Organic acid induced olefination reaction of lactones

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Supporting Information

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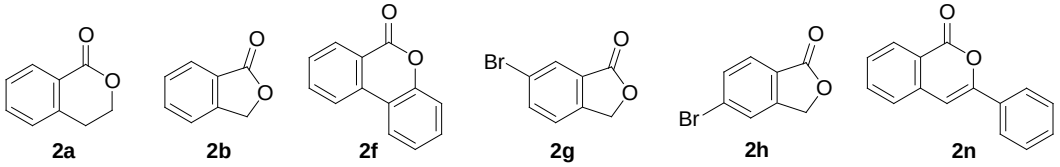
1. General and materials

All reactions were carried out under Ar atmosphere. Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were taken on a 400 MHz spectrometer, and chemical shifts were reported in parts per million (ppm) using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR, and $CDCl_3$ (77.01 ppm) for ^{13}C NMR as an internal standard, respectively. Mass spectra were recorded by an electrospray ionization-time of flight (ESI-TOF) mass spectrometer. Column chromatography was performed on neutral silica gel (Kanto Silica gel 60N, 63-210 μm and 40-100 μm) or basic alumina (ICN Alumina B–Super I). Tf_2CH_2 was supplied from Central Glass Co. and this compound can be also prepared by Waller's procedure in the laboratory.[1] $Tf_2CHCH_2CHTf_2$ **1a** and triple acid **1c** were prepared from Tf_2CH_2 by the reported procedure.[2]

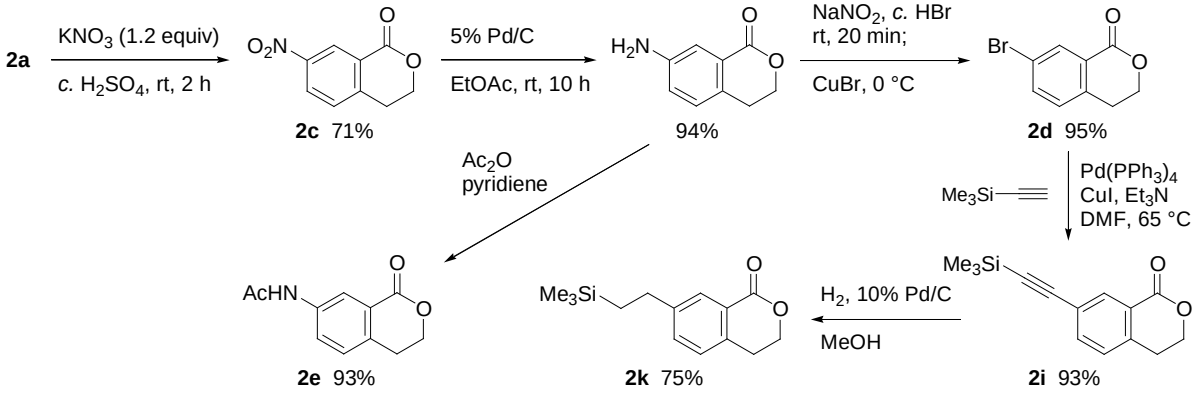
2. Preparation of lactone substrates

Isochroman-1-one **2a**, 6*H*-benzo[*c*]chromen-6-one **2f**,[3] and 6-bromoisobenzofuran-1(3*H*)-one **2g**[4], 3-phenyl-1*H*-isochromen-1-one **2n**[5] were prepared by the reported procedure. Isobenzofuran-1(3*H*)-one (phthalide) **2b** and 5-bromoisobenzofuran-1(3*H*)-one **2h**, and 6-aminoisobenzofuran-1(3*H*)-one were purchased.



7-Nitroisochroman-1-one **2c**, 7-bromoisocroman-1-one **2d**, *N*-(1-oxoisochroman-7-yl)acetamide **2e**,

7-((trimethylsilyl)ethynyl)isochroman-1-one **2i**, and 7-(2-(trimethylsilyl)ethyl)isochroman-1-one **2k** were prepared as follows.



7-Nitroisochroman-1-one (2c)

To a solution of potassium nitrate (2.5 g, 25 mmol) in concentrated sulfuric acid (6.0 mL), a suspension of isocroman-1-one **2a** (2.52 g, 17.0 mmol) in concentrated sulfuric acid (15 mL) was added at 0 °C. After being stirred for 1 h at room temperature, the reaction mixture was poured into iced water (15 mL) and filtrated through glass filter. The crude solid mass was carefully washed with water (15 mL x 3). The resulting solid was purified by column chromatography on silica gel (hexane/EtOAc = 1 : 1) to give nitrated 7-nitroisochroman-1-one **2c** in 71% yield (2.33 g, 12.1 mmol) as a sole product. Pale yellow crystals (EtOAc); Mp. 115-117 °C; IR (ATR) ν 3084, 1710, 1527, 1336, 1138, 851, 743, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (2H, t, J = 5.8 Hz), 4.60 (2H, t, J = 5.8 Hz), 7.50 (1H, d, J = 8.2 Hz), 8.39 (2H, d, J = 8.2 Hz), 8.95 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 66.8, 125.7, 126.8, 127.9, 128.8, 145.9, 147.7, 162.8; MS (ESI-TOF) m/z 216 $[M+Na]^+$; HRMS calcd for $C_9H_7NNaO_4$ $[M+Na]^+$, 216.0273; found, 216.0273. Anal. Calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. Found: C, 56.00; H, 3.59; N, 7.16.

7-Bromoisocroman-1-one (2d)

By stirring 7-nitroisochroman-1-one **2c** (1.31 g, 6.8 mmol) and 10% palladium on active carbon (50% wet, 200 mg) in EtOAc (50 mL) at room temperature for 10 h under H_2 atmosphere, hydrogenation completely proceeded. After removal of palladium on carbon by filtration, the reaction mixture was concentrated under reduced pressure to give 7-aminoisobenzofuran-1(3*H*)-one in 94% yield (1.05 g, 6.4 mmol). This lactone (718 mg, 4.4 mmol) was dissolved in a mixture of 46% aqueous hydrobromic acid (10 ml) and water (10 ml), then a solution of $NaNO_2$ (1.45 g, 21 mmol) in water (5 ml) was slowly added at 0 °C thereto. After being stirred for 20 min at 0 °C, a solution of copper(I) bromide (790 mg, 5.5 mmol) in 46% aqueous hydrobromic acid (5 ml) was added to the reaction mixture. The resulting mixture was stirred for 40 min at 80 °C and quenched with saturated NH_4Cl aqueous solution (50 mL). This mixture was extracted with EtOAc (50 mL x 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 1 : 1) to give 7-bromoisocroman-1-one **2d** in 95% yield (950 mg, 4.2 mmol). Colorless crystals (Et_2O); Mp. 79.0-81.5 °C; IR (ATR) ν 3073, 1709, 1595, 1422, 1271, 1066 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.02 (2H, t, J = 6.0 Hz), 4.54 (2H, t, J = 6.0 Hz), 7.16 (1H, d, J = 8.1 Hz), 7.66 (1H, d, J = 8.1 Hz), 8.24 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 67.1, 121.0, 126.7, 128.9, 132.7, 136.4, 138.2, 163.6; MS (ESI-TOF) m/z 227 $[M+H]^+$, 229 $[M+2+H]^+$; HRMS calcd for $C_9H_8BrO_2$

$[M+H]^+$, 226.9708; found, 226.9705. Anal. Calcd for $C_9H_7BrO_2$: C, 47.61; H, 3.11. Found: C, 47.39; H, 3.12.

***N*-(1-Oxoisochroman-7-yl)acetamide (2e)**

7-Aminoisocroman-1-one (163 mg, 1.00 mmol) was dissolved with pyridine (1.0 mL) and acetic anhydride (1.0 mL). After being stirred for 0.5 h at 40 °C, the reaction mixture was concentrated under reduced pressure. Chromatographic purification of the residue (silica gel, $CHCl_3$/MeOH = 10 : 1) gave *N*-(1-oxoisochroman-7-yl)acetamide **2e** in 93% yield (190 mg, 0.93 mmol). Colorless crystals ($CHCl_3$); Mp. 165-167 °C; IR (ATR) ν 3318, 1704, 1680, 1594, 1534, 1499, 1424, 1241, 1187, 839, 692, 537 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.22 (3H, s), 3.02 (2H, t, J = 6.0 Hz), 4.54 (2H, t, J = 6.0 Hz), 7.24 (1H, d, J = 8.3 Hz), 7.94 (1H, d, J = 2.1 Hz), 8.25 (1H, dd, J = 8.3, 2.1 Hz), 8.30 (1H, br, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 27.2, 67.7, 120.8, 125.3, 125.8, 128.1, 134.8, 138.2, 165.3, 169.1; MS (ESI-TOF) *m*/*z* 206 $[M+H]^+$; HRMS calcd for $C_{11}H_{12}NO_3$ $[M+H]^+$, 206.0817; found, 206.0819. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.02; H, 5.42; N, 6.90.

7-((Trimethylsilyl)ethynyl)isochroman-1-one (2i)

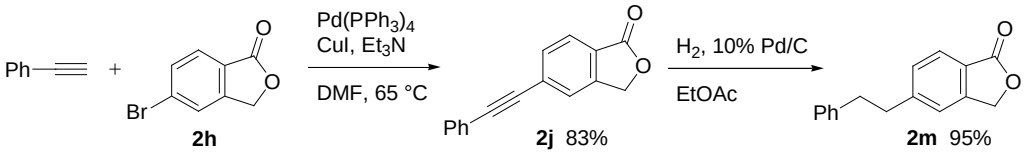
To a solution of 7-bromoisocroman-1-one **2i** (454 mg, 2.0 mmol), ethynyltrimethylsilane (786 mg, 8.0 mmol), and triethylamine (0.56 mL, 4.0 mmol) in DMF (4.0 mL), copper(I) iodide (133 mg, 0.7 mmol) and $Pd(PPh_3)_4$ (277 mg, 0.2 mmol) were added at room temperature. After being stirred for 17 h at 65 °C, the reaction mixture was poured into iced water (50 mL), extracted with Et_2O (30 mL x 3), and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give 7-((trimethylsilyl)ethynyl)isochroman-1-one **2i** in 97% yield (472 mg, 1.9 mmol). Colorless crystals (Et_2O); Mp. 104-105 °C; IR (ATR) ν 2157, 1718, 1610, 834, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (9H, s), 3.04 (2H, t, J = 5.8 Hz), 4.49-4.54 (2H, m), 7.19 (1H, d, J = 7.9 Hz), 7.57 (1H, d, J = 7.9 Hz), 8.17 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.2 (3C), 27.7, 67.1, 95.7, 103.2, 123.0, 125.4, 127.3, 133.8, 136.5, 139.4, 164.2; MS (ESI-TOF) *m*/*z* 245 $[M+H]^+$; HRMS calcd for $C_{14}H_{17}O_2Si$ $[M+H]^+$, 245.0998; found, 245.0990.

7-(2-(Trimethylsilyl)ethyl)isochroman-1-one (2k)

By stirring alkynylisochroman-1-one **2d** (245 mg, 1.0 mmol) and 10% palladium on active carbon (50% wet, 100 mg) in MeOH (5.0 mL) at room temperature for 18 h under H_2 atmosphere, hydrogenation completely proceeded. The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give 5-phenethylisobenzofuran-1(3*H*)-one **2k** in 75% yield (186 mg, 0.75 mmol). Colorless oil; IR (ATR) ν 1721, 1243, 858, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (9H, s), 0.81-0.88 (2H, m), 2.59-2.65 (2H, m), 3.00 (2H, t, J = 6.0 Hz), 4.49 (2H, t, J = 6.0 Hz), 7.14 (1H, d, J = 7.8 Hz), 7.35 (1H, d, J = 7.8 Hz), 7.92 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.9 (3C), 18.6, 27.4, 29.6, 67.3, 125.0, 127.1, 129.3, 133.3, 136.6, 145.0, 165.4; MS (ESI-TOF) *m*/*z* 249 $[M+H]^+$; HRMS calcd for $C_{14}H_{21}O_2Si$ $[M+H]^+$, 249.1311; found, 249.1316.

5-(Phenylethynyl)isobenzofuran-1(3*H*)-one **2j** and 5-phenethylisobenzofuran-1(3*H*)-one **2m** were prepared as

follows.



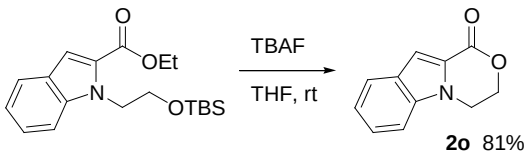
5-(Phenylethynyl)isobenzofuran-1(3*H*)-one (2j)

To a solution of 5-bromoisobenzofuran-1(3*H*)-one **2h** (0.33 g, 1.6 mmol), phenylacetylene (0.63 g, 6.2 mmol), CuI (72.3 mg, 0.38 mmol), and Et_3N (0.56 mL, 4.0 mmol) in DMF (3.0 mL), $Pd(PPh_3)_4$ (215 mg, 0.19 mmol) was added at room temperature. After being stirred at 65 °C for 5 h, the reaction mixture was quenched with H_2O (25 mL), and extracted with Et_2O (30 mL x 3). Combined organic layer was washed with brine (15 mL), dried over anhydrous Na_2SO_4, and evaporated. The oily residue was purified by flash column chromatography (hexane/EtOAc = 5 : 1) to give 5-(phenylethynyl)isobenzofuran-1(3*H*)-one **2j** in 83% yield (0.30 g, 1.3 mmol). Pale yellow crystals (EtOAc); Mp. 148-150 °C; IR (ATR) ν 2201, 1745, 1611, 1344, 1046, 997, 756, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.33 (2H, s), 7.36-7.42 (3H, m), 7.53-7.58 (2H, m), 7.64 (1H, s), 7.68 (1H, brd, J = 7.9 Hz), 7.91 (1H, d, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.3, 88.1, 93.3, 122.3, 124.9, 125.0, 125.7, 128.5 (2C), 129.1, 129.5, 131.8 (2C), 132.5, 146.6, 170.4; MS (ESI-TOF) m/z 235 $[M+H]^+$; HRMS calcd for $C_{16}H_{11}O_2$ $[M+H]^+$, 235.0759; found, 235.0767. Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.20; H, 4.25.

5-Phenethylisobenzofuran-1(3*H*)-one (2m)

By stirring alkynylisobenzofuranone **2j** (234.1 mg, 1.0 mmol) and 10% palladium on active carbon (50% wet, 100 mg) in EtOAc (20 mL) at room temperature for 3 h under H_2 atmosphere, hydrogenation completely proceeded. The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give 5-phenethylisobenzofuran-1(3*H*)-one **2m** in 95% yield (226.1 mg, 0.95 mmol). Pale yellow crystals ($CHCl_3$); Mp. 113-115 °C; IR (ATR) ν 1744, 1616, 1597, 1046, 997, 697, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.96 (2H, dd, J = 8.2, 6.0 Hz), 3.06 (2H, dd, J = 8.2, 6.0 Hz), 5.26 (2H, s), 7.14 (2H, d, J = 7.2 Hz), 7.18-7.36 (5H, m), 7.81 (1H, d, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.6, 38.2, 69.5, 122.0, 123.7, 125.6, 126.3, 128.4 (2C), 128.5 (2C), 129.8, 140.7, 147.1, 148.9, 171.1; MS (ESI-TOF) m/z 239 $[M+H]^+$; HRMS calcd for $C_{16}H_{15}O_2$ $[M+H]^+$, 239.1072; found, 239.1078.

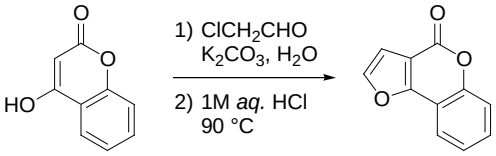
3,4-Dihydro-1*H*-[1,4]oxazino[4,3-*a*]indol-1-one (2o)



To a solution of ethyl 1-(2-(*tert*-butyldimethylsilyloxy)ethyl)-1*H*-indole-2-carboxylate[6] (3.48 g, 10 mmol) in THF (100 mL), tetrabutylammonium fluroride (1.0 M in THF, 20 mL, 20 mmol) was added at 0 °C. After being stirred for 2 h at room temperature, the reaction mixture was concentrated under reduced pressure. The resulting mixture was poured into H_2O (25 mL) and extracted with EtOAc (25 mL x 3). Combined organic

layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel to give 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indol-1-one **2o** in 81% yield (8.1 mmol, 1.52 g). Colorless crystals (EtOAc); Mp. 169-171 °C; IR (ATR) ν 2924, 1703, 1089, 751, 433 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.35 (2H, t, J = 5.2 Hz), 4.76 (2H, t, J = 5.2 Hz), 7.19-7.25 (1H, m), 7.35 (1H, d, J = 8.4 Hz), 7.39-7.45 (1H, m), 7.47 (1H, s), 7.75 (1H, d, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 66.6, 109.9, 110.3, 121.5, 123.2, 123.6, 126.1, 126.9, 136.6, 159.6; MS (ESI-TOF) m/z 188 $[M+H]^+$; HRMS calcd for $C_{11}H_{10}NO_2$ $[M+H]^+$, 188.0712; found, 188.0717. Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.66; H, 4.80; N, 7.65.

4*H*-furo[3,2-*c*]chromen-4-one (2p)

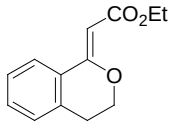


2p 45%

This compound was prepared by modifying the procedure reported by Majumdar.[7] To a mixture of K_2CO_3 (2.76 g, 20 mmol) and 4-hydroxycoumarin (1.62 g, 10 mmol) in water (20 mL), chloroacetaldehyde (40 % in water, 2.46 mL, 15 mmol) was slowly added. After being stirred for 1.5 h at room temperature, the precipitated solid was collected by filtration. The precipitate was treated by 1 M aqueous HCl (30 mL) for 1 h at 90 °C. The reaction mixture was extracted with EtOAc (30 mL x 3) and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure to give 4*H*-furo[3,2-*c*]chromen-4-one **2p** in 45% yield (0.84 g, 4.5 mmol). Colorless crystals (Et_2O); Mp. 81.0-82.5 °C; IR (ATR) ν 1718, 959, 750, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 (1H, d, J = 2.1 Hz), 7.34-7.39 (1H, m), 7.46 (1H, dd, J = 8.4, 0.7 Hz), 7.53 (1H, ddd, J = 8.4, 7.2, 1.4 Hz), 7.66 (1H, d, J = 2.1 Hz), 7.89 (1H, dd, J = 7.8, 1.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.6, 110.6, 112.8, 117.3, 120.9, 124.5, 130.7, 144.8, 152.5, 157.6, 158.3; MS (ESI-TOF) m/z 187 $[M+H]^+$; HRMS calcd for $C_{11}H_7O_3$ $[M+H]^+$, 187.0395; found, 187.0389.

3. Carbon acid induced olefination reaction of lactones

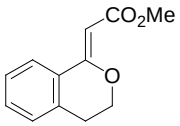
(*Z*)-Ethyl 2-(isochroman-1-ylidene)acetate (4aa)



To a solution of isochroman-1-one **2a** (73.8 mg, 0.50 mmol) and carbon acid **1c** (10.1 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (202 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump. After being stirred for additional 3 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4aa** in 85% yield (91.2 mg, 0.42 mmol). Pale yellow oil; IR (ATR) ν 2979, 1707, 1618, 1150, 1126, 1090, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, J = 7.2 Hz), 2.97 (2H, t, J = 5.7 Hz), 4.19 (2H, q, J = 7.2 Hz), 4.35 (2H,

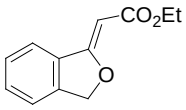
t, *J* = 5.7 Hz), 5.60 (1H, s), 7.20 (1H, brd, *J* = 7.5 Hz), 7.26-7.31 (1H, m), 7.37 (1H, td, *J* = 7.5, 1.3 Hz), 7.64 (1H, d, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 28.6, 59.2, 65.6, 92.0, 125.4, 127.2, 127.9, 128.5, 130.4, 135.6, 162.0, 165.8; MS (ESI-TOF) *m*/*z* 241 $[M+Na]^+$; HRMS calcd for $C_{13}H_{14}NaO_3$ $[M+Na]^+$, 241.0841; found, 241.0837. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.38; H, 6.50.

(*Z*)-Methyl 2-(isochroman-1-ylidene)acetate (4ab)



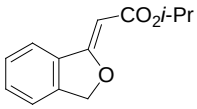
To a solution of isochroman-1-one **2a** (75.8 mg, 0.51 mmol) and carbon acid **1c** (9.8 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyldimethyl(1-methoxyvinyloxy)silane (188 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 3 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give the vinyl ether **4ab** in 82% yield (85.6 mg, 0.40 mmol). Pale yellow oil; IR (ATR) ν 2948, 1709, 1616, 1153, 1125, 1089, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (2H, t, *J* = 5.6 Hz), 3.68 (3H, s), 4.30 (1H, t, *J* = 5.6 Hz), 5.56 (1H, s), 7.15 (1H, d, *J* = 7.5 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 7.33 (1H, t, *J* = 7.5 Hz), 7.58 (1H, d, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 50.7, 65.6, 91.6, 125.4, 127.2, 127.9, 128.4, 130.5, 135.6, 162.0, 166.2; MS (ESI-TOF) *m*/*z* 205 $[M+H]^+$; HRMS calcd for $C_{12}H_{13}O_3$ $[M+H]^+$, 205.0865; found, 205.0864.

(*Z*)-Ethyl 2-(isobenzofuran-1(3*H*)-ylidene)acetate (4ba)



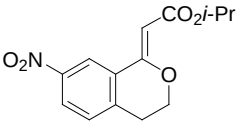
To a solution of isobenzofuran-1(3*H*)-one **2b** (68.0 mg, 0.51 mmol) and carbon acid **1c** (9.9 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (201 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 3 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give the vinyl ether **4ba** in 83% yield (85.9 mg, 0.42 mmol). The structure of the product was also confirmed by comparison of ^{1}H and ^{13}C NMR spectra in the literature.[8] Pale yellow oil; IR (ATR) ν 2980, 1702, 1635, 1146, 1065, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (3H, t, *J* = 7.1 Hz), 4.20 (2H, q, *J* = 7.1 Hz), 5.50 (1H, s), 5.55 (2H, s), 7.36-7.41 (2H, m), 7.44-7.50 (1H, m), 7.56 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 59.4, 76.5, 86.0, 121.2, 121.4, 128.4, 131.1, 132.9, 141.3, 166.2, 167.9; MS (ESI-TOF) *m*/*z* 227 $[M+Na]^+$; HRMS calcd for $C_{12}H_{12}NaO_3$ $[M+Na]^+$, 227.0680; found, 227.0684. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.68; H, 5.70.

(*Z*)-Isopropyl 2-(isobenzofuran-1(3*H*)-ylidene)acetate (4bc)



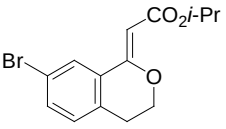
To a solution of isobenzofuran-1(3*H*)-one **1b** (67.2 mg, 0.50 mmol) and carbon acid **1c** (10.0 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-isopropyloxyvinyloxy)dimethylsilane (218 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 4 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give the vinyl ether **4bc** in 78% yield (85.1 mg, 0.39 mmol). Pale yellow oil; IR (ATR) ν 2981, 1732, 1102, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (3H, t, J = 7.1 Hz), 4.20 (2H, q, J = 7.1 Hz), 5.50 (1H, s), 5.55 (2H, s), 7.36-7.41 (2H, m), 7.44-7.50 (1H, m), 7.56 (1H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 59.4, 76.5, 86.0, 121.2, 121.4, 128.4, 131.1, 132.9, 141.3, 166.2, 167.9; MS (ESI-TOF) *m*/*z* 241 $[M+Na]^+$; HRMS calcd for $C_{13}H_{14}NaO_3$ $[M+Na]^+$, 241.0841; found, 241.0850. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.24; H, 6.30.

(*Z*)-Isopropyl 2-(7-nitroisochroman-1-ylidene)acetate (4cc)



To a solution of 7-nitroisochroman-1-one **2c** (47.6 mg, 0.25 mmol) and carbon acid **1c** (4.8 mg, 5 μmol) in CH_2Cl_2 (0.75 mL), a solution of *tert*-butyl(1-isopropyloxyvinyloxy)dimethylsilane (108 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 5 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 1 : 1) to give the vinyl ether **4cc** in 83% yield (57.0 mg, 0.21 mmol). Colorless crystals ($CHCl_3$); Mp. 85.5-88.0 °C; IR (ATR) ν 2982, 1703, 1620, 1518, 1342, 1104, 809, 793, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (6H, d, J = 6.2 Hz), 3.06 (2H, t, J = 5.7 Hz), 4.35 (2H, t, J = 5.7 Hz), 5.07 (1H, sept, J = 6.2 Hz), 5.68 (1H, s), 7.39 (1H, d, J = 8.4 Hz), 8.17 (1H, dd, J = 8.4, 2.1 Hz), 8.49 (1H, d, J = 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9 (2C), 28.9, 65.0, 66.8, 95.1, 120.5,124.5, 129.4, 130.0, 142.3, 147.3, 159.2, 164.6; MS (ESI-TOF) *m*/*z* 278 $[M+H]^+$; HRMS calcd for $C_{14}H_{16}NO_5$ $[M+H]^+$, 278.1028; found, 278.1037. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.60; H, 5.49; N, 5.15.

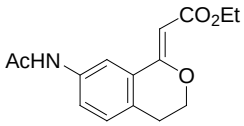
(*Z*)-Isopropyl 2-(7-bromoisochroman-1-ylidene)acetate (4dc)



To a solution of 7-bromoisochroman-1-one **2d** (113.4 mg, 0.50 mmol) and carbon acid **1** (10.1 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-isopropyloxyvinyloxy)dimethylsilane (216 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature

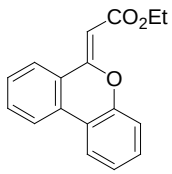
for 1 h. After being stirred for additional 6 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 2 : 1) to give the vinyl ether **4dc** in 84% yield (129.9 mg, 0.42 mmol). Colorless crystals (EtOAc); Mp. 98.5-99.5 °C; IR (ATR) ν 2982, 1698, 1612, 1161, 1091, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (6H, d, J = 6.2 Hz), 2.87 (2H, t, J = 5.6 Hz), 4.27 (2H, t, J = 5.6 Hz), 5.03 (1H, sept, J = 6.2 Hz), 5.49 (1H, s), 7.03 (1H, d, J = 8.1 Hz), 7.41 (1H, d, J = 8.1 Hz), 7.72 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 28.1, 65.4, 66.4, 93..6, 120.7, 128.1, 129.6, 130.4, 133.1, 134.4, 160.1, 164.9; MS (ESI-TOF) m/z 311 $[M+H]^+$, 313 $[M+2+H]^+$; HRMS calcd for $C_{14}H_{16}BrO_3$ $[M+H]^+$, 311.0283; found, 311.0292. Anal. Calcd for $C_{14}H_{15}BrO_3$: C, 54.04; H, 4.86. Found: C, 54.32; H, 4.71.

(*Z*)-Ethyl 2-(7-acetamidoisochroman-1-ylidene)acetate (4ea)



To a solution of *N*-(1-oxoisochroman-7-yl)acetamide **2e** (51.1 mg, 0.25 mmol) and carbon acid **1c** (5.1 mg, 5 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (152 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 4 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel ($CHCl_3$/MeOH = 10 : 1) to give the vinyl ether **4ea** in 87% yield (59.9 mg, 0.22 mmol). Colorless crystals ($CHCl_3$); Mp. 140-142 °C; IR (ATR) ν 3262, 2976, 1705, 1656, 1605, 1581, 1150, 1091, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 2.15 (3H, s), 2.81 (2H, t, J = 5.6 Hz), 4.13 (2H, q, J = 7.1 Hz), 4.13-4.17 (2H, m), 7.05 (1H, d, J = 8.2 Hz), 7.53 (1H, dd, J = 8.2, 1.8 Hz), 7.87 (1H, d, J = 1.8 Hz), 8.68 (1H, br, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.2, 28.0, 59.4, 65.6, 92.2, 116.7, 122.6, 128.4, 128.6, 131.6, 137.6, 162.0, 166.3, 169.1; MS (ESI-TOF) m/z 276 $[M+H]^+$; HRMS calcd for $C_{15}H_{18}NO_4$ $[M+H]^+$, 276.1236; found, 276.1230.

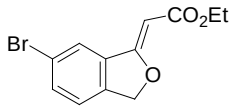
(*Z*)-Ethyl 2-(6*H*-benzo[*c*]chromen-6-ylidene)acetate (4fa)



To a solution of 6*H*-benzo[*c*]chromen-6-one **2f** (98.5 mg, 0.50 mmol) and carbon acid **1c** (9.9 mg, 10 μmol) in CH_2Cl_2 (0.75 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (201 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 8 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on alumina (hexane/EtOAc = 5 : 1) to give the vinyl ether **4fa** in 85% yield (113.6 mg, 0.43 mmol). Pale yellow oil; IR (ATR) ν 2970, 1695, 1627, 1588, 1277, 1143, 1107, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7.1 Hz), 4.25 (2H, q, J =

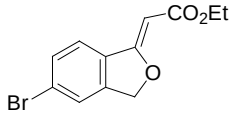
7.1 Hz), 5.85 (1H, s), 7.15-7.21 (1H, m), 7.29-7.42 (3H, m), 7.53-7.59 (1H, m), 7.78 (1H, dd, *J* = 8.1, 1.0 Hz), 7.88 (1H, dd, *J* = 7.9, 1.4 Hz), 7.96 (1H, brd, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 59.5, 91.3, 117.4, 118.3, 121.9, 122.2, 123.6, 124.3, 124.8, 128.8, 129.4, 130.1, 131.8, 150.6, 158.8, 165.4; MS (ESI-TOF) *m*/*z* 267 $[M+H]^+$; HRMS calcd for $C_{17}H_{15}O_3$ $[M+H]^+$, 267.1021; found, 267.1024. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30;. Found: C, 76.38; H, 5.27.

(*Z*)-Ethyl 2-(6-bromoisobenzofuran-1(3*H*)-ylidene)acetate (4ga)



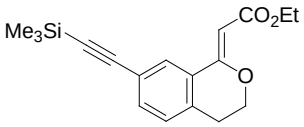
To a solution of 6-bromoisobenzofuran-1(3*H*)-one **2g** (105.5 mg, 0.50 mmol) and carbon acid **1c** (9.9 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (202 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 7 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4ga** in 72% yield (101.7 mg, 0.36 mmol). Colorless crystals (EtOAc); Mp. 105-107 °C; IR (ATR) ν 1701, 1639, 1154, 1078, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, *J* = 7.1 Hz), 4.21 (2H, q, *J* = 7.1 Hz), 5.48 (1H, s), 5.51 (2H, s), 7.28 (1H, d, *J* = 8.1 Hz), 7.59 (1H, brd, *J* = 8.1 Hz), 7.70 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 59.7, 76.3, 87.2, 122.5, 122.9, 124.5, 134.3, 135.2, 140.1, 165.9, 166.3; MS (ESI-TOF) *m*/*z* 283 $[M+H]^+$, 285 $[M+2+H]^+$; HRMS calcd for $C_{12}H_{12}BrO_3$ $[M+H]^+$, 282.9970; found, 282.9974. Anal. Calcd for $C_{12}H_{11}BrO_3$: C, 50.91; H, 3.92. Found: C, 50.77; H, 3.88.

(*Z*)-Ethyl 2-(5-bromoisobenzofuran-1(3*H*)-ylidene)acetate (4ha)



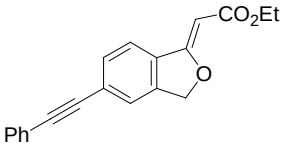
To a solution of 5-bromoisobenzofuran-1(3*H*)-one **2h** (104.5 mg, 0.49 mmol) and carbon acid **1c** (10.1 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (200 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 7 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4ha** in 75% yield (104.0 mg, 0.37 mmol). Colorless crystals (EtOAc); Mp. 121-124 °C; IR (ATR) ν 1709, 1654, 1145, 1059, 789 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, *J* = 7.1 Hz), 4.21 (2H, q, *J* = 7.1 Hz), 5.49 (1H, s), 5.54 (2H, s), 7.43 (1H, d, *J* = 8.2 Hz), 7.51-7.59 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 59.6, 75.8, 86.7, 122.67, 124.8, 125.7, 132.0, 132.1, 143.1, 166.0, 166.8; MS (ESI-TOF) *m*/*z* 305 $[M+Na]^+$, 307 $[M+2+Na]^+$; HRMS calcd for $C_{12}H_{11}BrNaO_3$ $[M+Na]^+$, 304.9789; found, 304.9790.

(*Z*)-Ethyl 2-(7-((trimethylsilyl)ethynyl)isochroman-1-ylidene)acetate (4ia)



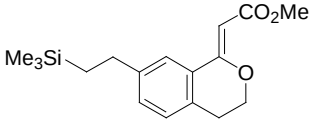
To a solution of 7-((trimethylsilyl)ethynyl)isochroman-1-one **2i** (60.7 mg, 0.25 mmol) and carbon acid **1c** (4.9 mg, 5 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyldimethyl(1-ethoxyvinyloxy)silane (102 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 5 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4ia** in 70% yield (54.4 mg, 0.17 mmol). Colorless crystals (Et_2O); Mp. 90.5-93.0 °C; IR (ATR) ν 2956, 2160, 1703, 1616, 1601, 1149, 1084, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.26 (9H, s), 1.29 (3H, t, J = 7.1 Hz), 2.95 (2H, t, J = 5.5 Hz), 4.18 (2H, q, J = 7.1 Hz), 4.32 (2H, t, J = 5.5 Hz), 5.61 (1H, s), 7.13 (1H, d, J = 7.8 Hz), 7.43 (1H, d, J = 7.8 Hz), 7.76 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.2 (3C), 14.4, 28.6, 59.4, 65.5, 92.8, 95.0, 103.8, 122.4, 128.1, 128.7, 129.0, 133.5, 135.9, 161.1, 165.7; MS (ESI-TOF) m/z 315 $[M+H]^+$; HRMS calcd for $C_{18}H_{23}O_3Si$ $[M+H]^+$, 315.1416; found, 315.1430. Anal. Calcd for $C_{18}H_{22}O_3Si$: C, 68.75; H, 7.05. Found: C, 68.99; H, 7.26.

(*Z*)-Ethyl 2-(5-(phenylethynyl)isobenzofuran-1(3*H*)-ylidene)acetate (4ja)



To a solution of 5-(phenylethynyl)isobenzofuran-1(3*H*)-one **2j** (58.7 mg, 0.25 mmol) and carbon acid **1c** (5.1 mg, 5 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyldimethyl(1-ethoxyvinyloxy)silane (101 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 7 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4ja** in 70% yield (53.1 mg, 0.17 mmol). Colorless crystals (Et_2O); Mp. 143-146 °C; IR (ATR) ν 1706, 1650, 1153, 1143, 1066, 794, 757, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.1 Hz), 4.22 (2H, q, J = 7.1 Hz), 5.52 (1H, s), 5.55 (2H, s), 7.32-7.40 (3H, m), 7.50-7.59 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 59.6, 76.2, 86.8, 88.5, 92.1, 121.3, 122.5, 124.2, 126.5, 128.4, 128.8, 131.7, 131.9, 132.6, 141.4, 166.1, 167.2; MS (ESI-TOF) m/z 327 $[M+Na]^+$; HRMS calcd for $C_{20}H_{16}NaO_3$ $[M+Na]^+$, 327.0997; found, 327.1011. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.60; H, 5.49.

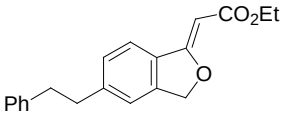
(*Z*)-Methyl 2-(7-(2-(trimethylsilyl)ethyl)isochroman-1-ylidene)acetate (4kb)



To a solution of 7-(2-(trimethylsilyl)ethyl)isochroman-1-one **2k** (63.2 mg, 0.25 mmol) and carbon acid **1c** (5.0

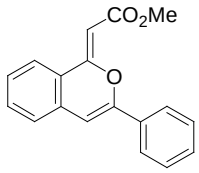
mg, 5 μmol) in CH_2Cl_2 (0.5 mL), a solution of *tert*-butyldimethyl(1-methoxyvinyloxy)silane (94 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 5 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4kb** in 72% yield (55.8 mg, 0.18 mmol). Colorless oil; IR (ATR) ν 2949, 1715, 1622, 1604, 1246, 1152, 1091, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.02 (9H, s), 0.81-0.88 (2H, m), 2.57-2.64 (2H, m), 2.92 (2H, t, J = 5.6 Hz), 3.72 (2H, s), 4.32 (2H, t, J = 5.6 Hz), 5.60 (1H, s), 7.09 (1H, d, J = 7.8 Hz), 7.21 (1H, brd, J = 7.8 Hz), 7.46 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0, 20.5, 30.1, 31.6, 52.6, 67.7, 93.2, 126.4, 129.7, 130.1, 132.2, 134.7, 146.3, 164.3, 168.2; MS (ESI-TOF) *m*/*z* 305 $[M+H]^+$; HRMS calcd for $C_{17}H_{25}O_3Si$ $[M+H]^+$, 305.1573; found, 305.1581.

(*Z*)-Ethyl 2-(5-phenethylisobenzofuran-1(3*H*)-ylidene)acetate (4ma)



To a solution of 5-phenethylisobenzofuran-1(3*H*)-one **2m** (59.7 mg, 0.25 mmol) and carbon acid **1c** (5.0 mg, 5 μmol) in chloroform (1.5 mL), a solution of *tert*-butyl(1-ethoxyvinyloxy)dimethylsilane (101 mg, 0.50 mmol) in chloroform (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 8 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the vinyl ether **4ma** in 63% yield (48.6 mg, 0.16 mmol). Colorless oil; IR (ATR) ν 2935, 1695, 1624, 1153, 1063, 793 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (3H, t, J = 7.1 Hz), 2.90-2.96 (2H, m), 2.97-3.04 (2H, m), 4.22 (2H, q, J = 7.1 Hz), 5.48 (1H, s), 5.52 (2H, s), 7.11-7.18 (3H, m), 7.19-7.23 (2H, m), 7.28 (2H, t, J = 7.0 Hz), 7.48 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 37.6, 38.0, 59.4, 76.4, 85.5, 121.2, 121.3, 126.2, 128.4 (4C), 129.1, 131.0, 140.9, 141.8, 145.9, 166.4, 168.2; MS (ESI-TOF) *m*/*z* 309 $[M+H]^+$; HRMS calcd for $C_{20}H_{21}O_3$ $[M+H]^+$, 309.1491; found, 304.1498.

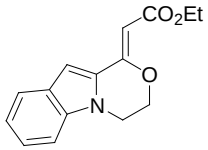
(*Z*)-Methyl 2-(3-phenyl-1*H*-isochromen-1-ylidene)acetate (4nb)



To a solution of 3-phenyl-1*H*-isochromen-1-one **2n** (108.7 mg, 0.49 mmol) and carbon acid **1c** (9.9 mg, 10 μmol) in CH_2Cl_2 (0.75 mL), a solution of *tert*-butyldimethyl(1-methoxyvinyloxy)silane (188 mg, 1.00 mmol) in CH_2Cl_2 (0.50 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred at the same temperature for 1 h. After being stirred for additional 8 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on alumina (hexane/EtOAc = 5 : 1) to give the vinyl ether **4nb** in 81% yield (110.2 mg, 0.40 mmol). Colorless oil; IR (ATR) ν 2946, 1702, 1649, 1590, 1271, 1148, 1127, 1093, 761, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (3H, s), 5.82

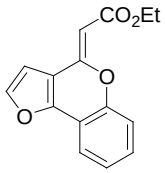
(1H, s), 6.68 (1H, s), 7.23-7.34 (2H, m), 7.37-7.51 (4H, m), 7.67-7.72 (1H, m), 8.09 (2H, d, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.8, 88.8, 100.4 (2C), 123.2, 123.9, 125.0 (2C), 126.2, 128.0, 128.7 (2C), 129.6, 132.0, 132.1, 151.6, 160.4, 166.0; MS (ESI-TOF) m/z 279 $[M+H]^+$; HRMS calcd for $C_{18}H_{15}O_3$ $[M+H]^+$, 279.1021; found, 279.1022.

(*Z*)-Ethyl 2-(3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indol-1-ylidene)acetate (4oa)



To a solution of 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indol-1-one **2o** (93.5 mg, 0.50 mmol) and carbon acid **1c** (10.1 mg, 10 μmol) in CH_2Cl_2 (1.5 mL), a solution of *tert*-butyldimethyl(1-ethoxyvinyloxy)silane (202 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 4 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (hexane/EtOAc = 1 : 1) to give the vinyl ether **4oa** in 90% yield (116.7 mg, 0.45 mmol). Pale yellow crystals (EtOAc); Mp. 85.5-87.0 °C; IR (ATR) ν 2980, 1686, 1613,1140, 1087, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.1 Hz), 4.17-4.27 (2H, m), 4.19 (2H, q, J = 7.1 Hz), 4.50 (2H, t, J = 5.0 Hz), 5.71 (1H, s), 6.91 (1H, s), 7.10-7.19 (1H, m), 7.23-7.30 (2H, m), 7.62 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143, 40.2, 59.4, 65.6, 93.0, 101.6, 108.8, 120.9, 121.7, 123.8, 127.2, 127.3, 136.4, 156.3, 165.3; MS (ESI-TOF) m/z 258 $[M+H]^+$; HRMS calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$, 258.1130; found, 258.1133.

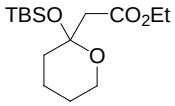
(Z)-Ethyl 2-(4*H*-furo[3,2-*c*]chromen-4-ylidene)acetate (4pa)



To a solution of 4*H*-furo[3,2-*c*]chromen-4-one **2p** (93.2 mg, 0.50 mmol) and carbon acid **1c** (10.0 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyldimethyl(1-ethoxyvinyloxy)silane (202 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at 0 °C over 1 h using a syringe pump and stirred for 1 h at the same temperature. After being stirred for additional 9 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on alumina (hexane/EtOAc = 10 : 1) to give the vinyl ether **4pa** in 75% yield (88.9 mg, 0.37 mmol). Yellow crystals (EtOAc-hexane); Mp. 94.5-95.5 °C; IR (ATR) ν 3158, 2973, 1704, 1630, 1584, 1159, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, t, J = 7.2 Hz), 4.22 (2H, q, J = 7.2 Hz), 5.53 (1H, s), 6.60 (1H, d, J = 2.0 Hz), 7.16-7.21 (1H, m), 7.34-7.40 (2H, m), 7.52 (1H, d, J = 2.0 Hz), 7.63 (1H, brd, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 59.3, 88.8, 106.5, 113.9, 114.0, 117.0, 119.9, 123.9, 129.9, 144.6, 150.2, 152.3, 156.9, 165.4; MS (ESI-TOF) m/z 257 $[M+H]^+$; HRMS calcd for $C_{15}H_{13}O_4$ $[M+H]^+$, 257.0814; found, 257.0806.

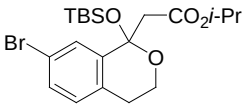
4. Preparation of Mukaiyama aldol products

Ethyl 2-(2-(*tert*-butyldimethylsilyloxy)tetrahydro-2*H*-pyran-2-yl)acetate



To a solution of δ-valerolactone (50.1 mg, 0.50 mmol) and carbon acid **1c** (5.0 mg, 5 μmol) in CH_2Cl_2 (0.5 mL), a solution of *tert*-butyl(1-ethyloxyvinyloxy)dimethylsilane (122 mg, 0.60 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at –78 °C over 1 h using a syringe pump. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (20 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of the resulting residue using silica gel (hexane/EtOAc = 50 : 1) gave the Mukaiyama aldol adduct in 71% yield (107.5 mg, 0.43 mmol). Colorless oil; IR (neat) ν 2936, 2857, 1741, 1017, 837, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (3H, s), 0.15 (3H, s), 0.90 (9H, s), 1.25 (3H, t, J = 7.1 Hz), 1.40-1.62 (3H, m), 1.67-1.94 (3H, m), 2.57 (1H, d, J = 13.6 Hz), 2.70 (1H, d, J = 13.6 Hz), 3.57-3.66 (1H, m), 3.86 (1H, td, J = 11.2, 3.9 Hz), 4.13 (1H, q, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.9 and –2.6, 14.2, 18.3, 19.2, 25.0, 25.9 (3C), 35.0, 47.1, 60.3, 62.0, 97.0, 169.7; MS (ESI-TOF) m/z 325 $[M+Na]^+$; HRMS calcd for $C_{15}H_{30}NaO_4Si$ $[M+Na]^+$, 325.1811; found, 325.1810. Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00. Found: C, 59.71; H, 9.76.

Isopropyl 2-(7-bromo-1-(*tert*-butyldimethylsilyloxy)isochroman-1-yl)acetate (3dc)



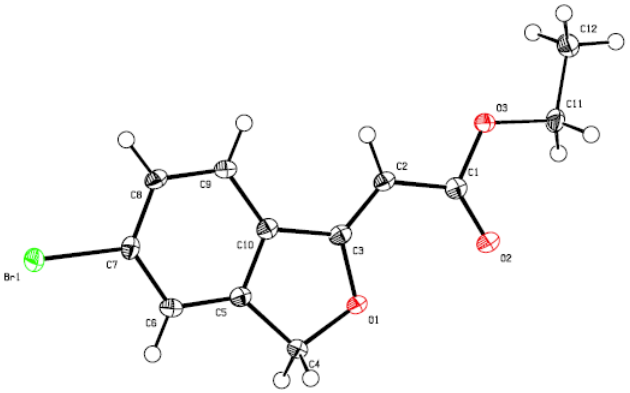
To a solution of 7-bromoisochroman-1-one **2d** (112.6 mg, 0.50 mmol) and carbon acid **1c** (9.9 mg, 10 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl(1-isopropyloxyvinyloxy)dimethylsilane (215 mg, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at –10 °C over 1 h using a syringe pump. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (20 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Chromatographic purification of the resulting residue using silica gel (hexane/EtOAc = 30 : 1) gave the Mukaiyama aldol adduct **3dc** in 86% yield (189.6 mg, 0.43 mmol). Colorless oil; IR (ATR) ν 2956, 1732, 1104, 1082, 1048, 835, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.03 (3H, s), 0.16 (3H, s), 0.87 (9H, s), 0.93 (3H, d, J = 6.3 Hz), 1.05 (3H, d, J = 6.3 Hz), 2.56 (1H, dt, J = 16.1, 3.3 Hz), 2.86 (1H, ddd, J = 16.1, 11.2, 5.1 Hz), 2.95 (2H, s), 3.86 (1H, td, J = 11.2, 3.3 Hz), 4.00 (1H, ddd, J = 11.2, 5.1, 3.3 Hz), 4.76 (1H, sept, J = 6.3 Hz), 6.93 (1H, d, J = 8.1 Hz), 7.29 (1H, dd, J = 8.1, 2.0 Hz), 7.46 (1H, d, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –3.3 and –2.8, 17.9, 21.3 and 21.5, 25.7 (3C), 28.2, 49.0, 60.3, 67.4, 96.9, 119.6, 129.4, 130.0, 130.4, 133.0, 140.5, 168.0; MS (ESI-TOF) m/z 465 $[M+Na]^+$, 467 $[M+2+H]^+$; HRMS calcd for $C_{20}H_{31}BrNaO_4Si$ $[M+Na]^+$, 465.1073; found, 465.1077.

A solution of Mukaiyama aldol adduct **3dc** (38.5 mg, 87 μmol) in CH_2Cl_2 (1.0 mL) was treated with carbon

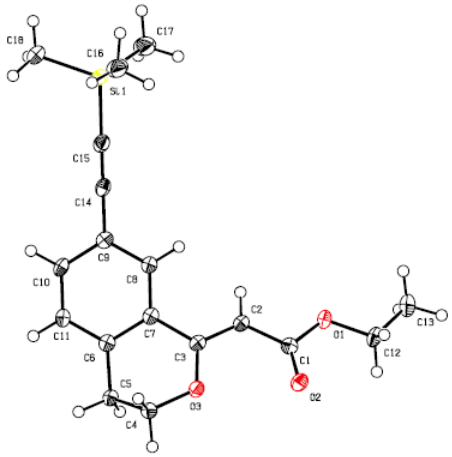
acid **1c** (2.0 mg, 2 μmol) at room temperature for 5 min. The reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (15 mL), extracted with Et_2O (20 mL x 3), and concentrated under reduced pressure. The resulting residue was purified by column chromatography on basic alumina (hexane/EtOAc = 5 : 1) to give the vinyl ether **4dc** in 98% yield (26.5 mg, 0.85 mmol). The structure of the product was confirmed by comparison of ^{1}H and ^{13}C NMR spectra with those of the authentic sample.

5. X-ray crystallographic data

X-ray crystallographic data of **4ha** and **4ia** have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication Nos. CCDC 881214 (**4ha**) and 881215 (**4ia**). These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.



X-ray structure of **4ha**



X-ray structure of **4ia**

Table S1. Crystal data and structure refinement for **4ha**.

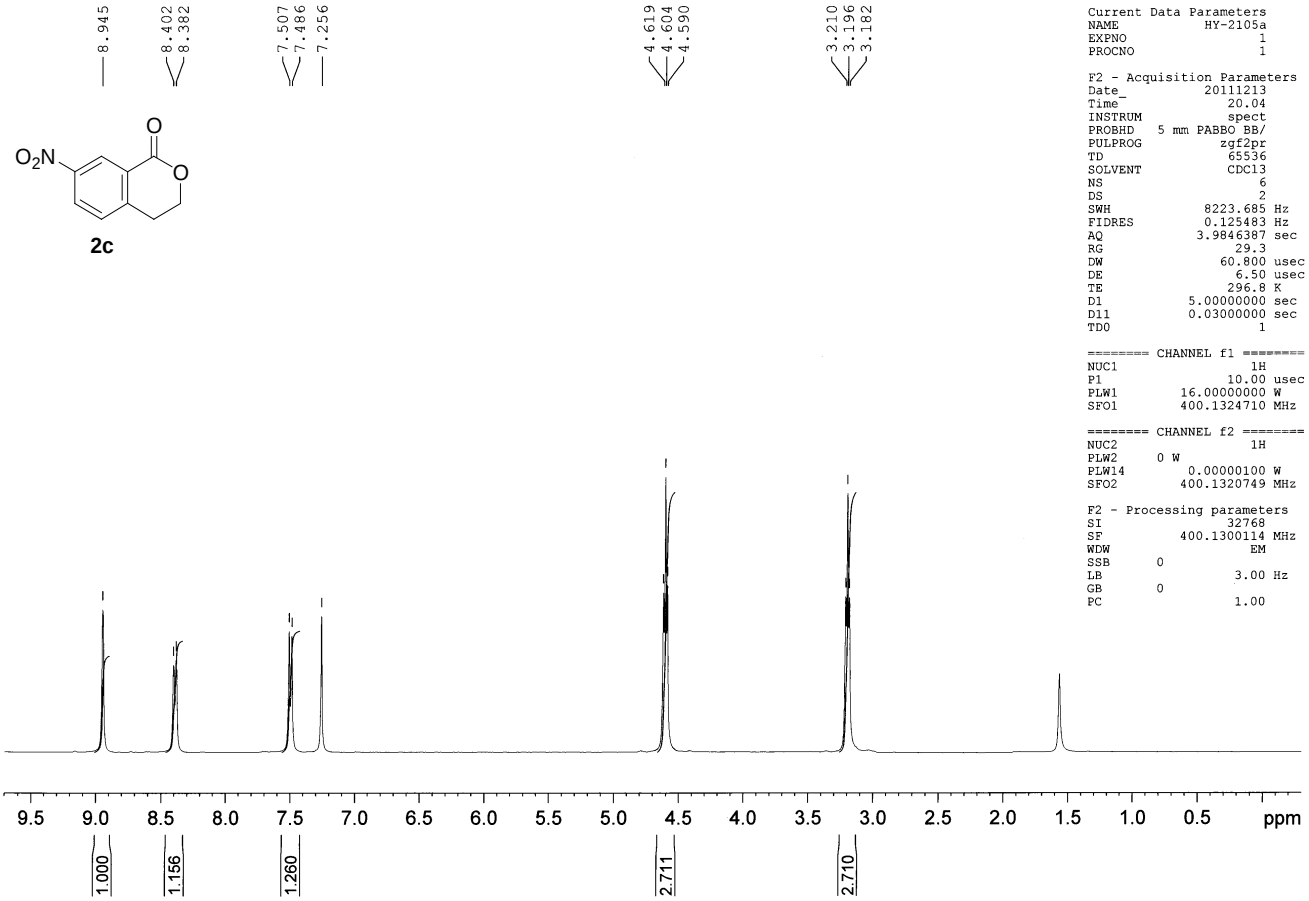
Empirical formula	$C_{12}H_{11}BrO_3$	
Formula weight	283.12	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.2003(10) Å	α = 90°.
	b = 11.6716(9) Å	β = 91.8430(10)°.
	c = 7.2810(6) Å	γ = 90°.
Volume	1121.19(15) $Å^3$	
Z	4	
Density (calculated)	1.677 Mg/m^3	
Absorption coefficient	3.654 mm^{-1}	
F(000)	568	
Crystal size	0.21 x 0.14 x 0.06 mm^3	
Theta range for data collection	2.33 to 25.03°.	
Index ranges	-15<=h<=9, -13<=k<=13, -8<=l<=8	
Reflections collected	5250	
Independent reflections	1974 [R(int) = 0.0210]	
Completeness to theta = 25.03°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.8106 and 0.5141	

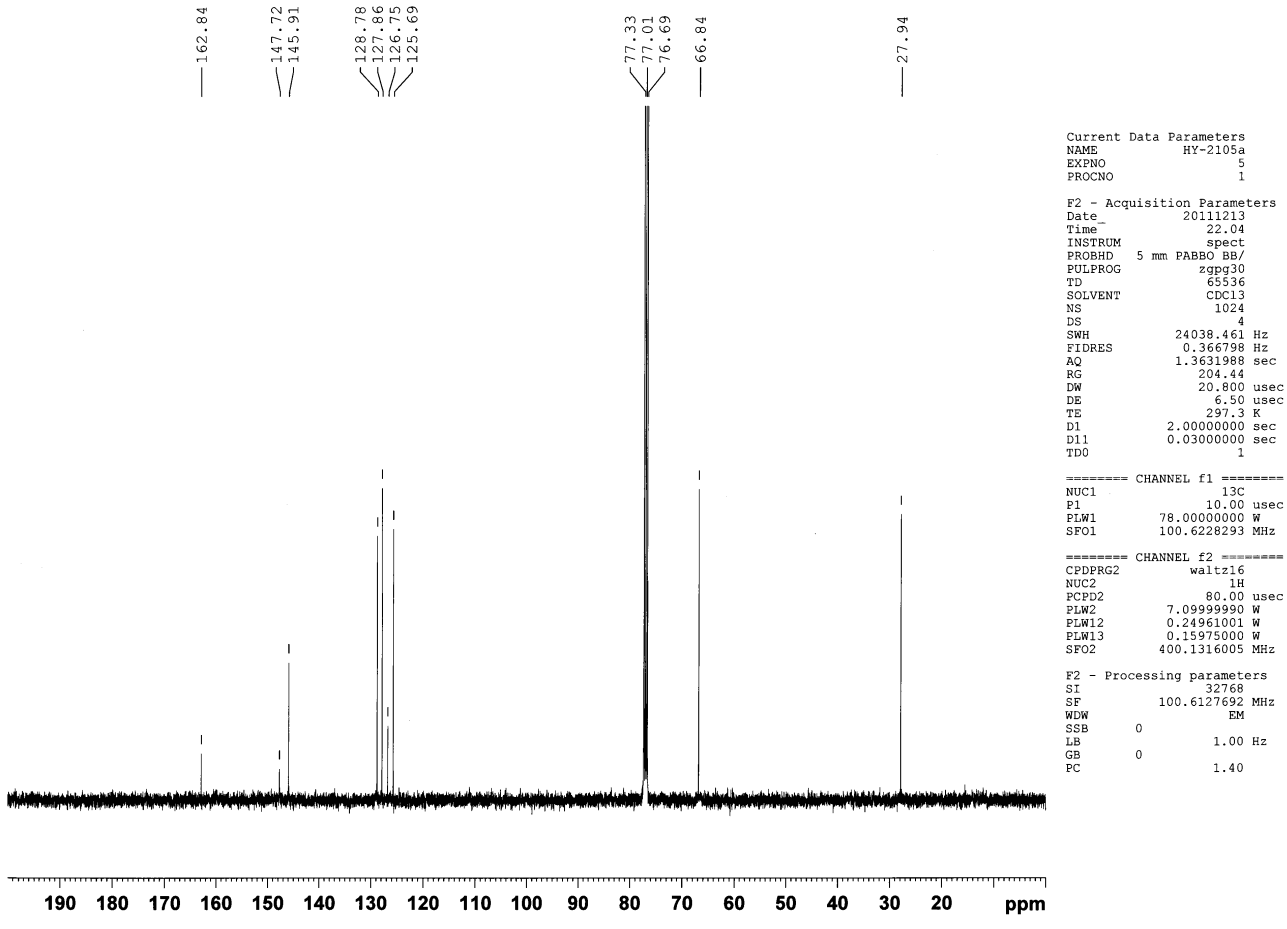
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1974 / 0 / 147
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0217, wR2 = 0.0507
R indices (all data)	R1 = 0.0258, wR2 = 0.0520
Largest diff. peak and hole	0.368 and -0.299 e.Å^{-3}

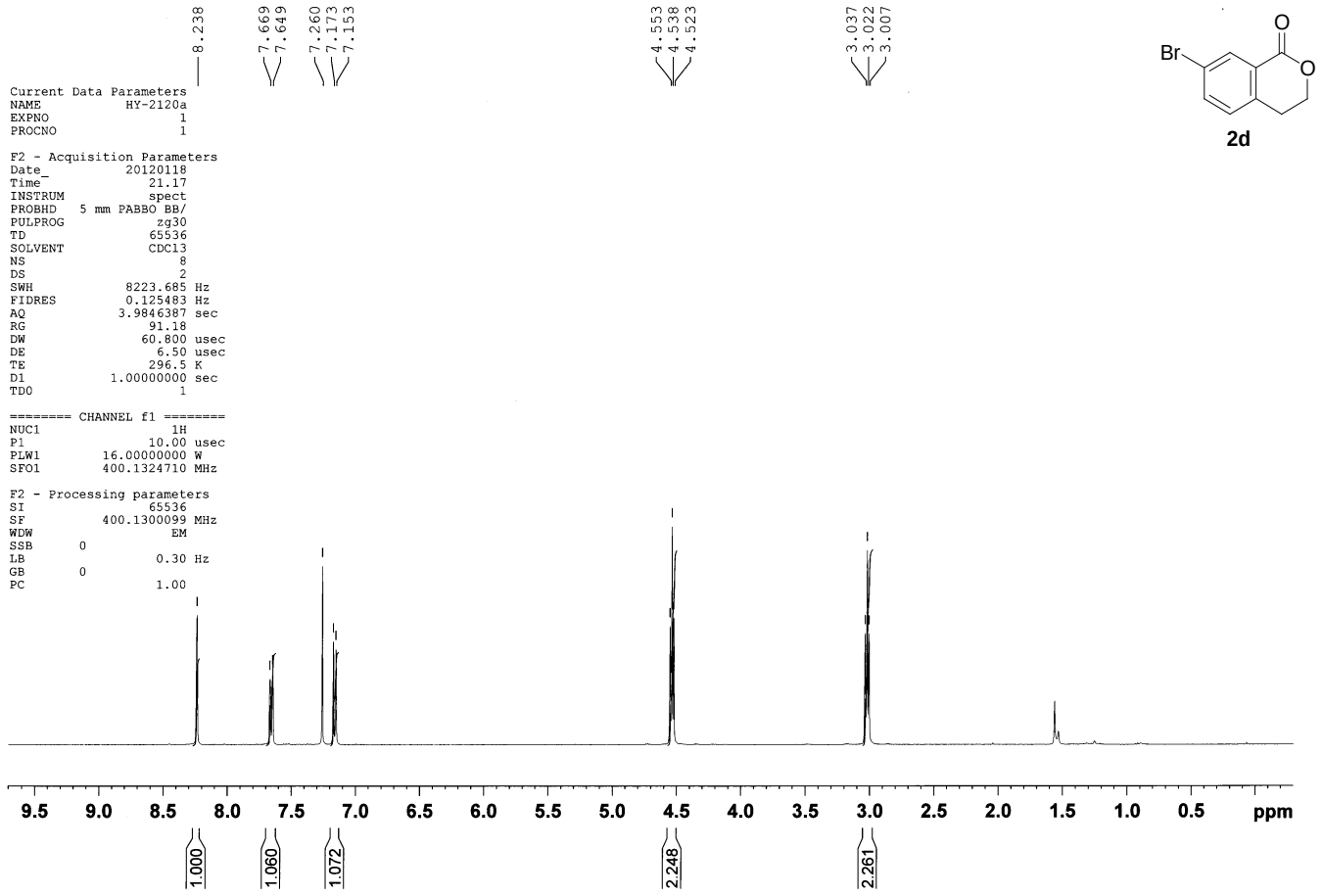
Table S2. Crystal data and structure refinement for **4ia**.

Empirical formula	$C_{18}H_{22}O_3Si$	
Formula weight	314.45	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.733(5) Å	α = 90°.
	b = 12.199(3) Å	β = 100.236(3)°.
	c = 7.4044(17) Å	γ = 90°.
Volume	1754.0(7) Å^3	
Z	4	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	0.143 mm^{-1}	
F(000)	672	
Crystal size	0.27 x 0.27 x 0.08 mm^3	
Theta range for data collection	2.10 to 25.02°.	
Index ranges	-23<=h<=17, -14<=k<=13, -8<=l<=8	
Reflections collected	7915	
Independent reflections	3091 [R(int) = 0.0248]	
Completeness to theta = 25.02°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.9886 and 0.9623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3091 / 0 / 203	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0921	
R indices (all data)	R1 = 0.0432, wR2 = 0.0959	
Largest diff. peak and hole	0.419 and -0.322 e.Å^{-3}	

6. ^{1}H and ^{13}C NMR spectra of all compounds



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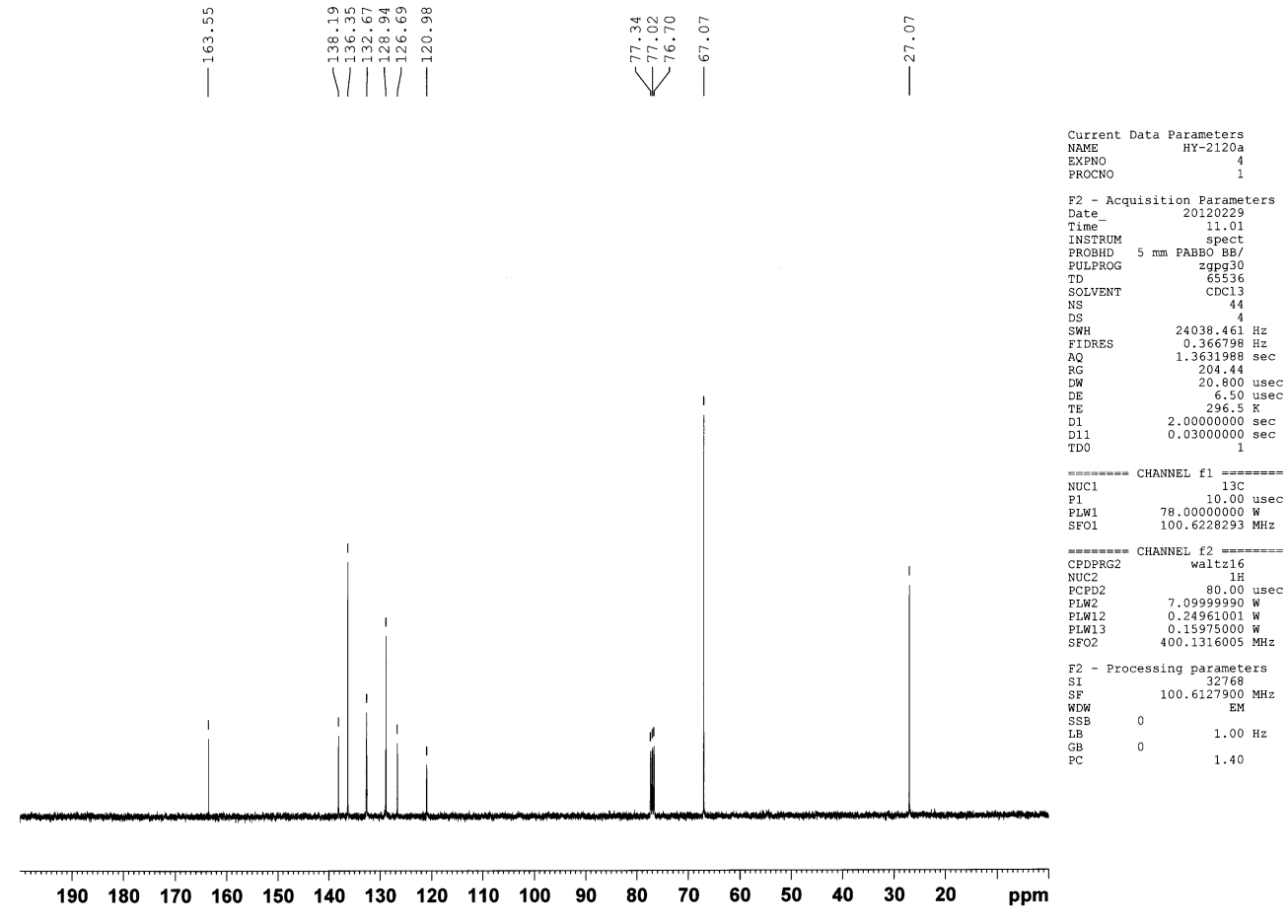
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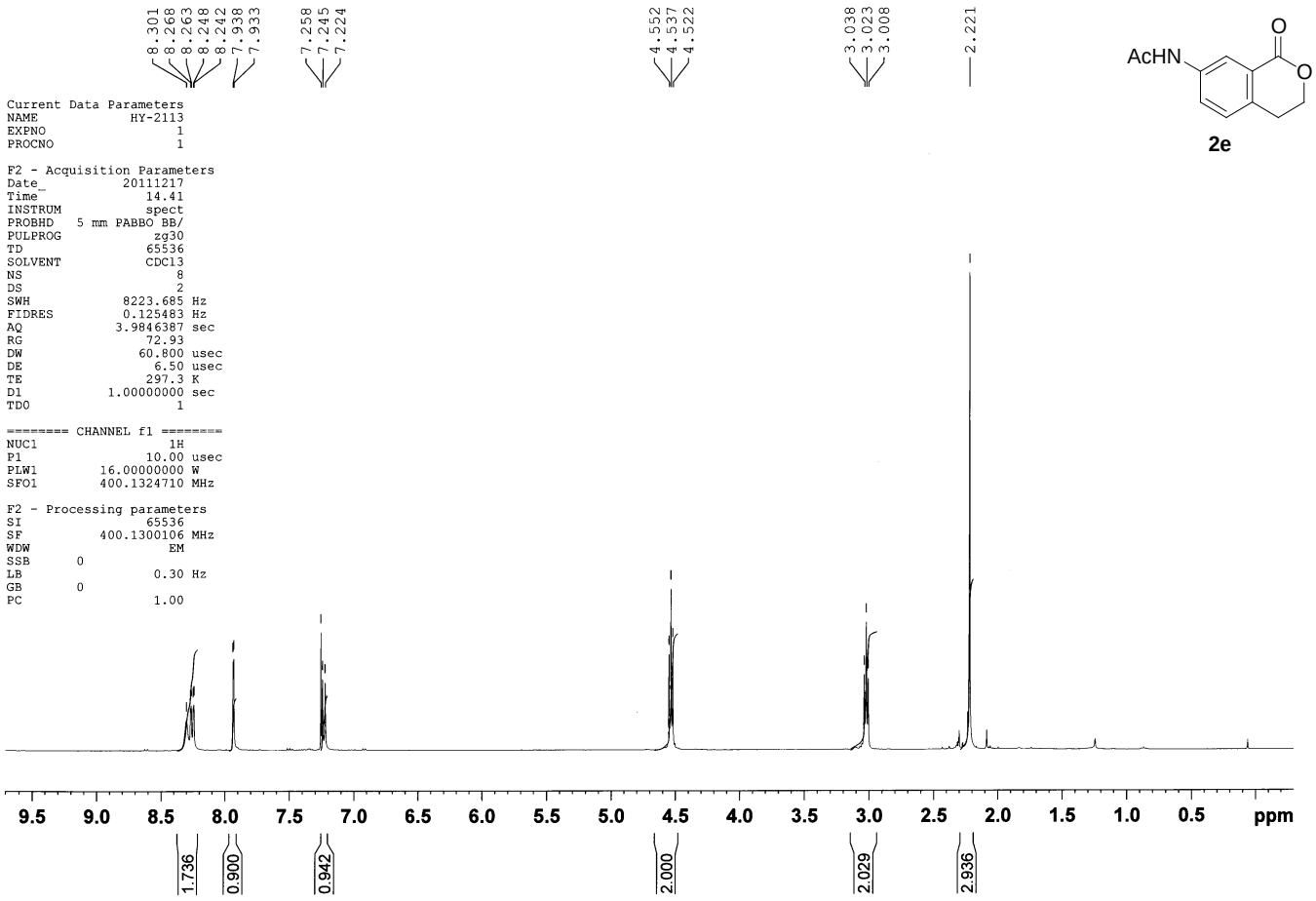
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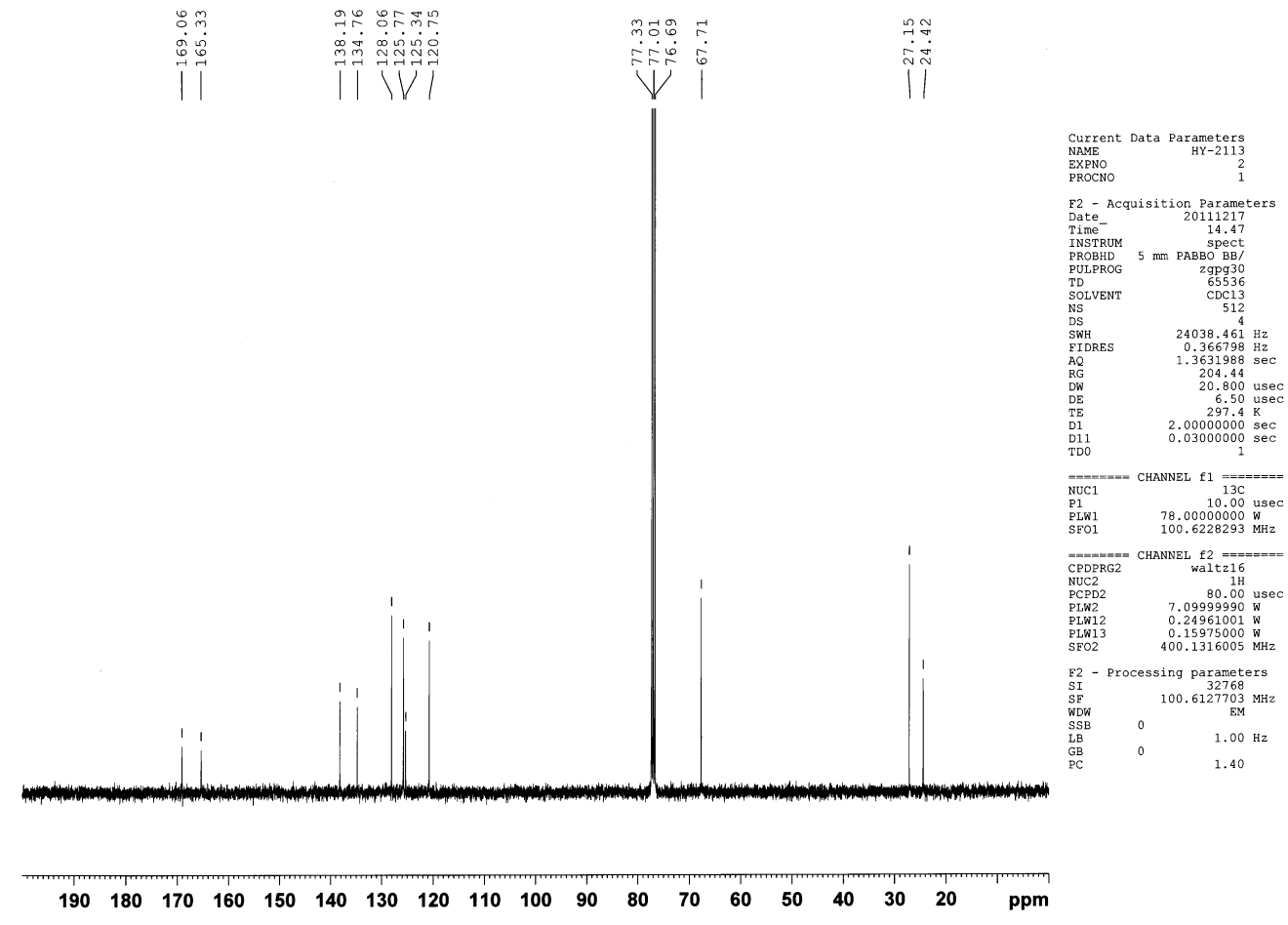
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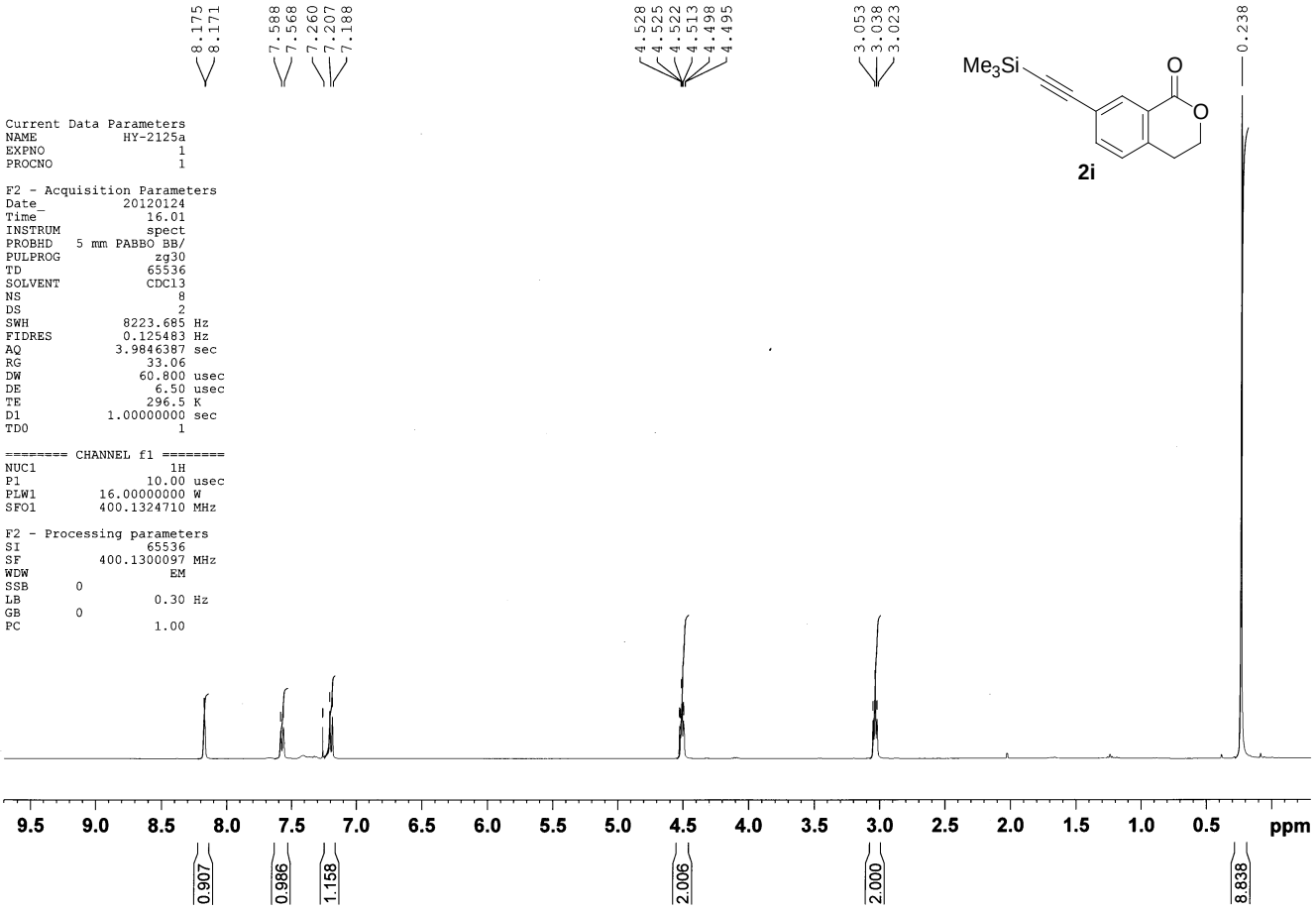
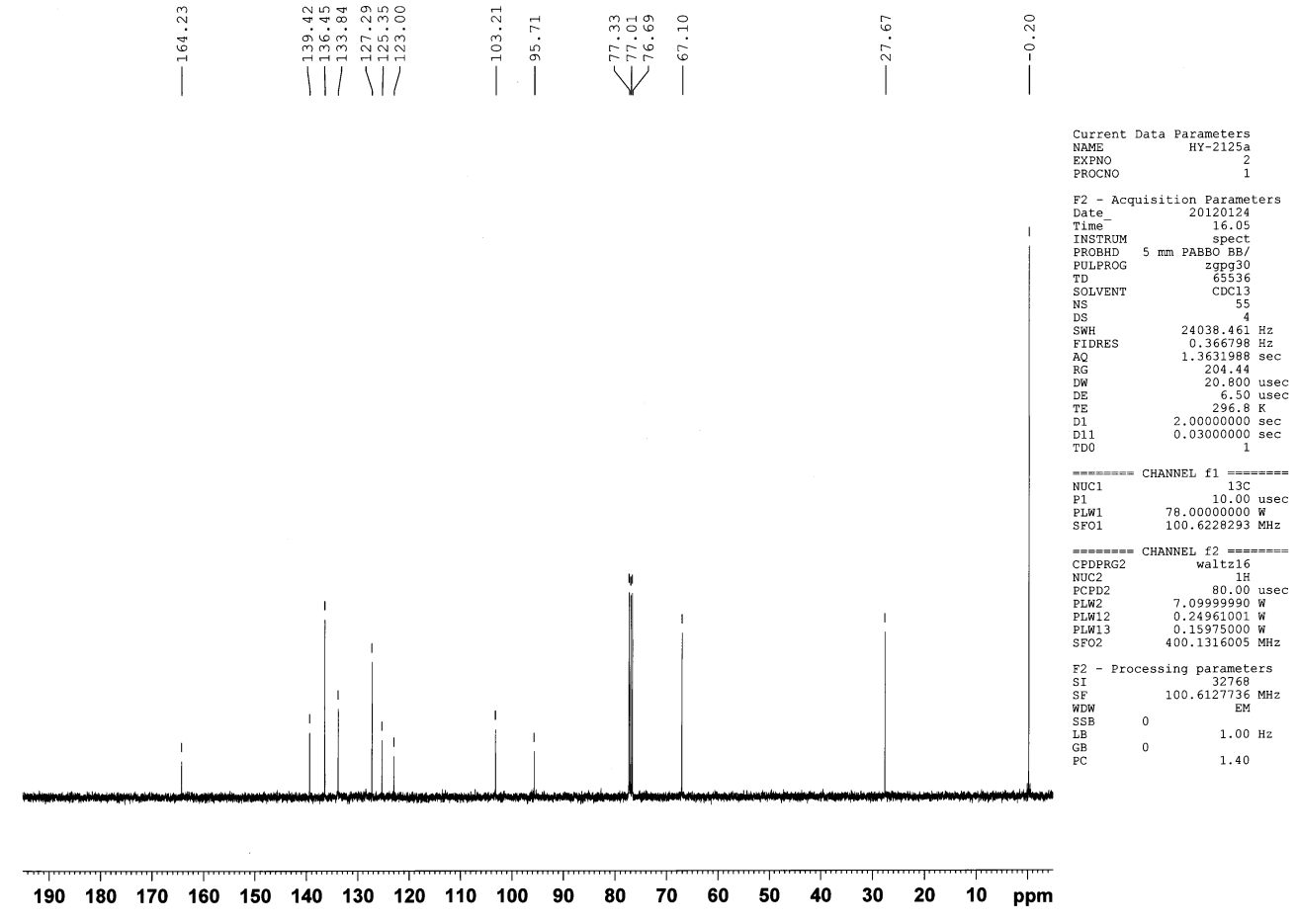
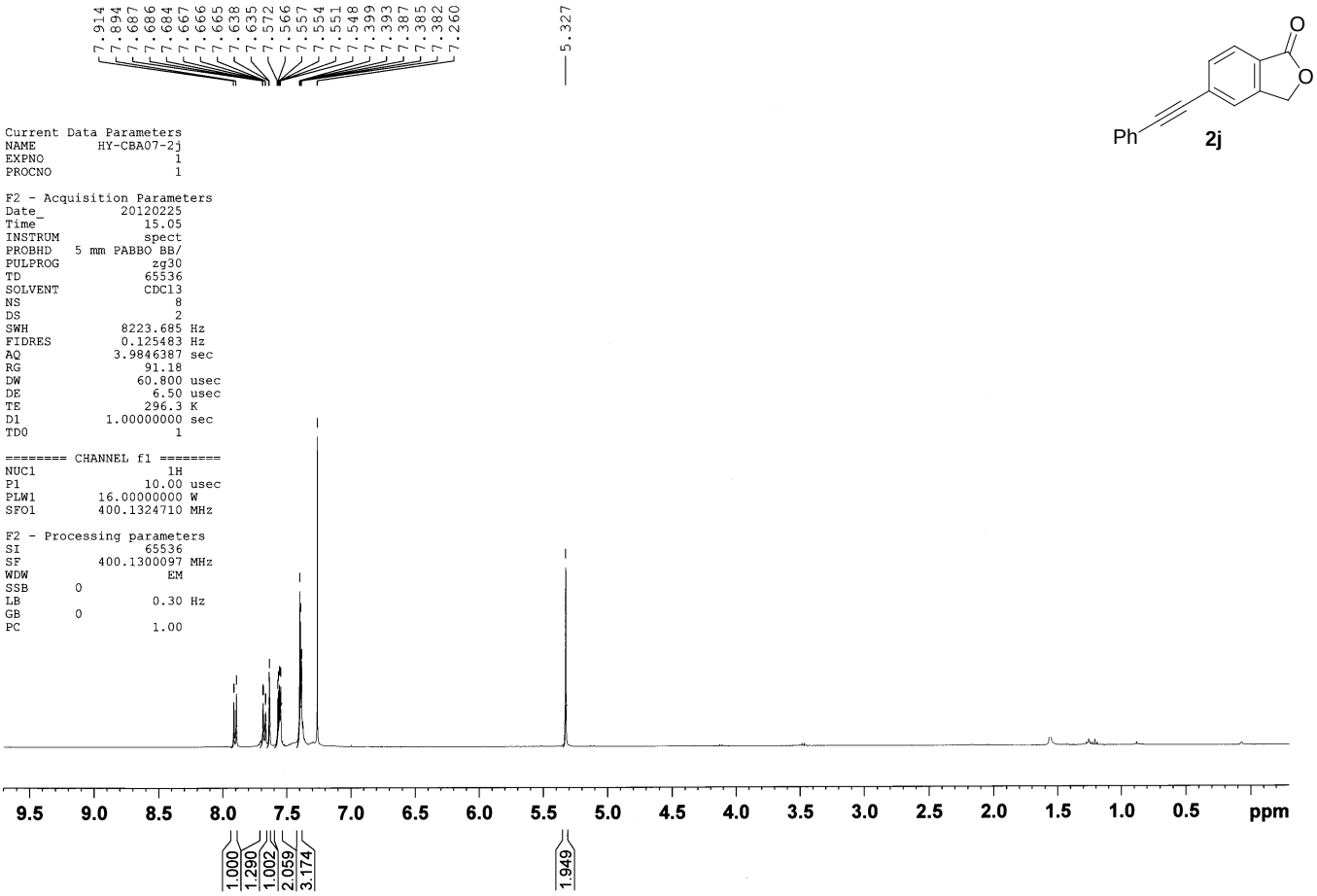
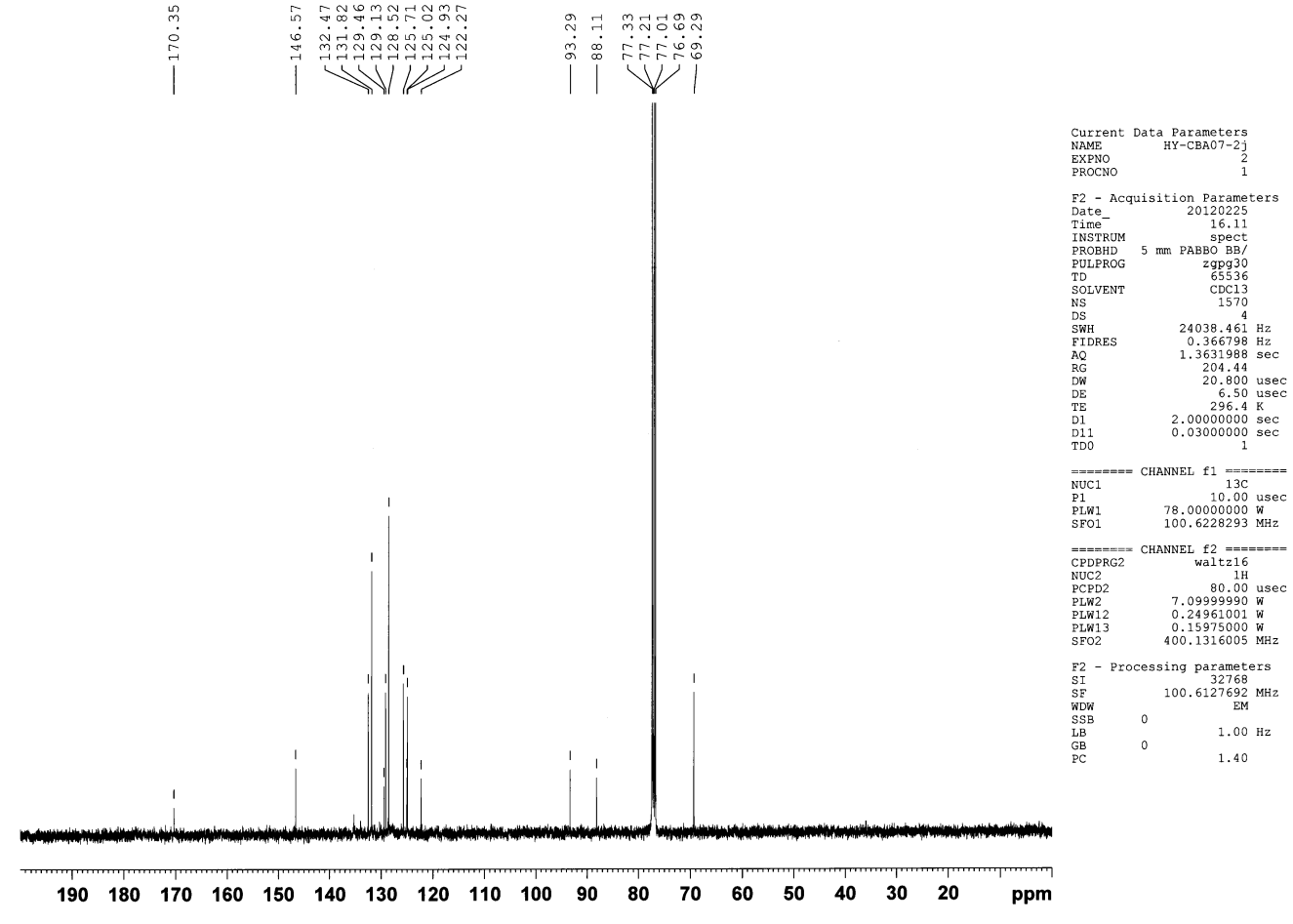
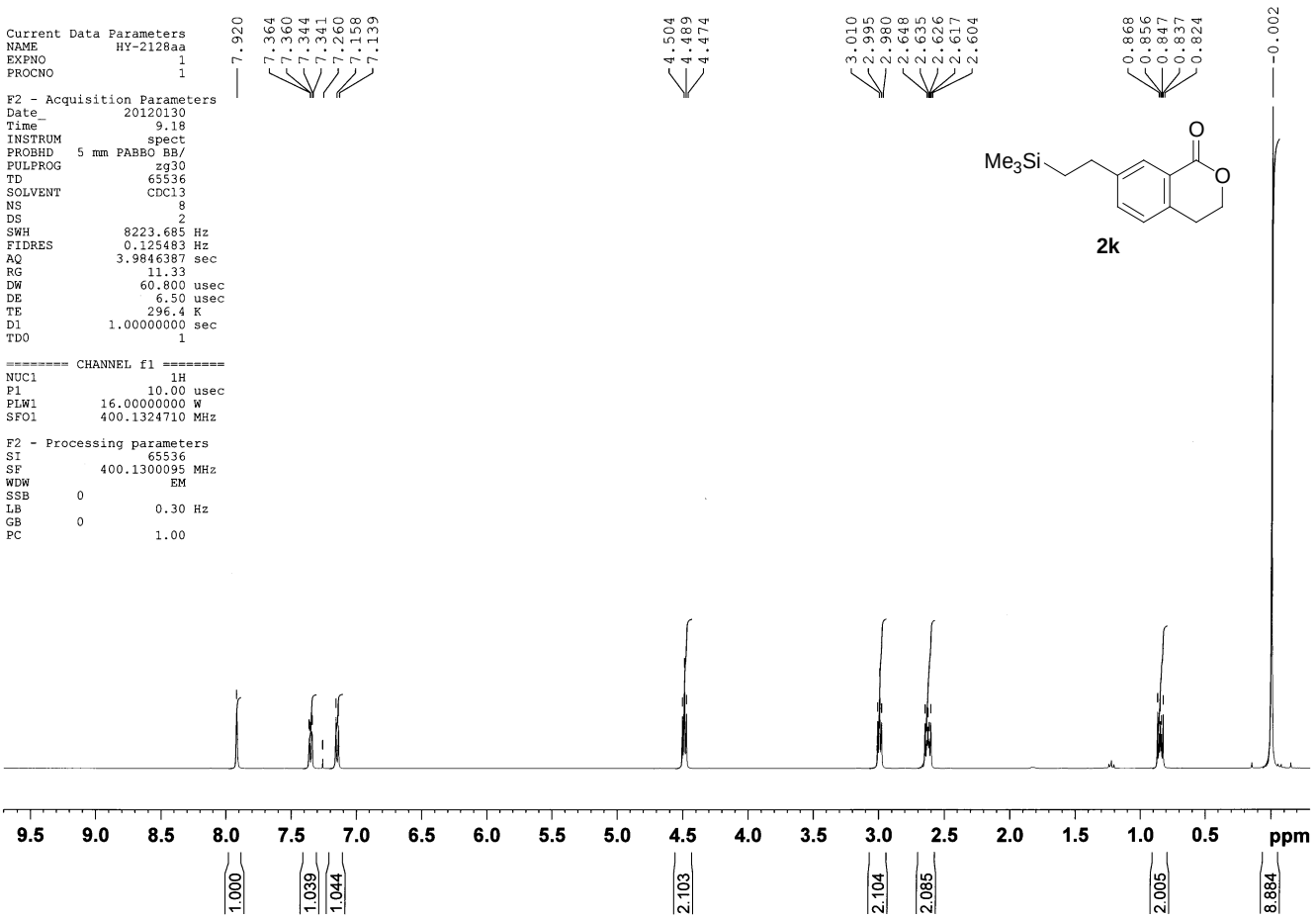
DW 20.800 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127703 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

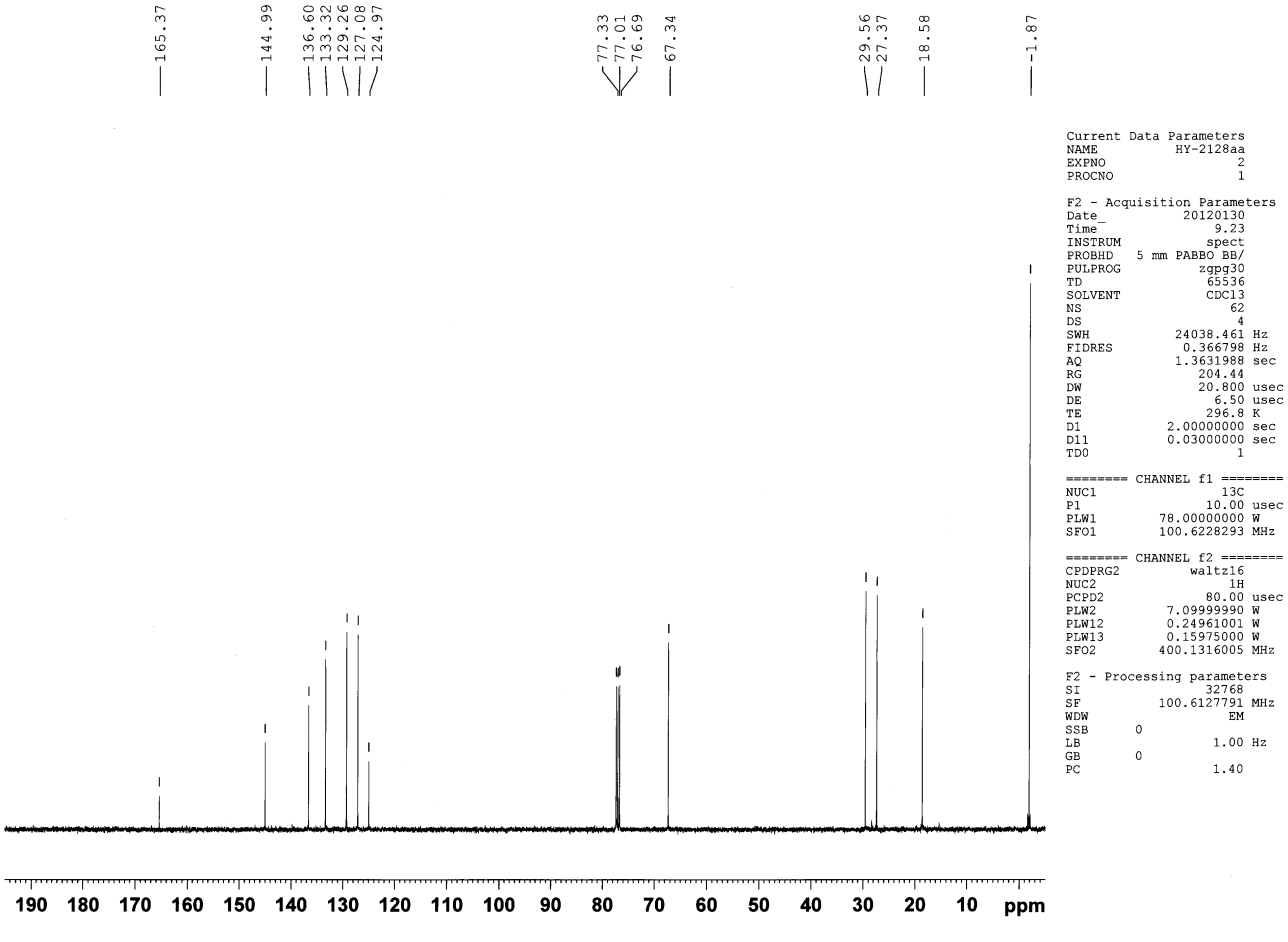

8.175
8.171
7.588
7.568
7.260
7.207
7.188
4.528
4.525
4.522
4.513
4.498
4.495
3.053
3.038
3.023
0.238
Me3Si
O
O
2i
Current Data Parameters
NAME HY-2125a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120124
Time 16.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.907
0.986
1.158
2.006
2.000
8.838

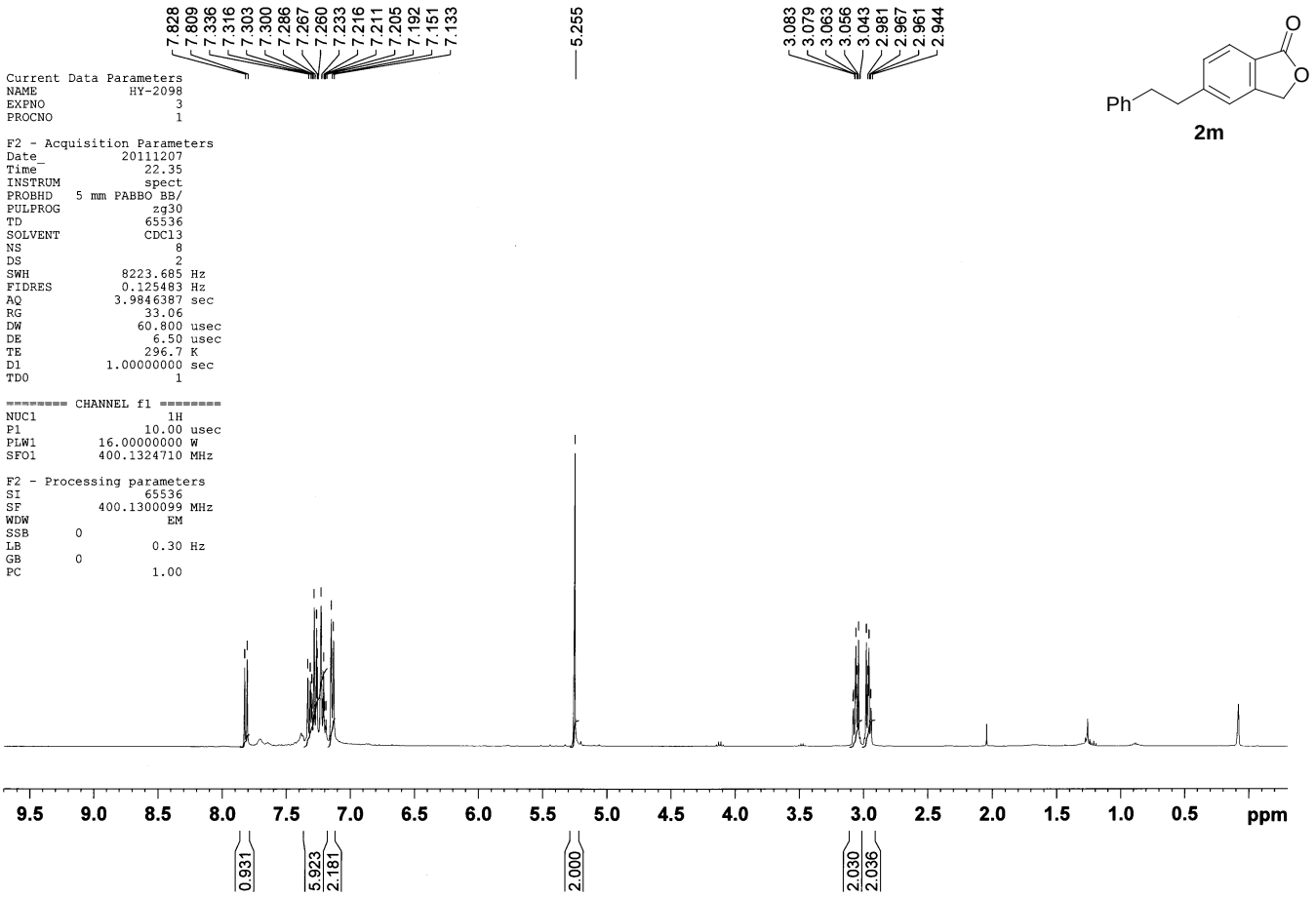

164.23
139.42
136.45
133.84
127.29
125.35
123.00
103.21
95.71
77.33
77.01
76.69
67.10
27.67
0.20
Current Data Parameters
NAME HY-2125a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120124
Time 16.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 55
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127736 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.914
7.894
7.687
7.686
7.684
7.667
7.666
7.665
7.638
7.635
7.572
7.566
7.557
7.554
7.551
7.548
7.399
7.393
7.387
7.385
7.382
7.260
5.327
Current Data Parameters
NAME HY-CBA07-2j
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120225
Time 15.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 91.18
DW 60.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.290
1.002
2.059
3.174
1.949

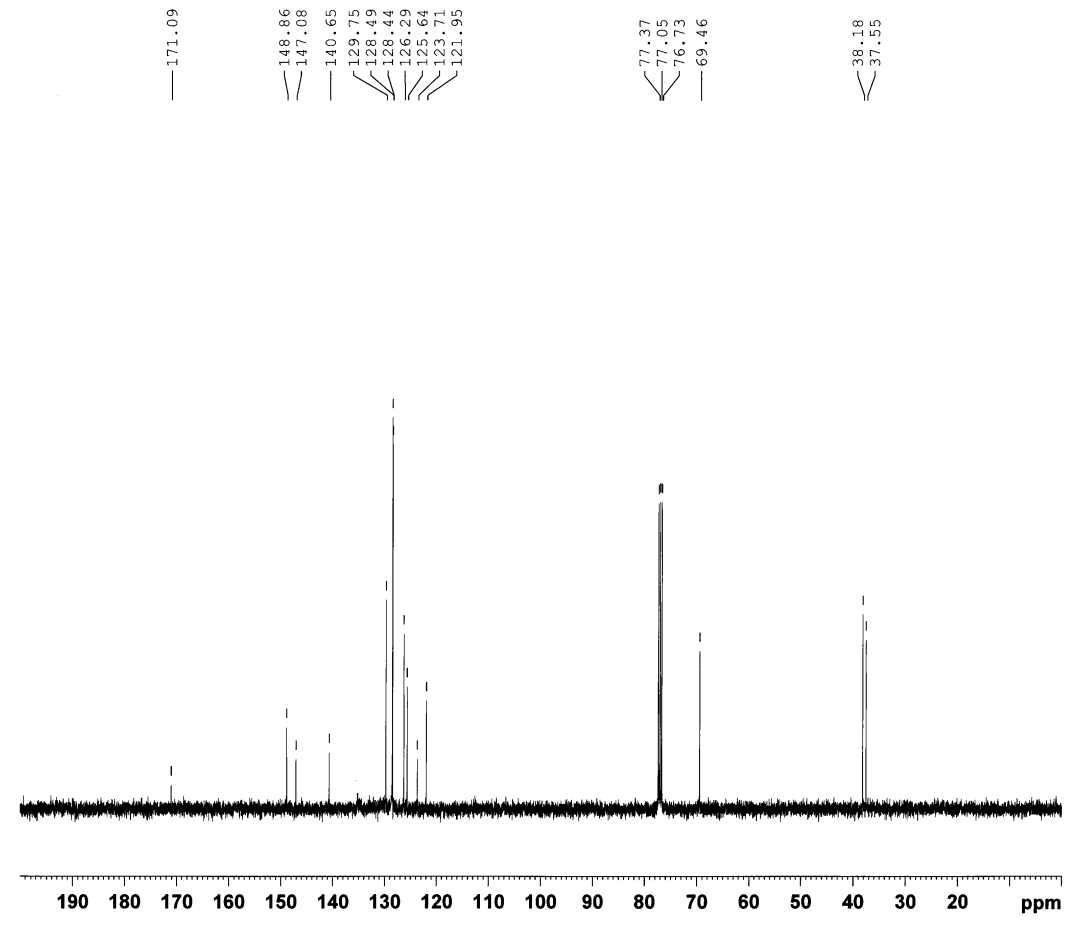

170.35
146.57
132.47
131.82
129.46
129.13
128.52
125.71
125.02
124.93
122.27
93.29
88.11
77.33
77.21
77.01
76.69
69.29
Current Data Parameters
NAME HY-CBA07-2j
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120225
Time 16.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1570
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127692 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Current Data Parameters
NAME HY-2128aa
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120130
Time 9.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 11.33
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.920
7.364
7.360
7.344
7.341
7.260
7.158
7.139
4.504
4.489
4.474
3.010
2.995
2.980
2.648
2.635
2.626
2.617
2.604
0.868
0.856
0.847
0.837
0.824
0.002
Me3Si
O
O
2k
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.039
1.044
2.103
2.104
2.085
2.005
8.884


165.37
144.99
136.60
133.32
129.26
127.08
124.97
77.33
77.01
76.69
67.34
29.56
27.37
18.58
1.87
Current Data Parameters
NAME HY-2128aa
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120130
Time 9.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 62
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127791 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



2m



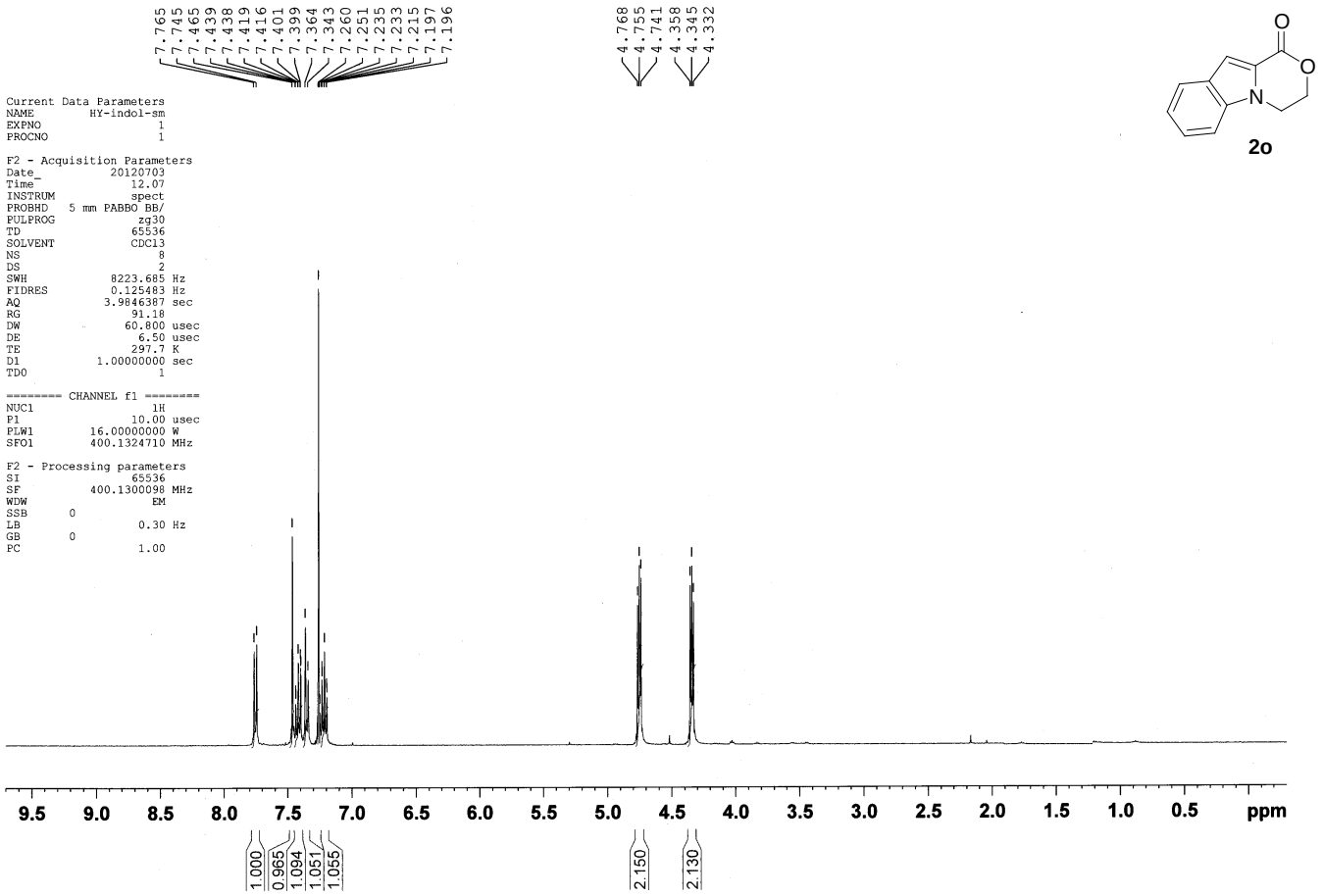
Current Data Parameters
NAME HY-2098
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111207
Time 22.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 53
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

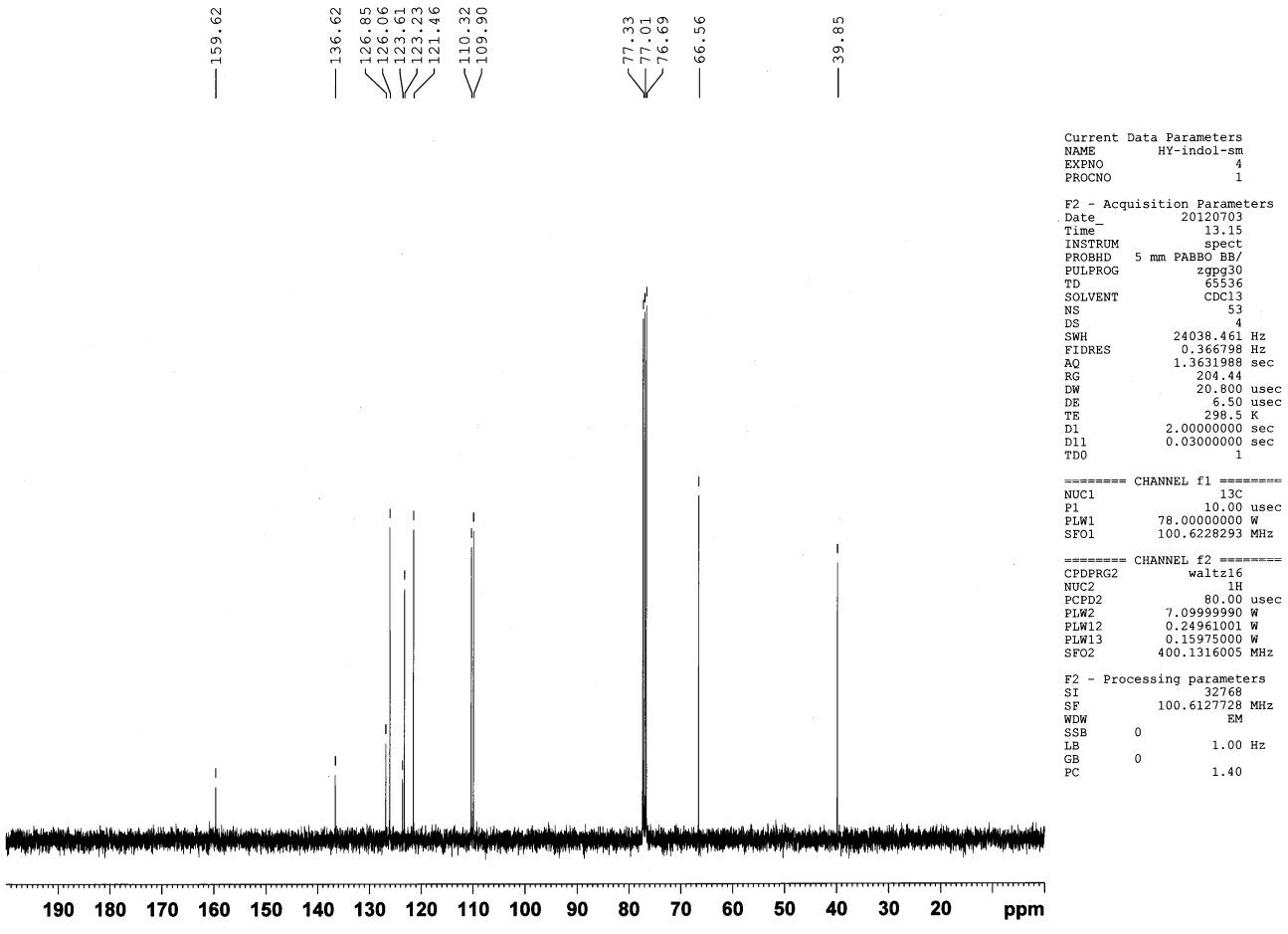
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

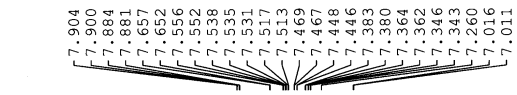
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

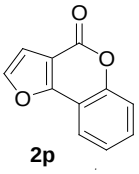

7.765
7.745
7.465
7.439
7.438
7.419
7.416
7.401
7.399
7.364
7.343
7.260
7.251
7.235
7.233
7.215
7.197
7.196
4.768
4.755
4.741
4.358
4.345
4.332
Current Data Parameters
NAME HY-indol-sm
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120703
Time 12.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 91.18
DW 60.800 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.965
1.094
1.051
1.055
2.150
2.130

O
O
N

2o


159.62
136.62
126.85
126.06
123.61
123.23
121.46
110.32
109.90
77.33
77.01
76.69
66.56
39.85
Current Data Parameters
NAME HY-indol-sm
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120703
Time 13.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 53
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm





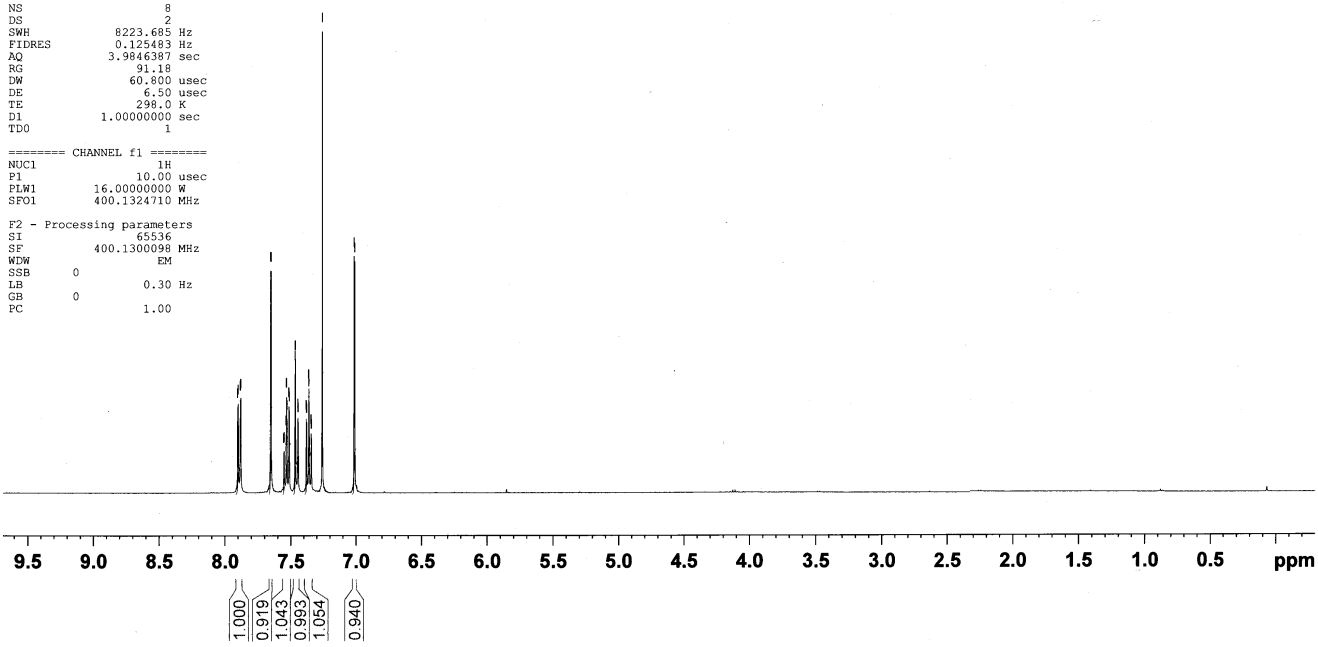
2p

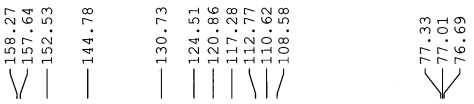
```
Current Data Parameters
NAME         HY-furan-sm
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120704
Time               12.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                 91.18
DW                60.800 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PLW1         16.00000000 W
SFO1         400.1324710 MHz

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





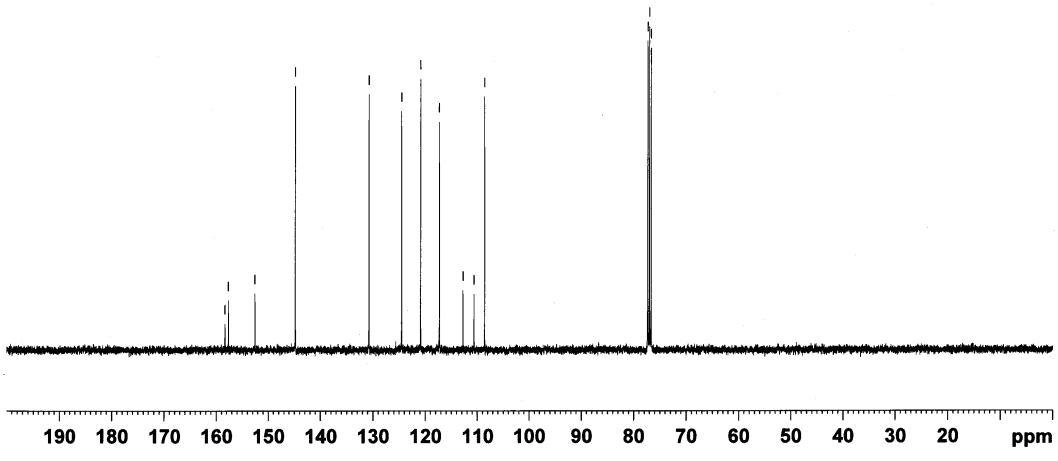

```
Current Data Parameters
NAME         HY-furan-sm
EXPNO                  2
PROCNO                 1

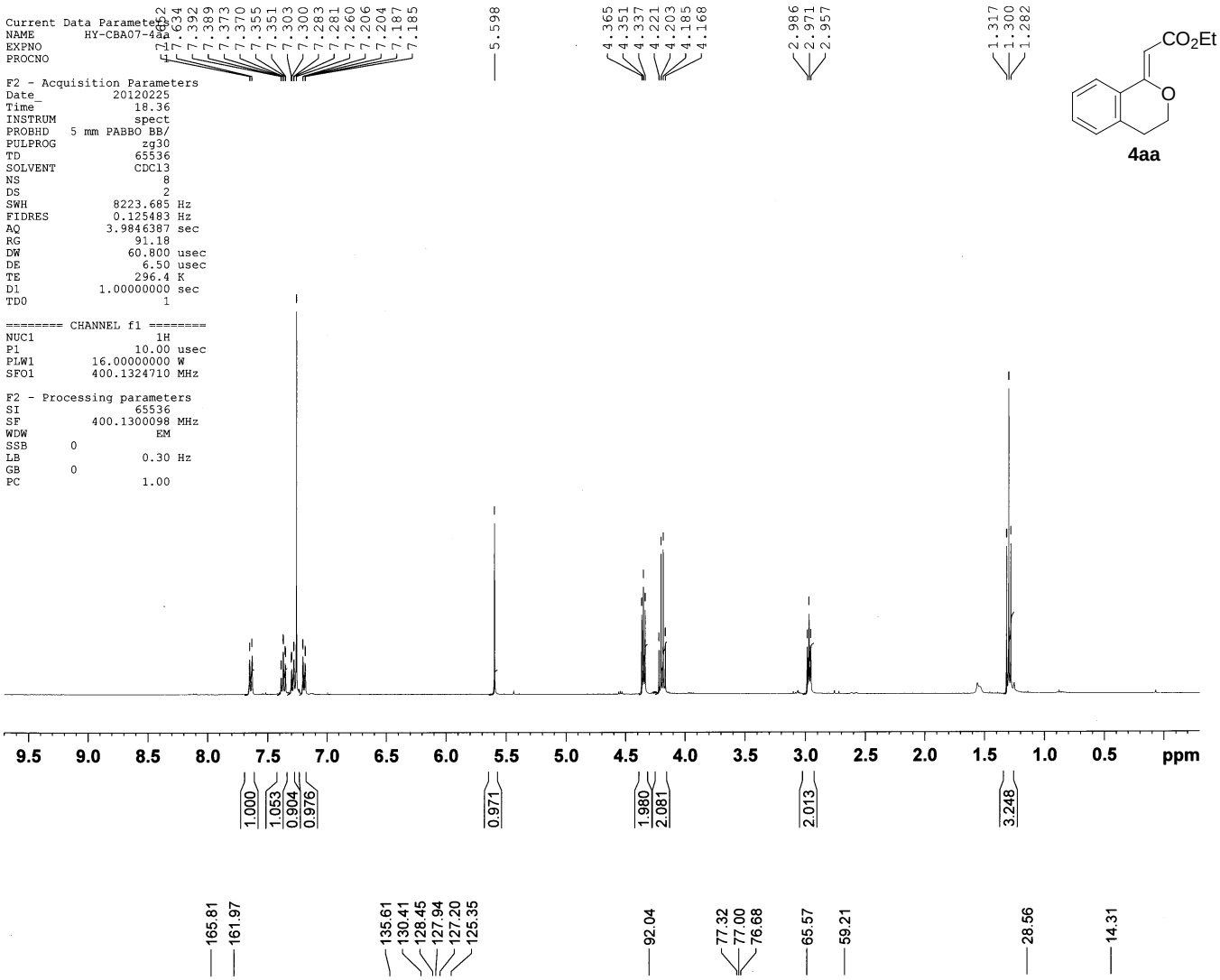
F2 - Acquisition Parameters
Date_           20120704
Time               12.42
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   160
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                204.44
DW                20.800 usec
DE                 6.50 usec
TE                298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

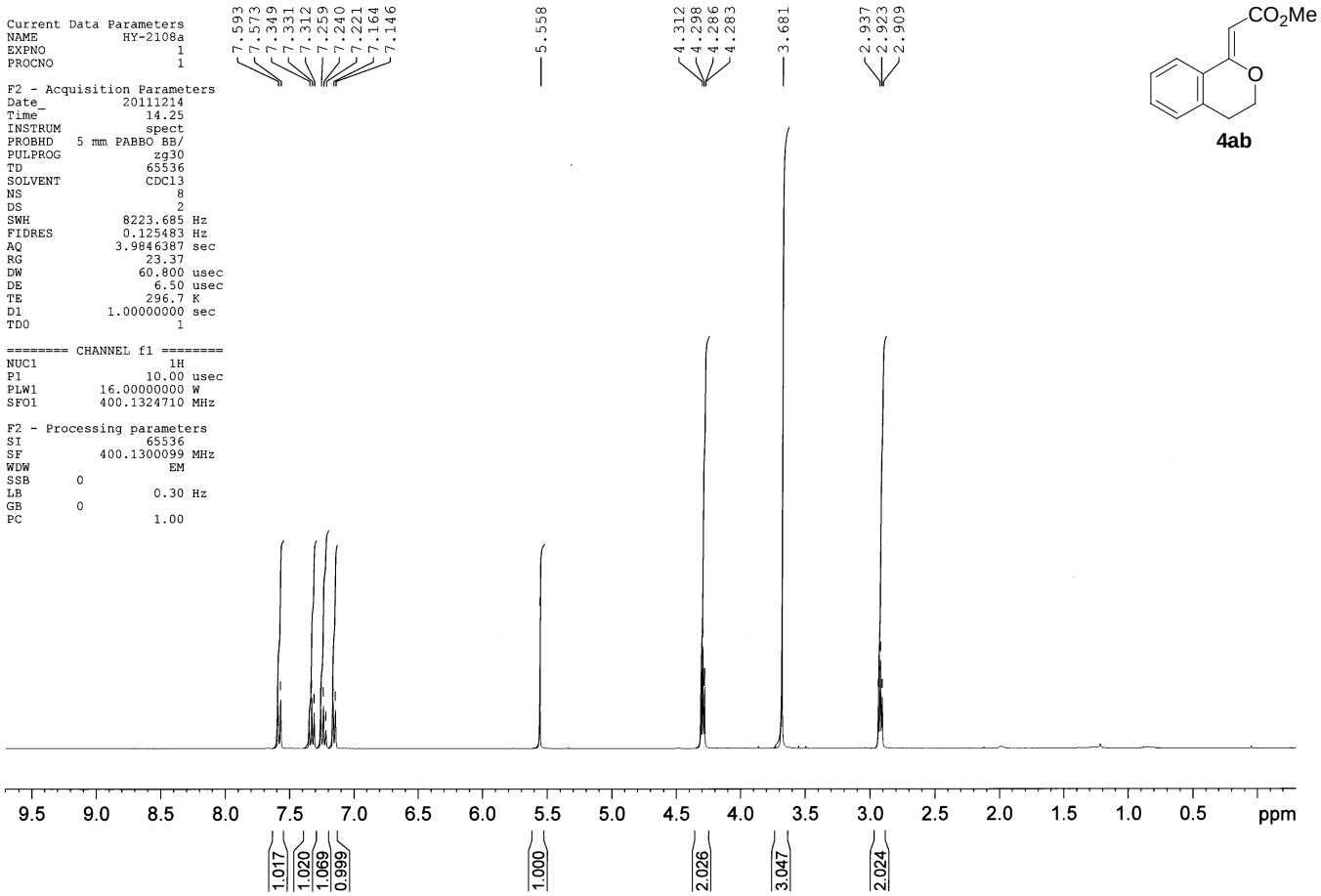
======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         78.00000000 W
SFO1         100.6228293 MHz

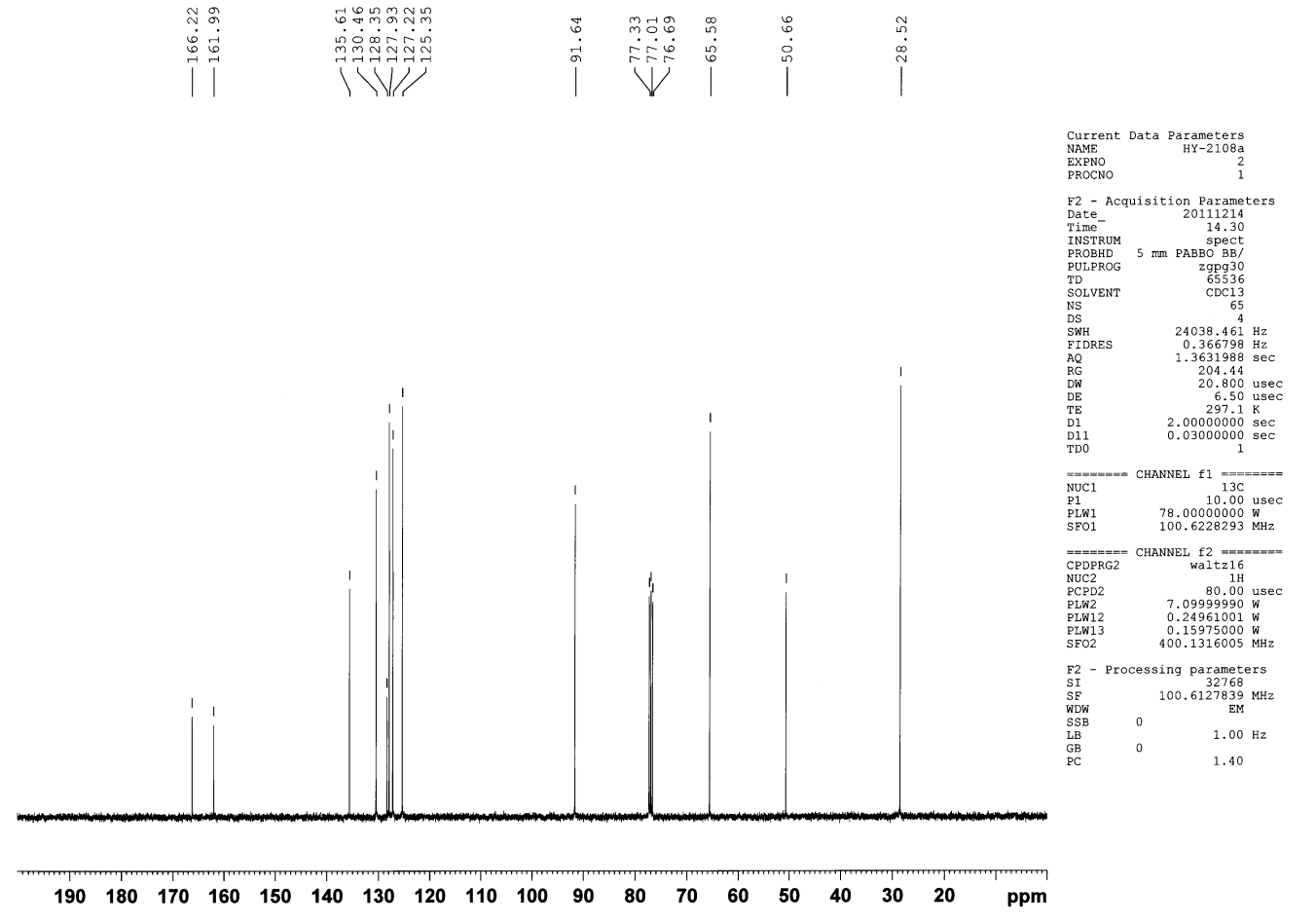
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2          7.09999990 W
PLW12         0.24961001 W
PLW13         0.15975000 W
SFO2         400.1316005 MHz

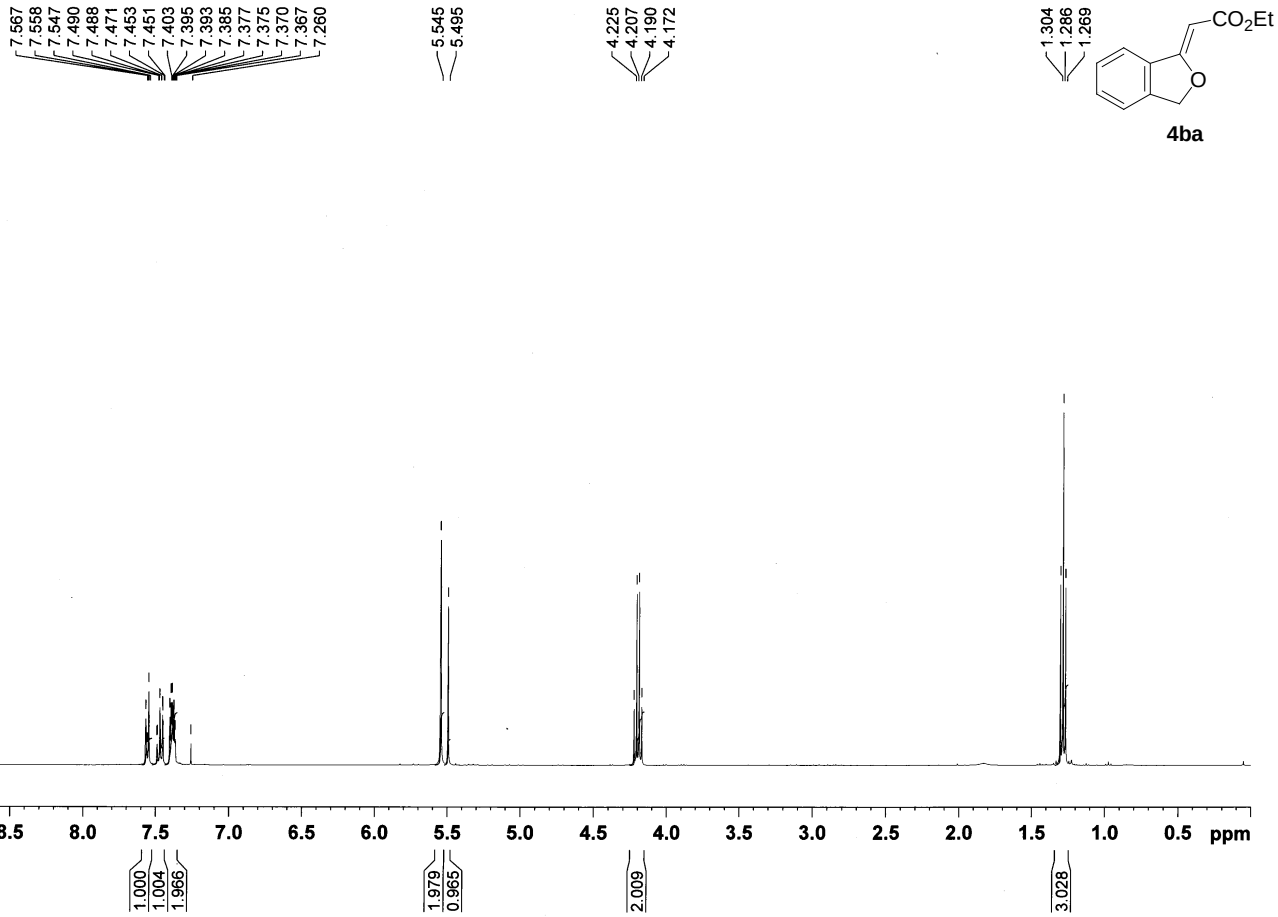
F2 - Processing parameters
SI                 32768
SF           100.6127729 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

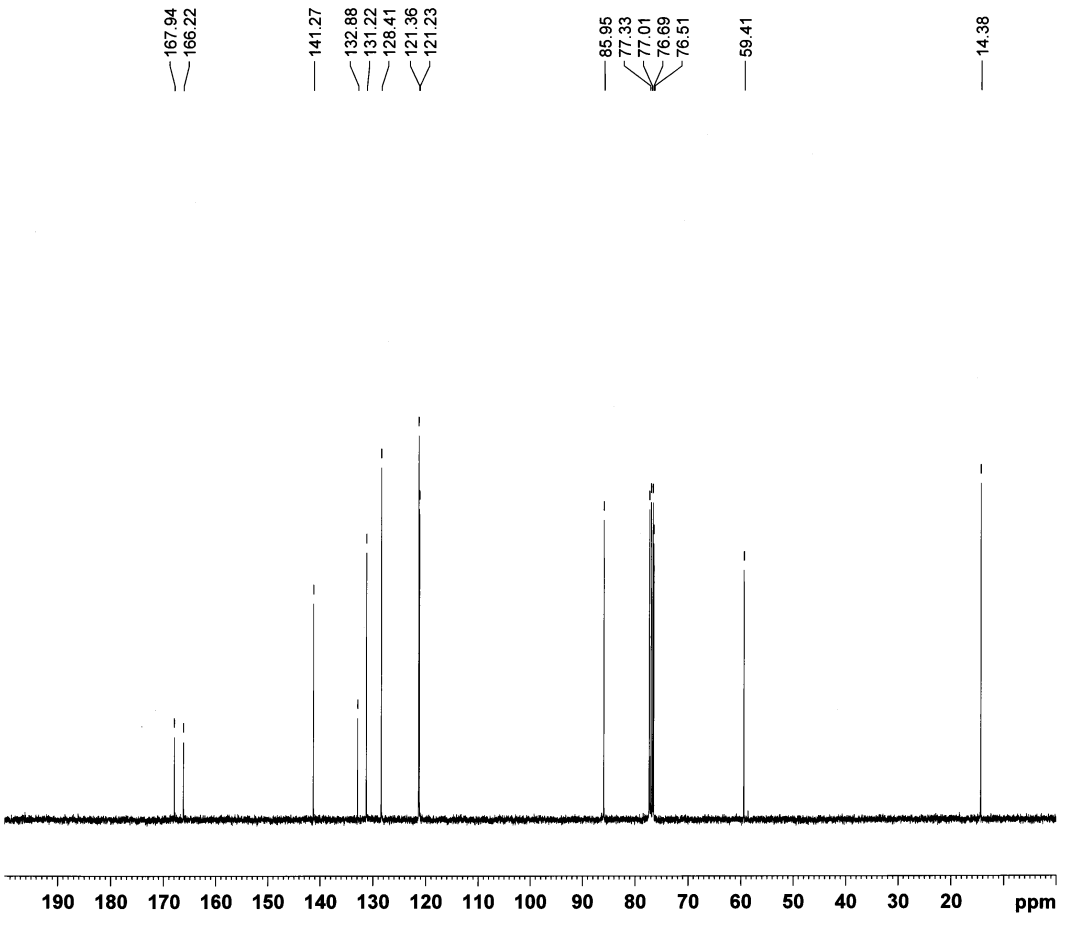



Current Data Parameters
NAME HY-CBA07-4aa
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120225
Time 18.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 91.18
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.652
7.634
7.392
7.389
7.373
7.370
7.355
7.351
7.303
7.300
7.283
7.281
7.260
7.206
7.204
7.187
7.185
5.598
4.365
4.351
4.337
4.221
4.203
4.185
4.168
2.986
2.971
2.957
1.317
1.300
1.282
CO2Et
O
4aa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.053
0.904
0.976
0.971
1.980
2.081
2.013
3.248
165.81
161.97
135.61
130.41
128.45
127.94
127.20
125.35
92.04
77.32
77.00
76.68
65.57
59.21
28.56
14.31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Current Data Parameters
NAME HY-2108a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111214
Time 14.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 23.37
DW 60.800 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.593
7.573
7.349
7.331
7.312
7.259
7.240
7.221
7.164
7.146
5.558
4.312
4.298
4.286
4.283
3.681
2.937
2.923
2.909
CO2Me
O
4ab
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.017
1.020
1.069
0.999
1.000
2.026
3.047
2.024


166.22
161.99
135.61
130.46
128.35
127.93
127.22
125.35
91.64
77.33
77.01
76.69
65.58
50.66
28.52
Current Data Parameters
NAME HY-2108a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111214
Time 14.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 65
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127839 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm





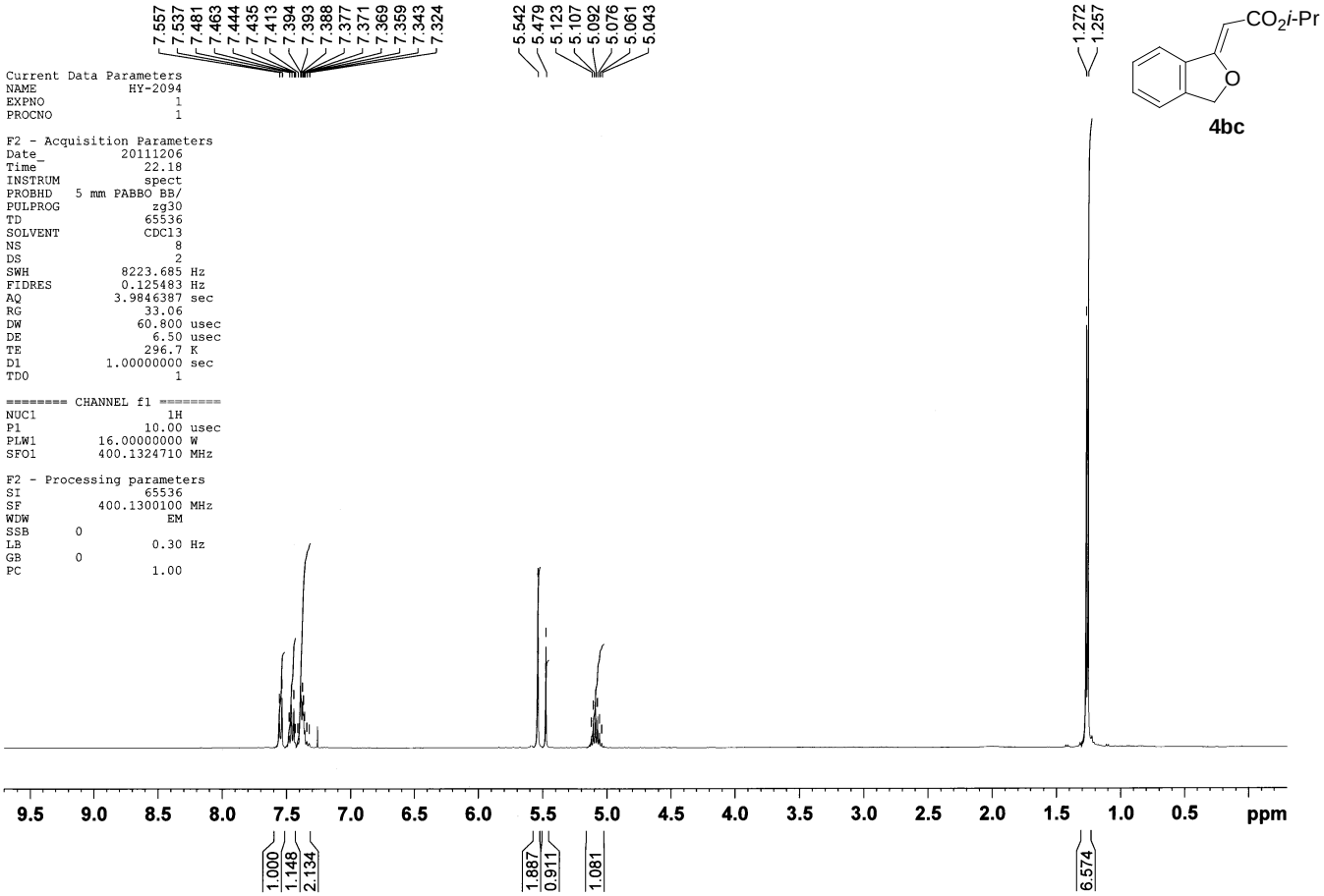

```
Current Data Parameters
NAME                  HY-51ac
EXPNO                       2
PROCNO                      1

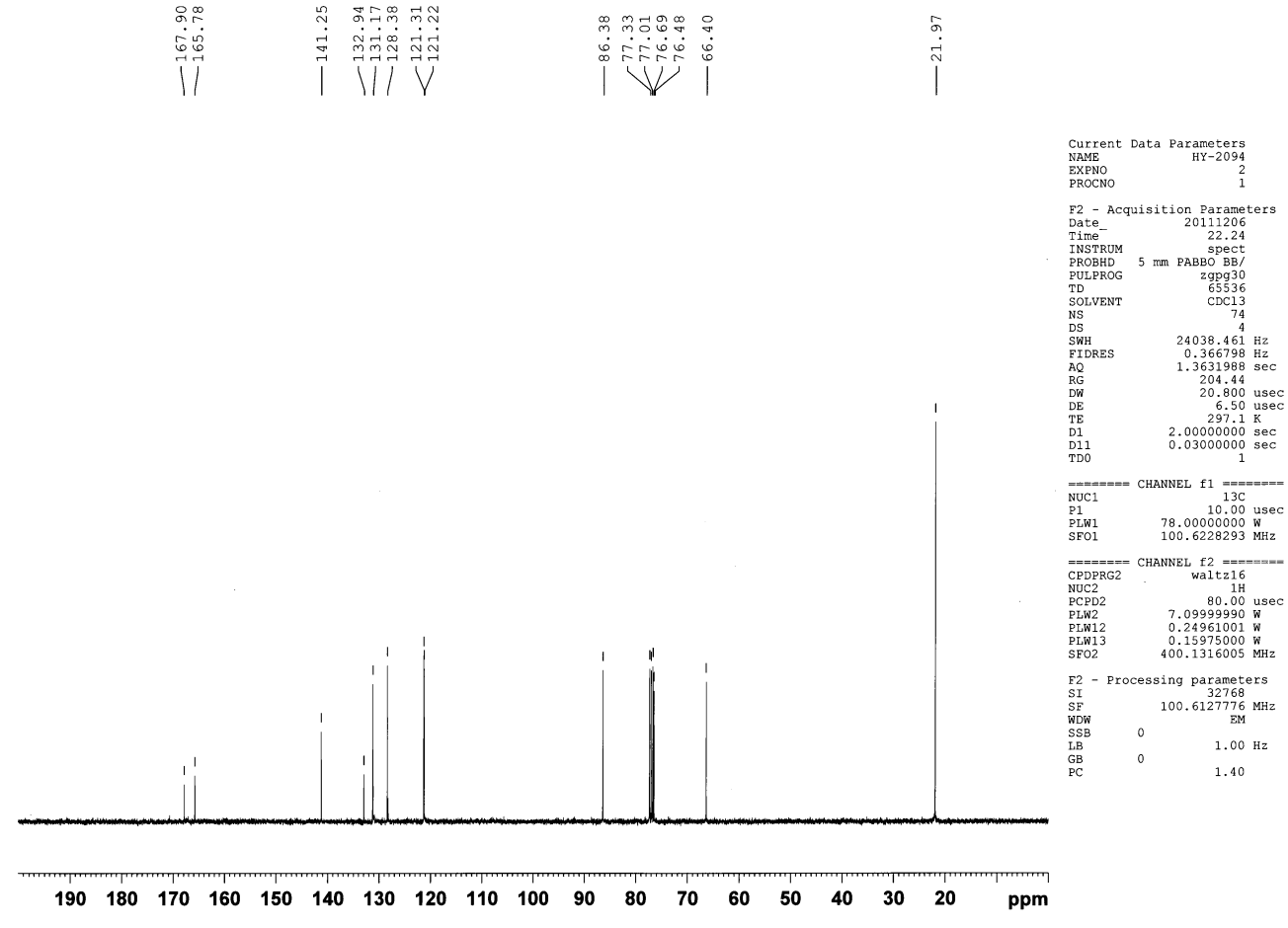
F2 - Acquisition Parameters
Date_              20111119
Time                   14.35
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        132
DS                          4
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                    204.44
DW                    20.800 usec
DE                     6.50 usec
TE                    297.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

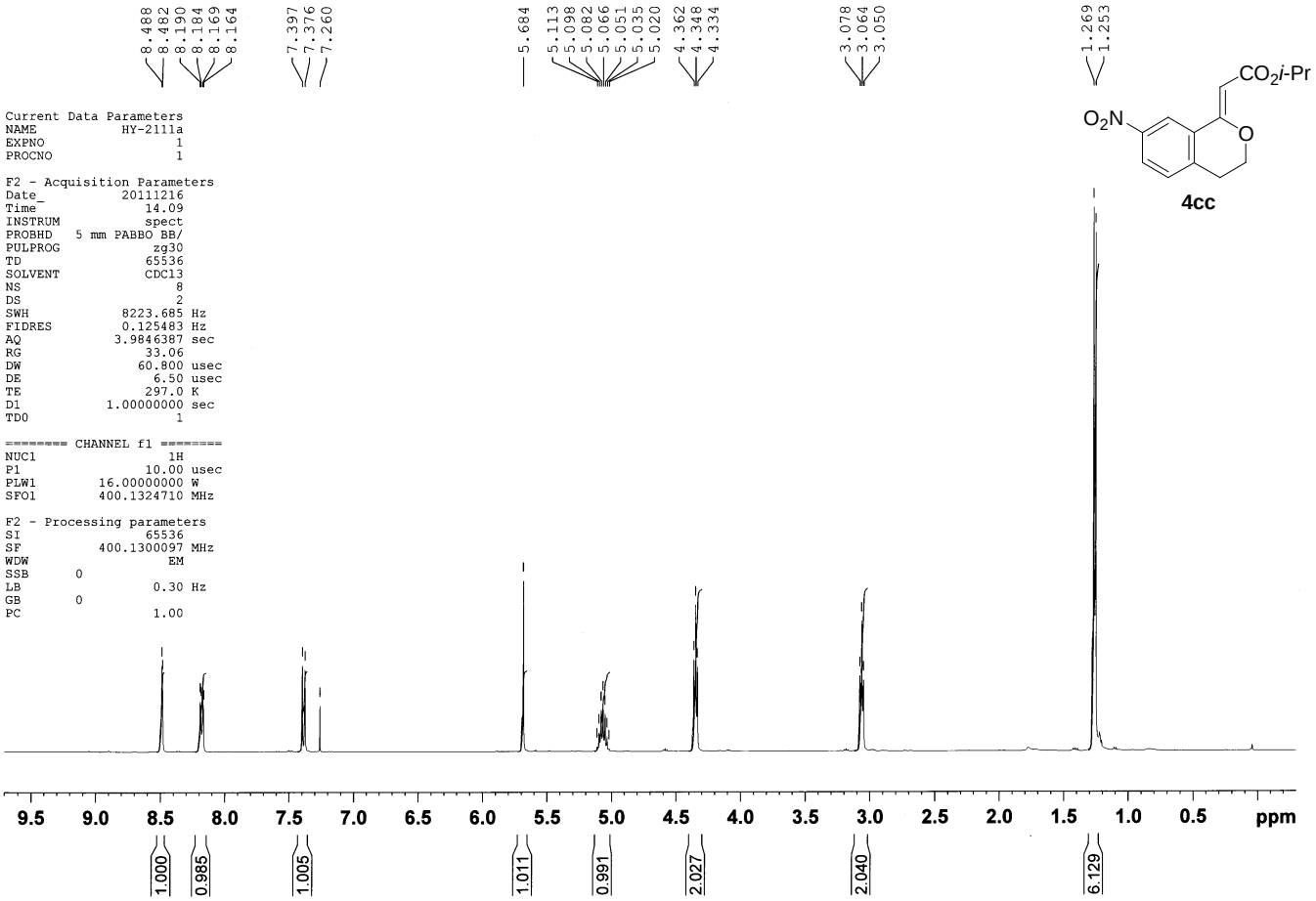
======== CHANNEL f1 ========
NUC1                      13C
P1                      10.00 usec
PLW1              78.00000000 W
SFO1             100.6228293 MHz

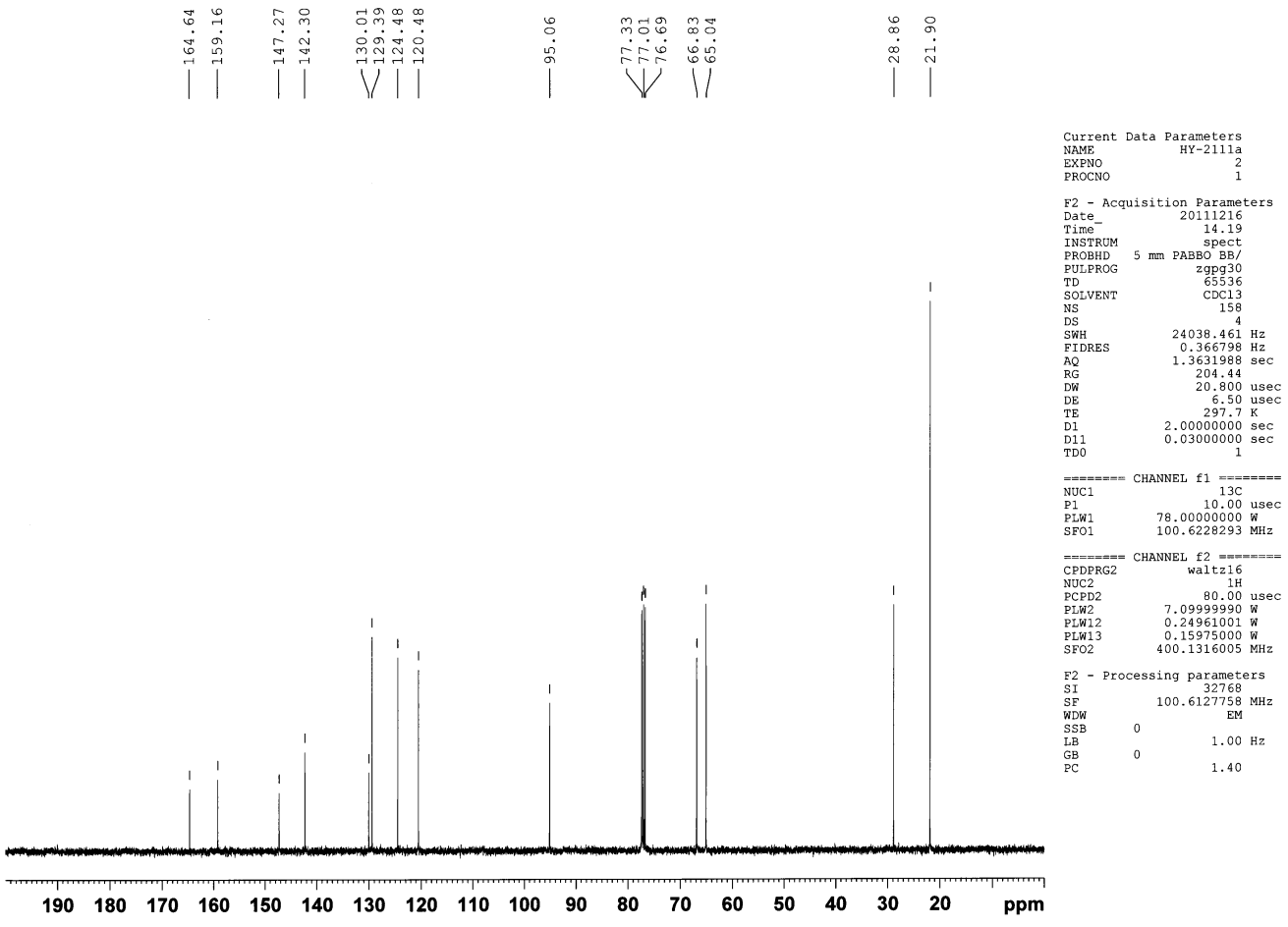
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PLW2               7.09999990 W
PLW12              0.24961001 W
PLW13              0.15975000 W
SFO2             400.1316005 MHz

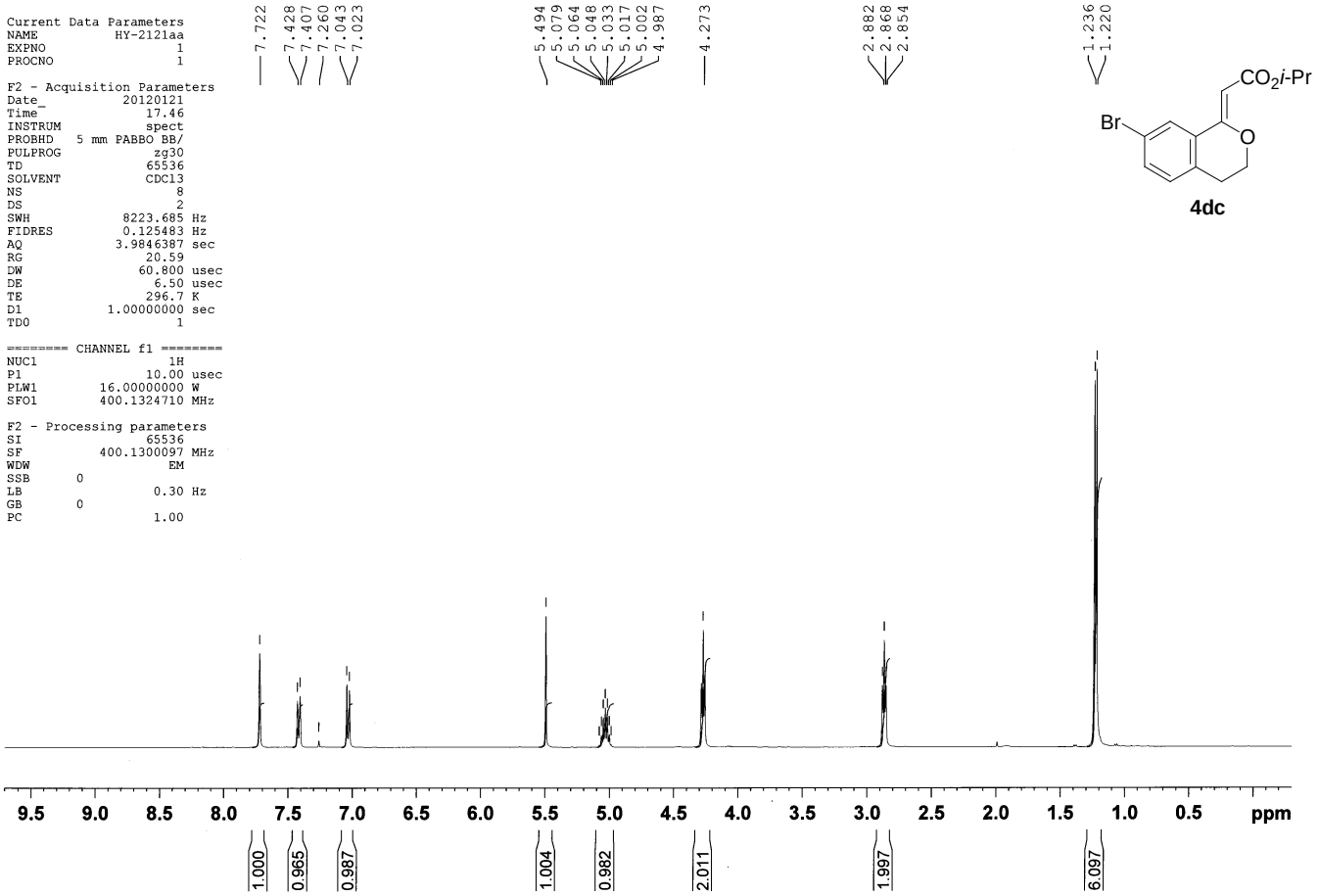
F2 - Processing parameters
SI                      32768
SF               100.6127778 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

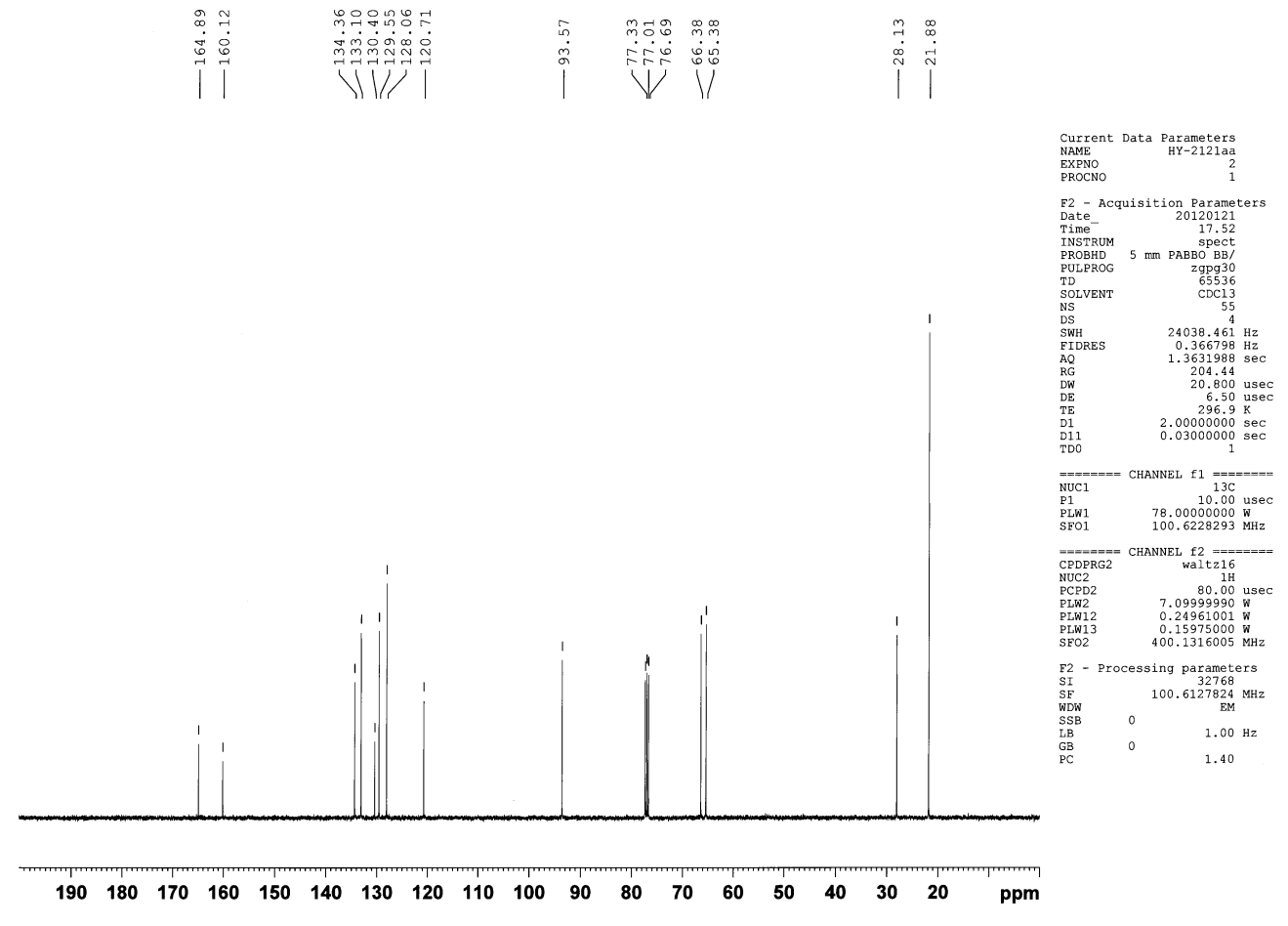

7.557
7.537
7.481
7.463
7.444
7.435
7.413
7.394
7.393
7.388
7.377
7.371
7.369
7.359
7.343
7.324
5.542
5.479
5.123
5.107
5.092
5.076
5.061
5.043
1.272
1.257
CO2i-Pr
O
4bc
Current Data Parameters
NAME HY-2094
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111206
Time 22.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.148
2.134
1.887
0.911
1.081
6.574

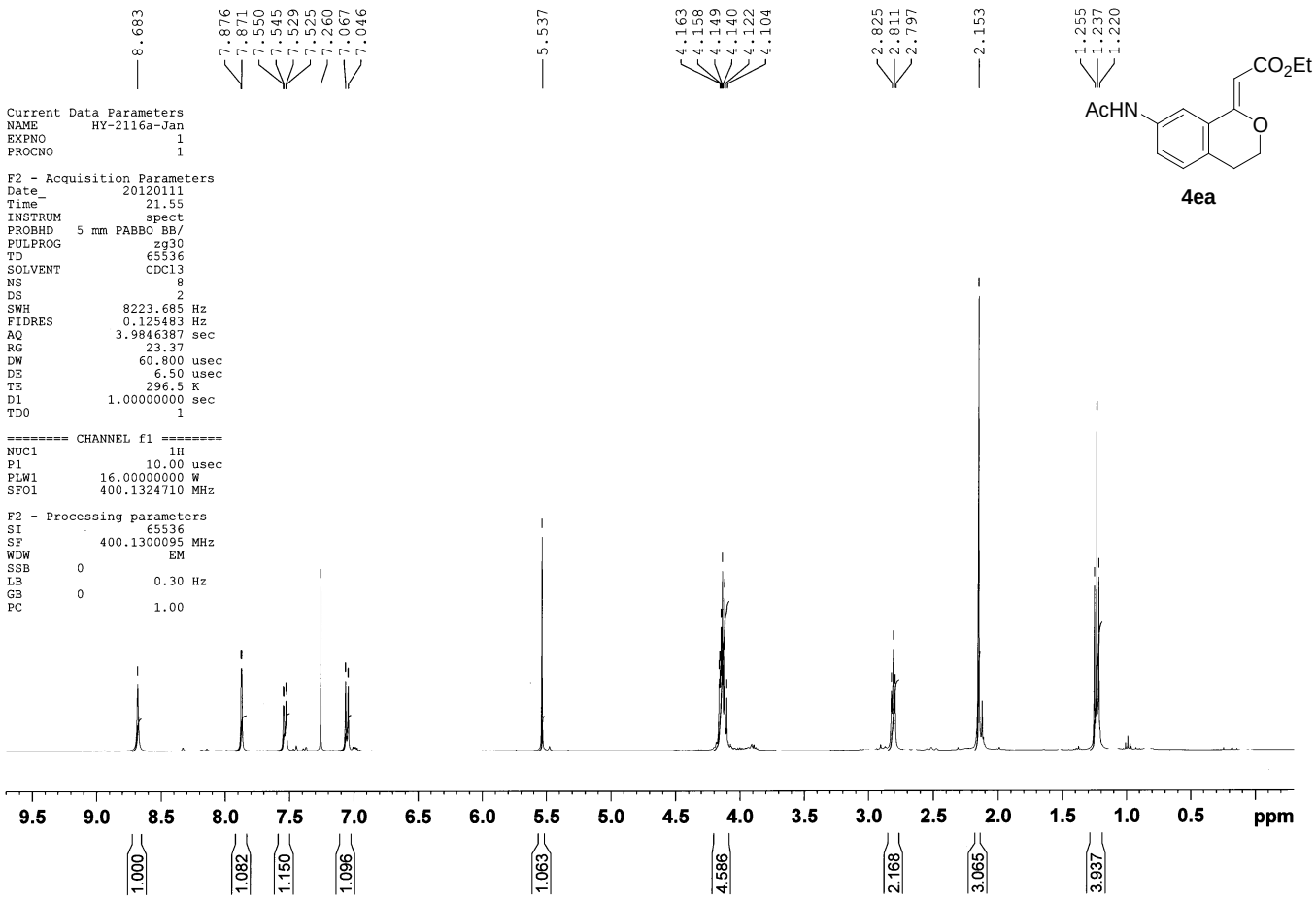

167.90
165.78
141.25
132.94
131.17
128.38
121.31
121.22
86.38
77.33
77.01
76.69
76.48
66.40
21.97
Current Data Parameters
NAME HY-2094
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111206
Time 22.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 74
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127776 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

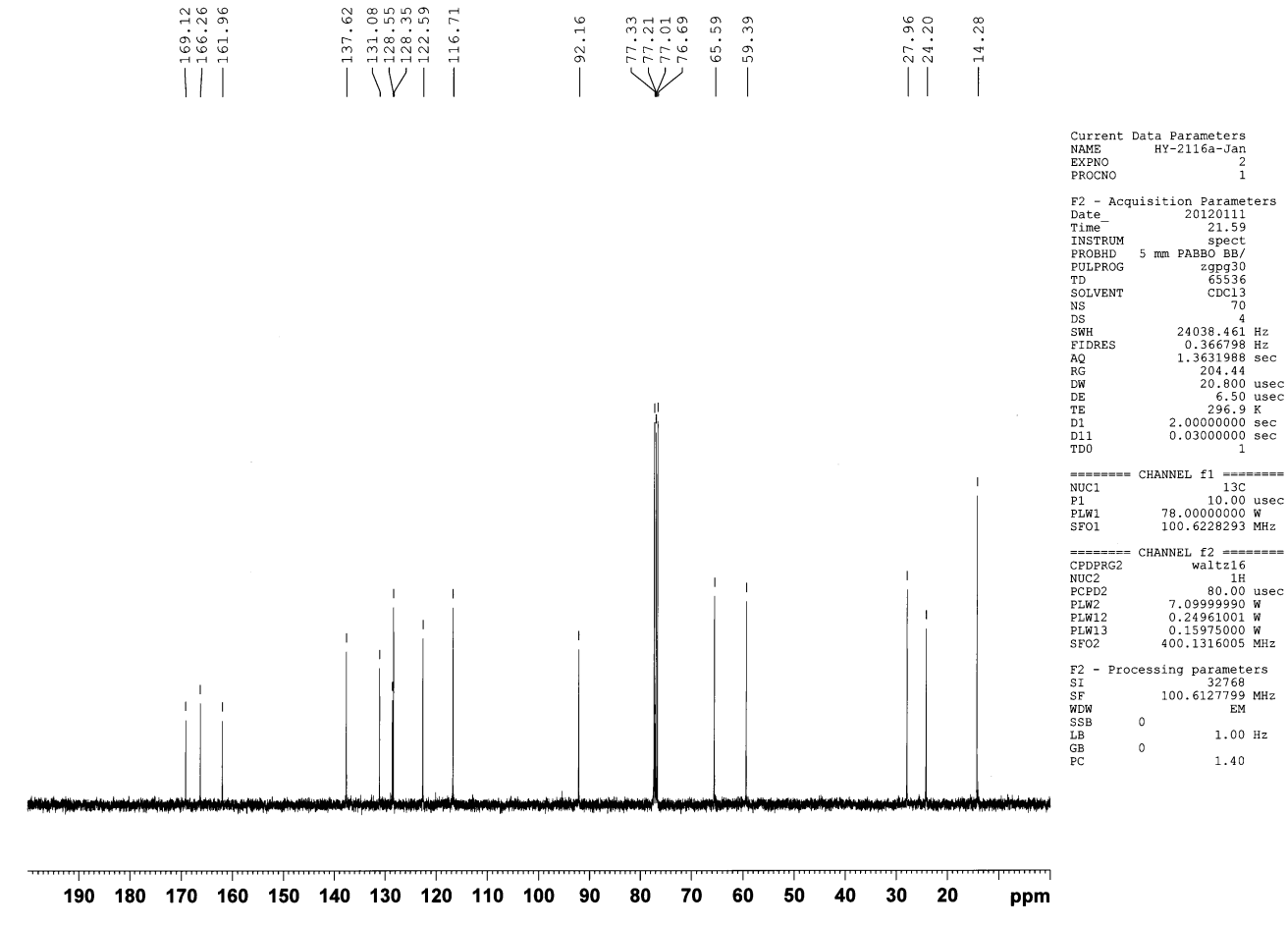

8.488
8.482
8.190
8.184
8.169
8.164
7.397
7.376
7.260
5.684
5.113
5.098
5.082
5.066
5.051
5.035
5.020
4.362
4.348
4.334
3.078
3.064
3.050
1.269
1.253
CO2i-Pr
O2N
O
4cc
Current Data Parameters
NAME HY-2111a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111216
Time 14.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.985
1.005
1.011
0.991
2.027
2.040
6.129

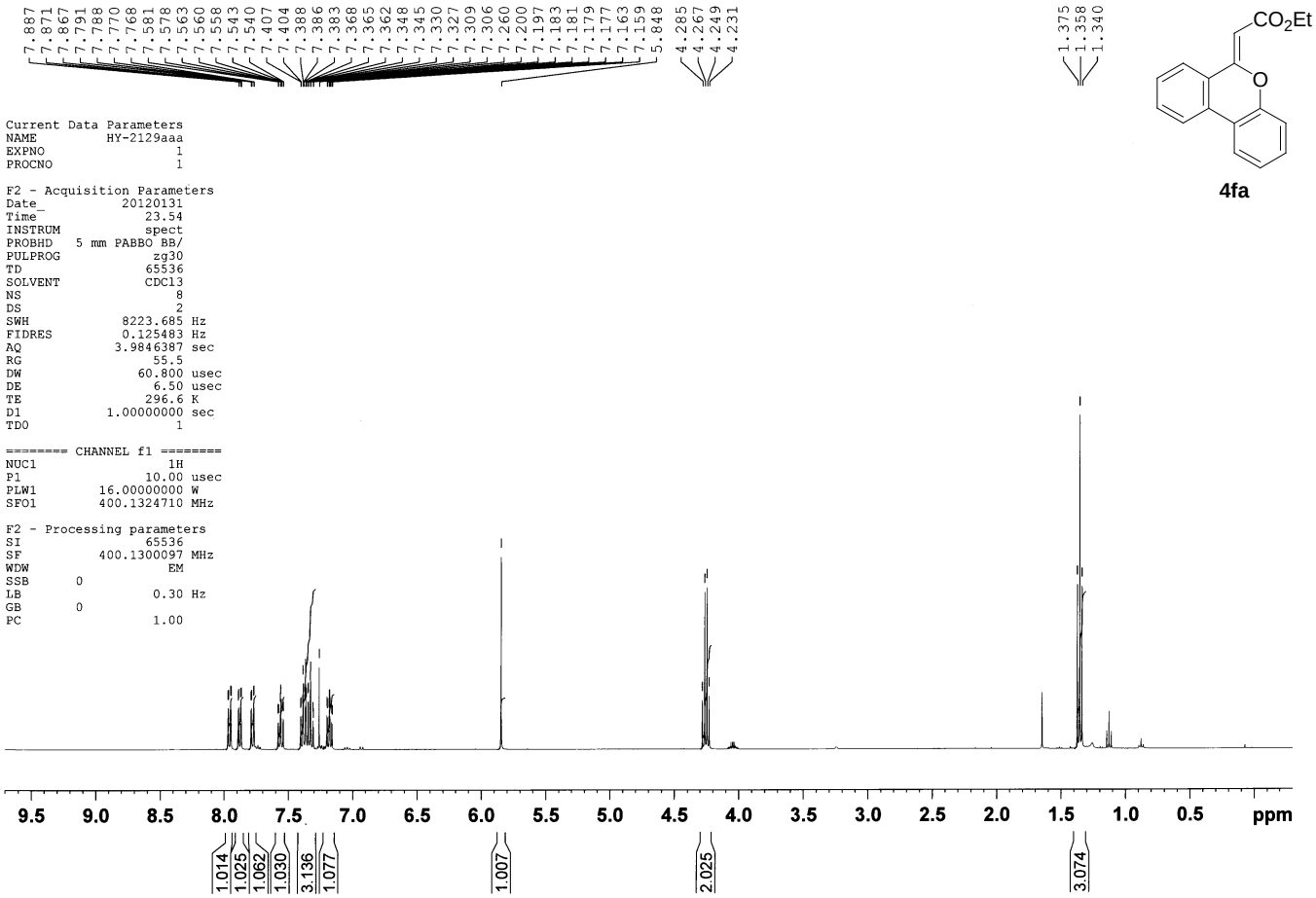

164.64
159.16
147.27
142.30
130.01
129.39
124.48
120.48
95.06
77.33
77.01
76.69
66.83
65.04
28.86
21.90
Current Data Parameters
NAME HY-2111a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111216
Time 14.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 158
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127758 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

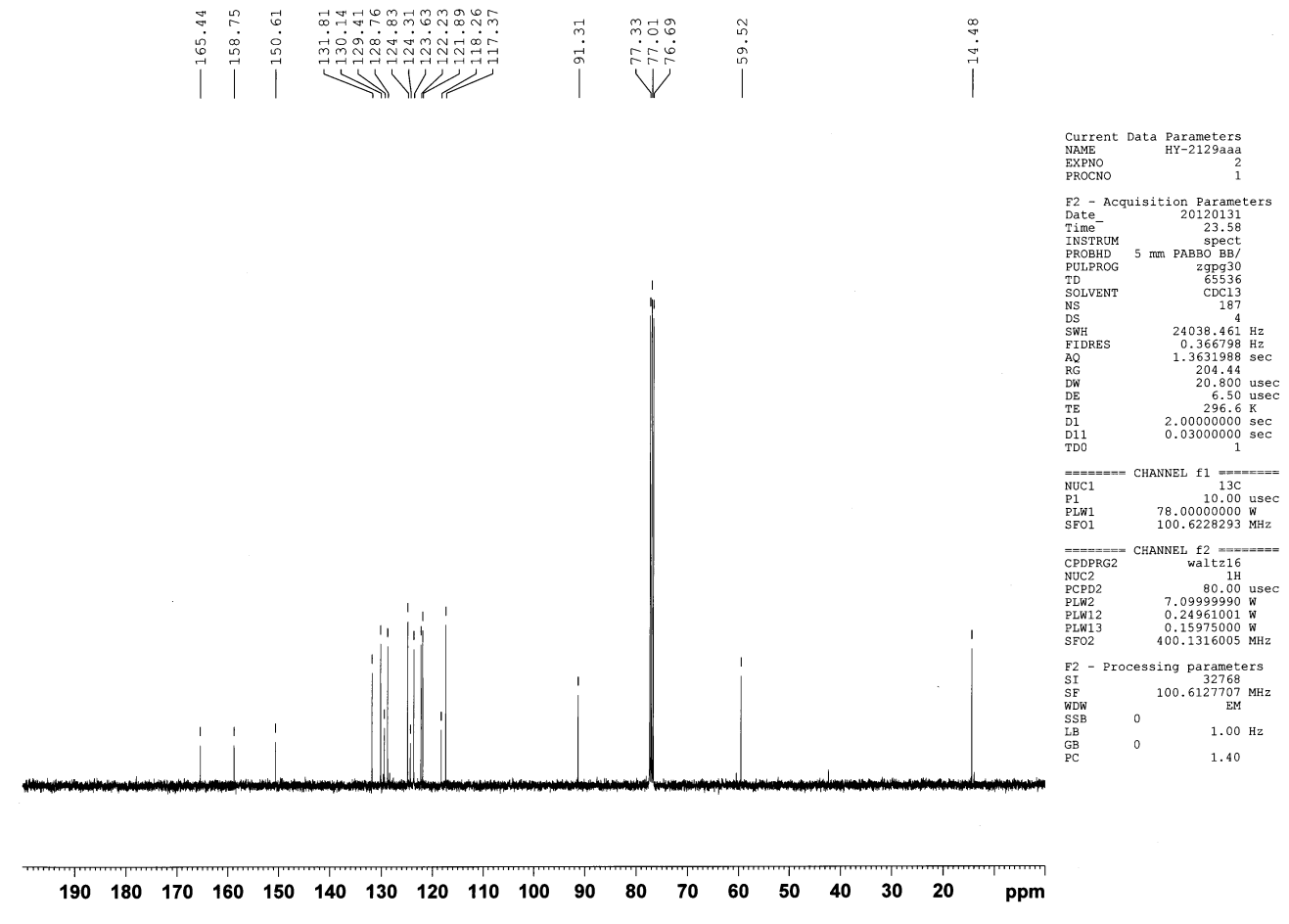

Current Data Parameters
NAME HY-2121aa
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120121
Time 17.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 20.59
DW 60.800 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.722
7.428
7.407
7.260
7.043
7.023
5.494
5.079
5.064
5.048
5.033
5.017
5.002
4.987
4.273
2.882
2.868
2.854
1.236
1.220
CO2i-Pr
Br
O
4dc
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.965
0.987
1.004
0.982
2.011
1.997
6.097

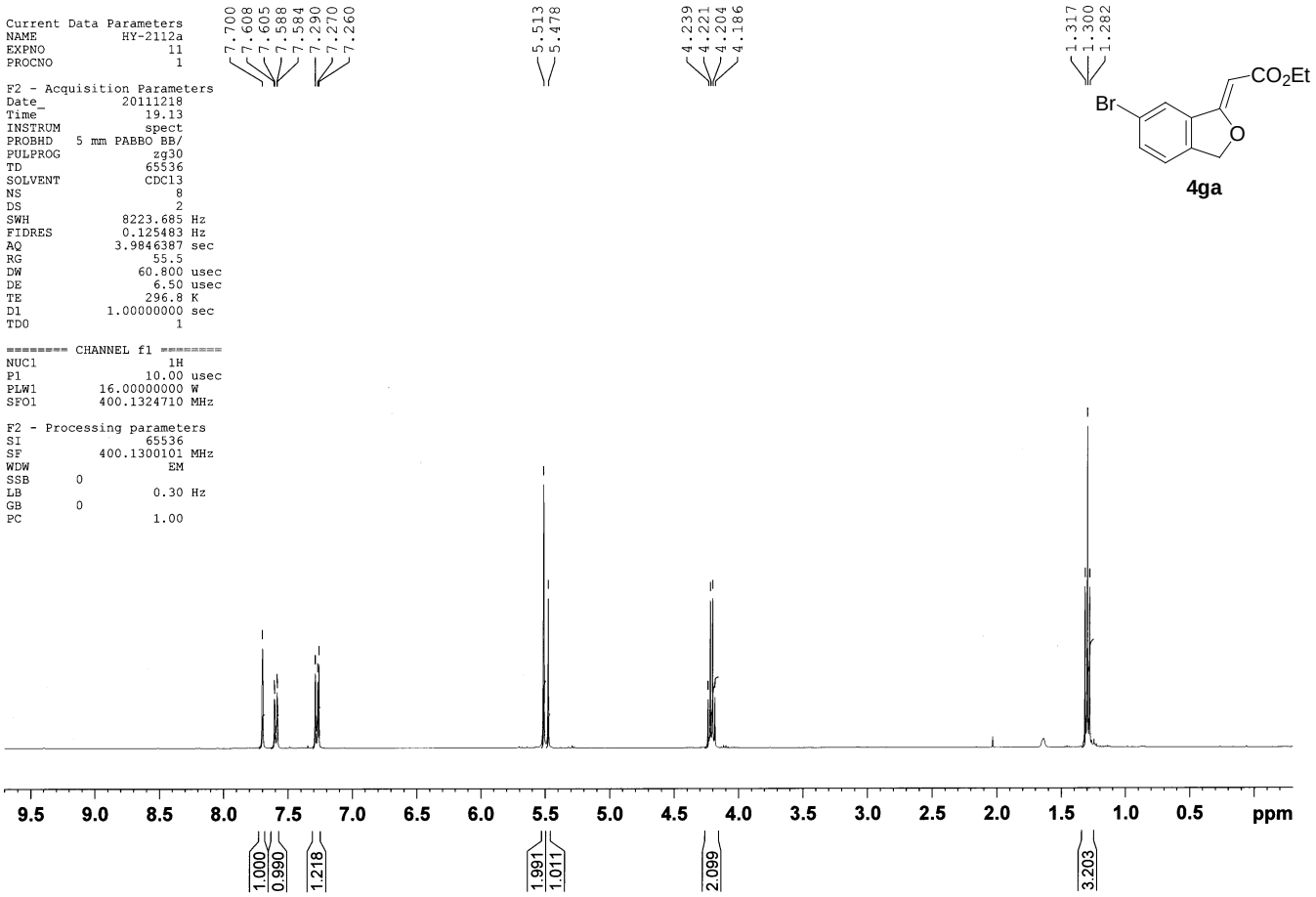

164.89
160.12
134.36
133.10
130.40
129.55
128.06
120.71
93.57
77.33
77.01
76.69
66.38
65.38
28.13
21.88
Current Data Parameters
NAME HY-2121aa
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120121
Time 17.52
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 55
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127824 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

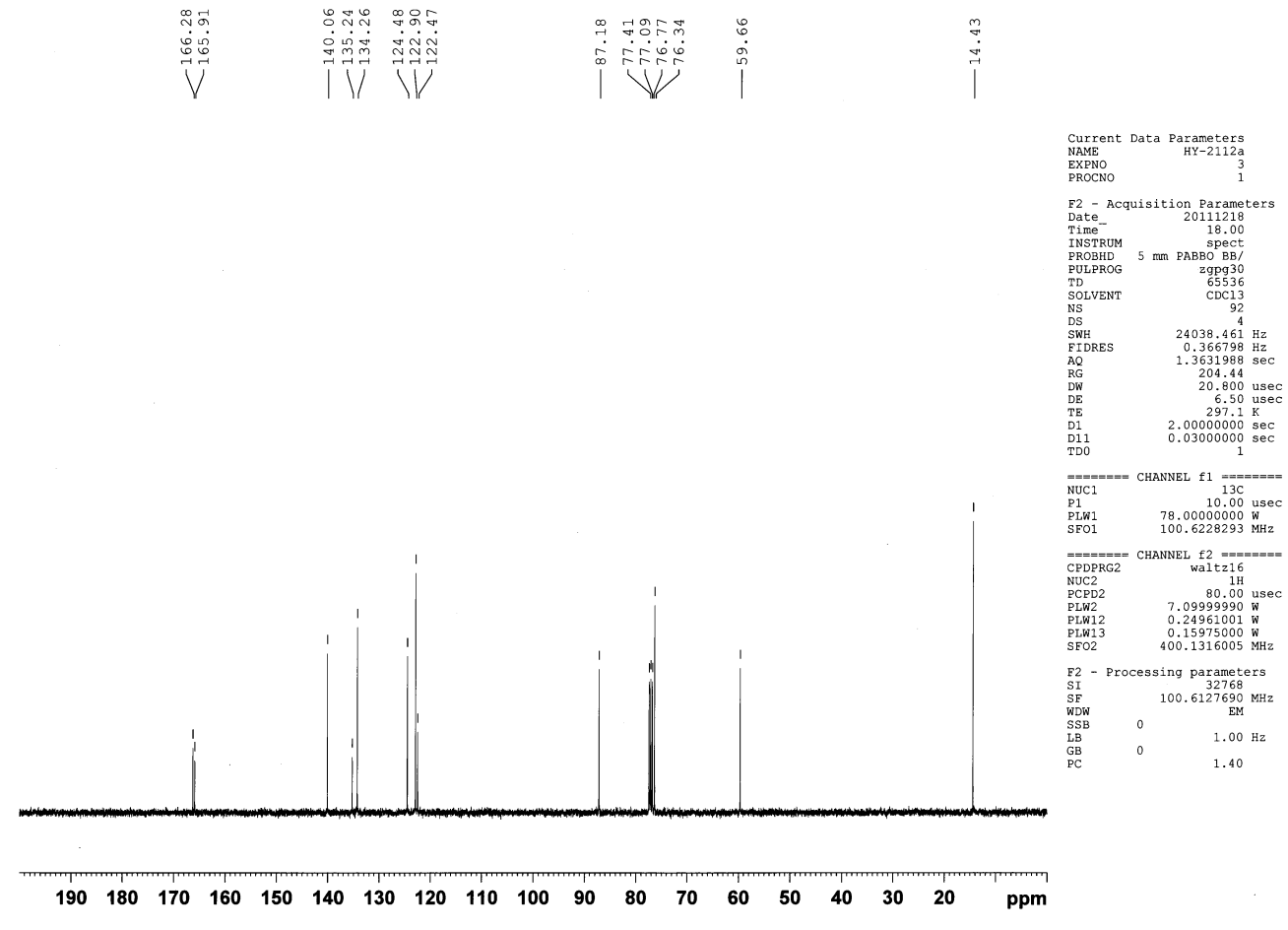

8.683
7.876
7.871
7.550
7.545
7.529
7.525
7.260
7.067
7.046
5.537
4.163
4.158
4.149
4.140
4.122
4.104
2.825
2.811
2.797
2.153
1.255
1.237
1.220
CO2Et
AcHN
O
4ea
Current Data Parameters
NAME HY-2116a-Jan
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120111
Time 21.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 23.37
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.082
1.150
1.096
1.063
4.586
2.168
3.065
3.937

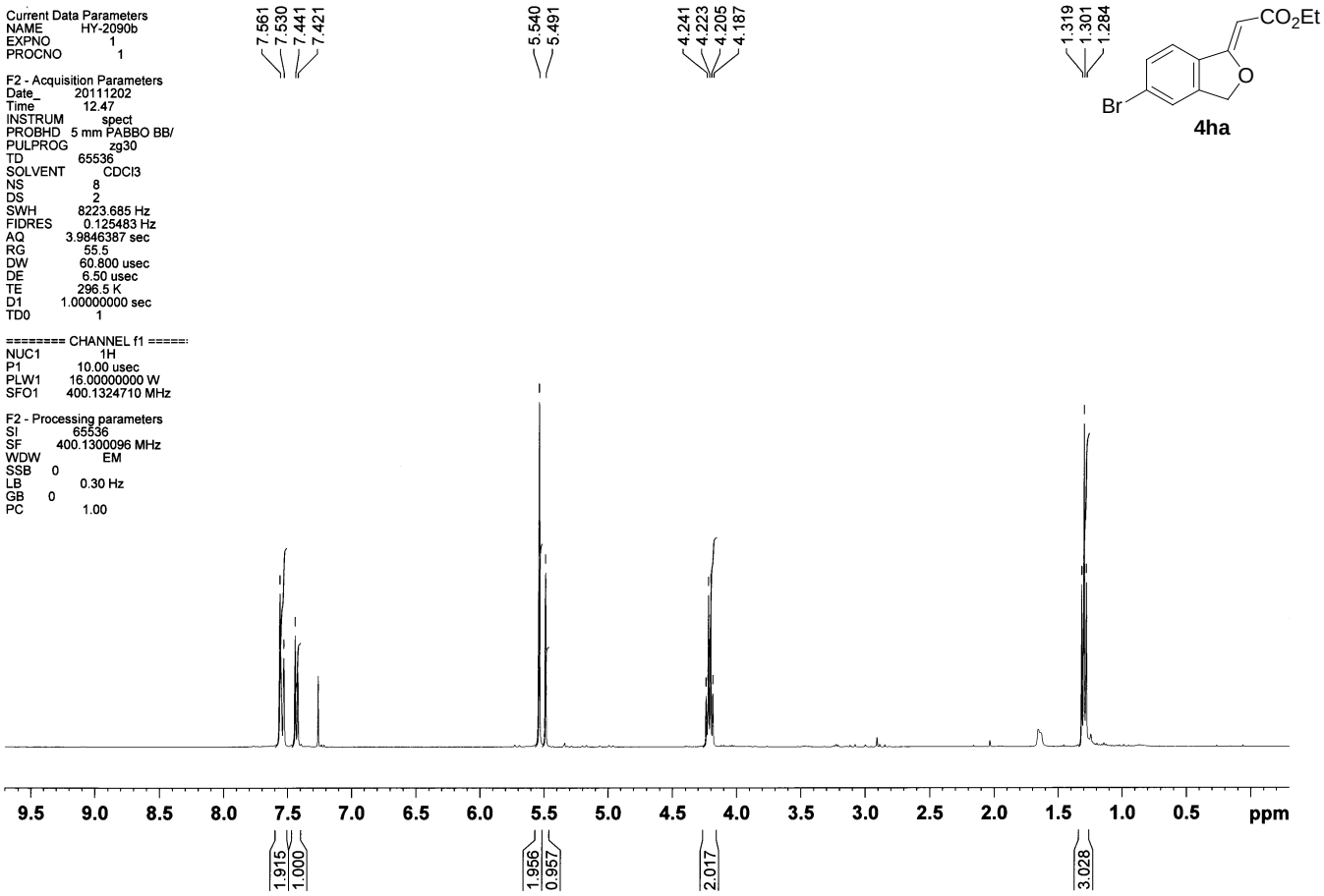

169.12
166.26
161.96
137.62
131.08
128.55
128.35
122.59
116.71
92.16
77.33
77.21
77.01
76.69
65.59
59.39
27.96
24.20
14.28
Current Data Parameters
NAME HY-2116a-Jan
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120111
Time 21.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 70
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127799 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

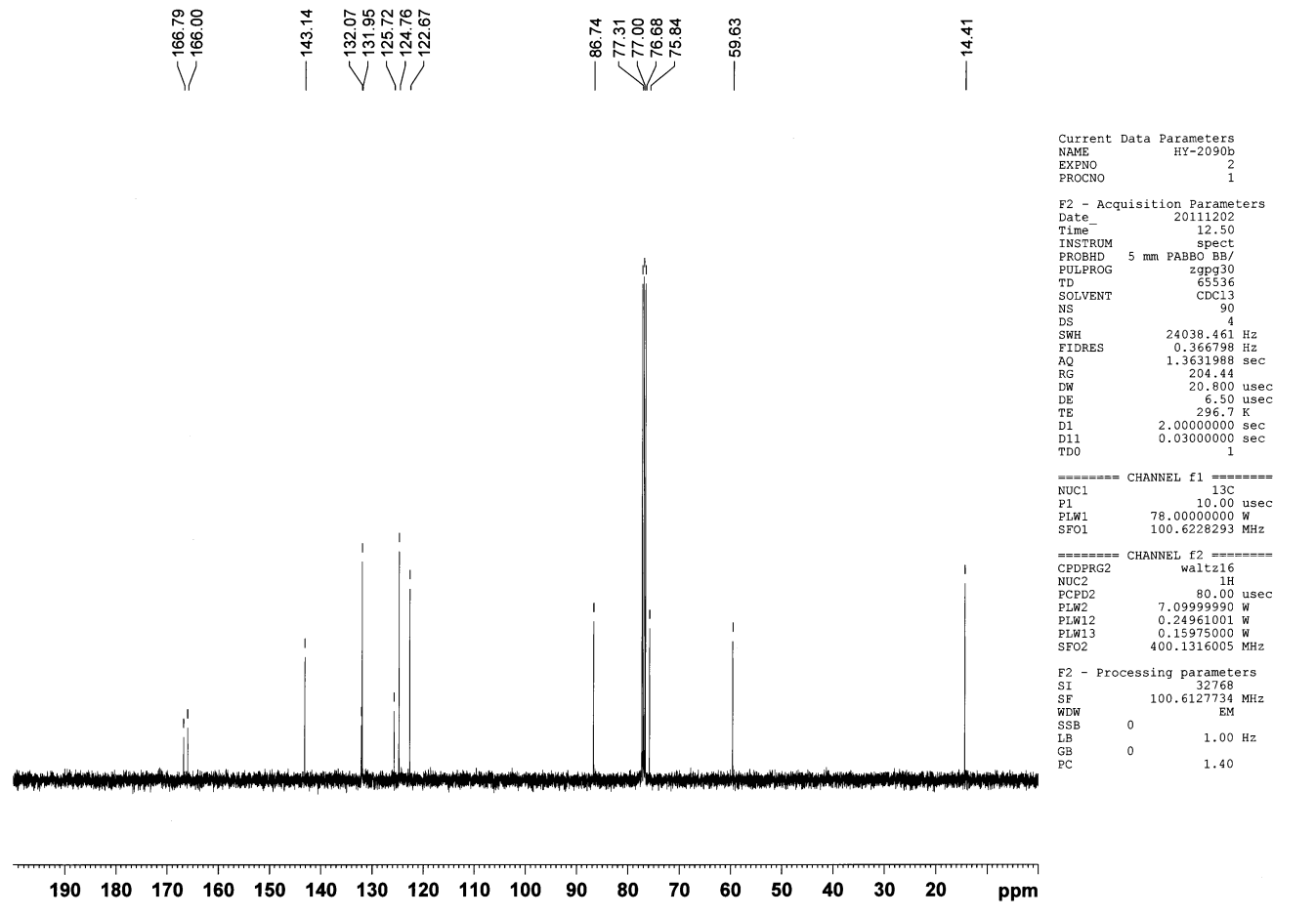

7.887
7.871
7.867
7.791
7.788
7.770
7.768
7.581
7.578
7.563
7.560
7.558
7.543
7.540
7.407
7.404
7.388
7.386
7.383
7.368
7.365
7.362
7.348
7.345
7.330
7.327
7.309
7.306
7.260
7.200
7.197
7.183
7.181
7.179
7.177
7.163
7.159
5.848
4.285
4.267
4.249
4.231
1.375
1.358
1.340
CO2Et
O
4fa
Current Data Parameters
NAME HY-2129aaa
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120131
Time 23.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.014
1.025
1.062
1.030
3.136
1.077
1.007
2.025
3.074

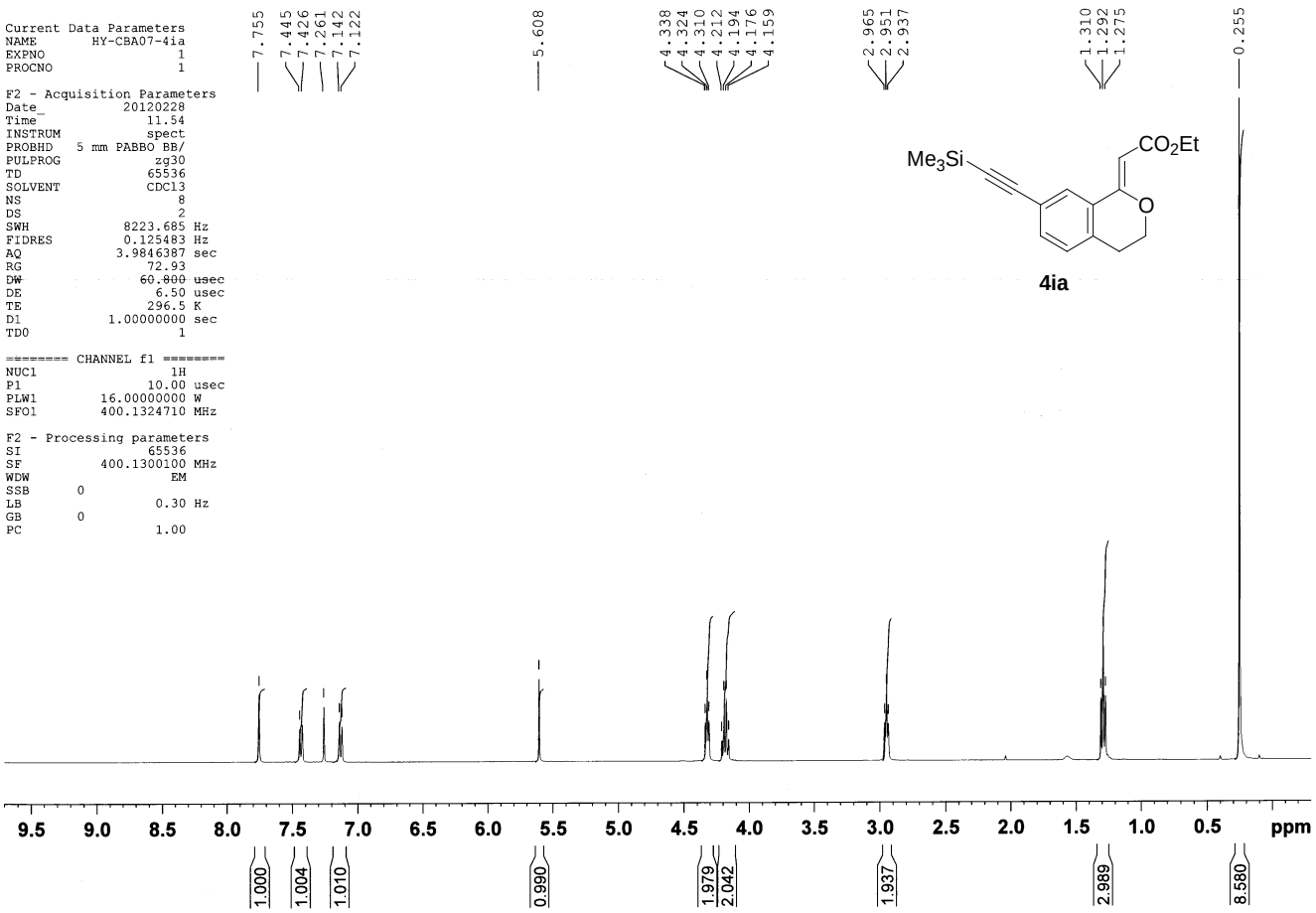

165.44
158.75
150.61
131.81
130.14
129.41
128.76
124.83
124.31
123.63
122.23
121.89
118.26
117.37
91.31
77.33
77.01
76.69
59.52
14.48
Current Data Parameters
NAME HY-2129aaa
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120131
Time 23.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 187
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

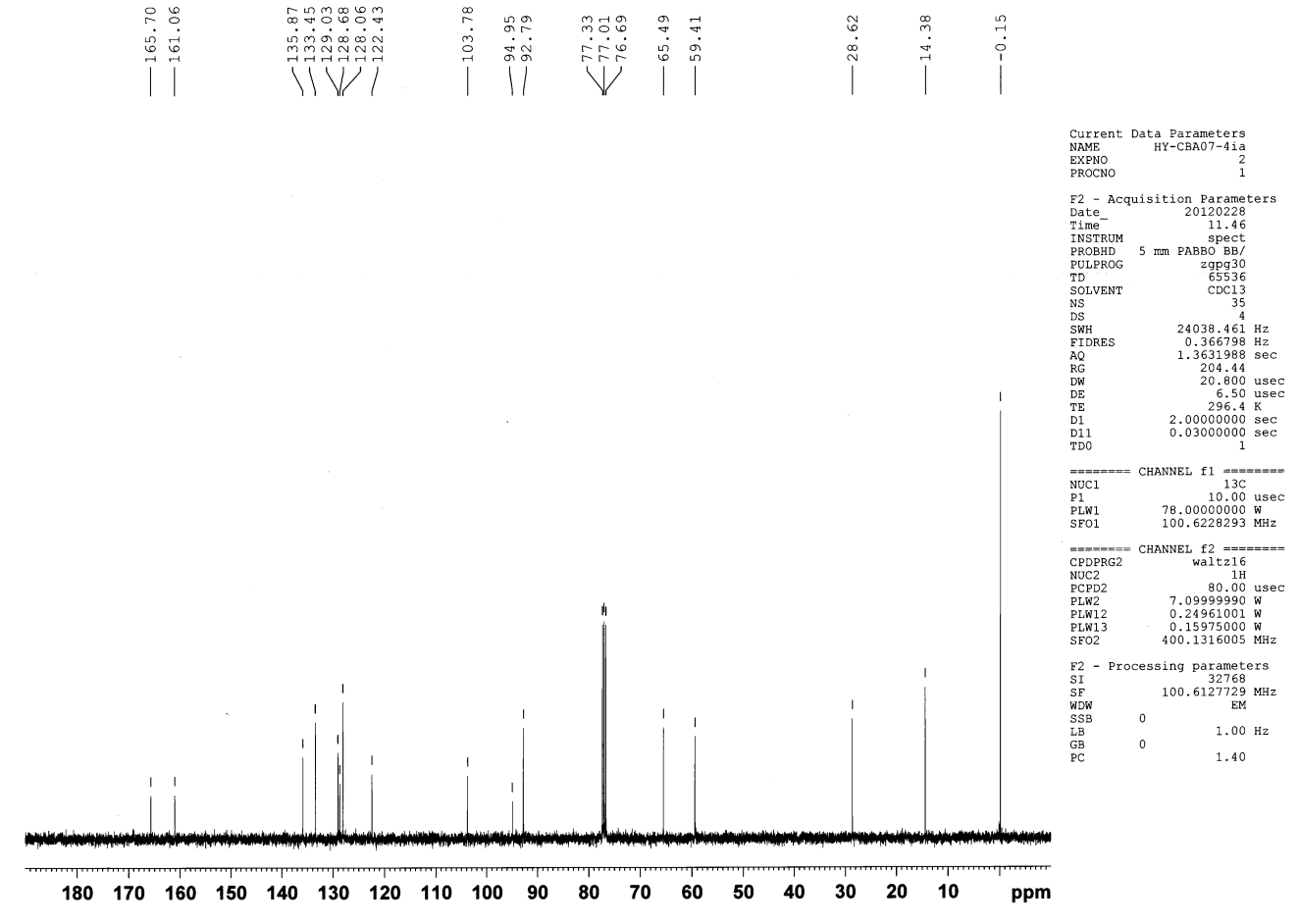

Current Data Parameters
NAME HY-2112a
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111218
Time 19.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.700
7.608
7.605
7.588
7.584
7.290
7.270
7.260
5.513
5.478
4.239
4.221
4.204
4.186
1.317
1.300
1.282
Br
CO2Et
O
4ga
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.990
1.218
1.991
1.011
2.099
3.203

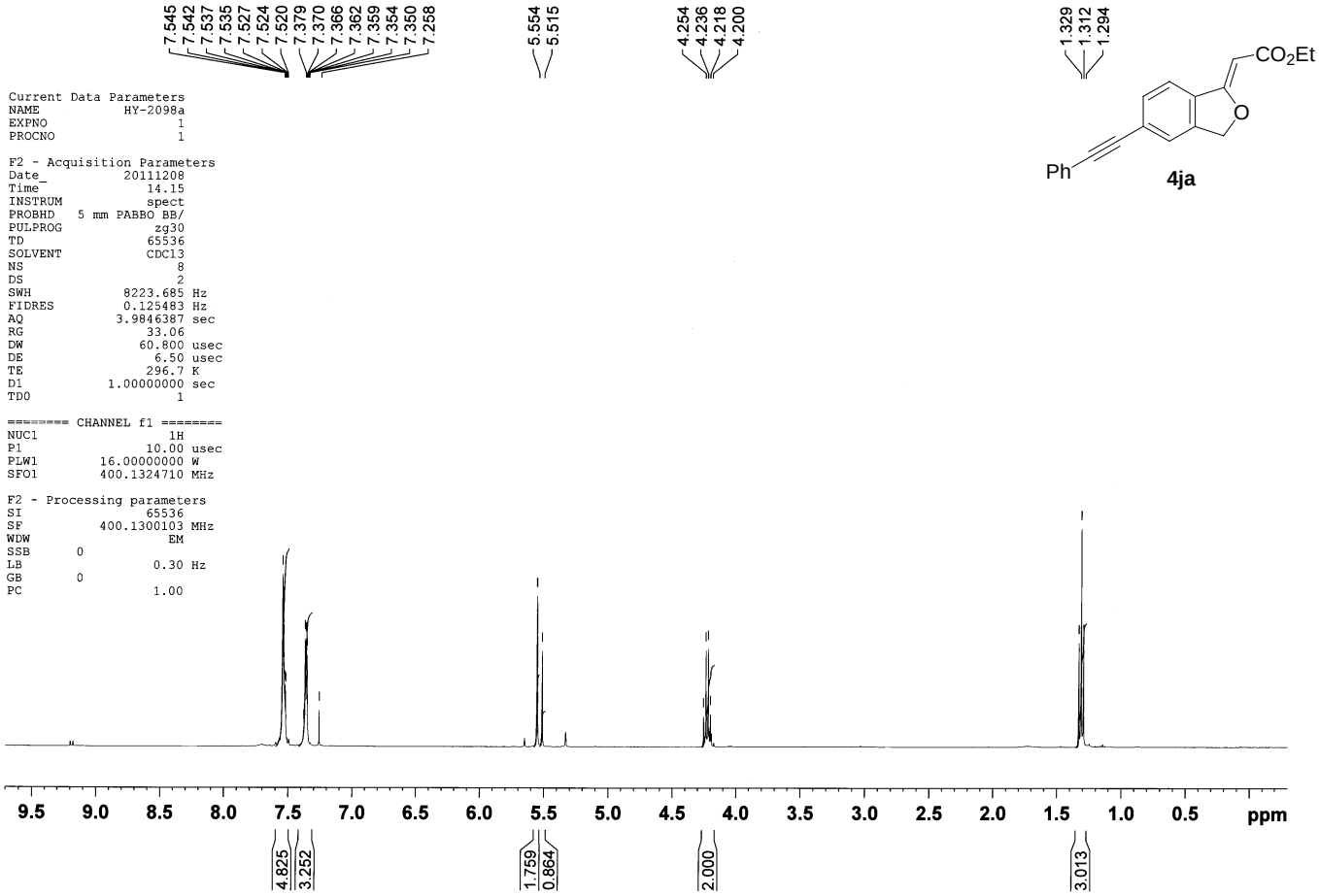

166.28
165.91
140.06
135.24
134.26
124.48
122.90
122.47
87.18
77.41
77.09
76.77
76.34
59.66
14.43
Current Data Parameters
NAME HY-2112a
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111218
Time 18.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 92
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

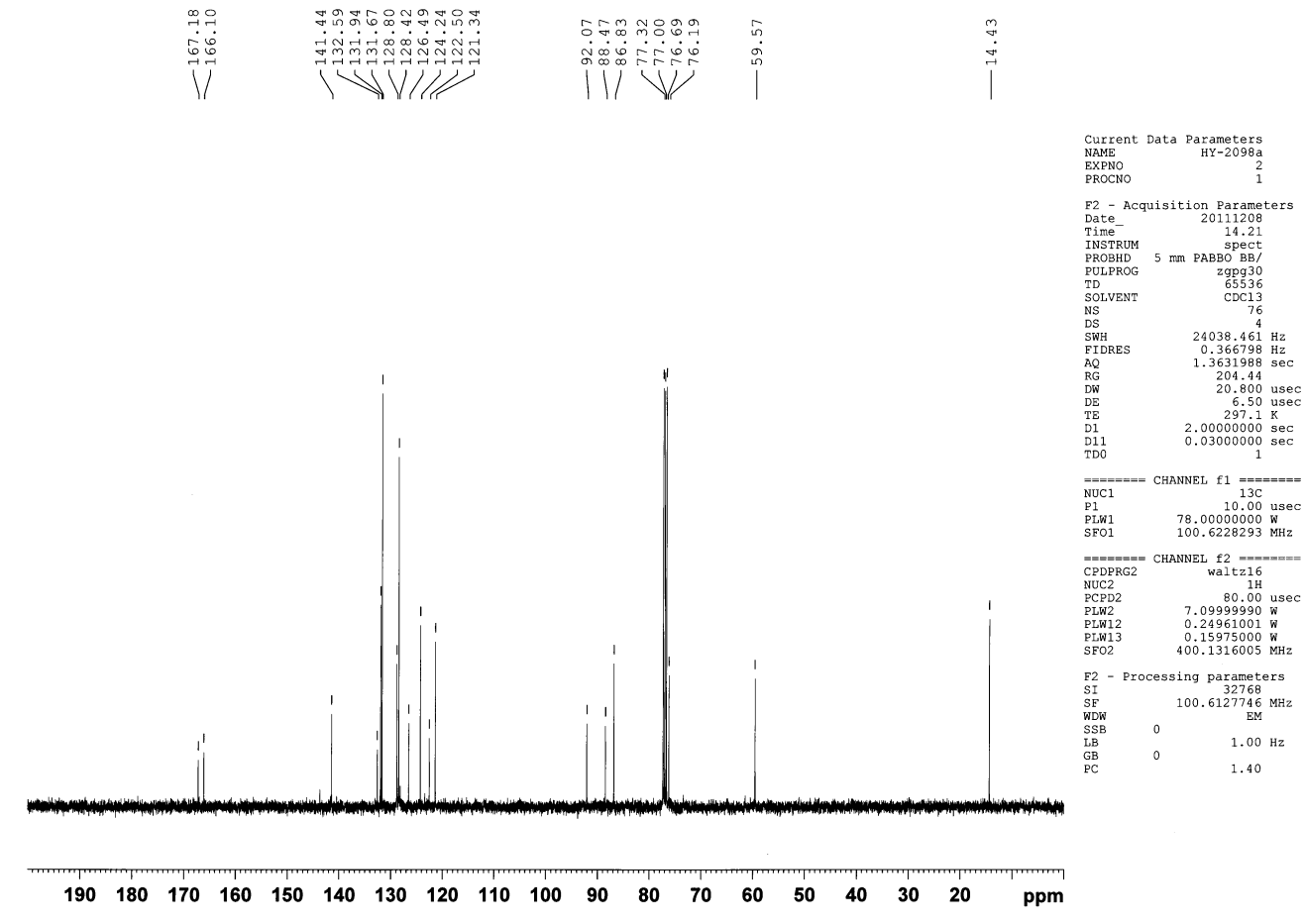

Current Data Parameters
NAME HY-2090b
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111202
Time 12.47
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 55.5
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.561
7.530
7.441
7.421
5.540
5.491
4.241
4.223
4.205
4.187
1.319
1.301
1.284
CO2Et
O
Br
4ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.915
1.000
1.956
0.957
2.017
3.028

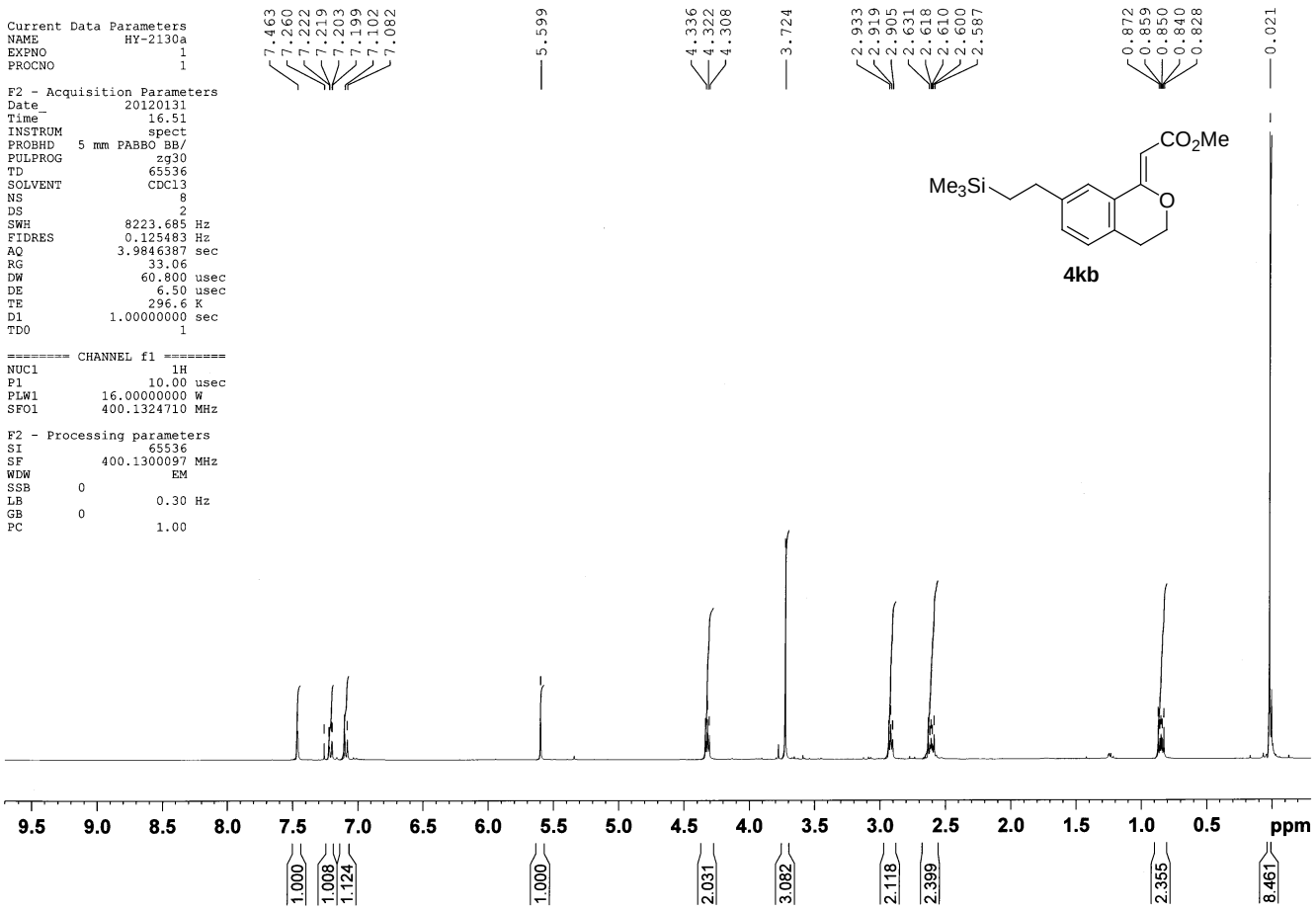

166.79
166.00
143.14
132.07
131.95
125.72
124.76
122.67
86.74
77.31
77.00
76.68
75.84
59.63
14.41
Current Data Parameters
NAME HY-2090b
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111202
Time 12.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 90
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127734 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

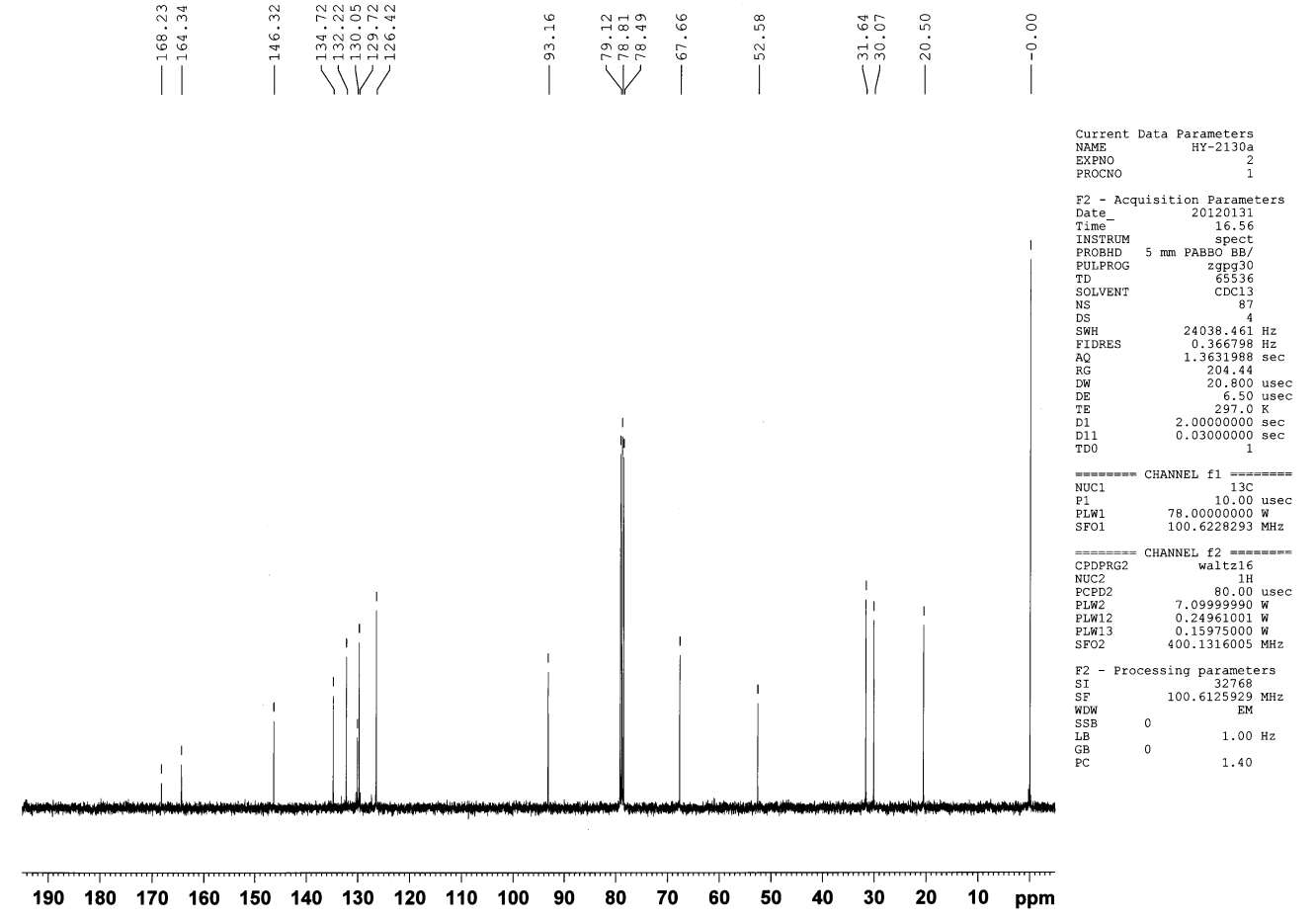

Current Data Parameters
NAME HY-CBA07-4ia
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120228
Time 11.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 72.93
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.755
7.445
7.426
7.261
7.142
7.122
5.608
4.338
4.324
4.310
4.212
4.194
4.176
4.159
2.965
2.951
2.937
1.310
1.292
1.275
0.255
Me3Si
CO2Et
O
4ia
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.004
1.010
0.990
1.979
2.042
1.937
2.989
8.580

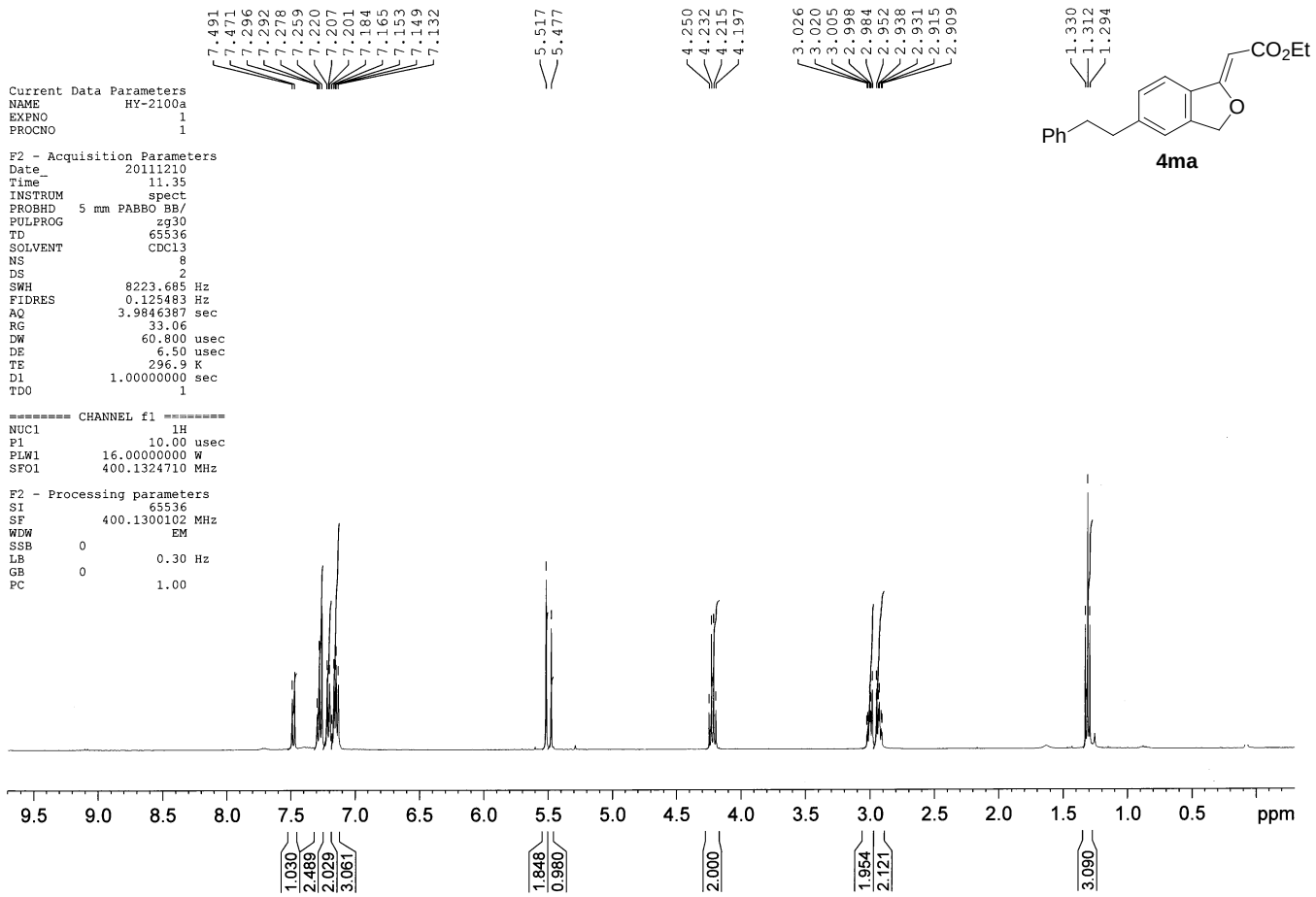

165.70
161.06
135.87
133.45
129.03
128.68
128.06
122.43
103.78
94.95
92.79
77.33
77.01
76.69
65.49
59.41
28.62
14.38
-0.15
Current Data Parameters
NAME HY-CBA07-4ia
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120228
Time 11.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 35
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

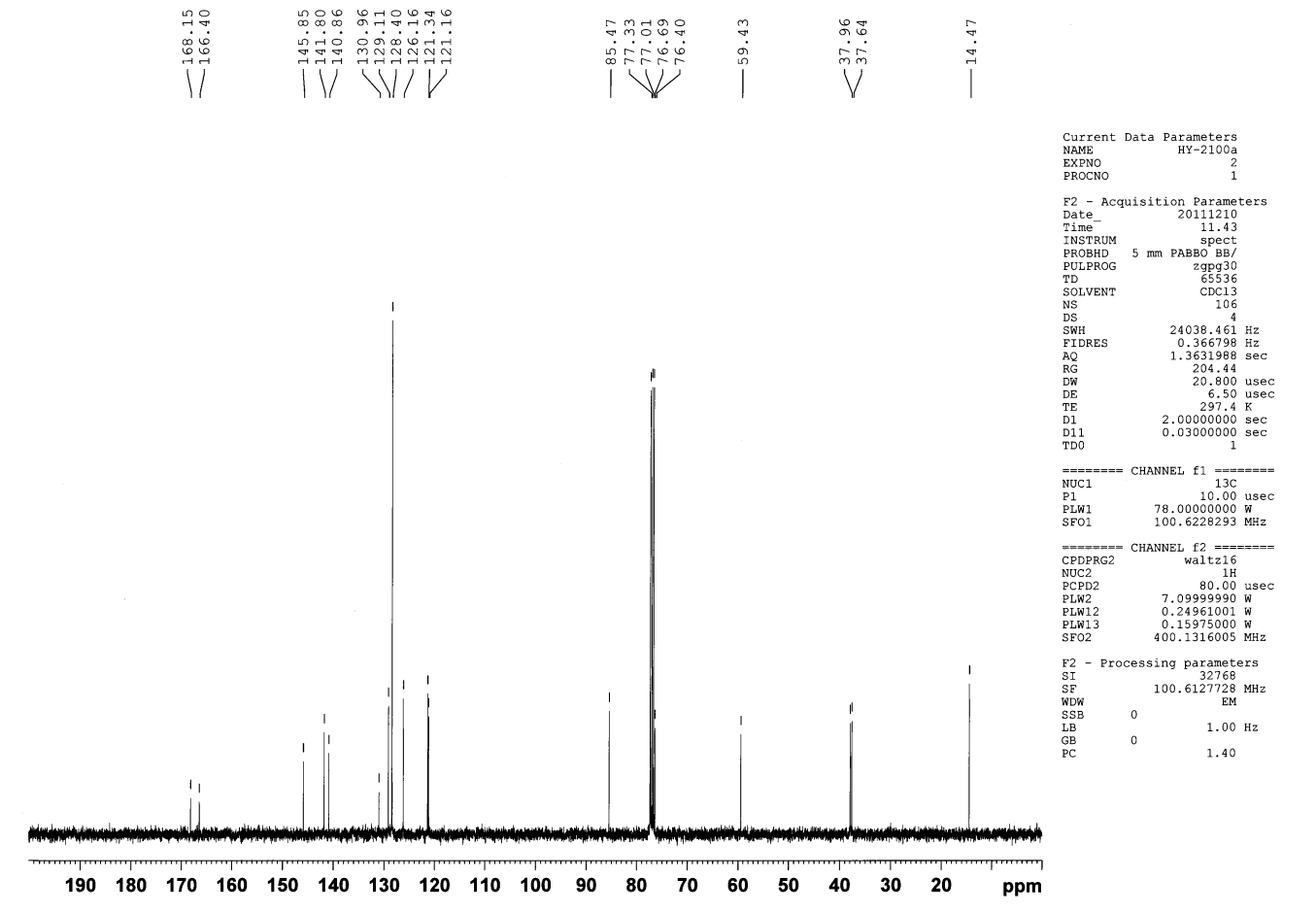

7.545
7.542
7.537
7.535
7.527
7.524
7.520
7.379
7.370
7.366
7.362
7.359
7.354
7.350
7.258
5.554
5.515
4.254
4.236
4.218
4.200
1.329
1.312
1.294
CO2Et
O
Ph
4ja
Current Data Parameters
NAME HY-2098a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111208
Time 14.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.825
3.252
1.759
0.864
2.000
3.013

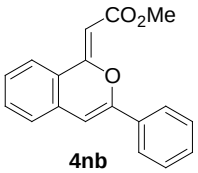

167.18
166.10
141.44
132.59
131.94
131.67
128.80
128.42
126.49
124.24
122.50
121.34
92.07
88.47
86.83
77.32
77.00
76.69
76.19
59.57
14.43
Current Data Parameters
NAME HY-2098a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111208
Time 14.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 76
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127746 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Current Data Parameters
NAME HY-2130a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120131
Time 16.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.463
7.260
7.222
7.219
7.203
7.199
7.102
7.082
5.599
4.336
4.322
4.308
3.724
2.933
2.919
2.905
2.631
2.618
2.610
2.600
2.587
0.872
0.859
0.850
0.840
0.828
0.021
CO2Me
Me3Si
O
4kb
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.008
1.124
1.000
2.031
3.082
2.118
2.399
2.355
8.461


168.23
164.34
146.32
134.72
132.22
130.05
129.72
126.42
93.16
79.12
78.81
78.49
67.66
52.58
31.64
30.07
20.50
-0.00
Current Data Parameters
NAME HY-2130a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120131
Time 16.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 87
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6125929 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.491
7.471
7.296
7.292
7.278
7.259
7.220
7.207
7.201
7.184
7.165
7.153
7.149
7.132
5.517
5.477
4.250
4.232
4.215
4.197
3.026
3.020
3.005
2.998
2.984
2.952
2.938
2.931
2.915
2.909
1.330
1.312
1.294
CO2Et
O
Ph
4ma
Current Data Parameters
NAME HY-2100a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111210
Time 11.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 33.06
DW 60.800 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.030
2.489
2.029
3.061
1.848
0.980
2.000
1.954
2.121
3.090


168.15
166.40
145.85
141.80
140.86
130.96
129.11
128.40
126.16
121.34
121.16
85.47
77.33
77.01
76.69
76.40
59.43
37.96
37.64
14.47
Current Data Parameters
NAME HY-2100a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111210
Time 11.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 106
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



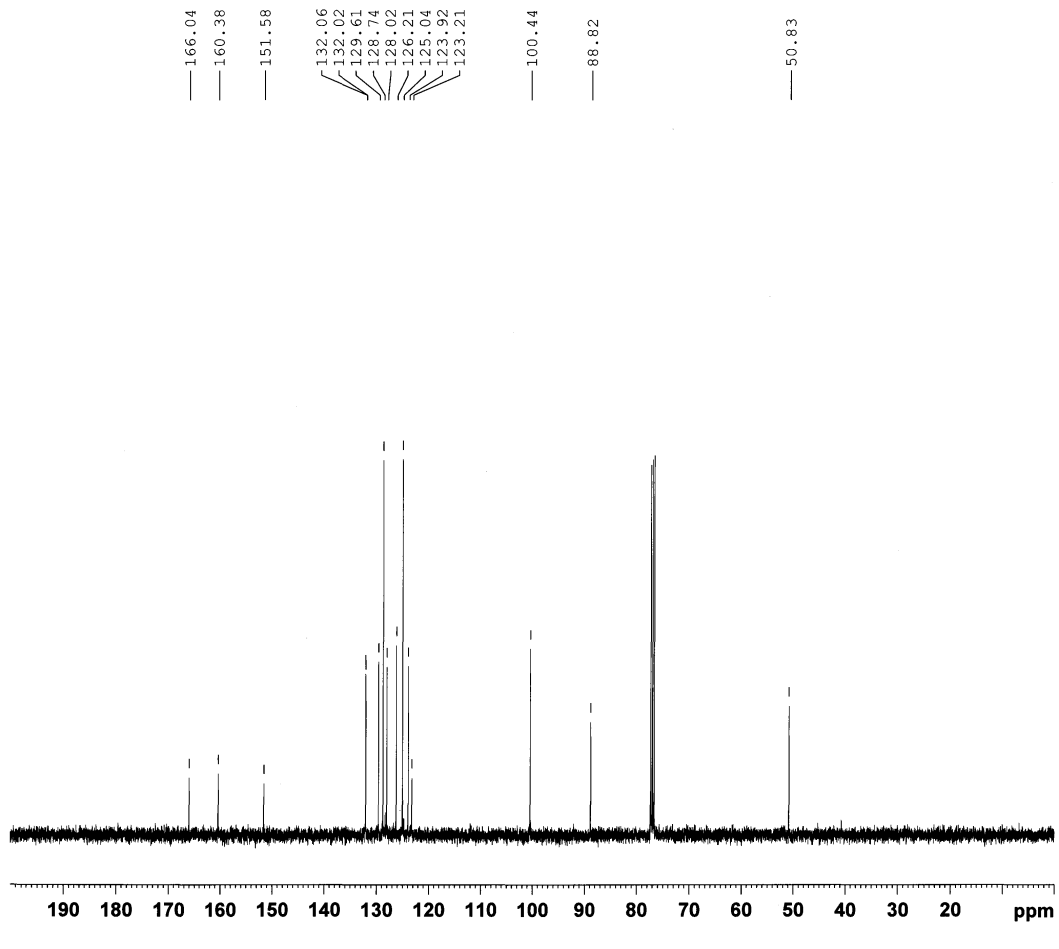
4nb

Current Data Parameters
NAME HY-2132a
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120202
Time 12.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 45.68
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



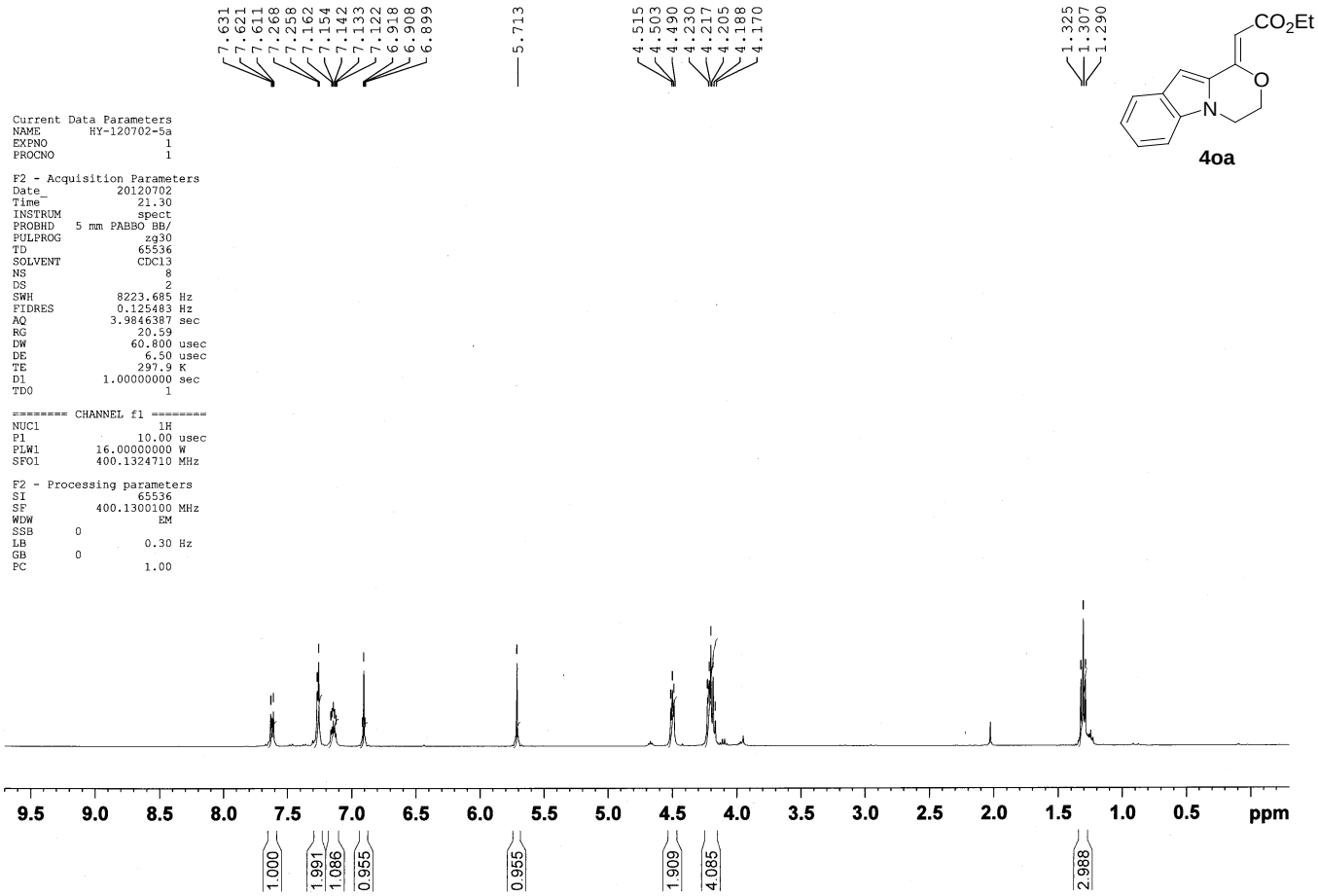
Current Data Parameters
NAME HY-2132a
EXPNO 2
PROCNO 1

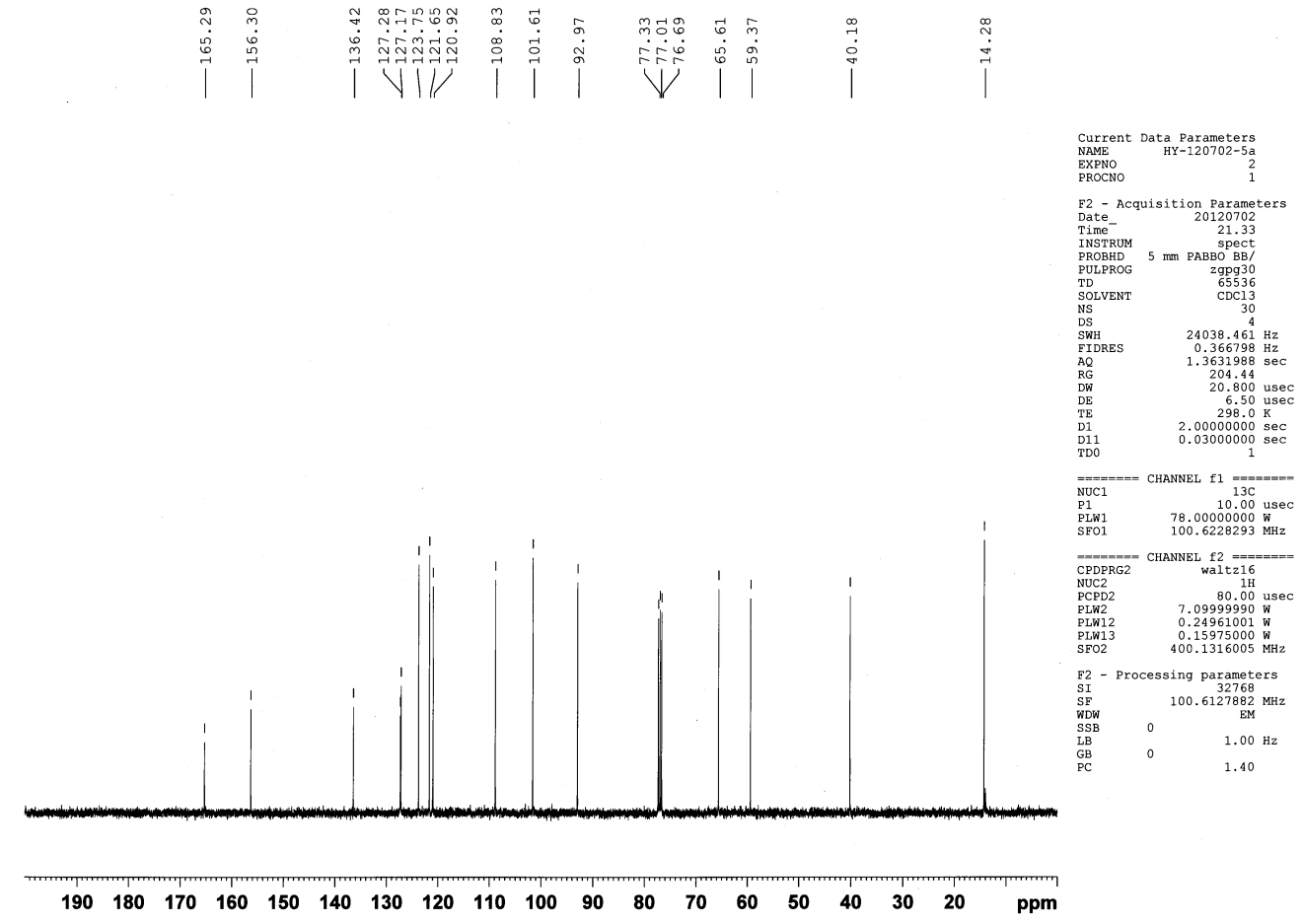
F2 - Acquisition Parameters
Date_ 20120202
Time 12.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

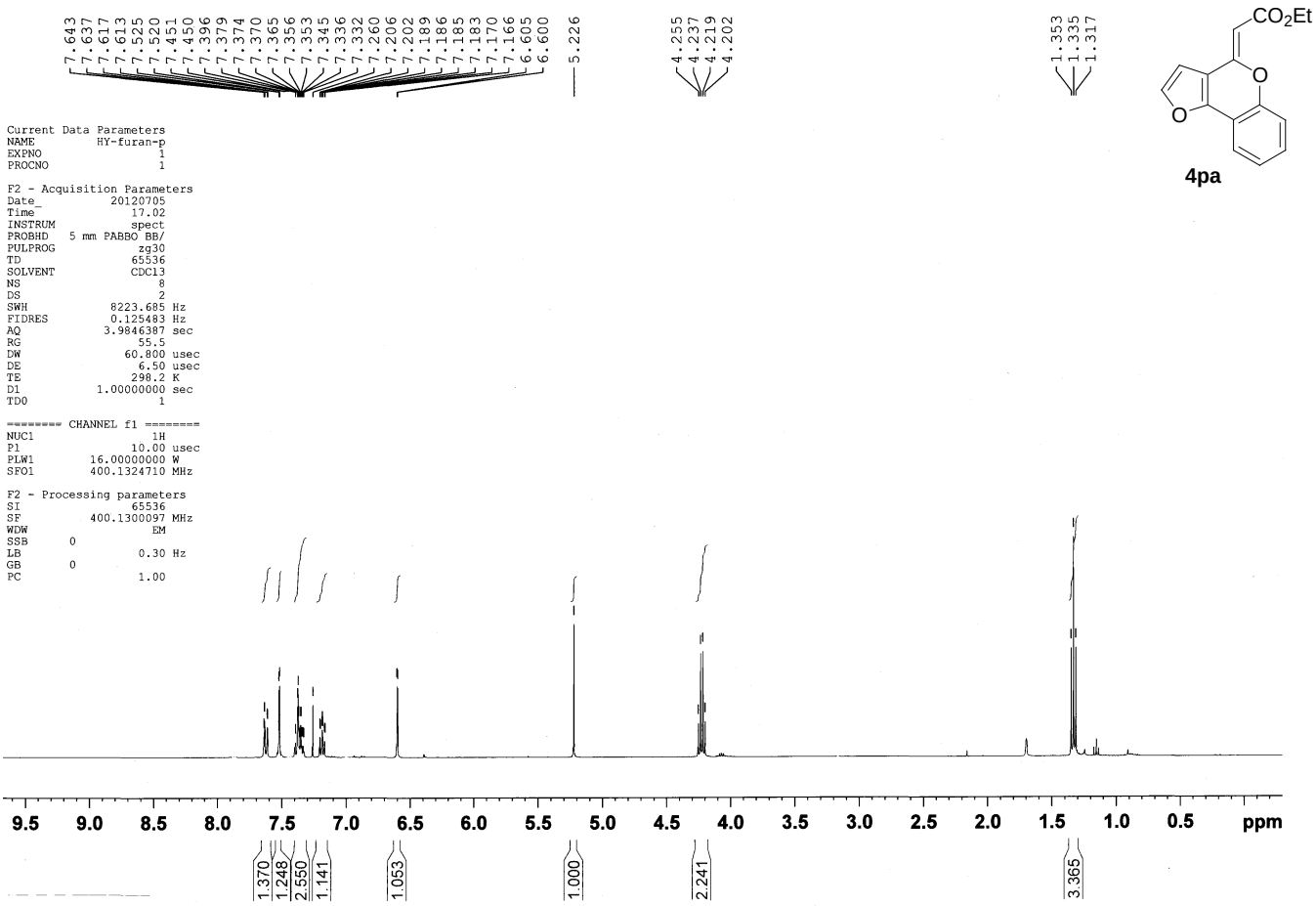
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz

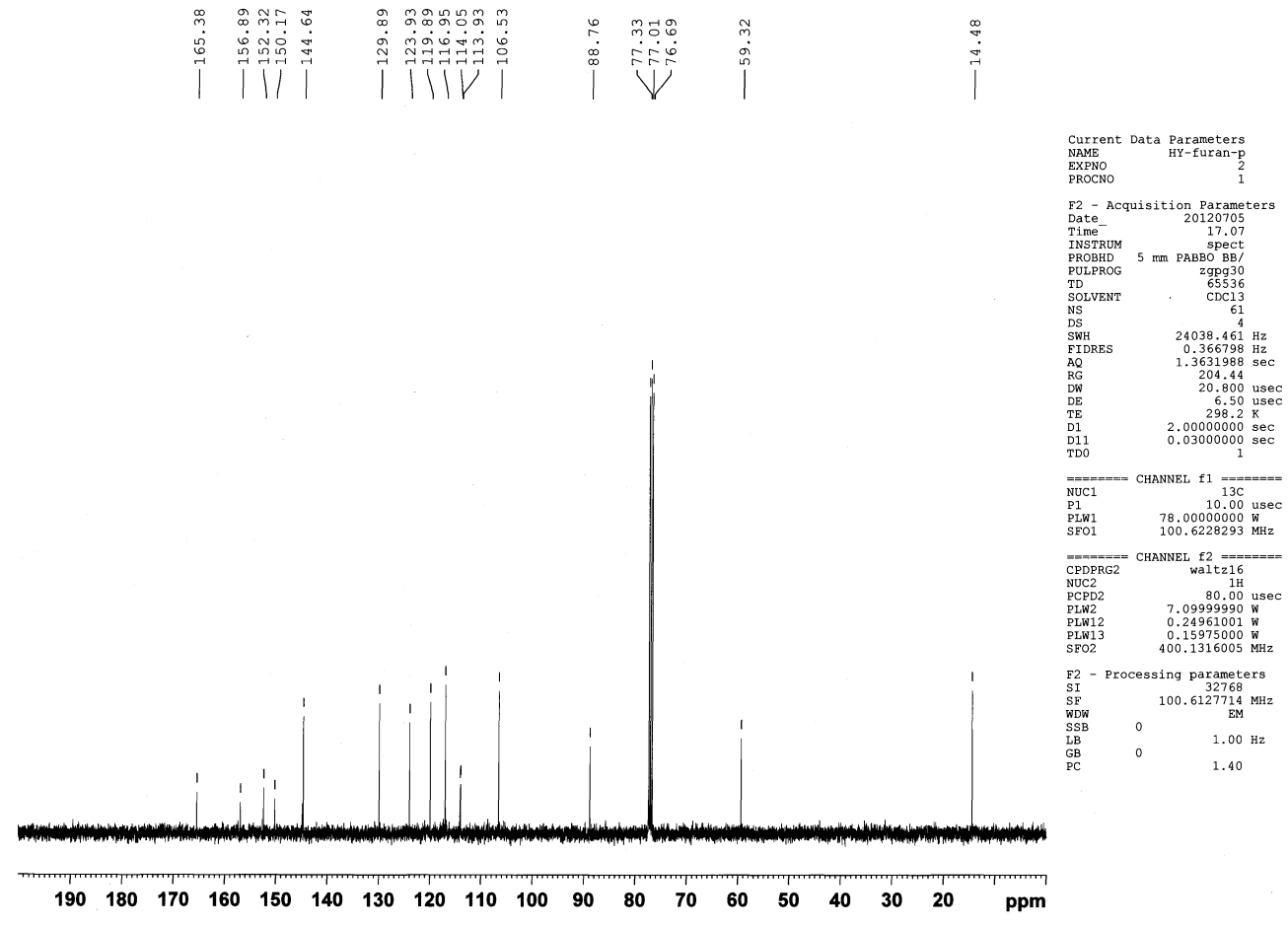
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz

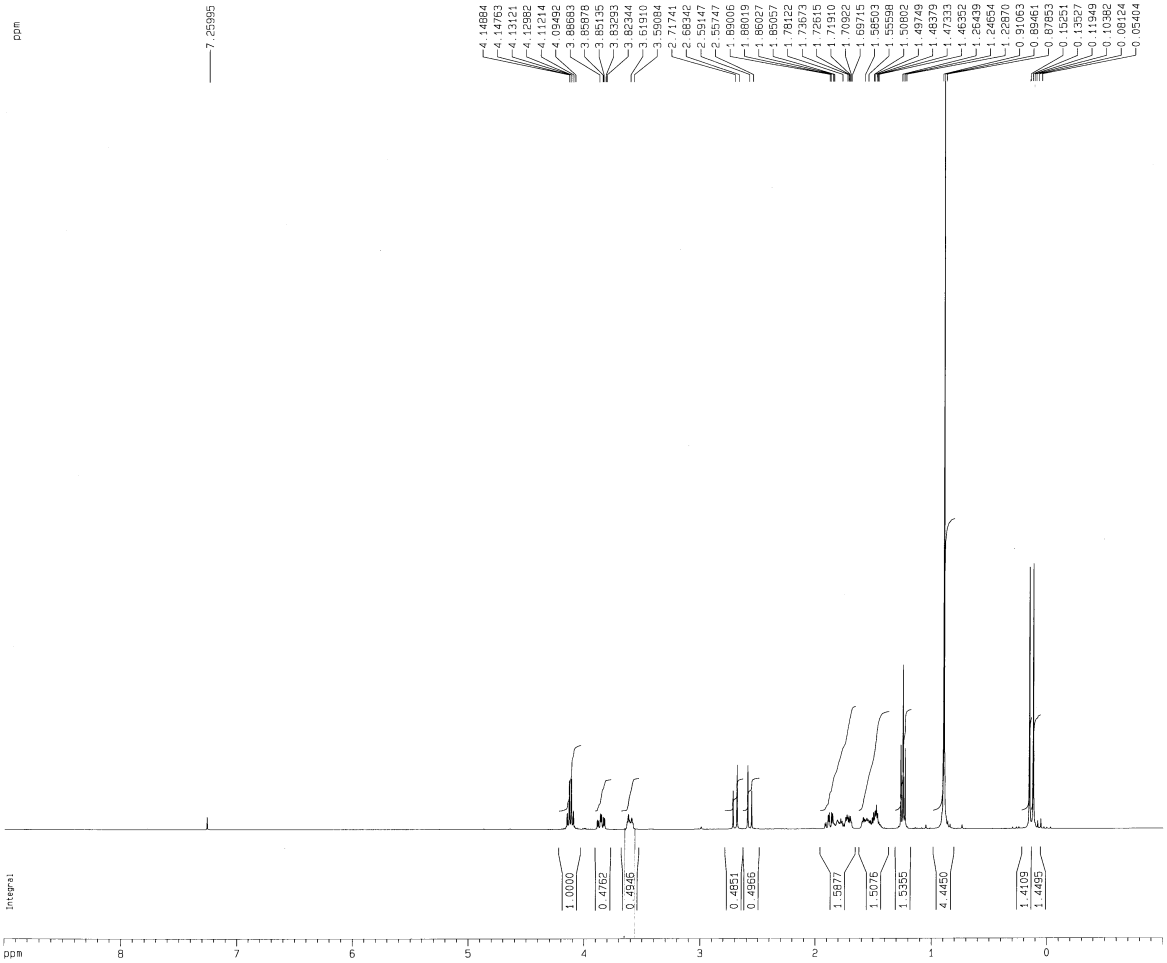
F2 - Processing parameters
SI 32768
SF 100.6127735 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

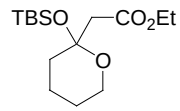

7.631
7.621
7.611
7.268
7.258
7.162
7.154
7.142
7.133
7.122
6.918
6.908
6.899
5.713
4.515
4.503
4.490
4.230
4.217
4.205
4.188
4.170
1.325
1.307
1.290
CO2Et
O
N
4oa
Current Data Parameters
NAME HY-120702-5a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120702
Time 21.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 20.59
DW 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.991
1.086
0.955
0.955
1.909
4.085
2.988


165.29
156.30
136.42
127.28
127.17
123.75
121.65
120.92
108.83
101.61
92.97
77.33
77.01
76.69
65.61
59.37
40.18
14.28
Current Data Parameters
NAME HY-120702-5a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120702
Time 21.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 30
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127882 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm









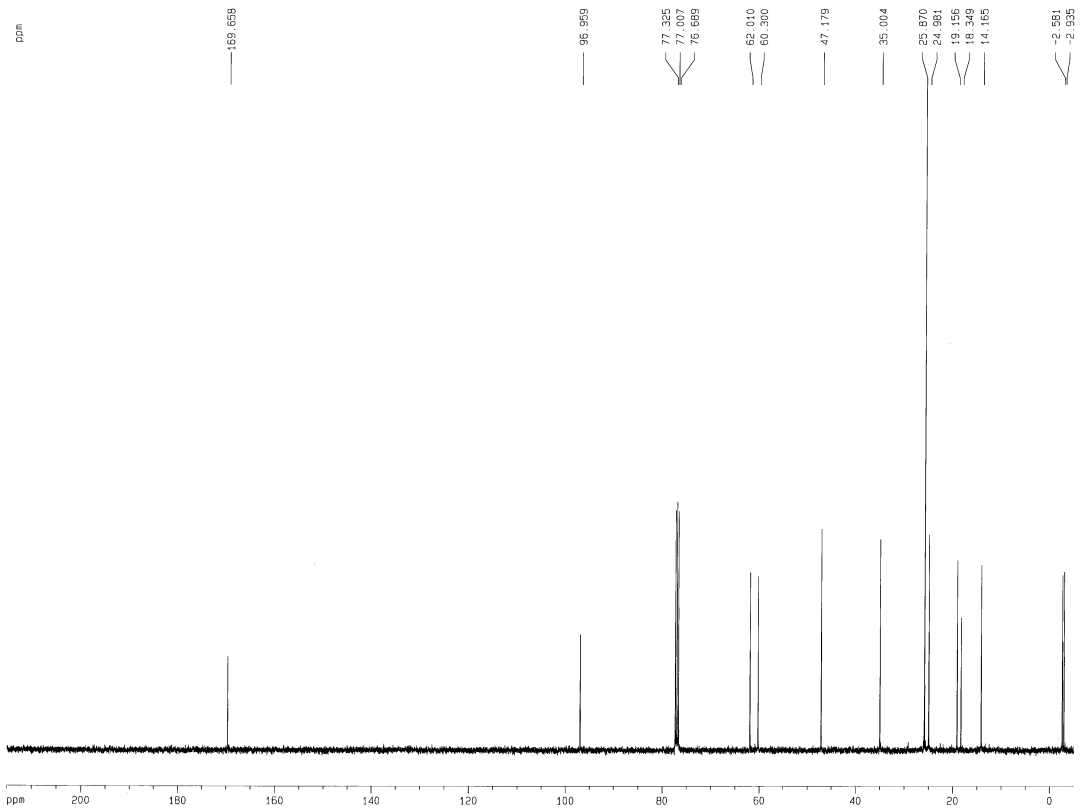

```
Current Data Parameters
NAME                  AK-177-Si
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20110908
Time                      15.47
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           11
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                         40.3
DW                       60.400 usec
DE                        6.00 usec
TE                       294.2 K
D1                     1.00000000 sec
MCREST                 0.00000000 sec
MCWRK                  0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        11.50 usec
PL1                       -4.00 dB
SFO1                400.0324703 MHz

F2 - Processing parameters
SI                           32768
SF                  400.0300070 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.00

1D NMR plot parameters
CX                           32.00 cm
CY                           21.00 cm
F1P                          9.000 ppm
F1                        3600.27 Hz
F2P                         -1.000 ppm
F2                         -400.03 Hz
PPMCM                     0.31250 ppm/cm
HZCM                    125.00938 Hz/cm
```

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Current Data Parameters
NAME                  AK-177-Si
EXPNO                         2
PROCNO                        1

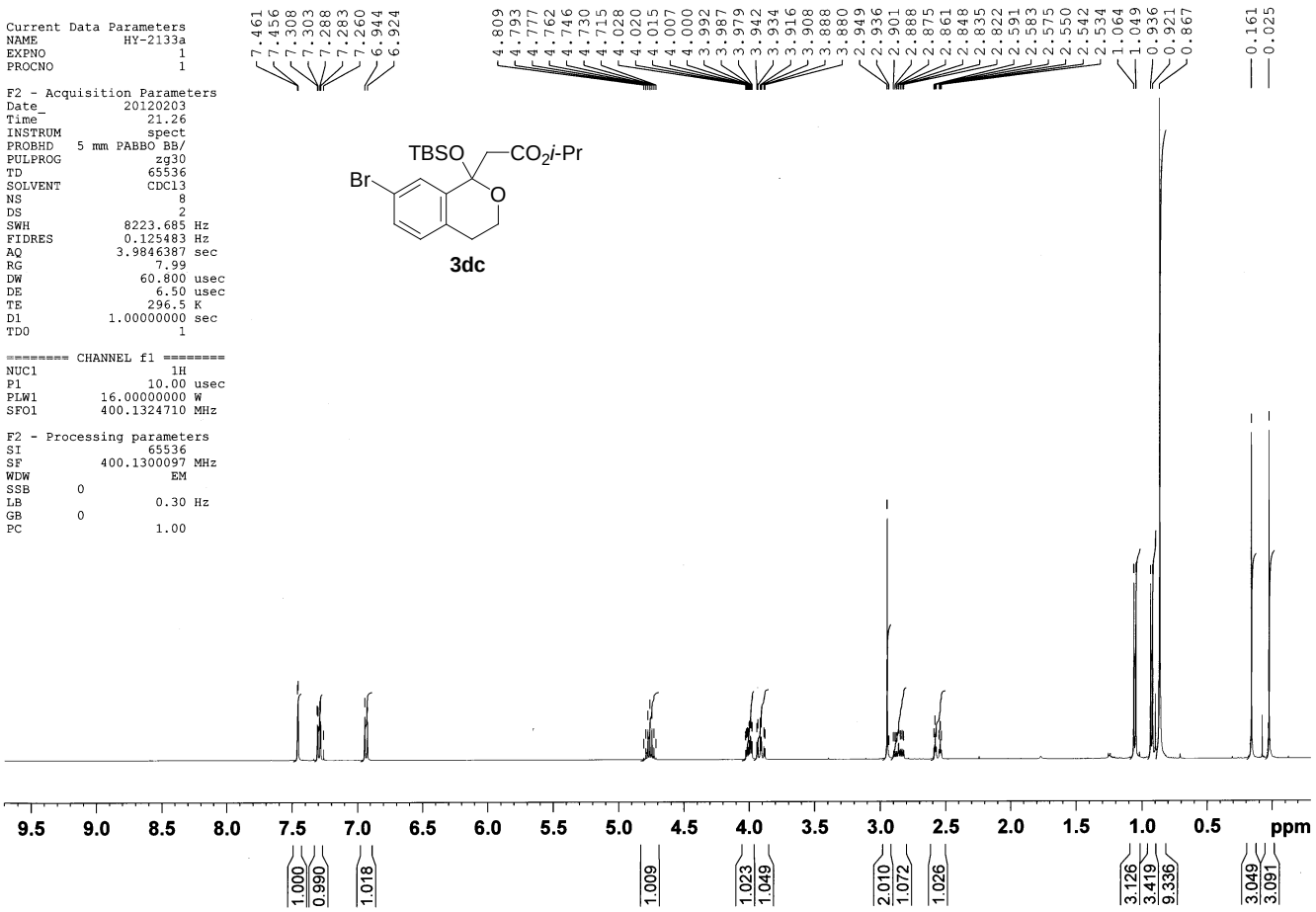
F2 - Acquisition Parameters
Date_                  20110908
Time                      15.57
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          168
DS                            4
SWH                   26178.010 Hz
FIDRES                 0.399445 Hz
AQ                     1.2517875 sec
RG                         8192
DW                       19.100 usec
DE                        6.00 usec
TE                       294.2 K
D1                     2.00000000 sec
d11                    0.03000000 sec
DELTA                  1.89999998 sec
MCREST                 0.00000000 sec
MCWRK                  0.01500000 sec

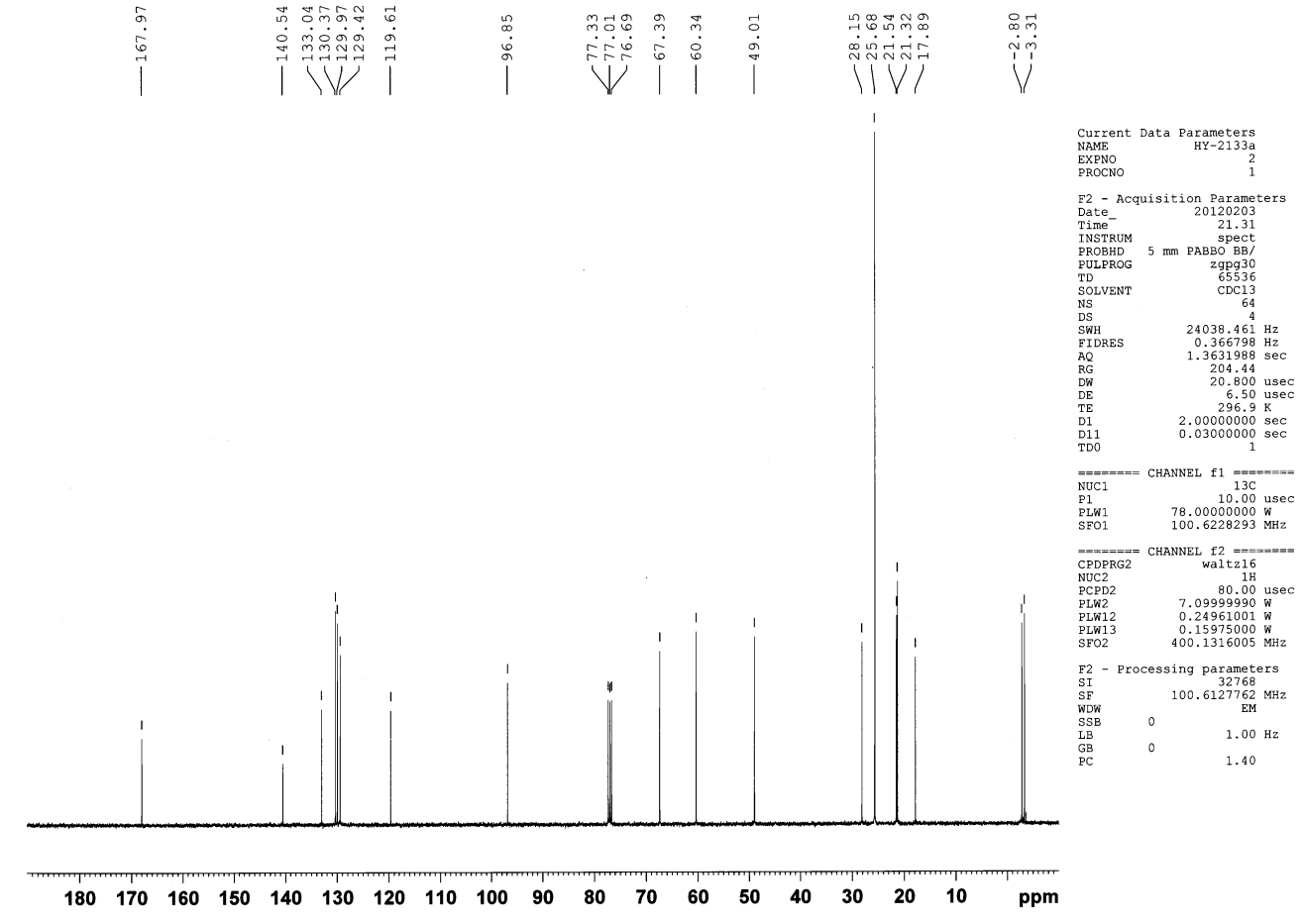
======== CHANNEL f1 ========
NUC1                         13C
P1                        10.00 usec
PL1                       -3.50 dB
SFO1                100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    100.00 usec
PL2                       -4.00 dB
PL12                      17.00 dB
PL13                      17.00 dB
SFO2                400.0316001 MHz

F2 - Processing parameters
SI                           32768
SF                  100.5876270 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40

1D NMR plot parameters
CX                           30.00 cm
CY                           19.00 cm
F1P                        215.000 ppm
F1                        21626.34 Hz
F2P                         -5.000 ppm
F2                         -502.94 Hz
PPMCM                     7.33333 ppm/cm
HZCM                    737.64258 Hz/cm
```


Current Data Parameters
NAME HY-2133a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120203
Time 21.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 7.99
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PLW1 16.00000000 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.461 7.456 7.308 7.303 7.288 7.283 7.260 6.944 6.924
4.809 4.793 4.777 4.762 4.746 4.730 4.715 4.028 4.020 4.015 4.007 4.000 3.992 3.987 3.979 3.942 3.934 3.916 3.908 3.888 3.880 2.949 2.936 2.901 2.888 2.875 2.861 2.848 2.835 2.822 2.591 2.583 2.575 2.550 2.542 2.534 1.064 1.049 0.936 0.921 0.867
0.161 0.025
TBSO
CO2i-Pr
Br
O
3dc
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000 0.990 1.018 1.009 1.023 1.049 2.010 1.072 1.026 3.126 3.419 9.336 3.049 3.091


167.97
140.54 133.04 130.37 129.97 129.42 119.61
96.85
77.33 77.01 76.69
67.39
60.34
49.01
28.15 25.68 21.54 21.32 17.89
-2.80 -3.31
Current Data Parameters
NAME HY-2133a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120203
Time 21.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 204.44
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 78.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 7.09999990 W
PLW12 0.24961001 W
PLW13 0.15975000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127762 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

7. References

1. (a) F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramprasad, R. M. McKinnell, A. J. P. White, D. J. Williams and R. J. Ducray, *J. Org. Chem.*, 1999, **64**, 2910–2913; (b) H. Yanai, A. Takahashi, T. Taguchi, *Tetrahedron*, 2007, **63**, 12149–12159.
2. H. Yanai, H. Ogura, H. Fukaya, A. Kotani, F. Kusu, T. Taguchi, *Chem.–Eur. J.*, 2011, **17**, 11742–11751.
3. K. Ruhland, A. Brück and E. Herdtweck, *Eur. J. Inorg. Chem.*, 2007, 944–964.
4. M. Mori, Y. Kagoshima, T. Uchida, T. Konosu, T. Shibayama, *Eur. Pat.*, 2003, 1362856.
5. M. Hellal, J.-J. Bourguignon and F. J.-J. Bihel, *Tetrahedron Lett.*, 2008, **49**, 62–65
6. J. T. Bamberg, T. Gabriel, N. E. Krauss, T. Mirzadegan, W. S. Palmer, D. B. Smith, *US Pat.* 77 646, 2004.
7. K. C. Majumdar, T. Bhattacharyya, *J. Chem . Res. (S)*, 1997, 244–245.
8. G. Sabitha, M. M. Reddy, D. Srinivas and J. S. Yadov, *Tetrahedron Lett.*, 1999, **40**, 165–166.