

Supporting information

An Entry to a Chiral Dihydropyrazole Scaffold: Enantioselective [3+2] Cycloaddition of Nitrile Imines

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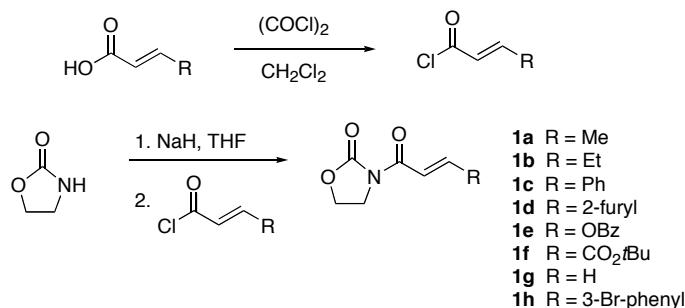
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General: Dichloromethane was distilled from calcium hydride under nitrogen prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Magnesium perchlorate, magnesium iodide, copper(II) triflate, zinc iodide, and nickel perchlorate were purchased from Aldrich chemicals. Magnesium triflimide and zinc triflimide were prepared according to literature procedure. Cyclopropyl bisoxazoline ligand {3aR-[2(3'aS, 8'aR), 3aa, 8aa]}-2,2'-(cyclopropylidene)-bis{3a,8a-dihydro-8H-indeno[1,2d]-oxazole} was prepared according to literature procedure. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh) or on an ISCOTM CombiFlash Companion with AnaLogixTM RS-4 columns. All glassware was oven dried, assembled hot and cooled under a stream of nitrogen before use. Reactions with air sensitive materials were carried out by standard syringe techniques.

Melting points were measured with a Fisher-Johns melting points apparatus and are uncorrected. ¹H-NMR were recorded on a Varian Unity/Inova-500 NB (500 MHz), Varian Unity/Inova-400 NB (400 MHz), or Varian Mercury-300 (300 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl₃ (7.27 ppm) as an internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. ¹³C-NMR was recorded on Varian Unity/Inova-500 NB (125 MHz), Varian Unity/Inova-400 NB (100 MHz), and Varian Mercury-300 (75MHz) spectrometers, using broadband proton decoupling. Chemical shifts are reported in parts per million (ppm) downfield from TMS, using the middle resonance of CDCl₃ (77.23) as an internal standard. HPLC analyses were carried out on Waters 515 HPLC pump and a 2487 dual λ absorbance detector connected to a PC with Empower workstation.

Rotations were recorded on a JASCO-DIP-370 instrument. FT-IR spectra were recorded on a Mettler-Toledo ReactIR-4000. High Resolution Mass Spectra (HRMS) (ESI+) were obtained from the Mass Spectrometry Laboratory, North Dakota State University, Fargo, North Dakota.

General procedure for the synthesis of 3-(2-Alkenoyl)-2-oxazolidinones (1a-1h):

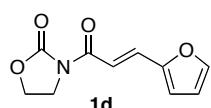


To a solution of α,β -unsaturated acid (11.0 mmol) in 15 mL of dichloromethane at 0 °C, under nitrogen, was added oxalyl chloride (12.1 mmol) followed by one drop of DMF. After 10 minutes the solution was allowed to warm to room temperature and stir for two hours. The solvent and excess oxalyl chloride were removed *in vacuo* to give crude acid chloride, which was used without further purification.

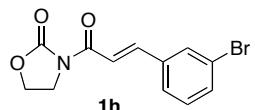
In a separate flask 2-oxazolidinone (11.0 mmol) was dissolved in THF (45 mL) and cooled to 0 °C under nitrogen. To this solution was added sodium hydride (15.0 mmol, 60% dispersion in mineral oil) in portions. This suspension was stirred at 0 °C for 10 min, then allowed to warm to room temperature and stir for an additional 45 minutes. Crude acid chloride was then added dropwise and the mixture allowed to stir for 4 hours at room temperature. The reaction was quenched with water (2 mL) and the THF was removed *in vacuo*. The reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic extracts were then washed with water (2 x 10 mL), and 1 M NaOH (2

x 10 mL), dried over MgSO_4 and concentrated. The crude product was purified by flash column silica gel chromatography using hexane/EtOAc as eluent.

Analytical characteristics for compounds **1a**¹, **1b**², **1c**³, **1e**⁴, **1f**⁵, and **1g**⁶ were in agreement with previously reported spectra and properties.

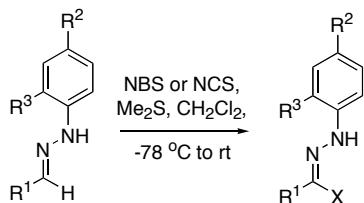


3-(3-Furan-2-yl-acryloyl)-oxazolidin-2-one (1d): This compound was obtained as an off white solid in 74% yield; m.p. = 135-137 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 4.11 (t, J = 8.0 Hz, 2H), 4.44 (t, J = 8.0 Hz, 2H), 6.47 (dd, J = 1.6 Hz, 3.6 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H), 7.51 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 15.2 Hz, 1H), 7.72 (d, J = 15.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 43.0, 62.2, 112.7, 114.3, 116.2, 132.5, 145.5, 151.5, 153.7, 165.5; IR (neat, cm^{-1}): 3110, 2997, 2912, 1762, 1667, 1611, 1555, 1339; HRMS Exact mass calcd. for $\text{C}_{10}\text{H}_9\text{NO}_4\text{Na}^+$ 230.0424 found 230.0416.



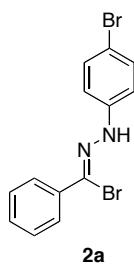
3-[3-(3-Bromo-phenyl)-acryloyl]-oxazolidin-2-one (1h): This compound was obtained as a white solid in 68% yield; m.p. = 153-155 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 4.13 (t, J = 6.4 Hz, 2H), 4.46 (t, J = 6.4 Hz, 2H), 7.26 (t, J = 6.0 Hz, 1H), 7.51 (t, J = 6.4 Hz, 2H), 7.72 (s, 1H), 7.75 (d, J = 12.8 Hz, 1H), 7.87 (d, J = 12.8 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 43.0, 62.3, 118.2, 123.2, 127.3, 130.6, 131.4, 133.6, 136.8, 144.6, 153.7, 165.1; IR (neat, cm^{-1}): 3091, 2923, 1764, 1676, 1621, 1555, 1474; HRMS Exact mass calcd. for $\text{C}_{12}\text{H}_{10}\text{BrNO}_3\text{Na}^+$ 317.9736 found 317.9740.

General procedure for the synthesis of hydrazoneoyl halides (2a-2e):

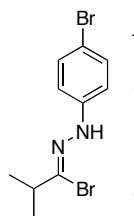


To NBS or NCS (73.2 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added methyl sulfide (147 mmol) over 5 minutes. After stirring for 15 minutes, the reaction was further cooled to –

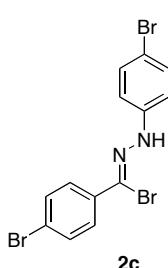
78 °C. Then the corresponding hydrazone (24.4 mmol) in CH_2Cl_2 (75 mL) was added. The reaction was allowed to stir at –78 °C for 1 h, then slowly allowed to warm to room temperature over 3 h. The reaction was quenched by addition of 200 mL of cold water. The organic layer was then washed with 200 mL cold water, 50 mL brine, 50 mL sat. aq. Na_2SO_3 , and 100 mL water. The organic layer was dried over MgSO_4 , filtered, and concentrated. Crude product was purified by flash column silica gel chromatography eluting first with 19:1 hexanes/EtOAc, then 9:1 hexanes/EtOAc to give the corresponding hydrazonoyl halides. Chromatography should be performed quickly as hydrazonoyl halides decompose over time on silica gel. Note: hydrazonoyl bromides **2b**, **2c**, and **8** were unstable and should be used immediately after preparation.



N-4-Bromophenylbenzohydrazonoyl bromide (2a). Obtained according to the general procedure in 95% yield as a red solid, m.p. = 94-96 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.07 (m, 2H), 7.35-7.43 (m, 5H), 7.89 (m, 2H), 8.02 (br s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 113.5, 115.4, 120.5, 127.9, 128.6, 129.8, 132.5, 135.7, 142.4; IR (neat, cm^{-1}): 3305, 3060, 3033, 1590, 1495, 1310; HRMS Exact mass calcd. for $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{N}_4^+$ (nitrile imine dimer + H^+) 544.9971 found 544.9995.

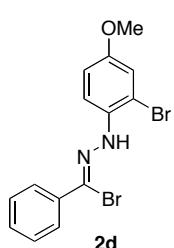


N-4-Bromophenylisopropohydrazonoyl bromide (2b). Obtained according to the general procedure in 46% yield as a red oil. ^1H NMR (CDCl_3 , 500 MHz) δ 1.26 (d, J = 6.5 Hz, 6H), 2.89 (sept, J = 6.5 Hz, 1H), 6.93 (dt, J = 9 Hz, 2.5 Hz, 2H), 7.34 (dt, J = 9 Hz, 2.5 Hz, 2H), 7.57 (br s, 1H). ^{13}C NMR and high resolution mass spectroscopy were not performed due to the instability of this compound.



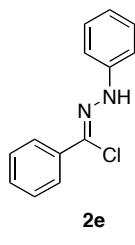
N-4-Bromophenyl-4-bromobenzohydrazonoyl bromide (2c). Obtained according to the general procedure in 92% yield as a purple solid, m.p. = 143-146 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 7.04 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H), 8.01 (br s, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 113.7,

115.4, 119.2, 124.0, 129.1, 131.8, 132.5, 134.6, 142.1; IR (neat, cm^{-1}): 3303, 3072, 1590, 1497, 1395; HRMS Exact mass calcd for $\text{C}_{26}\text{H}_{17}\text{Br}_2\text{N}_4^+$ (nitrile imine dimer + H^+) 700.8181 found 700.8146.

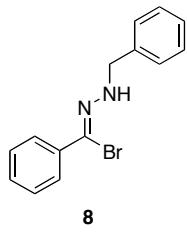


N-2-Bromo-4-methoxyphenylbenzohydrazonoyl bromide (2d).

Obtained according to the general procedure in 42% yield as a red oil. ^1H NMR (CDCl_3 , 500 MHz) δ 3.79 (s, 3H), 6.90 (dd, J = 9 Hz, 2.5 Hz, 1H), 7.08 (d, J = 2.5 Hz, 1H), 7.38-7.42 (m, 3H), 7.49 (d, J = 9.0 Hz, 1H), 7.91 (m, 2H), 8.42 (br s, 1H). ^{13}C NMR and high resolution mass spectroscopy were not performed due to the instability of this compound.

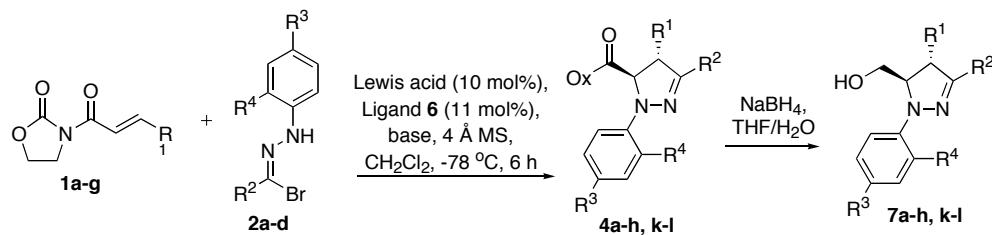


N-Phenylbenzohydrazonoyl chloride (2e). **2e** has been previously prepared.⁷ Obtained according to the general procedure in 88% yield as a yellow-red solid, m.p. = 127-128 °C (lit. 129-131 °C). ^1H NMR (CDCl_3 , 400 MHz) δ 6.93 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.30-7.42 (m, 5H), 7.92 (d, J = 7.2 Hz, 2H), 8.03 (br s, 1H). IR (neat, cm^{-1}): 3309, 1606, 1505, 1436. HRMS Exact mass calcd for $\text{C}_{26}\text{H}_{20}\text{N}_4^+$ (nitrile imine dimer) 388.1682 found 388.1688.

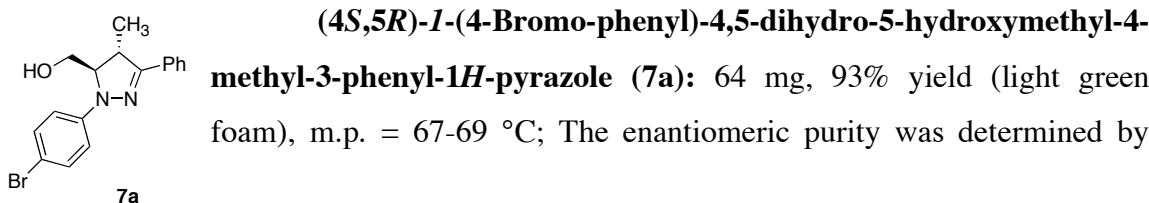


N-Benzylbenzohydrazonoyl bromide (8). Obtained according to the general procedure in 58% yield as a red oil. ^1H NMR (CDCl_3 , 400 MHz) δ 4.59 (s, 2H), 6.19 (br s, 1H), 7.30-7.42 (m, 4H), 7.84-7.87 (m, 2H), 7.30-7.42 (m, 4H). ^{13}C NMR and high resolution mass spectroscopy were not performed due to the instability of this compound.

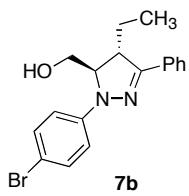
General Procedure for Enantioselective Nitrile Imine Cycloadditions (With Hydrazonoyl Bromides (2a-d) as Nitrile Imine Precursors):



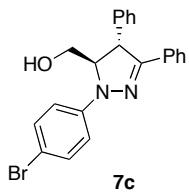
A flame-dried flask containing 4 Å molecular sieves (150 mg), Lewis acid (0.020 mmol), ligand **6** (0.022 mmol), and substrate **1a-g** (0.2 mmol) in CH_2Cl_2 (2 mL) was stirred for 30 minutes at room temperature. The flask was then cooled to $-78\text{ }^\circ\text{C}$ and stirred for 5 minutes. Then hydrazonoyl bromide **2a-d** (0.3 mmol) in CH_2Cl_2 (1 mL) was added to the reaction. After 5 minutes amine base (0.3 mmol) was added to the reaction. After stirring for 6 h at $-78\text{ }^\circ\text{C}$, the reaction was quenched with 0.5 M HCl (20 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1 g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude **4a-h, k-l**, which was analyzed by ^1H NMR to determine diastereomeric ratios. Crude **4a-h, k-l** was then reconcentrated and dissolved in THF (5 mL). To this solution was added NaBH_4 (1.32 mmol) in H_2O (1 mL). After 3 h at room temperature, the reaction was quenched with 1 M HCl (10 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1 g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude **7a-h, k-l**, which were purified by flash column silica gel chromatography on an ISCOTM CombiFlash Companion with AnaLogixTM RS-4 columns.



HPLC (254 nm, 25 °C) t_R 13.9 min (major); t_R 19.5 min (minor) [Chiracel AD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane *i*-PrOH, 95/5, 1.0 mL/min] as 99% ee. $[\alpha]_D^{25} = +501.6$ (*c* 0.30, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.32 (d, *J* = 7.2 Hz, 3H), 1.79 (br s, 1H), 3.61 (dq, *J* = 3.2 Hz, 7.2 Hz, 1H), 3.73 (m, 2H), 4.03 (m, 1H), 7.07 (m, 2H), 7.32-7.42 (m, 5H), 7.76 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 19.0, 43.2, 61.7, 69.4, 111.3, 114.9, 126.4, 128.9, 129.1, 131.7, 132.2, 144.0, 154.0; IR (neat, cm^{-1}): 3500-3300 (OH), 3058, 2968, 2931, 2873, 1590, 1486, 1393; HRMS Exact mass calcd. for $\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{OH}^+$ 345.0597 found 345.0580.

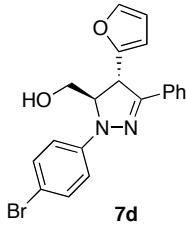


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-4-ethyl-5-hydroxymethyl-3-phenyl-1H-pyrazole (7b): 67 mg, 93% yield (yellow oil); The enantiomeric purity was determined before reduction by HPLC of the oxazolidinone derivative (**4b**) (254 nm, 25 °C) t_R 23.3 min (major); t_R 49.6 min (minor) [Chiracel AD (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 99% ee. $[\alpha]_D^{25} = +430.8$ (*c* 0.57, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.55-1.82 (m, 3H, $\text{CH}_2\text{-CH}_3$ + OH), 3.53 (app dt, *J* = 8.0 Hz, 3.5 Hz, 1H), 3.75 (m, 2H), 4.13 (app q, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.34-7.42 (m, 5H), 7.70 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 10.6, 24.9, 50.0, 62.5, 66.5, 111.2, 114.8, 126.5, 128.9, 129.1, 131.9, 132.2, 143.9, 152.6; IR (neat, cm^{-1}): 3500-3300 (OH), 3058, 2962, 2931, 2875, 1590, 1488; HRMS Exact mass calcd. for $\text{C}_{18}\text{H}_{19}\text{BrN}_2\text{ONa}^+$ 381.0573 found 381.0584.

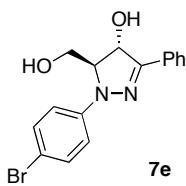


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-3,4-diphenyl-5-hydroxymethyl-1H-pyrazole (7c): 77 mg, 95% yield (light green foam), m.p. = 78-79 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 14.6 min (minor); t_R 20.6 min (major) [Chiracel AD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 97% ee. $[\alpha]_D^{25} = +268.6$ (*c* 0.52, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.76 (br s, 1H), 3.85 (m, 2H), 4.21 (app q, *J* = 4.0 Hz, 1H), 4.65 (d, *J* = 4.0 Hz, 1H), 7.08 (m, 2H), 7.16 (m, 2H), 7.22-7.29 (m, 6H), 7.36 (m, 2H), 7.65 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.2, 62.1, 71.5, 111.8, 115.2, 126.8, 127.6, 127.7, 128.7, 128.9, 129.5,

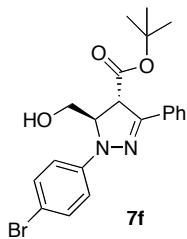
131.8, 132.3, 140.7, 143.8, 151.2; IR (neat, cm^{-1}): 3500-3300 (OH), 3062, 3027, 2931, 2877, 1588, 1488, 1391; HRMS Exact mass calcd. for $\text{C}_{22}\text{H}_{19}\text{BrN}_2\text{OH}^+$ 407.0735 found 407.0728.



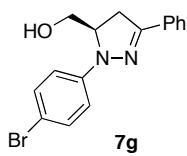
(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-4-furan-2-yl-5-hydroxymethyl-1H-pyrazole (7d): 75 mg, 94% yield (light green solid), m.p. = 156-158 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_{R} 31.7 min (minor); t_{R} 51.8 min (major) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 99% ee. $[\alpha]_{\text{D}}^{25} = +352.4$ (*c* 0.34, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.88 (br s, 1H), 3.83 (br d, $J = 11.5$ Hz, 1H), 3.91 (dd, $J = 11.5$ Hz, 5.0 Hz, 1H), 4.40 (dd, $J = 8.0$ Hz, 4.5 Hz, 1H), 4.86 (d, $J = 4.5$ Hz, 1H), 6.08 (d, $J = 3.5$ Hz, 1H), 6.26 (dd, $J = 3.0$ Hz, 2.0 Hz, 1H), 7.09 (d, $J = 9.0$ Hz, 2H), 7.29-7.34 (m, 4H), 7.38 (d, $J = 9.0$ Hz, 2H), 7.72 (dd, $J = 8.0$ Hz, 1.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 48.2, 61.7, 68.6, 107.4, 110.9, 112.1, 115.3, 126.5, 128.7, 129.1, 131.7, 132.2, 142.6, 143.7, 148.3, 152.5; IR (neat, cm^{-1}): 3500-3300 (OH), 3060, 2933, 2879, 1590, 1488, 1391; HRMS Exact mass calcd. for $\text{C}_{20}\text{H}_{17}\text{BrN}_2\text{O}_2\text{Na}^+$ 419.0366 found 419.0363.



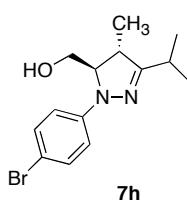
(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-hydroxymethyl-3-phenyl-1H-pyrazol-4-ol (7e): 67 mg, 97% yield (light green foam), m.p. = 82-83 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_{R} 18.8 min (major); t_{R} 23.3 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 93/7, 1.0 mL/min] as 96% ee. $[\alpha]_{\text{D}}^{25} = +364.6$ (*c* 0.55, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.97 (br s, 1H), 2.77 (br s, 1H), 3.63 (dd, $J = 11.5$ Hz, 6.5 Hz, 1H), 3.83 (dd, $J = 11.5$ Hz, 3.0 Hz, 1H), 4.16 (app quintet, $J = 3.0$ Hz, 1H), 5.32 (br s, 1H), 7.01 (d, $J = 9.0$ Hz, 2H), 7.33-7.39 (m, 5H), 7.82 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 60.3, 70.0, 77.5, 112.4, 115.2, 126.3, 129.0, 129.3, 131.0, 132.4, 143.0, 149.4; IR (neat, cm^{-1}): 3500-3200 (OH), 2952, 2890, 1592, 1490, 1396; HRMS Exact mass calcd. for $\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{O}_2\text{Na}^+$ 369.0209 found 369.0222.



(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-hydroxymethyl-3-phenyl-1H-pyrazole-4-carboxylic acid *tert*-butyl ester (7f): 77 mg, 90% yield (light green solid), m.p. = 155-157 °C. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 21.8 min (major); t_R 42.2 min (minor) [Chiracel AD (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 93% ee. $[\alpha]_D^{25} = +222.6$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 1.32 (s, 9H), 1.88 (br s, 1H), 3.78 (br d, J = 11.5 Hz, 1H), 3.90 (dd, J = 11.5 Hz, 4.5 Hz, 1H), 4.34 (d, J = 4.5 Hz, 1H), 4.66 (dd, J = 8.5 Hz, 4.5 Hz, 1H), 7.09 (m, 2H), 7.34-7.40 (m, 5H), 7.81 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.9, 55.7, 62.1, 66.3, 82.8, 112.1, 115.4, 126.8, 128.5, 129.2, 131.7, 132.2, 143.5, 146.8, 169.4; IR (neat, cm⁻¹): 3500-3300 (OH); 2979, 2933, 1727, 1588, 1490, 1393; HRMS Exact mass calcd. for C₂₁H₂₃BrN₂O₃Na⁺ 453.0784 found 453.0757.

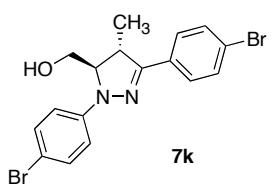


(5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-hydroxymethyl-3-phenyl-1H-pyrazole (7g): 63 mg, 95% yield (light green solid), m.p. = 156-159 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 20.7 min (major); t_R 26.4 min (minor) [Chiracel AD (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane *i*-PrOH, 95/5, 1.0 mL/min] as 84% ee. $[\alpha]_D^{25} = +343.7$ (c 0.57, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 1.60 (br s, 1H), 3.31 (dd, J = 5.5 Hz, 17.0 Hz, 1H), 3.47 (dd, J = 7.5 Hz, 17.0 Hz, 1H), 3.75 (dd, J = 2.5 Hz, 11.0 Hz, 1H), 3.90 (dd, J = 5.0 Hz, 11.0 Hz, 1H), 4.44-4.49 (m, 1H), 7.09 (d, J = 9.0 Hz, 2H), 7.34-7.41 (m, 5H), 7.73 (d, J = 7.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 36.4, 61.5, 62.7, 111.7, 115.1, 126.2, 128.8, 129.3, 132.2, 132.5, 144.3, 149.8; IR (neat, cm⁻¹): 3500-3300 (OH), 3060, 2929, 1590, 1488, 1397; HRMS Exact mass calcd. for C₁₆H₁₅BrN₂O₃Na⁺ 353.0260 found 353.0242.

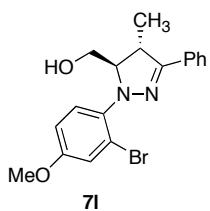


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-hydroxymethyl-3-isopropyl-1H-pyrazole (7h): 61 mg, 98% yield (pink oil); The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 35.1 min (major); t_R 40.5 min (minor) [Chiracel AD (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 99% ee.

$[\alpha]_D^{25} = +255.4$ (*c* 0.74, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.17 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.77 (br s, 1H) 2.65 (sept, *J* = 7.2 Hz, 1H), 3.17 (overlapping dq, *J* = 5.6 Hz, 6.8 Hz, 1H), 3.62-3.67 (m, 2H), 3.80 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.0, 19.9, 21.2, 28.0, 44.8, 62.4, 70.0, 111.3, 115.2, 132.0, 146.0, 163.4; IR (neat, cm^{-1}): 3500-3300 (OH), 2968, 2931, 2875, 1590, 1490, 1333; HRMS Exact mass calcd. for $\text{C}_{14}\text{H}_{19}\text{BrN}_2\text{ONa}^+$ 333.0573 found 333.0570.



(4S,5R)-1,3-Bis-(4-bromo-phenyl)-4,5-dihydro-5-hydroxymethyl-4-methyl-1H-pyrazole (7k): 80 mg, 95% yield (yellow-green foam), m.p. = 65-66 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 19.7 min (major); t_R 28.6 min (minor) [Chiracel OD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 1.0 mL/min] as 95% ee. $[\alpha]_D^{25} = +380.5$ (*c* 0.68, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.28 (d, *J* = 7.5 Hz, 3H), 2.09 (br s, 1H), 3.55 (dq, *J* = 3.0 Hz, 7.5 Hz, 1H), 3.68 (d, *J* = 5.0 Hz, 2H), 4.01 (dd, *J* = 7.5 Hz, 5.0 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 18.9, 42.9, 61.5, 69.3, 111.4, 114.9, 122.9, 127.8, 130.6, 132.0, 132.2, 143.5, 152.7; IR (neat, cm^{-1}): 3500-3300 (OH), 3062, 3029, 2931, 2877, 1590, 1486, 1385; HRMS Exact mass calcd. for $\text{C}_{17}\text{H}_{16}\text{Br}_2\text{N}_2\text{ONa}^+$ 444.9522 found 444.9523.

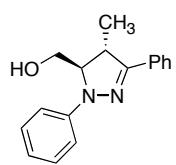


(4S,5R)-1-(2-Bromo-4-methoxy-phenyl)-4,5-dihydro-5-hydroxymethyl-4-methyl-3-phenyl-1H-pyrazole (7l): 72 mg, 96% yield (clear oil); The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 24.4 min (major); t_R 28.7 min (minor) [Chiracel AD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 96% ee. $[\alpha]_D^{25} = -99.6$ (*c* 0.45, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.40 (d, *J* = 7.0 Hz, 3H), 1.77 (br s, 1H), 3.51 (dd, *J* = 12.0 Hz, 3.5 Hz, 1H), 3.57 (dd, *J* = 12.0 Hz, 5 Hz, 1H), 3.74 (app. quintet, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 4.10 (app. quartet, *J* = 5.0 Hz, 1H), 6.87 (dd, *J* = 8.5 Hz, 2.5Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.34-7.41 (m, 4H), 7.72 (d, *J* =

8.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.6, 42.6, 55.9, 61.2, 74.4, 114.6, 118.3, 119.2, 126.5, 126.8, 128.7, 128.9, 132.1, 138.3, 155.4, 157.8; IR (neat, cm^{-1}): 3500-3300 (OH), 3058, 2966, 2937, 2836, 1600, 1567, 1488; HRMS Exact mass calcd for $\text{C}_{18}\text{H}_{19}\text{BrN}_2\text{O}_2\text{Na}^+$ 397.0522 found 397.0530.

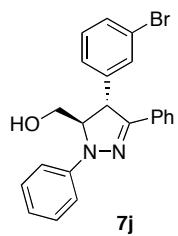
General Procedure for Enantioselective Nitrile Imine Cycloadditions (With Hydrazonoyl Chlorides (2e**) as the Nitrile Imine Precursor):** A flame-dried flask containing 4 Å molecular sieves (150 mg), Lewis acid (0.060 mmol), ligand **6** (0.066 mmol), and substrate **1a** or **1h** (0.2 mmol) in CH_2Cl_2 (2 mL) was stirred for 30 minutes at room temperature. The flask was then cooled to -20 °C and stirred for 5 minutes. Then hydrazonoyl chloride **2e** (0.3 mmol) in CH_2Cl_2 (1 mL) was added to the reaction. After 5 minutes NEt_3 (0.3 mmol) was added to the reaction. After stirring for 48 h at -20 °C, the reaction was quenched with 0.5 M HCl (20 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude **4i** or **4j**, which was analyzed by ^1H NMR to determine diastereomeric ratios. Crude **4i** or **4j** was then reconcentrated and dissolved in THF (5 mL). To this solution was added NaBH_4 (1.32 mmol) in H_2O (1 mL). After 3 h at room temperature, the reaction was quenched with 1 M HCl (10 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude **7i** or **7j**, which were purified by flash column silica chromatography on an ISCOTM CombiFlash Companion with AnaLogixTM RS-4 columns.

Note: The temperature of reactions using **2e** as the nitrile imine could be lowered to -78 °C if (tert-butylimino)tris(dimethylamino) phosphorane was used as the base.



(4*S*,5*R*)-4,5-dihydro-1,3-diphenyl-5-hydroxymethyl-4-methyl-1*H*-pyrazole (7i**):** 49 mg, 92% yield (light green foam or solid), m.p. = 90-91 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_{R}

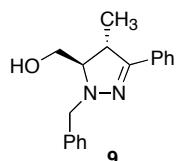
18.5 min (major); t_R 25.4 min (minor) [Chiracel AD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 97/3, 1.0 mL/min] as 95% ee. $[\alpha]_D^{25} = +582.0$ (*c* 0.34, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (d, *J* = 7.2 Hz, 3H), 1.72 (br s, 1H), 3.63 (dq, *J* = 3.2 Hz, 7.2 Hz, 1H), 3.77 (d, *J* = 4.8 Hz, 2H), 4.09 (m, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.29-7.35 (m, 3H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 19.1, 43.1, 61.9, 69.4, 113.4, 119.4, 126.4, 128.78, 128.82, 129.5, 132.0, 145.0, 153.3; IR (neat, cm^{-1}): 3500-3300 (OH), 3058, 2966, 2929, 2873, 1596, 1493, 1381, 1138; HRMS Exact mass calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}\text{Na}^+$ 289.1311 found 289.1315.



(4*S*,5*R*)-4-(3-Bromo-phenyl)-4,5-dihydro-1,3-diphenyl-5-hydroxymethyl-1*H*-pyrazole (7j): 77mg, 95% yield (light green foam), m.p. = 73-75 °C; The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 7.7 min (major); t_R 16.3 min (minor) [Chiracel AD (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 97% ee. $[\alpha]_D^{25} = +203.8$ (*c* 0.50, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.84 (br s, 1H), 3.88 (d, *J* = 4.25 Hz, 2H), 4.27 (q, *J* = 4.25 Hz, 1H), 4.67 (d, *J* = 4.25 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.26-7.33 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 54.4, 61.8, 71.2, 113.7, 112.0, 123.4, 126.3, 126.6, 128.7, 128.8, 129.6, 130.6, 130.8, 131.1, 131.8, 143.2, 144.4, 149.6; IR (neat, cm^{-1}): 3500-3300 (OH), 3058, 2935, 2879, 1606, 1501, 1397; HRMS Exact mass calcd. for $\text{C}_{22}\text{H}_{19}\text{BrN}_2\text{O}\text{Na}^+$ 429.0573 found 429.0578.

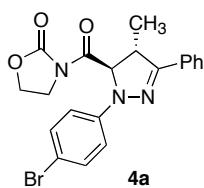
General Procedure for Enantioselective Nitrile Imine Cycloadditions (With *N*-Benzylbenzohydrazoneyl bromide (8) as the Nitrile Imine Precursors): A flame-dried flask containing 4 Å molecular sieves (150 mg), Lewis acid (0.060 mmol), ligand **6** (0.066 mmol), and substrate **1a** (0.2 mmol) in CH_2Cl_2 (2 mL) was stirred for 30 minutes at room temperature. The flask was then cooled to -78 °C and stirred for 5 minutes. Then hydrazoneyl bromide **8** (0.3 mmol) in CH_2Cl_2 (1 mL) was added to the reaction. After 5 minutes DBU or (tert-butylimino)tris(dimethylamino) phosphorane (0.3 mmol)

was added to the reaction. After stirring for 6 h at -78°C , the reaction was quenched with 0.5 M HCl (20 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1 g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude oxazolidinone intermediate, which was analyzed by ^1H NMR to determine diastereomeric ratios. The crude oxazolidinone intermediate was then reconcentrated and dissolved in THF (5 mL). To this solution was added NaBH_4 (1.32 mmol) in H_2O (1 mL). After 3 h at room temperature, the reaction was quenched with 1 M HCl (10 mL) and extracted with diethyl ether (10 mL). The organic layer was filtered through a pad of silica gel (1 g) and MgSO_4 (1 g). The separatory funnel was rinsed with diethyl ether (10 mL), which was used to wash the silica gel- MgSO_4 pad. The combined organic layers were concentrated to yield crude **9**, which was purified by flash column silica chromatography on an ISCOTM CombiFlash Companion with AnaLogixTM RS-4 columns.



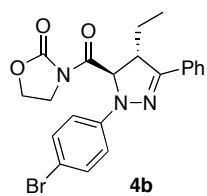
(4S,5R)-1-Benzyl-4,5-dihydro-5-hydroxymethyl-4-methyl-3-phenyl-1H-pyrazole (9): 32 mg, 57% yield (tan oil); The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_{R} 52.6 min (major); t_{R} 60.0 min (minor) [Chiracel OD-H (1 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 93/7, 1.0 mL/min] as 94% ee. $[\alpha]_D^{25} = +56.8$ (*c* 0.42, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz) δ 1.21 (d, *J* = 6.8 Hz, 3H), 2.20 (br s, 1H), 3.03 (dt, *J* = 10.0 Hz, 3.0 Hz, 1H), 3.51-3.59 (m, 3H), 4.40 (br s, 2H), 7.28-7.40 (m, 8H), 7.61 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.2, 42.8, 58.7, 61.0, 73.5, 126.7(2C), 127.8, 128.6 (4C), 128.7, 129.5(2C), 132.6, 137.1, 155.1; IR (neat, cm^{-1}): 3500-3300 (OH), 3062, 3029, 2962, 2929, 2873, 1663, 1453; HRMS Exact mass calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}\text{Na}^+$ 303.1468 found 303.1462.

Supporting Information for Intermediates 4a-l

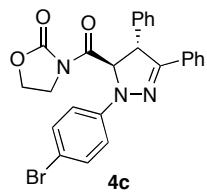


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-4-methyl-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazole (4a): Isolated as a yellow solid, m.p. = 221-225 °C. $[\alpha]_D^{25} = +207.8$ (*c* 0.41, CHCl_3), 99% ee;

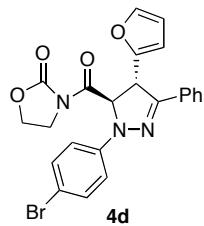
¹H NMR (CDCl₃, 500 MHz) δ 1.50 (d, J = 7.0 Hz, 3H), 3.61 (dq, J = 2.0 Hz, 7 Hz, 1H), 3.87-3.99 (m, 2H), 4.45 (app. dt, J = 2.0 Hz, 8.5 Hz, 2H), 5.68 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 2H), 7.32-7.40 (m, 5H), 7.40 (d, 7.5 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 18.2, 42.6, 46.7, 63.2, 68.3, 111.6, 114.7, 126.3, 128.8, 129.1, 131.1, 132.2, 143.7, 152.1, 154.1, 169.0; IR (neat, cm⁻¹): 3058, 2979, 2927, 1776, 1706, 1590, 1492, 1387; HRMS Exact mass calcd. for C₂₀H₁₈BrN₃O₃Na⁺ 450.0424 found 450.0426.



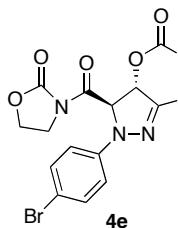
(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-4-ethyl-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazole (4b): Isolated as a white foam, m.p. = 77-79 °C. [α]_D²⁵ = +124.2 (c 0.39, CHCl₃), 99% ee; ¹H NMR (CDCl₃, 500 MHz) δ 0.89 (t, J = 7.0 Hz, 3H), 1.85 (m, 1H), 2.04 (m, 1H), 3.69 (m, 1H), 3.89-4.06 (m, 2H), 4.45-4.52 (m, 2H), 5.88 (d, J = 2.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 7.31-7.39 (m, 5H), 7.74 (d, J = 7.5 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 9.5, 24.6, 42.8, 52.6, 63.1, 65.4, 111.6, 114.5, 126.4, 128.8, 129.1, 131.6, 132.2, 143.3, 150.3, 154.0, 169.0; IR (neat, cm⁻¹): 3058, 2968, 2933, 2877, 1771, 1704, 1590, 1490, 1385; HRMS Exact mass calcd. for C₂₁H₂₀BrN₃O₃Na⁺ 464.0580 found 464.0566.



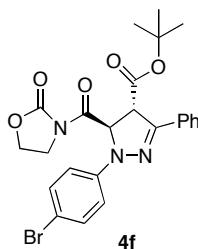
(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-3,4-diphenyl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4c): Isolated as a yellow foam, m.p. = 107-110 °C. [α]_D²⁵ = -47.7 (c 1.46, CHCl₃), 97% ee; ¹H NMR (CDCl₃, 500 MHz) δ 3.90-4.01 (m, 2H), 4.45 (t, J = 8.5 Hz, 2H), 4.63 (d, J = 2.0 Hz, 1H), 5.99 (d, J = 2.0 Hz, 1H), 7.03 (d, J = 9.0 Hz, 2H), 7.25-7.30 (m, 8H), 7.38 (d, J = 9.0 Hz, 2H), 7.67 (dd, J = 8.0 Hz, 1.5 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 42.7, 57.5, 63.1, 69.4, 112.0, 115.0, 126.5, 128.0, 128.2, 128.6, 129.2, 131.3, 132.3, 137.6, 143.5, 146.4, 150.6, 153.7, 168.6; IR (neat, cm⁻¹): 3060, 3031, 2989, 2923, 1775, 1700, 1588, 1490, 1387; HRMS Exact mass calcd. for C₂₅H₂₀BrN₃O₃Na⁺ 512.0580 found 512.0580.



(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-4-furan-2-yl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4d): Isolated as a yellow foam, m.p. = 105-107 °C. $[\alpha]_D^{25} = -7.9$ (*c* 0.58, CHCl_3), 99% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 3.96-4.07 (m, 2H), 4.50 (t, *J* = 8.5 Hz, 2H), 4.82 (d, *J* = 3.0 Hz, 1H), 6.19 (d, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 6.30 (dd, *J* = 2.0 Hz, 3.0 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 7.29-7.38 (m, 6H), 7.70 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 42.8, 50.7, 63.1, 67.2, 108.2, 111.0, 112.3, 115.0, 126.4, 128.7, 129.2, 131.3, 132.3, 142.7, 143.3, 147.2, 150.6, 153.7, 168.7; IR (neat, cm^{-1}): 3058, 2989, 2923, 1771, 1704, 1590, 1490, 1387; HRMS Exact mass calcd. for $\text{C}_{23}\text{H}_{18}\text{BrN}_3\text{O}_4\text{Na}^+$ 502.0373 found 502.0370.

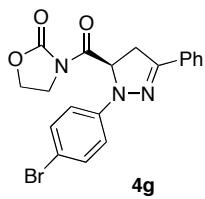


(4S,5R)-Benzoic acid 1-(4-bromo-phenyl)-4,5-dihydro-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazol-4-yl ester (4e): Isolated as a yellow foam, m.p. = 101-103 °C. $[\alpha]_D^{25} = -46.5$ (*c* 0.72, CHCl_3), 96% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 4.07-4.13 (m, 2H), 4.49-4.58 (m, 2H), 6.38 (d, *J* = 3.0 Hz, 1H), 6.80 (d, *J* = 3.0 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 7.31-7.43 (m, 7H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 8.03 (dd, *J* = 8.0 Hz, 1.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 43.0, 63.0, 66.9, 78.4, 113.0, 114.9, 126.1, 128.7, 128.9, 129.0, 129.4, 130.3, 130.4, 132.4, 134.0, 142.3, 144.4, 153.7, 165.9, 167.7; IR (neat, cm^{-1}): 3062, 2989, 2923, 1775, 1706, 1590, 1492, 1451, 1389; HRMS Exact mass calcd. for $\text{C}_{26}\text{H}_{20}\text{BrN}_3\text{O}_5\text{Na}^+$ 556.0479 found 556.0490.

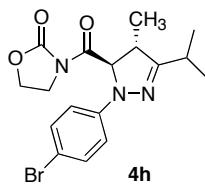


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazol-4-carboxylic acid *tert*-butyl ester (4f): Isolated as a yellow solid, m.p. = 115-118 °C. $[\alpha]_D^{25} = +50.6$ (*c* 0.63, CHCl_3), 93% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 1.37 (s, 9H), 3.97-4.10 (m, 2H), 4.29 (d, *J* = 4.0 Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 4.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.32-7.38 (m, 5H), 7.86 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 27.9, 42.7, 57.7, 63.2, 65.6, 83.4, 112.0, 114.7, 126.8, 128.5, 129.2, 131.1, 132.2, 142.6, 144.3, 153.7, 167.6, 168.2; IR (neat, cm^{-1}):

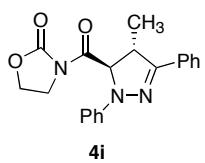
3060, 2979, 2931, 1775, 1710, 1590, 1492, 1380; HRMS Exact mass calcd. for $C_{24}H_{24}BrN_3O_5Na^+$ 536.0792 found 536.0785.



(5R)-1-(4-Bromo-phenyl)-4,5-dihydro-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazole (4g): Isolated as a off-white solid, m.p. = 240-243 °C. $[\alpha]_D^{25} = +274.5$ (*c* 0.57, $CHCl_3$), 84% ee; 1H NMR ($CDCl_3$, 500 MHz) δ 3.28 (dd, *J* = 5.5 Hz, 17.5 Hz, 1H), 3.90 (dd, *J* = 12.5 Hz, 17.5 Hz, 1H), 4.01-4.14 (m, 2H), 4.52-4.60 (m, 2H), 5.94 (dd, *J* = 5.5 Hz, 12.5 Hz, 1H), 6.20 (d, *J* = 9.0 Hz, 2H), 7.34-7.41 (m, 5H), 7.70 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 39.0, 42.7, 61.4, 63.2, 111.8, 114.7, 126.1, 128.8, 129.3, 132.0, 132.2, 143.5, 147.3, 153.8, 169.8; IR (neat, cm^{-1}): 2921, 1787, 1700, 1590, 1503, 1387; HRMS Exact mass calcd. for $C_{19}H_{16}BrN_3O_3Na^+$ 436.0267 found 436.0270.

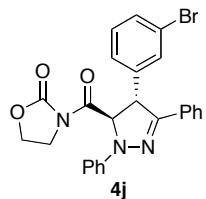


(4S,5R)-1-(4-Bromo-phenyl)-4,5-dihydro-3-isopropyl-4-methyl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4h): Isolated as a pink foam, m.p. = 74-75 °C. $[\alpha]_D^{25} = +12.1$ (*c* 0.69, $CHCl_3$), 99% ee; 1H NMR ($CDCl_3$, 500 MHz) δ 1.14 (d, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.38 (d, *J* = 7.0 Hz, 3H), 2.64 (sept, *J* = 7.0 Hz, 1H), 3.14 (dq, *J* = 2.5 Hz, 7.0 Hz, 1H), 3.94-4.05 (m, 2H), 4.50 (t, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 2.5 Hz, 1H), 6.08 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.6, 20.0, 21.4, 28.0, 42.6, 48.3, 63.1, 67.5, 110.8, 114.3, 132.1, 144.5, 154.0, 160.7, 169.9; IR (neat, cm^{-1}): 2970, 2933, 2875, 1773, 1706, 1592, 1403, 1387; HRMS Exact mass calcd. for $C_{17}H_{20}BrN_3O_3Na^+$ 416.0580 found 416.0577.

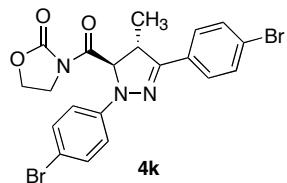


(4S,5R)-4,5-dihydro-4-methyl-1,3-diphenyl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4i): Isolated as a yellow foam, m.p. = 96-98 °C. $[\alpha]_D^{25} = +235.9$ (*c* 0.57, $CHCl_3$), 95% ee; 1H NMR ($CDCl_3$, 500 MHz) δ 1.50 (d, *J* = 7.5 Hz, 3H), 3.60 (dq, *J* = 2.0 Hz, 7.5 Hz, 1H), 3.89-4.01 (m, 2H), 4.46 (m, 2H), 5.72 (d, *J* = 2.0 Hz, 1H), 6.85 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 7.26-7.33 (m, 3H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.2, 42.6, 46.4, 63.2, 68.3, 113.0, 119.7, 126.2, 128.8,

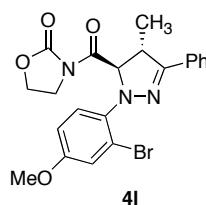
128.9, 129.5, 131.5, 144.5, 151.4, 154.2, 169.4; IR (neat, cm^{-1}): 3058, 3031, 2977, 2929, 1771, 1704, 1598, 1505, 1387; HRMS Exact mass calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_3\text{Na}^+$ 372.1319 found 372.1320.



(4S,5R)-4-(3-Bromo-phenyl)-4,5-dihydro-1,3-diphenyl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4j): Isolated as a yellow foam, m.p. = 118-121 °C. $[\alpha]_D^{25} = -93.1$ (*c* 0.64, CHCl_3), 97% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 3.97-4.07 (m, 2H), 4.52 (m, 2H), 4.58 (d, *J* = 2.0 Hz, 1H), 6.01 (d, *J* = 2.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.26-7.34 (m, 7 H), 7.41 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.48 (t, *J* = 1.5 Hz, 1H), 7.67 (dd, *J* = 8.0 Hz, 1.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 42.7, 56.7, 63.2, 69.3, 113.5, 120.3, 123.2, 126.4, 126.9, 128.7, 129.0, 129.6, 130.8, 131.0, 131.3, 131.4, 140.1, 144.2, 149.3, 153.8, 168.5; IR (neat, cm^{-1}): 3058, 2989, 2923, 1776, 1704, 1598, 1503, 1387; HRMS Exact mass calcd. for $\text{C}_{25}\text{H}_{21}\text{BrN}_3\text{ONa}^+$ 512.0580 found 512.0586.



(4S,5R)-1,3-Bis-(4-bromo-phenyl)-4,5-dihydro-4-methyl-5-(oxazolidin-2-one-3-carbonyl)-1H-pyrazole (4k): Isolated as a yellow solid, m.p. = 215-217 °C. $[\alpha]_D^{25} = +202.9$ (*c* 0.62, CHCl_3), 95% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 1.50 (d, *J* = 7.5 Hz, 3H), 3.58 (dq, *J* = 2.0 Hz, 7.5 Hz, 1H), 3.95-4.07 (m, 2H), 4.51-4.55 (m, 2H), 5.69 (d, *J* = 2.0 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 18.1, 42.6, 46.5, 63.3, 68.4, 112.1, 114.8, 123.1, 127.7, 130.1, 132.0, 132.3, 143.5, 151.1, 154.1, 168.9; IR (neat, cm^{-1}): 3056, 2977, 2925, 1771, 1704, 1594, 1788; HRMS Exact mass calcd. for $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{N}_3\text{O}_3\text{Na}^+$ 527.9529 found 527.9525.

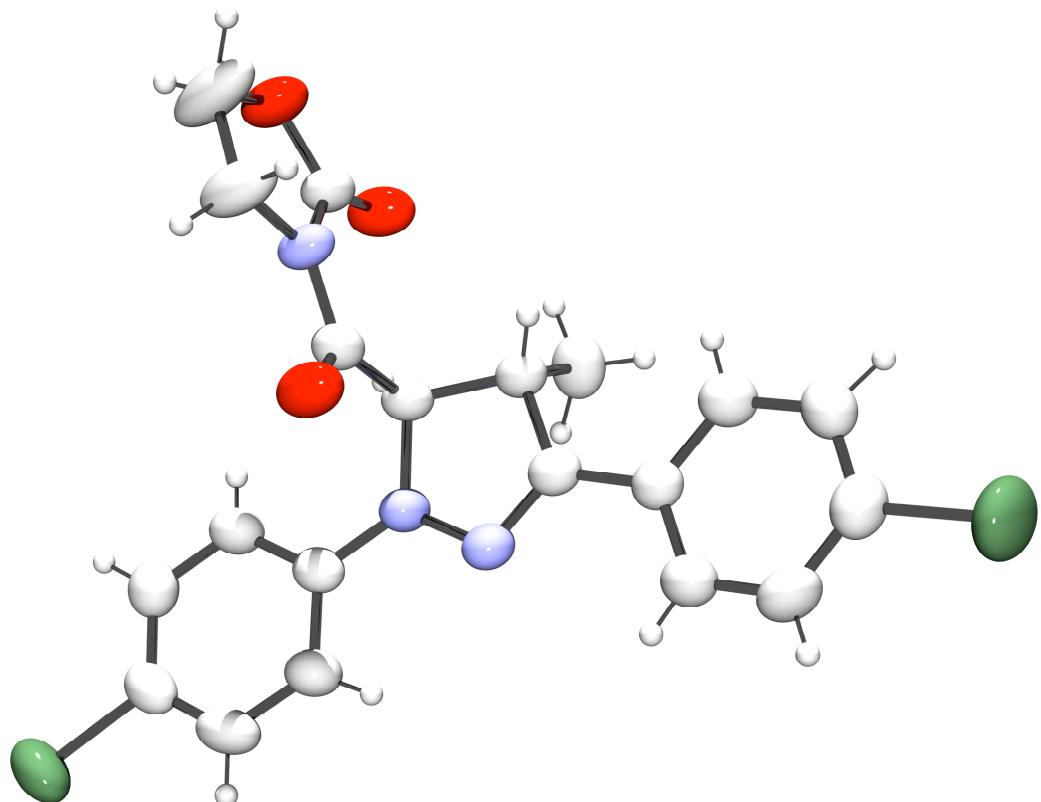


(4S,5R)-1-(2-Bromo-4-methoxy-phenyl)-4,5-dihydro-4-methyl-5-(oxazolidin-2-one-3-carbonyl)-3-phenyl-1H-pyrazole (4l): Isolated as a off-white foam, m.p. = 74-76 °C. $[\alpha]_D^{25} = +7.34$ (*c* 0.29, CHCl_3),

96% ee; ^1H NMR (CDCl_3 , 500 MHz) δ 1.57 (d, J = 7.0 Hz, 3H), 3.66 (dq, J = 1.5 Hz, 7.0 Hz, 1H), 3.79 (s, 3H), 3.90 (t, J = 8.0 Hz, 2H), 4.39-4.47 (m, 2H), 6.13 (d, J = 1.5 Hz, 1H), 6.87 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.72-7.76 (m, 3H). ^{13}C NMR (CDCl_3 , 500 MHz) δ 17.4, 42.6, 47.4, 55.9, 63.0, 71.4, 113.7, 114.9, 124.5, 126.1, 126.3, 128.8, 129.0, 131.4, 136.6, 152.4, 153.0, 156.4, 170.0; IR (neat, cm^{-1}): 3058, 2975, 2838, 1771, 1706, 1605, 1493, 1387; HRMS Exact mass calcd. for $\text{C}_{21}\text{H}_{20}\text{BrN}_3\text{O}_4\text{Na}^+$ 480.0529 found 480.0527.

Crystal Structure for Intermediate 4k

-(Crystal data and structure refinement for 4k can be found in the attached CIF file)



References:

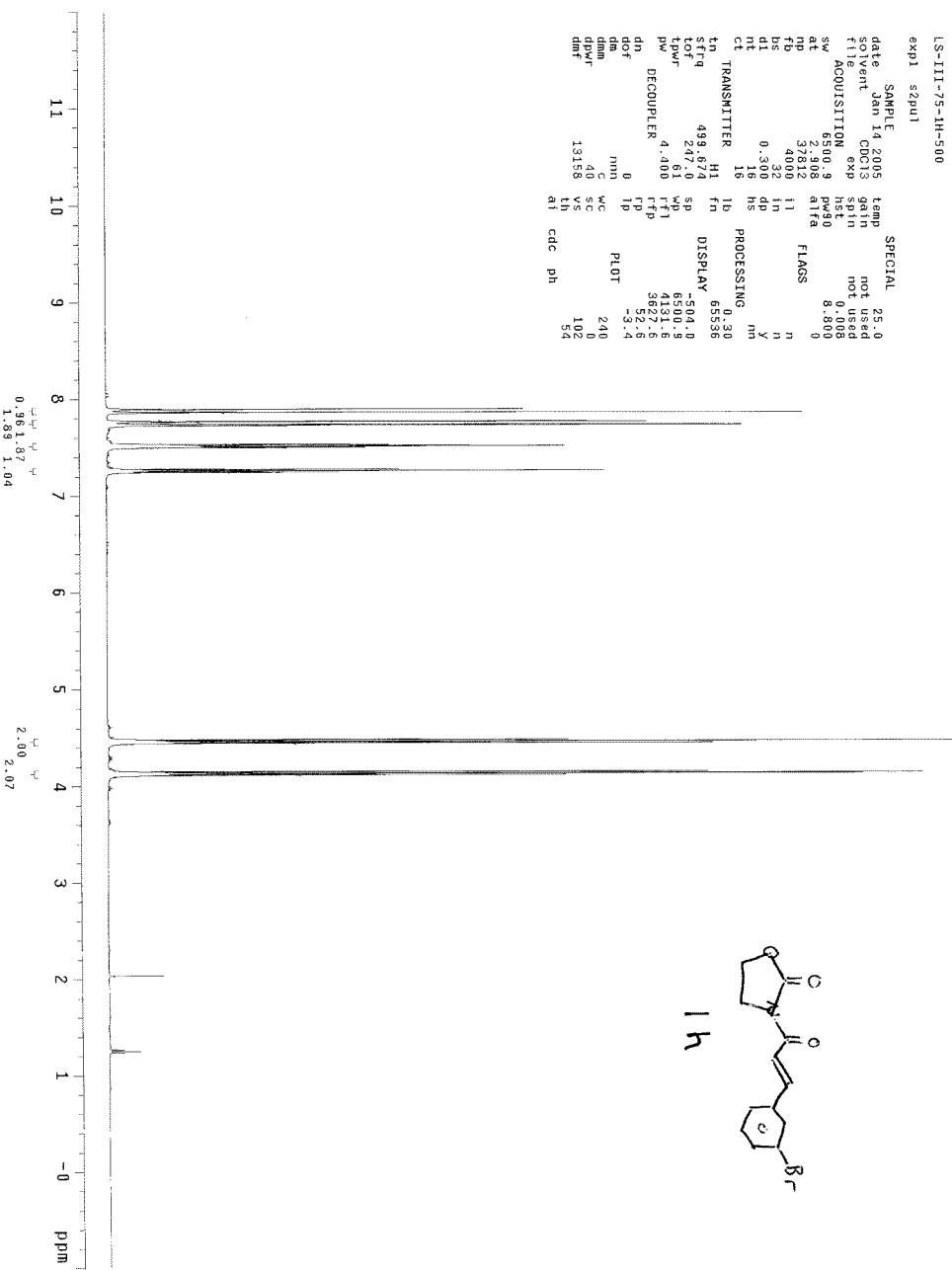
- 1) Kanemasa, S.; Kanai, T. *J. Am. Chem. Soc.* **2000**, *122*, 10710-10711.
- 2) Cai, C.; Soloshonok, V. A.; Hruby, V. J. *J. Org. Chem.* **2001**, *66*, 1339-1350.
- 3) Sibi, M. P.; Chen, J. *J. Am. Chem. Soc.* **2000**, *123*, 9472-9473.

- 4) Sibi, M. P.; Zimmerman, J.; Rheault, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4521-4523.
- 5) Sibi, M. P.; Hasegawa, H. *Org. Lett.* **2002**, *4*, 3347-3349.
- 6) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340-5345.
- 7) Patel, H. V.; Vyas, K. A.; Pandey, S. P.; Fernandes, P. S. *Tetrahedron* **1996**, *52*, 661-668.

LS-TII-75-1H-500

exp1 s2pul

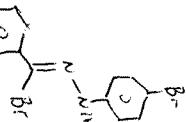
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np	2.908	alra	
fb	3.812		
ds	40.00	FLAGS	
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ct	0.316	in	n
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dof	0	fp	3.62.6
dm	0	ip	-3.4
dmm	0	PL0T	-3.4
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dt	cdc	ph	



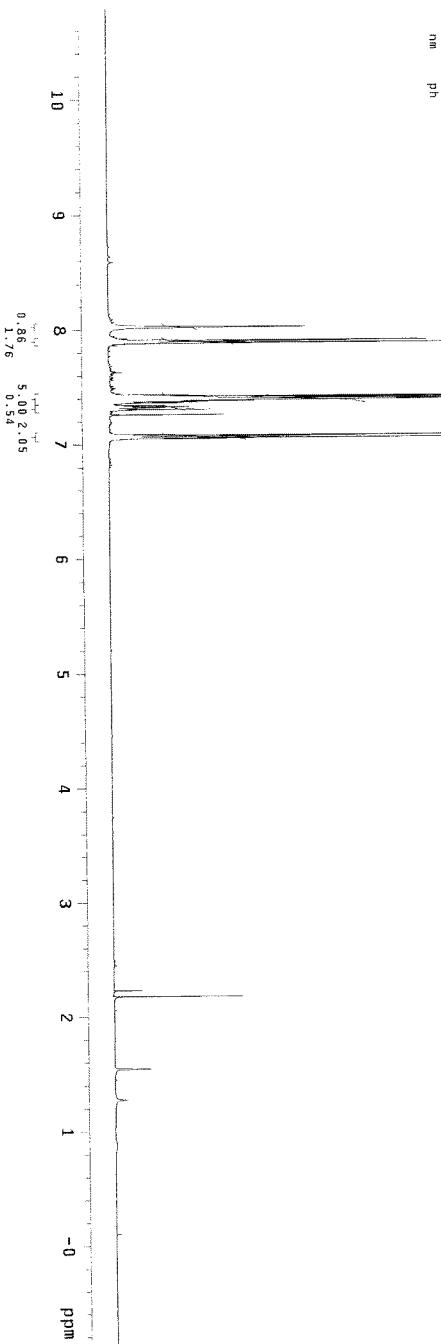
[(S)-N-bromophenyl]hydrazone bromide

exptl s2pu1

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np	31.036		dmf			
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fb	3800.0	homo		1.0		
bs	16					
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pw	4	temp	PROCESSING		25.0	
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tr1f	16	ft				
ct	16	fm				
atclck	16	math				
gain	n	werr				
FLAGS	not used	wexp				
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in	n	whit				
dp	y					
hs						
DISPLAY						
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ph						



2a



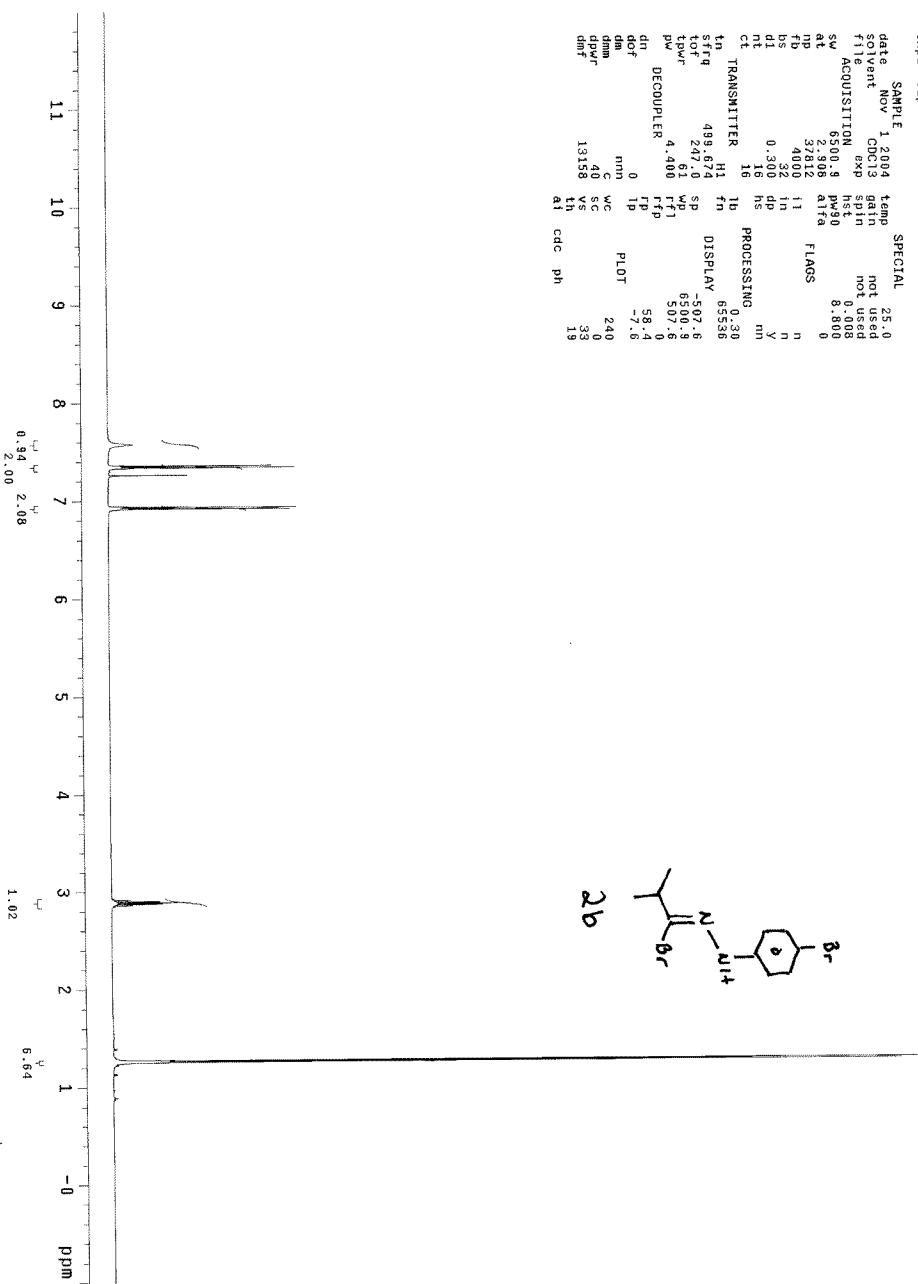
LS-II-281-1-1H-500

exp1 s2pu1

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FB	4.000	1
BS	0.332	1
DL	0.300	dp
RT	1.6	hs
CT	16	PROCESSING
TRANSMITTER	1b	0.30
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TOF	247.0	SP
TPWR	507.6	WP
PW	4.400	rpt
DECOPPLER	4.400	rfp
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MMR	0	65526
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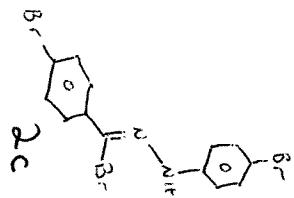
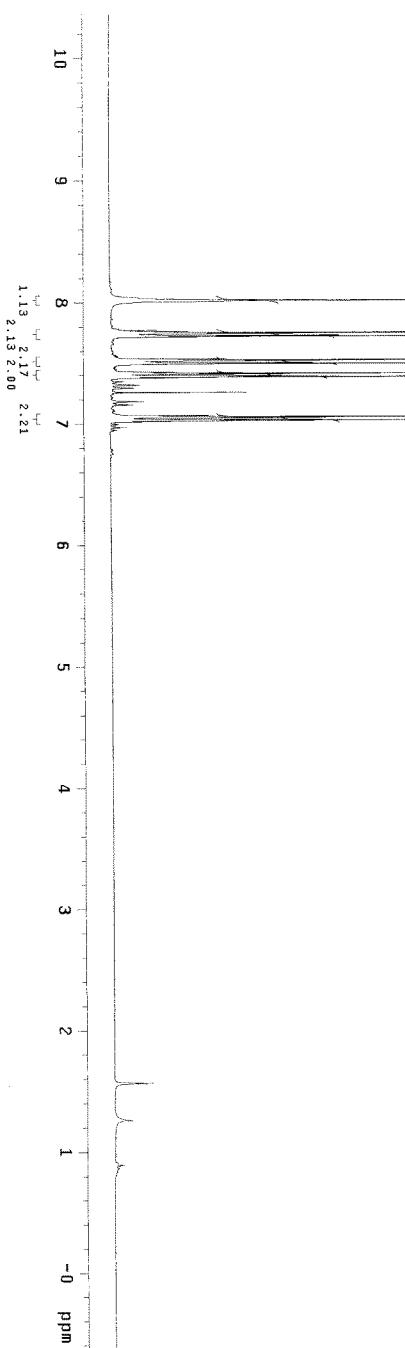
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STANDARD 1H OBSERVE

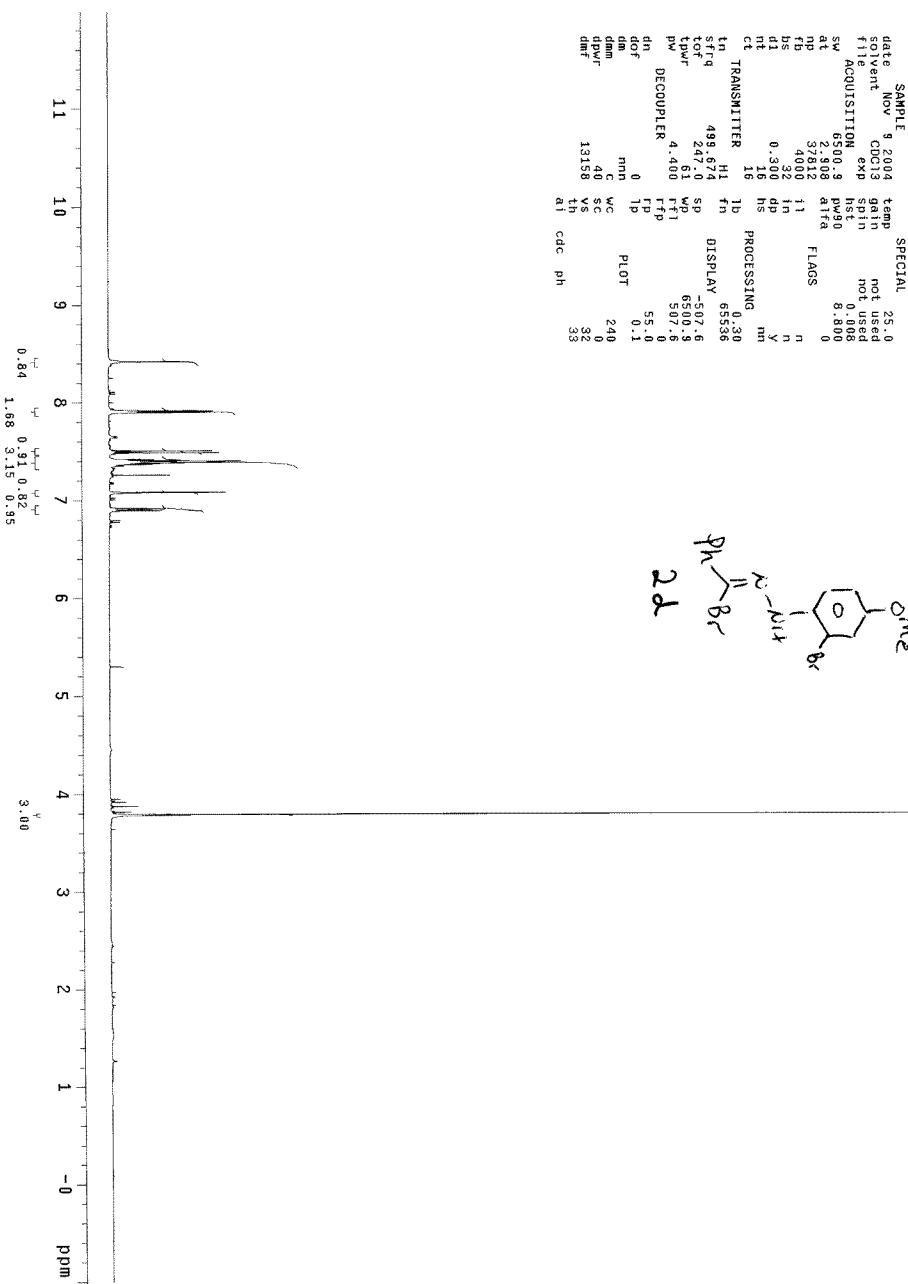
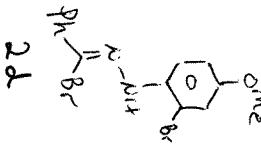
expt 5.01



LS-II-246-1B-500

exp11 s2pul

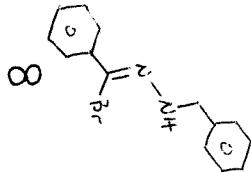
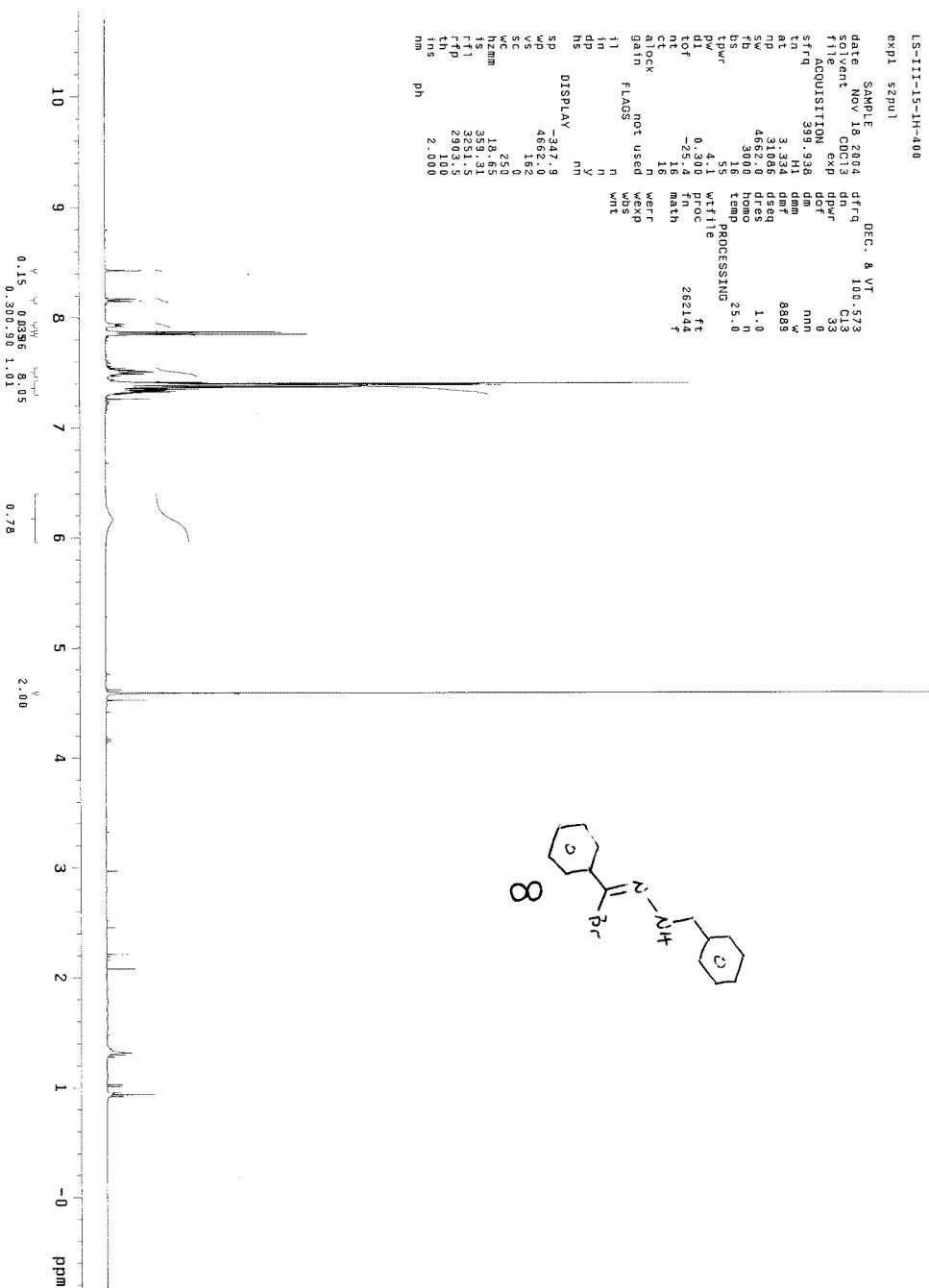
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ct	1.16	mn 0.30
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sfg	674	0.07.6
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dmr	40	sc 32
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dmr	33	th 33
ai	cdc	ph



LS-III-15-1H-400

- 1 -

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file				33.333
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dp	1.0	0.0	0.0	0.0
hs	1.0	0.0	0.0	0.0
DISPLAY	-347.9	0.0	0.0	0.0
sp	462.0	0.0	0.0	0.0
wp	462.0	0.0	0.0	0.0
vs	162	0.0	0.0	0.0
sc	0	0.0	0.0	0.0
wc	2.0	0.0	0.0	0.0
hzm	18.65	0.0	0.0	0.0
1s	359.31	0.0	0.0	0.0
r ¹	321.5	0.0	0.0	0.0
r ¹ p	2903.5	0.0	0.0	0.0
1h	100	0.0	0.0	0.0
1n	100	0.0	0.0	0.0
ph	2.000	0.0	0.0	0.0

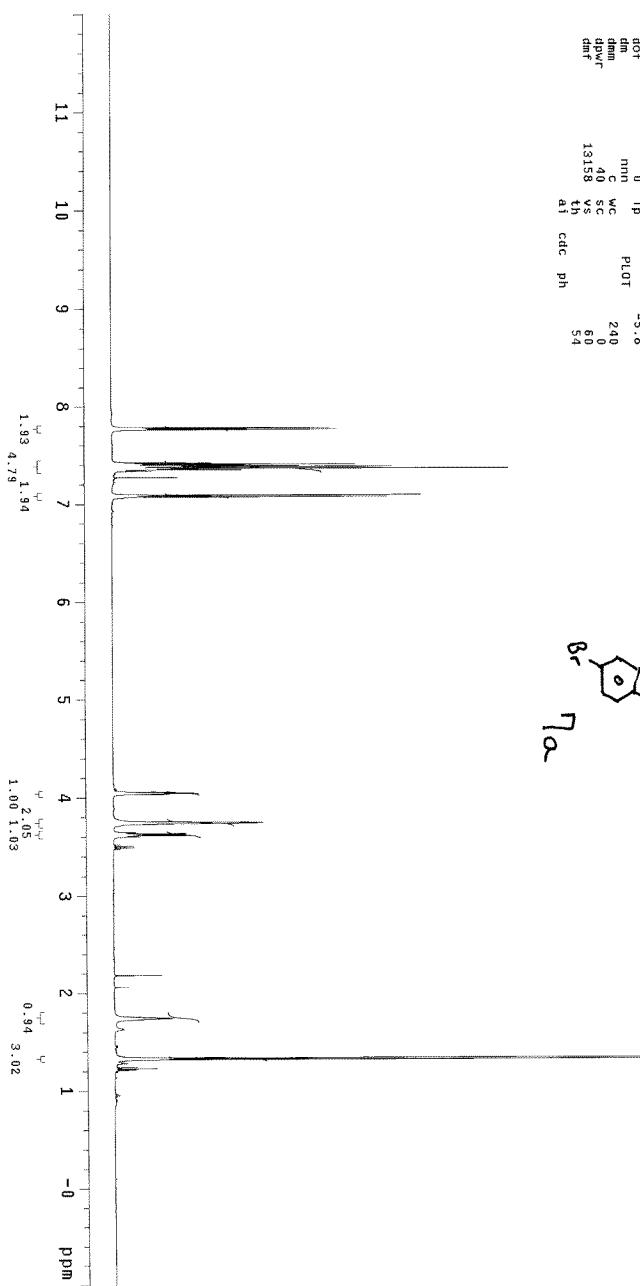
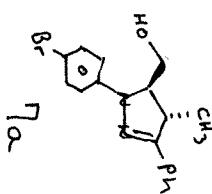


LS-III-264C

exp2

zspul

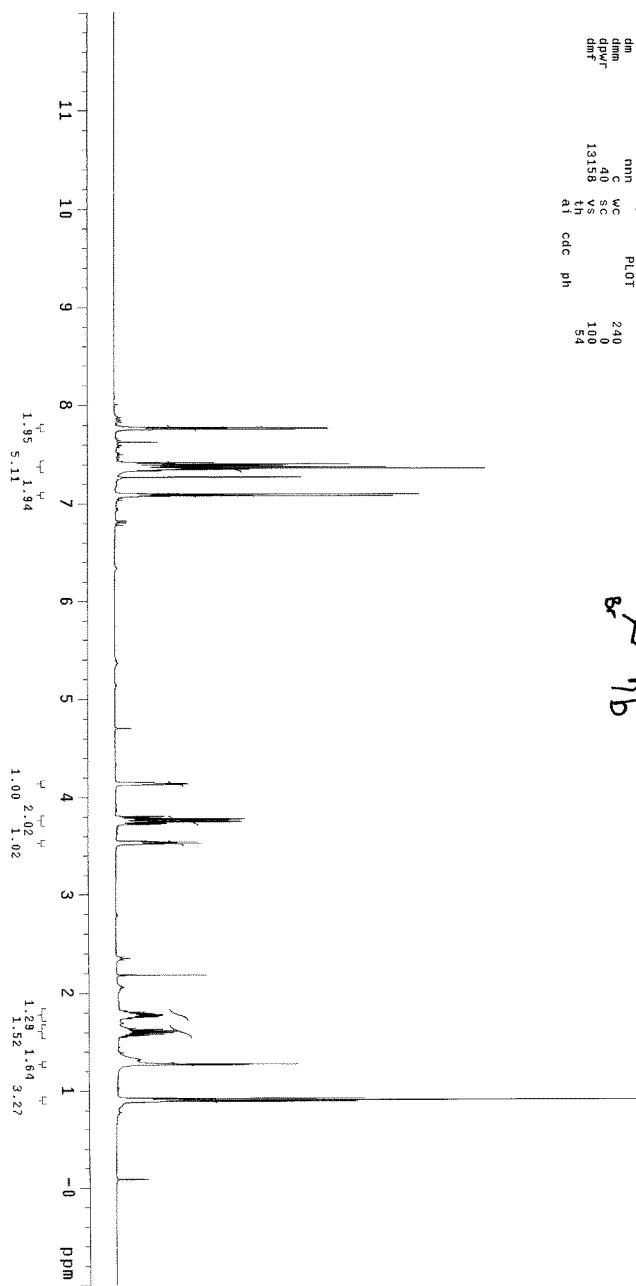
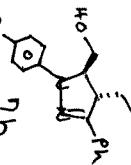
	SAMPLE	temp	SPECIAL
date	Apr 21, 2005	25.0	25.0
SOLVENT	CDCl ₃	not used	not used
file	exp2	0.008	0.008
ACQUISITION	exp	8.800	8.800
sw	6500.0	ps90	ps90
at	2.908	alra	0
np	37812		
fb	4000		
bs	32	in	n
d1	0.300	dp	y
dt	16	hs	nn
ct			
TRANSMITTER	16	PROCESSING	nn
tn	H1	0.30	
sf	499.674	653.6	
tof	499.674	DISPLAY	
tpwF	247.0	-500.6	
tpw	4.61	6500.9	
pw	4.400	rf1	4133.2
DECOUPLER		rf1	3832.6
dtw	0	rp	63.7
dtwF	0	1p	-5.3
dm	mm	PLOT	240
dm	sc		240
dpmF	13158	vs	6.0
dmF		th	54
		ai	cdc
		ph	ph



LS-III-2758

exp2 s2pul

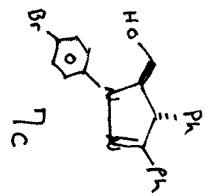
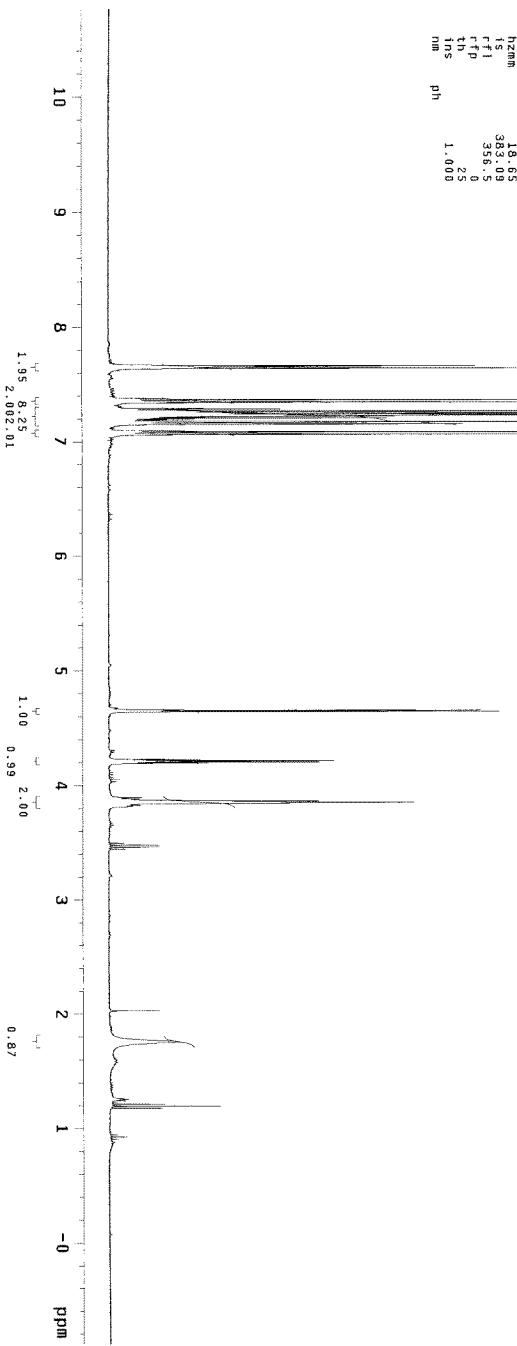
	SAMPLE	temp	SPECIAL
date	Apr 21	2005	25.0
solvent	CDCl ₃	gain	not used
file		exp	not used
ACQUISITION		spin	
sw	6500.9	freq	8.800
at	2.908	time	0
np	3812	alpha	
fb	4000	FLAGS	
bs	32	n	
di	0.300	dp	
nt	16	hs	y
ct			nn
TRANSMITTER	16	PROCESSING	0.30
tn	1b	H1	65336
sf	499.674	fn	
tf	247.0	sp	
tpw _r	4.611	wp	
pw	4.400	r _{f1}	4133.4
DECOUPLER		r _{f2}	3632.6
d1	0	rp	63.1
dof	0	1p	-4.3
dm		nm	
dmr		nc	
dpr	13158	sc	240
dnp	vs	th	100
dmf		ai	54
		cdc	
		ph	



L-S-11-272A-1H-400

exptl s2pul

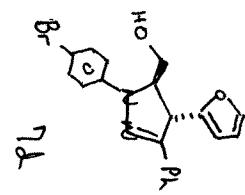
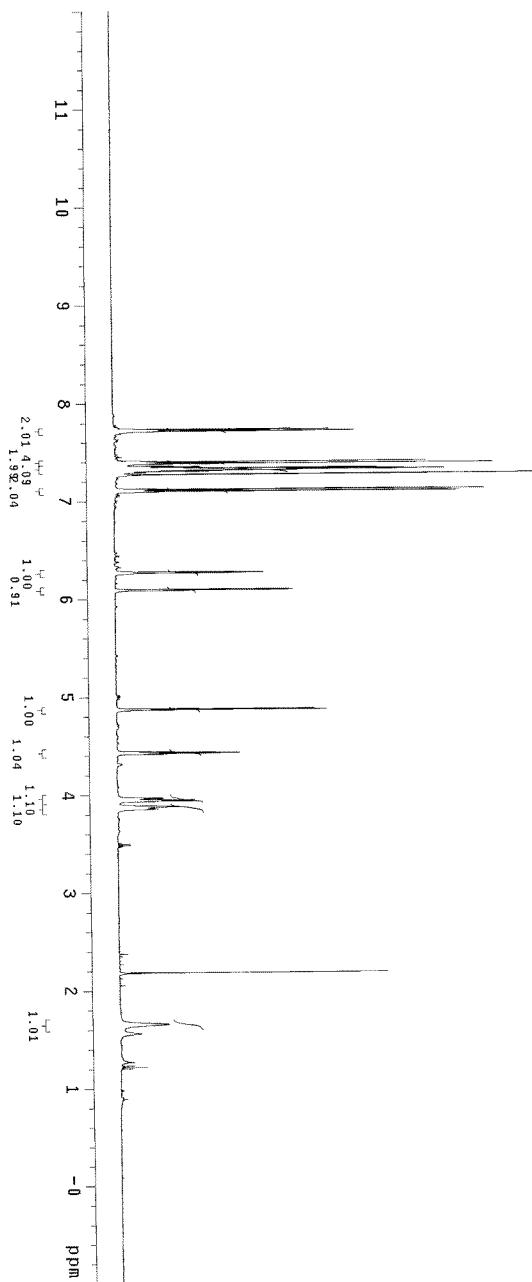
SAMPLE	DEC.	& VT
date Nov 22 2004	dfrq	100.573
solvent CDCl ₃	dn	C13
frq	dt	3.3
acquisition 399	dtw	0
spqr 399	dm	mn
tn H1	dmw	w
at 3.334	dmt	8889
np 31.056	dseq	
sw 48.210	dres	1.0
fb 38.010	dnmo	
bs 3.56	temp	25.0
tpur 3.55	PROCESSING	
pw 4.1	wrf1e	
dt 0.300	proc	
trf -25.4	fft	262144
nt 16	fn	
ct 16	math	
atlock	16	
gain	n	
FLAGS	not used	
ri	wns	
in	wnr	
dp	n	
hs	y	
DISPLAY		
sp -356.5		
wp 4682.0		
vs 151		
sc 0		
kc 250		
ncum 18.63		
l 383.1		
rfl 356.5		
rfp 25		
th 1.000		
ins		
nm		
ph		



LS-111-726

100

	DATE	APR 21, 2015	TEMP	SP. TEMP.
SOLVENT	CHCl ₃	30	25	not used
ACQUISITION	EXP	30	25	not used
SW	6500.9	30	25	not used
SPW	2.908	30	25	not used
APW	3.7812	30	25	not used
FB	4000	11	11	8.80
BS	32	11	11	
DI	0.300	10	10	
CT	1.6	10	10	
TRANSMITTER	1.6	10	10	
HI	449.674	30	25	
SPW	247.0	30	25	
TPWR	6.61	30	25	
TPWRF	4.400	30	25	
DECOUPLER	1.77	30	25	
RP	0	10	10	
MM	0	10	10	
PLOT	24	10	10	
SC	40	10	10	
VS	6	10	10	
TH	131.58	10	10	
CD	5	10	10	
PH	5	10	10	



LS-III-297C

temp

25.0

gain

not used

exp

not used

SW

0.008

ACQUISITION

0.008

time

8.800

at

0.008

ppm

8.800

atfa

0.008

np

0.008

37812

0.008

40000

1.0

FLAGS

n

fb

n

bs

n

322

0.300

dp

Y

0.300

hs

PROCESSING

nn

0.30

ct

TRANSMITTER

1b

fn

65536

DISPLAY

65536

sfq

499.674

H1

sp

-501.0

tof

247.0

sp

8500.9

tpur

4.61

wp

8500.9

pw

4.400

rfl

4138.6

decoupler

4.400

rtp

3632.6

dnf

0

1p

67.5

dmn

0

1.3

mc

240

sc

13158

vs

125

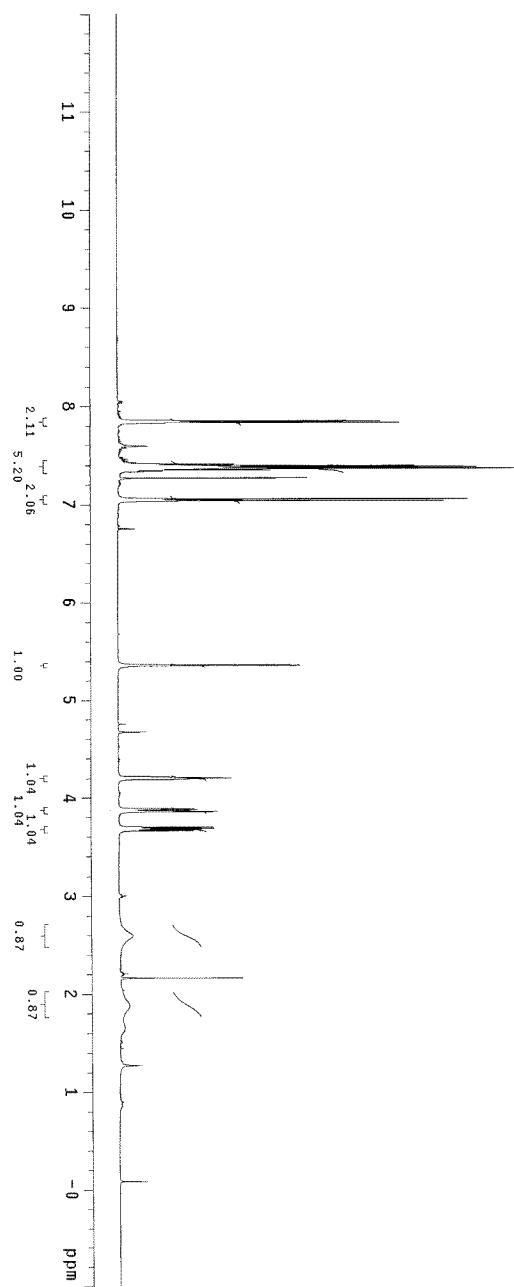
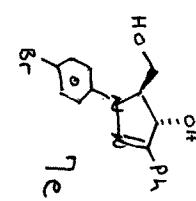
th

54

ai

cdc

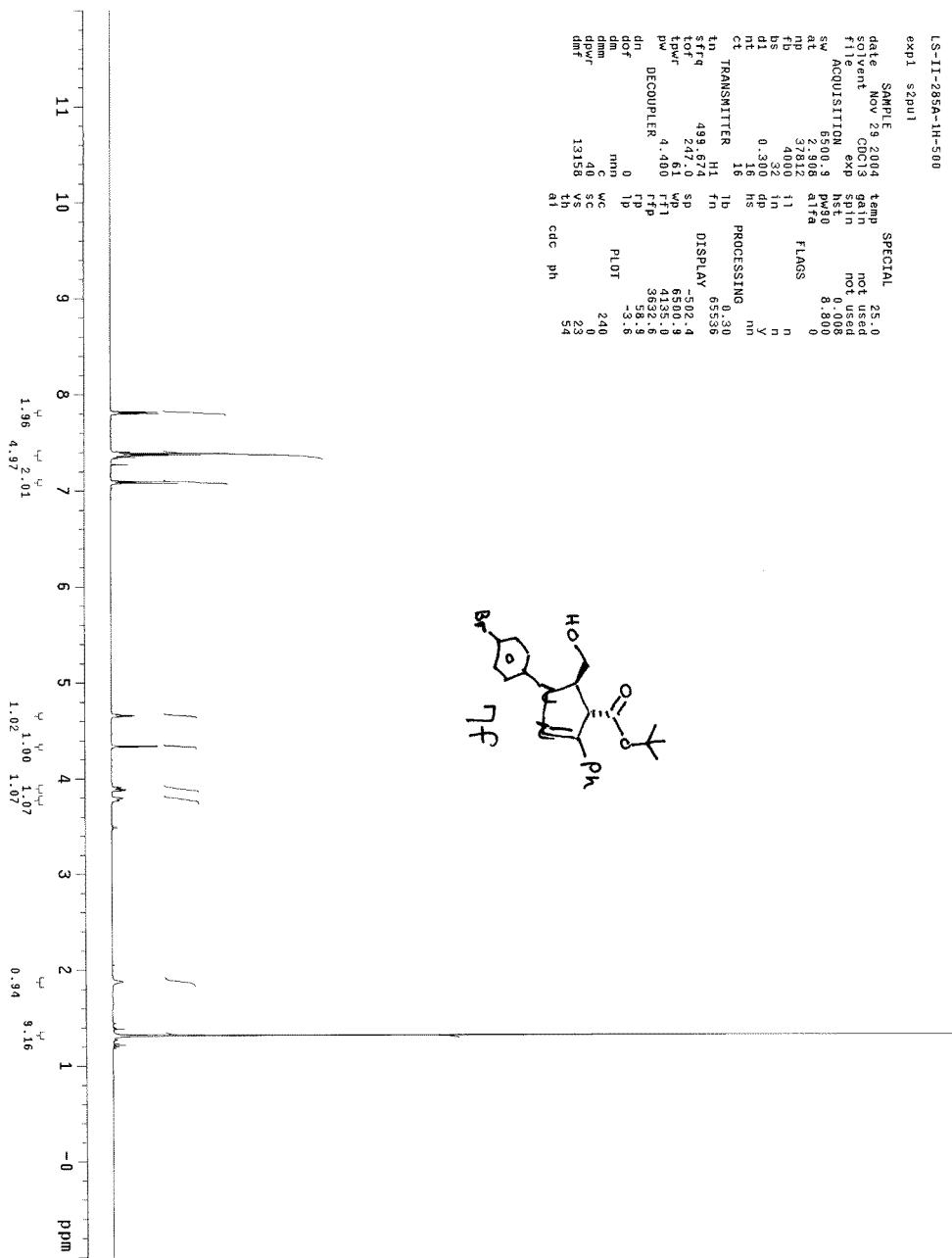
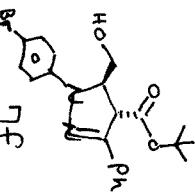
ph



LS-II-285A-1H-500

exp1 sspul

date	SAMPLE	temp	SPECIAL
so	Nov 29	2004	25.0
le	CDCl ₃	temp	not used
nt	file	spin	not used
ACQUISITION	64p	hist	0.008
sw	6500.9	pw0	8.800
at	2.908	alpha	0
np	37812	FLAGS	
fb	4000	n	
bs	322	n	
di	0.300	dp	y
rt	16	HS	nn
ct	16	PROCESSING	
TRANSMITTER	H1	0.30	
tn	H11	1b	
sfq	fn	DISPLAY	65336
tof	499.674	sp	-502.4
tpur	247.0	wp	6500.9
pw	61	wp1	4135.0
DECOUPLER	4.490	rp1	3632.6
dn	0	rp	551.9
do	0	1p	-35.6
dm	mn	PL0T	
dmn	c	240	
dpr	sc	23	
dmf	vs	54	
	th		
a1	cdc	ph	



LS-III-284B-1H-500

exp2 s2pu1

date	SAMPLE	SPECIAL
Feb 4 2005	CDCl ₃	25.0
SCV	gain	not used
f118	exp	not used
ACQUISITION	spn	0.008
SW	px10	8.800
AT	px10	0
TD	32712	FLAGS
RB	4000	
FB	11	
BS	32	
DT	0.300	
DP	in	
RT	0.300	
CT	16	
TRANSMITTER	hs	
TR	1b	
ST	439.574	
TRFQ	1b	
TOFR	247.0	
TPW	4.61	
PW	wp	
DECOPPLER	4.000	
DP	r ² 1	
DR	r ² p	
DPF	0	
DPW	1p	
DPW1	1p	
DPW2	1p	
DPW3	1p	
DPW4	1p	
DPW5	1p	
DPW6	1p	
DPW7	1p	
DPW8	1p	
DPW9	1p	
DPW10	1p	
DPW11	1p	
DPW12	1p	
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LSX-II-293C-1H-400

exptl

22pu1

sample

22pu1

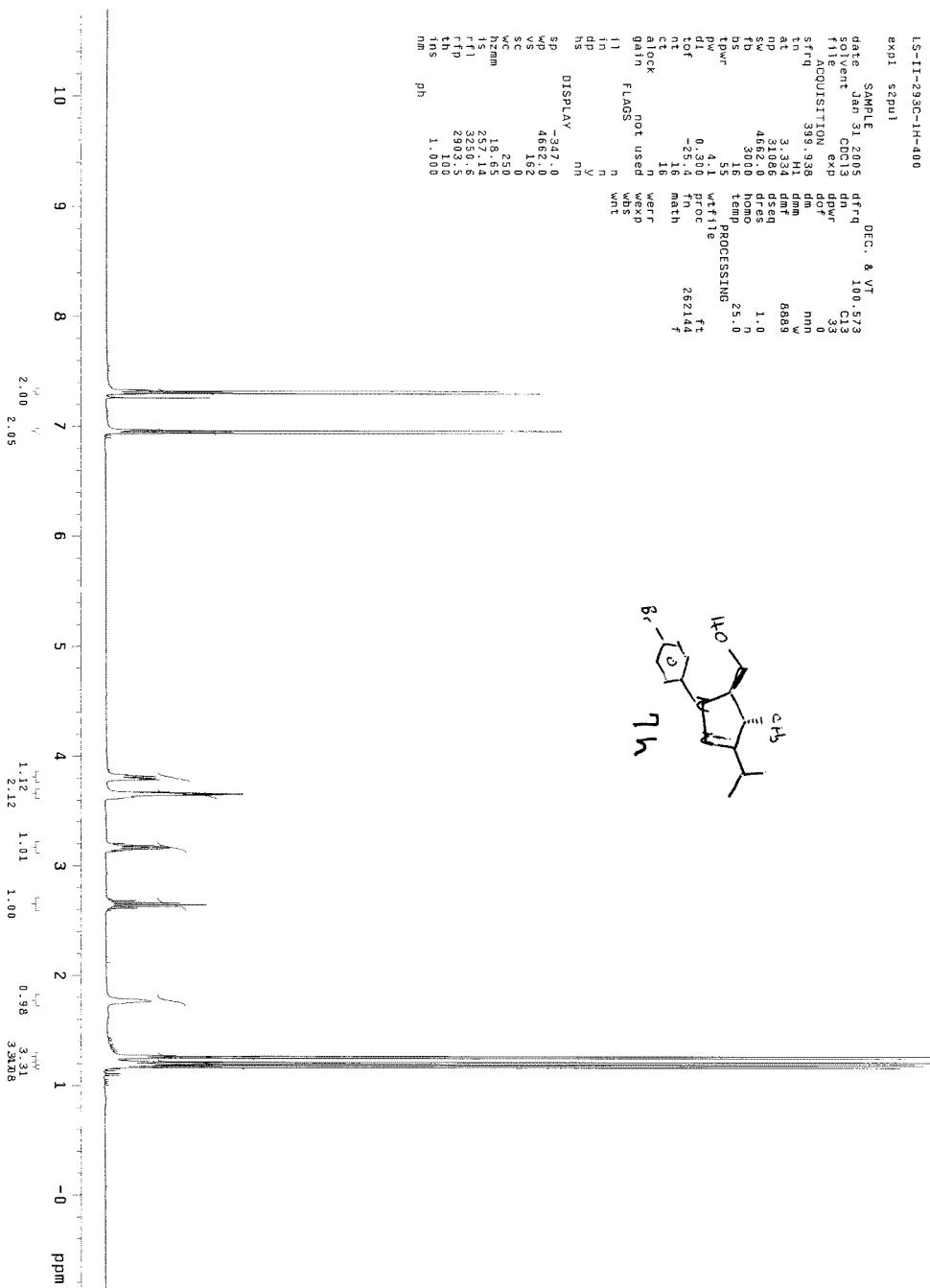
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scilent CNO13
f1e exp dpr
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tr H1 dmm
at 3.334 dmt
t1 31.986 dsn
sp 4681.0 dres
fb 301.6 dres
ds 1.6 temp
trpw 5.5 PROCESSING
pw 4.1 wtfile
dl 0.300 ft
tcf -25.4 fn
nt 16 math
ct 16

0EC. & VT
100.573
C13
33
0
nnn
w
8889

4681.0 dres
301.6 temp
trpw 5.5 PROCESSING
pw 4.1 wtfile
dl 0.300 ft
tcf -25.4 fn
nt 16 math
ct 16
alock
gain
not used
wewp
FLAGS
in
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dp
y
hs
DISPLAY
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sp
wp
sg
sc
wc
bzmm
18.65
15.14
rfl
3250.6
rfp
2903.5
th
1ns
nm
ph

0EC. & VT
100.573
C13
33
0
nnn
w
8889

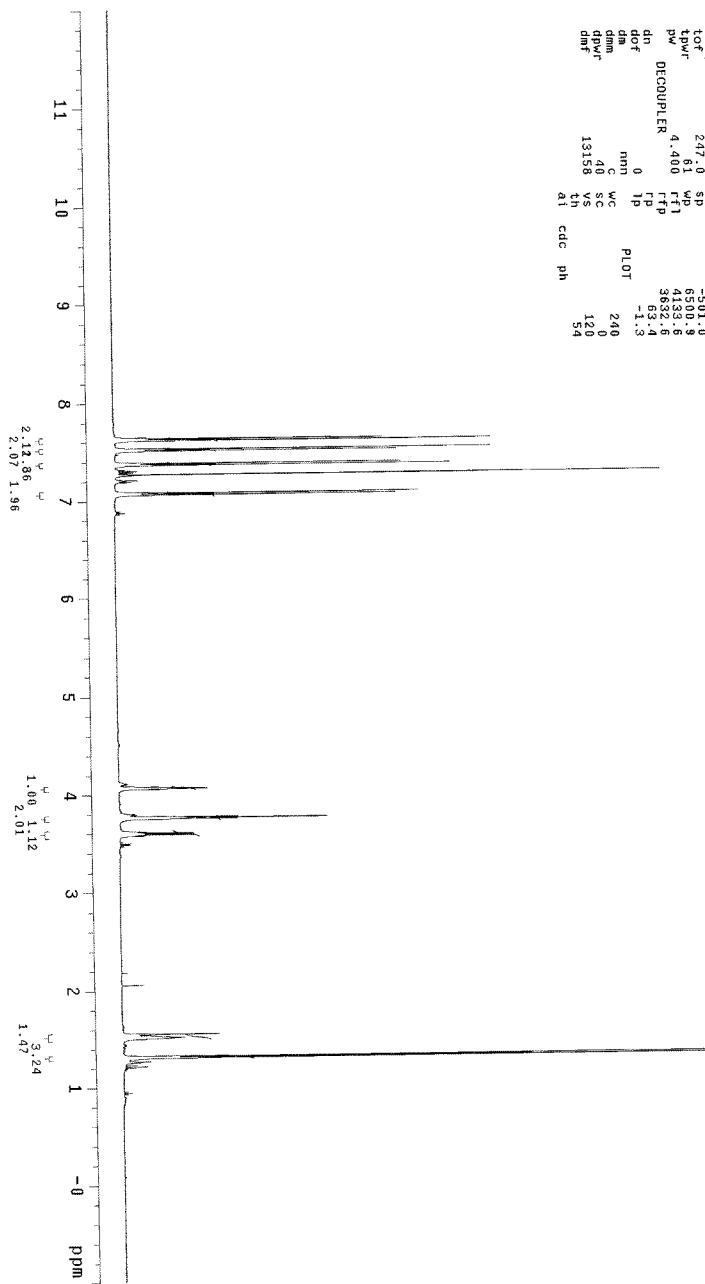
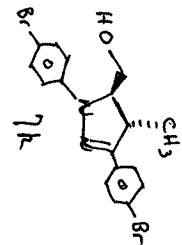
temp
trpw
pw
dl
tcf
nt
ct
alock
gain
not used
wewp
FLAGS
in
n
dp
y
hs
DISPLAY
-347.0
sp
wp
sg
sc
wc
bzmm
18.65
15.14
rfl
3250.6
rfp
2903.5
th
1ns
nm
ph



LS-III-290

exp2 s2pul

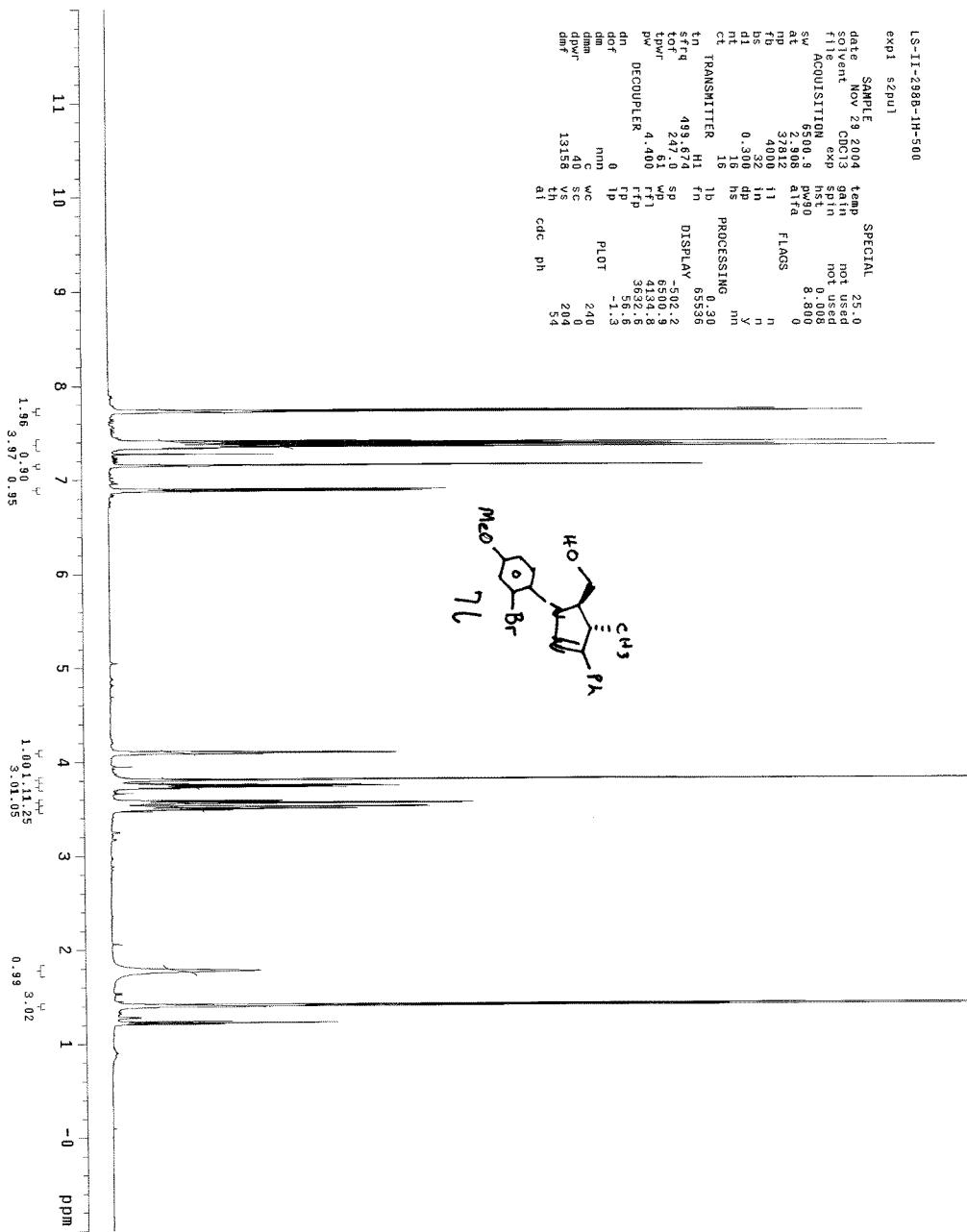
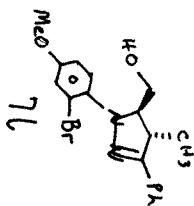
	SAMPLE	temp	SPECIAL
date	Apr 21	2005	25.0
sovent	CDCl ₃	gain	not used
frq	400.13	hetn	0.008
ACQUISITION	exp	hetn	8.800
sw	6500.9	psg0	0
at	2.908	alfa	
np	37812	FLAGS	
fb	40000		
bs	32		
d1	0.300	in	n
dt	16	dp	y
ct	16	hs	nn
TRANSMITTER	16	PROCESSING	0.30
tn	1b	1b	65336
sfq	499.674	fn	
toftr	247.0	sp	DISPLAY
tpwtr	499.674	wp	-501.0
pw	4.461	wp	6300.9
DECOPPLER	4.460	rf1	4133.6
d1n	0	rfp	3832.6
d1f	0	1p	63.4
d1m	0	nm	-1.3
d1m'	0	sc	240
d1w	13158	sc	0
d1f'	13158	vs	120
		th	54
		ai	
		cdc	
		ph	



LS-II-298B-1H-500

exp1 s2bu1

SAMPLE	Nov 29 2004	temp	25.0
SOLVENT	CDCl ₃	gain	not used
TIME	exp	height	0.008
ACQUISITION	8.800	pw0	8.800
Sy	65.00	psw0	0
at	2.908	alpha	0
np	3.812	FLACS	
fb	4.000		
bs	0.32	11	
d1	0.300	in	
nt	16	dp	Y
ct	16	hs	nn
TRANSMITTER	1b	PROCESSING	0.30
tn	4.93	H1	655.36
sfra	5.74	sp	
tr0f	2.47	wp	-502.2
tr0r	4.61	wp	650.9
pw	4.400	rf1	4134.8
DECOPPLER	rfp	rfp	3632.6
dn	0	1p	56.6
derf	0	rrm	-1.3
dm	40	sc	2.0
dmf	13158	sc	2.0
dtmf	vs	th	2.04
		ai	54
		cdc	
		ph	



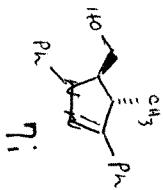
LS-III-820-1H-400

exp1 s2pu

SAMPLE DATE Jan 31 2005 DECR. & VIT. 11

alock	n	werr
gain	n	wxp
FLAGS	not used	wbs
ii	n	wnt
in	n	
dn	n	
v	v	

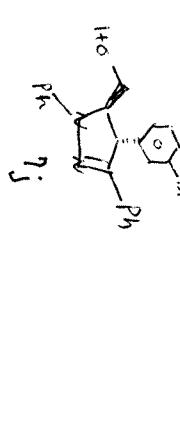
hs	hs	DISPLAY	-346.8
sp		wp	4662.0
		vs	152.0
		sc	0.0
		wc	25.0
h2mm			18.65
is			314.65
rfl			3250.4
rfp			2903.5
th			100.0
ins			1.0000
nm		ph	1.0000



LS-III-868-1H-500

exp2 s2bu1

SAMPLE	25.0
date	Jan 31, 2005
COVENT	CDCl ₃
TIME	6:13
ACQUISITION	temp
SW	not used
AT	not used
NP	0.008
FB	8.800
BS	0.000
D1	0.32
RT	0.500
CT	0.500
TRANSMITTER	16
TR	16
SP ¹	439.674
SP ²	427.740
SP ³	416.611
PW1	4.400
DECOUPLER	4.400
D1	0.000
DE	0.000
DM	0.000
SW1	13158
D1W1	1.00
SW2	1.370
D1W2	0.970
SW3	0.930
D1W3	0.940
SW4	0.960
D1W4	1.940
SW5	1.000
D1W5	1.970
SW6	1.370
D1W6	0.930
SW7	0.960
D1W7	1.940
SW8	1.000
D1W8	1.970
SW9	1.370
D1W9	0.930
SW10	0.960
D1W10	1.940
SW11	1.000
D1W11	1.970
SW12	1.370
D1W12	0.930
SW13	0.960
D1W13	1.940
SW14	1.000
D1W14	1.970
SW15	1.370
D1W15	0.930
SW16	0.960
D1W16	1.940
SW17	1.000
D1W17	1.970
SW18	1.370
D1W18	0.930
SW19	0.960
D1W19	1.940
SW20	1.000
D1W20	1.970
SW21	1.370
D1W21	0.930
SW22	0.960
D1W22	1.940
SW23	1.000
D1W23	1.970
SW24	1.370
D1W24	0.930
SW25	0.960
D1W25	1.940
SW26	1.000
D1W26	1.970
SW27	1.370
D1W27	0.930
SW28	0.960
D1W28	1.940
SW29	1.000
D1W29	1.970
SW30	1.370
D1W30	0.930
SW31	0.960
D1W31	1.940
SW32	1.000
D1W32	1.970
SW33	1.370
D1W33	0.930
SW34	0.960
D1W34	1.940
SW35	1.000
D1W35	1.970
SW36	1.370
D1W36	0.930
SW37	0.960
D1W37	1.940
SW38	1.000
D1W38	1.970
SW39	1.370
D1W39	0.930
SW40	0.960
D1W40	1.940
SW41	1.000
D1W41	1.970
SW42	1.370
D1W42	0.930
SW43	0.960
D1W43	1.940
SW44	1.000
D1W44	1.970
SW45	1.370
D1W45	0.930
SW46	0.960
D1W46	1.940
SW47	1.000
D1W47	1.970
SW48	1.370
D1W48	0.930
SW49	0.960
D1W49	1.940
SW50	1.000
D1W50	1.970
SW51	1.370
D1W51	0.930
SW52	0.960
D1W52	1.940
SW53	1.000
D1W53	1.970
SW54	1.370
D1W54	0.930
SW55	0.960
D1W55	1.940
SW56	1.000
D1W56	1.970
SW57	1.370
D1W57	0.930
SW58	0.960
D1W58	1.940
SW59	1.000
D1W59	1.970
SW60	1.370
D1W60	0.930
SW61	0.960
D1W61	1.940
SW62	1.000
D1W62	1.970
SW63	1.370
D1W63	0.930
SW64	0.960
D1W64	1.940
SW65	1.000
D1W65	1.970
SW66	1.370
D1W66	0.930
SW67	0.960
D1W67	1.940
SW68	1.000
D1W68	1.970
SW69	1.370
D1W69	0.930
SW70	0.960
D1W70	1.940
SW71	1.000
D1W71	1.970
SW72	1.370
D1W72	0.930
SW73	0.960
D1W73	1.940
SW74	1.000
D1W74	1.970
SW75	1.370
D1W75	0.930
SW76	0.960
D1W76	1.940
SW77	1.000
D1W77	1.970
SW78	1.370
D1W78	0.930
SW79	0.960
D1W79	1.940
SW80	1.000
D1W80	1.970
SW81	1.370
D1W81	0.930
SW82	0.960
D1W82	1.940
SW83	1.000
D1W83	1.970
SW84	1.370
D1W84	0.930
SW85	0.960
D1W85	1.940
SW86	1.000
D1W86	1.970
SW87	1.370
D1W87	0.930
SW88	0.960
D1W88	1.940
SW89	1.000
D1W89	1.970
SW90	1.370
D1W90	0.930
SW91	0.960
D1W91	1.940
SW92	1.000
D1W92	1.970
SW93	1.370
D1W93	0.930
SW94	0.960
D1W94	1.940
SW95	1.000
D1W95	1.970
SW96	1.370
D1W96	0.930
SW97	0.960
D1W97	1.940
SW98	1.000
D1W98	1.970
SW99	1.370
D1W99	0.930
SW100	0.960
D1W100	1.940
SW101	1.000
D1W101	1.970
SW102	1.370
D1W102	0.930
SW103	0.960
D1W103	1.940
SW104	1.000
D1W104	1.970
SW105	1.370
D1W105	0.930
SW106	0.960
D1W106	1.940
SW107	1.000
D1W107	1.970
SW108	1.370
D1W108	0.930
SW109	0.960
D1W109	1.940
SW110	1.000
D1W110	1.970
SW111	1.370
D1W111	0.930
SW112	0.960
D1W112	1.940
SW113	1.000
D1W113	1.970
SW114	1.370
D1W114	0.930
SW115	0.960
D1W115	1.940
SW116	1.000
D1W116	1.970
SW117	1.370
D1W117	0.930
SW118	0.960
D1W118	1.940
SW119	1.000
D1W119	1.970
SW120	1.370
D1W120	0.930
SW121	0.960
D1W121	1.940
SW122	1.000
D1W122	1.970
SW123	1.370
D1W123	0.930
SW124	0.960
D1W124	1.940
SW125	1.000
D1W125	1.970
SW126	1.370
D1W126	0.930
SW127	0.960
D1W127	1.940
SW128	1.000
D1W128	1.970
SW129	1.370
D1W129	0.930
SW130	0.960
D1W130	1.940
SW131	1.000
D1W131	1.970
SW132	1.370
D1W132	0.930
SW133	0.960
D1W133	1.940
SW134	1.000
D1W134	1.970
SW135	1.370
D1W135	0.930
SW136	0.960
D1W136	1.940
SW137	1.000
D1W137	1.970
SW138	1.370
D1W138	0.930
SW139	0.960
D1W139	1.940
SW140	1.000
D1W140	1.970
SW141	1.370
D1W141	0.930
SW142	0.960
D1W142	1.940
SW143	1.000
D1W143	1.970
SW144	1.370
D1W144	0.930
SW145	0.960
D1W145	1.940
SW146	1.000
D1W146	1.970
SW147	1.370
D1W147	0.930
SW148	0.960
D1W148	1.940
SW149	1.000
D1W149	1.970
SW150	1.370
D1W150	0.930
SW151	0.960
D1W151	1.940
SW152	1.000
D1W152	1.970
SW153	1.370
D1W153	0.930
SW154	0.960
D1W154	1.940
SW155	1.000
D1W155	1.970
SW156	1.370
D1W156	0.930
SW157	0.960
D1W157	1.940
SW158	1.000
D1W158	1.970
SW159	1.370
D1W159	0.930
SW160	0.960
D1W160	1.940
SW161	1.000
D1W161	1.970
SW162	1.370
D1W162	0.930
SW163	0.960
D1W163	1.940
SW164	1.000
D1W164	1.970
SW165	1.370
D1W165	0.930
SW166	0.960
D1W166	1.940
SW167	1.000
D1W167	1.970
SW168	1.370
D1W168	0.930
SW169	0.960
D1W169	1.940
SW170	1.000
D1W170	1.970
SW171	1.370
D1W171	0.930
SW172	0.960
D1W172	1.940
SW173	1.000
D1W173	1.970
SW174	1.370
D1W174	0.930
SW175	0.960
D1W175	1.940
SW176	1.000
D1W176	1.970
SW177	1.370
D1W177	0.930
SW178	0.960
D1W178	1.940
SW179	1.000
D1W179	1.970
SW180	1.370
D1W180	0.930
SW181	0.960
D1W181	1.940
SW182	1.000
D1W182	1.970
SW183	1.370
D1W183	0.930
SW184	0.960
D1W184	1.940
SW185	1.000
D1W185	1.970
SW186	1.370
D1W186	0.930
SW187	0.960
D1W187	1.940
SW188	1.000
D1W188	1.970
SW189	1.370
D1W189	0.930
SW190	0.960
D1W190	1.940
SW191	1.000
D1W191	1.970
SW192	1.370
D1W192	0.930
SW193	0.960
D1W193	1.940
SW194	1.000
D1W194	1.970
SW195	1.370
D1W195	0.930
SW196	0.960
D1W196	1.940
SW197	1.000
D1W197	1.970
SW198	1.370
D1W198	0.930
SW199	0.960
D1W199	1.940
SW200	1.000
D1W200	1.970



LS-III-45-1H-400

exp1 s2pul

SAMPLE

date Jan 23, 2015

solvent CDCl₃

exp

dtf

dtw

dtg

dtm

dtm

dtw

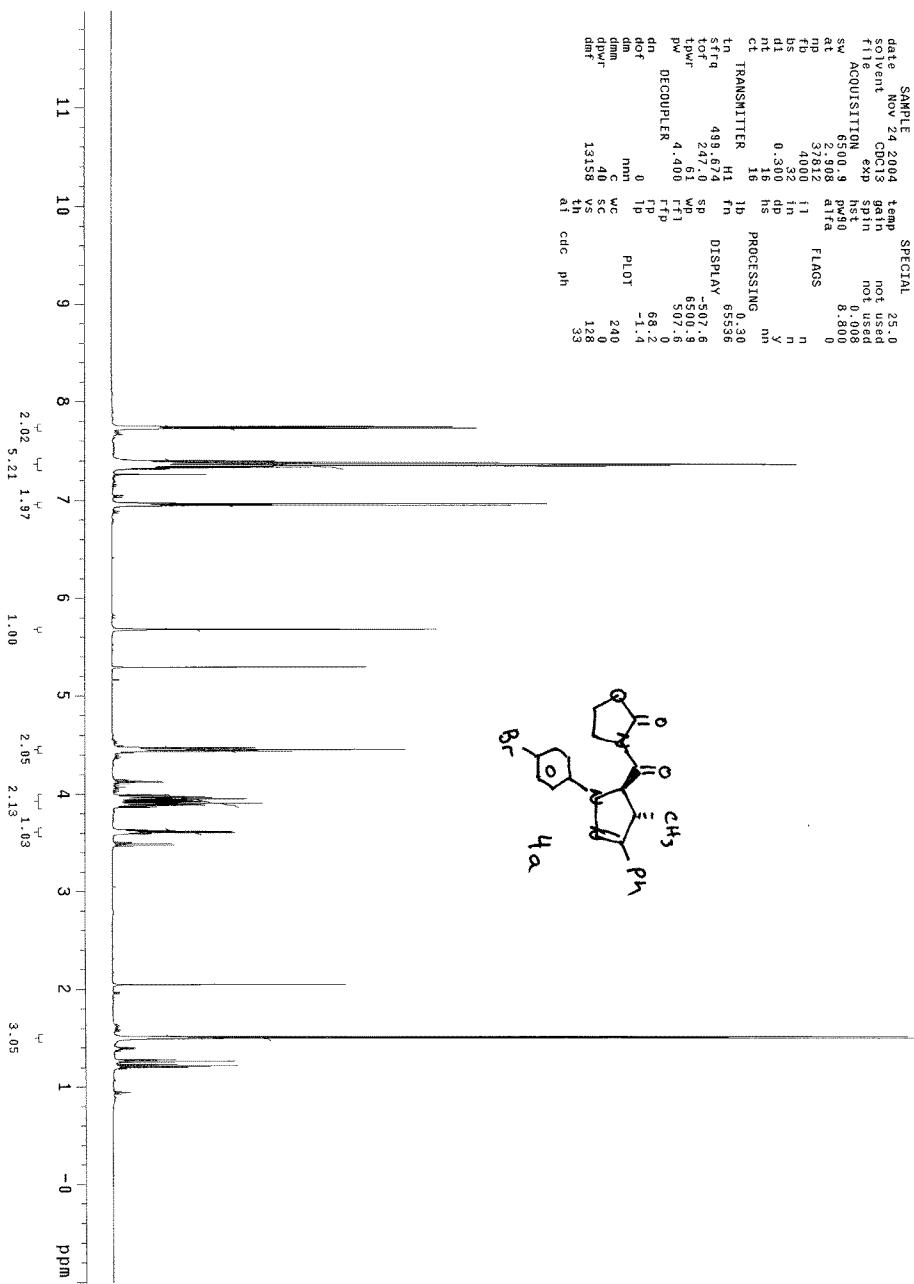
dtg

dtm

LS-III-18A-1H-500

exp1 s2pul

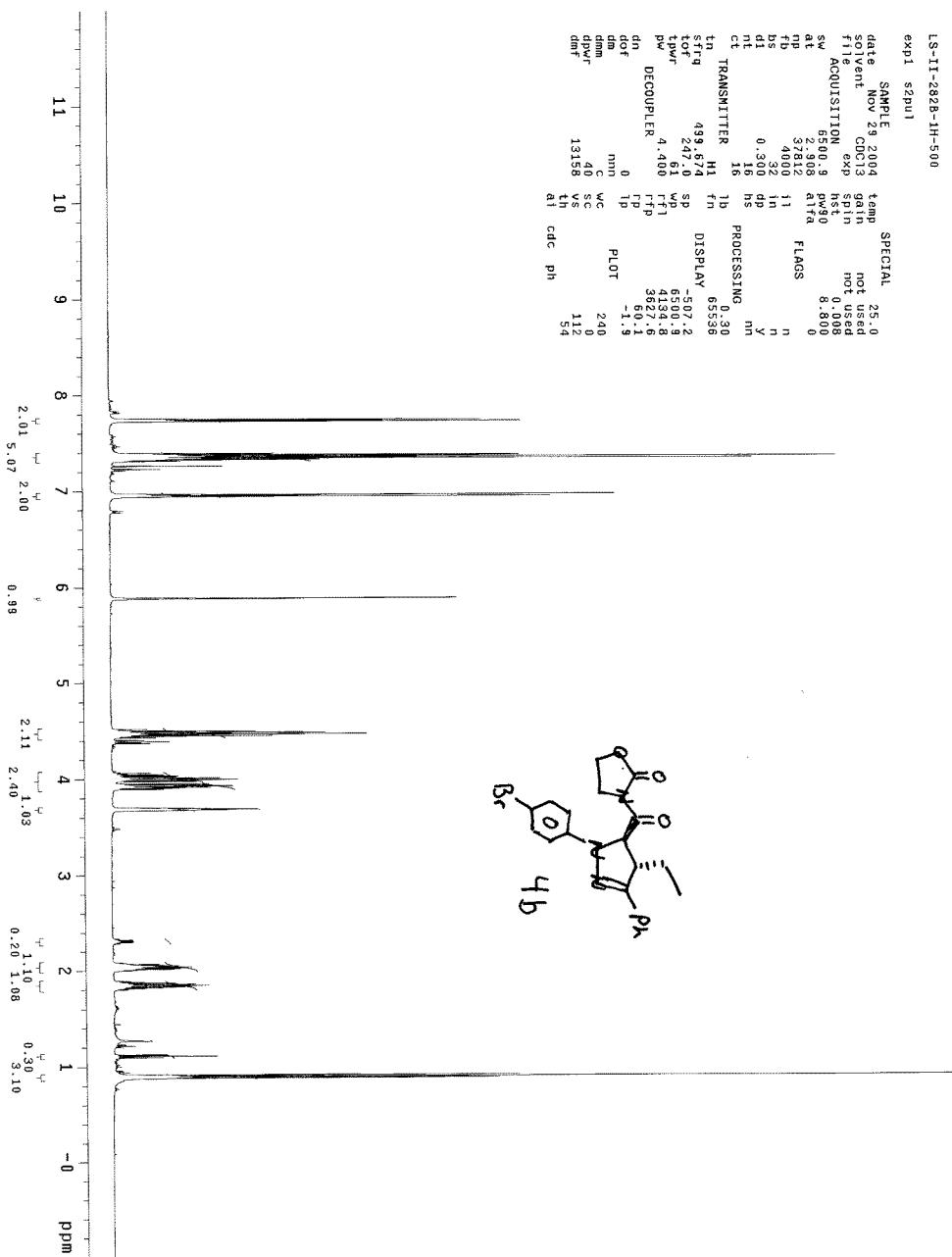
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date	Nov 24, 2004	25.0	
solvent	CDC13	gain	
file		not used	
ACQUISITION	exp	spin	
sw	6500.0	hist	0.008
at	2.908	pe90	8.800
np	38812	alra	0
fb	40000		
bs	0.332	FLAGS	
q1	0.300	11	n
mt	1.000	dp	y
ct	1.000	hs	nn
TRANSMITTER	1.00	PROCESSING	0.30
tn	H1	1b	0.30
sfq	674	DISPLAY	65536
tof	499.6		-507.6
tp ₁	247.0	s _p	
tp ₂	61.1	w _p	
pw	4.400	r _{f1}	6500.9
DECOUPLER		r _{f2}	507.6
dt		r _p	68.2
df	0	1p	-1.4
dm	0	PL0T	
dmr	C		
dpr	40	240	
dmf	VS	120	
	13158	128	
		33	
a1	ctc		
	ph		



LS-11-2828-1H-500

exp1 s2pu1

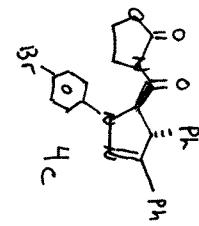
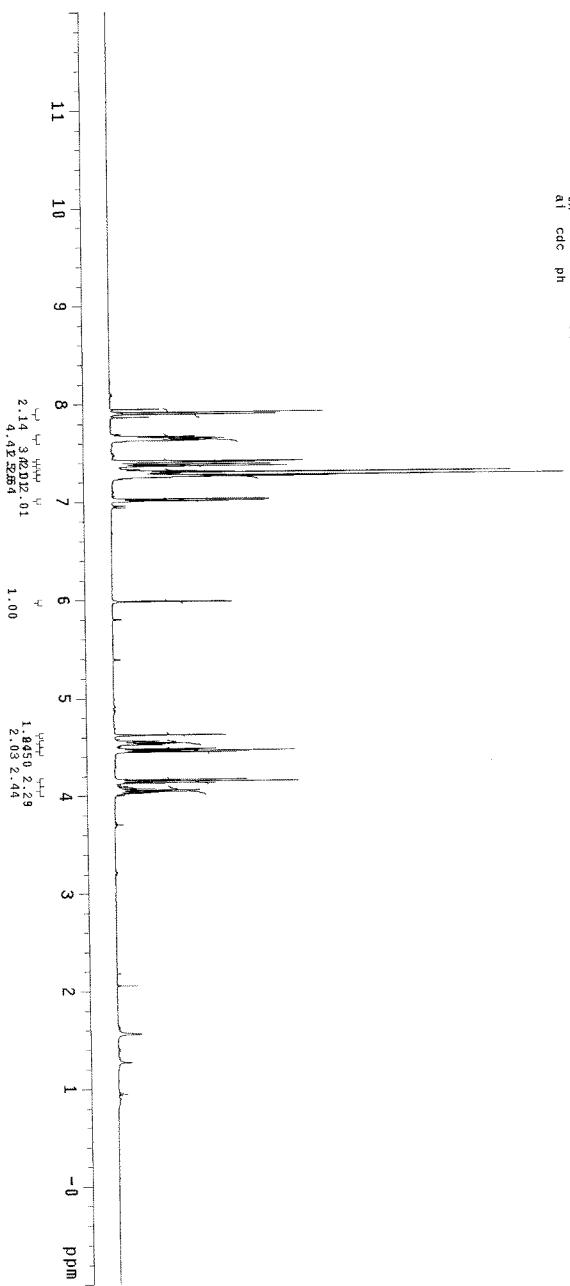
	SAMPLE	temp	SPECIAL
date	Nov 29 2004	25.0	25.0
COVENT	CDCl ₃	not used	not used
rt	exp	not used	not used
ACQUISITION	hsq	0.008	0.008
sw	65.00	8.800	8.800
et	2.908	0	0
pp	3.812	alpha	alpha
fb	4.000	11	11
bs	3.32	in	n
d1	0.300	dp	y
mt	16	hs	in
ct	16	PROCESSING	in
TRANSMITTER	1b	0.30	0.30
tr	4.39	H1	65.56
stf ^q	4.39	6.74	6.74
t0w ^q	2.47	7.0	7.0
t0w ^r	4.61	8.1	8.1
pw	4.400	wp	-5.07.2
DECOUPLER	4.400	r ^f 1	65.00.9
dn	0	r ^f p	4.34.8
dtf	0	tp	3.67.6
dtm	0	tp	60.1
dtm ^q	0	tp	-1.9
dtm ^r	131.58	PPM	2.40
dtm ^r	131.58	PPC	2.40
dtm ^r	131.58	SC	0
dtm ^r	131.58	VS	11.2
dtm ^r	131.58	TH	54
ai	cdc	ph	54



LS-III-19A

exp2 s2pu1

	SAMPLE	temp	SPECTRAL
date	Apr 21 2005	25.0	temp
solvent	CDCl ₃	25.0	gain
file	exp	not used	not used
ACQUISITION	16	ppm	ppm
sw	6500.0	0.008	0.008
at	2.008	8.800	8.800
np	37812	alpha	0
fb	4000	1	FLAVS
bs	0.32	in	n
dl	0.30	dp	y
nt	1.6	hs	Y
ct	16	PROCESSING	mm
TRANSMITTER	16	0.30	mm
tn	1.6	fr	mm
sfq	499.674	DISPLAY	6.536
tor	247.60	sp	-501.0
pw	6.61	wp	6500.9
DECOUPLER	4.400	r _{f1}	4133.6
dn	4.42	r _{fp}	3622.6
dor	0	rp	67.8
dm	0	ip	-9.2
dmr	40	PLDT	240
dpr	13158	vc	75
dmr	th	sc	75
dpr	th	cdc	54
dmr	th	ph	54

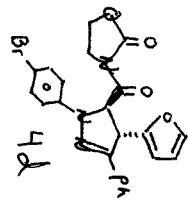


LS-III-89

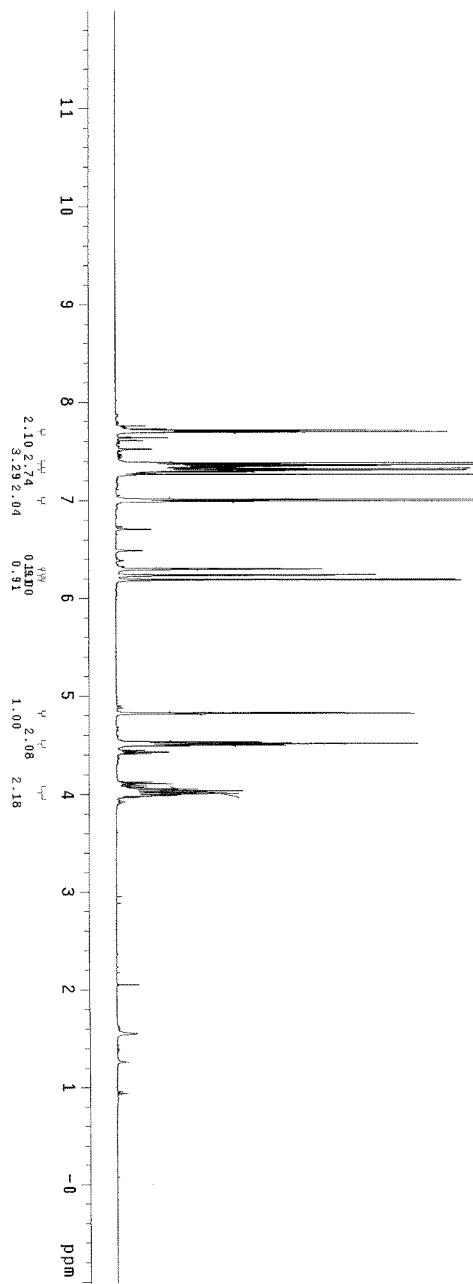
exp2

spul

	SAMPLE	temp	SPECIAL
date	Apr 21 2005	25.0	25.0
SOLVENT	CDCl ₃	spin	not used
file	exp2	spin	not used
ACQUISITION	16	htn	htn
sw	6.500	htn	htn
dt	2.908	htn	htn
np	37812	htn	htn
fb	4000	htn	htn
bs	32	n	n
dl	0.310	dp	y
nt	16	hs	nn
ct	16	PROCESSING	nn
TRANSMITTER	1b	0.30	0.30
tn	49.674	H1	fn
sf,q	49.674	H1	fn
tor	247.0	sp	DISPLAY
tpv,r	247.0	sp	65536
pw	4.400	wp	-505.8
DECOUPLER	4.400	r ¹	8500.9
dn	0	r ¹	4133.4
dn,r	0	r ¹	3627.6
dm	0	rp	70.7
dm,r	0	rp	-6.2
dpv,r	410	ip	240
dm,r	13158	sc	240
		th	75
ai	cdc	th	54
		ph	54



+ small amount
of starting material

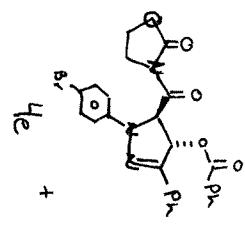


LS-III-90

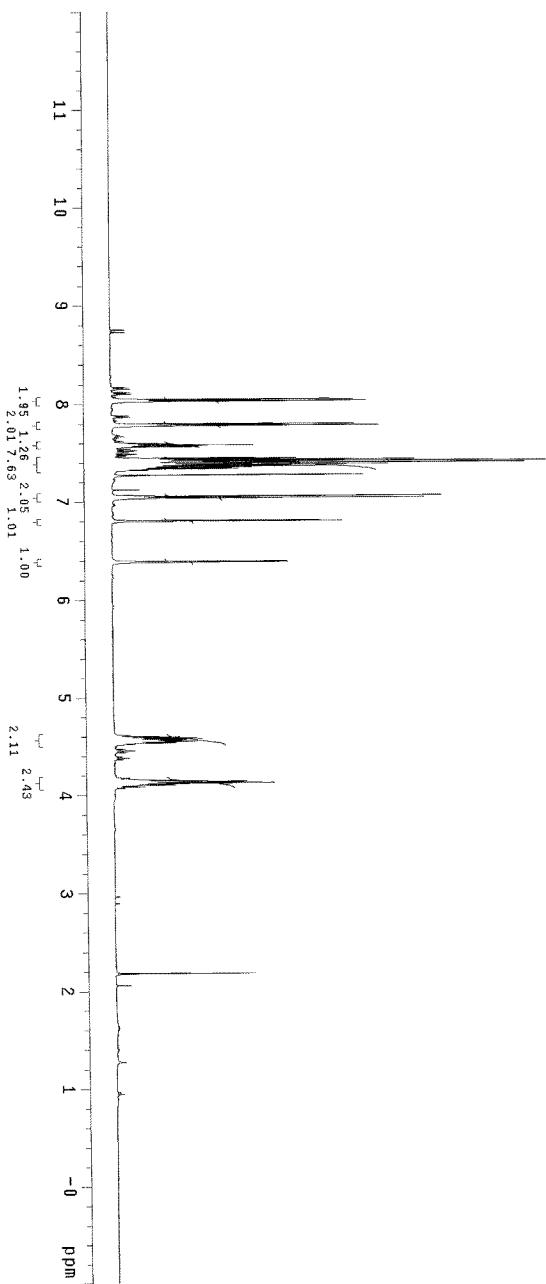
exp2

82pu1

SAMPLE: 21/05/2005 temp: 25.0
date: Apr 21/05/2005 gain: not used
solvent: CDCl₃ gain: not used
file: exp2: not used
ACQUISITION: 8.800
sw: 6500.0 Hz: 0.008
dt: 2.908 pw: 8.800
np: 37812 aifa: 0
fb: 40000 flags: 0
bs: 32 in: n
d1: 0.300 dp: y
nt: 16 hs: nn
ct: 16 processing: 0.30
TRANSMITTER: 1H fn: 65336
tn: 499.674 H1
sfr: 499.674
t0f: 247.0 sp: -501.0
t0r: 247.1 wp: 6500.9
pw: 4.400 r1f: 501.0
DECOUPLER: r1p: 74.6
dn: 0 tp: -11.6
d1f: 0 min: 240
d1m: 0 sc: 150
d1mf: 131.58 vs: 54
d1f: th: 54
ai: cdc: ph:



4e + small amount
of starting material

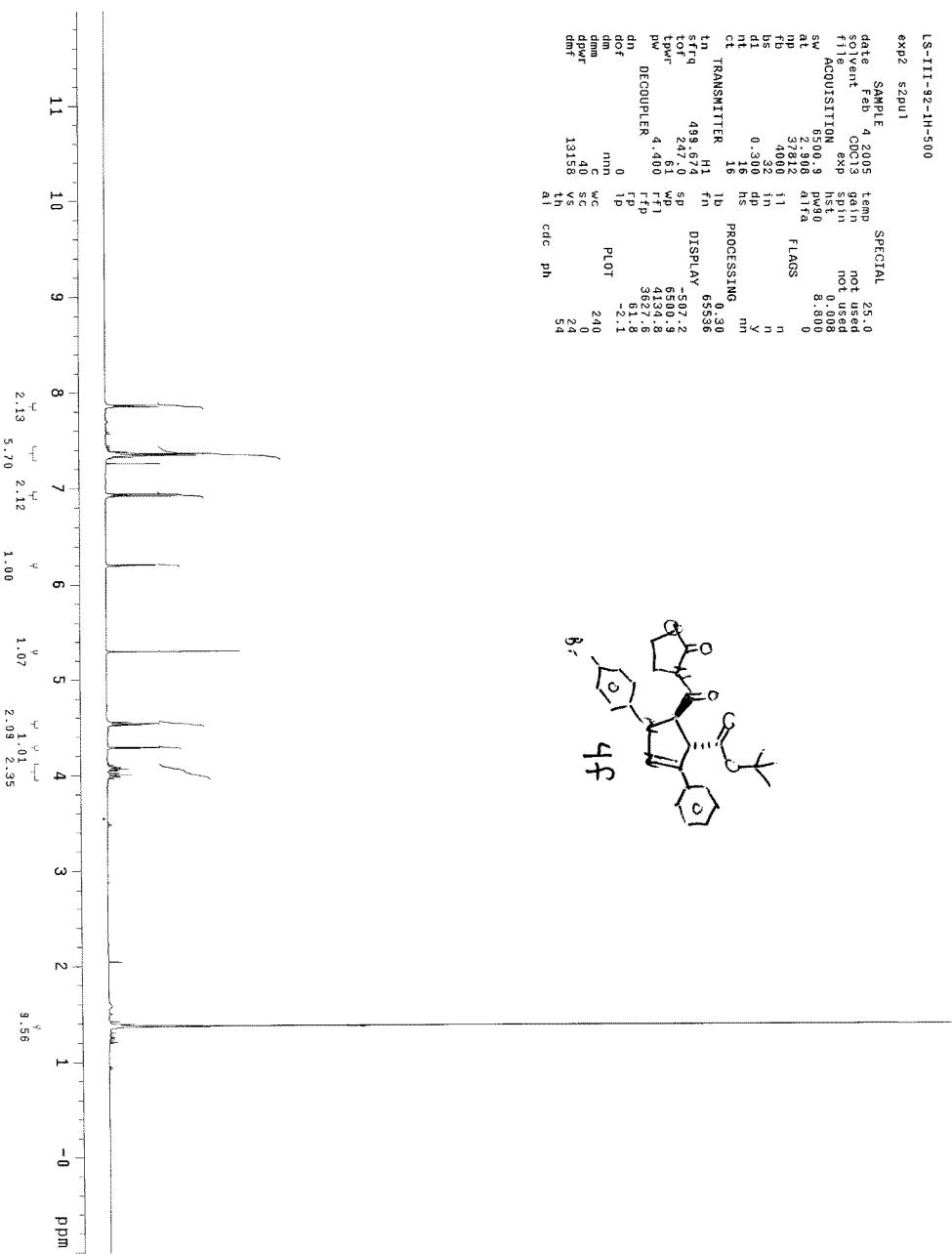


LS-III-92-1H-500

exp2

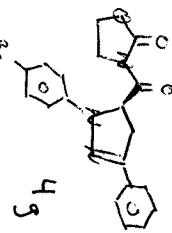
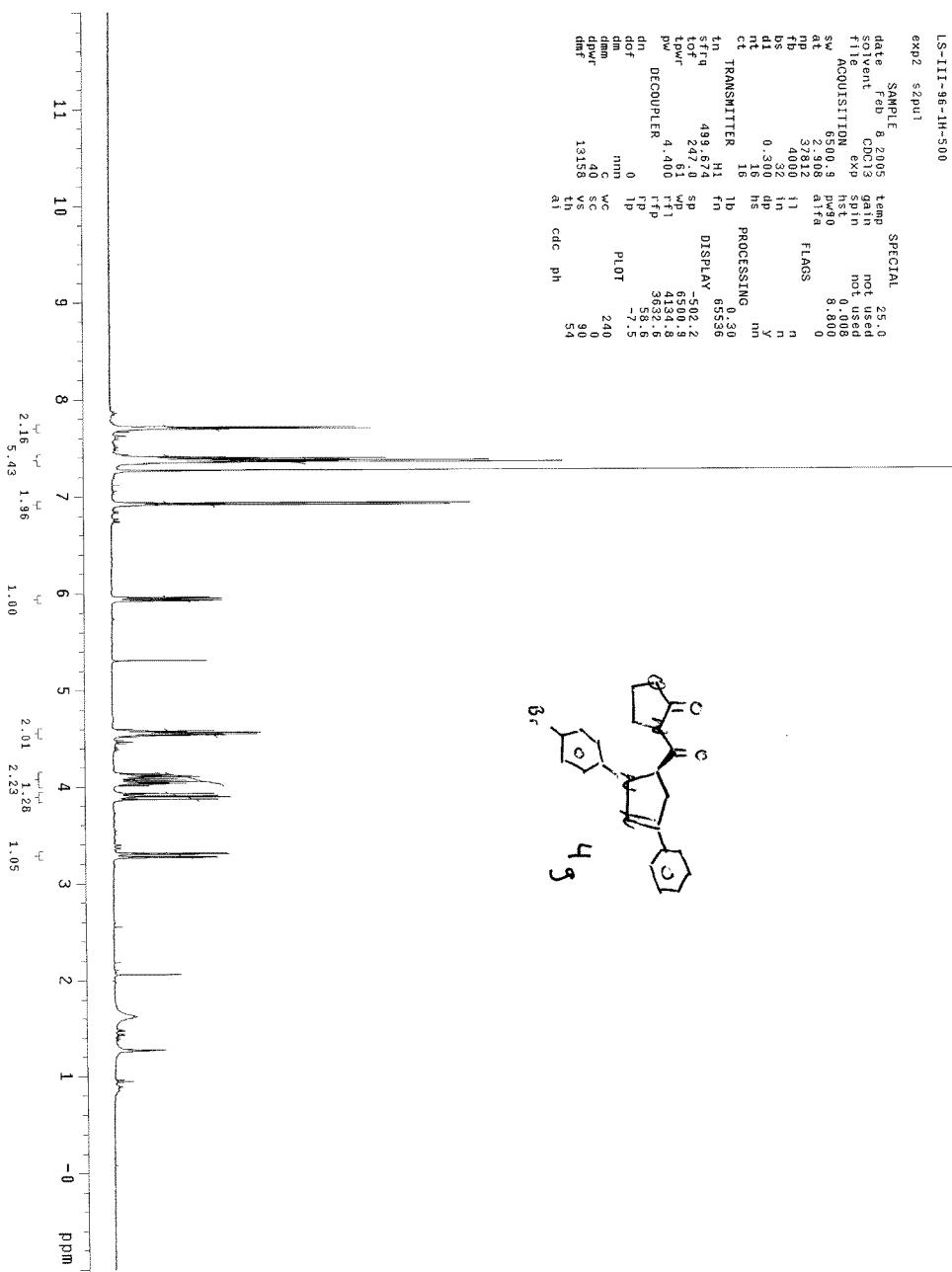
sz2u1

SAMPLE 4.005 temp 25.0
solvent CDCl₃ gain not used
file 13 exp not used
ACQUISITION 8.008
sw 65.00.9 hist 0.008
at 2.9.08 pwo 8.800
pp 3.8.12 aita 0.00
fb 4.000 flags
bs 1.1 n
dt 0.3.32 1h n
nt 0.3.00 dp y
ct 1.6 ns mn
TRANSMITTER 1b 0.30
tn 4.9.6.74 H1 fn DISPLAY 65.536
sfrq 4.9.6.74 tof -0.7.2
tppw 2.47.6.1 sp 6.00.9
tpwr 4.4.00 wp 6.00.9
pw 4.4.00 rrf1 4.3.4.8
dec 0 rfp 3.82.7.6
decf 0 1b 6.1.8
dim mn PLOT -2.1
dimc wc 2.40
dimw sc 2.40
dimf vs 13.15.8 th 5.4
ai cdc ph



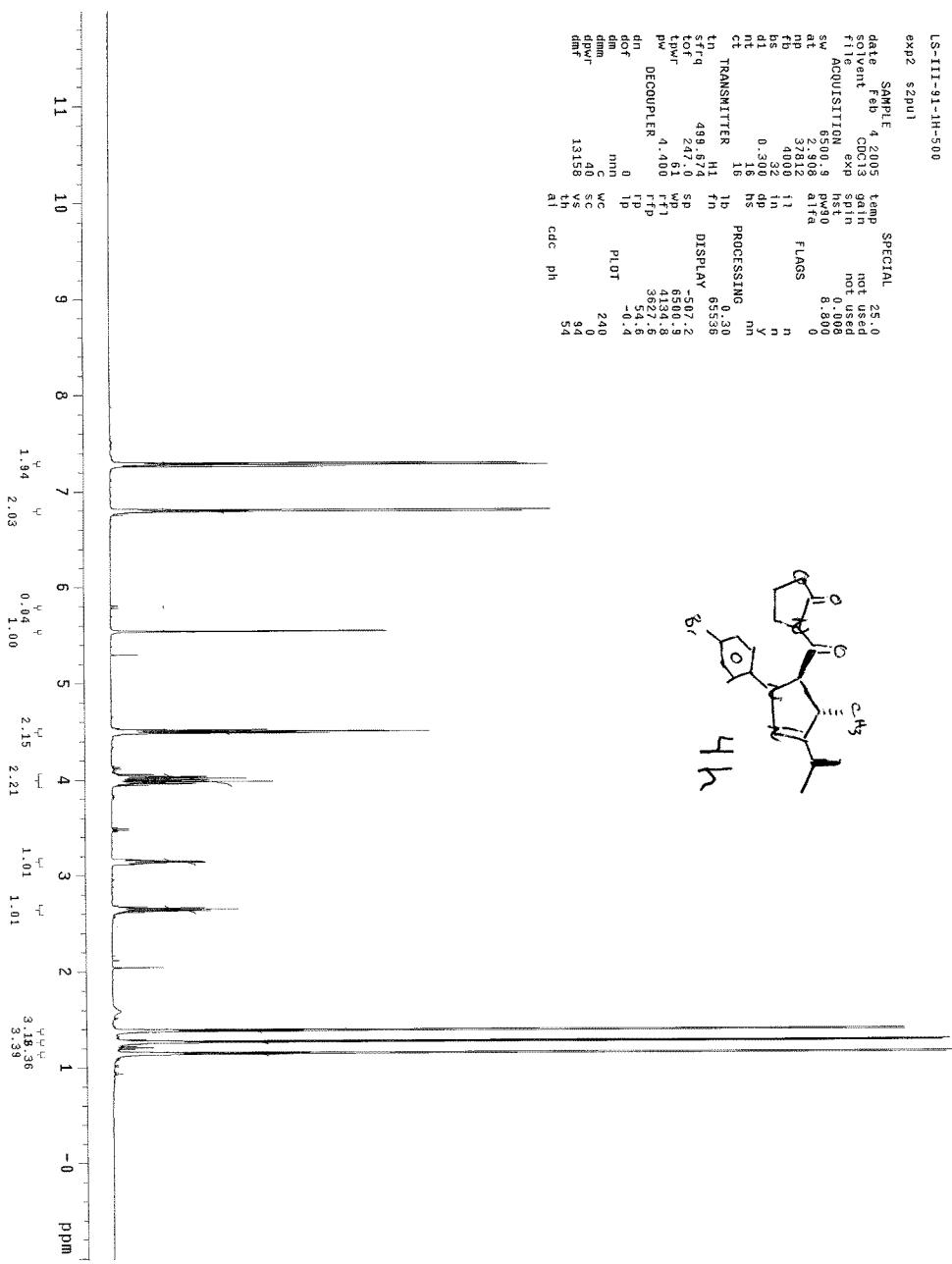
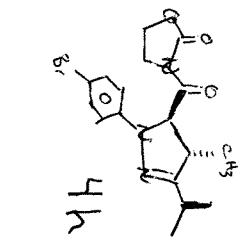
LS-III-96-1H-500

	SAMPLE	DATE	Feb 8, 2005	TEMP	SP. CTIAL	25.0	SOVENT	CUC13	GAIN	NOT USED
	FILE	FILE	ACQUISITION	EXP	SPIN	0.0000	ACQUISITION	6.510	9	8.8000
	SW	SW	ATT	HST	W90	0.0000	SW	6.510	9	0.0000
AT	fb	fb	4000.1	3.812	alpha	1.0000	AT	fb	fb	1.0000
BS	bs	bs	32.32	1.1	FLAG	1.0000	BS	bs	bs	1.0000
D1	d1	d1	300.00	dp	Y	1.0000	D1	d1	dp	1.0000
NT	nt	nt	16.00	hs	Y	1.0000	NT	nt	hs	1.0000
CT	ct	ct	16.00	hs	PROCESSING	0.3000	CT	ct	hs	0.3000
TRANSMITTER	TRANSMITTER	TRANSMITTER	1B	fb	DISPLAY	655.000	TRANSMITTER	49.9	H1	502.000
TIN	tin	tin	49.9	H1	DISPLAY	502.000	TIN	49.9	6.574	500.000
SFTQ	sftq	sftq	242.7	sp	DISPLAY	500.000	SFTQ	242.7	0.000	499.000
TPWR	tpwr	tpwr	8.01	wp	DISPLAY	499.000	TPWR	8.01	0.000	498.000
PW	pw	pw	4.490	rp	DISPLAY	498.000	PW	4.490	0.000	497.000
DECOUPLER	DECOUPLER	DECOUPLER	4.490	rp	DISPLAY	497.000	DECOUPLER	4.490	0.000	496.000
DIN	din	din	0.00	rp	DISPLAY	496.000	DIN	0.00	0.000	495.000
DOF	dof	dof	0.00	rp	DISPLAY	495.000	DOF	0.00	0.000	494.000
DMIN	dmn	dmn	0.00	rp	DISPLAY	494.000	DMIN	0.00	0.000	493.000
DMINN	dmnn	dmnn	0.00	rp	DISPLAY	493.000	DMINN	0.00	0.000	492.000
DQWTR	dqwr	dqwr	40.00	sc	PLOT	240.000	DQWTR	40.00	0.000	239.000
DQWTR	dqwr	dqwr	1315.8	vs	PLOT	239.000	DQWTR	1315.8	0.000	238.000
DM	dm	dm	1315.8	th	PLOT	238.000	DM	1315.8	0.000	237.000
AT	at	at	1315.8	cfc	PH	50.000	AT	at	cfc	50.000



LS-III-91-1H-500
exp2 s2pul

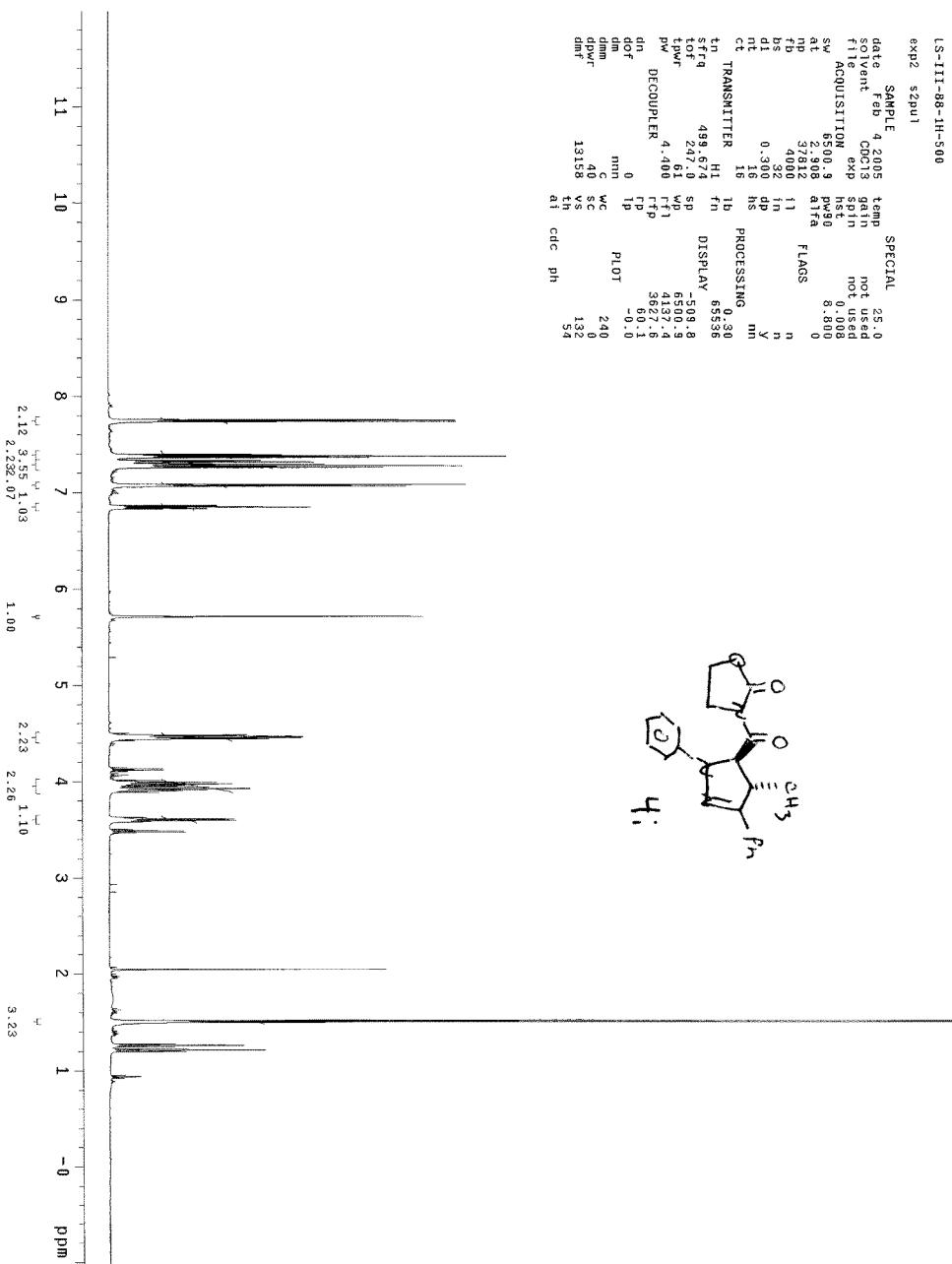
	SAMPLE	temp	SPECIAL
date	Feb 4, 2005	25.0	
solvent	CDCl ₃	0.01	not d
file	exp2	0.01	not used
ACQUISITION	6500.9	0.008	
sw	2.988	8.800	
at	37812	0	
np	4000	8.000	
fb	17		
bs	0.32		
dl	0.30		
nt	1.16	Y	
ct	hs	mn	
TRANSMITTER	1b		
tn	H1	0.30	
sfq	499.674	655.36	
top	247.0	-507.2	
tpv _r	61	6500.9	
pw	4.400	4134.3	
DECOUPLER	rp	3627.6	
dn _r	0	54.6	
dof	ip	-0.4	
dm	mn		
dm	mc		
dpr _r	40	240	
dpr _r	13158	vs	
th	54	94	
al	cdc		
	ph		



LS-TII-88-1H-500

exp2 s2pu1

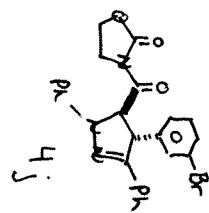
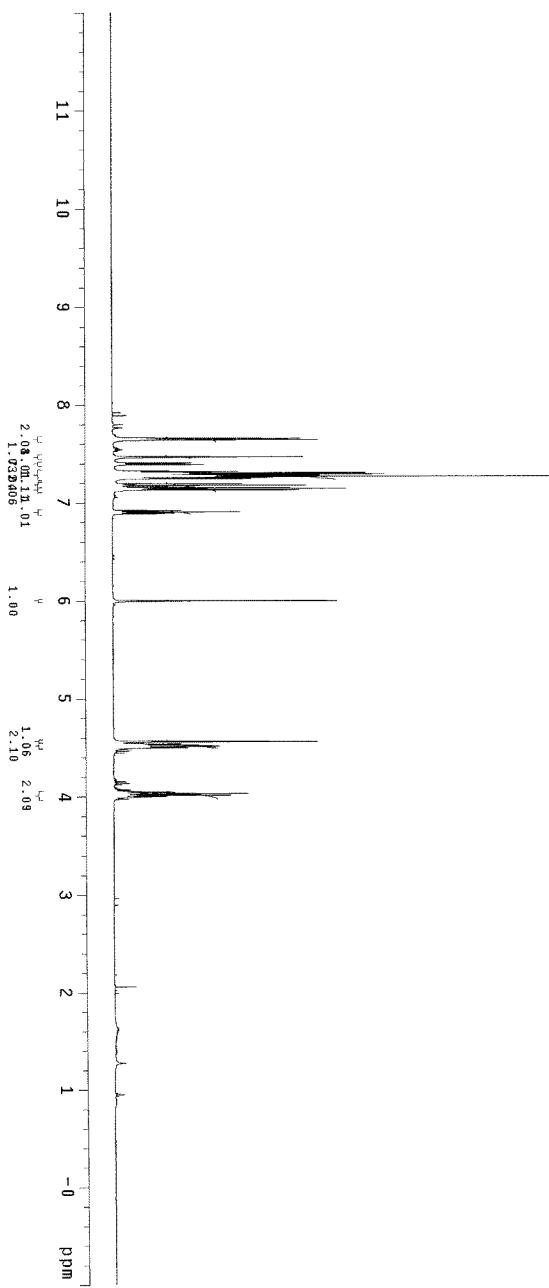
	SAMPLE	TEMP	SPECIAL
date	2005	25.0	
exp	CPC13	gain	not used
solvent	CDCl ₃	spin	not used
file	exp	hst	0.008
ACQUISITION		psg0	8.800
sw	6500.9	psg0	0
at	2.908	airfa	
np	3.812		
fb	400.0	FLAGS	
bs	40.0		
d1	0.300		
ds	0.16	in	n
nt	0.16	dp	y
ct	16	hs	nn
TRANSMITTER	1b	PROCESSING	0.30
tn	H1	1b	0.30
sf,q	499.674	fn	653.36
tof	247.0	sp	DISPLAY
tpw,r	4.61	wp	-509.8
pw	4.400	rp	-509.8
DECOUPLER	4.400	rp	435.4
dn	0	r	362.6
dof	0	ip	61.1
dm	0	mn	-0.0
dmm	0	sc	240
dmm	40	sc	240
dpr,r	131.58	vs	132
dmf	th	th	54
	at	cde	54
		ph	



exp2 52p

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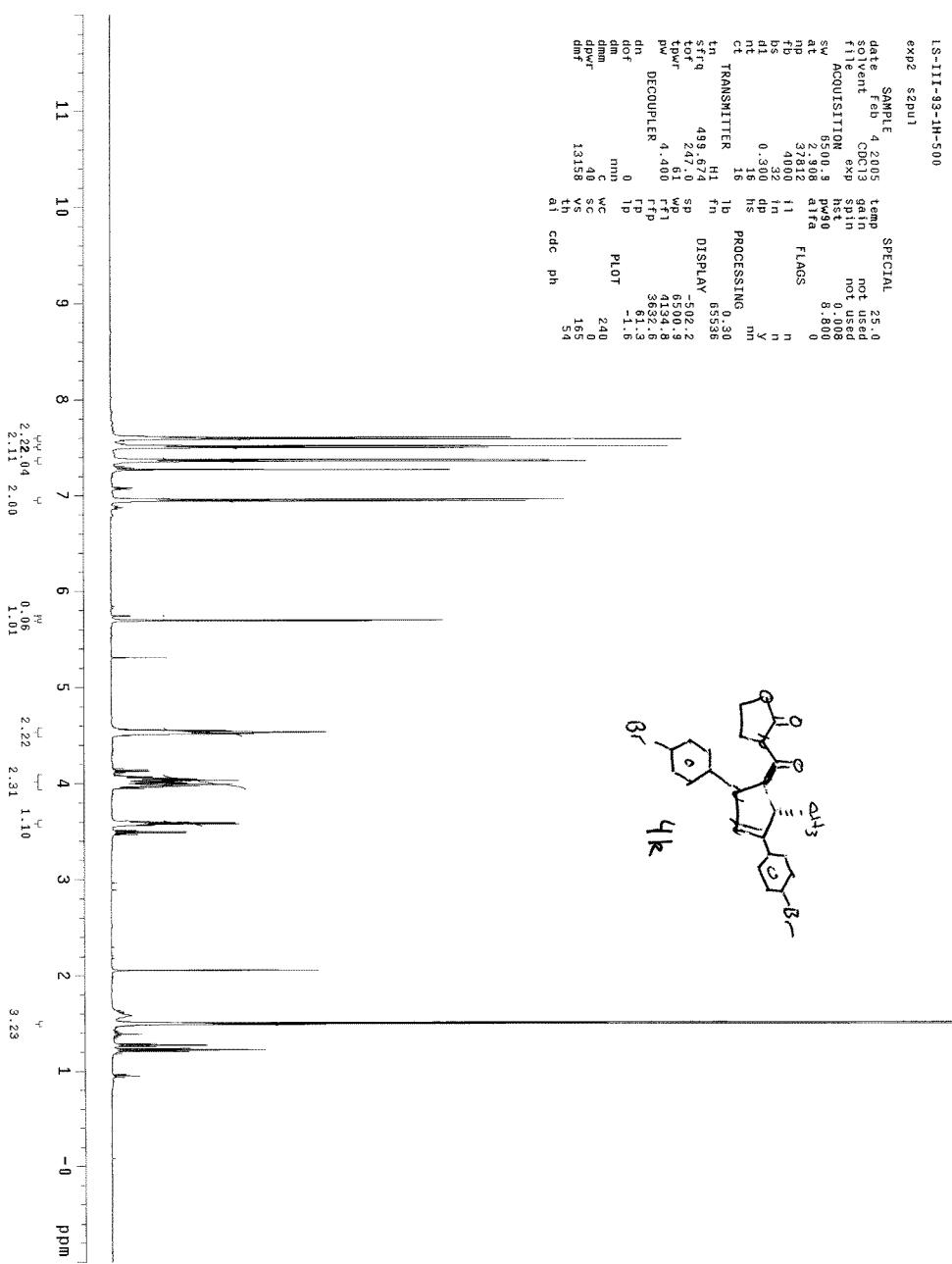
SAMPLE		SPECIAL	
date	APR 21, 2005	temp	25.0
solvent	CHCl ₃	run	not used
file	ACQUISITION	exp	not used
ACQUISITION	5.00	exp	not used
sw	9.00	run	not used
ap	3.7812	alfa	0
fb	4.0000	FLAGS	0
bs	.32	n	0
dt	0.300	in	0
nt	16	dp	0
ct	16	hs	0
TRANSMITTER	1.0	PROCESSING	0
tn	TRANSMITTER	9.0	0
5.00	H1	DISPLAY	65.5000
4.99	4.9	SP	-500.0
6.71	6.7	SP	-6500.0
2.47	2.47	SP	4133.6
6.61	6.61	SP	3622.5
4.400	4.400	RF1	0
DECOUPLER	0.0	RF1	0
d1	0	PP	0
d1n	0	PP	0
dof	0	PP	0
dmm	0	PP	0
dpm	0	PP	0
upper	4.00	SC	0
dtm	13.158	VS	0
dtm	13.158	TH	0
dt	0	CD	0
ct	0	PH	0



LS-III-93-1H-500

ext2 s�ur1

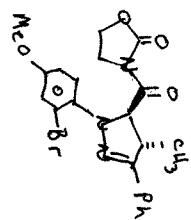
date	SAMP1C	temp	25.0
rebo	4/20/05	gain	not used
solvent	CDC13	SWIN	not used
file	8149	HT1	0.008
ACQUISITION	8149	HT2	8.800
sw	6500.9	PE90	0
at	2.908	ALFA	
np	38112		
fb	40000	FLAGS	
bs	3.32	in	n
q1	0.300	dp	y
mt	1.00	hs	nn
ct	1.00	PROCESSING	0.30
TRANSMITTER	1b	1b	65336
tn	H1	fn	
sfq	499.674	DISPLAY	
tr0f	247.0	sp	-502.2
tr0r	499.674	wp	-500.9
pw	4.400	rf1	4134.8
DECOUPLER	rf1	rf1	3632.6
dif	0	rp	61.3
dif	0	rp	1.6
din	0	PLT	
din	0	SC	
din	0	WC	
dprf	13158	240	
dif	0	th	
cdc	165	54	
ph	165		



LS-III-94

exp2 s2pu1

	SAMPLE	temp	SPECIAL
date	Apr 21 2005	25.0	
SOLVENT	CDCl ₃	not used	
FI	90	not used	
ACQUISITION	exp	0.008	
SW	6500.9	0.008	
AT	2.988	0	
NP	37812	0	
FB	4000	0	
BS	322	n	
D1	0.300	n	
RT	16	0	
CT	16	0	
TRANSMITTER	H1	0.30	
TN	H1	655.36	
SF/Q	499.674	DISPLAY	
TOF	247.0	6500.9	
TPR	61	-500.8	
PW	4.400	6500.9	
DECOPPLER	4.400	4133.4	
DP	0	3632.6	
DR	0	60.2	
DM	0	-1.7	
DMR	0	240	
DPR	4.0	240	
DPF	13158	0	
VS	30	54	
TH	54	54	
AI	CDCl ₃	0	
CD	0	0	
PH	0	0	



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