Supporting Information

Catalytic Asymmetric Hetero-Diels-Alder Reactions of Enones with Isatins to Access Functionalized Spirooxindole Tetrahydropyrans: Scope, Derivatization, and Discovery of Bioactives

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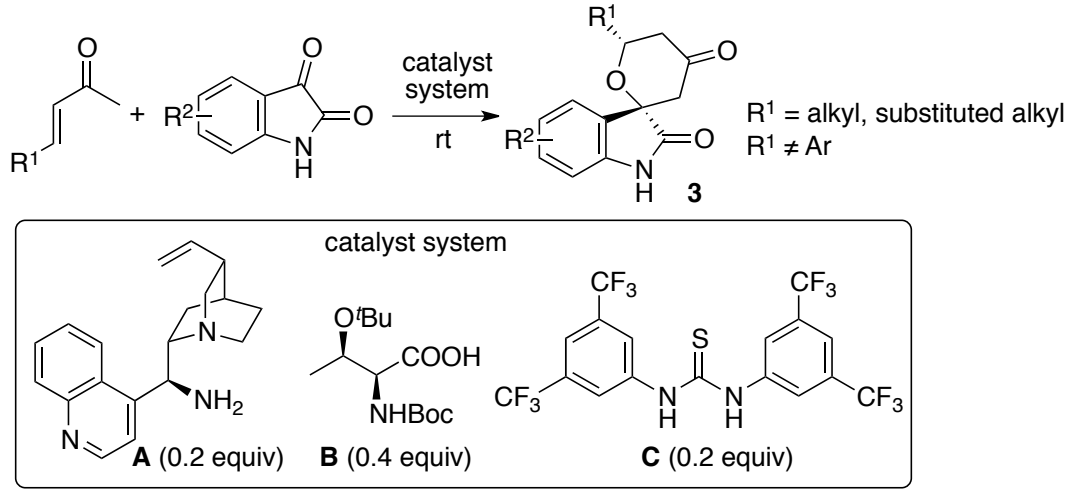
General

For thin layer chromatography (TLC), Merck silica gel 60 F254 aluminum sheets were used. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 400. Proton chemical shifts are given in relative to the residual proton signals of the deuterated solvent in CD_3OD (δ 3.31 ppm). Proton chemical shifts are reported in ppm downfield from tetramethylsilane or from the residual solvent as internal standard in $CDCl_3$ (δ 7.26 ppm), in CD_3OD (δ 3.31 ppm), and in $(CD_3)_2SO$ (δ 2.50 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.0 ppm), in CD_3OD (δ 49.0 ppm), and in $(CD_3)_2SO$ (δ 39.5 ppm). High-resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap ESI ion trap mass spectrometer. IR spectra were recorded on a Jasco FT IR-4100 spectrometer. Optical rotations were measured on a Jasco P2200 polarimeter.

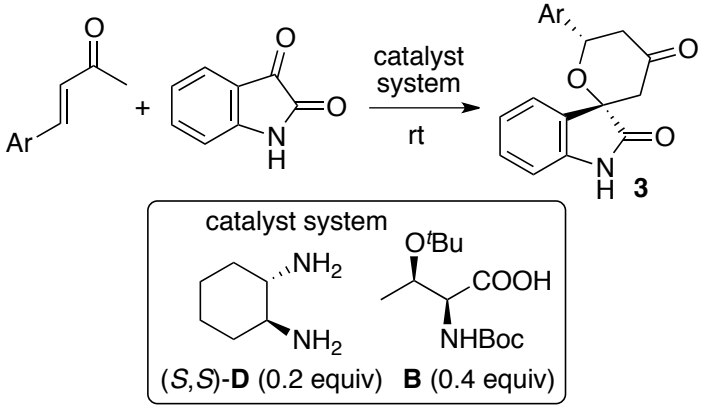
1. Catalytic Enantioselective Hetero-Diels-Alder Reactions

General Procedure for the Catalytic Enantioselective Hetero-Diels-Alder Reactions Using Catalyst System Composed of A, B, and C (Table 1 entry 5 and Charts 1 and 2)



Procedure for the catalytic enantioselective hetero-Diels-Alder Reactions using catalyst system composed of **A**, **B**, and **C** was reported in our recent communication.[S1] To a solution of amine **A** (0.04 mmol, 11.8 mg) and acid **B** (0.08 mmol, 22.0 mg) in toluene (super dehydrated, 0.4 mL) were added thiourea **C** (0.04 mmol, 20.0 mg), enone (1.0 mmol), and isatin (0.2 mmol) at room temperature (24 °C), and the resulting mixture (initially suspension) was stirred at the same temperature until isatin was consumed (monitored by TLC). The mixture was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1 or hexane/acetone = 3:1) to give product **3**. The major diastereomer was separated from the minor diastereomer. The minor diastereomer (if existed) was obtained with the major diastereomer. The dr values were determined by ^{1}H NMR analysis before purification. Synthesis of **3ga** in Chart 2 was reported in ref. S2. Reaction products **3aa**, **3ab**, **3ac**, **3ad**, **3ae**, **3af**, **3ba**, **3ca**, **3da**, **3ea**, **3fa**, **3ga**, **3ha**, and **3ia** shown in Charts 1 and 2 were reported in ref. S1. Crystallized **3aa** was reported in refs S1 and S2. Determination of the absolute stereochemistry of **3aa** was reported in ref. S1.

General Procedure for the Catalytic Enantioselective Hetero-Diels-Alder Reactions Using Catalyst System Composed of D and B (Scheme 4 and Chart 3)

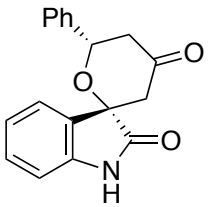


To a solution of amine (*S*,*S*)-**D** (0.02 mmol, 2.28 mg) and acid **B** (0.04 mmol, 11.0 mg) in CH_2Cl_2 (super dehydrated, 0.4 mL) were added enone (4-arylbut-3-ene-2-one) (0.5 mmol), and isatin (0.1 mmol) at room temperature (24 °C), and the mixture (initially suspension) was stirred

at the same temperature until isatin was consumed (monitored by TLC). The mixture was purified by silica gel flash column chromatography (hexane/EtOAc) to give product **3**. The diastereomers were separated each other by the column purification. The dr values were determined by ^{1}H NMR analysis before purification. Relative and absolute stereochemistries were assigned by analogy.

For the reactions of 4-arylbut-3-ene-2-ones, the initially formed major diastereomer decreased and the initially formed minor diastereomer become the major diastereomer under prolonged reaction time.[S2] The major diastereomers of **3ja**, **3ka**, and **3la** described below are initially formed major diastereomers.

Product 3ja



Product **3ja** was synthesized by the reaction of enone (1.0 mmol) and isatin (0.2 mmol) in the presence of (*S*,*S*)-**D** (0.04 mmol) and acid **B** (0.08 mmol) in CH_2Cl_2 (super dehydrated, 0.4 mL).[S1]

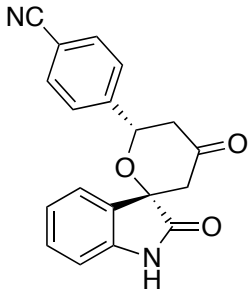
Product 3ja (major diastereomer)

Rf 0.23 (hexane/EtOAc = 2:1). See ref. S1 Supporting Information.

Product 3ja (minor diastereomer)

Rf 0.30 (hexane/EtOAc = 2:1). See ref. S1 Supporting Information.

Product 3ka (major diastereomer)

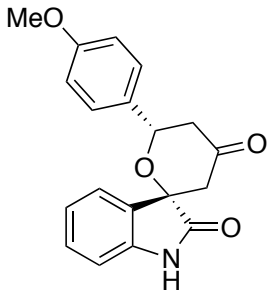


16 h, 12.0 mg (38%). Rf 0.42 (hexane/EtOAc = 1:1). Pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (brs, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.33 (dt, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.07 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.41 (dd, *J* = 11.2 Hz, 3.6 Hz, 1H), 3.19 (d, *J* = 14.8 Hz, 1H), 2.94 (dd, *J* = 14.8 Hz, 11.2 Hz, 1H), 2.87 (ddd, *J* = 14.8 Hz, 3.6 Hz, 1.2 Hz, 1H), 2.60 (dd, *J* = 14.8 Hz, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 174.7, 144.9, 140.5, 132.4, 130.8, 127.6, 126.4, 125.2, 123.0, 118.4, 112.4, 111.2, 78.9, 73.9, 48.9, 44.9. ESI-HRMS: calcd for $C_{19}H_{15}N_2O_3$ ($[M+H]^+$) 319.1083, found 319.1083. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 50/50, 0.6 mL/min, λ = 254 nm): t_R (major diastereomer, major enantiomer) = 9.3 min, t_R (major diastereomer, minor enantiomer) = 12.3 min, t_R (minor diastereomers) = 8.3 min and 12.3 min.

Product 3ka (minor diastereomer)

4.0 mg (13%). Rf 0.52 (hexane/EtOAc = 1:1). Pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$-CD_3OD): δ7.52 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.16 (dt, *J* =1.2 Hz, 7.6 Hz, 1H), 6.97 (dt, *J* = 1.2 Hz, 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.87 (dd, *J* = 11.2 Hz, 3.2 Hz, 1H), 2.83 (d, *J* = 14.8 Hz, 1H), 2.70 (ddd, *J* = 14.8 Hz, 3.2 Hz, 2.0 Hz, 1H), 2.50 (dd, *J* = 14.8 Hz, 11.2 Hz, 1H), 2.41 (dd, *J* = 14.8 Hz, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$-CD_3OD): δ 203.3, 176.1, 145.8, 140.9, 132.2, 130.5, 128.3, 126.3, 123.9, 122.9, 118.2, 111.2, 110.4, 78.3, 72.1, 47.8, 45.1. ESI-HRMS: calcd for $C_{19}H_{15}N_2O_3$ ($[M+H]^+$) 319.1083, found 319.1083.

Product 3la (major diastereomer)



16 h, 13.0 mg (40%). Rf 0.50 (hexane/EtOAc = 1:1). Pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (brs, 1H), 7.36-7.29 (m, 4H), 7.06 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.92 (dd, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.90-6.84 (m, 2H), 5.29 (dd, *J* = 11.6 Hz, 2.4 Hz, 1H), 3.77 (s, 3H), 3.19 (d, *J* = 14.8 Hz, 1H), 3.04 (dd, *J* = 14.8 Hz, 11.6 Hz, 1H), 2.80 (ddd, *J* = 14.8 Hz, 2.4 Hz, 1.6 Hz, 1H), 2.56 (dd, *J* = 14.8 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.8, 174.5, 159.6, 140.4, 131.9, 130.5, 128.2, 127.5, 125.4, 122.8, 114.0, 110.8, 78.7, 74.8, 55.3, 49.5, 45.1. ESI-HRMS: calcd for $C_{19}H_{18}NO_4$ ($[M+H]^+$) 324.1230, found 324.1222. HPLC (Daicel Chiralpak IA, Hexane/*i*-PrOH = 50/50, 0.6 mL/min, λ = 254 nm): *t*R (major diastereomer, major enantiomer) = 14.0 min, *t*R (major diastereomer, minor enantiomer) = 18.1 min, t_R (minor diastereomers) = 11.8 min and 13.2 min.

Product 3la (minor diastereomer)

7.2 mg (22%). Rf 0.50 (hexane/EtOAc = 1: 1). Pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (brs, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.89 (dd, *J* = 10.4 Hz, 3.6 Hz,1H), 3.78 (s, 3H), 2.92 (d, *J* = 14.8 Hz, 1H), 2.81 (ddd, *J* = 14.8 Hz, 3.6 Hz, 1.6 Hz, 1H), 2.75 (dd, *J* = 14.8 Hz, 10.4 Hz, 1H), 2.59 (dd, *J* = 14.8 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.6, 175.9, 159.5, 1401, 132.6, 130.5, 129.0, 127.5, 124.4, 123.4, 114.0, 110.2, 78.1, 73.3, 55.3, 48.7, 45.5. ESI-HRMS: calcd for $C_{19}H_{18}NO_4$ ($[M+H]^+$) 324.1230, found 324.1220.

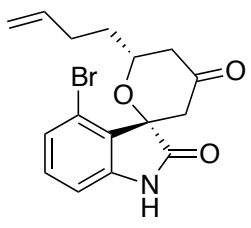
2. Synthesis of Racemic Hetero-Diels-Alder Reaction Products

General Procedure for the Synthesis of Racemic Products (Scheme 5)

To a solution of *cis*/(±)-*trans*-mixture of cyclohexane-1,2-diamine (0.08 mmol) and acid *N*-Boc-(±)-proline (0.16 mmol) in toluene (0.8 mL) were added enone (1.2 mmol) and isatin or substituted isatin (0.4 mmol) at room temperature (24 °C), and the resulting mixture was stirred at the same temperature until isatin was consumed (monitored by TLC). The mixture was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1 or hexane/acetone = 3:1) to give the desired product **3**.

Product 3fc

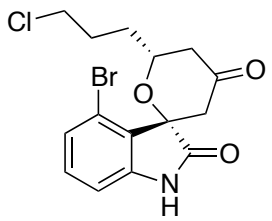
4-Bromoisatin 0.2 mmol-scale reaction, 24 h, 54.3 mg (78%, dr >20:1). Pale yellow solid. ^{1}H



NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.22 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.15 (dd, *J* = 8.0 Hz, 7.6 Hz, 1H), 6.84 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 5.85-5.79 (m, 1H), 5.03 (dq, *J* = 17.2 Hz, 0.8 Hz, 1H), 4.98-4.94 (m, 1H), 4.80-4.73 (m, 1H), 3.66 (d, *J* = 16.8 Hz, 1H), 2.98 (dd, *J* = 18.4 Hz, 12.4 Hz, 1H), 2.57 (dd, *J* = 18.4, 2.0 Hz, 1H), 2.37 (d, *J* = 16.8 Hz, 1H), 2.26-2.18 (m, 2H), 1.81-1.77 (m, 1H), 1.71-1.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 177.8, 142.3, 137.8, 131.6, 128.0,

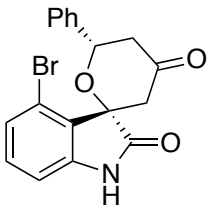
127.3, 119.6, 115.1, 110.0, 79.0, 72.0, 45.8, 40.7, 34.8, 29.1. ESI-HRMS: calcd for $C_{16}H_{17}BrNO_3$ ($[M+H]^+$) 350.0392, found 350.0395.

Product 3ic



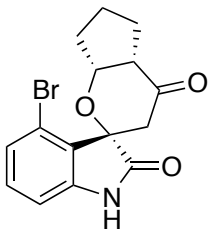
22 h, 135.1 mg (91%, dr >20:1). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.22 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.15 (dd, *J* = 8.0 Hz, 7.6 Hz, 1H), 6.85 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 4.82-4.75 (m, 1H), 3.67 (d, *J* = 16.8 Hz, 1H), 3.63-3.52 (m, 2H), 3.00 (dd, *J* = 18.4 Hz, 12.4 Hz, 1H), 2.57 (dd, *J* = 18.4 Hz, 2.0 Hz, 1H), 2.37 (d, *J* = 16.8 Hz, 1H), 2.09-1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.4, 177.6, 142.2, 131.6, 127.9, 127.3, 119.5, 110.0, 79.0, 71.9, 45.8, 44.9, 40.7, 32.9, 28.2. ESI-HRMS: calcd for $C_{15}H_{16}BrClNO_3$ ($[M+H]^+$) 371.9997, found 372.0006.

Product 3jc



Reaction in CH_2Cl_2, 9 h, 56.8 mg (38%, dr >20:1). Pale yellow solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.41-7.32 (m, 5H), 7.22-7.21 (m, 2H), 6.87 (dd, *J* = 6.0 Hz, 2.8 Hz, 1H), 5.81 (dd, *J* = 12.0 Hz, 2.0 Hz, 1H), 3.82 (d, *J* = 16.8 Hz, 1H), 3.03 (dd, *J* = 18.0 Hz, 12.0 Hz, 1H), 2.72 (dd, *J* = 18.0 Hz, 2.0 Hz, 1H), 2.43 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 204.8, 176.8, 143.8, 140.1, 132.0, 128.4, 128.1, 127.6, 126.5, 125.8, 118.7, 109.8, 78.9, 73.7, 46.8, 40.2. ESI-HRMS: calcd for $C_{18}H_{15}BrNO_3$ ($[M+H]^+$) 372.0230, found 372.0236.

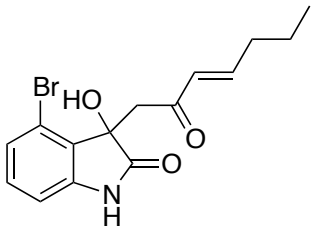
Product 3mc



4-Bromoisatin 0.2 mmol-scale reaction, 95 h, 36%, dr >8:1. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (brs, 1H), 7.22 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 7.17-7.13 (m, 1H), 6.85 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 5.32 (t, *J* = 4.4 Hz, 1H), 3.46 (d, *J* = 15.6 Hz, 1H), 2.82 (m, 1H), 2.49 (d, *J* = 15.6 Hz, 1H), 2.39-2.31 (m, 1H), 2.19-2.10 (m, 1H), 2.00-1.80 (m, 3H), 1.73-1.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 176.5, 142.8, 131.6, 128.3, 127.3, 119.7, 110.0, 80.5, 80.0, 54.2, 40.4, 34.2, 27.7, 23.0. ESI-HRMS: calcd for $C_{15}H_{15}BrNO_3$ ($[M+H]^+$) 336.0230, found 336.0226.

Aldol products **4** and **4c** were obtained with the corresponding hDA reaction products in the hDA reactions, and were also synthesized by the reported method.[S1,S3] Aldol **4** was reported in ref. S1.

Aldol 4c



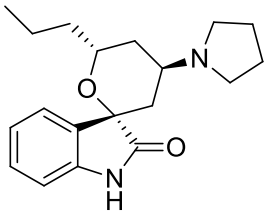
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 7.07-7.01 (m, 2H), 6.86-6.80 (m, 2H), 5.96 (dt, *J* = 16.0, 1.2 Hz, 1H), 4.66 (s, 1H), 4.04 (d, *J* = 16.8 Hz, 1H), 3.34 (d, *J* = 16.8 Hz, 1H), 2.18-2.12 (m, 2H), 1.50-1.40 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 178.8, 149.7, 143.7, 131.3, 130.0, 127.9, 126.8, 119.0, 110.1, 75.9, 44.3, 34.6, 21.2, 13.7. ESI-HRMS: calcd for $C_{15}H_{17}BrNO_3$ ($[M+H]^+$) 338.0386, found 338.0397.

3. Transformations of the Hetero-Diels-Alder Products

Compound 8

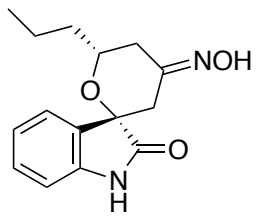
To a solution of compound (±)-**3aa** (100.0 mg, 0.39 mmol, dr >20:1) in CH_2Cl_2 (8.0 mL) were added pyrrolidine (94.4 μL, 1.16 mmol) and $NaBH(OAc)_3$ (243.7 mg, 1.16 mmol) at room temperature (24 °C), and the mixture was stirred at the same temperature for 36 h (consumption of the starting material was analyzed by TLC). To the mixture was added aqueous NaOH (1 N, 2.0 mL), and the mixture was extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel flash column chromatography (hexane/EtOAc = 1:1) gave **8** (92.1 mg, 76%).



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-7.85 (m, 2H), 7.22 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.37-4.19 (m, 1H), 3.13-2.27 (m, 5H), 2.25-2.13 (m, 1H), 2.13-1.64 (m, 7H), 1.64-1.48 (m, 1H), 1.48-1.13 (m, 3H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 140.2, 131.3, 129.1, 126.9, 122.6, 110.0, 77.2, 68.9, 56.6, 52.0, 38.1, 34.8, 33.1, 23.5, 18.6, 13.9. ESI-HRMS: calcd for $C_{19}H_{27}N_2O_2$ ($[M+H]^+$) 315.2067, found 315.2048.

Compound 9

A mixture of (±)-**3aa** (51.8 mg, 0.2 mmol, dr >20:1), K_2CO_3 (41.4 mg, 0.3 mmol), and hydroxylamine hydrochloride (41.9 mg, 0.6 mmol) in CH_2Cl_2 (2.0 mL) was stirred at room temperature (24°C) for 2 h. The mixture was diluted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel flash column chromatography (hexane/EtOAc = 2:1) to give **9** (32.0 mg, 58%, E/Z mixture).

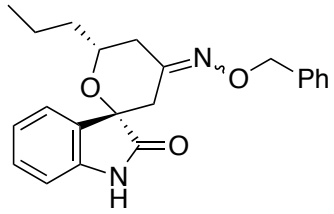


Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H x 1.0/2.7), 8.30 (s, 1H x 1.7/2.7), 7.37 (d, *J* = 7.6 Hz, 1H x 1.7/2.7), 7.30-7.26 (m, 1H + 1H x 1.0/2.7), 7.03-6.98 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.20-4.00 (m, 1H), 3.48 (dd, *J* = 14.0 Hz, 1.2 Hz, 1H x 1.0/1.7), 3.33 (dd, *J* = 14.0 Hz, 1.6 Hz, 1H x 1.7/2.7), 2.91 (d, *J* = 14.0 Hz, 1H x 1.0/2.7), 2.641-2.55 (m, 2H x 1.7/2.7), 2.11-2.04 (m, 1H x 1.0/2.7), 1.75-1.60 (m, 1H), 1.60-1.55 (m, 1H), 1.55-1.20 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H x 1.0/2.7), 0.82 (t, *J* = 7.2 Hz, 3H x 1.7/2.7). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 175.6, 154.4, 154.2, 140.4, 140.3, 130.0, 129.9, 129.1, 128.7, 126.1, 125.4, 122.7, 122.6, 110.7, 78.1, 77.2, 72.9, 71.2, 38.3, 38.1, 37.2, 36.1, 30.8, 29.6, 18.4, 18.3, 13.8. ESI-HRMS: calcd for $C_{15}H_{19}N_2O_3$ ($[M+H]^+$) 275.1390, found 275.1394.

Compound 10

A mixture of (±)-**3aa** (59.0 mg, 0.23 mmol) and *O*-benzylhydroxylamine (26.8 μL, 0.23 mmol) in MeOH (2.3 mL) was stirred under reflux for 2 h. The mixture was concentrated and purified

by flash column chromatography (hexane/EtOAc = 2:1) to give **10** (79.6 mg, 95 %, *E*/*Z* mixture).

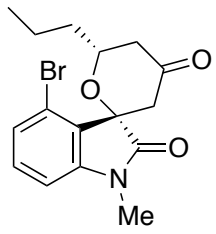


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76-8.63 (m, 1H), 7.40-6.75 (m, 9H), 5.07 (s, 2H x 1.3/2.3), 4.97 (s, 2H x 1/2.3), 4.09-3.98 (m, 1H x 1/2.3), 3.97-3.84 (m, 1H x 1.3/2.3), 3.45-3.33 (m, 1H x 1.3/2.3), 3.29-3.18 (m, 1H x 1/2.3), 2.80 (d, *J* = 13.9 Hz, 1H x 1.3/2.3), 2.61-2.45 (m, 2H x 1/2.3), 2.33-2.20 (m, 1H), 1.99 (dd, *J* = 14.6 Hz, 11.7 Hz, 1H x 1.3/2.3), 1.65-1.51 (m, 1H), 1.50-1.36 (m, 1H), 1.36-1.09 (m, 3H), 0.80-0.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 153.6, 153.4, 140.44, 140.42, 138.2, 137.9, 129.8, 129.7, 129.1, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 126.1, 125.4, 122.5, 122.4, 110.74, 110.68, 78.2, 77.2, 75.7, 75.5, 72.9, 71.2, 38.2, 38.1, 37.2, 36.2, 31.7, 30.5, 18.3, 18.2, 13.78, 13.77. ESI-HRMS: calcd for $C_{22}H_{25}N_2O_3$ ($[M+H]^+$) 365.1860, found 365.1849.

(2'*S*,6'*R*)-10. A mixture of (2'*S*,6'*R*)-**3aa** (36.8 mg, 0.14 mmol, single diastereomer, >99.5% ee) and *O*-benzylhydroxylamine (16.7 μL, 0.14 mmol) in MeOH (1.4 mL) was stirred at room temperature (24 °C) for 48 h. The mixture was concentrated and purified by flash column chromatography (hexane/EtOAc = 2:1) to give **10** (49.0 mg, 95 %, >99.5% ee, *E*/*Z* mixture). HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 85/15, 0.5 mL/min, λ = 254 nm): t_R (major enantiomers, (2'*S*,6'*R*)-**10**, *E*/*Z* mixture) = 51.6 min and 70.7 min, t_R (minor enantiomers, (2'*R*,6'*S*)-**10**, *E*/*Z* mixture) = 25.6 min and 32.0 min.

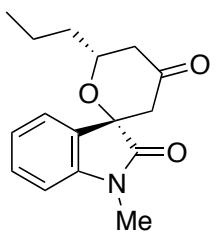
Compound 13

To a mixture of (±)-**3ac** (247.5 mg, 0.73 mmol, dr > 20:1) and K_2CO_3 (121.6 mg, 0.88 mmol) in DMSO (4.0 mL) was added MeI (162.0 μL, 1.46 mmol) at room temperature (24 °C), and the mixture was stirred at the same temperature for 4 h. To the mixture was added water, and the mixture was extracted with EtOAc (x3). Organic layers were combined, washed with water and brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel flash column chromatography (hexane/EtOAc = 2:1) to give **13** (198.0 mg, 77%).



Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.18 (m, 2H), 6.77 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 4.77-4.71 (m, 1H), 3.67 (d, *J* = 16.8 Hz, 1H), 3.13 (s, 3H), 3.02 (dd, *J* = 18.4 Hz, 12.0 Hz, 1H), 2.55 (dd, *J* = 18.4 Hz, 2.0 Hz, 1H), 2.27 (d, *J* = 16.8 Hz, 1H), 1.69-1.40 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 175.7, 145.2, 131.5, 127.6, 127.2, 119.5, 107.8, 78.6, 72.4, 45.8, 40.7, 37.8, 26.4, 18.2, 14.1. ESI-HRMS: calcd for $C_{16}H_{19}BrNO_3$ ($[M+H]^+$) 352.0543, found 352.0551.

Compound 11



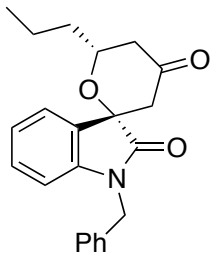
Compound **11** was synthesized from (±)-**3aa** (1.16 mmol) by the method used for the synthesis of compound **13**.

243.5 mg (77%). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dt, *J* = 1.2 Hz, 7.8 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.04 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.34-4.29 (m, 1H), 3.23 (s, 3H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.70-2.58 (m, 2H), 2.36 (dd, *J* = 14.4 Hz, 1.2 Hz, 1H),

1.77-1.67 (m, 1H), 1.59-1.50 (m, 1H), 1.42-1.26 (m, 2H), 0.83 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 173.3, 143.4, 130.3, 128.0, 125.0, 122.7, 109.0, 78.4, 73.1, 47.6, 45.6, 38.3, 26.5, 18.2, 13.8. ESI-HRMS: calcd for $C_{16}H_{20}NO_3$ ($[M+H]^+$) 274.1443, found 274.1444.

Compound 12

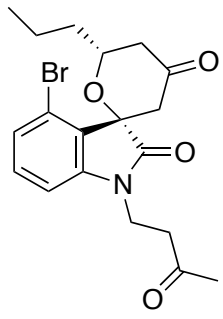
To a mixture of (±)-**3aa** (100.0 mg, 0.385 mmol, dr >20:1) and K_2CO_3(79.8 mg, 0.58 mmol,) in DMF (3.0 mL) was added benzyl chloride (66.5 μL, 0.58 mmol) at room temperature (24 °C), and the resulting mixture was stirred at the same temperature for 16 h. To the mixture was added water, and the mixture was extracted with EtOAc (x3). Organic layers were combined, washed with water and brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel flash column chromatography (hexane/EtOAc = 3:1) to give **12** (94.1 mg, 70 %).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.06 (m, 7H), 6.91 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.88 (d, J = 15.8 Hz, 1H), 4.79 (d, J = 15.8 Hz, 1H), 4.31-4.21 (m, 1H), 3.08 (d, J = 14.4 Hz, 1H), 2.66-2.49 (m, 2H), 2.35 (dd, J = 14.4, 1.2 Hz, 1H), 1.73-1.60 (m, 1H), 1.55-1.40 (m, 1H), 1.40-1.11 (m, 2H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5, 173.4, 142.4, 135.0, 130.1, 128.8, 128.0, 127.7, 127.0, 125.0, 122.6, 110.0, 78.4, 73.0, 47.6, 45.5, 43.8, 38.2, 18.2, 13.7. ESI-HRMS: calcd for $C_{22}H_{24}NO_3$ ($[M+H]^+$) 350.1751, found 350.1732.

Compound 14

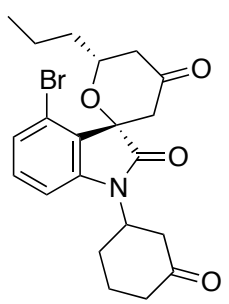
To a mixture of (±)-**3ac** (16.9 mg, 0.05 mmol, dr >20:1), methyl vinyl ketone (20.8 μL, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added PPh_3 (2.6 mg, 0.01 mmol) at room temperature (24 °C), and the resulting mixture was stirred at the same temperature for 120 h. The mixture was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1) to give **14** (20.0 mg, 98%).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.17 (m, 2H), 6.90 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 4.77-4.71 (m, 1H), 3.87 (dt, J = 3.2 Hz, 6.8 Hz, 2H), 3.66 (d, J = 16.8 Hz, 1H), 2.99 (dd, J = 18.4, 12.4 Hz, 1H), 2.83 (dt, J = 3.2 Hz, 6.8 Hz, 2H), 2.55 (dd, J = 18.0 Hz, 2.0 Hz, 1H), 2.24 (d, J = 16.8 Hz, 1H), 2.17 (s, 3H), 1.70-1.40 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.0, 205.9, 176.0, 144.1, 131.5, 127.6, 127.3, 119.6, 108.3, 78.4, 72.4, 45.8, 40.7, 40.6, 37.7, 35.1, 30.2, 18.2, 14.1. ESI-HRMS: calcd for $C_{19}H_{23}BrNO_4$ ($[M+H]^+$) 408.0805, found 408.0814.

Compound 15

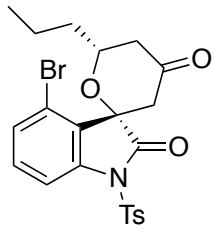
To a mixture of (±)-**3ac** (16.9 mg, 0.05 mmol, dr >20:1), cyclohexenone (97.0 μL, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added DBU (2.6 mg, 0.01 mmol) at room temperature (24 °C), and the resulting mixture was stirred at the same temperature for 22 h. The mixture was purified by silica gel flash column chromatography (hexane/EtOAc = 2:1) to give **15** (12.7 mg, 58%, dr 1:1).



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.17 (m, 2H), 6.85 (dd, *J* = 7.6 Hz, 0.4 Hz, 1H x 1/2), 6.84 (dd, *J* = 7.6 Hz, 0.4 Hz, 1H x 1/2), 4.76-4.73 (m, 1H), 4.13-4.10 (m, 1H), 3.67 (d, *J* = 16.8 Hz, 1H x 1/2), 3.66 (d, *J* = 16.8 Hz, 1H x 1/2), 3.33 (d, *J* = 16.8 Hz, 1H x 1/2), 3.31 (d, *J* = 16.8 Hz, 1H x 1/2), 3.00 (dd, *J* = 18.4 Hz, 2.0 Hz, 1H x 1/2), 2.62-2.32 (m, 5H), 2.24 (d, *J* = 16.8 Hz, 1H x 1/2), 2.23 (d, *J* = 16.8 Hz, 1H x 1/2), 2.19-2.10 (m, 1H), 2.04-1.92 (m, 1H), 1.73-1.25 (m, 5H), 0.941 (t, *J* = 7.2 Hz, 3H x 1/2), 0.936 (t, *J* = 7.2 Hz, 3H x 1/2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 207.4, 205.8, 205.7, 176.2, 176.1, 143.7, 143.6, 131.4, 127.7, 127.4, 120.1, 108.1, 108.0, 78.4, 72.5, 52.0, 51.9, 45.6, 44.0, 43.9, 40.84, 40.78, 40.50, 40.46, 37.7, 31.6, 27.52, 27.46, 22.33, 22.31, 18.2, 14.12, 14.06. ESI-HRMS: calcd for $C_{21}H_{25}BrNO_4$ ($[M+H]^+$) 434.0962, found 434.0962.

Compound 16

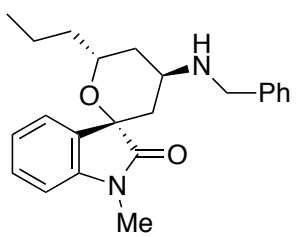
To a mixture of (±)-**3ac** (33.7 mg, 0.1 mmol, dr >20:1), Et_3N (16.7 μL, 0.12 mmol) in CH_2Cl_2 (0.5 mL) was added *p*-toluenesulfonyl chloride (21.0 mg, 0.11 mmol) at room temperature (24 °C), and the resulting mixture was stirred at the same temperature for 41 h. The mixture was purified by silica gel flash column chromatography (hexane/EtOAc = 3:1) to give **16** (10.9 mg, 22%).



Colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.90 (m, 3H), 7.38 (dd, *J* = 8.0 Hz, 0.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 4.70-4.64 (m, 1H), 3.57 (d, *J* = 16.8 Hz, 1H), 2.95 (dd, *J* = 18.4 Hz, 12.4 Hz, 1H), 2.51 (dd, *J* = 18.4 Hz, 2.0 Hz, 1H), 2.44 (s, 3H), 2.16 (d, *J* = 16.8 Hz, 1H), 1.66-1.26 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.4, 174.1, 146.3, 140.3, 134.5, 131.9, 130.1, 129.7, 127.9, 126.7, 119.6, 113.2, 78.5, 72.8, 45.3, 40.8, 37.5, 21.8, 18.0, 14.1. ESI-HRMS: calcd for $C_{22}H_{23}BrNO_5S$ ($[M+H]^+$) 492.0475, found 492.0474.

Compound 17

To a solution of compound **11** (21.0 mg, 0.077 mmol) in CH_2Cl_2 (1.5 mL) were added benzylamine (25.1 μL, 0.23 mmol) and $NaBH(OAc)_3$ (49.1 mg, 0.23 mmol) at room temperature (24 °C), and the mixture was stirred at the same temperature for 24 h (consumption of the starting material was analyzed by TLC). To the mixture was added aqueous NaOH (1 N, 0.5 mL), and the mixture was extracted with CH_2Cl_2 (x 3). Organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel flash column chromatography (hexane/EtOAc = 1:1) gave **17** (20.7 mg, 74 % yield).

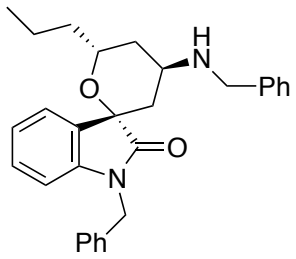


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.2 Hz, 1H), 7.31-7.14 (m, 6H), 6.97 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.32-4.20 (m, 1H), 3.67 (d, *J* = 12.4 Hz, 1H), 3.63 (d, *J* = 12.4 Hz, 1H), 3.47-3.39 (m, 1H), 3.09 (s, 3H), 2.20 (dd, *J* = 14.4, 4.8 Hz, 1H), 1.89-1.79 (m, 1H), 1.73 (m, 1H), 1.64 (m, 1H), 1.54-1.39 (m, 1H), 1.36-1.07 (m, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 143.3, 139.6, 131.2, 129.0, 128.5,

128.3, 127.2, 122.4, 108.0, 77.2, 68.1, 51.8, 49.5, 38.0, 35.8, 33.1, 26.2, 18.4, 13.9. ESI-HRMS: calcd For $C_{23}H_{29}N_2O_2$ ($[M+H]^+$) 365.2224, found 365.2210.

Compound 18

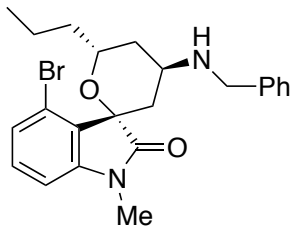
Compound **18** was synthesized from compound **12** (0.26 mmol) by the method used for the synthesis of compound **17**.



24 h, 61.0 mg (54%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.06 (m, 1H), 7.37-7.13 (m, 11H), 7.08 (dt, *J* = 1.2 Hz, 7.6 Hz, 1H), 6.93 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 4.39-4.20 (m, 1H), 3.70 (d, *J* = 12.8 Hz, 1H), 3.67 (d, *J* = 12.8 Hz, 1H), 3.58-3.44 (m, 1H), 2.26 (dd, *J* = 14.4 Hz, 4.8 Hz, 1H), 2.00-1.79 (m, 1H), 1.76-1.64 (m, 1H), 1.60-1.45 (m, 1H), 1.40-1.10 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 142.4, 135.6, 131.2, 129.0, 128.7, 128.6, 128.5, 127.5, 127.4, 127.1, 122.5, 109.1, 77.2, 68.5, 51.6, 49.3, 43.7, 38.0, 35.7, 33.3, 18.6, 13.9. ESI-HRMS: calcd for $C_{29}H_{33}N_2O_2$ ($[M+H)^+$) 441.2542, found 441.2518.

Compound 19

Compound **19** was synthesized from compound **13** (0.29 mmol) by the method used for the synthesis of compound **17**.



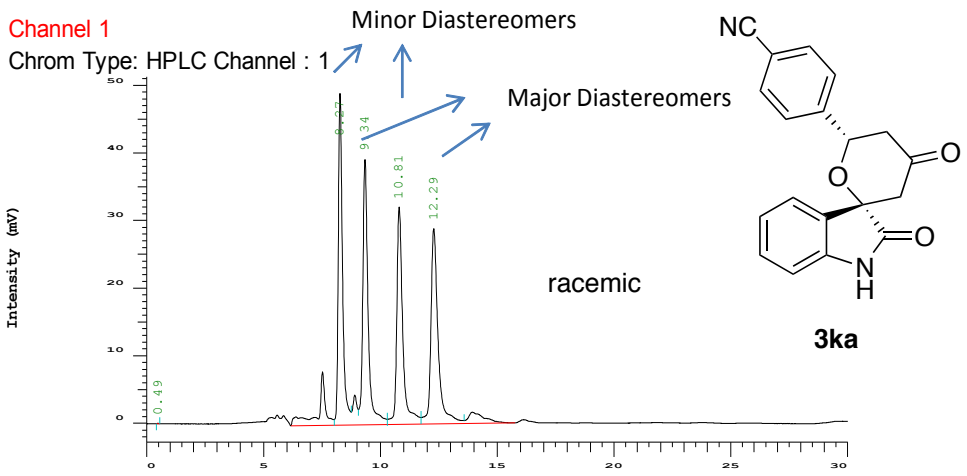
24 h, 91.0 mg (70%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.19 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 4.24-4.11 (m, 1H), 3.89 (d, *J* = 13.6 Hz, 1H), 3.87 (d, *J* = 13.6 Hz, 2H), 3.48-3.33 (m, 1H), 3.12 (s, 3H), 2.91 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 2.30 (m, 1H), 2.11-1.97 (m, 1H), 1.88 (d, *J* = 15.6 Hz, 1H), 1.66-1.30 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 144.6, 138.7, 130.8, 129.7, 128.5, 128.4, 127.6, 127.2, 119.0, 107.5, 79.1, 71.9, 50.3, 48.9, 38.4, 35.9, 29.8, 26.5, 18.4, 14.1. ESI-HRMS: calcd for $C_{23}H_{28}N_2O_2Br$ ($[M+H]^+$) 443.1329, found 443.1320.

4. References

S1. Cui, H.-L.; Tanaka, F. *Chem. Eur. J.* 2013, **19**, 6213.

S2. Cui, H.-L.; Chouthaiwale, P. V.; Yin, F.; Tanaka, F. *Asian J. Org. Chem.* in press, DOI: 10.1002/ajoc.201500412

S3. Guo, Q.; M. Bhanushali, Zhao, C.-G. *Angew. Chem. Int. Ed.* 2010, **49**, 9460.



No.	RT	Area	Area %
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3	9.34	619494	25.522
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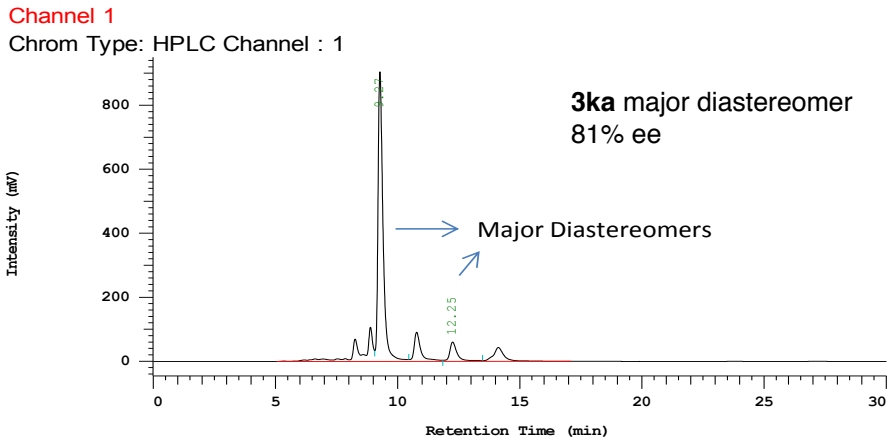
		2427254	100.000



No.	RT	Area	Area %
1	9.27	12821020	90.587
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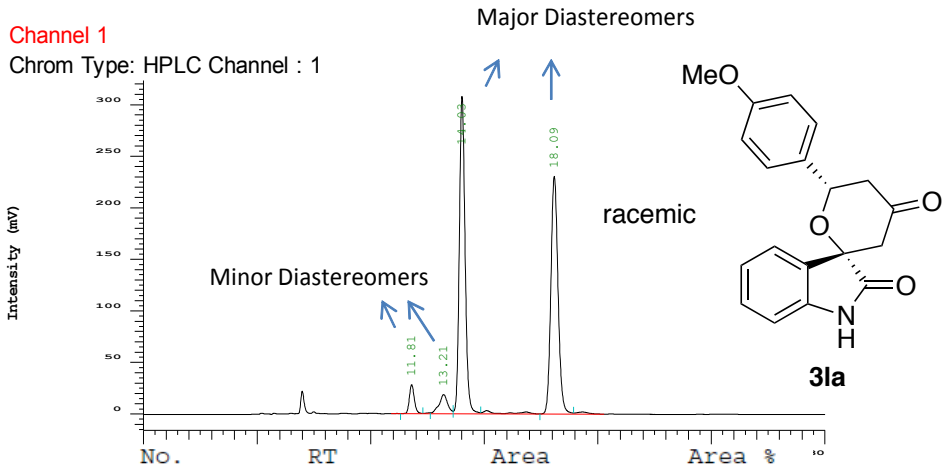
		14153208	100.000

Channel 1

Chrom Type: HPLC Channel : 1



No.	RT	Area	Area %
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Channel 1

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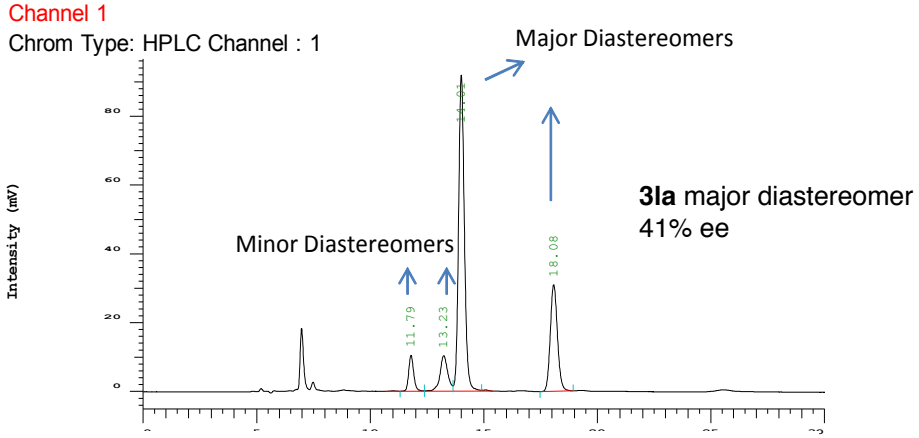

No.	RT	Area	Area %
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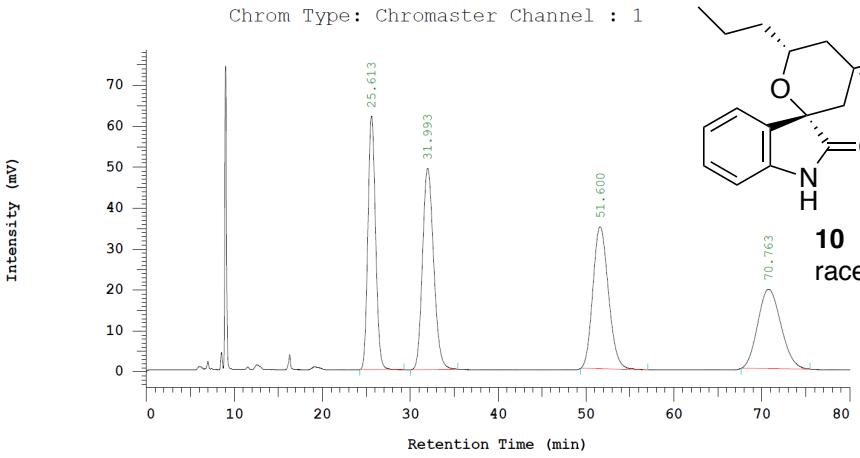
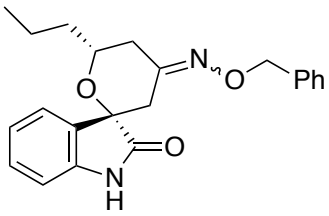
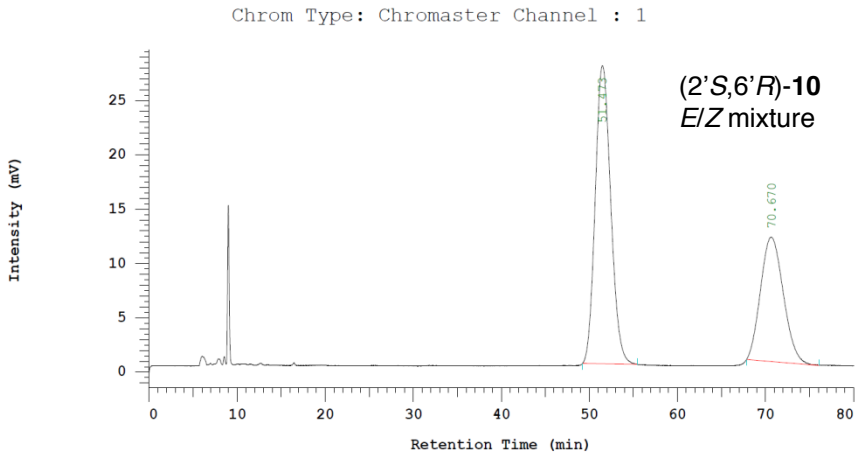




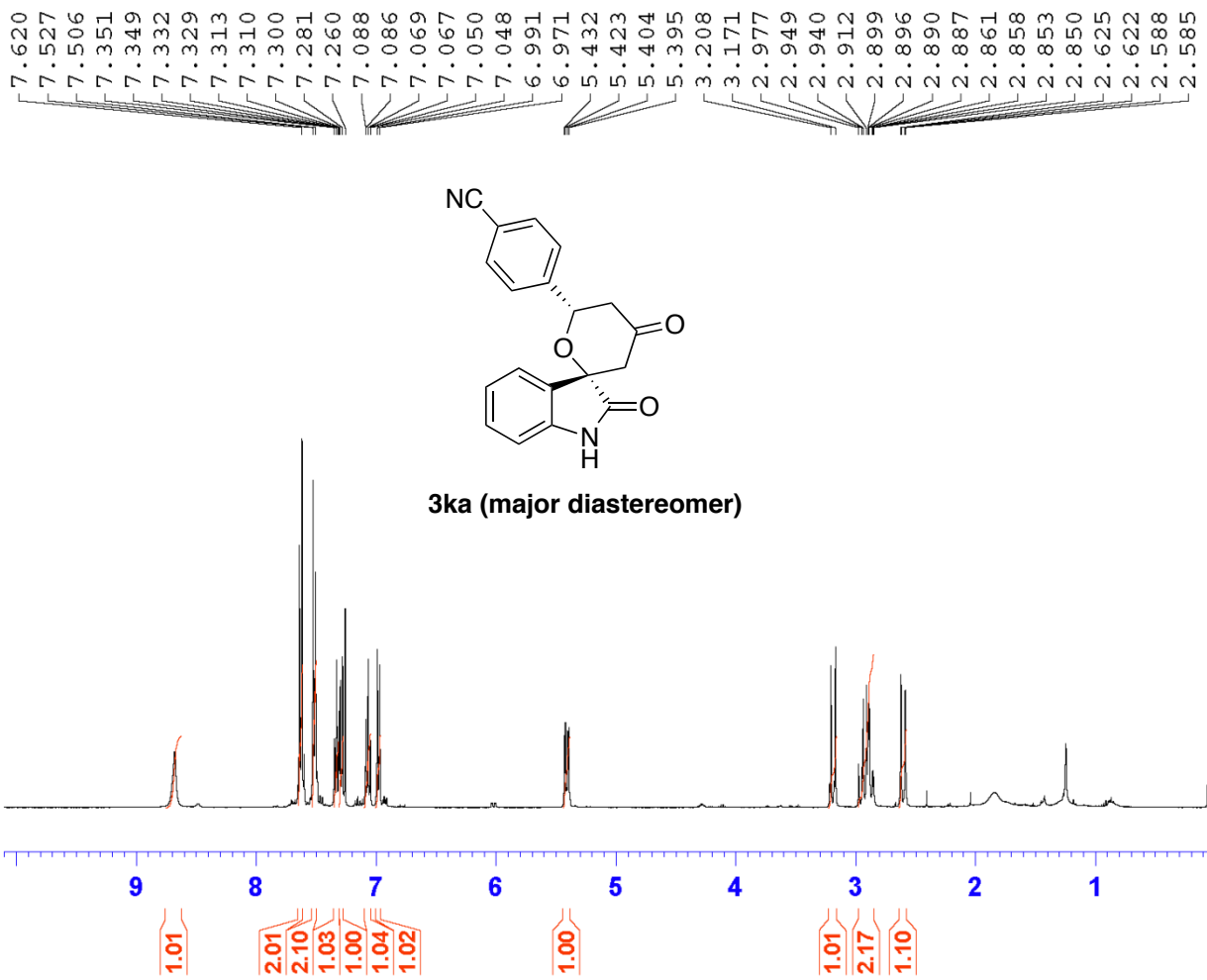
10
racemic, *E*/*Z* mixture

No.	RT	Area	Conc 1
1	25.613	3660102	23.372
2	31.993	4263810	27.227
3	51.600	4214978	26.915
4	70.763	3521407	22.486
		15660297	100.000

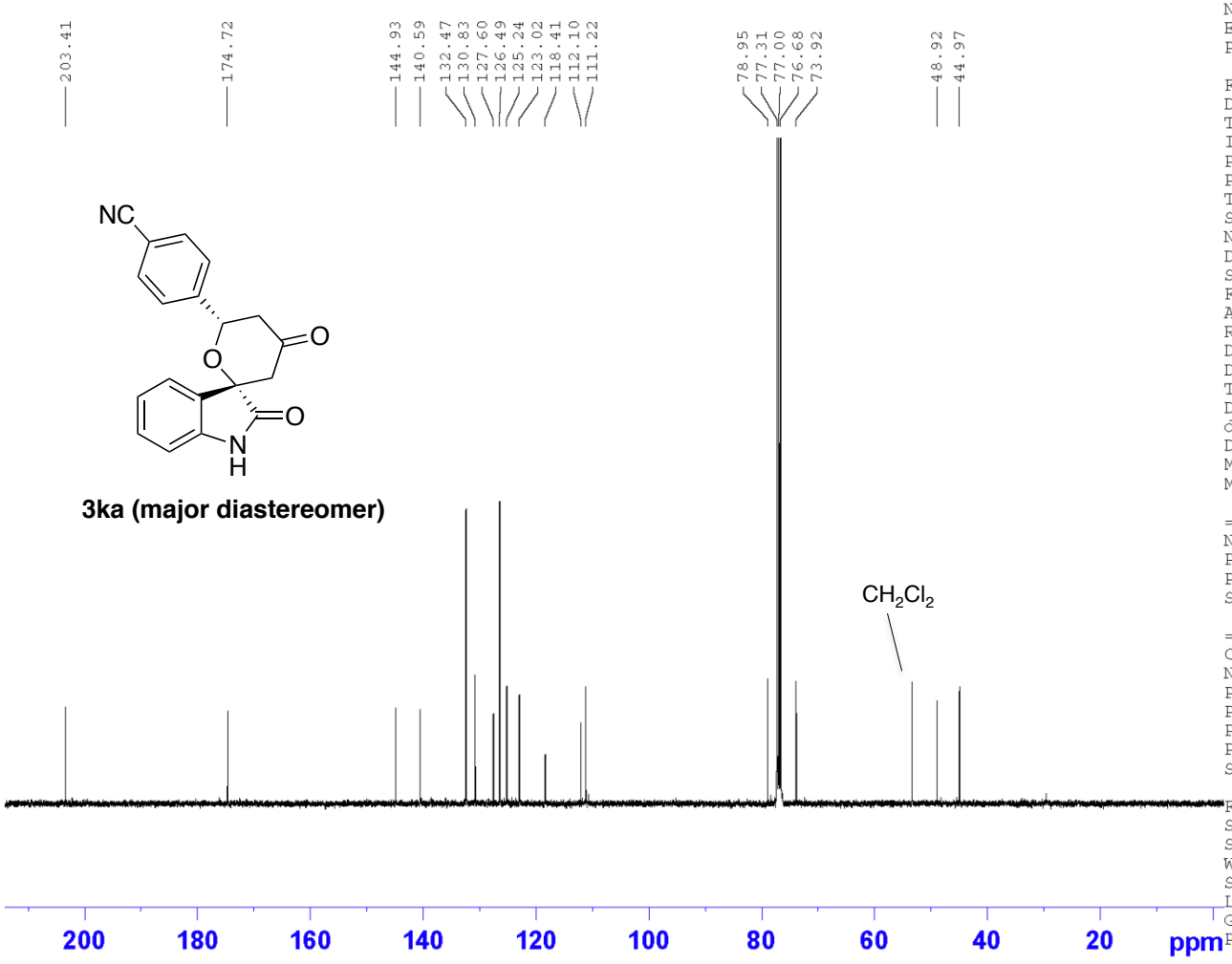


(2'*S*,6'*R*)-**10**
E/*Z* mixture

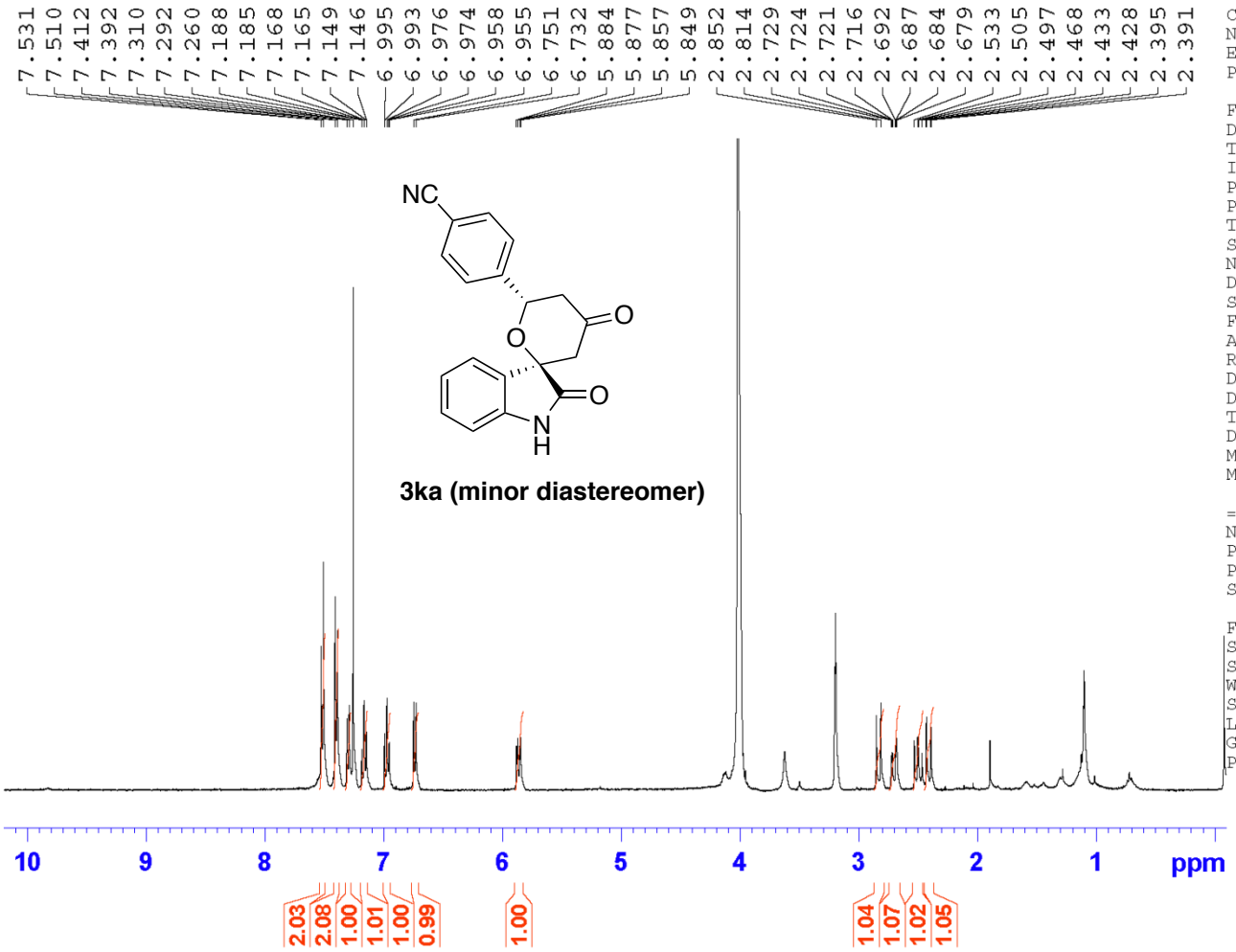
No.	RT	Area	Conc 1
1	51.473	3319960	61.981
2	70.670	2036456	38.019
		5356416	100.000



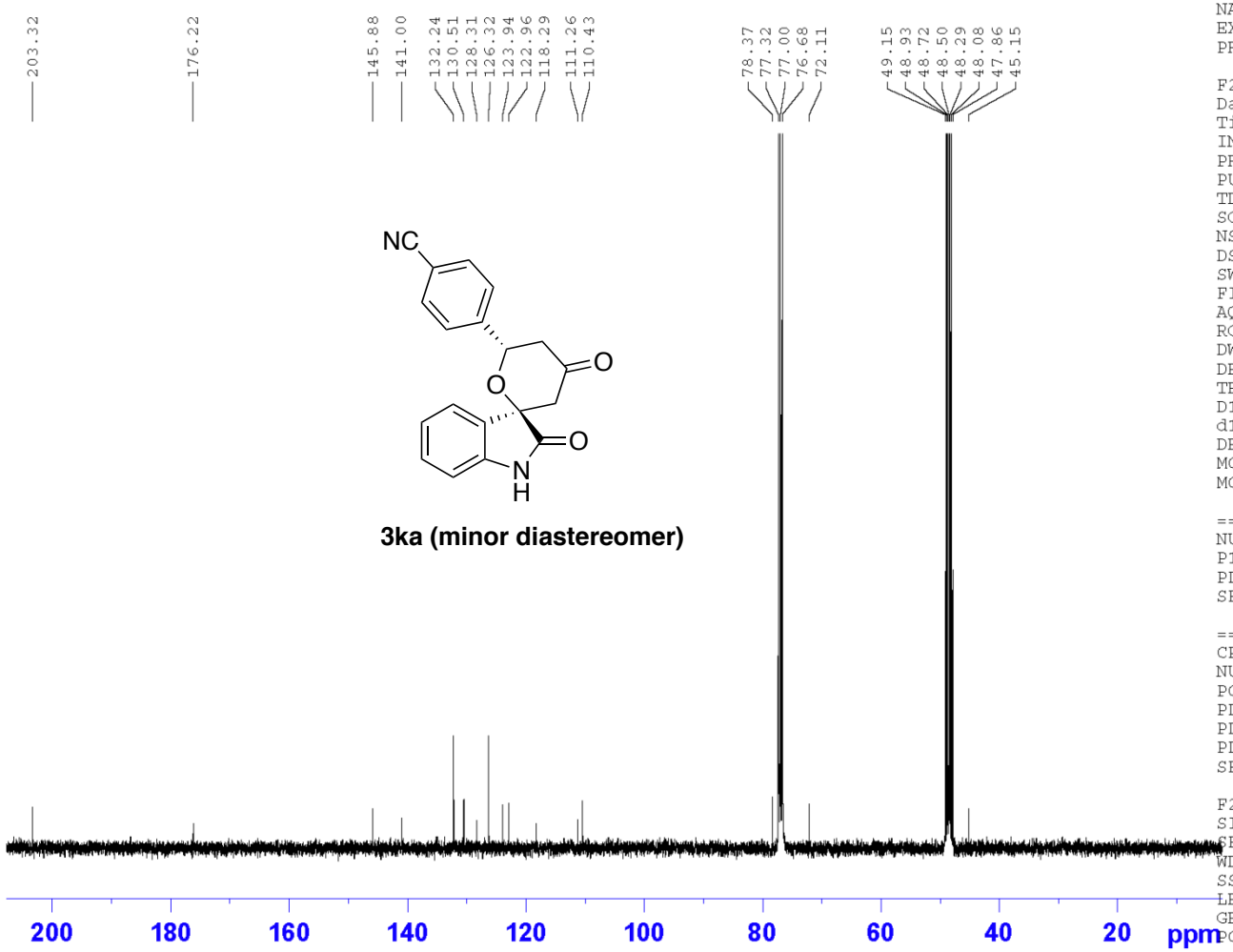

```
Current Data Parameters
NAME          Oct03-2013
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131003
Time               15.42
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715421 sec
RG                 228.1
DW                60.600 usec
DE                 6.00 usec
TE                296.9 K
D1             1.00000000 sec
MCREST    0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300054 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME          Oct04-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131005
Time                5.52
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 12000
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631696 sec
RG                 16384
DW                20.800 usec
DE                 6.00 usec
TE                298.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST    0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.70 dB
PL12               17.10 dB
PL13               17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                 32768
SF           100.6379184 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

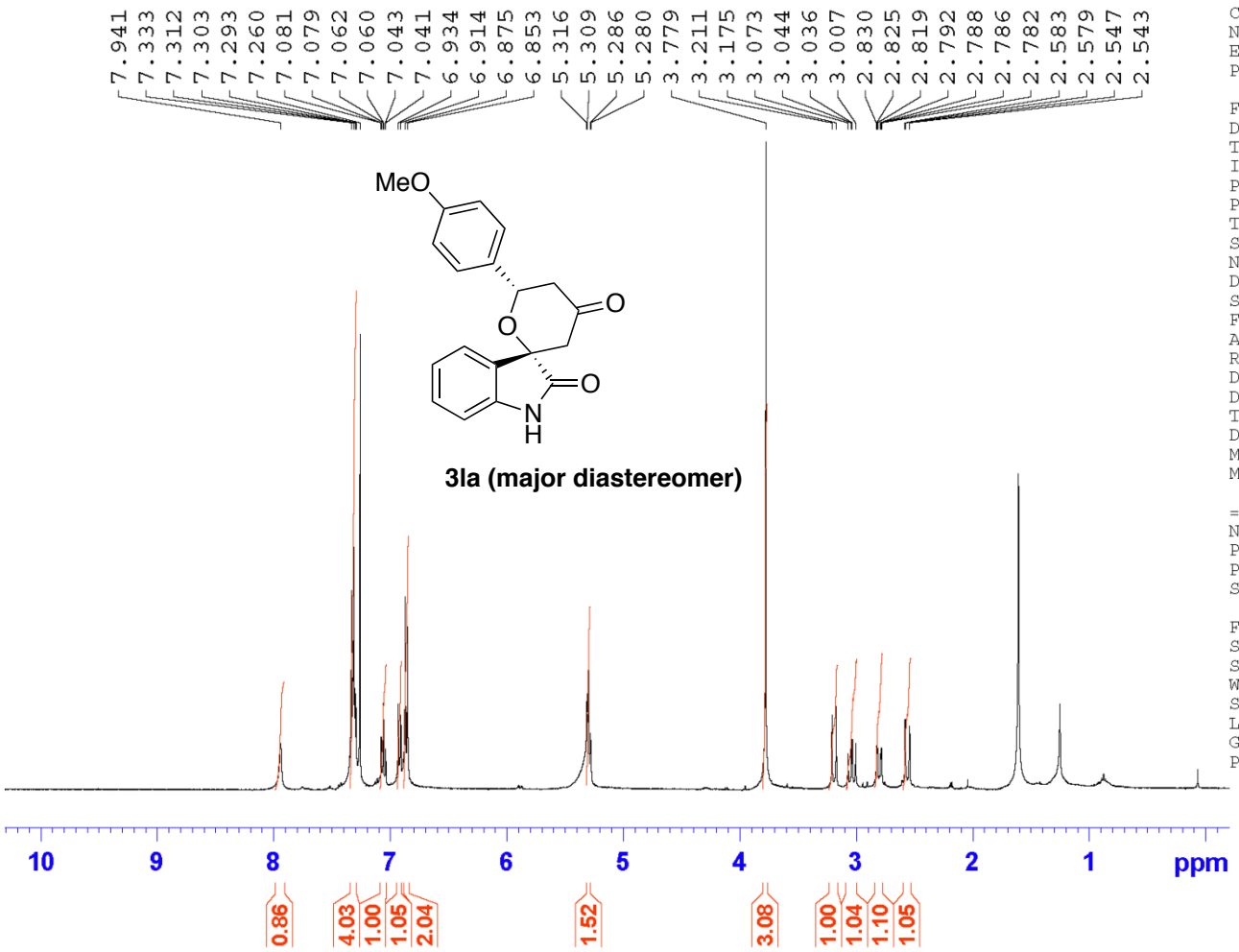



```
Current Data Parameters
NAME          Oct11-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131011
Time               18.18
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715421 sec
RG                   256
DW                60.600 usec
DE                 6.00 usec
TE                296.8 K
D1           1.00000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2316251 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

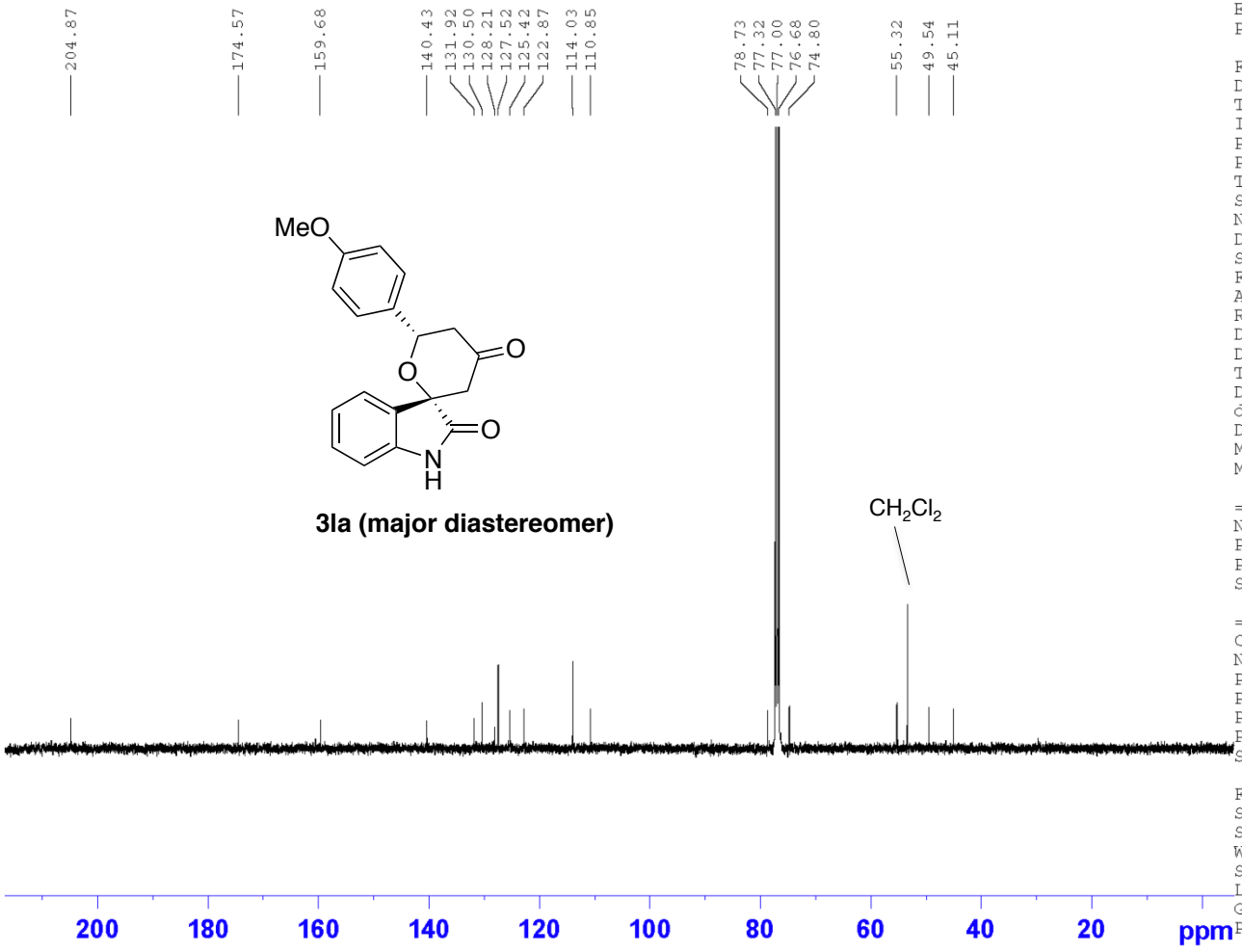


3ka (minor diastereomer)

```
Current Data Parameters
NAME          Oct11-2013
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131012
Time               12.45
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                19000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631696 sec
RG                29193
DW               20.800 usec
DE                6.00 usec
TE                297.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12               17.10 dB
PL13               17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6383317 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

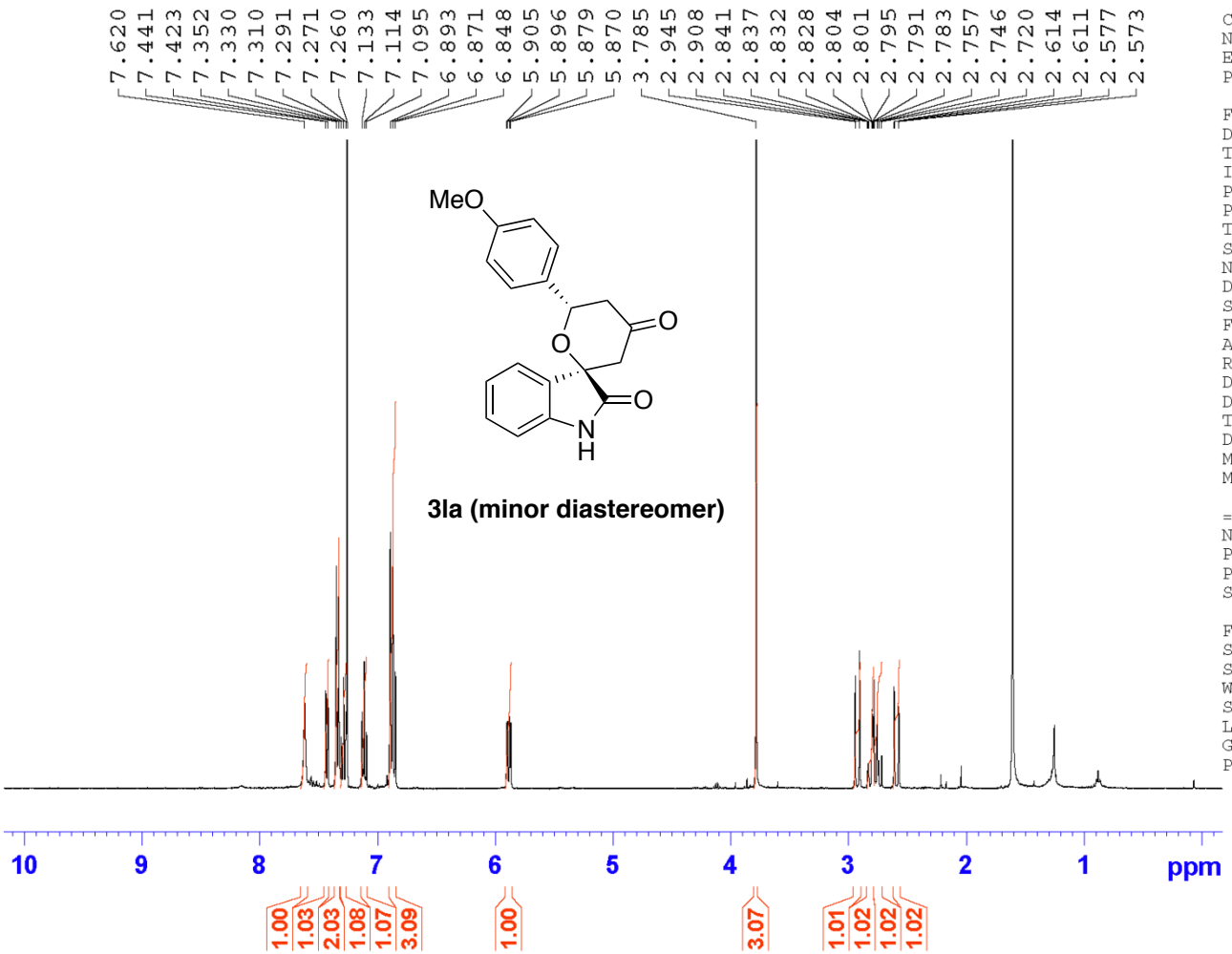



```
Current Data Parameters
NAME          Oct03-2013
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131003
Time              17.28
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715421 sec
RG                   256
DW                60.600 usec
DE                 6.00 usec
TE                297.0 K
D1           1.00000000 sec
MCREST    0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300052 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

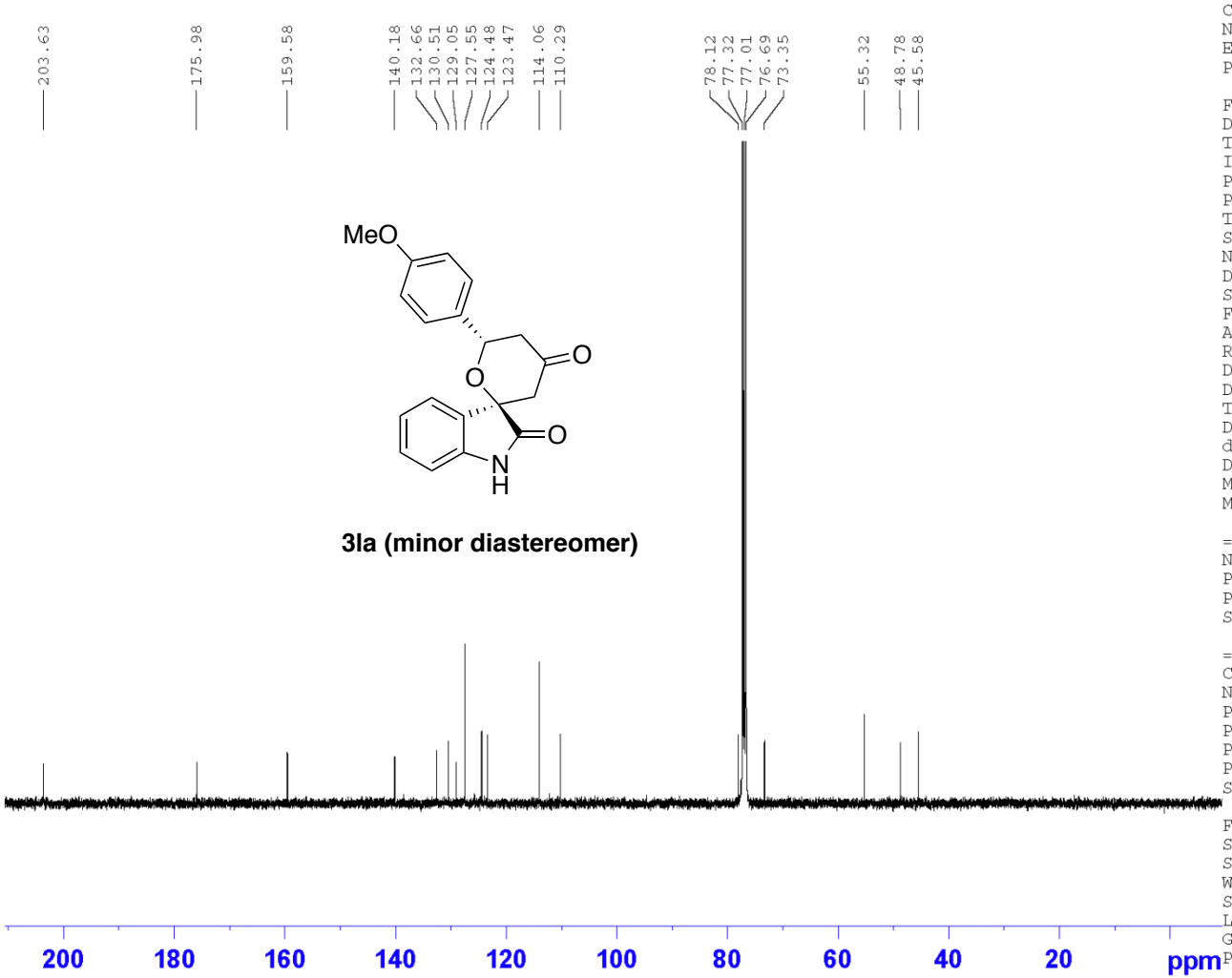


3la (major diastereomer)

```
Current Data Parameters
NAME          Oct03-2013
EXPNO                 60
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131004
Time                6.16
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                13000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631696 sec
RG                16384
DW               20.800 usec
DE                6.00 usec
TE                298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379149 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

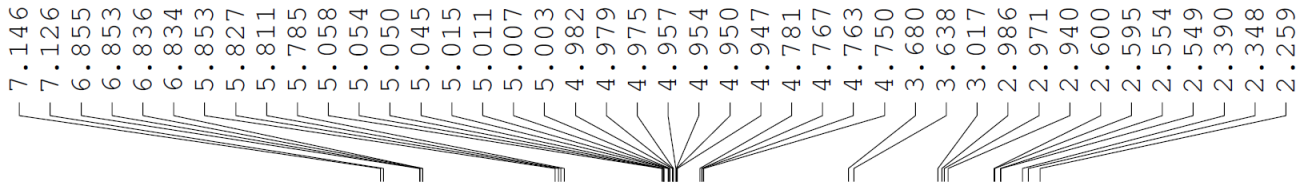


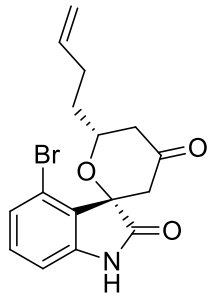

```
Current Data Parameters
NAME          Aug08-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130808
Time               12.48
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715421 sec
RG                 456.1
DW                60.600 usec
DE                 6.00 usec
TE                297.8 K
D1             1.00000000 sec
MCREST    0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF           400.2300054 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



3la (minor diastereomer)

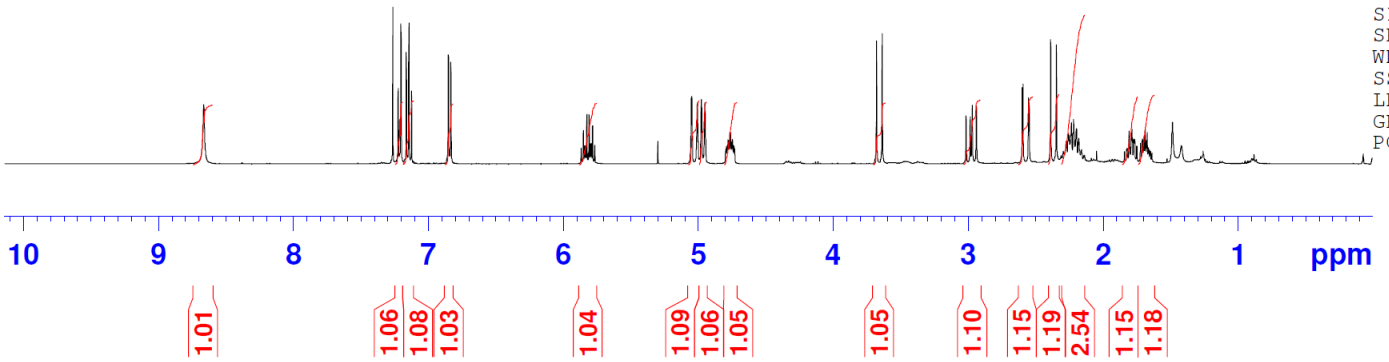
```
Current Data Parameters
NAME          Aug08-2013
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130809
Time                7.39
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                13000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631696 sec
RG                5160.6
DW                20.800 usec
DE                 6.00 usec
TE                298.4 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

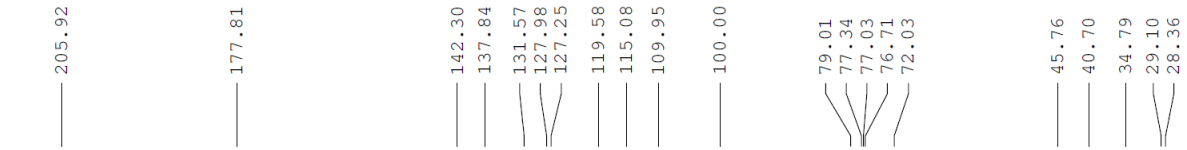


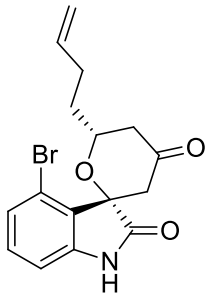


3fc

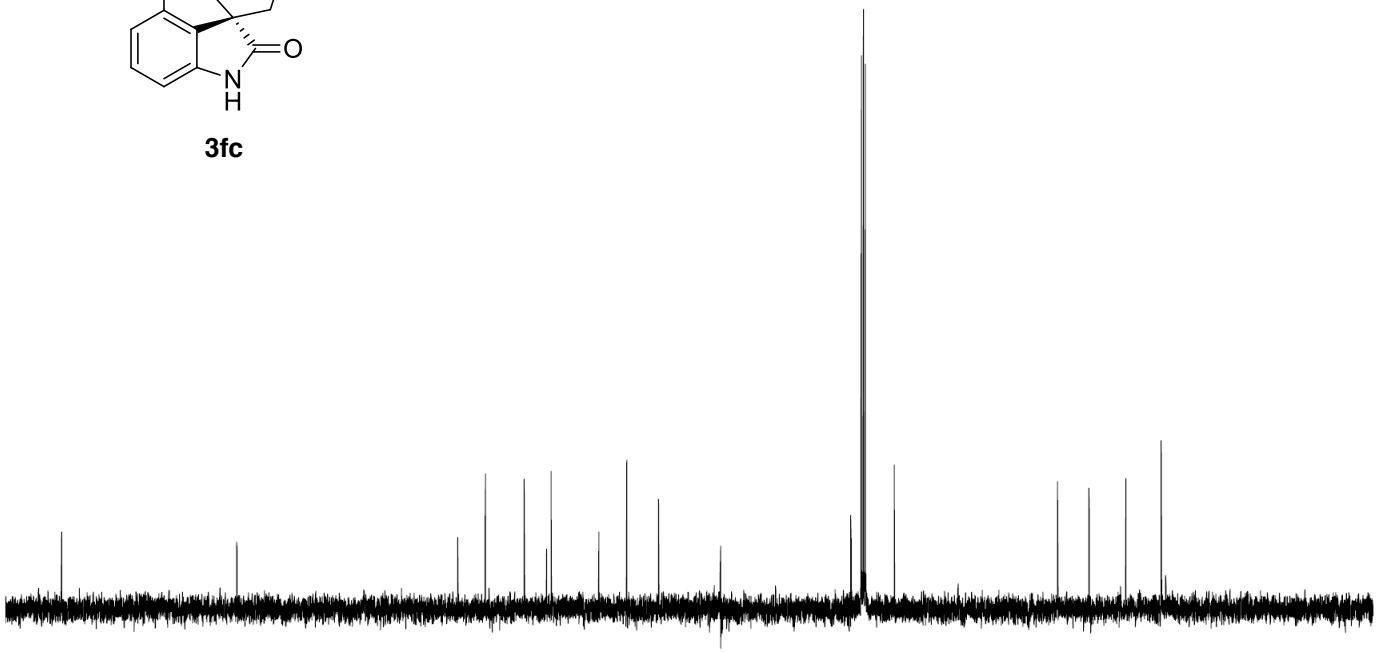
```
Current Data Parameters
NAME        03092012-Cui
EXPNO                 18
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120903
Time               21.12
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715922 sec
RG                 203.2
DW                60.600 usec
DE                 6.00 usec
TE                296.8 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300034 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



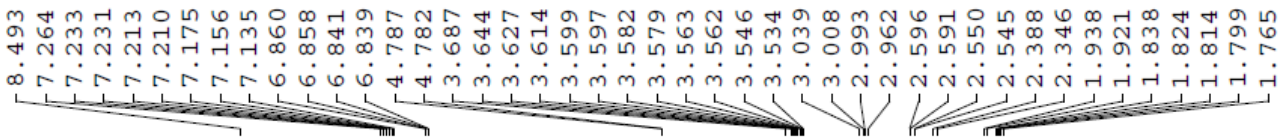


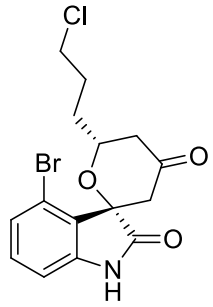


3fc

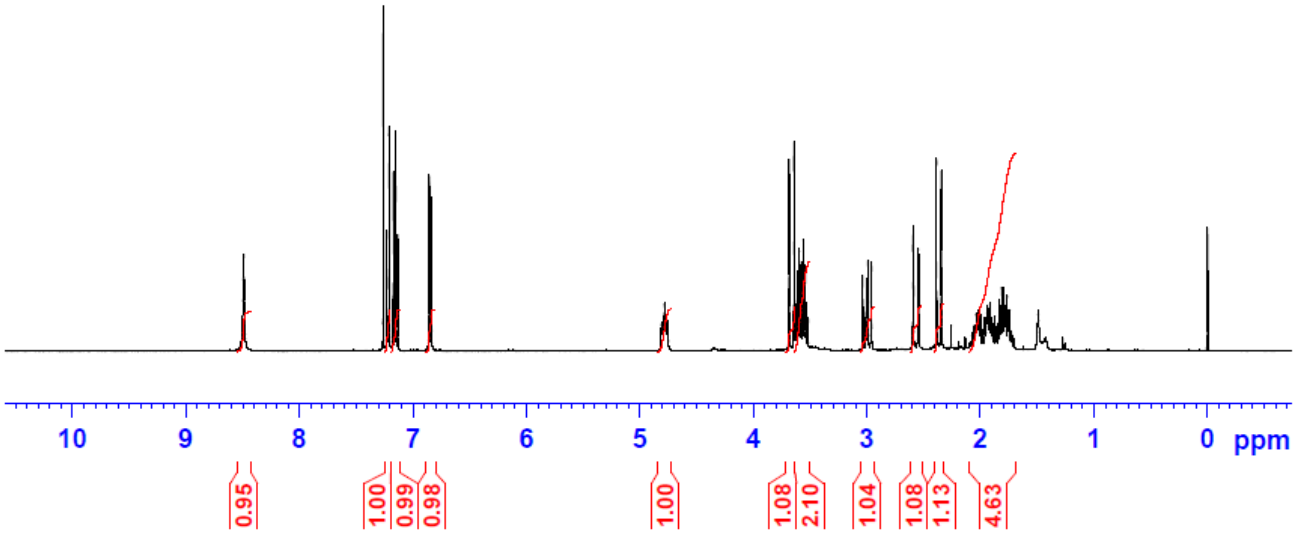



```
Current Data Parameters
NAME       03092012-Cui
EXPNO                19
PROCNO                1

F2 - Acquisition Parameters
Date_          20120903
Time              21.25
INSTRUM       avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3632196 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                297.4 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                10.00 usec
PL1               -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

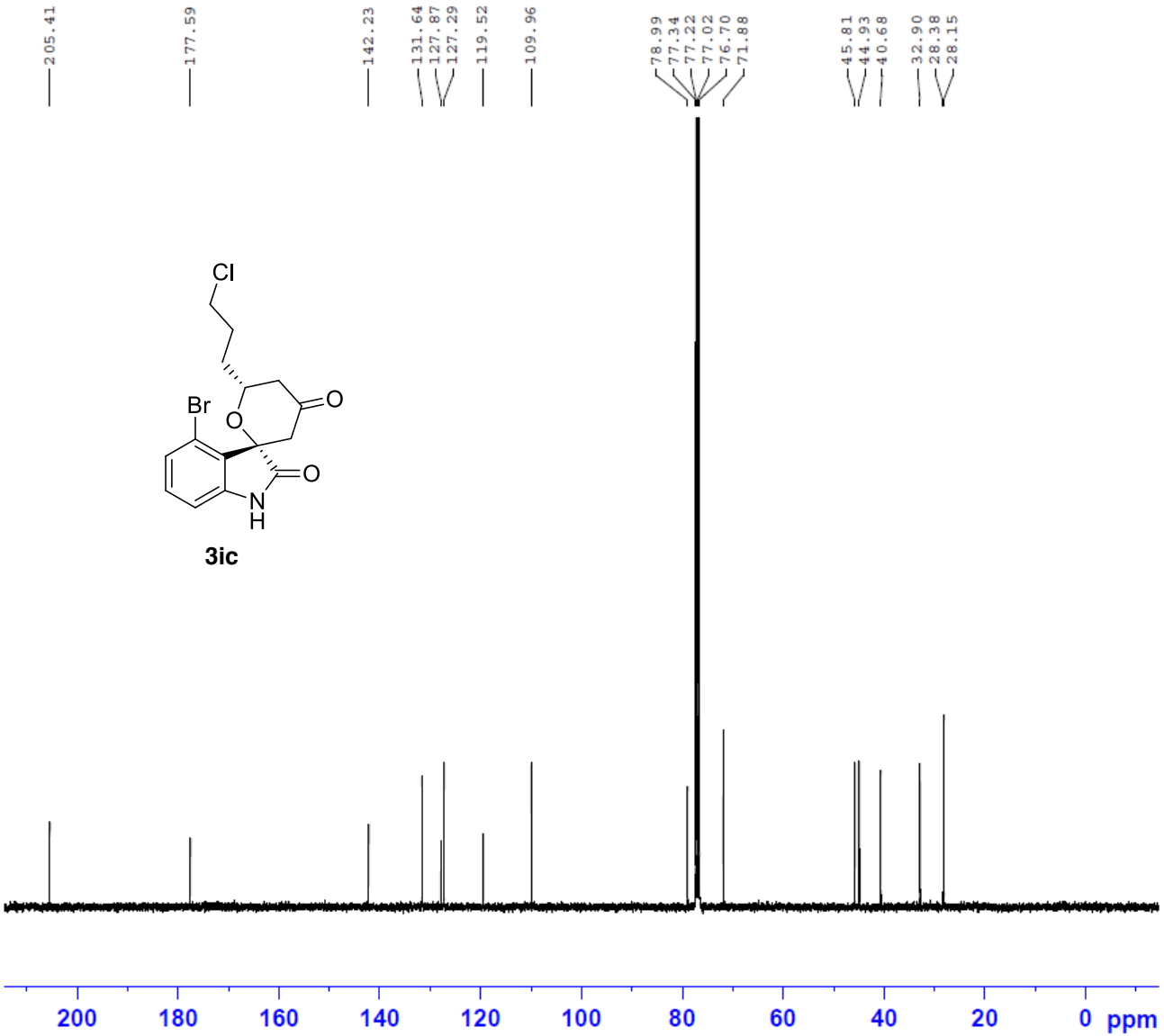




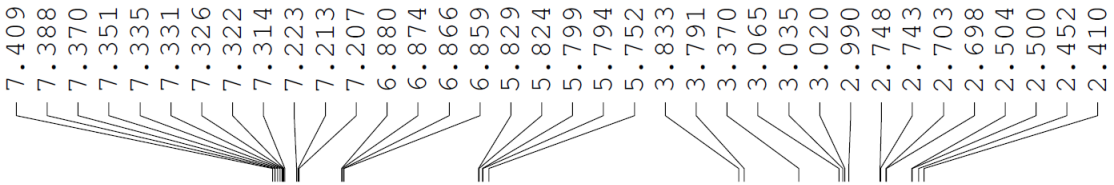
3ic

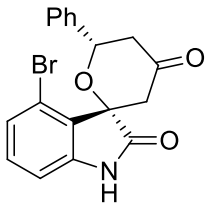



```
Current Data Parameters
NAME        18032014-CHL
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140318
Time              15.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG                62.88
DW               62.400 usec
DE                6.50 usec
TE               298.4 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                65536
SF           400.1300084 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



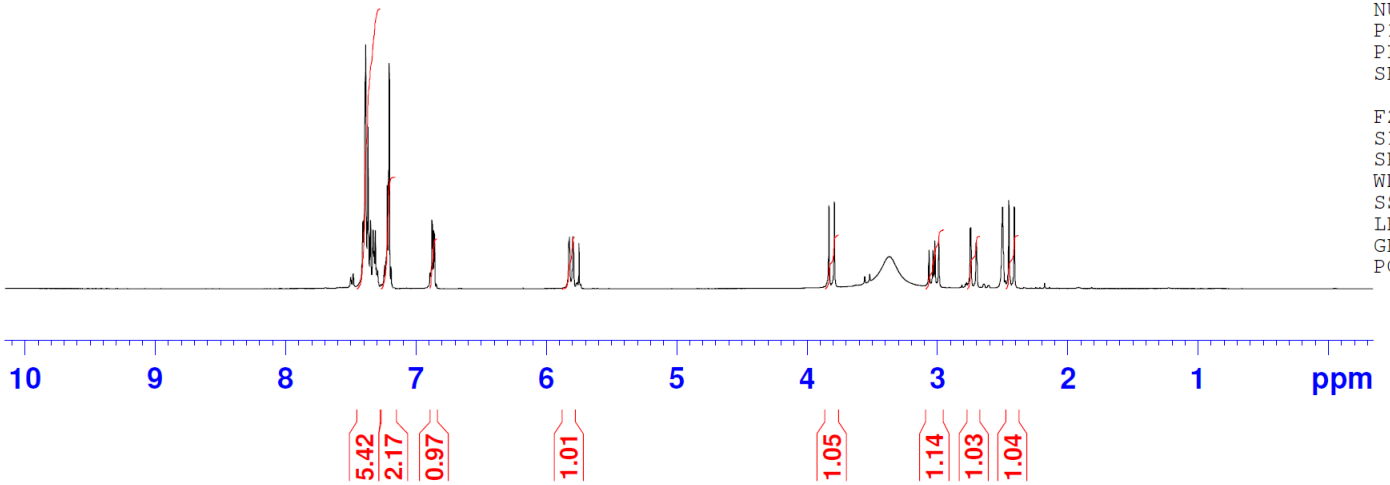

```
Current Data Parameters
NAME        18032014-CHL
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140318
Time              16.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               195.88
DW               20.800 usec
DE                6.50 usec
TE               299.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                 EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

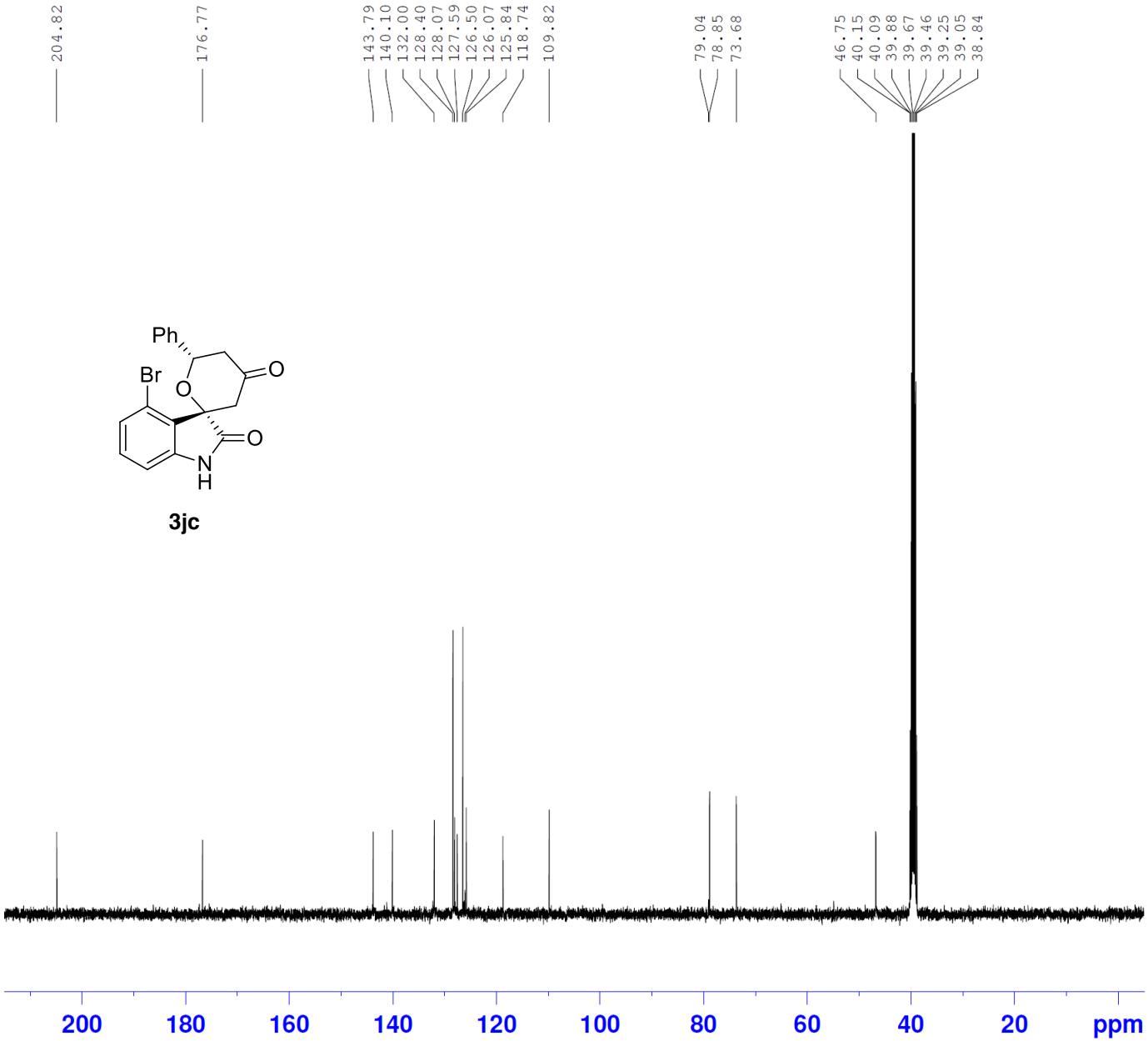




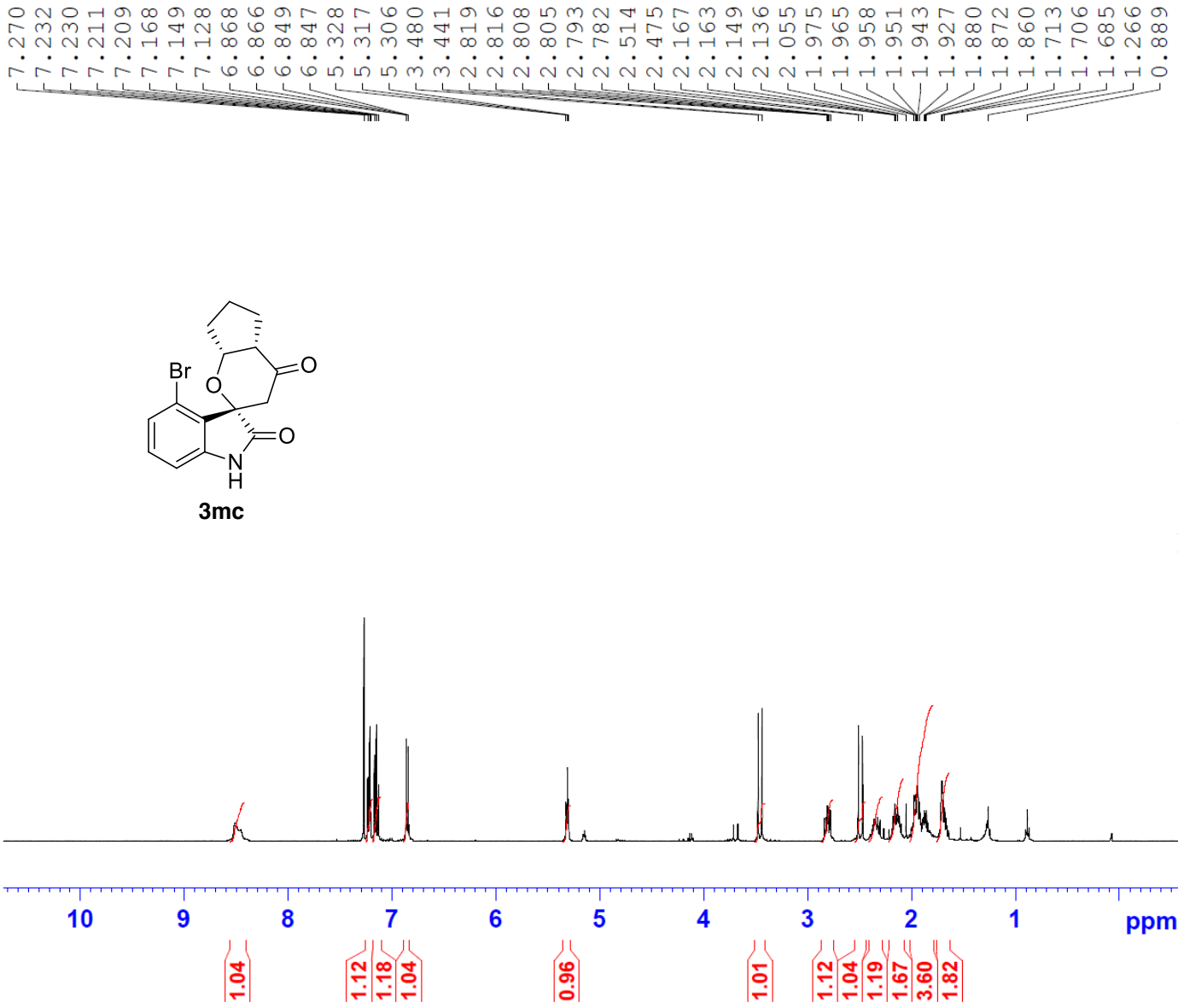
3jc

```
Current Data Parameters
NAME          05022013-Cui
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_              20130205
Time                  18.18
INSTRUM          avance400
PROBHD    5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               8250.825 Hz
FIDRES            0.125898 Hz
AQ                3.9715922 sec
RG                    161.3
DW                   60.600 usec
DE                    6.00 usec
TE                   296.5 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   15.00 usec
PL1                   2.70 dB
SFO1          400.2324716 MHz

F2 - Processing parameters
SI                    32768
SF            400.2299988 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```

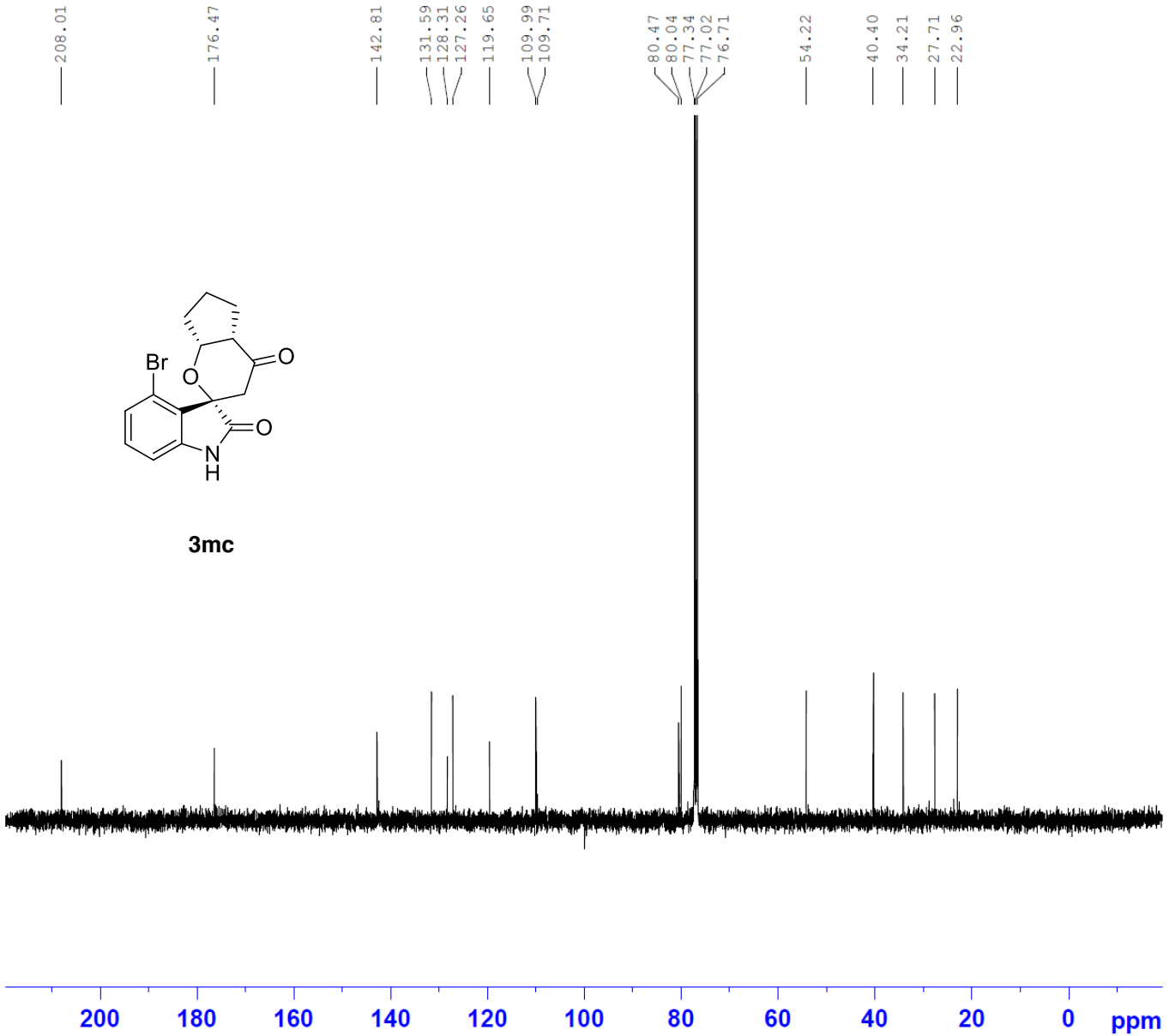





```
Current Data Parameters
NAME        05022013-Cui
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130205
Time               18.55
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                65536
SOLVENT            DMSO
NS                   300
DS                     2
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3632196 sec
RG                2580.3
DW                20.800 usec
DE                 6.00 usec
TE                297.4 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                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                 32768
SF          100.6379643 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

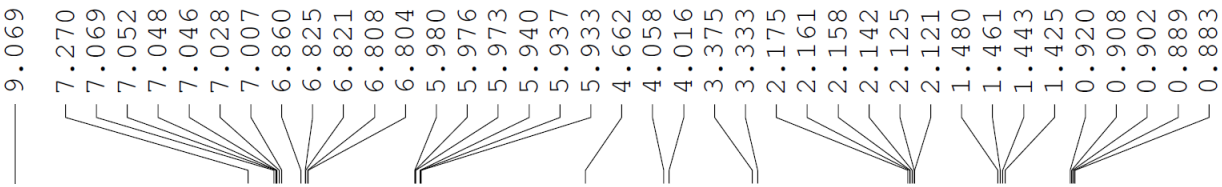


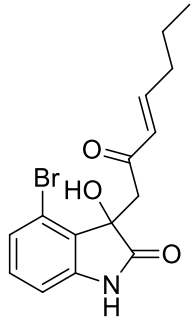

```
Current Data Parameters
NAME        15022013-Cui
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130215
Time               14.03
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715421 sec
RG                 287.4
DW                60.600 usec
DE                 6.00 usec
TE                296.4 K
D1           1.00000000 sec
MCREST    0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF           400.2300015 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



3mc

```
Current Data Parameters
NAME        15022013-Cui
EXPNO                 35
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130216
Time               18.06
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  300
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631696 sec
RG                143.7
DW               20.800 usec
DE                6.00 usec
TE               297.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST    0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1               -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                 1.40
```





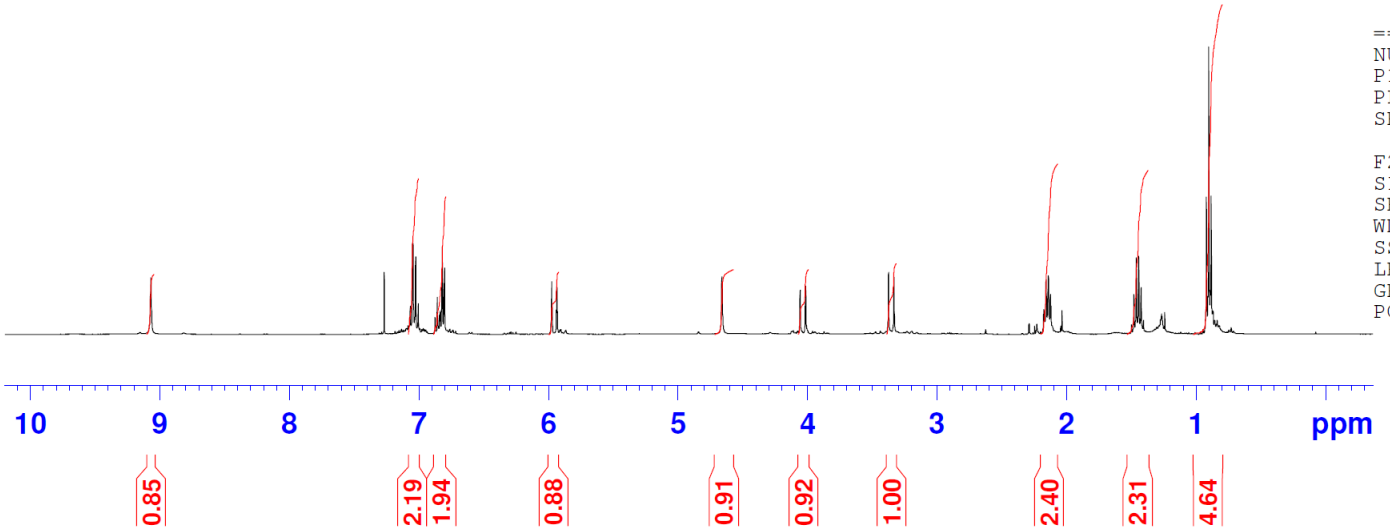
4c

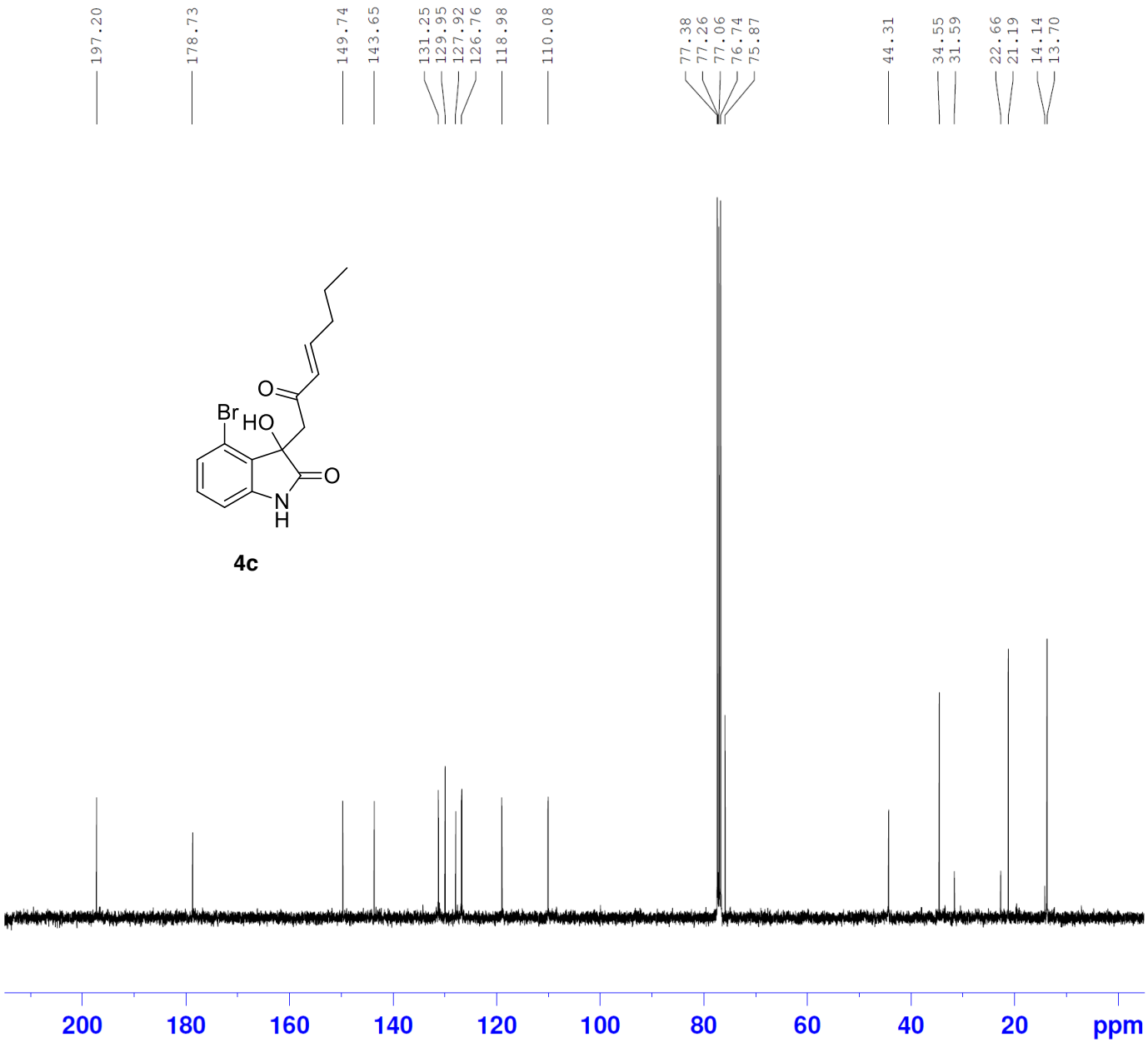
Current Data Parameters
NAME 12022013-Cui
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130212
Time 12.03
INSTRUM avance400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8250.825 Hz
FIDRES 0.125898 Hz
AQ 3.9715922 sec
RG 101.6
DW 60.600 usec
DE 6.00 usec
TE 293.7 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 2.70 dB
SFO1 400.2324716 MHz

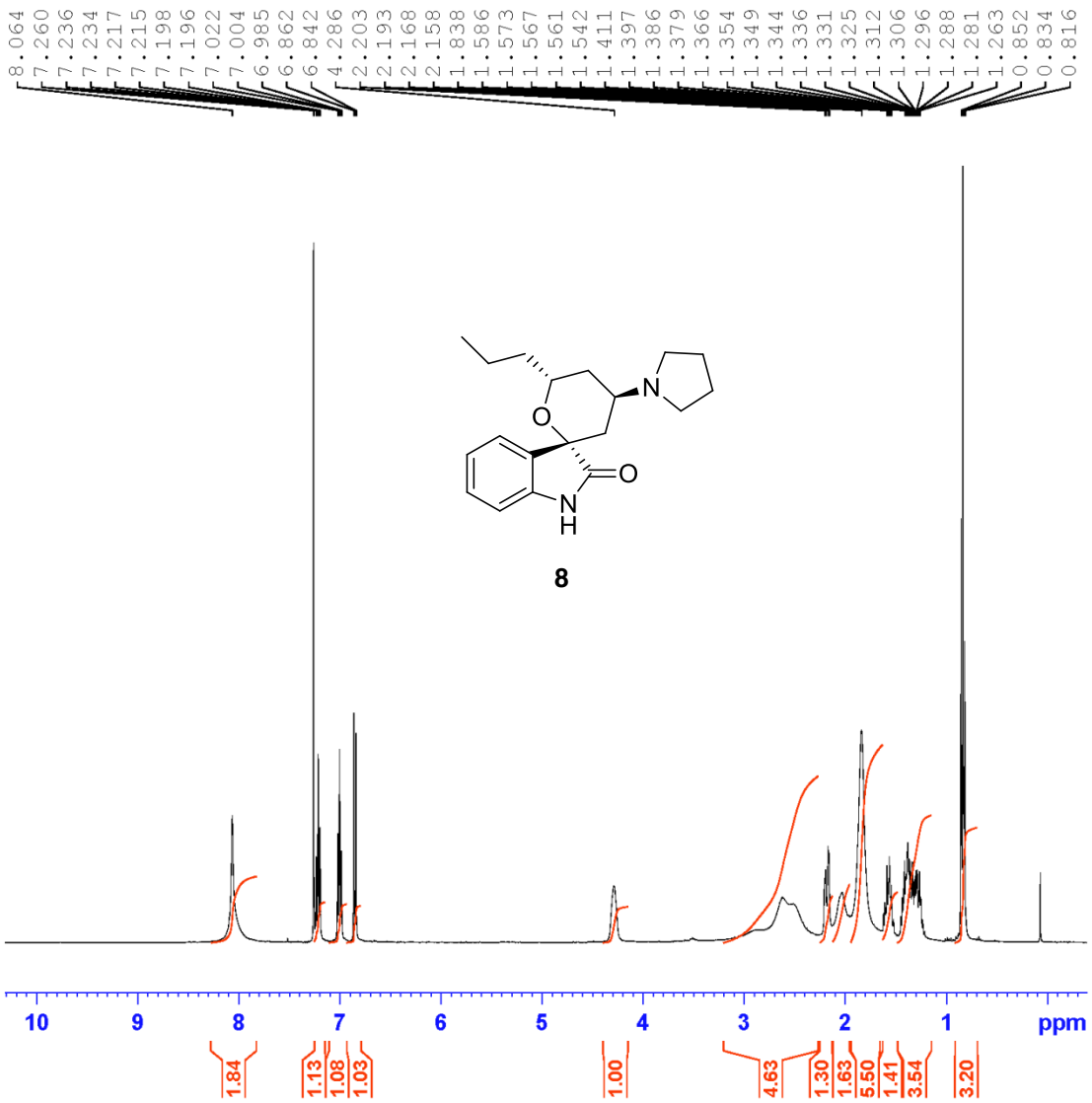
F2 - Processing parameters
SI 32768
SF 400.2300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





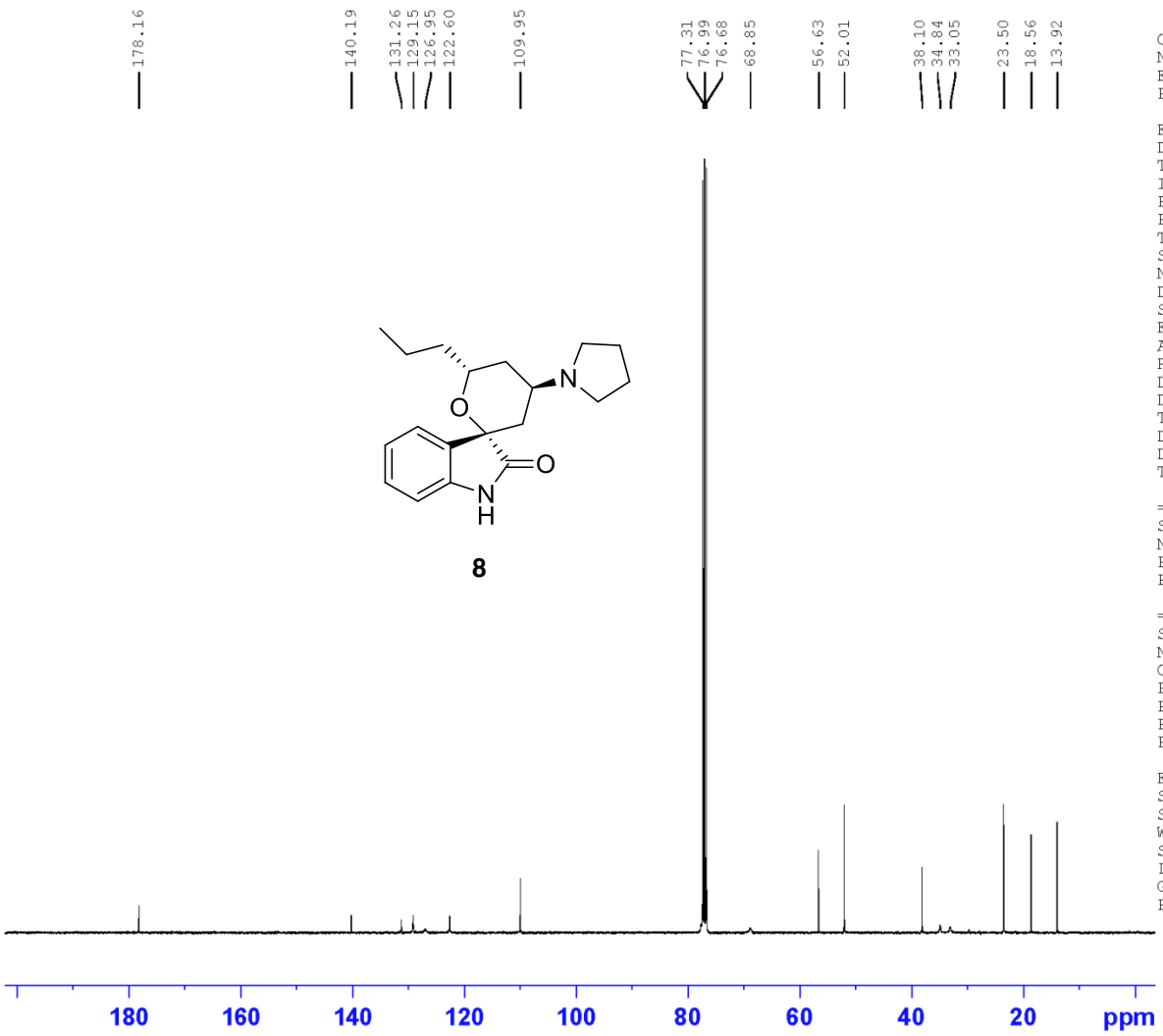
4c

```
Current Data Parameters
NAME       12022013-Cui
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20130212
Time              12.43
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  300
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3632196 sec
RG                161.3
DW               20.800 usec
DE                6.00 usec
TE                295.0 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                10.00 usec
PL1               -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

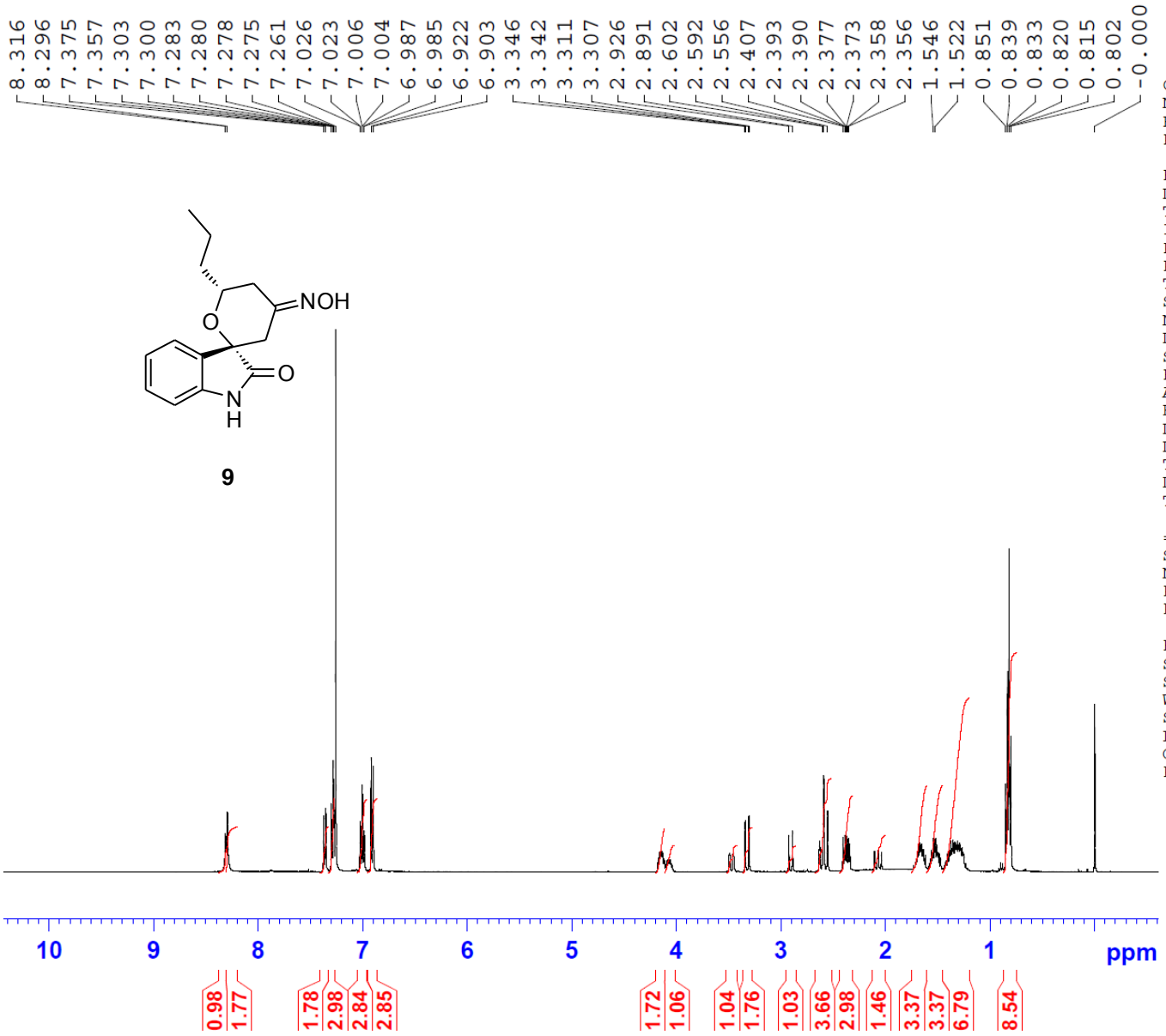


8

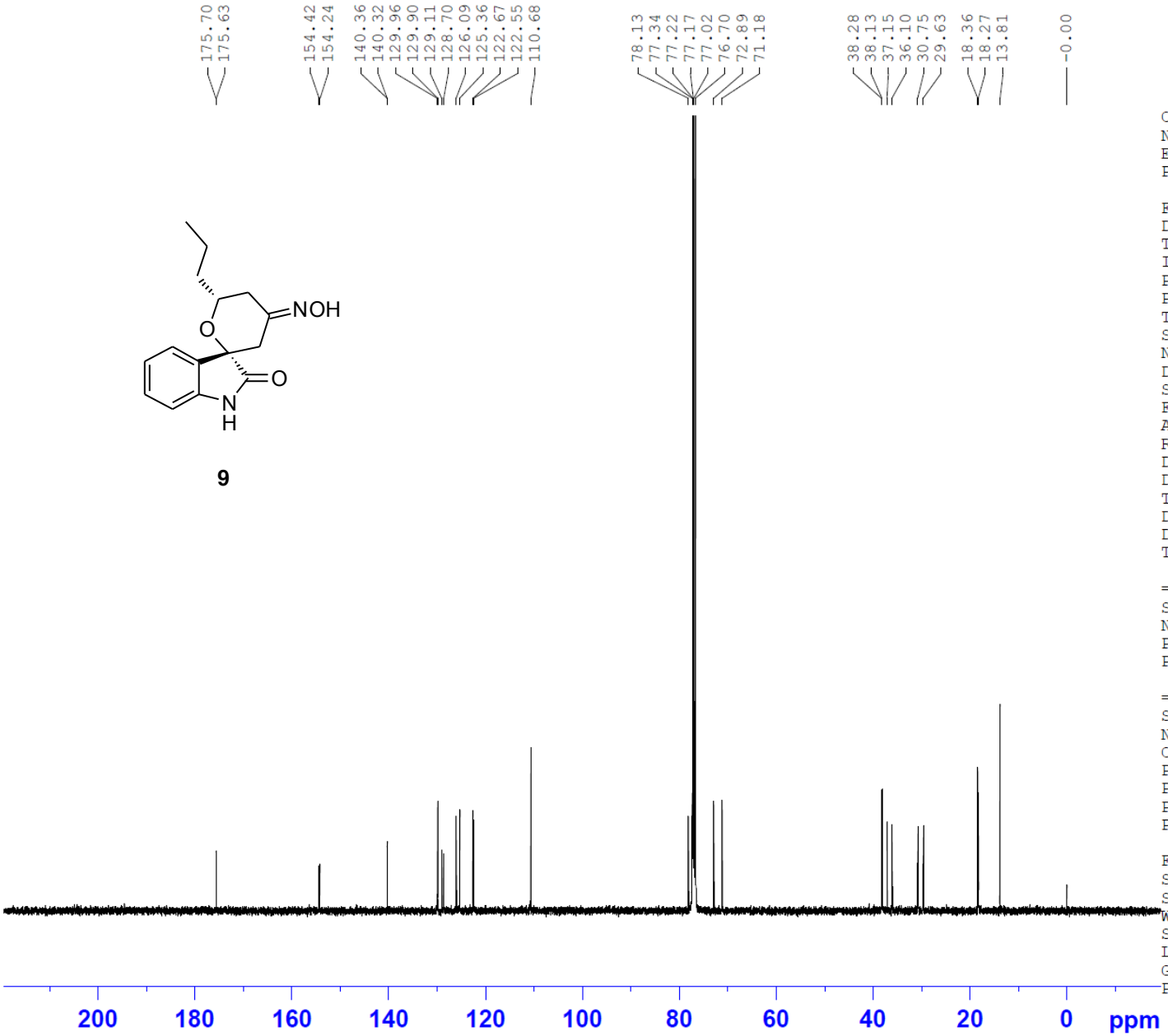
```
Current Data Parameters
NAME       YF-14-1210-52
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141210
Time_              17.29
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 62.88
DW                62.400 usec
DE                 6.50 usec
TE                298.5 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300098 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME       YF-14-1216-52
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141217
Time                8.02
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                12000
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG               195.88
DW               20.800 usec
DE                6.50 usec
TE                299.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                 32768
SF           100.6127714 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

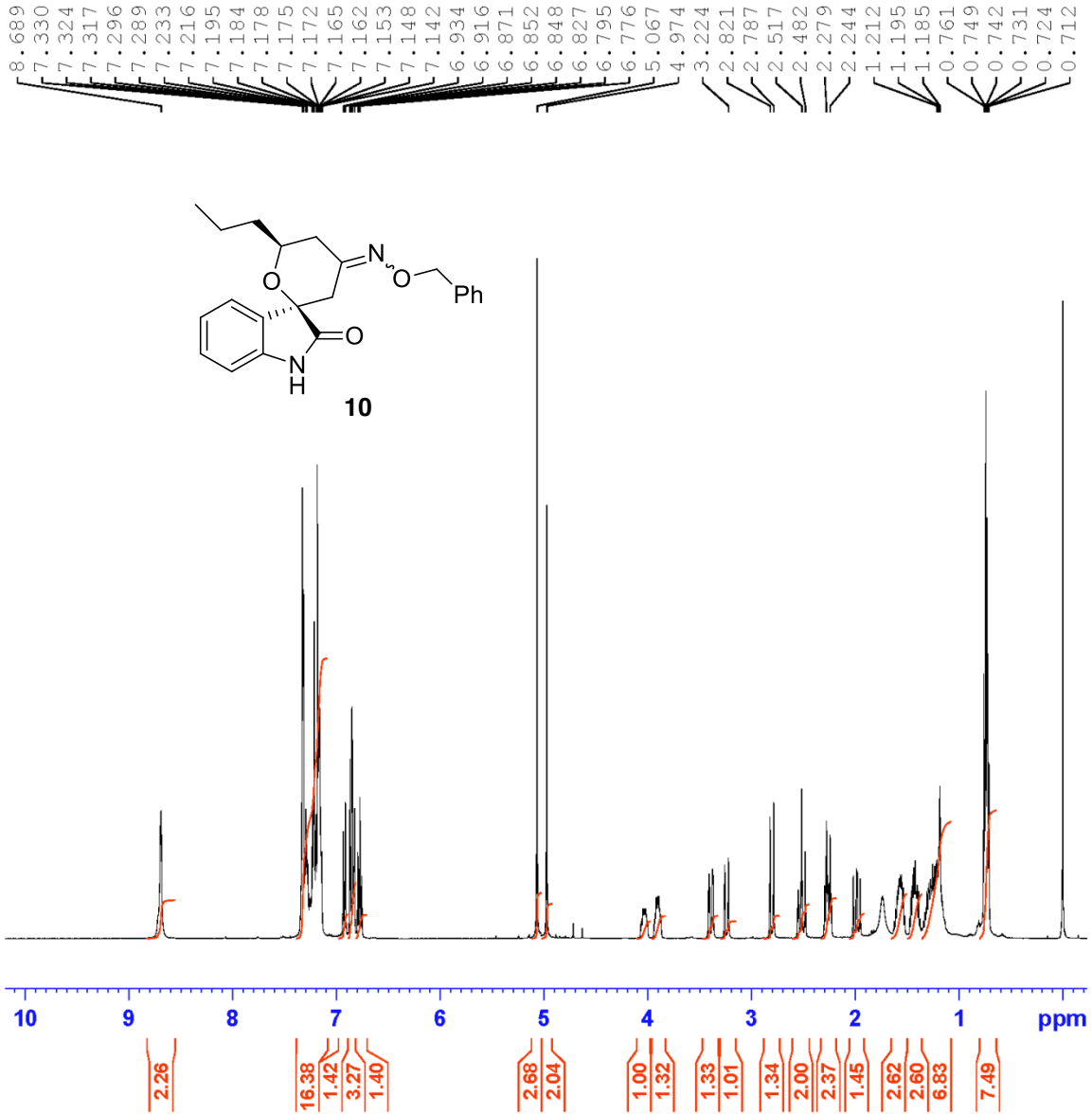



```
Current Data Parameters
NAME        01042014-CHL
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140401
Time              16.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ           4.0894465 sec
RG                77.81
DW              62.400 usec
DE               6.50 usec
TE               298.5 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                1H
P1                15.00 usec
PLW1         8.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1300093 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

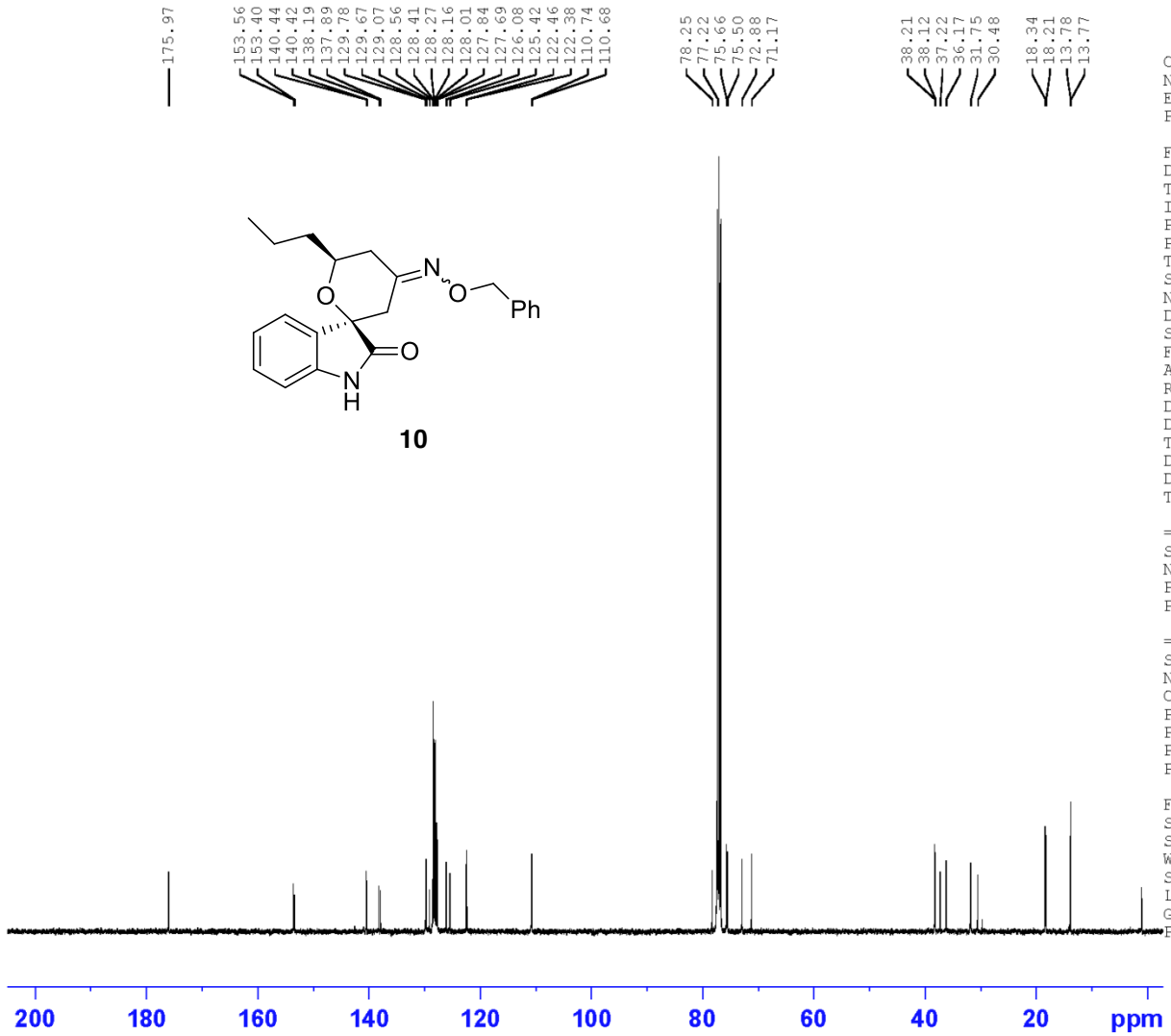


9

```
Current Data Parameters
NAME        01042014-CHL
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140402
Time               3.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                10000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                195.88
DW                20.800 usec
DE                 6.50 usec
TE                299.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                32768
SF           100.6127681 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

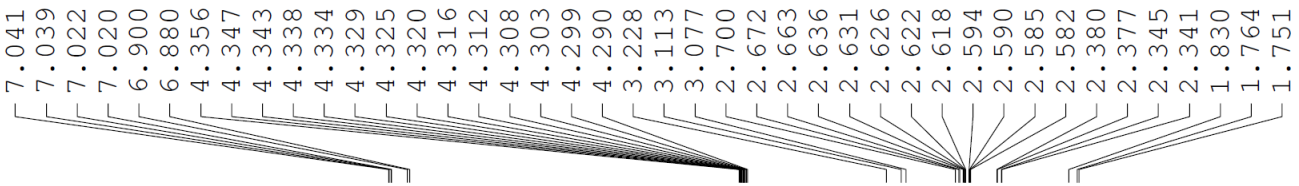



```
Current Data Parameters
NAME      YF-14-1211-54-64
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20141211
Time                11.37
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894465 sec
RG                  31.13
DW                 62.400 usec
DE                  6.50 usec
TE                 298.5 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                  65536
SF           400.1300400 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

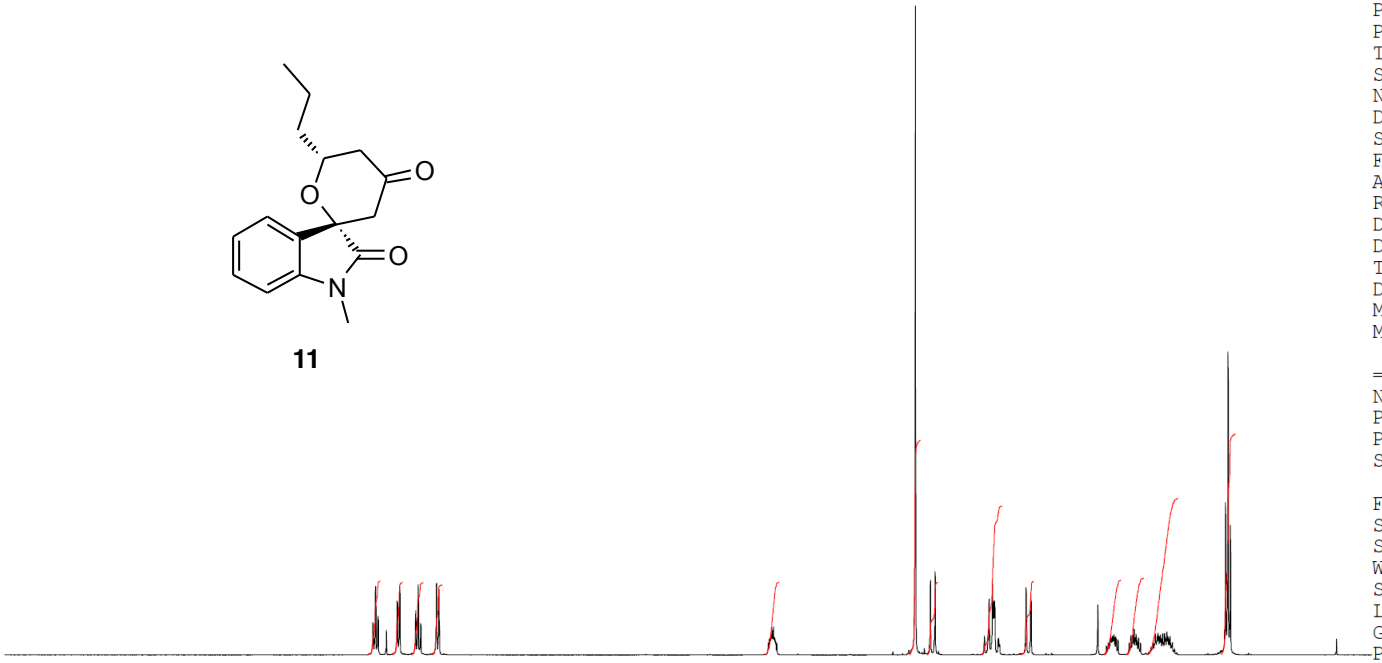


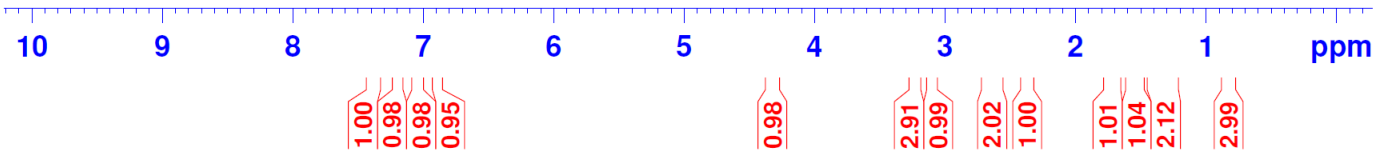
10

```
Current Data Parameters
NAME      YF-14-1211-54-64
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_           20141211
Time              13.50
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                195.88
DW                20.800 usec
DE                 6.50 usec
TE                299.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                 32768
SF           100.6127728 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

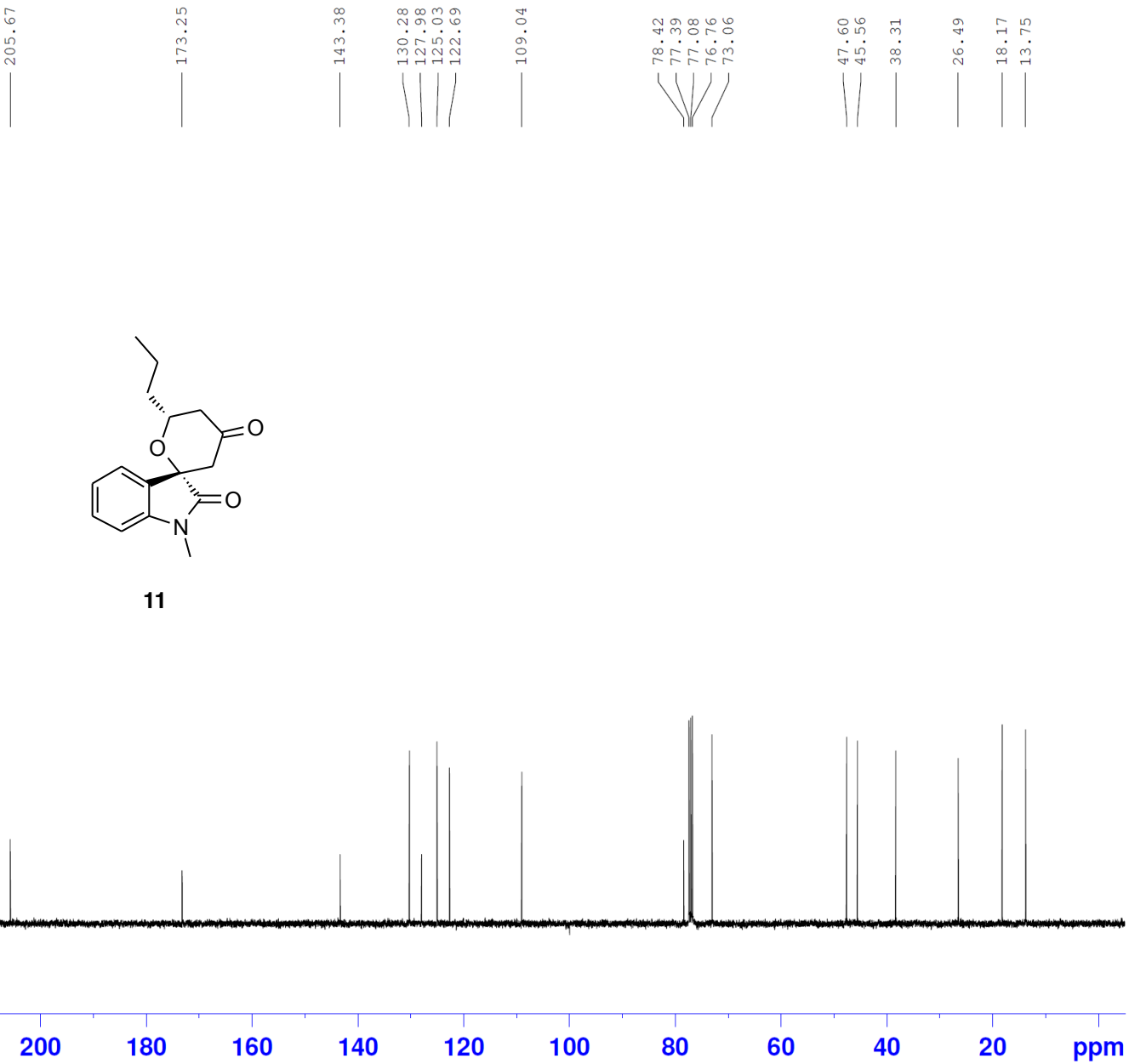


11



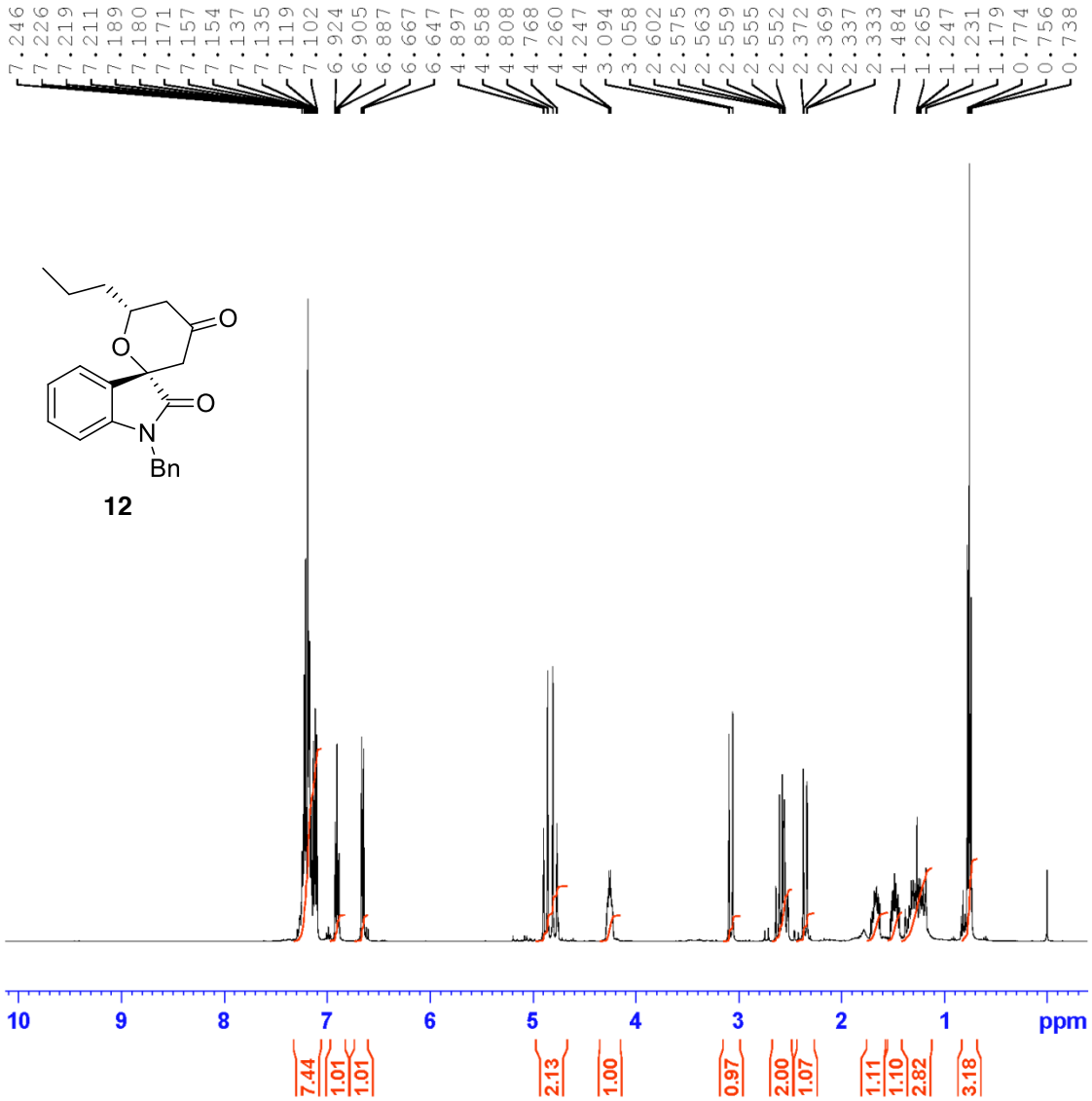



```
Current Data Parameters
NAME        21092012-Cui
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120921
Time               17.58
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715922 sec
RG                  80.6
DW                60.600 usec
DE                 6.00 usec
TE                296.1 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2299958 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

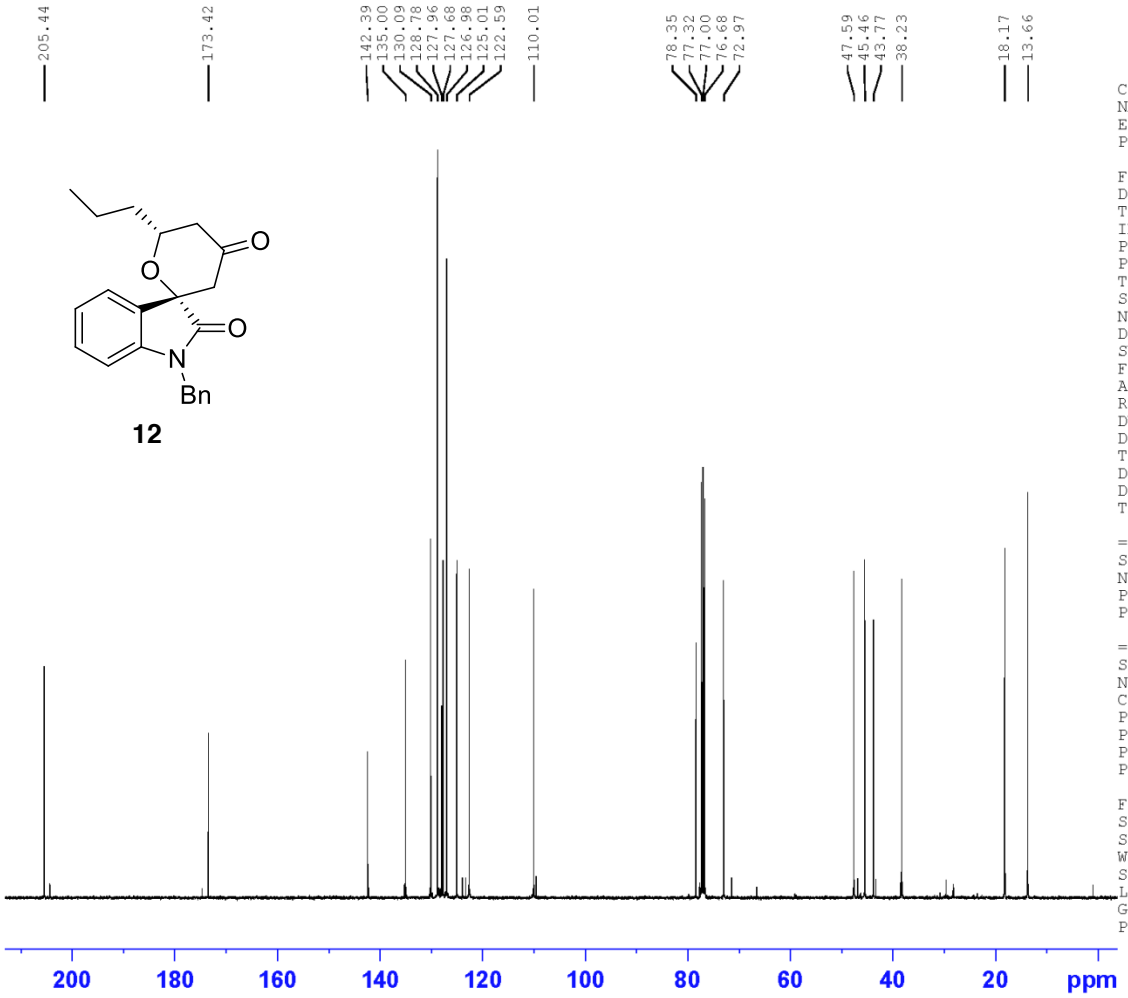


11

```
Current Data Parameters
NAME        21092012-Cui
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120921
Time               18.14
INSTRUM         avance400
PROBHD    5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     2
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3632196 sec
RG                   128
DW                20.800 usec
DE                 6.00 usec
TE                296.8 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                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                32768
SF           100.6379140 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

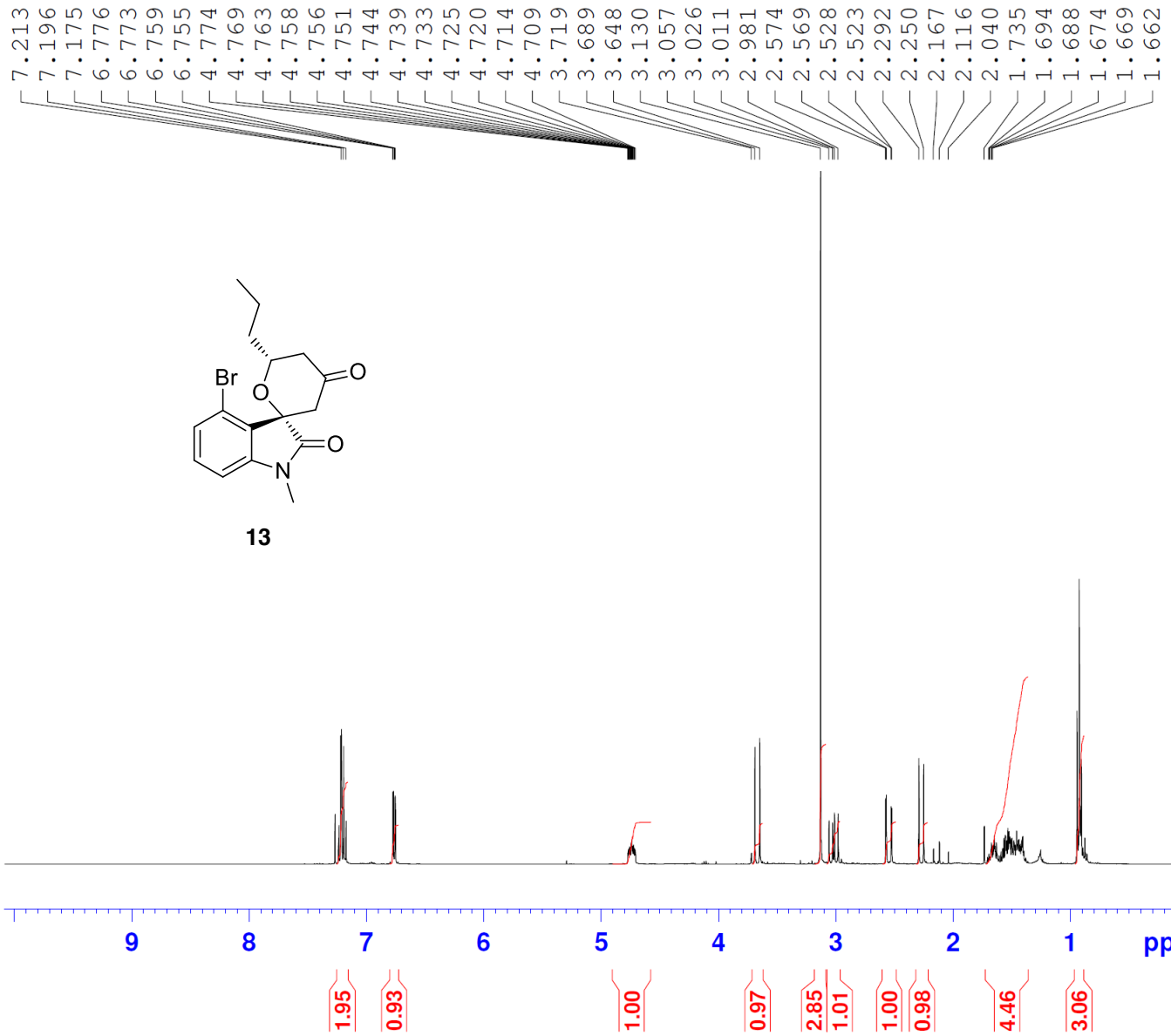



```
Current Data Parameters
NAME       YF-14-1212-58
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141212
Time                9.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 22.45
DW                62.400 usec
DE                 6.50 usec
TE                298.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300416 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

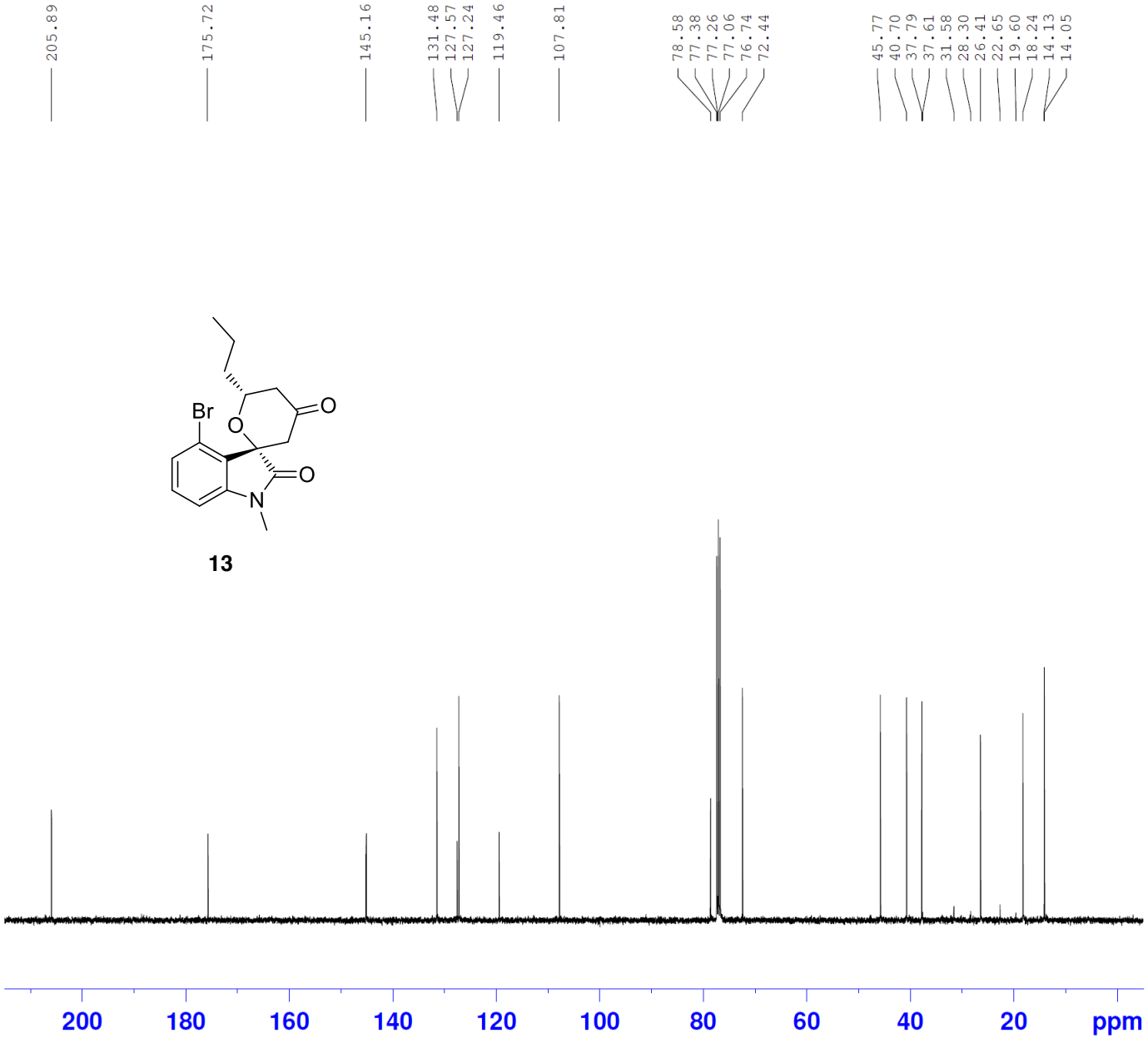


12

```
Current Data Parameters
NAME       YF-14-1212-58
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141212
Time              11.16
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1536
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG               195.88
DW               20.800 usec
DE                6.50 usec
TE               299.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        70.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         8.00000000 W
PLW12        0.28125000 W
PLW13        0.28125000 W

F2 - Processing parameters
SI                 32768
SF          100.6127794 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

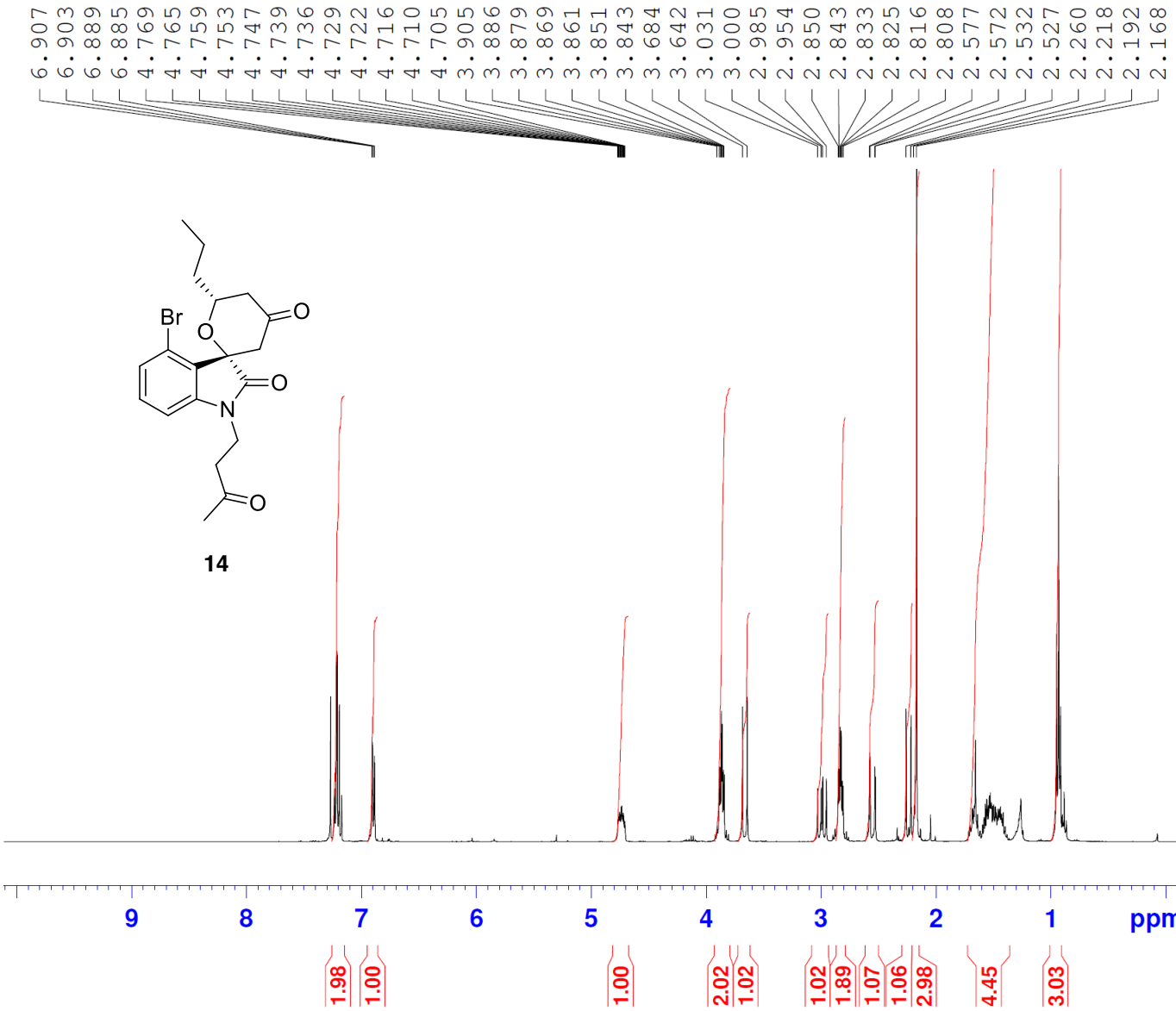



```
Current Data Parameters
NAME        07022013-Cui
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130207
Time               12.23
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715922 sec
RG                 101.6
DW                60.600 usec
DE                 6.00 usec
TE                295.7 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300015 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

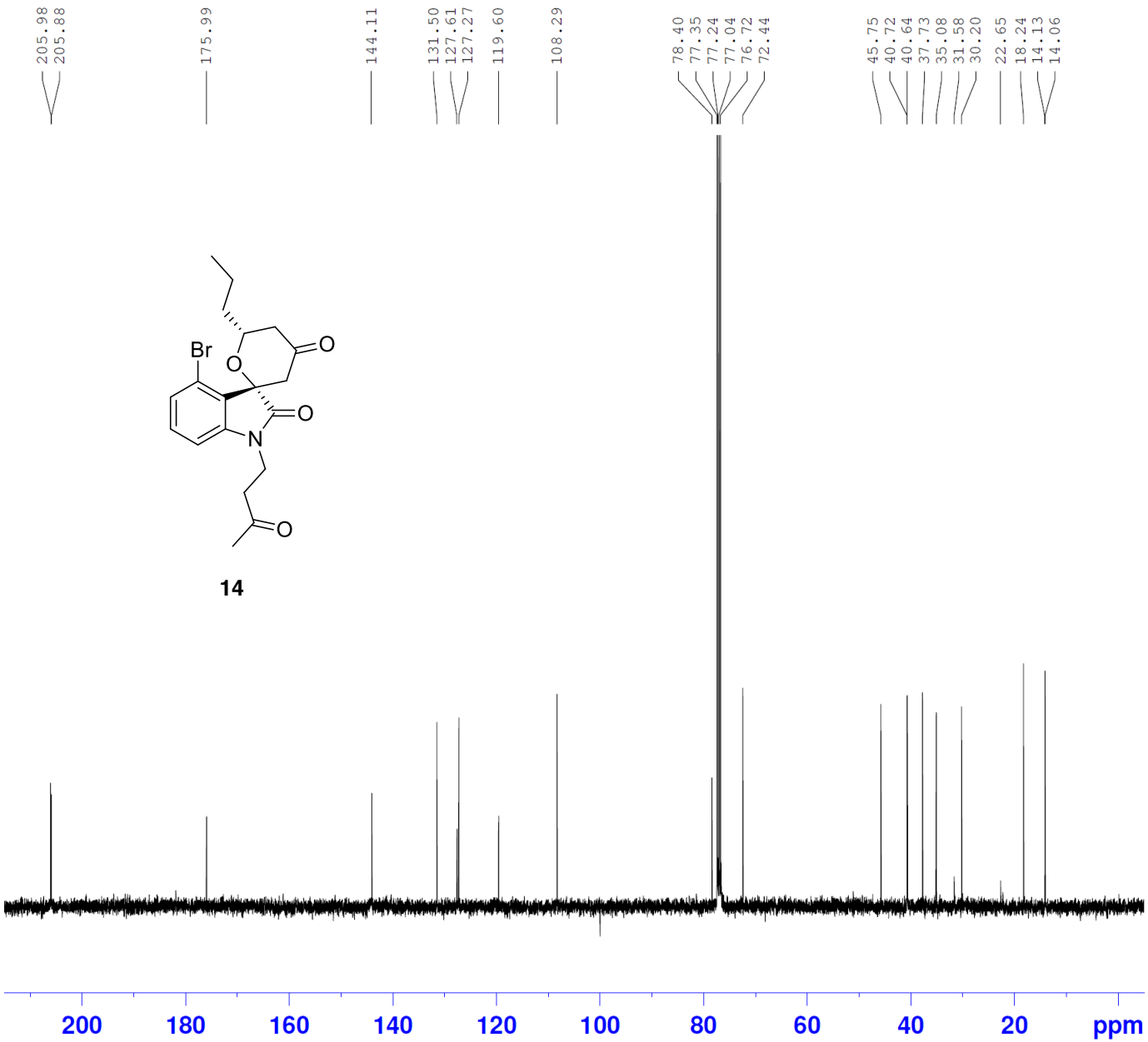


13

```
Current Data Parameters
NAME        07022013-Cui
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130207
Time               12.52
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  400
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3632196 sec
RG                143.7
DW                20.800 usec
DE                 6.00 usec
TE                296.8 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                10.00 usec
PL1               -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




```
Current Data Parameters
NAME        12022013-Cui
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130212
Time               16.41
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ             3.9715922 sec
RG                   181
DW                60.600 usec
DE                 6.00 usec
TE                294.8 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF           400.2300013 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



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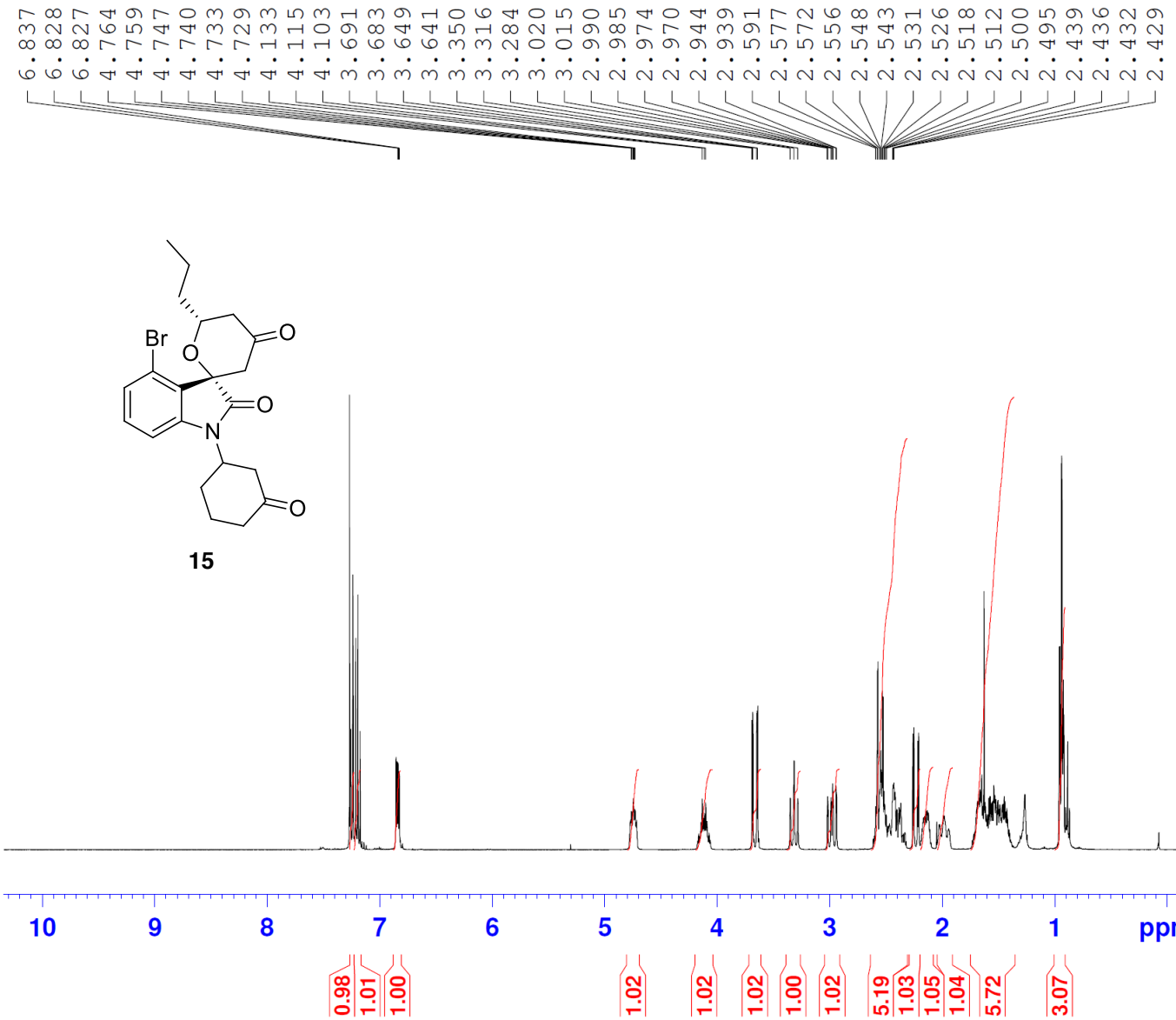
```
Current Data Parameters
NAME        12022013-Cui
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130212
Time               17.53
INSTRUM         avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  400
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3632196 sec
RG                143.7
DW               20.800 usec
DE                6.00 usec
TE                295.9 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               10.00 usec
PL1              -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               2.70 dB
PL12             17.10 dB
PL13             17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                32768
SF          100.6379140 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

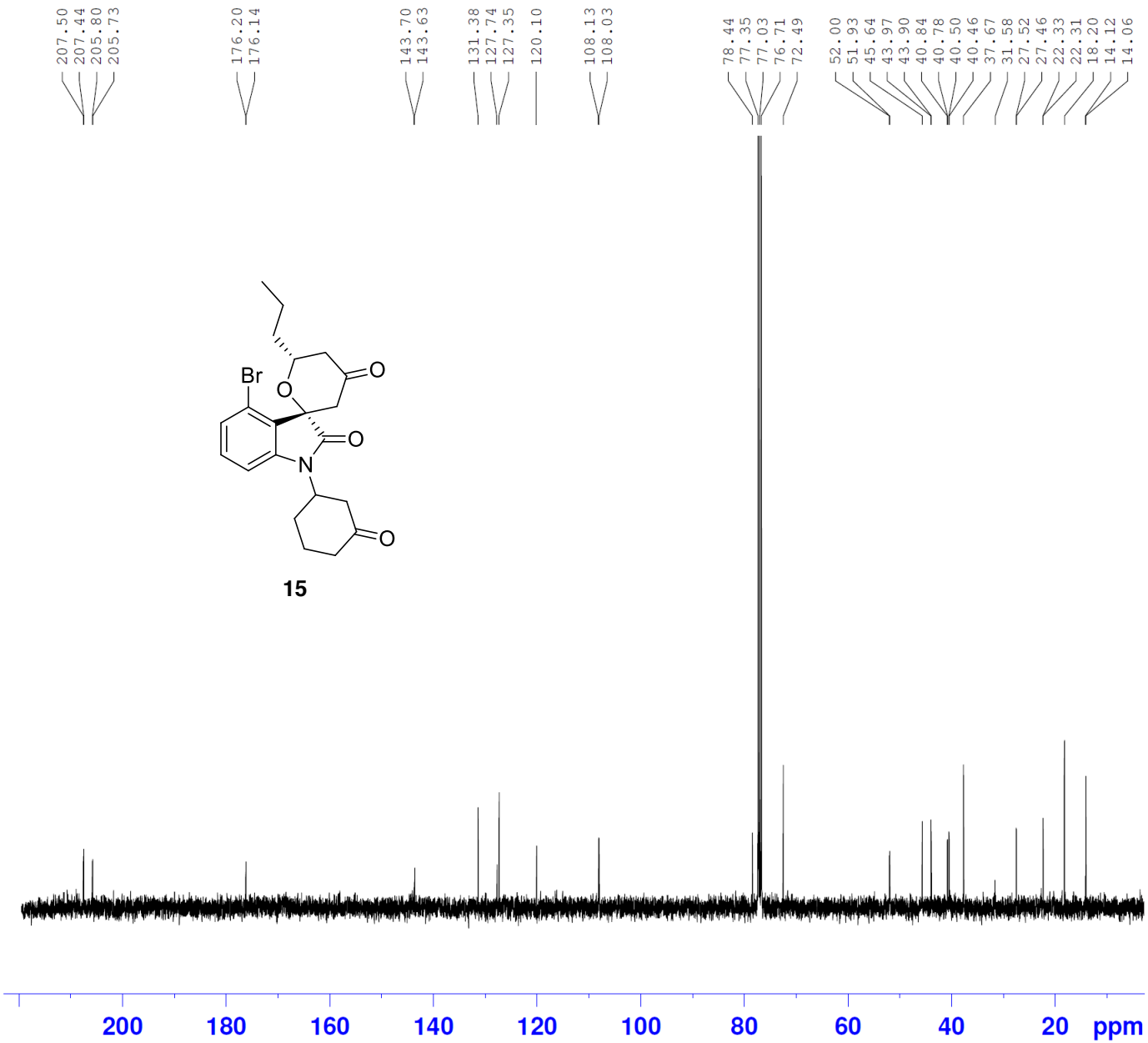



```
Current Data Parameters
NAME        14022013-Cui
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130214
Time               16.04
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ              3.9715922 sec
RG                 228.1
DW                60.600 usec
DE                 6.00 usec
TE                296.5 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300015 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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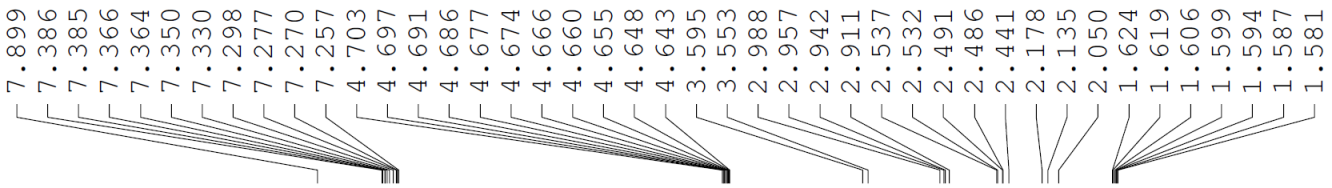
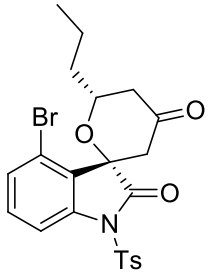
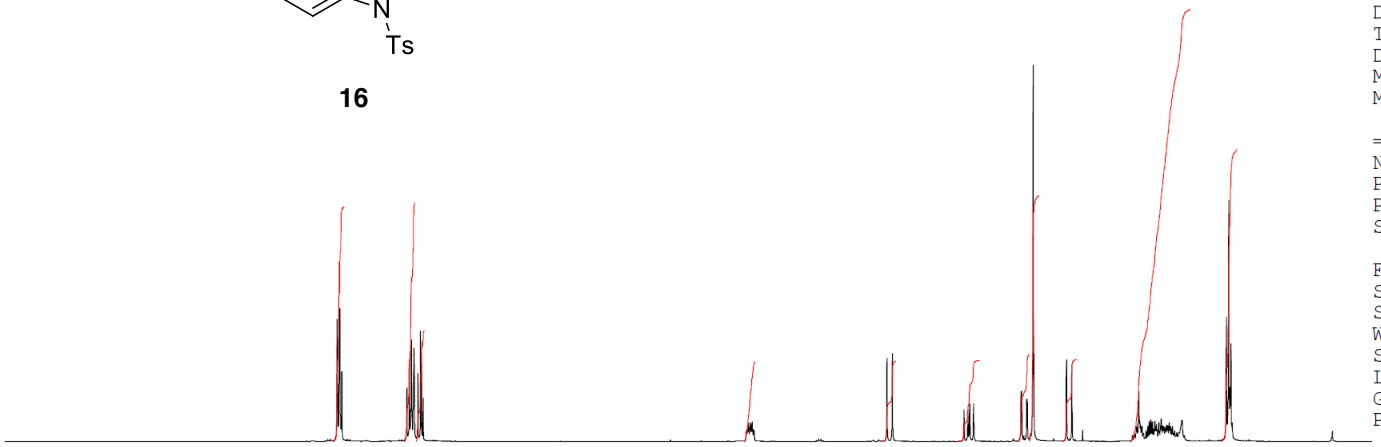
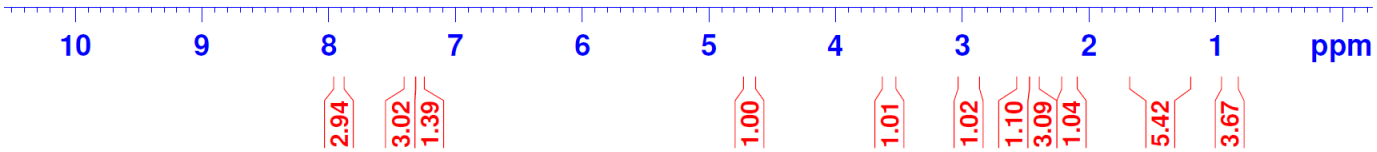
```
Current Data Parameters
NAME       14022013-Cui
EXPNO                31
PROCNO                1

F2 - Acquisition Parameters
Date_          20130214
Time              17.55
INSTRUM       avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3632196 sec
RG                 1024
DW               20.800 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                10.00 usec
PL1               -2.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2        400.2316009 MHz

F2 - Processing parameters
SI                 32768
SF          100.6379140 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



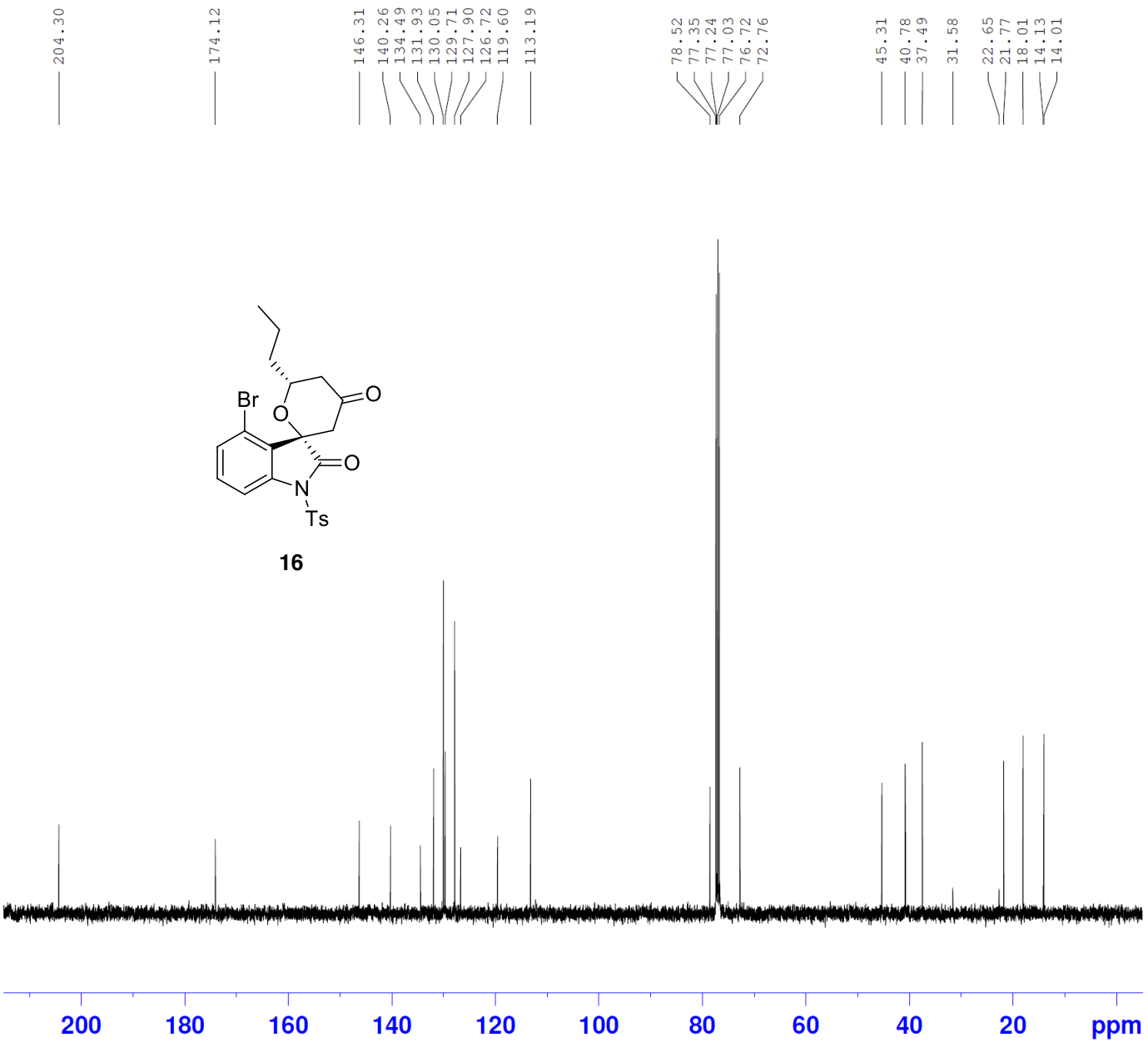


16






```
Current Data Parameters
NAME        14022013-Cui
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130214
Time               15.31
INSTRUM         avance400
PROBHD    5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8250.825 Hz
FIDRES          0.125898 Hz
AQ             3.9715922 sec
RG                   181
DW                60.600 usec
DE                 6.00 usec
TE                296.6 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                2.70 dB
SFO1         400.2324716 MHz

F2 - Processing parameters
SI                 32768
SF          400.2300015 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```



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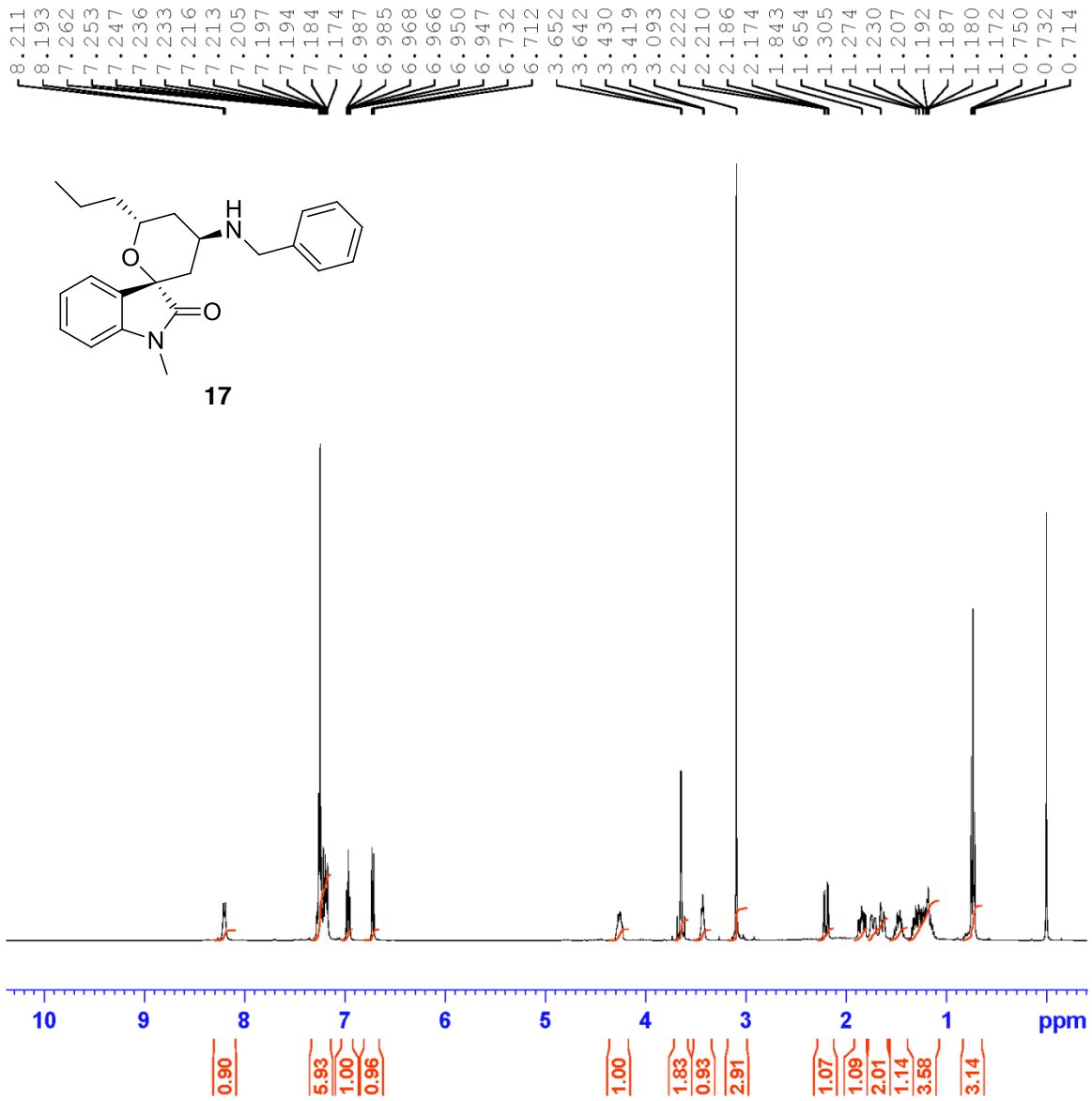
```
Current Data Parameters
NAME        14022013-Cui
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130214
Time               15.50
INSTRUM        avance400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3632196 sec
RG                 1024
DW                20.800 usec
DE                 6.00 usec
TE                297.3 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                10.00 usec
PL1               -2.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                2.70 dB
PL12              17.10 dB
PL13              17.10 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                 32768
SF           100.6379140 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

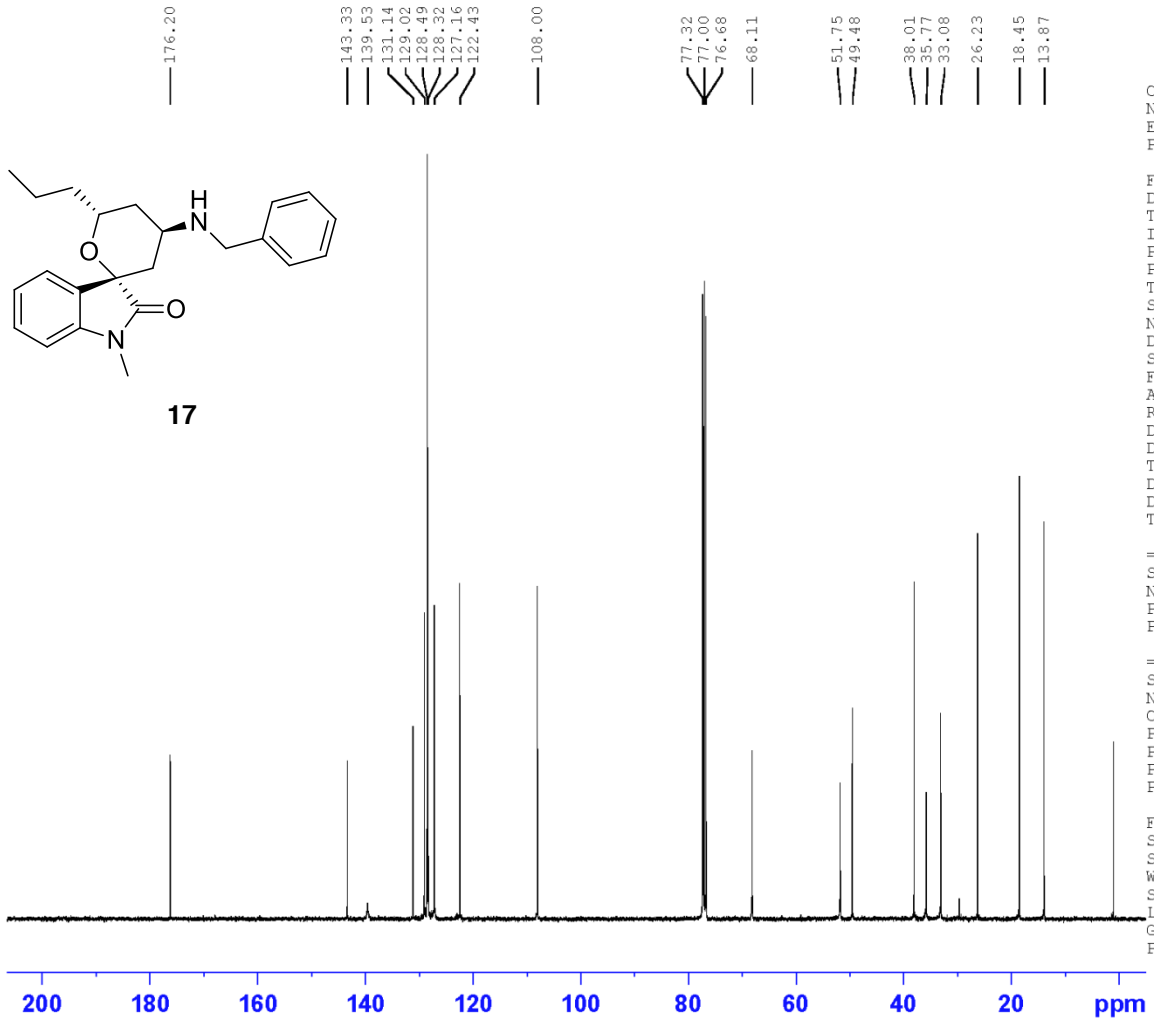



```
Current Data Parameters
NAME       YF-14-1211-59
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141211
Time                11.41
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894465 sec
RG                  27.4
DW                62.400 usec
DE                 6.50 usec
TE                298.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300441 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



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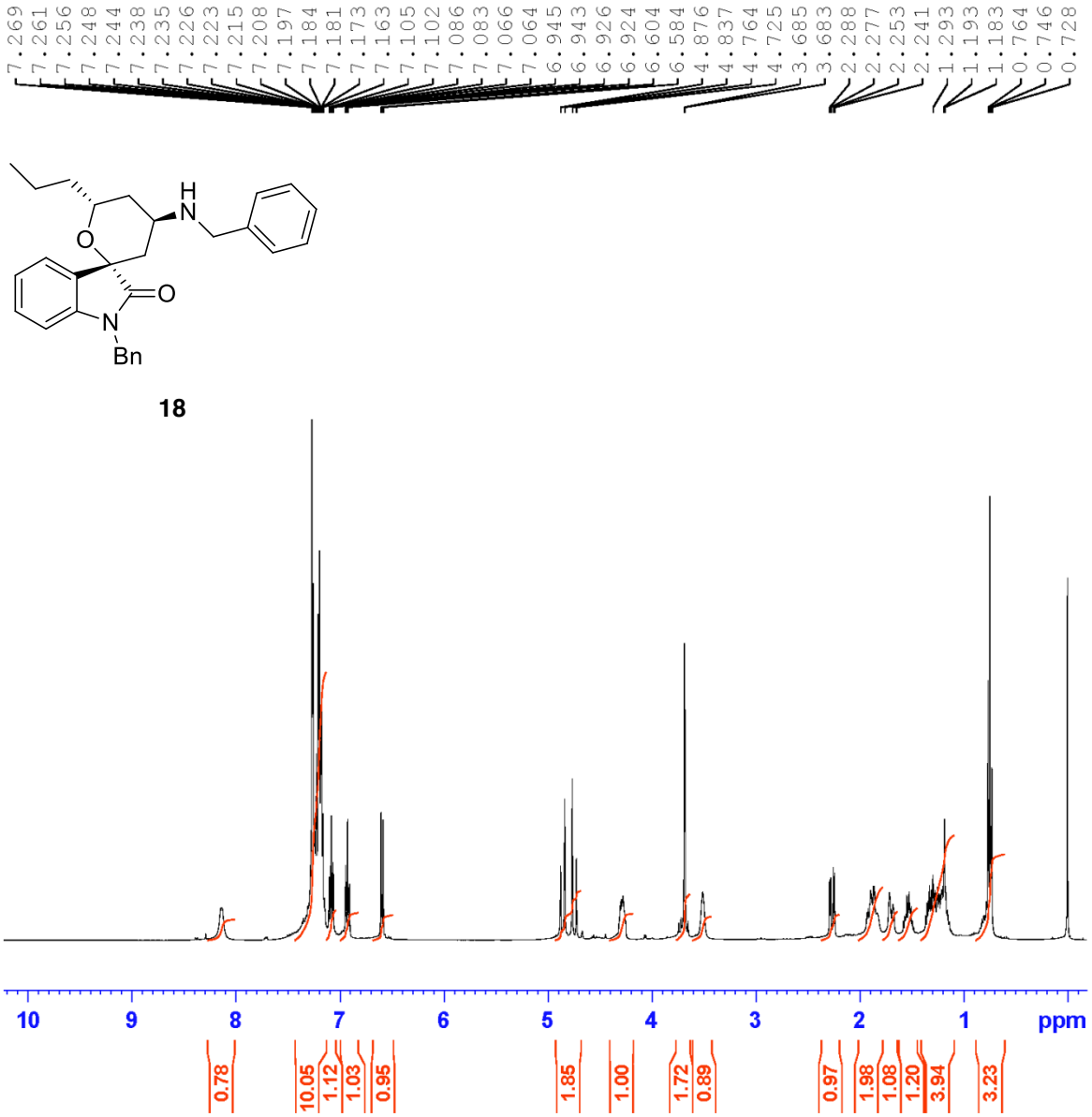
```
Current Data Parameters
NAME       YF-14-1211-59
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141211
Time               15.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                195.88
DW                20.800 usec
DE                 6.50 usec
TE                299.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                 10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                 32768
SF           100.6127772 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

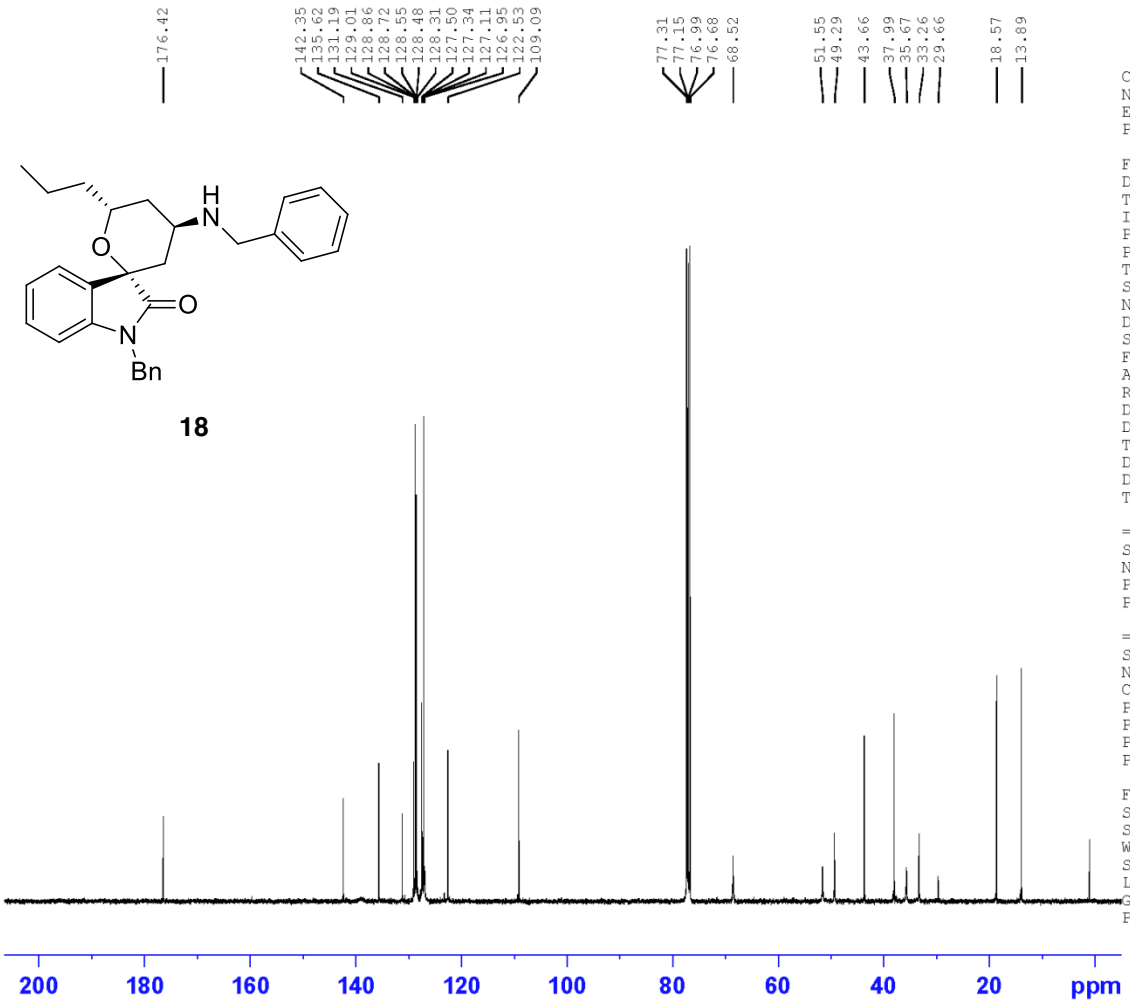



```
Current Data Parameters
NAME       YF-14-1211-60
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141211
Time              11.45
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894465 sec
RG                31.13
DW               62.400 usec
DE                6.50 usec
TE               298.5 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                65536
SF           400.1300445 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



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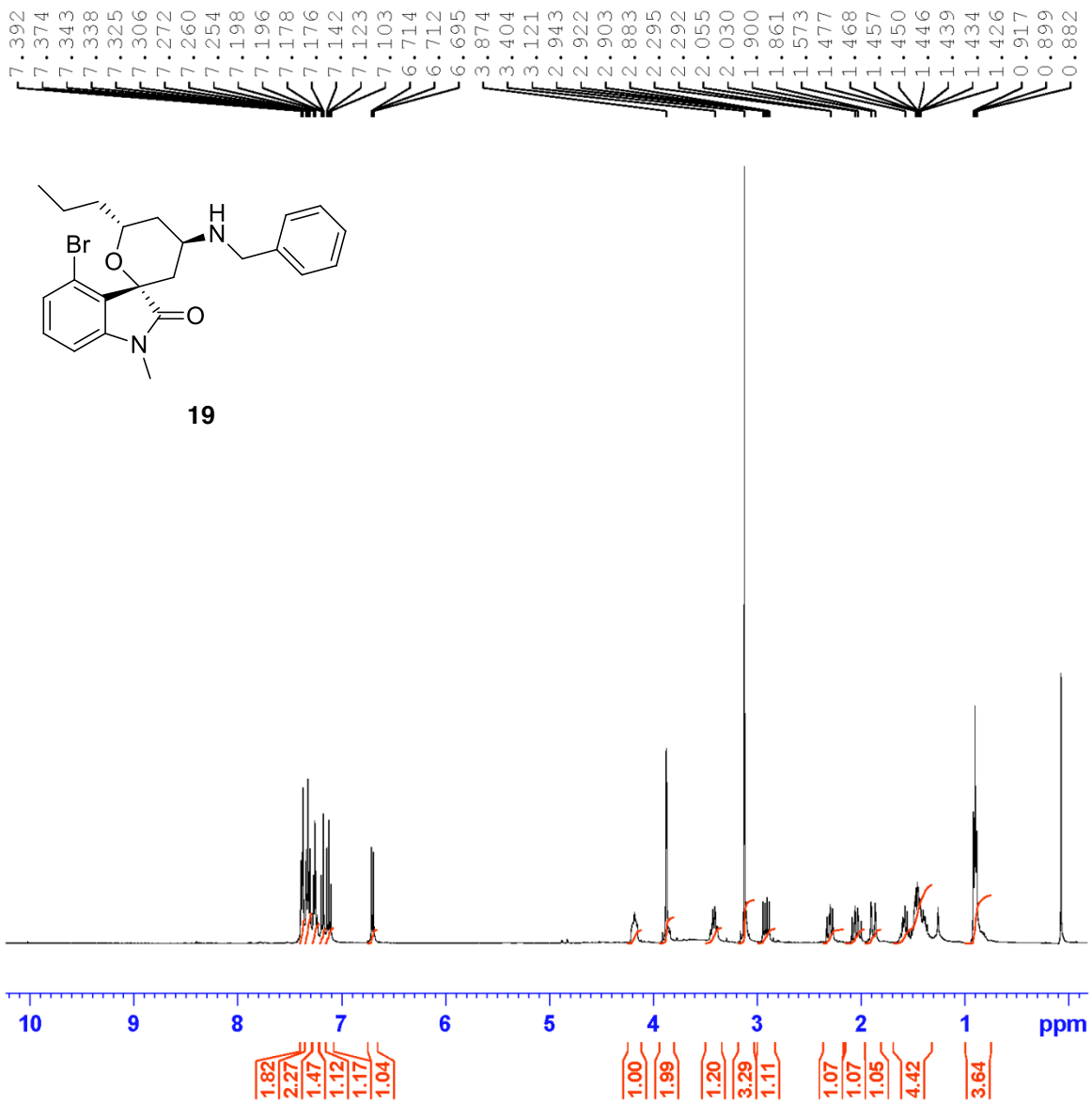
```
Current Data Parameters
NAME       YF-14-1211-60
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141211
Time               18.59
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               195.88
DW               20.800 usec
DE                6.50 usec
TE               299.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         70.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                 32768
SF          100.6127750 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



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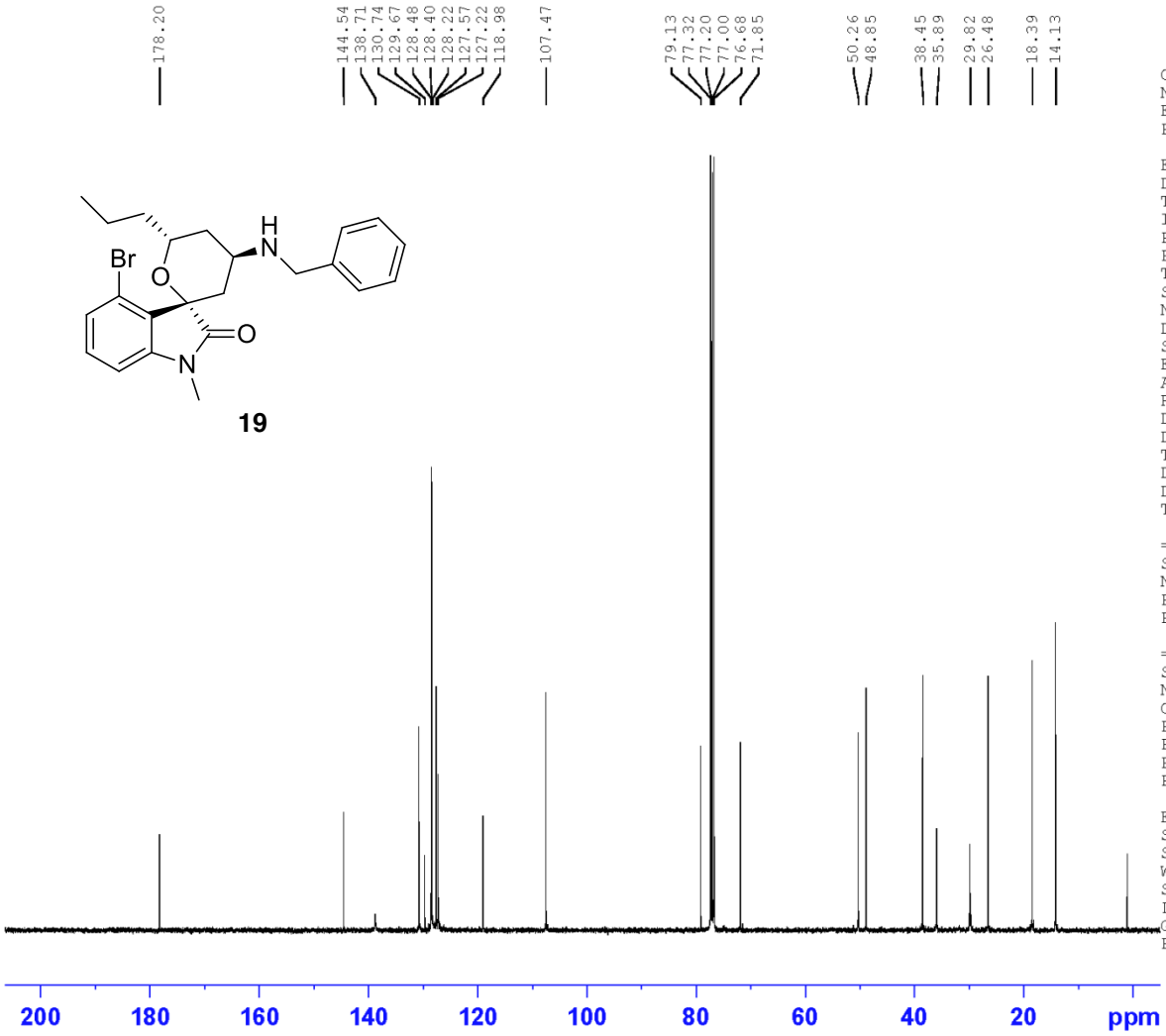
```
Current Data Parameters
NAME       YF-14-1211-61
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141211
Time               11.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 31.13
DW                62.400 usec
DE                 6.50 usec
TE                298.5 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                1H
P1                 15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300098 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```




```
Current Data Parameters
NAME      YF-14-1211-61
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20141211
Time              21.47
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               195.88
DW               20.800 usec
DE                6.50 usec
TE               299.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1               13C
P1               10.00 usec
PLW1        70.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2          8.00000000 W
PLW12         0.28125000 W
PLW13         0.28125000 W

F2 - Processing parameters
SI                32768
SF          100.6127743 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```