Electronic Supplementary Material (ESI) for ChemComm.

Sequential Mukaiyama–Michael reaction induced by carbon acids

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Electronic Supplementary Information

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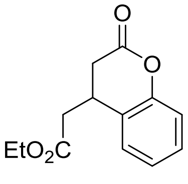
1. General and materials

All reactions were carried out under Ar atmosphere. Melting points were uncorrected. ^{1}H NMR spectra were recorded on a Bruker DPX400 (400 MHz) spectrometer or a Bruker Avance III 400 Nanobay spectrometer. Chemical shifts are reported in parts per million (ppm) using residual $CHCl_3$ (7.26 ppm) as an internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sex = sextet, m = multiplet), integration and coupling constants. ^{13}C NMR spectra were recorded on a Bruker DPX400 (100 MHz) spectrometer or a Bruker Avance III 400 Nanobay spectrometer (100 MHz), using broadband proton decoupling. Chemical shifts are reported in ppm using the middle resonance of $CDCl_3$ (77.01 ppm) as an internal standard. ^{19}F NMR spectra were taken on a Bruker Avance III 400 Nanobay spectrometer (376 MHz), and chemical shifts were reported in ppm using trifluoromethylbenzene (0 ppm) as a standard. Mass spectra were recorded by a Micromass LCT spectrometer (ESI-TOF). Column chromatography was performed on neutral silica gel (Kanto Chemical, 75-150 μm). MPLC was performed using 40 x 300 mm i. d. pre-packed column (silica gel, 50 μm) with UV and RI detectors. Size exclusion chromatography (SEC) measurements for polymers were performed at 40 °C using a Jasco GPC-900 system equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min^{-1}. The number average molecular weight ($M_{n(SEC)}$) and dispersity (M_w/M_n) were determined using poly(methyl methacrylate) standards with the M_w (M_w/M_n)s of 1.25×10^6 g mol^{-1} (1.07), 6.59×10^5 g mol^{-1} (1.02), 3.003×10^5 g mol^{-1} (1.02), 1.385×10^5 g mol^{-1} (1.05), 6.015×10^4 g mol^{-1} (1.03), 3.053×10^4 g mol^{-1} (1.02), and 1.155×10^4 g mol^{-1} (1.04), 4.90×10^3 g mol^{-1} (1.10), 2.87×10^3 g mol^{-1} (1.06), and 1.43×10^3 g mol^{-1} (1.15). Tf_2CH_2 was provided from Central Glass Co., Ltd. and it can be also prepared by the Waller's procedure in the laboratory.[1]

2. Mukaiyama–Michael reaction of α,β-unsaturated lactones

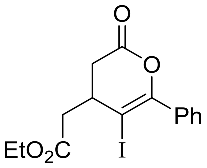
Ethyl 2-(2-oxochroman-4-yl)acetate (6a)



6a

To a solution of 2*H*-chromen-2-one **3a** (72.7 mg, 0.497 mmol) and triple carbon acid **1a** (5.3 mg, 5.3 μmol) in CH_2Cl_2 (1.5 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at –78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched with saturated $NaHCO_3$ aqueous solution (15 mL), then it was extracted with Et_2O (15 mL x 3) and washed with brine (15 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the adduct[2] in 91% yield (106 mg, 0.453 mmol). Colorless crystals (from EtOAc/hexane); Mp. 50.0-52.5 °C; IR (neat) ν 1762, 1715, 1145, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J = 7.1 Hz), 2.56 (1H, dd, J = 16.1, 7.9 Hz), 2.65 (1H, dd, J = 16.1, 6.8 Hz), 2.82 (1H, dd, J = 16.1, 4.6 Hz), 2.90 (1H, dd, J = 16.1, 5.8 Hz), 3.53-3.62 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 7.06 (1H, d, J = 8.1 Hz), 7.11 (1H, td, J = 7.5, 1.0 Hz), 7.22-7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 31.5, 34.5, 39.0, 60.9, 117.2, 124.7, 125.0, 127.4, 128.9, 151.3, 167.5, 170.8; MS (ESI-TOF) *m*/*z* 257 $[M+Na]^+$; HRMS calcd for $C_{13}H_{14}NaO_3$ $[M+Na]^+$, 257.0790; found, 257.0788. Anal. Calcd for $C_{13}H_{14}O_3$: C, 66.66; H, 6.02. Found: C, 66.81; H, 5.99.

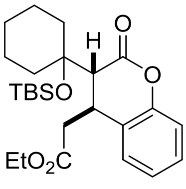
Ethyl 2-(5-iodo-2-oxo-6-phenyl-3,4-dihydro-2*H*-pyran-4-yl)acetate



According to the synthetic procedure for **6a**, this compound was obtained in 96% yield (187 mg, 0.484 mmol) by the reaction of 5-iodo-6-phenyl-2*H*-pyran-2-one[3] **3f** (150 mg, 0.503 mmol) with *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (127 mg, 0.628 mmol) in the presence of triple carbon acid **1a** (5.1 mg, 5.1 μmol) in CH_2Cl_2 (2.0 mL) for 30 min at –78 °C and the following column chromatography on silica gel (hexane/EtOAc = 5 : 1). Pale yellow oil; IR (neat) ν 2980, 1775, 1729, 1152, 1113, 1042, 1022, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (3H, t, J = 7.2 Hz), 2.53 (1H, dd, J = 16.6, 9.8 Hz), 2.78 (1H, dd, J = 16.6, 3.6 Hz), 2.87 (1H, dd, J = 16.4, 7.2 Hz), 3.08 (1H, dd, J = 16.4, 2.6 Hz), 3.24-3.32 (1H, m), 4.19 (2H, q, J = 7.2 Hz), 7.35-7.42 (3H, m), 7.52-7.57 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 34.0, 36.5, 40.9, 61.2, 75.3, 128.1, 129.3, 129.8, 134.4, 150.9, 166.3, 170.4; MS (ESI-TOF) *m*/*z* 387 $[M+H]^+$; HRMS calcd for $C_{15}H_{16}IO_4$ $[M+H]^+$, 387.0093; found, 387.0090. Anal. Calcd for $C_{15}H_{15}IO_4$: C, 46.65; H, 3.92. Found: C, 46.90; H, 4.04.

3. Mukaiyama–Michael/Mukaiyama aldol reaction

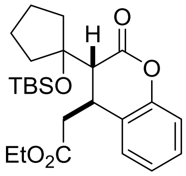
Ethyl 2-((3*R**,4*S**)-3-(1-((*tert*-butyldimethylsilyl)oxy)cyclohexyl)-2-oxochroman-4-yl)acetate (7a)



7a

To a solution of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol) and triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (3.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (243 mg, 1.20 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of cyclohexanone (199 mg, 2.03 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the resulting mixture was quenched with saturated $NaHCO_3$ aqueous solution (15 mL), extracted with Et_2O (15 mL x 3), and washed with brine (15 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Thus obtained residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20 : 1) to give the adduct in 99% yield (443 mg, 0.993 mmol). Its structure was also confirmed by an X-ray crystallographic analysis. Colorless crystals (from EtOAc); Mp. 90.0-91.5 °C; IR (ATR) ν 2928, 1750, 1732, 1151, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.44 (3H, s), 0.05 (3H, s), 0.70 (9H, s), 1.20 (3H, t, *J* = 7.1 Hz), 1.28-1.38 (1H, m), 1.38-1.49 (2H, m), 1.49-1.62 (3H, m), 1.65-1.75 (2H, m), 1.93-2.06 (2H, m), 2.48 (1H, dd, *J* = 15.9, 7.4 Hz), 2.54 (1H, dd, *J* = 15.9, 7.4 Hz), 3.10 (1H, s), 3.64 (1H, t, *J* = 7.4 Hz), 4.10 (2H, q, *J* = 7.1 Hz), 6.94 (1H, d, *J* = 8.0 Hz), 7.04 (1H, t, *J* = 7.4 Hz), 7.16-7.23 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.6, –0.7, 15.1, 19.2, 24.1, 24.6, 26.3, 26.9, 33.9, 37.7, 38.9, 42.8, 52.0, 61.8, 78.5, 118.0, 125.4, 125.7, 128.6, 129.2, 152.3, 169.1, 171.9; MS (ESI-TOF) *m*/*z* 469 $[M+Na]^+$; HRMS calcd for $C_{25}H_{38}NaO_5Si$ $[M+Na]^+$, 469.2386; found, 469.2383. Anal. Calcd for $C_{25}H_{38}O_5Si$: C, 67.23; H, 8.58. Found: C, 66.98; H, 8.62.

Ethyl 2-((3*R**,4*S**)-3-(1-((*tert*-butyldimethylsilyl)oxy)cyclopentyl)-2-oxochroman-4-yl)acetate (8a)

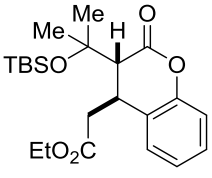


8a

According to the synthetic procedure for **7a**, this compound was obtained in 87% yield (375 mg, 0.867 mmol) by the reaction of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (243 mg, 1.20 mmol), and cyclopentanone (171 mg, 2.03 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following flash column chromatography on silica gel (hexane/EtOAc = 20 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2951, 2851, 1760, 1737, 1220, 1168, 1062, 837, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.02 (3H, s), 0.07 (3H, s), 0.80 (9H, s), 1.11-1.19 (1H, m), 1.19 (3H, t, *J* = 7.2 Hz), 1.34-1.44 (1H, m), 1.45-1.81 (5H, m), 2.03-2.15 (1H, m), 2.48 (1H, dd, *J* = 15.6, 8.0 Hz), 2.55 (1H, dd, *J* = 15.6, 6.9 Hz), 2.99

(1H, d, J = 0.9 Hz), 3.90 (1H, m), 4.08 (2H, q, J = 7.2 Hz), 6.96 (1H, d, J = 8.0 Hz), 7.07 (1H, t, J = 7.5 Hz), 7.17-7.25 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.78. –2.73, 14.1, 18.3, 22.1, 23.5, 25.9, 33.6, 37.78, 37.82, 42.0, 54.3, 60.8, 85.7, 116.7, 124.5, 124.7, 128.4, 128.5, 151.1, 168.1, 170.7; MS (ESI-TOF) m/z 433 $[M+H]^+$; HRMS calcd for $C_{24}H_{37}O_5Si$ $[M+H]^+$, 433.2410; found, 433.2417. Anal. Calcd for $C_{24}H_{36}O_5Si$: C, 66.63; H, 8.39. Found: C, 66.42; H, 8.45.

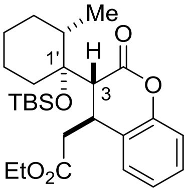
Ethyl 2-((3*R**,4*S**)-3-(2-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-yl)acetate (9a)



9a

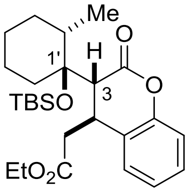
According to the synthetic procedure for **7a**, this compound was obtained in 97% yield (396 mg, 0.974 mmol) by the reaction of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (247 mg, 1.22 mmol), and acetone (118 mg, 2.03 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 15 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2936, 2853, 1764, 1736, 1253, 1221, 1162, 1038, 838, 779 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.14 (3H, s), 0.02 (3H, s), 0.77 (9H, s), 1.11 (3H, s), 1.20 (3H, t, J = 7.2 Hz), 1.40 (3H, s), 2.48 (1H, dd, J = 15.9, 7.2 Hz), 2.56 (1H, dd, J = 15.9, 7.2 Hz), 2.80 (1H, d, J = 0.9 Hz), 3.85 (1H, brt, J = 7.2 Hz), 4.08 (2H, q, J = 7.2 Hz), 7.07-7.09 (1H, m), 7.12-7.15 (1H, m), 7.18-7.22 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.5, –2.2, 14.1, 18.0, 25.7, 28.4, 29.8, 33.4, 42.0, 57.1, 60.8, 74.9, 116.8, 124.4, 124.6, 128.0, 128.4, 151.2, 167.7, 170.8; MS (ESI-TOF) m/z 407 $[M+H]^+$; HRMS calcd for $C_{22}H_{35}O_5Si$ $[M+H]^+$, 407.2254; found, 407.2258. Anal. Calcd for $C_{22}H_{34}O_5Si$: C, 64.99; H, 8.43. Found: C, 64.94; H, 8.48.

Ethyl 2-((3*R**,4*S**)-3-((1*R**,2*S**)-1-((*tert*-butyldimethylsilyl)oxy)-2-methylcyclohexyl)-2-oxochroman-4-yl) acetate (3,1'-*anti*-10a) and ethyl 2-((3*R**,4*S**)-3-((1*S**,2*S**)-1-((*tert*-butyldimethylsilyl)oxy)-2-methyl-cyclohexyl)-2-oxochroman-4-yl)acetate (3,1'-*syn*-10a)



3,1'-*anti*-**10a**

+



3,1'-*syn*-**10a**

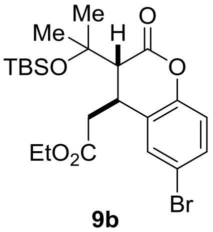
According to the synthetic procedure for **7a**, these compounds were obtained in 82% yield (380 mg, 0.794 mmol, 3'1-*anti*/*syn* = 8.1 : 1) by the reaction of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (242 mg, 1.20 mmol), and 2-methylcyclohexanone (170 mg, 1.52 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 15 : 1). Additional recycling HPLC (hexane/EtOAc = 15 : 1) was effective for separation the diastereomers to give less polar isomer 3,1'-*syn*-**10a**

(41.7 mg, 90.5 μmol, 9.1% yield) and more polar one 3,1'-*anti*-**10a** (338 mg, 0.734 mmol, 73% yield). The configurations of both diastereomers were assigned by their NOESY spectra.

For 3,1'-*syn*-**10a** Colorless oil; IR (neat) ν 2935, 2852, 1763, 1738, 1459, 1222, 1167, 1063, 837, 774 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.22 (3H, s), 0.24 (3H, s), 0.75-0.85 (1H, m), 0.96 (9H, s), 1.04-1.13 (1H, m), 1.11 (3H, d, J = 6.5 Hz), 1.16 (3H, t, J = 7.1 Hz), 1.19-1.28 (2H, m), 1.30-1.44 (3H, m), 1.52 (1H, brd, J = 12.8 Hz), 1.62-1.72 (1H, m), 2.49 (1H, dd, J = 15.2, 10.1 Hz), 2.56 (1H, dd, J = 15.2, 4.6 Hz), 3.17 (1H, s), 3.82 (1H, dd, J = 10.1, 4.6 Hz), 4.05 (2H, q, J = 7.1 Hz), 6.97 (1H, d, J = 7.9 Hz), 7.03-7.09 (1H, m), 7.22 (1H, d, J = 7.5 Hz), 7.22-7.26 (1H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ –1.5, 14.0, 16.2, 19.7, 21.6, 25.0, 26.5, 30.5, 32.4, 34.2, 396.1, 42.7, 53.3, 60.7, 81.0, 116.5, 124.67, 124.70, 128.1, 128.7, 150.08, 167.4, 170.5; MS (ESI-TOF) *m/z* 406 [M+Na]$^{+}$; HRMS calcd for C$_{26}$H$_{40}$NaO$_5$Si [M+Na]$^{+}$, 483.2543; found, 483.2548. Anal. Calcd for C$_{26}$H$_{40}$O$_5$Si: C, 67.79; H, 8.75. Found: C, 68.00; H, 8.85.

For 3,1'-*anti*-**10a** Colorless oil; IR (neat) ν 2978, 2851, 1769, 1732, 1460, 1142, 1087, 839, 778, 760 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.09 (3H, s), 0.16 (3H, s), 0.67-0.78 (1H, m), 0.87-0.96 (1H, m), 0.90 (9H, s), 0.99 (3H, d, J = 6.6 Hz), 1.15-1.24 (1H, m), 1.20 (3H, t, J = 7.2 Hz), 1.33-1.69 (6H, m), 2.50 (2H, d, J = 7.6 Hz), 3.19 (1H, d, J = 0.8 Hz), 3.52-3.61 (1H, m), 4.03-4.17 (2H, m), 6.98 (1H, d, J = 7.5 Hz), 7.08 (1H, td, J = 7.5, 0.9 Hz), 7.21 (1H, d, J = 7.5 Hz), 7.23-7.29 (1H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ –2.0, –1.7, 14.1, 15.5, 19.7, 21.4, 24.5, 26.7, 30.5, 34.2, 34.7, 38.0, 41.8, 54.3, 60.9, 80.2, 116.7, 124.1, 124.6, 128.0, 128.9, 151.4, 167.7, 170.7; MS (ESI-TOF) *m/z* 406 [M+Na]$^{+}$; HRMS calcd for C$_{26}$H$_{40}$NaO$_5$Si [M+Na]$^{+}$, 483.2543; found, 483.2549. Anal. Calcd for C$_{26}$H$_{40}$O$_5$Si: C, 67.79; H, 8.75. Found: C, 67.59; H, 8.80.

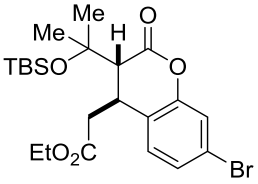
Ethyl 2-((3*R,4*S**)-6-bromo-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-yl)acetate (9b)**



9b

Due to low solubility of the starting lactone **3b**, this reaction was conducted under highly diluted conditions. To a solution of 6-bromo-2*H*-chromen-2-one[4] **3b** (112 mg, 0.498 mmol) and triple carbon acid **1a** (4.9 mg, 4.9 μmol) in CH$_2$Cl$_2$ (9.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol) in CH$_2$Cl$_2$ (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of acetone (55 μL, 0.75 mmol) in CH$_2$Cl$_2$ (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. After usual extractive workup, the obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give the adduct in 89% yield (214 mg, 0.441 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2939, 2854, 1766, 1734, 1479, 1163, 1034, 838, 778 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ –0.13 (3H, s), 0.03 (3H, s), 0.75 (9H, s), 1.17 (3H, s), 1.21 (3H, t, J = 7.1 Hz), 1.41 (3H, s), 2.49 (1H, dd, J = 16.1, 7.0 Hz), 2.56 (1H, dd, J = 16.1, 7.3 Hz), 2.77 (1H, d, J = 0.8 Hz), 3.76-3.83 (1H, m), 4.07-4.15 (2H, m), 6.86 (1H, brd, J = 7.8 Hz), 7.31-7.35 (1H, m), 7.34 (1H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ –0.3, –0.0, 16.3, 20.2, 27.9, 30.9, 31.6, 35.5, 44.0, 59.0, 63.2, 77.2, 119.1, 120.7, 128.8, 132.9, 133.5, 152.6, 169.2, 172.7; MS (ESI-TOF) *m*/*z* 507 $[M+Na]^+$, 509 $[M+2+Na]^+$; HRMS calcd for $C_{22}H_{33}BrNaO_5Si$ $[M+Na]^+$, 507.1178; found, 507.1184. Anal. Calcd for $C_{22}H_{33}BrO_5Si$: C, 54.43; H, 6.85. Found: C, 54.20; H, 6.84.

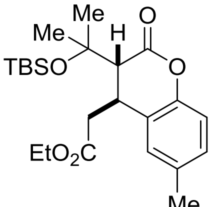
Ethyl 2-((3*R**,4*S**)-7-bromo-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-yl)acetate (9c)



9c

According to the synthetic procedure for **9b**, this compound was obtained in 89% yield (214 mg, 0.441 mmol) by the reaction of 7-bromo-2*H*-chromen-2-one[4] **3c** (112 mg, 0.498 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (122 mg, 0.603 mmol), and acetone (55 μL, 0.75 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (10 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 2950, 2930, 2850, 1750, 1730, 1600, 1580, 1480, 1405, 1160, 940, 835, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.14 (3H, s), 0.03 (3H, s), 0.75 (9H, s), 1.15 (3H, s), 1.20 (3H, t, *J* = 7.1 Hz), 1.40 (3H, s), 2.47 (1H, dd, *J* = 16.1, 7.2 Hz), 2.53 (1H, dd, *J* = 16.1, 7.2 Hz), 2.77 (1H, d, *J* = 0.8 Hz), 3.81 (1H, brt, *J* = 7.2 Hz), 4.09 (2H, q, *J* = 7.1 Hz), 7.08 (1H, d, *J* = 8.1 Hz), 7.13 (1H, d, *J* = 1.9 Hz), 7.20 (1H, dd, *J* = 8.1, 1.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.5, –2.2, 14.1, 18.0, 25.6, 28.6, 29.6, 33.0, 41.7, 56.8, 60.9, 75.0, 120.1, 121.2, 123.6, 127.6, 129.3, 151.8, 166.9, 170.6; MS (ESI-TOF) *m*/*z* 507 $[M+Na]^+$, 509 $[M+2+Na]^+$; HRMS calcd for $C_{22}H_{33}BrNaO_5Si$ $[M+Na]^+$, 507.1178; found, 507.1183. Anal. Calcd for $C_{22}H_{33}BrO_5Si$: C, 54.43; H, 6.85. Found: C, 54.22; H, 6.90.

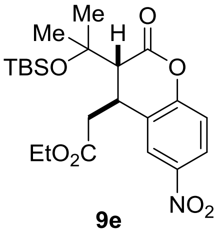
Ethyl 2-((3*R**,4*S**)-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-6-methyl-2-oxochroman-4-yl)acetate (9d)



9d

According to the synthetic procedure for **7a**, this compound was obtained in 90% yield (190 mg, 0.452 mmol) by the reaction of 6-methyl-2*H*-chromen-2-one **3d** (80.1 mg, 0.500 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (122 mg, 0.603 mmol), and acetone (55 μL, 0.75 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2932, 2852, 1759, 1736, 1498, 1214, 1162, 1036, 837, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.01 (3H,s), 0.03 (3H, s), 0.78 (9H, s), 1.10 (3H, s), 1.20 (3H, s), 1.40 (3H, s), 2.30 (3H, s), 2.48 (1H, dd, *J* = 15.8, 7.2 Hz), 2.54 (1H, dd, *J* = 15.8, 7.2 Hz), 2.78 (1H, brs), 3.80 (1H, t, *J* = 7.2 Hz), 4.10 (2H, q, *J* = 7.2 Hz), 6.85 (1H, d, *J* = 8.1 Hz), 6.97-7.03 (1H, m), 6.99 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.5, –1.2, 15.1, 19.0, 21.7, 26.7, 29.3, 30.9, 34.4, 43.0, 58.1, 61.7, 75.9, 117.4, 125.0, 129.3, 130.0, 135.2, 150.1, 169.0, 171.9; MS (ESI-TOF) *m*/*z* 443 [M+Na]$^+$; HRMS calcd for $C_{23}H_{36}NaO_5Si$ [M+Na]$^+$, 443.2230; found, 443.2246. Anal. Calcd for $C_{23}H_{36}O_5Si$: C, 65.68; H, 8.63. Found: C, 65.38; H, 8.63.

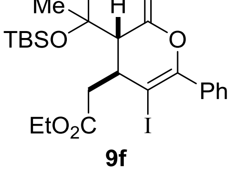
Ethyl 2-((3*R,4*S**)-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-6-nitro-2-oxochroman-4-yl)acetate (9e)**



9e

To a solution of 6-nitro-2*H*-chromen-2-one[5] **3e** (95.6 mg, 0.500 mmol) and triple carbon acid **1a** (15 mg, 15 μmol) in CH_2Cl_2 (9.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (155 mg, 0.766 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, the reaction mixture was treated with a solution of acetone (74 μL, 1.0 mmol) in CH_2Cl_2 (0.5 mL) for 30 min at the same temperature. Since a small amount of *in situ*-generated KSA was observed by TLC analysis at this stage, further acetone (74 μL, 1.0 mmol) was added to the reaction mixture and the resulting mixture was stirred for 30 min at –78 °C. After usual extractive workup, the obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 6 : 1) to give the adduct in 90% yield (183 mg, 0.451 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 2960, 2930, 2850, 1770, 1730, 1530, 1340, 1250, 1160, 1030, 838, 780 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.21 (3H, s), 0.02 (3H, s), 0.71 (9H, s), 1.22 (3H, t, *J* = 7.1 Hz), 1.24 (3H, s), 1.44 (3H, s), 2.54 (1H, dd, *J* = 16.5, 6.6 Hz), 2.64 (1H, dd, *J* = 16.5, 7.2 Hz), 2.82 (1H, d, *J* = 0.4 Hz), 3.89-3.95 (1H, m), 4.11 (2H, q, *J* = 7.1 Hz), 7.09 (1H, d, *J* = 7.1 Hz), 8.11-8.17 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.5, –2.3, 14.1, 18.0, 25.7, 29.0, 29.4, 33.3, 41.7, 56.4, 61.2, 75.2, 117.7, 123.9, 124.3, 125.7, 144.2, 155.9, 165.9, 170.2; MS (ESI-TOF) *m*/*z* 474 [M+Na]$^+$; HRMS calcd for $C_{22}H_{33}NNaO_7Si$ [M+Na]$^+$, 474.1924; found, 474.1933. Anal. Calcd for $C_{22}H_{33}NO_7Si$: C, 58.51; H, 7.37; N, 3.10. Found: C, 58.75; H, 7.58; N, 3.12.

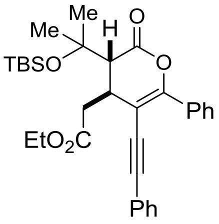
Ethyl 2-((3*R,4*S**)-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-5-iodo-2-oxo-6-phenyl-3,4-dihydro-2*H*-pyran-4-yl)acetate (9f)**



9f

According to the synthetic procedure for **7a**, this compound was obtained in 90% yield (251 mg, 0.449 mmol) by the reaction of 5-iodo-6-phenyl-2*H*-pyran-2-one[3] **3f** (149 mg, 0.500 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (124 mg, 0.613 mmol), and acetone (55 μL, 0.75 mmol) in the presence of triple carbon acid **1a** (5.1 mg, 5.1 μmol) in CH_2Cl_2 (2.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 6 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Yellow crystals (from CH_2Cl_2); Mp. 37.0-38.5 °C; IR (ATR) ν 2956, 2927, 2853, 1760, 1729, 1148, 1045, 831, 771, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (3H, s), 0.17 (3H, s), 0.89 (9H, s), 1.27 (3H, t, *J* = 7.2 Hz), 1.40 (3H, s), 1.50 (3H, s), 2.55 (1H, dd, *J* = 16.2, 4.4 Hz), 2.82 (1H, dd, *J* = 16.2, 6.8 Hz), 2.89 (1H, brs), 3.57 (1H, ddd, *J* = 6.8, 4.4, 0.9 Hz), 4.12-4.21 (2H, m), 7.36-7.40 (3H, m), 7.48-7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.2, –1.0, 15.2, 19.1, 26.8, 27.9, 30.9, 39.5, 43.7, 58.7, 62.0, 76.0, 77.3, 129.0, 130.1, 130.7, 135.7, 150.6, 167.5, 171.6; MS (ESI-TOF) *m*/*z* 581 [M+Na]$^+$; HRMS calcd for $C_{24}H_{35}INaO_5Si$ [M+Na]$^+$, 581.1196; found, 581.1193. Anal. Calcd for $C_{24}H_{35}IO_5Si$: C, 51.61; H, 6.32. Found: C, 51.57; H, 6.44.

Ethyl 2-((3*R**,4*S**)-3-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-2-oxo-6-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-4-yl)acetate (9g)

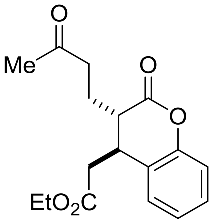


9g

According to the synthetic procedure for **7a**, this compound was obtained in 86% yield (231 mg, 0.434 mmol) by the reaction of 6-phenyl-5-(phenylethynyl)-2*H*-pyran-2-one[6] **3g** (137 mg, 0.503 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (185 mg, 0.916 mmol), and acetone (74 μL, 1.0 mmol) in the presence of triple carbon acid **1a** (9.9 mg, 9.9 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Yellow oil; IR (neat) ν 2961, 2926, 2852, 1764, 1729, 1159, 1035, 837, 778, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (3H, s), 0.13 (3H, s), 0.86 (9H, s), 1.24 (3H, t, *J* = 7.2 Hz), 1.37 (3H, s), 1.50 (3H, s), 2.66 (1H, dd, *J* = 16.0, 5.5 Hz), 2.72 (1H, dd, *J* = 16.0, 7.6 Hz), 2.82 (1H, d, *J* = 0.7 Hz), 3.50-3.56 (1H, m), 4.14 (2H, q, *J* = 7.2 Hz), 7.31-7.36 (3H, m), 7.38-7.44 (5H, m), 8.01-8.05 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ –2.14, –2.12, 14.1, 18.1, 25.8, 27.4, 30.1, 35.8, 39.1, 55.9, 60.9, 75.0, 86.7, 95.5, 99.8, 123.2, 127.5, 127.9, 128.3, 128.4, 129.6, 131.2, 132.2, 152.8, 166.6, 171.0; MS (ESI-TOF) *m*/*z* 555 [M+Na]$^+$; HRMS calcd for $C_{32}H_{40}NaO_5Si$ [M+Na]$^+$, 555.2543; found, 555.2543. Anal. Calcd for $C_{32}H_{40}O_5Si$: C, 72.14; H, 7.57. Found: C, 71.99; H, 7.60.

4. Sequential Mukaiyama–Michael reaction

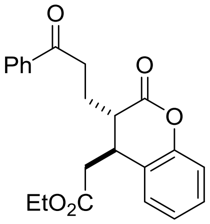
Ethyl 2-((3*S**,4*S**)-2-oxo-3-(3-oxobutyl)chroman-4-yl)acetate (11a)



11a

To a solution of 2*H*-chromen-2-one **3a** (73.0 mg, 0.499 mmol) and triple carbon acid **1a** (5.1 mg, 5.1 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (123 mg, 0.608 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of freshly distillated methyl vinyl ketone (63 μL, 0.76 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture over 1 h using a syringe pump. This mixture was additionally stirred for 30 min at –78 °C, then the resultant was treated with a 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. After extractive workup and evaporation, thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give this product in 59% yield (90.1 mg, 0.296 mmol) along with isolation of simple Michael adduct **6a** (24.1 mg, 0.103 mmol, 21% yield). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless crystals (from CH_2Cl_2); Mp. 34.0-35.0 °C; IR (ATR) ν 1767, 1709, 1219, 1174, 1137, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, t, J = 7.1 Hz), 1.62-1.74 (1H, m), 1.77-1.88 (1H, m), 2.13 (3H, s), 2.47-2.67 (4H, m), 2.82 (1H, ddd, J = 10.3, 5.6, 1.7 Hz), 3.34 (1H, td, J = 7.4, 1.7 Hz), 4.11 (2H, q, J = 7.1 Hz), 7.03 (1H, d, J = 8.1 Hz), 7.11 (1H, td, J = 7.4, 1.0 Hz), 7.22-7.31 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.1, 300.1, 37.9, 40.0, 40.3, 44.4, 60.9, 116.8, 123.1, 124.9, 129.0, 129.1, 150.3, 169.3, 170.7, 207.0; MS (ESI-TOF) *m*/*z* 327 $[M+Na]^+$; HRMS calcd for $C_{17}H_{20}NaO_5$ $[M+Na]^+$, 327.1208; found, 327.1203. Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.86; H, 6.68.

Ethyl 2-((3*S**,4*S**)-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12a)

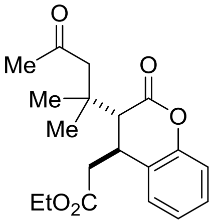


12a

To a solution of 2*H*-chromen-2-one **3a** (72.9 mg, 0.499 mmol) and triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of phenyl vinyl ketone[7] (101 mg, 0.764 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the reaction mixture was treated with TfOH (0.1 mL) for 30 min at –78 °C. The resulting mixture was quenched with a saturated $NaHCO_3$ aqueous solution (15 mL), extracted with Et_2O (20 mL x 3), and washing with brine (20 mL). The combined organic layer was dried over anhydrous $MgSO_4$

and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give the adduct in 83% yield (152 mg, 0.415 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless crystals (from CH_2Cl_2); Mp. 62.0-63.0 °C; IR (ATR) ν 2947, 1767, 1734, 1719, 1682, 1221, 1209, 1173, 1133, 764, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.2 Hz), 1.92-1.97 (1H, m), 1.98-2.04 (1H, m), 2.54 (1H, dd, *J* = 16.2, 7.5 Hz), 2.61 (1H, dd, *J* = 16.2, 7.7 Hz), 2.95 (1H, ddd, *J* = 10.2, 5.5, 1.7 Hz), 3.06 (1H, ddd, *J* = 18.1, 8.6, 5.6 Hz), 3.19 (1H, ddd, *J* = 18.1, 8.3, 6.8 Hz), 3.43 (1H, td, *J* = 7.4, 1.7 Hz), 4.13 (2H, q, *J* = 7.2 Hz), 7.06 (1H, d, *J* = 7.2 Hz), 7.09-7.15 (1H, m), 7.24-7.32 (2H, m), 7.41-7.48 (2H, m), 7.52-7.59 (1H, m), 7.89-7.96 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.6, 35.6, 38.0, 40.0, 44.6, 61.0, 116.9, 123.2, 124.9, 128.0, 128.6, 129.0, 129.1, 133.4, 136.6, 150.4, 169.4, 170.7, 198.4; MS (ESI-TOF) *m*/*z* 389 $[M+Na]^+$; HRMS calcd for $C_{22}H_{22}NaO_5$ $[M+Na]^+$, 389.1365; found, 389.1360. Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.12; H, 6.05. Found: C, 72.22; H, 6.23.

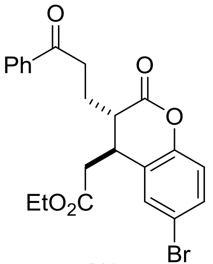
Ethyl 2-((3*R**,4*S**)-3-(2-methyl-4-oxopentan-2-yl)-2-oxochroman-4-yl)acetate (13a)



13a

According to the synthetic procedure for **11a**, the reaction of 2*H*-chromen-2-one **3a** (73.4 mg, 0.502 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (121 mg, 0.598 mmol), and mesityl oxide (73.7 mg, 0.751 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (2.0 mL) was carried out at –78 °C for 30 min. Then, the mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature and quenched with a saturated $NaHCO_3$ aqueous solution (15 mL). After usual extractive workup, column chromatography of the resulting mixture on silica gel (hexane/EtOAc = 4 : 1) gave this product (102 mg, 0.305 mmol, 61% yield) and 1,2-adduct (21.2 mg, 63.3 μmol, 13% yield). Relative configuration of **13a** was assigned by its NOESY spectrum. Yellow crystals (from CH_2Cl_2); Mp. 52.0-53.0 °C; IR (ATR) ν 2973, 2930, 1756, 1729, 1718, 1145, 1028, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.76 (3H, s), 1.09 (3H, s), 1.21 (3H, t, *J* = 7.2 Hz), 2.10 (3H, s), 2.31 (1H, d, *J* = 17.5 Hz), 2.50 (1H, dd, *J* = 15.9, 7.4 Hz), 2.57 (1H, dd, *J* = 15.9, 7.4 Hz), 2.61 (1H, d, *J* = 17.5 Hz), 3.22 (1H, brs), 3.57 (1H, t, *J* = 7.4 Hz), 4.05-4.18 (2H, m), 6.98 (1H, dd, *J* = 7.2, 0.9 Hz), 7.09 (1H, td, *J* = 7.4, 0.9 Hz), 7.20-7.28 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 25.6, 26.3, 31.7, 33.7, 36.5, 42.0, 51.0, 52.7, 60.9, 116.6, 124.5, 124.9, 128.1, 128.8, 151.0, 168.5, 170.7, 207.2; MS (ESI-TOF) *m*/*z* 335 $[M+Na]^+$; HRMS calcd for $C_{19}H_{24}NaO_5$ $[M+Na]^+$, 335.1521; found, 335.1520. Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.41; H, 7.30.

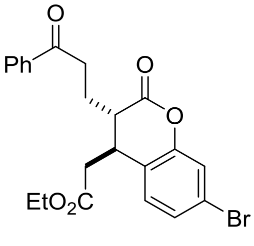
Ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12b)



12b

To a solution of 6-bromo-2*H*-chromen-2-one[4] **3b** (113 mg, 0.502 mmol) and triple carbon acid **1a** (5.2 mg, 5.2 μmol) in CH_2Cl_2 (9.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (122 mg, 0.603 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of phenyl vinyl ketone[7] (102 mg, 0.772 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the reaction mixture was treated with TfOH (0.1 mL) for 1 h at –78 °C. The resulting mixture was quenched with a saturated $NaHCO_3$ aqueous solution (15 mL), extracted with Et_2O (20 mL x 3), and washing with brine (20 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the adduct in 83% yield (186 mg, 0.418 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2980, 2930, 1765, 1730, 1690, 1480, 1220, 1180, 820, 750, 735, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.1 Hz), 1.81-1.93 (1H, m), 1.96-2.07 (1H, m), 2.53 (1H, dd, *J* = 16.3, 7.6 Hz), 2.61 (1H, dd, *J* = 16.3, 7.2 Hz), 2.94 (1H, ddd, *J* = 10.2, 5.5, 1.7 Hz), 3.06 (1H, ddd, *J* = 18.2, 7.7, 6.6 Hz), 3.17 (1H, dt, *J* = 18.2, 7.2 Hz), 3.36-3.43 (1H, m), 4.14 (2H, q, *J* = 7.1 Hz), 6.94 (1H, d, *J* = 8.4 Hz), 7.38-7.48 (4H, m), 7.56 (1H, t, *J* = 7.7 Hz), 7.92 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.6, 35.4, 37.9, 39.8, 44.3, 61.1, 117.4, 118.6, 125.4, 128.0, 128.6, 131.9, 132.0, 133.3, 136.5, 149.5, 168.6, 170.4, 198.2; MS (ESI-TOF) *m/z* 467 $[M+H]^+$, 469 $[M+2+H]^+$; HRMS calcd for $C_{22}H_{21}BrNaO_5$ $[M+Na]^+$, 467.0470; found, 467.0469. Anal. Calcd for $C_{22}H_{21}BrO_5$: C, 59.34; H, 4.75. Found: C, 59.53; H, 4.86.

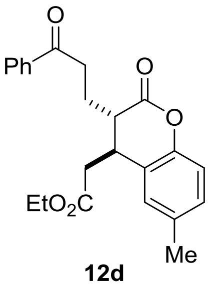
Ethyl 2-((3*S**,4*S**)-7-bromo-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12c)



12c

According to the synthetic procedure for **12b**, this compound was obtained in 73% yield (162 mg, 0.365 mmol) by the reaction of 7-bromo-2*H*-chromen-2-one[4] **3c** (113 mg, 0.502 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (124 mg, 0.613 mmol), and phenyl vinyl ketone[7] (102 mg, 0.772 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (10 mL) for 30 min at –78 °C and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 3 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 2980, 2930, 1771, 1730, 1680, 1600, 1481, 1408, 1212, 1179, 1075, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.1 Hz), 1.81-1.92 (1H, m), 1.97-2.08 (1H, m), 2.52 (1H, dd, *J* = 16.3, 7.7 Hz), 2.60 (1H, dd, *J* = 16.3, 7.1 Hz), 2.94 (1H, ddd, *J* = 10.2, 5.4, 1.4 Hz), 3.05 (1H, ddd, *J* = 18.2, 8.0, 5.9 Hz), 3.17 (1H, dt, *J* = 18.2, 7.5 Hz), 3.37-3.43 (1H, m), 4.08-4.17 (2H, m), 7.16 (1H, d, *J* = 8.0 Hz), 7.22-7.28 (2H, m), 7.45 (2H, t, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.0 Hz), 7.92 (2H, d, *J* = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.6, 35.4, 37.7, 39.8, 44.4, 61.0, 120.2, 121.9, 122.3, 128.0, 128.6, 130.4, 133.3, 136.5, 151.0, 168.5, 170.5, 198.2; MS (ESI-TOF) *m/z* 467 [M+Na]$^+$, 469 [M+2+Na]$^+$; HRMS calcd for $C_{22}H_{21}BrNaO_5$ [M+Na]$^+$, 467.0470; found, 467.0471. Anal. Calcd for $C_{22}H_{21}BrO_5$: C, 59.34; H, 4.75. Found: C, 59.24; H, 4.77.

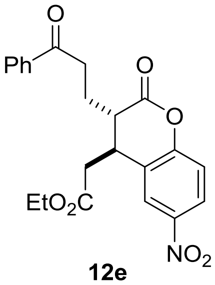
Ethyl 2-((3*S,4*S**)-6-methyl-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12d)**



12d

According to the synthetic procedure for **12a**, this compound was obtained in 79% yield (151 mg, 0.397 mmol) by the reaction of 6-methyl-2*H*-chromen-2-one **3d** (80.1 mg, 0.500 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (124 mg, 0.613 mmol), and phenyl vinyl ketone[7] (101 mg, 0.764 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (4.0 mL) at –78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2980, 2920, 1760, 1730, 1680, 1494, 1203, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.1 Hz), 1.82-1.93 (1H, m), 1.95-2.06 (1H, m), 2.31 (3H, s), 2.53 (1H, dd, *J* = 16.2, 7.3 Hz), 2.58 (1H, dd, *J* = 16.2, 7.6 Hz), 2.92 (1H, ddd, *J* = 10.0, 5.5, 1.5 Hz), 3.05 (1H, ddd, *J* = 18.0, 8.6, 5.6 Hz), 3.17 (1H, ddd, *J* = 18.0, 8.6, 6.8 Hz), 3.33-3.40 (1H, m), 4.13 (2H, q, *J* = 7.1 Hz), 6.93 (1H, d, *J* = 8.0 Hz), 7.05 (1H, s), 7.07 (1H, d, *J* = 8.0 Hz), 7.40-7.48 (2H, m), 7.55 (1H, tt, *J* = 7.3, 1.2 Hz), 7.90-7.94 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.7, 24.6, 35.6, 38.0, 40.0, 44.6, 60.5, 116.5, 122.8, 128.0, 128.6, 129.42, 129.44, 133.2, 134.5, 136.5, 148.3, 169.6, 170.8, 198.4; MS (ESI-TOF) *m/z* 403 [M+Na]$^+$; HRMS calcd for $C_{23}H_{24}NaO_5$ [M+Na]$^+$, 403.1521; found, 403.1520.

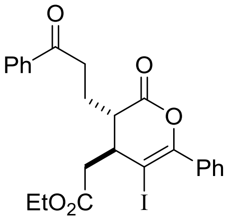
Ethyl 2-((3*S,4*S**)-6-nitro-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12e)**



12e

According to the synthetic procedure for **12b**, this compound was obtained in 77% yield (157 mg, 0.382 mmol) by the reaction of 6-nitro-2*H*-chromen-2-one[5] **3e** (95.3 mg, 0.499 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (153 mg, 0.756 mmol), and phenyl vinyl ketone[7] (106 mg, 0.802 mmol) in the presence of triple carbon acid **1a** (15 mg, 15 μmol) in CH_2Cl_2 (10 mL) at –78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2975, 2925, 1779, 1748, 1682, 1525, 1341, 1230, 1091, 751, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, *J* = 7.1 Hz), 1.83-1.96 (1H, m), 2.00-2.12 (1H, m), 2.59 (1H, dd, *J* = 16.6, 7.5 Hz), 2.69 (1H, dd, *J* = 16.6, 6.9 Hz), 3.03 (1H, ddd, *J* = 10.2, 5.4, 2.0 Hz), 3.09 (1H, ddd, *J* = 18.2, 7.5, 6.0 Hz), 3.19 (1H, dt, *J* = 18.2, 7.3 Hz), 3.52-3.58 (1H, m), 4.15 (2H, q, *J* = 7.1 Hz), 7.20 (1H, d, *J* = 8.0 Hz), 7.43-7.49 (2H, m), 7.57 (1H, t, *J* = 7.3 Hz), 7.90-7.94 (2H, m), 8.21 (1H, dd, *J* = 8.0, 2.6 Hz), 8.25 (1H, d, *J* = 2.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.6, 35.2, 37.9, 43.9, 61.3, 117.8, 124.5, 125.0, 125.2, 128.0, 128.7, 133.4, 136.4, 144.4, 155.0, 167.5, 170.0, 198.0; MS (ESI-TOF) *m*/*z* 434 $[M+Na]^+$; HRMS calcd for $C_{22}H_{21}NaNO_6$ $[M+Na]^+$, 434.1216; found, 434.1213. Anal. Calcd for $C_{22}H_{21}NO_6$: C, 64.23; H, 5.15; N, 3.40. Found: C, 64.22; H, 5.16; N, 3.36.

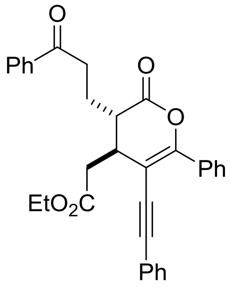
Ethyl 2-((3*S,4*S**)-5-iodo-2-oxo-3-(3-oxo-3-phenylpropyl)-6-phenyl-3,4-dihydro-2*H*-pyran-4-yl)acetate (12f)**



12f

According to the synthetic procedure for **12a**, this compound was obtained in 84% yield (218 mg, 0.421 mmol) by the reaction of 5-iodo-6-phenyl-2*H*-pyran-2-one[3] **3f** (149 mg, 0.500 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol), and phenyl vinyl ketone[7] (102 mg, 0.772 mmol) in the presence of triple carbon acid **1a** (5.1 mg, 5.1 μmol) in CH_2Cl_2 (3.0 mL) at –78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 4 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 3050, 2970, 2920, 1760, 1730, 1680, 1600, 1580, 1495, 1450, 1370, 1230, 1180, 1105, 1000, 960, 760, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (3H, t, *J* = 7.2 Hz), 2.21-2.32 (1H, m), 2.32-2.41 (1H, m), 2.56 (1H, dd, *J* = 16.7, 9.8 Hz), 2.79 (1H, dd, *J* = 16.7, 3.7 Hz), 2.92 (1H, ddd, *J* = 9.8, 6.0, 1.2 Hz), 3.09-3.27 (3H, m), 4.19 (2H, q, *J* = 7.2 Hz), 7.38-7.42 (3H, m), 7.46 (2H, t, *J* = 7.4 Hz), 7.54-7.61 (3H, m), 7.97 (2H, brd, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 26.3, 36.6, 37.4, 45.7, 48.6, 62.2, 74.5, 129.0, 129.1, 129.6, 130.3, 134.2, 129.44, 133.2, 134.3, 135.1, 150.9, 169.5, 171.4, 199.3; MS (ESI-TOF) *m*/*z* 541 $[M+Na]^+$; HRMS calcd for $C_{24}H_{23}INaO_5$ $[M+Na]^+$, 541.0488; found, 541.0485. Anal. Calcd for $C_{24}H_{23}IO_5$: C, 55.61; H, 4.47. Found: C, 55.45; H, 4.65.

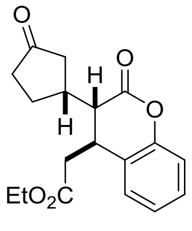
Ethyl 2-((3*S**,4*S**)-2-oxo-3-(3-oxo-3-phenylpropyl)-6-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-4-yl)acetate (12g)



12g

According to the synthetic procedure for **12a**, this compound was obtained in 72% yield (177 mg, 0.359 mmol) by the reaction of 6-phenyl-5-(phenylethynyl)-2*H*-pyran-2-one[6] **3g** (136 mg, 0.499 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (155 mg, 0.766 mmol), and phenyl vinyl ketone[7] (119 mg, 0.902 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (5.0 mL) at –78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 3153, 2991, 2938, 1964, 1892, 1769, 1730, 1681, 1597, 1487, 1443, 1374, 1260, 1229, 1180, 1099, 1000, 759, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, t, *J* = 7.1 Hz), 2.25 (2H, q, *J* = 7.5 Hz), 2.63 (1H, dd, *J* = 16.6, 9.0 Hz), 2.83 (1H, dd, *J* = 16.6, 4.8 Hz), 2.95 (1H, td, *J* = 7.5, 2.6 Hz), 3.10-3.20 (2H, m), 3.25 (1H, dt, *J* = 18.0, 7.5 Hz), 4.17 (2H, q, *J* = 7.1 Hz), 7.31-7.36 (3H, m), 7.38-7.48 (7H, m), 7.53-7.59 (1H, m), 7.94-7.99 (2H, m), 8.02-8.07 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.8, 35.6, 37.2, 40.0, 42.9, 61.1, 86.3, 95.8, 99.2, 122.9, 127.7, 128.0, 128.4, 128.5, 128.6, 129.9, 131.1, 131.9, 133.2, 136.6, 153.0, 168.6, 171.0, 198.4; MS (ESI-TOF) *m/z* 493 $[M+H]^+$; HRMS calcd for $C_{32}H_{29}O_5$ $[M+H]^+$, 493.2015; found, 493.2018.

Ethyl 2-((3*S**,4*S**)-2-oxo-3-((*R**)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-*syn*-14a) and ethyl 2-((3*S**,4*S**)-2-oxo-3-((*S**)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-*anti*-14a)



3,3'-*syn*-**14a**

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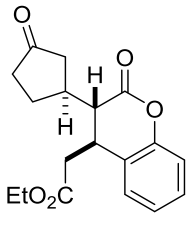


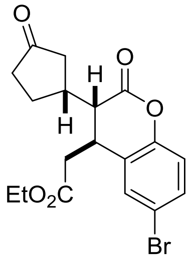
3,3'-*anti*-**14a**

According to the synthetic procedure for **12a**, the reaction of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (251 mg, 1.24 mmol), and cyclopent-2-en-1-one (124 mg, 1.51 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (4.0 mL) was conducted. After being stirred for 30 min at –78 °C, this mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was quenched with a saturated $NaHCO_3$ aqueous solution (10 mL) and extracted with Et_2O (15 mL x 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and evaporated. Column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue gave a mixture of two diastereomers in 84% yield (267 mg, 0.844 mmol, 3,3'-*syn*/*anti* = 1 : 2.9) by. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2 : 1) to give less polar isomer 3,3'-*syn*-**14a** and more polar one 3,3'-*anti*-**14a** in 21% (67 mg, 0.212 mmol) and 59% (188 mg, 0.595 mmol) yields, respectively. Structure of 3,3'-*syn*-**14a** was confirmed by an X-ray crystallographic analysis. 3,4-*Anti* configuration of 3,3'-*anti*-**14a** was assigned by its NOESY spectrum.

For 3,3'-*syn*-**14a** Colorless crystals (from EtOAc/hexane); Mp. 89.0-90.5 °C; IR (ATR) ν 2964, 1753, 1735, 1458, 1134, 910, 850, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.2 Hz), 1.75-1.89 (1H, m), 1.97-2.21 (4H, m), 2.29-2.46 (2H, m), 2.56 (2H, d, *J* = 7.3 Hz), 2.79 (1H, dd, *J* = 10.1, 1.4 Hz), 3.35-3.42 (1H, m), 4.13 (2H, q, *J* = 7.2 Hz), 7.07 (1H, dd, *J* = 8.1, 1.0 Hz), 7.14 (1H, td, *J* = 7.6, 1.0 Hz), 7.24 (1H, dd, *J* = 7.6, 1.7 Hz), 7.29-7.35 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.9, 36.4, 36.8, 37.4, 39.8, 43.0, 50.6, 61.1, 116.9, 122.9, 125.2, 128.9, 129.2, 150.6, 167.8, 170.6, 216.0; MS (ESI-TOF) *m*/*z* 339 [M+Na]$^+$; HRMS calcd for $C_{18}H_{20}NaO_5$ [M+Na]$^+$, 339.1208; found, 339.1211. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.13; H, 6.34.

For 3,3'-*anti*-**14a** Colorless crystals (from EtOAc/hexane); Mp. 40.0-42.5 °C; IR (ATR) ν 2957, 1765, 1738, 1725, 1457, 1215, 1160, 855, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, t, *J* = 7.1 Hz), 1.63-1.76 (1H, m), 1.98-2.38 (6H, m), 2.56 (2H, d, *J* = 7.5 Hz), 2.79 (1H, d, *J* = 9.0 Hz), 3.55 (1H, t, *J* = 7.5 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 7.03 (1H, d, *J* = 8.1 Hz), 7.13 (1H, t, *J* = 7.3 Hz), 7.24-7.33 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.6, 35.4, 36.2, 38.1, 39.8, 43.1, 50.4, 61.0, 116.9, 122.9, 125.1, 128.9, 129.2, 150.5, 168.2, 170.7, 216.2; MS (ESI-TOF) *m*/*z* 339 [M+Na]$^+$; HRMS calcd for $C_{18}H_{20}NaO_5$ [M+Na]$^+$, 339.1208; found, 339.1209. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.16; H, 6.37.

Ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-((*R**)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-*syn*-14b) and Ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-((*S**)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-*anti*-14b)



3,3'-*syn*-**14b**

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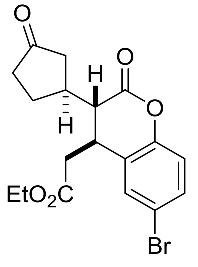


3,3'-*anti*-**14b**

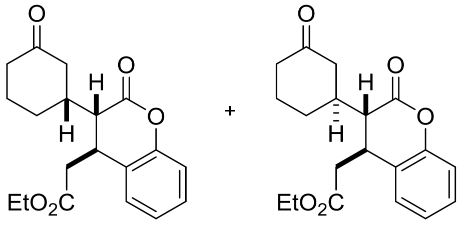
According to the synthetic procedure for **12b**, the reaction of 6-bromo-2*H*-chromen-2-one[4] **3b** (113 mg, 0.502 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (123 mg, 0.608 mmol), and cyclopent-2-en-1-one (62 mg, 0.755 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (10 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 72% yield (143 mg, 0.362 mmol, 3,3'-*syn*/*anti* = 1 : 2.4) by column chromatography on silica gel (hexane/EtOAc =

3 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1.5 : 1) to give less polar isomer 3,3'-*syn*-**14b** and more polar one 3,3'-*anti*-**14b** in 18% (35.9 mg, 90.8 μmol) and 42% (83.8 mg, 0.212 mmol) yields, respectively. Structure of 3,3'-*syn*-**14b** was confirmed by an X-ray crystallographic analysis. 3,4-*Anti* configuration of 3,3'-*anti*-**14b** was assigned by its NOESY spectrum.

For 3,3'-*syn*-**14b** Colorless crystals (from EtOAc/hexane); Mp. 94.0-95.5 °C. IR (ATR) ν 2948, 1765, 1735, 1720, 1478, 1160, 1138, 824, 486 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.1 Hz), 1.73-1.87 (1H, m), 1.96-2.20 (4H, m), 2.29-2.48 (2H, m), 2.55 (2H, d, *J* = 7.5 Hz), 2.77 (1H, d, *J* = 10.2 Hz), 3.35 (1H, t, *J* = 7.5 Hz), 4.14 (2H, q, *J* = 7.1 Hz), 6.95 (1H, d, *J* = 8.5 Hz), 7.37-7.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.9, 36.4, 36.6, 38.4, 39.6, 42.9, 50.2, 61.2, 117.6, 118.7, 125.0, 131.6, 132.2, 149.6, 167.0, 170.2, 215.6; MS (ESI-TOF) *m*/*z* 417 $[M+Na]^+$, 419 $[M+2+Na]^+$; HRMS calcd for $C_{18}H_{19}BrNaO_5$ $[M+Na]^+$, 417.0314; found, 417.0310. Anal. Calcd for $C_{18}H_{19}BrO_5$: C, 54.70; H, 4.85. Found: C, 54.75; H, 4.86.

For 3,3'-*anti*-**14b** Colorless oil; IR (neat) ν 2991, 1778, 1741, 1731, 1480, 1220, 1169, 821, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, *J* = 7.1 Hz), 1.60-1.76 (1H, m), 2.05-2.19 (3H, m), 2.19-2.31 (2H, m), 2.36 (1H, dd, *J* = 18.1, 7.1 Hz), 2.56 (2H, d, *J* = 7.5 Hz), 2.76 (1H, d, *J* = 10.2 Hz), 3.53 (1H, t, *J* = 7.5 Hz), 4.07-4.20 (2H, m), 6.92-6.97 (1H, m), 7.39-7.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.7, 35.3, 36.1, 38.0, 39.5, 43.0, 50.0, 61.2, 117.5, 118.2, 125.0, 131.6, 132.3, 149.6, 167.4, 170.3, 215.8; MS (ESI-TOF) *m*/*z* 417 $[M+Na]^+$, 419 $[M+2+Na]^+$; HRMS calcd for $C_{18}H_{19}BrNaO_5$ $[M+Na]^+$, 417.0314; found, 417.0318. Anal. Calcd for $C_{18}H_{19}BrO_5$: C, 54.70; H, 4.85. Found: C, 54.46; H, 4.80.

Ethyl 2-((3*S,4*S**)-2-oxo-3-((*R**)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-*syn*-15a) and ethyl 2-((3*S**,4*S**)-2-oxo-3-((*S**)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-*anti*-15a)**



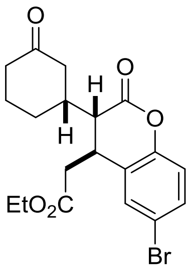
3,3'-*syn*-**15a** 3,3'-*anti*-**15a**

According to the synthetic procedure for **12a**, the reaction of 2*H*-chromen-2-one **3a** (147 mg, 1.01 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (243 mg, 1.20 mmol), and cyclohex-2-en-1-one (146 mg, 1.52 mmol) in the presence of triple carbon acid **1a** (10 mg, 10 μmol) in CH_2Cl_2 (4.0 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 93% yield (308 mg, 0.929 mmol, 3,3’-*syn*/*anti* = 1.1 : 1) by column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1.5 : 1) to give less polar isomer 3,3'-*syn*-**15a** and more polar one 3,3'-*anti*-**15a** in 46% (154 mg, 0.466 mmol) and 42% (140 mg, 0.424 mmol) yields, respectively. Structure of 3,3'-*syn*-**15a** was confirmed by an X-ray crystallographic analysis. 3,4-*Anti* configuration of 3,3'-*anti*-**15a** was assigned by its NOESY spectrum.

For 3,3'-*syn*-**15a** Colorless crystals (from hexane); Mp. 97.5-99.0 °C; IR (ATR) ν 2961, 1758, 1732, 1707, 1487, 1223, 1148, 764, 504 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.2 Hz), 1.42-1.62 (2H, m), 1.71-1.89 (2H, m), 2.00-2.16 (2H, m), 2.18-2.29 (1H, m), 2.29-2.38 (1H, m), 2.50-2.58 (1H, m), 2.53 (2H, d, *J* = 7.5 Hz), 2.73 (1H, dd *J* = 9.3, 1.5 Hz), 3.47 (1H, td, *J* = 7.5, 1.5 Hz), 4.13 (2H, q, *J* = 7.2 Hz), 7.03 (1H, dd, *J* = 8.1, 1.0 Hz), 7.12 (1H, td, *J* = 7.6, 1.0 Hz), 7.23 (1H, dd, *J* = 7.6, 1.6 Hz), 7.26-7.32 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.4, 29.5, 34.8, 37.6, 39.8, 41.0, 45.3, 50.9, 61.0, 116.8, 122.9, 125.1, 128.9, 129.2, 150.6, 167.9, 170.5, 209.2; MS (ESI-TOF) *m*/*z* 353 $[M+Na]^+$; HRMS calcd for $C_{19}H_{22}NaO_5$ $[M+Na]^+$, 353.1365; found, 353.1354. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.05; H, 6.70.

For 3,3'-*anti*-**15a** Pale yellow oil; IR (neat) ν 2945, 1766, 1729, 1711, 1484, 1458, 1223, 1180, 1146, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.1 Hz), 1.47-1.54 (2H, m), 1.72-1.85 (1H, m), 2.01-2.11 (2H, m), 2.17-2.36 (4H, m), 2.55 (2H, d, 7.5 Hz), 2.73 (1H, d, *J* = 9.0 Hz), 3.56 (1H, t, *J* = 7.5 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 7.05 (1H, brd, *J* = 8.1 Hz), 7.11 (1H, td, *J* = 7.5, 1.0 Hz), 7.22 (1H, dd, *J* = 7.5, 1.4 Hz), 7.25-7.32 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.5, 29.2, 35.4, 37.9, 39.9, 40.9, 45.8, 50.9, 61.0, 117.0, 123.0, 125.0, 128.7, 129.2, 150.5, 167.7, 170.7, 209.2; MS (ESI-TOF) *m*/*z* 353 $[M+Na]^+$; HRMS calcd for $C_{19}H_{22}NaO_5$ $[M+Na]^+$, 353.1365; found, 353.1362. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.13; H, 6.81.

Ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-((*R**)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-*syn*-15b) and ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-((*S**)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-*anti*-15b)



3,3'-*syn*-**15b**

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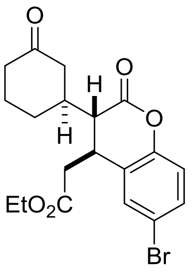


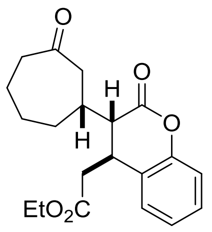
3,3'-*anti*-**15b**

According to the synthetic procedure for **12b**, the reaction of 6-bromo-2*H*-chromen-2-one[4] **3b** (113 mg, 0.502 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol), and cyclohex-2-en-1-one (73 mg, 0.76 mmol) in the presence of triple carbon acid **1a** (5.1 mg, 5.1 μmol) in CH_2Cl_2 (10 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 87% yield (177 mg, 0.432 mmol, 3,3'-*syn*/*anti* = 1.1 : 1) by column chromatography on silica gel (hexane/EtOAc = 4 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2 : 1) to give less polar isomer 3,3'-*syn*-**15b** and more polar one 3,3'-*anti*-**15b** in 43% (88.4 mg, 0.216 mmol) and 40% (82.3 mg, 0.201 mmol) yields, respectively. Structure of 3,3'-*syn*-**15b** was confirmed by an X-ray crystallographic analysis. 3,4-*Anti* configuration of 3,3'-*anti*-**15b** was assigned by its NOESY spectrum.

For 3,3'-*syn*-**15b** Colorless crystals (from Et_2O); Mp. 97.0-98.5 °C; IR (ATR) ν 2950, 1757, 1732, 1702, 1474, 1218, 1151, 819, 503 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.47-1.61 (2H, m), 1.72-1.87 (2H, m), 2.02-2.17 (2H, m), 2.20-2.30 (1H, m), 2.31-2.40 (1H, m), 2.50-2.57 (1H, m), 2.53 (2H, d, J = 7.5 Hz), 2.72 (1H, dd J = 9.2, 1.3 Hz), 3.41-3.47(1H, m), 4.15 (2H, q, J = 7.1 Hz), 6.93 (1H, d, J = 8.5 Hz), 7.37-7.44 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.3, 29.4, 34.7, 37.6, 39.6, 40.9, 45.2, 50.4, 61.2, 117.5, 118.5, 125.0, 131.6, 132.2, 149.6, 167.1, 170.1, 208.9; MS (ESI-TOF) *m*/*z* 431 $[M+Na]^+$, 433 $[M+2+Na]^+$; HRMS calcd for $C_{19}H_{21}BrNaO_5$ $[M+Na]^+$, 431.0470; found, 431.0475. Anal. Calcd for $C_{19}H_{21}BrO_5$: C, 55.76; H, 5.17. Found: C, 55.73; H, 5.04.

For 3,3'-*anti*-**15b** Colorless oil; IR (neat) ν 2949, 1769, 1734, 1717, 1480, 1221, 1182, 1144, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J = 7.2 Hz), 1.36-1.58 (2H, m), 1.71-1.83 (1H, m), 2.01-2.13 (2H, m) , 2.17-2.37 (4H, m) , 2.54 (2H, d, 7.4 Hz) , 2.72 (1H, dd, J = 9.2, 1.4 Hz) , 3.53 (1H, td, J = 7.4, 1.4 Hz) , 4.14 (2H, q, J = 7.2 Hz) , 6.93 (1H, d, J = 8.5 Hz) , 7.36-7.42 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.4, 29.1, 35.1, 37.8, 39.7, 40.8, 45.8, 50.5, 61.2, 117.4, 118.7, 125.1, 131.5, 132.2, 149.6, 166.9, 170.3, 209.0; MS (ESI-TOF) *m*/*z* 431 $[M+Na]^+$, 433 $[M+2+Na]^+$; HRMS calcd for $C_{19}H_{21}BrNaO_5$ $[M+Na]^+$, 431.0470; found, 431.0465. Anal. Calcd for $C_{19}H_{21}BrO_5$: C, 55.76; H, 5.17. Found: C, 55.55.; H, 5.27.

Ethyl 2-((3*S**,4*S**)-2-oxo-3-((*R**)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-*syn*-16a) and ethyl 2-((3*S**,4*S**)-2-oxo-3-((*S**)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-*anti*-16a)



3,3'-*syn*-**16a**

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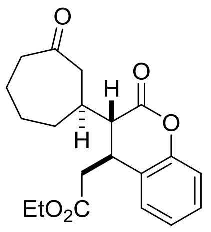


3,3'-*anti*-**16a**

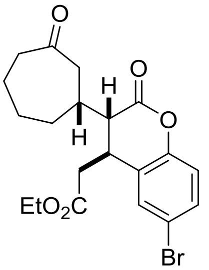
According to the synthetic procedure for **12a**, the reaction of 2*H*-chromen-2-one **3a** (146 mg, 0.999 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (243 mg, 1.20 mmol), and cyclohept-2-en-1-one (167 mg, 1.52 mmol) in the presence of triple carbon acid **1a** (9.9 mg, 9.9 μmol) in CH_2Cl_2 (4.0 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 88% yield (304 mg, 0.883 mmol, 3,3'-*syn*/*anti* = 3.9 : 1) by column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2 : 1) to give less polar isomer 3,3'-*syn*-**16a** and more polar one 3,3'-*anti*-**16a** in 65% (224 mg, 0.650 mmol) and 18% (62.0 mg, 0.180 mmol) yields, respectively. 3,4-*Anti* configurations of both isomers were assigned by their NOESY spectra.

For 3,3'-*syn*-**16a** Colorless oil; IR (neat) ν 2931, 1762, 1731, 1700, 1457, 1220, 1158, 762 cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$) δ 1.21 (3H, t, *J* = 7.1 Hz), 1.29-1.41 (1H, m), 1.46-1.57 (1H, m), 1.58-1.94 (5H, m), 2.30-2.47 (2H, m), 2.48-2.59 (2H, m), 2.52 (2H, d, *J* = 7.5 Hz), 2.72 (1H, dd, *J* = 9.7, 1.0 Hz), 3.54 (1H, td, *J* = 7.5, 1.0 Hz), 4.11 (2H, q, *J* = 7.1 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 7.11 (1H, t, *J* = 7.5 Hz), 7.23-7.31 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 23.7, 27.1, 34.2, 35.1, 35.2, 39.9, 43.6, 46.7, 49.9, 60.9, 116.7, 123.1, 125.0, 128.9, 129.1, 150.6, 168.2, 170.4, 212.1; MS (ESI-TOF) *m*/*z* 345 $[M+H]^+$; HRMS calcd for $C_{20}H_{25}O_5$ $[M+H]^+$, 345.1702; found, 345.1711. Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.58; H, 6.97.

For 3,3'-*anti*-**16a** Colorless oil; IR (neat) ν 2928, 1747, 1728, 1704, 1458, 1157, 1139, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.2 Hz), 1.23-1.39 (2H, m), 1.55-1.65 (1H, m), 1.72-1.87 (2H, m), 1.87-1.99 (2H, m), 2.31-2.49 (3H, m), 2.55 (2H, d, *J* = 7.4 Hz), 2.60 (1H, dd, *J* = 14.4, 11.1 Hz), 2.71 (1H, dd, *J* = 9.0, 1.4 Hz), 3.51-3.57 (1H, m), 4.13 (2H, q, *J* = 7.2 Hz), 7.05 (1H, d, *J* = 8.1 Hz), 7.12 (1H, t, *J* = 7.4 Hz), 7.21-7.33 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 24.0, 27.6, 33.7, 35.2, 35.7, 40.0, 43.5, 47.2, 50.6, 61.0, 116.9, 123.2, 125.0, 128.6, 129.2, 150.6, 168.3, 1707, 211.8; MS (ESI-TOF) *m*/*z* 367 $[M+Na]^+$; HRMS calcd for $C_{20}H_{24}NaO_5$ $[M+Na]^+$, 367.1521; found, 367.1508. Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.67; H, 7.21.

Ethyl 2-((3*S,4*S**)-6-bromo-2-oxo-3-((*R**)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-*syn*-16b) and ethyl 2-((3*S**,4*S**)-6-bromo-2-oxo-3-((*S**)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-*anti*-16b)**



3,3'-*syn*-**16b**

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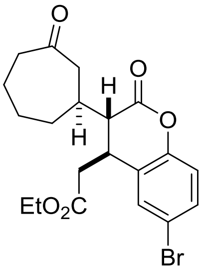


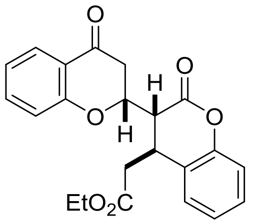
3,3'-*anti*-**16b**

According to the synthetic procedure for **12b**, the reaction of 6-bromo-2*H*-chromen-2-one[4] **3b** (112 mg, 0.498 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (122 mg, 0.604 mmol), and cyclohept-2-en-1-one (166 mg, 1.51 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (10 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 82% yield (173 mg, 0.409 mmol, 3,3'-*syn*/*anti* = 5.8 : 1) by column chromatography on silica gel (hexane/EtOAc = 4 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 3 : 1) to give less polar isomer 3,3'-*syn*-**16b** and more polar one 3,3'-*anti*-**16b** in 64% (135 mg, 0.319 mmol) and 13% (27.4 mg, 64.7 μmol) yields, respectively. Structures of both isomers were confirmed by X-ray crystallographic analyses.

For 3,3'-*syn*-**16b** Colorless solid (from hexane); Mp. 84.0-85.0 °C; IR (neat) ν 2930, 1754, 1732, 1704, 1475, 1216, 1153, 1119, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, *J* = 7.2 Hz), 1.33-1.44 (1H, m), 1.48-1.59 (1H, m), 1.61-1.94 (5H, m), 2.35-2.43 (2H, m), 2.43-2.61 (2H, m), 2.52 (2H, d, *J* = 7.4 Hz), 2.72 (1H, dd, *J* = 9.6, 1.5 Hz), 3.53 (1H, td, *J* = 7.4, 1.5 Hz), 4.14 (2H, q, *J* = 7.2 Hz), 6.93 (1H, d, *J* = 8.4 Hz), 7.38-7.43 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 23.6, 27.0, 34.2, 35.0, 35.2, 39.7, 43.6, 46.6, 49.4, 61.1, 117.4, 118.4, 125.3, 131.7, 132.1, 149.6, 167.4, 170.1, 211.9; MS (ESI-TOF) *m*/*z* 445 $[M+Na]^+$, 447 $[M+2+Na]^+$; HRMS calcd for $C_{20}H_{23}BrNaO_5$ $[M+Na]^+$, 445.0627; found, 445.0634. Anal. Calcd for $C_{20}H_{23}BrO_5$: C, 56.75; H, 5.48. Found: C, 56.52; H, 5.50.

For 3,3'-*anti*-**16b** Colorless solid (from hexane); Mp. 127-130 °C; IR (neat) ν 2932, 1755, 1732, 1694, 1474, 1218, 1162, 1113, 824 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.1 Hz), 1.27-1.39 (2H, m), 1.53-1.66 (1H, m), 1.70-1.88 (2H, m), 1.88-1.98 (2H, m), 2.32-2.42 (2H, m), 2.46 (1H, dt, *J* = 15.2, 4.9 Hz), 2.54 (2H, d, *J* = 7.4 Hz), 2.60 (1H, dd, *J* = 15.2, 11.2 Hz), 2.70 (1H, dd, *J* = 9.0, 1.6 Hz), 3.47-3.54 (1H, m), 4.14 (2H, q, *J* = 7.1 Hz), 6.94 (1H, d, *J* = 8.5 Hz), 7.38 (1H, d, *J* = 2.1 Hz), 7.40 (1H, dd, *J* = 8.5, 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 23.9, 27.5, 33.8, 35.0, 35.7, 39.8, 43.5, 47.0, 50.3, 61.2, 117.4, 118.7, 125.3, 131.3, 132.2 149.7, 167.5, 170.4, 211.6; MS (ESI-TOF) *m*/*z* 445 $[M+Na]^+$, 447 $[M+2+Na]^+$; HRMS calcd for $C_{20}H_{23}BrNaO_5$ $[M+Na]^+$, 445.0627; found, 445.0631. Anal. Calcd for $C_{20}H_{23}BrO_5$: C, 56.75; H, 5.48. Found: C, 57.02; H, 5.63.

Ethyl 2-((2*R**,3'*R**,4'*S**)-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-*syn*-17) and ethyl 2-((2*S**,3'*R**,4'*S**)-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-*anti*-17)



3,2'-*syn*-**17**

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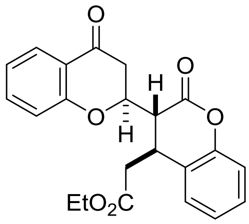


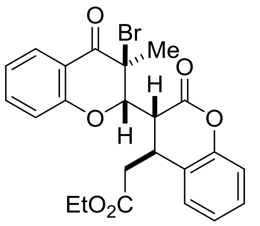
3,2'-*anti*-**17**

According to the synthetic procedure for **12a**, the reaction of 2*H*-chromen-2-one **3a** (73.1 mg, 0.500 mmol), *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (125 mg, 0.618 mmol), and 4*H*-chromen-4-one (109 mg, 0.746 mmol) in the presence of triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (2.5 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H_2O (20 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and evaporated. A mixture of two diastereomers was obtained in 99% yield (189 mg, 0.497 mmol, 3,2'-*syn*/*anti* = 8.5 : 1) by column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1 : 1) to give less polar isomer 3,2'-*anti*-**17** and more polar one 3,2'-*syn*-**17** in 81% (154 mg, 0.405 mmol) and 9.2% (17.5 mg, 46.0 μmol) yields, respectively. Structure of 3,2'-*anti*-**17** was confirmed by an X-ray crystallographic analysis. 3,4-*Anti* configuration of 3,2'-*syn*-**17** was assigned by its NOESY spectrum.

For 3,2'-*syn*-**17** Pale yellow oil; IR (neat) ν 2978, 2922, 1757, 1730, 1688, 1603, 1460, 1221, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.1 Hz), 2.63 (1H, dd, *J* = 16.7, 6.8 Hz), 2.68 (1H, dd, *J* = 16.7, 7.8 Hz), 2.78 (1H, dd, *J* = 16.8, 3.2 Hz), 2.89 (1H, dd, *J* = 16.8, 12.7 Hz), 3.31 (1H, dd, *J* = 6.6, 1.6 Hz), 3.53-3.59 (1H, m), 4.14 (2H, q, *J* = 7.1 Hz), 4.52 (1H, ddd *J* = 12.7, 6.6, 3.2 Hz), 6.67 (1H, brd, *J* = 8.4 Hz), 6.99 (1H, td, *J* = 7.5, 1.0 Hz), 7.08 (1H, dd, *J* = 8.2, 1.0 Hz), 7.14 (1H, td, *J* = 7.5, 1.0 Hz), 7.24 (1H, dd, *J* = 7.5, 1.7 Hz), 7.28-7.35 (1H, m), 7.37-7.44 (1H, m), 7.81 (1H, dd, *J* = 7.2, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 35.3, 40.0, 40.9, 49.4, 61.2, 76.9, 117.0, 118.0, 120.7, 122.1, 122.8, 125.1, 126.9, 128.3, 129.3, 136.3, 150.9, 160.4, 165.7 ,170.4, 190.5; MS (ESI-TOF) *m*/*z* 403 [M+Na]$^+$; HRMS calcd for $C_{22}H_{20}NaO_6$ [M+Na]$^+$, 403.1158; found, 403.1167.

For 3,2'-*anti*-**17** Colorless crystals (from Et_2O); Mp. 86.0-87.5 °C; IR (ATR) ν 2983, 2926, 1761, 1728, 1682, 1605, 1216, 1149, 1029, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, *J* = 7.1 Hz), 2.61 (1H, dd, *J* = 16.2, 7.5 Hz), 2.66 (1H, dd, *J* = 16.2, 7.5 Hz), 2.70 (1H, dd, *J* = 16.9, 2.9 Hz), 2.92 (1H, dd, *J* = 16.9, 12.8 Hz), 3.33 (1H, dd, *J* = 8.9, 1.4 Hz), 4.00 (1H, td, *J* = 7.5, 1.4 Hz), 4.13 (2H, q, *J* = 7.1 Hz), 4.34 (1H, ddd *J* = 12.8, 8.9, 2.9 Hz), 6.94 (1H, brd, *J* = 8.4 Hz), 6.99-7.04 (1H, m), 7.06 (1H, d, *J* = 8.0 Hz), 7.12 (1H, td, *J* = 7.5, 1.1 Hz), 7.26-7.30 (1H, m), 7.30 (1H, d, *J* = 7.5 Hz), 7.44-7.50 (1H, m), 7.83 (1H, dd, *J* = 7.8, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 33.6, 39.8, 41.3, 50.6, 61.1, 74.1, 117.0, 117.8, 120.9, 122.1, 122.7, 125.3, 127.0, 129.1, 129.3, 136.2, 150.5, 160.3, 165.8, 170.5, 190.3; MS (ESI-TOF) *m*/*z* 403 [M+Na]$^+$; HRMS calcd for $C_{22}H_{20}NaO_6$ [M+Na]$^+$, 403.1158; found, 403.1148. Anal. Calcd for $C_{22}H_{20}O_6$: C, 69.46; H, 5.30. Found: C, 69.48; H, 5.31.

Ethyl-2-((2*S**,3*S**,3'*R**,4'*S**)-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-*syn*-18) and ethyl 2-((2*R**,3*R**,3'*R**,4'*S**)-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-*anti*-18)



3,2'-*syn*-**18**

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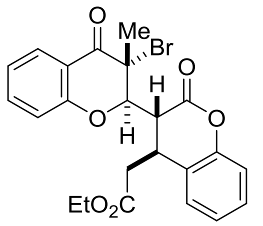


3,2'-*anti*-**18**

To a solution of 2*H*-chromen-2-one **3a** (73.2 mg, 0.501 mmol) and triple carbon acid **1a** (5.0 mg, 5.0 μmol) in CH_2Cl_2 (1.0 mL), a solution of *tert*-butyl((1-ethoxyvinyl)oxy)dimethylsilane **4** (124 mg, 0.613 mmol) in CH_2Cl_2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of 3-methylchromone[8] (120 mg, 0.749 mmol) in CH_2Cl_2 (1.0 mL) was added to the reaction mixture and it was additionally stirred for 1.5 h at the same temperature. After that, the reaction mixture was treated with a solution of bromine (170 mg, 1.06 mmol) for 30 min at –78 °C. The resulting mixture was quenched with a saturated aqueous $Na_2S_2O_3$ solution (15 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/ EtOAc = 6 : 1) to give an inseparable mixture of the desired adduct and a small amount of **6a**. Isolation of the products was achieved by recycling HPLC technique (hexane/EtOAc = 4 : 1) to give less polar isomer 3,2'-*anti*-**18** and more polar isomer 3,2'-*syn*-**18** in 42% (100 mg, 0.212 mmol) and 30% (70.3 mg, 0.149 mmol) yields, respectively. Structure of 3,2'-*anti*-**18** was determined by an X-ray crystallographic analysis. 3,4-*Anti* and 2',3'-*anti* configurations of 3,2'-*syn*-**18** were assigned by its NOESY spectrum.

For 3,2'-*syn*-**18** Colorless crystals (from EtOAc); Mp. 117-118 °C; IR (ATR) ν 2980, 1748, 1727, 1693, 1606, 1459, 1166, 1156, 1145, 1040, 751, 478 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.23 (3H, t, *J* = 7.2 Hz), 2.07(3H, s), 2.59 (1H, dd, *J* = 16.4, 7.2 Hz) , 2.64 (1H, dd, *J* = 16.4, 8.0 Hz), 3.58-3.63 (1H, m), 3.65 (1H, dd, *J* = 3.7, 1.6 Hz), 4.09-4.19 (2H, m), 4.53 (1H, d, *J* = 3.7 Hz), 6.38 (1H, brd, *J* = 8.3 Hz), 6.99-7.07 (2H, m), 7.13 (1H, td, *J* = 7.5, 1.1 Hz), 7.28-7.32 (2H, m), 7.32-7.38 (1H, m), 7.87 (1H, dd, *J* = 7.9, 1.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1, 21.6, 38.9, 39.5, 46.3, 61.2, 64.5, 85.0, 116.9, 117.4, 117.7, 122.6, 123.0, 125.1, 128.3, 129.0, 129.3, 136.5, 151.1, 158.1, 165.6, 170.3, 186.6; MS (ESI-TOF) *m*/*z* 495 [M+Na]$^+$, 497 [M+2+Na]$^+$; HRMS calcd for $C_{23}H_{21}BrNaO_6$ [M+Na]$^+$, 495.0419; found, 495.0418. Anal. Calcd for $C_{23}H_{21}BrO_6$: C, 58.37; H, 4.47. Found: C, 58.41; H, 4.59.

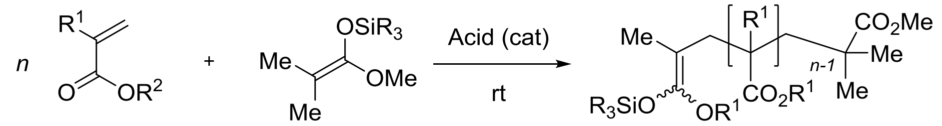
For 3,2'-*anti*-**18** Colorless crystals (from EtOAc); Mp. 149-150 °C; IR (ATR) ν 2932, 1751, 1725, 1685, 1608, 1459, 1202, 1179, 1028, 749, 479 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.18 (3H, t, *J* = 7.2 Hz), 2.12 (3H, s), 2.47 (2H, d, *J* = 7.5 Hz), 3.42 (1H, dd, *J* = 6.2, 1.2 Hz), 3.49 (1H, brt, *J* = 7.4 Hz), 4.03-4.13 (2H, m), 4.83 (1H, d, *J* = 6.2 Hz), 6.52 (1H, d, *J* = 8.3 Hz), 6.79 (1H, d, *J* = 7.2 Hz), 6.85-6.92 (1H, m), 7.00 (1H, t, *J* = 8.1 Hz), 7.05 (1H, d, *J* = 8.1 Hz), 7.18-7.24 (1H, m), 7.28-7.34 (1H, m), 7.86 (1H, dd, *J* = 7.8, 1.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1, 21.8, 34.1, 39.9, 46.6, 61.1, 61.3, 84.0, 116.8, 117.3, 117.5, 112.3, 112.8, 125.1, 127.7, 128.3, 129.1, 136.8, 150.3, 158.3, 166.7, 170.1, 186.3; MS (ESI-TOF) *m*/*z* 495 [M+Na]$^+$, 497 [M+2+Na]$^+$; HRMS calcd for $C_{23}H_{21}BrNaO_6$ [M+Na]$^+$, 495.0419; found, 495.0417. Anal. Calcd for $C_{23}H_{21}BrO_6$: C, 58.37; H, 4.47. Found: C, 58.40; H, 4.94.

5. GTP studies by using carbon acids

Typical procedure: $Tf_2CHCH_2CHTf_2$ **1b** (1.43 mg, 2.50 μmol) was added to a solution of methyl methacrylate **19a** (500 mg, 5.00 mmol) and KSA **20** (8.7 mg, 50 μmol) in CH_2Cl_2 (4.50 mL) under an argon atmosphere at room temperature. After stirring for 3 h, the polymerization was quenched by adding a small amount of methanol. Aliquots were removed from the reaction mixture to determine the conversion of **19a** based on its ^1H NMR spectrum. The reaction mixture was purified by reprecipitated to large amount of *n*-hexane, followed by drying the product to give the **21a** as a white solid. Yield, 495 mg (99 %). SEC (RI): $M_{n(SEC)}$, 11,300 g mol^{-1}; M_w/M_n, 1.04.

The GTPs of methyl methacrylate **19a** and butyl acrylate **19b** in the presence of carbon acid **1a** (3.56 mg, 5.0 μmol) or zwitterion **2** (2.63 mg, 5.0 μmol) as an acid catalyst were carried out with KSA **20** or **22** by a similar procedure. These results are summarized in Table S1. $Tf_2CHCH_2CHTf_2$ **1b** nicely promoted desired polymerization in both cases of **19a** and **19b** (entries 1, 4 and 5), while triple carbon acid **1a** did not show a considerable level of catalysis in the GTP of **19a** with KSA **20** (entry 2). On the other hand, monomer **19b** was polymerized with KSA **22** to give the corresponding polymer **21b** in the presence of a catalytic amount of **1a** (entry 6). Compared to methacrylate **19a**, acrylate **19b** has relatively higher reactivity. For this, less effective carbon acid **1a** worked as a suitable polymerization catalyst for **19b**.

Table S1. GTP of methyl methacrylate **19a** and butyl acrylate **19b**



19a ($R^1 = R^2 = Me$)
19b ($R^1 = H$, $R^2 = Bu$)

20 ($R_3Si = Me_3Si$)
22 ($R_3Si = i\text{-}Pr_3Si$)

21a, **21b**

Entry	19	Acid (equiv)	KSA	Solvent	Conversion of **19**^{b} (%)	$M_{n(SEC)}$^{c} (g mol^{-1})	M_w/M_n^{c}
1	**19a**	$Tf_2CHCH_2CHTf_2$ **1b** (0.02 equiv)	**20**	CH_2Cl_2	>99	11,300	1.04
2	**19a**	Carbon acid **1a** (0.05 equiv)	**20**	CH_2Cl_2	<1	--	--
3	**19a**	Zwitterion **2** (0.05 equiv)	**20**	CH_2Cl_2	<1	--	--
4	**19b**	$Tf_2CHCH_2CHTf_2$ **1b** (0.02 equiv)	**20**	CH_2Cl_2	77.0	11,400	1.47
5	**19b**	$Tf_2CHCH_2CHTf_2$ **1b** (0.02 equiv)	**22**	toluene	>99	14,400	1.02
6	**19b**	Carbon acid **1a** (0.02 equiv)	**22**	toluene	>99	14,500	1.02
7	**19b**	Zwitterion **2** (0.05 equiv)	**22**	toluene	<1	--	--

[a] Ar atmosphere; **19**/KSA/Acid = 100 : 1 : 0.02-0.05, $[\mathbf{19}]_0$ = 1.0 mol L^{-1}.
Reaction time; 3 h for GTP of **19a**, 5 min for GTP of **19b**.

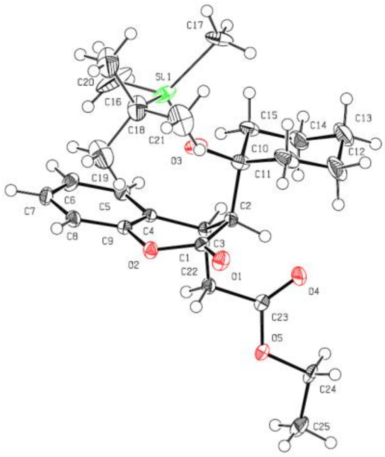
[b] Determined by ^1H NMR in $CDCl_3$.

[c] Determined by size exclusion chromatography (SEC) in THF using poly(methyl methacrylate) standards.

6. X-ray crystallographic data

Crystallographic data for the X-ray crystal structure analysis of **7a**, 3,3’-*syn*-**14a**, 3,3’-*syn*-**14b**, 3,3’-*syn*-**15a**, 3,3’-*syn*-**15b**, 3,3’-*syn*-**16b**, 3,3’-*anti*-**16b**, 3,2’-*anti*-**17**, and 3,2’-*anti*-**18** have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication Nos. CCDC 1440383 (**7a**), 1440387 (3,3’-*syn*-**14a**), 1440388 (3,3’-*syn*-**14b**), 1440389 (3,3’-*syn*-**15a**), 1440390 (3,3’-*syn*-**15b**), 1440391 (3,3’-*syn*-**16b**), 1440384 (3,3’-*anti*-**16b**), 1440385 (3,2’-*anti*-**17**), and 1440386 (3,2’-*anti*-**18**). These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

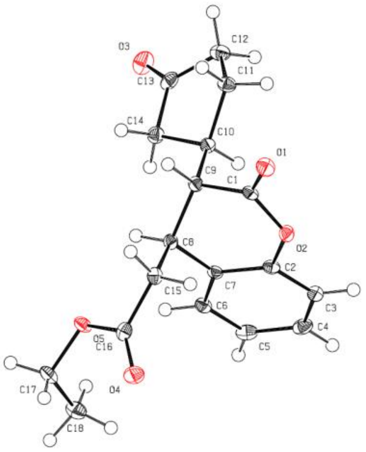
Table S2. Crystal data and structure refinement for **7a**.



$C_{25}H_{38}O_5Si$	$F(000) = 968$
$M_r = 446.64$	$D_x = 1.178$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5017 reflections
$a = 10.5246$ (7) Å	$\theta = 2.5–27.5°$
$b = 7.1824$ (5) Å	$\mu = 0.12$ mm^{-1}
$c = 33.424$ (2) Å	$T = 90$ K
$\beta = 94.7154$ (10)°	Block, colorless
$V = 2518.0$ (3) Å^3	0.29 × 0.17 × 0.06 mm
$Z = 4$	
Bruker APEXII CCD area detector diffractometer	4464 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	3789 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	$R_{int} = 0.021$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
phi and ω scans	$h = -9\rightarrow12$
Absorption correction: analytical	$k = -8\rightarrow7$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.965$, $T_{max} = 0.993$	$l = -39\rightarrow37$
11783 measured reflections	
Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 1.2637P]$
	where $P = (F_o^2 + 2F_c^2)/3$
4464 reflections	$(\Delta/\sigma)_{max} < 0.001$
355 parameters	$\Delta\rangle_{max} = 0.26$ e Å^{-3}
48 restraints	$\Delta\rangle_{min} = -0.23$ e Å^{-3}

Table S3. Crystal data and structure refinement for 3,3'-*syn*-**14a**.



$C_{18}H_{20}O_5$	$F(000) = 1344$
$M_r = 316.34$	$D_x = 1.372$ Mg m^{-3}
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 5810 reflections
$a = 25.583$ (3) Å	$\theta = 2.3$–$27.5°$
$b = 6.8787$ (8) Å	$\mu = 0.10$ mm^{-1}
$c = 17.4038$ (19) Å	$T = 90$ K
$V = 3062.7$ (6) Å^3	Block, colourless
$Z = 8$	0.20 × 0.18 × 0.08 mm
Bruker APEXII CCD area detector diffractometer	4775 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	4424 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	$R_{int} = 0.029$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.6°$
phi and ω scans	$h = -30\rightarrow27$
Absorption correction: analytical	$k = -8\rightarrow8$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.980$, $T_{max} = 0.992$	$l = -18\rightarrow20$
14062 measured reflections	
Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.080$

$S = 1.04$

4775 reflections

417 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.7653P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

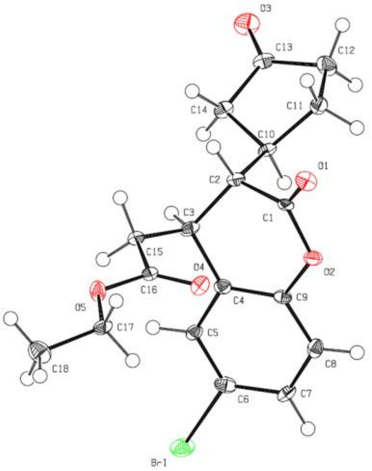
$\Delta\rangle_{max} = 0.16$ e Å^{-3}

$\Delta\rangle_{min} = -0.19$ e Å^{-3}

Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881

Flack parameter: 1.0 (7)

Table S4. Crystal data and structure refinement for 3,3'-*syn*-**14b**.



$C_{18}H_{19}BrO_5$

$M_r = 395.24$

Monoclinic, *Pc*

Hall symbol: P -2yc

$a = 11.3068 (19)$ Å

$b = 9.6829 (16)$ Å

$c = 24.116 (4)$ Å

$\beta = 103.091 (2)°$

$V = 2571.7 (7)$ Å^3

$Z = 6$

$F(000) = 1212$

$D_x = 1.531$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3963 reflections

$\theta = 3.1–27.1°$

$\mu = 2.42$ mm^{-1}

$T = 90$ K

Block, colourless

0.15 × 0.13 × 0.06 mm

Bruker APEXII CCD area detector diffractometer

Radiation source: Bruker TXS fine-focus rotating anode

Bruker Helios multilayer confocal mirror

Detector resolution: 8.333 pixels mm^{-1}

phi and ω scans

6361 independent reflections

5637 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$

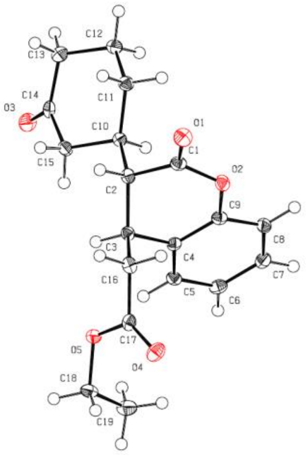
$\theta_{max} = 25.0°$, $\theta_{min} = 1.7°$

$h = -12\rightarrow13$

Absorption correction: analytical	$k = -9 \rightarrow 11$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.713$, $T_{max} = 0.868$	$l = -28 \rightarrow 15$
12184 measured reflections	

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} = 0.001$
6361 reflections	$\Delta\rangle_{max} = 0.49$ e Å^{-3}
652 parameters	$\Delta\rangle_{min} = -0.47$ e Å^{-3}
452 restraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Flack parameter: -0.001 (6)

Table S5. Crystal data and structure refinement for 3,3'-*syn*-**15a**.



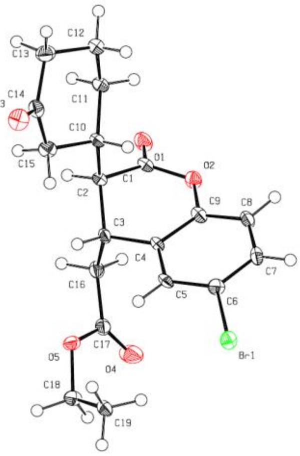
$C_{19}H_{22}O_5$	$F(000) = 704$
$M_r = 330.37$	$D_x = 1.362$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3451 reflections
$a = 15.1059$ (12) Å	$\theta = 2.5–27.6°$
$b = 7.0831$ (6) Å	$\mu = 0.10$ mm^{-1}
$c = 16.4912$ (13) Å	$T = 90$ K
$\beta = 114.080$ (1)°	Block, colourless
$V = 1610.9$ (2) Å^3	0.22 × 0.14 × 0.07 mm
$Z = 4$	

Bruker APEXII CCD area detector diffractometer	2841 independent reflections

Radiation source: Bruker TXS fine-focus rotating anode	2505 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	$R_{int} = 0.020$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.5°$
phi and ω scans	$h = -15 \rightarrow 17$
Absorption correction: analytical	$k = -8 \rightarrow 8$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{min} = 0.979$, $T_{max} = 0.993$	$l = -19 \rightarrow 19$
7482 measured reflections	

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.6685P]$
	where $P = (F_o^2 + 2F_c^2)/3$
2841 reflections	$(\Delta/\sigma)_{max} = 0.001$
218 parameters	$\Delta\rangle_{max} = 0.24$ e Å^{-3}
156 restraints	$\Delta\rangle_{min} = -0.20$ e Å^{-3}

Table S6. Crystal data and structure refinement for 3,3’-*syn*-**15b**.



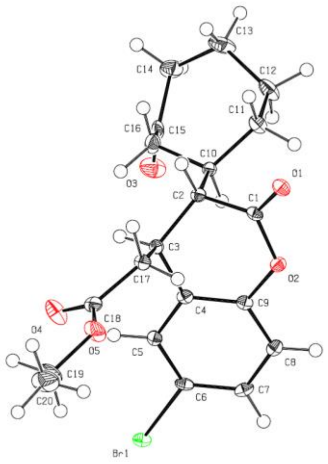
$C_{19}H_{21}BrO_5$	$Z = 4$
$M_r = 409.27$	$F(000) = 840$
Triclinic, $P\bar{1}$	$D_x = 1.546$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.854$ (3) Å	Cell parameters from 4477 reflections
$b = 14.268$ (4) Å	$\theta = 2.4–27.4°$
$c = 14.396$ (4) Å	$\mu = 2.37$ mm^{-1}
$\alpha = 94.289$ (4)°	$T = 90$ K
$\beta = 102.730$ (4)°	Block, colourless
$\gamma = 95.207$ (4)°	0.31 × 0.11 × 0.05 mm

V = 1758.1 (9) Å^3

Bruker APEXII CCD area detector diffractometer	6156 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	4996 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	R_{int} = 0.049
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.4°
phi and ω scans	h = -10→10
Absorption correction: analytical	k = -16→16
Crystal Faces plugin in Bruker *APEX2* software	
T_{min} = 0.528, T_{max} = 0.891	l = -17→17
17095 measured reflections	

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.074	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.199	H-atom parameters constrained
S = 1.18	$w = 1/[\sigma^2(F_o^2) + (0.0009P)^2 + 30.7076P]$
	where $P = (F_o^2 + 2F_c^2)/3$
6156 reflections	$(\Delta/\sigma)_{max}$ = 0.001
453 parameters	$\Delta\rangle_{max}$ = 2.06 e Å^{-3}
312 restraints	$\Delta\rangle_{min}$ = -0.94 e Å^{-3}

Table S7. Crystal data and structure refinement for 3,3'-*syn*-**16b**.



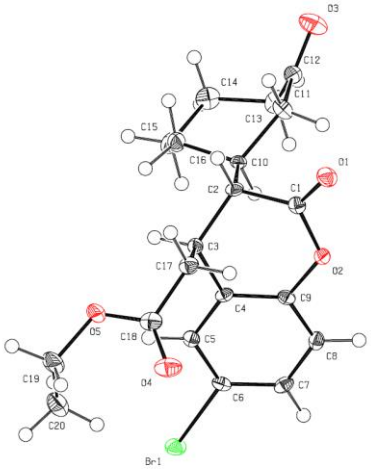
$C_{20}H_{23}BrO_5$	$F(000)$ = 872
M_r = 423.29	D_x = 1.481 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 5070 reflections
a = 12.0177 (12) Å	θ = 3.0–27.6°
b = 6.6196 (6) Å	μ = 2.19 mm^{-1}
c = 23.898 (2) Å	T = 90 K
β = 93.302 (1)°	Block, colourless

V = 1898.0 (3) Å^3	0.22 × 0.12 × 0.06 mm
Z = 4	

Bruker APEXII CCD area detector diffractometer	3352 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	3025 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	R_{int} = 0.021
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{\max}$ = 25.0°, $\theta_{\min}$ = 1.7°
phi and ω scans	h = -14→14
Absorption correction: analytical	k = -7→7
Crystal Faces plugin in Bruker *APEX2* software	
$T_{\min}$ = 0.644, $T_{\max}$ = 0.880	l = -28→15
8856 measured reflections	

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.023	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.056	H-atom parameters constrained
S = 1.06	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 1.0095P]$
	where $P = (F_o^2 + 2F_c^2)/3$
3352 reflections	$(\Delta/\sigma)_{\max}$ = 0.004
236 parameters	$\Delta\rangle_{\max}$ = 0.33 e Å^{-3}
162 restraints	$\Delta\rangle_{\min}$ = -0.21 e Å^{-3}

Table S8. Crystal data and structure refinement for 3,3'-*anti*-**16b**.



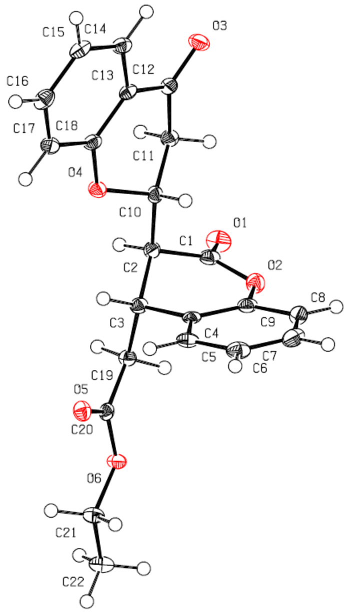
$C_{20}H_{23}BrO_5$	$F(000)$ = 872
M_r = 423.29	D_x = 1.559 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 3254 reflections
a = 7.1552 (8) Å	θ = 2.4–27.4°
b = 17.356 (2) Å	μ = 2.31 mm^{-1}

c = 14.5825 (17) Å	T = 90 K
β = 95.177 (2)°	Block, colourless
V = 1803.5 (4) Å^3	0.13 × 0.11 × 0.11 mm
Z = 4	

Bruker APEXII CCD area detector diffractometer	3188 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	2741 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	R_{int} = 0.027
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.8°
phi and ω scans	h = -8→4
Absorption correction: analytical	k = -20→20
Crystal Faces plugin in Bruker *APEX2* software	
T_{min} = 0.754, T_{max} = 0.785	l = -17→16
8683 measured reflections	

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.029	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.074	H-atom parameters constrained
S = 1.04	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.4382P]$
	where $P = (F_o^2 + 2F_c^2)/3$
3188 reflections	$(\Delta/\sigma)_{\text{max}}$ = 0.001
236 parameters	$\Delta\rangle_{\text{max}}$ = 0.50 e Å^{-3}
162 restraints	$\Delta\rangle_{\text{min}}$ = -0.37 e Å^{-3}

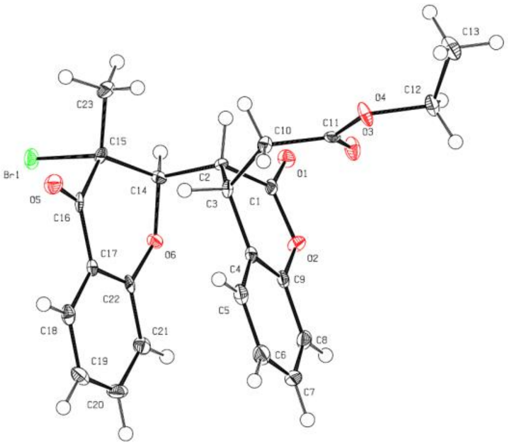
Table S9. Crystal data and structure refinement for 3,2’-*anti*-**17**.



$C_{22}H_{20}O_6$	$F(000)$ = 1600
M_r = 380.38	D_x = 1.338 Mg m^{-3}

Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: P 2c -2ac	Cell parameters from 5244 reflections
a = 34.732 (4) Å	θ = 2.4–26.2°
b = 13.1317 (14) Å	μ = 0.10 mm^{-1}
c = 8.2791 (9) Å	T = 90 K
V = 3776.0 (7) Å^3	Block, colourless
Z = 8	0.18 × 0.07 × 0.05 mm
Bruker APEXII CCD area detector diffractometer	6383 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	5777 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	R_{int} = 0.032
Detector resolution: 8.333 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.2°
phi and ω scans	h = -41→39
Absorption correction: analytical	k = -11→15
Crystal Faces plugin in Bruker *APEX2* software	
T_{min} = 0.983, T_{max} = 0.995	l = -9→9
17978 measured reflections	
Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.033	H-atom parameters constrained
$wR(F^2)$ = 0.075	$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.5188P]$
	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.001
6383 reflections	$\Delta\rangle_{max}$ = 0.15 e Å^{-3}
507 parameters	$\Delta\rangle_{min}$ = -0.16 e Å^{-3}

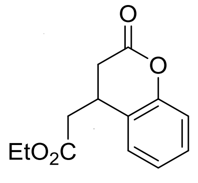
Table S10. Crystal data and structure refinement for 3,2'-*anti*-**18**.



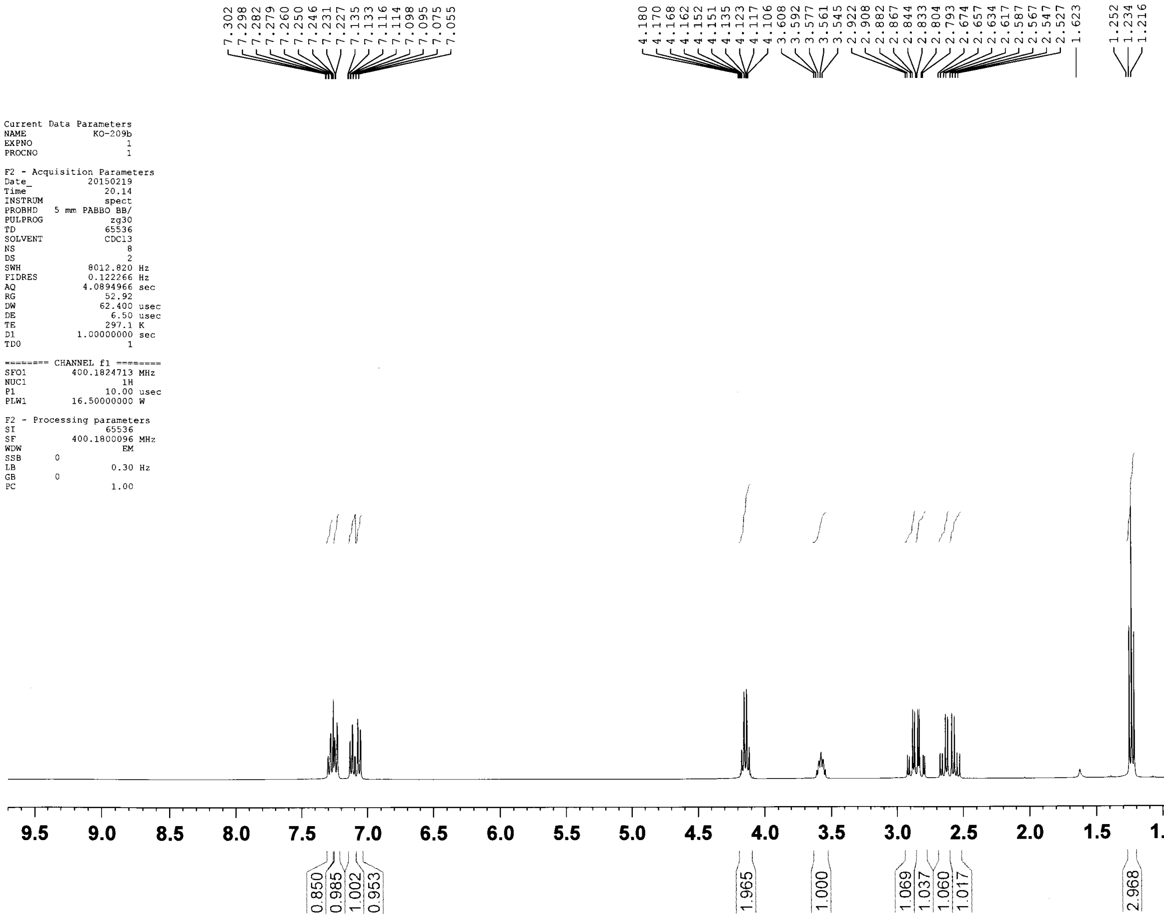
$C_{23}H_{21}BrO_6$	$F(000)$ = 968
M_r = 473.31	D_x = 1.578 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2685 reflections

$a = 12.6704\ (12)$ Å	$\theta = 2.5–26.5°$
$b = 9.7676\ (9)$ Å	$\mu = 2.10\ \mathrm{mm}^{-1}$
$c = 16.2166\ (16)$ Å	$T = 90$ K
$\beta = 97.059\ (1)°$	Block, colourless
$V = 1991.7\ (3)$ Å^3	0.11 × 0.09 × 0.04 mm
$Z = 4$	
Bruker APEXII CCD area detector diffractometer	3501 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	2887 reflections with $I > 2\sigma(I)$
Bruker Helios multilayer confocal mirror	$R_{\mathrm{int}} = 0.033$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{\mathrm{max}} = 25.0°$, $\theta_{\mathrm{min}} = 1.9°$
phi and ω scans	$h = -15 \rightarrow 14$
Absorption correction: analytical	$k = -11 \rightarrow 11$
Crystal Faces plugin in Bruker *APEX2* software	
$T_{\mathrm{min}} = 0.802$, $T_{\mathrm{max}} = 0.921$	$l = -14 \rightarrow 19$
9184 measured reflections	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.063$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 0.658P]$
	where $P = (F_o^2 + 2F_c^2)/3$
3501 reflections	$(\Delta/\sigma)_{\mathrm{max}} = 0.001$
273 parameters	$\Delta\rangle_{\mathrm{max}} = 0.39$ e Å^{-3}
192 restraints	$\Delta\rangle_{\mathrm{min}} = -0.32$ e Å^{-3}

7. ^{1}H and ^{13}C NMR spectra



6a



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Current Data Parameters
NAME              KO-209b
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150219
Time                20.14
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  52.92
DW                 62.400 usec
DE                   6.50 usec
TE                  297.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1824713 MHz
NUC1                   1H
P1                  10.00 usec
PLW1          16.50000000 W

F2 - Processing parameters
SI                  65536
SF            400.1800096 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
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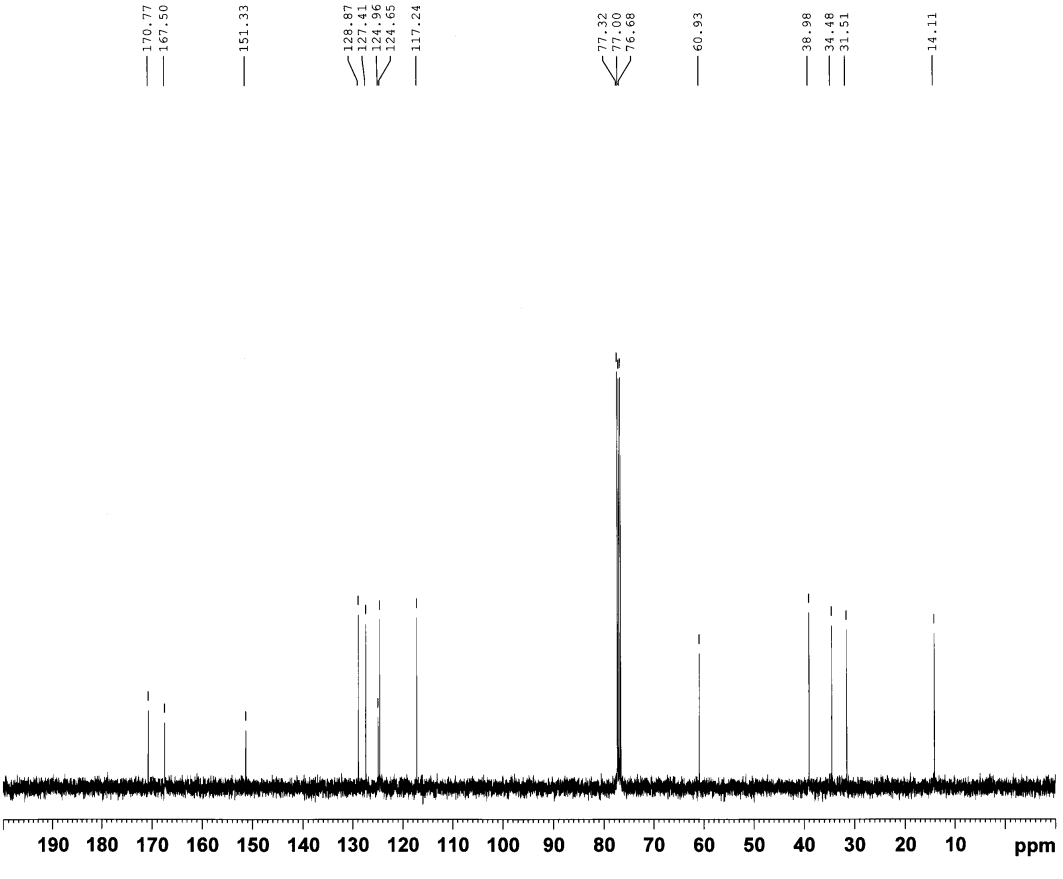

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Current Data Parameters
NAME              KO-209b
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150219
Time                20.24
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDC13
NS                     40
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 206.25
DW                 20.800 usec
DE                   6.50 usec
TE                  297.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6354031 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          63.50000000 W

======== CHANNEL f2 ========
SFO2          400.1816007 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          16.50000000 W
PLW12          0.20370001 W
PLW13          0.16500001 W

F2 - Processing parameters
SI                  32768
SF            100.6253459 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
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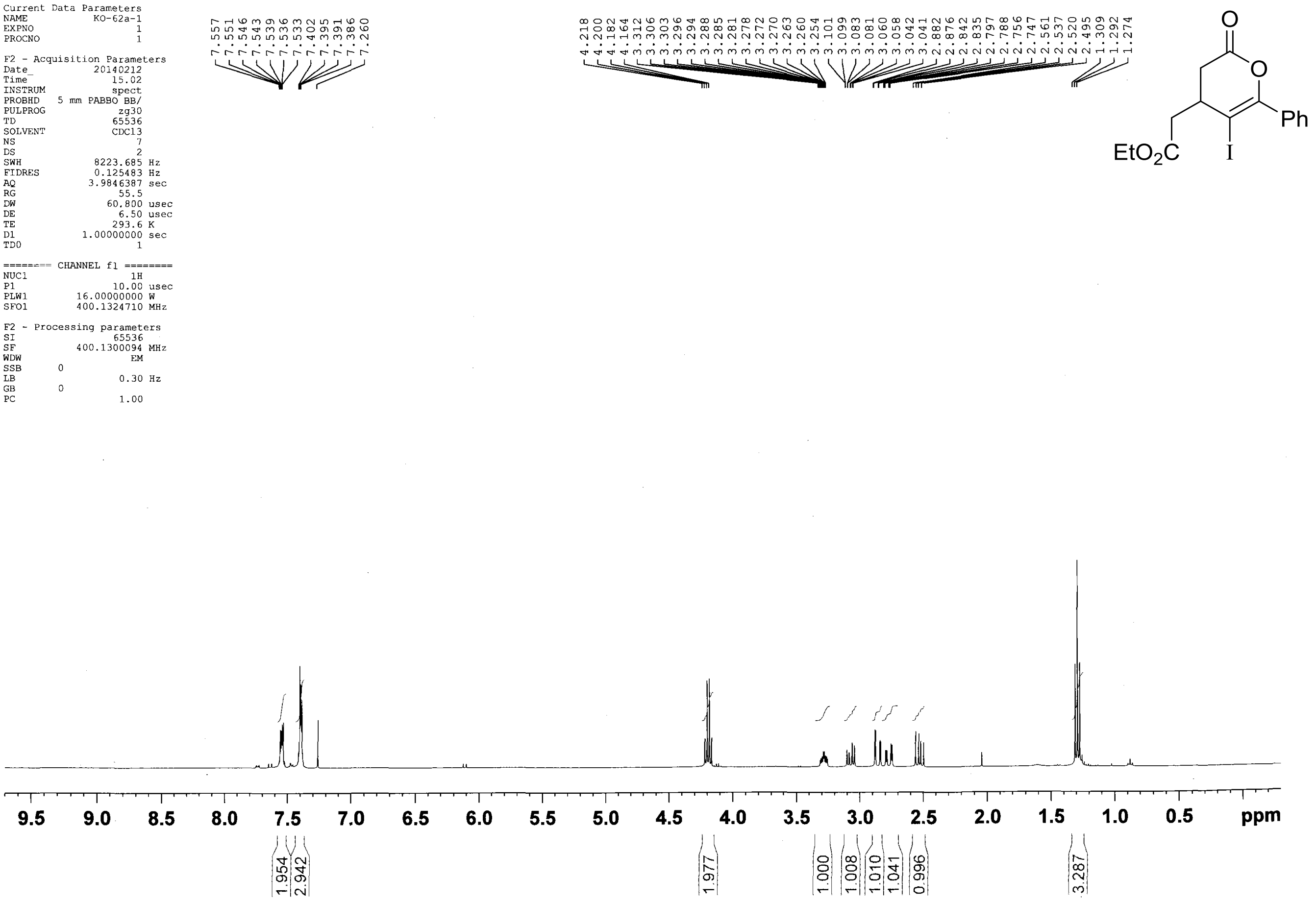

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Current Data Parameters
NAME            KO-62a-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140212
Time               15.02
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
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                 293.6 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           400.1300094 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
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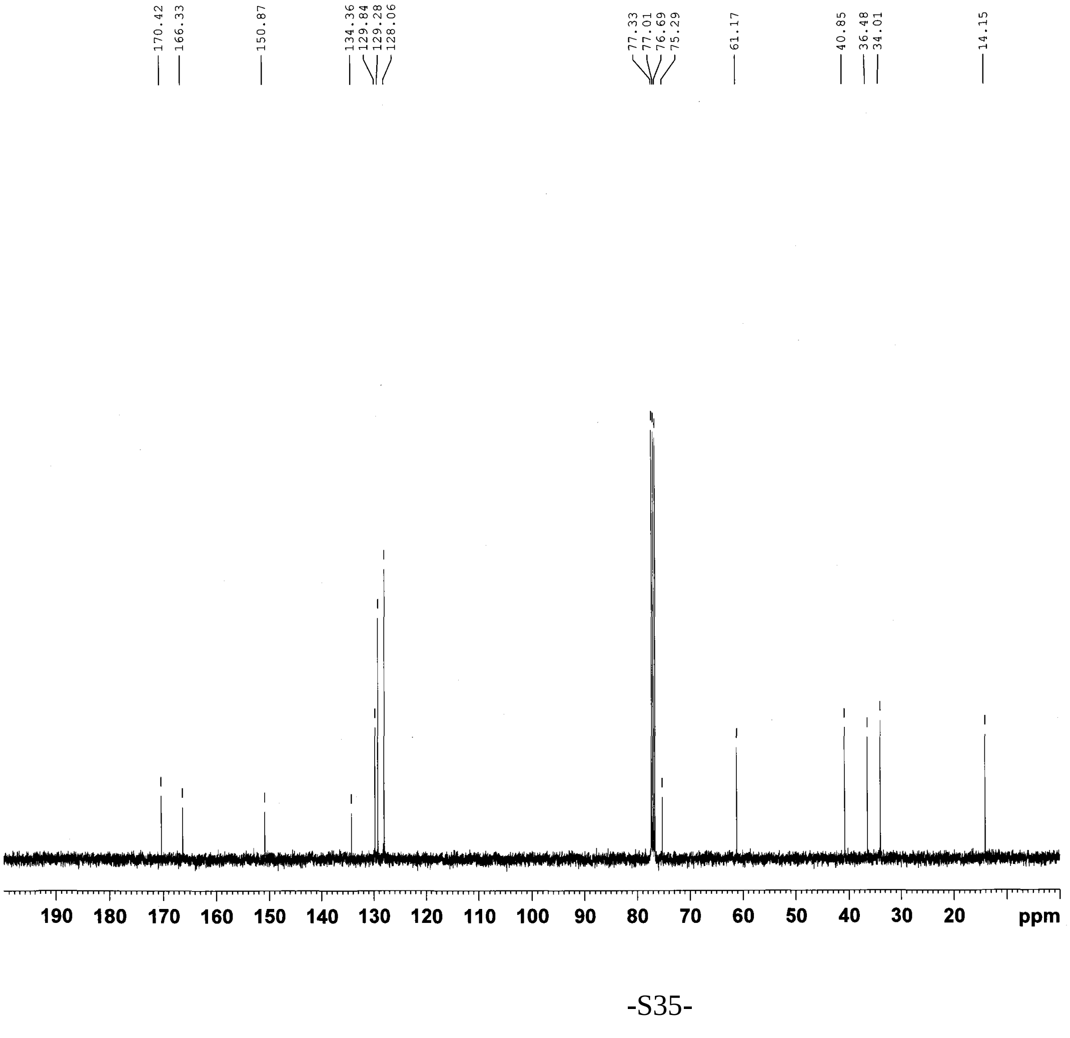

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Current Data Parameters
NAME            KO-62a-1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140212
Time               15.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    80
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                 294.1 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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 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
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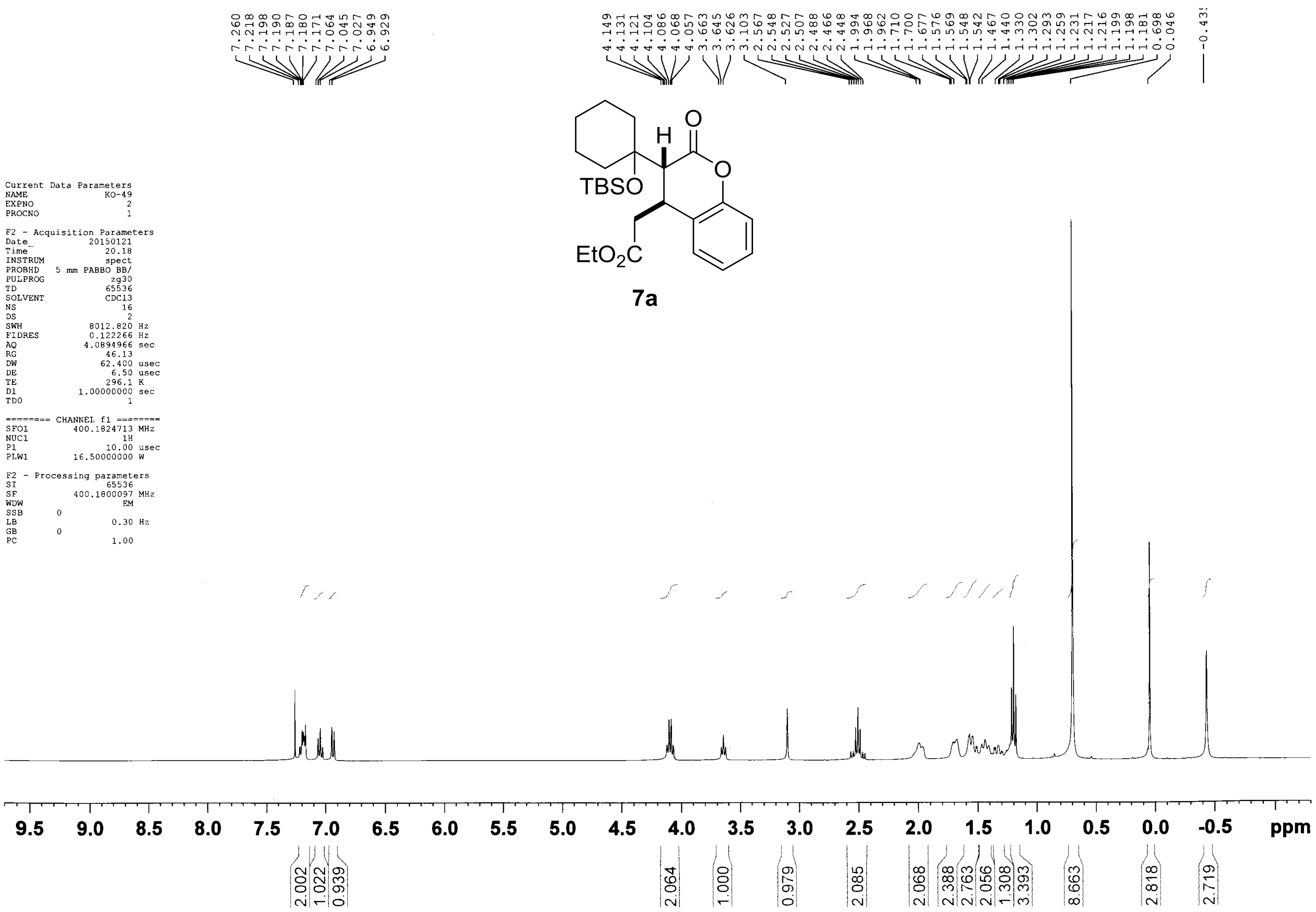

7a

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Current Data Parameters
NAME              KO-49
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150121
Time              20.18
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                46.13
DW               62.400 usec
DE                 6.50 usec
TE                296.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1824713 MHz
NUC1                 1H
P1                10.00 usec
PLW1        16.50000000 W

F2 - Processing parameters
SI                65536
SF          400.1800097 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
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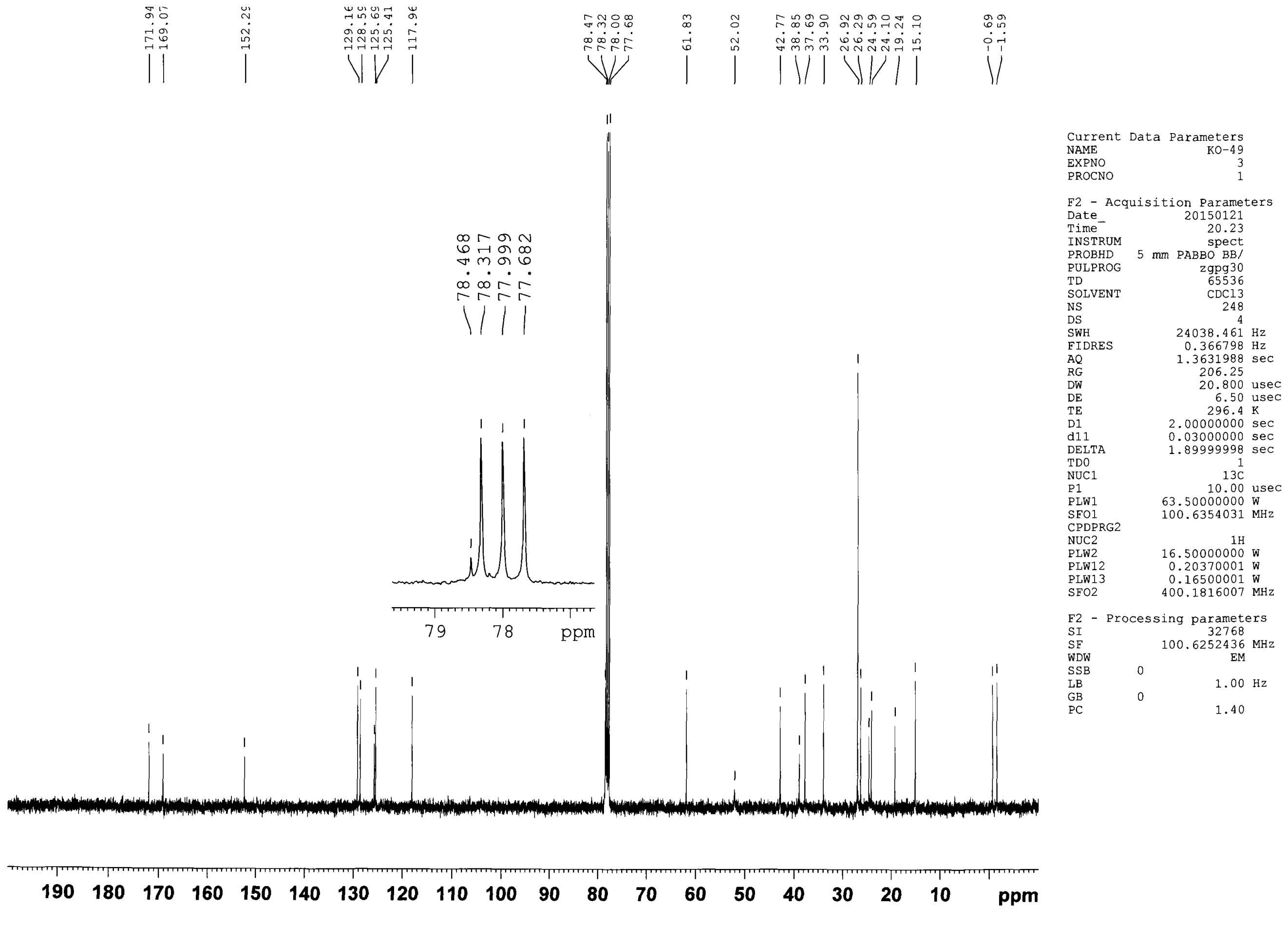

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Current Data Parameters
NAME              KO-49
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150121
Time              20.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  248
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               206.25
DW               20.800 usec
DE                 6.50 usec
TE                296.4 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1
NUC1                13C
P1                10.00 usec
PLW1        63.50000000 W
SFO1        100.6354031 MHz
CPDPRG2
NUC2                 1H
PLW2        16.50000000 W
PLW12        0.20370001 W
PLW13        0.16500001 W
SFO2        400.1816007 MHz

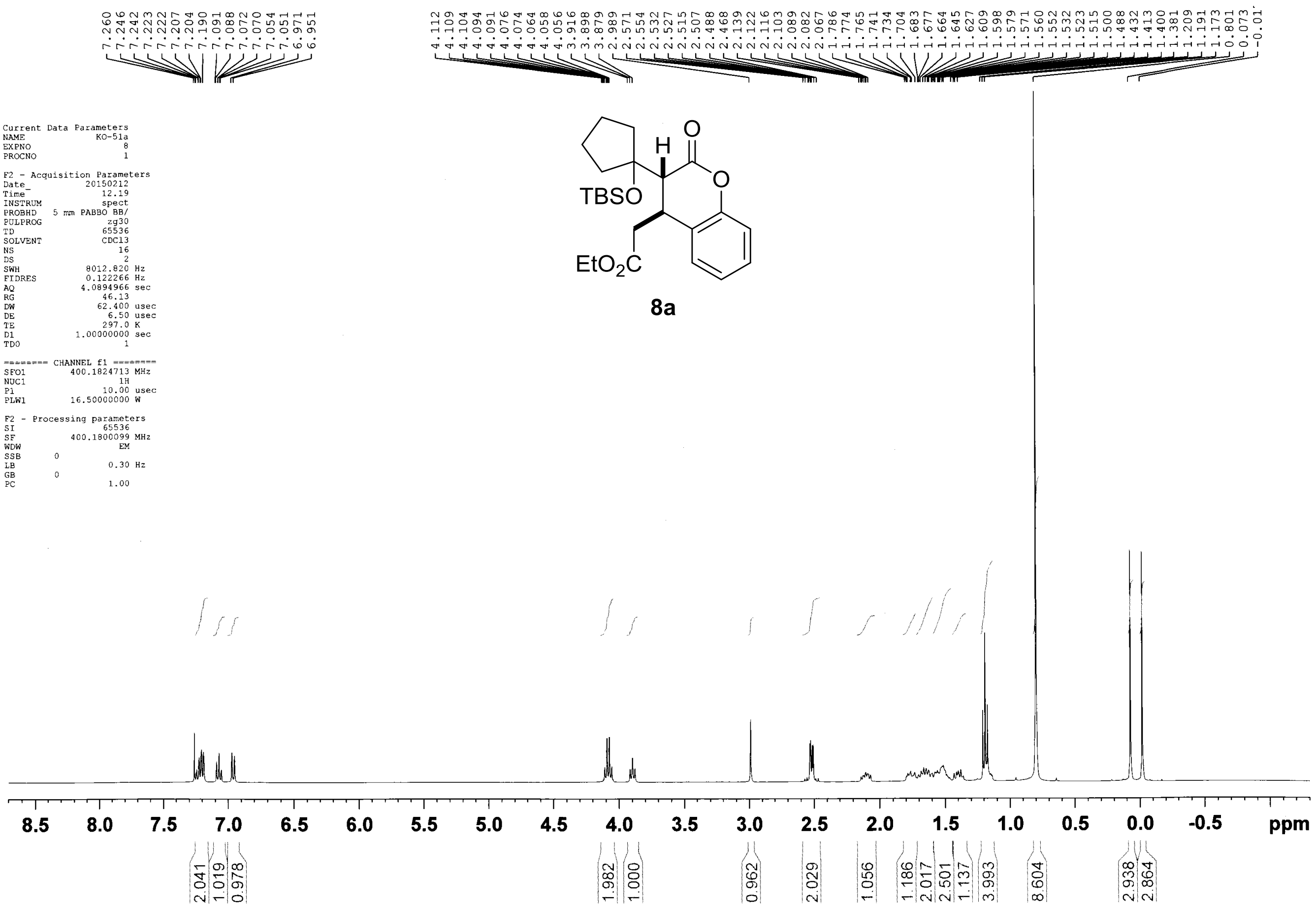
F2 - Processing parameters
SI                32768
SF          100.6252436 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

```
Current Data Parameters
NAME              KO-51a
EXPNO                  8
PROCNO                 1

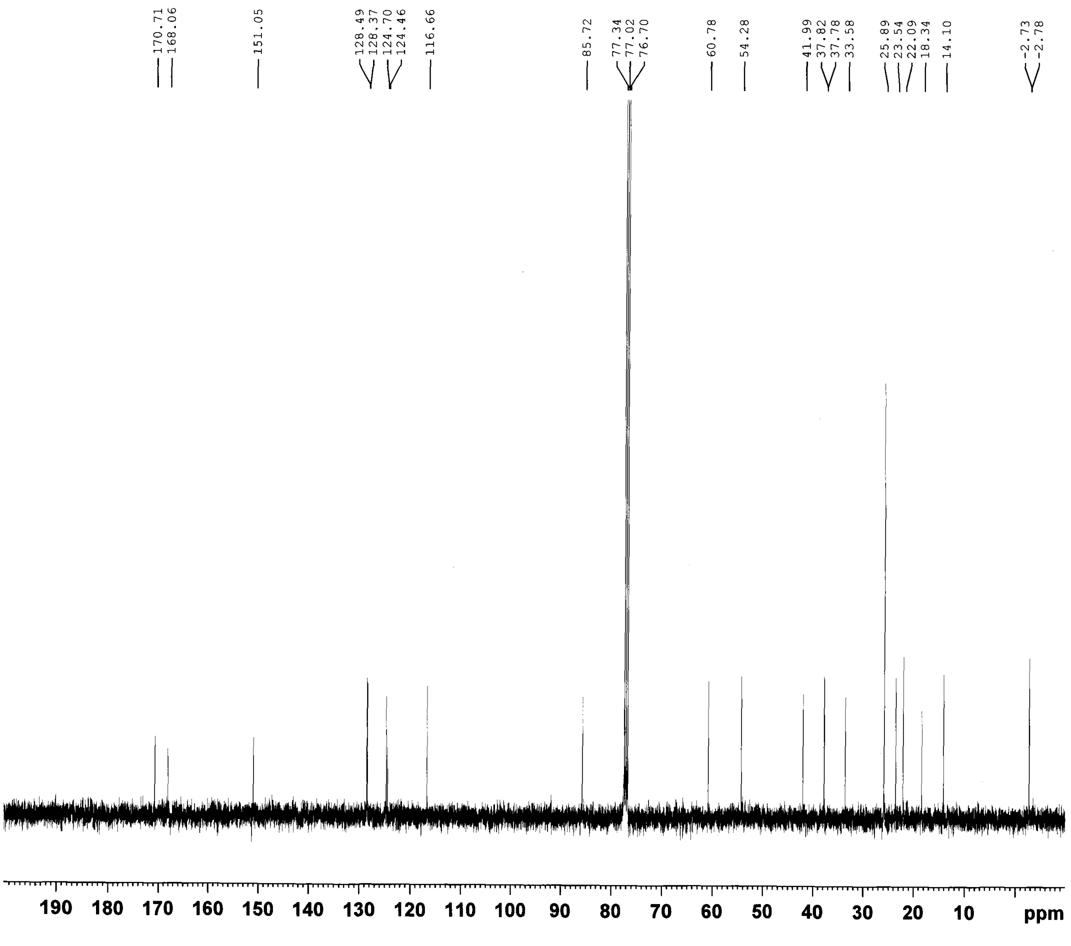
F2 - Acquisition Parameters
Date_           20150212
Time               12.19
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 46.13
DW                62.400 usec
DE                  6.50 usec
TE                 297.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1824713 MHz
NUC1                  1H
P1                 10.00 usec
PLW1         16.50000000 W

F2 - Processing parameters
SI                 65536
SF           400.1800099 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



8a



```
Current Data Parameters
NAME               KO-51
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150212
Time               12.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    65
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                206.25
DW                20.800 usec
DE                  6.50 usec
TE                 297.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6354031 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         63.50000000 W

======== CHANNEL f2 ========
SFO2         400.1816007 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.50000000 W
PLW12         0.20370001 W
PLW13         0.16500001 W

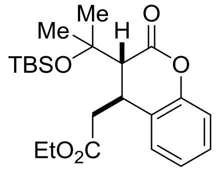
F2 - Processing parameters
SI                 32768
SF           100.6253420 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

```
Current Data Parameters
NAME            KO-57
EXPNO               1
PROCNO              1

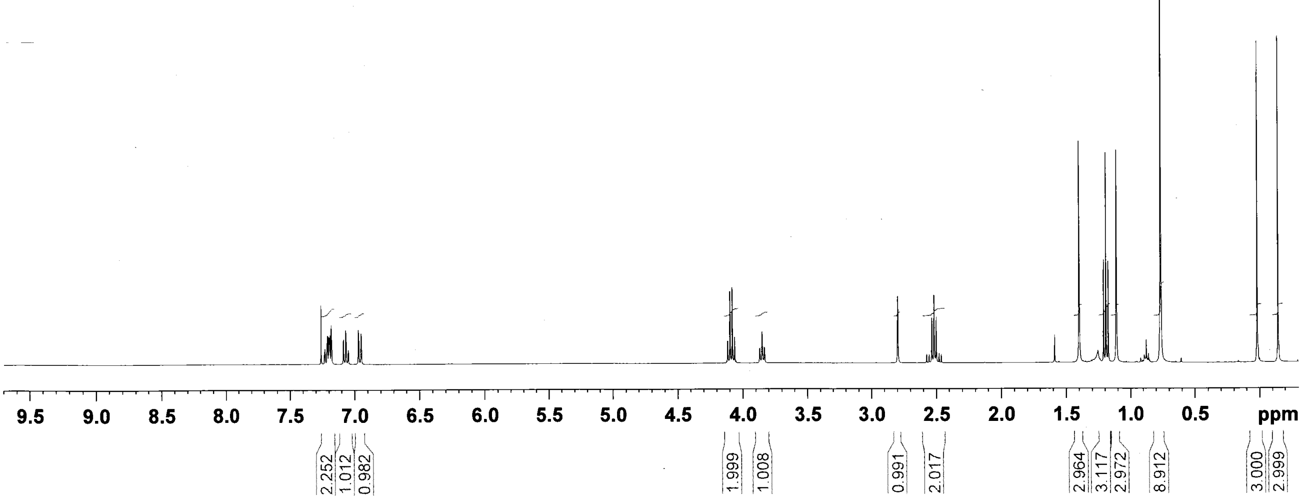
F2 - Acquisition Parameters
Date_        20140212
Time            18.52
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ          3.9846387 sec
RG              33.06
DW             60.800 usec
DE               6.50 usec
TE              293.7 K
D1         1.00000000 sec
TD0                 1

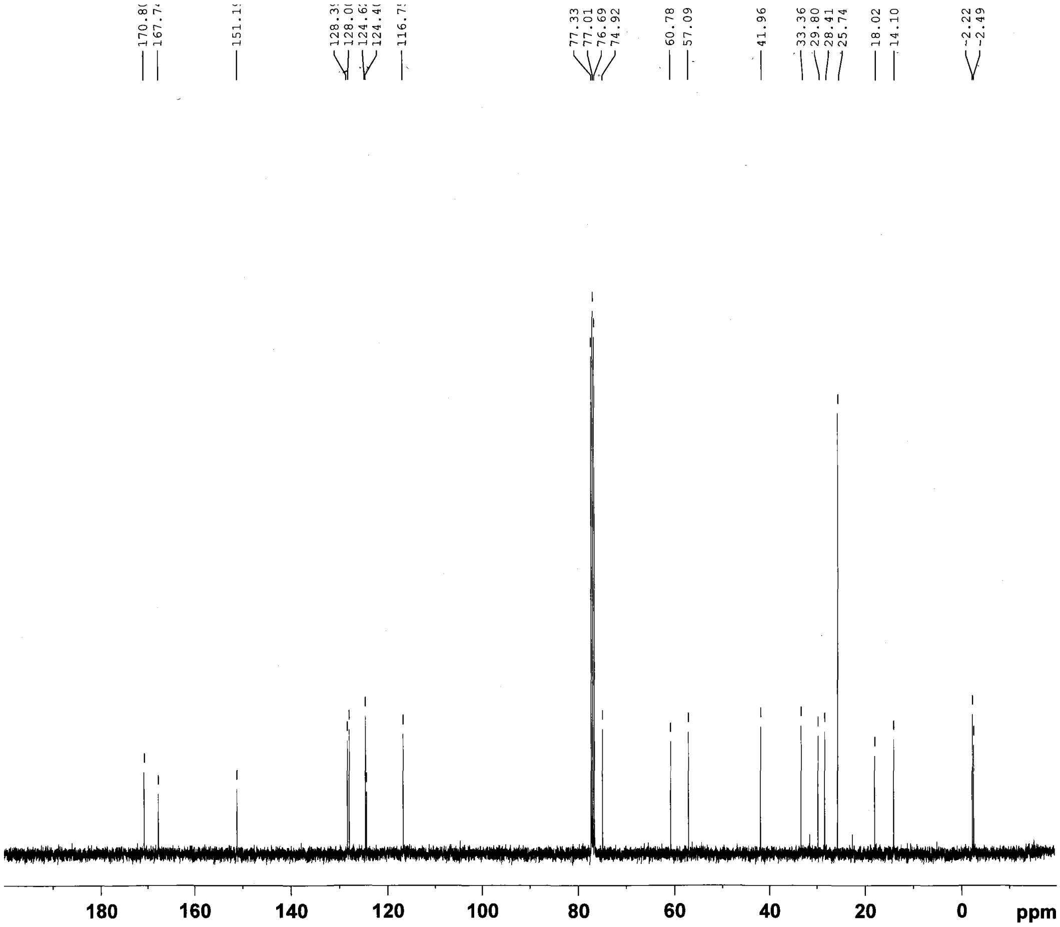
======== CHANNEL f1 ========
NUC1               1H
P1              10.00 usec
PLW1      16.00000000 W
SFO1      400.1324710 MHz

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



9a





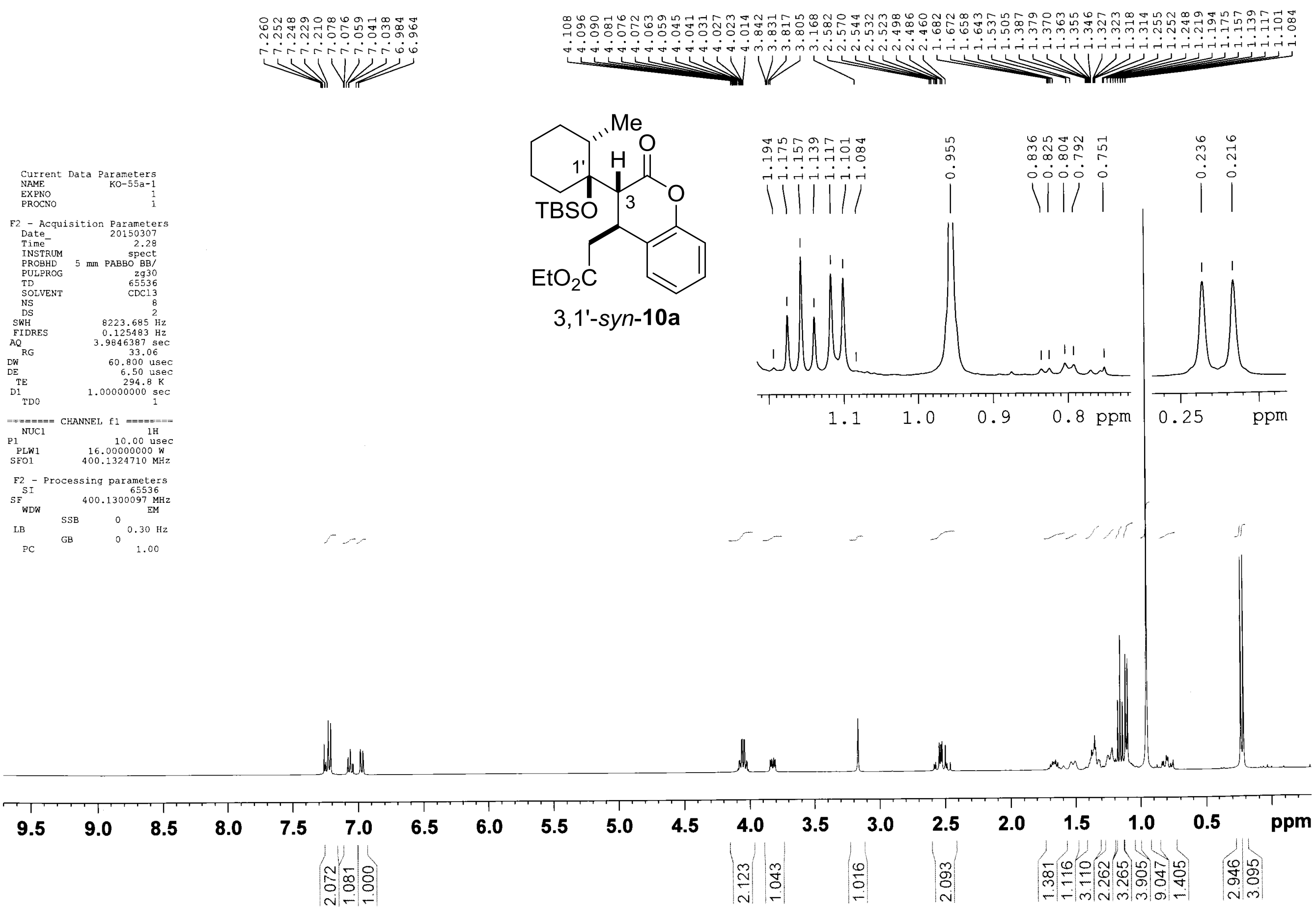
```
Current Data Parameters
NAME            KO-57
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_        20140212
Time            18.58
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 85
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              294.1 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           90.00 usec
PLW2      16.00000000 W
PLW12      0.19753000 W
PLW13      0.16000000 W
SFO2      400.1316005 MHz

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



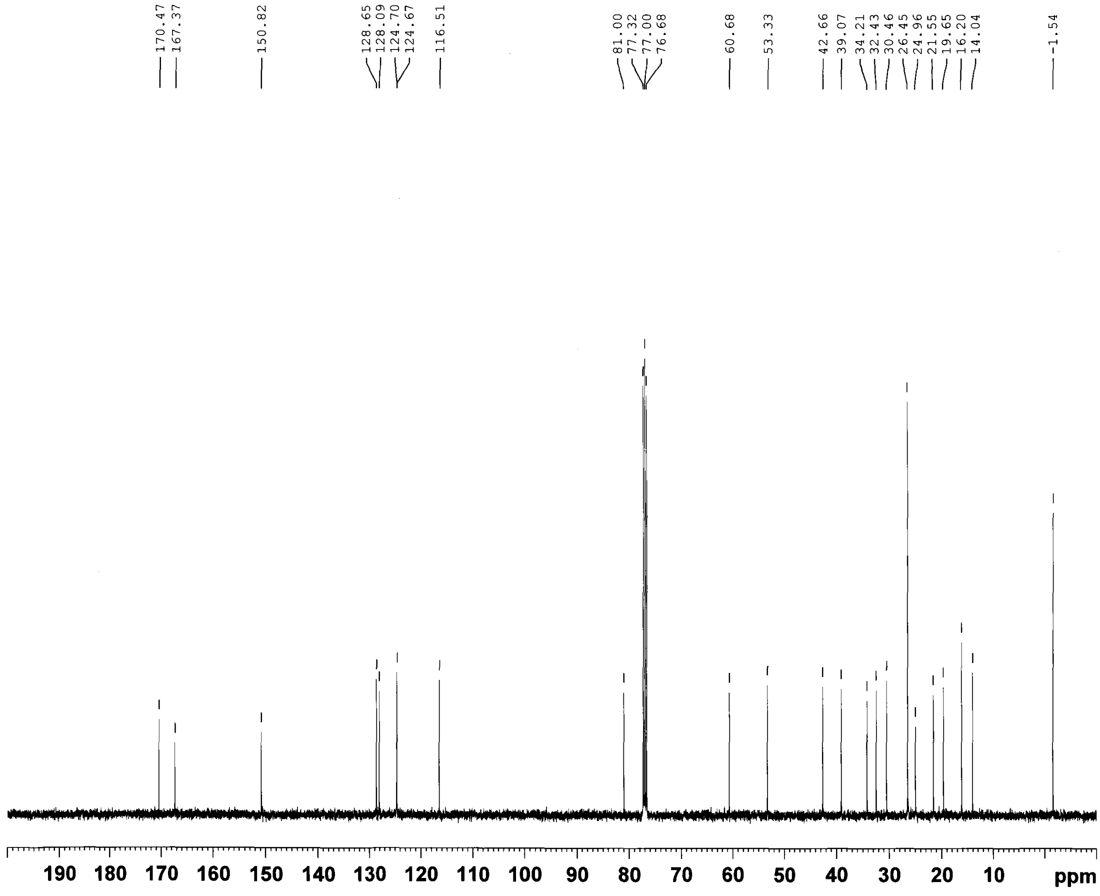
3,1'-*syn*-**10a**

```
  Current Data Parameters
  NAME             KO-55a-1
  EXPNO                   1
  PROCNO                  1

F2 - Acquisition Parameters
  Date_            20150307
  Time                 2.28
  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                   294.8 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             400.1300097 MHz
  WDW                    EM
          SSB        0
LB                     0.30 Hz
          GB         0
  PC                   1.00
```



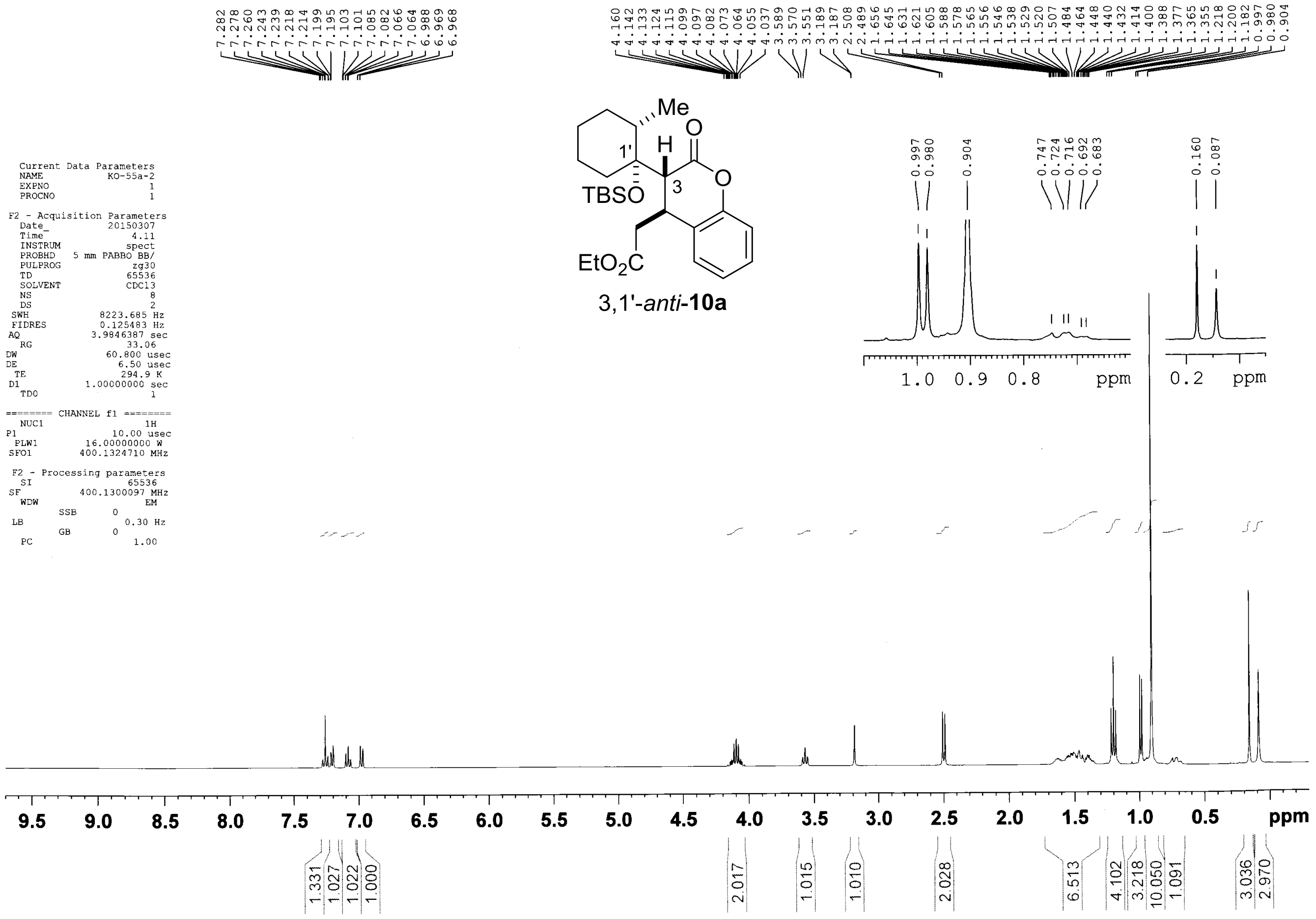
```
Current Data Parameters
NAME             KO-55a-1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150307
Time                 2.37
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    148
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                  295.4 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF             100.6127724 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```



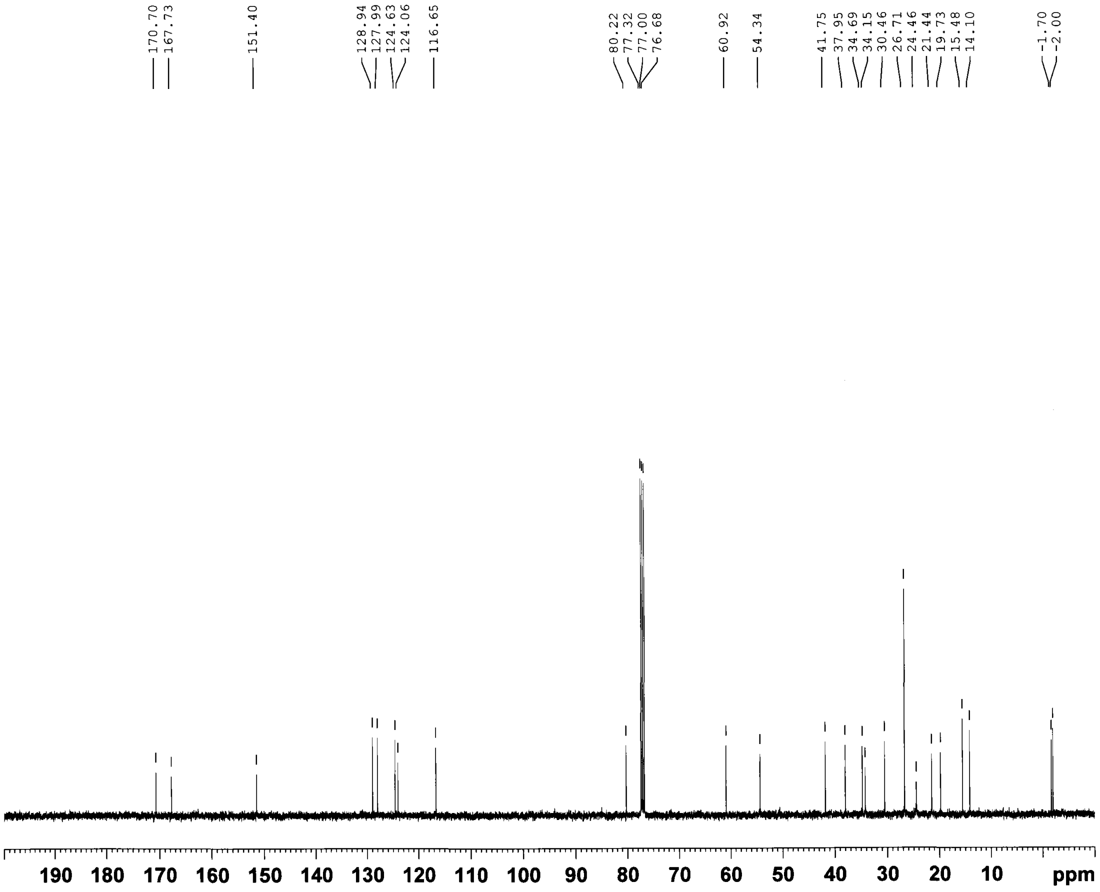
3,1'-*anti*-**10a**

```
Current Data Parameters
NAME              KO-55a-2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150307
Time                  4.11
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                 294.9 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          400.1300097 MHz
WDW                     EM
        SSB       0
LB                 0.30 Hz
        GB        0
PC                    1.00
```



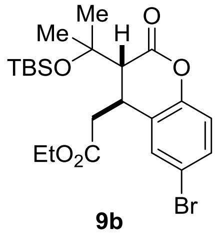
```
Current Data Parameters
NAME              KO-55a-2
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150307
Time                  4.18
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     105
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                 295.5 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            90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF          100.6127717 MHz
WDW                     EM
SSB        0
LB                 1.00 Hz
GB         0
PC                    1.40
```



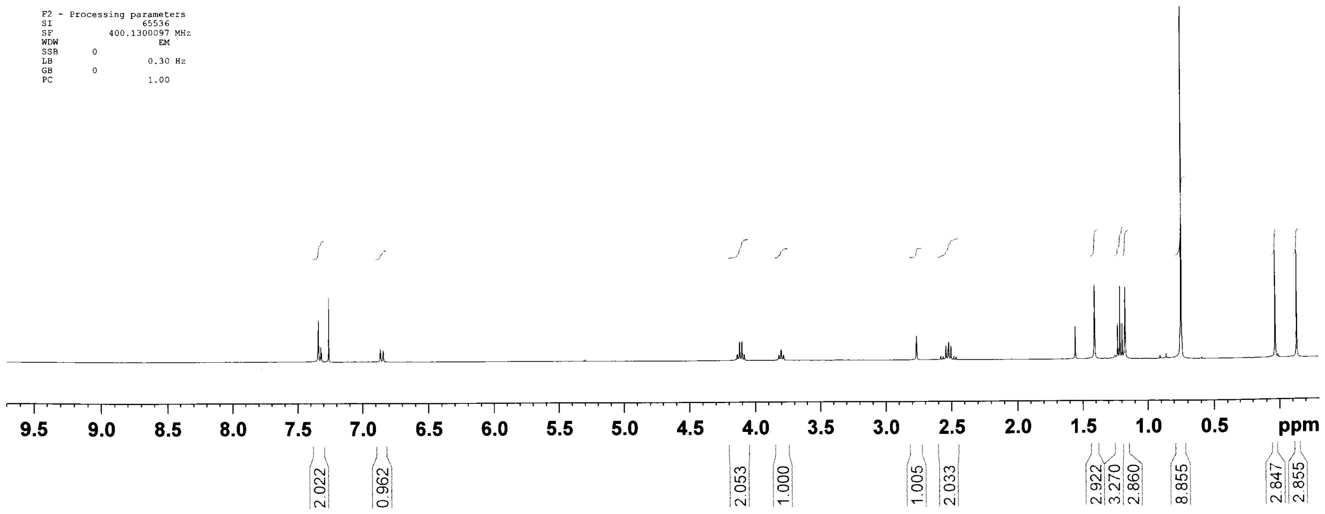
9b

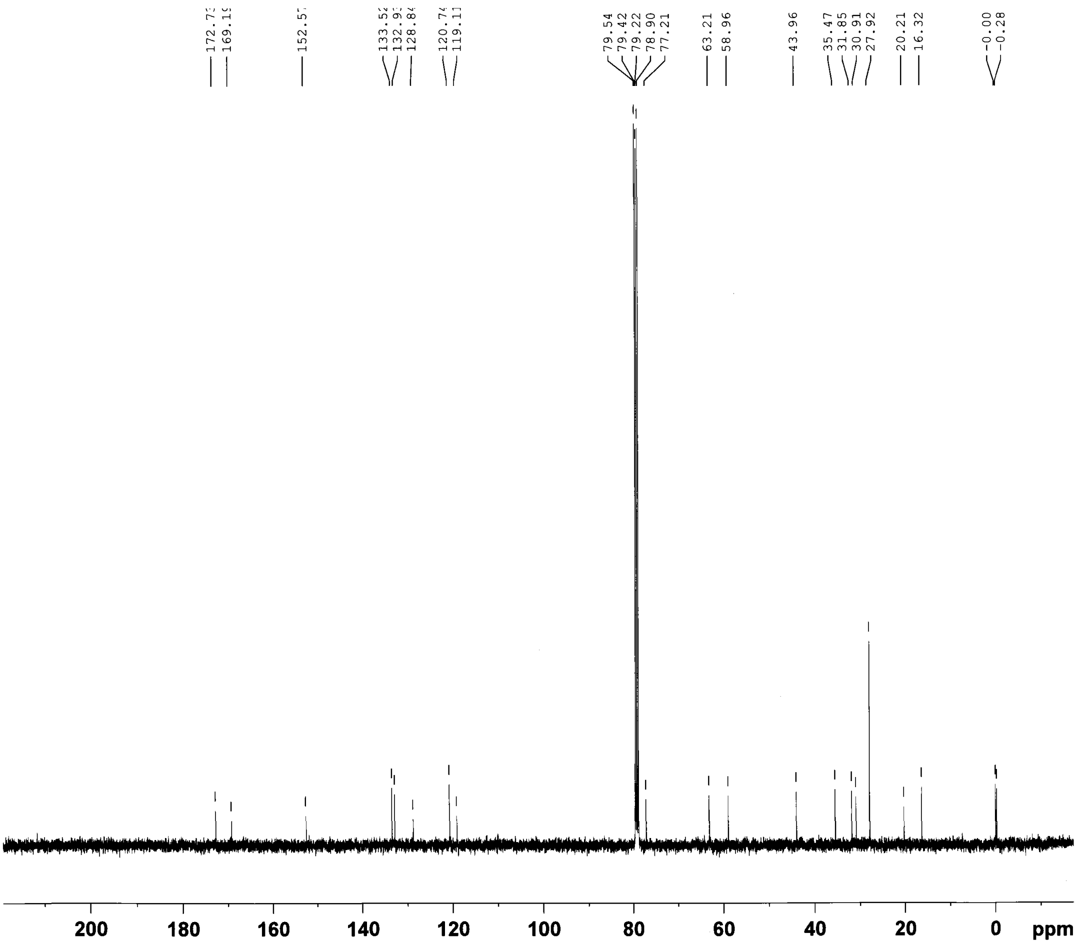
```
Current Data Parameters
NAME             KO-182a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150120
Time               22.19
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                 80.57
DW                60.800 usec
DE                  6.50 usec
TE                 294.8 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           400.1300097 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```





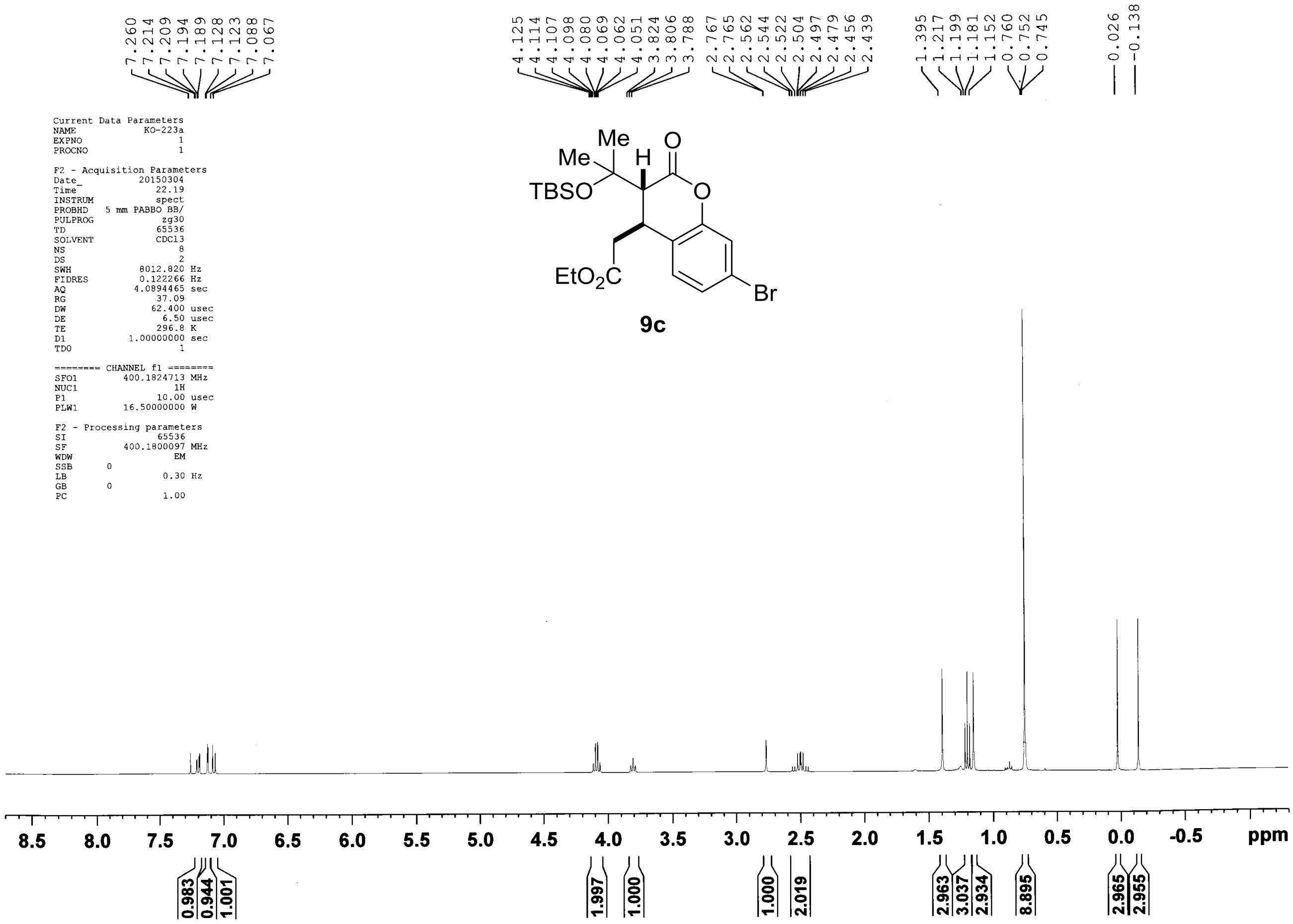
```
Current Data Parameters
NAME             KO-182a
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150120
Time               22.34
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   254
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                 295.2 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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6125479 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



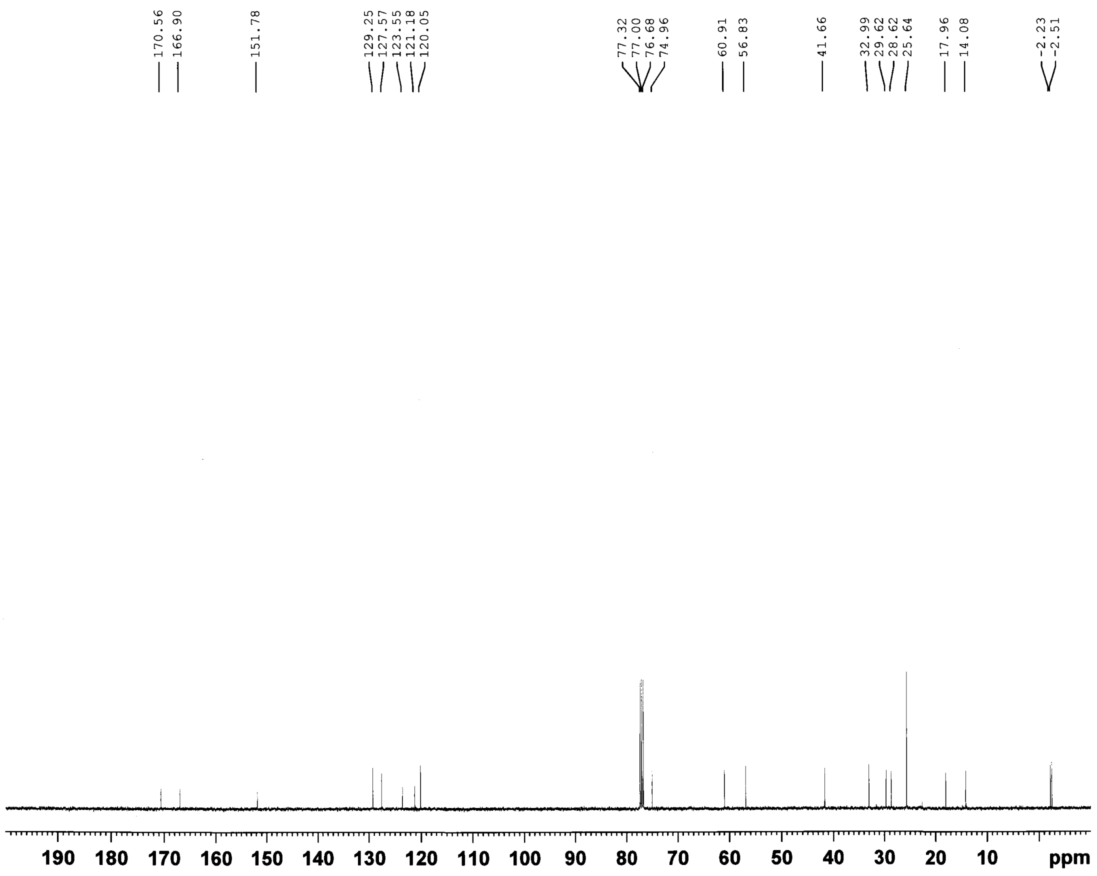
9c

```
Current Data Parameters
NAME            KO-223a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150304
Time              22.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                37.09
DW               62.400 usec
DE                 6.50 usec
TE                296.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1824713 MHz
NUC1                 1H
P1                10.00 usec
PLW1        16.50000000 W

F2 - Processing parameters
SI                65536
SF          400.1800097 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



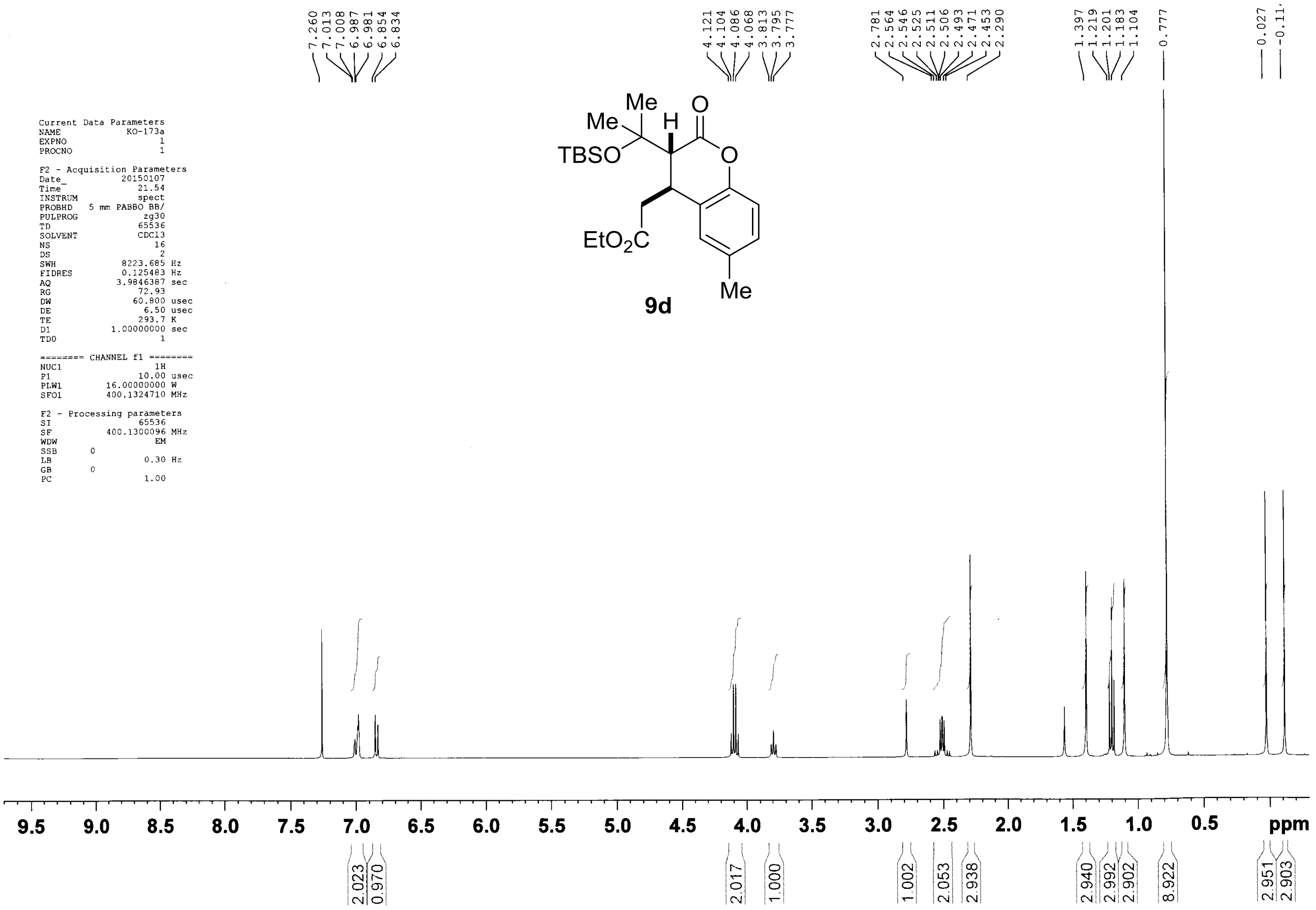
```
Current Data Parameters
NAME            KO-223a
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150304
Time              22.21
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            1.3631488 sec
RG               206.25
DW               20.800 usec
DE                 6.50 usec
TE                297.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6354031 MHz
NUC1                13C
P1                10.00 usec
PLW1        63.50000000 W

======== CHANNEL f2 ========
SFO2        400.1816007 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.50000000 W
PLW12        0.20370001 W
PLW13        0.16500001 W

F2 - Processing parameters
SI                32768
SF          100.6253445 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



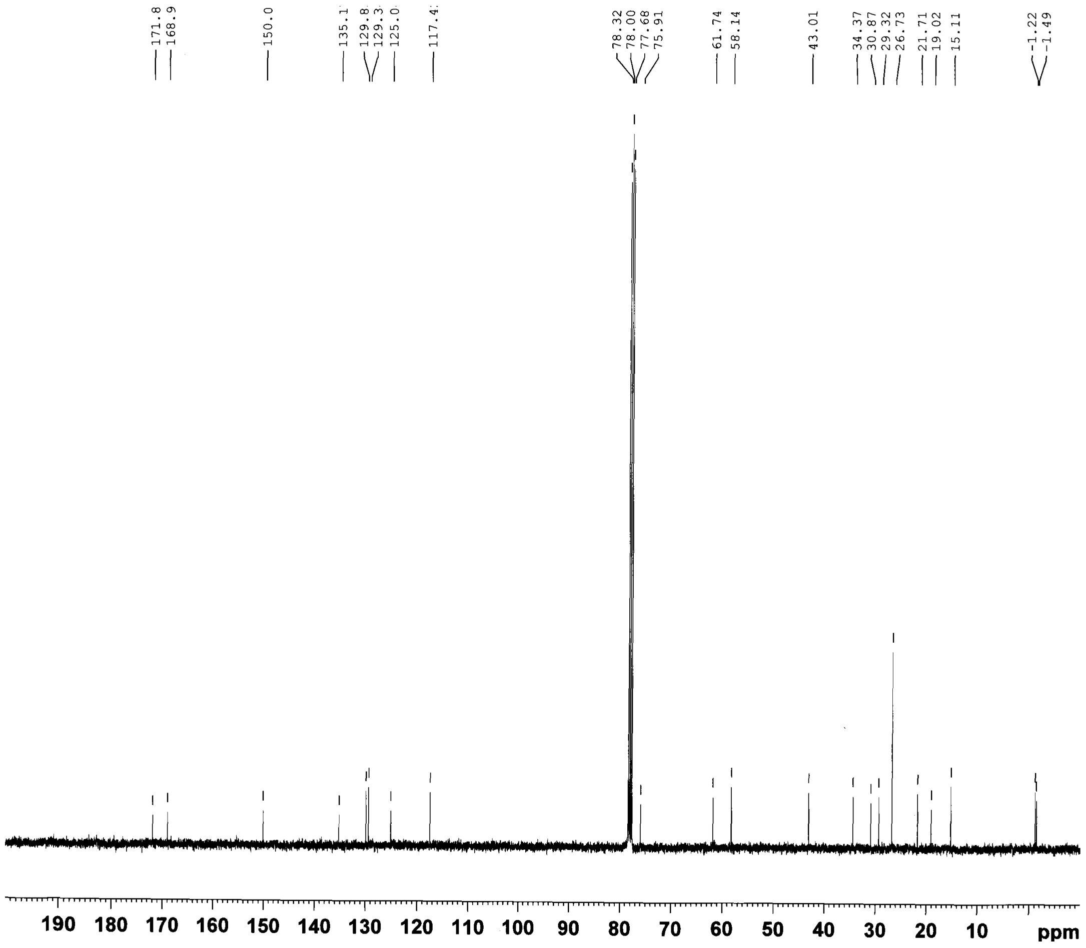
9d

```
Current Data Parameters
NAME             KO-173a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150107
Time               21.54
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
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                 293.7 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           400.1300096 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



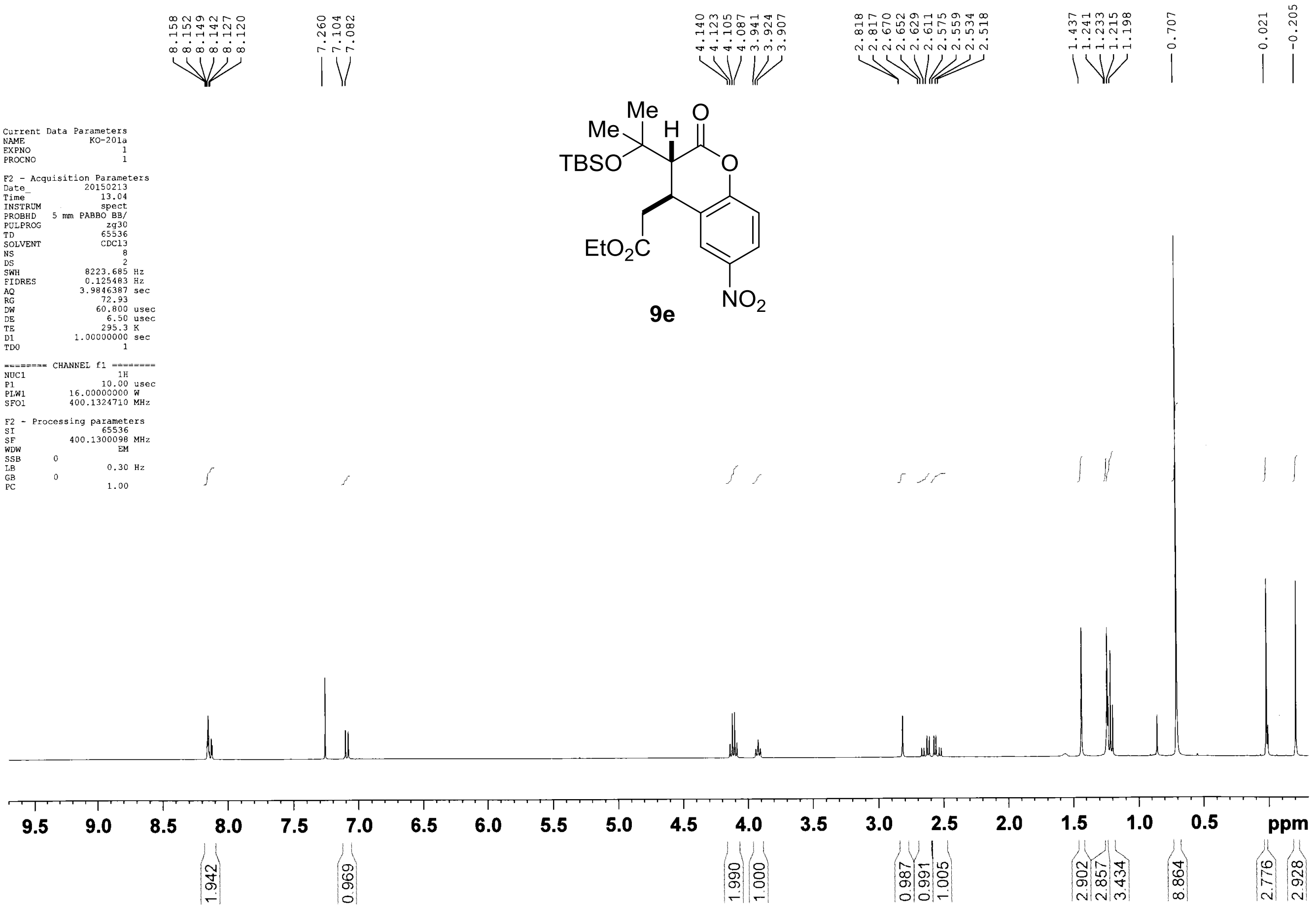
```
Current Data Parameters
NAME             KO-173a
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150107
Time               22.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   382
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                 294.3 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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126711 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



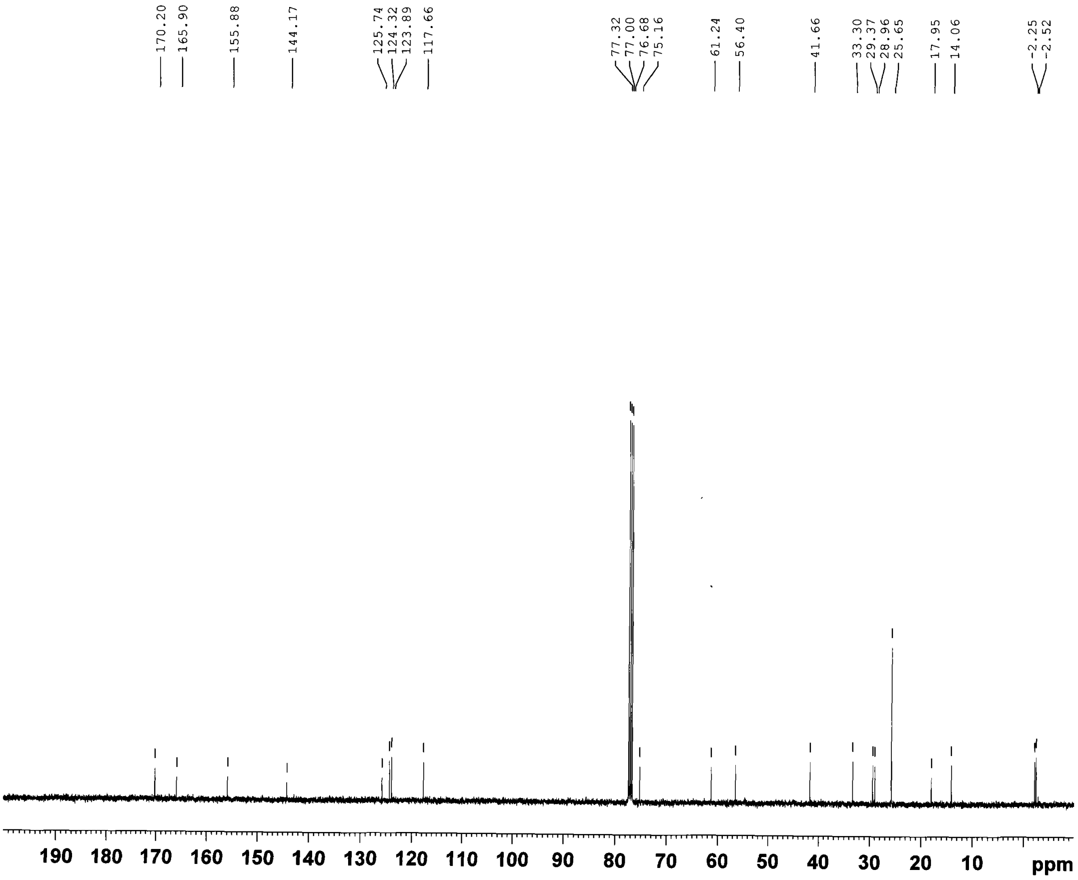
9e

```
Current Data Parameters
NAME              KO-201a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150213
Time                13.04
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                  295.3 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            400.1300098 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



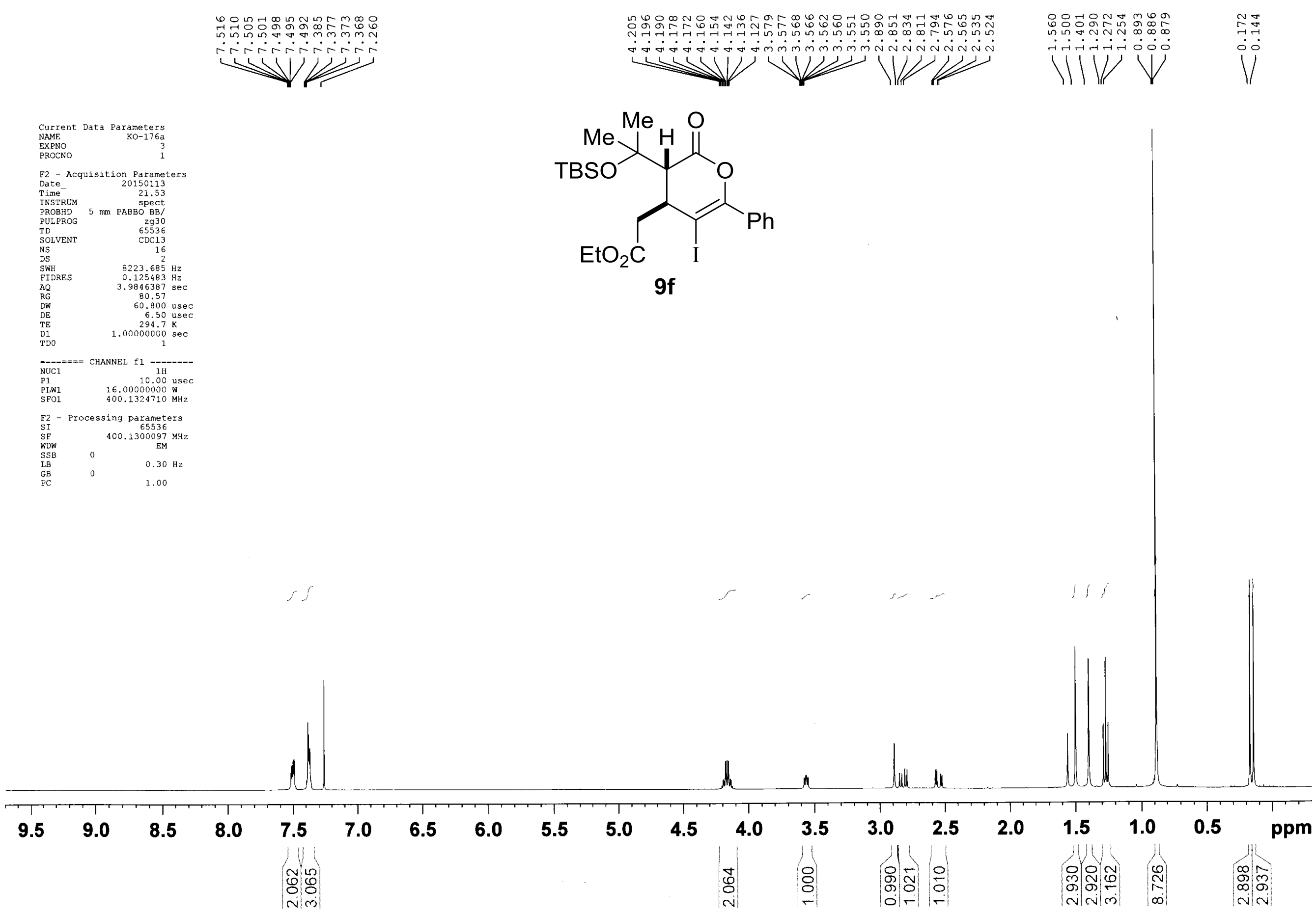
```
Current Data Parameters
NAME              KO-201a
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150213
Time                13.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
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                  295.7 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127710 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



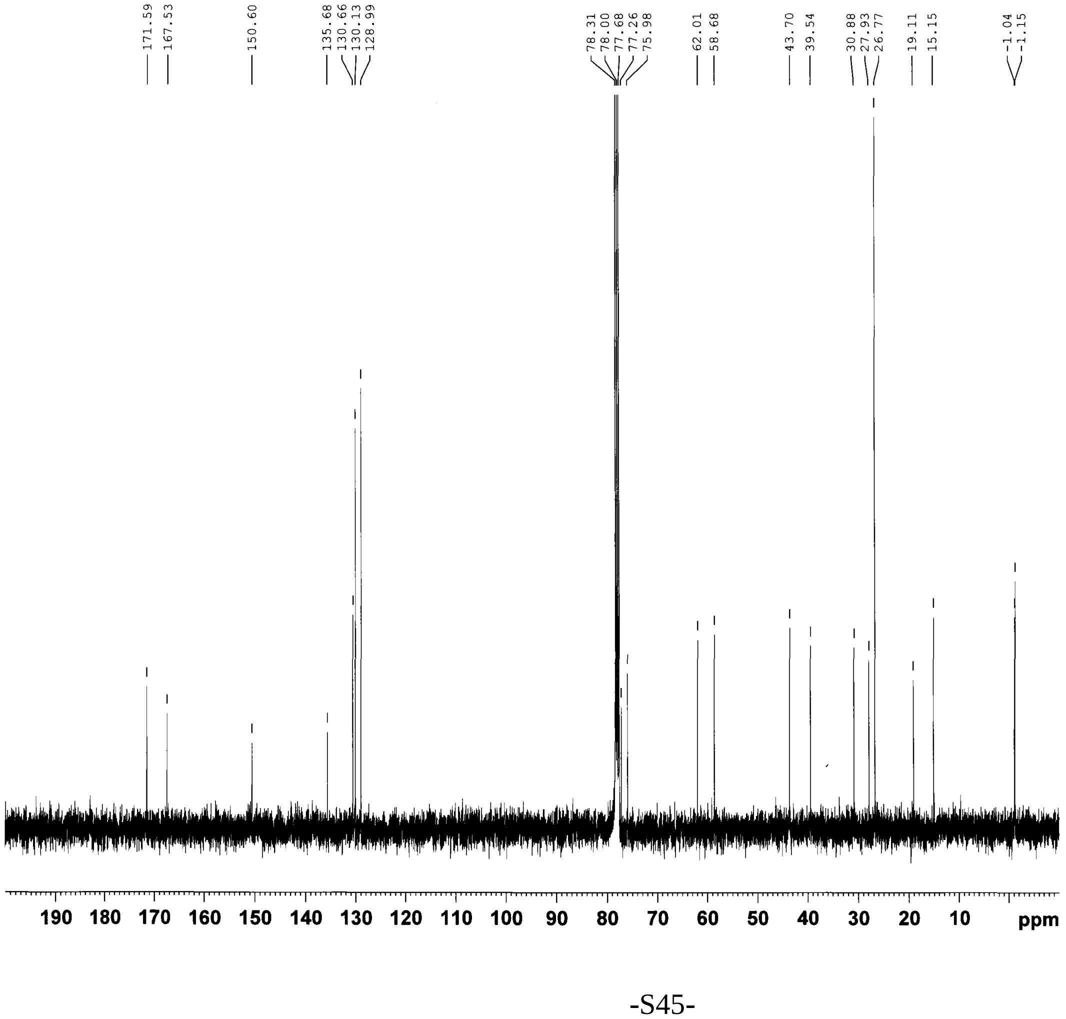
9f

```
Current Data Parameters
NAME              KO-176a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150113
Time                21.53
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                  80.57
DW                 60.800 usec
DE                   6.50 usec
TE                  294.7 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
```



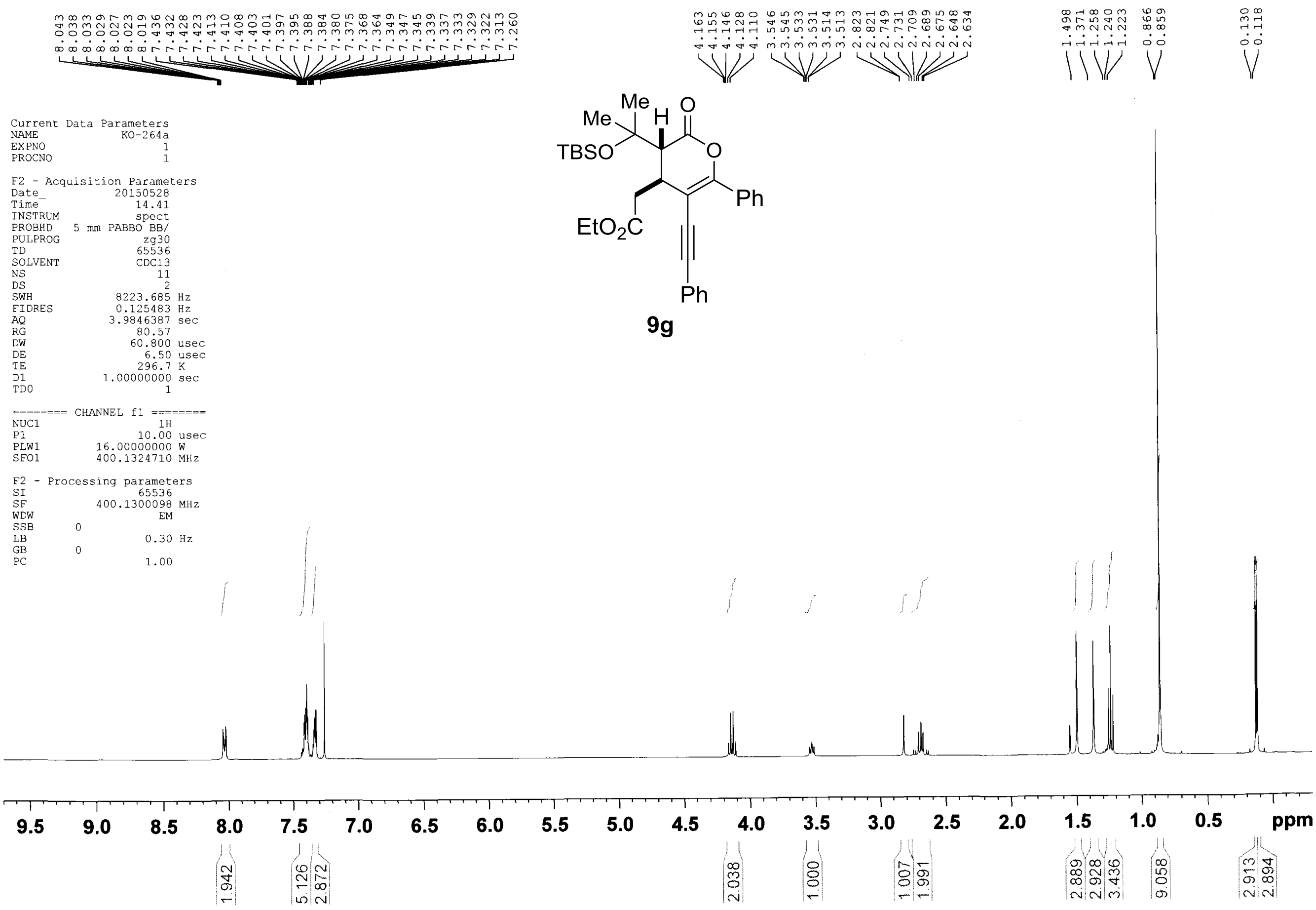
```
Current Data Parameters
NAME              KO-176a
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150113
Time                21.57
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
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                  295.1 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6126711 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```



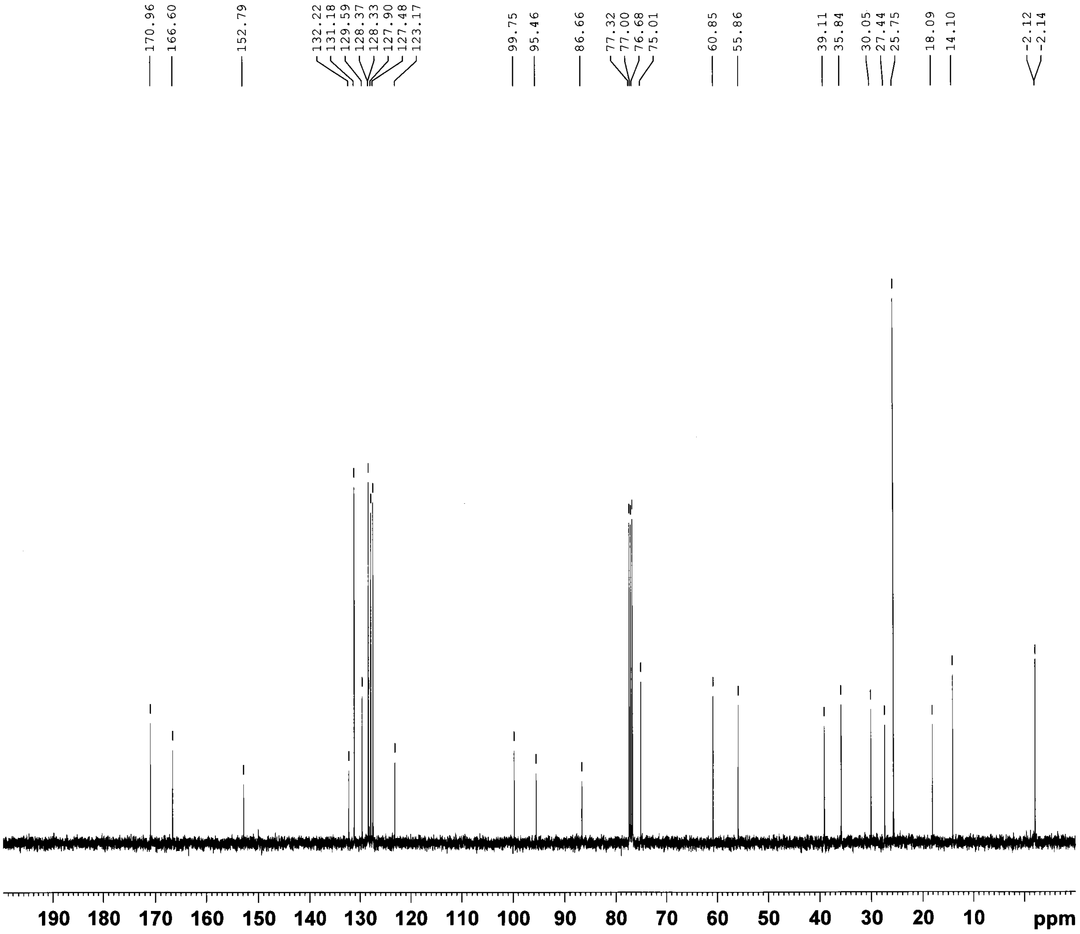
9g

```
Current Data Parameters
NAME             KO-264a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150528
Time               14.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    11
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                 80.57
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           400.1300098 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



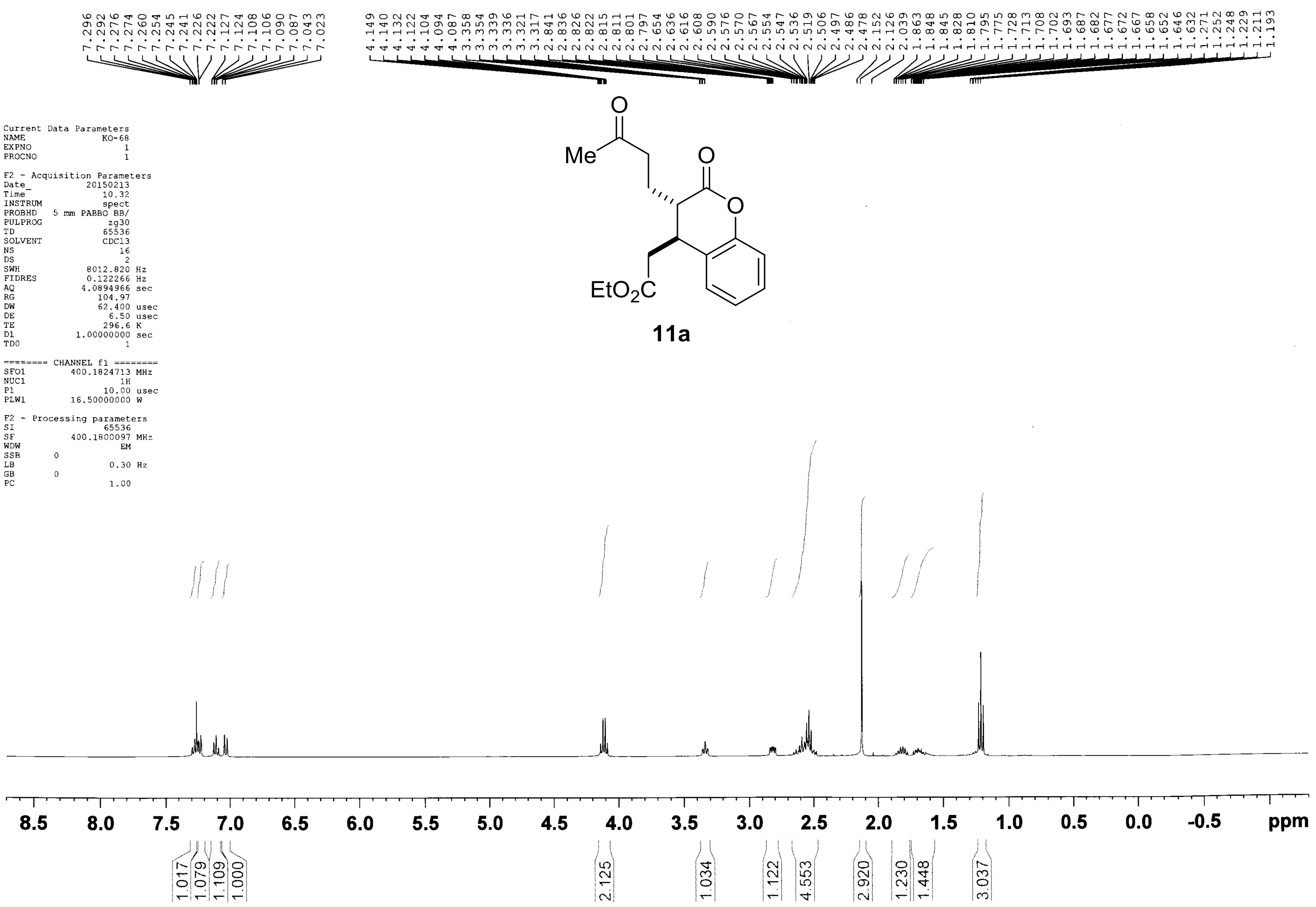
```
Current Data Parameters
NAME             KO-264a
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150528
Time               15.21
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    36
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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127749 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



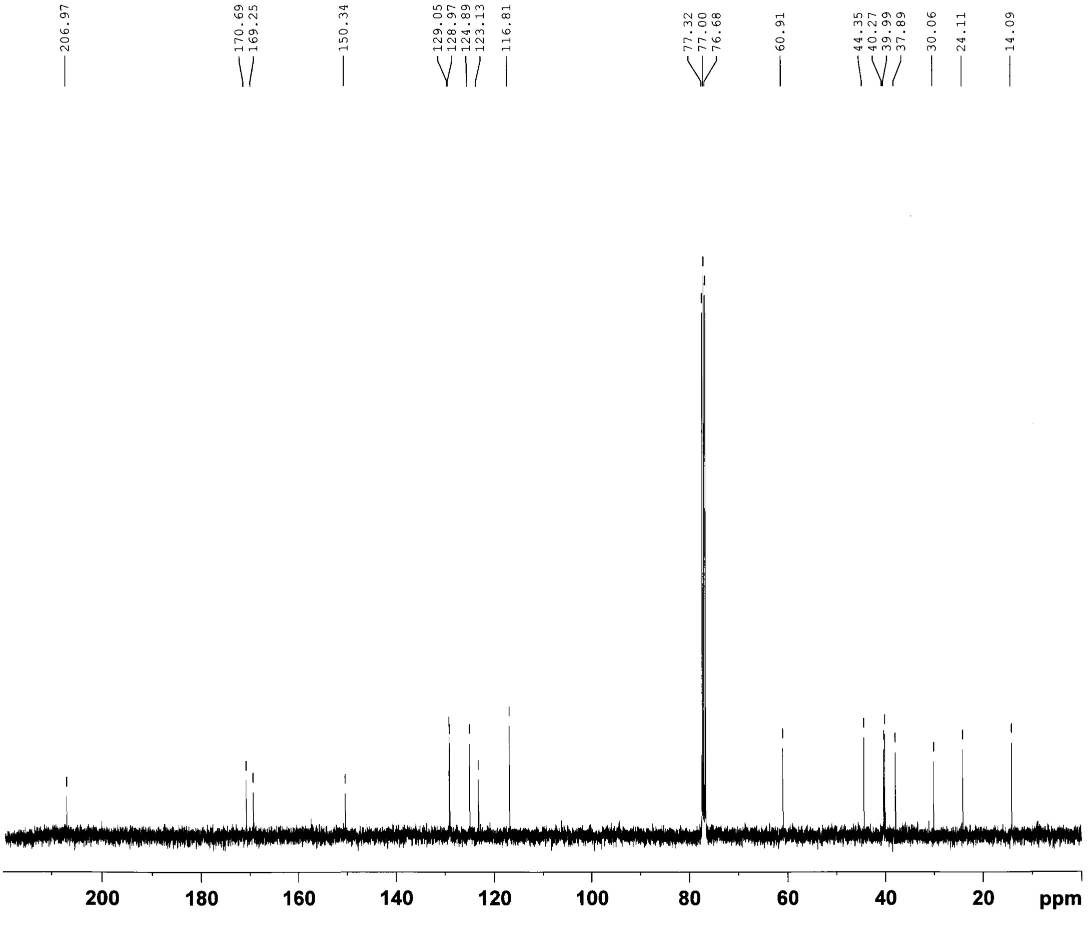
11a

```
Current Data Parameters
NAME             KO-68
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20150213
Time             10.32
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG              104.97
DW              62.400 usec
DE                6.50 usec
TE               296.6 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       400.1824713 MHz
NUC1                1H
P1               10.00 usec
PLW1       16.50000000 W

F2 - Processing parameters
SI               65536
SF         400.1800097 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



```
Current Data Parameters
NAME             KO-68
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20150213
Time             10.35
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                  81
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              206.25
DW              20.800 usec
DE                6.50 usec
TE               297.4 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                  1
NUC1               13C
P1               10.00 usec
PLW1       63.50000000 W
SFO1       100.6354031 MHz
CPDPRG2
NUC2                1H
PLW2       16.50000000 W
PLW12       0.20370001 W
PLW13       0.16500001 W
SFO2       400.1816007 MHz

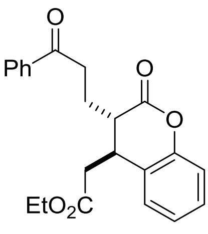
F2 - Processing parameters
SI               32768
SF         100.6253445 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

```
Current Data Parameters
NAME              KO-150a
EXPNO                   2
PROCNO                  1

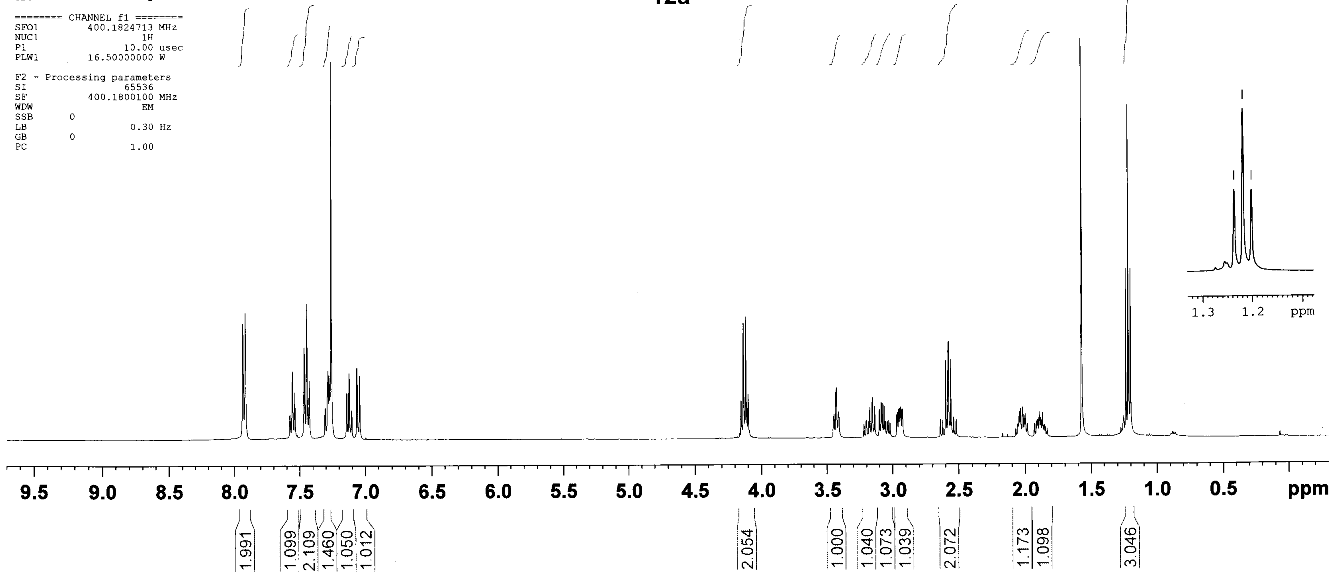
F2 - Acquisition Parameters
Date_            20141210
Time                18.28
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 104.97
DW                 62.400 usec
DE                   6.50 usec
TE                  296.5 K
D1             1.00000000 sec
TD0                     1

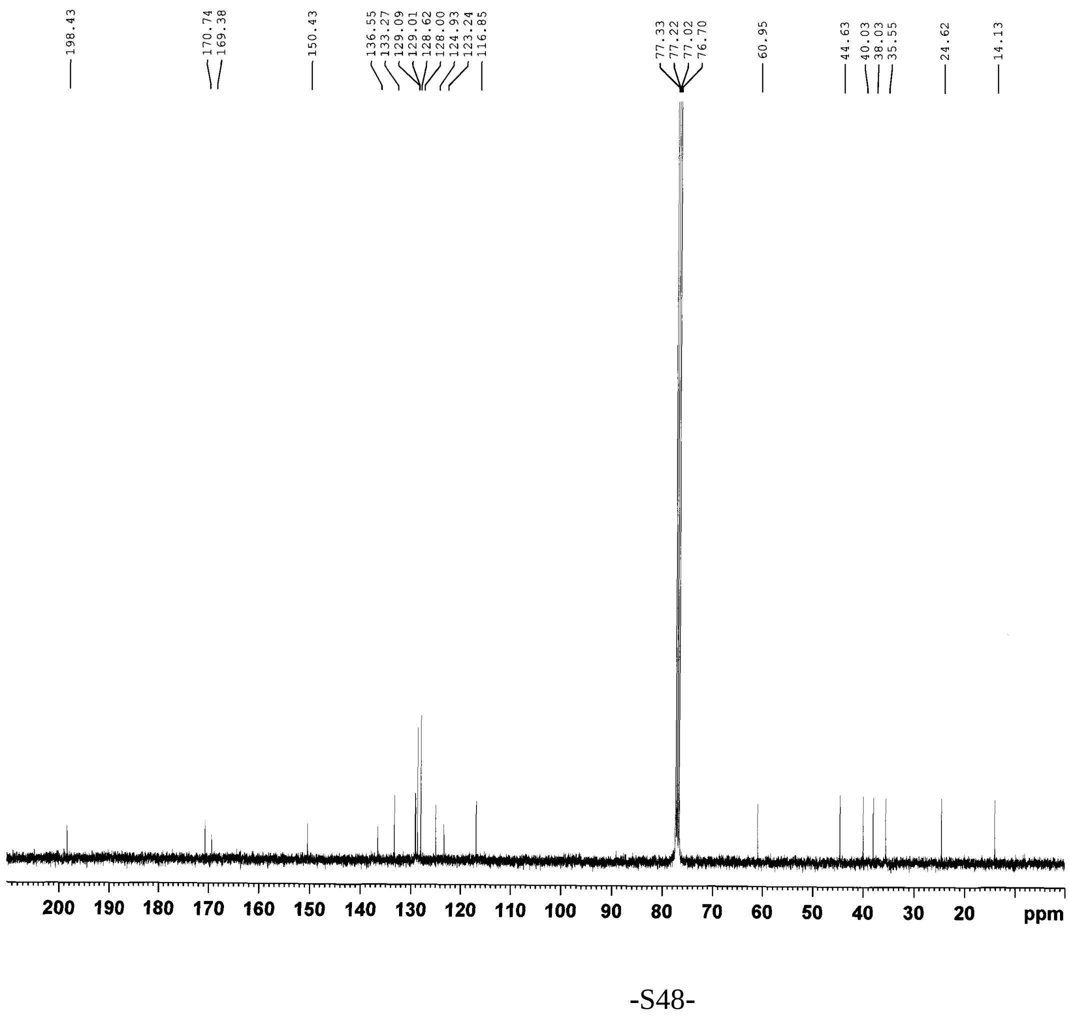
======== CHANNEL f1 ========
SFO1          400.1824713 MHz
NUC1                   1H
P1                  10.00 usec
PLW1          16.50000000 W

F2 - Processing parameters
SI                  65536
SF            400.1800100 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



12a





```
Current Data Parameters
NAME              KO-150a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20141210
Time                18.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 206.25
DW                 20.800 usec
DE                   6.50 usec
TE                  297.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6354031 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          63.50000000 W

======== CHANNEL f2 ========
SFO2          400.1816007 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          16.50000000 W
PLW12          0.20370001 W
PLW13          0.16500001 W

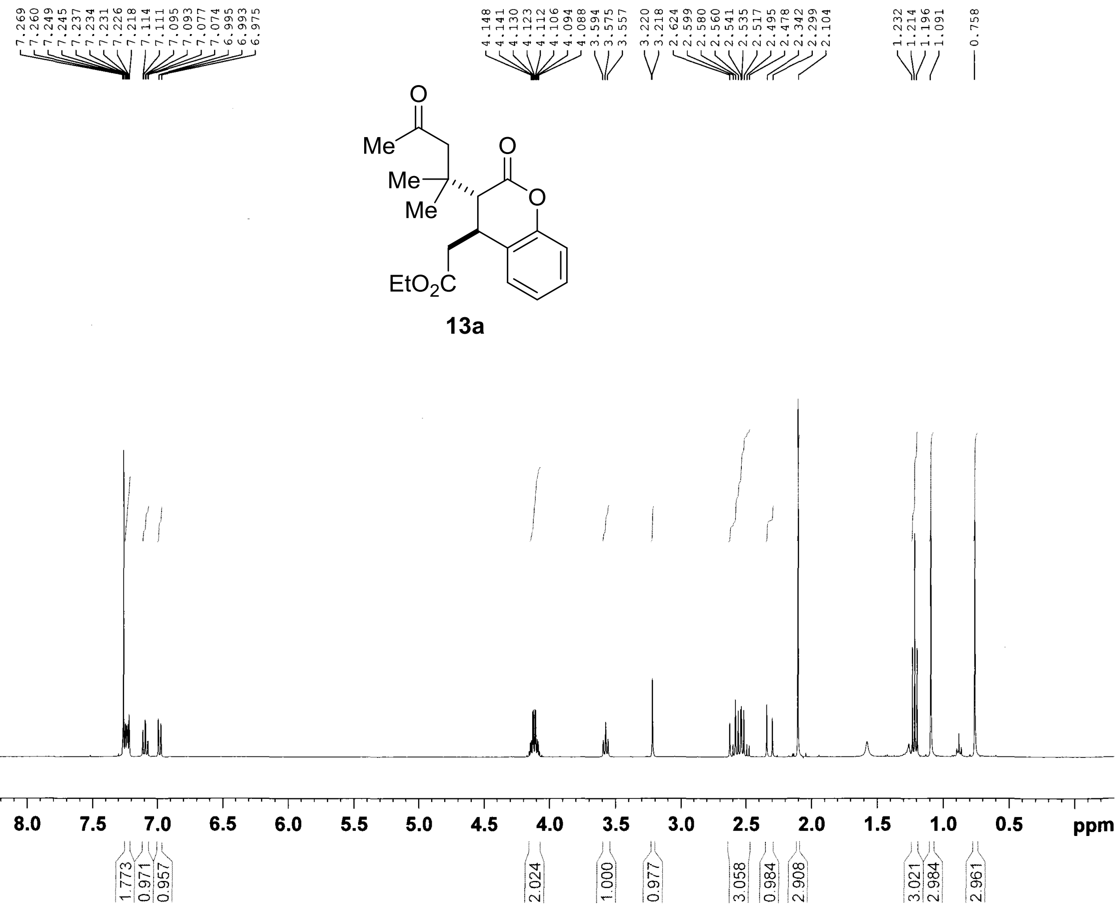
F2 - Processing parameters
SI                  32768
SF            100.6253420 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

```
Current Data Parameters
NAME              Ko-80f
EXPNO                  1
PROCNO                 1

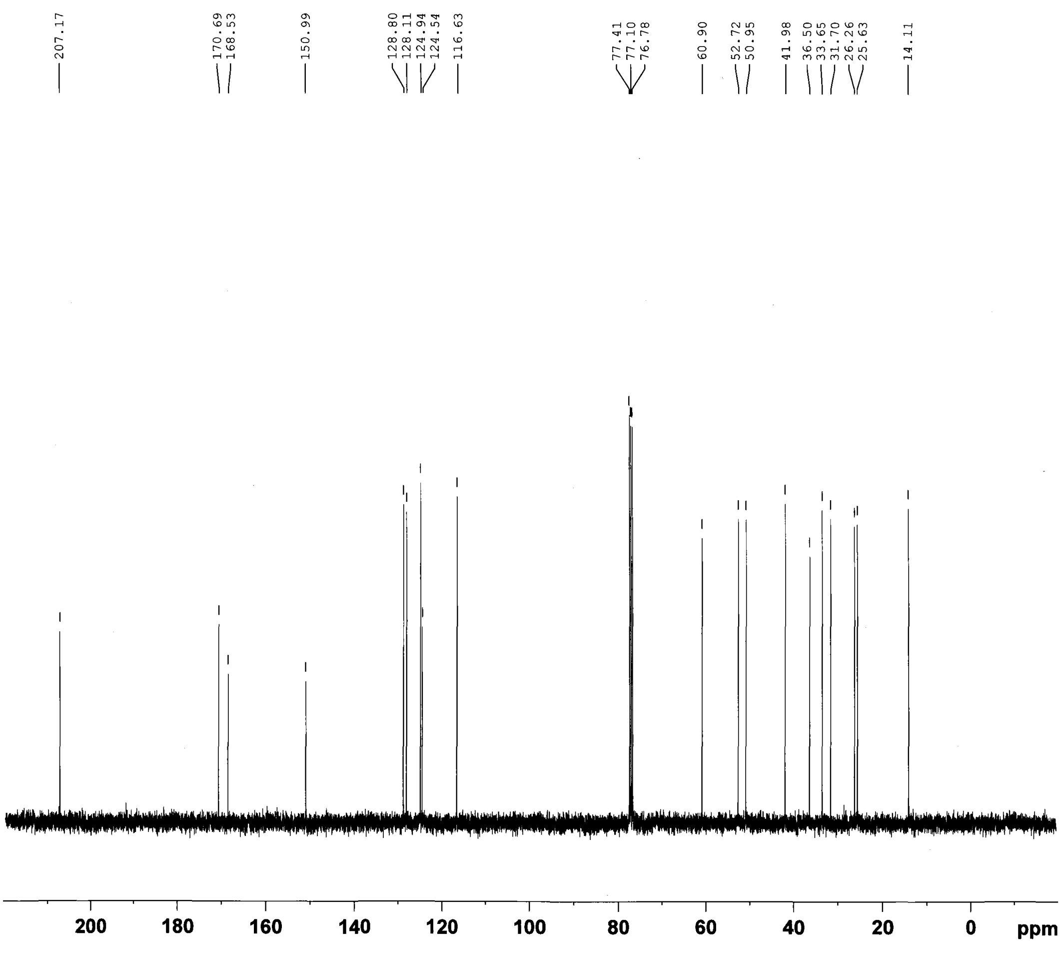
F2 - Acquisition Parameters
Date_           20140226
Time               17.42
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                 91.18
DW                60.800 usec
DE                  6.50 usec
TE                 294.3 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           400.1300098 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



13a



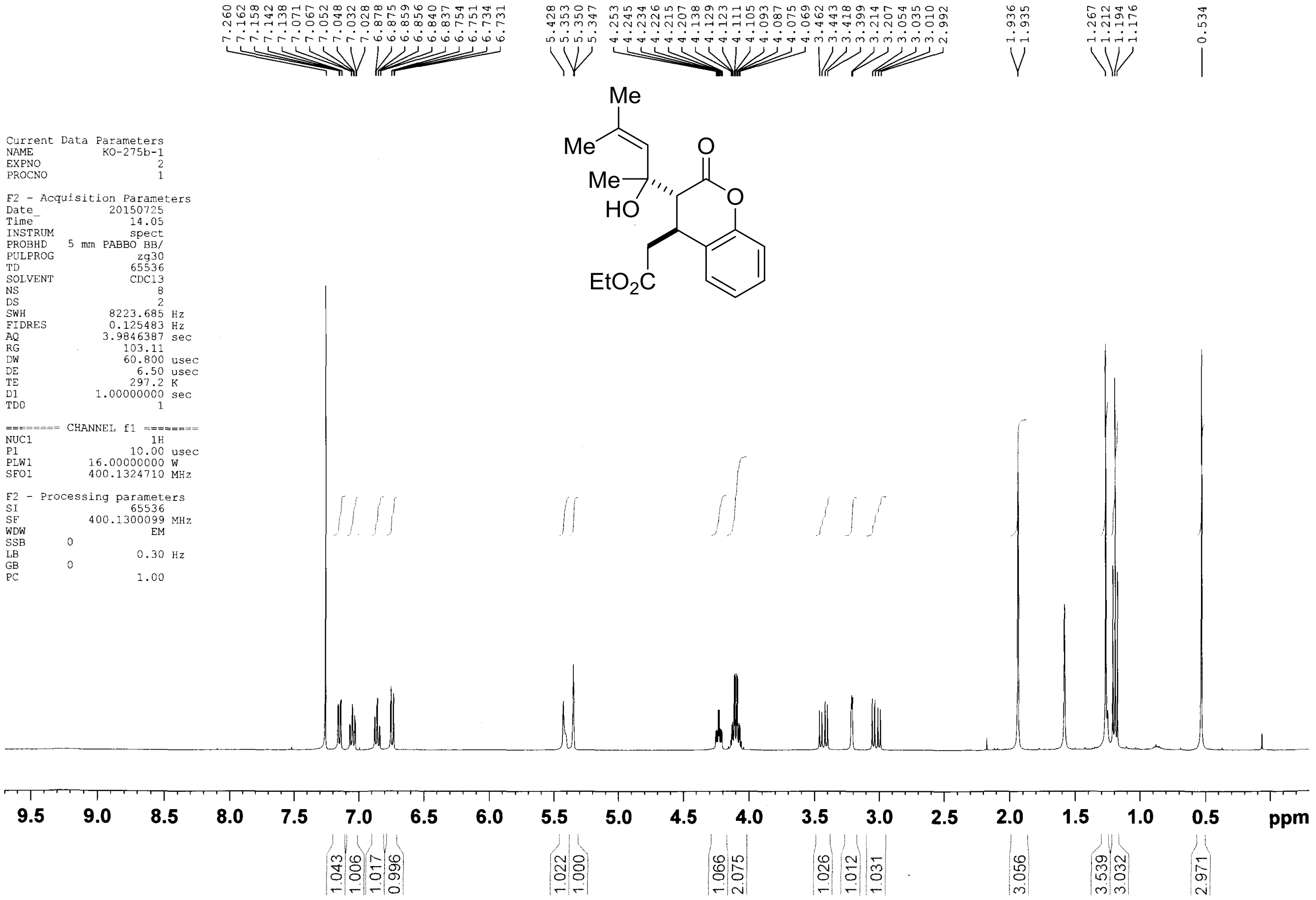
```
Current Data Parameters
NAME              Ko-80f
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140227
Time               18.24
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    28
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                 294.3 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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 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
```

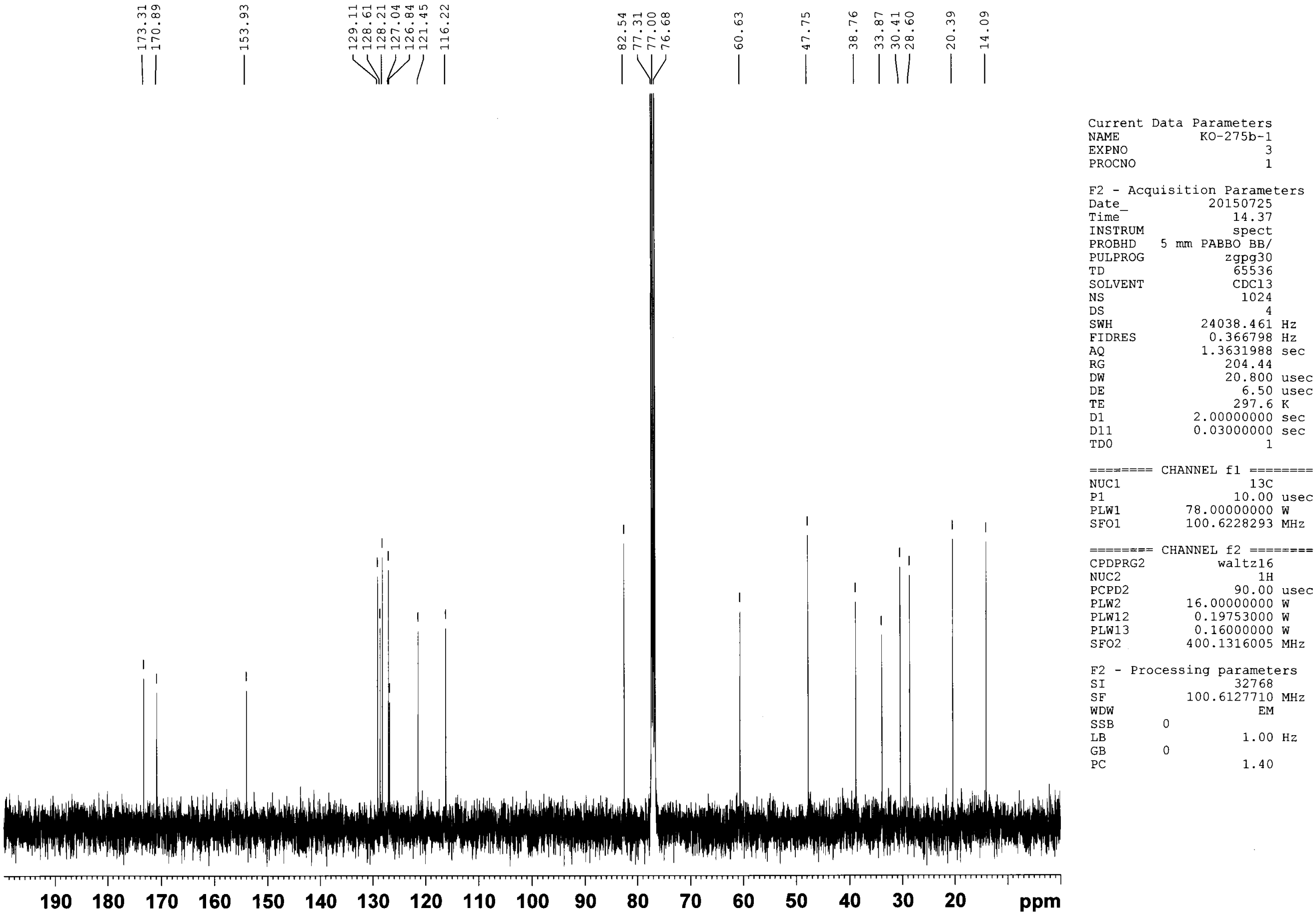


```
Current Data Parameters
NAME          KO-275b-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150725
Time              14.05
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               103.11
DW               60.800 usec
DE                 6.50 usec
TE                297.2 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
```



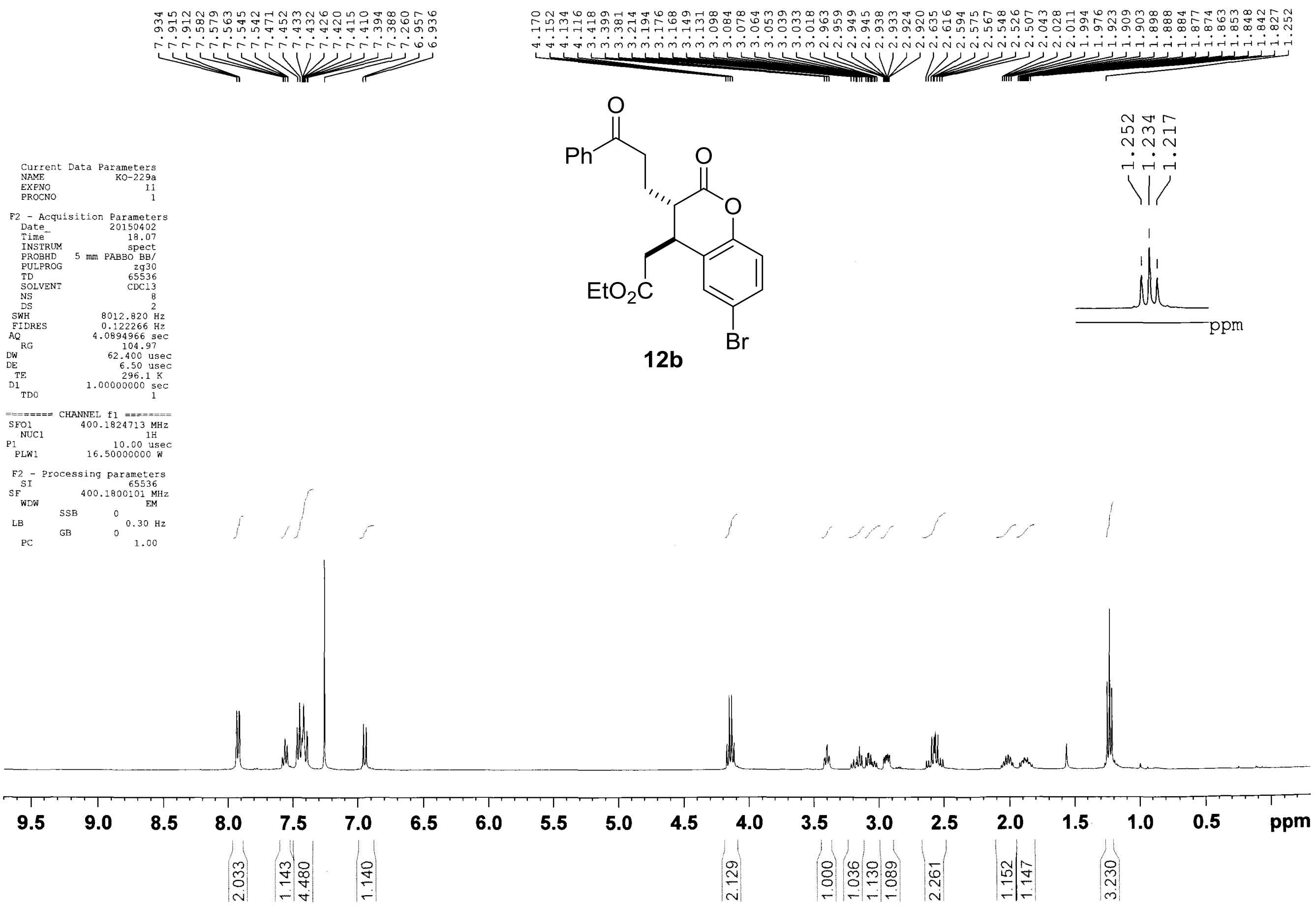
```
Current Data Parameters
NAME          KO-275b-1
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150725
Time              14.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               204.44
DW               20.800 usec
DE                 6.50 usec
TE                297.6 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127710 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



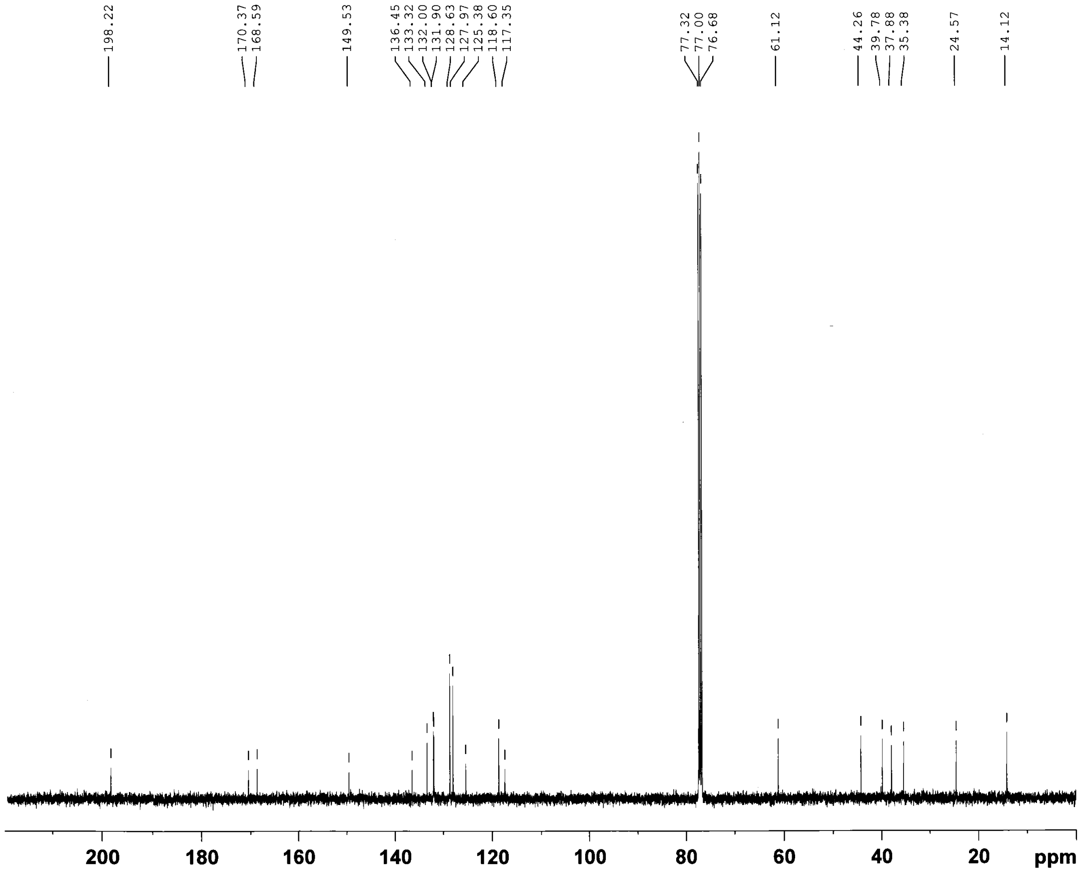
12b

```
Current Data Parameters
NAME              KO-229a
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150402
Time                18.07
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                 104.97
DW             62.400 usec
DE               6.50 usec
TE                296.1 K
D1         1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1       400.1824713 MHz
NUC1                   1H
P1              10.00 usec
PLW1       16.50000000 W

F2 - Processing parameters
SI                  65536
SF         400.1800101 MHz
WDW                    EM
SSB      0
LB                0.30 Hz
GB       0
PC                   1.00
```



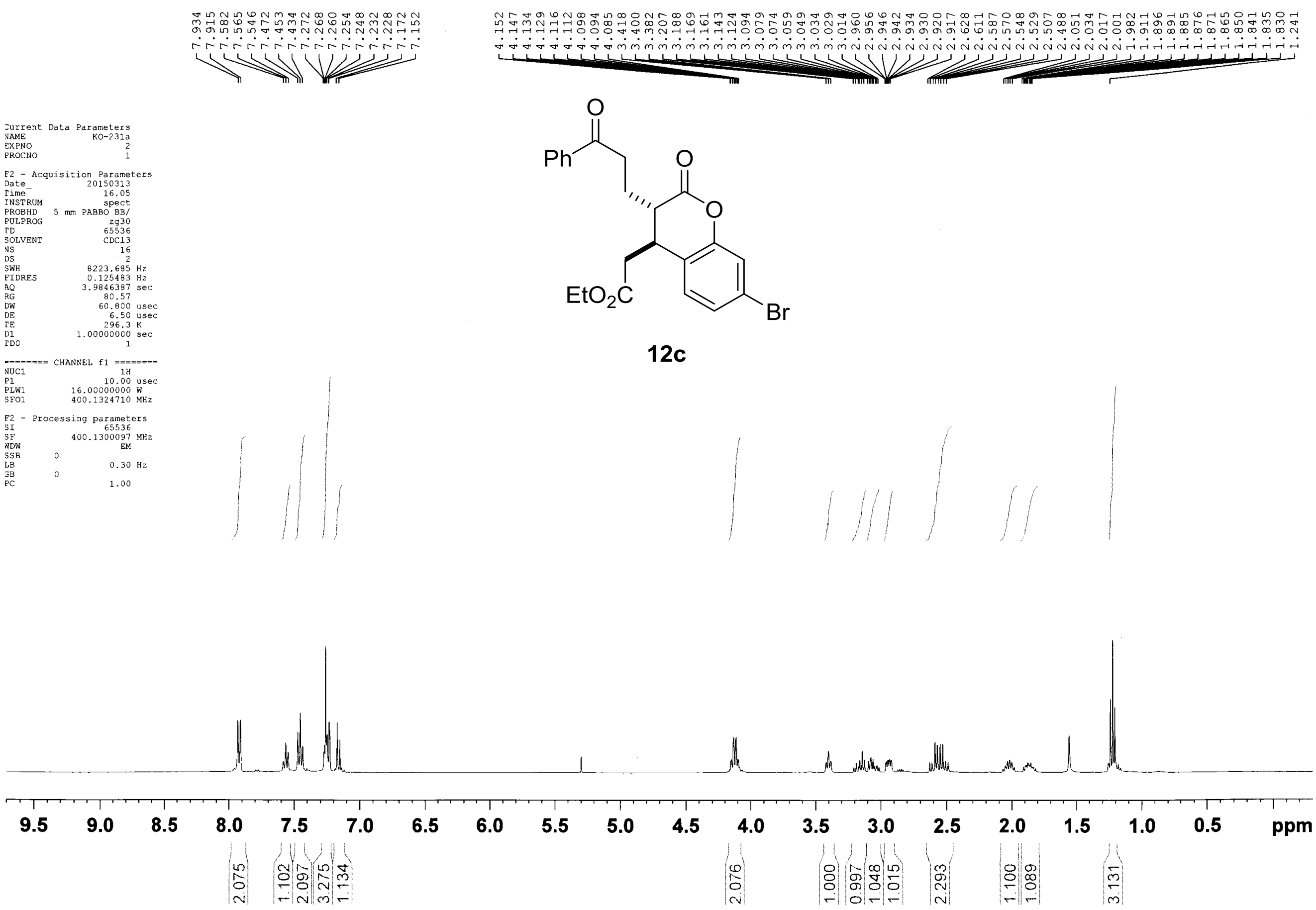
```
Current Data Parameters
NAME              KO-229a
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150310
Time                 4.08
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    322
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                296.0 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            90.00 usec
PLW2       16.00000000 W
PLW12       0.19753000 W
PLW13       0.16000000 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF         100.6127717 MHz
WDW                    EM
SSB      0
LB                1.00 Hz
GB       0
PC                   1.40
```



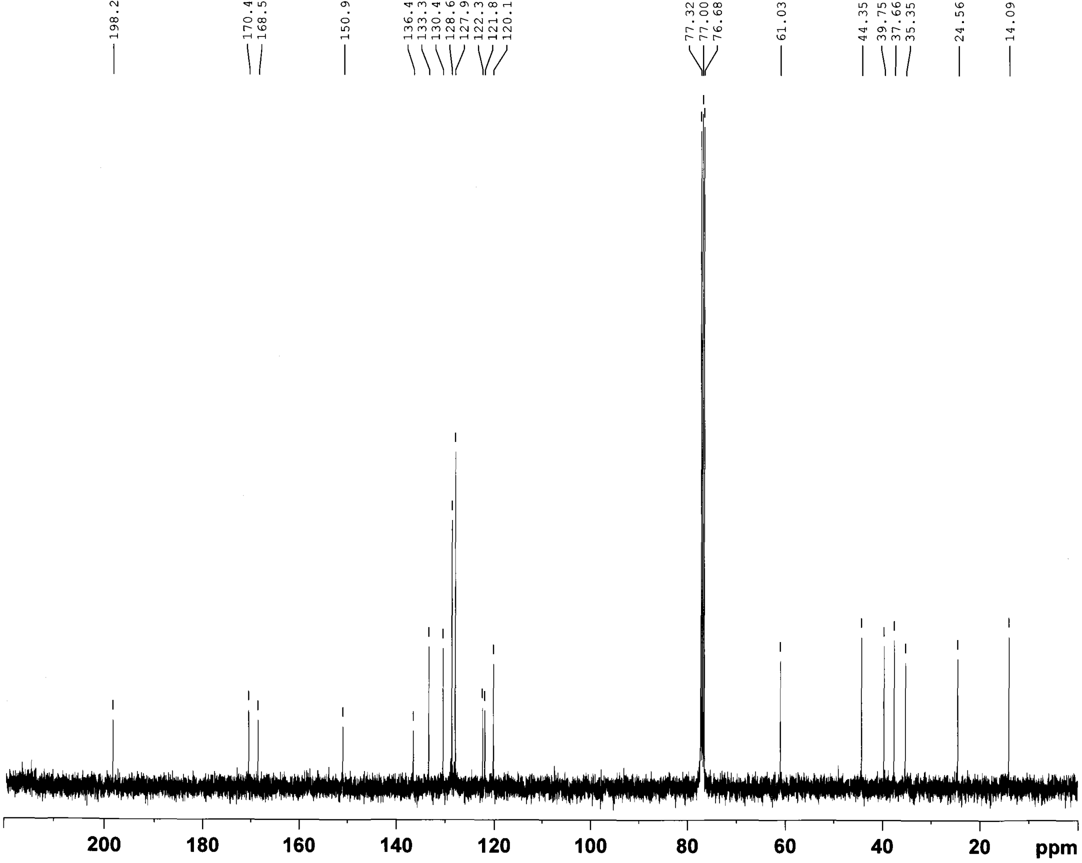
12c

```
Current Data Parameters
NAME            KO-231a
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150313
Time              16.05
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                80.57
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
```



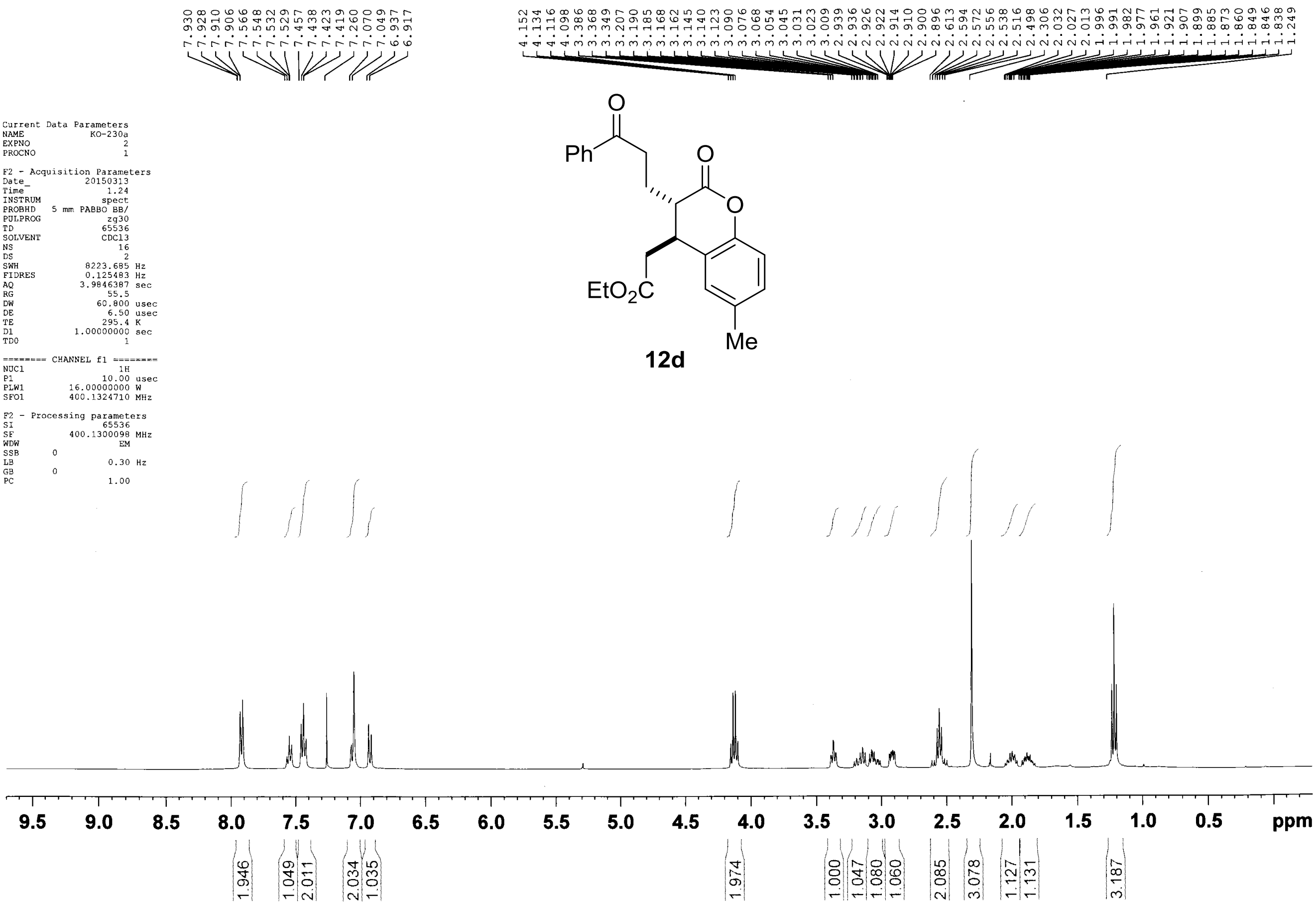
```
Current Data Parameters
NAME            KO-231a
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20150404
Time              18.58
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  193
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                297.6 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127723 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



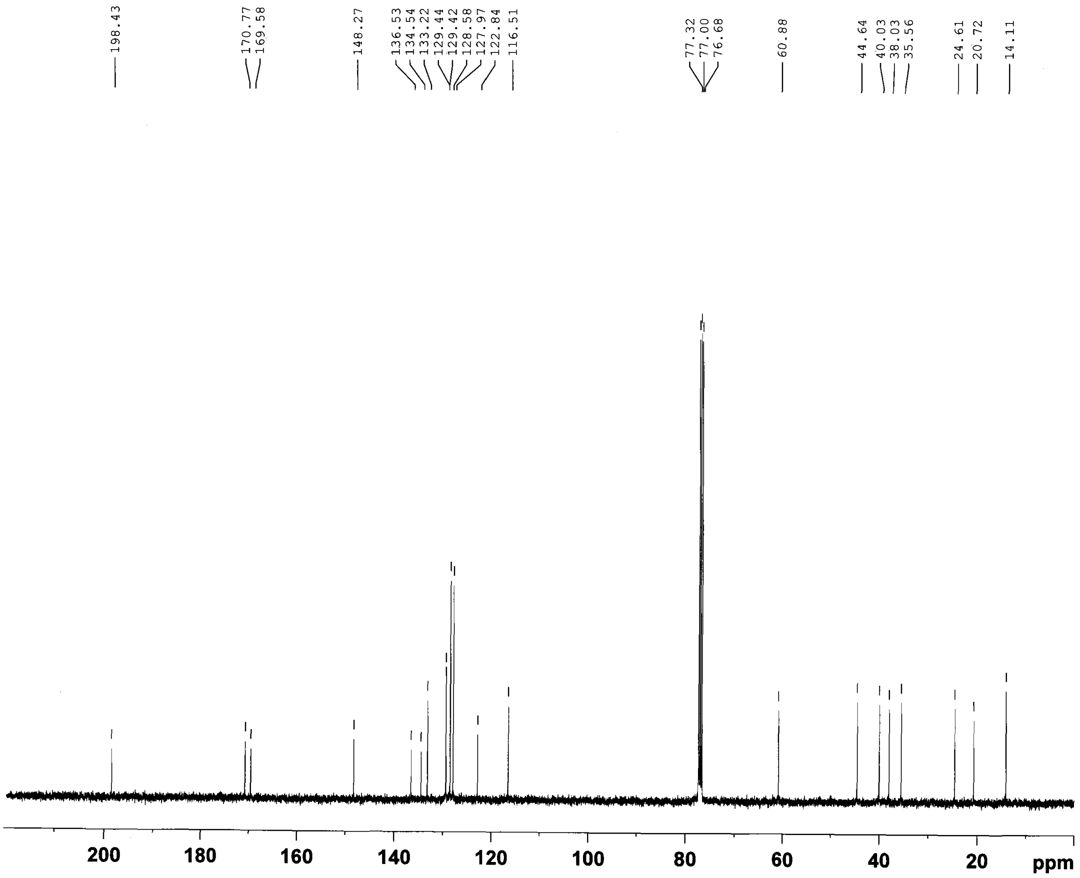
12d

```
Current Data Parameters
NAME              KO-230a
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150313
Time                 1.24
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
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                  295.4 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
```



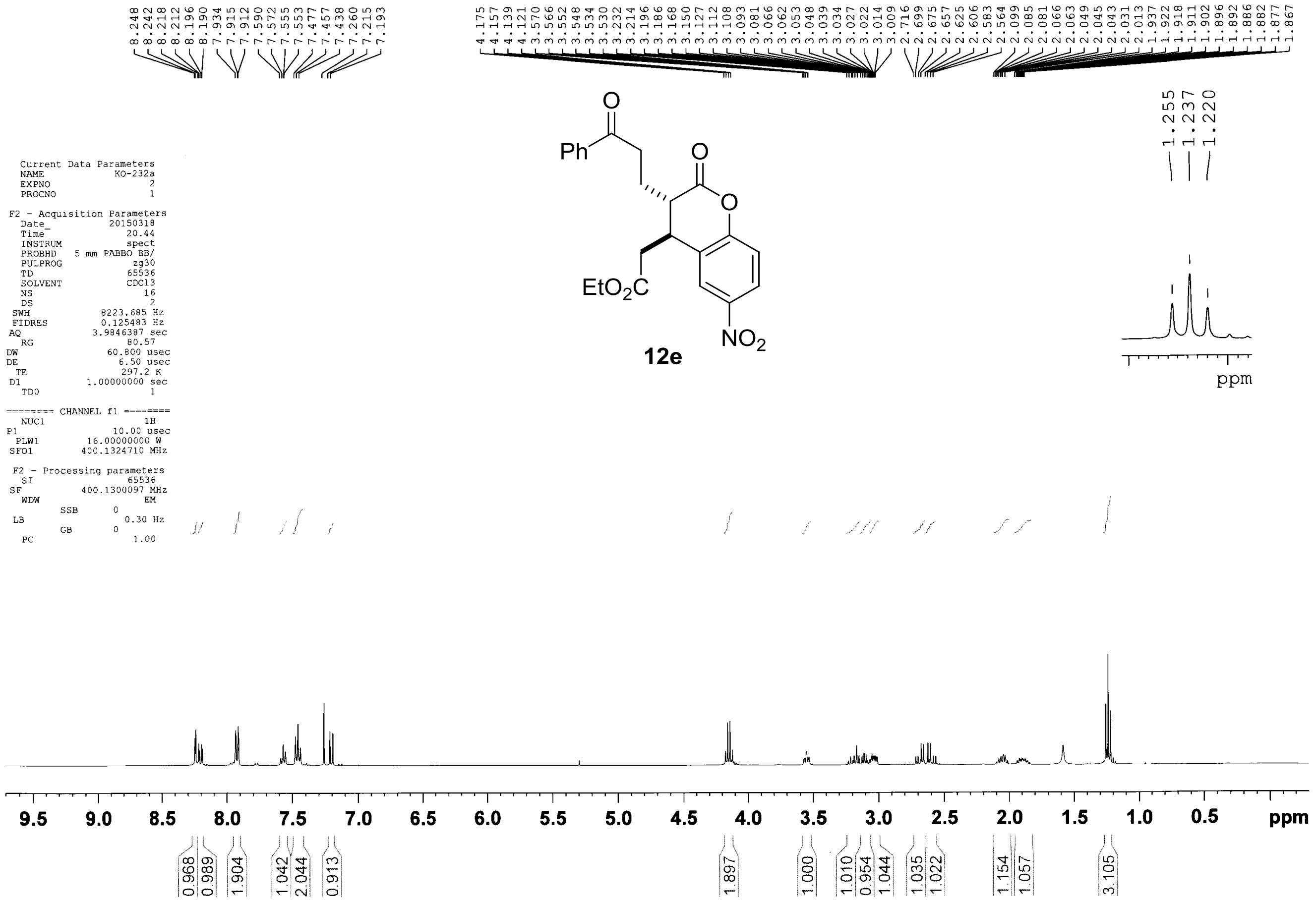
```
Current Data Parameters
NAME              KO-230a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150313
Time                 1.31
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
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                  295.5 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127724 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



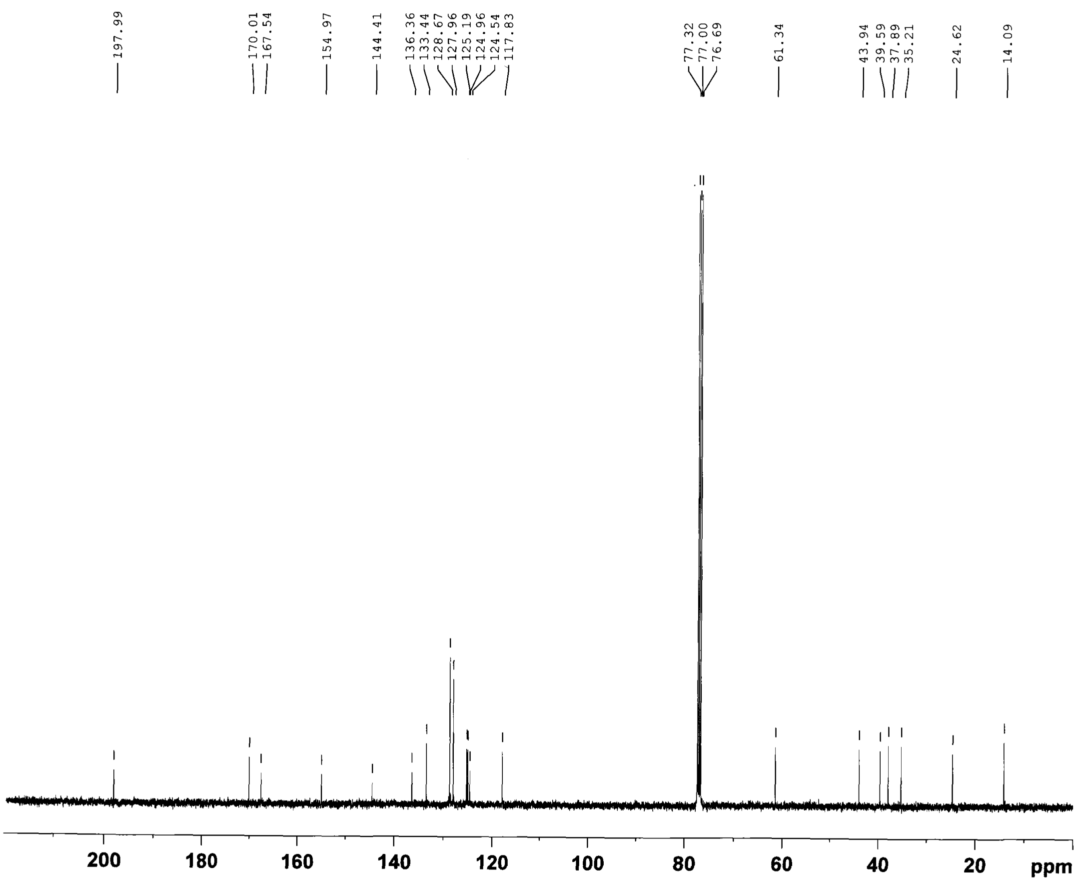
12e

```
Current Data Parameters
NAME             KO-232a
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150318
Time               20.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ          3.9846387 sec
RG                 80.57
DW            60.800 usec
DE              6.50 usec
TE               297.2 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
```



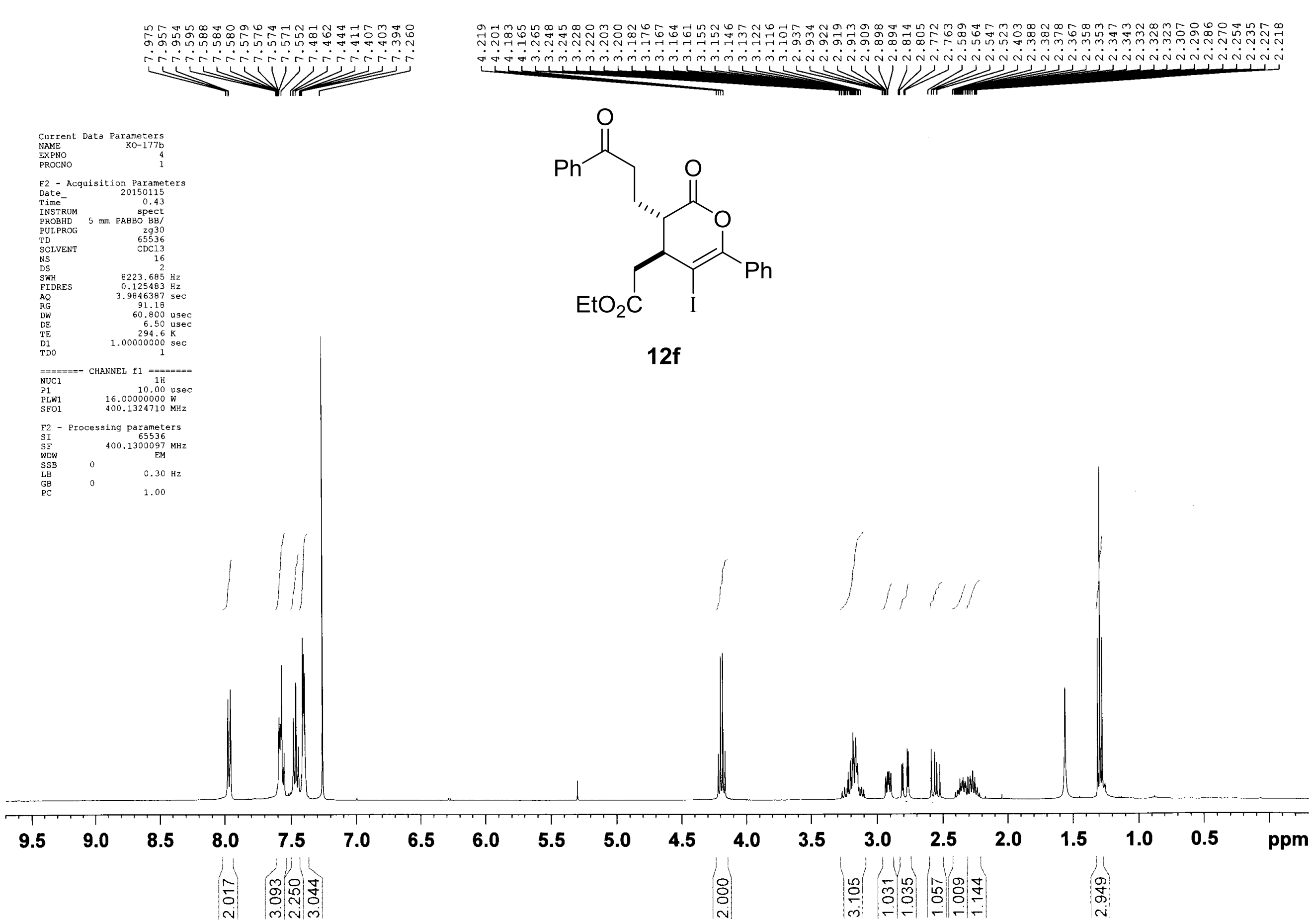
```
Current Data Parameters
NAME             KO-232a
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150318
Time               20.55
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   498
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               297.9 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          90.00 usec
PLW2      16.00000000 W
PLW12      0.19753000 W
PLW13      0.16000000 W
SFO2      400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF        100.6127710 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                  1.40
```



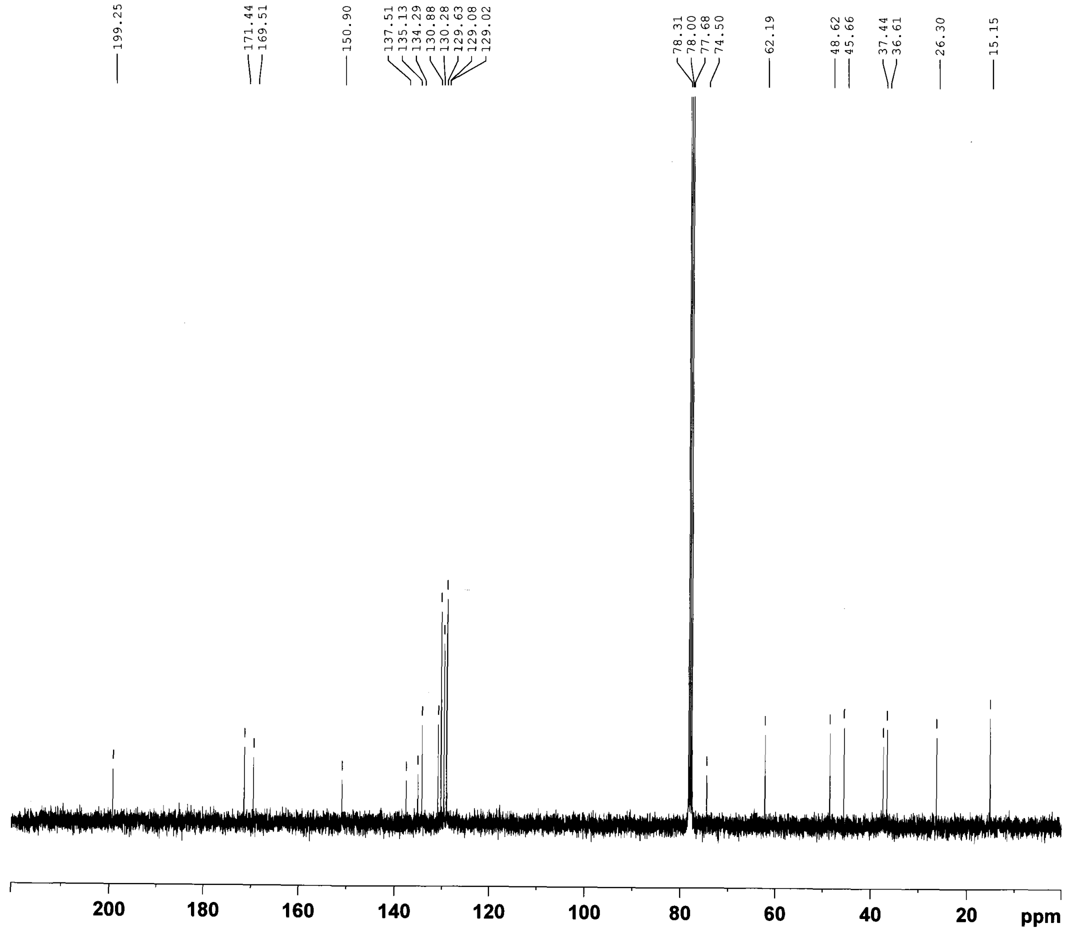
12f

```
Current Data Parameters
NAME              KO-177b
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150115
Time                 0.43
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
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                  294.6 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
```



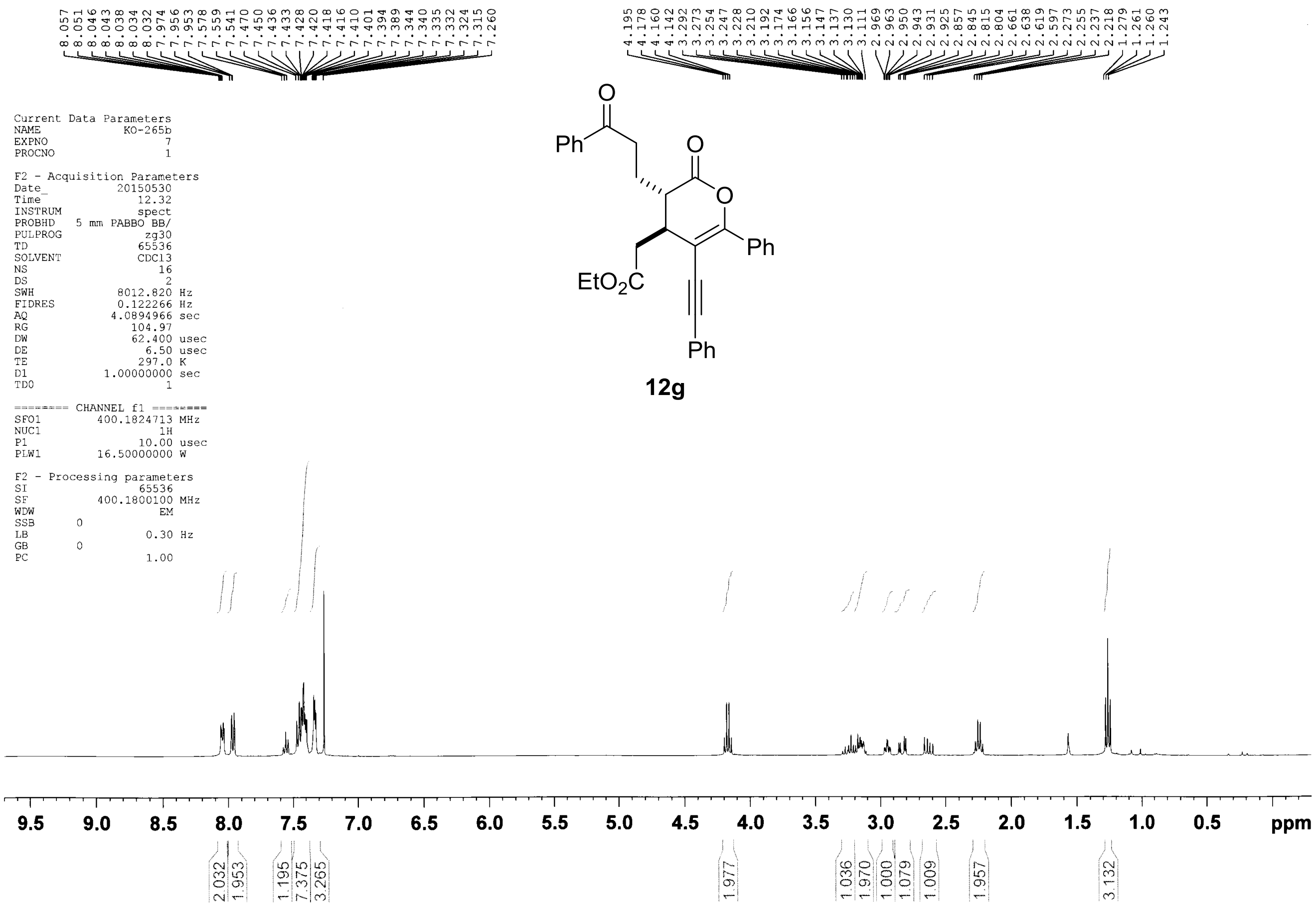
```
Current Data Parameters
NAME              KO-177b
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150114
Time                22.07
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    145
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                  295.4 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6126718 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



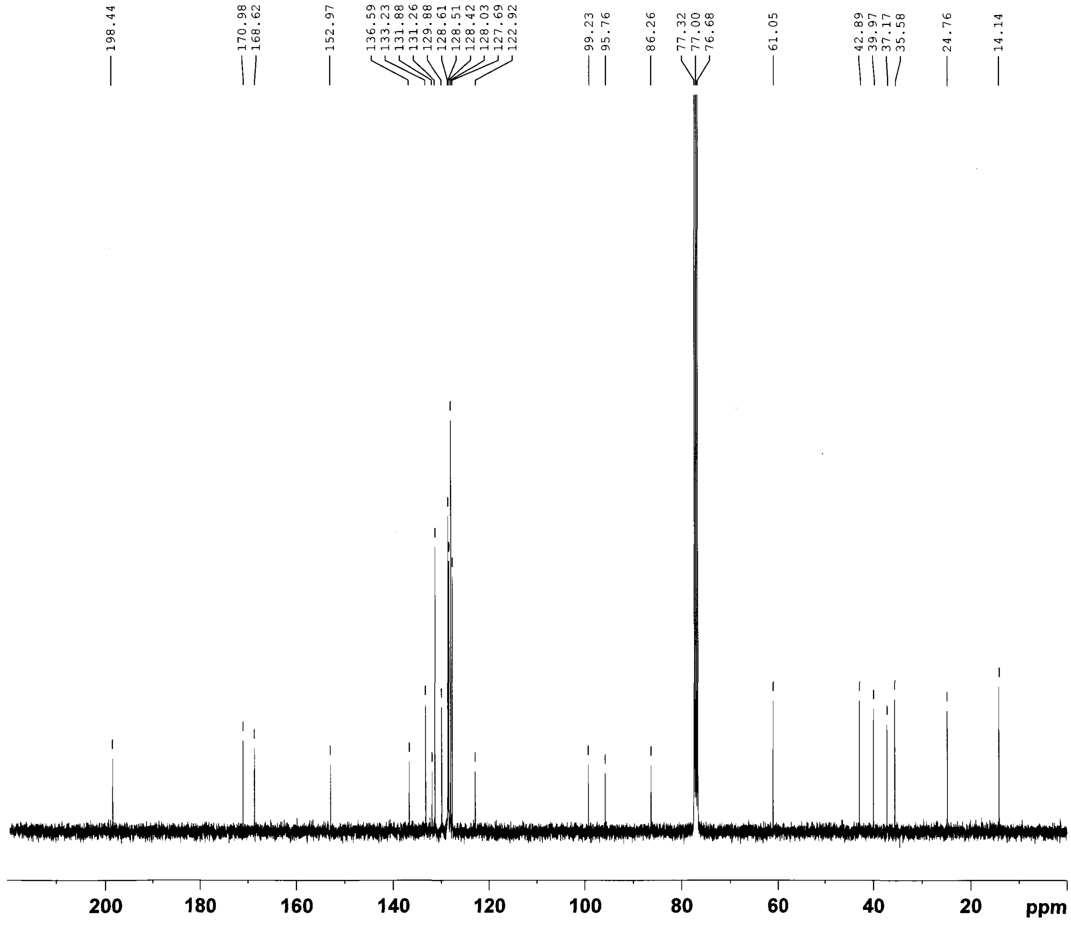
12g

```
Current Data Parameters
NAME            KO-265b
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20150530
Time              12.32
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG               104.97
DW               62.400 usec
DE                 6.50 usec
TE                297.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1824713 MHz
NUC1                 1H
P1                10.00 usec
PLW1        16.50000000 W

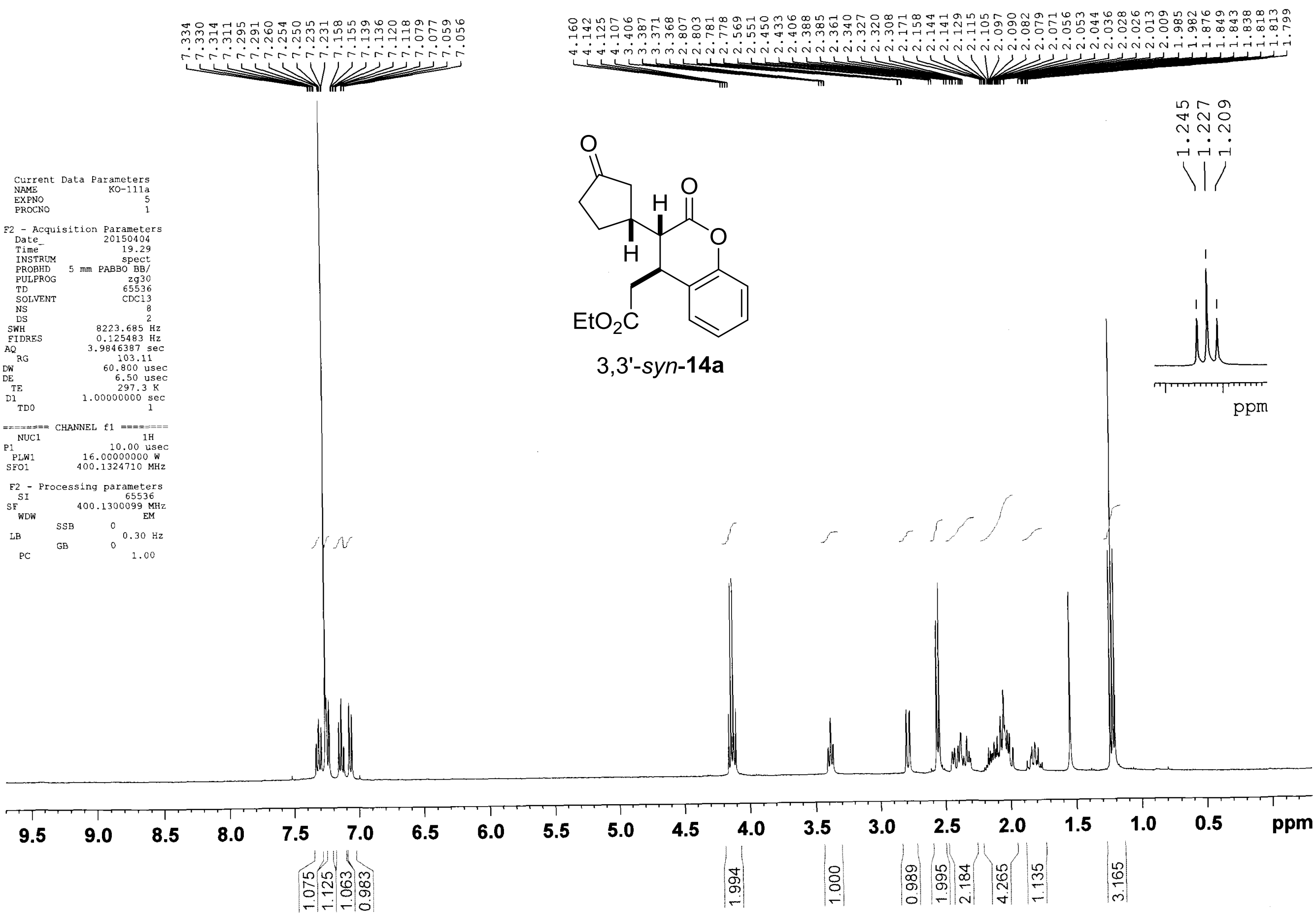
F2 - Processing parameters
SI                65536
SF          400.1800100 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



```
Current Data Parameters
NAME            KO-265b
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20150530
Time              13.33
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               206.25
DW               20.800 usec
DE                 6.50 usec
TE                297.4 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1
NUC1                13C
P1                10.00 usec
PLW1        63.50000000 W
SFO1        100.6354031 MHz
CPDPRG2
NUC2                 1H
PLW2        16.50000000 W
PLW12        0.20370001 W
PLW13        0.16500001 W
SFO2        400.1816007 MHz

F2 - Processing parameters
SI                32768
SF          100.6253439 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



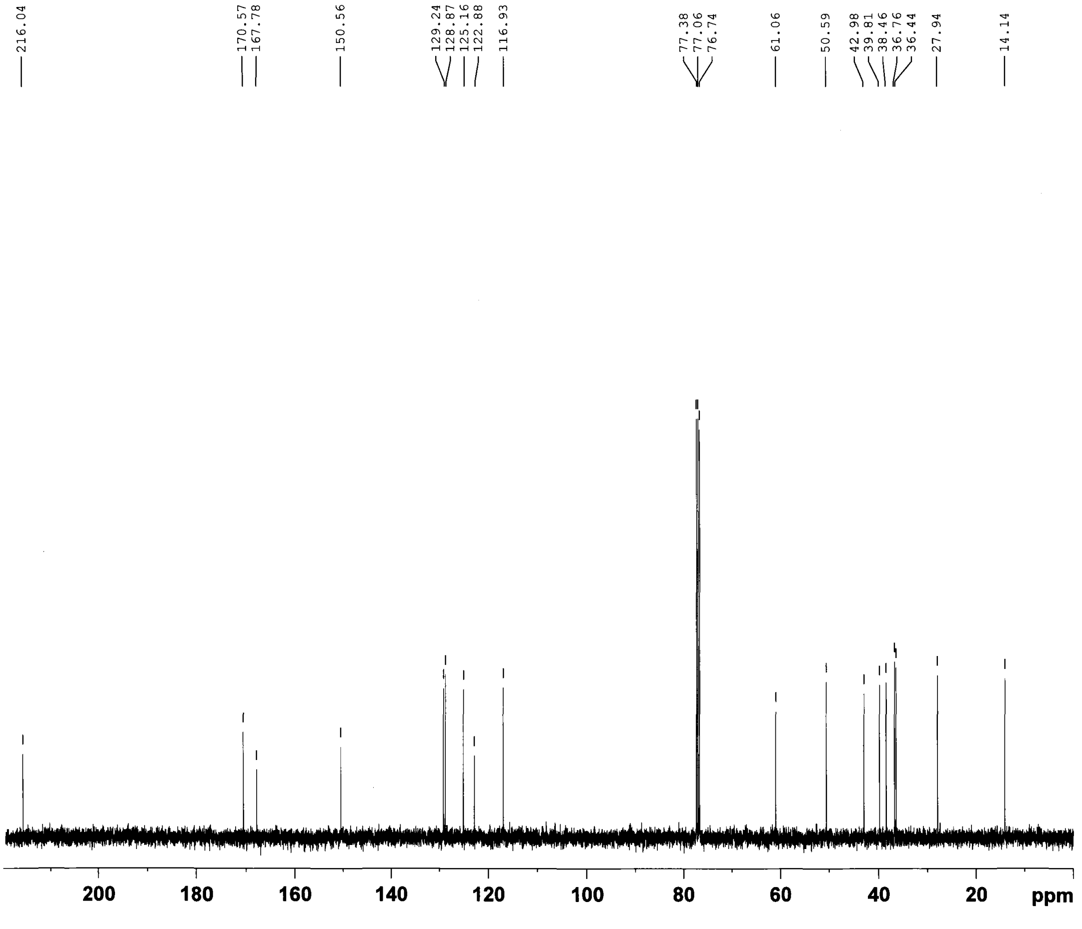
3,3'-*syn*-**14a**

```
Current Data Parameters
NAME            KO-111a
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20150404
Time              19.29
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               103.11
DW           60.800 usec
DE             6.50 usec
TE              297.3 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       400.1300099 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.00
```



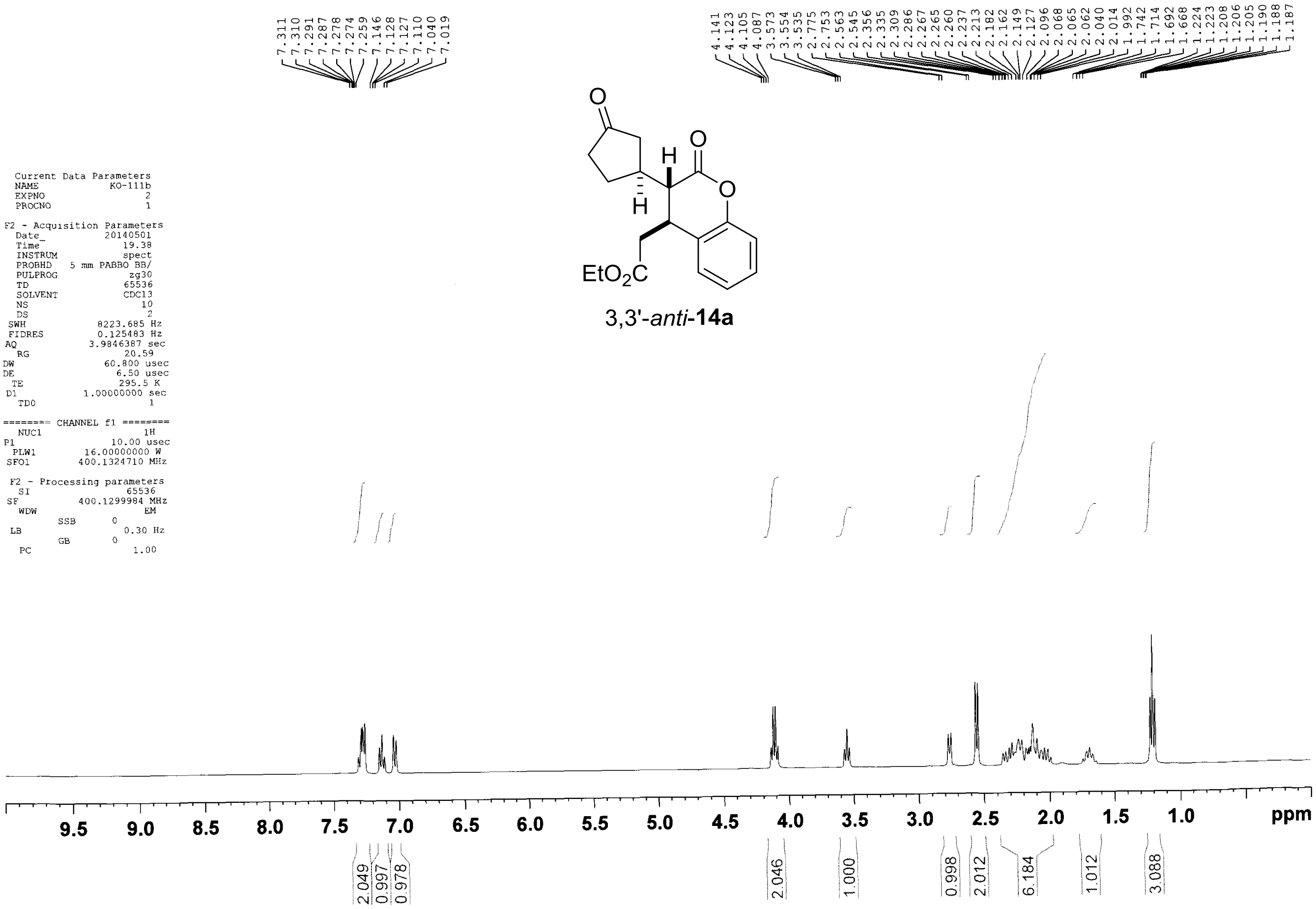
```
Current Data Parameters
NAME            KO-111a
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140501
Time              15.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   27
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              295.3 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        90.00 usec
PLW2     16.00000000 W
PLW12     0.19753000 W
PLW13     0.16000000 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
```



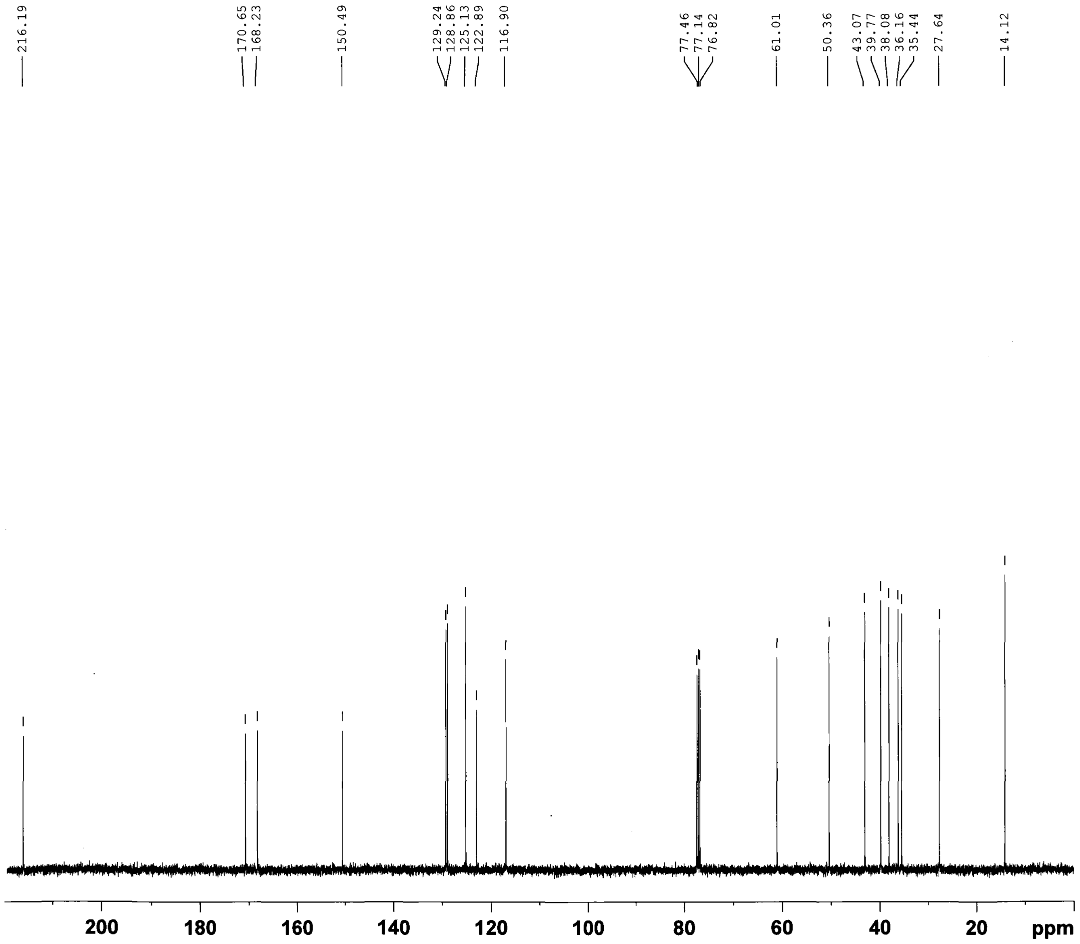
3,3'-*anti*-**14a**

```
Current Data Parameters
NAME              KO-111b
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140501
Time                19.38
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     10
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                  295.5 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            400.1299984 MHz
WDW                    EM
         SSB      0
LB                   0.30 Hz
         GB       0
PC                   1.00
```



```
Current Data Parameters
NAME              KO-111b
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140501
Time                19.41
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     26
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                  295.7 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

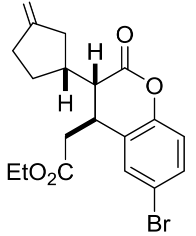
F2 - Processing parameters
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

```
Current Data Parameters
NAME             KO-171a-1
EXPNO                    1
PROCNO                   1

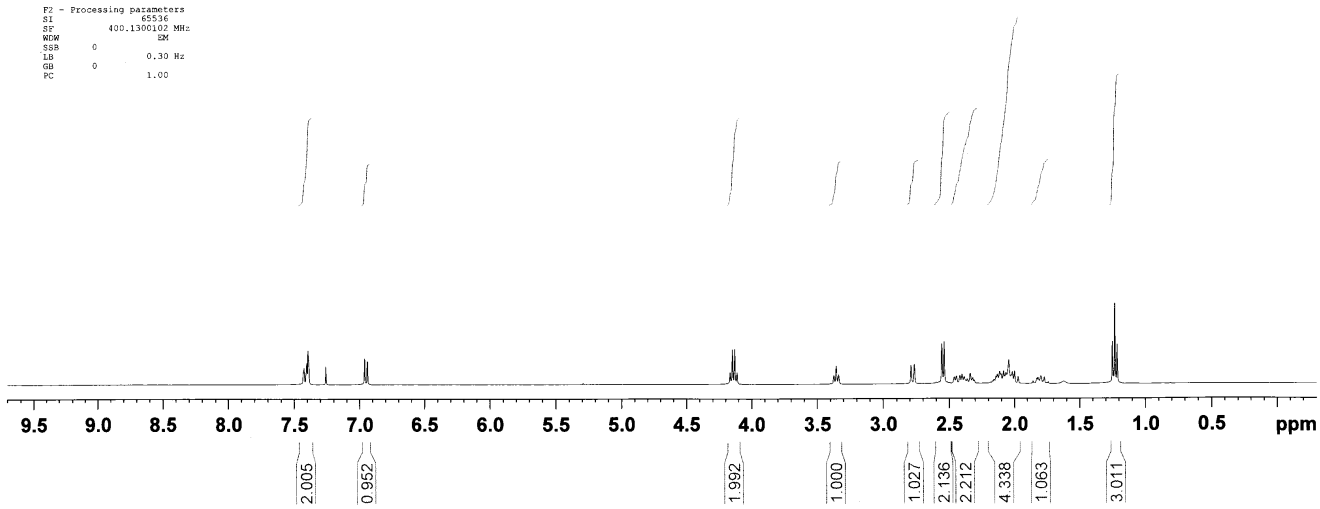
F2 - Acquisition Parameters
Date_             20150108
Time                 23.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                    55.5
DW                  60.800 usec
DE                    6.50 usec
TE                   294.4 K
D1              1.00000000 sec
TD0                      1

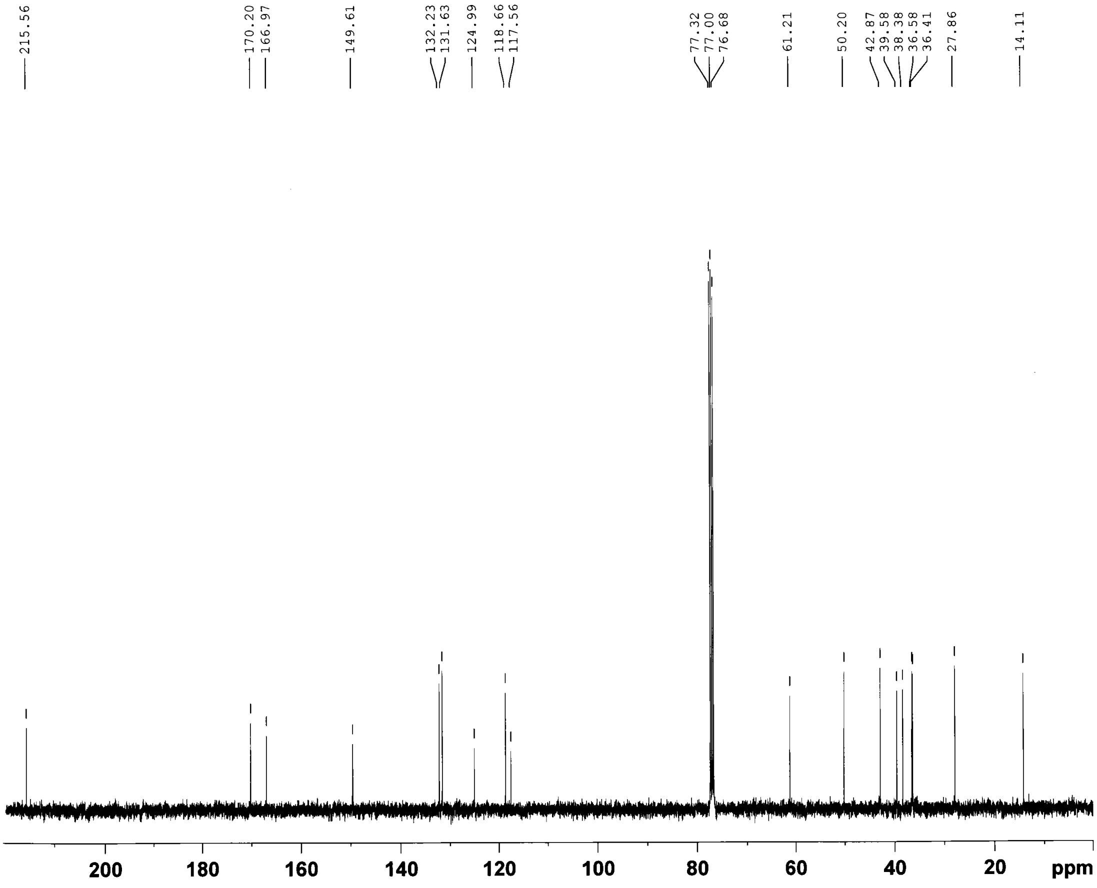
======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PLW1           16.00000000 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300102 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



3,3'-*syn*-**14b**





```
Current Data Parameters
NAME             KO-171a-1
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150108
Time                 23.11
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     101
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                   294.7 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                90.00 usec
PLW2           16.00000000 W
PLW12           0.19753000 W
PLW13           0.16000000 W
SFO2           400.1316005 MHz

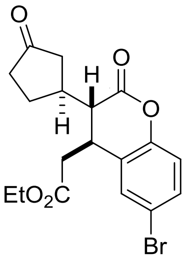
F2 - Processing parameters
SI                   32768
SF             100.6127731 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

```
Current Data Parameters
NAME          KO-171a-2
EXPNO                 3
PROCNO                1

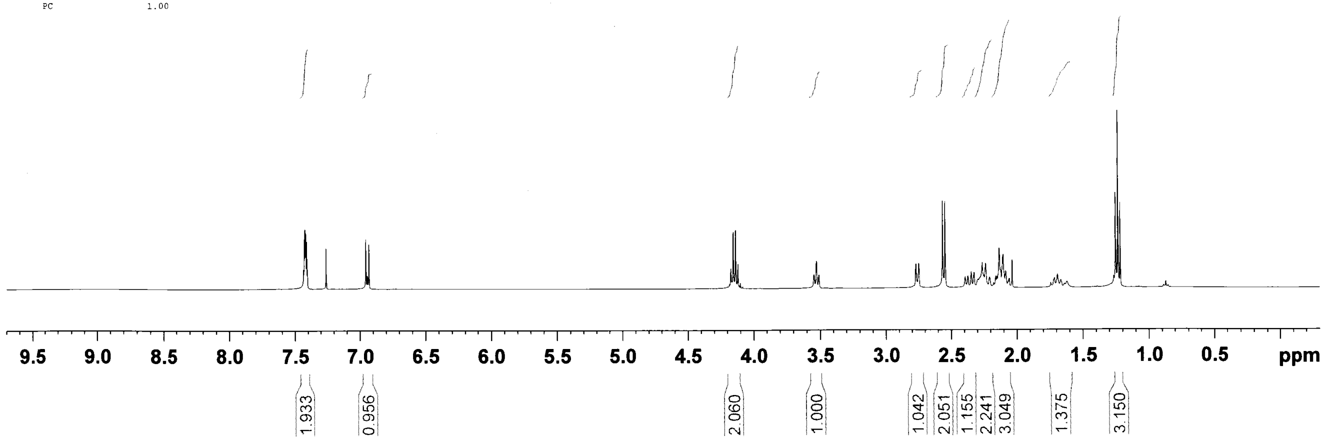
F2 - Acquisition Parameters
Date_          20150108
Time              15.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                 55.5
DW               60.800 usec
DE                 6.50 usec
TE                295.1 K
D1           1.00000000 sec
TD0                   1

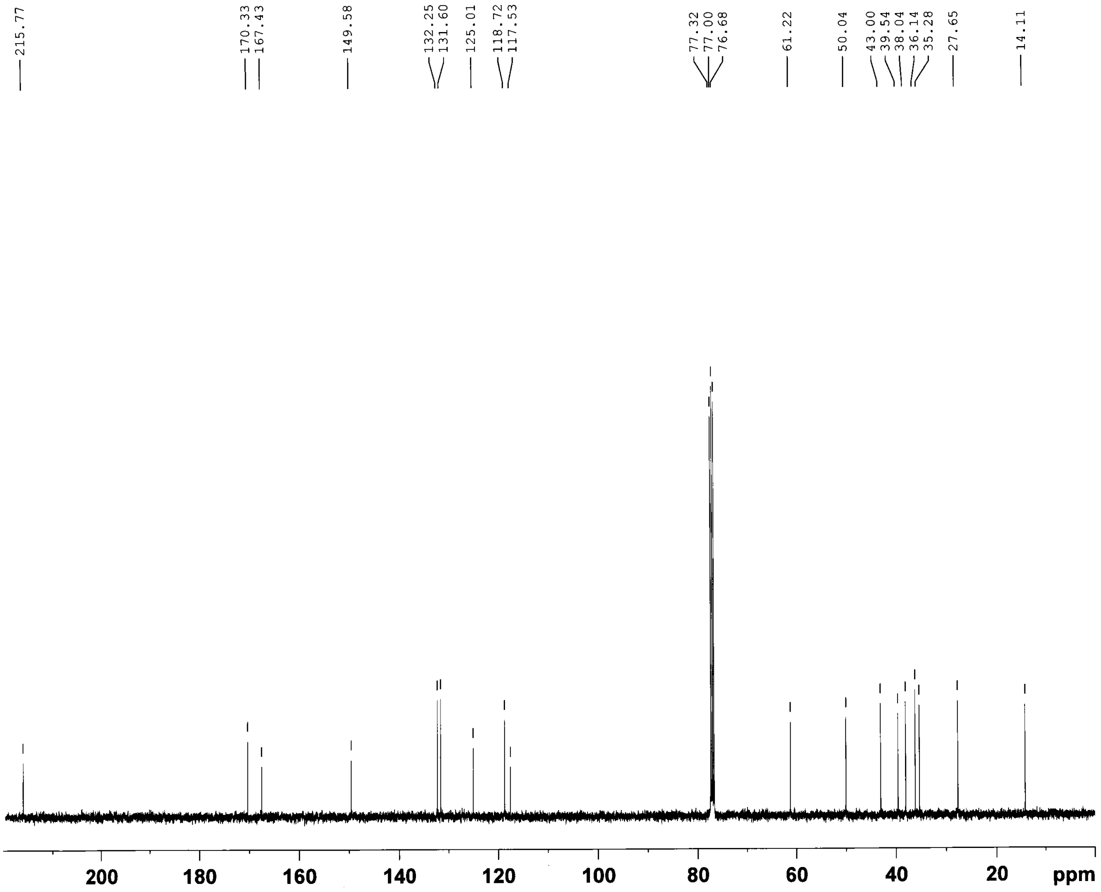
======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PLW1        16.00000000 W
SFO1        400.1324710 MHz

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



3,3'-*anti*-**14b**





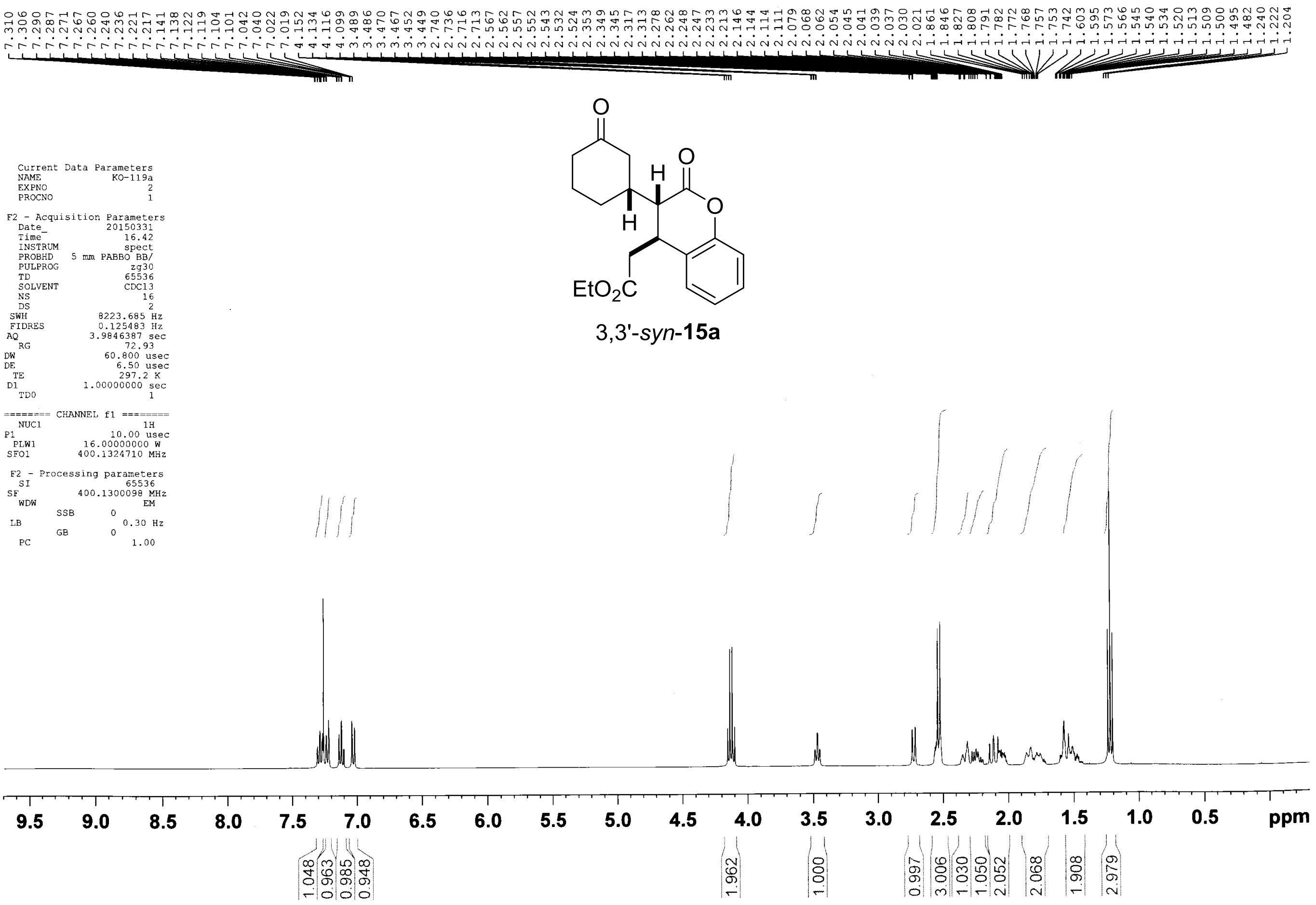
```
Current Data Parameters
NAME          KO-171a-2
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20150108
Time              15.55
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  165
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                295.6 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127732 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



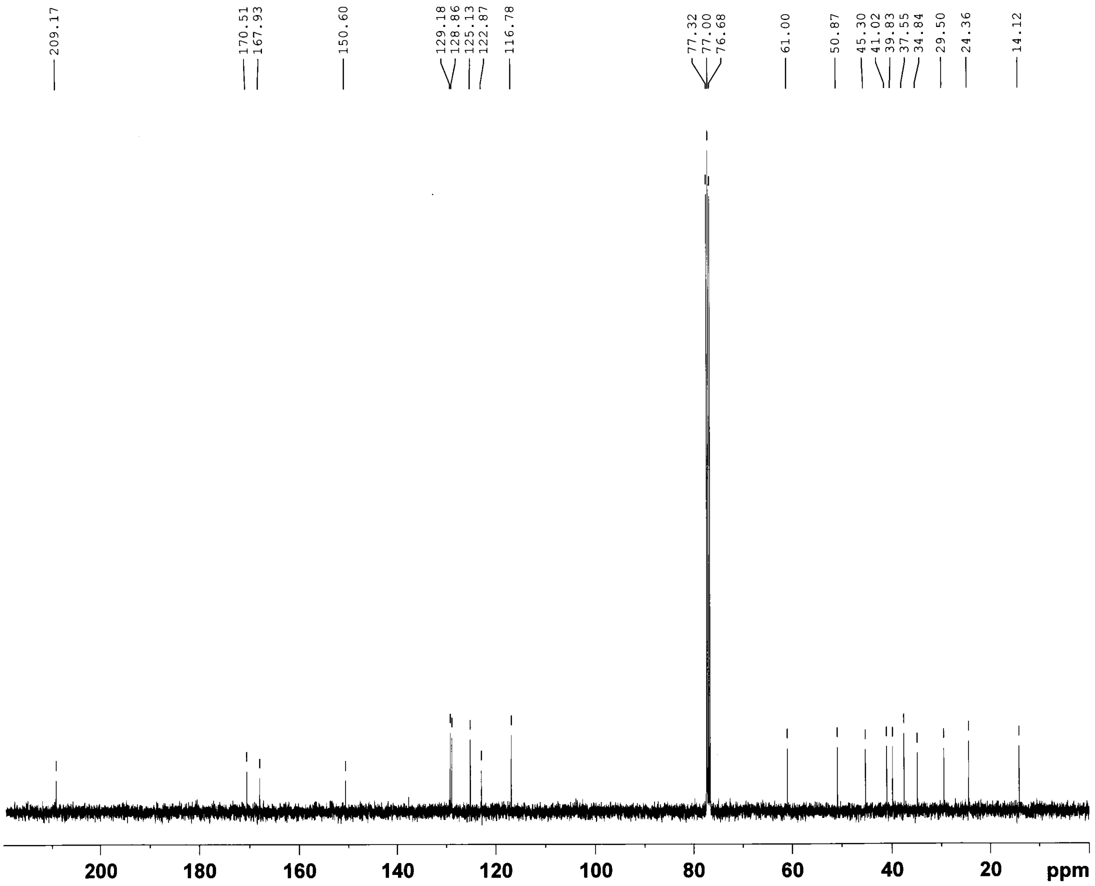
3,3'-*syn*-**15a**

```
Current Data Parameters
NAME              KO-119a
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150331
Time                16.42
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
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                  297.2 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
```



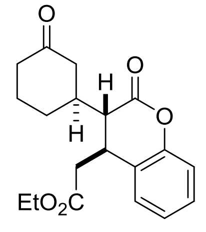
```
Current Data Parameters
NAME              KO-119a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150331
Time                16.50
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    143
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                  297.9 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127710 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```



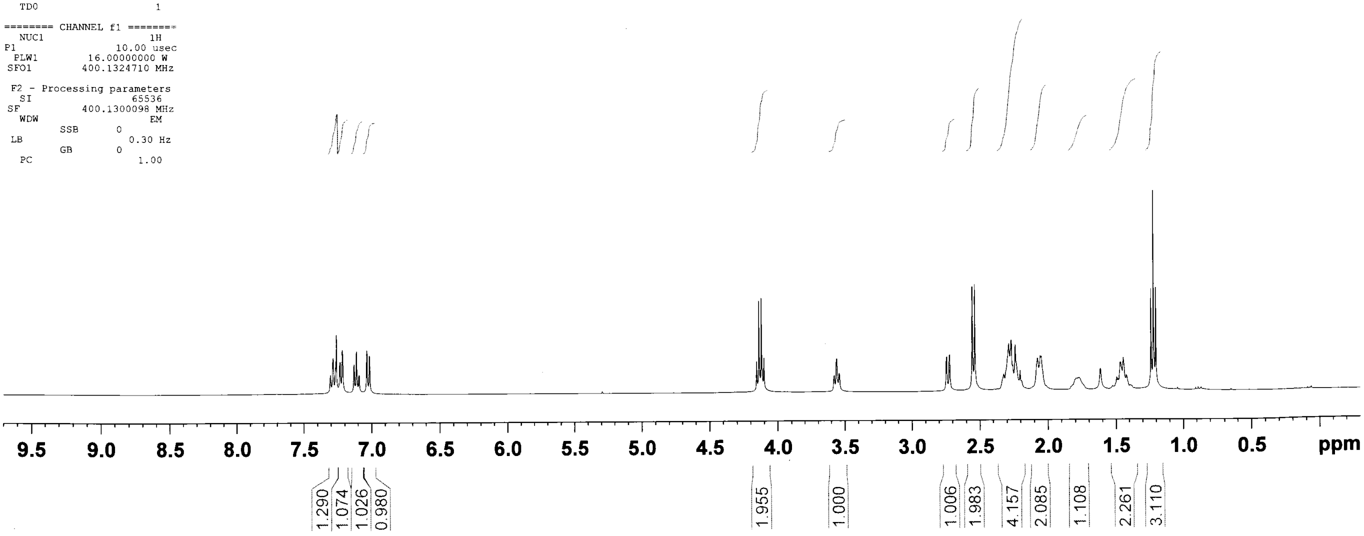
3,3'-*anti*-**15a**

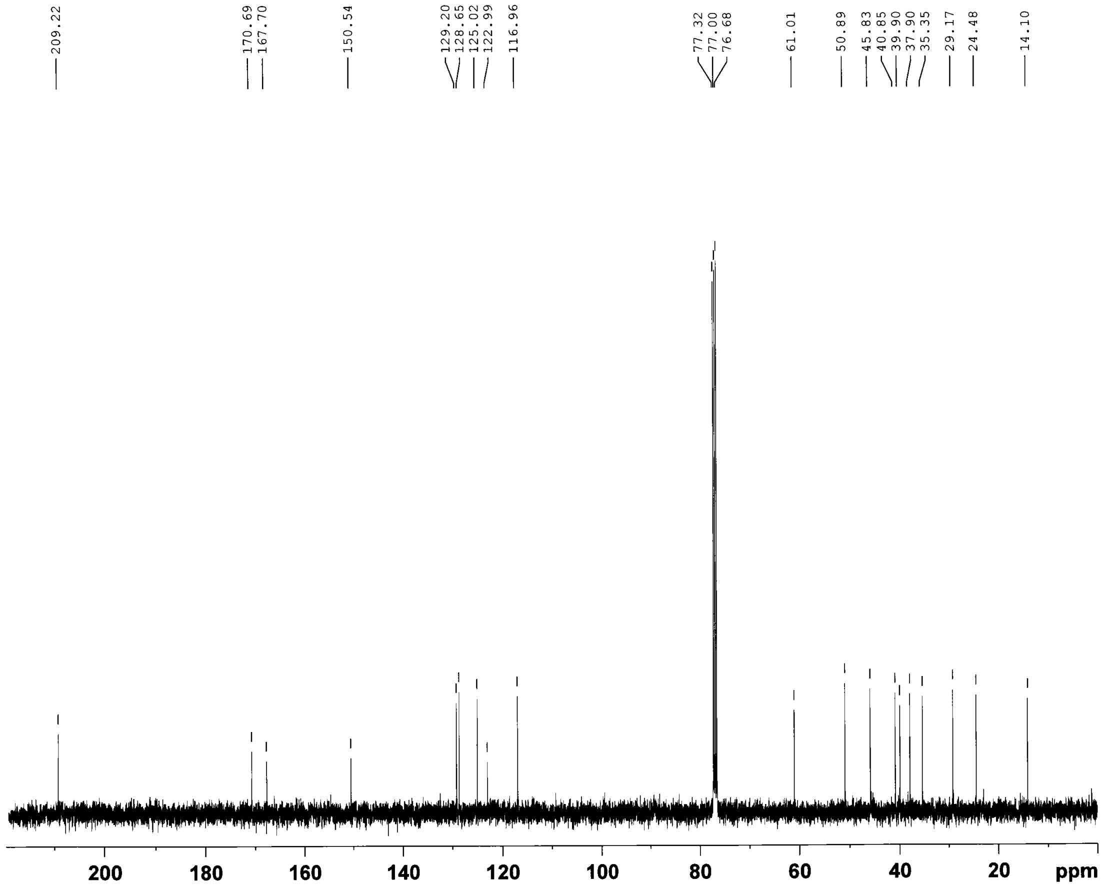
```
Current Data Parameters
NAME              KO-120a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150401
Time                11.13
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
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                  297.2 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
```





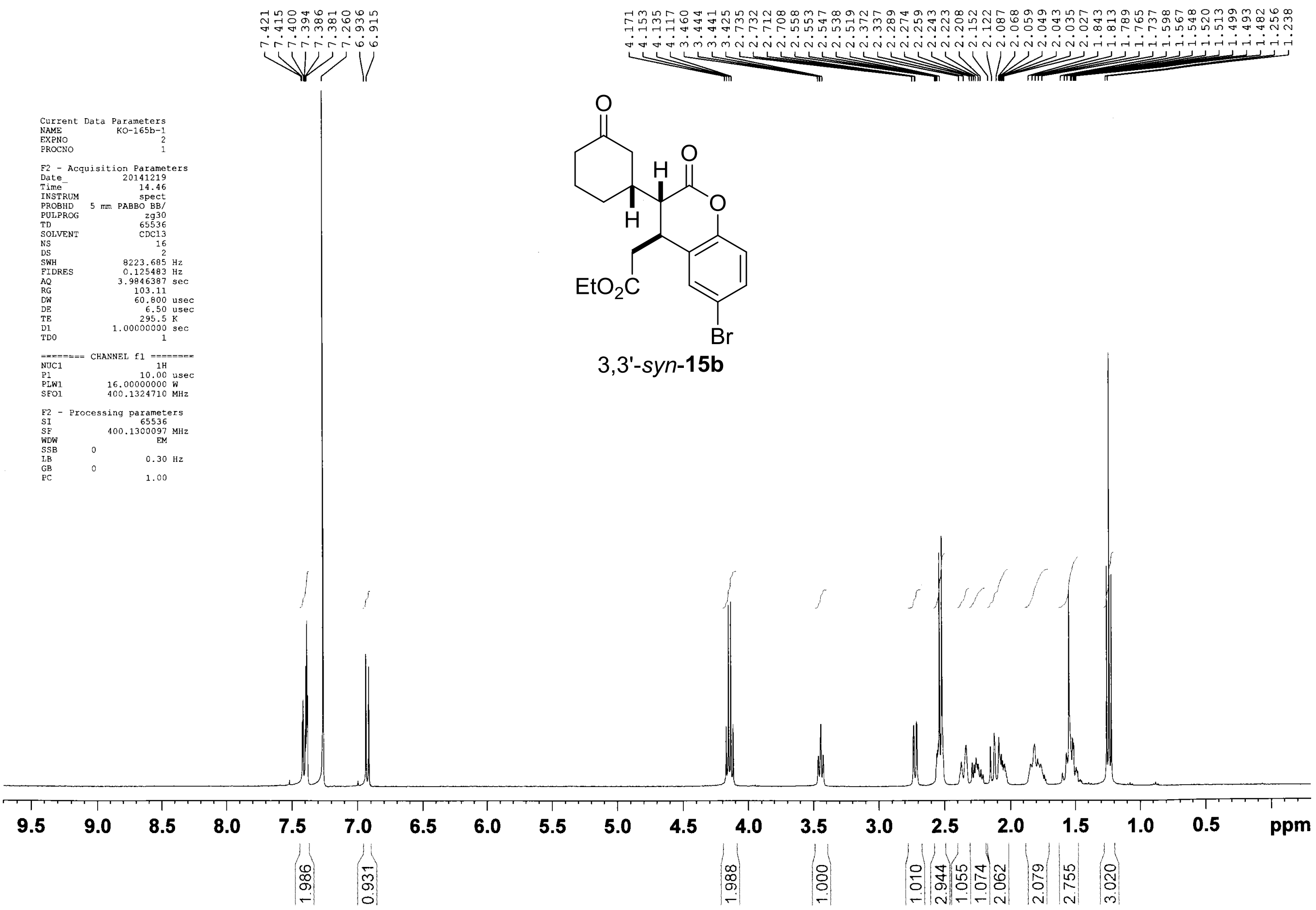
```
Current Data Parameters
NAME              KO-120a
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150401
Time                11.20
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     88
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                  297.8 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127722 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



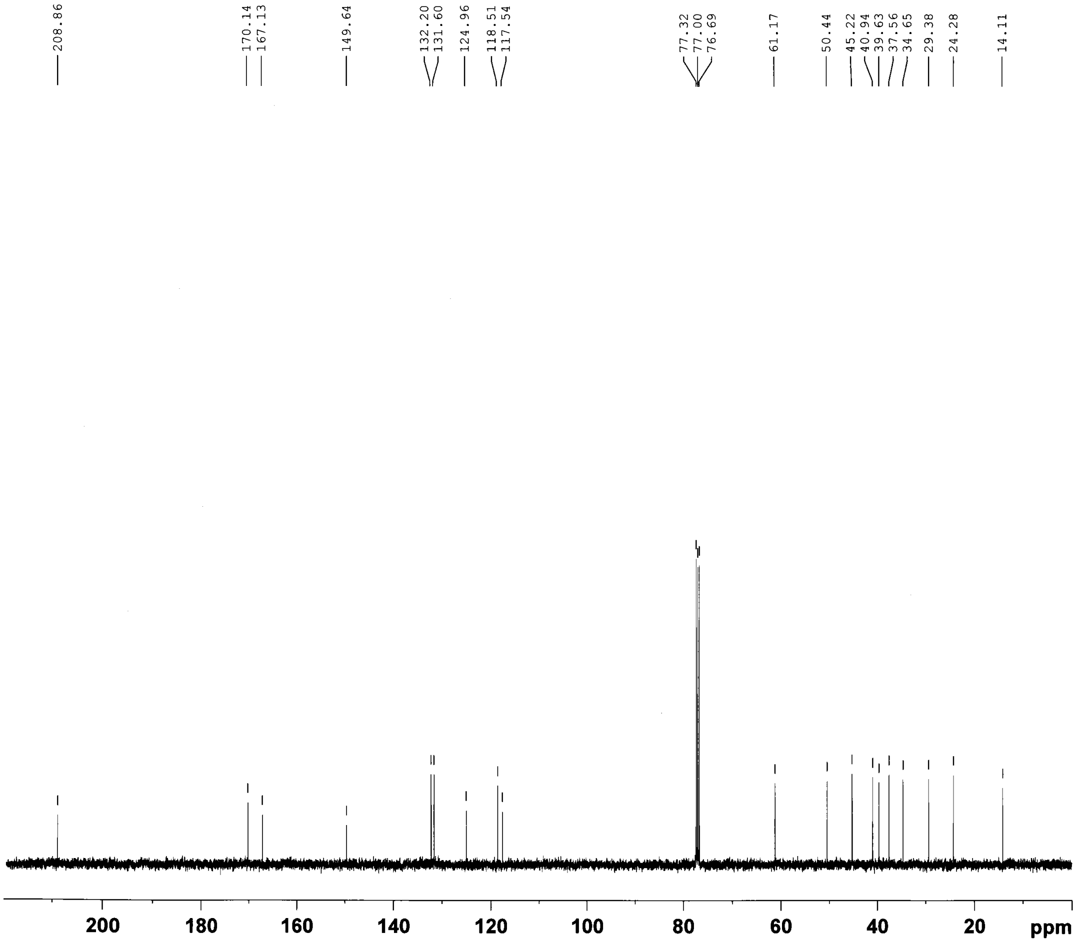
3,3'-*syn*-**15b**

```
Current Data Parameters
NAME          KO-165b-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20141219
Time              14.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG               103.11
DW               60.800 usec
DE                 6.50 usec
TE                295.5 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
```



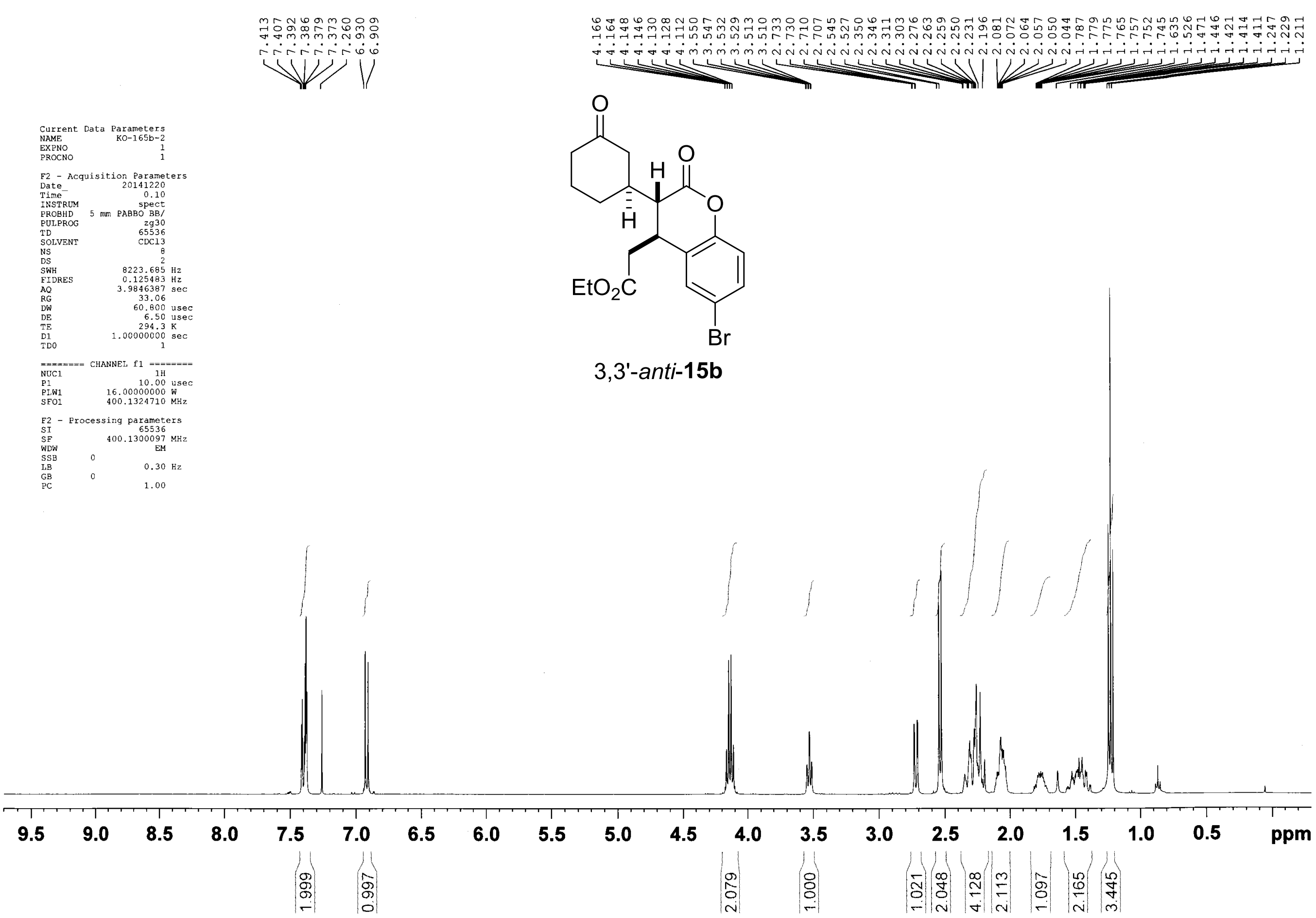
```
Current Data Parameters
NAME          KO-165b-1
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20141219
Time              23.38
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   39
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                294.7 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127739 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



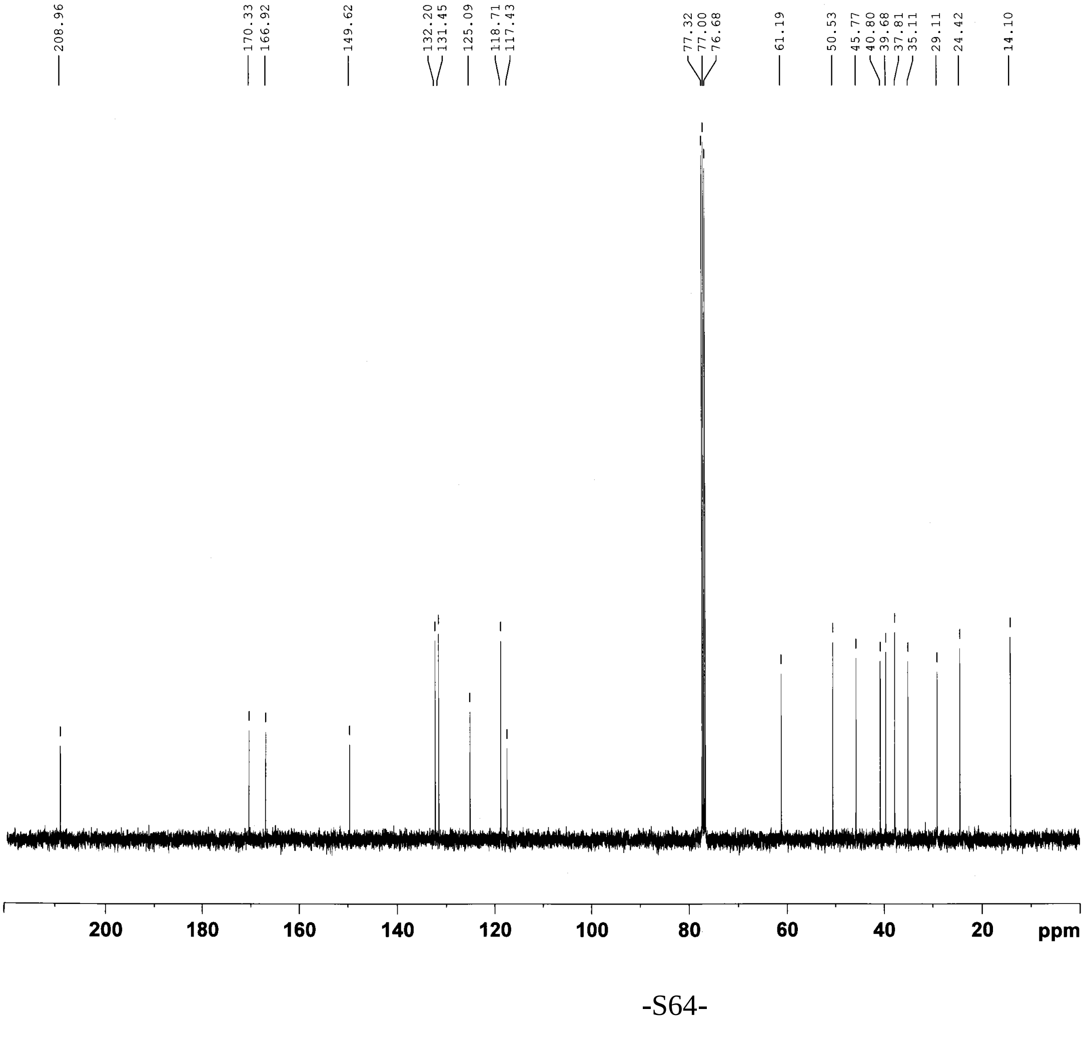
3,3'-*anti*-**15b**

```
Current Data Parameters
NAME            KO-165b-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20141220
Time                 0.10
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                  294.3 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
```



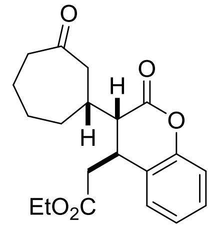
```
Current Data Parameters
NAME            KO-165b-2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20141220
Time                 0.15
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                  294.8 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127739 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



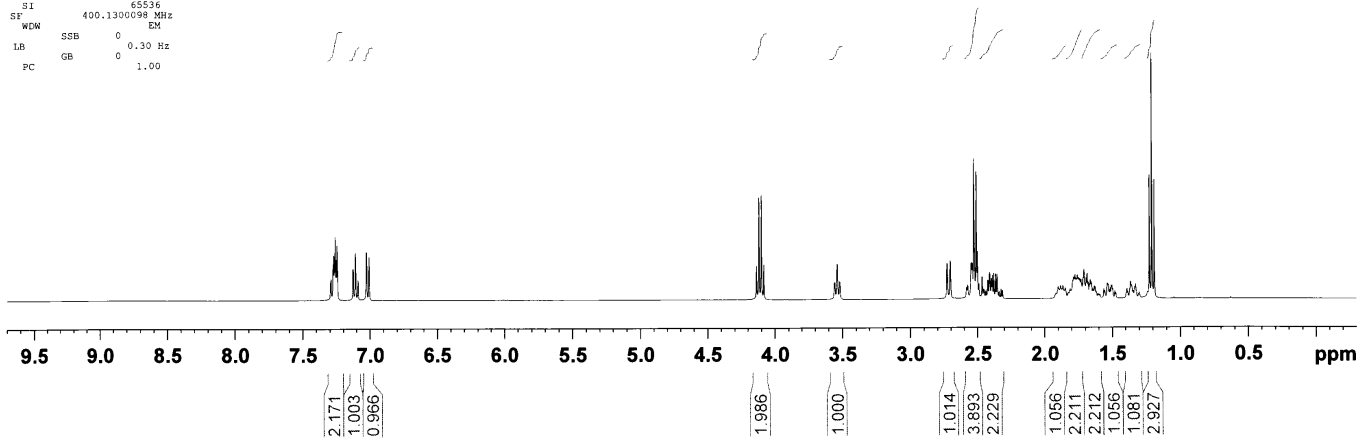
3,3'-*syn*-**16a**

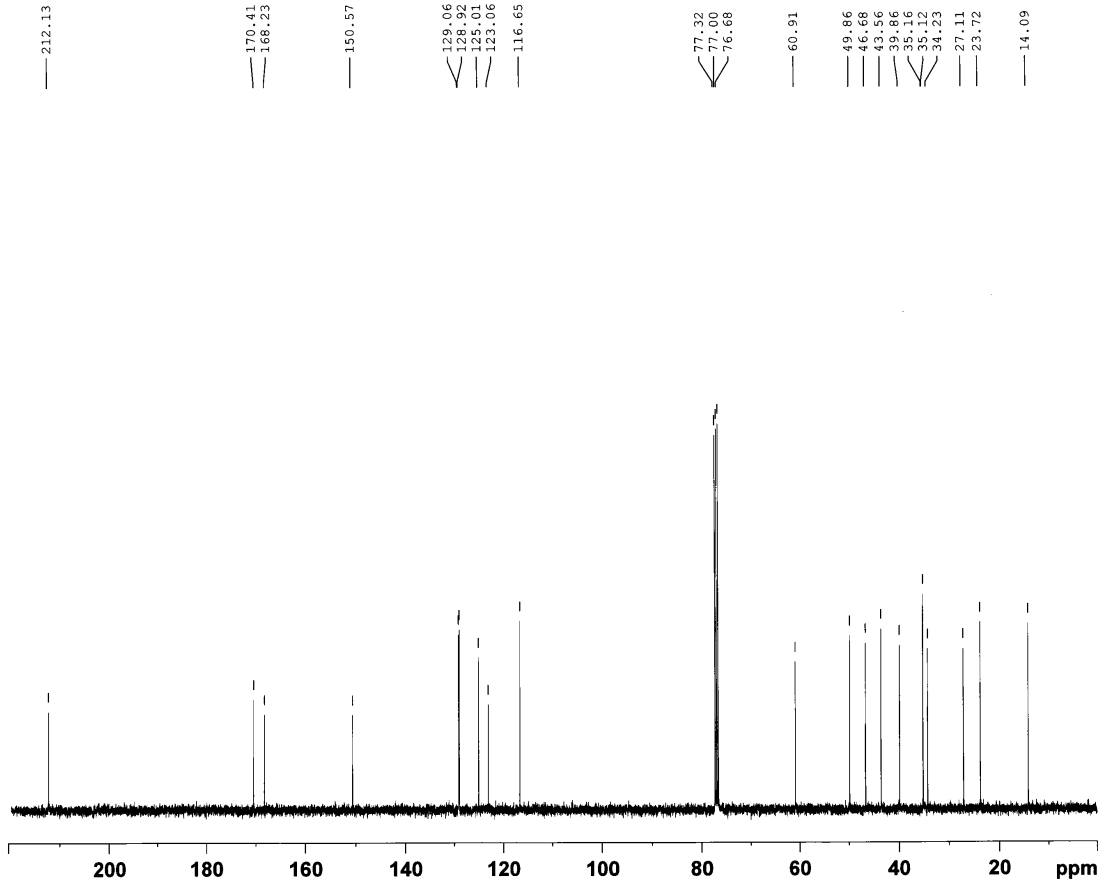
```
  Current Data Parameters
  NAME             KO-122a
  EXPNO                  1
  PROCNO                 1

F2 - Acquisition Parameters
  Date_           20150403
  Time               20.59
  INSTRUM            spect
  PROBHD   5 mm PABBO BB/
  PULPROG             zg30
  TD                 65536
  SOLVENT            CDCl3
  NS                     9
  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                  297.2 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
```





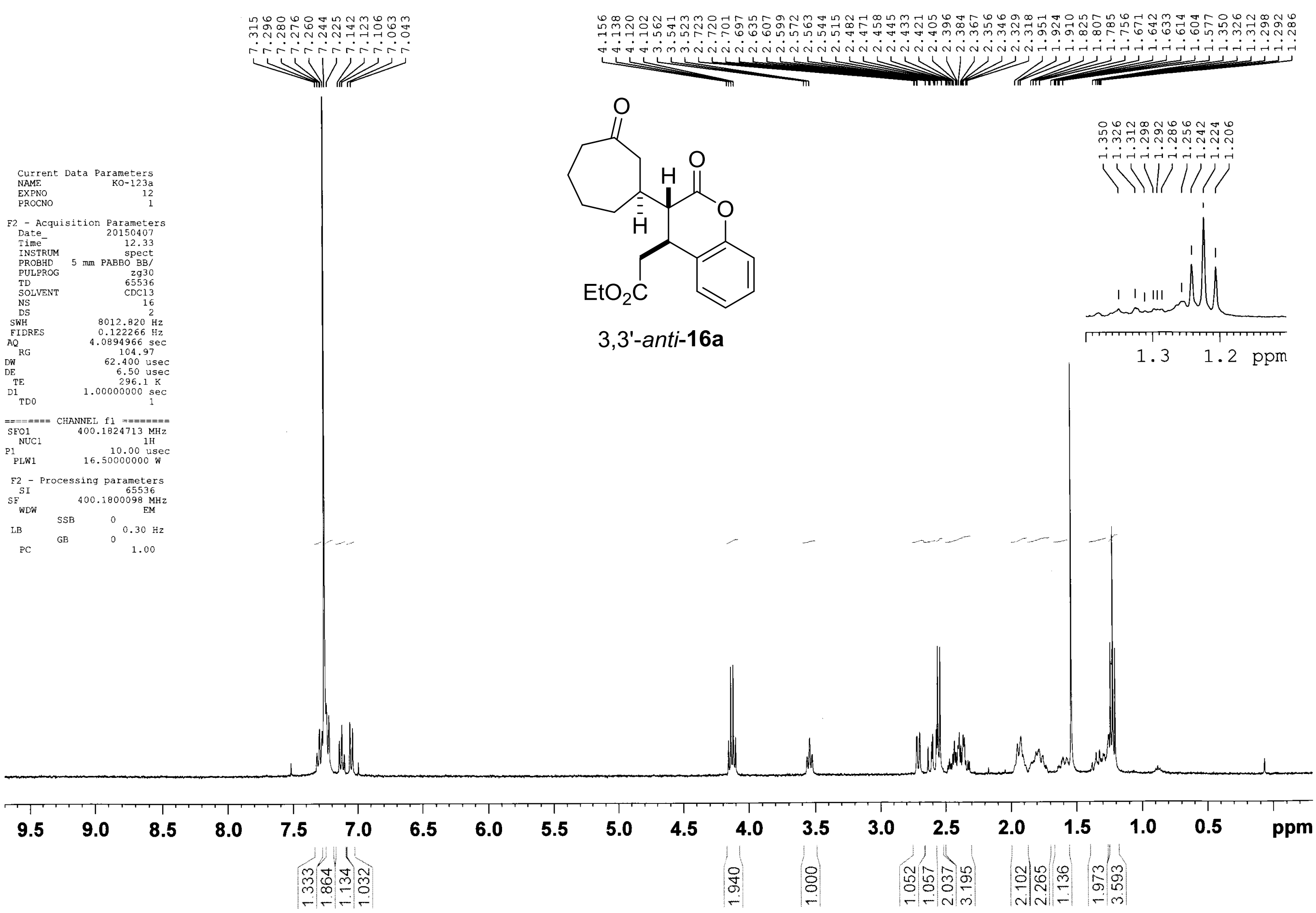
```
Current Data Parameters
NAME             KO-122a
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150403
Time               21.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    83
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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2         400.1316005 MHz

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



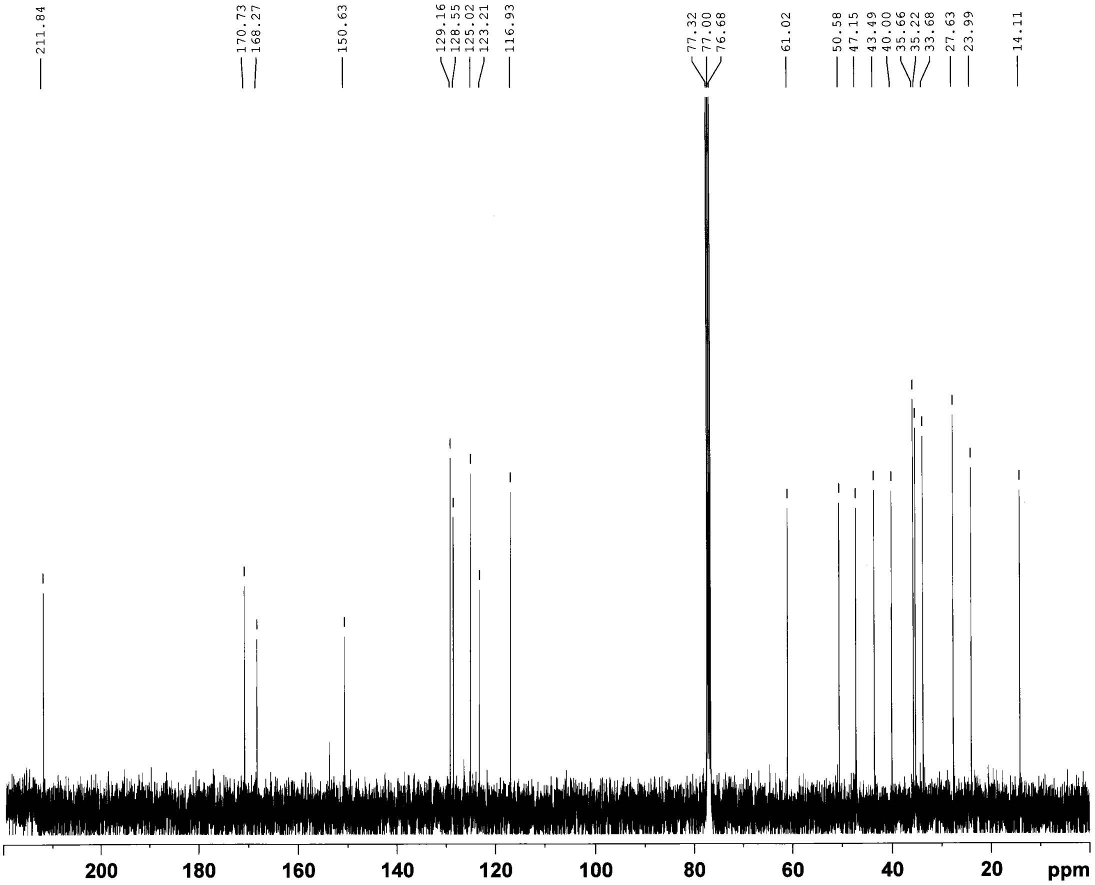
3,3'-*anti*-**16a**

```
Current Data Parameters
NAME             KO-123a
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150407
Time               12.33
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                104.97
DW                62.400 usec
DE                  6.50 usec
TE                 296.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1824713 MHz
NUC1                  1H
P1                 10.00 usec
PLW1         16.50000000 W

F2 - Processing parameters
SI                 65536
SF           400.1800098 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



```
Current Data Parameters
NAME             KO-123a
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               22.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   543
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                 297.8 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              90.00 usec
PLW2         16.00000000 W
PLW12         0.19753000 W
PLW13         0.16000000 W
SFO2         400.1316005 MHz

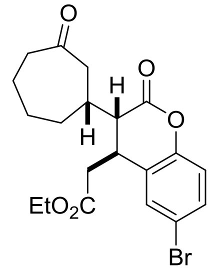
F2 - Processing parameters
SI                 32768
SF           100.6127707 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

```
Current Data Parameters
NAME          KO-234b-1
EXPNO                 1
PROCNO                1

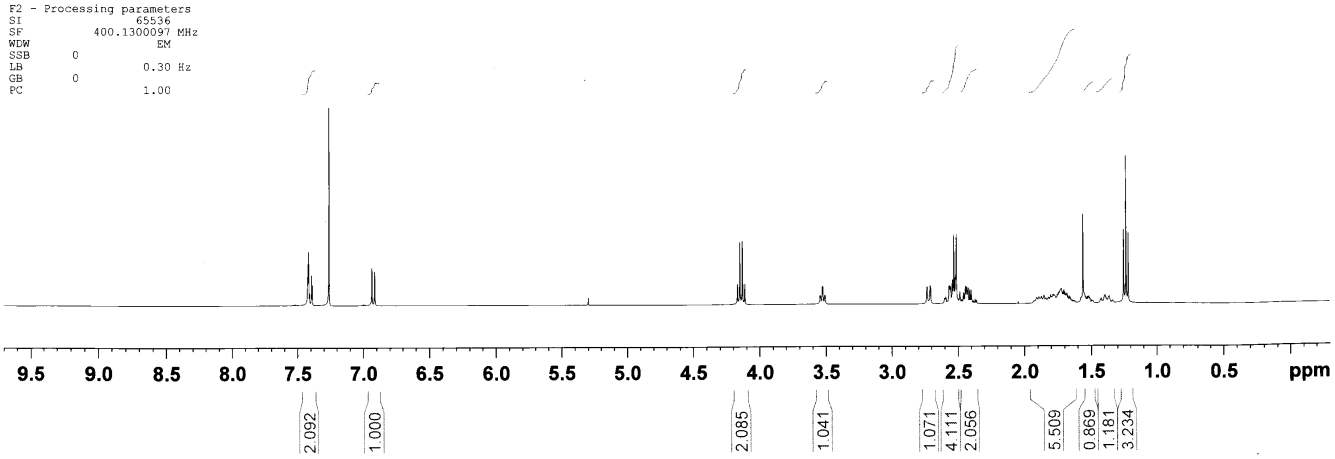
F2 - Acquisition Parameters
Date_          20150409
Time               0.31
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                91.18
DW               60.800 usec
DE                 6.50 usec
TE                294.9 K
D1           1.00000000 sec
TD0                   1

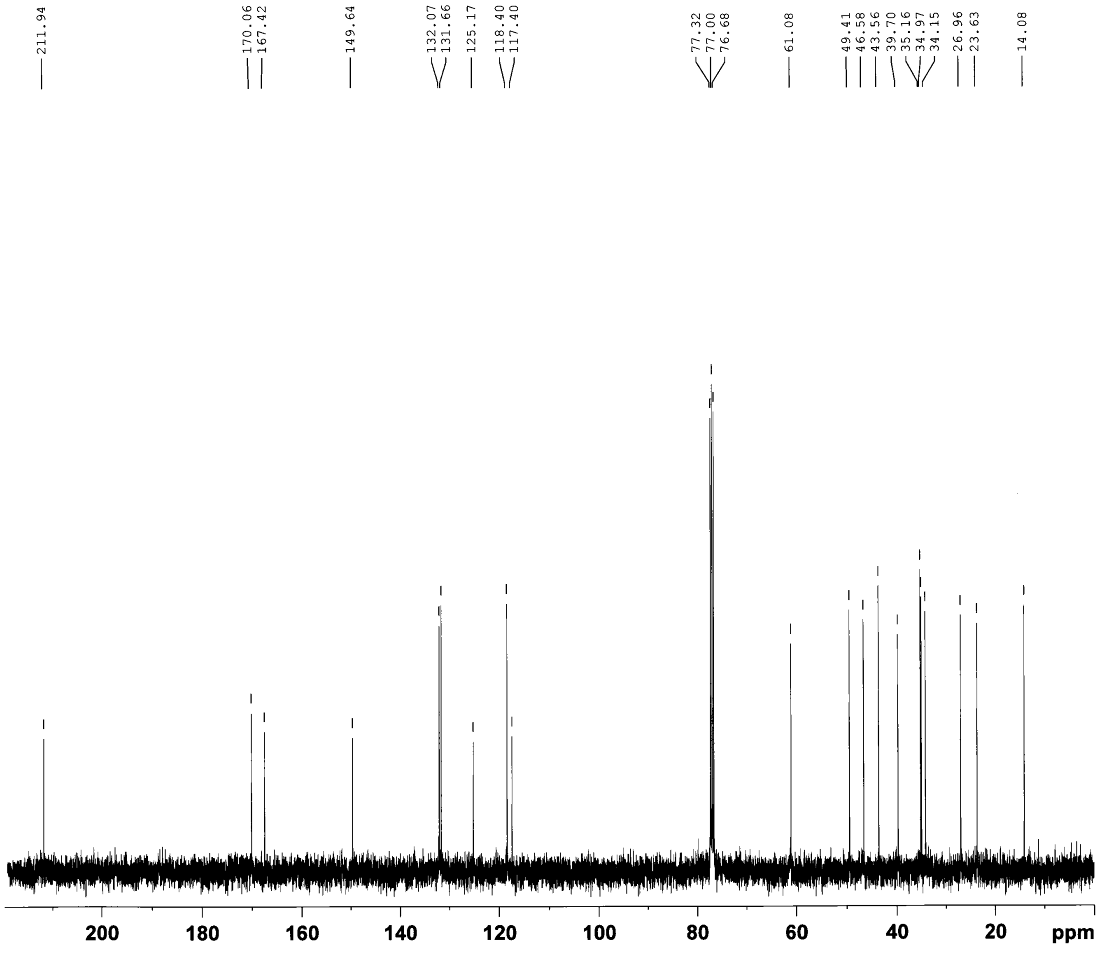
======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PLW1        16.00000000 W
SFO1        400.1324710 MHz

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



3,3'-*syn*-**16b**





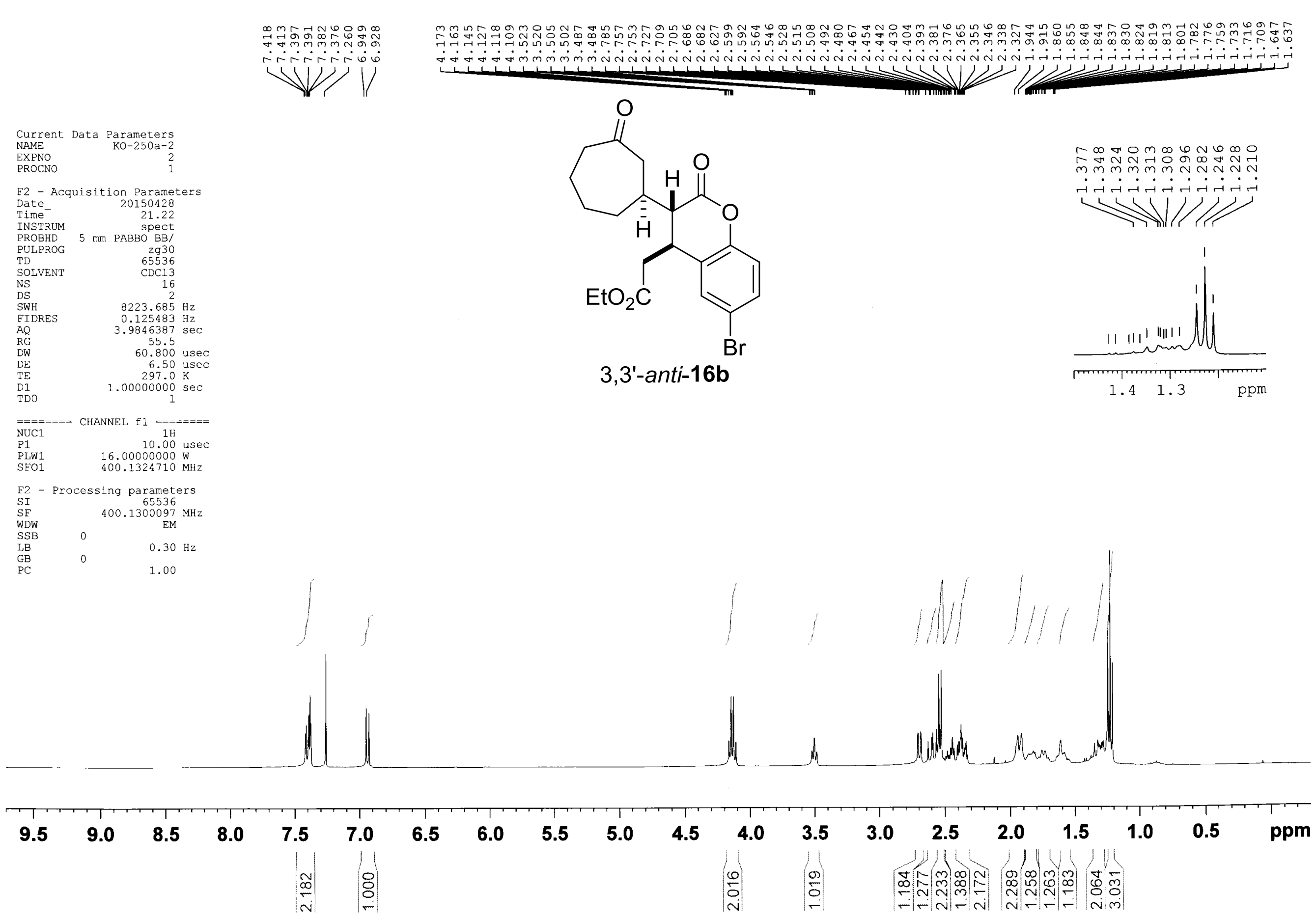
```
Current Data Parameters
NAME          KO-234b-1
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20150409
Time               3.12
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   49
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                295.3 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127766 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



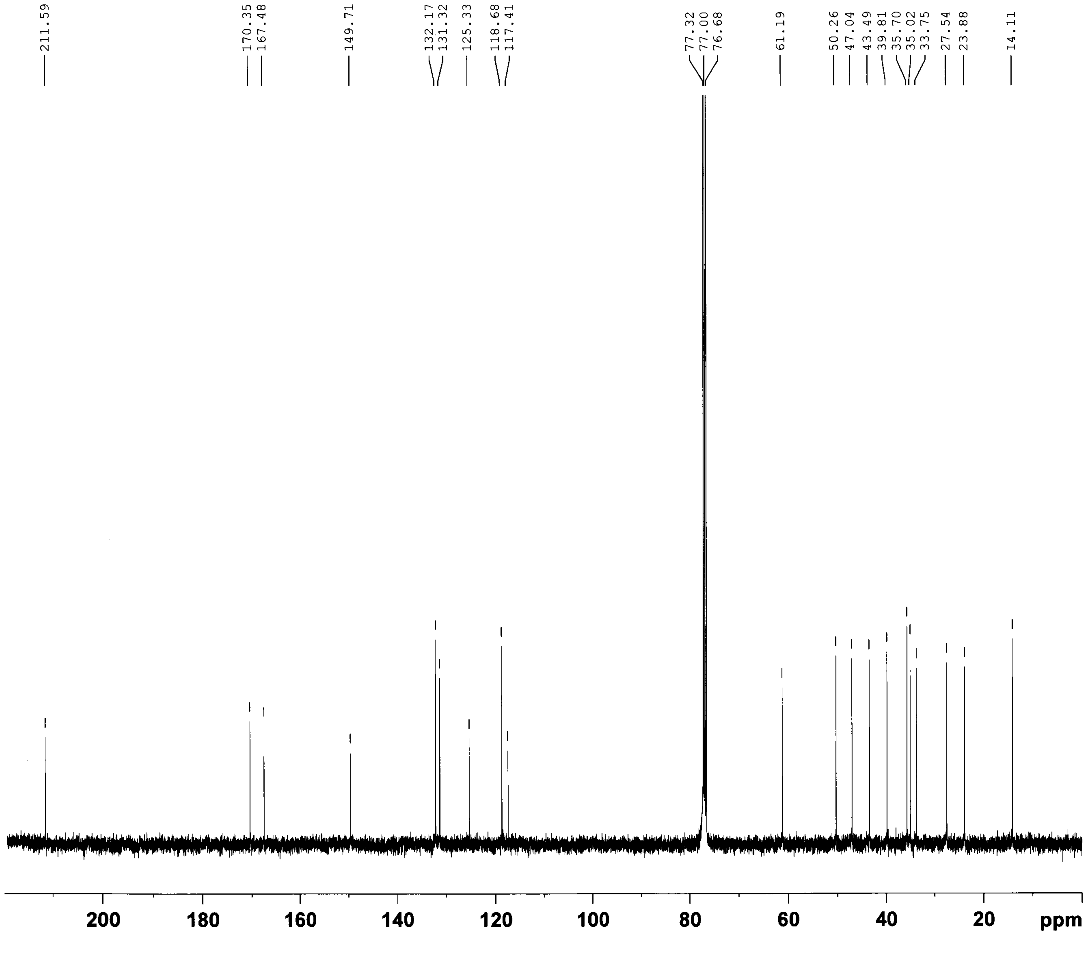
3,3'-*anti*-**16b**

```
Current Data Parameters
NAME          KO-250a-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150428
Time              21.22
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
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                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
```



```
Current Data Parameters
NAME          KO-250a-2
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150428
Time              21.53
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 W
SFO2        400.1316005 MHz

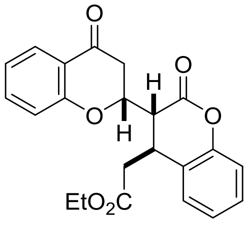
F2 - Processing parameters
SI                32768
SF          100.6127724 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

```
Current Data Parameters
NAME          KO-186d 2
EXPNO                 1
PROCNO                1

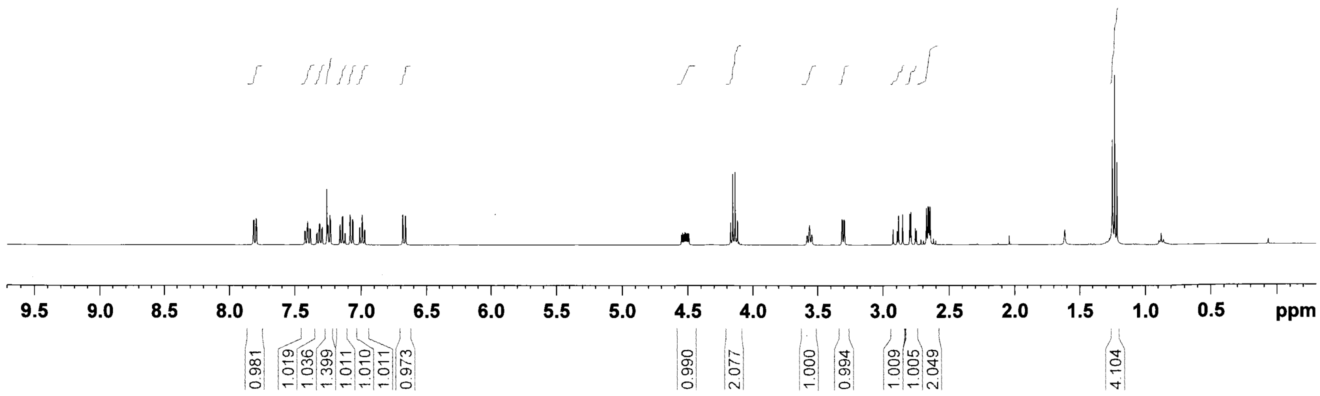
F2 - Acquisition Parameters
Date_          20150125
Time               0.07
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                    8
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                62.25
DW               60.800 usec
DE                 6.50 usec
TE                294.0 K
D1           1.00000000 sec
TD0                   1

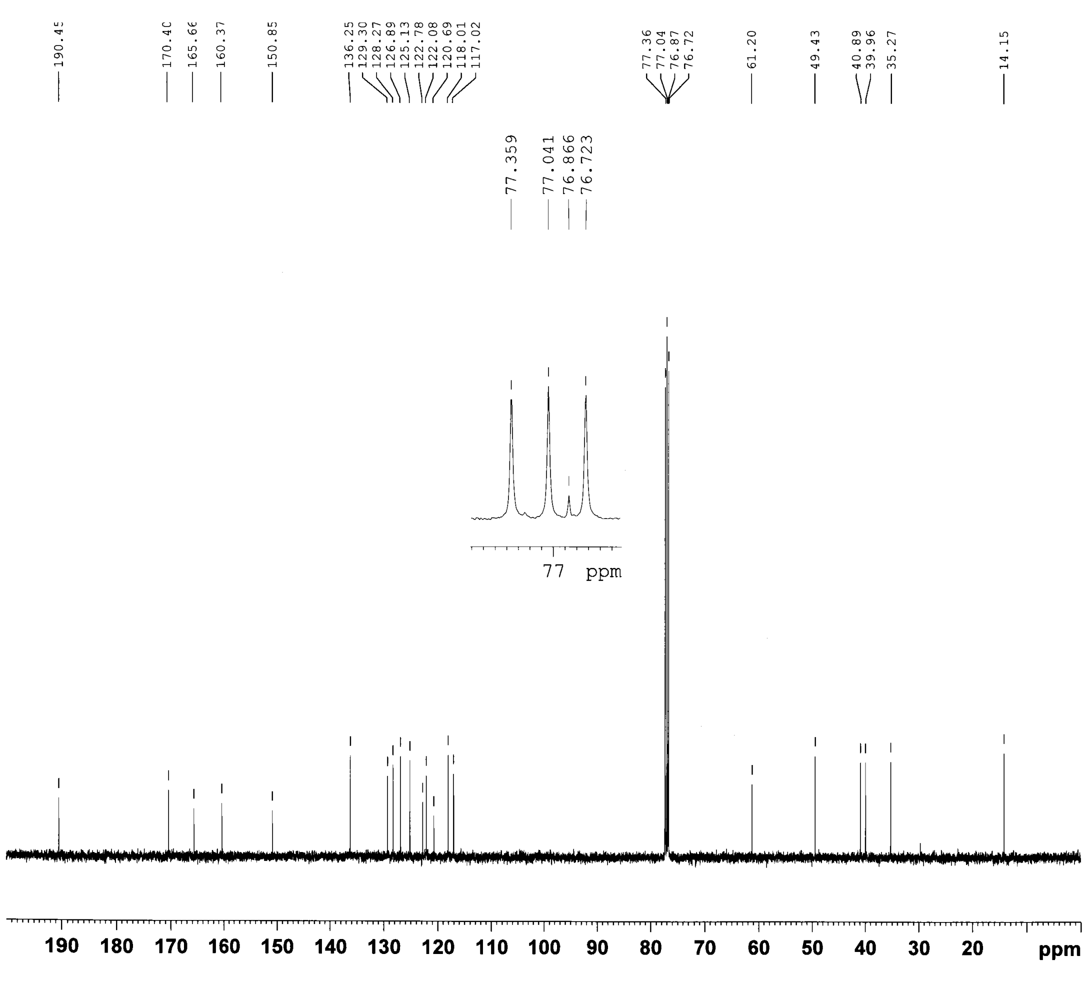
======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PLW1        16.00000000 W
SFO1        400.1324710 MHz

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



3,2'-*syn*-**17**





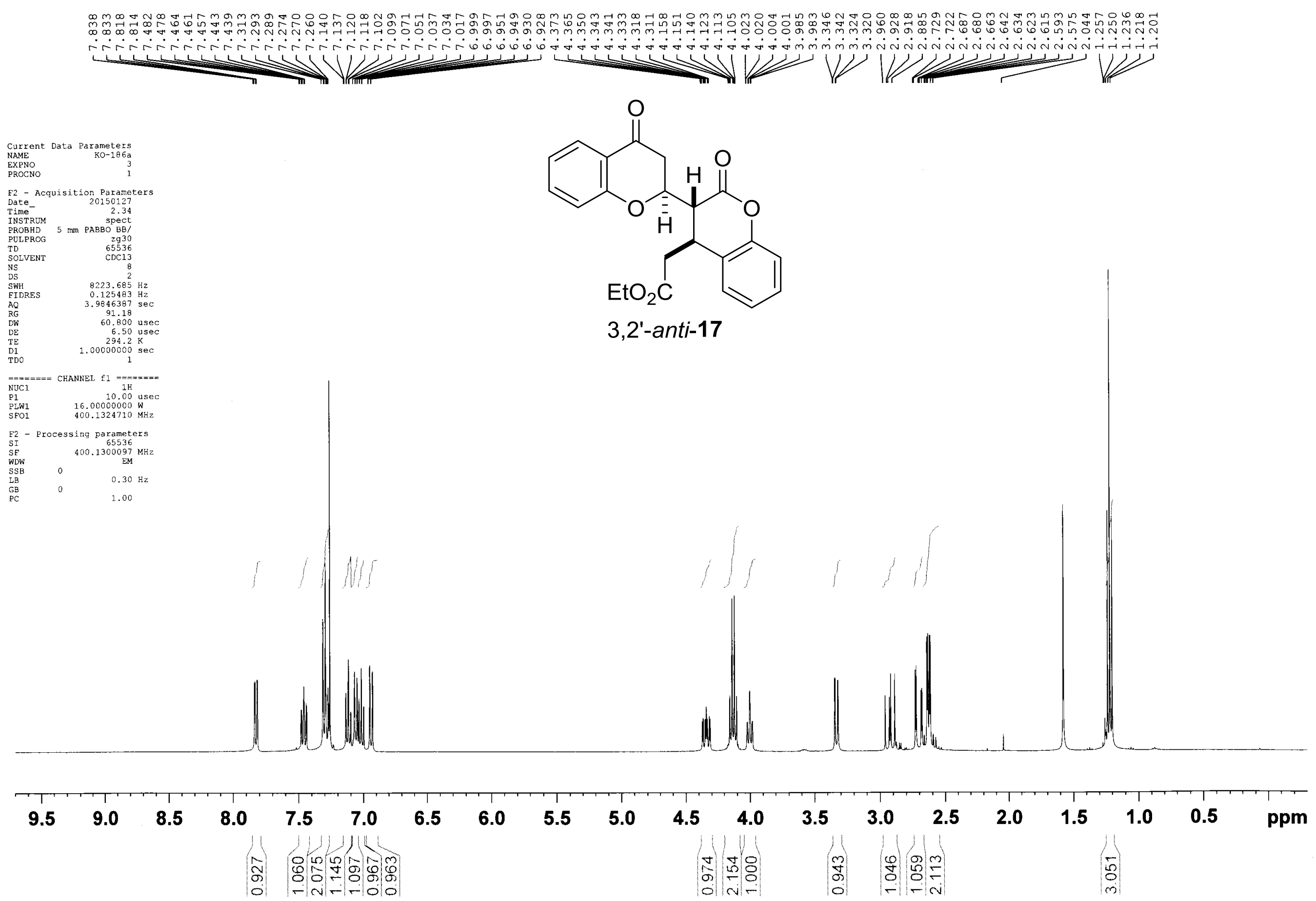
```
Current Data Parameters
NAME          KO-186d 2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150125
Time               0.15
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                  159
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                294.4 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             90.00 usec
PLW2        16.00000000 W
PLW12        0.19753000 W
PLW13        0.16000000 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
```



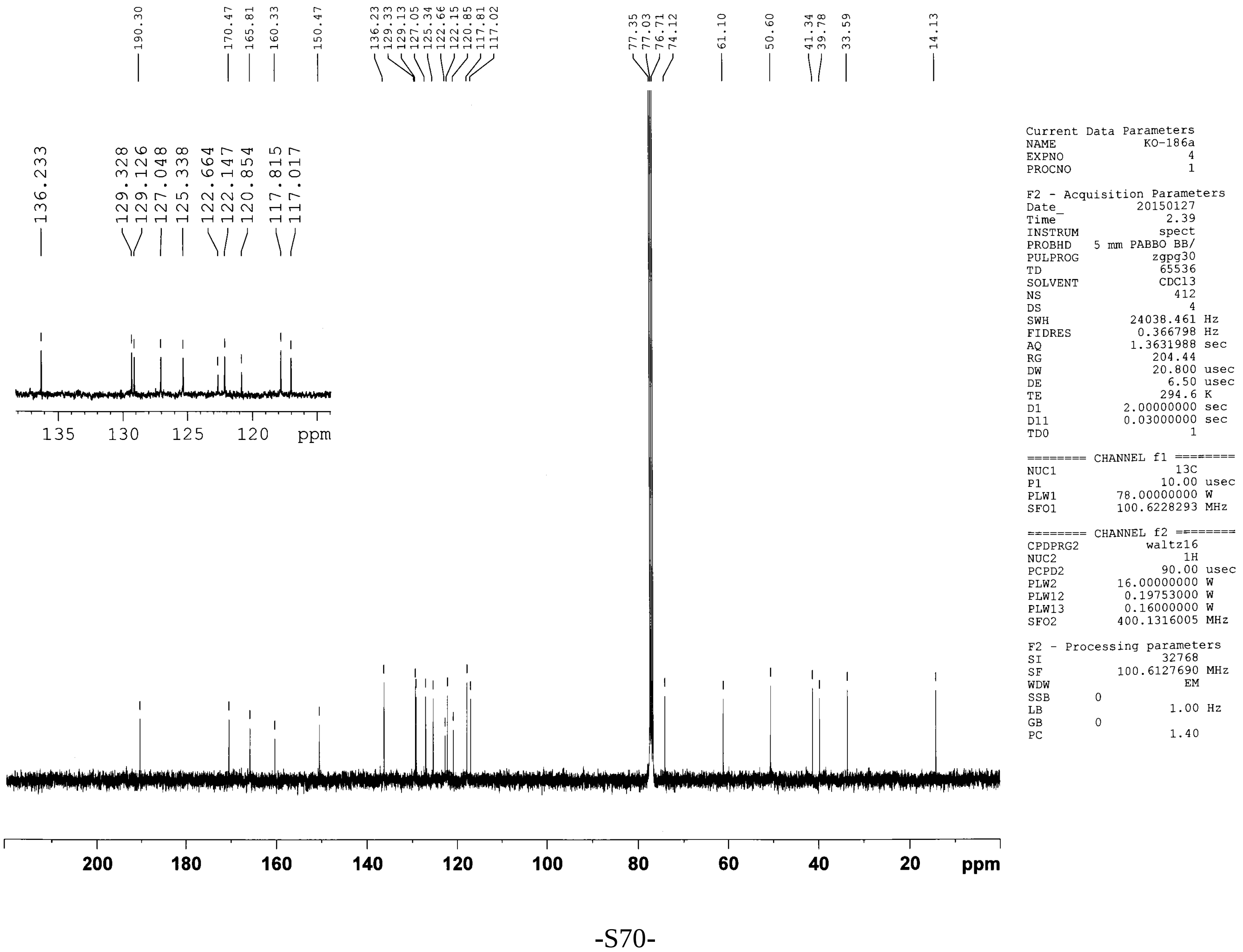
3,2'-*anti*-**17**

```
Current Data Parameters
NAME              KO-186a
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150127
Time                 2.34
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                  294.2 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
```



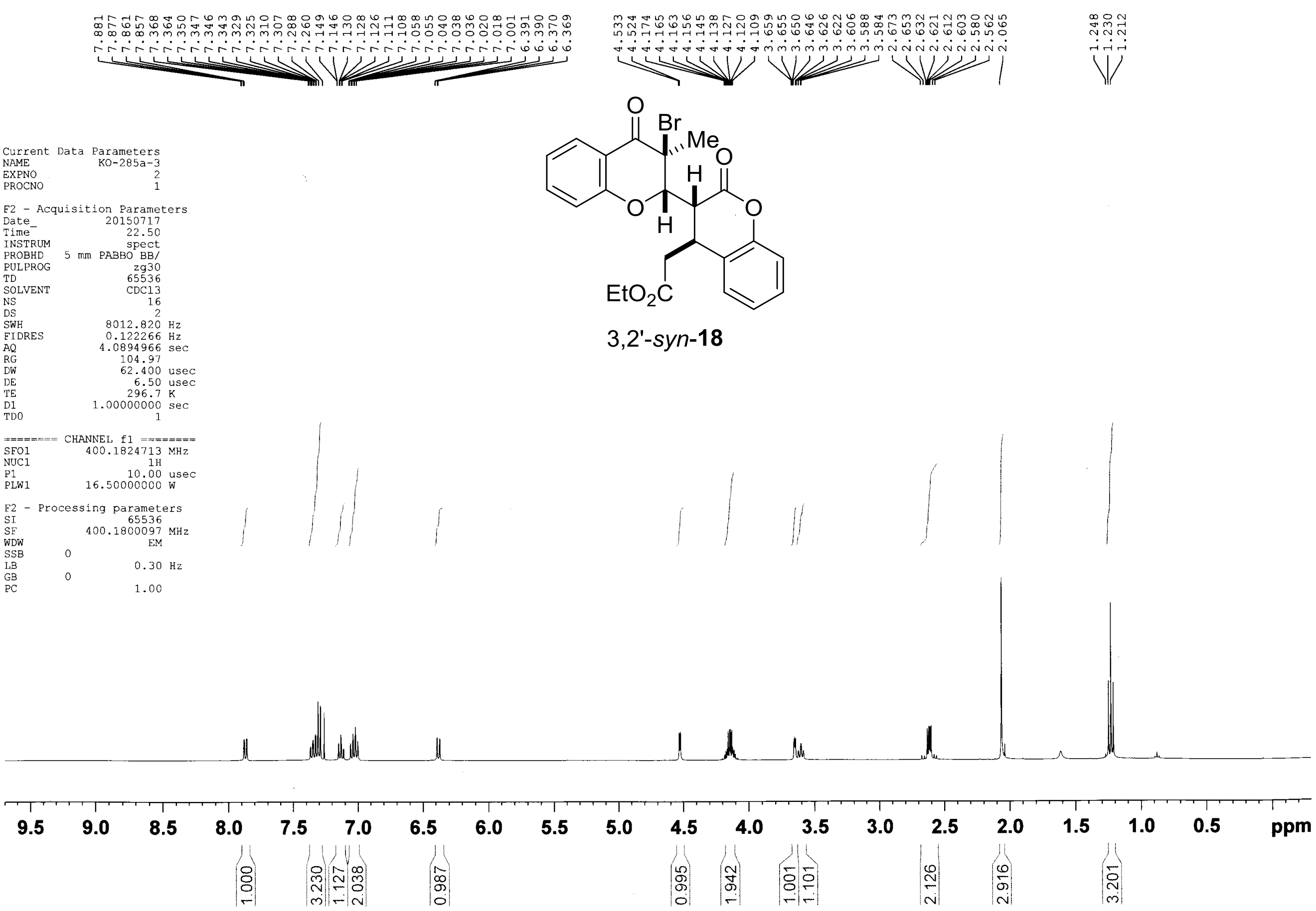
```
Current Data Parameters
NAME              KO-186a
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150127
Time                 2.39
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    412
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                  294.6 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               90.00 usec
PLW2          16.00000000 W
PLW12          0.19753000 W
PLW13          0.16000000 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
```



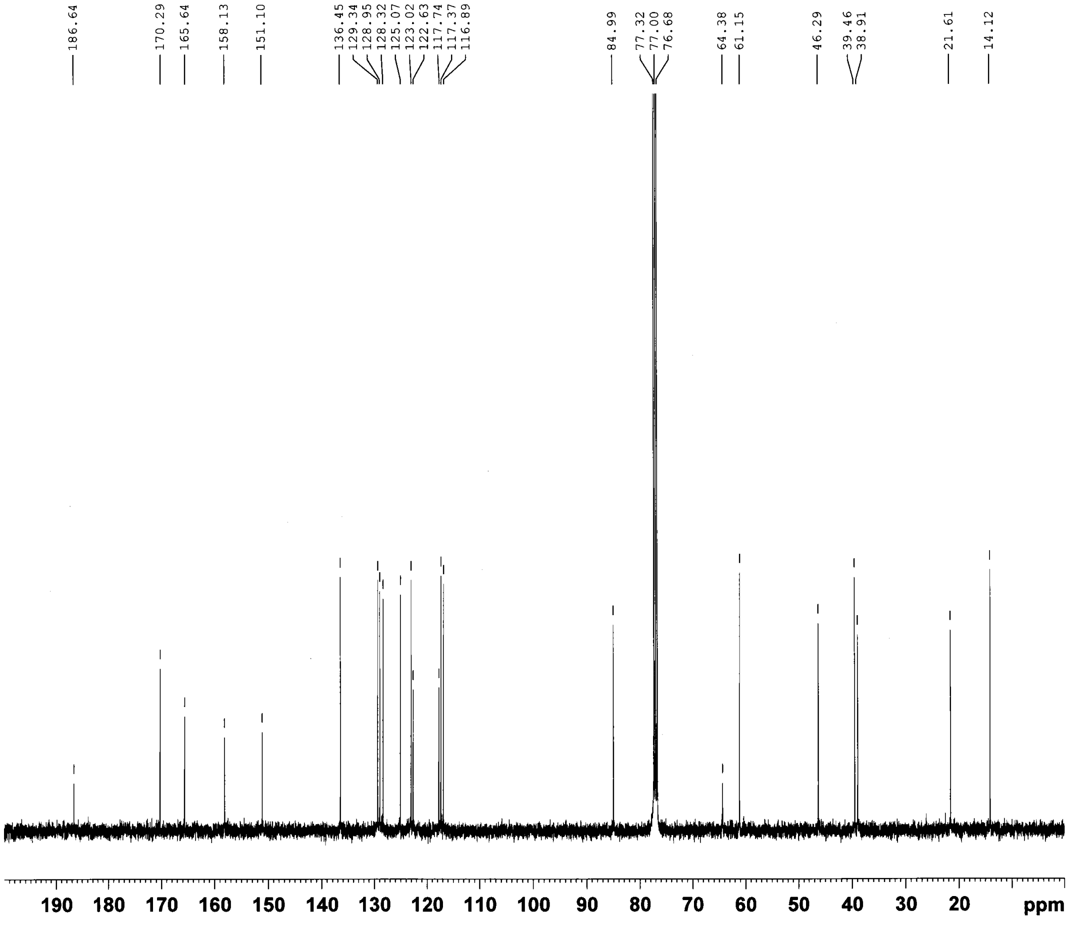
3,2'-*syn*-**18**

```
Current Data Parameters
NAME            KO-285a-3
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150717
Time                22.50
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 104.97
DW                 62.400 usec
DE                   6.50 usec
TE                  296.7 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1824713 MHz
NUC1                   1H
P1                  10.00 usec
PLW1          16.50000000 W

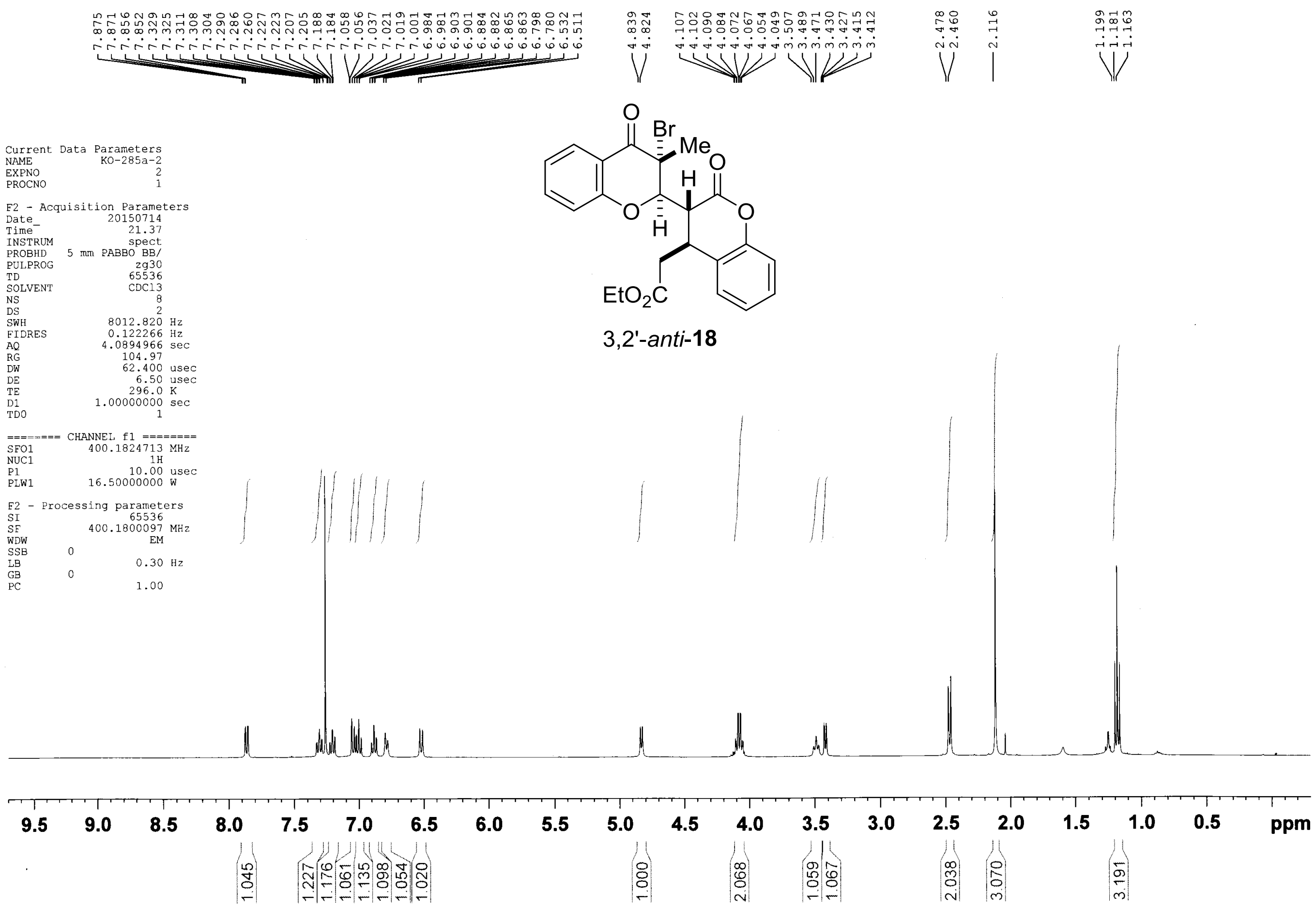
F2 - Processing parameters
SI                  65536
SF            400.1800097 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



```
Current Data Parameters
NAME            KO-285a-3
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150717
Time                22.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    499
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 206.25
DW                 20.800 usec
DE                   6.50 usec
TE                  297.6 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
NUC1                  13C
P1                  10.00 usec
PLW1          63.50000000 W
SFO1          100.6354031 MHz
CPDPRG2
NUC2                   1H
PLW2          16.50000000 W
PLW12          0.20370001 W
PLW13          0.16500001 W
SFO2          400.1816007 MHz

F2 - Processing parameters
SI                  32768
SF            100.6253452 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



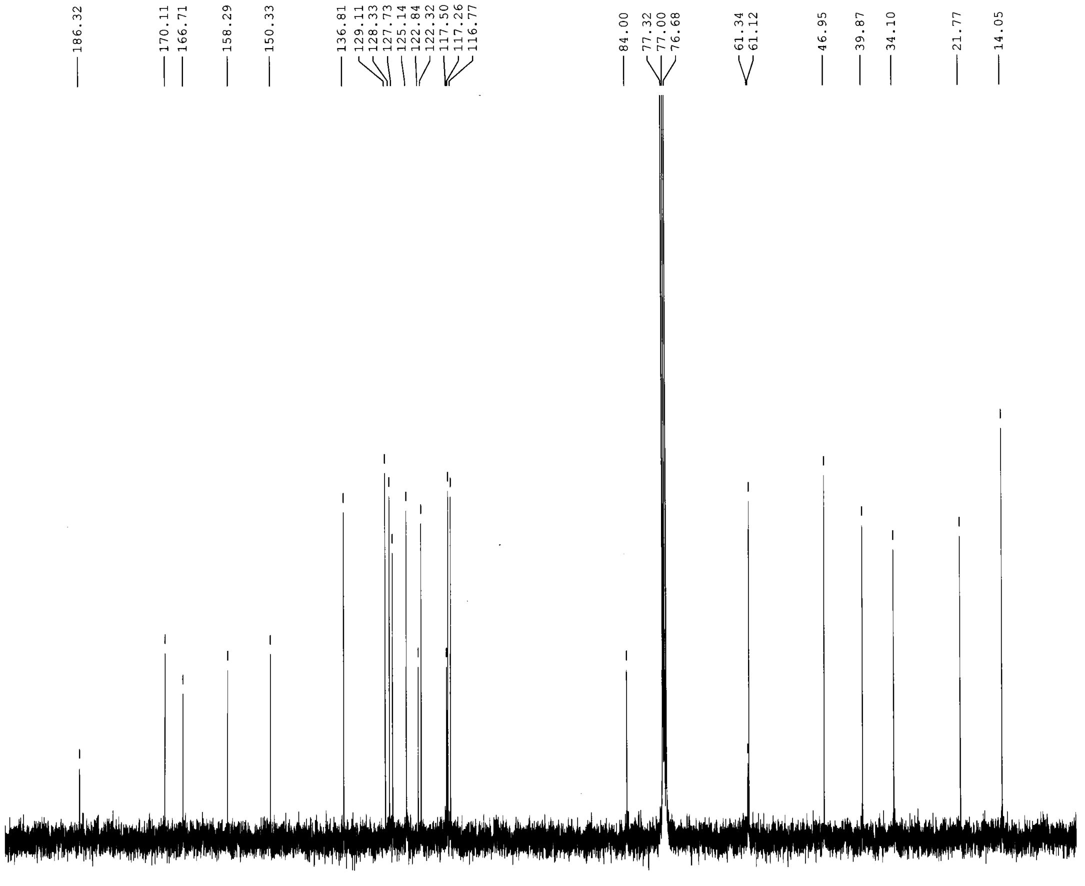
3,2'-*anti*-**18**

```
Current Data Parameters
NAME           KO-285a-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150714
Time               21.37
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                104.97
DW                62.400 usec
DE                  6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1824713 MHz
NUC1                  1H
P1                 10.00 usec
PLW1         16.50000000 W

F2 - Processing parameters
SI                 65536
SF           400.1800097 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



```
Current Data Parameters
NAME           KO-285a-2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150714
Time               21.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   331
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                206.25
DW                20.800 usec
DE                  6.50 usec
TE                 296.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1
NUC1                 13C
P1                 10.00 usec
PLW1         63.50000000 W
SFO1         100.6354031 MHz
CPDPRG2
NUC2                  1H
PLW2         16.50000000 W
PLW12         0.20370001 W
PLW13         0.16500001 W
SFO2         400.1816007 MHz

F2 - Processing parameters
SI                 32768
SF           100.6253445 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

8. References

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