A Chiral Azolium-Catalyzed, Enantioselective Claisen Rearrangement

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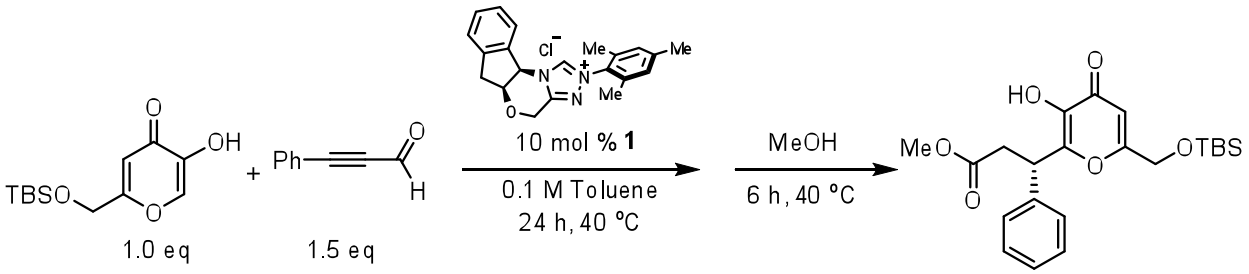
General methods. All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry N_2. Dichloromethane (CH_2Cl_2) was distilled over CaH_2; EtOH was distilled over Na. THF and toluene were dried by passage over activated alumina under an Ar atmosphere. For all mechanistic investigations, the reactions were performed in deuterated toluene (distilled from sodium and benzophenone). The derivatives of ynals were synthesized according to literature procedure.[1] Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) and were visualized by fluorescence quenching under UV light or by staining with phosphomolybdic acid. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Kieselgel 60 PF_{254} (Art 7747). Flash column chromatography was performed on E. Merck Silica Gel 60 (230–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR and ^{13}C NMR were measured on Bruker Avance II 500 MHz, 125 MHz respectively. Chemical shifts are expressed in parts per million (ppm) downfield from residual solvent peaks, and coupling constants are reported in Hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The enolic proton of the products is not usually observed in the proton spectra. Infrared (IR) spectra were recorded on a JASCO FT:IR-4100 spectrophotometer and reported as wavenumber (cm^{-1}). Optical rotations were measured on a JASCO P-1010 polarimeter operating at the sodium D line with a 100 mm path length cell, and were reported as follows: $[\alpha]_D^T$ (concentration (g/100 ml), solvent).

HPLC conditions. Column, Daicel Chiralpak IA (4.6 × 250mm), Daicel Chiralpak IB (4.6 × 250 mm); Daicel Chiralpak ODH (4.6 × 250 mm); eluent: hexanes:*i*-PrOH; flow rate 1.0 mL/min; detection wavelength: 220 nm.

SFC conditions. Column, Daicel Chiralpak AS-H (4.6 × 250 mm), Diacel Chiralcel OJ-H (4.6 x 250 mm); eluent: CO_2: *i*PrOH; oven temperature: 40 ^oC; outlet pressure 100 bar; flow rate 2.0 mL/min; detection wavelength: 220 nm.

(1) (a) Journet, M.; Cai, D.; Dimichele, L. M.; Larsen, R. D. *Tetrahedron Lett.* **1998**, *39(36)*, 6427–6428. (b) Serra, S.; Fuganti, C. *Synlett.* **2002**, *10*, 1661–1664.

General procedure for enantioselective annulation of ynals and kojic acid derivatives: 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4h-pyran-4-one

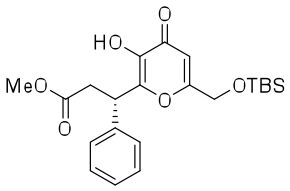


The reaction of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one[2] and 3-phenylpropiolaldehyde is representative. Into an oven dried 10.0 mL round bottom flask, 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (102.5 mg, 0.40 mmol, 1.0 equiv) and (*S,R*) triazolium precatalyst (**1**)[3] (15.8 mg, 0.10 equiv) were added, followed by 4.0 mL toluene (0.1 M) and 3-phenylpropiolaldehyde (78.0 mg, 0.60 mmol, 1.50 equiv). The flask was sealed with a polyethylene cap. The resulting solution was heated to 40 ^{o}C and stirred for 24 h before it was diluted with EtOAc and poured into sat aq NH_4Cl solution. The mixture was extracted with 3 x 5.0 mL EtOAc. The combined organic extract was dried over Na_2SO_4. After filtration and concentration in vacuo, the residue was dissolved in 5.0 mL MeOH and stirred for 6 h. MeOH was removed, and the crude product was purified by flash chromatography (gradient, 0%–5% MeOH in dichlorometane) to give the product as a pale brown-yellow solid (133.3 mg, 80%).

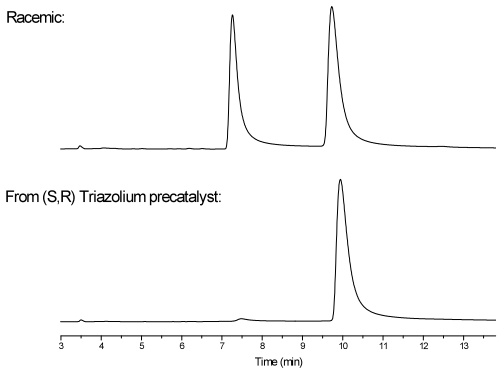
Racemic standards of the chiral products were prepared by the use of 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride (**19**)[4] as the catalyst. In most cases, this achiral catalyst was less efficient in terms of chemical yield than the chiral triazolium counterpart.

(2) Kamino, T.; Kuramochi, K.; Kobayashi, S. *Tetrahedron Lett*. **2003**, *44*, 7349–7351
(3) Both (*S,R*) chiral triazolium salt (**1**) and its (*R,S*) enantiomer are commercially available from Sigma-Aldrich (catalog number 683981 and 683973).
(4) (a) Sohn. S. S.; Bode. J. W. *Org. Lett.* **2005**, *7*, 3873–3876. (b) This achiral triazolium salt (**19**) is also commercially available from Sigma-Aldrich (catalog number 688487).

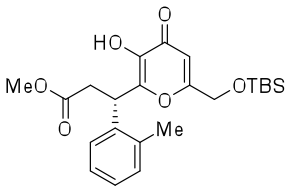
Preparations and characterizations of products 2–14



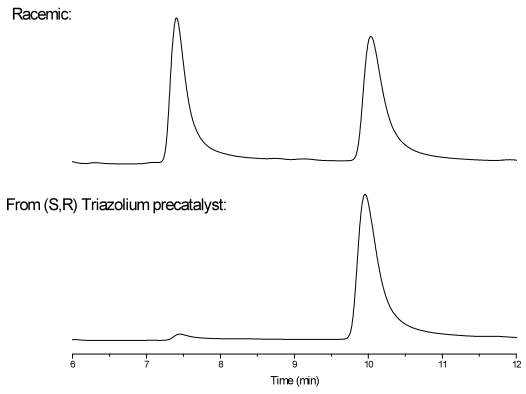
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-phenylpropanoate *(Table 1,* **2***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-phenylpropiolaldehyde using 10 mol % **1** as the catalyst in 80% yield as a pale yellow solid. $[\alpha]_D^{20}$ (c 1.05, $CHCl_3$): –14.26; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.31 (m, 5H), 6.46 (s, 1H), 4.80–4.77 (m, 1H), 4.46 (s, 2H), 3.63 (s, 3H), 3.21 (dd, 1H, *J* = 9.0, 16.0 Hz), 3.02 (dd, 1H, *J* = 7.5, 16.0 Hz), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 171.4, 167.2, 149.6, 141.5, 139.4, 129.0, 128.8, 127.8, 127.6, 108.5, 61.6, 52.0, 40.8, 36.8, 29.8, 25.8, 18.3, -5.3; IR (thin film) ν 3254, 2929, 1740, 1629, 1453, 1254, 838, 700 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{30}O_6Si$, 441.1709 found, 441.1694; 97% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH), t_r = 7.2 and 9.6 min. Ozonolysis[5] of **2**, followed by KOH saponification, afforded (*S*)-(+)-phenylsuccinic acid which was confirmed by ^{1}H and ^{13}C NMR comparison with literature values.[6] The absolute configuration of the experimentally obtained (*S*)-(+)-phenylsuccinic acid was confirmed by comparison with a commercial sample from Sigma-Aldrich. The measured optical rotation was recorded as $[\alpha]_D^{20}$ (c = 0.20, acetone): +101.9, and Sigma-Aldrich reported $[\alpha]_D^{20}$ (c = 1%, acetone): +171±4.

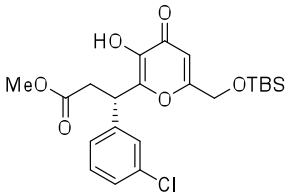


(5) Johnson, S. C.; Crasto, C.; Hecht, S. M. *Chem. Commun*. **1998**, *9*, 1019–1020.
(6) Makosza, M.; Marcinowicz, A. *Synthesis*. **2001**, *9*, 1311–1312.

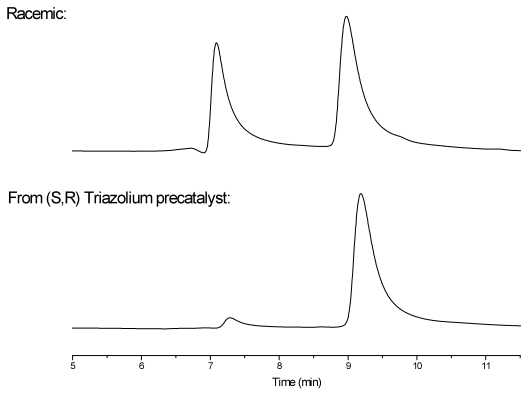


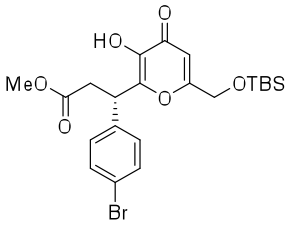
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-o-tolylpropanoate *(Table 1,* **3***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-*o*-tolylpropiolaldehyde using 10 mol % **1** as the catalyst in 95% yield as a brown oil. $[\alpha]_D^{20}$ (c 1.04, $CHCl_3$): –2.59; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 1H), 7.16–7.15 (m, 3H), 6.46 (s, 1H), 5.04 (t, 1H, *J* = 8.5 Hz), 4.45 (s, 2H), 3.62 (s, 3H), 3.17 (dd, 1H, *J* = 8.5, 16.0 Hz), 2.98 (dd, 1H, *J* = 7.0, 16.0 Hz), 2.47 (s, 3H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 171.5, 167.3,149.6, 141.5, 137.6, 136.6, 131.0, 127.4, 126.9, 126.5, 108.5, 61.6, 52.0, 37.1, 36.4, 25.9, 19.9, 18.3, -5.3; IR (thin film) ν 3249, 2953, 2857, 1741, 1630, 1255, 1165, 839, 781 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{23}H_{32}O_6Si$, 455.1866 found, 455.1866; 95% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 7.4 and 10.0 min.



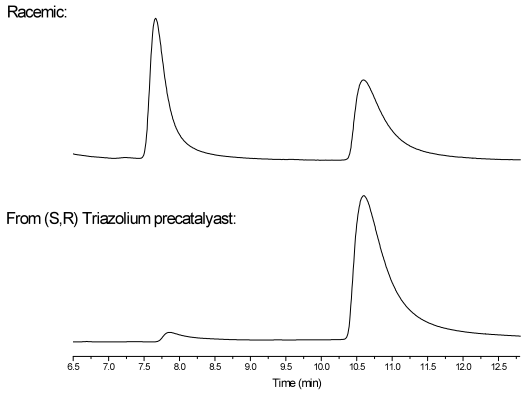


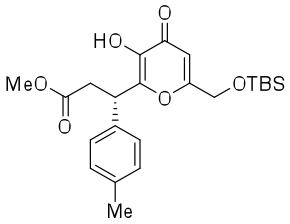
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-(3-chlorophenyl)propanoate *(Table 1,* **4***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(3-chlorophenyl)propiolaldehyde using 10 mol % **1** as the catalyst in 87% yield as a white solid. $[\alpha]_D^{20}$ (c 0.50, $CHCl_3$): –19.23; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.26–7.24 (m, 3H), 6.47 (s, 1H), 4.75 (t, 1H, J = 16.0 Hz), 4.46 (s, 2H), 3.64 (s, 3H), 3.18 (dd, 1H, J = 8.5, 16.0 Hz), 3.01 (dd, 1H, J = 7.5, 16.0 Hz), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 171.2, 167.4, 148.4, 141.4, 141.3, 134.8, 130.3, 128.0, 127.9, 126.0, 108.3, 61.6, 52.2, 40.6, 36.5, 25.8, 18.3, -5.34; IR (thin film) ν 3261, 2928, 1735, 1624, 1587, 1254, 1233, 838, 781 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{29}ClO_6Si$, 475.1320 found, 475.1313; 99% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 23.8 and 39.4 min.



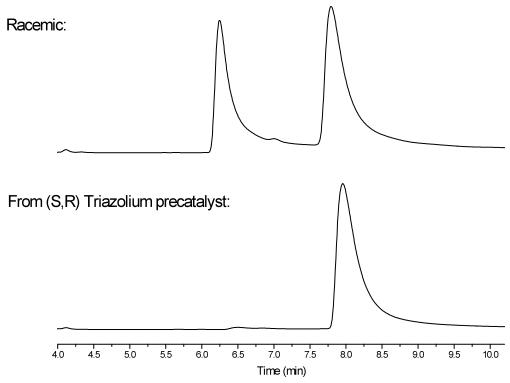


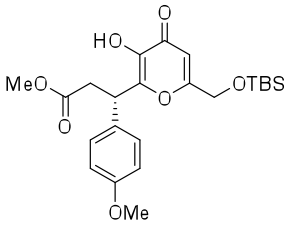
(*S*)-methyl-3-(4-bromophenyl)-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)propanoate *(Table 1,* **5***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(4-bromophenyl) propiolaldehyde using 10 mol % **1** as the catalyst in 82% yield as a pale yellow solid. $[\alpha]_D^{20}$ (c 0.59, $CHCl_3$): –27.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 2H, J = 8.5 Hz), 7.22 (d, 2H, J = 8.5 Hz), 6.46 (s, 1H), 4.71–4.62 (m, 1H), 4.46 (s, 2H), 3.64 (s, 3H), 3.16 (dd, 1H, J = 8.5, 16.5 Hz), 3.00 (dd, 1H, J = 8.5, 16.5 Hz), 0.93 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 174.2, 171.2, 168.6, 167.2, 149.0, 145.7, 141.4, 138.3, 137.4, 132.1, 130.8, 129.5, 129.3, 121.6, 109.1, 108.5, 61.6, 61.5, 52.1, 40.3, 36.5, 29.8, 25.9, 25.8, 18.4, 18.3; IR (thin film) ν 3248, 2953, 2928, 1741, 1630, 1254, 1164, 839, 780 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{29}BrO_6Si$, 519.0814 found, 519.0804; 92% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 7.8 and 10.7 min.



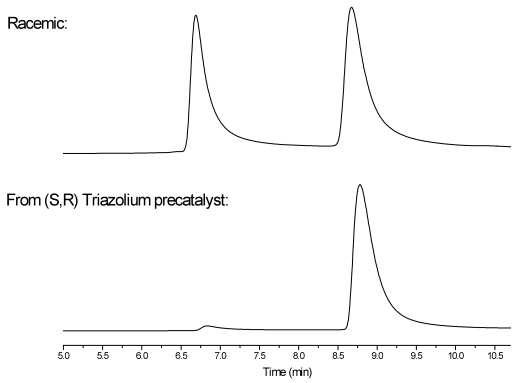


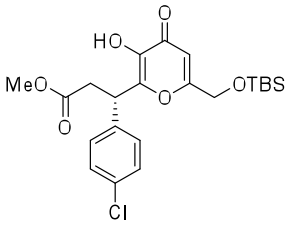
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-p-tolylpropanoate *(Table 1,* **6***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-*p*-tolylpropiolaldehyde using 10 mol % **1** as the catalyst in 98% yield as a pale yellow solid. $[\alpha]_D^{20}$ (c 1.42, $CHCl_3$): –25.87; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, 2H, *J* = 8.0 Hz), 7.11 (d, 2H, *J* = 8.0 Hz), 6.47 (s, 1H), 4.78 (t, 1H, *J* = 8.0 Hz), 4.40 (s, 2H), 3.62 (s, 3H), 3.18 (dd, 1H, *J* = 8.5, 16.0 Hz), 3.00 (dd, 1H, *J* = 7.5, 16.0 Hz), 2.31 (s, 3H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 171.5, 167.1, 150.0, 141.4, 137.3, 136.4, 129.6, 127.6, 108.5, 61.6, 52.0, 40.4, 38.9, 25.8, 21.2, 18.3, -5.3; IR (thin film) ν cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{23}H_{32}O_6Si$, 455.1866 found, 455.1872; 98% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 6.4 and 7.9 min.



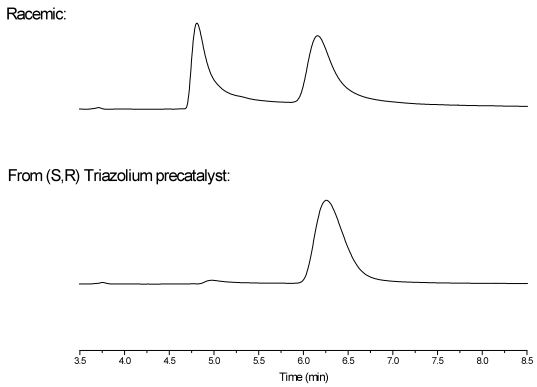


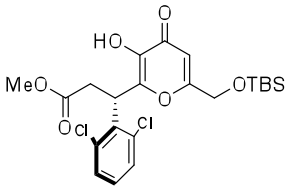
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-(4-methoxyphenyl)propanoate *(Table 1,* **7***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(4-methoxyphenyl) propiolaldehyde using 10 mol % **1** as the catalyst in 88% yield as a yellow-brown solid. $[\alpha]_D^{20}$ (c 1.10, $CHCl_3$): –23.29; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, 2H, *J* = 8.5 Hz), 6.84 (d, 2H, *J* = 8.5 Hz), 6.46 (s, 1H), 4.74 (t, 1H, *J* = 8.0 Hz), 4.46 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H), 3.15 (dd, 1H, *J* = 8.5, 16.0 Hz), 2.99 (dd, 1H, *J* = 7.0, 16.0 Hz), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 171.5, 167.1, 159.0, 150.1, 141.2, 131.4, 128.8, 114.3, 108.5, 61.6, 55.3, 52.0, 40.0, 37.0, 25.8, 18.3, -5.3; IR (thin film) ν 3250, 2953, 2930, 1740, 1630, 1253, 838, 780 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{23}H_{32}O_7Si$, 471.1815 found, 471.1831; 96% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 6.8 and 8.8 min.



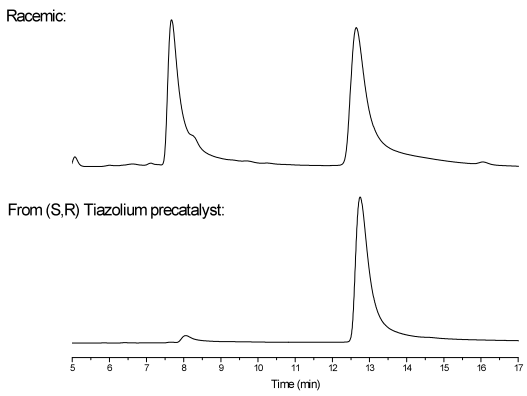


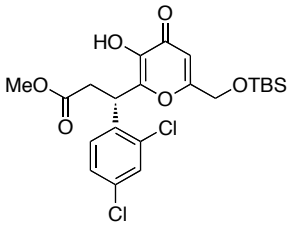
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-(4-chlorophenyl)propanoate *(Table 1,* **8***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(4-chlorophenyl)propiolaldehyde using 10 mol % **1** as the catalyst in 90% yield as a pale-brown yellow solid. $[\alpha]_D^{20}$ (c 0.52, $CHCl_3$): –28.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.26 (m, 4H), 6.46 (s, 1H), 4.76 (t, 1H, *J* = 8.5 Hz), 4.45 (s, 2H), 3.63 (s, 3H), 3.17 (dd, 1H, *J* = 9.0, 16.5 Hz), 3.00 (dd, 1H, *J* = 8.0, 16.5 Hz), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 171.2, 167.1, 149.4, 141.5, 137.8, 133.5, 129.2, 129.1, 108.7, 61.5, 61.4, 58.4, 52.1, 40.1, 36.6, 25.8, 25.7, 18.4, 18.3, -5.3; IR (thin film) ν 3241, 2928, 2361, 1760, 1684, 1168, 1091, 779, 668 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{29}ClO_6Si$, 475.1320 found, 475.1316; 96% ee as determined by SFC (OJ-H, 15% *i*-PrOH in CO_2) t_r = 5.0 and 6.3 min..



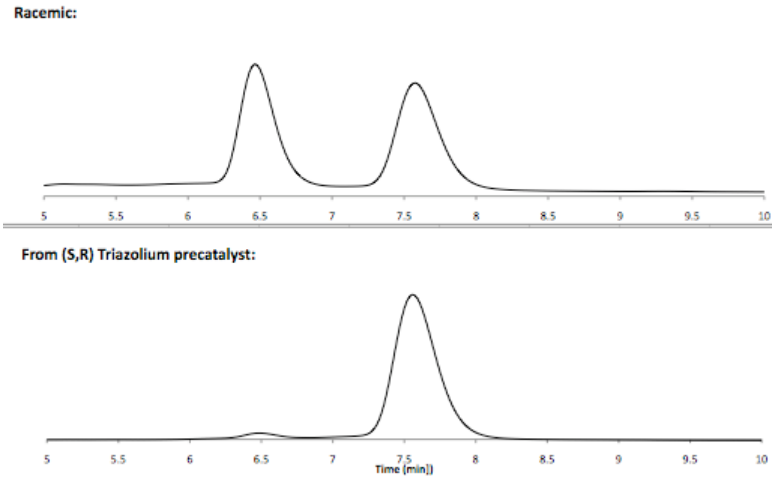


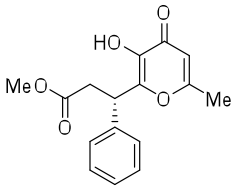
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-(2,6-dichlorophenyl)propanoate *(Table 1,* **9***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(2,6-dichlorophenyl)propiolaldehyde using 10 mol % **1** as the catalyst in 95% yield as a dark-brown solid. $[\alpha]_D^{20}$ (c 0.10, $CHCl_3$): +109.3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.10 (s, 1H), 6.46 (s, 1H), 5.64–5.61 (m, 1H), 4.45 (d, 1H, *J* = 5.5 Hz), 4.34 (d, 1H, *J* = 5.5 Hz), 3.65 (s, 3H), 3.52–3.46 (m, 1H), 2.76–2.72 (m, 1H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 171.4, 166.7, 147.0, 142.4, 134.9, 129.3, 129.1, 108.6, 61.4, 52.1, 38.3, 33.2, 25.8, 18.3, -5.4; IR (thin film) ν 2952, 1741, 1631, 1435, 1250, 838, 776 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{28}Cl_2O_6Si$, 509.0930 found, 509.0955; 94% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH) t_r = 8.0 and 12.8 min.



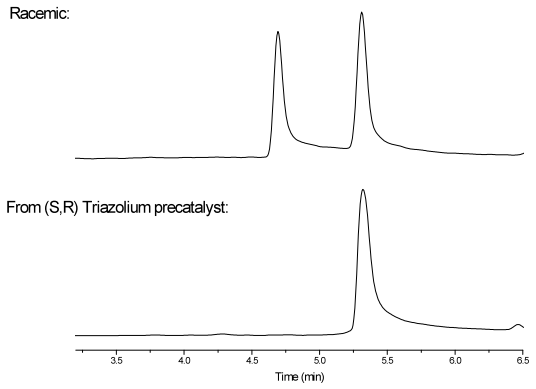


(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-(2,4-dichlorophenyl)propanoate *(Table 1,* **10***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-(2,4-dichlorophenyl)propiolaldehyde[7] using 10 mol % **1** as the catalyst in 95% yield as a dark-brown solid. $[\alpha]_D^{20}$ (c 0.94, $CHCl_3$): +17.48; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.28–7.25 (m, 1H), 7.22–7.20 (m, 1H), 6.49 (s, 1H), 5.18–5.15 (m, 1H), 4.44 (d, 2H, J = 2.5 Hz), 3.65 (s, 3H), 3.19 (dd, 1H, J = 9.0, 16.5 Hz), 2.97 (dd, 1H, J = 6.5, 16.5 Hz), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 171.0, 167.5, 147.6, 142.1, 135.5, 134.6, 134.1, 129.9, 129.7, 127.7, 108.4, 61.5, 52.2, 38.0, 36.2, 25.8, 18.3, -5.4; IR (thin film) ν 3230, 2953, 2857, 1742, 1652, 1253, 861, 781 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{28}Cl_2O_6Si$, 509.0930 found, 509.0955; 95% ee as determined by HPLC (ODH, 9:1 hexanes:*i*-PrOH) t_r = 6.5 and 7.6 min.

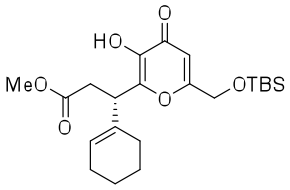




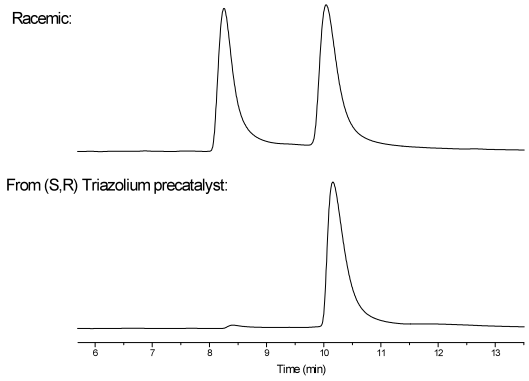
(*S*)-methyl-3-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-3-phenylpropanoate *(Table 1,* **11***)*. Prepared according to the general procedure from 5-hydroxy-2-methyl-4H-pyran-4-one[7] and 3-phenylpropiolaldehyde using 10 mol % **1** as a catalyst in 90% yield as a pale yellow solid. $[\alpha]_D^{20}$ (c 0.62, $CHCl_3$): –38.22; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.26 (m, 5H), 6.17 (s, 1H), 4.77 (t, 1H, *J* = 8.5 Hz), 3.64 (s, 3H), 3.22 (dd, 1H, *J* = 9.0, 16.5 Hz), 3.01 (dd, 1H, *J* = 7.0, 16.5 Hz), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 171.5, 165.4, 149.5, 140.9, 139.5, 129.0, 127.7, 127.6, 110.5, 52.0, 40.8, 36.8, 20.2; IR (thin film) ν 3246, 2925, 1738, 1621, 1436, 1211, 733, 701 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{16}H_{16}O_5$, 311.0895 found, 311.0901; 99% ee as determined by SFC (ASH, gradient 5%–80% *i*-PrOH in CO_2, rate 10%/min) t_r = 4.3 and 5.3 min.

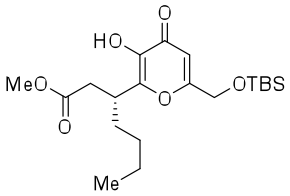


(9) Őztürk, G.; Erol, D. D.; Aytemir, M. D.; Uzbay, T. *Eur. J. Med. Chem.* **2002**, *37*, 829–834

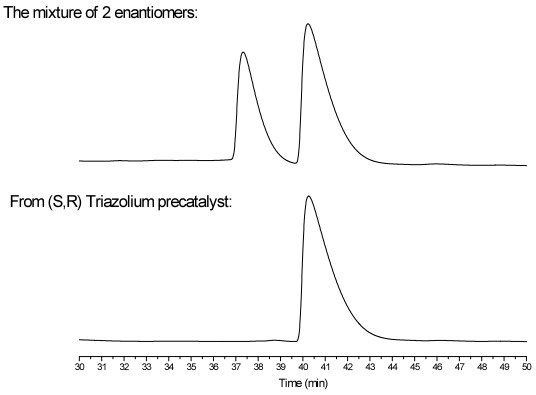


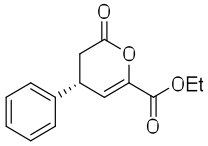
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-cyclohexenylpropanoate *(Table 1,* **12***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and 3-cyclohexenyl propiolaldehyde using 10 mol % **1** as the catalyst in 98% yield as a pale brown solid. $[\alpha]_D^{20}$ (c 1.10, $CHCl_3$): –22.76; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (s, 1H), 5.61 (s, 1H), 4.46 (s, 2H), 4.05 (t, 1H, J = 7.5 Hz), 3.64 (s, 3H), 2.88 (dd, 1H, J = 9.0, 16.0 Hz), 2.79 (dd, 1H, J = 7.0, 16.0 Hz), 2.00–1.95 (m, 4H), 1.61–1.57 (m, 4H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 172.0, 167.0, 150.0, 142.0, 135.1, 124.4, 108.4, 61.6, 51.9, 42.2, 34.8, 27.1, 25.8, 25.4, 22.8, 22.2, 18.3, -5.4; IR (thin film) ν 3263, 2929, 1729, 1627, 1252, 1164, 839, 781 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{22}H_{34}O_6Si$, 445.2022 found, 445.1968; 97% ee as determined by HPLC (IB, 20:1 hexanes:*i*-PrOH) t_r = 8.4 and 10.2 min.





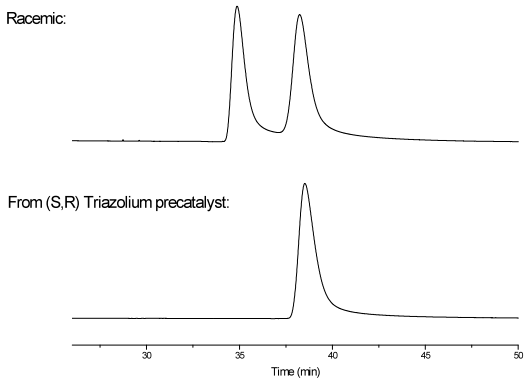
(*R*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)heptanoate *(Table 1,* **13***)*. Prepared according to the general procedure from 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one and hept-2-ynal using 10 mol % **1** as the catalyst in 78% yield as pale yellow solid. $[\alpha]_D^{20}$ (c 0.28, $CHCl_3$): –11.70; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 1H), 4.50 (s, 2H), 3.66 (s, 3H), 3.51–3.47 (m, 1H), 2.71 (dd, 1H, J = 8.0, 15.5 Hz), 2.60 (dd, 1H, J = 6.5, 15.5 Hz), 1.72–1.67 (m, 3H), 1.64–1.59 (m, 6H), 0.93 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 172.1, 167.2, 151.2, 142.1, 108.4, 61.6, 51.9, 37.0, 35.5, 32.1, 29.3, 25.8, 22.5, 18.3, 14.0, -5.3; IR (thin film) ν cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{20}H_{34}O_6Si$, 399.2203 found, 399.2206; >99% ee as determined by HPLC (IA, 100:1 hexanes:*i*-PrOH) t_r = 35.0 and 38.5 min.

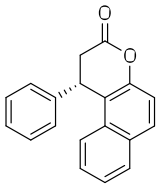




(*R*)-ethyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate *(Scheme 2,* **14***)*. Prepared according to the generalprocedure from ethyl pyruvate and 3-phenylpropiolaldehyde (The

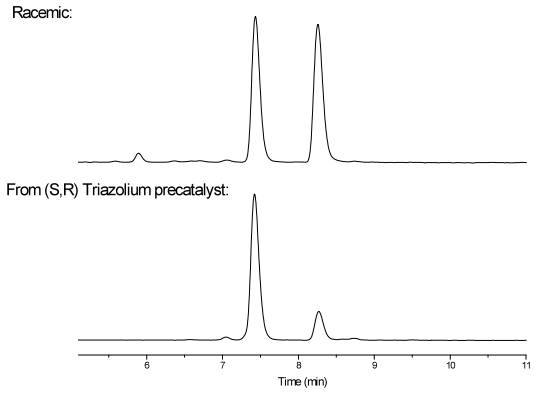
aldehyde was added 2 portions: 1.5 equiv, and after 12 h, another 1.0 equiv) using 10 mol % **1** as catalyst and 20 mol % $^{i}Pr_2NEt$ as a base in 74% yield as a pale yellow oil. $[\alpha]_D^{20}$ (c 0.35, $CHCl_3$): +120.0; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.32–7.31 (m, 1H), 7.20–7.18 (m, 2H), 6.64 (d, 1H, J = 4.5 Hz), 4.35–4.31 (m, 2H), 3.96–3.92 (m, 1H), 2.98 (dd, 1H, J = 7.0, 16.0 Hz), 2.76 (dd, 1H, J = 8.5, 16.0 Hz), 1.35 (t, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 160.5, 143.0, 140.0, 129.4, 128.1, 127.0, 117.9, 62.1, 37.3, 35.9, 14.3; IR (thin film) ν 2882, 1779, 1734, 1208, 1102, 760, 700 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{14}H_{14}O_4$, 269.0790 found, 269.0789; 99% ee as determined by HPLC (IB, 30:1 hexanes:*i*-PrOH) t_r = 40.6 and 42.8 min.



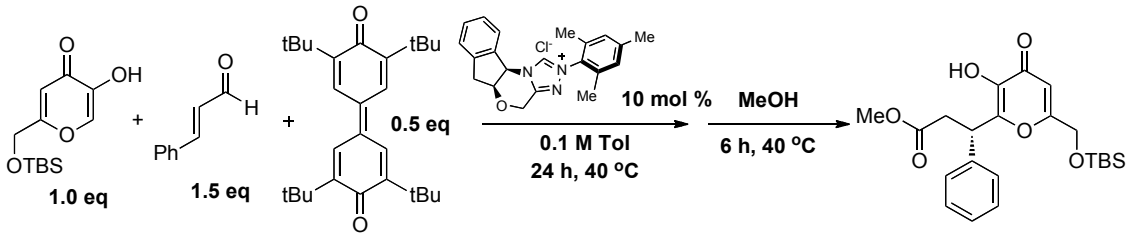


(*S*)-1-phenyl-1H-benzo[f]chromen-3(2H)-one *(Scheme 2,* **15***)*. Prepared according to the general procedure from 2-naphthol and 3-phenylpropiolaldehyde using 10 mol % **1** as a catalyst in 79% yield as a yellow solid. $[\alpha]_D^{20}$ (c 0.60, $CHCl_3$): +57.34; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 7.80 (d, 1H, J = 8.5 Hz), 7.49–7.45 (m, 2H), 7.43 (d, 1H, J = 7.0 Hz), 7.28–7.25 (m, 2H), 7.23–7.20 (m, 1H), 7.13 (d, 2H, J = 7.5 Hz), 4.96 (d, 1H, J = 6.5 Hz), 3.25–3.14 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 150.0, 140.7, 131.2, 131.1, 130.1, 129.4, 128.9,

127.7, 127.6, 127.1, 125.4, 123.2, 117.7, 37.8, 37.6; IR (thin film) ν 3061, 1781, 1515, 1209, 1135, 816, 789 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{19}H_{14}O_2$, 297.0891 found, 297.0905; 68% ee as determined by SFC (ASH, gradient 10%–80% *i*-PrOH in CO_2, rate 5%/min) t_r = 7.4 and 8.2 min.



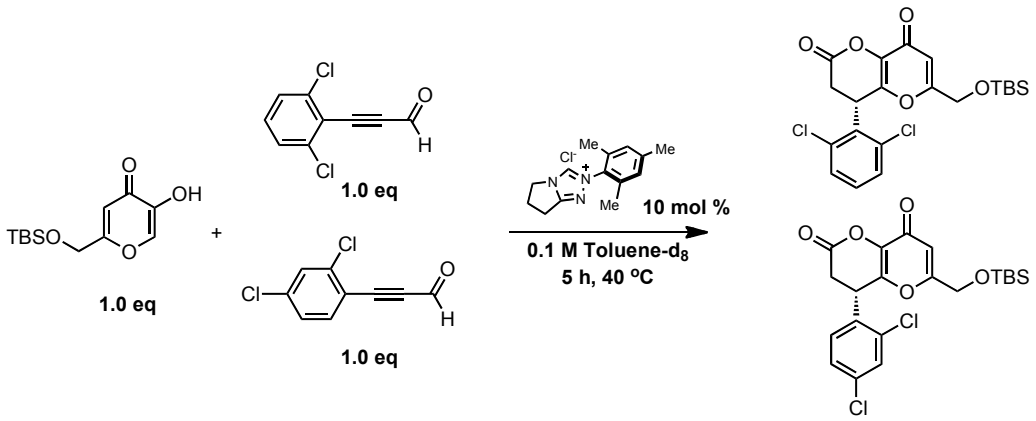
An azolium-catalyzed Claisen rearrangement via oxidation of α,β-unsaturated aldehyde



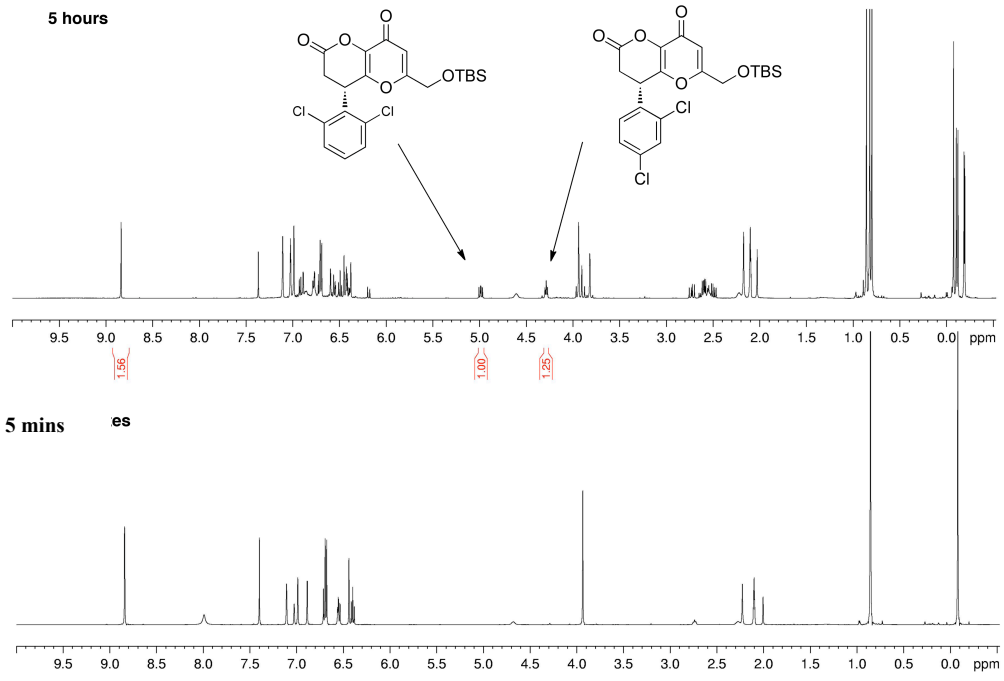
(*S*)-methyl-3-(6-((*tert*-butyldimethylsilyloxy)methyl)-3-hydroxy-4-oxo-4H-pyran-2-yl)-3-phenylpropanoate *(Table 1,* **2***)*. As an alternative method, inspired by the work of Studer[8], 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (25.6 mg, 0.1 mmol, 1 equiv), cinnamaldehyde (19.8 mg, 0.15 mmol, 1.5 equiv), 3,3',5,5'-tetra-tert-butyl-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-dione (20.4 mg, 0.05 mmol, 0.5 equiv an an oxidant), and **1 (**10 mol% as the catalyst) were combined and diluted in toluene (0.1 M) at 40°C overnight. Ring opening of the reaction with MeOH (6 hours at 40°C) afforded product **2**: 66% conversion (based on ^{1}H NMR relative to the starting materials) and 97% ee.

(8) De Sarkar, S.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2010**, *132*, 1190–1191.

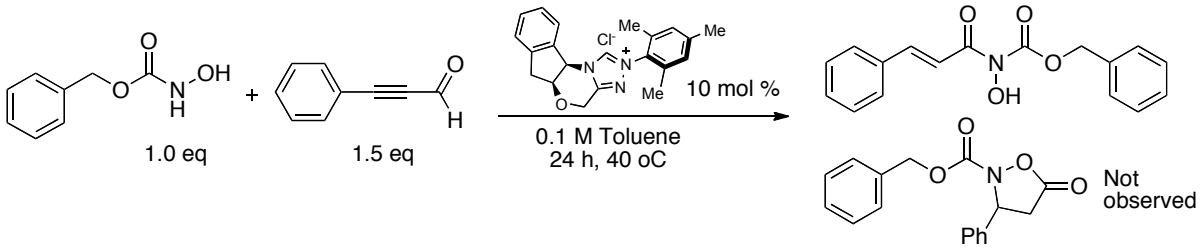
Relative reactivity of *o,o*-dichloro and *o,p*-dichloro phenylpropiolaldehyde



In a dried 10.0 mL NMR tube, 3-(2,4-dichlorophenyl)propiolaldehyde (10.0 mg, 0.05 mmol, 1.0 equiv), 3-(2,6-dichlorophenyl)propiolaldehyde (10.0 mg, 0.05 mmol, 1.0 equiv) and 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (13.0 mg, 0.05 mmol, 1.0 equiv) were mixed with 10 mol% of catalyst **18** in $C_6D_6CD_3$ (0.50 mL). The reaction mixture was monitored by ^{1}H NMR. After 5 hours, the ratio of products was determined from ^{1}H NMR spectra (below) to be 1.25 (*o,p*-dichloro) to 1.00 (*o,o*-dichloro) products.

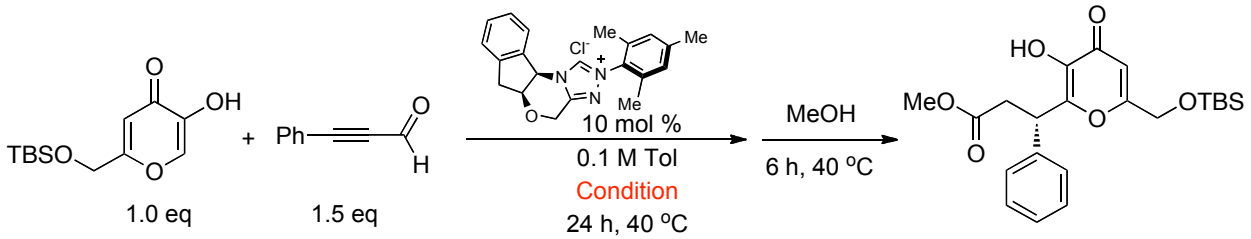


1,2 Addition of *N*-Cbz hydroxamic acid



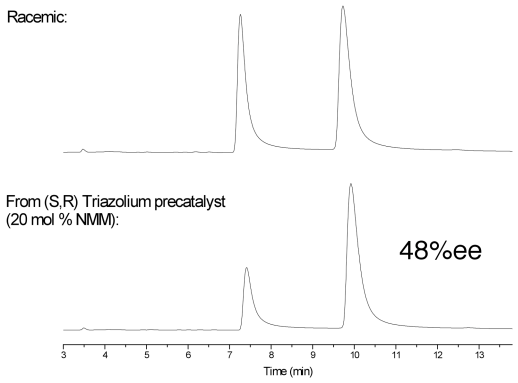
Prepared according to the general procedure from *N*-Cbz hydroxamic acid and 3-phenylpropiolaldehyde using 10 mol % of **1** as the catalyst to afford the product **20** in 53% yield as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.86 (d, 1H, J = 16.0 Hz), 7.55–7.54 (m, 2H), 7.44–7.34 (m, 8H), 6.53 (d, 1H, J = 16.0 Hz), 5.25 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 156.5, 148.3, 135.2, 133.8, 131.3, 129.2, 128.8, 128.8, 128.6, 128.5, 113.3, 68.5; IR (thin film) ν 3266, 1746, 1633, 1450, 1219, 1118, 766, 697 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{17}H_{15}NO_4$, 320.0899 found, 320.0861.

Epimerization by an addition of base experiment



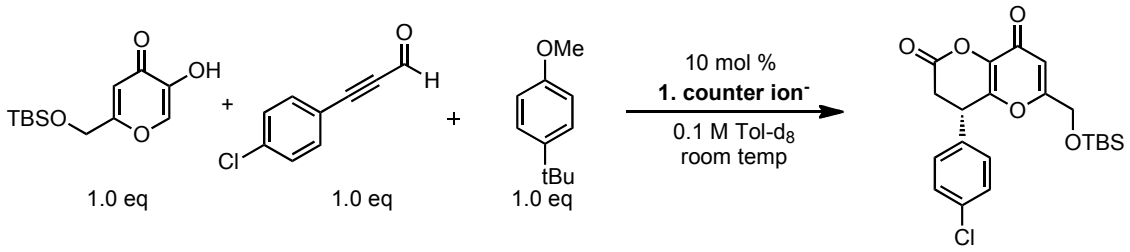
Prepared according to the general procedure, except that *N*-methylmorpholine (NMM) (20 mol %) was added as a base. The crude product mixture was purified by preparative TLC (3:1 hexanes:EtOAc) to give **2** (48% ee as determined by HPLC (IB, 9:1 hexanes:*i*-PrOH), t_r = 7.2 and 9.6 min. Alternatively, based-induced epimerization of the final adduct could be confirmed by stirring high-enantiomeric excess product in a weak amine base (see table below).

Reaction condition	% ee of the final adduct (from chiral HPLC)
No base	97%
20% AcOH added at t = 0	47%
20% NMM added at t = 0	48%
20% NMM added at t = 2 hours	14%
20% NMM added at t = 24 hours (after the reaction completed by ^{1}H NMR)	74%



Catalyst counter ions comparison

Preparation: The counter ions exchanges between 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride (**1**) and various silver salts (AgOAc, $AgClO_4$, $AgSbF_6$, $AgOCOCF_3$) were performed according to a literature procedure.[9]



Comparison Experiment: A solution of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (1.0 equiv), 3-(4-chlorophenyl)propiolaldehydeis (1.0 equiv), and 1-(tert-butyl)-4-methoxybenzene (1.0 equiv as internal standard) was prepared using deuterated toluene (with 10% deuterated dichloromethane to ensure complete solubility) and mixed with the precatalyst with different counter ions (X, 0.1 equiv): Cl^-, OAc^-, ClO_4^-, $CF_3CO_2^-$, and SbF_6^-. A control reaction was done using the same solution and the precatalyst with SbF_6^- and 20% N-methylmorpholine (NMM). The reactions were performed in dried NMR tubes at room temperature. Percentage conversions were measured using ^{1}H NMR by the disappearance of the ynal, from the integration of the peak at 8.90 ppm (1H) against the internal standard peak at 1.22 ppm (9H). The conversion of the ynal was found to be influenced by the counter ion with the

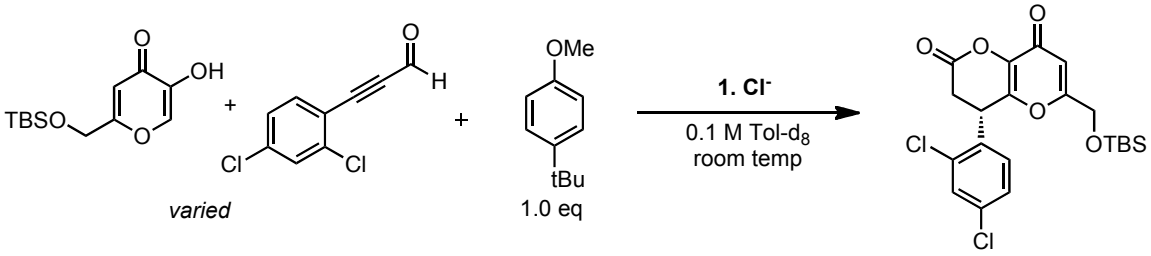
(9) Kim, J.H.; Jo, K.A.; Son, Y.H.; Park, S.R.; Ahn, K-H.; Kang, E.J. *Bull. Korean Chem. Soc*. **2009**, *30*, 2464-2466.

following treand: OAc^- > SbF_6^- with NMM > Cl^- > $CF_3CO_2^-$ > ClO_4^- (trace) > SbF_6^- (no reaction). The table below compares percent conversions (% conv.) at 1.0, 2.5, and 12 hours.

Effect of azolium counterion on conversion.

X (counter ion)	% conv. 1 h	% conv. 2.5 h	% conv. 12 h
Cl^-	10	16	70
OAc^-	100	na	na
$CF_3CO_2^-$	7	10	20
ClO_4^-	0	0	trace
SbF_6^-	0	0	0
SbF_6^- + NMM(30%)	30	35	86
[a]Determined by ^{1}H NMR analysis against an internal standard.			

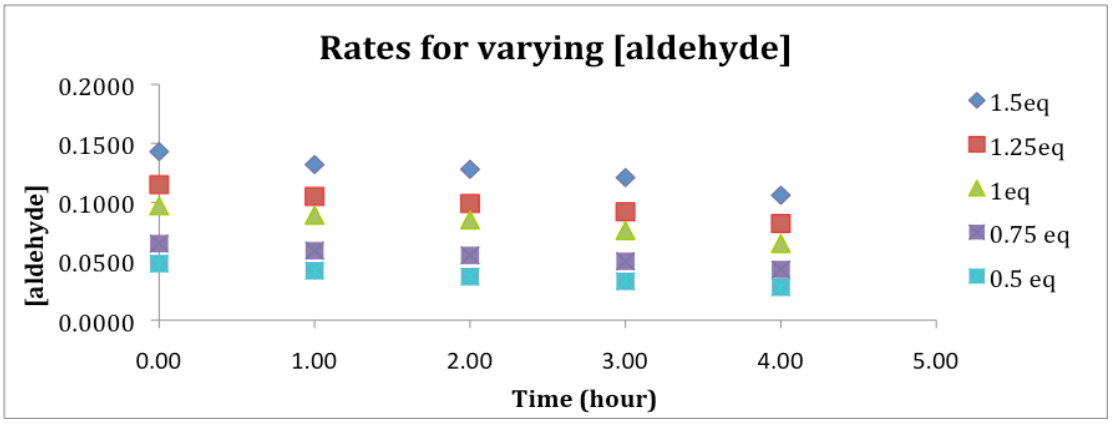
Experimental rate orders measurements

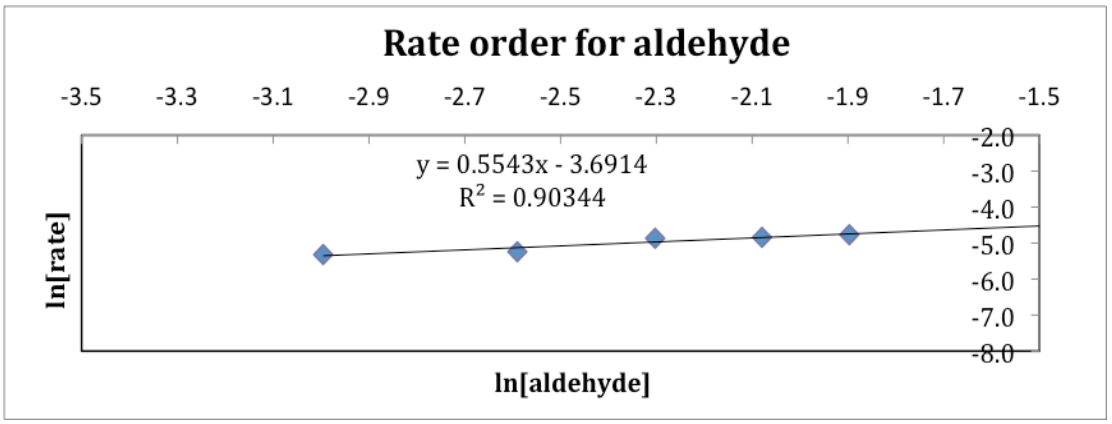


Rate order for aldehyde: A solution of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (1.0 equiv) and 1-(tert-butyl)-4-methoxybenzene (1.0 equiv as internal standard) was prepared using deuterated toluene (with 10% deuterated dichloromethane to ensure complete solubility) and degassed. Then, 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride (0.1 equiv) was added to the solution, and the final solution was transferred to dried NMR tubes containing varied amounts of 3-(2,4-dichlorophenyl) propiolaldehyde: 0.50, 0.75, 1.00, 1.25, and 1.50 equiv. The reactions were performed at room temperature; percentage conversions were measured using ^{1}H NMR by the disappearance of the ynal from the integration of the peak at 8.85 ppm (1H) against the internal standard peak at 1.22 ppm (9H). The plots of molar concentration of the ynal versus time (hour) were generated; the rates were determined from the slope of each plot.[10] The rate order was calculated from the plot of ln(rate) against ln(aldehyde concentration) to be 0.55 (R^2 = 0.90). Below, the table reports raw data; the plots shows [aldehyde] vs. time, and the ln[rate] vs. ln[aldehyde].

(10) As a verification of the method validity, the plot of molar concentration of the product versus time (hour) was performed additionally. Percentage deviations of the rates were calculated to be <3.00% for three cases: *para* methyl, no substitution, and *para* chloro ynals.

time (h)	Aldehyde concentration for the reactions (varying aldehyde equiv).				
	1.50 equiv.	1.25 equiv.	1.00 equiv.	0.75 equiv.	0.50 equiv.
0.00	0.1430	0.1150	0.0970	0.0650	0.0480
1.00	0.1320	0.1050	0.0890	0.0590	0.0420
2.00	0.1280	0.0990	0.0850	0.0550	0.0370
3.00	0.1210	0.0920	0.0760	0.0500	0.0330
4.00	0.1060	0.0820	0.0650	0.0430	0.0280
Rate [M/h]	**-8.50×10^{-3}**	**-7.90×10^{-3}**	**-7.70×10^{-3}**	**-5.30×10^{-3}**	**-4.90×10^{-3}**
R^2	**0.98**	**1.00**	**0.99**	**1.00**	**1.00**

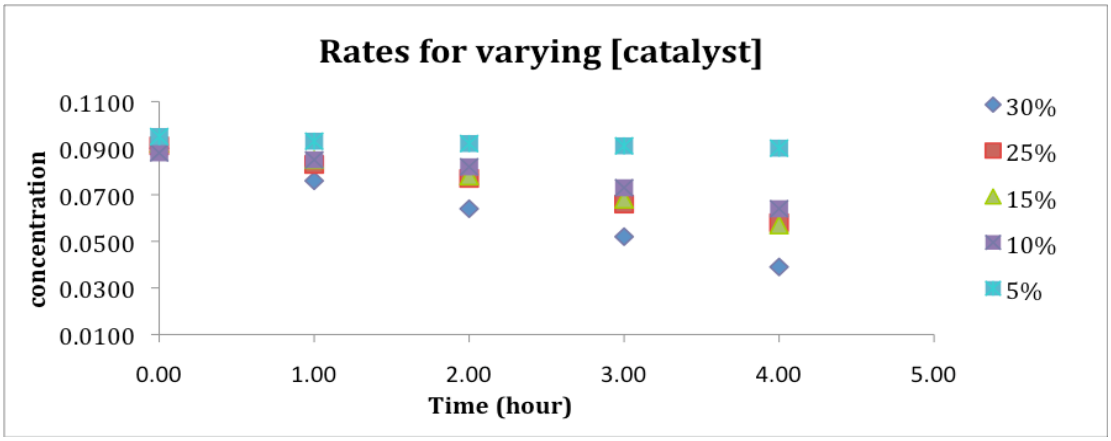


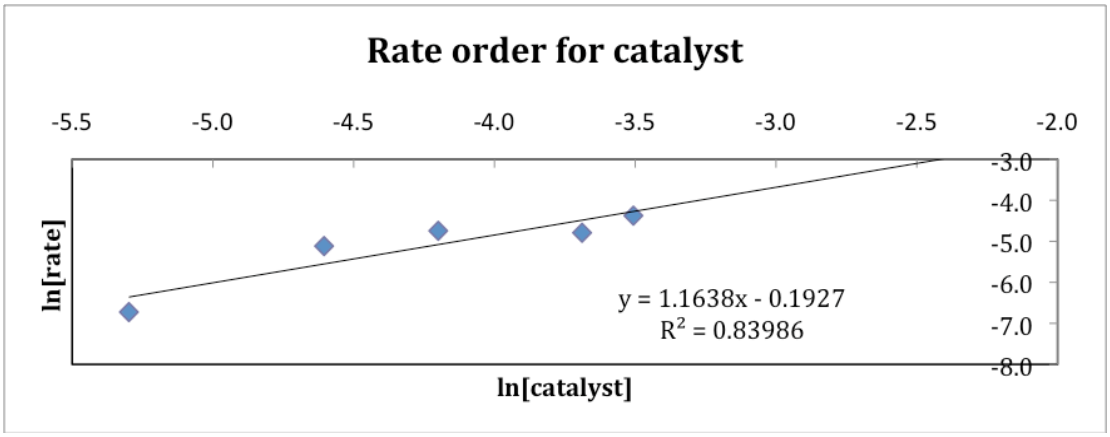


Rate order for the catalyst: A solution of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (1.0 equiv), 3-(2,4-dichlorophenyl) propiolaldehyde (1.0 equiv), and 1-(tert-butyl)-4-methoxybenzene (1.0 equiv as internal standard) was prepared using deuterated toluene (with 10% deuterated dichloromethane) and degassed. Then the solution was transferred to dried NMR tubes containing varied amounts of the precatalyst (**1**): 0.10, 0.15, 0.20, 0.25, and 0.30 equiv. The reactions were performed, the percentage conversions were measured, and the plots were generated as described above. The rate order was calculated from the plot of ln(rate) against

ln(aldehyde concentration) to be 1.16 (R^2 = 0.84). Below, the table reports raw data; the plots shows [aldehyde] vs. time, and the ln[rate] vs. ln[precatalyst].

	Aldehyde concentration for the reactions (varying precatalyst concentration)				
time (h)/M	30% precat.	25% precat.	15% precat.	10% precat.	5% precat.
0.00	0.0900	0.0910	0.0920	0.0880	0.0950
1.00	0.0760	0.0830	0.0850	0.0850	0.0930
2.00	0.0640	0.0770	0.0780	0.0820	0.0920
3.00	0.0520	0.0660	0.0680	0.0730	0.0910
4.00	0.0390	0.0580	0.0570	0.0640	0.0900
Rate [M/h]	**-1.26×10^{-2}**	**-8.30×10^{-3}**	**-8.70×10^{-3}**	**-6.00×10^{-3}**	**-1.20×10^{-3}**
R^2	**1.00**	**1.00**	**0.99**	**0.97**	**0.99**

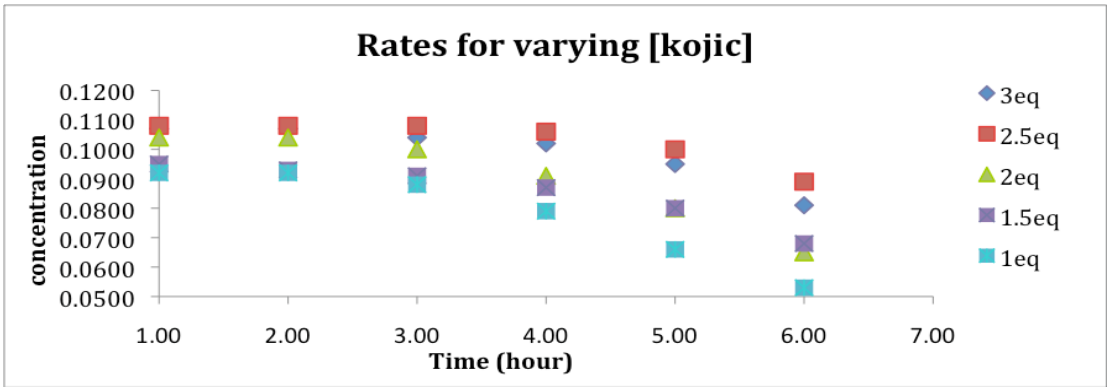


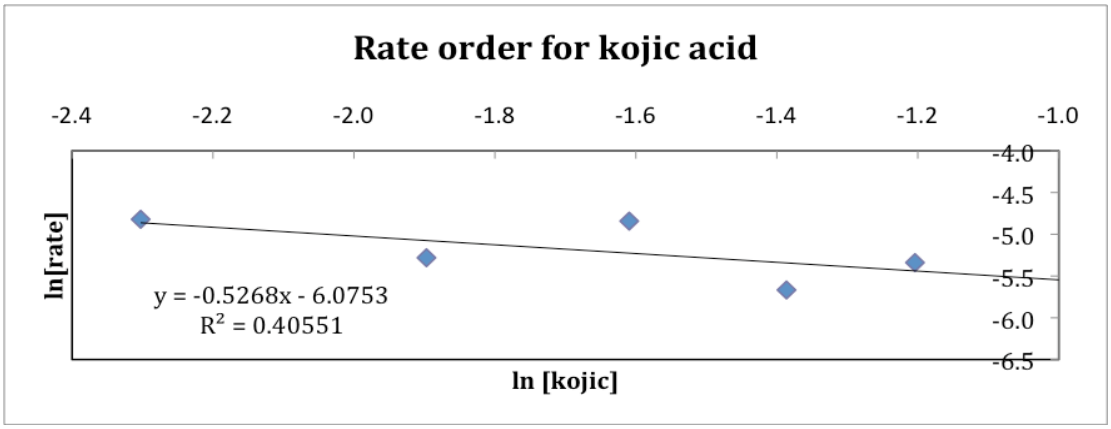


Rate order for TBS-kojic acid: A solution of the precatalyst (**1,** 0.1 equiv) and 1-(tert-butyl)-4-methoxybenzene (1.0 equiv as internal standard) was prepared using deuterated toluene (with 10% deuterated dichloromethane) and degassed. Then, 3-(2,4-dichlorophenyl) propiolaldehyde was added to the solution, and the final solution was quickly transferred to dried NMR tubes containing varied amounts of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one

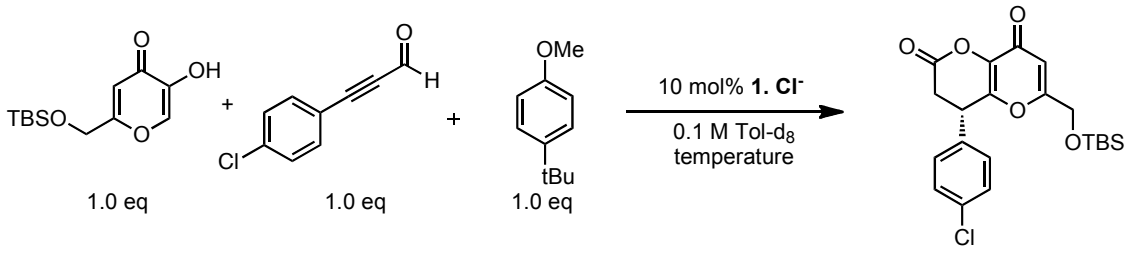
or TBS-kojic acid: 1.0, 1.5, 2.0, 2.5, and 3.0 equiv. The reactions were performed, the percentage conversions were measured, and the plots were generated as described above. The rate order was calculated from the plot of ln(rate) against ln(aldehyde concentration) to be -0.53 (R^2 = 0.41). Below, the table reports raw data; the plots shows [aldehyde] vs. time, and the ln[rate] vs. ln[TBS-kojic acid].

	Aldehyde concentration for the reactions (varying equiv of TBS-kojic acid)				
time (h)/M	3.0 equiv	2.5 equiv	2.0 equiv	1.5 equiv	1.0 equiv
1.00	0.1070	0.1080	0.1040	0.0950	0.0920
2.00	0.1070	0.1080	0.1040	0.0930	0.0920
3.00	0.1040	0.1080	0.1000	0.0910	0.0880
4.00	0.1020	0.1060	0.0910	0.0870	0.0790
5.00	0.0950	0.1000	0.0800	0.0800	0.0660
6.00	0.0810	0.0890	0.0650	0.0680	0.0530
Rate [M/h]	**-4.80×10^{-3}**	**-3.46×10^{-3}**	**-7.89×10^{-3}**	**-5.09×10^{-3}**	**-8.06×10^{-3}**
R^2	**0.90**	**0.85**	**0.95**	**0.94**	**0.95**





Activation parameters measurement and analysis



A solution of 2-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxy-4H-pyran-4-one (1.0 equiv), 3-(4-chlorophenyl)propiolaldehyde (1.0 equiv), and 1-(tert-butyl)-4-methoxybenzene (1.0 equiv as internal standard), and 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride (1, 2.0 mg, 0.005 mmol, 0.1 equiv) was prepared using 0.5 mL deuterated toluene (with 10% deuterated dichloromethane to ensure complete solubility). The reactions were performed in NMR tubes and placed in the preheated NMR instrument (temp at 30, 35, 40, 45, and 50^{o}C). Percentage conversions were measured using ^{1}H NMR by the disappearance of the ynal from the integration of the peak at 8.90 ppm (1H) against the internal standard peak at 1.22 ppm (9H).

The plots of molar concentration of the ynal versus time (hour) were generated; the rates were determined from the slope of each plot. The rate constants (k_{obs}) were calculated from the experimentally determined rate law (1). The plot of ln(k/T) vs 1/T (in K) was then generated. Using the Eyring equation (2), the activation enthalpy ($\Delta H^{\ddagger}$) was calculated from the slope to be 15.25 Kcal/mol, while the entropy of activation ($\Delta S^{\ddagger}$) was calculated from the y-intercept to be -25.48 cal/K.mol. The table below reports raw data; the plot below shows ln(k/T) vs 1/T.

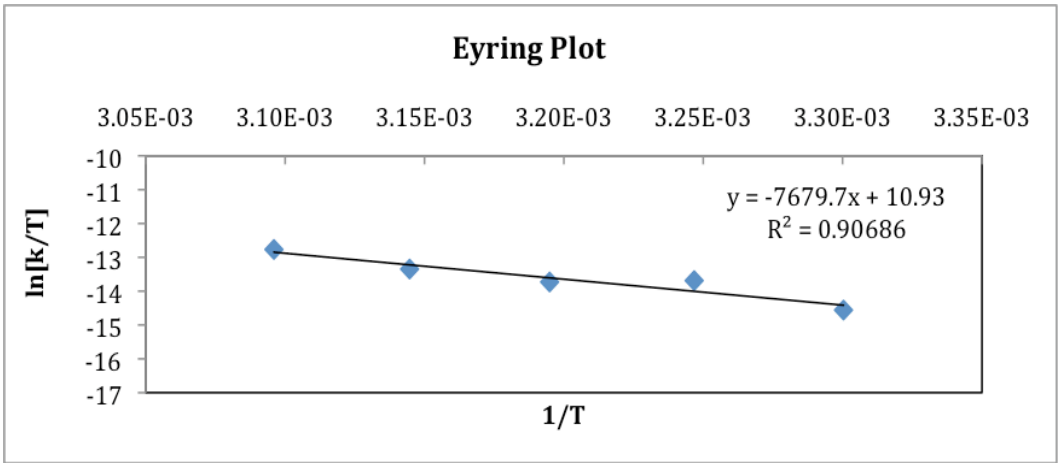
$$Rate = k_{obs}\,[triazolium\ precatalyst]^{1}[RCHO]^{1/2}[kojic\ acid]^{-1/2} \quad (1)$$

$$ln(k/T) = -(\Delta H^{\ddagger}/RT) + (\Delta S^{\ddagger}/R) + ln(k_B/h) \quad (2)$$

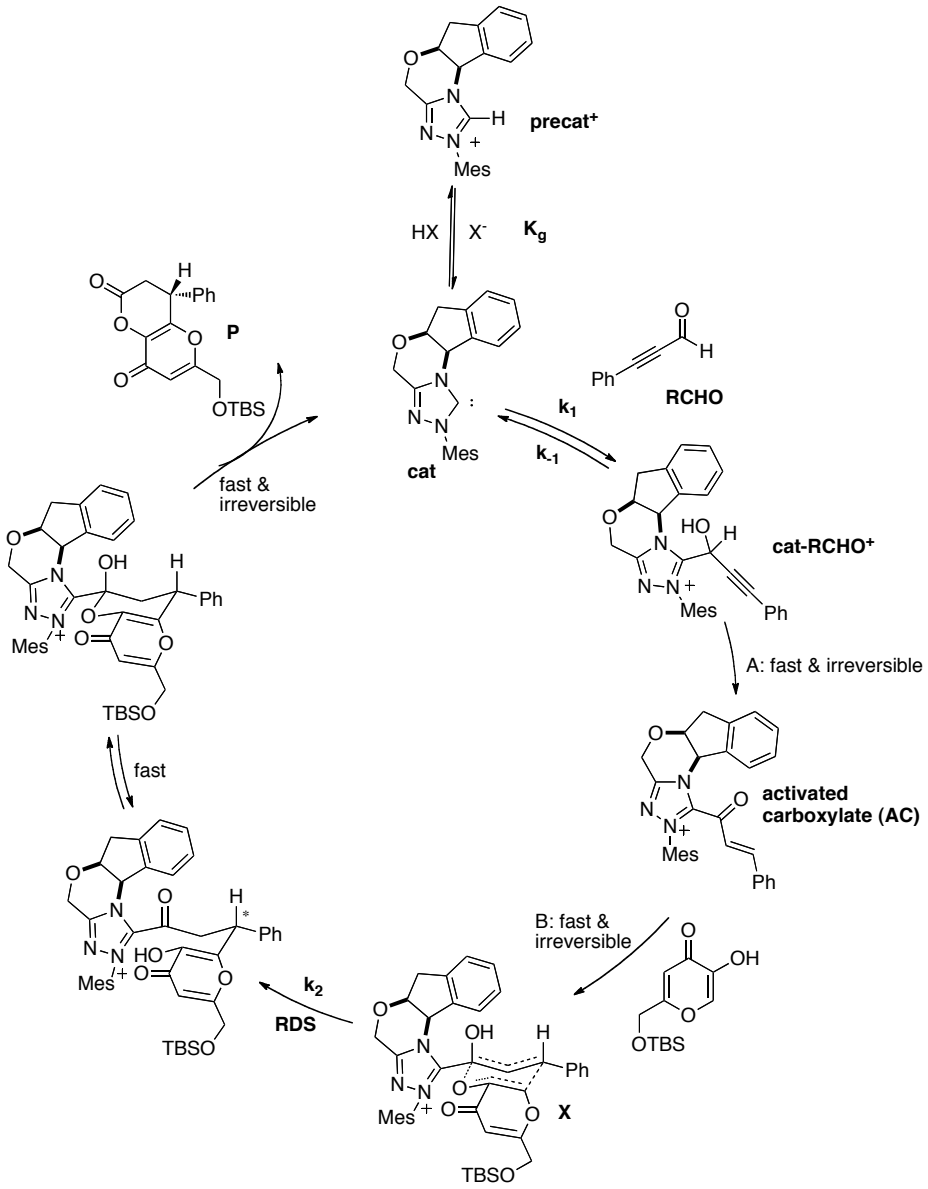
where R = the gas constant; k_B = Boltzmann constant; and h = Planck's constant.

	Aldehyde concentration for the reactions (varying temperatures)				
time(s)/T(K)	**323 K**	**318 K**	**313 K**	**308 K**	**303 K**
600	0.0639	0.0715	0.0718	0.0741	0.0681
900	0.0601	0.0708	0.0712	0.0732	0.0677
1200	0.0567	0.0692	0.0701	0.0716	0.0670
1500	0.0537	0.0673	0.0691	0.0703	0.0663
1800	0.0510	0.0655	0.0682	0.0694	0.0663
2100	0.0478	0.0641	0.0674	0.0683	0.0659
2400	0.0466	0.0627	0.0657	0.0674	0.0656
2700	0.0442	0.0612	0.0649	0.0665	0.0648
3000	0.0402	0.0597	0.0642	0.0658	0.0647
3300	0.0384	0.0584	0.0627	0.0644	0.0640
Rate [M/sec]	**-9.21×10^{-6}**	**-5.08×10^{-6}**	**-3.41×10^{-6}**	**-3.50×10^{-6}**	**-1.44×10^{-6}**
R^2	**0.99**	**1.00**	**0.99**	**0.99**	**0.98**
k_{obs} [sec^{-1}]	**9.21×10^{-4}**	**5.08×10^{-4}**	**3.41×10^{-4}**	**3.50×10^{-4}**	**1.44×10^{-4}**

ln(k/T)	1/T (K^{-1})	**Constants**		**Parameters**	
-12.77	3.096×10^{-3}	R(cal/Kmol)	1.986	slope	-7679.66
-13.35	3.145×10^{-3}	k_B ($m^2 kg\ s^{-2}\ K^{-1}$)	1.38×10^{-23}	R^2	0.91
-13.73	3.195×10^{-3}	h ($m^2\ kg\ s^{-1}$)	6.63×10^{-34}	y-intercept	10.93
-13.69	3.247×10^{-3}	$\Delta H^{\ddagger}$ = ***15.25 (Kcal/mol)***			
-14.56	3.300×10^{-3}	$\Delta S^{\ddagger}$ = ***-25.48 (cal/mol.K)***			



Derivation of the rate law for azolium-catalyzed Claisen rearrangement pathway



The unimolecular sigmatropic rearrangement is proposed to be the rate-determining step. Assuming that redox reaction, protonation steps, and 1,2-addition step are fast and irreversible, that is $[\text{cat}-\text{RCHO}^+] \approx [\text{X}]$, the overall rate is defined as:

$$\frac{d[P]}{dt} = k_2[cat - RCHO^+]$$

The equilibrium constant (K_g) for the generation of the active catalyst is defined as:

$$K_g = \frac{[cat][HX]}{[precat^+][X^-]} \text{ or } [precat^+] = \frac{1}{K_g}\frac{[cat][HX]}{[X^-]} \quad \text{eq 1.}$$

The overall catalyst concentration is defined as:

$$[cat]_0 = [cat] + [precat^+] + [cat - RCHO^+] \quad \text{eq 2.}$$

Substitute eq. 1 into eq. 2 to obtain:

$$[cat]_0 = [cat] + \frac{1}{K_g}\frac{[cat][HX]}{[X^-]} + [cat - RCHO^+] \text{ or } (1 + \frac{1}{K_g}\frac{[HX]}{[X^-]})[cat] = [cat]_0 - [cat - RCHO^+]$$

$$[cat] = \frac{[cat]_0 - [cat - RCHO^+]}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}} \quad \text{eq 3.}$$

The rate of the catalyst-aldehyde complex can be expressed by:

$$\frac{d[cat - RCHO^+]}{dt} = k_1[cat][RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] \quad \text{eq 4.}$$

Assuming that the concentration of catalyst-aldehyde complex does not change over time (steady state approximation); thus,

$$\frac{d[cat - RCHO^+]}{dt} = k_1[cat][RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] = 0 \quad \text{eq 5.}$$

Substitute eq. 3 into eq. 5 to obtain:

$$k_1\frac{[cat]_0 - [cat - RCHO^+]}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] = 0$$

$$\frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[cat]_0[RCHO] = (k_{-1} + k_2 + \frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[RCHO])[cat - RCHO^+]$$

$$[cat-RCHO^{+}] = \frac{\dfrac{k_1}{1+\dfrac{1}{K_g}\dfrac{[HX]}{[X^-]}}[cat]_0[RCHO]}{k_{-1}+k_2+\dfrac{k_1}{1+\dfrac{1}{K_g}\dfrac{[HX]}{[X^-]}}[RCHO]}$$

$$[cat-RCHO^{+}] = \frac{[cat]_0[RCHO]}{[RCHO]+\dfrac{k_{-1}+k_2}{k_1}(1+\dfrac{1}{K_g}\dfrac{[HX]}{[X^-]})} \quad \text{eq 6.}$$

Assuming that the sigmatropic rearrangement is the rate-determining step; thus,

$$\frac{d[P]}{dt} = k_2[cat-RCHO^{+}] \quad \text{eq 7.}$$

Substituted eq. 6 into the rate equation 7, the rate law may be expressed as:

$$\frac{d[P]}{dt} = k_2\frac{[cat]_0[RCHO]}{[RCHO]+\dfrac{k_{-1}+k_2}{k_1}(1+\dfrac{1}{K_g}\dfrac{[HX]}{[X^-]})} \quad \text{eq 8.}$$

Where $K_g = \dfrac{[cat][HX]}{[precat^{+}][X^-]}$.

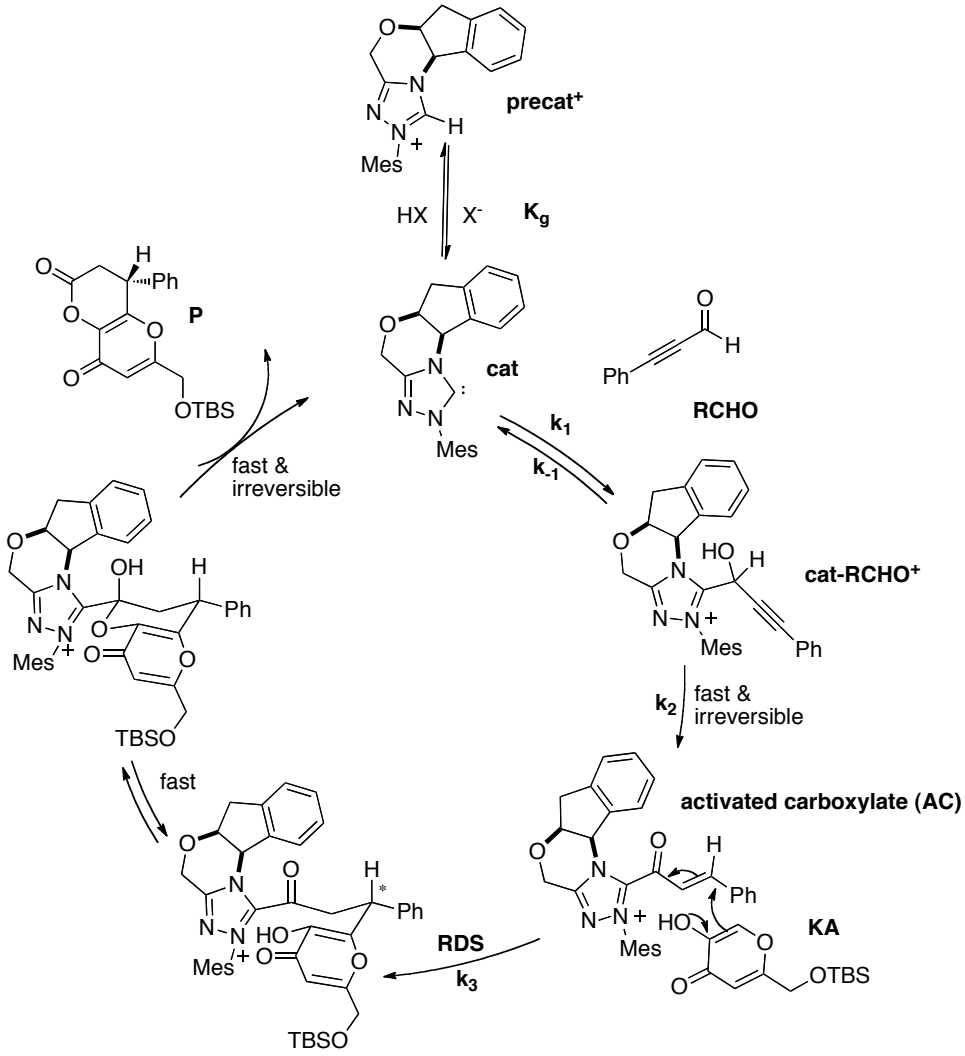
Alternatively, eq. 8 may be expressed in terms of the dissociation constant (K_a) of a general acid (HX):

$$K_a = \frac{[H^+][X^-]}{[HX]} \text{ or } \frac{[HX]}{[X^-]} = \frac{[H^+]}{K_a} \quad \text{eq 9.}$$

Substitute eq. 9 into eq. 8, the rate law may be expressed as:

$$\frac{d[P]}{dt} = k_2\frac{[cat]_0[RCHO]}{[RCHO]+\dfrac{k_{-1}+k_2}{k_1}(1+\dfrac{1}{K_gK_a}[H^+])} \quad \text{eq 10.}$$

Derivation of the rate law for azolium-catalyzed conjugate addition pathway



The bimolecular conjugation addition is proposed to be the rate-determining step. Assuming that redox and protonation step is fast and irreversible, that is $[\text{cat}-\text{RCHO}^+] \approx [\text{AC}]$, the overall rate is defined as:

$$\frac{d[P]}{dt} = k_3[cat - RCHO^+][KA]$$

The equilibrium constant (K_g) for the generation of the active catalyst is defined as:

$$K_g = \frac{[cat][HX]}{[precat^+][X^-]} \quad \text{or} \quad [precat^+] = \frac{1}{K_g}\frac{[cat][HX]}{[X^-]} \qquad \text{eq 11.}$$

The overall catalyst concentration is defined as:

$$[cat]_0 = [cat] + [precat^+] + [cat - RCHO^+] \quad \text{eq 12.}$$

Substitute eq. 11 into eq. 12 to obtain:

$$[cat]_0 = [cat] + \frac{1}{K_g}\frac{[cat][HX]}{[X^-]} + [cat - RCHO^+] \quad \text{or} \quad (1 + \frac{1}{K_g}\frac{[HX]}{[X^-]})[cat] = [cat]_0 - [cat - RCHO^+]$$

$$[cat] = \frac{[cat]_0 - [cat - RCHO^+]}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}} \quad \text{eq 13.}$$

The rate of the catalyst-aldehyde complex can be expressed by:

$$\frac{d[cat - RCHO^+]}{dt} = k_1[cat][RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] \quad \text{eq 14.}$$

Assuming that the concentration of catalyst-aldehyde complex does not change over time (steady state approximation); thus,

$$\frac{d[cat - RCHO^+]}{dt} = k_1[cat][RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] = 0 \quad \text{eq 15.}$$

Substitute eq. 13 into eq. 15 to obtain:

$$k_1\frac{[cat]_0 - [cat - RCHO^+]}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[RCHO] - k_{-1}[cat - RCHO^+] - k_2[cat - RCHO^+] = 0$$

$$\frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[cat]_0[RCHO] = (k_{-1} + k_2 + \frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[RCHO])[cat - RCHO^+]$$

$$[cat - RCHO^+] = \frac{\frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[cat]_0[RCHO]}{k_{-1} + k_2 + \frac{k_1}{1 + \frac{1}{K_g}\frac{[HX]}{[X^-]}}[RCHO]}$$

$$[cat - RCHO^{+}] = \frac{[cat]_0[RCHO]}{[RCHO] + \frac{k_{-1} + k_2}{k_1}(1 + \frac{1}{K_g}\frac{[HX]}{[X^{-}]})}$$ eq 16.

Assuming that the bimolecular conjugate addition is the rate-determining step; thus,

$$\frac{d[P]}{dt} = k_3[cat - RCHO^{+}][KA]$$ eq 17.

Substitute eq. 16 into eq. 17, the rate law may be expressed as:

$$\frac{d[P]}{dt} = k_3 \frac{[cat]_0[RCHO][KA]}{[RCHO] + \frac{k_{-1} + k_2}{k_1}(1 + \frac{1}{K_g}\frac{[HX]}{[X^{-}]})}$$ eq 18.

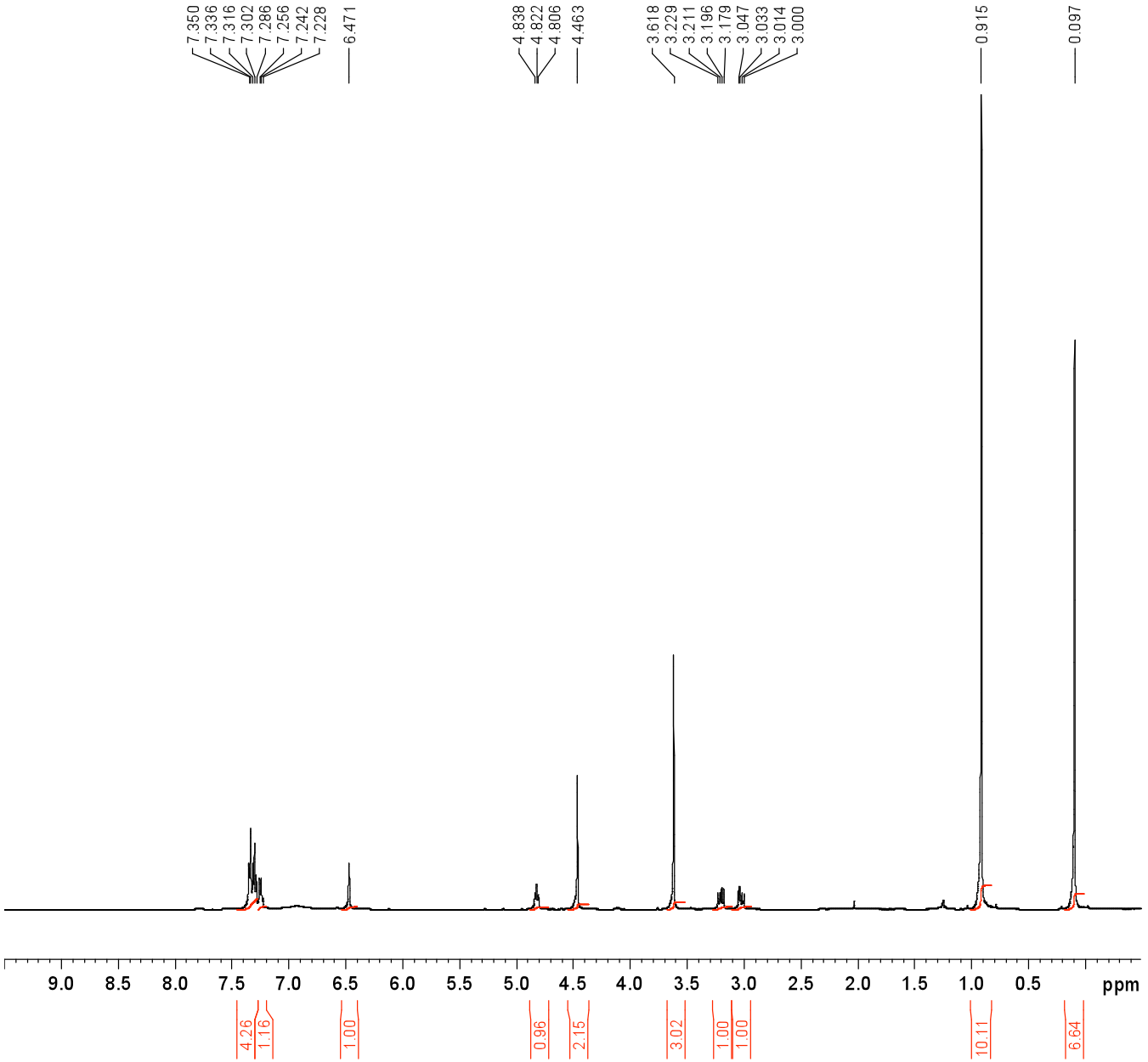
Where $K_g = \frac{[cat][HX]}{[precat^{+}][X^{-}]}$.

Alternatively, eq. 18 may be expressed in terms of the dissociation constant (K_a) of a general acid (HX):

$$K_a = \frac{[H^{+}][X^{-}]}{[HX]} \text{ or } \frac{[HX]}{[X^{-}]} = \frac{[H^{+}]}{K_a}$$ eq 19.

Substitute eq. 19 into eq. 18, the rate law may be expressed as:

$$\frac{d[P]}{dt} = k_3 \frac{[cat]_0[RCHO][KA]}{[RCHO] + \frac{k_{-1} + k_2}{k_1}(1 + \frac{1}{K_g K_a}[H^{+}])}$$ eq 20.

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TE                297.3 K
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PC                 1.00
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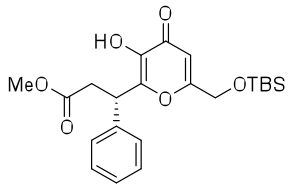

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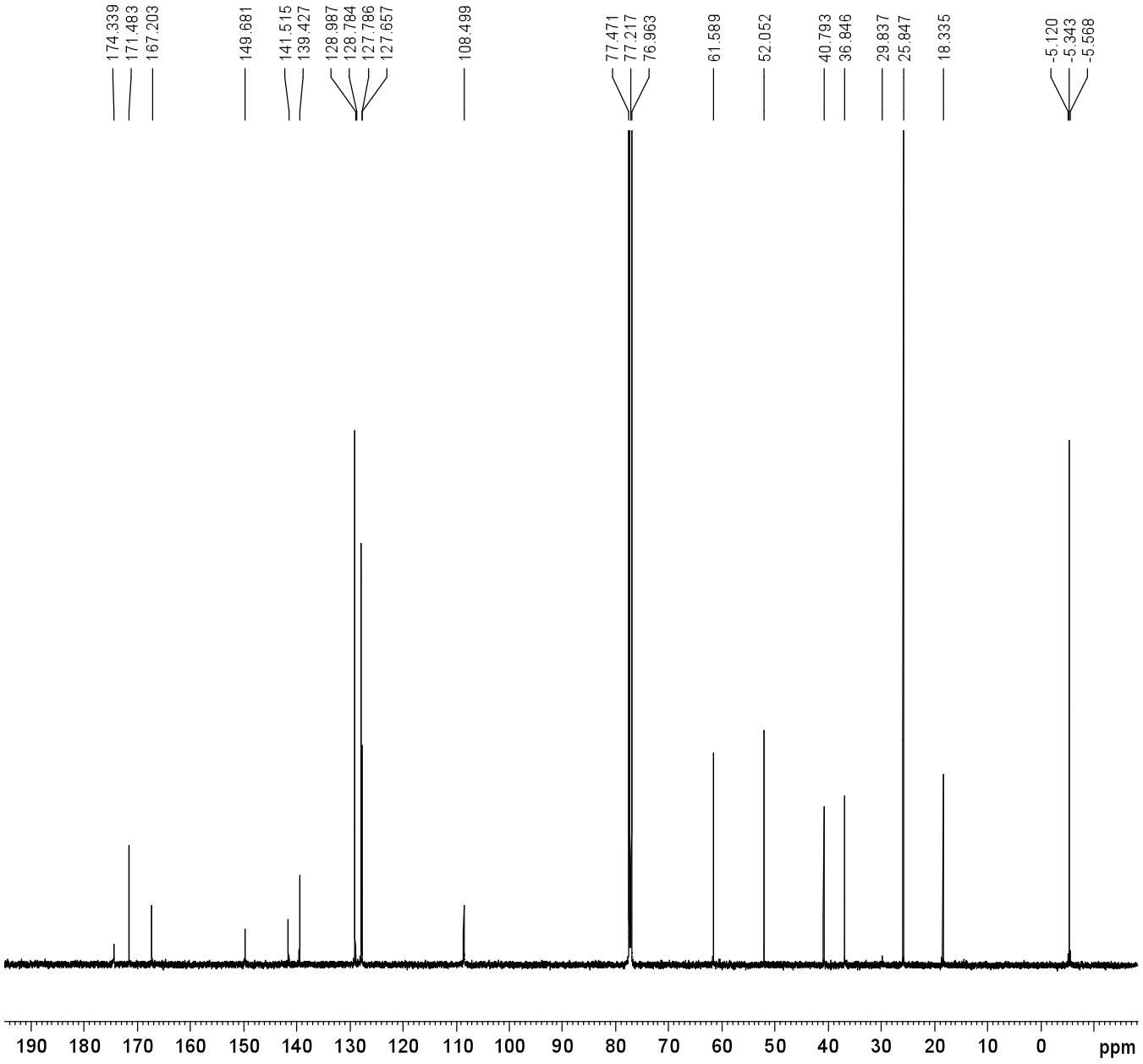


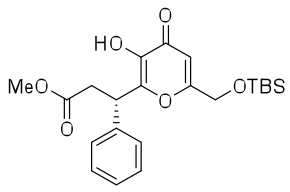

```
Current Data Parameters
NAME        I-JM-59carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20090825
Time                19.53
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  722
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 1290
DW               16.800 usec
DE                6.50 usec
TE              298.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.50 usec
PL1                 1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL12               17.43 dB
PL13               18.43 dB
PL2                 0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                  32768
SF          125.8231500 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



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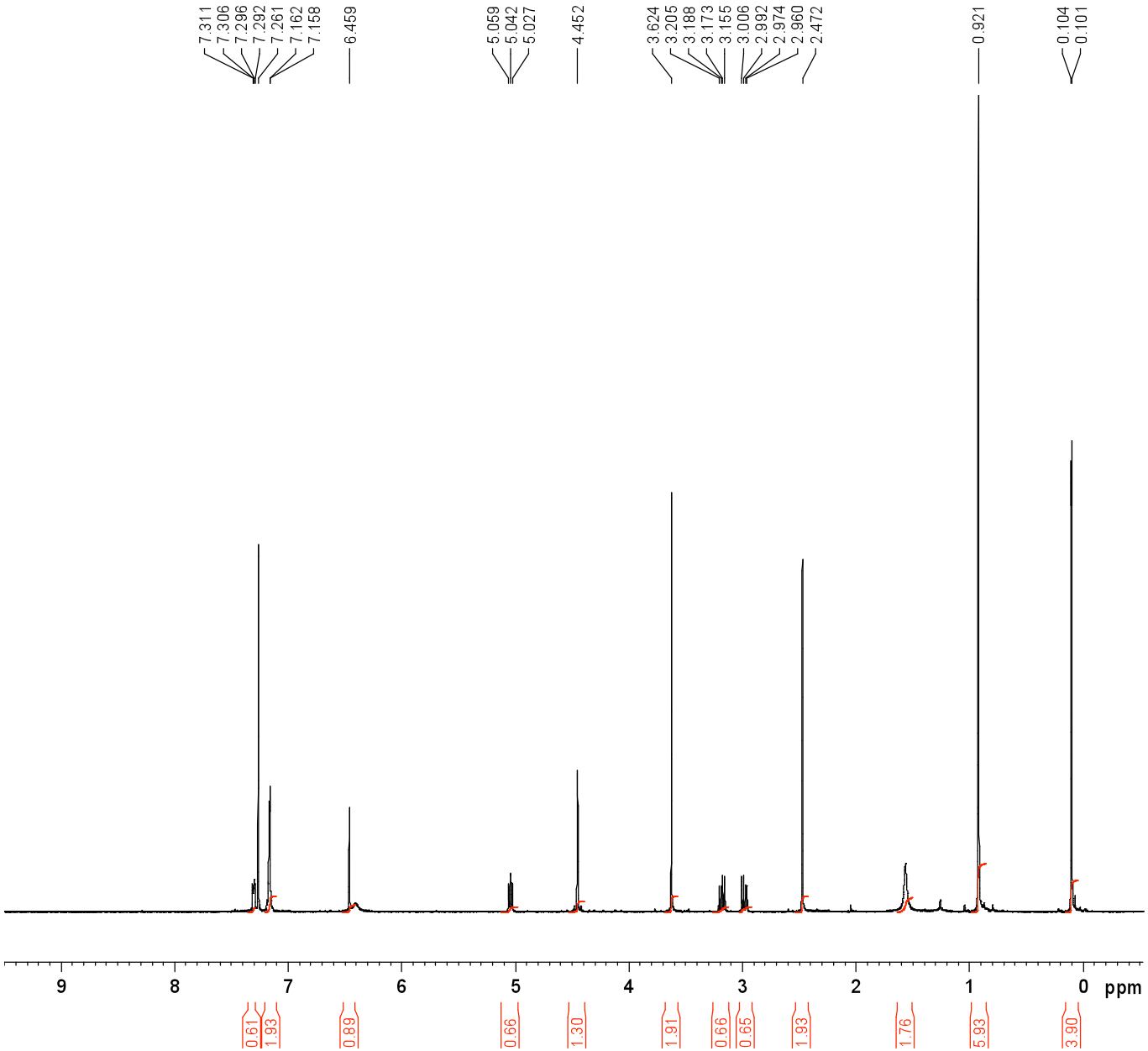
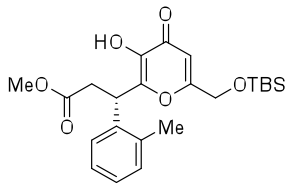



```
Current Data Parameters
NAME                  V95Racc
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20090923
Time                   19.14
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 7002.801 Hz
FIDRES              0.106854 Hz
AQ                  4.6793203 sec
RG                       512
DW                    71.400 usec
DE                     6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    10.76 usec
PL1                    0.00 dB
SFO1             500.3932525 MHz

F2 - Processing parameters
SI                       32768
SF                500.3900160 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```



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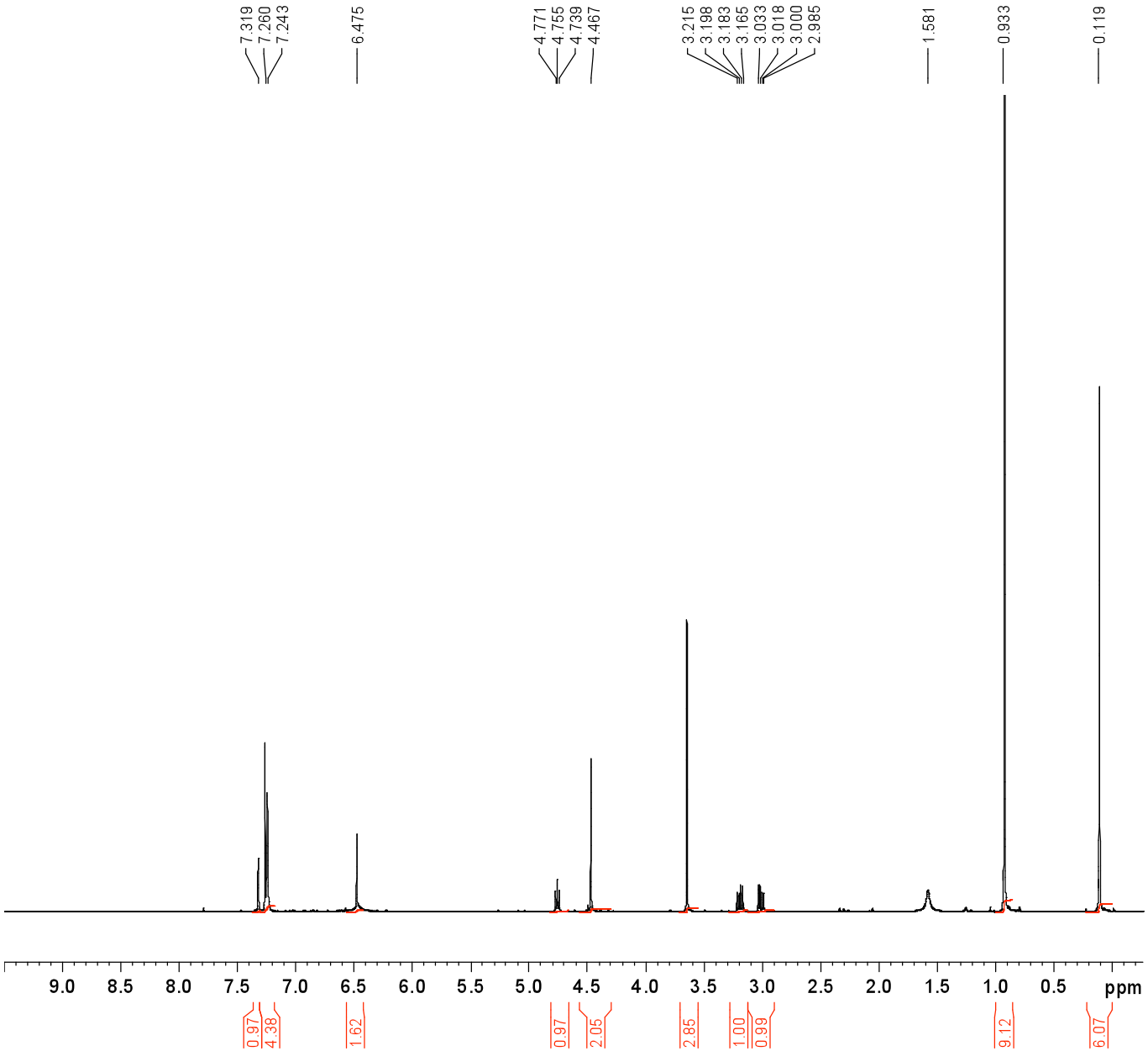
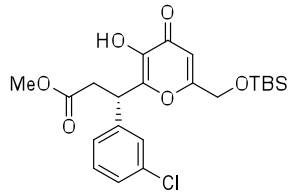
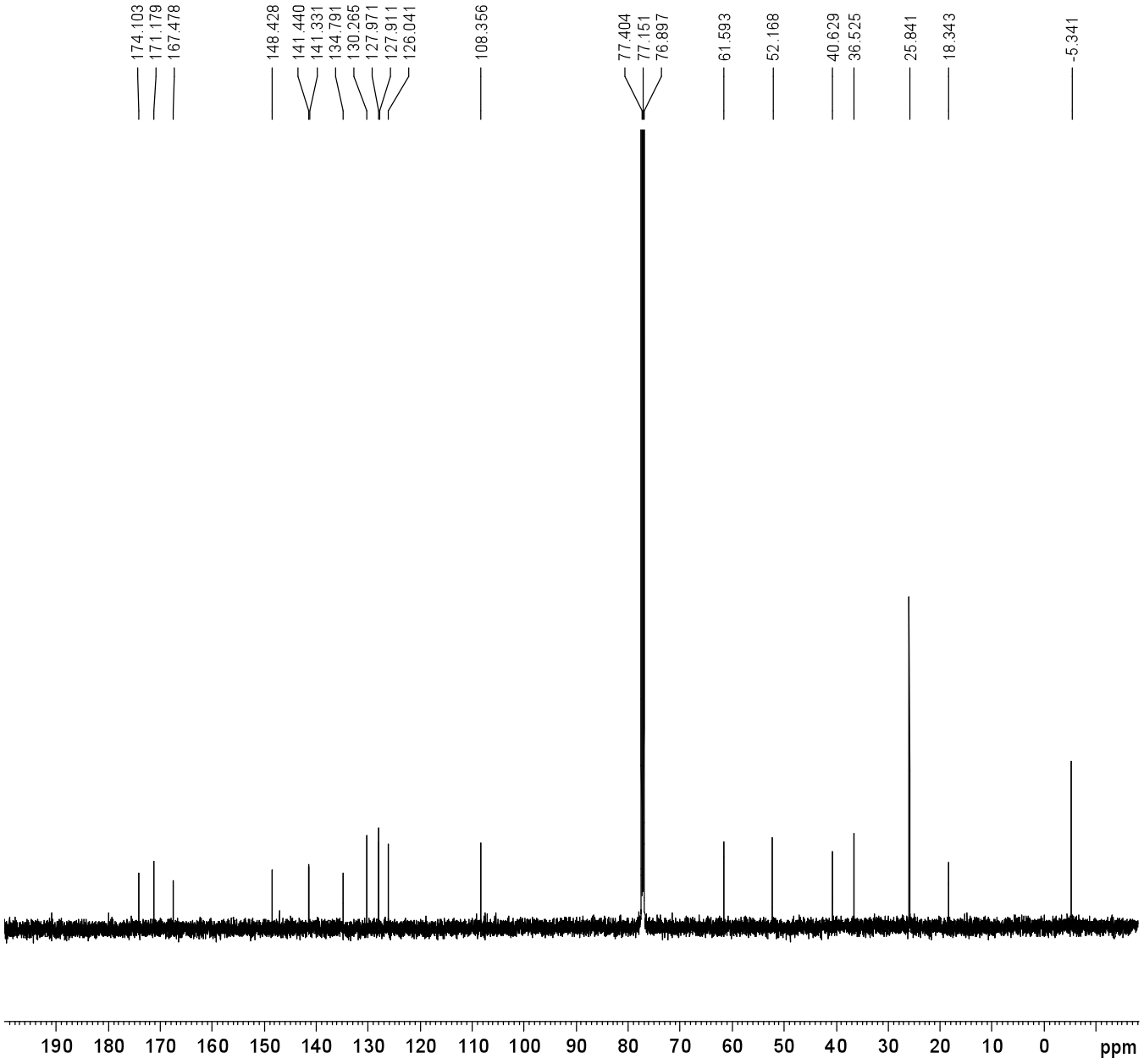
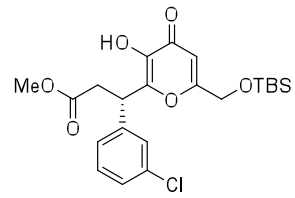


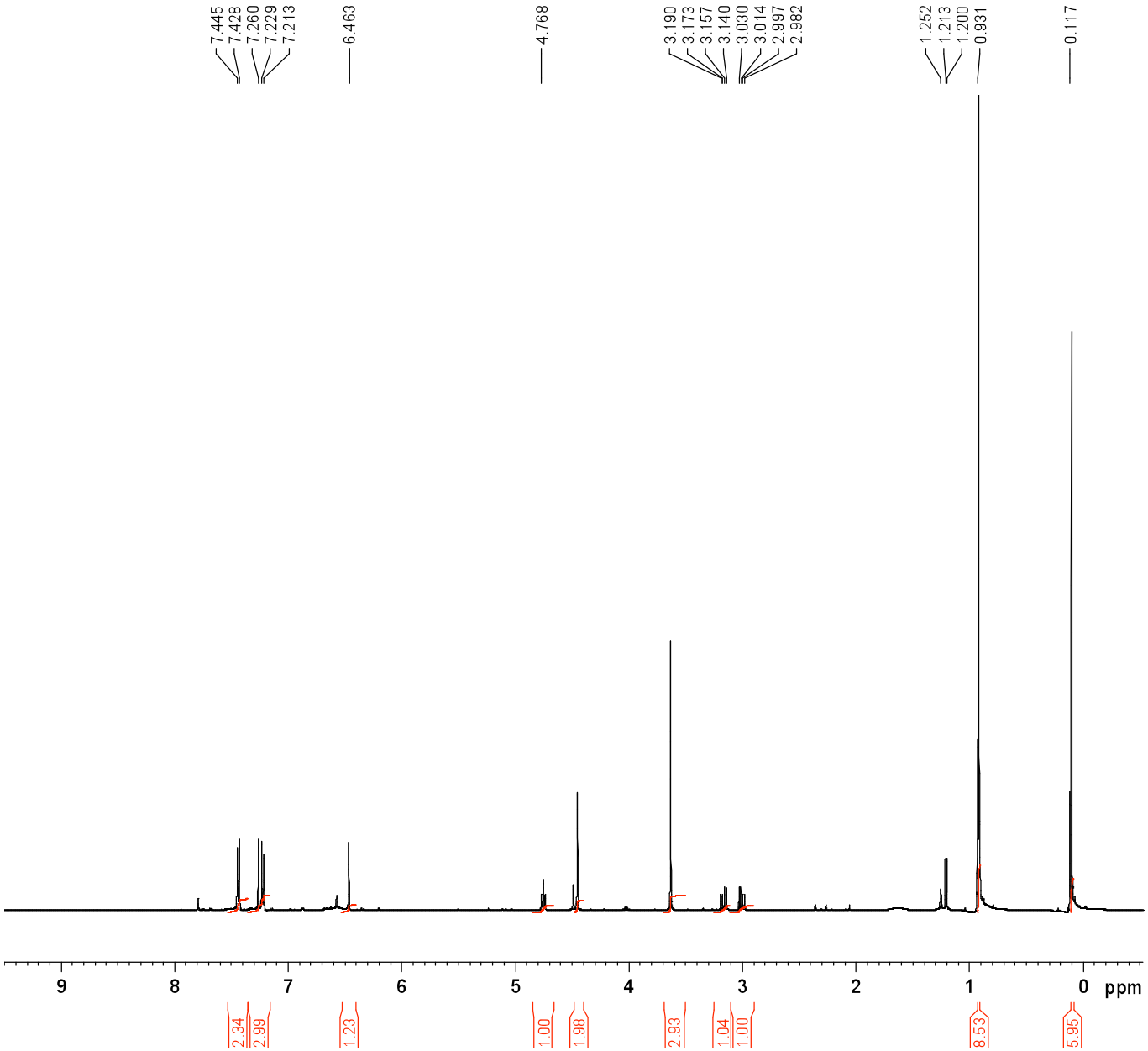

```
Current Data Parameters
NAME          I-JM-66prep
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090919
Time                17.48
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     10
DS                      2
SWH              7002.801 Hz
FIDRES           0.106854 Hz
AQ               4.6793203 sec
RG                    575
DW                 71.400 usec
DE                  6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.76 usec
PL1                 0.00 dB
SFO1         500.3932525 MHz

F2 - Processing parameters
SI                  32768
SF           500.3900160 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



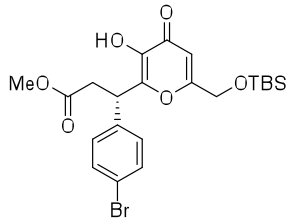



```
Current Data Parameters
NAME      I-JM-66prep13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090919
Time              18.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1000
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 1290
DW               16.800 usec
DE                6.50 usec
TE              298.7 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL12             17.43 dB
PL13             18.43 dB
PL2               0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                 32768
SF          125.8231500 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```






```
Current Data Parameters
NAME        I-JM-65_prep
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090919
Time              19.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   13
DS                    2
SWH            7002.801 Hz
FIDRES        0.106854 Hz
AQ            4.6793203 sec
RG                  256
DW             71.400 usec
DE              6.50 usec
TE              298.3 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                1H
P1             10.76 usec
PL1             0.00 dB
SFO1       500.3932525 MHz

F2 - Processing parameters
SI                 32768
SF         500.3900160 MHz
WDW                   EM
SSB                    0
LB              0.30 Hz
GB                     0
PC                  1.00
```



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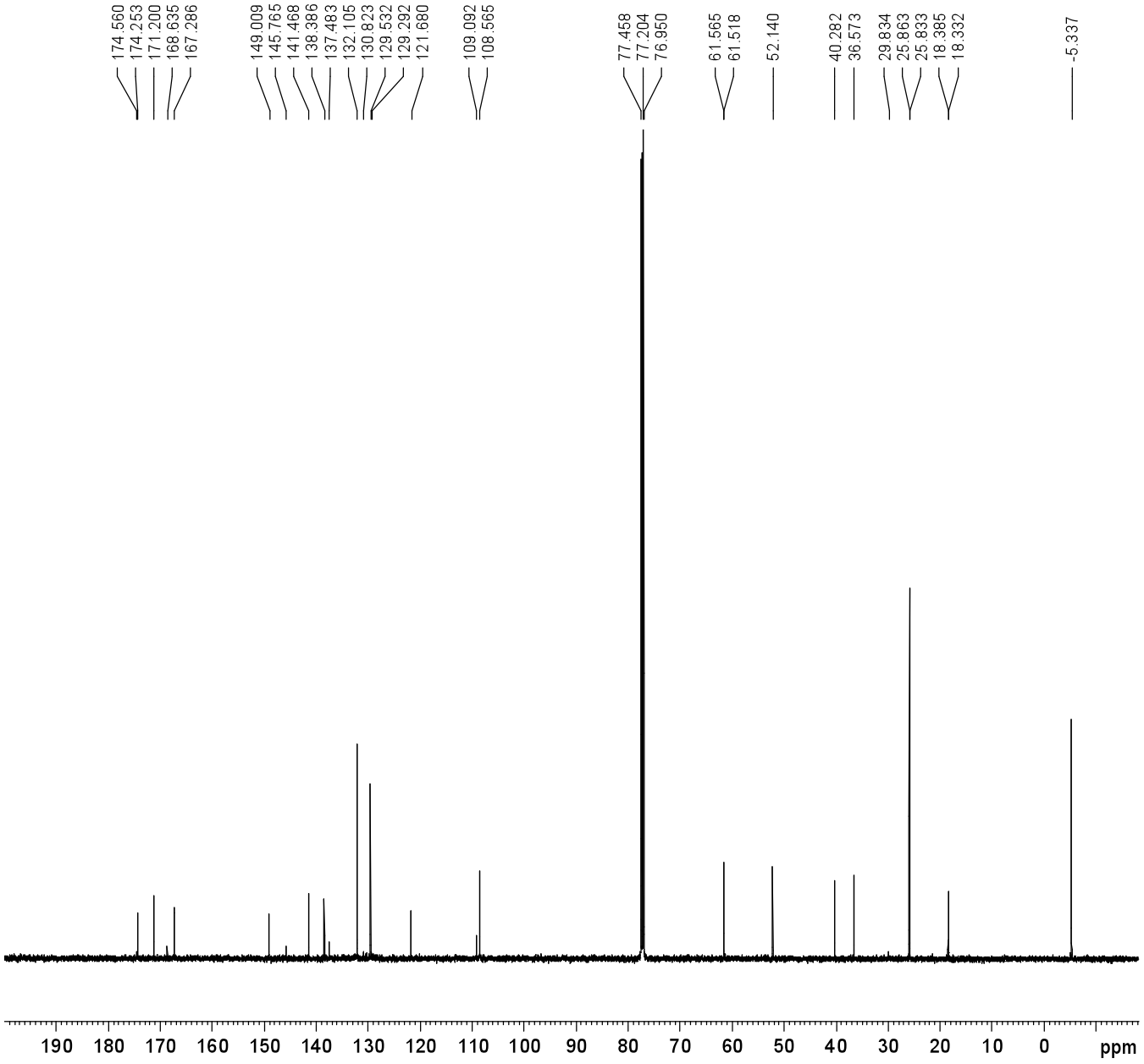


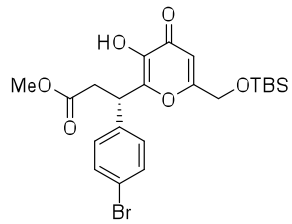

```
Current Data Parameters
NAME        I-JM-65carbon
EXPNO                   9
PROCNO                  1

F2 - Acquisition Parameters
Date_           20090831
Time              20.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  276
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 1290
DW               16.800 usec
DE                6.50 usec
TE              298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL12             17.43 dB
PL13             18.43 dB
PL2               0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                 32768
SF          125.8231500 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```



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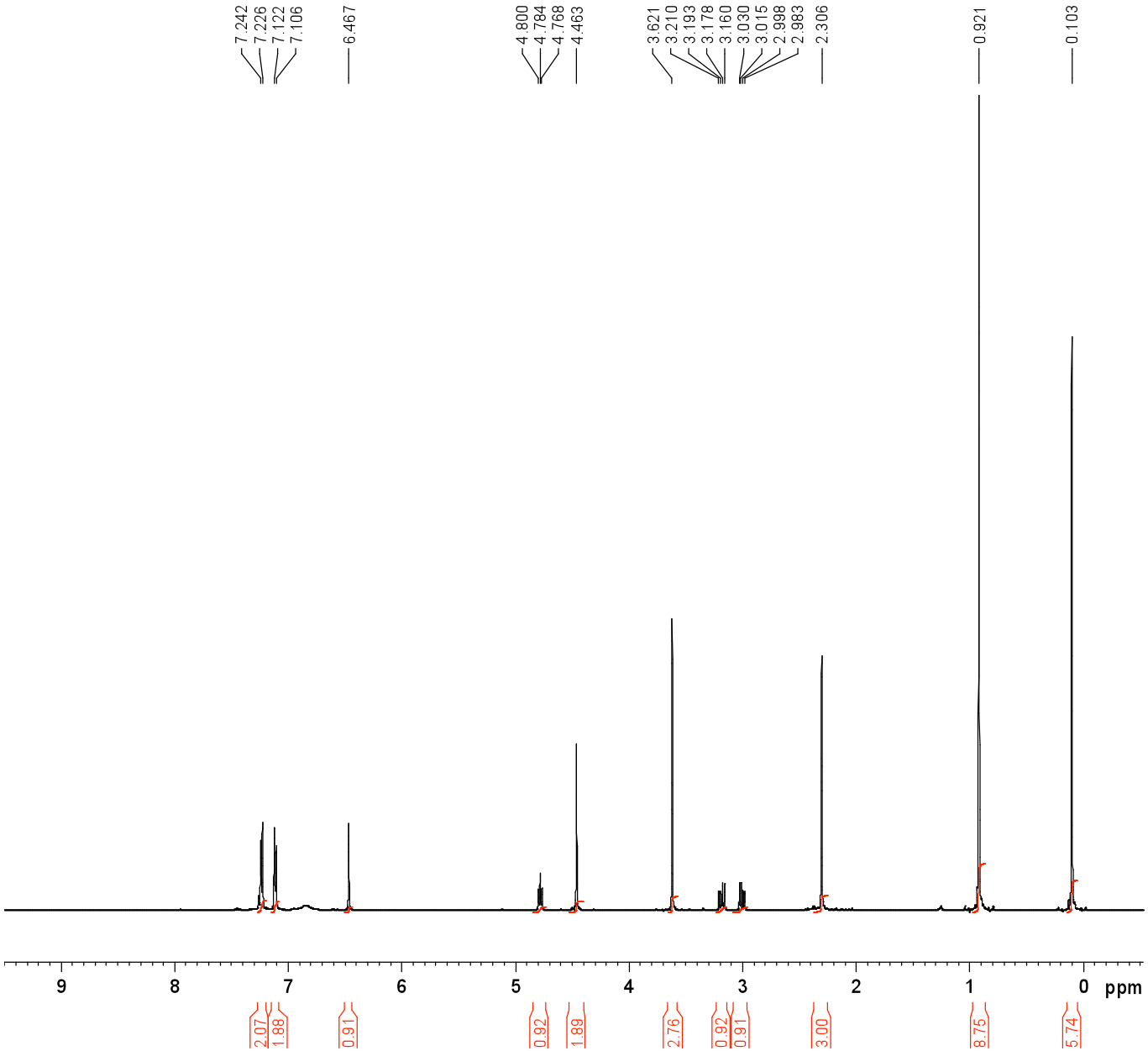
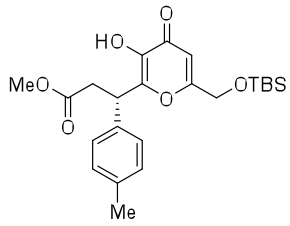



```
Current Data Parameters
NAME                  V97
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090903
Time                13.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     15
DS                      2
SWH              7002.801 Hz
FIDRES           0.106854 Hz
AQ               4.6793203 sec
RG                   80.6
DW                 71.400 usec
DE                  6.50 usec
TE                 297.3 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.76 usec
PL1                 0.00 dB
SF01         500.3932525 MHz

F2 - Processing parameters
SI                  32768
SF           500.3900160 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```



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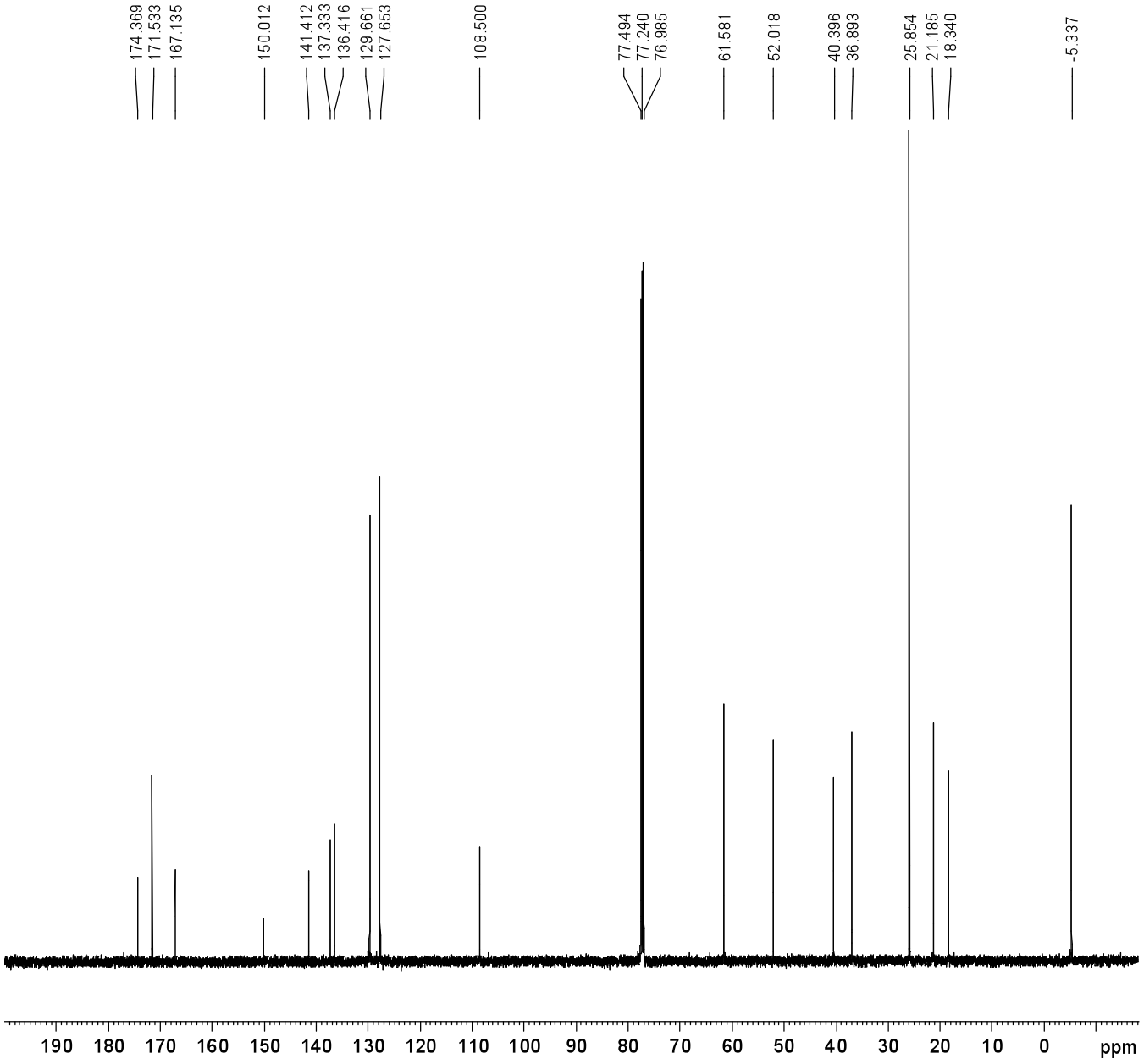
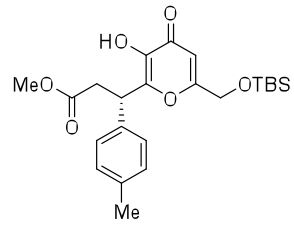
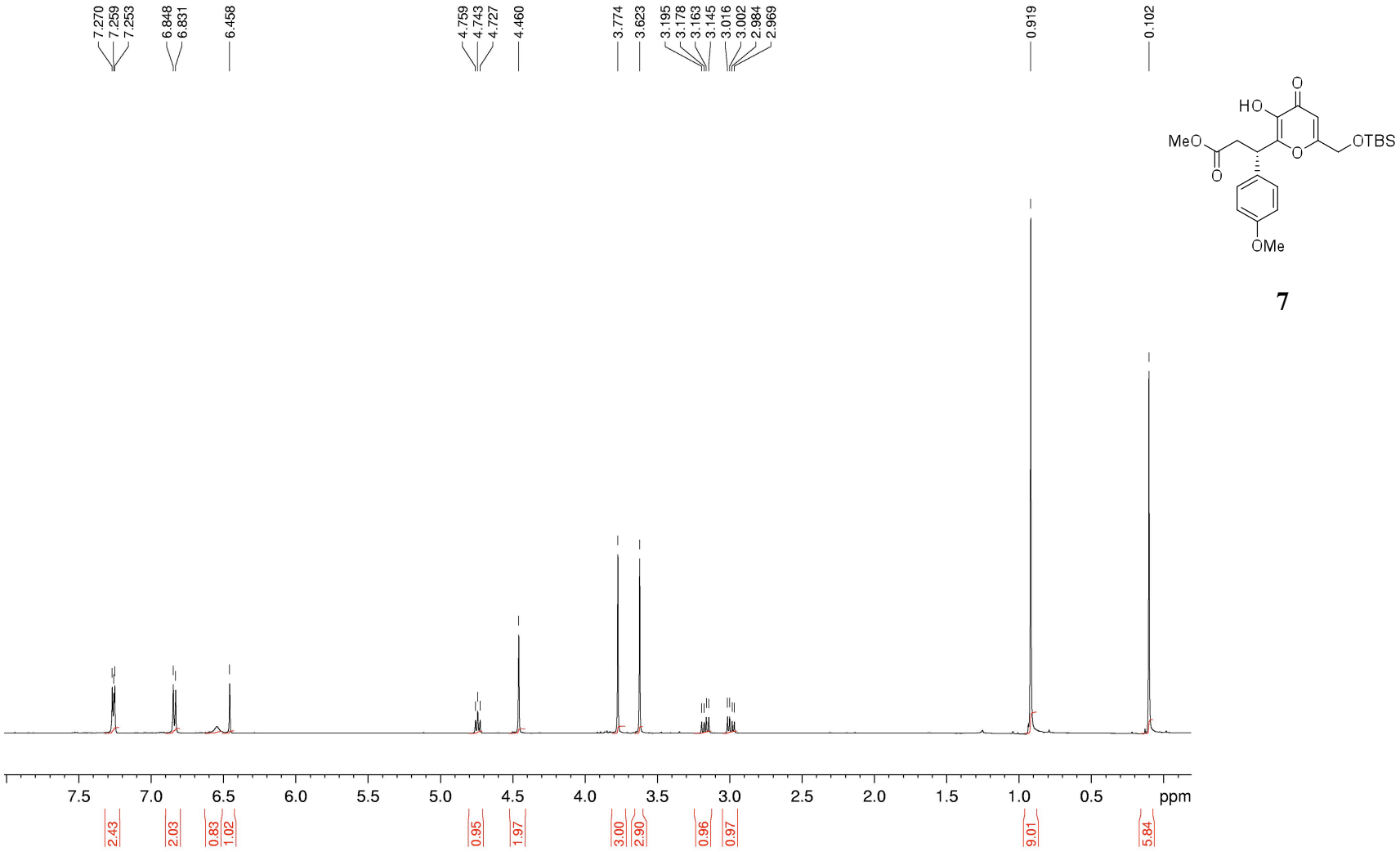


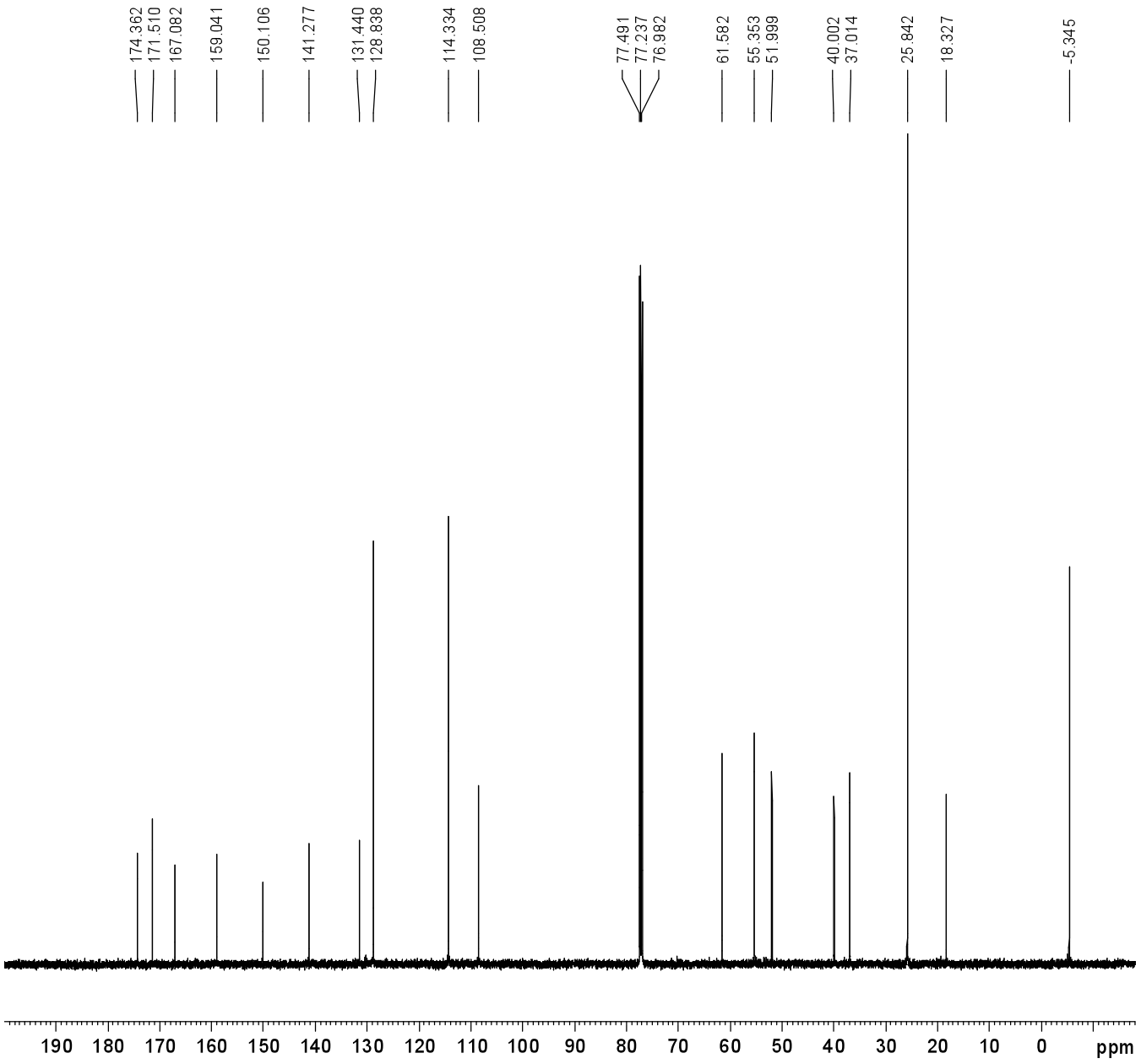

```
Current Data Parameters
NAME                 V97carbon
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090923
Time                   18.09
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT                CDCl3
NS                       116
DS                         4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      1030
DW                   16.800 usec
DE                    6.50 usec
TE                   298.5 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                       7.50 usec
PL1                      1.00 dB
SF01             125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL12                    17.43 dB
PL13                    18.43 dB
PL2                      0.00 dB
SF02             500.3920016 MHz

F2 - Processing parameters
SI                       32768
SF               125.8231500 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```



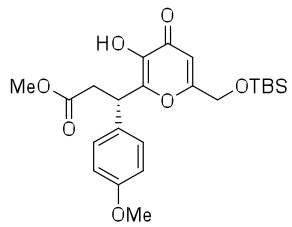
6


7.270
7.259
7.253
6.848
6.831
6.458
4.759
4.743
4.727
4.460
3.774
3.623
3.195
3.178
3.163
3.145
3.016
3.002
2.984
2.969
0.919
0.102
HO
O
MeO
O
O
OTBS
OMe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.43
2.03
0.83
1.02
0.95
1.97
3.00
2.90
0.96
0.97
9.01
5.84

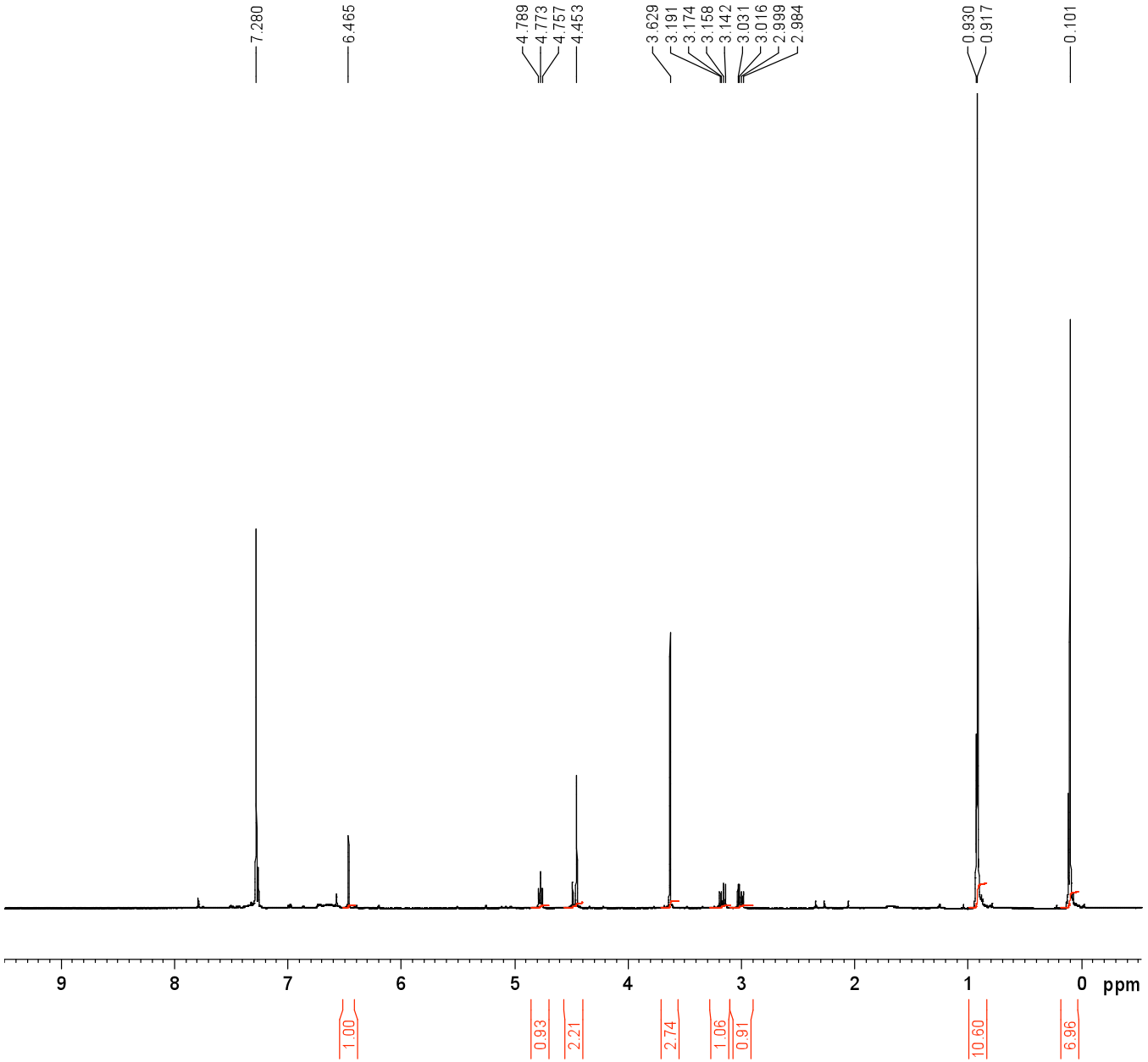
7



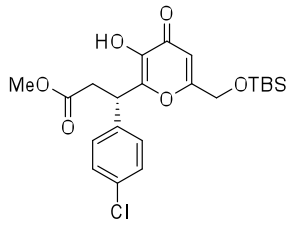

```
Current Data Parameters
NAME                  V86carbon
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20090921
Time                   18.01
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     123
DS                       4
SWH                29761.904 Hz
FIDRES             0.454121 Hz
AQ                 1.1010548 sec
RG                      1620
DW                    16.800 usec
DE                     6.50 usec
TE                   298.7 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                           1

======== CHANNEL f1 =======
NUC1                      13C
P1                       7.50 usec
PL1                      1.00 dB
SF01             125.8357479 MHz

======== CHANNEL f2 =======
CPDPRG2              waltz16
NUC2                      1H
PCPD2                   80.00 usec
PL12                    17.43 dB
PL13                    18.43 dB
PL2                      0.00 dB
SF02             500.3920016 MHz

F2 - Processing parameters
SI                       32768
SF               125.8231500 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



7




```
Current Data Parameters
NAME                  Vpchloro
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_              20091013
Time                   19.31
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                CDCl3
NS                        10
DS                         2
SWH                7002.801 Hz
FIDRES             0.106854 Hz
AQ                 4.6793203 sec
RG                       203
DW                  71.400 usec
DE                   6.50 usec
TE                  298.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                   10.76 usec
PL1                   0.00 dB
SFO1           500.3932525 MHz

F2 - Processing parameters
SI                        32768
SF              500.3900160 MHz
WDW                         EM
SSB                          0
LB                    0.30 Hz
GB                           0
PC                        1.00
```



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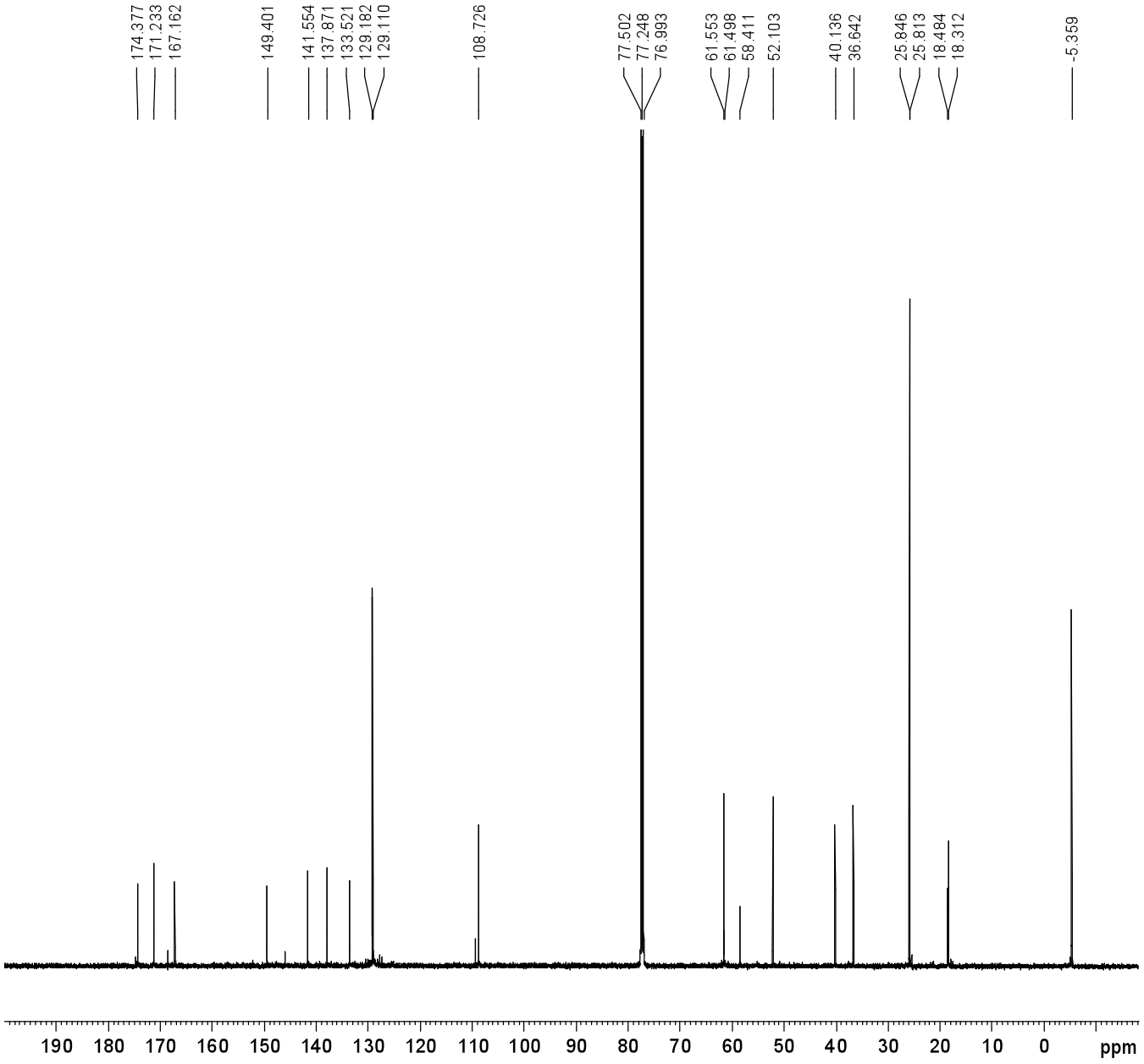
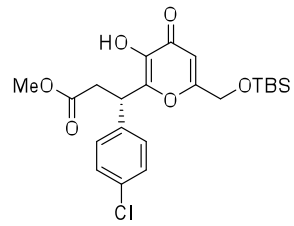
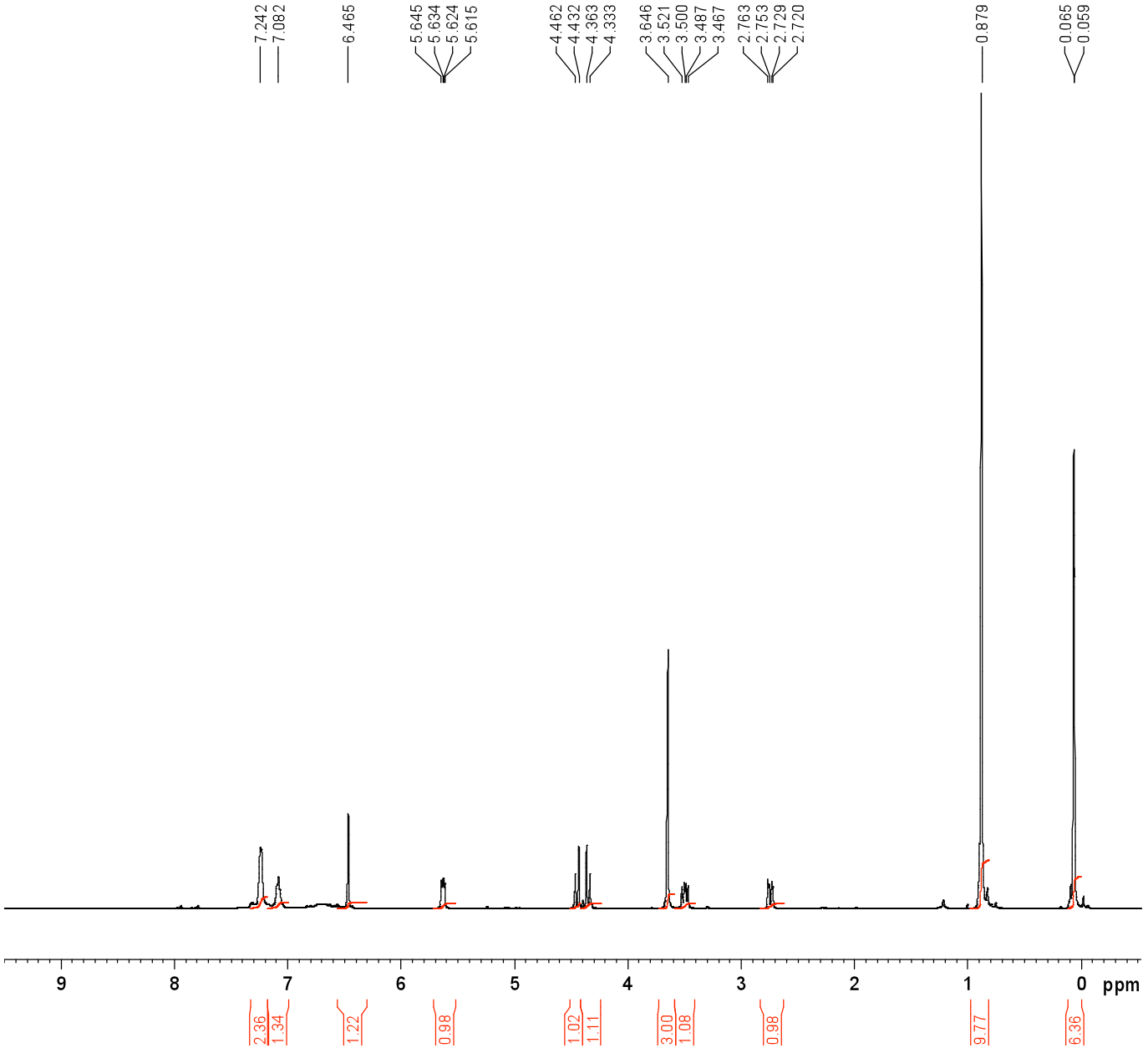


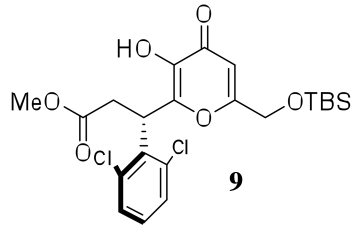

```
Current Data Parameters
NAME      Vp-chloroCarbon
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20090928
Time               12.03
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  502
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  456
DW               16.800 usec
DE                6.50 usec
TE              298.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 7.50 usec
PL1                1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL12              17.43 dB
PL13              18.43 dB
PL2                0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                 32768
SF          125.8231500 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



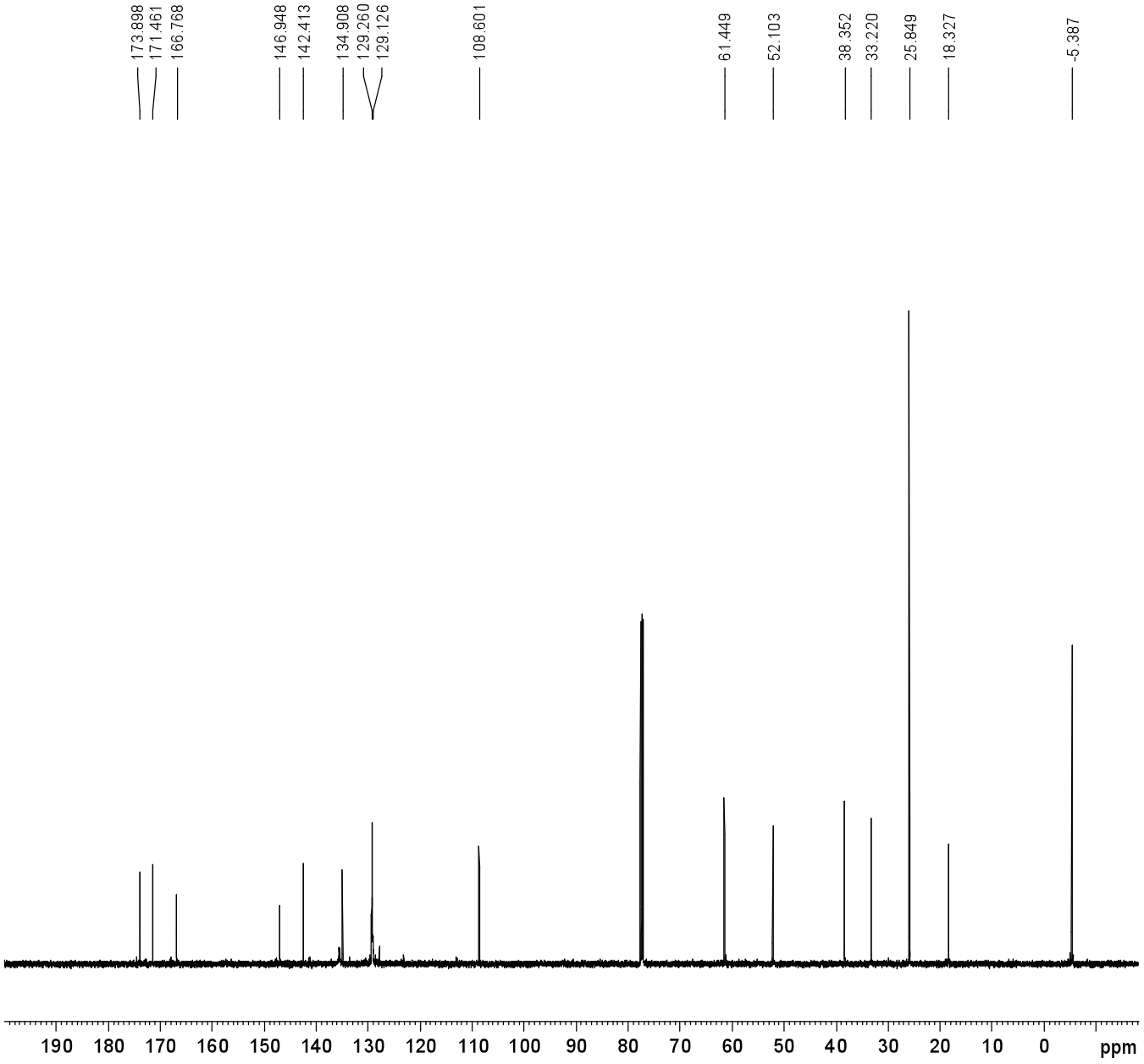
8



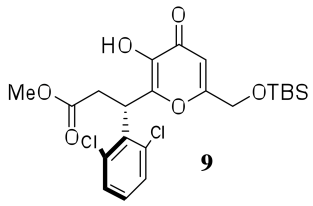

```
Current Data Parameters
NAME          I-JM-90prep
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090926
Time                16.20
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              7002.801 Hz
FIDRES           0.106854 Hz
AQ               4.6793203 sec
RG                     36
DW                 71.400 usec
DE                  6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.76 usec
PL1                 0.00 dB
SFO1         500.3932525 MHz

F2 - Processing parameters
SI                  32768
SF           500.3900160 MHz
WDW                    EM
SSB                     0
LB                  0.30 Hz
GB                      0
PC                   1.00
```



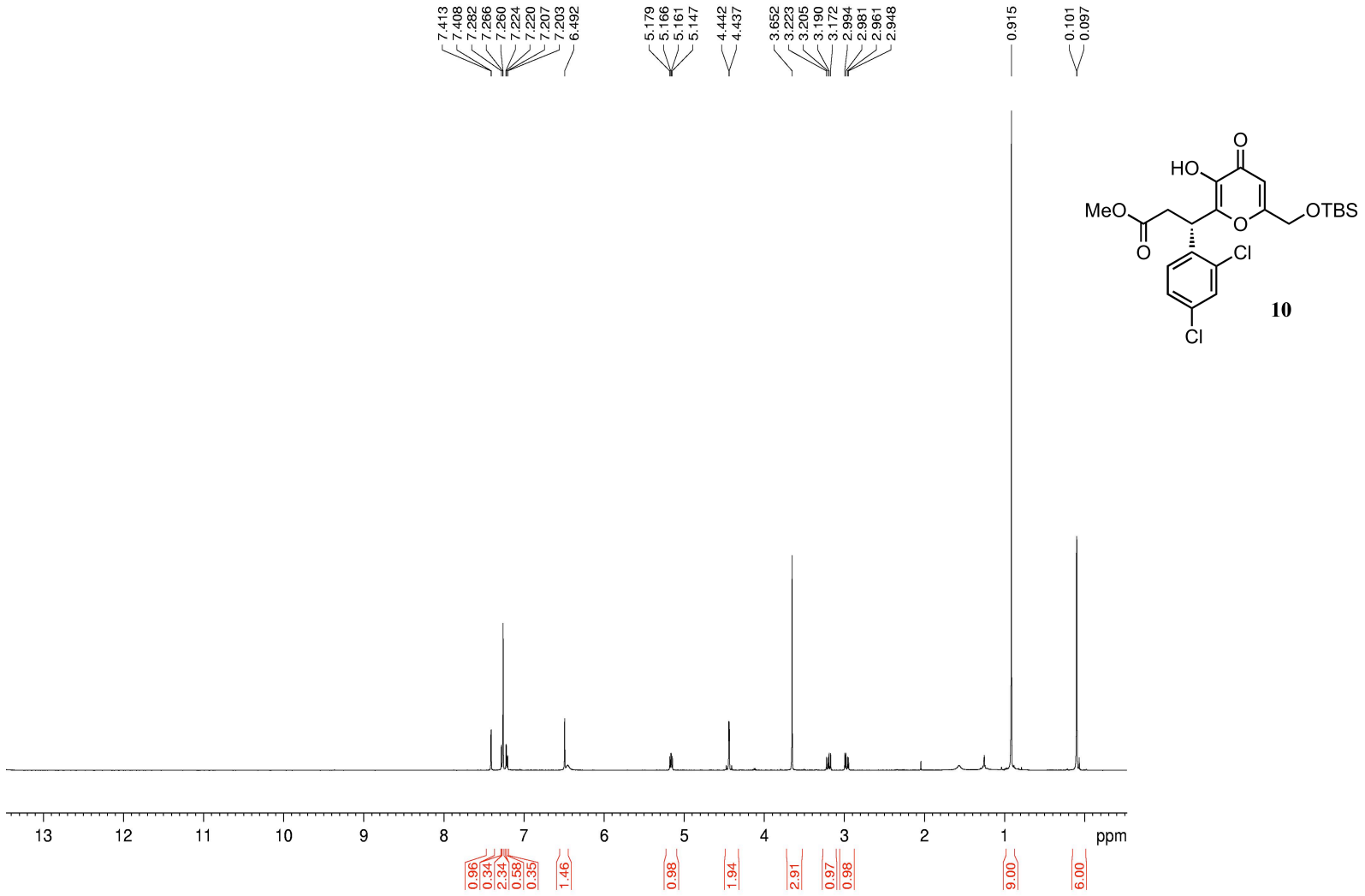
9

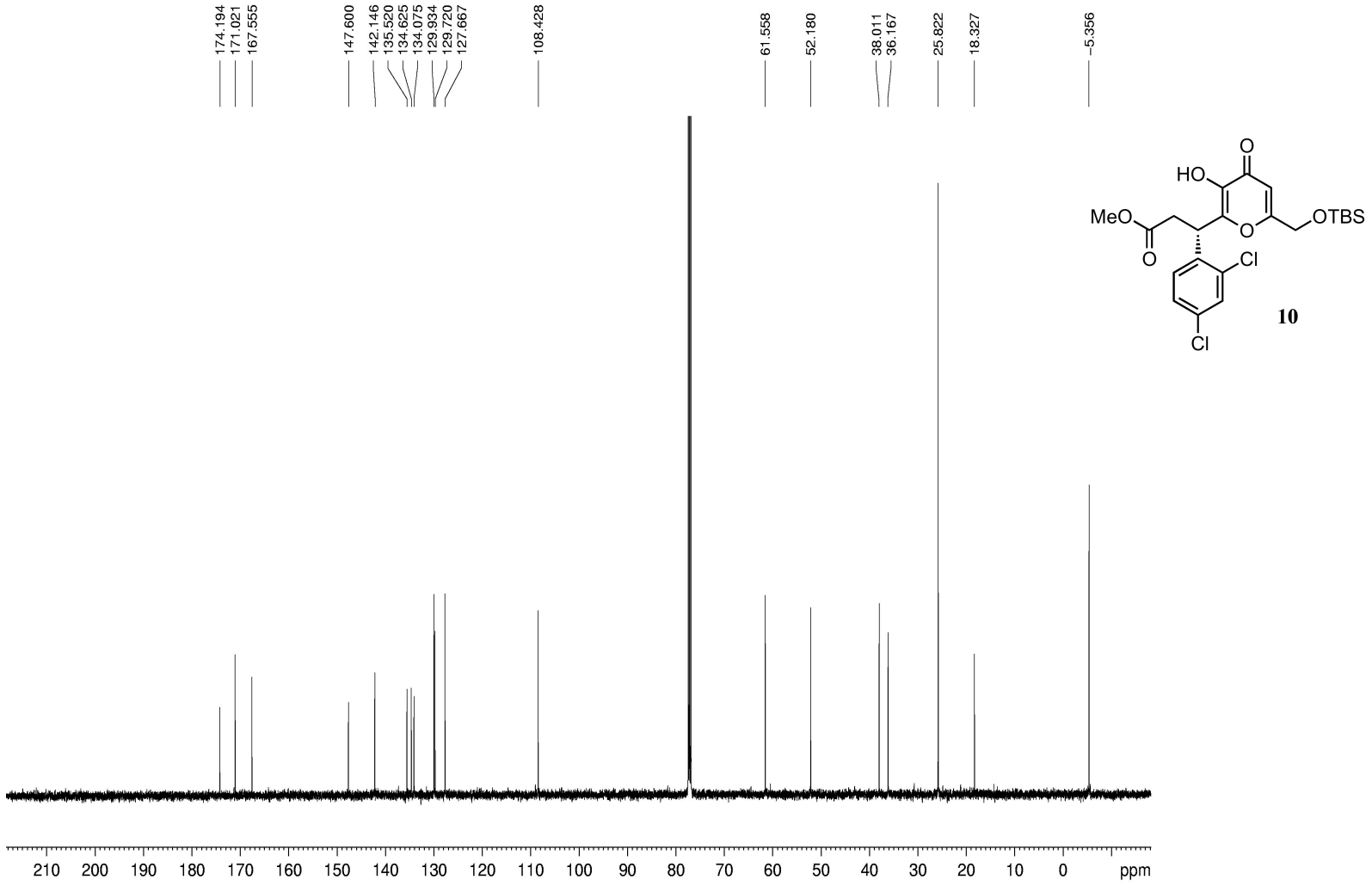


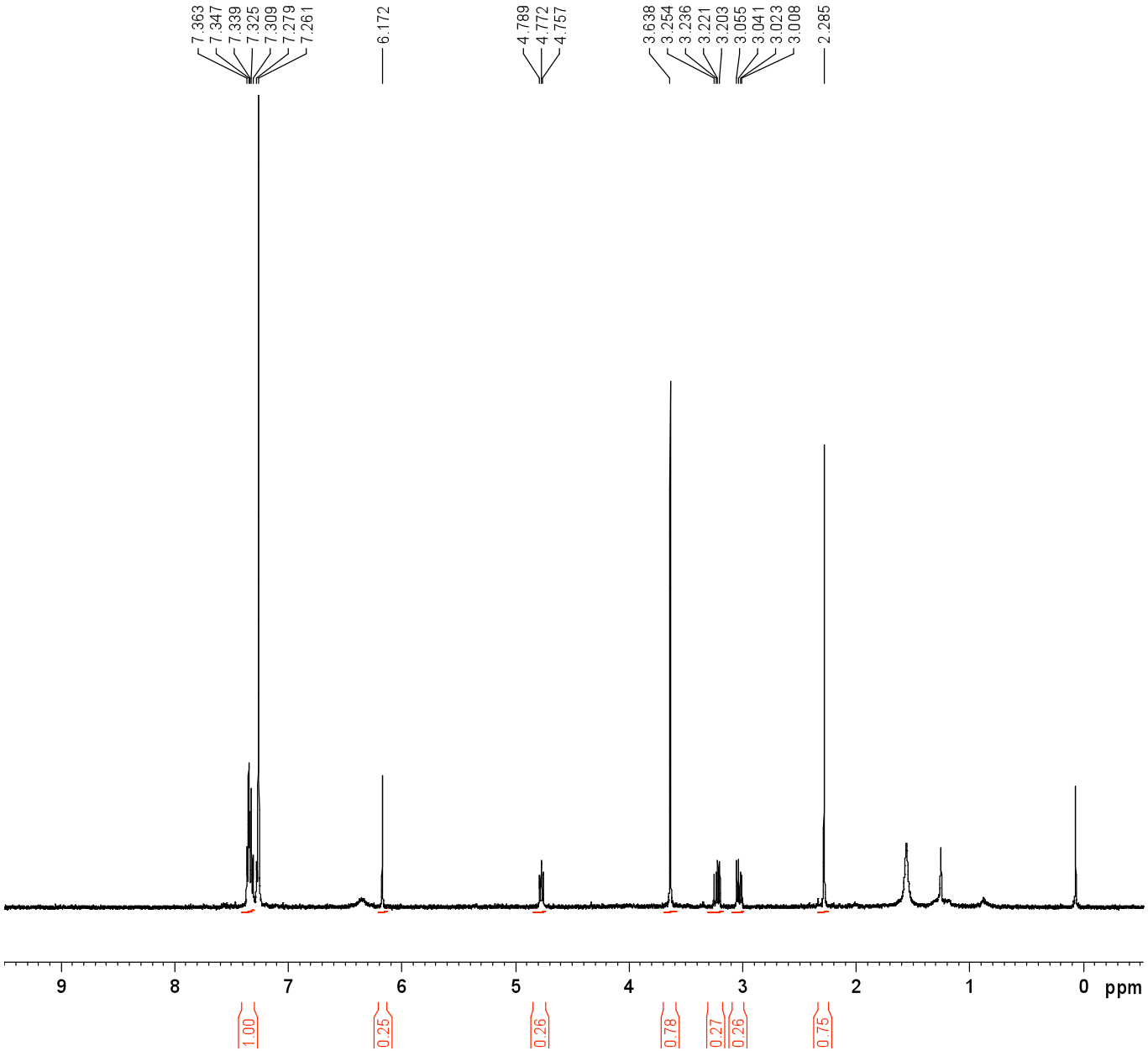

```
Current Data Parameters
NAME          I-JM-90prepC
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_          20090926
Time               16.23
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   67
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 2050
DW               16.800 usec
DE                6.50 usec
TE              298.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.50 usec
PL1                 1.00 dB
SF01         125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL12               17.43 dB
PL13               18.43 dB
PL2                 0.00 dB
SF02         500.3920016 MHz

F2 - Processing parameters
SI                  32768
SF           125.8231500 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



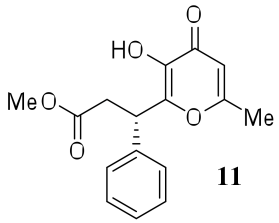
9


7.413
7.408
7.282
7.266
7.260
7.224
7.220
7.207
7.203
6.492
5.179
5.166
5.161
5.147
4.442
4.437
3.652
3.223
3.205
3.190
3.172
2.994
2.981
2.961
2.948
0.915
0.101
0.097
HO
O
MeO
O
O
OTBS
Cl
Cl
10
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
0.34
2.34
0.58
0.35
1.46
0.98
1.94
2.91
0.97
0.98
9.00
6.00

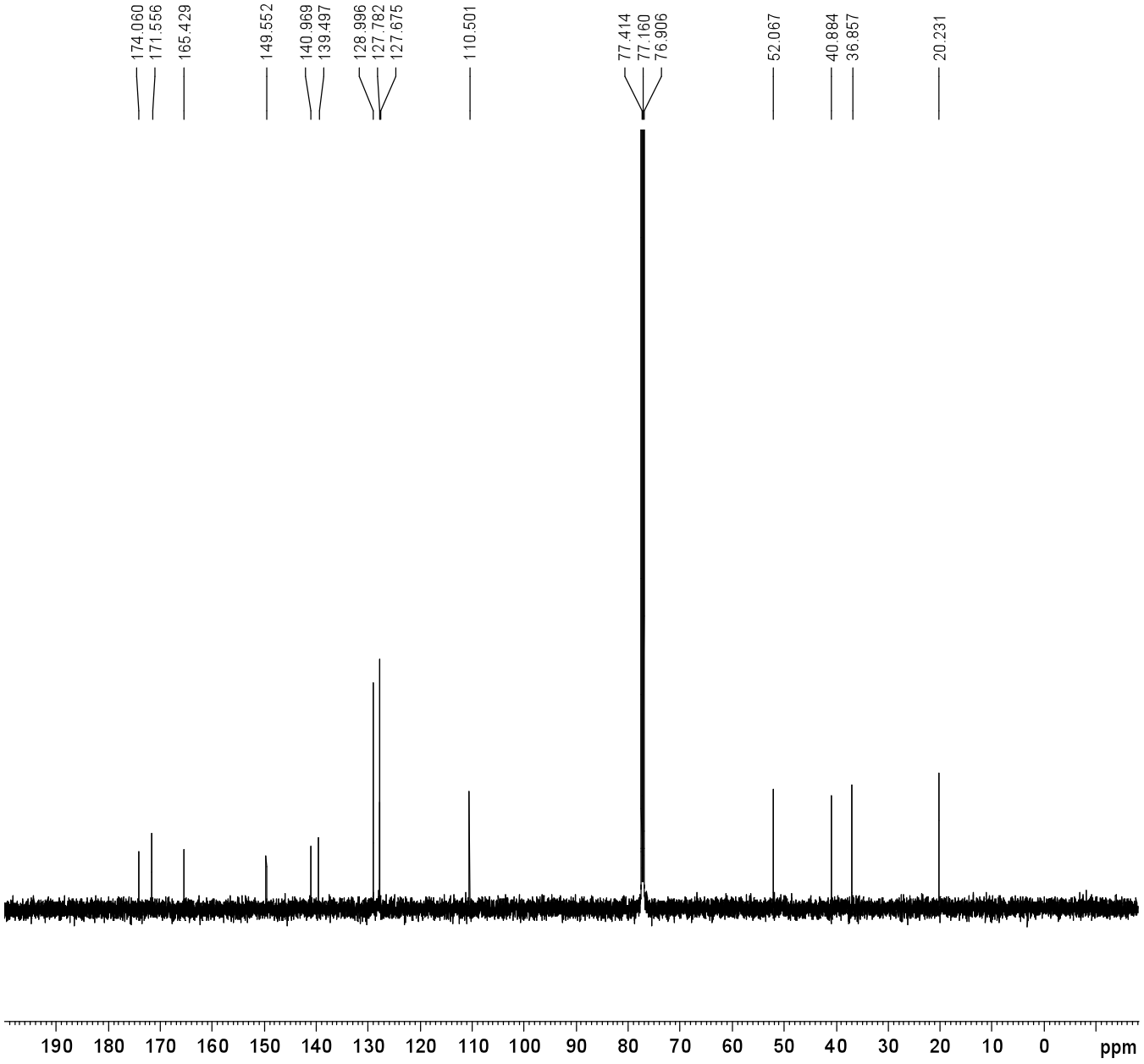

174.194
171.021
167.555
147.600
142.146
135.520
134.625
134.075
129.934
129.720
127.667
108.428
61.558
52.180
38.011
36.167
25.822
18.327
-5.356
HO
O
MeO
O
O
OTBS
Cl
Cl
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



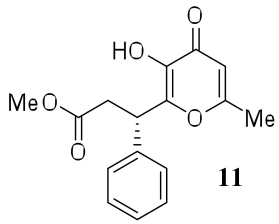

```
Current Data Parameters
NAME                  V106-1
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090917
Time                  10.52
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       10
DS                        2
SWH                7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6793203 sec
RG                     1030
DW                   71.400 usec
DE                    6.50 usec
TE                   298.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    10.76 usec
PL1                    0.00 dB
SF01          500.3932525 MHz

F2 - Processing parameters
SI                     32768
SF            500.3900160 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00
```



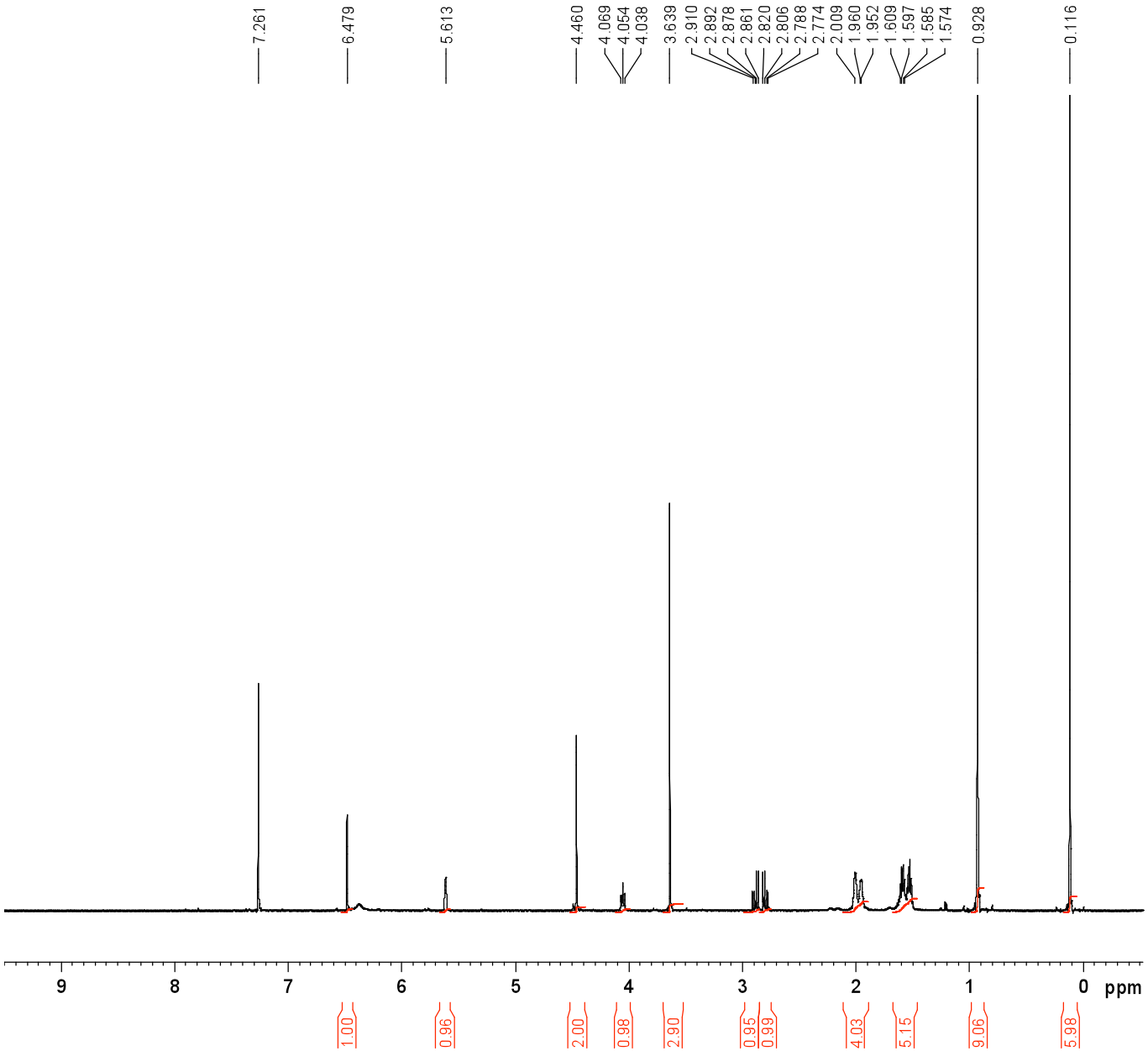
11



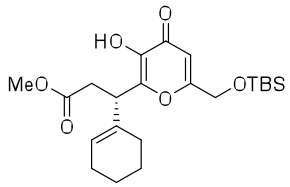

```
Current Data Parameters
NAME            V112carbon
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090917
Time                 19.38
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH              29761.904 Hz
FIDRES           0.454121 Hz
AQ               1.1010548 sec
RG                    1150
DW                  16.800 usec
DE                   6.50 usec
TE                  298.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.50 usec
PL1                   1.00 dB
SF01          125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PL12                17.43 dB
PL13                18.43 dB
PL2                  0.00 dB
SF02          500.3920016 MHz

F2 - Processing parameters
SI                    32768
SF            125.8231500 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```



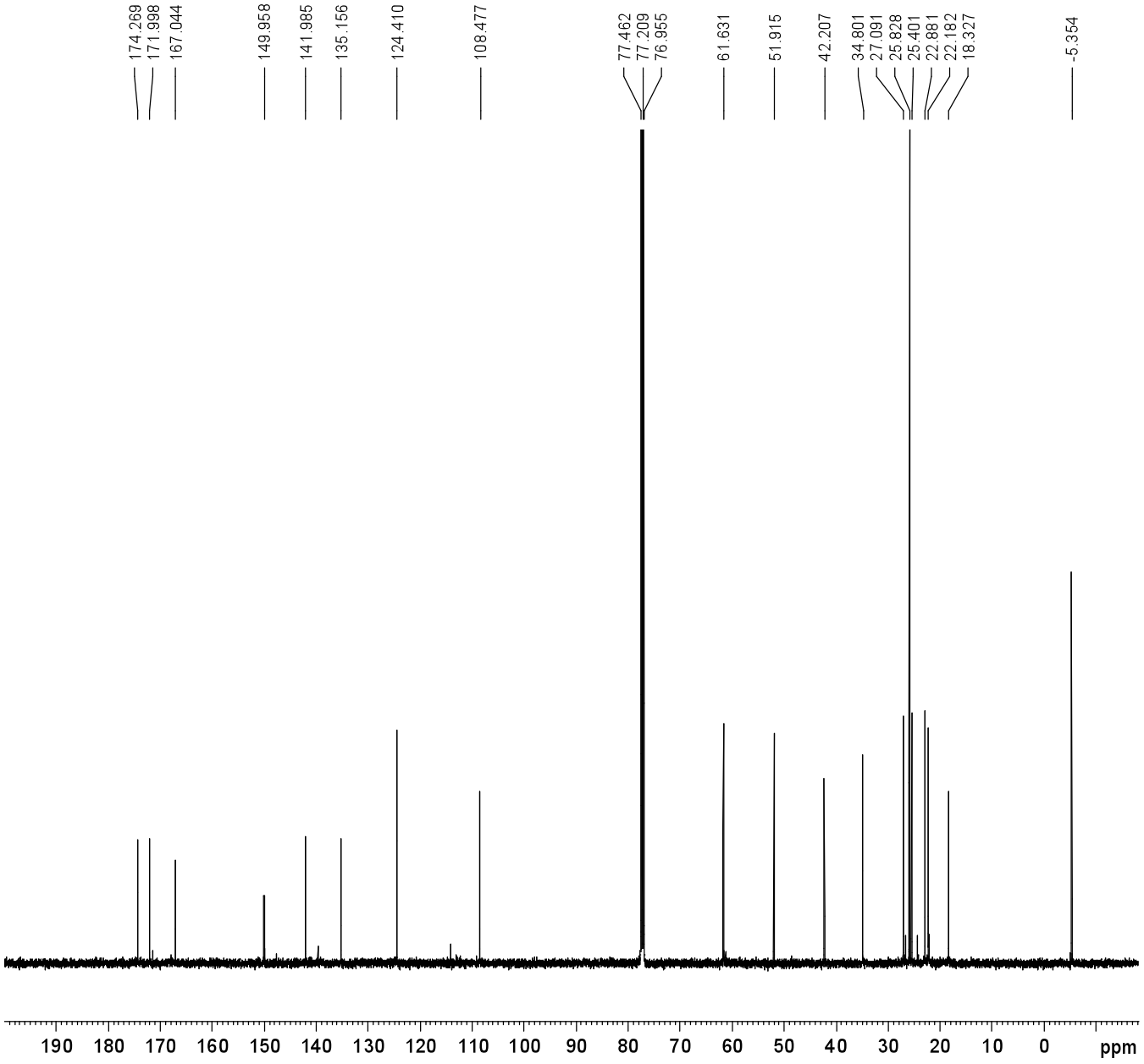
11



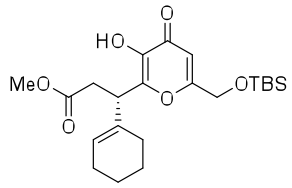

```
Current Data Parameters
NAME                  V113
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20090918
Time                 10.50
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      15
DS                       2
SWH                7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6793203 sec
RG                     406
DW                  71.400 usec
DE                   6.50 usec
TE                  298.3 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.76 usec
PL1                   0.00 dB
SFO1          500.3932525 MHz

F2 - Processing parameters
SI                   32768
SF             500.3900160 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



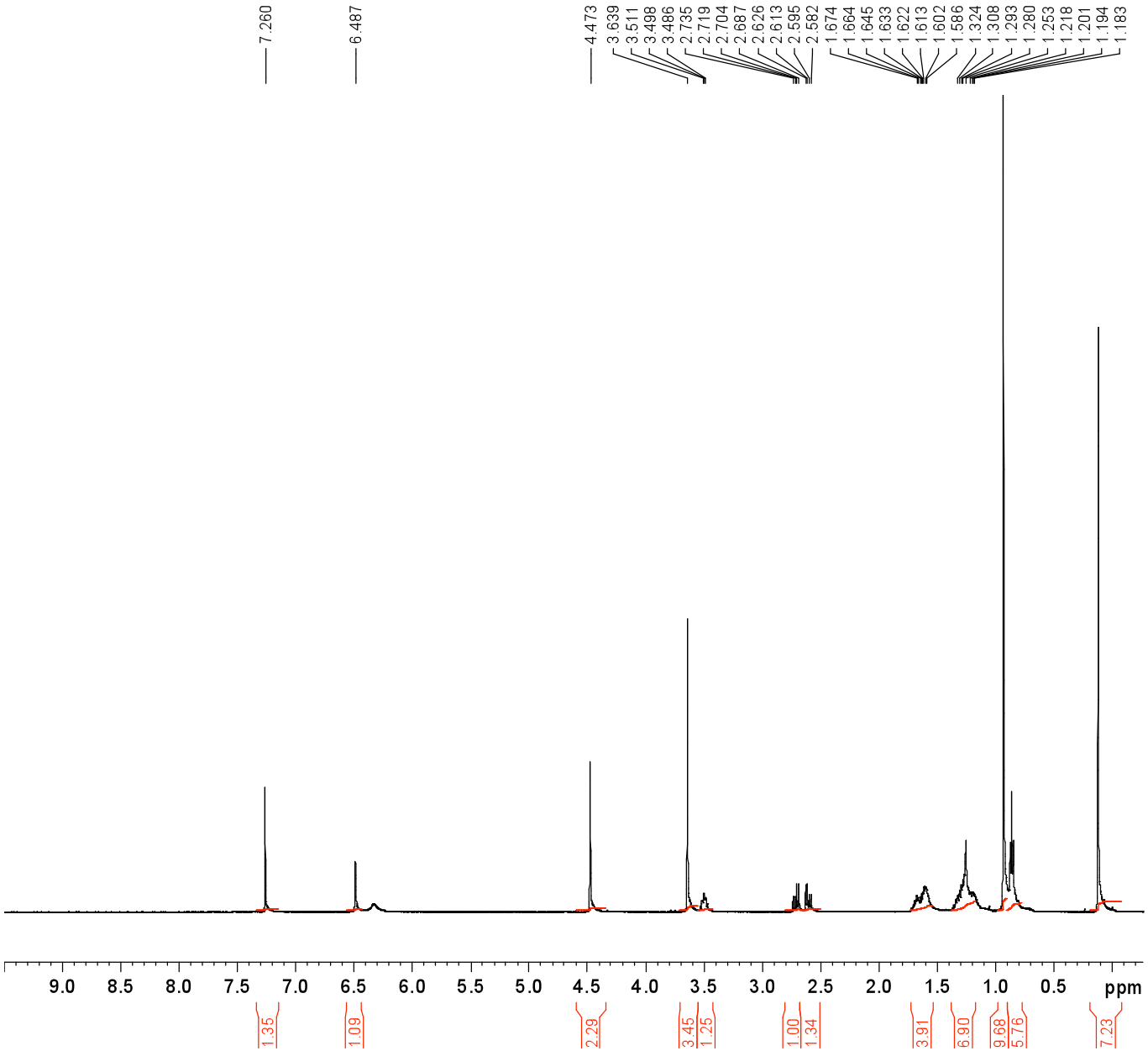
12



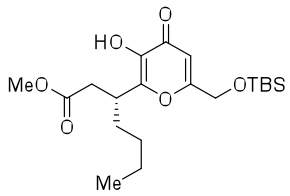

```
Current Data Parameters
NAME          Vl13carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090919
Time              14.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 308
DS                   4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                1290
DW               16.800 usec
DE                6.50 usec
TE              298.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                7.50 usec
PL1               1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL12             17.43 dB
PL13             18.43 dB
PL2               0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                32768
SF          125.8231500 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```



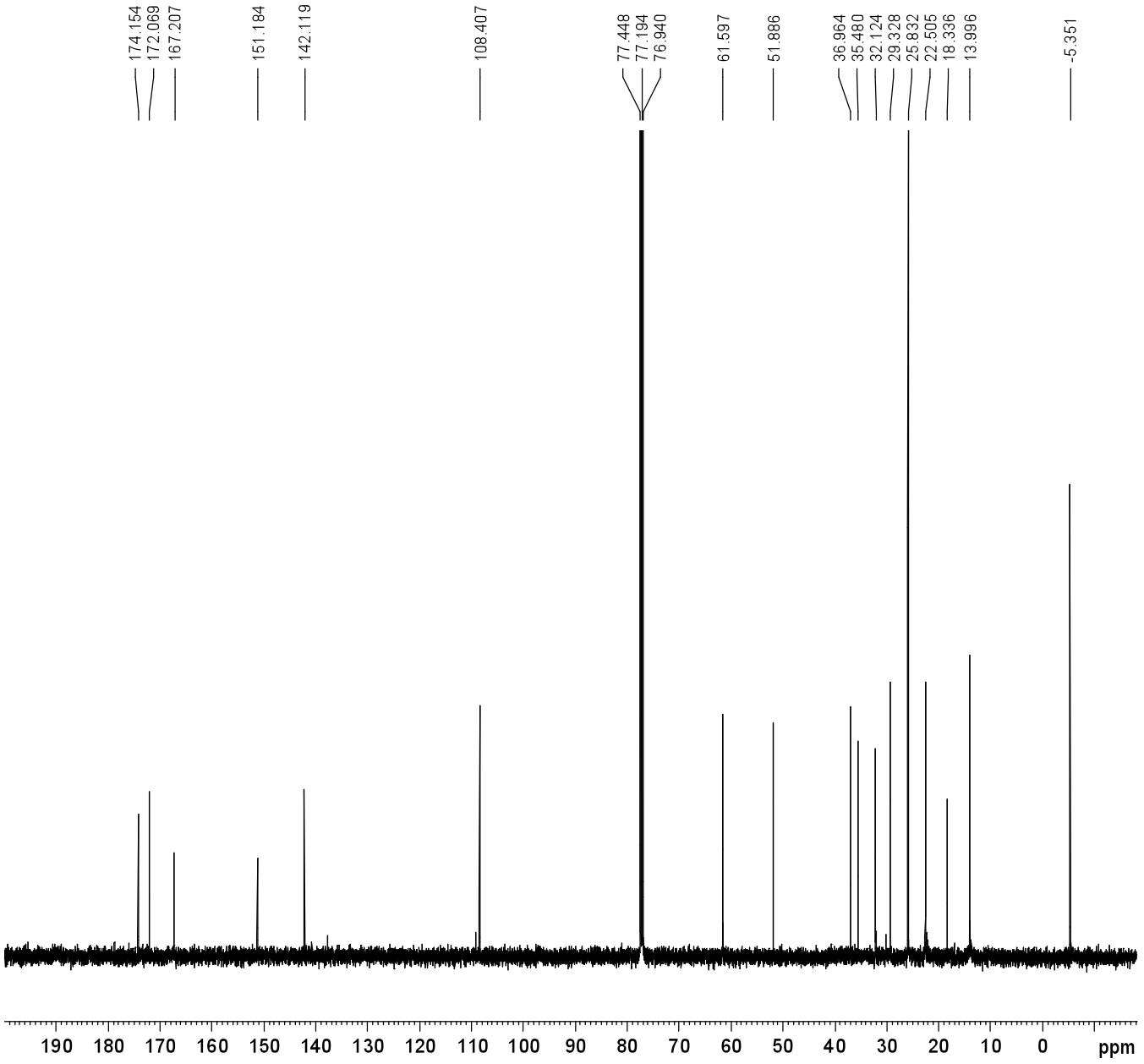
12



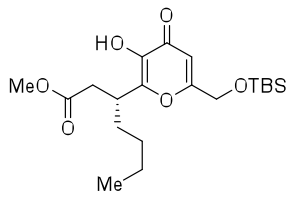

```
Current Data Parameters
NAME         I-JM-79ptlc
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090917
Time              21.14
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            7002.801 Hz
FIDRES        0.106854 Hz
AQ            4.6793203 sec
RG                  322
DW             71.400 usec
DE              6.50 usec
TE             300.0 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1             10.76 usec
PL1             0.00 dB
SF01        500.3932525 MHz

F2 - Processing parameters
SI                32768
SF          500.3900160 MHz
WDW                  EM
SSB                   0
LB             0.30 Hz
GB                    0
PC                 1.00
```



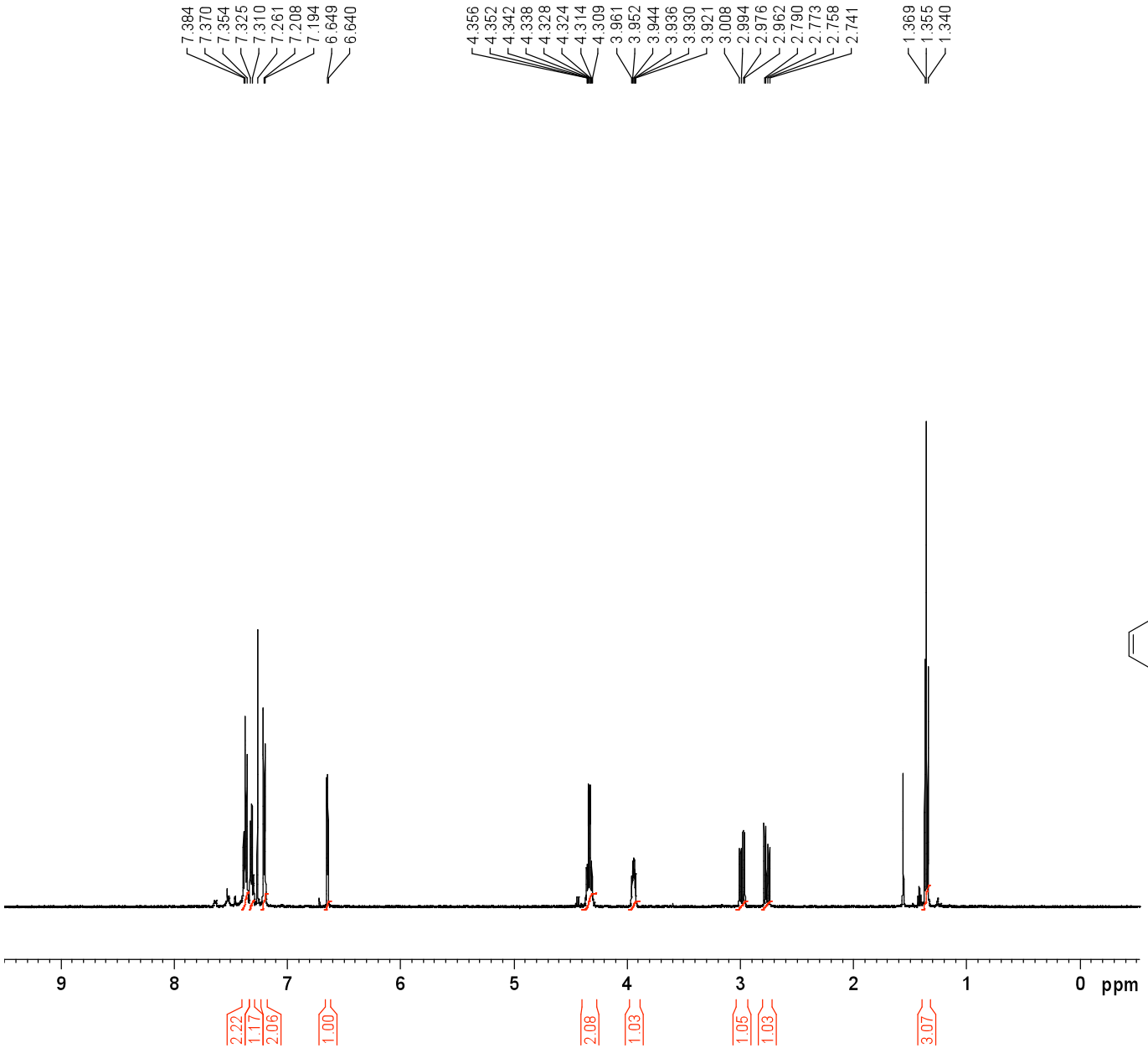
13



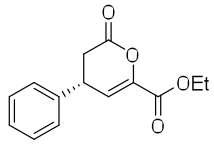

```
Current Data Parameters
NAME      VjessNBuCarbon
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090924
Time              21.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  146
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  456
DW               16.800 usec
DE                6.50 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               1.00 dB
SF01        125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL12             17.43 dB
PL13             18.43 dB
PL2               0.00 dB
SF02        500.3920016 MHz

F2 - Processing parameters
SI                 32768
SF          125.8231500 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```



13




```
Current Data Parameters
NAME                  V120
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20090922
Time                 11.31
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      11
DS                       2
SWH               7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6793203 sec
RG                     456
DW                  71.400 usec
DE                   6.50 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.76 usec
PL1                   0.00 dB
SFO1          500.3932525 MHz

F2 - Processing parameters
SI                   32768
SF            500.3900160 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



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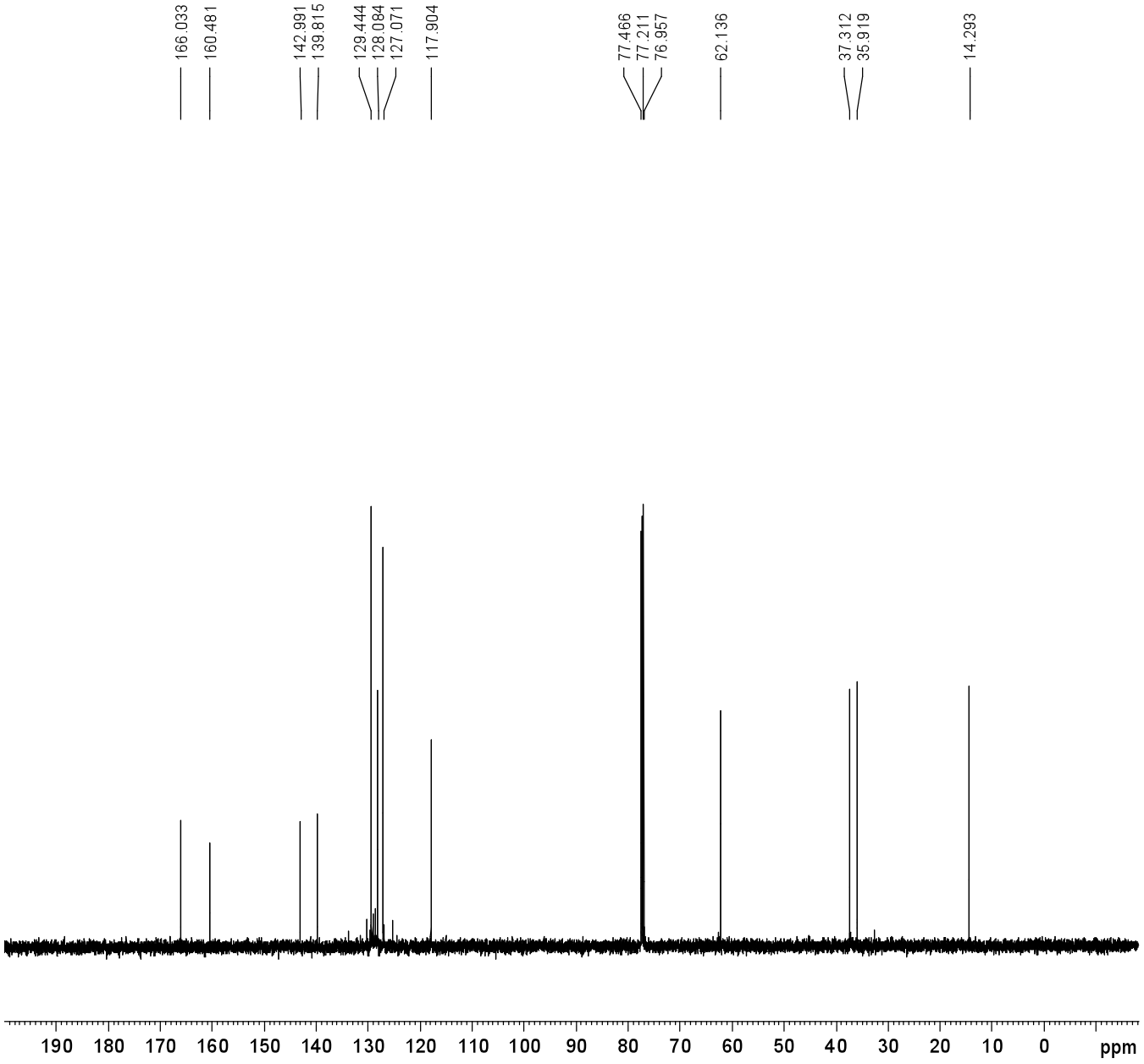


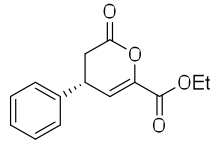

```
Current Data Parameters
NAME              V120carbon
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_           20090922
Time                 10.12
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT              CDCl3
NS                      74
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                     456
DW                16.800 usec
DE                 6.50 usec
TE                298.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.50 usec
PL1                   1.00 dB
SF01          125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL12                 17.43 dB
PL13                 18.43 dB
PL2                   0.00 dB
SF02          500.3920016 MHz

F2 - Processing parameters
SI                     32768
SF            125.8231500 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```



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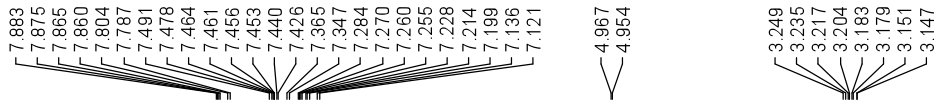
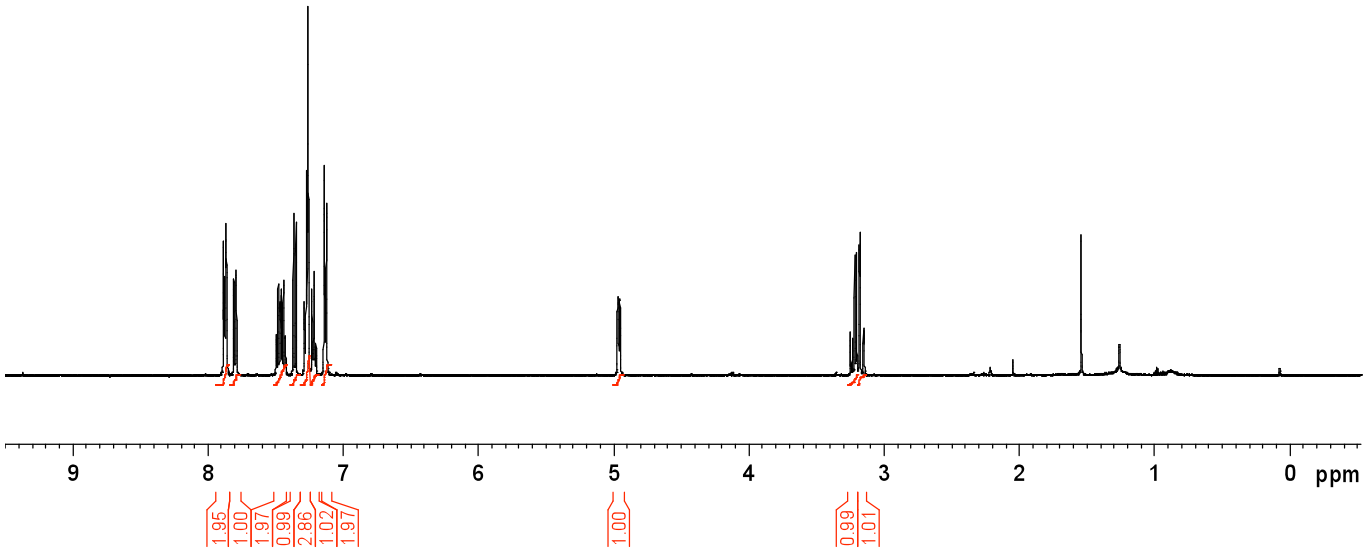


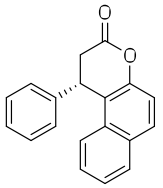

```
Current Data Parameters
NAME                  IV225-3
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20090304
Time                   13.16
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       15
DS                        2
SWH                7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6793203 sec
RG                      724
DW                   71.400 usec
DE                    6.50 usec
TE                   298.4 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    10.76 usec
PL1                    0.00 dB
SFO1           500.3932525 MHz

F2 - Processing parameters
SI                      32768
SF             500.3900160 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```





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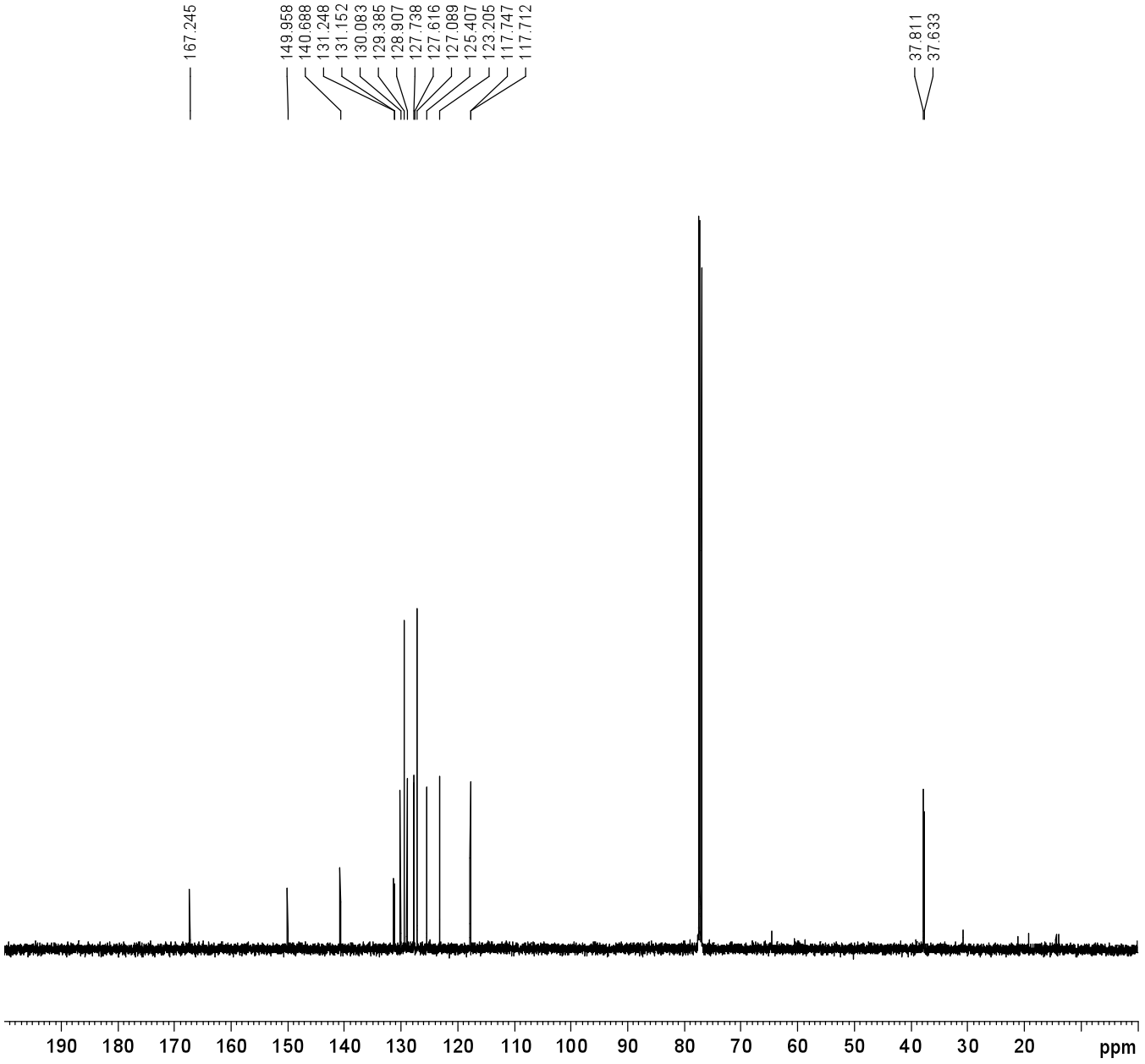


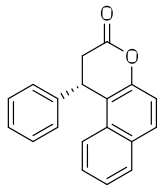

```
Current Data Parameters
NAME          IV189Carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20090206
Time              22.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 201
DS                   4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 456
DW              16.800 usec
DE               6.50 usec
TE              298.4 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               7.50 usec
PL1              1.00 dB
SF01       125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           80.00 usec
PL12            17.43 dB
PL13            18.43 dB
PL2              0.00 dB
SF02       500.3920016 MHz

F2 - Processing parameters
SI                32768
SF         125.8231500 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



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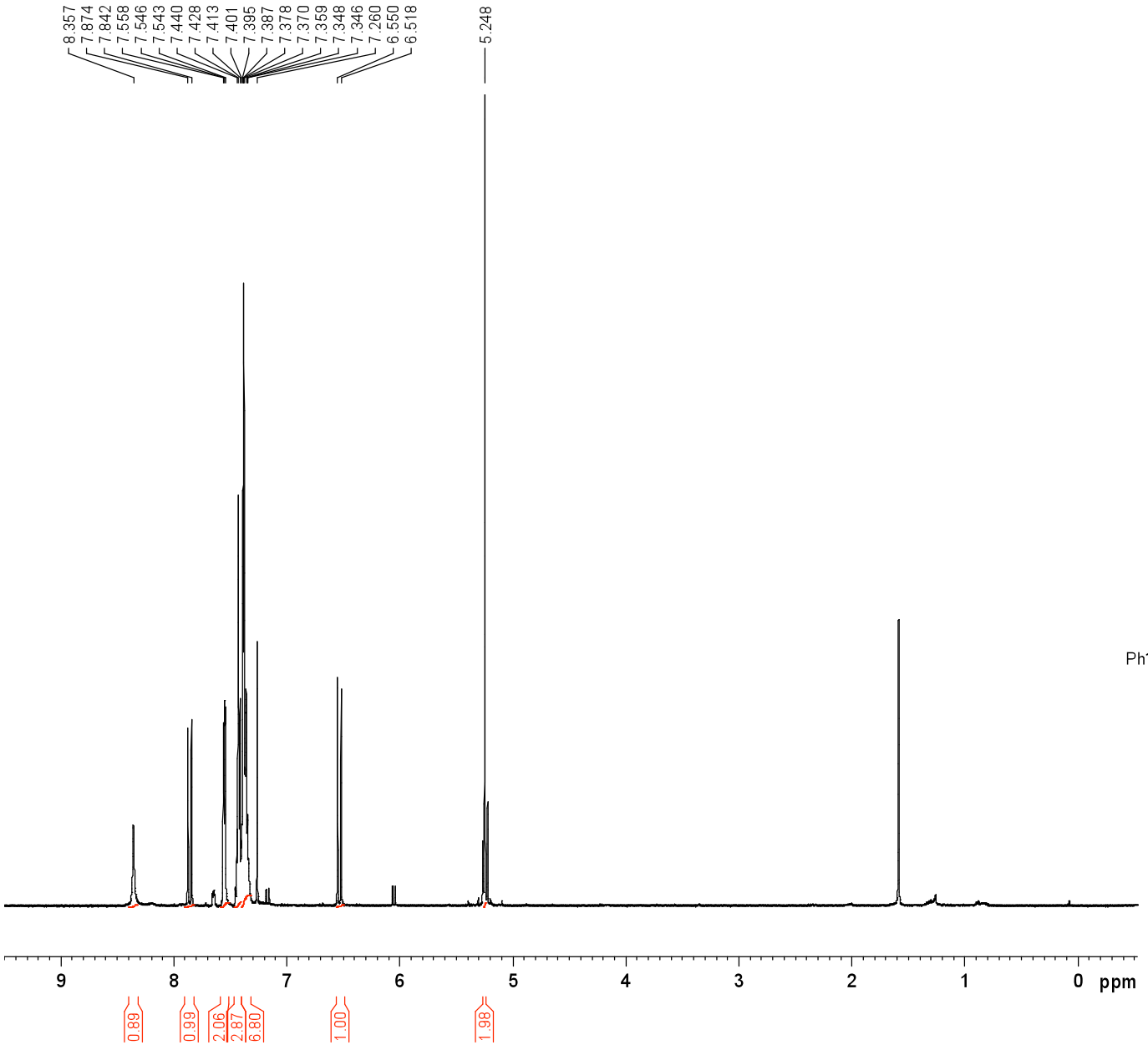
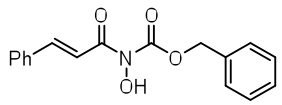



```
Current Data Parameters
NAME                  V119
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_              20091007
Time                 20.06
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      13
DS                       2
SWH               7002.801 Hz
FIDRES            0.106854 Hz
AQ                4.6793203 sec
RG                     362
DW                  71.400 usec
DE                   6.50 usec
TE                  298.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.76 usec
PL1                  0.00 dB
SF01          500.3932525 MHz

F2 - Processing parameters
SI                   32768
SF            500.3900160 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



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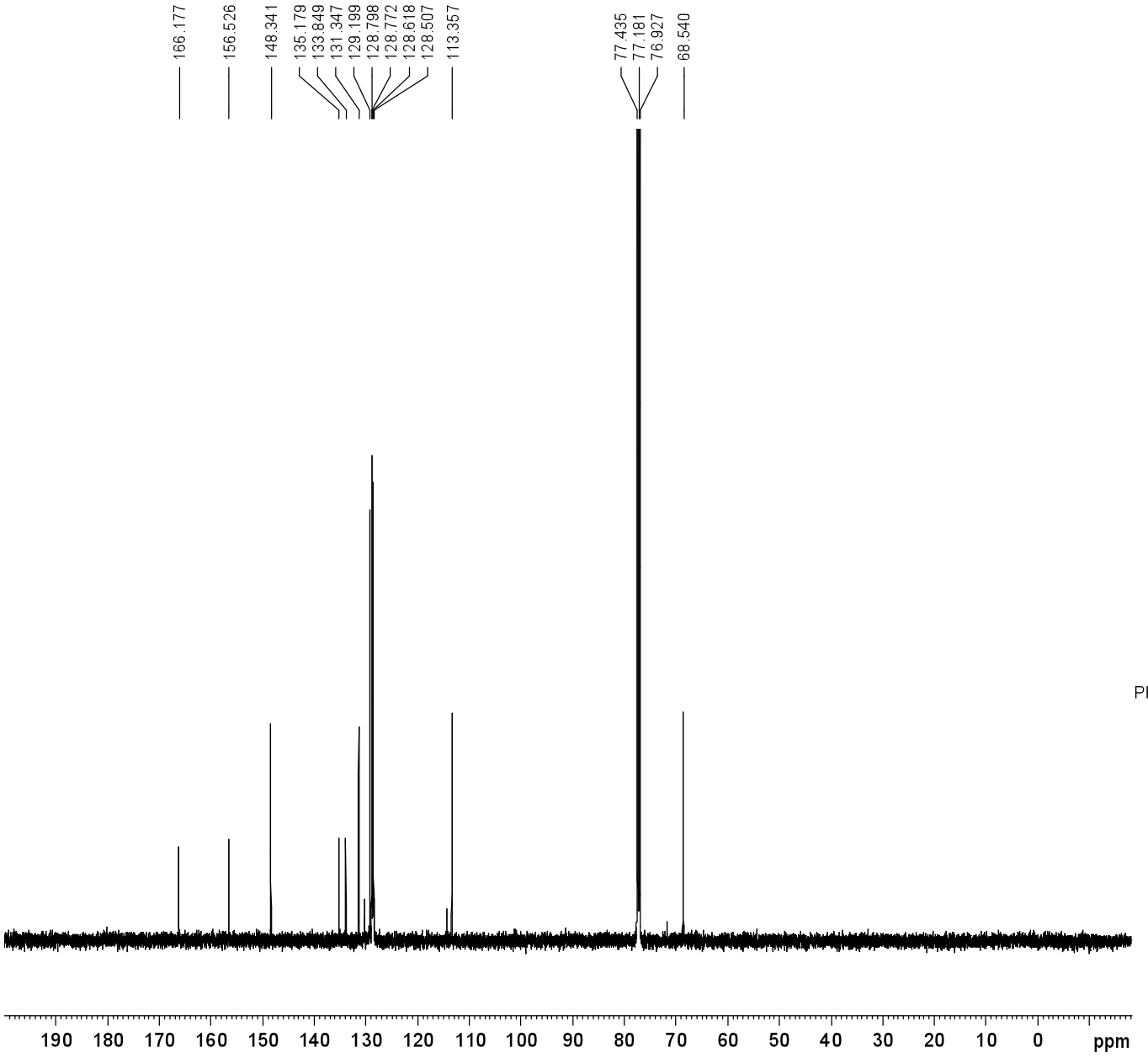


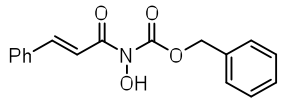

```
Current Data Parameters
NAME          V11Scarbon
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091007
Time              20.31
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 808
DS                   4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 456
DW              16.800 usec
DE               6.50 usec
TE              298.7 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               7.50 usec
PL1              1.00 dB
SF01       125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           80.00 usec
PL12            17.43 dB
PL13            18.43 dB
PL2              0.00 dB
SF02       500.3920016 MHz

F2 - Processing parameters
SI                32768
SF         125.8231500 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



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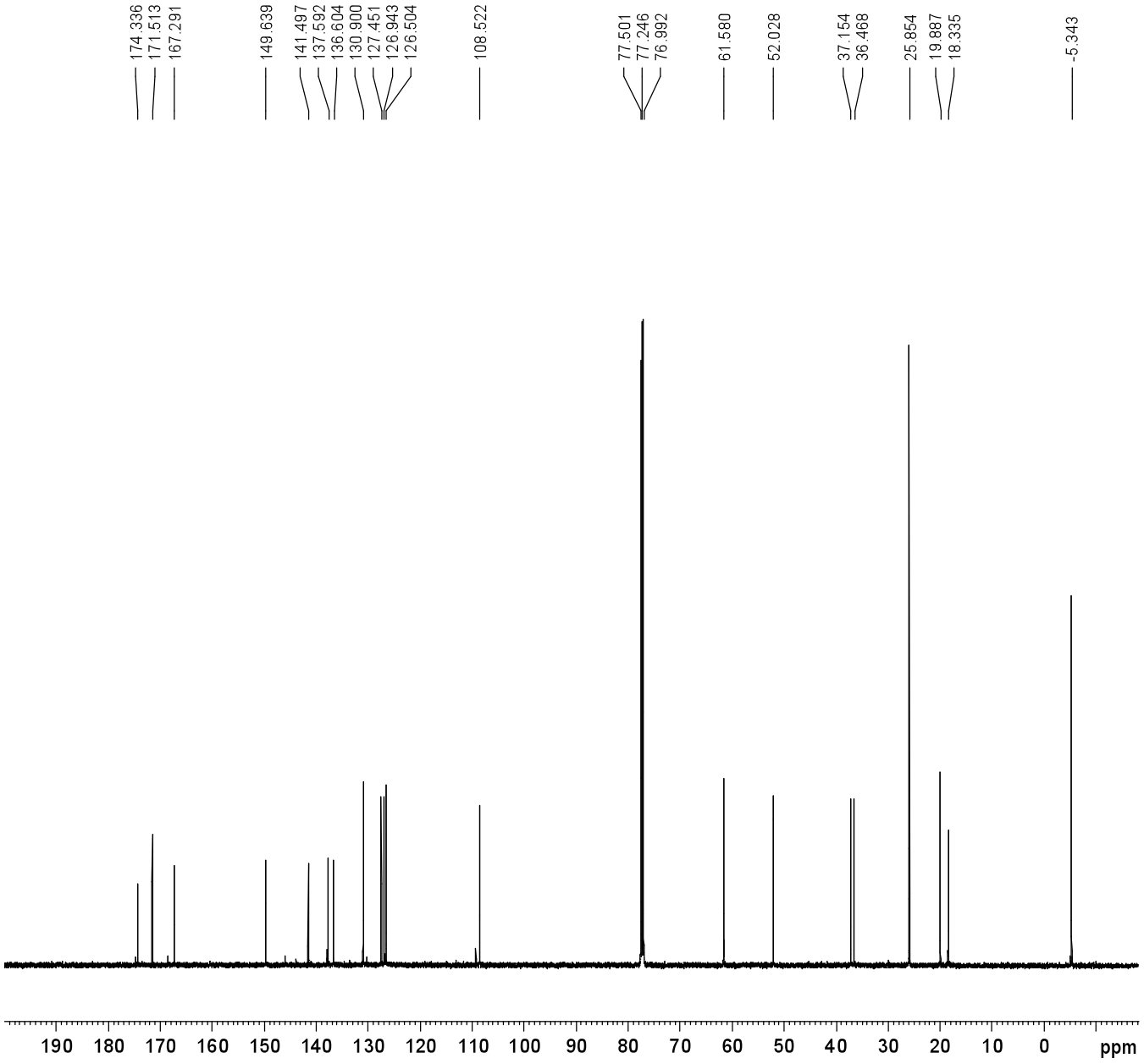


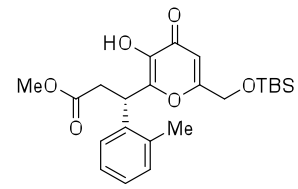

```
Current Data Parameters
NAME                  V95carbon
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20090924
Time                      10.34
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         328
DS                           4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      1290
DW                    16.800 usec
DE                     6.50 usec
TE                    298.5 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         7.50 usec
PL1                        1.00 dB
SF01             125.8357479 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL12                      17.43 dB
PL13                      18.43 dB
PL2                        0.00 dB
SF02             500.3920016 MHz

F2 - Processing parameters
SI                        32768
SF               125.8231500 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



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