A Broadly Applicable NHC–Cu-Catalyzed Approach for Efficient, Site- and Enantioselective Coupling of Readily Accessible (Pinacolato)alkenylboron Compounds to Allylic Phosphates and Applications to Natural Product Synthesis

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SUPPORTING INFORMATION

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General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by GLC analysis (gas liquid chromatography) with an Agilent chromatograph (Alltech Associated Chiral dex CD-BDM column (30 m x 0.25 mm)), HPLC analysis (high-performance liquid chromatography) with a Shimadzu chromatograph (Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), Chiral Technologies Chiralpak AD-H (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm) Chiral Technologies Chiralpak AS-H (4.6 x 250 mm)) in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Diethylether, benzene and dichloromethane (Fisher Scientific) were purified by passing through two alumina columns under a positive pressure of dry argon by a modified Innovative Technologies purification system. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) under air. All substrates are prepared according to previously reported procedures and the characterization data of the unknown compounds will be disclosed within this text;[1] all substrates possess *E* olefin geometry and purities are established by ^1H NMR analysis (400 MHz). Allylic phosphate that yields product **16** is prepared according to a previously reported procedure[1b] from the corresponding alcohol, which has been disclosed before.[2]Allylic phosphates **1d**[3a] and **39**[3b] are synthesized according to the general phosphorylation procedure[1] from the corresponding alcohols reported in previous studies.[3]

■ **Reagents and Imidazolinium Salts:**

9-Borabicyclo[3.3.1]nonane (0.5 M in thf): purchased from Aldrich Chemical Co. and used as received.

(*Z*)-2-(9-Bromonon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: prepared according to a previously disclosed procedure.[4]

***tert*-Butanol:** purchased from Aldrich Chemical Co. and used as received.

(*Z*)-2-(2-Butoxyvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: prepared according to a previously disclosed procedure.[4]

***tert*-Butyl hydroperoxide solution (5.0~6.0 M in decane):** purchased from Aldrich Chemical Co. and used as received.

***tert*-Butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate (56):** prepared according to a previously disclosed procedure.[5]

***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dihydropyridine-1(2*H*)-carboxylate (41):** purchased from Frontier Scientific Inc. and used as received.

***tert*-Butyl (*Z*)-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate:** prepared according to a previously disclosed procedure.[4]

(*Z*)-*tert*-Butyldimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane (24): prepared according to a previously reported procedure.[4]

(*Z*)-*tert*-Butyldimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)oxy)silane (34): prepared according to a previously disclosed procedure.[6]

Copper(I) chloride: purchased from Strem Chemicals Inc. and used as received.

Dess-Martin Periodinane: purchased from TCI America and used as received.

1,2-Dichloroethane: purchased from Aldrich Chemical Co. and used as received.

(*E*)-2-(3,3-Diethoxyprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10): generously donated to us by Frontier Scientific Inc. and used as received.

2-(3,4-Dihydro-2*H*-pyran-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: purchased from Frontier Scientific Inc. and used as received.

2-(3,6-Dihydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49): purchased from Frontier Scientific Inc. as a dark brown oil and used as a white solid after purification through silica gel column chromatography.

Di*iso*butylaluminum hydride (neat): purchased from Aldrich Chemical Co. and used as received.

Ethanol (200 proof): purchased from Fisher Scientific and used as received.

(*E*)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (14): generously donated to us by Frontier Scientific Inc. and used as received.

Imidazolinium salt 9a and 9b: prepared according to a previously reported procedure.[1e]

Imidazolinium salt 9c: prepared according to a previously reported procedure.[7]

Imidazolinium salt 52: prepared according to a previously reported procedure.[8]

Imidazolinium salts 4 and 5: prepared according to a previously reported procedure.[9]

Imidazolinium salt 6: prepared according to a previously reported procedure.[10]

Imidazolinium salt 7: prepared according to a previously reported procedure.[11]

Imidazolinium salt 8: prepared according to a previously reported procedure.[1d]

Lithium borohydride solution (2.0 M in tetrahydrofuran): purchased from Aldrich Chemical Co. and used as received.

(*Z*)-2-(9-((4-Methoxybenzyl)oxy)non-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: prepared according to a previously reported procedure.[4]

(*Z*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32): prepared according to a previously reported procedure.[4]

Methyllithium (1.6 M solution in diethylether): purchased from Acros Organics and used as received from an Acroseal container.

Methylmagnesium iodide (~1.0 M solution in Et_2O): prepared from methyl iodide and Mg turnings in diethylether and used immediately after titration.

Poly(methylhydrosiloxane): purchased from Aldrich Chemical Co. and used as received.

Potassium hydroxide: purchased from Fisher Scientific and used as received.

Pyridinium chlorochromate: purchased from Aldrich Chemical Co. and used as received.

Pyridinium *p*-toluenesulfonate: purchased from Aldrich Chemical Co. and used as received.

Sodium bicarbonate: purchased from Fisher Scientific and used as received.

Sodium methoxide: purchased from Strem Chemicals Inc. and used as received.

Sodium perborate tetrahydrate: purchased from Aldrich Chemical Co. and used as received.

Tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran): purchased from Aldrich Chemical Co. and used as received.

4,4,5,5-Tetramethyl-2-(2-methylprop-1-en-1-yl)-1,3,2-dioxaborolane (40): purchased from Frontier Scientific Inc. and used as received.

(*E*)-4,4,5,5-Tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (2): purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

4,4,5,5-Tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane: purchased from Aldrich Chemical Co. and used as received.

(*Z*)-4,4,5,5-Tetramethyl-2-(prop-1-en-1-yl)-1,3,2-dioxaborolane (18): purchased from Aldrich Chemical Co. and used as received.

(*Z*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (30): prepared according to a previously reported procedure.[4]

Titanium(IV) *iso*propoxide: purchased from Aldrich Chemical Co. and used as received.

Vinylboronic acid pinacol ester (22): purchased from Aldrich Chemical Co. and used immediately after vacuum transfer under N_2 atmosphere.

■ Characterization Data for Allylic Phosphates

(*E*)-4-((Diethoxyphosphoryl)oxy)-3-methylbut-2-en-1-yl acetate (substrate that leads to compound 17, Scheme 4): IR (neat): 2985 (w), 2934 (w), 1737 (s), 1444 (w), 1368 (w), 1230 (s), 1166 (w), 1004 (s), 955 (s), 877 (m), 801 (m), 750 (w), 590 (w), 506 (m), 421 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.66–5.62 (1H, m), 4.60 (2H, dd, *J* = 7.2, 0.8 Hz), 4.22 (2H, d, *J* = 6.4 Hz), 4.09 (4H, ddq, *J* = 7.6, 6.8, 0.8 Hz), 2.02 (3H, s), 1.73 (3H, d, *J* = 0.8 Hz), 1.31 (6H, dt, *J* = 6.8, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 136.0 (d, *J* = 7.6 Hz), 122.0, 71.5 (d, *J* = 5.3 Hz), 63.9 (d, *J* = 6.0 Hz), 60.6, 21.0, 16.0 (d, *J* = 6.8 Hz), 13.8; HRMS (ESI+): Calcd for $C_{11}H_{21}P_1Na_1O_6$ $[M+Na]^+$: 303.0968, Found: 303.0966.

(*E*)-3-(2,5-Dimethoxy-4-methylphenyl)allyl diethyl phosphate (1d): IR (neat): 2984 (w), 2937 (w), 2833 (w), 1508 (m), 1466 (m), 1401 (m), 1271 (m), 1211 (s), 1038 (s), 975 (s), 860 (w), 818 (w), 543 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (1H, d, *J* = 15.6 Hz), 6.90 (1H, s), 6.70 (1H, s), 6.29 (1H, dt, *J* = 16.0, 6.0 Hz), 4.70 (2H, ddd, *J* = 8.0, 5.6, 1.6 Hz), 4.14 (4H, dq, *J* = 7.2, 7.2 Hz), 3.81 (3H, s), 3.80 (3H, s), 2.22 (3H, s), 1.35 (6H, dt, *J* = 7.2, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.1, 129.4, 128.2, 123.2 (d, *J* = 6.9 Hz), 122.8, 114.7, 109.0, 68.8 (d, *J* = 5.3 Hz), 63.9 (d, *J* = 6.0 Hz), 56.4, 56.1, 16.6, 16.3 (d, *J* = 6.9 Hz); HRMS (ESI+): Calcd for $C_{16}H_{25}P_1O_6$ $[M]^+$: 344.13887, Found: 344.13780.

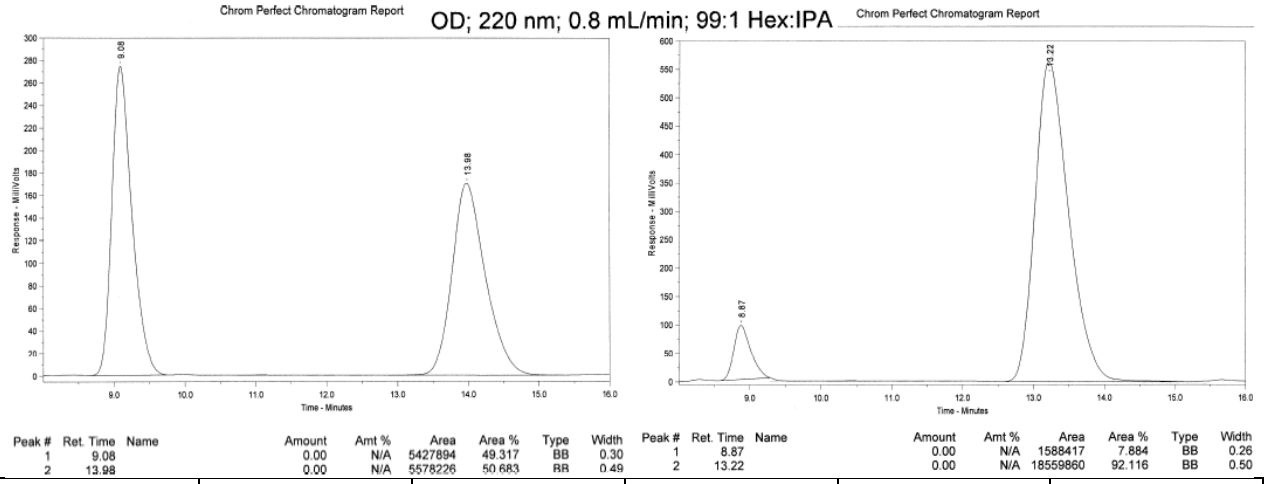
(*E*)-Diethyl (4-hydroxy-4-methylpent-2-en-1-yl) phosphate (39): IR (neat): 3410 (w), 2972 (w), 2925 (w), 1464 (w), 1372 (w), 1256 (m), 1164 (w), 1019 (s), 968 (s), 802 (m), 547 (w), 526 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.93 (1H, dt, *J* = 15.6, 1.2 Hz), 5.78 (1H, dt, *J* = 15.6, 6.0 Hz), 4.51 (2H, ddd, *J* = 8.0, 5.6, 0.8 Hz), 4.10 (4H, dq, *J* = 7.2, 7.2 Hz), 1.33 (6H, dt, *J* = 7.2, 0.8 Hz), s), 1.31 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 121.4 (d, *J* = 6.9 Hz), 70.5, 67.6 (d, *J* = 5.3 Hz), 63.9 (d, *J* = 6.1 Hz), 29.7 (d, *J* = 8.3 Hz), 16.3 (d, *J* = 6.8 Hz); HRMS (ESI+): Calcd for $C_{10}H_{21}P_1Na_1O_5$ $[M+Na]^+$: 275.1019, Found: 275.1017.

■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with *trans*-1,2-Disubstituted Alkenylboron Reagents (Table 1):** In an N_2-filled glove box, an oven-dried 1-dram vial (15 x 45 mm) with a magnetic stir bar is charged with imidazolinium salt **9b** (4.7 mg, 0.0055 mmol), NaOMe (10.8 mg, 0.200 mmol) and CuCl (0.5 mg, 0.005 mmol). The vial is sealed with a cap (phenolic open top cap with a red PTFE/white silicone septum) and electrical tape before removal from the glove box. To the vial under an N_2 atmosphere is added tetrahydrofuran (thf, 0.5 mL) and the resulting suspension is allowed to stir at 22 °C for one hour. The suspension turns from off-white to light-yellow during catalyst formation. Meanwhile, in a separate vial, cinnamyl diethyl phosphate **1a** (27.0 mg, 0.100 mmol) and (*E*)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane **2** (47.6 mg, 0.200 mmol) are weighted out and the vial is sealed and purged with N_2 flow for 10 min before thf (0.5 mL) is added through a syringe. The stock solution is transferred through a syringe to the reaction vessel that contains the in situ-formed catalyst and the resulting yellow solution is allowed to stir at 22 °C for additional 24 h. At this point, the mixture is allowed to pass through a short plug of silica gel eluted with Et_2O. The filtrate is concentrated under reduced pressure to provide a

yellow oil residue, which is purified by silica gel column chromatography (100% hexanes) to afford product **3** as colorless oil (22.1 mg, 0.0968 mmol, 97% yield). **(*S*,*E*)-Undeca-1,4-dien-3-ylbenzene (3, Table 1).** The product has been previously reported and spectral data match those previously described.[1b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.28 (2H, m), 7.21–7.18 (3H, m), 6.02 (1H, ddd, *J* = 16.8, 10.0, 6.8 Hz), 5.60 (1H, ddt, *J* = 15.6, 7.2, 1.6 Hz), 5.50 (1H, ddt, *J* = 15.2, 6.8, 0.8 Hz), 5.11 (1H, d, *J* = 10.0 Hz), 5.05 (1H, d, *J* = 17.2 Hz), 4.06 (1H, dd, *J* = 6.8, 6.8 Hz), 2.05 (2H, dt, *J* = 7.2, 7.2 Hz), 1.37–1.25 (8H, m), 0.88 (3H, t, *J* = 7.2 Hz). Specific Rotation: $[\alpha]_D^{20}$ +15.1 (*c* 0.467, $CHCl_3$) for an enantiomerically enriched sample of 92:8 er.

Determination of stereochemical identity: Literature value ($[\alpha]_D^{20}$ –11.0 (*c* 1.49, $CHCl_3$), 89.5:10.5 er) is assigned to the (*R*) enantiomer.[1b]

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (92:8 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



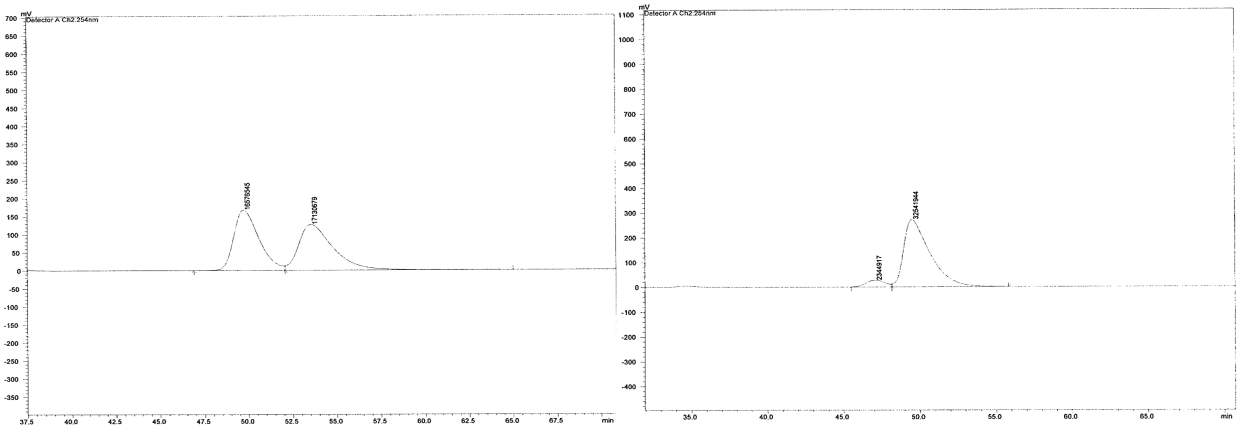
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	9.08	49.3	1	8.87	7.9
2	13.98	50.7	2	13.22	92.1

■ **Representative Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Acetal-Containing *trans*-1,2-Disubstituted Alkenylboron Reagents (Scheme 3):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

(*S*,*E*)-1-(6,6-Diethoxyhexa-1,4-dien-3-yl)-4-nitrobenzene (11, Scheme 3). Same procedure as described in Table 1 is followed. The title compound is isolated by column chromatography with basified silica gel (5% NEt_3). IR (neat): 2976 (w), 2928 (w), 2876 (w), 1598 (w), 1521 (s), 1346 (s), 1133 (w), 1052 (m), 996 (w), 854 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.16 (2H, m), 7.39–7.35 (2H, m), 6.04–5.95 (2H, m), 5.58 (1H, ddd, *J* = 17.2, 5.2, 1.6 Hz), 5.22 (1H, ddd,

J = 10.4, 1.2, 1.2 Hz), 5.10 (1H, ddd, *J* = 17.2, 1.2, 1.2 Hz), 4.93 (1H, dd, *J* = 6.0, 0.8 Hz), 4.20 (1H, dd, *J* = 6.8, 6.8 Hz), 3.67–3.60 (2H, m), 3.54–3.45 (2H, m), 1.24–1.19 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.9, 138.3, 134.1, 130.2, 129.1, 124.0, 117.3, 101.0, 61.2, 51.5, 15.39, 15.40; HRMS (ESI+): Calcd for $C_{14}H_{16}N_1O_3$ $[M–OEt]^+$: 246.11302, Found: 246.11300. Specific Rotation: $[\alpha]_D^{20}$ +3.79 (*c* 0.327, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (93:7 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).



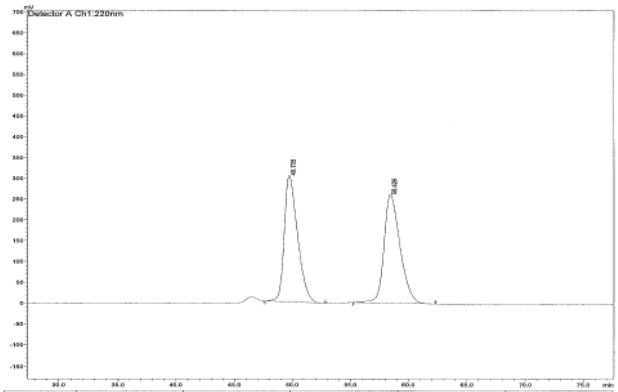
Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.706	16576545	166872	49.178	56.845
2	53.528	17130679	126687	50.822	43.155
Total		33707225	293559	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.062	2344917	27231	6.721	9.125
2	49.485	32541944	271196	93.279	90.875
Total		34886861	298427	100.000	100.000

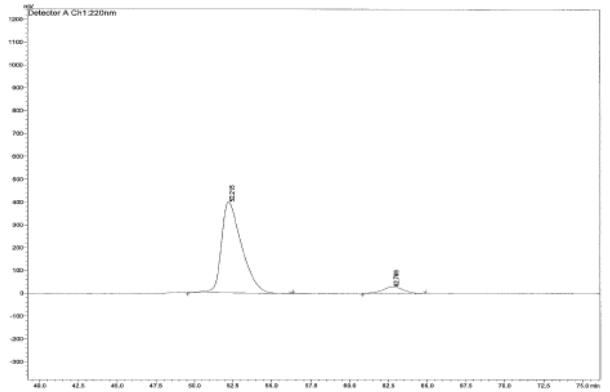
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	49.71	49.2	1	47.06	6.7
2	53.53	50.8	2	49.49	93.3

(*S*,*E*)-4-(4-Nitrophenyl)hexa-2,5-dienal (12b, Scheme 3). Same procedure as described in Table 1 is followed. The reaction mixture is dissolved in Et_2O and treated with solid silica gel (ca. 100 mg). The resulting suspension is allowed to stir at 22 °C for one hour before it is passed through a cotton plug eluted with Et_2O. Solvent is removed by rotory evaporation to afford a yellow oil residue, which is purified by regular silica gel column chromatography. IR (neat): 2985 (w), 2827 (w), 1699 (s), 1634 (w), 1472 (m), 1433 (w), 1166 (w), 1031 (m), 985 (w), 927 (m), 754 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (1H, dd, *J* = 8.0, 2.8 Hz), 8.24–8.20 (2H, m), 7.41–7.37 (2H, m), 6.96 (1H, dd, *J* = 16.0, 6.8 Hz), 6.15 (1H, ddd, *J* = 17.2, 7.6, 1.6 Hz), 6.03 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz), 5.36 (1H, dd, *J* = 10.0, 0.8 Hz), 5.20 (1H, dd, *J* = 17.2, 0.8 Hz), 4.45 (1H, dd, *J* = 6.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 155.7, 147.4, 147.2, 136.1, 133.9, 129.2, 124.3, 118.9, 51.7; HRMS (ESI+): Calcd for $C_{12}H_{12}N_1O_3$ $[M+H]^+$: 218.08172, Found: 218.08203. Specific Rotation: $[\alpha]_D^{20}$ +17.2 (*c* 0.492, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (93:7 er shown; Chiralcel OJ-H column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.735	24237585	303774	49.411	53.799
2	58.426	24815053	260872	50.589	46.201
Total		49052638	564646	100.000	100.000

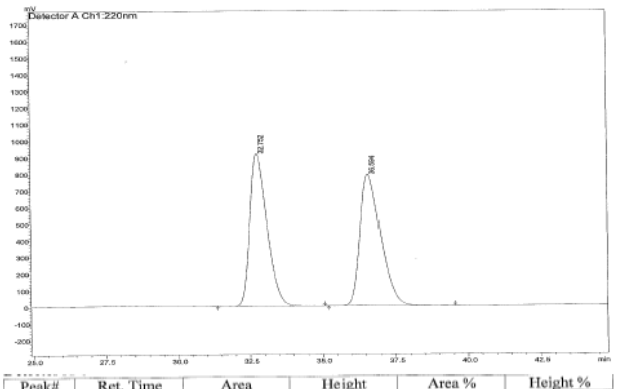


Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.215	36366606	400479	93.233	93.057
2	62.768	2639421	29878	6.767	6.943
Total		39006027	430356	100.000	100.000

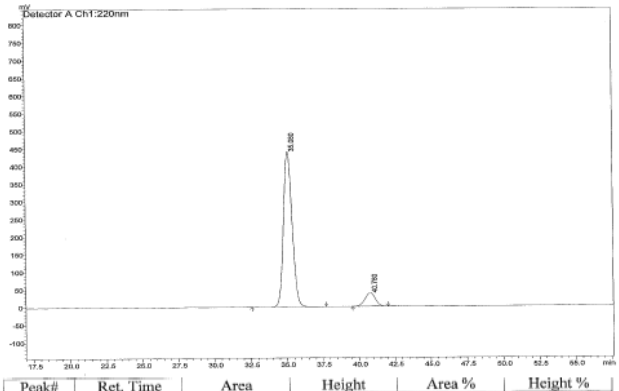
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	49.74	49.4	1	52.22	93.2
2	58.43	50.6	2	62.77	6.8

(*S*,*E*)-4-Phenylhexa-2,5-dienal (12a, Scheme 3). The title compound is prepared by the same procedure as with **12b**. IR (neat): 3083 (w), 3061 (w), 3029 (w), 2980 (w), 2818 (w), 2735 (w), 1687 (s), 1631 (w), 1600 (w), 1492 (w), 1453 (w), 1111 (m), 978 (m), 923 (m), 758 (m), 701 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.51 (1H, d, *J* = 8.0 Hz), 7.31–7.26 (2H, m), 7.23–7.19 (1H, m), 7.13 (2H, dd, *J* = 8.4, 1.2 Hz), 6.92 (1H, dd, *J* = 15.6, 6.8 Hz), 6.09–5.94 (2H, m), 5.19 (1H, ddd, *J* = 10.4, 1.2, 1.2 Hz), 5.07 (1H, ddd, *J* = 17.2, 1.6, 0.8 Hz), 4.25 (1H, dd, *J* = 6.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 158.3, 140.1, 137.6, 133.1, 129.1, 128.2, 127.5, 117.5, 52.2; HRMS (ESI+): Calcd for $C_{12}H_{13}O_1$ $[M+H]^+$: 173.09664, Found: 173.09718. Specific Rotation: $[\alpha]_D^{20}$ +16.0 (*c* 0.807, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (91:9 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.752	37711294	916162	49.879	53.776
2	36.594	37894913	787511	50.121	46.224
Total		75606207	1703673	100.000	100.000



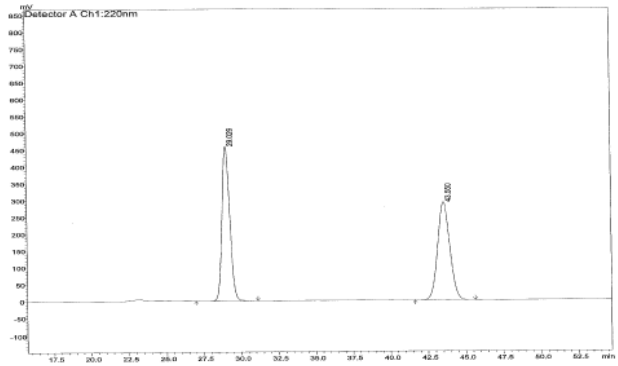
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.080	18475818	440415	90.872	92.033
2	40.780	1855931	38126	9.128	7.967
Total		20331749	478540	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	32.75	49.9	1	35.08	90.8
2	36.59	50.1	2	40.78	9.1

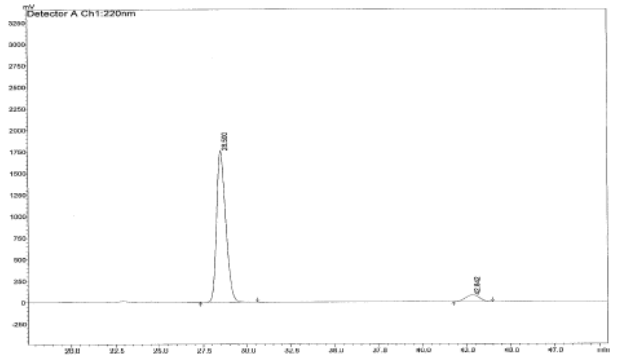
(*S*,*E*)-1-Bromo-2-(6,6-diethoxyhexa-1,4-dien-3-yl)benzene (S1, Scheme 3). The title compound is prepared by the same procedure as with **11**. IR (neat): 2975 (m), 2929 (w), 2878 (w), 1468 (w), 1439 (w), 1339 (w), 1300 (w), 1133 (m), 1051 (s), 1022 (w), 996 (m), 920 (w), 754 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (1H, dd, *J* = 8.0, 1.6 Hz), 7.27 (1H, ddd, *J* = 7.6, 7.2, 1.2 Hz), 7.21 (1H, dd, *J* = 7.6, 2.0 Hz), 7.08 (1H, ddd, *J* = 9.2, 7.2, 1.6 Hz), 6.02–5.93 (2H, m), 5.55 (1H, ddd, *J* = 16.0, 5.2, 1.6 Hz), 5.20 (1H, ddd, *J* = 10.4, 1.6, 1.6 Hz), 5.08 (1H, ddd, *J* = 17.2, 1.6, 1.6 Hz), 4.93 (1H, ddd, *J* = 5.2, 0.8, 0.8 Hz), 4.62 (1H, ddd, *J* = 6.4, 6.0, 0.8 Hz), 3.68–3.59 (2H, m), 3.54–3.45 (2H, m), 1.23–1.18 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.4, 134.5, 133.2, 129.8, 129.7, 128.2, 127.7, 124.9, 116.7, 101.3, 61.0, 49.9, 15.42, 15.40; HRMS (ESI+): Calcd for $C_{14}H_{16}O_1Br_1$ $[M–EtO]^+$: 279.03845, Found: 279.03902. Specific Rotation: $[\alpha]_D^{20}$ –18.5 (*c* 0.780, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er. Enantiomeric purity is determined by HPLC analysis of the derived enal (see below).

(*S*,*E*)-4-(2-Bromophenyl)hexa-2,5-dienal (12c, Scheme 3). The title compound is prepared using the same procedure as with **12b**. IR (neat): 3063 (w), 2981 (w), 2816 (w), 2734 (w), 1691 (s), 1630 (w), 1469 (w), 1437 (w), 1122 (w), 1023 (w), 979 (w), 926 (w), 756 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.60 (1H, d, *J* = 7.6 Hz), 7.60 (1H, dd, *J* = 8.0, 1.2 Hz), 7.32 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.21–7.13 (2H, m), 6.95 (1H, dd, *J* = 15.6, 6.0 Hz), 6.11 (1H, ddd, *J* = 15.6, 7.6, 1.6 Hz), 6.02 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz), 5.32 (1H, ddd, *J* = 10.0, 1.2, 0.8 Hz), 5.16 (1H, ddd, *J* = 17.2, 1.6, 0.8 Hz), 4.89–4.85 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 157.0, 139.2, 136.3, 133.8, 133.5, 129.7, 129.1, 128.1, 124.8, 118.3, 50.5; HRMS (ESI+): Calcd for $C_{12}H_{12}Br_1O_1$ $[M+H]^+$: 251.00715, Found: 251.00766. Specific Rotation: $[\alpha]_D^{20}$ –14.6 (*c* 0.467, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (94:6 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.029	16311175	458748	49.983	61.187
2	43.550	16322571	291001	50.017	38.813
Total		32633745	749750	100.000	100.000



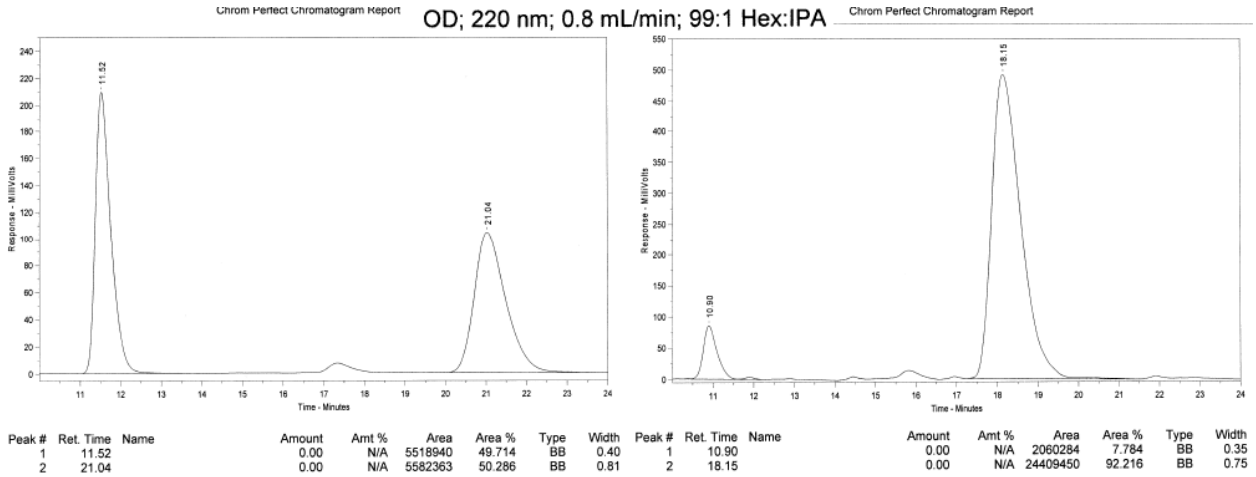
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.500	64083321	1759240	93.871	95.766
2	42.842	4184373	77787	6.129	4.234
Total		68267694	1837027	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)

1	29.03	50.0	1	28.50	93.9
2	43.55	50.0	2	42.84	6.1

Methyl (*S*,*E*)-3-(4-chlorophenyl)-6,6-diethoxy-2-methylenehex-4-enoate (13, Scheme 3). The title compound is prepared by the same procedure as with **11**, except in the presense of 2.5 mol % **9b**, 25 mol % CuCl and 1.5 equiv NaOMe. IR (neat): 2972 (w), 2928 (w), 2870 (w), 1720 (s), 1599 (w), 1488 (m), 1340 (s), 1243 (s), 1234 (m), 1134 (w), 1128 (s), 1080 (m), 1052 (s), 997 (m), 825 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (2H, d, *J* = 8.4 Hz), 7.12 (2H, d, *J* = 8.4 Hz), 6.37 (1H, app s), 6.06 (1H, ddd, *J* = 15.6, 6.8, 1.2 Hz), 5.60 (1H, t, *J* = 1.2 Hz), 5.38 (1H, ddd, *J* = 15.6, 4.8, 1.6 Hz), 4.91 (1H, dt, *J* = 5.2, 0.8 Hz), 4.65 (1H, br d, *J* = 6.8 Hz), 3.68 (3H, s), 3.64–3.55 (2H, m), 3.51–3.43 (2H, m), 1.19 (6H, dt, *J* = 7.2, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 143.6, 139.4, 134.3, 133.9, 130.7, 126.9, 124.5, 124.1, 100.9, 61.1, 52.1, 50.5, 15.39, 15.41; HRMS (ESI^+): Calcd for $C_{16}H_{18}{}^{35}ClO_3$ $[M–OEt]^+$: 293.0945, Found: 293.0921.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (92:8 er shown; Chiralcel OD column, 99/1 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).

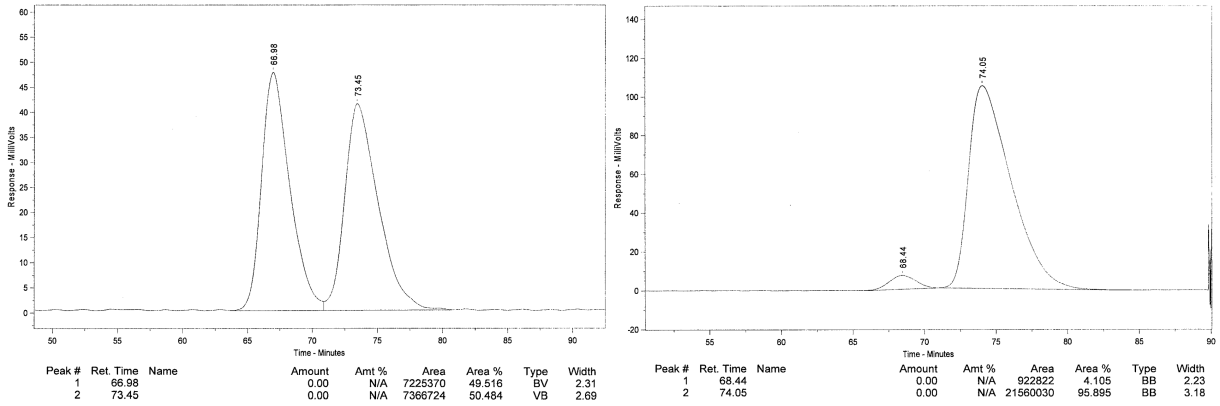


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	11.52		0.00	N/A	5518940	49.714	BB	0.40
2	21.04		0.00	N/A	5582363	50.286	BB	0.81

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.90		0.00	N/A	2060284	7.784	BB	0.35
2	18.15		0.00	N/A	24409450	92.216	BB	0.75

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	11.52	49.7	1	10.90	7.8
2	21.04	50.3	2	18.15	92.2

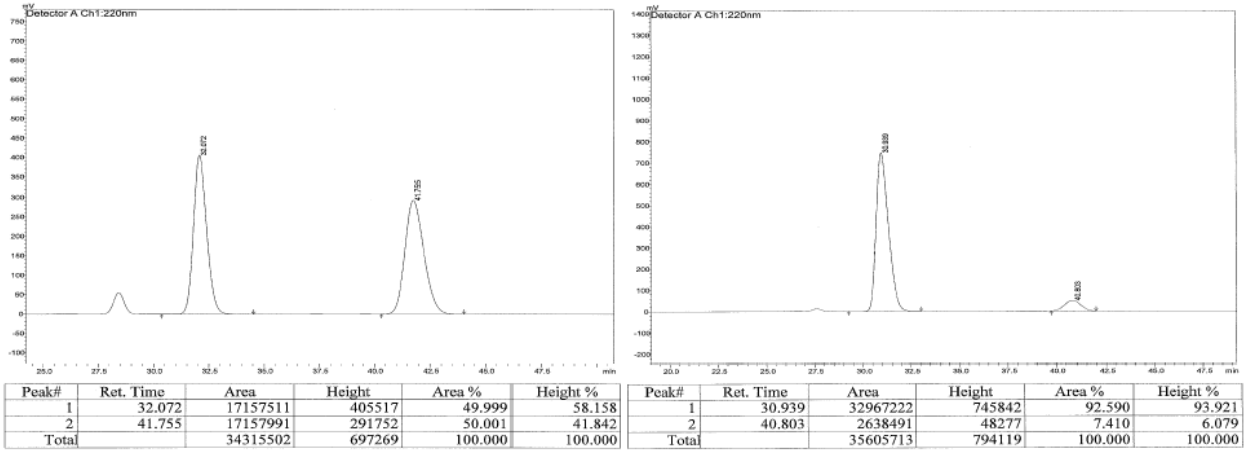
■ **Representative Experimental Procedure for Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Ester-Containing *trans* 1,2-Disubstituted Alkenylboron Reagents (Scheme 4):** In this section, the reactions are performed following the same representative procedure as described for Table 1. Compound **15c** and **16** are inseparable mixture by column chromatography; therefore, the yield is determined through analysis of ^1H NMR spectra with an internal standard. Enantioselectivity of **15c** is determined from the mixture in comparison with authentic racemic material (96:4 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	66.98	49.5	1	68.44	4.1
2	73.45	50.5	2	74.05	95.9

Ethyl (*S*,*E*)-4-phenylhexa-2,5-dienoate (15a, Scheme 4). IR (neat): 2980 (w), 1718 (s), 1651 (w), 1493 (w), 1452 (w), 1367 (w), 1312 (w), 1265 (m), 1231 (w), 1172 (m), 1041 (w), 986 (w), 922 (w), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (1H, m), 7.24–8.20 (1H, m), 7.18–7.09 (3H, m), 6.00 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz), 5.81 (1H, dd, *J* = 16.0, 1.6 Hz), 5.18 (1H, dd, *J* = 11.2, 1.2 Hz), 5.09 (1H, dd, *J* = 17.2, 1.2 Hz), 4.19–4.13 (3H, m), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 149.4, 140.7, 138.3, 128.9, 128.2, 127.2, 122.2, 116.9, 60.5, 51.8, 14.4; HRMS (ESI+): Calcd for $C_{14}H_{16}N_1O_3$ $[M+H]^+$: 217.12285, Found: 217.12381. Specific Rotation: $[\alpha]_D^{20}$ +5.78 (*c* 1.45, $CHCl_3$) for an enantiomerically enriched sample of 92.5:7.5 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (92.5:7.5 er shown; Chiralcel OJ-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).

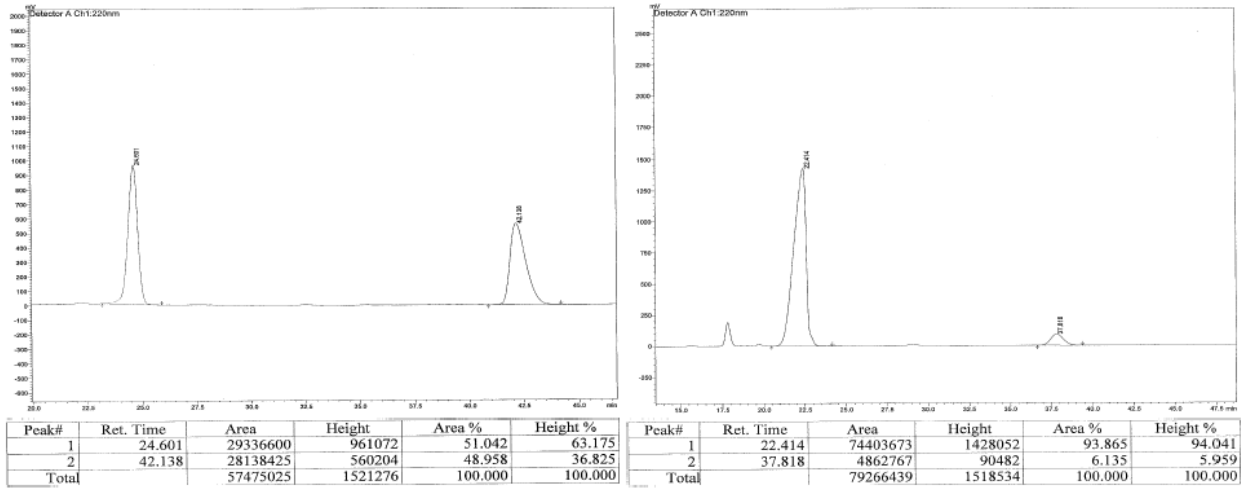


Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	32.07	50.0	1	30.94	92.6

2	41.76	50.0	2	40.80	7.4

Ethyl (*S*,*E*)-4-(*o*-tolyl)hexa-2,5-dienoate (15d, Scheme 4). IR (neat): 3065 (w), 2980 (w), 1718 (s), 1650 (w), 1489 (w), 1462 (w), 1367 (w), 1309 (w), 1264 (m), 1234 (w), 1179 (m), 1040 (m), 987 (w), 922 (w), 759 (w), 729 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.11 (5H, m), 6.00 (1H, ddd, *J* = 16.4, 10.0, 6.4 Hz), 5.80 (1H, dd, *J* = 15.6, 1.6 Hz), 5.23 (1H, ddd, *J* = 10.4, 1.2, 1.2 Hz), 5.07 (1H, ddd, *J* = 17.2, 1.6, 1.2 Hz), 4.43–4.39 (1H, m), 4.19 (2H, q, *J* = 6.8 Hz), 2.32 (3H, s), 1.27 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 149.3, 136.6, 137.9, 136.2, 130.8, 128.0, 127.1, 126.5, 122.3, 117.0, 60.5, 47.5, 19.6, 14.4; HRMS (ESI+): Calcd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.13850, Found: 231.13894. Specific Rotation: $[\alpha]_D^{20}$ +7.96 (*c* 0.950, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (94:6 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.601	29336600	961072	51.042	63.175
2	42.138	28138425	560204	48.958	36.825
Total		57475025	1521276	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.414	74403673	1428052	93.865	94.041
2	37.818	4862767	90482	6.135	5.959
Total		79266439	1518534	100.000	100.000

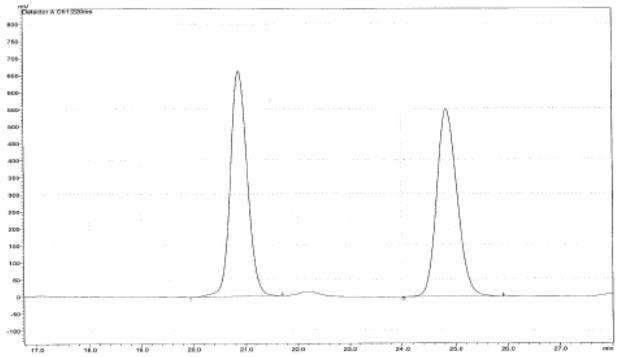
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	24.60	51.0	1	22.41	93.9
2	42.14	49.0	2	37.82	6.1

■ **Synthesis of Irregular Monoterpenoid from Enoate 17 (Scheme 4):** Enoate **17** is prepared following the procedure described in Scheme 4 with the exception that imidazolinium salt **9c** is used as the optimal ligand on copper. **17** cannot be separated from alkenylboron **14** and thus the characterization is carried out after the transformation into the natural product.

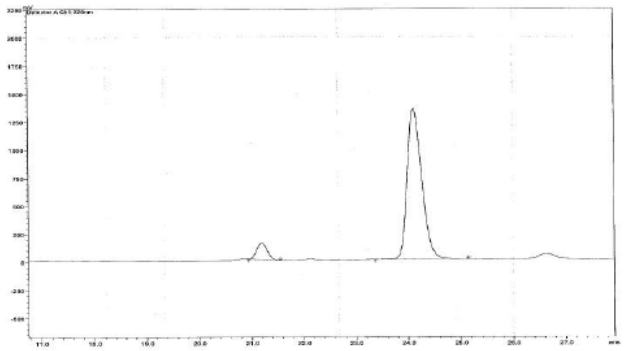
To an oven-dried 2-dram vial equipped with a magnetic stir bar is charged with enoate **17** (ca. 32.0 mg, 0.141 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, diethyl ether (1.5 mL) is added through a syringe. The solution is allowed to cool to –78 °C in a dry ice/acetone bath followed by dropwise addition of a solution of MeLi (353 μL, 0.564 mmol, 1.6 M in Et_2O) over 5 minutes. The resulting solution is allowed to stir at –78 °C for an additional hour; then it is allowed to warm to 0 °C and kept stirring at this temperature for

another 30 minutes before it is quenched by addition of a saturated NH_4Cl solution (1.0 mL). The layers are separated and the aqueous layer is washed with Et_2O (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford a crude light yellow oil residue, which is purified by silica gel column chromatography (3:1 hexanes/ethyl acetate) to deliver the irregular monoterpenoid as colorless oil (17.0 mg, 0.100 mmol, 71% yield). **(*R*,*E*)-5-Methyl-2-(prop-1-en-2-yl)hex-3-ene-1,5-diol (irregular monoterpenoid, Scheme 4).** The compound has been previously isolated and the spectral data match those reported.[12] IR (neat): 3334 (s), 2970 (s), 2922 (m), 2874 (w), 1645 (w), 1453 (w), 1374 (s), 1230 (w), 1152 (s), 1042 (s), 973 (s), 891 (s), 604 (w), 548 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.74 (1H, dd, *J* = 15.6, 0.8 Hz), 5.56 (1H, dd, *J* = 15.6, 8.0 Hz), 4.90 (1H, ddd, *J* = 2.8, 1.6, 1.2 Hz), 4.81 (1H, dd, *J* = 0.8, 0.4 Hz), 3.66 (1H, dd, *J* = 10.4, 7.2 Hz), 3.58 (1H, dd, *J* = 10.8, 7.2 Hz), 2.89 (1H, dt, *J* = 7.2, 7.2 Hz), 1.73 (3H, d, *J* = 0.8 Hz), 1.32 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.8, 125.6, 112.5, 70.8, 63.9, 52.4, 30.1, 29.9, 20.9; HRMS (ESI+): Calcd for $C_{10}H_{17}O_1$ $[M+H-H_2O]^+$: 153.12794, Found: 153.12809. Specific Rotation: $[\alpha]_D^{20}$ –23.1 (*c* 0.267, $CHCl_3$) for an enantiomerically enriched sample of 92.5:7.5 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (92.5:7.5 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.868	14908942	660924	50.032	54.563
2	24.832	14889622	550382	49.968	45.437
Total		29798564	1211306	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.288	4744242	149163	7.475	9.979
2	24.140	58721733	1345546	92.525	90.021
Total		63465975	1494709	100.000	100.000

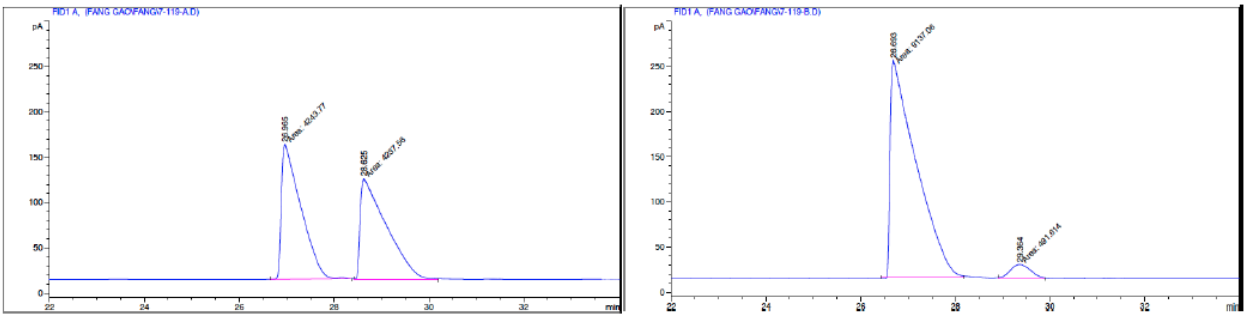
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	20.87	50.0	1	21.29	7.5
2	24.83	50.0	2	24.14	92.5

■ **Representative Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Methyl-Substituted *cis*-1,2-Disubstituted Alkenylboron Reagents (Scheme 5):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

(*S*,*Z*)-Hexa-1,4-dien-3-ylbenzene (19a, Scheme 5). The title compound is prepared in 8 h at 22 °C following the general procedure. IR (neat): 3060 (w), 3019 (w), 2974 (w), 2917 (w), 1635 (w),

1480 (m), 1462 (w), 1371 (m), 996 (m), 913 (m), 795 (w), 755 (s), 727 (m), 661 (w), 545 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (2H, dd, *J* = 7.5, 7.5 Hz), 7.26–7.19 (3H, m), 5.99 (1H, ddd, *J* = 17.0, 10.5, 6.5 Hz), 5.65–5.55 (2H, m), 5.14–5.10 (2H, m), 4.37 (1H, dd, *J* = 7.5, 7.5 Hz), 1.71 (3H, dd, *J* = 6.0, 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 140.5, 131.8, 128.6, 127.8, 126.3, 124.7, 114.7, 46.8, 13.2; HRMS (ESI+): Calcd for $C_{12}H_{15}$ $[M+H]^+$: 159.11738, Found: 159.11756. Specific Rotation: $[\alpha]_D^{20}$ +17.3 (*c* 0.41, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (95:5 er shown; CDB/DM column, 80 °C, 15 psi).



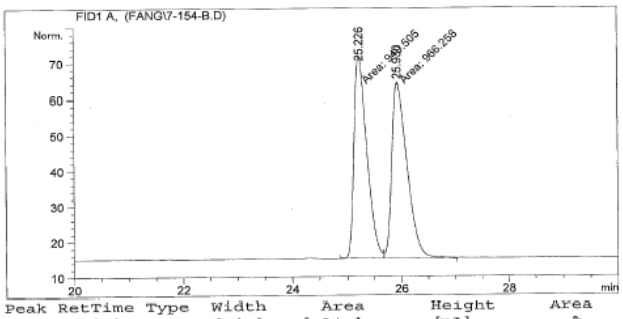
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.965	MM	0.4739	4243.76660	149.23819	50.03660
2	28.625	MM	0.6333	4237.55762	111.51509	49.96340

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.693	MM	0.6328	9137.05859	240.64719	94.89427
2	29.364	MM	0.5091	491.61389	16.09519	5.10573

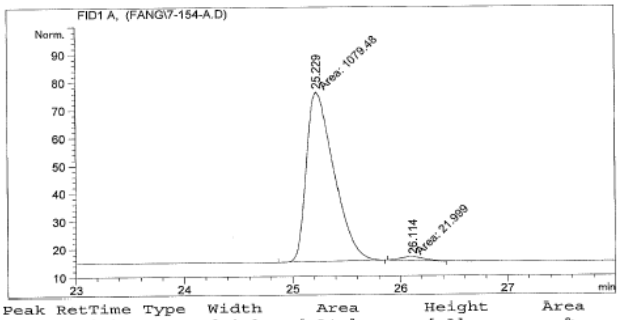
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	26.97	50.0	1	26.69	94.9
2	28.63	50.0	2	29.36	5.1

(*S*,*Z*)-1-(Hexa-1,4-dien-3-yl)-3-(trifluoromethyl)benzene (19b, Scheme 5). The title compound is prepared in 8 h at 22 °C following the general procedure. IR (neat): 3020 (w), 2980 (w), 2921 (w), 1444 (w), 1328 (s), 1248 (w), 1162 (s), 1121 (s), 1072 (s), 993 (w), 917 (m), 801 (m), 777 (w), 720 (m), 701 (s), 682 (w), 655 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.41 (4H, m), 5.97 (1H, ddd, *J* = 16.8, 10.4, 6.4 Hz), 5.72–5.64 (1H, m), 5.58–5.52 (1H, m), 5.18–5.12 (2H, m), 4.42 (1H, dd, *J* = 8.4, 6.8 Hz), 1.71 (3H, dd, *J* = 6.8, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 139.6, 131.3, 130.9 (q, *J* = 32.0 Hz), 130.88, 129.0, 125.7, 124.5 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 245.0 Hz), 115.6, 46.5, 13.2; HRMS (ESI+): Calcd for $C_{13}H_{14}F_3$ $[M+H]^+$: 227.10476, Found: 227.10569. Specific Rotation: $[\alpha]_D^{20}$ –8.76 (*c* 1.14, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (98:2 er shown; CDB/DM column, 80 °C, 15 psi).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.226	MF	0.2768	940.50464	56.62022	49.32469
2	25.930	FM	0.3272	966.25787	49.21194	50.67531

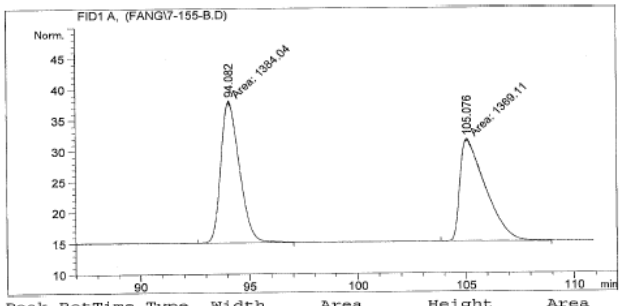


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.229	MM	0.2952	1079.47913	60.95594	98.00278
2	26.114	MM	0.2787	21.99896	1.31538	1.99722

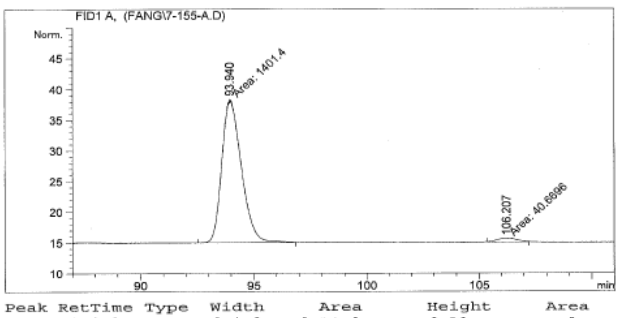
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	25.23	49.3	1	25.23	98.0
2	25.93	50.7	2	26.11	2.0

(*S*,*Z*)-1-(Hexa-1,4-dien-3-yl)-2-methoxybenzene (19c, Scheme 5). The title compound is prepared in 8 h at 22 ºC following the general procedure. IR (neat): 3078 (w), 3012 (w), 2936 (w), 2835 (w), 1634 (w), 1598 (w), 1586 (w), 1490 (s), 1463 (m), 1438 (m), 1288 (w), 1238 (s), 1105 (m), 1051 (m), 1030 (s), 993 (w), 912 (m), 855 (w), 750 (s), 715 (s), 662 (m), 577 (w), 492 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–7.17 (2H, m), 6.92 (1H, ddd, J = 7.5, 7.5, 1.0 Hz), 6.87 (1H, dd, J = 8.5, 1.0 Hz), 6.04 (1H, ddd, J = 17.0, 10.0, 5.5 Hz), 5.60–5.53 (2H, m), 5.11–5.05 (2H, m), 4.82–4.79 (1H, m), 3.84 (3H, s), 1.71 (3H, d, J = 5.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 140.7, 132.5, 131.6, 128.5, 127.3, 124.7, 120.9, 114.0, 111.0, 55.6, 39.8, 13.1; HRMS (ESI+): Calcd for $C_{13}H_{17}O_1$ $[M+H]^+$: 189.12794, Found: 189.12772. Specific Rotation: $[\alpha]_D^{20}$ +87.3 (*c* 1.03, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (97:3 er shown; CDB/DM column, 80 ºC, 15 psi).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	94.082	MM	0.9979	1384.03589	23.11509	50.27115
2	105.076	MM	1.3731	1369.10559	16.61872	49.72885

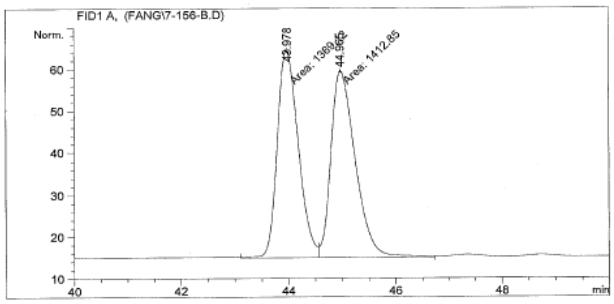


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	93.940	MM	0.9970	1401.40137	23.42776	97.17978
2	106.207	MM	1.0305	40.66960	6.57783e-1	2.82022

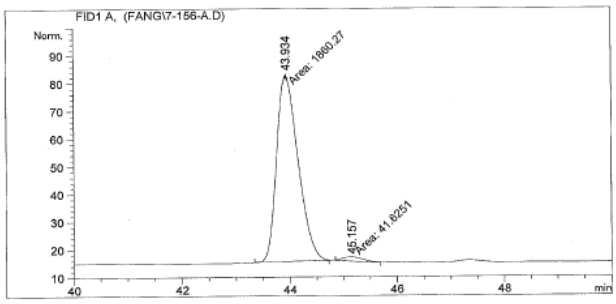
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	94.08	50.3	1	93.94	97.2
2	105.08	49.7	2	106.21	2.8

(*S*,*Z*)-1-(Hexa-1,4-dien-3-yl)-2-methylbenzene (19d, Scheme 5). The title compound is prepared in 8 h at 22 ºC based on the general procedure. IR (neat): 3066 (w), 3018 (w), 2975 (w), 2916 (w), 1634 (w), 1487 (m), 1461 (m), 1396 (w), 1369 (w), 993 (m), 915 (s), 848 (w), 794 (w), 753 (s), 728 (s), 658 (w), 547 (w), 454 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.10 (4H, m), 6.02 (1H, ddd, *J* = 17.0, 10.0, 5.0 Hz), 5.65–5.58 (1H, m), 5.51–5.46 (1H, m), 5.13–5.06 (2H, m), 4.54–4.51 (1H, m), 2.35 (3H, s), 1.70 (3H, dd, *J* = 6.5, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 140.4, 135.9, 131.5, 130.5, 127.4, 126.4, 126.3, 124.9, 114.5, 43.0, 19.6, 13.2; HRMS (ESI+): Calcd for $C_{13}H_{17}$ $[M+H]^+$: 173.13303, Found: 173.13231. Specific Rotation: $[\alpha]_D^{20}$ +0.67 (*c* 0.90, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (98:2 er shown; CDB/DM column, 80 ºC, 15 psi).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	43.978	MF	0.4559	1369.12305	50.04856	49.21411
2	44.965	FM	0.5260	1412.84937	44.76710	50.78589

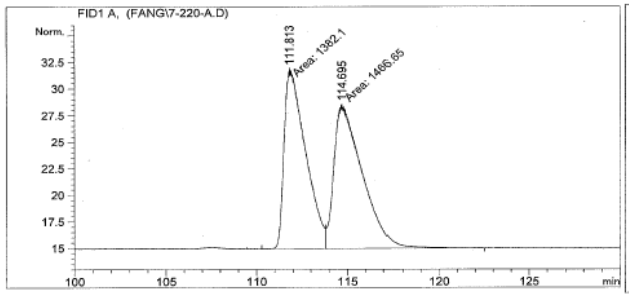


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	43.934	MM	0.4576	1860.26843	67.74814	97.81139
2	45.157	MM	0.4507	41.62508	1.53918	2.18861

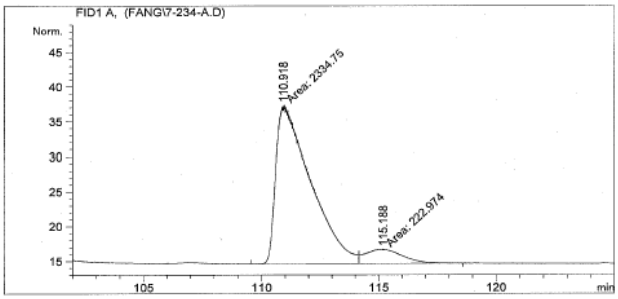
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	43.98	49.2	1	43.93	97.8
2	44.97	50.8	2	45.16	2.2

(*R*,*Z*)-(2-Methylhexa-1,4-dien-3-yl)benzene (20a, Scheme 5). The title compound with **9c** is prepared in 24 h at 22 °C following the general procedure. IR (neat): 3062 (w), 3022 (w), 2971 (w), 2917 (w), 1644 (w), 1599 (w), 1491 (w), 1450 (w), 1371 (w), 1073 (w), 1032 (w), 893 (m), 755 (m), 739 (m), 697 (s), 536 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.28 (2H, m), 7.26–7.18 (3H, m), 5.74–5.68 (1H, m), 5.66–5.58 (1H, m), 4.90–4.86 (2H, m), 4.29 (1H, d, *J* = 9.2 Hz), 1.68 (3H, dd, *J* = 6.4, 1.6 Hz), 1.66 (3H, dd, *J* = 0.8, 0.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 143.3, 131.9, 128.5, 128.0, 126.3, 124.9, 111.8, 50.2, 21.3, 13.1; HRMS (ESI+): Calcd for $C_{13}H_{17}$ $[M+H]^+$: 173.13303, Found: 173.13295. Specific Rotation: $[\alpha]_D^{20}$ +21.2 (*c* 0.970, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (91:9 er shown; CDB/DM column, 60 ºC, 15 psi).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	111.813	MF	1.3545	1382.09973	17.00585	48.51595
2	114.695	FM	1.7932	1466.65369	13.63160	51.48405

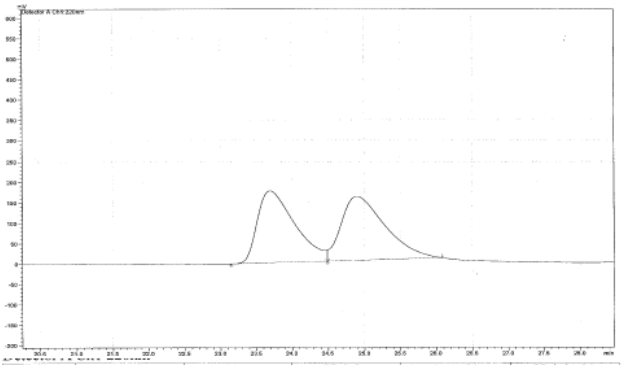


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	110.918	MF	1.7138	2334.74805	22.70551	91.28231
2	115.188	FM	1.8038	222.97417	2.06024	8.71769

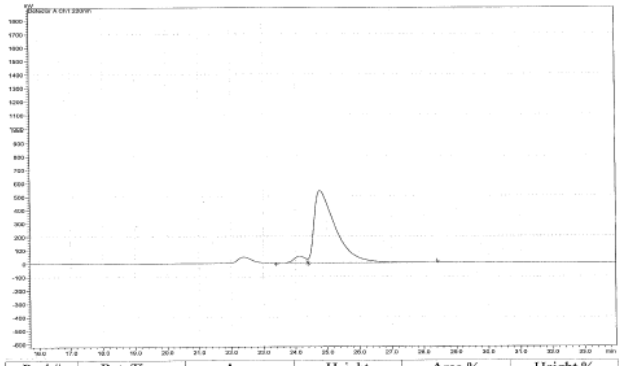
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	111.81	48.5	1	110.92	91.3
2	114.70	51.5	2	115.19	8.7

(*R*,*Z*)-1-(2-Methylhexa-1,4-dien-3-yl)-4-nitrobenzene (20b, Scheme 5). The title compound is prepared with **9c** in 24 h at 22 ºC following the general procedure. IR (neat): 3078 (w), 3020 (w), 2973 (w), 2917 (w), 2856 (w), 1646 (w), 1596 (w), 1518 (s), 1448 (w), 1343 (s), 1109 (w), 1015 (w), 899 (m), 847 (m), 744 (w), 696 (m), 539 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (2H, dd, *J* = 8.0, 2.5 Hz), 7.39 (2H, dd, *J* = 8.0, 2.5 Hz), 5.72–5.62 (2H, m), 4.95 (1H, s), 4.87 (1H, s), 4.38 (1H, d, *J* = 9.0 Hz), 1.68 (3H, d, *J* = 6.0 Hz), 1.65 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 146.6, 145.9, 130.2, 128.9, 126.6, 123.8, 113.2, 50.1, 21.2, 13.2; HRMS (ESI+): Calcd for $C_{13}H_{15}N_1O_2$ $[M]^+$: 217.1103, Found: 217.1099. Specific Rotation: $[\alpha]_D^{20}$ +147 (*c* 2.11, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (95:5 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.692	6410323	175707	49.330	52.949
2	24.894	6584433	156134	50.670	47.051
Total		12994756	331840	100.000	100.000

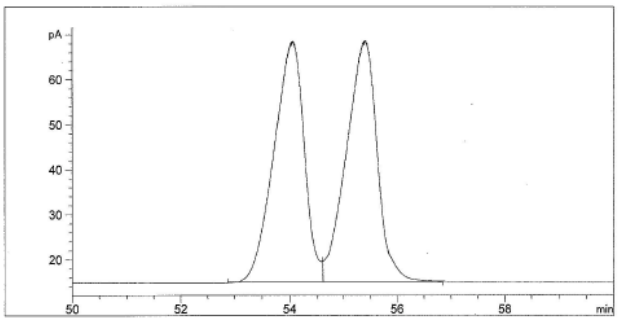


Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.126	1246131	49221	4.743	8.376
2	24.767	25026124	538447	95.257	91.624
Total		26272255	587668	100.000	100.000

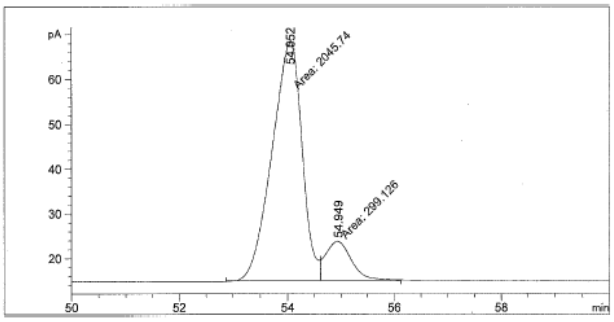
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	23.69	49.3	1	24.13	4.7
2	24.89	50.7	2	24.77	95.3

(*R*,*Z*)-1-Methyl-2-(2-methylhexa-1,4-dien-3-yl)benzene (20c, Scheme 5). The title compound with **9c** is prepared in 24 h at 22 °C based on the general procedure. IR (neat): 3067 (w), 3018 (w), 2970 (w), 2915 (w), 2858 (w), 1646 (w), 1487 (m), 1449 (m), 1371 (w), 1052 (w), 1033 (w), 894 (s), 751 (s), 721 (s), 705 (s), 463 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.21–7.09 (4H, m), 5.62–5.56 (2H, m), 4.89 (1H, s), 4.76 (1H, s), 4.39 (1H, d, *J* = 6.5 Hz), 2.33 (3H, s), 1.68–1.66 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 141.6, 136.3, 132.3, 130.4, 127.4, 126.2, 126.1, 124.7, 111.7, 46.4, 22.3, 19.7, 13.2; HRMS (ESI+): Calcd for $C_{14}H_{18}$ $[M]^+$: 186.1409, Found: 186.1408. Specific Rotation: $[\alpha]_D^{20}$ +130 (*c* 1.31, $CHCl_3$) for an enantiomerically enriched sample of 87:13 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (87:13 er shown; CDB/DM column, 80 ºC, 15 psi).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	54.069	MF	0.6364	2245.56255	56.93786	49.84947
2	55.549	FM	0.6374	2259.12371	56.79375	50.15053

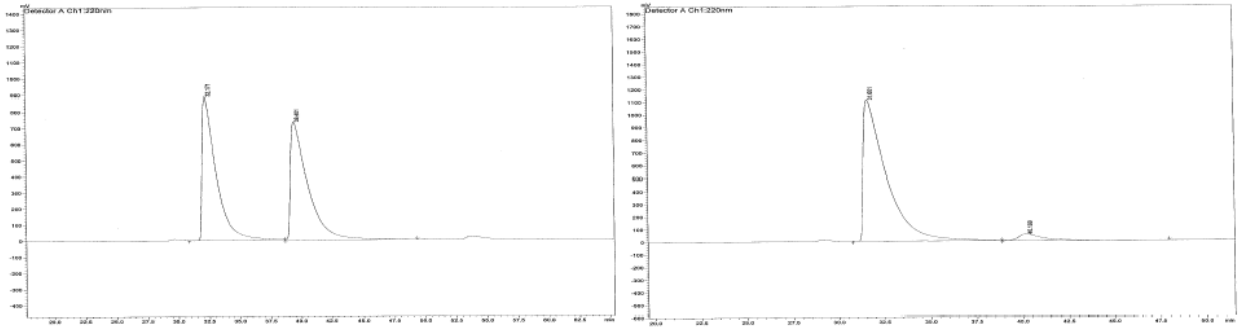


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	54.052	MF	0.6321	2045.73645	53.93697	87.24336
2	54.949	FM	0.5674	299.12561	8.78665	12.75664

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	54.07	49.8	1	54.05	87.2
2	55.55	50.2	2	54.95	12.8

Methyl (*S*,*Z*)-2-methylene-3-(*p*-tolyl)hex-4-enoate (21a, Scheme 5). The title compound is prepared with 1.0 mol % **9b**, 10 mol % CuCl and 1.5 equiv NaOMe in 24 h at 60 ºC following the general procedure. IR (neat): 3019 (w), 2950 (w), 2921 (w), 1721 (s), 1627 (w), 1512 (m), 1436 (m), 1315 (m), 1244 (s), 1190 (m), 1144 (s), 945 (m), 811 (s), 740 (s), 680 (w), 529 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.12–7.08 (4H, m), 6.28 (1H, dd, *J* = 1.2, 0.8 Hz), 5.66–5.56 (3H, m), 4.86 (1H, d, *J* = 8.0 Hz), 3.68 (3H, d, *J* = 0.8 Hz), 2.30 (3H, s), 1.70 (3H, dd, *J* = 5.6, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 143.4, 139.9, 136.0, 131.5, 129.3, 127.7, 125.5, 125.2, 52.0, 44.0, 21.2, 13.2; HRMS (ESI+): Calcd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.13850, Found: 231.13787. Specific Rotation: $[\alpha]_D^{20}$ –17.8 (*c* 1.40, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (95.5:4.5 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



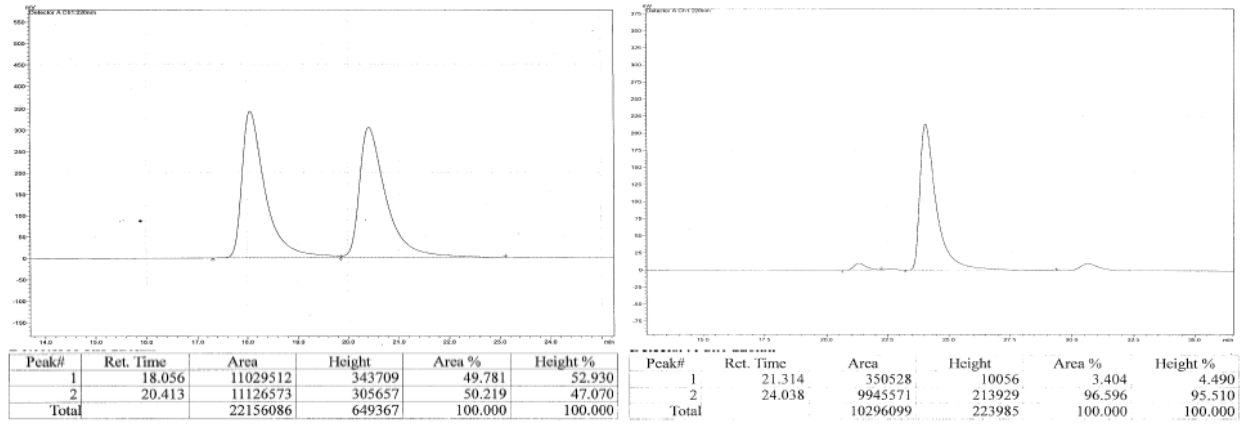
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.171	71045914	887170	49.476	54.754
2	39.401	72550866	733122	50.524	45.246
Total		143596780	1620292	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.601	96792729	1109805	95.354	95.589
2	40.199	4716070	51213	4.646	4.411
Total		101508799	1161018	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	32.17	49.5	1	31.60	95.4
2	39.40	50.5	2	40.20	4.6

Methyl (*S*,*Z*)-2-methylene-3-(4-(trifluoromethyl)phenyl)hex-4-enoate (21b, Scheme 5). The title compound is prepared with 1.0 mol % **9b**, 10 mol % CuCl and 1.5 equiv NaOMe in 24 h at 60 °C based on the general procedure. IR (neat): 3021 (w), 2954 (w), 2917 (w), 2849 (w), 1723 (s), 1617 (w), 1438 (w), 1418 (w), 1324 (s), 1251 (w), 1162 (m), 1121 (s), 1068 (s), 1019 (w), 953 (w), 832 (w), 733 (w), 604 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (2H, d, J = 8.0 Hz), 7.33 (2H, d, J = 8.0 Hz), 6.35 (1H, d, J = 2.5 Hz), 5.71–5.56 (3H, m), 4.93 (1H, d, J = 9.0 Hz), 3.68 (3H, s), 1.70 (3H, dd, J = 6.5, 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 147.1, 142.4, 128.6 (q, J = 32 Hz), 128.2, 126.7, 126.2, 125.6 (q, J = 3.7 Hz), 124.2 (q, J = 269 Hz), 52.1, 44.3, 13.3; HRMS (ESI+): Calcd for $C_{15}H_{15}F_3O_2$ $[M]^+$: 284.1024, Found: 284.1029. Specific Rotation: $[\alpha]_D^{20}$ +135 (*c* 1.70, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.056	11029512	343709	49.781	52.930
2	20.413	11126573	305657	50.219	47.070
Total		22156086	649367	100.000	100.000

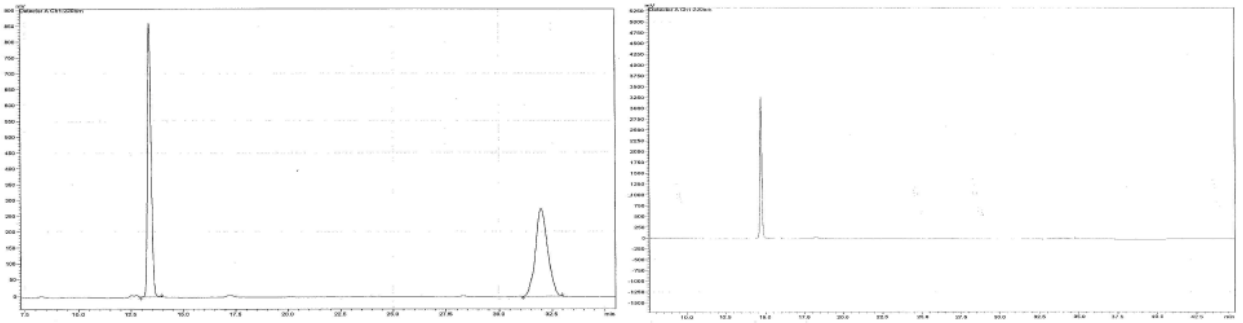
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.314	350528	10056	3.404	4.490
2	24.038	9945571	213929	96.596	95.510
Total		10296099	223985	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	18.06	49.8	1	21.31	3.4

2	20.41	50.2	2	24.04	96.6

Methyl (*S*,*Z*)-3-(2-(methoxymethoxy)phenyl)-2-methylenehex-4-enoate (21c, Scheme 5). The title compound is prepared with 1.0 mol % **9b**, 10 mol % CuCl and 1.5 equiv NaOMe in 24 h at 60 °C following the general procedure. IR (neat): 2951 (w), 2917 (w), 2849 (w), 2826 (w), 1722 (s), 1488 (m), 1403 (m), 1317 (w), 1231 (s), 1200 (m), 1150 (s), 1078 (m), 1001 (s), 923 (w), 754 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.17–7.14 (2H, m), 7.06 (1H, d, *J* = 8.0 Hz), 6.94 (1H, dd, *J* = 8.0, 7.5 Hz), 6.25 (1H, s), 5.64–5.50 (3H, m), 5.30 (1H, d, *J* = 9.5 Hz), 5.20 (2H, s), 3.68 (3H, s), 3.46 (3H, s), 1.71 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 154.3, 143.4, 132.0, 130.8, 128.1, 127.6, 125.9, 124.9, 121.8, 114.3, 94.3, 66.0, 56.1, 52.0, 13.2; HRMS (ESI+): Calcd for $C_{16}H_{20}O_4$ $[M]^+$: 276.1362, Found: 276.1368. Specific Rotation: $[\alpha]_D^{20}$ +98.3 (*c* 2.54, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.388	10520048	859915	49.960	75.866
2	31.989	10537033	273544	50.040	24.134
Total		21057081	1133459	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.718	27992522	3259557	96.808	99.435
2	33.925	923067	18531	3.192	0.565
Total		28915589	3278088	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	13.39	50.0	1	14.72	96.8
2	31.99	50.0	2	33.93	3.2

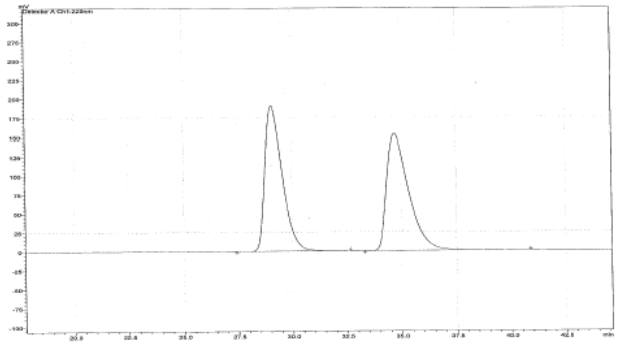
■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Alkyl-Substituted *cis*-1,2-Disubstituted Alkenylboron Reagents (Scheme 6):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

(*S*,*Z*)-*tert*-Butyl((4-(2,5-dimethoxy-4-methylphenyl)hexa-2,5-dien-1-yl)oxy)dimethylsilane (25, Scheme 6). The title compound is prepared in the presence of 1.5 equiv of the corresponding alkenylboron reagent (96% *Z*) and 1.5 equiv of NaOMe based on the same representative procedure. IR (neat): 2952 (w), 2929 (w), 2855 (w), 1502 (m), 1464 (m), 1396 (m), 1252 (w), 1205 (s), 1087 (s), 1046 (s), 1004 (m), 914 (w), 834 (s), 774 (s), 715 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.68 (1H, s), 6.63 (1H, s), 6.00 (1H, ddd, *J* = 17.6, 10.0, 5.2 Hz),

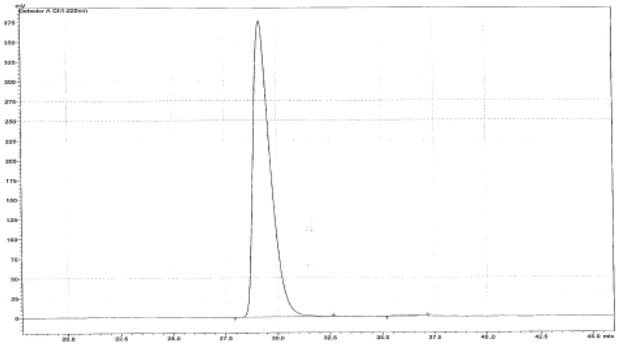
5.63–5.53 (2H, m), 5.12–5.08 (2H, m), 4.67 (1H, dd, *J* = 8.8, 7.2 Hz), 4.39 (1H, dd, *J* = 13.6, 5.2 Hz), 4.28 (1H, dd, *J* = 14.0, 4.4 Hz), 3.774 (3H, s), 3.769 (3H, s), 2.20 (3H, s), 0.90 (9H, s), 0.07 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 150.4, 140.4, 130.8, 130.6, 129.7, 125.4, 114.6, 114.5, 111.0, 60.0, 56.4, 56.2, 40.3, 26.1, 18.5, 16.3, –4.98, –.5.00; HRMS (ESI+): Calcd for $C_{21}H_{35}O_3Si_1$ $[M+H]^+$: 363.23555, Found: 363.23475. Specific Rotation: $[\alpha]_D^{20}$ +85.5 (*c* 1.17, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity is determined by HPLC analysis of the derived *Z* allylic alcohol (see below).

(*S*,*Z*)-4-(2,5-Dimethoxy-4-methylphenyl)hexa-2,5-dien-1-ol (S2, Scheme 6). To a 2-dram vial equipped with a magnetic stir bar is charged with **25** (27.4 mg, 0.0756 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, tetrahydrofuran (thf, 1.0 mL) is added through a syringe. The solution is allowed to cool to 0 ^oC in an ice bath followed by dropwise addition of tetrabutylammonium fluoride solution (151 μL, 0.151 mmol, 1.0 M in thf). The resulting light yellow solution is allowed to warm to 22 °C and stir for an additional 30 minutes before it is quenched by addition of saturated NH_4Cl solution (1.0 mL). The layers are separated and the aqueous layer is washed with EtOAc (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford a crude yellowish oil residue, which is purified by silica gel column chromatography (3:1 hexanes/EtOAc) to deliver **S2** as colorless oil (18.8 mg, 0.0756 mmol, >98% yield). IR (neat): 3371 (m), 2997 (w), 2933 (w), 2848 (w), 1501 (m), 1464 (m), 1395 (m), 1316 (w), 1236 (w), 1205 (s), 1041 (s), 915 (m), 861 (w), 767 (w), 695 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (1H, s), 6.65 (1H, s), 6.04 (1H, ddd, *J* = 16.8, 10.4, 4.8 Hz), 5.76 (1H, dddd, *J* = 11.2, 7.6, 6.4, 0.8 Hz), 5.60 (1H, dddd, *J* = 10.4, 10.4, 1.2, 1.2 Hz), 5.18–5.12 (2H, m), 4.83–4.80 (1H, m), 4.35 (1H, dd, *J* = 12.4, 7.6 Hz), 4.17–4.11 (1H, m), 3.81 (3H, s), 3.78 (3H, s), 2.20 (3H, s), 1.78 (1H, bs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.1, 140.2, 133.9, 129.3, 128.6, 125.7, 115.2, 114.8, 110.8, 58.6, 56.6, 56.2, 39.7, 16.3; HRMS (ESI+): Calcd for $C_{15}H_{19}O_2$ $[M+H–H_2O]^+$: 231.13850, Found: 231.13793. Specific Rotation: $[\alpha]_D^{20}$ +198.2 (*c* 1.05, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.059	10591055	190768	49.853	55.433
2	34.709	10653475	153376	50.147	44.567
Total		21244530	344145	100.000	100.000



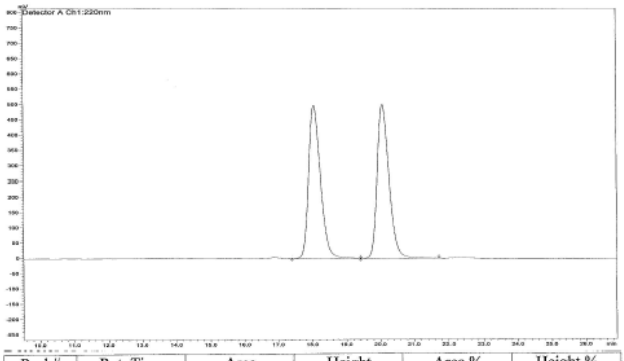
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.173	21523401	375925	99.622	99.687
2	36.191	81702	1182	0.378	0.313
Total		21605103	377106	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	29.06	49.9	1	29.17	99.6
2	34.71	50.1	2	36.19	0.4

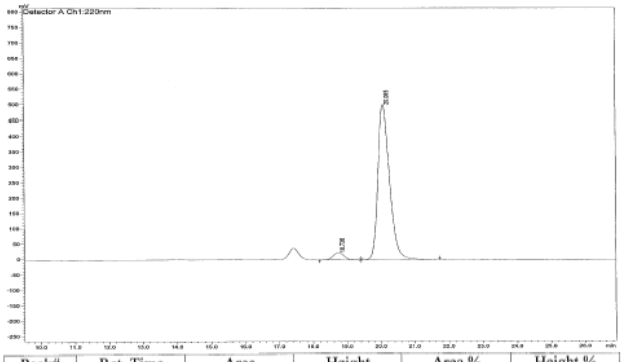
(*S*,*Z*)-4-(2,5-Dimethoxy-4-methylphenyl)hexa-2,5-dienal (26, Scheme 6). To a 2-dram vial equipped with a magnetic stir bar is charged with **S2** (18.8 mg, 0.0756 mmol) and solid sodium bicarbonate (50.8 mg, 0.605 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, CH_2Cl_2 (1.0 mL) is added through a syringe. The solution is allowed to cool to 0 °C in an ice bath followed by addition of Dess-Martin periodinane (48.1 mg, 0.113 mmol) in one portion as a solid. The resulting white suspension is allowed to stir for an additional 60 minutes before the reactions is quenched by passing the suspension through a celite plug eluted with EtOAc. The volatiles are removed under reduced pressure to afford colorless oil residue, which is purified by silica gel column chromatography (8:1 hexanes/EtOAc) to deliver **26** as colorless oil (14.5 mg, 0.0590 mmol, 78% yield). IR (neat): 2936 (w), 2849 (w), 2831 (w), 1767 (w), 1678 (s), 1504 (m), 1466 (m), 1397 (m), 1207 (s), 1044 (s), 998 (w), 921 (w), 863 (w), 785 (s), 697 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 10.25 (1H, d, *J* = 8.0 Hz), 6.70 (1H, s), 6.67 (1H, s), 6.60 (1H, dd, *J* = 11.2, 11.2 Hz), 6.11 (1H, ddd, *J* = 17.6, 10.4, 5.2 Hz), 5.93 (1H, dd, *J* = 10.8, 8.0 Hz), 5.46–5.42 (1H, m), 5.28 (1H, d, *J* = 10.8 Hz), 5.20 (1H, d, *J* = 17.2 Hz), 3.79 (3H, s), 3.76 (3H, s), 2.21 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 152.1, 151.4, 150.5, 138.6, 129.0, 126.8, 126.6, 116.8, 114.2, 110.7, 56.3, 56.0, 40.2, 16.4; HRMS (ESI+): Calcd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.13342, Found: 247.13346. Specific Rotation: $[\alpha]_D^{20}$ +297 (*c* 0.327, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity is further confirmed by converting the title compound to the corresponding enone **S3**, **Scheme 8** (see below).

(*S*,*Z*)-(11-Bromoundeca-1,4-dien-3-yl)benzene (27a, Scheme 6). The title compound is prepared with 1.0 equiv of the alkenylboron reagent (96% *Z*) as the limiting reagent, 1.25 equiv of NaOMe and 1.25 equiv of the corresponding allylic phosphate following the same representative procedure. The compound was characterized with 6% *E* isomer. IR (neat): 3081 (w), 3006 (w), 2929 (m), 2855 (m), 1634 (w), 1600 (w), 1492 (w), 1451 (w), 1256 (w), 1230 (w), 944 (w), 915 (m), 851 (w), 741 (m), 699 (s), 563 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (2H, m), 7.26–7.18 (3H, m), 5.99 (1H, ddd, *J* = 17.6, 10.0, 6.4 Hz), 5.58–5.48 (2H, m), 5.14–5.08 (2H, m), 4.34 (1H, dd, *J* = 6.8, 6.8 Hz), 3.39 (2H, t, *J* = 7.2 Hz), 2.19–2.09 (2H, m), 1.87–1.80 (2H, m), 1.46–1.26 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 140.7, 131.0, 130.5, 128.6, 127.8, 126.4, 114.8, 47.1, 34.1, 32.9, 29.4, 28.5, 28.2, 27.4; HRMS (ESI+): Calcd for $C_{17}H_{24}Br_1$ $[M+H]^+$: 307.10614, Found: 307.10584. Specific Rotation: $[\alpha]_D^{20}$ +57.5 (*c* 0.740, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.019	12552318	523008	50.066	49.969
2	20.229	12519292	523650	49.934	50.031
Total		25071610	1046658	100.000	100.000

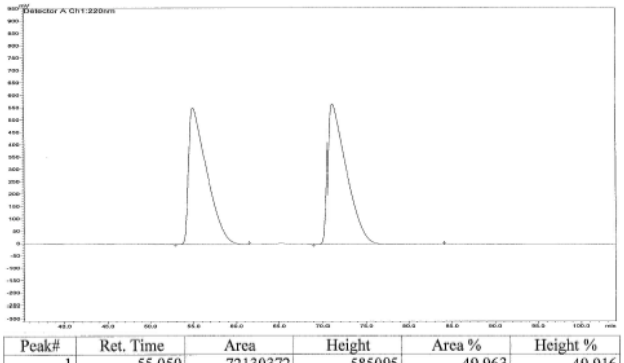


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.736	491918	23151	3.897	4.421
2	20.065	12131008	500450	96.103	95.579
Total		12622925	523601	100.000	100.000

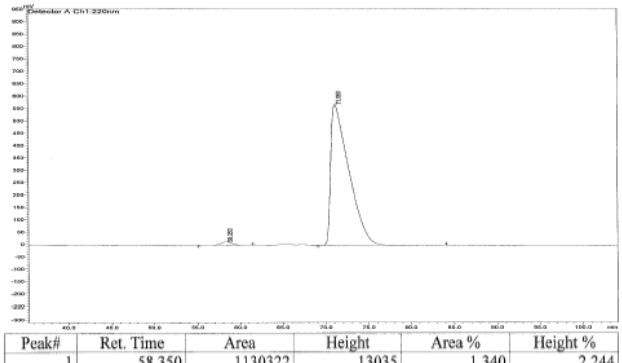
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	18.02	50.1	1	18.74	3.9
2	20.23	49.9	2	20.07	96.1

(*S*,*Z*)-1-Methoxy-4-(((9-phenylundeca-7,10-dien-1-yl)oxy)methyl)benzene (27b, Scheme 6). The title compound is prepared with 1.0 equiv of the alkenylboron reagent (97% *Z*) as the limiting reagent, 1.25 equiv of NaOMe and 1.25 equiv of the corresponding allylic phosphate following the same representative procedure. The compound was characterized with 7% *E* isomer. IR (neat): 3057 (w), 2930 (m), 2854 (m), 1612 (w), 1512 (s), 1453 (w), 1362 (w), 1301 (w), 1246 (s), 1172 (w), 1097 (m), 1036 (m), 914 (w), 820 (m), 741 (m), 699 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.17 (7H, m), 6.88 (2H, d, J = 8.8 Hz), 6.03–5.95 (1H, m), 5.57–5.48 (2H, m), 5.13–5.09 (2H, m), 4.43 (2H, s), 4.34 (1H, dd, J = 7.6, 7.6 Hz), 3.80 (3H, s), 3.42 (2H, t, J = 6.8 Hz), 2.17–2.07 (2H, m), 1.59 (2H, dt, J = 13.2, 6.0 Hz), 1.44–1.26 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.9, 140.7, 131.0, 130.8, 130.7, 129.4, 128.6, 127.8, 126.3, 114.7, 113.9, 72.7, 70.3, 55.4, 47.1, 29.9, 29.6, 29.3, 27.5, 26.2; HRMS (ESI+): Calcd for $C_{25}H_{33}O_2$ $[M+H]^+$: 365.24806, Found: 365.24830. Specific Rotation: $[\alpha]_D^{20}$ +41.2 (*c* 0.650, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.050	72130372	585095	49.963	49.916
2	71.322	72237530	587054	50.037	50.084
Total		144367902	1172149	100.000	100.000

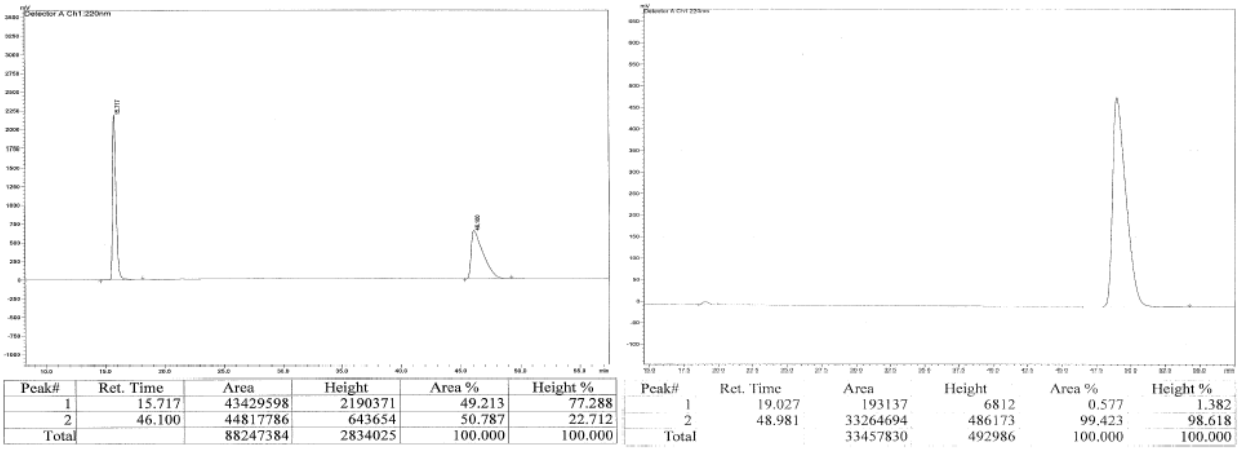


Peak#	Ret. Time	Area	Height	Area %	Height %
1	58.350	1130322	13035	1.340	2.244
2	71.060	83242530	567984	98.660	97.756
Total		84372853	581019	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	55.05	50.0	1	58.35	1.3
2	71.32	50.0	2	71.06	98.7

(*S*,*Z*)-(1-Butoxypenta-1,4-dien-3-yl)benzene (27c, Scheme 6). The title compound is prepared in the presence of 1.5 equiv of the corresponding alkenylboron reagent (>98% *Z*) and 1.5 equiv of NaOMe based the representative procedure. IR (neat): 3083 (w), 3029 (w), 2959 (m), 2931 (m), 2872 (m), 1660 (m), 1492 (w), 1452 (w), 1372 (w), 1275 (w), 1102 (s), 994 (w), 913 (m), 744 (m), 699 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.24 (4H, m), 7.21–7.16 (1H, m), 6.07–5.97 (2H, m), 5.13 (1H, ddd, *J* = 17.6, 1.6, 1.2 Hz), 5.08 (1H, ddd, *J* = 10.4, 2.0, 1.2 Hz), 4.58–4.57 (2H, m), 3.76 (2H, dddd, *J* = 16.8, 12.4, 9.6, 6.4 Hz), 1.64–1.57 (2H, m), 1.44–1.35 (2H, m), 0.93 (3H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 144.4, 141.1, 128.5, 127.7, 126.2, 114.2, 108.0, 72.3, 44.0, 32.0, 19.2, 14.0; HRMS (ESI+): Calcd for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.15924, Found: 217.15902. Specific Rotation: $[\alpha]_D^{20}$ +79.2 (*c* 1.64, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.717	43429598	2190371	49.213	77.288
2	46.100	44817786	643654	50.787	22.712
Total		88247384	2834025	100.000	100.000

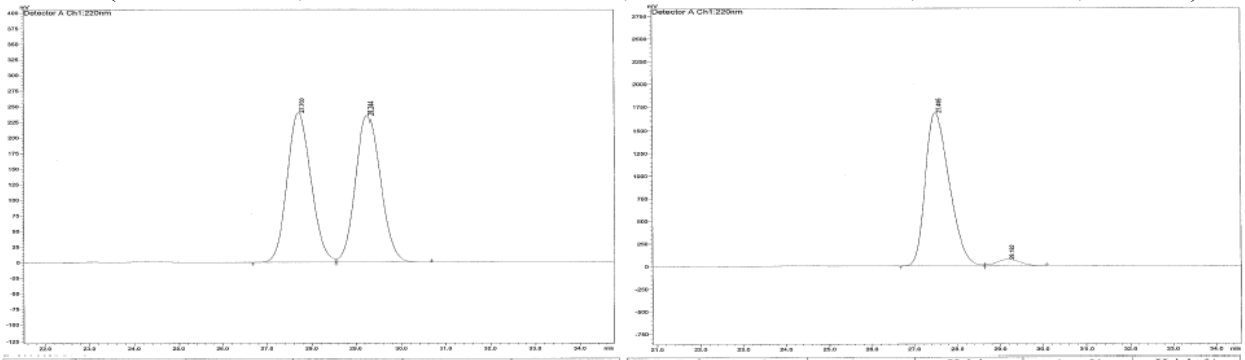
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.027	193137	6812	0.577	1.382
2	48.981	33264694	486173	99.423	98.618
Total		33457830	492986	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	15.72	49.2	1	19.03	0.6
2	46.10	50.8	2	48.98	99.4

***tert*-Butyl-(*S*,*Z*)-(4-(3-bromophenyl)hexa-2,5-dien-1-yl)carbamate (28, Scheme 6).** The title compound is prepared in the presence of 1.5 equiv of the corresponding alkenylboron reagent (>98% *Z*) and 1.5 equiv of NaOMe following the same representative procedure, except with 5.5 mol % imidazolinium salt **9c**. IR (neat): 3062 (w), 3022 (w), 2971 (w), 2917 (w), 1644 (w), 1599 (w), 1491 (w), 1450 (w), 1371 (w), 1073 (w), 1032 (w), 893 (m), 755 (m), 739 (m), 697 (s), 536 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.33 (2H, m), 7.19–7.13 (2H, m), 5.93 (1H, ddd, *J* = 17.2, 10.0, 6.4 Hz), 5.67–5.55 (2H, m), 5.17–5.10 (2H, m), 4.50 (1H, bs), 4.36 (1H, bdd, *J* = 7.6, 7.6 Hz), 3.83 (2H, dd, *J* = 5.6, 5.6 Hz), 1.45 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 145.4, 139.3, 133.1, 130.9, 130.3, 129.8, 127.3, 126.5, 122.9, 116.0, 77.4, 46.8, 37.9, 28.6;

HRMS (ESI+): Calcd for $C_{13}H_{17}$ [M+H–Boc]$^+$: 251.03096, Found: 251.03077. Specific Rotation: $[\alpha]_D^{20}$ +99.1 (*c* 1.21, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.700	8954626	240033	50.122	50.497
2	29.244	8910868	235309	49.878	49.503
Total		17865494	475342	100.000	100.000

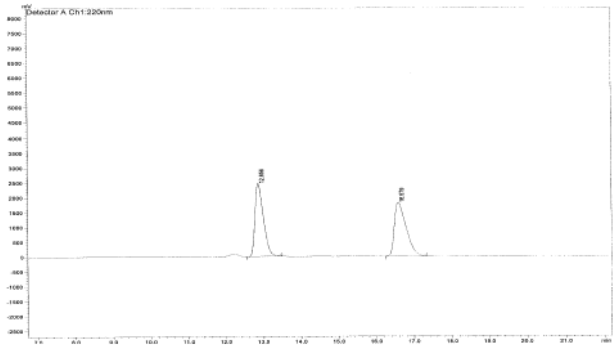
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.495	65605465	1678893	96.012	95.897
2	29.192	2725106	71826	3.988	4.103
Total		68330571	1750719	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	27.70	50.1	1	27.50	96.0
2	29.24	49.9	2	29.19	4.0

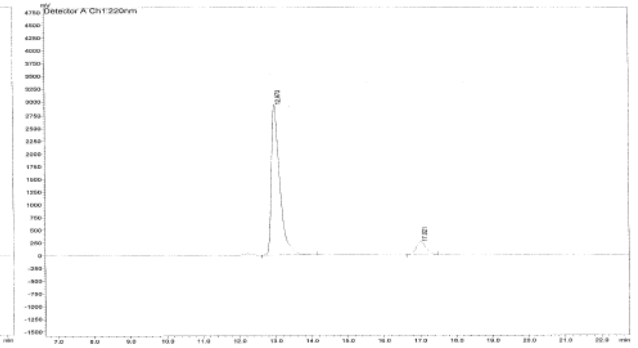
■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Aryl-Substituted *cis*-1,2-Disubstituted Alkenylboron Reagents (Scheme 7 & 8):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

(*R*,*Z*)-(3-Cyclohexylpenta-1,4-dien-1-yl)benzene (31, Scheme 7). The title compound is prepared in the presence of 1.5 equiv of the corresponding alkenylboron reagent (95% *Z*) and 1.5 equiv of NaOMe following the same representative procedure. IR (neat): 3078 (w), 3058 (w), 3023 (w), 2921 (s), 2850 (s), 1633 (m), 1600 (w), 1493 (m), 1447 (s), 1415 (w), 1261 (w), 1074 (w), 1029 (w), 994 (m), 971 (w), 911 (s), 812 (m), 768 (s), 698 (s), 652 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.18 (5H, m), 6.52 (1H, d, *J* = 11.6 Hz), 5.80 (1H, ddd, *J* = 17.6, 10.8, 7.2 Hz), 5.58 (1H, dd, *J* = 11.6, 10.4 Hz), 5.07–5.01 (2H, m), 3.11–3.04 (1H, m), 1.74–1.57 (5H, m), 1.33–1.02 (4H, m), 0.95–0.83 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 137.9, 133.7, 129.5, 128.8, 128.2, 126.6, 114.9, 48.3, 42.0, 30.8, 30.5, 26.7, 26.6; HRMS (ESI+): Calcd for $C_{17}H_{23}$ [M+H]$^+$: 227.17998, Found: 227.18093. Specific Rotation: $[\alpha]_D^{20}$ –171 (*c* 1.58, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (91:9 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.856	38227803	2467504	49.850	57.566
2	16.579	38457304	1818903	50.150	42.434
Total		76685107	4286407	100.000	100.000

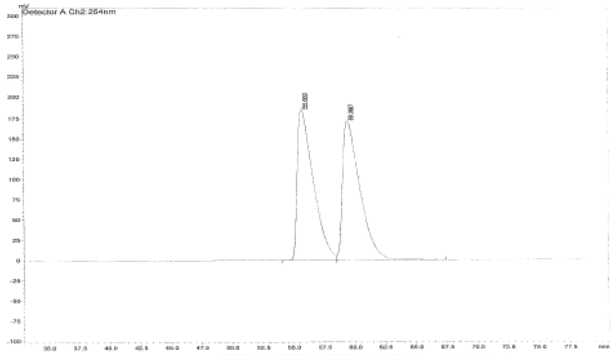


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.973	48037031	2932785	91.031	91.970
2	17.021	4732933	256068	8.969	8.030
Total		52769964	3188853	100.000	100.000

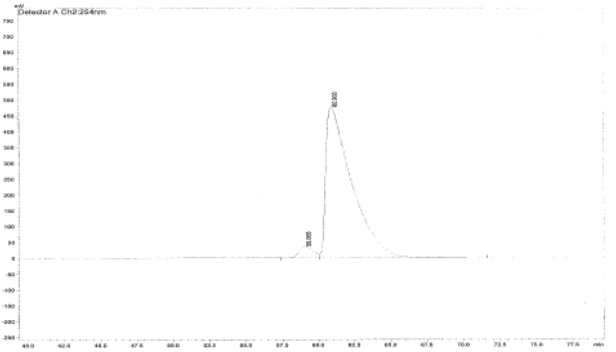
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	12.86	49.9	1	12.97	91.0
2	16.58	50.1	2	17.02	9.0

(*S*,*Z*)-4-(1-(4-Methoxyphenyl)penta-1,4-dien-3-yl)phenyl 4-methylbenzenesulfonate (33, Scheme 8). The title compound is prepared in the presence of 1.5 equiv of the corresponding alkenylboron reagent (93% *Z*) and 1.5 equiv of NaOMe based on the same representative procedure. IR (neat): 3008 (w), 2956 (w), 2927 (w), 2837 (w), 1607 (m), 1509 (s), 1490 (s), 1372 (s), 1303 (w), 1248 (s), 1198 (s), 1176 (s), 1153 (s), 1093 (s), 1033 (m), 1018 (m), 922 (w), 864 (s), 839 (s), 815 (m), 750 (m), 669 (m), 570 (s), 552 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.70 (2H, m), 7.30 (2H, dd, *J* = 8.8, 0.8 Hz), 7.21–7.13 (4H, m), 6.93–6.85 (4H, m), 6.56 (1H, d, *J* = 11.6 Hz), 5.99 (1H, ddd, *J* = 16.8, 10.4, 6.0 Hz), 5.63 (1H, dd, *J* = 11.2, 10.0 Hz), 5.20–5.15 (2H, m), 4.54 (1H, dd, *J* = 9.6, 6.0 Hz), 3.81 (3H, s), 2.45 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.2, 145.4, 142.5, 140.0, 132.7, 130.9, 129.90, 129.86, 129.5, 129.0, 128.6, 122.5, 115.9, 113.9, 55.4, 47.1, 21.9; HRMS (ESI+): Calcd for $C_{25}H_{25}O_4S_1$ $[M+H]^+$: 421.14735, Found: 421.14770. Specific Rotation: $[\alpha]_D^{20}$ +60.7 (*c* 1.81, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 254 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.660	16803700	185975	49.559	51.926
2	59.387	17102659	172181	50.441	48.074
Total		33906359	358156	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	59.065	2483807	35928	4.038	7.011
2	60.900	59031591	476532	95.962	92.989
Total		61515398	512460	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	55.66	49.6	1	59.07	4.0
2	59.39	50.4	2	60.90	96.0

(–)-Nyasol (Scheme 8): To a 10-mL round-bottom flask with a magnetic stir bar is charged with **33** (40.2 mg, 0.0956 mmol); the flask is equipped with a reflux condenser and the whole apparatus is sealed with a septum and purged with N_2 for five minutes. EtOH (2.0 mL) is added through a syringe followed by the addition of 2.0 N aqueous solution of KOH (112 mg in 1.0 mL H_2O). The resulting solution is allowed to warm to 80 °C and stir for one hour, after which it is allowed to cool to 22 °C and quenched by addition of an aqueous solution of 1.0 N HCl (2.0 mL). The solution was washed with EtOAc (3 x 1.0 mL); the combined organic layers are dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford a yellow oil residue, which is dried under high vacuum. The unpurified mixture is placed in a flame-dried 6-dram vial with a magnetic stir bar and the vessel is sealed with a septum and purged with N_2 flow for 10 minutes. Freshly prepared MeMgI in diethyl ether (956 μL, 0.478 mmol) is added to the reaction vessel through a syringe and solvent is carefully removed under reduced pressure. The resulting mixture is allowed to warm to 180 °C in an oil bath and kept for 10 minutes (white smoke generated as the reaction proceeds, disappearing in 10 minutes), after which it is allowed to cool to 22 °C and diluted with EtOAc (5.0 mL). A saturated solution of NH_4Cl (2.0 mL) is added to quench the reaction and the layers are separated. The aqueous layer is washed with EtOAc (3 x 2.0 mL) and the combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a brown oil residue, which is subjected to silica gel chromatography (4:1 hexanes/EtOAc) to furnish (–)-nyasol. (19.1 mg, 0.0755 mmol, 79% yield). The product has been previously reported and spectral data match those previously described.[13] IR (neat): 3300 (br), 2975 (w), 2961 (w), 2928 (w), 1634 (m), 1509 (s), 1440 (w), 1366 (w), 1224 (s), 1168 (s), 1099 (m), 913 (m), 829 (s), 732 (m), 649 (w), 623 (w), 542 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (2H, dt, *J* = 8.4, 2.4 Hz), 7.10 (2H, dt, *J* = 8.8, 2.4 Hz), 6.79 (2H, dt, *J* = 8.8, 2.4 Hz), 6.78 (2H, dt, *J* = 8.4, 2.4 Hz), 6.52 (1H, d, *J* = 11.6 Hz), 6.00 (1H, ddd, *J* = 16.8, 10.4, 6.0 Hz), 5.68 (1H, dd, *J* = 11.6, 10.0 Hz), 5.16–5.14 (2H, m), 4.75 (1H, s), 4.66 (1H, s), 4.49 (1H, dd, *J* = 10.0, 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 153.9, 140.6, 135.5, 131.8, 130.0, 129.9, 128.7, 128.4, 115.4, 115.2, 115.0, 46.7; HRMS (ESI+): Calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.12285. Found: 253.12318. Specific rotation: $[\alpha]_D^{20}$ +195 (*c* 0.947, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er. Assuming the enantiomeric purity is kept the same as compound **33** (see above).

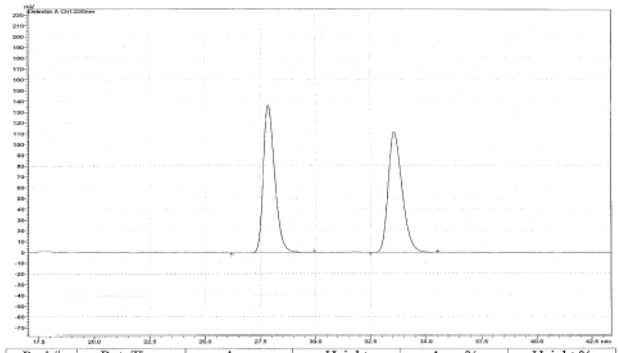
Determination of stereochemical identity: Literature value ($[\alpha]_D^{20}$ –201.9 (*c* 0.42, $CHCl_3$), 98.5:1.5 er) is assigned to the (*R*) enantiomer.[1d]

■ **Formal Synthesis of Heliespirone A and Heliannuol E (Scheme 9):** In this section, the synthesis of compound **35** is performed at 22 °C for 36 h following the representative procedure described in Table 1. Silyl ether **35** is formed as an inconsequential 4:1 diastereomer mixture in 79% yield. The mixture is subsequently deprotected; the resulting secondary alcohol is oxidized

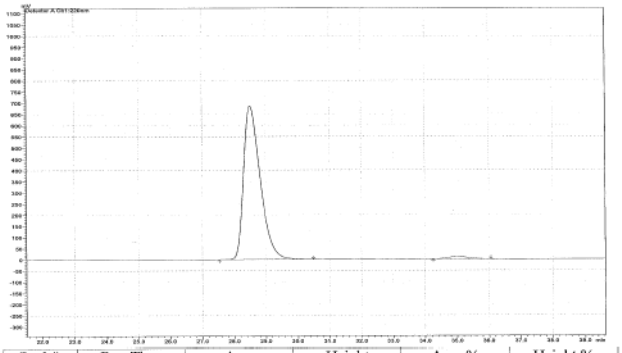
to deliver the *Z* enone and the compound is characterized at this stage (for procedure details, see below).

To a 2-dram vial equipped with a magnetic stir bar is charged with **35** (29.8 mg, 0.0791 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, tetrahydrofuran (thf, 1.0 mL) is added through a syringe. The solution is allowed to cool to 0 °C in an ice bath followed by dropwise addition of tetrabutylammonium fluoride solution (158 μL, 0.158 mmol, 1.0 M in thf). The resulting light yellow solution is allowed to warm to 22 °C and stir for an additional 12 h before it is quenched by addition of a saturated NH_4Cl solution (1.0 mL). The layers are separated and the aqueous layer is washed with EtOAc (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford yellow oil, which is directly placed into a 2-dram vial equipped with a magnetic stir bar and solid sodium bicarbonate (53.2 mg, 0.633 mmol) is added to the vessel. The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, CH_2Cl_2 (1.0 mL) is added through a syringe. The solution is allowed to cool to 0 °C followed by addition of Dess-Martin periodinane (50.5 mg, 0.119 mmol) in one portion as a solid. The resulting white suspension is allowed to warm to 22 °C and stir for an additional 60 minutes before it is quenched by passing the suspension through a celite plug eluted with EtOAc. The volatiles are removed under reduced pressure to afford a colorless oil residue, which is purified by silica gel column chromatography (8:1 hexanes/EtOAc) to deliver the *Z* enone **S3** as colorless oil (13.4 mg, 0.0514 mmol, 65% yield). **(*S*,*Z*)-5-(2,5-Dimethoxy-4-methylphenyl)hepta-3,6-dien-2-one (S3, Scheme 9).** IR (neat) 2932 (m) 2850 (w) 1694 (m) 1611 (w) 1504 (m) 1465 (m) 1397 (m), 1209 (s), 1176 (m), 1045 (s), 916 (w), 866 (w) 789 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.74 (1H, s), 6.69 (1H, s), 6.27 (1H, dd, *J* = 11.5, 10.0 Hz), 6.14 (1H, d, *J* = 11.5 Hz), 6.09 (1H, ddd, *J* = 17.0, 10.0, 6.0 Hz), 5.52–5.49 (1H, m), 5.14–5.09 (2H, m), 3.79 (3H, s), 3.75 (3H, s), 2.25 (3H, s), 2.19 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 152.0, 151.1, 146.5, 139.2, 128.5, 126.7, 126.0, 115.3, 114.9, 111.8, 56.4, 56.2, 43.3, 31.7, 29.8; HRMS (ESI+): Calcd for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.14907, Found: 261.14862. Specific Rotation: $[\alpha]_D^{20}$ +119.7 (*c* 0.670, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown; Chiralcel OD-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.850	4944303	136601	50.024	54.969
2	33.561	4939639	111904	49.976	45.031
Total		9883942	248505	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.513	25098393	686930	98.118	98.467
2	35.013	481389	10697	1.882	1.533
Total		25579783	697628	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	27.85	50.0	1	28.51	98.1
2	33.56	50.0	2	35.01	1.9

To an oven-dried 2-dram vial equipped with a magnetic stir bar is charged with enone **S3** (52.2 mg, 0.201 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, Et_2O (1.5 mL) is added through a syringe. The solution is allowed to cool to –78 °C in a dry ice/acetone bath followed by dropwise addition of MeLi solution (251 μL, 0.402 mmol, 1.6 M in Et_2O) over 5 minutes. The resulting solution is allowed to stir at –78 °C for additional two hours; then it is allowed to warm to 22 °C after which the reaction is quenched by the addition of a aturated solution of NH_4Cl (1.0 mL). The layers are separated and the aqueous layer is washed with Et_2O (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford yellow oil, which is purified by silica gel column chromatography (6:1 hexanes/EtOAc) to deliver **36** as colorless oil (51.1 mg, 0.185 mmol, 92% yield). **(*S*,*Z*)-5-(2,5-Dimethoxy-4-methylphenyl)-2-methylhepta-3,6-dien-2-ol (36, Scheme 9).** IR (neat): 3500 (w), 2972 (w), 2830 (w), 1768 (w), 1504 (m), 1466 (m), 1397 (m), 1208 (s), 1045 (m), 1001 (w), 957 (w), 916 (w), 863 (w), 778 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.71 (1H, s), 6.67 (1H, s), 6.06 (1H, ddd, J = 17.2, 10.4, 4.4 Hz), 5.57 (1H, d, J = 11.2 Hz), 5.38–5.27 (2H, m), 5.23–5.17 (2H, m), 3.82 (3H, s), 3.78 (3H, s), 3.15 (1H, bs), 2.20 (3H, s), 1.39 (3H, s), 1.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.0, 140.6, 137.0, 130.3, 129.7, 125.6, 115.2, 114.4, 110.9, 71.7, 56.3, 56.2, 39.9, 32.0, 30.8, 16.3; HRMS (ESI+): Calcd for $C_{17}H_{23}O_2$ $[M+H–H_2O]^+$: 259.16980, Found: 259.16932. Specific Rotation: $[\alpha]_D^{20}$ +183.9 (*c* 0.560, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Assuming the enantiomeric purity is kept the same as the *Z* enone **S3** (see above).

To an oven-dried 2-dram vial equipped with a magnetic stir bar is charged with tertiary alcohol **36** (51.1 mg, 0.185 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, CH_2Cl_2 (2.0 mL) is added through a syringe. The solution is allowed to cool to –20 °C in a cryogenic bath followed by dropwise addition of titanium (IV) isopropoxide (110 μL, 0.370 mmol). The resulting solution is allowed to stir for an additional 10 minutes, after which time *tert*-butyl peroxide (~5.5 M in decane, 101 μL, 0.555 mmol) is added through a syringe.

The solution is allowed to stir for an additional 18 h before the reaction is quenched by addition of 0.1 M aqueous solution of HCl (2.0 mL). The mixture is allowed to warm to ambient temperature and stir for another 30 minutes. Layers are separated and the aqueous layer is washed with Et_2O (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford colorless oil, which is purified by silica gel column chromatography (4:1 hexanes/EtOAc) to deliver **37** as colorless oil (41.1 mg, 0.141 mmol, 76% yield). **2-((2*S*,3*S*)-3-((*R*)-1-(2,5-Dimethoxy-4-methylphenyl)allyl)oxiran-2-yl)propan-2-ol (37, Scheme 9).** In the unpurified mixture, ~15% mono epoxidation at the terminal alkene is also observed. The major epoxidation product is obtained as a 92:8 diastereomer mixture; the minor diastereomer can be separated from the desired **37**. IR (neat): 3489 (w), 3455 (w), 2972 (m), 2831 (w), 1505 (m), 1466 (m), 1397 (m), 1210 (s), 1044 (s), 998 (w), 968 (w), 922 (w), 866 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.74 (1H, s), 6.69 (1H, s), 6.16 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz), 5.21 (1H, ddd, *J* = 17.6, 1.6, 1.6 Hz), 5.16 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz), 4.29–4.24 (1H, m), 3.78 (6H, s), 3.41 (1H, dd, *J* = 9.6, 4.0 Hz), 2.82 (1H, d, *J* = 4.4 Hz), 2.21 (3H, s), 1.36 (3H, s), 1.10 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.2, 139.1, 126.8, 126.3, 115.7, 115.2, 112.1, 68.5, 63.9, 61.1, 56.6, 56.2, 41.2, 29.7, 25.9, 16.4; HRMS (ESI+): Calcd for $C_{17}H_{25}O_4$ $[M+H]^+$: 293.17528, Found: 293.17594. Specific Rotation: $[\alpha]_D^{20}$ +25.8 (*c* 0.387, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

To an oven-dried 2-dram vial equipped with a magnetic stir bar is charged with epoxy alcohol **37** (41.1 mg, 0.141 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, tetrahydrofuran (thf, 1.0 mL) is added through a syringe. The vessel is charged with titanium (IV) isopropoxide (83 μL, 0.282 mmol) in a dropwise fashion and the resulting solution is allowed to stand at 22 °C for 10 minutes before $LiBH_4$ solution (282 μL, 0.564 mmol, 2 M in thf) is introduced through a syringe. The resulting mixture is allowed to warm to 50 °C and stir for an additional 18 h, after which time it is allowed to cool to 22 °C and the reaction is quenched by addition of a 0.1 M solution of aqueous HCl (1.0 mL). The mixture is allowed to stir for another 30 minutes. Layers are separated and the aqueous layer is washed with EtOAc (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford yellow oil, which is purified by silica gel chromatography (1:1 hexanes/EtOAc) to deliver **38** as colorless oil (22.8 mg, 0.0776 mmol, 55% yield). **(3*S*,5*R*)-5-(2,5-Dimethoxy-4-methylphenyl)-2-methylhept-6-ene-2,3-diol (38, Scheme 9).** The compound has been previously prepared and the spectral data match those reported.[14] ^1H NMR (400 MHz, $CDCl_3$): δ 6.70 (1H, s), 6.66 (1H, s), 6.03 (1H, ddd, *J* = 18.0, 10.4, 9.6 Hz), 5.17–5.10 (2H, m), 3.90 (1H, dt, *J* = 9.6, 4.8 Hz), 3.80 (3H, s), 3.78 (3H, s), 3.52 (1H, dd, *J* = 9.2, 4.0 Hz), 2.19 (3H, s), 2.08 (1H, d, *J* = 4.4 Hz), 2.06 (1H, bs), 1.94 (1H, dd, *J* = 14.0, 10.0 Hz), 1.64–1.58 (1H, m), 1.21 (3H, s), 1.15 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 150.4, 140.4, 131.3, 125.2, 115.5, 114.8, 110.9, 76.4, 73.1, 56.5, 56.2, 40.6, 37.2, 26.3, 23.7, 16.3; HRMS (ESI+): Calcd for $C_{17}H_{26}O_4$ $[M]^+$: 294.18311, Found: 294.18332. Specific Rotation: $[\alpha]_D^{20}$ –33.3 (*c* 0.330, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

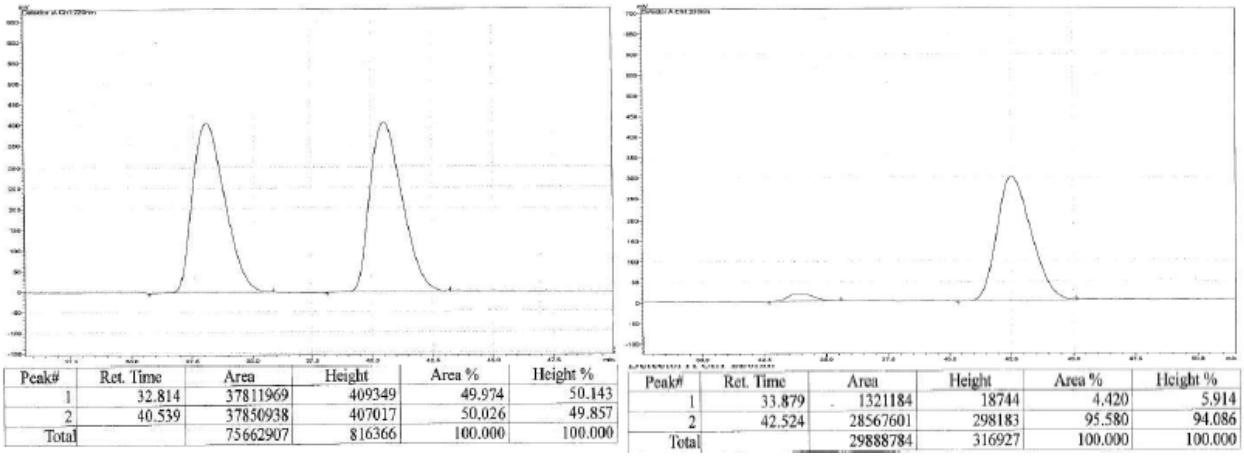
Determination of stereochemical identity: Literature value ($[\alpha]_D^{20}$ +36.3 (*c* 0.25, $CHCl_3$), 98:2 er) is assigned to the (3*R*, 5*S*) enantiomer.[14]

■ **Synthesis of Santolina Alcohol (eq 1):** In this section, the synthesis of santolina alcohol is performed with 2.5 equiv of the corresponding alkenylboron reagent at 4 °C for 24 h following the same representative procedure as described for Table 1. The product is volatile and therefore the loss of santolina alcohol occurs during the work-up and isolation processes.

(*S*)-2,5-Dimethyl-3-vinylhex-4-en-2-ol (santolina alcohol). The compound is commercially available and the spectral data match those collected from a sample obtained through a purchase. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84–5.75 (1H, m), 5.16 (1H, dddd, *J* = 10.0, 2.4, 1.6, 0.8 Hz), 5.11–5.06 (2H, m), 2.98 (1H, dd, *J* = 9.2, 8.8 Hz), 1.76 (3H, d, *J* = 1.6 Hz), 1.69 (1H, bs), 1.66 (3H, d, *J* = 1.2 Hz), 1.18 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 135.0, 122.8, 116.6, 72.7, 54.7, 27.1, 26.8, 26.4, 18.4; HRMS (ESI+): Calcd for $C_{10}H_{17}$ $[M+H–H_2O]^+$: 137.13303, Found: 137.13342. Specific Rotation: $[\alpha]_D^{20}$ +3.24 (*c* 0.440, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Determination of stereochemical identity: Specific rotation value ($[\alpha]_D^{20}$ +15.0 (neat), >98:2 er) from Aldrich Chemical Co. is assigned to the (*S*) enantiomer.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.814	37811969	409349	49.974	50.143
2	40.539	37850938	407017	50.026	49.857
Total		75662907	816366	100.000	100.000

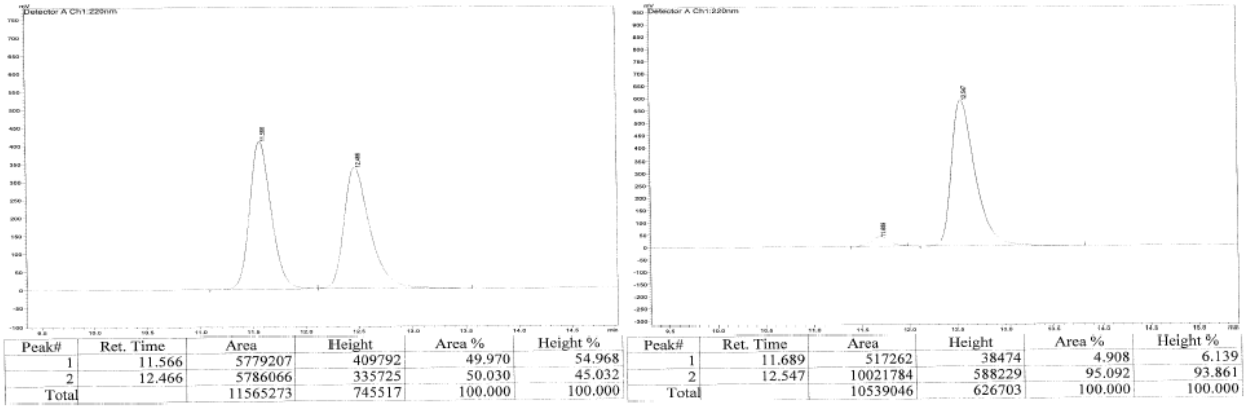
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.879	1321184	18744	4.420	5.914
2	42.524	28567601	298183	95.580	94.086
Total		29888784	316927	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	32.81	50.0	1	33.88	4.4
2	40.54	50.0	2	42.52	95.6

■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Heterocycle-Substituted Alkenylboron Reagents (Scheme 10):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

***tert*-Butyl (*S*)-4-(1-(2-bromophenyl)allyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (42a, Scheme 10).** IR (neat): 2976 (w), 2827 (w), 2837 (w), 1696 (s), 1467 (w), 1415 (m), 1365 (m), 1286 (w), 1240 (m), 1171 (s), 1112 (m), 1022 (w), 921 (w), 754 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (1H, dd, *J* = 8.0, 1.2 Hz), 7.25 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz), 7.16 (1H, dd, *J* = 8.0, 2.0 Hz), 7.09–7.05 (1H, m), 5.96 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz), 5.37 (1H, br s), 5.18 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz), 4.95 (1H, ddd, *J* = 17.2, 1.6, 1.2 Hz), 4.40 (1H, d, *J* = 6.8 Hz), 3.90 (2H, br s), 3.48–3.36 (2H, m), 1.98 (2H, br s), 1.44 (9H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 140.6, 137.9, 137.2 (br), 133.2, 129.7, 128.2, 127.5, 125.7, 121.0 (br), 117.1, 79.7, 54.5, 43.6 (br), 41.2 (br), 40.0 (br), 28.6; HRMS (ESI+): Calcd for $C_{14}H_{17}Br_1N_1$ $[M+2H–Boc]^+$: 278.05444, Found: 278.05322. Specific Rotation: $[\alpha]_D^{20}$ –30.1 (*c* 1.99, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (95:5 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



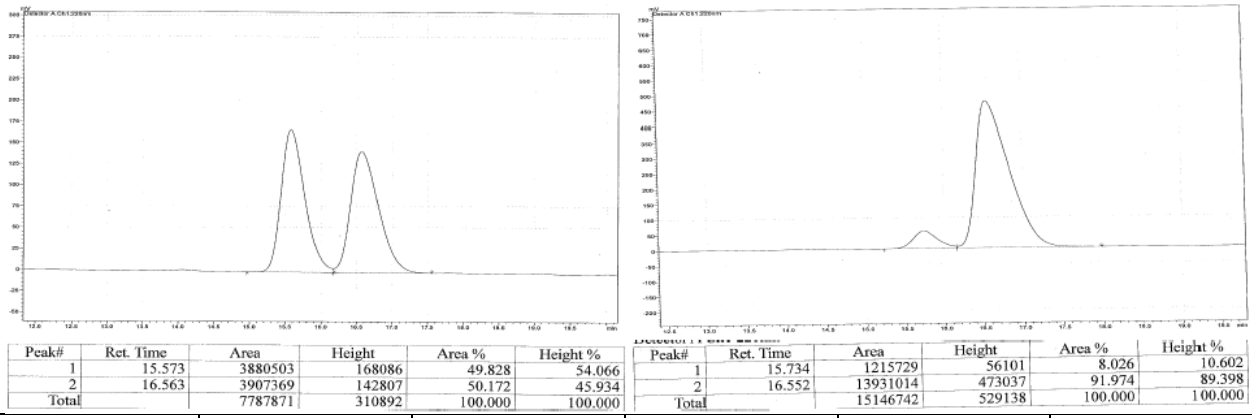
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.566	5779207	409792	49.970	54.968
2	12.466	5786066	335725	50.030	45.032
Total		11565273	745517	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.689	517262	38474	4.908	6.139
2	12.547	10021784	588229	95.092	93.861
Total		10539046	626703	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	11.57	50.0	1	11.69	4.9
2	12.47	50.0	2	12.55	95.1

***tert*-Butyl (*S*)-4-(2-methyl-1-phenylallyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (43a, Scheme 10).** The title compound is prepared at 60 ºC for 24 h following the same representative procedure. IR (neat): 2975 (m), 2928 (m), 2853 (w), 1699 (s), 1417 (m), 1365 (w), 1338 (w), 1285 (w), 1241 (m), 1173 (s), 1110 (m), 959 (w), 897 (w), 865 (w), 770 (w), 701 (w), 656 (w), 539 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31–7.27 (2H, m), 7.24–7.20 (1H, m), 7.17–7.14 (2H, m), 5.24 (1H, br s), 5.00 (1H, dd, *J* = 1.5, 1.0 Hz), 4.62 (1H, s), 3.89–3.86 (3H, m), 3.48 (2H, t, *J* = 6.0), 2.12 (2H, br s), 1.73 (3H, s), 1.46 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 145.7, 140.8, 129.2, 128.3, 126.6, 125.4, 121.2, 113.7, 79.6, 59.7, 43.5, 29.9, 28.6, 25.3, 23.3; HRMS (ESI+): Calcd for $C_{16}H_{18}N_1O_2$ $[M–C_4H_9]^+$: 256.1338, Found: 256.1327. Specific Rotation: $[\alpha]_D^{20}$ +8.90 (*c* 1.91, $CHCl_3$) for an enantiomerically enriched sample of 92:8 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (92:8 er shown; Chiralpak AD-H column, 99.7/0.3 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



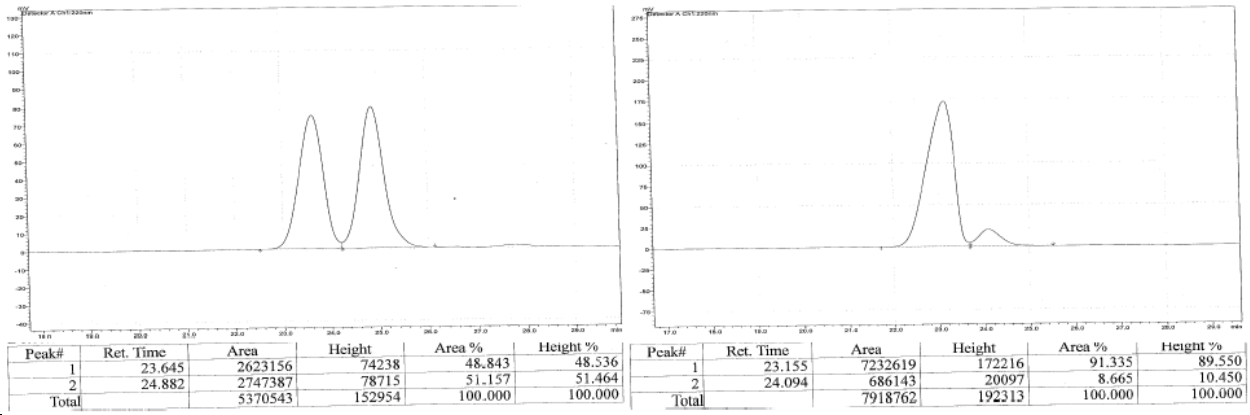
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.573	3880503	168086	49.828	54.066
2	16.563	3907369	142807	50.172	45.934
Total		7787871	310892	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.734	1215729	56101	8.026	10.602
2	16.552	13931014	473037	91.974	89.398
Total		15146742	529138	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	15.57	49.8	1	15.73	8.0
2	16.56	50.2	2	16.55	92.0

***tert*-Butyl (*S*)-4-(2-methyl-5-phenylpent-1-en-3-yl)-3,6-dihydropyridine-1(2*H*)-carboxylate (43b, Scheme 10).** The title compound is prepared at 60 °C for 24 h based on the same representative procedure. IR (neat): 2975 (m), 2930 (m), 2859 (w), 1699 (s), 1418 (m), 1365 (w), 1285 (w), 1241 (m), 1173 (s), 1111 (m), 892 (w), 770 (w), 700 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.30–7.25 (2H, m), 7.20–7.15 (3H, m), 5.45 (1H, br s), 4.87 (1H, dd, *J* = 1.5, 1.0 Hz), 4.78 (1H, br s), 3.88 (2H, dt, *J* = 6.0, 2.5 Hz), 3.51–3.44 (2H, m), 3.39 (1H, ddd, J = 12.5, 6.5, 4.5 Hz), 2.61–2.51 (3H, m), 2.13 (1H, ddt, *J* = 7.0, 4.0, 3.5 Hz), 1.83 (2H, ddt, *J* = 9.0, 7.5, 2.0 Hz), 1.60 (3H, s), 1.47 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 145.7, 142.6, 128.6, 128.4, 125.9, 125.3, 119.4, 111.9, 79.6, 53.2, 43.5, 34.0, 31.8, 28.6, 26.3, 25.3, 20.5; HRMS (ESI+): Calcd for $C_{18}H_{22}N_1O_2$ $[M–C_4H_9]^+$: 284.1651, Found: 284.1689. Specific Rotation: $[\alpha]_D^{20}$ –16.1 (*c* 2.68, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (91:9 er shown; Chiralpak AD-H column, 99.7/0.3 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.645	2623156	74238	48.843	48.536
2	24.882	2747387	78715	51.157	51.464
Total		5370543	152954	100.000	100.000

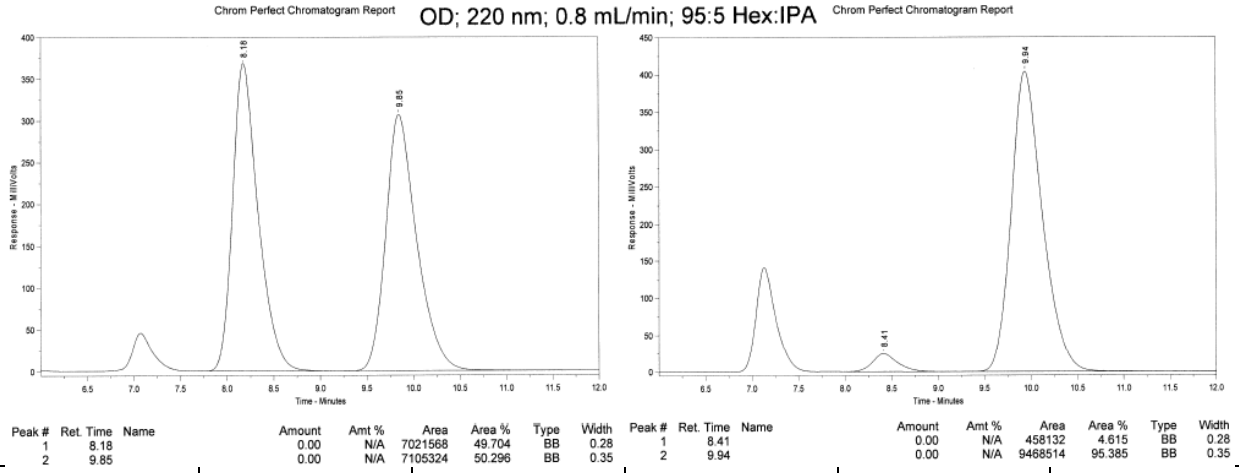
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.155	7232619	172216	91.335	89.550
2	24.094	686143	20097	8.665	10.450
Total		7918762	192313	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	23.65	48.8	1	23.16	91.3

2	24.88	51.2	2	24.09	8.7

Methyl (*S*)-2-((4-bromophenyl)(3,6-dihydro-2*H*-pyran-4-yl)methyl)acrylate (44, Scheme 10). The title compound is prepared with 2.5 mol % **9c** and 25 mol % CuCl at 60 ºC for 24 h following the same representative procedure. IR (neat): 2956 (w), 2924 (w), 2835 (m), 1720 (s), 1598 (w), 1486 (s), 1464 (m), 1340 (s), 1287 (w), 1243 (s), 1233 (m), 1132 (s), 1128 (m), 1052 (s), 917 (m), 828 (w), 749 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, d, *J* = 8.4 Hz), 7.05 (2H, d, *J* = 8.4 Hz), 6.40 (1H, app s), 5.34 (1H, t, *J* = 1.2 Hz), 5.28 (1H, dt, *J* = 2.8, 1.2 Hz), 4.54 (1H, br s), 4.15 (2H, dtt, *J* = 11.2, 5.2, 2.8 Hz), 3.73 (3H, s), 3.86–3.71 (2H, m), 2.18–1.95 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 140.3, 138.9, 136.6, 131.5, 130.7, 126.9, 121.9, 120.8, 65.8, 64.7, 52.3, 49.6, 28.2; HRMS (ESI$^+$): Calcd for $C_{16}H_{18}{}^{79}BrO_3$ $[M+H]^+$: 337.04393, Found: 337.04357.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (95:5 er shown; Chiralcel OD column, 95/5 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



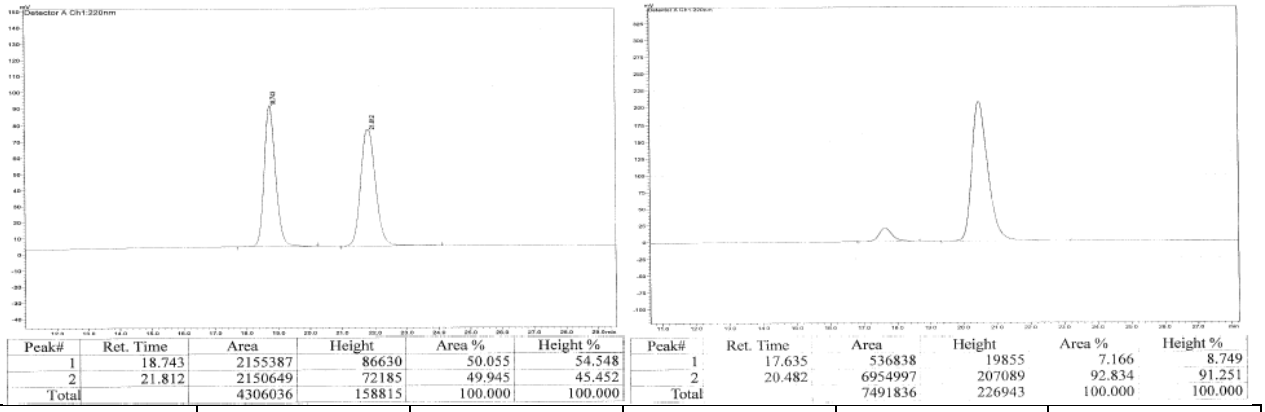
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	8.18		0.00	N/A	7021568	49.704	BB	0.28
2	9.85		0.00	N/A	7105324	50.296	BB	0.35

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	8.41		0.00	N/A	458132	4.615	BB	0.28
2	9.94		0.00	N/A	9468514	95.385	BB	0.35

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	8.18	49.7	1	8.41	4.6
2	9.85	50.3	2	9.94	95.4

(*S*)-4-(1-(2-Methoxyphenyl)allyl)-3,6-dihydro-2*H*-pyran (45, Scheme 10). IR (neat): 2956 (w), 2922 (m), 2834 (m), 1634 (w), 1598 (w), 1490 (s), 1463 (m), 1439 (w), 1288 (w), 1243 (s), 1130 (s), 1031 (m), 917 (m), 754 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (1H, ddd, *J* = 9.2, 7.6, 2.0 Hz), 7.13 (1H, dd, *J* = 7.6, 2.0 Hz), 6.92 (1H, ddd, *J* = 7.2, 7.2, 0.8 Hz), 6.88 (1H, dd, *J* = 8.0, 1.2 Hz), 6.05 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz), 5.46–5.44 (1H, m), 5.12 (1H, ddd, *J* = 11.2, 2.0, 1.2 Hz), 4.95 (1H, ddd, *J* = 16.8, 1.6, 1.6 Hz), 4.40 (1H, d, *J* = 6.8 Hz), 4.19–4.16 (2H, m), 3.81 (3H, s), 3.74 (2H, ddd, *J* = 22.0, 11.2, 5.6 Hz), 2.02–1.98 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 139.0, 137.1, 129.9, 128.7, 127.6, 121.7, 120.6, 115.9, 110.9, 65.9, 64.7, 55.8, 48.0, 28.4; HRMS (ESI+): Calcd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.13850, Found: 231.13929. Specific Rotation: $[\alpha]_D^{20}$ –15.2 (*c* 1.28, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (93:7 er shown; Chiralcel OJ-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



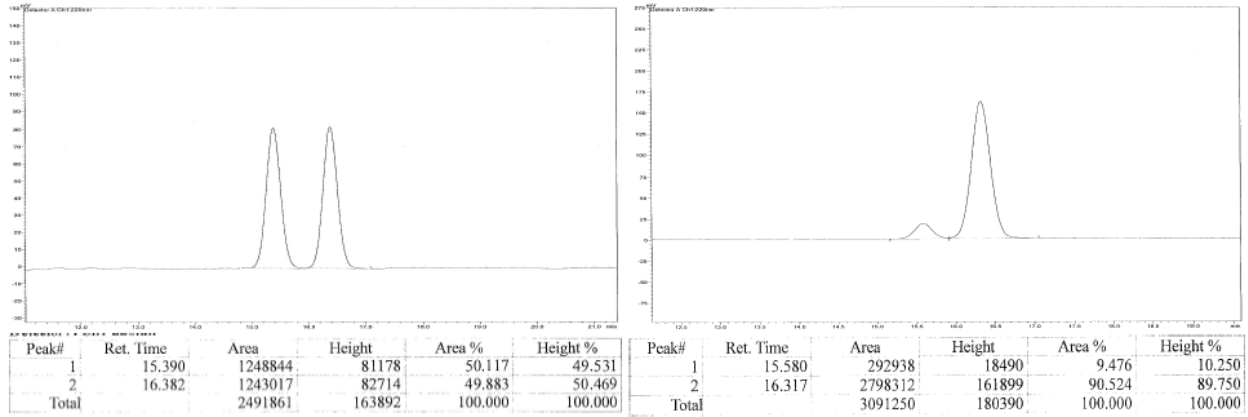
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.743	2155387	86630	50.055	54.548
2	21.812	2150649	72185	49.945	45.452
Total		4306036	158815	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.635	536838	19855	7.166	8.749
2	20.482	6954997	207089	92.834	91.251
Total		7491836	226943	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	18.74	50.1	1	17.64	7.2
2	21.81	49.9	2	20.48	92.8

(*S*)-4-(2-Methyl-5-phenylpent-1-en-3-yl)-3,6-dihydro-2*H*-pyran (46, Scheme 10). The title compound is prepared at 60 ºC for 24 h following the same representative procedure. IR (neat): 3063 (w), 3025 (w), 2928 (m), 2849 (m), 1643 (w), 1603 (w), 1495 (w), 1453 (m), 1371 (w), 1234 (w), 1126 (s), 1029 (w), 971 (w), 890 (m), 851 (w), 747 (m), 698 (s), 572 (w), 478 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (2H, m), 7.20–7.16 (3H, m), 5.53–5.50 (1H, m), 4.89–4.88 (1H, m), 4.80–4.79 (1H, m), 4.18–4.16 (2H, m), 3.80–3.71 (2H, m), 2.60–2.55 (3H, m), 2.08–1.99 (1H, m), 1.95–1.82 (3H, m), 1.63 (3H, dd, J = 1.2, 0.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 142.7, 136.3, 128.6, 128.5, 125.9, 121.2, 112.0, 65.7, 64.8, 53.2, 34.0, 31.6, 26.5, 20.4; HRMS (ESI+): Calcd for $C_{13}H_{21}O_1$ $[M+H]^+$: 243.17489, Found: 243.17497. Specific Rotation: $[\alpha]_D^{20}$ –11.1 (*c* 1.13, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (91:9 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.390	1248844	81178	50.117	49.531
2	16.382	1243017	82714	49.883	50.469
Total		2491861	163892	100.000	100.000

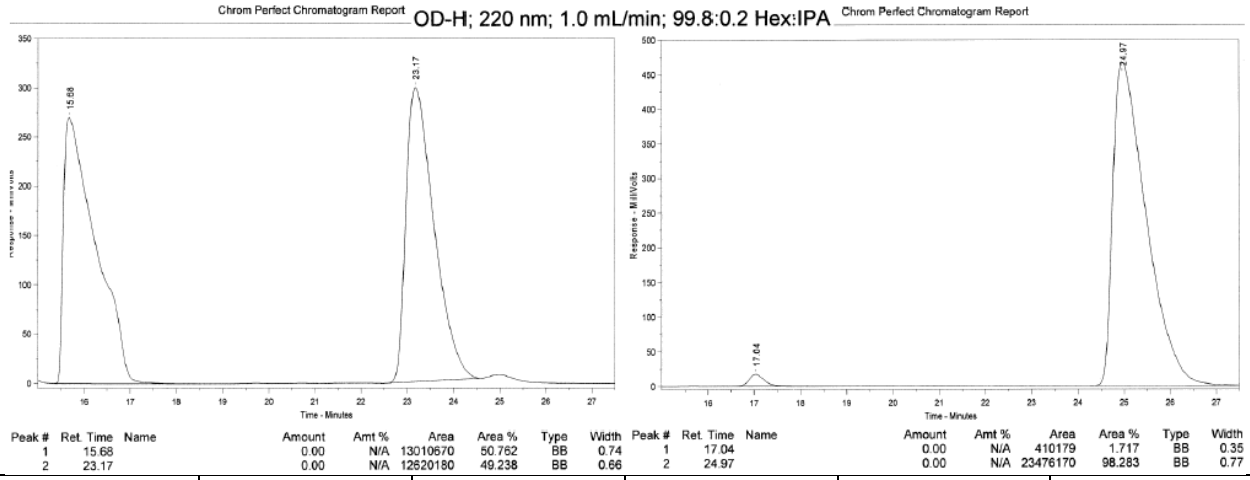
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.580	292938	18490	9.476	10.250
2	16.317	2798312	161899	90.524	89.750
Total		3091250	180390	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	15.39	50.1	1	15.58	9.5
2	16.38	49.9	2	16.32	90.5

Methyl (*S*)-2-((4-bromophenyl)(3,4-dihydro-2*H*-pyran-6-yl)methyl)acrylate (47a, Scheme 10). The title compound is prepared with 2.5 mol % **9c** and 25 mol % CuCl at 60 ºC for 24 h based on the representative procedure. IR (neat): 1720 (s), 1490 (m), 1240 (s), 1230 (m), 1150 (m), 1130 (s), 1080 (m), 1060 (s), 1010 (m), 820 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (2H, d, *J* = 8.4 Hz), 7.11 (2H, d, *J* = 8.4 Hz), 6.38 (1H, app s), 5.52 (1H, t, *J* = 1.2 Hz), 4.59 (1H, s), 4.47 (1H, t, *J* = 3.6 Hz), 3.96 (2H, dd, *J* = 5.2, 4.8 Hz), 3.71 (3H, s), 2.04–2.00 (2H, m), 1.79 (2H, dt, *J* = 10.4, 5.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 152.6, 140.6, 138.9, 131.5, 130.7, 127.2, 120.8, 99.9, 66.6, 52.2, 50.9, 22.3, 20.5; HRMS (ESI^+): Calcd for $C_{16}H_{18}{}^{79}BrO_3$ $[M+H]^+$: 337.0439, Found: 337.0441.

Determination of stereochemical identity: The absolute stereochemistry is secured by X-ray crystallography of the title compound (see the last section).

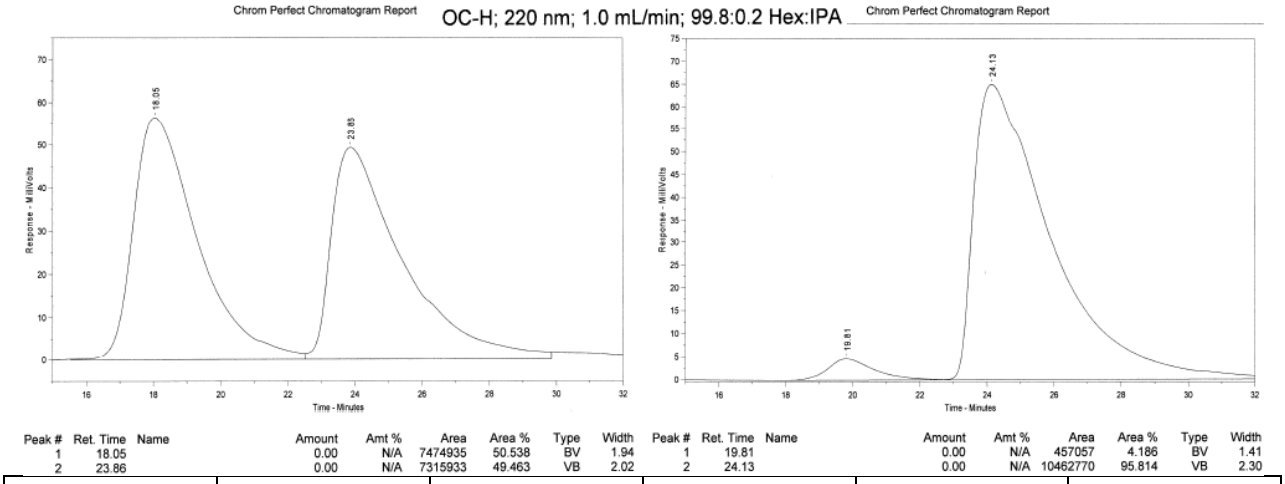
Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown; Chiralcel OD-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	15.68	50.8	1	17.04	1.7
2	23.17	49.2	2	24.97	98.3

Methyl (*S*)-2-((3,4-dihydro-2*H*-pyran-6-yl)(*o*-tolyl)methyl)acrylate (47b, Scheme 10). The title compound is prepared with 2.5 mol % **9c** and 25 mol % CuCl at 60 °C for 24 h based on the representative procedure. IR (neat,): 1720 (s), 1290 (w), 1250 (m), 1230 (m), 1150 (m), 1130 (s), 1060 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.13 (4H, m), 6.36 (1H, dd, *J* = 1.2, 0.8 Hz), 5.43 (1H, t, *J* = 1.2 Hz), 4.79 (1H, br s), 4.39 (1H, t, *J* = 4.0 Hz), 3.99 (2H, dd, *J* = 6.0, 4.0 Hz), 3.72 (3H, s), 2.30 (3H, s), 2.05–2.00 (2H, m), 1.81 (2H, dt, *J* = 10.4, 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 153.5, 140.6, 137.9, 136.9, 130.6, 127.7, 126.9, 126.8, 125.8, 99.8, 66.6, 52.1, 47.8, 22.4, 20.6, 19.5; HRMS (ESI^+): Calcd for $C_{17}H_{21}O_3$ $[M+H]^+$: 273.1491, Found: 273.1487.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OC-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



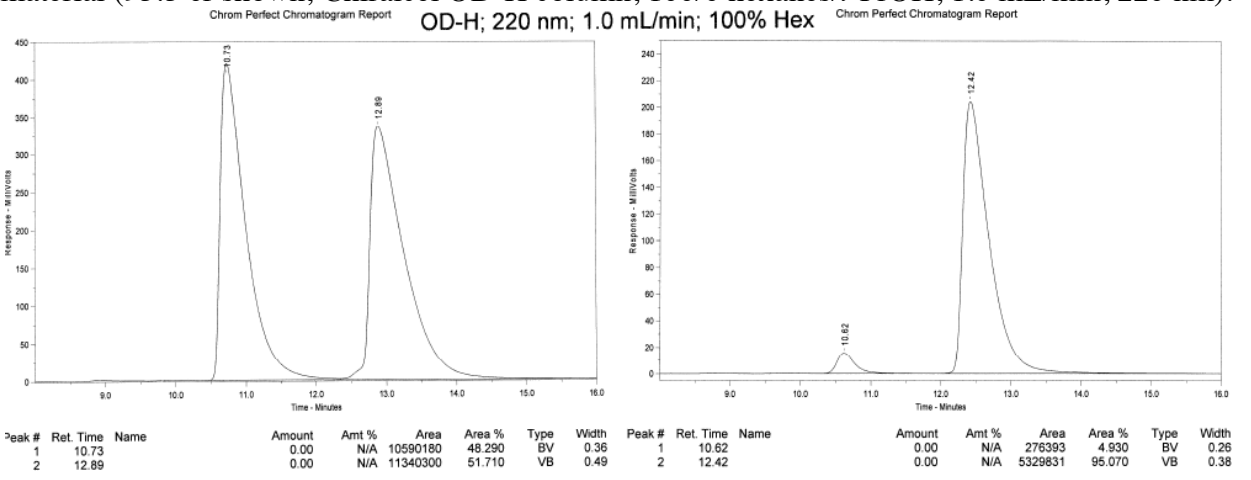
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	18.05		0.00	N/A	7474935	50.538	BV	1.94
2	23.86		0.00	N/A	7315933	49.463	VB	2.02

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	19.81		0.00	N/A	457057	4.186	BV	1.41
2	24.13		0.00	N/A	10462770	95.814	VB	2.30

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	18.05	50.5	1	19.81	4.2
2	23.86	49.5	2	24.13	95.8

Methyl (*S*)-2-(cyclohexyl(3,4-dihydro-2*H*-pyran-6-yl)methyl)acrylate (48, Scheme 10). The title compound is prepared with 2.5 mol % **9c** and 25 mol % CuCl at 60 ºC for 24 h following the same representative procedure. IR (neat) 2930 (m), 2850 (w), 1720 (s), 1670 (w), 1250 (s), 1230 (w), 1150 (m), 1120 (w), 1090 (w), 1060 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.24 (1H, dd, *J* = 1.6, 0.8 Hz), 5.80 (1H, dd, *J* = 1.6, 0.8 Hz), 4.58 (1H, t, *J* = 3.6 Hz), 3.97–3.86 (2H, m), 3.74 (3H, s), 2.99 (1H, d, *J* = 10.4 Hz), 1.99–1.94 (2H, m), 1.82–1.57 (8H, m), 1.30–1.07 (3H, m), 0.96–0.76 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.1, 140.9, 124.9, 98.0, 66.3, 52.0, 50.9, 39.2, 31.6, 31.1, 26.7, 26.5, 26.4, 22.6, 20.6; HRMS (ESI^+): $[M+H]^+$ Calcd for $C_{16}H_{25}O_3$: 265.1804, found 265.1811.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (95:5 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.73		0.00	N/A	10590180	48.290	BV	0.36
2	12.89		0.00	N/A	11340300	51.710	VB	0.49

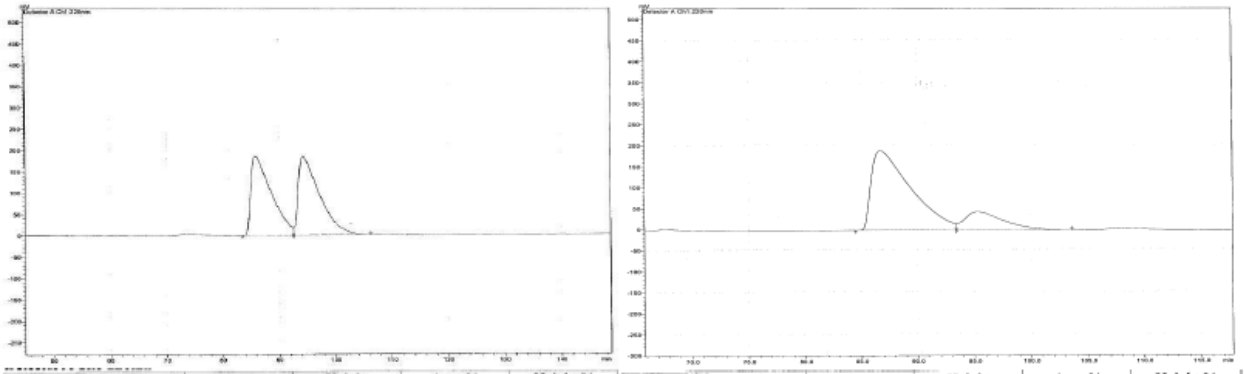
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.62		0.00	N/A	276393	4.930	BV	0.26
2	12.42		0.00	N/A	5329831	95.070	VB	0.38

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	10.73	48.3	1	10.62	4.9
2	12.89	51.7	2	12.42	95.1

■ **Synthesis of Semburin (Scheme 11):** In this section, the EAS product **50** is prepared with imidazolinium salt **9c** following the same representative procedure, as described for Table 1. **(*S*)-*tert*-Butyl((2-(3,6-dihydro-2*H*-pyran-4-yl)but-3-en-1-yl)oxy)dimethylsilane (50, Scheme 11).** IR (neat): 2955 (w), 2928 (w), 2888 (w), 2855 (w), 1472 (w), 1384 (w), 1362 (w), 1253 (m), 1100 (s), 1005 (w), 915 (w), 833 (s), 773 (s), 665 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.82–5.73 (1H, m), 5.49–5.47 (1H, m), 5.10–5.05 (2H, m), 4.13 (2H, ddd, *J* = 5.2, 2.4, 0.8 Hz), 3.81–3.72 (2H, m), 3.67 (2H, ddd, *J* = 22.0, 10.0, 6.4 Hz), 2.81 (1H, dt, *J* = 7.6, 7.6 Hz), 2.11–2.05 (2H, m), 0.88 (9H, s), 0.04 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 135.4, 121.8, 116.1, 65.7, 64.8, 64.6, 53.1, 27.2, 26.0, 18.4, –5.16, –5.22; HRMS (ESI+): Calcd for $C_{15}H_{29}O_2Si_1$ $[M+H]^+$: 269.19368, Found: 269.19423. Specific Rotation: $[\alpha]_D^{20}$ +15.8 (*c* 1.83, $CHCl_3$) for an enantiomerically enriched sample of 83:17 er. Enantiomeric purity is determined by HPLC analysis of the derived lactone (see below).

To a 2-dram vial equipped with a magnetic stir bar is charged with dihydropyran **50** (53.7 mg, 0.200 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, dichloroethane (2.0 mL) is added through a syringe. The vessel is charged with pyridinium chlorochromate (PCC, 43.1 mg, 0.200 mmol) in one portion as a solid. The vial containing the orange suspension is sealed with a teflon-lined cap and allowed to warm to 80 °C and stir for 4 h (the orange suspension turns to dark brown suspension). At this time, an additional equivalent of PCC (43.1 mg, 0.200 mmol) is added to the above mixture and the resulting dark brown suspension is sealed again and allowed to stir at 80 °C for another 4 h. The third equivalent of PCC is introduced the same way, and the reaction is quenched 4 hours later through addition of *i*PrOH (2.0 mL). The mixture is allowed to cool to ambient temperature and stir for another 30 minutes, after which time it is passed through a plug of celite eluted with EtOAc. The volatiles are removed under reduced pressure to afford a brown oil residue, which is purified by silica gel column chromatography (4:1 hexanes/EtOAc) to deliver **51** as colorless oil (44.1 mg, 0.156 mmol, 78% yield). **(*S*)-4-(1-((*tert*-Butyldimethylsilyl)oxy)but-3-en-2-yl)-5,6-dihydro-2*H*-pyran-2-one (51, Scheme 11).** IR (neat): 2954 (m), 2929 (m), 2896 (w), 2857 (m), 1727 (s), 1471 (w), 1420 (w), 1257 (m), 1220 (m), 1102 (s), 1086 (s), 1003 (w), 922 (w), 838 (s), 777 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.88–5.87 (1H, m), 5.77 (1H, ddd, *J* = 18.0, 10.4, 7.6 Hz), 5.21 (1H, ddd, *J* = 10.4, 1.2, 1.2 Hz), 5.16 (1H, ddd, *J* = 17.2, 1.2, 1.2 Hz), 4.36 (2H, t, *J* = 6.0 Hz), 3.80–3.72 (2H, m), 3.09 (1H, dt, *J* = 6.4, 6.4 Hz), 2.43 (2H, dt, *J* = 6.0, 0.8 Hz), 0.87 (9H, s), 0.04 (6H, d, *J* = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 161.2, 134.7, 118.5, 117.3, 66.3, 64.4, 52.7, 26.6, 25.9, 18.3, –5.31, –5.38; HRMS (ESI+): Calcd for $C_{15}H_{27}O_3Si_1$ $[M+H]^+$: 283.17295, Found: 283.17397. Specific Rotation: $[\alpha]_D^{20}$ +5.33 (*c* 0.912, $CHCl_3$) for an enantiomerically enriched sample of 83:17 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (82:18 er shown; Chiralcel OD-H column, 99.8/0.2 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	85.908	47105369	185748	49.877	50.242
2	94.738	47337605	183957	50.123	49.758
Total		94442974	369705	100.000	100.000

Peak#	Ret. Time	Area	Height	Area %	Height %
1	86.730	46362129	189633	81.992	81.431
2	95.304	10182242	43243	18.008	18.569
Total		56544371	232876	100.000	100.000

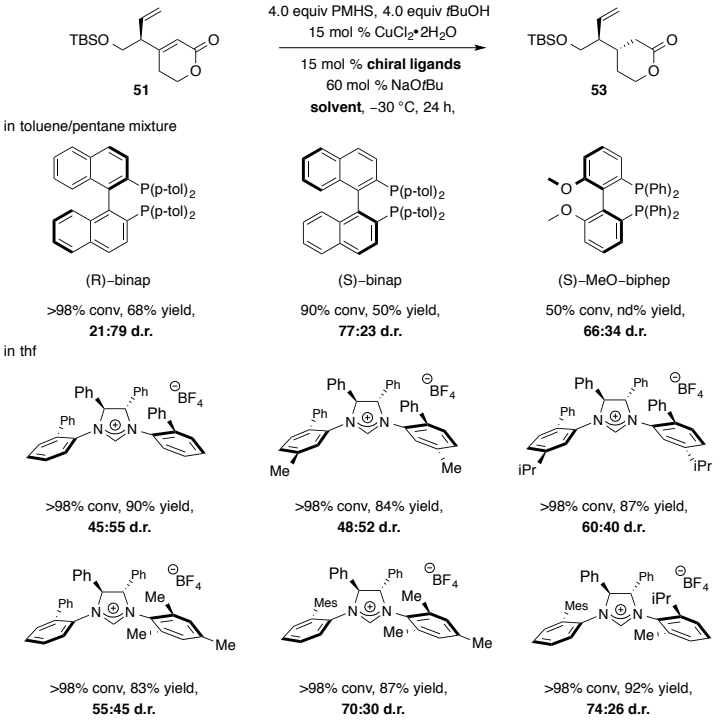
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	85.91	49.9	1	86.73	82.0
2	94.74	50.1	2	95.30	18.0

In an N_2-filled glove box, an oven-dried 1-dram vial (15 x 45 mm) with a magnetic stir bar is charged with imidazolinium salt **52** (3.2 mg, 0.0050 mmol), NaO*t*Bu (1.9 mg, 0.020 mmol) and CuCl (0.5 mg, 0.005 mmol). The vial is sealed with a cap (phenolic open top cap with a red PTFE/white silicon septum) and electrical tape before removal from the glove box. To the vial under an N_2 atmosphere is added tetrahydrofuran (thf, 0.5 mL) and the resulting suspension is allowed to stir at 22 °C for one hour. The suspension turns from off-white to light yellow during catalyst formation. Poly(methylhydrosiloxane) (PMHS, 24.1 mg, 0.400 mmol) is introduced into the reaction vessel through a micro-syringe (the light yellow suspension turns to orange solution immediately). Meanwhile, in a separate vial, lactone **51** (28.2 mg, 0.100 mmol) and *t*-BuOH (29.6 mg, 0.400 mmol) are weighted out and the vial is sealed and purged with N_2 flow for 10 min before thf (0.5 mL) is added through a syringe. Both vials are allowed to cool to –50 °C in a dry ice/acetone bath and the substrate solution is transferred through a syringe to the vessel that contains the in situ-formed catalyst. The resulting bright yellow solution is allowed to stir at –50 °C for an additional 24 h. The mixture is then passed through a short plug of silica gel eluted with Et_2O when it is still cold. The filtrate is concentrated under reduced pressure to provide a yellow oil residue, which is purified by silica gel column chromatography (4:1 hexanes/EtOAc) to afford product **53** as colorless oil (26.2 mg, 0.0921 mmol, 92% yield). **(*S*)-4-((*S*)-1-((*tert*-Butyldimethylsilyl)oxy)but-3-en-2-yl)tetrahydro-2*H*-pyran-2-one (53, Scheme 11).** The compound is characterized in the presence of 22% minor diastereomer. IR (neat): 2954 (w), 2928 (w), 2897 (w), 2857 (w), 1738 (s), 1472 (w), 1401 (w), 1252 (m), 1218 (m), 1079 (s), 1001 (m), 918 (w), 834 (s), 774 (s), 666 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (1H, ddd, *J* = 17.2, 10.0, 9.6 Hz), 5.15 (1H, dd, *J* = 10.4, 1.6 Hz), 5.09 (1H, ddd, *J* = 17.2, 2.0, 0.8 Hz), 4.43–4.36 (1H, m), 4.24 (1H, ddd, *J* = 11.6, 10.8, 3.6 Hz), 3.67 (1H, dd, *J* = 10.4, 4.8 Hz), 3.59 (1H, dd, *J* =

10.4, 6.0 Hz), 2.64–2.60 (1H, m), 2.29–2.20 (2H, m), 2.10 (1H, ddd, J = 14.8, 6.0, 4.8 Hz), 1.98–1.92 (1H, m), 1.70–1.60 (1H, m), 0.87 (9H, s), 0.03 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 136.2, 118.4, 68.7, 63.8, 50.9, 33.7, 31.5, 27.2, 26.0, 18.4, –5.3, –5.4; HRMS (ESI+): Calcd for $C_{15}H_{29}O_3Si_1$ $[M+H]^+$: 285.18860, Found: 285.18790. Specific Rotation: $[\alpha]_D^{20}$ –27.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er (major diastereomer). Enantiomeric purity is determined by GLC analysis of natural product semburin (see below).

■ Screening Data for Cu-Catalyzed Enantioselective Reduction of Unsaturated Lactone with Poly(methylhydrosiloxane):

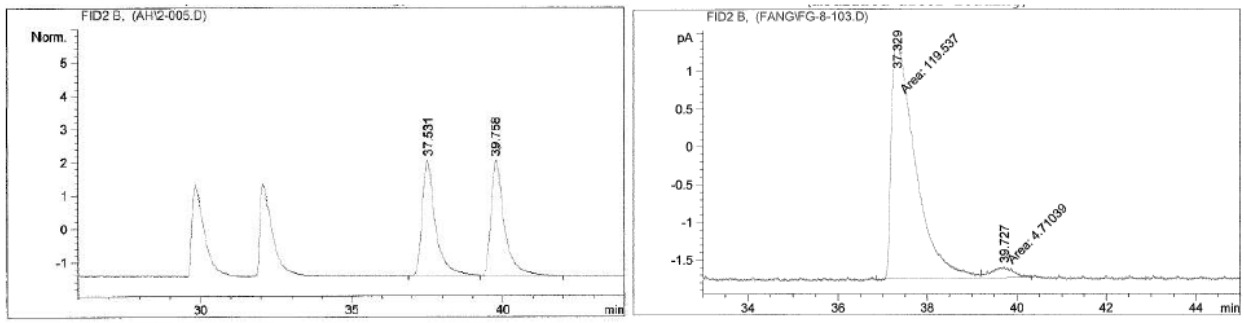
Figure S1. Screening Data of Various Phosphines and NHCs for Cu-Catalyzed Reduction



To a 2-dram vial equipped with a magnetic stir bar is charged with lactone **53** (26.2 mg, 0.0921 mmol). The vessel is evacuated and refilled with N_2 three times; under N_2 atmosphere, tetrahydrofuran (thf, 1.0 mL) is added through a syringe. The solution is allowed to cool to 0 °C in an ice bath followed by dropwise addition of tetrabutylammonium fluoride solution (184 μL, 0.184 mmol, 1.0 M in thf). The resulting light yellow solution is allowed to stir for an additional 30 minutes at 0 °C before the reaction is quenched by the addition of a saturated solution of NH_4Cl (1.0 mL). The layers are separated and the aqueous phase is washed with EtOAc (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and volatiles removed under reduced pressure to afford a light yellow oil residue, which is purified by silica gel column chromatography. A flame-dried 6-dram vial (23 x 85 mm) is charged with the alcohol product (15.7 mg, 0.0.921 mmol, >98% yield) and a stir bar. The vial is sealed with a septum and purged with N_2 flow for 10 minutes. CH_2Cl_2 (1.0 mL) is added to the vessel through a syringe. The vial is allowed to cool to –78 °C in a dry ice/acetone bath followed by dropwise

addition of diisobutyl aluminum hydride as a solution in CH_2Cl_2 (0.5 M stock solution, 202 μL, 0.101 mmol). The resulting solution is allowed to stir for one hour at –78 °C before the reaction is quenched by addition of methyl alcohol (0.5 mL). The solution is then allowed to warm to 22 °C; saturated Rochelle's salt solution (1.0 mL) is added. The mixture is allowed to stir until two clear layers formed and the aqueous layer is washed with Et_2O (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a colorless oil residue. A separate 6-dram vial (23 x 85 mm) is charged with the residue, pyridinium *p*-toluenesulfonate (25.4 mg, 0.101 mmol) and a stir bar. The vial is sealed with a septum and purged with N_2 flow for 10 minutes before 1.0 mL benzene is added through a syringe. The septum is quickly switched to a teflon-lined cap and the resulting suspension is allowed to warm to 80 °C and stir for additional 20 h, after which time the reaction is quenched by passing through a plug of silica gel eluted with Et_2O. The filtrate is concentrated under reduced pressure to afford a colorless oil residue, which is purified by preparative thin-layer chromatography to separate the diastereomers (100% CH_2Cl_2), furnishing the desired natural product as colorless oil (9.2 mg, 0.060 mmol, 65% yield). Note: the separation of diastereomers can be tedious. Usually the first half of the TLC band is collected and the second half is resubjected to preparative TLC. The process is repeated two more times to maximize the yield (semburin can be volatile; minimum Et_2O should be used to retrieve the natural product and careful evaporation should be performed). **Semburin (Scheme 11).** The natural product has been previously reported and the spectral data match those described before.[15] ^{1}H NMR (500 MHz, C_6D_6): δ 5.38 (1H, ddd, *J* = 17.5, 11.0, 6.5 Hz), 5.31 (1H, d, *J* = 1.0 Hz), 4.91 (1H, ddd, *J* = 10.5, 1.5, 1.0 Hz), 4.79 (1H, ddd, *J* = 17.5, 1.5, 1.5 Hz), 4.06 (1H, dd, *J* = 12.0, 11.5 Hz), 3.73–3.66 (2H, m), 3.42–3.37 (1H, m), 2.39–2.32 (1H, m), 1.70–1.57 (3H, m), 1.36–1.25 (2H, m); ^{13}C NMR (125 MHz, C_6D_6): δ 137.8, 115.6, 92.4, 61.6, 60.3, 44.0, 30.3, 25.9, 23.9; HRMS (ESI+): Calcd for $C_9H_{15}O_2$ $[M+H]^+$: 155.10720, Found: 155.10705. Specific Rotation: $[\alpha]_D^{20}$ +1.49 (*c* 0.267, $CHCl_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (96:4 er shown; CDGTA column, 100 °C, 15 psi). The first set of racemic enantiomers corresponds to the diastereomer of semburin.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.531	MM	0.5234	108.93215	3.47582	50.00478
2	39.758	MM	0.5221	108.72426	3.47049	49.95522

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.329	MF	0.6348	119.53748	3.13850	96.20888
2	39.727	FM	0.5367	4.71039	1.46288e-1	3.79112

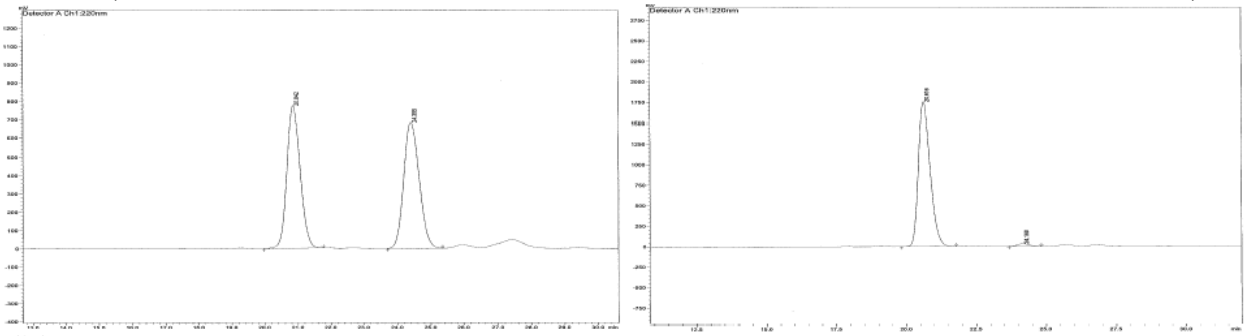
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)

1	37.53	50.0	1	37.33	96.2
2	39.76	50.0	2	39.73	3.8

■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with 1,1-Disubstituted Alkenylboron Reagents (Scheme 12):** In this section, the reactions are performed following the same representative procedure as described for Table 1. The specific differences are included within the characterization data of each compound.

***tert*-Butyl (*R*)-(3-(3-bromophenyl)-2-methylenepent-4-en-1-yl)carbamate (57a, Scheme 12).** The title compound is prepared at 60 °C for 24 h following the same general procedure. IR (neat): 3348 (w), 2977 (w), 2928 (w), 1701 (s), 1567 (w), 1508 (m), 1473 (w), 1391 (w), 1366 (m), 1271 (m), 1169 (s), 1073 (w), 1049 (w), 997 (w), 945 (m), 862 (w), 781 (w), 702 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (2H, m), 7.18 (1H, dd, *J* = 7.6, 7.6 Hz), 7.13 (1H, ddd, *J* = 7.6, 1.2, 1.2 Hz), 6.05 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz), 5.20–5.17 (2H, m), 4.99–4.94 (2H, m), 4.55 (1H, br s), 4.00 (1H, d, *J* = 7.2 Hz), 3.64 (2H, br s), 1.43 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 148.7, 146.0, 138.6, 132.9, 130.5, 128.9, 127.7, 126.1, 117.4, 111.4, 79.1, 45.3, 40.8, 28.4; HRMS (ESI+): Calcd for $C_{12}H_{14}Br_1N_1$ $[M+H–Boc]^+$: 251.03096, Found: 251.03035. Specific Rotation: $[\alpha]_D^{20}$ +67.1 (*c* 0.532, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.842	21899279	773288	50.080	53.108
2	24.395	21829267	682790	49.920	46.892
Total		43728546	1456077	100.000	100.000

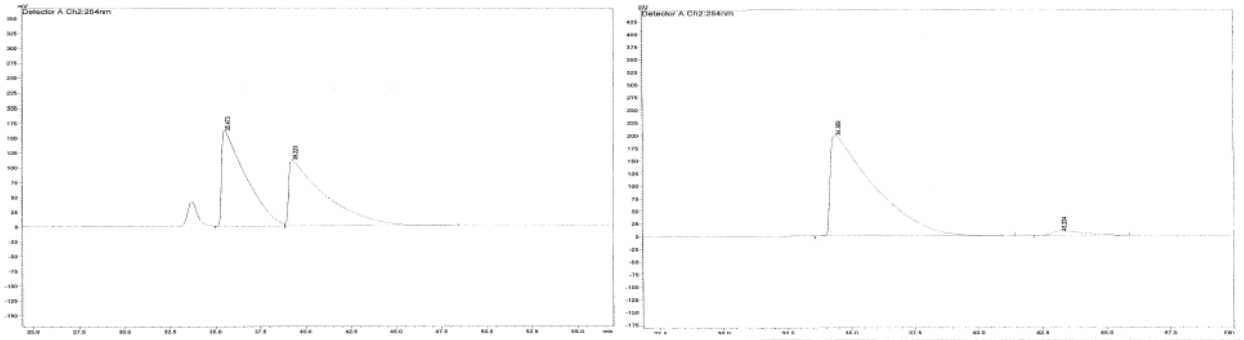
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.616	51552876	1752120	98.177	98.222
2	24.168	957452	31710	1.823	1.778
Total		52510328	1783829	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	20.84	50.1	1	20.62	98.2
2	24.40	49.9	2	24.17	1.8

(*S*)-Dimethyl(phenyl)(2-phenylpenta-1,4-dien-3-yl)silane (57b, Scheme 12). IR (neat): 3070 (w), 3052 (w), 3023 (w), 2958 (w), 2898 (w), 1616 (w), 1491 (w), 1426 (w), 1301 (w), 1249 (m), 1112 (m), 995 (w), 897 (m), 830 (s), 813 (s), 772 (s), 724 (s), 696 (s), 654 (s), 469 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.42 (2H, m), 7.36–7.18 (8H, m), 5.98 (1H, ddd, *J* = 17.6, 12.4 9.2 Hz), 5.21 (1H, dd, *J* = 0.8, 0.8 Hz), 4.98–4.93 (2H, m), 4.83 (1H, s), 3.14 (1H, d, *J* = 9.6 Hz), 0.252 (3H, s), 0.246 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 144.4, 138.9, 137.2, 134.4, 129.2, 128.2, 127.6, 127.3, 126.6, 112.6, 111.9, 42.7, –3.7, –4.4; HRMS (ESI+): Calcd for

$C_{19}H_{23}Si_1$ $[M+H]^+$: 279.15690, Found: 279.15733. Specific Rotation: $[\alpha]_D^{20}$ –144 (*c* 1.73, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 254 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.473	14992124	161331	49.612	59.098
2	39.223	15226647	111657	50.388	40.902
Total		30218771	272988	100.000	100.000

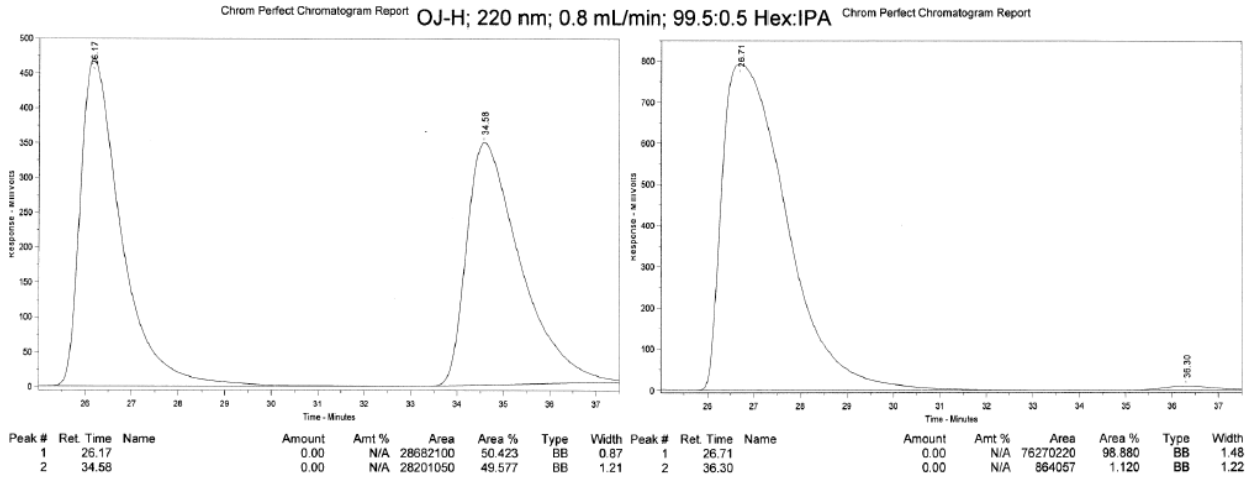
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.369	23361038	199627	96.840	95.764
2	43.204	762258	8830	3.160	4.236
Total		24123296	208457	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	35.47	49.6	1	34.37	96.8
2	39.23	50.4	2	43.20	3.2

■ **Experimental Procedure for NHC–Cu-Catalyzed Enantioselective Allylic Substitution (EAS) with Vinyl–B(pin) (Scheme 13):** In a nitrogen-filled glovebox, an oven-dried vial equipped with a magnetic stir bar is charged with imidazolinium salt **9b** (2.1 mg, 0.0025 mmol), NaOMe (8.1 mg, 0.15 mmol) and CuCl (2.5 mg, 0.025 mmol). The vial is sealed with a screw cap fitted with a Teflon septum and removed from the glovebox. Tetrahydrofuran (thf, 0.5 mL) is added and the suspension is allowed to stir for 2 h at 22 °C. A solution of methyl (*E*)-2-(((diethoxyphosphoryl)oxy)methyl)-3-(naphthalen-2-yl)acrylate (37.8 mg, 0.100 mmol) and vinylboronic acid pinacol ester (**22**, 30.8 mg, 0.200 mmol) in thf (0.4 mL) is then prepared in an oven-dried vial equipped with a septum. The solution is transferred to the vessel that contains the catalyst solution, with the vial further rinsed with thf (0.1 mL). The septum-fitted screw cap is rapidly exchanged for a standard screw cap, the vial sealed with electrical tape and allowed to warm to 60 °C and kept stirring for 20 h. After this time the mixture is allowed to cool to ambient temperature and partitioned between water and ethyl acetate. The aqueous solution is washed with more ethyl acetate (3 x 1.0 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The oil residue is purified by silica gel column chromatography (50:1 to 25:1 hexanes/Et_2O) to deliver the desired product **59a** as colorless oil (17.4 mg, 0.0690 mmol, 69% yield). **Methyl (*S*)-2-methylene-3-(naphthalen-2-yl)pent-4-enoate (59a, Scheme 13).** IR (neat): 1720 (s), 1190 (s), 1100 (s), 920 (m), 900 (m), 820 (s), 750 (s), 470 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (3H, m), 7.63 (1H, br d, *J* = 1.2 Hz), 7.46 (1H, ddd, *J* = 7.2, 7.2, 2.8 Hz), 7.43 (1H, ddd, *J* = 7.2, 6.4, 2.8 Hz), 7.33 (1H, d, *J* = 8.4, 1.2 Hz), 6.42 (1H, dd, *J* = 0.8, 0.4 Hz), 7.17 (1H, ddd, *J* = 17.2, 10.0, 6.8 Hz), 5.64 (1H, t, *J* = 1.2 Hz), 5.23 (1H, dt, *J* = 10.0, 1.2 Hz), 4.99 (1H, dt, *J* = 17.2, 1.2 Hz), 4.84 (1H, d, *J* = 6.8

Hz), 3.68 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 142.5, 138.9, 138.4, 133.6, 132.5, 128.2, 127.9, 127.7, 127.3, 127.0, 126.6, 126.1, 125.7, 117.1, 52.1, 50.3; HRMS (ESI$^+$): Calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1229, Found: 253.1233.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown; Chiralcel OJ-H column, 99.5/0.5 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



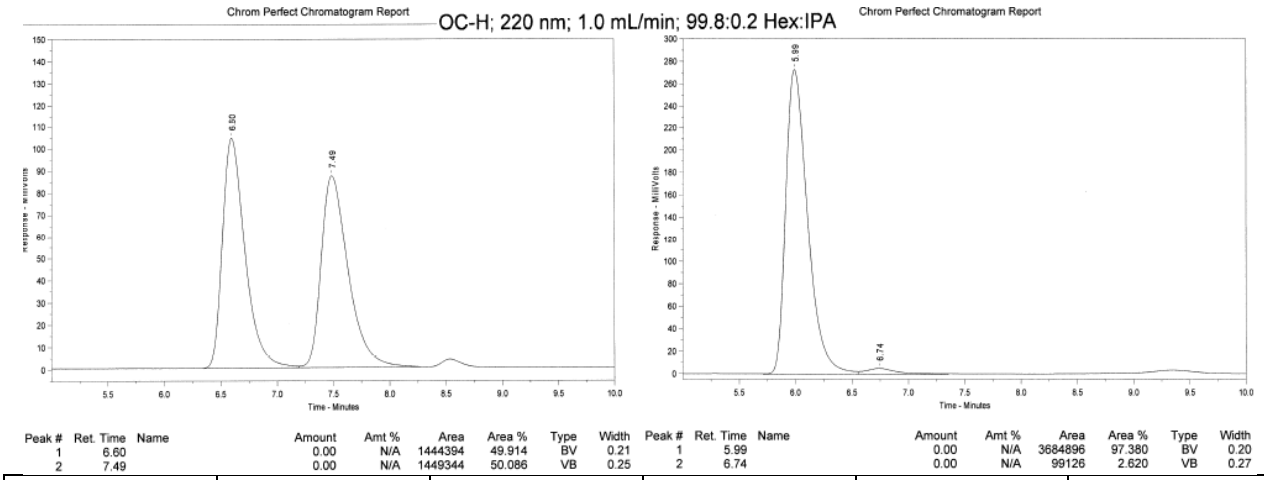
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	26.17		0.00	N/A	28682100	50.423	BB	0.87
2	34.58		0.00	N/A	28201050	49.577	BB	1.21

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	26.71		0.00	N/A	76270220	98.880	BB	1.48
2	36.30		0.00	N/A	864057	1.120	BB	1.22

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	26.17	50.4	1	26.71	98.9
2	34.58	49.6	2	36.30	1.1

Methyl (*S*)-2-methylene-3-(4-(trifluoromethyl)phenyl)pent-4-enoate (59b, Scheme 13). The title compound is prepared with 10 mol % imidazolinium salt **9b** and 10 mol % CuCl following the same representative procedure. IR (neat): 1720 (m), 1320 (s), 1250 (w), 1160 (m), 1120 (s), 1070 (s), 1000 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, J = 8.2 Hz), 7.31 (2H, d, J = 8.2 Hz), 6.42 (1H, s), 6.08 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.64 (1H, s), 5.23 (1H, br d, J = 10.0 Hz), 4.94 (1H, dt, J = 17.2, 1.2 Hz), 4.71 (1H, br d, J = 6.8 Hz), 3.69 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 145.0, 141.9, 138.2, 129.3, 128.9, 127.0, 125.6, 125.5, 125.5, 117.6, 52.2, 50.2, 24.9; HRMS (ESI$^+$): Calcd for $C_{14}H_{14}F_3O_2$ $[M+H]^+$: 271.0946, Found: 271.0939.

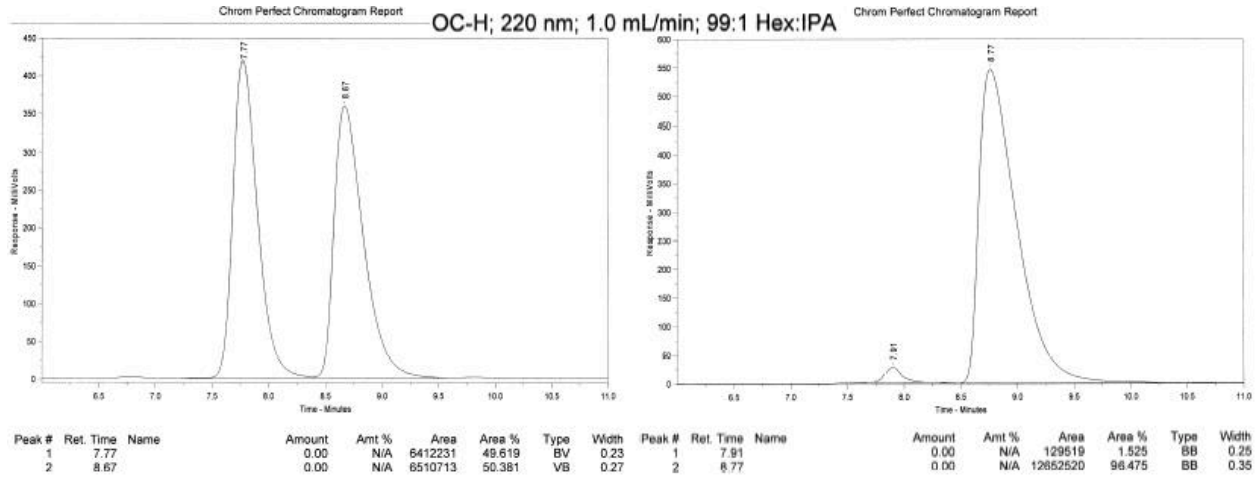
Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown; Chiralcel OC-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	6.60	49.9	1	5.99	97.4
2	7.49	50.1	2	6.74	2.6

Methyl (*S*)-3-(2-(methoxymethoxy)phenyl)-2-methylenepent-4-enoate (59c, Scheme 13). The title compound is prepared with 3.0 equiv of **22** following the same representative procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (1H, ddd, *J* = 8.0, 7.2, 1.6 Hz), 7.11 (1H, dd, 7.6, 1.6 Hz), 7.08 (1H, dd, *J* = 8.0, 1.2 Hz), 6.96 (1H, ddd, *J* = 7.6, 7.2, 1.2 Hz), 6.34 (1H, dd, *J* = 1.2, 0.8 Hz), 6.06 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz), 5.49 (1H, dd, *J* = 1.2, 0.8 Hz), 5.19 (2H, s), 5.18 (1H, dt, *J* = 10.4, 1.6 Hz), 5.11 (1H, br dd, *J* = 6.4, 0.8 Hz), 4.94 (1H, dt, *J* = 17.2, 1.6 Hz), 3.70 (3H, s), 3.46 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 154.6, 142.4, 138.4, 130.1, 128.9, 128.0, 126.2, 121.7, 116.6, 114.4, 94.4, 56.2, 52.0, 43.1; HRMS (ESI$^+$): Calcd for $C_{15}H_{19}O_4$ $[M+H]^+$: 263.1283.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (98.5:1.5 er shown; Chiralcel OC-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

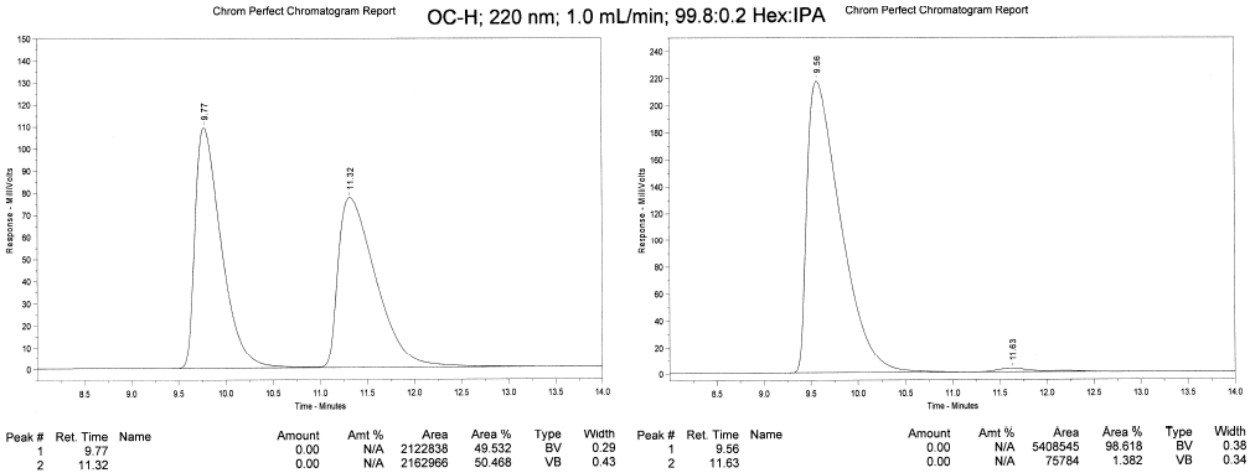


Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	7.77	49.6	1	7.91	1.5

2	8.67	50.4	2	8.77	98.5

Methyl (*S*)-2-methylene-3-phenylpent-4-enoate (59d, Scheme 13). The title compound is prepared with 10 mol % imidazolinium salt **9b** and 10 mol % CuCl following the same representative procedure. IR (neat): 1720 (s), 1440 (w), 1250 (m), 1140 (m), 920 (w), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (2H, m), 7.24–7.18 (3H, m), 6.36 (1H, dd, *J* = 1.0, 0.6 Hz), 6.10 (1H, ddd, *J* = 17.0, 10.0, 6.8 Hz), 5.58 (1H, t, *J* = 1.2 Hz), 5.18 (1H, dt, *J* = 10.4, 1.2 Hz), 4.95 (1H, dt, *J* = 17.0, 1.2 Hz), 4.67 (1H, br d, *J* = 6.8 Hz), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 142.7, 140.8, 139.0, 128.6, 128.5, 126.7, 126.4, 116.8, 52.1, 50.3; HRMS (ESI^+): $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$: 203.10720, found 203.10777.

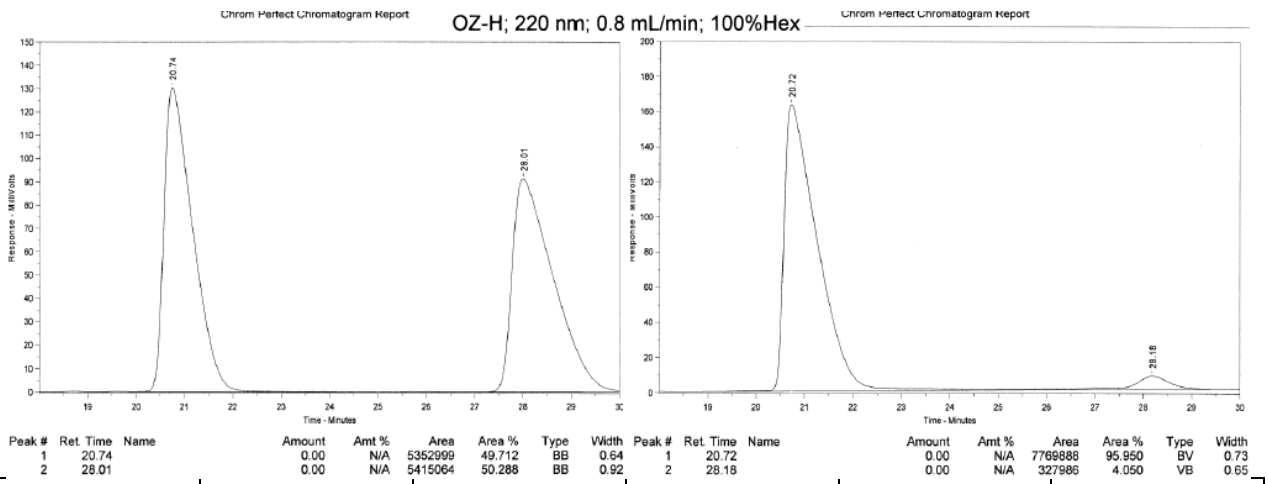
Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown; Chiralcel OC-H column, 99.8/0.2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	9.77	49.5	1	9.56	98.6
2	11.32	50.5	2	11.63	1.4

Methyl (*R*)-3-cyclohexyl-2-methylenepent-4-enoate (61, Scheme 13). The title compound is prepared with 1.0 mol % imidazolinium salt **9c** and 10 mol % CuCl following the same representative procedure. IR (neat): 2920 (m), 2850 (w), 1720 (s), 1250 (m), 1190 (w), 1160 (m), 1130 (m), 910 (w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.20 (1H, d, *J* = 1.2 Hz), 5.84 (1H, dddd, *J* = 17.6, 13.2, 9.2, 6.4 Hz), 5.51 (1H, t, *J* = 1.2 Hz), 5.03 (1H, dt, *J* = 17.6, 1.2 Hz), 5.00 (1H, dt, *J* = 13.2, 1.3 Hz), 3.75 (3H, s), 2.96 (1H, t, *J* = 9.2 Hz), 1.82–1.60 (5H, m), 1.58–1.48 (1H, m), 1.25–1.05 (3H, m), 0.93–7.90 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 142.7, 139.5, 125.0, 116.0, 52.8, 51.9, 40.3, 31.5, 30.8, 26.6, 26.5, 26.4; HRMS (ESI^+): Calcd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1542, Found: 209.1550.

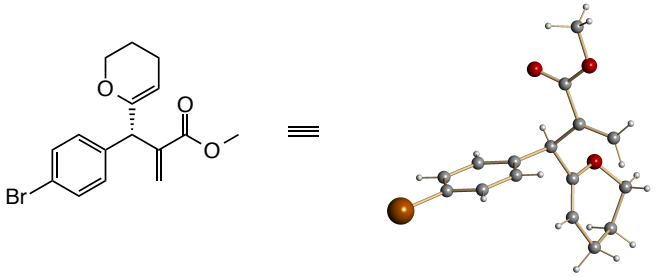
Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown; Chiralcel OZ-H column, 100/0 hexanes/*i*-PrOH, 0.8 mL/min, 220 nm).



Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	20.74	49.7	1	20.72	96.0
2	28.01	50.3	2	28.18	4.0

■ ***Determination of stereochemical identity*: Crystal Structure of 47a (Scheme 10).** The crystal structure secured for **47a** is assigned to the (*S*) enantiomer. For details, refer to the crystallography data attached.

Figure S2. Crystal Structure of Compound **47a**



■ Data for X-ray Crystallography of Compound 47a:

Table 1. Crystal data and structure refinement for $C_{16}H_{17}BrO_3$**.**

Identification code	C16H17BrO3	
Empirical formula	C16 H17 Br O3	
Formula weight	337.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.1590(3) Å	$\alpha = 90^{o}$.

	b = 9.1136(5) Å	β= 90°.
	c = 25.9848(13) Å	γ = 90°.
Volume	1458.54(13) Å^3	
Z	4	
Density (calculated)	1.536 Mg/m^3	
Absorption coefficient	2.823 mm^{-1}	
F(000)	688	
Crystal size	0.24 x 0.14 x 0.06 mm^3	
Theta range for data collection	2.37 to 28.41°.	
Index ranges	-8<=h<=8, -12<=k<=9, -34<=l<=34	
Reflections collected	26659	
Independent reflections	3643 [R(int) = 0.0216]	
Completeness to theta = 28.41°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8489 and 0.5507	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3643 / 4 / 194	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0168, wR2 = 0.0452	
R indices (all data)	R1 = 0.0176, wR2 = 0.0455	
Absolute structure parameter	0.018(6)	
Extinction coefficient	na	
Largest diff. peak and hole	0.312 and -0.469 e. Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $C_{16}H_{17}BrO_3$. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

Br(1)	9961(1)	-2636(1)	2472(1)	21(1)
O(1)	2648(2)	3595(1)	3922(1)	19(1)
O(2)	2389(2)	-1268(1)	4346(1)	23(1)
O(3)	3796(2)	-770(1)	5124(1)	19(1)
C(1)	8198(2)	-1468(1)	2909(1)	15(1)
C(2)	8992(2)	-1038(1)	3383(1)	16(1)
C(3)	7697(2)	-171(1)	3700(1)	15(1)
C(4)	5624(2)	263(1)	3545(1)	14(1)
C(5)	4869(2)	-199(1)	3066(1)	16(1)
C(6)	6131(2)	-1069(1)	2746(1)	17(1)
C(7)	4186(2)	1236(1)	3880(1)	13(1)
C(8)	4481(2)	2849(2)	3769(1)	15(1)
C(9)	6248(2)	3487(2)	3575(1)	18(1)
C(10)	6390(2)	5100(2)	3471(1)	22(1)
C(11)	4170(3)	5818(2)	3537(1)	26(1)
C(12)	2997(2)	5142(2)	3990(1)	22(1)
C(13)	4457(2)	921(1)	4452(1)	14(1)
C(14)	5490(2)	1786(2)	4779(1)	20(1)
C(15)	3433(2)	-477(1)	4626(1)	15(1)
C(16)	2881(2)	-2118(2)	5318(1)	19(1)

Table 3. Bond lengths [Å] and angles [^{o}] for $C_{16}H_{17}BrO_3$.

Br(1)-C(1)	1.8983(12)
O(1)-C(8)	1.3761(15)
O(1)-C(12)	1.4372(16)

O(2)-C(15)	1.2079(16)
O(3)-C(15)	1.3404(14)
O(3)-C(16)	1.4428(16)
C(1)-C(2)	1.3806(17)
C(1)-C(6)	1.3905(17)
C(2)-C(3)	1.3925(17)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3955(17)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3930(16)
C(4)-C(7)	1.5256(18)
C(5)-C(6)	1.3877(17)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.5094(18)
C(7)-C(13)	1.5228(17)
C(7)-H(7)	0.993(13)
C(8)-C(9)	1.3327(18)
C(9)-C(10)	1.4976(19)
C(9)-H(9)	0.937(13)
C(10)-C(11)	1.525(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.511(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900

C(13)-C(14)	1.3235(18)
C(13)-C(15)	1.4918(17)
C(14)-H(14A)	0.962(13)
C(14)-H(14B)	0.971(13)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

C(8)-O(1)-C(12)	113.41(11)
C(15)-O(3)-C(16)	116.28(10)
C(2)-C(1)-C(6)	121.51(12)
C(2)-C(1)-Br(1)	119.31(9)
C(6)-C(1)-Br(1)	119.18(9)
C(1)-C(2)-C(3)	118.99(11)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	120.97(12)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	118.51(12)
C(5)-C(4)-C(7)	119.39(11)
C(3)-C(4)-C(7)	122.10(11)
C(6)-C(5)-C(4)	121.40(12)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.62(11)
C(5)-C(6)-H(6)	120.7
C(1)-C(6)-H(6)	120.7

C(8)-C(7)-C(13)	110.84(10)
C(8)-C(7)-C(4)	112.84(10)
C(13)-C(7)-C(4)	112.55(10)
C(8)-C(7)-H(7)	103.9(9)
C(13)-C(7)-H(7)	106.5(9)
C(4)-C(7)-H(7)	109.6(9)
C(9)-C(8)-O(1)	124.29(12)
C(9)-C(8)-C(7)	126.52(12)
O(1)-C(8)-C(7)	109.14(10)
C(8)-C(9)-C(10)	122.96(13)
C(8)-C(9)-H(9)	118.5(10)
C(10)-C(9)-H(9)	118.5(10)
C(9)-C(10)-C(11)	110.39(12)
C(9)-C(10)-H(10A)	109.6
C(11)-C(10)-H(10A)	109.6
C(9)-C(10)-H(10B)	109.6
C(11)-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	108.1
C(12)-C(11)-C(10)	109.96(12)
C(12)-C(11)-H(11A)	109.7
C(10)-C(11)-H(11A)	109.7
C(12)-C(11)-H(11B)	109.7
C(10)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
O(1)-C(12)-C(11)	112.07(12)
O(1)-C(12)-H(12A)	109.2
C(11)-C(12)-H(12A)	109.2
O(1)-C(12)-H(12B)	109.2

C(11)-C(12)-H(12B)	109.2
H(12A)-C(12)-H(12B)	107.9
C(14)-C(13)-C(15)	121.16(11)
C(14)-C(13)-C(7)	124.62(12)
C(15)-C(13)-C(7)	114.22(10)
C(13)-C(14)-H(14A)	119.9(10)
C(13)-C(14)-H(14B)	123.3(10)
H(14A)-C(14)-H(14B)	116.7(14)
O(2)-C(15)-O(3)	123.34(12)
O(2)-C(15)-C(13)	123.58(11)
O(3)-C(15)-C(13)	113.08(11)
O(3)-C(16)-H(16A)	109.5
O(3)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(3)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for $C_{16}H_{17}BrO_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	19(1)	23(1)	20(1)	-5(1)	5(1)	1(1)
O(1)	18(1)	14(1)	25(1)	-1(1)	3(1)	3(1)
O(2)	29(1)	22(1)	18(1)	2(1)	-5(1)	-9(1)

O(3)	26(1)	16(1)	14(1)	3(1)	-2(1)	-4(1)
C(1)	18(1)	12(1)	16(1)	0(1)	5(1)	0(1)
C(2)	15(1)	16(1)	17(1)	3(1)	0(1)	0(1)
C(3)	17(1)	15(1)	13(1)	0(1)	-2(1)	-1(1)
C(4)	16(1)	12(1)	15(1)	2(1)	0(1)	-1(1)
C(5)	16(1)	16(1)	17(1)	2(1)	-2(1)	0(1)
C(6)	20(1)	17(1)	12(1)	0(1)	-2(1)	-2(1)
C(7)	14(1)	13(1)	13(1)	-1(1)	-1(1)	0(1)
C(8)	17(1)	14(1)	13(1)	-1(1)	-1(1)	2(1)
C(9)	20(1)	15(1)	17(1)	-1(1)	3(1)	1(1)
C(10)	29(1)	18(1)	20(1)	0(1)	7(1)	-4(1)
C(11)	36(1)	14(1)	26(1)	2(1)	4(1)	3(1)
C(12)	27(1)	12(1)	28(1)	-2(1)	6(1)	3(1)
C(13)	14(1)	14(1)	14(1)	1(1)	1(1)	1(1)
C(14)	25(1)	19(1)	17(1)	2(1)	-2(1)	-4(1)
C(15)	14(1)	16(1)	15(1)	1(1)	1(1)	2(1)
C(16)	20(1)	17(1)	20(1)	4(1)	2(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{16}H_{17}BrO_3$.

	x	y	z	U(eq)
H(2)	10402	-1330	3491	19
H(3)	8232	130	4026	18
H(5)	3460	89	2957	19
H(6)	5594	-1385	2422	20
H(7)	2640(20)	1050(17)	3797(6)	16
H(9)	7470(20)	2903(17)	3508(6)	21
H(10A)	6918	5264	3116	27
H(10B)	7439	5555	3712	27
H(11A)	4352	6885	3595	31
H(11B)	3300	5680	3220	31
H(12A)	3859	5305	4306	27
H(12B)	1578	5637	4035	27
H(14A)	6200(30)	2660(16)	4657(6)	24
H(14B)	5680(30)	1549(18)	5141(5)	24
H(16A)	1369	-1950	5420	28
H(16B)	3718	-2447	5618	28
H(16C)	2935	-2871	5049	28

Table 6. Torsion angles [°] for $C_{16}H_{17}BrO_3$.

C(6)-C(1)-C(2)-C(3)	-0.76(19)
Br(1)-C(1)-C(2)-C(3)	179.44(9)
C(1)-C(2)-C(3)-C(4)	0.05(19)
C(2)-C(3)-C(4)-C(5)	0.35(19)
C(2)-C(3)-C(4)-C(7)	-178.85(12)
C(3)-C(4)-C(5)-C(6)	-0.04(18)
C(7)-C(4)-C(5)-C(6)	179.17(11)
C(4)-C(5)-C(6)-C(1)	-0.64(19)
C(2)-C(1)-C(6)-C(5)	1.05(19)
Br(1)-C(1)-C(6)-C(5)	-179.14(9)
C(5)-C(4)-C(7)-C(8)	-88.14(13)
C(3)-C(4)-C(7)-C(8)	91.04(14)
C(5)-C(4)-C(7)-C(13)	145.49(11)
C(3)-C(4)-C(7)-C(13)	-35.32(16)
C(12)-O(1)-C(8)-C(9)	-16.48(17)
C(12)-O(1)-C(8)-C(7)	161.12(11)
C(13)-C(7)-C(8)-C(9)	101.60(14)
C(4)-C(7)-C(8)-C(9)	-25.67(17)
C(13)-C(7)-C(8)-O(1)	-75.94(12)
C(4)-C(7)-C(8)-O(1)	156.79(10)
O(1)-C(8)-C(9)-C(10)	-3.6(2)
C(7)-C(8)-C(9)-C(10)	179.20(12)
C(8)-C(9)-C(10)-C(11)	-8.96(19)
C(9)-C(10)-C(11)-C(12)	38.75(16)
C(8)-O(1)-C(12)-C(11)	48.46(15)
C(10)-C(11)-C(12)-O(1)	-60.51(16)

C(8)-C(7)-C(13)-C(14)	-20.91(17)
C(4)-C(7)-C(13)-C(14)	106.52(14)
C(8)-C(7)-C(13)-C(15)	158.81(10)
C(4)-C(7)-C(13)-C(15)	-73.76(13)
C(16)-O(3)-C(15)-O(2)	0.64(18)
C(16)-O(3)-C(15)-C(13)	-179.13(10)
C(14)-C(13)-C(15)-O(2)	176.47(13)
C(7)-C(13)-C(15)-O(2)	-3.27(17)
C(14)-C(13)-C(15)-O(3)	-3.76(17)
C(7)-C(13)-C(15)-O(3)	176.50(10)

Symmetry transformations used to generate equivalent atoms:

References:

(1) (a) Kacprzynski, M. A.; May T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *49*, 4554–4558. (b) Lee, Y.; Akiyama, K.; Gillingham, D. G.; Brown, M. K.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2008**, *130*, 446–447. (c) Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 11625–11633. (d) Akiyama, K.; Gao, F.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 419–423. (e) Jung, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 1490–1493. (f) Dabrowski, J. A.; Haeffner, F.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 7694–7699 and references cited therein.
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(9) Lee, K-s.; Hoveyda, A. H. *J. Org. Chem.* **2009**, *74*, 4455–4462.
(10) Martin, D.; Kehrli, S.; d'Augustin, M.; Clavier, H.; Mauduit, M.; Alexakis, A. *J. Am. Chem. Soc.* **2006**, *128*, 8416–8417.
(11) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1097–1100.
(12) (a) Sy, L.-K.; Brown, G. D. *Phytochemistry* **2001**, *58*, 1159–1166. (b) Araki, S.; Kambe, S.; Kameda, K.; Hirashita, T. *Synthesis* **2003**, *5*, 751–754.
(13) (a) Ref 1d. (b) Iida, Y.; Oh, K-B.; Saito, M.; Matsuoka, H.; Kurata, H.; Natsume, M.; Abe, H. *J. Agric. Food. Chem.* **1999**, *47*, 584–587. (c) Jeong, S-J.; Higuchi, R.; Ono, M.; Kuwano, M.; Kim, Y-C.; Miyamoto, T. *Biol. Pharm. Bull.* **2003**, *26*, 1721–1724.
(14) Huang, C.; Liu, B. *Chem. Commun.* **2010**, *46*, 5280–5282.
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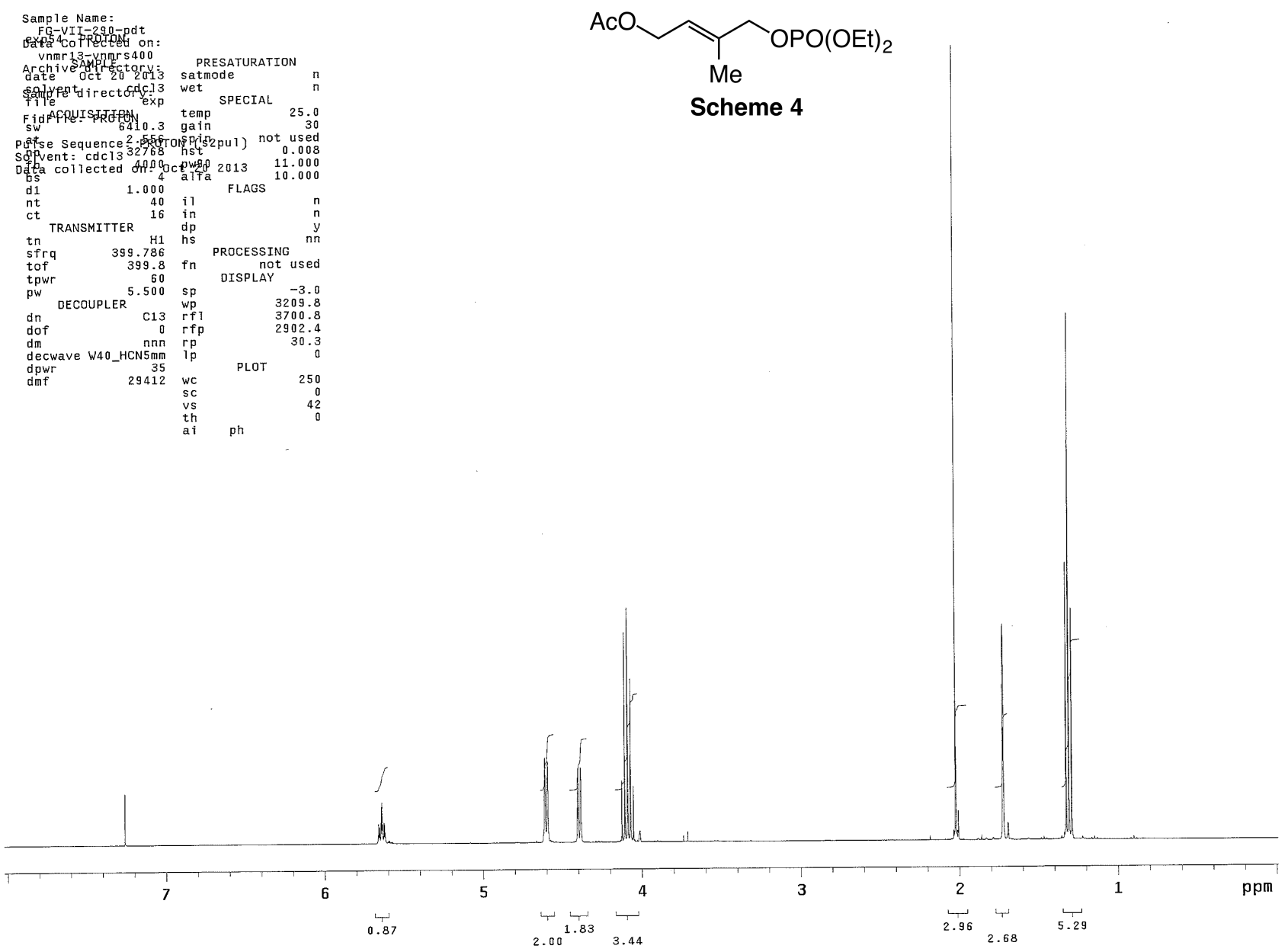
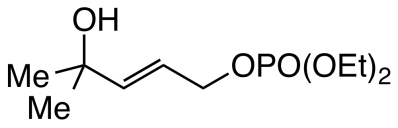

Sample Name:
FG-VII-290-pdt
exp54 PROTON
Data Collected on:
vnmr13-vnmrs400
Archive directory:
SAMPLE
date Oct 20 2013
solvent cdcl3
Sample directory:
file exp
ACQUISITION
Fidfile: PROTON
sw 6410.3
at 2.556
np 32768
fb 4000
bs 4
d1 1.000
nt 40
ct 16
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_HCN5mm
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin not used
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 20 2013
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -3.0
wp 3209.8
rfl 3700.8
rfp 2902.4
rp 30.3
lp 0
PLOT
wc 250
sc 0
vs 42
th 0
ai ph
AcO
OPO(OEt)2
Me
7
6
5
4
3
2
1
ppm
0.87
2.00
1.83
3.44
2.96
2.68
5.29

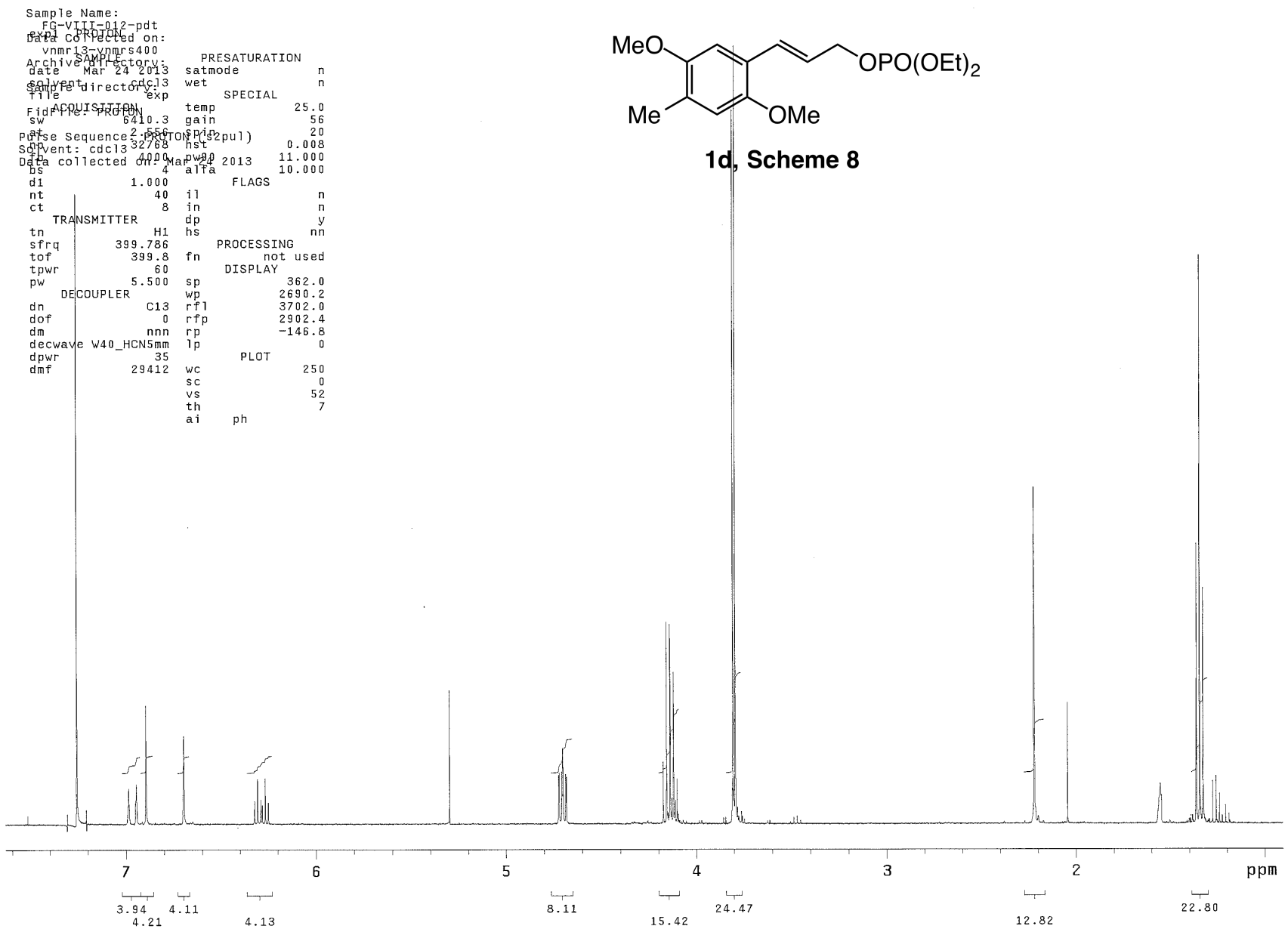
Scheme 4

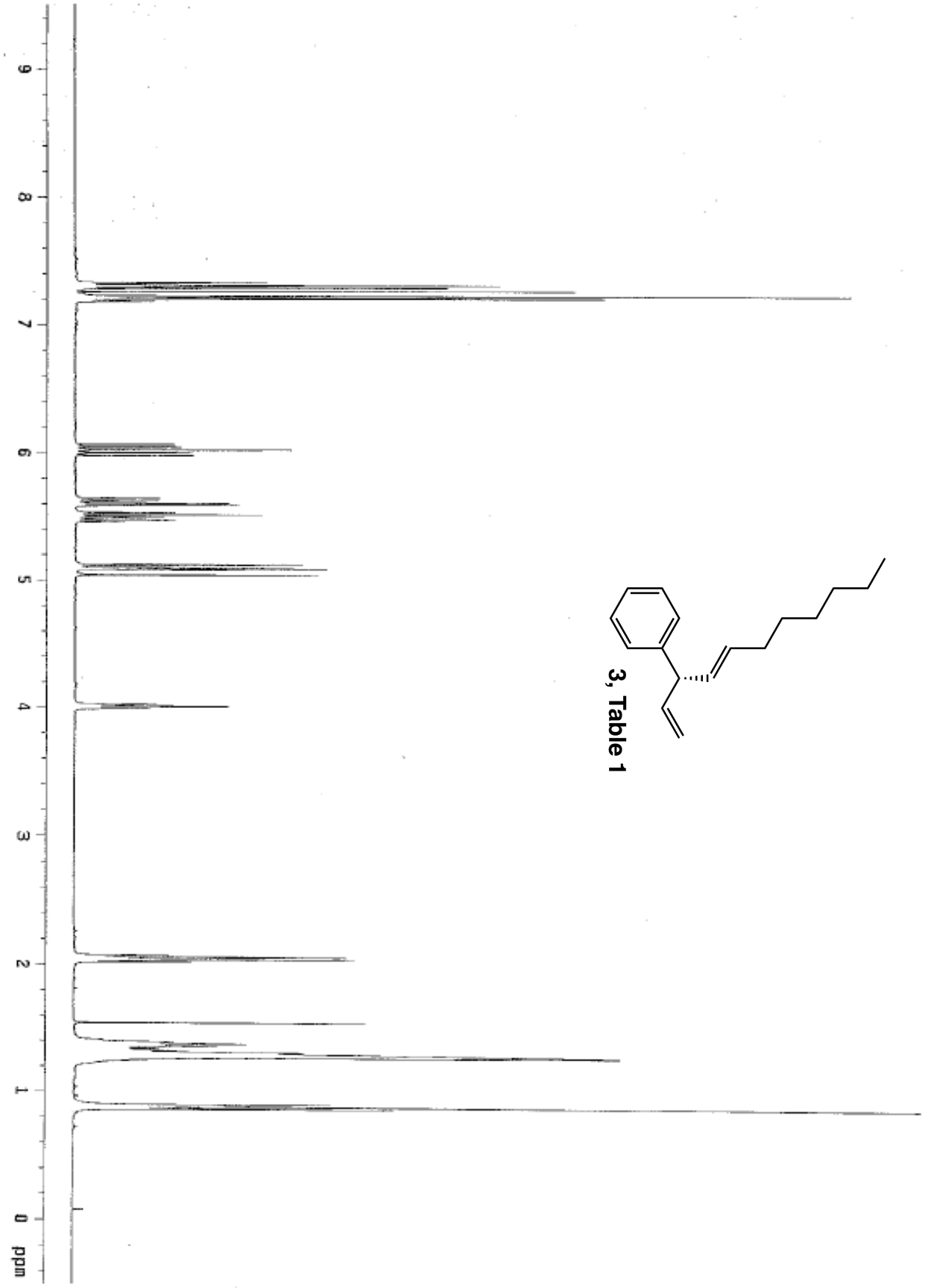
```
Sample Name:
  FG-VIII-040-pdt
  exp4  PROTON
Data collected on:
  vnmr13-vnmrs400
Archive directory:
    SAMPLE
Sample directory:
  exp4
File:
    ACQUISITION
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 20 2013
```

date	Oct 20 2013	satmode	n
solvent	cdcl3	wet	n
file	exp	SPECIAL	
ACQUISITION		temp	25.0
sw	6410.3	gain	30
at	2.556	spin	not used
np	32768	hst	0.008
fb	4000	pw90	11.000
bs	4	alfa	10.000
d1	1.000	FLAGS	
nt	40	il	n
ct	16	in	n
TRANSMITTER		dp	y
tn	H1	hs	nn
sfrq	399.786	PROCESSING	
tof	399.8	fn	not used
tpwr	60	DISPLAY	
pw	5.500	sp	11.5
DECOUPLER		wp	3199.7
dn	C13	rfl	3700.8
dof	0	rfp	2902.4
dm	nnn	rp	28.9
decwave	W40_HCN5mm	lp	0
dpwr	35	PLOT	
dmf	29412	wc	250
		sc	0
		vs	51
		th	7
		ai	ph

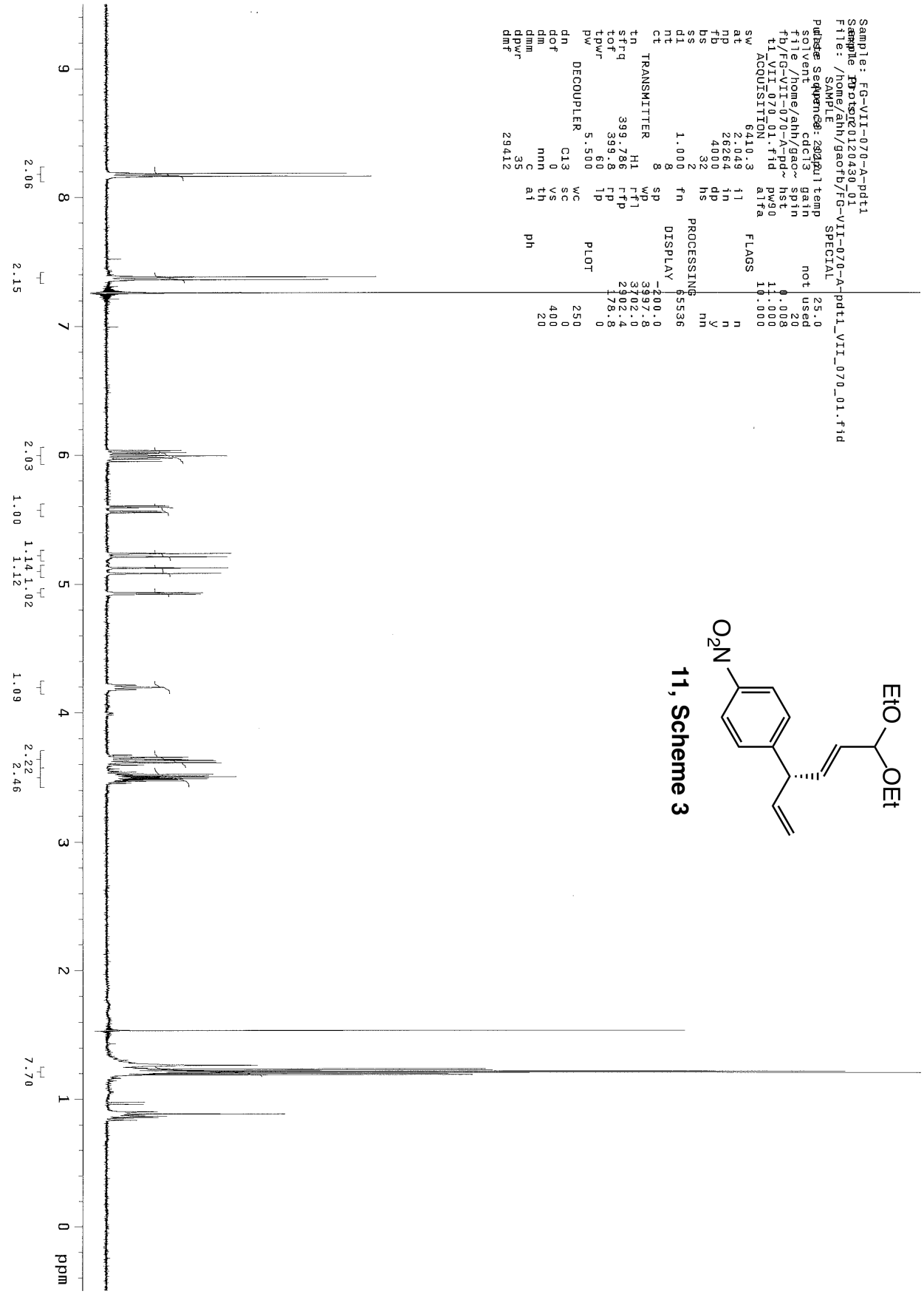


39, Eq. 1


Sample Name:
FG-VIII-012-pdt
exp1 PROTON
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
File exp
Fidfile: PROTON
Pulse Sequence: PROTON(s2pul)
Solvent: cdcl3
Data collected on: Mar 24 2013
SAMPLE
date Mar 24 2013
solvent cdcl3
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 4
d1 1.000
nt 40
ct 8
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_HCN5mm
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 56
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 362.0
wp 2690.2
rfl 3702.0
rfp 2902.4
rp -146.8
lp 0
PLOT
wc 250
sc 0
vs 52
th 7
ai ph
MeO
OPO(OEt)2
Me
OMe
1d, Scheme 8
7
6
5
4
3
2
ppm
3.94
4.11
4.21
4.13
8.11
15.42
24.47
12.82
22.80



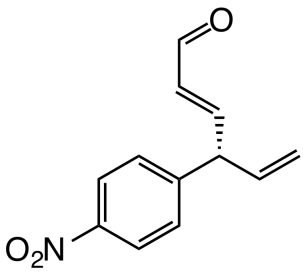
3, Table 1


Sample: FG-VII-070-A-pdt1
Sample ID: tsoc20120430_01
File: /home/ahh/gaofb/FG-VII-070-A-pdt1_VII_070_01.fid
SAMPLE
SPECIAL
solvent cdcl3 gain not used 20
file /home/ahh/gao~ spin 0.008
fb/FG-VII-070-A-pd~ hst 11.000
t1_VII_070_01.fid pw90 10.000
ACQUISITION FLAGS
sw 6410.3 fl n
at 2.049 in n
np 26264 dp y
fb 4000 hs nn
bs 32
ss 2 PROCESSING
d1 1.000 fn 65536
nt 8 DISPLAY
ct 8 sp -200.0
TRANSMITTER wp 3997.8
tn H1 rfl 3702.0
sfrq 399.786 rfp 2902.4
tof 399.8 rp 178.8
tpwr 60 lp 0
pw 5.500 PLOT
DECOUPLER wc 250
dn C13 sc 0
dof 0 vs 400
dm nnn th 20
dmm c ai
dmf 35 ph
dpwr
dmf 29412
EtO
OEt
O2N
11, Scheme 3
ppm
2.06
2.15
2.03
1.00
1.14
1.02
1.12
1.09
2.22
2.46
7.70

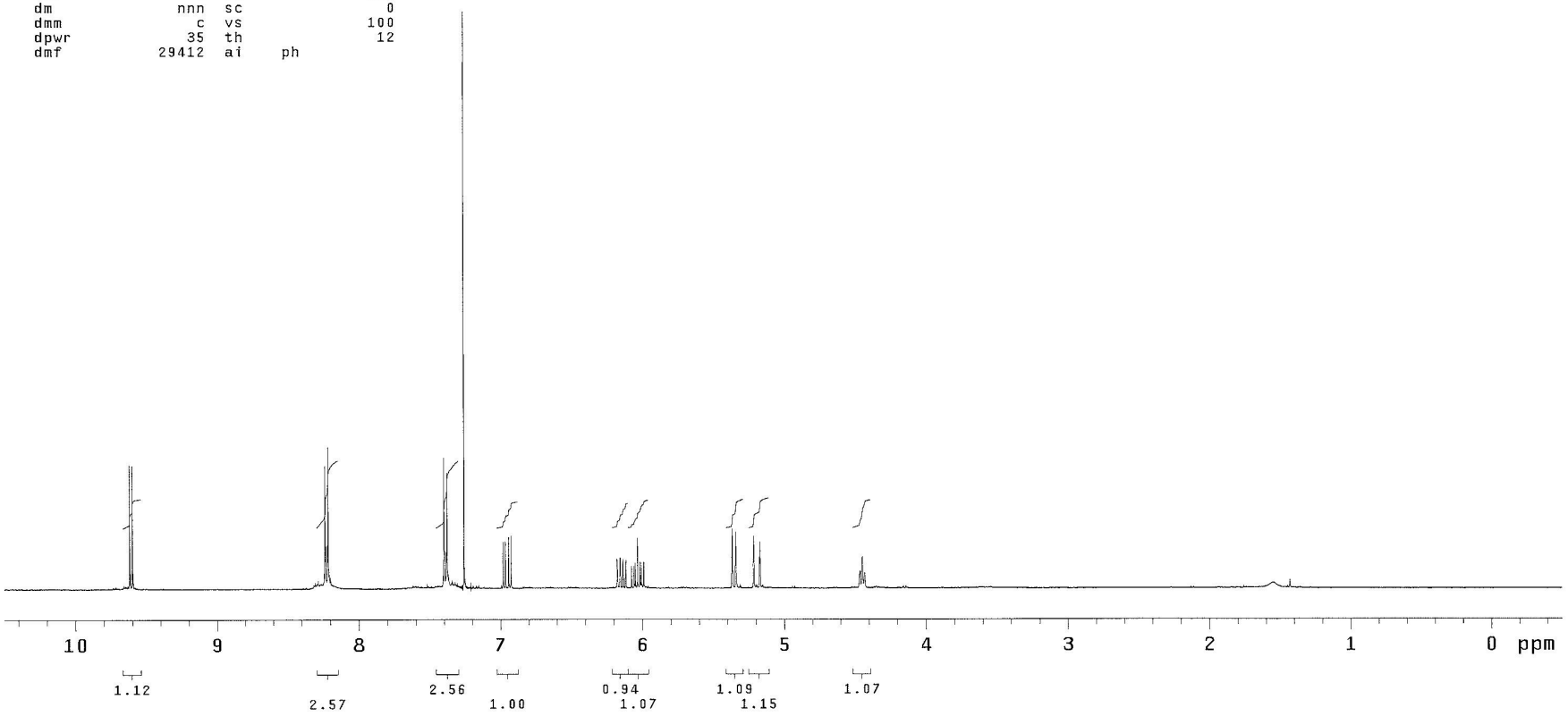
Sample: FG-VII-070-B-pdt2
Exp1 exp Proton

Pulse Sequence: s2pul SAMPLE SPECIAL

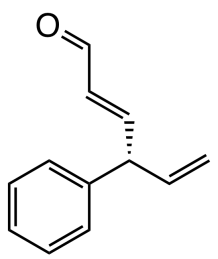
date	Apr 30 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	20	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.0
sfrq	399.786	wp	4397.5
tof	399.8	rfl	3701.8
tpwr	60	rfp	2902.4
pw	5.500	rp	-175.2
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	100
dpwr	35	th	12
dmf	29412	ai ph	



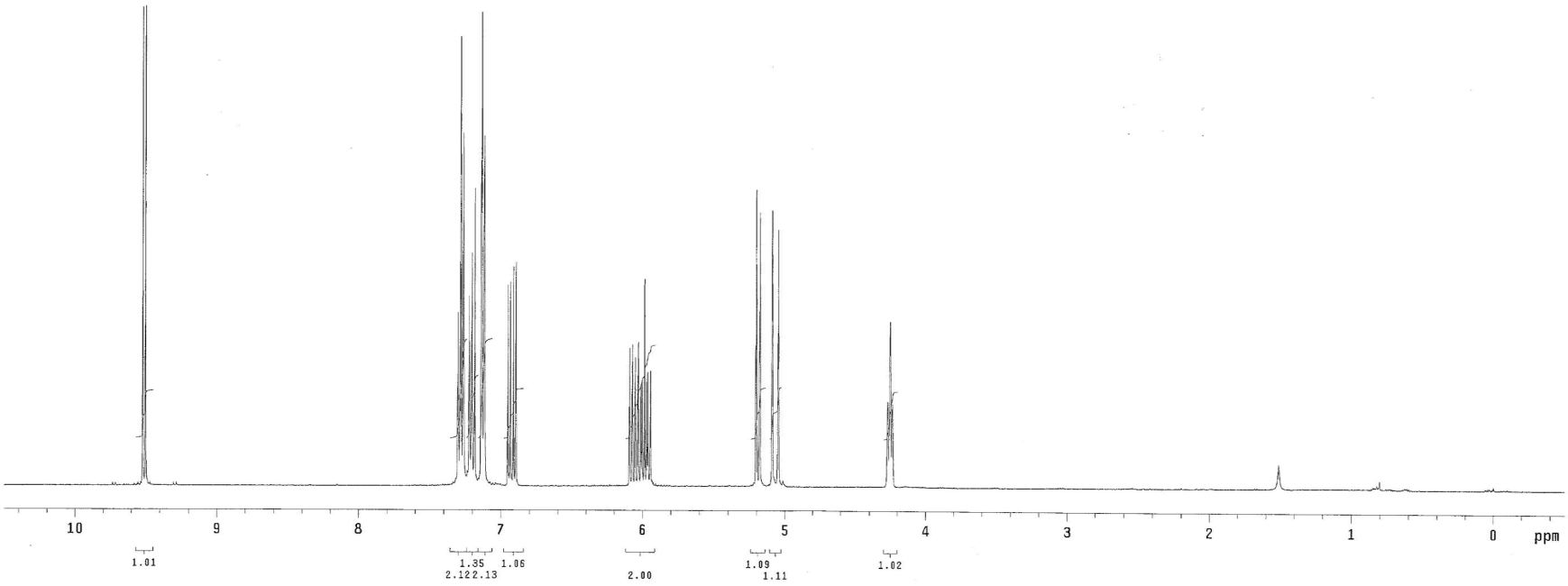
12b, Scheme 3

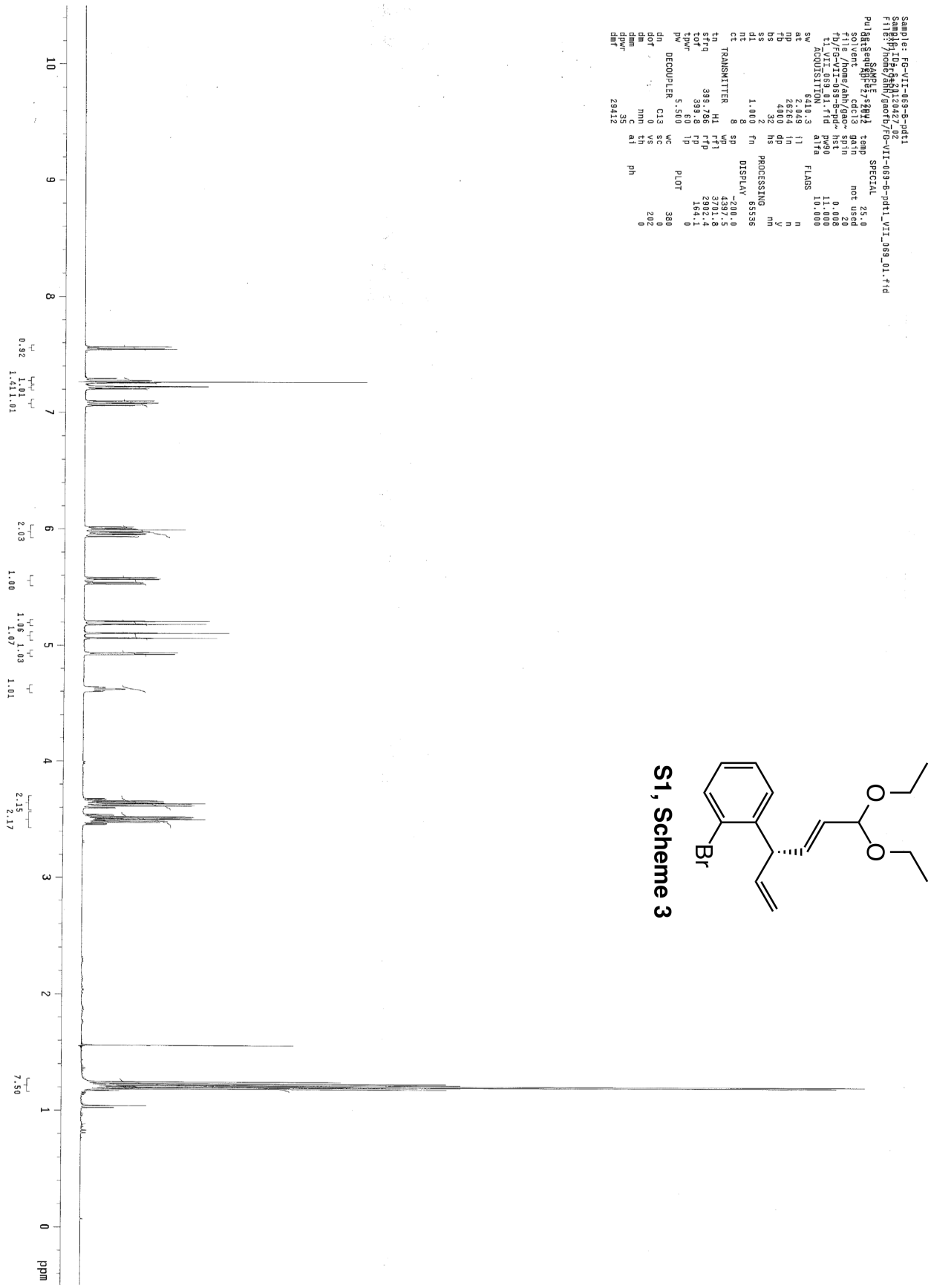


```
Sample: FG-VII-067-A-pdt2
Sample ID: ps_20120426_02
File: /home/ahh/gaofb/FG-VII-067-A-pdt2_VII_067_01.fid
Pulse Sequence: s2pul
        SAMPLE              SPECIAL
   date  Apr 26 2012   temp          25.0
   solvent      cdcl3   gain       not used
   file /home/ahh/gao~  spin            20
   fb/FG-VII-067-A-pd~  hst          0.008
    t2_VII_067_01.fid   pw90         11.000
      ACQUISITION       alfa         10.000
   sw          6410.3          FLAGS
   at             2.049  il                n
   np           26264    in                n
   fb            4000    dp                y
   bs              32    hs               nn
   ss               2        PROCESSING
   d1           1.000    fn            65536
   nt               8      DISPLAY
   ct               8    sp           -199.9
      TRANSMITTER       wp           4397.5
   tn              H1    rfl           830.0
   sfrq       399.786    rfp               0
   tof          399.8    rp             91.3
   tpwr            60    lp                0
   pw           5.500       PLOT
       DECOUPLER         wc              380
   dn              C13    sc                0
   dof               0    vs              400
   dm              nnn    th                1
   dmm               c    ai    ph
   dpwr             35
   dmf           29412
```

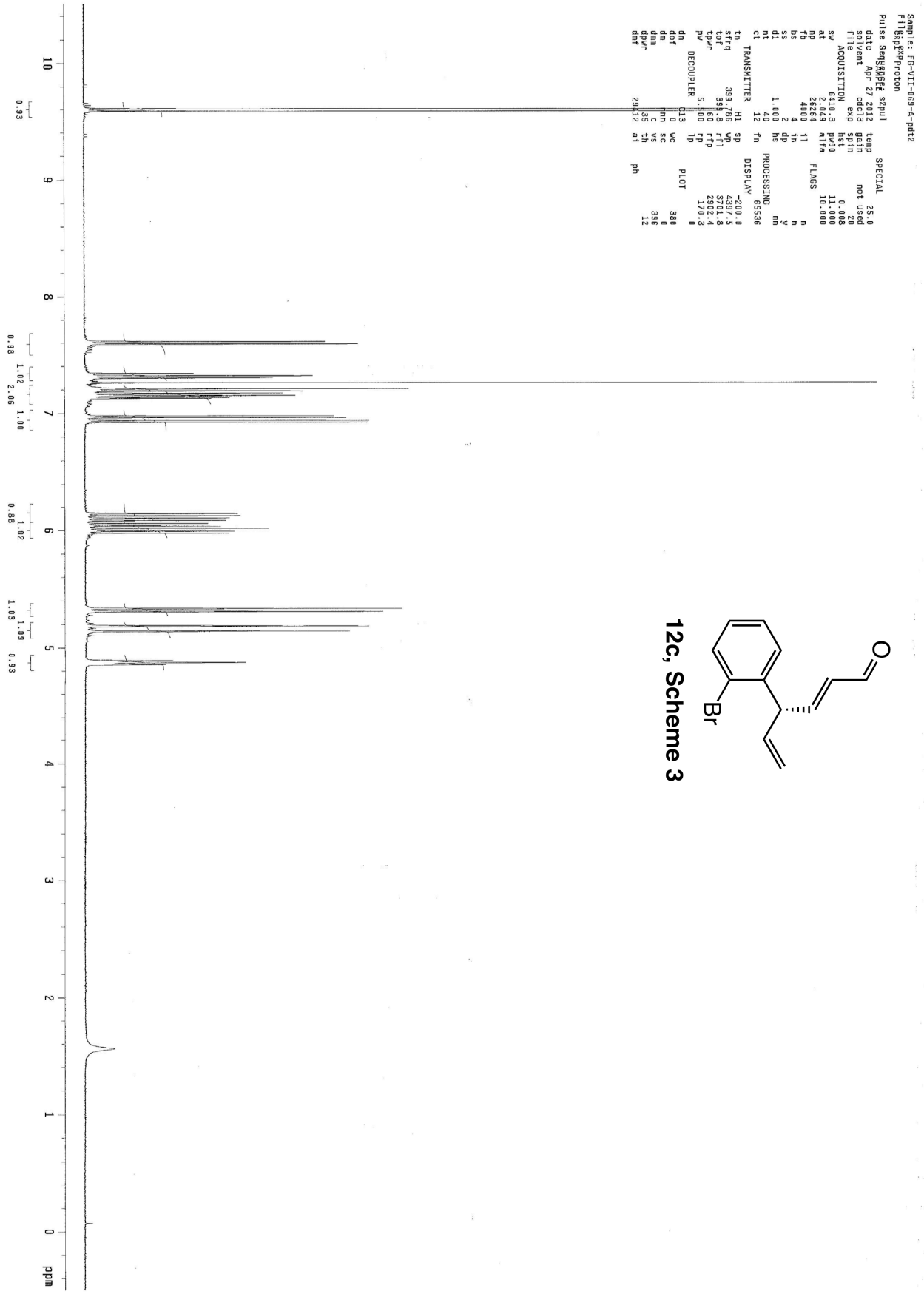


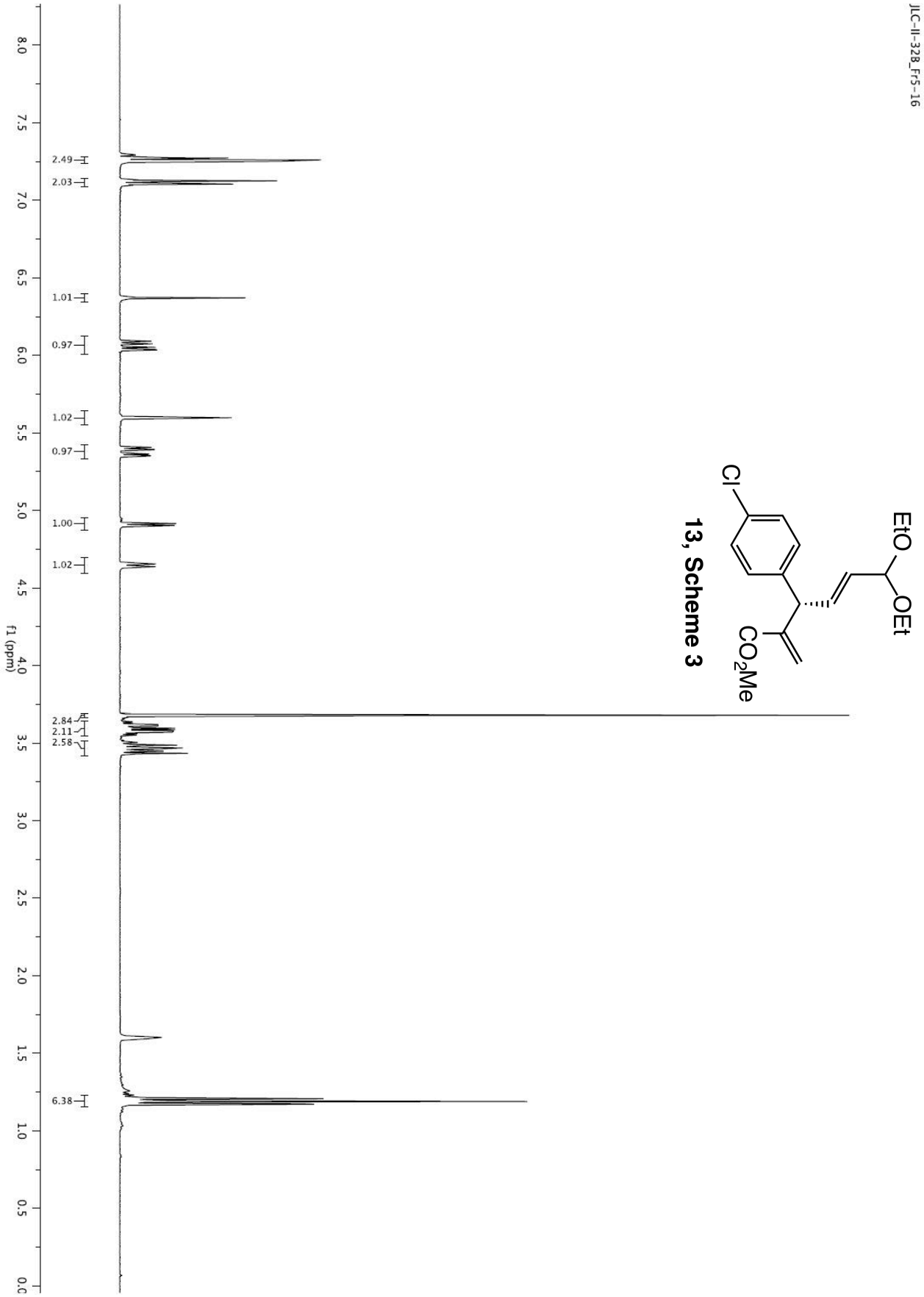
12a, Scheme 3

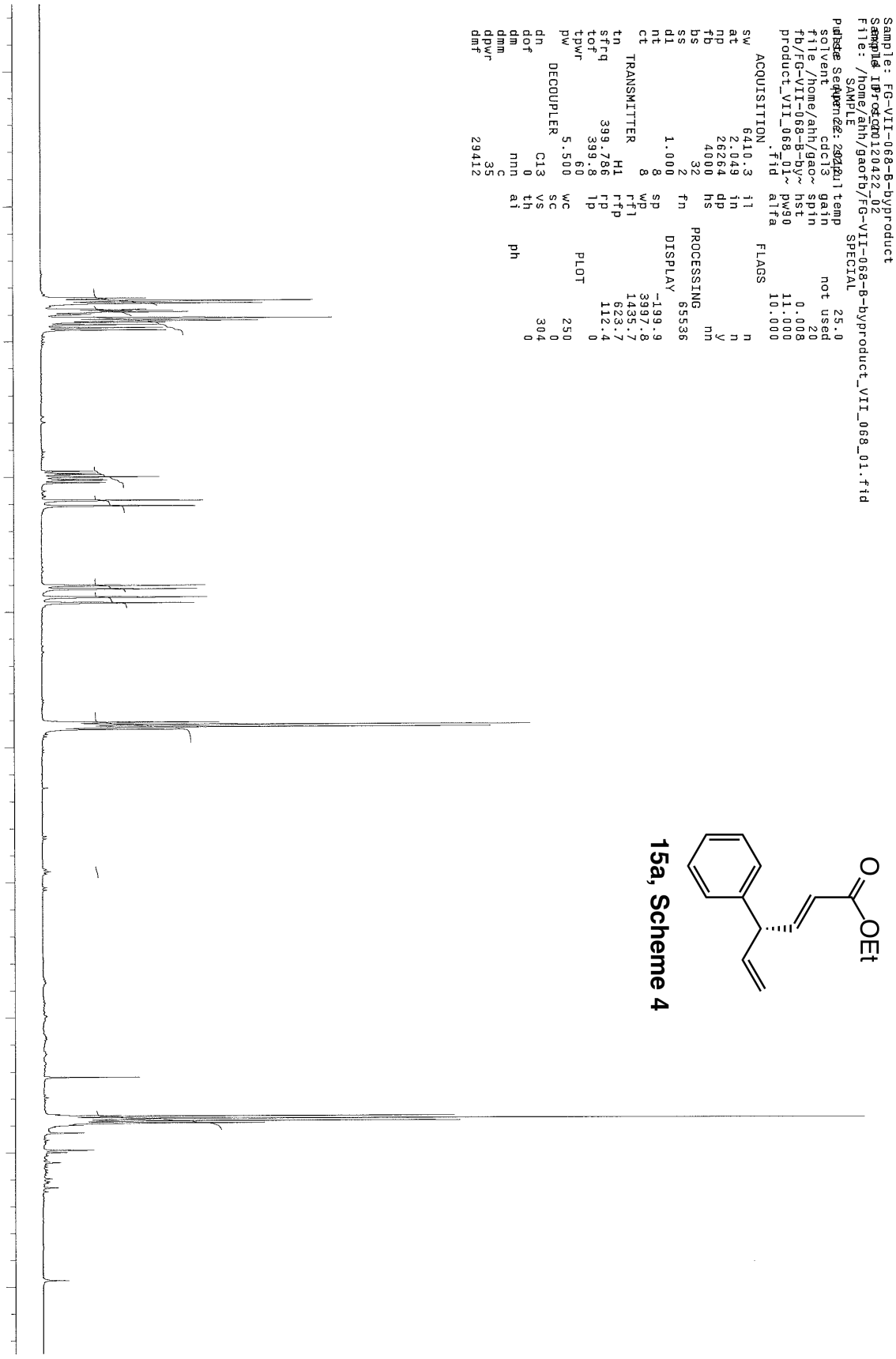


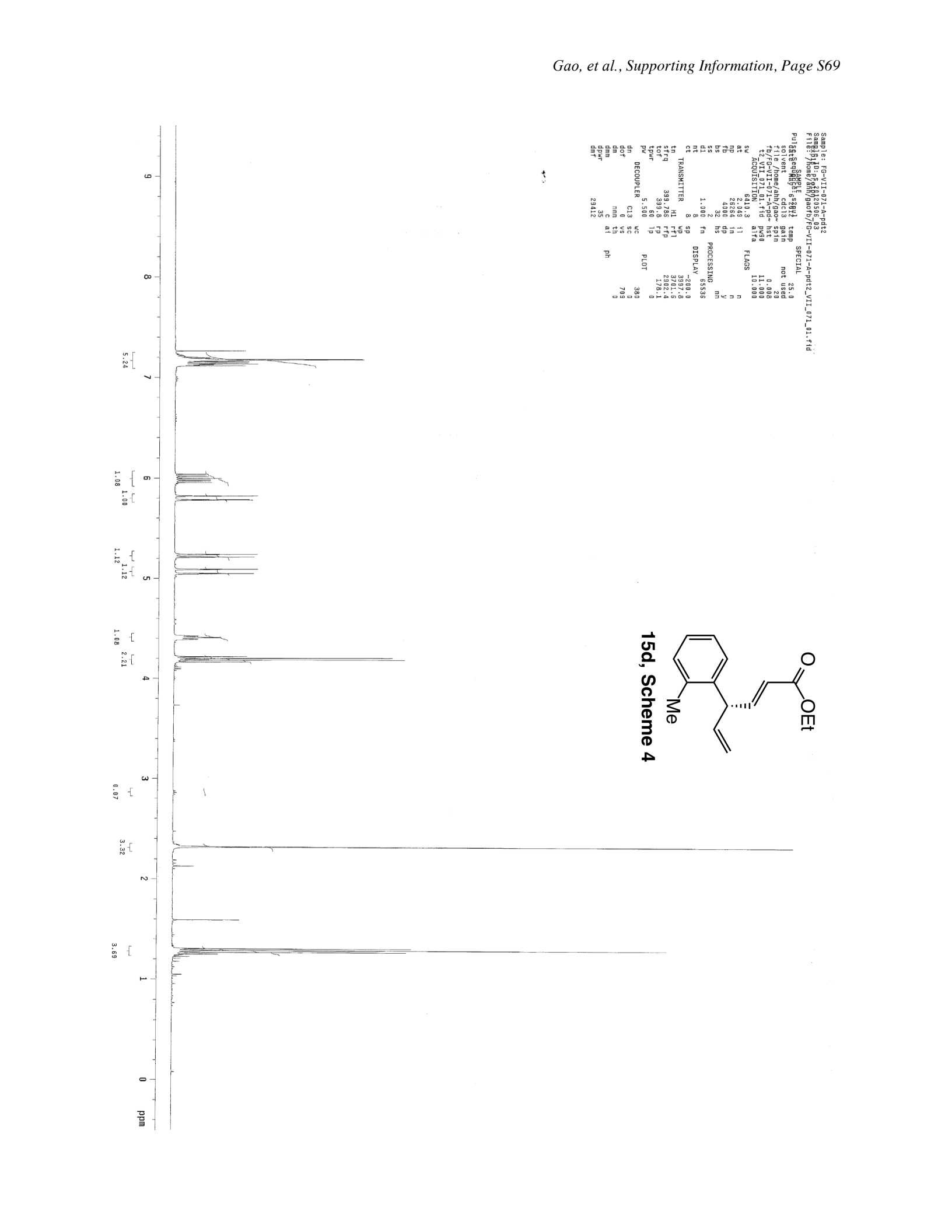

Sample: FG-VII-069-B-pdt1
Sample ID: 6_20120427_02
File: /home/ahb/gaofb/FG-VII-069-B-pdt1_VII_069_01.fid
SAMPLE
Pulse Sequence: s2pul
solvent: cdcl3
file: /home/ahb/gao~
fb/FG-VII-069-B-pd~
t1_VII_069_01.fid
ACQUISITION
sw 6410.3
at 2.049
fb 2604
bs 40
ss 2
d1 1.000
nt 8
ct 8
tn H1
sfrq 399.786
tof 399.6
tpwr 61
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dmf 35
dpwr 29412
temp gain
spin not used 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in y
dp n
hs nn
PROCESSING
fn 65536
DISPLAY
sp -200.0
wp 4397.5
rf1 3701.8
rfp 2902.4
rp 164.1
lp 0
PLOT
wc 380
sc 0
vs 202
th 0
ph
0.92
1.01
1.61
1.01
2.03
1.00
1.06
1.07
1.03
1.01
2.15
2.17
7.50
ppm
Br
O
O

S1, Scheme 3


Sample: FG-VII-069-A-pdt2
File: exp
Pulse Sequence: s2pul
date Apr 27 2012
solvent
file
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 400
bs
ss 2
d1 1.000
nt 40
ct 12
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
pw 5.60
DECOUPLER
dn C13
dof 0
dm nnn
dm c
dmm s
dpwr 35
dmf 2912
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -200.0
wp 4397.5
rf1 3701.8
rfp 2902.4
lp 170.3
PLOT
wc 380
sc 0
vs 396
th 12
al
ph
Br
O
12c, Scheme 3
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.98
1.02
2.06
1.00
0.88
1.02
1.03
1.09
0.93


JLC-II-328_Fr5-16
EtO
OEt
Cl
CO2Me
13, Scheme 3
f1 (ppm)
2.49
2.03
1.01
0.97
1.02
0.97
1.00
1.02
2.84
2.11
2.58
6.38

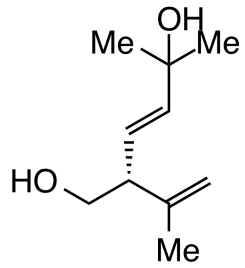

Sample: FG-VII-068-B-byproduct
Sample Id: FG-VII-068-B-byproduct_VII_068_01.fid
File: /home/ahh/gaofb/FG-VII-068-B-byproduct_VII_068_01.fid
SAMPLE
SPECIAL
25.0
not used
20
0.008
11.000
10.000
FLAGS
n
n
y
nn
PROCESSING
65536
DISPLAY
-199.9
3997.8
1435.7
623.7
112.4
0
PLOT
250
0
304
0
ppm
1.92
2.80
1.18
0.93
0.91
1.00
0.96
3.01
0.06
3.95
O
OEt
15a, Scheme 4


Me
15d, Scheme 4
ppm

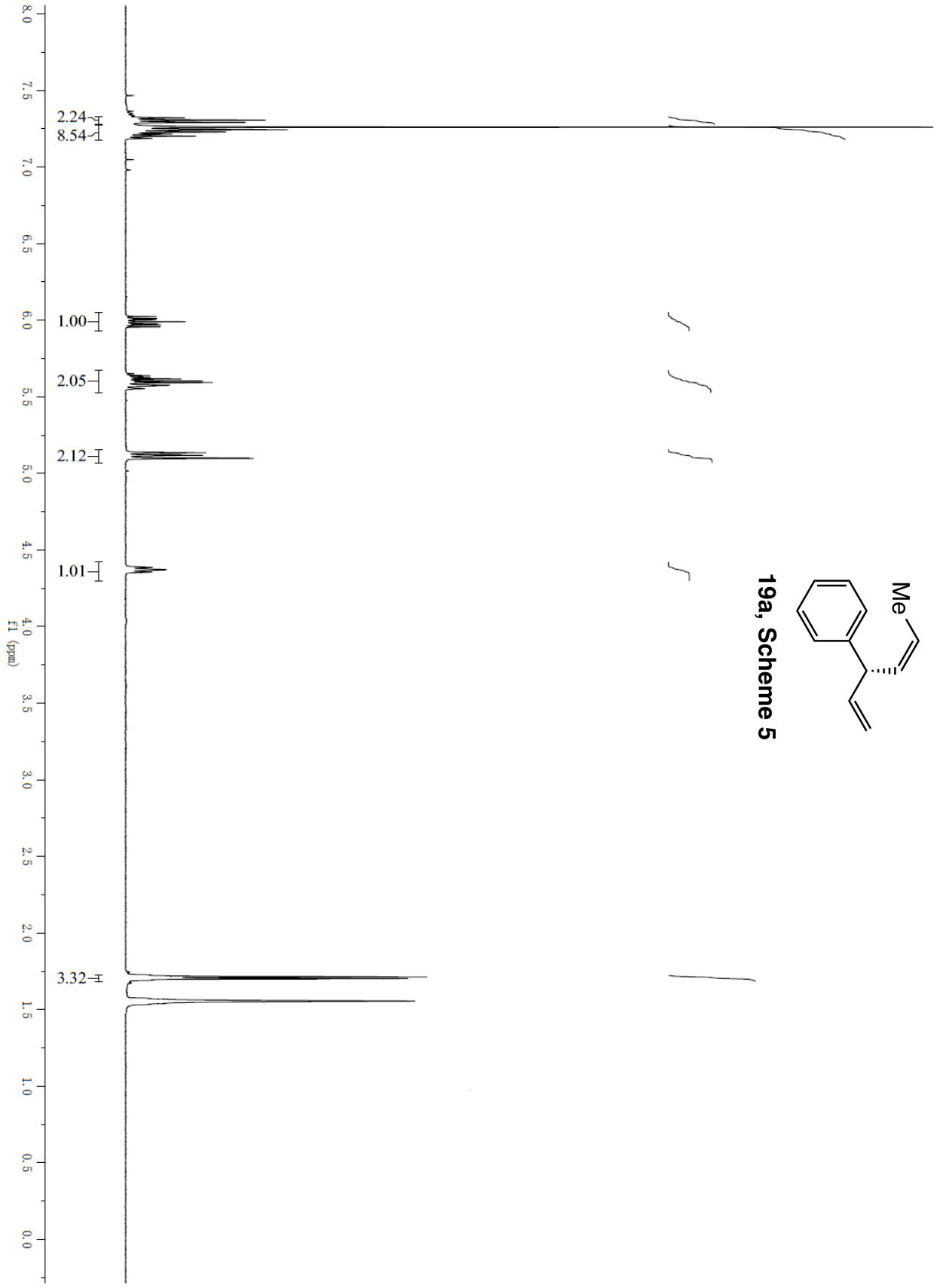
Sample Name:
FG-VII-301-pdt
exp2 proton
Data collected on:
vnmr13-vnmrs400
Archive directory:
SAMPLE
date Mar 20 2013
solvent cdcl3
Sample directory:
file exp
ACQUISITION
Fidfile: PROTON
sw 6410.3
at 2.556
np 32768
fb 4000
bs 4
d1 1.000
nt 40
ct 12
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_HCN5mm
dpwr 35
dmf 29412

PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 312.3
wp 2671.1
rfl 3701.6
rfp 2902.4
rp -156.4
lp 0
PLOT
wc 250
sc 0
vs 103
th 7
ai ph

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 20 2013



irregular monoterpene, Scheme 4

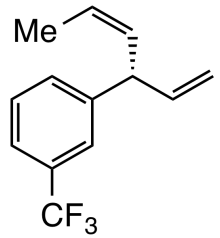


19a, Scheme 5

Sample: FG-VII-154-B-pdt
Exp 10 Proton

Pulse Sequence: s2pul SAMPLE

date	Sep 21 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	**FLAGS**	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	**PROCESSING**	
ct	4	fn	65536
TRANSMITTER		**DISPLAY**	
tn	H1	sp	-7.9
sfrq	399.786	wp	3240.5
tof	399.8	rfl	3701.6
tpwr	60	rfp	2902.4
pw	5.500	rp	112.8
DECOUPLER		lp	0
dn	C13	**PLOT**	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	174
dpwr	35	th	12
dmf	29412	ai	ph

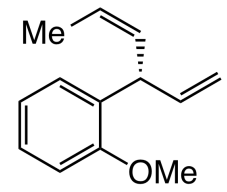


19b, Scheme 5

Sample: FG-VII-155-B-pdt
Exp1 exp Proton

Pulse Sequence: s2pul SAMPLE

date	Sep 21 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	8012.8	pw90	8.900
at	2.049	alfa	10.000
np	32830	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	8	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	1.3
sfrq	499.884	wp	3998.1
tof	499.8	rfl	4635.6
tpwr	59	rfp	3629.1
pw	4.450	rp	159.5
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	136
dpwr	35	th	12
dmf	32258	ai ph	

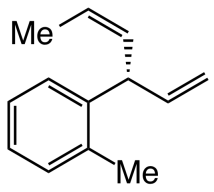


19c, Scheme 5

Sample: FG-VII-156-B-pdt
Exp1 exp Proton

Pulse Sequence: s2pul SAMPLE

date	Sep 21 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	8012.8	pw90	8.900
at	2.049	alfa	10.000
np	32830	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	8	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	22.5
sfrq	499.884	wp	3961.2
tof	499.8	rfl	4635.6
tpwr	59	rfp	3629.1
pw	4.450	rp	-175.3
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	191
dpwr	35	th	12
dmf	32258	ai ph	

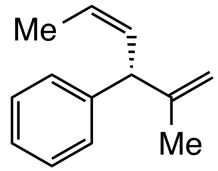


19d, Scheme 5

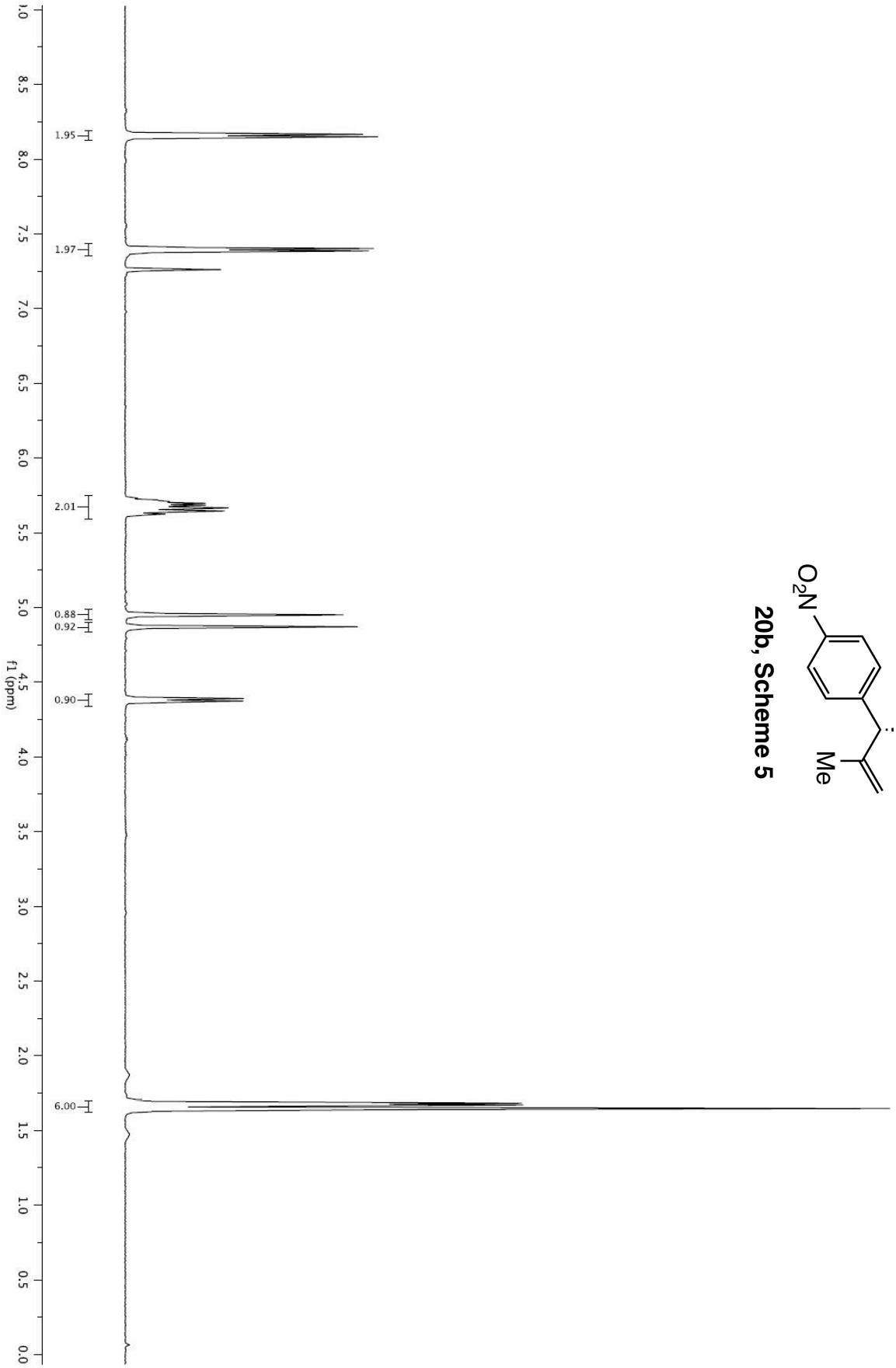
Sample: FG-VII-220-B-pdt
Fekp19exp Proton

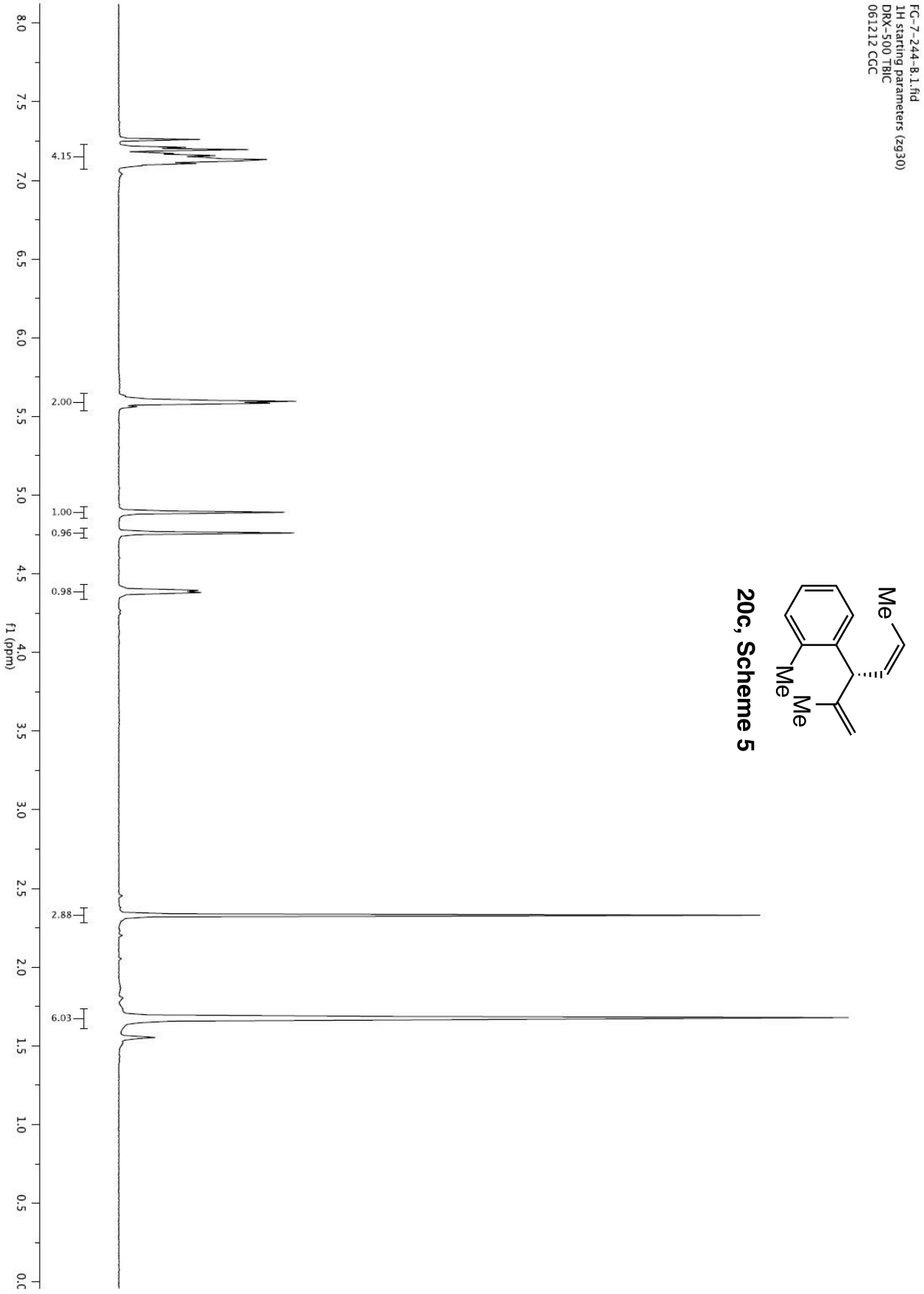
Pulse Sequence: s2pul SAMPLE SPECIAL

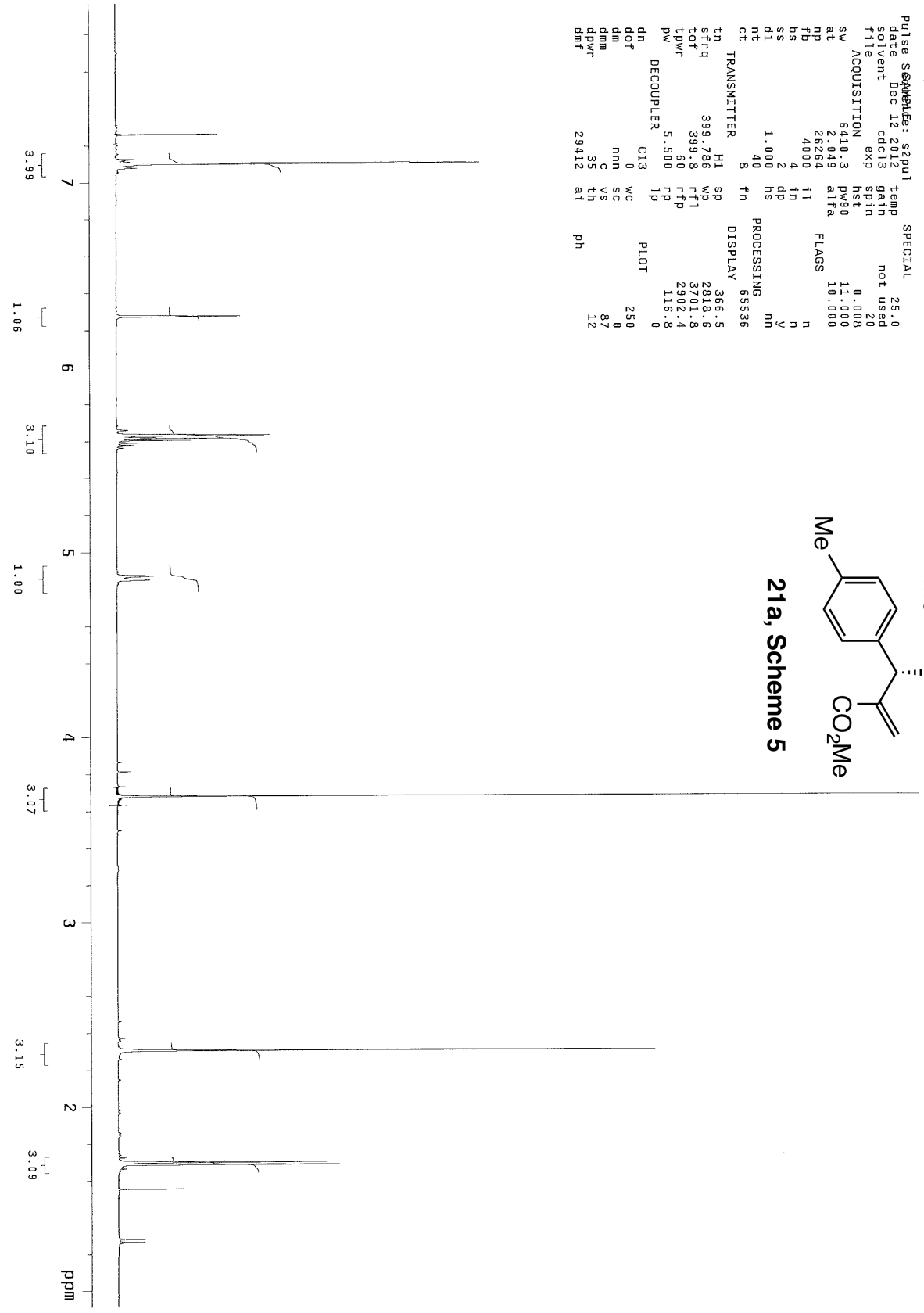
date	Dec 12 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	16	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	188.9
sfrq	399.786	wp	3020.1
tof	399.8	rfl	3701.6
tpwr	60	rfp	2902.4
pw	5.500	rp	115.6
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	203
dpwr	35	th	12
dmf	29412	ai ph	

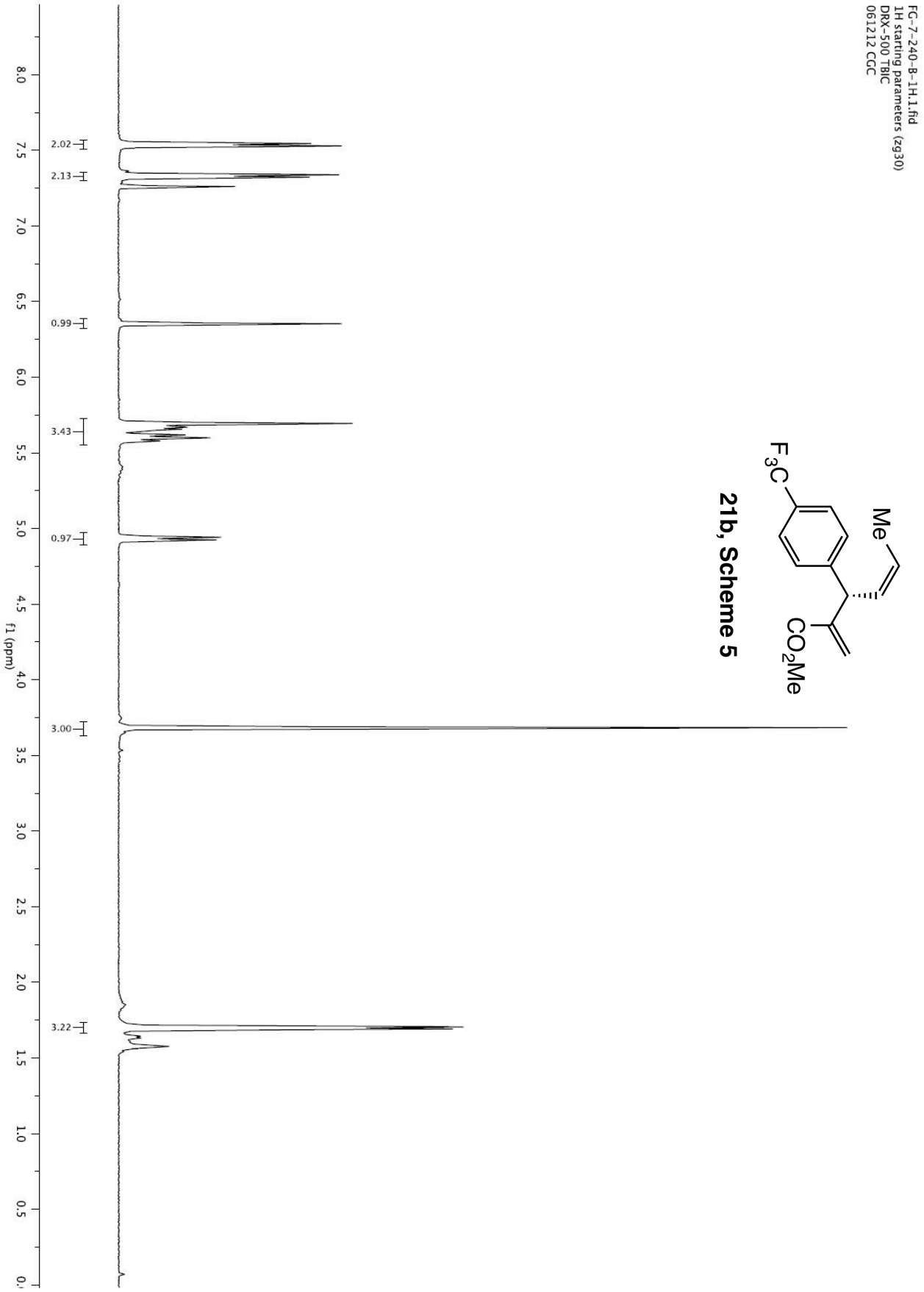


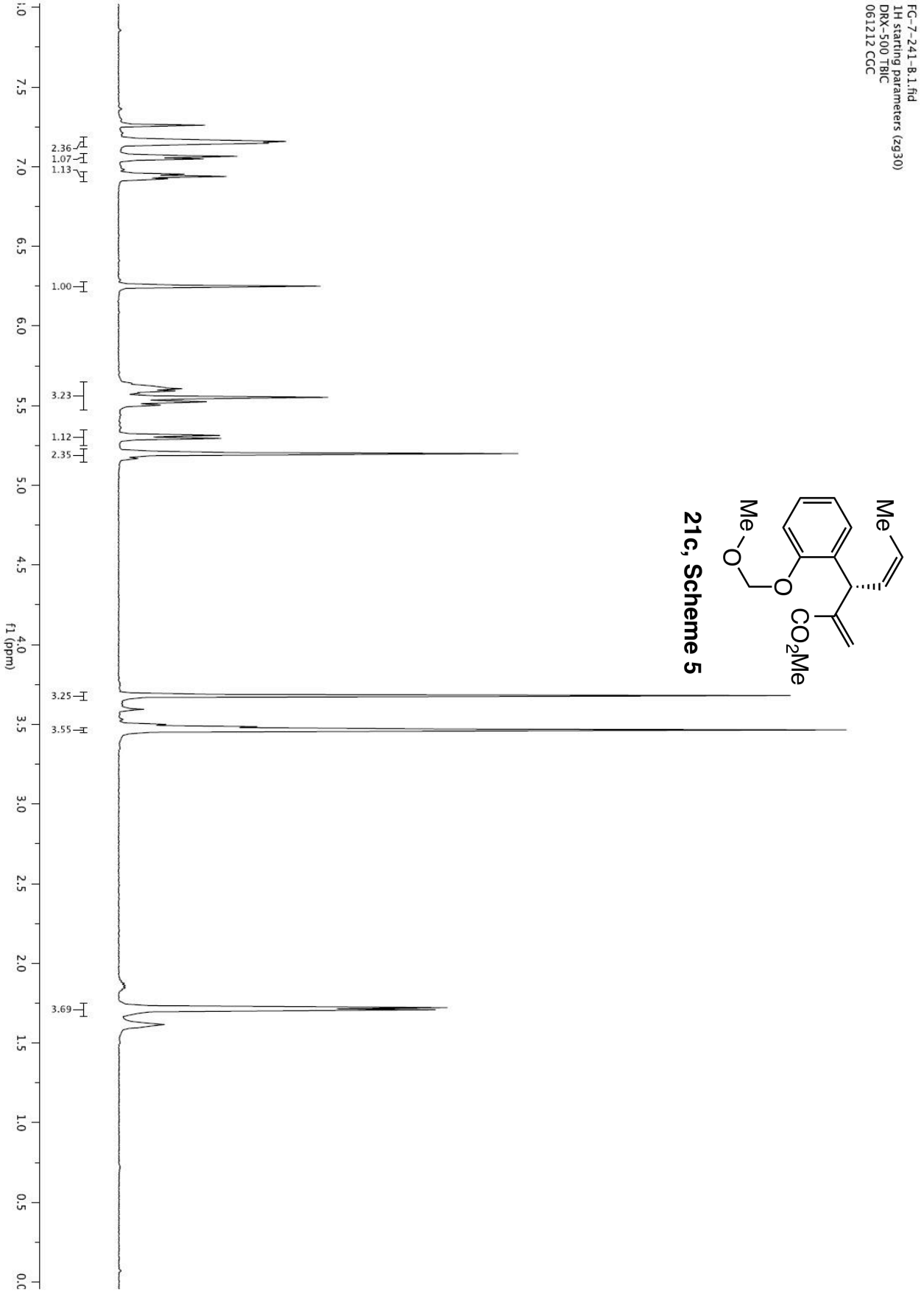
20a, Scheme 5

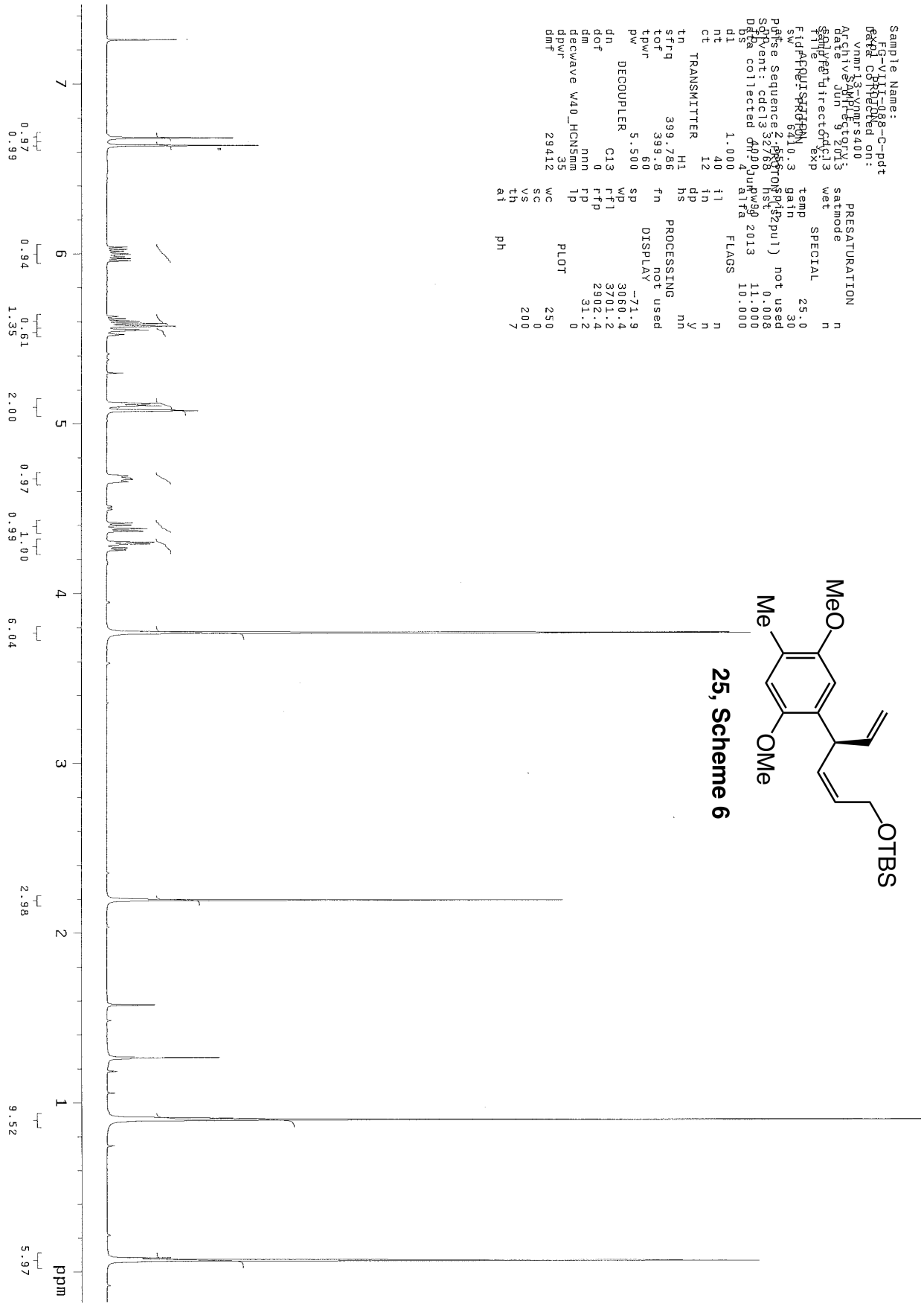

FG-7-243-B.1.fid
1H starting parameters (zg30)
DRX-500 TBC
061212 CGC
Me
Me
O2N
20b, Scheme 5
1.95
1.97
2.01
0.88
0.92
0.90
6.00
f1 (ppm)


FG-7-244-B.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
Me
Me
20c, Scheme 5
4.15
2.00
1.00
0.96
0.98
2.88
6.03
f1 (ppm)


Sample: FG-VII-214-A-pdt
Exp: 1Exp Proton
Pulse Sequence: s2pul SPECIAL
date Dec 12 2012 temp 25.0
solvent cdcl3 gain not used
file exp spin 20
ACQUISITION hst 0.008
sw 6410.3 pw90 11.000
at 2.049 alfa 10.000
np 26264 FLAGS
fb 4000 il n
bs 4 in n
ss 2 dp y
d1 1.000 hs nn
nt 40 PROCESSING
ct 8 fn 65536
TRANSMITTER DISPLAY
tn H1 sp 366.5
sfrq 399.786 wp 2818.6
tof 399.8 rfl 3701.8
tpwr 60 rfp 2902.4
pw 5.500 rp 116.8
DECOUPLER lp 0
dn C13 PLOT
dof 0 wc 250
dm nnn sc 0
dmm c vs 87
dpwr 35 th 12
dmf 29412 ai
ph
Me
CO2Me
Me
21a, Scheme 5
7
6
5
4
3
2
ppm
3.99
1.06
3.10
1.00
3.07
3.15
3.09

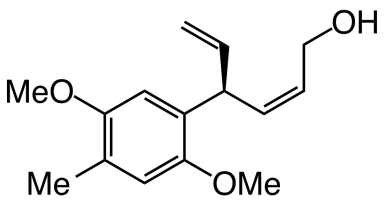

FG-7-240-B-1H.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
F3C
CO2Me
21b, Scheme 5
2.02
2.13
0.99
3.43
0.97
3.00
3.22
f1 (ppm)


FG-7-241-B.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
O
Me
O
CO2Me
21c, Scheme 5
2.36
1.07
1.13
1.00
3.23
1.12
2.35
3.25
3.55
3.69
f1 (ppm)

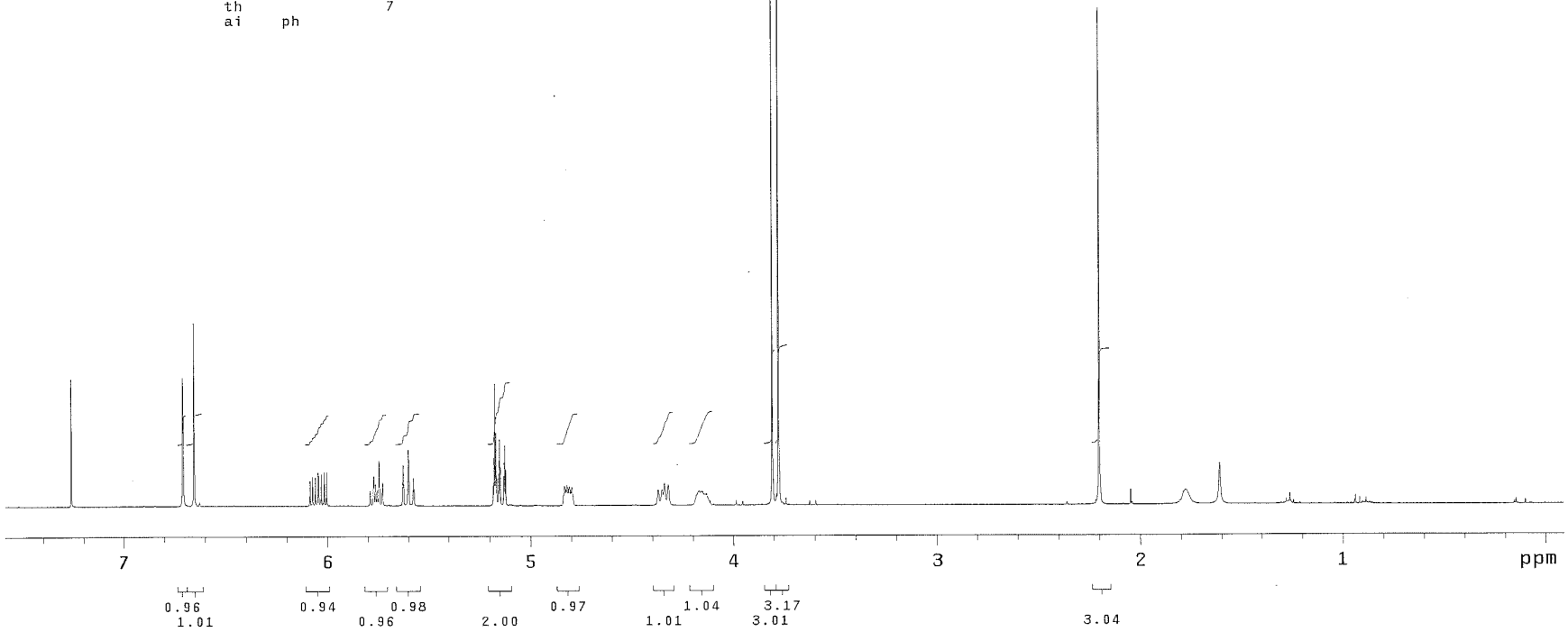

MeO
Me
OMe
OTBS
25, Scheme 6
ppm

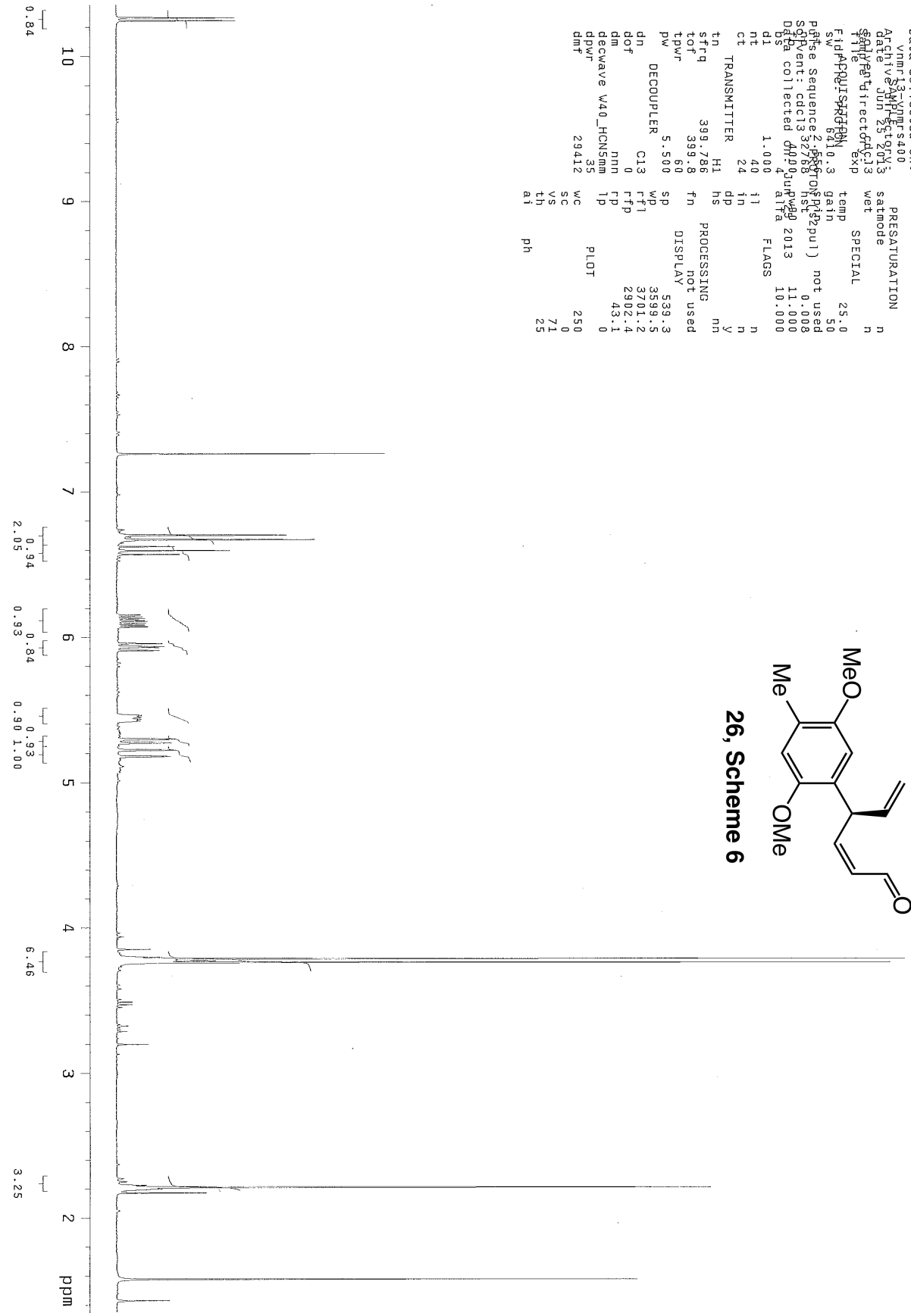
```
Sample Name:
  FG-VIII-093-crude
Data collected on:
  vnmrj3-vnmrs400
Archive directory:
  SAMPLE
Sample directory:
  exp24_PROTON
File:
  exp
Fidfile: PROTON
Pulse Sequence: PROTON(s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2013
```

SAMPLE		PRESATURATION	
date	Jun 11 2013	satmode	n
solvent	cdcl3	wet	n
file	exp	SPECIAL	
ACQUISITION		temp	25.0
sw	6410.3	gain	44
at	2.556	spin	not used
np	32768	hst	0.008
fb	4000	pw90	11.000
bs	4	alfa	10.000
d1	1.000	FLAGS	
nt	40	il	n
ct	12	in	n
TRANSMITTER		dp	y
tn	H1	hs	nn
sfrq	399.786	PROCESSING	
tof	399.8	fn	not used
tpwr	60	DISPLAY	
pw	5.500	sp	-36.7
DECOUPLER		wp	3069.4
dn	C13	rfl	3700.8
dof	0	rfp	2902.4
dm	nnn	rp	38.3
decwave	W40_HCN5mm	lp	0
dpwr	35	PLOT	
dmf	29412	wc	250
		sc	0
		vs	35
		th	7
		ai	ph



S2, Scheme 6

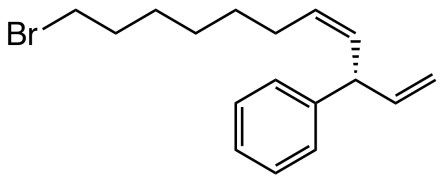



Sample Name:
exp-vnmrs400
Data corrected on:
vnmrj3-vnmrs400
Archive directory
date Jun 25 2013
solvent cdcl3
file exp
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 50
not used
0.008
hst 11.000
Jun 25 2013 10.000
FLAGS
y
nn
PROCESSING
not used
DISPLAY
3599.5
3701.2
2902.4
43.1
0
PLOT
250
0
71
25
ph
MeO
Me
OMe
O
26, Scheme 6
ppm

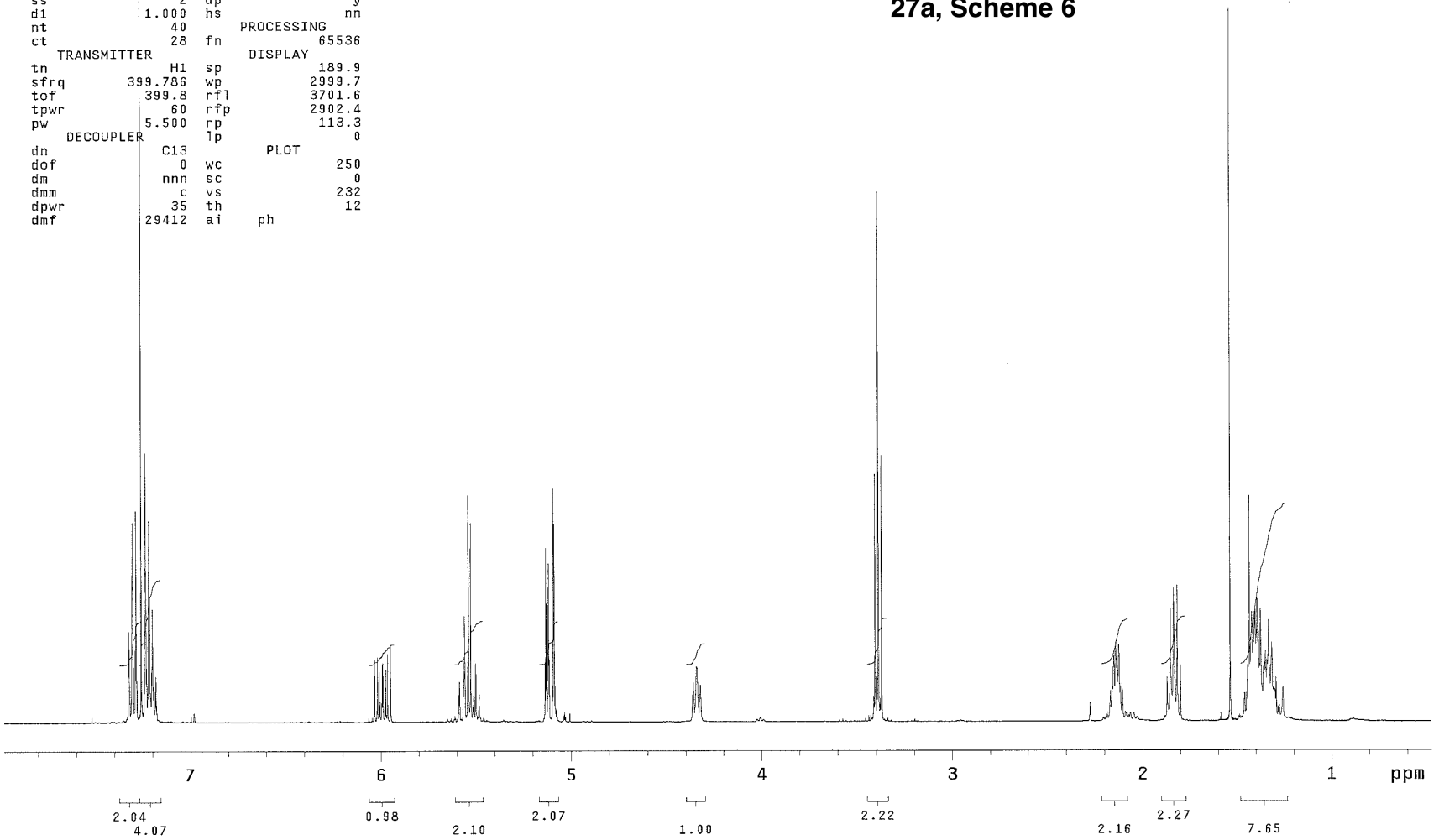
Sample: FG-VII-238-pdt-2
File: exp22exp1 Proton

Pulse Sequence: s2pul SAMPLE

date	Dec 18 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	28	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	189.9
sfrq	399.786	wp	2999.7
tof	399.8	rfl	3701.6
tpwr	60	rfp	2902.4
pw	5.500	rp	113.3
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	232
dpwr	35	th	12
dmf	29412	ai ph	



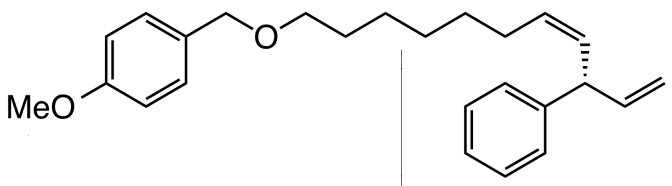
27a, Scheme 6



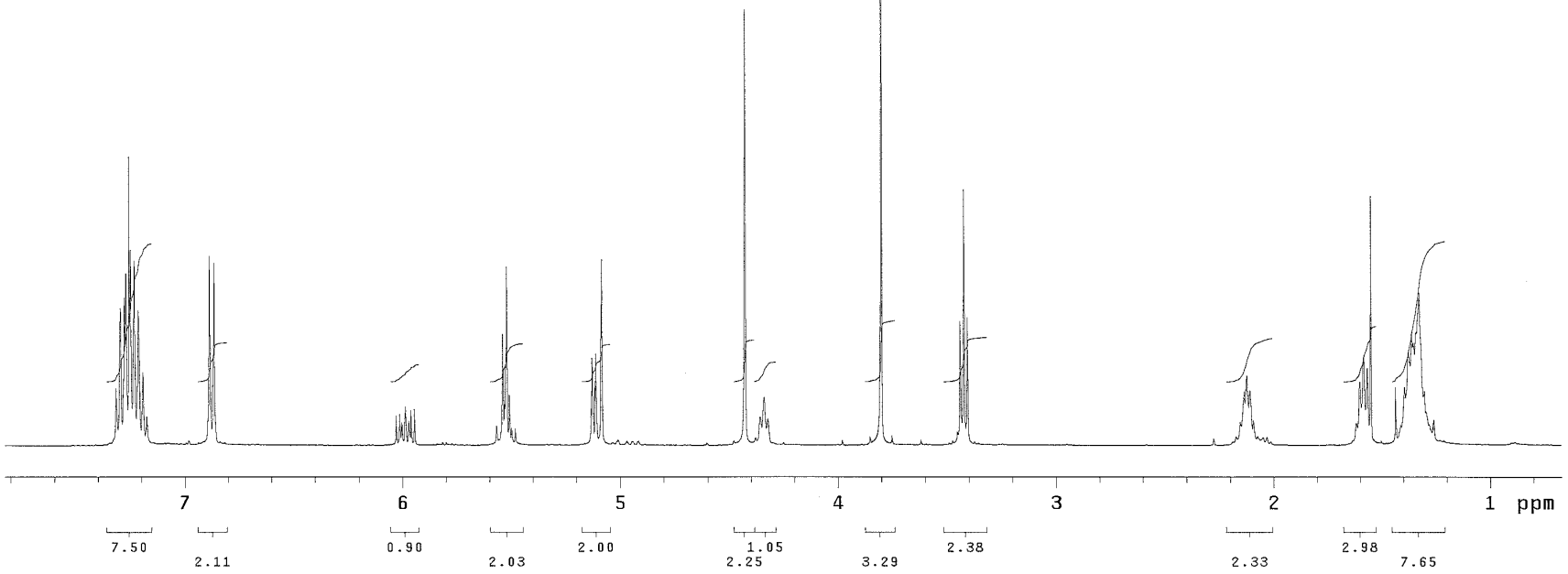
Sample: FG-VII-237-pdt
Exp: 20exp Proton

Pulse Sequence: s2pul SAMPLE

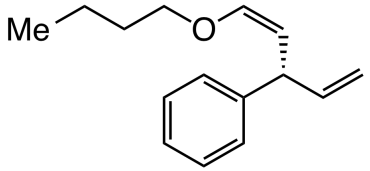
date	Dec 18 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	36	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	268.9
sfrq	399.786	wp	2859.7
tof	399.8	rfl	3702.0
tpwr	60	rfp	2902.4
pw	5.500	rp	108.7
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	271
dpwr	35	th	12
dmf	29412	ai ph	



27b, Scheme 6



Sample: FG-VII-216-A-pdt
File: exp
SAMPLE
Pulse Sequence: s2pul
date Dec 8 2012
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 40
ct 8
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -15.9
wp 3221.4
rfl 3701.6
rfp 2902.4
rp 117.2
lp 0
PLOT
wc 250
sc 0
vs 179
th 12
ai ph

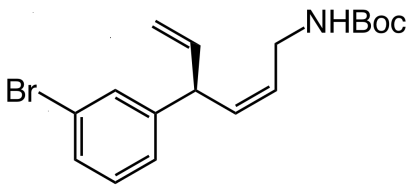


27c, Scheme 6

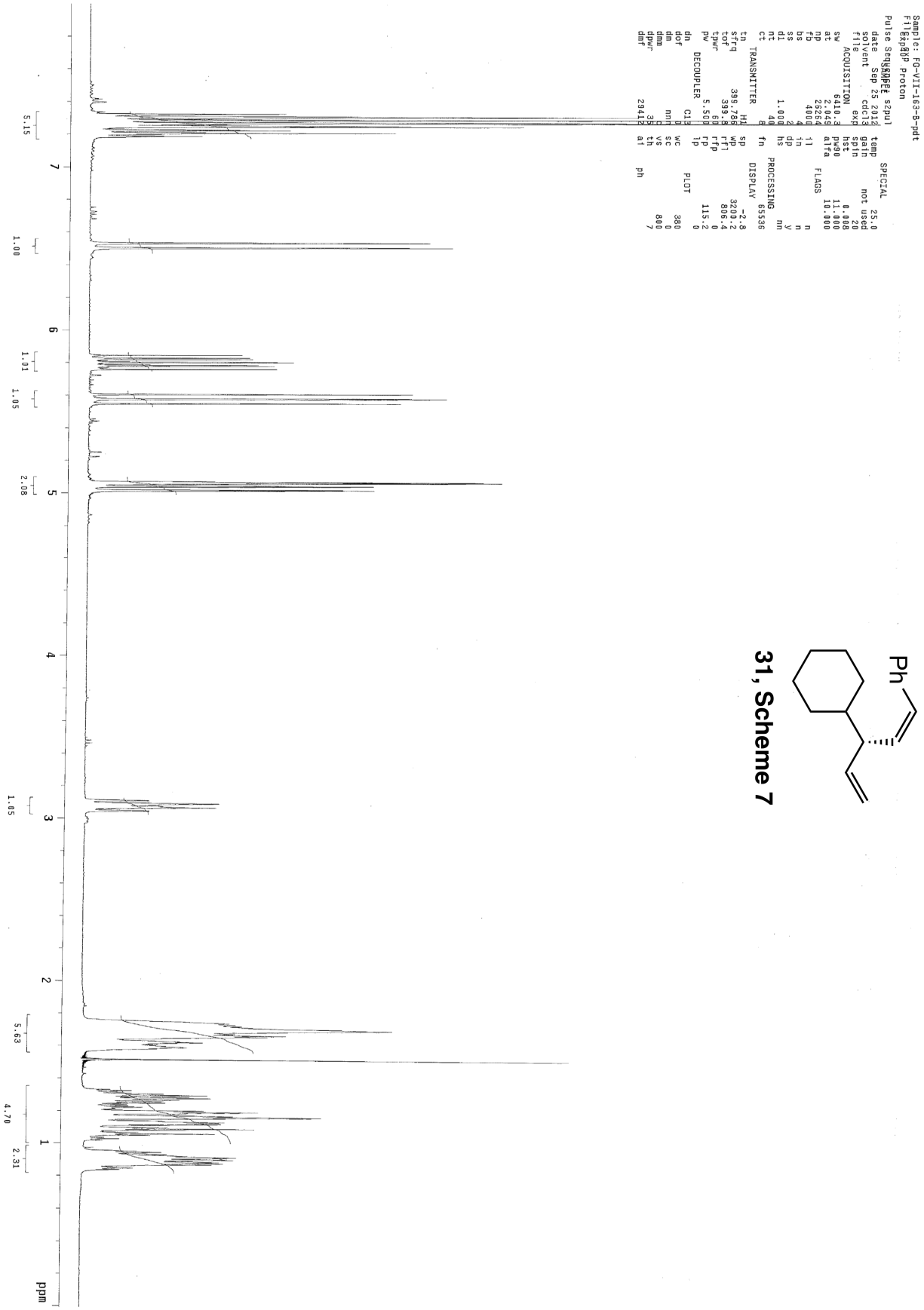
Sample: FG-VII-207-B-pdt
File: exp1

Pulse Sequence: s2pul
Solvent: cdcl3

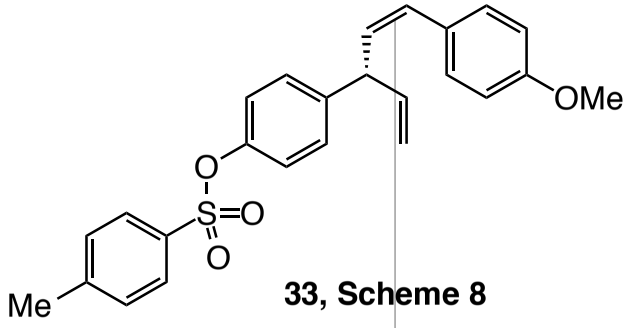
date	Nov 20 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	12	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	239.6
sfrq	399.786	wp	2984.3
tof	399.8	rfl	3702.0
tpwr	60	rfp	2902.4
pw	5.500	rp	116.6
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	76
dpwr	35	th	12
dmf	29412	ai ph	



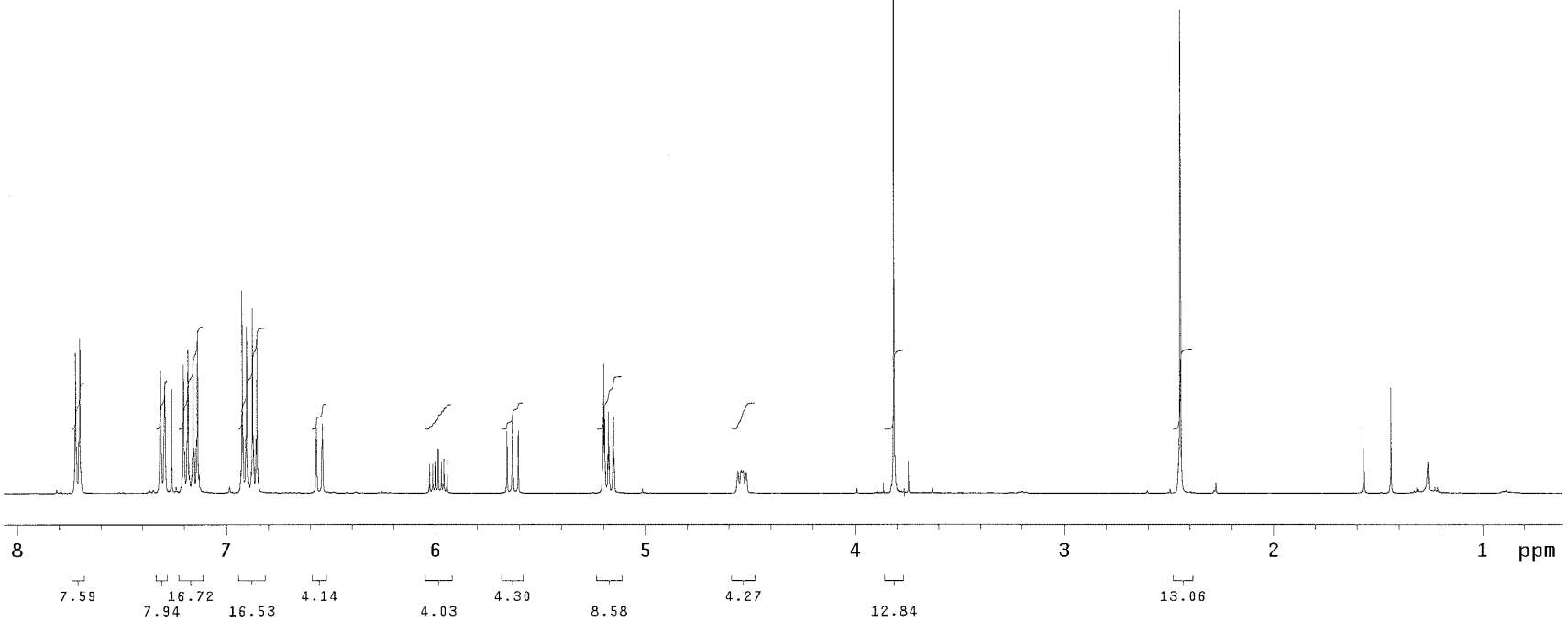
28, Scheme 6

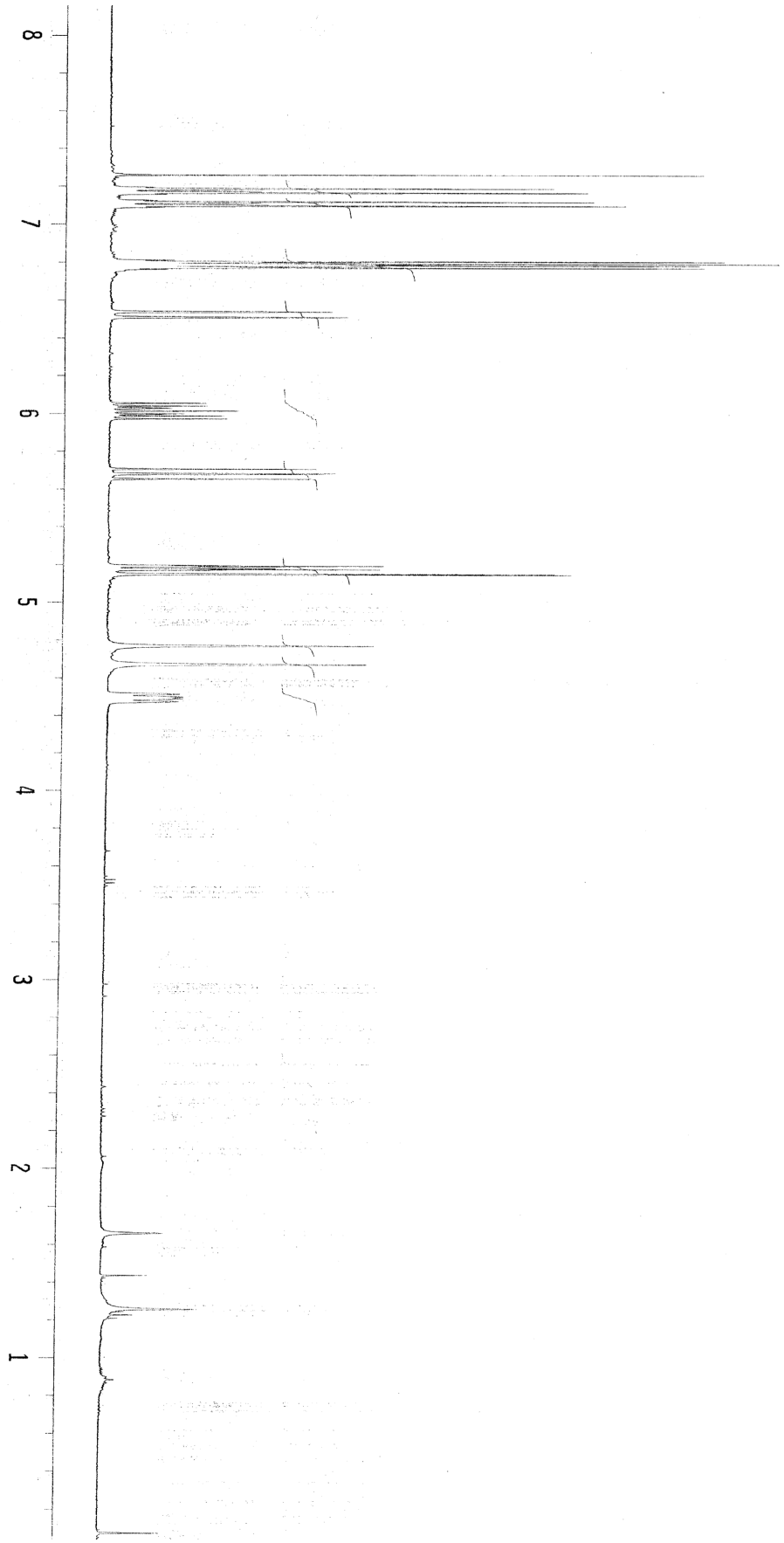

Sample: FG-VII-163-B-pdt
File: exp
1H proton
Pulse Sequence: s2pul
SAMPLE
date Sep 25 2012
solvent cdcl3
file
ACQUISITION
sw 6410.3
at 2.045
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 4
ct 0
TRANSMITTER
tn H1
sfrq 399.788
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 2941.2
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.000
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -2.8
wp 3200.2
rfl 806.4
rfp 0
rp 115.2
lp 0
PLOT
wc 380
sc 0
vs 800
th 7
ph
Ph
31, Scheme 7
5.15
1.00
1.01
1.05
2.06
1.05
5.63
4.70
2.31
ppm

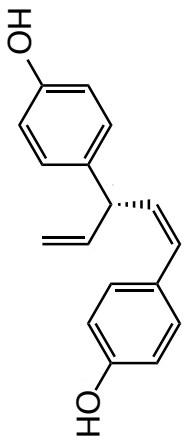
```
Sample: FG-VII-198-A-pdt
Exp5 exp                Proton

Pulse Sequence: s2pul      SPECIAL
  date   Nov  8 2012  temp          25.0
  solvent      cdcl3  gain       not used
  file           exp  spin            20
     ACQUISITION      hst          0.008
  sw          6410.3  pw90        11.000
  at            2.049 alfa        10.000
  np            26264       FLAGS
  fb             4000  il              n
  bs                4  in              n
  ss                2  dp              y
  d1            1.000  hs             nn
  nt               40     PROCESSING
  ct                8  fn           65536
     TRANSMITTER      DISPLAY
  tn               H1  sp           245.6
  sfrq       399.786  wp          2978.0
  tof          399.8  rfl         3701.6
  tpwr            60  rfp         2902.4
  pw           5.500  rp           116.5
     DECOUPLER        lp               0
  dn              C13          PLOT
  dof               0  wc            250
  dm              nnn  sc              0
  dmm               c  vs            120
  dpwr             35  th             12
  dmf           29412  ai     ph
```



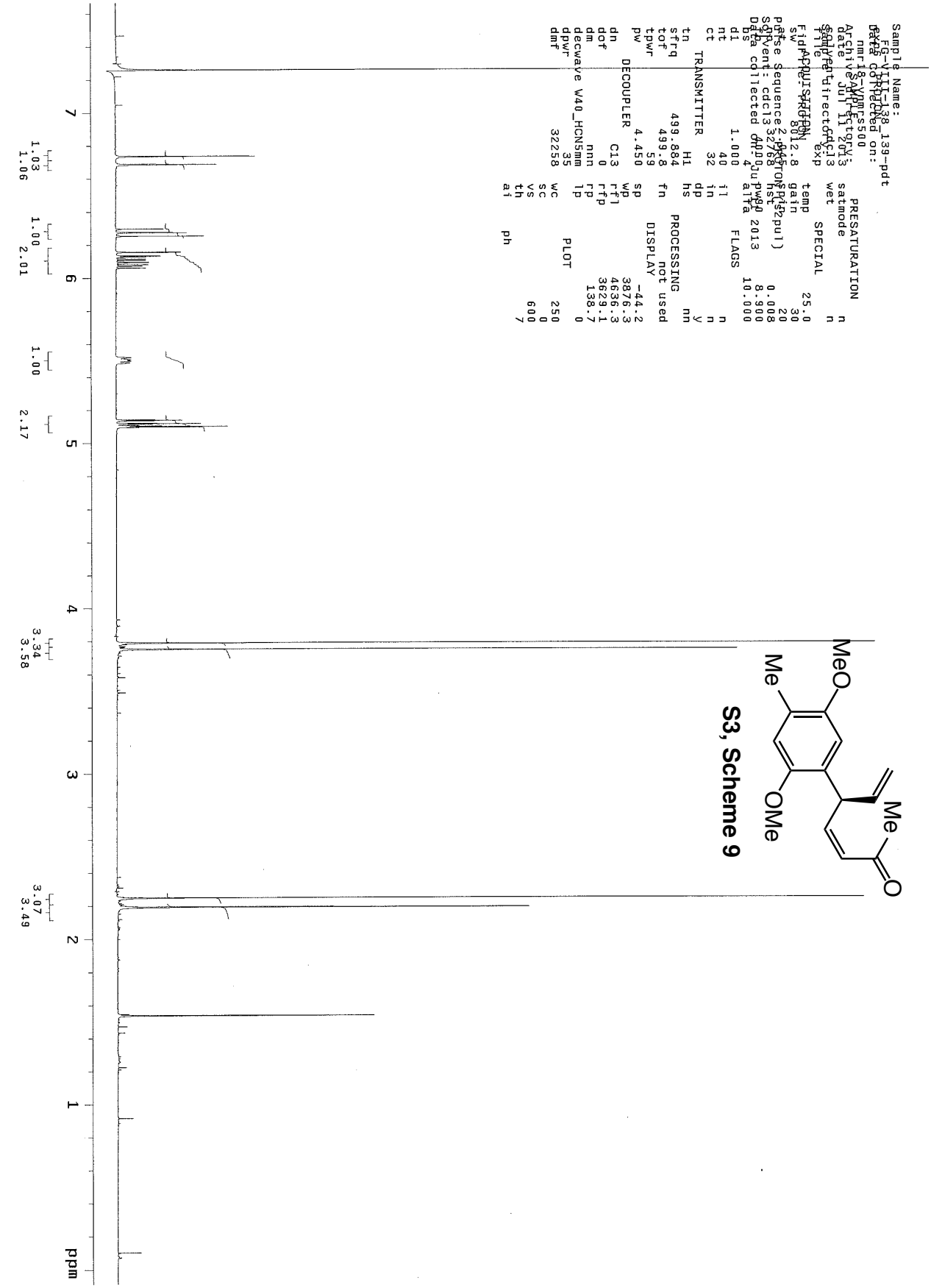
33, Scheme 8

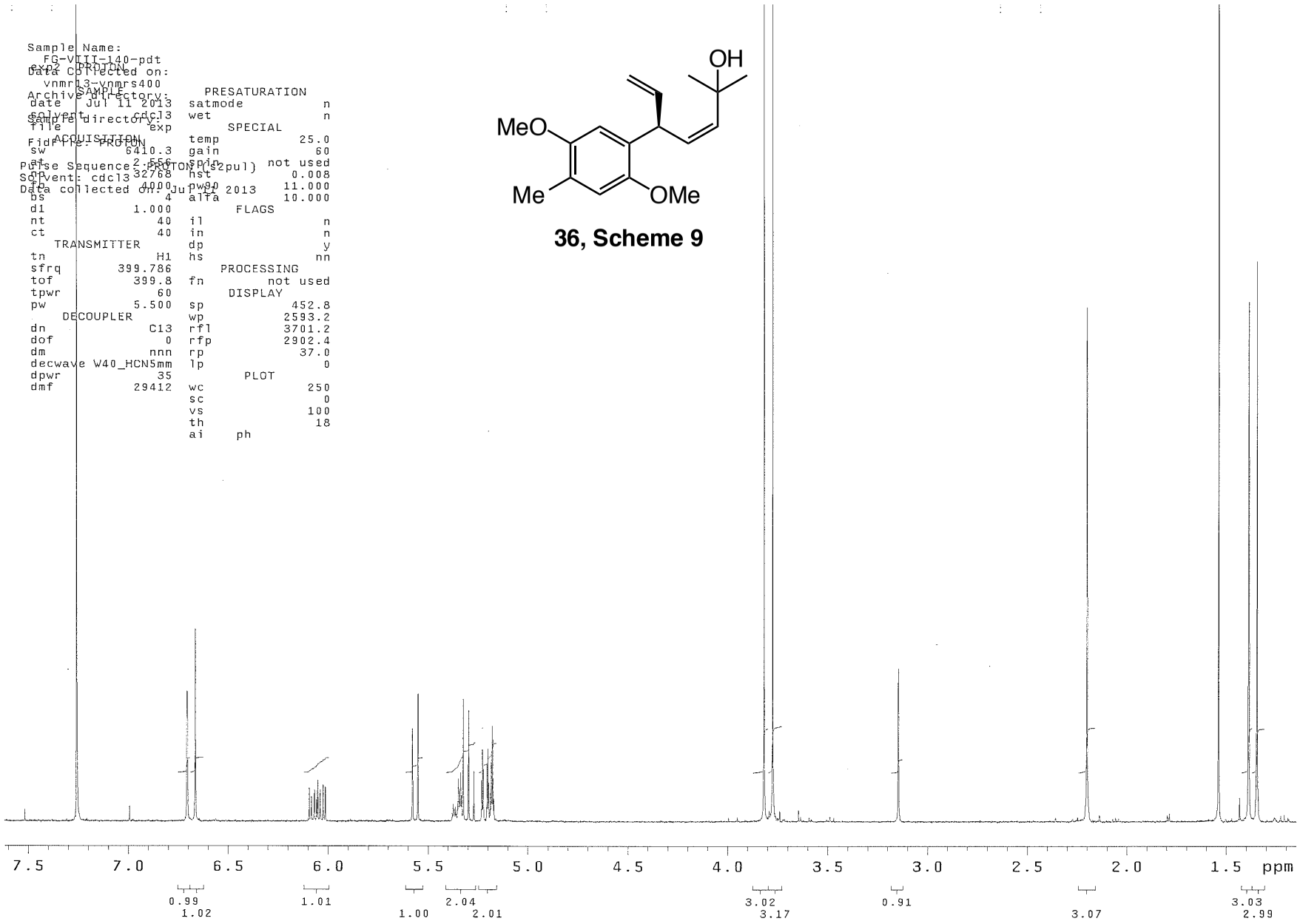


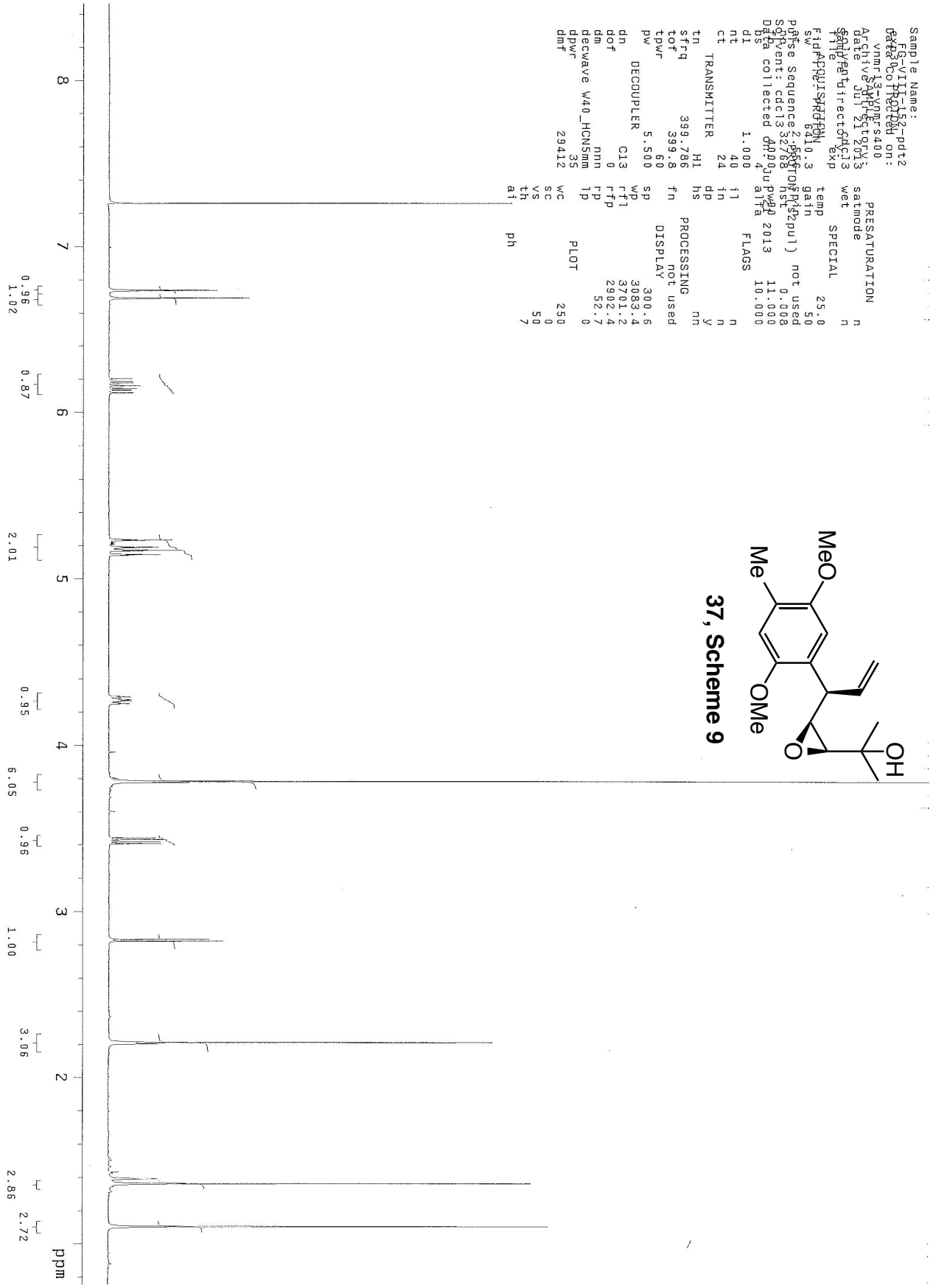


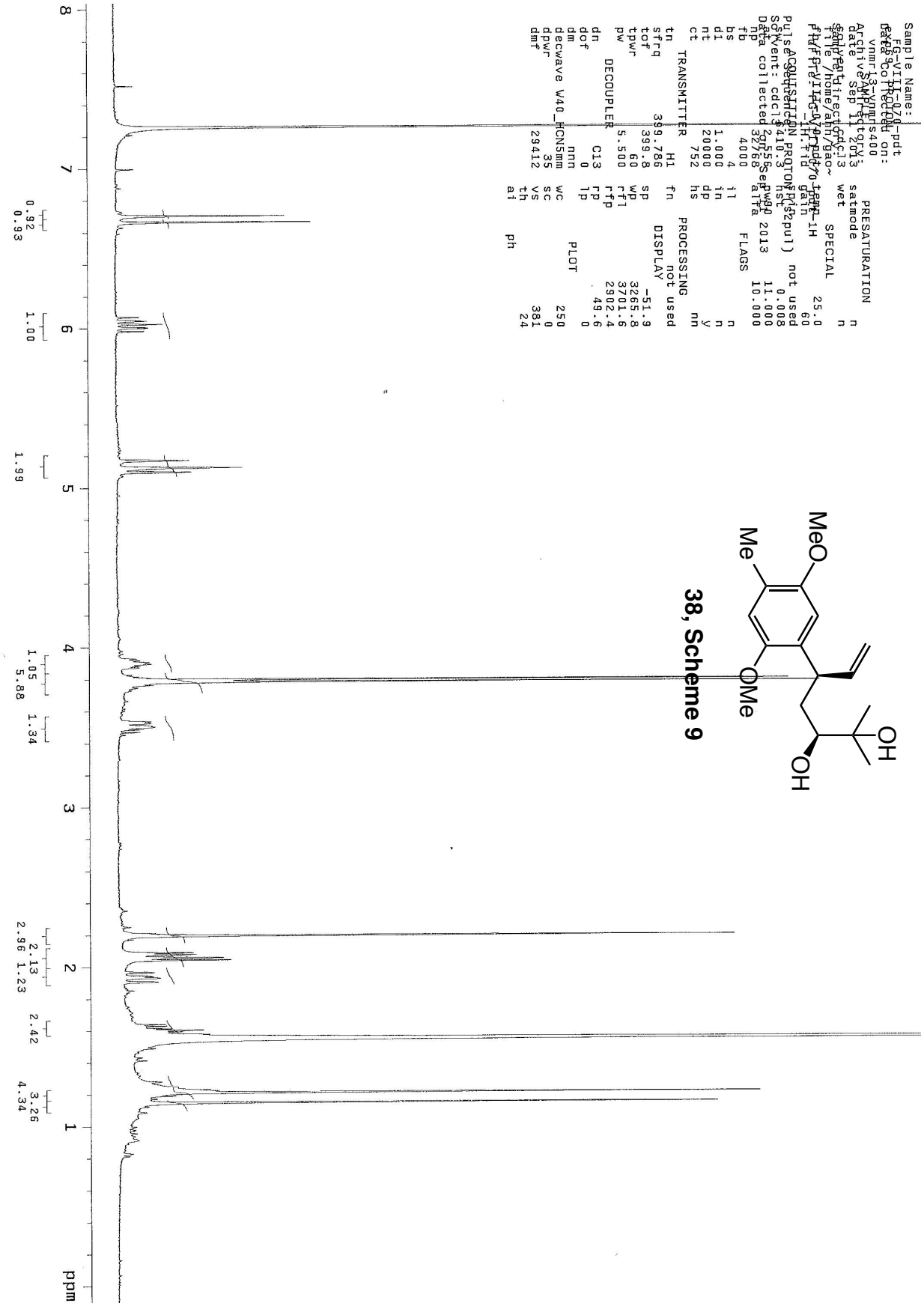


nyasol, Scheme 8

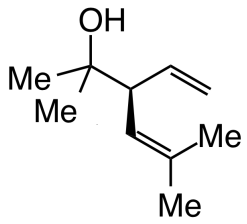

Sample Name:
FG-VIII-138_139-pdt
Data collected on:
nmr18-VNMRS500
Archive directory:
Date Jul 11 2013
Solvent: cdcl3
Temp. 25.0
Pulse Sequence: s2pul
Solvent: cdcl3
Data collected on: Thu Aug 8 2013
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
dp y
PROCESSING
not used
DISPLAY
-44.2
3876.3
4636.3
3629.1
138.7
0
PLOT
250
0
600
7
1.03
1.06
1.00
2.01
1.00
2.17
3.34
3.58
3.07
3.49
ppm
MeO
Me
OMe
Me
O
S3, Scheme 9


Sample Name:
FG-VIII-140-pdt
Data Collected on:
vnmrj3-vnmrs400
Archive directory:
date Jul 11 2013
solvent cdcl3
sample directory: exp
file ACQUISITION
Fidfile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 11 2013
SAMPLE
sw 6410.3
at 2.555
np 32768
fb 4000
bs 4
d1 1.000
nt 40
ct 40
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_HCN5mm
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 60
spin not used
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 452.8
wp 2593.2
rfl 3701.2
rfp 2902.4
rp 37.0
lp 0
PLOT
wc 250
sc 0
vs 100
th 18
ai ph
OH
MeO
Me
OMe
36, Scheme 9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.99
1.02
1.01
1.00
2.04
2.01
3.02
3.17
0.91
3.07
3.03
2.99

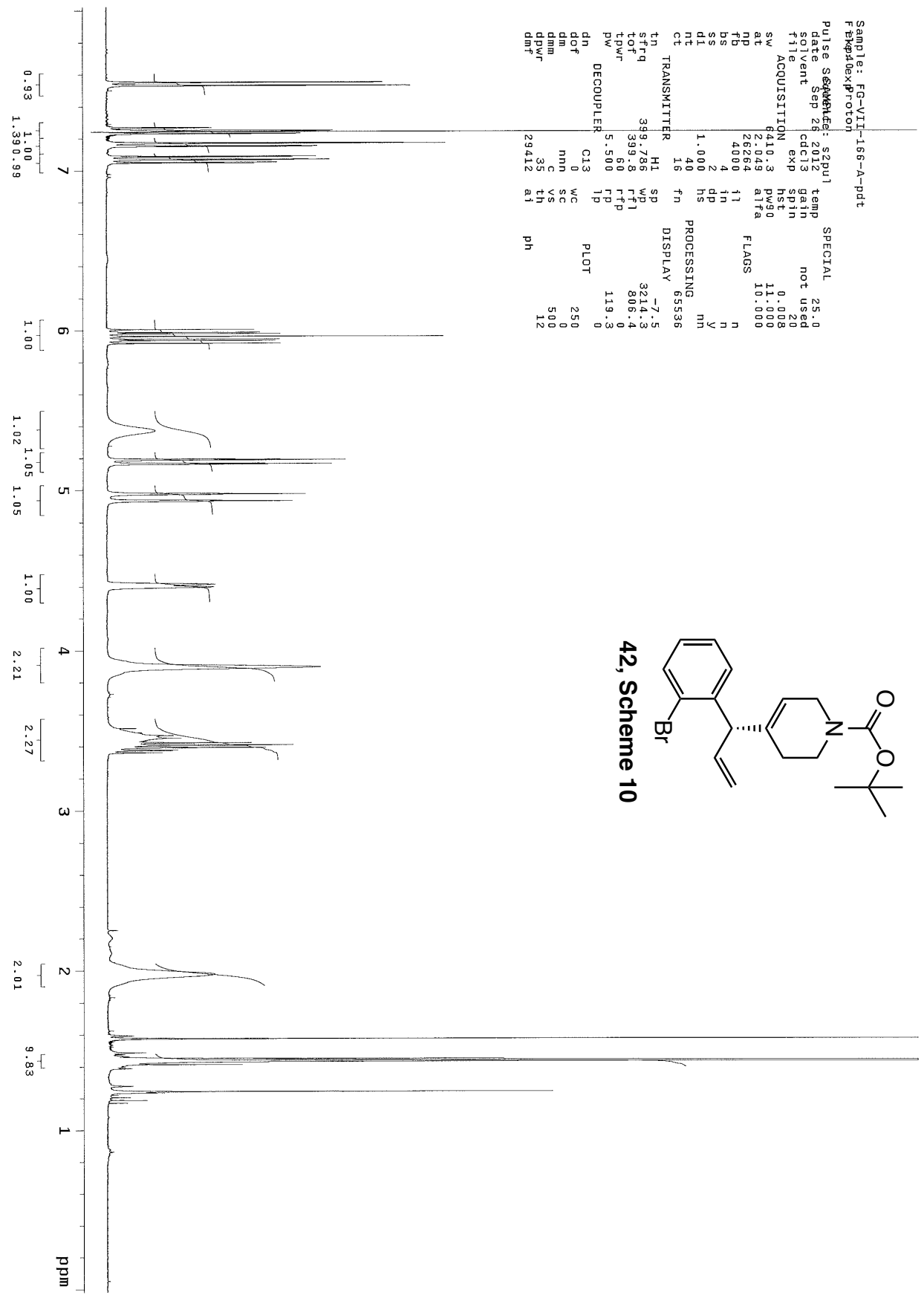

MeO
Me
OMe
O
OH
37, Scheme 9
ppm
0.96
1.02
0.87
2.01
0.95
6.05
0.96
1.00
3.06
2.86
2.72

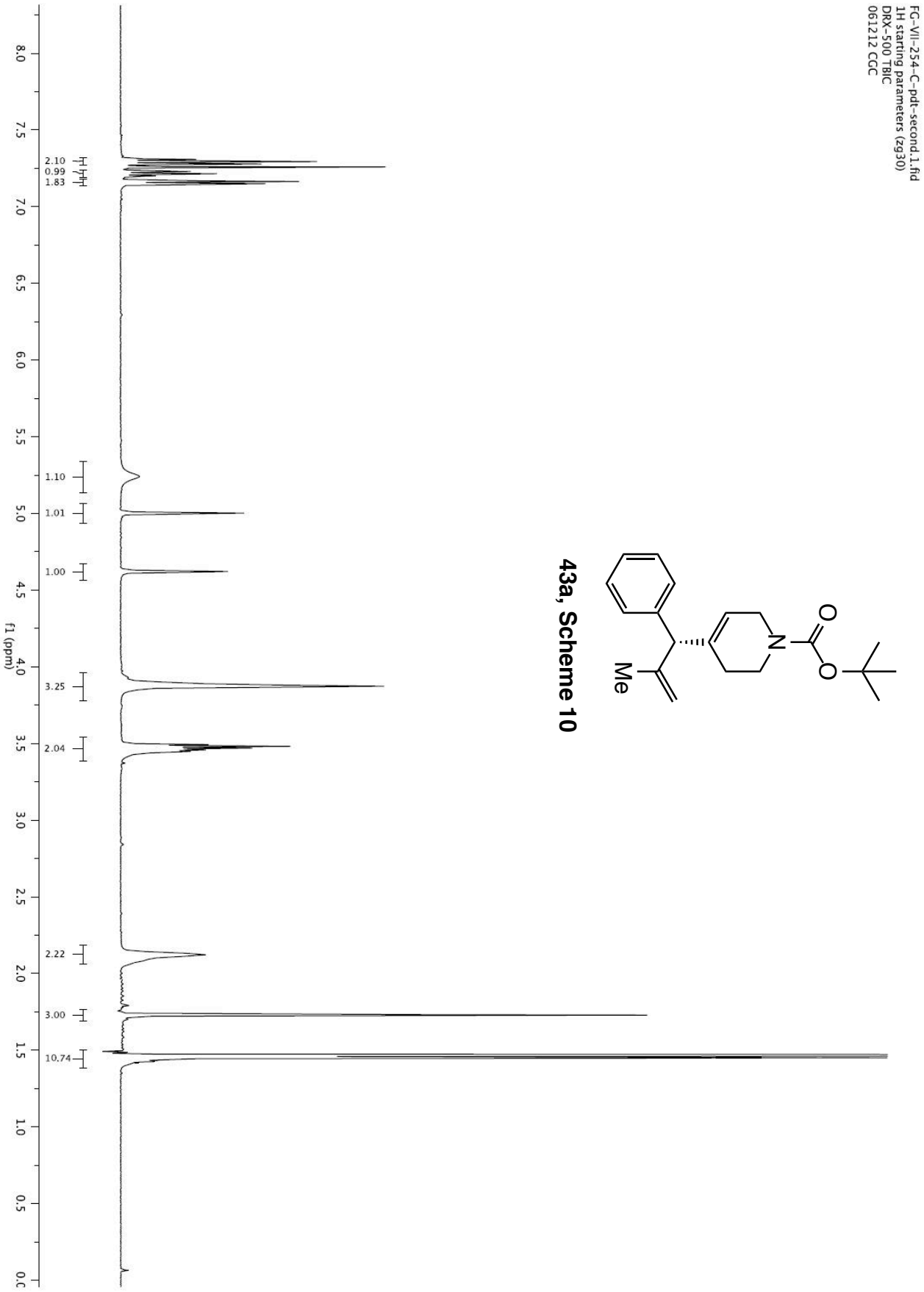

MeO
Me
OMe
OH
OH
38, Scheme 9
ppm
0.92
0.93
1.00
1.99
1.05
5.88
1.34
2.96
1.23
2.13
2.42
3.26
4.34

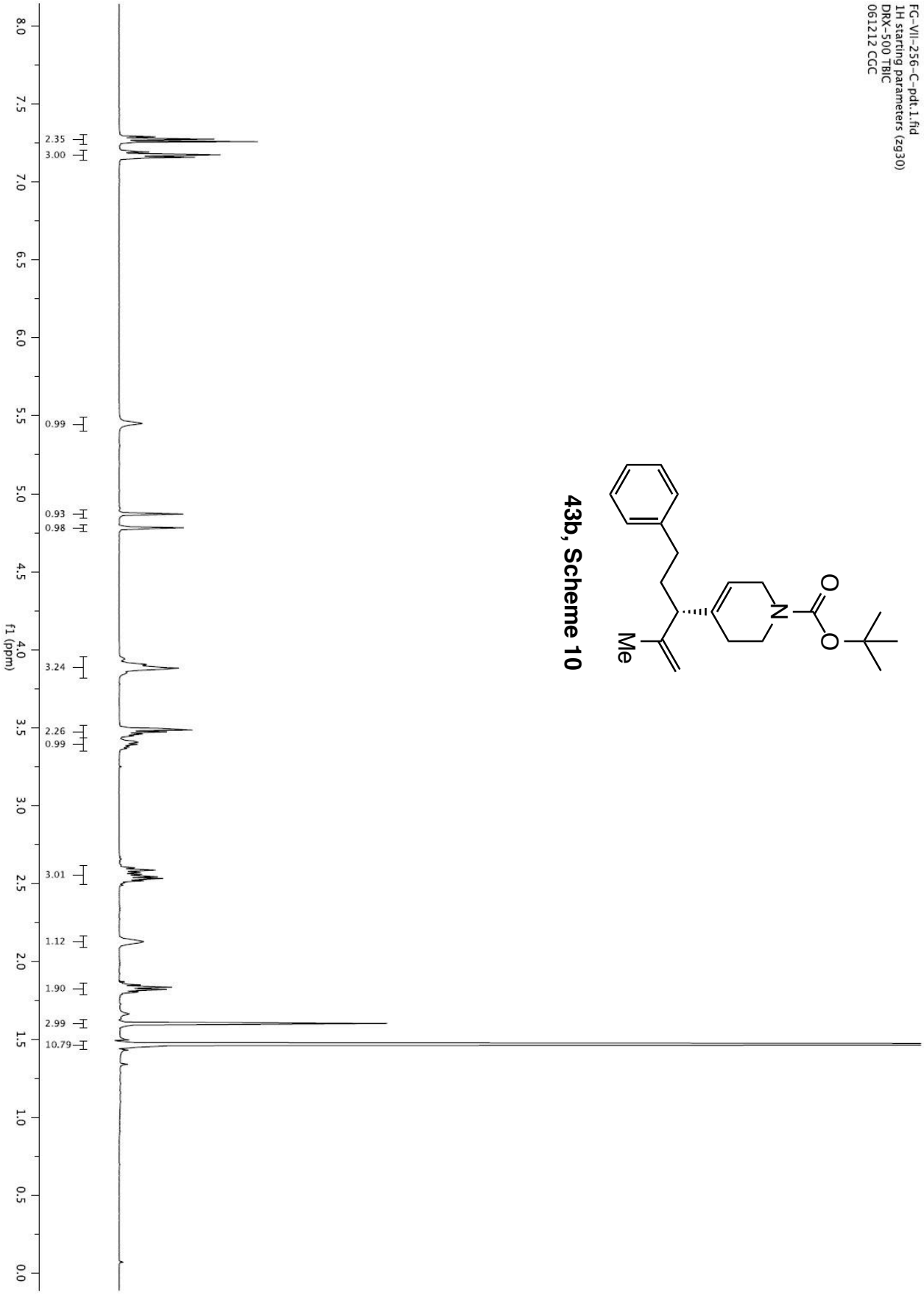
```
Sample Name:
  FG-VIII-041-pdt
exp1  PROTON
Date Collected on:
  vnmr13-vnmrs400
Archive directory:
    SAMPLE
date    May  5 2013
solvent     cdcl3
Sample directory:
file            exp
    ACQUISITION
Fidfile: PROTON
sw            6410.3
at             2.556
np              32768
fb               4000
bs                  4
d1              1.000
nt                 40
ct                 16
   TRANSMITTER
tn                 H1
sfrq          399.786
tof             399.8
tpwr               60
pw              5.500
    DECOUPLER
dn                C13
dof                 0
dm                nnn
decwave W40_HCN5mm
dpwr               35
dmf             29412

   PRESATURATION
satmode             n
wet                 n
      SPECIAL
temp             25.0
gain               46
spin               20
hst             0.008
pw90           11.000
alfa           10.000
       FLAGS
il                  n
in                  n
dp                  y
hs                 nn
     PROCESSING
fn           not used
      DISPLAY
sp              286.9
wp             2740.7
rfl            3700.8
rfp            2902.4
rp              -53.3
lp                  0
        PLOT
wc                250
sc                  0
vs                 49
th                  7
ai     ph

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 5 2013
```



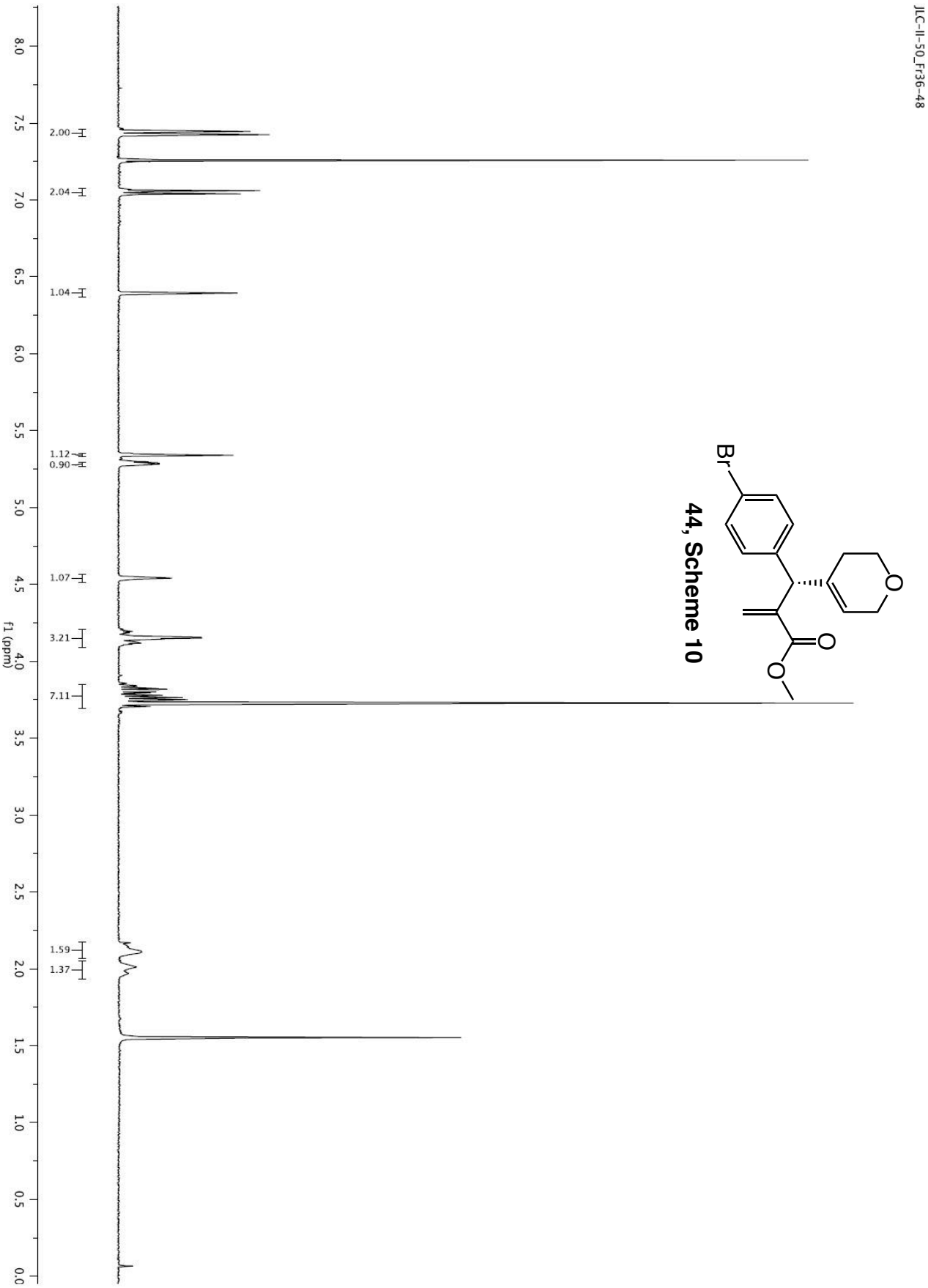
santolina alcohol, Eq 1


Sample: FG-VII-166-A-pdt
Exp: 10exp proton
Pulse Sequence: s2pul
date Sep 26 2012
solvent cdcl3
file
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 40
ct 16
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -7.5
wp 3214.3
rfl 806.4
rfp 0
rp 119.3
lp 0
PLOT
wc 250
sc 0
vs 500
th 12
ph
ai
Br
42, Scheme 10
0.93
1.00
1.39
0.99
1.00
1.02
1.05
1.05
1.00
2.21
2.27
2.01
9.83
ppm


FG-VII-254-C-pdt-second.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
43a, Scheme 10
Me
N
O
O
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.10
0.99
1.83
1.10
1.01
1.00
3.25
2.04
2.22
3.00
10.74



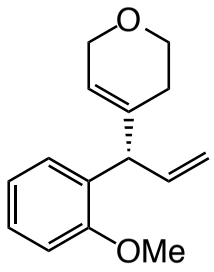
43b, Scheme 10


JLC-II-50_Fr36-48
Br
O
O
O
44, Scheme 10
2.00
2.04
1.04
1.12
0.90
1.07
3.21
7.11
1.59
1.37
f1 (ppm)

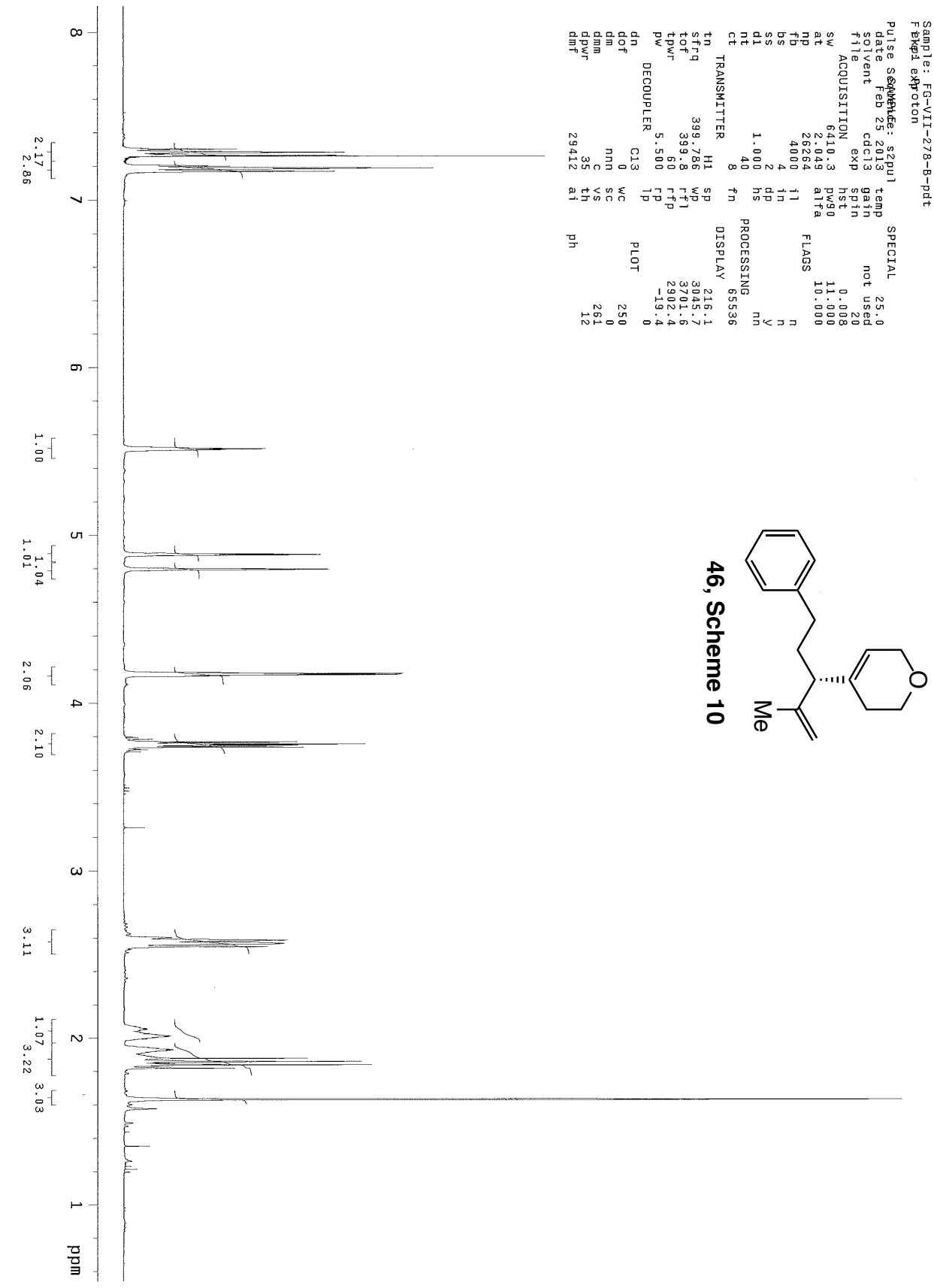
Sample: FG-VII-192-B-pdt
File: exp
Proton

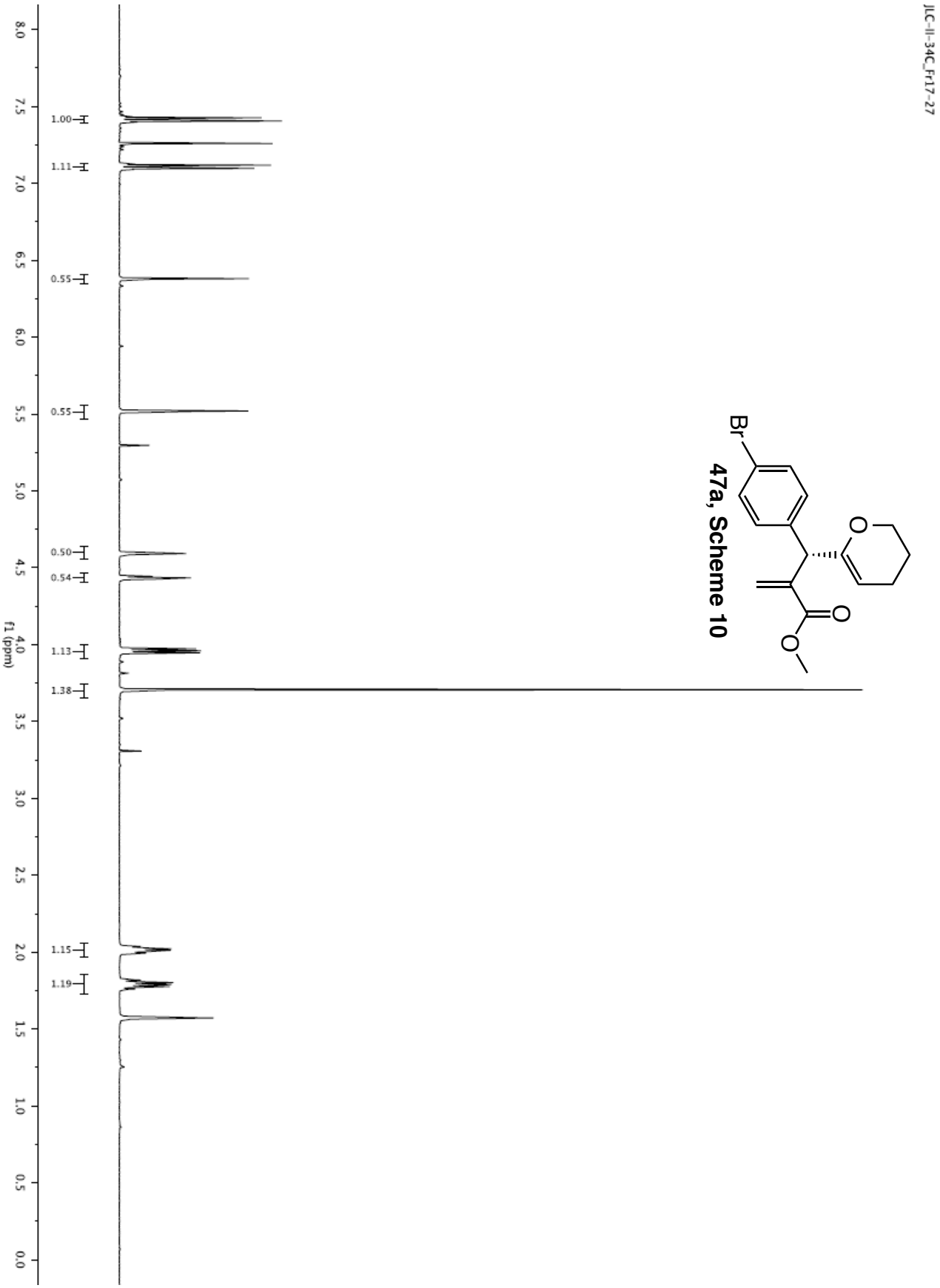
Pulse Sequence: s2pul
SAMPLE

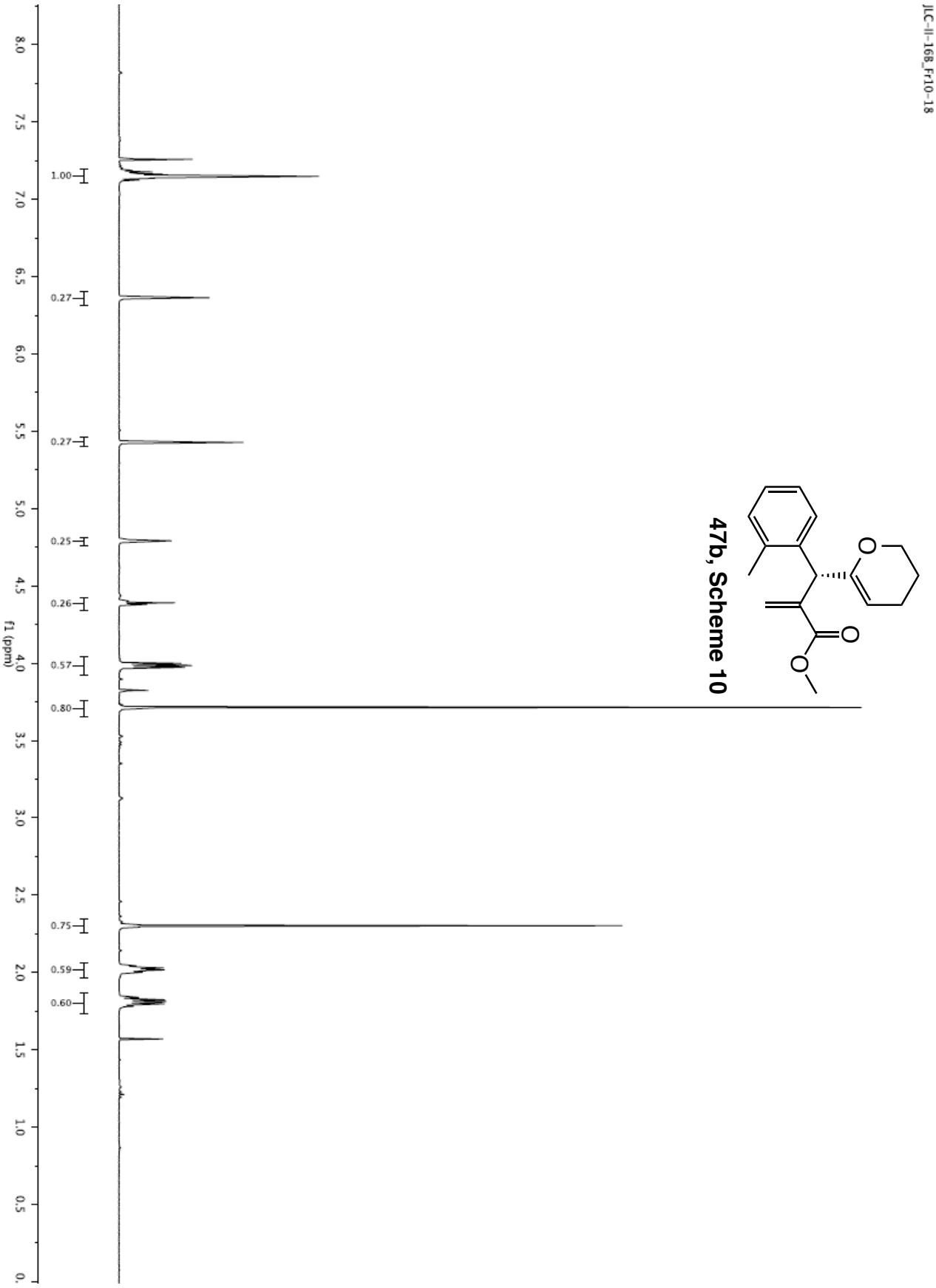
date	Oct 22 2012	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	11.000
at	2.049	alfa	10.000
np	26264	FLAGS	
fb	4000	il	n
bs	4	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	40	PROCESSING	
ct	12	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	143.9
sfrq	399.786	wp	3095.4
tof	399.8	rfl	3701.6
tpwr	60	rfp	2902.4
pw	5.500	rp	59.9
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	72
dpwr	35	th	12
dmf	29412	ai ph	

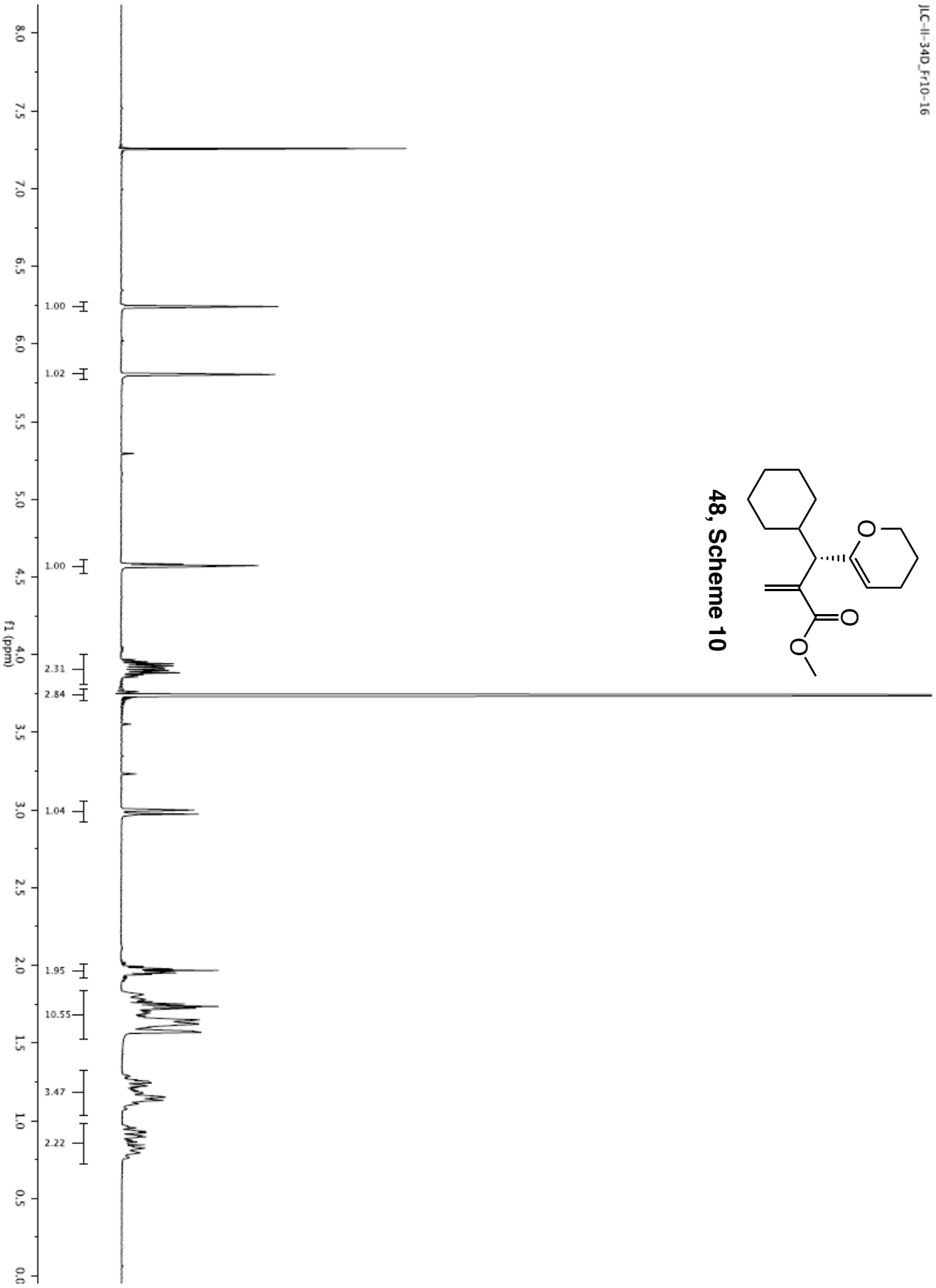


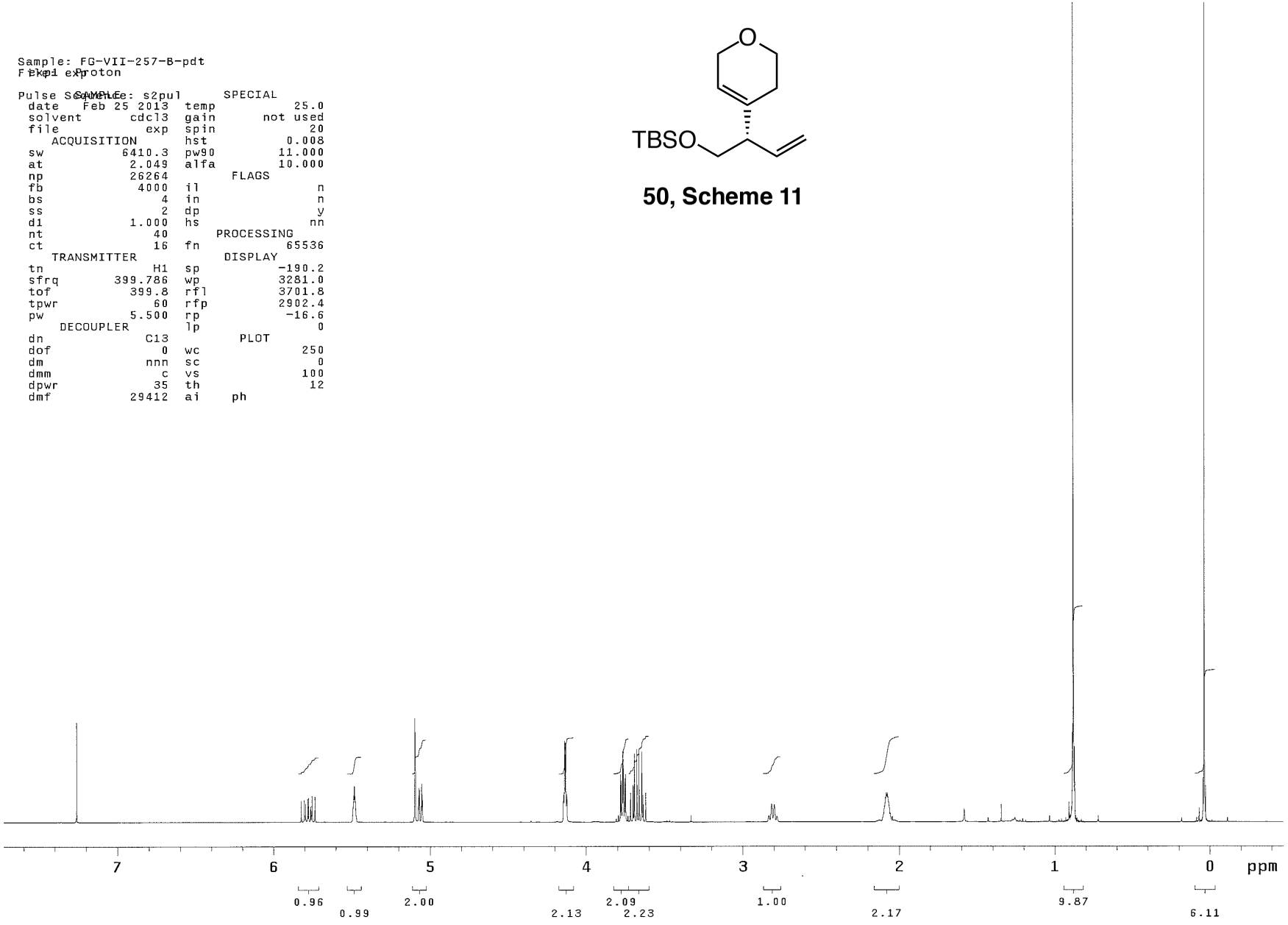
45, Scheme 10

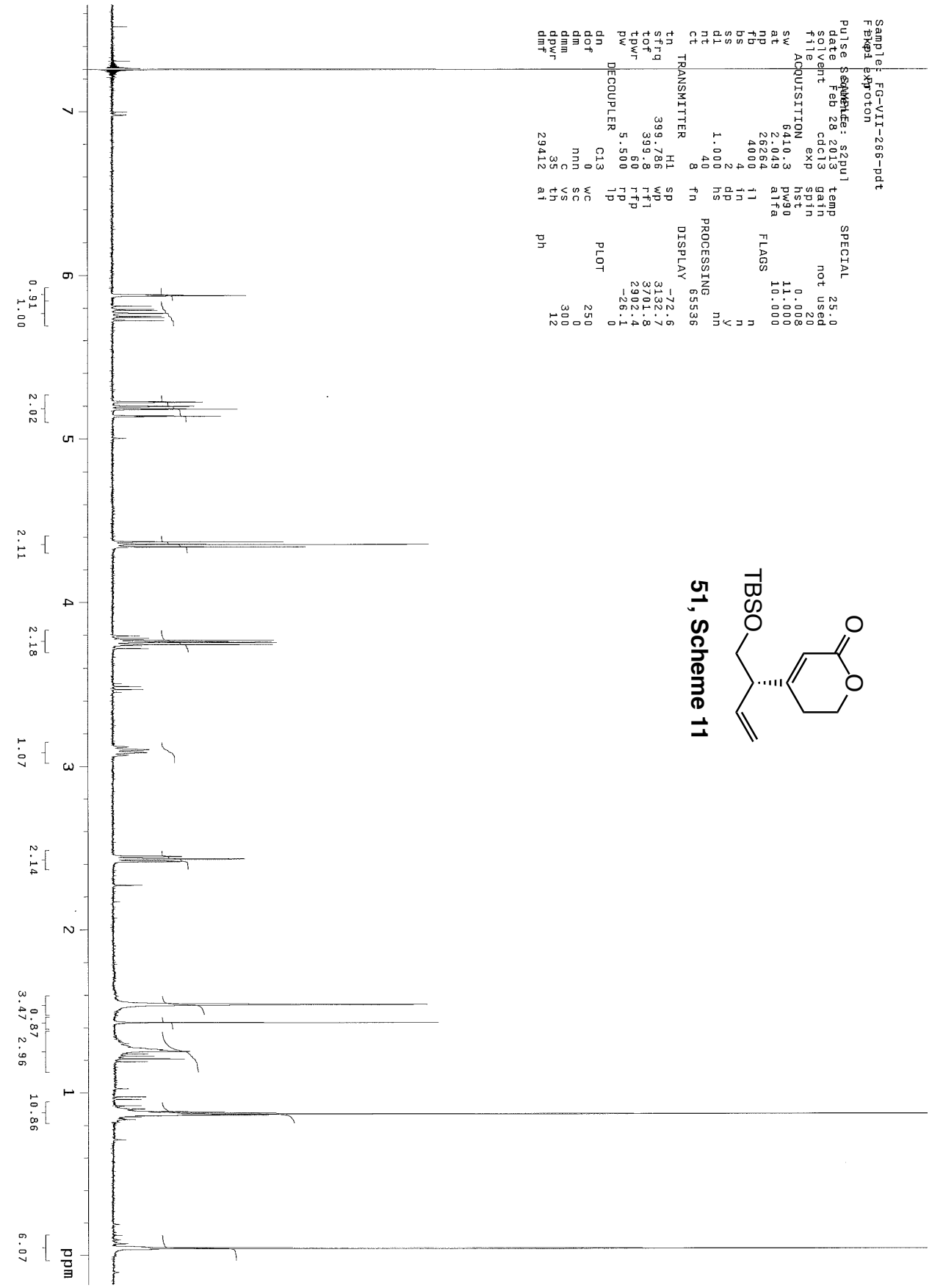

Sample: FG-VII-278-B-pdt
Exp: 1 exp proton
Pulse Sequence: s2pul
date Feb 25 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 40
ct 8
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
SPECIAL 25.0
temp not used
gain 20
spin 0.008
hst 11.000
pw90 10.000
alfa
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp 216.1
wp 3045.7
rfl 3701.6
rfp 2902.4
rp -19.4
lp 0
PLOT
250
0
wc
sc
vs
th
261
12
ph
ai
2.17
2.86
1.00
1.04
1.01
2.06
2.10
3.11
1.07
3.22
3.03
8
7
6
5
4
3
2
1
ppm
O
Me
46, Scheme 10


JLC-II-34C_Fr17-27
Br
O
O
O
47a, Scheme 10
f1 (ppm)
1.00
1.11
0.55
0.55
0.50
0.54
1.13
1.38
1.15
1.19


JLC-II-168_Fr10-18
47b, Scheme 10
f1 (ppm)
1.00
0.27
0.27
0.25
0.26
0.57
0.80
0.75
0.59
0.60


JLC-II-34D_Fr10-16
48, Scheme 10
f1 (ppm)
1.00
1.02
1.00
2.31
2.84
1.04
1.95
10.55
3.47
2.22

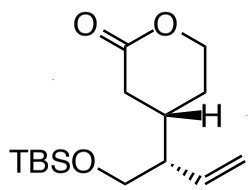

Sample: FG-VII-257-B-pdt
Exp: Proton
Pulse Sequence: s2pul
SAMPLE
date Feb 25 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 40
ct 16
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -190.2
wp 3281.0
rfl 3701.8
rfp 2902.4
rp -16.6
lp 0
PLOT
wc 250
sc 0
vs 100
th 12
ai ph
TBSO
O
50, Scheme 11
7
6
5
4
3
2
1
0
ppm
0.96
0.99
2.00
2.13
2.09
2.23
1.00
2.17
9.87
6.11


Sample: FG-VII-266-pdt
Exp: 1 exp proton
Pulse Sequence: s2pul
date Feb 28 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 4
ss 2
d1 1.000
nt 40
ct 8
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
temp
gain
spin
hst
pw90
alfa
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -72.6
wp 3132.7
rfl 3701.8
rfp 2902.4
rp -26.1
lp 0
PLOT
wc 250
sc 0
vs 300
th 12
ai
ph
SPECIAL
25.0
not used
20
0.008
11.000
10.000
n
n
y
nn
0
TBSO
51, Scheme 11
ppm
7
6
5
4
3
2
1
0.91
1.00
2.02
2.11
2.18
1.07
2.14
0.87
3.47
2.96
10.86
6.07

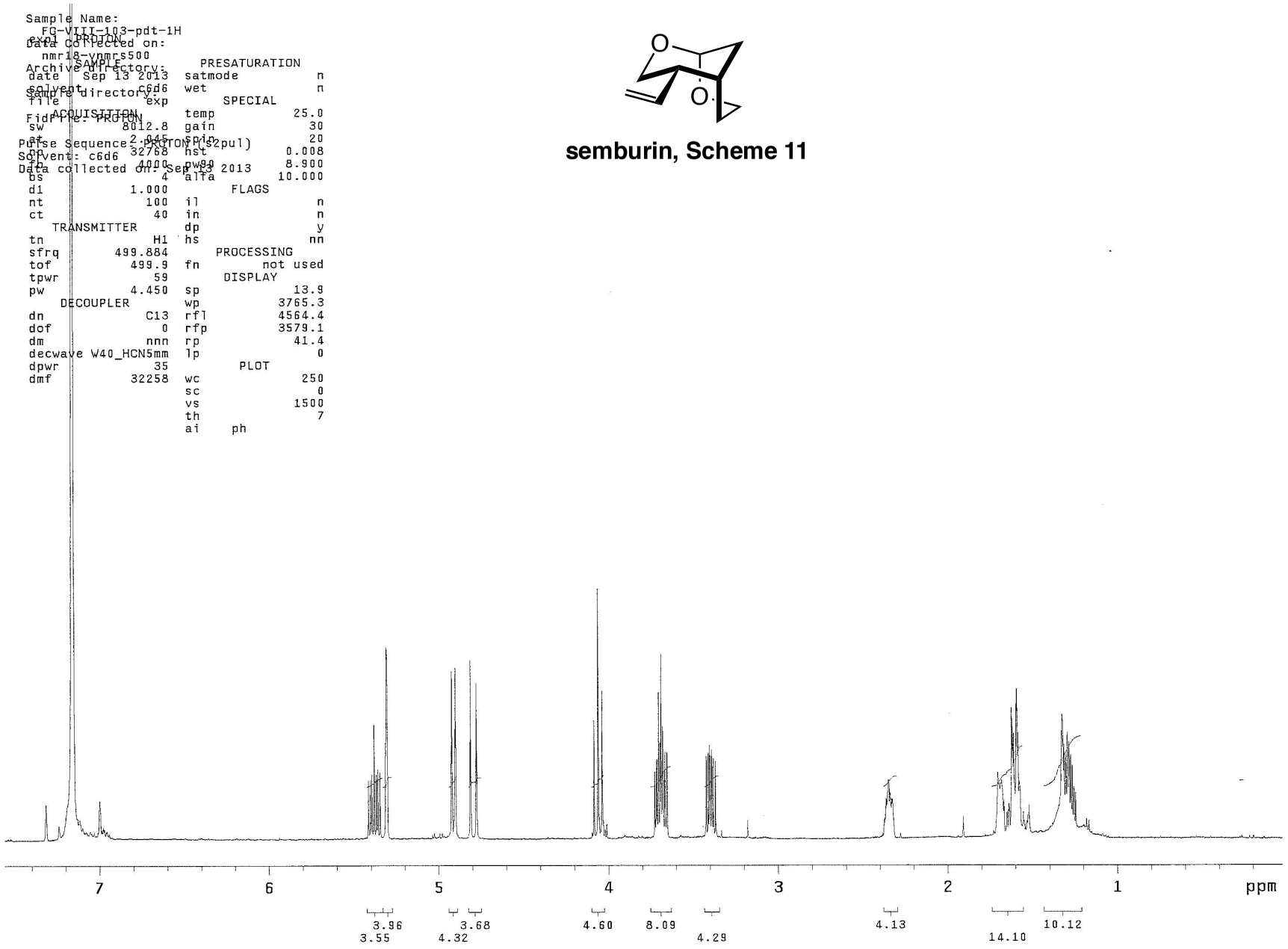
Sample Name:
FG-VIII-095-pdt
exp24 proton
Data collected on:
vnmr13-vnmrs400
SAMPLE
Archive directory:
date Jun 18 2013
solvent cdcl3
Sample directory:
file exp
ACQUISITION
Fidfile: PROTON
sw 6410.3
at 2.556
np 32768
fb 4000
bs 4
d1 1.000
nt 40
ct 20
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_HCN5mm
dpwr 35
dmf 29412

PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin not used
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -206.1
wp 3209.4
rfl 3701.2
rfp 2902.4
rp 40.8
lp 0
PLOT
wc 250
sc 0
vs 500
th 7
ai ph

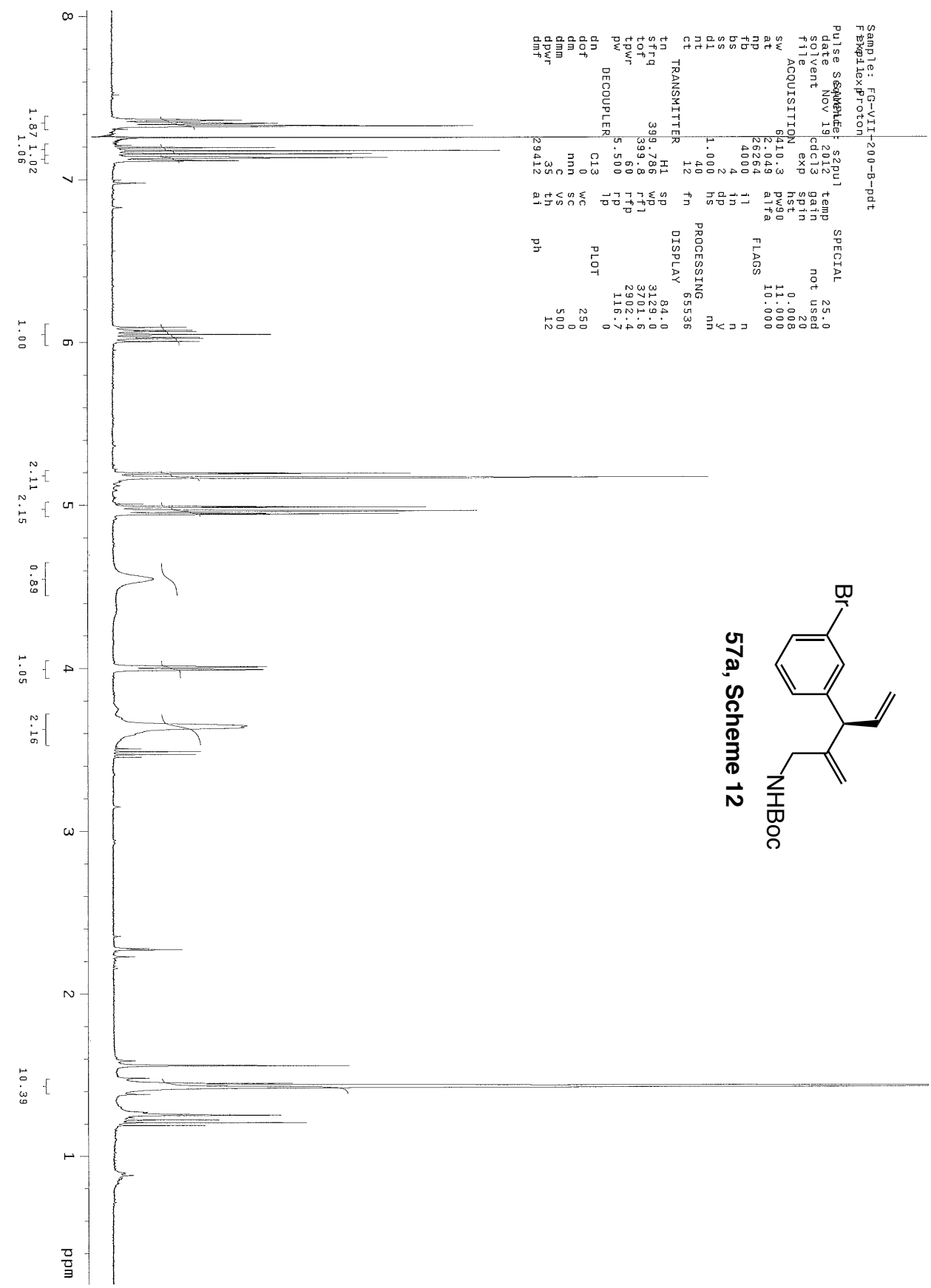
Pulse Sequence: PROTON(s2pul)
Solvent: cdcl3
Data collected on: Jun 18 2013

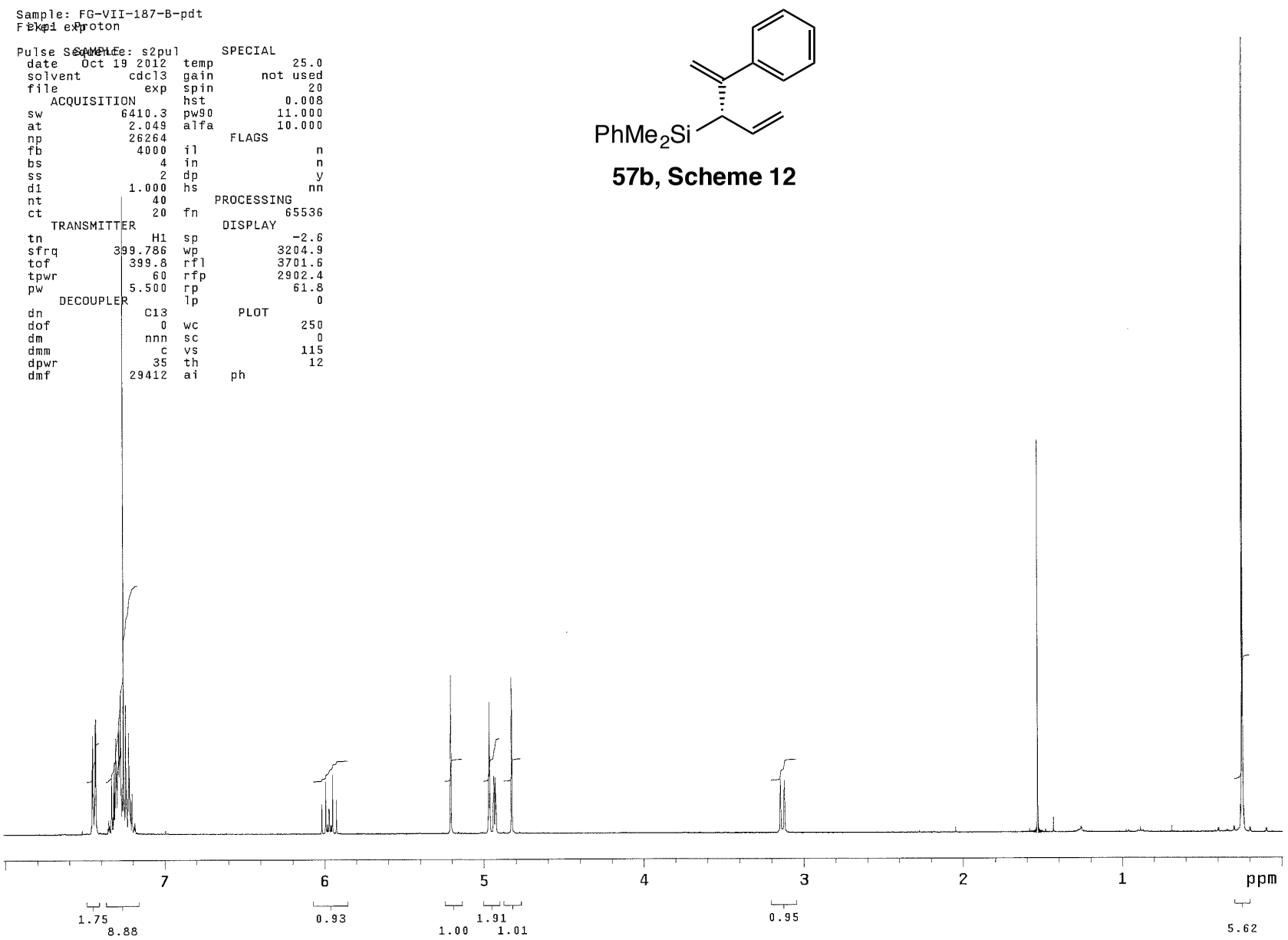


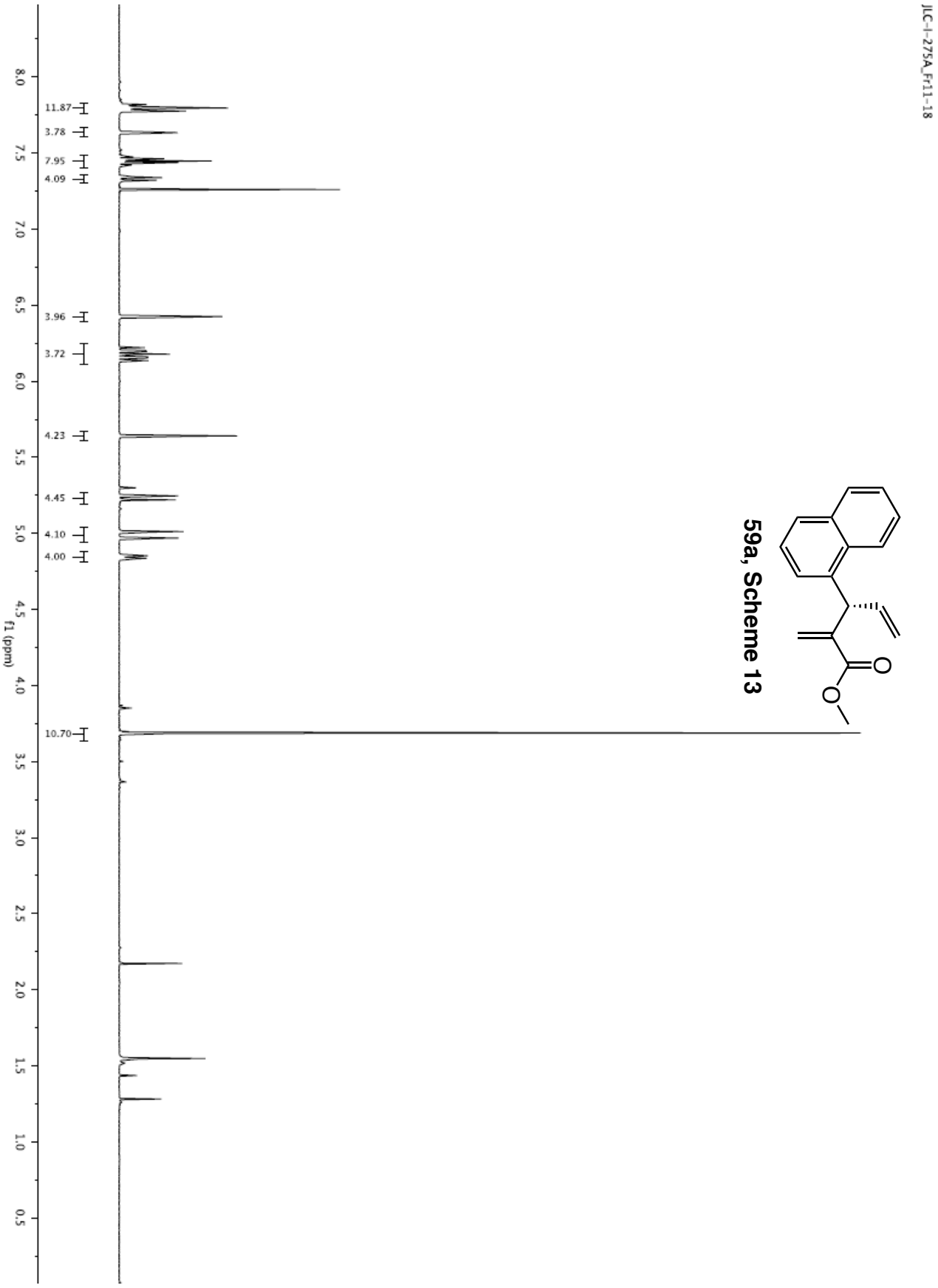
53, Scheme 11

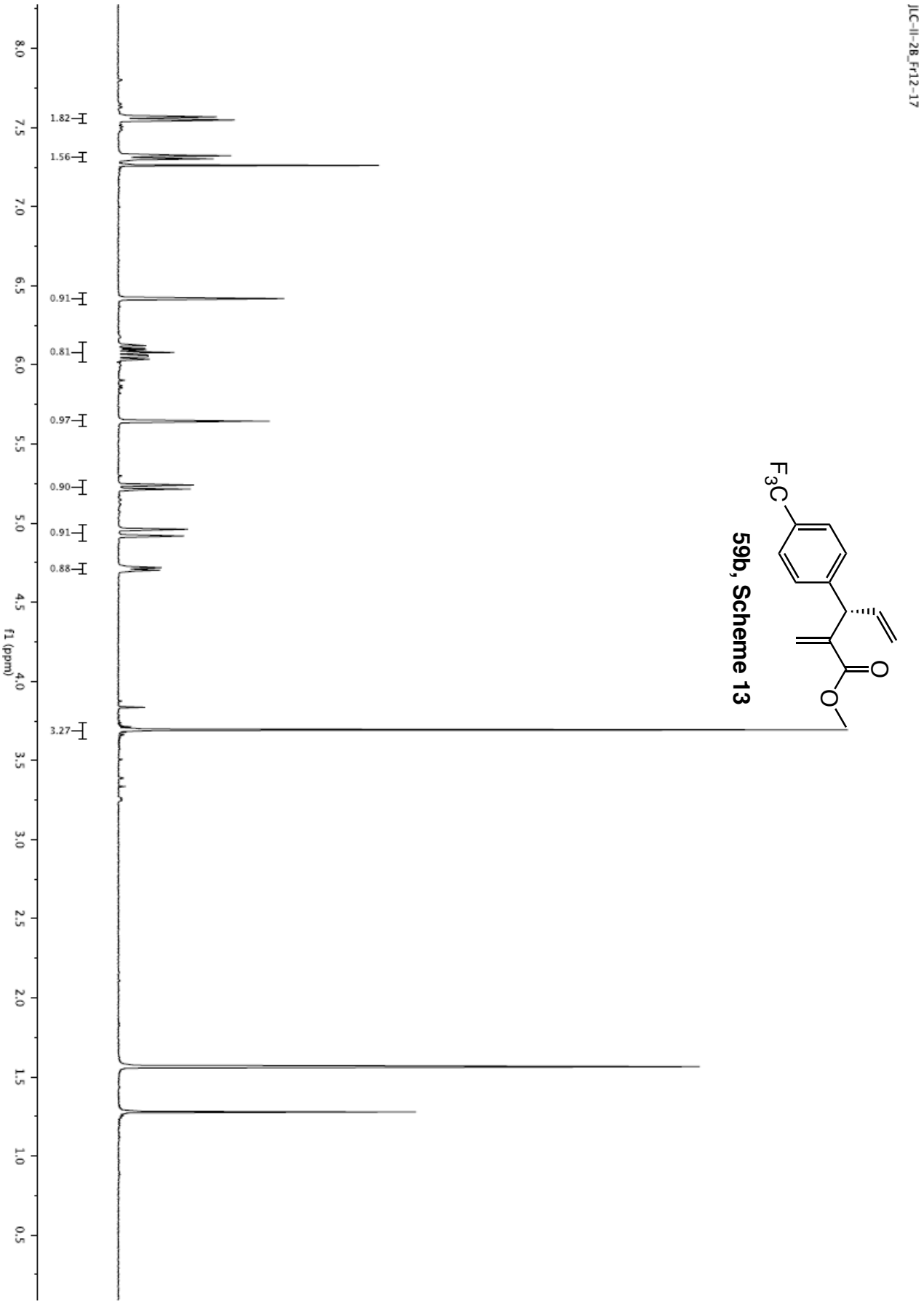


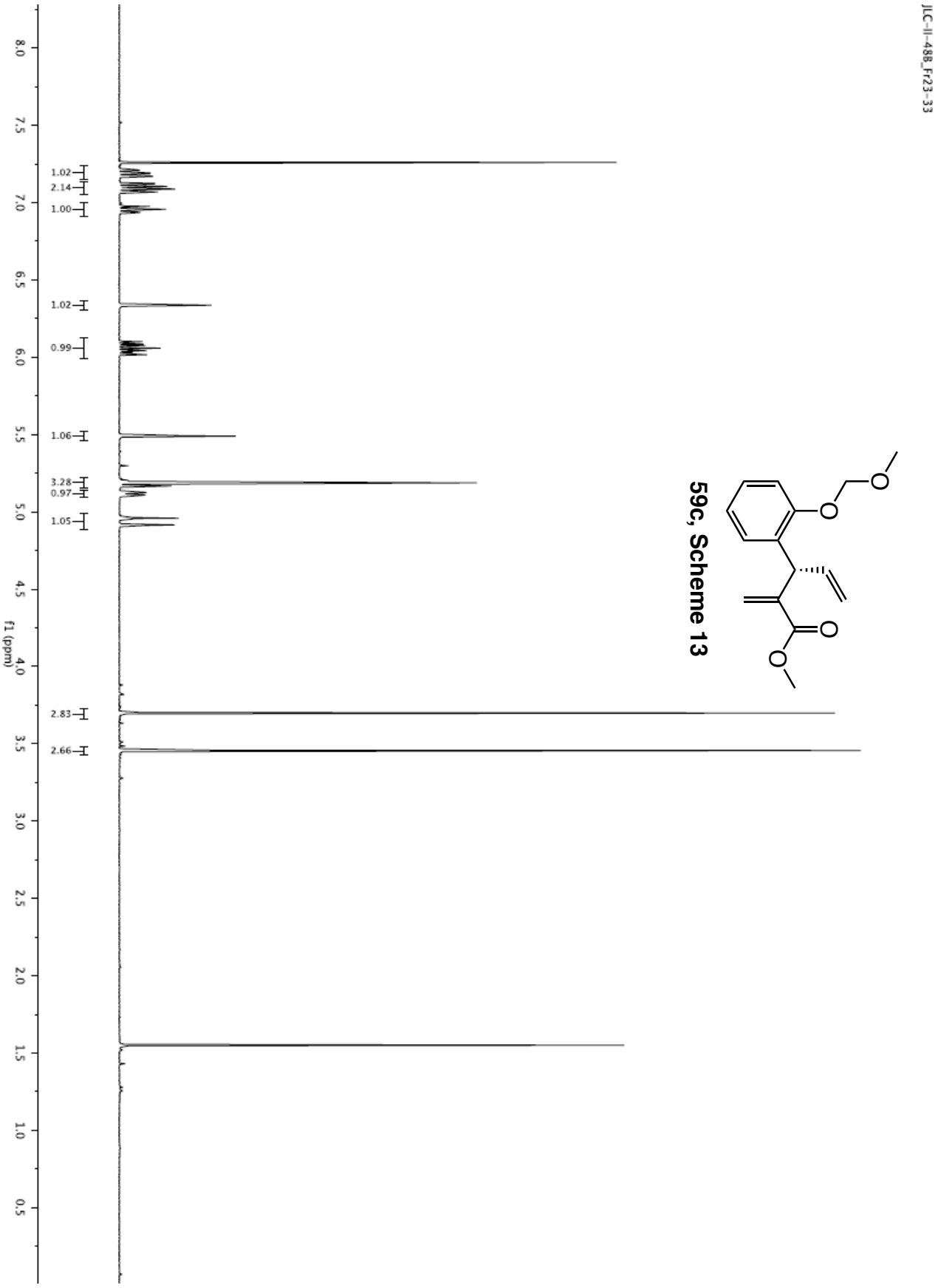
semburin, Scheme 11

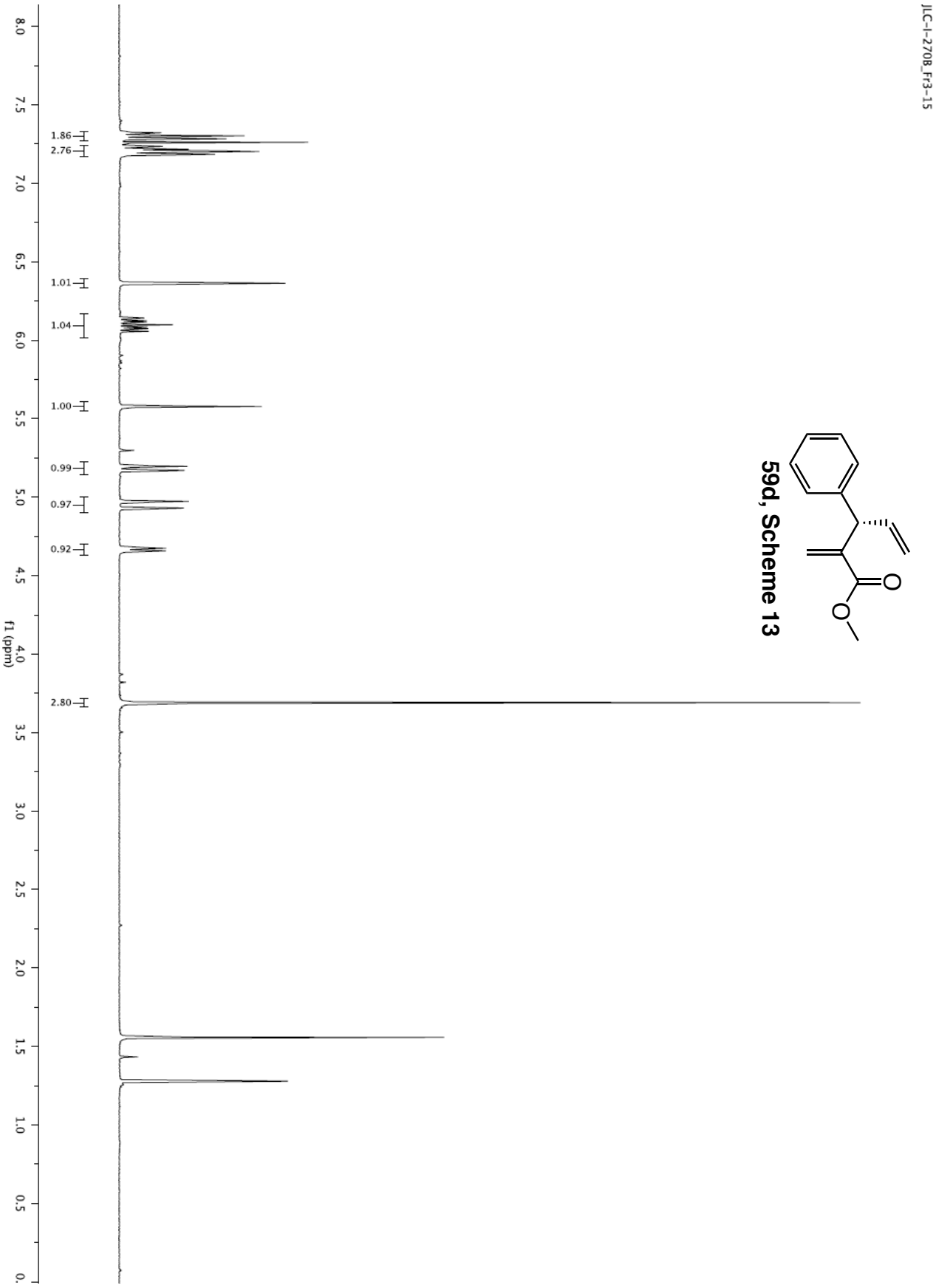

Sample: FG-VII-200-B-pdt
Exp: 1exp1
Proton
Pulse Sequence: s2pul SPECIAL
date Nov 19 2012 temp 25.0
solvent cdcl3 gain not used
file exp spin 20
ACQUISITION hst 0.008
sw 6410.3 pw90 11.000
at 2.049 alfa 10.000
np 26264 FLAGS
fb 4000 il n
bs 4 in n
ss 2 dp y
d1 1.000 hs nn
nt 40 PROCESSING
ct 12 fn 65536
TRANSMITTER DISPLAY
tn H1 sp 84.0
sfrq 399.786 wp 3129.0
tof 399.8 rfl 3701.6
tpwr 60 rfp 2902.4
pw 5.500 rp 116.7
DECOUPLER lp 0
dn C13 PLOT
dof 0 wc 250
dm nnn sc 0
dmm c vs 500
dpwr 35 th 12
dmf 29412 ai
ph
Br
NHBoc
57a, Scheme 12
1.87 1.02
1.06
1.00
2.11
2.15
0.89
1.05
2.16
10.39
8
7
6
5
4
3
2
1
ppm

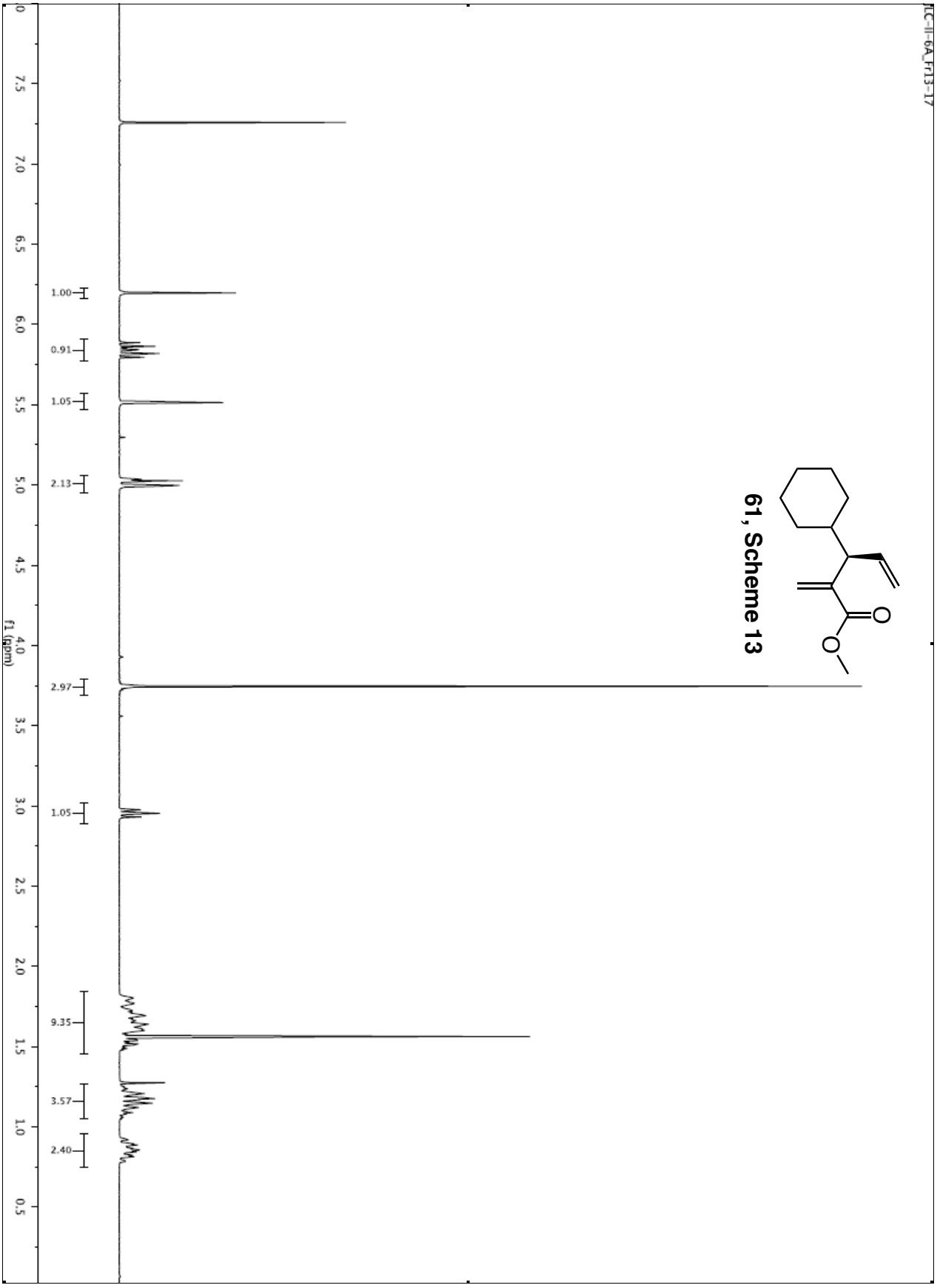

Sample: FG-VII-187-B-pdt
Exp1 exp Proton
Pulse Sequence: s2pul SPECIAL
date Oct 19 2012 temp 25.0
solvent cdcl3 gain not used
file exp spin 20
ACQUISITION hst 0.008
sw 6410.3 pw90 11.000
at 2.049 alfa 10.000
np 26264 FLAGS
fb 4000 il n
bs 4 in n
ss 2 dp y
d1 1.000 hs nn
nt 40 PROCESSING
ct 20 fn 65536
TRANSMITTER DISPLAY
tn H1 sp -2.6
sfrq 399.786 wp 3204.9
tof 399.8 rfl 3701.6
tpwr 60 rfp 2902.4
pw 5.500 rp 61.8
DECOUPLER lp 0
dn C13 PLOT
dof 0 wc 250
dm nnn sc 0
dmm c vs 115
dpwr 35 th 12
dmf 29412 ai ph
PhMe2Si
57b, Scheme 12
7
6
5
4
3
2
1
ppm
1.75
8.88
0.93
1.00
1.91
1.01
0.95
5.62


JLC-I-275A_Fr11-18
59a, Scheme 13
11.87
3.78
7.95
4.09
3.96
3.72
4.23
4.45
4.10
4.00
10.70
f1 (ppm)


JLC-II-28_Fr12-17
F3C
O
O
59b, Scheme 13
1.82
1.56
0.91
0.81
0.97
0.90
0.91
0.88
3.27
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


JLC-II-488_Fr23-33
59c, Scheme 13
f1 (ppm)
1.02
2.14
1.00
1.02
0.99
1.06
3.28
0.97
1.05
2.83
2.66


JLC-I-270B_Fr3-15
59d, Scheme 13
1.86
2.76
1.01
1.04
1.00
0.99
0.97
0.92
2.80
f1 (ppm)


JLC-II-6A_ft13-17
61, Scheme 13
O
O
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
0.91
1.05
2.13
2.97
1.05
9.35
3.57
2.40