Cascade Intramolecular *N*-Arylation/Intermolecular Carboamination Reactions for the Construction of Tricyclic Heterocycles.

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Supporting Information

Experimental procedures and characterization data for new compounds in Table 2 and Scheme 2.

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General: All reactions were carried out under a nitrogen atmosphere in oven- or flame-dried glassware. $Pd(OAc)_2$, $Pd_2(dba)_3$, and all phosphine ligands were purchased from Strem Chemical Co. or Aldrich Chemical Co. and used without further purification. All aryl chlorides and common reagents were obtained from commercial sources and were used as received. Toluene, diethyl ether, methylene chloride, and THF were purified using a GlassContour solvent purification system. Flash chromatography was conducted using silica gel unless otherwise noted. Bulk quantities of NaO^tBu were stored in a nitrogen-filled glovebox. Small amounts (ca 1 g) were removed and stored in a dessicator for up to a few days prior to use, and quantities needed for individual experiment were weighed in the air. 3-(2-bromophenyl)propanal[1] and 2-(2-

bromophenoxy)acetic acid[2] were synthesized according to literature procedure. Ratios of diastereomers were determined by ^{1}H NMR analysis of crude reaction mixtures. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR analysis. The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in Table 2 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Table 2.

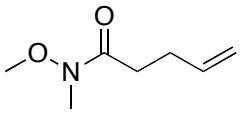
Preparation and Characterization of Substrates

General Procedure 1: Generation of Grignard Reagents

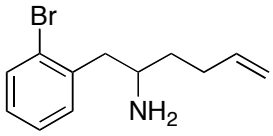
A flame- or oven-dried flask equipped with a reflux condenser and a magnetic stir bar was cooled under a stream of nitrogen and charged with an appropriate alkyl bromide (2.0 equiv relative to substrate) and diethyl ether (0.2–1 M). Freshly ground magnesium turnings were added (4.0 equiv relative to substrate) and the flask was purged with nitrogen. When self-reflux began, the reaction mixture was placed in an ambient temperature water bath for 5 min, then was removed from the bath and stirred for an additional 30 min at rt. Stirring was then halted, and the reaction mixture was allowed to stand at rt for 20 min. During this time a finely divided particulate suspension settled to the bottom of the flask. Only the solution above the solid material was employed in subsequent addition reactions to electrophiles.

General Procedure 2: Synthesis of *N*-Sulfinyl Imines

A flame-dried flask equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with an appropriate aldehyde or ketone (1.0 equiv), 2-methylpropane-2-sulfinamide (1.05 equiv), THF (0.5 M), and titanium ethoxide (2.0 equiv). The resulting mixture was stirred under a nitrogen atmosphere at rt (aldehyde) or reflux (ketone) until the starting material was consumed as judged by TLC analysis. The reaction mixture was cooled to rt, quenched with brine (0.5 M) and quickly filtered through a plug of Celite. The plug was rinsed thoroughly with ethyl acetate. The filtrate was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated *in vacuo* and purified by flash chromatography on silica gel.

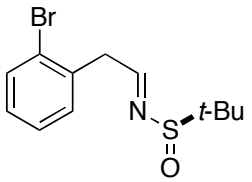


***N*-Methoxy-*N*-methylpent-4-enamide (S1).**[3] An oven-dried flask equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with 4-pentenoic acid (10.2 mL, 100 mmol) and chloroform (400 mL, 0.25 M). *N,O*-dimethylhydroxylamine hydrochloride (14.63 g, 150 mmol), *N*-methylmorpholine (27.5 mL, 250 mmol), 1-hydroxybenzotriazole hydrate (14.86 g, 110 mmol), and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (21.09 g, 110 mmol) were added, and the reaction flask was purged with N_2. The resulting mixture was stirred at rt overnight, then was filtered through a fritted funnel. The solids were rinsed with 1:1 EtOAc/ hexanes, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 7.76 g (54%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93–5.81 (m, 1 H), 5.11–5.04 (m, 1 H), 5.02–4.98 (m, 1 H), 3.69 (s, 3 H), 3.19 (s, 3 H), 2.56–2.51 (m, 2 H), 2.41–2.36 (m, 2 H).



(±)-1-(2-Bromophenyl)hex-5-en-2-amine (**5a**) A solution of 2-bromobenzyl bromide (16.41 g, 66 mmol) in diethyl ether (300 mL) was converted to 2-bromobenzylmagnesium bromide according to General Procedure 1. The freshly made Grignard reagent was added dropwise to a 0 ºC solution of *N*-methoxy-*N*-methylpent-4-enamide (4.70 g, 33 mmol) in diethyl ether (30 mL) via cannula over 25 min. After the addition was complete, the reaction vessel was removed from the ice bath and stirred at rt overnight. The mixture was then cooled to 0 °C and slowly quenched with saturated ammonium chloride. The resulting mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with methylene chloride (3 x 50 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on basic alumina to afford 1-(2-bromophenyl)hex-5-en-2-one (**S2**) as a clear oil (6.15 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J = 1.0, 8.1 Hz, 1 H), 7.30–7.26 (m, 1 H), 7.21 (dd, J = 1.7, 7.6 Hz, 1 H), 7.16–7.12 (m, 1 H), 5.85–5.76 (m, 1 H), 5.05–4.96 (m, 2 H), 3.86 (s, 2 H), 2.60 (t, J = 7.3, 2 H), 2.38–2.33 (m, 2 H).

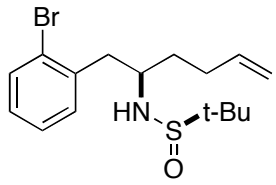
A portion of the 1-(2-bromophenyl)hex-5-en-2-one (1.27 g, 5.0 mmol) was stirred with ammonium acetate (3.93 g, 5.1 mmol) and sodium cyanoborohydride (223 mg, 3.6 mmol) in anhydrous methanol (15 mL, 0.33 M) under nitrogen at rt for 4 d. The reaction was quenched with 1 M HCl and concentrated *in vacuo* to remove methanol. The mixture was taken to pH 14 by addition of 3 M NaOH, and the resulting solution was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on basic alumina to afford the title compound as a pale yellow oil (642 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 1 H), 7.27–7.22 (m, 2 H), 7.11–7.07 (m, 1 H), 5.89–5.80 (m, 1 H), 5.07 (dd, J = 2.0, 3.4 Hz, 1 H), 5.04–4.95 (m, 1 H), 3.15–3.09 (m, 1 H), 2.97 (dd, J = 4.9, 13.7 Hz, 1 H), 2.60 (dd, J = 8.8, 13.7 Hz, 1 H), 2.29–2.19 (m, 1 H), 2.18–2.13 (m, 1 H), 1.66–1.58 (m, 1 H), 1.53–1.45 (m, 1 H), 1.22 (s, br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.5, 133.0, 131.6, 128.0, 127.3, 125.0, 114.7, 50.8, 44.8, 36.9, 30.5; IR (film) 3371, 3287, 2920, 1640 cm^{-1}. MS (ESI) *m/z* 254.0554 (245.0544 calcd for $C_{12}H_{16}BrN$, M + H$^+$).



(–)-(*R*,*E*)-*N*-[2-(2-Bromophenyl)ethylidene]-2-methylpropane-2-sulfinamide (10a). An oven-dried round bottom flask equipped with a magnetic stir bar was charged with 2-(2-bromophenyl)ethanol (1.00 g, 5.0 mmol) and purged with nitrogen. Methylene chloride (16 mL, 0.32 M) was added and the resulting solution was cooled to 0 ºC. Trichloroisocyanuric acid (1.16 g, 5.0 mmol) was added and the mixture was stirred at 0 ºC for 5 min. 2,2,6,6-Tetramethyl-piperidin-1-oxyl (81 mg, 0.50 mmol) was then added and the reaction mixture was stirred at 0 °C for an additional 10 min. The reaction mixture was then filtered through Celite, and the Celite was rinsed with fresh methylene chloride. The filtrate was transferred to a separatory funnel and washed with 10% Na_2CO_3 (3 x 50 mL), 1 M HCl (3 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford 2-(2-bromophenyl)acetaldehyde[4] (**9a**) as a clear oil. This material was used without additional

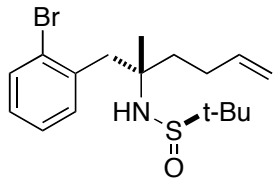
purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.7 Hz 1 H), 7.62 (dd, *J* = 1.0, 8.1 Hz, 1 H), 7.34–7.30 (m, 1 H), 7.27–7.23 (m, 1 H), 7.21–7.17 (m, 1 H), 3.87 (d, *J* = 1.7 Hz, 2 H).

The crude 2-(2-bromophenyl)acetaldehyde (**9a**) was then condensed with (*R*)-2-methylpropane-2-sulfinamide (641 mg, 5.30 mmol) according to General Procedure 2 to afford 619 mg (41% over two steps) of the title compound as a clear oil. $[\alpha]^{23}_D$ –201.6 (*c* 2.42, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (t, *J* = 4.6 Hz, 1 H), 7.58 (dd, *J* = 1.0, 8.1 Hz, 1 H), 7.31–7.23 (m, 2 H), 7.17–7.13 (m, 1 H), 3.99 (d, *J* = 4.6 Hz, 2 H), 1.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 135.0, 133.0, 131.2, 128.9, 127.7, 124.8, 57.0, 42.7, 22.4; IR 3059, 2959, 1619 cm^{-1}. MS (ESI) 302.0202 (302.0209 calcd for $C_{12}H_{16}BrNOS$, M + H^+).



(+)-(*R*$_s$,*R*)-*N*-[1-(2-Bromophenyl)hex-5-en-2-yl]-2-methylpropane-2-sulfinamide (11a). A solution of 4-bromo-1-butene (0.41 mL, 4.0 mmol) in diethyl ether (4 mL) was converted to the corresponding Grignard reagent via General Procedure 1. The freshly made Grignard solution was added dropwise to a –55 ºC solution of **10a** (602 mg, 2.0 mmol) in methylene chloride (10 mL) over 5 min. The resulting mixture was slowly warmed from –55 ºC to –15 ºC over 4 h. TLC analysis indicated the reaction had not proceeded to completion. The reaction was cooled to –78 ºC and allowed to warm slowly overnight (12 h) to +10 ºC. The reaction was then quenched with saturated ammonium chloride and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with methylene chloride (4 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 478 mg (67%) of the title compound as a 22:1 mixture of diastereomers as a clear oil which solidified upon standing to give a white solid, mp 69–75 ºC $[\alpha]^{23}_D$ +9.2 (*c* 2.48, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.51 (m, 1 H), 7.28–7.21 (m, 2 H), 7.09–7.04 (m, 1 H), 5.88–5.79 (m, 1 H), 5.12–5.06 (m, 1 H), 5.03–4.99 (m, 1H), 3.63–3.56 (m, 1 H), 3.17 (d, *J* = 7.6 Hz, 1 H), 2.99 (dd, *J* = 5.4, 11.7 Hz, 1 H), 2.95–2.90 (m, 1 H), 2.33–2.22 (m, 2 H), 1.93–1.85 (m, 1 H), 1.82–1.74 (m, 1 H), 1.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.8, 132.8, 132.0, 128.1, 127.3, 125.1, 115.3, 57.4, 55.8, 42.5,

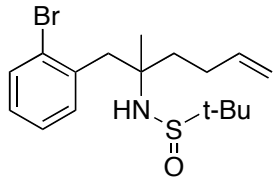
35.5, 30.0, 22.4; IR (film) 3216, 3071, 2924, 1640. MS (ESI) *m/z* 358.0835 (358.0835 calcd for $C_{16}H_{24}BrNOS$, M + H^+).



(–)-(*R*$_s$,*S*)-*N*-[1-(2-Bromophenyl)-2-methylhex-5-en-2-yl]-2-methylpropane-2-sulfinamide (S4). Ketone **S2** (1.92 g, 7.57 mmol) was condensed with (*R*)-2-methylpropane-2-sulfinamide (963 mg, 7.94 mmol) according to General Procedure 2. This procedure afforded 1.88 g (70%) of (–)-(*R*)-*N*-[1-(2-bromophenyl)hex-5-en-2-ylidene]-2-methylpropane-2-sulfinamide (**S3**) as a 1:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. $[\alpha]^{23}_D$ –85.0 (*c* 3.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 2 H), 7.32–7.23 (m, 4 H), 7.20–7.09 (m, 2 H), 5.93–5.82 (m, 1 H), 5.78–5.69 (m, 1 H), 5.12 (d, *J* = 17.6 Hz, 1 H), 5.05 (d, *J* = 10.4 Hz, 1 H), 4.99–4.91 (m, 2 H), 4.37 (d, *J* = 15.8 Hz, 1 H), 4.22 (d, *J* = 15.6 Hz, 1 H), 3.92–3.83 (m, 2 H), 2.99–2.91 (m, 1 H), 2.89–2.80 (m, 1 H), 2.51–2.44 (m, 2 H), 2.37–2.32 (m, 4 H), 1.31 (s, 9 H), 1.04 (s, 9 H).

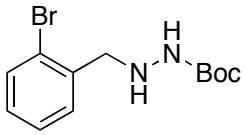
A flame dried flask was cooled under a stream of nitrogen, charged with a portion of **S3** (772 mg, 2.17 mmol), then purged with nitrogen. Toluene (2.2 mL) was added and the resulting solution was cooled to –78 ºC. Trimethylaluminum (2.0 M in toluene, 1.2 mL, 2.4 mmol) was added and the resulting mixture was stirred at –78 ºC for 5 min, then was added via cannula over 10 min to a flask containing a –78 ºC solution of methyllithium (1.6 M in diethyl ether, 3.0 mL, 4.8 mmol) and toluene (6.6 mL). The mixture was stirred at –78 ºC for 4 h, then the reaction vessel was placed in an ice bath and saturated aqueous ammonium chloride was added until bubbling stopped. The layers were separated, and the organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated *in vacuo* and purified via flash chromatography on silica gel to afford 385 mg (50% recovery) of **S3** and 285 mg (35%) of the title compound as a yellow oil which was a 12:1 mixture of diastereomers as determined by ^{1}H NMR analysis. Data are for the major isomer. $[\alpha]^{23}_D$ –4.2 (*c* 2.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.50 (dd, *J* = 1.7, 7.6 Hz, 1 H), 7.29–7.24 (m, 1 H), 7.12–7.07 (m, 1 H), 5.86–5.75 (m, 1 H), 5.05–4.93 (m, 2 H), 3.33 (s, 1 H), 3.21 (d, *J* = 13.6 Hz,

1 H), 3.08 (d, J = 13.6 Hz, 1 H), 2.15–2.12 (m, 2 H), 1.83–1.75 (m, 1 H), 1.64–1.55 (m, 1 H), 1.43 (s, 3 H), 1.21 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 136.7, 133.3, 133.1, 128.3, 127.2, 126.4, 114.5, 58.9, 56.0, 47.1, 39.4, 27.9, 26.2, 22.8; IR (film) 3301, 3220, 3071, 2976, 1640 cm^{-1}. MS (ESI) 372.0992 (372.0991 calcd for $C_{17}H_{26}BrNOS$, M + H$^+$).

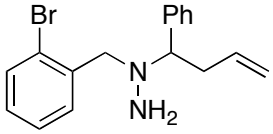


(±)-*N*-[1-(2-Bromophenyl)-2-methylhex-5-en-2-yl]-2-methylpropane-2-sulfinamide (S4). Ketone **S2** (2.23 g, 8.8 mmol) was condensed with (±)-2-methylpropane-2-sulfinamide (1.12 g, 9.2 mmol) according to General Procedure 2. This procedure afforded 1.98 g (63%) of (±)-*N*-[1-(2-bromophenyl)hex-5-en-2-ylidene]-2-methylpropane-2-sulfinamide (**S3**) as a 1:1 mixture of diastereomers as judged by ^{1}H NMR analysis. NMR data were identical to those reported above for (–)-**S3**.

A flame dried flask was cooled under a stream of nitrogen and charged with **S3** (1.98 g, 5.52 mmol). The reaction vessel was purged with nitrogen, toluene (5.5 mL) was added, and the resulting solution was cooled to –78 ºC. Trimethylaluminum (2.0 M in toluene, 3.0 mL, 6.0 mmol) was added and the resulting mixture was stirred at –78 ºC for 5 min, then was added via cannula over 10 min to a flask containing a –78 ºC solution of methyllithium (1.6 M in diethyl ether, 7.5 mL, 12.1 mmol) and toluene (18 mL). The mixture was stirred at –78 ºC for 4 h, then the reaction vessel was placed in an ice bath and saturated aqueous ammonium chloride was added until bubbling stopped. The layers were separated, and the organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated *in vacuo* and purified to afford 1.25g (63% recovery) of **S3** and 588 mg (29%) of the title compound as a yellow oil which was a 12:1 mixture of diastereomers as determine by ^{1}H NMR. ^{1}H NMR data were identical to that those reported above for (–)-**S4**.



***tert*-Butyl 2-(2-bromobenzyl)hydrazinecarboxylate (S5)**. An oven-dried flask equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with *tert*-butyl carbazate (1.13 g, 8.6 mmol). The flask was purged with nitrogen. THF (11 mL) and 2-bromobenzaldehyde (1.0 mL, 8.6 mmol) were added, and the resulting mixture was stirred at rt for 18 h. Additional THF (23 mL), sodium cyanoborohydride (808 mg, 13 mmol), and acetic acid (14 mL) were added, and stirring was continued for an additional 24 h at rt. The reaction mixture was then diluted with water (60 mL) and ethyl acetate (60 mL), then saturated aqueous sodium bicarbonate was slowly added until bubbling ceased. The mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with ethyl acetate (2 x 75 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude material was dissolved in methanol (40 mL), and 1.5 M sodium hydroxide (30 mL) was added. The resulting mixture was stirred at 60 ºC for 1.5 h. The reaction mixture was then cooled to rt and transferred to a separatory funnel. The mixture was extracted with diethyl ether (3 x 50 mL), and the combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The product was taken up in additional diethyl ether (10 mL) and re-dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to afford 2.19 g (85%) of a white solid, mp 67–71 ºC, which was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.54 (m, 1 H), 7.40–7.39 (m, 1 H), 7.28–7.26 (m, 1 H), 7.15–7.12 (m, 1 H), 6.16 (s, br, 1 H), 4.33 (s, br, 1 H), 4.10 (d, J = 11.5 Hz, 2 H), 1.45 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 137.1, 132.8, 131.0, 129.0, 127.4, 124.6, 80.5, 55.6, 28.3; IR (film) 3314, 2976, 1695 cm^{-1}. MS (ESI) 301.0542 (301.0546 calcd for $C_{12}H_{17}BrN_2O_2$, M + H$^+$).

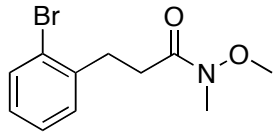


1-(2-Bromobenzyl)-1-(1-phenylbut-3-en-1-yl)hydrazine (16). A flame dried flask was cooled under a stream of nitrogen and charged with **S5** (4.10 g, 14 mmol), benzotriazole (2.43 g, 20

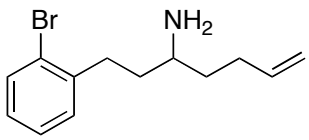
mmol), benzene (68 mL), and benzaldehyde (2.1 mL, 20 mmol). The flask was equipped with a Dean-Stark apparatus and purged with nitrogen. The reaction mixture was heated to reflux for 26 h, then was cooled to rt and quenched with 2 M sodium hydroxide (75 mL). The mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The flask containing the resulting viscous benzotriazole adduct was purged with nitrogen, in diethyl ether (132 mL) was added, and the solution was cooled to 0 ºC. A solution of allyl magnesium bromide (1 M in ether, 27 mL, 27 mmol) was added in slowly over 5 min, then the cooling bath was removed and the reaction mixture was stirred at rt until the benzotriazole adduct was consumed as judged by TLC analysis. The reaction mixture was then cooled to 0 ºC and quenched with 2 M sodium hydroxide (20 mL). The mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 4.10 g (70%) of *tert*-butyl 2-(2-bromobenzyl)-2-(1-phenylbut-3-en-1-yl)hydrazinecarboxylate (**S6**) as a white solid, mp 88–92 ºC. ^{1}H NMR (500 MHz, C_7D_8, 80 ºC) δ 7.52 (s, br, 1 H), 7.29 (d, J = 8.1 Hz, 1 H), 7.23 (d, J = 7.3 Hz, 2 H), 7.14–7.11 (m, 2 H), 7.06–7.03 (m, 2 H), 7.00–6.97 (m, 1 H), 6.73 (t, J = 7.6 Hz, 1 H), 5.80–5.75 (m, 1 H), 5.08 (s, br, 1 H), 4.95–4.86 (m, 2 H), 4.00–3.90 (m, 2 H), 3.70–3.66 (m, 1 H), 2.81–2.75 (m, 1 H), 2.49–2.43 (m, 1 H), 1.29 (s, 9 H).

A flame-dried flask was cooled under a stream of nitrogen and charged with portion of **S6** (4.03 g, 9.3 mmol). Dichloromethane (9.3 mL) was added, and the resulting solution was cooled to 0 ºC. Trifluoroacetic acid (9.3 mL) was added over 5 min and the resulting mixture was stirred and slowly warmed from 0 °C to rt over 2 h. The mixture was then cooled to 0 ºC and solid potassium carbonate was added slowly until the bubbling stopped. A solution of 2 M sodium hydroxide (25 mL) was added, the mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel to afford 1.64 g (53%) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2 H), 7.39–7.35 (m, 4 H), 7.32–7.27 (m, 2 H), 7.11–7.07 (m, 1 H), 5.84–5.76 (m, 1 H), 5.06–5.02 (m, 1 H), 4.98–4.95

(m, 1 H), 3.79–3.76 (m, 1 H), 3.73 (d, J = 14.2 Hz, 1 H), 3.57 (d, J = 14.2 Hz, 1 H), 2.99–2.93 (m, 1 H), 2.75–2.60 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 137.8, 136.3, 132.7, 130.8, 128.9, 128.5, 128.2, 127.5, 127.3, 124.6, 116.2, 71.0, 62.5, 37.4; IR (film) 3347, 3065, 3027, 2918 cm^{-1}. MS (ESI) 331.0801 (331.0804 calcd for $C_{17}H_{19}BrN_2$, M + H$^+$).



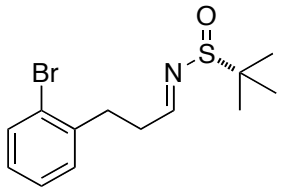
3-(2-Bromophenyl)-*N*-methoxy-*N*-methylpropanamide (S7). A round bottom flask equipped with a magnetic stir bar was charged with 3-(2-bromophenyl)propanoic acid (4.00 g, 17.5 mmol), *N,O*-dimethyl hydroxylamine hydrochloride (2.90 g, 29.7 mmol), THF (35 mL, 0.5 M), water (35 mL, 0.5 M), and aqueous 1 M NaOH (3 mL). A solution of EDCI (8.39 g, 43.8 mmol) and 1 M NaOH (7 mL) in water (117 mL) was then added dropwise over 20 min. After the addition was complete, 1 M NaOH (5.5 mL) was added to raise the pH of the solution to 4.5 and the mixture was then stirred at rt for 8 h. The reaction mixture was then saturated with solid sodium chloride, transferred to a separatory funnel, and extracted with ethyl acetate (5 x 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford the title compound as a clear oil (4.43 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 1.0, 8.0 Hz, 1 H), 7.30 (dd, J = 1.5, 7.5 Hz, 1 H), 7.24 (dt, J = 1.0, 7.5 Hz, 1 H), 7.07 (dt, J = 1.5, 7.5 Hz, 1 H), 3.63 (s, 3 H), 3.18 (s, 3 H), 3.10–3.06 (m, 2 H), 2.76 (t, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 140.4, 132.7, 130.7, 127.8, 127.5, 124.3, 61.1, 31.9, 31.3, 31.1; IR (film) 3312, 2936, 1664 cm^{-1}. MS (ESI) *m/z* 272.0274 (272.0281 calcd for $C_{11}H_{14}BrNO_2$, M + H$^+$).



(±)-1-(2-Bromophenyl)hept-6-en-3-amine (**5b**) A solution of 4-bromo-1-butene (0.75 mL, 7.35 mmol) in diethyl ether (15 mL) was converted to the corresponding Grignard reagent according to General Procedure 1. The freshly made Grignard reagent was added dropwise to a 0 ºC

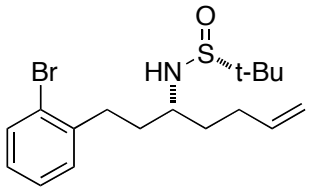
solution of **S7** (1.00 g, 3.67 mmol) in diethyl ether (7 mL) via cannula over 25 min. After the addition was complete, the reaction vessel was removed from the ice bath and stirred at rt for 1.5 h. The mixture was then cooled to 0 °C and slowly quenched with saturated ammonium chloride. The resulting mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 1-(2-bromophenyl)hept-6-en-3-one[5] (**S8**) as a clear oil (858 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 1 H), 7.25–7.22 (m, 2 H), 7.09–7.04 (m, 1 H), 5.84–5.75 (m, 1 H), 5.04–4.96 (m, 2 H), 3.03–2.99 (m, 2 H), 2.77–2.73 (m, 2 H), 2.53–2.49 (m, 2 H), 2.36–2.30 (m, 2 H).

S8 (858 mg, 3.21 mmol) was stirred with ammonium acetate (2.54 g, 32.7 mmol) and sodium cyanoborohydride (202 mg, 3.21 mmol) in anhydrous methanol (10 mL, 0.33 M) under nitrogen at reflux for 1 d. The mixture was then cooled to rt, quenched with 1 M HCl, and concentrated *in vacuo* to remove methanol. The resulting solution was basified to pH 14 with 3 M NaOH and then was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on basic alumina to afford the title compound as a clear oil (549 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1 H), 7.24–7.22 (m, 2 H), 7.08–7.02 (m, 1 H), 5.89–5.77 (m, 1 H), 5.07–5.00 (m, 1 H), 4.98–4.94 (m, 1 H), 2.90–2.71 (m, 3 H), 2.22–2.08 (m, 2 H), 1.80–1.70 (m, 1 H), 1.64–1.51 (m, 2 H), 1.47–1.37 (m, 1 H), 1.25 (s, br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.6, 132.8, 130.3, 127.52, 127.47, 124.4, 114.6, 50.6, 38.3, 37.2, 32.9, 30.5; IR (film) 3375, 3283, 3068, 2927, 1639 cm^{-1}. MS (ESI) *m/z* 268.0696 (268.0701 calcd for $C_{13}H_{18}BrN$, M + H$^+$).

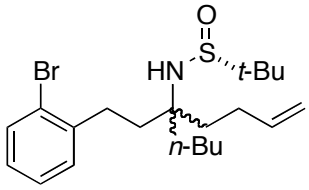


(*R*,*E*)-*N*-[3-(2-Bromophenyl)propylidene]-2-methylpropane-2-sulfinamide[6] (10b). 3-(2-bromophenyl)propanal[1] (765 mg, 3.59 mmol) was condensed with (*R*)-2-methylpropane-2-sulfinamide (414 mg, 3.42 mmol) according to General Procedure 2 to afford 870 mg (77%) of

the title compound as a clear oil, $[\alpha]^{23}_D$ –117.6 (*c* 0.92, $CHCl_3$) [lit.[6] $[\alpha]^{22}_D$ –156.2 (*c* 0.98, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, *J* = 4.1 Hz, 1 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.25–7.23 (m, 2 H), 7.11–7.06 (m, 1 H), 3.12–3.07 (m, 2 H), 2.90–2.84 (m, 2 H), 1.17 (s, 9 H).



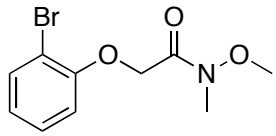
(–)-(*R*$_s$,*R*)-*N*-[1-(2-Bromophenyl)hept-6-en-3-yl]-2-methylpropane-2-sulfinamide (11b). A solution of 4-bromo-1-butene (0.41 mL, 4.0 mmol) in diethyl ether (4 mL) was converted to the corresponding Grignard reagent according to General Procedure 1. The freshly made Grignard solution was added dropwise to a –55 ºC solution of **10b** (602 mg, 2.0 mmol) in methylene chloride (10 mL) over 5 min. The resulting mixture was slowly warmed from –55 ºC to –10 ºC over 3.5 h at a rate of approximately 13 °C/hr. The reaction was then quenched with saturated ammonium chloride and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford 596 mg (62%) of the title compound as a 10:1 mixture of diastereomers as a yellow oil. Data are for the major diastereomer. $[\alpha]^{23}_D$ –30.4 (*c* 1.19, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.51 (m, 1 H), 7.26–7.20 (m, 2 H), 7.08–7.04 (m, 1 H), 5.86–5.80 (m, 1 H), 5.09–5.03 (m, 1 H), 4.99 (dd, *J* = 1.7, 10.3 Hz, 1 H), 3.36–3.31 (m, 1 H), 3.15 (d, *J* = 6.8 Hz, 1 H), 2.94–2.87 (m, 1 H), 2.74–2.67 (m, 1 H), 2.18 (dd, *J* = 7.6, 14.4 Hz, 2 H), 1.90–1.69 (m, 4 H), 1.24 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 137.9, 132.8, 130.3, 127.7, 127.6, 124.3, 115.3, 56.3, 55.9, 35.9, 35.5, 32.4, 30.0, 22.8; IR (film) 3222, 3071, 2925, 1690, 1640 cm^{-1}. MS (ESI) 372.0990 (372.0991 calcd for $C_{17}H_{26}BrNOS$, M + H$^+$).



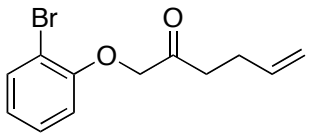
(–)-(R_s,*R)-*N*-[5-(2-Bromophenethyl)non-1-en-5-yl]-2-methylpropane-2-sulfinamide (S10).** Ketone **S8** (1.50 g, 5.60 mmol) was condensed with (*R*)-2-methylpropane-2-sulfinamide (715 mg, 5.90 mmol) according to General Procedure 2 to afford 1.62 g (78%) of (*R*)-*N*-[1-(2-bromophenyl)hept-6-en-3-ylidene]-2-methylpropane-2-sulfinamide (**S9**) as a 1:1 mixture of *E*:Z diastereomers, as determined by ^{1}H and ^{13}C NMR analysis. Data is reported for the mixture. $[\alpha]^{23}_D$ –125.2 (*c* 2.41, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 7.3 Hz, 1 H), 7.26–7.21 (m, 3 H), 7.10–7.05 (m, 2 H), 5.87–5.78 (m, 2 H), 5.10–4.98 (m, 4 H), 3.09–2.98 (m, 5 H), 2.94–2.86 (m, 2 H), 2.82–2.71 (m, 3 H), 2.61–2.48 (m, 2 H), 2.42–2.35 (m, 4 H), 1.30 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 185.7, 140.3, 139.5, 137.3, 136.4, 132.8, 132.7, 130.8, 130.2, 128.2, 127.9, 127.8, 127.5, 124.3, 124.0, 115.9, 115.3, 56.6, 56.5, 40.7, 40.5, 36.7, 35.7, 33.9, 32.1, 31.4, 29.3, 22.3 (one signal is missing due to incidental equivalence).

A flame dried flask was cooled under a stream of nitrogen and charged with a portion of **S9** (1.44 mg, 3.88 mmol). The reaction vessel was purged with nitrogen, toluene (4 mL) was added, and the resulting solution was cooled to –78 ºC. Trimethylaluminum (2.0 M in toluene, 2.1 mL, 4.2 mmol) was added and the resulting mixture was stirred at –78 ºC for 5 min, then was added via cannula over 10 min to a flask containing a –78 ºC solution of of *n*-butyllithium (2.0 M in diethyl ether, 4.3 mL, 8.6 mmol) and toluene (13 mL). The mixture was stirred at –78 ºC for 7 h, then the reaction vessel was placed in an ice bath and saturated aqueous ammonium chloride was added until bubbling stopped. The layers were separated, and the organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated *in vacuo* and purified via flash chromatography on silica gel to afford 1.39 g (83 %) of the title compound as a white solid, mp 51–56 ºC which was a 1:1 mixture of diastereomers as determined by ^{1}H and ^{13}C NMR analysis. Data is for the mixture. $[\alpha]^{23}_D$ –48.1 (*c* 3.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2 H), 7.34–7.29 (m, 2 H), 7.25–7.21 (m, 2 H), 7.07–7.01 (m, 2 H), 5.89–5.79 (m, 2 H), 5.10–5.02 (m, 2 H), 5.00–4.94 (m, 2 H), 3.24 (s, 2 H), 2.83–2.72 (m, 4 H), 2.19–2.12 (m, 4 H), 1.85–1.78 (m, 4 H), 1.76–1.57 (m, 8 H), 1.38–1.32 (m, 8 H), 1.25 (s, 18 H), 0.97–0.91 (m, 6

H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.47, 141.45, 138.4, 138.3, 132.61, 132.59, 130.7, 130.6, 127.7, 127.6, 124.1, 114.7, 114.6, 60.1, 55.9, 39.01, 38.96, 37.7, 37.3, 37.0, 29.9, 27.5, 27.4, 25.1, 25.0, 23.1, 23.0, 22.8, 14.0 (nine signals are missing due to incidental equivalence); IR (film) 3307, 3236, 3070, 2953, 1640 cm^{-1}. MS (ESI) *m/z* 428.1607 (428.1617 calcd for $C_{21}H_{34}BrNOS$, M + H$^+$).

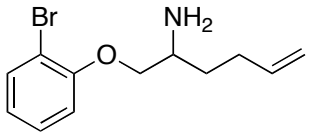


2-(2-Bromophenoxy)-*N*-methoxy-*N*-methylacetamide (S11). A round bottom flask equipped with a magnetic stir bar was charged with 2-(2-bromophenoxy)acetic acid[2] (1.11 g, 4.80 mmol) and purged with nitrogen. Methylene chloride (9.6 mL) was added, the mixture was cooled to 0 ºC, 1,1′-carbonyldiimidazole (1.01 g, 6.24 mmol) was added, and the reaction vessel was briefly purged with nitrogen. The resulting mixture was stirred at rt for 30 min, then triethylamine (0.94 mL, 0.68 g, 6.7 mmol) was added and the mixture was cooled to 0 ºC. *N,O*-dimethyl hydroxylamine hydrogen chloride was added in one portion, the vessel was briefly purged with nitrogen, then was stirred at rt for 14 h. The reaction was then quenched with 1 M HCl (15 mL) and the mixture was transferred to a separatory funnel. The layers were separated, the aqueous layer was extracted with methylene chloride (3 x 10 mL), and the combined organic layers were dried over magnesium sulfate and filtered. The filtrate was concentrated *in vacuo* and purified by flash chromatography to afford 1.23 g (94%) of the title compound as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.53 (m, 1 H), 7.26–7.22 (m, 1 H), 6.91–6.85 (m, 2 H), 4.90 (s, 2 H), 3.77 (s, 3 H), 3.24 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 154.8, 133.5, 128.4, 122.7, 114.0, 112.3, 66.8, 61.8, 32.3; IR (film) 2941, 1686, 1479 cm^{-1}. MS (ESI) *m/z* 274.0072 (274.0073 calcd for $C_{10}H_{12}BrNO_3$, M + H$^+$).



1-(2-Bromophenoxy)hex-5-en-2-one (S12). A solution of 4-bromo-1-butene (0.89 mL, 8.8 mmol) in diethyl ether (12 mL) was converted to the corresponding Grignard reagent according

to General Procedure 1. The freshly made Grignard reagent was added dropwise to a 0 ºC solution of **S11** (1.20 g, 4.4 mmol) in diethyl ether (5 mL) via cannula over 15 min. After the addition was complete, the reaction vessel was removed from the ice bath and the mixture was stirred at rt for 1 h. The mixture was then cooled to 0 °C and slowly quenched with saturated ammonium chloride. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 871 mg (74%) of the title compound as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 1.5, 6.4 Hz, 1 H), 7.28–7.23 (m, 1 H), 6.91–6.87 (m, 1 H), 6.77 (d, J = 8.3 Hz, 1 H), 5.89–5.81 (m, 1 H), 5.10–5.05 (m, 1 H), 5.00 (dd, J = 1.0, 9.3 Hz), 4.56 (s, 2 H), 2.84 (t, J = 7.3 Hz, 2 H), 2.43–2.38 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8, 154.2, 136.7, 133.7, 128.6, 122.9, 115.5, 113.1, 112.2, 73.5, 38.4, 27.0; IR (film) 2917, 1723 1480 cm^{-1}. MS (ESI) *m/z* 290.9991 (290.9991 calcd for $C_{12}H_{13}BrO_2$, M + Na^+).



(±)-1-(2-Bromophenoxy)hex-5-en-2-amine (5c). Ketone **S10** (1.41 g, 5.22 mmol) was stirred with ammonium acetate (4.10 g, 53.2 mmol) and sodium cyanoborohydride (328 mg, 5.22 mmol) in anhydrous methanol (16 mL, 0.33 M) under nitrogen at reflux 1 d. The reaction mixture was cooled to rt then was quenched with 1 M HCl and concentrated *in vacuo* to remove methanol. The pH was raised 14 with 3 M NaOH and the resulting solution was extracted with methylene chloride (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on basic alumina to afford the title compound as a clear oil (630 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 1.7, 6.1 Hz, 1 H), 7.27–7.22 (m, 1 H), 6.89–6.81 (m, 2 H), 5.89–5.80 (m, 1 H), 5.10–4.98 (m, 2 H), 4.01–3.98 (m, 1 H), 3.80–3.75 (m, 1 H), 3.26–3.21 (m, 1 H), 2.30–2.15 (m, 2 H), 1.72–1.64 (m, 1 H), 1.58–1.49 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 138.1, 133.2, 128.4, 121.9, 115.0, 113.3, 112.3, 74.2, 50.1, 33.1, 30.3; IR (film)

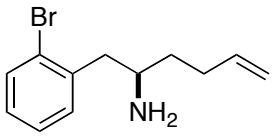
3375, 3282, 3073, 2925 cm^{-1}. MS (ESI) *m/z* 270.0491 (270.0488 calcd for $C_{12}H_{16}BrNO$, M + H^+).

General Procedure 3 - Deprotection of Sulfinamides.

A flame-dried flask equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with the sulfinamide (1 equiv) and anhydrous methanol (1 M) under nitrogen. A 4 M solution of hydrogen chloride in 1,4-dioxane (4 equiv) was added via syringe. The resulting solution was stirred at rt for 15 min, then the solvent was evaporated via a nitrogen purge. The crude reaction mixture was diluted with methylene chloride and the pH was raised to 14 with aqueous sodium hydroxide. The layers were separated, the aqueous layer was extracted with methylene chloride (4 x), and the combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on basic alumina.

General Procedure 4 - Mosher Amide Analysis

In order to assess enantiomeric purity of the amine substrates, the Mosher amides were generated using the following procedure. A flame dried vial equipped with a magnetic stir bar was cooled under a stream of nitrogen and charged with amine (1.0 equiv), methylene chloride (10 mL solvent/mmol amine), either (*S*)- or (*R*)-α-methoxy-α-trifluoromethylphenylacetic acid (1.2 equiv), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (1.2 equiv), and triethylamine (1.2 equiv). The vial was purged with nitrogen and stirred at rt for 36 h. The mixture was then concentrated *in vacuo* and the crude product was purified by flash chromatography on silica gel. Enantiomeric purity was determined by ^{19}F NMR analysis.

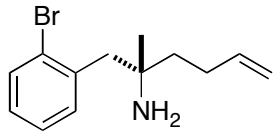


(+)-(*R*)-1-(2-Bromophenyl)hex-5-en-2-amine (**5a**). The deprotection of (+)-(R_s,*R*)-*N*-[1-(2-bromophenyl)hex-5-en-2-yl]-2-methylpropane-2-sulfinamide (**11a**) (475 mg, 1.30 mmol) was conducted according to General Procedure 3 to afford 264 mg (80 %) of the title compound as a pale yellow oil. $[\alpha]^{23}_D$ +13.4 (*c* 2.60, CH_2Cl_2). ^1H NMR data were identical to those reported

above for (±)-**11a**. The enantiomeric purity of the title compound was determined by conversion of 64 mg (0.25 mmol) of **5a** to the corresponding Mosher amide using General Procedure 4. This procedure afforded 13 mg (11%) of **S13**. The enantiopurity was determined to be 92% ee by ^{19}F NMR analysis.

(2*S*,1'*R*)-*N*-[1-(2-Bromophenyl)hex-5-en-2-yl]-3,3,3-trifluoro-2-methoxy-2-phenylpropanamide (S13). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 3 H), 7.41–7.37 (m, 3 H), 7.26–7.20 (m, 2 H), 7.11–7.05 (m, 1 H), 6.61 (d, *J* = 8.6 Hz, 1 H), 5.80–5.68 (m, 1 H), 5.00–4.93 (m, 2 H), 4.37–4.26 (m, 1 H), 3.27–3.26 (m, 3 H), 3.01–2.97 (m, 2 H), 2.11–1.99 (m, 2 H), 1.74–1.61 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.71 (s); IR (film) 3400, 3339, 2925, 1695, 1686 cm^{-1}. MS (ESI) 470.0940 (470.0937 calcd for $C_{22}H_{23}BrF_3NO_2$, M + H$^+$).

The absolute stereochemistry of the product was assigned based on models established by Ellman.[7]



(–)-(*S*)-1-(2-Bromophenyl)-2-methylhex-5-en-2-amine (5d). The deprotection of (–)-(*R*$_s$,*S*)-*N*-[1-(2-bromophenyl)-2-methylhex-5-en-2-yl]-2-methylpropane-2-sulfinamide (**S4**) (415 mg, 1.11 mmol) was conducted according to General Procedure 3 to afford 240 mg (81%) of the title compound as a clear oil. $[\alpha]^{23}_{D}$ –14.6 (*c* 2.60, CH_2Cl_2). ^{1}H HMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.2, 6.8 Hz, 1 H), 7.30–7.23 (m, 2 H), 7.10–7.07 (m, 1 H), 5.91–5.83 (m, 1 H), 5.09–5.04 (m, 1 H), 4.99–4.95 (m, 1 H), 2.91 (s, 2 H), 2.24–2.17 (m, 2 H), 1.64–1.51 (m, 2 H), 1.29 (s, br, 2 H), 1.09 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 137.9, 133.1, 132.4, 127.9, 126.9, 126.3, 114.3, 53.4, 47.6, 42.6, 28.5, 27.3; IR (film) 3367, 3298, 3071, 2921, 1640 cm^{-1}. MS (ESI) *m/z* 268.0696 (268.0695 calcd for $C_{13}H_{18}BrN$, M + H$^+$).

The enantiomeric purity of the title compound was determined by conversion of 76 mg (0.28 mmol) of **5d** to the corresponding Mosher amide using General Procedure 4. This procedure afforded 12 mg (8%) of **S14**. The enantiopurity was determined to be 87% ee by ^{19}F NMR analysis.

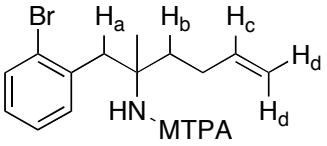
(2*S*,1'*S*)-*N*-[1-(2-Bromophenyl)-2-methylhex-5-en-2-yl]-3,3,3-trifluoro-2-methoxy-2-phenylpropanamide (S15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 3 H), 7.40–7.37 (m, 3

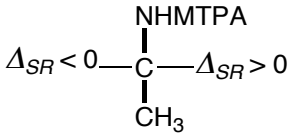
H), 7.22–7.17 (m, 2 H), 7.11–7.06 (m, 1 H), 6.71 (s, 1 H), 5.81–5.72 (m, 1 H), 5.00–4.92 (m, 2 H), 3.47 (d, J = 11.2 Hz, 1 H), 3.38–3.37 (m, 3 H), 3.12 (d, J = 11.1 Hz, 1 H), 2.13–1.94 (m, 3 H), 1.87–1.79 (m, 1 H), 1.34 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.92 (s, 3 F); IR (film) 3404, 3377, 2923, 1697 cm^{-1}. MS (ESI) 484.1093 (484.1094 calcd for $C_{23}H_{25}BrF_3NO_2$, M + H$^+$).

To determine the absolute stereochemistry of the title compound, 55 mg (0.21 mmol) was reacted with (*R*)-α-methoxy-α-trifluoromethylphenylacetic acid in an analogous to General Procedure 4 to afford 13 mg (12%) of **S15**. Modified Mosher amide analysis was conducted as described below.

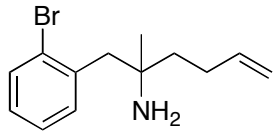
(2*R*,1'*S*)-*N*-[1-(2-Bromophenyl)-2-methylhex-5-en-2-yl]-3,3,3-trifluoro-2-methoxy-2-phenylpropanamide (**S15**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 3 H), 7.47–7.43 (m, 3 H), 7.13–7.05 (m, 2 H), 7.00–6.97 (m, 1 H), 6.68 (s, 1 H), 5.86–5.75 (m, 1 H), 5.05–4.94 (m, 2 H), 3.40–3.34 (m, 4 H), 3.08 (d, J = 13.8 Hz, 1 H), 2.19–2.03 (m, 3 H), 1.90–1.82 (m, 1 H), 1.34 (s, 3 H); ^{19}F (376 MHz, $CDCl_3$) δ –68.05 (s); IR (film) 3396, 2929, 1699 cm^{-1}. MS 484.1096 (484.1094 calcd for $C_{23}H_{25}BrF_3NO_2$, M + H$^+$).

The absolute stereochemistry of **5d** was tentatively assigned based on a modified Mosher amide analysis, using Δ_{SR}.[8] The methyl signal does not shift between **S14** and **S15**, thus the methyl group was assigned the place of the hydrogen in the model reported by Kusumi and coworkers.[8] Signals reported in this table are centers for multiplets or the peak if a defined splitting pattern.

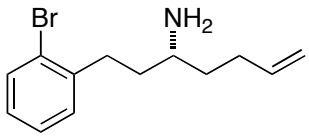




Proton	*S*-MTPA (ppm)	*R*-MTPA (ppm)	Δ_{SR} (Hz)
H_a	3.12	3.08	16
CH_3	1.34	1.34	0
H_b	2.04	2.11	-30
H_c	5.77	5.81	-16
H_d	4.96	5.00	-14



(±)-1-(2-Bromophenyl)-2-methylhex-5-en-2-amine (5d). The deprotection of (±)-*N*-(1-(2-bromophenyl)-2-methylhex-5-en-2-yl)-2-methylpropane-2-sulfinamide (**S4**) (588 mg, 1.6 mmol) was conducted according to General Procedure 3 to afford 376 mg (88%) of the title compound as a clear oil. ^{1}H NMR data matched that reported above for (–)-**5d**.

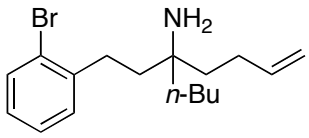


(+)-(*R*)-1-(2-Bromophenyl)hept-6-en-3-amine (**5b**)

The deprotection of (–)-(R_s,*R*)-*N*-[1-(2-bromophenyl)hept-6-en-3-yl]-2-methylpropane-2-sulfinamide (**11b**) (550 mg, 1.48 mmol) was conducted according to General Procedure 3 to afford 317 mg (80%) of the title compound as a clear oil. In order to increase the level of optical purity, the amine was stirred with (L)-tartaric acid (176 mg, 1.17 mmol) in methanol (1.2 mL) and water (2 mL). After 1 min, a voluminous white precipitate formed, which was collected by filtration. The white solid was recrystallized from an ethanol/ethyl acetate/water mixture. The recrystallized salt was suspended in EtOAc and aqueous NaOH was added until a solution of pH 14 was obtained. The mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with methylene chloride (3 x 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered through alumina, and concentrated *in vacuo* to afford 152 mg (38%) of the title compound as a clear oil. $[\alpha]^{23}_D$ +10.5 (*c* 2.73, CH_2Cl_2). ^{1}H NMR data were identical to those reported above for (±)-**5b**. The enantiomeric purity of the title compound was determined by conversion of 67 mg (0.25 mmol) of **5b** to the corresponding Mosher amide using General Procedure 4. This procedure afforded 17 mg (14 %) of **S16**. The enantiopurity was determined to be 88% ee by ^{19}F NMR analysis.

(2*S*,1'*R*)-*N*-[1-(2-Bromophenyl)hept-6-en-3-yl]-3,3,3-trifluoro-2-methoxy-2-phenylpropanamide (S16). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 3 H), 7.45–7.40 (m, 3 H), 7.26–7.19 (m, 2 H), 7.10–7.03 (m, 1 H), 6.67 (d, *J* = 9.1 Hz, 1 H), 5.79–5.70 (m, 1 H), 5.00–4.92 (m, 2 H), 4.12–4.02 (m, 1 H), 3.46 (s, 3 H), 2.89–2.80 (m, 1 H), 2.76–2.67 (m, 1 H), 2.05–

1.99 (m, 2 H), 1.93–1.83 (m, 1 H), 1.78–1.52 (m, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.60 (s); IR (film) 3408, 3339, 2925, 1686 cm^{-1}. MS (ESI) 484.1094 (484.1094 calcd for $C_{23}H_{25}BrF_3NO_2$, M + H^+).



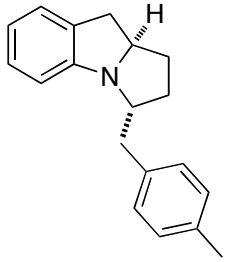
(±)-5-(2-Bromophenethyl)non-1-en-5-amine (5e). The reaction of (±)-*N*-[5-(2-bromophenethyl)non-1-en-5-yl]-2-methylpropane-2-sulfinamide (**S8**) (1.312 g, 3.06 mmol) was conducted according to General Procedure 3 to afford 907 mg (91%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1 H), 7.24–7.21 (m, 2 H), 7.07–7.02 (m, 1 H), 5.91–5.80 (m, 1 H) 5.05 (dd, *J* = 1.7, 17.1 Hz, 1 H), 4.96 (d, *J* = 10.1 Hz, 1 H), 2.75–2.70 (m, 2 H), 2.15–2.08 (m, 2 H), 1.62–1.47 (m, 2 H), 1.44–1.39 (m, 2 H), 1.37–1.30 (m, 6 H), 1.10 (s, br, 2 H), 0.95–0.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.1, 132.8, 130.3, 127.5, 127.4, 124.2, 114.2, 53.3, 40.7, 39.7, 39.2, 30.7, 28.0, 25.6, 23.4, 14.1; IR (film) 3371, 3310, 3071, 2930 cm^{-1}. MS (ESI) *m/z* 324.1321 (324.1321 calcd for $C_{17}H_{26}BrN$, M + H^+).

Preparation and Characterization of Heterocyclic Products.

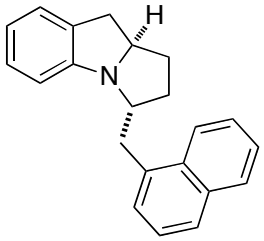
General Procedure 5 - Palladium Catalyzed Tandem Intramolecular *N*-Arylation/Intermolecular Carboamination.

An oven-dried Schlenk tube equipped with a magnetic stirbar was cooled under a stream of nitrogen and charged with $Pd_2(dba)_3$ (2 mol % complex, 4 mol % Pd) or $Pd(OAc)_2$ (4 mol %), $PCy_3{\cdot}HBF_4$ (4 or 8 mol %), Cy_4Dpe-Phos (4 mol%), or X-Phos (8 mol%), sodium *tert*-butoxide (2.4 equiv), and the aryl chloride if solid (1.2 equiv). The Schlenk tube was evacuated and refilled with nitrogen three times. The primary amine substrate (1.0 equiv) was added as a solution in toluene (4 mL/mmol substrate), along with the aryl chloride if liquid. The resulting mixture was heated to 100 °C until the intermediate was consumed as judged by GC analysis. The reaction mixture was cooled to rt and treated with saturated aqueous ammonium chloride (2 mL) and ethyl acetate (5 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (2 x 5 mL), and the combined organic layers were dried over anhydrous sodium

sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel.

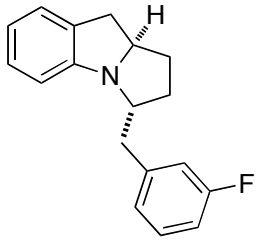


(±)-(3*R,9a*R**)-3-(4-Methylbenzyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8a).** The reaction of **5a** (64 mg, 0.25 mmol) with 4-chlorotoluene (36 μL, 38 mg, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 51 mg (77%) of the title compound as an off-white solid, mp 42–45 ºC. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 20:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.8, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 7.03 (d, *J* = 6.8 Hz, 1 H), 6.98–6.94 (m, 1 H), 6.68 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.13 (d, *J* = 7.8 Hz, 1 H), 4.00–3.94 (m, 1 H), 3.51–3.47 (m, 1 H), 3.15 (dd, *J* = 9.3, 15.6 Hz, 1 H), 2.96 (dd, *J* = 6.8, 13.2 Hz, 1 H), 2.91 (dd, *J* = 2.0, 16.1 Hz, 1 H), 2.79 (dd, *J* = 6.3, 13.2 Hz, 1 H), 2.33 (s, 3 H), 2.01 (dtd, *J* = 1.5, 7.3, 12.3 Hz, 1 H), 1.85–1.81 (m, 1 H), 1.64–1.55 (m, 2 H), 1.38–1.28 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 136.8, 135.5, 129.4, 129.1, 129.0, 127.4, 124.8, 118.9, 110.0, 67.4, 64.9, 43.8, 33.4, 32.9, 31.9, 21.0; IR (film) 3021, 2923, 1603 cm^{-1}. MS (ESI) *m/z* 264.1752 (264.1752 calcd for $C_{19}H_{21}N$, M + H$^+$).



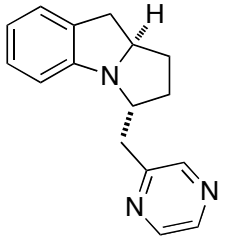
(±)-(3*R,9a*R**)-3-(Naphthalen-1-ylmethyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8b).** The reaction of **5a** (64 mg, 0.25 mmol) with 1-chloronapthalene (41 mg, 0.30 mmol) was

conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 59 mg (79%) of the title compound as a tan solid, mp 65–78 ºC. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 5:1 mixture of diastereomers. The product was isolated as an 8:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 1 H), 7.88–7.85 (m, 1 H), 7.80–7.72 (m, 1 H), 7.55–7.36 (m, 4 H), 7.00–6.98 (m, 1 H), 6.83 (t, *J* = 7.8 Hz, 1 H), 6.63 (dt, *J* = 1.2, 7.4 Hz, 1 H), 5.83 (d, *J* = 7.8 Hz, 1 H), 4.09–4.02 (m, 1 H), 3.76–3.68 (m, 1 H), 3.42 (dd, *J* = 7.1, 13.7 Hz, 1 H), 3.31 (dd, *J* = 6.7, 13.7 Hz, 1 H), 3.14 (dd, *J* = 9.4, 16.1 Hz, 1 H), 2.92 (d, *J* = 2.3 Hz, 1 H), 2.03–1.95 (m, 1 H), 1.90–1.82 (m, 1 H), 1.74–1.63 (m, 1 H), 1.38–1.27 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 136.1, 133.9, 132,2, 129.1, 128.8, 127.6, 127.4, 126.9, 125.8, 125.6, 125.4, 124.8, 124.0, 119.0, 110.0, 66.3, 64.9, 41.2, 33.5, 33.1, 32.0; IR (film) 3045, 2927, 1603 cm^{-1}. MS (ESI) *m/z* 300.1753 (300.1752 calcd for $C_{22}H_{21}N$, M + H^+).



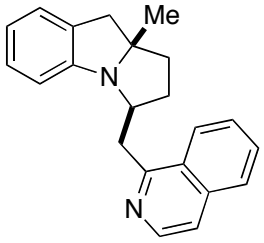
(±)-(3*R,9a*R**)-3-(3-Fluorobenzyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8c).** The reaction of **5a** (64 mg, 0.25 mmol) with 1-chloro-3-fluorobenzene (32 µL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.020 mmol) to afford 28 mg (42%) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 5:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 1 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 7.05–7.01 (m, 2 H), 6.97–6.90 (m, 2 H), 6.69 (dt, *J* = 1.0, 7.3 Hz, 1 H0, 6.04 (d, *J* = 7.8 Hz, 1 H), 4.00–3.93 (m, 1 H), 3.53–3.46 (m, 1 H), 3.15 (dd, *J* = 9.4, 16.0 Hz, 1 H), 2.98–2.90 (m, 2 H), 2.86–2.82 (m, 1 H), 2.08–2.01 (m, 1 H), 1.88–1.82 (m, 1 H), 1.64–1.55 (m, 1 H), 1.39–1.29 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, *J* = 243.6 Hz), 154.5, 142.6 (d, *J* = 7.3 Hz), 129.7 (d, *J* = 8.3 Hz), 129.1, 127.5, 125.2 (d, *J* = 2.9

Hz), 124.9, 119.1, 116.4 (d, J = 20.4 Hz), 113.0 (d, J = 20.9 Hz), 109.9, 67.1, 64.9, 43.9 (d, J = 1.5 Hz), 33.4, 32.9, 31.9; IR (film) 3043, 2927 cm^{-1}. MS (ESI) *m/z* 268.1499 (268.1496 calcd for $C_{18}H_{18}FN$, $M + H^+$).

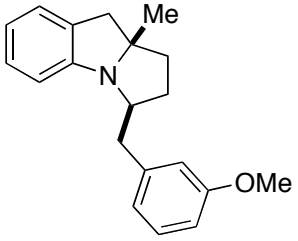


(±)-(3*R,9a*R**)-3-(Pyrazin-2-ylmethyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8d).** The reaction of (±)-**5a** (64 mg, 0.25 mmol) with 2-chloropyrazine (27 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 37 mg (59%) of the title compound as a brown solid, mp 83–87 ºC. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 7:1 mixture of diastereomers. The product was isolated as an 8:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 2 H), 8.46–8.44 (m, 1 H), 7.05–7.01 (m, 1 H), 6.96–6.92 (m, 1 H), 6.69 (t, J = 7.3 Hz, 1 H), 6.02 (d, J = 7.8 Hz, 1 H), 4.00–3.93 (m, 1 H), 3.83–3.77 (m, 1 H), 3.17–3.05 (m, 3 H), 2.92 (d, J = 15.6 Hz, 1 H), 2.16–2.09 (m, 1 H), 1.91–1.85 (m, 1 H), 1.71–1.62 (m, 1 H), 1.44–1.33 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 154.1, 145.8, 144.0, 142.4, 128.9, 127.4, 124.9, 119.2, 109.8, 65.2, 64.7, 43.4, 33.4, 32.8, 31.7; IR (film) 3043, 2925, 1603. MS (ESI) *m/z* 252.1497 (252.1495 calcd for $C_{16}H_{17}N_3$, $M + H^+$).

(–)-(3*R*,9a*R*)-3-(Pyrazin-2-ylmethyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8d). The reaction of **(+)-5a** (64 mg, 0.25 mmol) with 2-chloropyrazine (27 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 33 mg (53%) of the title compound as a brown solid, mp 60–64 ºC, $[\alpha]^{23}_D$ –133.3 (*c* 1.13, CH_2Cl_2). The product was determined to be 86% ee by chiral HPLC analysis [Chiralcel OD-H, 0.46 cm x 15 cm, 8% isopropanol/ hexanes, 1.0 mL/min, RT = 5.6 and 6.6 min]. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 7:1 mixture of diastereomers. The product was isolated as an 8:1 mixture of diastereomers. ^{1}H NMR data were identical to those reported above for (±)-**8d**.



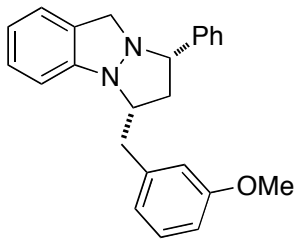
(±)-(3*S,9a*S**)-3-(Isoquinolin-1-ylmethyl)-9a-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8e).** The reaction of **5d** (67 mg, 0.25 mmol) with 1-chloroisoquinoline (49 mg, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 38 mg (47%) of the title compound as a bright yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 5:1 mixture of diastereomers. The product was isolated as a 14:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1 H), 8.05–8.02 (m, 1 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.74–7.70 (m, 1 H), 7.53–7.51 (m, 1 H), 7.47 (dd, *J* = 2.0, 13.2 Hz, 1 H), 6.97 (d, *J* = 7.1 Hz, 1 H), 6.81–6.78 (m, 1 H), 6.65–6.61 (m, 1 H), 5.84 (d, *J* = 7.8 Hz, 1 H), 3.85– 3.80 (m, 1 H), 3.29 (dd, *J* = 1.7, 6.8 Hz, 2 H)), 3.11 (d, *J* = 15.9 Hz, 1 H), 2.86 (d, *J* = 15.9 Hz, 1 H), 2.23–2.16 (m, 1 H), 2.00–1.91 (m, 1 H), 1.78–1.74 (m, 1 H), 1.66–1.59 (m, 2 H), 1.39 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 155.0, 147.9, 136.0, 129.2, 128.95, 128.93, 127.6, 127.4, 126.9, 125.8, 124.4, 123.2, 119.0, 110.3, 72.3, 66.7, 48.4, 42.5, 37.0, 32.0, 28.2; IR (film) 2957, 1600 cm^{-1}. MS (ESI) 315.1859 (315.1856 cald for $C_{22}H_{22}N_2$, M + H$^+$).



(+)-(3*S*,9a*S*)-3-(3-Methoxybenzyl)-9a-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8f). The reaction of **(–)-5d** (67 mg, 0.25 mmol) with 3-chloroanisole (37 µL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 55 mg (75%) of the title compound as a pale yellow oil, $[\alpha]^{23}_D$ +97.5 (*c* 1.95, CH_2Cl_2). The product was determined to be

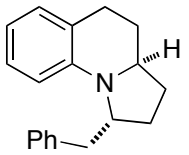
91% ee by chiral HPLC analysis [Chiralcel OJ-H, 0.46 cm x 25 cm, 0.1% isopropanol/ hexanes, 0.8 mL/min, RT = 9.3 and 12.7 min]. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed a 10:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 1 H), 6.99–6.89 (m, 3 H), 6.84 (s, 1 H), 6.79–6.75 (m, 1 H), 6.69–6.65 (m, 1 H), 6.03 (d, *J* = 7.9 Hz, 1 H), 3.79 (s, 3 H), 3.49–3.41 (m, 1 H), 3.10 (d, *J* = 16.1 Hz, 1 H), 3.00 (dd, *J* = 7.4, 13.0 Hz, 1 H), 2.87–2.79 (m, 2 H), 2.08–2.01 (m, 1 H), 1.86–1.70 (m, 2 H), 1.62–1.54 (m, 1 H), 1.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 155.2, 141.6, 129.2, 129.1, 127.5, 124.4, 122.1, 119.0, 115.4, 111.3, 110.3, 72.1, 68.1, 55.2, 45.7, 42.6, 37.1, 31.9, 28.4; IR (film) 2957, 1602 cm^{-1}. MS (ESI) 294.1857 (294.1852 calcd for calcd for $C_{20}H_{23}NO$, M + H^+).

(±)-(3*S,9a*S**)-3-(3-Methoxybenzyl)-9a-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8f).** The reaction of (±)-**5d** (67 mg, 0.25 mmol) with 3-chloroanisole (37 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 55 mg (75 %) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 10:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR data were identical to those reported above for (+)-**8f**.

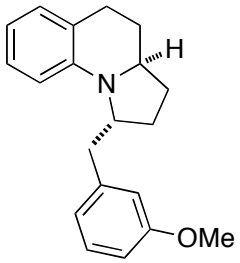


(±)-(1*R,3*R**)-3-(3-Methoxybenzyl)-1-phenyl-1,2,3,9-tetrahydropyrazolo[1,2-*a*]indazole (17)** The reaction of **16** (83 mg, 0.25 mmol) with 3-chloroanisole (37 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and X-Phos (9.5 mg, 0.020 mmol) to afford 42 mg (48%) of the title compound as a yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed a 3:1 mixture of diastereomers. The product was isolated as a 15:1 mixture of diastereomers; data are for the

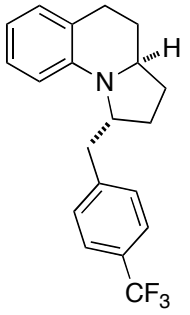
major diastereomer. ^{1}H NMR (500 MHz, C_6D_6) δ 7.32 (d, *J* = 7.3 Hz, 2 H), 7.20–7.09 (m, 4 H), 7.05 (s, br, 1 H), 6.97–6.73 (m, 3 H), 6.26 (d, *J* = 7.8 Hz, 1 H), 3.98 (d, *J* = 14.7 Hz, 1 H), 3.79 (d, *J* = 14.9 Hz, 1 H), 3.70–3.64 (m, 1 H), 3.43 (dd, *J* = 6.1, 11.0 Hz, 1 H), 3.32 (s, 3 H), 3.16 (dd, *J* = 9.0 Hz, 13.4 Hz, 1 H), 2.75 (dd, *J* = 4.6, 13.4 Hz, 1 H), 2.18–2.12 (m, 1 H), 1.91–1.86 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 152.8, 141.4, 139.5, 129.5, 128.6, 128.0, 127.8, 126.2, 123.6, 121.7, 121.0, 115.0, 111.8, 109.9, 67.1, 66.6, 55.2, 53.2, 44.5, 43.7 (one signal is missing due to incidental equivalence); IR (film) 3028, 2935, 2852 cm^{-1}. MS (EI) 356.1893 (356.1888 calcd for $C_{24}H_{24}N_2O$, M^+).



(±)-(1*R,3a*R**)-1-Benzyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8g).** The reaction of **5b** (67 mg, 0.25 mmol) with chlorobenzene (31 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 45 mg (68%) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 12:1 mixture of diastereomers. The product was isolated as a 25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.28 (m, 2 H), 7.24–7.20 (m, 3 H), 7.14–7.10 (m, 1 H), 7.05–6.99 (m, 1 H), 6.62 (d, *J* = 8.3 Hz, 1 H), 6.58–6.54 (m, 1 H), 4.02–3.96 (m, 1 H), 3.48–3.42 (m, 1 H), 3.17 (dd, *J* = 3.4, 13.7 Hz, 1 H), 2.84–2.77 (m, 1 H), 2.73–2.68 (m, 1 H), 2.62 (dd, *J* = 9.3, 13.2 Hz, 1 H), 2.09–1.96 (m, 3 H), 1.77–1.69 (m, 1 H), 1.44–1.34 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.2, 129.5, 128.6, 128.3, 127.2, 126.1, 122.0, 114.6, 109.6, 59.8, 58.1, 38.9, 31.8, 29.5, 28.4, 27.4; IR (film) 3024, 2934 cm^{-1}. MS (ESI) 264.1740 (264.1752 calcd for for $C_{19}H_{21}N$, M + H^+).

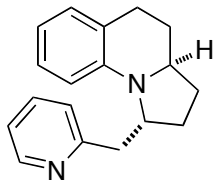


(±)-(1*R,3a*R**)-1-(3-Methoxybenzyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8h).** The reaction of **8b** (67 mg, 0.25 mmol) with 3-chloroanisole (37 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 49 mg (67%) of the title compound as a yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as an 8:1 mixture of diastereomers. The product was isolated as a 22:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.19 (m, 1 H), 7.13–7.09 (m, 1 H), 6.99 (d, *J* = 7.3 Hz, 1 H), 6.83 (d, *J* = 7.8 Hz, 1 H), 6.78–6.75 (m, 2 H), 6.61 (d, *J* = 8.3 Hz, 1 H), 6.55 (dt, *J* = 1.0, 7.3 Hz, 1 H), 4.02–3.96 (m, 1 H), 3.78 (s, 3 H), 3.48–3.42 (m, 1 H), 3.15 (dd, *J* = 3.0, 13.3 Hz, 1 H), 2.84–2.76 (m, 1 H), 2.73–2.67 (m, 1 H), 2.60 (dd, *J* = 9.3, 13.2 Hz, 1 H), 2.09–1.97 (m, 3 H), 1.77–1.69 (m, 1 H), 1.43–1.30 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 143.6, 140.8, 129.2, 128.6, 127.2, 122.0, 115.4, 114.6, 111.3, 109.6, 59.6, 58.1, 55.1, 38.9, 31.8, 29.6, 28.4, 27.4 (one signal is missing due to incidental equivalence); IR (film) 2934, 2838 cm^{-1}. MS (ESI) 294.1859 (294.1852 calcd for $C_{20}H_{23}NO$, M + H^+).



(±)-(1*R,3a*R**)-1-[4-(Trifluoromethyl)benzyl]-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8i).** The reaction of **5b** (64 mg, 0.25 mmol) with 4-chlorobenzotrifluoride (40 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.020 mmol) to afford 48 mg (58%) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the

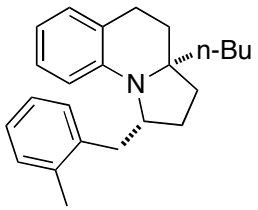
product was formed as a 3:1 mixture of diastereomers. The product was isolated as a 7:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 2 H) 7.31 (d, J = 7.9 Hz, 2 H), 7.14–7.09 (m, 1 H), 7.01 (d, J = 7.1 Hz, 1 H), 6.60–6.56 (m, 2 H), 4.04–3.99 (m, 1 H), 3.42–3.36 (m, 1 H), 3.18 (dd, J = 2.9, 13.4 Hz, 1 H), 2.83–2.67 (m, 3 H), 2.09–1.97 (m, 3 H), 1.71–1.64 (m, 1 H), 1.42–1.29 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.2, 129.9, 128.7, 128.0, 127.2, 125.1 (q, J = 3.5 Hz), 124.3 (q, J = 270 Hz), 122.1, 114.9, 109.5, 59.4, 58.3, 38.7, 31.7, 29.5, 28.4, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ 62.3 (s, 3 F). IR (film) 2934, 1602 cm^{-1}. MS (EI) 331.1548 (331.1548 calcd for $C_{20}H_{20}F_3N$, M^+).



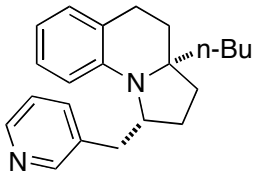
(±)-(1*R,3a*R**)-1-(Pyridin-2-ylmethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8j).** The reaction of **(±)-5b** (67 mg, 0.25 mmol) with 3-chloropyridine (29 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 38 mg (57%) of the title compound as a yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 10:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59–8.57 (m, 1 H), 7.60–7.55 (m, 1 H), 7.16–7.08 (m, 3 H), 6.99 (d, J = 7.2 Hz, 1 H), 6.66 (dd, J = 2.8, 5.2 Hz, 1 H), 6.58–6.53 (m, 1 H), 4.24–4.16 (m, 1 H), 3.52–41 (m, 1 H), 3.41–3.36 (m, 1 H), 2.85–2.68 (m, 3 H), 2.10–1.95 (m, 3 H), 1.85–1.75 (m, 1 H), 1.49–1.35 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.3, 143.6, 136.1, 128.5, 127.3, 124.0, 121.8, 121.2. 114.7, 109.9, 58.9, 57.9, 41.3, 31.7, 29.4, 28.4, 27.5; IR (film) 3062, 2932 cm^{-1}. MS (EI) 264.1632 (264.1626 calcd for $C_{18}H_{20}N_2$, M^+).

(+)-(1*R*,3a*R*)-1-(Pyridin-2-ylmethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8j). The reaction of **(+)-5b** (67 mg, 0.25 mmol) with 3-chloropyridine (29 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 43 mg (65%) of the title

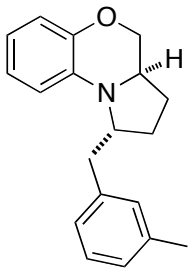
compound as a yellow oil, $[\alpha]^{23}_{D}$ +19.4 (*c* 0.34, CH_2Cl_2). The product was determined to be 92% ee by chiral HPLC analysis [Chiralcel OD-H, 0.46 cm x 15 cm, 0.5% isopropanol/ hexanes, 2.0 mL/min, RT = 4.8 and 11.2 min]. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 10:1 mixture of diastereomers. The product was isolated as a >25:1 mixture of diastereomers. ^{1}H NMR data were identical to those reported above for (±)-**8j**.



(±)-(1*R,3a*R**)-3a-Butyl-1-(2-methylbenzyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8k).** The reaction of **5e** (81 mg, 0.25 mmol) with 2-chlorotoluene (35 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 66 mg (79%) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 12:1 mixture of diastereomers. The product was isolated as an 11:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.24 (m, 1 H), 7.21–7.15 (m, 3 H), 7.11–7.01 (m, 2 H), 6.64–6.58 (m, 2 H), 4.00–3.94 (m, 1 H), 2.26 (dd, *J* = 4.0, 14.5 Hz, 1 H), 2.85–2.77 (m), 2.72 (dd, *J* = 10.0, 14.0 Hz, 1 H), 2.65–2.59 (m, 1 H), 2.44 (s, 3 H), 2.15–2.07 (m, 1 H), 2.00–1.95 (m, 1 H), 1.94–1.86 (m, 1 H), 1.80–1.71 (m, 2 H), 1.68–1.61 (m, 1 H), 1.38–1.19 (m, 7 H), 0.94–0.90 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 138.0, 136.4, 130.3, 129.9, 129.1, 126.9, 126.2, 125.9, 121.0, 115.1, 112.3, 63.1, 63.0, 39.3, 38.8, 36.3, 28.1, 27.9, 26.7, 24.6, 23.4, 20.3, 14.2; IR (film) 2927 cm^{-1}. MS (EI) 333.2459 (333.2457 calcd for $C_{24}H_{31}N$, M^+).

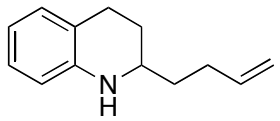


(±)-(1*R,3a*R**)-3a-Butyl-1-(pyridin-3-ylmethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinoline (8l).** The reaction of **5e** (81 mg, 0.25 mmol) with 3-chloropyridine (29 μL, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol) and $PCy_3{\cdot}HBF_4$ (3.7 mg, 0.010 mmol) to afford 38 mg (47%) of the title compound as a red solid, mp 76–85 ºC. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed as a 7:1 mixture of diastereomers. The product was isolated as a 10:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56–8.53 (m, 1 H), 8.49 (dd, *J* = 1.5, 6.3 Hz, 1 H), 7.58 (dt, *J* = 7.7, 9.5 Hz, 1 H), 7.26–7.22 (m, 1 H), 7.11–7.07 (m, 1 H), 7.04–7.02 (m, 1 H), 6.63–6.57 (m, 2 H), 3.89–2.83 (m, 1 H), 3.25 (dd, *J* = 3.9, 11.8 Hz, 1 H), 2.83–2.75 (m, 1 H), 2.72–2.66 (m, 1 H), 2.64–2.59 (m, 1 H), 2.12–1.92 (m, 3 H), 1.80–1.72 (m, 1 H), 1.69–1.54 (m, 2 H), 1.34–1.14 (m, 6 H), 0.92–0.88 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 147.8, 144.0, 136.7, 134.8, 129.1, 127.0, 123.4, 121.3, 115.3, 111.5; IR (film) 2928 cm^{-1}. MS (ESI) *m/z* 321.2326 (321.2325 calcd for $C_{22}H_{28}N_2$, M + H$^+$).

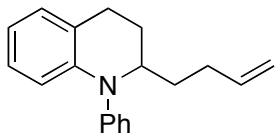


(±)-(1*R,3a*R**)-1-(3-Methylbenzyl)-2,3,3a,4-tetrahydro-1*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazine (8m).** The reaction of **5c** (68 mg, 0.25 mmol) with 3-chlorotoluene (36 μL, 38 mg, 0.30 mmol) was conducted according to General Procedure 5 using a catalyst composed of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and Cy_4Dpe-Phos (5.6 mg, 0.010 mmol) to afford 24 mg (35%) of the title compound as a pale yellow oil. ^{1}H NMR analysis of the crude reaction mixture indicated the product was formed a 5:1 mixture of diastereomers. The product was isolated as a 15:1 mixture of diastereomers; data are for the major diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.17 (m, 1 H), 7.08–7.02 (m, 3 H), 6.90–6.85 (m, 2 H), 6.70 (dd, *J* = 1.5, 7.9 Hz, 1 H),

6.63–6.58 (m, 1 H), 4.27 (dd, *J* = 3.9, 10.3 Hz, 1 H), 4.05–3.90 (m, 1 H), 3.65–3.58 (m, 1 H), 3.35 (t, *J* = 10.0 Hz, 1 H), 3.11 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.66 (dd, *J* = 8.8, 13.3 Hz, 1 H), 2.33 (s, 3 H), 2.04–1.96 (m, 1 H), 1.95–1.87 (m, 1 H), 1.80–1.73 (m, 1 H), 1.50–1.43 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 138.8, 138.0, 134.4, 130.3, 128.3, 127.0, 126.5, 122.0, 116.3, 112.2, 67.5, 62.8, 55.2, 40.4, 28.4, 26.7, 21.4 (one signal is missing due to incidental equivalence); IR (film) 2920, 1500 cm^{-1}. MS (EI) 279.1616 (279.1623 calcd for $C_{19}H_{21}NO$, M^+).



(±)-2-(But-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (6a). In order to obtain a pure sample of **6a** for the purposes of characterization, the reaction of **5b** (351 mg, 1.31 mmol) was conducted via a modification of General Procedure 5 in which a catalyst composed of $Pd_2(dba)_3$ (11 mg, 0.012 mmol) and Dpe-Phos (13 mg, 0.024 mmol) was employed, and the aryl chloride was omitted. This procedure afforded 187 mg (76%) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97–6.93 (m, 2 H), 6.59 (t, *J* = 7.3 Hz, 1 H), 6.46 (d, *J* = 8.1 Hz, 1 H), 5.89–5.80 (m, 1 H), 5.05 (dd, *J* = 1.7, 17.2 Hz, 1 H), 4.98 (dd, *J* = 0.5, 10.0 Hz, 1 H), 3.78 (s, br, 1 H), 3.30–3.25 (m, 1 H), 2.84–2.77 (m, 1 H), 2.75–2.69 (m, 1 H), 2.20–2.15 (m, 2 H), 1.99–1.93 (m, 1 H), 1.66–1.57 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 138.2, 129.2, 126.7, 121.3, 116.9, 114.9, 114.1, 51.0, 35.6, 30.0, 27.9, 26.2; IR (film) 3405, 3076, 2924, 2845, 1608 cm^{-1}. MS (ESI) 188.1432 (188.1434 calcd for $C_{13}H_{17}N$, M + H^+).

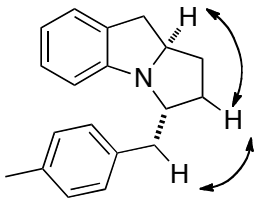


(±)-2-(but-3-en-1-yl)-1-phenyl-1,2,3,4-tetrahydroquinoline (12). In order to obtain a pure sample of **12** for the purposes of characterization, the reaction of **5b** (67 mg, 0.25 mmol) with bromobenzene (27 μL, 0.26 mmol) was conducted via a modification of General Procedure 5 in which a catalyst composed of (RuPhos) palladium(II) phenethylamine chloride (1.8 mg, 0.0025 mmol) and BrettPhos (1.3 mg, 0.0025 mmol) was employed, using 1,4-dioxane (2 mL/ mmol) as solvent. This procedure afforded 7 mg (11%) of the title compound as a clear oil.[9] ^{1}H NMR of the crude reaction mixture indicated that the title compound was generated as a 1:1 mixture with

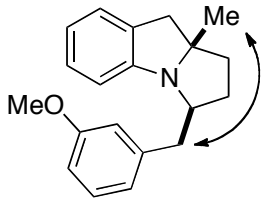
8g. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2 H), 7.24–7.17 (m, 2 H), 7.08–7.05 (m, 2 H), 6.94–6.91 (m, 1 H), 6.73–6.68 (m, 2 H), 5.81–5.75 (m, 1 H), 5.00 (ddd, *J* = 1.7, 3.4, 17.2 Hz, 1 H), 4.95–4.93 (m, 1 H), 3.78–3.74 (m, 1 H), 2.89–2.83 (m, 1 H), 2.80–2.75 (m, 1 H), 2.22–2.16 (m, 1 H), 2.14–2. 08 (m, 1 H), 2.03–1.97 (m, 1 H), 1.91–1.86 (m, 1 H), 1.78–1.72 (m, 1 H), 1.63–1.53 (m, 1 H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.8, 143.3, 138.3, 129.34, 129.30, 126.3, 125.2, 124.5, 123.4, 118.5, 118.3, 114.7, 58.7, 31.2, 30.4, 24.2, 23.5; IR (film) 3063, 2929, 2847 cm^{-1}. MS 264.1743 (264.1747 calcd for $C_{19}H_{21}N$, M + H^+).

Assignment of Stereochemistry

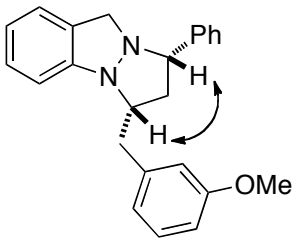
The relative stereochemistry of **8a** was determined based on the nOe signals depicted below. The stereochemistry of **8b–d** were assigned based on analogy to **8a**.



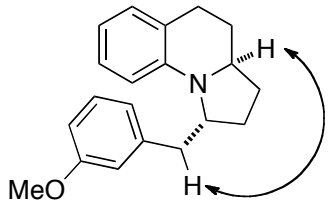
The relative stereochemistry of **8f** was determined based on the nOe signals depicted below. The stereochemistry of **8e** was assigned based on analogy to **8f**.



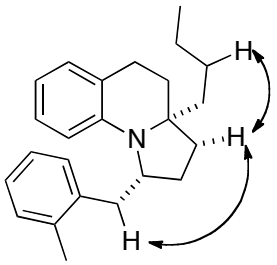
The relative stereochemistry of **17** was determined based on the nOe signals depicted below.



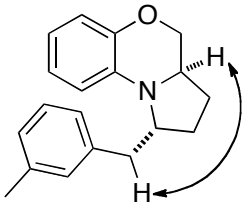
The relative stereochemistry of **8h** was determined based on the nOe signals depicted below. The stereochemistry of **8g**, and **8i–j** were assigned based on analogy to **8h**.



The relative stereochemistry of **8k** was determined based on the nOe signals depicted below. The stereochemistry of **8l** was assigned based on analogy to **8k**.



The relative stereochemistry of **8m** was determined based on the nOe signals depicted below.



References

[1] Padwa, A.; Zanka, A.; Cassidy, M. P.; Harris, J. M. *Tetrahedron* **2003**, *59*, 4939–4944.

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gsl-VII-204-3

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

Sample directory:

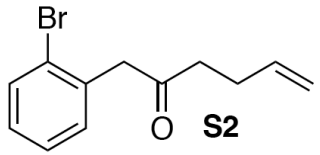
FidFile: gsl-VII-204-3

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 6 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
12 repetitions
OBSERVE H1, 499.9042603 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 56 sec

VARIAN



S2

gsl-IV-31-3

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

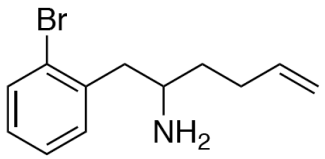
Sample directory:

FidFile: gsl-IV-31-3

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 30 2009

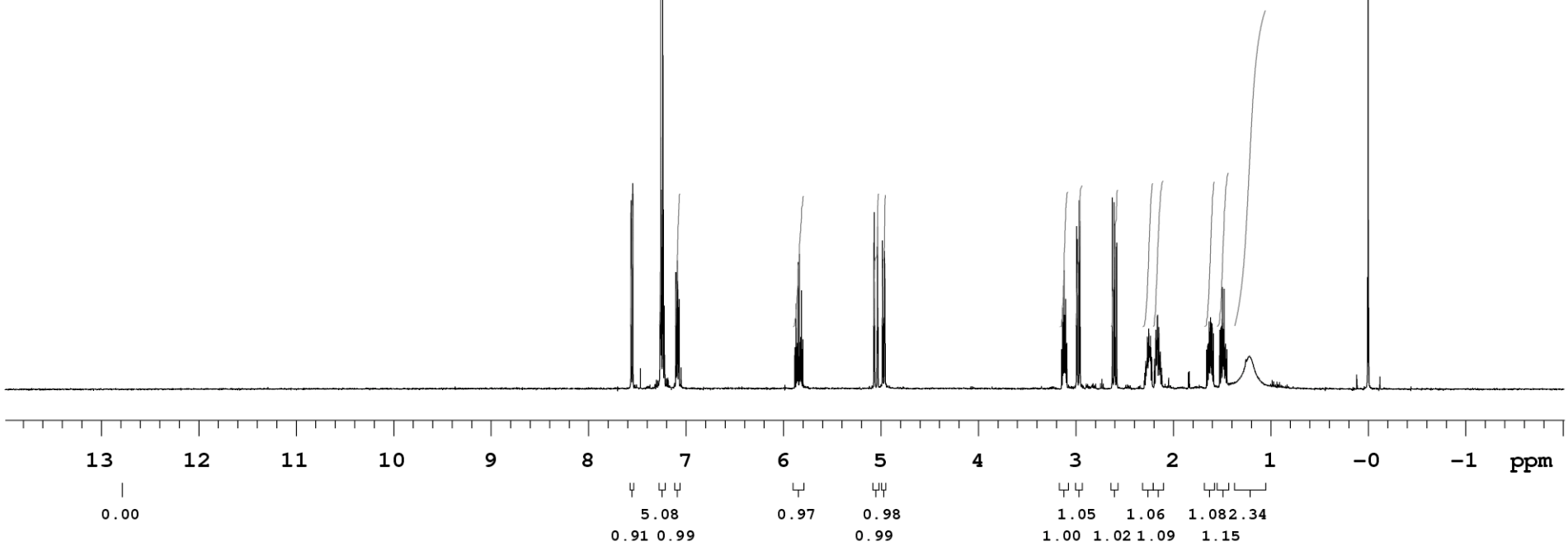
Operator: geolemen

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
10 repetitions
OBSERVE H1, 499.9042605 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 41 sec



5a

VARIAN



VARIAN

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

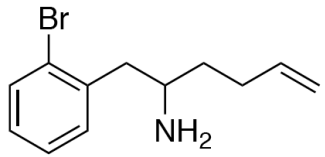
Sample directory:

FidFile: gsl-IV-31-3carbon

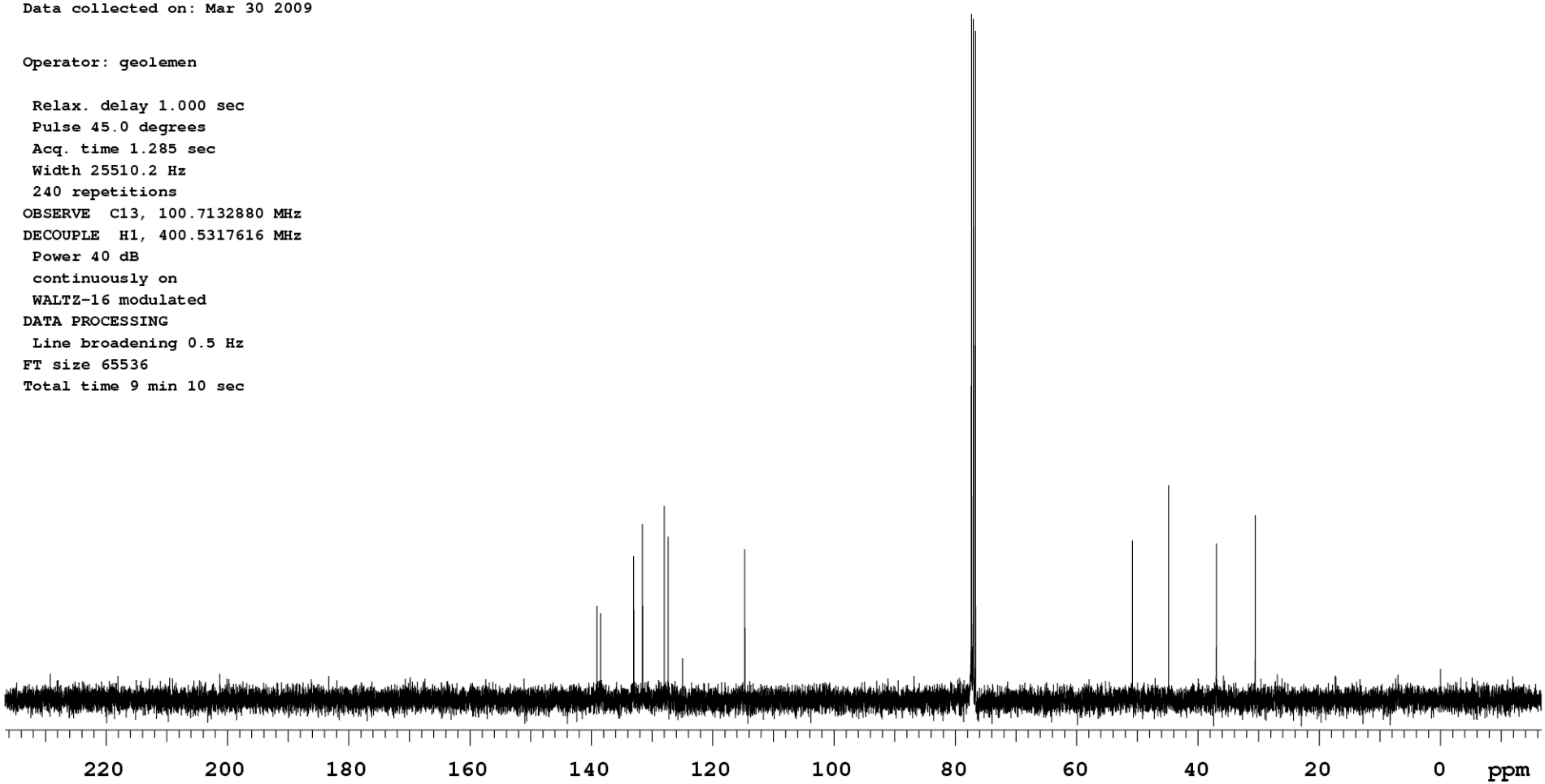
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 30 2009

Operator: geolemen

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
240 repetitions
OBSERVE C13, 100.7132880 MHz
DECOUPLE H1, 400.5317616 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 10 sec



5a



gsl-VIII-79-2

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

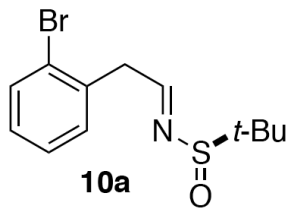
Sample directory:

FidFile: gsl-VIII-79-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 13 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
12 repetitions
OBSERVE H1, 499.9042596 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 56 sec



10a

VARIAN

gsl-VIII-89-2 carbon

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

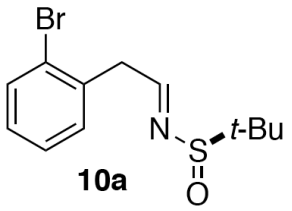
FidFile: gsl-VIII-89-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 20 2011

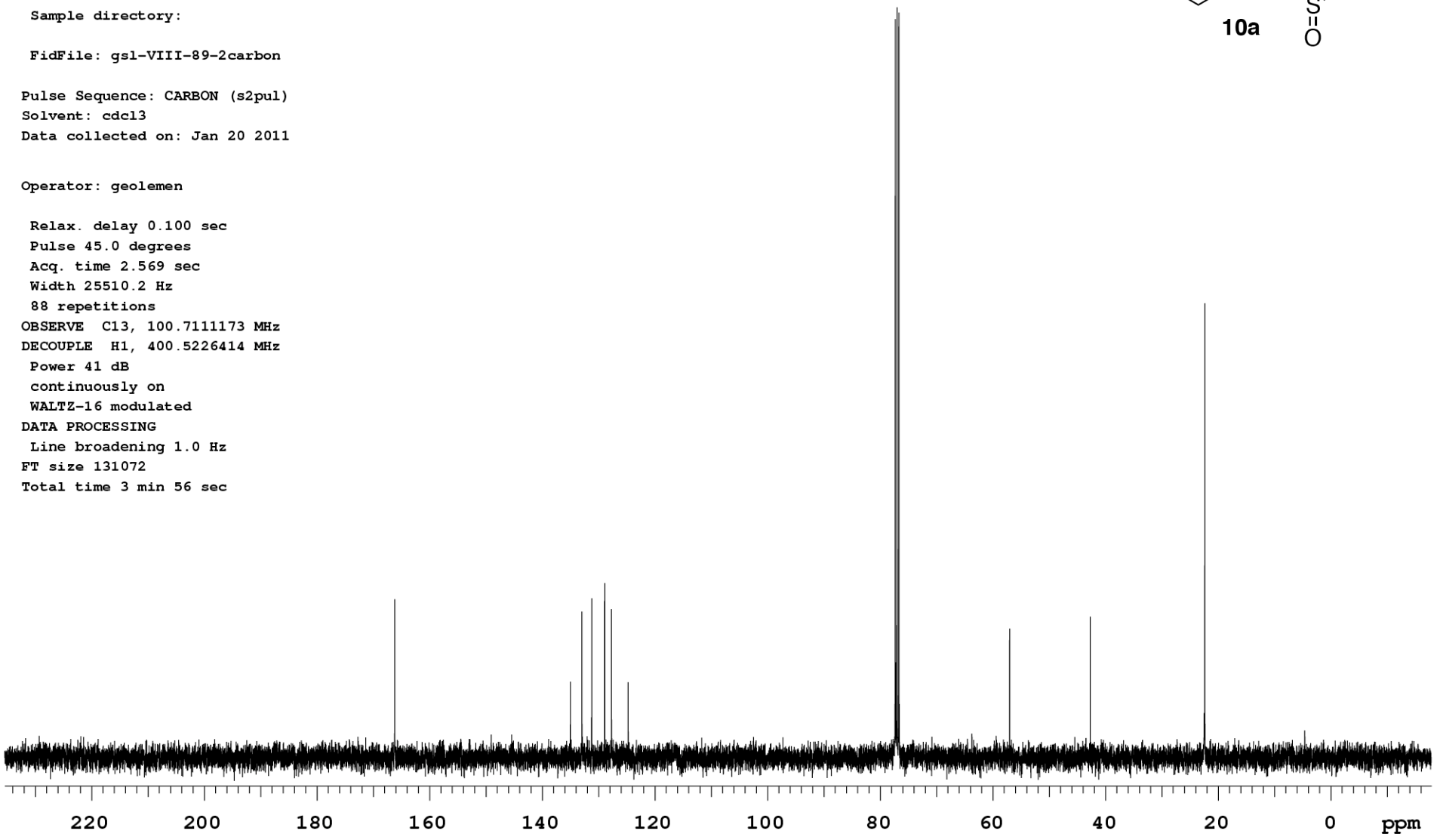
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
88 repetitions
OBSERVE C13, 100.7111173 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min 56 sec

VARIAN



10a



gsl-VIII-90-2

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

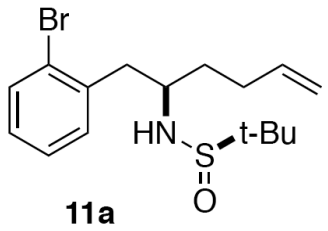
Sample directory:

FidFile: gsl-VIII-90-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 14 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
20 repetitions
OBSERVE H1, 499.9042598 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 28 sec



11a

VARIAN

VARIAN

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

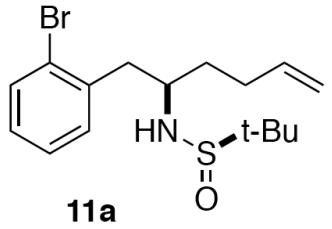
Sample directory:

FidFile: gsl-VIII-90-2carbon

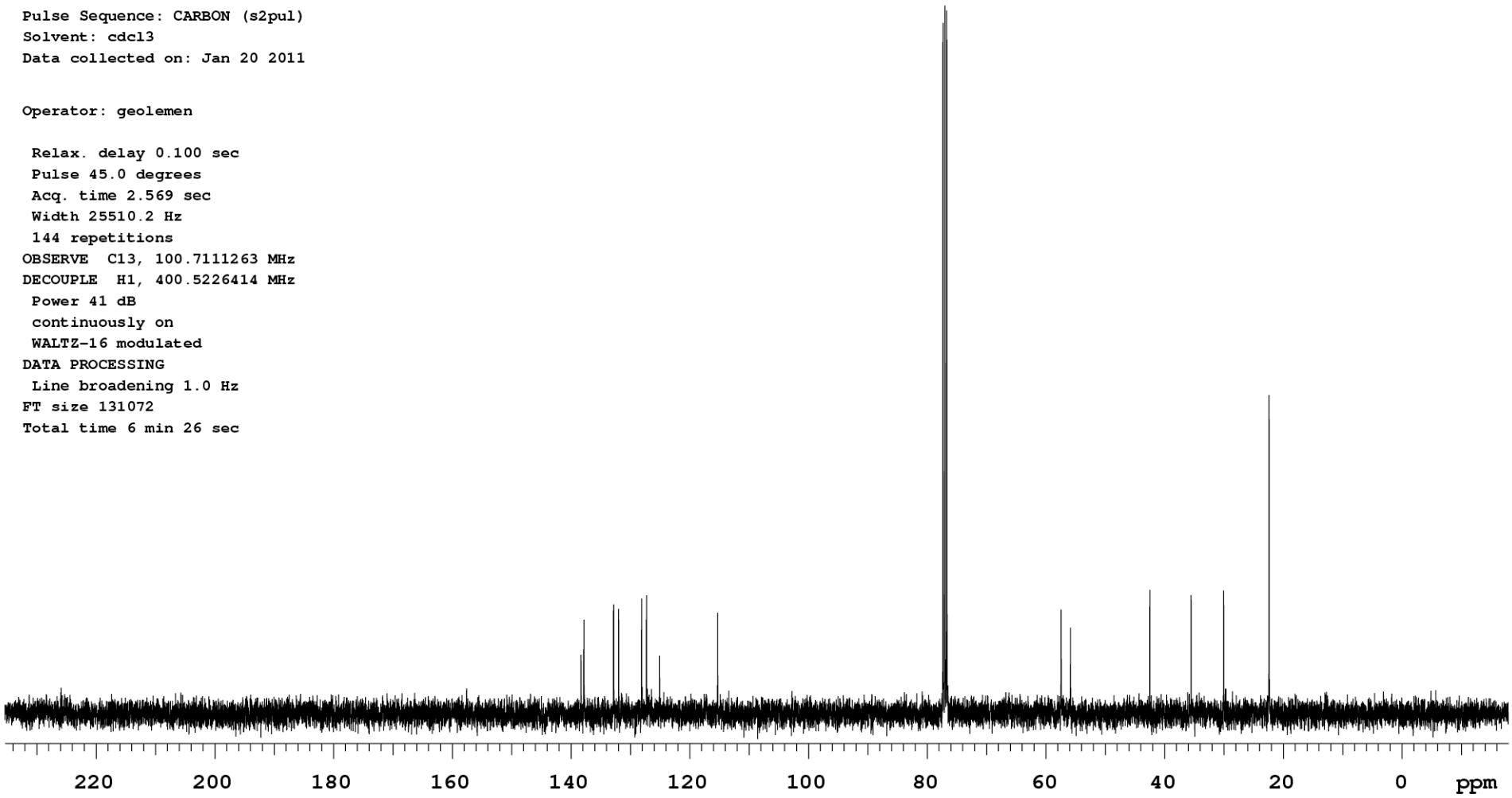
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 20 2011

Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
144 repetitions
OBSERVE C13, 100.7111263 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 min 26 sec



11a



gsl-VII-190-2

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

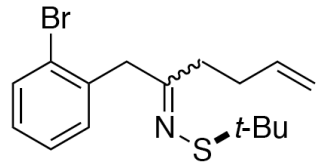
FidFile: gsl-VII-190-2frac10-26

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 23 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 5.112 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.5389187 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 56 sec

VARIAN



S3

gsl-VII-199-2frac35-48

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

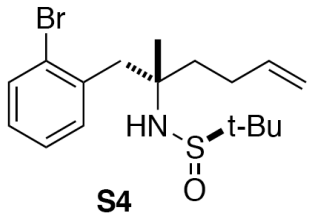
Sample directory:

FidFile: gsl-VII-199-2frac35-48

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 2 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
4 repetitions
OBSERVE H1, 400.5206313 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 4 sec



S4

VARIAN

gsl-VII-199-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

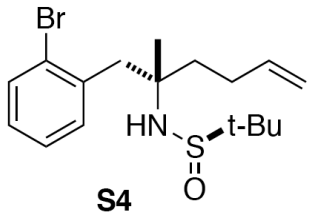
FidFile: gsl-VII-199-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Jan 26 2011

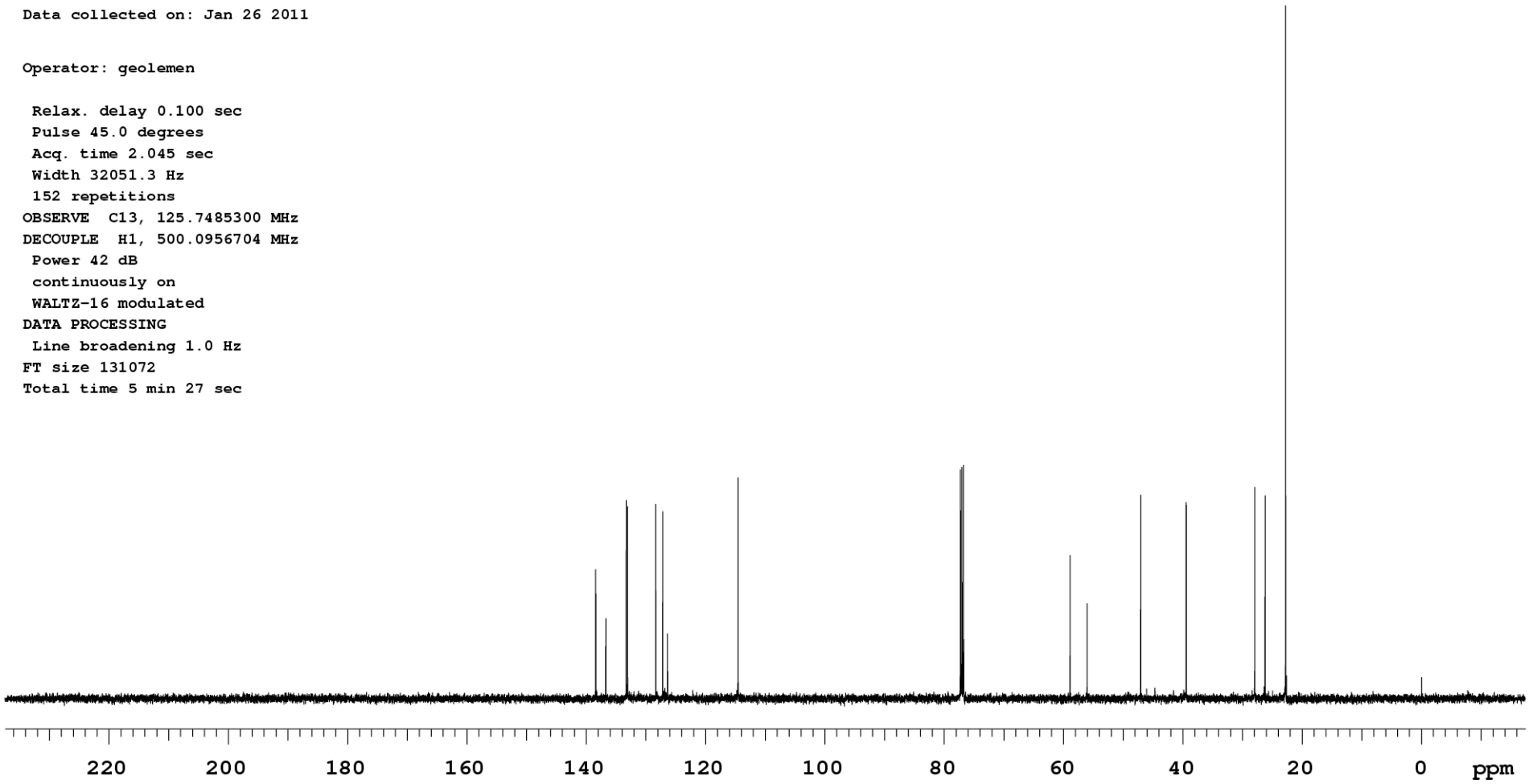
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
152 repetitions
OBSERVE C13, 125.7485300 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 5 min 27 sec

VARIAN



S4



gsl-VIII-144-3

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

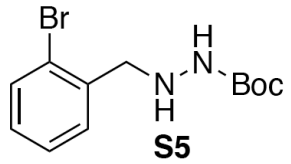
Sample directory:

FidFile: gsl-VIII-144-3

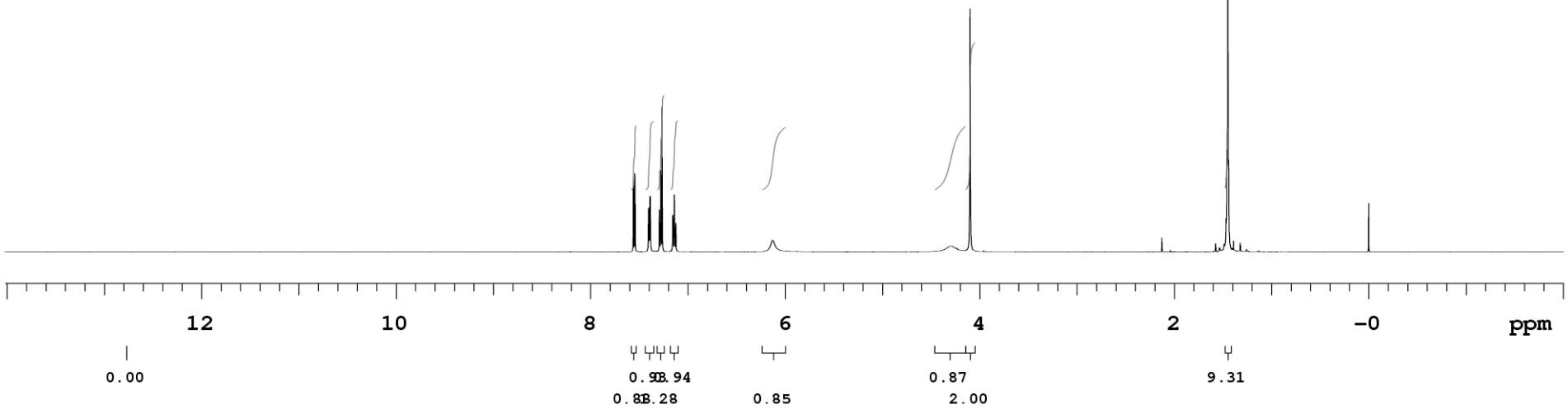
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 14 2011

Operator: geolemen

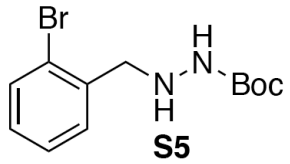
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 500.0931657 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 46 sec



S5



VARIAN



S5

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

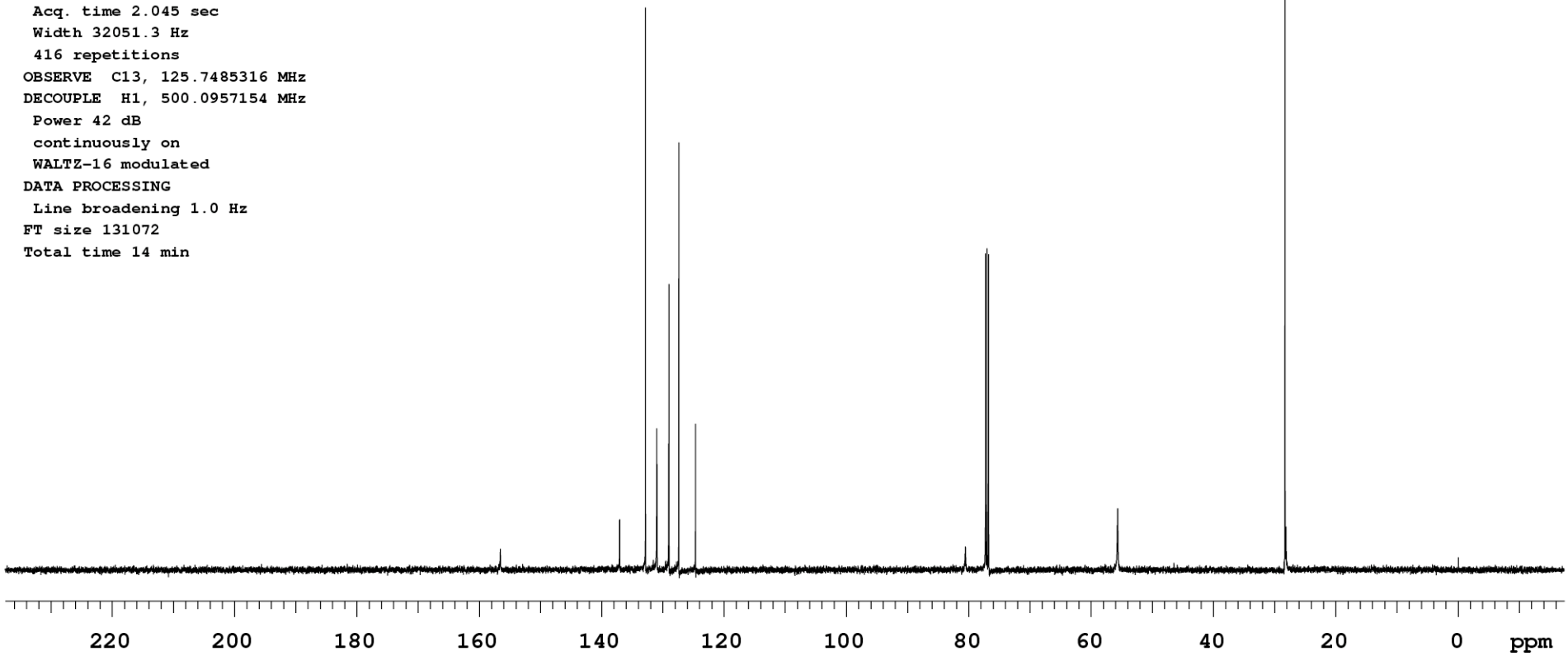
Sample directory:

FidFile: gsl-VIII-144-3carbonrerun

Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Apr 14 2011

Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
416 repetitions
OBSERVE C13, 125.7485316 MHz
DECOUPLE H1, 500.0957154 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 14 min



gsl-VIII-145-3
d8-toluene
80 degrees

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

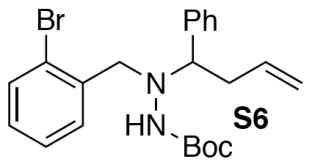
Sample directory:

FidFile: gsl-VIII-145-3toluene80degrees

Pulse Sequence: PROTON (s2pul)
Solvent: toluene
Data collected on: Apr 14 2011

Temp. 80.0 C / 353.1 K
Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
20 repetitions
OBSERVE H1, 500.0957485 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 41 sec



S6

VARIAN

gsl-VIII-146-4

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

Sample directory:

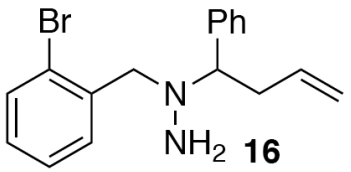
FidFile: gsl-VIII-146-4

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 14 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
4 repetitions
OBSERVE H1, 500.0931806 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 28 sec

VARIAN



16

gsl-VIII-164-2

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

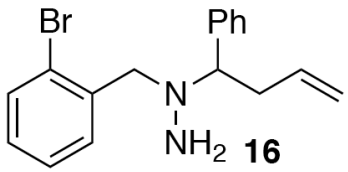
Sample directory:

FidFile: gsl-VIII-146-4carbon

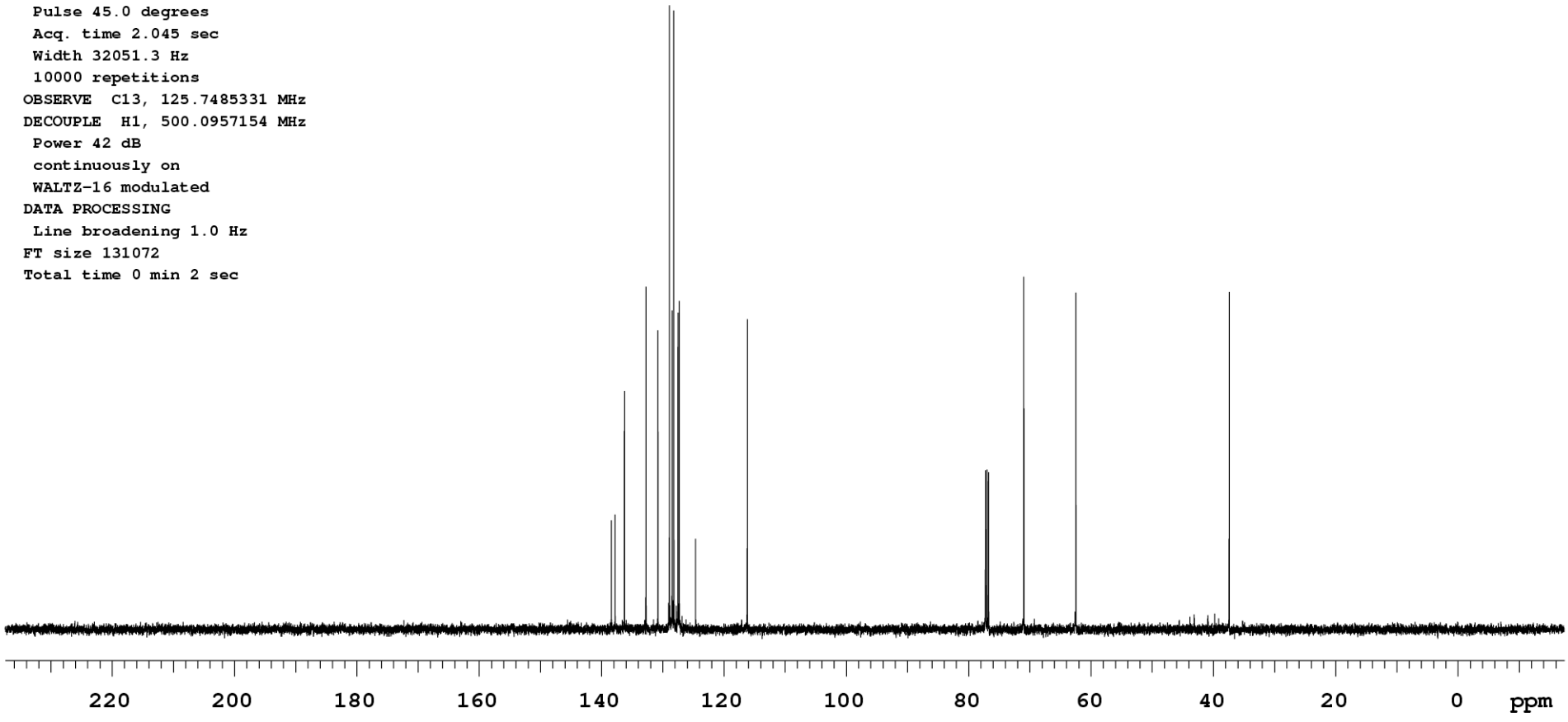
Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Apr 14 2011

Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
10000 repetitions
OBSERVE C13, 125.7485331 MHz
DECOUPLE H1, 500.0957154 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 0 min 2 sec



16



gsl-VII-154-2

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

Sample directory:

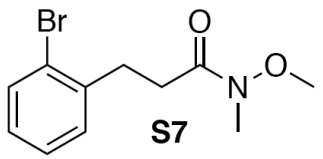
FidFile: gsl-VII-154-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 29 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
10 repetitions
OBSERVE H1, 499.9042598 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 48 sec

VARIAN



S7

gsl-VII-154-2 carbon

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

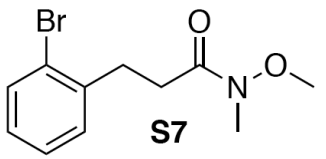
FidFile: gsl-VII-154-2carbon

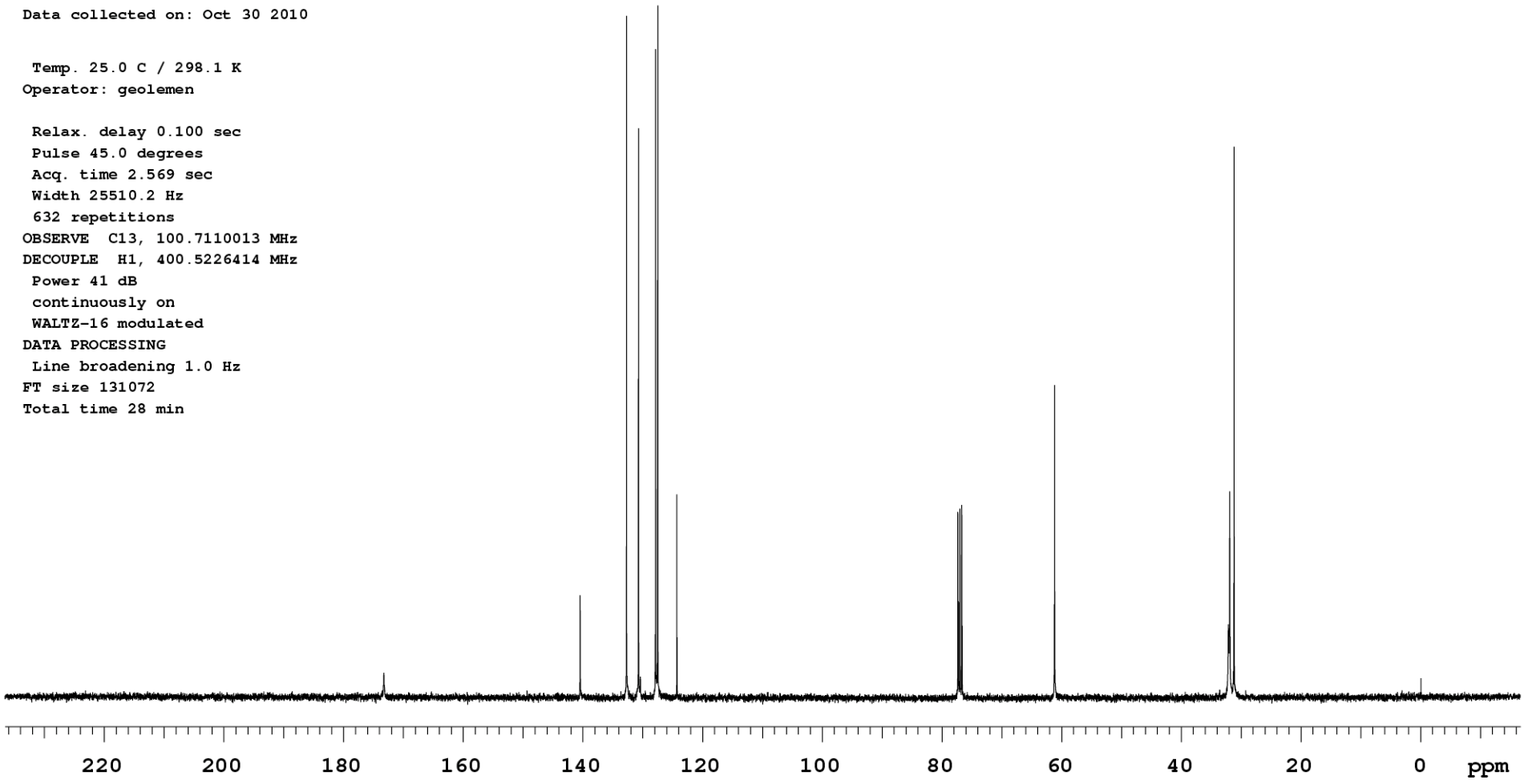
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 30 2010

Temp. 25.0 C / 298.1 K
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
632 repetitions
OBSERVE C13, 100.7110013 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 28 min

VARIAN





gsl-VII-183-3

Sample Name:

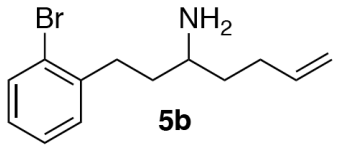
Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:
/export/home/chempack/vnmrsys/data
Sample directory:

FidFile: gsl-VII-183-3

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 19 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6399.5 Hz
8 repetitions
OBSERVE H1, 399.9649483 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 40 sec



5b

VARIAN

gsl-III-208-1 carbon

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

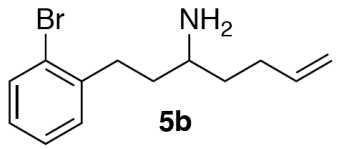
FidFile: gsl-III-208-1carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 24 2009

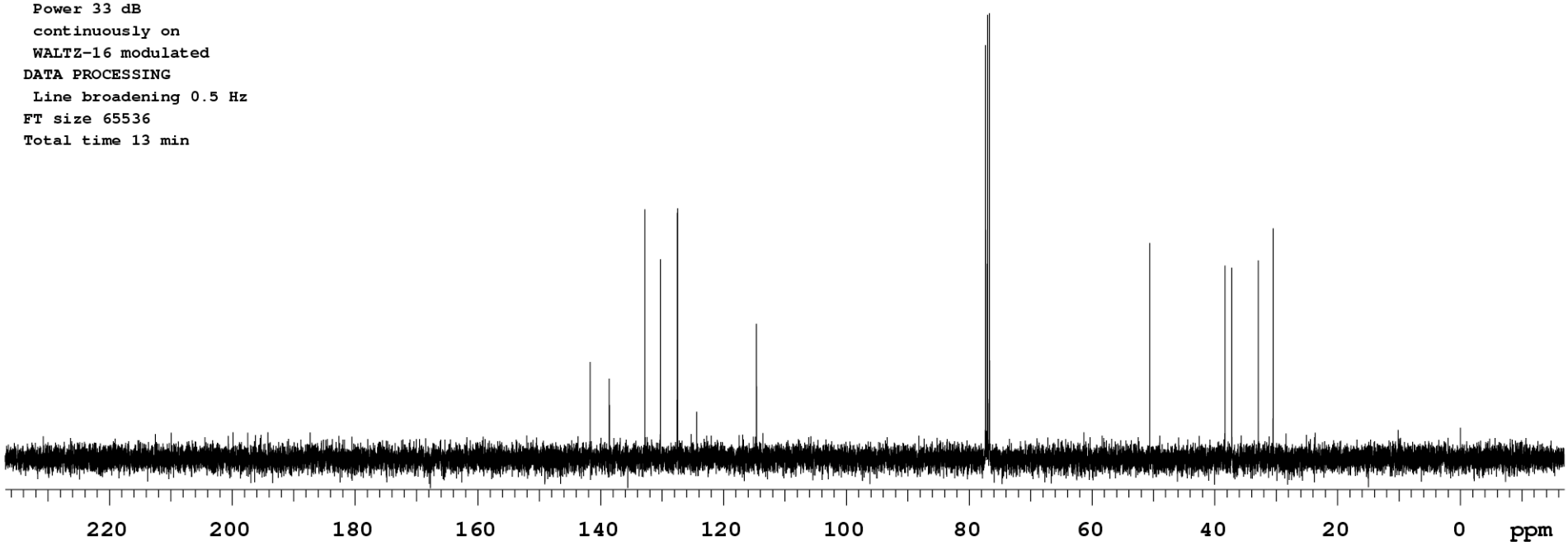
Operator: geolemen

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
352 repetitions
OBSERVE C13, 100.4641417 MHz
DECOUPLE H1, 399.5409236 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 13 min

VARIAN



5b



gsl-VII-171-2frac63-92

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

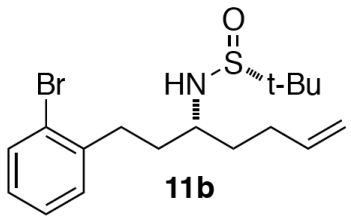
Sample directory:

FidFile: gsl-VII-171-2frac63-92

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 8 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.097 sec
Width 7998.4 Hz
12 repetitions
OBSERVE H1, 499.9042603 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 4 sec



11b

VARIAN

gsl-VII-171-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

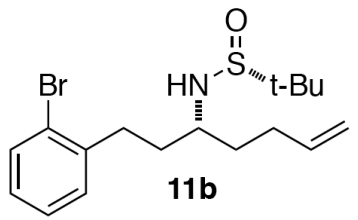
FidFile: gsl-VII-171-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Jan 27 2011

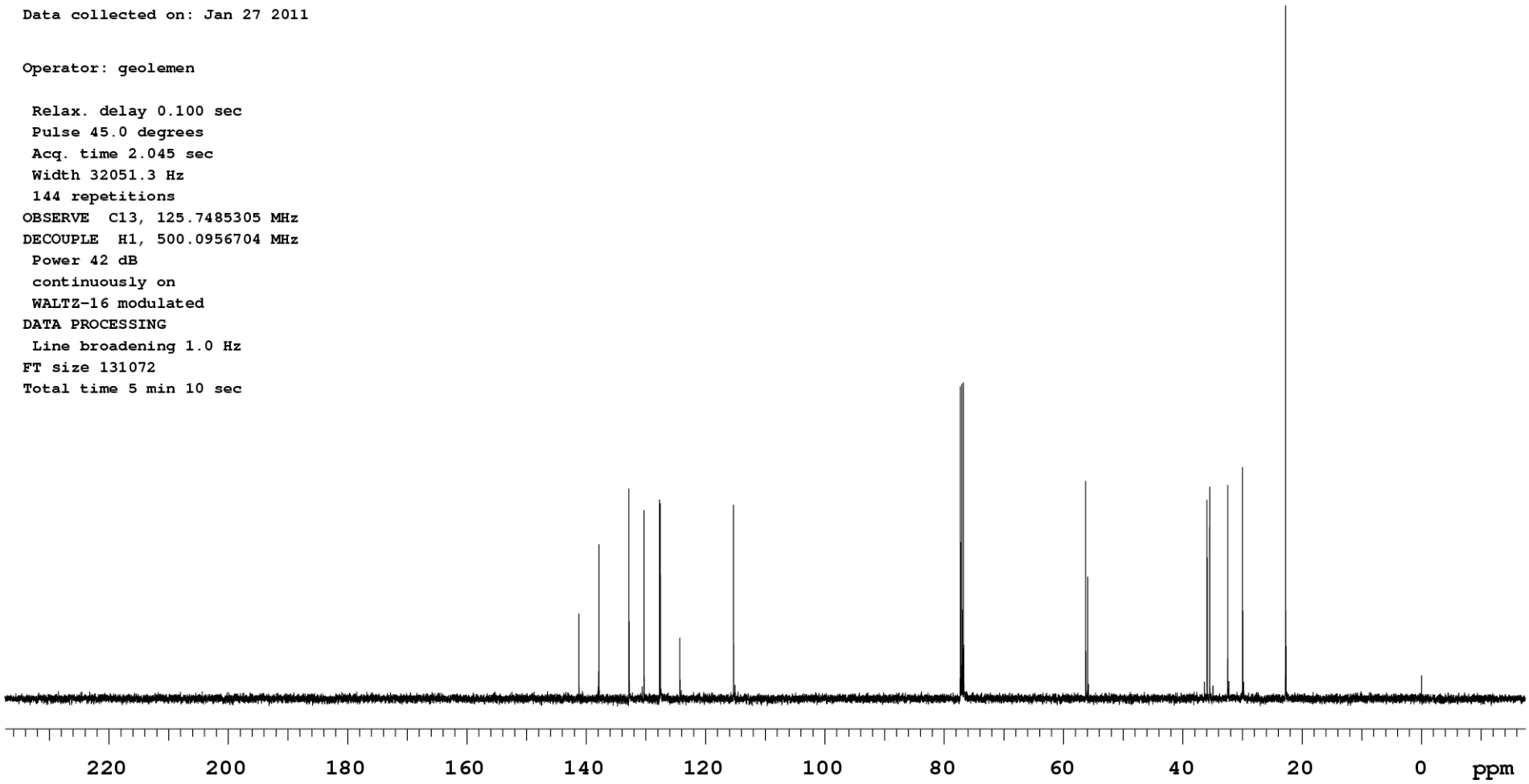
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
144 repetitions
OBSERVE C13, 125.7485305 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 5 min 10 sec

VARIAN



11b



gsl-VIII-76-2

Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

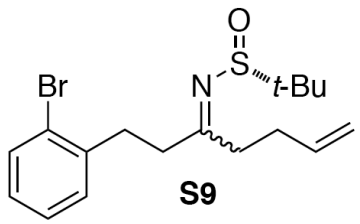
Sample directory:

FidFile: gsl-VIII-76-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 17 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
12 repetitions
OBSERVE H1, 499.9042596 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 56 sec



S9

VARIAN

gsl-VIII-76-2 carbon

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

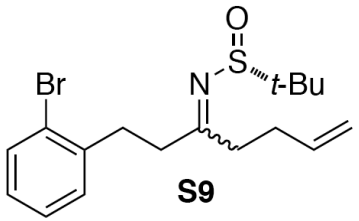
Sample directory:

FidFile: gsl-VIII-76-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 18 2010

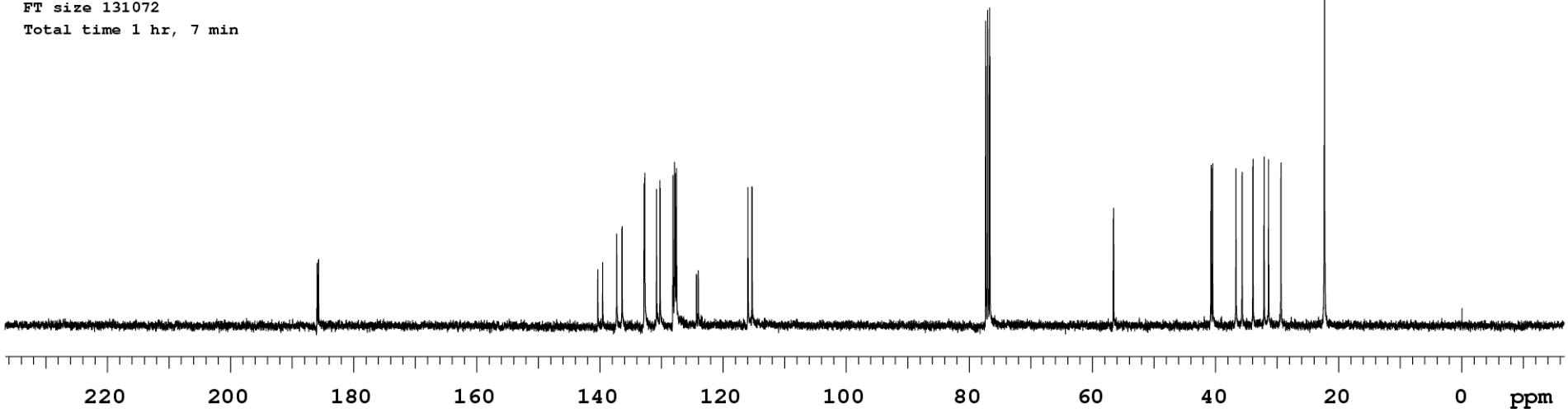
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
1512 repetitions
OBSERVE C13, 100.7109994 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 7 min



S9

VARIAN



gsl-VIII-84-2

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

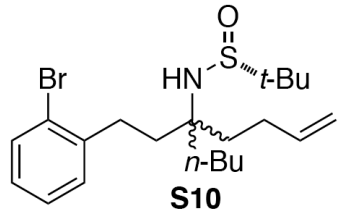
FidFile: gsl-VIII-84-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 25 2011

Temp. 25.0 C / 298.1 K
Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 5.112 sec
Width 6410.3 Hz
10 repetitions
OBSERVE H1, 399.5334909 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 7 sec

VARIAN



S10

VARIAN

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

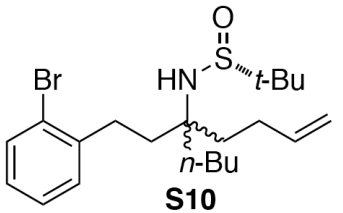
Sample directory:

FidFile: gsl-VIII-84-2carbon

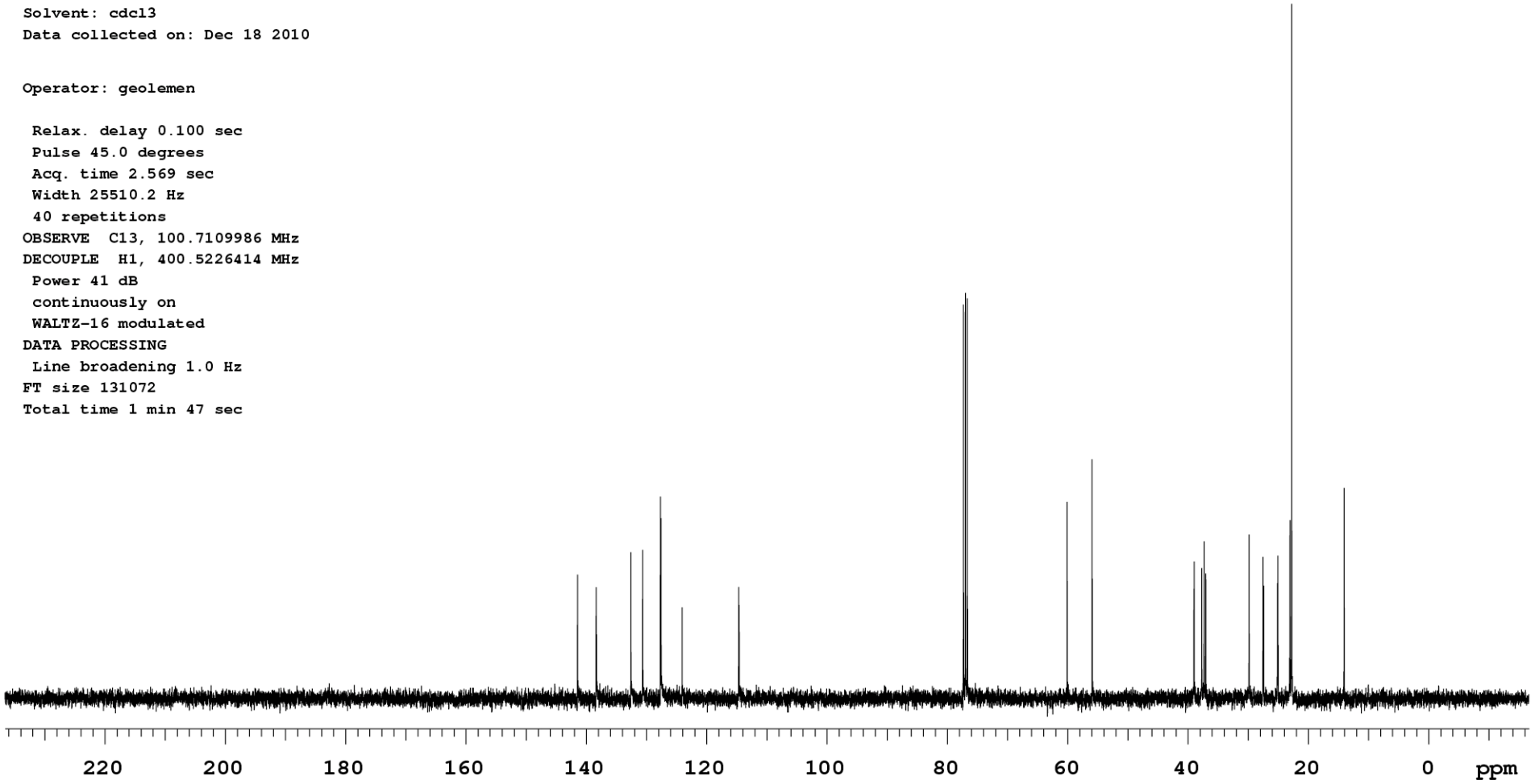
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 18 2010

Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
40 repetitions
OBSERVE C13, 100.7109986 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 min 47 sec



S10



gsl-VIII-104-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

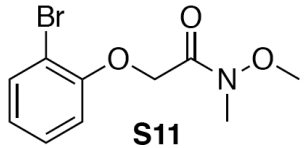
FidFile: gsl-VIII-104-2

Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Feb 16 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
4 repetitions
OBSERVE H1, 500.0931679 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 28 sec

VARIAN



S11

gsl-VIII-104-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

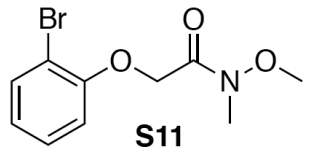
FidFile: gsl-VIII-104-2carbon30degreepulse

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Feb 17 2011

Operator: geolemen

Relax. delay 0.100 sec
Pulse 30.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
2488 repetitions
OBSERVE C13, 125.7485305 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 29 min

VARIAN



S11

gsl-VIII-105-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

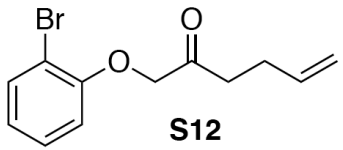
FidFile: gsl-VIII-105-2

Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Feb 16 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
4 repetitions
OBSERVE H1, 500.0931691 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 28 sec

VARIAN



S12

gsl-VIII-105-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

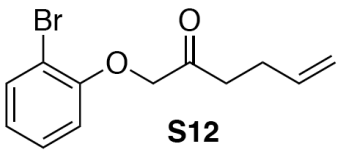
FidFile: gsl-VIII-105-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Feb 16 2011

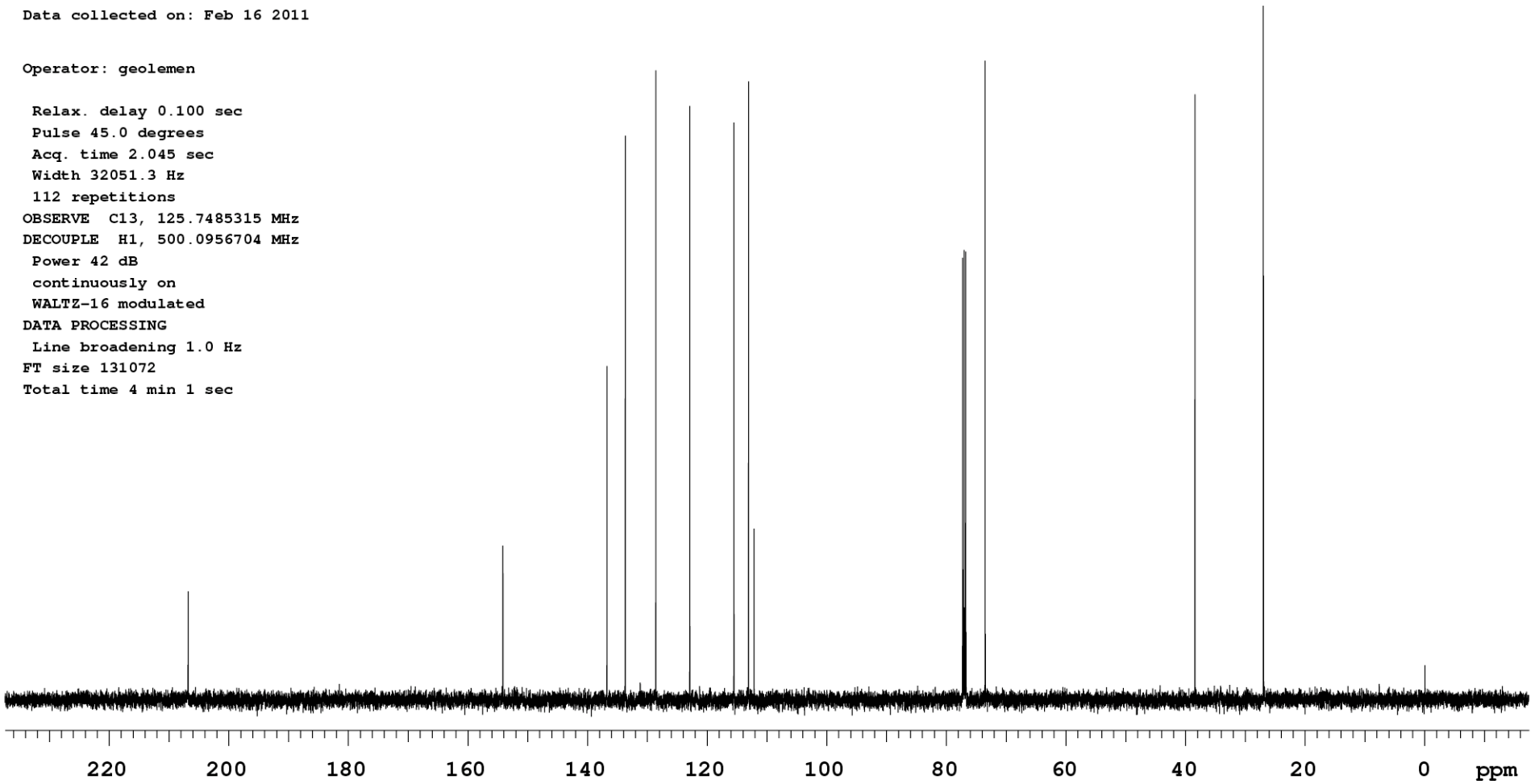
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
112 repetitions
OBSERVE C13, 125.7485315 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 min 1 sec

VARIAN



S12



gsl-VIII-113-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

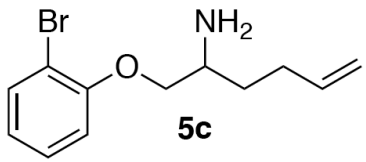
FidFile: gsl-VIII-113-2

Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Feb 22 2011

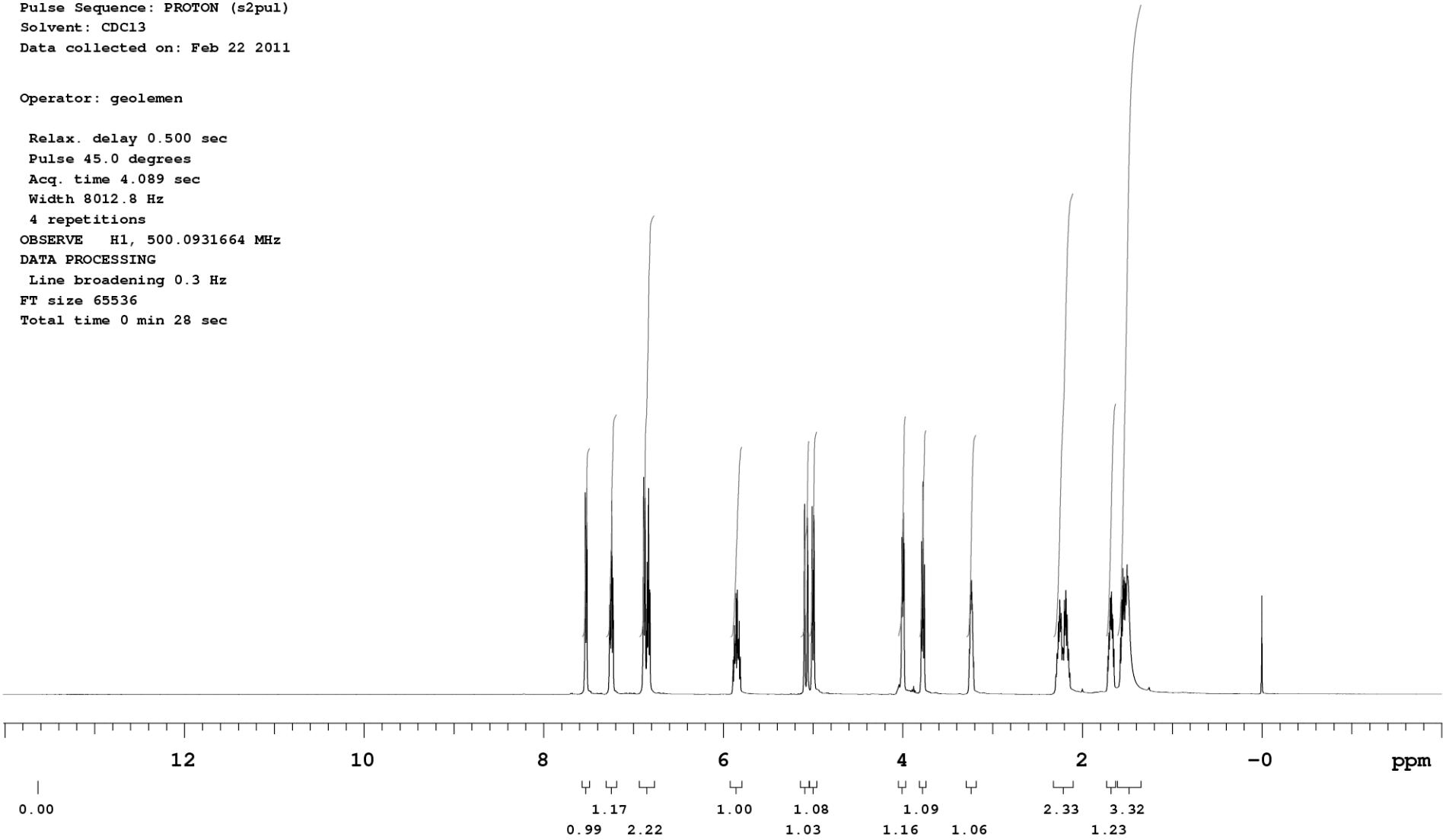
Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
4 repetitions
OBSERVE H1, 500.0931664 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 28 sec

VARIAN



5c



gsl-VIII-113-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

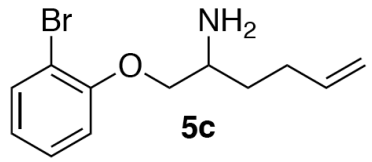
FidFile: gsl-VIII-113-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Feb 22 2011

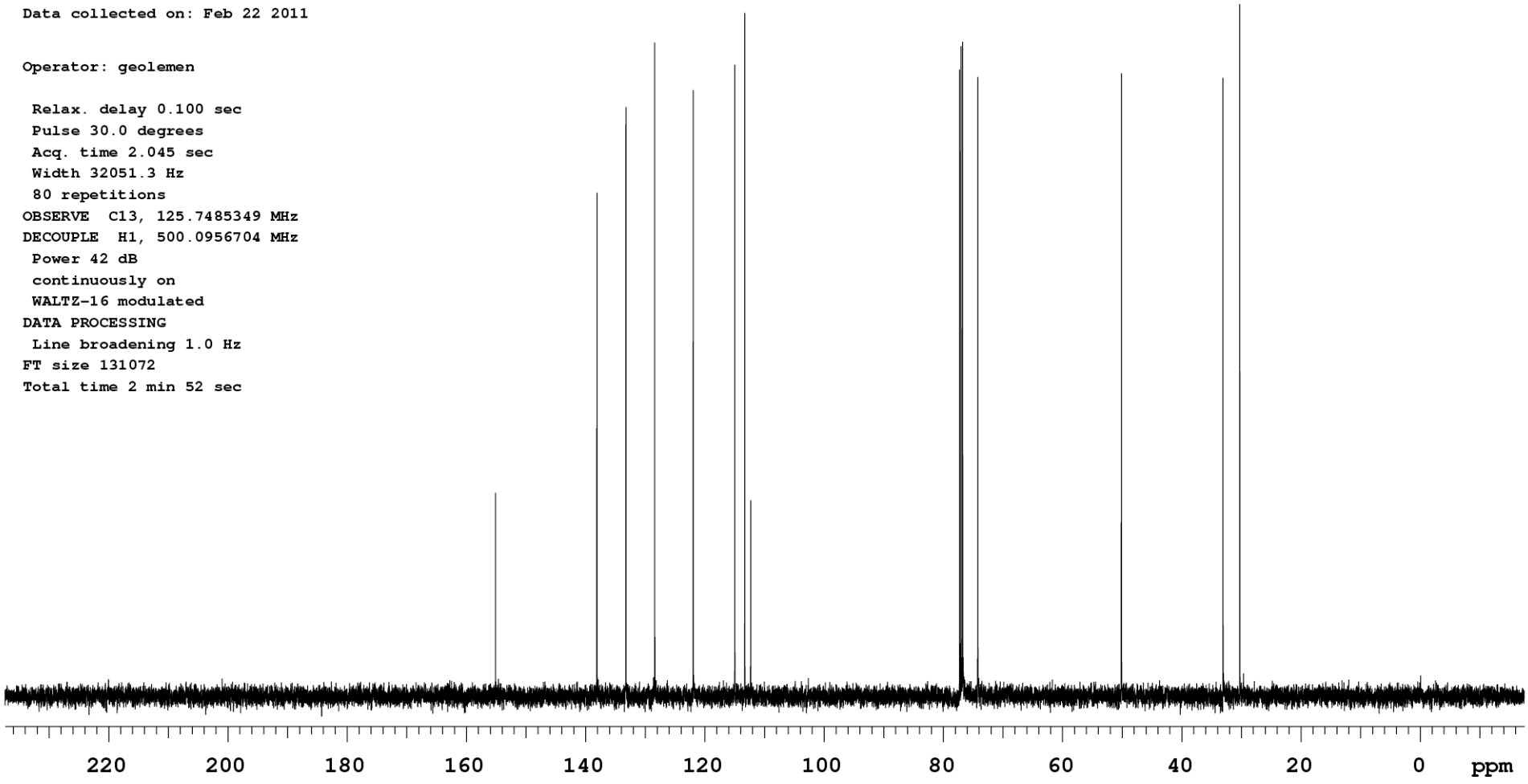
Operator: geolemen

Relax. delay 0.100 sec
Pulse 30.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
80 repetitions
OBSERVE C13, 125.7485349 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 2 min 52 sec

VARIAN



5c



gsl-VIII-87-2B

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

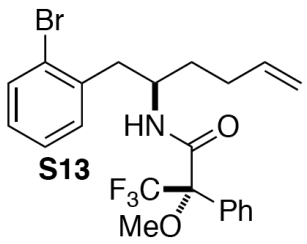
FidFile: gsl-VIII-87-2B

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 21 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
6 repetitions
OBSERVE H1, 400.5206324 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 26 sec

VARIAN



S13

gsl-VIII-87-2A racemic

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

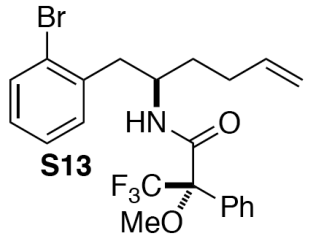
FidFile: gsl-VIII-87-2Bfluorine

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Dec 21 2010

Temp. 25.0 C / 298.1 K
Operator: geolemen

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659204 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 31 sec

VARIAN



S13

gsl-VII-198-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

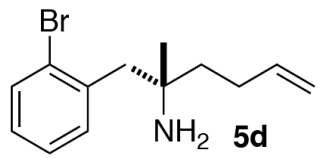
FidFile: gsl-VII-198-2

Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Jan 27 2011

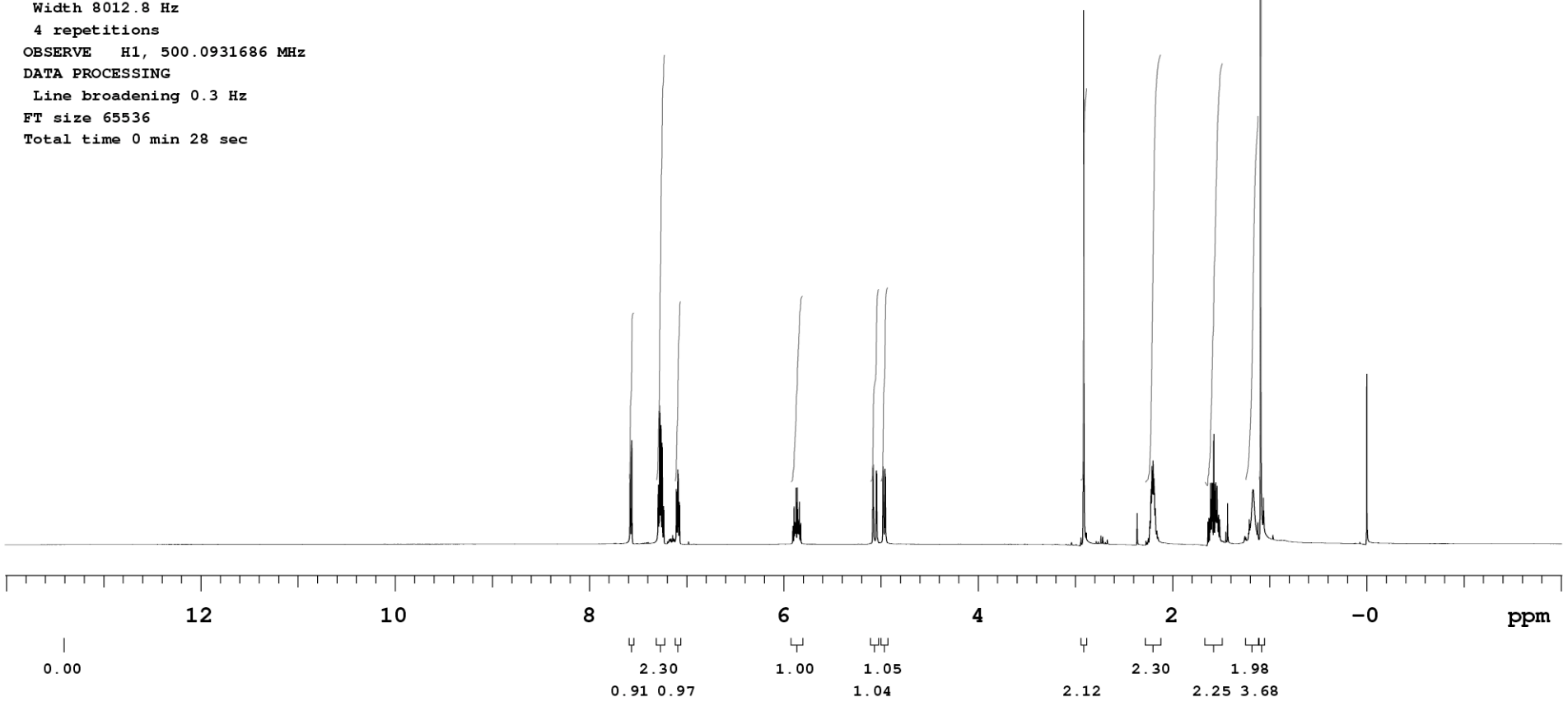
Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
4 repetitions
OBSERVE H1, 500.0931686 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 28 sec

VARIAN



5d



gsl-VII-198-2 carbon

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

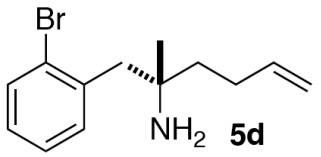
FidFile: gsl-VII-198-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Jan 27 2011

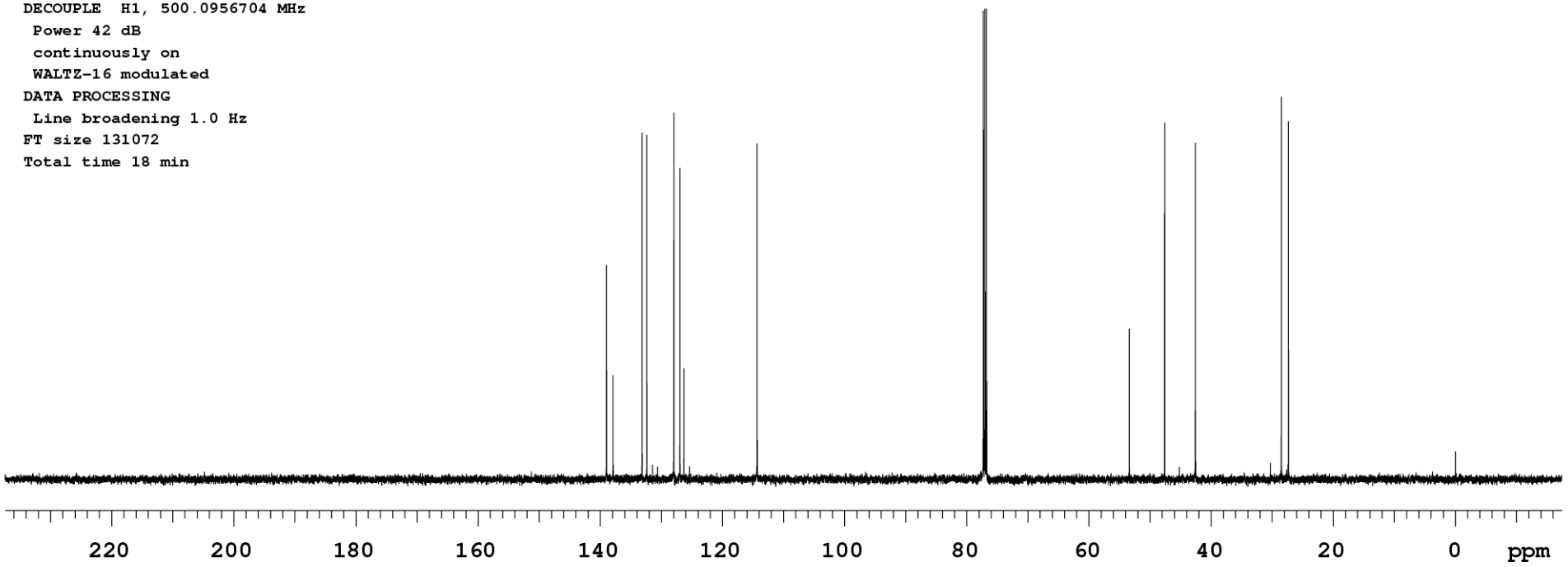
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
504 repetitions
OBSERVE C13, 125.7485295 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 18 min

VARIAN



5d



gsl-VIII-115B-2frac8-20

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

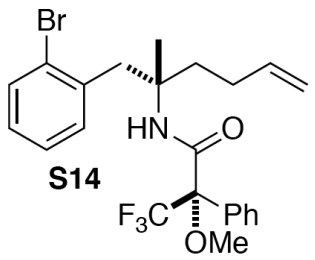
Sample directory:

FidFile: gsl-VIII-115B-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
2 repetitions
OBSERVE H1, 400.5206323 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 0 min 43 sec



S14

VARIAN

gsl-VIII-115A-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

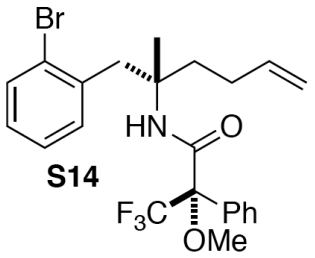
FidFile: gsl-VIII-115B-2fluorine

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2011

Operator: geolemen

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
32 repetitions
OBSERVE F19, 376.8659278 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 59 sec

VARIAN



S14

gsl-VIII-136-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

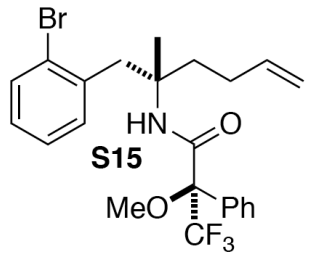
FidFile: gsl-VIII-136-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 4 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.5206322 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 47 sec

VARIAN



S15

gs1-VIII-136-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

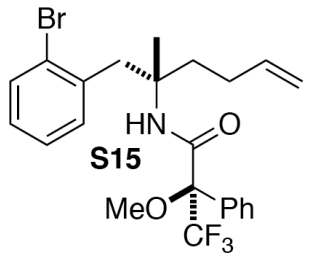
FidFile: gs-VIII-136-2fluorine

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Mar 4 2011

Operator: geolemen

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
32 repetitions
OBSERVE F19, 376.8659248 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 59 sec

VARIAN



S15

gsl-VII-196-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

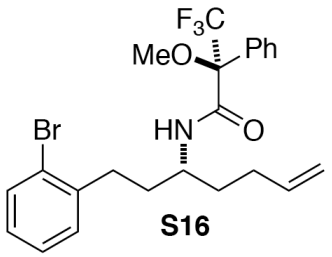
FidFile: gsl-VII-196-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 1 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
4 repetitions
OBSERVE H1, 400.5206327 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 4 sec

VARIAN



S16

gsl-VII-196-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

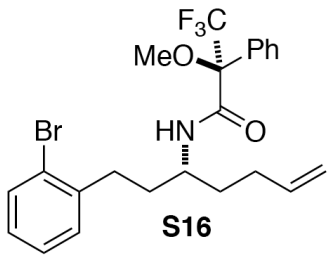
FidFile: gsl-VII-196-2fluorine

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Dec 1 2010

Temp. 25.0 C / 298.1 K
Operator: geolemen

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659384 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 31 sec

VARIAN



S16

gsl-VIII-88-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

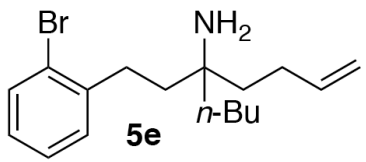
Sample directory:

FidFile: gsl-VIII-88-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 21 2010

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 10.224 sec
Width 6410.3 Hz
6 repetitions
OBSERVE H1, 400.5206283 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 26 sec



5e

VARIAN

gsl-VIII-88-2 carbon

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

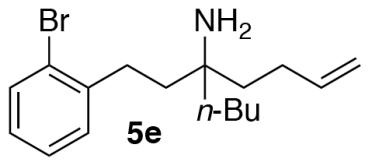
FidFile: gsl-VIII-88-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 21 2010

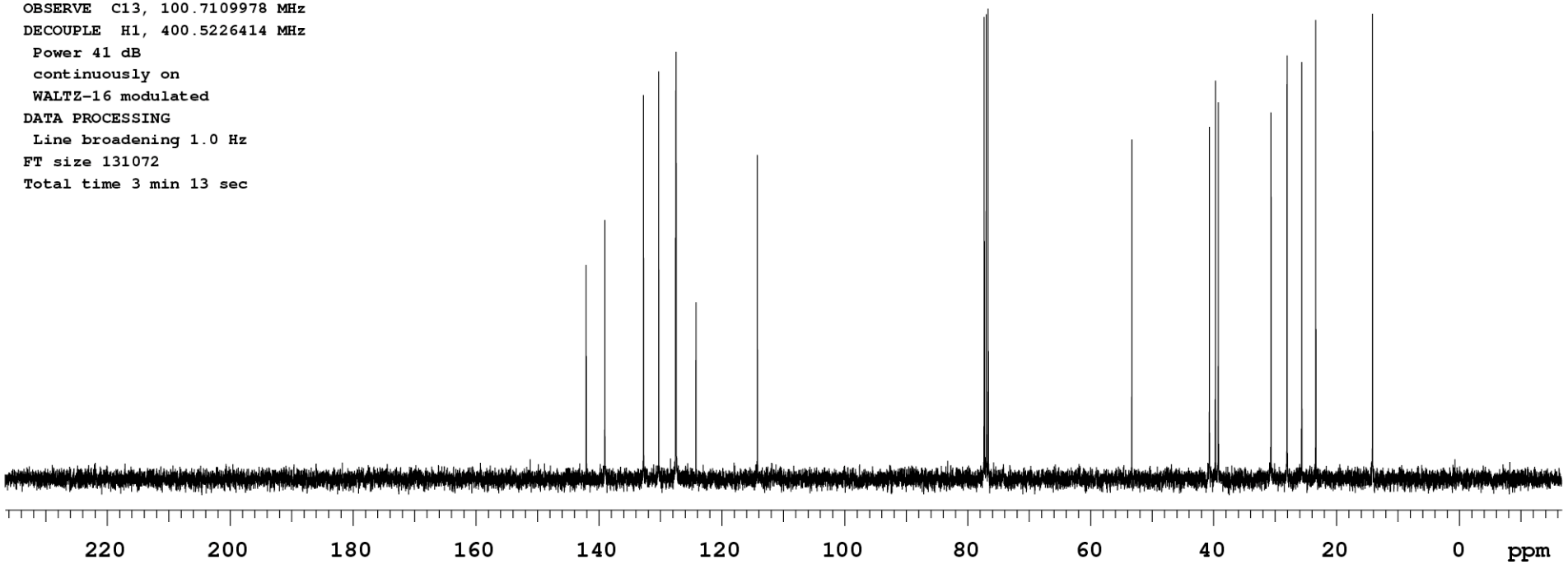
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
72 repetitions
OBSERVE C13, 100.7109978 MHz
DECOUPLE H1, 400.5226414 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min 13 sec

VARIAN



5e



gsl-III-198-2

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

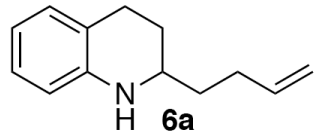
Sample directory:

FidFile: gsl-III-198-2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 25 2011

Operator: geolemen

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.089 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931823 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 23 sec



6a

gsl-VIII-164-2

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

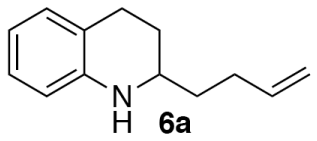
Sample directory:

FidFile: gsl-III-198-2carbon

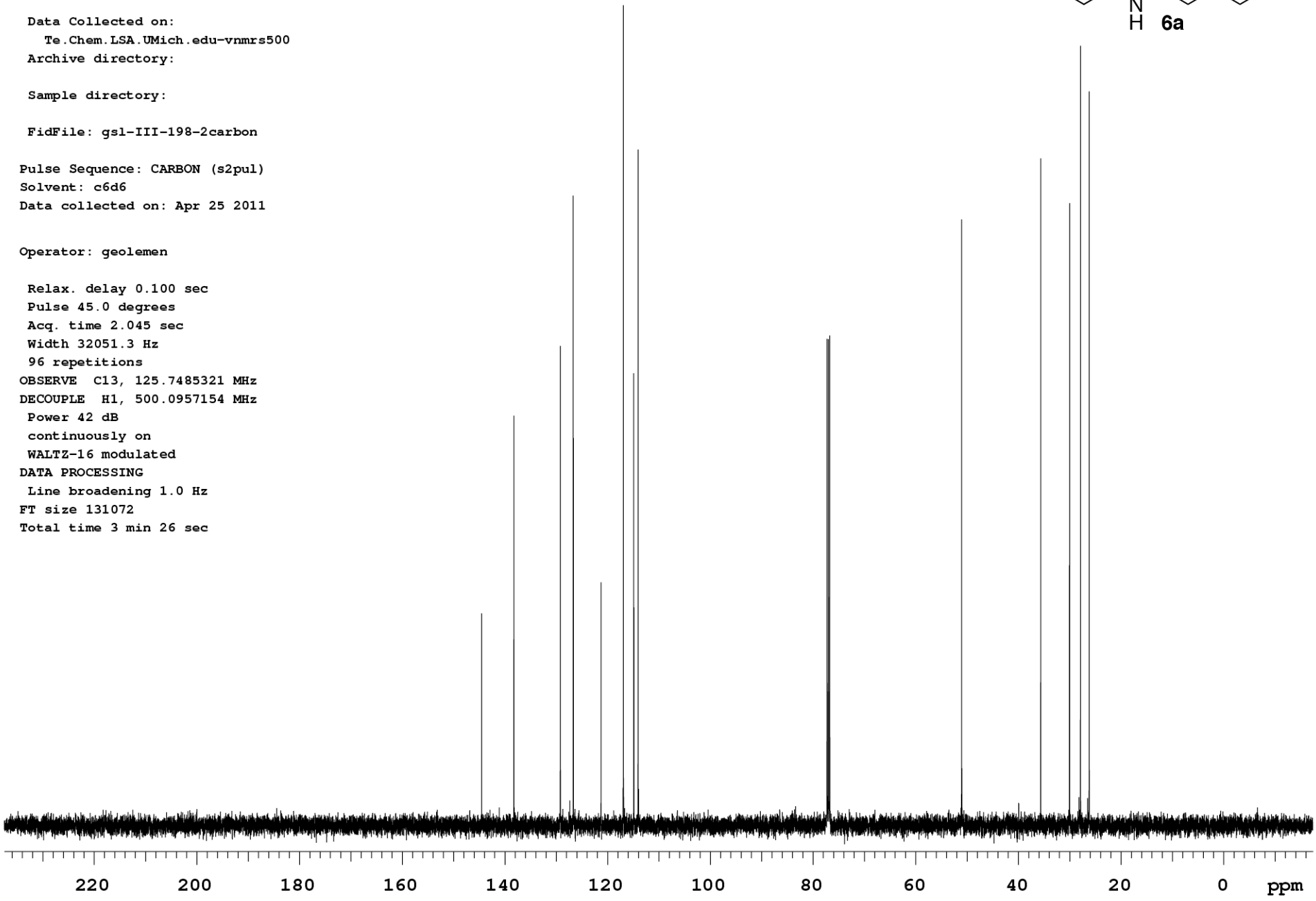
Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Apr 25 2011

Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 32051.3 Hz
96 repetitions
OBSERVE C13, 125.7485321 MHz
DECOUPLE H1, 500.0957154 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min 26 sec



6a



gsl-III-198-2

Sample Name:

Data Collected on:
Te.Chem.LSA.UMich.edu-vnmrs500
Archive directory:

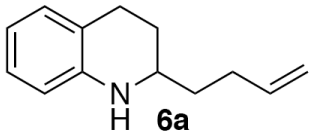
Sample directory:

FidFile: gsl-III-198-2cosy

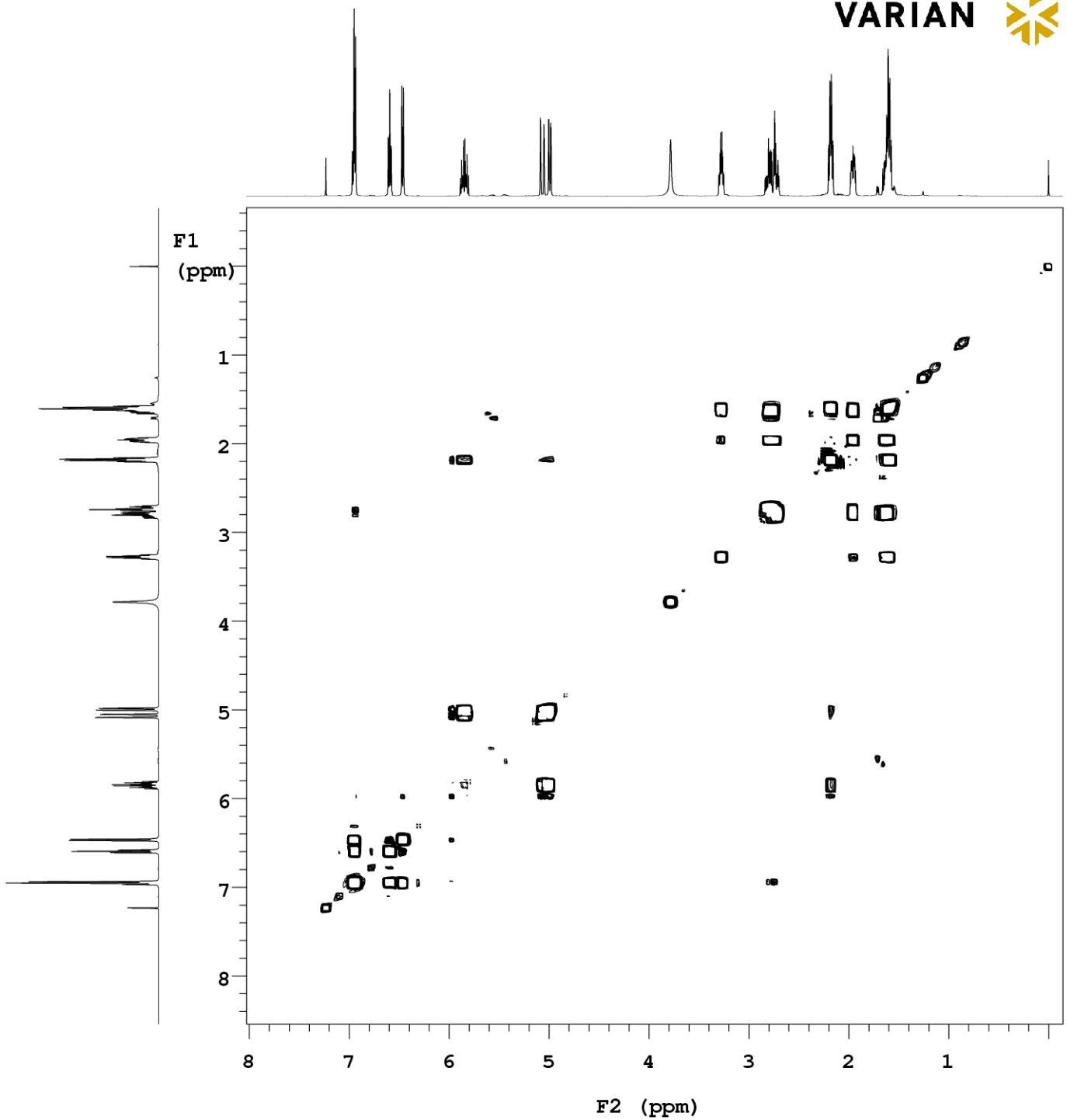
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Apr 25 2011

Operator: geolemen

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 8012.8 Hz
2D Width 8012.8 Hz
Single scan
128 increments
OBSERVE H1, 500.0931823 MHz
DATA PROCESSING
Sq. sine bell 0.064 sec
F1 DATA PROCESSING
Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 3 min 11 sec



6a



STANDARD PROTON PARAMETERS
Atropine

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

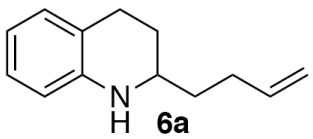
Sample directory:

FidFile: gsl-VIII-174-2frac11-24

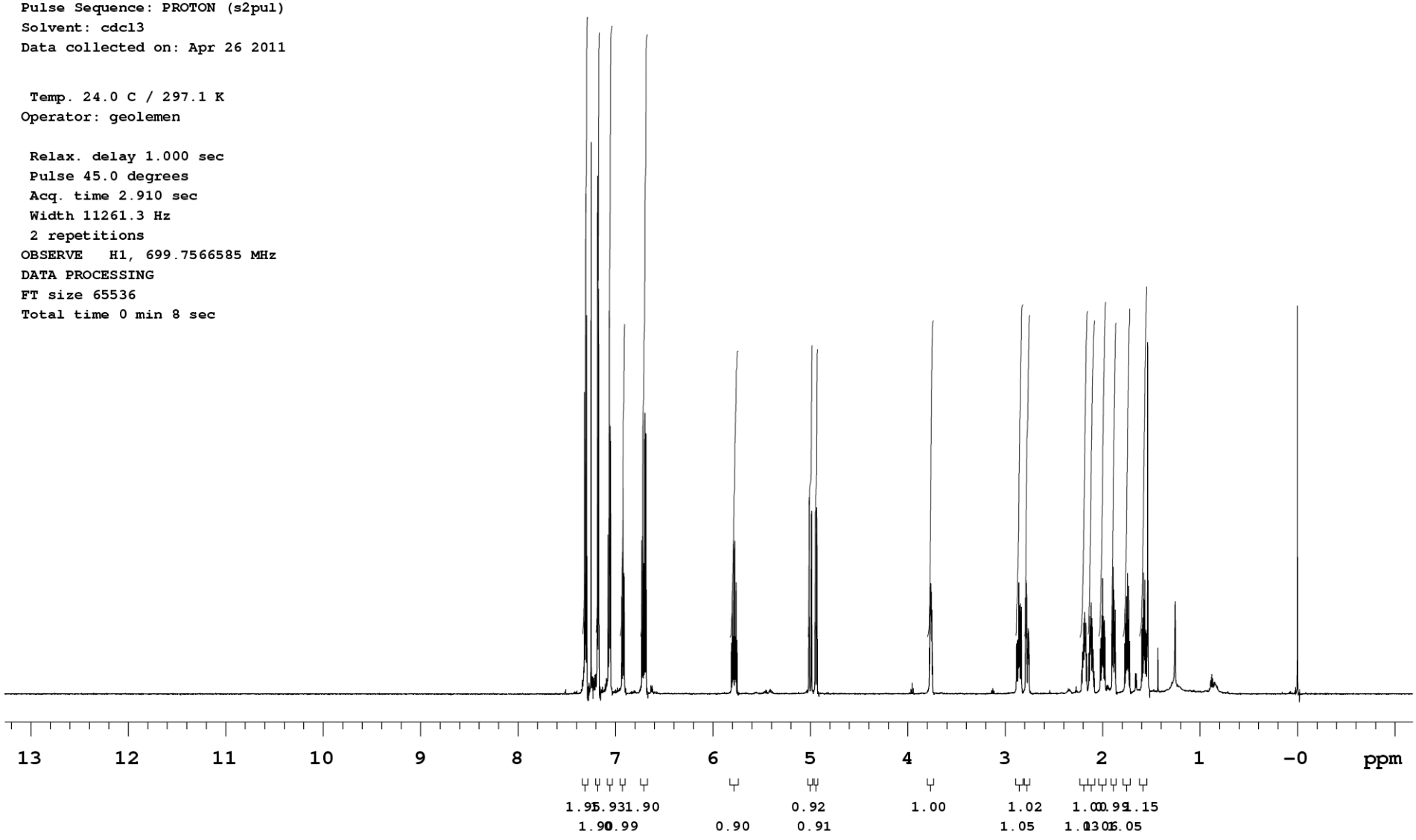
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 26 2011

Temp. 24.0 C / 297.1 K
Operator: geolemen

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.910 sec
Width 11261.3 Hz
2 repetitions
OBSERVE H1, 699.7566585 MHz
DATA PROCESSING
FT size 65536
Total time 0 min 8 sec



6a



Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

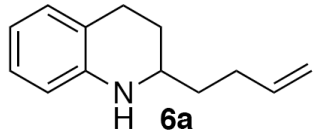
Sample directory:

FidFile: gsl-VIII-174-2carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 26 2011

Temp. 24.0 C / 297.1 K
Operator: geolemen

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
96 repetitions
OBSERVE C13, 175.9539809 MHz
DECOUPLE H1, 699.7602734 MHz
Power 47 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 2 min 31 sec



6a

STANDARD PROTON PARAMETERS
Atropine

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

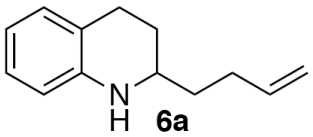
Sample directory:

FidFile: gsl-VIII-174-2cosy

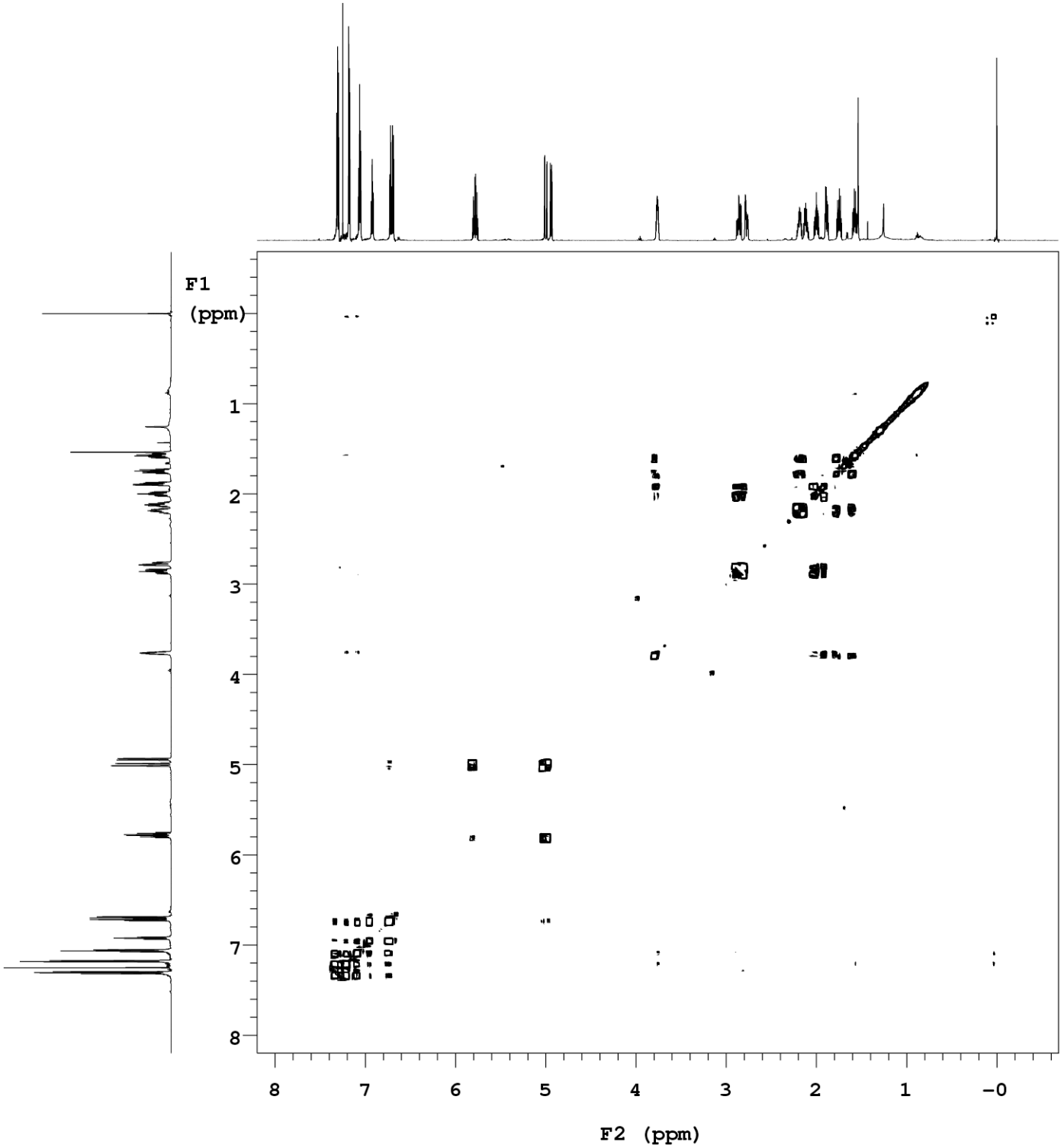
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Apr 26 2011

Temp. 24.0 C / 297.1 K
Operator: geolemen

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6218.9 Hz
2D Width 6218.9 Hz
Single scan
128 increments
OBSERVE H1, 699.7566536 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
FT size 2048 x 2048
Total time 3 min 10 sec



6a



STANDARD PROTON PARAMETERS
Atropine

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

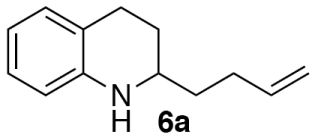
Sample directory:

FidFile: gsl-VIII-174-2hsqc

Pulse Sequence: gHSQC
Solvent: cdcl3
Data collected on: Apr 26 2011

Temp. 24.0 C / 297.1 K
Operator: geolemen

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6218.9 Hz
2D Width 36951.5 Hz
2 repetitions
2 x 64 increments
OBSERVE H1, 699.7566536 MHz
DECOUPLE C13, 175.9706957 MHz
Power 38 dB
on during acquisition
off during delay
W40_autoxbb modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.004 sec
FT size 2048 x 2048
Total time 10 min



6a