

Enantioselective Total Synthesis of (+)-Conicol via Cascade Three-Component Organocatalysis.

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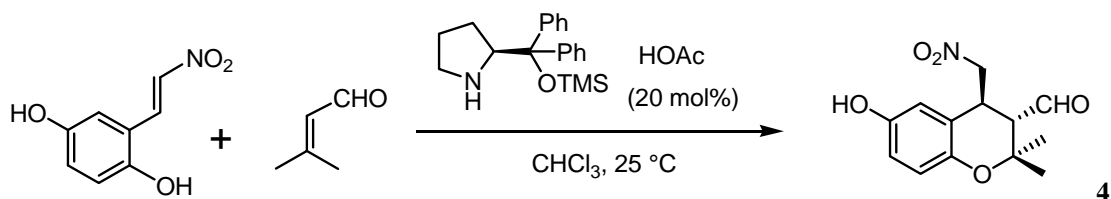
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SUPPORTING INFORMATION:

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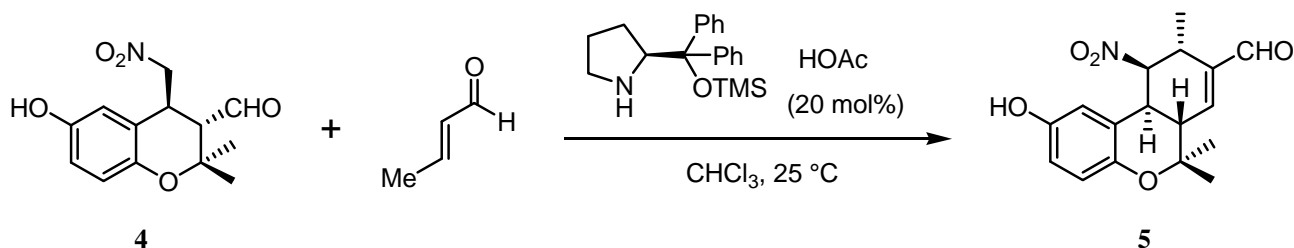
General Procedure. All solvents were reagent grade. L-proline (99+%) was purchased from Bachem. Other chemicals were purchased from Aldrich or Acros Chemical Co. Reactions were normally carried out under argon atmosphere in flame-dried glassware. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography. Melting points are uncorrected. ¹H NMR spectra were obtained in CDCl₃ unless otherwise noted at 400 MHz (Bruker DPX-400) or 500 MHz (Varian-Unity INOVA-500). ¹³C NMR spectra were obtained at 100 MHz or 125 MHz. *E.e.* values were measured by HPLC on a chiral column (chiralpak IA or chiralcel OD-H, 0.46 cm ID x 25 cm, particle size 5 μ) by elution with IPA-hexane or THF-hexane. The flow rate of the indicated elution solvent is maintained at 1 mL/min, and the retention time of a compound is recorded accordingly. HPLC was equipped with the ultraviolet and refractive index detectors. The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. The optical rotation values were recorded with a Jasco-P-2000 digital polarimeter

Preparation of 4.



To a solution of 3-methylbut-2-enal (696 mg, 8.28 mmol), (*S*)-diphenylprolinol-*O*-TMS-ether (358 mg, 1.10 mmol) and acetic acid (60 mg, 1.10 mmol) in CHCl_3 (25 mL) was added 2-((*E*)-2-nitrovinyl)benzene-1,4-diol (1.00 g, 5.52 mmol). The resulting solution was stirred at 25 °C for 1 h, and diluted with EtOAc (50 mL). The solution was washed with brine (20 mL), dried over MgSO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 20% EtOAc-Hexane (R_f = 0.33 for **4** in 30% EtOAc-hexane) to give **4** as yellow solid (1100 mg, 76% yield): mp 96-98 °C. Selected spectroscopic data for **4**: $[\alpha]_D^{26} +31.2$ (c 1 CHCl_3); IR (neat): 3420, 2980, 1718, 1552, 1375, 1150, 927 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 9.87 (s, 1 H), 6.73-6.64 (m, 3H), 4.70-4.59 (m, 2 H), 3.94 (dt, J = 4.9, 10.1 Hz, 1 H), 3.18 (d, J = 10.5 Hz, 1 H), 1.65 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.3 (CH), 149.9 (C), 146.6 (C), 119.7 (C), 119.2 (CH), 116.5 (CH), 113.0 (CH), 77.8 (CH_2), 74.3 (C), 57.5 (CH), 31.3 (CH), 28.4 (CH_3), 21.1 (CH_3); MS (m/z , relative intensity): 265 (M^+ , 100), 218 (46), 203 (28), 175 (95), 147 (42), 136 (47); exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_5$ (M^+): 265.0950; found 265.0949.

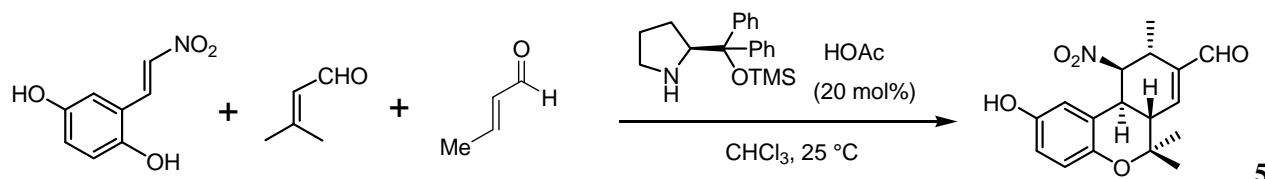
Preparation of 5



To a solution of **4** (59 mg, 0.22 mmol), (*S*)-diphenylprolinol-*O*-TMS-ether (15 mg, 0.046 mmol) and acetic acid (2.8 mg, 0.046 mmol) in CHCl_3 (3.0 mL) was added crotonaldehyde (16 mg, 0.23 mmol). The resulting solution was stirred at ambient temperature for 12 h, and added another crotonaldehyde (16 mg, 0.23 mmol). The resulting mixture was stirred at ambient temperature for 12 h and diluted with EtOAc (10 mL). The solution was washed with brine (2 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 30 % EtOAc-hexane (R_f = 0.35 in 30% EtOAc-hexane) to give **5** (white solid, 52 mg, 74% yield); mp. 75-78 °C. Selected data for **5**: $[\alpha]_D^{22} -107.6$ (c 2.95 CHCl_3); IR (neat): 3381, 2976, 2931, 1682, 1549, 1492, 1455, 1372 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 9.47 (s, 1 H), 6.77

(d, $J = 8.5$ Hz, 1 H), 6.64 (dd, $J = 2.3, 8.4$ Hz, 1 H), 6.53 (br. s., 1 H), 6.23 (br. s., 1 H), 4.92 (dd, $J = 5.7, 12.1$ Hz, 1 H), 3.59 - 3.48 (m, 2 H), 2.33 (d, $J = 10.7$ Hz, 1 H), 1.46 (s, 3 H), 1.34 (s, 3 H), 1.07 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 191.5 (CH), 150.2 (C), 147.2 (C), 145.3 (CH), 143.4 (C), 129.5 (C), 119.0 (CH), 114.9 (CH), 109.3 (CH), 85.3 (CH), 78.9 (C), 50.8 (CH), 31.5 (CH), 30.8 (CH), 28.2 (CH_3), 24.1 (CH_3), 15.6 (CH_3); MS (m/z , relative intensity): 317 (M^+ , 53), 270 (18), 255 (100), 241 (48), 227 (14), 105 (12), 91 (11); exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_5$ (M^+): 317.1263; found 317.1265.

One-pot procedure for the preparation of **5**.



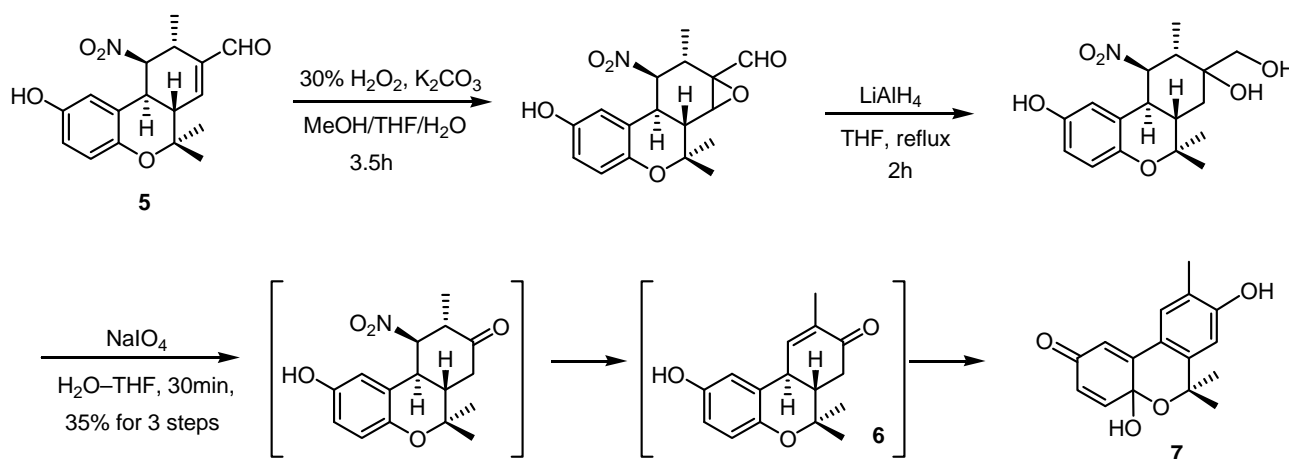
(Method A)

To a solution of 2-((*E*)-2-nitrovinyl)benzene-1,4-diol (41.7 mg, 0.23 mmol) (*S*)-diphenyl-prolinol-*O*-TMS-ether (15 mg, 0.046 mmol) and acetic acid (2.8 mg, 0.046 mmol) in CHCl_3 (2.5 mL) was added 3-methylbut-2-enal (19.3 mg, 0.23 mmol). The resulting solution was stirred at 25 °C for 1.2 h, followed by the addition of crotonaldehyde (16.1 mg, 0.23 mmol) and stirred for additional 12 h at ambient temperature. To this solution was added crotonaldehyde (16.1 mg, 0.23 mmol), the mixture was stirred at ambient temperature for additional 12 h. The solution was diluted with EtOAc (10 mL), washed with brine (2 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 30 % EtOAc-hexane ($R_f = 0.35$ in 30% EtOAc-hexane) to give **5** (white solid, 48 mg, 66% yield).

(Method B)

To a solution of 2-((*E*)-2-nitrovinyl)benzene-1,4-diol (41.7 mg, 0.23 mmol) (*S*)-diphenyl-prolinol-*O*-TMS-ether (15 mg, 0.046 mmol) and acetic acid (2.8 mg, 0.046 mmol) in CHCl_3 (2.5 mL) was added 3-methylbut-2-enal (19.3 mg, 0.23 mmol). The resulting solution was stirred at 25 °C for 5 min, followed by the addition of crotonaldehyde (16.1 mg, 0.23 mmol) and stirred for additional 12 h at ambient temperature. To this solution was added crotonaldehyde (16.1 mg, 0.23 mmol), the mixture was stirred at ambient temperature for additional 12 h. The solution was diluted with EtOAc (10 mL), washed with brine (2 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 30 % EtOAc-hexane ($R_f = 0.35$ in 30% EtOAc-hexane) to give **5** (white solid, 23 mg, 32% yield).

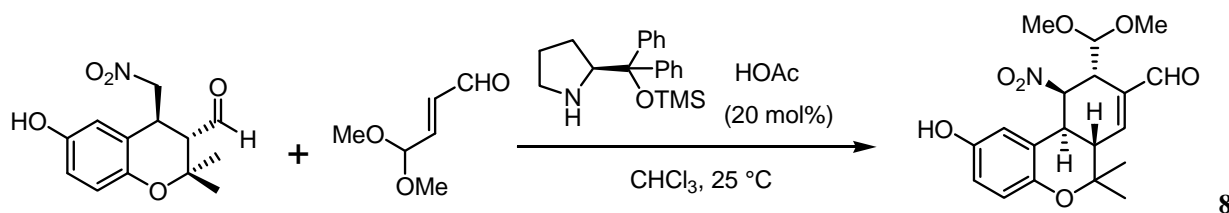
Preparation of 7



To a solution of **5** (50.0 mg, 0.158 mmol), K_2CO_3 (44 mg, 0.32 mmol) and H_2O (0.2 mL) in $\text{MeOH}-\text{THF}$ (1:1, 1 mL) was added dropwise at 0 °C a solution of 30–35% H_2O_2 (0.03 mL, 0.31 mmol). The resulting mixture was stirred at ambient temperature for 3.5 h and diluted with EtOAc (10 mL). The solution was washed with brine (2 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. The residue was directly used for the next-step reaction without further purification.

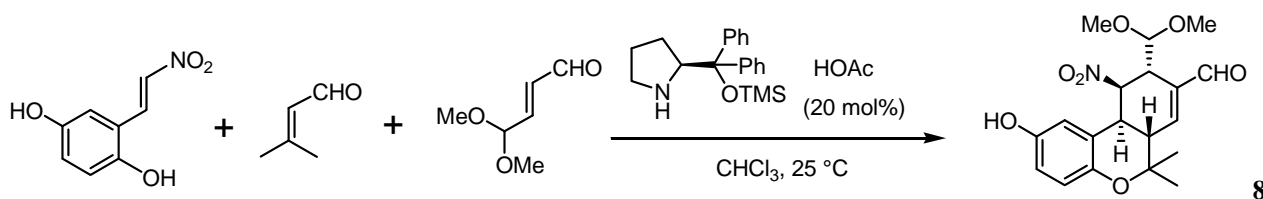
To a solution of crude epoxide product in dry THF (4 mL) was added LiAlH_4 (24 mg, 0.63 mmol). The solution was heated to reflux under nitrogen for 2 h, and the reaction was quenched by the addition of EtOAc (20 mL) and aqueous solution of NH_4Cl . The solution was washed with brine (5 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. A solution of the crude diol product in THF (0.3 mL) was added to a stirred solution of NaIO_4 (34 mg, 0.16 mmol), H_2O (2 mL) and THF (0.5 mL) at room temperature. The resulting mixture was stirred at ambient temperature for 0.5 h and diluted with EtOAc (20 mL). The solution was washed with brine (2 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 40 % EtOAc -hexane ($R_f = 0.31$ in 50% EtOAc -hexane) to give **7** (yellow solid, 14 mg, 35% overall yield from **5**): mp. 135–137 °C. Selected data for **7**: IR (neat): 3381, 2976, 2931, 1682, 1549, 1492, 1455, 1372, 1281 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 7.36 (s, 1 H), 6.80 (d, $J = 10.0$ Hz, 1 H), 6.67 (s, 1 H), 6.32 (d, $J = 1.2$ Hz, 1 H), 6.18 (dd, $J = 1.5, 10.0$ Hz, 1 H), 2.26 (s, 3 H), 1.76 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 186.4 (C), 157.1 (C), 149.2 (C), 144.4 (CH), 143.2 (C), 128.2 (CH), 127.3 (CH), 124.2 (C), 119.2 (C), 116.6 (CH), 111.3 (CH), 87.7 (C), 76.1 (C), 33.8 (CH_3), 31.7 (CH_3), 15.6 (CH_3); MS (m/z , relative intensity): 272 (M^+ , 62), 257 (58), 241 (100), 215 (60), 175 (51), 147 (29), 115 (16); exact mass calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$ (M^+): 272.1049; found 272.1050.

Representative procedure for the preparation of 8.



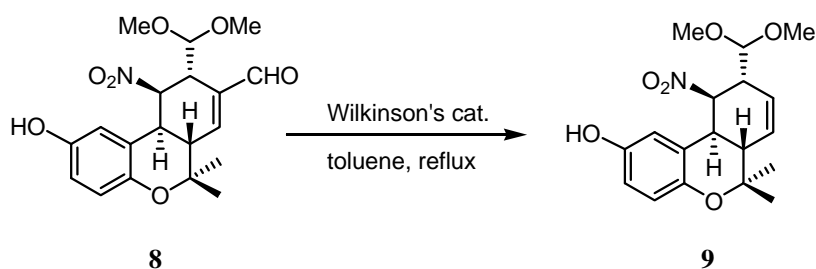
To a solution of (E)-4,4-dimethoxybut-2-enal (982 mg, 7.54 mmol), (S)-diphenyl-prolinol-O-TMS-ether (245 mg, 0.75 mmol) and acetic acid (45 mg, 0.75 mmol) in CHCl₃ (25 mL) was added compound **4** (1000 mg, 3.77 mmol). The resulting solution was stirred at 25 °C for 35 h, and diluted with EtOAc (50 mL). The solution was washed with brine (20 mL), dried over MgSO₄, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 25% EtOAc-Hexane (*R_f* = 0.22 for **3** in 30% EtOAc-hexane) to give **3** as yellow solid (990 mg, 69% yield): mp 56-59 °C. Selected spectroscopic data for **3**: [α]_D²⁵ -159.3 (c 1.4 CHCl₃); IR (neat): 3413, 2974, 2838, 1687, 1647, 1553, 1371, 755 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 9.52 (s, 1 H), 6.77 (d, *J* = 8.5 Hz, 1 H), 6.68 (br. s., 1 H), 6.63 (d, *J* = 8.1 Hz, 1 H), 6.24 (br. s., 1 H), 4.91 (dd, *J* = 6.0, 11.6 Hz, 1 H), 4.26 (d, *J* = 2.9 Hz, 1 H), 4.01 (t, *J* = 11.1 Hz, 1 H), 3.86 (br. s., 1 H), 3.39 (s, 3 H), 3.35 (s, 3 H), 2.25 (d, *J* = 10.7 Hz, 1 H), 1.46 (s, 3 H), 1.36 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 190.8 (CH), 150.1 (C), 147.1 (C), 146.4 (CH), 137.6 (C), 130.0 (C), 118.9 (CH), 114.6 (CH), 109.3 (CH), 104.6 (CH), 83.5 (CH), 79.0 (C), 56.4 (CH₃), 56.2 (CH₃), 50.7 (CH), 38.0 (CH), 33.5 (CH), 28.4 (CH₃), 23.8 (CH₃); MS (*m/z*, relative intensity): 377 (M⁺, 6), 265 (6), 227 (4), 175 (5), 147 (4), 75 (100); exact mass calcd for C₁₉H₂₃NO₇ (M⁺): 377.1475; found 377.1475.

One-pot procedure for the preparation of **8**.



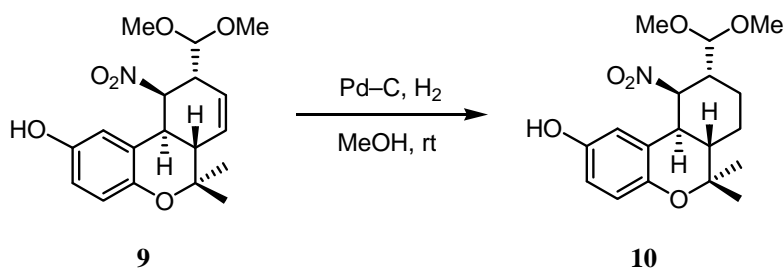
To a solution of 3-methylbut-2-enal (24 mg, 0.29 mmol), (S)-diphenyl-prolinol-O-TMS-ether (13 mg, 0.03 mmol) and acetic acid (2 mg, 0.03 mmol) in CHCl₃ (4 mL) was added 2-((E)-2-nitrovinyl)benzene-1,4-diol (35 mg, 0.19 mmol). The resulting solution was stirred at 25 °C for 1 h, followed by the addition of (E)-4,4-dimethoxybut-2-enal (50 mg, 0.39 mmol) and stirred for additional 35h at ambient temperature. The solution was diluted with EtOAc (15 mL), washed with brine (5 mL), dried over MgSO₄ and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 25% EtOAc-Hexane (*R_f* = 0.22 for **8** in 30% EtOAc-hexane) to give **8** as yellow solid (40 mg, 55% overall yield).

Preparation of **9**



To a solution of **8** (600 mg, 1.59 mmol) in toluene (15 mL) was added Wilkinson's catalyst (1.42 g, 1.59 mmol). The resulting solution was heated to reflux for 4 h, followed by the dilution with EtOAc (30 mL). The solution was filtered through celite, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 20% EtOAc-hexane ($R_f = 0.40$ for **9** in 30% EtOAc-hexane) to give **9** as a pale yellow solid (300 mg, 54% yield): mp 206-209 °C. Selected spectroscopic data for **9**: $[\alpha]_D^{25} -92.4$ (c 0.5 CHCl₃); IR (neat): 3395, 2977, 2838, 1591, 1372, 1219, 1067, 756 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 6.70-6.62 (m, 3 H), 6.03-5.87 (m, 2 H), 5.21 (t, $J = 7.3$ Hz, 1 H), 4.62 (br. s., 1 H), 4.28 (d, $J = 6.6$ Hz, 1 H), 3.38 (d, $J = 3.2$ Hz, 6 H), 3.23-3.18 (m, 1 H), 2.90 (br. s., 1 H), 2.11 (d, $J = 11.5$ Hz, 1 H), 1.43 (s, 3 H), 1.22 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 149.4 (C), 146.9 (C), 129.3 (CH), 126.0 (CH), 125.3 (C), 118.5 (CH), 115.4 (CH), 111.8 (CH), 104.1 (CH), 87.9 (CH), 77.4 (C), 56.0 (CH₃), 54.0 (CH₃), 45.1 (CH), 41.9 (CH), 38.5 (CH), 28.3 (CH₃), 21.4 (CH₃); MS (m/z , relative intensity): 349 (M^+ , 15), 325 (57), 269 (10), 227 (14), 115 (6), 77 (5), 75 (100); exact mass calcd for C₁₈H₂₃NO₆ (M^+): 349.1525; found 349.1525.

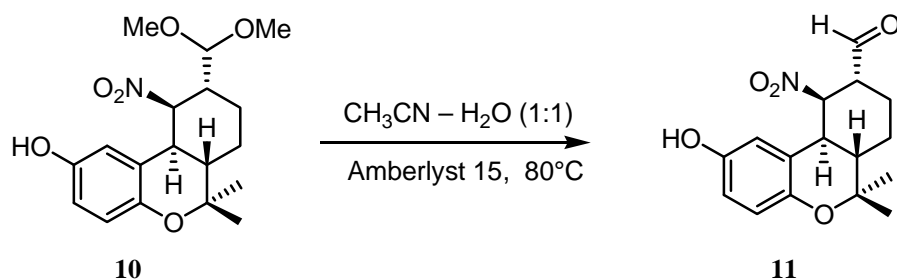
Preparation of **10**



A suspension of **9** (300 mg, 0.85 mmol) and Pd-C (150 mg, 10%) in MeOH (10 mL) was stirred at room temperature under hydrogen (1 atm) for 1 h. The mixture was filtered through Celite, and the filtrate was concentrated *in vacuo* to give the crude product. The crude residue was purified by silica gel flash column chromatography with 20% EtOAc-hexane ($R_f = 0.40$ for **10** in 30% EtOAc-hexane) to give **10** as a white solid (215 mg, 72% yield): mp 142-145 °C. Selected spectroscopic data for **10**: $[\alpha]_D^{25} +50.1$ (c 0.8 CHCl₃); IR (neat): 3373, 2936, 1548, 1370, 1218, 1060, 768 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 6.66 (s, 2 H), 6.42 (s, 1 H), 5.01-4.96 (m, $J = 8.1$ Hz, 1 H), 4.94 (s, 1 H), 4.20 (d, $J = 6.8$ Hz, 1 H), 3.41-3.36 (m, 1H), 3.35 (s, 6 H), 2.50-2.45 (m, 1 H), 2.13-2.04 (m, $J = 12.0$ Hz,

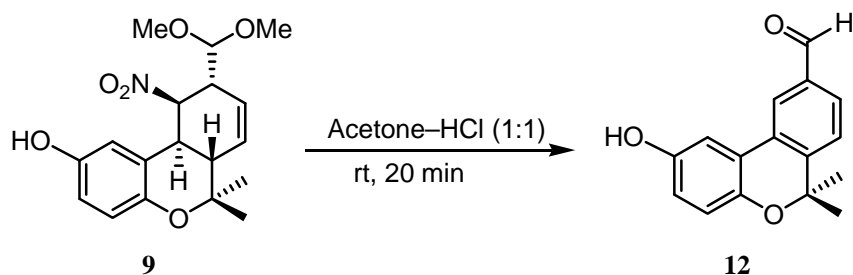
1 H), 1.79-1.70 (m, 1 H), 1.67 (td, $J = 4.9, 12.1$ Hz, 2 H), 1.55-1.47 (m, 1 H), 1.35 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 149.3 (C), 146.8 (C), 124.7 (C), 118.4 (CH), 115.6 (CH), 111.8 (CH), 104.2 (CH), 89.4 (CH), 77.5 (C), 55.7 (CH_3), 53.6 (CH_3), 41.2 (CH), 39.7 (CH), 36.3 (CH), 27.9 (CH_3), 21.8 (CH_2), 19.9 (CH_3), 19.5 (CH_2); MS (m/z , relative intensity): 351 (M^+ , 21), 325 (53), 279 (23), 239 (34), 219 (29), 191 (65), 107 (67), 95 (39), 77 (41), 75 (92), 57 (64); exact mass calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_6$ (M^+): 351.1682; found 351.1683.

Preparation of **11**



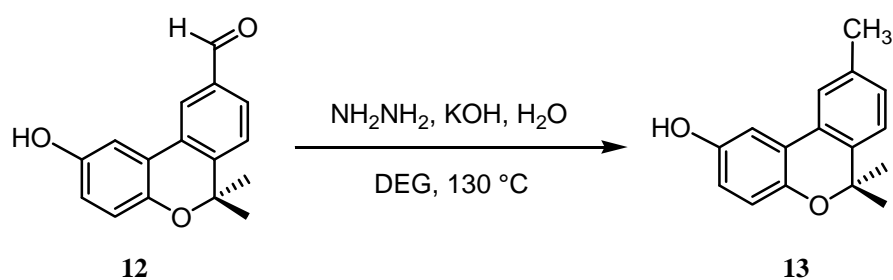
To a solution of **10** (100 mg, 0.28 mmol) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1, 6 mL) was added Amberlyst 15 (50 mg). The resulting solution was heated to 80°C and stirred at the same temperature for 5 h. After cooling to room temperature, the solution was diluted with EtOAc (15 mL), washed with brine (5 mL), dried over MgSO_4 , and concentrated *in vacuo* to give the crude product. To the crude residue CHCl_3 was added (0.5 mL), followed by the addition of hexane (2 mL), and lead to the formation of solid precipitation. After decanting the solvent, the precipitate was dried under *vacuo* ($R_f = 0.28$ for **11** in 30% EtOAc-hexane) to give pure **11** as a pale yellow solid along with the recovery of 20 mg of pure **10** in solvent layer (48 mg, 69% yield, based on the recovered **10**): mp $191-193^\circ\text{C}$. Due to the instability of **11** in solution (decomposition), the above procedure, the incomplete transformation as well as the precipitation of product, was adapted for the routine preparation and purification. Purification of **11** by silica gel chromatography led to the decomposition of product. However, **11** was stable in solid form for months as long as it is not in solution or in silica gel condition. Selected spectroscopic data for **11**: $[\alpha]_{\text{D}}^{25} -15.4$ (c 0.15 EtOAc); IR (neat): 3377, 2930, 1698, 1547, 1370, 1226, 1138, 768 cm^{-1} ; ^1H NMR (CD_3CN , 500 MHz): δ 9.85 (d, $J = 2$ Hz, 1 H), 6.61 (s, 2 H), 6.28 (s, 1 H), 5.07 (dd, $J = 5.2, 10.4$ Hz, 1 H), 3.55 (t, $J = 11.2$ Hz, 1 H), 3.35 (d, $J = 3.9$ Hz, 1H), 1.90-1.80 (m, 1 H), 1.78-1.72 (m, 1 H), 1.64 (td, $J = 3.7, 12.3$ Hz, 1 H), 1.61-1.30 (m, 1 H), 1.31 (s, 3H), 1.20-1.18 (m, 1 H), 1.17 (s, 3H); ^{13}C NMR (CD_3CN , 125 MHz): δ 202.3 (CH), 151.4 (C), 147.5 (C), 125.3 (C), 119.3 (CH), 116.4 (CH), 112.3 (CH), 89.1 (CH), 78.1 (C), 50.3 (CH), 46.2 (CH), 36.3 (CH), 28.5 (CH_3), 24.2 (CH_2), 23.0 (CH_2), 21.2 (CH_3); MS (m/z , relative intensity): 305 (M^+ , 52), 258 (62), 229 (100), 215 (31), 187 (26), 161 (28), 107 (6), 105 (6), 77 (10); exact mass calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_5$ (M^+): 305.1263; found 305.1260.

Preparation of 12



To a solution of Acetone–HCl (1:1, 4 mL), compound **9** (50 mg, 0.14 mmol) was added portion-wise at room temperature. The resulting solution was stirred for 20 min, diluted with EtOAc (20 mL), and the organic layer was washed with saturated aqueous solution of NaHCO₃ (10 mL), followed by brine (10 mL), and dried over anhydrous MgSO₄, concentrated in *vacuo* to give crude product. The residue was purified by column chromatography with 15% EtOAc-hexane (R_f = 0.38 for **12** in 20 % EtOAc-hexane) to give **12** as a yellow oil (25 mg, 69% yield). Selected spectroscopic data for **12**: IR (neat): 3387, 2925, 1689, 1496, 1213, 770 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 10.03 (s, 1 H), 8.15 (d, J = 0.7 Hz, 1 H), 7.79 (dd, J = 1.2, 7.8 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 1 H), 7.31 (d, J = 2.7 Hz, 1H), 6.87-6.83 (m, 1 H) 6.82-6.78 (m, 1 H), 1.63 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz): δ 192.2 (CH), 150.7 (C), 146.4 (C), 146.1 (C), 135.7 (C), 129.8 (C), 129.7 (CH), 124.1 (CH), 123.2 (CH), 122.0 (C), 119.0 (CH), 117.5 (CH), 109.5 (CH), 77.3 (C), 27.1 (two CH₃); MS (m/z , relative intensity): 254 (M^+ , 45), 239 (100), 210 (9), 185 (45), 180 (28), 179 (100), 112 (5), 90 (5), 55 (4); exact mass calcd for C₁₆H₁₄O₃ (M^+): 254.0943; found 254.0935.

Preparation of 13



To a solution of **12** (15 mg, 0.06 mmol) and KOH (10 mg, 0.7 mmol) in diethylene glycol (1 mL) was added dropwise a solution of aqueous hydrazine hydrate (0.3 mL of hydrazine hydrate in 0.5 mL diethylene glycol). The solution was stirred for 20 min at room temperature and then 130 °C for 8 h. The reaction mixture was cooled to room temperature and diluted with EtOAc (15 mL). The organic layer was washed with H₂O (5 mL), followed by brine (5 mL), dried over MgSO₄, and concentrated in *vacuo* to give crude product. The residue was purified by flash column chromatography with 5 % EtOAc-Hexane (R_f = 0.51 for **12** in 20% EtOAc-Hexane) to give **12** as a

yellow oil. (9 mg, 63% yield). Selected spectroscopic data for **13**: IR (neat): 3395, 2976, 2927, 1614, 1569, 1321, 1210, 1040, 941, 869, 765 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 7.43 (br.s, 1 H), 7.18 (d, $J = 3.0$ Hz, 1 H), 7.10 (br.s., 2 H), 6.80 (d, $J = 8.5$ Hz, 1 H), 6.68 (dd, $J = 8.5, 3.0$ Hz, 1 H), 2.37 (s, 3 H), 1.58 (s, 6 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 150.0 (C), 146.8 (C), 137.2 (C), 137.1 (C), 128.9 (CH), 128.2 (C), 123.4 (C), 123.1 (CH), 122.9 (CH), 118.7 (CH), 116.2 (CH), 109.3 (CH), 77.3 (C), 27.4 (two CH_3), 21.3 (CH_3); MS (m/z , relative intensity): 240 (M^+ , 41), 226 (34), 225 (100), 120 (6), 112 (20), 76 (4); exact mass calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ (M^+): 240.1150; found 240.1145.

^1H NMR Data for didehydroconicol

Lit. ^{a,1}		Obs.	
δ	mult, J (Hz)	δ	mult, J (Hz), H
7.43	(bs), 1H	7.43	(bs), 1H
7.18	d (2.0), 1H	7.18	d (3.0), 1H
7.11	(AB), 1H	7.10	(br. s., 2 H),
7.09	(AB), 1H		
6.80	d (8.0), 1H	6.80	(d, $J = 8.5$ Hz, 1 H),
6.68	dd (8.0; 2.0), 1H	6.68	dd (8.5; 3.0, 1 H),
2.37	s, 3H	2.37	(s, 3 H),
1.58	s, 3H	1.58	(s, 3 H);
1.58	s, 3H	1.58	(s, 3 H);

^a Spectrum recorded at 400 MHz (JEOL EX 400) in CDCl_3 .

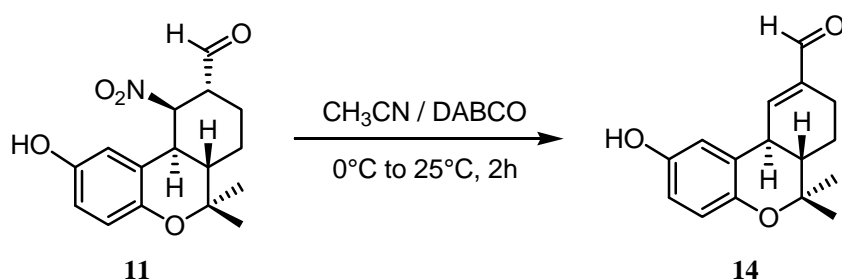
^b Spectrum recorded at 500 MHz (Varian Unity INOVA 500) in CDCl_3 .

^{13}C NMR Data for didehydroconicol

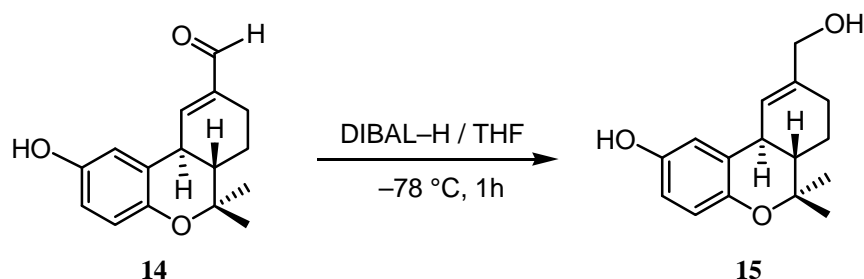
Lit. ^{a,1}	Obs. ^b	
δ	δ	Type
150.2	150.0	C
146.8	146.8	C
137.3	137.2	C
137.2	137.1	C
129.0	128.9	CH
128.3	128.2	C
123.5	123.4	C
123.2	123.1	CH
123.0	122.9	CH
118.8	118.7	CH
116.2	116.2	CH
109.4	109.3	CH
77.4	77.3	C
27.5	27.4	CH_3
27.5	27.4	CH_3
21.3	21.3	CH_3

^a Spectrum recorded at 100 MHz in CDCl_3 . ^b Spectrum recorded at 125 MHz in CDCl_3 .

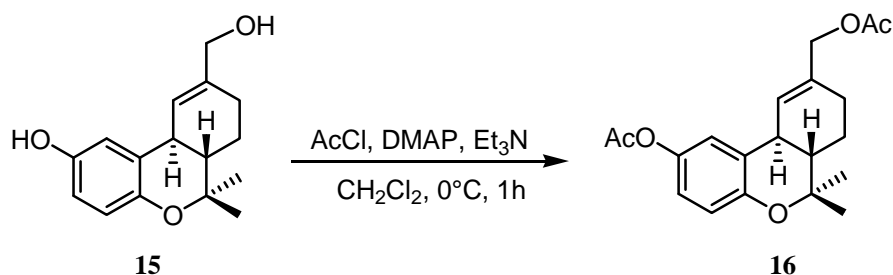
¹ Simon-Levert, A.; Arrault, A.; Bontemps-Subielos, N. Canal, C.; Banaigs, B. *J. Nat. Prod.* **2005**, *68*, 1412-1415.

Preparation of **14**

To a solution of **11** (45 mg, 0.15 mmole) in CH₃CN (4 mL) was added DABCO (24 mg, 0.22 mmol) at 0 °C. The solution was stirred at 0 °C for 20 min and warmed up to room temperature over 2 h until the completion of reaction, monitored by ¹H NMR (*R_f* = 0.28 for **14** in 30% EtOAc-hexane). The solution was diluted with EtOAc (15 mL), washed with brine (10 mL) dried over anhydrous MgSO₄ and concentrated *in vacuo* to give **14** as a yellow oil (30 mg, 79% yield). The product obtained was pure enough for NMR analysis and for the next step reaction without further purification. Moreover, due to the instability of **14** in solution (decomposition), for routine preparation, **14** was directly subjected to the next step reaction without further purification. For the purpose of spectra analysis, a pure sample was obtained by fast passing through a silica gel column with CHCl₃. Selected spectroscopic data for **14**: [α]_D²⁵ +89.8 (c 0.9 CHCl₃); IR (neat): 3394, 2930, 1671, 1550, 1370, 1154, 756 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 9.52 (s, 1 H), 7.17 (br. s., 1 H), 6.86 (br. s., 1 H), 6.70-6.67 (m, 1 H), 6.66-6.63 (m, 1 H), 4.78 (s, 1H), 3.43 (d, *J* = 11.0 Hz, 1 H), 2.55 (dd, *J* = 5.1, 18.3 Hz, 1 H), 2.25-2.03 (m, 1 H), 2.01 (dd, *J* = 6.6, 12.2 Hz, 1 H), 1.70-1.65 (m, 1 H), 1.43 (s, 3 H), 1.36 (dd, *J* = 6.2, 12.3 Hz, 1 H), 1.16 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 194.0 (CH), 150.4 (CH), 148.9 (C), 147.3 (C), 141.4 (C), 122.4 (C), 118.4(CH), 115.3(CH), 111.6, (CH), 77.3 (C), 44.1 (CH), 36.1 (CH), 27.8 (CH₃), 23.3 (CH₂), 22.2 (CH₂), 20.2 (CH₃) ; MS (*m/z*, relative intensity): 258 (M⁺, 33), 245 (40), 244 (43), 241 (37), 239 (100), 229 (77), 201 (30), 77 (23); exact mass calcd for C₁₆H₁₈O₃ (M⁺): 258.1256; found 258.1254.

Preparation of **15**

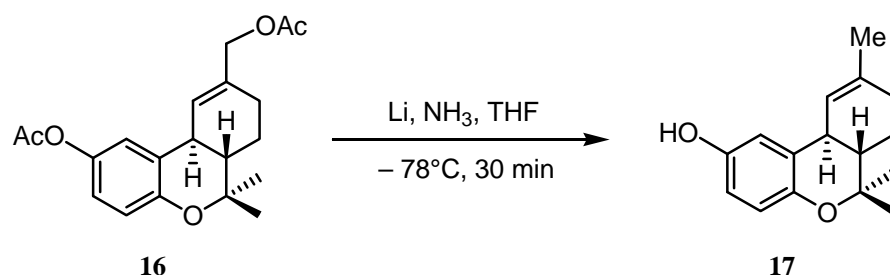
To a solution of **14** (30 mg, 0.11 mmol) in THF (5 mL) was added DIBAL-H (0.34 mL, 1M in toluene, 0.34 mmol) at $-78\text{ }^{\circ}\text{C}$, and the resulting solution was stirred for 1 h at the same temperature. The reaction was quenched by adding H_2O (4 mL), followed by EtOAc (15 mL), and allowed to warm up at room temperature. Then filter over celite, and organic layer was dried over anhydrous MgSO_4 , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 35% EtOAc-hexane ($R_f = 0.25$ for **15** in 40% EtOAc-hexane) to give **15** as a yellow oil (22 mg, 73% yield). Selected spectroscopic data for **15**: $[\alpha]_{\text{D}}^{25} +78.3$ (c 0.4 CHCl_3); IR (neat): 3429, 2927, 1641, 1489, 1375, 1257, 1021, 803 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz): δ 7.03 (br. s., 1 H), 6.92 (d, $J = 8.5$ Hz, 1 H), 6.70 (dd, $J = 2.0, 8.5$ Hz, 1 H), 6.17 (br. s., 1 H), 6.14 (s, 1 H), 3.92 (s, 2 H), 3.03 (d, $J = 10.5$ Hz, 1H), 1.88-1.86 (m, 1 H), 1.84-1.79 (m, 1 H), 1.52-1.44 (m, 2 H), 1.30 (s, 3 H), 1.00 (s, 3 H), 0.96 (dd, $J = 6.6, 12.0$ Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz): δ 150.0 (C), 147.6 (C), 138.1 (C), 125.4 (C), 122.8 (CH), 118.3 (CH), 115.0 (CH), 112.5 (CH), 77.1 (C), 66.7 (CH_2), 45.0 (CH), 34.5 (CH), 28.0 (CH_3), 26.5 (CH_2), 24.3 (CH_2), 20.6 (CH_3); MS (m/z , relative intensity): 259 ($\text{M}^+ - 1$, 24), 245 (35), 244 (42), 241 (57), 229 (100), 201 (31), 187 (26), 149 (38), 137 (34); exact mass calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ (M^+): 260.1412; found 260.1412.

Preparation of **16**

To a solution of **15** (25 mg, 0.096 mmol), in CH_2Cl_2 (5 mL) was added DMAP (47 mg, 0.38 mmol), followed by triethyl amine (30 mg, 0.28 mmol) and acetyl chloride (15 mg, 0.19 mmol) at $0\text{ }^{\circ}\text{C}$, and allowed to warm at room temperature for 1 h. Then diluted with EtOAc (15 mL) and washed by H_2O (10 mL), followed by brine (10 mL), dried over MgSO_4 , and concentrated *in vacuo* to give

the crude product. The residue was purified by flash column chromatography with 10% EtOAc-hexane ($R_f = 0.35$ for **16** in 20% EtOAc-hexane) to give **16** as a colorless oil (25 mg, 76 % yield). Selected spectroscopic data for **16**: $[\alpha]_D^{25} +72$ (c 0.5 CHCl_3); IR (neat): 2924, 1744, 1640, 1485, 1372, 1210, 1020, 929 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 6.97 (s, 1 H), 6.81-6.77 (m, 1 H), 6.76-6.74 (m, 1 H), 6.16 (br. s., 1 H), 4.55-4.44 (m, 2 H), 3.23 (d, $J = 11.2$ Hz, 1 H), 2.26 (s, 3 H), 2.21 (d, $J = 5.9$ Hz, 1 H), 2.18-2.11 (m, 1 H), 2.07 (s, 3 H), 1.92 (dd, $J = 6.1, 12.5$ Hz, 1 H), 1.64-1.59 (m, 1 H), 1.46-1.35 (m, 1 H), 1.41 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 170.9 (C), 170.1 (C), 151.0 (C), 143.4 (C), 134.0 (C), 126.4 (CH), 124.3 (C), 120.5 (CH), 118.7 (CH), 117.8 (CH), 77.9 (C), 68.2 (CH_2), 43.8 (CH), 34.1 (CH), 27.9 (CH_3), 26.7 (CH_2), 24.0 (CH_2), 21.1 (CH_3), 21.0 (CH_3), 20.8 (CH_3); MS (m/z , relative intensity): 344 (M^+ , 23), 343 (100), 334 (46), 327 (41), 316 (24), 177 (41), 149 (37), 77 (13), 57 (45); exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5$ (M^+): 344.1624; found 344.1624

Preparation of **17**



The acetate **16** (25 mg, 0.07 mmol) in THF (5 mL) was added to a solution of lithium (6 mg, 0.87 mmol) in liquid ammonia (5 mL) at -78°C and stirred for 0.5 h. an aqueous saturated ammonium chloride solution (3 mL) was carefully added and the ammonia allowed to evaporate. The residue was diluted with EtOAc (20 mL), and washed by H_2O (10 mL) followed by brine (10 mL) and organic layer was dried over anhydrous MgSO_4 and concentrated in *vacuo* to give crude product. The crude was purified by flash column chromatography with 10 % EtOAc-Hexane, ($R_f = 0.38$ for **17** in 20 % EtOAc-hexane) to give **17** as colorless oil (13 mg, 73% yield). Selected spectroscopic data for **17**: $[\alpha]_D^{25} +51.8$ (c 2 CHCl_3);^{2,3} IR (neat): 3390, 2930, 1617, 1490, 1375, 1213, 1130, 928, 759 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 6.78 (d, $J = 1.7$ Hz, 1 H), 6.65 (d, $J = 8.5$ Hz, 1 H), 6.60-6.54 (m, 1 H), 5.83 (br. s., 1 H), 4.47 (br. s., 1 H), 3.13 (d, $J = 10.7$ Hz, 1 H), 2.08 (d, $J = 5.9$ Hz, 2 H), 1.85 (dt, $J = 2.4, 12.5$ Hz, 1 H), 1.71 (s, 3 H), 1.54 (dd, $J = 12.0, 12.0$ Hz, 1 H),

² Garrido, L.; Zuba, E.; Ortega, M. J.; Salv, J. *J. Nat. Prod.*, **2002**, 65, 1328-1331. Lit. $[\alpha]_D^{27} = +1.0$ (C 0.4, CHCl_3). The optical rotation value is somewhat different from those reported for the natural product and raises earlier suspicions that the natural products have an enantiomeric excess in the opposite sense, and were not isolated as pure single enantiomers. Or, this lack of optical purity in the natural products may be due to their facile racemization and/or decomposition. In fact, storage of our enantiopure **17** in neat at 25°C for a week gave some decomposition products. Moreover, the compound was completely decomposed in CHCl_3 and gave a complex mixture after standing in CHCl_3 for 24 h at ambient temperature. Refer to the above reference on page 1330 and the note 6, 7 and 13 in that paper for the discussion of the low optical value.

³ However, Alcohol **15** and acetate **16** were the stable compounds.

1.44-1.34 (m, 1 H), 1.39 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 148.6 (C), 147.2 (C), 135.2 (C), 125.8 (C), 121.6 (CH), 111.7 (CH), 114.2 (CH), 112.0 (CH), 77.5 (C), 44.5 (CH), 34.2 (CH), 30.8 (CH_2), 28.0 (CH_3), 24.6 (CH_2), 23.5 (CH_3), 20.7 (CH_3); MS (m/z , relative intensity): 244 (M^+ , 34), 225 (29), 201 (23), 161 (28), 111 (38), 97 (56), 83 (63), 69 (71), 57 (100); exact mass calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$ (M^+): 244.1463; found 244.1459.

^1H NMR Data for (+)-Conicol

Lit. ^{a,4}		Obs.	
δ	mult, J (Hz)	δ	mult, J (Hz), H
6.80	br d (2.8)	6.78	d (1.7), 1 H
6.66	d (8.7)	6.65	d (8.5), 1H
6.59	br dd (8.7, 3.0)	6.60-6.54	m, 1H
5.84	br s	5.83	br s, 1H
4.45	br s	4.47	br s, 1H
3.15	br d (11.4)	3.13	d (10.7), 1H
2.10	m	2.08	d (5.9), 2H
1.87	dddd (12.5, 5.2, 2.8, 2.3)	1.85	dt (12.5, 2.4), 1H
1.73	d (0.9)	1.71	s, 3H
1.56	ddd (12.3, 11.4, 2.2)	1.54	dd (12.0, 12.0), 1H
1.41	s	1.39	s, 3 H
1.39	m	1.34-1.44	m, 1H
1.15	s	1.13	s, 3 H

^a Spectrum recorded at 400 MHz (Varian Unity 400) in CDCl_3 .

^b Spectrum recorded at 500 MHz (Varian Unity INOVA 500) in CDCl_3 .

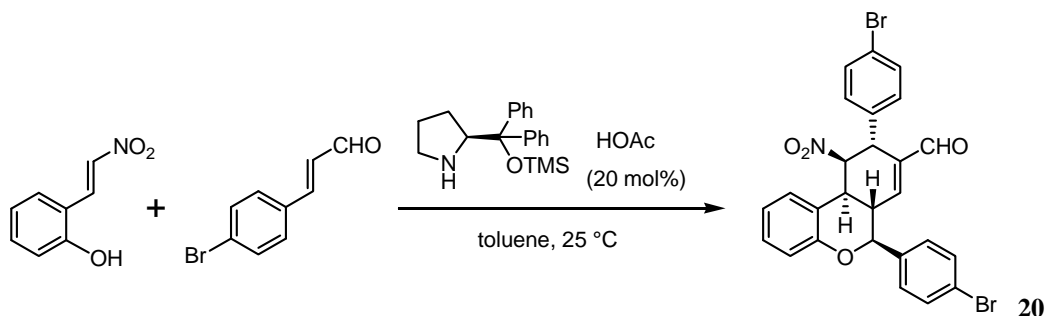
^{13}C NMR Data for (+)-Conicol

Lit. ^{a,4}		Obs. ^b	
δ	mult	δ	Type
148.6	s	148.6	C
147.3	s	147.3	C
135.2	s	135.2	C
125.9	s	125.8	C
121.7	d	121.6	CH
117.7	d	117.7	CH
114.2	d	114.2	CH
112.0	d	112.0	CH
77.5	s	77.5	C
44.6	d	44.5	CH
34.3	d	34.2	CH
30.8	t	30.8	CH_2
28.0	q	28.0	CH_3
24.6	t	24.6	CH_2
23.5	q	23.5	CH_3
20.7	q	20.7	CH_3

^a Spectrum recorded at 100 MHz in CDCl_3 . ^b Spectrum recorded at 125 MHz in CDCl_3 .

⁴ Garrido, L.; Zuba, E.; Ortega, M. J.; Salv, J. *J. Nat. Prod.*, **2002**, *65*, 1328-1331.

Preparation of 20.



To a solution of (*E*)-3-(4-bromophenyl)acrylaldehyde (191.6 mg, 0.9 mmol), (*S*)-diphenyl-prolinol-O-TMS-ether (19.70 mg, 0.06 mmol) and acetic acid (3.63 mg, 0.06 mmol) in toluene (5mL) was added *trans*-2-Hydroxy- β -nitrostyrene (50 mg, 0.3 mmol). The resulting solution was stirred for 10 h at 25 °C, and the reaction mixture was directly loaded on to a column and purified by silica gel chromatography with 4% EtOAc-Hexane (R_f = 0.75 for **20** in 20 % EtOAc-hexane) to give **20** as white solid (94 mg, 55% yields): mp 219-221 °C. Selected spectroscopic data for **20**: $[\alpha]_D^{25}$ +29.3 (c 1.2 CHCl₃); IR (neat): 2924, 1690, 1549, 1487, 1364, 1232, 1009, 754 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 9.36 (s, 1 H), 7.66 (d, J = 8.5 Hz, 2 H), 7.50 (d, J = 8.5 Hz, 2 H), 7.42 (d, J = 8.5 Hz, 2 H), 7.18-7.15 (m, 1H), 7.12 (m, 1H), 7.09 (d, J = 8.5Hz, 2 H), 6.92 (m, 2 H), 6.58 (s, 1 H), 5.40 (d, J = 2.5Hz, 1 H), 5.05 (d, J = 10.5Hz, 1 H), 4.58 (s, 1 H), 3.50-3.48 (m, 1H), 3.47 (t, J = 10.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ 191.1 (CH), 154.4 (C), 146.8 (CH), 139.9 (C), 137.4 (C), 136.4 (C), 132.5 (two CH), 132.4 (two CH), 129.4 (CH), 129.3 (two CH), 129.2 (two CH), 124.5 (CH), 123.6 (C), 122.4 (C), 121.1 (CH), 118.4 (C), 117.3 (CH), 84.8 (CH), 81.29 (CH), 42.4 (CH), 39.5 (CH), 35.8 (CH); MS (m/z , relative intensity): 569 (M^+ +2, 13), 567 (M^+ , 7), 522 (6), 443 (3), 369 (5), 295 (5), 221 (9), 171 (21), 169 (22), 43 (100); exact mass calcd for C₂₆H₁₉Br₂NO₄ (M^+): 566.9681; found 566.9680.

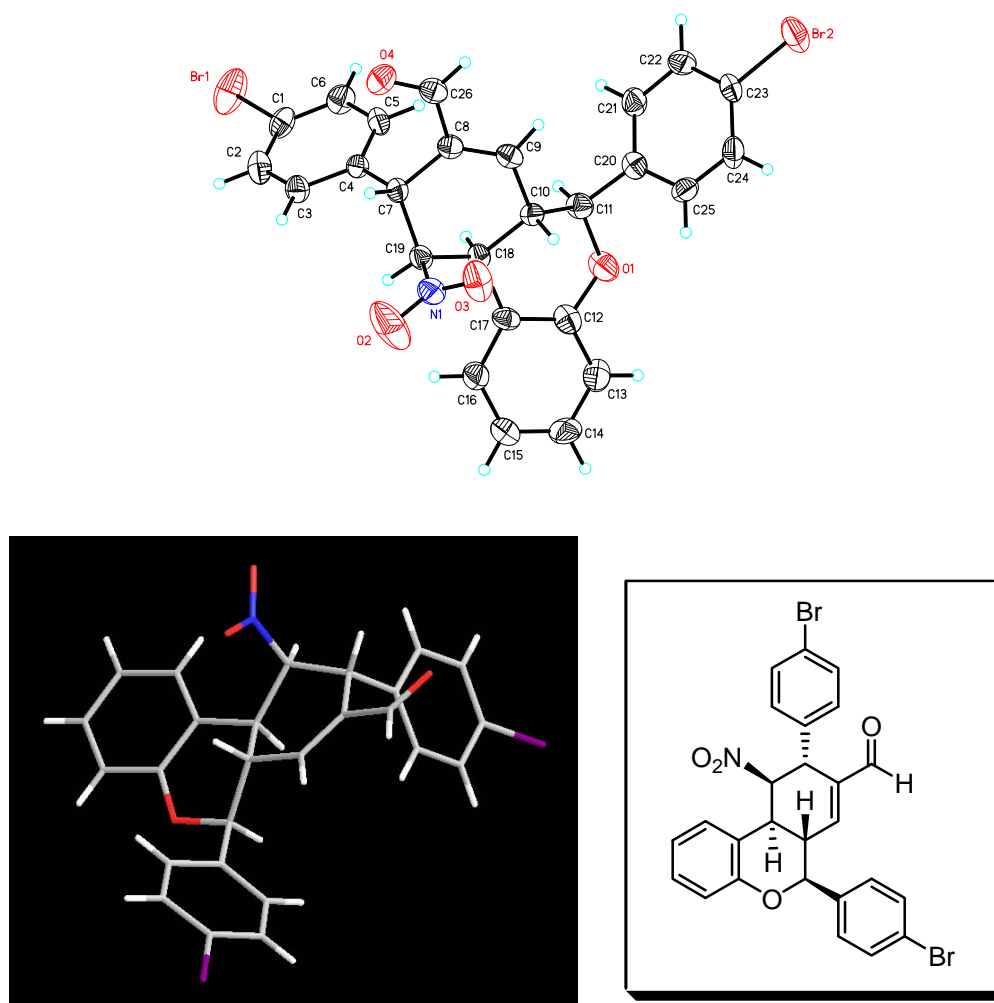
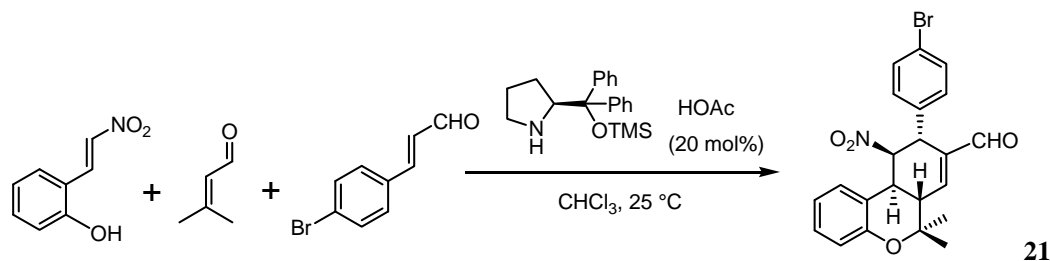


Figure S1. ORTEP and stereo plots for X-ray crystal structures of (+)-**20**.

CCDC 751181 contains the supplementary crystallographic data for (+)-**20**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for (+)-**20**: $C_{26}H_{19}Br_2NO_4$, $M = 569.24$, orthorhombic, space group $P 2_1 2_1 2_1$, $T = 298(2)K$, $a = 10.7996(6)$, $b = 11.8516(7)$, $c = 17.5643(10)$ Å, $\beta = 90.00^\circ$, $V = 2248.1(2)$ Å³, $Z = 4$, $D = 1.682$ g/cm³, λ (Mo- $K\alpha$) = 0.71073 Å, 26471 reflections collected, 5456 unique reflections, 298 parameters refined on F^2 , $R = 0.0656$, $wR2[F^2] = 0.1029$ [3703 data with $F^2 > 2\sigma(F^2)$].

Preparation of **21**.

To a solution of 3-methylbut-2-enal (15.2 mg, 0.18 mmol), (*S*)-diphenylprolinol-O-TMS-ether (9.83 mg, 0.03 mmol), and acetic acid (1.81 mg, 0.03 mmol) in CHCl₃ (3 mL) was added *trans*-2-Hydroxy- β -nitrostyrene (25 mg, 0.15 mmol). The resulting solution was stirred at 25 °C for 0.5 h, followed by the addition of (*E*)-3-(4-bromophenyl)acrylaldehyde (38.2 mg, 0.18 mmol), and stirred at room temperature for 24 h. The reaction mixture was diluted with EtOAc (15 mL), washed with brine (5 mL), dried over anhydrous MgSO₄, and concentrated in *vacuo* to give crude product. The residue was purified by flash column chromatography with 12% EtOAc-hexane, (*R_f* = 0.62 for **21** in 20% EtOAc-hexane) to give **21** as a white solid (35 mg, 52% yield): mp 187-190 °C. Selected spectroscopic data for **21**: [α]_D²⁵ -60 (c 0.75 CHCl₃); IR (neat): 2968, 1690, 1547, 1510, 1366, 1255, 1019, 759 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 9.58 (s, 1 H), 7.49 (d, *J* = 8.1 Hz, 2 H), 7.18-7.11 (m, 2 H), 7.09 (d, *J* = 8.1 Hz, 3 H), 6.87-6.79 (m, 2 H), 5.43 (br. s., 1 H), 4.59 (s, 1 H), 3.27 (d, *J* = 1.2 Hz, 1 H), 3.04 (d, *J* = 12.2 Hz, 1 H), 1.74 (s, 3 H), 1.28 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 191.6 (CH), 153.6 (C), 148.6 (CH), 140.2 (C), 137.9 (C), 132.8 (CH), 129.8 (two CH), 129.3 (two CH), 124.9 (CH), 122.6 (C), 120.6 (CH), 118.0 (CH), 117.6 (C), 85.6 (CH), 77.5 (C), 42.6 (CH), 42.5 (CH), 32.0 (CH), 28.2 (CH₃), 22.6 (CH₃); MS (*m/z*, relative intensity): 442 (*M*⁺+1, 100), 440 (*M*⁺-1, 87), 395 (49), 379 (43), 381 (82), 379 (94), 273 (32), 246 (33), 202 (56), 115 (65), 77 (40); exact mass calcd for C₂₂H₂₀BrNO₄ (*M*⁺): 441.0576; found 441.0574..

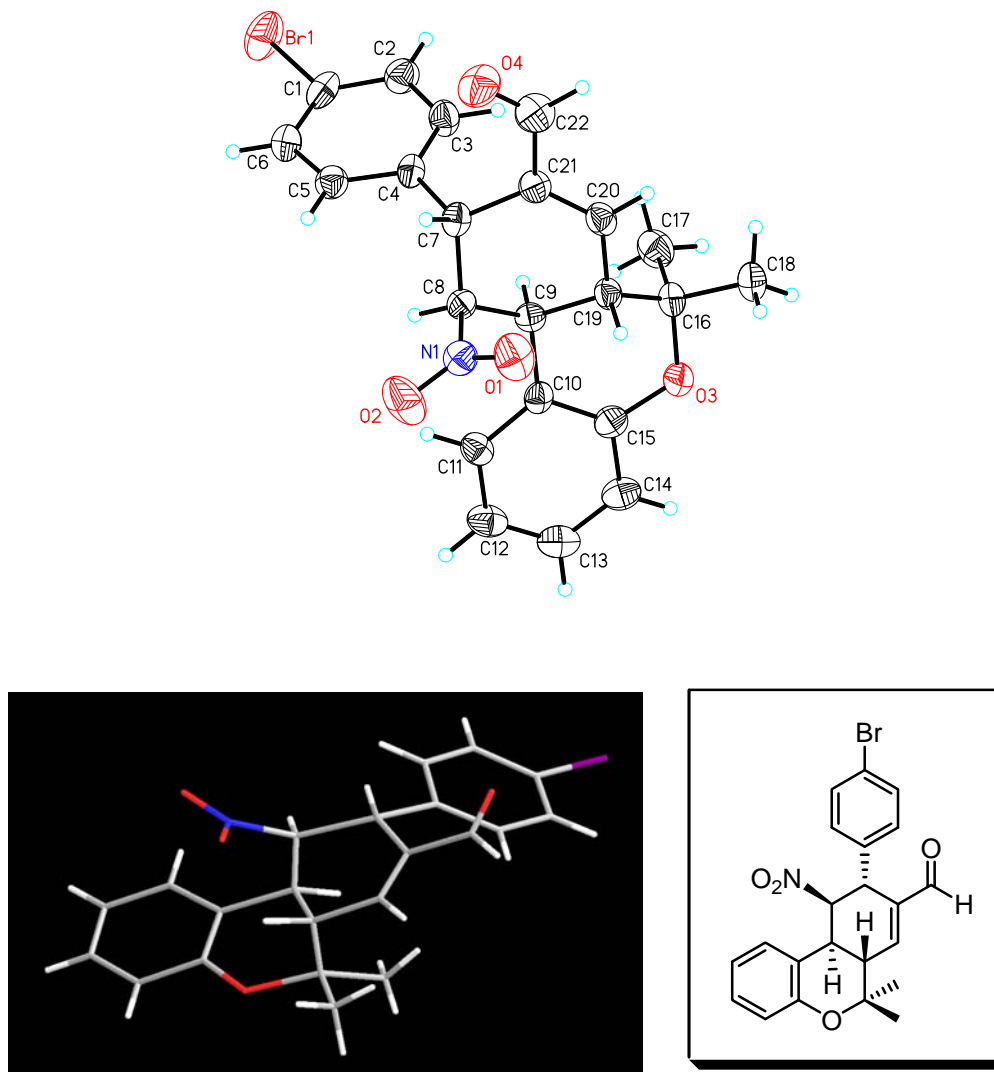


Figure S2. ORTEP and stereo plots for X-ray crystal structures of (-)-**21**.

CCDC 751182 contains the supplementary crystallographic data for (-)-**21**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for (-)-**21**: $C_{22}H_{20}BrNO_4$, $M = 442.30$, Hexagonal, space group $P\ 6_1$, $T = 295(2)\text{K}$, $a = 18.5358(18)$, $b = 18.5358(18)$, $c = 10.8967(15)\text{ \AA}$, $\beta = 90.00^\circ$, $V = 3242.3(6)\text{ \AA}^3$, $Z = 6$, $D = 1.359\text{ g/cm}^3$, $\lambda\text{ (Mo-}K\alpha) = 0.71073\text{ \AA}$, 23088 reflections collected, 3693 unique reflections, 275 parameters refined on F^2 , $R = 0.0528$, $wR2[F^2] = 0.1005$ [2291 data with $F^2 > 2\sigma(F^2)$].

Fig S18. ¹H NMR of compound 4 (500 MHz, CDCl₃).

S18

PMK-01-203

exp32 s2pul

```

SAMPLE
date Mar 28 2009 dfrq 125.695
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vnmr1/vnmrsys/data~ dof 0
/PMK/PMK-01-203/H.~ dm nnn
fid dmm c
ACQUISITION dmf 200
sfrq 499.836 dseq
tn H1 dres 1.0
at 3.000 homo n
np 48000
sw 8000.0 wtfile
fb 4000 proc
bs 4 fn not used
tpwr 57 math f
pw 4.8
d1 1.000 werr react
tof 499.7 wexp procplot
nt 4 wbs
ct 4 wnt wft
alock y
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5498.0
vs 50
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wc 210
hzmm 26.18
ls 128.15
rfl 4631.6
rfp 3618.8
th 1
ins 100.000
nm ph
    
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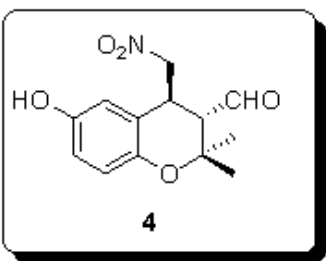
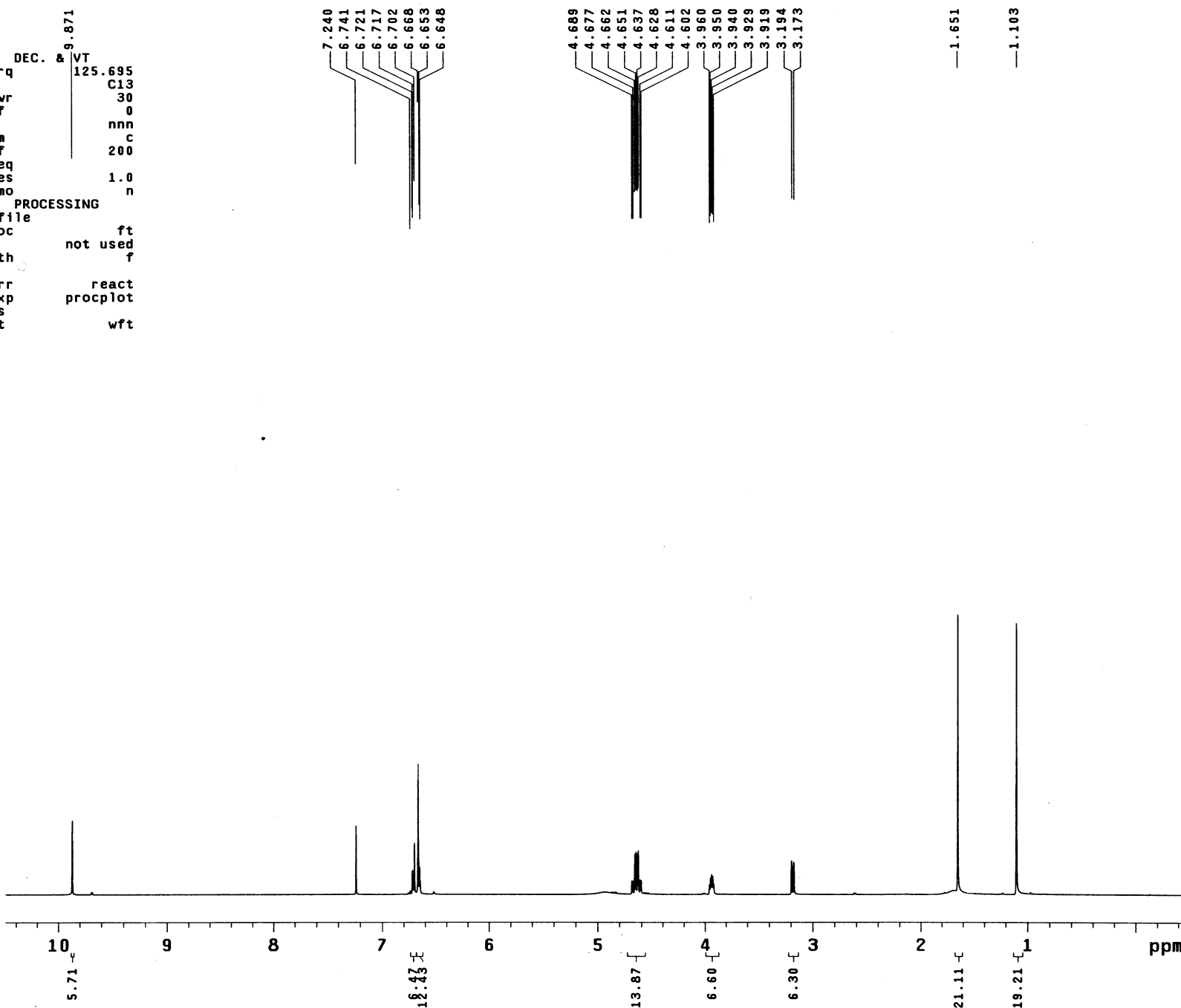


Fig S19. 13C NMR of compound 4 (125 MHz, CDCl₃).

S19

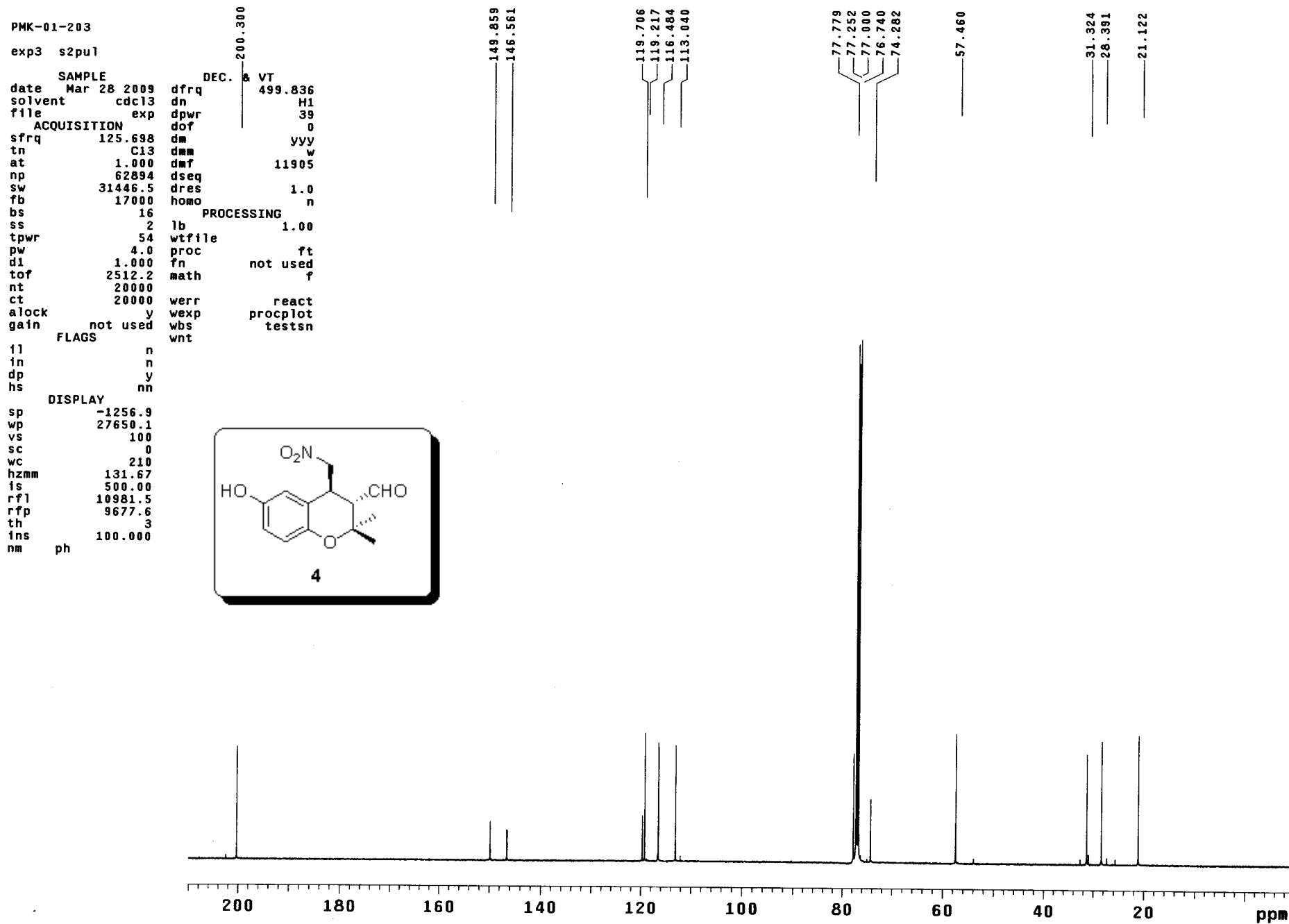


Fig S20. DEPT of compound 4 (CDCl₃).

S20

PMK-01-203

exp2 DEPT

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solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	40	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	900	wp	27650.1		
ct	900	sp	-1257.2		
TRANSMITTER		rp	113.9		
tn	C13	lp	82.5		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.7		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	225		
dmm	ccw	hzmm	131.67		
dmf	11905	th	68		
pplv1	49				
pp	29.400				

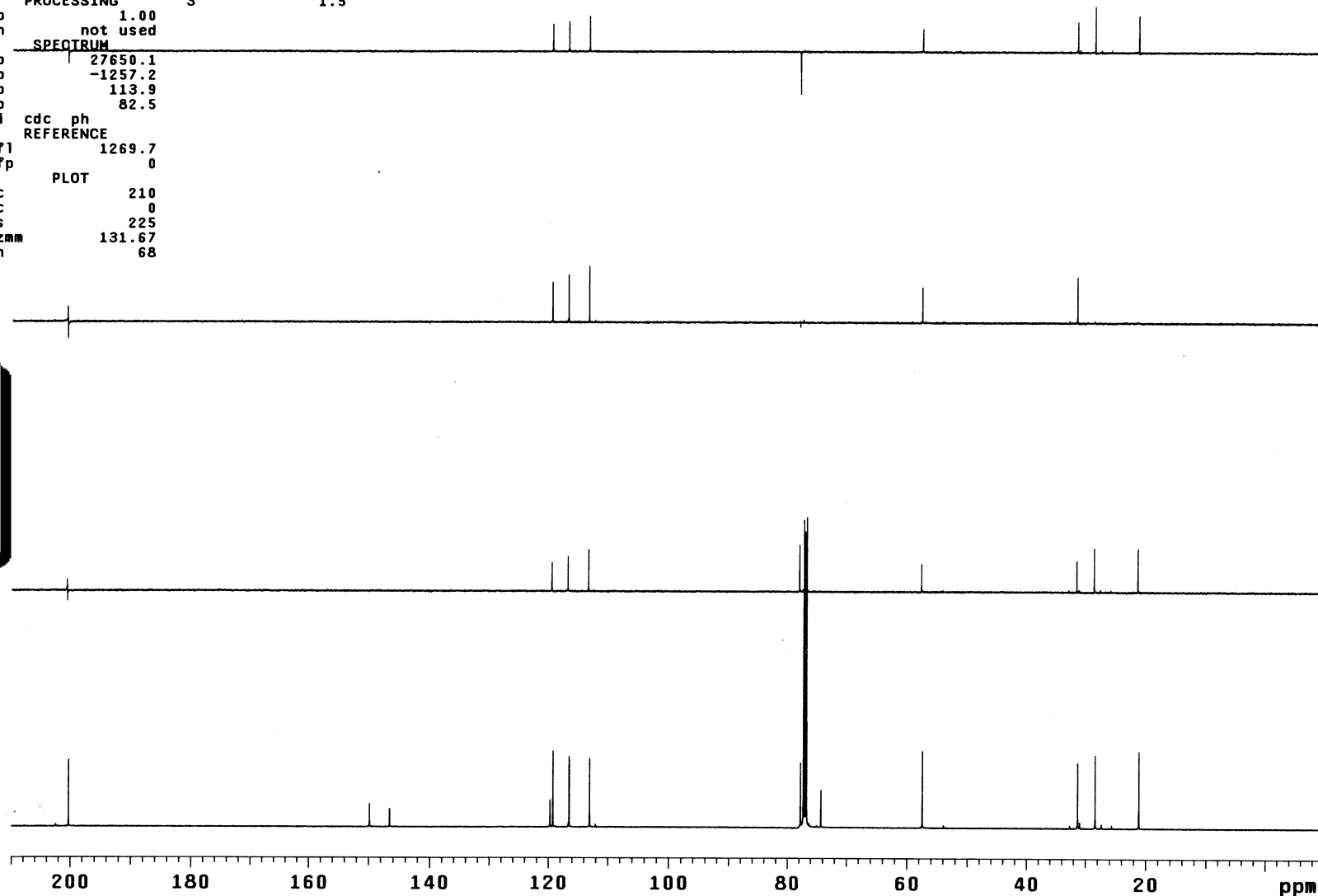
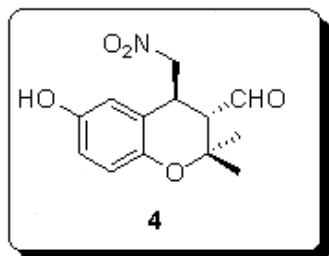


Fig S21. HMQC of compound 4 (CDCl₃).

S21

PMK-01-203

exp32 gHMQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	Apr 6 2009	hs	n	array	phase
solvent	cdc13	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglvi	1026	i	phase
sw	4698.4	SPECIAL		1	1
at	0.218	temp	not used	2	2
np	2048	gain	34		
fb	3000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1026		
nt	16	gt1	0.001000		
2D ACQUISITION		gzlv13	516		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.101		
tn	H1	gfs	not used		
sfrq	499.836	fn	2048		
tof	249.8	F1 PROCESSING			
tpwr	57	gf1	0.006		
pw	13.000	gfs1	not used		
DECOUPLER		proc1	lp		
dn	C13	fni	2048		
dof	-2515.1	DISPLAY			
dm	nny	sp	411.4		
dmm	ccp	wp	3381.6		
dmf	32258	sp1	1734.2		
dpwr	35	wp1	14439.8		
pxwlv1	51	rfl	1205.6		
pxw	14.700	rfp	1589.5		
HMQC		rfl1	8513.2		
j1xh	140.0	rfp1	7221.8		
nullflg	y	PLOT			
		wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	113		
		th	5		
		ai	cdc	ph	

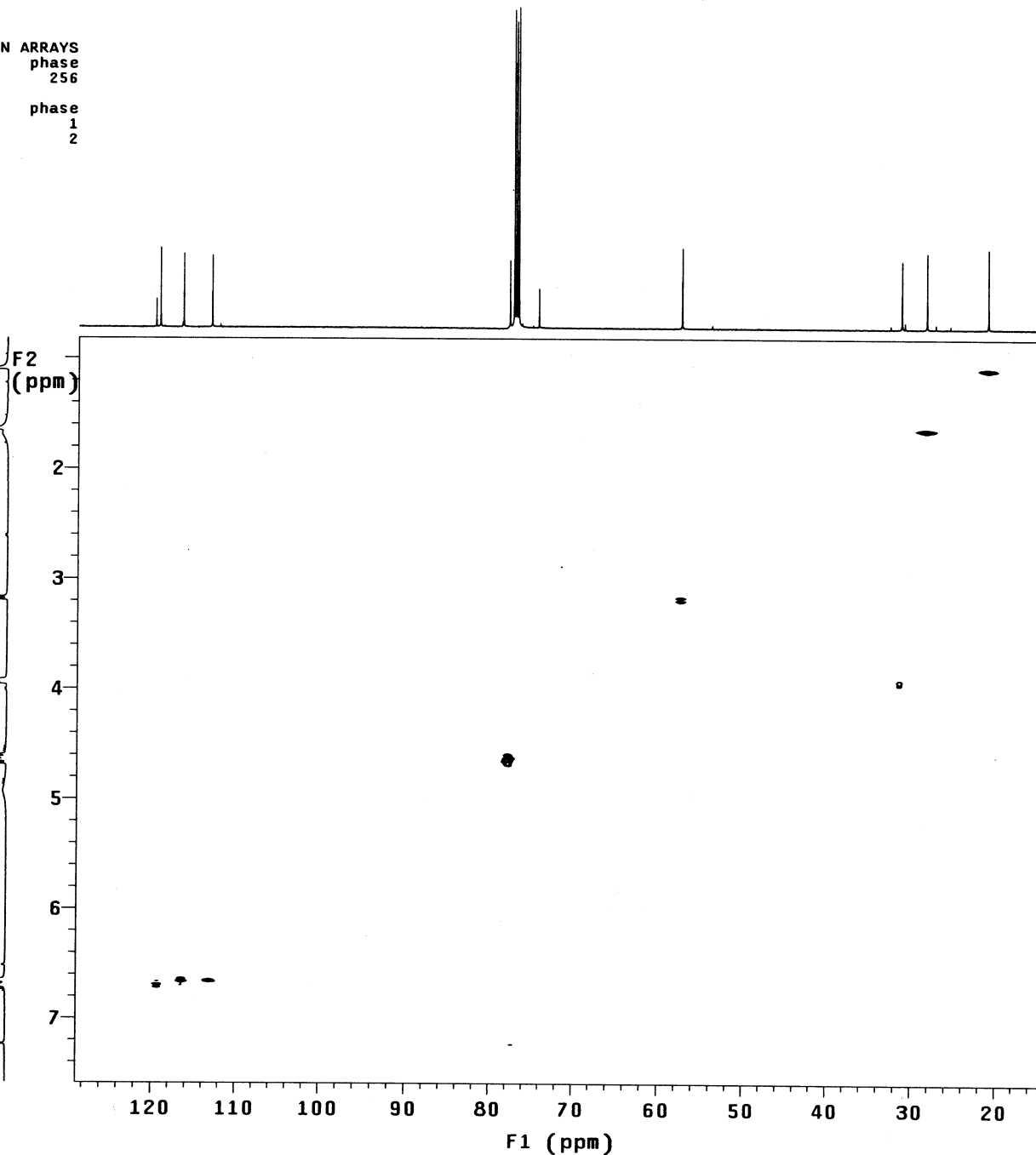
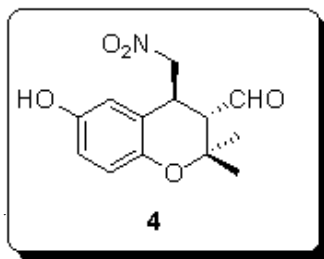


Fig S22. COSY of compound 4 (CDCl₃).

S22

PMK-01-203

exp25 gCOSY

SAMPLE		FLAGS	
date	Apr 18 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	4998.4	temp	21.0
at	0.205	gain	40
np	2048	spin	0
fb	3000	F2 PROCESSING	
ss	16	sb	-0.102
dl	1.000	sbs	not used
nt	16	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4998.4	sb1	-0.026
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.836	DISPLAY	
tof	249.8	sp	241.6
tpwr	57	wp	4993.6
pw	13.000	sp1	243.0
GRADIENTS		wp1	
gzlv11	1026	rfl	4993.6
gt1	0.001000	rfp	3382.0
gstab	0.000500	rfl1	3618.8
DECOUPLER		rfp1	
dn	C13	3618.8	
dm	nnn	PLOT	
		wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	1814
		th	5
		ai	cdc av

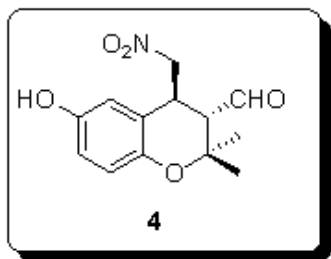
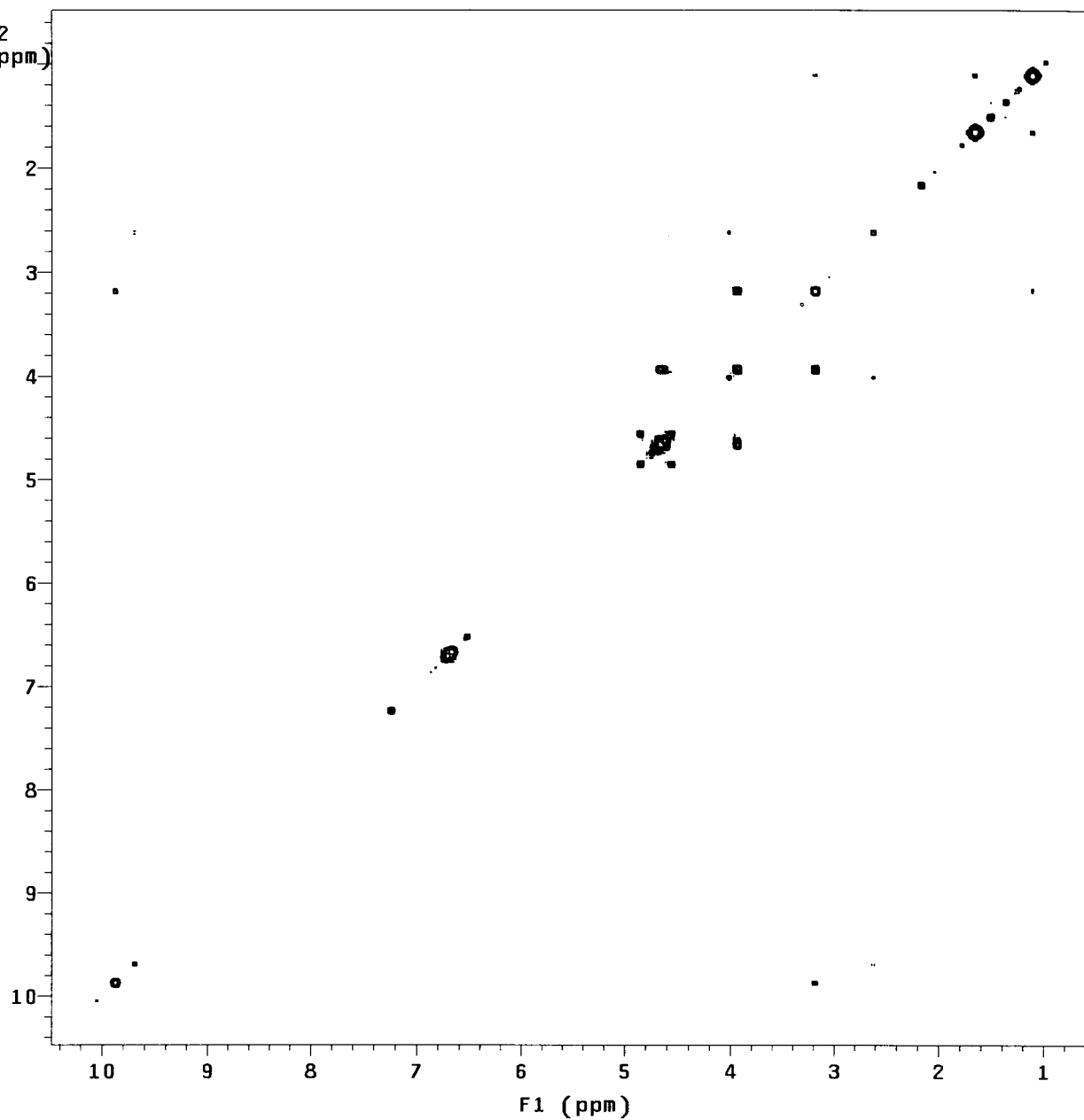
F2
(ppm)

Fig S23. NOESY of compound 4 (CDCl₃).

S23

PMK-01-203

exp27 NOESY

SAMPLE		FLAGS	
date	Apr 18 2009	hs	n
solvent	cdc13	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1026
sw	4998.4	SPECIAL	
at	0.205	temp	21.0
np	2048	gain	40
fb	3000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.095
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4998.4	F1 PROCESSING	
ni	200	gf1	0.037
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.836	fn1	2048
tof	249.8	DISPLAY	
tpwr	57	sp	243.5
pw	13.000	wp	4993.6
NOESY		sp1	244.4
mix	0.600	wp1	4993.6
PRESATURATION		rfl	3380.2
satmode	nnnn	rfp	3618.8
satpwr	0	rfl1	3379.3
satdly	0	rfp1	3618.8
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	1814
		th	1
		ai	ph

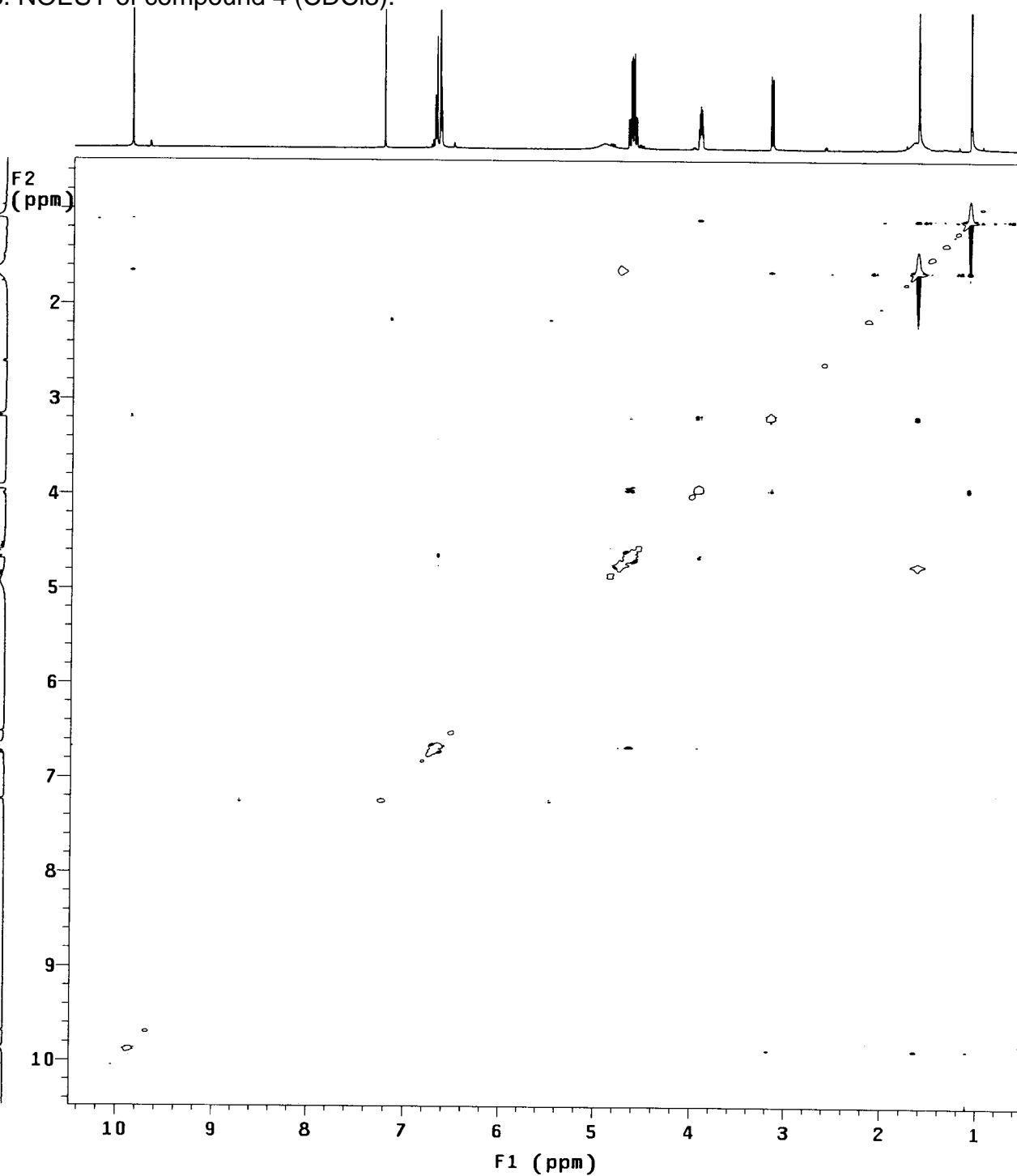
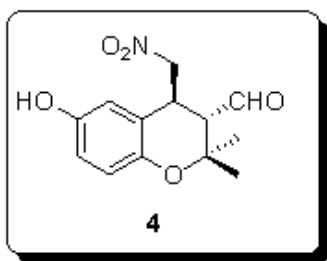


Fig S24. ¹H NMR of compound 5 (500 MHz, CDCl₃).

S24

tcw-6-6
exp22 s2pu1

SAMPLE		DEC. & VT	
date	Oct 17 2009	dfrq	125.655
solvent	cdc13	dn	013
file	exp	dpwr	30

ACQUISITION

sfrq	499.836	dof	0
tn	H1	dm	rnn
at	3.000	dmm	c
np	48000	dmf	200
sw	8000.0	dseq	1.0
fb	4000	dres	n
bs	4	homo	

PROCESSING

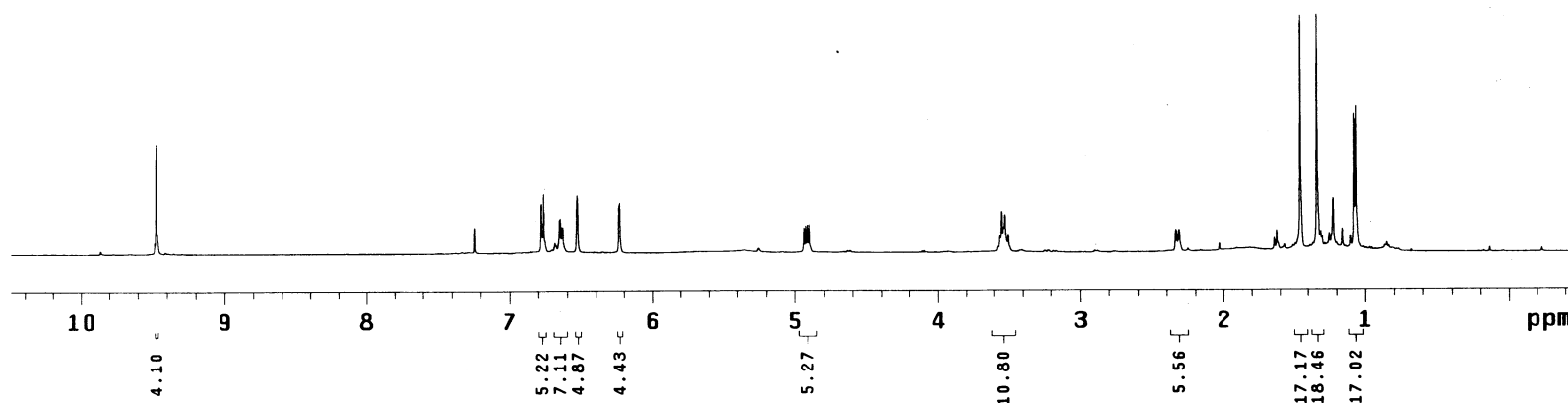
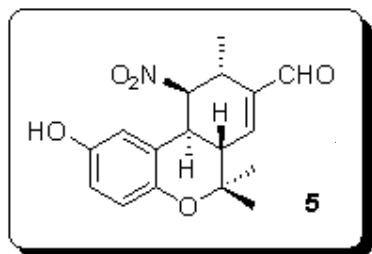
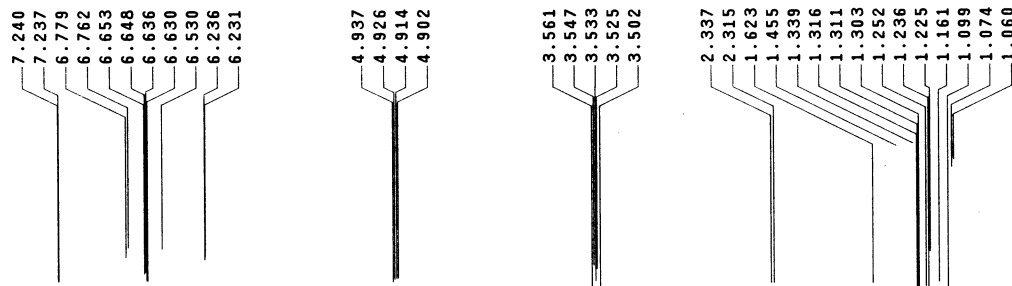
tpwr	59	wtfile	ft
pw	4.8	proc	not used
d1	1.000	fn	f
tof	499.7	math	
nt	4	werr	react
ct	4	wexp	procplot
alock	y	wbs	
gain	not used	wnt	wft

FLAGS

il	n
in	n
dp	y
hs	nn

DISPLAY

sp	-250.1
wp	5498.0
vs	32
sc	0
wc	210
hzmm	26.18
is	85.01
rfl	4646.0
rfp	3618.8
th	2
ins	100.000
nm	ph



```

tcw-6-6
exp21 s2pu1

SAMPLE
date Sep 26 2009 dfrq 499 836
solvent cdc13 dn H1
file exp dpwr 39
ACQUISITION dof 0
sfrq 125.698 dm yyy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 lb 1.00
tpwr 54 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 10000
ct 10000 werr react
alock y wexp procplot
gain not used wbs testsn
wnt

FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -1256.9
wp 27650.1
vs 50
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10981.5
rfp 9677.6
th 5
ins 100.000
nm cdc ph

```

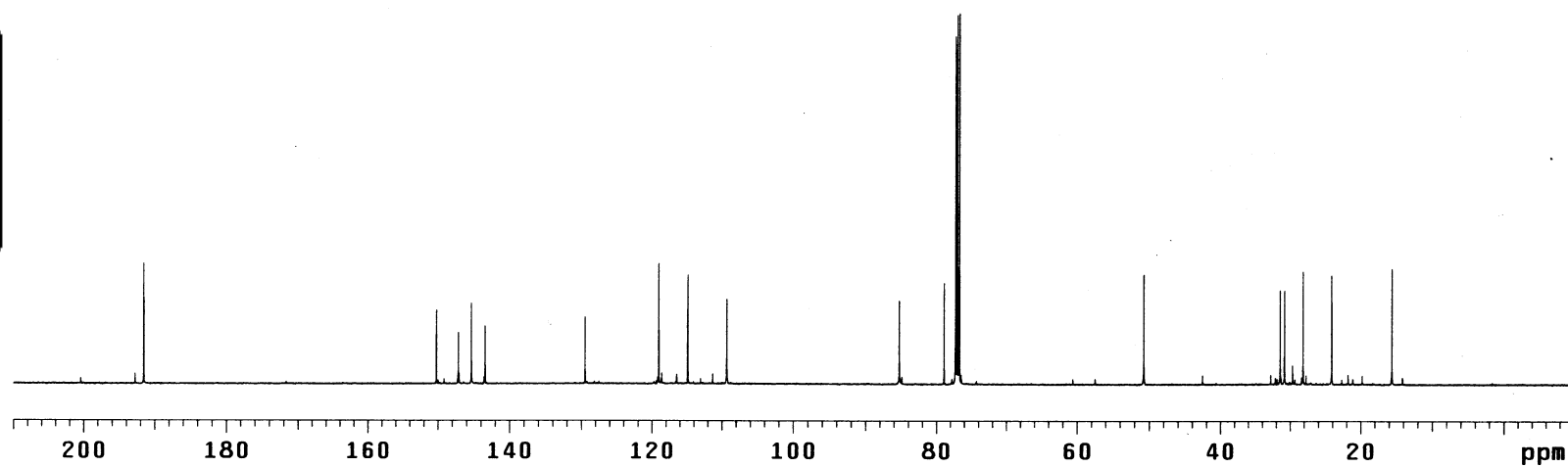
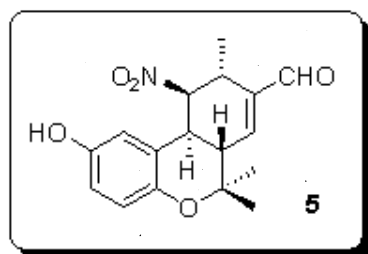
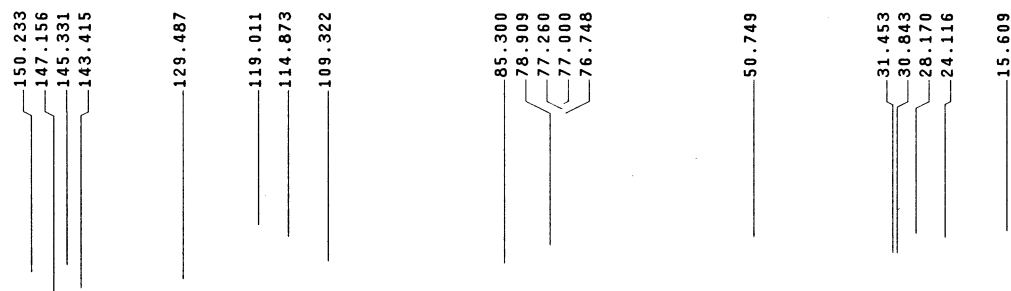


Fig S25. ¹³C NMR of compound 5 (125 MHz, CDCl₃).

Fig S26. DEPT of compound 5 (CDCl₃).

tcw-6-6

exp23 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Sep 26 2009	j1xh 140.0	array	mult
solvent	cdcl3	mult arrayed	arraydim	3
sample	undefined	SPECIAL		
ACQUISITION		temp not used	i	mult
sw	31446.5	gain 34	1	0.5
at	1.000	spin 0	2	1
np	62894	PROCESSING	3	1.5
bs	16	lb 1.00		
ss	-4	fn not used		
d1	1.000	SPECTRUM		
nt	1000	wp 27650.1		
ct	1000	sp -1257.2		
TRANSMITTER		rp -156.5		
tn	C13	lp 78.7		
tof	2512.2	ai cdc ph		
tpwr	54	REFERENCE		
pw	9.400	rfl 1269.7		
DECOUPLER		rfl 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	39	sc 0		
dm	nny	vs 118		
dmm	ccw	hzmm 131.67		
dmf	11905	th 68		
pp1v1	49			
pp	29.400			

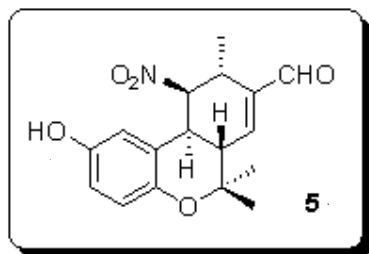
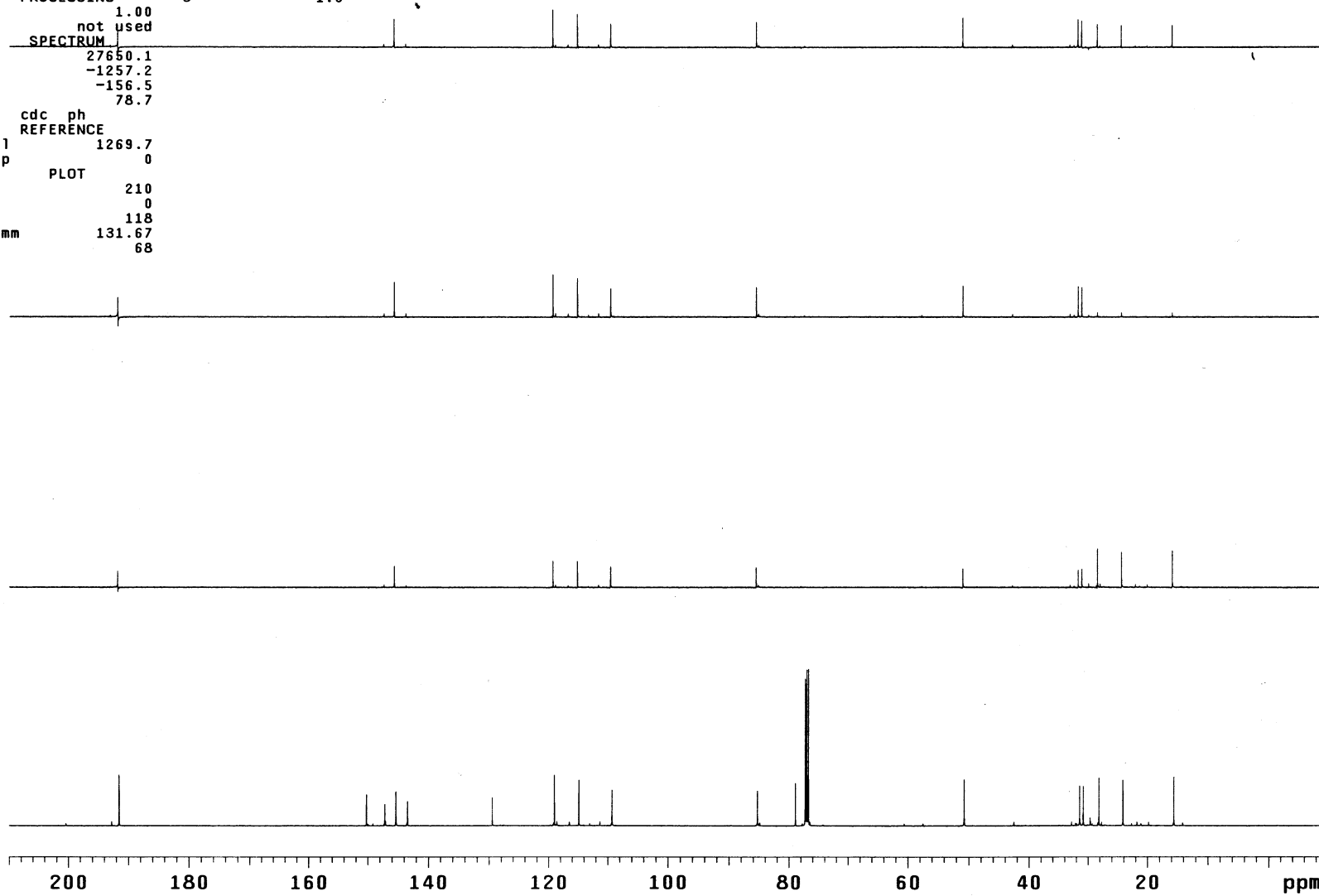


Fig S27. COSY of compound 5 (CDCl₃).

tcw-6-6

exp25 gCOSY

SAMPLE
date Sep 26 2009
solvent cdc13
sample undefined

ACQUISITION
sw 4498.4
at 0.228
np 2048
fb 3000
ss 16
dl 1.000
nt 16

2D ACQUISITION
sw1 4498.4
n1 128

TRANSMITTER
tn H1
sfrq 499.836
tof 249.8
tpwr 57
pw 13.000

GRADIENTS
gzlv11 1026
gt1 0.001000
gstab 0.000500

DECOUPLER
dn C13
dm nnn

FLAGS
hs nn
sspul n
hsglv1 1026

SPECIAL
temp not used
gain 34
spin 0

F2 PROCESSING
sb -0.114
sbs not used
fn 2048

F1 PROCESSING
sb1 -0.028
sbs1 not used
proc1 lp
fn1 2048

DISPLAY
sp 491.3
wp 4494.0
sp1 492.3
wp1 4494.0
rf1 2629.0
rfp 3116.0
rf11 2628.0
rfp1 3115.9

PLOT
wc 155.0
sc 10.0
wc2 155.0
sc2 0
vs 113
th 4
a1 cdc av

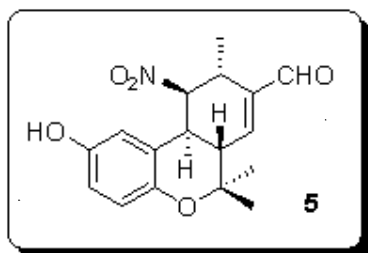
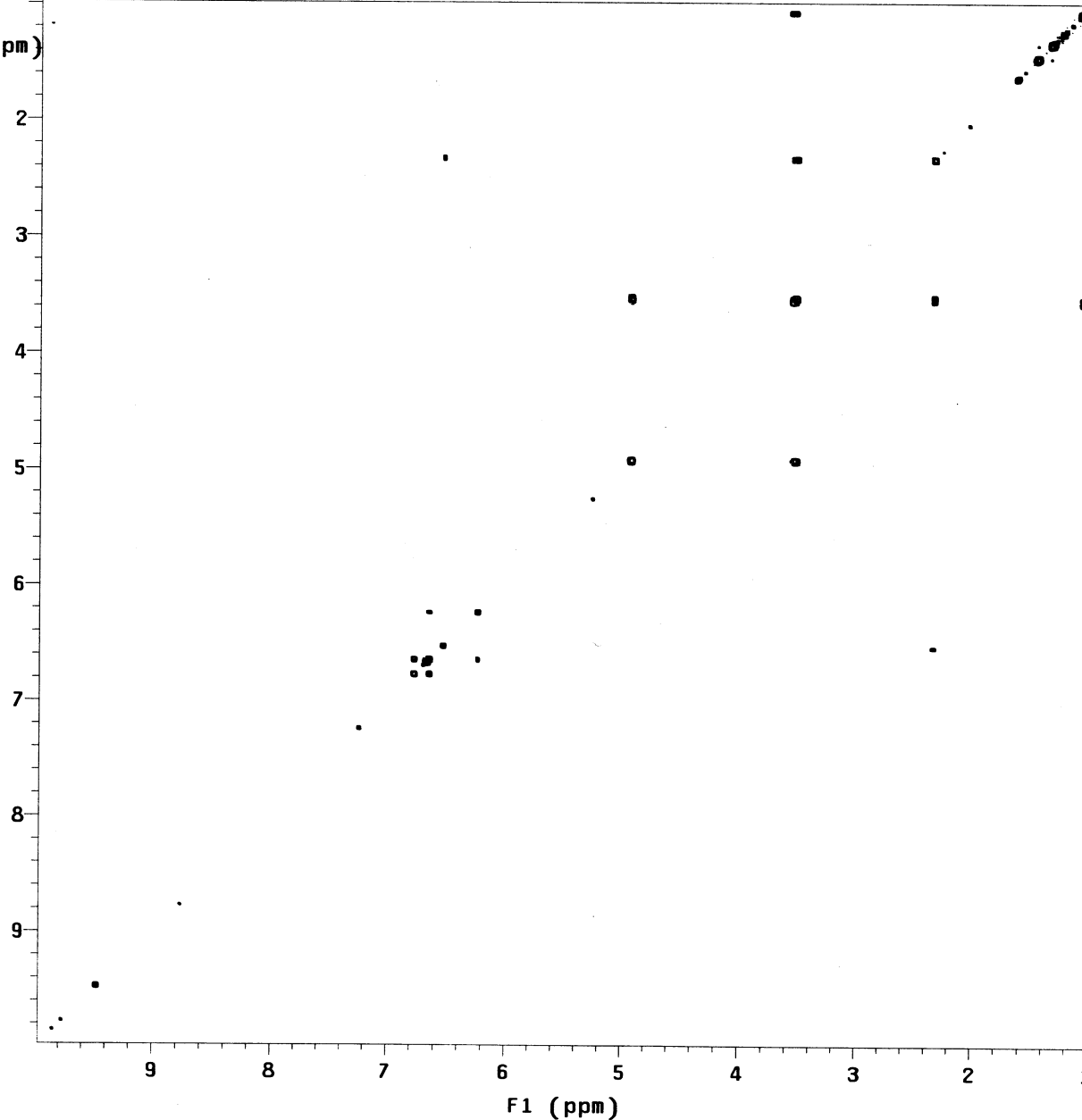
F2
(ppm)

Fig S28. HMQC of compound 5 (CDCl₃).

tcw-6-6

exp27 gHMQC

SAMPLE		FLAGS		ACQUISITION ARRAYS	
date	Sep 26 2009	hs	n	array	phase
solvent	cdcl3	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1026	i	phase
sw	4498.4	SPECIAL	1	1	
at	0.228	temp	not used	2	2
np	2048	gain	20		
fb	3000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1026		
nt	16	gt1	0.001000		
2D ACQUISITION		gzlv13	516		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.105		
tn	H1	gfs	not used		
sfrq	499.836	fn	2048		
tof	249.8	F1 PROCESSING			
tpwr	57	gf1	0.006		
pw	13.000	gfs1	not used		
DECOUPLER		proc1	lp		
dn	C13	fn1	2048		
dof	-2515.1	DISPLAY			
dm	nny	sp	512.0		
dmm	ccp	wp	3154.2		
dmf	32258	sp1	1420.1		
dpwr	35	wp1	17319.4		
pxlv1	51	rfl	1969.2		
pxw	14.700	rfp	2459.2		
HMQC		rfl1	12013.4		
j1xh	140.0	rfp1	10720.8		
nullflg	y	PLOT			
		wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	3506		
		th	3		
		ai	cdc ph		

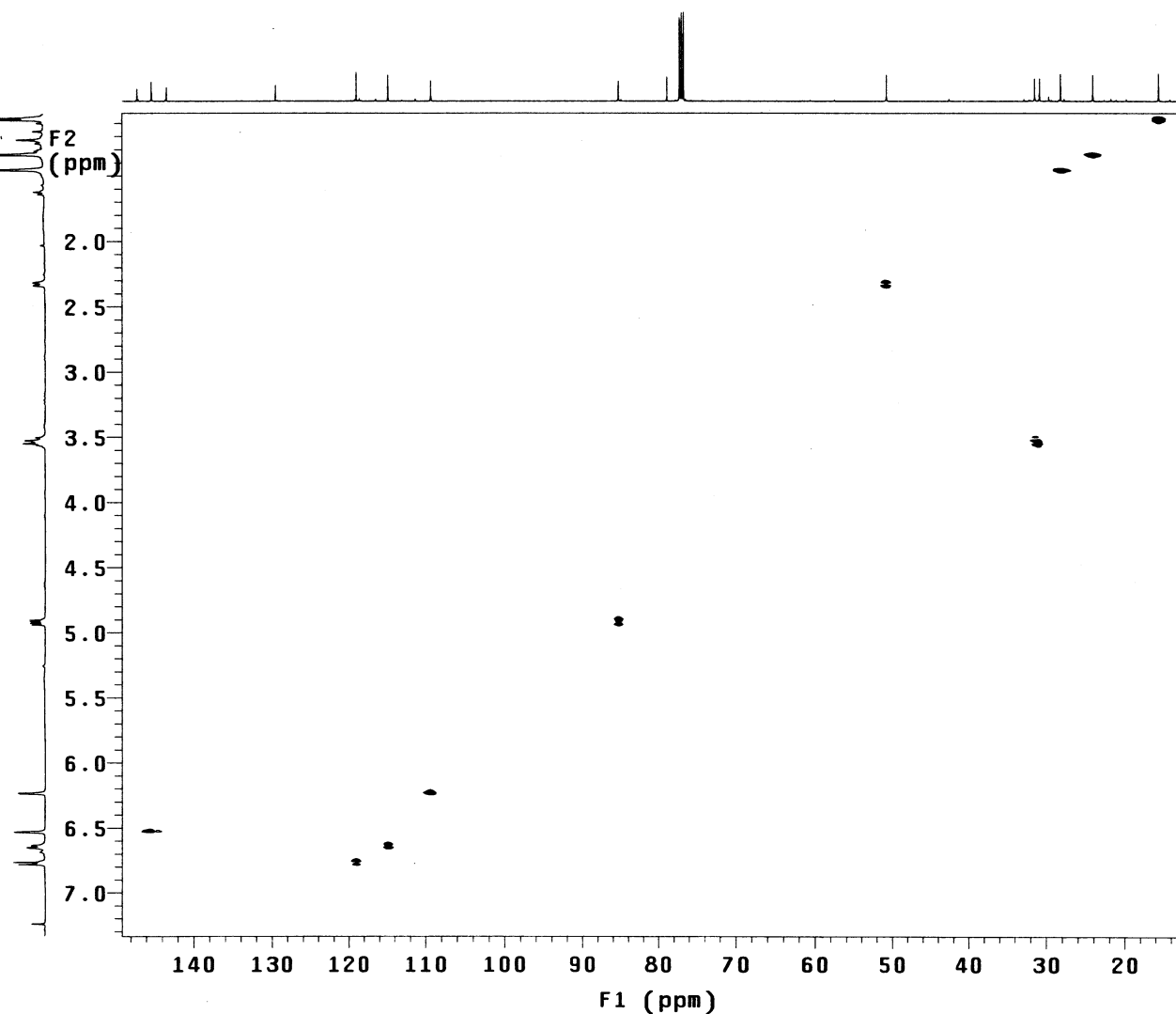
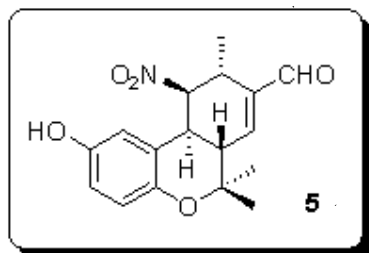


Fig S29. NOESY of compound 5 (CDCl₃).

S29

tcw-6-6

exp26 NOESY

SAMPLE		FLAGS		n
date	Sep 26 2009	hs		y
solvent	cdcl3	sspul		y
sample	undefined	PFGflg		y
ACQUISITION		hsglvi	1026	
sw	4498.4	SPECIAL	not used	
at	0.228	temp		
np	2048	gain	34	
fb	3000	spin	0	
ss	32	F2 PROCESSING		
d1	1.000	gf	0.105	
nt	8	gfs	not used	
2D ACQUISITION		fn	2048	
sw1	4498.4	F1 PROCESSING		
ni	200	gf1	0.041	
TRANSMITTER		gfs1	not used	
tn	H1	proc1	lp	
sfrq	499.836	fn1	2048	
tof	249.8	DISPLAY		
tpwr	57	sp	490.7	
pw	13.000	wp	4494.0	
NOESY		sp1	494.7	
mix	0.600	wp1	4494.0	
PRESATURATION		rfl	2629.7	
satmode	nnnn	rfp	3116.0	
satpwr	0	rfl1	2625.7	
satdly	0	rfp1	3115.9	
satfrq	0	PLOT		
DECOUPLER		wc	155.0	
dn	C13	sc	10.0	
dm	nnn	wc2	155.0	
		sc2	0	
		vs	113	
		th	1	
		ai	ph	

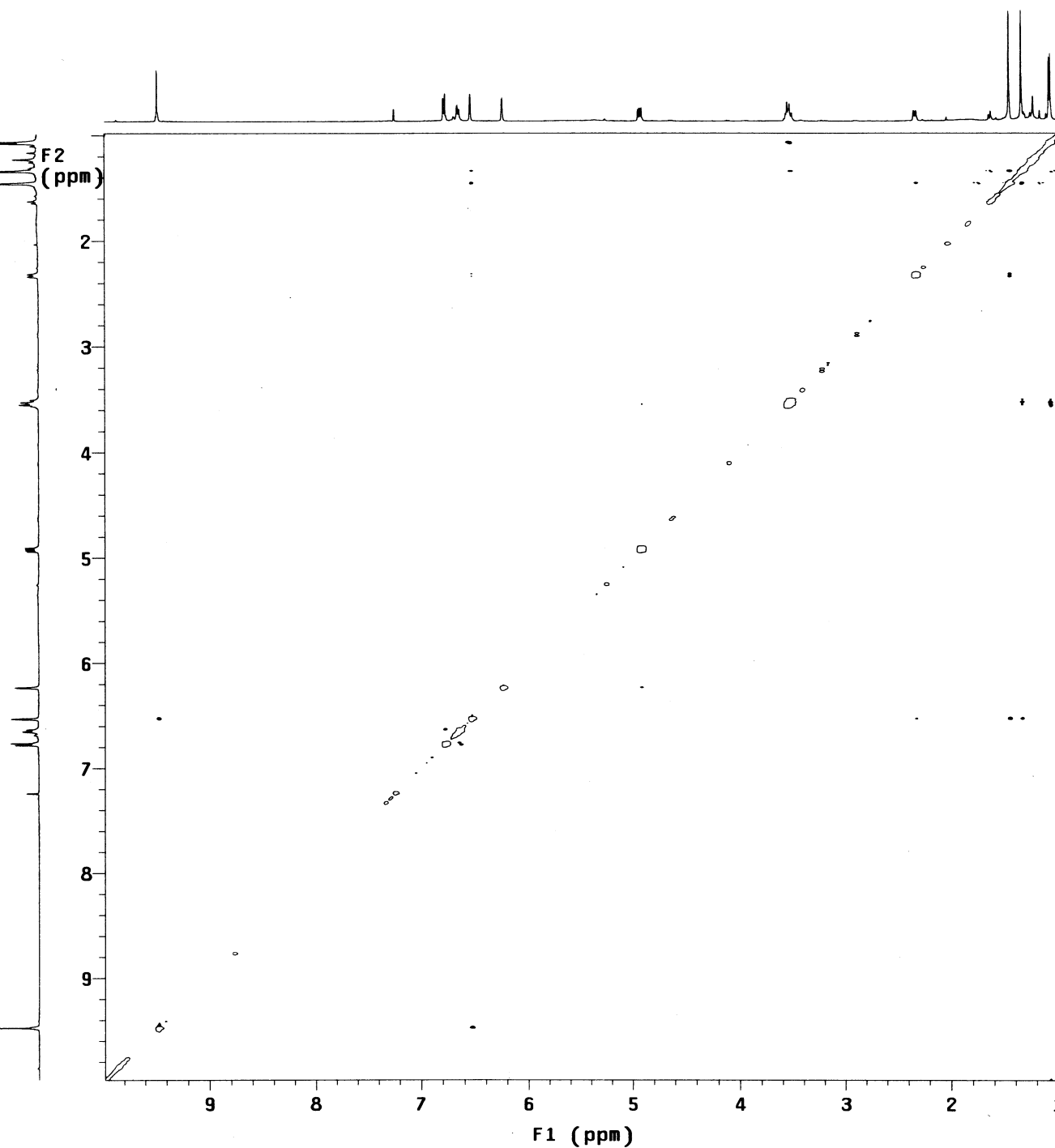
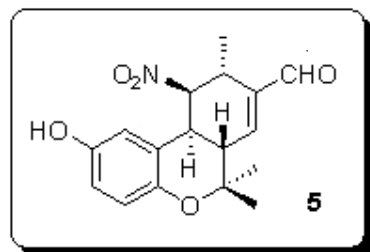


Fig S30. ¹H NMR of compound 7 (500 MHz, CDCl₃).

tcw-5-61-F2

exp23 s2pu1

SAMPLE DEC. & VT
date Nov 5 2009 dfrq 125.693
solvent cdc13 dn C13
file exp dpwr 30
ACQUISITION dof 0
sfrq 499.830 dm nnn
tn H1 dmm c
at 3.000 dmf 200
np 48000 dseq
sw 8000.0 dres 1.0
fb 4000 homo n
bs 4 temp 20.0
tpwr 59
pw 4.8 wtfile
dl 1.000 proc ft
tof 499.7 fn not used
nt 1000 math f
ct 20
alock y werr react
gain not used wexp procplot
FLAGS
il n wnt wft
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 4998.0
vs 35
sc 0
wc 210
hzmm 23.80
is 65.05
rfl 4637.9
rfp 3618.7
th 4
ins 100.000
ai ph

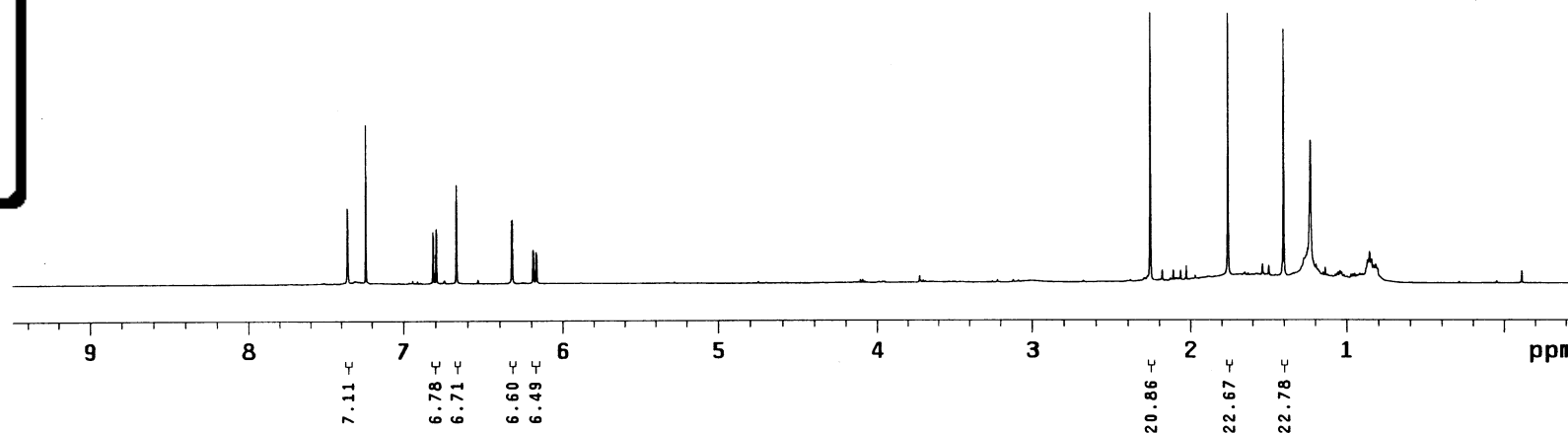
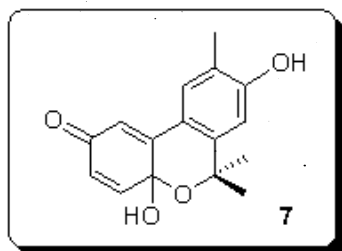
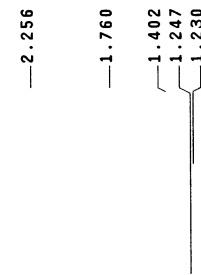
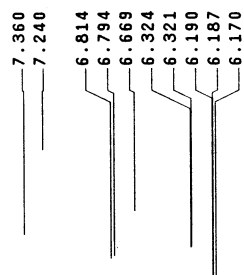


Fig S31. ¹³C NMR of compound 7 (125 MHz, CDCl₃).

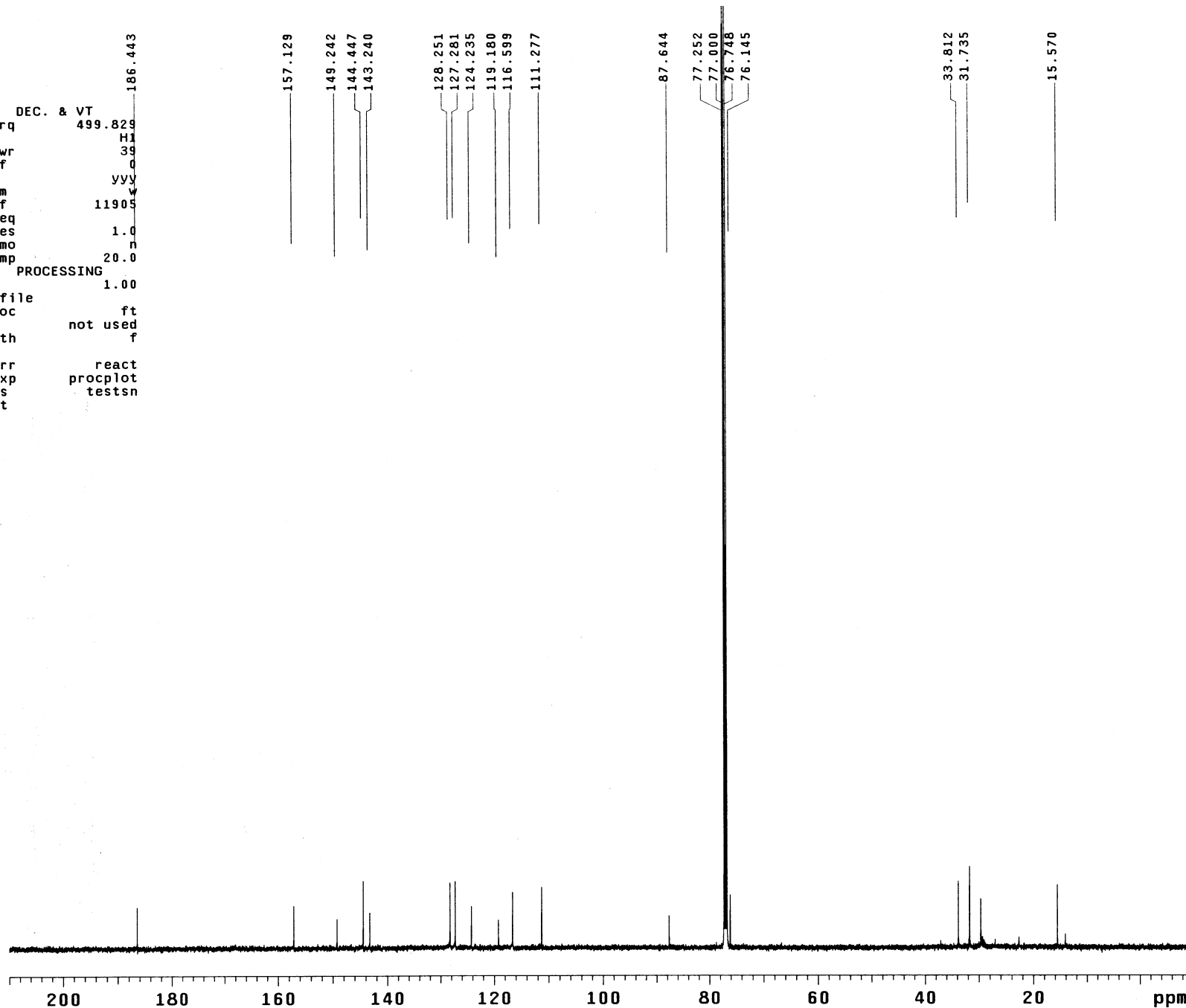
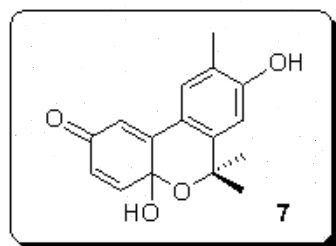
S31

tcw-6-61-F2
exp25 s2pul

SAMPLE
date Nov 5 2009
solvent cdc13
file exp
ACQUISITION
sfrq 125.696
tn C13
at 1.000
np 62894
sw 31446.5
fb 17000
bs 16
ss 2
tpwr 54
pw 4.0
d1 1.000
tof 2512.2
nt 4000
ct 4000
alock y
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1257.0
wp 27649.1
vs 200
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10981.5
rfp 9677.5
th 4
ins 100.000
nm ph

DEC. & VT
dfrq 499.829
dn H1
dpwr 39
dof 0
dm vvy
dmm w
dmf 11905
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr react
wexp procplot
wbs testsn
wnt

157.129
149.242
144.447
143.240
128.251
127.281
124.235
119.180
116.599
111.277
87.644
77.252
77.000
76.748
76.145
33.812
31.735
15.570



tcw-6-61-F2

exp24 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Nov 5 2009	j1xh 140.0	array	mult
solvent	cdcl3	mult	arrayed	3
sample	undefined	SPECIAL		
ACQUISITION		temp 20.0	i	mult
sw	31446.5	gain 20	1	0.5
at	1.000	spin 0	2	5
np	62894	PROCESSING	3	1.5
bs	16	lb 1.00		
ss	-4	fn not used		
d1	1.000	SPECTRUM		
nt	1200	wp 27649.1		
ct	1200	sp -1257.4		
TRANSMITTER		rp -61.1		
tn	C13	lp 28.8		
tof	2512.2	ai cdc ph		
tpwr	54	REFERENCE		
pw	10.500	rfl 1269.9		
DECOUPLER		rfl 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	39	sc 0		
dm	nny	vs 541		
dmm	ccw	hzmm 131.67		
dmt	11905	th 9		
pp1v1	51			
pp	24.000			

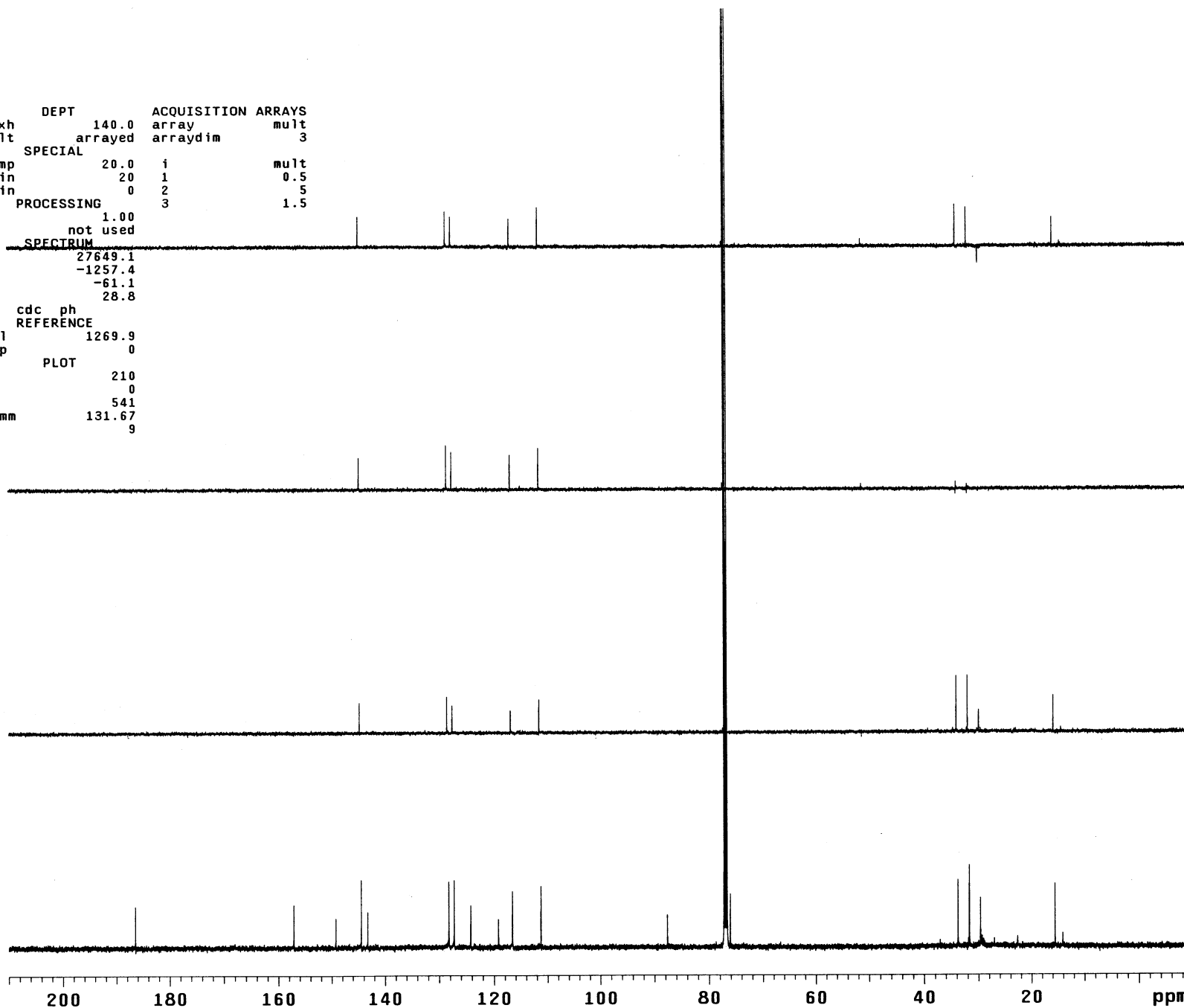
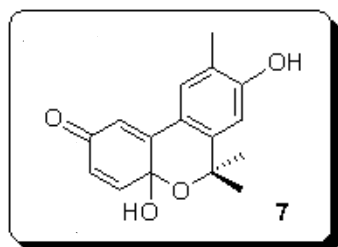
Fig S32. DEPT of compound 7 (CDCl₃).

Fig S33. COSY of compound 7 (CDCl₃).

tcw-6-61-F2

exp26 gCOSY

SAMPLE		FLAGS	
date	Nov 5 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	3348.8	temp	20.0
at	0.153	gain	34
np	1024	spin	0
fb	2000	F2 PROCESSING	
ss	16	sb	-0.076
d1	1.000	sbs	not used
nt	16	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	3348.8	sb1	-0.038
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	1024
sfrq		DISPLAY	
tof	-175.0	sp	637.4
tpwr	59	wp	3342.3
pw	13.500	sp1	637.8
GRADIENTS		wp1	
gzlv11	1026	rfl	3342.3
gt1	0.001000	rfl	2529.0
gstab	0.000500	rfl1	3159.9
DECOUPLER		rfl1	
dn	C13	3159.9	
dm	nnn	PLOT	
		wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	28
		th	6
		a1	cdc av

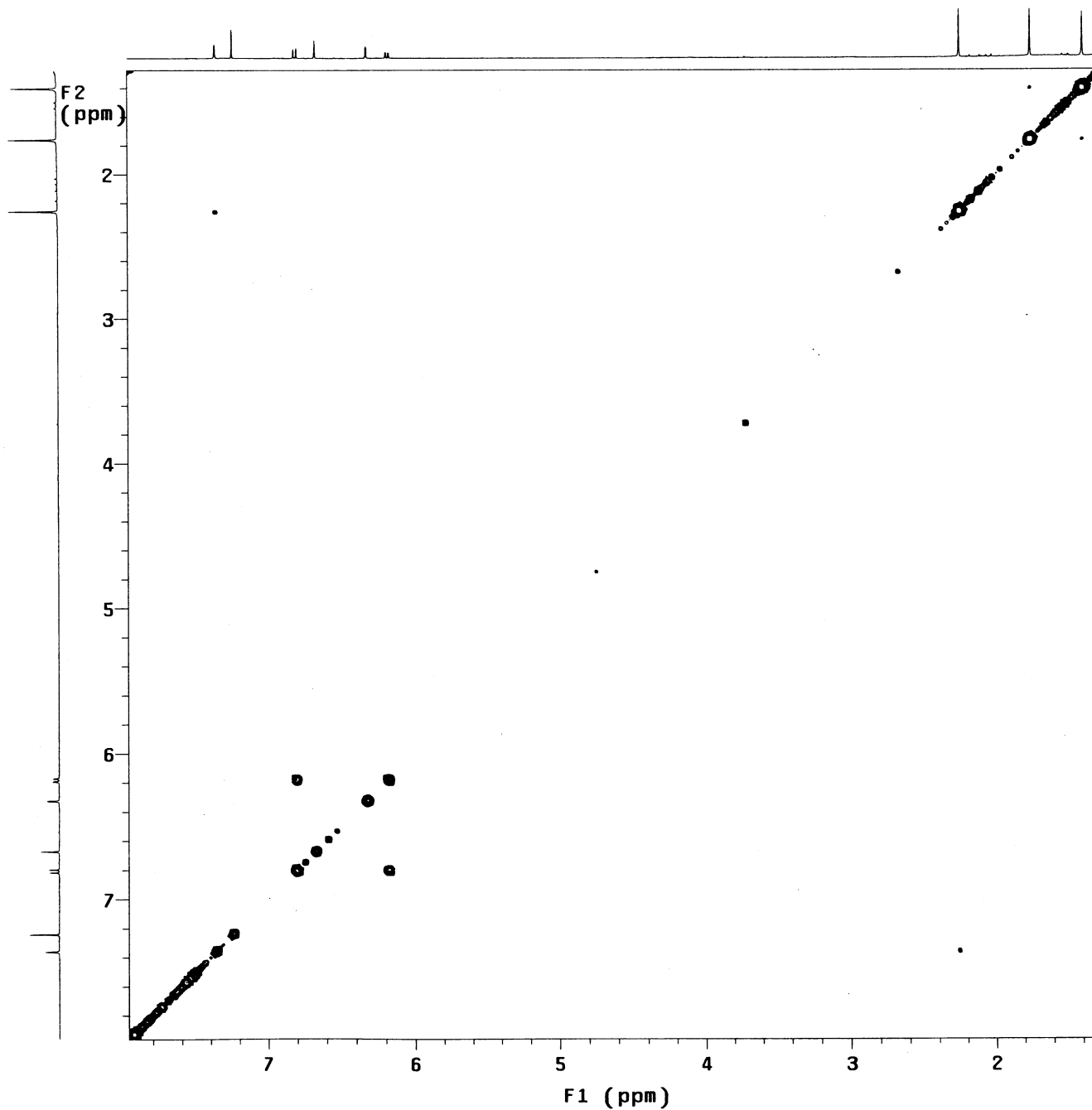
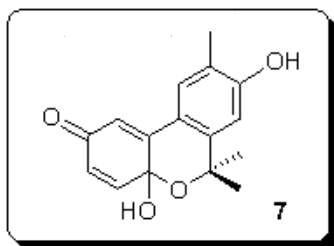


Fig S34. HSQC of compound 7 (CDCl3).

tcw-6-61-F2

exp32 gHSQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	Nov 5 2009	hs	n	array	phase
solvent	cdc13	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1026	1	phase
sw	3348.8	SPECIAL	1	1	1
at	0.153	temp	20.0	2	2
np	1024	gain	54		
fb	2000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1026		
nt	16	gt1	0.002000		
2D ACQUISITION		gzlv13	516		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.071		
tn	H1	gfs	not used		
sfrq	499.829	fn	1024		
tof	-175.0	F1 PROCESSING			
tpwr	59	gf1	0.005		
pw	13.500	gfs1	not used		
DECOUPLER		proc1	1p		
dn	C13	fn1	2048		
dof	-2515.2	DISPLAY			
dm	nny	sp	648.5		
dmm	ccp	wp	3139.5		
dmf	32258	sp1	1445.4		
dpwr	35	wp1	16964.6		
pwxlvl	51	rf1	2530.0		
pw	14.700	rfl	3158.9		
HSQC		rfl1	15958.3		
j1xh	140.0	rfl1	14649.3		
nullflg	y	PLOT			
mult	2	wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	524		
		th	6		
		ai	cdc	ph	

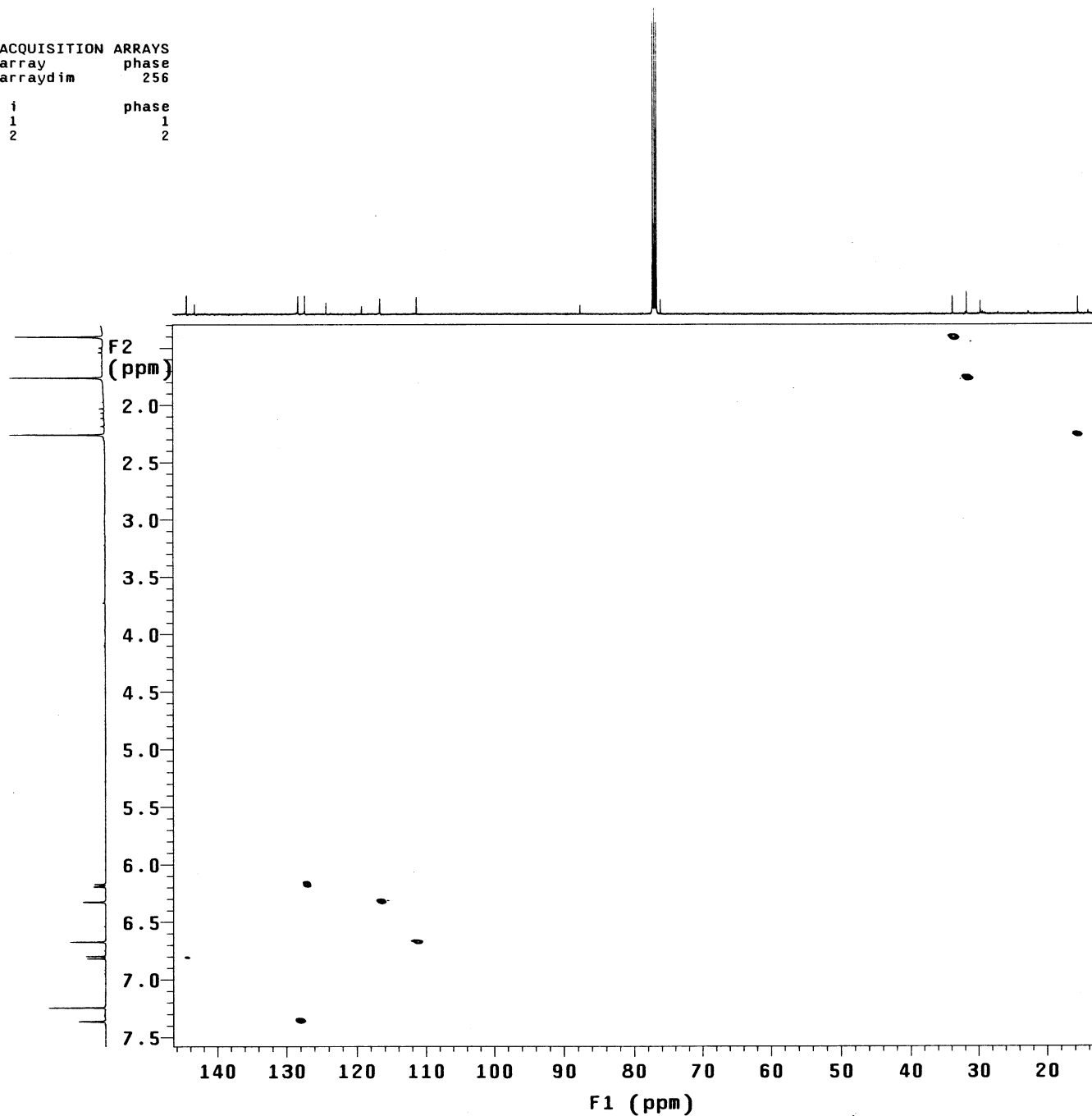
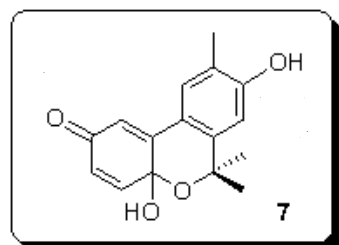


Fig S35. NOESY of compound 7 (CDCl₃).

tcw-6-61-F2

exp27 NOESY

SAMPLE		FLAGS		n
date	Nov 5 2009	hs		y
solvent	cdcl3	sspul		y
sample	undefined	PFGflg		y
ACQUISITION		hsglvi	1026	
sw	3348.8	SPECIAL		
at	0.153	temp	20.0	
np	1024	gain	54	
fb	2000	spin	0	
ss	32	F2 PROCESSING		
dl	1.000	gf	0.071	
nt	8	gfs	not used	
2D ACQUISITION		fn	1024	
sw1	3348.8	F1 PROCESSING		
ni	200	gf1	0.027	
TRANSMITTER		gfs1	not used	
tn	H1	fn1	1024	
sfrq	499.829	DISPLAY		
tof	-175.0	sp	650.5	
tpwr	59	wp	3244.2	
pw	13.500	sp1	654.1	
NOESY		wp1	3244.2	
mix	0.600	rfl	2528.0	
PRESATURATION		rfp	3158.9	
satmode	nnnn	rfl1	2524.4	
satpwr	0	rfp1	3158.9	
satdly	0	PLOT		
satfrq	0	wc	155.0	
DECOUPLER		sc	10.0	
dn	C13	wc2	155.0	
dm	nnn	sc2	0	
		vs	301	
		th	4	
		ai	ph	

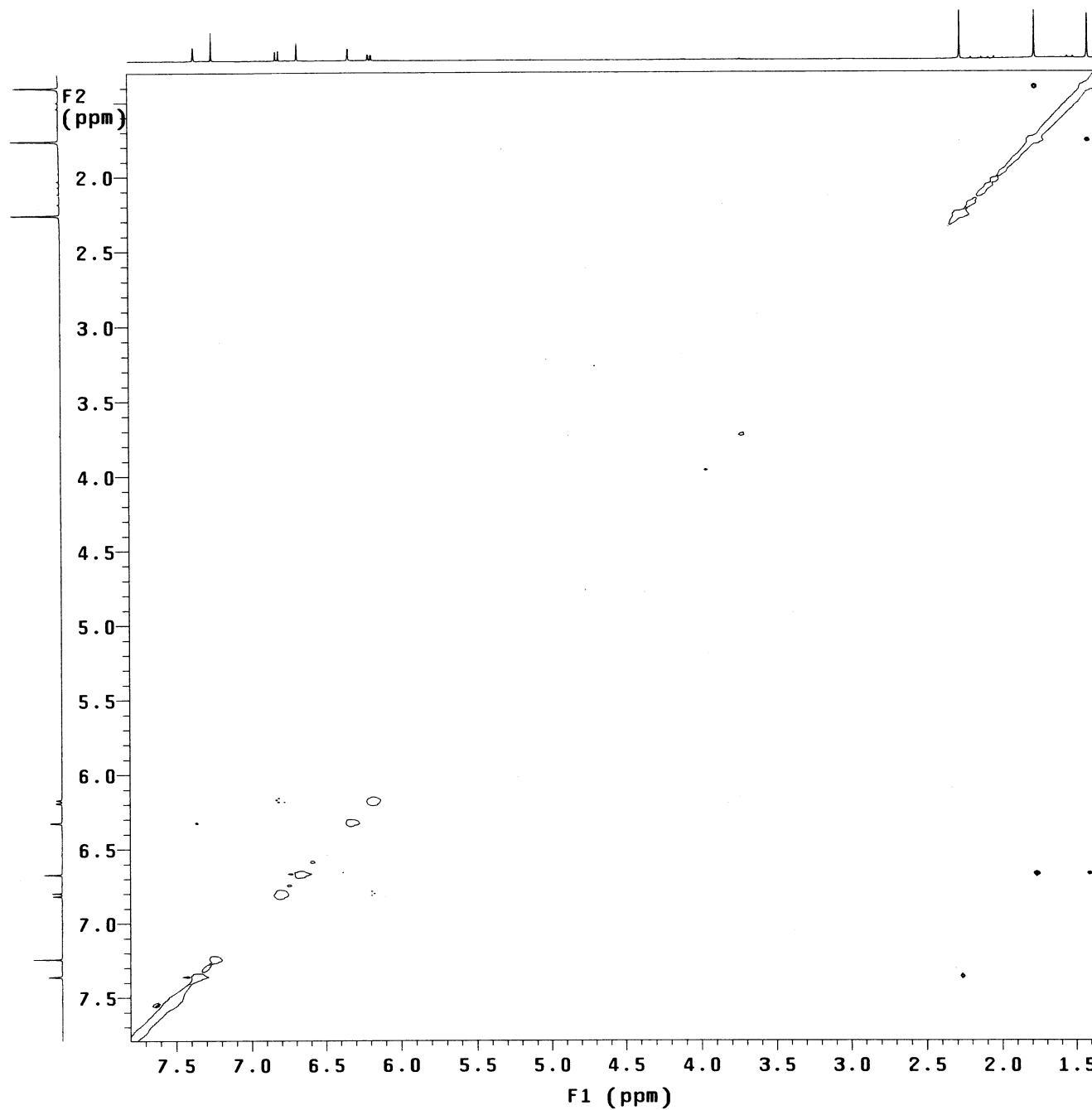
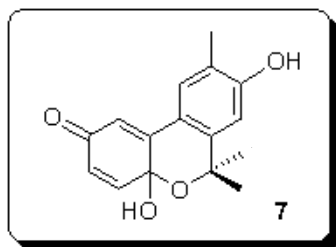


Fig S36. ¹H NMR of compound 8 (500 MHz, CDCl₃).

PMK-01-204

exp31 s2pul

SAMPLE
 date Mar 31 2009 dfrq 125.695
 solvent cdc13 dn C13
 file /export/home/~ dpwr 30
 vnmr1/vnmrSYS/data~ dof 0
 /PMK/PMK-01-204/H.~ dm hnn
 fid dmm c
 dm 200
 ACQUISITION
 sfrq 499.836 dseq
 tn H1 dres 1.0
 at 3.000 homo n
 np 48000
 sw 8000.0 wtfile
 fb 4000 proc
 bs 4 fn not used
 tpwr 57 math f
 pw 4.8
 d1 1.000 werr
 tof 499.7 wexp react
 nt 4 wbs
 ct 4 wnt
 wft
 alock y
 gain not used
 FLAGS
 il n
 in n
 dp y
 hs nn
 DISPLAY
 sp -250.1
 wp 5498.0
 vs 41
 sc 0
 wc 210
 hzmm 26.18
 is 147.72
 rfl 4632.8
 rfp 3618.8
 th 2
 ins 100.000
 nm ph

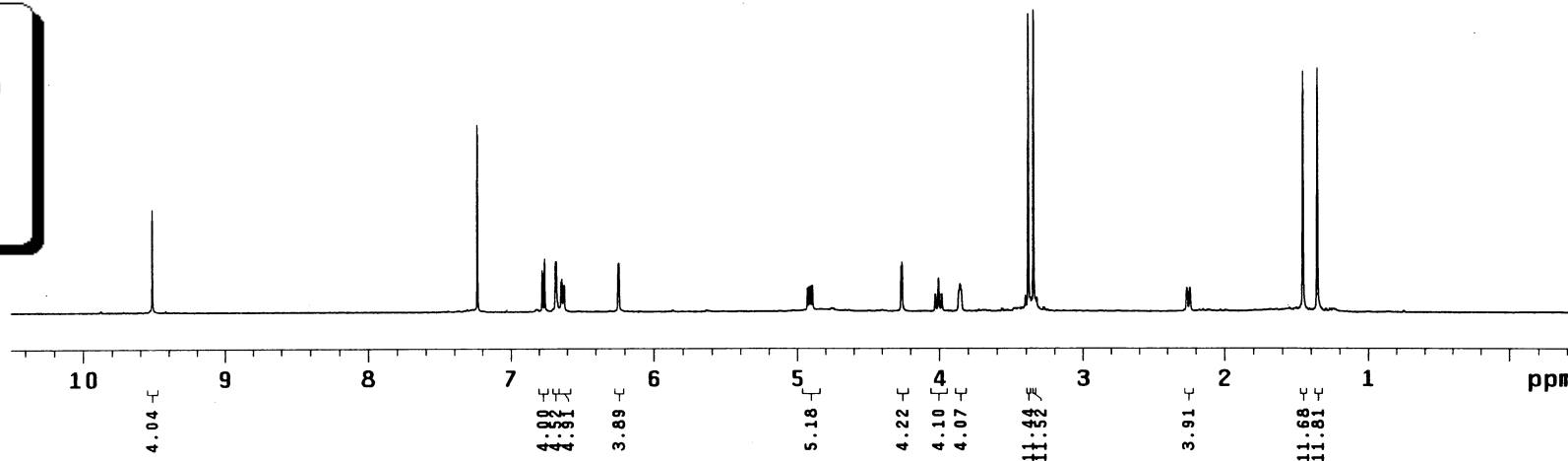
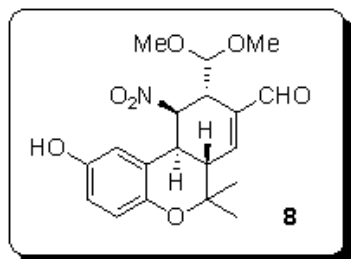
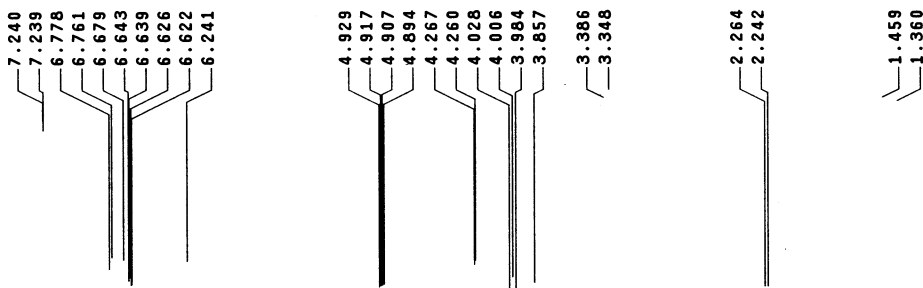


Fig S37. ¹³C NMR of compound 8 (125 MHz, CDCl₃).

S37

PMK-01-204
exp43 s2pul

SAMPLE		DEC. & VT	
date	Mar 31 2009	dfrq	499.836
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION			
sfrq	125.698	dof	0
tn	C13	dm	yyy
at	1.000	dmm	w
np	62894	dmf	11905
sw	31446.5	dseq	
fb	17000	dres	1.0
bs	16	homo	n
PROCESSING			
ss	2	lb	1.00
tpwr	54	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	20000		
ct	9552	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
flags		wnt	
fl	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	27650.1		
vs	326		
sc	0		
wc	210		
hzmm	131.67		
is	500.00		
rfl	10981.5		
rfp	9677.6		
th	7		
ins	100.000		
nm	ph		

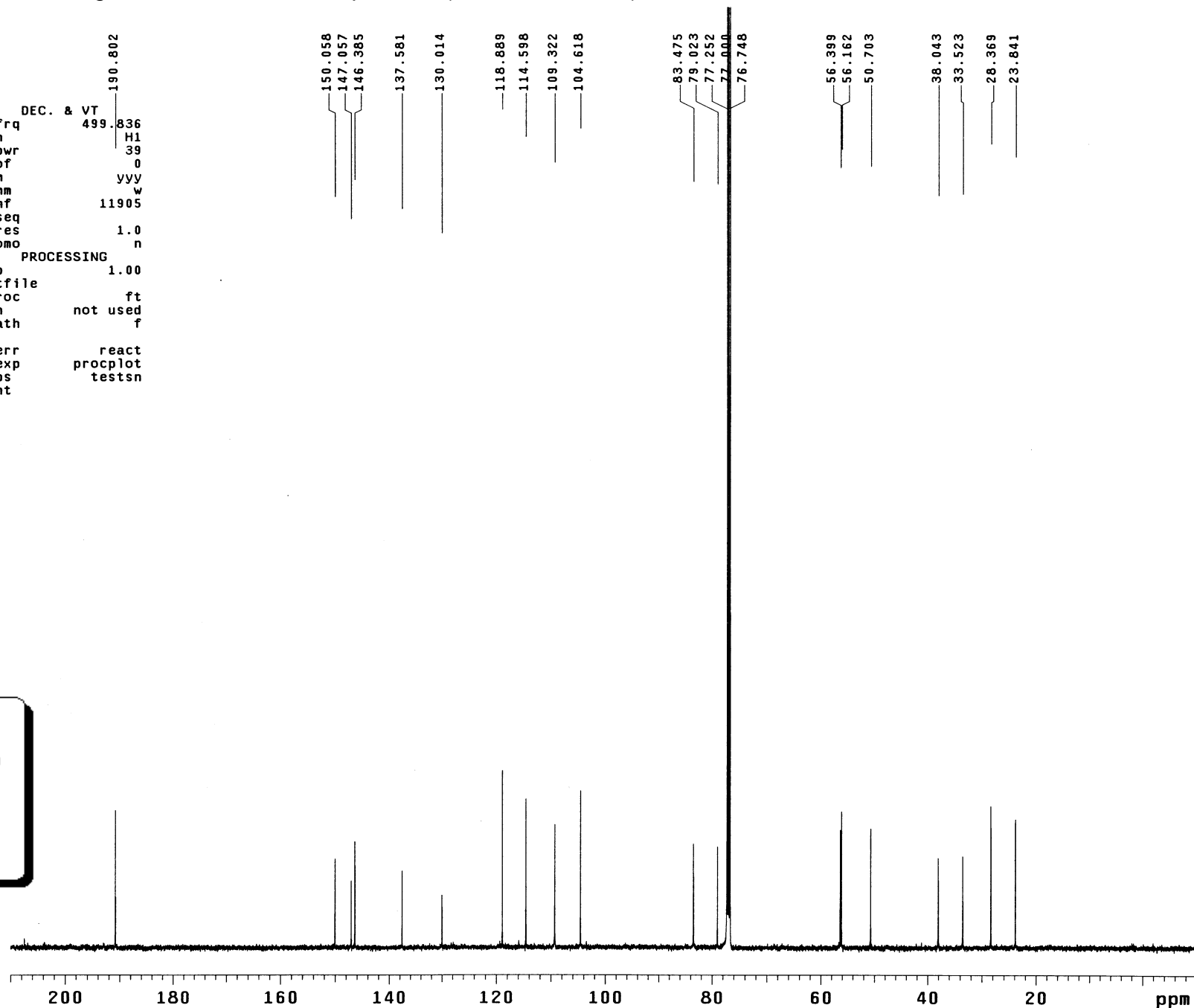
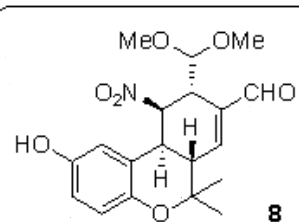


Fig S38. DEPT of compound 8 (CDCl₃).

S38

PMK-01-204

exp21 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	Apr 28 2009	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	54	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	3000	wp	27690.1		
ct	2656	sp	-1257.2		
TRANSMITTER		rp	-57.8		
tn	C13	lp	69.0		
tof	2512.2	al	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.7		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	566		
dmm	ccw	hzmm	131.67		
dmf	11905	th	68		
pp1v1	49				
pp	29.400				

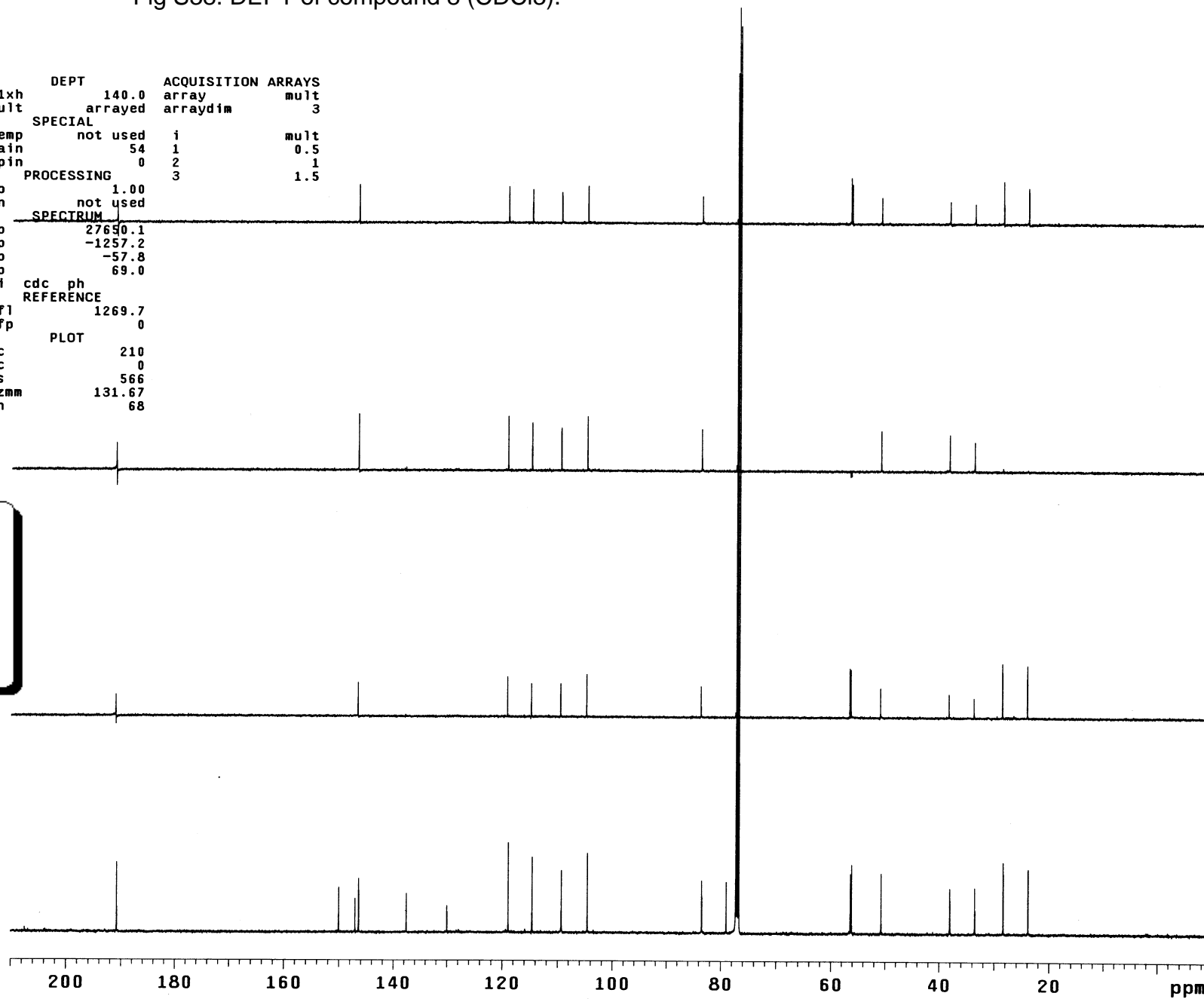
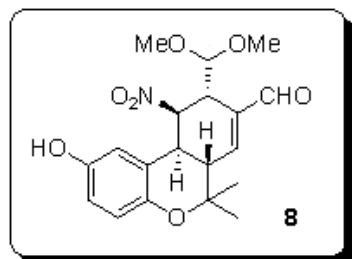


Fig S39. HSQC of compound 8 (CDCl₃).

S39

PMK-01-204

exp18 gHSQC

SAMPLE		FLAGS	ACQUISITION ARRAYS	
date	Apr 15 2009	hs	n	array
solvent	cdc13	sspul	y	arraydim
sample	undefined	PFGflg	y	phase
ACQUISITION		hsglv1	1026	256
sw	4498.4	SPECIAL	1	phase
at	0.228	temp	21.0	1
np	2048	gain	60	2
fb	3000	spin	0	
ss	32	GRADIENTS		
d1	1.000	gzlv11	1026	
nt	16	gt1	0.002000	
2D ACQUISITION		gzlv13	516	
sw1	21367.5	gt3	0.001000	
ni	128	gstab	0.000500	
phase	arrayed	F2 PROCESSING		
TRANSMITTER		gf	0.105	
tn	H1	gfs	not used	
sfrq	499.836	fn	2048	
tof	249.8	F1 PROCESSING		
tpwr	57	gf1	0.006	
pw	13.000	gfs1	not used	
DECOUPLER		procl	1p	
dn	C13	fn1	2048	
dof	-2515.1	DISPLAY		
dm	nny	sp	512.6	
dmm	ccp	wp	3409.0	
dmf	32258	sp1	2173.8	
dpwr	35	wp1	16589.0	
pwxlvl	51	rf1	2633.2	
pw	14.700	rfl	3119.5	
HSQC		rfl1	15030.0	
j1xh	140.0	rflp1	13739.9	
nullflg	y	PLOT		
mult	2	wc	150.0	
		sc	6.2	
		wc2	150.2	
		sc2	0	
		vs	113	
		th	4	
		al	cdc	ph

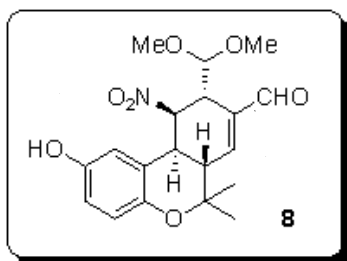
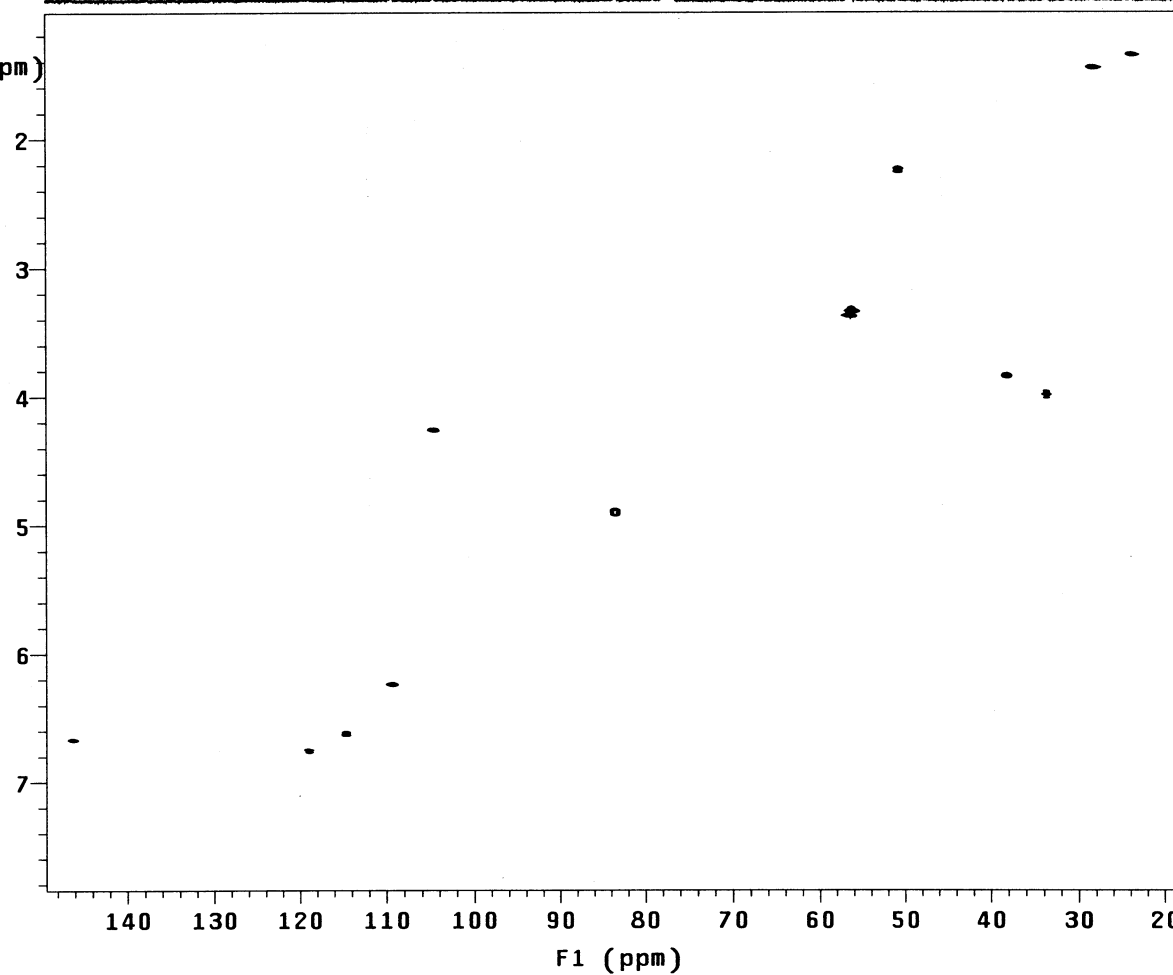
F2
(ppm)

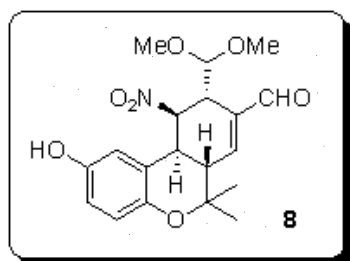
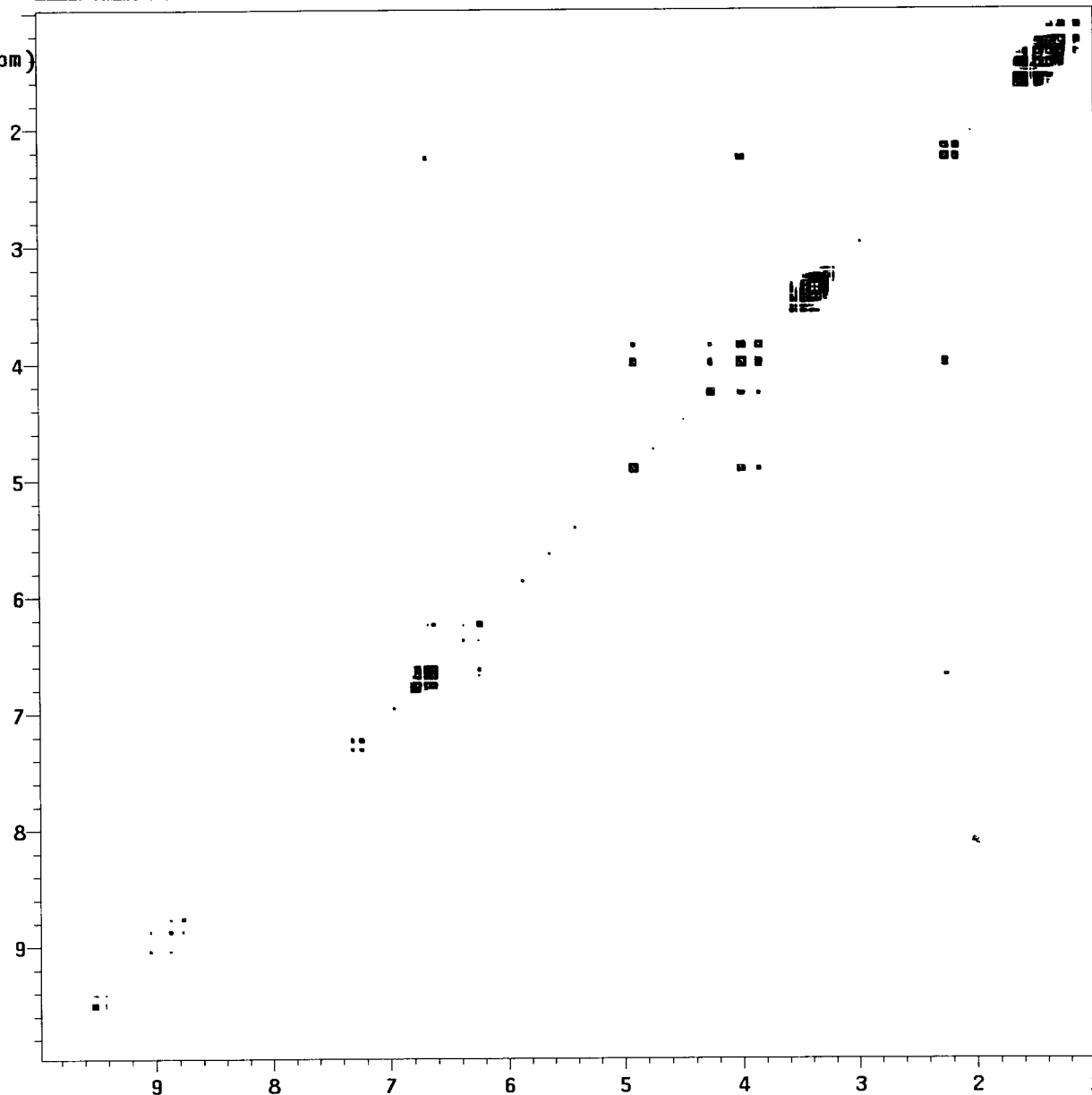
Fig S40. COSY of compound 8 (CDCl₃).

S40

PMK-01-204

exp12 gCOSY

SAMPLE		FLAGS	
date	Apr 27 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglvl	1026
ACQUISITION		SPECIAL	not used
sw	4498.4	temp	40
at	0.228	gain	0
np	2048	spin	0
fb	3000	F2 PROCESSING	
ss	16	sb	-0.114
d1	1.000	sbs	not used
nt	16	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4498.4	sb1	-0.006
n1	128	sbs1	not used
TRANSMITTER		proc1	1p
tn	H1	fni	2048
sfrq	499.836	DISPLAY	
tof	249.8	sp	488.8
tpwr	57	wp	4494.0
pw	13.000	sp1	4494.0
GRADIENTS		wp1	2635.0
gzlv11	1026	rfl	3119.5
gt1	0.001000	rfp	2632.1
gstab	0.000500	rfl1	3119.4
DECOUPLER		rfp1	
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	113
		th	7
		a1	cdc av

F2
(ppm)

F1 (ppm)

Fig S41. NOESY of compound 8 (CDCl₃).

PMK-01-204

exp22 NOESY

SAMPLE		FLAGS		
date	Apr 28 2009	hs		n
solvent	cdc13	sspu1		y
sample	undefined	PFGflg		y
ACQUISITION		hsglv1	1026	
sw	4498.4	SPECIAL		
at	0.228	temp	not used	
np	2048	gain	54	
fb	3000	spin	0	
ss	32	F2 PROCESSING		
d1	1.000	gf	0.105	
nt	16	gfs	not used	
2D ACQUISITION		fn	2048	
sw1	4498.4	F1 PROCESSING		
ni	200	gf1	0.041	
TRANSMITTER		gfs1	not used	
tn	H1	proc1	lp	
sfrq	499.836	fn1	2048	
tof	249.8	DISPLAY		
tpwr	57	sp	489.5	
pw	13.000	wp	4494.0	
NOESY		sp1	494.4	
mix	0.600	wp1	4494.0	
PRESATURATION		rfl	3133.7	
satmode	nnnn	rfp	3618.8	
satpwr	0	rfl1	3128.8	
satdly	0	rfl1	3618.8	
satfrq	0	PLOT		
DECOUPLER		wc	155.0	
dn	C13	sc	10.0	
dm	nnn	wc2	155.0	
		sc2	0	
		vs	1814	
		th	1	
		ai		
		ph		

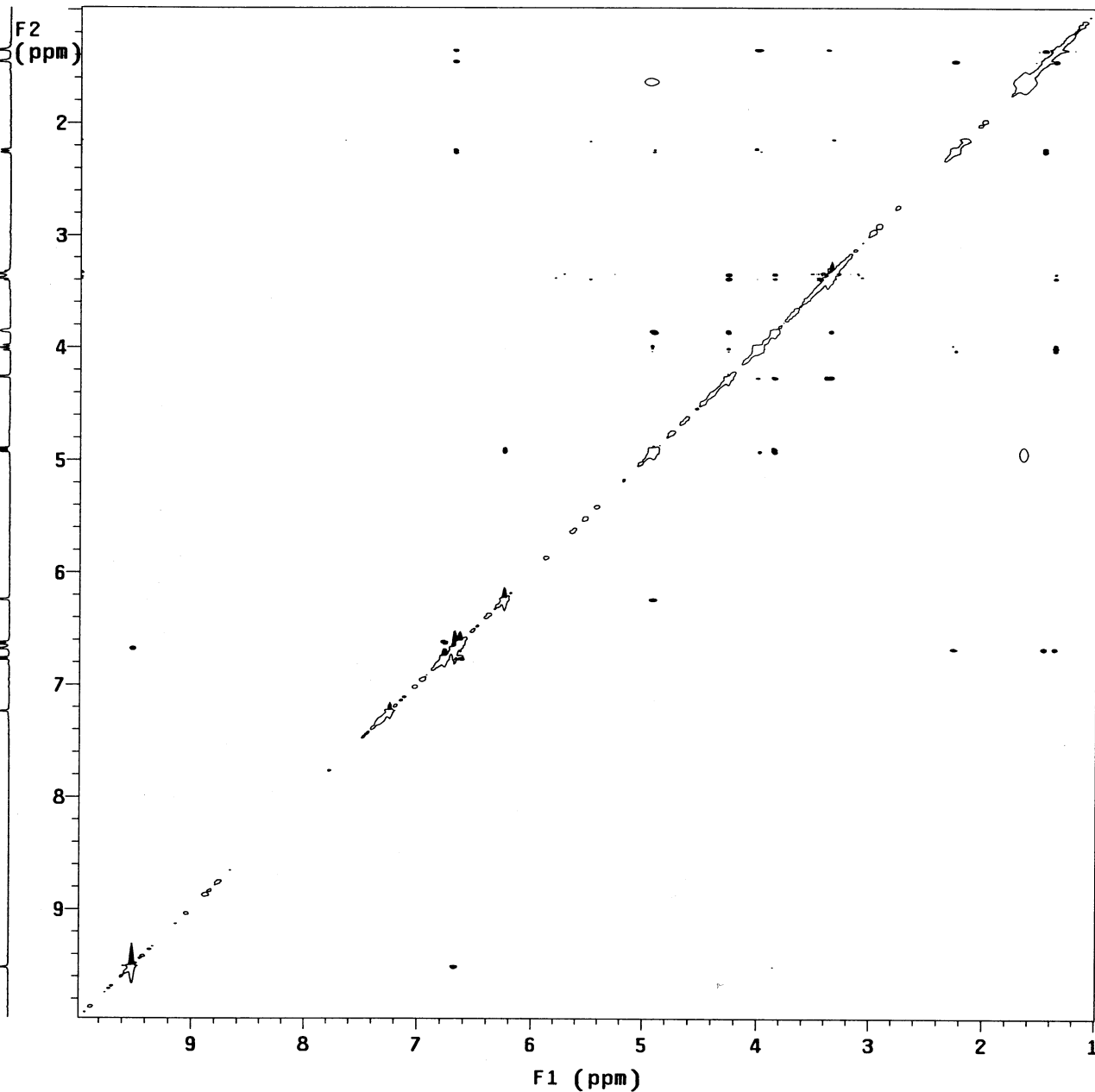
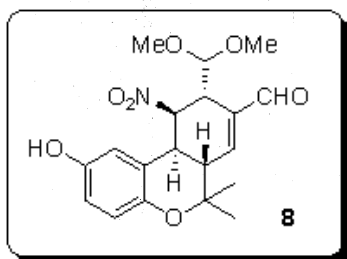


Fig S42. ¹H NMR of compound 9 (500 MHz, CDCl₃).

S42

PMK-01-206

exp11 s2pul

SAMPLE DEC. & VT
 date May 1 2009 dfrq 125.695
 solvent cdc13 dn C13
 file exp dpwr 30
 ACQUISITION dof 0
 sfrq 499.836 dm nnn
 tn H1 dmm c
 at 3.000 dmf 200
 np 48000 dseq
 sw 8000.0 dres 1.0
 fb 4000 homo n
 bs 4
 tpwr 57
 pw 4.8
 d1 1.000
 tof 499.7
 nt 4
 ct 4
 alock y
 gain not used
 FLAGS
 il n
 in n
 dp y
 hs nn
 DISPLAY
 sp -250.1
 wp 4998.3
 vs 113
 sc 0
 wc 210
 hzmm 23.80
 is 148.31
 rfl 4631.3
 rfp 3618.8
 th 2
 ins 100.000
 nm ph
 PROCESSING
 wtfile
 proc ft
 fn not used
 math f
 werr react
 wexp procplot
 wbs
 wnt wft

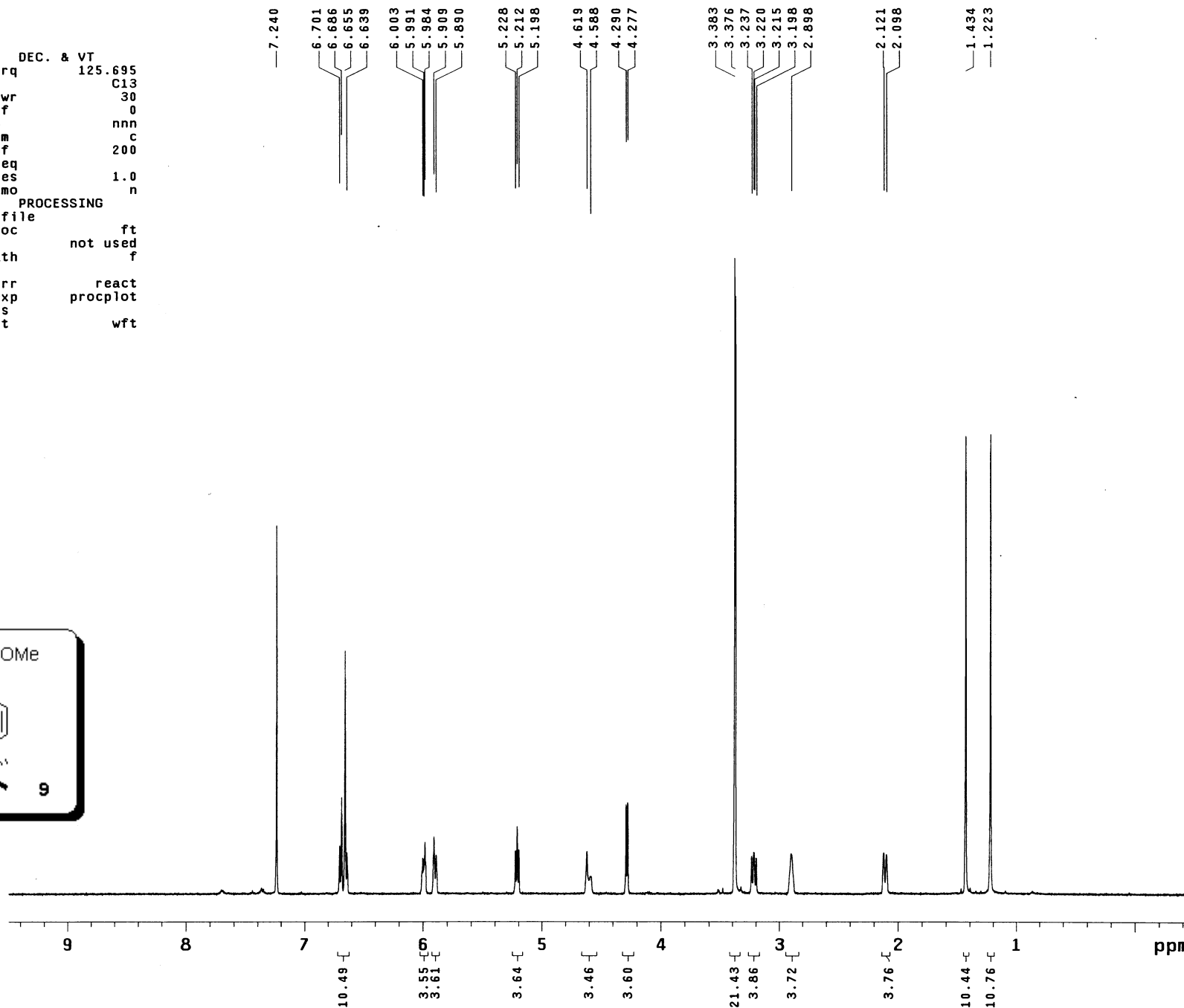
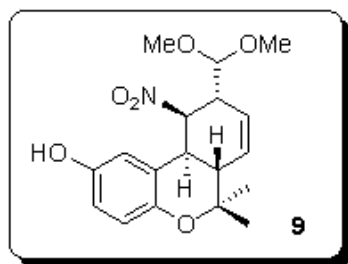
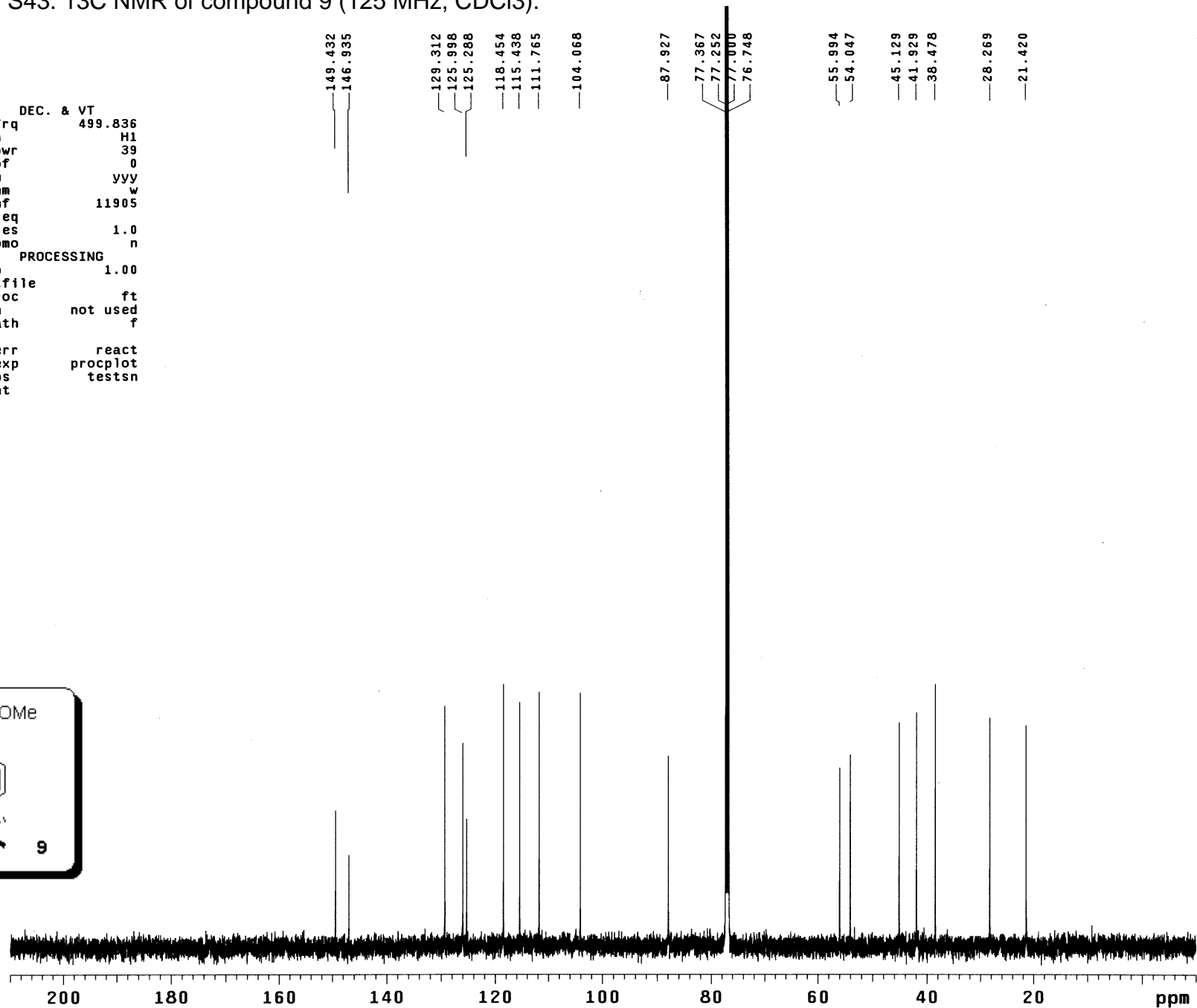
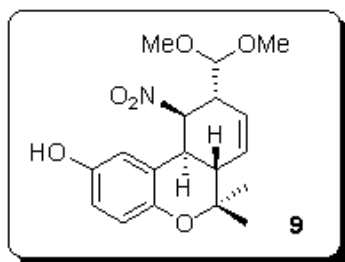


Fig S43. ¹³C NMR of compound 9 (125 MHz, CDCl₃).

PMK-01-206

exp12 s2pu1

SAMPLE DEC. & VT
date May 1 2009 dfrq 499.836
solvent cdc13 dn H1
file exp dpwr 39
ACQUISITION dof 0
sfrq 125.698 dm yvy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 PROCESSING lb 1.00
tpwr 54 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 20000
ct 2560 werr react
aLOCK y wexp procplot
gain not used wbs testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1256.9
wp 27650.1
vs 562
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10979.6
rfp 9677.6
th 8
ins 100.000
nm ph



S43

Fig S44. ¹³C NMR of compound 9 (125 MHz, CDCl₃), expanded.

S44

PMK-01-206

exp31 s2pu1

SAMPLE		DEC. & VT	
date	May 1 2009	dfrq	499.836
solvent	cdcl3	dn	H1
file	/export/home/~	dpwr	39
vnmr1/vnmrsys/data~		dof	0
/PMK/PMK-01-206/C.~		dm	yyv
	fid	dmm	w
ACQUISITION		dmf	11905
sfrq	125.698	dseq	
tn	C13	dres	1.0
at	1.000	homo	n
np	62894	PROCESSING	
sw	31446.5	lb	1.00
fb	17000	wtfile	
bs	16	proc	ft
ss	2	fn	not used
tpwr	54	math	f
pw	4.0		
d1	1.000	werr	react
tof	2512.2	wexp	procplot
nt	20000	wbs	testsn
ct	2560	wnt	
alock	y		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	8169.0		
wp	2513.4		
vs	68		
sc	0		
wc	210		
hzmm	11.97		
is	500.00		
rfl	10979.6		
rfp	9677.6		
th	3		
ins	100.000		
nm	ph		

77.367
77.252
77.000
76.748

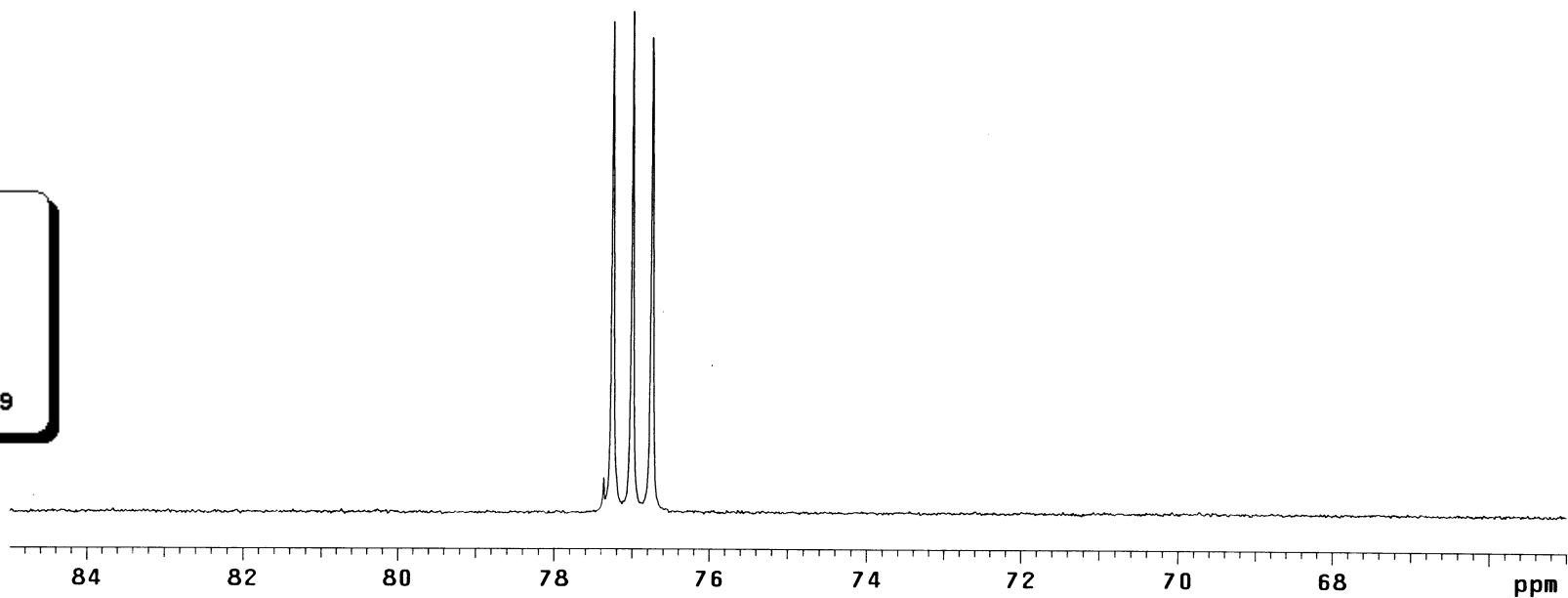
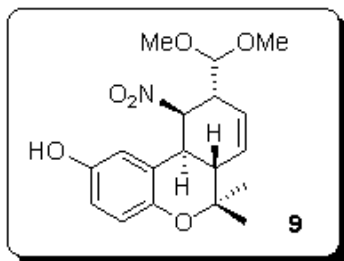


Fig S45. DEPT of compound 9 (CDCl₃).

S45

PMK-01-206

exp13 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	May 1 2009	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	20	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	3000	wp	27650.1		
ct	3000	sp	-1257.2		
TRANSMITTER		rp	-66.6		
tn	C13	lp	60.3		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.7		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	82344		
dmm	ccw	hzmm	131.67		
dmf	11905	th	68		
pplvl	49				
pp	29.400				

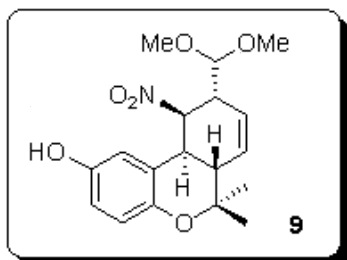
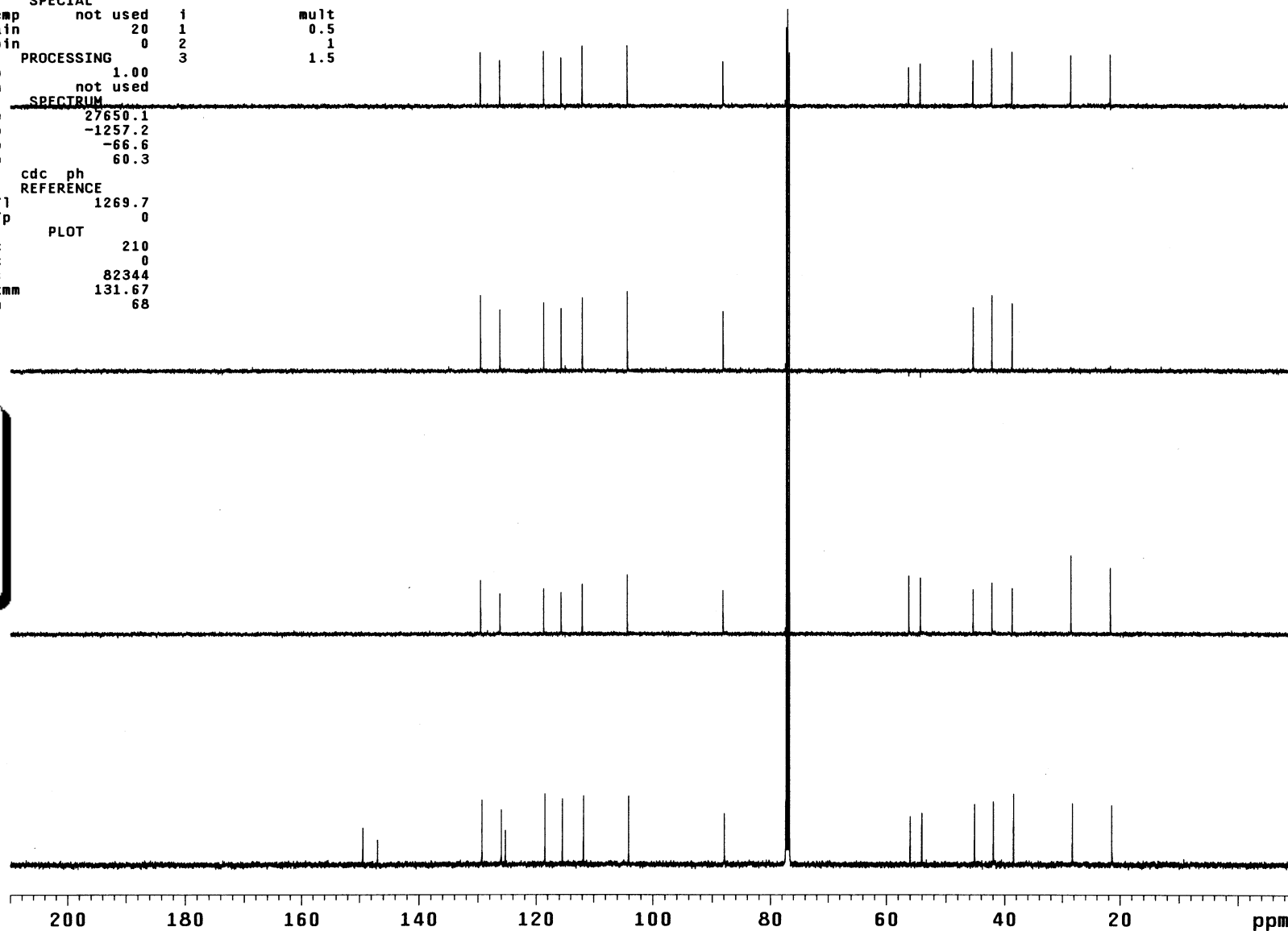


Fig S46. DEPT of compound 9 (CDCl₃), expanded.

S46

PMK-01-206

exp32 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	May 1 2009	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	1	mult
sw	31446.5	gain	20	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	3000	wp	2513.4		
ct	3000	sp	8168.7		
TRANSMITTER		rp	-66.6		
tn	C13	lp	60.3		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.7		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	82344		
dmm	ccw	hzmm	11.97		
dmf	11905	th	68		
pp1v1	49				
pp	29.400				

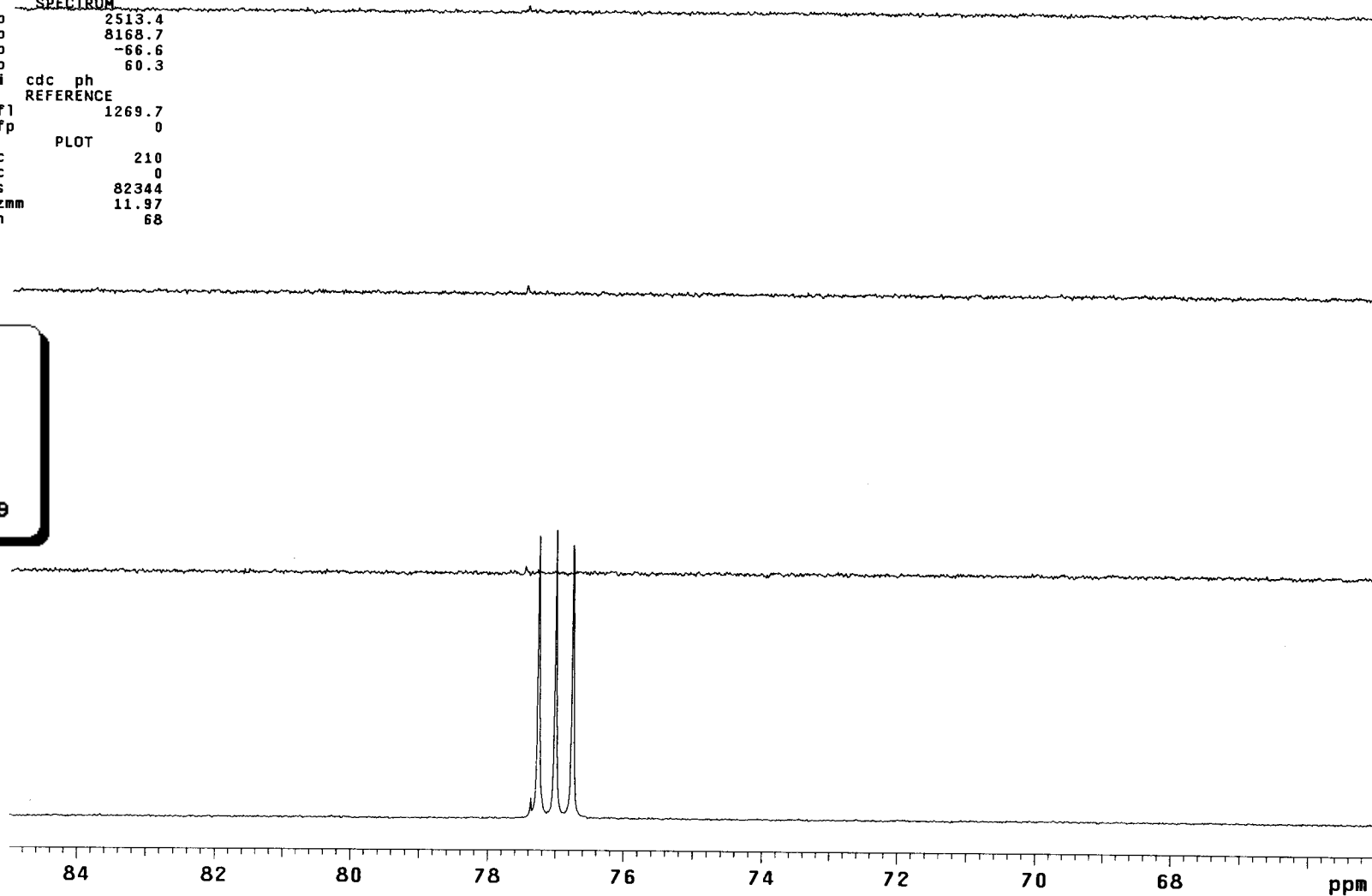
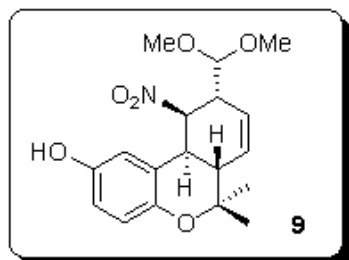


Fig S47. HMQC of compound 9 (CDCl₃).

S47

PMK-01-206

exp15 gHMQC

SAMPLE		FLAGS	ACQUISITION	ARRAYS
date	May 1 2009	hs	n	array
solvent	cdcl3	sspul	y	arraydim
sample	undefined	PFGflg	y	phase
ACQUISITION	hsglv1	1026	i	phase
sw	3498.8	SPECIAL	1	1
at	0.146	temp	not used	2
np	1024	gain	20	
fb	2000	spin	0	
ss	32			
d1	1.000	GRADIENTS		
nt	16	gzlv11	1026	
2D ACQUISITION		gt1	0.001000	
sw1	21367.5	gzlv13	516	
ni	128	gt3	0.001000	
phase	arrayed	gstab	0.000500	
TRANSMITTER		F2 PROCESSING		
tn	H1	gf	0.068	
sfrq	499.835	gfs	not used	
tof	-250.0	fn	1024	
tpwr	57	F1 PROCESSING		
pw	13.000	gf1	0.006	
DECOUPLER		gfs1	not used	
dn	C13	proc1	lp	
dof	-2515.1	fn1	2048	
dm	nny	DISPLAY		
dmm	ccp	sp	510.0	
dmf	32258	wp	2993.1	
dpwr	35	sp1	1856.3	
pwxlvl	51	wp1	14878.0	
pw	14.700	rfl	1651.3	
j1xh	140.0	rfp	2140.8	
HMQC		rfl1	14374.2	
nullflg	y	rfp1	13079.6	
		PLOT		
		wc	150.0	
		sc	6.2	
		wc2	116.2	
		sc2	0	
		vs	227	
		th	5	
		ai	cdc	ph

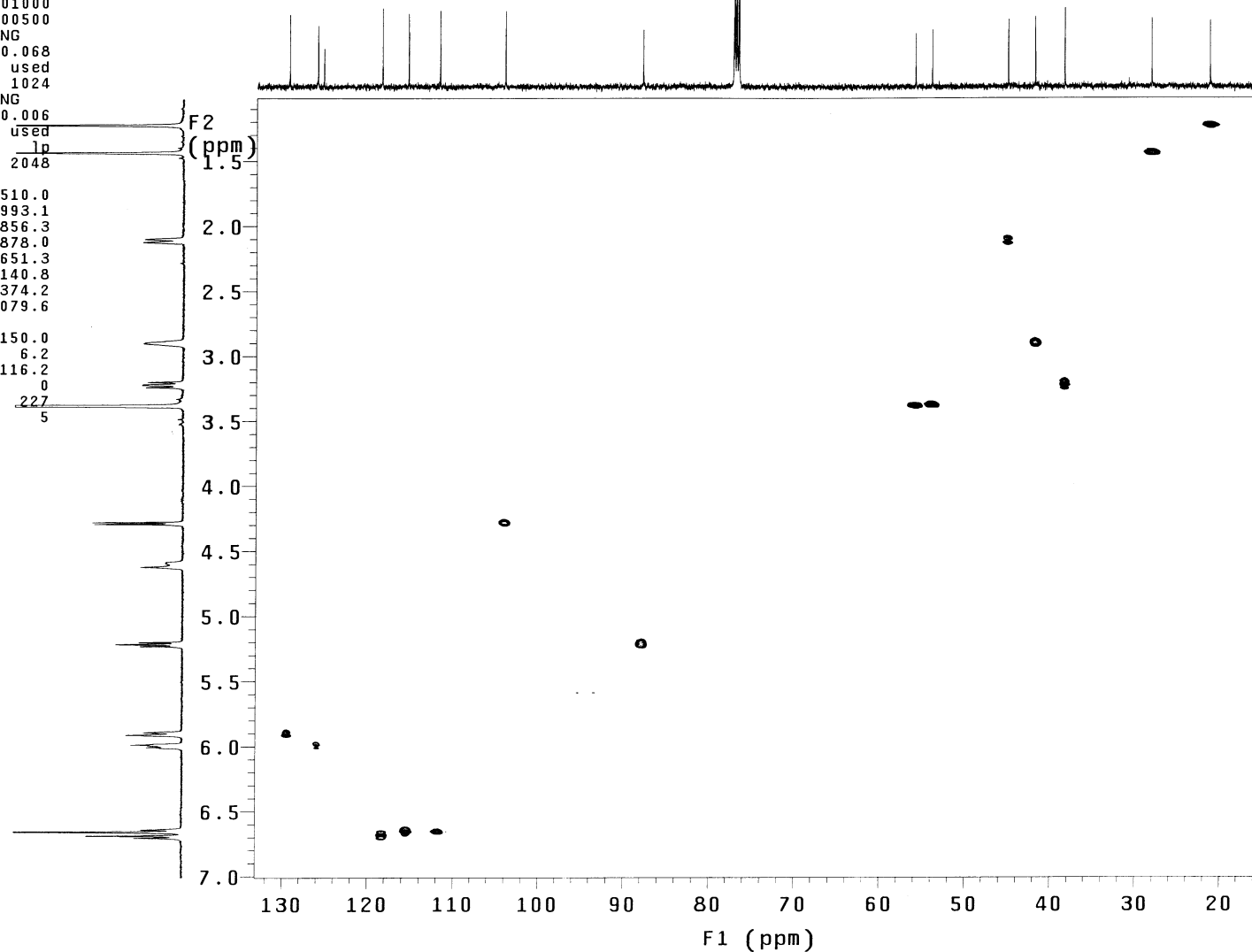
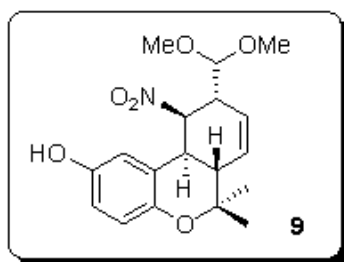


Fig S48. COSY of compound 9 (CDCl₃).

S48

PMK-01-206

expl4 gCOSY

SAMPLE		FLAGS	
date	May 1 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	3498.8	temp	not used
at	0.146	gain	20
np	1024	spin	0
fb	2000	F2 PROCESSING	
ss	16	sb	-0.073
d1	1.000	sbs	not used
nt	16	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	3498.8	sb1	-0.037
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	1024
sfrq	499.835	DISPLAY	
tof	-250.0	sp	489.8
tpwr	57	wp	3492.0
pw	13.000	sp1	493.9
GRADIENTS		wp1	3492.0
gzlv11	1026	rfl	3135.9
gt1	0.001000	rfp	3618.8
gstab	0.000500	rfl1	3131.8
DECOUPLER		rfp1	3618.8
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	227
		th	6
		ai	cdc av

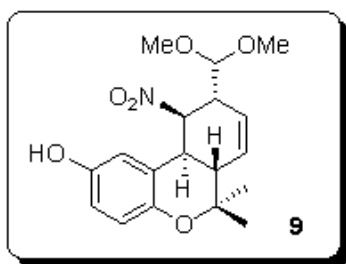
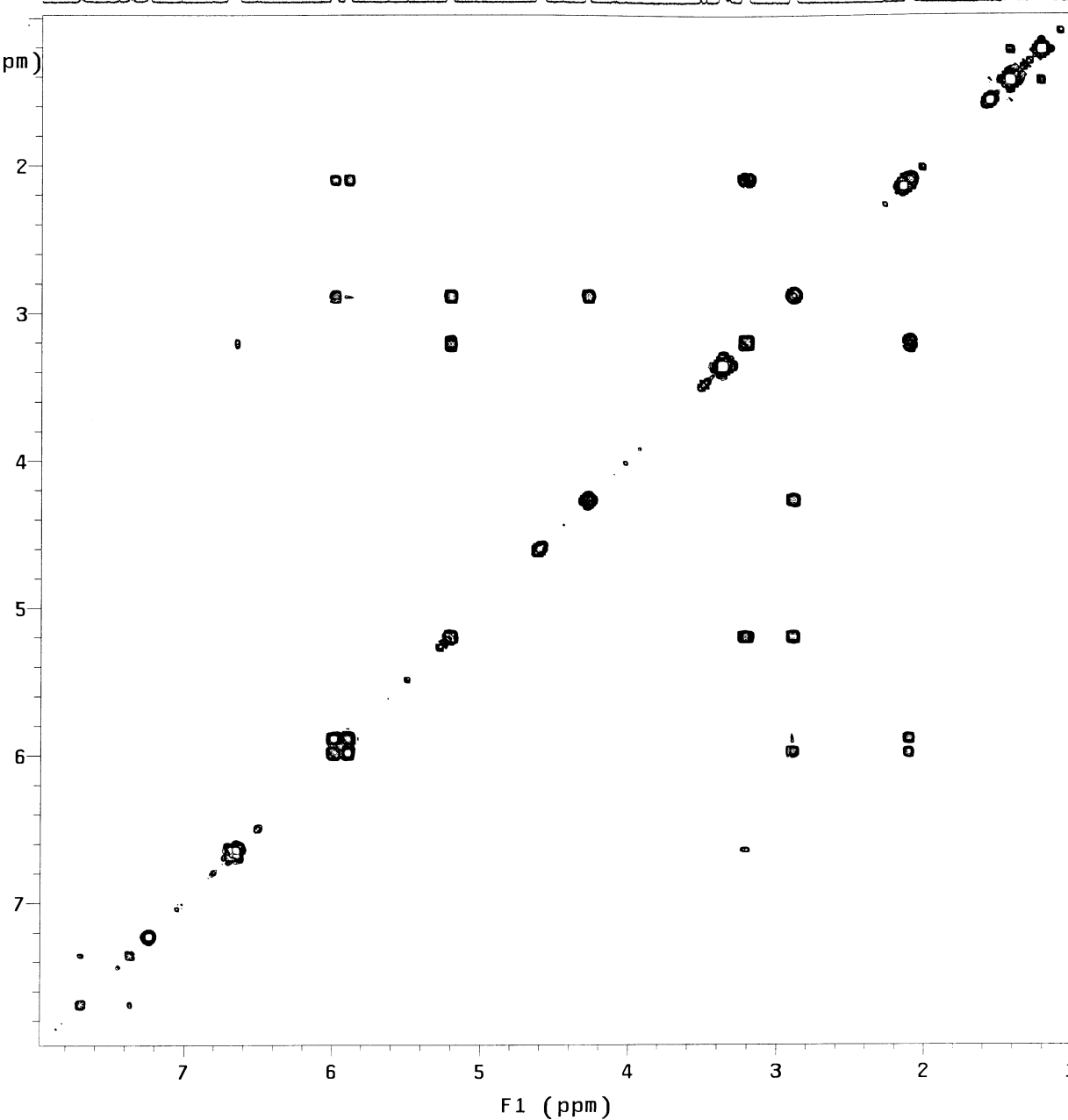
F2
(ppm)

Fig S49. NOESY of compound 9 (CDCl₃).

S49

PMK-01-206

exp16 NOESY

SAMPLE		FLAGS	
date	May 1 2009	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	1026
sw	3498.8	SPECIAL	
at	0.146	temp	not used
np	1024	gain	20
fb	2000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.068
nt	8	gfs	not used
2D ACQUISITION		fn	1024
sw1	3498.8	F1 PROCESSING	
ni	200	gf1	0.053
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.835	fn1	1024
tof	-250.0	DISPLAY	
tpwr	57	sp	492.5
pw	13.000	wp	3492.0
NOESY		sp1	505.8
mix	0.600	wp1	3492.0
PRESATURATION		rfl	3133.1
satmode	nnnn	rfp	3618.8
satpwr	0	rfl1	3129.8
satdly	0	rfp1	3628.8
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	227
		th	1
		ai	ph

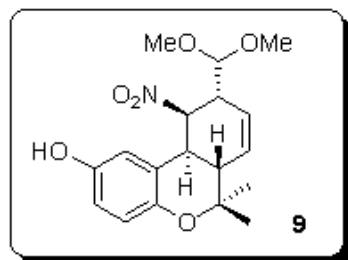
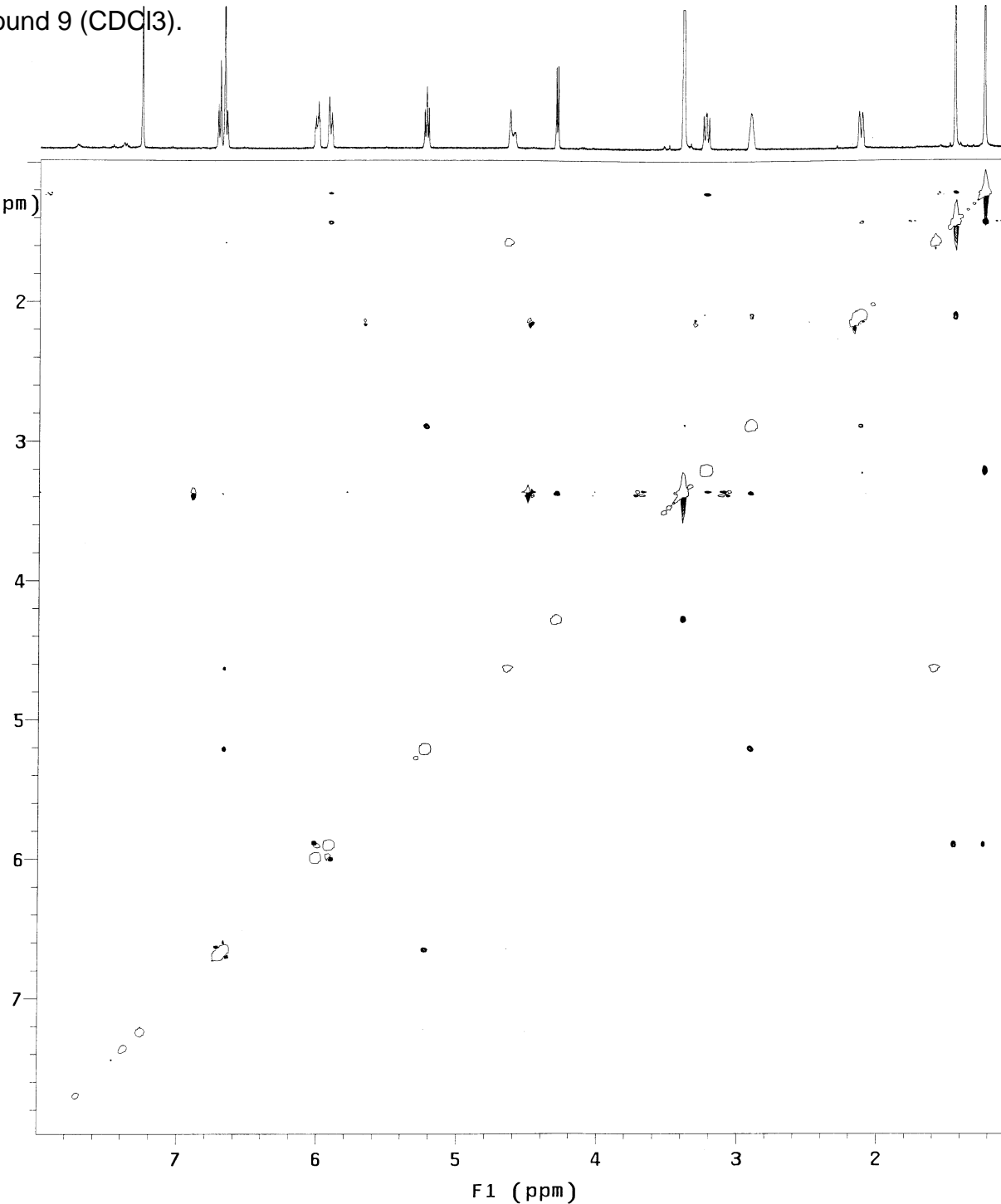
F2
(ppm)

Fig S50. ¹H NMR of compound 10 (500 MHz, CDCl₃).

S50

PMK-01-207

exp46 s2pu1

SAMPLE		DEC. & VT	
date	Apr 8 2009	dfrq	125.695
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION			
sfrq	499.836	dof	0
tn	H1	dm	nnn
at	3.000	dmm	c
np	48000	dmf	200
sw	8000.0	dseq	
fb	4000	dres	1.0
bs	4	homo	n
PROCESSING			
tpwr	57	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wft	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5498.0		
vs	142		
sc	0		
wc	210		
hzmm	26.18		
is	109.02		
rfl	4633.1		
rfp	3628.8		
th	2		
ins	100.000		
nm	ph		

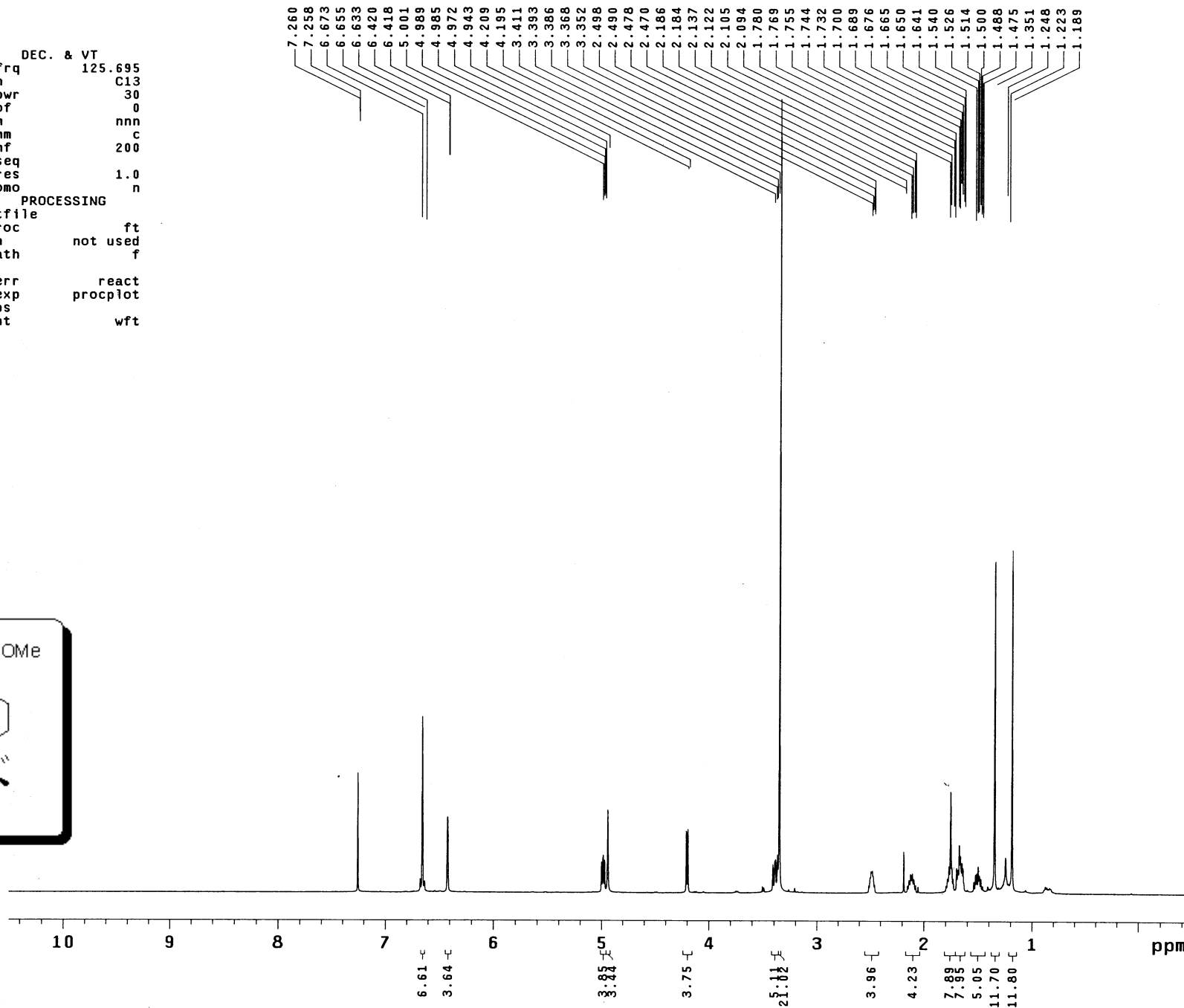
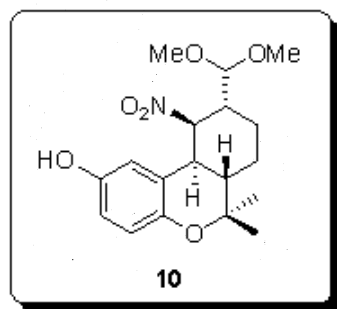


Fig S51. ¹³C NMR of compound 10 (125 MHz, CDCl₃).

S51

PMK-01-207

exp48 s2pu1

SAMPLE DEC. & VT
date Apr 8 2009 dfrq 499.836
solvent cdcl3 dn H1
file exp dpwr 39
ACQUISITION dof 0
sfrq 125.698 dm yyy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 PROCESSING
tpwr 54 lb 1.00
pw 4.0 wtfile
d1 1.000 fn not used
tof 2512.2 math f
nt 5000
ct 5000 werr react
alock y wexp procplot
gain not used wbs testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1256.9
wp 27650.1
vs 125
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10983.4
rfp 9677.6
th 9
ins 100.000
nm ph

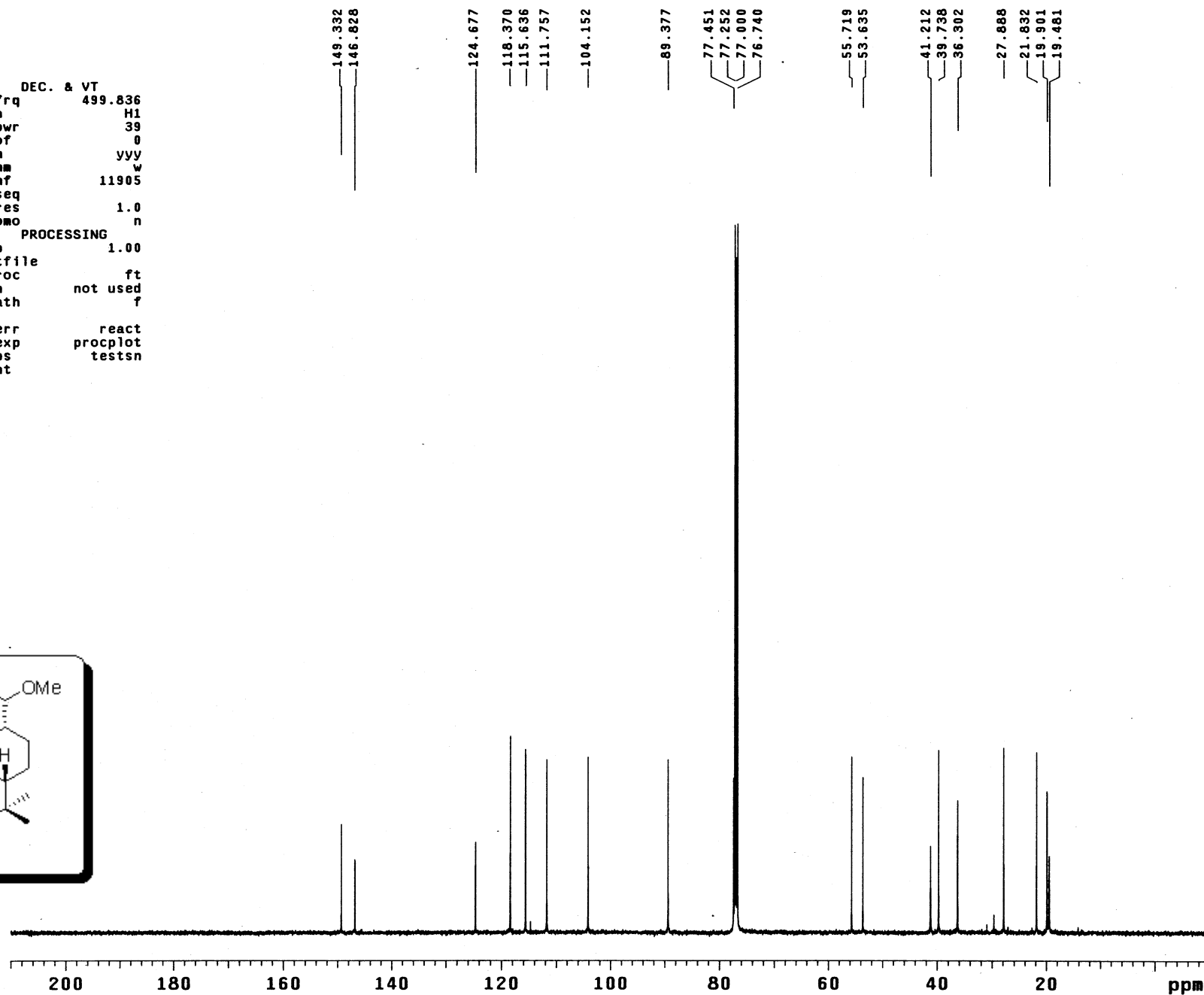
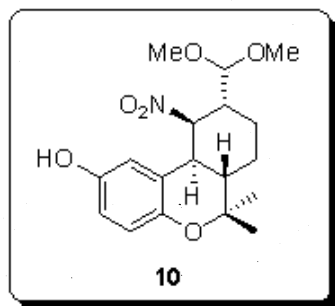


Fig S52. ¹³C NMR of compound 10 (125 MHz, CDCl₃), expanded.

S52

PMK-01-207

exp32 s2pu1

```

SAMPLE          DEC. & VT
date Apr 8 2009  dfrq      499.836
solvent cdc13      dn       H1
file /export/home/~ dpwr      39
vnmr1/vnmrsys/data~ dof       0
/PMK/PMK-01-207/C.~ dm        yyy
                  fid        w
ACQUISITION      dmf      11905
sfrq      125.698  dseq
tn         C13      dres      1.0
at         1.000    homo      n
np         62894
sw         31446.5  lb        1.00
fb         17000    wtfile
bs         16       proc      ft
ss         2        fn        not used
tpwr       54       math      f
pw         4.0
d1         1.000    werr      react
tof        2512.2   wexp      procplot
nt         5000     wbs       testsn
ct         5000     wnt
alock      y
gain       not used
          FLAGS
fl         n
in         n
dp         y
hs         nn
          DISPLAY
sp         8169.0
wp         2513.4
vs         94
sc         0
wc         210
hzmm       11.97
is         500.00
rfl        10983.4
rfp        9677.6
th         12
ins        100.000
nm         ph
    
```

77.451
77.252
77.000
76.740

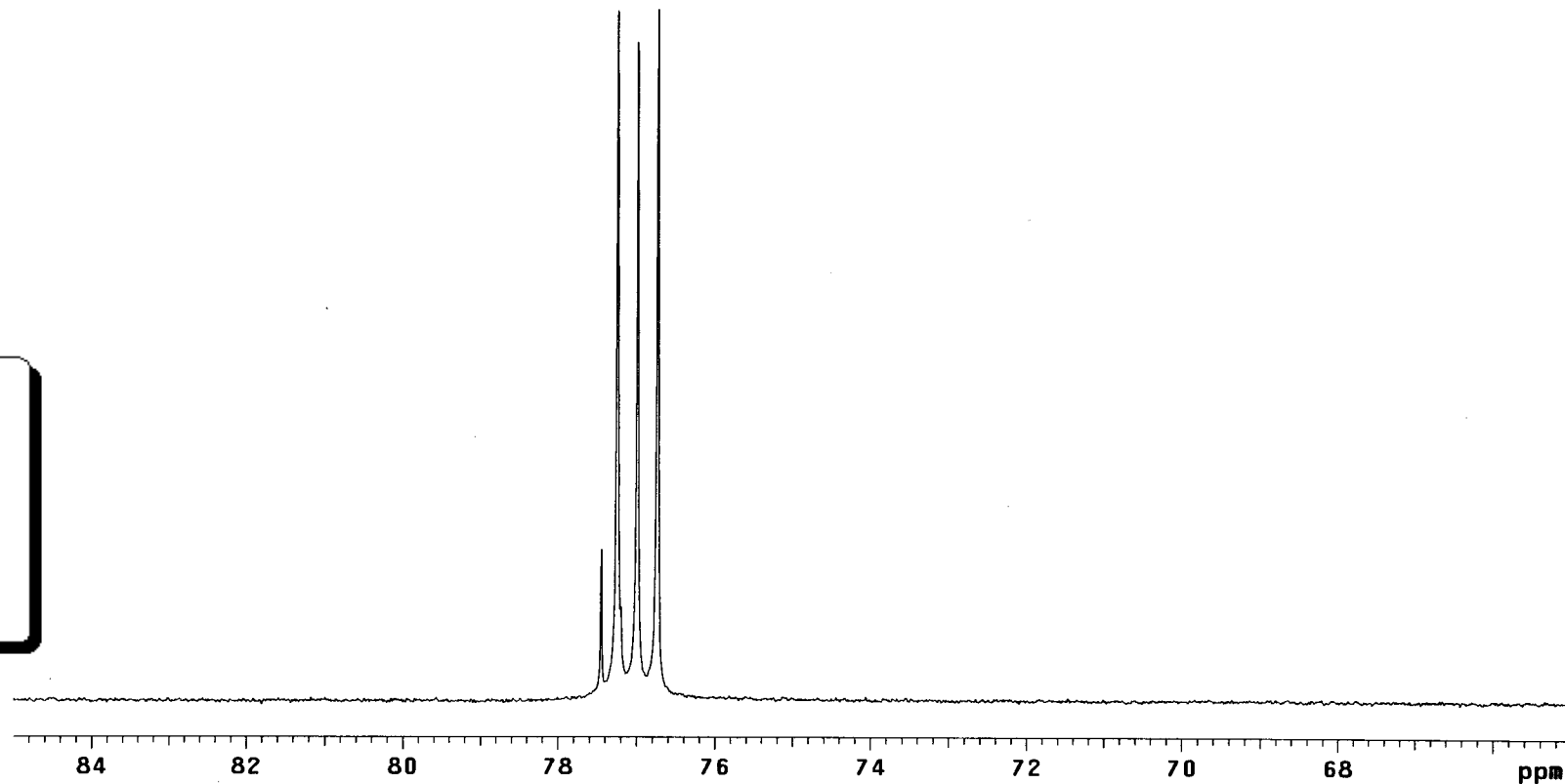
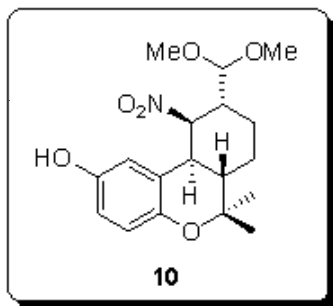


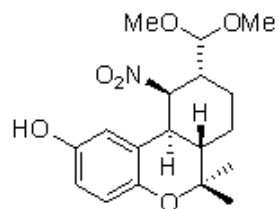
Fig S53. DEPT of compound 10 (CDCl₃).

S53

PMK-01-207

exp47 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Apr 8 2009	j1xh 140.0	array	mult
solvent	cdcl3	mult	arraydim	3
sample	undefined	SPECIAL		
ACQUISITION		temp not used	i	mult
sw	31446.5	gain 54	1	0.5
at	1.000	spin 0	2	1
np	62894	PROCESSING	3	1.5
bs	16	lb 1.00		
ss	-4	fn not used		
d1	1.000	SPECTRUM		
nt	1000	wp 27650.1		
ct	1000	sp -1257.2		
TRANSMITTER		rp -52.7		
tn	C13	lp 41.6		
tof	2512.2	ai cdc ph		
tpwr	54	REFERENCE		
pw	9.400	rfl 1269.7		
DECOUPLER		rfl 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	39	sc 0		
dm	nny	vs 175		
dmm	ccw	hzmm 131.67		
dmf	11905	th 68		
pp1v1	49			
pp	29.400			



10

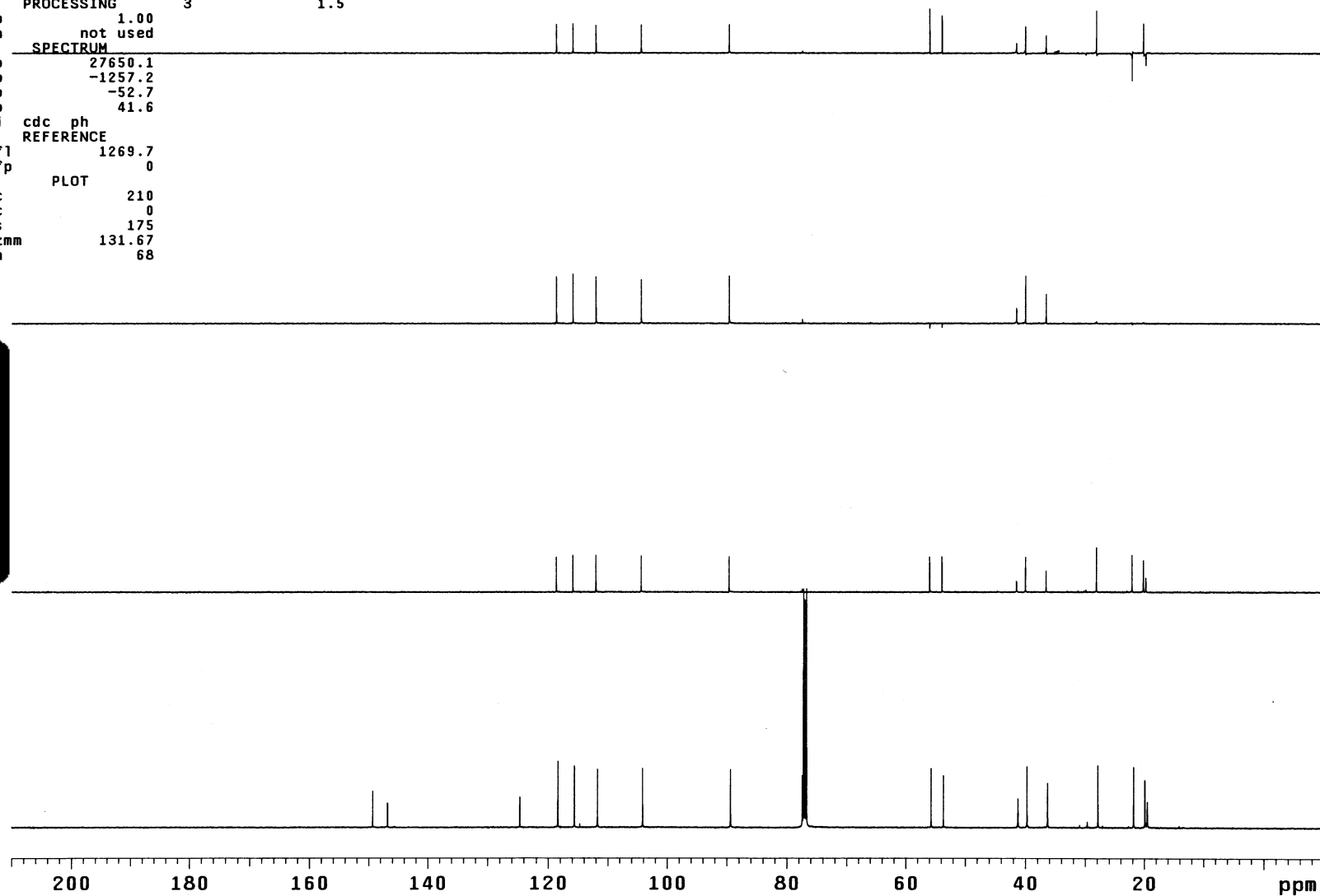


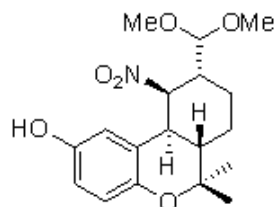
Fig S54. DEPT of compound 10 (CDCl₃), expanded.

S54

PMK-01-207

exp33 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	Apr 8 2009	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	54	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	1000	wp	2513.4		
ct	1000	sp	8168.7		
TRANSMITTER		rp	-52.5		
tn	C13	lp	36.5		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.7		
DECOUPLER		rtp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	230		
dmm	ccw	hzmm	11.97		
dmf	11905	th	68		
pp1v1	49				
pp	29.400				



10

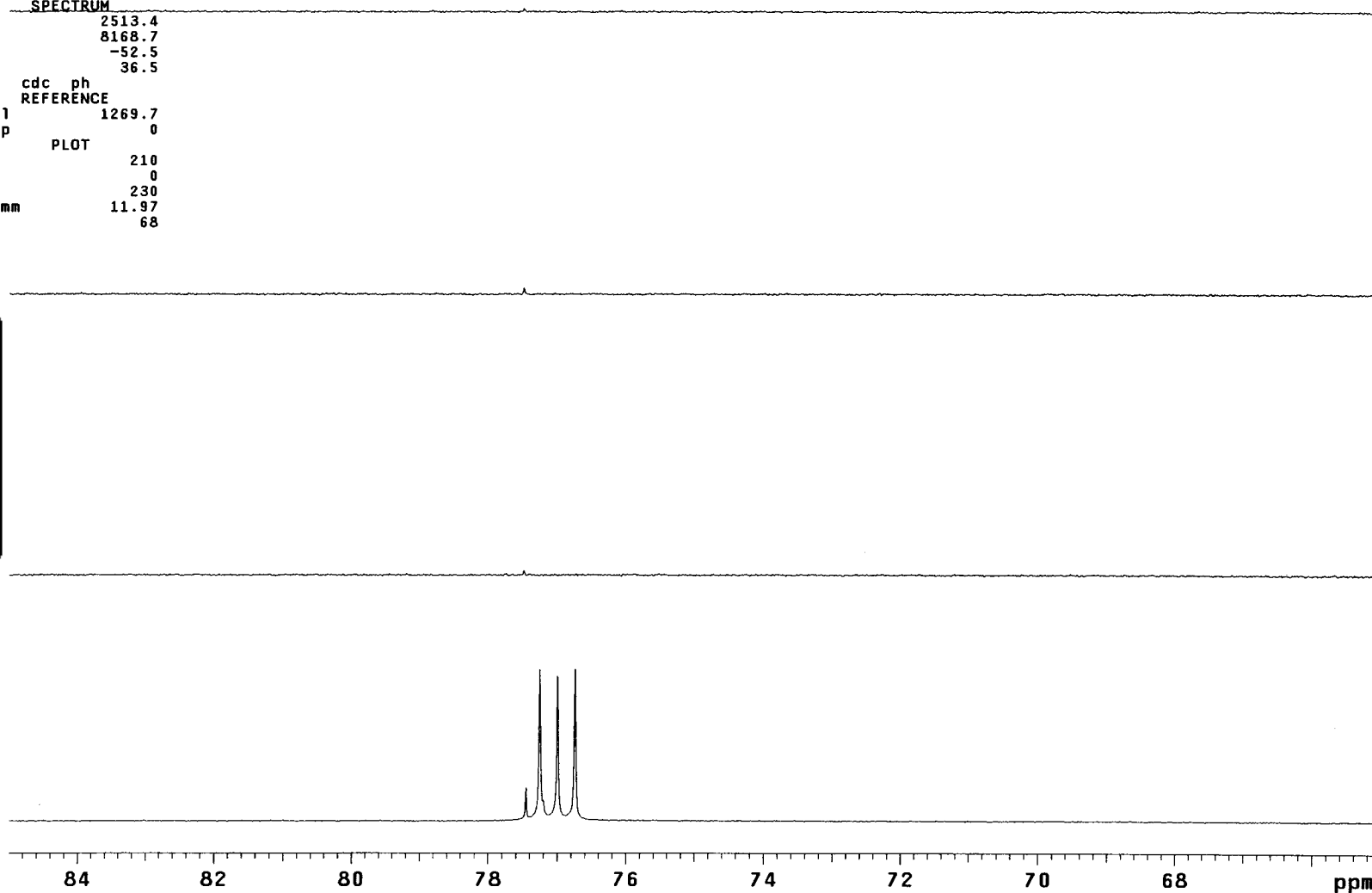


Fig S55. HMQC compound 10 (CDCl₃).

S55

PMK-01-207

exp33 gHMQC

SAMPLE		FLAGS	ACQUISITION	ARRAYS
date	Apr 13 2009	hs	n	phase
solvent	cdc13	sspul	y	256
sample	undefined	PFGflg	y	
ACQUISITION		hsglv1	1026	phase
sw	3748.8	SPECIAL	1	1
at	0.137	temp	21.0	2
np	1024	gain	54	
fb	2000	spin	0	
ss	32	GRADIENTS		
d1	1.000	gzlv11	1026	
nt	16	gt1	0.001000	
2D ACQUISITION		gzlv13	516	
sw1	21367.5	gt3	0.001000	
n1	128	gstab	0.000500	
phase	arrayed	F2 PROCESSING		
TRANSMITTER		gf	0.063	
tn	H1	gfs	not used	
sfrq	499.835	fn	1024	
tof	-375.0	F1 PROCESSING		
tpwr	57	gf1	0.006	
pw	13.000	gfs1	not used	
DECOUPLER		proc1	1p	
dn	C13	fn1	2048	
do1	-2515.1	DISPLAY		
dm	nny	sp	443.3	
dmm	ccp	wp	3067.9	
dmf	32258	sp1	2026.7	
dpwr	35	wp1	13667.7	
pwxlvl	51	rfl	2959.7	
pw	14.700	rfl	3197.9	
HMQC		rfl1	15357.9	
j1xh	140.0	rfl1	14046.0	
nullflg	y	PLOT		
		wc	150.0	
		sc	6.2	
		wc2	116.2	
		sc2	0	
		vs	453	
		th	4	
		al	cdc ph	

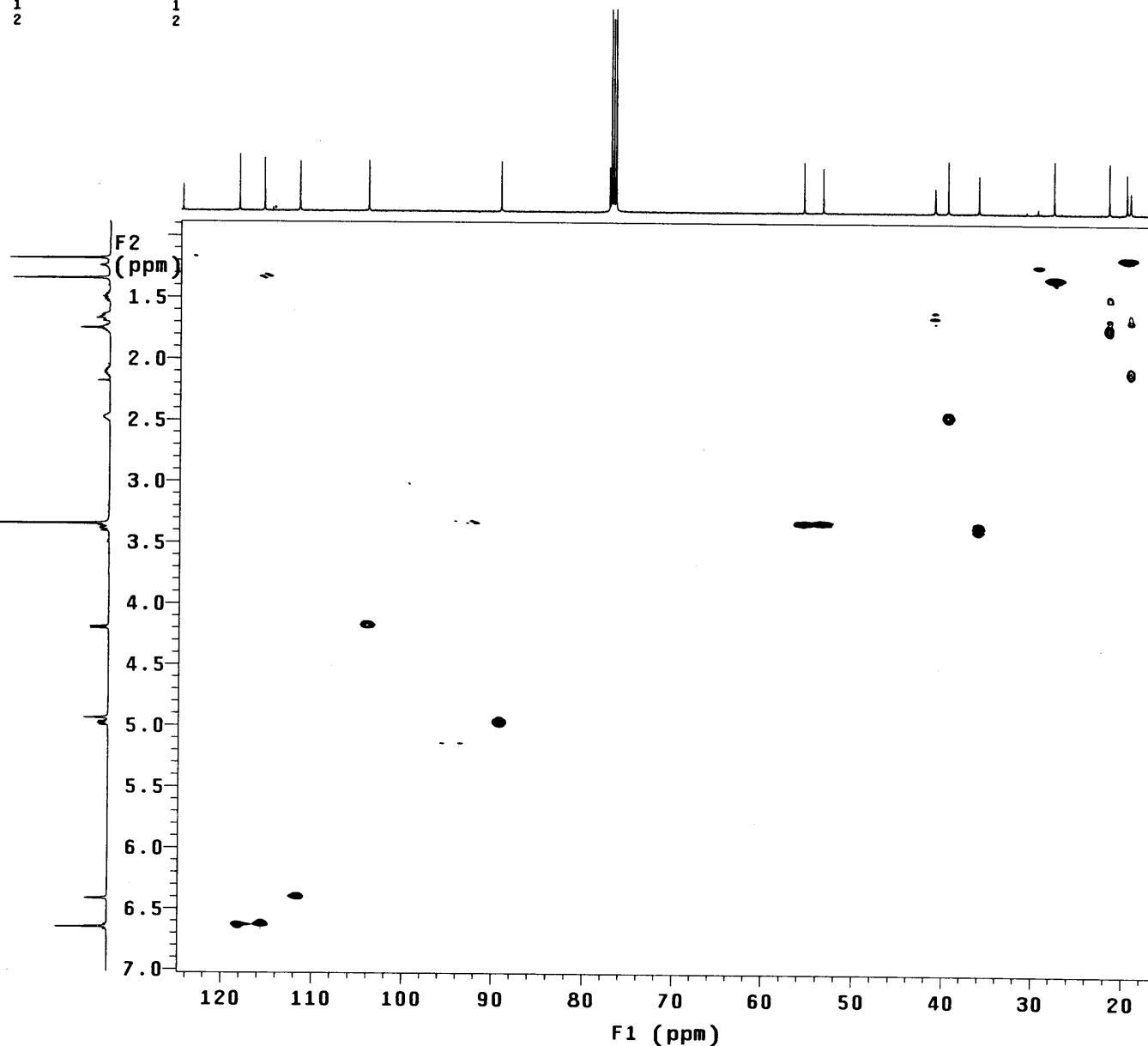
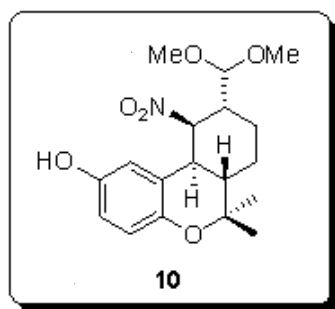


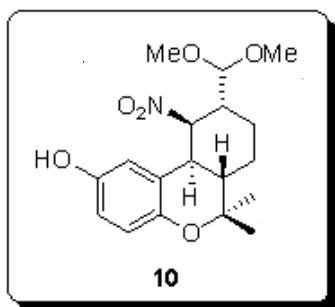
Fig S56. COSY of compound 10 (CDCl₃).

S56

PMK-01-207

exp41 gCOSY

SAMPLE		FLAGS	
date	Apr 13 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	3748.8	temp	21.0
at	0.137	gain	34
np	1024	spin	0
fb	2000	F2 PROCESSING	
ss	16	sb	-0.068
d1	1.000	sbs	not used
nt	16	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	3748.8	sb1	-0.034
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	lp	
sfrq	499.835	fn1	1024
tof	-375.0	DISPLAY	
tpwr	57	sp	245.6
pw	13.000	wp	3741.5
GRADIENTS		sp1	247.8
gzlv11	1026	wp1	3741.5
gt1	0.001000	rfl	3380.5
gstab	0.000500	rfp	3618.8
DECOUPLER		rfl1	3378.3
dn	C13	rfp1	3618.8
dm	nnn	PLOT	
		wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	453
		th	4
		ai	cdc av

F2
(ppm)

1

2

3

4

5

6

7

F1 (ppm)

7

6

5

4

3

2

1

Fig S57. NOESY of compound 10 (CDCl₃).

S57

PMK-01-207

exp43 NOESY

SAMPLE		FLAGS	
date	Apr 13 2009	hs	n
solvent	cdc13	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1026
sw	3748.8	SPECIAL	
at	0.137	temp	21.0
np	1024	gain	34
fb	2000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.063
nt	8	gfs	not used
2D ACQUISITION		fn	1024
sw1	3748.8	F1 PROCESSING	
ni	200	gf1	0.049
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.835	fn1	1024
tof	-375.0	DISPLAY	
tpwr	57	sp	244.9
pw	13.000	wp	3741.5
NOESY		sp1	247.1
mix	0.600	wp1	3741.5
PRESATURATION		rfl	3381.2
satmode	nnnn	rfp	3618.8
satpwr	0	rfl1	3379.0
satdly	0	rfp1	3618.8
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	453
		th	1
		ai	ph

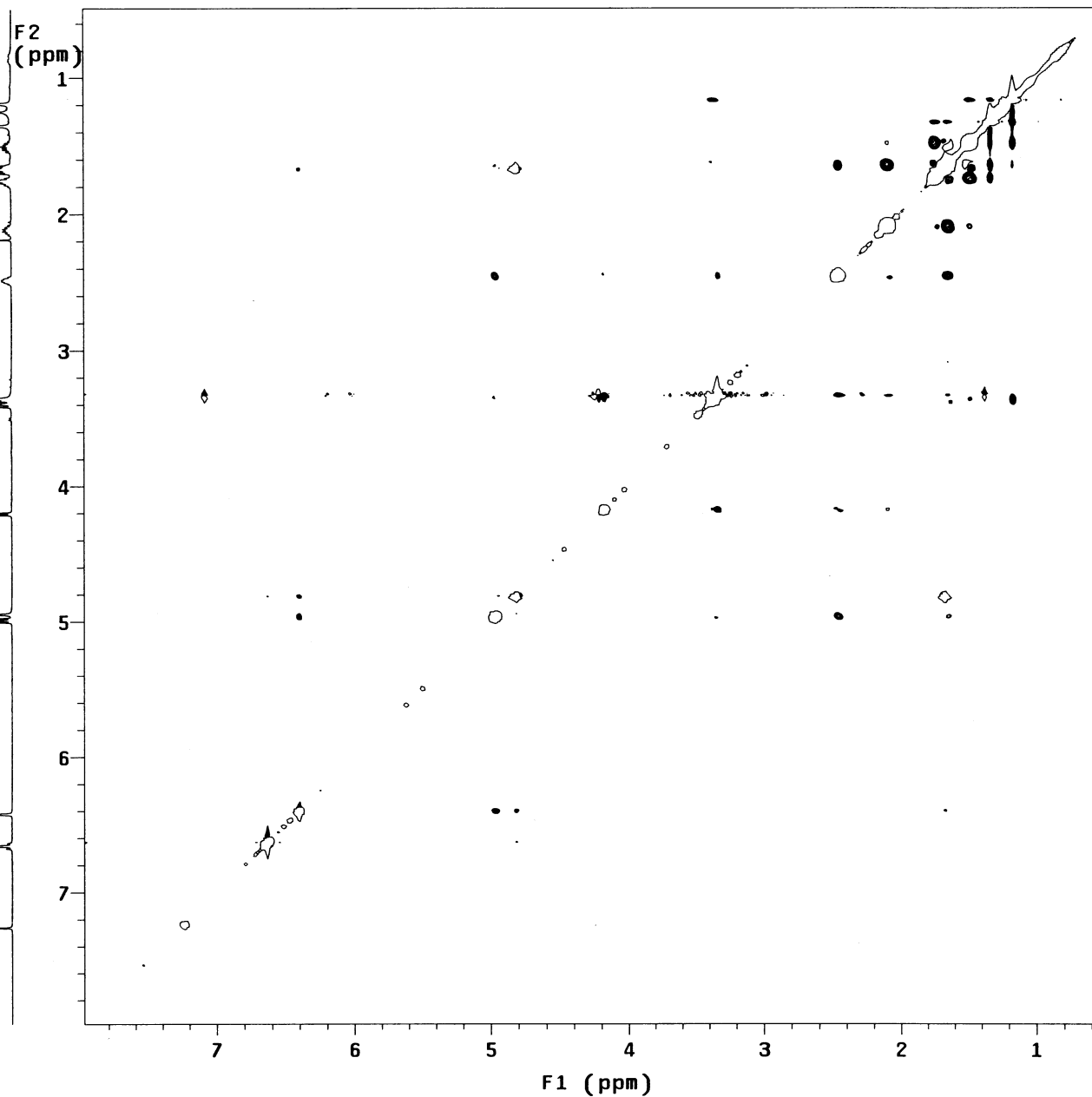
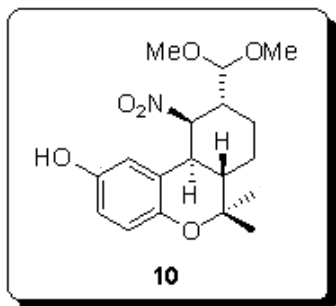
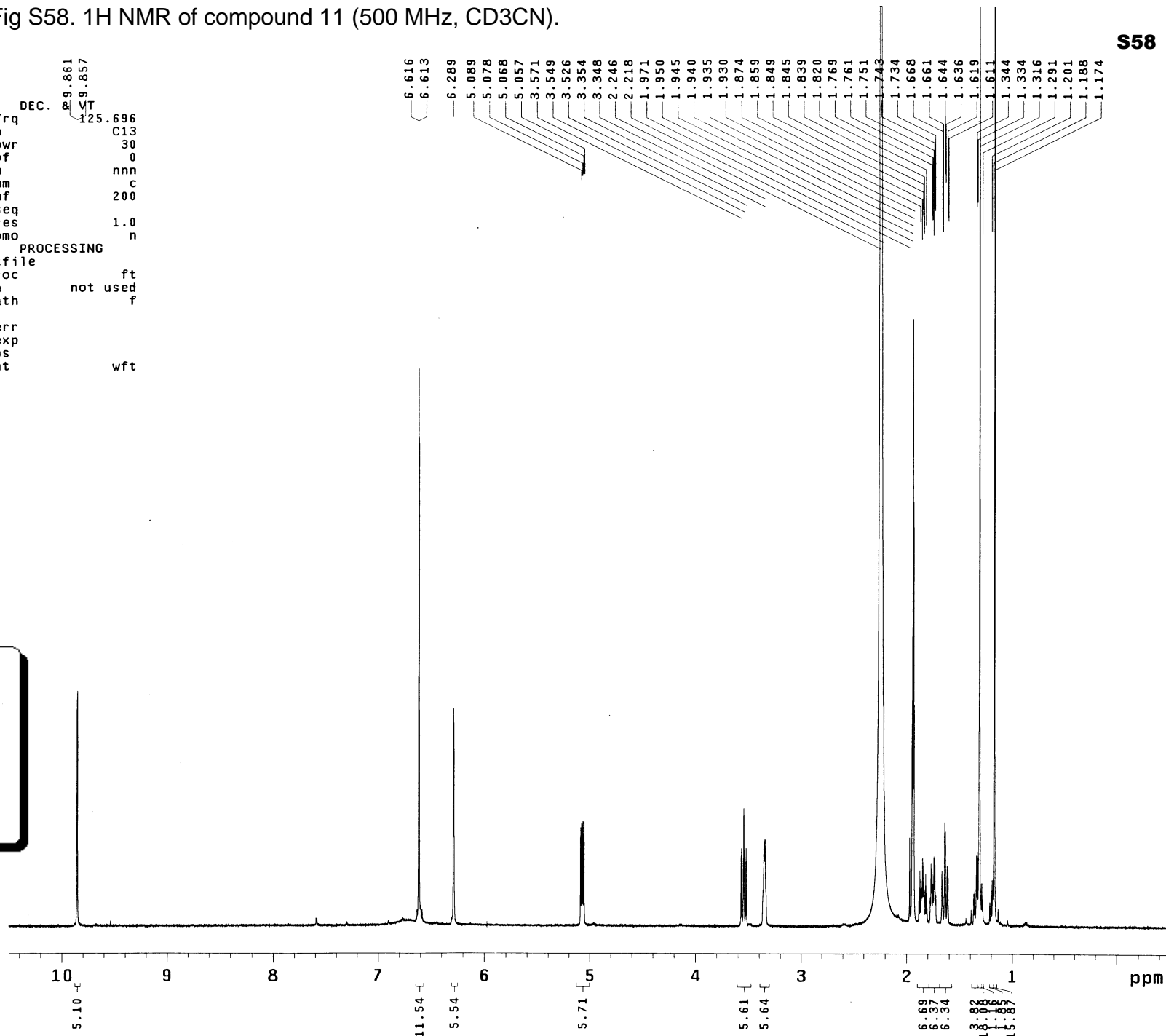
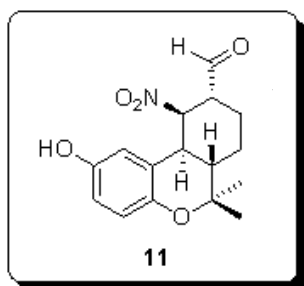


Fig S58. ¹H NMR of compound 11 (500 MHz, CD₃CN).

PMK-01-255

exp33 s2pul

SAMPLE DEC. 8 9.861 9.857
 date Sep 15 2009 dfrq 125.696
 solvent ch3cn dn C13
 file exp dpwr 30
 ACQUISITION dof 0
 sfrq 499.839 dm nnn
 tn H1 dmm c
 at 3.000 dmf 200
 np 48000 dseq
 sw 8000.0 dres 1.0
 fb 4000 homo n
 bs 4
 PROCESSING
 tpwr 57 wtfile
 pw 4.8 proc ft
 d1 1.000 fn not used f
 tof 499.7 math
 nt 4
 ct 4 werr
 alock y wexp
 gain not used wbs
 wnt wft
 FLAGS
 il n
 in n
 dp y
 hs nn
 DISPLAY
 sp -250.0
 wp 5498.0
 vs 873
 sc 0
 wc 210
 hzmm 26.18
 is 230.40
 rfl 1982.7
 rfp 969.7
 th 7
 ins 100.000
 nm ph

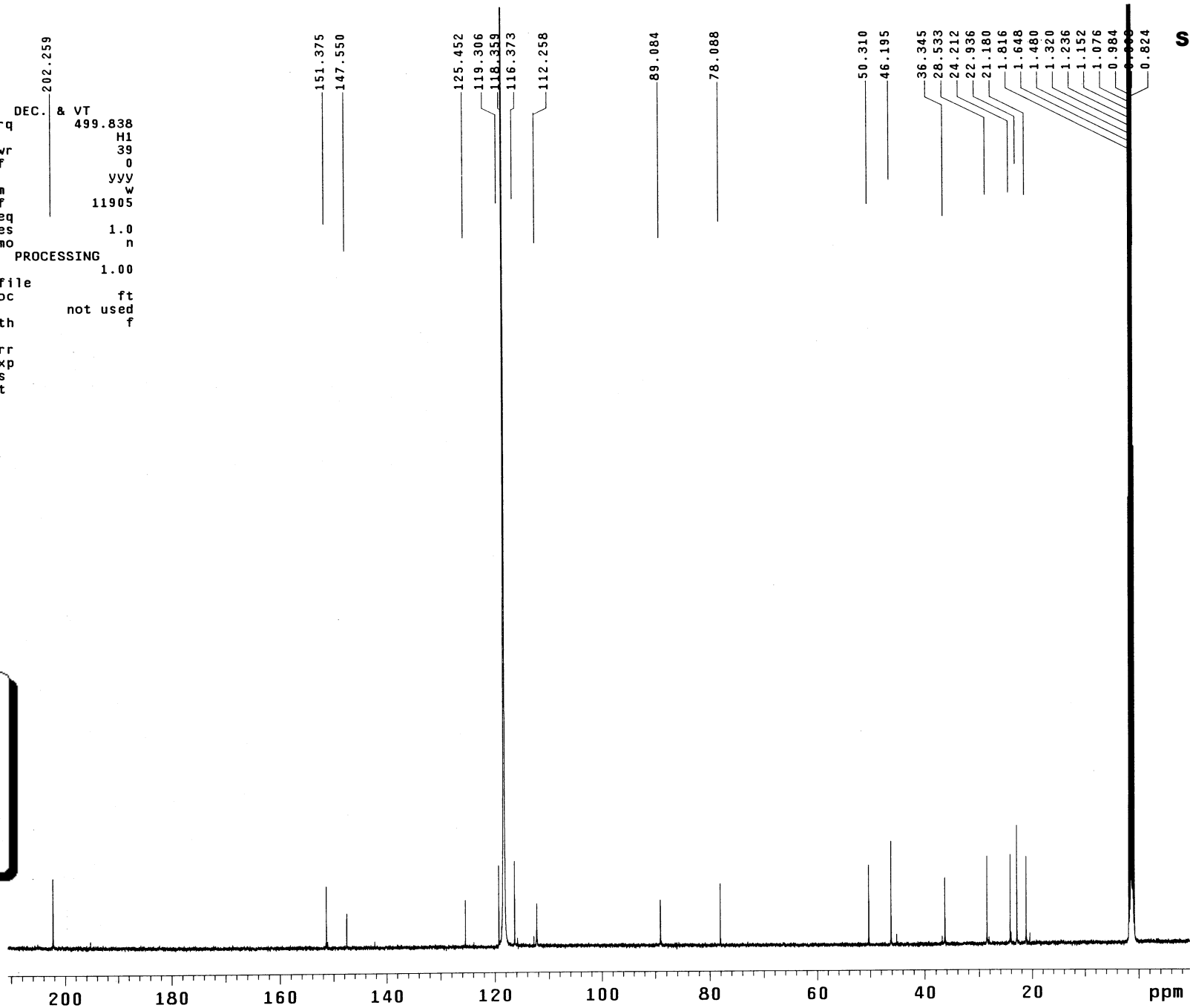


PMK-01-255

exp35 s2pu1

```

SAMPLE
date Sep 15 2009 dfrq 499.838
solvent ch3cn dn H1
file exp dpwr 39
ACQUISITION
sfrq 125.698 dm yvy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 lb 1.00
tpwr 54 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 20000
ct 16640 werr
alock y wexp
gain not used wbs
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1175.7
wp 27650.1
vs 788
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 1342.6
rfp 165.9
th 3
ins 100.000
nm ph
  
```



S59

Fig S59. ¹³C NMR of compound 11 (125 MHz, CD₃CN).

Fig S60. DEPT of compound 11 (CD₃CN).

S60

PMK-01-255

exp34 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	Sep 15 2009	j1xh	140.0	array	mult
solvent	ch3cn	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	54	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	2000	wp	27650.1		
ct	2000	sp	-1257.2		
TRANSMITTER		rp	-72.0		
tn	C13	lp	150.8		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	9.400	rfl	1269.6		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	872		
dmm	ccw	hzmm	131.67		
dmf	11905	th	30		
pp1v1	49				
pp	29.400				

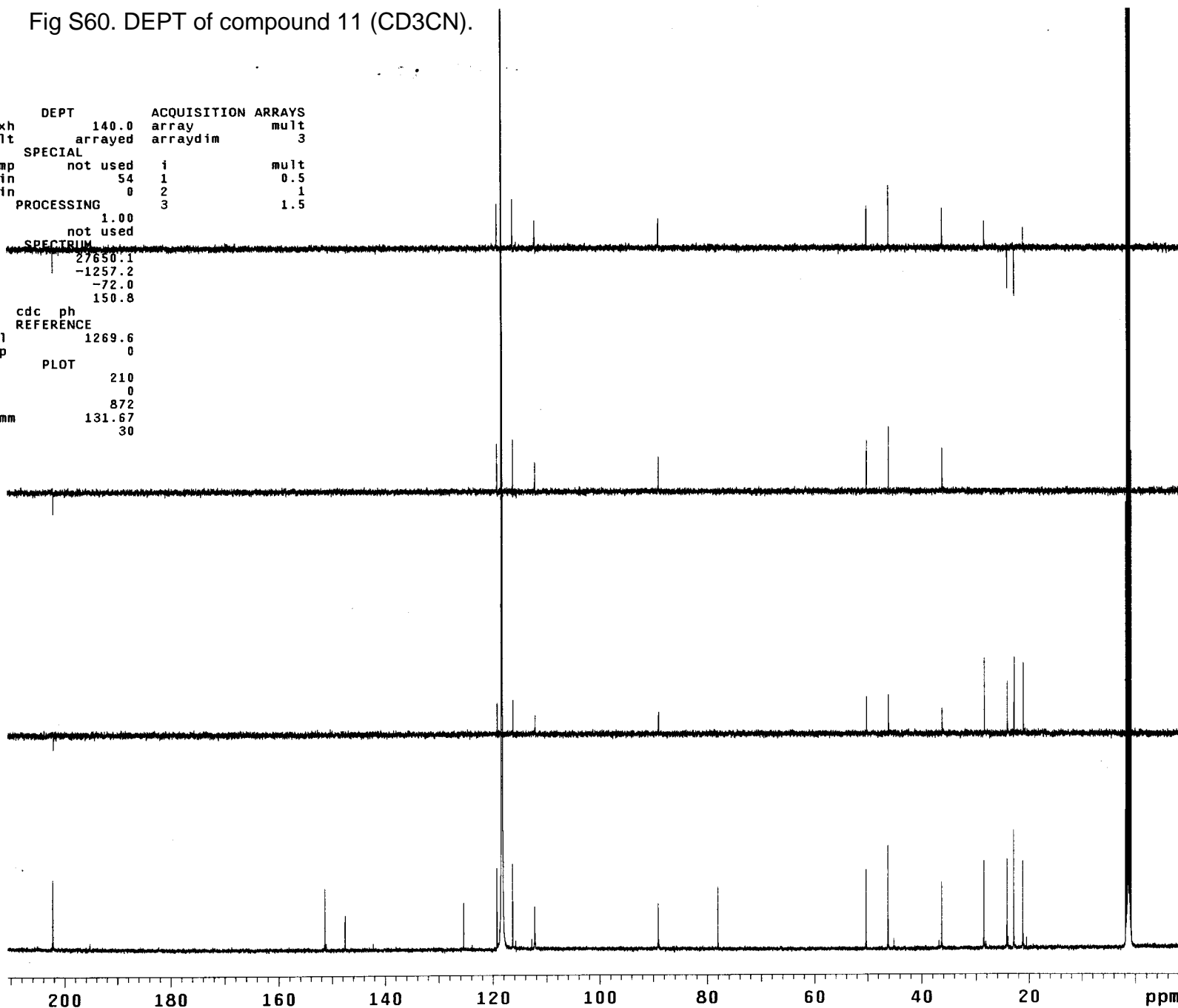
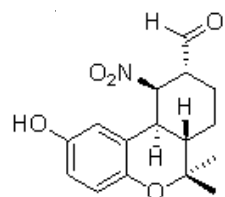


Fig S61. ¹H NMR of compound 12 (500 MHz, CDCl₃).

S61

PMK-01-222
exp40 s2pu1

SAMPLE		DEC. & VT	
date	Jul 29 2009	dfrq	125 695
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.836	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	1.0
sw	8000.0	dres	n
fb	4000	homo	
bs	4	PROCESSING	
tpwr	57	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	16		
ct	16	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	100		
sc	0		
wc	210		
hzmm	27.37		
is	42.72		
rfl	4631.3		
rfp	3628.8		
th	3		
ins	100.000		
nm	cdc ph		

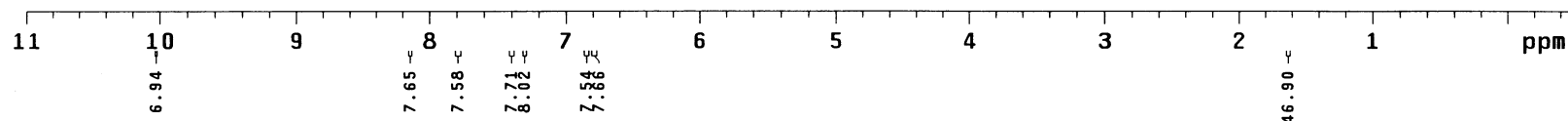
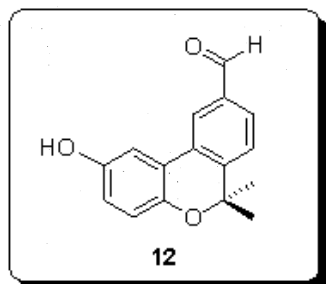
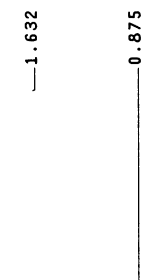
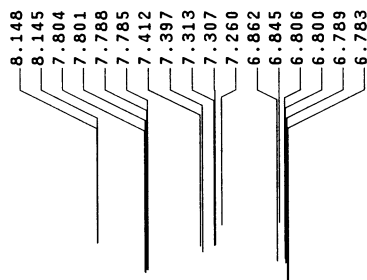


Fig S62. ¹³C NMR of compound 12 (125 MHz, CDCl₃).

S62

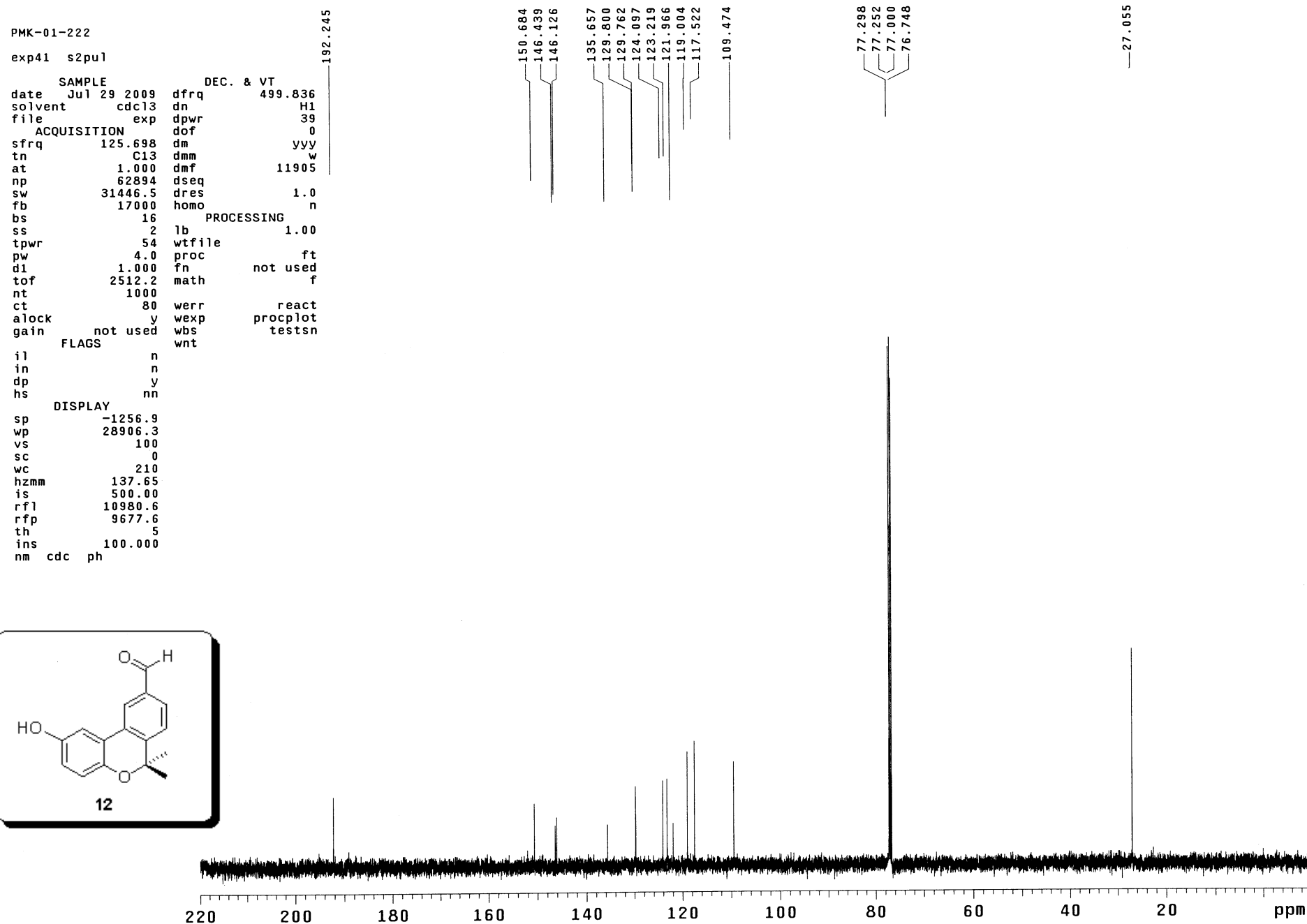


Fig S63. ¹³C NMR of compound 12 (125 MHz, CDCl₃), expanded.

S63

PMK-01-222
exp40 s2pul

SAMPLE		DEC. & VT	
date	Jul 29 2009	dfrq	499.836
solvent	cdcl3	dn	H1
file	/export/home/~	dpwr	39
vnmr1/vnmrsys/data/~		dof	0
/PMK/PMK-01-222/C.~		dm	yyy
	fid	dmm	w
ACQUISITION		dmf	11905
sfrq	125.698	dseq	
tn	C13	dres	1.0
at	1.000	homo	n
np	62894	PROCESSING	
sw	31446.5	lb	1.00
fb	17000	wtfile	
bs	16	proc	ft
ss	2	fn	not used
tpwr	54	math	f
pw	4.0		
d1	1.000	werr	react
tof	2512.2	wexp	procplot
nt	1000	wbs	testsn
ct	80	wnt	
alock	y		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	9614.3		
wp	124.8		
vs	100		
sc	0		
wc	210		
hzmm	0.60		
is	500.00		
rfl	10980.6		
rfp	9677.6		
th	5		
ins	100.000		
nm	cdc	ph	

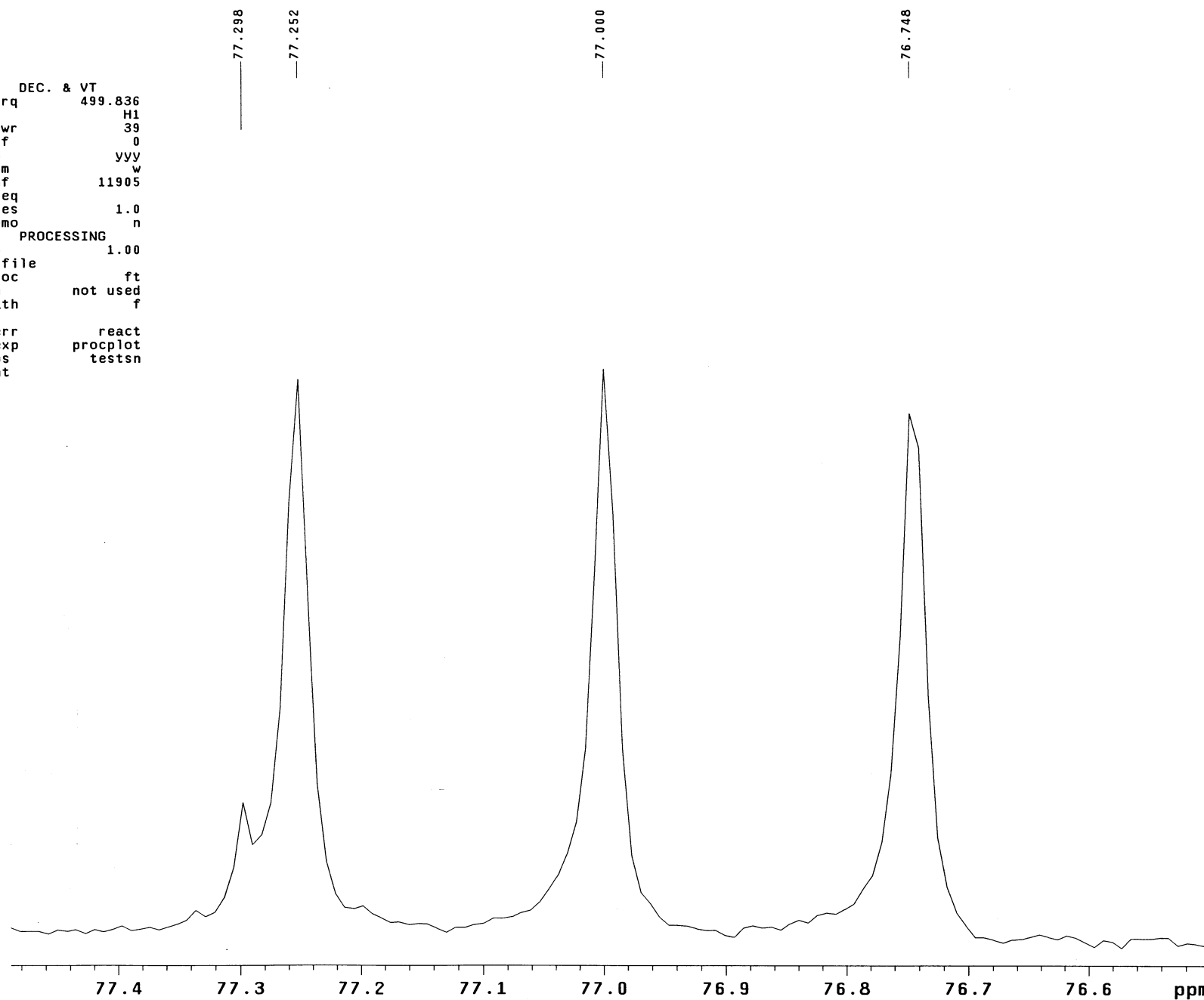
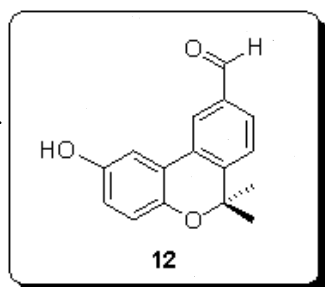


Fig S64. DEPT of compound 12 (CDCl₃).

S64

PMK-01-222

exp41 s2pu1

```

SAMPLE          DEC. & VT
date Jul 29 2009 dfrq      499.836
solvent cdc13      dn       H1
file exp          dpwr     39
ACQUISITION      dof      0
sfrq 125.698      dm       yyy
tn C13            dmm      w
at 1.000          dmf     11905
np 62894          dseq
sw 31446.5        dres     1.0
fb 17000          homg
bs 16            PROCESSING
ss 2             lb       1.00
tpwr 54          wtfile
pw 4.0          proc     ft
d1 1.000        fn       not used
tof 2512.2      math     f
nt 1000
ct 80          werr      react
alock y        wexp     procplot
gain not used   wbs      testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1256.9
wp 28906.3
vs 30
sc 0
wc 210
hzmm 137.65
is 500.00
rfl 10980.6
rfp 9677.6
th 5
ins 100.000
nm cdc ph
```

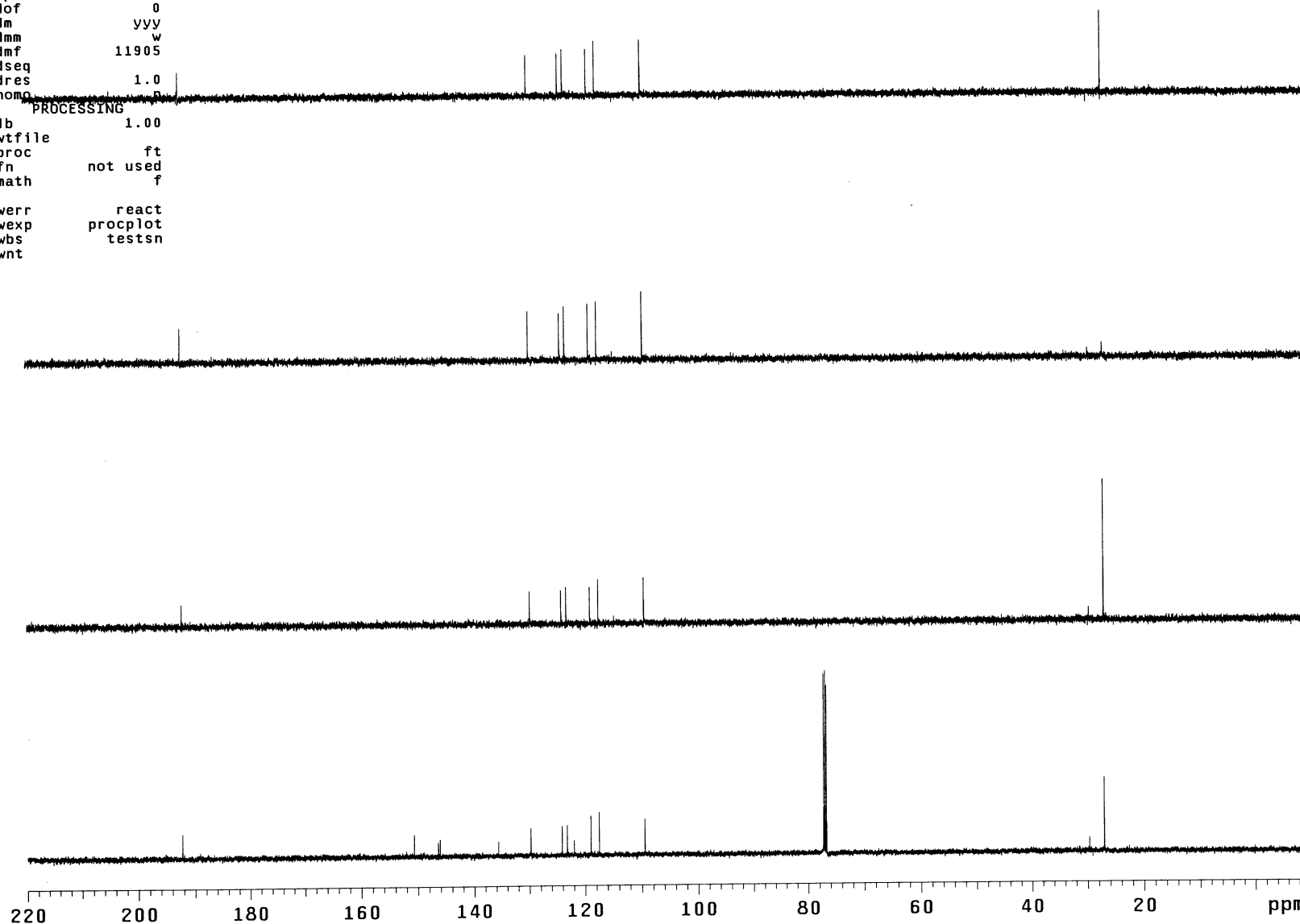
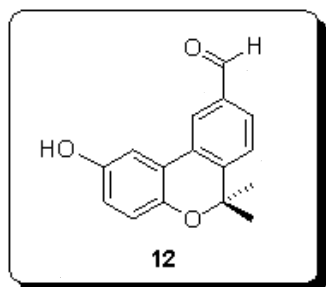


Fig S65. ¹H NMR of compound 13 (500 MHz, CDCl₃).

S65

PMK-01-233

exp12 s2pul

SAMPLE		DEC. & VT	
date	Nov 30 2009	dfrq	125.693
solvent	CDCl ₃	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.830	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	58	wtfile	
pw	4.8	proc	ft
dl	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	
alock	y	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	4998.0		
vs	98		
sc	0		
wc	210		
hzmm	23.80		
is	64.27		
rfl	4638.2		
rfp	3618.7		
th	3		
ins	100.000		
nm	ph		

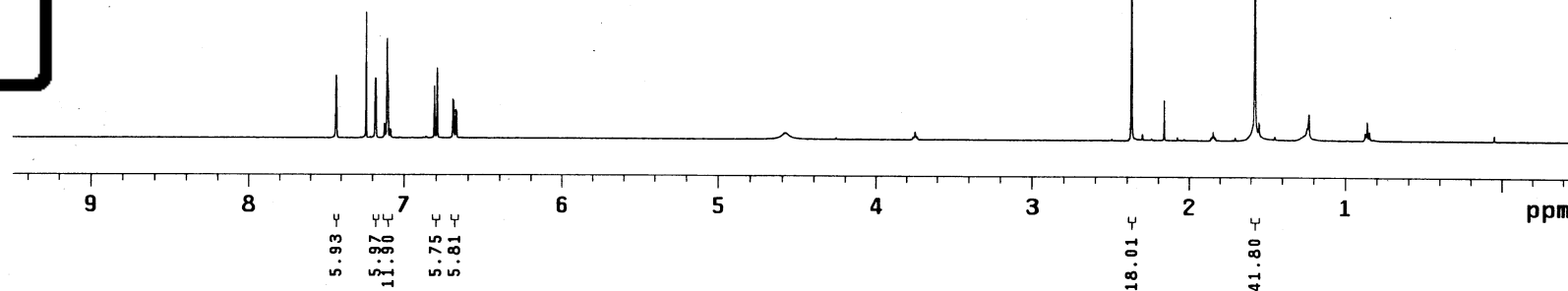
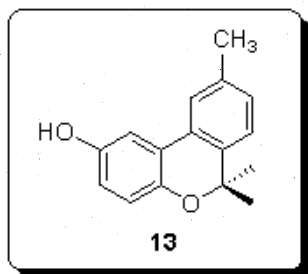
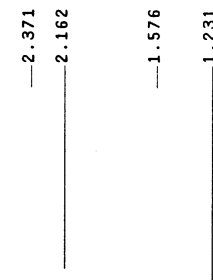
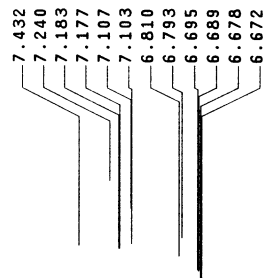
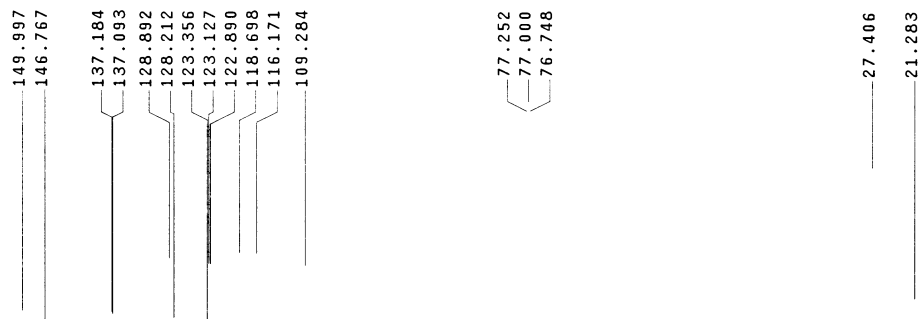


Fig S66. ¹³C NMR of compound 13 (125 MHz, CDCl₃).

PMK-1-233
exp43 s2pu1

SAMPLE		DEC. & VT	
date	Aug 4 2009	dfrq	499.836
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION		dof	0
sfrq	125.698	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	11905
np	62894	dseq	
sw	31446.5	dres	1.0
fb	17000	homo	n
bs	16	PROCESSING	
ss	2	lb	1.00
tpwr	54	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	10000		
ct	10000	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	28906.3		
vs	100		
sc	0		
wc	210		
hzmm	137.65		
is	500.00		
rfl	10980.6		
rfp	9677.6		
th	2		
ins	100.000		
nm	cdc ph		



S66

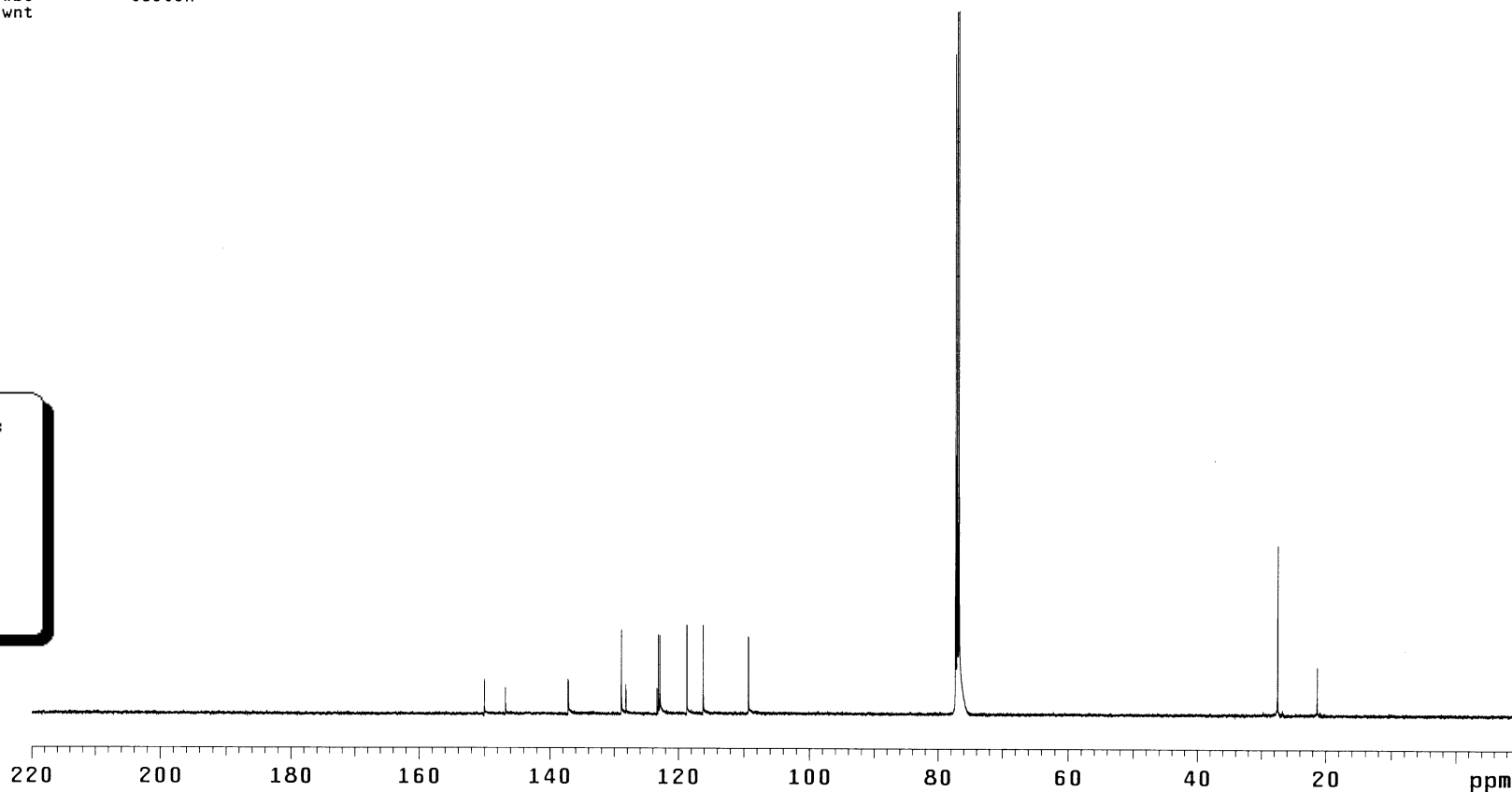
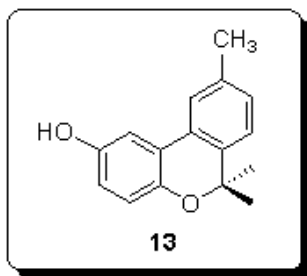


Fig S67. DEPT of compound 13 (CDCl₃).

S67

PMK-1-233

exp43 s2pu1

SAMPLE		DEC. & VT	
date	Aug 4 2009	dfrq	499.836
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION		do	0
sfrq	125.698	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	11905
np	62894	dseq	
sw	31446.5	dres	1.0
fb	17000	homo	n
bs	16	PROCESSING	
ss	2	lb	1.00
tpwr	54	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	10000		
ct	10000	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	28906.3		
vs	100		
sc	0		
wc	210		
hzmm	137.65		
is	500.00		
rfl	10980.6		
rfp	9677.6		
th	2		
ins	100.000		
nm	cdc ph		

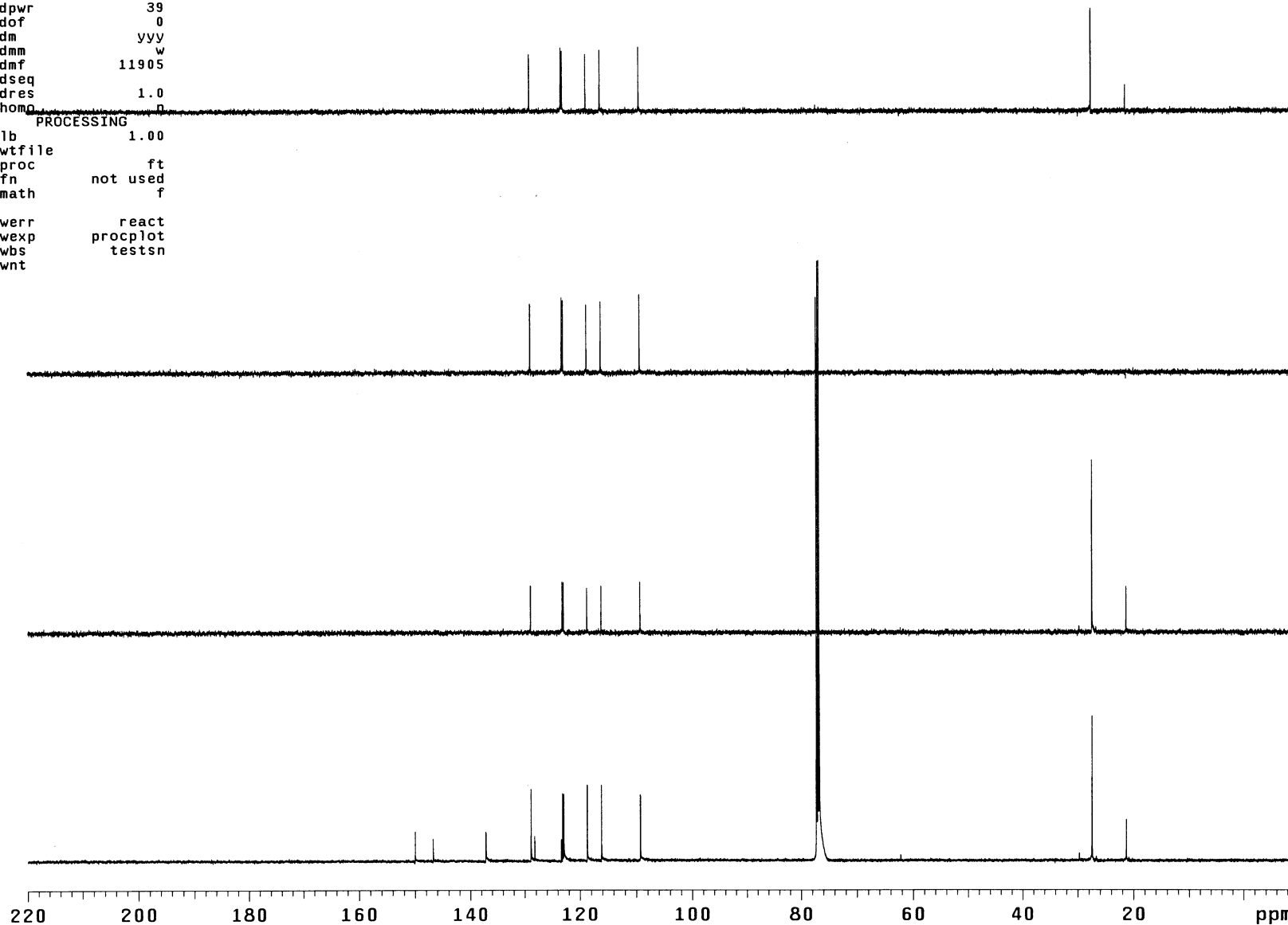
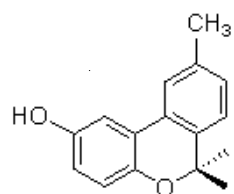


Fig S68. HSQC of compound 13 (CDCl₃).

S68

PMK-01-233

exp16 gHSQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	Nov 30 2009	hs	n	array	phase
solvent	cdcl3	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1003	i	phase
sw	4001.6	SPECIAL	1	1	1
at	0.128	temp	not used	2	2
np	1024	gain	34		
fb	not used	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1003		
nt	8	gt1	0.002000		
2D ACQUISITION		gzlv13	505		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.059		
tn	H1	gfs	not used		
sfrq	499.829	fn	1024		
tof	-250.0	F1 PROCESSING			
tpwr	58	gf1	0.006		
pw	11.100	gfs1	not used		
DECOUPLER		procl	lp		
dn	C13	fn1	2048		
dof	-2515.2	DISPLAY			
dm	nny	sp	662.6		
dmm	ccp	wp	3282.6		
dmf	32258	sp1	2289.7		
dpwr	36	wp1	14439.8		
pxwlv1	52	rfl	-248.4		
pxw	14.300	rfl1	1257.6		
HSQC		rflp1	0		
j1xh	140.0	PLOT			
nullflg	y	wc	150.0		
mult	2	sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	227		
		th	4		
		ai	cdc	ph	

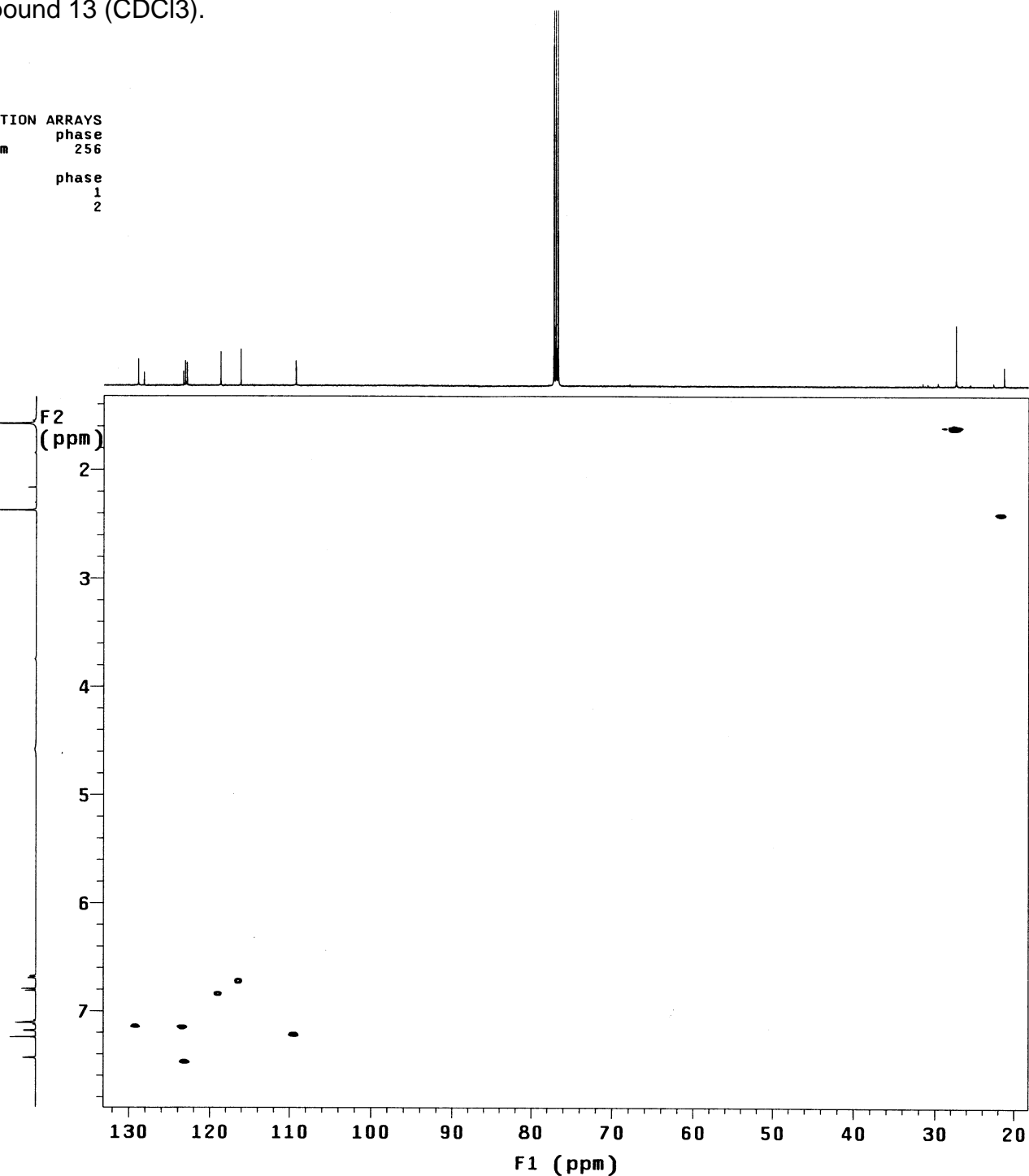
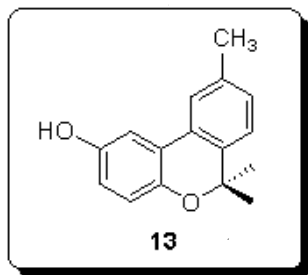


Fig S69. COSY of compound 13 (CDCl₃).

S69

PMK-01-233

exp15 gCOSY

SAMPLE		FLAGS	
date	Nov 30 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglvl	1003
ACQUISITION		SPECIAL	
sw	4001.6	temp	not used
at	0.128	gain	34
np	1024	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.064
d1	1.000	sbs	not used
nt	8	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	4001.6	sb1	-0.032
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	1024
sfrq	499.829	DISPLAY	
tof	-250.0	sp	235.9
tpwr	58	wp	3993.8
pw	11.100	sp1	238.0
GRADIENTS		wp1	
gzlv11	1003	rfl	957.0
gt1	0.001000	rfl1	1185.1
gstab	0.000500	rfl1	954.9
DECOUPLER		rfl1	
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	227
		th	5
		ai	cdc av

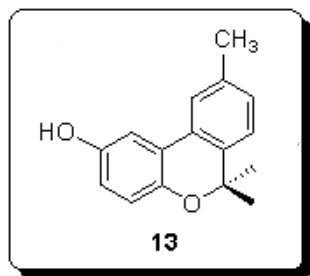
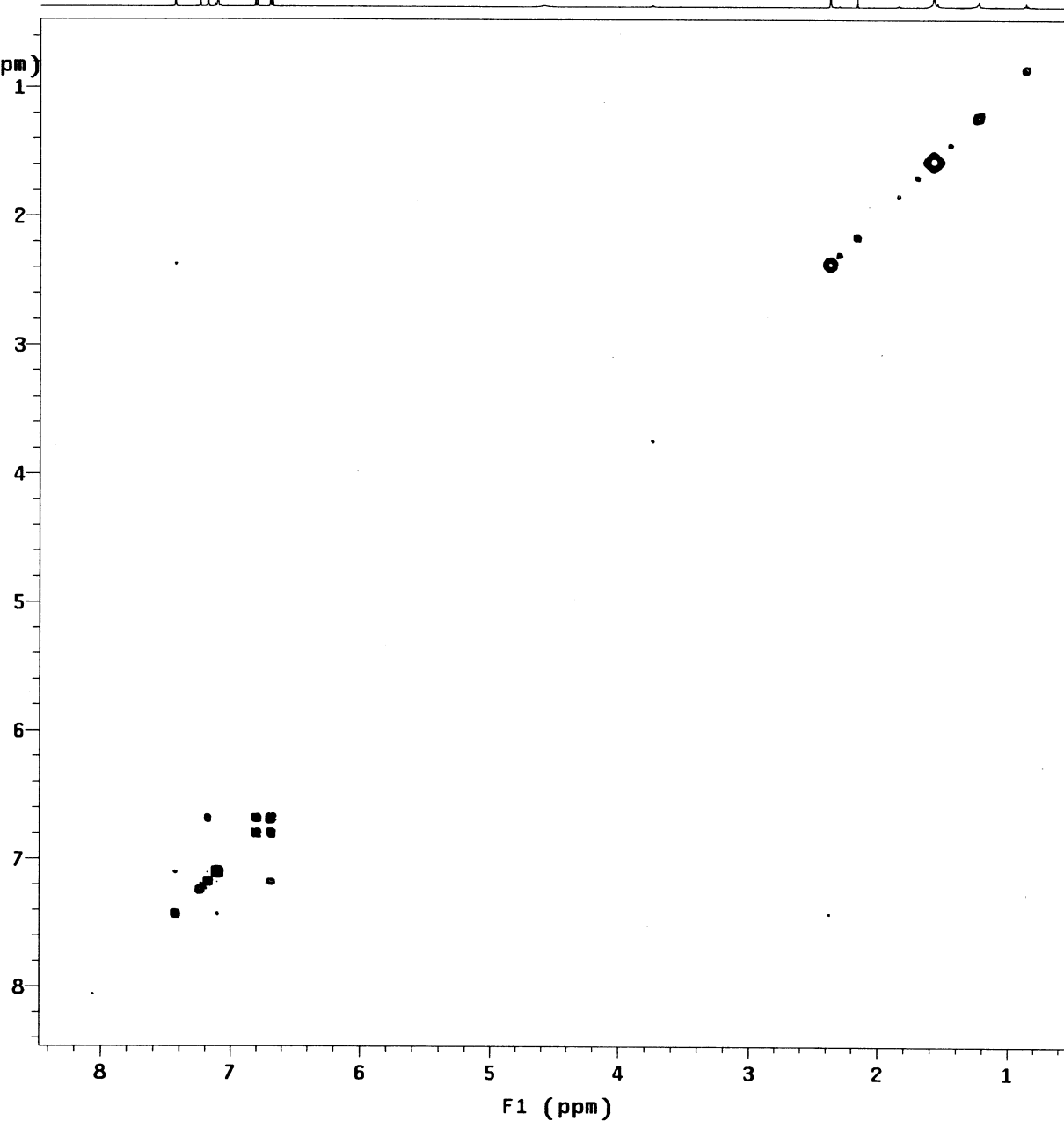
F2
(ppm)

Fig S70. ¹H NMR of compound 14 (500 MHz, CDCl₃).

S70

PMK-01-209
exp31 s2pu1

SAMPLE		DEC. & VT	
date	May 20 2009	dfrq	125.695
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.836	dm	hnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs		PROCESSING	
tpwr	57	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5498.0		
vs	60		
sc	0		
wc	210		
hzmm	26.18		
is	192.38		
rfl	4630.9		
rfp	3618.8		
th	1		
ins	100.000		
nm	ph		

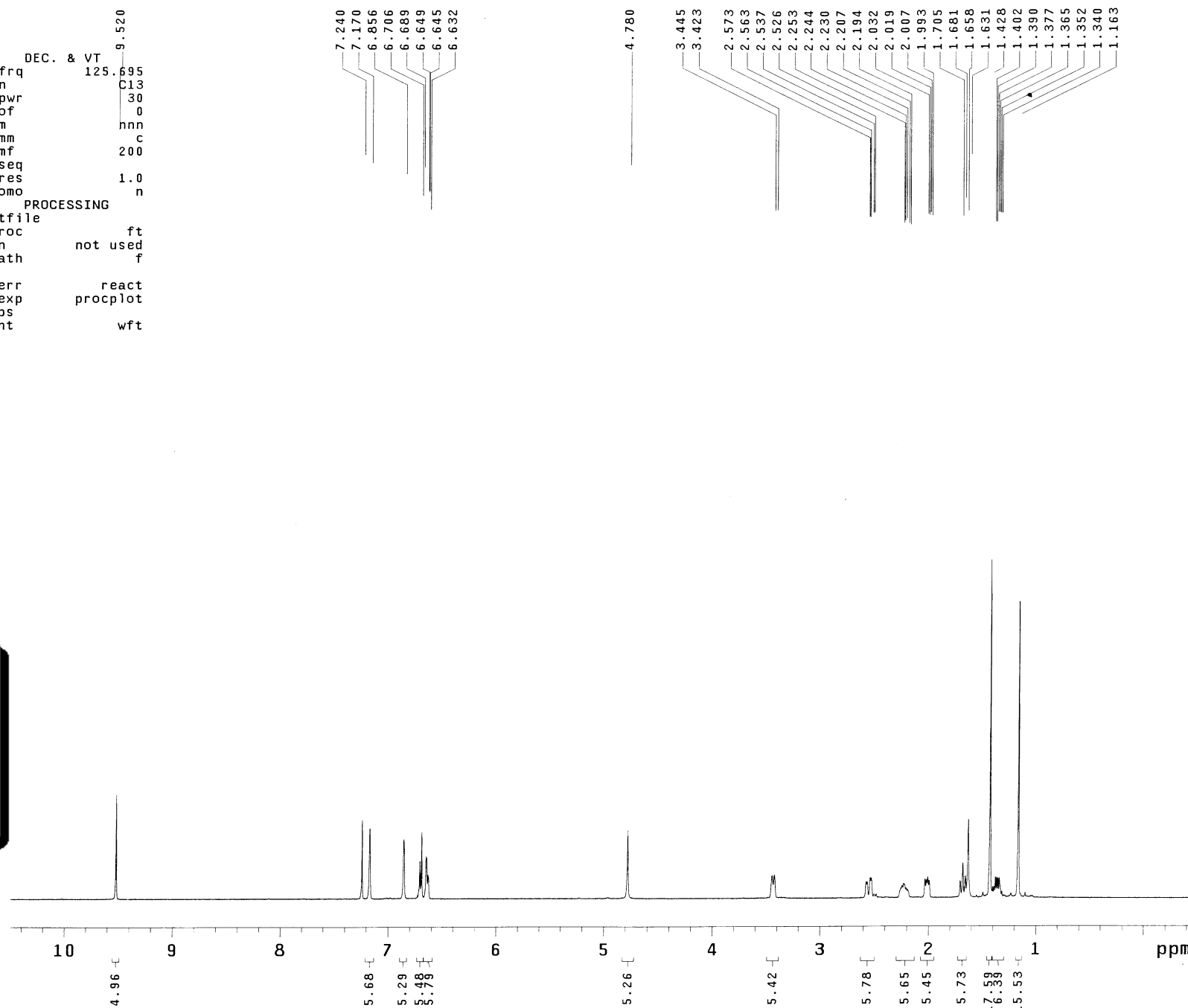
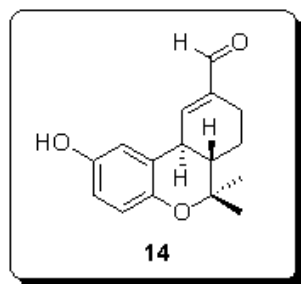


Fig S71. ¹³C NMR of compound 14 (125 MHz, CDCl₃).

S71

PMK-01-209
exp33 s2pu1

SAMPLE
date May 20 2009
solvent cdc13
file exp

ACQUISITION
sfrq 125.698
tn C13
at 1.000
np 62894
sw 31446.5
fb 17000
bs 16
ss 2
tpwr 54
pw 4.0
d1 1.000
tof 2512.2
nt 20000
ct 20000
alock y
gain not used

DEC. & VT
dfrq 499.836
dn H1
dpwr 39
dof 0
dm yyy
dmm w
dmf 11905
dseq
dres 1.0
homo n

PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr react
wexp procplot
wbs testsn
wnt

FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -1256.9
wp 27650.1
vs 145
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10978.7
rfp 9677.6
th 6
ins 100.000
nm ph

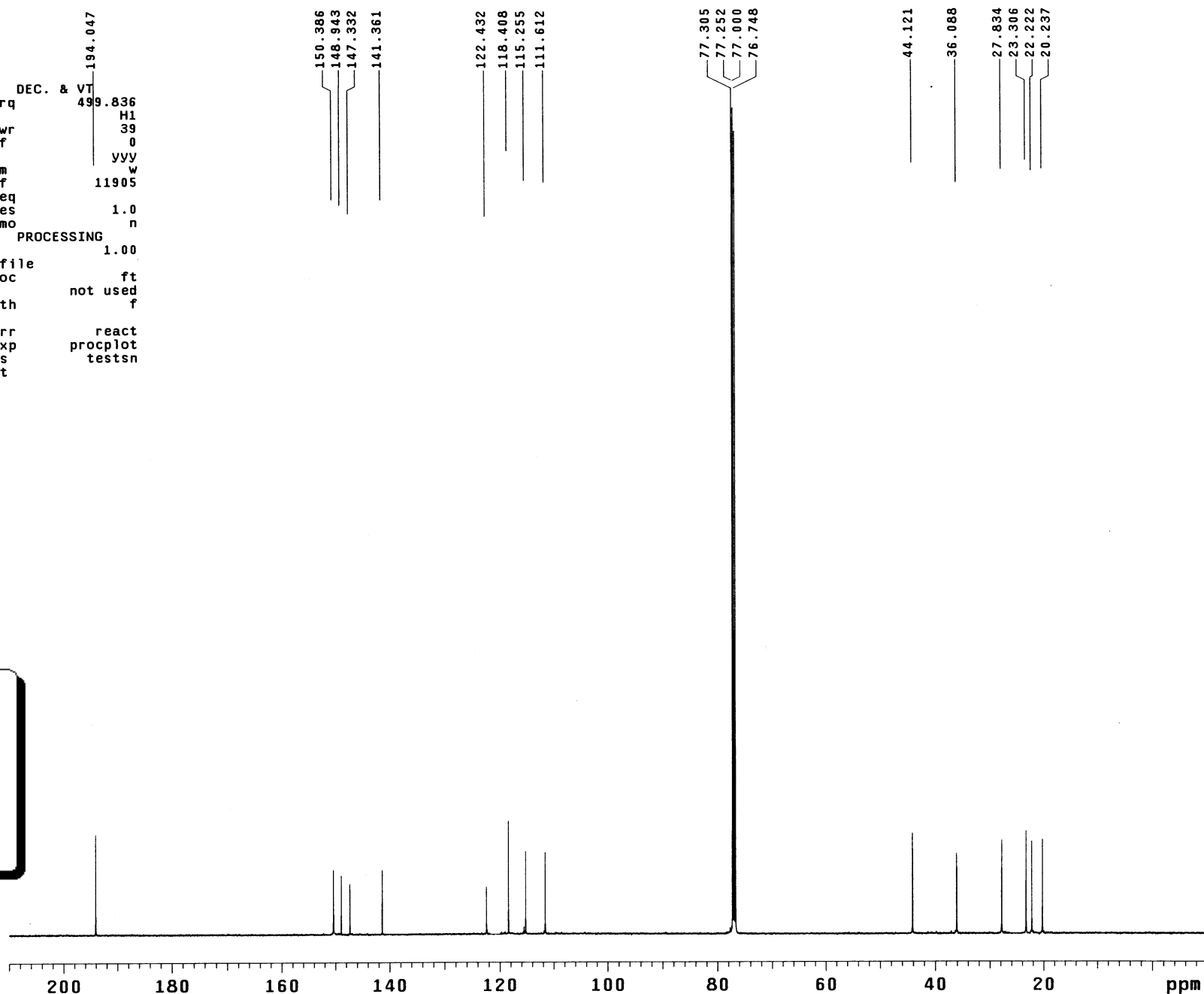
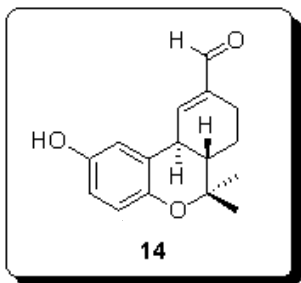


Fig S72. ¹³C NMR of compound 14 (125 MHz, CDCl₃), expanded.

S72

PMK-01-209

exp33 s2pu1

SAMPLE DEC. & VT
date May 20 2009 dfrq 499.836
solvent cdcl3 dn H1
file exp dpwr 39
ACQUISITION dof 0
sfrq 125.698 dm yvy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 PROCESSING lb 1.00
tpwr 54 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 20000
ct 20000 werr react
alock y wexp procplot
gain not used wbs testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 9383.0
wp 468.3
vs 81
sc 0
wc 210
hzmm 2.23
is 500.00
rfl 10978.7
rfp 9677.6
th 6
ins 100.000
nm ph

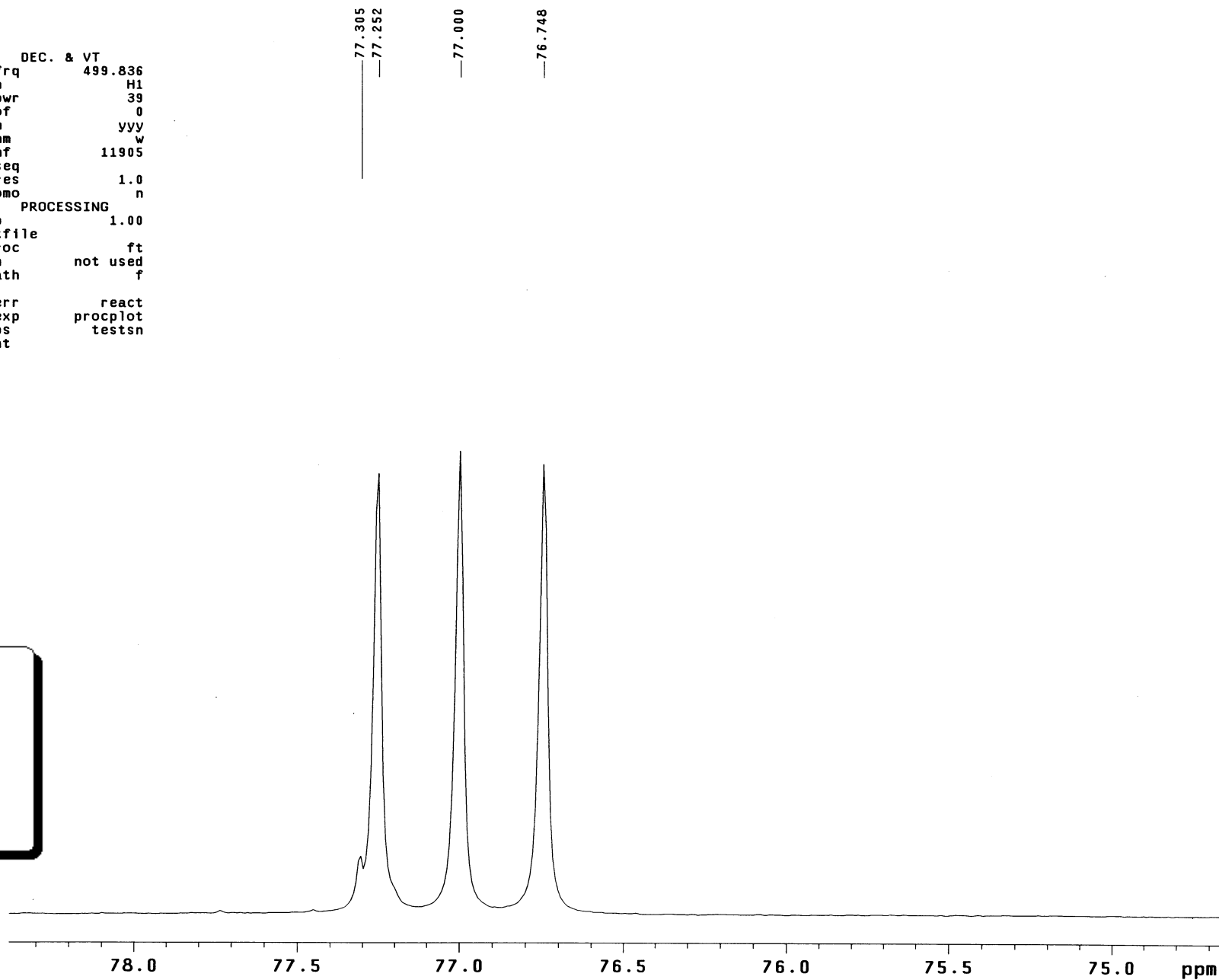
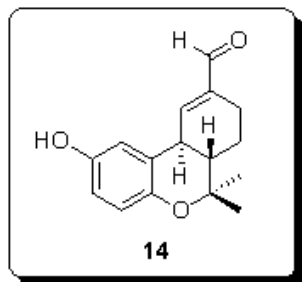


Fig S73. DEPT of compound 14 (CDCl3).

S73

PMK-01-209

exp32 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	May 20 2009	j1xh 140.0	array	mult
solvent	cdcl3	mult	arrayed	3
sample	undefined	SPECIAL	arraydim	
ACQUISITION		temp	not used	i mult
sw	31446.5	gain	20	1 0.5
at	1.000	spin	0	2 1
np	62894	PROCESSING	3	1.5
bs	16	lb	1.00	
ss	-4	fn	not used	
d1	1.000	SPECTRUM		
nt	1000	wp	27650.1	
ct	1000	sp	-1257.2	
TRANSMITTER		rp	33.5	
tn	C13	lp	52.4	
tof	2512.2	ai	ph	
tpwr	54	REFERENCE		
pw	9.400	rfl	1269.7	
DECOUPLER		rfl	0	
dn	H1	PLOT		
dof	0	wc	210	
dpwr	39	sc	0	
dm	nny	vs	256	
dmm	ccw	hzmm	131.67	
dmf	11905	th	68	
pp1v1	49			
pp	29.400			

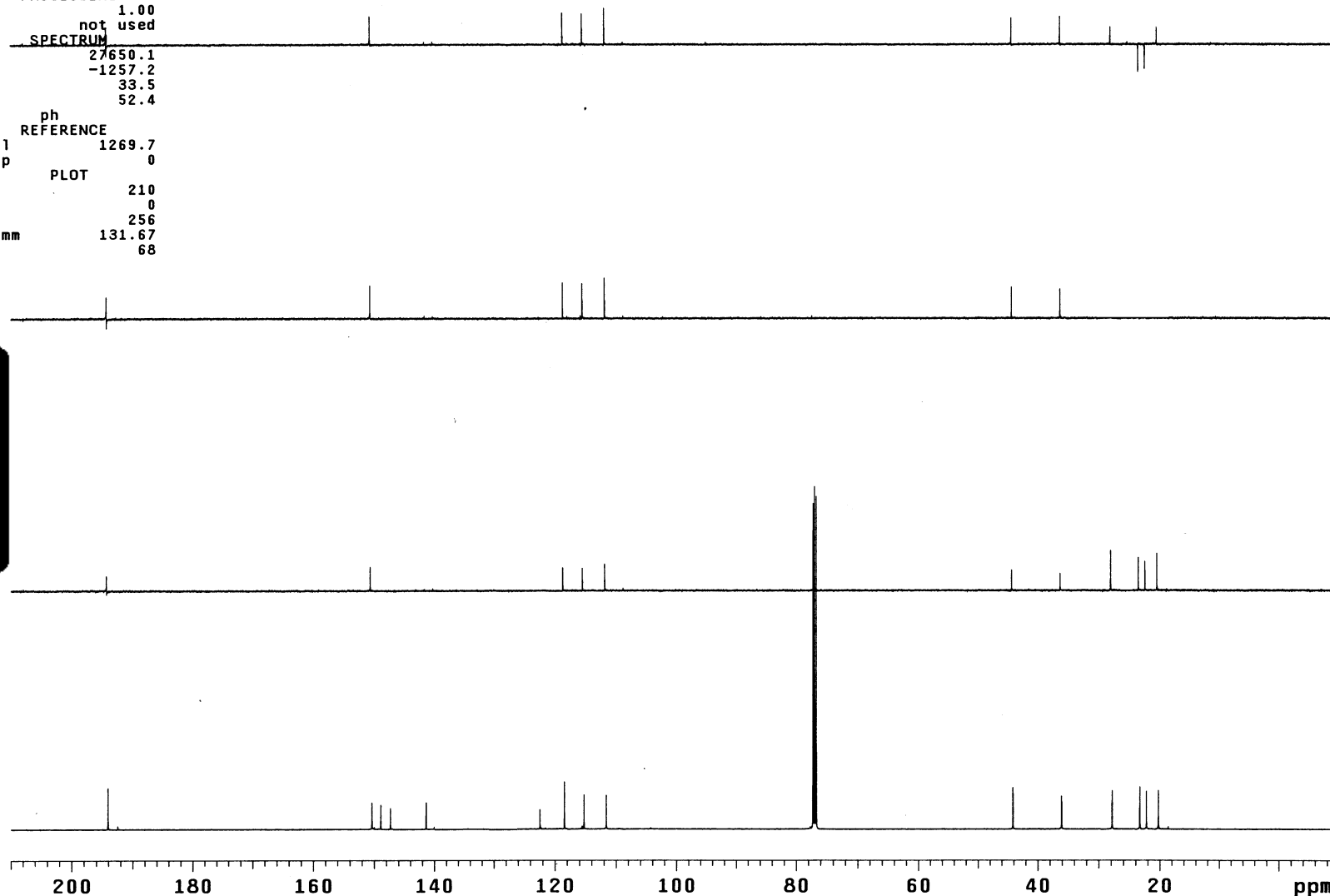
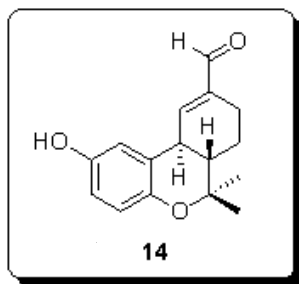


Fig S74. DEPT of compound 14 (CDCl₃), expanded.

S74

PMK-01-209

exp32 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	May 20 2009	j1xh	140.0	array
solvent	cdcl3	mult	arrayed	mult
sample	undefined		arraydim	3
ACQUISITION		SPECIAL		
sw	31446.5	temp	not used	i
at	1.000	gain	20	1
np	62894	spin	0	2
bs	16	PROCESSING	3	1.5
ss	-4	lb	1.00	
d1	1.000	fn	not used	
nt	1000	SPECTRUM		
ct	1000	wp	3142.0	
TRANSMITTER		sp	7540.1	
tn	C13	rp	33.5	
tof	2512.2	lp	52.4	
tpwr	54	ai	ph	
pw	9.400	REFERENCE		
DECOUPLER		rfl	1269.7	
dn	H1	rtp	0	
dof	0	PLOT		
dpwr	39	wc	210	
dm	nny	sc	0	
dmm	ccw	vs	256	
dmf	11905	hzmm	14.96	
pplv1	49	th	68	
pp	29.400			

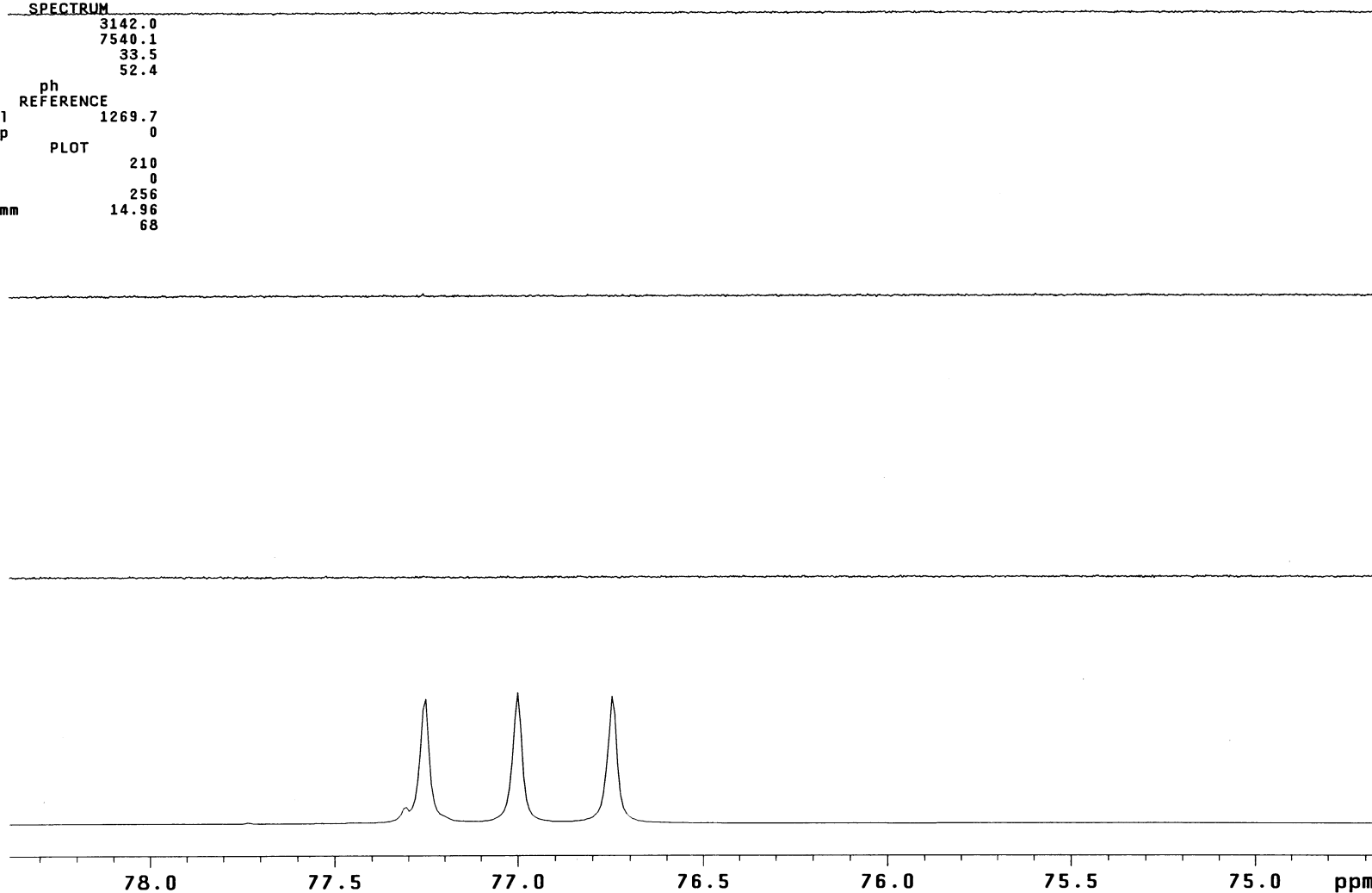
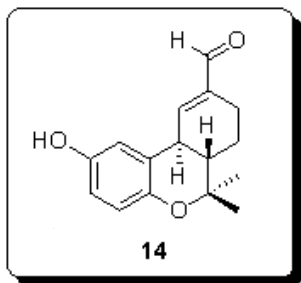


Fig S75. HMQC of compound 14 (CDCl₃).

S75

PMK-01-209

exp35 gHMQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	May 20 2009	hs	n	array	phase
solvent	cdcl3	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1026	i	phase
sw	4498.4	SPECIAL	1	1	1
at	0.228	temp	not used	2	2
np	2048	gain	44		
fb	3000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1026		
nt	16	gt1	0.001000		
2D ACQUISITION		gzlv13	516		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.105		
tn	H1	gfs	not used		
sfrq	499.836	fn	2048		
		F1 PROCESSING			
tof	249.8	gf1	0.006		
tpwr	57	gfs1	not used		
pw	13.000	proc1	1p		
DECOUPLER		fn1	2048		
dn	C13	DISPLAY			
dof	-2515.1	sp	526.2		
dm	nnv	wp	3400.2		
dmm	ccp	sp1	1851.6		
dmf	32258	wp1	17882.8		
dpwr	35	rfl	-499.8		
pwxlvl	51	rfp	0		
pw	14.700	rfl1	1257.5		
HMQC		rflp1	0		
j1xh	140.0	PLOT			
nullflg	y	wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	227		
		th	4		
		ai	cdc		
			ph		

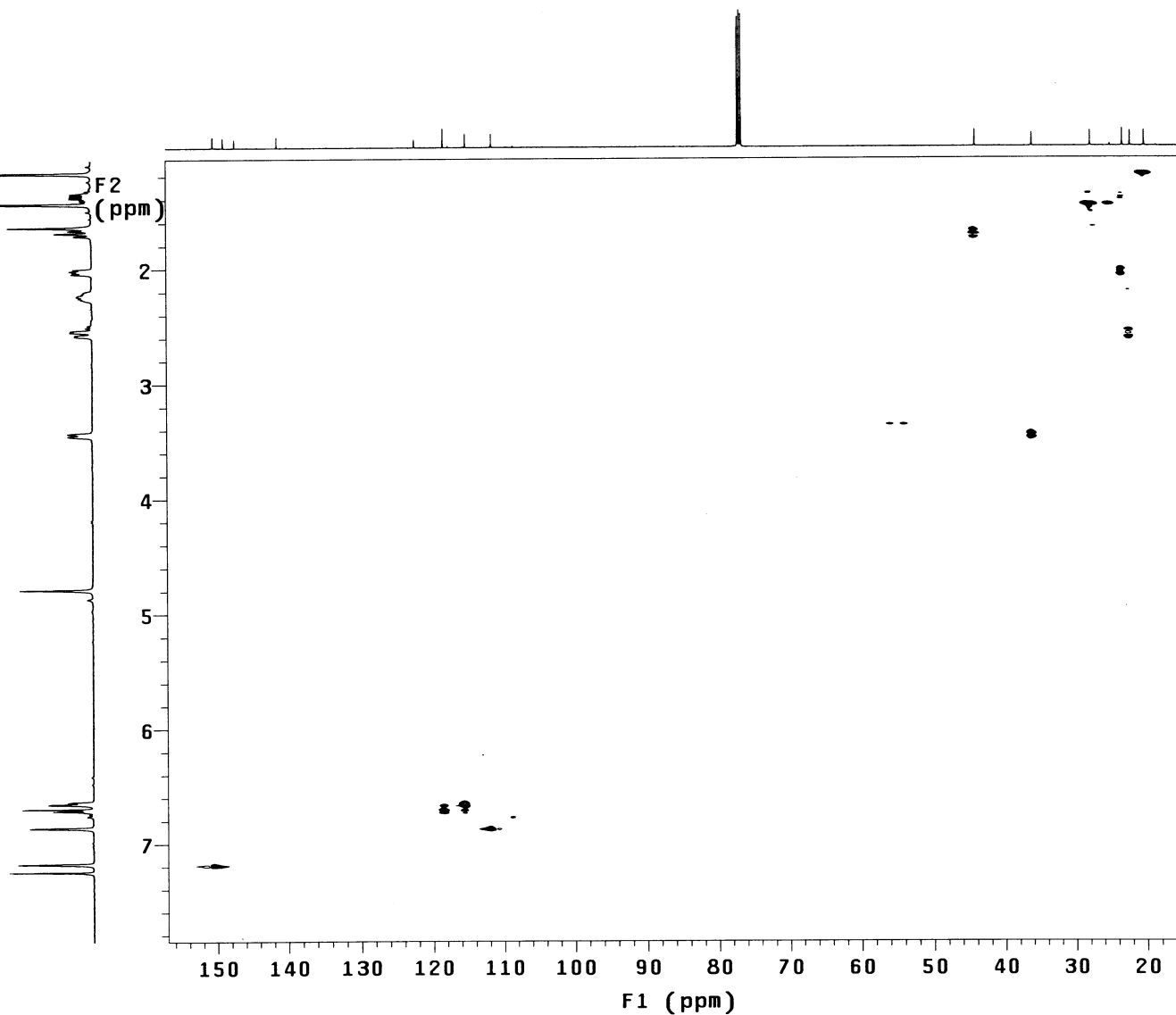
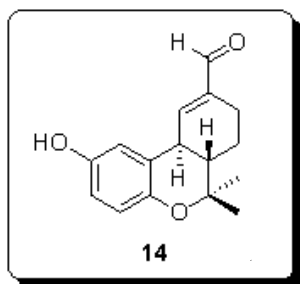


Fig S76. COSY of compound 14 (CDCl₃).

S76

PMK-01-209

exp34 gCOSY

SAMPLE		FLAGS	
date	May 20 2009	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	4498.4	temp	not used
at	0.228	gain	44
np	2048	spin	0
fb	3000	F2 PROCESSING	
ss	16	sb	-0.114
d1	1.000	sbs	not used
nt	16	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4498.4	sb1	-0.028
ni	128	sbs1	not used
TRANSMITTER		proc1	lp
tn	H1	fn1	2048
sfrq	499.836	DISPLAY	
tof	249.8	sp	489.1
tpwr	57	wp	4494.0
pw	13.000	sp1	491.5
GRADIENTS		wp1	4494.0
gzlv11	1026	rfl	3134.1
gt1	0.001000	rfp	3618.8
gstab	0.000500	rfl1	3131.7
DECOUPLER		rfp1	3618.8
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	1814
		th	5
		ai	cdc av

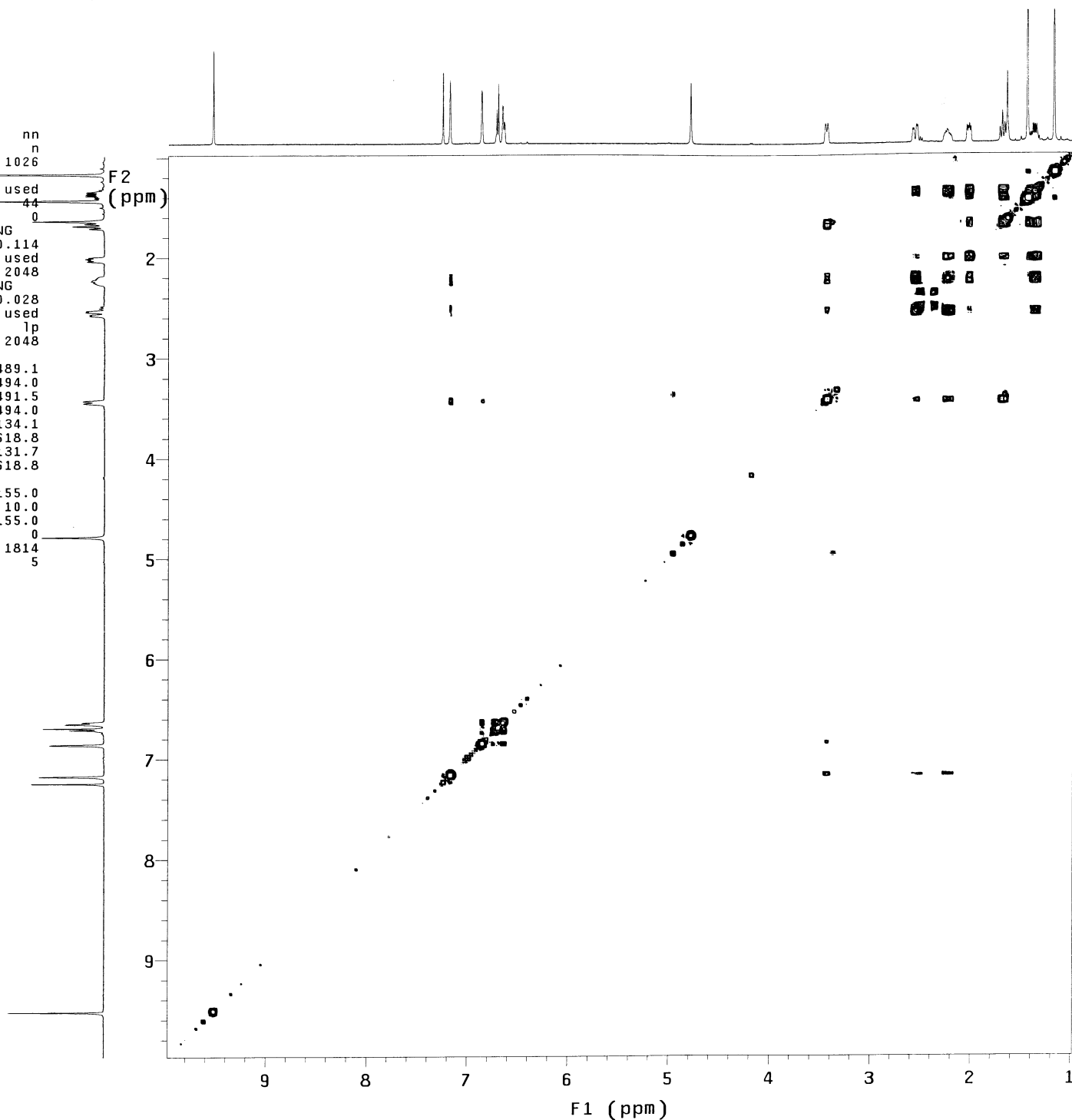
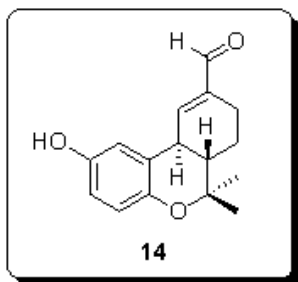


Fig S77. NOESY of compound 14 (CDCl₃).

S77

PMK-01-209
exp36 NOESY

SAMPLE		FLAGS	
date	May 20 2009	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	1026
sw	4498.4	SPECIAL	
at	0.228	temp	not used
np	2048	gain	44
fb	3000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.105
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4498.4	F1 PROCESSING	
ni	200	gf1	0.041
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.836	fn1	2048
tof	249.8	DISPLAY	
tpwr	57	sp	490.6
pw	13.000	wp	4494.0
NOESY		sp1	491.5
mix	0.600	wp1	4494.0
PRESATURATION		rfl	3132.6
satmode	nnnn	rfp	3618.8
satpwr	0	rfl1	3131.6
satdly	0	rfp1	3618.8
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	1814
		th	1
		ai	ph

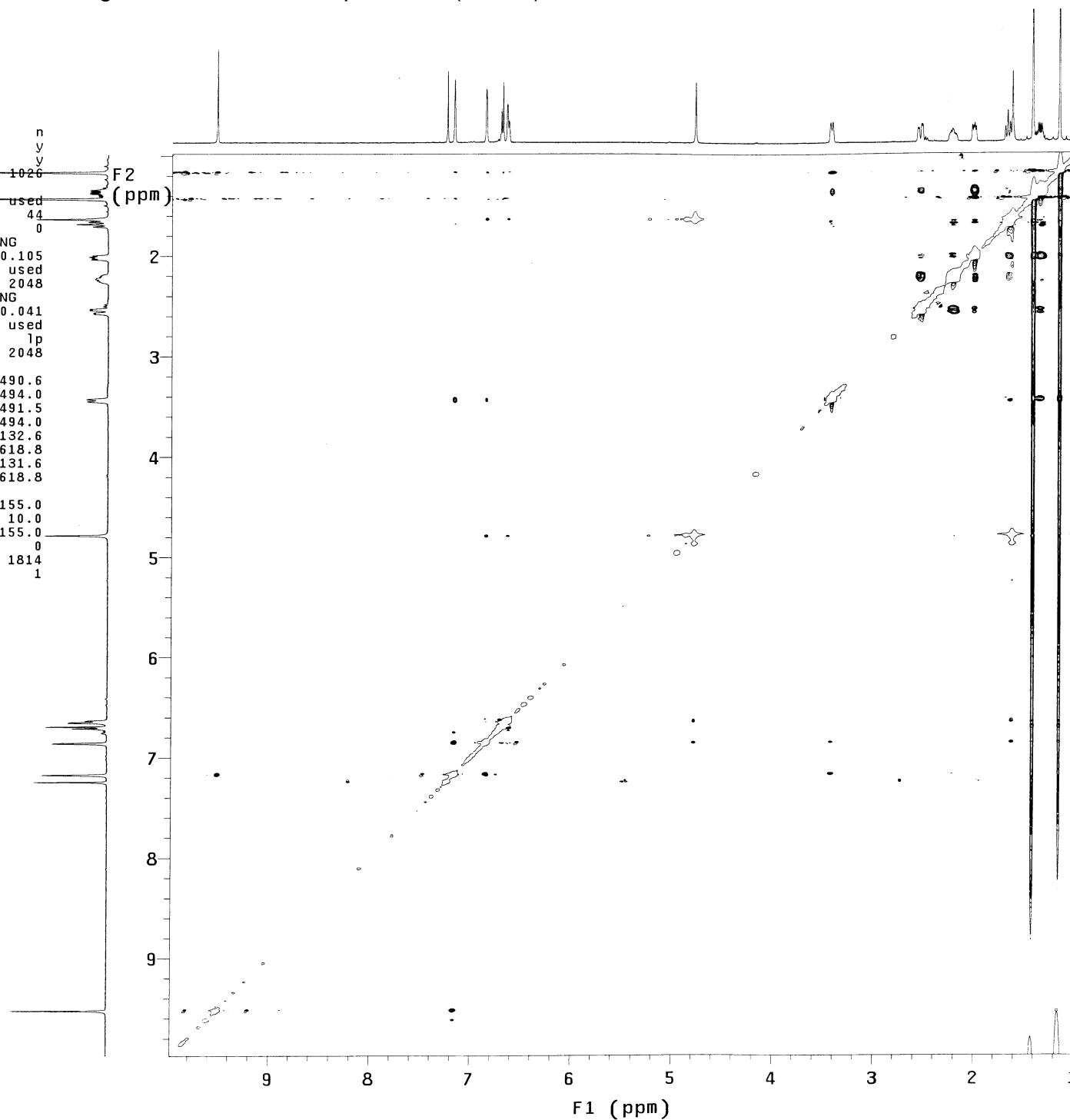
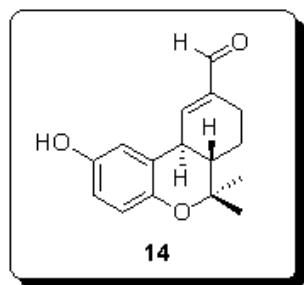


Fig S78. NOESY of compound 14 (CDCl₃).

S78

PMK-01-209

exp3 NOESY

SAMPLE		FLAGS	
date	May 21 2009	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1026
sw	4498.4	SPECIAL	
at	0.228	temp	not used
np	2048	gain	44
fb	3000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.105
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4498.4	F1 PROCESSING	
ni	400	gf1	0.041
TRANSMITTER		gfs1	not used
tn	H1	fn1	2048
sfrq	499.836	DISPLAY	
tof	249.8	sp	489.4
tpwr	57	wp	4349.1
pw	13.000	sp1	501.0
NOESY		wp1	4344.7
mix	0.600	rfl	1917.4
PRESATURATION		rfp	2389.2
satmode	nnnn	rfl1	1901.4
satpwr	0	rfp1	2389.2
satdly	0	PLOT	
satfrq	0	wc	155.0
DECOUPLER		sc	10.0
dn	C13	wc2	155.0
dm	nnn	sc2	0
		vs	113
		th	1
		ai	ph

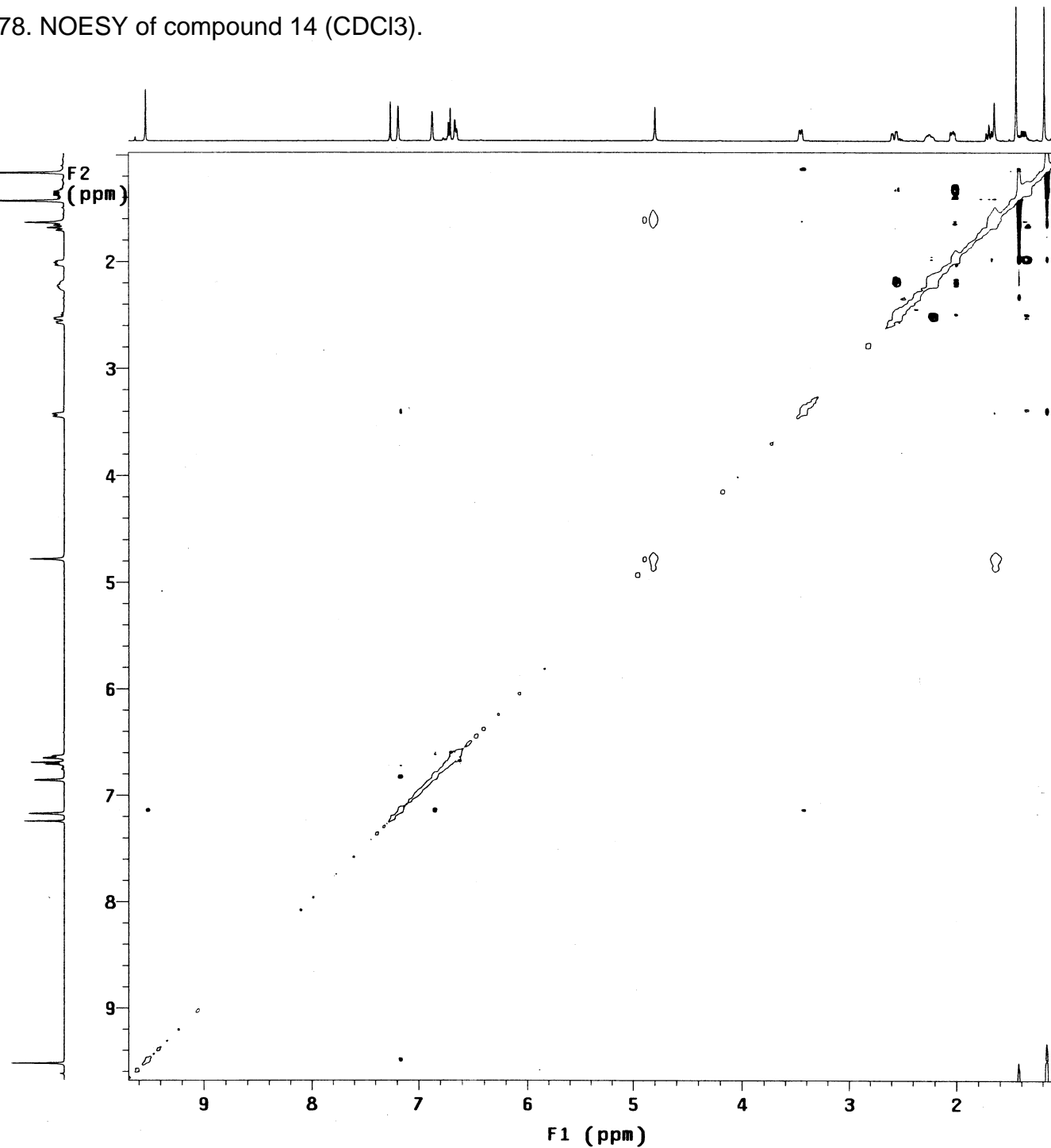
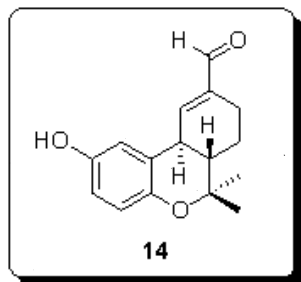
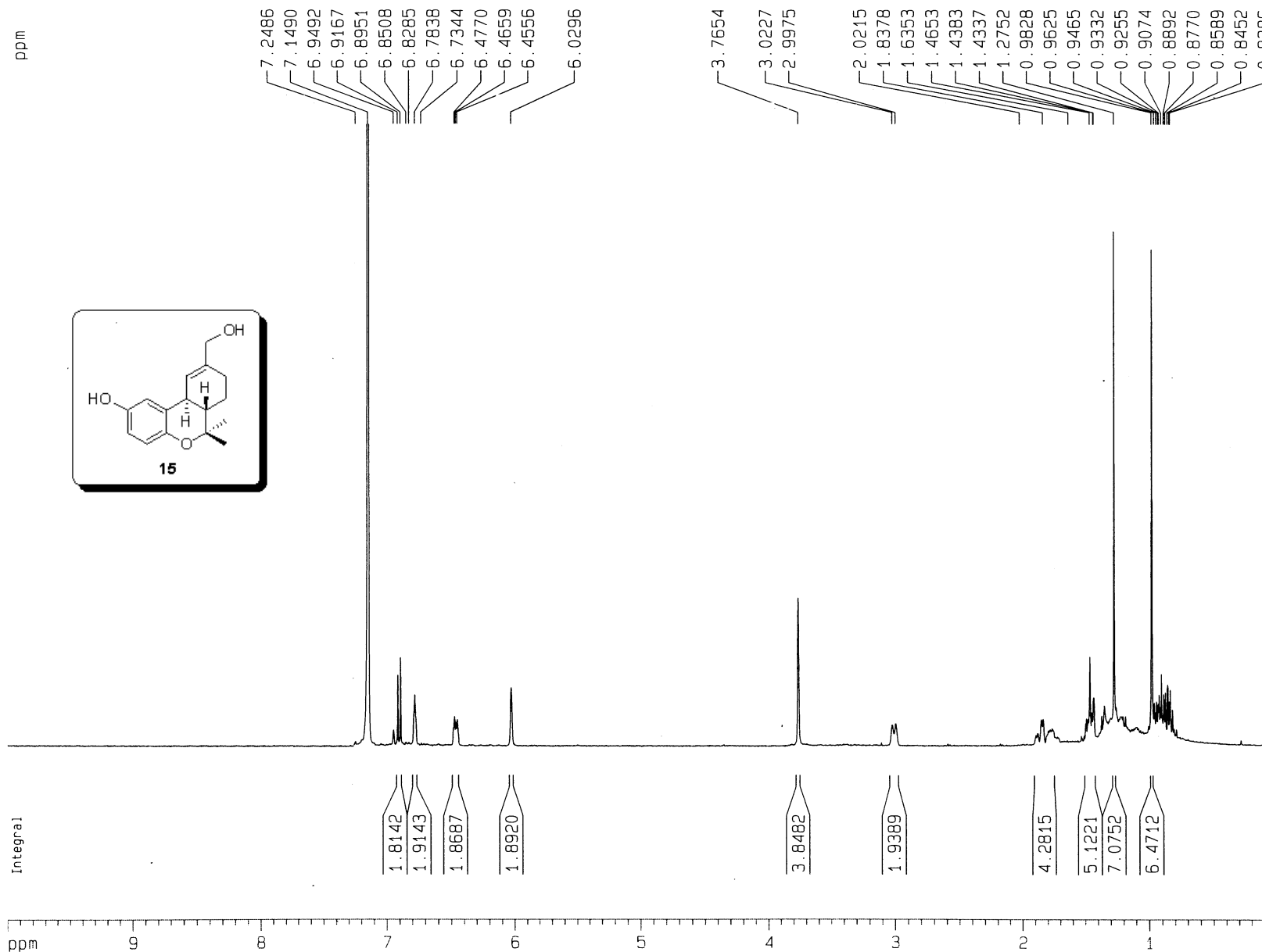


Fig S79. ¹H NMR of compound 15 (400 MHz, C₆D₆).

S79



Current Data Parameters
NAME PMK-01-262
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090921
Time 23.29
INSTRUM spect
PROBHD 5 mm GNP 1H
PULPROG zg30
TD 16384
SOLVENT C6D6
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1448.2
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.50000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.90 usec
PL1 -3.00 dB
SF01 400.1326008 MHz

F2 - Processing parameters
SI 8192
SF 400.1300495 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 21.50 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.46512 ppm/cm
HZCM 186.10698 Hz/cm

Fig S80. ¹H NMR of compound 15 (500 MHz, C6D6).

S80

PMK-01-262

exp9 s2pul

```

SAMPLE          DEC. & VT
date Nov 18 2009 dfrq 125.693
solvent Benzene  dn  C13
file exp         dpwr 30
ACQUISITION     dof  0
sfrq 499.830     dm   nnn
tn      H1       dmm   c
at      3.000     dmf  200
np      48000     dseq
sw      8000.0    dres 1.0
fb      not used  homo
bs      4
PROCESSING
tpwr 58          wtfile
pw 4.8           proc   ft
d1 1.000         fn     not used
tof 499.7        math   f
nt 4
ct 4             werr
alock y          wexp   wft
gain not used    wbs    wft
wnt             wnt     wft
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 4998.0
vs 39
sc 0
wc 210
hzmm 23.80
is 102.59
rfl 4567.1
rfp 3578.8
th 1
ins 100.000
ai ph
  
```

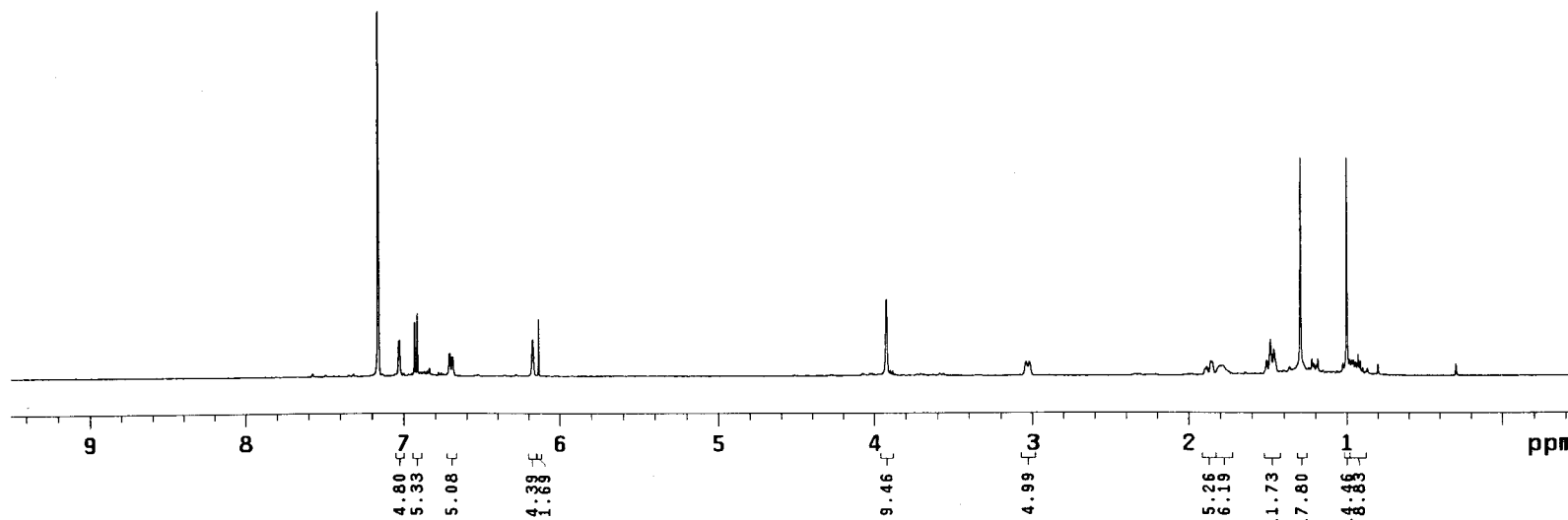
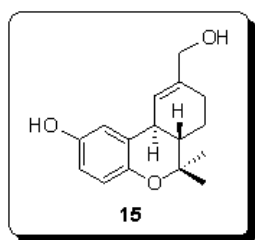
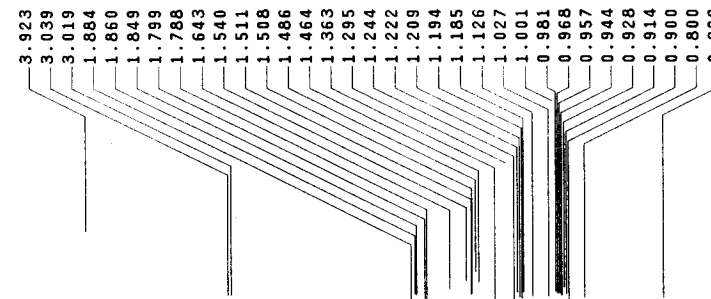
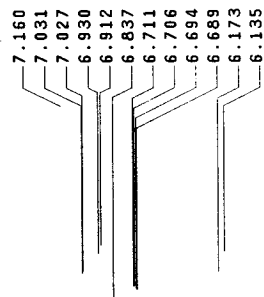


Fig S81. ¹H NMR of compound 15 (125 MHz, C₆D₆).

PMK-01-262

exp11 s2pu1

SAMPLE		DEC. & VT	
date	Nov 18 2009	dfrq	499.829
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION			
sfrq	125.696	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	11905
np	62894	dseq	
sw	31446.5	dres	1.0
fb	not used	homo	n
PROCESSING			
bs	16	lb	1.00
ss	2	wtfile	
tpwr	54	proc	ft
pw	4.0	fn	not used
d1	1.000	math	f
tof	2512.2	werr	react
nt	6000	wexp	procplot
ct	3056	wbs	testsn
alock	y	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	27649.1		
vs	1123		
sc	0		
wc	210		
hzmm	131.67		
is	500.00		
rfl	17355.7		
rfp	16087.2		
th	5		
ins	100.000		
nm	ph		

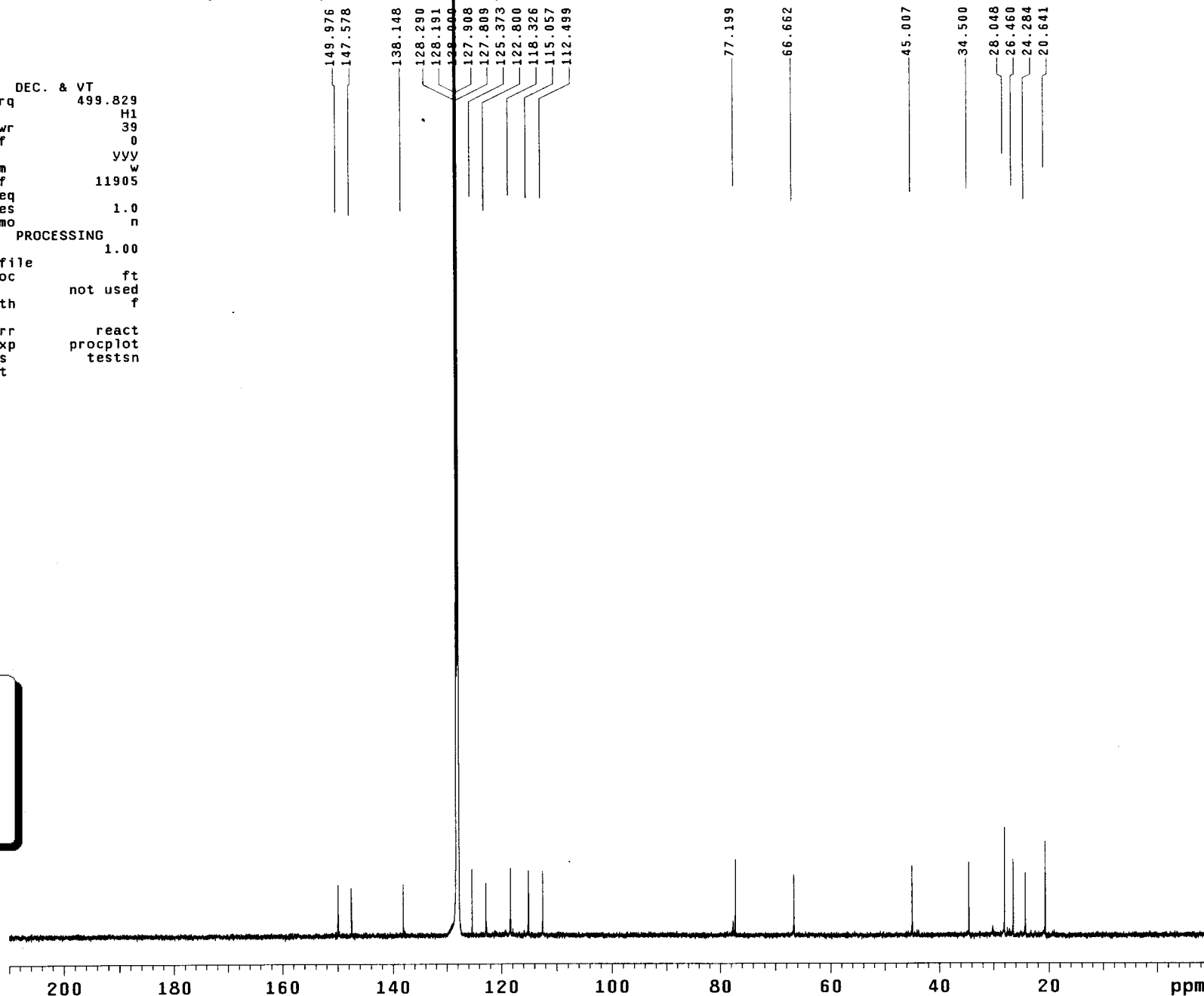
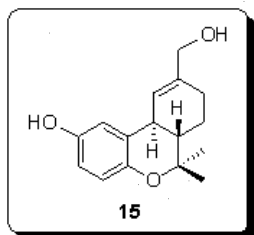


Fig S82. DEPT of compound 15, (C6D6).

S82

PMK-01-262

exp10 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	Nov 18 2009	j1xh	140.0	array	mult
solvent	Benzene	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	20	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
dl	1.000	SPECTRUM			
nt	1200	wp	27649.1		
ct	1200	sp	-1257.4		
TRANSMITTER		rp	-114.1		
tn	C13	lp	174.6		
tof	2512.2	ai	cdc ph		
tpwr	54	REFERENCE			
pw	10.500	rfl	1269.9		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	39	sc	0		
dm	nny	vs	603		
dmm	ccw	hzmm	131.67		
dmf	11905	th	18		
pplvl	51				
pp	24.000				

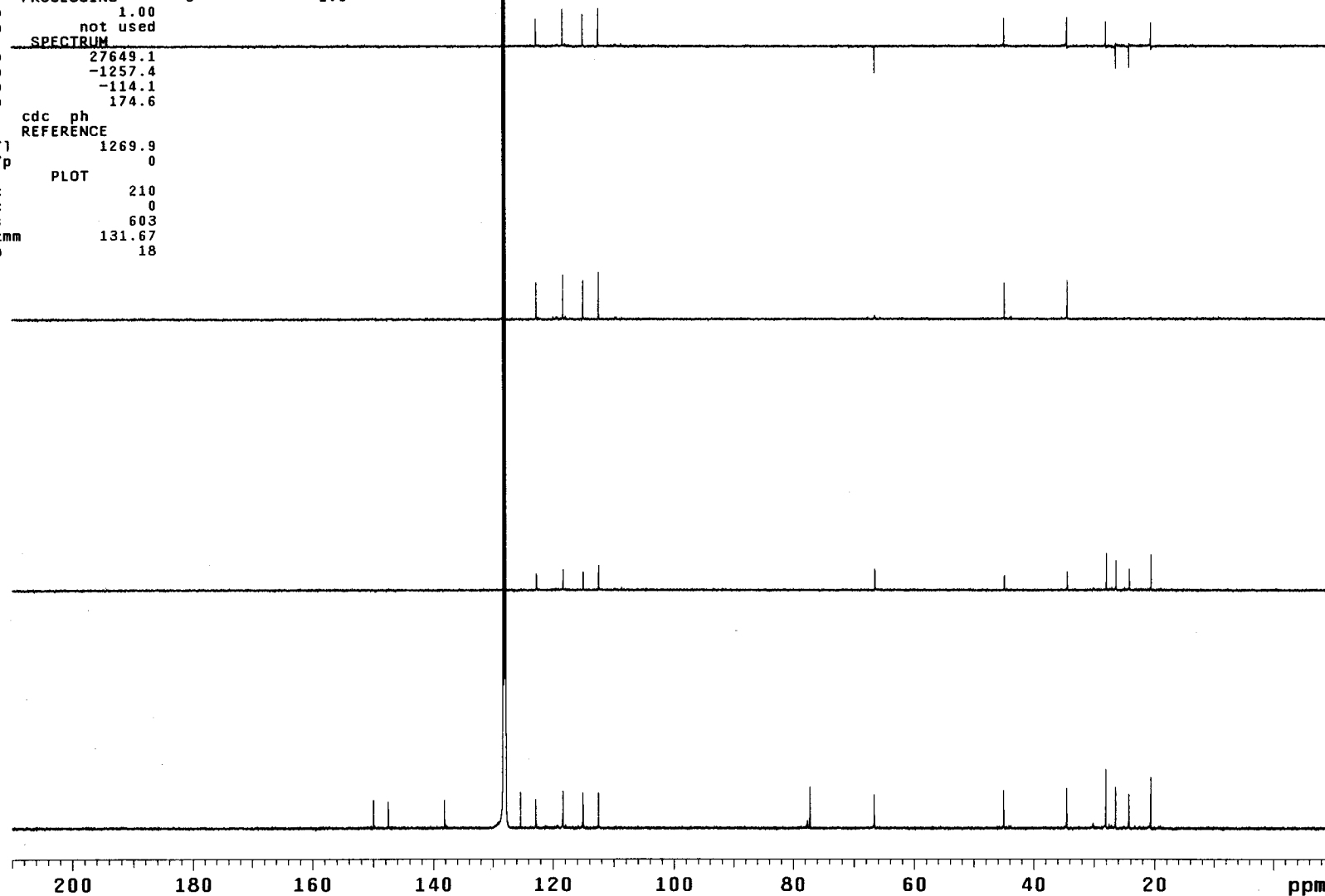
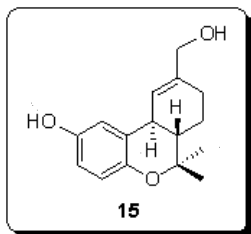


Fig S83. COSY of compound 15 (C6D6).

S83

PMK-01-262

exp12 gCOSY

SAMPLE		FLAGS	
date	Nov 18 2009	hs	nn
solvent	Benzene	sspul	n
sample	undefined	hsglv1	1003
ACQUISITION		SPECIAL	
sw	4490.3	temp	not used
at	0.228	gain	28
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.114
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4490.3	sb1	-0.029
n1	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.829	DISPLAY	
tof	-499.9	sp	-234.4
tpwr	58	wp	4486.0
pw	11.100	sp1	-234.3
GRADIENTS		wp1	4486.0
gzlv1	1003	rfl	1748.2
gt1	0.001000	rfp	1509.5
gstab	0.000500	rfl1	1748.1
DECOUPLER		rfp1	1509.5
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	113
		th	5
		af	cdc av

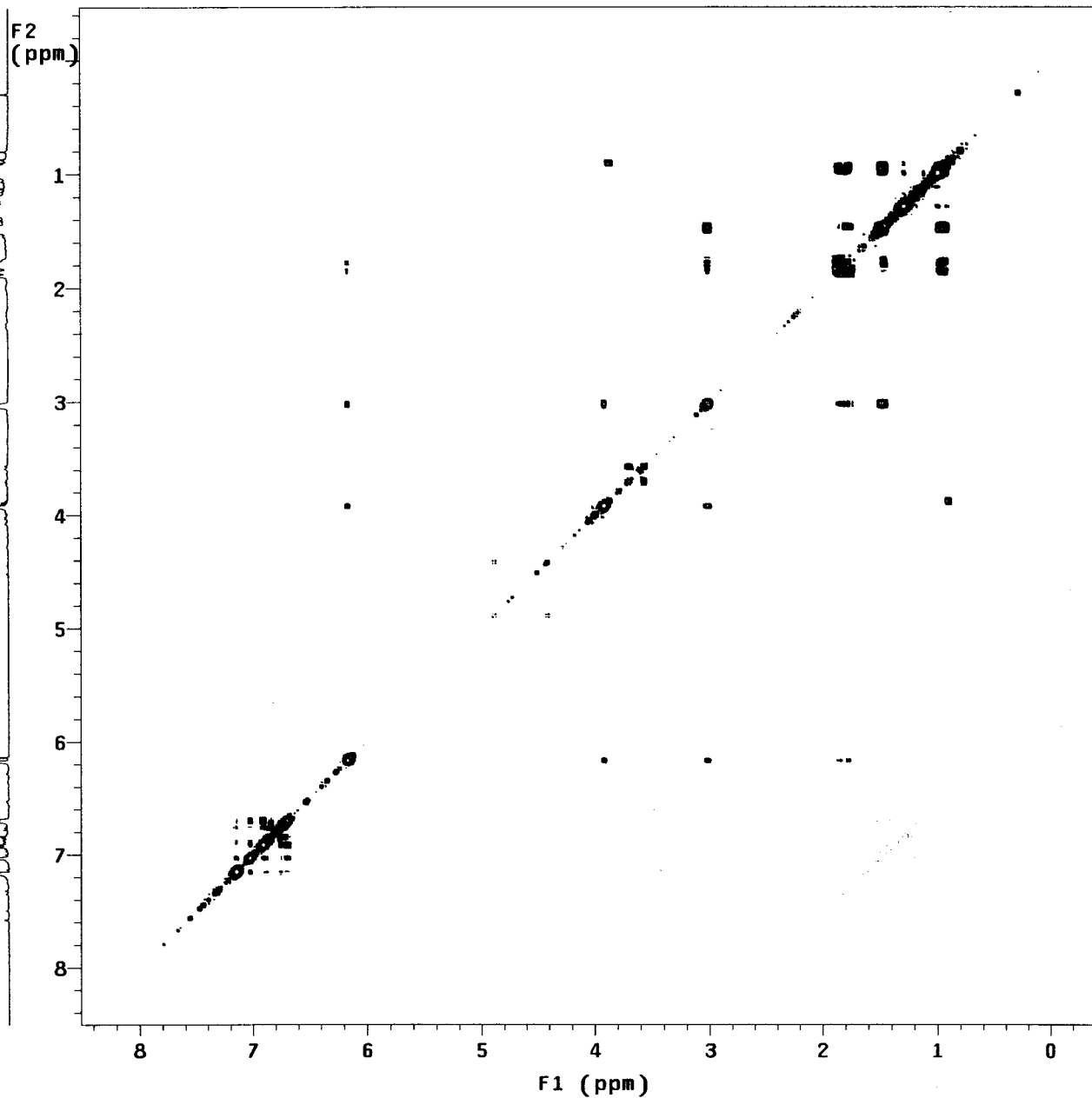
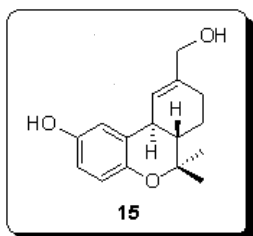


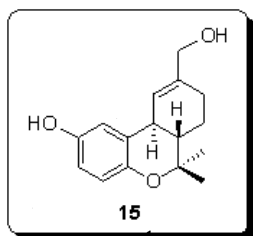
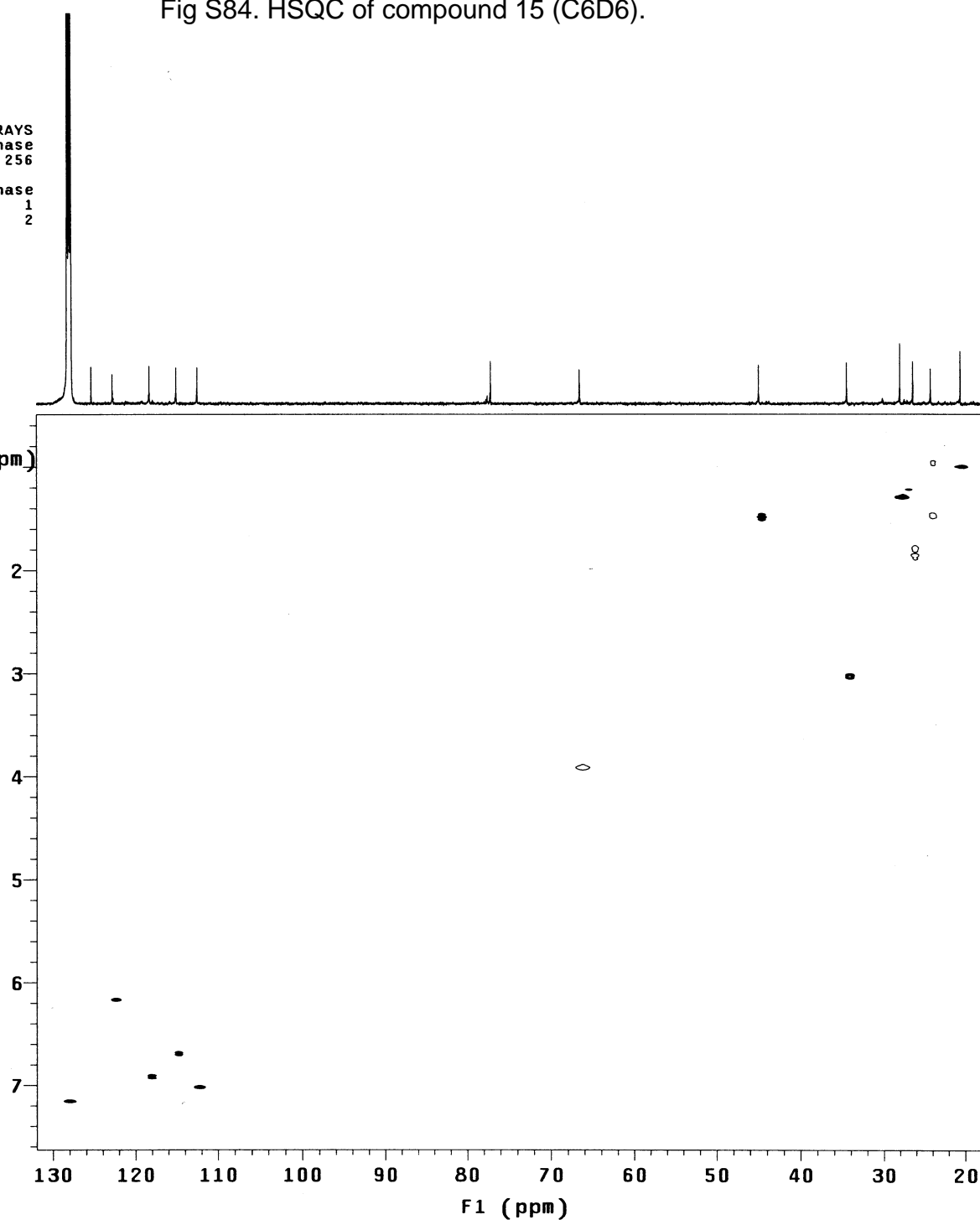
Fig S84. HSQC of compound 15 (C6D6).

S84

STANDARD PROTON PARAMETERS

exp5 gHSQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	Nov 19 2009	hs	n	array	phase
solvent	Benzene	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1003	i	phase
sw	4490.3	SPECIAL		1	1
at	0.228	temp	not used	2	2
np	2048	gain	24		
fb	not used	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1003		
nt	16	gt1	0.002000		
2D ACQUISITION		gzlv13	505		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
tn	TRANSMITTER	gf	0.105		
sfrq	H1	gfs	not used		
tof	499.829	fn	2048		
tpwr	-499.9	F1 PROCESSING			
pw	58	gf1	0.006		
DECOUPLER	11.100	gfs1	not used		
dn	C13	proc1	lp		
dof	-2515.2	fn1	2048		
dm	nny	DISPLAY			
dmm	ccp	sp	248.3		
dmf	32258	wp	3565.1		
dpwr	36	sp1	2135.0		
pxwlv1	52	wp1	14439.8		
pxw	14.300	rfl	3812.8		
HSQC	140.0	rfl1	3578.8		
j1xh	140.0	rfl1	17374.4		
nullflg	y	rfl1	16087.2		
mult	2	PLOT			
		wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	157		
		th	4		
		ai	cdc	ph	

F2
(ppm)

F1 (ppm)

Fig S85. NOESY of compound 15 (500 MHz, C6D6).

S85

PMK-01-262

exp6 NOESY

SAMPLE		FLAGS	
date	Nov 19 2009	hs	n
solvent	Benzene	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1003
sw	4490.3	SPECIAL	
at	0.228	temp	not used
np	2048	gain	24
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.105
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4490.3	F1 PROCESSING	
n1	200	gf1	0.041
TRANSMITTER		gfs1	not used
tn	H1	proc1	1p
sfrq	499.829	fn1	2048
tof	-499.9	DISPLAY	
tpwr	58	sp	-241.5
pw	11.100	wp	4486.0
NOESY		sp1	-241.5
mix	0.600	wp1	4486.0
PRESATURATION		rfl	245.8
satmode	nnnn	rfp	0
satpwr	0	rfl1	245.8
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	157
		th	1
		ai	ph

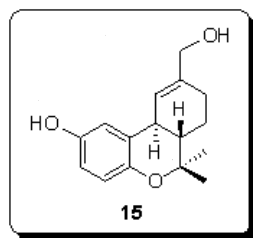
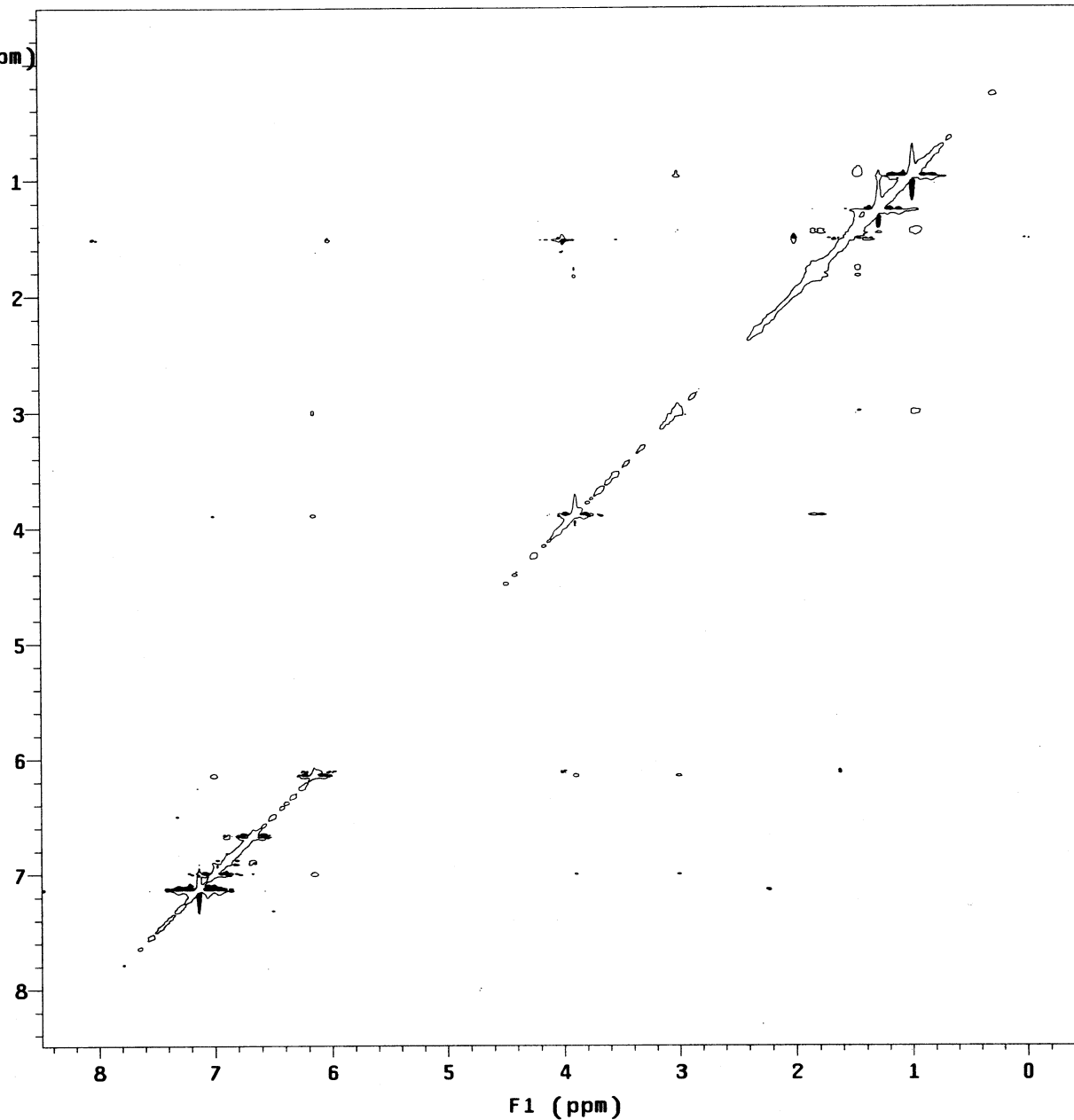
F2
(ppm)

Fig S86. ¹H NMR of compound 16 (500 MHz, CDCl₃).

PMK-01-269

exp12 s2pu1

SAMPLE		DEC. & VT	
date	Oct 27 2009	dfrq	125.693
solvent	cdc13	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.830	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	4	PROCESSING	
tpwr	59	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	4998.0		
vs	97		
sc	0		
wc	210		
hzmm	23.80		
is	75.25		
rfl	4638.2		
rfp	3618.7		
th	2		
ins	1.000		
nm	ph		

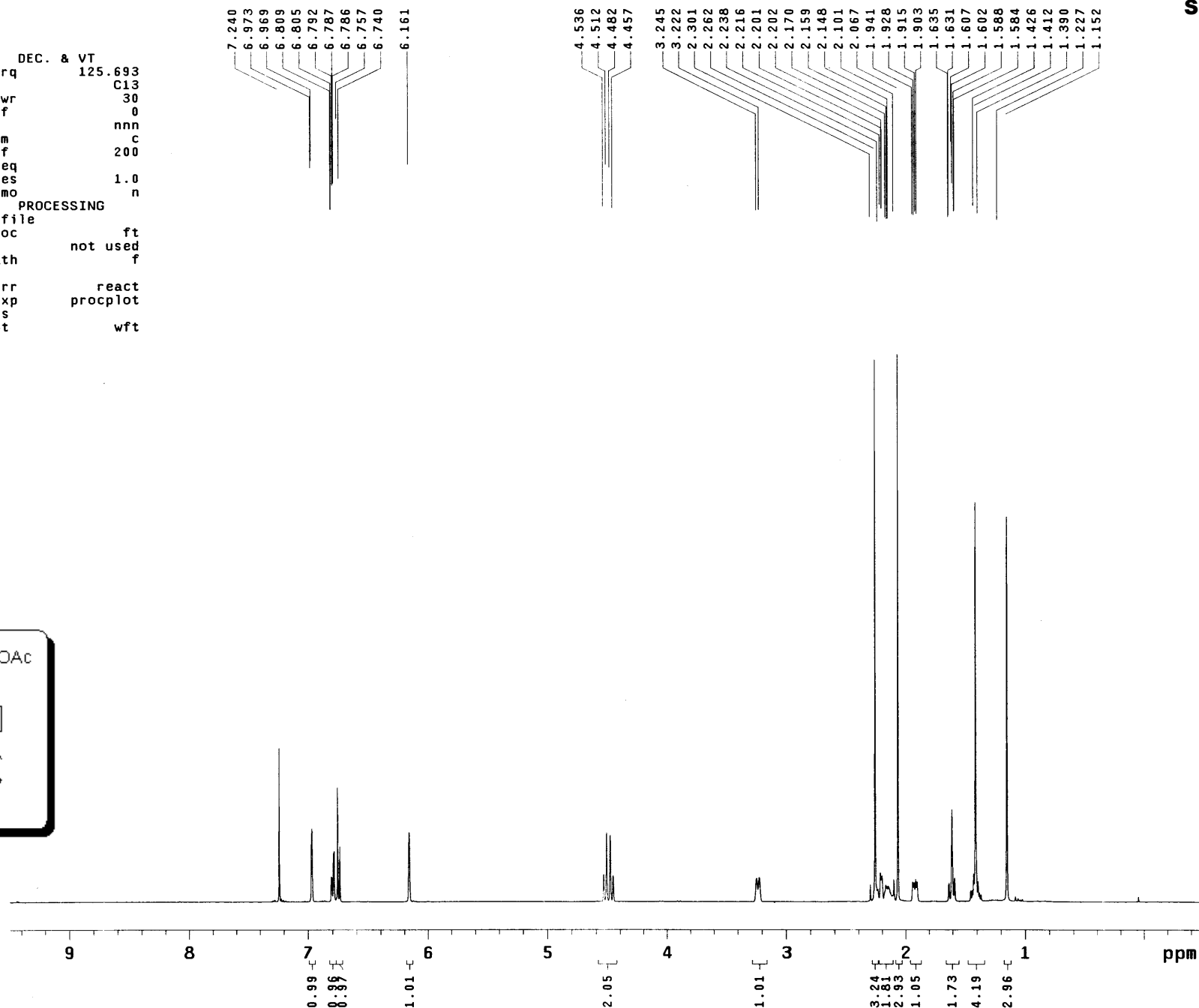
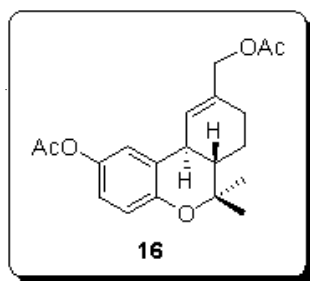
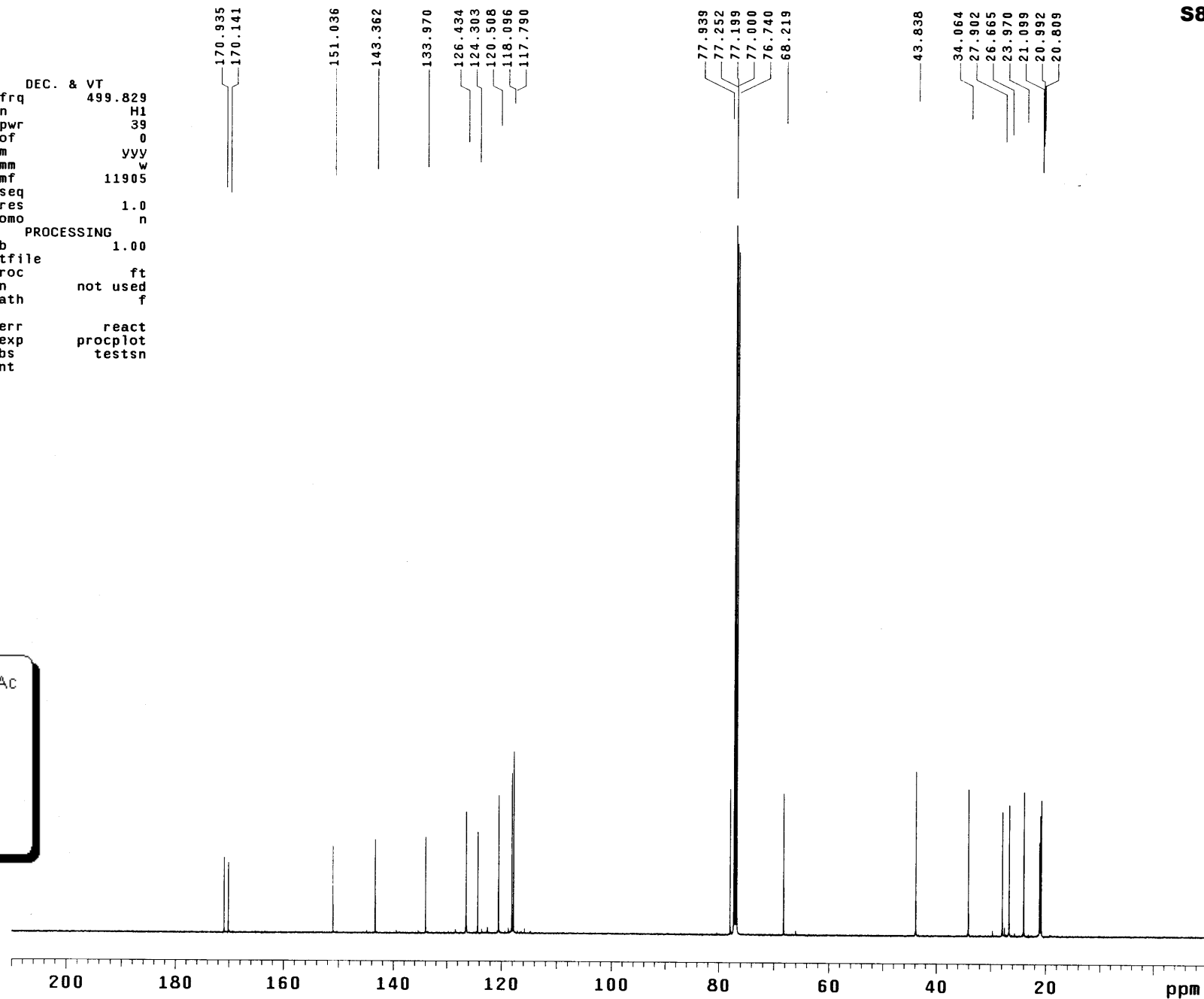
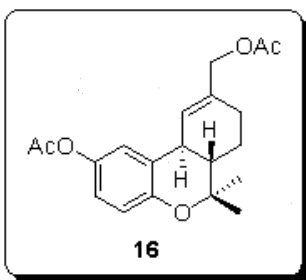


Fig S87. ¹³C NMR of compound 16 (125 MHz, CDCl₃).

PMK-01-269

exp13 s2pu1

SAMPLE DEC. & VT
date Oct 27 2009 dfrq 499.829
solvent cdcl3 dn H1
file exp dpwr 39
ACQUISITION dof 0
sfrq 125.696 dm yyy
tn C13 dmm w
at 1.000 dmf 11905
np 62894 dseq
sw 31446.5 dres 1.0
fb 17000 homo n
bs 16
ss 2 PROCESSING
tpwr 54 lb 1.00
pw 4.0 wtfile
d1 1.000 proc ft
tof 2512.2 fn not used
nt 10000 math f
ct 10000 werr react
alock y wexp procplot
gain not used wbs testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1257.0
wp 27649.1
vs 125
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10985.4
rfp 9677.5
th 8
ins 100.000
nm ph



S87

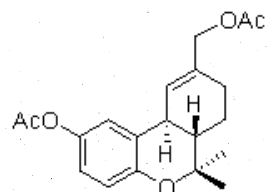
Fig S88. DEPT of compound 16 (CDCl₃).

S88

PMK-01-269

exp13 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Oct 27 2009	j1xh	140.0	array
solvent	CdCl ₃	mult	arrayed	mult
sample	undefined	SPECIAL	arraydim	3
ACQUISITION		temp	not used	i
sw	31446.5	gain	20	1
at	1.000	spin	0	2
np	62894	PROCESSING	3	1.5
bs	16	lb	1.00	
ss	-4	fn	not used	
d1	1.000	SPECTRUM		
nt	1200	wp	27649.1	
ct	1200	sp	-1257.0	
TRANSMITTER		rp	18.0	
tn	C13	lp	68.5	
tof	2512.2	ai	ph	
tpwr	54	REFERENCE		
pw	10.500	rfl	9881.7	
DECOUPLER		rfp	8573.9	
dn	H1	PLOT		
dof	0	wc	210	
dpwr	39	sc	0	
dm	nny	vs	106	
dmm	ccw	hzmm	131.67	
dmf	11905	th	3	
pp1v1	51			
pp	24.000			



16

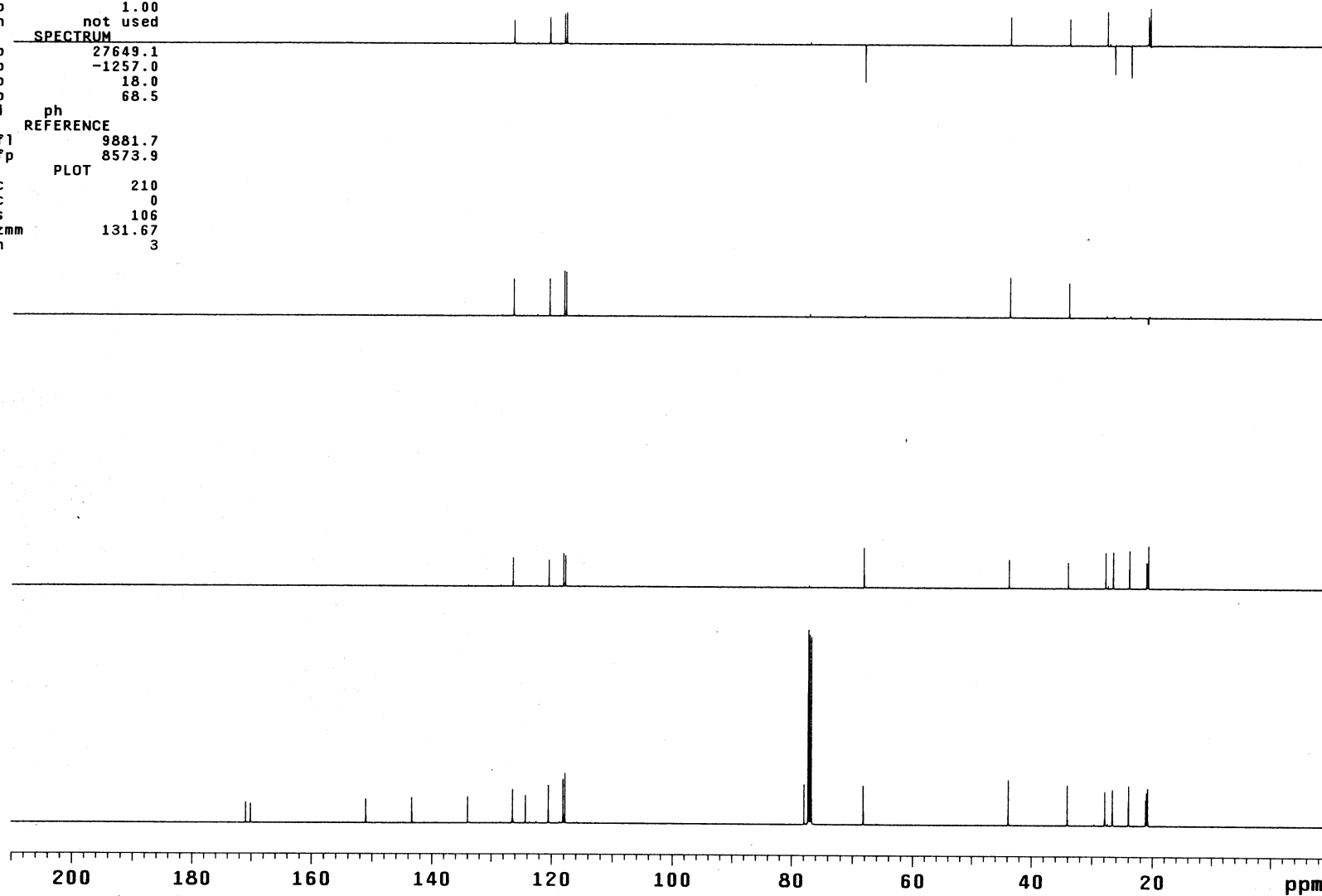


Fig S89. COSY of compound 16 (CDCl₃).

S89

PMK-01-269

exp15 gCOSY

SAMPLE
date Oct 27 2009
solvent cdc13
sample undefined

FLAGS

hs nn
sspul n
hsglv1 1026

ACQUISITION

SPECIAL

sw 3498.8 temp not used
at 0.146 gain 34
np 1024 spin 0
fb 2000
ss 16 sb -0.073
d1 1.000 sbs not used
nt 8 fn 1024

F2 PROCESSING

2D ACQUISITION

F1 PROCESSING

sw1 3498.8 sb1 -0.037
ni 128 sbs1 not used

TRANSMITTER

proc1 tp

tn H1 fn1 1024

DISPLAY

sfrq 499.829 sp 482.0
tof -250.0 wp 3492.0

tpwr 59 sp1 483.2
pw 13.500 wp1 3492.0

GRADIENTS

gzlv1 1026 rfl 1135.2
gt1 0.001000 rfp 1610.4

gstab 0.000500 rfl1 1134.0
rflp1 1610.4

DECOUPLER

dn C13 PLOT
dm nnn wc 155.0

wc 10.0

wc2 155.0

sc2 0

vs 113

th 4

ai cdc av

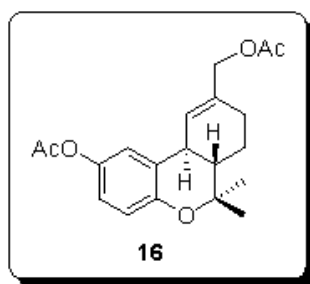
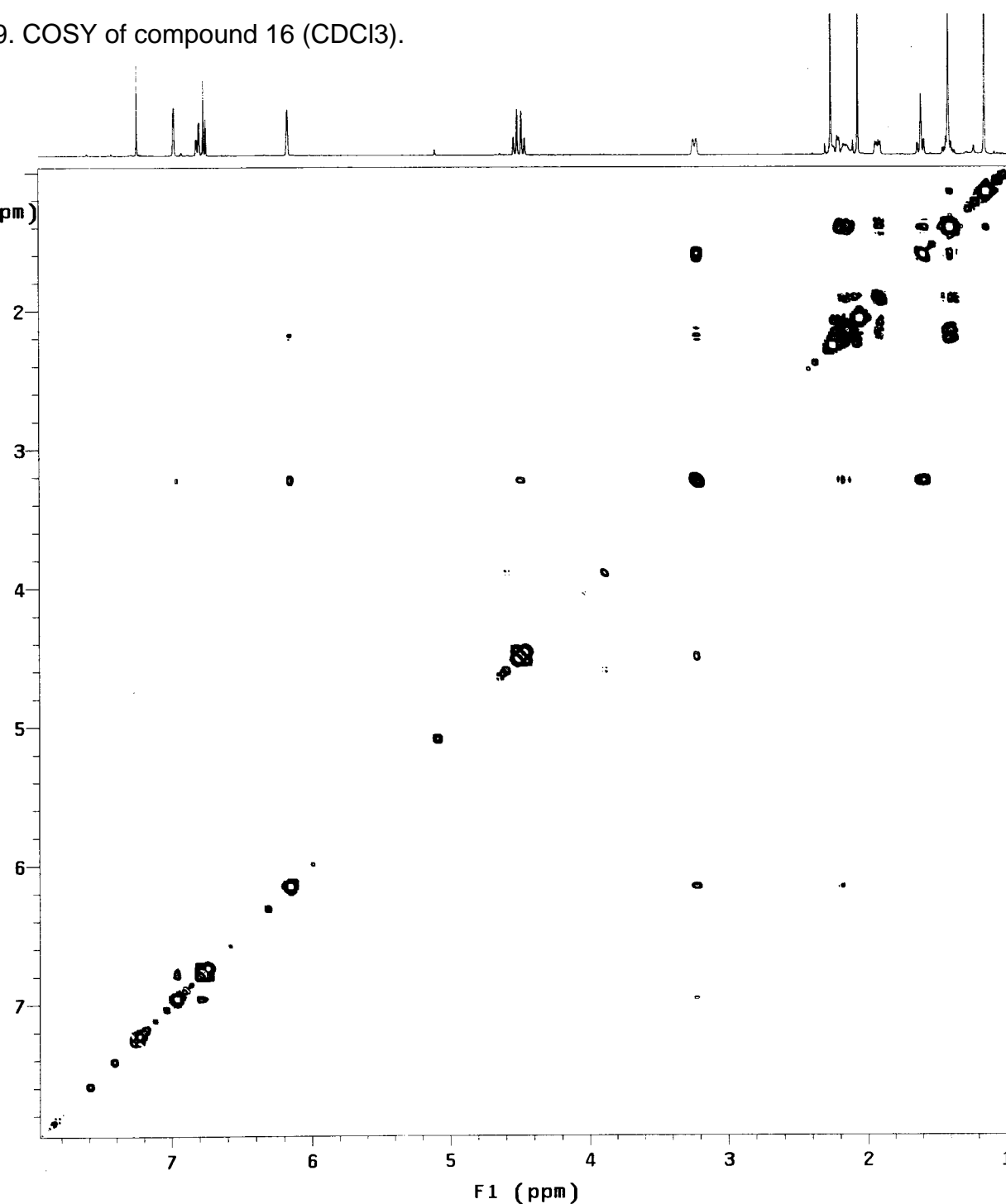
F2
(ppm)

Fig S90. NOESY of compound 16 (CDCl₃).

S90

PMK-01-269

exp17 NOESY

SAMPLE		FLAGS	
date	Oct 27 2009	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1026
sw	3498.8	SPECIAL	
at	0.146	temp	not used
np	1024	gain	34
fb	2000	spin	0
ss	32	F2 PROCESSING	
d1	1.500	gf	0.068
nt	8	gfs	not used
2D ACQUISITION		fn	1024
sw1	3498.8	F1 PROCESSING	
ni	200	gf1	0.053
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.829	fn1	1024
tof	-250.0	DISPLAY	
tpwr	59	sp	481.5
pw	13.500	wp	3492.0
NOESY		sp1	482.9
mix	0.600	wp1	3492.0
PRESATURATION		rf1	1135.8
satmode	nnnn	rfp	1610.4
satpwr	0	rf11	1134.4
satdly	0	rfp1	1610.4
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	113
		th	1
		ai	ph

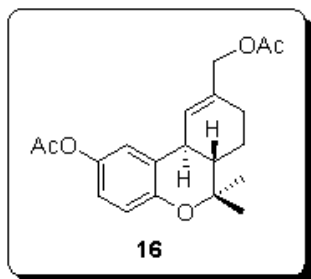
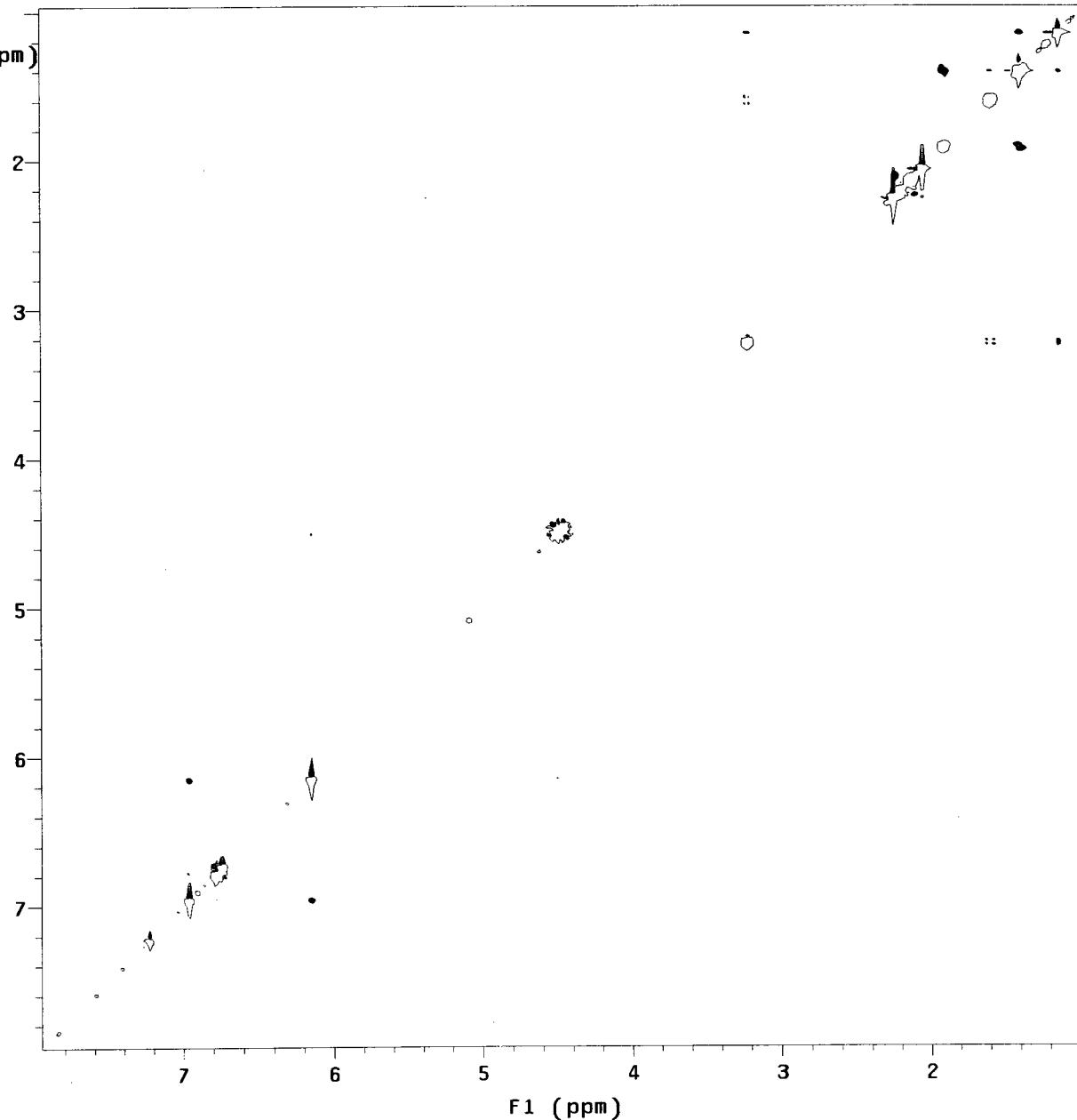
F2
(ppm)

Fig S91. HMQC of compound 16 (500 MHz, CDCl₃).

S91

PMK-01-269

exp17 gHMQC

SAMPLE		FLAGS		ACQUISITION		ARRAYS	
date	Oct 14 2009	hs	n	array	phase		
solvent	cdcl3	sspul	y	arraydim	256		
sample	undefined	PFGflg	y				
ACQUISITION		hsglv1	1026	i	phase		
sw	3498.8	SPECIAL		1	1		
at	0.146	temp	not used	2	2		
np	1024	gain	54				
fb	2000	spin	0				
ss	32	GRADIENTS					
d1	1.000	gzlv1	1026				
nt	16	gt1	0.001000				
2D ACQUISITION		gzlv13	516				
sw1	21367.5	gt3	0.001000				
ni	128	gstab	0.000500				
phase		F2 PROCESSING					
TRANSMITTER		gf	0.068				
tn	H1	gfs	not used				
sfrq	499.835	fn	1024				
tof		F1 PROCESSING					
tpwr	57	gf1	0.006				
pw	13.000	gfs1	not used				
DECOUPLER		proc1	lp				
dn	C13	fn1	2048				
dof	-2515.1	DISPLAY					
dm	nny	sp	511.5				
dmm	ccp	wp	3095.6				
dmf	32258	sp1	1732.5				
dpwr	35	wp1	14794.5				
pwxlvl	51	rfl	2588.0				
pxw	14.700	rfp	3079.0				
HMQC		rfl1	17164.0				
j1xh	140.0	rfl1	15891.8				
nullflg		PLOT					
	y	wc	150.0				
		sc	6.2				
		wc2	116.2				
		sc2	0				
		vs	406				
		th	5				
		ai	cdc ph				

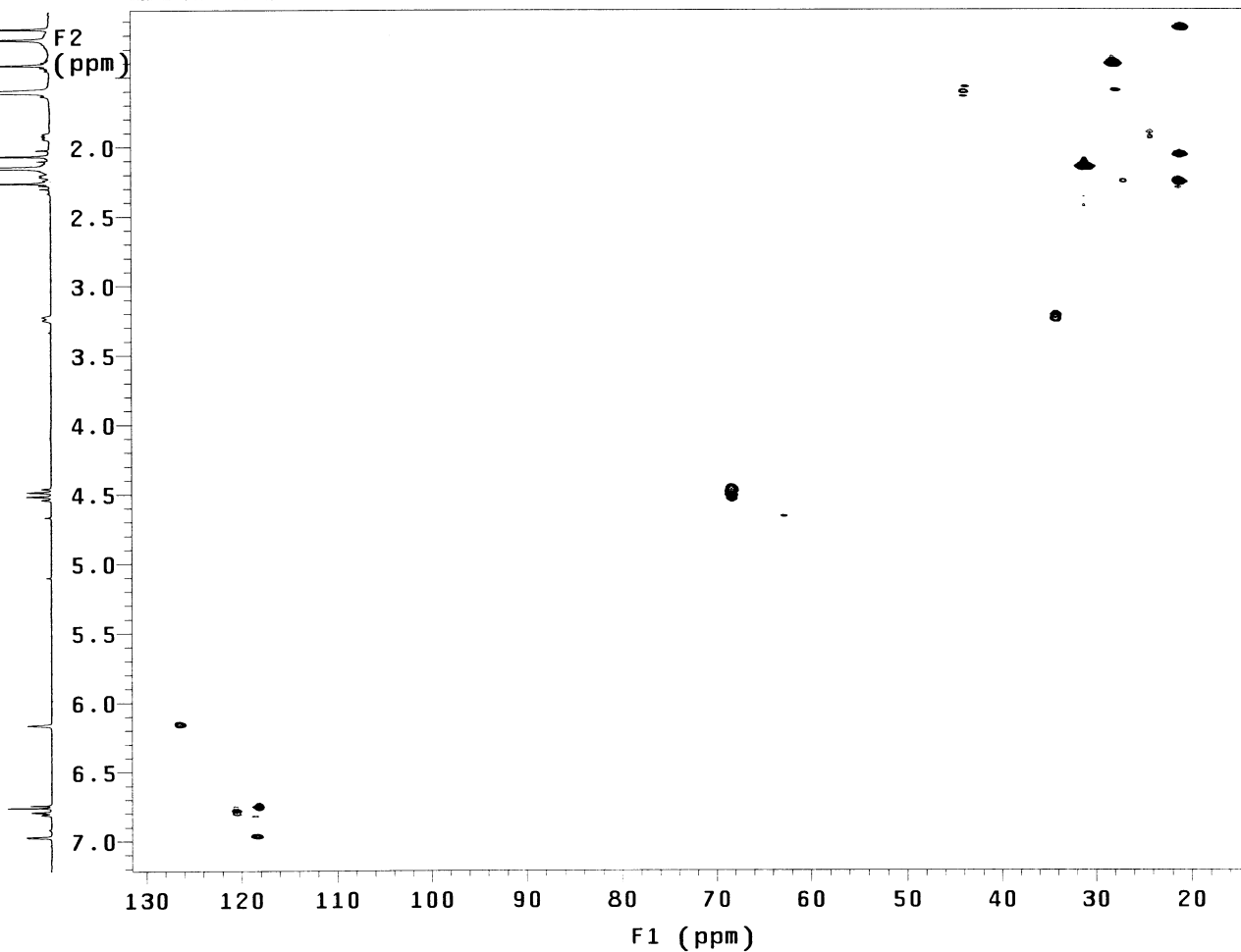
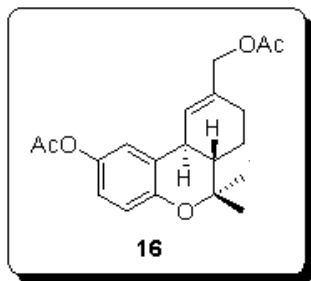


Fig S92. ¹H NMR of compound 17 (500 MHz, CDCl₃).

S92

PMK-01-271-3rd

exp12 s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2009	dfrq	125.693
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.830	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	4	PROCESSING	
tpwr	59	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	4998.0		
vs	184		
sc	0		
wc	210		
hzmm	23.80		
is	104.54		
rfl	4637.5		
rfp	3618.7		
th	4		
ins	100.000		
nm	ph		

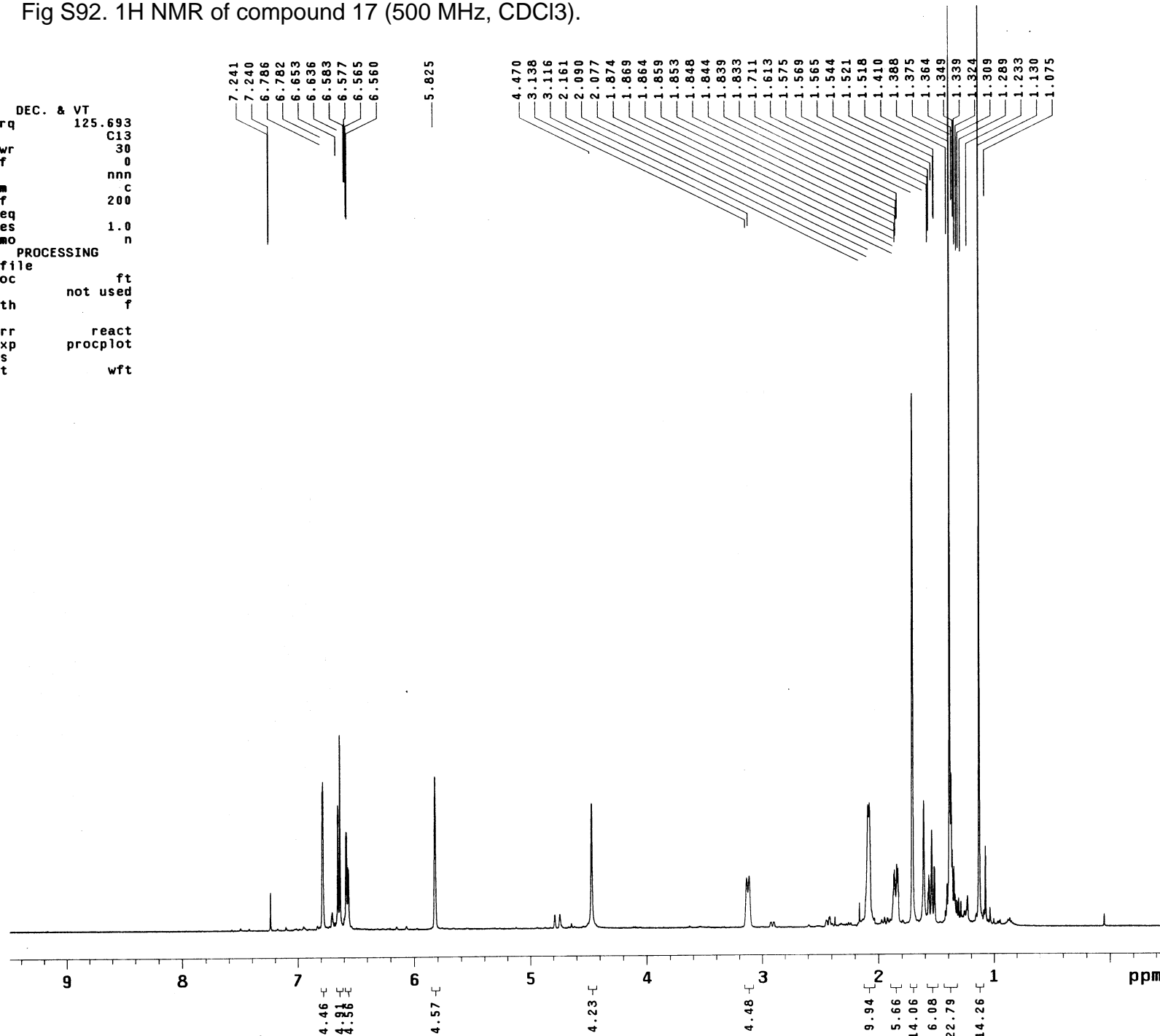
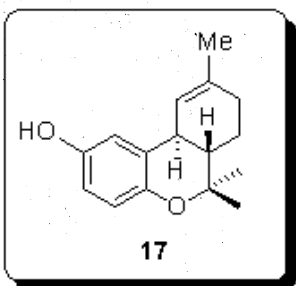


Fig S93. ¹³C NMR of compound 17 (125 MHz, CDCl₃).

S93

PMK-01-271-3rd

exp13 s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2009	dfrq	499.829
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION		dof	0
sfrq	125.696	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	11905
np	62894	dseq	
sw	31446.5	dres	1.0
fb	17000	homo	n
bs	16	PROCESSING	
ss	2	lb	1.00
tpwr	54	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	20000		
ct	1376	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1257.0		
wp	27649.1		
vs	200		
sc	0		
wc	210		
hzmm	131.67		
is	500.00		
rfl	10982.5		
rfp	9677.5		
th	6		
ins	100.000		
nm	ph		

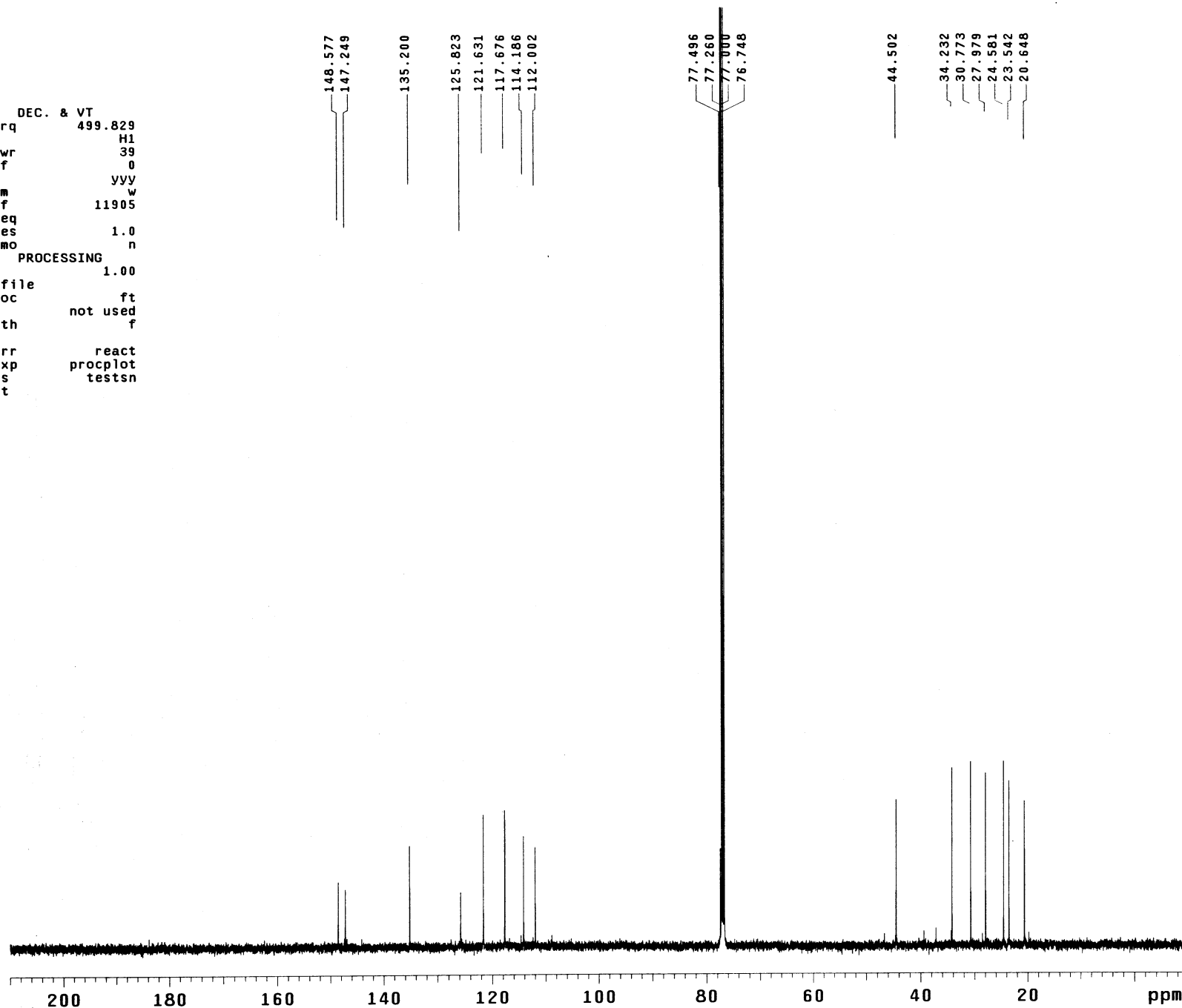
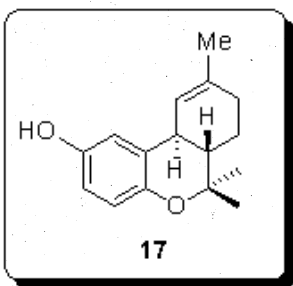


Fig S94. ¹³C NMR of compound 17 (125 MHz, CDCl₃), expanded.

S94

PMK-01-271-3rd

exp13 s2pu1

SAMPLE		DEC. & VT	
date	Oct 28 2009	dfrq	499.829
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION			
sfrq	125.696	dof	0
tn	C13	dm	YVY
at	1.000	dmm	w
np	62894	dmf	11905
sw	31446.5	dseq	
fb	17000	dres	1.0
bs	16	homo	n
ss	2	PROCESSING	
tpwr	54	lb	1.00
pw	4.0	wtfile	
d1	1.000	proc	ft
tof	2512.2	fn	not used
nt	20000	math	f
ct	1392	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
	FLAGS	wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	8797.5		
wp	1256.2		
vs	100		
sc	0		
wc	210		
hzmm	5.98		
is	500.00		
rfl	10982.5		
rfp	9677.5		
th	6		
ins	100.000		
nm	ph		

77.496
77.260
77.000
76.748

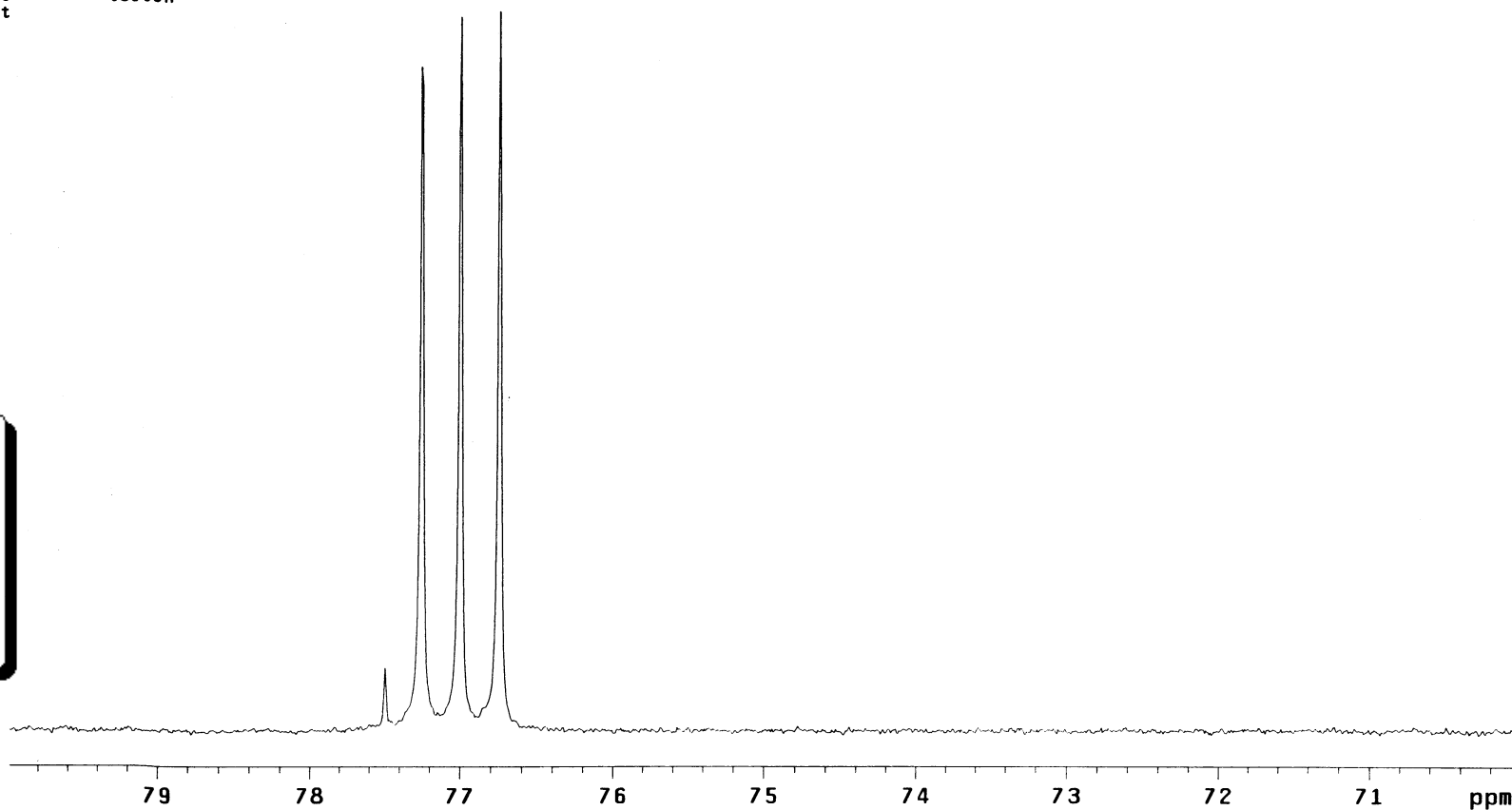
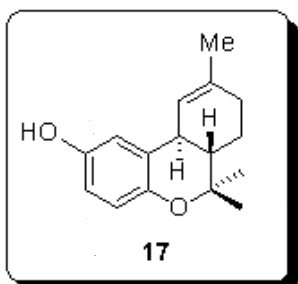


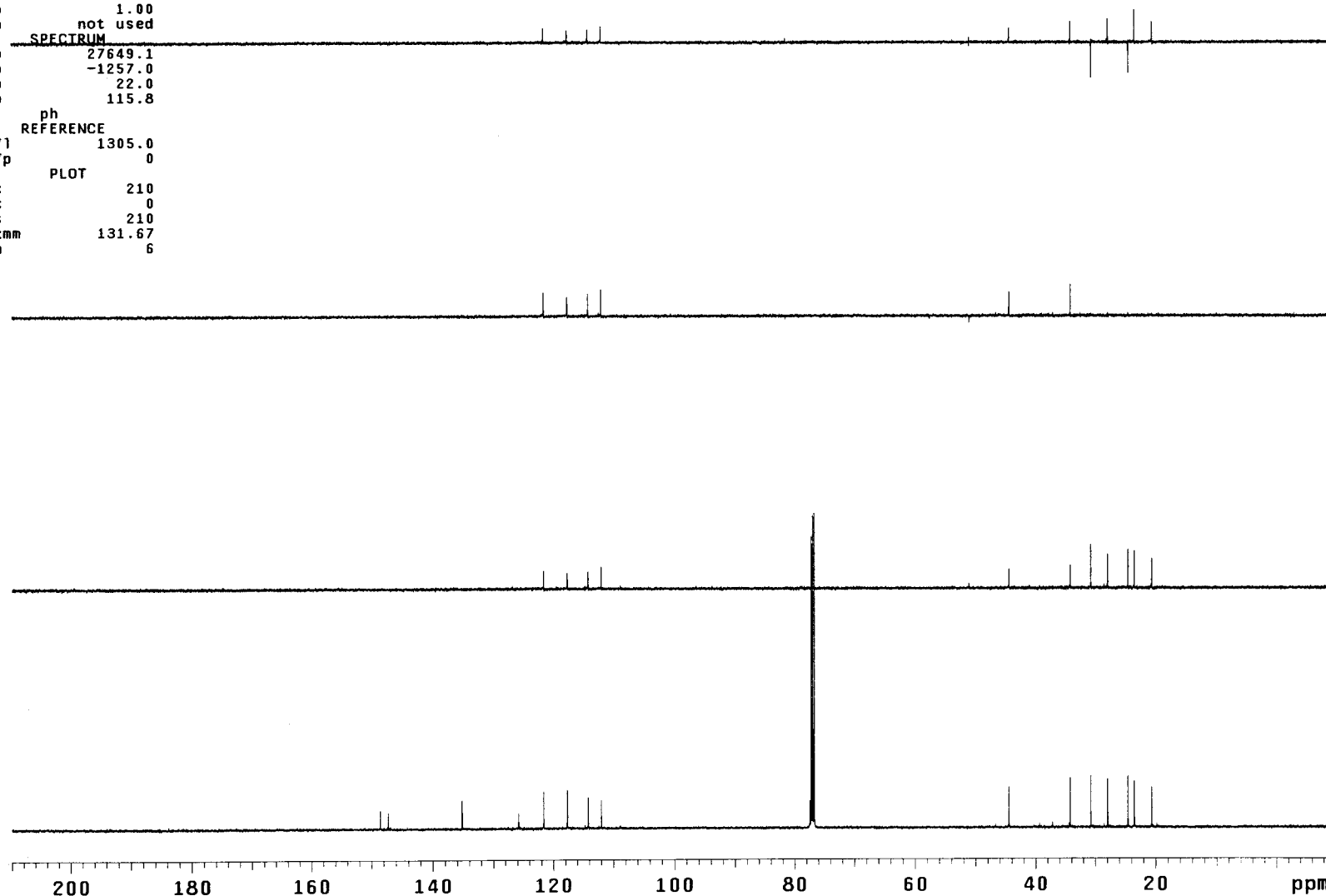
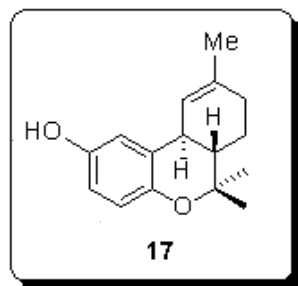
Fig S95. DEPT of compound 17 (CDCl₃).

S95

PMK-01-271-3rd

exp14 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Oct 28 2009	j1xh 140.0	array	mult
solvent	cdcl3	mult arrayed	arraydim	3
sample	undefined	SPECIAL		
ACQUISITION		temp not used	1	mult
sw	31446.5	gain 54	1	0.5
at	1.000	spin 0	2	1
np	62894	PROCESSING	3	1.5
bs	16	lb 1.00		
ss	-4	fn not used		
d1	1.000	SPECTRUM		
nt	300	wp 27649.1		
ct	300	sp -1257.0		
TRANSMITTER		rp 22.0		
tn	C13	lp 115.8		
tof	2512.2	ai ph		
tpwr	54	REFERENCE		
pw	10.500	rfl 1305.0		
DECOUPLER		rtp 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	39	sc 0		
dm	nny	vs 210		
dmm	ccw	hzmm 131.67		
dmf	11905	th 6		
pplv1	51			
pp	24.000			



exp14 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Oct 28 2009	j1xh	140.0	
solvent	cdc13	mult	arrayed	mult
sample	undefined		arraydim	3
ACQUISITION		temp	not used	i
sw	31446.5	gain	54	1
at	1.000	spin	0	2
np	62894	PROCESSING	3	1.5
bs	16	lb	1.00	
ss	-4	fn	not used	
dl	1.000	SPECIAL		
nt	300	wp	1256.2	
ct	300	sp	8797.5	
TRANSMITTER		rp	-16.5	
tn	C13	lp	207.1	
tof	2512.2	ai	ph	
tpwr	54	REFERENCE		
pw	10.500	rfl	1305.0	
DECOUPLER		rff	0	
dn	H1	PLOT		
dof	0	wc	210	
dpwr	39	sc	0	
dm	nny	vs	178	
dmm	ccw	hzmm	5.98	
dmt	11905	th	6	
pp1v1	51			
pp	24.000			

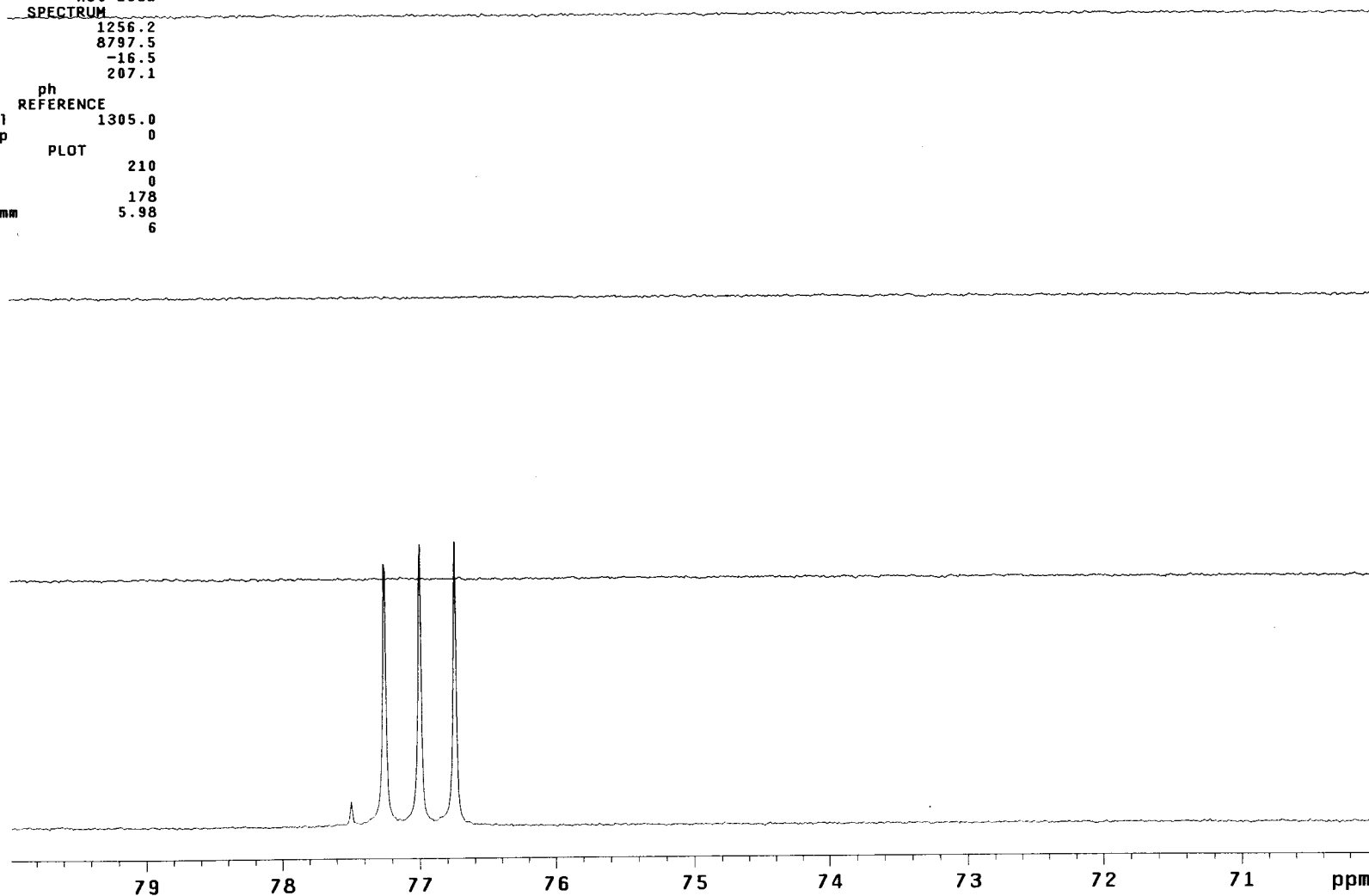
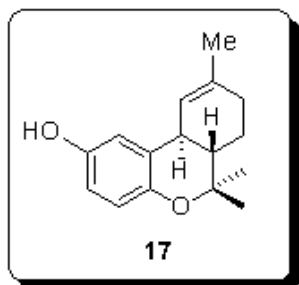


Fig S97. COSY of compound 17 (CDCl₃).

S97

PMK-01-271-3rd

exp16 gCOSY

SAMPLE
date Oct 28 2009
solvent cdc13
sample undefined

ACQUISITION
sw 2999.0
at 0.171
np 1024
fb 2000
ss 16
dl 1.000
nt 8

2D ACQUISITION
sw1 2999.0
ni 128

TRANSMITTER
tn H1
sfrq 499.829
tof -499.9
tpwr 59
pw 13.500

GRADIENTS
gzlv11 1026
gt1 0.001000
gstab 0.000500

DECOUPLER
dn C13
dm nnn

FLAGS
hs nn
sspu1 n
hsglv1 1026

SPECIAL
temp not used
gain 34
spin 0
F2 PROCESSING
sb -0.085
sbs not used
fn 1024

F1 PROCESSING
sb1 -0.043
sbs1 not used
proc1 lp
fn1 1024

DISPLAY
sp 479.8
wp 2993.1
sp1 478.7
wp1 2993.1
rf1 1760.3
rfp 2234.2
rf11 1761.4
rfp1 2234.2

PLOT
wc 155.0
sc 10.0
wc2 155.0
sc2 0
vs 170
th 5
ai cdc av

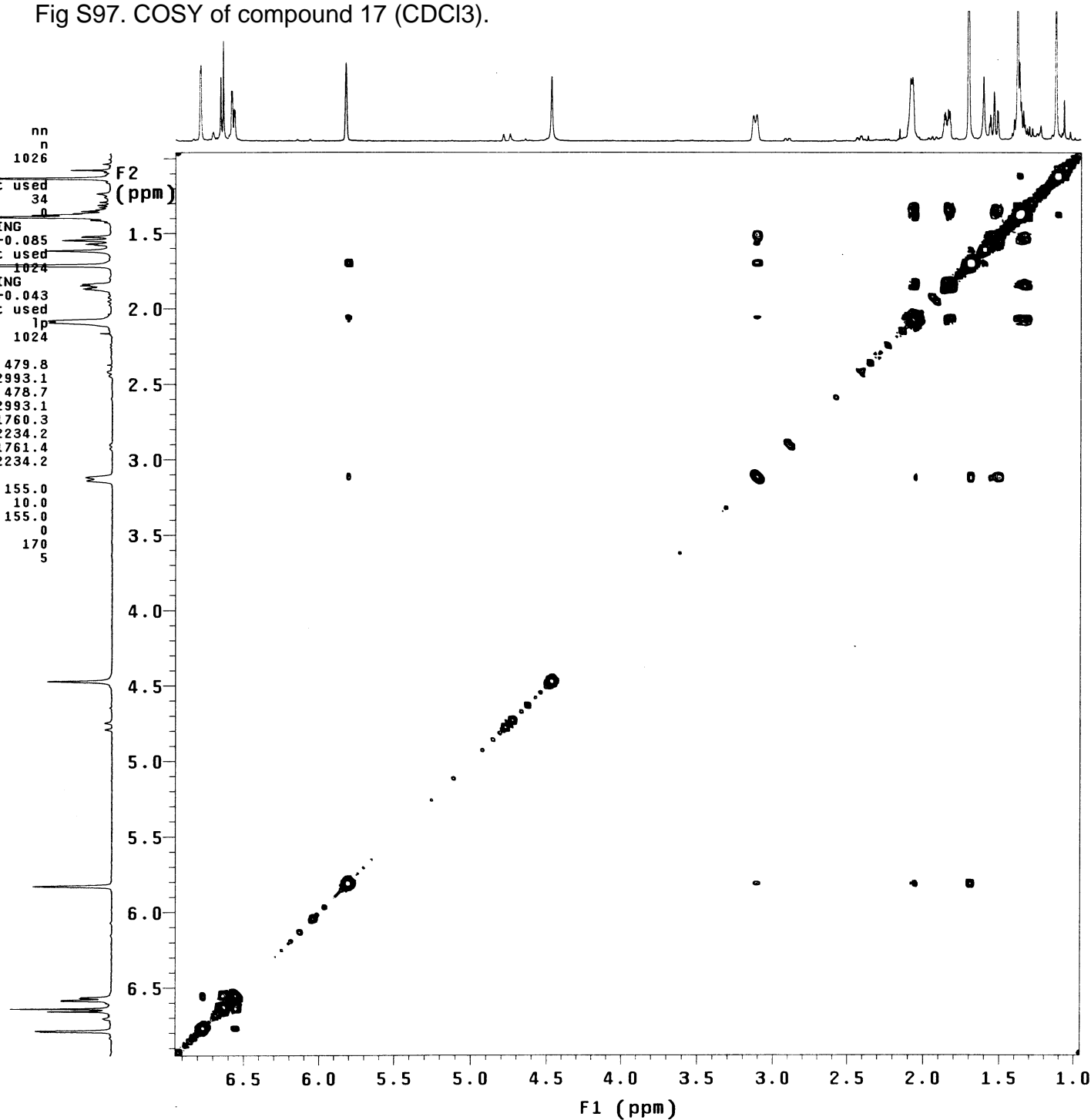
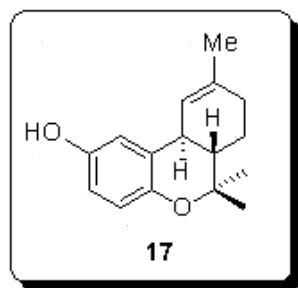


Fig S98. NOESY of compound 17 (CDCl₃).

S98

PMK-01-271-3rd

exp2 NOESY

SAMPLE		FLAGS	
date	Oct 28 2009	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1026
sw	2999.0	SPECIAL	
at	0.171	temp	20.0
np	1024	gain	34
fb	2000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	8	gfs	not used
2D ACQUISITION		fn	1024
sw1	2999.0	F1 PROCESSING	
ni	200	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	fn1	1024
sfrq	499.829	DISPLAY	
tof	-499.9	sp	494.4
tpwr	59	wp	2922.8
pw	13.500	sp1	495.8
NOESY		wp1	2928.7
mix	0.600	rfl	1751.5
PRESATURATION		rfp	2234.2
satmode	nnnn	rfl1	1750.1
satpwr	0	rfp1	2234.2
satdly	0	PLOT	
satfrq	0	wc	155.0
DECOUPLER		sc	10.0
dn	C13	wc2	155.0
dm	nnn	sc2	0
		vs	170
		th	4
		ai	ph

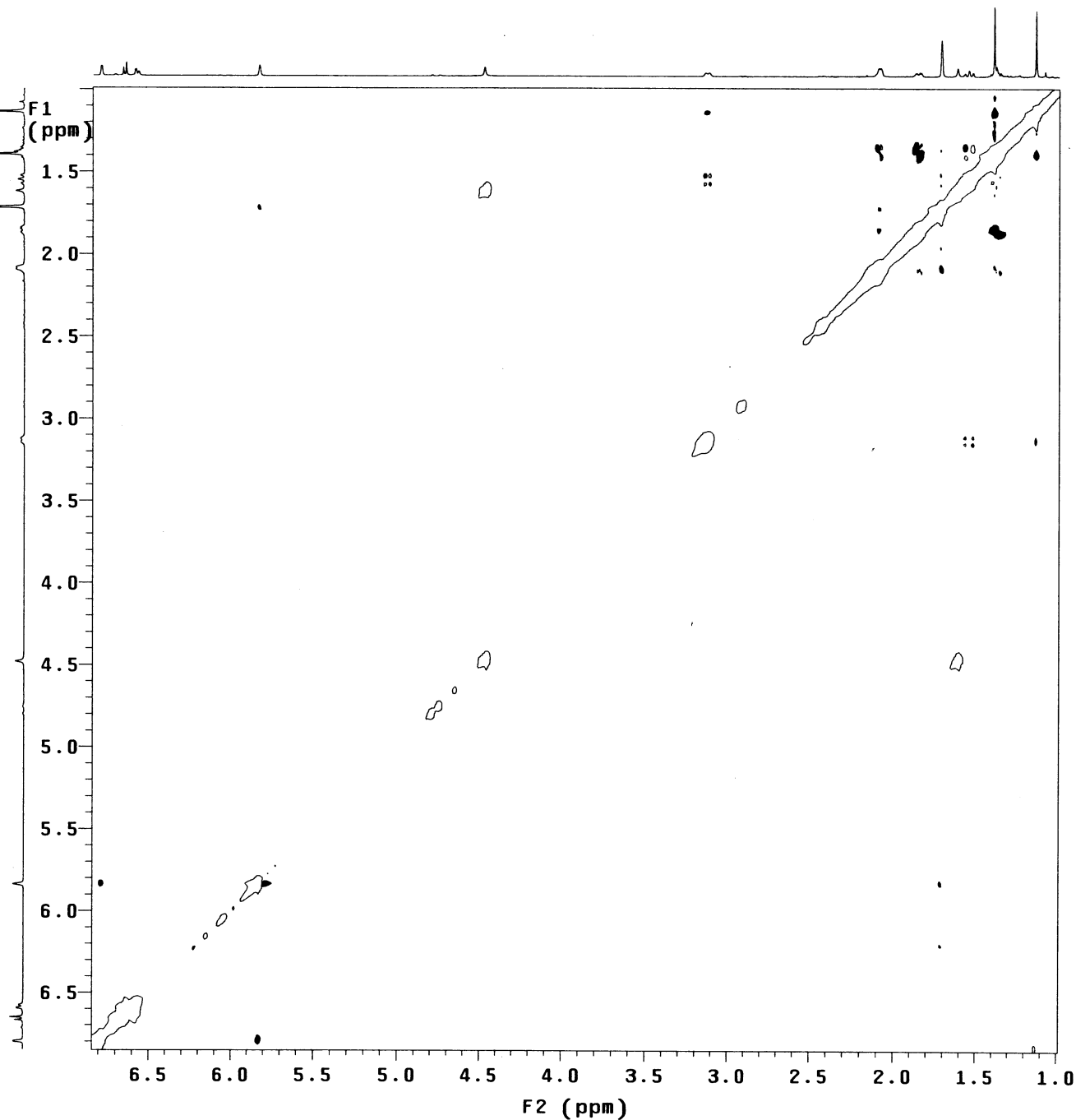
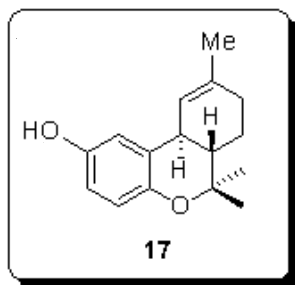


Fig S99. ¹H NMR of compound 20 (500 MHz, CDCl₃).

S99

pmk-01-72

exp41 s2pu1

SAMPLE		DEC. & VT	
date	May 23 2008	dfrq	125.695
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		do	0
sfrq	499.836	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	57	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	500		
ct	12	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5498.0		
vs	282		
sc	0		
wc	210		
hzmm	26.18		
is	146.28		
rfl	4627.0		
rfp	3618.8		
th	5		
ins	100.000		
nm	ph		

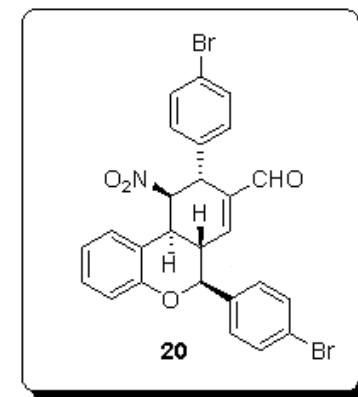
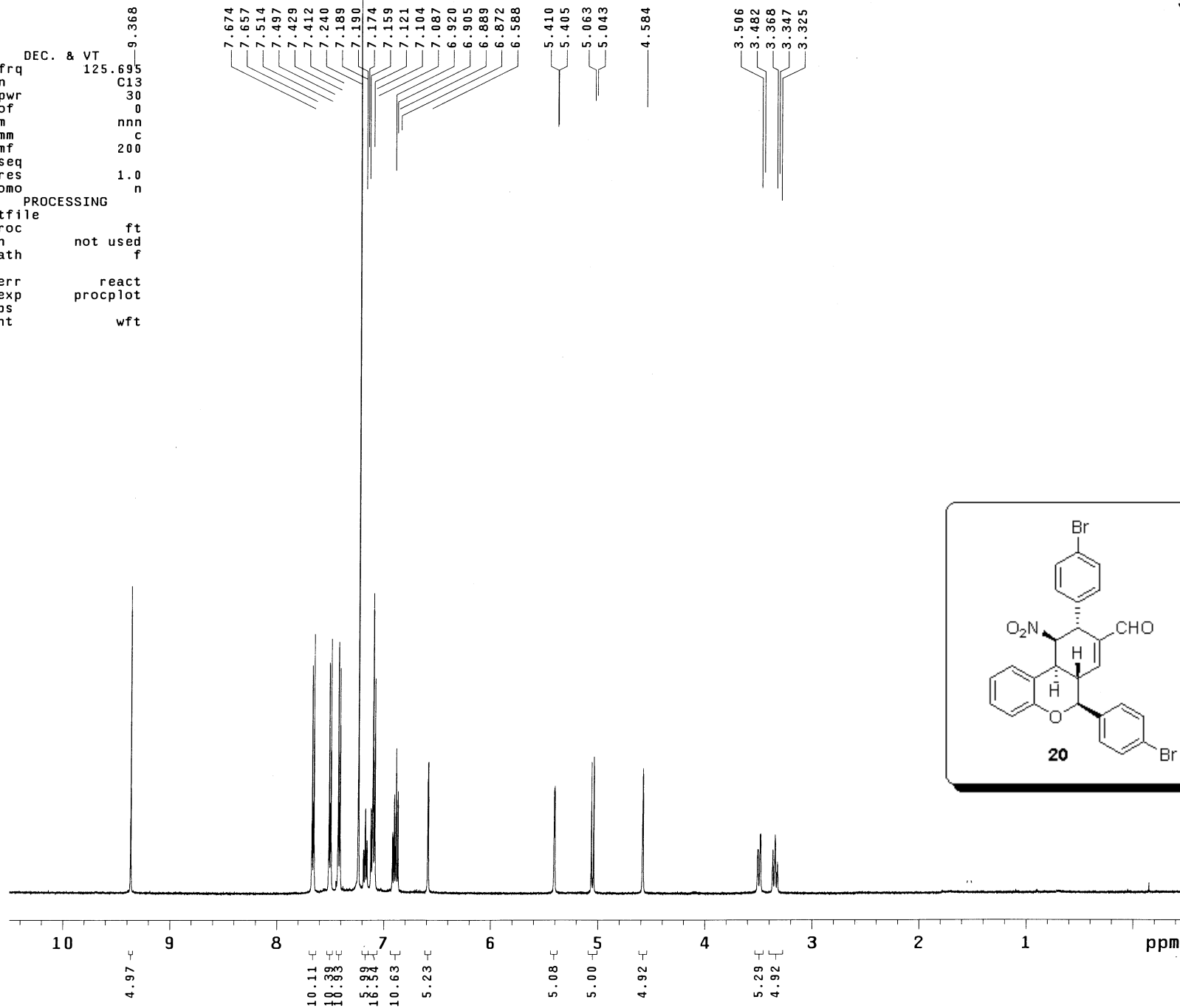


Fig S100. ¹³C NMR of compound 20 (125 MHz, CDCl₃).

S100

pmk-01-72
exp31 s2pu1

SAMPLE		DEC. & VT	
date	May 15 2008	dfrq	499.836
solvent	cdcl3	dn	H1
file	exp	dpwr	37
ACQUISITION			
sfrq	125.698	dof	0
tn	C13	dm	yyy
at	1.000	dmm	w
np	62894	dmf	10870
sw	31446.5	dseq	
fb	not used	dres	1.0
bs	16	homo	n
PROCESSING			
ss	2	lb	1.00
tpwr	53	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	10000		
ct	10000	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
	FLAGS	wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1256.9		
wp	28906.3		
vs	425		
sc	0		
wc	210		
hzmm	137.65		
is	500.00		
rfl	10978.7		
rfp	9677.6		
th	5		
ins	100.000		
nm	ph		

191.153

154.448
146.851
139.933
137.474
136.405
132.565
132.404
129.426
129.304
129.266
124.532
123.669
122.447
121.134
118.431
117.309

84.880
81.299
77.260
77.000
76.748

42.495
39.593
35.821

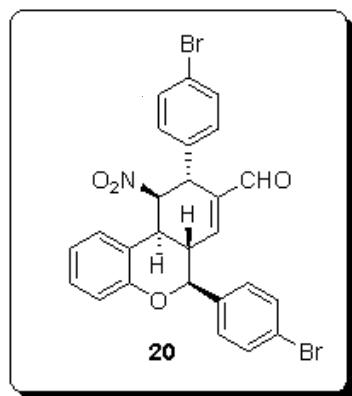


Fig S101. DEPT of compound 20 (CDCl₃).

S101

pmk-01-72
exp27 DEPT

SAMPLE		DEPT		ACQUISITION ARRAYS	
date	May 15 2008	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	i	mult
sw	31446.5	gain	34	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	1000	wp	28906.3		
ct	1000	sp	-1257.2		
TRANSMITTER		rp	-174.2		
tn	C13	lp	133.2		
tof	2512.2	ai	cdc ph		
tpwr	53	REFERENCE			
pw	8.600	rfl	1269.7		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	37	sc	0		
dm	nny	vs	99543		
dmm	ccw	hzmm	137.65		
dmf	10870	th	6		
pplvl	51				
pp	21.300				

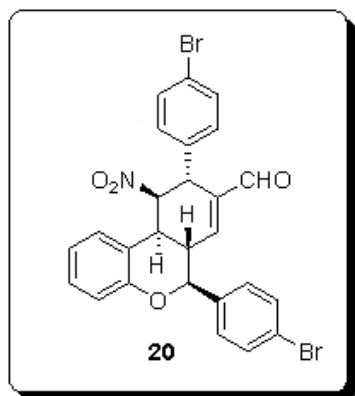
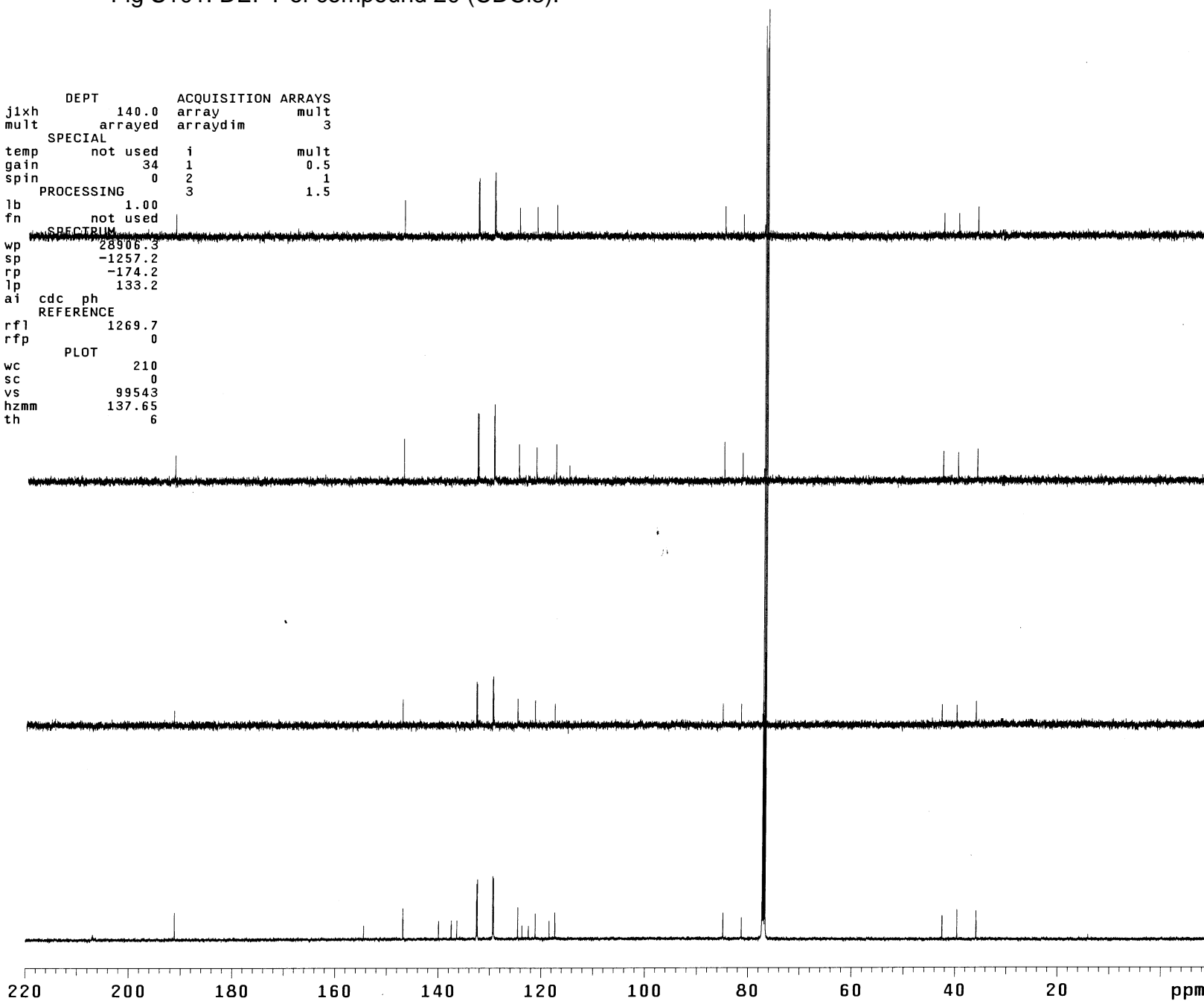


Fig S102. HMQC of compound 20 (CDCl₃).

S102

pmk-01-72
exp29 gHMQC

SAMPLE		FLAGS	ACQUISITION		ARRAYS
date	May 15 2008	hs	n	array	phase
solvent	cdcl3	sspul	y	arraydim	256
sample	undefined	PFGflg	y		
ACQUISITION		hsglv1	1006	i	phase
sw	3501.4	SPECIAL	1		1
at	0.146	temp	not used	2	2
np	1024	gain	54		
fb	not used	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlv11	1006		
nt	16	gt1	0.001000		
2D ACQUISITION		gzlv13	506		
sw1	21367.5	gt3	0.001000		
ni	128	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		gf	0.068		
tn	H1	gfs	not used		
sfrq	499.836	fn	1024		
tof	749.7	F1 PROCESSING			
tpwr	57	gf1	0.006		
pw	9.600	gfs1	not used		
DECOUPLER		proc1	lp		
dn	C13	fn1	2048		
dof	-2515.1	DISPLAY			
dm	nny	sp	1600.8		
dmm	ccp	wp	3214.2		
dmf	32258	sp1	2686.3		
dpwr	33	wp1	16401.2		
pwxlvl	49	rfl	-1498.3		
pw	14.000	rfp	0		
HMQC		rfl1	1257.5		
j1xh	140.0	rfp1	0		
nullflg	y	PLOT			
		wc	150.0		
		sc	6.2		
		wc2	116.2		
		sc2	0		
		vs	1814		
		th	5		
		ai	cdc	ph	

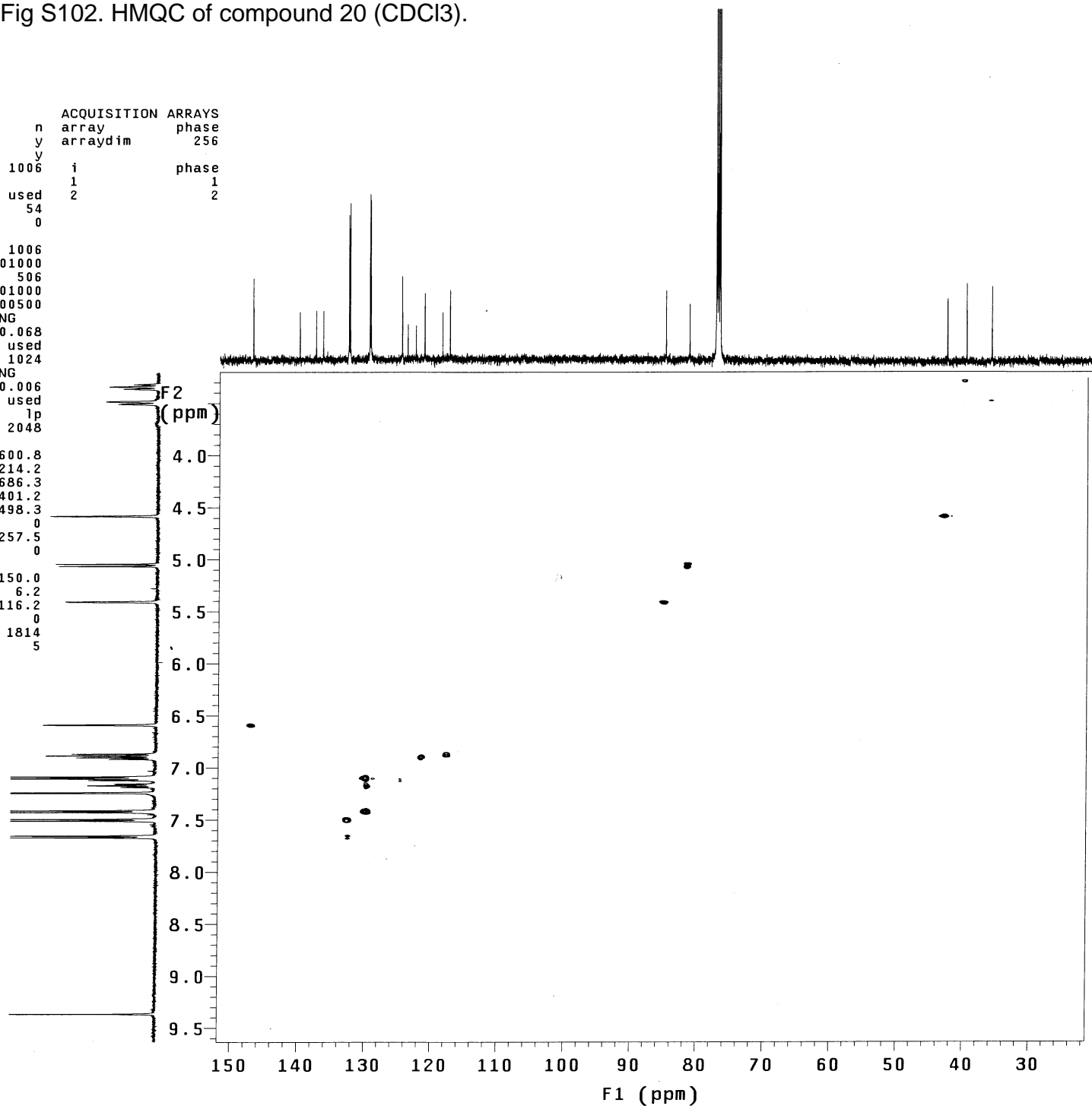
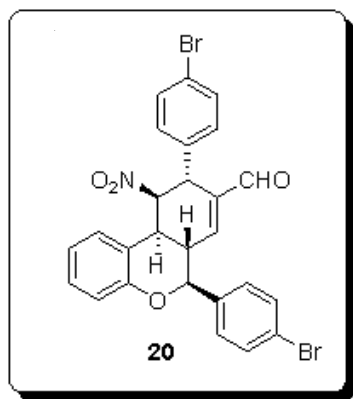


Fig S103. COSY of compound 20 (CDCl3).

S103

pmk-01-72
exp28 gCOSY

SAMPLE		FLAGS	
date	May 15 2008	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1006
ACQUISITION		SPECIAL	
sw	3501.4	temp	not used
at	0.146	gain	34
np	1024	spin	0
fb	not used	F2	PROCESSING
ss	16	sb	-0.073
d1	1.000	sbs	not used
nt	16	fn	1024
2D ACQUISITION		F1	PROCESSING
sw1	3501.4	sb1	-0.037
ni	128	sbs1	not used
TRANSMITTER		proc1	lp
tn	H1	fn1	1024
sfrq		499.836	DISPLAY
tof	749.7	sp	1566.0
tpwr	57	wp	3303.1
pw	9.600	sp1	1558.0
GRADIENTS		wp1	3303.1
gzlv11	1006	rfl	798.4
gt1	0.001000	rfl	2289.2
gstab	0.000500	rfl1	1799.2
DECOUPLER		rflp1	3288.9
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	1814
		th	6
		ai	cdc av

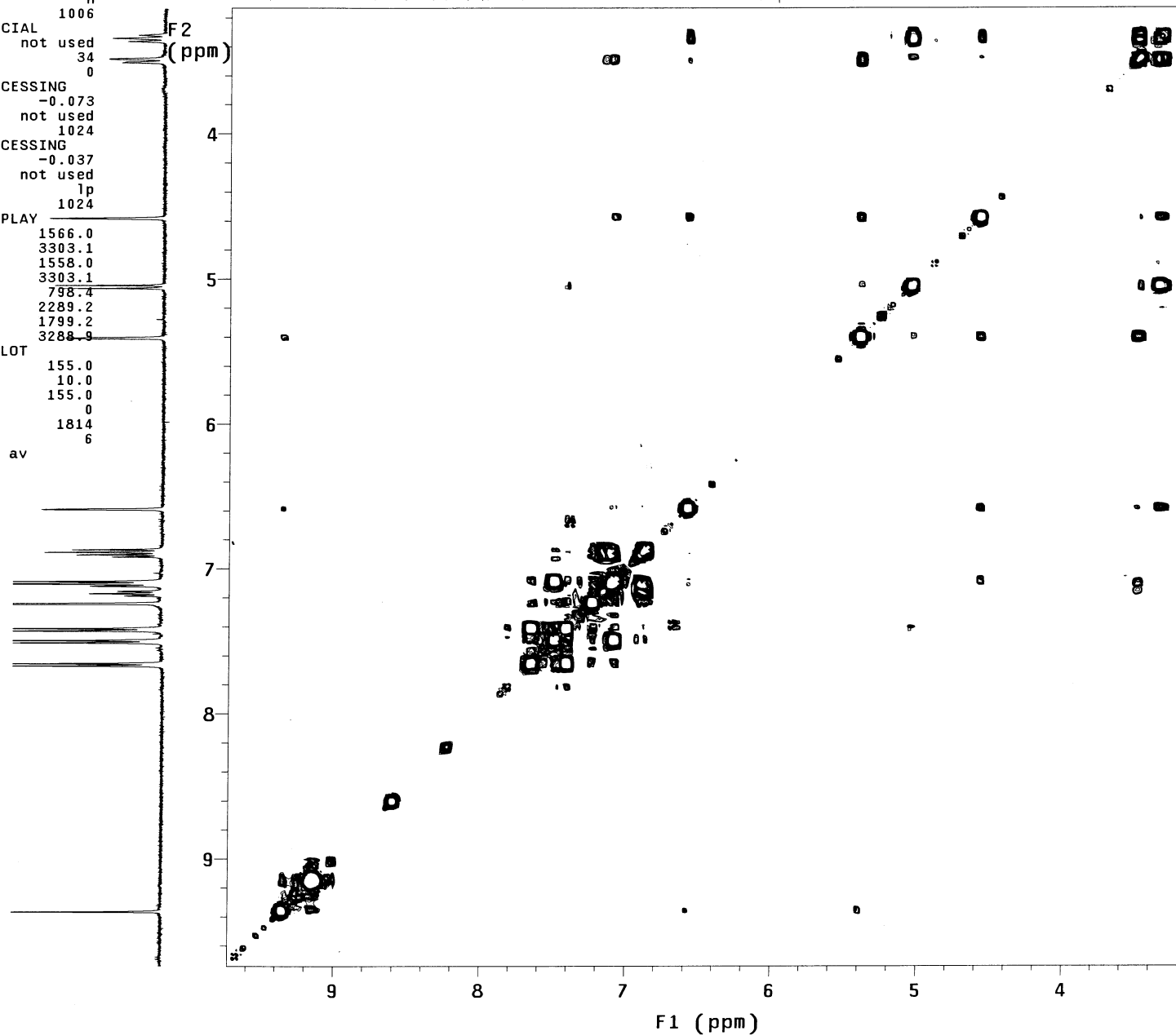
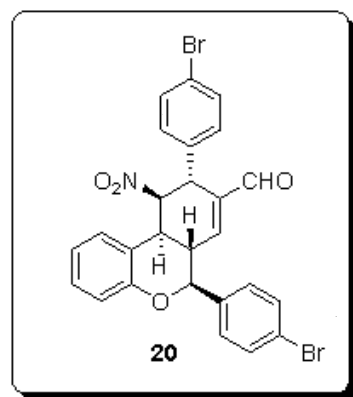


Fig S104. NOESY of compound 20 (CDCl₃).

S104

pmk-01-72

exp30 NOESY

SAMPLE		FLAGS	
date	May 15 2008	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1006
sw	3501.4	SPECIAL	
at	0.146	temp	not used
np	1024	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.068
nt	8	gfs	not used
2D ACQUISITION		fn	1024
sw1	3501.4	F1 PROCESSING	
ni	200	gf1	0.053
TRANSMITTER		gfs1	not used
tn	H1	procl	lp
sfrq	499.836	fn1	1024
tof	749.7	DISPLAY	
tpwr	57	sp	1559.8
pw	9.600	wp	3275.7
NOESY		sp1	1573.5
mix	0.600	wp1	3262.0
PRESATURATION		rfl	-1498.3
satmode	nnnn	rfp	0
satpwr	0	rfl1	-1498.3
satlly	0	rfl1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	1814
		th	1
		ai	ph

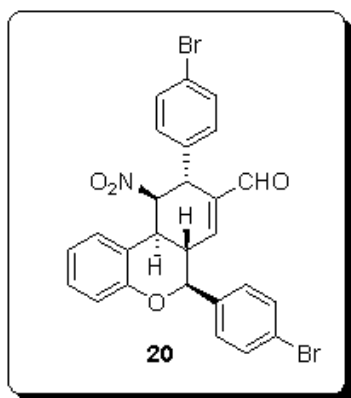
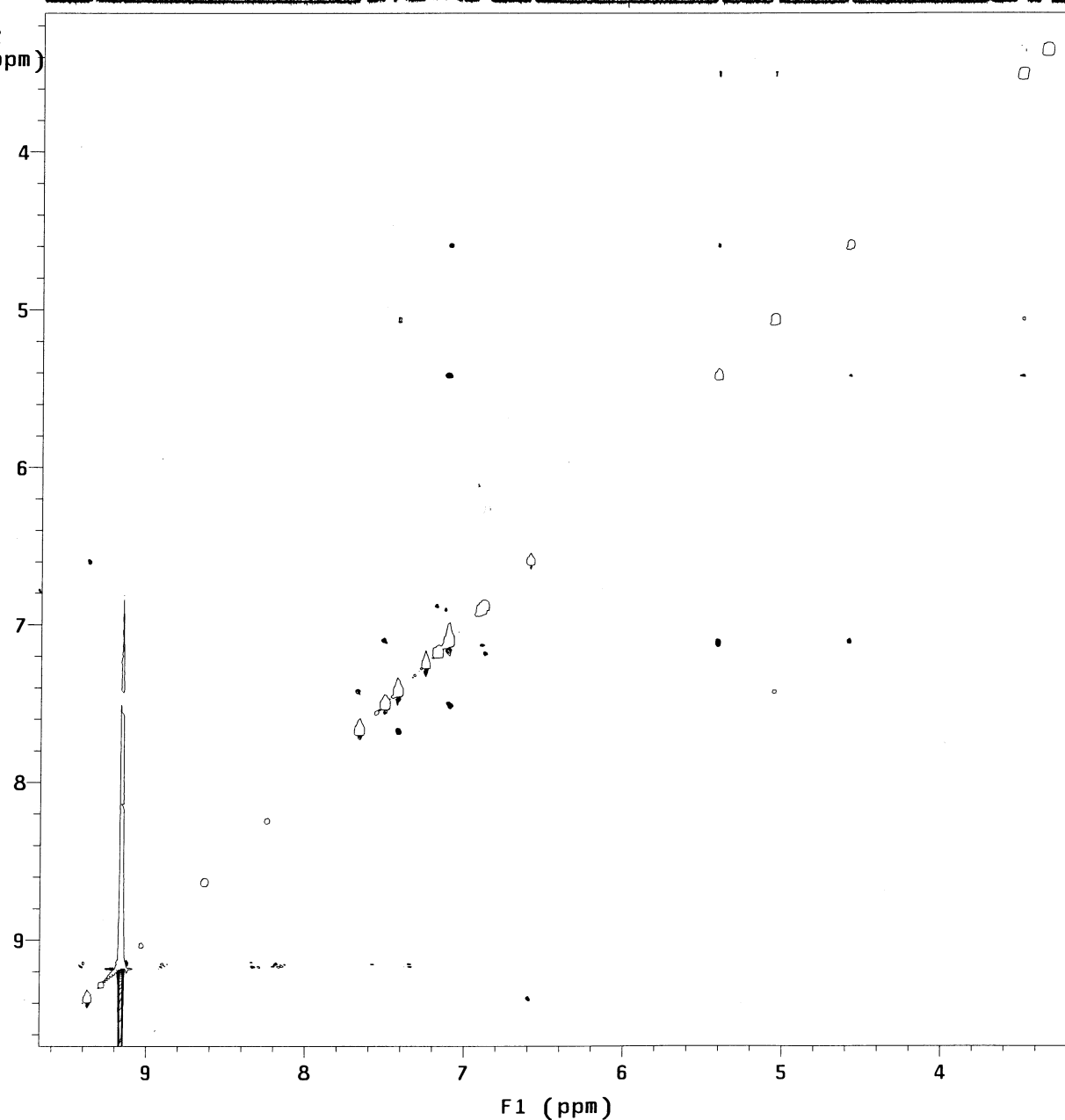
F2
(ppm)

Fig S105. ¹H NMR of compound 21 (500 MHz, CDCl₃).

S105

PMK-01-166

exp11 s2pu1

SAMPLE		DEC. & VT	
date	Dec 11 2008	dfrq	125.695
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.836	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs		PROCESSING	
tpwr	57	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5498.0		
vs	57		
sc	0		
wc	210		
hzmm	26.18		
is	83.74		
rfl	4628.4		
rfp	3618.8		
th	3		
ins	100.000		
nm	ph		

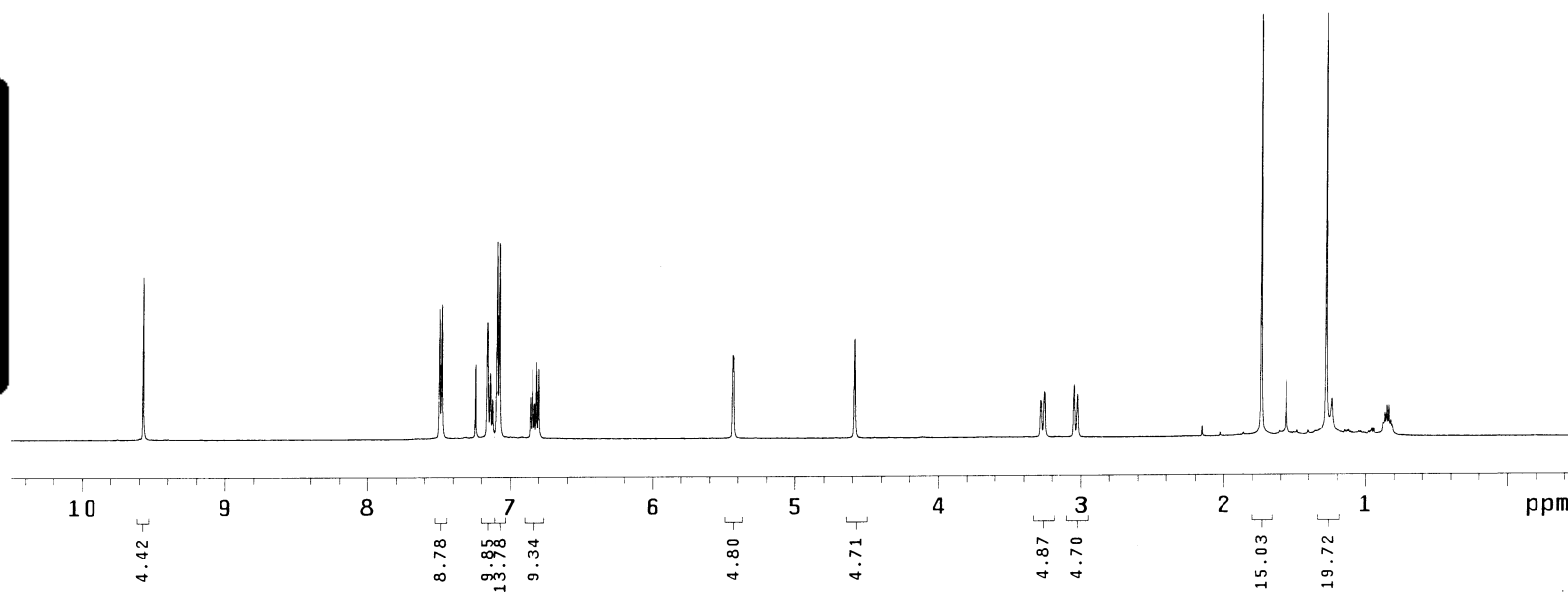
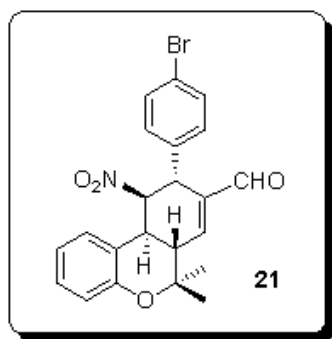
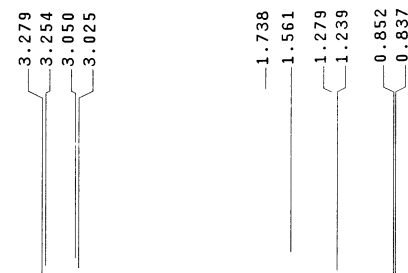
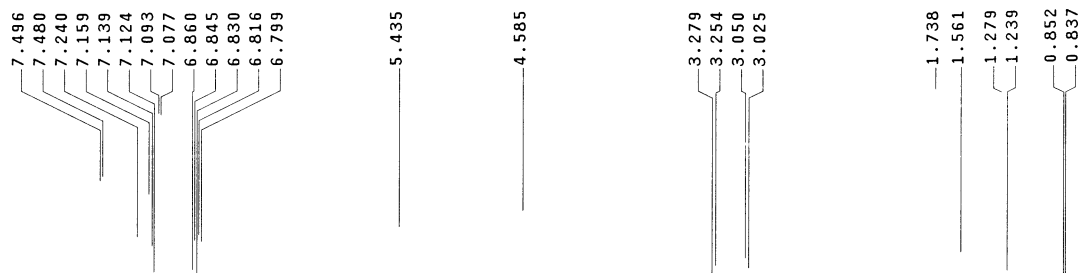


Fig S106. ¹³C NMR of compound 21 (125 MHz, CDCl₃).

S106

PMK-01-166

exp12 s2pul

SAMPLE		DEC. & VT	
date	Dec 11 2008	dfrq	499.836
solvent	cdcl3	dn	H1
file	exp	dpwr	39
ACQUISITION		dof	0
sfrq	125.698	dm	VVY
tn	C13	dmm	w
at	1.000	dmf	11905
np	62894	dseq	
sw	31446.5	dres	1.0
fb	17000	homo	n
bs	16	PROCESSING	
ss	2	lb	1.00
tpwr	54	wtfile	
pw	4.0	proc	ft
d1	1.000	fn	not used
tof	2512.2	math	f
nt	10000		
ct	6496	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1257.2		
wp	27650.1		
vs	112		
sc	0		
wc	210		
hzmm	131.67		
is	500.00		
rfl	1269.7		
rfp	0		
th	6		
ins	100.000		
nm	ph		

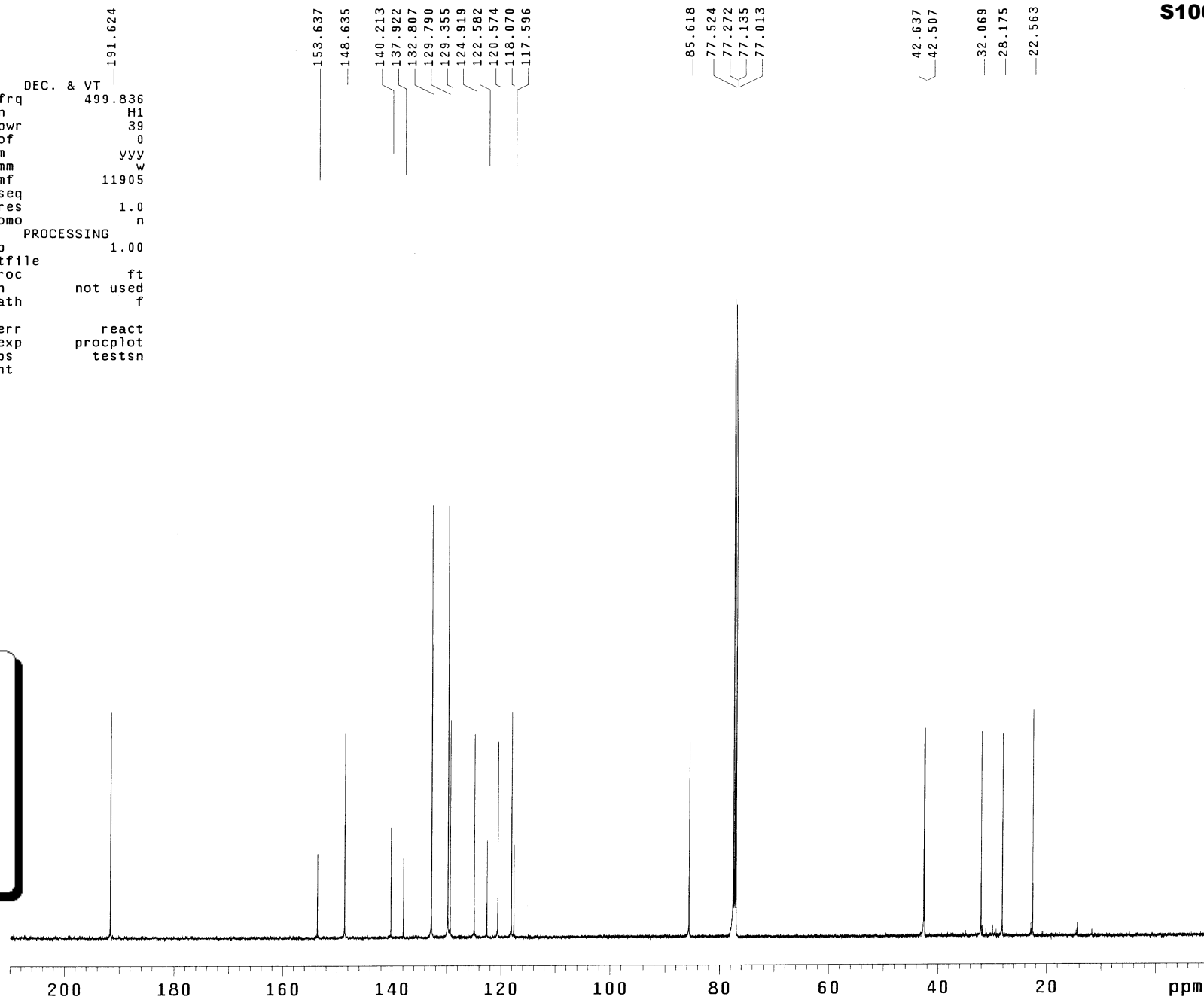
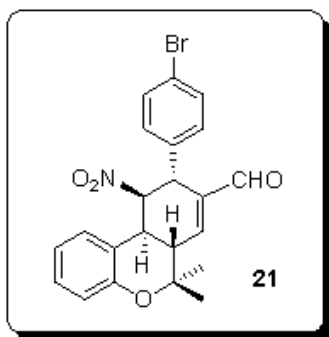


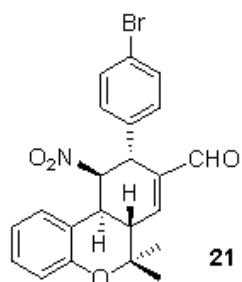
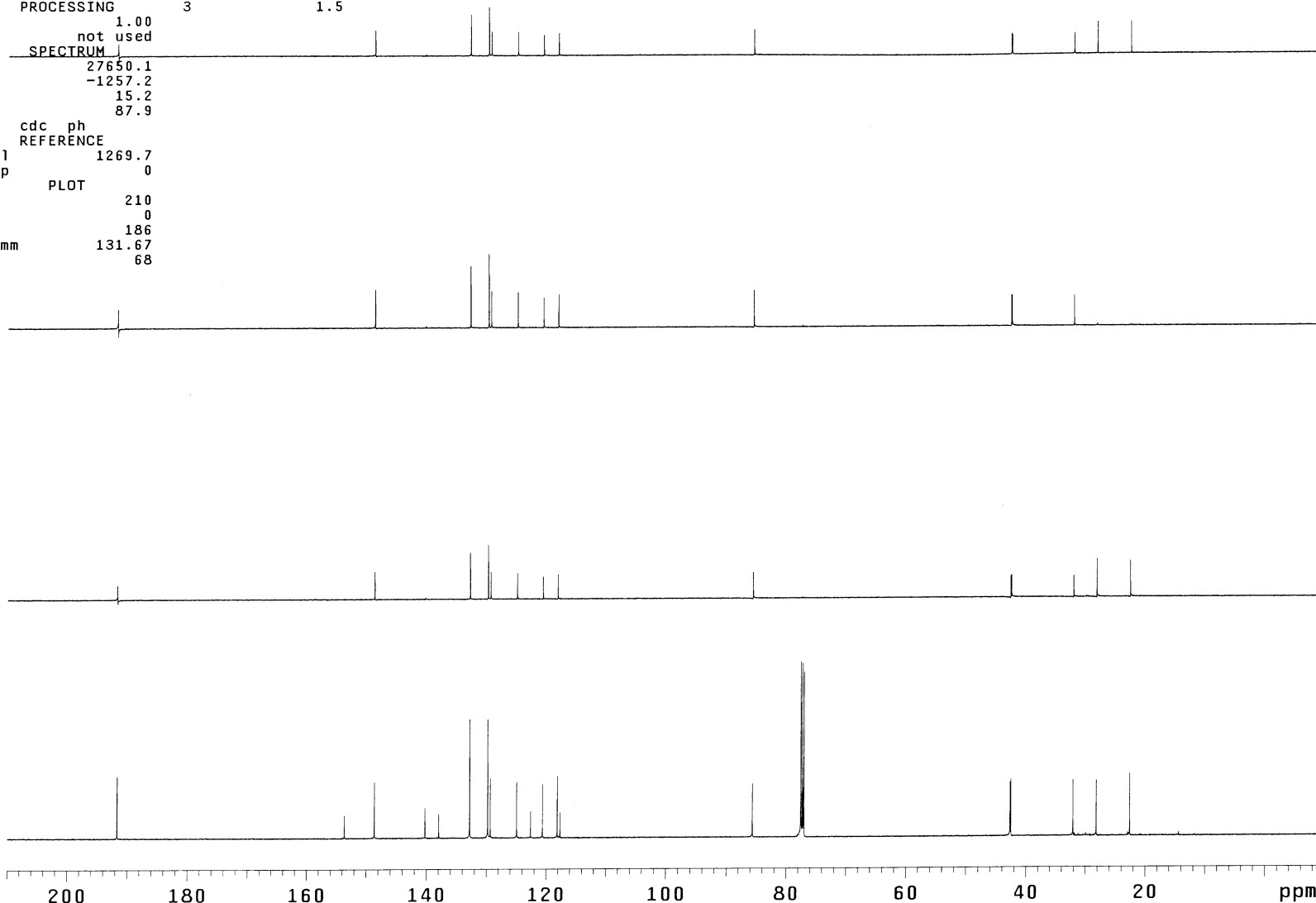
Fig S107. DEPT of compound 21 (CDCl₃).

S107

PMK-01-166

exp13 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Dec 11 2008	j1xh	140.0	mult
solvent	cdcl3	mult	arrayed	arraydim
sample	undefined	SPECIAL	not used	mult
ACQUISITION		temp	not used	mult
sw	31446.5	gain	20	1
at	1.000	spin	0	2
np	62894	PROCESSING	3	1.5
bs	16	lb	1.00	
ss	-4	fn	not used	
d1	1.000	SPECTRUM		
nt	1000	wp	27650.1	
ct	1000	sp	-1257.2	
TRANSMITTER		rp	15.2	
tn	C13	lp	87.9	
tof	2512.2	ai	cdc ph	
tpwr	54	REFERENCE		
pw	9.400	rfl	1269.7	
DECOUPLER		rflp	0	
dn	H1	PLOT		
dof	0	wc	210	
dpwr	39	sc	0	
dm	nnv	vs	186	
dmm	ccw	hzmm	131.67	
dmf	11905	th	68	
pplv1	49			
pp	29.400			



21

Fig S108. HMQC of compound 21 (CDCl₃).

S108

STANDARD PROTON PARAMETERS

exp15 gHMQC

SAMPLE		FLAGS	ACQUISITION	ARRAYS
date	Dec 11 2008	hs	n	phase
solvent	cdcl3	sspul	y	256
sample	undefined	PFGflg	y	
ACQUISITION		hsglv1	1026	phase
sw	4498.4	SPECIAL	1	1
at	0.228	temp	not used	2
np	2048	gain	30	
fb	3000	spin	0	
ss	32	GRADIENTS		
d1	1.000	gzlv11	1026	
nt	16	gt1	0.001000	
2D ACQUISITION		gzlv13	516	
sw1	21367.5	gt3	0.001000	
ni	128	gstab	0.000500	
phase	arrayed	F2 PROCESSING		
TRANSMITTER		gf	0.105	
tn	H1	gfs	not used	
sfrq	499.836	fn	2048	
tof	249.8	F1 PROCESSING		
tpwr	57	gf1	0.006	
pw	13.000	gfs1	not used	
DECOUPLER		proc1	lp	
dn	C13	fn1	2048	
dof	-2515.1	DISPLAY		
dm	nny	sp	515.8	
dmm	ccp	wp	3571.5	
dmf	32258	sp1	2374.8	
dpwr	35	wp1	16860.3	
pxlv1	51	rfl	2227.2	
pxw	14.700	rfp	2716.6	
HMQC		rfl1	12016.8	
j1xh	140.0	rfp1	10760.7	
nullflg	y	PLOT		
		wc	150.0	
		sc	6.2	
		wc2	116.2	
		sc2	0	
		vs	57	
		th	4	
		ai	cdc	ph

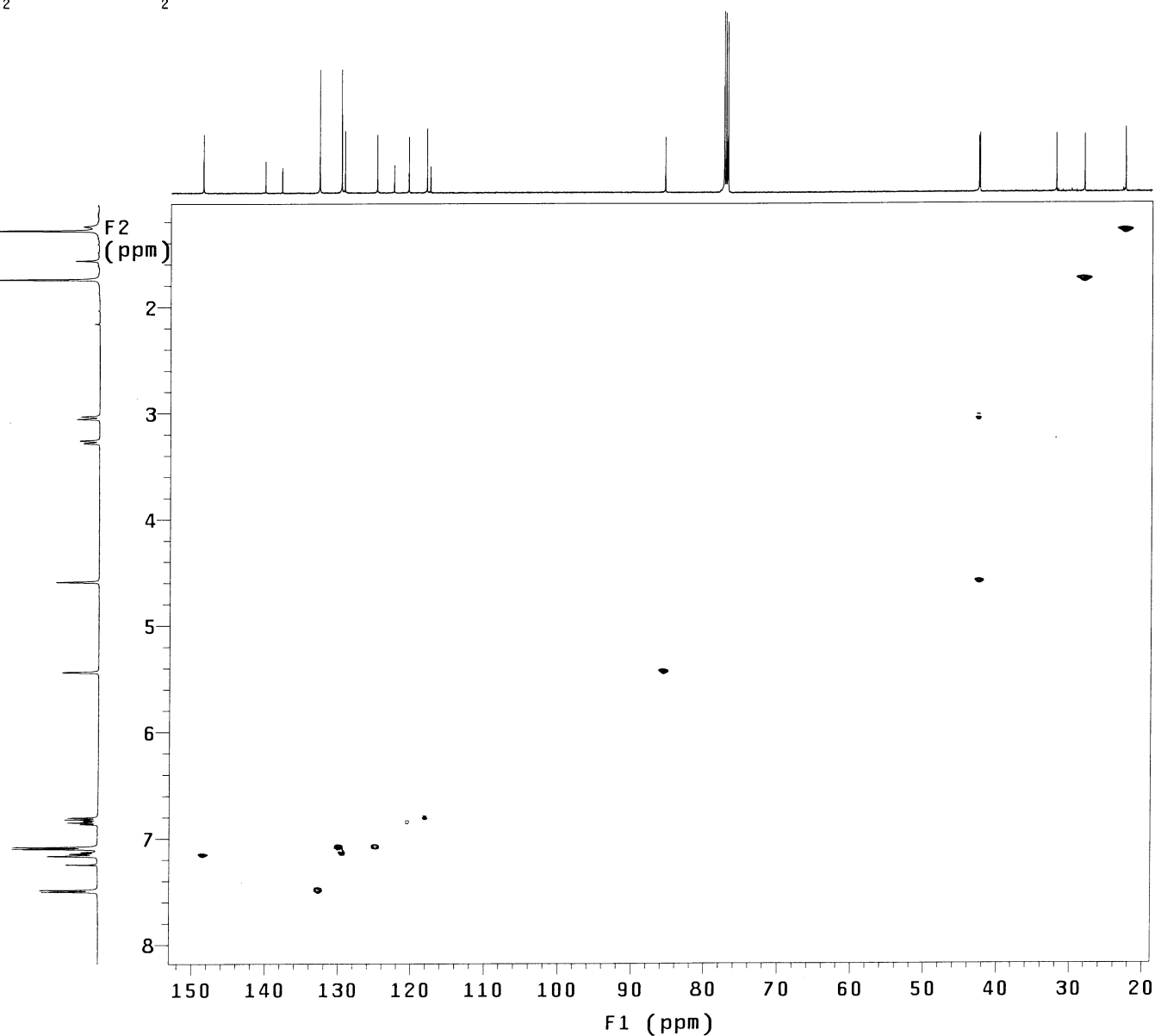
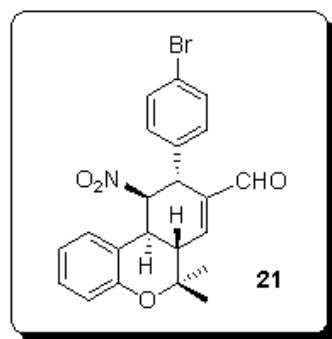


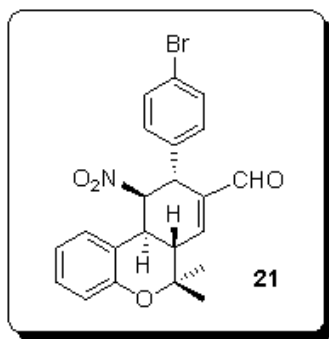
Fig S109. COSY of compound 21 (CDCl₃).

S109

PMK-01-166

exp14 gCOSY

SAMPLE		FLAGS	
date	Dec 11 2008	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1026
ACQUISITION		SPECIAL	
sw	4498.4	temp	not used
at	0.228	gain	30
np	2048	spin	0
fb	3000	F2 PROCESSING	
ss	16	sb	-0.114
d1	1.000	sbs	not used
nt	16	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4498.4	sb1	-0.028
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.836	DISPLAY	
tof	249.8	sp	493.2
tpwr	57	wp	4494.0
pw	13.000	sp1	504.2
GRADIENTS		wp1	4494.0
gzlv11	1026	rfl	2227.8
gt1	0.001000	rfp	2716.6
gstab	0.000500	rfl1	-499.8
DECOUPLER		rfp1	0
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	57
		th	4
		ai	cdc av



F2
(ppm)

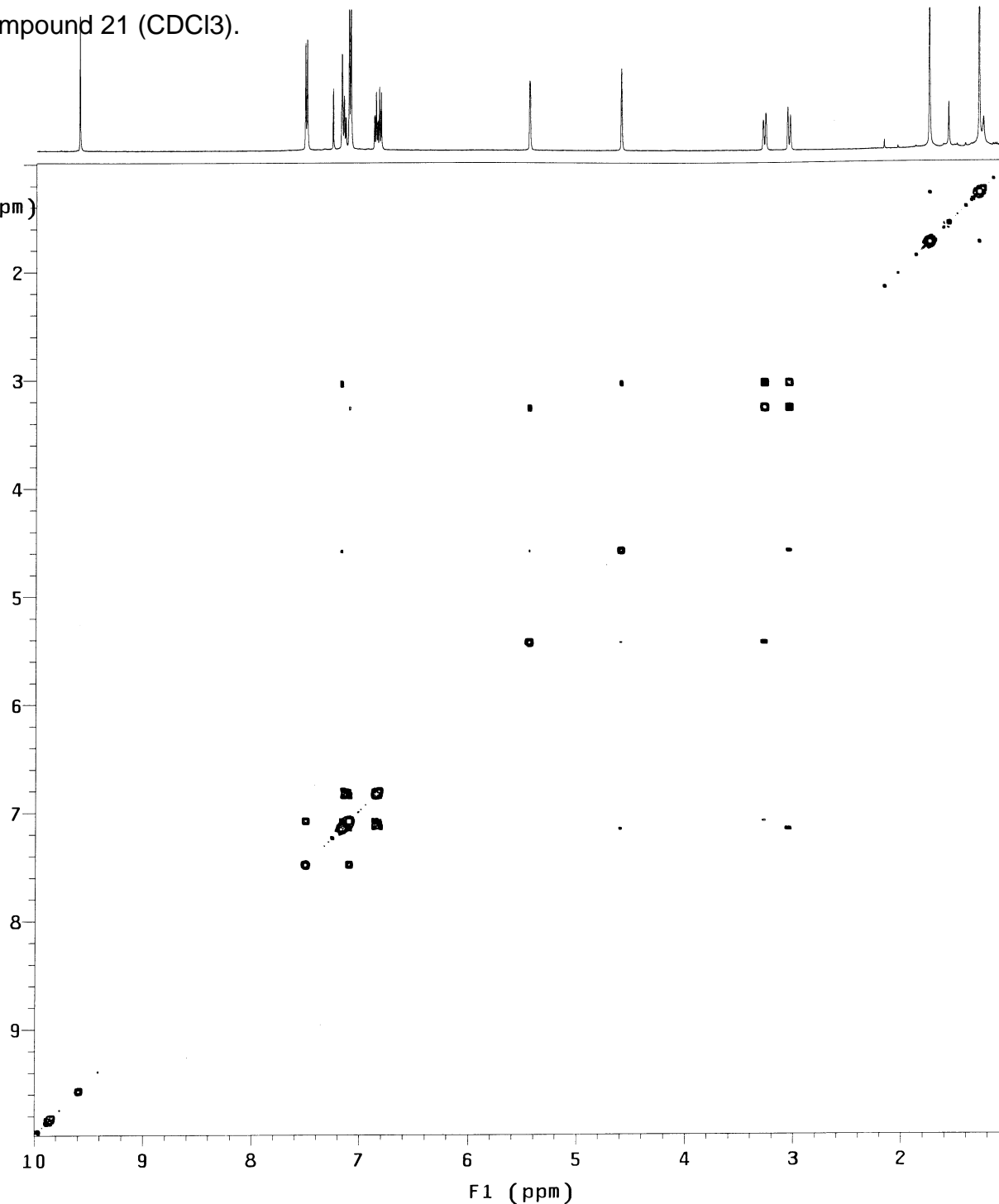


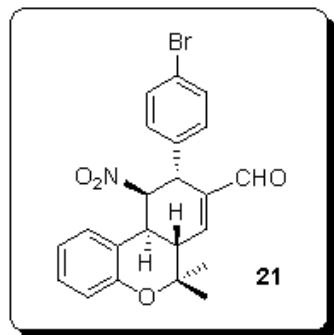
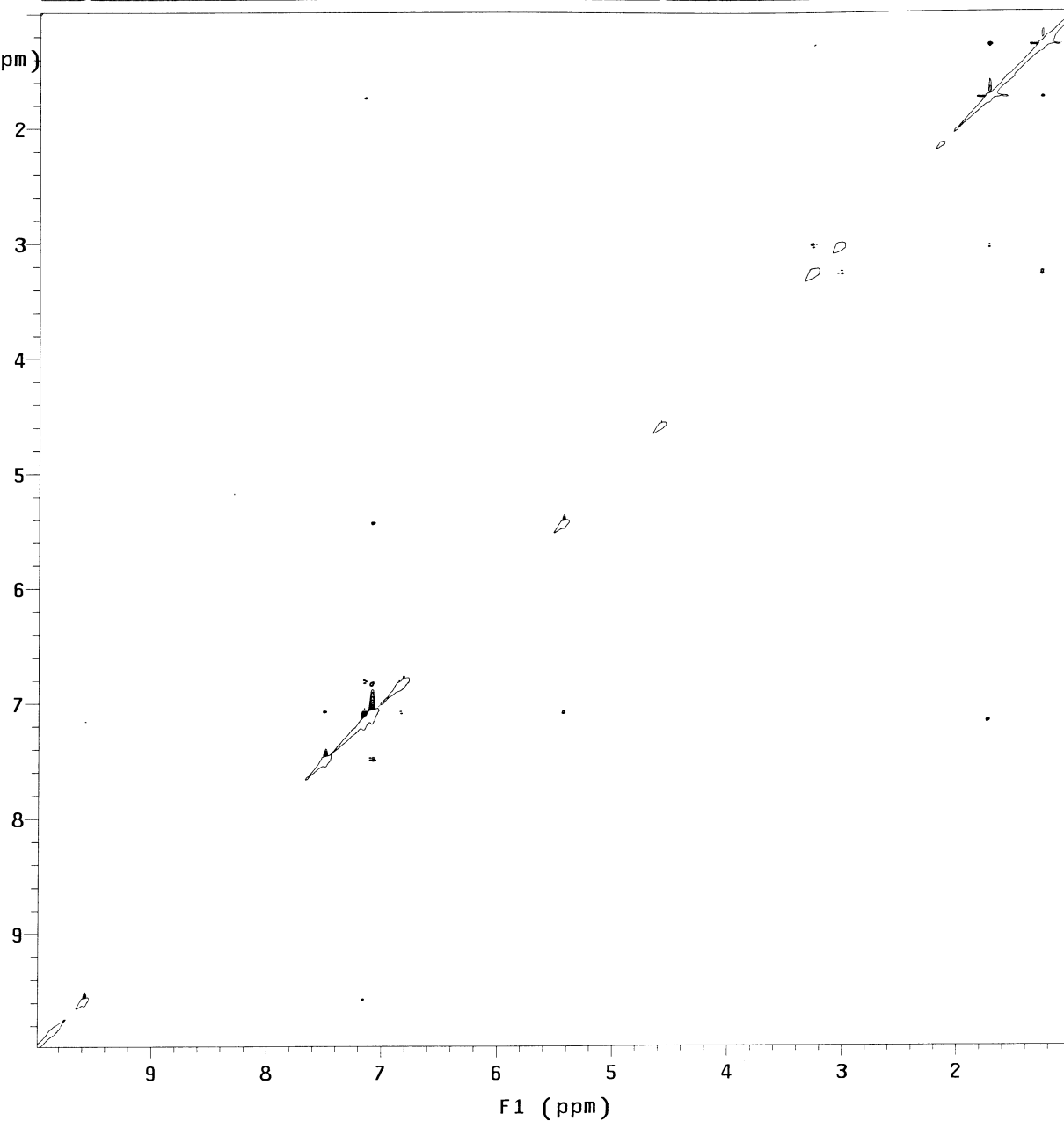
Fig S110. NOESY of compound 21 (CDCl₃).

S110

STANDARD PROTON PARAMETERS

exp16 NOESY

SAMPLE		FLAGS	
date	Dec 11 2008	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1026
sw	4498.4	SPECIAL	
at	0.228	temp	not used
np	2048	gain	30
fb	3000	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.105
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4498.4	F1 PROCESSING	
ni	200	gf1	0.041
TRANSMITTER		gfs1	not used
tn	H1	proc1	1p
sfrq	499.836	fn1	2048
tof	249.8	DISPLAY	
tpwr	57	sp	493.7
pw	13.000	wp	4494.0
NOESY		sp1	496.9
mix	0.200	wp1	4494.0
PRESATURATION		rfl	2227.2
satmode	nnnn	rfp	2716.6
satpwr	0	rfl1	2224.1
satdly	0	rfp1	2716.6
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	1814
		th	2
		ai	ph

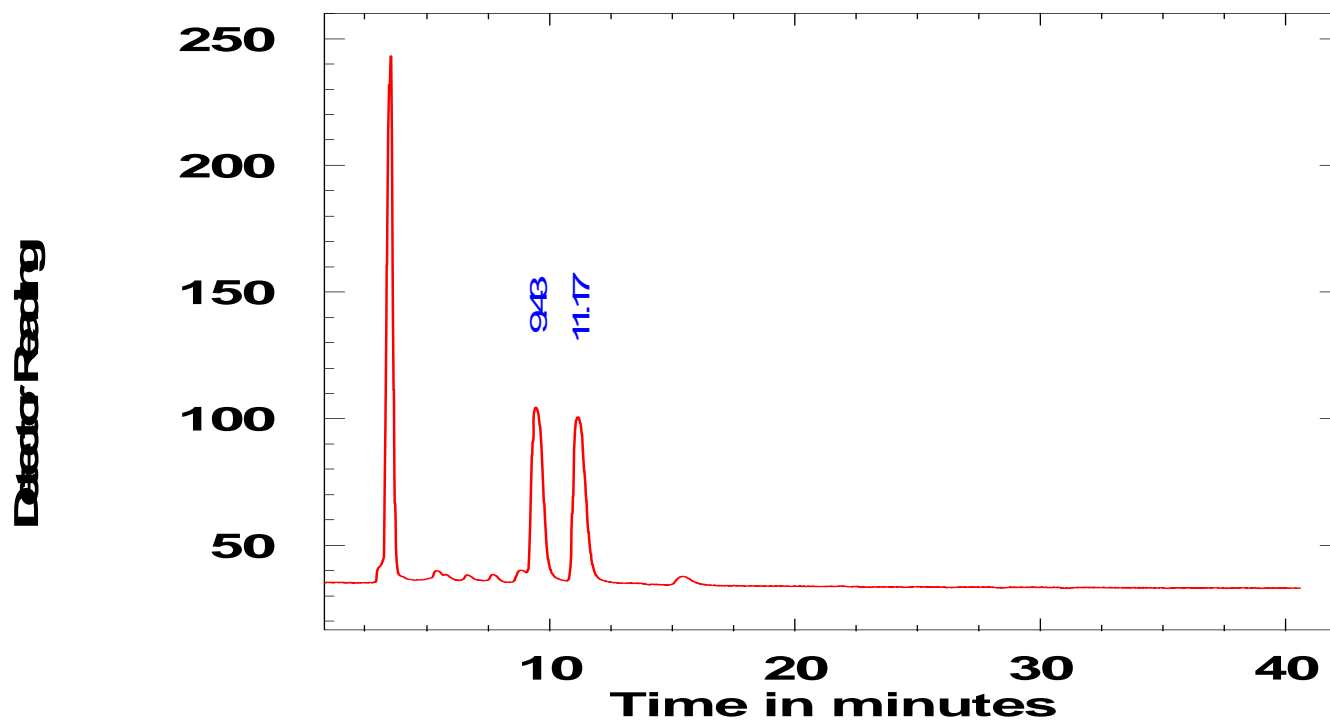
F2
(ppm)



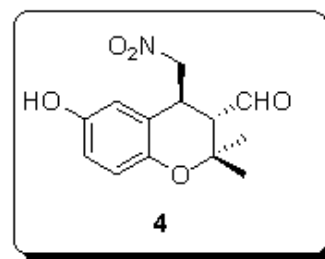
Peak Report

pmk-01-203-racemate-colmn-1A-20%ipa-hexane

Report produced on 2009/11/7 at 下午 04:18:24 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	9.11	10.12	1992	104.50	9.43	49.4	Baseline
2	10.76	11.83	2041	100.67	11.17	50.6	Baseline





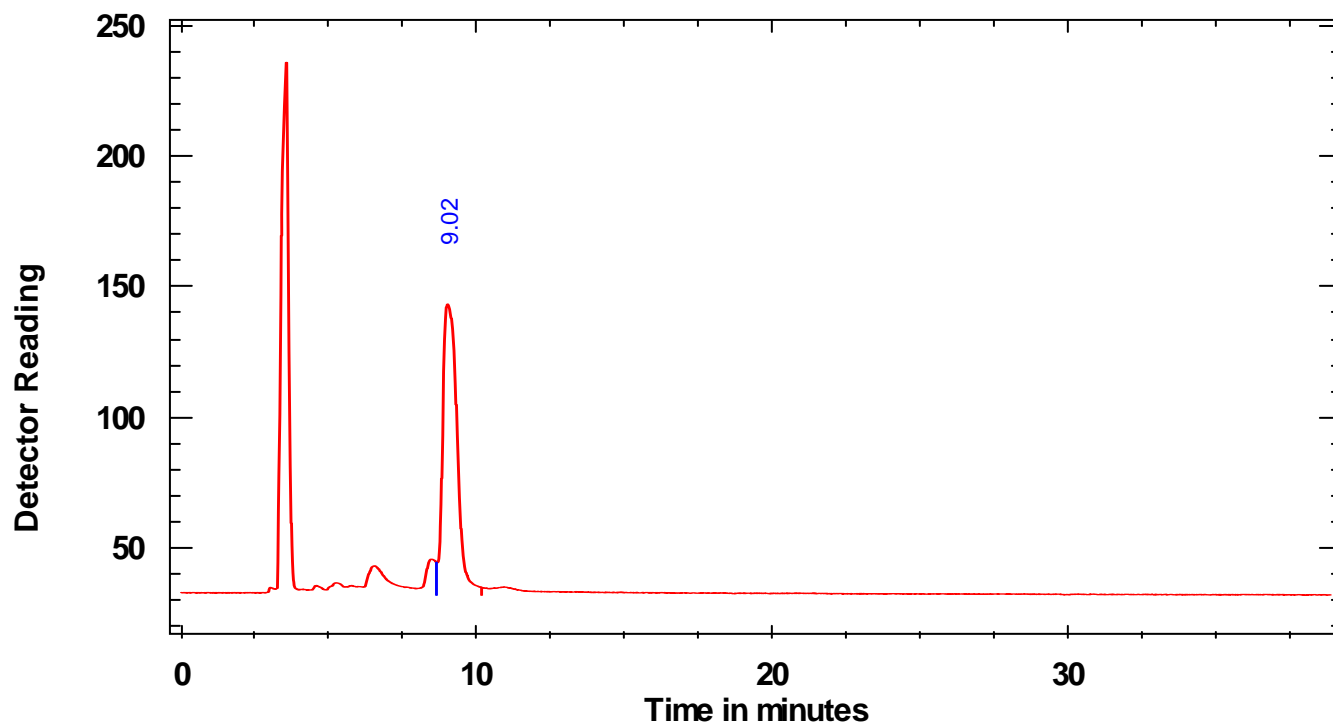
Chromatogram Report

First line of organization's address

Second line of organization's address

pmk-01-203-chiral-column-IA-20%ipa-hexane

Report produced on 2009/11/30 at 下午 03:26:00 by Put your name here

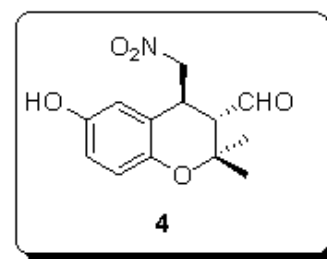


2009/11/7 02:23:03 Flow set to 1.00 at 0.00 minutes

2009/11/7 03:02:01 Run stopped by operator

PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	8.65	10.17	3094	100.0	142.84	9.02	Baseline	

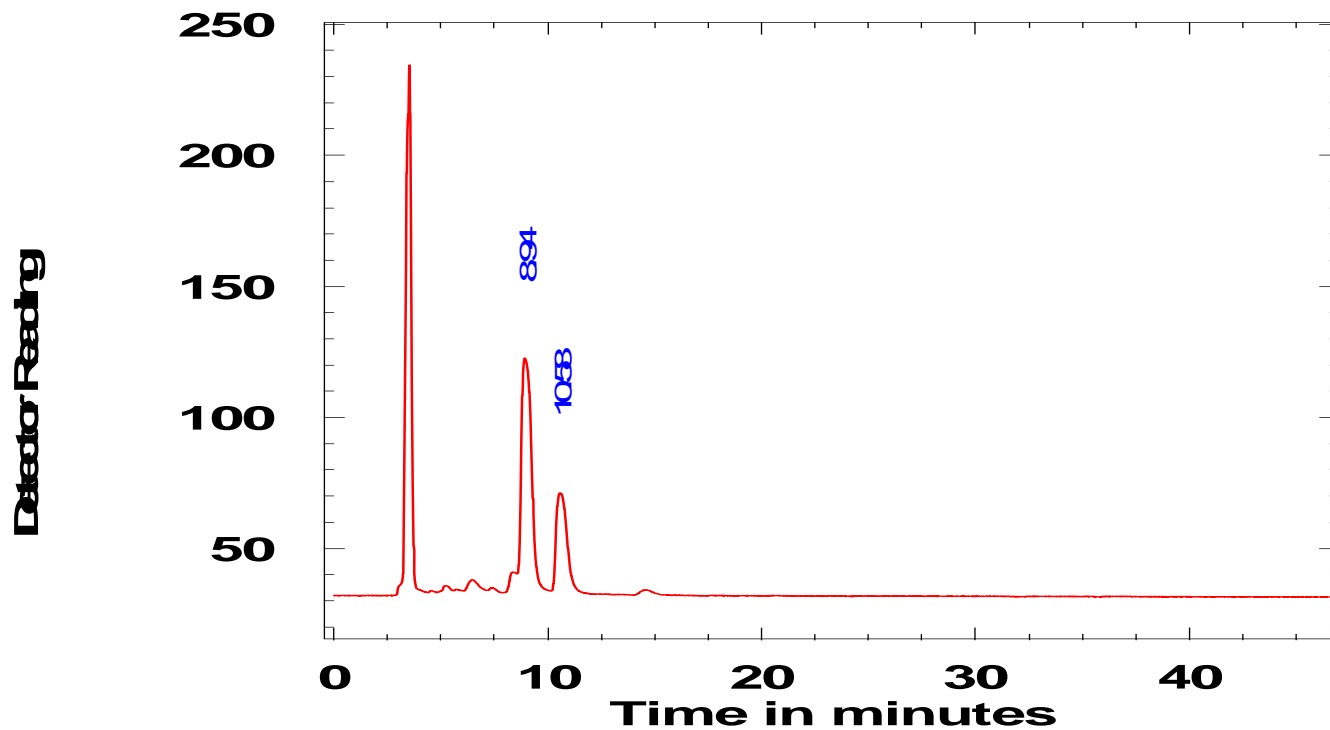




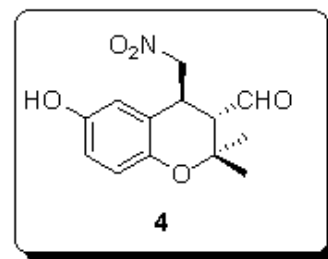
Peak Report

pmk-01-203-chiral+racemate-column-1A-20%ipa-hexane

Report produced on 2009/11/7 at 下午 04:25:30 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	8.43	9.66	2604	122.63	8.94	67.8	Baseline
2	10.06	11.35	1235	71.20	10.58	32.2	Baseline

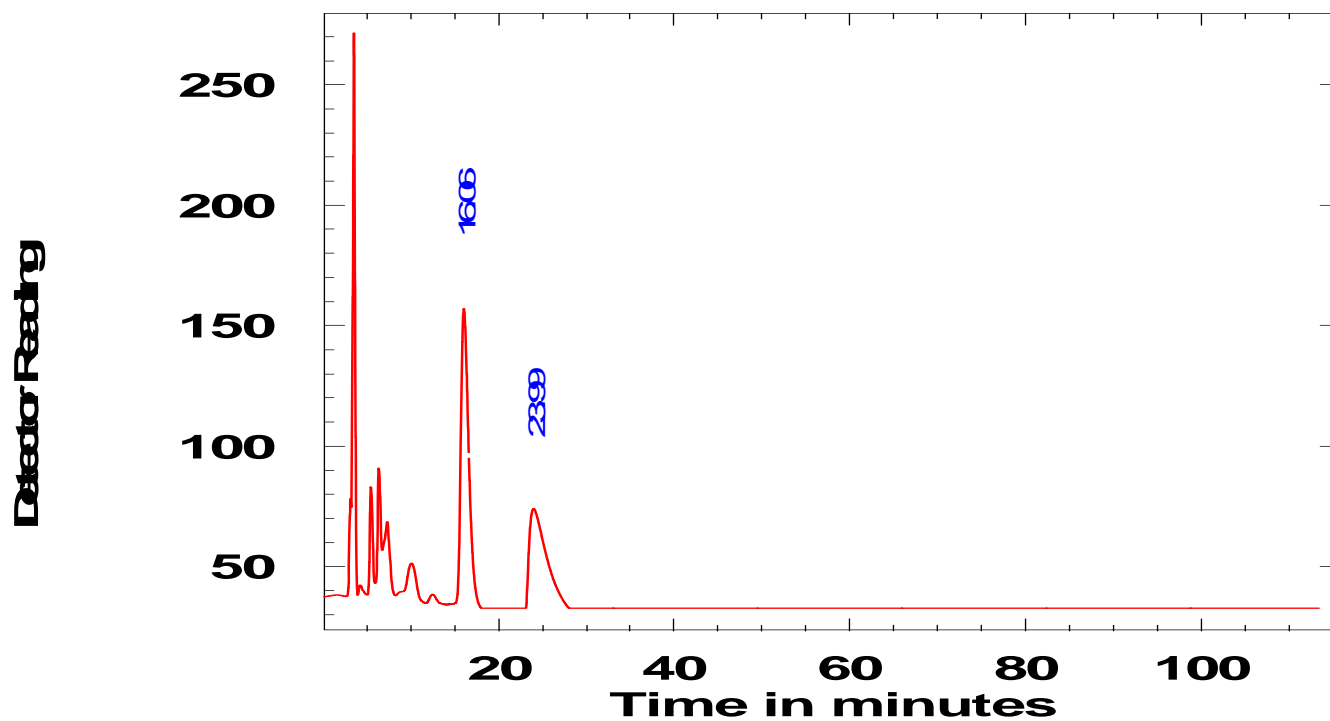




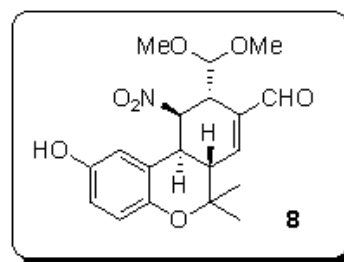
Peak Report

PMK-01-204

Report produced on 2009/9/30 at 下午 06:32:00 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	15.04	17.34	6883	157.01	16.06	48.9	Baseline
2	22.46	31.70	7204	73.93	23.99	51.1	Baseline

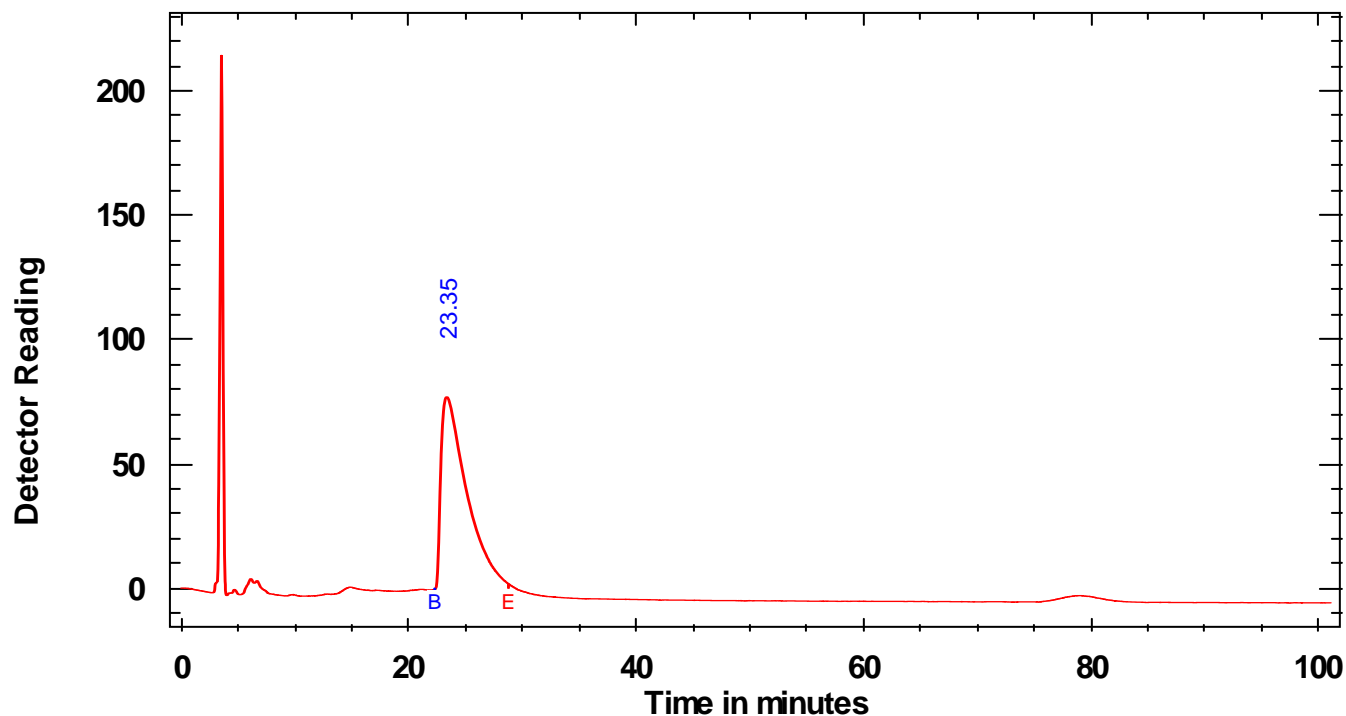




Chromatogram Report

PMK-01-204-Chiral -20%ipa/hex/colm-od

Report produced on 2009/11/30 at 下午 03:40:39 by Put your name here

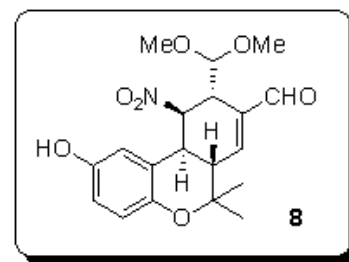


2009/9/30 02:20:05 Flow set to 1.00 at 0.00 minutes

2009/9/30 04:01:12 Run stopped by operator

PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	22.30	28.78	11950	100.0	76.93	23.35	Baseline	

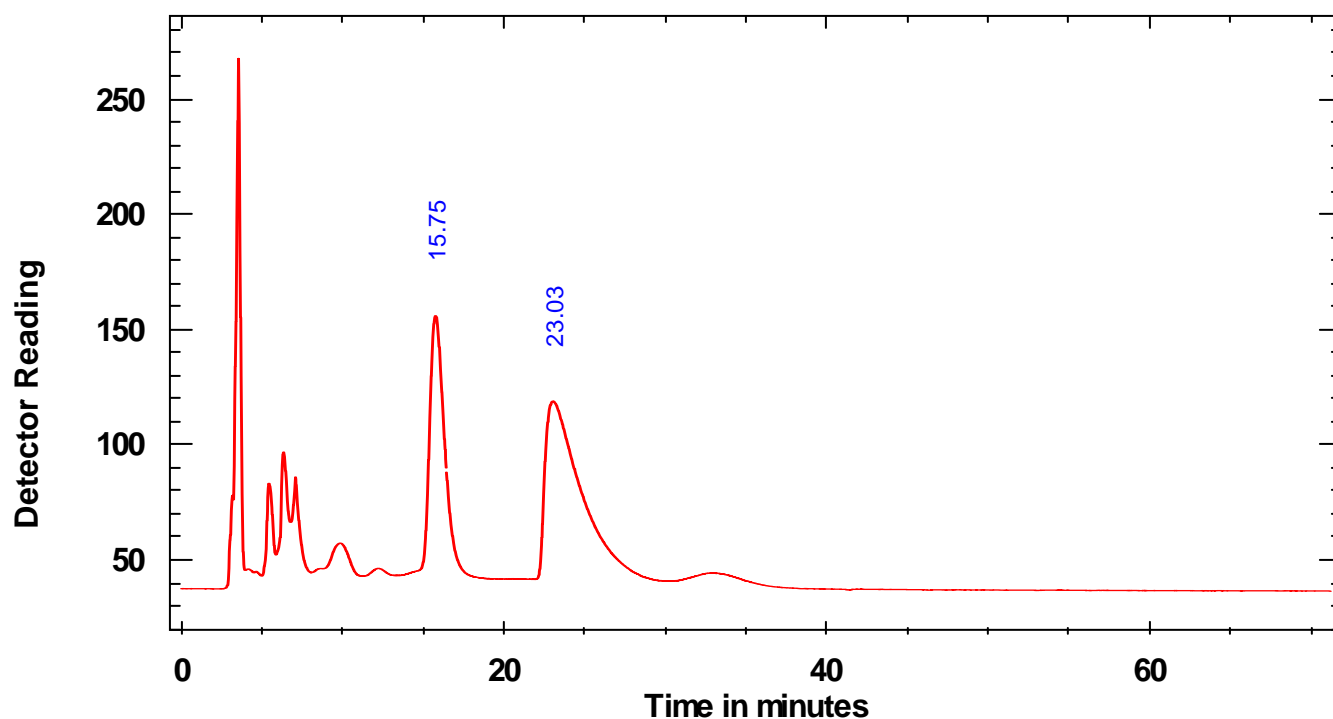




Chromatogram Report

PMK-01-204-racemate+chiral-%ipa/hex-colm OD

Report produced on 2009/11/30 at 下午 04:20:35 by Put your name here

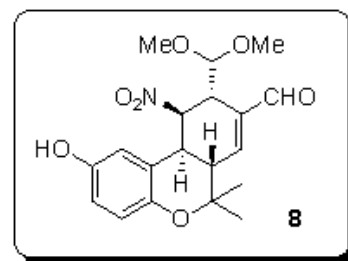


2009/9/30 04:58:46 Flow set to 1.00 at 0.00 minutes

2009/9/30 06:10:03 Run stopped by operator

PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	15.00	17.80	6676	37.1	86.84	15.77	Baseline	
2	22.02	28.06	11332	62.9	49.98	23.03	Baseline	

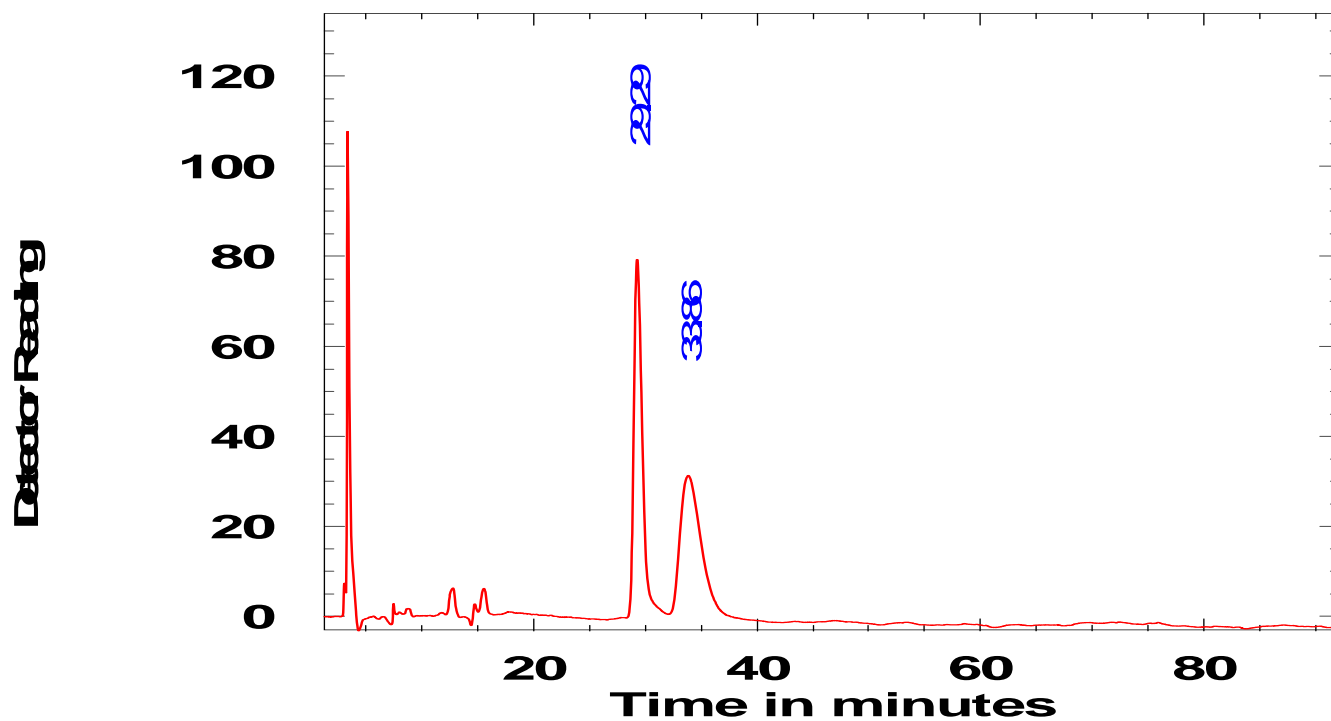




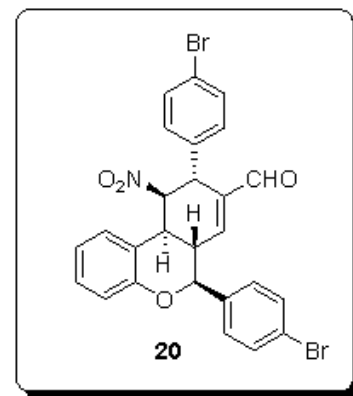
Peak Report

PMK-01-72-CO-coltm-IA-8%-THF-Hex

Report produced on 2008/10/11 at 下午 04:24:49 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	28.63	31.39	3844	79.25	29.29	49.3	Baseline
2	32.03	37.52	3957	31.27	33.86	50.7	Baseline

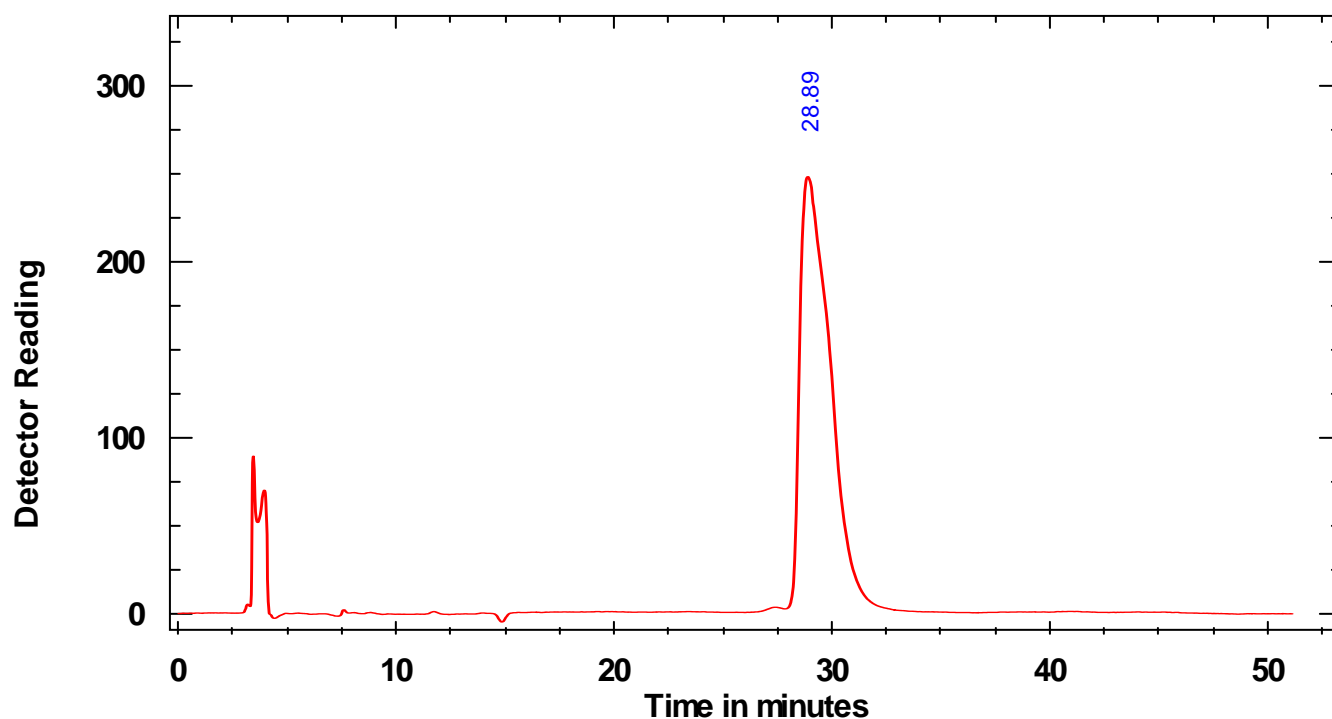




Chromatogram Report

PMK-01-72-chiral-colum-IA-8%-THF-Hex

Report produced on 2008/10/11 at 下午 01:08:24 by Put your name here

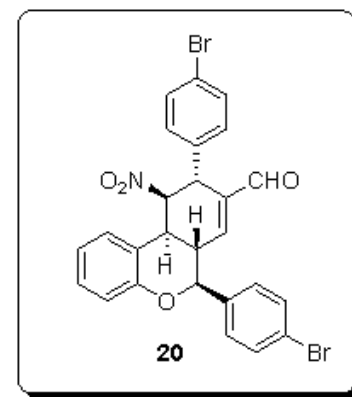


2008/10/11 12:14:49 Flow set to 1.00 at 0.00 minutes

2008/10/11 01:06:01 Run stopped by operator

PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	26.58	27.83	59	98.8	3.47	27.43	Baseline	



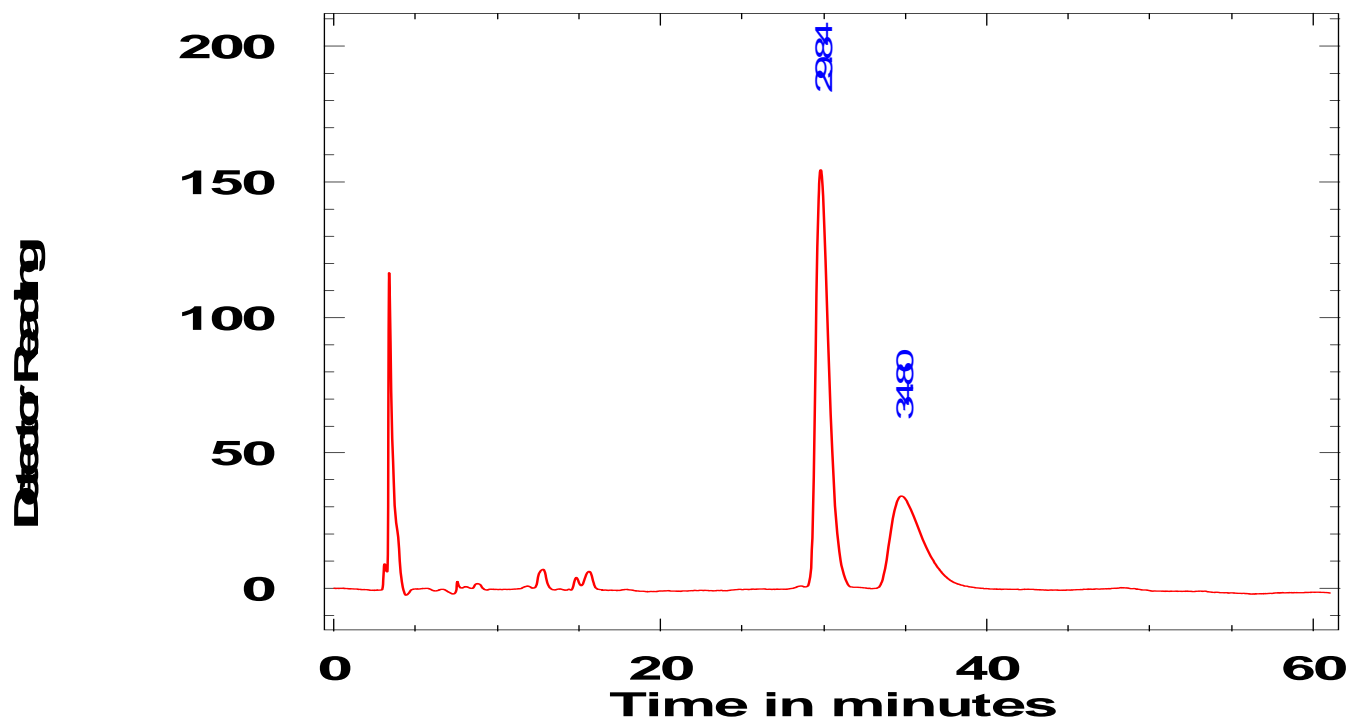
(For comparison)



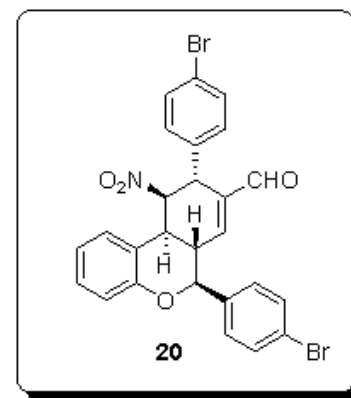
Peak Report

PMK-01-72-CO-collm-IA-8%-THF-Hex

Report produced on 2008/10/11 at 下午 02:20:16 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	29.17	31.65	8393	154.39	29.84	69.2	Baseline
2	33.34	37.24	3727	34.05	34.80	30.8	Baseline

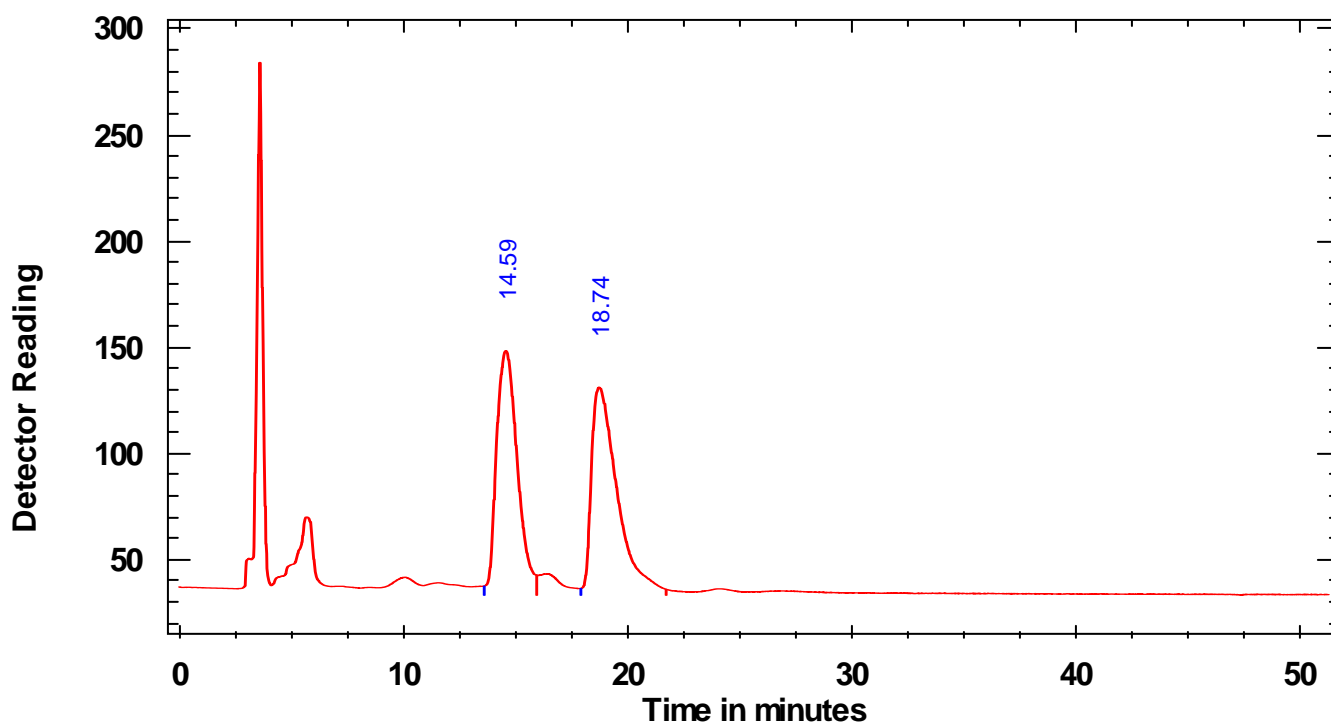




Chromatogram Report

PMK--01-166-racemate-15%ipa/hex/colm/OD

Report produced on 2009/11/30 at 下午 04:13:01 by Put your name here

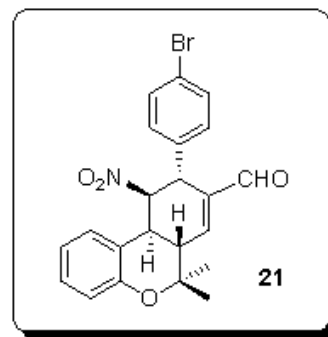


2009/10/15 02:21:07 Flow set to 1.00 at 0.00 minutes

2009/10/15 03:12:28 Run stopped by operator

PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	13.62	15.96	6548	47.3	148.18	14.59	Baseline	
2	17.93	21.74	7285	52.7	130.95	18.74	Baseline	

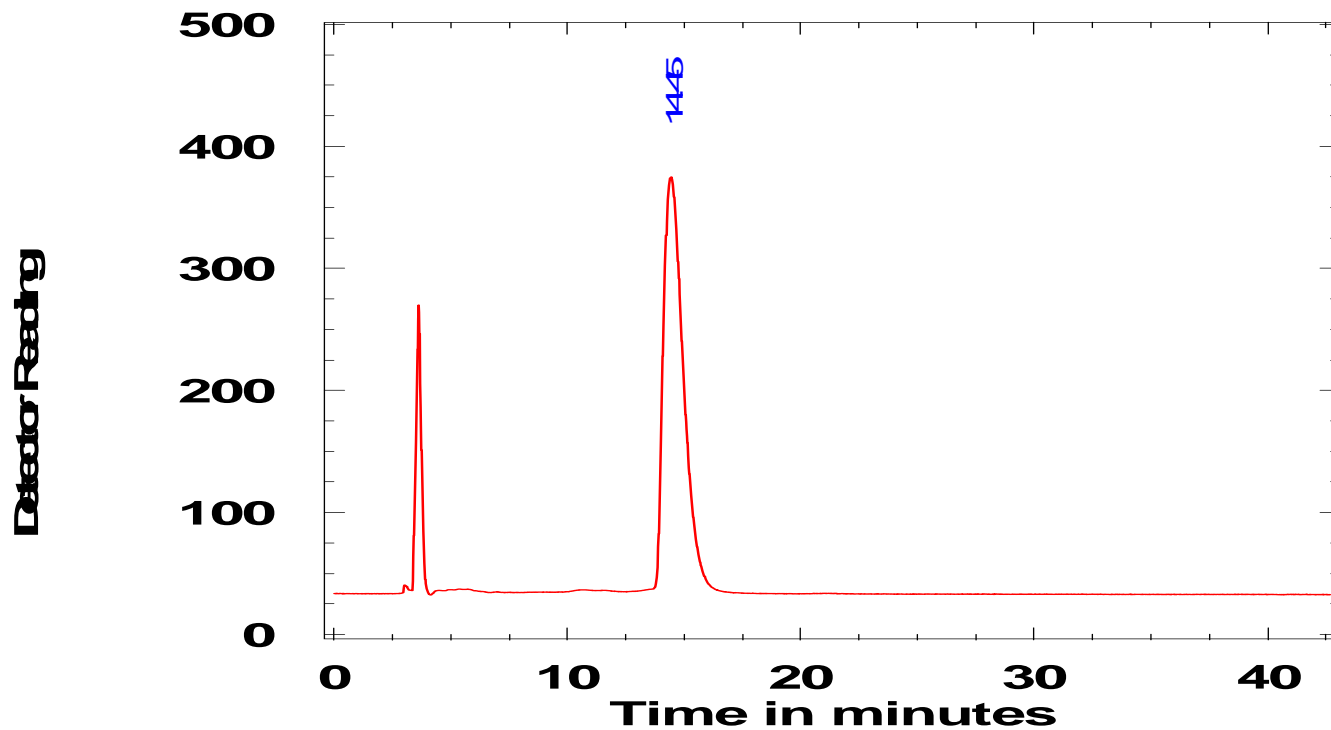




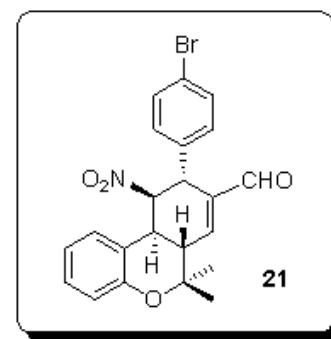
Peak Report

PMK-01-166

Report produced on 2009/10/15 at 下午 04:00:49 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	13.75	16.87	20019	374.94	14.45	100.0	Baseline

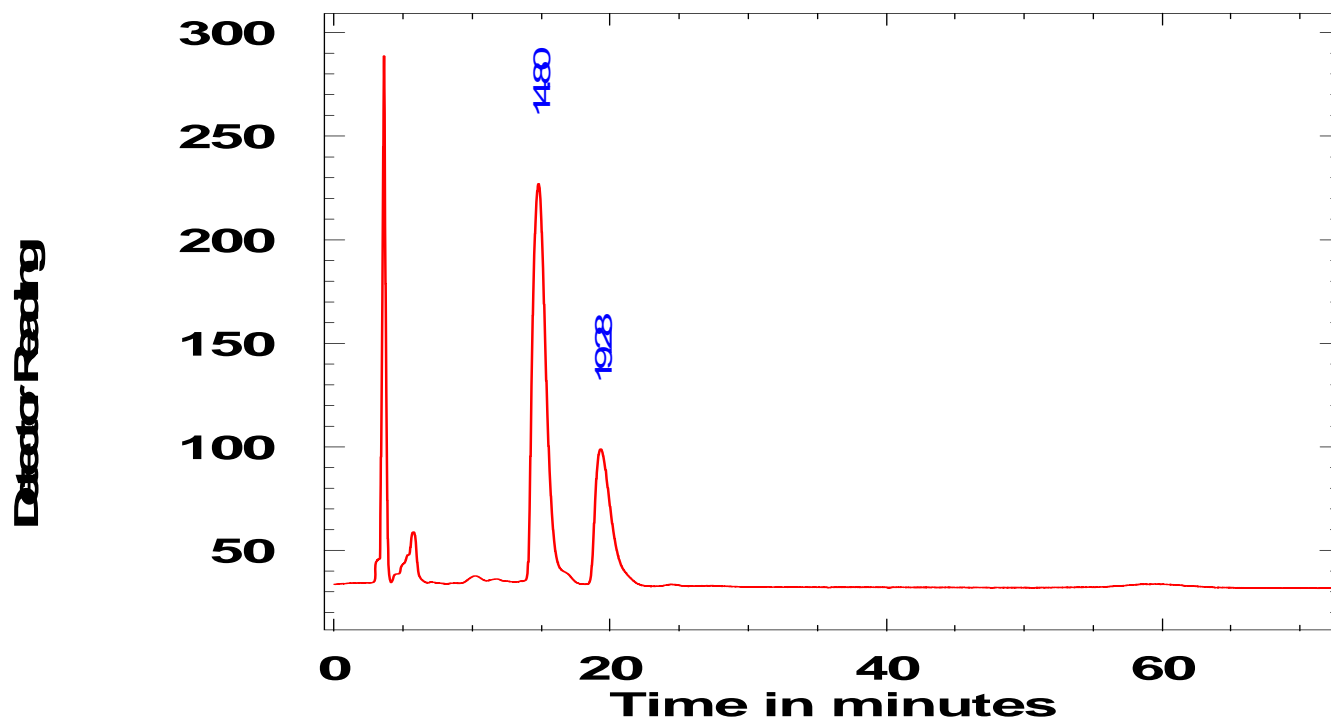




Peak Report

PMK-01-166

Report produced on 2009/10/15 at 下午 05:21:10 by Put your name here



Peak #	Begin	End	Peak Area	Maximum	Time	Area %	Begins as
1	14.11	16.52	10961	227.10	14.80	72.0	Baseline
2	18.61	21.13	4271	98.99	19.28	28.0	Baseline

