Supporting Informations

$Pd^{(II)}/CuBr_2$ catalysed keto α-C_{sp3}–H benzoxylation of *N*,*N*-dialkylamides directed by *o*-hydroxy groups

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Contents:

Instrumentation and Chemicals:

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H NMR (400

and 600 MHz) $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 and 150 MHz). MS spectra were recorded using ESI mode. IR spectra were recorded in KBr or neat.

Crystallographic Description:

Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite monochromatedMoKα radiation (λ = 0.71073 Å) at 298 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in SHELX-97[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. colourless crystals were isolated in rectangular shape from acetonitrile at room temperature.

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
b. SAINT V 4.035 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
c. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997.

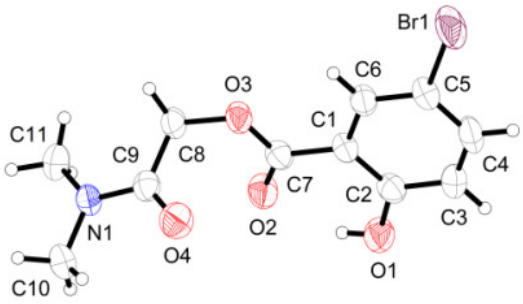
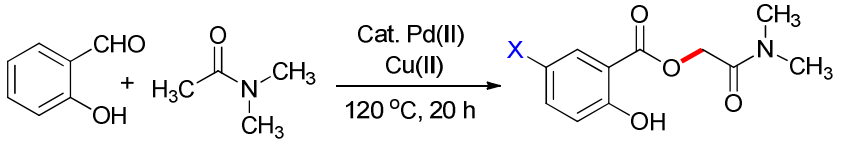


Fig. S1 Ortep view of compound (**1a**).

CCDC number for compound 1a: CCDC 1429212. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Crystallographic description of 1a: Crystal dimension (mm): 0.38 x 0.24 x 0.22. $C_{11}H_{12}BrNO_4$, Mr = 302.13. monoclinic, space group p 21/n; a = 5.4464 (3) Å, b = 8.7160 (5) Å, c = 25.2572 (4) Å; $\alpha = 90^o$, $\beta = 91.713$ (2) ^{o}, $\gamma = 90^o$, V = 1198.44 (12) $Å^3$; Z = 4; ρ_{cal}= 1.674 g/cm^3; μ (mm^{-1}) = 3.432; *F (000)* = 608.0; Reflection collected / unique = 2071 / 2164; Refinement method = Full-matrix least-squares on F^2; Final R indices [I>2σ_I] R1 = 0.0402, wR2 = 0.0928, R indices (all data) R1 = 0.0779, wR2 = 0.1047; goodness of fit = 1.039.

Table S1 Screening of reaction conditions[a,b]



(1) (a) X = H, (**1a'**); X = Br, (**1a**); X = Cl, (**1a''**)

Entry	Catalyst (mol%)	Oxidant (equiv.)	Yield (%) (**1a/1a′/1a′′**)
1	-	$Cu(OAc)_2$ (1 equiv.)	00/00/00
2	$Pd(OAc)_2$ (5.0)	$Cu(OAc)_2$ (1 equiv.)	00/12/00
3	$Pd(OAc)_2$ (5.0)	$CuBr_2$ (1 equiv.)	64/00/00
4	$Pd(OAc)_2$ (5.0)	$CuCl_2$ (1 equiv.)	00/00/40
5	$PdCl_2$ (5.0)	$CuBr_2$ (1 equiv.)	54/00/trace
6	$PdBr_2$ (5.0)	$CuBr_2$ (1 equiv.)	58/00/00
7	$Pd(TFA)_2$ (5.0)	$CuBr_2$ (1 equiv.)	62/00/00
8	**$Pd(OAc)_2$ (5.0)**	**$CuBr_2$ (1.2 equiv.)**	**72/00/00**
9	-	$CuBr_2$ (1.2 equiv.)	00/00/00
10	$Pd(OAc)_2$ (5.0)	-	00/00/00
11	$Pd(OAc)_2$ (10.0)	$CuBr_2$ (1.2 equiv.)	75/00/00

[a] Reaction conditions: salicylaldehyde (0.5 mmol), DMA (1 mL) and Cu-salts(0.5 mmol and 0.6 mmol) at 120 ^{o}C for 20 h. [b]Isolated yield.

Experimental procedure:

*Synthesis of 2-(dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (**1a**) from 2-hydroxybenzaldehyde (**1**).*

To an oven-dried 10 mL round bottom flask were added sequentially 2-hydroxybenzaldehyde (**1**) (0.061 g, 0.5 mmol), $CuBr_2$ (0.134 g, 0.6 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol) and *N*,*N*-dimethylacetamide (1.0 mL). The reaction mixture was then heated in an oil bath preheated at 120 ^oC. After completion of the reaction (20 h) the crude product was admixed with ethyl acetate (25 mL) and the organic layer was washed with saturated sodium bicarbonate solution (2 x 5 mL), dried over anhydrous sodium sulphate (Na_2SO_4), and evaporated under reduced pressure. The crude product so obtained was purified by silica gel column chromatography (hexane / ethyl acetate, 8:2) to give pure 2-(dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (**1a**) (0.109 g, yield 72%). The identity and purity of the product was confirmed by spectroscopic analysis.

Mechanistic Investigation:

^{1}H NMR study for the detection of reaction intermediates during α-bromo-esterification of 5-chlorosalicylaldehyde (3)

In order to detect the intermediate species in the reaction mixture for this α-bromo-esterification ^{1}H NMR spectroscopy was performed. In this study, an oven-dried flask was charged with 5-chlorosalicylaldehyde (**3**) (0.078g, 0.5 mmol), $CuBr_2$ (0.134g, 0.6 mmol), $Pd(OAc)_2$ (0.006g, 0.025 mmol) and *N*,*N*-dimethylacetamide (1.0 mL). Then the reaction mixture was stirred in an oil bath at 120 ^oC. After 1 h of reaction, aliquot (100 μL) was withdrawn and crude product was extracted with ethyl acetate (5 mL) and evaporated under reduced pressure. The crude product so obtained was used for ^{1}H NMR study in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz). In the ^{1}H NMR spectra both brominated (**3A**) and non brominated 5-chlorosalicylaldehyde (**3**) were observed. After 3 h α-bromo-esterification product (**3a**) and α-esterification product (**3a´**) formation were observed. However, during progress of the reaction α-bromo-esterification product (**3a**) formation was increased faster compare to α-esterification product (**3a´**) formation. This is taken as the representative example.

^{1}H NMR study during α-bromo-esterification of 5-Chlorosalicylaldehyde (3) at different time interval: ^{1}H NMR ($CDCl_3$, 400 MHz)

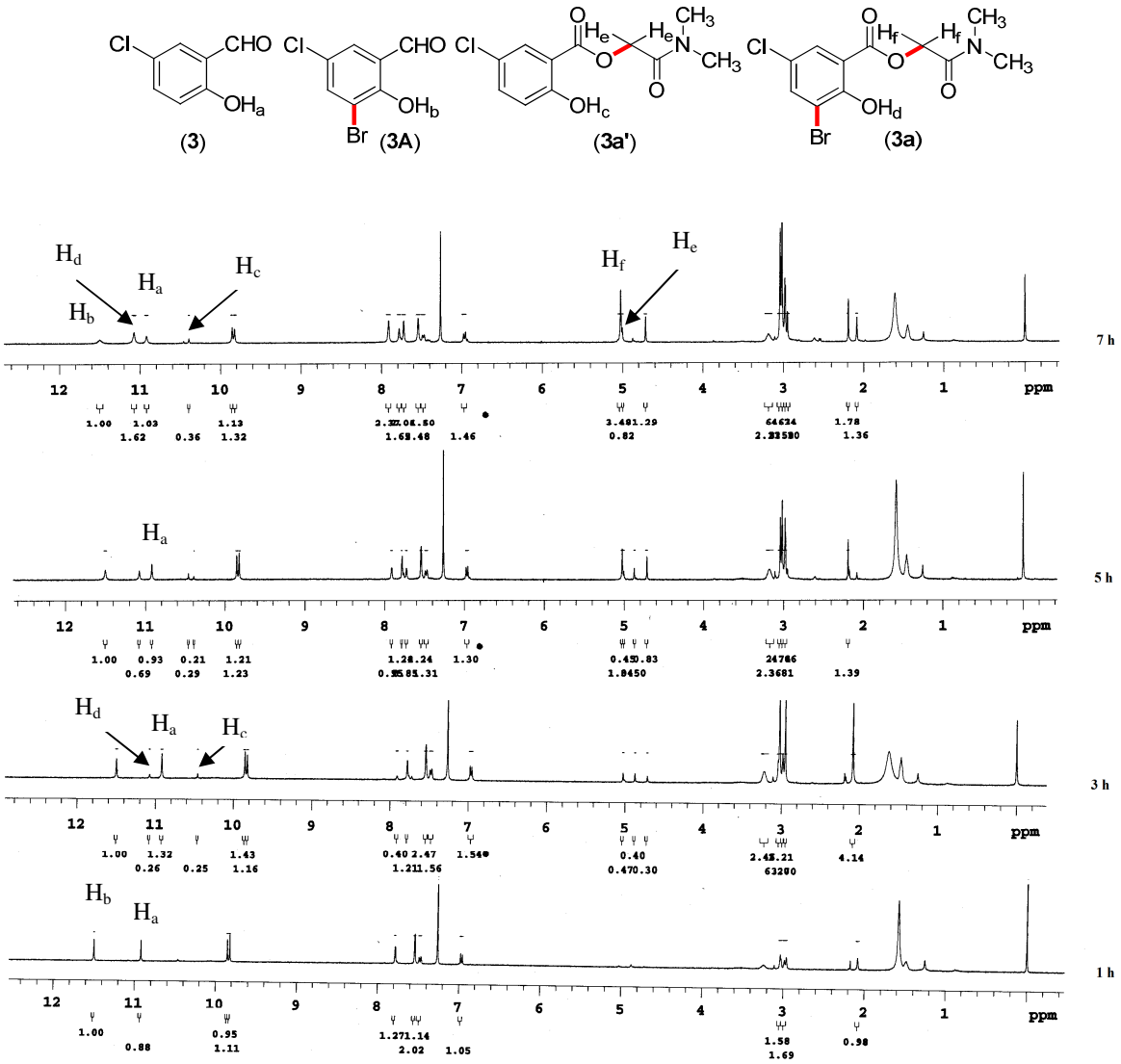


Fig. S2 Progress of the reaction monitored by ^{1}H NMR.

HRMS Spectra of ester (1a) from $H_2{}^{18}O$ labelling experiment:

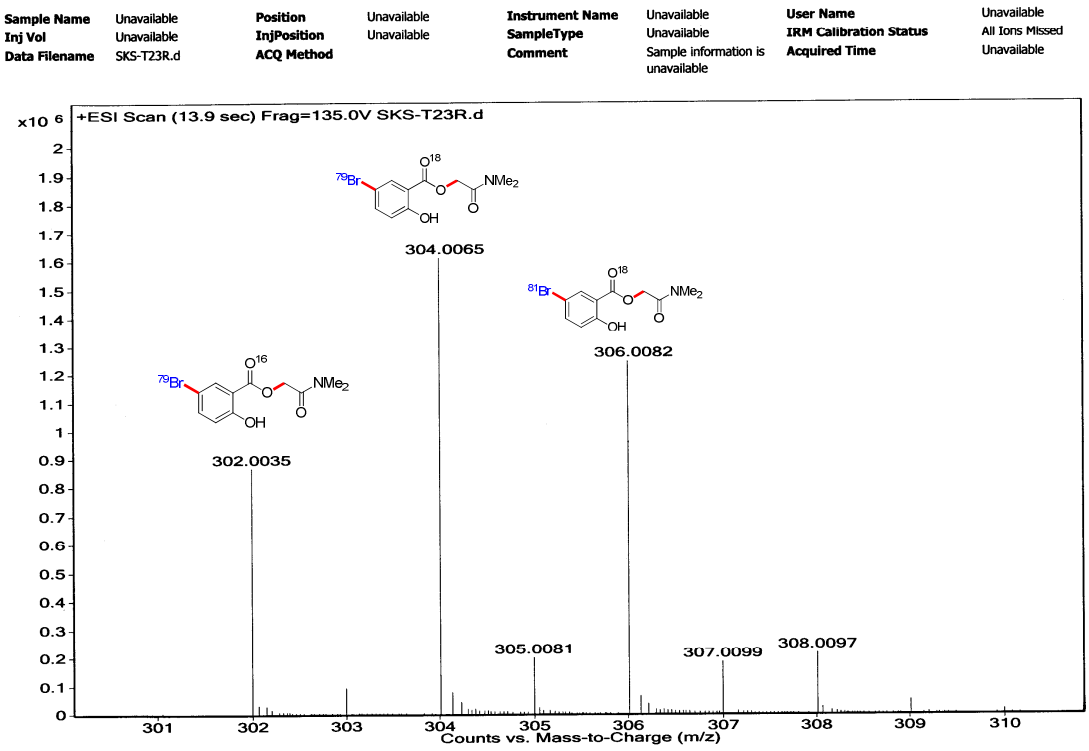


Fig. S3 HRMS spectrum of ^{18}O labeled (**1a**), water as the source of ^{18}O.

$^{18}O_2$ Labelling experiment:

To an oven-dried 10 mL round bottom flask were added sequentially 2-hydroxybenzaldehyde (**1**) (0.061 g, 0.5 mmol), $CuBr_2$ (0.134 g, 0.6 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol) and *N*,*N*-dimethylacetamide (1.0 mL). The reaction was carried out in $^{18}O_2$ atmosphere. After completion of the reaction (20 h) the crude product was admixed with ethyl acetate (25 mL) and the organic layer was washed with saturated sodium bicarbonate solution (2 x 5 mL), dried over anhydrous sodium sulphate (Na_2SO_4), and evaporated under reduced pressure. The identity of the product was confirmed by HRMS analysis (Fig. S4).

HRMS Spectra of ester (1a) from $^{18}O_2$ labelling experiment:

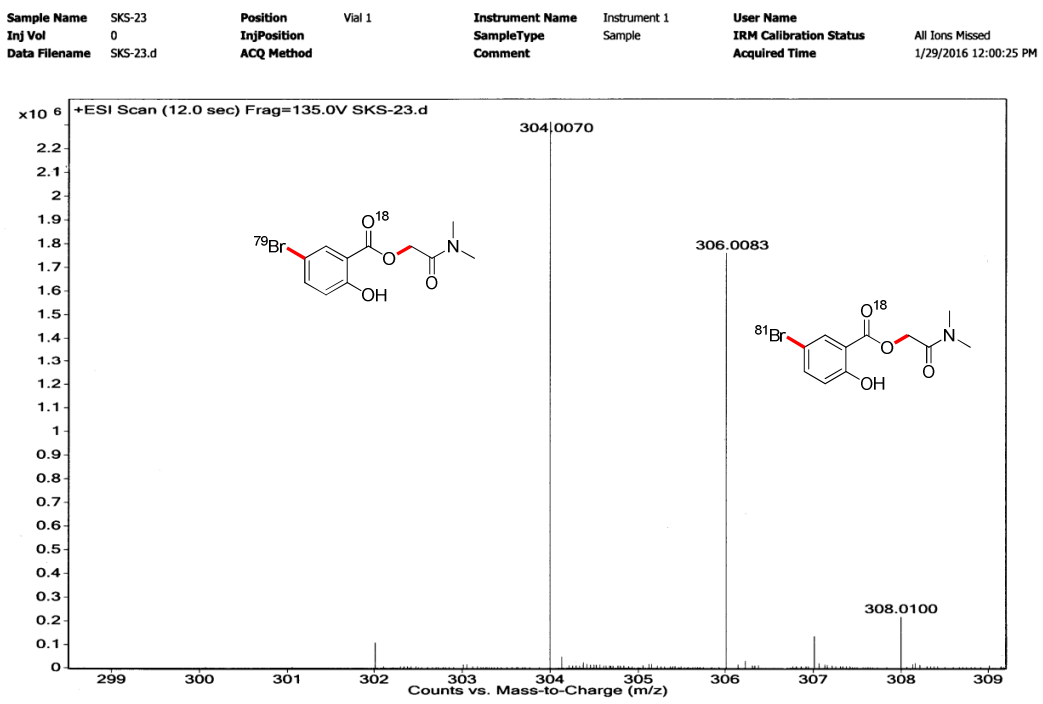


Fig. S4 HRMS spectrum of ^{18}O labeled (**1a**), ^{18}O oxygen as the source of ^{18}O.

Labeled 2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (1a): ^{13}C NMR ($CDCl_3$, 100 MHz)

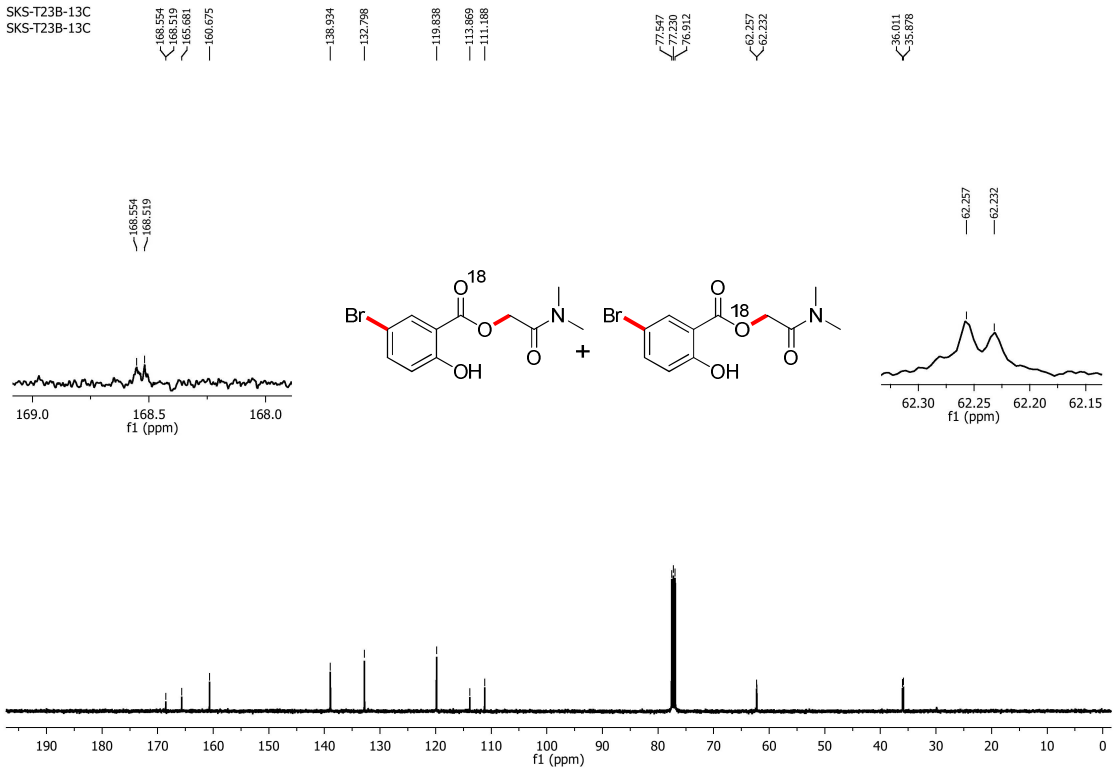


Fig. S5 ^{13}C NMR spectrum of ^{18}O labeled (**1a**), ^{18}O oxygen as the source of ^{18}O.

HRMS study for the detection of reaction intermediates during α-bromo-esterification:

In order to detect the intermediate species in the reaction mixture an electrospray mass spectrometry of crude reaction mixture was performed. In this study, an oven-dried flask was charged with 2-hydroxybenzaldehyde (**1**) (0.061 g, 0.5 mmol), $CuBr_2$ (0.134 g, 0.6 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol) and *N*,*N*-dimethylacetamide (1.0 mL). Then the reaction mixture was stirred in an oil bath at 120 ^{o}C. After 2 h of reaction, aliquot (100 µL) was withdrawn and diluted with acetonitrile (2 mL). A 20 µL of the diluted solution was injected to run APCl and ESI-MS analysis. Various intermediates viz (**C**) and (**E**) were detected in the MS analysis as shown below in Fig. S6 and S7. The species observed in the spectrum are as follows: peaks at m/z 380.5093 corresponding to [$C_9H_7BrO_5Pd$(II)] (**C**) (Fig. S6) and at m/z 553.2541 corresponding to [$C_{15}H_{19}NO_8Pd_2$(II)] (**E**) (Fig. S7).

HRMS Spectra of the reaction mixture after 2 hours:

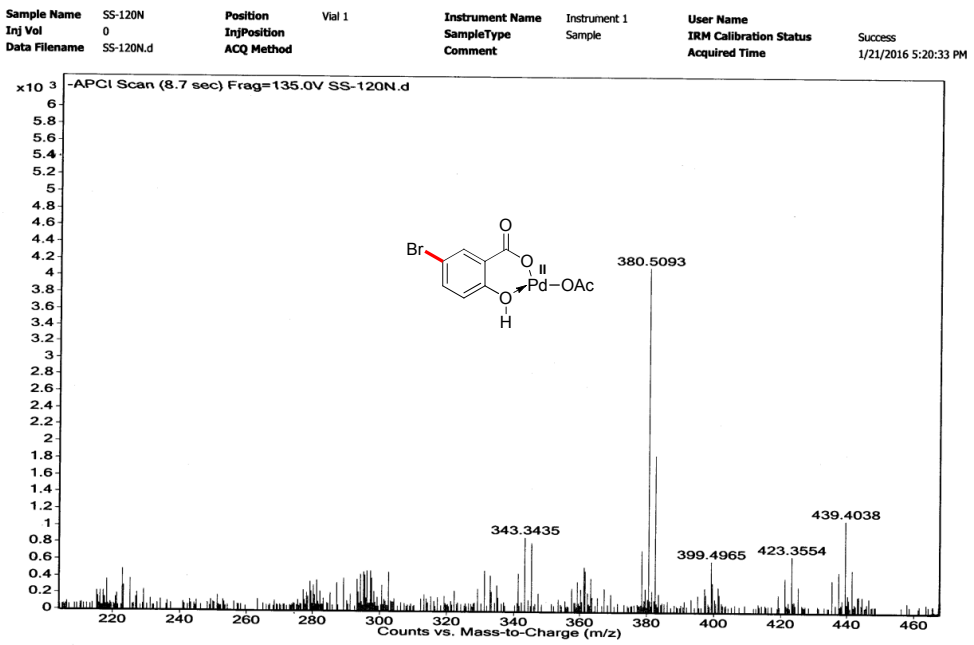


Fig. S6 HRMS spectrum of the reaction mixture after 2 h.

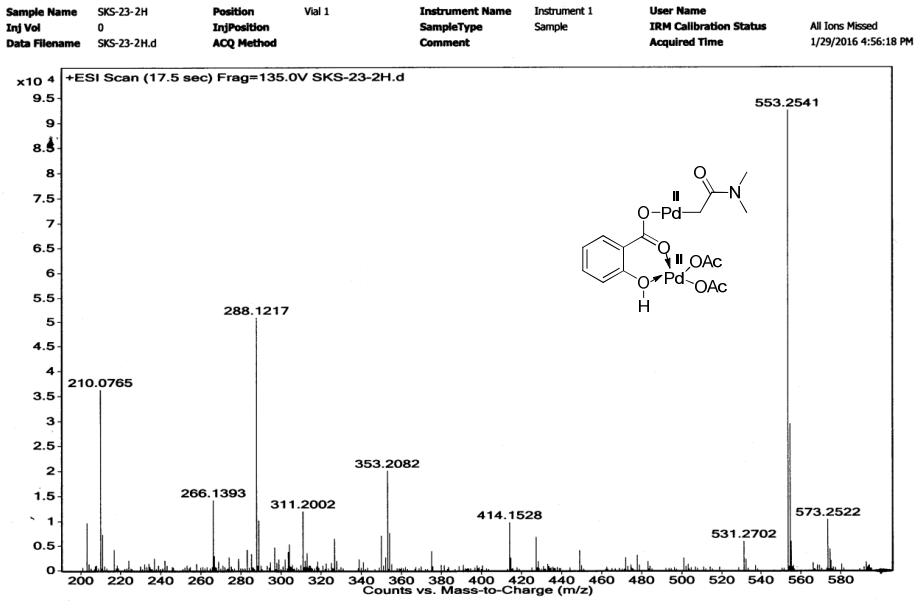
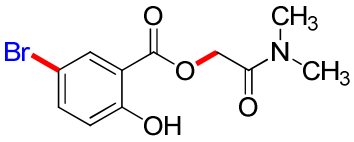


Fig. S7 HRMS spectrum of the reaction mixture after 2 h.

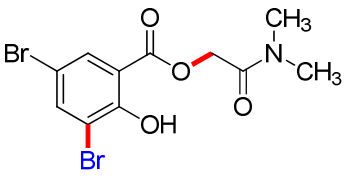
Spectral Data:

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (1a):



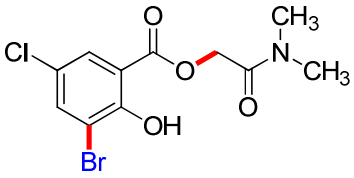
Solid; M.p. 82.6 °C–84.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.39 (s, 1H), 8.01 (s, 1H), 7.27 (d, 1H, J = 9.2 Hz), 6.84 (d, 1H, J = 8.8 Hz), 4.96 (s, 2H), 2.99 (s, 3H), 2.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 165.6, 160.6, 138.8, 132.7, 119.8, 113.9, 111.1, 62.2, 35.9, 35.8; IR (KBr, cm^{-1}): 3203, 2998, 2956, 2923, 1689, 1667, 1604, 1573, 1471, 1435, 1399, 1133, 1243, 1177, 1137, 1100, 1023, 1000, 830, 788, 751; HRMS (ESI) calcd for $C_{11}H_{12}BrNO_4$ (M + H$^+$) 302.0029, found 302.0037.

2-(Dimethylamino)-2-oxoethyl 3,5-dibromo-2-hydroxybenzoate (2a):



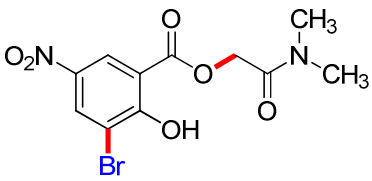
Solid; M.p. 171.3 °C–173.8 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.09 (s, 1H), 8.03 (s, 1H), 7.84 (s, 1H), 5.02 (s, 2H), 3.03 (s, 3H), 3.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.2, 165.4, 157.3, 141.4, 132.2, 114.7, 112.6, 111.1, 62.6, 35.95, 35.87; IR (KBr, cm^{-1}): 3168, 2998, 2961, 2923, 2880, 1664, 1595, 1501, 1438, 1419, 1367, 1334, 1313, 1235, 1177, 1152, 1110, 1025, 872, 812, 787, 757; HRMS (ESI) calcd for $C_{11}H_{11}Br_2NO_4$ (M + H$^+$) 381.9114, found 381.9119.

2-(Dimethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3a):



Solid; M.p. 146.9 °C–149.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.07 (s, 1H), 7.87 (s, 1H), 7.69 (s, 1H), 5.00 (s, 2H), 3.01 (s, 3H), 2.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.2, 165.4, 156.9, 138.7, 129.2, 124.5, 114.1, 112.2, 62.6, 35.9, 35.8; IR (KBr, cm^{-1}): 3164, 2993, 2952, 2926, 2877, 2850, 1668, 1596, 1501, 1442, 1424, 1395, 1369, 1338, 1314, 1274, 1260, 1234, 1179, 1153, 1143, 1116, 1093, 1061, 1026, 872, 812, 787, 758; HRMS (ESI) calcd for $C_{11}H_{11}BrClNO_4$ (M + H$^+$) 335.9639, found 335.9636.

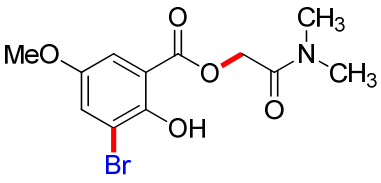
2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-nitrobenzoate (4a):



Solid; M.p. 120.0 °C–123.4 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.91 (s, 1H), 8.84 (s, 1H), 8.64 (s, 1H), 5.09 (s, 2H), 3.07 (s, 3H), 3.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.9, 162.9, 140.2, 133.9, 130.9, 125.9, 113.2, 112.5, 63.1, 35.9; IR (KBr, cm^{-1}): 3255, 3095, 2925, 2853, 1738, 1653, 1612, 1571, 1523, 1477, 1438, 1423, 1348, 1284, 1264, 1240, 1143, 1082, 1025, 917, 800, 782, 744, 728;

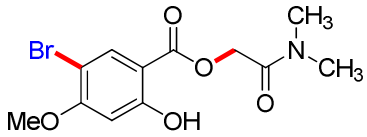
HRMS (ESI) calcd for $C_{11}H_{11}BrN_2O_6$ (M + H^+) 346.9880, found 346.9891.

2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methoxybenzoate (5a):



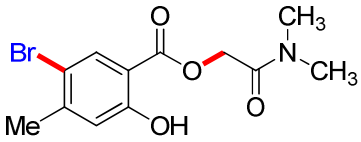
Gummy solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.69 (s, 1H), 7.41 (s, 1H), 7.37 (s, 1H), 5.00 (s, 2H), 3.77 (s, 3H), 3.03 (s, 3H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.0, 165.7, 152.8, 152.2, 127.3, 112.9, 112.8, 111.8, 62.4, 56.3, 35.9, 35.8; IR (KBr, cm^{-1}): 3203, 2952, 2929, 2853, 2834, 1734, 1659, 1608, 1498, 1471, 1431, 1368, 1332, 1298, 1273, 1238, 1226, 1152, 1095, 1067, 1041, 1025, 860, 813, 784, 735; HRMS (ESI) calcd for $C_{12}H_{14}BrNO_5$ (M + H^+) 332.0135, found 332.0144.

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methoxybenzoat (6a):



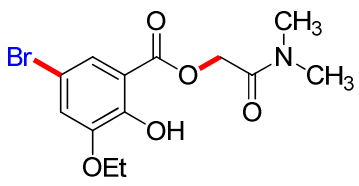
Solid; M.p. 174.2 °C–176.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.63 (s, 1H), 8.07 (s, 1H), 6.64 (s, 1H), 4.94 (s, 2H), 3.89 (s, 3H), 3.01 (s, 3H), 2.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.5, 165.9, 163.2, 161.8, 134.3, 106.2, 101.8, 100.5, 61.9, 56.7, 35.9, 35.8; IR (KBr, cm^{-1}): 3333, 3036, 2955, 2942, 1714, 1671, 1608, 1563, 1489, 1443, 1357, 1320, 1271, 1232, 1190, 1170, 1117, 1040, 1021, 974, 893, 865, 778; HRMS (ESI) calcd for for $C_{12}H_{14}BrNO_5$ (M + H^+) 332.0135, found 332.0141.

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methylbenzoate (7a):



Solid; M.p. 120.7 °C–124.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.29 (s, 1H), 8.07 (s, 1H), 6.88 (s, 1H), 4.97 (s, 2H), 3.03 (s, 3H), 3.00 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.5, 165,8, 160.6, 146.9, 133.4, 119.8, 114.2, 111.7, 62.1, 36.0, 35.9, 23.7; IR (KBr, cm^{-1}): 3212, 2955, 2926, 2874, 2847, 1668, 1614, 1559, 1502, 1477, 1436, 1418, 1398, 1368, 1331, 1252, 1229, 1197, 1167, 1112, 1066, 1022, 947, 903, 857, 807, 787, 749; HRMS (ESI) calcd for $C_{12}H_{14}BrNO_4$ (M + H^+) 316.0186, found 316.0179.

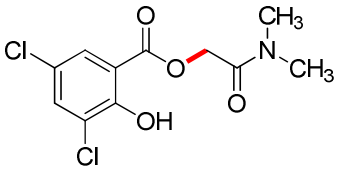
2-(Dimethylamino)-2-oxoethyl 5-bromo-3-ethoxy-2-hydroxybenzoate (8a):



Solid; M.p. 181.4 °C–183.8 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.65 (s, 1H), 7.65 (s, 1H), 7.11 (s, 1H), 4.98 (s, 2H), 4.08 (q, 2H, J = 6.6 Hz), 3.02 (s, 3H), 2.99 (s, 3H), 1.46 (t, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.9, 165.6, 151.8, 148.9, 123.7, 121.4, 113.5, 110.5, 65.3, 62.3, 35.9, 35.8, 14.8; IR (KBr, cm^{-1}):

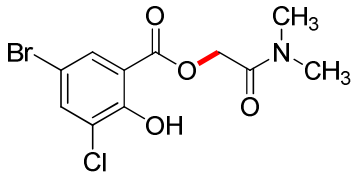
3201, 3077, 2978, 2944, 2926, 2850, 1680, 1657, 1575, 1504, 1466, 1438, 1401, 1368, 1336, 1285, 1252, 1226, 1178, 1155, 1108, 1066, 965, 786, 756; HRMS (ESI) calcd for $C_{13}H_{16}BrNO_5$ (M + H^+) 346.0291, found 346.0301.

2-(Dimethylamino)-2-oxoethyl 3,5-dichloro-2-hydroxybenzoat (9a):



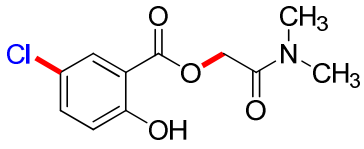
Solid; M.p. 132.2 °C–135.5 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.96 (s, 1H), 7.82 (s, 1H), 7.53 (s, 1H), 5.00 (s, 2H), 3.01 (s, 3H), 2.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.3, 165.4, 155.9, 135.7, 128.4, 124.0, 123.4, 114.3, 62.5, 35.9, 35.8; IR (KBr, cm^{-1}): 3177, 2996, 2961, 2931, 1670, 1601, 1501, 1445, 1429, 1414, 1369, 1339, 1315, 1262, 1235, 1176, 1163, 1147, 1094, 1064, 1028, 951, 872, 850, 817, 788, 757, 728; HRMS (ESI) calcd for $C_{11}H_{11}Cl_2NO_4$ (M + H^+) 292.0145, found 292.0147.

2-(Dimethylamino)-2-oxoethyl 5-bromo-3-chloro-2-hydroxybenzoate (10a):



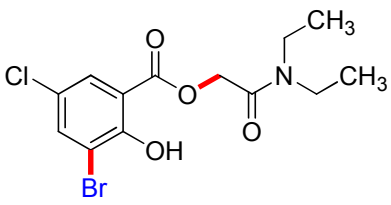
Solid; M.p. 165.8 °C–168.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.08 (s, 1H), 8.01 (s, 1H), 7.83 (s, 1H), 5.00 (s, 2H), 3.01 (s, 3H), 2.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.1, 165.4, 157.3, 141.3, 132.1, 131.4, 114.7, 112.5, 62.6, 35.9, 35.8; IR (KBr, cm^{-1}): 3169, 3074, 2996, 2958, 2928, 1665, 1595, 1502, 1438, 1419, 1394, 1368, 1335, 1313, 1285, 1234, 1177, 1152, 1110, 1090, 1061, 1026, 871, 813, 787, 757, 733; HRMS (ESI) calcd for $C_{11}H_{11}BrClNO_4$ (M + H^+) 335.9639, found 335.9630.

2-(Dimethylamino)-2-oxoethyl 5-chloro-2-hydroxybenzoate (1a´´):



Solid; M.p. 93.6 °C–97.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.41 (s, 1H), 7.92 (s, 1H), 7.42 (d, 1H, J = 9.0 Hz), 6.94 (d, 1H, J = 9.0 Hz), 5.01 (s, 2H), 3.05 (s, 3H), 3.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.6, 165.7, 160.2, 136.2, 129.8, 124.3, 119.5, 113.3, 62.3, 36.0, 35.9; IR (KBr, cm^{-1}): 3200, 2950, 2934, 2920, 1750, 1688, 1668, 1609, 1470, 1431, 1378, 1329, 1281, 1241, 1200, 1105, 1082, 1019, 1003, 832, 801, 758, 717; HRMS (ESI) calcd for $C_{11}H_{12}ClNO_4$ (M + H^+) 258.0534, found 258.0538.

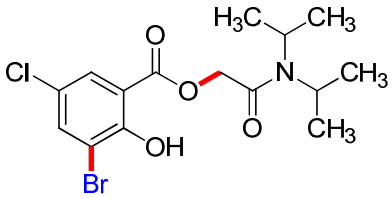
2-(Diethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3b):



Solid; M.p. 94.1°C–96.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.11 (s, 1H), 7.91 (s, 1H), 7.71 (s, 1H), 5.02 (s, 2H), 3.42 (q, 2H, J = 7.2 Hz), 3.29 (q, 2H, J = 7.2 Hz), 1.27 (t, 3H, J = 7.2 Hz), 1.16 (t, 3H,

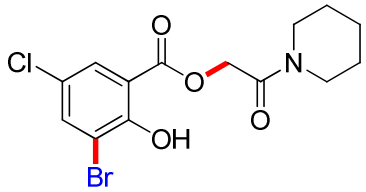
J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.3, 164.6, 156.9, 138.7, 129.3, 124.6, 114.2, 112.3, 62.6, 41.2, 40.9, 14.4, 13.1; IR (KBr, cm^{-1}): 3158, 3071, 2974, 2923, 2872, 1678, 1644, 1496, 1467, 1432, 1381, 1331, 1340, 1269, 1232, 1171, 1117, 1093, 1032, 1015, 946, 904, 887, 813, 790, 725; HRMS (ESI) calcd for $C_{13}H_{15}BrClNO_4$ (M + H^+) 363.9952, found 363.9962.

2-(Diisopropylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3c):



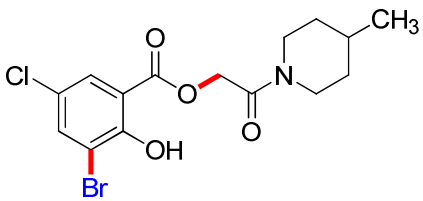
Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.17 (s, 1H), 7.90 (s, 1H), 7.70 (s, 1H), 4.97 (s, 2H), 3.77–3.74 (m, 1H), 3.51–3.48 (m, 1H), 1.41 (d, 6H, J = 5.4 Hz), 1.28 (d, 6H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.0, 163.8, 156.7, 138.5, 129.3, 124.5, 114.5, 112.2, 63.3, 47.9, 46.6, 20.9, 20.6; IR (KBr, cm^{-1}): 3222, 2996, 2969, 2935, 1689, 1662, 1598, 1473, 1448, 1369, 1302, 1284, 1235, 1171, 1152, 1135, 1092, 1043, 1019, 884, 826, 788; HRMS (ESI) calcd for $C_{15}H_{19}BrClNO_4$ (M + H^+) 392.0265, found 392.0260.

2-Oxo-2-(piperidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3d):



Solid; M.p. 97.5 °C–100.9 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.09 (s, 1H), 7.87 (s, 1H), 7.69 (s, 1H), 5.01 (s, 2H), 3.55 (t, 2H, J = 4.8 Hz), 3.33 (t, 2H, J = 5.4 Hz), 1.66–1.65 (m, 2H), 1.62–1.61 (m, 2H), 1.57–1.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.2, 163.6, 156.8, 138.6, 129.1, 124.4, 114.2, 112.2, 62.7, 45.7, 43.4, 26.3, 25.4, 24.4; IR (KBr, cm^{-1}): 3216, 2998, 2935, 2917, 2856, 1702, 1668, 1473, 1454, 1435, 1368, 1316, 1264, 1254, 1223, 1151, 1136, 1091, 1032, 1004, 951, 875, 849, 837, 826, 778, 759; HRMS (ESI) calcd for $C_{14}H_{15}BrClNO_4$ (M + H^+) 375.9952, found 375.9954.

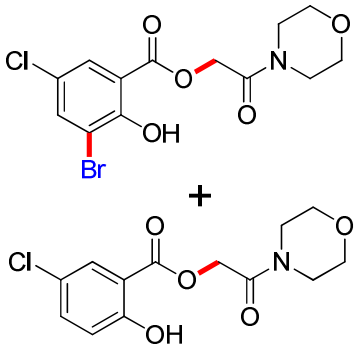
2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3e):



Solid; M.p. 115.0 °C–118.4 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.09 (s, 1H), 7.89 (s, 1H), 7.71 (s, 1H), 5.02 (s, 2H), 4.51 (d, 1H, J = 13.2 Hz), 3.61 (d, 1H, J = 13.2 Hz), 3.08 (t, 1H, J = 12.6 Hz), 2.65 (t, 1H, J = 12.6 Hz), 1.76–1.63 (m, 3H), 1.21–1.14 (m, 2H), 1.13 (d, 3H, J = 3.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.3, 163.7, 156.9, 138.7, 129.2, 124.5, 114.2, 112.3, 62.7, 45.0, 42.9, 34.5, 33.6, 31.1, 21.8; IR (KBr, cm^{-1}): 3234, 3001, 2954, 2907, 2857, 1704, 1671, 1651, 1473, 1451, 1430, 1316, 1270, 1238, 1222, 1149, 1087, 1036, 1013, 971, 876, 802, 786, 732; HRMS

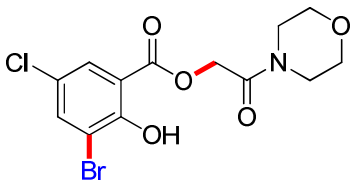
(ESI) calcd for $C_{15}H_{17}BrClNO_4$ (M + H^+) 390.0109, found 390.0118.

2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Morpholino-2-oxoethyl 5-chloro-2-hydroxybenzoate (3f and 3f´):



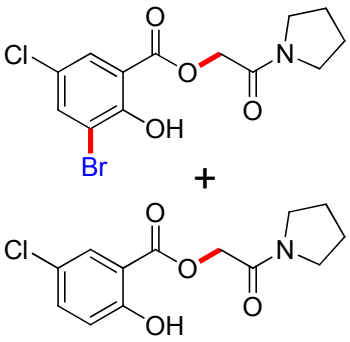
Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.01 (s, 1H), 10.33 (s, 1H), 7.88 (s, 2H), 7.72 (s, 1H), 7.41 (d, 1H, J = 9.0 Hz), 6.93 (d, 1H, J = 8.4 Hz), 5.01 (s,2H), 4.99 (s,2H), 3.72 (bs, 8H), 3.64 (bs, 4H); 3.43 (bs, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.6, 168.3, 164.5, 164.2, 160.3, 156.9, 138.9, 136.3, 129.7, 129.1, 124.6, 124.3, 119.5, 113.8, 113.1, 112.3, 66.9, 66.4, 62.4, 62.0, 45.2, 45.1, 42.5; IR (KBr, cm^{-1}): 3220, 3063, 2965, 2923, 2856, 1684, 1673, 1609, 1475, 1450, 1362, 1334, 1274, 1229, 1170, 1114, 1068, 1042, 1003, 854, 829, 791, 783, 718; HRMS (ESI) calcd for $C_{13}H_{13}BrClNO_5$ (M + H^+) 377.9745, found 377.9756, and HRMS (ESI) calcd for $C_{13}H_{14}ClNO_5$ (M + H^+) 300.0640, found 300.0647.

2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3f):



Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.02 (s, 1H), 7.91 (s, 1H), 7.74 (s, 1H), 5.03 (s,2H), 3.75 (bs, 4H), 3.66 (bs, 2H); 3.45 (bs, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.4, 164.2, 156.9, 138.9, 129.1, 124.4, 113.9, 112.7, 66.8, 66.5, 62.7, 45.2, 42.5; IR (KBr, cm^{-1}): 3228, 3053, 2961, 2933, 2858, 1663, 1601, 1461, 1448, 1361, 1334, 1274, 1231, 1164, 1062, 1003, 832, 784, 728; HRMS (ESI) calcd for $C_{13}H_{13}BrClNO_5$ (M + H^+) 377.9745, found 377.9751.

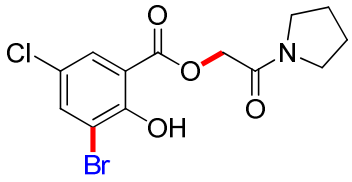
2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Oxo-2-(pyrrolidin-1-yl)ethyl 5-chloro-2-hydroxybenzoate (3g and 3g´):



Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.08 (s, 1H), 10.39 (s, 1H), 7.91 (s, 2H), 7.71 (s, 1H), 7.40 (d, 1H, J = 8.4 Hz), 6.93 (d, 1H, J = 8.4 Hz), 4.92 (s, 2H), 4.90 (s, 2H), 3.54 (t, 4H, J = 7.2 Hz), 3.44 (t, 4H, J = 6.6 Hz); 2.05–2.02 (m, 4H), 1.91–1.89 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.7, 168.3, 164.4, 164.0, 160.3, 156.9, 138.8, 136.1, 129.8, 129.2, 124.6, 124.3, 119.5, 114.1, 113.3, 112.2, 63.1, 62.7, 46.41, 46.37, 45.51, 45.46, 26.3, 24.1; IR (KBr, cm^{-1}): 3182, 2965, 2923, 2878, 1672, 1606, 1574, 1468, 1459, 1430, 1361, 1315, 1285, 1233, 1187, 1164, 1107, 1085, 976, 875, 825, 786, 741, 724; HRMS (ESI) calcd for $C_{13}H_{13}BrClNO_4$

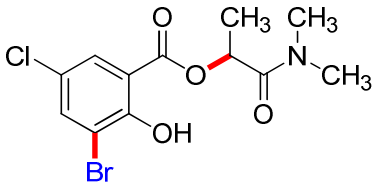
(M + H^+) 361.9796, found 361.9799 and HRMS (ESI) calcd for $C_{13}H_{14}ClNO_4$ (M + H^+) 284.0691, found 284.0695

2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3g):



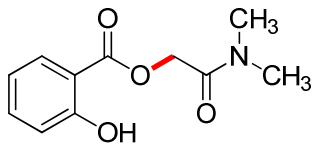
Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.06 (s, 1H), 7.88 (s, 1H), 7.70 (s, 1H), 4.92 (s,2H), 3.54 (t, 2H, J = 7.2 Hz), 3.45 (t, 2H, J = 6.8 Hz); 2.06–2.03 (m, 2H), 1.92–1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.4, 164.2, 157.0, 138.8, 129.2, 124.6, 114.0, 112.3, 63.1, 46.5, 45.5, 26.2, 24.0; IR (KBr, cm^{-1}): 3211, 2985, 2915, 2858, 1662, 1606, 1574, 1468, 1433, 1351, 1321, 1284, 1189, 1158, 1100, 1075, 875, 828, 748, 718; HRMS (ESI) calcd for $C_{13}H_{13}BrClNO_4$ (M + H^+) 361.9796, found 361.9806.

1-(Dimethylamino)-1-oxopropan-2-yl 3-bromo-5-chloro-2-hydroxybenzoate (3h):



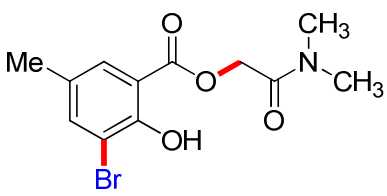
Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.10 (s, 1H), 7.89 (s, 1H), 7.70 (s, 1H), 5.63 (q, 1H, J = 6.6 Hz), 3.12 (s, 3H), 3.00 (s, 3H), 1.60 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.4, 168.3, 157.0, 138.8, 129.2, 124.5, 113.9, 112.2, 69.1, 37.0, 36.3, 16.8; IR (KBr, cm^{-1}): 3092, 2992, 2934, 2853, 1746, 1664, 1602, 1506, 1429, 1371, 1317, 1233. 1173, 1115, 1079, 1026, 880, 793, 728; HRMS (ESI) calcd for $C_{12}H_{13}BrClNO_4$ (M + H^+) 349.9796, found 349.9804.

2-(Dimethylamino)-2-oxoethyl 2-hydroxybenzoate (1a´):



Solid; M.p. 56.0 °C–58.2 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.45 (s, 1H), 7.95 (d, 1H, J = 6.6 Hz), 7.46 (t, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 8.4 Hz), 6.89 (t, 1H, J = 7.5 Hz), 4.98 (s, 2H), 3.03 (s, 3H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.6, 166.0, 161.7, 136.2, 130.6, 119.5, 117.8, 112.4, 62.1, 36.1, 35.8; IR (KBr, cm^{-1}): 3220, 2957, 2922, 2850, 1685, 1659, 1613, 1584, 1501, 1482, 1435, 1415, 1329, 1303, 1246, 1197, 1180, 1151, 1131, 1096, 850, 793 ,737; HRMS (ESI) calcd for $C_{11}H_{13}NO_4$ (M + H^+) 224.0924, found 224.0927.

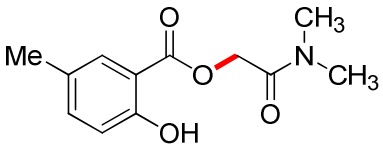
2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methylbenzoate (12a):



Solid; M.p. 140.2 °C–143.6 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.92 (s, 1H), 7.73 (s, 1H), 7.56 (s, 1H), 4.99 (s, 2H), 3.03 (s, 3H), 3.00 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.3, 165.7, 156.0, 140.1, 129.83, 129.80, 113.1, 110.9, 62.3, 35.9, 35.8, 20.3; IR (KBr, cm^{-1}): 3225, 2948, 2927, 2853, 1667, 1613, 1494,

1438, 1397, 1362, 1326, 1214, 1166, 1148, 1101, 1061, 1026, 927, 869, 787, 782, 743; HRMS (ESI) calcd for $C_{12}H_{14}BrNO_4$ (M + H^+) 316.0186, found 316.0180.

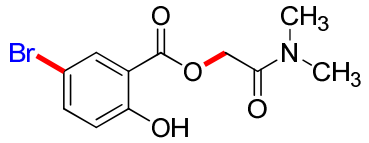
2-(Dimethylamino)-2-oxoethyl 2-hydroxy-5-methylbenzoate (12a´):

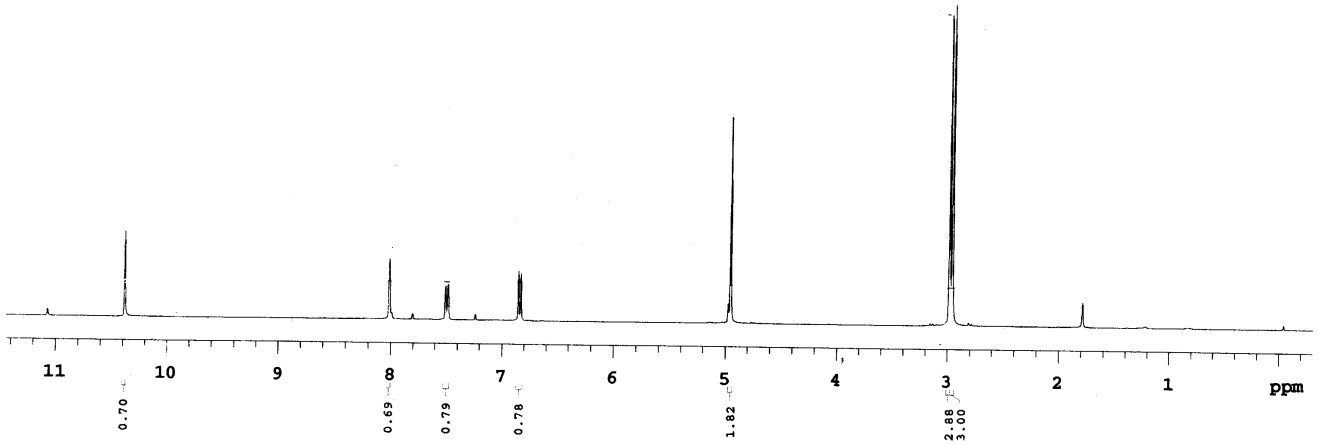


Solid; M.p. 86.4 ^oC–89.8 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ 10.28 (s, 1H), 7.75 (s, 1H), 7.28 (d, 1H, J = 10.2 Hz), 6.89 (d, 1H, J = 8.4 Hz), 4.99 (s, 2H), 3.05 (s, 3H), 3.02 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.6, 166.2, 159.6, 137.3, 130.2, 128.7, 117.6, 111.8, 61.9, 36.1, 35.9, 20.5; IR (KBr, cm^{-1}): 3236, 2959, 2925, 2856, 1663, 1495, 1435, 1365, 1335, 1290, 1249, 1211, 1187, 1155, 1099, 1022, 825, 789, 740; HRMS (ESI) calcd for $C_{12}H_{15}NO_4$ (M + H^+) 238.1081, found 238.1089.

Spectra

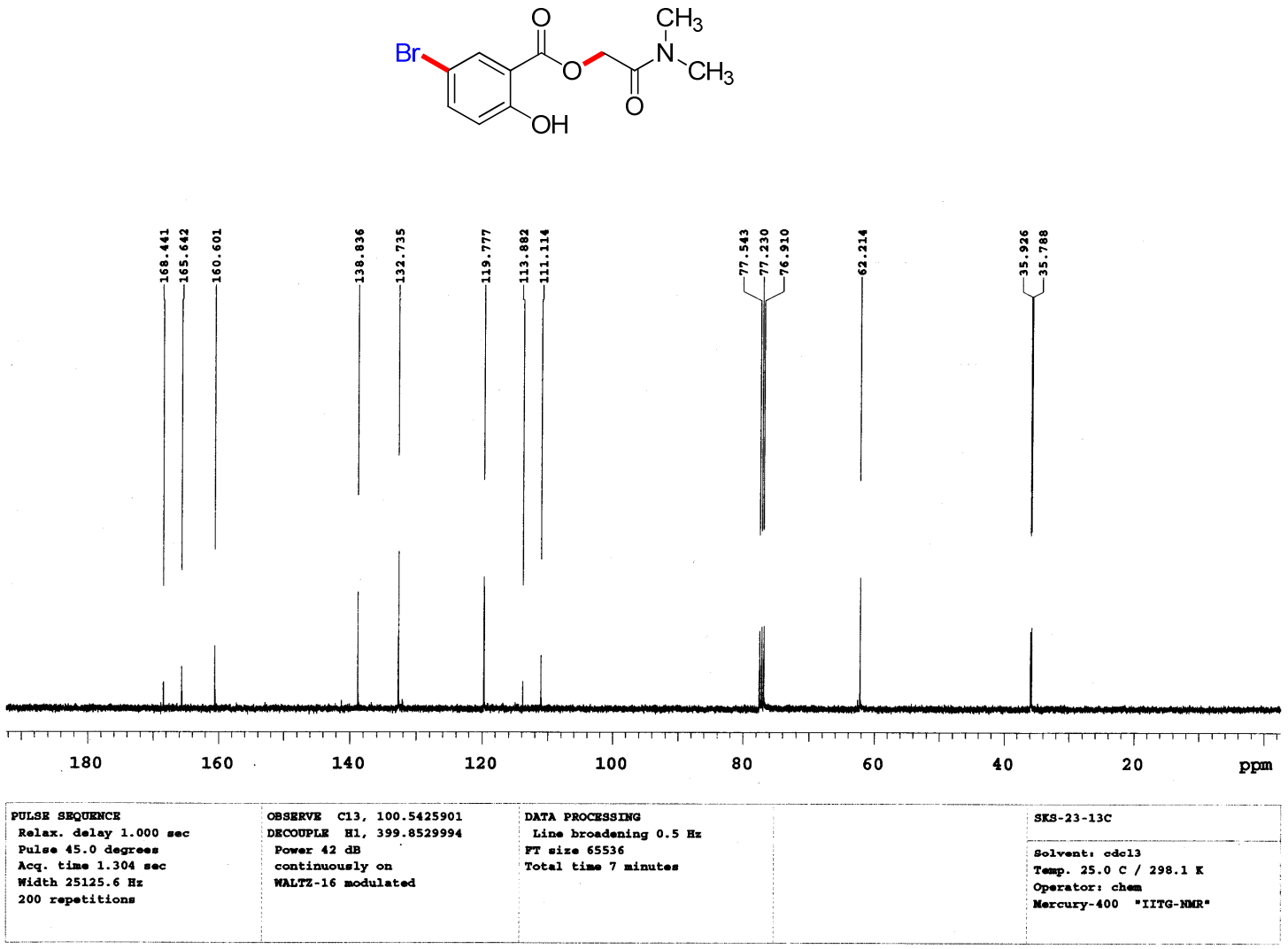
2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (1a): ^{1}H NMR ($CDCl_3$, 400 MHz)



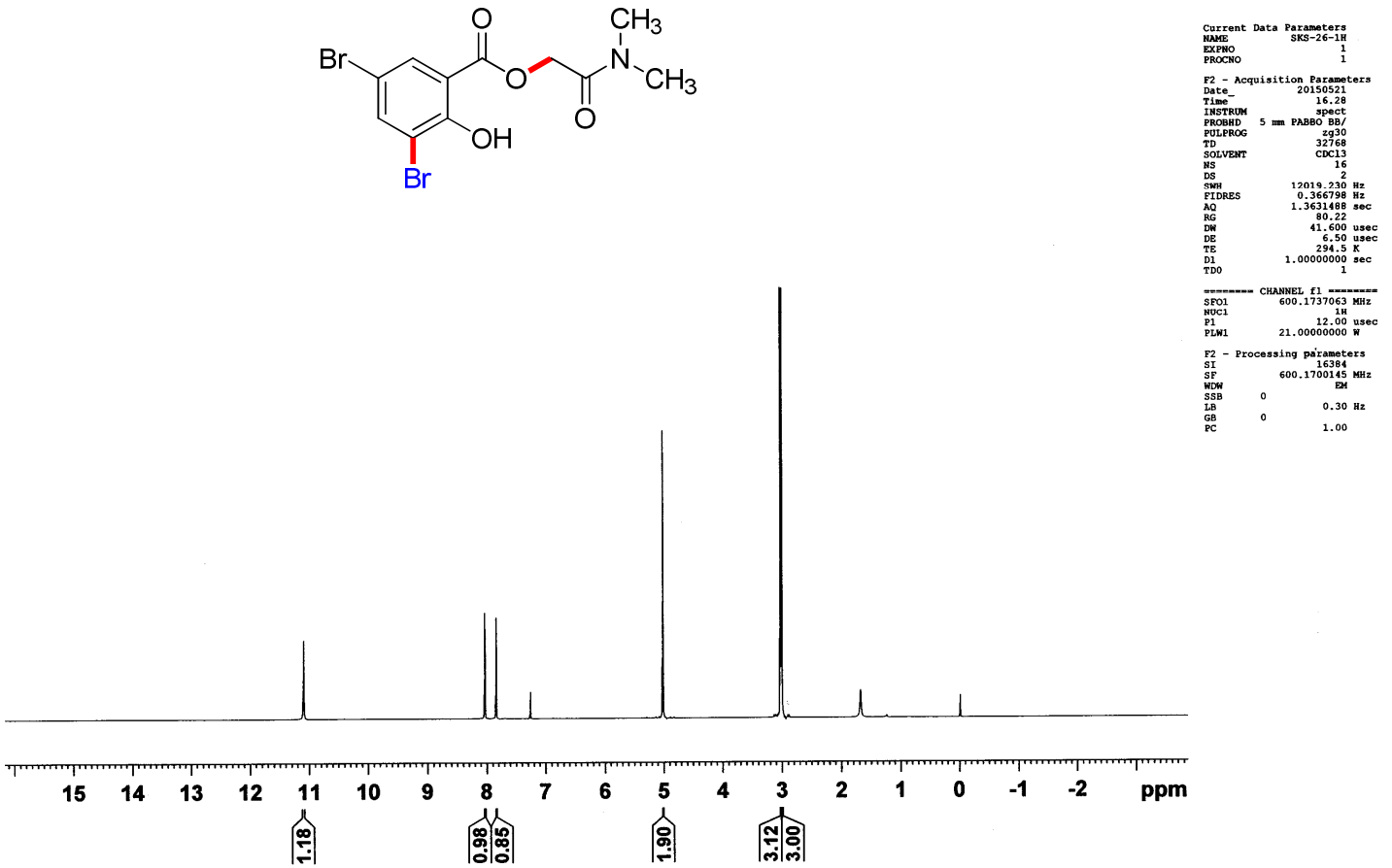


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.561 sec Width 6398.0 Hz 32 repetitions	OBSERVE H1, 399.8509729	DATA PROCESSING FT size 32768 Total time 1 minutes		SKS-23-1H Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem File: SKS-23-1H Mercury-400 "IITG-NMR"

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxybenzoate (1a): ^{13}C NMR ($CDCl_3$, 100 MHz)



2-(Dimethylamino)-2-oxoethyl 3,5-dibromo-2-hydroxybenzoate (2a): ^{1}H NMR ($CDCl_3$, 600 MHz)

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PROCNO                        1

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TD                       32768
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AQ                    1.3631488 sec
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DW                       41.600 usec
DE                        6.50 usec
TE                       294.5 K
D1                    1.00000000 sec
TD0                           1

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NUC1                        1H
P1                       12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
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SF                  600.1700145 MHz
WDW                          EM
SSB       0
LB                        0.30 Hz
GB        0
PC                        1.00
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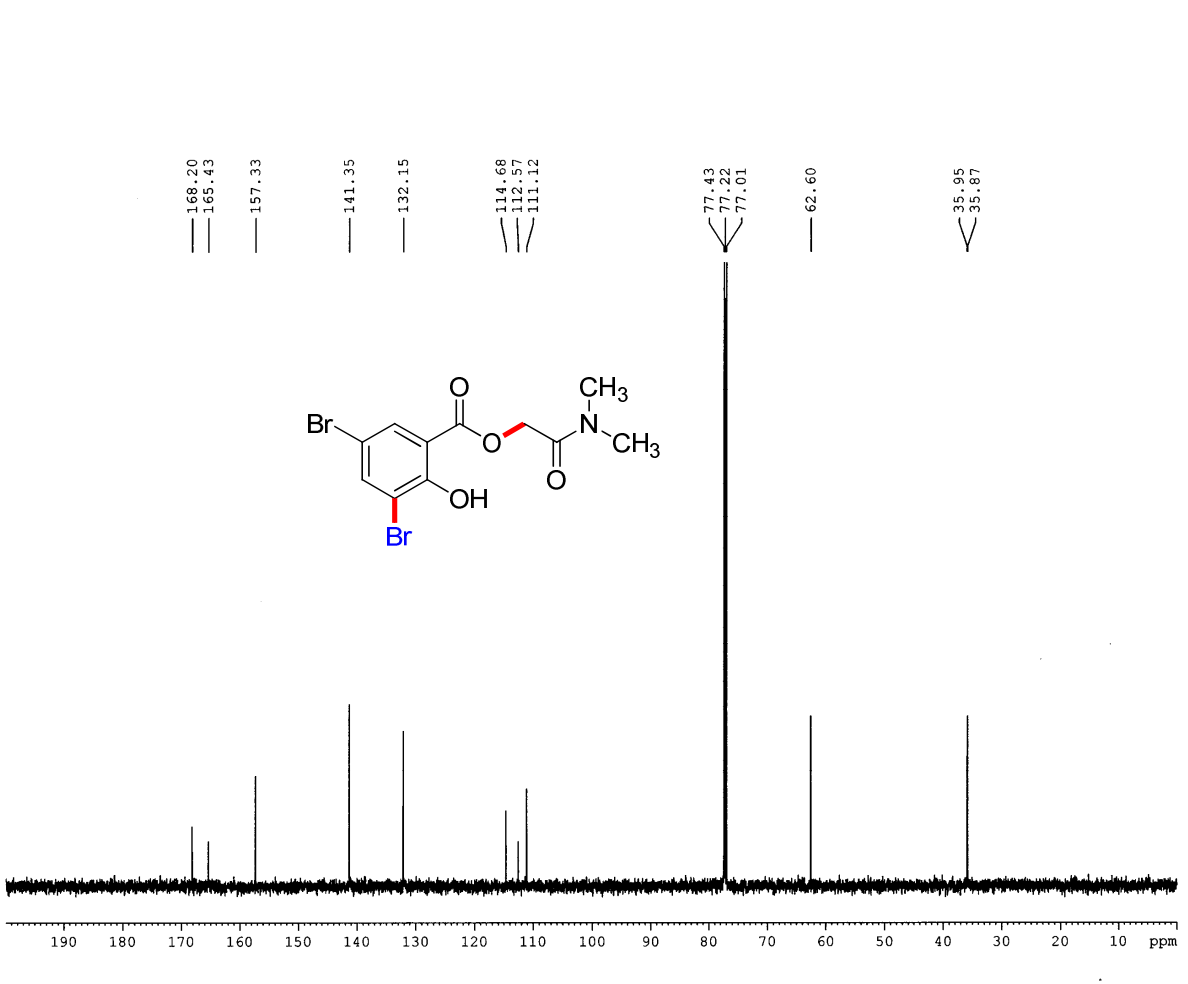
2-(Dimethylamino)-2-oxoethyl 3,5-dibromo-2-hydroxybenzoate (2a): ^{13}C NMR ($CDCl_3$, 150 MHz)

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PROCNO                 1

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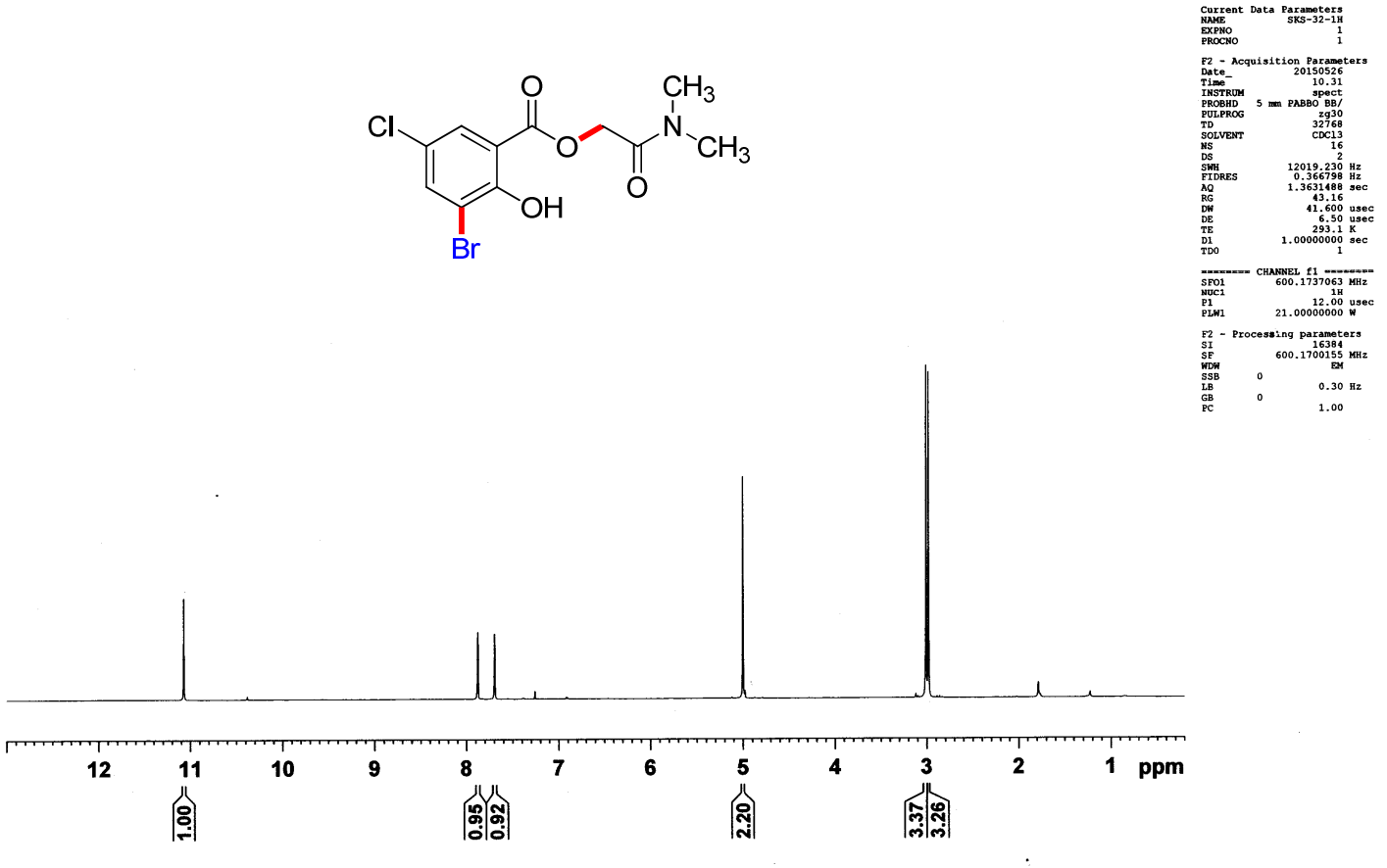
Time               13.01
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                32768
SOLVENT           CDCl3
NS                   51
DS                    2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ             0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE                297.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1                13C
P1                10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                16384
SF          150.9128415 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3a): ^{1}H NMR ($CDCl_3$, 600 MHz)



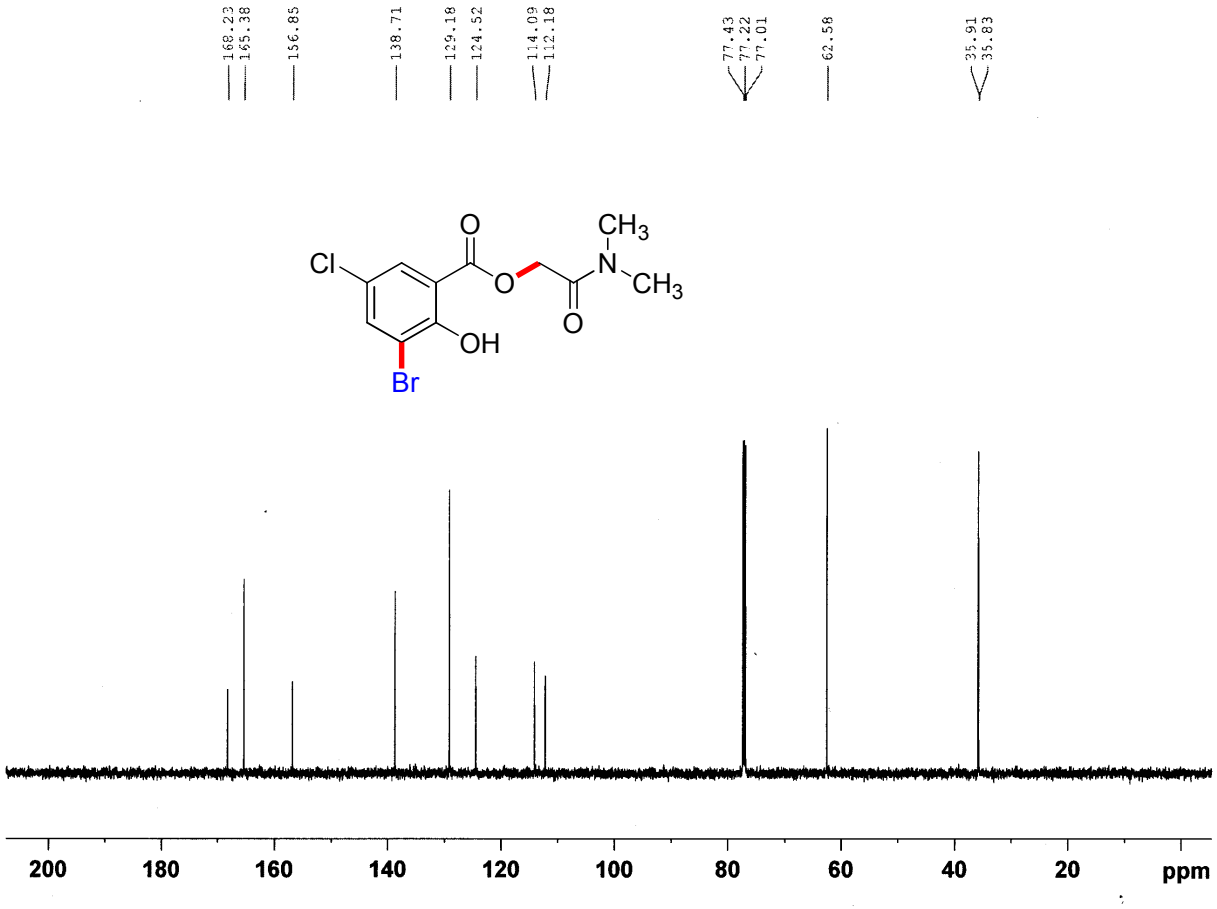

```
Current Data Parameters
NAME                  SKS-32-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20150526
Time                      10.31
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                           16
DS                            2
SWH                12019.230 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                       43.16
DW                     41.600 usec
DE                      6.50 usec
TE                      293.1 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               600.1737063 MHz
NUC1                        1H
P1                       12.00 usec
PLW1              21.00000000 W

F2 - Processing parameters
SI                        16384
SF                 600.1700155 MHz
WDW                          EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3a): ^{13}C NMR ($CDCl_3$, 150 MHz)



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```
Current Data Parameters
NAME          SKS-32-13C
EXPNO                  1
PROCNO                 1

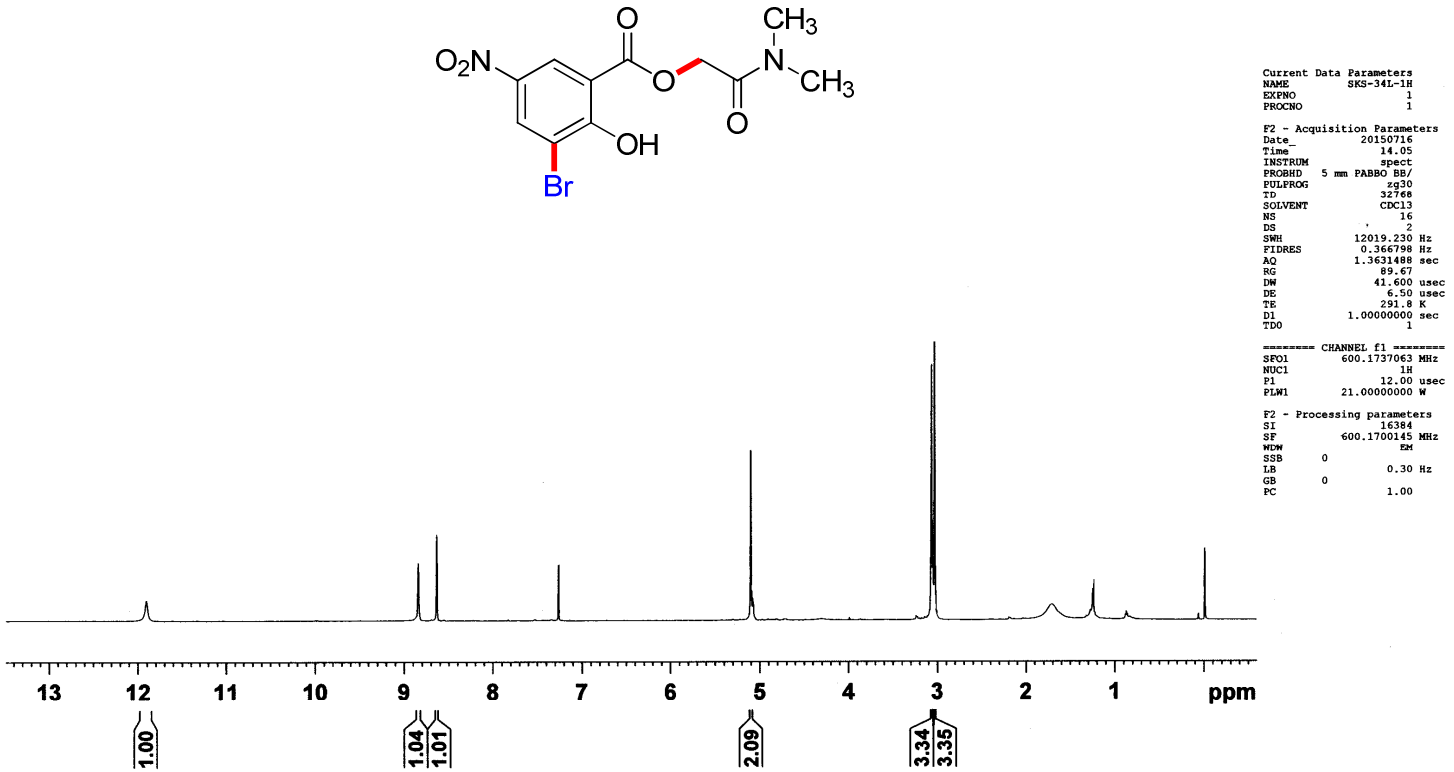
F2 - Acquisition Parameters
Date_           20150601
Time              10.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               32768
SOLVENT          CDCl3
NS                 102
DS                   2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ             0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE                298.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1               13C
P1                10.50 usec
PLW1        95.00000000 W

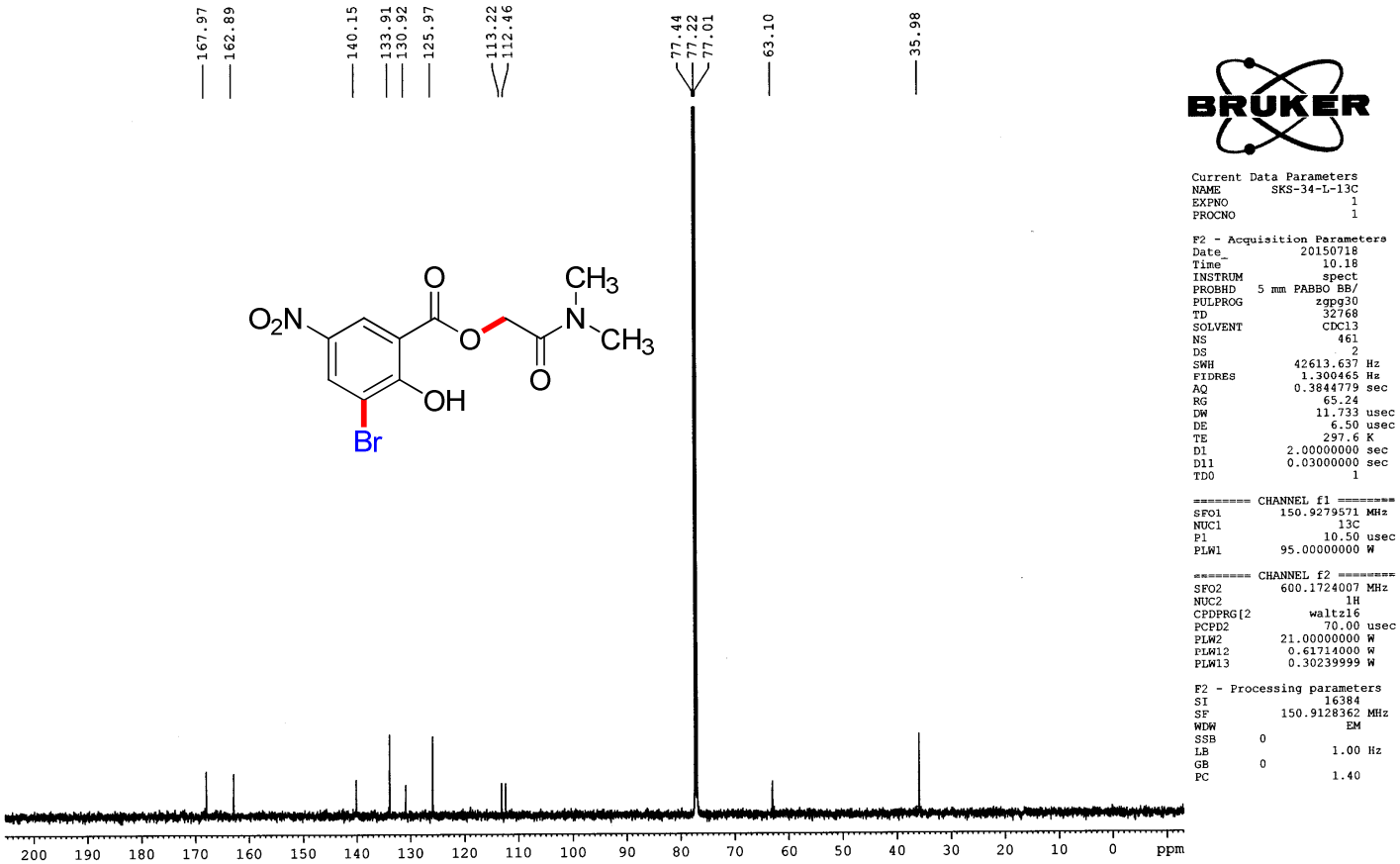
======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                16384
SF          150.9128447 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-nitrobenzoate (4a): ^{1}H NMR ($CDCl_3$, 600 MHz)



2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-nitrobenzoate (4a): ^{13}C NMR ($CDCl_3$, 150 MHz)




```
Current Data Parameters
NAME        SKS-34-L-13C
EXPNO                  1
PROCNO                 1

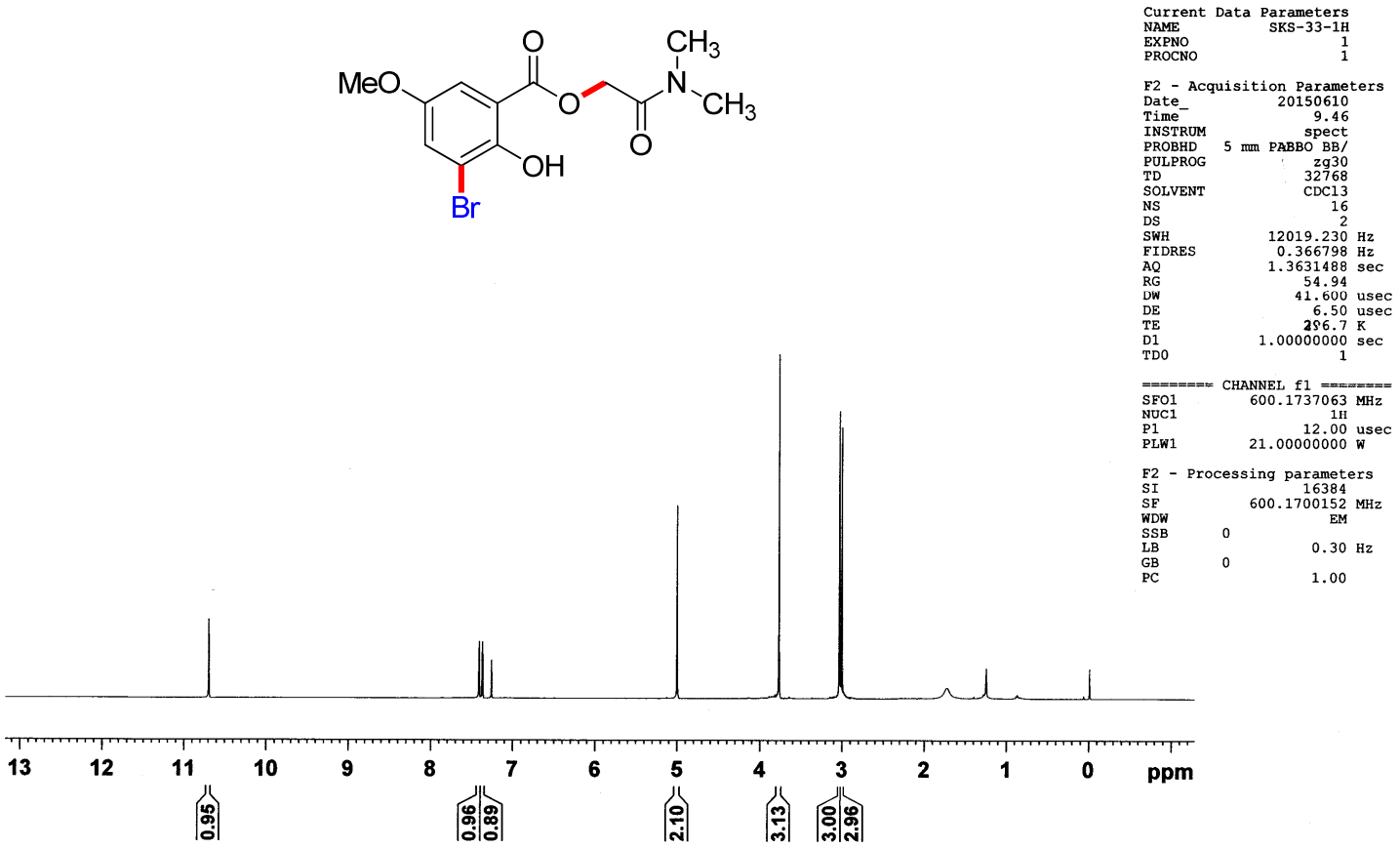
F2 - Acquisition Parameters
Date_           20150718
Time              10.18
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              32768
SOLVENT           CDCl3
NS                  461
DS                    2
SWH           42613.637 Hz
FIDRES         1.300465 Hz
AQ            0.3844779 sec
RG                65.24
DW               11.733 usec
DE                6.50 usec
TE                297.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       150.9279571 MHz
NUC1               13C
P1               10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2       600.1724007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                16384
SF          150.9128362 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methoxybenzoate (5a): ^{1}H NMR ($CDCl_3$, 600 MHz)



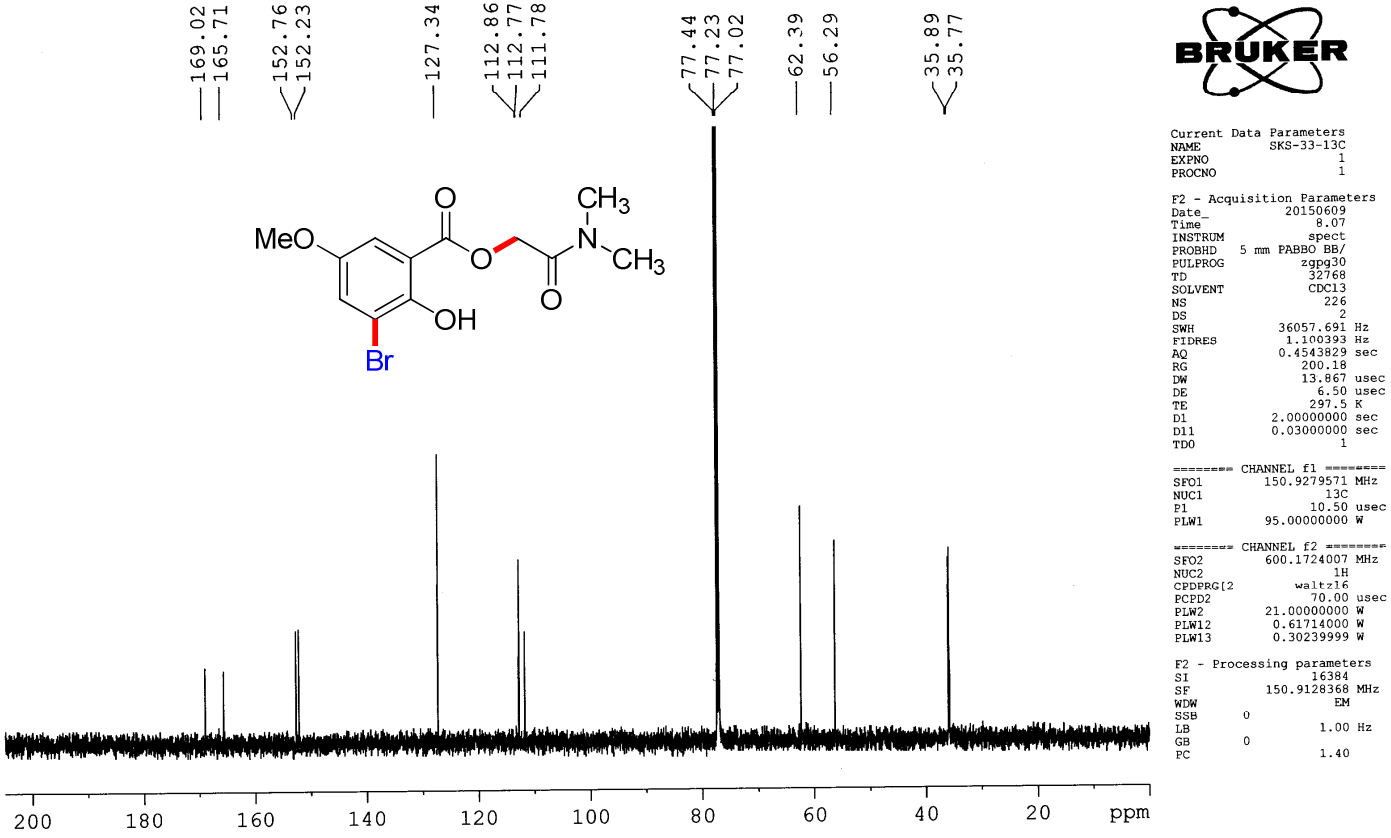

```
Current Data Parameters
NAME                  SKS-33-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20150610
Time                       9.46
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                12019.230 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                      54.94
DW                     41.600 usec
DE                      6.50 usec
TE                     296.7 K
D1                 1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               600.1737063 MHz
NUC1                        1H
P1                         12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
SI                        16384
SF                 600.1700152 MHz
WDW                          EM
SSB          0
LB                          0.30 Hz
GB           0
PC                         1.00
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methoxybenzoate (5a): ^{13}C NMR ($CDCl_3$, 150 MHz)




```
Current Data Parameters
NAME                  SKS-33-13C
EXPNO                          1
PROCNO                         1

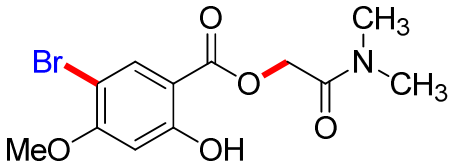
F2 - Acquisition Parameters
Date_                   20150609
Time                        8.07
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           226
DS                             2
SWH                    36057.691 Hz
FIDRES                 1.100393 Hz
AQ                     0.4543829 sec
RG                        200.18
DW                        13.867 usec
DE                          6.50 usec
TE                         297.5 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 150.9279571 MHz
NUC1                         13C
P1                         10.50 usec
PLW1                 95.00000000 W

======== CHANNEL f2 ========
SFO2                 600.1724007 MHz
NUC2                         1H
CPDPRG[2                 waltz16
PCPD2                      70.00 usec
PLW2                 21.00000000 W
PLW12                 0.61714000 W
PLW13                 0.30239999 W

F2 - Processing parameters
SI                         16384
SF                   150.9128368 MHz
WDW                           EM
SSB                  0
LB                         1.00 Hz
GB                   0
PC                         1.40
```

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methoxybenzoat (6a): ^{1}H NMR ($CDCl_3$, 600 MHz)

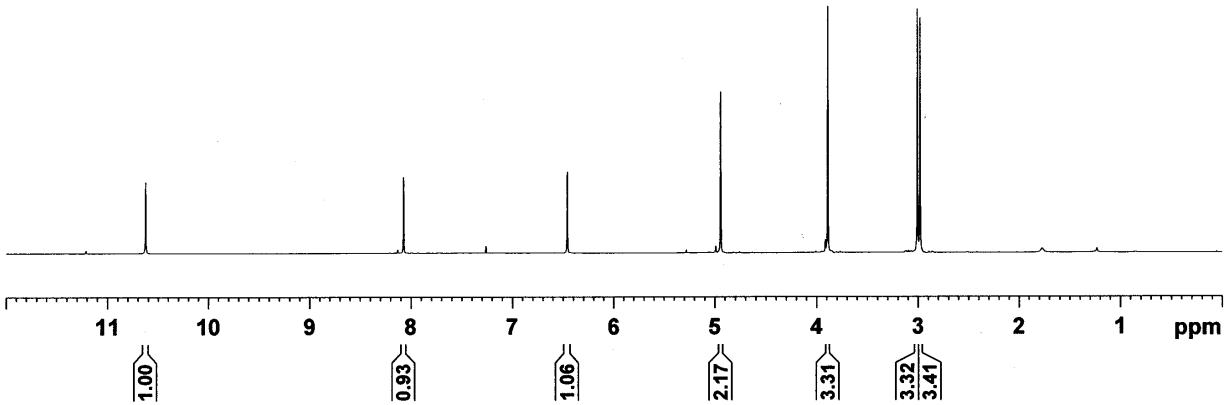



```
Current Data Parameters
NAME                  SKS-31-1H
EXPNO                         1
PROCNO                        1

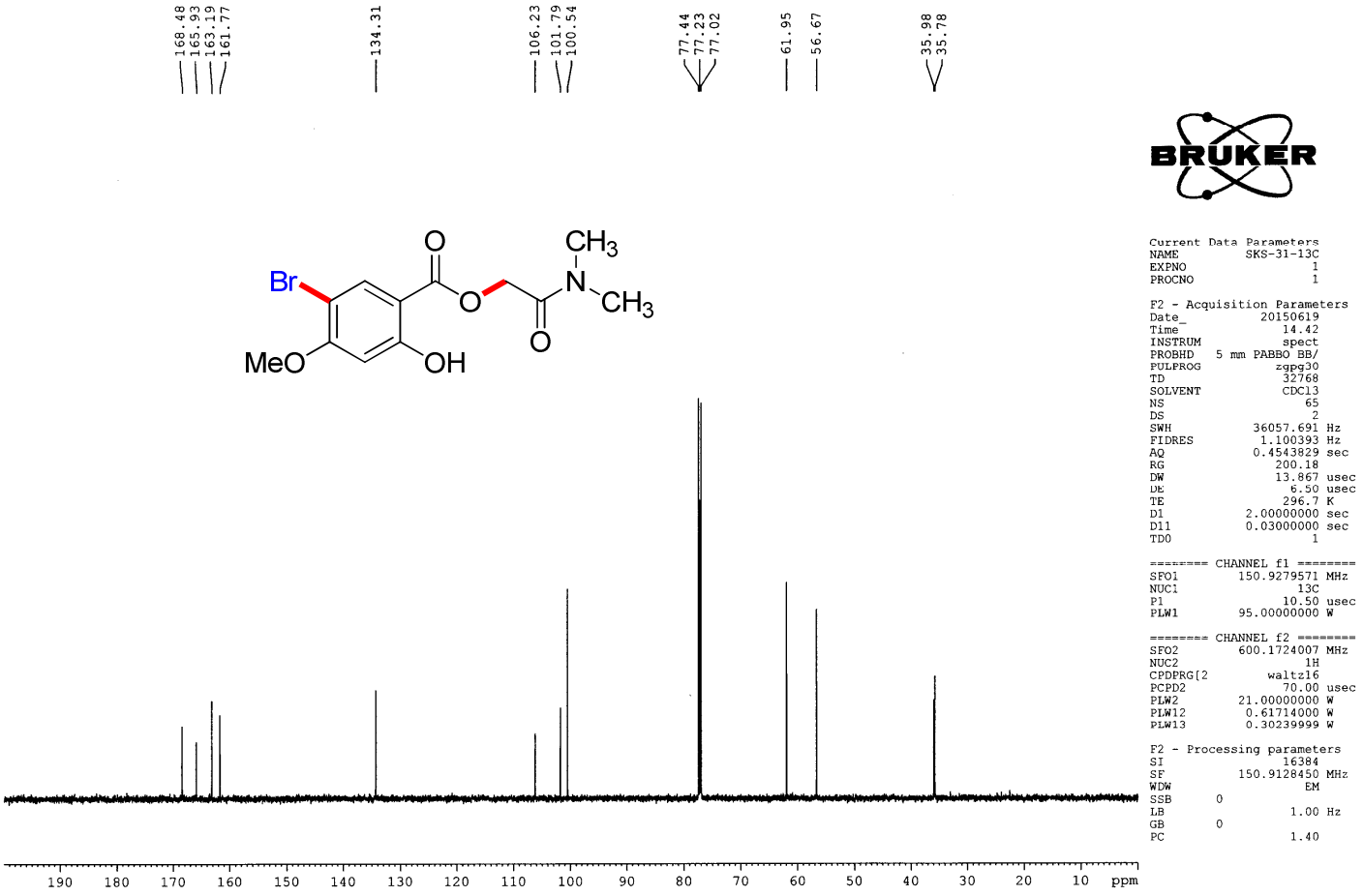
F2 - Acquisition Parameters
Date_                  20150619
Time                      14.11
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                           16
DS                            2
SWH                   12019.230 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                        54.94
DW                       41.600 usec
DE                        6.50 usec
TE                       296.2 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1737063 MHz
NUC1                         1H
P1                       12.00 usec
PLW1                21.00000000 W

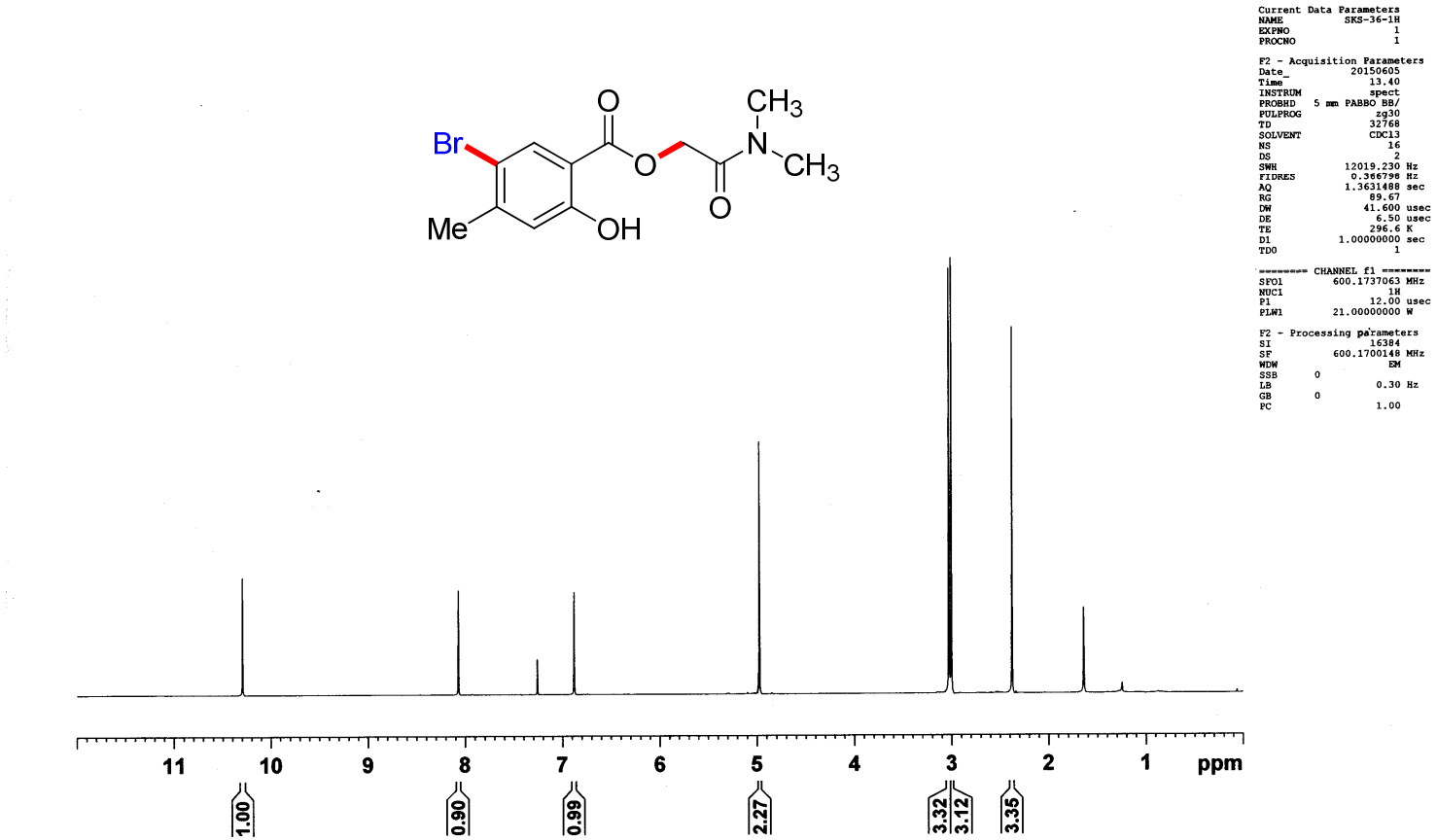
F2 - Processing parameters
SI                           16384
SF                  600.1700146 MHz
WDW                          EM
SSB                   0
LB                            0.30 Hz
GB                    0
PC                            1.00
```



2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methoxybenzoat (6a): ^{13}C NMR ($CDCl_3$, 150 MHz)



2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methylbenzoate (7a): ^{1}H NMR ($CDCl_3$, 600 MHz)



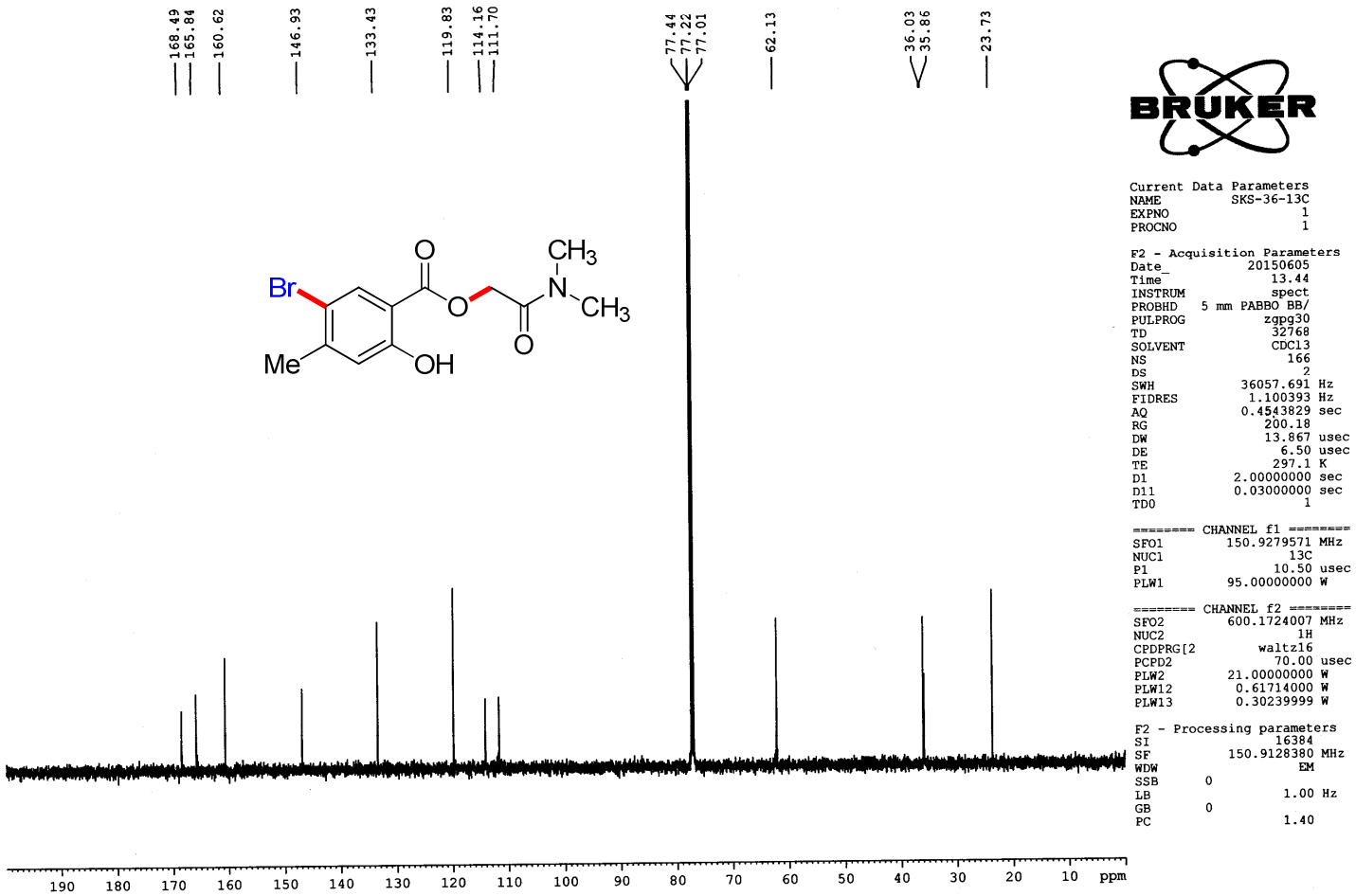

```
Current Data Parameters
NAME                  SKS-36-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20150605
Time                      13.40
INSTRUM                   spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                12019.230 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                       89.67
DW                     41.600 usec
DE                      6.50 usec
TE                     296.6 K
D1                  1.00000000 sec
TD0                          1

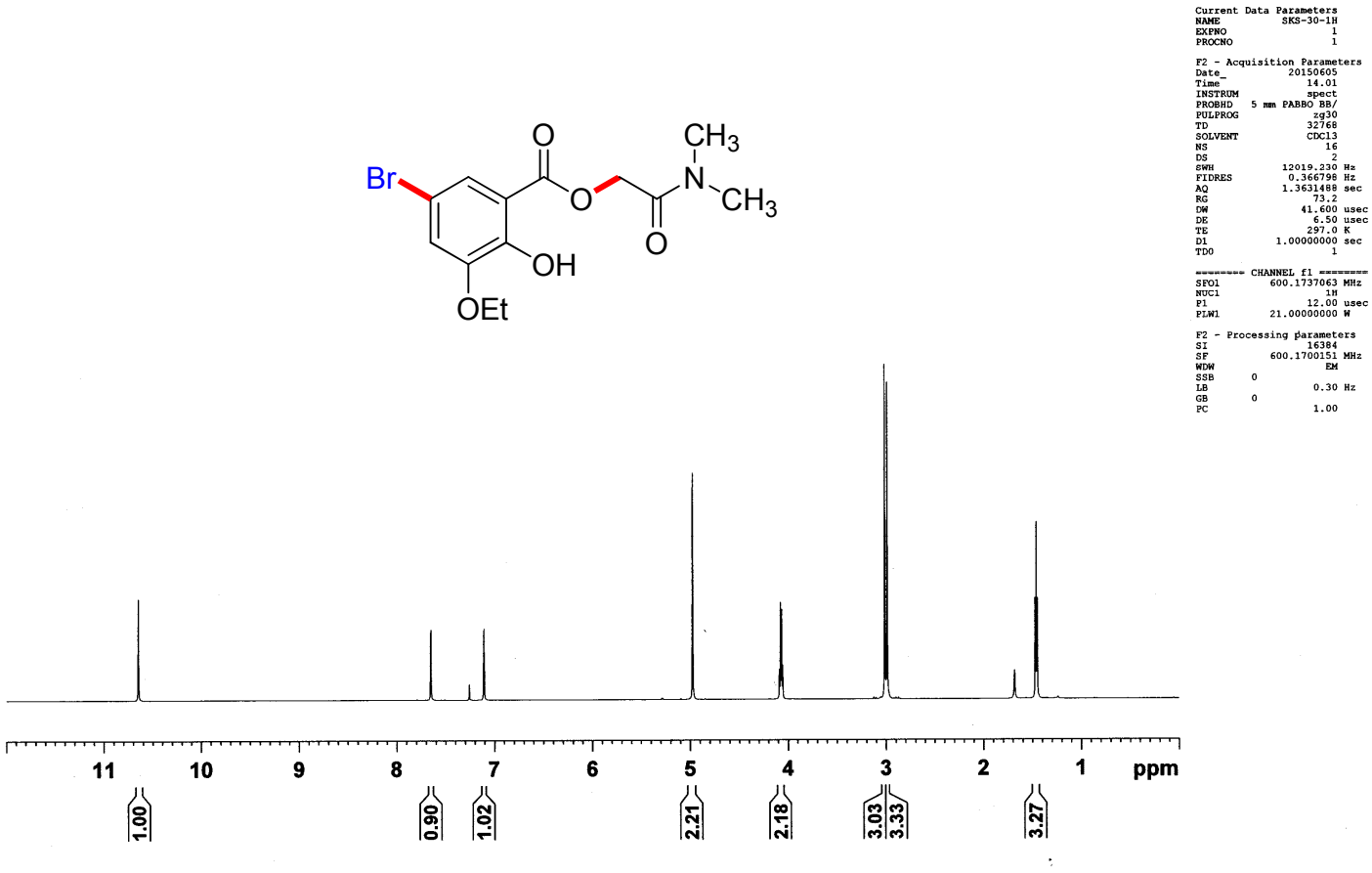
======== CHANNEL f1 ========
SFO1               600.1737063 MHz
NUC1                       1H
P1                      12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
SI                       16384
SF                 600.1700148 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

2-(Dimethylamino)-2-oxoethyl 5-bromo-2-hydroxy-4-methylbenzoate (7a): ^{13}C NMR ($CDCl_3$, 150 MHz)



2-(Dimethylamino)-2-oxoethyl 5-bromo-3-ethoxy-2-hydroxybenzoate (8a): ^{1}H NMR ($CDCl_3$, 600 MHz)



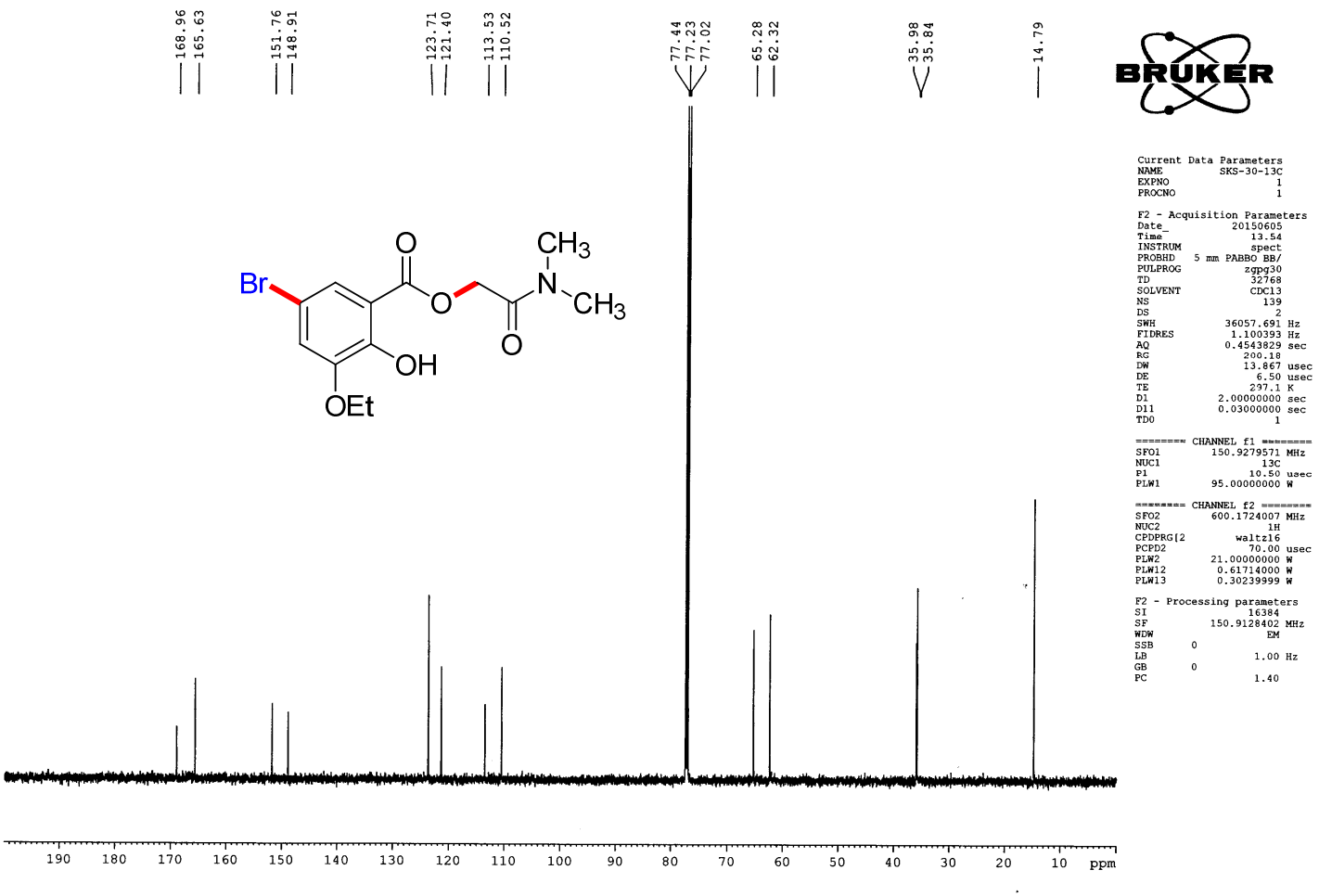

```
Current Data Parameters
NAME                  SKS-30-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20150605
Time                     14.01
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  12019.230 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                         73.2
DW                       41.600 usec
DE                        6.50 usec
TE                       297.0 K
D1                    1.00000000 sec
TD0                           1

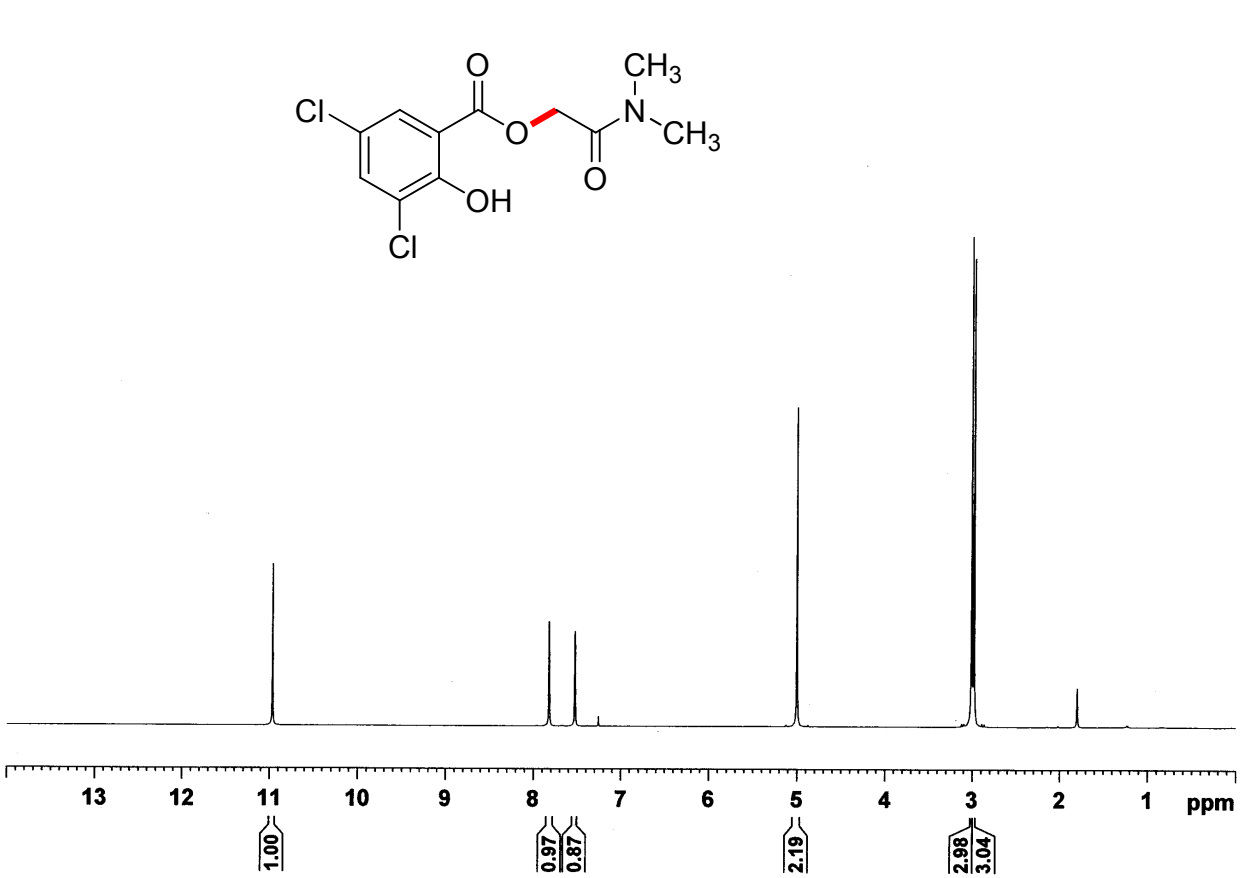
======== CHANNEL f1 ========
SFO1                600.1737063 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                21.00000000 W

F2 - Processing parameters
SI                          16384
SF                  600.1700151 MHz
WDW                            EM
SSB                  0
LB                            0.30 Hz
GB                   0
PC                            1.00
```

2-(Dimethylamino)-2-oxoethyl 5-bromo-3-ethoxy-2-hydroxybenzoate (8a): ^{13}C NMR ($CDCl_3$, 150 MHz)



2-(Dimethylamino)-2-oxoethyl 3,5-dichloro-2-hydroxybenzoat (9a): ^{1}H NMR ($CDCl_3$, 600 MHz)



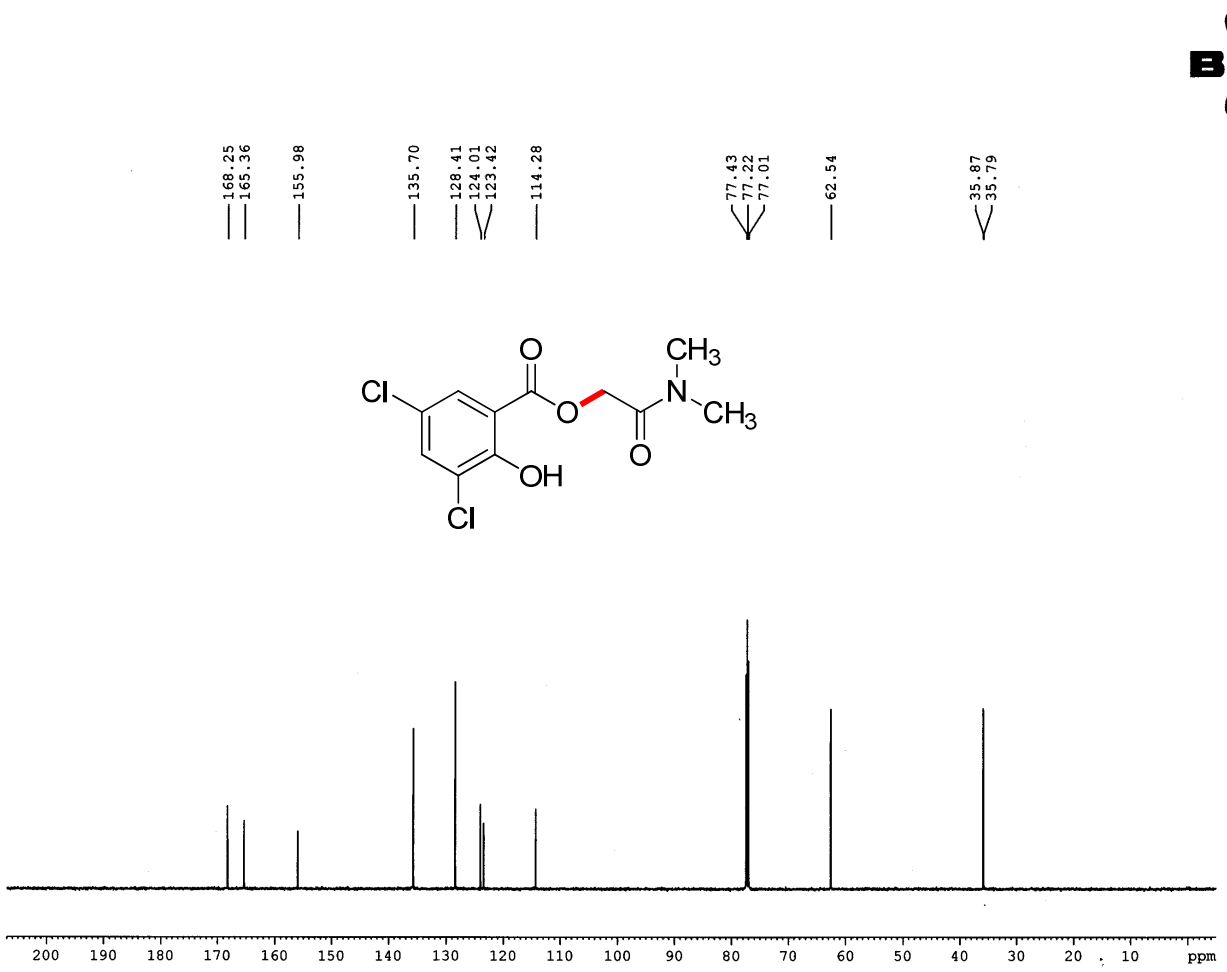

```
Current Data Parameters
NAME                  SKS-27-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20150526
Time                    10.51
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                     43.16
DW                    41.600 usec
DE                     6.50 usec
TE                    293.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              600.1737063 MHz
NUC1                      1H
P1                     12.00 usec
PLW1              21.00000000 W

F2 - Processing parameters
SI                        16384
SF                600.1700155 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

2-(Dimethylamino)-2-oxoethyl 3,5-dichloro-2-hydroxybenzoat (9a): ^{13}C NMR ($CDCl_3$, 150 MHz)




```
Current Data Parameters
NAME                  SKS-27_13C
EXPNO                          1
PROCNO                         1

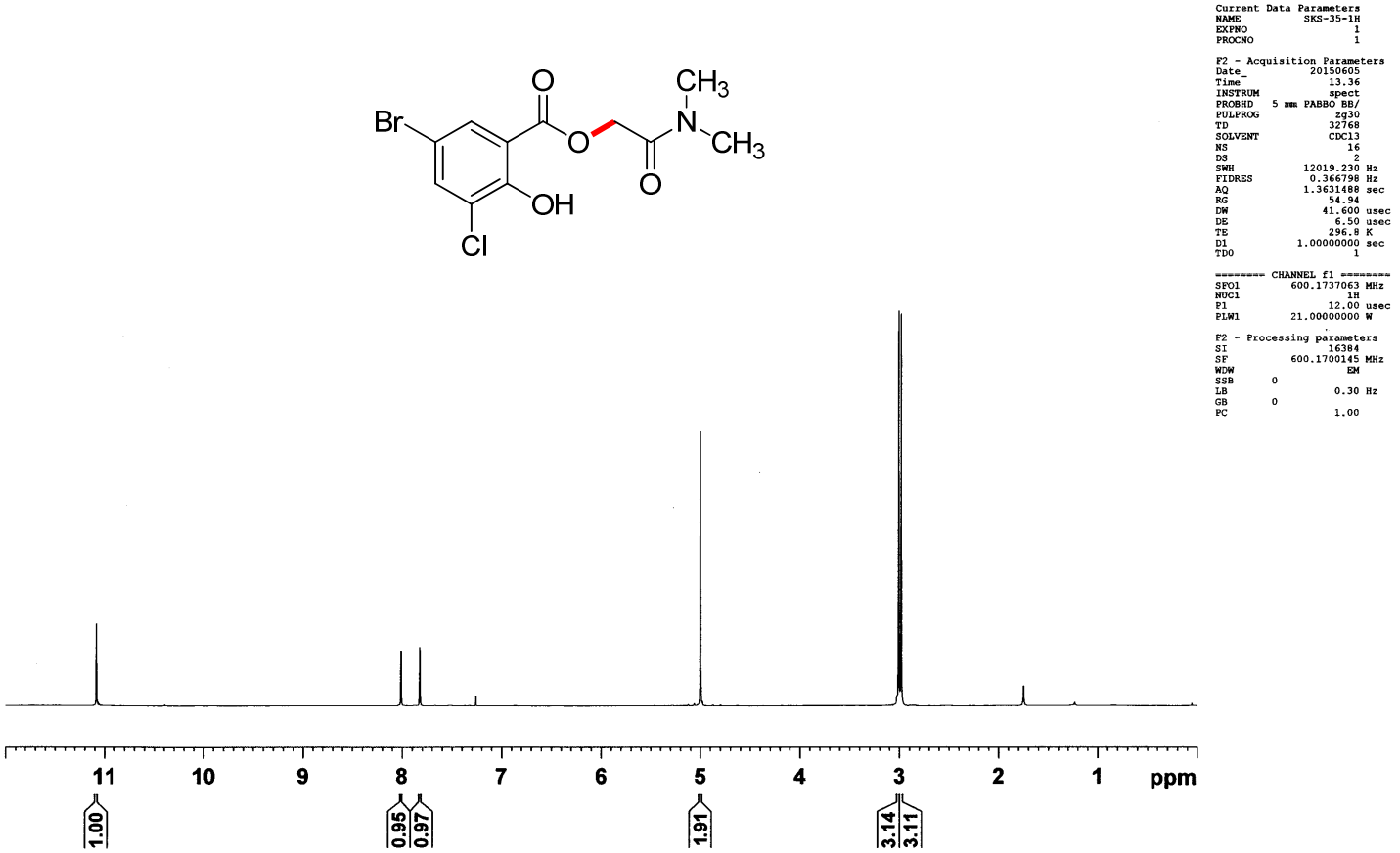
F2 - Acquisition Parameters
Date_                   20150529
Time                       12.56
INSTRUM                    spect
PROBHD   5 mm PABBO BB/
PULPROG                 zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           262
DS                             2
SWH                    36057.691 Hz
FIDRES                 1.100393 Hz
AQ                     0.4543829 sec
RG                         65.24
DW                        13.867 usec
DE                          6.50 usec
TE                         294.8 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 150.9279571 MHz
NUC1                         13C
P1                         10.50 usec
PLW1                95.00000000 W

======== CHANNEL f2 ========
SFO2                 600.1724007 MHz
NUC2                         1H
CPDPRG[2                waltz16
PCPD2                      70.00 usec
PLW2                21.00000000 W
PLW12                0.61714000 W
PLW13                0.30239999 W

F2 - Processing parameters
SI                         16384
SF                   150.9128490 MHz
WDW                           EM
SSB                0
LB                         1.00 Hz
GB                 0
PC                         1.40
```

2-(Dimethylamino)-2-oxoethyl 5-bromo-3-chloro-2-hydroxybenzoate (10a): ^{1}H NMR ($CDCl_3$, 600 MHz)



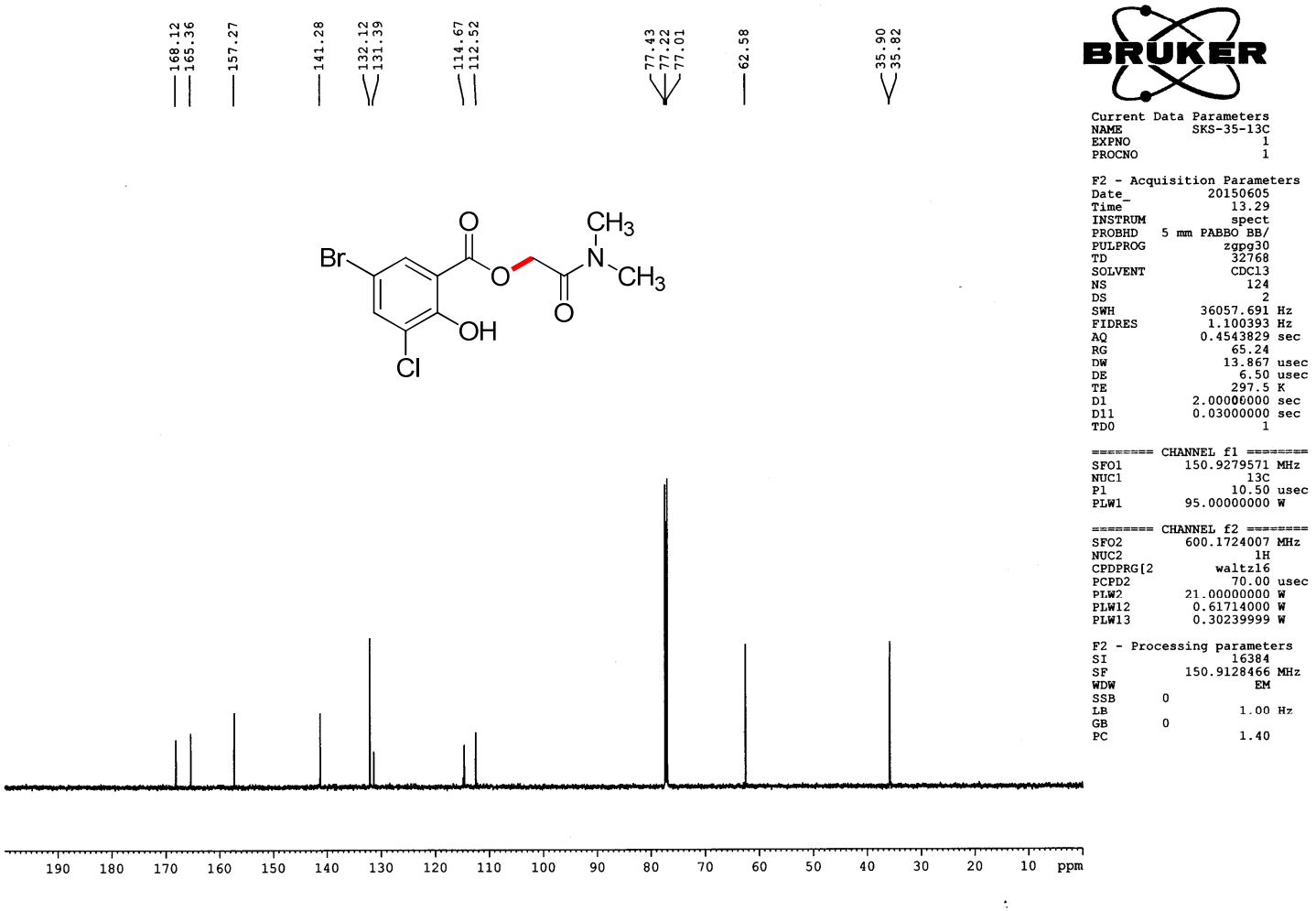

```
Current Data Parameters
NAME                  SKS-35-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20150605
Time                      13.36
INSTRUM                   spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  12019.230 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                        54.94
DW                       41.600 usec
DE                        6.50 usec
TE                       296.8 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1737063 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                21.00000000 W

F2 - Processing parameters
SI                        16384
SF                  600.1700145 MHz
WDW                          EM
SSB                 0
LB                        0.30 Hz
GB                  0
PC                        1.00
```

2-(Dimethylamino)-2-oxoethyl 5-bromo-3-chloro-2-hydroxybenzoate (10a): ^{13}C NMR ($CDCl_3$, 150 MHz)



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```
Current Data Parameters
NAME          SKS-35-13C
EXPNO                  1
PROCNO                 1

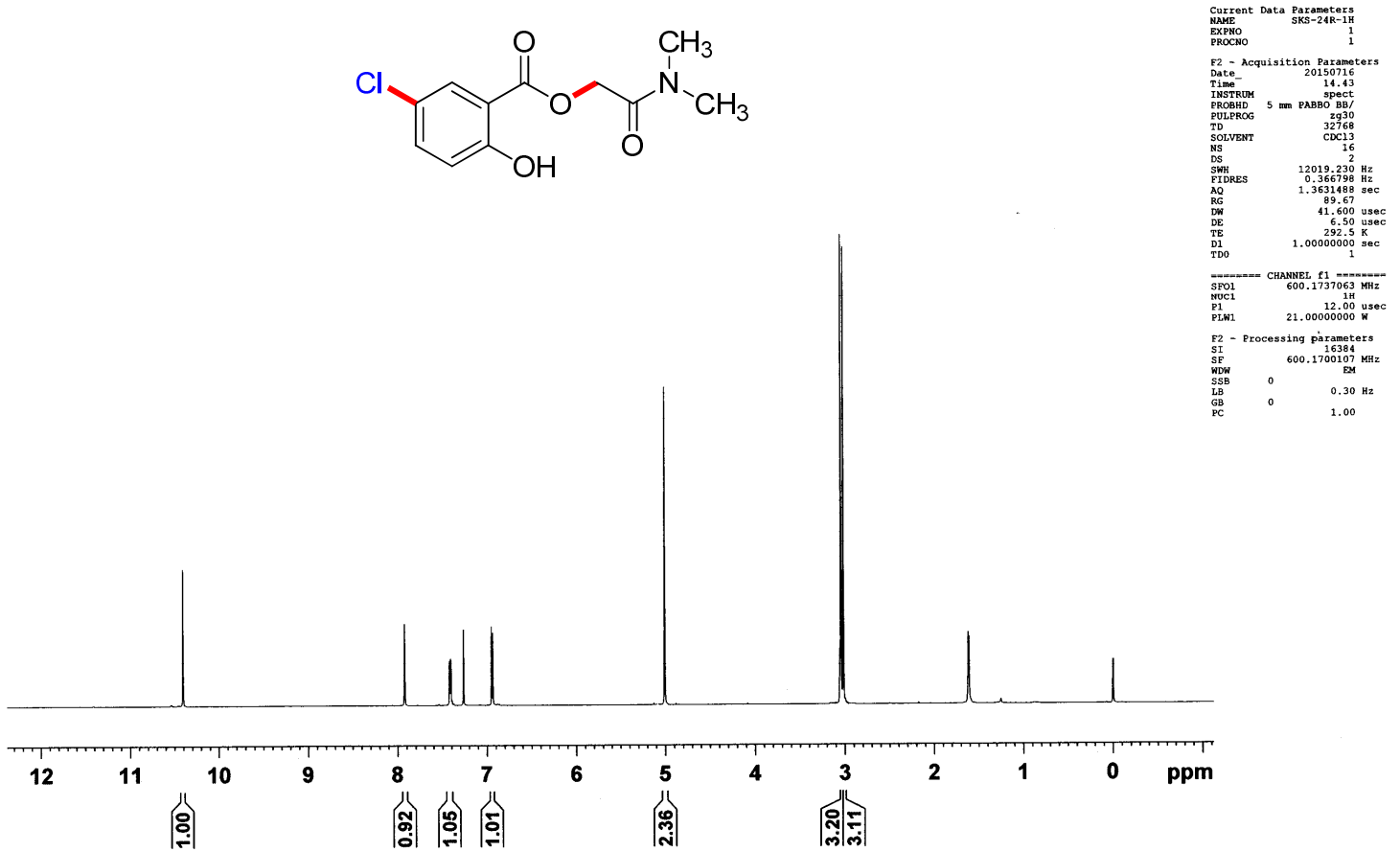
F2 - Acquisition Parameters
Date_           20150605
Time               13.29
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  124
DS                    2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE               297.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1                13C
P1                10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                 16384
SF          150.9128466 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

2-(Dimethylamino)-2-oxoethyl 5-chloro-2-hydroxybenzoate (1a´´): ^{1}H NMR ($CDCl_3$, 600 MHz)



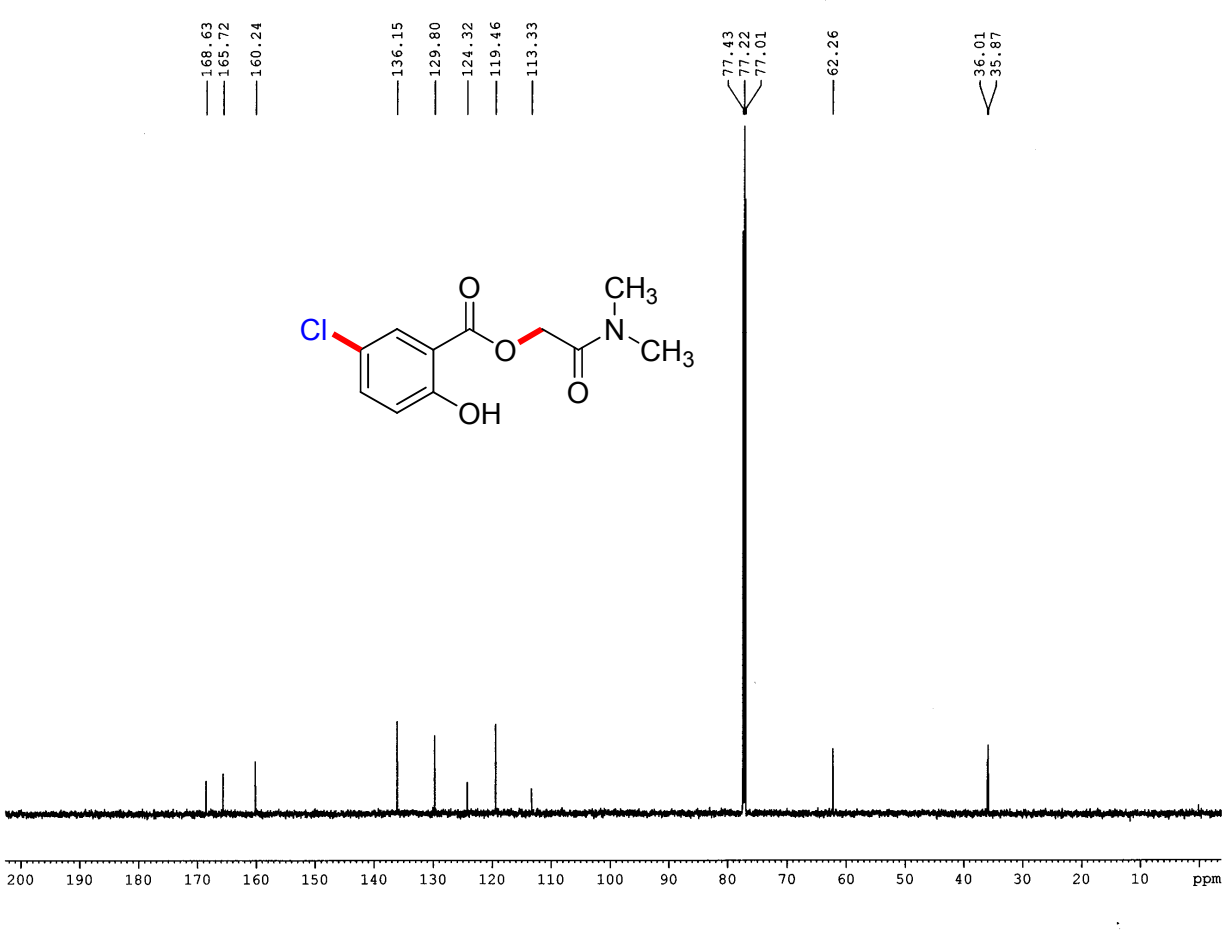

```
Current Data Parameters
NAME                  SKS-24R-1H
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150716
Time                       14.43
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        32768
SOLVENT                   CDCl3
NS                            16
DS                             2
SWH                   12019.230 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                        89.67
DW                       41.600 usec
DE                        6.50 usec
TE                       292.5 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                600.1737063 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                21.00000000 W

F2 - Processing parameters
SI                         16384
SF                  600.1700107 MHz
WDW                           EM
SSB                0
LB                           0.30 Hz
GB                 0
PC                           1.00
```

2-(Dimethylamino)-2-oxoethyl 5-chloro-2-hydroxybenzoate (1a´´): ^{13}C NMR ($CDCl_3$, 150 MHz)




```
Current Data Parameters
NAME        SKS-24-R-13C
EXPNO                  1
PROCNO                 1

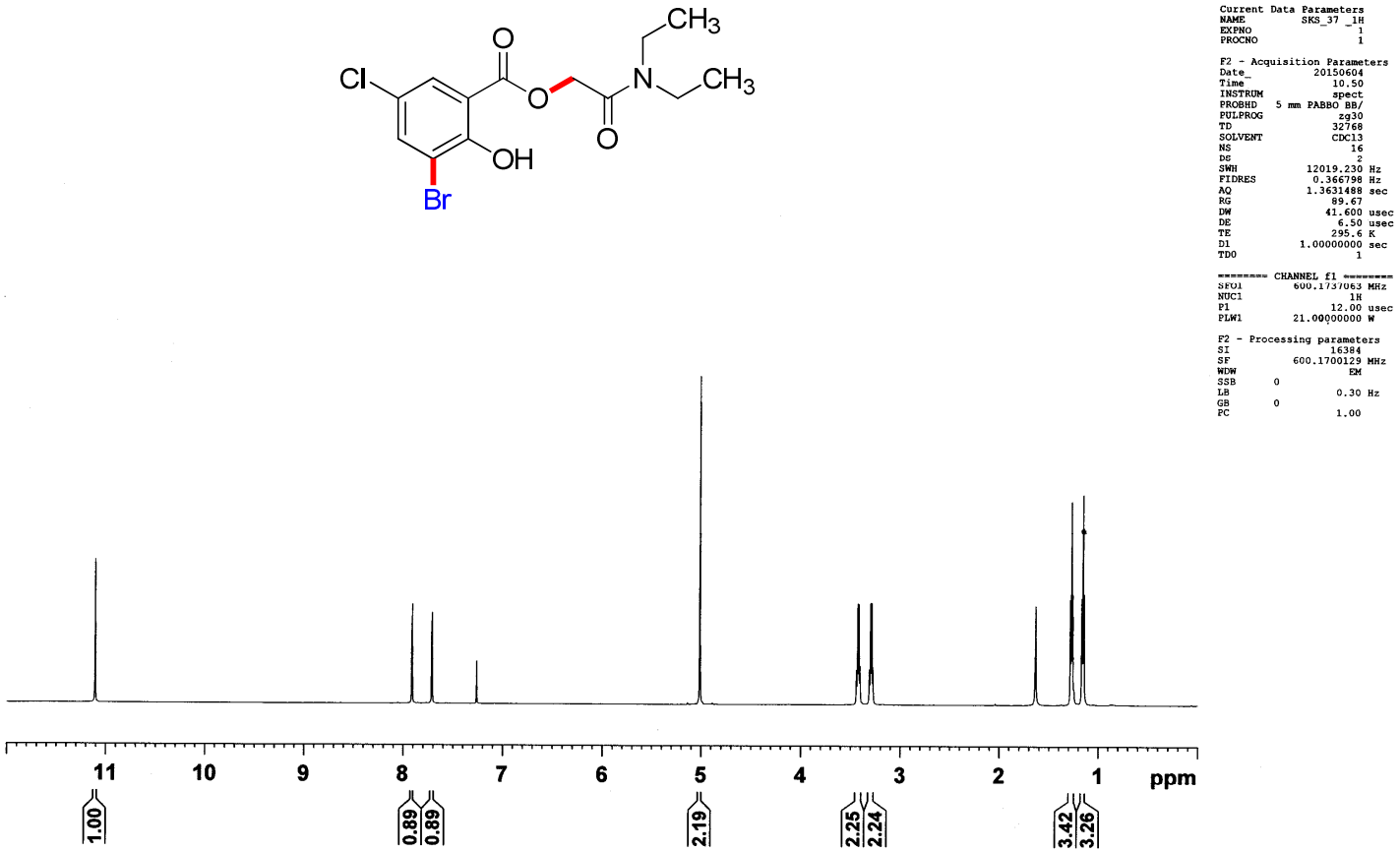
F2 - Acquisition Parameters
Date_           20150718
Time                9.56
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           42613.637 Hz
FIDRES         1.300465 Hz
AQ             0.3844779 sec
RG                65.24
DW               11.733 usec
DE                6.50 usec
TE               296.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1               13C
P1                10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                16384
SF          150.9128378 MHz
WDW                EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

2-(Diethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3b): ^{1}H NMR ($CDCl_3$, 600 MHz)

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Current Data Parameters
NAME          SKS_37 _1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150604
Time               10.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12019.230 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG                89.67
DW               41.600 usec
DE                6.50 usec
TE               295.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1737063 MHz
NUC1                   1H
P1                 12.00 usec
PLW1        21.00000000 W

F2 - Processing parameters
SI                 16384
SF          600.1700129 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```
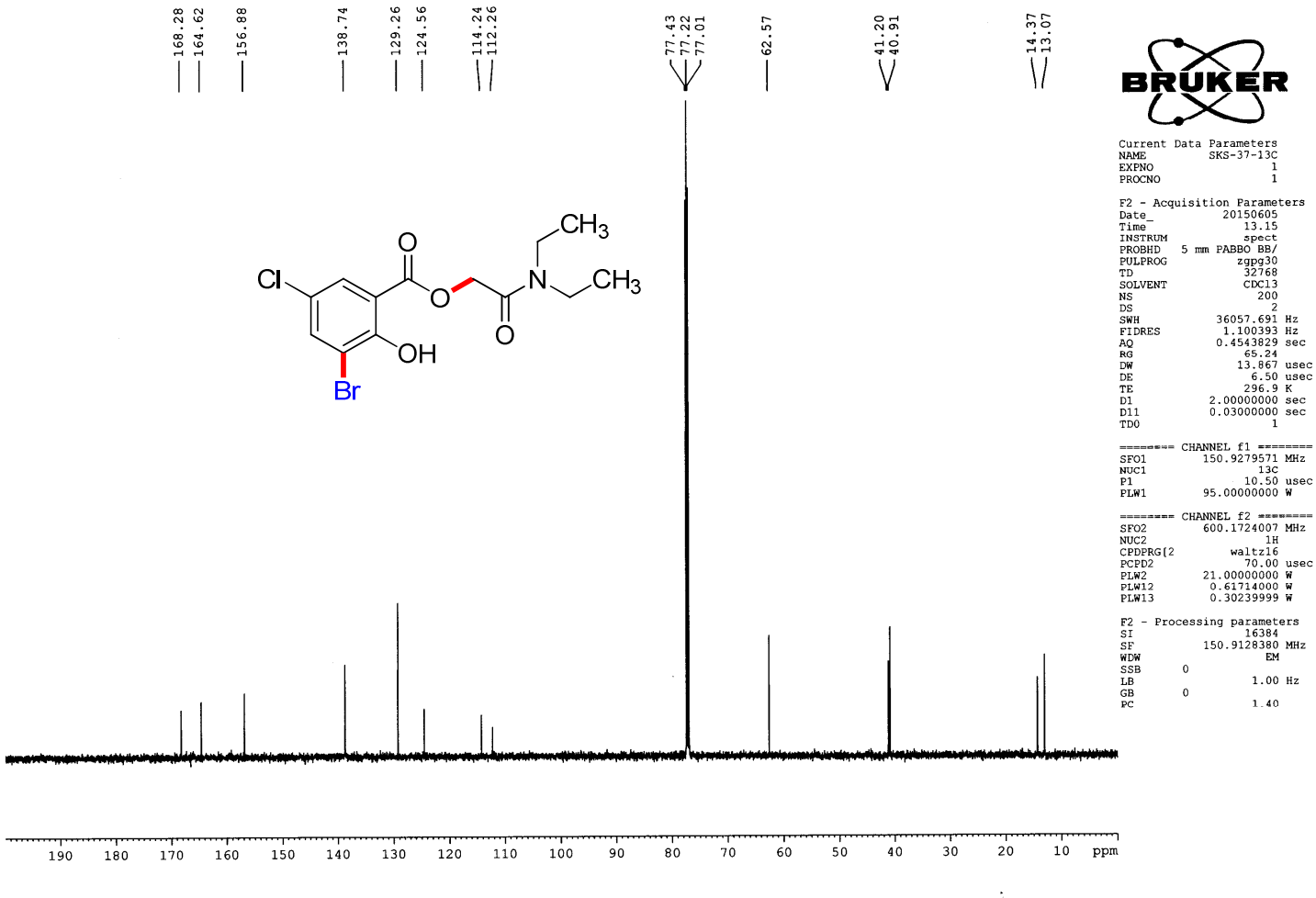
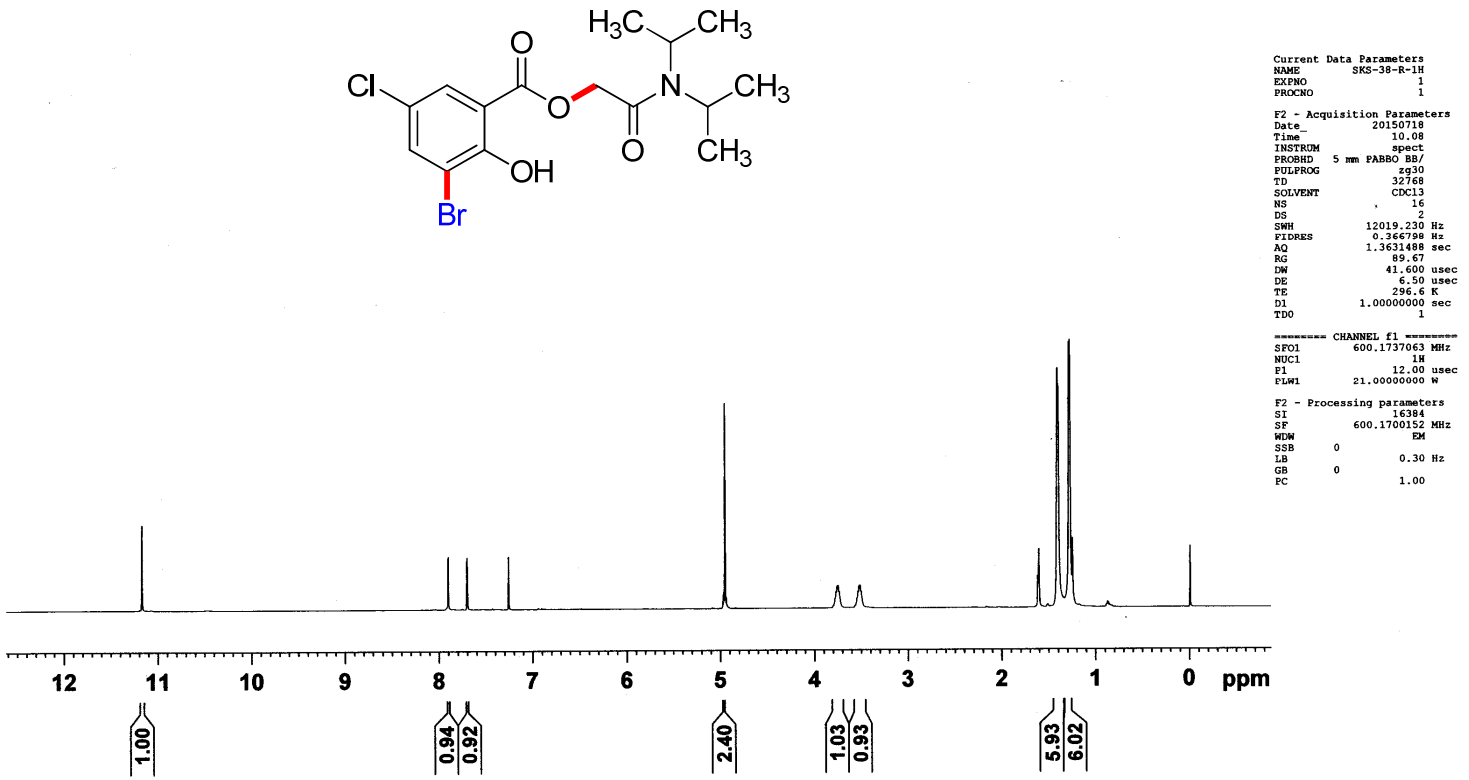
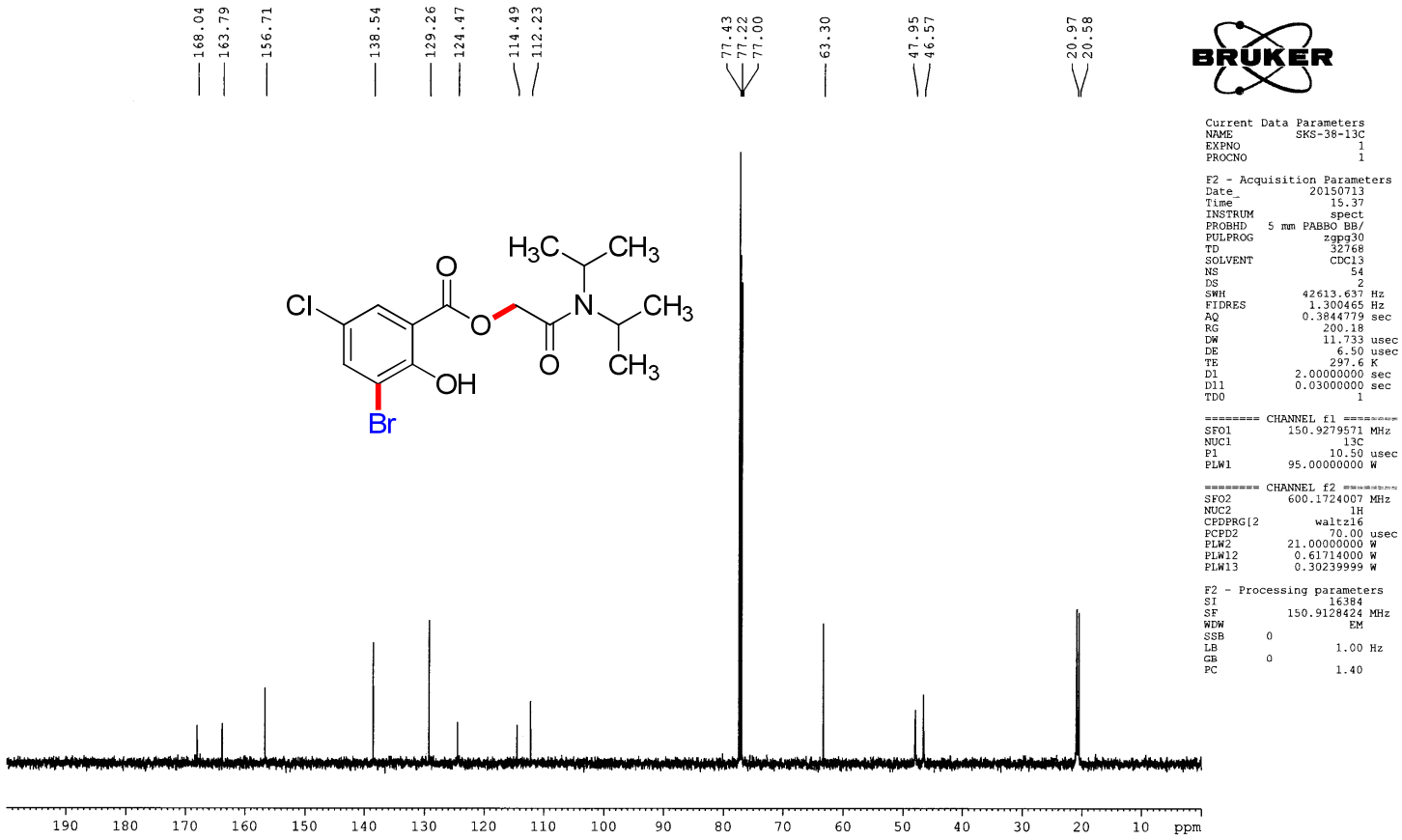

2-(Diethylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3b): ^{13}C NMR ($CDCl_3$, 150 MHz)



2-(Diisopropylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3c): ^{1}H NMR ($CDCl_3$, 600 MHz)

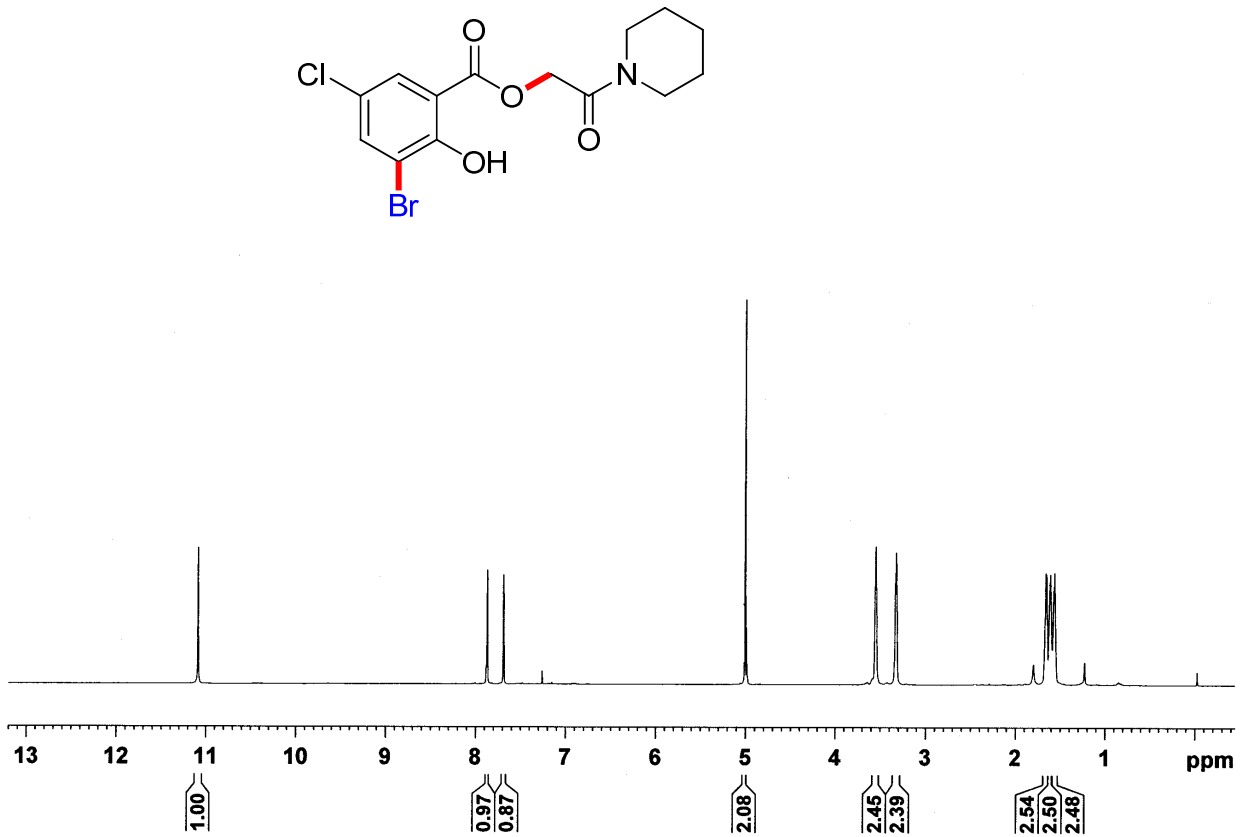


2-(Diisopropylamino)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3c): ^{13}C NMR ($CDCl_3$, 150 MHz)



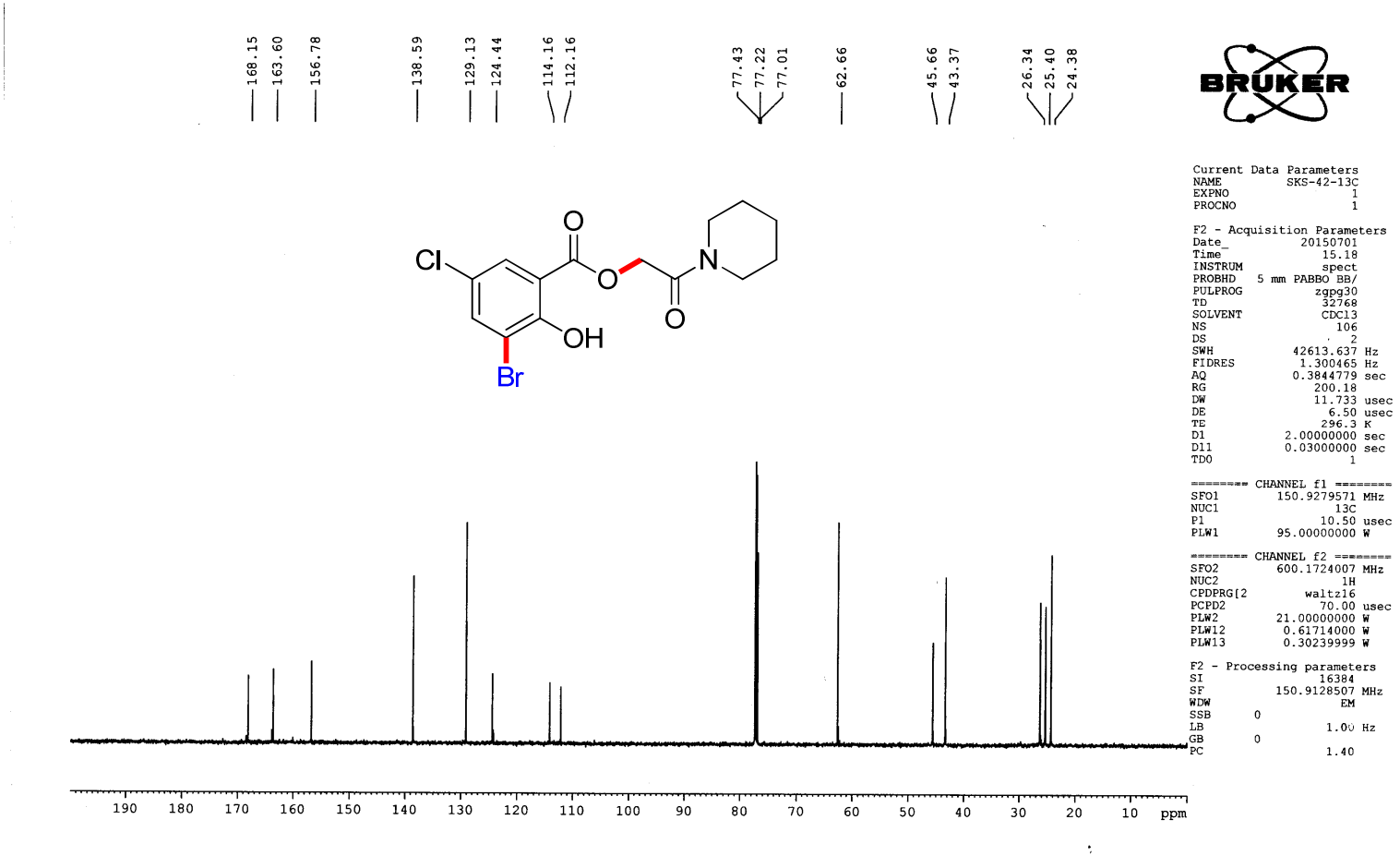

```
Current Data Parameters
NAME                  SKS-38-13C
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150713
Time                       15.37
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                            54
DS                             2
SWH                    42613.637 Hz
FIDRES                 1.300465 Hz
AQ                     0.3844779 sec
RG                        200.18
DW                        11.733 usec
DE                          6.50 usec
TE                        297.6 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 150.9279571 MHz
NUC1                         13C
P1                         10.50 usec
PLW1                95.00000000 W

======== CHANNEL f2 ========
SFO2                 600.1724007 MHz
NUC2                         1H
CPDPRG[2                 waltz16
PCPD2                      70.00 usec
PLW2                21.00000000 W
PLW12                0.61714000 W
PLW13                0.30239999 W

F2 - Processing parameters
SI                         16384
SF                   150.9128424 MHz
WDW                           EM
SSB                0
LB                         1.00 Hz
GB                 0
PC                         1.40
```

2-Oxo-2-(piperidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3d): ^{1}H NMR ($CDCl_3$, 600 MHz)

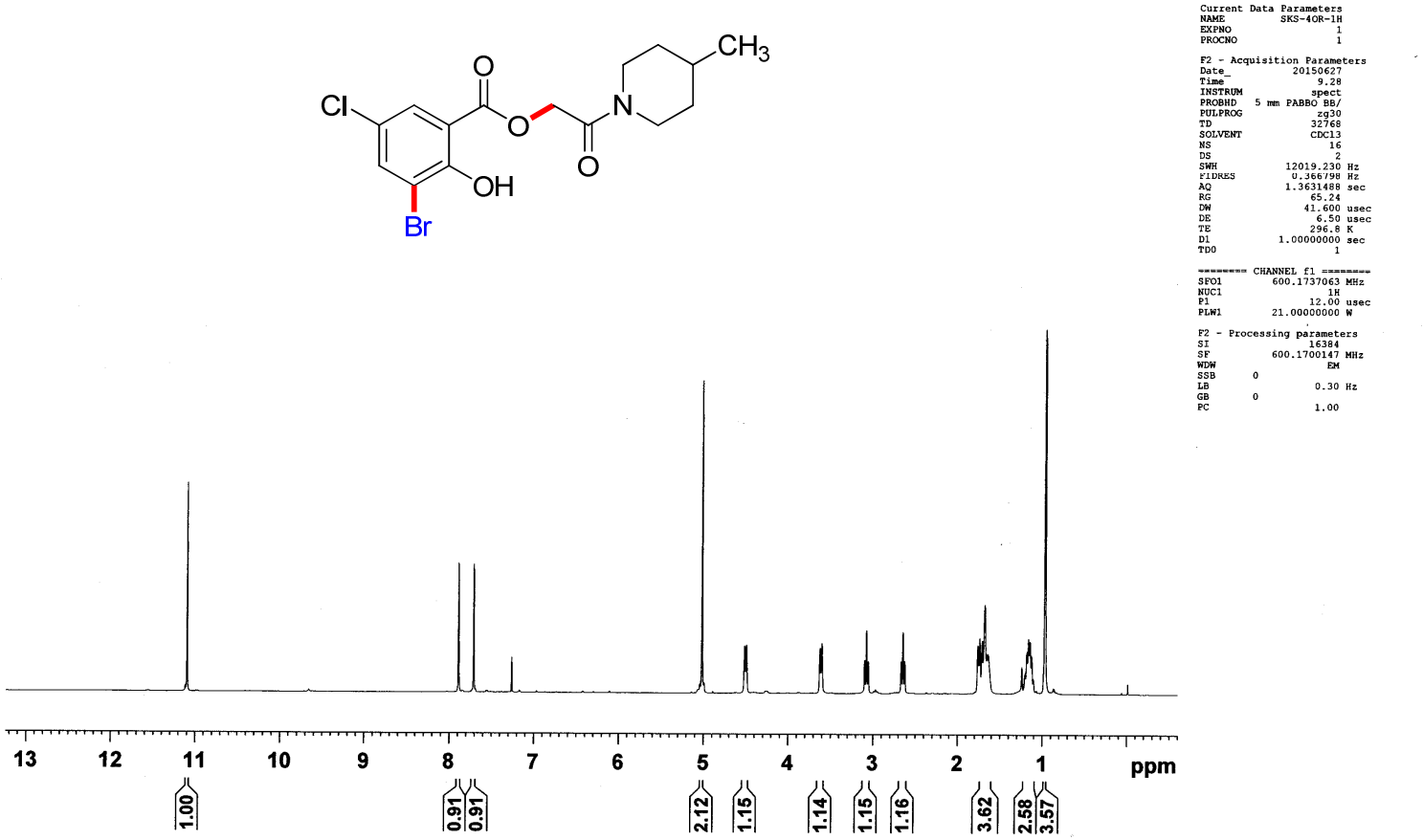



```
Current Data Parameters
NAME                  SKS-42-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20150627
Time                      9.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                      39.59
DW                     41.600 usec
DE                      6.50 usec
TE                     296.8 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             600.1737063 MHz
NUC1                       1H
P1                      12.00 usec
PLW1            21.00000000 W

F2 - Processing parameters
SI                      16384
SF               600.1700149 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

2-Oxo-2-(piperidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3d): ^{13}C NMR ($CDCl_3$, 150 MHz)

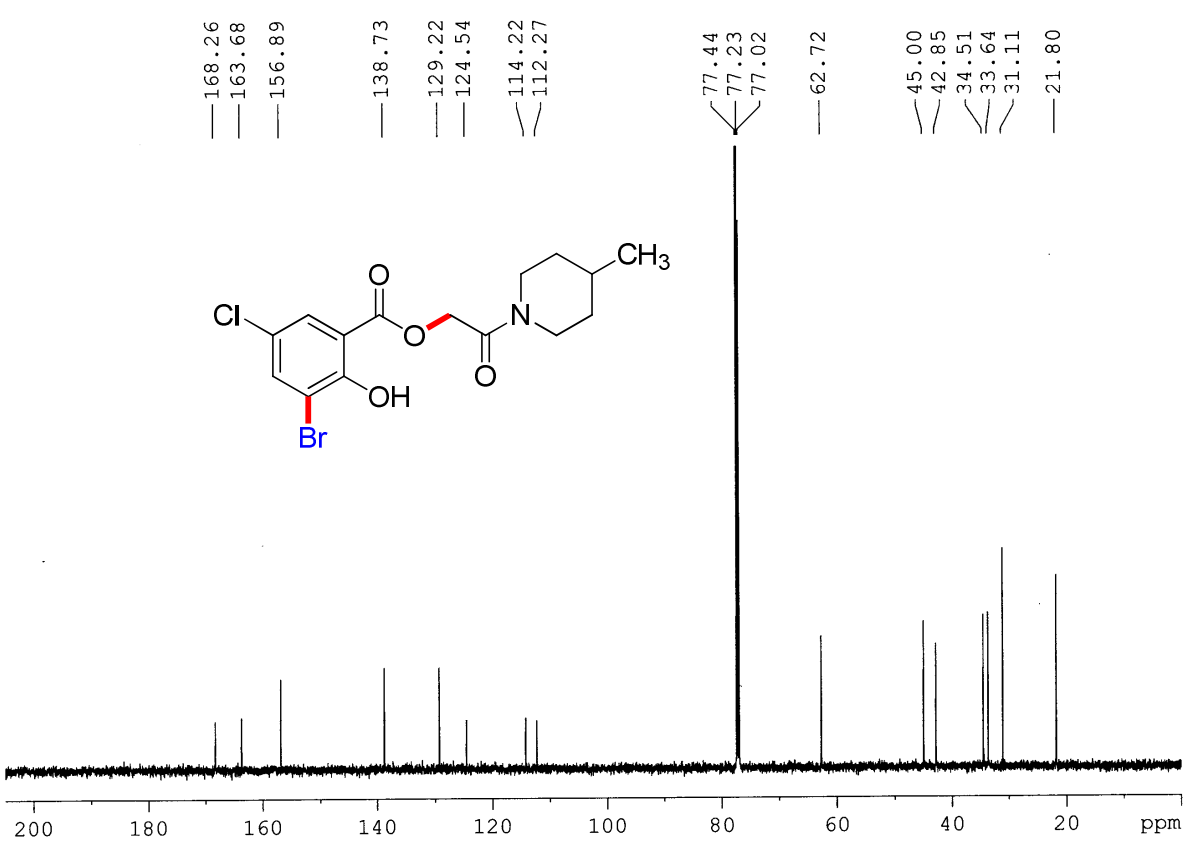


2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3e):^{1}H NMR ($CDCl_3$, 600 MHz)




```
Current Data Parameters
NAME                 SKS-4OR-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20150627
Time                    9.28
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                     65.24
DW                    41.600 usec
DE                     6.50 usec
TE                    296.8 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             600.1737063 MHz
NUC1                       1H
P1                      12.00 usec
PLW1            21.00000000 W

F2 - Processing parameters
SI                     16384
SF               600.1700147 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3e):^{13}C NMR ($CDCl_3$, 150 MHz)



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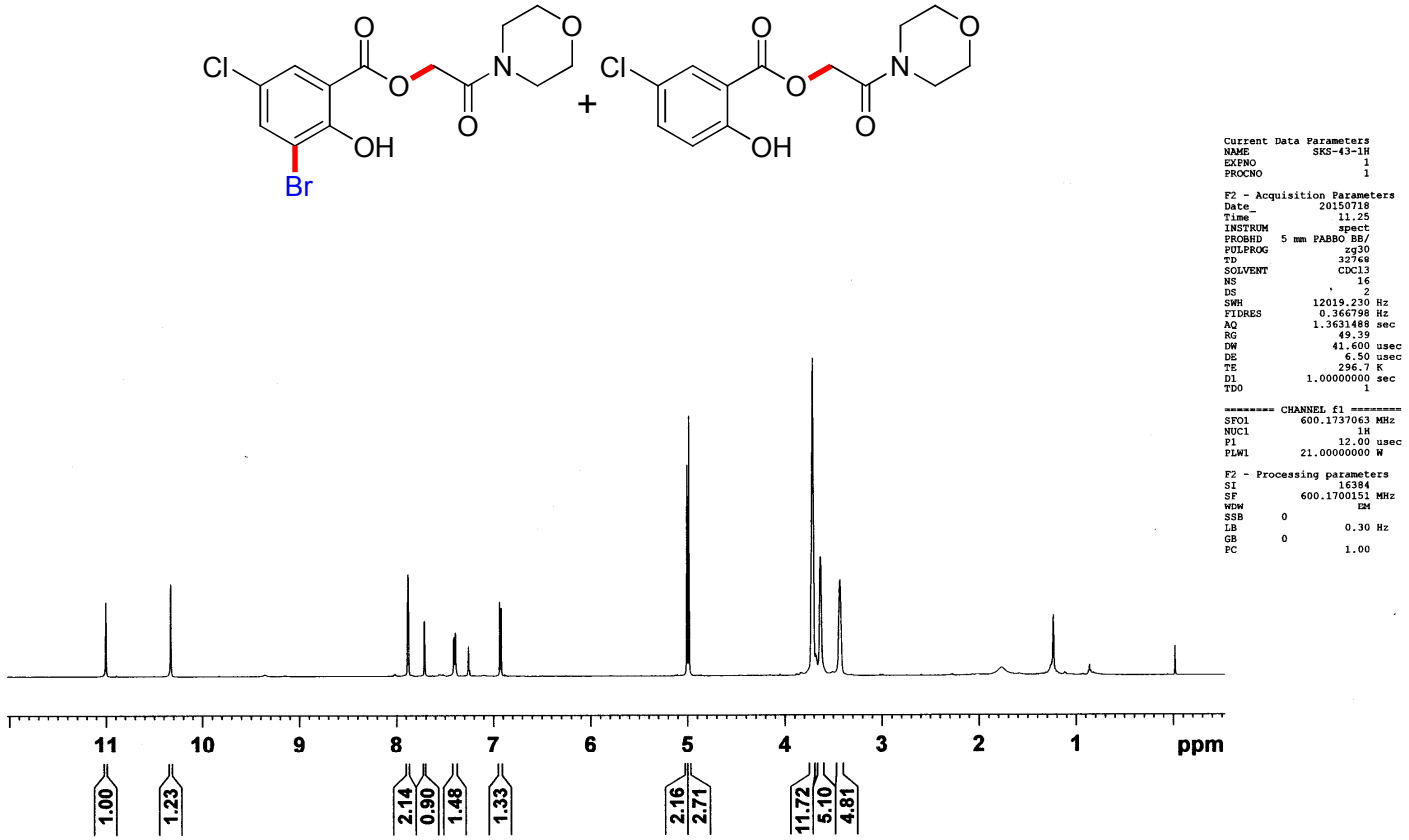
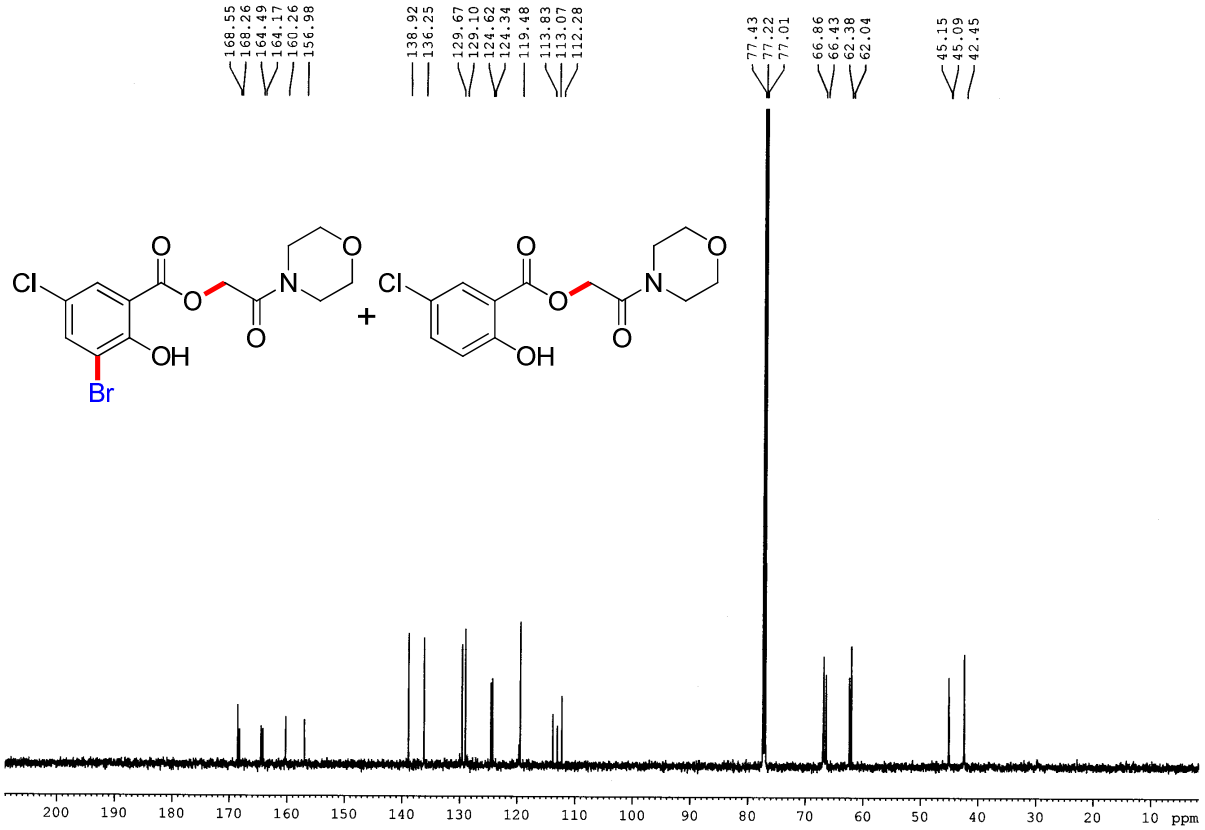
```
Current Data Parameters
NAME         SKS-40R-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150707
Time              13.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               32768
SOLVENT          CDCl3
NS                 102
DS                   2
SWH          42613.637 Hz
FIDRES        1.300465 Hz
AQ            0.3844779 sec
RG                6[illegible].24
DW               11.733 usec
DE                6.50 usec
TE              297.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       150.9279571 MHz
NUC1              13C
P1              10.50 usec
PLW1       95.00000000 W

======== CHANNEL f2 ========
SFO2       600.1724007 MHz
NUC2              1H
CPDPRG[2        waltz16
PCPD2           70.00 usec
PLW2       21.00000000 W
PLW12       0.61714000 W
PLW13       0.30239999 W

F2 - Processing parameters
SI               16384
SF         150.9128390 MHz
WDW                 EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
```

2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Morpholino-2-oxoethyl 5-chloro-2-hydroxybenzoate (3f and 3f´): ^{1}H NMR ($CDCl_3$, 600 MHz)



2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Morpholino-2-oxoethyl 5-chloro-2-hydroxybenzoate (3f and 3f´): ^{13}C NMR ($CDCl_3$, 150 MHz)



BRUKER

Current Data Parameters
NAME SKS-43-13c
EXPNO 1
PROCNO 1

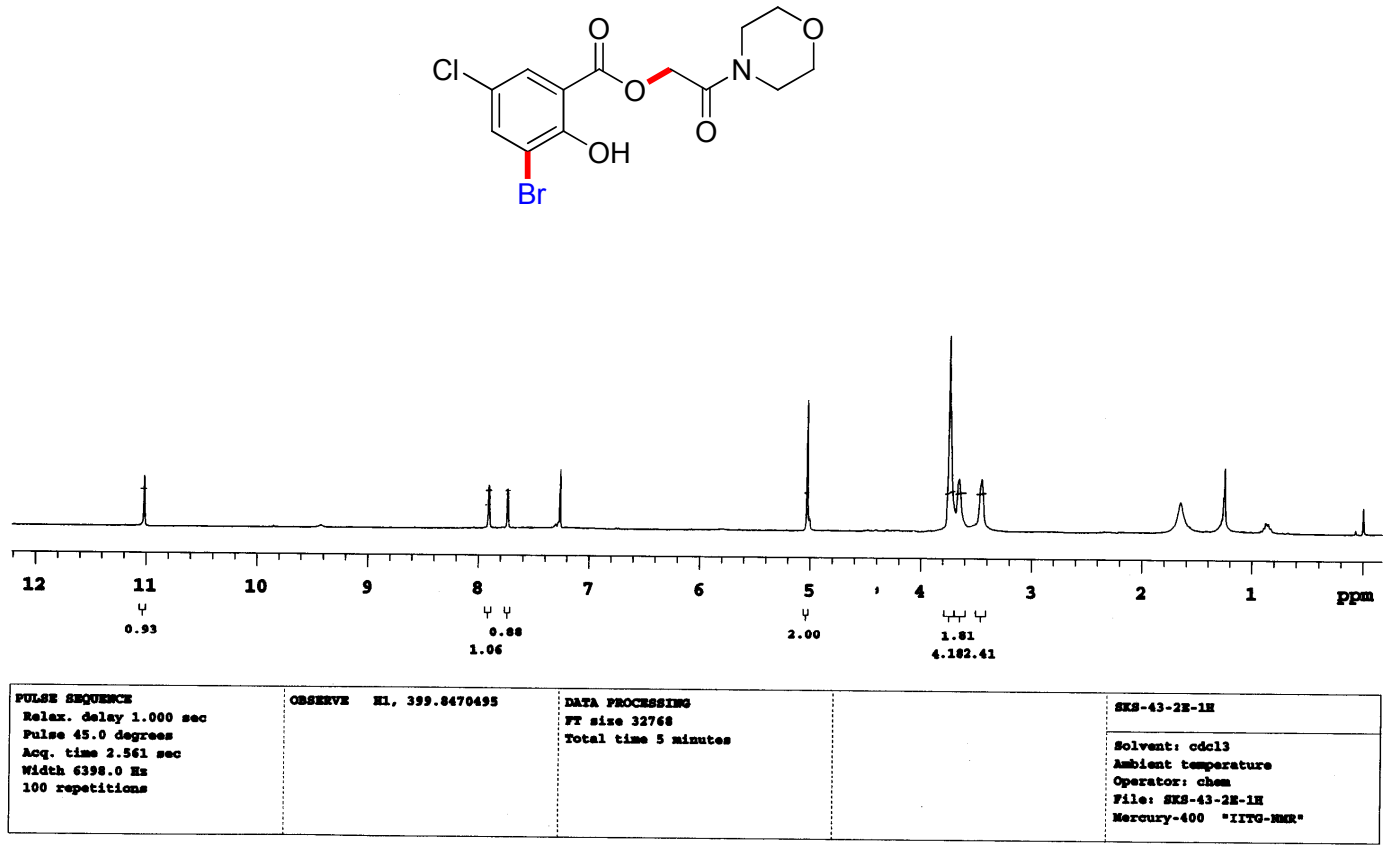
F2 - Acquisition Parameters
Date_ 20150718
Time 11.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 251
DS 2
SWH 42613.637 Hz
FIDRES 1.300465 Hz
AQ 0.3844779 sec
RG 65.24
DW 11.733 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

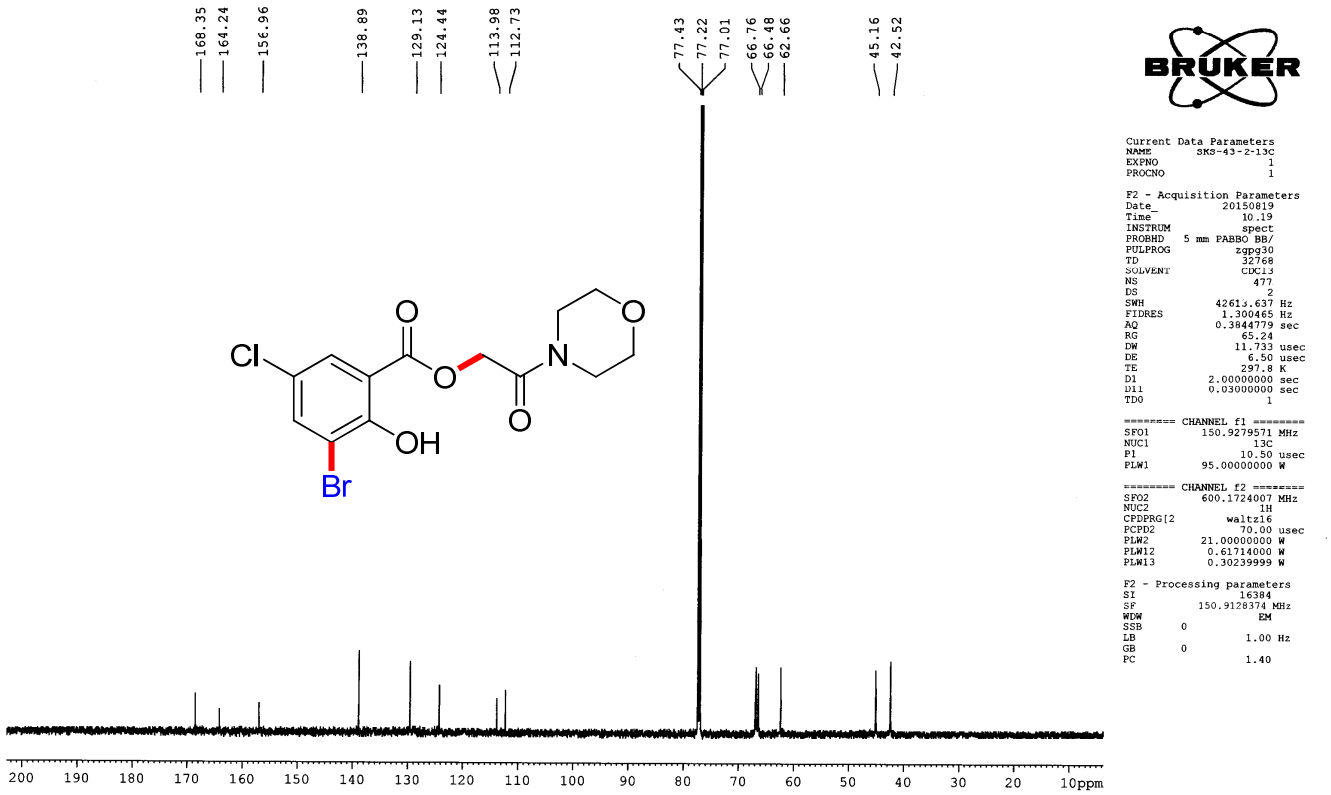
======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128429 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

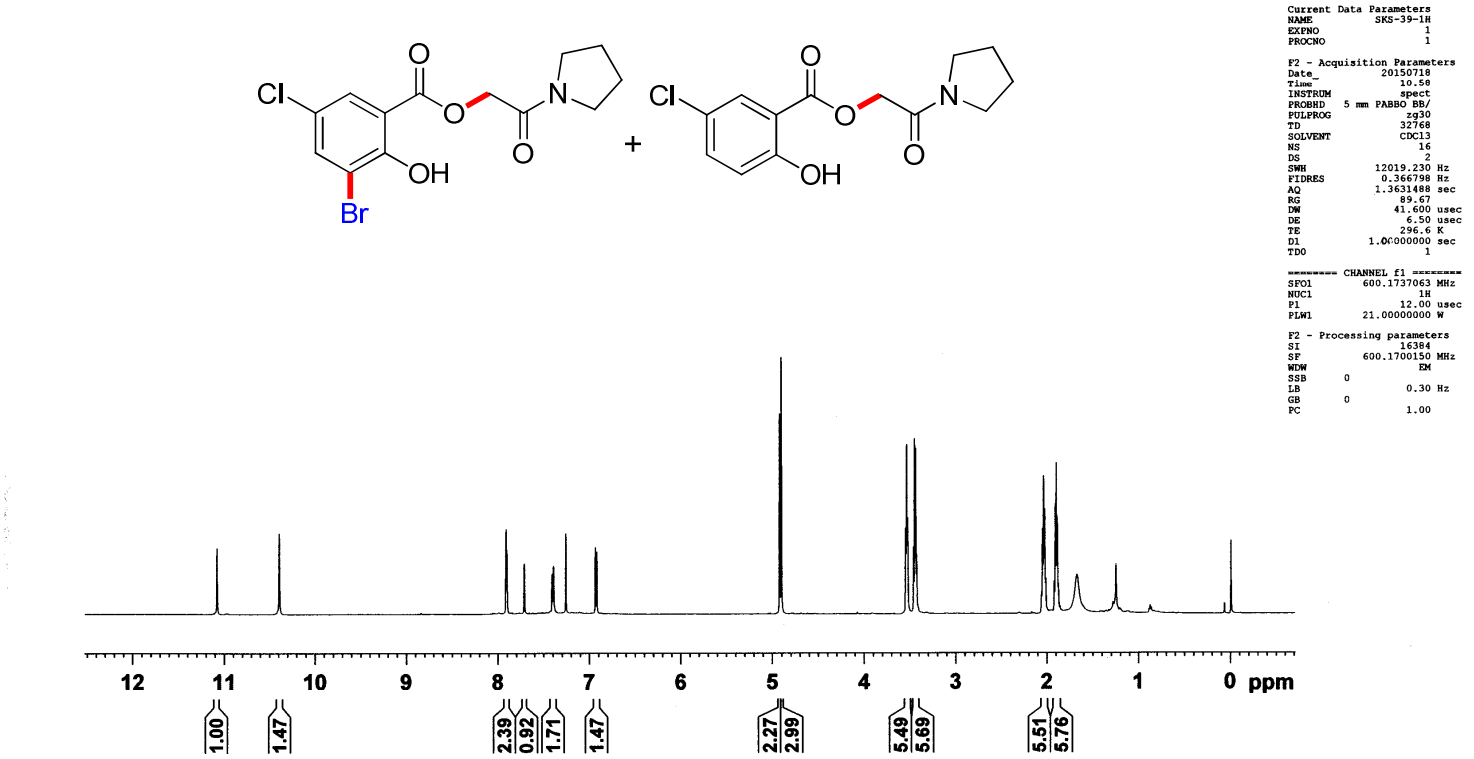
2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3f): ^{1}H NMR ($CDCl_3$, 400 MHz)



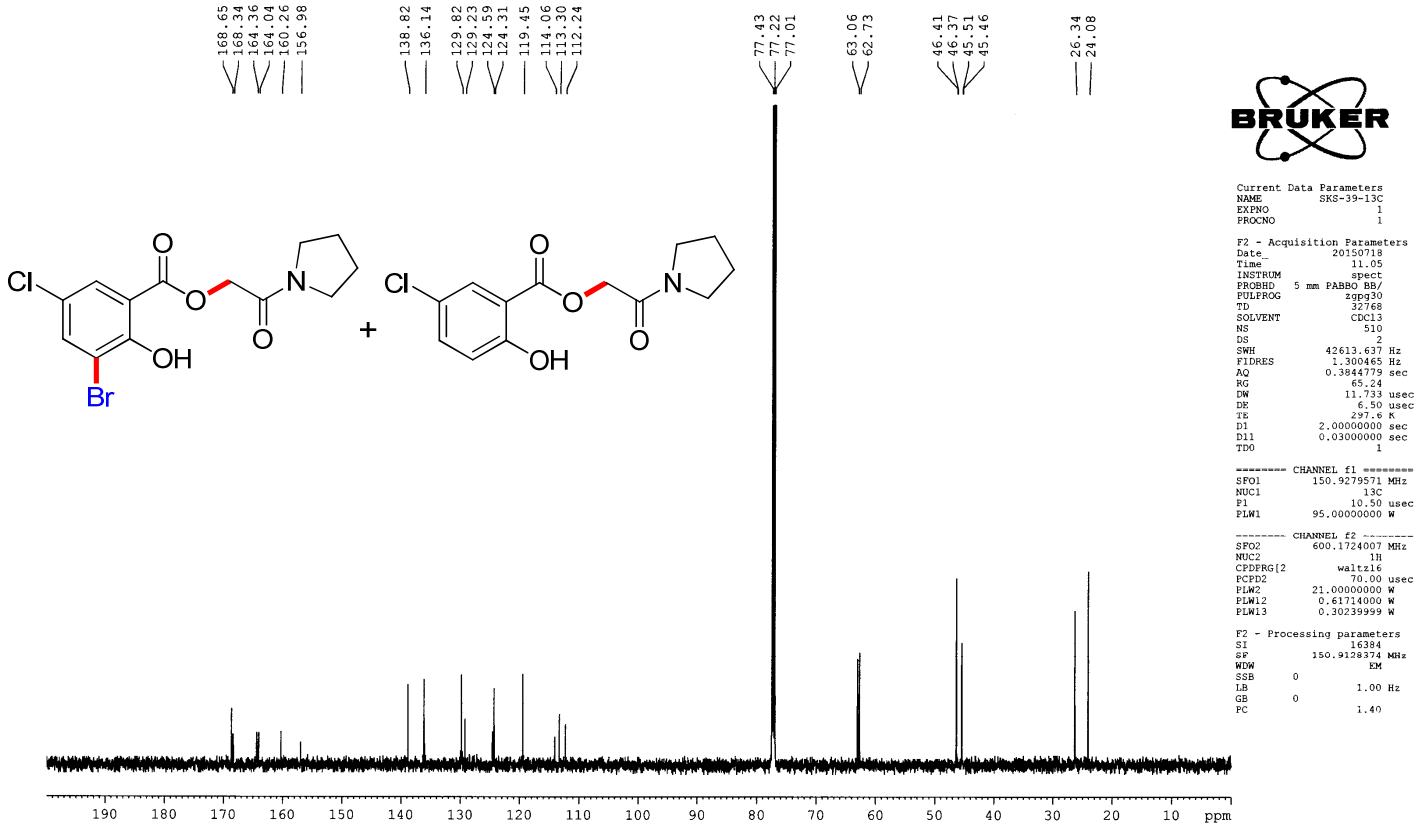
2-Morpholino-2-oxoethyl 3-bromo-5-chloro-2-hydroxybenzoate (3f): ^{13}C NMR ($CDCl_3$, 150 MHz)



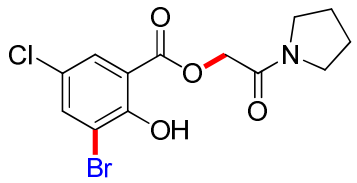
2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Oxo-2-(pyrrolidin-1-yl)ethyl 5-chloro-2-hydroxybenzoate (3g and 3g´): ^{1}H NMR ($CDCl_3$, 600 MHz)

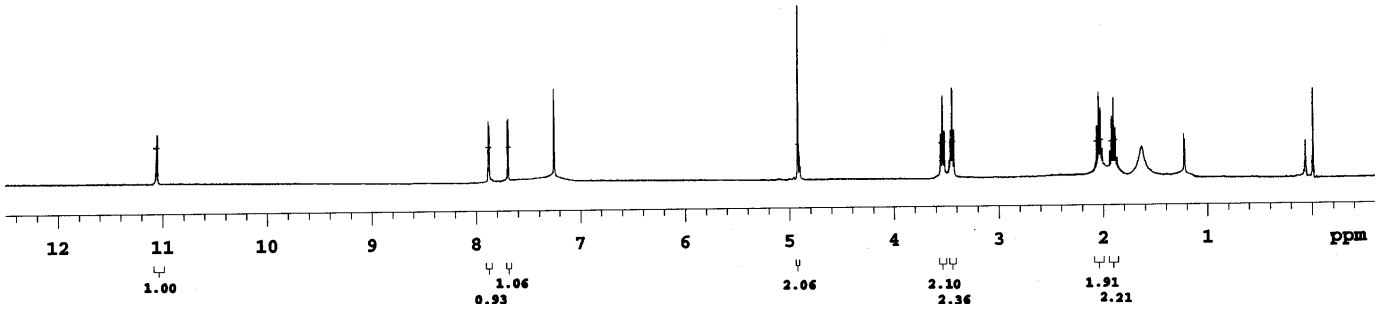


2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate and 2-Oxo-2-(pyrrolidin-1-yl)ethyl 5-chloro-2-hydroxybenzoate (3g and 3g´): ^{13}C NMR ($CDCl_3$, 150 MHz)



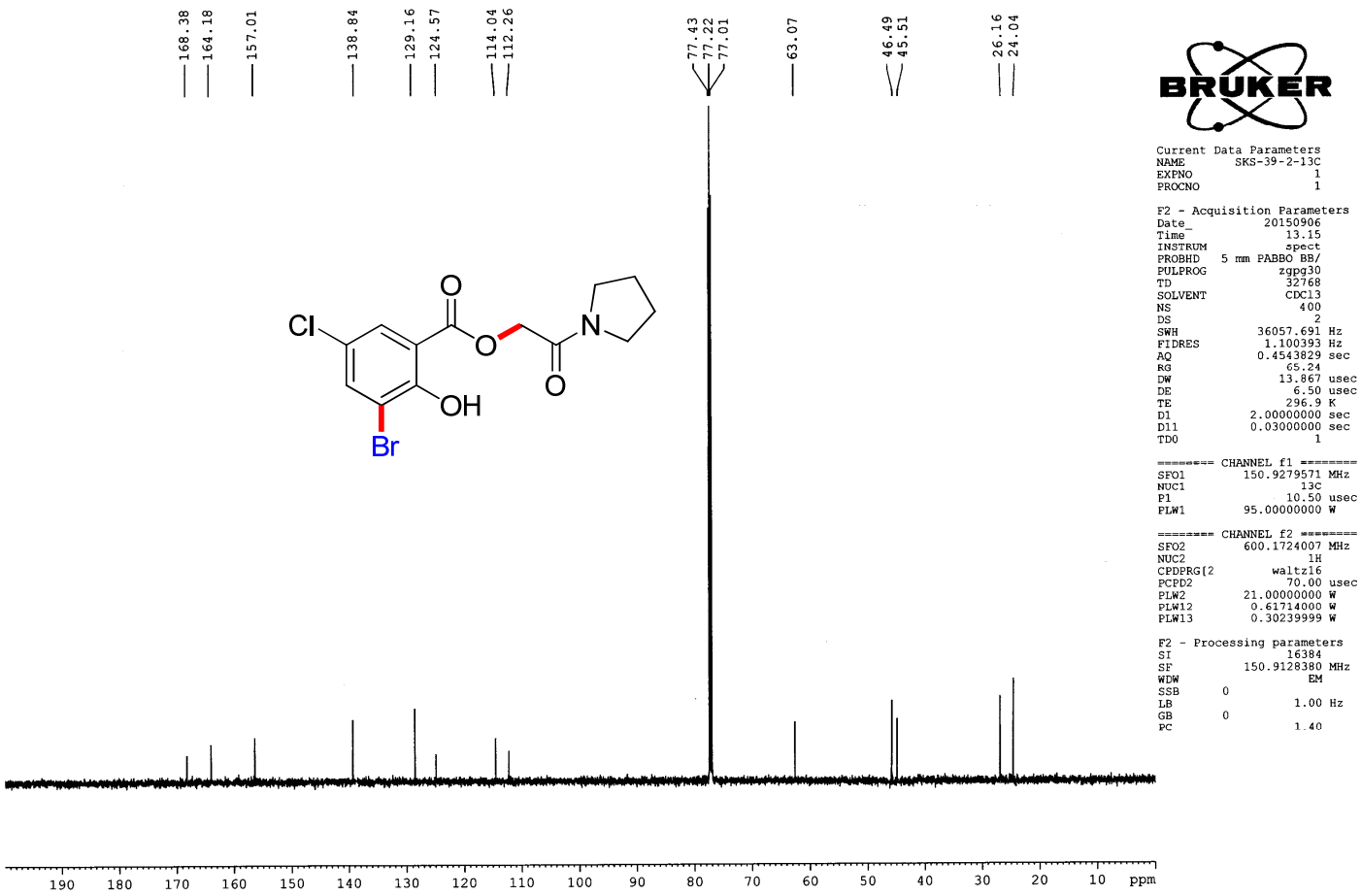
2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3g): ^{1}H NMR ($CDCl_3$, 400 MHz)





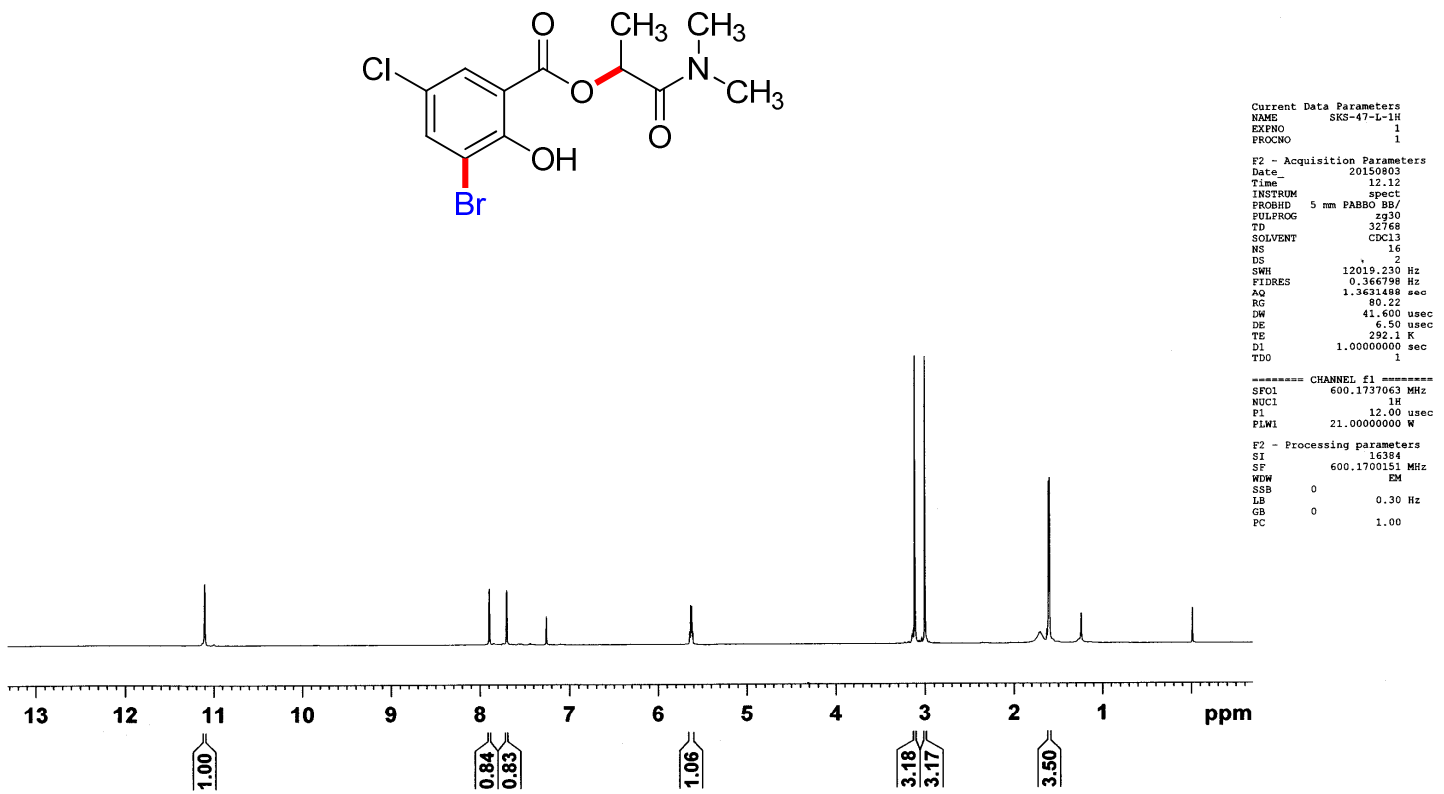
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.561 sec Width 6398.0 Hz 100 repetitions	OBSERVE H1, 399.8470548	DATA PROCESSING FT size 32768 Total time 5 minutes		SKS-39-1H Solvent: cdcl3 Ambient temperature Operator: chem File: SKS-39-1H Mercury-400 "IITG-NMR"

2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromo-5-chloro-2-hydroxybenzoate (3g): ^{13}C NMR ($CDCl_3$, 150 MHz)



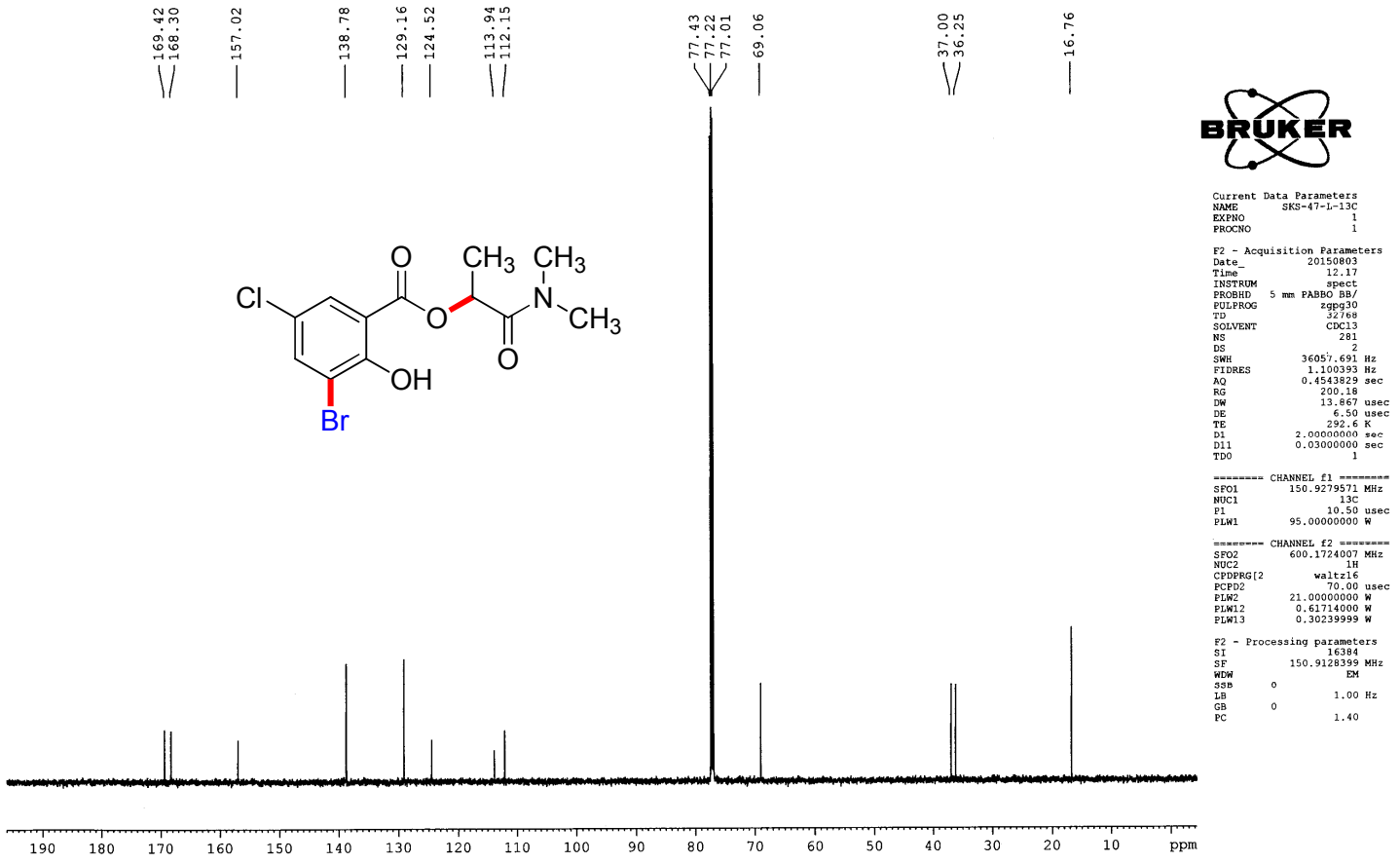

```
Current Data Parameters
NAME          SKS-39-2-13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150906
Time                 13.15
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                32768
SOLVENT           CDCl3
NS                  400
DS                    2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE                296.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         150.9279571 MHz
NUC1                 13C
P1                10.50 usec
PLW1         95.00000000 W

======== CHANNEL f2 ========
SFO2         600.1724007 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2         21.00000000 W
PLW12         0.61714000 W
PLW13         0.30239999 W

F2 - Processing parameters
SI                  16384
SF           150.9128380 MHz
WDW                    EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

1-(Dimethylamino)-1-oxopropan-2-yl 3-bromo-5-chloro-2-hydroxybenzoate (3h): ^{1}H NMR ($CDCl_3$, 600 MHz)




```
Current Data Parameters
NAME         SKS-47-L-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150803
Time              12.12
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           12019.230 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                80.22
DW               41.600 usec
DE                6.50 usec
TE               292.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1737063 MHz
NUC1                 1H
P1                12.00 usec
PLW1         21.00000000 W

F2 - Processing parameters
SI                 16384
SF           600.1700151 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

1-(Dimethylamino)-1-oxopropan-2-yl 3-bromo-5-chloro-2-hydroxybenzoate (3h): ^{13}C NMR ($CDCl_3$, 150 MHz)



BRUKER

Current Data Parameters
NAME SKS-47-L-13C
EXPNO 1
PROCNO 1

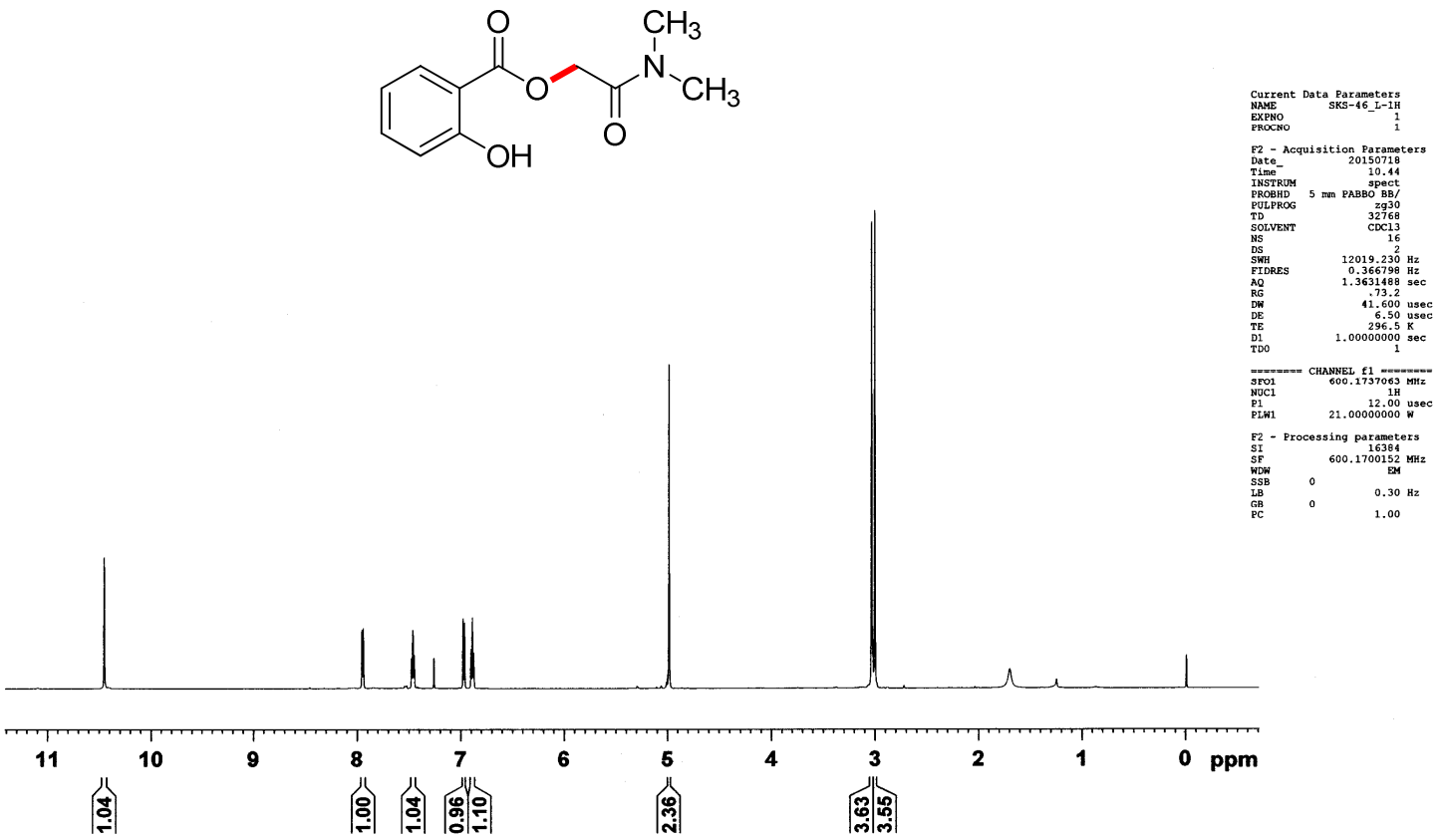
F2 - Acquisition Parameters
Date_ 20150803
Time 12.17
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 281
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 200.18
DW 13.867 usec
DE 6.50 usec
TE 292.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

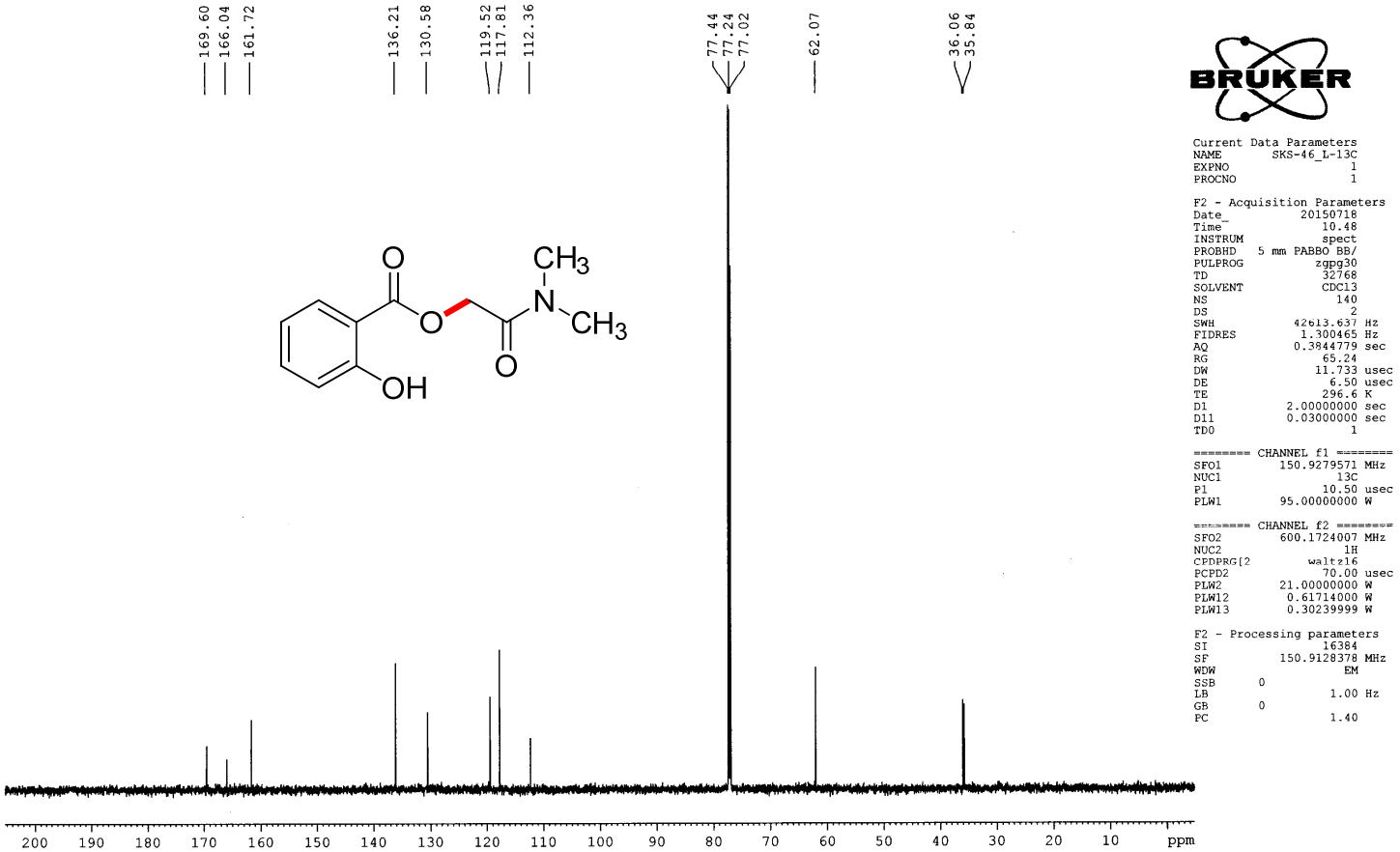
======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128399 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

2-(Dimethylamino)-2-oxoethyl 2-hydroxybenzoate (1a´): ^{1}H NMR ($CDCl_3$, 600 MHz)

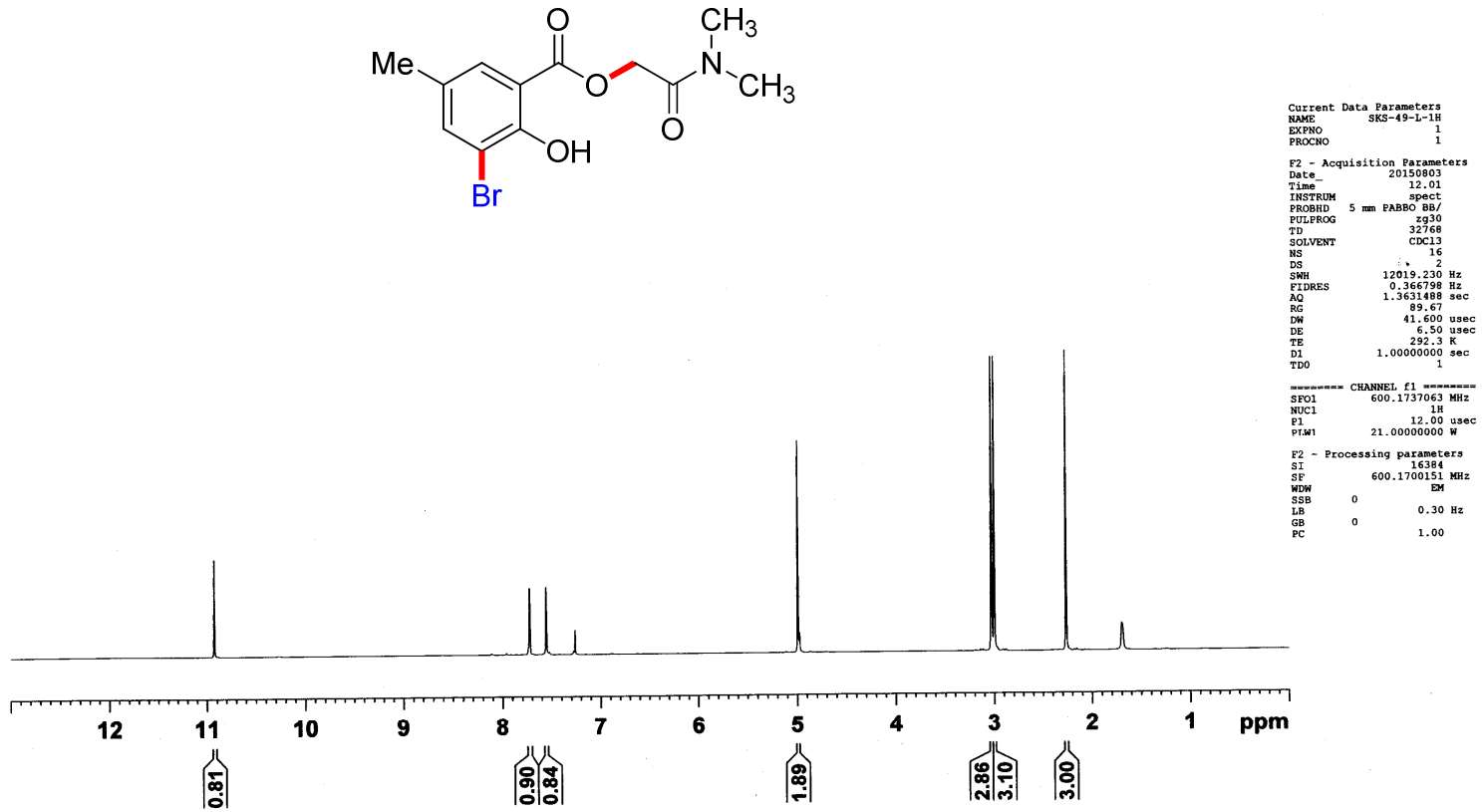


2-(Dimethylamino)-2-oxoethyl 2-hydroxybenzoate (1a´): ^{13}C NMR ($CDCl_3$, 150 MHz)



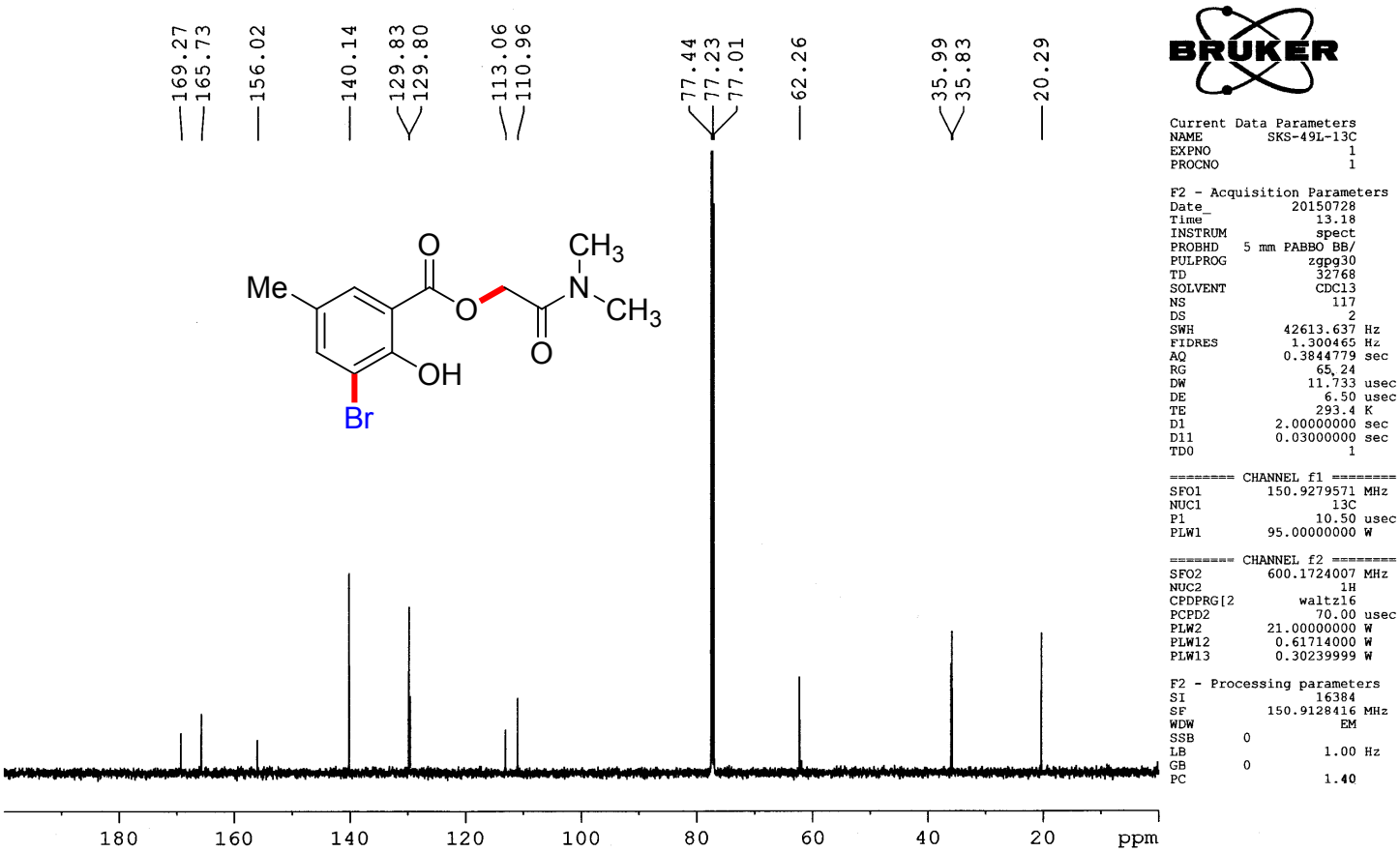

```
Current Data Parameters
NAME        SKS-46_L-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150718
Time              10.48
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               32768
SOLVENT          CDCl3
NS                 140
DS                   2
SWH           42613.637 Hz
FIDRES         1.300465 Hz
AQ            0.3844779 sec
RG                65.24
DW               11.733 usec
DE                6.50 usec
TE               296.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1               13C
P1               10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                 16384
SF          150.9128378 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC                 1.40
```

2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methylbenzoate (12a): ^{1}H NMR ($CDCl_3$, 600 MHz)

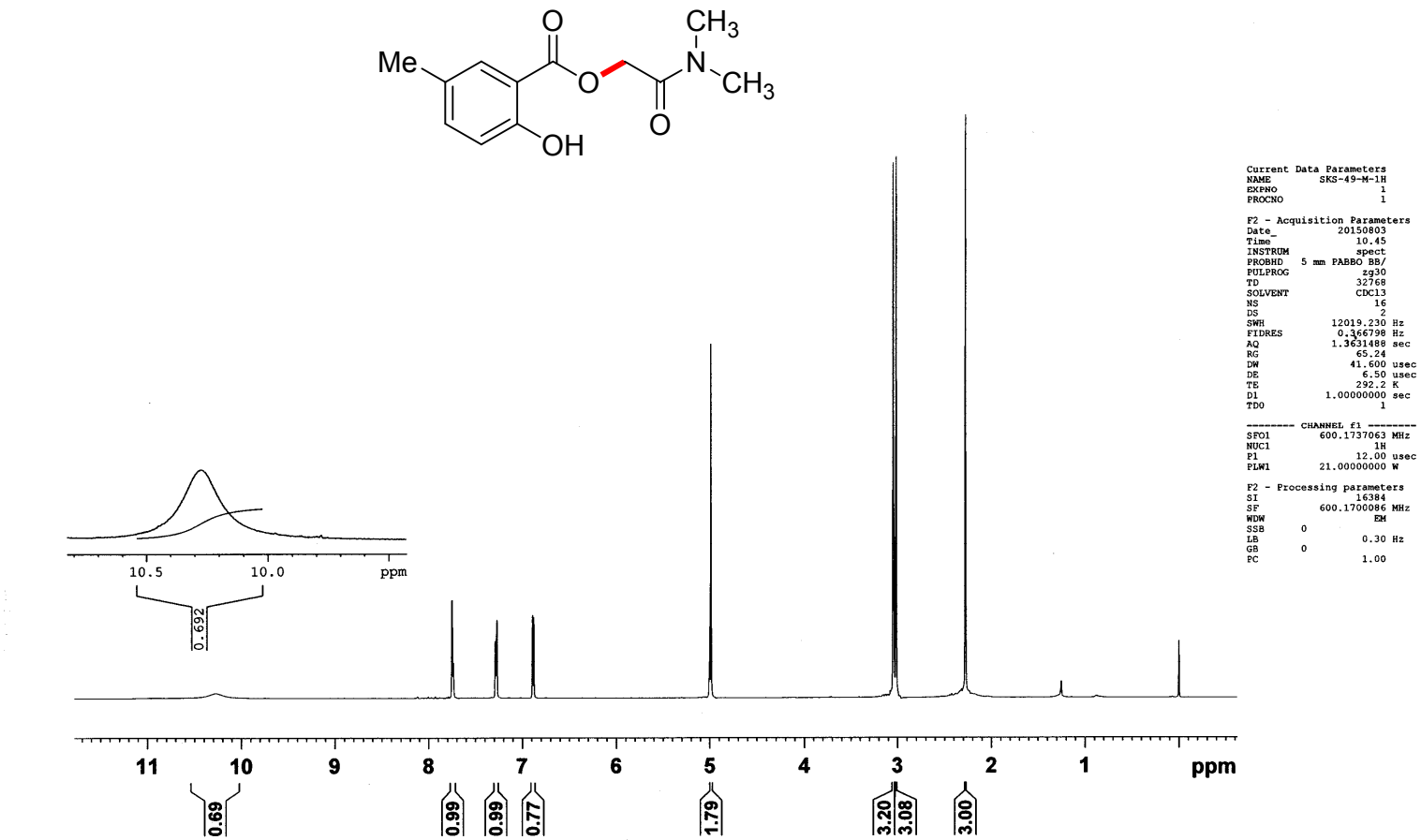



```
Current Data Parameters
NAME          SKS-49-L-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20150803
Time              12.01
INSTRUM           spect
PROBHD  5 mm PABBO BB/
PULPROG           zg30
TD               32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12019.230 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   89.67
DW                41.600 usec
DE                 6.50 usec
TE                292.3 K
D1             1.00000000 sec
TD0                     1

========== CHANNEL f1 ========
SFO1          600.1737063 MHz
NUC1                    1H
P1                 12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                   16384
SF            600.1700151 MHz
WDW                     EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

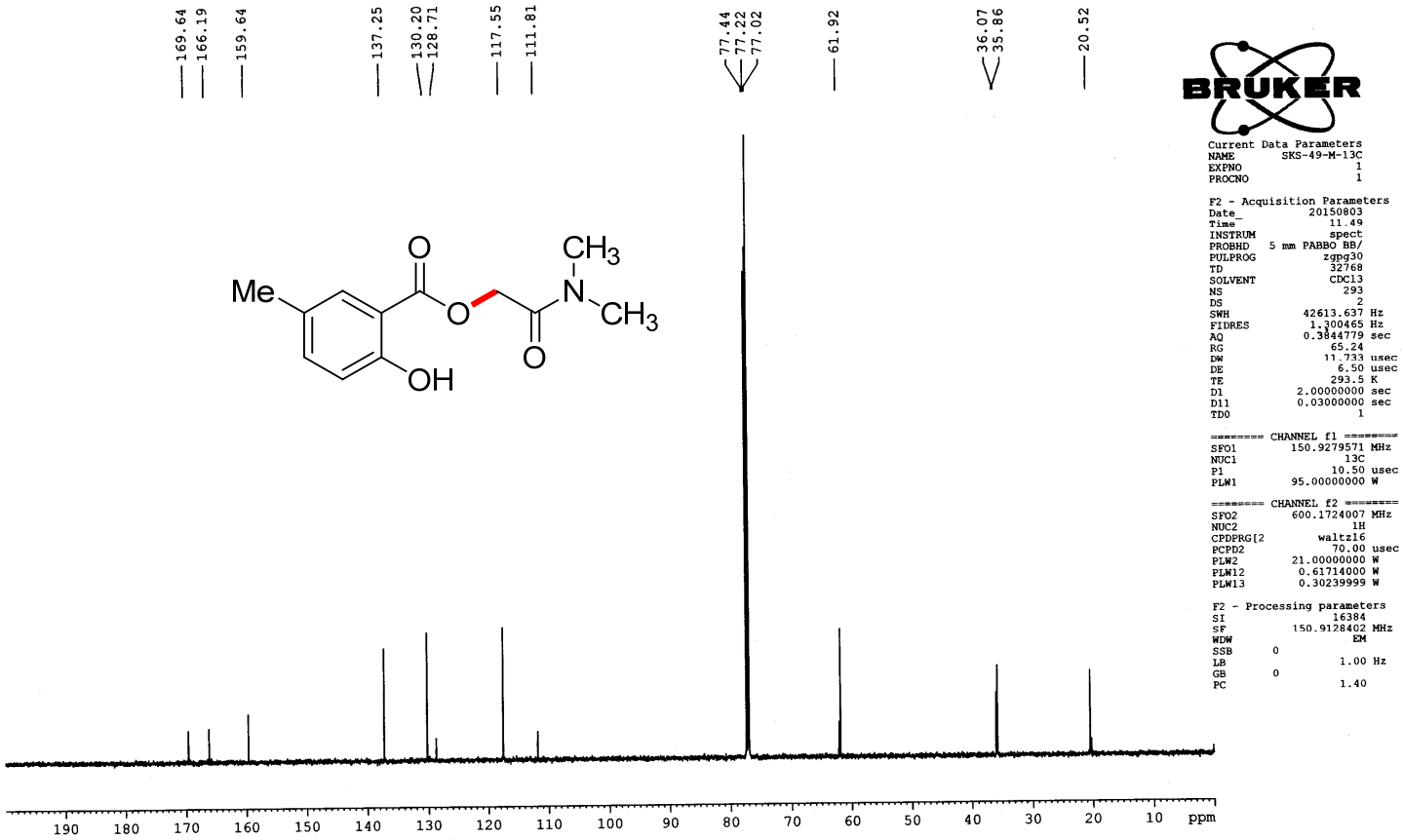
2-(Dimethylamino)-2-oxoethyl 3-bromo-2-hydroxy-5-methylbenzoate (12a): ^{13}C NMR ($CDCl_3$, 150 MHz)



2-(Dimethylamino)-2-oxoethyl 2-hydroxy-5-methylbenzoate (12a´): ^{1}H NMR (600 MHz, $CDCl_3$):



2-(Dimethylamino)-2-oxoethyl 2-hydroxy-5-methylbenzoate (12a´): ^{13}C NMR (150 MHz, $CDCl_3$):



BRUKER

Current Data Parameters
NAME SKS-49-M-13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150803
Time 11.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 293
DS 2
SWH 42613.637 Hz
FIDRES 1.300465 Hz
AQ 0.3844779 sec
RG 65.24
DW 11.733 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128402 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40