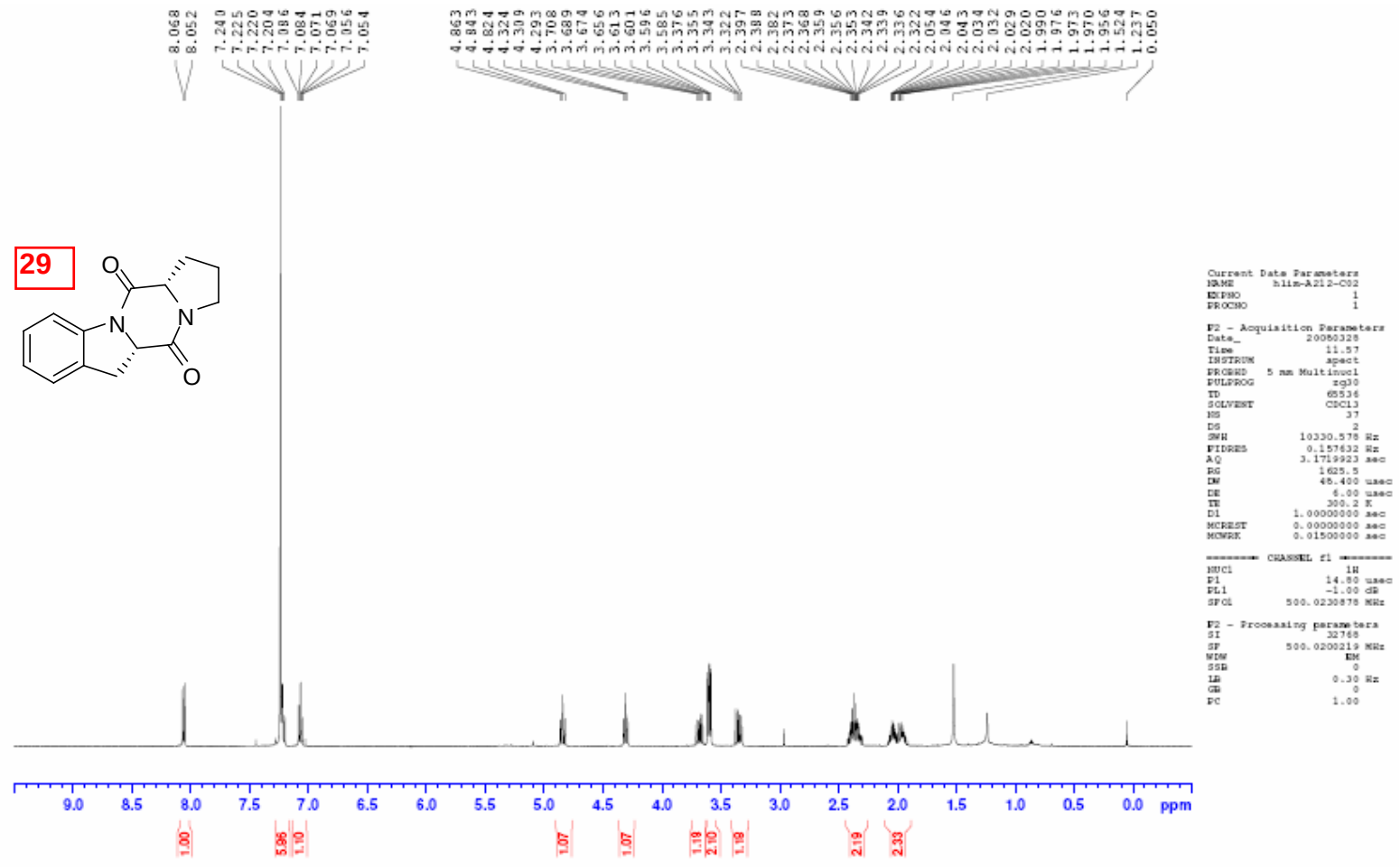
F2 - Processing parameters
SI 32768
SF 500.0200210 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

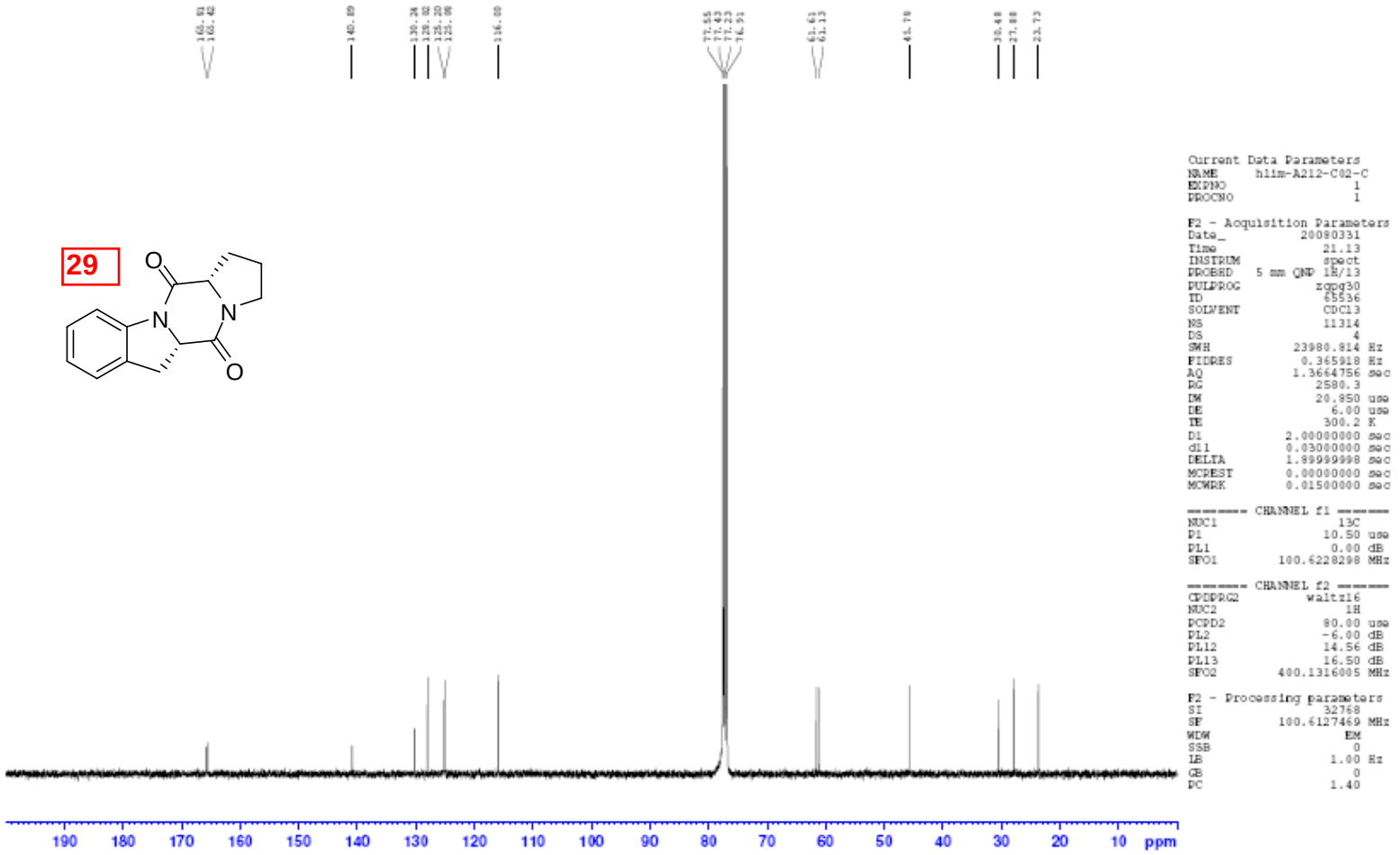


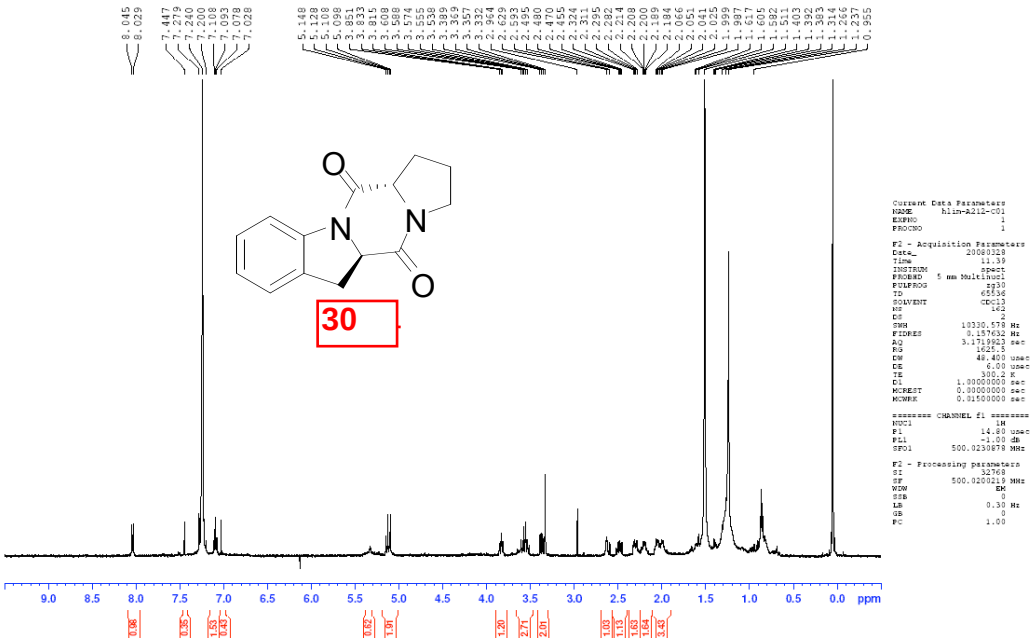

```
Current Data Parameters
NAME        hlim-A168-A01
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071127
Time                14.31
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    571
DS                      4
SWH             23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                11585.2
DW                 20.850 usec
DE                  6.00 usec
TE                301.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PL1                  0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                14.56 dB
PL13                16.50 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127469 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```


8.066
8.047
7.240
7.224
7.206
7.101
7.080
7.063
5.277
4.873
4.848
4.823
3.687
3.669
3.563
3.538
3.522
3.497
3.410
3.385
3.369
3.344
3.155
3.084
2.311
2.294
2.277
2.259
1.565
1.264
1.234
1.162
1.144
1.124
1.107
ent-28
Current Data Parameters
NAME hlim-A193-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080212
Time 15.19
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
------- CHANNEL f1 ------
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.96
3.29
1.13
0.99
0.95
0.92
1.11
3.16
1.00
6.89

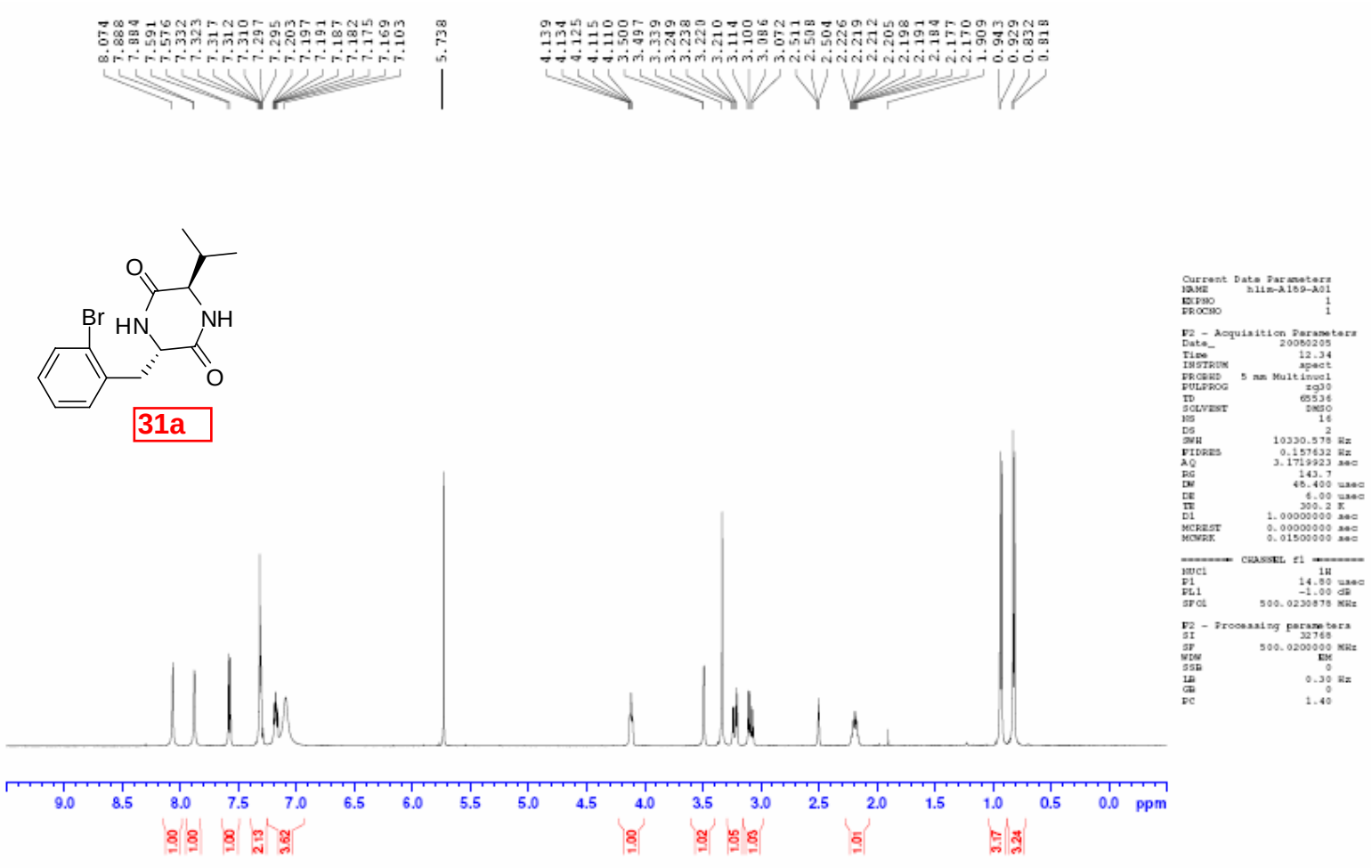

167.19
160.84
140.12
129.63
127.76
127.07
124.81
116.50
77.33
77.02
76.70
71.87
67.12
59.44
35.34
32.22
31.97
20.06
19.27
ent-28
Current Data Parameters
NAME hlim-A193-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080212
Time 15.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 329
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2048
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

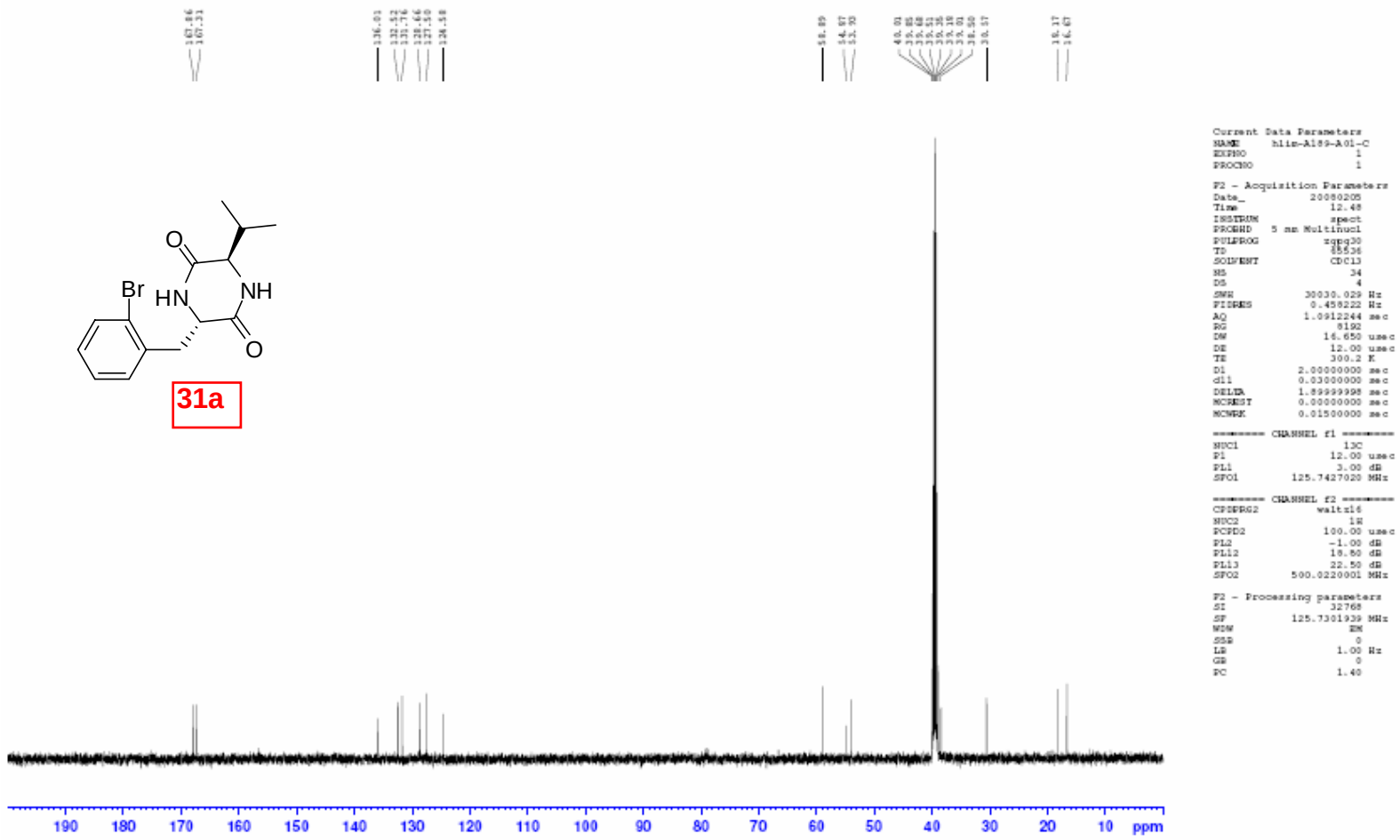

29
8.068
8.052
7.240
7.225
7.220
7.204
7.086
7.084
7.071
7.069
7.056
7.054
4.863
4.843
4.824
4.324
4.309
4.293
3.708
3.689
3.674
3.656
3.613
3.601
3.596
3.585
3.376
3.355
3.343
3.322
2.397
2.388
2.382
2.373
2.368
2.359
2.356
2.353
2.342
2.339
2.336
2.322
2.054
2.046
2.043
2.034
2.032
2.029
2.020
1.990
1.976
1.973
1.970
1.956
1.524
1.237
0.050
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
5.96
1.10
1.07
1.07
1.19
2.10
1.18
2.19
2.33
Current Data Parameters
NAME hlim-A212-C02
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080328
Time 11.57
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 37
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 1625.5
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

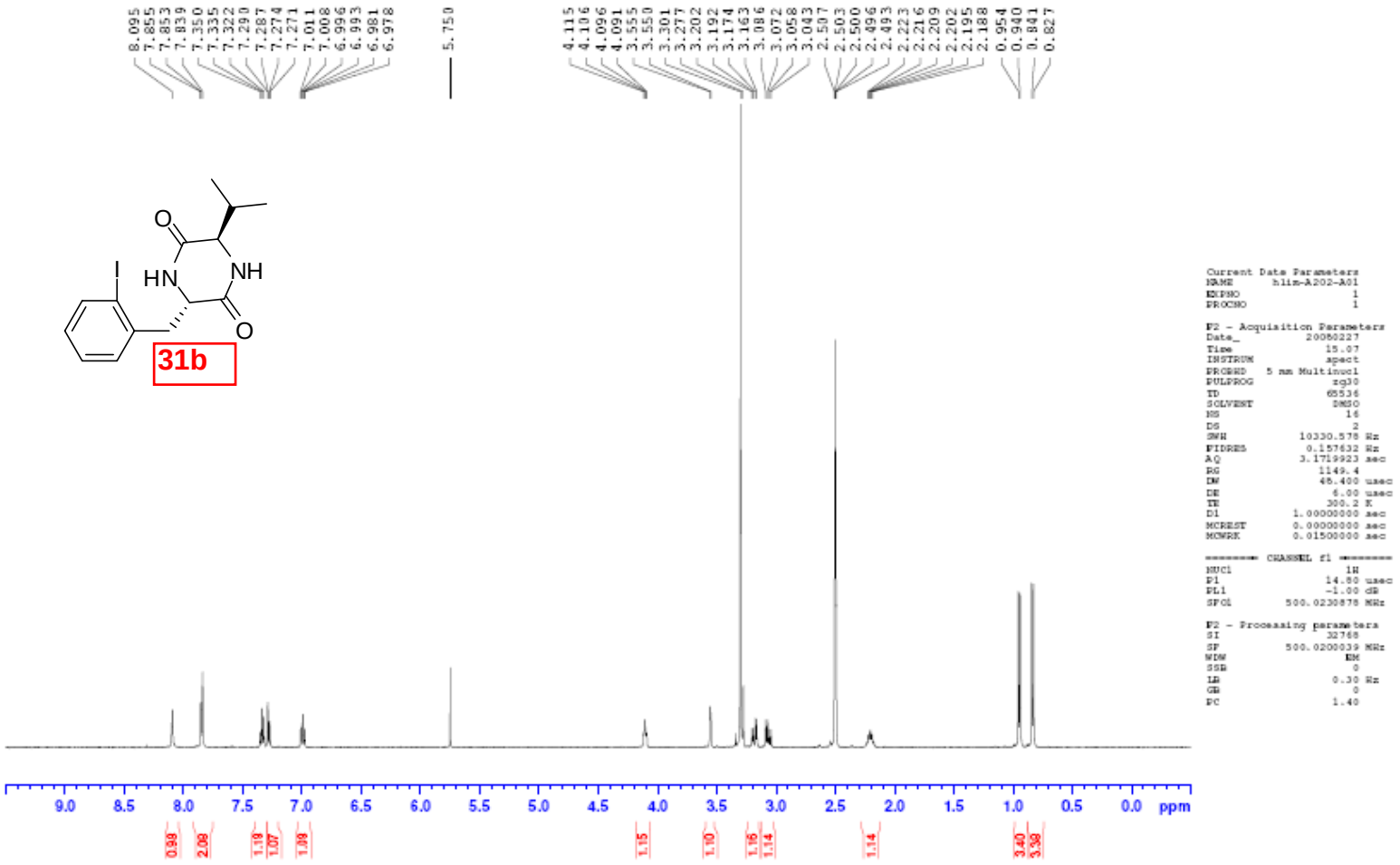

29
O
N
N
O
165.51
165.42
140.89
130.24
128.02
125.20
125.08
116.00
77.55
77.43
77.23
76.91
61.61
61.13
45.70
30.48
27.88
23.73
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Current Data Parameters
NAME hlim-A212-C02-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080331
Time 21.13
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 11314
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2580.3
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127469 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



^{1}H NMR spectrum of **30**


8.074
7.888
7.884
7.591
7.576
7.332
7.323
7.317
7.312
7.310
7.297
7.295
7.203
7.197
7.191
7.187
7.182
7.175
7.169
7.103
5.738
4.139
4.134
4.125
4.115
4.110
3.500
3.497
3.339
3.249
3.238
3.220
3.210
3.114
3.100
3.086
3.072
2.511
2.508
2.504
2.226
2.219
2.212
2.205
2.198
2.191
2.184
2.177
2.170
1.909
0.943
0.929
0.832
0.818
O
HN
NH
Br
O
31a
Current Data Parameters
NAME hlim-A169-A01
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080205
Time 12.34
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 143.7
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.00
1.00
2.13
3.62
1.00
1.02
1.05
1.05
1.01
3.17
3.24


167.86
167.31
136.01
132.52
131.76
128.66
127.50
124.58
58.89
54.67
53.93
40.01
39.85
39.68
39.51
39.35
39.18
39.01
38.50
30.57
19.17
16.67
O
HN
NH
O
Br
31a
Current Data Parameters
NAME hlin-A189-A01-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080205
Time 12.48
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 34
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 8192
DW 16.650 usec
DE 12.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
SFO1 125.7427020 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.60 dB
PL13 22.50 dB
SFO2 500.0220001 MHz
F2 - Processing parameters
SI 32768
SF 125.7301939 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

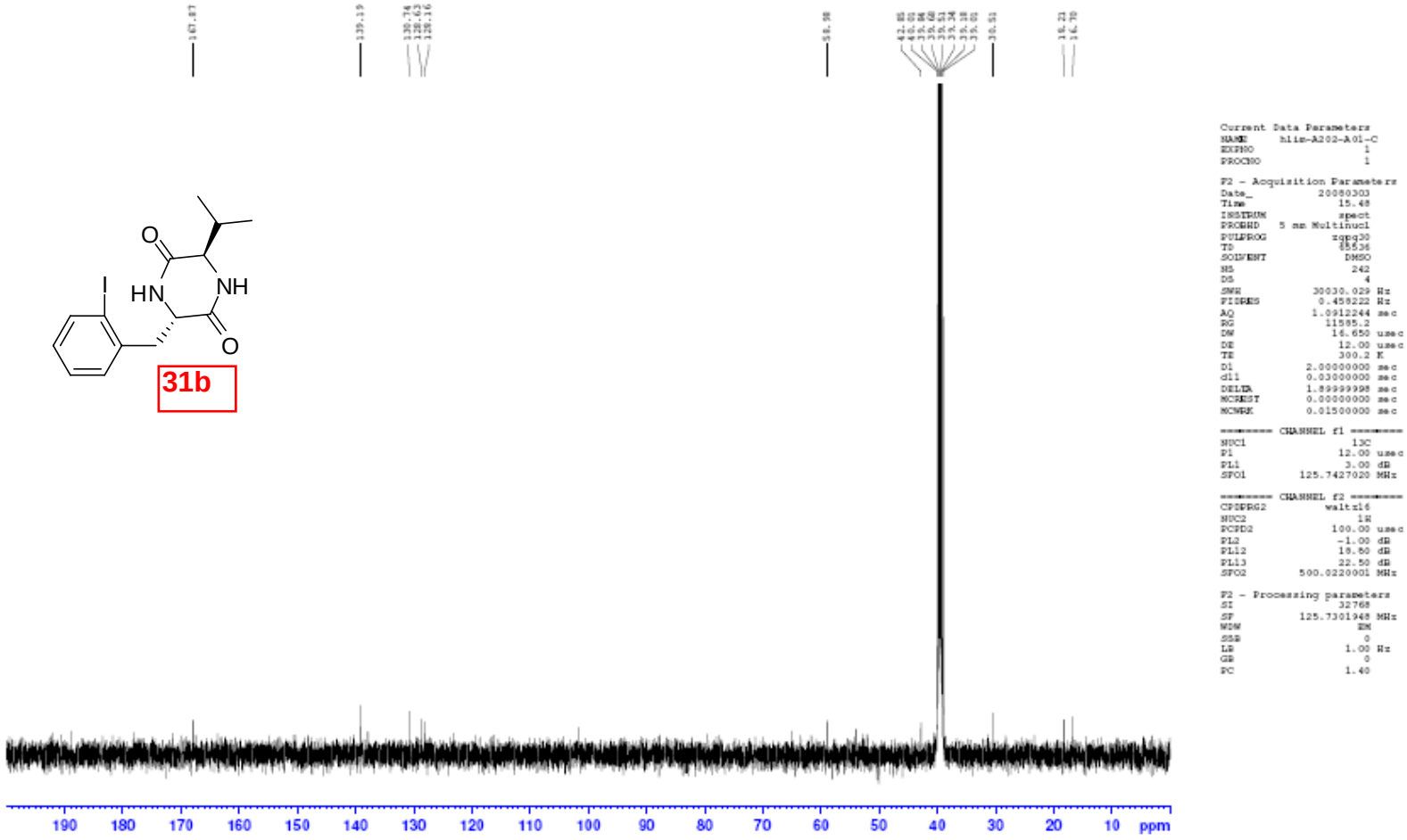


Current Data Parameters
NAME hlm-A202-A01
EXPNO 1
PROCNO 1

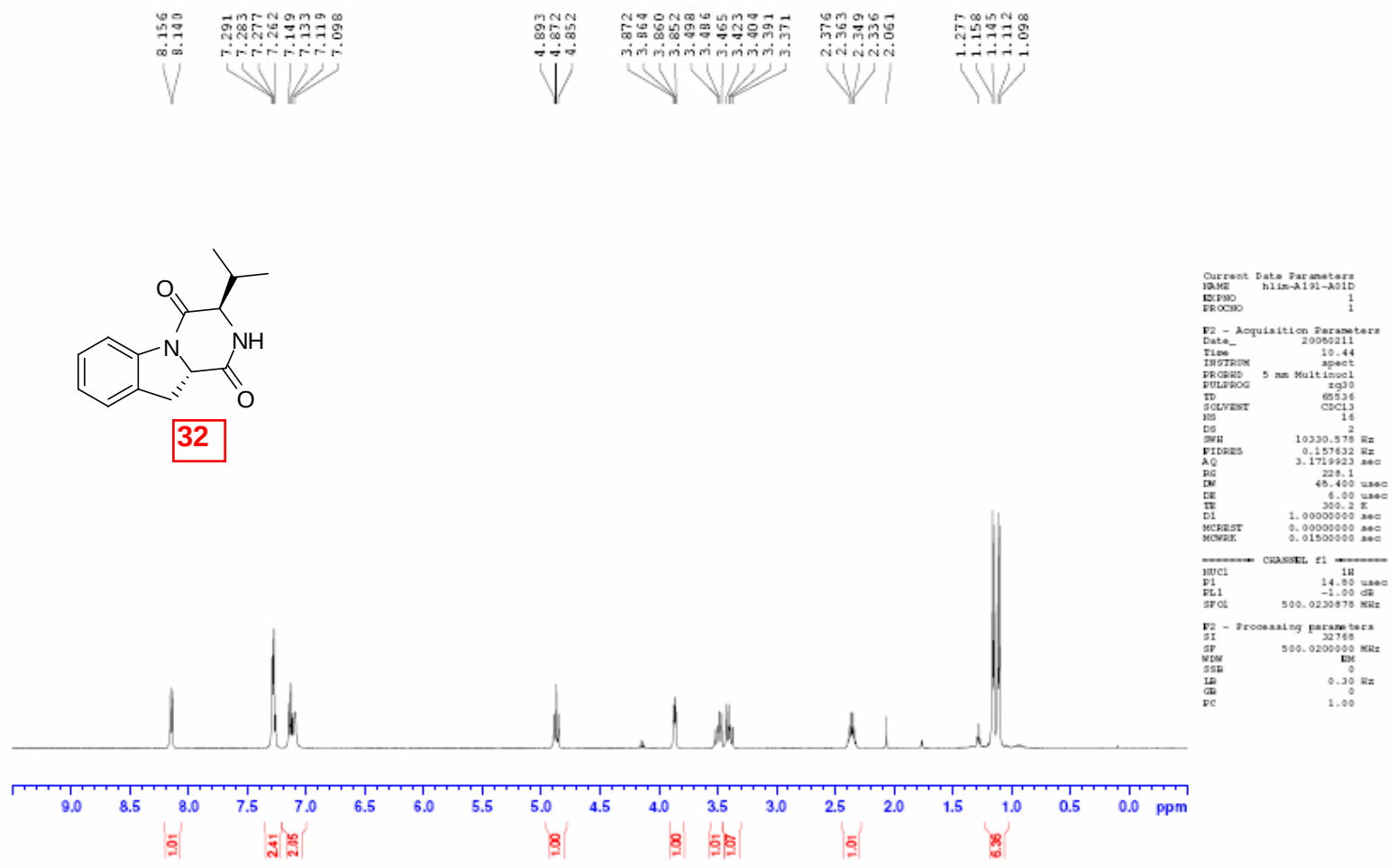
F2 - Acquisition Parameters
Date_ 20060227
Time 15.07
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 1149.4
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

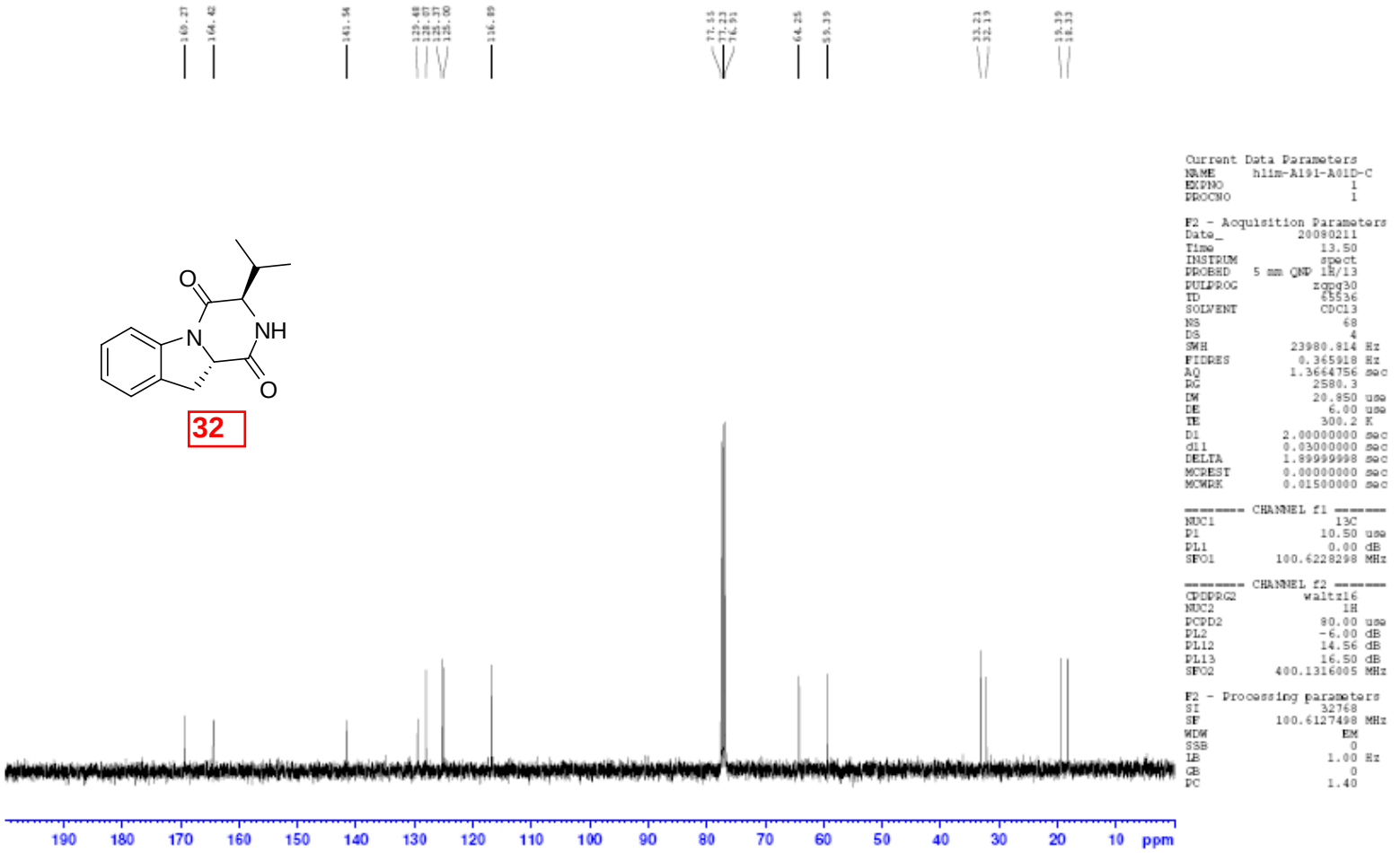
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz

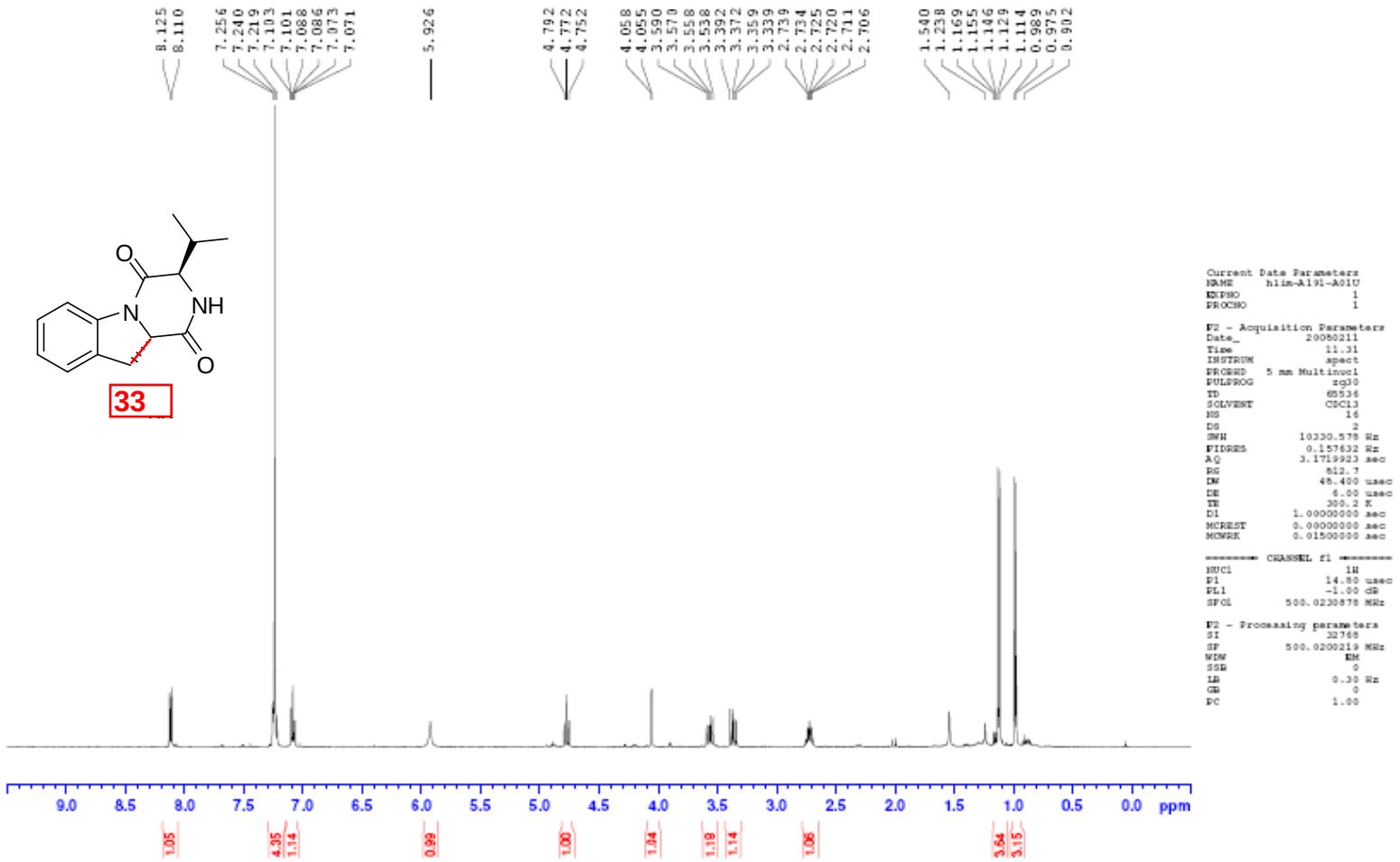
F2 - Processing parameters
SI 32768
SF 500.0200039 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

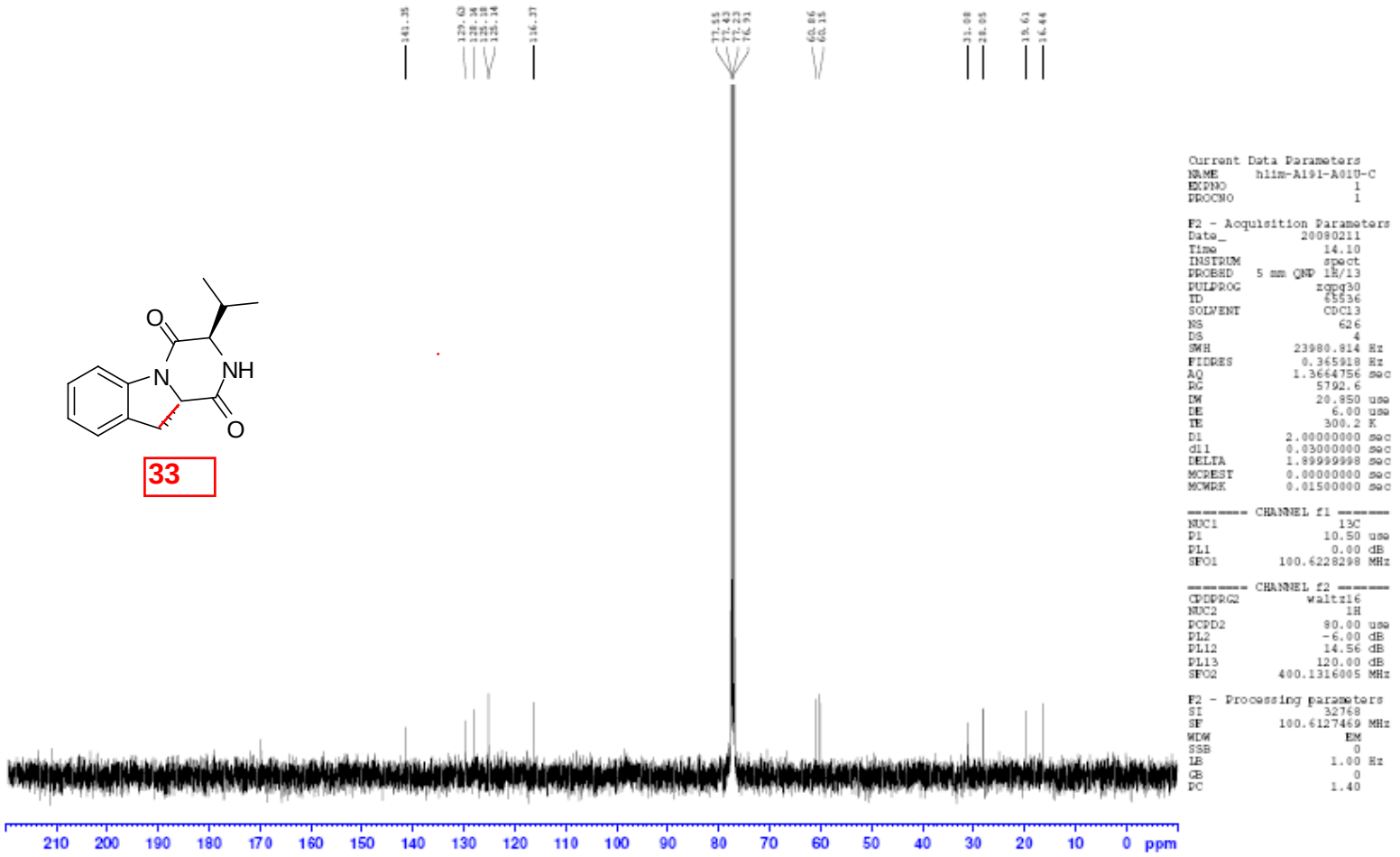



```
Current Data Parameters
NAME      hlim-A202-A01-C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              20080303
Time                  15.48
INSTRUM                spect
PROBHD   5 mm Multinucl
PULPROG            zgpg30
TD                  65536
SOLVENT             DMSO
NS                    242
DS                      4
SWH               30030.029 Hz
FIDRES            0.458222 Hz
AQ                1.0912244 sec
RG                  11585.2
DW                   16.650 usec
DE                   12.00 usec
TE                   300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.00 usec
PL1                   3.00 dB
SFO1          125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                100.00 usec
PL2                  -1.00 dB
PL12                 18.60 dB
PL13                 22.50 dB
SFO2          500.0220001 MHz

F2 - Processing parameters
SI                    32768
SF            125.7301948 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```


8.156
8.140
7.291
7.283
7.277
7.262
7.149
7.133
7.119
7.098
4.893
4.872
4.852
3.872
3.864
3.860
3.852
3.498
3.486
3.465
3.423
3.404
3.391
3.371
2.376
2.363
2.349
2.336
2.061
1.277
1.158
1.145
1.112
1.098
O
N
NH
O
32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
2.41
2.05
1.00
1.00
1.01
1.07
1.01
6.36
Current Data Parameters
NAME hlim-A191-A01D
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060211
Time 10.44
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 228.1
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


169.27
164.42
141.54
139.48
129.07
125.37
125.00
116.89
77.55
77.23
76.91
64.25
59.39
33.21
32.19
18.39
18.33
O
N
NH
O
32
Current Data Parameters
NAME hlim-A191-A01D-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080211
Time 13.50
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 68
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2580.3
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 16.50 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127498 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.125
8.110
7.256
7.240
7.219
7.103
7.101
7.088
7.086
7.073
7.071
5.926
4.792
4.772
4.752
4.058
4.055
3.590
3.570
3.558
3.538
3.392
3.372
3.359
3.339
2.739
2.734
2.725
2.720
2.711
2.706
1.540
1.238
1.169
1.155
1.146
1.129
1.114
0.989
0.975
0.902
O
N
NH
O
33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05
4.35
1.14
0.99
1.00
1.04
1.18
1.14
1.06
3.64
3.15
Current Data Parameters
NAME hlim-A191-A01U
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060211
Time 11.31
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 512.7
DW 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz
F2 - Processing parameters
SI 32768
SF 500.0200219 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


141.35
129.63
128.94
128.38
125.14
136.37
77.55
77.13
77.33
76.91
60.86
60.15
31.08
28.05
19.61
16.44
O
N
NH
O
33
Current Data Parameters
NAME hlim-A191-A01D-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080211
Time 14.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 626
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 120.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127469 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

ORTEP Diagram of Tetracyclic Adduct 14 (see CIF for details)