Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Desymmetrizing Reductive Aldol Cyclizations of Enethioate Derivatives of 1, 3-Diones Catalyzed by Chiral Copper Hydride

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Supporting Information

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1. General Experimental

Preparative: All reactions were performed in oven-dried round-bottomed flasks under a positive pressure of dry argon. Reactions were monitored by thin layer chromatography (TLC) using E. Merck silica gel plates, Kieselgel 60 F_{254} with 0.2 mm thickness. Components were visualized by illumination with short-wavelength ultra-violet light and/or staining. Flash column chromatography was performed with E. Merck silica gel 60 (230-400 mesh ASTM). Solvents and chemicals were purified according to standard procedures. HPLC grade dichloromethane (DCM) was used as received. Toluene was distilled from CaH_2 under argon. Reagents were used as received.

Analytical: All ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform ($CDCl_3$), with tetramethylsilane (TMS) as an internal standard at ambient temperature on a Bruker DPX 400, or 500 MHz Fourier Transform Spectrometer, operating at 400 MHz, or 500 MHz respectively for ^{1}H, and at 100 MHz, or 125 MHz respectively for ^{13}C. All spectra were calibrated at δ 7.26 ppm for ^{1}H and δ 77.03 ppm for ^{13}C. Spectral features are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = mutiplet and br = broad. IR absorption spectra were recorded as a solution in CH_2Cl_2 on a BioRad Fourier Transform 165 Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1}. Mass Spectra were recorded on a Finnigan MAT 95 mass spectrometer or API QSTAR PULSAR LC/MS/TOF System for both low resolution and high resolution, with accurate mass reported for the molecular ion (M^{+}) or next largest fragment thereof. Optical rotations were obtained on a Perkin Elmer polarimeter operating at 589 nm. Analytical HPLC was carried out on a Waters HPLC system equipped with a 1525 Binary HPLC Pump, Waters 2707 autosampler with a Waters 2489 variable wavelength UV/Visible detector or Waters 2998 PDA detector, operated using Breeze2 software. The enantiomeric excesses of the products were determined using a Daicel CHIRALCEL AS-3 column.

A. General procedure for the preparation of keto-enethioates 3

The thioester derived phosphoranes were prepared as previously described.[1]

To a solution of 1,3-dione **1** (1.0 equiv.) in H_2O/THF (30 mL, 1:1) was added acrolein (2.0 equiv.). The reaction mixture was stirred for 24-48 h. The solvent was removed to give the crude aldehyde, which was used in the next reaction without further purification.

To the crude aldehyde in CH_2Cl_2 was added the phosphorane **2** (1.2 equiv.). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed by in vacuo, and the residue was subjected to flash chromatography on silica gel to give the corresponding enethioates **3** as mixture of (*E*)- and (*Z*)-isomers.

The preparation of enethioates **3a-e, i-j,** have been previously reported.[2]

(*E*)-3f: According to the general procedure A, the reaction of **1a** (0.499 g, 4.46 mmol), and acrolein (0.445 g, 8.92 mmol) produced a crude aldehyde which was treated with phosphorane **2f** (2.58 g, 5.35 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3f** (0.54 g, 32% yield, *E*: *Z* >98:2) was obtained as white solid. **(*E*)-3f**: mp = 92-93 ^oC; R_f (25% EtOAc in hexane): 0.43; IR (CH_2Cl_2): 3047, 2978, 1720 (C=O, ketone), 1666 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.73 (dt, *J* = 15.0, 6.9 Hz, 1H), 6.04 (d, *J* = 15.0 Hz, 1H), 4.15 (s, 2H), 2.88-2.51 (m, 4H), 2.12-2.04 (m, 2H), 1.83-1.79 (m, 2H), 1.29 (s, 9H), 1.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.8, 189.1, 150.2, 143.5, 134.3, 129.1, 128.5, 125.6, 56.1, 34.9, 34.5, 32.6, 32.5, 31.3, 27.3, 20.1 ppm. LRMS (EI, 20 eV): m/z 372.1 (M^+, 6), 193.1 (M^+-$SC_{11}H_{15}$, 9), 165.1 (M^+-$COSC_{11}H_{15}$, 11); HRMS (EI, 20 eV): calcd for $C_{22}H_{28}O_3S$ (M^+), 372.1759, found 372.1754.

(*E*)-3g: According to the general procedure A, the reaction of **1a** (0.499 g, 4.46 mmol), and acrolein (0.445 g, 8.92 mmol) produced a crude aldehyde which was treated with phosphorane **2g** (2.51 g, 5.35 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3g** (1.05 g, 66% yield, *E*: *Z* >98:2) was obtained as a yellow oil. **(*E*)-3g**: R_f (25% EtOAc in hexane): 0.44; IR (CH_2Cl_2): 3063, 2985, 1720 (C=O, ketone), 1666 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 2H), 6.73 (td, *J* = 15.2, 6.9 Hz, 1H), 6.04 (d, *J* = 15.2 Hz, 1H), 4.21 (s, 2H), 2.84-2.69 (m, 4H), 2.29 (s, 6H), 2.24 (s, 3H), 2.08 (td, J = 15.2, 7.0 Hz, 2H), 1.80 (t, *J* = 8.0 Hz, 2H), 1.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.8, 190.1, 143.3, 137.2, 137.0, 129.2, 129.0, 56.1, 34.9, 32.6, 28.0, 27.3, 20.9, 20.0, 19.8 ppm; LRMS (EI, 20 eV): m/z 358.1 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{21}H_{26}O_3S$ (M^+), 358.1603, found 358.1597.

(*E*)-3h: According to the general procedure A, the reaction of **1a** (1.14 g, 10.2 mmol), and acrolein (1.14 g, 20.4 mmol) produced a crude aldehyde which was treated with phosphorane **2d** (4.85 g, 11.0 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3h** (2.13 g, 64% yield, *E*: *Z* >95:5) was obtained as a yellow oil. **(*E*)-3h**: R_f (25% EtOAc in hexane): 0.44; IR (CH_2Cl_2): 3047, 2985, 1720 (C=O, ketone), 1658 (C=O, unsaturated thioester) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.30-7.22 (m, 5H), 6.53 (t, *J* = 9.0 Hz, 1H), 4.14 (s, 2H), 2.84-2.66 (m, 4H), 2.09-2.04 (m, 2H), 1.84 (s, 3H), 1.82-1.76 (m, 2H), 1.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.8, 192.8, 138.6, 137.7, 136.9, 128.9, 128.6, 127.2, 56.2, 35.1, 35.0, 34.6, 33.2, 32.9, 23.9, 20.0, 12.4 ppm; LRMS (EI, 20 eV): m/z 330.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{19}H_{22}O_3S$ (M^+), 330.1284, found 330.1284.

(*E*)-3k: To a 10 mL EtOH solution of 3-bromobenzaldehyde (0.56 g, 3.0 mmol) and 1,3-indanedione (0.44 g, 3.0 mmol) was added *L*-proline (69 mg, 0.60 mmol) and diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.76 g, 3 mmol). The resulting mixture was stirred for 12 h, after which the volatiles were removed, and the crude product was purified by flash chromatography to afford 2-(3-bromobenzyl)-1H-indene-1,3(2H)-dione (**1k**) as a yellow oil (0.47 g, 50% yield). **1k:** R_f (10% EtOAc in hexane): 0.32; ^1H NMR (300 MHz, $CDCl_3$): 7.93-7.89 (m, 2H), 7.81-7.76 (m, 2H), 7.36 (s, 1H), 7.25-7.22 (m,1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 12.9 Hz, 1H), 3.35-3.27 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 199.4, 142.3, 139.5, 135.7, 132.5, 129.8, 128.2, 123.2, 122.3, 54.8, 31.5 ppm, LRMS (EI, 20 eV): m/z 314.0 (M^+, 62), 316.0 (M^+, 57); HRMS (EI, 20 eV): calcd for $C_{16}H_{11}{}^{79}BrO_2$ (M^+), 313.9942, $C_{16}H_{11}{}^{81}BrO_2$ (M^+), 315.9922, found 313.9950, 315.9937.

According to the general procedure A, the reaction of acrolein (0.18 g, 3.0 mmol) and **1k** (0.47 g, 1.5 mmol) produced a crude aldehyde which was treated with phosphorane **2d** (0.78 g, 1.8 mmol) in CH_2Cl_2 (20 mL). After workup and purification by flash chromatography, **3k** (0.57 g, 73% yield, *E*: *Z*= >95:5) was obtained as a yellow oil. **(*E*)-3k**: R_f (25% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3067, 2995, 2093, 1736, 1715, 1565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.79-7.78 (m, 2H), 7.67-7.64 (m, 2H), 7.29-7.26 (m, 5H), 7.10-7.07 (m, 2H), 6.87-6.85 (m, 2H), 6.68(dt, *J* = 8.7, 6.7 Hz, 1H), 5.85 (d, *J* = 14.3 Hz, 1H), 4.12 (s, 2H), 3.07 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 203.7, 189.4, 144.0, 142.9, 138.3, 138.0, 136.6, 136.4, 133.4, 130.7, 130.3, 129.7, 129.6, 129.2, 127.9, 123.5, 122.8, 60.1, 41.4, 33.8, 33.6, 28.3 ppm; LRMS (EI, 20 eV): m/z 518.1 (M^+, 2.4), 520.1 (M^+, 2.6); HRMS (EI, 20 eV): calcd for $C_{28}H_{23}{}^{79}BrO_3S$ (M^+) 518.0551, $C_{28}H_{23}{}^{81}BrO_3S$ (M^+) 520.0531; found 518.0536, 520.0540.

(*E*)-3l: According to the general procedure A, the reaction of **1l** (1.28 g, 10.2 mmol), and acrolein (1.14 g, 20.4 mmol) produced a crude aldehyde which was treated with phosphorane **2d** (5.10 g, 12.0 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3l** (2.42 g, 73% yield, *E*: *Z* = 9:1) was obtained as a yellow oil. **(*E*)-3l**: R_f (25% EtOAc in hexane): 0.25; IR (CH_2Cl_2): 3047, 2978, 1728 (C=O, ketone), 1697 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ7.30-1.23 (m, 5H), 6.80 (dt, *J* = 15.6, 6.7, Hz, 1H), 6.08 (dt, *J* = 15.3, 1.5 Hz, 1H), 4.17 (s, 2H), 2.69-2.63 (m, 4H), 2.04-1.90 (m, 6H), 1.28 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 189.1, 144.2, 137.6, 128.9, 128.7, 128.6, 127.3, 64.8, 37.9, 34.1, 33.7, 32.9, 27.6, 21.7, 17.5 ppm; LRMS (EI, 20 eV): m/z 330.1 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{19}H_{22}O_3S$ (M^+), 330.1290, found 330.1286.

(*E*)-3m: According to the general procedure A, the reaction of **1l** (0.76 g, 6.0 mmol), and acrolein (0.67 g, 12 mmol) produced a crude aldehyde which was treated with phosphorane **2f** (3.5 g, 7.2 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3m** (1.53 g, 66% yield, *E*: *Z* >95:5) was obtained as a white solid. **(*E*)-3m**: mp = 79-81 ^oC; R_f (25% EtOAc in hexane): 0.35; IR (CH_2Cl_2): 3047, 2970, 1728 (C=O, ketone), 1697 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.8 Hz, 2H) 7.23 (d, *J* = 7.8, 2H), 6,82 (dt, *J* =15.6, 6.4, 1H), 6.07 (dt, *J* = 15.6, 1.5, 1H), 4.15 (s, 2H), 2.73-2.58 (m, 4H), 2.06-1.90 (m, 6H), 1.29 (s, 9H), 1.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 189.2, 150.2, 144.1, 134.4, 128.8, 128.5, 125.6, 64.8, 37.9, 34.5, 33.8, 32.6, 31.3, 27.6, 21.6, 17.5 ppm; LRMS (EI, 20 eV): m/z 386.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{23}H_{30}O_3S$ (M^+), 386.1916, found 386.1910.

(*E*)-3n: According to the general procedure A, the reaction of **1l** (0.76 g, 6.0 mmol), and acrolein (0.67 g, 12 mmol) produced a crude aldehyde which was treated with phosphorane **2a** (2.63 g, 7.2 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3n** (1.0 g, 62% yield, *E*: *Z* >95:5) was obtained as a yellow oil. **(*E*)-3n**: R_f (25% EtOAc in hexane): 0.22; IR (CH_2Cl_2): 3047, 2985, 1728 (C=O, ketone), 1666 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.76 (dt, *J* = 15.4, 6.4, Hz, 1H), 6.06 (dt, *J* = 15.2, 1.5 Hz, 1H), 2.93 (q, *J* = 7.3 Hz, 2H), 2.69-2.63 (m, 4H), 2.06-1.90 (m, 6H), 1.26-1.24 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 189.9, 143.5, 129.2, 64.8, 37.9, 33.8, 27.5, 23.1, 21.5, 21.5, 17.5, 14.8 ppm. LRMS (EI, 20 eV): m/z 268.1 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{14}H_{20}O_3S$ (M^+), 268.1133, found 268.1126.

(*E*)-3o: According to the general procedure A, the reaction of **1o** (0.81 g, 4.0 mmol), and acrolein (0.45 g, 8.0 mmol) produced a crude aldehyde which was treated with phosphorane **2d** (2.1 g, 4.8 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3o** (0.5 g, 30 % yield, *E*: *Z* >98:2) was obtained as a yellow oil. **(*E*)-3o**: R_f (25% EtOAc in hexane): 0.35; IR (CH_2Cl_2): 3047, 2978, 1722 (C=O, ketone), 1669 (C=O, unsaturated thioester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ7.39-7.23 (m, 8H), 7.01-6.89 (m, 2H), 6,77 (dt, *J* =15.5, 6.7, 1H), 6.07 (d, *J* = 15.6, 1H), 4.19 (s, 2H), 3.07 (s, 2H), 2.46 (dd, *J* = 7.4, 4.7 Hz, 1H), 2.42 (dd, *J* = 7.4, 4.7 Hz, 1H), 2.18 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.14 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.09-2.04 (m, 2H), 2.01-1.94 (m, 2H), 1.64 (dtt, *J* = 14.1, 9.4, 4.7 Hz, 1H), 1.38-1.31 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5, 189.7, 144.5, 138.3, 136.5, 134.7, 134.6, 130.5, 130.1, 129.5, 129.3, 129.2, 1280, 127.9, 127.6, 69.5, 46.6, 41.4, 35.9, 33.6, 28.7, 16.5 ppm; LRMS (EI, 20 eV): m/z 406.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{25}H_{26}O_3S$ (M^+), 406.1597, found 406.1596.

(*E*)-3p: According to the general procedure A, the reaction of acrolein (1.36 g, 24.0 mmol) and 3-allylpentane-2,4-dione[3] (1.73 g, 12.4 mmol) produced aldehyde (2.43 g, 12.4 mmol) which was treated with phosphorane **2d** (5.80 g, 13.6 mmol) in CH_2Cl_2 (30 mL). After workup and purification by flash chromatography, **3p** (1.0 g, 55 % yield, *E*: *Z* >95:5) was obtained as a pale yellow oil. **(*E*)-3p**: R_f (25% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3047, 2986, 1697, 1666 (C=O, unsaturated thioester), 1635 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ7.32-7.23 (m, 5H), 6.86 (dt, *J* = 15.4, 6.4 Hz, 1H), 6.12 (d, *J* = 16.0 Hz, 1H), 5.47 (ddt, *J* = 16.0, 11, 7.5 Hz, 1H), 5.15-5.09 (m, 2H), 4.18 (s, 2H), 2.66 (d, *J* = 7.3 Hz, 2H), 2.10 (s, 6H), 2.04-1.94 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 189.0, 143.8, 137.6, 131.6, 128.9, 128.8, 128.7, 127.3, 119.4, 69.9, 34.9, 32.9, 28.7, 26.9, 26.3 ppm; LRMS (EI, 20 eV): m/z 344.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{20}H_{24}O_3S$ (M^+), 344.1446, found 344.1437.

(*E*)-3t: According to the general procedure A, the reaction of acrolein (1.36 g, 24.0 mmol) and 2-allyl-5,5-dimethylcyclohexane-1,3-dione[4] (1.8 g, 10.0 mmol) produced a crude aldehyde which was treated with phosphorane **2d** (5.2 g, 12.0 mmol) in CH_2Cl_2 (40 mL). After purification by chromatography, **3n** (2.0 g, 52% yield, *E*: *Z* >95:5) was obtained as an orange oil. **(*E*)-3t**: R_f (25% EtOAc in hexane): 0.40; IR (CH_2Cl_2): 3047, 2962, 1720 (C=O, ketone), 1689 (C=O, unsaturated thioester), 1635 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.30-7.21 (m, 5H), 6.86 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.10 (dt, *J* = 15.6, 1.4 Hz, 1H), 5.55 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.11-5.06 (m, 2H), 4.18 (s, 2H), 2.16-2.46 (m, 6H), 2.05-2.00 (m, 2H), 1.88-1.84 (m, 2H), 1.06 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 208.5, 189.2, 144.6, 131.3, 128.9, 128.6, 128.5, 127.3,

119.9, 67.9, 51.6, 40.8, 32.9, 30.7, 30.5, 29.5, 27.7, 27.2 ppm; LRMS (EI, 20 eV): m/z 384.2; HRMS (EI, 20 eV): calcd for $C_{23}H_{28}O_3S$ (M^+),384.1754, found 384.1759.

(*E*)-3u: To a solution of **3a** (0.805 g, 3.00 mmol) in acetone (100 mL) was added $Pd(OAc)_2$ (0.067 g, 0.3 mmol) under Ar, then Et_3SiH (2.1 g, 18.0 mmol) was added by syringe. After stirring for 2 h at RT, MeOH was added to quench the reaction. The volatiles were removed in vacuo to give an aldehyde, which was treated with phosphorane **2f** (1.24 g, 2.56 mmol) in CH_2Cl_2 (40 mL). After workup and purification by flash chromatography, **3u** (0.620 g, 50% yield over two steps, *E*: *Z*= 100:0) was obtained as an orange oil. **(*E*)-3u**: R_f (25% EtOAc in hexane): 0.42; IR (CH_2Cl_2): 2962, 1720 (C=O, ketone), 1689 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.33-7.31 (m, 2H), 7.25-7.23 (m, 2H), 6.86 (dt, *J* = 16.0, 4.0 Hz, 1H), 6.08 (dt, *J* = 16.0, 4.0 Hz, 1H), 4.16 (s, 2H), 2.71-2.58 (m, 4H), 2.16 (q, *J* = 8.0 Hz, 2H), 2.03-1.84 (m, 2H), 1.80-1.75 (m, 2H), 1.45-1.37 (m, 2H), 1.30 (s, 9H), 1.23 (s, 3H), 1.18-1.09 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 210.3, 189.4, 150.2, 145.1, 134.5, 128.5, 128.5, 125.6, 65.4, 38.0, 36.7, 34.5, 32.6, 31.8, 31.3, 28.2, 24.4, 19.9, 17.6 ppm; LRMS (EI, 20 eV): m/z 414.3; HRMS (EI, 20 eV): calcd for $C_{25}H_{34}O_3S$ (M^+),414.2229, found 414.2224.

B. General procedure for the synthesis of 3q-3s

To a solution of **1r** or **1s** (1.0 equiv.) in THF (22 mL) and H_2O (4.5 mL) was added OsO_4 (0.1 eq.) in *t*BuOH (0.5 mL). When the reaction mixture turned black, NMO (2.0 eq.) was added in portions to the reaction mixture. The black color faded and stirring was continued overnight at room temperature. The crude mixture was filtered through a Celite pad (1 inch). The filtrate was extracted with Et_2O (3 × 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo.

To the crude residue in DCM (15 mL) and H_2O (6 mL) was added $NaIO_4$ (2.2 eq.). The reaction mixture was stirred overnight at room temperature. The mixture was filtered through a Celite pad (1 inch). The filtrate was extracted with DCM (3 x 3 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo.

The residue dissolved in CH_2Cl_2 was treated with phosphorane **2c** or **2d** (0.55 eq.). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, and the residue was subjected to flash chromatography on silica gel to give the corresponding enethioates **3q-s**.

(*E*)-3q: 2.0 g, 26% yield overteps; orange solid; mp = 45-48 ^{o}C; R_f (25% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3039, 2978, 1728 (C=O, ketone), 1674 (C=O, unsaturated thioester), 1635 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.30-7.22 (m, 5H), 6.63 (dt, *J* = 16.0, 8.0 Hz, 1H), 6.10 (dt, *J* = 15.4, 1.2 Hz, 1H), 4.16 (s, 2H), 2.87-2.64 (m, 4H), 2.47 (dd, *J* = 7.7, 1.3 Hz, 2H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 188.6, 137.6, 137.3, 128.9, 128.6, 127.3, 56.1, 36.7, 35.1, 33.1, 20.1 ppm; LRMS (EI, 20 eV): m/z 302.1 (M^+, 3); HRMS (EI, 20 eV): calcd for $C_{17}H_{18}O_3S$ (M^+), 302.0974, found 302.0971.

(*E*)-3r: 1.1 g, 13% yield over 3 steps; orange solid; mp = 68-71 ^{o}C; R_f (25% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3047, 2986, 1728 (C=O, ketone), 1697 (C=O, unsaturated thioester), 1635 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.29-7.23 (m, 5H), 6.65 (dt, *J* = 16.0, 8.0 Hz, 1H), 6.11 (dt, *J* = 15.4, 1.3 Hz, 1H), 4.14 (s, 2H), 2.75 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.70 (dd, *J* = 9.5, 5.6 Hz, 1H), 2.66 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.59 (dd, *J* = 7.1, 5.1 Hz, 1H), 2.55 (dd, *J* = 7.1, 5.1 Hz, 1H), 2.07-1.97 (m, 1H), 1.91-1.81 (m, 1H), 1.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 188.9, 139.7, 137.5, 131.5, 128.9, 128.6, 127.3, 64.6, 37.9, 36.9, 33.0, 23.0, 17.3 ppm; LRMS (EI, 20 eV): m/z 316.2 (M^+, 5); HRMS (EI, 20 eV): calcd for $C_{18}H_{20}O_3S$ (M^+), 316.1128, found 316.1142.

(*E*)-3s: 2.0 g, 26% yield over 3 steps; orange oil;. R_f (25% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3047, 2985, 1728 (C=O, ketone), 1697 (C=O, unsaturated thioester), 1627 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (dt, *J* = 20.0, 8.0 Hz, 1H), 6.11 (d, *J* = 20 Hz, 1H), 2.78-2.55 (m, 6H), 2.08-1.85 (m, 2H), 1.47 (s, 9H), 1.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 190.3, 137.6, 132.6, 64.6, 48.06, 37.9, 37.1, 29.8, 22.5 ,17.3 ppm; LRMS (EI, 20 eV): m/z 282.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{15}H_{22}O_3S$ (M^+), 282.1284, found 282.1282.

C. General procedure for asymmetric reductive aldol cyclizations

$Cu(OAc)_2$•H_2O (0.015 mmol), **L8** (TaniaPhos SL-T001-1, 0.015 mmol) and bipy (0.015 mmol) were transferred into an oven-dried 5 mL round-bottomed flask, to which anhydrous PhMe (1.0 mL) and phenylsilane (0.75 mmol) were added under argon. The reaction mixture was stirred at room temperature until a characteristic greenish-yellow color was observed. The reaction mixture was cooled to –20 °C. Substrate **3** (0.15 mmol) in PhMe (1.0 mL) was added to the reaction mixture via cannula. The progress of the reaction was monitored by TLC. The reaction was quenched by the addition of 1 M HCl (1.0 mL), The organic layer was separated, and the aqueous layer was back-extracted with EtOAc (3 x 5 mL). The combined organics were dried over

anhydrous $MgSO_4$ and concentrated *in vacuo*. Flash chromatography of the residue on silica gel using 5%-20% EtOAc in hexane afforded the aldol products.

The corresponding reductive aldol reactions to obtain racemic products were similarly executed, but using either BDP or dppf as achiral ligands.

The reductions of **3a-c, e, i** have been previously reported.[2]

Reduction of 3d: According to general procedure C, **L8** (10.0 mg, 0.015 mmol), $Cu(OAc)_2•H_2O$ (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.015 mmol) and $PhSiH_3$ (76.0 μL, 0.60 mmol) in 2.0 mL PhMe at –20 °C were treated with **3d** (94.8 mg, 0.30 mmol) in PhMe (2 x 0.5 mL) at -20 °C for 18 h. After workup and chromatographic purification, **4d** was obtained as a colourless oil (77 mg, 81% yield, 91% ee). **4d**: $[\alpha]_D^{20}$ = –58.7 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL AY-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 30.890 min (major), 38.272 min (minor); R_f (25% EtOAc in hexane): 0.40; IR (CH_2Cl_2): 3053, 1739 (C=O, cyclopentanone), 1652 (C=O, thioester) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.33-7.24 (m, 5H), 4.27 (br s, 1H), 4.18 (d, *J*= 13.9 Hz, 1H), 4.14 (d, *J*= 13.9 Hz, 1H), 2.55 (ddd, *J* = 19.7, 10.3, 2.4 Hz, 1H), 2.39 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.23 (ddd, *J* = 19.2, 10.0, 9.6 Hz, 1H), 2.11 (dt, *J* = 13.5, 10.1 Hz, 1H), 2.00 (ddd, *J* = 13.2, 9.3, 1.9 Hz, 1H), 1.90 (dm, *J* = 13.9 Hz, 1H), 1.83 (dtd, *J* = 12.7, 12.5, 3.4 Hz, 1H), 1.72 (dm, *J*= 13.0 Hz, 1H), 1.71-1.60 (m, 1H), 1.37 (ddd, *J* = 13.6, 13.3, 4.5 Hz, 1H), 1.19 (dtt, *J* = 13.3, 13.0, 3.8 Hz, 1H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 217.7, 204.2, 136.6, 128.8, 128.7, 127.6, 77.9, 56.2, 53.8, 34.5, 33.5, 30.9, 28.3, 26.0, 22.5, 19.1 ppm; LRMS (EI, 20 eV): m/z 318.2 (M^+, 3), 195.1 (M^+-SC_7H_7, 5), 167.1 (M^+-$COSC_7H_7$, 18); HRMS (EI, 20 eV): calcd for $C_{18}H_{22}O_3S$ (M^+), 318.1284, found 318.1285.

Reduction of 3f: According to general procedure C, **L8** (10.0 mg, 0.015 mmol), $Cu(OAc)_2•H_2O$ (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.0.15 mol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe at -20 °C were treated with **3f** (55.9 mg, 0.15 mmol) in PhMe (2 x 0.3 mL) and stirred at -20 °C for 15 h. After workup and chromatographic purification, **4f** was obtained as a pale-yellow solid (105 mg, 94% yield, 90% ee). **4f**: mp = 76-78 °C; $[\alpha]_D^{20}$ = –34.9 (c = 2, CH_2Cl_2); DAICEL CHIRALCEL OD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 16.538 min (minor), 17.324 min (major); R_f (25% EtOAc in hexane): 0.50; IR (CH_2Cl_2): 3680 (OH), 3487 (hydrogen-bonded OH), 3047, 2970, 1735 (C=O, ketone), 1658 (C=O, thioester), 1604 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.30 (br, 1H), 4.14 (s, 2H), 2.55 (ddd, *J* = 19.7, 10.3, 2.4 Hz, 1H), 2.39 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.23 (ddd, *J* = 19.2, 10.0, 9.6 Hz, 1H), 2.11 (dt, *J* = 13.5, 10.1 Hz, 1H), 2.00 (ddd, *J* = 13.2,

9.3, 1.9 Hz, 1H), 1.90 (dm, *J* = 13.9 Hz, 1H), 1.83 (dtd, *J* = 12.7, 12.5, 3.4 Hz, 1H), 1.75-1.72 (m, *J*= 13.0 Hz, 1H), 1.71-1.60 (m, 1H), 1.37 (ddd, *J* = 13.6, 13.3, 4.5 Hz, 1H), 1.30 (s, 9H), 1.19 (dtt, *J* = 13.3, 13.0, 3.8 Hz, 1H), 1.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 217.8, 204.4, 150.6, 133.4, 128.4, 125.7, 77.9, 56.1, 53.8, 34.5, 33.1, 31.3, 30.9, 28.4, 26.0, 22.5, 19.1 ppm; LRMS (EI, 20 eV): m/z 374.2 (M^+, 6), 195.1 (M^+-SC_7H_7, 5); HRMS (EI, 20 eV): calcd for $C_{22}H_{30}O_3S$ (M^+), 374.1910, found 374.1901.

Reduction of 3g: According to general procedure C, **L8** (10.0 mg, 0.015 mmol), $Cu(OAc)_2$•H_2O (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.0.15 mol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe at -20 °C were treated with **3g** (112.0 mg, 0.31 mmol) in PhMe (2 x 0.6 mL) and stirred at -20 °C for 15 h. After workup and chromatographic purification, **4g** was obtained as a colourless oil (107 mg, 93% yield, 93% ee). **4g**: $[\alpha]_D^{20}$ = –30.4 (c=1, CH_2Cl_2); DAICEL CHIRALCEL OD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 15.572 min (minor), 27.364 min (major); R_f (25% EtOAc in hexane): 0.65; IR (CH_2Cl_2): 3680 (OH), 3487 (hydrogen-bonded OH), 2939, 1735 (C=O, ketone), 1658 (C=O, thioester), 1604 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (s, 2H), 4.26 (d, *J* = 13.4 Hz, 1H), 4.18 (d, *J*= 13.4 Hz, 1H), 2.55 (ddd, *J* = 19.7, 10.3, 2.4 Hz, 1H), 2.39 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.28 (s, 6H), 2.25 (s, 3H), 2.23 (ddd, *J* = 19.2, 10.0, 9.6 Hz, 2H), 2.11 (dt, *J* = 13.5, 10.1 Hz, 1H), 2.00 (ddd, *J* = 13.2, 9.3, 1.9 Hz, 1H), 1.90 (dm, *J* = 13.9 Hz, 1H), 1.83 (dtd, *J* = 12.7, 12.5, 3.4 Hz, 1H), 1.72 (dm, *J*= 13.0 Hz, 1H), 1.71-1.60 (m, 1H), 1.37 (ddd, *J* = 13.6, 13.3, 4.5 Hz, 1H), 1.19 (dtt, *J* = 13.3, 13.0, 3.8 Hz, 1H), 1.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 217.7, 205.1, 137.4, 137.1, 129.2, 128.6, 77.9, 56.2, 53.8, 34.5, 30.9, 28.3, 28.2, 26.1, 22.5, 20.9, 19.8, 19.1 ppm; LRMS (EI, 20 eV): m/z 360.1 (M^+, 3); HRMS (EI, 20 eV): calcd for $C_{21}H_{28}O_3S$ (M^+), 360.1754, found 360.1751.

Reduction of 3j: According to general procedure C, $Cu(OAc)_2$•H_2O (4.0 mg, 0.020 mmol), **L8** (14.0 mg, 0.020 mmol), bipyridine (3.0 mg, 0.19 mol) and $PhSiH_3$ (100 μL, 0.80 mmol) in anhydrous PhMe (3.0 mL) were treated with **3j** (153.4 mg, 0.39 mmol) in PhMe (1.0 mL) and stirred at -20 °C for 48 h. After workup and chromatographic purification, **4j** was obtained as a yellow oil (80.1 mg, 52% yield, 95% ee), and **6j** was obtained as a yellow oil (12.6 mg, 8 % yield, 73 % ee). **4j**: $[\alpha]_D^{20}$ = –137.8 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL AS-3, *n*-hexane/2-propanol = 96/4, flow rate = 1 mL/min, λ = 254 nm, retention times: 9.29 min (major), 28.43 min (minor); R_f (25% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3456 (OH), 2939, 2862, 1712 (C=O, ketone), 1651 (C=O, thioester), 1604 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71-7.70 (m, 1H), 7.39-7.23 (m, 8H), 5.55 (dddd, *J* = 23.4, 15.0, 8.4, 6.5 Hz, 1H), 5.3, (s, 1H), 4.90 (dd, *J* =

10.1, 0.78 Hz,1H), 4.85 (dd, *J* = 16.9, 1.4 Hz, 1H), 4.15 (d, *J* = 13.9 Hz, 1H), 4.00 (d, *J* = 13.9 Hz, 1H), 2.42 (dd, *J* = 14.2, 8.5 Hz, 1H), 2.29 (dt, *J* = 14.2, 3.1 Hz, 1H), 2.21 (dd, *J* = 12.3, 3.3 Hz, 1H), 1.88-1.73 (m, 3H), 1.53 (td, *J* = 14.1, 4.5 Hz, 1H), 1.30-1.21 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.8, 203.8, 155.9, 136.7, 134.1, 133.9, 133.4, 128.8, 128.7, 128.6, 127.5, 123.7, 123.5, 117.7, 78.7, 62.5, 60.2, 41.9, 33.4, 26.7, 25.9, 22.7 ppm; LRMS (EI, 20 eV): m/z 392.1 (M^+, 0.6), 268.1 (M^+-SC_7H_7, 2.59); HRMS (EI, 20 eV): calcd for $C_{24}H_{24}O_3S$ (M^+), 392.1446, found 392.1441. **6j**: $[\alpha]_D^{20}$ = –65.9 (c= 0.88, CH_2Cl_2); DAICEL CHIRALCEL AD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 67.504 min (minor), 72.897 min (major); R_f (10% EtOAc in hexane): 0.23; IR (CH_2Cl_2): 2955, 1713 (ketone, C=O), 1643 (thioester, C=O), 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 9.6 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.34-7.29 (m, 6H), 7.11 (d, *J* = 7.7 Hz, 1H), 5.68 (ddt, *J* = 16.0, 12.0, 7.2 Hz, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.18 (s, 2H), 3.14 (dd, *J* = 13.8, 3.0 Hz, 1H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.91 (dt, *J* = 14.2, 5.3 Hz, 1H), 1.86-1.80 (m, 1H), 1.70-1.64 (m, 1H), 1.61-1.56 (m, 2H), 1.01-0.91 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.9, 203.2, 152.1, 137.0, 135.9, 134.8, 134.6, 129.5, 129.1, 128.6, 127.4, 125.4, 122.9, 117.6, 81.2, 59.2, 56.5, 39.2, 33.5, 26.5, 20.4, 18.0 ppm; LRMS (EI, 20 eV): m/z 392.1 (M^+, 2), 268.1 (M^+-SC_7H_7, 7.1); HRMS (EI, 20 eV): calcd for $C_{24}H_{24}O_3S$: 392.1446, found 392.1439.

Reduction of 3k: According to the general procedure, **L8** (10.3 mg, 0.015 mmol), $Cu(OAc)_2$-H_2O (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.015 mol), and $PhSiH_3$ (76.0 μL, 0.60 mmol) in 2.0 mL PhMe were treated with **3k** (155.4 mg, 0.30 mmol) in PhMe (2×0.5 mL) and stirred at -20 °C for 30 h. After workup and chromatographic purification, **4k** was obtained as a yellow oil (80.0 mg, 51% yield, 98% ee) and **6k** was obtained as a yellow oil (22.5 mg, 14% yield, 91% ee). **4k**: $[\alpha]_D^{20}$ = –133.4 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL AD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 48.097 min (major), 59.360 min (minor); R_f (25% EtOAc in hexane): 0.56; IR (CH_2Cl_2): 3688 (OH), 3063, 2985, 2306, 1712 (C=O, ketone), 1651 (C=O, thioester), 1604， 1550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.68-7.66 (m, 1 H), 7.37-7.30 (m, 4H), 7.25-7.19 (m, 4H), 7.05 (t, *J* = 1.5 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.75 (d, J = 7.7 Hz, 1H), 5.44 (s, 1H), 4.14 (d, *J* = 13.9, 1H), 4.00 (d, *J* = 13.9, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.62 (d, *J* = 13.6, 1H), 2.20 (dd, *J* = 12.6, 7.2 Hz, 1H), 2.13 (dm, *J* = 13.9 Hz,1H), 1.90-1.73 (m, 3H), 1.63 (dt, *J* = 13.7, 4.6 Hz, 1H), 1.27-1.20 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 205.5, 203.7, 156.5, 139.8, 137.3, 134.9, 134.7, 134.0, 130.1, 129.7, 129.6, 129.5, 129.4, 129.3, 128.2, 124.3, 124.1, 122.3, 79.3, 63.5, 62.4, 43.8, 34.1, 27.9, 26.7, 23.5 ppm; LRMS (EI, 20 eV): m/z 520.1 (5.4), 522.1 (5.8); HRMS (EI, 20 eV): calcd for $C_{28}H_{25}{}^{79}BrO_3S$: 520.0708,

$C_{28}H_{25}{}^{81}BrO_3S$ 522.0687; found 520.0706, 522.0694. **6k**: $[\alpha]_D{}^{20}$ = –35.3 (c = 0.5, CH_2Cl_2); DAICEL CHIRALCEL AD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 92.032 min (major), 102.633 min (minor); R_f (25% EtOAc in hexane): 0.56; ^{1}H NMR (400 MHz, $CDCl_3$): 7.65 (d, *J* = 7.4 Hz, 1H), 7.35-7.21 (m, 10H), 7.09-7.00 (m, 3H), 4.64 (s, 1H), 4.12 (d, *J* = 7.1, 2H), 3.06 (dd, *J* = 13.2, 2.9 Hz, 1H), 2.96 (d, *J* = 13.7 Hz, 1H), 2.88 (d, *J* = 13.7 Hz, 1H), 1.85-1.80 (m, 2H), 1.75-1.69 (m, 1H), 1.49-1.44 (m, 1H), 1.10-0.90 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 205.8, 204.7, 152.4, 140.4, 137.4, 136.3, 135.2, 134.7, 130.4, 130.0, 129.9, 129.7, 129.3, 128.2, 125.9, 123.9, 122.3, 81.7, 60.9, 57.2, 39.7, 34.1, 27.3, 21.1, 19.2 ppm; LRMS (EI, 20 eV): m/z 520.1 (M^+, 1.6), 522.1 (M^+, 1.9); HRMS (EI, 20 eV): calcd for $C_{28}H_{25}{}^{79}BrO_3S$ 520.0708, $C_{28}H_{25}{}^{81}BrO_3S$ 522.0687; found 520.0692, 522.0676.

Reduction of 3l: According to the general procedure, **L8** (10.3 mg, 0.015 mmol), $Cu(OAc)_2$-H_2O (3.0 mg, 0.015 mmol), and $PhSiH_3$ (76.0 μL, 0.60 mmol) in 2.0 mL PhMe were treated with **3l** (99 mg, 0.30 mmol) in PhMe (2 x 0.6 mL) and stirred at –20 °C for 15 h. After workup and chromatographic purification, **4l** (72.3 mg, 72%,93%ee) was obtained as a pale-yellow oil: **4l:** $[\alpha]_D{}^{20}$ = –2.4 (c = 0.7, CH_2Cl_2); DAICEL CHIRALCEL AS-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 11.555 min (minor),4.674 min (major); R_f (25% EtOAc in hexane): 0.65; IR (CH_2Cl_2): 3680 (OH), 3502 (hydrogen-bonded OH), 3063, 2955, 1705 (C=O, ketone), 1651 (C=O, thioester), 1604 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.23 (m, 5H), 4.13 (d, *J* = 2.7, 2H), 3.76 (s, 1H), 2.65-2.54 (m, 2H), 2.26 (ddt, *J* = 16.0, 4.0, 1.6 Hz, 1H), 2.18 (td, *J* = 16.0, 4.0 Hz, 1H), 2.01-1.92 (m, 2H), 1.09-1.82 (m, 1H), 1.75-1.45 (m, 6H), 1.19 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 204.1, 136.7, 128.7, 127.5, 75.4, 55.3, 54.4, 36.4, 33.3, 32.1, 28.9, 26.6, 22.4, 21.7, 19.5 ppm; LRMS (EI, 20 eV): m/z 332.1 (M^+, 3); HRMS (EI, 20 eV): calcd for $C_{19}H_{24}O_3S$: 332.1441, found 332.1444.

Reduction of 3m According to the general procedure, **L8** (10.0 mg, 0.015 mmol), $Cu(OAc)_2$•H_2O (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.015 mmol) and $PhSiH_3$ (76.0 μL, 0.60 mmol) in 2.0 mL PhMe at -10 °C were treated with **3m** (116 mg, 0.30 mmol) in PhMe (2 x 0.5 mL) and stirred at –20 °C for 20 h. After workup and chromatographic purification, **4m** was obtained as a pale-yellow oil (89.2 mg, 77% yield, 88% ee) and **6m** was obtained as a pale-yellow oil (10.8 mg, 9% yield, 74% ee); **4m**: $[\alpha]_D{}^{20}$ = –11.8 (c = 2, CH_2Cl_2); DAICEL CHIRALCEL AS-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 16.910 min (minor), 21.141 min(major); R_f (25% EtOAc in hexane): 0.79; IR (CH_2Cl_2): 3688 (OH), 3063,

2962, 1705 (C=O, ketone), 1643 (C=O, thioester), 1604 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.10 (q, *J* = 13.8 Hz, 2H), 3.79 (s, 1H), 2.65-2.54 (m, 2H), 2.26-2.18 (m, 2H), 2.01-1.81 (m, 3H), 1.75-1.50 (m, 6H), 1.29 (s, 9H), 1.19 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ213.2, 204.2, 150.5, 133.4, 128.3, 125.6, 75.3, 55.2, 54.4, 36.4, 34.5, 32.9, 32.0, 31.3, 28.9, 26.5, 22.4, 21.7, 19.5 ppm; LRMS (EI, 20 eV): m/z 388.3 (M^+, 2); HRMS (EI, 20 eV): calcd for $C_{23}H_{32}O_3S$ (M^+), 388.2067, found 388.2070. **6m**: $[\alpha]_D^{20}$ = –1.9 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL OD-3, *n*-hexane/2-propanol = 96/4, flow rate = 1 mL/min, λ = 254 nm, retention times: 40.865 min (minor), 46.578 min (major); R_f (25% EtOAc in hexane): 0.76; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, *J* = 6.5 Hz, 2H), 7.20 (d, *J* = 6.5 Hz, 2H), 4.10 (q, *J* = 13.8 Hz, 2H), 3.22 (s, 1H), 2.92 (dd, *J* = 13.2, 4.1 Hz, 1H), 2.56 (ddd, *J* = 14.1, 14.1, 6.8 Hz, 1H), 2.31-2.25 (m, 2H), 2.23-2.04 (m, 2H), 1.90 (ddd, J = 27.4, 13.5, 4.4 Hz, 1H), 1.85-1.75 (m, 2H), 1.74-1.62 (m, 1H), 1.60-1.55 (m, 1H), 1.30 (s, 9H), 1.20 (s, 3H) ppm ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.1, 203.5, 150.5, 133.7, 128.5, 125.7, 78.0, 56.5, 54.7, 36.9, 34.5, 33.9, 33.0, 31.3, 28.0, 25.3, 20.3, 19.9, 14.7 ppm; LRMS (EI, 20 eV): m/z 388.2 (M^+, 5); HRMS (EI, 20 eV): calcd for $C_{23}H_{32}O_3S$ 388.2067, found 388.2061.

Reduction of 3o: According to the general procedure, **L8** (10 mg, 0.015 mmol), $Cu(OAc)_2$•H_2O (3.0 mg, 0.015 mmol), bipyridine (2.30 mg, 0.015 mmol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe were treated with **3o** (121 mg, 0.30 mmol) in PhMe (2 x 0.5 mL) and stirred at –20 °C for 20 h. After workup and chromatographic purification, **3o** was obtained as a colorless oil (80 mg, 66% yield, 93% ee). **4o**: $[\alpha]_D^{20}$ = –4.5 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL AD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 42.577 min (minor), 45.459 min (major); R_f (25% EtOAc in hexane): 0.70; IR (CH_2Cl_2): 3688 (OH), 3063, 2993, 2337, 1705 (C=O, ketone), 1658 (C=O, thioester), 1604 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.25 (m, 5H), 7.24-7.15 (m, 3H), 6.96 (dd, *J* = 6.4, 1.7 Hz, 2H), 4.14 (q, *J* = 13.9 Hz, 2H), 3.93, (s, 1H), 3.26 (d, *J* = 13.9 Hz, 1H), 3.14 (d, *J* = 13.9 Hz, 1H), 2.91 (ddd, *J* = 21.9, 13.7, 7.9 Hz, 1H), 2.68 (dd, *J* = 12.5, 3.3 Hz, 1H), 2.44-2.36 (m, 2H), 2.00- 1.91 (m, 2H), 1.79 (ddt, *J* = 32.9, 14.0, 5.1 Hz, 1H), 1.71 (dm, *J* = 16.7 Hz, 1H), 1.64 (dm, *J* = 16.7 Hz, 1H), 1.54-1.35 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5, 204.2, 136.7, 136.6, 130.0, 128.7, 128.0, 127.5, 126.6, 75.9, 58.8, 55.6, 39.6, 37.6, 33.4, 31.9, 26.4, 26.2, 21.4, 19.9 ppm; LRMS (EI, 20 eV): m/z 408.2 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{25}H_{28}O_3S$ (M^+), 408.1754, found 408.1753.

Reduction of 3p: According to the general procedure, **L8** (5.0 mg, 0.0075 mmol), $Cu(OAc)_2$•H_2O (1.5 mg, 0.0075 mmol) and $PhSiH_3$ (38 μL, 0.3 mmol) in 1.0 mL PhMe at -10 °C

were treated with **3p** (51.7 mg, 0.15 mmol) in PhMe (2 x 0.3 mL) and stirred at –10 °C for 18 h. After workup and chromatographic purification, **4p** was obtained as a colorless oil (17.6 mg, 35% yield, 68% ee) and conjugate reduction product **3p-H$_2$** as a colorless oil (8.4 mg, 17% yield) **4p**: $[\alpha]_D^{20}$ = +4.8 (c = 1.2, CH_2Cl_2); DAICEL CHIRALCEL AS-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 10.603 min (minor), 13.602 min (major); R_f (25% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3680 (OH), 3479 (hydrogen-bonded OH), 3047, 2985, 1681 (C=O, ketone), 1604 (C=O, thioester)，1604 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.21 (m, 5H), 5.49 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.11-5.06 (m, 2H), 4.16 (d, *J* = 11.1 Hz, 1H), 4.10 (d, *J* = 11.1 Hz, 1H), 3.01 (ddd, *J* = 14.3, 6.8, 1.1 Hz, 1H), 2.94 (dd, *J* = 12.9, 3.7 Hz, 1H), 2.45 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.23 (s, 3H), 1.89 (dm, *J* = 8.4 Hz, 1H), 1.82 (dm, *J* = 8.4 Hz, 1H), 1.72-1.62 (m, 3H), 1.47 (tt, *J* = 13.7, 4.5 Hz, 1H), 1.19 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 216.2, 202.2, 137.2, 133.1, 128.8, 128.6, 127.3, 118.8, 74.7, 58.6, 56.5, 33.6, 30.3, 26.5, 257, 20.9, 19.7 ppm; LRMS (EI, 20 eV): m/z 346.2 (M^+, 5); HRMS (EI, 20 eV): calcd for $C_{20}H_{26}O_3S$ (M^+), 346.1597, found 346.1596. **3p-H$_2$**: IR (CH_2Cl_2): 3047, 2970, 1740, 1657 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.22 (m, 5H), 5.49 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.11-5.06 (m, 2H), 4.11 (s, 2H), 2.61 (d, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 6H), 1.88-1.85 (m, 2H), 1.67 (q, *J* = 7.4, 2H), 1.11-1.04 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.2, 198.3, 137.6, 132.1, 128.8, 128.6, 127.3, 119.0, 70.4, 43.2, 34.8, 33.2, 30.9, 30.0, 29.7, 26.9, 25.8, 22.8, 14.1 ppm; LRMS (EI, 20 eV): m/z 346.2 (M^+, 10); HRMS (EI, 20 eV): calcd for $C_{20}H_{26}O_3S$ 346.1597, found 346.1602.

Reduction of 3q: According to the general procedure, **L8** (10 mg, 0.015 mmol), $Cu(OAc)_2$•H_2O (3.0 mg, 0.015 mmol), bipyridine (2.30 mg, 0.015 mmol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe were treated with **3q** (91.0 mg, 0.30 mmol) in PhMe (2 x 0.3 mL) and stirred at –20 °C for 15 h. After workup and chromatographic purification, **4q** was obtained as a colorless oil (52.6 mg, 56% yield, 27% ee). **4q**: $[\alpha]_D^{20}$ = –17.2 (c = 0.92, CH_2Cl_2); DAICEL CHIRALCEL AS-3, *n*-hexane/2-propanol = 96/4, flow rate = 1 mL/min, λ = 254 nm, retention times: 34.123 min (minor), 41.514 min (major); R_f (25% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3680 (OH), 2970, 1735 (C=O, ketone), 1666 (C=O, thioester), 1604 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.24 (m, 5H), 4.17 (s, 2H), 3.32 (s, 1H), 2.87 (dd, *J* = 10.0, 7.8 Hz, 1H), 2.56 (ddd, *J* = 19.2, 10.4, 4.3 Hz, 1H), 2.33 (ddd, *J* = 10.5, 10.5, 9.1 Hz, 1H), 2.24 (ddd, *J* = 13.3, 9.0, 4.1 Hz, 1H), 2.19-1.91 (m, 4H), 1.70 (ddd, *J* = 10.4, 9.7, 3.8 Hz, 1H), 1.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 136.7, 128.8, 128.7, 127.5, 88.0, 60.2, 59.8, 35.5, 33.5, 33.1, 31.1, 28.1, 16.4 ppm; LRMS (EI, 20 eV): m/z 304.1 (M^+, 3); HRMS (EI, 20 eV): calcd for $C_{17}H_{20}O_3S$ (M^+), 304.1128, found

304.1119.

Reduction of 3r: According to the general procedure, **L8** (10 mg, 0.015 mmol), $Cu(OAc)_2•H_2O$ (3.0 mg, 0.015 mmol), bipyridine (2.30 mg, 0.015 mmol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe were treated with **3r** (95.0 mg, 0.30 mmol) in PhMe (2 x 0.3 mL) and stirred at –20 °C for 15 h. After workup and chromatographic purification, **3r** was obtained as a colorless oil (41.8 mg, 44% yield, 59% ee). **4r**: $[\alpha]_D^{20}$ = –6.3 (c = 1, CH_2Cl_2); DAICEL CHIRALCEL AD-3, *n*-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, λ = 254 nm, retention times: 44.257 min (minor), 57.504 min (major); R_f (25% EtOAc in hexane): 0.56; IR (CH_2Cl_2): 3680 (OH), 3502 (hydrogen-bonded OH), 3063, 2947, 1705 (C=O, ketone), 1666 (C=O, thioester)，1604 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32-7.23 (m, 5H), 4.15 (s, 2H), 3.58 (s, 1H), 2.85 (t, *J* = 9.8 Hz, 1H), 2.63 (ddd, *J* = 13.8, 9.6, 4.7 Hz, 1H), 2.55 (ddd, *J* = 14.2, 14.2, 6.9 Hz, 1H), 2.27 (dm, *J* = 12.6 Hz, 1H), 2.05-1.88 (m, 5H), 1.61-1.52 (m, 2H), 1.22 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.6, 202.2, 136.7, 128.8, 128.7, 127.5, 84.4, 62.2, 56.1, 36.7, 33.4, 30.6, 29.5, 25.1, 20.2, 18.5 ppm; LRMS (EI, 20 eV): m/z 318.1 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{18}H_{22}O_3S$ (M^+), 318.1284, found 318.1283.

Reduction of 3u: According to the general procedure, **L8** (10 mg, 0.015 mmol), $Cu(OAc)_2•H_2O$ (3.0 mg, 0.015 mmol), bipyridine (2.3 mg, 0.0015 mmol) and $PhSiH_3$ (76 μL, 0.6 mmol) in 2.0 mL PhMe at –20 °C were treated with **3u** (47.4 mg, 0.15 mmol) in PhMe (2 x 0.5 mL) and stirred at –20 °C for 18 h. After workup and chromatographic purification, conjugate reduction product **3u-H$_2$** was obtained as a colorless oil (95.4 mg, 76% yield). **3u-H$_2$**: R_f (25% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 2939, 1720 (C=O, ketone), 1689 (C=O, unsaturated thioester) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.09 (s, 2H), 2.69-2.60 (m, 4H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.05-1.96 (m, 1H), 1.89-1.81 (m, 1H), 1.78-1.72 (m, 2H), 1.66-1.58 (m, 2H), 1.29-1.23 (m, 13H), 1.21 (s, 3H), 1.12-1.08 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.3, 198.8, 150.1, 134.4, 128.4, 125.5, 65.6, 43.7, 37.9, 37.4, 34.5, 32.7, 31.3, 29.5, 28.6, 25.4, 24.5, 19.1, 17.7 ppm; LRMS (EI, 20 eV): m/z 416.3 (M^+, 3); HRMS (EI, 20 eV): calcd for $C_{25}H_{36}O_3S$ (M^+), 416.2380, found 416.2375.

D. Other synthetic procedures

Synthesis of 7d: To a solution of **4d** (38 mg, 0.12 mmol) in acetone (4 mL) was added $Pd(OAc)_2$ (8.8 mg, 0.039 mmol) under Ar, then Et_3SiH (195 mg, 1.70 mmol) was added by

syringe. After stirring for 15 min at room temperature, MeOH was added to quench the reaction. The volatiles were removed in vacuo to give a residue which was purified by flash chromatography to furnish the aldehyde **7d** as colorless oil (20.3 mg, 86% yield). **7d**: $[\alpha]_D^{20}$ = +13.4 (c = 0.25, CH_2Cl_2); R_f (25% EtOAc in hexane): 0.10; ^{1}H NMR (400 MHz, $CDCl_3$):δ 9.75 (d, *J* = 0.5 Hz, 1H), 3.42 (s, 1H), 2.59-2.52 (m, 1H), 2.34-2.30 (m, 1H), 2.30-2.20 (m, 2H), 2.09-2.02 (m, 1H), 1.87-1.83 (m, 3H), 1.62-1.53 (m, 1H), 1.38-1.30 (m, 2H), 1.03 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 218.3, 205.2, 78.5, 54.0, 53.8, 34.0, 31.2, 29.9, 22.5, 21.0, 17.5 ppm. The ^{1}H and ^{13}C NMR data of **7d** were identical to that previous reported for racemic **7d**.[5]

Synthesis of 8d: To a DCM solution of **7d** (20.3 mg, 0.100 mmol) was added phosphorane **2a** (55.0 mg, 0.150 mmol). The reaction was stirred for 12 h, and the volatiles were removed in vacuo. The residue was subjected to flash chromatography and yielded **8d** as a white solid (25.1 mg, 89% yield). **8d**: mp = 67-69 ^{o}C; R_f (25% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3670 (OH), 3600 (hydrogen-bonded OH), 2060, 2984, 1736 (C=O, ketone), 1680 (C=O, unsaturated thioester), 1637 (C=C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (dd, *J* = 15.6, 8.6 Hz, 1H), 6.16 (dd, *J* = 15.7, 0.7 Hz, 1H), 2.96 (q, *J* = 7.4 Hz, 2H), 2.55 (ddd, *J* = 19.7, 10.5, 2.8 Hz, 1H), 2.27 (dd, *J* = 18.3, 9 Hz, 1H), 2.17-2.15 9m, 1H), 2.14-2.00 (m, 1H), 1.94-1.86 (m, 2H), 1.65-1.52 (m, 3H), 1.35-1.20 (m, 5H), 1.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ218.1, 190.1, 144.2, 130.5, 78.5, 53.7, 46.4, 34.1, 30.9, 29.1, 26.7, 23.2, 21.3, 19.2, 14.7 ppm; LRMS (EI, 20 eV): m/z 282.1 (M^+, 1); HRMS (EI, 20 eV): calcd for $C_{15}H_{22}O_3S$ (M^+), 282.1206, found 282.1204.

Synthesis of 9: TaniaPhos (SL-T001-1, **L8**) (350 mg, 0.510 mmol) and CuBr•SMe_2 (102 mg, 0.510 mmol) were introduced to a round-bottomed flask under Ar. The addition of CH_3CN (6 mL) produced a clear solution. After stirring for 5 minutes, a yellow suspension started to form, and stirring was continued for 1 h. After removing the volatiles in vacuo, **9** (448 mg, 0.500 mmol) was obtained as yellow solid.

The crude **9** was dissolved in 2.0 mL DCM, then 4.0 mL CH_3CN was layered on. After slow evaporation over 1-2 days, orange crystals of **9** were obtained, which were subjected to X-ray diffraction analysis. **9**: $[\alpha]_D^{20}$ = +139.5 (c = 0.47, CH_2Cl_2); IR (CH_2Cl_2): 3047, 2955, 2777, 2739, 1473, 1427, 1311, 1257, 1149, 1095, 1026 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (brs, 2H), 8.06 (brs, 2H), 7.45 (brs, 6H), 7.34 (brs, 1H), 7.17 (brs, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.10 (s, 3H), 6.98 (brs, 2H), 6.75 (brs, 1H), 6.28 (brs, 3H), 5.68 (brs, 1H), 5.28 (s, 1H), 4.96 (brs, 1H), 4.60 (s, 1H), 4.13 (s, 1H), 4.05 (s, 4H), 1.98 (brs, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 136.2, 136.1, 133.2, 133.1, 131.0, 130.9, 10.8, 130.7, 129.0, 128.9, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 100.2, 71.2, 70.6, 69.9, 67.2, 67.1, 66.4, 53.4, 45.3, 41.0 ppm; LRMS (FAB): m/z 829.1

(M^+, 10); HRMS (EI, 20 eV): calcd for $C_{43}H_{39}{}^{79}BrCuFeNP_2$ 829.0387, $C_{43}H_{63}{}^{81}BrCuFeNP_2$ 831.0366, found 829.0371, 831.0408.

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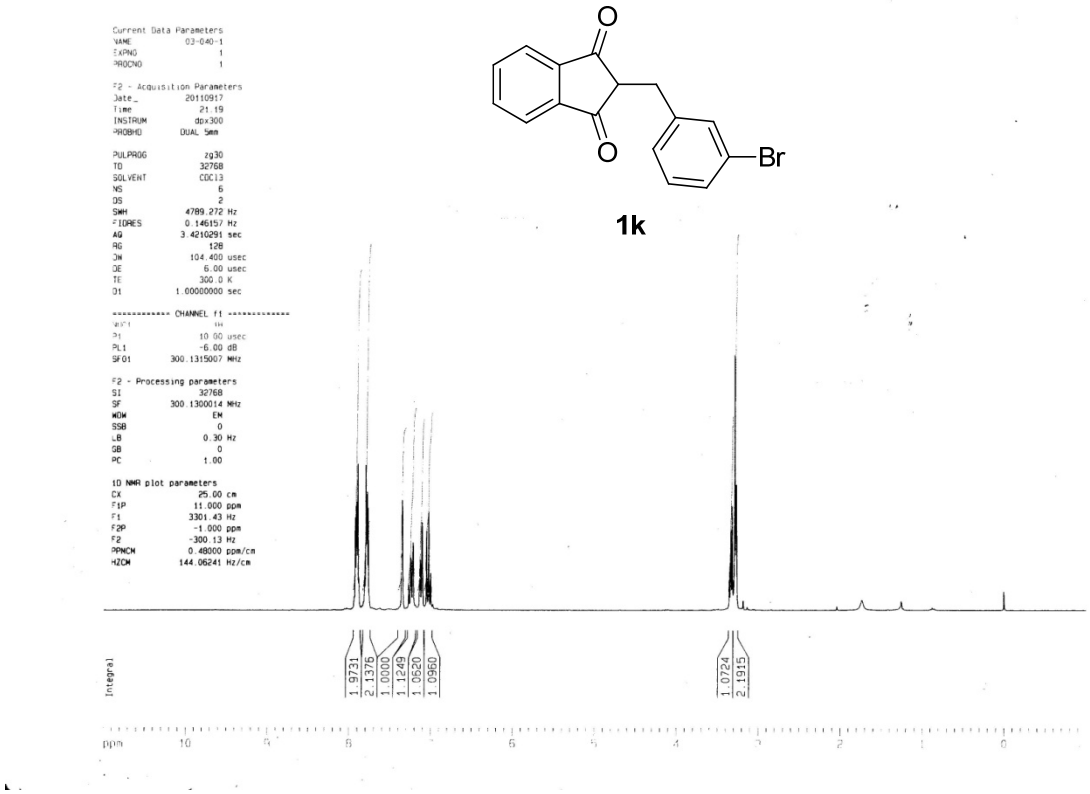
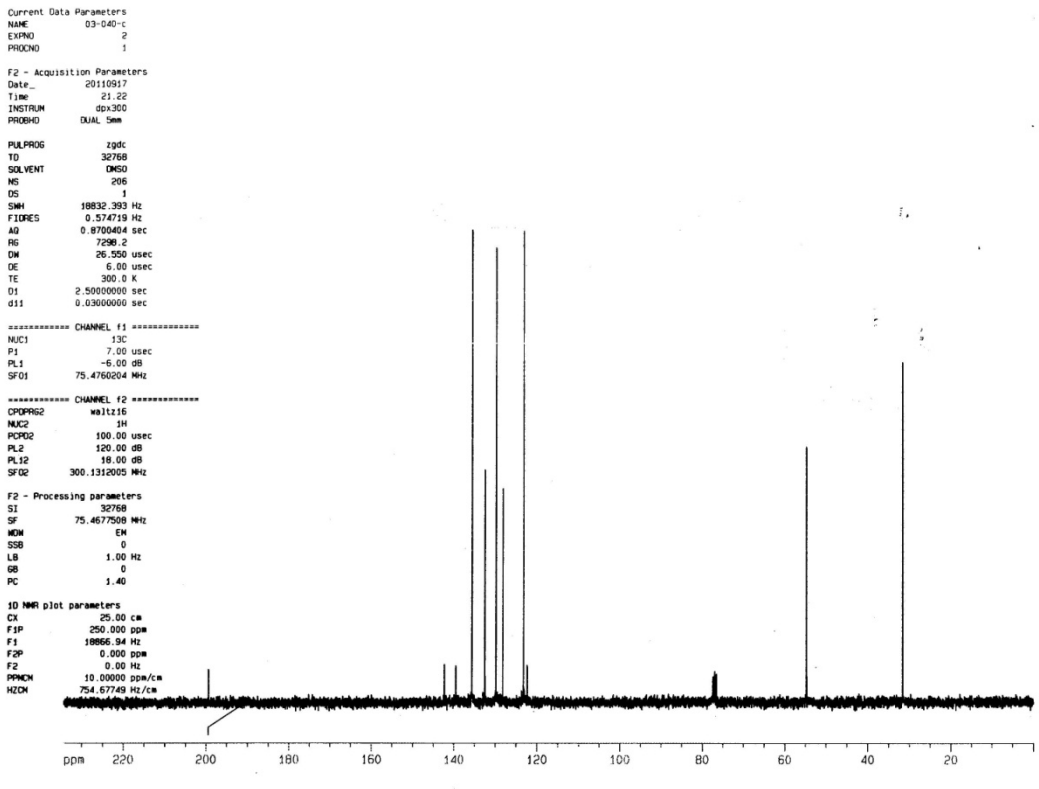
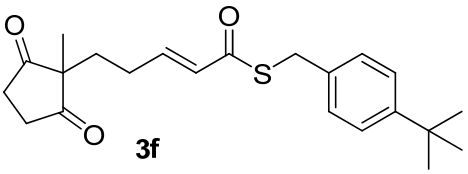
NMR data of all new compounds







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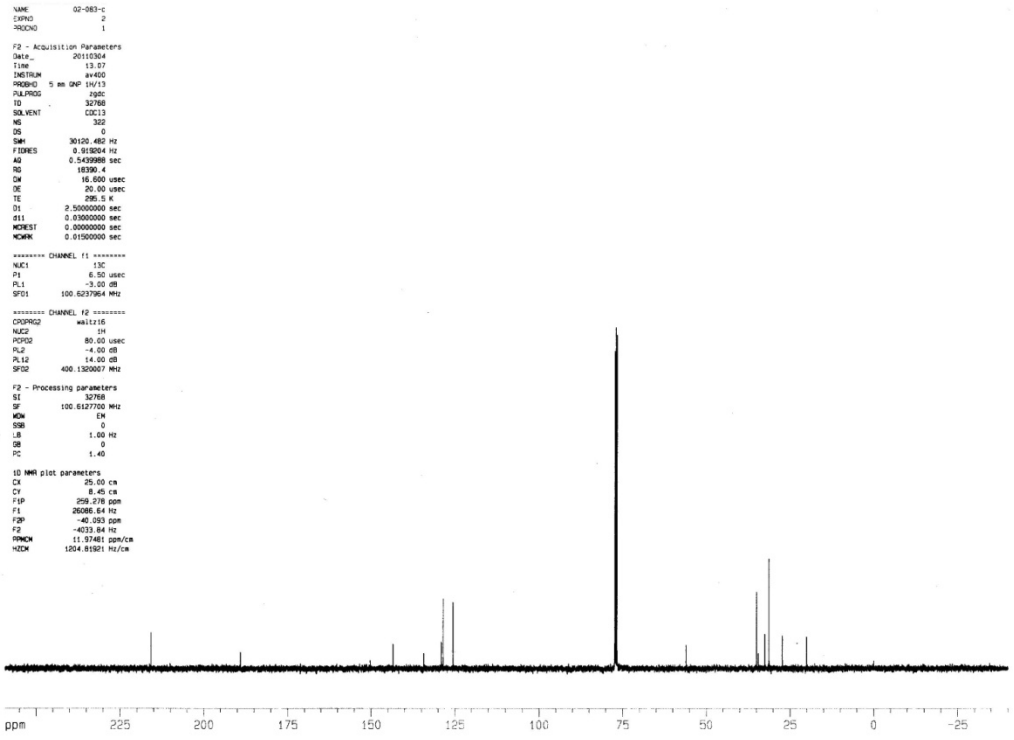


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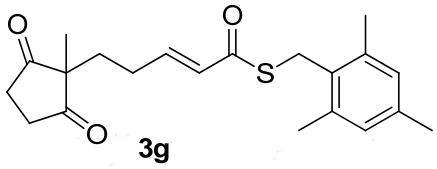
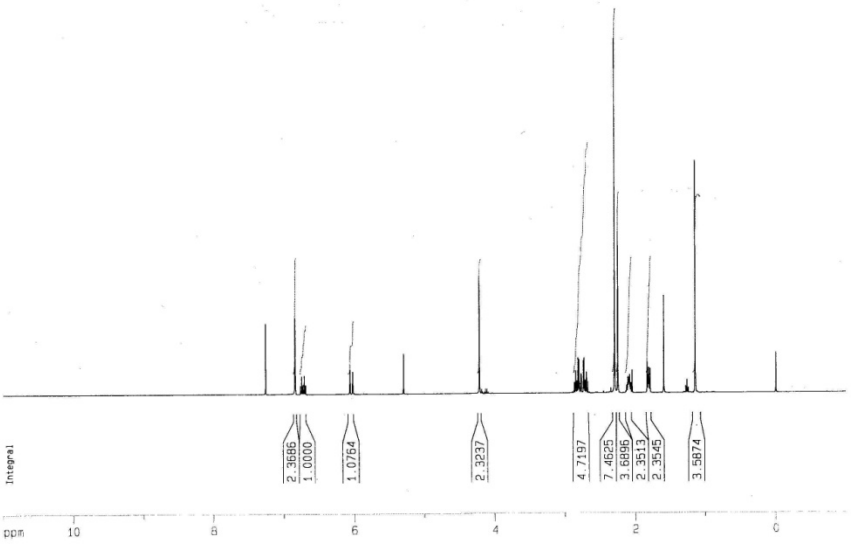
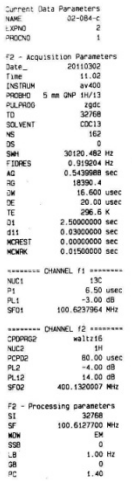
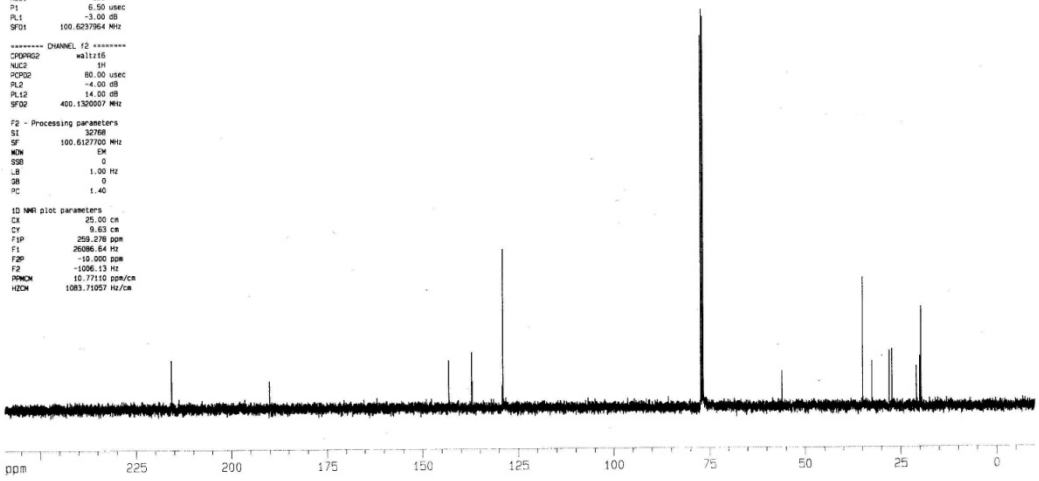
CY 8.79 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.57143 ppm/cm
HZCM 228.64572 Hz/cm

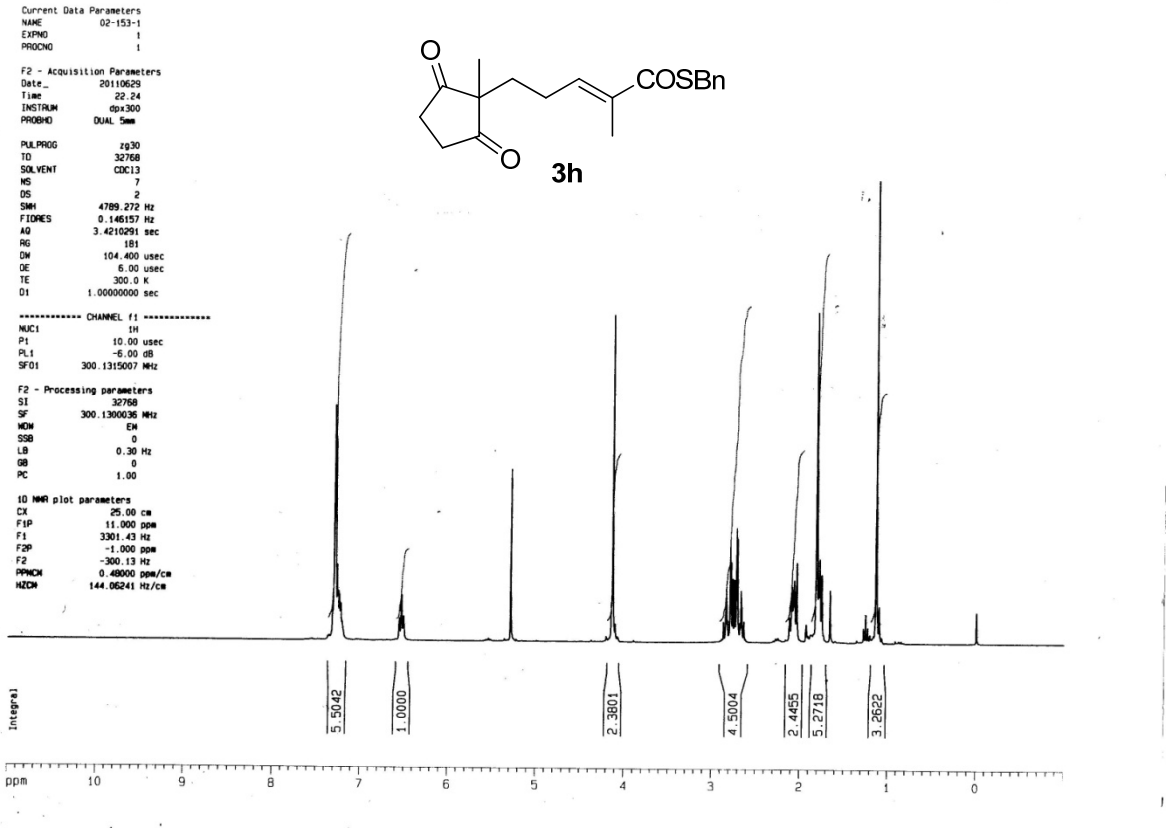

O
O
O
S

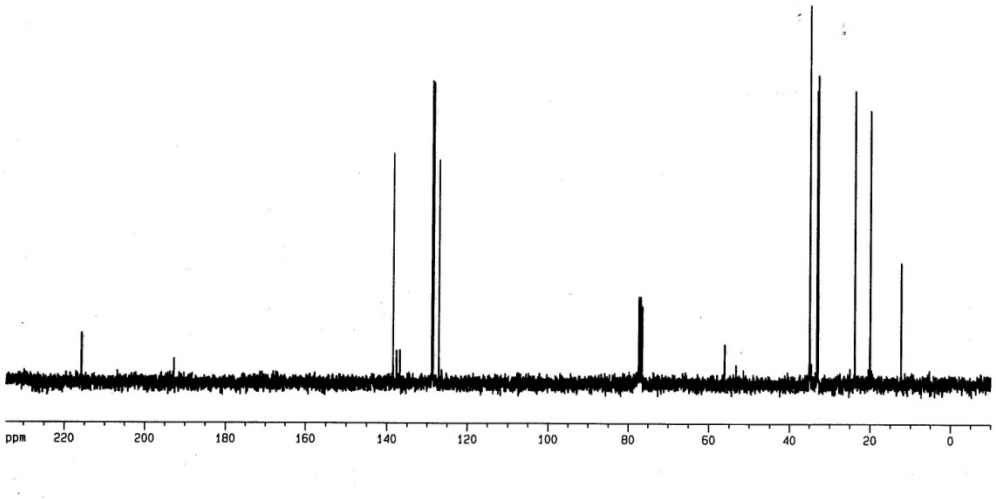
3g

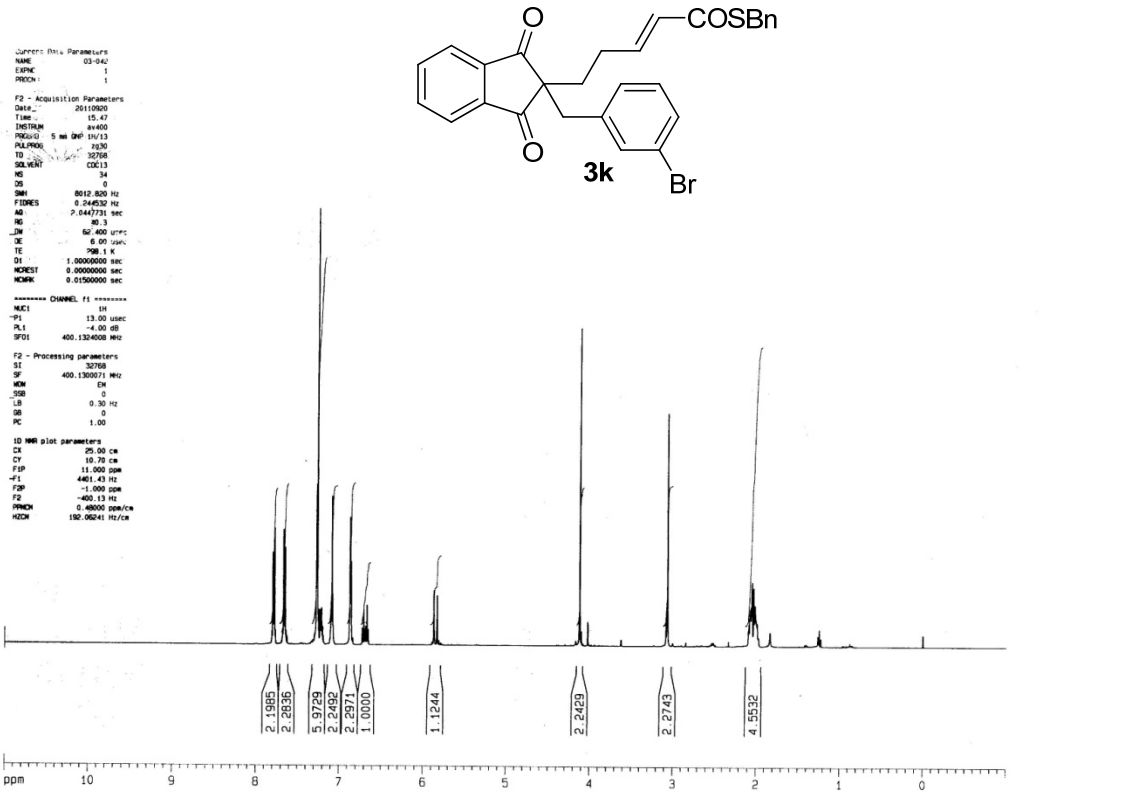

Integral
2.3686
1.0000
1.0764
2.3237
4.7197
7.4625
3.6896
2.3513
2.3545
3.5874
ppm
10
8
6
4
2
0

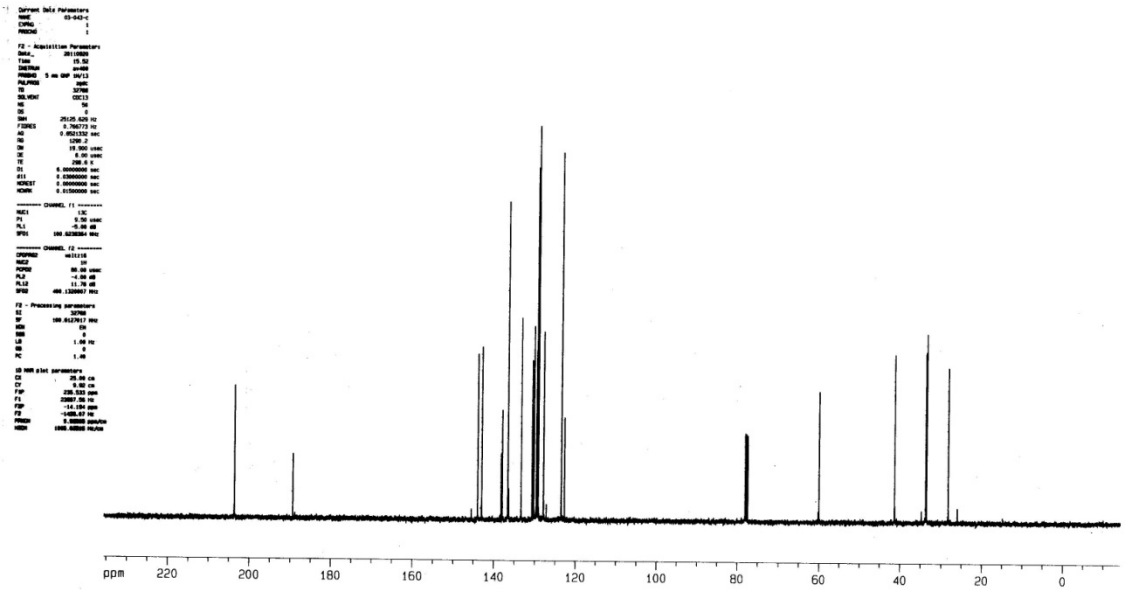

Current Data Parameters
NAME 02-084-c
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110302
Time 11.02
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 162
DS 0
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 0.5439088 sec
RG 18390.4
DW 16.600 usec
DE 20.00 usec
TE 296.6 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
PL1 -3.00 dB
SFO1 100.6233964 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 9.63 cm
F1P 259.278 ppm
F1 26086.64 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 10.77110 ppm/cm
HZCM 1083.71057 Hz/cm

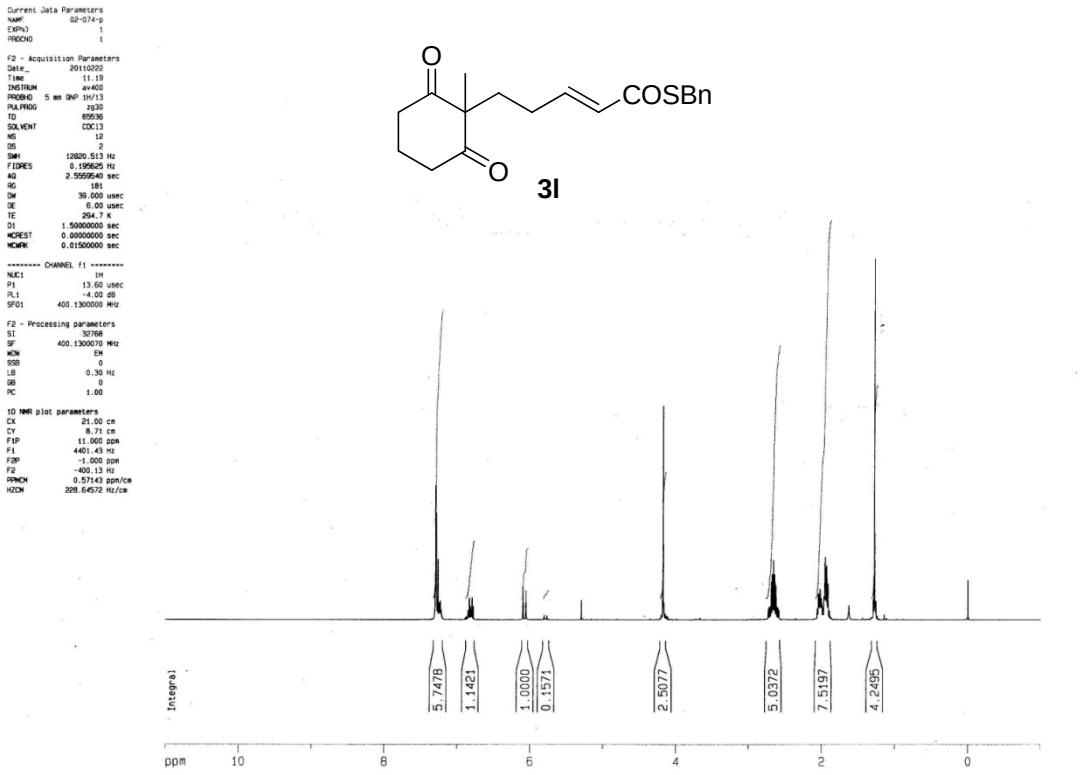

ppm
225
200
175
150
125
100
75
50
25
0

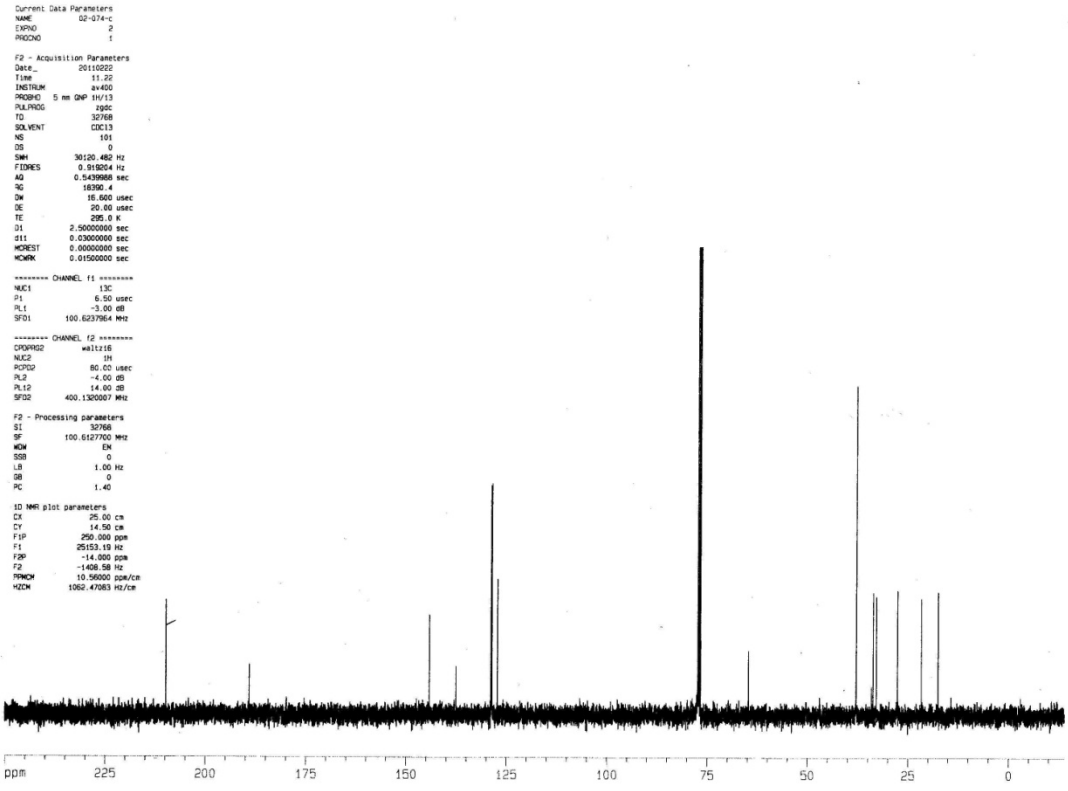


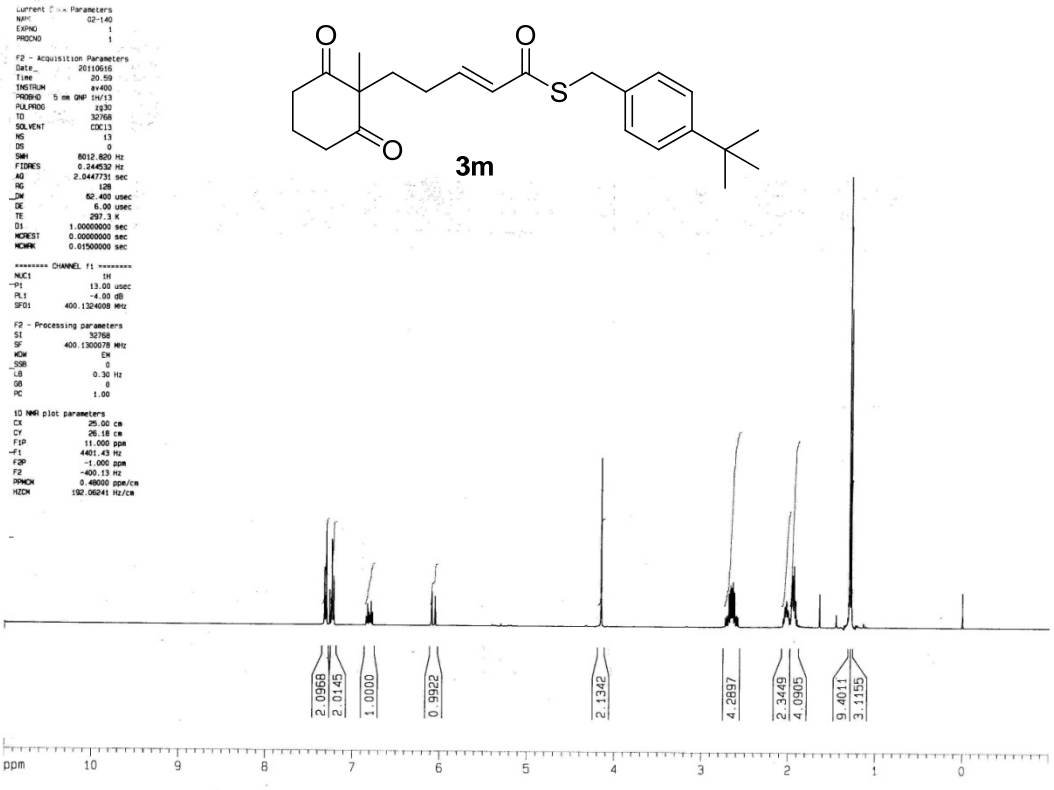


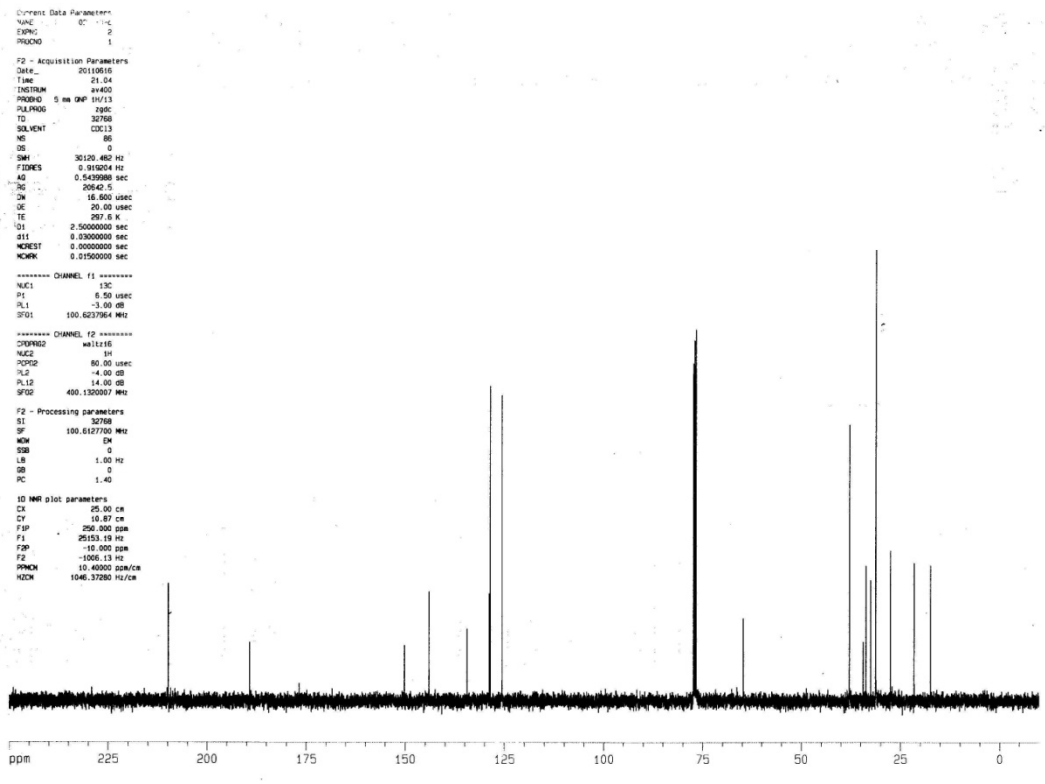

O
COSBn
O
3k
Br
2.1985
2.2836
5.9729
2.2492
2.2971
1.0000
1.1244
2.2429
2.2743
4.5532
ppm
10
9
8
7
6
5
4
3
2
1
0

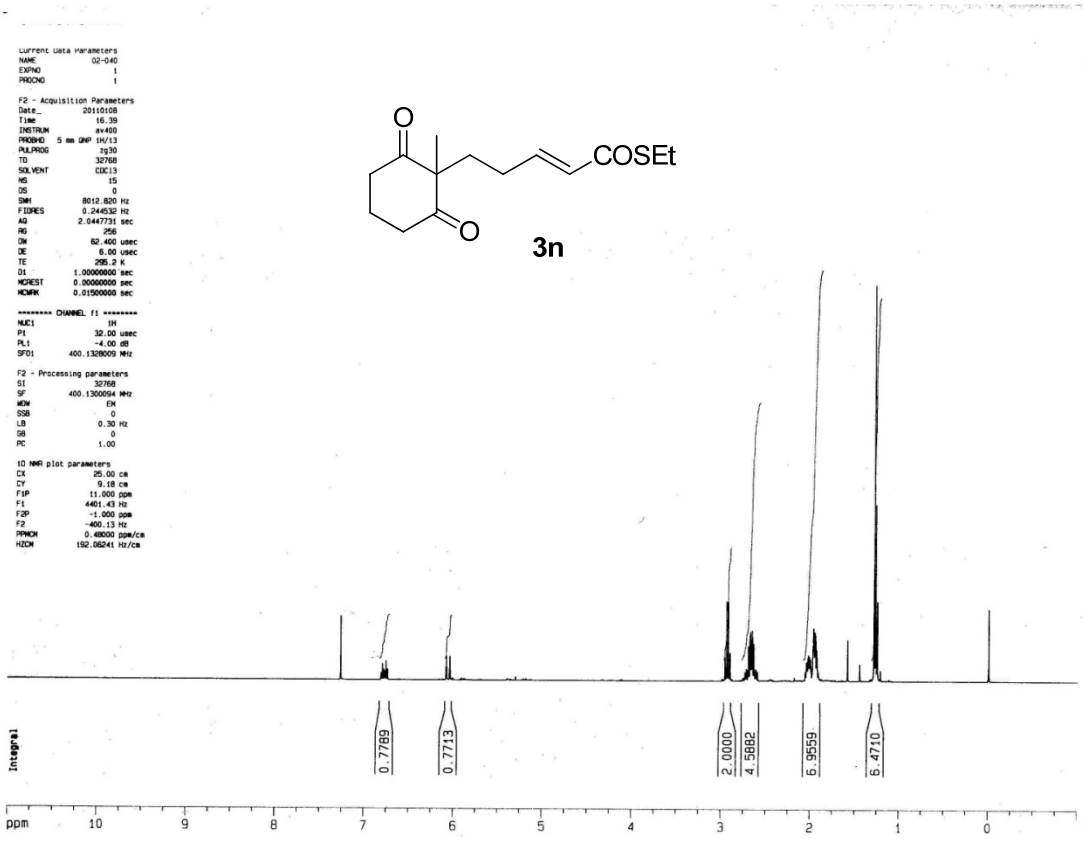

ppm
220
200
180
160
140
120
100
80
60
40
20
0

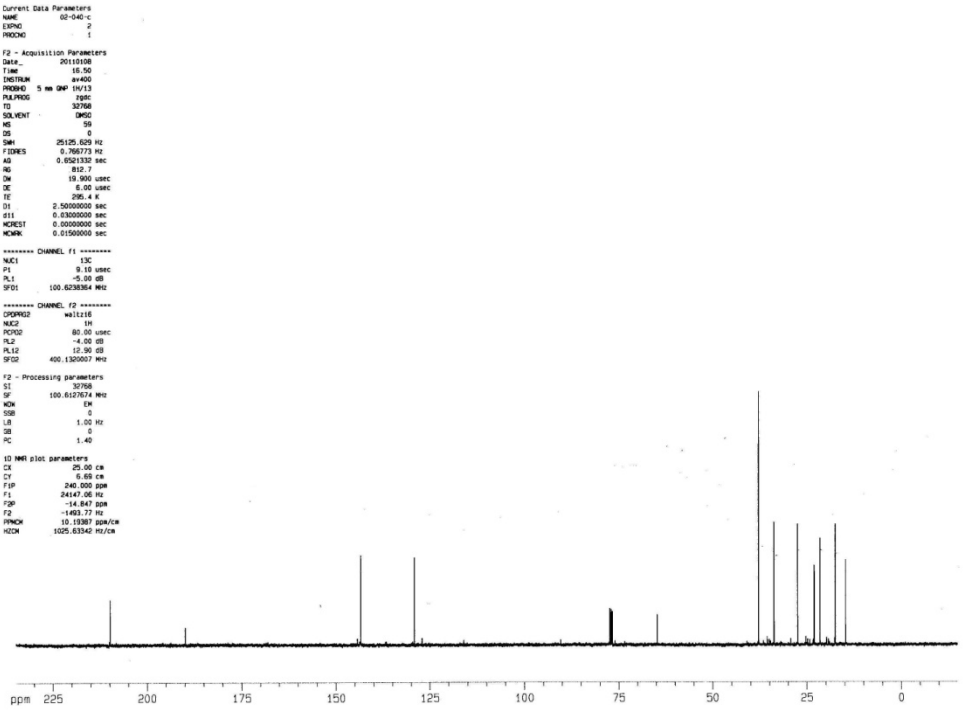


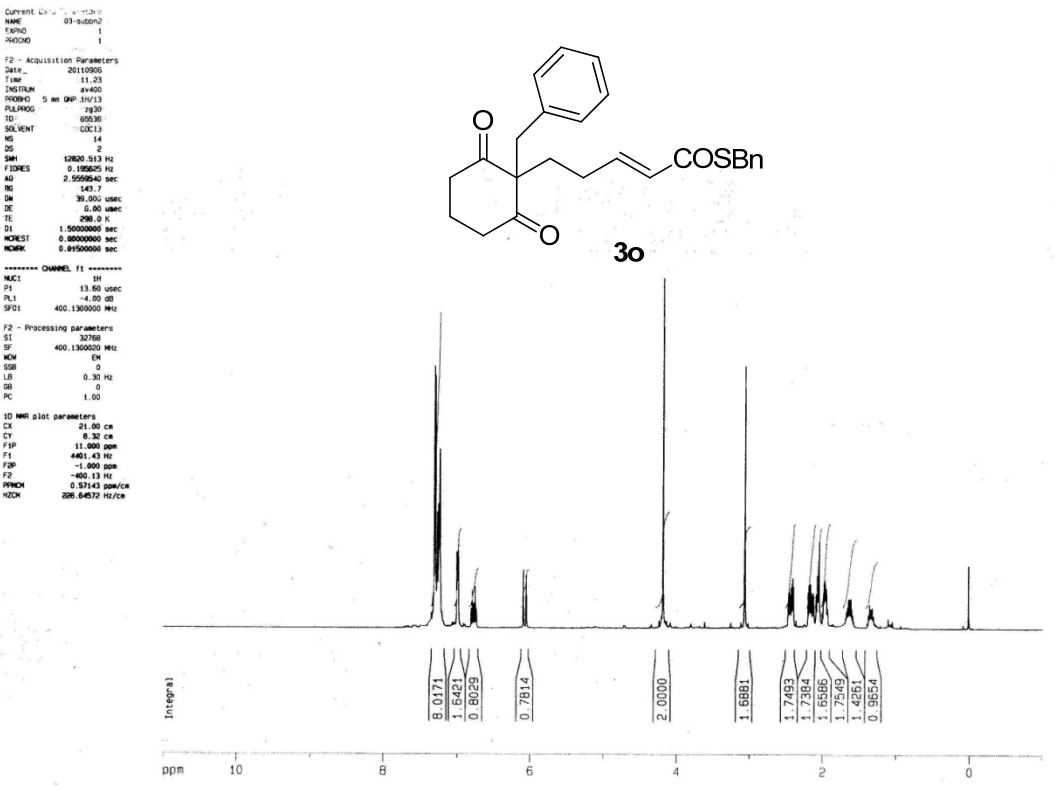


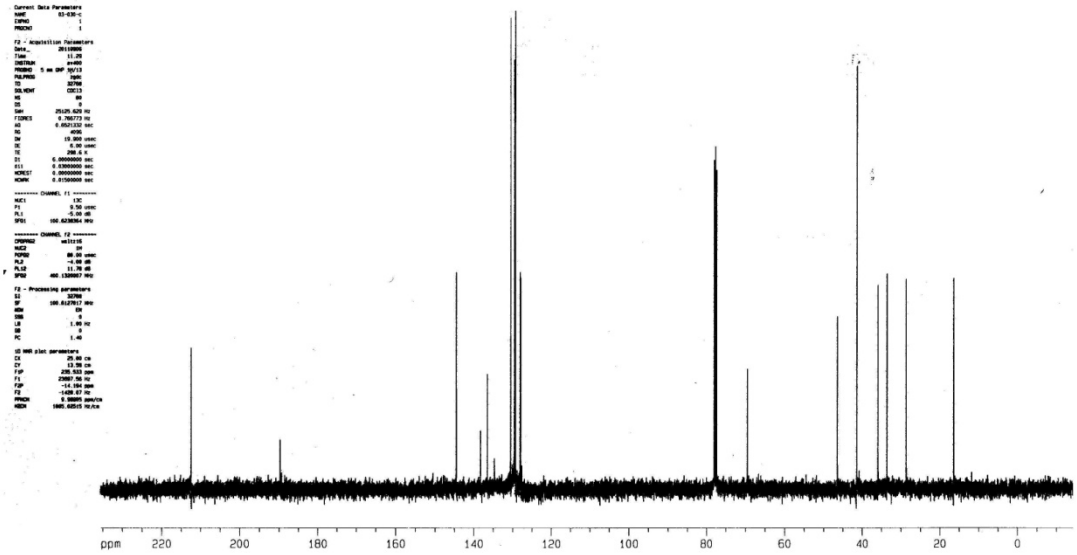

3m
2.0968
2.0145
1.0000
0.9922
2.1342
4.2897
2.3449
4.0905
9.4011
3.1155
ppm

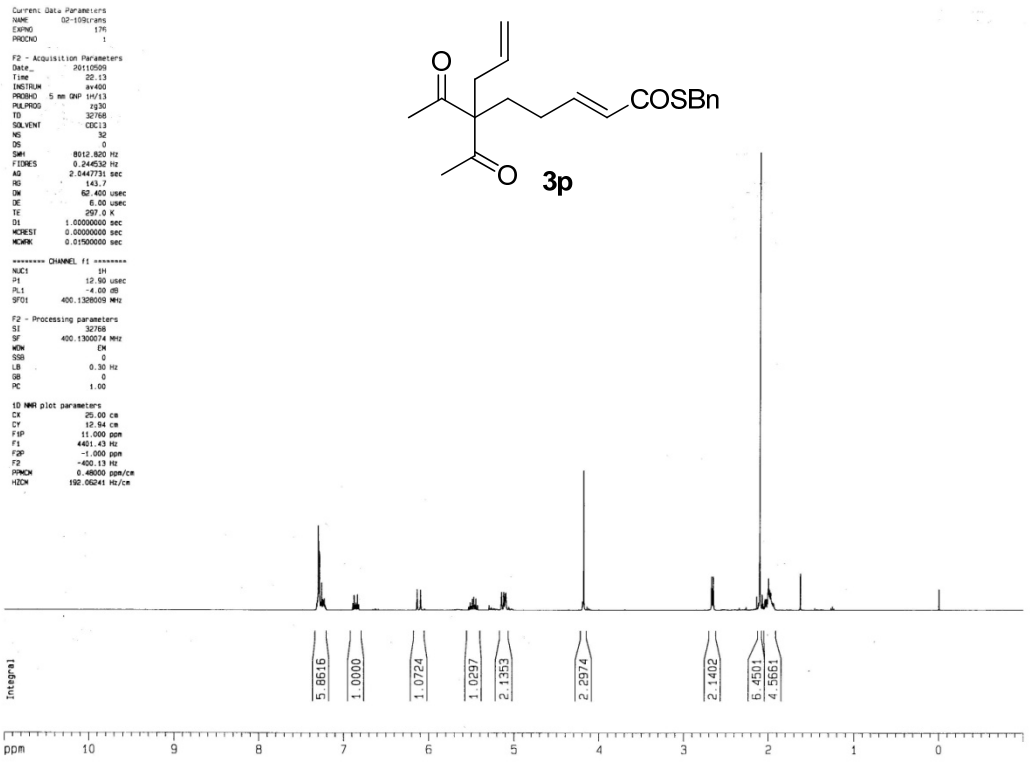

ppm

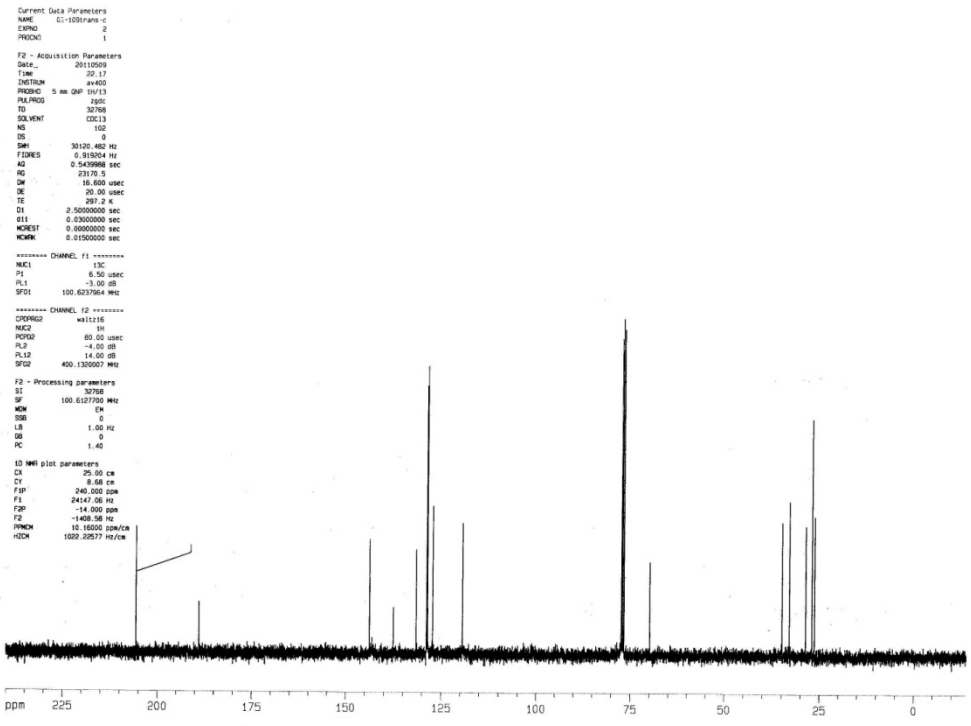

Current Data Parameters
NAME 02-040
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110108
Time 16.39
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 256
DW 62.400 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 32.00 usec
PL1 -4.00 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 9.18 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.48000 ppm/cm
HZCM 192.06241 Hz/cm
O
O
COSEt
3n
Integral
0.7789
0.7713
2.0000
4.5882
6.9559
6.4710
ppm
10
9
8
7
6
5
4
3
2
1
0

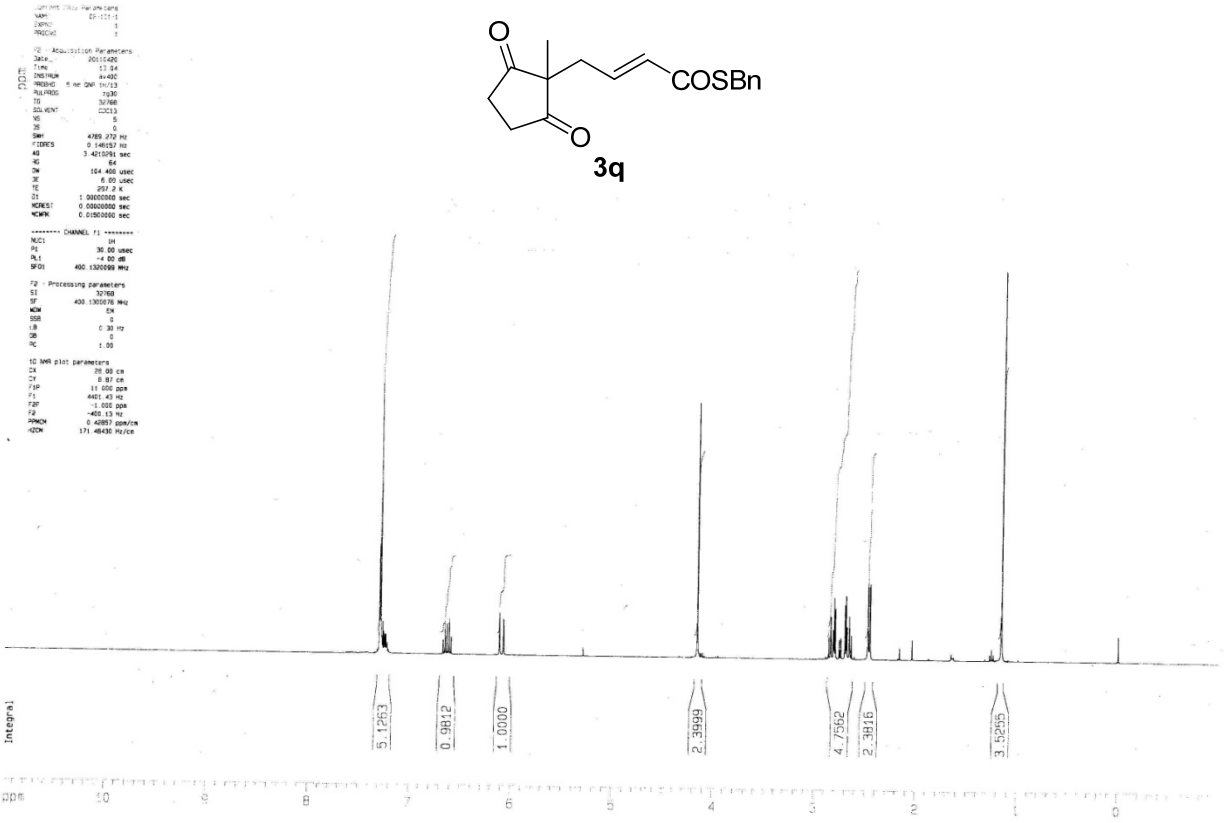

Current Data Parameters
NAME 02-040-c
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110108
Time 16.50
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 59
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 812.7
DW 19.900 usec
DE 6.00 usec
TE 295.4 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCP02 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127674 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 6.69 cm
F1P 240.000 ppm
F1 24147.06 Hz
F2P -14.847 ppm
F2 -1493.77 Hz
PPMCM 10.19387 ppm/cm
HZCM 1025.63342 Hz/cm
ppm
225
200
175
150
125
100
75
50
25
0

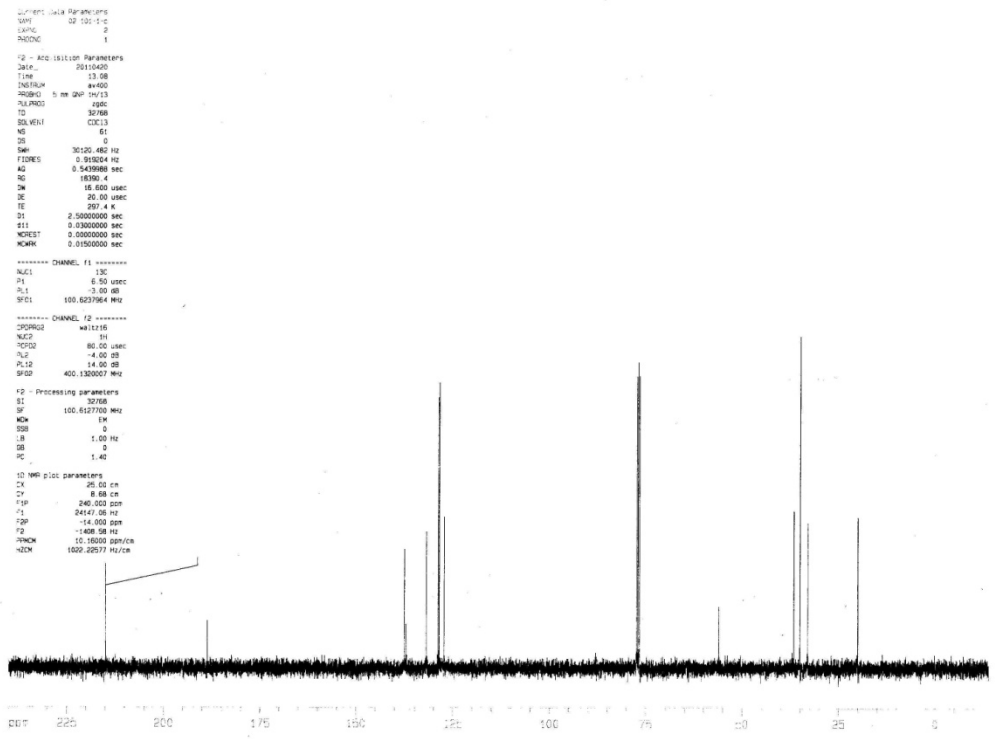


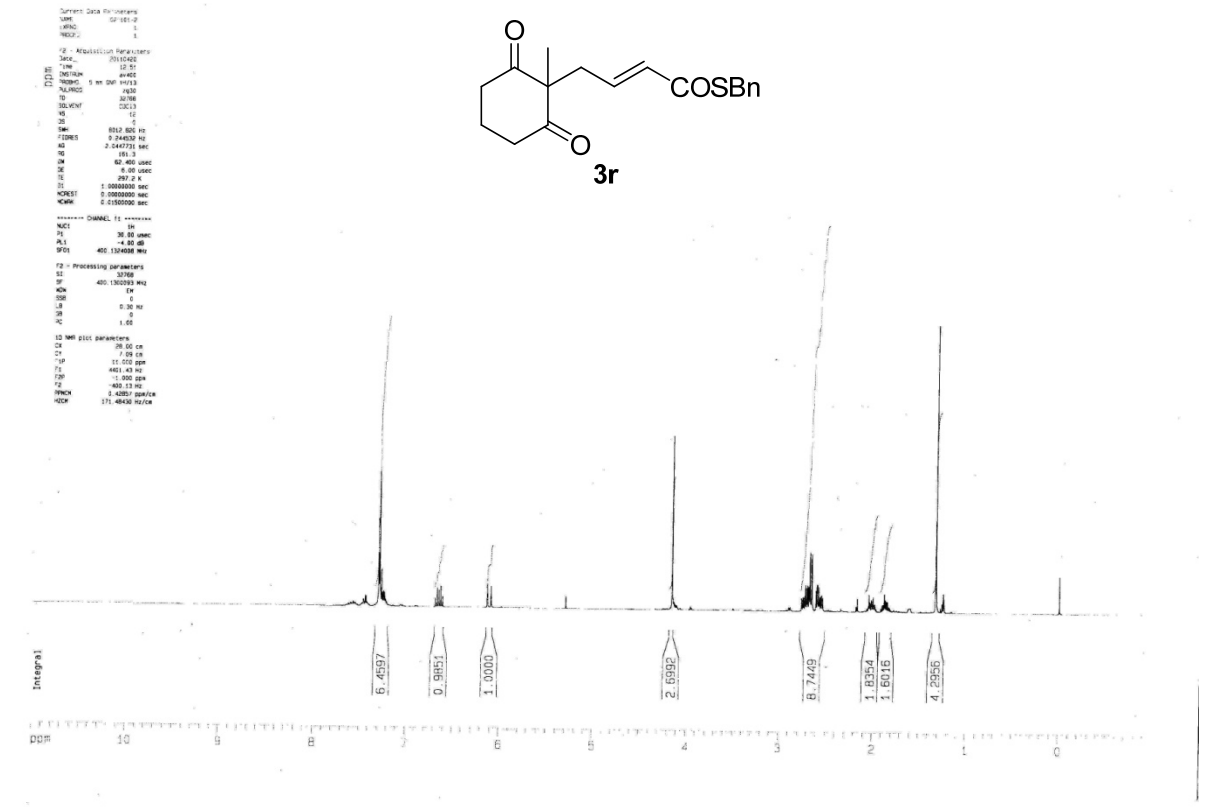


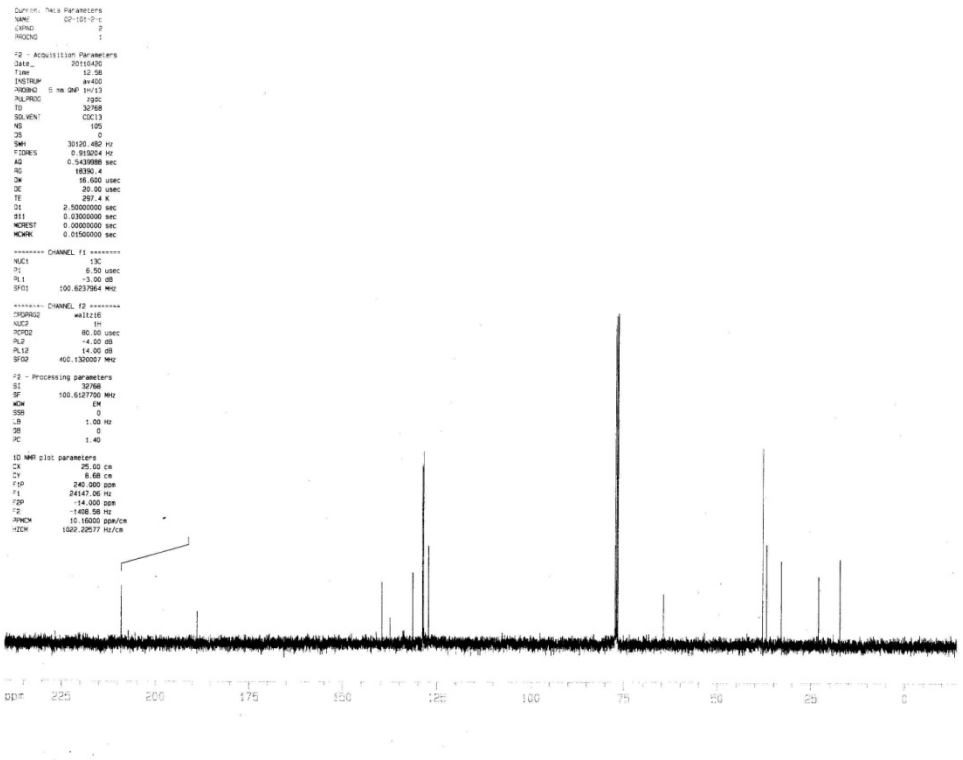

COSBn
3p
Integral
5.8616
1.0000
1.0724
1.0297
2.1353
2.2974
2.1402
6.4501
4.5661
ppm

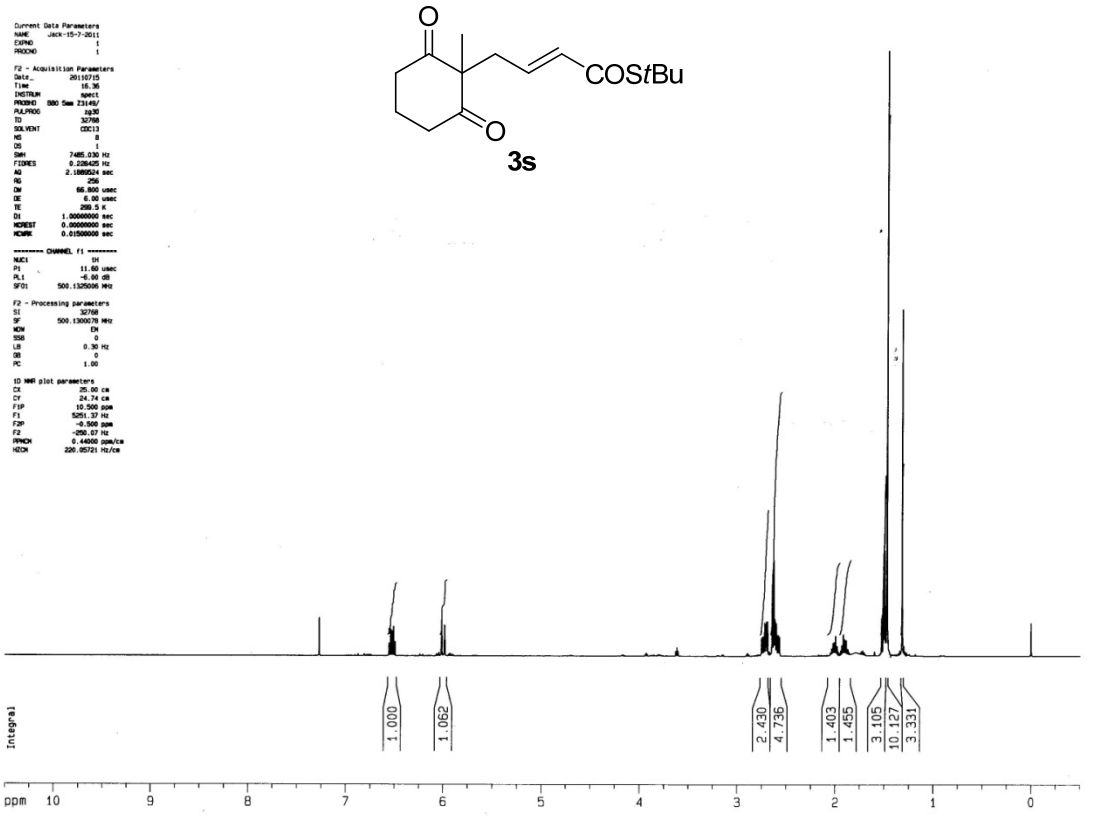

ppm

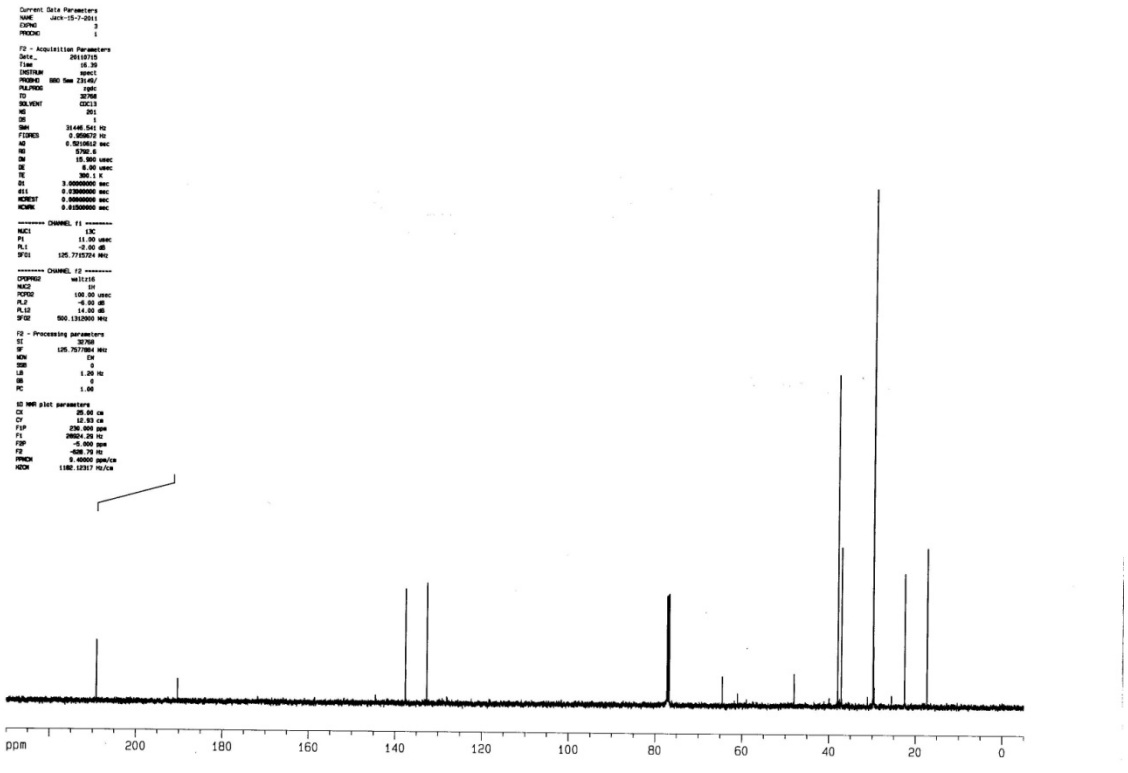


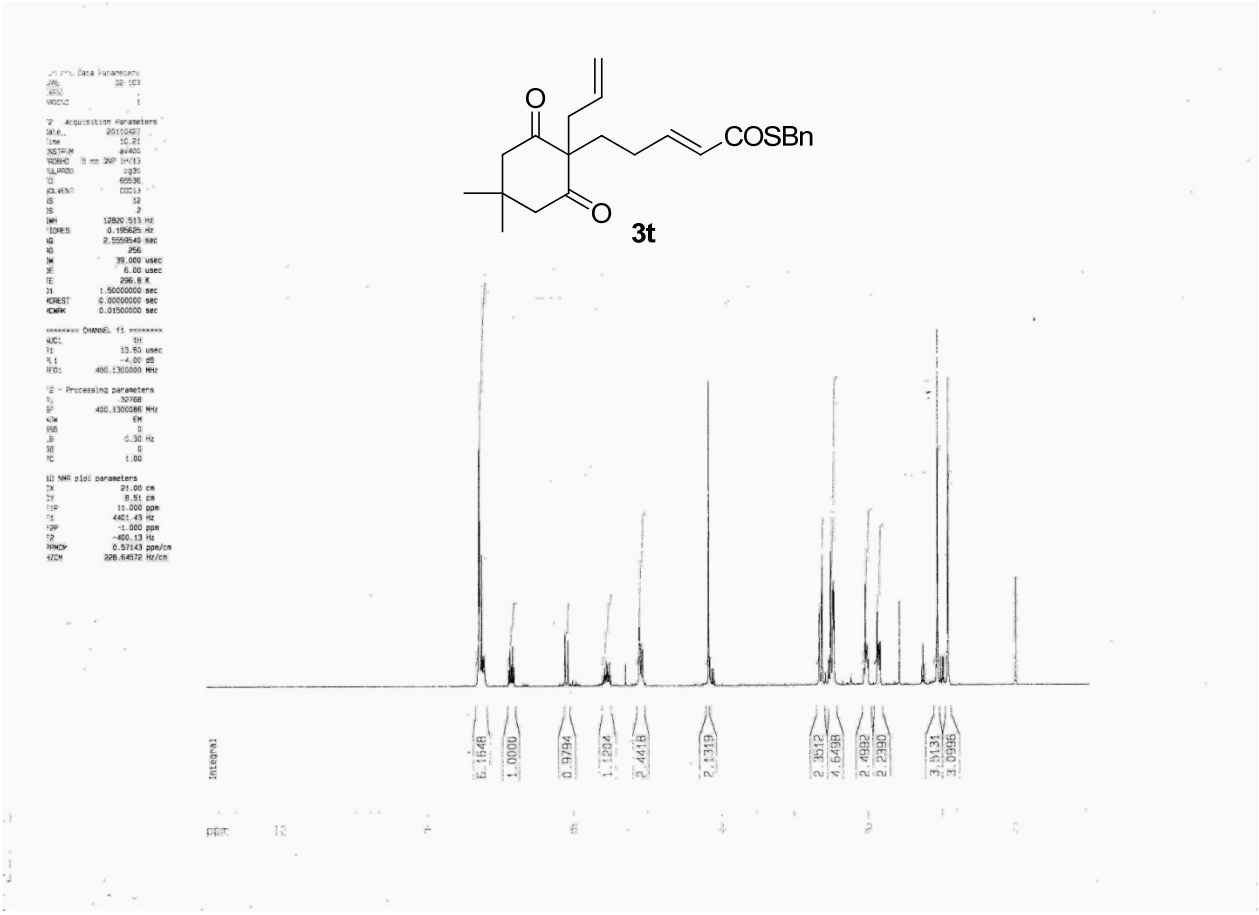


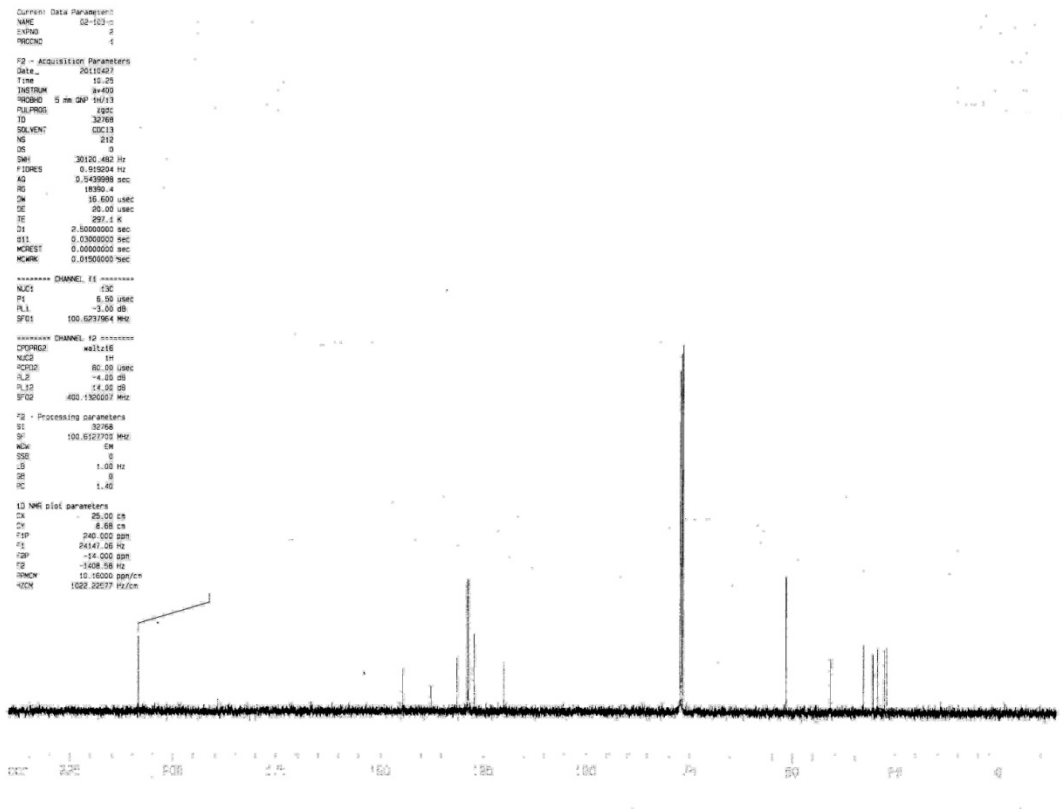


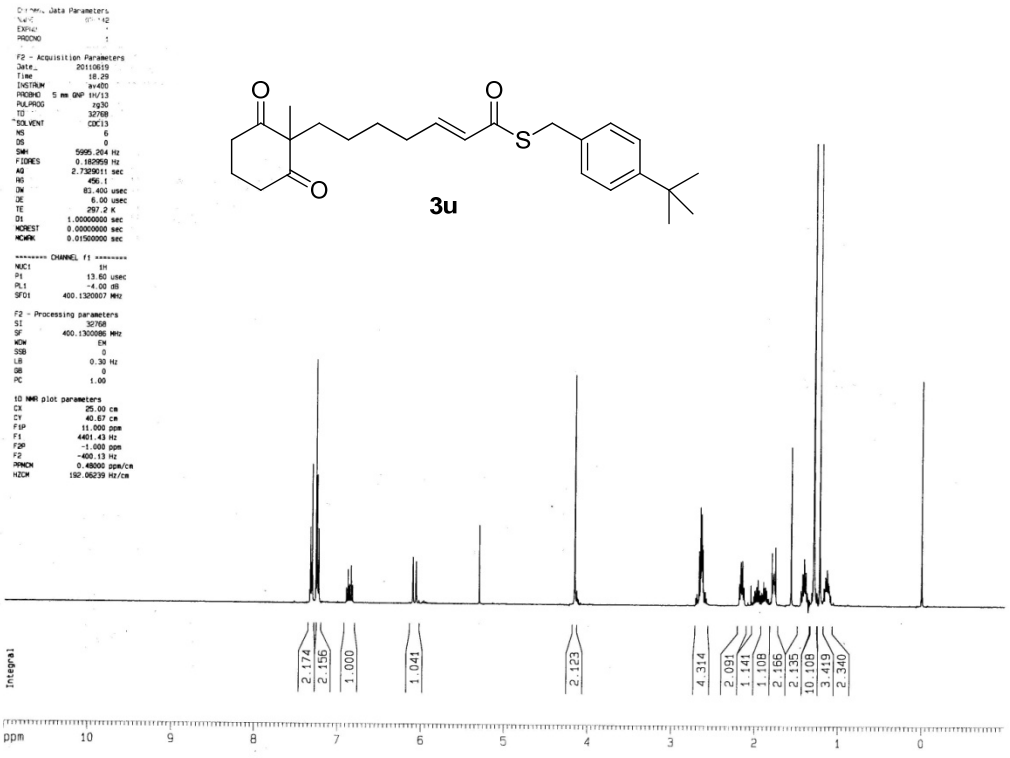


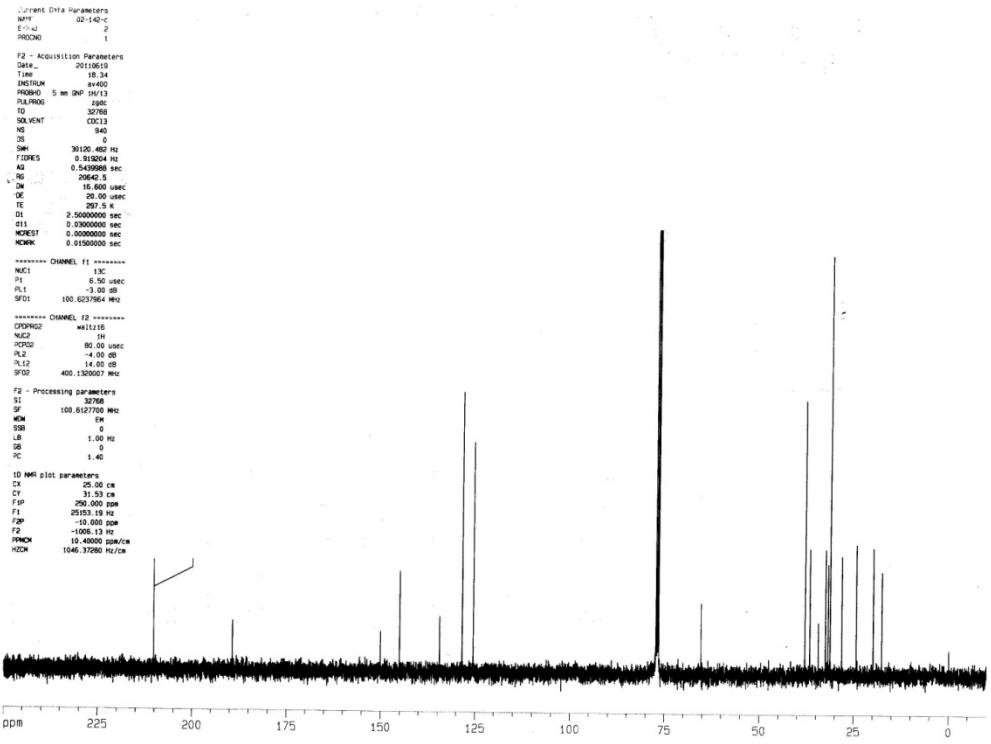

O
COS*t*Bu
O
3s
Integral
1.000
1.062
2.430
4.736
1.403
1.455
3.105
10.127
3.331
ppm 10 9 8 7 6 5 4 3 2 1 0

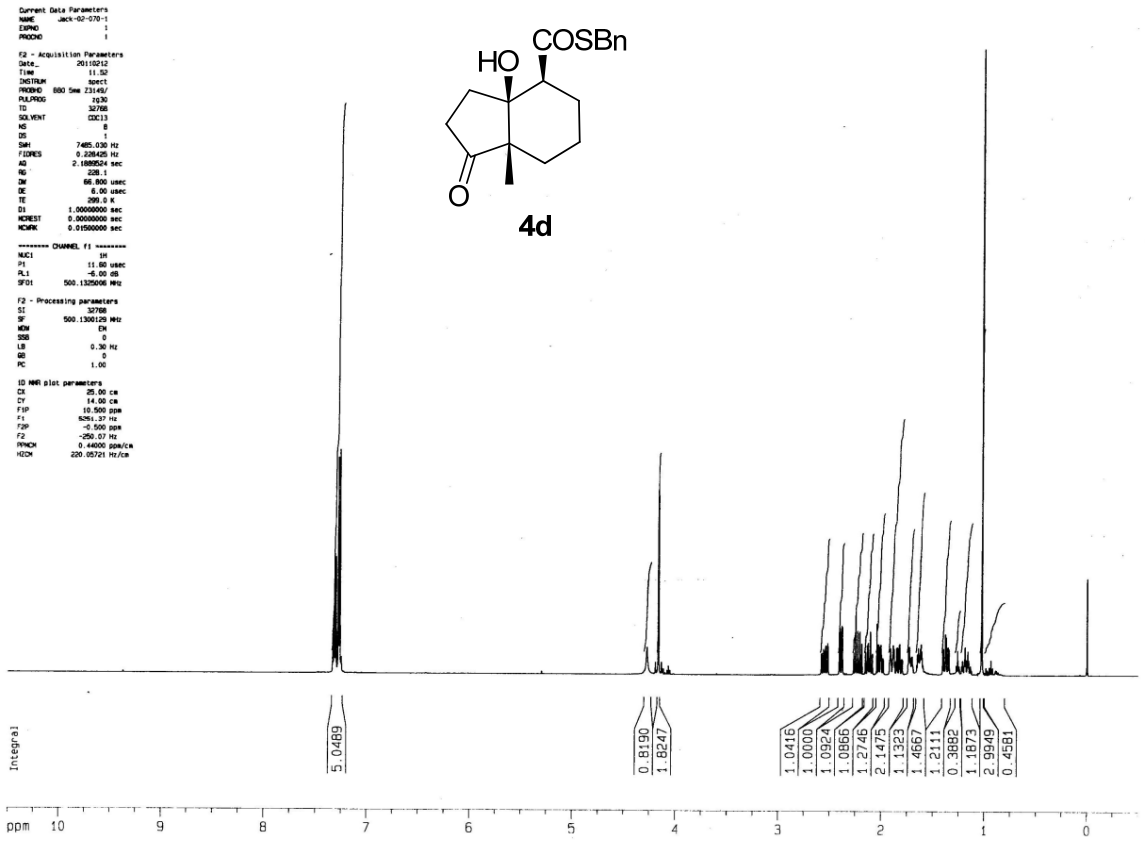

ppm 200 180 160 140 120 100 80 60 40 20 0

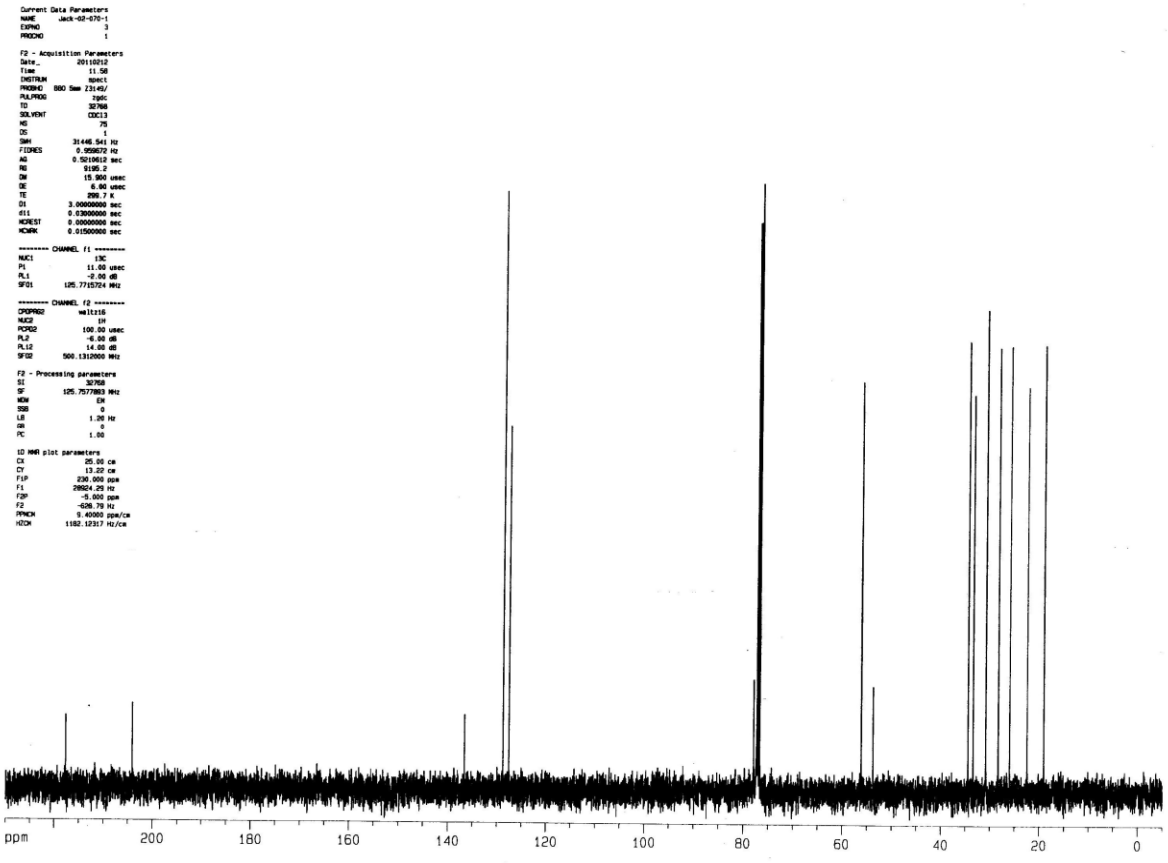




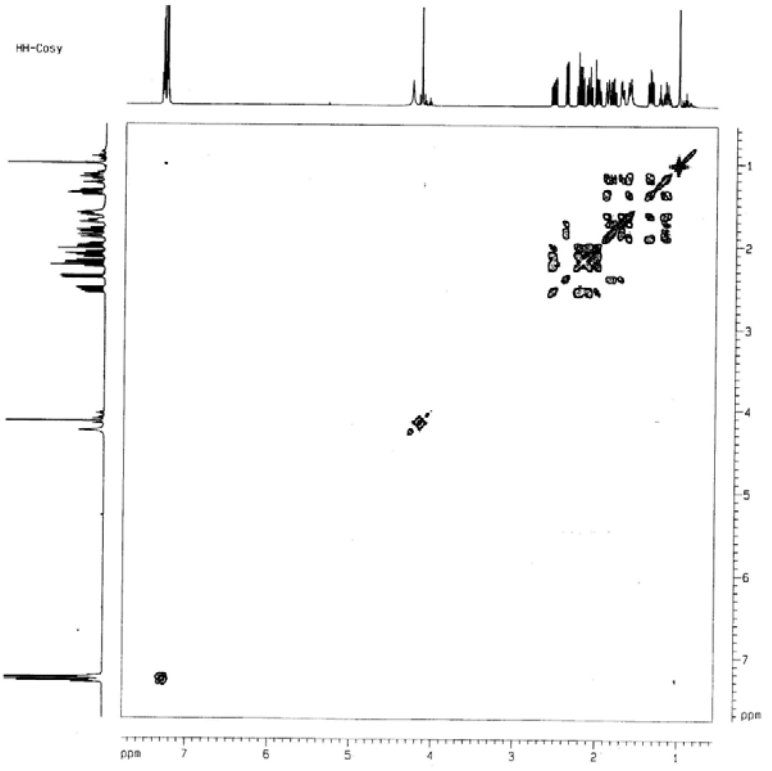





HO
COSBn
O
4d
Integral
5.0489
0.8190
1.8247
1.0416
1.0000
1.0924
1.0866
1.2746
2.1475
1.1323
1.4667
1.2111
0.3882
1.1873
2.9949
0.4581
ppm

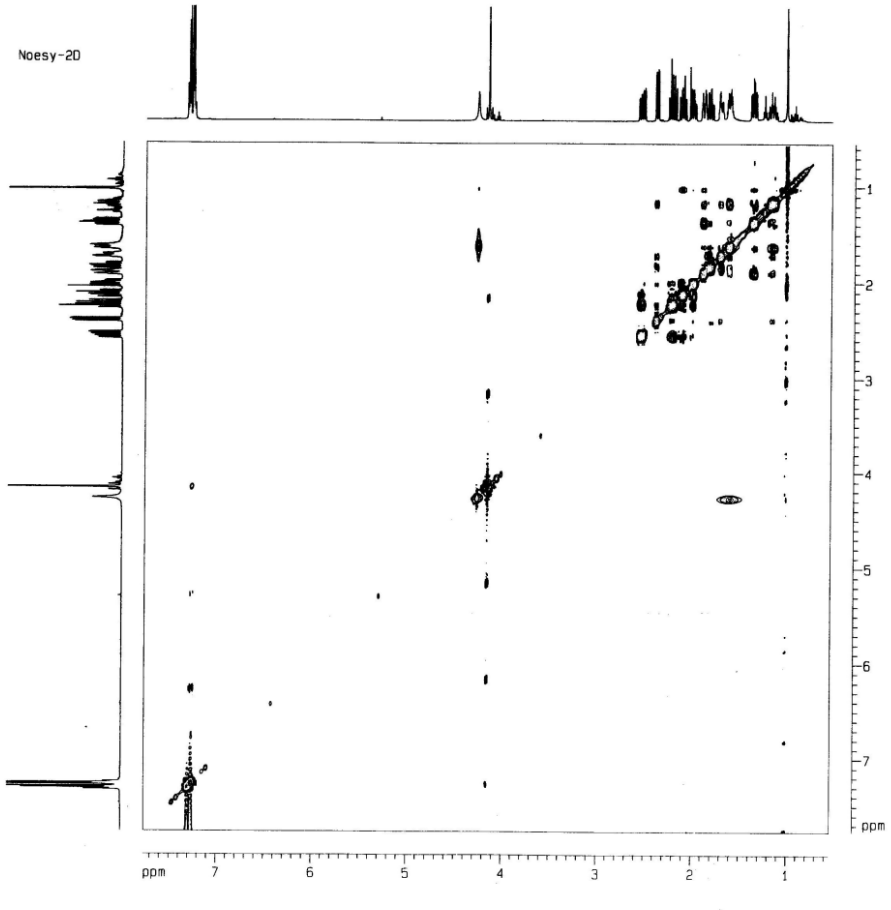

ppm

HH-COSY of 4d



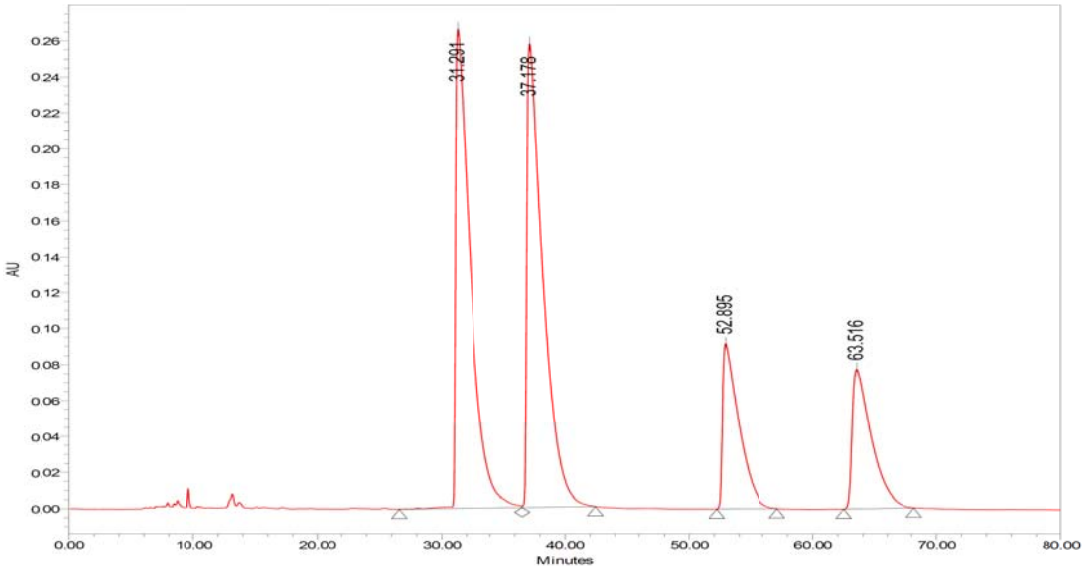

```
Current Data Parameters
NAME        Jack-02-070-1
EXPNO               4
PROCNO              1

F2 - Acquisition Parameter
Date_         20110210
Time             12.00
INSTRUM          spect
PROBHD   BBO 5mm Z3149/
PULPROG          cosy45
TD               1024
SOLVENT          CDCl3
NS                  4
DS                 16
SWH          3612.717 Hz
FIDRES       3.528044 Hz
AQ           0.1417716 sec
RG                228.1
DW           138.400 usec
DE             6.00 usec
TE             299.5 K
d0          0.00000300 sec
D1          2.00000000 sec
IN0         0.00027680 sec

======== CHANNEL f1 ========
NUC1               1H
P1              11.90 usec
PL1             -6.00 dB
SFO1       500.1320920 MHz

F1 - Acquisition parameters
ND0                 1
TD                256
SFO1       500.13 MHz
FIDRES     14.112175 Hz
SW          7.224 ppm
FnMODE       undefined

F2 - Processing parameters
SI               1024
SF         500.1300096 MHz
WDW              SINE
SSB                 0
LB           0.00 Hz
GB                  0
PC               1.00

F1 - Processing parameters
SI                512
MC2               QF
SF         500.1279217 MHz
WDW              SINE
SSB                 0
LB           0.00 Hz
GB                  0

2D NMR plot parameters
CX2              15.00 cm
CX1              15.00 cm
F2PLO          7.776 ppm
F2LO         3888.78 Hz
F2PHI          0.552 ppm
F2HI          276.06 Hz
F1PLO          7.767 ppm
F1LO         3884.70 Hz
F1PHI          0.544 ppm
F1HI          271.98 Hz
F2PPMCM      0.48157 ppm/cm
F2HZCM     240.84775 Hz/cm
F1PPMCM      0.48157 ppm/cm
F1HZCM     240.84787 Hz/cm
```

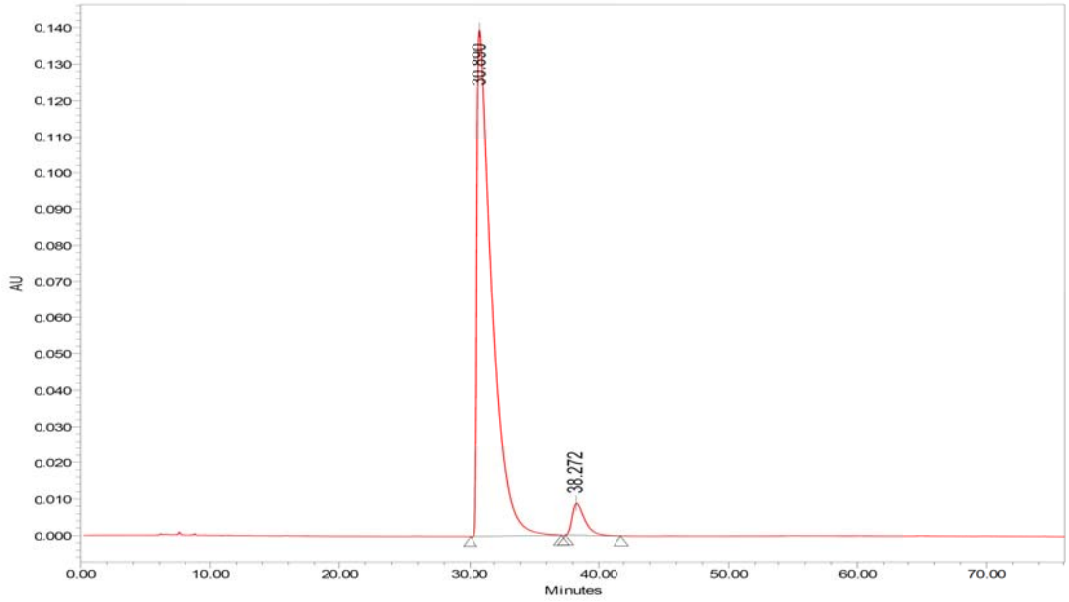
HH-NOESY of 4d




```
Current Data Parameters
NAME        Jack-02-070-1
EXPNO               5
PROCNO              1

F2 - Acquisition Parameters
Date_         20110212
Time             12.39
INSTRUM          spect
PROBHD   BBO 5mm Z3149/
PULPROG          noesytp
TD               1024
SOLVENT          CDCl3
NS                  8
DS                 16
SWH          3612.717 Hz
FIDRES       3.528044 Hz
AQ           0.1417716 sec
RG                228.1
DW           138.400 usec
DE             6.00 usec
TE             299.0 K
d0          0.00000300 sec
D1          2.00000000 sec
D8          0.69999999 sec
IN0         0.00013840 sec

======== CHANNEL f1 ========
NUC1               1H
P1              11.90 usec
PL1             -6.00 dB
SFO1       500.1320920 MHz

F1 - Acquisition parameters
ND0                 2
TD                256
SFO1       500.1321 MHz
FIDRES     14.112175 Hz
SW          7.224 ppm
FnMODE       undefined

F2 - Processing parameters
SI               1024
SF         500.1300123 MHz
WDW              SINE
SSB                 2
LB           0.00 Hz
GB                  0
PC               1.00

F1 - Processing parameters
SI                512
MC2              TPPI
SF         500.1300130 MHz
WDW              SINE
SSB                 2
LB           0.00 Hz
GB                  0

2D NMR plot parameters
CX2              15.00 cm
CX1              15.00 cm
F2PLO          7.770 ppm
F2LO         3886.05 Hz
F2PHI          0.547 ppm
F2HI          273.33 Hz
F1PLO          7.769 ppm
F1LO         3885.41 Hz
F1PHI          0.545 ppm
F1HI          272.69 Hz
F2PPMCM      0.48157 ppm/cm
F2HZCM     240.84779 Hz/cm
F1PPMCM      0.48157 ppm/cm
F1HZCM     240.84779 Hz/cm
```

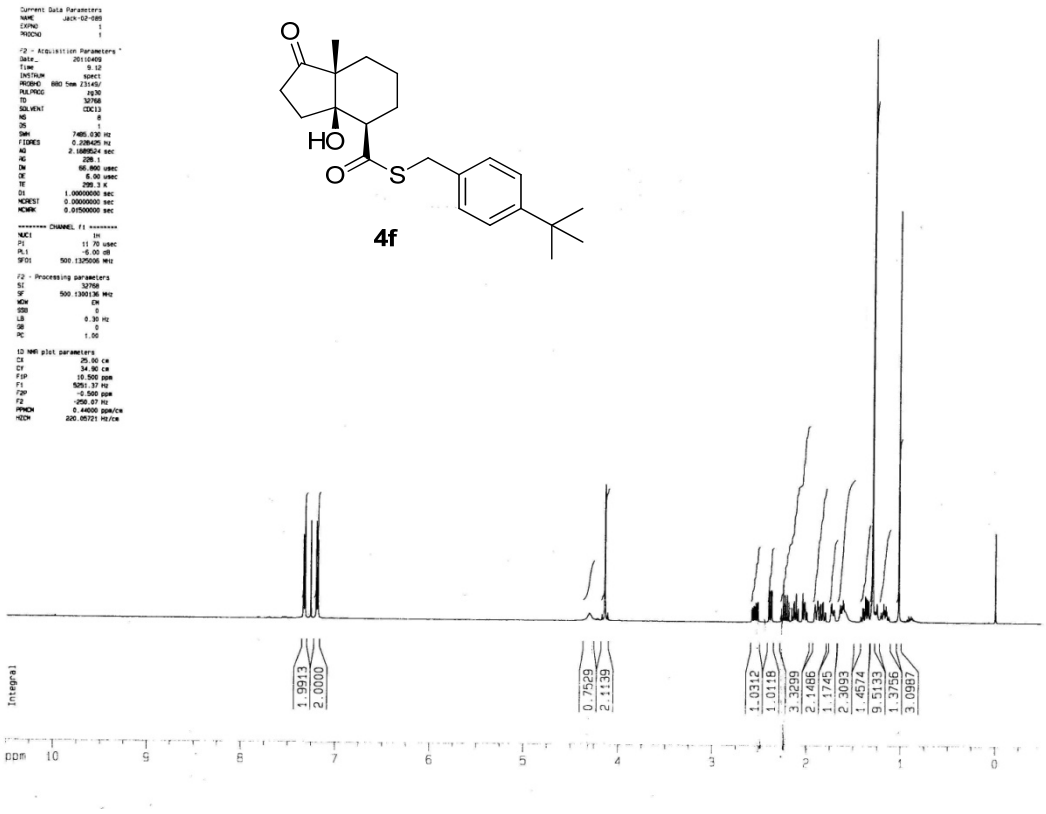
HPLC data for **4d**

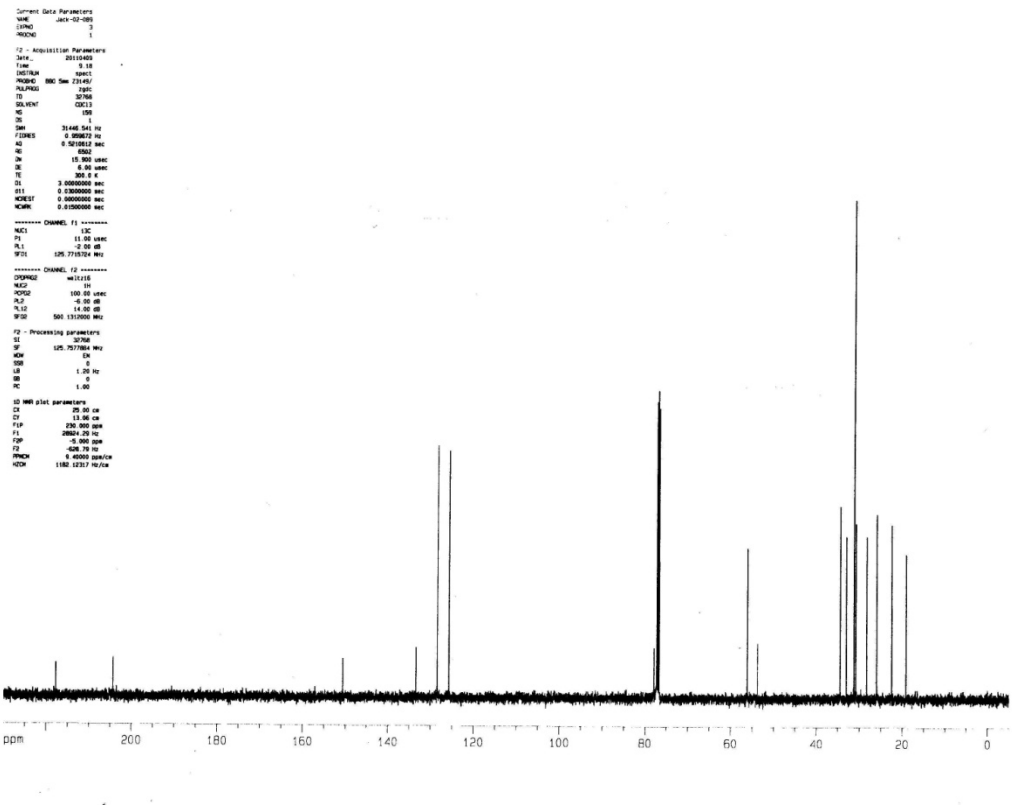




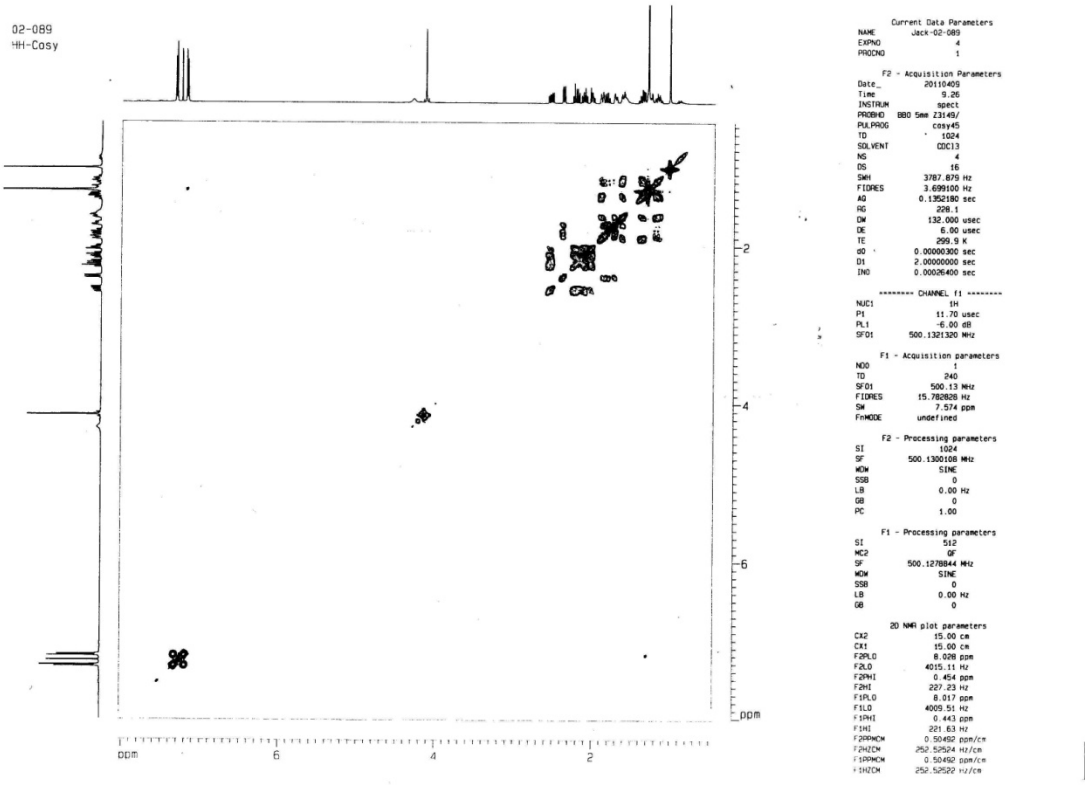
Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (猩*sec)	% Area	Height (猩)
1	02-073-2	1:B,1	1	38.272	582787	4.97	8786
2	02-073-2	1:B,1	1	30.890	11142957	95.03	139600
Mean				34.581	5862872.169		74193.056
Std. Dev.				5.220	7467167.627		92499.40
% RSD				15.09	127.36		124.674

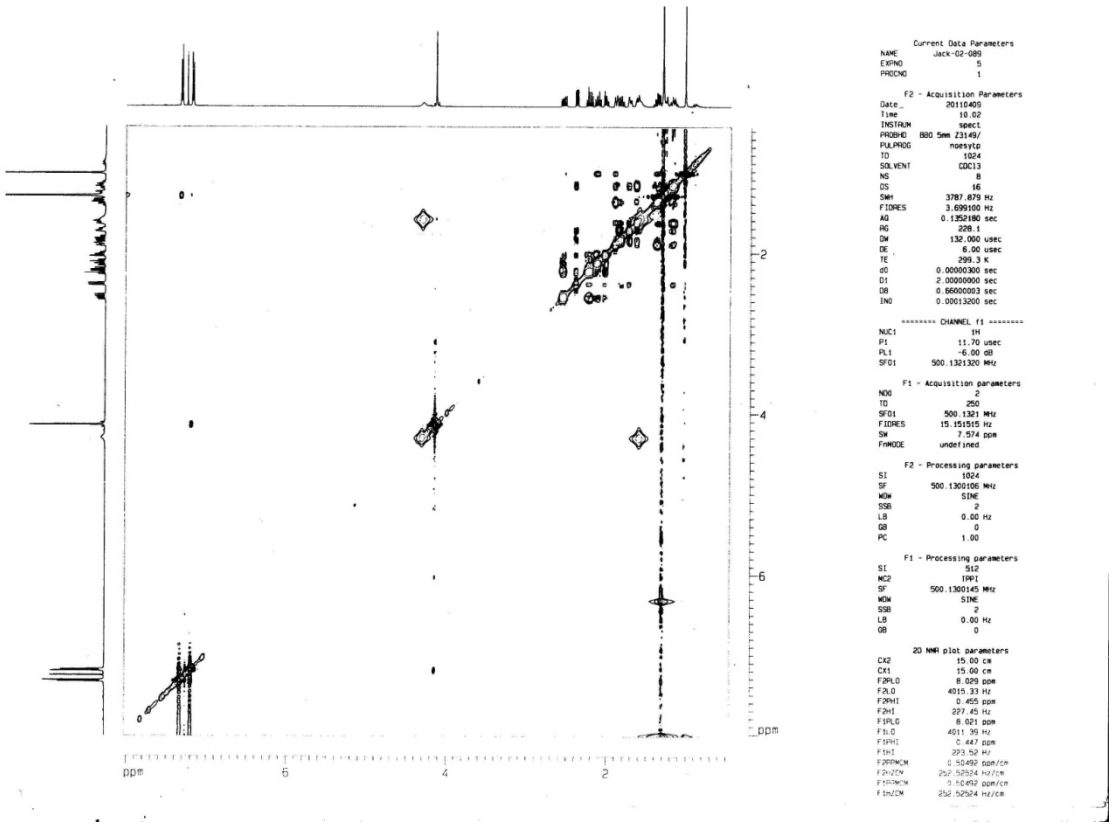




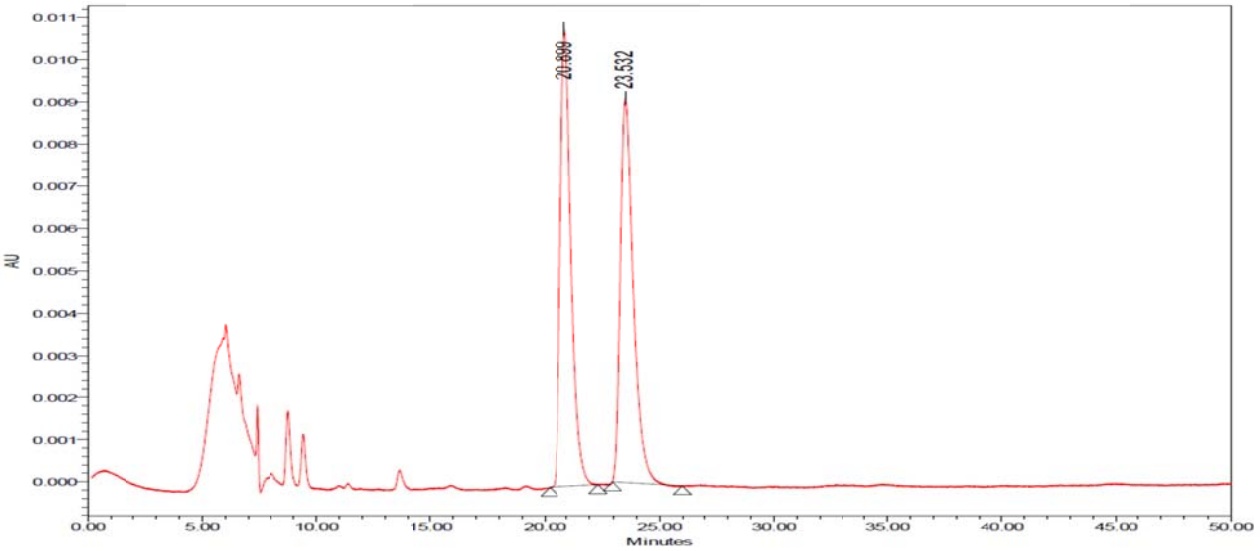
HH-COSY of **4f**

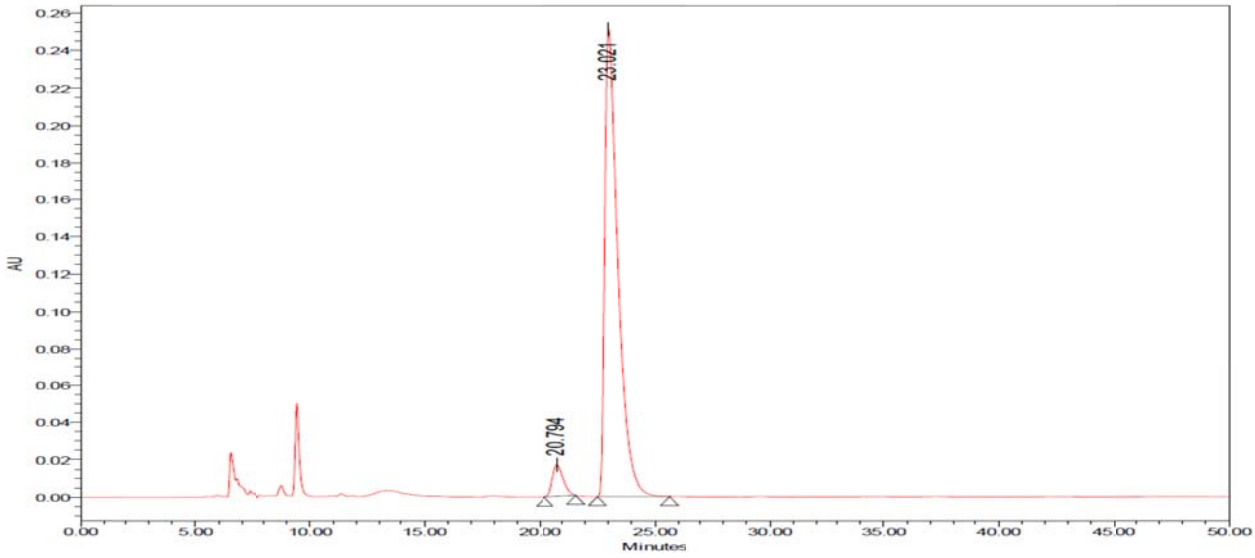


NOESY of 4f



HPLC data for **4g**

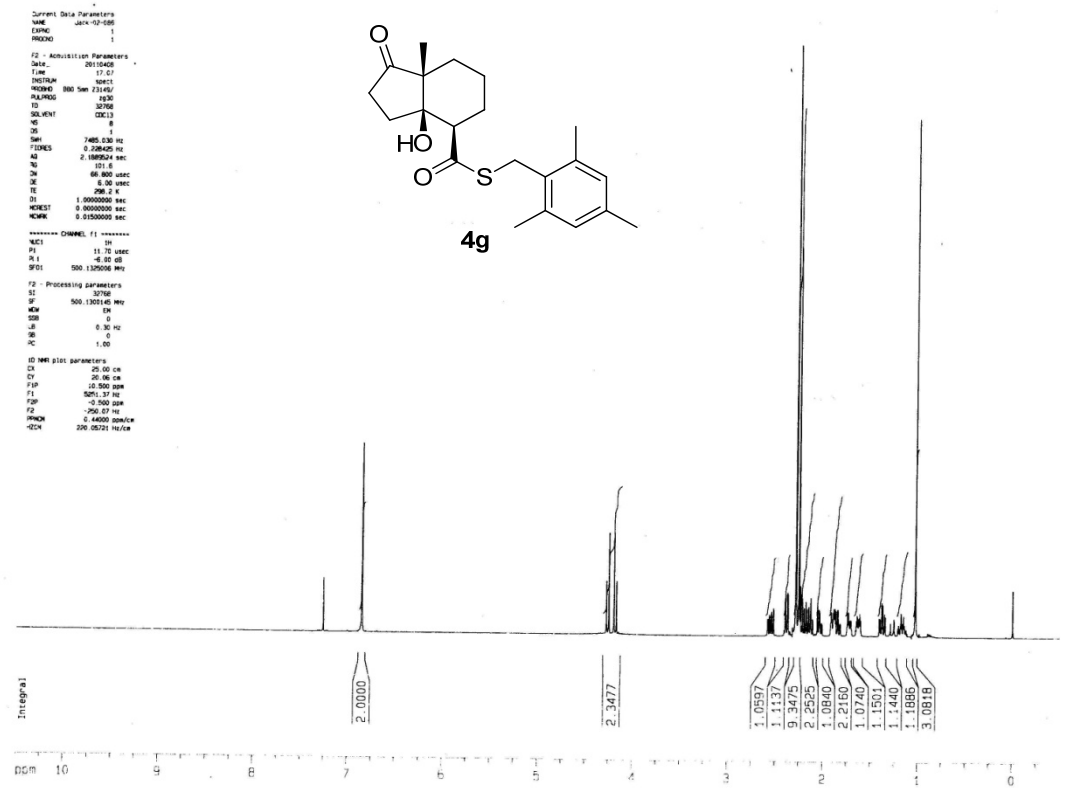


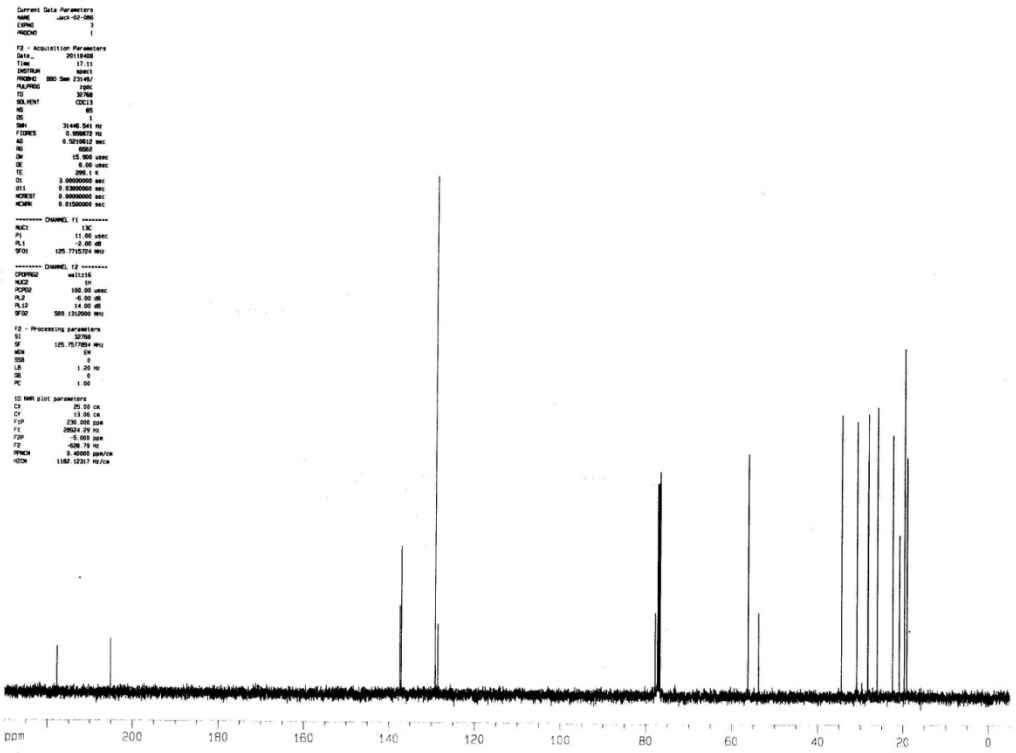


Peak Summary with Statistics

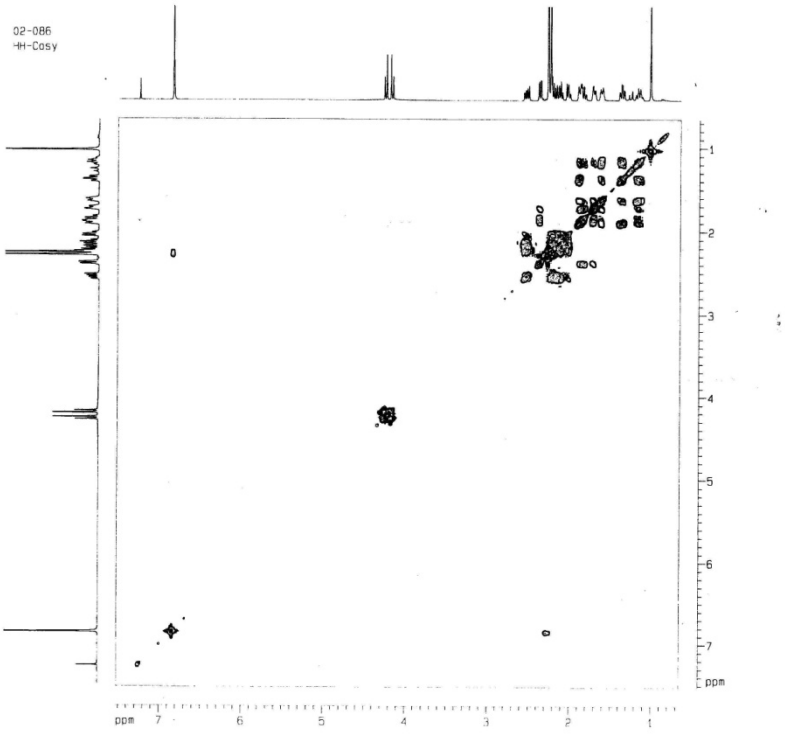
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-135	1:D,2	1	23.021	9823667	94.82	250912
2	02-135	1:D,2	1	20.794	536944	5.18	16641
Mean				21.907	5180305.815		133776.516
Std. Dev.				1.575	6566704.876		165654.22
% RSD				7.19	126.76		123.829


HO
O
S
4g
2.0000
2.3477
1.0597
1.1137
9.3475
2.2525
1.0840
2.2160
1.0740
1.1501
1.1440
1.1886
3.0818
ppm

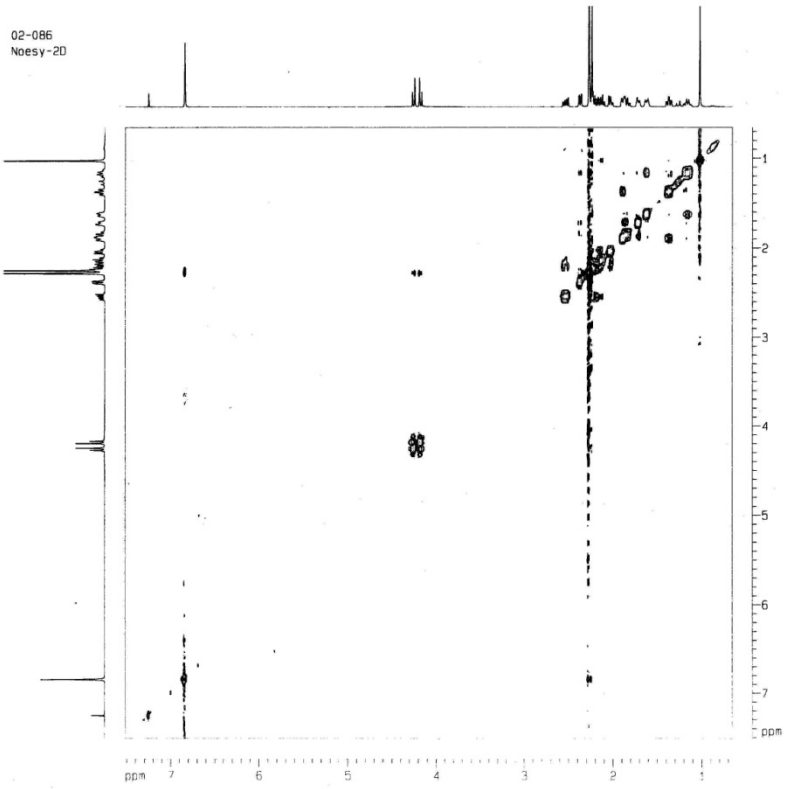

ppm

HH-COSY of **4g**



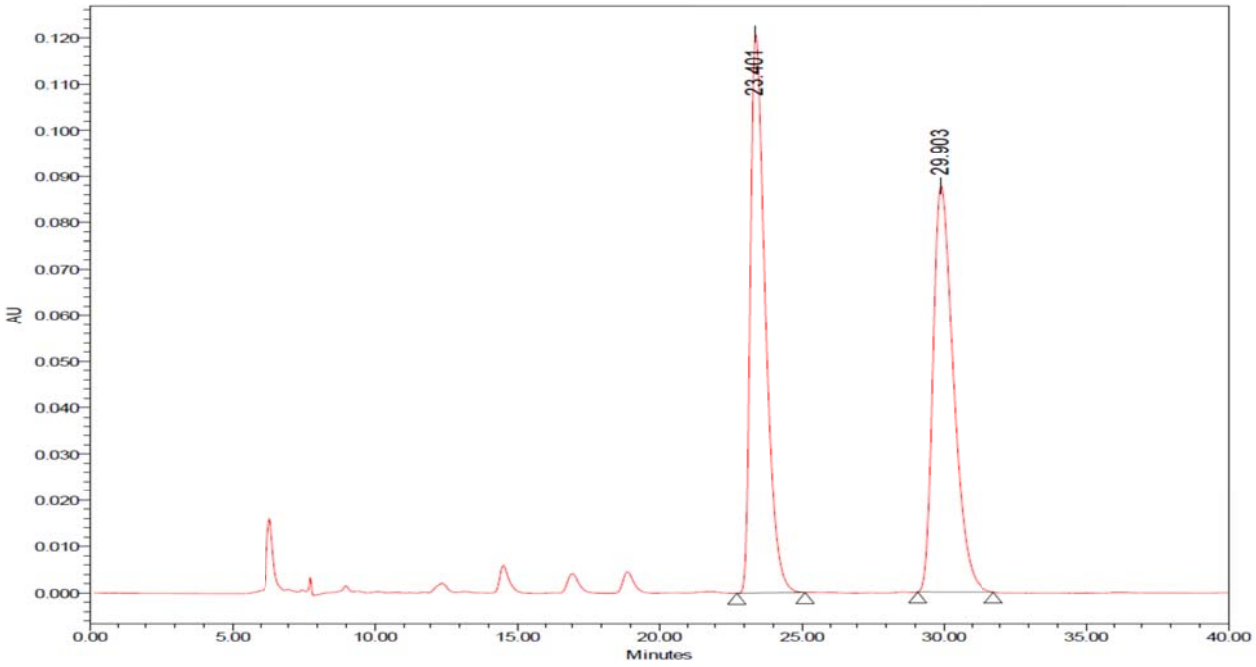

```
Current Data Parameters
NAME                  Jack-02-086
EXPNO                           4
PROCNO                          1

F2 - Acquisition Parameters
Date_               20110408
Time                      15.10
INSTRUM                   spect
PROBHD   BBIz 5mm 28107
PULPROG                 cosy45
TD                        1024
SOLVENT                   CDCl3
NS                             4
DS                            16
SWH                 3434.066 Hz
FIDRES              3.353580 Hz
AQ                  0.1491444 sec
RG                          80.6
DW                  145.600 usec
DE                    6.00 usec
TE                      301.3 K
d0                  0.00000300 sec
D1                  2.00000000 sec
IN0                 0.00029120 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        12.40 usec
PL1                        0.00 dB
SFO1                500.1320600 MHz

F1 - Acquisition parameters
ND0                            1
TD                           220
SFO1                 500.13 MHz
FIDRES              15.609390 Hz
SW                     6.866 ppm
FnMODE                 undefined

F2 - Processing parameters
SI                          1024
SF                  500.1300139 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00

F1 - Processing parameters
SI                           512
MC2                           QF
SF                  500.1279564 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0

2D NMR plot parameters
CX2                        15.00 cm
CX1                        15.00 cm
F2PLO                      7.524 ppm
F2LO                    3763.17 Hz
F2PHI                      0.658 ppm
F2HI                     329.10 Hz
F1PLO                      7.519 ppm
F1LO                    3760.59 Hz
F1PHI                      0.653 ppm
F1HI                     326.53 Hz
F2PPMCM                 0.45776 ppm/cm
F2HZCM                228.53773 Hz/cm
F1PPMCM                 0.45776 ppm/cm
F1HZCM                228.53773 Hz/cm
```

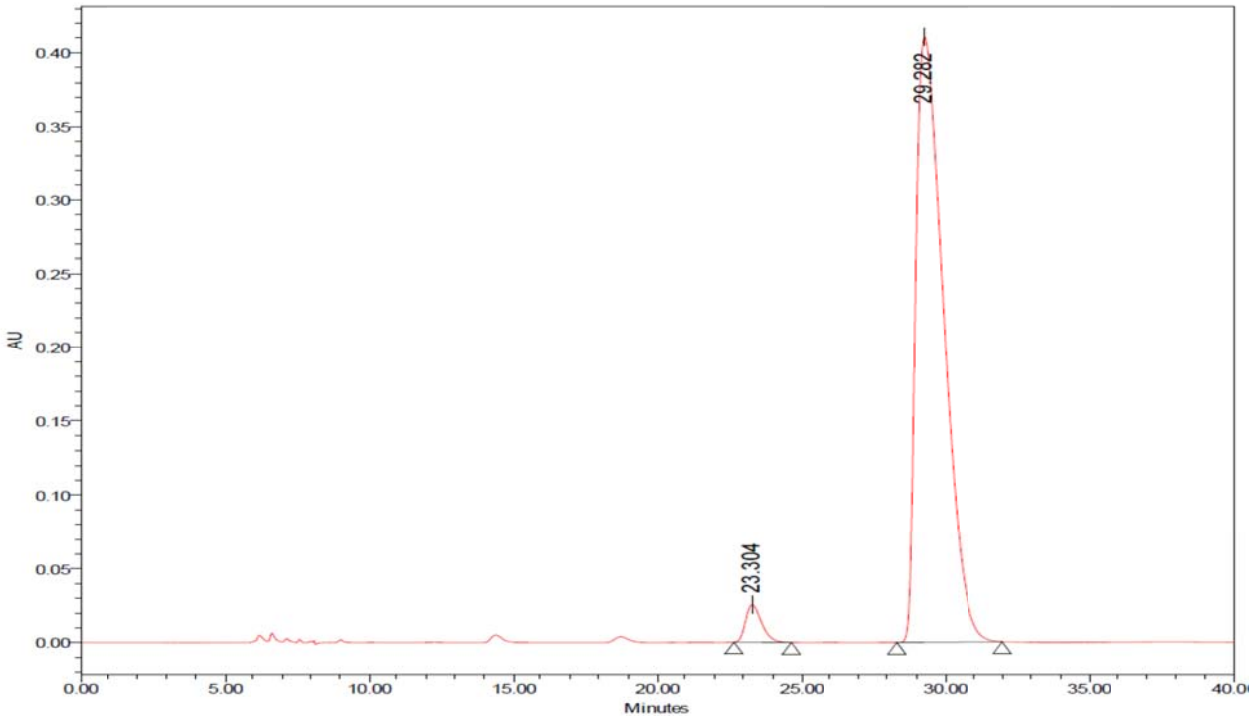
NOESY of **4g**




```
Current Data Parameters
NAME                  Jack-02-086
EXPNO                           5
PROCNO                          1

F2 - Acquisition Parameters
Date_               20110408
Time                      15.43
INSTRUM                   spect
PROBHD   BBIz 5mm 28107
PULPROG                 noesytp
TD                        1024
SOLVENT                   CDCl3
NS                             8
DS                            16
SWH                 3434.066 Hz
FIDRES              3.353580 Hz
AQ                  0.1491444 sec
RG                          80.6
DW                  145.600 usec
DE                    6.00 usec
TE                      300.4 K
d0                  0.00000300 sec
D1                  2.00000000 sec
D8                  0.63000000 sec
IN0                 0.00014560 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        12.40 usec
PL1                        0.00 dB
SFO1                500.1320600 MHz

F1 - Acquisition parameters
ND0                            2
TD                           200
SFO1                500.1321 MHz
FIDRES              17.170330 Hz
SW                     6.866 ppm
FnMODE                 undefined

F2 - Processing parameters
SI                          1024
SF                  500.1300145 MHz
WDW                         SINE
SSB                            2
LB                          0.00 Hz
GB                             0
PC                          1.00

F1 - Processing parameters
SI                           512
MC2                         TPPI
SF                  500.1300173 MHz
WDW                         SINE
SSB                            2
LB                          0.00 Hz
GB                             0

2D NMR plot parameters
CX2                        15.00 cm
CX1                        15.00 cm
F2PLO                      7.523 ppm
F2LO                    3762.54 Hz
F2PHI                      0.657 ppm
F2HI                     328.47 Hz
F1PLO                      7.517 ppm
F1LO                    3759.71 Hz
F1PHI                      0.651 ppm
F1HI                     325.65 Hz
F2PPMCM                 0.45776 ppm/cm
F2HZCM                228.53773 Hz/cm
F1PPMCM                 0.45776 ppm/cm
```

HPLC data for **4g**

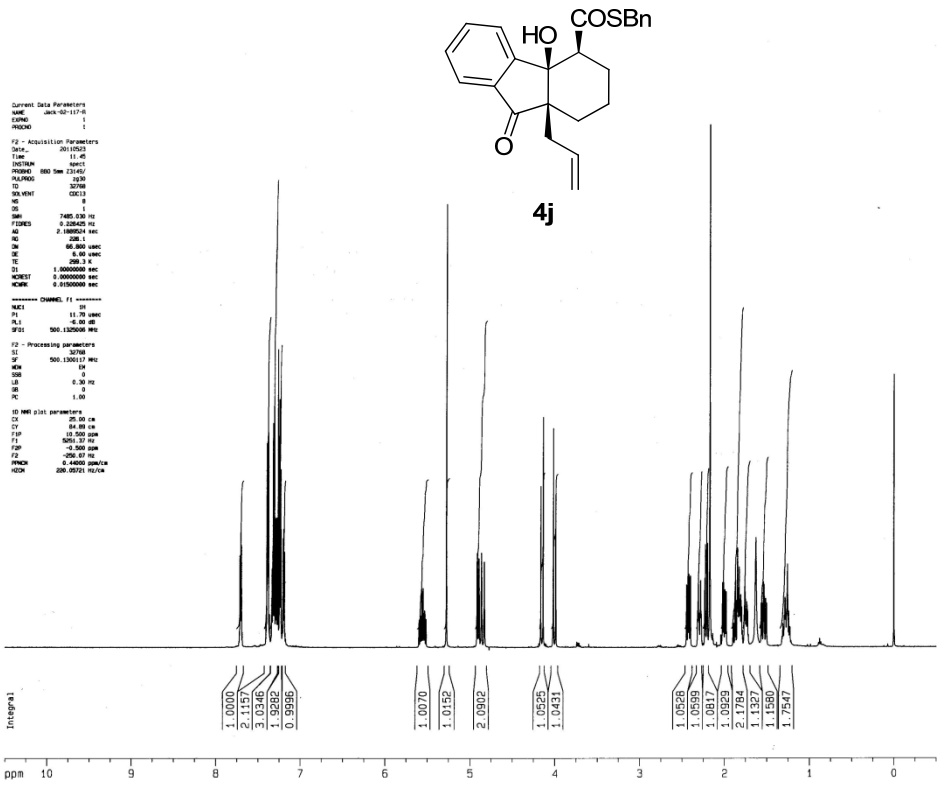


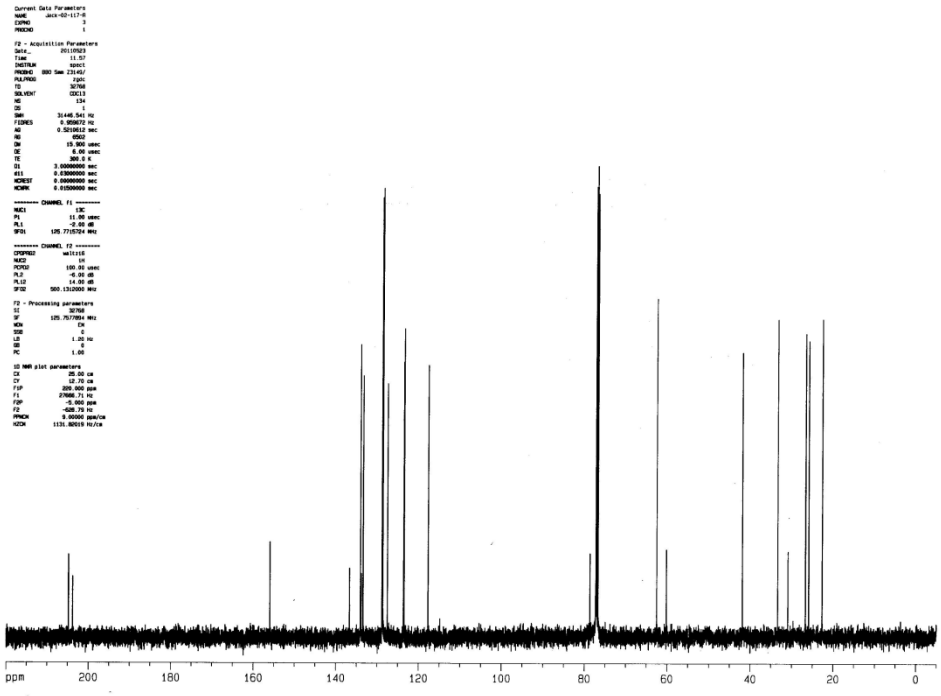


Peak Summary with Statistics

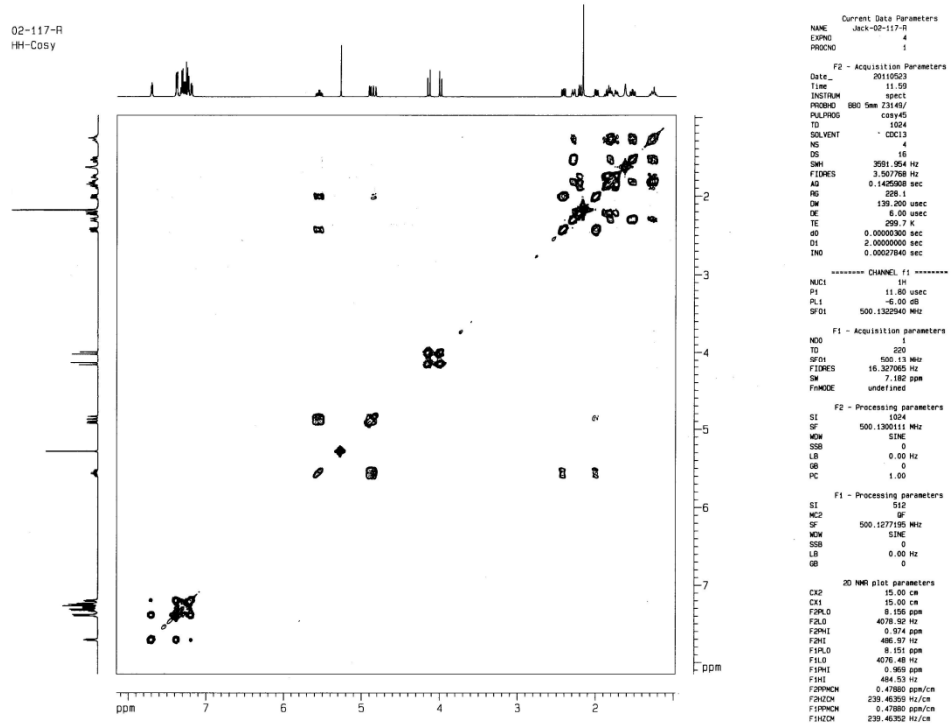
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-137c	1:D,2	1	29.282	27240195	96.59	410363
2	02-137c	1:D,2	1	23.304	960429	3.41	25353
Mean				26.293	14100312.267		217858.197
Std. Dev.				4.227	18582600.605		272243.53
% RSD				16.08	131.79		124.964



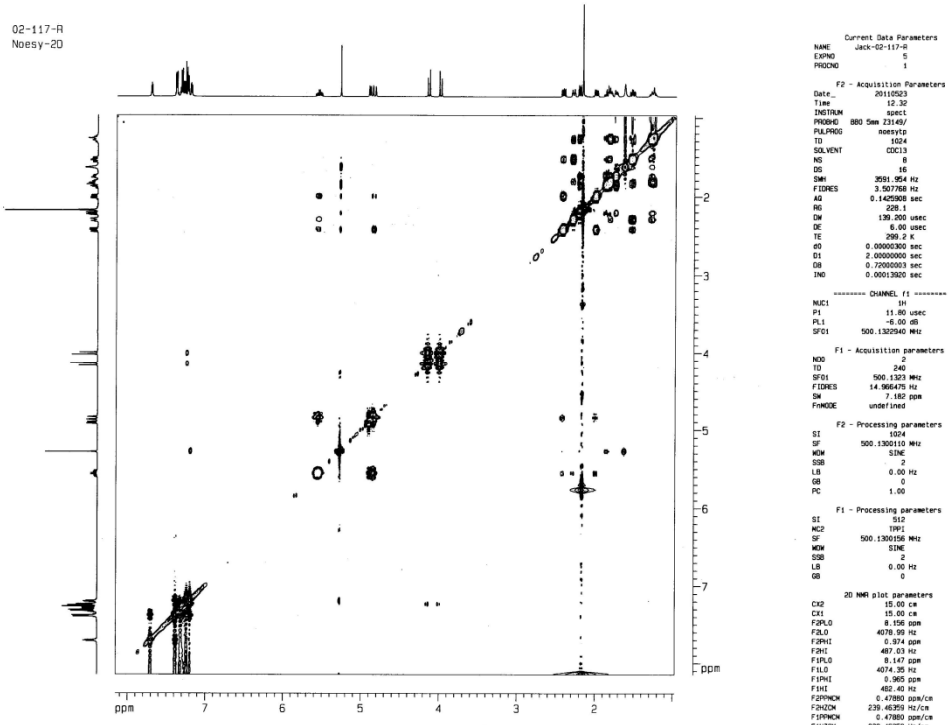


H-H COSY of **4j**



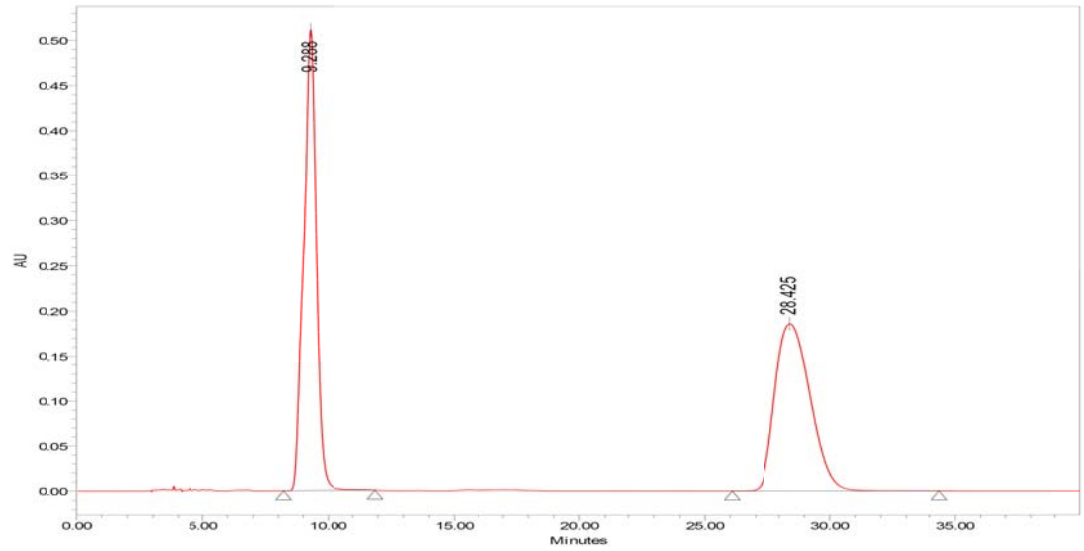

```
Current Data Parameters
NAME          Jack-02-117-R
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_              20110523
Time                 11.59
INSTRUM              spect
PROBHD  BBO 5mm Z3149/
PULPROG            cosy45
TD                   1024
SOLVENT             CDCl3
NS                      4
DS                     16
SWH               3591.954 Hz
FIDRES            3.507768 Hz
AQ                0.1425908 sec
RG                    228.1
DW                  139.200 usec
DE                    6.00 usec
TE                  299.7 K
d0                0.00000300 sec
D1                2.00000000 sec
INO               0.00027840 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.80 usec
PL1                  -6.00 dB
SFO1           500.1322940 MHz

F1 - Acquisition parameters
NDO                     1
TD                    220
SFO1           500.13 MHz
FIDRES           16.327065 Hz
SW                 7.182 ppm
FnMODE           undefined

F2 - Processing parameters
SI                    1024
SF             500.1300111 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                     512
MC2                     QF
SF             500.1277195 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                8.156 ppm
F2LO               4078.92 Hz
F2PHI                0.974 ppm
F2HI                486.97 Hz
F1PLO                8.151 ppm
F1LO               4076.48 Hz
F1PHI                0.969 ppm
F1HI                484.53 Hz
F2PPMCM          0.47880 ppm/cm
F2HZCM          239.46359 Hz/cm
F1PPMCM          0.47880 ppm/cm
F1HZCM          239.46352 Hz/cm
```

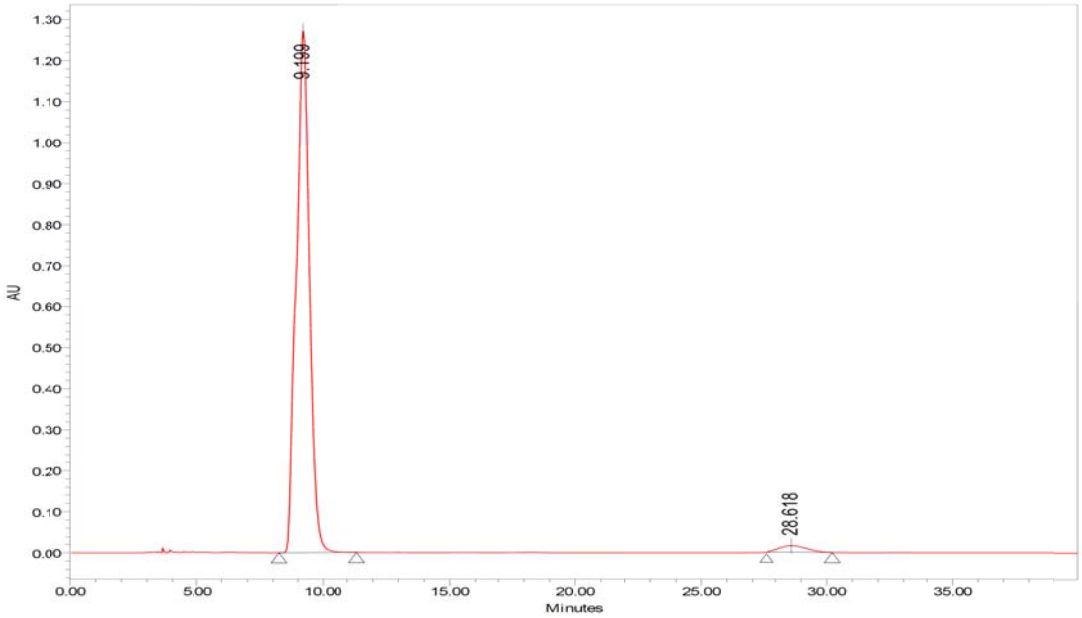
NOESY of **4j**




```
Current Data Parameters
NAME          Jack-02-117-R
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_              20110523
Time                 12.32
INSTRUM              spect
PROBHD  BBO 5mm Z3149/
PULPROG           noesytp
TD                   1024
SOLVENT             CDCl3
NS                      8
DS                     16
SWH               3591.954 Hz
FIDRES            3.507768 Hz
AQ                0.1425908 sec
RG                    228.1
DW                  139.200 usec
DE                    6.00 usec
TE                  299.2 K
d0                0.00000300 sec
D1                2.00000000 sec
D8                0.72000003 sec
INO               0.00013920 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.80 usec
PL1                  -6.00 dB
SFO1           500.1322940 MHz

F1 - Acquisition parameters
NDO                     2
TD                    240
SFO1           500.1323 MHz
FIDRES           14.966475 Hz
SW                 7.182 ppm
FnMODE           undefined

F2 - Processing parameters
SI                    1024
SF             500.1300110 MHz
WDW                   SINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                     512
MC2                   TPPI
SF             500.1300156 MHz
WDW                   SINE
SSB                      2
LB                    0.00 Hz
GB                       0

2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                8.156 ppm
F2LO               4078.99 Hz
F2PHI                0.974 ppm
F2HI                487.03 Hz
F1PLO                8.147 ppm
F1LO               4074.35 Hz
F1PHI                0.965 ppm
F1HI                482.40 Hz
F2PPMCM          0.47880 ppm/cm
F2HZCM          239.46359 Hz/cm
F1PPMCM          0.47880 ppm/cm
F1HZCM          239.46359 Hz/cm
```

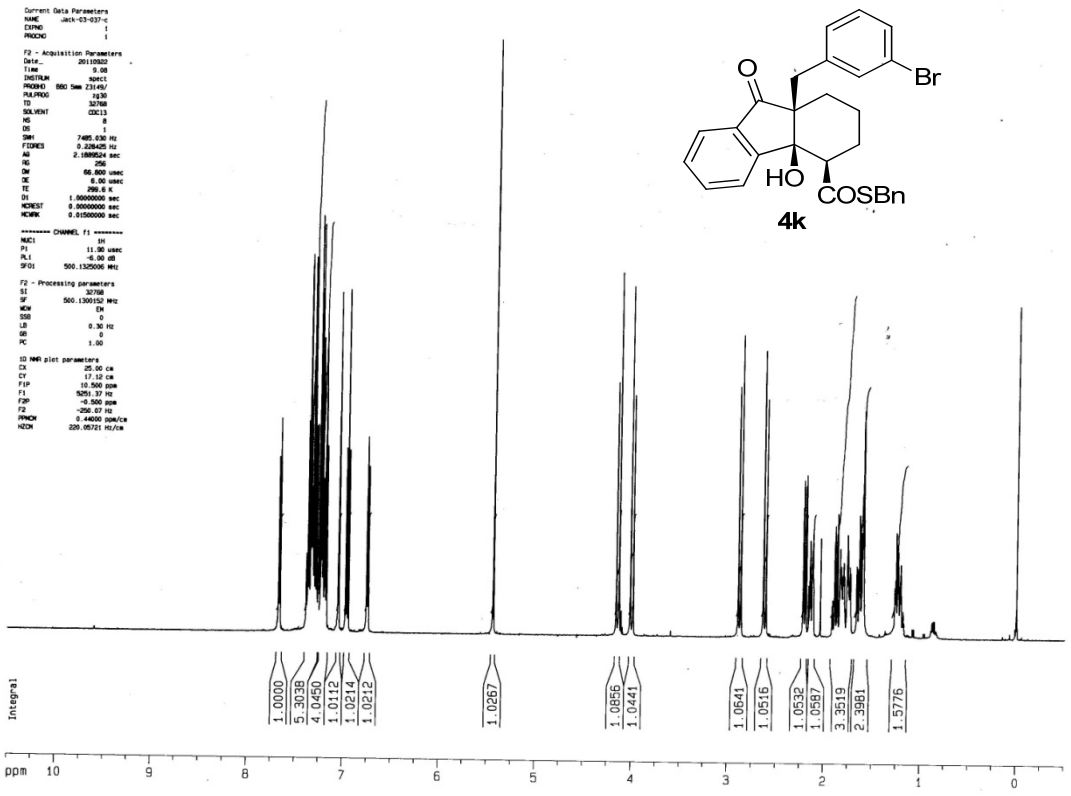
HPLC data of **4j**

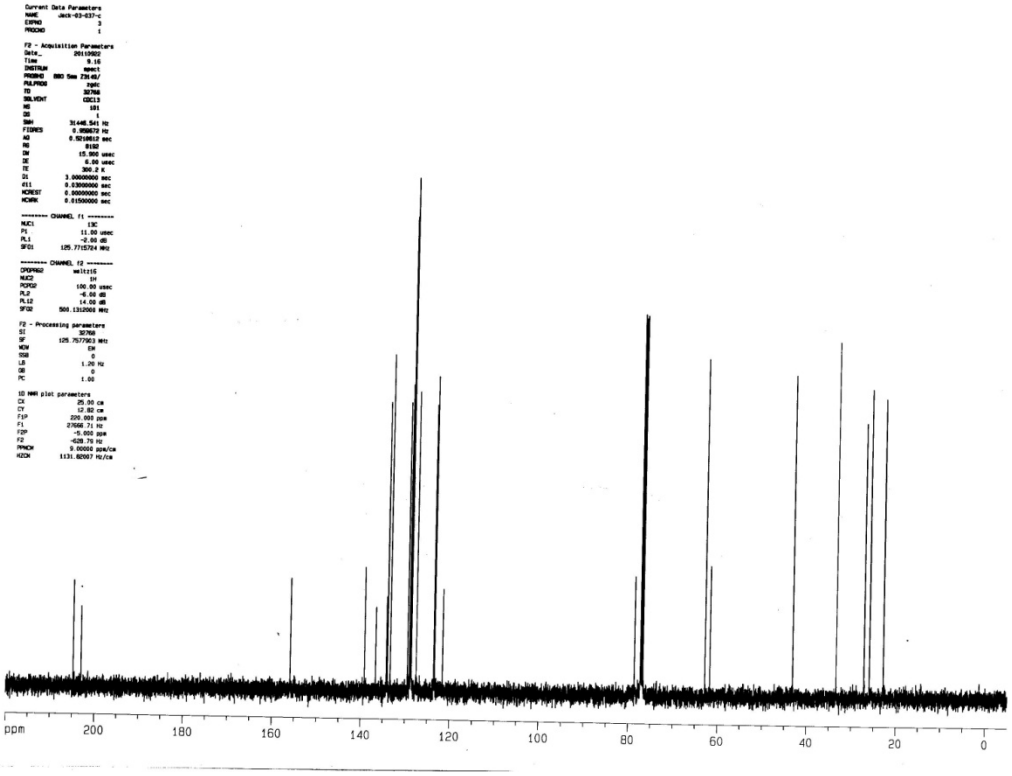


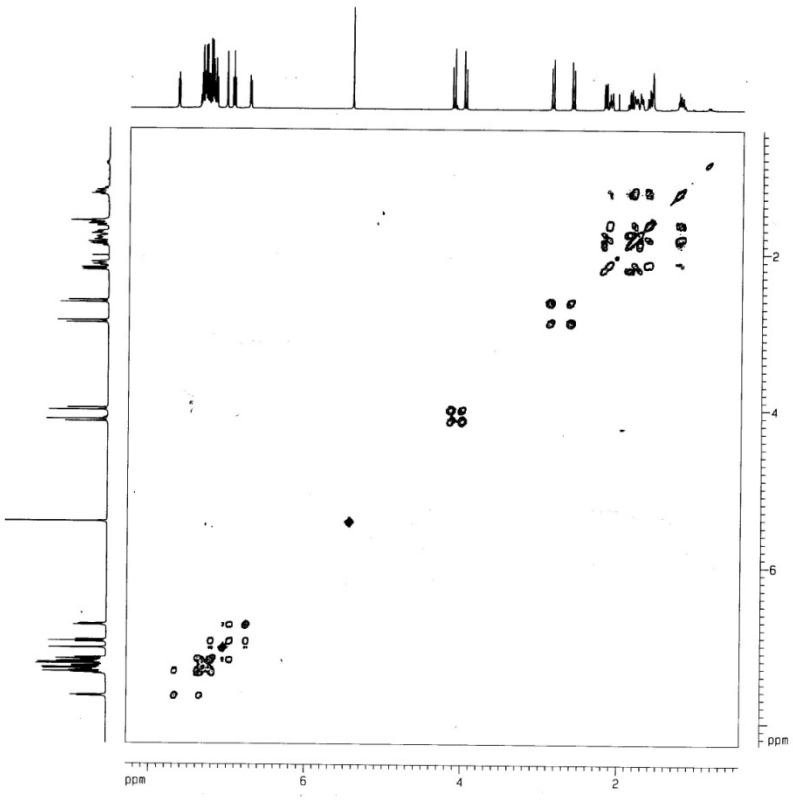


Peak Summary with Statistics
Peak Name:

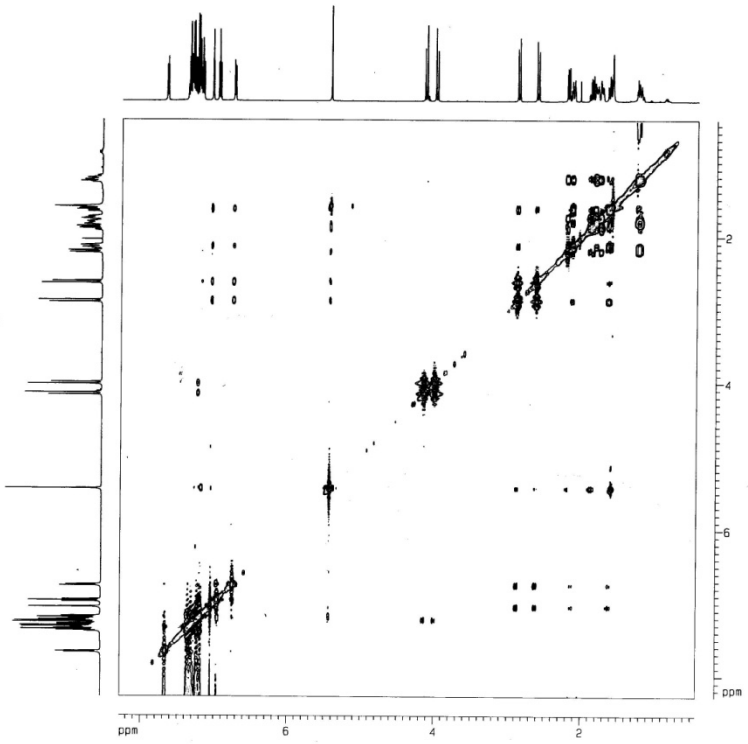
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-132C	1:D,2	1	28.618	1197737	2.55	15896
2	02-132C	1:D,2	1	9.199	45795210	97.45	1271689
Mean				18.908	23496473.239		643792.570
Std. Dev.				13.731	31535175.333		887980.27
% RSD				72.62	134.21		137.930


O
Br
HO
COSBn
4k
Integral
1.0000
5.3038
4.0450
1.0112
1.0214
1.0212
1.0267
1.0856
1.0441
1.0641
1.0516
1.0532
1.0587
3.3519
2.3981
1.5776
ppm 10 9 8 7 6 5 4 3 2 1 0


ppm 200 180 160 140 120 100 80 60 40 20 0

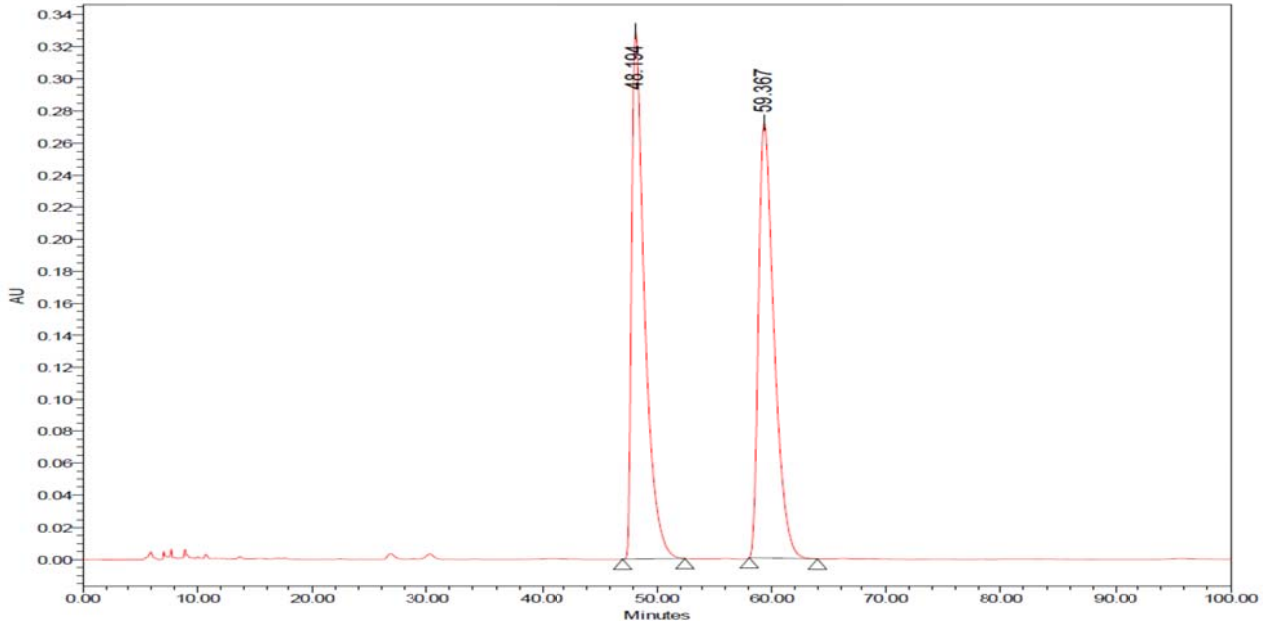


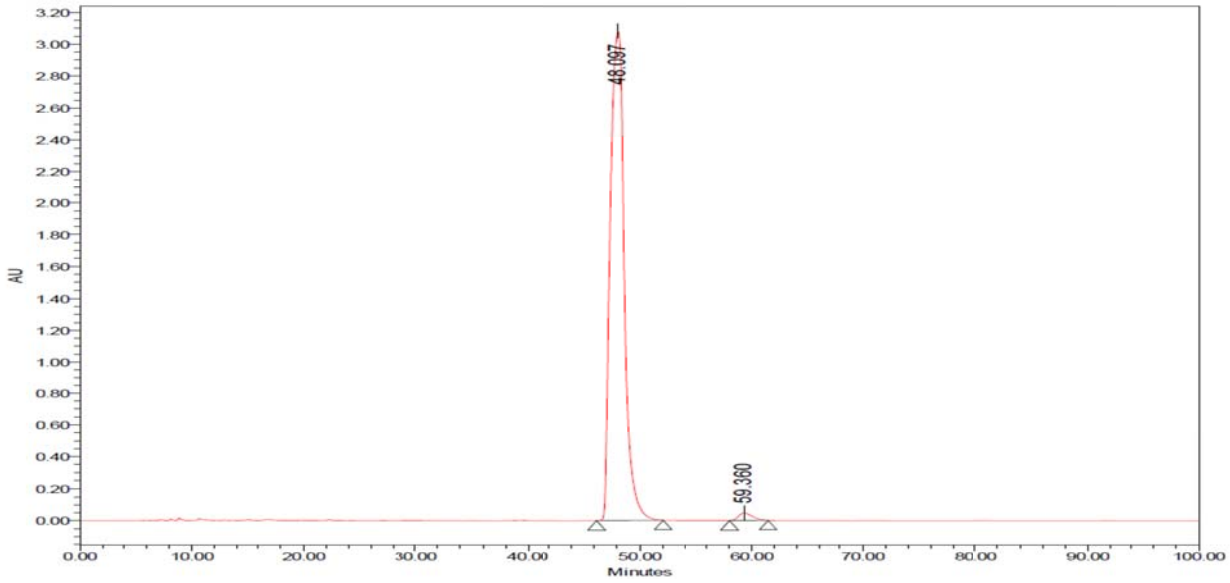

```
Current Data Parameters
NAME                  Jack-03-037-c
EXPNO                             4
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20110922
Time                           9.21
INSTRUM                       spect
PROBHD     BBO 5mm Z3145/
PULPROG                     cosy45
TD                            1024
SOLVENT                       CDCl3
NS                                4
DS                               16
SWH                      3930.818 Hz
FIDRES                   3.838689 Hz
AQ                       0.1303028 sec
RG                              256
DW                       127.200 usec
DE                         6.00 usec
TE                           300.1 K
d0                       0.00000300 sec
D1                       2.00000000 sec
IN0                      0.00025440 sec

======== CHANNEL f1 ========
NUC1                             1H
P1                         11.80 usec
PL1                         -6.00 dB
SFO1                  500.1321940 MHz

F1 - Acquisition parameters
NDO                               1
TD                              256
SFO1                  500.13 MHz
FIDRES                15.354756 Hz
SW                         7.860 ppm
FnMODE                    undefined

F2 - Processing parameters
SI                             1024
SF                    500.1300120 MHz
WDW                            SINE
SSB                               0
LB                             0.00 Hz
GB                                0
PC                             1.00

F1 - Processing parameters
SI                              512
MC2                              QF
SF                    500.1278232 MHz
WDW                            SINE
SSB                               0
LB                             0.00 Hz
GB                                0

2D NMR plot parameters
CX2                           15.00 cm
CY1                           15.00 cm
F2PLO                      8.253 ppm
F2LO                     4147.40 Hz
F2PHI                      0.433 ppm
F2HI                     216.58 Hz
F1PLO                      8.282 ppm
F1LO                     4142.20 Hz
F1PHI                      0.423 ppm
F1HI                     211.39 Hz
F2PPMCM                    0.52397 ppm/cm
F2HZCM                   262.05450 Hz/cm
F1PPMCM                    0.52397 ppm/cm
F1HZCM                   262.05426 Hz/cm
```




```
Current Data Parameters
NAME                  Jack-03-037-c
EXPNO                             5
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20110922
Time                           9.59
INSTRUM                       spect
PROBHD     BBO 5mm Z3145/
PULPROG                     noesytp
TD                            1024
SOLVENT                       CDCl3
NS                                8
DS                               16
SWH                      3930.818 Hz
FIDRES                   3.838689 Hz
AQ                       0.1303028 sec
RG                              256
DW                       127.200 usec
DE                         6.00 usec
TE                           299.8 K
d0                       0.00000300 sec
D1                       2.00000000 sec
D8                       0.67000002 sec
IN0                      0.00012720 sec

======== CHANNEL f1 ========
NUC1                             1H
P1                         11.80 usec
PL1                         -6.00 dB
SFO1                  500.1321940 MHz

F1 - Acquisition parameters
NDO                               2
TD                              220
SFO1                  500.1322 MHz
FIDRES                17.867353 Hz
SW                         7.860 ppm
FnMODE                    undefined

F2 - Processing parameters
SI                             1024
SF                    500.1300135 MHz
WDW                            SINE
SSB                               2
LB                             0.00 Hz
GB                                0
PC                             1.00

F1 - Processing parameters
SI                              512
MC2                         TPPI
SF                    500.1300185 MHz
WDW                            SINE
SSB                               2
LB                             0.00 Hz
GB                                0

2D NMR plot parameters
CX2                           15.00 cm
CY1                           15.00 cm
F2PLO                      8.290 ppm
F2LO                     4145.96 Hz
F2PHI                      0.430 ppm
F2HI                     215.14 Hz
F1PLO                      8.280 ppm
F1LO                     4140.80 Hz
F1PHI                      0.420 ppm
F1HI                     210.08 Hz
F2PPMCM                    0.52397 ppm/cm
F2HZCM                   262.05450 Hz/cm
F1PPMCM                    0.52397 ppm/cm
```

HPLC data of **4k**

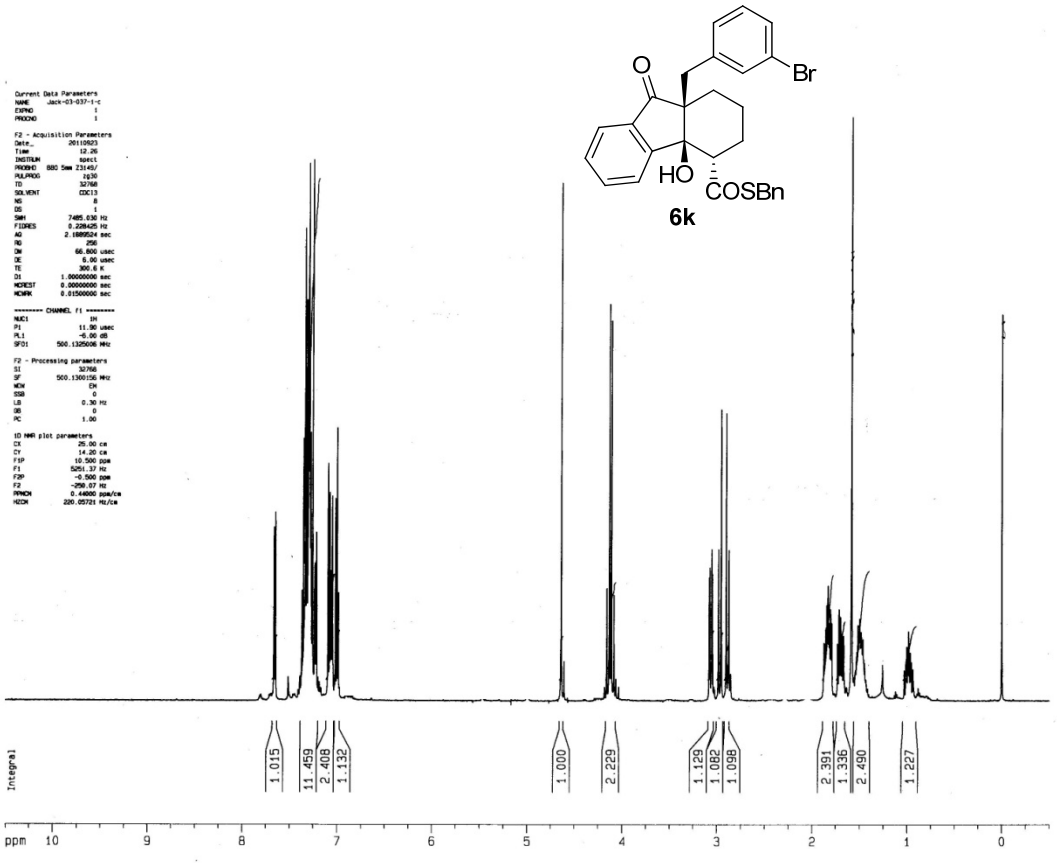


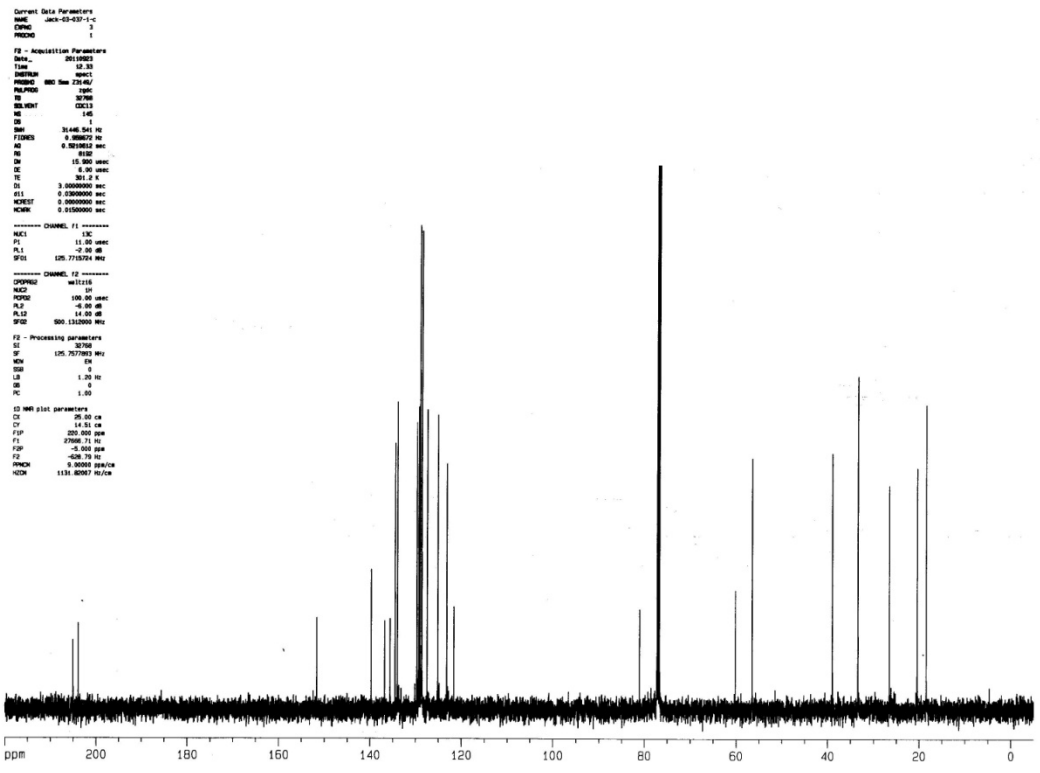


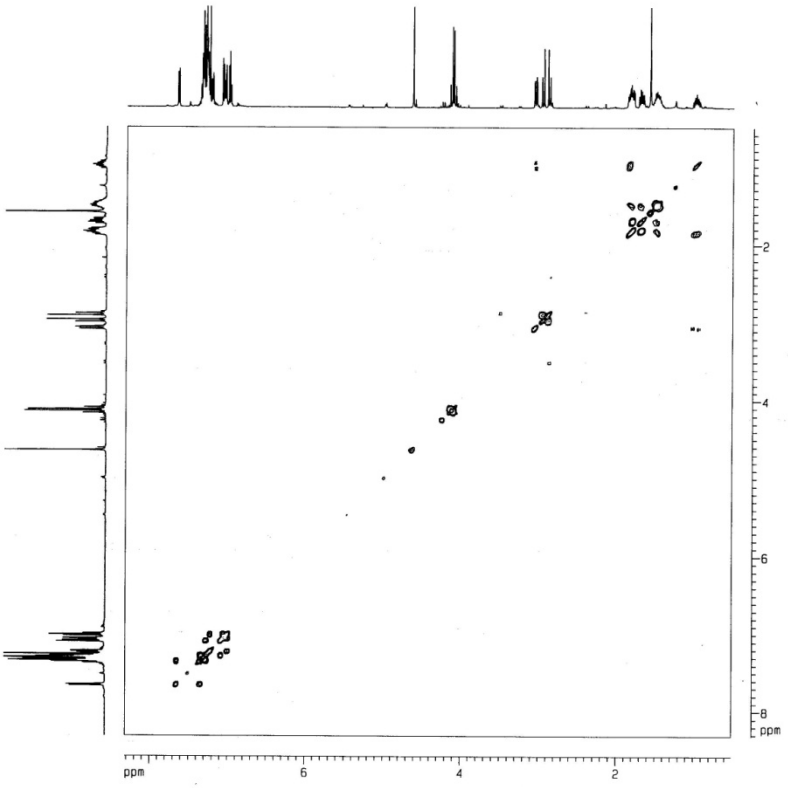
Peak Summary with Statistics

Peak Name:

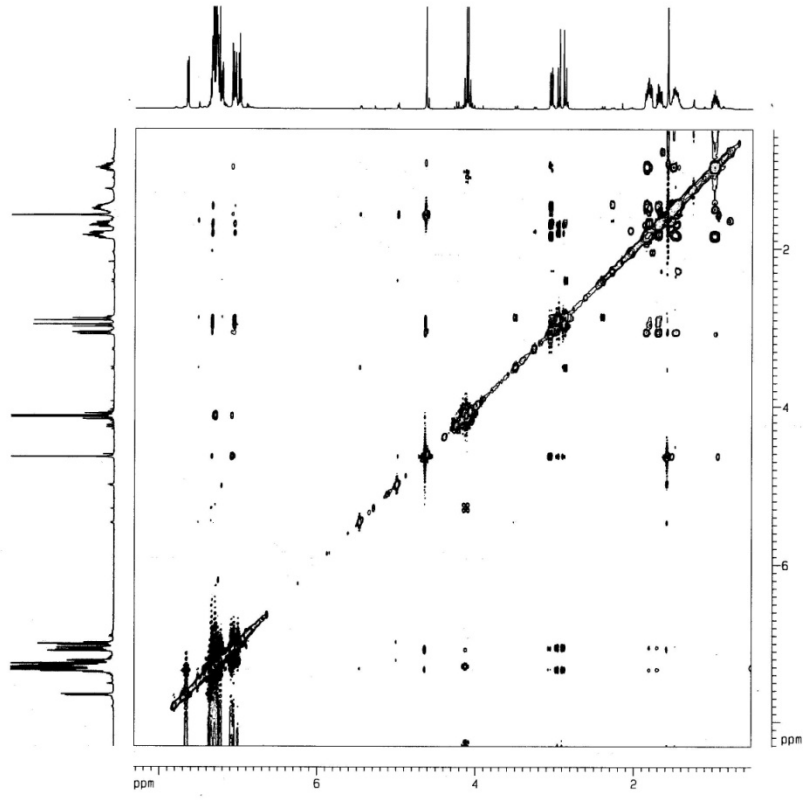
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	03-037-c	1:D,2	1	59.360	3995855	1.50	47580
2	03-037-c	1:D,2	1	48.097	263225297	98.50	3083520
Mean				53.728	133610575.985		1565549.899
Std. Dev.				7.964	183302895.688		2146733.63
% RSD				14.82	137.19		137.123





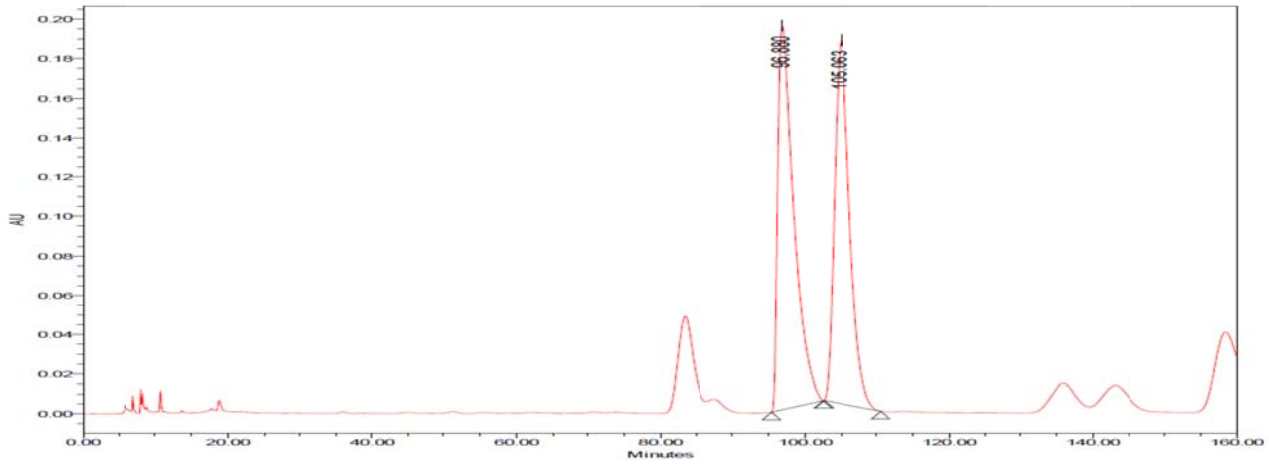


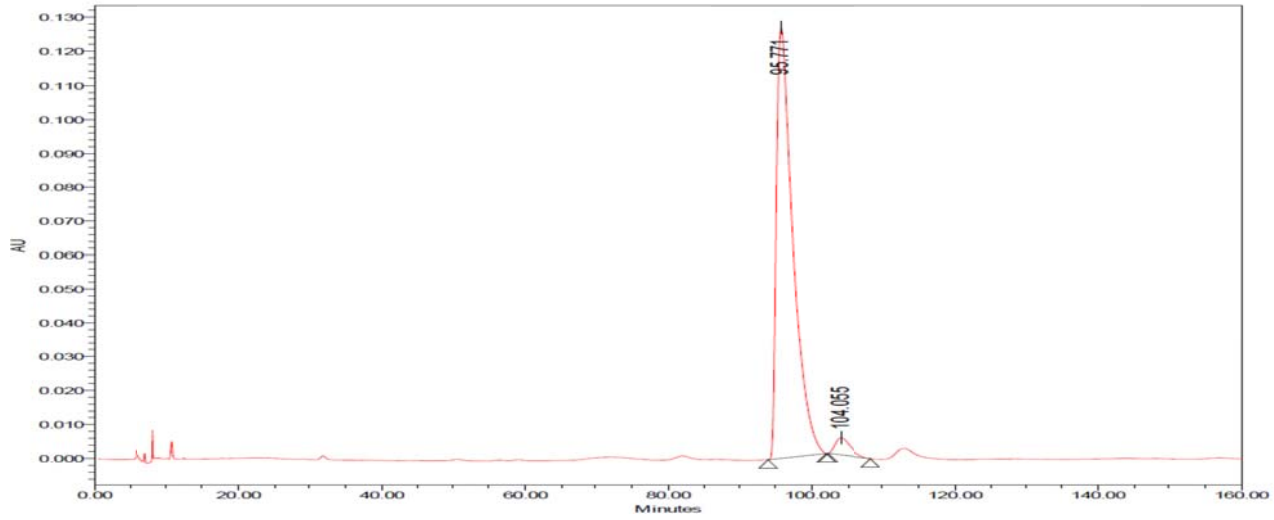

```
                Current Data Parameters
NAME        Jack-03-037-1-c
EXPNO                    4
PROCNO                   1

        F2 - Acquisition Parameters
Date_              20110923
Time                  12.40
INSTRUM               spect
PROBHD   BBO 5mm Z3149/
PULPROG              cosy45
TD                     1024
SOLVENT             - CDCl3
NS                        4
DS                       16
SWH                3906.250 Hz
FIDRES             3.814697 Hz
AQ                 0.1311220 sec
RG                       256
DW                 128.000 usec
DE                   6.00 usec
TE                   301.1 K
d0                 0.00000300 sec
D1                 2.00000000 sec
INO                0.00025600 sec

        ======== CHANNEL f1 ========
NUC1                      1H
P1                    12.10 usec
PL1                   -6.00 dB
SFO1           500.1322230 MHz

        F1 - Acquisition parameters
NDO                       1
TD                      256
SFO1               500.13 MHz
FIDRES          15.256789 Hz
SW                  7.810 ppm
FnMODE          undefined

        F2 - Processing parameters
SI                     1024
SF             500.1300141 MHz
WDW                    SINE
SSB                       0
LB                 0.00 Hz
GB                        0
PC                     1.00

        F1 - Processing parameters
SI                      512
MC2                      QF
SF             500.1277952 MHz
WDW                    SINE
SSB                       0
LB                 0.00 Hz
GB                        0

        2D NMR plot parameters
CX2                   15.00 cm
CX1                   15.00 cm
F2PLO              8.322 ppm
F2LO              4162.07 Hz
F2PHI                0.512 ppm
F2HI               255.82 Hz
F1PLO              8.314 ppm
F1LO              4157.91 Hz
F1PHI                0.503 ppm
F1HI               251.66 Hz
F2PPMCM           0.52070 ppm/cm
F2HZCM          260.41666 Hz/cm
F1PPMCM           0.52070 ppm/cm
F1HZCM          260.41666 Hz/cm
```




```
                Current Data Parameters
NAME        Jack-03-037-1-c
EXPNO                    5
PROCNO                   1

        F2 - Acquisition Parameters
Date_              20110923
Time                  13.18
INSTRUM               spect
PROBHD   BBO 5mm Z3149/
PULPROG              noesytp
TD                     1024
SOLVENT              CDCl3
NS                        8
DS                       16
SWH                3906.250 Hz
FIDRES             3.814697 Hz
AQ                 0.1311220 sec
RG                       256
DW                 128.000 usec
DE                   6.00 usec
TE                   300.5 K
d0                 0.00000300 sec
D1                 2.00000000 sec
D8                 0.64999998 sec
INO                0.00012800 sec

        ======== CHANNEL f1 ========
NUC1                      1H
P1                    12.10 usec
PL1                   -6.00 dB
SFO1           500.1322230 MHz

        F1 - Acquisition parameters
NDO                       2
TD                      220
SFO1               500.1322 MHz
FIDRES          17.755682 Hz
SW                  7.810 ppm
FnMODE          undefined

        F2 - Processing parameters
SI                     1024
SF             500.1300140 MHz
WDW                    SINE
SSB                       2
LB                 0.00 Hz
GB                        0
PC                     1.00

        F1 - Processing parameters
SI                      512
MC2                    TPPI
SF             500.1300193 MHz
WDW                    SINE
SSB                       2
LB                 0.00 Hz
GB                        0

        2D NMR plot parameters
CX2                   15.00 cm
CX1                   15.00 cm
F2PLO              8.322 ppm
F2LO              4162.11 Hz
F2PHI                0.512 ppm
F2HI               255.86 Hz
F1PLO              8.311 ppm
F1LO              4156.81 Hz
F1PHI                0.501 ppm
F1HI               250.56 Hz
F2PPMCM           0.52070 ppm/cm
F2HZCM          260.41666 Hz/cm
F1PPMCM           0.52070 ppm/cm
F1HZCM          260.41666 Hz/cm
```

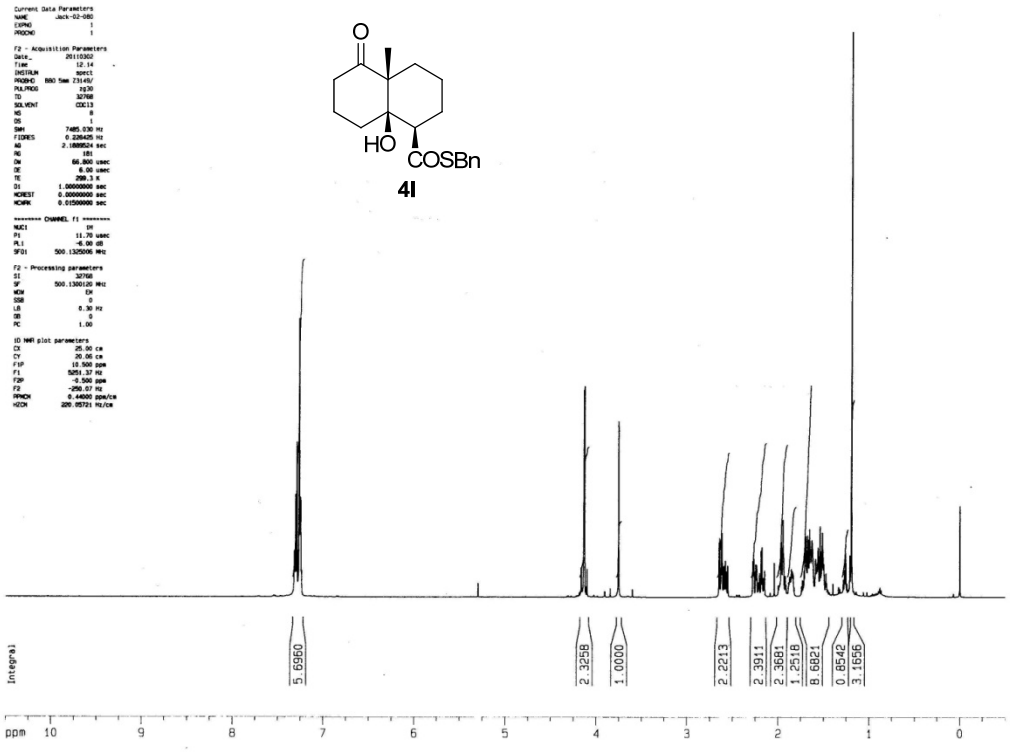
HPLC data of **6k**

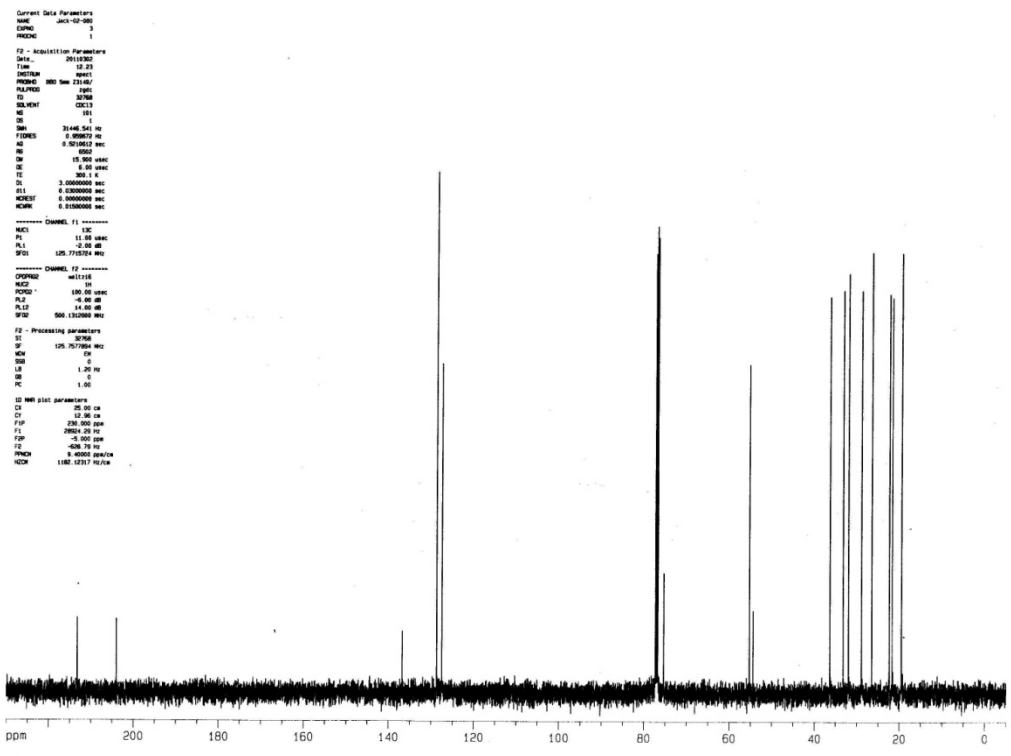


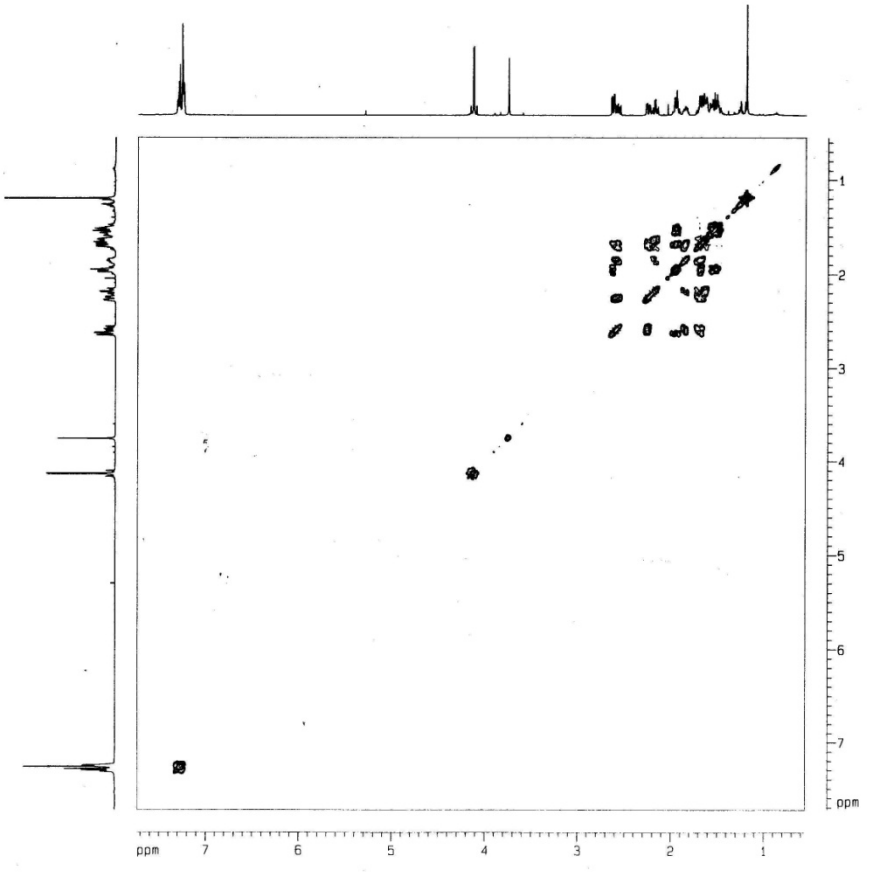


Peak Summary with Statistics
Peak Name:

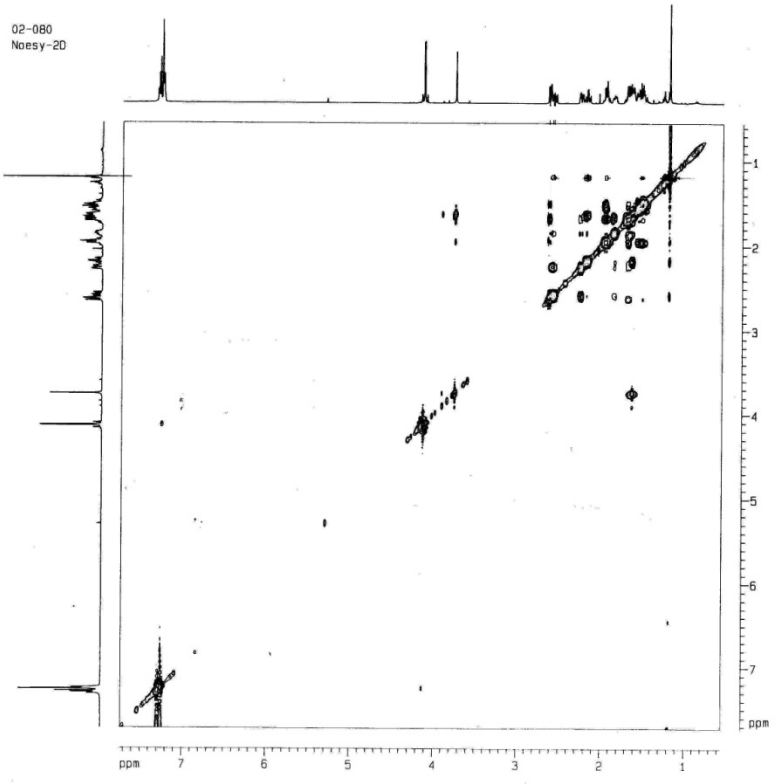
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	03-037-1-C	1:D,2	1	104.055	761393	3.66	5075
2	03-037-1-C	1:D,2	1	95.771	20017595	96.34	126806
Mean				99.913	10389494.014		65940.446
Std. Dev.				5.858	13616190.459		86076.87
% RSD				5.86	131.06		130.537





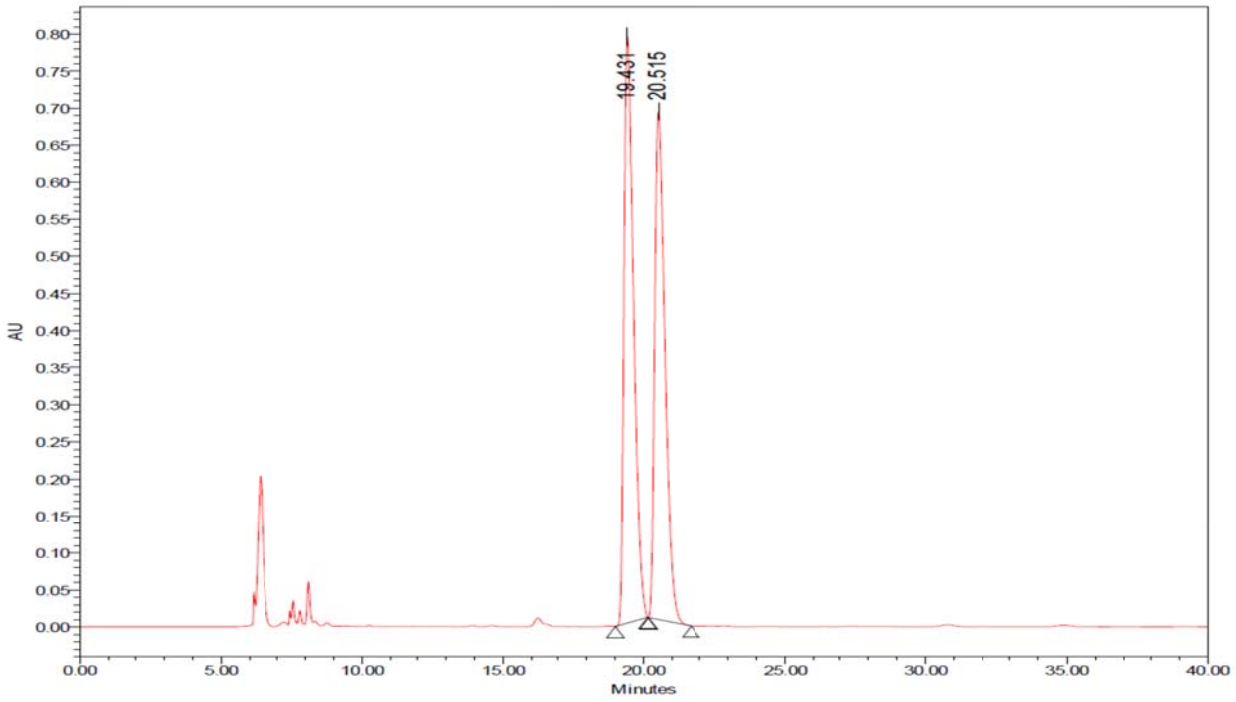


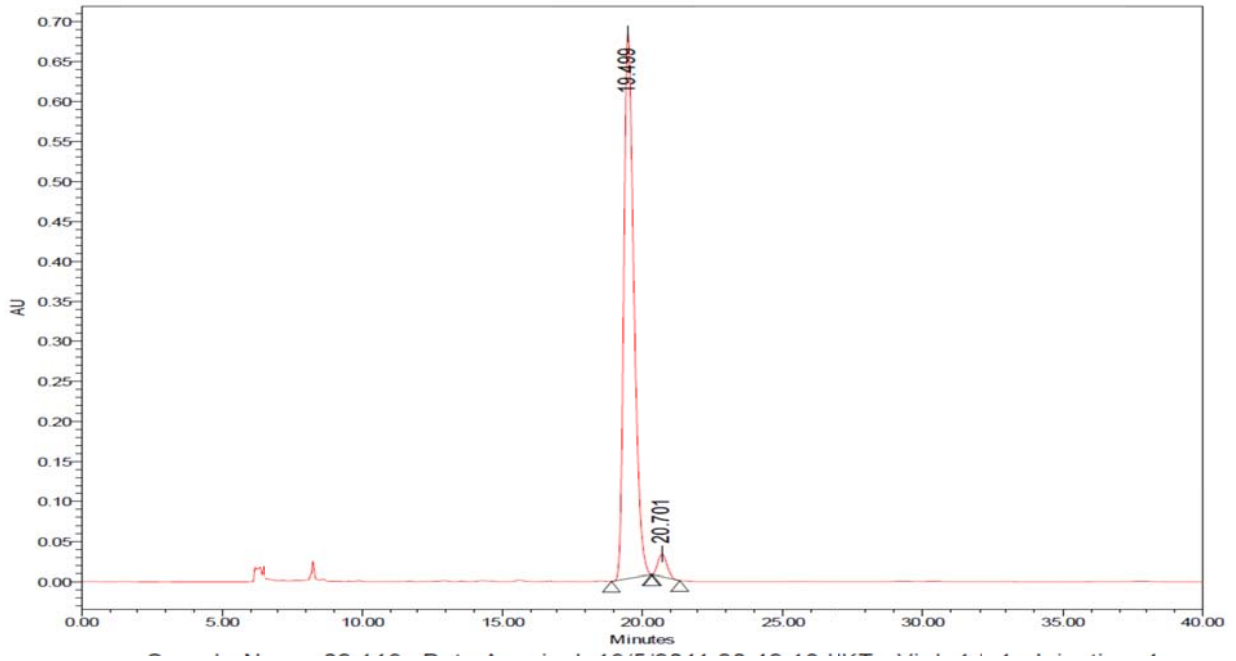

```
Current Data Parameters
NAME            Jack-02-080
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_          20110302
Time              12.25
INSTRUM           spect
PROBHD    BBO 5mm Z3149/
PULPROG          cosy45
TD                1024
SOLVENT           CDCl3
NS                   4
DS                  16
SWH            3591.954 Hz
FIDRES         3.507768 Hz
AQ             0.1425908 sec
RG                 181
DW              139.200 usec
DE                6.00 usec
TE                299.8 K
d0             0.00000300 sec
D1             2.00000000 sec
IN0            0.00027840 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                11.70 usec
PL1               -6.00 dB
SFO1         500.1320850 MHz

F1 - Acquisition parameters
ND0                  1
TD                 256
SFO1          500.13 MHz
FIDRES       14.031071 Hz
SW            7.182 ppm
FnMODE        undefined

F2 - Processing parameters
SI                1024
SF          500.1300106 MHz
WDW               SINE
SSB                  0
LB             0.00 Hz
GB                   0
PC                1.00

F1 - Processing parameters
SI                 512
MC2                QF
SF          500.1279315 MHz
WDW               SINE
SSB                  0
LB             0.00 Hz
GB                   0

2D NMR plot parameters
CX2              15.00 cm
CX1              15.00 cm
F2PLO             7.739 ppm
F2LO           3870.40 Hz
F2PHI             0.557 ppm
F2HI            278.45 Hz
F1PLO             7.727 ppm
F1LO           3864.50 Hz
F1PHI             0.545 ppm
F1HI            272.55 Hz
F2PPMCM       0.47880 ppm/cm
F2HZCM      239.46359 Hz/cm
F1PPMCM       0.47880 ppm/cm
F1HZCM      239.46326 Hz/cm
```




```
Current Data Parameters
NAME            Jack-02-080
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_          20110302
Time              13.03
INSTRUM           spect
PROBHD    BBO 5mm Z3149/
PULPROG         noesytp
TD                1024
SOLVENT           CDCl3
NS                   8
DS                  16
SWH            3591.954 Hz
FIDRES         3.507768 Hz
AQ             0.1425908 sec
RG                 181
DW              139.200 usec
DE                6.00 usec
TE                299.2 K
d0             0.00000300 sec
D1             2.00000000 sec
D8             0.68000001 sec
IN0            0.00013920 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                11.70 usec
PL1               -6.00 dB
SFO1         500.1320850 MHz

F1 - Acquisition parameters
ND0                  2
TD                 210
SFO1          500.1321 MHz
FIDRES       17.104544 Hz
SW            7.182 ppm
FnMODE        undefined

F2 - Processing parameters
SI                1024
SF          500.1300117 MHz
WDW               SINE
SSB                  2
LB             0.00 Hz
GB                   0
PC                1.00

F1 - Processing parameters
SI                 512
MC2               TPPI
SF          500.1300165 MHz
WDW               SINE
SSB                  2
LB             0.00 Hz
GB                   0

2D NMR plot parameters
CX2              15.00 cm
CX1              15.00 cm
F2PLO             7.737 ppm
F2LO           3869.27 Hz
F2PHI             0.554 ppm
F2HI            277.32 Hz
F1PLO             7.727 ppm
F1LO           3864.46 Hz
F1PHI             0.545 ppm
F1HI            272.51 Hz
F2PPMCM       0.47880 ppm/cm
F2HZCM      239.46359 Hz/cm
F1PPMCM       0.47880 ppm/cm
F1HZCM      239.46359 Hz/cm
```

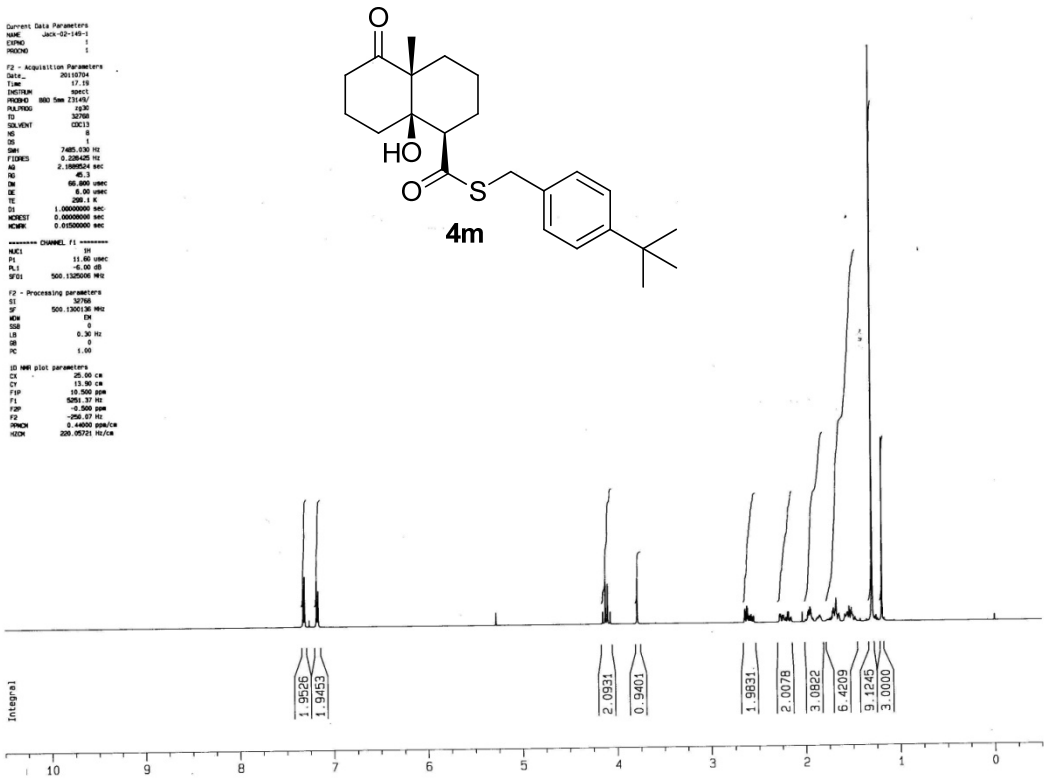
HPLC data for **4l**

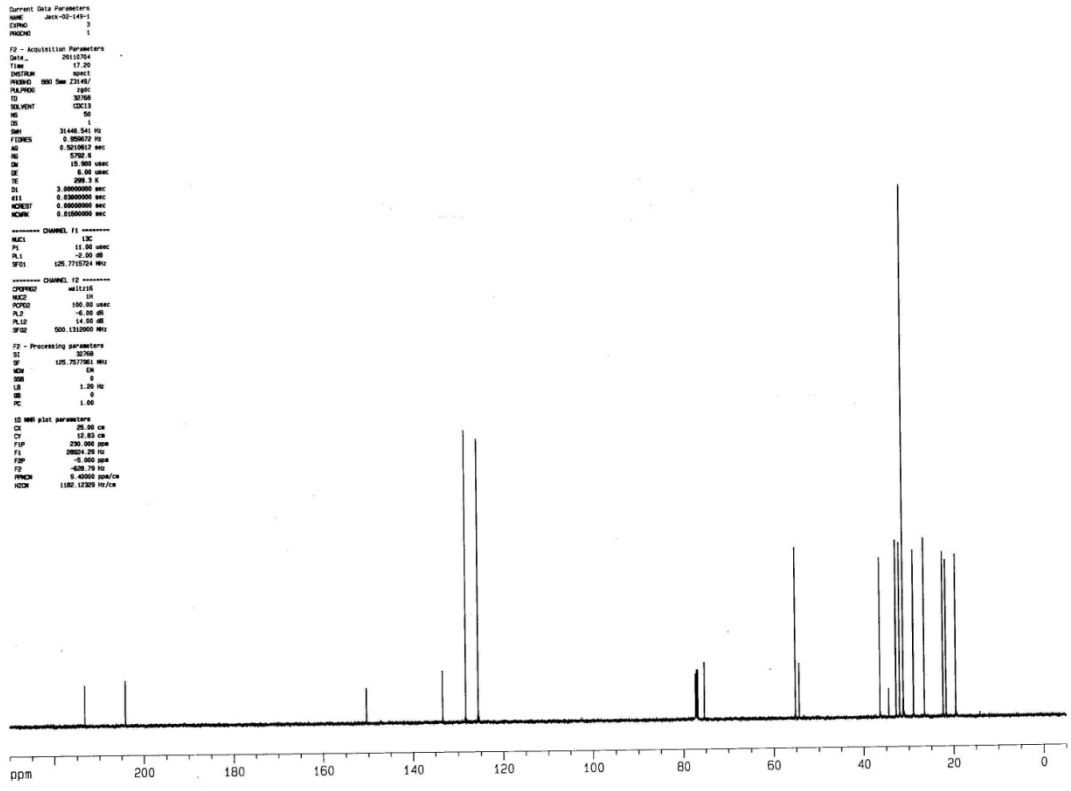


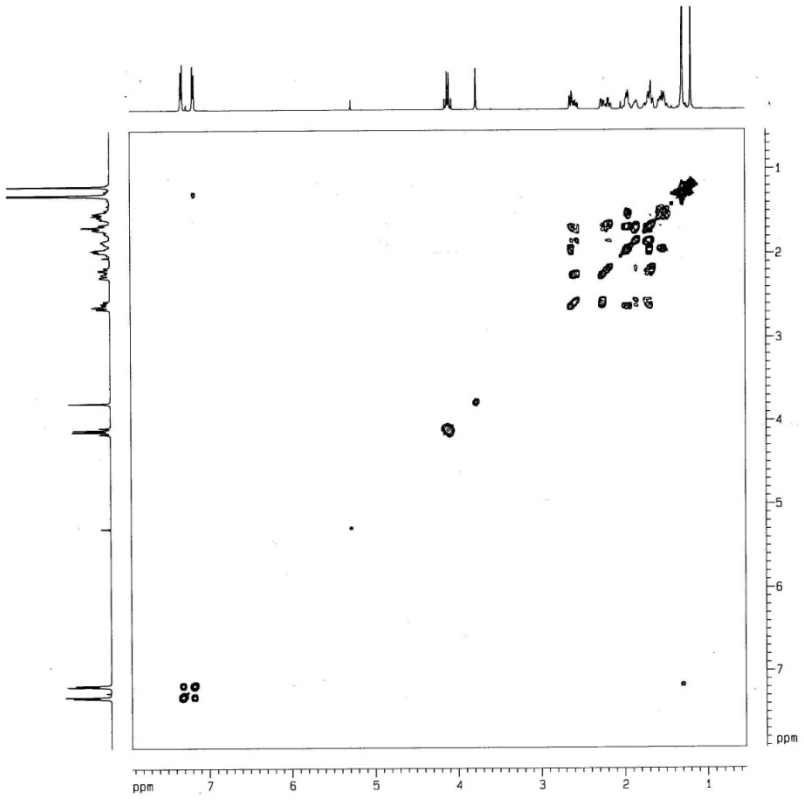


Peak Summary with Statistics
Peak Name:

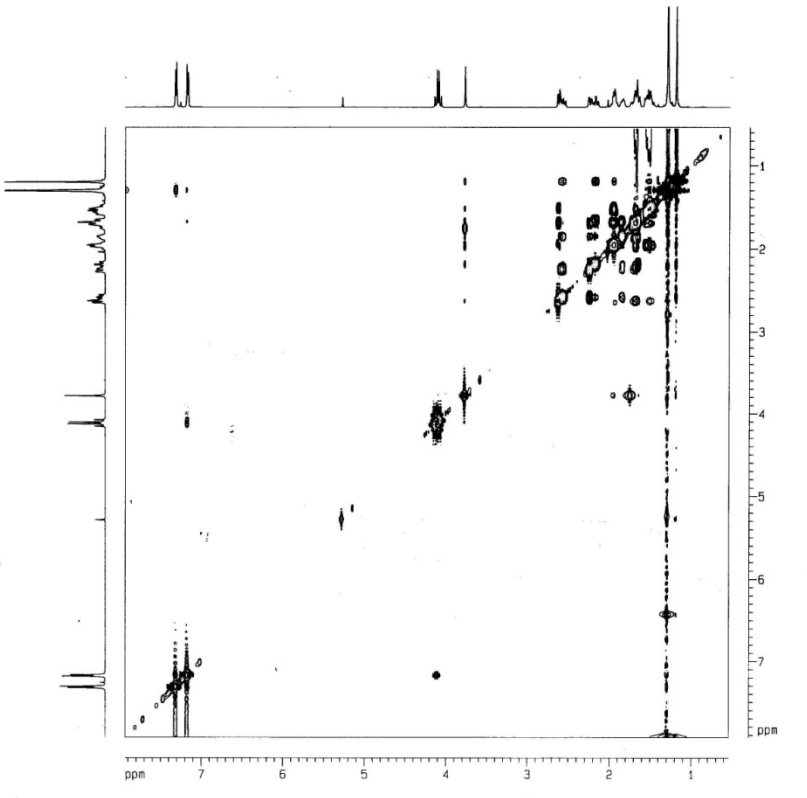
	Sample Name	Vial	Inj.	RT (min)	Area (寘*sec)	% Area	Height (寘)
1	02-119	1:b,1	1	20.701	616850	3.55	27843
2	02-119	1:b,1	1	19.499	16771820	96.45	681028
Mean				20.100	8694335.001		354435.464
Std. Dev.				0.850	11423288.798		461871.48
% RSD				4.23	131.39		130.312


O
HO
O
S
4m
Integral
1.9526
1.9453
2.0931
0.9401
1.9831
2.0078
3.0822
6.4209
9.1245
3.0000
10
9
8
7
6
5
4
3
2
1
0


ppm
200
180
160
140
120
100
80
60
40
20
0

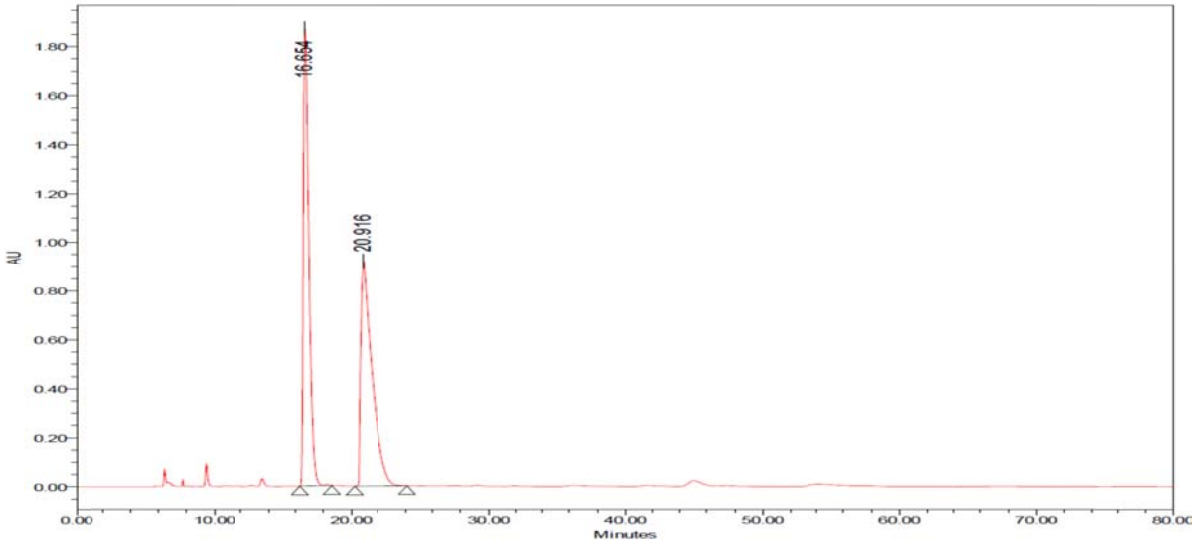


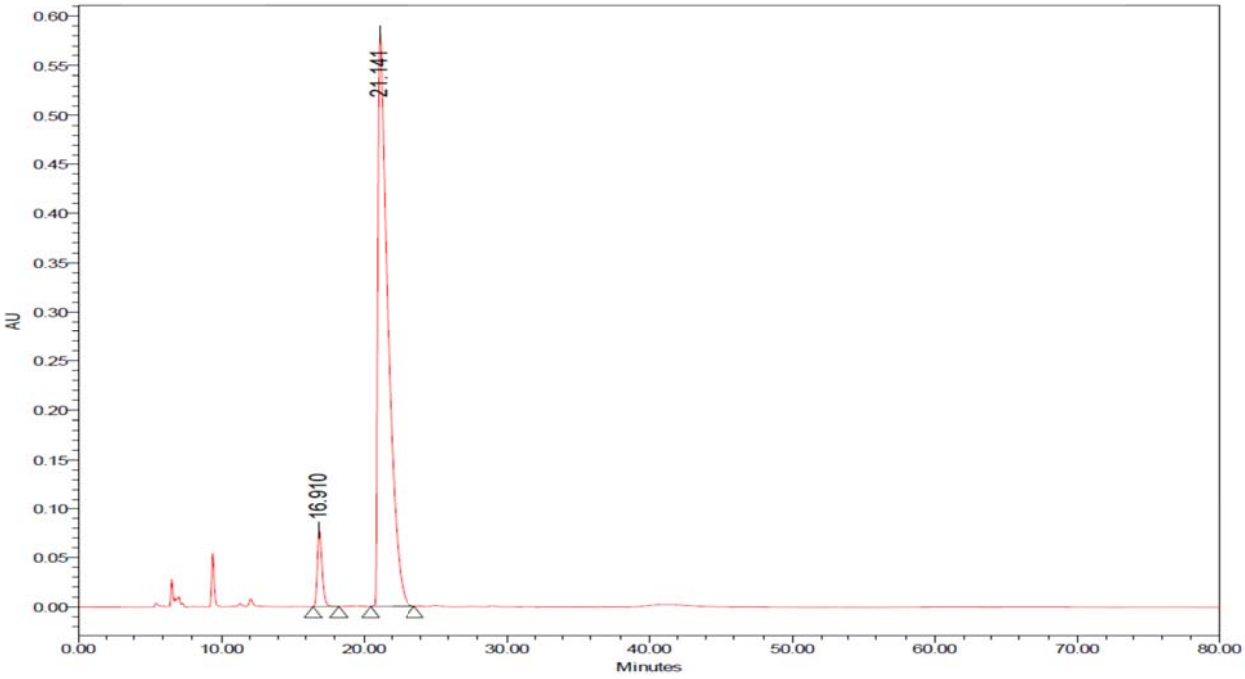

```
                Current Data Parameters
NAME            Jack-02-149-1
EXPNO                       4
PROCNO                      1

            F2 - Acquisition Parameters
Date_               20110704
Time                   11.15
INSTRUM                spect
PROBHD     BBIz 5mm Z8107
PULPROG             cosy45
TD                    1024
SOLVENT              CDCl3
NS                          4
DS                         16
SWH               3698.225 Hz
FIDRES            3.611548 Hz
AQ                0.1384948 sec
RG                         16
DW                  135.200 usec
DE                    6.00 usec
TE                   301.5 K
d0                0.00000300 sec
D1                2.00000000 sec
IN0               0.00027040 sec

            ======== CHANNEL f1 ========
NUC1                       1H
P1                    12.60 usec
PL1                    0.00 dB
SFO1          500.1321330 MHz

            F1 - Acquisition parameters
NDO                         1
TD                        180
SFO1                500.13 MHz
FIDRES            20.545694 Hz
SW                 7.395 ppm
FnMODE            undefined

            F2 - Processing parameters
SI                        1024
SF                500.1300114 MHz
WDW                       SINE
SSB                          0
LB                    0.00 Hz
GB                           0
PC                        1.00

            F1 - Processing parameters
SI                         512
MC2                         GF
SF                500.1278840 MHz
WDW                       SINE
SSB                          0
LB                    0.00 Hz
GB                           0

            2D NMR plot parameters
CX2                      15.00 cm
CX1                      15.00 cm
F2PLO                     7.939 ppm
F2LO                   3970.66 Hz
F2PHI                     0.545 ppm
F2HI                    272.44 Hz
F1PLO                     7.928 ppm
F1LO                   3965.10 Hz
F1PHI                     0.534 ppm
F1HI                    266.88 Hz
F2PPMCM                0.49297 ppm/cm
F2HZCM               246.54832 Hz/cm
F1PPMCM                0.49297 ppm/cm
F1HZCM               246.54834 Hz/cm
```




```
                Current Data Parameters
NAME            Jack-02-149-1
EXPNO                       5
PROCNO                      1

            F2 - Acquisition Parameters
Date_               20110704
Time                   11.42
INSTRUM                spect
PROBHD     BBIz 5mm Z8107
PULPROG             noesytp
TD                    1024
SOLVENT              CDCl3
NS                          8
DS                         16
SWH               3698.225 Hz
FIDRES            3.611548 Hz
AQ                0.1384948 sec
RG                         16
DW                  135.200 usec
DE                    6.00 usec
TE                   300.5 K
d0                0.00000300 sec
D1                2.00000000 sec
D8                0.72000003 sec
IN0               0.00013520 sec

            ======== CHANNEL f1 ========
NUC1                       1H
P1                    12.60 usec
PL1                    0.00 dB
SFO1          500.1321330 MHz

            F1 - Acquisition parameters
NDO                         2
TD                        180
SFO1                500.1321 MHz
FIDRES            20.545694 Hz
SW                 7.394 ppm
FnMODE            undefined

            F2 - Processing parameters
SI                        1024
SF                500.1300114 MHz
WDW                       SINE
SSB                          2
LB                    0.00 Hz
GB                           0
PC                        1.00

            F1 - Processing parameters
SI                         512
MC2                       TPPI
SF                500.1300165 MHz
WDW                       SINE
SSB                          2
LB                    0.00 Hz
GB                           0

            2D NMR plot parameters
CX2                      15.00 cm
CX1                      15.00 cm
F2PLO                     7.939 ppm
F2LO                   3970.66 Hz
F2PHI                     0.545 ppm
F2HI                    272.44 Hz
F1PLO                     7.929 ppm
F1LO                   3965.65 Hz
F1PHI                     0.535 ppm
F1HI                    267.43 Hz
F2PPMCM                0.49297 ppm/cm
F2HZCM               246.54832 Hz/cm
F1PPMCM                0.49297 ppm/cm
F1HZCM               246.54832 Hz/cm
```

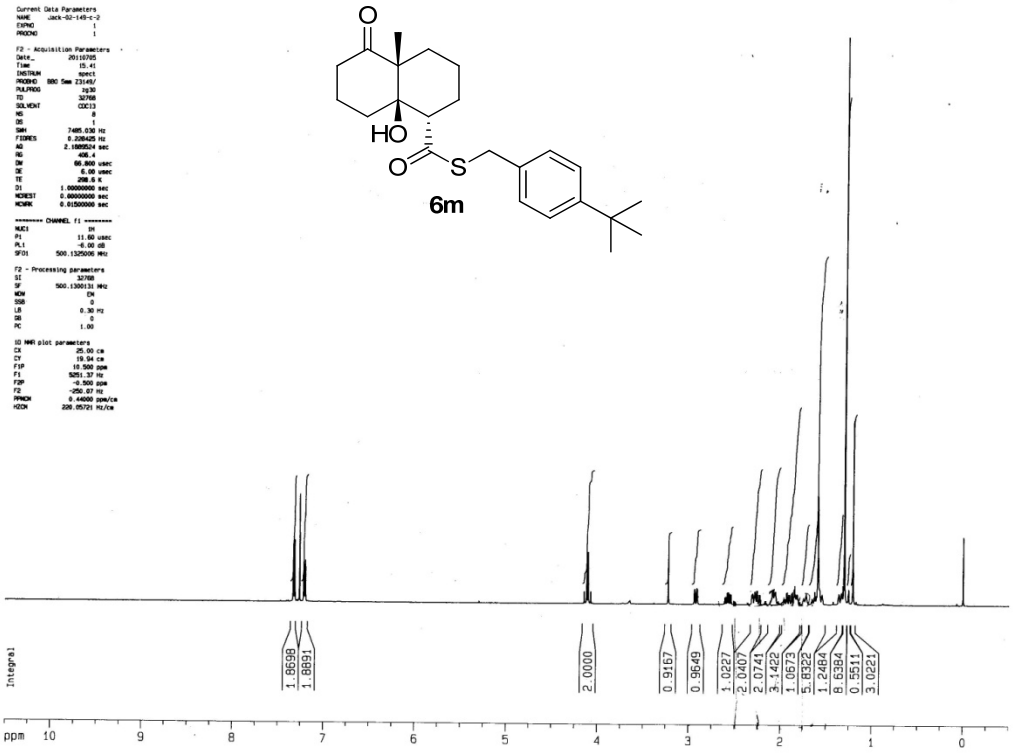
HPLC data for**4m**

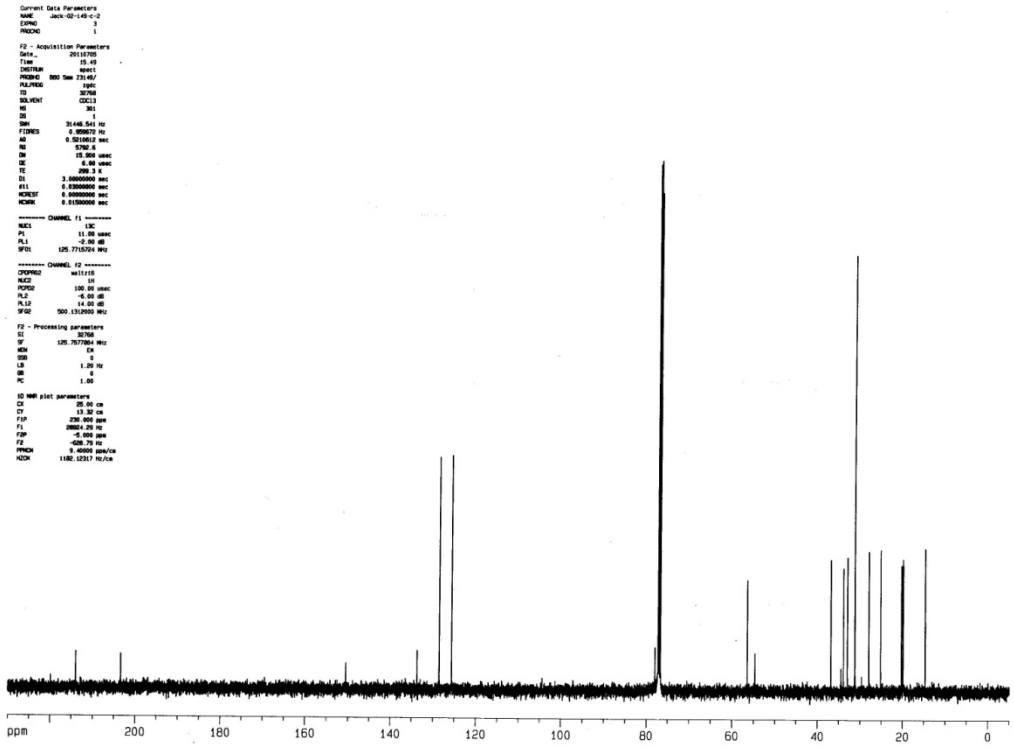


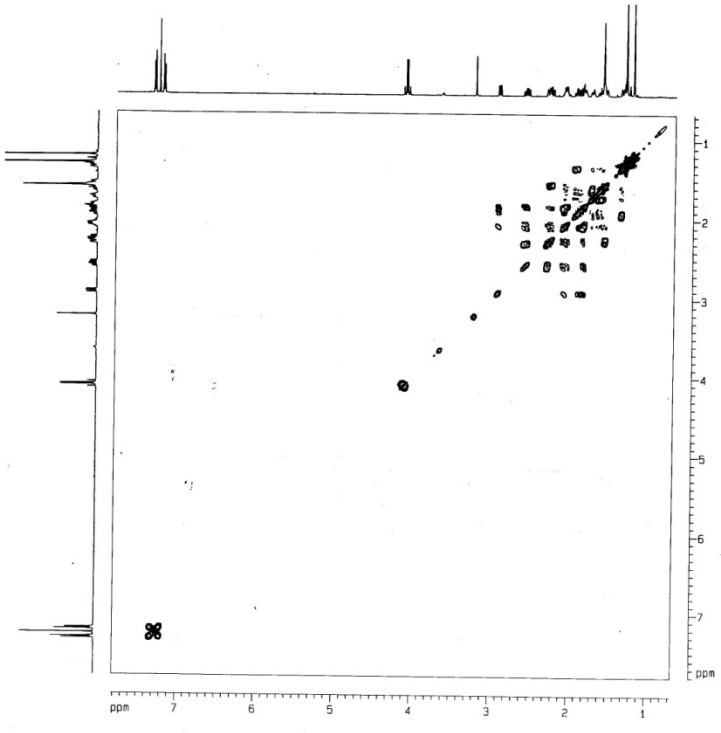


Peak Summary with Statistics
Peak Name:

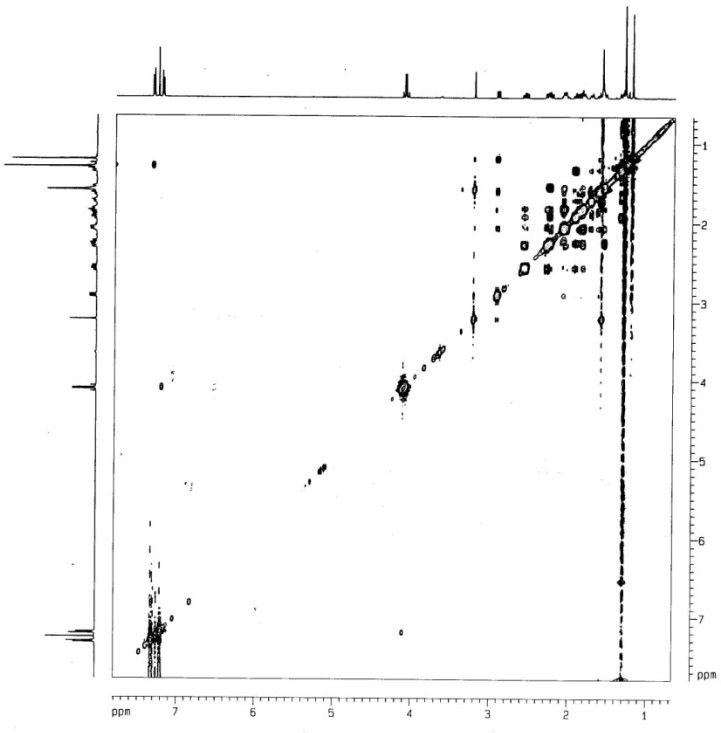
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-149-C-1	1:d,4	1	21.141	28743386	94.29	581074
2	02-149-C-1	1:d,4	1	16.910	1740957	5.71	77202
Mean				19.025	15242171.221		329138.242
Std. Dev.				2.992	19093600.450		356291.21
% RSD				15.73	125.27		108.250





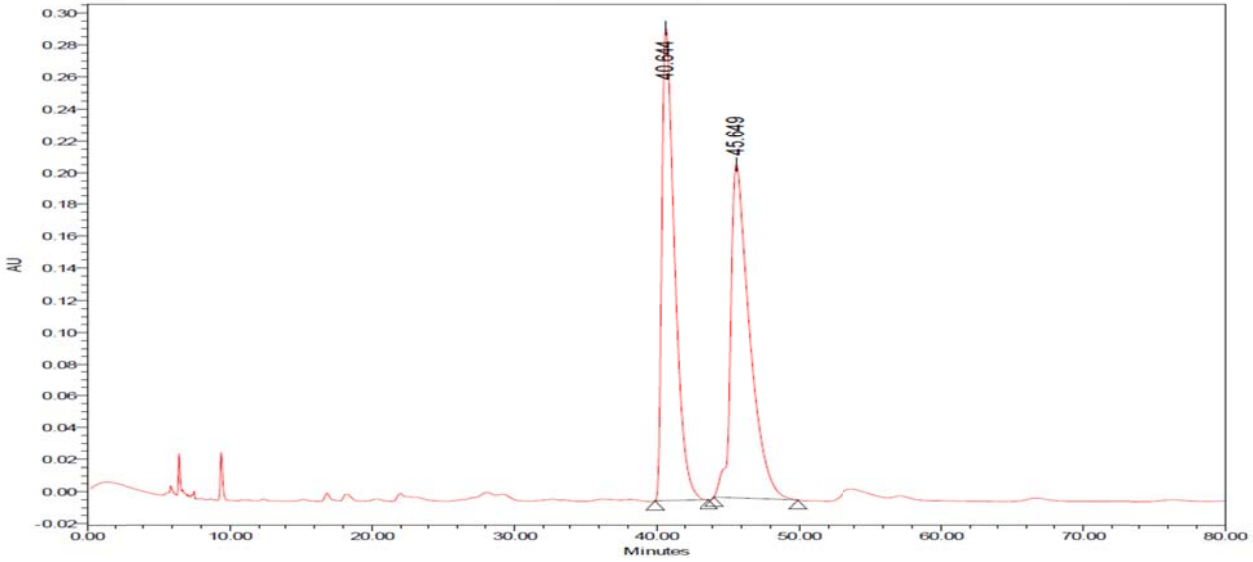


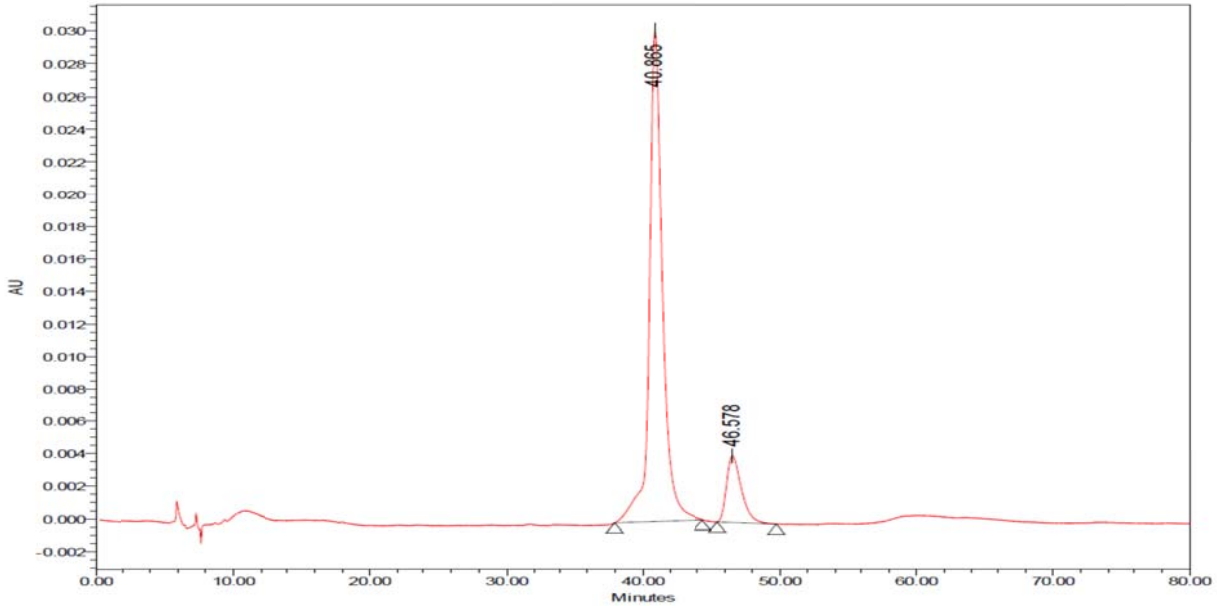

```
                Current Data Parameters
NAME            Jack-02-149-c-2
EXPNO                         4
PROCNO                        1

                F2 - Acquisition Parameters
Date_                  20110705
Time                      16.05
INSTRUM                   spect
PROBHD     BBO 5mm Z3145/
PULPROG                 cosy45
TD                        1024
SOLVENT                   CDCl3
NS                            4
DS                           16
SWH                    3571.426 Hz
FIDRES                 3.487723 Hz
AQ                     0.1434100 sec
RG                        406.4
DW                     140.000 usec
DE                       6.00 usec
TE                       299.1 K
d0                     0.00000300 sec
D1                     2.00000000 sec
IN0                    0.00028000 sec

                ======== CHANNEL f1 ========
NUC1                          1H
P1                         12.00 usec
PL1                        -6.00 dB
SFO1                  500.1321320 MHz

                F1 - Acquisition parameters
NDO                           1
TD                          220
SFO1                   500.13 MHz
FIDRES                 16.233767 Hz
SW                        7.141 ppm
FnMODE                undefined

                F2 - Processing parameters
SI                         1024
SF                  500.1300104 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00

                F1 - Processing parameters
SI                          512
MC2                          QF
SF                  500.1278839 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0

                2D NMR plot parameters
CX2                       15.00 cm
CX1                       15.00 cm
F2PLO                     7.813 ppm
F2LO                   3907.36 Hz
F2PHI                     0.672 ppm
F2HI                    335.93 Hz
F1PLO                     7.802 ppm
F1LO                   3901.78 Hz
F1PHI                     0.661 ppm
F1HI                    330.35 Hz
F2PPMCM                0.47607 ppm/cm
F2HZCM                 238.09523 Hz/cm
F1PPMCM                0.47607 ppm/cm
F1HZCM                 238.09525 Hz/cm
```




```
                Current Data Parameters
NAME            Jack-02-149-c-2
EXPNO                         5
PROCNO                        1

                F2 - Acquisition Parameters
Date_                  20110706
Time                      9.17
INSTRUM                   spect
PROBHD     BBO 5mm Z3145/
PULPROG                 noesytp
TD                        1024
SOLVENT                   CDCl3
NS                            8
DS                           16
SWH                    3571.426 Hz
FIDRES                 3.487723 Hz
AQ                     0.1434100 sec
RG                        406.4
DW                     140.000 usec
DE                       6.00 usec
TE                       298.7 K
d0                     0.00000300 sec
D1                     2.00000000 sec
D8                     0.64999998 sec
IN0                    0.00014000 sec

                ======== CHANNEL f1 ========
NUC1                          1H
P1                         12.00 usec
PL1                        -6.00 dB
SFO1                  500.1321320 MHz

                F1 - Acquisition parameters
NDO                           2
TD                          220
SFO1                   500.1321 MHz
FIDRES                 16.233767 Hz
SW                        7.141 ppm
FnMODE                undefined

                F2 - Processing parameters
SI                         1024
SF                  500.1300114 MHz
WDW                        SINE
SSB                           2
LB                         0.00 Hz
GB                            0
PC                         1.00

                F1 - Processing parameters
SI                          512
MC2                        TPPI
SF                  500.1300186 MHz
WDW                        SINE
SSB                           2
LB                         0.00 Hz
GB                            0

                2D NMR plot parameters
CX2                       15.00 cm
CX1                       15.00 cm
F2PLO                     7.811 ppm
F2LO                   3906.28 Hz
F2PHI                     0.670 ppm
F2HI                    334.86 Hz
F1PLO                     7.796 ppm
F1LO                   3899.07 Hz
F1PHI                     0.655 ppm
F1HI                    327.64 Hz
F2PPMCM                0.47607 ppm/cm
F2HZCM                 238.09523 Hz/cm
F1PPMCM                0.47607 ppm/cm
F1HZCM                 238.09523 Hz/cm
```

HPLC data for **6m**

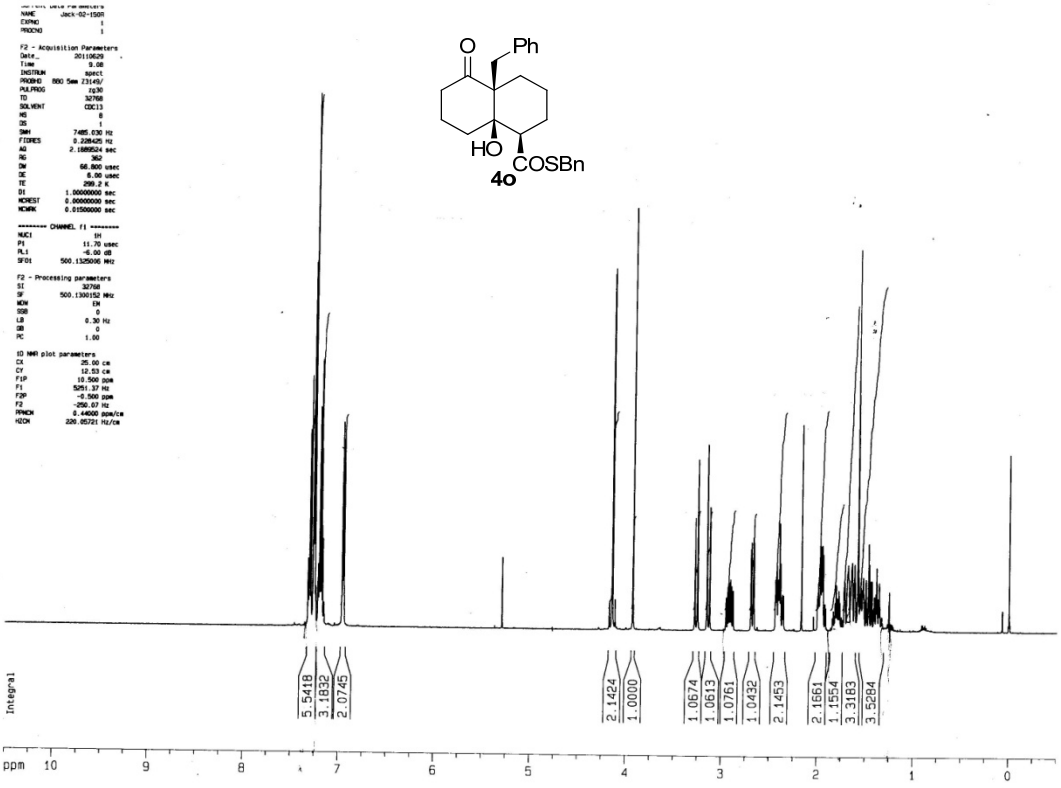


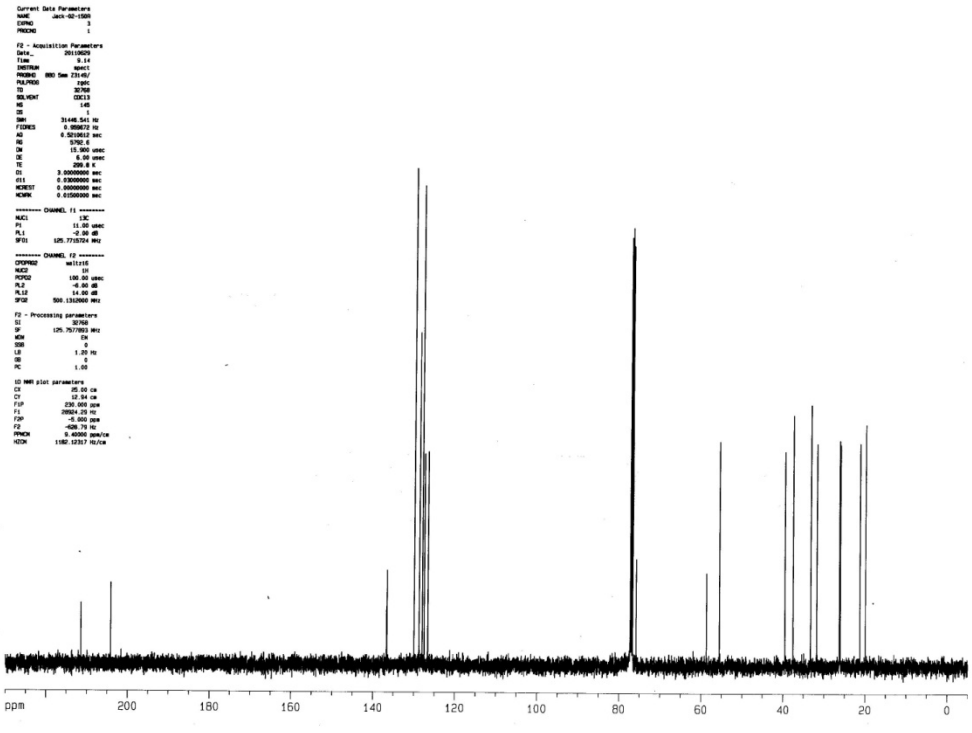


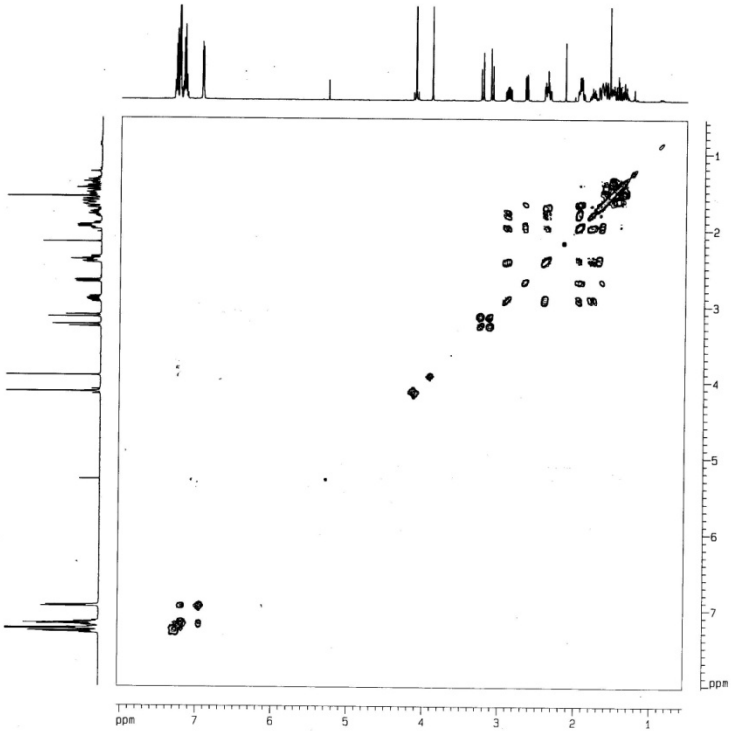
Peak Summary with Statistics

Peak Name:

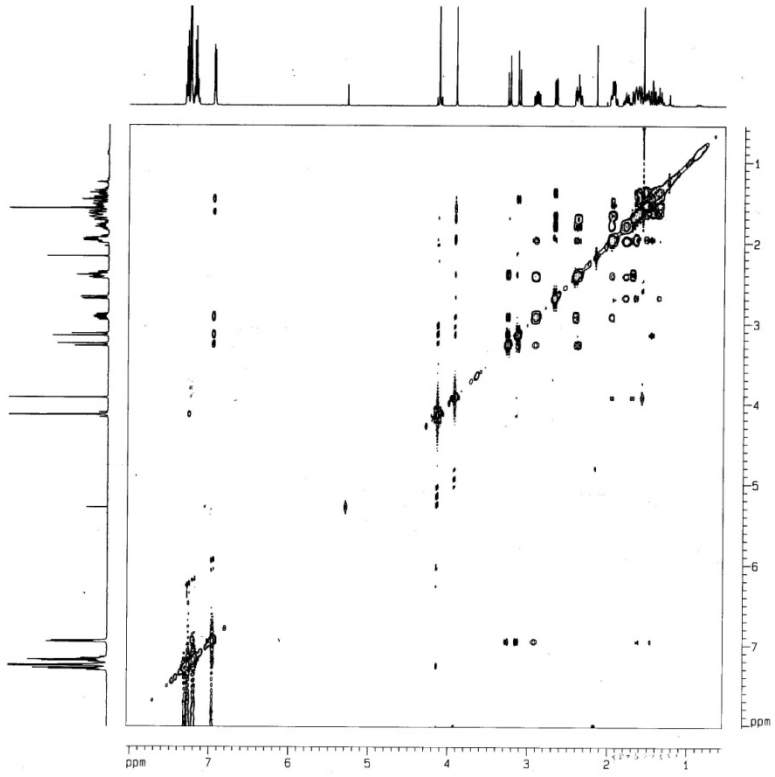
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-149-C-2	1:d,6	1	46.578	302759	13.16	4098
2	02-149-C-2	1:d,6	1	40.865	1998293	86.84	30219
Mean				43.722	1150525.885		17158.500
Std. Dev.				4.040	1198923.290		18470.99
% RSD				9.24	104.21		107.649


O
Ph
HO
COSBn
4o
Integral
5.5418
3.1832
2.0745
2.1424
1.0000
1.0674
1.0613
1.0761
1.0432
2.1453
2.1661
1.1554
3.3183
3.5284
ppm


ppm

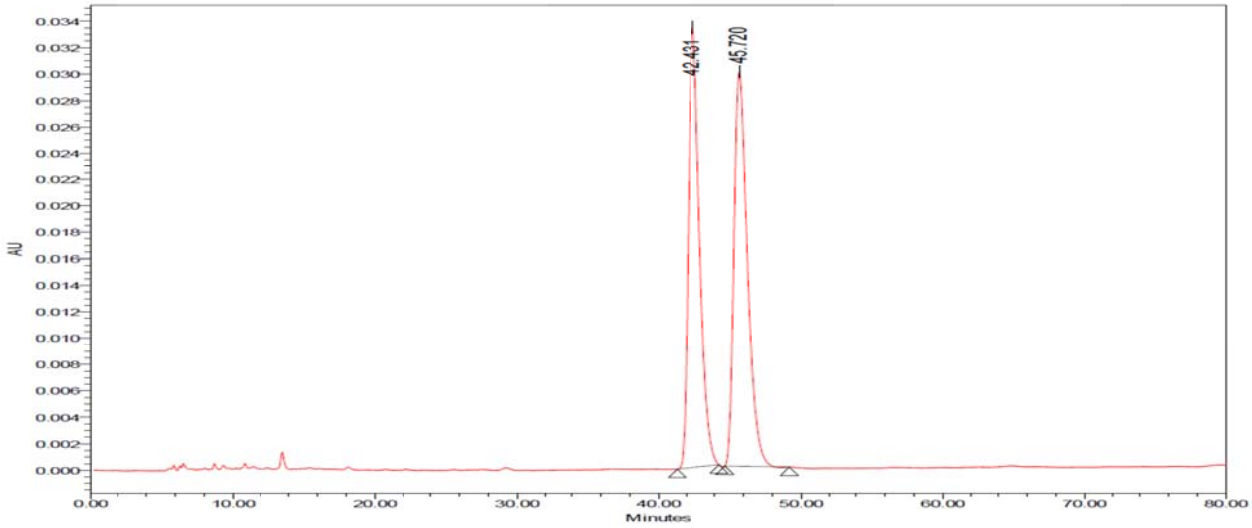


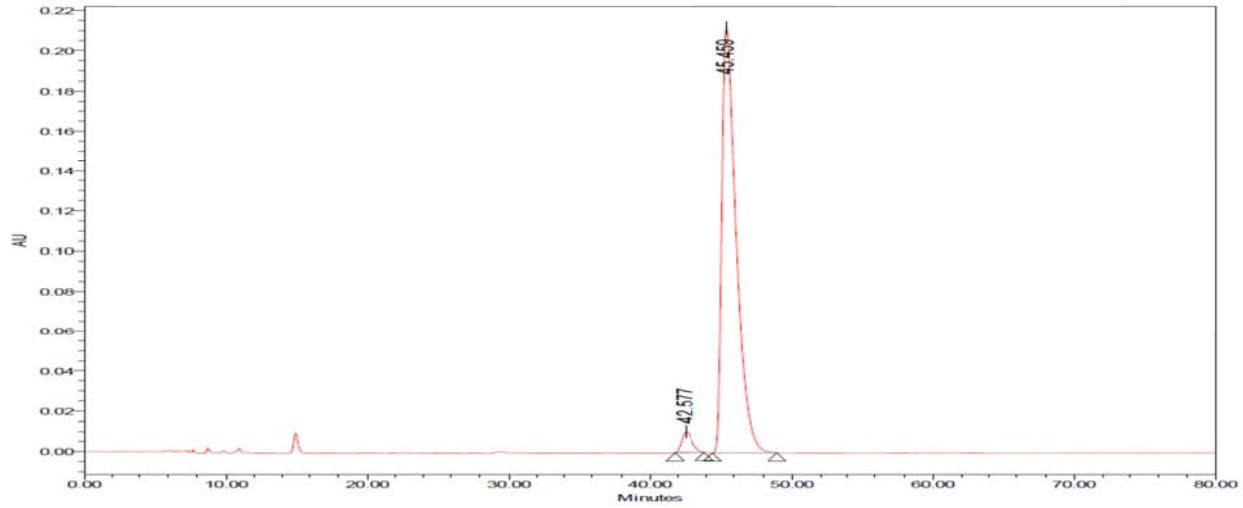

```
Current Data Parameters
NAME                 Jack-02-150R
EXPNO                           4
PROCNO                          1

F2 - Acquisition Parameters
Date_               20110629
Time                    9.21
INSTRUM                 spect
PROBHD     BBO 5mm Z3149/
PULPROG             cosy45
TD                        1024
SOLVENT                   CDCl3
NS                           4
DS                          16
SWH                 3742.515 Hz
FIDRES              3.654800 Hz
AQ                  0.13685564 sec
RG                         362
DW                  133.600 usec
DE                    6.00 usec
TE                    299.7 K
d0                  0.00000300 sec
D1                  2.00000000 sec
INO                 0.00026720 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.10 usec
PL1                     -6.00 dB
SFO1                500.1321630 MHz

F1 - Acquisition parameters
NDO                         1
TD                        221
SFO1                500.13 MHz
FIDRES              16.934458 Hz
SW                     7.483 ppm
FnMODE              undefined

F2 - Processing parameters
SI                        1024
SF                  500.1300133 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                         512
MC2                         QF
SF                  500.1278550 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0

2D NMR plot parameters
CX2                      15.00 cm
CX1                      15.00 cm
F2PLO                    8.040 ppm
F2LO                  4020.98 Hz
F2PHI                    0.557 ppm
F2HI                   278.47 Hz
F1PLO                    8.031 ppm
F1LO                  4016.30 Hz
F1PHI                    0.547 ppm
F1HI                   273.79 Hz
F2PPMCM              0.49887 ppm/cm
F2HZCM             249.50099 Hz/cm
F1PPMCM              0.49887 ppm/cm
```




```
Current Data Parameters
NAME                 Jack-02-150R
EXPNO                           5
PROCNO                          1

F2 - Acquisition Parameters
Date_               20110629
Time                    9.54
INSTRUM                 spect
PROBHD     BBO 5mm Z3149/
PULPROG             noesytp
TD                        1024
SOLVENT                   CDCl3
NS                           8
DS                          16
SWH                 3742.515 Hz
FIDRES              3.654800 Hz
AQ                  0.13685564 sec
RG                         362
DW                  133.600 usec
DE                    6.00 usec
TE                    299.3 K
d0                  0.00000300 sec
D1                  2.00000000 sec
D8                  0.55000001 sec
INO                 0.00013360 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.10 usec
PL1                     -6.00 dB
SFO1                500.1321630 MHz

F1 - Acquisition parameters
NDO                         2
TD                        200
SFO1                500.1322 MHz
FIDRES              18.712574 Hz
SW                     7.483 ppm
FnMODE              undefined

F2 - Processing parameters
SI                        1024
SF                  500.1300134 MHz
WDW                       SINE
SSB                          2
LB                        0.00 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                         512
MC2                       TPPI
SF                  500.1300171 MHz
WDW                       SINE
SSB                          2
LB                        0.00 Hz
GB                           0

2D NMR plot parameters
CX2                      15.00 cm
CX1                      15.00 cm
F2PLO                    8.040 ppm
F2LO                  4020.91 Hz
F2PHI                    0.557 ppm
F2HI                   278.39 Hz
F1PLO                    8.032 ppm
F1LO                  4017.12 Hz
F1PHI                    0.549 ppm
F1HI                   274.60 Hz
F2PPMCM              0.49887 ppm/cm
F2HZCM             249.50099 Hz/cm
F1PPMCM              0.49887 ppm/cm
```

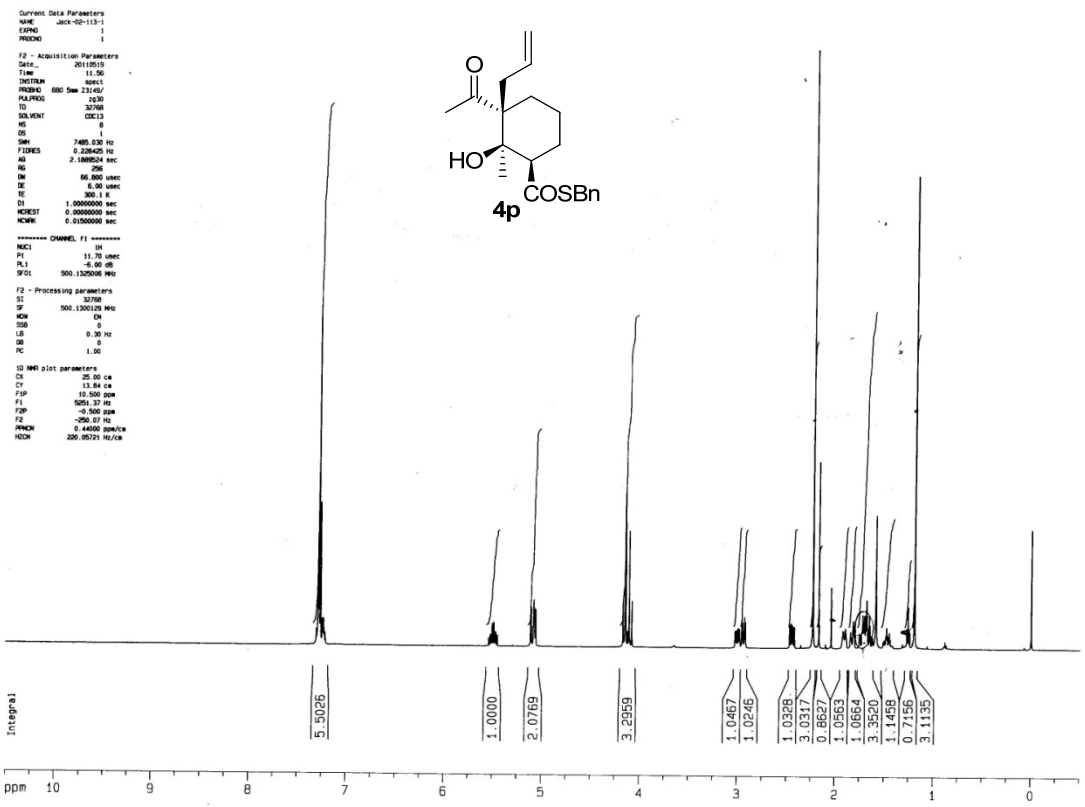
HPLC data for **4o**

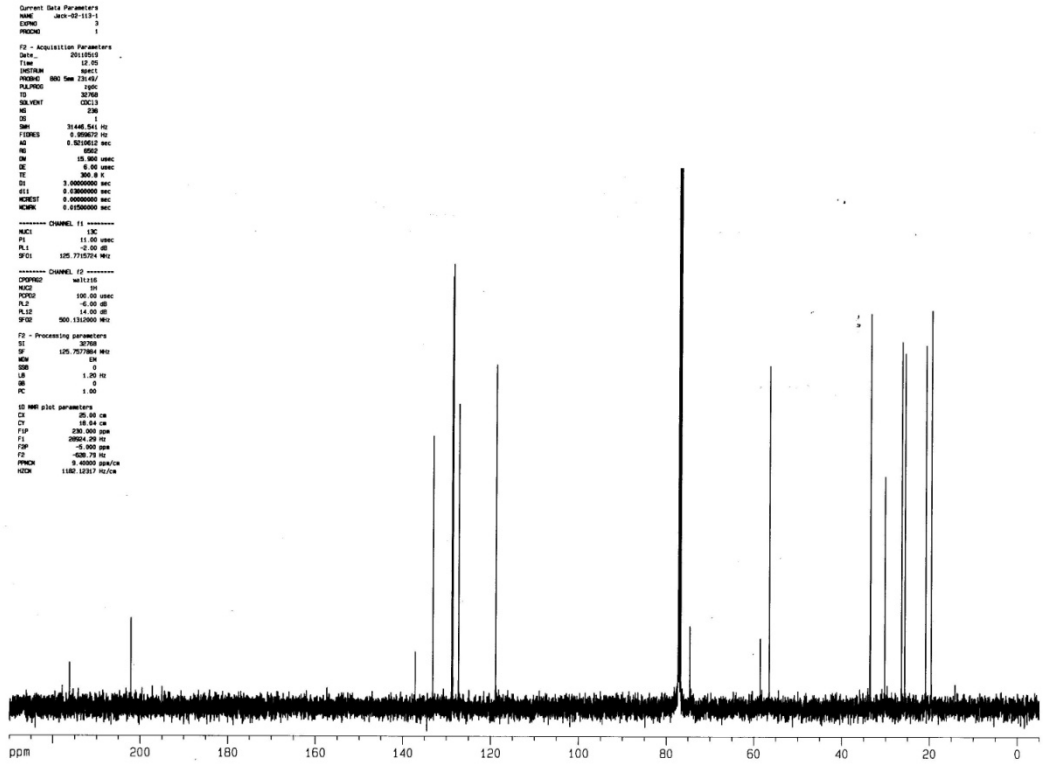


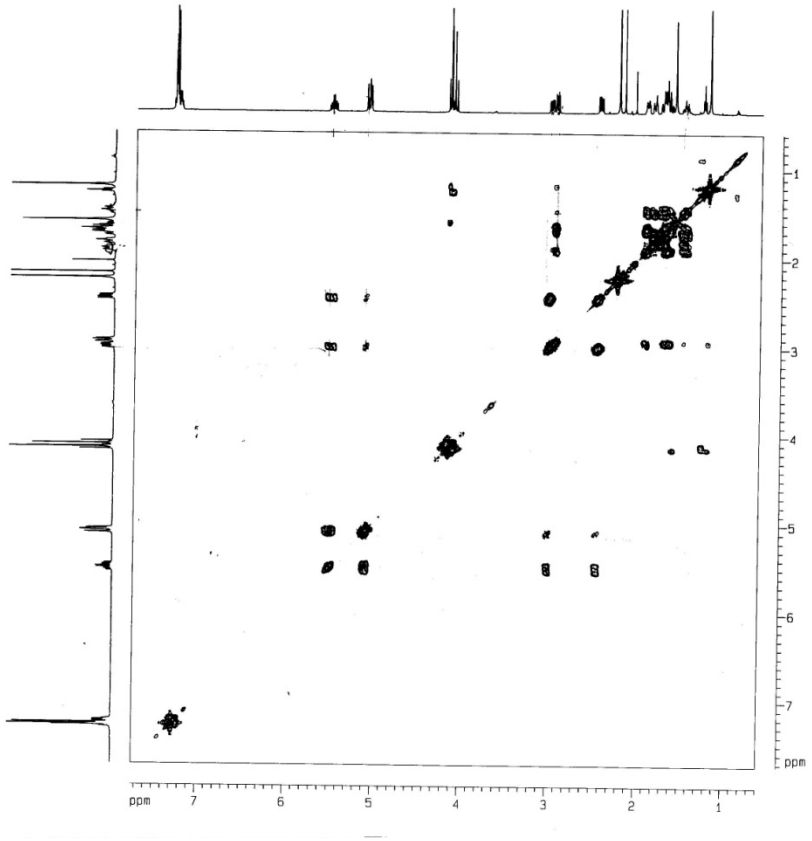


Peak Summary with Statistics
Peak Name:

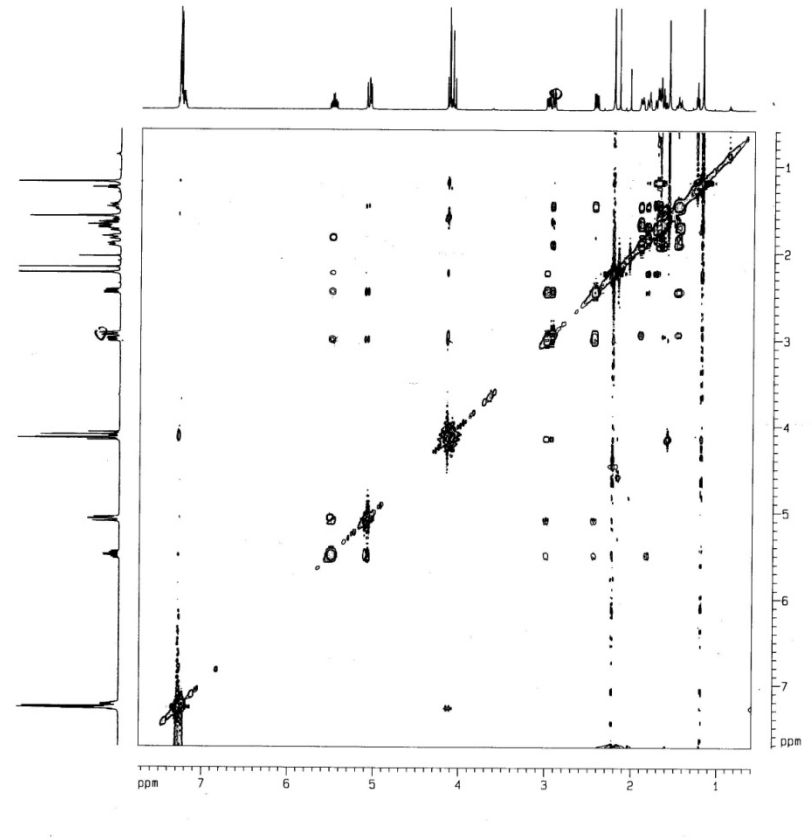
	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	02-122C	1:d,2	1	45.459	14779761	96.36	211945
2	02-122C	1:d,2	1	42.577	557593	3.64	10386
Mean				44.018	7668676.694		111165.607
Std. Dev.				2.038	10056591.265		142523.34
% RSD				4.63	131.14		128.208





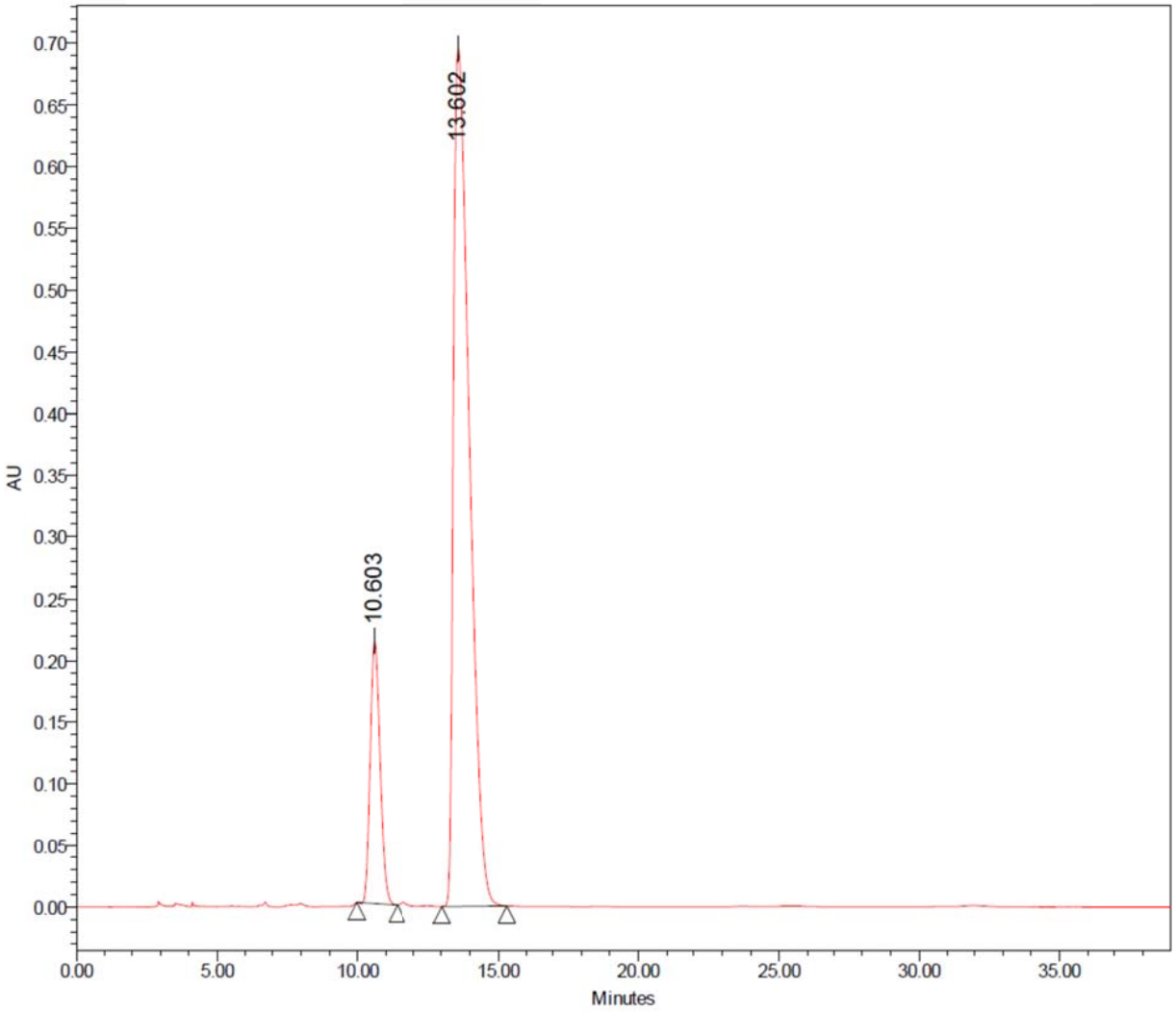



```
                Current Data Parameters
NAME            Jack-02-113-1
EXPNO                       4
PROCNO                      1

                F2 - Acquisition Parameters
Date_                20110519
Time                    12.16
INSTRUM                 spect
PROBHD     BBO 5mm Z3149/
PULPROG                 cosy45
TD                        1024
SOLVENT                 CDCl3
NS                           4
DS                          16
SWH                  3571.428 Hz
FIDRES               3.487723 Hz
AQ                   0.1434100 sec
RG                          256
DW                   140.000 usec
DE                     6.00 usec
TE                     300.5 K
d0                   0.00000300 sec
D1                   2.00000000 sec
IN0                  0.00028000 sec

                ======== CHANNEL f1 ========
NUC1                        1H
P1                     11.60 usec
PL1                    -6.00 dB
SFO1                500.1320950 MHz

                F1 - Acquisition parameters
NO0                         1
TD                        256
SFO1                500.13 MHz
FIDRES              13.950892 Hz
SW                    7.141 ppm
FnMODE              undefined

                F2 - Processing parameters
SI                        1024
SF                  500.1300106 MHz
WDW                     SINE
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.00

                F1 - Processing parameters
SI                         512
MC2                         QF
SF                  500.1279214 MHz
WDW                     SINE
SSB                        0
LB                    0.00 Hz
GB                         0

                2D NMR plot parameters
CX2                   15.00 cm
CX1                   15.00 cm
F2PLO                 7.738 ppm
F2LO                3870.14 Hz
F2PHI                 0.597 ppm
F2HI                 298.71 Hz
F1PLO                 7.727 ppm
F1LO                3864.34 Hz
F1PHI                 0.586 ppm
F1HI                 292.91 Hz
F2PPMCM              0.47607 ppm/cm
F2HZCM             238.09523 Hz/cm
F1PPMCM              0.47607 ppm/cm
F1HZCM             238.09529 Hz/cm
```




```
                Current Data Parameters
NAME            Jack-02-113-1
EXPNO                       5
PROCNO                      1

                F2 - Acquisition Parameters
Date_                20110519
Time                    12.55
INSTRUM                 spect
PROBHD     BBO 5mm Z3149/
PULPROG                 .noesytp
TD                        1024
SOLVENT                 CDCl3
NS                           8
DS                          16
SWH                  3571.428 Hz
FIDRES               3.487723 Hz
AQ                   0.1434100 sec
RG                          256
DW                   140.000 usec
DE                     6.00 usec
TE                     299.6 K
d0                   0.00000300 sec
D1                   2.00000000 sec
D8                   0.80000001 sec
IN0                  0.00014000 sec

                ======== CHANNEL f1 ========
NUC1                        1H
P1                     11.60 usec
PL1                    -6.00 dB
SFO1                500.1320950 MHz

                F1 - Acquisition parameters
NO0                         2
TD                        220
SFO1                500.1321 MHz
FIDRES              16.233767 Hz
SW                    7.141 ppm
FnMODE              undefined

                F2 - Processing parameters
SI                        1024
SF                  500.1300123 MHz
WDW                     SINE
SSB                        2
LB                    0.00 Hz
GB                         0
PC                      1.00

                F1 - Processing parameters
SI                         512
MC2                       TPPI
SF                  500.1300137 MHz
WDW                     SINE
SSB                        2
LB                    0.00 Hz
GB                         0

                2D NMR plot parameters
CX2                   15.00 cm
CX1                   15.00 cm
F2PLO                 7.735 ppm
F2LO                3868.40 Hz
F2PHI                 0.594 ppm
F2HI                 296.98 Hz
F1PLO                 7.732 ppm
F1LO                3867.04 Hz
F1PHI                 0.591 ppm
F1HI                 295.61 Hz
F2PPMCM              0.47607 ppm/cm
F2HZCM             238.09523 Hz/cm
F1PPMCM              0.47607 ppm/cm
F1HZCM             238.09523 Hz/cm
```

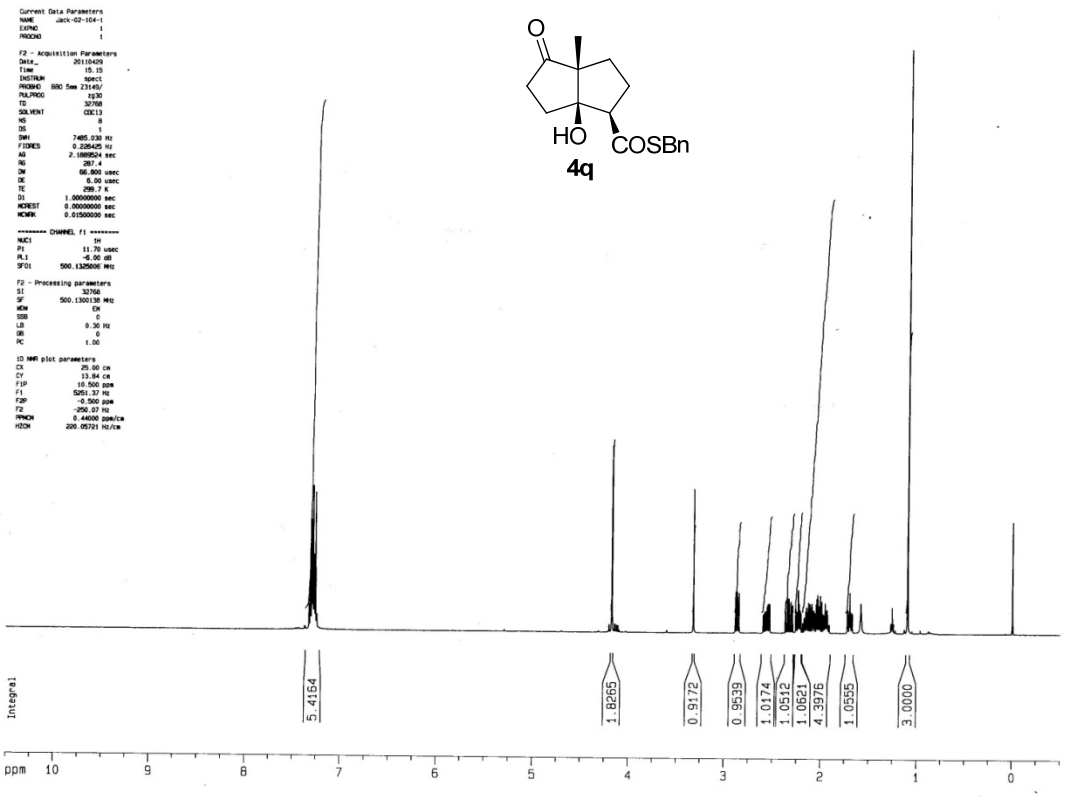
HPLC data for **4p**

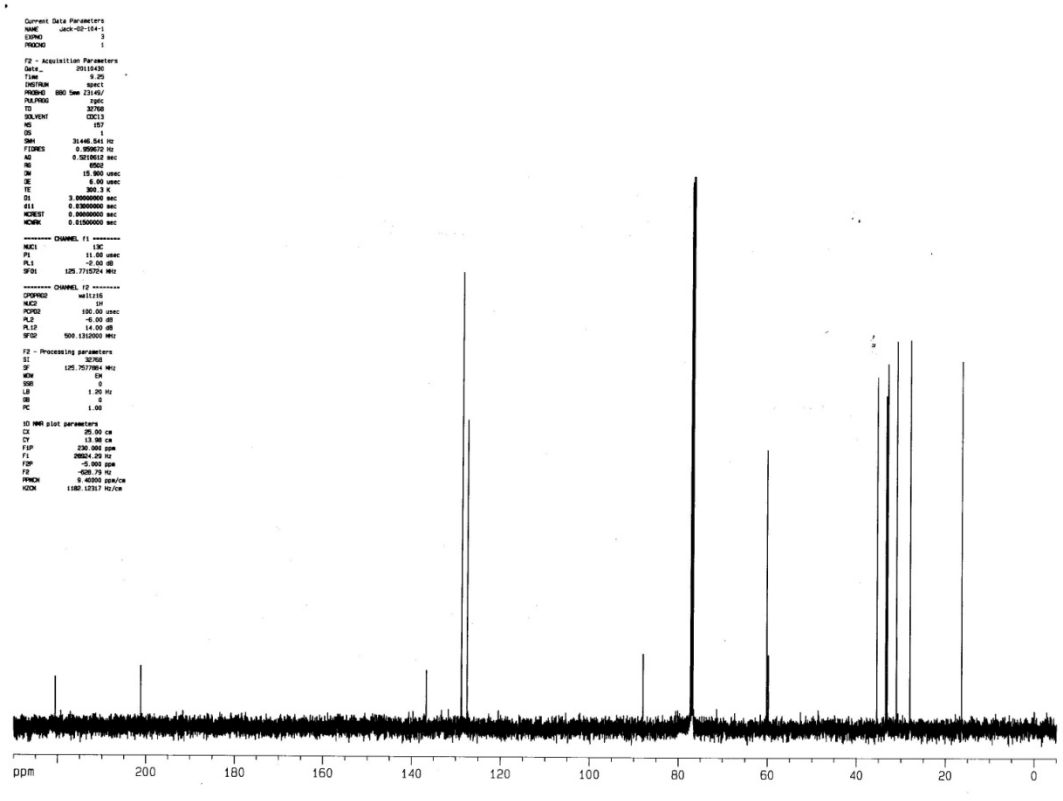


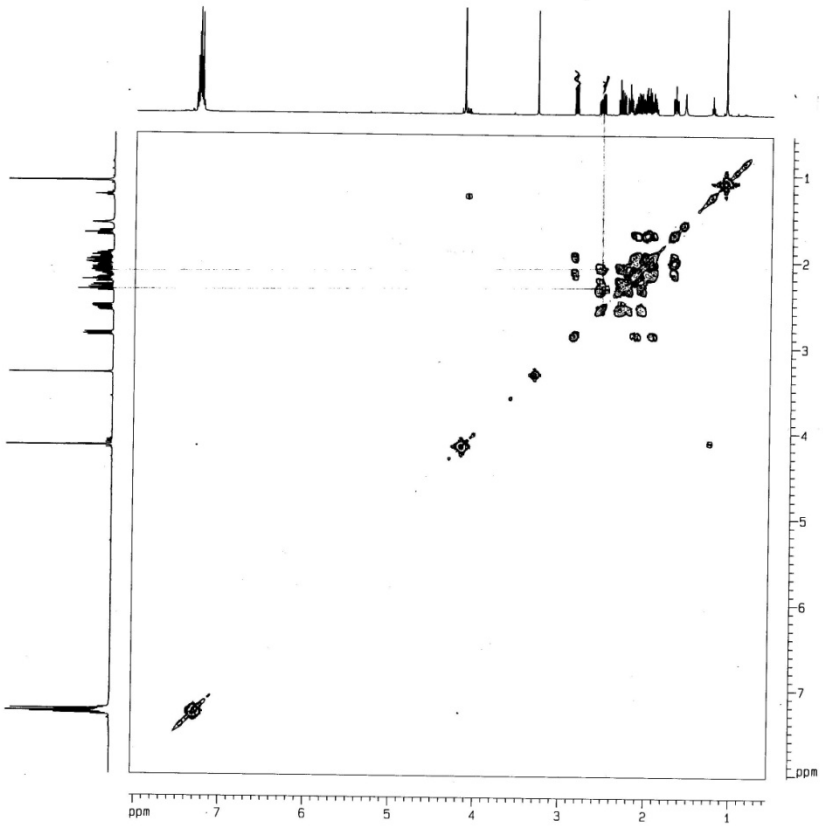
Peak Summary with Statistics

Peak Name:

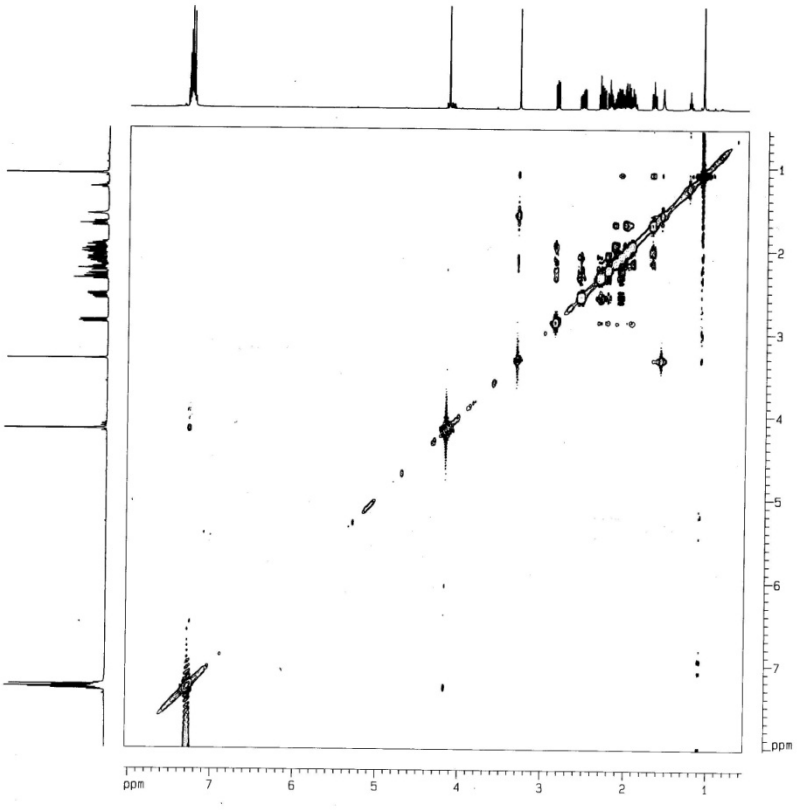
	Sample Name	Vial	Inj	RT (min)	Area (猩*sec)	% Area	Height (猩)
1	02-113-c-1	1:b,3	1	13.602	26939465	83.91	695673
2	02-113-c-1	1:b,3	1	10.603	5165224	16.09	213398
Mean				12.102	16052344.561		454535.593
Std. Dev.				2.121	15396713.679		341020.37
% RSD				17.52	95.92		75.026


O
HO
COSBn
4q
Integral
5.4164
1.8265
0.9172
0.9539
1.0174
1.0512
1.0621
4.3976
1.0555
3.0000
ppm


ppm

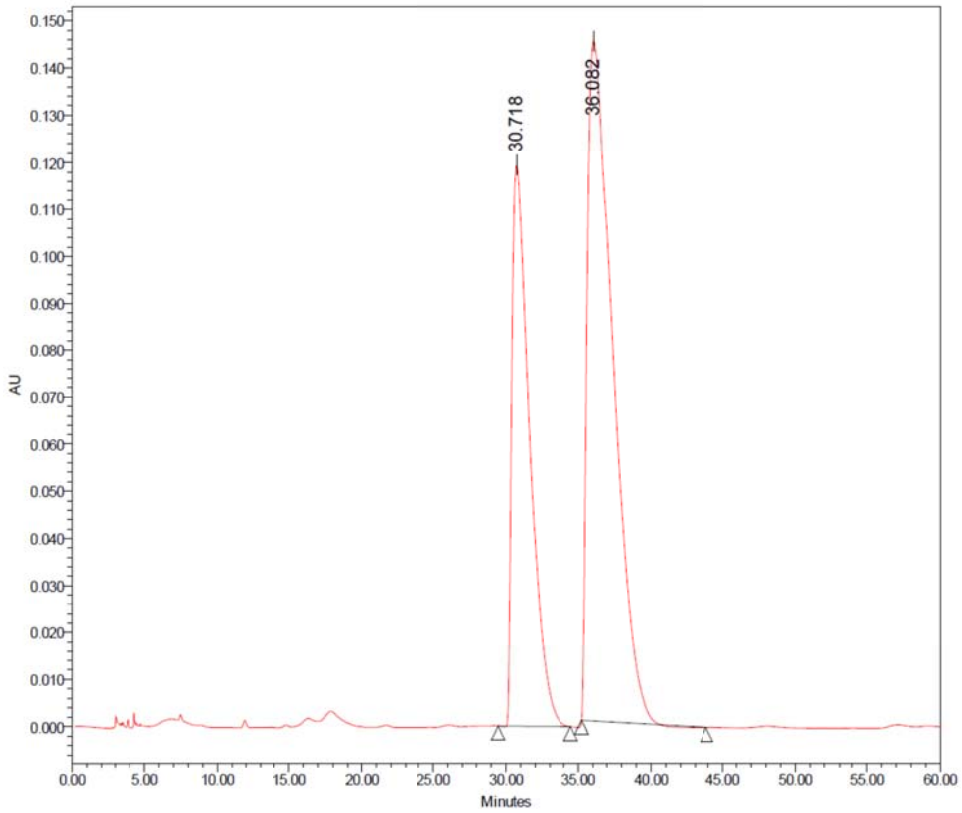



```
Current Data Parameters
NAME            Jack-02-104-1
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_            20110429
Time                16.51
INSTRUM             spect
PROBHD   BBO 5mm Z3149/
PULPROG          cosy45
TD                  1024
SOLVENT             CDCl3
NS                     4
DS                    16
SWH              3742.515 Hz
FIDRES           3.654800 Hz
AQ               0.1368564 sec
RG                  287.4
DW                133.600 usec
DE                  6.00 usec
TE                299.3 K
d0             0.00000300 sec
D1             2.00000000 sec
INO            0.00026720 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.10 usec
PL1                -6.00 dB
SFO1        500.1321610 MHz

F1 - Acquisition parameters
NDO                    1
TD                   202
SFO1          500.13 MHz
FIDRES       18.527302 Hz
SW                7.483 ppm
FnMODE          undefined

F2 - Processing parameters
SI                  1024
SF          500.1300117 MHz
WDW                 SINE
SSB                    0
LB                0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                   512
MC2                   QF
SF          500.1278570 MHz
WDW                 SINE
SSB                    0
LB                0.00 Hz
GB                     0

2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              8.039 ppm
F2LO             4020.56 Hz
F2PHI              0.956 ppm
F2HI              278.04 Hz
F1PLO              8.027 ppm
F1LO             4014.28 Hz
F1PHI              0.543 ppm
F1HI              271.78 Hz
F2PPMCM         0.49887 ppm/cm
F2HZCM        249.50099 Hz/cm
F1PPMCM         0.49887 ppm/cm
F1HZCM        249.50055 Hz/cm
```



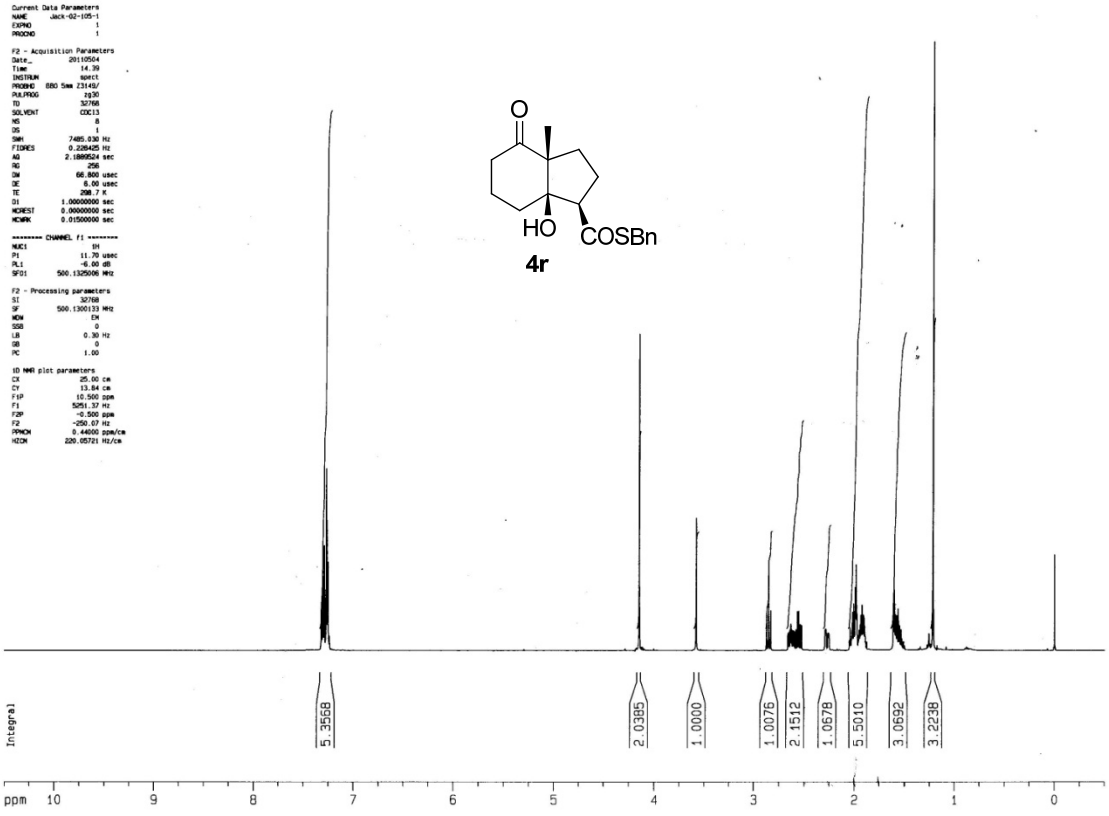

```
Current Data Parameters
NAME            Jack-02-104-1
EXPNO                       5
PROCNO                      1

F2 - Acquisition Parameters
Date_            20110429
Time                15.21
INSTRUM             spect
PROBHD   BBO 5mm Z3149/
PULPROG          noesytp
TD                  1024
SOLVENT             CDCl3
NS                     8
DS                    16
SWH              3742.515 Hz
FIDRES           3.654800 Hz
AQ               0.1368564 sec
RG                  287.4
DW                133.600 usec
DE                  6.00 usec
TE                299.5 K
d0             0.00000300 sec
D1             2.00000000 sec
D8             0.82999998 sec
INO            0.00013360 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.10 usec
PL1                -6.00 dB
SFO1        500.1321610 MHz

F1 - Acquisition parameters
NDO                    2
TD                   324
SFO1          500.1322 MHz
FIDRES       16.707857 Hz
SW                7.483 ppm
FnMODE          undefined

F2 - Processing parameters
SI                  1024
SF          500.1300126 MHz
WDW                 SINE
SSB                    2
LB                0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                   512
MC2                TPPI
SF          500.1300169 MHz
WDW                 SINE
SSB                    2
LB                0.00 Hz
GB                     0

2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              8.037 ppm
F2LO             4019.66 Hz
F2PHI              0.954 ppm
F2HI              277.15 Hz
F1PLO              8.029 ppm
F1LO             4015.35 Hz
F1PHI              0.546 ppm
F1HI              272.84 Hz
F2PPMCM         0.49887 ppm/cm
F2HZCM        249.50099 Hz/cm
F1PPMCM         0.49887 ppm/cm
```

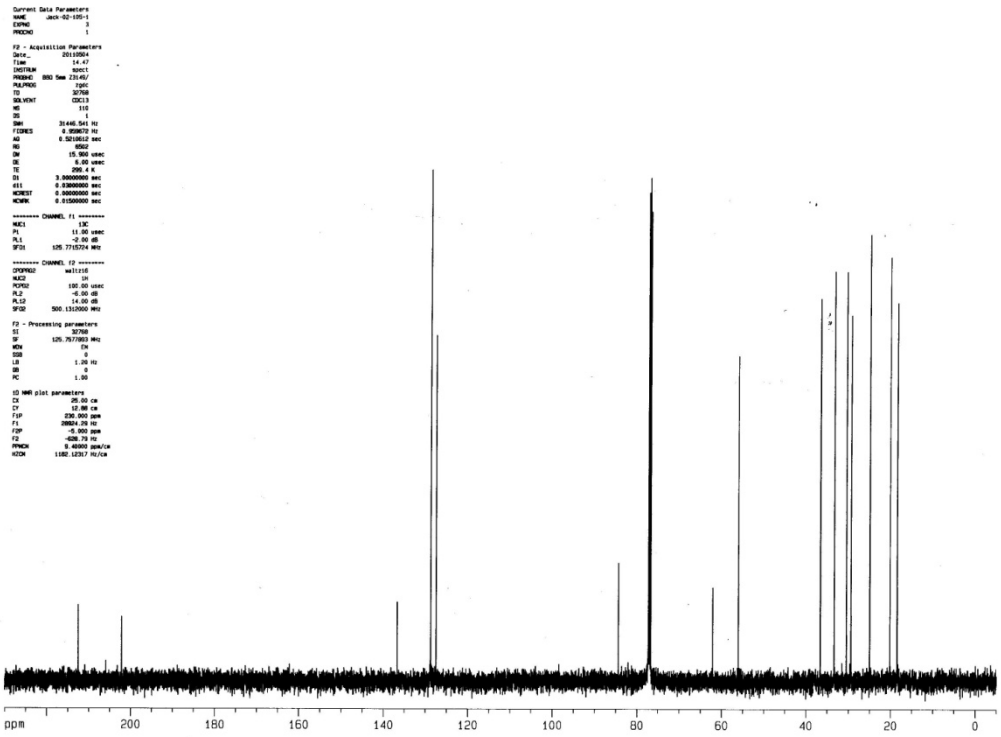
HPLC data of **4r**



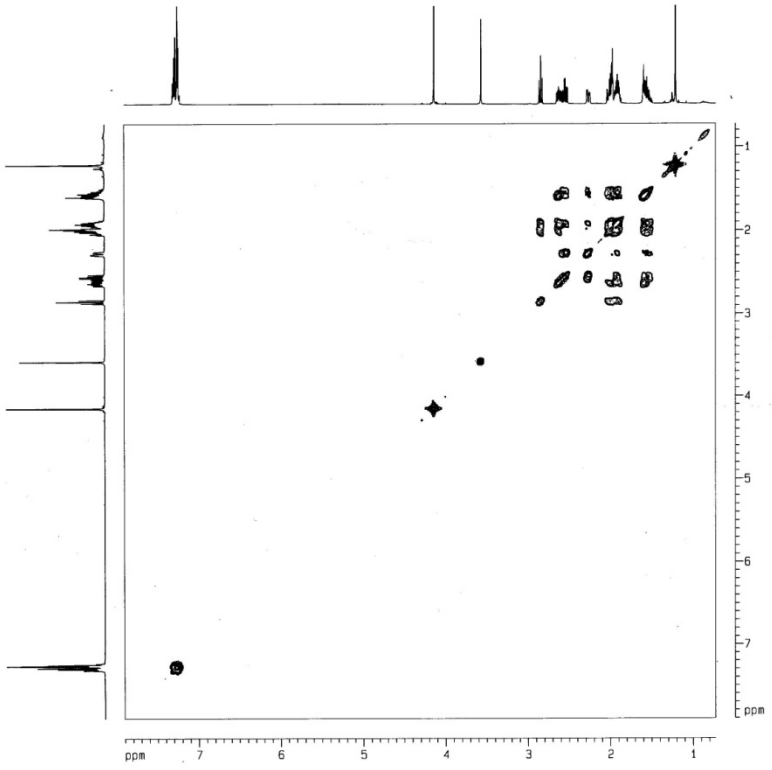
Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (猩*sec)	% Area	Height (猩)
1	02-121-C	1:B,2	1	36.082	17707962	63.47	144627
2	02-121-C	1:B,2	1	30.718	10190904	36.53	119274
Mean				33.400	13949432.977		131950.329
Std. Dev.				3.793	5315362.327		17927.15
% RSD				11.36	38.10		13.586



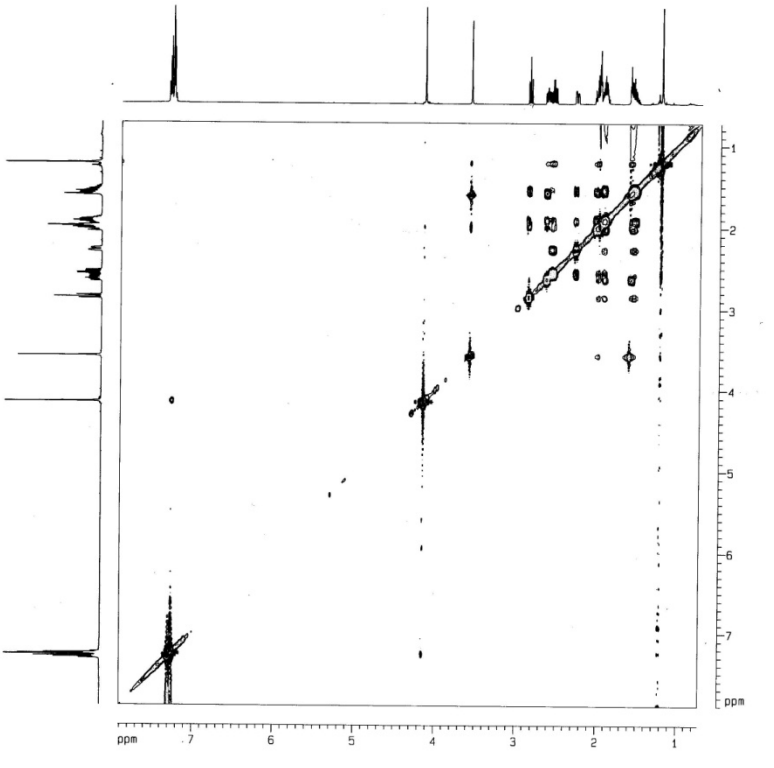


HH-COSY of 4r




```
Current Data Parameters
NAME          Jack-02-105-1
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20110504
Time                  14.52
INSTRUM               spect
PROBHD   BBO 5mm Z3149/
PULPROG             cosy45
TD                    1024
SOLVENT          -  CDCl3
NS                       4
DS                      16
SWH               3591.954 Hz
FIDRES            3.507768 Hz
AQ                0.1425908 sec
RG                      256
DW                139.200 usec
DE                  6.00 usec
TE                  299.3 K
d0                0.00000300 sec
D1                2.00000000 sec
IN0               0.00027840 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.90 usec
PL1                   -6.00 dB
SFO1          500.1321710 MHz

F1 - Acquisition parameters
ND0                       1
TD                      221
SFO1            500.13 MHz
FIDRES          16.253185 Hz
SW                7.182 ppm
FnMODE          undefined

F2 - Processing parameters
SI                     1024
SF          500.1300113 MHz
WDW                    SINE
SSB                       0
LB                 0.00 Hz
GB                        0
PC                     1.00

F1 - Processing parameters
SI                      512
MC2                      QF
SF          500.1278423 MHz
WDW                    SINE
SSB                       0
LB                 0.00 Hz
GB                        0

2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                7.909 ppm
F2LO              3955.70 Hz
F2PHI                0.727 ppm
F2HI               363.75 Hz
F1PLO                7.905 ppm
F1LO              3953.64 Hz
F1PHI                0.723 ppm
F1HI               361.69 Hz
F2PPMCM          0.47880 ppm/cm
F2HZCM         239.46359 Hz/cm
F1PPMCM          0.47880 ppm/cm
F1HZCM         239.46359 Hz/cm
```

NOESY of **4r**

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Current Data Parameters
NAME          Jack-02-105-1
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
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Time                  15.25
INSTRUM               spect
PROBHD   BBO 5mm Z3149/
PULPROG             noesytp
TD                    1024
SOLVENT               CDCl3
NS                        8
DS                       16
SWH               3591.954 Hz
FIDRES            3.507768 Hz
AQ                0.1425908 sec
RG                      256
DW                139.200 usec
DE                  6.00 usec
TE                  298.8 K
d0                0.00000300 sec
D1                2.00000000 sec
D8                0.75000000 sec
IN0               0.00013920 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.90 usec
PL1                   -6.00 dB
SFO1          500.1321710 MHz

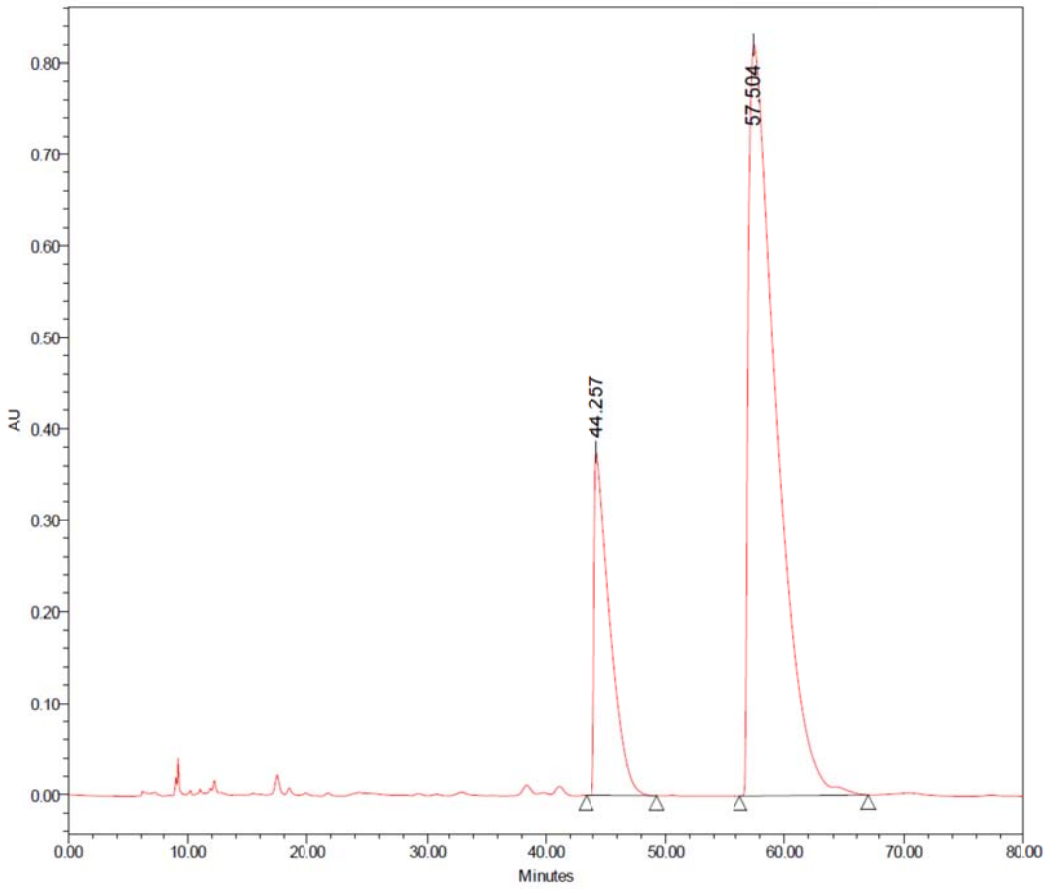
F1 - Acquisition parameters
ND0                       2
TD                      220
SFO1            500.1322 MHz
FIDRES          16.327065 Hz
SW                7.182 ppm
FnMODE          undefined

F2 - Processing parameters
SI                     1024
SF          500.1300106 MHz
WDW                    SINE
SSB                       2
LB                 0.00 Hz
GB                        0
PC                     1.00

F1 - Processing parameters
SI                      512
MC2                    TPPI
SF          500.1300153 MHz
WDW                    SINE
SSB                       2
LB                 0.00 Hz
GB                        0

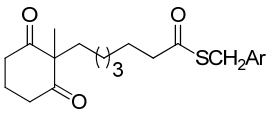
2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                7.911 ppm
F2LO              3956.40 Hz
F2PHI                0.729 ppm
F2HI               364.45 Hz
F1PLO                7.901 ppm
F1LO              3951.72 Hz
F1PHI                0.719 ppm
F1HI               359.77 Hz
F2PPMCM          0.47880 ppm/cm
F2HZCM         239.46359 Hz/cm
F1PPMCM          0.47880 ppm/cm
F1HZCM         239.46359 Hz/cm
```

HPLC data of **4s**

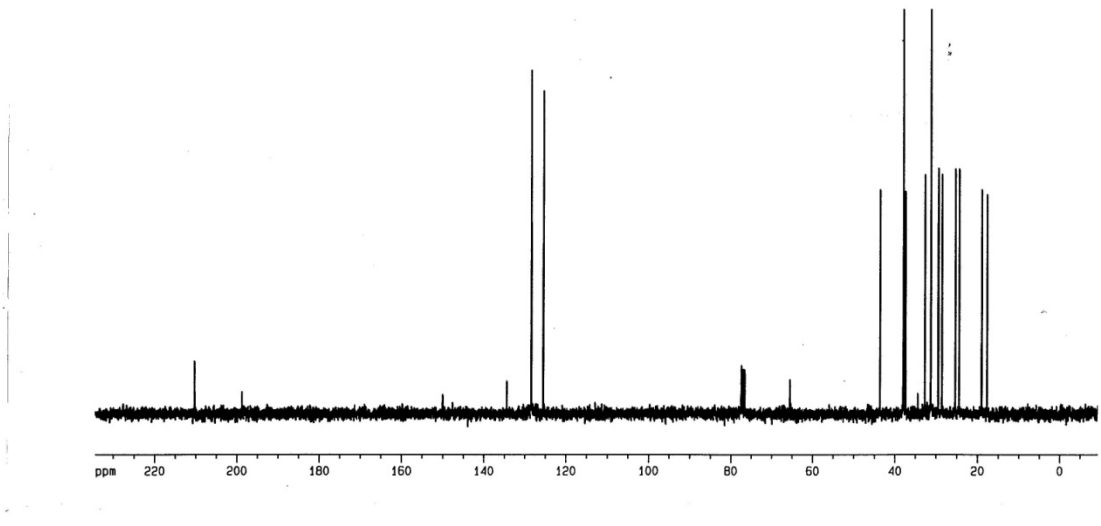


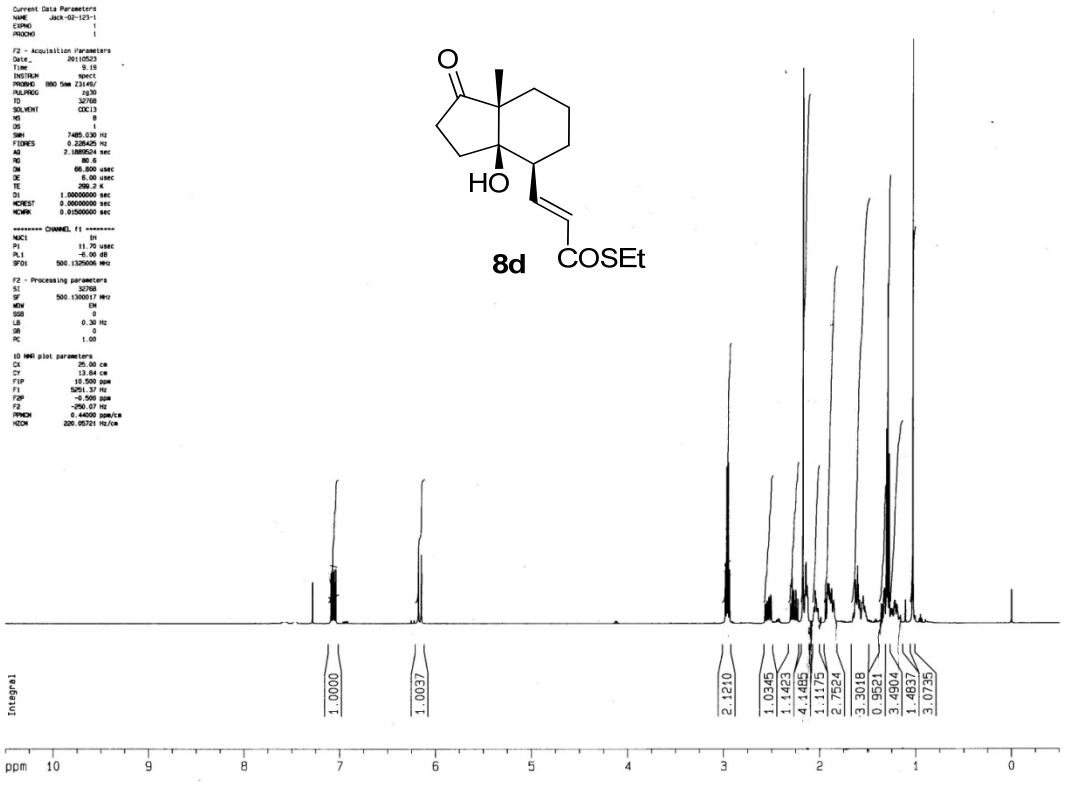
Peak Summary with Statistics
Peak Name:

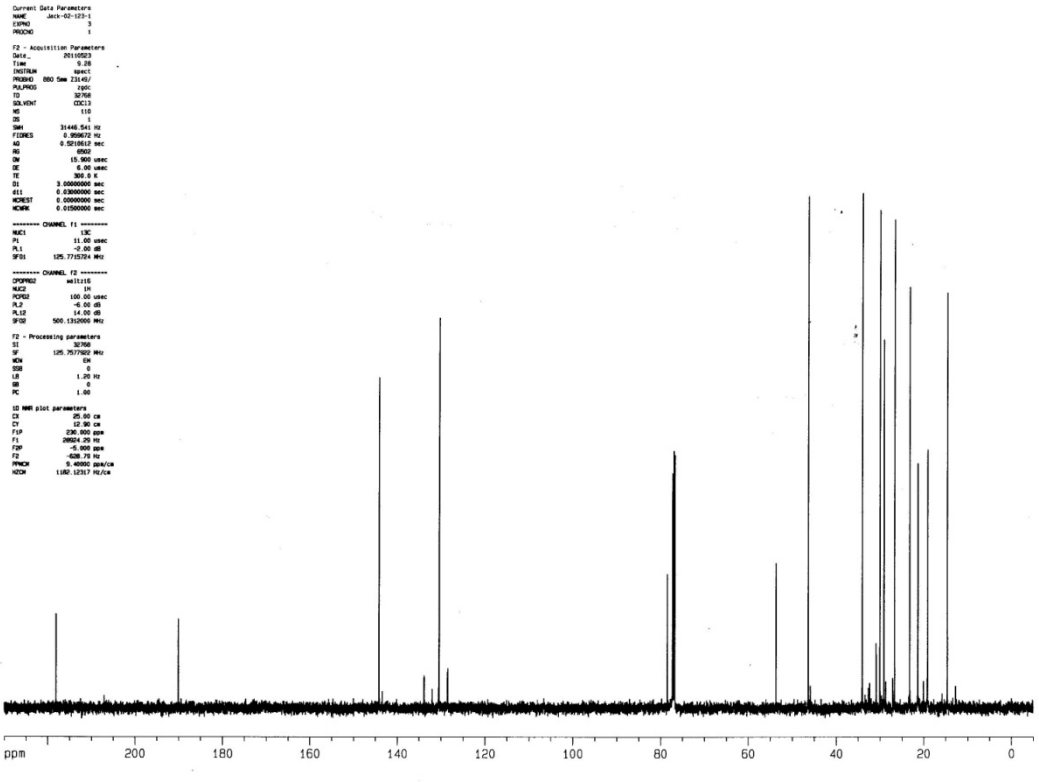
	Sample Name	Vial	Inj.	RT (min)	Area (猩*sec)	% Area	Height (猩)
1	02-120c	1:b,2	1	57.504	132016430	79.71	821253
2	02-120c	1:b,2	1	44.257	33605839	20.29	375321
Mean				50.881	82811134.665		598287.257
Std. Dev.				9.367	69586796.660		315321.43
% RSD				18.41	84.03		52.704

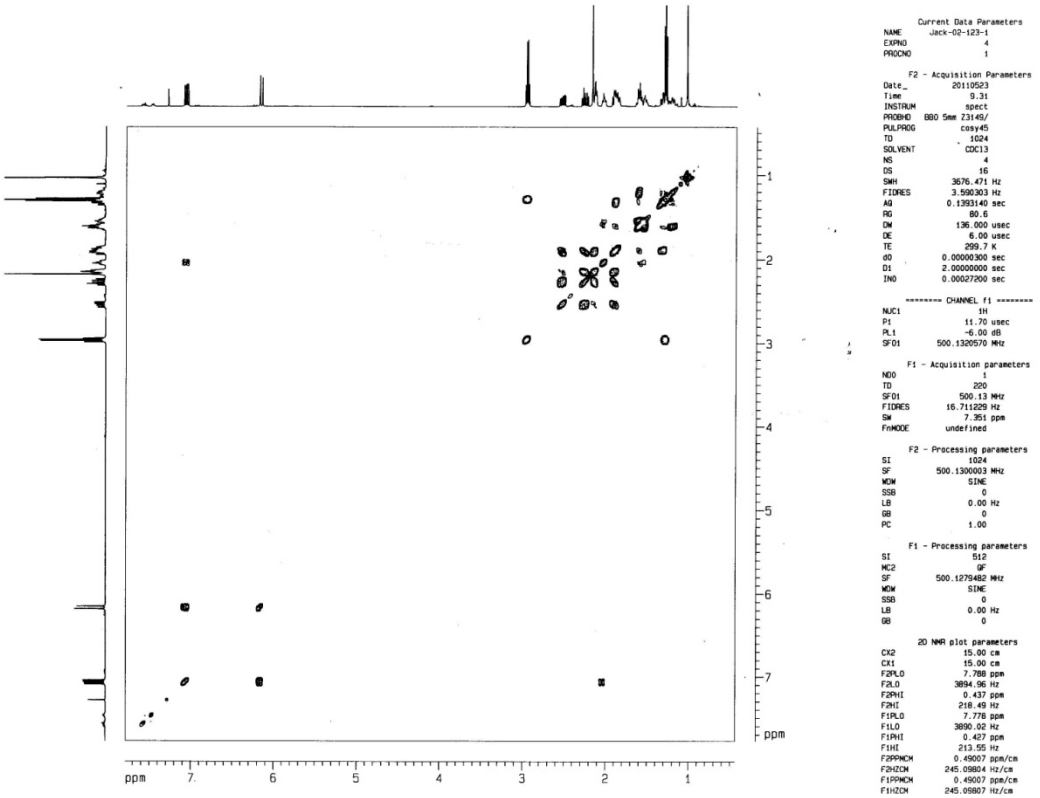


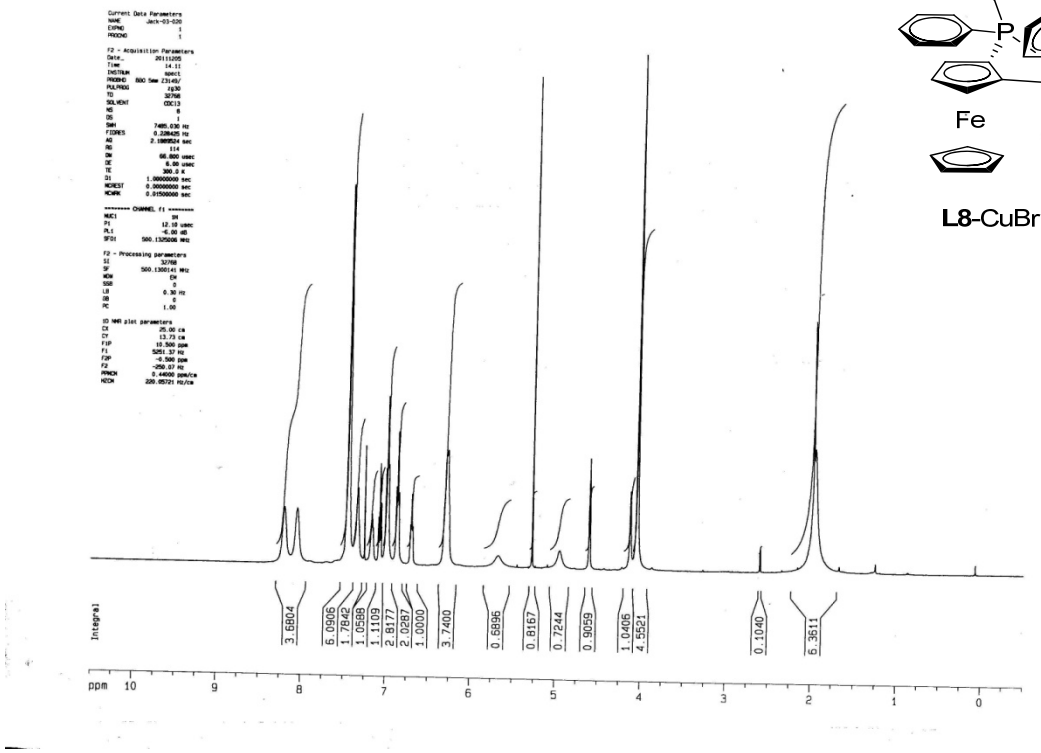
3u-H$_2$ Ar= 4-^{t}BuCH$_4$

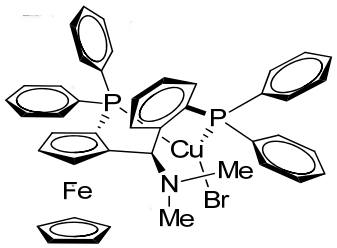




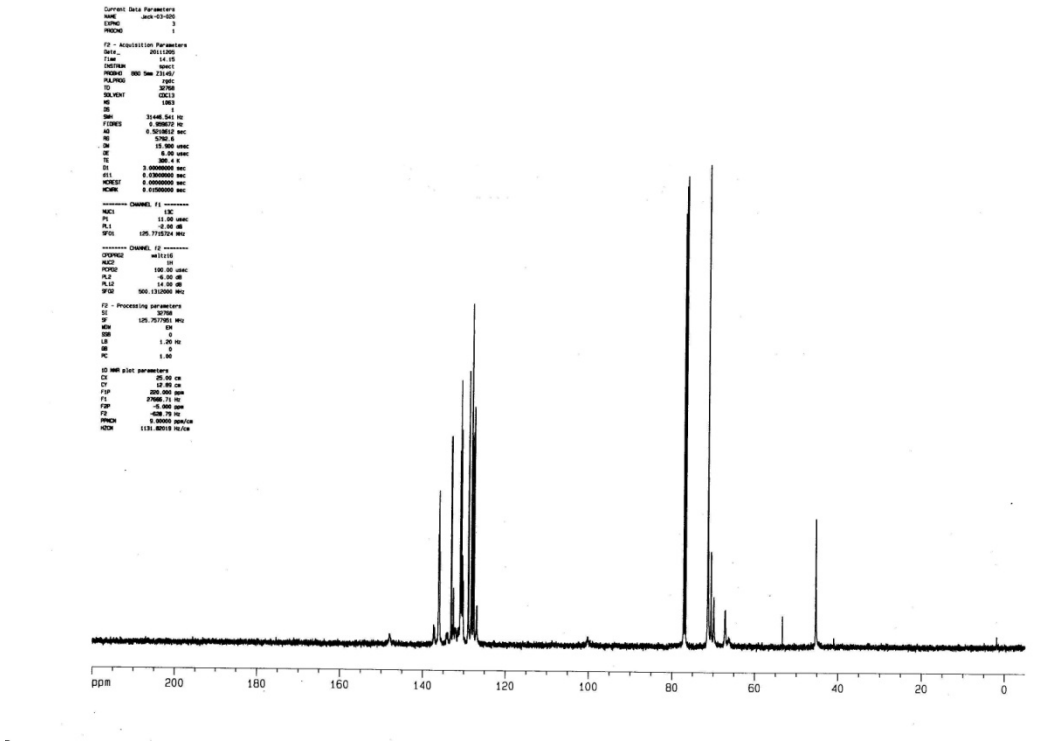




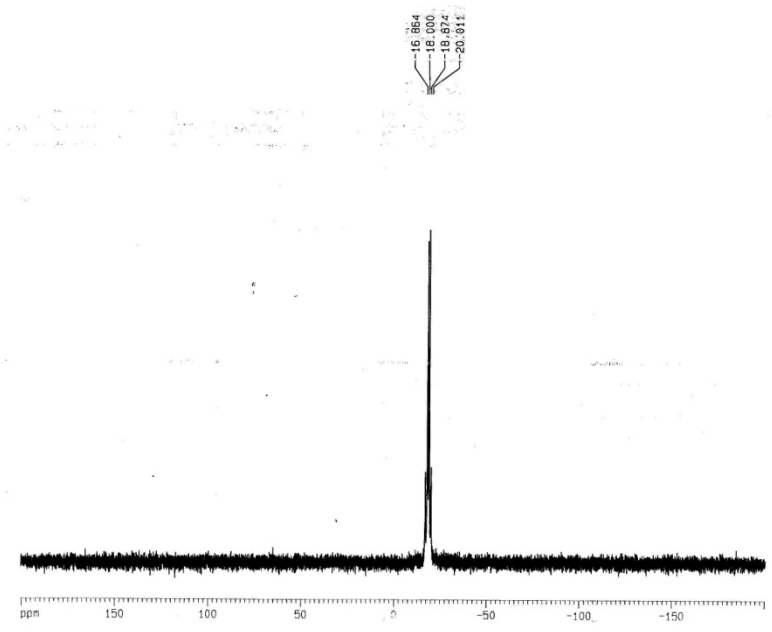




L8-CuBr complex **9**



^{31}P NMR for **L8**-copper bromide complex **9** in $CDCl_3$

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EXPNO
PROCNO

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PULPROG                 zgpg
TD                     32768
SOLVENT                 CDCl3
NS                         20
DS                          0
SWH                64935.066 Hz
FIDRES             1.981661 Hz
AQ                 0.2523636 sec
RG                   10321.3
DW                     7.700 usec
DE                     6.00 usec
TE                     298.6 K
D1                 2.00000000 sec
d11                0.03000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                     31P
P1                      8.80 usec
PL1                    -5.00 dB
SF01             161.9755730 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                  70.00 usec
PL2                    -5.00 dB
PL12                   12.00 dB
SF02             400.1317250 MHz

F2 - Processing parameters
SI                       32768
SF               161.9755740 MHz
WDW                         EM
SSB                          0
LB                      2.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                      20.00 cm
CY                       8.90 cm
F1P                   200.441 ppm
F1                   32466.53 Hz
F2P                  -200.453 ppm
F2                  -32468.53 Hz
PPMCM                20.04471 ppm/cm
HZCM                 3246.75317 Hz/cm
```

Crystallographic Analyses

General: X-ray crystallographic data was either collected on a Bruker *SMART 1000* CCD diffractometer or Bruker *SMART Apex II* CCD diffractometer with graphite monochromated Mo-Kα radiation. Diffraction data were corrected for absorption. The data reduction was performed with either Bruker *SMART*[1] program package or Bruker *APEX*[2] suite package. Structure solutions were found with the SHELXS97[3] package and were refined with SHELXL97[4] package against F^2. All C-bound H-atoms were could be located from difference Fourier map but were placed at calculated positions with C-H = 0.93, 0.96, 0.97 and 0.98Å for vinyl/phenyl, methyl, methylene and methine H-atoms respectively. All C-bound H-atoms were refined using riding model with $U_{iso}(H) = 1.2U_{eq}(Carrier)$. The O-bound hydrogen atoms were located from difference Fourier map and also refined using riding model of $U_{iso}(H) = 1.2U_{eq}(Carrier)$.

[1] Bruker AXS Inc. (2006). *SMART*, Madison, Wisconsin, USA.
[2] Bruker AXS Inc. (2007). *APEX II*, Madison, Wisconsin, USA.
[3] Sheldrick, G.M. (2008). *SHELX* programs. *SHELXL97* & *SHELXS97*. *Acta Cryst*. **E64**, 112-122.
[4] Sheldrick, G.M. (2008). *SHELX* programs. *SHELXL97* & *SHELXS97*. *Acta Cryst*. **E64**, 112-122.

X-ray data for **L8**-copper bromide complex **9**

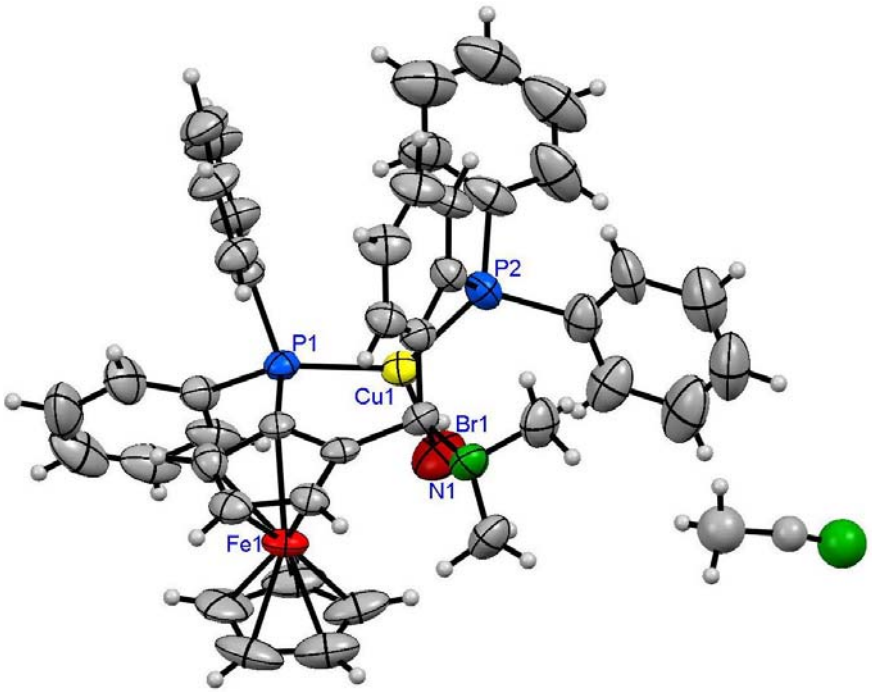


Table 1. Crystal data and structure refinement for PC_03_020.

Identification code	pc_03_020
Empirical formula	C88 H81 Br2 Cu2 Fe2 N3 P4
Formula weight	1703.04
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.3018(3) A alpha = 90 deg. b = 16.8469(5) A beta = 90 deg. c = 25.9616(8) A gamma = 90 deg.
Volume	4068.4(2) A^3
Z, Calculated density	2, 1.390 Mg/m^3
Absorption coefficient	1.971 mm^-1
F(000)	1740
Crystal size	0.52 x 0.40 x 0.36 mm
Theta range for data collection	2.62 to 26.37 deg.
Limiting indices	-11<=h<=11, -21<=k<=20, -32<=l<=32
Reflections collected / unique	47426 / 8295 [R(int) = 0.0634]
Completeness to theta = 26.37	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5371 and 0.4271
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8295 / 57 / 457

Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1375
R indices (all data)	R1 = 0.0811, wR2 = 0.1487
Absolute structure parameter	0.044(15)
Largest diff. peak and hole	0.555 and -0.320 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for PC_03_020. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	1110(1)	-792(1)	4517(1)	59(1)
Cu(1)	-1534(1)	131(1)	3304(1)	54(1)
Br(1)	-2027(1)	-1134(1)	2988(1)	99(1)
P(1)	-1624(2)	428(1)	4148(1)	45(1)
P(2)	-647(2)	1137(1)	2818(1)	58(1)
N(1)	3293(6)	409(3)	3470(2)	63(1)
C(1)	1072(10)	-1737(4)	4014(5)	101(3)
C(2)	2176(11)	-1814(5)	4379(5)	102(3)
C(3)	1587(13)	-1847(4)	4856(5)	110(4)
C(4)	11(13)	-1737(4)	4821(5)	109(3)
C(5)	-235(9)	-1687(4)	4285(5)	91(3)
C(6)	1972(7)	29(3)	5010(3)	63(2)
C(7)	455(7)	117(4)	4955(2)	59(1)
C(8)	140(6)	294(3)	4424(2)	46(1)
C(9)	1499(6)	285(2)	4156(2)	46(1)
C(10)	2577(6)	123(3)	4526(2)	51(1)
C(11)	-2847(6)	-100(3)	4577(3)	58(1)
C(12)	-3449(6)	-812(4)	4411(3)	73(2)
C(13)	-4250(7)	-1252(5)	4762(5)	90(3)
C(14)	-4484(10)	-1017(7)	5239(5)	113(4)
C(15)	-3981(11)	-343(8)	5406(4)	119(4)
C(16)	-3084(8)	158(5)	5080(3)	88(2)
C(17)	-2093(6)	1459(3)	4307(2)	49(1)
C(18)	-3493(7)	1692(4)	4202(3)	71(2)
C(19)	-3901(9)	2469(5)	4293(4)	98(3)
C(20)	-2947(10)	2999(4)	4481(4)	92(2)
C(21)	-1570(9)	2760(4)	4603(3)	81(2)
C(22)	-1136(7)	1977(3)	4514(3)	63(2)
C(23)	1775(6)	554(3)	3611(2)	50(1)
C(24)	3547(8)	-434(5)	3374(3)	81(2)
C(25)	3791(8)	865(5)	3023(3)	81(2)
C(26)	1447(6)	1437(3)	3573(2)	51(1)
C(27)	490(6)	1773(4)	3215(2)	55(1)
C(28)	395(8)	2597(4)	3185(3)	71(2)
C(29)	1206(9)	3089(4)	3513(3)	86(2)
C(30)	2060(9)	2763(4)	3870(3)	79(2)
C(31)	2226(7)	1939(4)	3898(3)	61(2)
C(32)	-2062(8)	1781(4)	2567(3)	78(2)

C(33)	-2409(10)	1790(7)	2045(4)	116(4)
C(34)	-3619(13)	2210(8)	1886(5)	136(5)
C(35)	-4452(13)	2616(8)	2243(6)	130(4)
C(36)	-4117(12)	2597(7)	2746(6)	130(4)
C(37)	-2917(9)	2173(5)	2910(4)	99(3)
C(38)	477(8)	932(4)	2260(3)	77(2)
C(39)	625(8)	144(5)	2099(3)	94(2)
C(40)	1562(11)	-28(9)	1687(4)	134(5)
C(41)	2282(14)	596(8)	1457(4)	131(4)
C(42)	2084(12)	1376(8)	1597(4)	124(4)
C(43)	1196(9)	1549(6)	2021(3)	95(3)
N(1A)	5678(17)	-673(10)	1132(6)	100(4)
C(1A)	5765(13)	-403(7)	1520(5)	54(3)
C(2A)	5780(20)	-187(11)	2008(7)	95(5)

Table 3. Bond lengths [A] and angles [deg] for PC_03_020.

Fe(1)-C(7)	2.002(6)
Fe(1)-C(2)	2.019(8)
Fe(1)-C(3)	2.033(7)
Fe(1)-C(6)	2.047(6)
Fe(1)-C(4)	2.051(8)
Fe(1)-C(5)	2.051(7)
Fe(1)-C(8)	2.054(5)
Fe(1)-C(10)	2.058(5)
Fe(1)-C(1)	2.061(8)
Fe(1)-C(9)	2.073(5)
Cu(1)-P(1)	2.2484(16)
Cu(1)-P(2)	2.2687(17)
Cu(1)-Br(1)	2.3292(9)
P(1)-C(8)	1.805(6)
P(1)-C(11)	1.824(6)
P(1)-C(17)	1.837(5)
P(2)-C(38)	1.820(7)
P(2)-C(27)	1.824(6)
P(2)-C(32)	1.827(7)
N(1)-C(24)	1.461(9)
N(1)-C(25)	1.468(9)
N(1)-C(23)	1.479(8)
C(1)-C(2)	1.405(14)
C(1)-C(5)	1.407(13)
C(1)-H(1A)	0.9800
C(2)-C(3)	1.356(15)
C(2)-H(2A)	0.9800
C(3)-C(4)	1.480(15)
C(3)-H(3A)	0.9800
C(4)-C(5)	1.414(14)
C(4)-H(4A)	0.9800
C(5)-H(5A)	0.9800
C(6)-C(10)	1.386(9)
C(6)-C(7)	1.426(10)
C(6)-H(6A)	0.9800
C(7)-C(8)	1.440(8)
C(7)-H(7A)	0.9800
C(8)-C(9)	1.443(8)
C(9)-C(10)	1.414(8)
C(9)-C(23)	1.509(8)
C(10)-H(10A)	0.9800
C(11)-C(12)	1.392(9)

C(11)-C(16)	1.394(11)
C(12)-C(13)	1.391(11)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.317(15)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.303(16)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.457(13)
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.9300
C(17)-C(22)	1.359(8)
C(17)-C(18)	1.387(9)
C(18)-C(19)	1.383(10)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.351(12)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.380(12)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.398(9)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-C(26)	1.521(8)
C(23)-H(23A)	0.9800
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(31)	1.398(8)
C(26)-C(27)	1.406(8)
C(27)-C(28)	1.394(9)
C(28)-C(29)	1.407(10)
C(28)-H(28A)	0.9300
C(29)-C(30)	1.338(11)
C(29)-H(29A)	0.9300
C(30)-C(31)	1.399(9)
C(30)-H(30A)	0.9300
C(31)-H(31A)	0.9300
C(32)-C(37)	1.364(12)
C(32)-C(33)	1.392(12)
C(33)-C(34)	1.392(15)
C(33)-H(33A)	0.9300

C(34)-C(35)	1.389(18)
C(34)-H(34A)	0.9300
C(35)-C(36)	1.342(17)
C(35)-H(35A)	0.9300
C(36)-C(37)	1.392(14)
C(36)-H(36A)	0.9300
C(37)-H(37A)	0.9300
C(38)-C(43)	1.383(9)
C(38)-C(39)	1.397(9)
C(39)-C(40)	1.410(10)
C(39)-H(39)	0.9300
C(40)-C(41)	1.383(11)
C(40)-H(40A)	0.9300
C(41)-C(42)	1.376(11)
C(41)-H(41A)	0.9300
C(42)-C(43)	1.405(10)
C(42)-H(42A)	0.9300
C(43)-H(43)	0.9300
N(1A)-C(1A)	1.108(17)
C(1A)-C(2A)	1.32(2)
C(2A)-H(2AA)	0.9600
C(2A)-H(2AB)	0.9600
C(2A)-H(2AC)	0.9600
C(7)-Fe(1)-C(2)	154.5(4)
C(7)-Fe(1)-C(3)	119.3(4)
C(2)-Fe(1)-C(3)	39.1(4)
C(7)-Fe(1)-C(6)	41.2(3)
C(2)-Fe(1)-C(6)	119.6(3)
C(3)-Fe(1)-C(6)	103.5(4)
C(7)-Fe(1)-C(4)	102.9(4)
C(2)-Fe(1)-C(4)	69.5(5)
C(3)-Fe(1)-C(4)	42.5(4)
C(6)-Fe(1)-C(4)	118.6(4)
C(7)-Fe(1)-C(5)	122.9(3)
C(2)-Fe(1)-C(5)	67.7(3)
C(3)-Fe(1)-C(5)	67.5(4)
C(6)-Fe(1)-C(5)	156.9(4)
C(4)-Fe(1)-C(5)	40.3(4)
C(7)-Fe(1)-C(8)	41.6(2)
C(2)-Fe(1)-C(8)	162.7(4)
C(3)-Fe(1)-C(8)	157.7(4)
C(6)-Fe(1)-C(8)	69.1(2)
C(4)-Fe(1)-C(8)	121.2(3)

C(5)-Fe(1)-C(8)	110.6(3)
C(7)-Fe(1)-C(10)	67.9(2)
C(2)-Fe(1)-C(10)	108.4(3)
C(3)-Fe(1)-C(10)	120.4(3)
C(6)-Fe(1)-C(10)	39.5(2)
C(4)-Fe(1)-C(10)	155.2(4)
C(5)-Fe(1)-C(10)	163.4(4)
C(8)-Fe(1)-C(10)	68.0(2)
C(7)-Fe(1)-C(1)	161.1(3)
C(2)-Fe(1)-C(1)	40.3(4)
C(3)-Fe(1)-C(1)	66.6(4)
C(6)-Fe(1)-C(1)	157.7(3)
C(4)-Fe(1)-C(1)	68.6(4)
C(5)-Fe(1)-C(1)	40.0(4)
C(8)-Fe(1)-C(1)	127.3(3)
C(10)-Fe(1)-C(1)	126.7(3)
C(7)-Fe(1)-C(9)	68.9(2)
C(2)-Fe(1)-C(9)	125.5(4)
C(3)-Fe(1)-C(9)	157.3(4)
C(6)-Fe(1)-C(9)	67.9(2)
C(4)-Fe(1)-C(9)	160.1(4)
C(5)-Fe(1)-C(9)	128.1(3)
C(8)-Fe(1)-C(9)	40.9(2)
C(10)-Fe(1)-C(9)	40.0(2)
C(1)-Fe(1)-C(9)	113.1(3)
P(1)-Cu(1)-P(2)	112.90(6)
P(1)-Cu(1)-Br(1)	122.70(5)
P(2)-Cu(1)-Br(1)	123.96(6)
C(8)-P(1)-C(11)	105.3(3)
C(8)-P(1)-C(17)	104.2(2)
C(11)-P(1)-C(17)	100.1(3)
C(8)-P(1)-Cu(1)	109.00(18)
C(11)-P(1)-Cu(1)	120.6(2)
C(17)-P(1)-Cu(1)	115.99(19)
C(38)-P(2)-C(27)	103.2(3)
C(38)-P(2)-C(32)	104.0(4)
C(27)-P(2)-C(32)	105.7(3)
C(38)-P(2)-Cu(1)	120.7(3)
C(27)-P(2)-Cu(1)	109.60(19)
C(32)-P(2)-Cu(1)	112.3(2)
C(24)-N(1)-C(25)	108.8(6)
C(24)-N(1)-C(23)	110.9(5)
C(25)-N(1)-C(23)	114.2(5)

C(2)-C(1)-C(5)	107.4(10)
C(2)-C(1)-Fe(1)	68.3(5)
C(5)-C(1)-Fe(1)	69.6(5)
C(2)-C(1)-H(1A)	126.3
C(5)-C(1)-H(1A)	126.3
Fe(1)-C(1)-H(1A)	126.3
C(3)-C(2)-C(1)	109.0(9)
C(3)-C(2)-Fe(1)	71.0(5)
C(1)-C(2)-Fe(1)	71.5(4)
C(3)-C(2)-H(2A)	125.5
C(1)-C(2)-H(2A)	125.5
Fe(1)-C(2)-H(2A)	125.5
C(2)-C(3)-C(4)	109.8(10)
C(2)-C(3)-Fe(1)	69.9(5)
C(4)-C(3)-Fe(1)	69.4(4)
C(2)-C(3)-H(3A)	125.1
C(4)-C(3)-H(3A)	125.1
Fe(1)-C(3)-H(3A)	125.1
C(5)-C(4)-C(3)	103.2(10)
C(5)-C(4)-Fe(1)	69.8(5)
C(3)-C(4)-Fe(1)	68.1(5)
C(5)-C(4)-H(4A)	128.3
C(3)-C(4)-H(4A)	128.3
Fe(1)-C(4)-H(4A)	128.3
C(1)-C(5)-C(4)	110.4(9)
C(1)-C(5)-Fe(1)	70.3(4)
C(4)-C(5)-Fe(1)	69.8(5)
C(1)-C(5)-H(5A)	124.8
C(4)-C(5)-H(5A)	124.8
Fe(1)-C(5)-H(5A)	124.8
C(10)-C(6)-C(7)	107.4(6)
C(10)-C(6)-Fe(1)	70.7(3)
C(7)-C(6)-Fe(1)	67.7(4)
C(10)-C(6)-H(6A)	126.3
C(7)-C(6)-H(6A)	126.3
Fe(1)-C(6)-H(6A)	126.3
C(6)-C(7)-C(8)	108.6(6)
C(6)-C(7)-Fe(1)	71.1(4)
C(8)-C(7)-Fe(1)	71.2(3)
C(6)-C(7)-H(7A)	125.7
C(8)-C(7)-H(7A)	125.7
Fe(1)-C(7)-H(7A)	125.7
C(7)-C(8)-C(9)	106.3(5)

C(7)-C(8)-P(1)	126.3(4)
C(9)-C(8)-P(1)	127.3(4)
C(7)-C(8)-Fe(1)	67.3(3)
C(9)-C(8)-Fe(1)	70.3(3)
P(1)-C(8)-Fe(1)	123.9(3)
C(10)-C(9)-C(8)	107.2(5)
C(10)-C(9)-C(23)	125.0(5)
C(8)-C(9)-C(23)	126.7(5)
C(10)-C(9)-Fe(1)	69.4(3)
C(8)-C(9)-Fe(1)	68.8(3)
C(23)-C(9)-Fe(1)	135.7(3)
C(6)-C(10)-C(9)	110.5(5)
C(6)-C(10)-Fe(1)	69.8(3)
C(9)-C(10)-Fe(1)	70.6(3)
C(6)-C(10)-H(10A)	124.8
C(9)-C(10)-H(10A)	124.8
Fe(1)-C(10)-H(10A)	124.8
C(12)-C(11)-C(16)	119.7(6)
C(12)-C(11)-P(1)	118.8(5)
C(16)-C(11)-P(1)	121.2(5)
C(13)-C(12)-C(11)	118.2(8)
C(13)-C(12)-H(12A)	120.9
C(11)-C(12)-H(12A)	120.9
C(14)-C(13)-C(12)	122.9(8)
C(14)-C(13)-H(13A)	118.5
C(12)-C(13)-H(13A)	118.5
C(15)-C(14)-C(13)	121.1(8)
C(15)-C(14)-H(14A)	119.5
C(13)-C(14)-H(14A)	119.5
C(14)-C(15)-C(16)	121.2(10)
C(14)-C(15)-H(15A)	119.4
C(16)-C(15)-H(15A)	119.4
C(11)-C(16)-C(15)	116.9(9)
C(11)-C(16)-H(16A)	121.5
C(15)-C(16)-H(16A)	121.5
C(22)-C(17)-C(18)	120.7(5)
C(22)-C(17)-P(1)	122.8(5)
C(18)-C(17)-P(1)	116.5(4)
C(19)-C(18)-C(17)	119.5(7)
C(19)-C(18)-H(18A)	120.3
C(17)-C(18)-H(18A)	120.3
C(20)-C(19)-C(18)	120.5(7)
C(20)-C(19)-H(19A)	119.7

C(18)-C(19)-H(19A)	119.7
C(19)-C(20)-C(21)	120.0(7)
C(19)-C(20)-H(20A)	120.0
C(21)-C(20)-H(20A)	120.0
C(20)-C(21)-C(22)	120.4(7)
C(20)-C(21)-H(21A)	119.8
C(22)-C(21)-H(21A)	119.8
C(17)-C(22)-C(21)	118.9(6)
C(17)-C(22)-H(22A)	120.6
C(21)-C(22)-H(22A)	120.6
N(1)-C(23)-C(9)	110.1(5)
N(1)-C(23)-C(26)	109.7(5)
C(9)-C(23)-C(26)	108.6(4)
N(1)-C(23)-H(23A)	109.5
C(9)-C(23)-H(23A)	109.5
C(26)-C(23)-H(23A)	109.5
N(1)-C(24)-H(24A)	109.5
N(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
N(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(1)-C(25)-H(25A)	109.5
N(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(31)-C(26)-C(27)	118.9(5)
C(31)-C(26)-C(23)	116.7(5)
C(27)-C(26)-C(23)	124.3(5)
C(28)-C(27)-C(26)	118.6(6)
C(28)-C(27)-P(2)	121.1(5)
C(26)-C(27)-P(2)	120.2(5)
C(27)-C(28)-C(29)	121.2(6)
C(27)-C(28)-H(28A)	119.4
C(29)-C(28)-H(28A)	119.4
C(30)-C(29)-C(28)	119.7(7)
C(30)-C(29)-H(29A)	120.1
C(28)-C(29)-H(29A)	120.1
C(29)-C(30)-C(31)	120.6(7)
C(29)-C(30)-H(30A)	119.7
C(31)-C(30)-H(30A)	119.7

C(26)-C(31)-C(30)	120.7(6)
C(26)-C(31)-H(31A)	119.6
C(30)-C(31)-H(31A)	119.6
C(37)-C(32)-C(33)	119.6(8)
C(37)-C(32)-P(2)	118.4(6)
C(33)-C(32)-P(2)	121.4(8)
C(32)-C(33)-C(34)	118.8(12)
C(32)-C(33)-H(33A)	120.6
C(34)-C(33)-H(33A)	120.6
C(35)-C(34)-C(33)	120.2(11)
C(35)-C(34)-H(34A)	119.9
C(33)-C(34)-H(34A)	119.9
C(36)-C(35)-C(34)	120.5(11)
C(36)-C(35)-H(35A)	119.7
C(34)-C(35)-H(35A)	119.7
C(35)-C(36)-C(37)	119.7(13)
C(35)-C(36)-H(36A)	120.1
C(37)-C(36)-H(36A)	120.1
C(32)-C(37)-C(36)	121.1(11)
C(32)-C(37)-H(37A)	119.5
C(36)-C(37)-H(37A)	119.5
C(43)-C(38)-C(39)	122.1(7)
C(43)-C(38)-P(2)	119.5(6)
C(39)-C(38)-P(2)	118.3(6)
C(38)-C(39)-C(40)	118.9(9)
C(38)-C(39)-H(39)	120.6
C(40)-C(39)-H(39)	120.6
C(41)-C(40)-C(39)	118.1(11)
C(41)-C(40)-H(40A)	120.9
C(39)-C(40)-H(40A)	120.9
C(42)-C(41)-C(40)	123.1(11)
C(42)-C(41)-H(41A)	118.4
C(40)-C(41)-H(41A)	118.4
C(41)-C(42)-C(43)	118.9(10)
C(41)-C(42)-H(42A)	120.6
C(43)-C(42)-H(42A)	120.6
C(38)-C(43)-C(42)	118.7(9)
C(38)-C(43)-H(43)	120.7
C(42)-C(43)-H(43)	120.7
N(1A)-C(1A)-C(2A)	171.0(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for PC_03_020.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	61(1)	32(1)	84(1)	7(1)	-11(1)	2(1)
Cu(1)	56(1)	45(1)	62(1)	-6(1)	-6(1)	-2(1)
Br(1)	110(1)	70(1)	117(1)	-40(1)	-7(1)	-18(1)
P(1)	48(1)	32(1)	56(1)	0(1)	4(1)	-2(1)
P(2)	57(1)	62(1)	54(1)	9(1)	-5(1)	-2(1)
N(1)	54(3)	64(3)	70(3)	0(2)	5(3)	11(2)
C(1)	82(5)	42(3)	179(9)	-29(4)	-16(6)	11(3)
C(2)	86(5)	56(4)	163(8)	-10(5)	-27(6)	15(4)
C(3)	128(8)	47(4)	156(10)	36(5)	-54(8)	-7(5)
C(4)	142(9)	32(3)	152(9)	29(4)	19(7)	-1(4)
C(5)	73(5)	34(3)	167(9)	-5(4)	-17(5)	-5(3)
C(6)	76(4)	40(3)	74(4)	-1(3)	-6(3)	-4(3)
C(7)	69(4)	55(3)	54(3)	0(3)	3(3)	-7(3)
C(8)	58(3)	27(2)	53(3)	-1(2)	2(3)	3(2)
C(9)	49(3)	25(2)	65(3)	-1(2)	-1(3)	2(2)
C(10)	55(3)	38(2)	61(3)	3(2)	-4(3)	-5(2)
C(11)	48(3)	49(3)	77(4)	11(3)	11(3)	-3(2)
C(12)	47(3)	51(3)	123(6)	25(4)	-12(4)	-7(3)
C(13)	49(4)	60(4)	160(8)	36(5)	-4(5)	-19(3)
C(14)	72(5)	114(7)	153(9)	73(7)	5(6)	-27(5)
C(15)	110(7)	161(11)	85(6)	27(6)	40(6)	16(7)
C(16)	81(5)	88(5)	96(6)	26(4)	30(4)	-14(4)
C(17)	59(3)	37(2)	52(3)	-3(2)	14(3)	-3(2)
C(18)	57(4)	54(3)	102(5)	-10(3)	-4(4)	10(3)
C(19)	68(4)	69(5)	156(8)	-4(5)	9(5)	28(4)
C(20)	103(6)	56(4)	116(6)	-16(4)	27(5)	14(4)
C(21)	83(5)	44(3)	117(6)	-24(3)	8(5)	-1(3)
C(22)	58(3)	51(3)	79(4)	-8(3)	5(3)	-4(3)
C(23)	47(3)	47(3)	55(3)	-5(2)	1(2)	6(2)
C(24)	68(4)	87(5)	87(5)	-15(4)	13(4)	17(4)
C(25)	60(4)	102(5)	81(5)	2(4)	23(4)	-5(4)
C(26)	47(3)	45(3)	62(3)	4(2)	7(3)	0(2)
C(27)	56(3)	56(3)	54(3)	7(3)	1(3)	-2(3)
C(28)	76(4)	51(3)	87(5)	27(3)	-10(4)	-1(3)
C(29)	90(5)	51(3)	116(6)	17(4)	-11(5)	-12(4)
C(30)	75(4)	55(4)	107(6)	-3(4)	-9(4)	-15(3)
C(31)	60(3)	53(3)	70(4)	6(3)	-1(3)	-7(3)

C(32)	58(4)	75(4)	103(6)	42(4)	-16(4)	-15(3)
C(33)	80(6)	172(10)	96(6)	46(7)	-24(5)	-14(6)
C(34)	102(8)	161(11)	146(10)	71(9)	-47(8)	-20(8)
C(35)	89(6)	127(8)	173(10)	63(8)	-22(7)	-1(6)
C(36)	98(6)	106(7)	186(10)	33(7)	1(7)	11(6)
C(37)	67(5)	88(5)	142(8)	31(5)	21(5)	15(4)
C(38)	70(4)	107(6)	54(4)	-7(4)	-6(3)	2(4)
C(39)	72(4)	118(7)	92(6)	-37(5)	-6(4)	-8(5)
C(40)	121(8)	202(13)	79(6)	-53(8)	-22(6)	15(9)
C(41)	113(7)	204(11)	76(6)	-10(7)	22(5)	-4(8)
C(42)	111(7)	180(10)	81(6)	12(6)	7(5)	-18(7)
C(43)	97(6)	142(8)	46(4)	19(4)	6(4)	-7(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for PC_03_020.

	x	y	z	U(eq)
H(1A)	1192	-1710	3639	121
H(2A)	3204	-1858	4301	122
H(3A)	2128	-1909	5178	132
H(4A)	-697	-1737	5100	130
H(5A)	-1179	-1607	4125	109
H(6A)	2491	-84	5330	76
H(7A)	-251	85	5234	71
H(10A)	3603	67	4448	62
H(12A)	-3320	-988	4075	88
H(13A)	-4638	-1734	4655	108
H(14A)	-5017	-1337	5459	136
H(15A)	-4197	-179	5739	143
H(16A)	-2688	629	5202	106
H(18A)	-4152	1329	4071	85
H(19A)	-4840	2627	4225	117
H(20A)	-3218	3526	4528	110
H(21A)	-927	3121	4746	98
H(22A)	-208	1815	4595	75
H(23A)	1146	261	3375	60
H(24A)	4486	-503	3227	121
H(24B)	2835	-631	3139	121
H(24C)	3487	-721	3693	121
H(25A)	4724	679	2920	122
H(25B)	3848	1417	3112	122
H(25C)	3127	797	2743	122
H(28A)	-215	2827	2943	86
H(29A)	1149	3638	3481	103
H(30A)	2548	3088	4101	95
H(31A)	2861	1723	4137	73
H(33A)	-1844	1520	1808	139
H(34A)	-3869	2220	1539	163
H(35A)	-5249	2903	2133	156
H(36A)	-4684	2866	2984	156
H(37A)	-2695	2156	3259	119
H(39)	113	-259	2261	112
H(40A)	1692	-547	1574	160
H(41A)	2931	483	1194	157
H(42A)	2531	1782	1415	149

H(43)	1094	2067	2138	114
H(2AA)	5950	374	2031	142
H(2AB)	6525	-467	2186	142
H(2AC)	4865	-309	2162	142

Table 6. Torsion angles [deg] for PC_03_020.

P(2)-Cu(1)-P(1)-C(8)	-80.56(18)
Br(1)-Cu(1)-P(1)-C(8)	92.10(18)
P(2)-Cu(1)-P(1)-C(11)	157.6(2)
Br(1)-Cu(1)-P(1)-C(11)	-29.7(2)
P(2)-Cu(1)-P(1)-C(17)	36.6(2)
Br(1)-Cu(1)-P(1)-C(17)	-150.8(2)
P(1)-Cu(1)-P(2)-C(38)	144.0(3)
Br(1)-Cu(1)-P(2)-C(38)	-28.6(3)
P(1)-Cu(1)-P(2)-C(27)	24.4(2)
Br(1)-Cu(1)-P(2)-C(27)	-148.1(2)
P(1)-Cu(1)-P(2)-C(32)	-92.7(3)
Br(1)-Cu(1)-P(2)-C(32)	94.7(3)
C(7)-Fe(1)-C(1)-C(2)	-149.4(10)
C(3)-Fe(1)-C(1)-C(2)	-37.1(6)
C(6)-Fe(1)-C(1)-C(2)	30.4(13)
C(4)-Fe(1)-C(1)-C(2)	-83.2(7)
C(5)-Fe(1)-C(1)-C(2)	-119.5(9)
C(8)-Fe(1)-C(1)-C(2)	163.2(6)
C(10)-Fe(1)-C(1)-C(2)	74.3(8)
C(9)-Fe(1)-C(1)-C(2)	118.2(7)
C(7)-Fe(1)-C(1)-C(5)	-29.9(14)
C(2)-Fe(1)-C(1)-C(5)	119.5(9)
C(3)-Fe(1)-C(1)-C(5)	82.4(7)
C(6)-Fe(1)-C(1)-C(5)	149.8(8)
C(4)-Fe(1)-C(1)-C(5)	36.2(6)
C(8)-Fe(1)-C(1)-C(5)	-77.4(7)
C(10)-Fe(1)-C(1)-C(5)	-166.3(5)
C(9)-Fe(1)-C(1)-C(5)	-122.3(6)
C(5)-C(1)-C(2)-C(3)	2.6(9)
Fe(1)-C(1)-C(2)-C(3)	61.4(6)
C(5)-C(1)-C(2)-Fe(1)	-58.8(5)
C(7)-Fe(1)-C(2)-C(3)	38.9(11)
C(6)-Fe(1)-C(2)-C(3)	74.2(7)
C(4)-Fe(1)-C(2)-C(3)	-37.9(7)
C(5)-Fe(1)-C(2)-C(3)	-81.3(7)
C(8)-Fe(1)-C(2)-C(3)	-169.2(9)
C(10)-Fe(1)-C(2)-C(3)	115.8(6)
C(1)-Fe(1)-C(2)-C(3)	-118.6(9)
C(9)-Fe(1)-C(2)-C(3)	156.9(5)
C(7)-Fe(1)-C(2)-C(1)	157.5(7)
C(3)-Fe(1)-C(2)-C(1)	118.6(9)

C(6)-Fe(1)-C(2)-C(1)	-167.2(6)
C(4)-Fe(1)-C(2)-C(1)	80.7(7)
C(5)-Fe(1)-C(2)-C(1)	37.3(6)
C(8)-Fe(1)-C(2)-C(1)	-50.6(13)
C(10)-Fe(1)-C(2)-C(1)	-125.6(6)
C(9)-Fe(1)-C(2)-C(1)	-84.5(7)
C(1)-C(2)-C(3)-C(4)	-3.7(10)
Fe(1)-C(2)-C(3)-C(4)	58.0(6)
C(1)-C(2)-C(3)-Fe(1)	-61.7(5)
C(7)-Fe(1)-C(3)-C(2)	-161.9(5)
C(6)-Fe(1)-C(3)-C(2)	-120.7(6)
C(4)-Fe(1)-C(3)-C(2)	121.5(10)
C(5)-Fe(1)-C(3)-C(2)	81.8(6)
C(8)-Fe(1)-C(3)-C(2)	171.6(7)
C(10)-Fe(1)-C(3)-C(2)	-81.8(6)
C(1)-Fe(1)-C(3)-C(2)	38.2(6)
C(9)-Fe(1)-C(3)-C(2)	-56.1(12)
C(7)-Fe(1)-C(3)-C(4)	76.5(7)
C(2)-Fe(1)-C(3)-C(4)	-121.5(10)
C(6)-Fe(1)-C(3)-C(4)	117.8(7)
C(5)-Fe(1)-C(3)-C(4)	-39.7(6)
C(8)-Fe(1)-C(3)-C(4)	50.0(12)
C(10)-Fe(1)-C(3)-C(4)	156.6(6)
C(1)-Fe(1)-C(3)-C(4)	-83.3(7)
C(9)-Fe(1)-C(3)-C(4)	-177.6(7)
C(2)-C(3)-C(4)-C(5)	3.3(9)
Fe(1)-C(3)-C(4)-C(5)	61.6(5)
C(2)-C(3)-C(4)-Fe(1)	-58.3(6)
C(7)-Fe(1)-C(4)-C(5)	126.3(5)
C(2)-Fe(1)-C(4)-C(5)	-79.2(6)
C(3)-Fe(1)-C(4)-C(5)	-114.2(9)
C(6)-Fe(1)-C(4)-C(5)	167.4(5)
C(8)-Fe(1)-C(4)-C(5)	85.6(6)
C(10)-Fe(1)-C(4)-C(5)	-168.9(6)
C(1)-Fe(1)-C(4)-C(5)	-36.0(5)
C(9)-Fe(1)-C(4)-C(5)	63.1(13)
C(7)-Fe(1)-C(4)-C(3)	-119.5(7)
C(2)-Fe(1)-C(4)-C(3)	35.0(6)
C(6)-Fe(1)-C(4)-C(3)	-78.4(8)
C(5)-Fe(1)-C(4)-C(3)	114.2(9)
C(8)-Fe(1)-C(4)-C(3)	-160.1(6)
C(10)-Fe(1)-C(4)-C(3)	-54.7(11)
C(1)-Fe(1)-C(4)-C(3)	78.2(7)

C(9)-Fe(1)-C(4)-C(3)	177.3(9)
C(2)-C(1)-C(5)-C(4)	-0.4(8)
Fe(1)-C(1)-C(5)-C(4)	-58.4(5)
C(2)-C(1)-C(5)-Fe(1)	58.0(5)
C(3)-C(4)-C(5)-C(1)	-1.7(8)
Fe(1)-C(4)-C(5)-C(1)	58.7(5)
C(3)-C(4)-C(5)-Fe(1)	-60.4(5)
C(7)-Fe(1)-C(5)-C(1)	168.9(5)
C(2)-Fe(1)-C(5)-C(1)	-37.5(6)
C(3)-Fe(1)-C(5)-C(1)	-79.9(7)
C(6)-Fe(1)-C(5)-C(1)	-151.0(7)
C(4)-Fe(1)-C(5)-C(1)	-121.7(8)
C(8)-Fe(1)-C(5)-C(1)	124.0(5)
C(10)-Fe(1)-C(5)-C(1)	41.9(12)
C(9)-Fe(1)-C(5)-C(1)	80.9(6)
C(7)-Fe(1)-C(5)-C(4)	-69.4(6)
C(2)-Fe(1)-C(5)-C(4)	84.3(7)
C(3)-Fe(1)-C(5)-C(4)	41.8(7)
C(6)-Fe(1)-C(5)-C(4)	-29.2(10)
C(8)-Fe(1)-C(5)-C(4)	-114.3(6)
C(10)-Fe(1)-C(5)-C(4)	163.6(9)
C(1)-Fe(1)-C(5)-C(4)	121.7(8)
C(9)-Fe(1)-C(5)-C(4)	-157.3(5)
C(7)-Fe(1)-C(6)-C(10)	-119.1(5)
C(2)-Fe(1)-C(6)-C(10)	83.1(6)
C(3)-Fe(1)-C(6)-C(10)	121.7(5)
C(4)-Fe(1)-C(6)-C(10)	164.6(4)
C(5)-Fe(1)-C(6)-C(10)	-174.3(7)
C(8)-Fe(1)-C(6)-C(10)	-80.4(4)
C(1)-Fe(1)-C(6)-C(10)	61.0(10)
C(9)-Fe(1)-C(6)-C(10)	-36.2(3)
C(2)-Fe(1)-C(6)-C(7)	-157.8(5)
C(3)-Fe(1)-C(6)-C(7)	-119.2(5)
C(4)-Fe(1)-C(6)-C(7)	-76.3(5)
C(5)-Fe(1)-C(6)-C(7)	-55.2(9)
C(8)-Fe(1)-C(6)-C(7)	38.7(4)
C(10)-Fe(1)-C(6)-C(7)	119.1(5)
C(1)-Fe(1)-C(6)-C(7)	-179.9(9)
C(9)-Fe(1)-C(6)-C(7)	82.9(4)
C(10)-C(6)-C(7)-C(8)	-1.8(7)
Fe(1)-C(6)-C(7)-C(8)	-61.6(4)
C(10)-C(6)-C(7)-Fe(1)	59.8(4)
C(2)-Fe(1)-C(7)-C(6)	49.6(10)

C(3)-Fe(1)-C(7)-C(6)	76.6(5)
C(4)-Fe(1)-C(7)-C(6)	119.0(5)
C(5)-Fe(1)-C(7)-C(6)	157.4(5)
C(8)-Fe(1)-C(7)-C(6)	-118.2(5)
C(10)-Fe(1)-C(7)-C(6)	-36.8(4)
C(1)-Fe(1)-C(7)-C(6)	179.9(11)
C(9)-Fe(1)-C(7)-C(6)	-80.0(4)
C(2)-Fe(1)-C(7)-C(8)	167.8(8)
C(3)-Fe(1)-C(7)-C(8)	-165.2(4)
C(6)-Fe(1)-C(7)-C(8)	118.2(5)
C(4)-Fe(1)-C(7)-C(8)	-122.8(5)
C(5)-Fe(1)-C(7)-C(8)	-84.4(5)
C(10)-Fe(1)-C(7)-C(8)	81.4(4)
C(1)-Fe(1)-C(7)-C(8)	-61.9(12)
C(9)-Fe(1)-C(7)-C(8)	38.2(3)
C(6)-C(7)-C(8)-C(9)	1.9(6)
Fe(1)-C(7)-C(8)-C(9)	-59.7(3)
C(6)-C(7)-C(8)-P(1)	177.8(4)
Fe(1)-C(7)-C(8)-P(1)	116.2(4)
C(6)-C(7)-C(8)-Fe(1)	61.6(4)
C(11)-P(1)-C(8)-C(7)	-23.3(5)
C(17)-P(1)-C(8)-C(7)	81.5(5)
Cu(1)-P(1)-C(8)-C(7)	-154.1(4)
C(11)-P(1)-C(8)-C(9)	151.8(4)
C(17)-P(1)-C(8)-C(9)	-103.3(4)
Cu(1)-P(1)-C(8)-C(9)	21.1(5)
C(11)-P(1)-C(8)-Fe(1)	61.8(4)
C(17)-P(1)-C(8)-Fe(1)	166.7(3)
Cu(1)-P(1)-C(8)-Fe(1)	-68.9(3)
C(2)-Fe(1)-C(8)-C(7)	-162.2(10)
C(3)-Fe(1)-C(8)-C(7)	36.0(9)
C(6)-Fe(1)-C(8)-C(7)	-38.4(4)
C(4)-Fe(1)-C(8)-C(7)	73.2(5)
C(5)-Fe(1)-C(8)-C(7)	116.8(5)
C(10)-Fe(1)-C(8)-C(7)	-80.9(4)
C(1)-Fe(1)-C(8)-C(7)	158.9(5)
C(9)-Fe(1)-C(8)-C(7)	-118.3(5)
C(7)-Fe(1)-C(8)-C(9)	118.3(5)
C(2)-Fe(1)-C(8)-C(9)	-43.9(11)
C(3)-Fe(1)-C(8)-C(9)	154.2(8)
C(6)-Fe(1)-C(8)-C(9)	79.8(3)
C(4)-Fe(1)-C(8)-C(9)	-168.5(5)
C(5)-Fe(1)-C(8)-C(9)	-124.9(4)

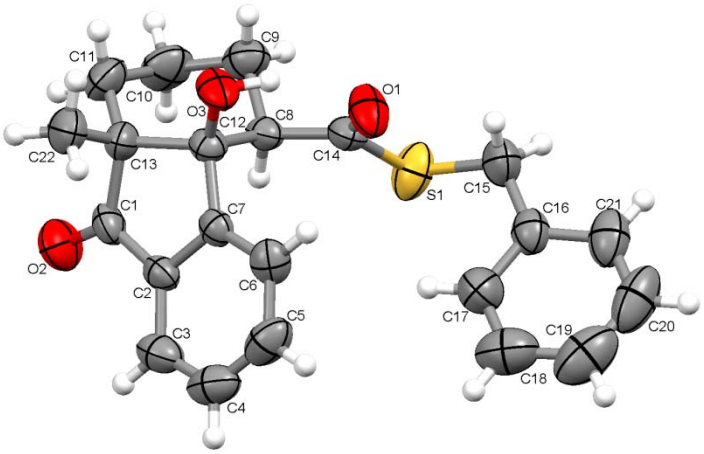
C(10)-Fe(1)-C(8)-C(9)	37.3(3)
C(1)-Fe(1)-C(8)-C(9)	-82.8(5)
C(7)-Fe(1)-C(8)-P(1)	-119.4(5)
C(2)-Fe(1)-C(8)-P(1)	78.4(11)
C(3)-Fe(1)-C(8)-P(1)	-83.4(9)
C(6)-Fe(1)-C(8)-P(1)	-157.8(4)
C(4)-Fe(1)-C(8)-P(1)	-46.2(6)
C(5)-Fe(1)-C(8)-P(1)	-2.6(5)
C(10)-Fe(1)-C(8)-P(1)	159.7(4)
C(1)-Fe(1)-C(8)-P(1)	39.5(6)
C(9)-Fe(1)-C(8)-P(1)	122.3(5)
C(7)-C(8)-C(9)-C(10)	-1.2(5)
P(1)-C(8)-C(9)-C(10)	-177.1(4)
Fe(1)-C(8)-C(9)-C(10)	-59.0(3)
C(7)-C(8)-C(9)-C(23)	-170.2(5)
P(1)-C(8)-C(9)-C(23)	13.9(7)
Fe(1)-C(8)-C(9)-C(23)	132.0(5)
C(7)-C(8)-C(9)-Fe(1)	57.8(4)
P(1)-C(8)-C(9)-Fe(1)	-118.1(4)
C(7)-Fe(1)-C(9)-C(10)	80.2(4)
C(2)-Fe(1)-C(9)-C(10)	-75.7(5)
C(3)-Fe(1)-C(9)-C(10)	-35.7(11)
C(6)-Fe(1)-C(9)-C(10)	35.7(3)
C(4)-Fe(1)-C(9)-C(10)	149.0(11)
C(5)-Fe(1)-C(9)-C(10)	-163.8(4)
C(8)-Fe(1)-C(9)-C(10)	119.0(4)
C(1)-Fe(1)-C(9)-C(10)	-120.1(4)
C(7)-Fe(1)-C(9)-C(8)	-38.8(3)
C(2)-Fe(1)-C(9)-C(8)	165.3(4)
C(3)-Fe(1)-C(9)-C(8)	-154.7(10)
C(6)-Fe(1)-C(9)-C(8)	-83.2(4)
C(4)-Fe(1)-C(9)-C(8)	30.0(12)
C(5)-Fe(1)-C(9)-C(8)	77.2(5)
C(10)-Fe(1)-C(9)-C(8)	-119.0(4)
C(1)-Fe(1)-C(9)-C(8)	120.9(4)
C(7)-Fe(1)-C(9)-C(23)	-160.2(6)
C(2)-Fe(1)-C(9)-C(23)	43.9(7)
C(3)-Fe(1)-C(9)-C(23)	83.9(12)
C(6)-Fe(1)-C(9)-C(23)	155.3(6)
C(4)-Fe(1)-C(9)-C(23)	-91.4(12)
C(5)-Fe(1)-C(9)-C(23)	-44.2(7)
C(8)-Fe(1)-C(9)-C(23)	-121.4(7)
C(10)-Fe(1)-C(9)-C(23)	119.6(7)

C(1)-Fe(1)-C(9)-C(23)	-0.5(6)
C(7)-C(6)-C(10)-C(9)	1.1(6)
Fe(1)-C(6)-C(10)-C(9)	59.0(4)
C(7)-C(6)-C(10)-Fe(1)	-57.9(4)
C(8)-C(9)-C(10)-C(6)	0.1(6)
C(23)-C(9)-C(10)-C(6)	169.3(5)
Fe(1)-C(9)-C(10)-C(6)	-58.5(4)
C(8)-C(9)-C(10)-Fe(1)	58.6(3)
C(23)-C(9)-C(10)-Fe(1)	-132.1(5)
C(7)-Fe(1)-C(10)-C(6)	38.4(4)
C(2)-Fe(1)-C(10)-C(6)	-114.6(5)
C(3)-Fe(1)-C(10)-C(6)	-73.5(6)
C(4)-Fe(1)-C(10)-C(6)	-33.7(9)
C(5)-Fe(1)-C(10)-C(6)	172.1(9)
C(8)-Fe(1)-C(10)-C(6)	83.5(4)
C(1)-Fe(1)-C(10)-C(6)	-155.5(5)
C(9)-Fe(1)-C(10)-C(6)	121.6(5)
C(7)-Fe(1)-C(10)-C(9)	-83.2(3)
C(2)-Fe(1)-C(10)-C(9)	123.8(5)
C(3)-Fe(1)-C(10)-C(9)	164.9(5)
C(6)-Fe(1)-C(10)-C(9)	-121.6(5)
C(4)-Fe(1)-C(10)-C(9)	-155.4(8)
C(5)-Fe(1)-C(10)-C(9)	50.5(10)
C(8)-Fe(1)-C(10)-C(9)	-38.2(3)
C(1)-Fe(1)-C(10)-C(9)	82.8(5)
C(8)-P(1)-C(11)-C(12)	-107.5(5)
C(17)-P(1)-C(11)-C(12)	144.6(5)
Cu(1)-P(1)-C(11)-C(12)	16.1(6)
C(8)-P(1)-C(11)-C(16)	66.7(6)
C(17)-P(1)-C(11)-C(16)	-41.1(6)
Cu(1)-P(1)-C(11)-C(16)	-169.7(5)
C(16)-C(11)-C(12)-C(13)	-1.4(9)
P(1)-C(11)-C(12)-C(13)	173.0(5)
C(11)-C(12)-C(13)-C(14)	1.4(11)
C(12)-C(13)-C(14)-C(15)	0.8(15)
C(13)-C(14)-C(15)-C(16)	-2.9(16)
C(12)-C(11)-C(16)-C(15)	-0.6(11)
P(1)-C(11)-C(16)-C(15)	-174.8(6)
C(14)-C(15)-C(16)-C(11)	2.8(14)
C(8)-P(1)-C(17)-C(22)	9.0(6)
C(11)-P(1)-C(17)-C(22)	117.7(5)
Cu(1)-P(1)-C(17)-C(22)	-110.7(5)
C(8)-P(1)-C(17)-C(18)	-171.3(5)

C(11)-P(1)-C(17)-C(18)	-62.6(5)
Cu(1)-P(1)-C(17)-C(18)	68.9(5)
C(22)-C(17)-C(18)-C(19)	2.2(11)
P(1)-C(17)-C(18)-C(19)	-177.5(6)
C(17)-C(18)-C(19)-C(20)	0.3(13)
C(18)-C(19)-C(20)-C(21)	-2.7(14)
C(19)-C(20)-C(21)-C(22)	2.6(14)
C(18)-C(17)-C(22)-C(21)	-2.2(10)
P(1)-C(17)-C(22)-C(21)	177.4(6)
C(20)-C(21)-C(22)-C(17)	-0.2(12)
C(24)-N(1)-C(23)-C(9)	75.0(6)
C(25)-N(1)-C(23)-C(9)	-161.6(5)
C(24)-N(1)-C(23)-C(26)	-165.4(5)
C(25)-N(1)-C(23)-C(26)	-42.1(7)
C(10)-C(9)-C(23)-N(1)	15.9(7)
C(8)-C(9)-C(23)-N(1)	-177.0(5)
Fe(1)-C(9)-C(23)-N(1)	-80.1(6)
C(10)-C(9)-C(23)-C(26)	-104.3(5)
C(8)-C(9)-C(23)-C(26)	62.9(6)
Fe(1)-C(9)-C(23)-C(26)	159.7(4)
N(1)-C(23)-C(26)-C(31)	-61.8(7)
C(9)-C(23)-C(26)-C(31)	58.6(7)
N(1)-C(23)-C(26)-C(27)	114.1(6)
C(9)-C(23)-C(26)-C(27)	-125.4(6)
C(31)-C(26)-C(27)-C(28)	2.4(9)
C(23)-C(26)-C(27)-C(28)	-173.4(6)
C(31)-C(26)-C(27)-P(2)	-175.3(5)
C(23)-C(26)-C(27)-P(2)	8.8(8)
C(38)-P(2)-C(27)-C(28)	94.3(6)
C(32)-P(2)-C(27)-C(28)	-14.7(6)
Cu(1)-P(2)-C(27)-C(28)	-135.9(5)
C(38)-P(2)-C(27)-C(26)	-88.1(5)
C(32)-P(2)-C(27)-C(26)	163.0(5)
Cu(1)-P(2)-C(27)-C(26)	41.7(5)
C(26)-C(27)-C(28)-C(29)	-1.7(10)
P(2)-C(27)-C(28)-C(29)	176.0(6)
C(27)-C(28)-C(29)-C(30)	-1.6(12)
C(28)-C(29)-C(30)-C(31)	4.1(13)
C(27)-C(26)-C(31)-C(30)	0.0(9)
C(23)-C(26)-C(31)-C(30)	176.2(6)
C(29)-C(30)-C(31)-C(26)	-3.4(12)
C(38)-P(2)-C(32)-C(37)	-166.8(6)
C(27)-P(2)-C(32)-C(37)	-58.4(7)

Cu(1)-P(2)-C(32)-C(37)	61.0(7)
C(38)-P(2)-C(32)-C(33)	22.4(7)
C(27)-P(2)-C(32)-C(33)	130.8(7)
Cu(1)-P(2)-C(32)-C(33)	-109.8(7)
C(37)-C(32)-C(33)-C(34)	0.8(14)
P(2)-C(32)-C(33)-C(34)	171.5(8)
C(32)-C(33)-C(34)-C(35)	0.4(16)
C(33)-C(34)-C(35)-C(36)	-1.1(19)
C(34)-C(35)-C(36)-C(37)	0.5(18)
C(33)-C(32)-C(37)-C(36)	-1.4(13)
P(2)-C(32)-C(37)-C(36)	-172.4(7)
C(35)-C(36)-C(37)-C(32)	0.7(16)
C(27)-P(2)-C(38)-C(43)	-46.7(7)
C(32)-P(2)-C(38)-C(43)	63.4(7)
Cu(1)-P(2)-C(38)-C(43)	-169.4(5)
C(27)-P(2)-C(38)-C(39)	130.9(6)
C(32)-P(2)-C(38)-C(39)	-118.9(6)
Cu(1)-P(2)-C(38)-C(39)	8.2(7)
C(43)-C(38)-C(39)-C(40)	1.5(12)
P(2)-C(38)-C(39)-C(40)	-176.1(6)
C(38)-C(39)-C(40)-C(41)	-0.7(14)
C(39)-C(40)-C(41)-C(42)	-2.6(17)
C(40)-C(41)-C(42)-C(43)	5.1(18)
C(39)-C(38)-C(43)-C(42)	1.0(12)
P(2)-C(38)-C(43)-C(42)	178.6(7)
C(41)-C(42)-C(43)-C(38)	-4.2(15)

X-ray data for 4i



Comment

The compound, 4a-hydroxy-9a-methyl-9-oxo-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene-4-carbothioic acid *S*-benzyl ester, crystallizes in a chiral primitive triclinic space group, *P*1 (#1). The compound is chiral. There are 2 asymmetric units in the unit cell.

The cyclo-hexyl ring is in the chair form, and the five-membered ring in the envelop form. The atoms C8, C13, C30 and C35 are of the same configuration, all *R*, while C12 and C34 are *S*-configurations. All the bonding parameters were within the normal ranges.

Intra-molecular, O3—H3O···O1 and O6—H6O···O4; and inter-molecular, O3—H3O···O4, H-bond inter-actions are present in the crystal lattice that connects the molecules into dimer. Weak C—H··· inter-actions (Table 2) are also observed.

The Flack parameter of 0.10(14) indicated that the current configuration is correct. (Inverting the structure resulted in a Flack parameter of close to one.)

Experimental

A colourless block crystal of $C_{22}H_{22}O_3S$, having approximate dimensions of 0.16 *x* 0.34 *x* 0.76 mm was mounted in glass capillary. All measurements were made on a Bruker *Apex II* CCD detector with graphite monochromated Mo—K radiation. The crystal-to-detector distance was 55.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 8.6495(6)Å b = 8.6869(6)Å c = 13.4401(9)Å V = 958.09(11)Å^3

= 72.062 (4)° = 89.472(4)° = 85.803(5)°

For *Z* = 2 and F.W. = 366.46, the calculated density is 1.270 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: *P*1 (#1)

The data were collected at a temperature of 23 (1)°C to a maximum 2 value of 50.05°. The exposure rate was 20.0 [sec./°]. The crystal-to-detector distance was 55.00 mm.

Of the 13175 reflections that were collected, 5970 reflections were unique. (R_{int} = 0.0479); equivalent reflections were merged.

Refinement

The structure was solved by direct methods (*SHELXS-97*) and expanded using Fourier techniques. All non-H atoms were refined anisotropically.

All of the C-bound H atoms were observable from difference Fourier map but were all placed at geometrical positions with C—H = 0.93, 0.96, 0.97 and 0.98Å for phenyl, methyl, methyl-ene and methine H-atoms respectively. All C-bound H-atoms were refined using riding model with U_{iso}(H) = 1.2U_{eq}(Carrier). The O-bound hydrogen atoms were located from difference Fourier map and also refined using riding model of U_{iso}(H) = 1.2U_{eq}(Carrier).

Floating origin restraints (three) were used.

Highest peak is 0.42 at (0.0238, 0.5878, 0.5136) [1.00Å from C32] Deepest hole is -0.32 at (0.0916, 0.1768, 0.7216) [0.52Å from H22A]

(PC-O2-145-C-shelxl)

Crystal data

$C_{22}H_{22}O_3S$	Z = 2
M_r = 366.46	F(000) = 388
Triclinic, P1	D_x = 1.270 Mg m^{-3}
Hall symbol: P 1	Mo K radiation, = 0.71073 Å
a = 8.6495 (6) Å	Cell parameters from 13175 reflections
b = 8.6869 (6) Å	= 2.8–25.0°
c = 13.4401 (9) Å	= 0.19 mm^{-1}
= 72.062 (4)°	T = 296 K
= 89.472 (4)°	Block, colourless
= 85.803 (5)°	0.76 × 0.34 × 0.16 mm
V = 958.09 (11) Å^3	

Data collection

Bruker APEX CCD diffractometer	5970 independent reflections
Radiation source: fine-focus sealed tube	4860 reflections with I > 2 (I)
graphite	R_{int} = 0.048
& scans	$_{max}$ = 25.0°, $_{min}$ = 2.8°
Absorption correction: multi-scan *SADABS* (Sheldrick, 2008)	h = -10 10
T_{min} = 0.871, T_{max} = 0.971	k = -10 10
13175 measured reflections	l = -15 15

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2 \quad (F^2)] = 0.071$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.236$	H-atom parameters constrained
$S = 1.11$	$w = 1/[\quad ^2(F_o^2) + (0.1452P)^2 + 0.2104P]$ where $P = (F_o^2 + 2F_c^2)/3$
5970 reflections	$(\quad / \quad)_{max} = 0.005$
472 parameters	$_{max} = 0.42$ e Å^{-3}
3 restraints	$_{min} = -0.32$ e Å^{-3}
Flack parameter: 0.10 (14)	Absolute structure: Flack (1983), 2596 Friedel pairs

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

The structure was solved by direct methods (*SHELXS-97*) and expanded using Fourier techniques. All non-H atoms were refined anisotropically.

All of the C-bound H atoms were observable from difference Fourier map but were all placed at geometrical positions with C—H = 0.93, 0.96, 0.97 and 0.98Åfor phenyl, methyl, methyl-ene and methine H-atoms respectively. All C-bound H-atoms were refined using riding model with U_{iso}(H) = 1.2U_{eq}(Carrier). The O-bound hydrogen atoms were located from difference Fourier map and also refined using riding model of U_{iso}(H) = 1.2U_{eq}(Carrier).

Floating origin restraints (three) were used.

Highest peak is 0.42 at (0.0238, 0.5878, 0.5136) [1.00Å from C32] Deepest hole is -0.32 at (0.0916, 0.1768, 0.7216) [0.52Å from H22A]

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.76747 (18)	0.30429 (18)	0.82338 (15)	0.0742 (5)
S2	0.62126 (18)	0.4288 (2)	0.30329 (16)	0.0792 (6)
O1	0.5731 (5)	0.4779 (5)	0.6769 (3)	0.0744 (13)
O2	0.2139 (6)	-0.1345 (5)	0.8744 (4)	0.0795 (13)
O3	0.3258 (5)	0.3521 (5)	0.6150 (3)	0.0621 (10)
H3O	0.4192	0.3978	0.6155	0.075*

O4	0.5166 (6)	0.5569 (6)	0.4457 (3)	0.0725 (12)
O5	1.0393 (5)	0.9972 (6)	0.2396 (4)	0.0726 (12)
O6	0.6741 (5)	0.7816 (5)	0.5005 (3)	0.0594 (10)
H6O	0.5932	0.7358	0.4948	0.071*
C1	0.2343 (6)	0.0091 (6)	0.8296 (4)	0.0496 (11)
C2	0.2228 (5)	0.1413 (6)	0.8751 (4)	0.0449 (10)
C3	0.1576 (7)	0.1484 (8)	0.9705 (4)	0.0634 (15)
H3	0.1176	0.0575	1.0168	0.076*
C4	0.1545 (8)	0.2892 (10)	0.9930 (5)	0.0728 (17)
H4	0.1124	0.2944	1.0560	0.087*
C5	0.2115 (8)	0.4248 (9)	0.9258 (6)	0.0713 (17)
H5	0.2085	0.5198	0.9441	0.086*
C6	0.2743 (6)	0.4230 (6)	0.8300 (5)	0.0542 (12)
H6	0.3108	0.5162	0.7837	0.065*
C7	0.2809 (5)	0.2779 (6)	0.8056 (4)	0.0426 (10)
C8	0.5284 (5)	0.1938 (6)	0.7390 (4)	0.0444 (10)
H8	0.5388	0.1208	0.8109	0.053*
C9	0.6054 (7)	0.1036 (8)	0.6667 (5)	0.0654 (15)
H9A	0.5902	0.1688	0.5941	0.078*
H9B	0.7160	0.0840	0.6813	0.078*
C10	0.5321 (9)	-0.0563 (9)	0.6862 (6)	0.0786 (19)
H10A	0.5814	-0.1155	0.6425	0.094*
H10B	0.5500	-0.1212	0.7586	0.094*
C11	0.3625 (8)	-0.0327 (8)	0.6637 (5)	0.0681 (16)
H11A	0.3200	-0.1380	0.6872	0.082*
H11B	0.3472	0.0092	0.5885	0.082*
C12	0.3552 (6)	0.2333 (6)	0.7139 (3)	0.0433 (10)
C13	0.2696 (7)	0.0804 (6)	0.7130 (4)	0.0526 (12)
C14	0.6094 (6)	0.3446 (7)	0.7338 (4)	0.0519 (12)
C15	0.8297 (8)	0.5075 (9)	0.7943 (6)	0.0742 (18)
H15A	0.9421	0.5006	0.7937	0.089*
H15B	0.7938	0.5688	0.7241	0.089*
C16	0.7778 (7)	0.6005 (7)	0.8655 (5)	0.0579 (13)
C17	0.6382 (9)	0.5736 (9)	0.9214 (6)	0.0767 (18)
H17	0.5803	0.4896	0.9174	0.092*
C18	0.5865 (12)	0.6666 (12)	0.9807 (6)	0.097 (2)
H18	0.4955	0.6453	1.0183	0.116*
C19	0.6719 (16)	0.7956 (13)	0.9849 (9)	0.112 (3)
H19	0.6352	0.8630	1.0233	0.134*
C20	0.8093 (14)	0.8232 (9)	0.9326 (8)	0.101 (3)

H20	0.8671	0.9066	0.9378	0.122*
C21	0.8615 (9)	0.7287 (8)	0.8731 (6)	0.0778 (19)
H21	0.9538	0.7496	0.8371	0.093*
C22	0.1108 (8)	0.1289 (9)	0.6594 (6)	0.0716 (16)
H22A	0.0525	0.1998	0.6907	0.086*
H22B	0.0564	0.0334	0.6674	0.086*
H22C	0.1238	0.1839	0.5863	0.086*
C23	0.9196 (6)	0.9631 (6)	0.2844 (4)	0.0488 (11)
C24	0.7631 (6)	0.9985 (6)	0.2383 (4)	0.0482 (11)
C25	0.7091 (9)	1.1059 (7)	0.1434 (5)	0.0671 (16)
H25	0.7776	1.1655	0.0957	0.080*
C26	0.5507 (9)	1.1232 (8)	0.1208 (6)	0.0739 (18)
H26	0.5145	1.1941	0.0569	0.089*
C27	0.4459 (8)	1.0375 (8)	0.1908 (6)	0.0675 (15)
H27	0.3404	1.0510	0.1747	0.081*
C28	0.5018 (6)	0.9298 (6)	0.2867 (5)	0.0555 (13)
H28	0.4329	0.8717	0.3349	0.067*
C29	0.6567 (5)	0.9097 (5)	0.3097 (4)	0.0425 (10)
C30	0.7774 (5)	0.6278 (5)	0.3859 (4)	0.0427 (10)
H30	0.8179	0.6487	0.3150	0.051*
C31	0.8994 (8)	0.5168 (7)	0.4602 (5)	0.0662 (15)
H31A	0.9105	0.4121	0.4481	0.079*
H31B	0.8687	0.5002	0.5321	0.079*
C32	1.0538 (8)	0.5975 (8)	0.4401 (7)	0.0781 (18)
H32A	1.1332	0.5283	0.4867	0.094*
H32B	1.0854	0.6100	0.3688	0.094*
C33	1.0391 (8)	0.7629 (9)	0.4576 (6)	0.0744 (17)
H33A	1.0294	0.7468	0.5320	0.089*
H33B	1.1339	0.8158	0.4351	0.089*
C34	0.7457 (5)	0.7943 (5)	0.4042 (3)	0.0392 (9)
C35	0.9028 (6)	0.8754 (6)	0.4009 (4)	0.0509 (12)
C36	0.6280 (6)	0.5450 (6)	0.3889 (4)	0.0484 (11)
C37	0.4401 (7)	0.3365 (7)	0.3413 (6)	0.0668 (15)
H37A	0.4537	0.2241	0.3427	0.080*
H37B	0.4172	0.3371	0.4120	0.080*
C38	0.3028 (7)	0.4161 (6)	0.2724 (5)	0.0544 (12)
C39	0.2907 (10)	0.5753 (8)	0.2063 (6)	0.0778 (19)
H39	0.3742	0.6396	0.1985	0.093*
C40	0.1494 (13)	0.6384 (10)	0.1508 (6)	0.102 (3)
H40	0.1404	0.7444	0.1060	0.123*

C41	0.0274 (9)	0.5447 (11)	0.1629 (6)	0.083 (2)
H41	-0.0645	0.5863	0.1257	0.099*
C42	0.0389 (7)	0.3918 (9)	0.2283 (6)	0.0694 (16)
H42	-0.0463	0.3296	0.2379	0.083*
C43	0.1717 (8)	0.3283 (8)	0.2799 (5)	0.0635 (14)
H43	0.1771	0.2209	0.3226	0.076*
C44	0.8804 (9)	1.0139 (8)	0.4511 (5)	0.0730 (18)
H44A	0.7926	1.0855	0.4191	0.088*
H44B	0.9716	1.0733	0.4407	0.088*
H44C	0.8631	0.9685	0.5247	0.088*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0628 (9)	0.0665 (9)	0.0968 (12)	0.0042 (7)	-0.0300 (8)	-0.0313 (8)
S2	0.0564 (9)	0.0939 (12)	0.1169 (15)	-0.0133 (8)	0.0062 (9)	-0.0742 (11)
O1	0.072 (3)	0.067 (3)	0.066 (2)	-0.025 (2)	-0.018 (2)	0.011 (2)
O2	0.102 (4)	0.049 (2)	0.082 (3)	-0.026 (2)	0.011 (3)	-0.008 (2)
O3	0.061 (2)	0.071 (2)	0.0399 (19)	-0.0170 (18)	-0.0089 (16)	0.0069 (17)
O4	0.086 (3)	0.083 (3)	0.060 (2)	-0.043 (2)	0.036 (2)	-0.031 (2)
O5	0.060 (3)	0.082 (3)	0.079 (3)	-0.032 (2)	0.025 (2)	-0.024 (2)
O6	0.071 (2)	0.072 (2)	0.0465 (19)	-0.0283 (19)	0.0220 (17)	-0.0303 (18)
C1	0.048 (3)	0.045 (2)	0.051 (3)	-0.017 (2)	0.002 (2)	-0.004 (2)
C2	0.036 (2)	0.053 (3)	0.042 (2)	-0.0072 (19)	0.0047 (18)	-0.009 (2)
C3	0.057 (3)	0.079 (4)	0.047 (3)	-0.005 (3)	0.007 (2)	-0.009 (3)
C4	0.066 (4)	0.099 (5)	0.056 (3)	0.009 (3)	0.001 (3)	-0.032 (3)
C5	0.066 (4)	0.079 (4)	0.083 (4)	0.011 (3)	-0.009 (3)	-0.049 (4)
C6	0.044 (3)	0.046 (3)	0.073 (4)	0.003 (2)	0.002 (2)	-0.021 (2)
C7	0.033 (2)	0.047 (2)	0.046 (2)	-0.0034 (18)	0.0003 (18)	-0.012 (2)
C8	0.042 (2)	0.054 (3)	0.036 (2)	-0.0045 (19)	0.0037 (18)	-0.011 (2)
C9	0.058 (3)	0.085 (4)	0.060 (3)	0.000 (3)	0.004 (3)	-0.033 (3)
C10	0.086 (5)	0.080 (4)	0.085 (5)	0.007 (3)	0.009 (4)	-0.051 (4)
C11	0.083 (4)	0.070 (4)	0.063 (3)	-0.013 (3)	-0.003 (3)	-0.037 (3)
C12	0.049 (3)	0.042 (2)	0.036 (2)	-0.0037 (19)	0.0003 (19)	-0.0069 (19)
C13	0.062 (3)	0.053 (3)	0.049 (3)	-0.020 (2)	0.005 (2)	-0.021 (2)
C14	0.054 (3)	0.060 (3)	0.039 (2)	-0.013 (2)	0.007 (2)	-0.011 (2)
C15	0.058 (4)	0.092 (5)	0.083 (4)	-0.026 (3)	0.005 (3)	-0.037 (4)
C16	0.053 (3)	0.058 (3)	0.060 (3)	-0.010 (2)	-0.010 (2)	-0.012 (3)
C17	0.082 (5)	0.080 (4)	0.072 (4)	-0.020 (3)	0.011 (3)	-0.026 (4)
C18	0.104 (6)	0.112 (7)	0.074 (5)	0.013 (5)	0.004 (4)	-0.033 (5)

C19	0.142 (10)	0.097 (6)	0.105 (7)	0.022 (6)	-0.032 (7)	-0.050 (5)
C20	0.131 (8)	0.059 (4)	0.117 (7)	-0.003 (4)	-0.049 (6)	-0.032 (4)
C21	0.074 (4)	0.066 (4)	0.087 (5)	-0.013 (3)	-0.026 (4)	-0.013 (3)
C22	0.061 (4)	0.091 (4)	0.069 (4)	-0.022 (3)	-0.004 (3)	-0.030 (3)
C23	0.053 (3)	0.043 (2)	0.054 (3)	-0.017 (2)	0.011 (2)	-0.017 (2)
C24	0.054 (3)	0.040 (2)	0.051 (3)	-0.008 (2)	0.008 (2)	-0.015 (2)
C25	0.090 (4)	0.052 (3)	0.057 (3)	-0.015 (3)	0.012 (3)	-0.013 (3)
C26	0.081 (4)	0.065 (4)	0.068 (4)	0.002 (3)	-0.022 (3)	-0.010 (3)
C27	0.061 (3)	0.064 (3)	0.079 (4)	0.007 (3)	-0.012 (3)	-0.027 (3)
C28	0.047 (3)	0.048 (3)	0.074 (4)	0.003 (2)	-0.004 (2)	-0.023 (3)
C29	0.048 (3)	0.036 (2)	0.045 (2)	-0.0080 (18)	0.0048 (19)	-0.0142 (19)
C30	0.048 (3)	0.043 (2)	0.037 (2)	-0.0081 (19)	0.0037 (19)	-0.0109 (19)
C31	0.082 (4)	0.045 (3)	0.066 (4)	0.007 (3)	-0.007 (3)	-0.012 (3)
C32	0.065 (4)	0.071 (4)	0.095 (5)	0.015 (3)	-0.018 (3)	-0.025 (4)
C33	0.054 (4)	0.091 (5)	0.078 (4)	-0.013 (3)	-0.005 (3)	-0.024 (4)
C34	0.042 (2)	0.042 (2)	0.035 (2)	-0.0068 (18)	0.0051 (17)	-0.0138 (18)
C35	0.052 (3)	0.055 (3)	0.051 (3)	-0.021 (2)	-0.004 (2)	-0.019 (2)
C36	0.055 (3)	0.039 (2)	0.047 (3)	-0.006 (2)	0.002 (2)	-0.008 (2)
C37	0.065 (4)	0.045 (3)	0.094 (4)	-0.010 (2)	-0.006 (3)	-0.026 (3)
C38	0.059 (3)	0.049 (3)	0.061 (3)	-0.009 (2)	0.004 (2)	-0.024 (2)
C39	0.092 (5)	0.051 (3)	0.076 (4)	-0.007 (3)	0.015 (4)	0.001 (3)
C40	0.150 (9)	0.070 (4)	0.065 (4)	0.027 (5)	0.023 (5)	0.004 (4)
C41	0.071 (4)	0.109 (6)	0.069 (4)	0.007 (4)	-0.002 (3)	-0.030 (4)
C42	0.054 (3)	0.084 (4)	0.081 (4)	-0.006 (3)	0.004 (3)	-0.042 (4)
C43	0.065 (4)	0.059 (3)	0.071 (4)	-0.005 (3)	0.002 (3)	-0.026 (3)
C44	0.100 (5)	0.071 (4)	0.062 (3)	-0.037 (3)	0.010 (3)	-0.035 (3)

Geometric parameters (Å, º)

S1—C14	1.773 (6)	C20—C21	1.364 (14)
S1—C15	1.808 (7)	C20—H20	0.9300
S2—C36	1.753 (6)	C21—H21	0.9300
S2—C37	1.810 (6)	C22—H22A	0.9600
O1—C14	1.196 (7)	C22—H22B	0.9600
O2—C1	1.232 (6)	C22—H22C	0.9600
O3—C12	1.421 (6)	C23—C24	1.466 (8)
O3—H3O	0.9272	C23—C35	1.527 (7)
O4—C36	1.242 (7)	C24—C25	1.388 (9)
O5—C23	1.202 (6)	C24—C29	1.412 (7)
O6—C34	1.407 (6)	C25—C26	1.394 (10)

O6—H6O	0.8453	C25—H25	0.9300
C1—C2	1.455 (8)	C26—C27	1.383 (10)
C1—C13	1.535 (7)	C26—H26	0.9300
C2—C7	1.389 (7)	C27—C28	1.405 (9)
C2—C3	1.412 (8)	C27—H27	0.9300
C3—C4	1.346 (10)	C28—C29	1.364 (7)
C3—H3	0.9300	C28—H28	0.9300
C4—C5	1.367 (11)	C29—C34	1.527 (7)
C4—H4	0.9300	C30—C36	1.518 (7)
C5—C6	1.397 (9)	C30—C31	1.522 (8)
C5—H5	0.9300	C30—C34	1.545 (6)
C6—C7	1.394 (7)	C30—H30	0.9800
C6—H6	0.9300	C31—C32	1.537 (10)
C7—C12	1.525 (7)	C31—H31A	0.9700
C8—C14	1.513 (7)	C31—H31B	0.9700
C8—C12	1.529 (7)	C32—C33	1.522 (11)
C8—C9	1.543 (8)	C32—H32A	0.9700
C8—H8	0.9800	C32—H32B	0.9700
C9—C10	1.517 (10)	C33—C35	1.521 (9)
C9—H9A	0.9700	C33—H33A	0.9700
C9—H9B	0.9700	C33—H33B	0.9700
C10—C11	1.487 (10)	C34—C35	1.571 (6)
C10—H10A	0.9700	C35—C44	1.550 (8)
C10—H10B	0.9700	C37—C38	1.501 (9)
C11—C13	1.524 (9)	C37—H37A	0.9700
C11—H11A	0.9700	C37—H37B	0.9700
C11—H11B	0.9700	C38—C39	1.392 (8)
C12—C13	1.570 (7)	C38—C43	1.398 (9)
C13—C22	1.526 (9)	C39—C40	1.421 (14)
C15—C16	1.478 (10)	C39—H39	0.9300
C15—H15A	0.9700	C40—C41	1.358 (13)
C15—H15B	0.9700	C40—H40	0.9300
C16—C21	1.401 (9)	C41—C42	1.346 (11)
C16—C17	1.413 (9)	C41—H41	0.9300
C17—C18	1.351 (11)	C42—C43	1.339 (10)
C17—H17	0.9300	C42—H42	0.9300
C18—C19	1.401 (15)	C43—H43	0.9300
C18—H18	0.9300	C44—H44A	0.9600
C19—C20	1.374 (16)	C44—H44B	0.9600
C19—H19	0.9300	C44—H44C	0.9600

C14—S1—C15	99.1 (3)	H22A—C22—H22C	109.5
C36—S2—C37	100.4 (3)	H22B—C22—H22C	109.5
C12—O3—H3O	93.4	O5—C23—C24	126.8 (5)
C34—O6—H6O	101.5	O5—C23—C35	126.0 (5)
O2—C1—C2	126.9 (5)	C24—C23—C35	107.2 (4)
O2—C1—C13	125.0 (5)	C25—C24—C29	119.5 (5)
C2—C1—C13	108.0 (4)	C25—C24—C23	130.7 (5)
C7—C2—C3	120.4 (5)	C29—C24—C23	109.8 (4)
C7—C2—C1	109.4 (4)	C24—C25—C26	119.1 (6)
C3—C2—C1	130.1 (5)	C24—C25—H25	120.5
C4—C3—C2	118.8 (6)	C26—C25—H25	120.5
C4—C3—H3	120.6	C27—C26—C25	121.7 (6)
C2—C3—H3	120.6	C27—C26—H26	119.2
C3—C4—C5	121.7 (6)	C25—C26—H26	119.2
C3—C4—H4	119.2	C26—C27—C28	118.7 (6)
C5—C4—H4	119.2	C26—C27—H27	120.6
C4—C5—C6	121.1 (6)	C28—C27—H27	120.6
C4—C5—H5	119.4	C29—C28—C27	120.4 (6)
C6—C5—H5	119.4	C29—C28—H28	119.8
C7—C6—C5	118.3 (5)	C27—C28—H28	119.8
C7—C6—H6	120.9	C28—C29—C24	120.6 (5)
C5—C6—H6	120.9	C28—C29—C34	130.2 (4)
C2—C7—C6	119.7 (5)	C24—C29—C34	109.1 (4)
C2—C7—C12	109.5 (4)	C36—C30—C31	111.3 (4)
C6—C7—C12	130.6 (4)	C36—C30—C34	110.9 (4)
C14—C8—C12	111.5 (4)	C31—C30—C34	113.4 (4)
C14—C8—C9	111.4 (4)	C36—C30—H30	106.9
C12—C8—C9	111.0 (4)	C31—C30—H30	106.9
C14—C8—H8	107.6	C34—C30—H30	106.9
C12—C8—H8	107.6	C30—C31—C32	108.2 (5)
C9—C8—H8	107.6	C30—C31—H31A	110.1
C10—C9—C8	108.4 (5)	C32—C31—H31A	110.1
C10—C9—H9A	110.0	C30—C31—H31B	110.1
C8—C9—H9A	110.0	C32—C31—H31B	110.1
C10—C9—H9B	110.0	H31A—C31—H31B	108.4
C8—C9—H9B	110.0	C33—C32—C31	111.1 (6)
H9A—C9—H9B	108.4	C33—C32—H32A	109.4
C11—C10—C9	112.1 (6)	C31—C32—H32A	109.4
C11—C10—H10A	109.2	C33—C32—H32B	109.4

C9—C10—H10A	109.2	C31—C32—H32B	109.4
C11—C10—H10B	109.2	H32A—C32—H32B	108.0
C9—C10—H10B	109.2	C35—C33—C32	114.9 (5)
H10A—C10—H10B	107.9	C35—C33—H33A	108.5
C10—C11—C13	116.4 (5)	C32—C33—H33A	108.5
C10—C11—H11A	108.2	C35—C33—H33B	108.5
C13—C11—H11A	108.2	C32—C33—H33B	108.5
C10—C11—H11B	108.2	H33A—C33—H33B	107.5
C13—C11—H11B	108.2	O6—C34—C29	114.1 (4)
H11A—C11—H11B	107.4	O6—C34—C30	112.4 (4)
O3—C12—C7	114.3 (4)	C29—C34—C30	108.8 (4)
O3—C12—C8	112.6 (4)	O6—C34—C35	109.0 (4)
C7—C12—C8	107.3 (4)	C29—C34—C35	102.7 (4)
O3—C12—C13	106.9 (4)	C30—C34—C35	109.3 (4)
C7—C12—C13	102.7 (4)	C33—C35—C23	117.6 (5)
C8—C12—C13	112.6 (4)	C33—C35—C44	107.0 (5)
C11—C13—C22	109.6 (5)	C23—C35—C44	104.3 (4)
C11—C13—C1	116.0 (5)	C33—C35—C34	115.5 (4)
C22—C13—C1	104.7 (4)	C23—C35—C34	102.4 (4)
C11—C13—C12	114.0 (5)	C44—C35—C34	109.3 (5)
C22—C13—C12	111.4 (5)	O4—C36—C30	124.4 (5)
C1—C13—C12	100.6 (4)	O4—C36—S2	120.9 (4)
O1—C14—C8	125.1 (5)	C30—C36—S2	114.6 (4)
O1—C14—S1	122.3 (4)	C38—C37—S2	115.5 (5)
C8—C14—S1	112.6 (4)	C38—C37—H37A	108.4
C16—C15—S1	117.0 (5)	S2—C37—H37A	108.4
C16—C15—H15A	108.0	C38—C37—H37B	108.4
S1—C15—H15A	108.0	S2—C37—H37B	108.4
C16—C15—H15B	108.0	H37A—C37—H37B	107.5
S1—C15—H15B	108.0	C39—C38—C43	116.7 (6)
H15A—C15—H15B	107.3	C39—C38—C37	125.2 (6)
C21—C16—C17	117.5 (7)	C43—C38—C37	117.9 (5)
C21—C16—C15	120.1 (6)	C38—C39—C40	119.1 (7)
C17—C16—C15	122.2 (5)	C38—C39—H39	120.4
C18—C17—C16	121.8 (7)	C40—C39—H39	120.4
C18—C17—H17	119.1	C41—C40—C39	120.3 (7)
C16—C17—H17	119.1	C41—C40—H40	119.8
C17—C18—C19	119.1 (10)	C39—C40—H40	119.8
C17—C18—H18	120.5	C42—C41—C40	120.2 (7)
C19—C18—H18	120.5	C42—C41—H41	119.9

C20—C19—C18	120.4 (9)	C40—C41—H41	119.9
C20—C19—H19	119.8	C43—C42—C41	120.7 (7)
C18—C19—H19	119.8	C43—C42—H42	119.7
C21—C20—C19	120.3 (8)	C41—C42—H42	119.7
C21—C20—H20	119.8	C42—C43—C38	122.9 (6)
C19—C20—H20	119.8	C42—C43—H43	118.6
C20—C21—C16	120.9 (8)	C38—C43—H43	118.6
C20—C21—H21	119.6	C35—C44—H44A	109.5
C16—C21—H21	119.6	C35—C44—H44B	109.5
C13—C22—H22A	109.5	H44A—C44—H44B	109.5
C13—C22—H22B	109.5	C35—C44—H44C	109.5
H22A—C22—H22B	109.5	H44A—C44—H44C	109.5
C13—C22—H22C	109.5	H44B—C44—H44C	109.5

Hydrogen-bond geometry (Å, º)

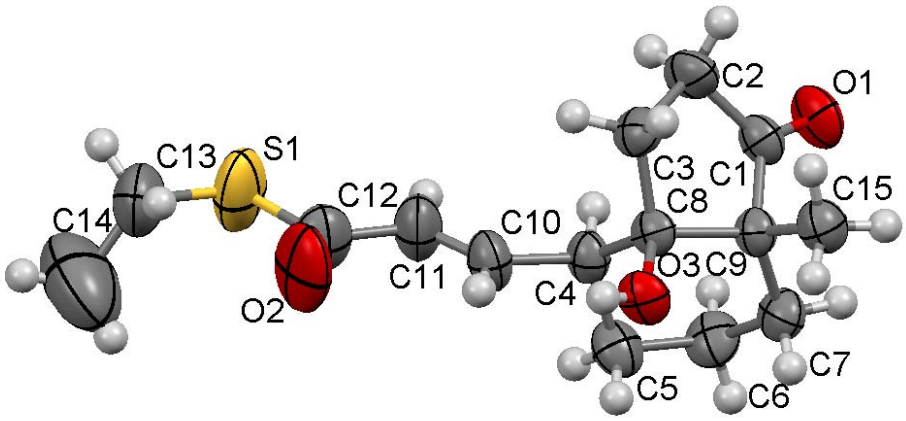
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O1	0.93	1.86	2.720 (5)	153.9
O3—H3*O*···O4	0.93	2.45	2.989 (5)	116.8
O6—H6*O*···O4	0.85	2.02	2.739 (6)	142.5

Figures

Fig. 1. The compound was shown at 50% probability thermal ellipsoids with the atom numbering scheme.

Fig. 2. The unit cell packing diagram of the compound projected along the *a*-axis and showing the H-bonding interactions (cyan lines).

X-ray data for 8d



Comment

The compound, 3(3a-hydroxy-7a-methyl-1-oxo-octa- hydro-inden-4-yl)-thio-acrlic acid *S*-ethyl ester, crystallizes in a chiral primitive monoclinic space group, $P2_1$ (#4). The compound is chiral. There are 2 asymmetric units in the unit cell.

The cyclo-hexyl ring is in the chair form, and the five-membered ring in the envelop form. The atoms C8 and C9 are *R*-configuration, while atom C4 is *S*-configurations. All the bonding parameters were within the normal ranges.

Inter-molecular, O3—H3O···O1 H-bond inter-action is present in the crystal lattice that connects the molecules into 1-D chain along *a*-axis.

The Flack parameter of the current configuration was found to be 0.1(2), and for the inverted configuration was 0.9(2) which indicated that the current configuration is the correct one.

Experimental

A colourless block crystal of $C_{22}H_{22}O_3S$, having approximate dimensions of 0.16mm *x* 0.34mm *x* 0.76mm was mounted in glass capillary. All measurements were made on a Bruker *Apex II* CCD detector with graphite monochromated Mo—K radiation. The crystal-to-detector distance was 55.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 6.8058(3)Å b = 8.7130(4)Å c = 13.1696(5)Å V = 780.58 (6) Å^3

= 91.746 (3)°.

For Z = 2 and F.W. = 282.40, the calculated density is 1.201 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1$ (#4)

The data were collected at a temperature of 23(1)°C to a maximum 2 value of 50.05°. The exposure rate was 20.0 [sec./°]. The crystal-to-detector distance was 55.00 mm.

Of the 7329 reflections that were collected, 2515 reflections were unique. (R_{int} = 0.0291); equivalent reflections were merged.

Refinement

The structure was solved by direct methods (*SHELXS-97*) and expanded using Fourier techniques. All

non-H atoms were refined anisotropically.

All of the C-bound H atoms were observable from difference Fourier map but were all placed at geometrical positions with C—H = 0.93, 0.96, 0.97 and 0.98Å for vinyl, methyl, methylene and methine H-atoms respectively. All C-bound H-atoms were refined using riding model with U_{iso}(H) = 1.2U_{eq}(Carrier). The O-bound hydrogen atoms were located from difference Fourier map and also refined using riding model of U_{iso}(H) = 1.2U_{eq}(Carrier).

The thio-ethyl group was refined as two disordered groups and their occupancies were found to be 0.728(9) and 0.272(9) respectively.

Seventeen restraints have been used during the refinement. Twelve restraints used in the anisotropic refinement of atoms C14 and C14' using isotropic restraints of standard deviation of 0.01 (six restraints for each atom). One restraint used to fix the C13—C14 distance to be 1.53(1)Å. The bond distances of the disordered group, thio-ethyl, were refined with same distance restrants which accounted for three restraints. The final restraint was used for the floating origin restraint.

Highest peak 0.39 at (-0.0007, 0.2208, 0.9729) [0.93 A from C12] Deepest hole -0.28 at (0.1489, 0.6169, 0.9039) [0.72 A from S1']

(PC-O2-123-1_2-shelxl)

Crystal data

$C_{15}H_{22}O_3S$	$F(000)$ = 304
M_r = 282.39	D_x = 1.201 Mg m^{-3}
Monoclinic, $P2_1$	Mo K radiation, = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 7329 reflections
a = 6.8058 (3) Å	= 2.8–25.0°
b = 8.7130 (4) Å	= 0.21 mm^{-1}
c = 13.1696 (5) Å	T = 296 K
= 91.746 (3)°	Plate, colourless
V = 780.58 (6) Å^3	0.44 × 0.22 × 0.04 mm
Z = 2	

Data collection

Bruker Apex CCD diffractometer	2515 independent reflections
Radiation source: fine-focus sealed tube	1908 reflections with $I > 2$ (I)
graphite	R_{int} = 0.029
scans	max = 25.0°, min = 2.8°
Absorption correction: multi-scan *SADABS* (Sheldrick, 2008)	h = -8 8
T_{min} = 0.914, T_{max} = 0.992	k = -10 10
7329 measured reflections	l = -15 14

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2 \quad (F^2)] = 0.062$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.185$	H-atom parameters constrained
$S = 1.10$	$w = 1/[\quad ^2(F_o^2) + (0.110P)^2 + 0.0373P]$ where $P = (F_o^2 + 2F_c^2)/3$
2515 reflections	$(\quad / \quad)_{max} = 0.008$
198 parameters	$_{max} = 0.39$ e Å^{-3}
17 restraints	$_{min} = -0.28$ e Å^{-3}
Flack parameter: 0.1(2)	Absolute structure: Flack (1983). 1908 Friedel pairs

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.1253 (5)	0.7768 (8)	-0.0727 (2)	0.1228 (16)	0.728 (9)
C13	-0.1352 (13)	0.8031 (12)	-0.0975 (7)	0.110 (3)	0.728 (9)
H13A	-0.1960	0.8330	-0.0348	0.132*	0.728 (9)
H13B	-0.1539	0.8865	-0.1456	0.132*	0.728 (9)
C14	-0.237 (2)	0.6641 (19)	-0.1386 (16)	0.202 (8)	0.728 (9)
H14A	-0.1615	0.6201	-0.1916	0.242*	0.728 (9)
H14B	-0.3649	0.6922	-0.1655	0.242*	0.728 (9)
H14C	-0.2513	0.5903	-0.0851	0.242*	0.728 (9)
S1'	0.1301 (15)	0.6874 (19)	-0.0692 (8)	0.1228 (16)	0.272 (9)
C13'	-0.121 (3)	0.653 (3)	-0.1059 (14)	0.096 (8)	0.272 (9)
H13C	-0.1227	0.5810	-0.1623	0.115*	0.272 (9)
H13D	-0.1830	0.6019	-0.0498	0.115*	0.272 (9)
C14'	-0.243 (5)	0.785 (4)	-0.136 (4)	0.166 (14)	0.272 (9)
H14D	-0.2288	0.8641	-0.0854	0.199*	0.272 (9)
H14E	-0.3783	0.7539	-0.1416	0.199*	0.272 (9)
H14F	-0.2020	0.8235	-0.2001	0.199*	0.272 (9)

O1	1.0541 (3)	0.8743 (4)	0.3625 (2)	0.0700 (8)	
O2	-0.0213 (5)	0.7338 (7)	0.1014 (3)	0.1238 (17)	
O3	0.4024 (3)	0.7104 (3)	0.42017 (19)	0.0574 (7)	
H3O	0.2848	0.7336	0.4158	0.069*	
C1	0.8752 (5)	0.8724 (5)	0.3662 (3)	0.0505 (8)	
C2	0.7459 (5)	0.9979 (5)	0.3230 (4)	0.0683 (12)	
H2A	0.7631	1.0086	0.2505	0.082*	
H2B	0.7759	1.0953	0.3558	0.082*	
C3	0.5378 (5)	0.9474 (4)	0.3448 (3)	0.0576 (10)	
H3A	0.4486	0.9724	0.2884	0.069*	
H3B	0.4916	0.9966	0.4057	0.069*	
C4	0.5537 (5)	0.6900 (5)	0.2553 (3)	0.0512 (9)	
H4	0.6518	0.7412	0.2141	0.061*	
C5	0.6162 (6)	0.5214 (5)	0.2675 (3)	0.0631 (11)	
H5A	0.5260	0.4687	0.3113	0.076*	
H5B	0.6112	0.4711	0.2017	0.076*	
C6	0.8211 (6)	0.5122 (5)	0.3126 (3)	0.0647 (11)	
H6A	0.9117	0.5609	0.2671	0.078*	
H6B	0.8591	0.4054	0.3200	0.078*	
C7	0.8346 (6)	0.5899 (5)	0.4147 (3)	0.0582 (9)	
H7A	0.9715	0.5924	0.4374	0.070*	
H7B	0.7642	0.5281	0.4629	0.070*	
C8	0.5522 (4)	0.7722 (4)	0.3595 (2)	0.0450 (8)	
C9	0.7537 (4)	0.7528 (4)	0.4172 (2)	0.0447 (8)	
C10	0.3587 (6)	0.7042 (5)	0.2003 (3)	0.0645 (11)	
H10	0.2487	0.6888	0.2392	0.077*	
C11	0.3247 (7)	0.7351 (7)	0.1056 (3)	0.0784 (14)	
H11	0.4304	0.7536	0.0642	0.094*	
C12	0.1196 (8)	0.7423 (7)	0.0601 (4)	0.0854 (15)	
C15	0.7420 (6)	0.8069 (6)	0.5285 (3)	0.0612 (10)	
H15A	0.8679	0.7941	0.5623	0.073*	
H15B	0.6456	0.7471	0.5626	0.073*	
H15C	0.7052	0.9133	0.5299	0.073*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0968 (12)	0.203 (5)	0.0679 (9)	-0.031 (2)	-0.0167 (8)	0.050 (2)
C13	0.113 (7)	0.125 (8)	0.089 (6)	-0.007 (6)	-0.038 (5)	0.010 (5)
C14	0.176 (13)	0.180 (13)	0.245 (15)	-0.003 (11)	-0.058 (11)	-0.077 (12)

S1'	0.0968 (12)	0.203 (5)	0.0679 (9)	-0.031 (2)	-0.0167 (8)	0.050 (2)
C13'	0.117 (19)	0.13 (2)	0.042 (9)	-0.010 (16)	-0.009 (10)	-0.001 (10)
C14'	0.18 (2)	0.136 (19)	0.18 (2)	-0.020 (17)	-0.030 (17)	0.036 (17)
O1	0.0303 (13)	0.0912 (19)	0.0885 (19)	-0.0047 (13)	0.0043 (11)	-0.0091 (16)
O2	0.0384 (17)	0.203 (5)	0.130 (3)	-0.009 (2)	-0.0089 (19)	0.021 (3)
O3	0.0354 (12)	0.0716 (17)	0.0659 (16)	-0.0042 (12)	0.0146 (10)	0.0008 (12)
C1	0.0363 (18)	0.059 (2)	0.056 (2)	-0.0047 (16)	0.0040 (14)	-0.0052 (17)
C2	0.041 (2)	0.065 (3)	0.099 (3)	-0.0117 (18)	0.002 (2)	0.017 (2)
C3	0.0423 (19)	0.054 (2)	0.077 (3)	0.0084 (17)	-0.0007 (17)	0.009 (2)
C4	0.0362 (17)	0.067 (2)	0.0508 (19)	-0.0030 (16)	0.0012 (14)	0.0016 (16)
C5	0.060 (2)	0.067 (3)	0.063 (2)	0.003 (2)	0.0023 (18)	-0.0193 (19)
C6	0.056 (2)	0.062 (2)	0.076 (3)	0.018 (2)	0.0046 (19)	-0.006 (2)
C7	0.045 (2)	0.059 (2)	0.070 (2)	0.0083 (17)	-0.0030 (17)	0.0005 (19)
C8	0.0273 (15)	0.051 (2)	0.0571 (19)	0.0027 (13)	0.0065 (13)	0.0037 (16)
C9	0.0335 (16)	0.052 (2)	0.0488 (17)	0.0036 (14)	0.0019 (13)	-0.0012 (15)
C10	0.046 (2)	0.087 (3)	0.061 (2)	-0.007 (2)	-0.0057 (16)	-0.005 (2)
C11	0.060 (3)	0.116 (4)	0.059 (2)	-0.010 (3)	-0.0075 (18)	0.011 (3)
C12	0.076 (3)	0.116 (4)	0.065 (3)	-0.010 (3)	0.009 (2)	0.012 (3)
C15	0.058 (2)	0.069 (2)	0.057 (2)	-0.0035 (19)	0.0015 (16)	-0.0042 (18)

Geometric parameters (Å, º)

S1—C12	1.776 (6)	C3—C8	1.542 (5)
S1—C13	1.808 (9)	C3—H3A	0.9700
C13—C14	1.490 (9)	C3—H3B	0.9700
C13—H13A	0.9700	C4—C10	1.498 (5)
C13—H13B	0.9700	C4—C5	1.536 (6)
C14—H14A	0.9600	C4—C8	1.549 (5)
C14—H14B	0.9600	C4—H4	0.9800
C14—H14C	0.9600	C5—C6	1.502 (5)
S1'—C12	1.773 (13)	C5—H5A	0.9700
S1'—C13'	1.787 (16)	C5—H5B	0.9700
C13'—C14'	1.468 (19)	C6—C7	1.505 (6)
C13'—H13C	0.9700	C6—H6A	0.9700
C13'—H13D	0.9700	C6—H6B	0.9700
C14'—H14D	0.9600	C7—C9	1.523 (5)
C14'—H14E	0.9600	C7—H7A	0.9700
C14'—H14F	0.9600	C7—H7B	0.9700
O1—C1	1.220 (4)	C8—C9	1.556 (4)
O2—C12	1.119 (6)	C9—C15	1.545 (5)

O3—C8	1.420 (4)	C10—C11	1.289 (6)
O3—H3O	0.8259	C10—H10	0.9300
C1—C9	1.502 (5)	C11—C12	1.504 (6)
C1—C2	1.505 (6)	C11—H11	0.9300
C2—C3	1.519 (5)	C15—H15A	0.9600
C2—H2A	0.9700	C15—H15B	0.9600
C2—H2B	0.9700	C15—H15C	0.9600
C12—S1—C13	98.6 (4)	C6—C5—H5B	109.7
C14—C13—S1	114.0 (9)	C4—C5—H5B	109.7
C14—C13—H13A	108.8	H5A—C5—H5B	108.2
S1—C13—H13A	108.8	C5—C6—C7	111.1 (3)
C14—C13—H13B	108.8	C5—C6—H6A	109.4
S1—C13—H13B	108.8	C7—C6—H6A	109.4
H13A—C13—H13B	107.7	C5—C6—H6B	109.4
C12—S1'—C13'	103.9 (9)	C7—C6—H6B	109.4
C14'—C13'—S1'	118 (2)	H6A—C6—H6B	108.0
C14'—C13'—H13C	107.8	C6—C7—C9	115.2 (3)
S1'—C13'—H13C	107.8	C6—C7—H7A	108.5
C14'—C13'—H13D	107.8	C9—C7—H7A	108.5
S1'—C13'—H13D	107.8	C6—C7—H7B	108.5
H13C—C13'—H13D	107.2	C9—C7—H7B	108.5
C13'—C14'—H14D	109.5	H7A—C7—H7B	107.5
C13'—C14'—H14E	109.5	O3—C8—C3	113.7 (3)
H14D—C14'—H14E	109.5	O3—C8—C4	110.3 (3)
C13'—C14'—H14F	109.5	C3—C8—C4	110.4 (3)
H14D—C14'—H14F	109.5	O3—C8—C9	108.7 (3)
H14E—C14'—H14F	109.5	C3—C8—C9	102.7 (3)
C8—O3—H3O	125.4	C4—C8—C9	110.6 (2)
O1—C1—C9	126.3 (4)	C1—C9—C7	115.6 (3)
O1—C1—C2	123.2 (4)	C1—C9—C15	104.9 (3)
C9—C1—C2	110.5 (3)	C7—C9—C15	109.5 (3)
C1—C2—C3	104.8 (3)	C1—C9—C8	101.3 (3)
C1—C2—H2A	110.8	C7—C9—C8	113.9 (3)
C3—C2—H2A	110.8	C15—C9—C8	111.1 (3)
C1—C2—H2B	110.8	C11—C10—C4	128.0 (4)
C3—C2—H2B	110.8	C11—C10—H10	116.0
H2A—C2—H2B	108.9	C4—C10—H10	116.0
C2—C3—C8	104.8 (3)	C10—C11—C12	122.1 (4)
C2—C3—H3A	110.8	C10—C11—H11	119.0

C8—C3—H3A	110.8	C12—C11—H11	119.0
C2—C3—H3B	110.8	O2—C12—C11	127.1 (5)
C8—C3—H3B	110.8	O2—C12—S1'	120.6 (6)
H3A—C3—H3B	108.9	C11—C12—S1'	107.9 (5)
C10—C4—C5	111.6 (3)	O2—C12—S1	122.3 (5)
C10—C4—C8	111.1 (3)	C11—C12—S1	110.6 (4)
C5—C4—C8	111.0 (3)	C9—C15—H15A	109.5
C10—C4—H4	107.6	C9—C15—H15B	109.5
C5—C4—H4	107.6	H15A—C15—H15B	109.5
C8—C4—H4	107.6	C9—C15—H15C	109.5
C6—C5—C4	110.0 (3)	H15A—C15—H15C	109.5
C6—C5—H5A	109.7	H15B—C15—H15C	109.5
C4—C5—H5A	109.7		

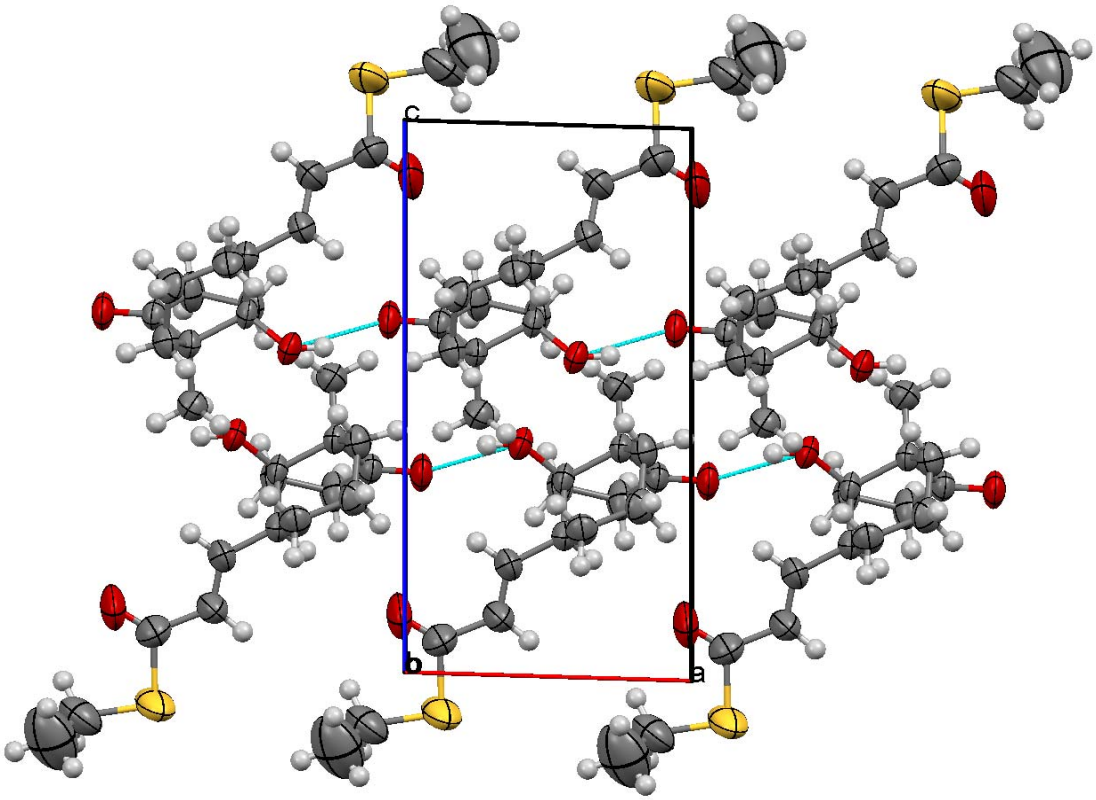
Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O1^{i}	0.83	2.10	2.851 (4)	151.8

Symmetry code: (i) *x*-1, *y*, *z*.

Figures

The unit cell packing diagram of the compound projected along the *b*-axis and showing the H-bonding interactions (cyan lines) connect the molecules into 1-D chain along *a*-axis (showing major component only).



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