Supporting Information

Palladium-Catalyzed Carbocyclizations of Unactivated Alkyl Bromides with Alkenes Involving Auto-Tandem Catalysis

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General Experimental Details

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were obtained using a Bruker model AVANCE III 600 (^{1}H NMR at 600 MHz and ^{13}C NMR at 100 MHz) spectrometer with solvent resonance as internal reference (^{1}H NMR: $CDCl_3$ at 7.28 ppm, ^{13}C NMR: $CDCl_3$ at 77.00 ppm). ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using either a Thermo LTqFT mass spectrometer with electrospray introduction and external calibration or a Thermo GC Exactive GC/MS in chemical ionization mode with methane as the mobile phase.

Flash chromatography was performed using SiliaFlash P60 silica gel (40-63μm) purchased from Silicycle. Visualization was achieved using a short wave UV light (254 nm) and aqueous basic potassium permanganate solution. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM), toluene ($PhCH_3$), acetonitrile (MeCN), and dimethylformamide (DMF) were dried by passage through a column of neutral alumina under nitrogen prior to use. Acetone, 1,4-dioxane, and α,α,α-trifluorotoluene were dried over 3Å molecular sieves and degassed with

argon prior to use. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted.

Substrate Preparation

General Procedure A: Reduction of Esters and Carboxylic Acids.

To a 0°C solution of ester or carboxylic acid (1 equiv.) in THF (0.5 M) was added $LiAlH_4$ (1 equiv.). The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was cooled to 0°C and diluted with Et_2O. This mixture was quenched successively with H_2O (1 mL/g $LiAlH_4$), 15% aqueous NaOH (2 mL/g $LiAlH_4$), and H_2O (3 mL/g $LiAlH_4$). The quenched reaction mixture was allowed to warm to ambient temperature and was stirred for 30 minutes. $MgSO_4$ was added and the reaction was stirred for 30 more minutes. Aluminum and magnesium solids were removed by filtration and the crude product was concentrated under reduced pressure. The crude product was purified by flash chromatography or distillation.

General Procedure B: Bromoetherification of Enol Ethers.

To a 0°C solution of alcohol (1 equiv.) and enol ether (1.2 equiv.) in CH_2Cl_2 (1.0 M) was added *N*-bromosuccinimide (1 equiv). The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

General Procedure C: Bromoetherification of Methoxystyrene.

To a -78°C solution of styrene (1 equiv.) and alcohol (2 equiv.) in CH_2Cl_2 (0.25 M) was added *N*-bromosuccinimide (1.5 equiv). The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was quenched with saturated $Na_2S_2O_4$ and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

General Procedure D: Bromination of Allylic and Homoallylic Alcohols.

To a 0°C solution of alcohol (1 equiv.) in CH_2Cl_2 (1.0 M) was added phosphorus tribromide (0.5 equiv.) dropwise. The reaction mixture was stirred at room temperature for 1 hour, and was then quenched with H_2O. The aqueous layer was back extracted with CH_2Cl_2 (3x) and the combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography or distillation.

General Procedure E: Alkylation of Alkyl Sulfonamides.

To a solution of sulfonamide (1 equiv.) in acetone (0.5 M) was added allylic or homoallylic bromide (1.5 equiv.), K_2CO_3 (1.5 equiv.), and KI (0.1 equiv.). The reaction mixture was heated to reflux and stirred for 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

General Procedure F: Bromination of Primary and Secondary Alcohols.

To a 0°C solution of triphenylphosphine (3 equiv.) in THF (0.25 M) was added CBr_4 (3 equiv.). This solution was stirred at 0°C for 5 minutes until the solution turned bright yellow. Alcohol (1 equiv.) was then added dropwise, and the reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

General Procedure G: Alkylation of Allylic and Homoallylic Sulfonamides.

To a solution of allylic or homoallylic sulfonamide (1 equiv.) in MeCN (0.5 M) was added alkyl bromide (10 equiv.), and Cs_2CO_3 (1.5 equiv.). The reaction mixture was heated to reflux and stirred for 72 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

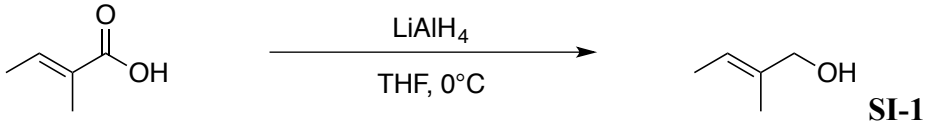
General Procedure H: Alkylation of α-Aryl Acetates.

To a 0°C solution of $^{i}Pr_2NH$ (1.1 equiv.) in THF (0.25 M) was added $^{n}BuLi$ (1.1 equiv.). This solution was stirred for 15 minutes and then cooled to -78°C. α-Aryl acetate (1 equiv.) was then added dropwise, and the reaction mixture was stirred for 30 minutes at -78°C. Alkyl bromide (1.2 equiv.) and HMPA (0.6 equiv.) were then added and the reaction was allowed to warm to room temperature and stirred for 16 hours. The reaction was quenched with saturated NH_4Cl and the aqueous layer was extracted with 1:1 hexanes : ethyl acetate (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

General Procedure I: Alternative Bromination Method for Primary Alcohols.

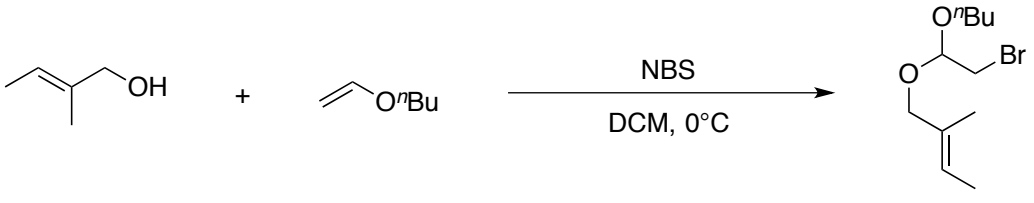
To a 0°C solution of triphenylphosphine (1.6 equiv.) and imidazole (1.5 equiv.) in DCM (0.5 M) was added Br_2 (1.5 equiv.). This solution was stirred at 0°C for 5 minutes until a color change had occurred. Alcohol (1 equiv.) was then added dropwise, and the reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with saturated $Na_2S_2O_3$, brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Experimental Data



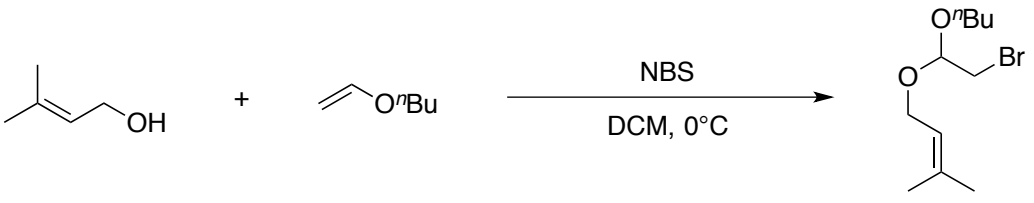
SI-1

(SI-1): *trans*-2-Methyl-2-buten-1-ol. *trans*-2-Methyl-2-butenoic acid (20 g, 200 mmol) was reduced by $LiAlH_4$ (7.6 g, 200 mmol) according to General Procedure A. The crude product was purified by distillation to provide alcohol **SI-1** as a clear oil (7.5 g, 46% Yield). All physical and spectroscopic data were in accordance with literature data.[1]



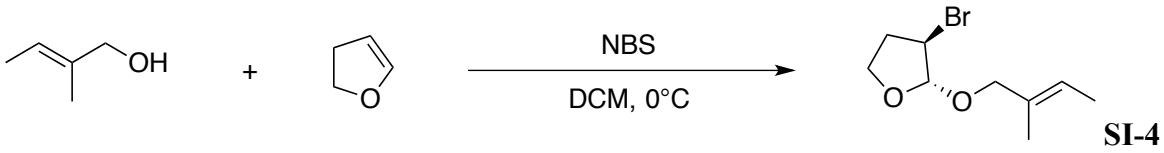
SI-2

(SI-2): 2-Bromoethanal butyl tiglic acetal. *n*-Butyl vinyl ether (2.8 g, 27.9 mmol) was bromoetherified by alcohol **SI-1** (2.0 g, 23.2 mmol) according to General Procedure B. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-2** as a clear oil (4.4 g, 72% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 5.54 (m, 1H), 4.68 (t, J = 5.4 Hz, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.95 (d, J = 11.4 Hz, 1H), 3.62 (m, 1H), 3.52 (m, 1H), 3.39 (m, 2H), 1.70 (s, 3H), 1.65 (m, 3H), 1.60 (m, 2H), 1.41 (m, 2H), 1.94 (t, J = 7.8 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 132.21, 123.57, 100.54, 73.07, 66.37, 31.78, 31.77, 19.29, 13.85, 13.76, 13.24. **HRMS** (ESI): Calculated for $[C_{11}H_{21}BrO_2H]^+$ 266.0837, found 266.1209.



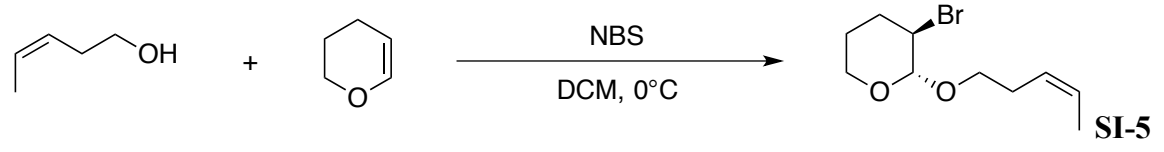
SI-3

(SI-3): 2-Bromoethanal butyl prenyl acetal. *n*-Butyl vinyl ether (2.3 g, 23.2 mmol) was bromoetherified by 3-methyl-2-buten-1-ol (2.4 g, 27.8 mmol) according to General Procedure B. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-3** as a clear oil (5.0 g, 81% Yield). All physical and spectroscopic data were in accordance with literature data.[2]



SI-4

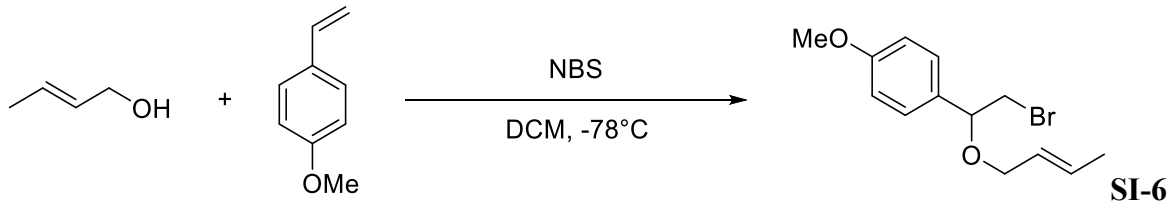
(SI-4): *trans*-3-Bromo-2-(((E)-2-methylbut-2-en-1-yl)oxy)tetrahydrofuran. Dihydrofuran (3.9 g, 55.7 mmol) was bromoetherified by alcohol **SI-1** (4.0 g, 46.5 mmol) according to General Procedure B. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-4** as a clear oil (4.3 g, 40% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 5.51 (m, 1H), 5.20 (s, 1H), 4.23 (dd, *J* = 6.0 Hz, 1.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 4.06 (td, *J* = 8.4 Hz, 3.6 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.85 (d, *J* = 10.8 Hz, 1H), 2.64 (m, 1H), 2.20 (m, 1H), 1.63 (s, 3H), 1.62 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 131.95, 123.26, 107.37, 73.15, 66.50, 50.09, 33.85, 33.85, 13.55, 13.14. **HRMS** (ESI): Calculated for $[C_9H_{15}BrO_2]$-Br 155.1072, found 155.1065.



SI-5

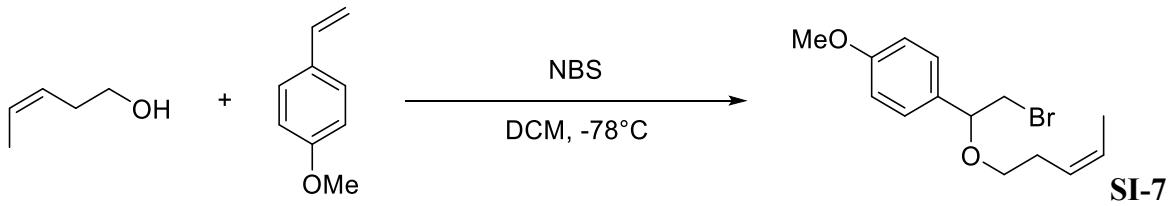
(SI-5): *trans*-3-Bromo-2-((Z)-3-pentene-1-yloxy)tetrahydropyran. Dihydropyran (3.5 g, 41.8 mmol) was bromoetherified by *cis*-3-penten-1-ol (3.0 g, 34.8 mmol) according to General Procedure B. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide bromide **SI-5** as a clear oil (6.9 g, 80% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 5.57 (m, 1H), 5.44 (m, 1H), 4.63 (d, *J* = 4.8 Hz, 1H), 3.99 (m, 1H), 3.94 (m, 1H), 3.78 (m, 1H), 3.59 (m, 1H), 3.51 (m, 1H), 2.39 (m, 3H), 1.94 (m, 2H), 1.65 (d, *J* = 7.2 Hz, 3H), 1.56

(m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 126.08, 126.06, 101.09, 67.90, 62.59, 49.51, 30.19, 27.37, 23.38, 12.90. **HRMS** (ESI): Calculated for $[C_{10}H_{18}BrO_2H]^+$ 249.0569, found 250.0899.



SI-6

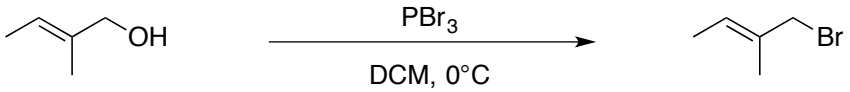
(SI-6): 1-(But-2-enyl)oxy-2-bromo-1-(4-methoxyphenyl)ethane. *para*-Methoxystyrene (2.0 g, 14.9 mmol) was bromoetherified by *trans*-2-buten-1-ol (2.2 g, 29.8 mmol) according to General Procedure C. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-6** as a clear oil (1.0 g, 25% Yield, 9:1 E:Z). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.28 (m, 2H), 6.93 (m, 2H), 5.69 (m, 1H), 5.62 (m, 1H), 4.52 (m, 1H), 3.93 (m, 1H), 3.84 (s, 3H), 3.80 (m, 1H), 3.57 (m, 1H), 3.46 (m, 1H), 1.73 (m, 2.7H), 1.59 (m, 0.3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 159.58, 131.35, 129.90, 128.06, 128.04, 127.11, 113.92, 78.00, 69.62, 55.21, 36.57, 17.77. **HRMS** (ESI): Calculated for $[C_{13}H_{17}BrO_2]$-HBr 204.1150, found 204.1141.



SI-7

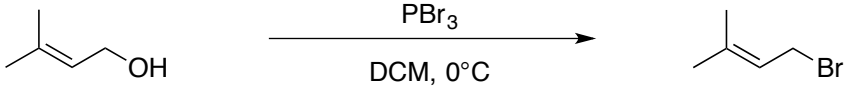
(SI-7): 1-(Pent-3-enyl)oxy-2-bromo-1-(4-methoxyphenyl)ethane. *para*-Methoxystyrene (1.6 mL, 12 mmol) was bromoetherified by *cis*-3-penten-1-ol (2.5 mL, 24 mmol) according to General Procedure C. The crude product was purified by flash chromatography using hexanes/ethyl acetate (30:1) to provide bromide **SI-7** as a clear oil (1.4 g, 39% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 5.57 (m, 1H), 5.22 (m, 1H), 4.65 (m, 1H), 2.98 (q, J = 6.6 Hz, 2H), 2.44 (s, 3H), 2.22 (q, J = 7.2 Hz, 2H), 1.57 (d, J = 6.6 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.34, 136.79, 129.65, 127.67, 127.06, 125.52,

42.60, 26.93, 21.48, 12.87. **HRMS** (ESI): Calculated for $[C_{14}H_{19}BrO_2]$-HBr 218.1307, found 218.1301.



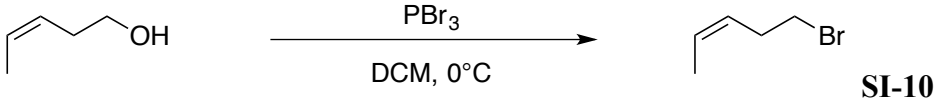
SI-8

(SI-8): *trans*-1-Bromo-2-methyl-2-butene. Alcohol **SI-1** (22 g, 256 mmol) was brominated with PBr_3 (34.6 g, 128 mmol) according to General Procedure D. The crude product was purified by distillation to provide bromide **SI-8** as a clear oil (26.3 g, 69% Yield). All physical and spectroscopic data were in accordance with literature data.[3]



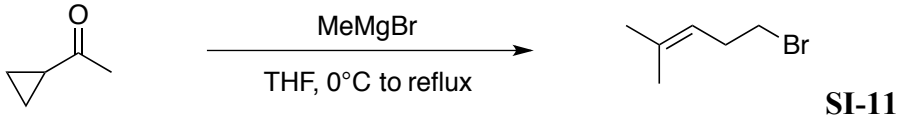
SI-9

(SI-9): 1-Bromo-3-methyl-2-butene. 3-methyl-2-buten-1-ol (21.5 g, 250 mmol) was brominated with PBr_3 (33.8 g, 125 mmol) according to General Procedure D. The crude product was purified by distillation to provide bromide **SI-9** as a clear oil (23.1 g, 62% Yield). All physical and spectroscopic data were in accordance with literature data.



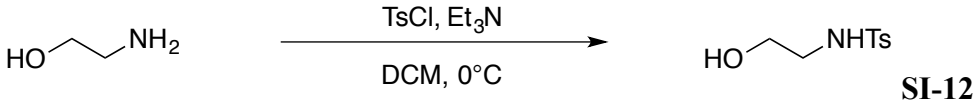
SI-10

(SI-10): *cis*-1-Bromo-3-pentene. *cis*-3-penten-1-ol (10.0 g, 116 mmol) was brominated with PBr_3 (15.7 g, 58.1 mmol) according to General Procedure D. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide bromide **SI-10** as a clear oil (10.1 g, 59% Yield). All physical and spectroscopic data were in accordance with literature data.[4]



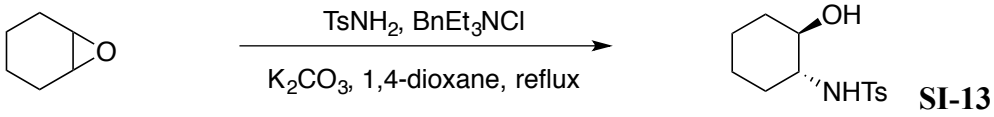
SI-11

(SI-11): 1-Bromo-4-methylpent-3-ene. To a 0°C solution of cyclopropyl methyl ketone (16.8 g, 200 mmol, 1 equiv.) in THF (2.0 M) was added MeMgBr (80 mL, 3.0 M in THF, 1.2 equiv.). The reaction mixture was heated to reflux stirred for 20 minutes. The reaction was cooled to 0°C and 2:1 H_2O:H_2SO_4 was added and stirred, warming to room temperature, for 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by distillation to provide bromide **SI-11** as a clear oil (10.4g, 33% Yield) All physical and spectroscopic data were in accordance with literature data.[5]



SI-12

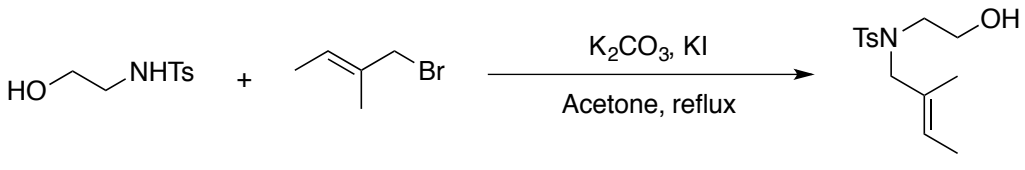
(SI-12): *N*-(2-Hydroxyethyl)-4-toluenesulfonamide. To a 0°C solution of ethanolamine (5.0 g, 82 mmol, 1 equiv.) and toluenesulfonyl chloride (17.2 g, 90.2 mmol, 1.1 equiv.) in CH_2Cl_2 (180 mL, 0.45 M) was added triethylamine (12.6 mL, 90.2 mmol, 1.1 equiv.). The reaction mixture was allowed to warm to ambient temperature and was stirred for 24 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product, sulfonamide **SI-12** (17.6 g, 99% Yield), was carried on without further purification. All physical and spectroscopic data were in accordance with literature data.[6]



SI-13

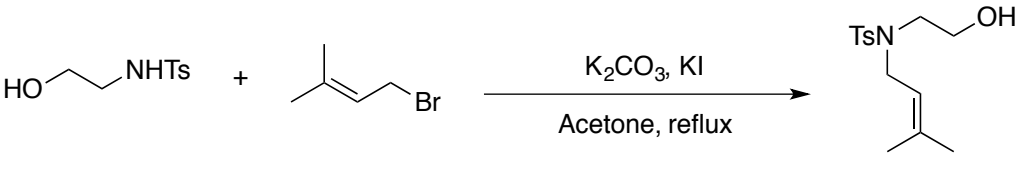
(SI-13): *N*-(2-Hydroxycyclohexyl)-4-toluenesulfonamide. To a 0°C solution of cyclohexene oxide (8.0 g, 81.5 mmol, 1 equiv.) in 1,4-dioxane (50 mL, 1.6 M) was added toluenesulfonamide (16.8 g, 97.9 mmol, 1.2 equiv.), K_2CO_3 (1.1 g, 8.2 mmol, 0.1 equiv.), and $BnEt_3NCl$ (1.9 g, 8.2 mmol, 0.1 equiv.). The reaction mixture was heated to reflux and stirred at 96 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with CH_2Cl_2 (3x). The

combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide sulfonamide **SI-13** as a clear oil (9.1 g, 42% Yield). All physical and spectroscopic data were in accordance with literature data.[7]



SI-14

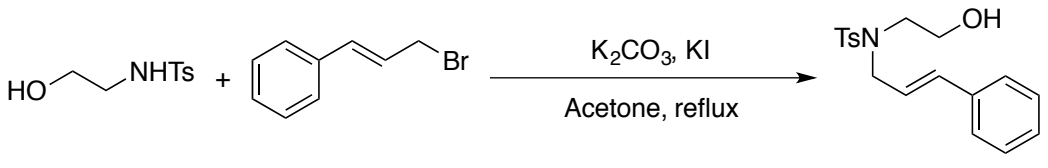
(SI-14): *N*-(2-Hydroxyethyl)-4-methyl-*N*-((E)-2-methylbut-2-en-1-yl)benzene sulfonamide. Sulfonamide **SI-12** (20 g, 92.9 mmol) was alkylated with bromide **SI-8** (20.8 g, 139 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-14** as a white solid (19.2 g, 73% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.39 (m, 1H), 3.67 (s, 2H), 3.64 (t, *J* = 5.4 Hz, 2H), 3.15 (t, *J* = 5.4 Hz, 2H), 2.44 (s, 3H), 1.63 (s, 3H), 1.61 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.46, 135.76, 131.11, 129.69, 127.22, 124.52, 61.16, 58.17, 50.02, 21.48, 13.67, 13.43. **HRMS** (ESI): Calculated for $[C_{14}H_{21}NO_3SNa]^+$ 306.1140, found 306.1136.



SI-15

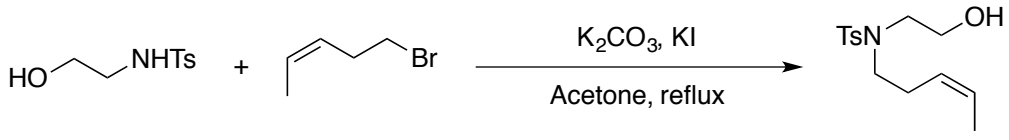
(SI-15): *N*-(2-Hydroxyethyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide. Sulfonamide **SI-12** (15 g, 70 mmol) was alkylated with bromide **SI-9** (15.6 g, 105 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-15** as a white solid (12.3 g, 62% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz), 5.03 (m, 1H), 3.84 (d, *J* = 7.2 Hz, 2H), 3.73 (m, 2H), 3.21 (t, *J* = 4.8 Hz, 2H), 2.44 (s, 3H), 2.41 (m, 1H), 1.68 (s, 3H), 1.63 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.39, 137.55, 136.22, 129.65, 127.24,

118.71, 61.17, 49.63, 46.92, 25.74, 21.48, 17.77. **HRMS** (ESI): Calculated for $[C_{14}H_{21}NO_3SH]^+$ 284.1321, found 284.1314.



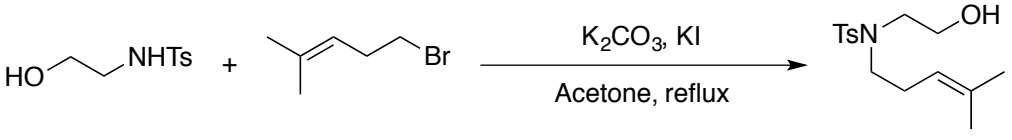
SI-16

(SI-16): *N*-Cinnamyl-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide. Sulfonamide **SI-12** (6.0 g, 27.9 mmol) was alkylated with cinnamyl bromide (8.2 g, 41.8 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-16** as a thick brown sludge (5.8 g, 63% Yield). All physical and spectroscopic data were in accordance with literature data.[8]



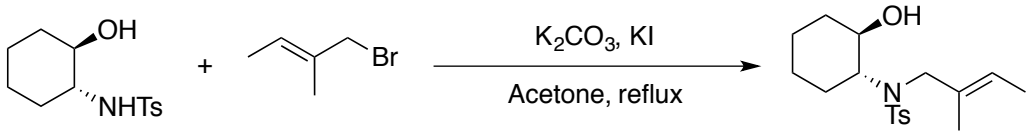
SI-17

(SI-17): *N*-(2-Hydroxyethyl)-4-methyl-*N*-((Z)-pent-3-en-1-yl)benzenesulfonamide. Sulfonamide **SI-12** (1.7 g, 8.0 mmol) was alkylated with bromide **SI-10** (2.0 g, 13 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-17** as a white solid (1.2 g, 53% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.56 (m, 1H), 5.32 (m, 1H), 3.77 (t, *J* = 5.4 Hz, 2H), 3.25 (m, 2H), 3.17 (m, 2H), 2.57 (bs, 1H), 2.43 (s, 3H), 2.32 (q, *J* = 7.8 Hz, 2H), 1.60 (dd, *J* = 7.2 Hz, 1.2 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.47, 135.85, 129.70, 127.17, 126.88, 125.73, 61.24, 50.98, 49.37, 37.61, 26.59, 21.44, 12.87. **HRMS** (ESI): Calculated for $[C_{14}H_{21}NO_3SH]^+$ 284.1321, found 284.1316.



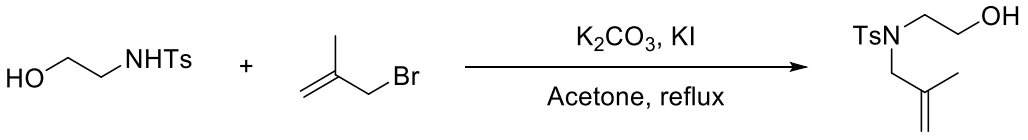
SI-18

(SI-18): *N*-(2-Hydroxyethyl)-4-methyl-*N*-(4-methylpent-3-en-1-yl)benzenesulfonamide. Sulfonamide **SI-12** (5.4 g, 25 mmol) was alkylated with bromide **SI-11** (6.0 g, 37 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-18** as a white solid (5.1 g, 68% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.04 (m, 1H), 3.77 (m, 2H), 3.26 (t, *J* = 5.4 Hz, 2H), 3.15 (m, 2H), 2.44 (s, 3H), 2.26 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.44, 135.94, 134.78, 129.71, 127.22, 119.80, 61.30, 50.97, 49.64, 27.75, 25.65, 21.47, 17.80. **HRMS** (ESI): Calculated for $[C_{15}H_{22}NO_3SNa]^+$ 320.1297, found 320.1289.



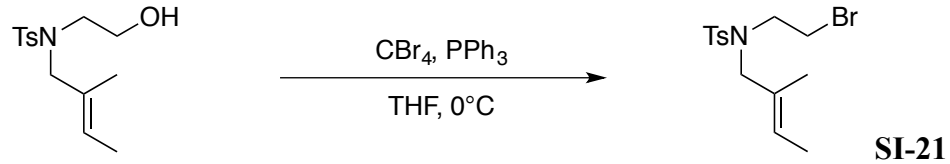
SI-19

(SI-19): *N*-(2-Hydroxycyclohexyl)-4-methyl-*N*-((E)-2-methylbut-2-en-1-yl)benzene sulfonamide. Sulfonamide **SI-13** (6.0 g, 22.4 mmol) was alkylated with bromide **SI-8** (5.0 g, 33.6 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate/methylene chloride (4:2:1) to provide alcohol **SI-19** as a pale yellow oil (4.8 g, 64% Yield). All physical and spectroscopic data were in accordance with literature data.[9]



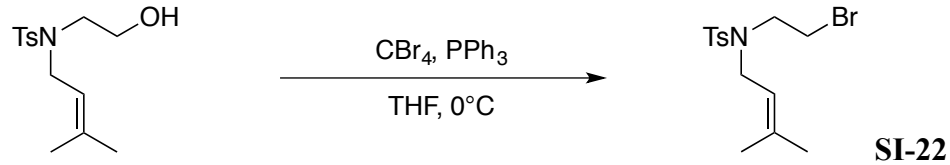
SI-20

(SI-20): N-(2-hydroxyethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide. Sulfonamide **SI-12** (2.0 g, 9.3 mmol) was alkylated with 3-bromo-2methylpropene (1.4 mL, 14 mmol) according to General Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (2:1) to provide alcohol **SI-20** as a white solid (1.4 g, 56% Yield). All physical and spectroscopic data were in accordance with literature data.[10]



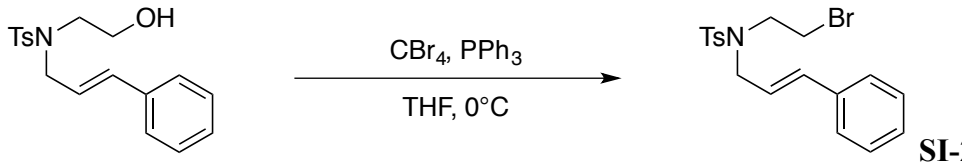
SI-21

(SI-21): (E)-*N*-(2-Bromoethyl)-4-methyl-*N*-((E)-2-methylbut-2-en-1-yl)benzenesulfonamide. Alcohol **SI-14** (7.5 g, 26.5 mmol) was brominated with CBr_4 (26.3 g, 79.4 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide bromide **SI-21** as a white solid (6.4 g, 70% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



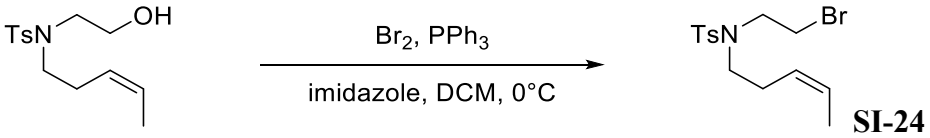
SI-22

(SI-22): *N*-(2-Bromoethyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide. Alcohol **SI-15** (2.5 g, 8.8 mmol) was brominated with CBr_4 (8.8 g, 26.5 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide bromide **SI-22** as a white solid (2.1 g, 69% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.33, (d, J = 7.8 Hz, 2H), 5.03 (m, 1H), 3.82 (d, J = 6.6 Hz, 2H), 3.46 (m, 2H), 3.39 (m, 2H), 2.45 (s, 3H), 1.71 (s, 3H), 1.65 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.49, 138.07, 136.37, 129.73, 127.16, 118.59, 48.81, 46.67, 29.61, 25.80, 21.52, 17.78. **HRMS** (ESI): Calculated for $[C_{14}H_{20}BrNO_2SH]^+$ 346.0477, found 346.0470.



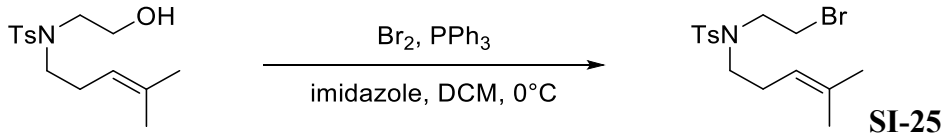
SI-23

(SI-23): *N*-Cinnamyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide. Alcohol **SI-16** (3.0 g, 9.1 mmol) was brominated with CBr_4 (9.0 g, 27.2 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide bromide **SI-23** as a white solid (2.6 g, 72% Yield). All physical and spectroscopic data were in accordance with literature data.[12]



SI-24

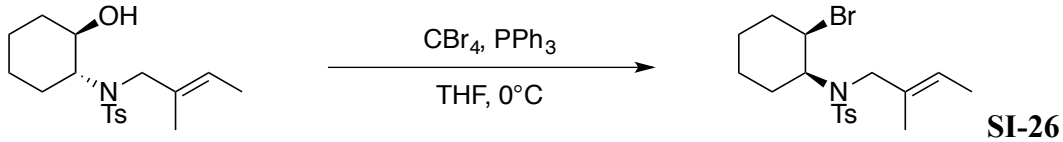
(SI-24): *N*-(2-Bromoethyl)-4-methyl-*N*-((Z)-pent-3-en-1-yl)benzenesulfonamide. Alcohol **SI-17** (0.9 g, 3.0 mmol) was brominated with Br_2 (0.23 mL, 4.5 mmol) according to General Procedure I. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide bromide **SI-24** as a white solid (0.53 g, 50% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.58 (m, 1H), 5.31 (m, 1H), 3.49 (m, 4H), 3.18 (m, 2H), 2.46 (s, 3H), 2.33 (q, *J* = 7.2 Hz, 2H), 1.63 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.62, 136.17, 129.82, 129.79, 127.14, 127.04, 125.49, 50.15, 49.15, 29.45, 26.83, 21.53, 12.96. **HRMS** (ESI): Calculated for $[C_{14}H_{21}BrNO_2S]^+$ 346.0477, found 346.0470.



SI-25

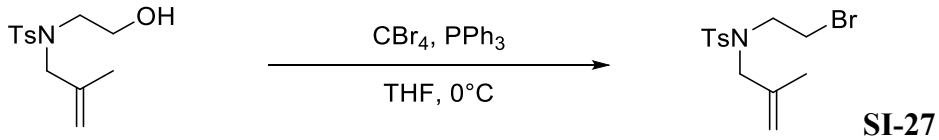
(SI-25): *N*-(2-Bromoethyl)-4-methyl-*N*-(4-methylpent-3-en-1-yl)benzenesulfonamide. Alcohol **SI-18** (1.5 g, 5 mmol) was brominated with Br_2 (0.38 mL, 7.5 mmol) according to General Procedure I. The crude product was purified by flash chromatography using hexanes/ethyl acetate (6:1) to provide bromide **SI-25** as a white solid (1.1 g, 61% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.01 (m, 1H), 3.48 (m, 2H), 3.48 (m, 2H), 3.14 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.25 (q, *J* = 7.8 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.54, 136.22, 134.85, 129.78, 127.13,

119.59, 50.07, 49.33, 29.45, 27.95, 25.69, 21.52, 17.86. **HRMS** (ESI): Calculated for $[C_{15}H_{22}BrNO_2SH]^+$ 360.0633, found 360.0630.



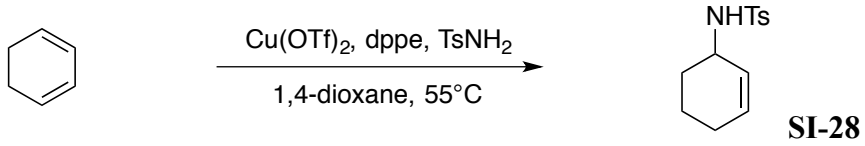
SI-26

(SI-26): ***N*-(2-Bromocyclohexyl)-4-methyl-*N*-(2-methylbut-2-en-1-yl)benzenesulfonamide.** Alcohol **SI-19** (2.5 g, 7.4 mmol) was brominated with CBr_4 (7.4 g, 22.2 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate/methylene chloride (8:4:1) to provide bromide **SI-26** as a thick orange oil (2.4 g, 82% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.43 (m, 1H), 4.68 (m, 1H), 4.01 (m, 1H), 3.98 (m, 1H), 3.50 (q, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.06 (m, 1H), 1.95 (m, 2H), 1.86 (m, 2H), 1.72 (m, 2H), 1.61 (m, 1H), 1.58 (d, J = 15.6 Hz, 3H), 1.56 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.03, 138.50, 132.50, 129.41, 127.17, 121.65, 60.29, 59.89, 52.33, 35.02, 26.16, 25.84, 21.56, 19.84, 14.01, 13.30. **HRMS** (ESI): Calculated for $[C_{18}H_{26}BrNO_2SH]^+$ 400.0946, found 400.0938.



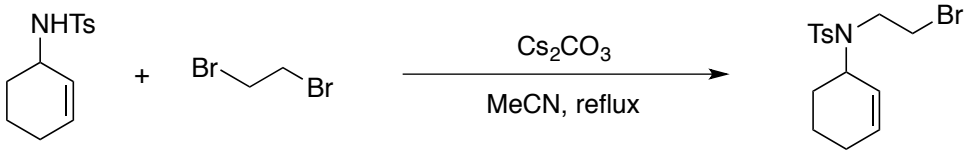
SI-27

(SI-27): N-(2-bromoethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide. Alcohol **SI-20** (1.0 g, 3.7 mmol) was brominated with CBr_4 (3.7 g, 11.1 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide bromide **SI-27** as a colorless oil (580 mg, 48% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.97 (s, 1H), 4.92 (s, 1H), 3.71 (s, 2H), 3.44 (m, 2H), 3.39 (m, 2H), 2.46 (s, 3H), 1.76 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.72, 140.48, 136.04, 129.86, 127.19, 115.45, 55.92, 49.55, 28.99, 21.59, 19.78.



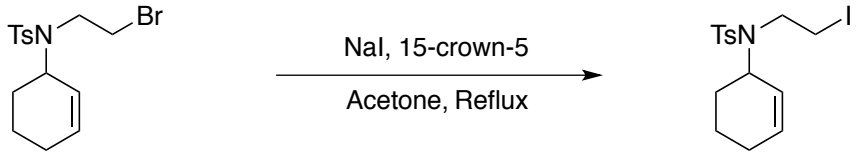
SI-28

(SI-28): *N*-Cyclohex-2-enyl-4-methyl-benzenesulfonamide. To a solution of $Cu(OTf)_2$ (1.1 g, 3.1 mmol, 5 mol %) in 1,4-dioxane (100 mL, 0.6 M) was added dppe (1.2 g, 3.1 mmol, 5 mol %). The reaction mixture was allowed to stir for 10 minutes at room temperature. Cyclohexadiene (5.0 g, 62 mmol) and toluenesulfonamide (16.1 g, 94 mmol) were then added, and the reaction mixture was heated to 55°C and stirred at 16 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (4:1) to provide sulfonamide **SI-28** as white solid (5.8 g, 37% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



SI-29

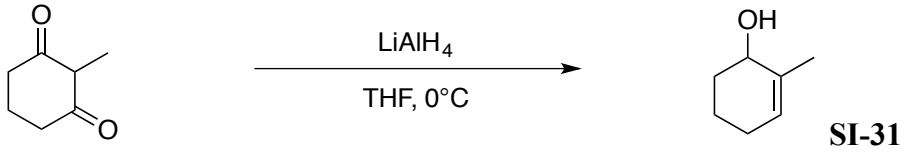
(SI-29): *N*-(2-Bromoethyl)-*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide. Sulfonamide **SI-28** (3.0 g, 11.9 mmol) was alkylated with 1,2-dibromoethane (22.6 g, 119 mmol) according to General Procedure G. The crude product was purified by flash chromatography using hexanes/ethyl acetate (6:1) to provide bromide **SI-29** as a white solid (1.5 g, 35% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



SI-30

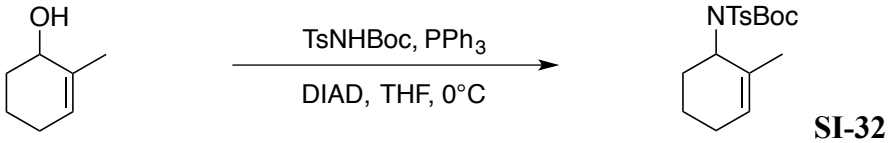
(SI-30): *N*-(2-Iodoethyl)-*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide. To a solution of bromide **SI-29** (5.0 g, 14.0 mmol, 1 equiv.) in actone (60 mL, 0.3 M) was added NaI (6.3 g,

41.9 mmol, 3 equiv.) and 15-crown-5 (310 mg, 1.4 mmol, 0.1 equiv.). The reaction mixture was heated to reflux and stirred at 42 hours. The reaction was quenched with H_2O and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with saturated $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide sulfonamide **SI-30** as white solid (4.2 g, 74% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



SI-31

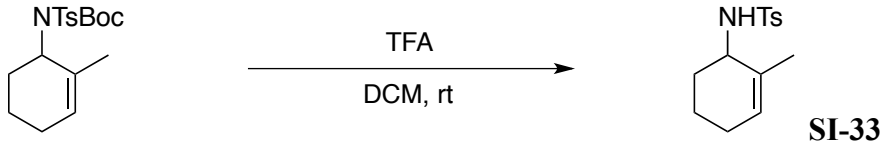
(SI-31): 2-Methylcyclohex-2-en-1-ol. To a 0°C solution of 2-methyl-1,3-cyclohexadione (15.1 g, 120 mmol, 1 equiv.) in Et_2O (0.5 M) was added $LiAlH_4$ (11.4 g, 300 mmol, 2.5 equiv.). The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 hours. The reaction was cooled to 0°C and diluted with Et_2O. This mixture was quenched successively with H_2O (12 mL), 15% aqueous NaOH (24 mL), and H_2O (36 mL). The quenched reaction mixture was allowed to warm to ambient temperature and was stirred for 30 minutes. $MgSO_4$ was added to this crude mixture, it was stirred for 30 more minutes. Aluminum and magnesium solids were removed by filtration and the crude product was concentrated under reduced pressure. The crude product was purified by distillation to provide enol **SI-31** as a clear oil (10.1 g, 75% Yield). All physical and spectroscopic data were in accordance with literature data.[13]



SI-32

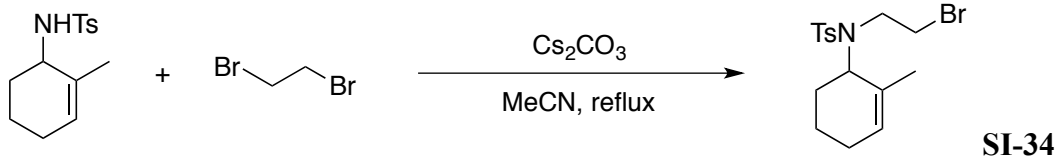
(SI-32): *tert*-Butyl *N*-(4-methylbenzenesulfonyl)-*N*-(2-methylcyclohex-2-en-1-yl)carbamate. To a 0°C solution of enol **SI-31** (8.4 g, 75 mmol, 2 equiv.), TsNHBoc (10.2 g, 37 mmol, 1 equiv.), and PPh_3 (29.5 g, 112.5 mmol, 3 equiv.) in THF (200 mL, 0.2 M) was added DIAD

(19.7 g, 97.5 mmol, 2.6 equiv.). The reaction mixture was allowed to warm to ambient temperature and was stirred for 24 hours. The reaction was concentrated under reduced pressure and filtered through silica. The silica plug was flushed with Et_2O (2x) and the combined organics were concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide sulfonamide **SI-32** as a white solid (12.4 g, 90% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.54 (m, 1H), 4.99 (m, 1H), 2.46 (s, 3H), 2.16 (m, 1H), 2.07 (m, 2H), 1.99 (m, 1H), 1.86 (m, 1H), 1.67 (m, 1H), 1.56 (bs, 3H), 1.38 (s, 9H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 150.36, 143.91, 137.36, 132.94, 129.14, 128.07, 124.69, 83.83, 59.28, 29.06, 27.84, 24.79, 22.77, 21.61, 20.33. **HRMS** (ESI): Calculated for $[C_{19}H_{27}NO_4SNa]^+$ 388.1559, found 388.1557.



SI-33

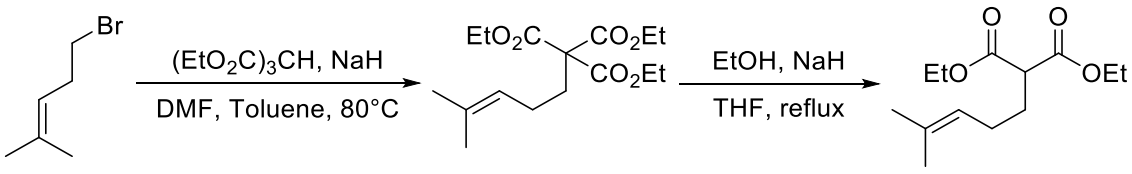
(SI-33): 4-Methyl-*N*-(2-methyl-2-cyclohexen-1-yl)benzenesulfonamide. To a solution of sulfonamide **SI-32** (10 g, 27.4 mmol, 1 equiv.) in DCM (70 mL, 0.4 M) was added TFA (15.6 g, 137 mmol, 5 equiv.). The reaction mixture stirred for 16 hours at room temperature. The reaction was quenched with saturated $NaHCO_3$ and the aqueous layer was extracted with DCM (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide sulfonamide **SI-33** as a white solid (7.1 g, 98% Yield). All physical and spectroscopic data were in accordance with literature data.[14]



SI-34

(SI-34): *N*-(2-Bromoethyl)-*N*-(2-methylcyclohex-2-en-1-yl)-4-methylbenzenesulfonamide. Sulfonamide **SI-33** (1.7 g, 6.4 mmol) was alkylated with 1,2-dibromoethane (12 g, 64 mmol) according to General Procedure G. The crude product was purified by flash chromatography

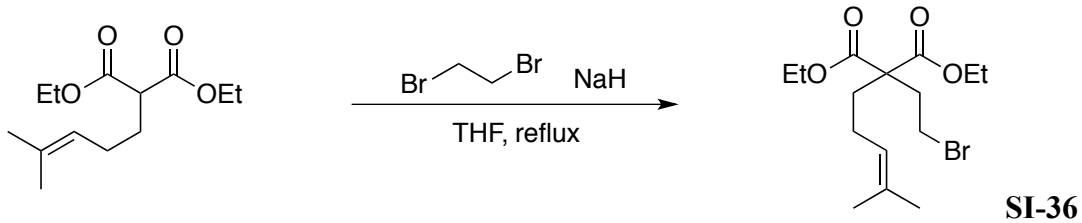
using hexanes/ethyl acetate (20:1) to provide bromide **SI-34** as a white solid (1.1 g, 46% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.71 (m, 1H), 4.27 (m, 1H), 3.71 (m, 1H), 3.55 (m, 1H), 3.48 (m, 1H), 3.22 (m, 1H), 2.45 (s, 3H), 2.01 (m, 1H), 1.94 (m, 1H), 1.84 (m, 1H), 1.65-1.52 (m, 3H), 1.28 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.46, 137.51, 131.64, 129.94, 129.71, 127.06, 57.70, 45.89, 30.57, 30.09, 24.94, 21.54, 20.91, 20.60. **HRMS** (ESI): Calculated for $[C_{16}H_{22}BrNO_2SNa]^+$ 395.0531, found 395.0487.



SI-35

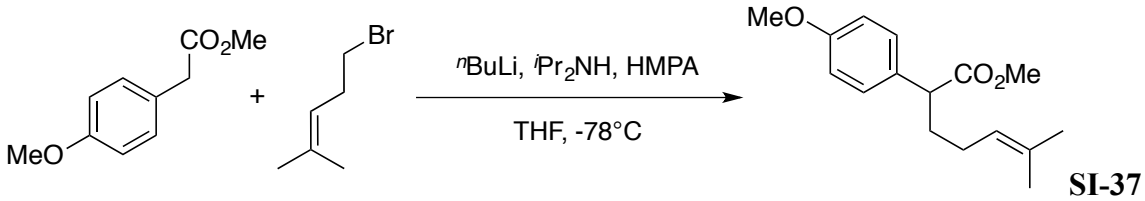
(SI-35): Diethyl 2-(4-methylpent-3-en-1-yl)malonate. To a suspension of sodium hydride (0.74 g, 60 %, 18.4 mmol, 1.02 equiv) in 1:1 DMF:Toluene (60 mL, 0.3 M) was added triethyl methanetricarboxylate (4.2 g, 18.0 mmol, 1 equiv.). The solution was stirred for 30 minutes at room temperature before the addition of bromide **SI-11** (3.0 g, 18.4 mmol, 1.02 equiv). The reaction mixture was heated to reflux and stirred for 20 hours. The reaction was quenched with H_2O, extracted with EtOAc (5x) and washed with H_2O, saturated $NaHCO_3$, and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated. The crude product was then decarboxylated without further purification.

To a suspension of sodium hydride (0.81 g, 60%, 20.2 mmol, 1.1 equiv) in THF (50 mL, 0.4 M) was added ethanol (1.0 g, 22.1 mmol, 1.2 equiv) and stirred for 30 minutes at room temperature. Alkyl triester (6.0 g, 18.4 mmol, 1 equiv) was then added, and the solution was heated to reflux and stirred for 16 hours. The reaction mixture was quenched with 1N HCl, extracted with Et_2O, and washed with H_2O, saturated $NaHCO_3$, and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide alkylmalonate **SI-35** as a clear oil (2.8 g, 63% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



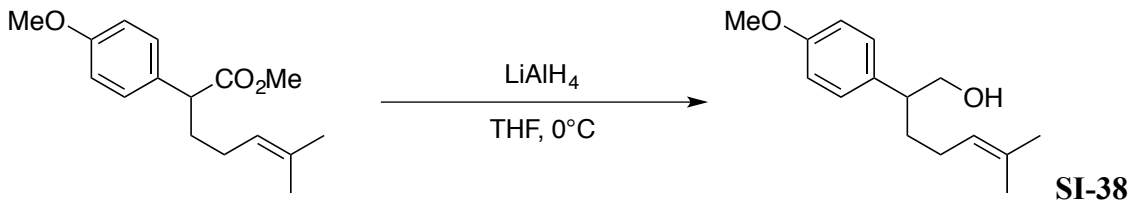
SI-36

(SI-36): Diethyl 2-(2-bromoethyl)-2-(4-methylpent-3-en-1-yl)malonate. To a suspension of sodium hydride (0.58 g, 60%, 14.5 mmol, 1.3 equiv) in THF (40 mL, 0.3 M) was added diethyl alkylmalonate **SI-35** (2.7 g, 11.1 mmol, 1 equiv). The solution was stirred for 30 minutes at room temperature and 1,2-dibromoethane (20.9 g, 111 mmol, 10 equiv) was then added. The reaction mixture was heated to reflux, stirred for 24 hours. The reaction was quenched with H_2O, extracted with Et_2O (3x), washed with brine, Dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-36** as a clear oil (1.8 g, 46% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



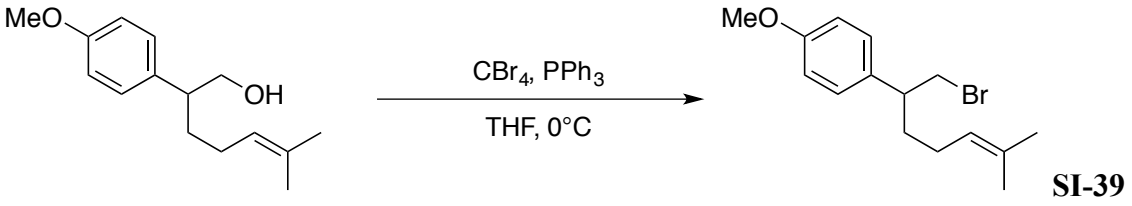
SI-37

(SI-37): Methyl 2-(4-methoxyphenyl)-6-methylhept-5-enoate. Methyl 4-methoxyphenyl acetate (4.0 g, 22.4 mmol) was alkylated with bromide **SI-11** (4.0 g, 26.8 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide methyl ester **SI-37** as a clear oil (5.1 g, 91% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



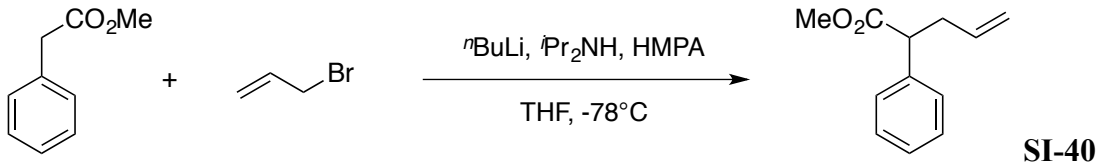
SI-38

(SI-38): 2-(4-Methoxyphenyl)-6-methylhept-5-enol. Methyl ester **SI-37** (5.0 g, 20.1 mmol) was reduced by $LiAlH_4$ (1.5 g, 40.2 mmol) according to General Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (3:1) to provide alcohol **SI-38** as a clear oil (2.2 g, 50% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



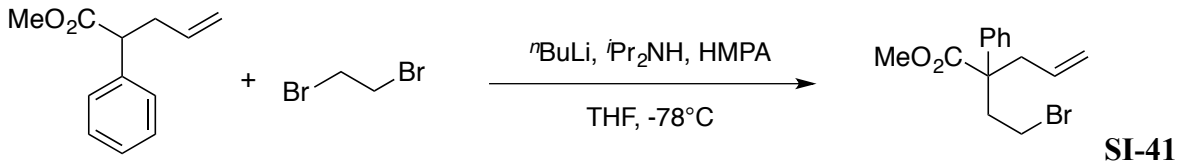
SI-39

(SI-39): 1-(1-Bromo-6-methylhept-5-en-2-yl)-4-methoxybenzene. Alcohol **SI-38** (1.5 g, 6.4 mmol) was brominated with CBr_4 (6.4 g, 19.2 mmol) according to General Procedure F. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide bromide **SI-39** as a clear oil (1.6 g, 84% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.09 (m, 1H), 3.82 (s, 3H), 3.54 (d, *J* = 7.2 Hz, 2H), 2.92 (m, 1H), 1.94 (m, 1H), 1.87 (m, 2H), 1.69 (s, 3H), 1.65 (m, 1H), 1.49 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 158.44, 134.18, 132.15, 128.63, 123.66, 113.84, 55.19, 46.62, 39.48, 34.18, 25.71, 25.69, 17.70. **HRMS** (ESI): Calculated for $[C_{15}H_{21}BrOH]^+$ 297.0854, found 297.0672.



SI-40

(SI-40): Methyl allylphenylacetate. Methyl phenylacetate (3.8 g, 25.5 mmol) was alkylated with allyl bromide (3.7 g, 30.7 mmol) according to General Procedure H. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide methyl ester **SI-40** as a clear oil (4.1 g, 85% Yield). All physical and spectroscopic data were in accordance with literature data.[15]



SI-41

(SI-41): Methyl allyl(2-bromoethyl)phenylacetate. Methyl ester **SI-40** (3.8 g, 20 mmol) was alkylated with dibromoethane (4.5 g, 24 mmol) according to General Procedure H. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-41** as a clear oil (3.7 g, 62% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 5.61 (m, 1H), 5.15 (m, 2H), 3.71 (s, 3H), 3.24 (m, 1H), 3.14 (m, 1H), 2.88 (m, 1H), 2.75 (m, 1H), 2.65 (m, 1H), 2.54 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 174.67, 140.51, 132.78, 128.70, 127.29, 126.16, 119.17, 54.50, 52.29, 39.98, 38.83, 27.86. **HRMS** (ESI): Calculated for $[C_{14}H_{17}BrO_2H]^+$ 297.0490, found 297.1085.

Palladium-Catalyzed Cross-Coupling Reactions

Cross-Coupling Procedure A: 5-Membered Ring Formation

To a one-dram vial in a glove box under argon atmosphere was added primary or secondary bromide (1.0 mmol, 1 equiv) dissolved in $PhCF_3$ (0.25 M). $[Pd(allyl)Cl]_2$ (5 mol%), dtbpf (20 mol%), and Et_3N (2 equiv.) were then added. The reaction vial was removed from the glove box and heated to 100°C, stirring for 3-24 hours. The reaction mixture was allowed to cool to ambient temperature, was quenched with 1N HCl and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Cross-Coupling Procedure B: Reaction with Terminal Alkenes

To a one-dram vial in a glove box under argon atmosphere was added primary or secondary bromide (1.0 mmol, 1 equiv) dissolved in $PhCF_3$ (0.25 M). $[Pd(allyl)Cl]_2$ (5 mol%), dtbpf (20 mol%), and DBU (2 equiv.) were then added. The reaction vial was removed from the glove box and heated to 100°C, stirring for 16 hours. The reaction mixture was allowed to cool to ambient temperature, was quenched with 1N HCl and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Cross-Coupling Procedure C: 6-Membered Ring Formation

To a one-dram vial in a glove box under argon atmosphere was added primary or secondary bromide (1.0 mmol, 1 equiv) dissolved in $PhCF_3$ (0.25 M). $[Pd(allyl)Cl]_2$ (5 mol%), dtbpf (20 mol%), and Cy_2NMe (2 equiv.) were then added. The reaction vial was removed from the glove box and heated to 120°C, stirring for 16-48 hours. The reaction mixture was allowed to cool to ambient temperature, was quenched with 1N HCl and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Cross-Coupling Procedure D: Intermolecular Alkyl Mizoroki-Heck

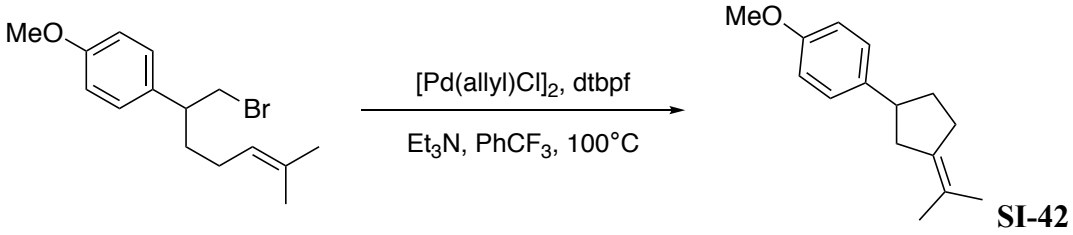
To a one-dram vial in a glove box under argon atmosphere was added primary or secondary bromide (0.25 mmol, 1 equiv) dissolved in $PhCF_3$ (0.25 M). $[Pd(allyl)Cl]_2$ (5 mol%), dtbpf (20

mol%), styrene (3 equiv.) and Cy_2NH (2 equiv.) were then added. The reaction vial was removed from the glove box and heated to 100°C, stirring for 16 hours. The reaction mixture was allowed to cool to ambient temperature, was quenched with 1N HCl and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated.

Cross-Coupling Procedure E: Atom-Transfer Radical Cyclization

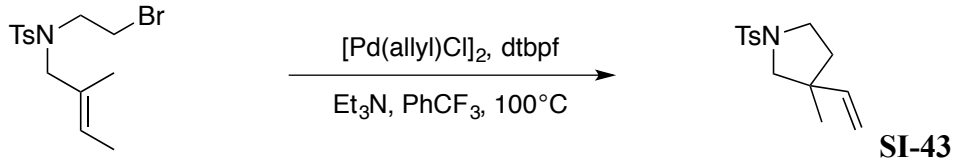
To a one-dram vial in a glove box under argon atmosphere was added primary or secondary bromide (0.125 mmol, 1 equiv) dissolved in $PhCF_3$ (0.25 M). $[Pd(allyl)Cl]_2$ (5 mol%), dtbpf (20 mol%), and Et_3N (0.5 equiv.) were then added. The reaction vial was removed from the glove box and heated to 80°C, stirring for 30 minutes. The reaction mixture was allowed to cool to ambient temperature, was quenched with 1N HCl and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Experimental Data



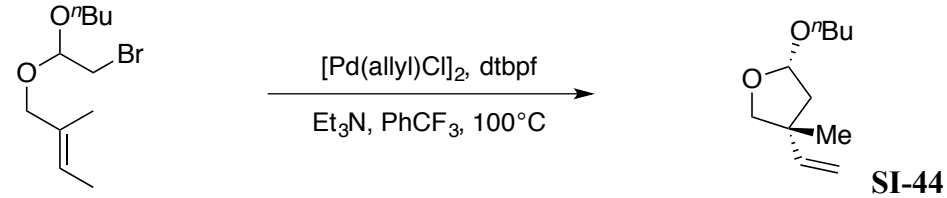
SI-42

(SI-42): 1-methoxy-4-(3-(propan-2-ylidene)cyclopentyl)benzene. Primary bromide **SI-39** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide Heck product **SI-42** as a yellow oil (195.3 mg, 90% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



SI-43

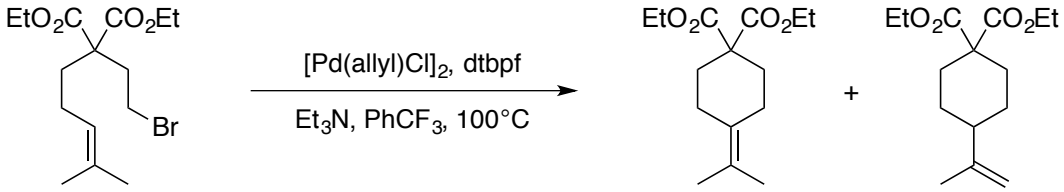
(SI-43): 3-methyl-1-tosyl-3-vinylpyrrolidine. Primary bromide **SI-21** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck product **SI-43** as a yellow solid (213.6 mg, 80% Yield). All physical and spectroscopic data were in accordance with literature data.[11]



SI-44

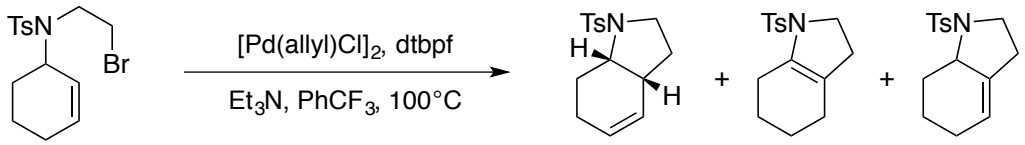
(SI-44): 2-butoxy-4-methyl-4-vinyltetrahydrofuran. Primary bromide **SI-2** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide Heck product **SI-**

44 as a yellow oil (134.4 mg, 73% Yield, 89:11 dr). All physical and spectroscopic data were in accordance with literature data.[11]



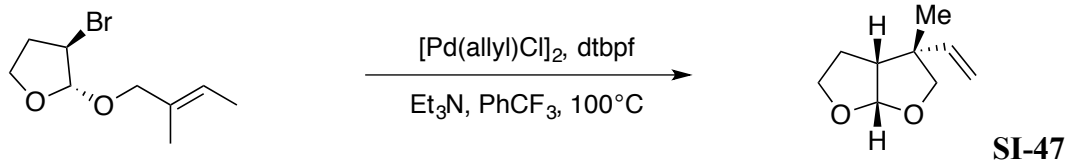
SI-45a **SI-45b**

(SI-45): Diethyl 4-(propan-2-ylidene)cyclohexane-1,1-dicarboxylate. Primary bromide **SI-36** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide Heck products **SI-45a** and **SI-45b** as a yellow oil (221.1 mg, 82% Yield, 4.3:1 rr). All physical and spectroscopic data were in accordance with literature data.[11]



SI-46a **SI-46b** **SI-46c**

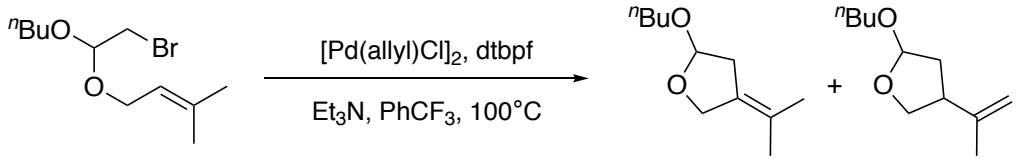
(SI-46): 1-tosyl-2,3,3a,6,7,7a-hexahydro-1H-indole. Primary bromide **SI-29** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck products **SI-46a**, **SI-46b,** and **SI-46c** as a yellow solid (214.5 mg, 77% Yield, 7.2:3:1 rr). All physical and spectroscopic data were in accordance with literature data.[11]



SI-47

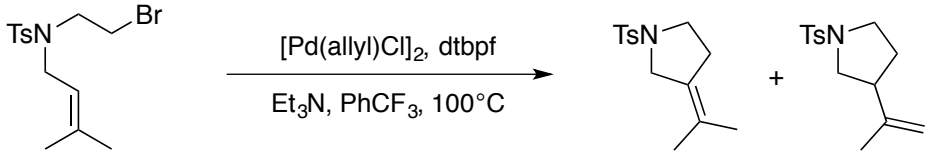
(SI-47): 3-methyl-3-vinylhexahydrofuro[2,3-*b*]furan. Secondary bromide **SI-4** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The product was

found to decompose after prolonged contact with silica. The crude reaction mixture was dissolved in Et_2O and flushed multiple times through silica gel until no residue or color remained in the silica, providing Heck product **SI-47** as a red oil (143.6 mg, 93% Yield >95:5 dr). All physical and spectroscopic data were in accordance with literature data.[11]



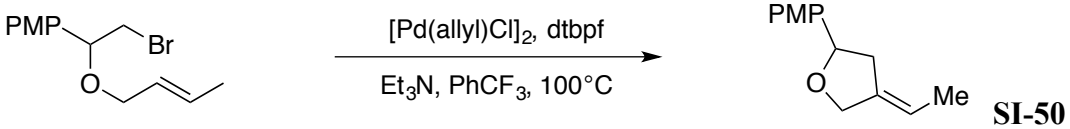
SI-48a **SI-48b**

(SI-48): 2-butoxy-4-(propan-2-ylidene)tetrahydrofuran. Primary bromide **SI-3** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (40:1) to provide Heck products **SI-48a** and **SI-48b** as a yellow oil (158.3 mg, 86% Yield, 17:1 rr). All physical and spectroscopic data were in accordance with literature data.[2,16]



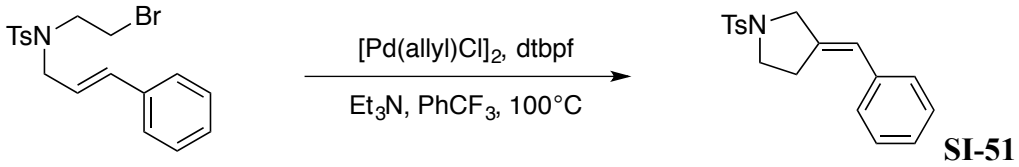
SI-49a **SI-49b**

(SI-49): 3-(propan-2-ylidene)-1-tosylpyrrolidine. Primary bromide **SI-22** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck products **SI-49a** and **SI-49b** as a yellow oil (214.1 mg, 81% Yield, 6.0:1 dr). All physical and spectroscopic data were in accordance with literature data.[17]



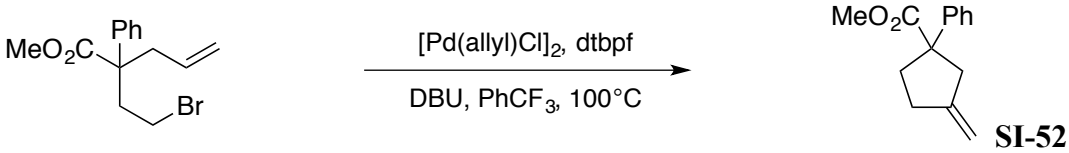
SI-50

(SI-50): 4-ethylidene-2-(4-methoxyphenyl)tetrahydrofuran. Primary bromide **SI-6** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck product **SI-50** as a light yellow oil (144.2 mg, 71% Yield, 1:1 E:Z). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.33 (m, 2H), 6.91 (m, 2H), 5.43 (m, 1H), 4.89 (m, 1H), 4.60 (m, 1H), 4.39 (m, 1H), 3.83 (s, 3H), 2.88 (m, 1H), 2.58-2.39 (m, 1H), 1.65 (m, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 159.00, 139.29, 134.08, 133.79, 127.28, 127.26, 114.48, 113.70, 1113.67, 55.22, 40.89, 37.38, 15.07, 14.54. **HRMS** (ESI): Calculated for $[C_{13}H_{16}O_2Na]^+$ 227.1048, found 227.1562.



SI-51

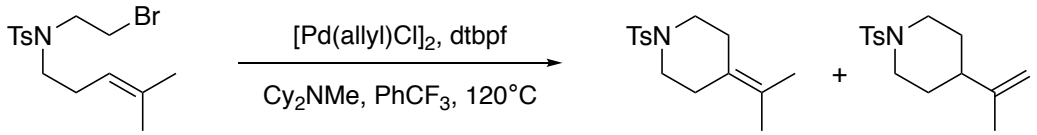
(SI-51): 3-benzylidene-1-tosylpyrrolidine. Primary bromide **SI-23** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck product **SI-51** as a light yellow oil (202.7 mg, 65% Yield, 1:1 E:Z). All physical and spectroscopic data were in accordance with literature data.[18]



SI-52

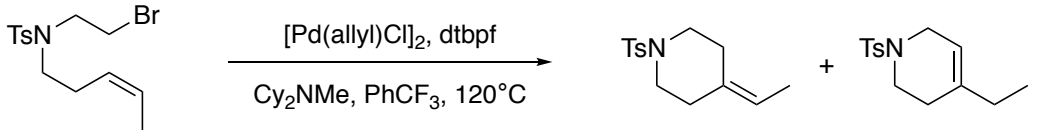
(SI-52): Methyl 3-methylene-1-phenylcyclopentane-1-carboxylate. Primary bromide **SI-41** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure B. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck product **SI-52** as a yellow oil (140.0 mg, 65% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.41 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.28 (m, 1H), 5.03 (s, 1H), 4.93 (s, 1H), 3.65 (s, 3H), 3.35 (d, J = 15.6 Hz, 1H), 2.79 (m, 2H), 2.46 (m, 2H), 3.07 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.65, 149.08, 142.26, 128.33, 126.93, 126.59, 106.75, 58.05,

52.40, 43.09, 35.80, 30.53. **HRMS** (ESI): Calculated for $[C_{14}H_{16}O_2H]^+$ 217.1229, found 217.1220.



SI-53a **SI-53b**

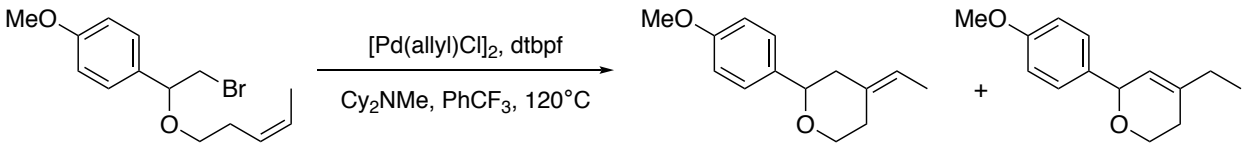
(SI-53): 4-(propan-2-ylidene)-1-tosylpiperidine. Primary bromide **SI-25** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure C, stirring for 16 hours. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide Heck products **SI-53a** and **SI-53b** as a yellow solid (255.7 mg, 92% Yield, 1.9:1 rr). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.71 (s, 0.5H), 4.65 (s, 0.5H), 3.84 (m, 1H), 3.85 (t, *J* = 6.0 Hz, 4H), 2.43 (s, 1.5H), 2.41 (s, 3H), 2.36 (t, *J* = 5.4 Hz, 4H), 2.24 (m, 1H), 1.75 (m, 1H), 1.67 (s, 1.5H), 1.59 (s, 6H), 1.55 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 147.95, 143.33, 143.26, 132.83, 129.46, 129.44, 127.58, 127.56, 125.43, 124.13, 109.40, 47.24, 46.51, 42.41, 29.97, 28.74, 21.39, 20.56, 19.74. **HRMS** (APPI): Calculated for $[C_{15}H_{21}NO_2SNa]^+$ 302.1186, found 302.1185.



SI-54a **SI-54b**

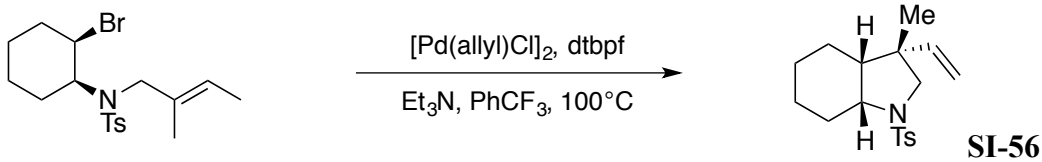
(SI-54): 4-ethylidene-1-tosylpiperidine. Primary bromide **SI-24** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure C, stirring for 48 hours. The crude product was purified by flash chromatography using hexanes/ethyl acetate (9:1) to provide Heck products **SI-54a** and **SI-54b** as a yellow solid (187.6 mg, 71% Yield, 3.3:1 rr). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 0.6H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.32 (m, 2.6H), 5.29 (m, 0.3H), 5.22 (m, 1H), 3.55 (m, 0.6H), 3.16 (t, *J* = 6.0 Hz, 0.6H), 3.00 (m, 4H), 2.43 (s, 3.9H), 2.32

(m, 2H), 2.25 (m, 2H), 2.13 (m, 0.6H), 1.95 (m, 0.6H), 1.52 (d, J = 6.6 Hz, 3H), 0.95 (t, J = 7.8 Hz, 0.9H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.39, 143.36, 138.07, 133.53, 133.10, 129.57, 129.57, 129.54, 129.51, 127.68, 127.61, 118.74, 114.80, 47.93, 47.08, 44.80, 42.90, 35.10, 29.53, 28.26, 27.07, 21.47, 12.57, 11.79. **HRMS** (APPI): Calculated for $[C_{14}H_{18}O_2H]^+$ 288.1029, found 288.1028.



SI-55a **SI-55b**

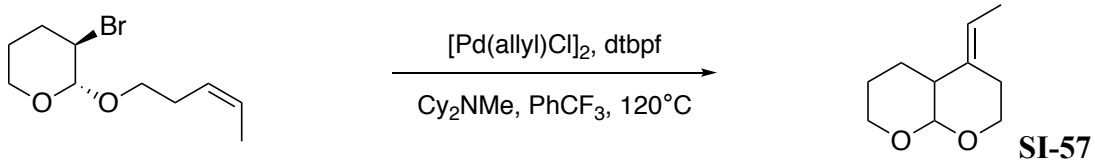
(SI-55): 4-ethylidene-2-(4-methoxyphenyl)tetrahydro-2*H*-pyran. Primary bromide **SI-7** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure C, stirring for 48 hours. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck products **SI-55a** and **SI-55b** as a yellow solid (90.3 mg, 41% Yield, 7.0:1 rr, 1:1 E:Z). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.38 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 6.93 (m, 2H), 5.53 (m, 0.15H), 5.38 (m, 1H), 4.53 (d, J = 7.8 Hz, 0.15H), 4.38 (s, 0.3H), 4.27 (m, 2H), 3.84 (s, 3.45H), 3.54 (m. 1H), 2.77 (d, J = 7.8 Hz, 0.5H), 2.56 (d, J = 7.8 Hz, 0.5H), 2.46 (m, 0.45H), 2.36 (m, 1H), 2.15 (m, 2H), 1.68 (m, 3H), 1.10 (t, J = 5.4 Hz, 0.45H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 158.90, 158.83, 134.80, 134.75, 134.71, 134.68, 127.15, 127.08, 127.02, 127.00, 117.98, 117.61, 117.55, 113.59, 113.55, 80.62, 79.70, 75.33, 69.28, 68.40, 66.45, 55.10, 55.08, 44.25, 36.49, 36.15, 36.04, 29.51, 28.58, 12.53, 12.40, 11.63. **HRMS** (APPI): Calculated for $[C_{14}H_{18}O_2H]^+$ 219.1380, found 219.1379.



SI-56

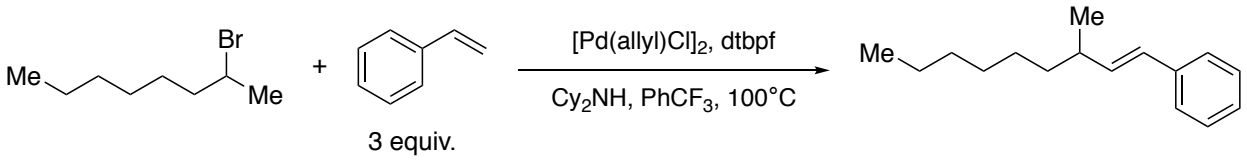
(SI-56): 3-methyl-1-tosyl-3-vinyloctahydro-1*H*-indole. Secondary bromide **SI-26** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck

product **SI-56** as a yellow solid (191.1 mg, 60% Yield, >95:5 dr). The major diastereomer was determined by 2D NMR analysis. **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.80 (dd, *J* = 17.4 Hz, 10.8 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 17.4 Hz, 1H), 3.67 (d, *J* = 10.8 Hz, 1H), 3.60 (m, 1H), 3.12 (d, *J* = 10.8 Hz, 1H), 2.51 (m, 1H), 2.45 (s, 3H), 1.67-1.48 (m, 8H), 0.56 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.24, 141.43, 134.05, 129.49, 127.51, 113.56, 58.62, 57.50, 48.04, 45.07, 28.84, 25.17, 24.13, 23.93, 21.54, 20.37. **HRMS** (ESI): Calculated for $[C_{18}H_{25}NO_2SNa]^+$ 342.1504, found 342.1496.



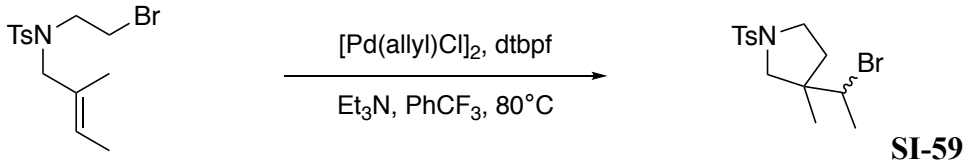
SI-57

(SI-57): (*E*)-4-ethylidenehexahydro-2*H*,5*H*-pyrano[2,3-*b*]pyran. Secondary bromide **SI-5** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure C, stirring for 48 hours. The crude product was purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide Heck product **SI-57** as a yellow oil (126.4 mg, 75% Yield, >95:5 dr, 1.5:1 E:Z). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 5.34 (m, 1H), 4.70 (d, J = 3.0 Hz, 0.6H), 4.63 (d, J = 2.4 Hz, 0.4H), 4.10 (m, 1H), 3.92 (m, 1H), 3.68 (m, 1H), 3.42 (m, 1H), 2.77 (m, 0.4 H), 2.53 (m, 0.51H), 2.31 (m, 0.6H), 2.24 (m, 1.49H), 2.01-1.68 (m, 4H), 1.62 (m, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 137.46, 137.39, 119.63, 119.32, 98.24, 97.51, 66.57, 65.60, 61.42, 60.93, 45.86, 38.50, 31.79, 24.85, 24.60, 24.53, 24.12, 22.38, 12.81, 12.10. **HRMS** (ESI): Calculated for $[C_{10}H_{16}O_2H]^+$ 169.1229, found 169.1223.



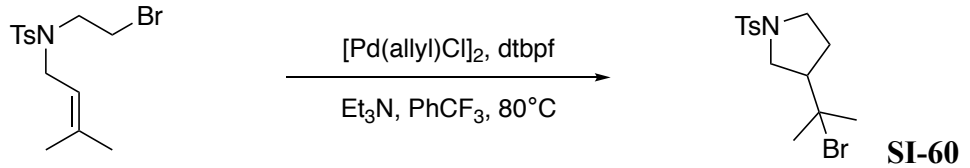
SI-58

(SI-58): (*E*)-β-(1-methylheptyl)styrene. 3-Bromooctane and styrene were made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure D. The yield of the crude product was determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard (40% Yield). All physical and spectroscopic data were in accordance with literature data.[19]



SI-59

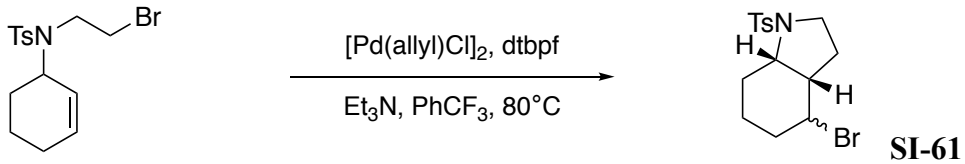
(SI-59): 3-(1-bromoethyl)-3-methyl-1-tosylpyrrolidine. Primary bromide **SI-21** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide ATRC product **SI-59** as a colorless oil (19.6 mg, 45% Yield, 1.3:1 dr). **Major Diastereomer: ^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 4.01 (q, *J* = 6.6 Hz, 1H), 3.47 (m, 1H), 3.37 (m, 1H), 3.21 (d, *J* = 10.2 Hz, 1H), 3.12 (d, *J* = 10.2 Hz, 1H), 2.46 (s, 3H), 1.70 (m, 2H), 1.67 (d, *J* = 6.6 Hz, 3H), 0.99 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.56, 133.53, 129.72, 127.53, 60.36, 57.99, 47.59, 47.56, 36.01, 21.92, 21.60, 18.78. **HRMS** (ESI): Calculated for $[C_{14}H_{20}BrNO_2SH]^+$ 346.0477, found 346.0468. **Minor Diastereomer: ^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 4.02 (q, J = 6.6 Hz, 1H), 3.39 (m, 1H), 3.31 (m, 1H), 3.12 (m, 2H), 2.47 (s, 3H), 1.84 (m, 1H), 1.75 (m, 1H), 1.62 (d, J = 6.6 Hz, 3H), 1.00 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.65, 133.49, 129.74, 127.50, 57.97, 56.90, 47.58, 46.56, 38.41, 22.33, 21.60, 19.28. **HRMS** (ESI): Calculated for $[C_{14}H_{20}BrNO_2SH]^+$ 346.0477, found 346.0468.



SI-60

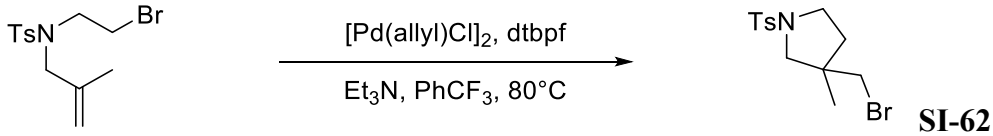
(SI-60): 3-(2-bromopropan-2-yl)-1-tosylpyrrolidine. Primary bromide **SI-22** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E, stirring for 10 minutes. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide ATRC product **SI-60** as a colorless oil (11.3 mg, 26% yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 3.49 (m, 1H), 3.41 (m, 1H), 3.24 (m, 1H), 3.16 (m, 1H), 2.46 (s, 3H), 2.34 (m, 0.5H), 2.17 (m, 0.5H), 1.97 (m, 1H), 1.79 (m,

1H), 1.75 (s, 3H), 1.52 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.59, 143.57, 133.31, 133.28, 129.73, 129.72, 127.70, 127.67, 70.56, 67.82, 51.81, 50.84, 50.60, 49.44, 47.96, 47.94, 33.20, 32.66, 31.54, 31.04, 29.73, 28.50, 27.29, 21.60. **HRMS** (ESI): Calculated for $[C_{14}H_{20}BrNO_2SH]^+$ 346.0477, found 346.0470.



SI-61

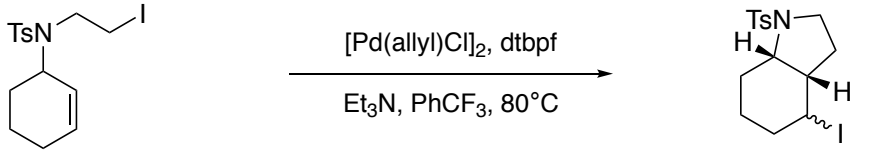
(SI-61): 4-bromo-1-tosyloctahydro-1*H*-indole. Primary bromide **SI-29** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide ATRC product **SI-61** as a colorless oil (26.7 mg, 60% Yield, 1:1 dr). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.22 (m, 1H), 4.20 (m, 1H), 3.74 (m, 1H), 3.69 (m, 1H), 3.60 (m, 1H), 3.57 (m, 1H), 3.29 (m, 1H), 3.16 (m, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 2.22 (m, 1H), 2.16 (m, 1H), 2.07 (m, 2H), 2.06 (m, 4H), 1.93 (m, 1H), 1.85 (m, 2H), 1.77 (m, 2H), 1.74 (m, 1H), 1.46 (m, 2H), 1.39 (m, 1H), 1.26 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.55, 143.46, 135.18, 134.06, 129.83, 129.77, 127.47, 127.20, 59.79, 59.01, 52.92, 50.09, 48.06, 47.19, 46.04, 45.35, 33.15, 31.85, 29.06, 28.58, 27.73, 27.01, 25.78, 24.23, 21.58, 20.32. **HRMS** (ESI): Calculated for $[C_{15}H_{20}BrNO_2SH]^+$ 358.0477, found 358.0472.



SI-62

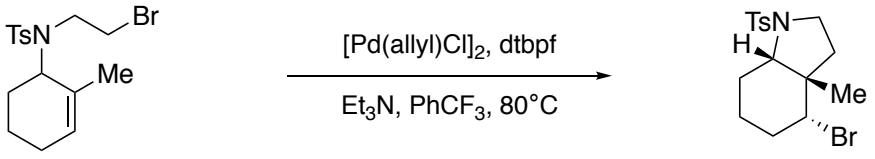
(SI-62): 3-(bromomethyl)-3-methyl-1-tosylpyrrolidine. Primary bromide **SI-27** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E, stirring for 16 hours. The crude product was purified by flash chromatography using hexanes/ethyl acetate (5:1) to provide ATRC product **SI-62** as a light yellow oil (12.5 mg, 30% Yield). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 3.35 (m, 2H), 3.26 (d, *J* = 10.2 Hz,

1H), 3.23 (d, *J* = 1.8 Hz, 2H), 3.06 (d, *J* = 10.2 Hz, 1H), 2.47 (s, 3H), 1.86 (m, 1H), 1.68 (m, 1H), 1.09 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.65, 133.38, 129.75, 127.53, 57.57, 46.80, 43.46, 41.57, 36.23, 23.27, 21.62.



SI-63

(SI-63): 4-iodo-1-tosyloctahydro-1*H*-indole. Primary iodide **SI-30** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E, stirring for 60 seconds. The crude product was purified by flash chromatography using hexanes/ethyl acetate (10:1) to provide ATRC product **SI-63** as a white solid (257.0 mg, 63% Yield, 1:1 dr). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.72 (m, 2H), 7.35 (m, 2H), 4.38 (m, 0.5H), 4.31 (m, 0.5H), 3.74 (m, 0.5H), 3.67 (m, 0.5H), 3.59 (m, 1H), 3.29 (m, 0.5H), 3.17 (m, 0.5H), 2.46 (s, 3H), 2.30 (m, 0.5H), 2.16-1.91 (m, 5.5H), 1.64 (m, 2H), 1.44 (m, 0.5H), 1.27 (m, 0.5H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.51, 143.41, 135.19, 134.01, 129.79, 129.74, 127.41, 127.15, 58.91, 58.86, 49.53, 47.17, 46.31, 45.63, 34.97, 33.93, 32.36, 29.11, 28.69, 28.61 28.49, 27.56, 25.89, 21.95, 21.54. **HRMS** (ESI): Calculated for $[C_{15}H_{20}INO_2SNa]^+$ 428.0157, found 428.0156.

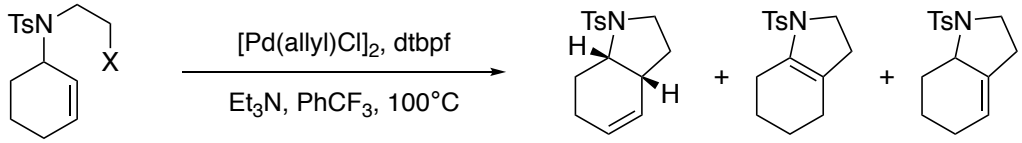


SI-64

(SI-64): 4-bromo-3a-methyl-1-tosyloctahydro-1*H*-indole. Primary bromide **SI-32** was made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure E. The yield of the crude product was determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard (84% Yield, 1.5:1 dr). The crude product was then purified by flash chromatography using hexanes/ethyl acetate (20:1) to provide bromide **SI-64** as a white solid. The major diastereomer was determined by 2D NMR analysis. **Major Diastereomer: ^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.97 (dd, *J* = 12.6, 4.8 Hz, 1H), 3.53

(m, 1H), 3.42 (m, 1H), 3.21 (m, 1H), 2.45 (s, 3H), 2.17 (m, 3H), 1.87 (m, 1H), 1.69 (m, 2H), 1.40 (m, 1H), 1.25 (m, 1H), 0.72 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.28, 135.82, 129.64, 127.12, 65.38, 60.02, 47.02, 43.99, 33.75, 31.69, 31.14, 25.46, 24.16, 21.58. **HRMS** (ESI): Calculated for $[C_{16}H_{22}BrNO_2SH]^+$ 372.0633, found 372.0629. **Minor Diastereomer: ^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.30 (dd, J = 12.0, 4.2 Hz, 1H), 3.57 (m, 1H), 3.39 (m, 1H), 3.01 (m, 1H), 2.47 (s, 3H), 2.17 (m, 1H), 2.07 (m, 1H), 1.95 (m, 1H), 1.79 (m, 1H), 1.64 (m, 2H), 1.12 (m, 1H), 1.09 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 143.62, 133.27, 129.75, 127.60, 66.27, 58.55, 46.81, 46.66, 34.95, 33.30, 24.85, 21.81, 21.61, 20.13. **HRMS** (ESI): Calculated for $[C_{16}H_{22}BrNO_2SH]^+$ 372.0633, found 372.0629.

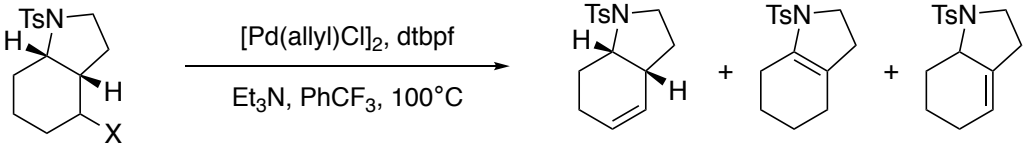
Mechanistic Experiments



SI-46a **SI-46b** **SI-46c**

***N*-(2-Haloethyl)-*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide.** Primary bromide **SI-29** and iodide **SI-30** were each made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A with the modifications described below. The yields of the crude products were determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Entry	Conditions	SM (%)	SI-46a (%)	SI-46b (%)	SI-46c (%)
1	X = Br, no additive	0	50	7	20
2	X = I, no additive	0	27	10	11
3	X = Br, with 10 mol % dinitrobenzene	99	0	0	0
4	X = I, with 10 mol % dinitrobenzene	0	32	<2	46
5	X = Br, with 1 equiv TEMPO	69	0	0	0
6	X = I, with 1 equiv TEMPO	0	31	4	20

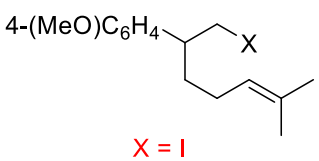
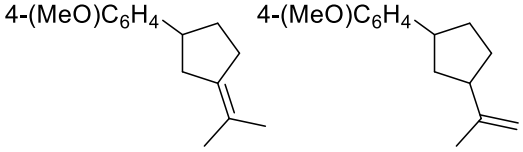
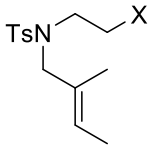
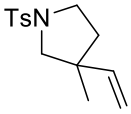
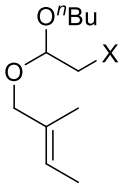
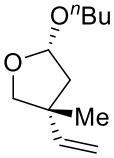
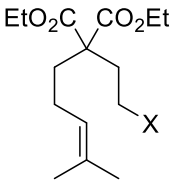
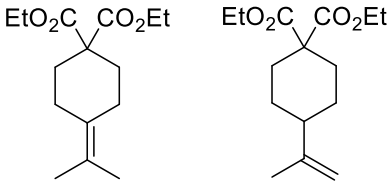
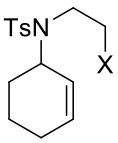
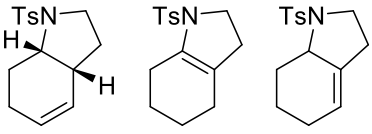


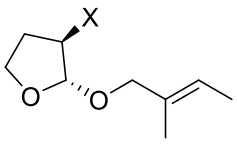
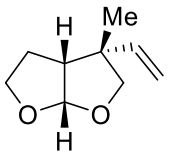
SI-46a **SI-46b** **SI-46c**

4-Halo-1-(4-Methylbenzensulfonyl)-*cis*-octahydro-1H-indole. Secondary bromide **SI-61** and iodide **SI-63** were each made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A with the modifications described below. The yields of the crude products were determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Entry	Conditions	SM (%)	SI-46a (%)	SI-46b (%)	SI-46c (%)
1	X = Br, no additive	0	65	<2	33
2	X = I, no additive	0	35	37	25
3	X = Br, with 10 mol % dinitrobenzene	78	3	2	4
4	X = I, with 10 mol % dinitrobenzene	0	32	30	38
5	X = Br, without [Pd] or dtbpf	100	0	0	0
6	X = I, without [Pd] or dtbpf	44	16	14	7

Comparison of Iodides and Bromides Using Current Protocol. Primary or secondary iodide[11] or bromide were each made to react with $[Pd(allyl)Cl]_2$ and dtbpf following Cross-Coupling Procedure A. [a]Isolated yield from Table 2. [b]Yield determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Entry	Substrate	Product	Yield (%)[a]
			
1	X = I		98 (19:1 rr)[b]
2	X = Br		90 (>20:1 rr)
			
3	X = I		22[b]
4	X = Br		80
			
5	X = I		14[b]
6	X = Br		73 (89:11 dr)
			
7	X = I		69 (4.3:1 rr)[b]
8	X = Br		82 (4.3:1 rr)
			
9	X = I		48 (2.7:1:1 rr)[b]
10	X = Br		77 (7.2:3:1 rr)

11	 X = I		23 (>95:5 dr)[b]
12	X = Br		93 (>95:5 dr)

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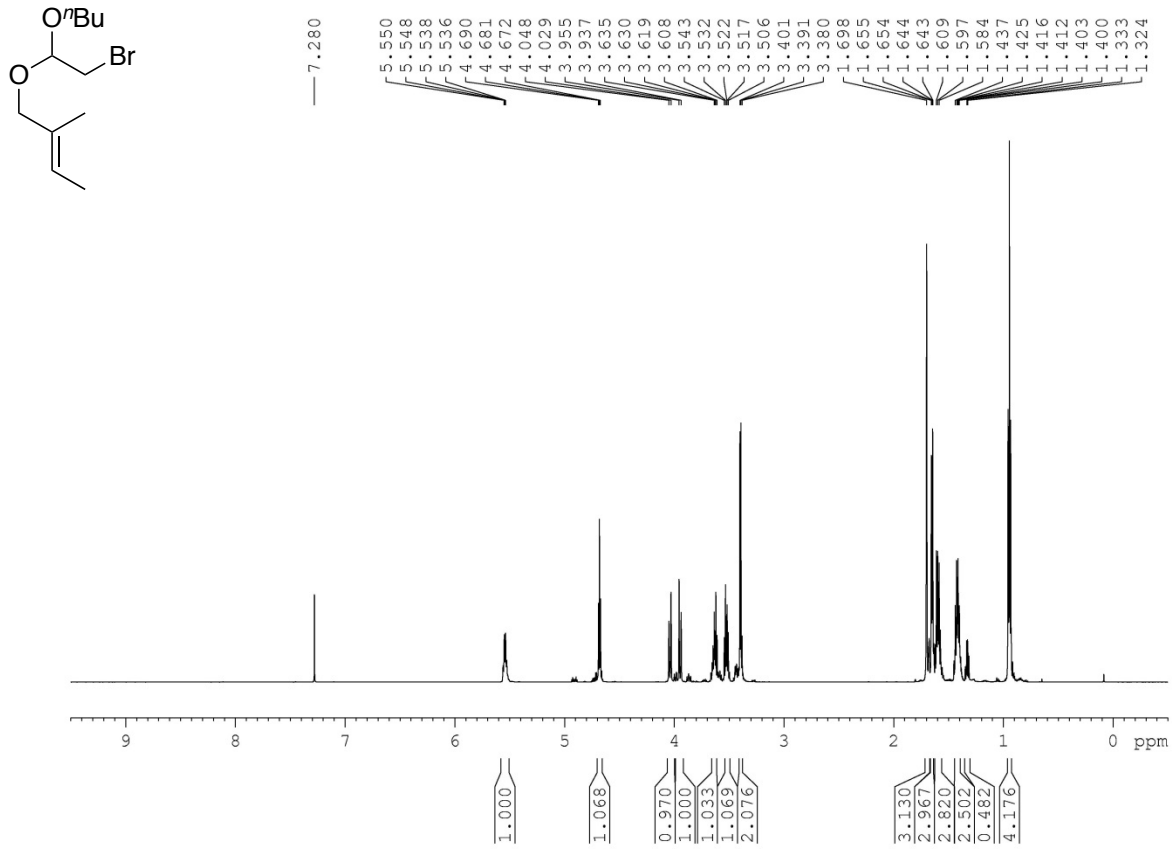
NMR Spectra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Br
O
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5.548
5.538
5.536
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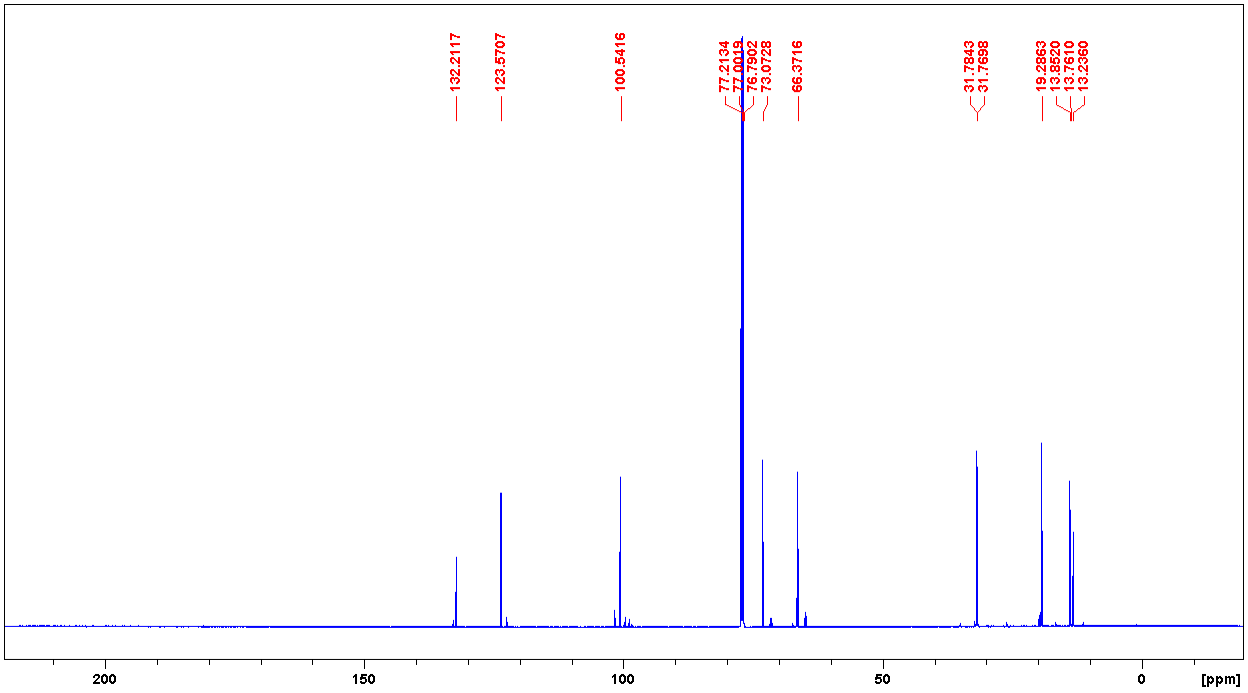
4.681
4.672
4.048
4.029
3.955
3.937
3.635
3.630
3.619
3.608
3.543
3.532
3.522
3.517
3.506
3.401
3.391
3.380
1.698
1.655
1.654
1.644
1.643
1.609
1.597
1.584
1.437
1.425
1.416
1.412
1.403
1.400
1.333
1.324
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.068
0.970
1.000
1.033
1.069
2.076
3.130
2.967
2.820
2.502
0.482
4.176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100.5416
77.2134
77.0019
76.7902
73.0728
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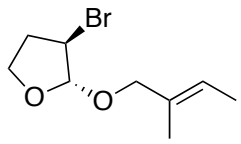
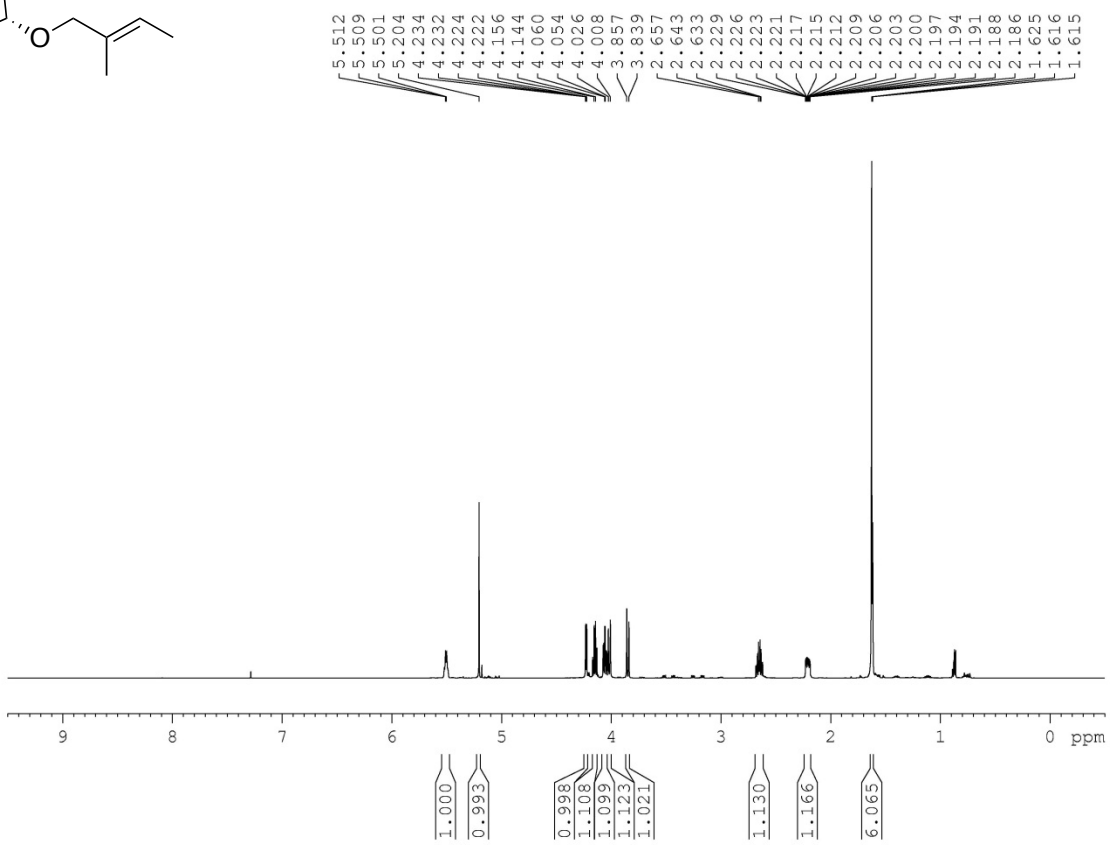
31.7843
31.7698
19.2863
13.8520
13.7610
13.2360
200
150
100
50
0
[ppm]


Br
O
O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5.509
5.501
5.204
4.234
4.232
4.224
4.222
4.156
4.144
4.060
4.054
4.026
4.008
3.857
3.839
2.657
2.643
2.633
2.229
2.226
2.223
2.221
2.217
2.215
2.212
2.209
2.206
2.203
2.200
2.197
2.194
2.191
2.188
2.186
1.625
1.616
1.615
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.993
0.998
1.108
1.099
1.123
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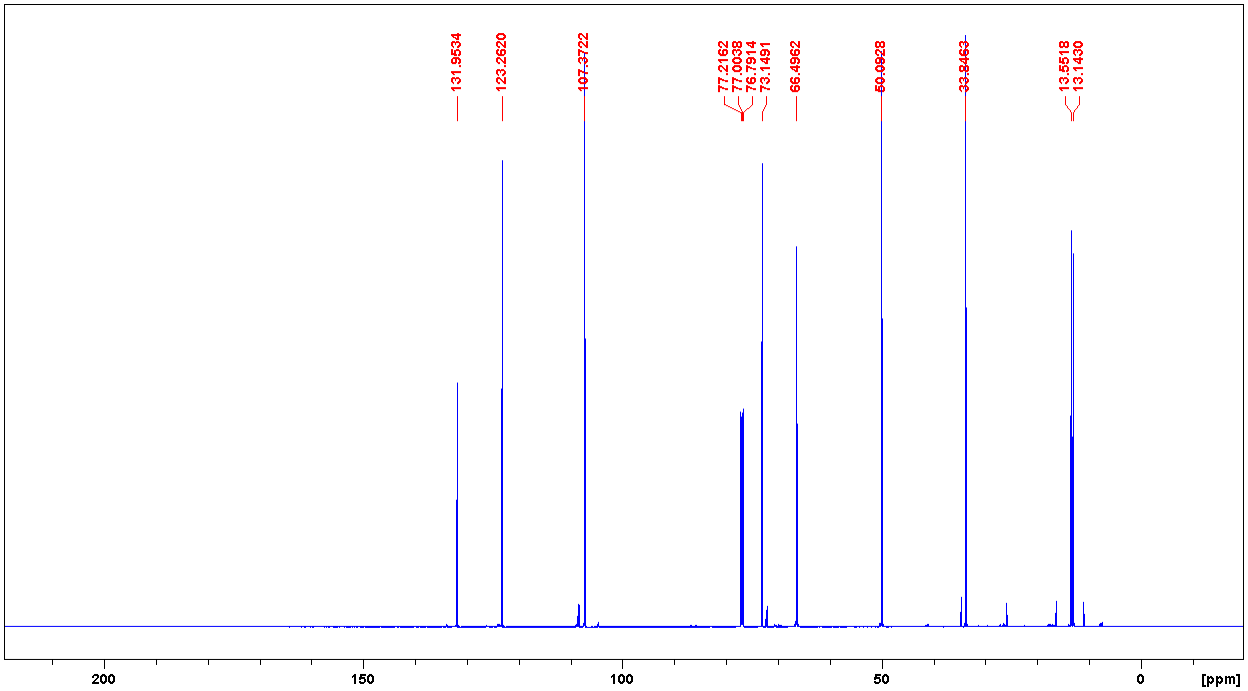
1.130
1.166
6.065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107.3722
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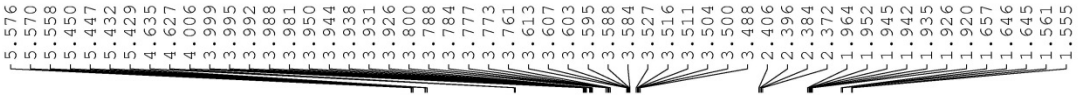
13.5518
13.1430
200
150
100
50
0
[ppm]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5.558
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5.447
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5.429
4.635
4.627
4.006
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3.995
3.992
3.988
3.981
3.950
3.944
3.938
3.931
3.926
3.800
3.788
3.784
3.777
3.773
3.761
3.613
3.607
3.603
3.595
3.588
3.584
3.527
3.516
3.511
3.504
3.500
3.488
2.406
2.396
2.384
2.372
1.964
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1.942
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1.657
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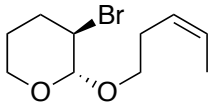
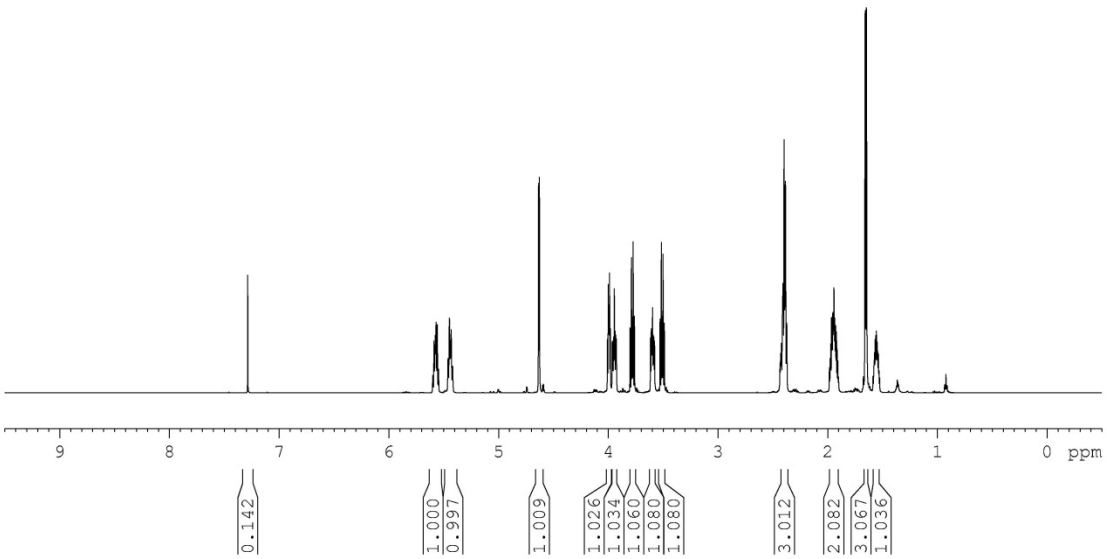
1.645
1.561
1.555


Br
O
O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5
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3
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1.080
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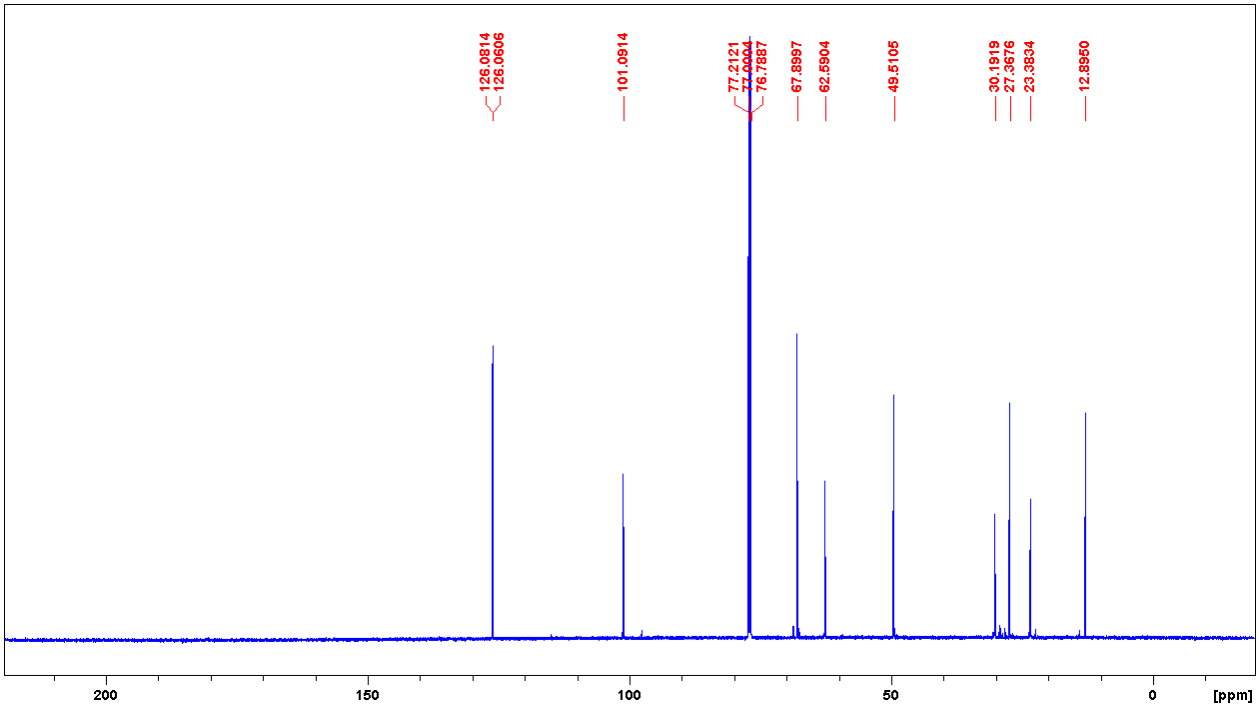
1.036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101.0914
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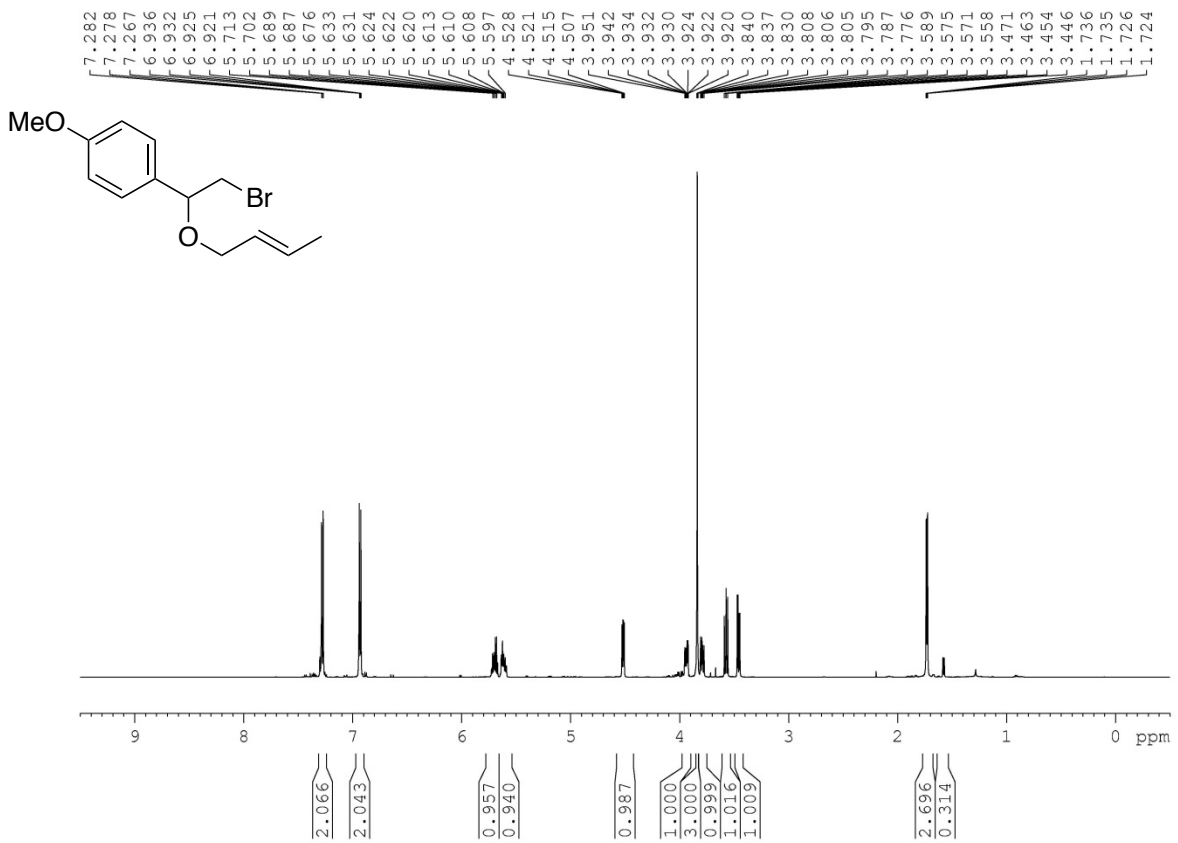
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5.633
5.631
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5.622
5.620
5.613
5.610
5.608
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4.521
4.515
4.507
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3.942
3.934
3.932
3.930
3.924
3.922
3.920
3.840
3.837
3.830
3.808
3.806
3.805
3.795
3.787
3.776
3.589
3.575
3.571
3.558
3.471
3.463
3.454
3.446
1.736
1.735
1.726
1.724
MeO
Br
O
9
8
7
6
5
4
3
2
1
0 ppm
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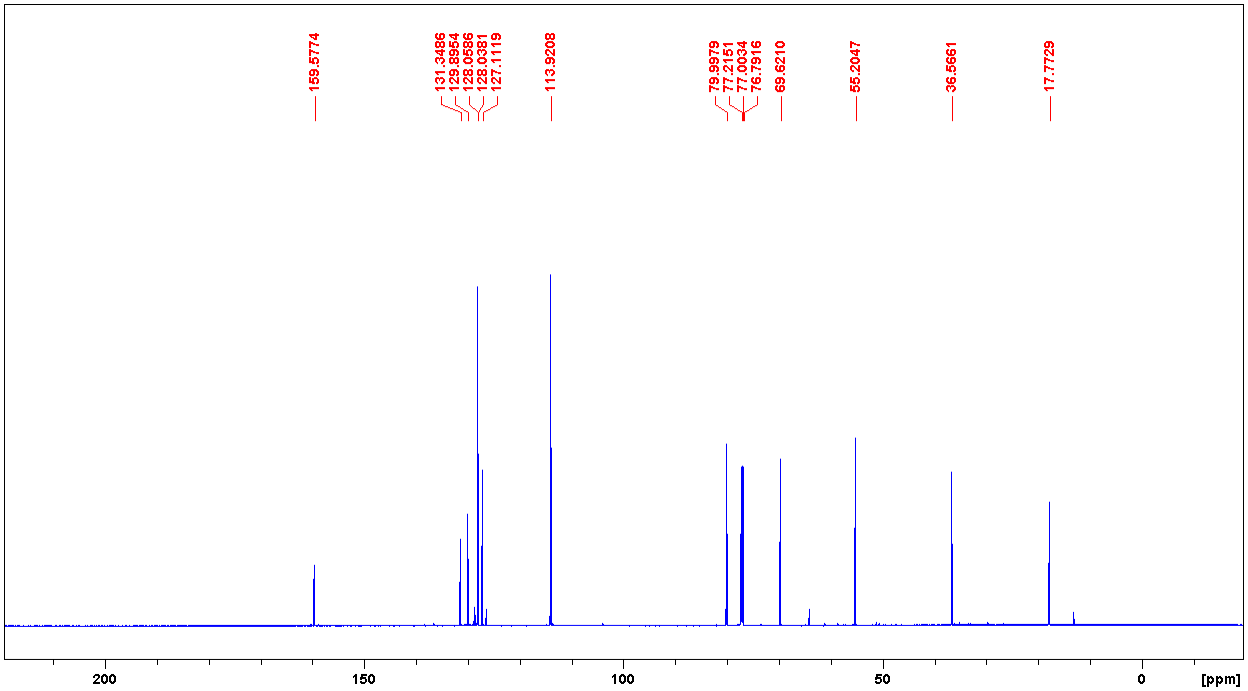
0.314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128.0586
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76.7916
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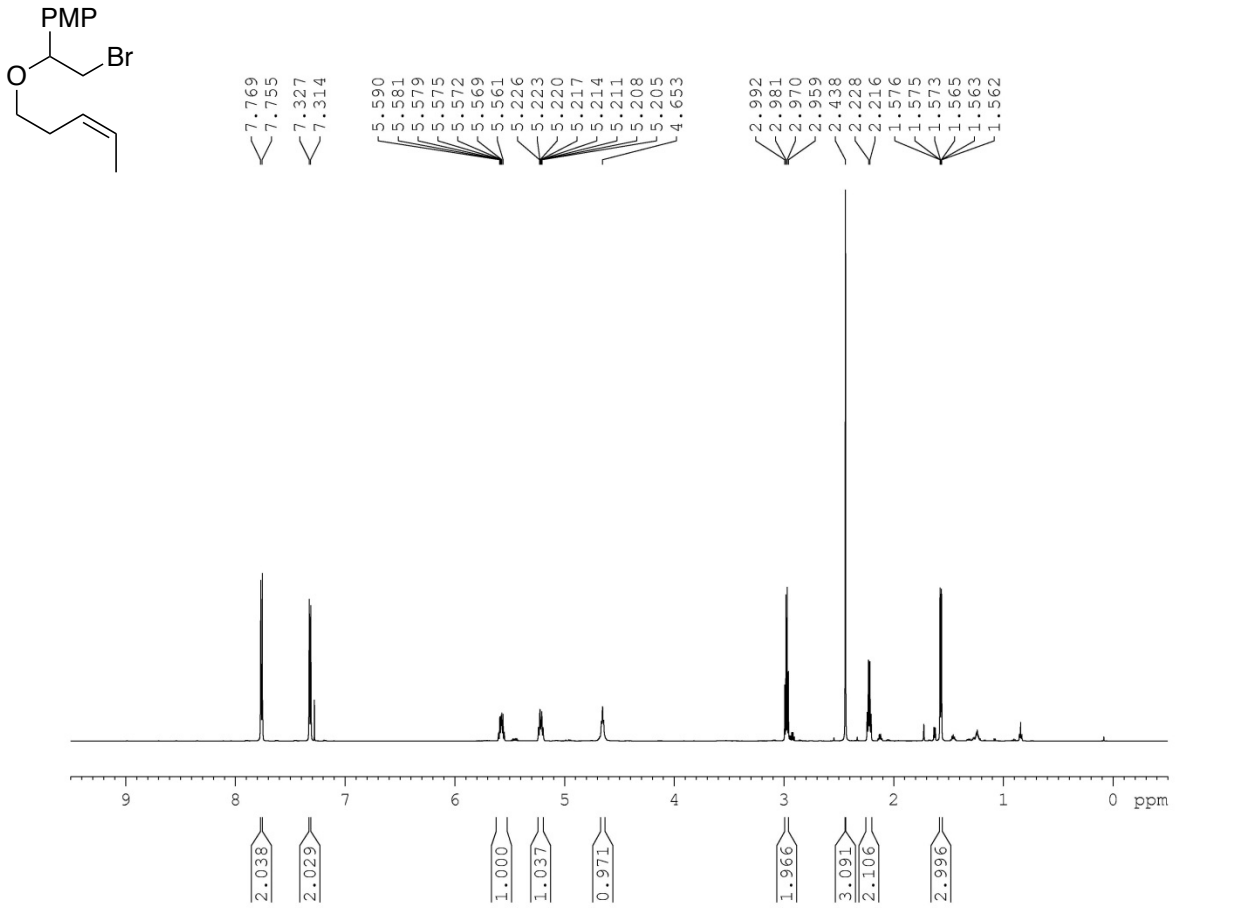
150
100
50
0
[ppm]


PMP
Br
O
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5.579
5.575
5.572
5.569
5.561
5.226
5.223
5.220
5.217
5.214
5.211
5.208
5.205
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2.981
2.970
2.959
2.438
2.228
2.216
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1.573
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1.563
1.562
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8
7
6
5
4
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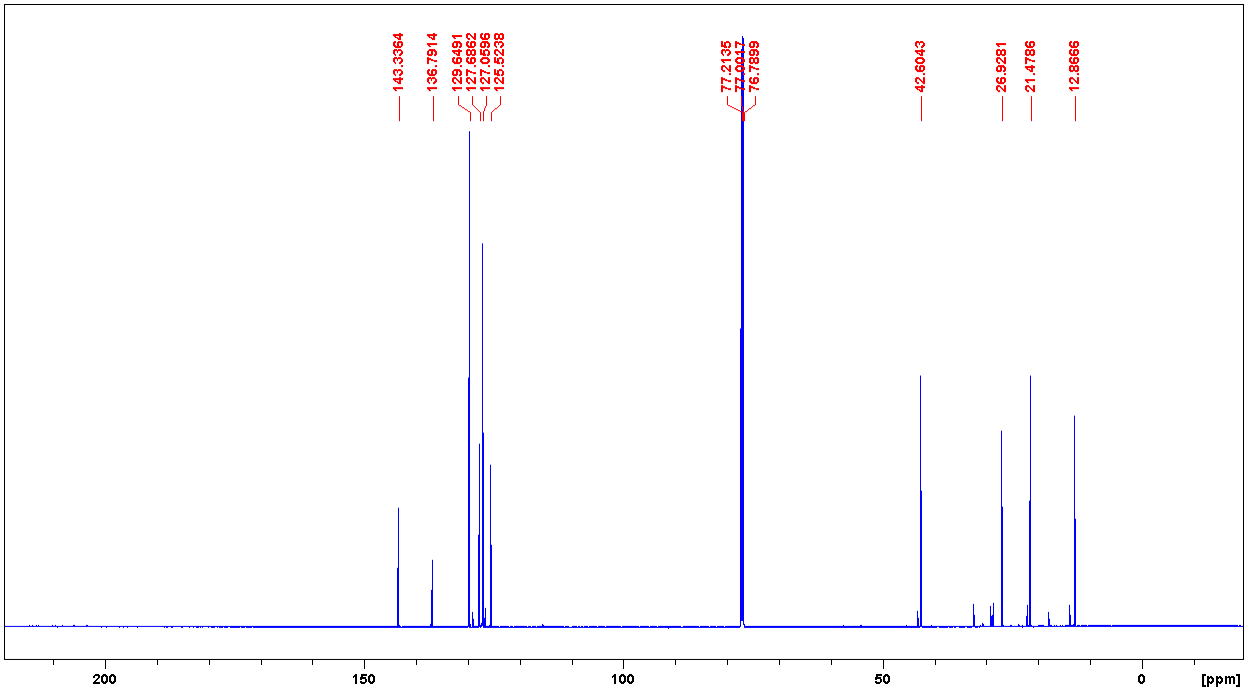
2.996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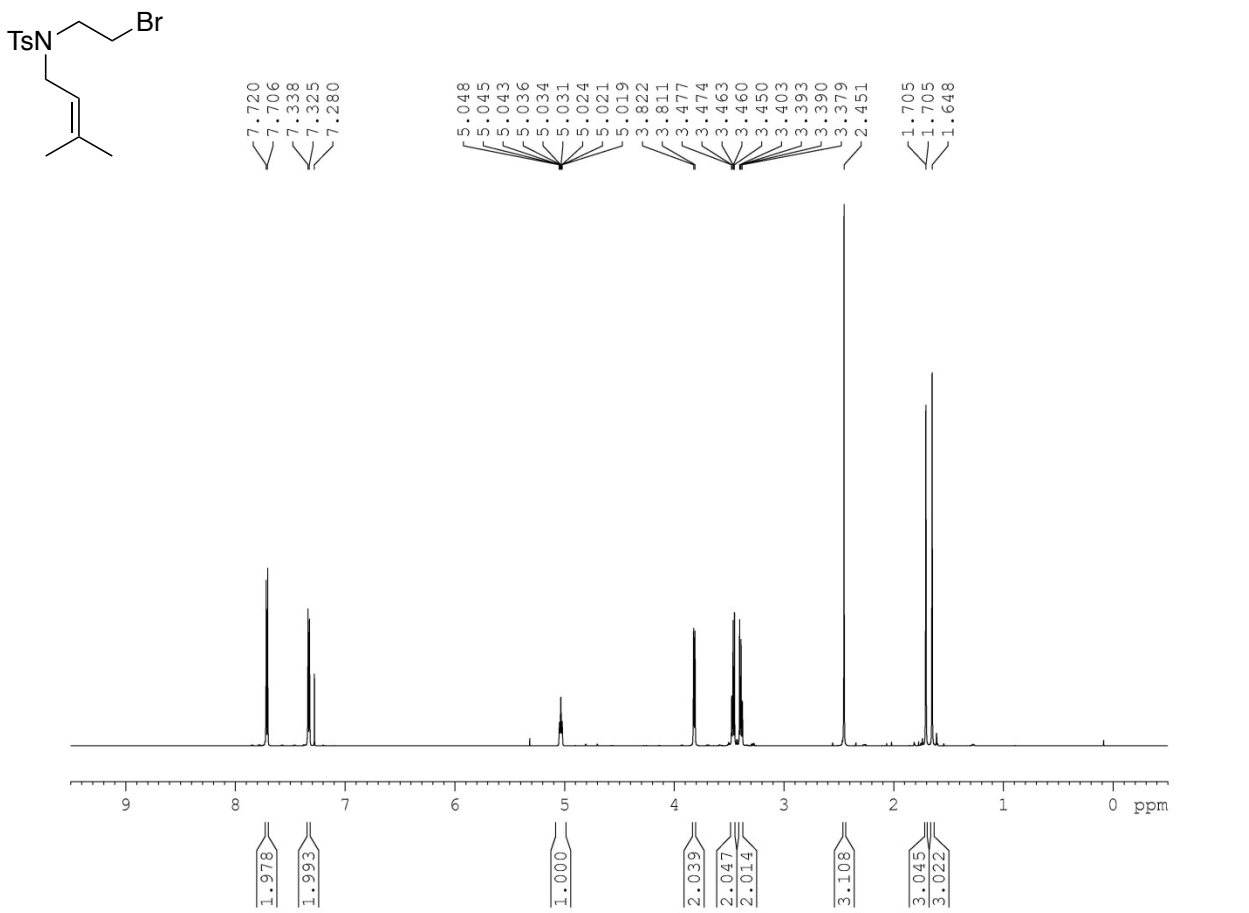
100
50
0
[ppm]


TsN
Br
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7.325
7.280
5.048
5.045
5.043
5.036
5.034
5.031
5.024
5.021
5.019
3.822
3.811
3.477
3.474
3.463
3.460
3.450
3.403
3.393
3.390
3.379
2.451
1.705
1.705
1.648
9
8
7
6
5
4
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ppm
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2.047
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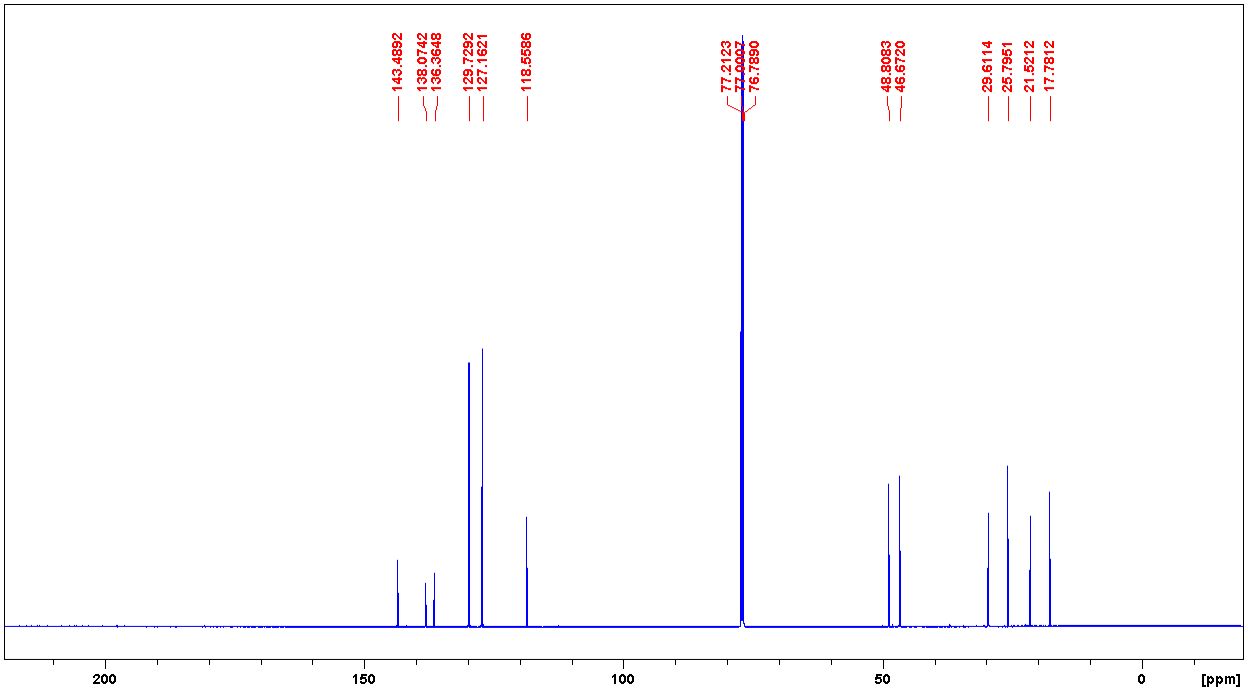
3.022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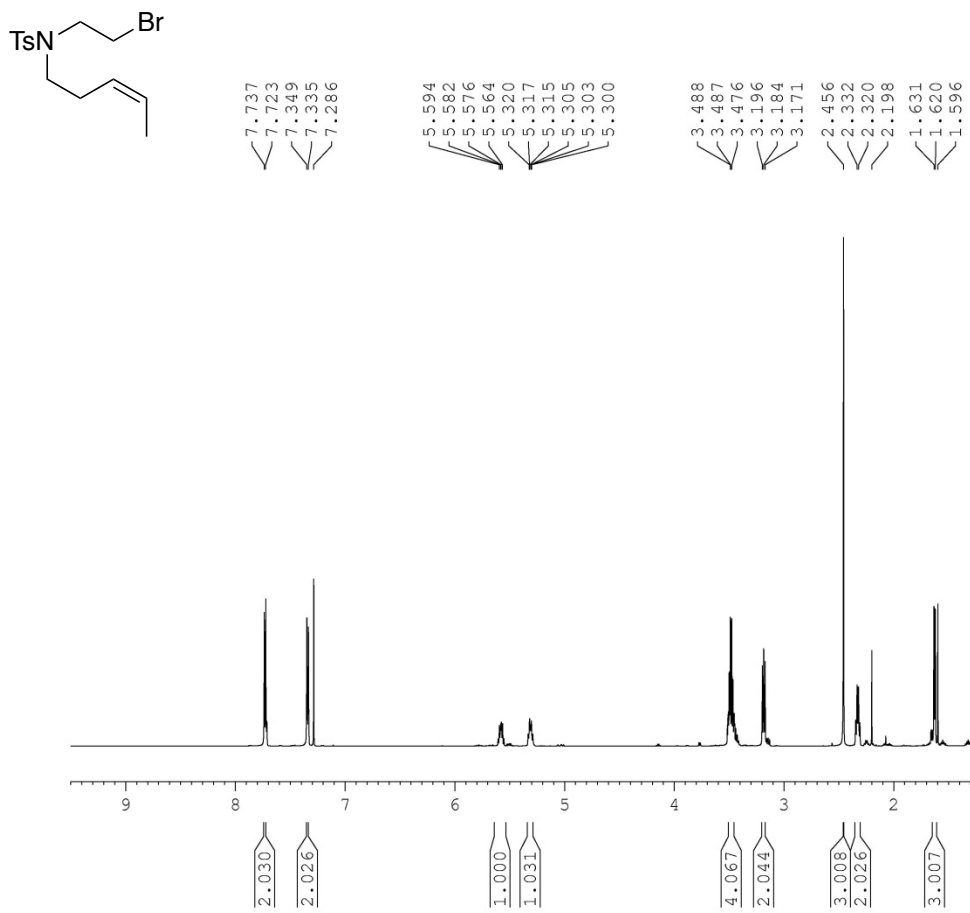
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Br
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7.335
7.286
5.594
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5.564
5.320
5.317
5.315
5.305
5.303
5.300
3.488
3.487
3.476
3.196
3.184
3.171
2.456
2.332
2.320
2.198
1.631
1.620
1.596
9
8
7
6
5
4
3
2
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ppm
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1.031
4.067
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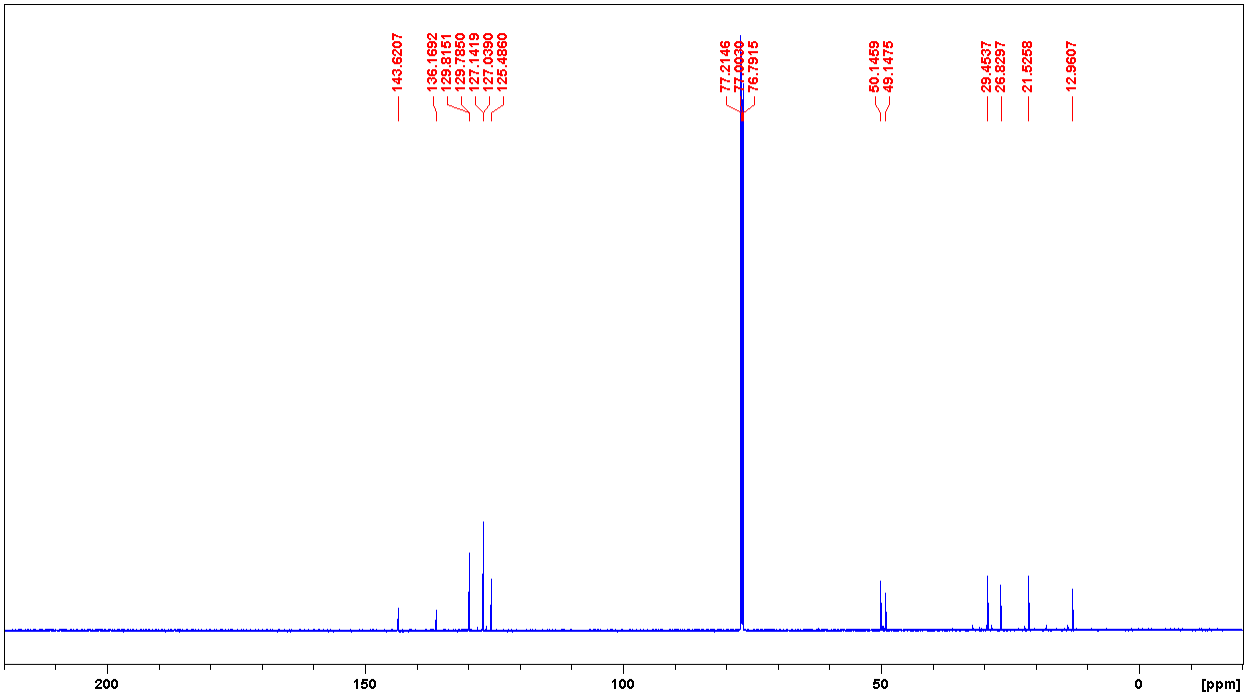
3.008
2.026
3.007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77.0030
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29.4537
26.8297
21.5258
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100
50
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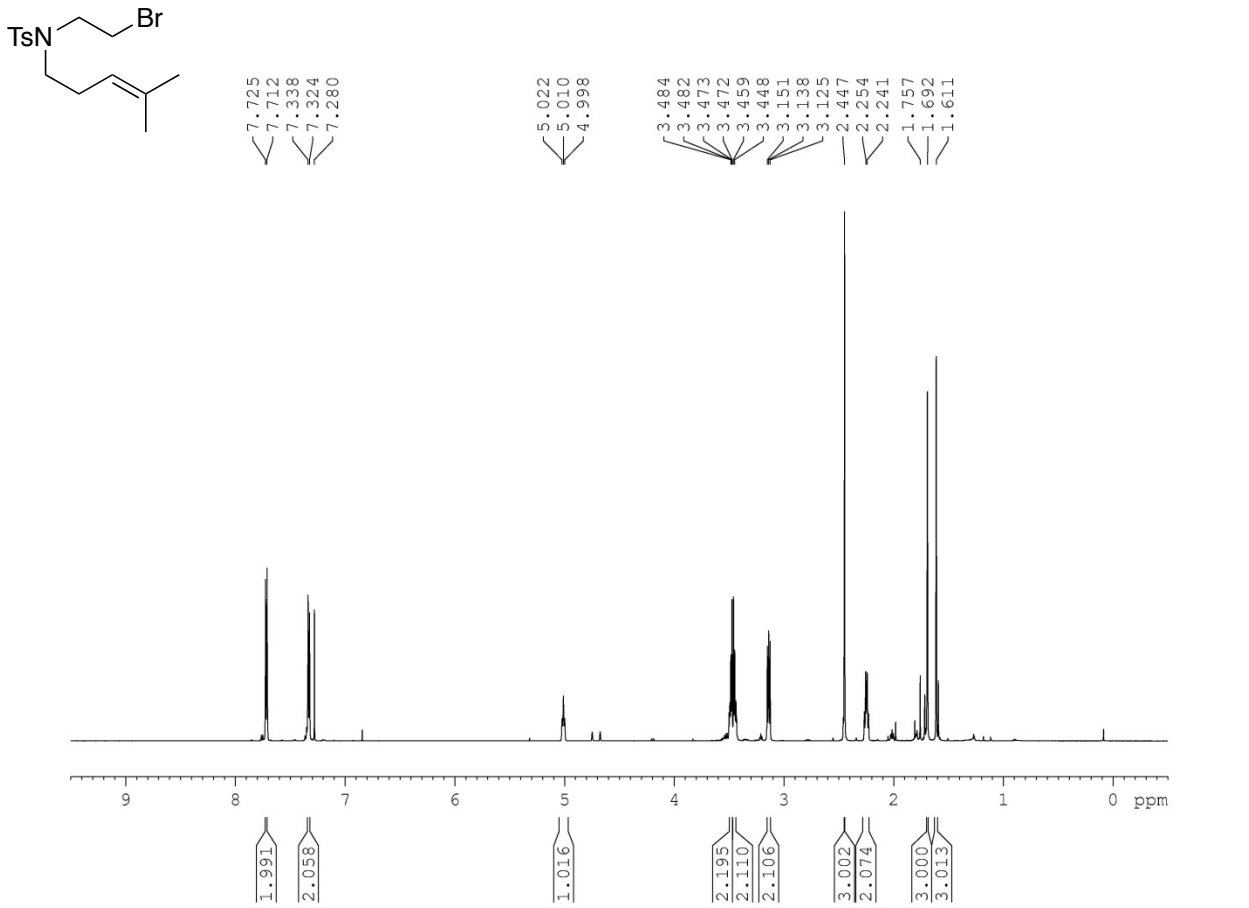
[ppm]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Br
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7.338
7.324
7.280
5.022
5.010
4.998
3.484
3.482
3.473
3.472
3.459
3.448
3.151
3.138
3.125
2.447
2.254
2.241
1.757
1.692
1.611
9
8
7
6
5
4
3
2
1
0 ppm
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2.195
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2.106
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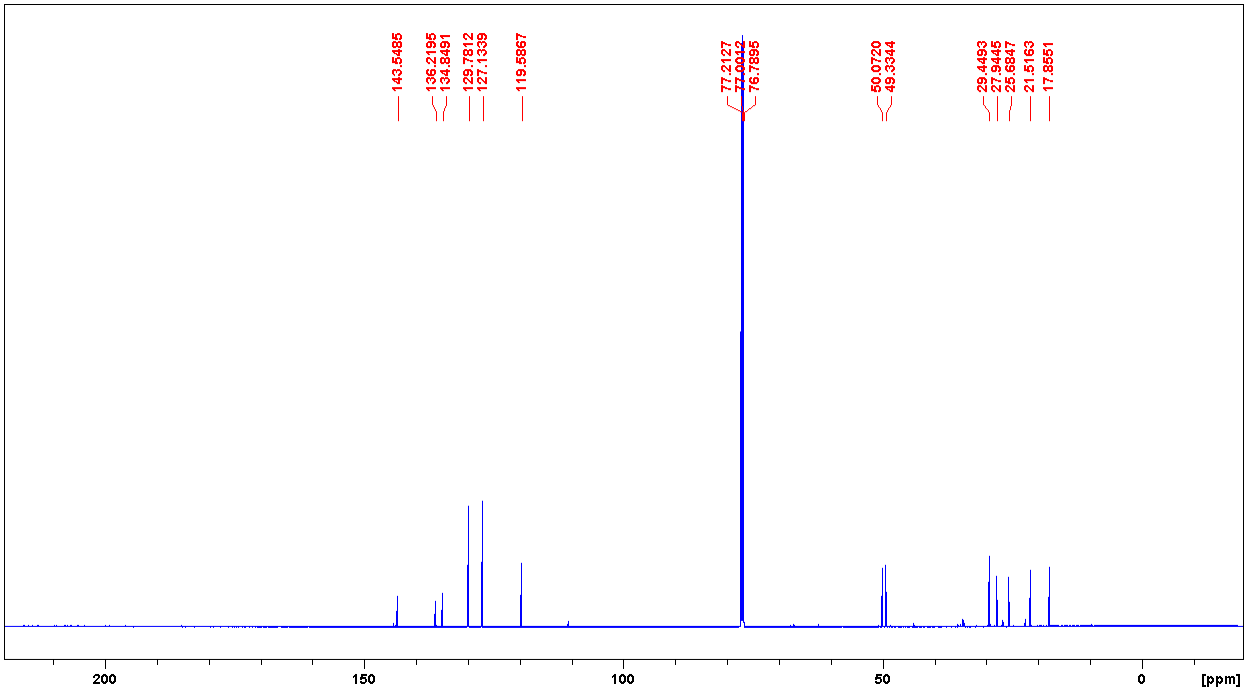
2.074
3.000
3.013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76.7895
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29.4493
27.9445
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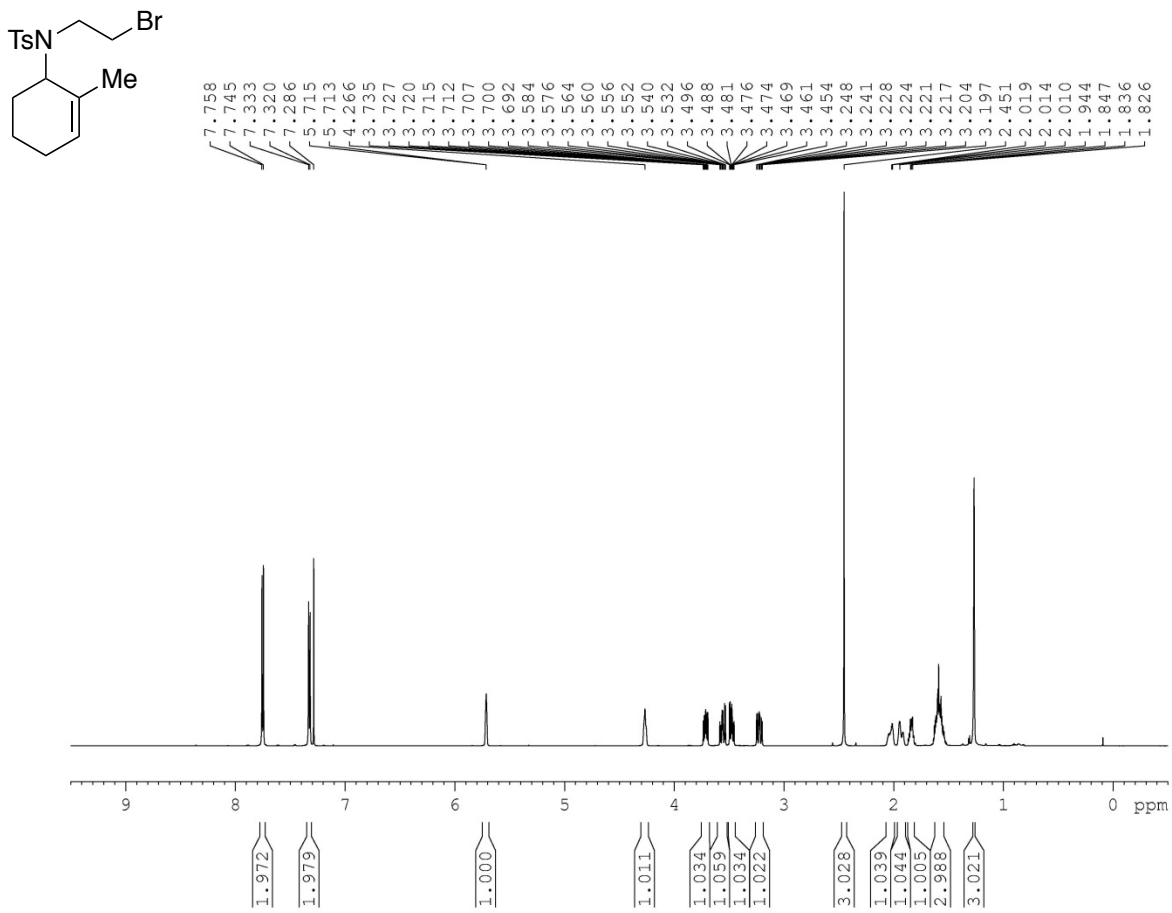
TsN
Br
Me
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7.320
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5.713
4.266
3.735
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3.715
3.712
3.707
3.700
3.692
3.584
3.576
3.564
3.560
3.556
3.552
3.540
3.532
3.496
3.488
3.481
3.476
3.474
3.469
3.461
3.454
3.248
3.241
3.228
3.224
3.221
3.217
3.204
3.197
2.451
2.019
2.014
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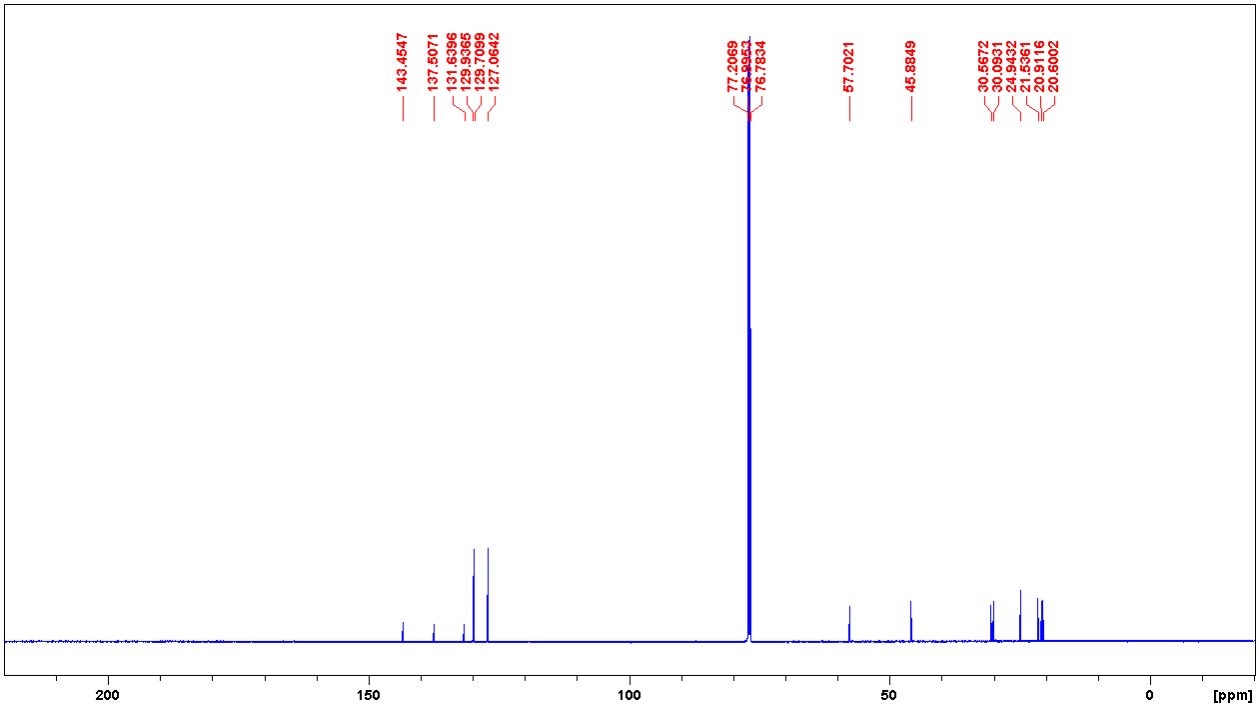
1.847
1.836
1.826
9
8
7
6
5
4
3
2
1
0 ppm
1.972
1.979
1.000
1.011
1.034
1.059
1.034
1.022
3.028
1.039
1.044
1.005
2.988
3.021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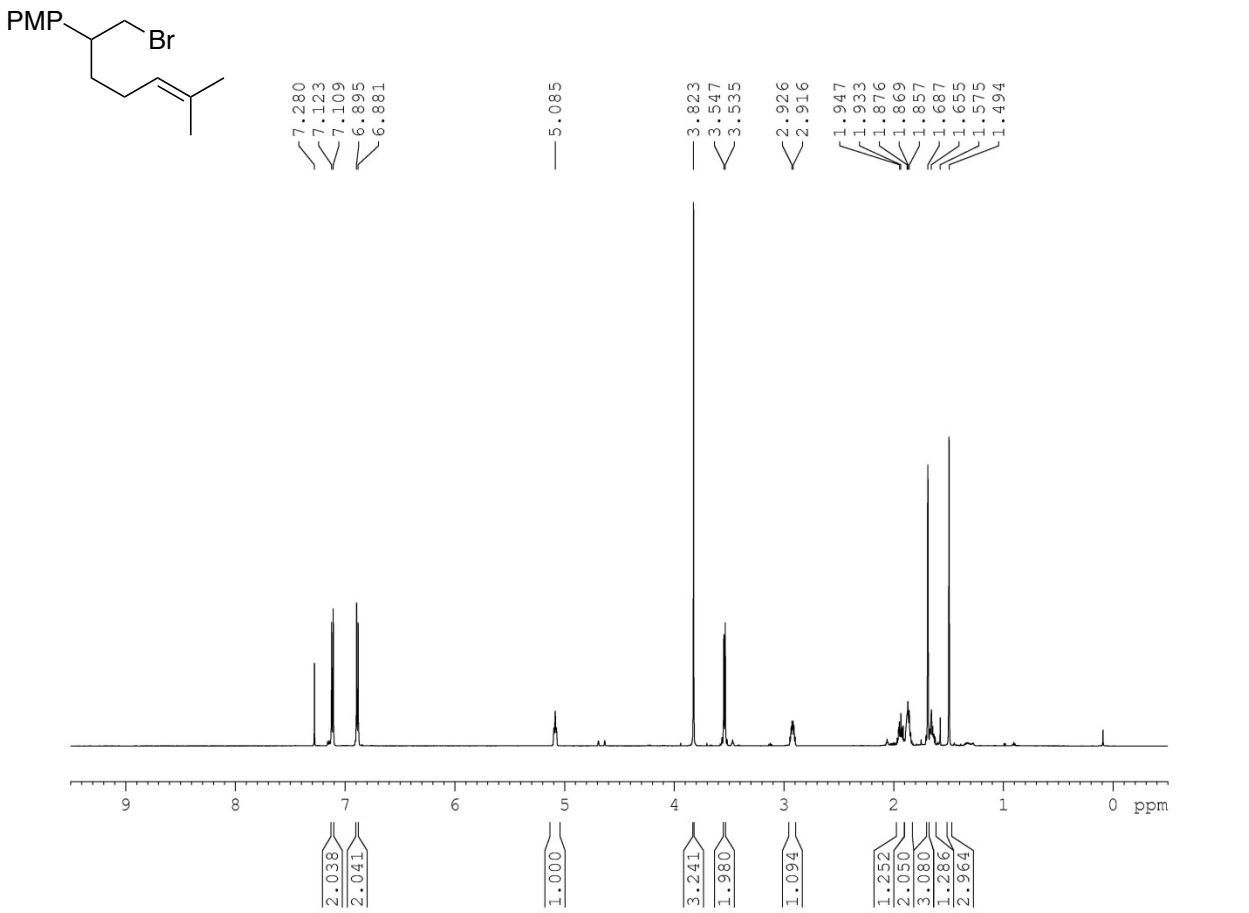
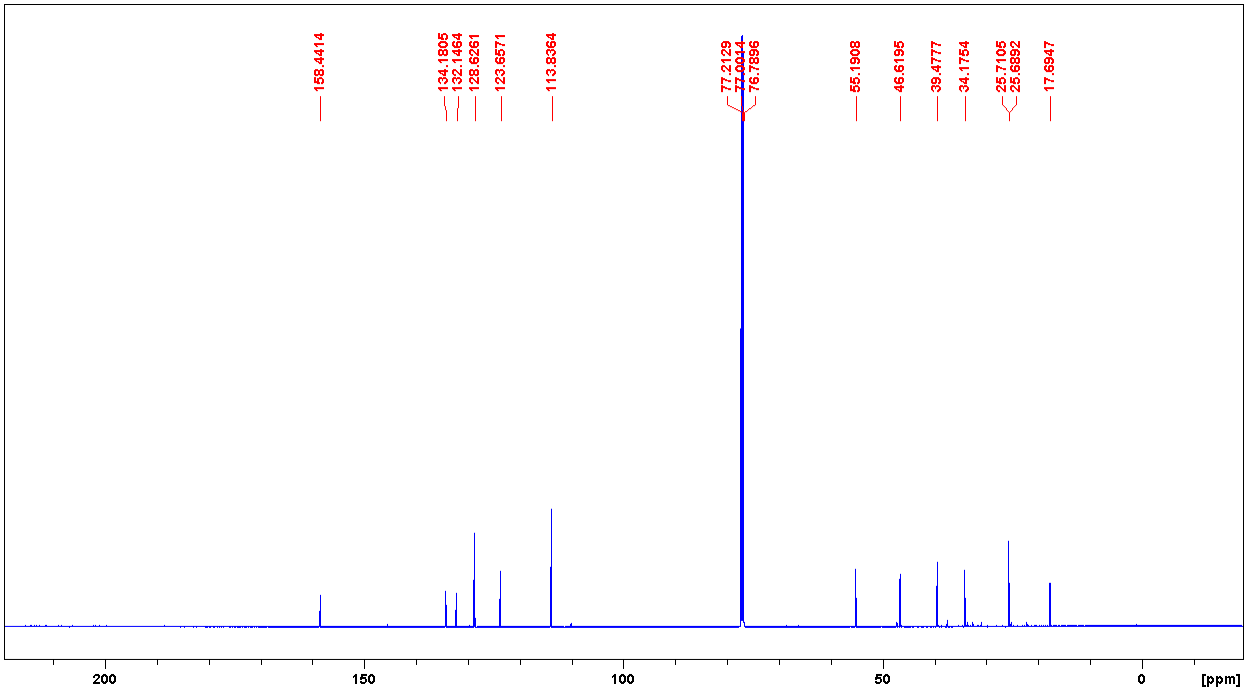
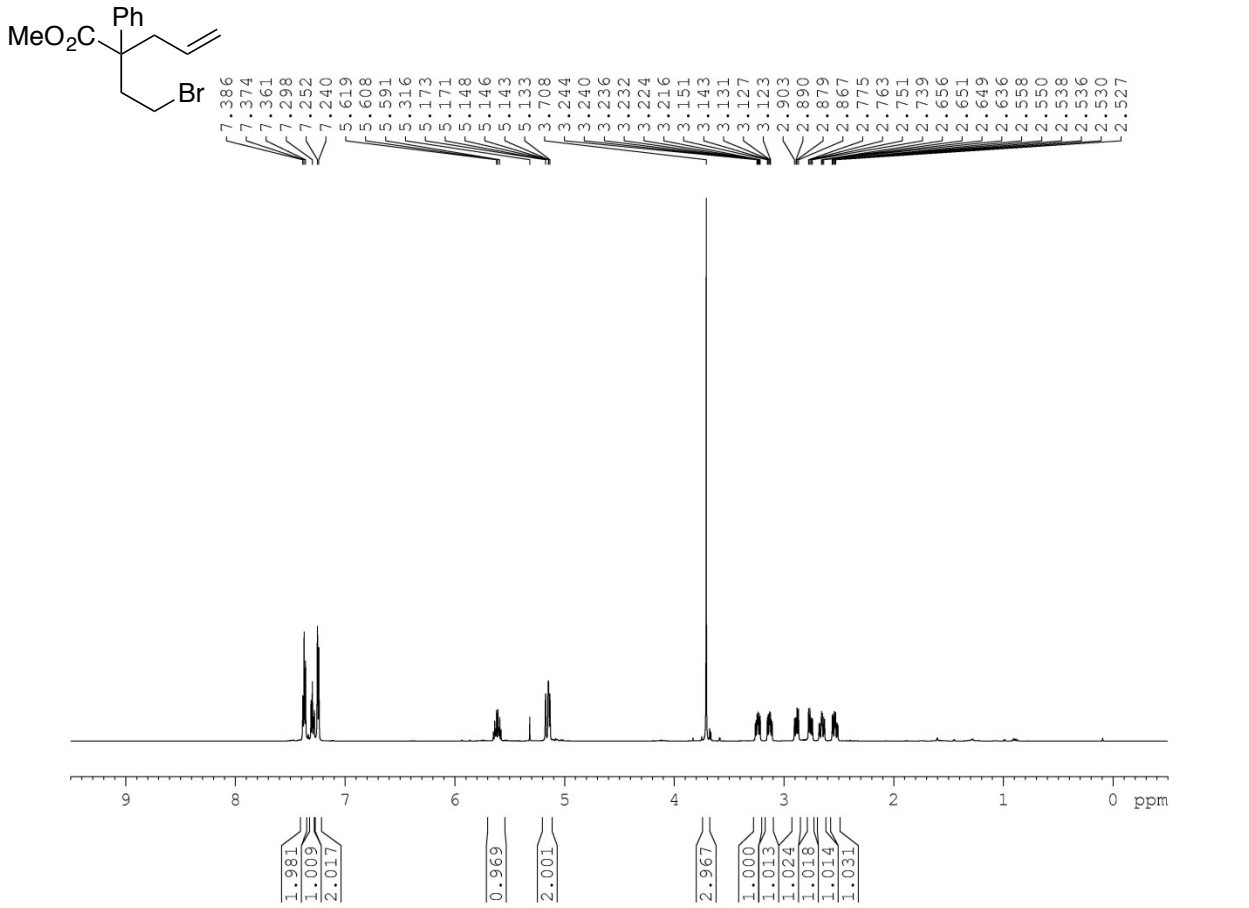
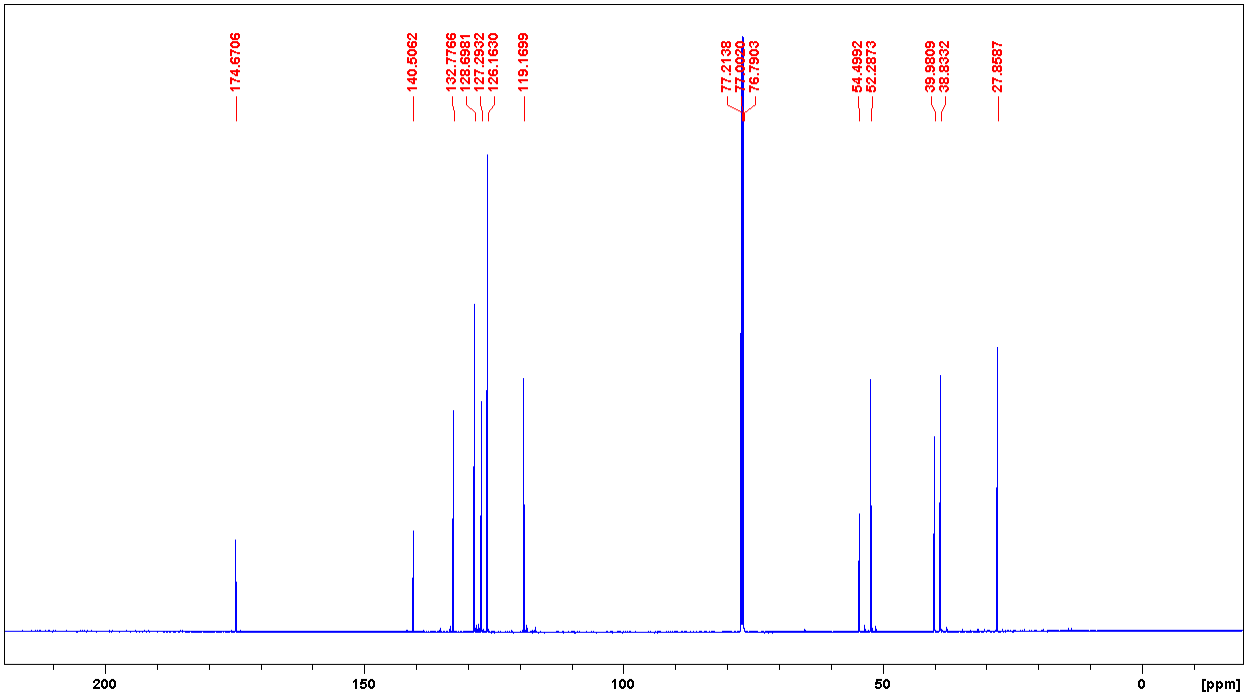
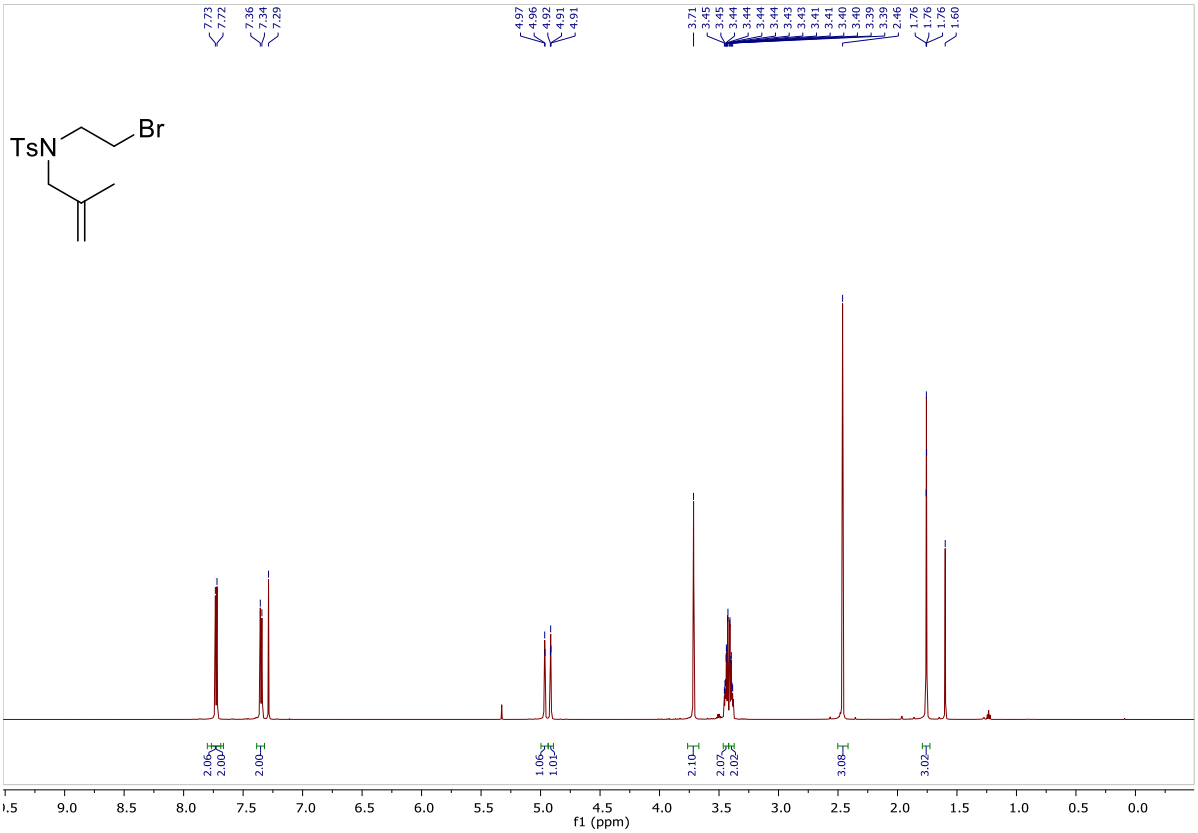
137.5071
131.6396
129.9365
129.7099
127.0642
77.2069
76.9563
76.7834
57.7021
45.8849
30.5672
30.0931
24.9432
21.5361
20.9116
20.6002
200
150
100
50
0
[ppm]

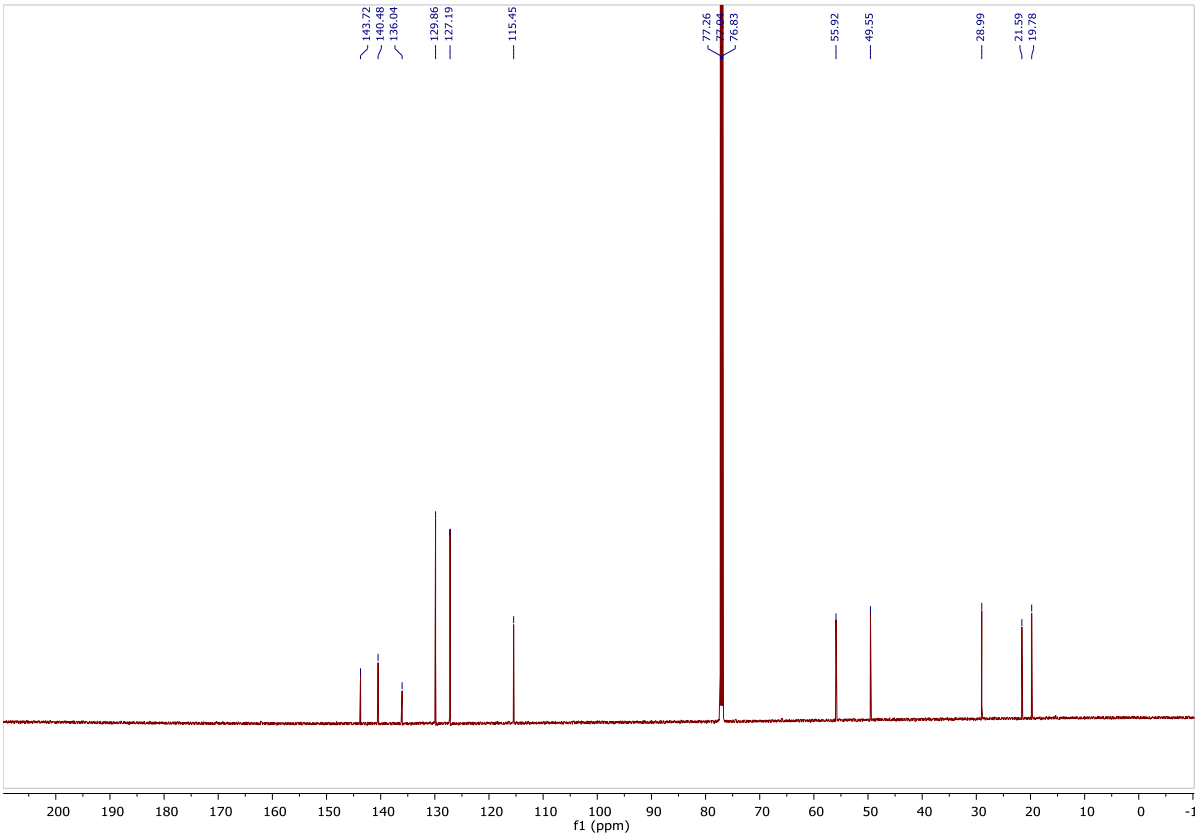

PMP
Br
7.280
7.123
7.109
6.895
6.881
5.085
3.823
3.547
3.535
2.926
2.916
1.947
1.933
1.876
1.869
1.857
1.687
1.655
1.575
1.494
9
8
7
6
5
4
3
2
1
0
ppm
2.038
2.041
1.000
3.241
1.980
1.094
1.252
2.050
3.080
1.286
2.964

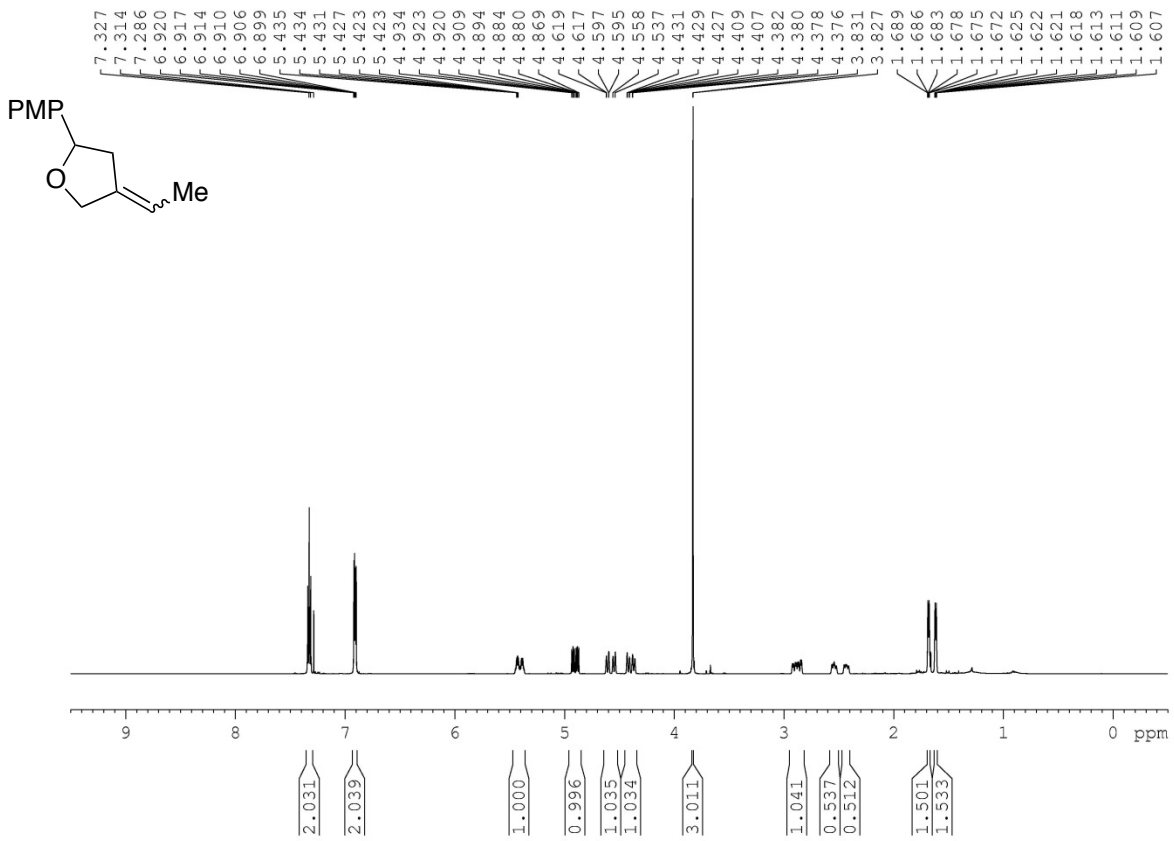

158.4414
134.1805
132.1464
128.6261
123.6571
113.8364
77.2129
77.0014
76.7896
55.1908
46.6195
39.4777
34.1754
25.7105
25.6892
17.6947
200
150
100
50
0
[ppm]

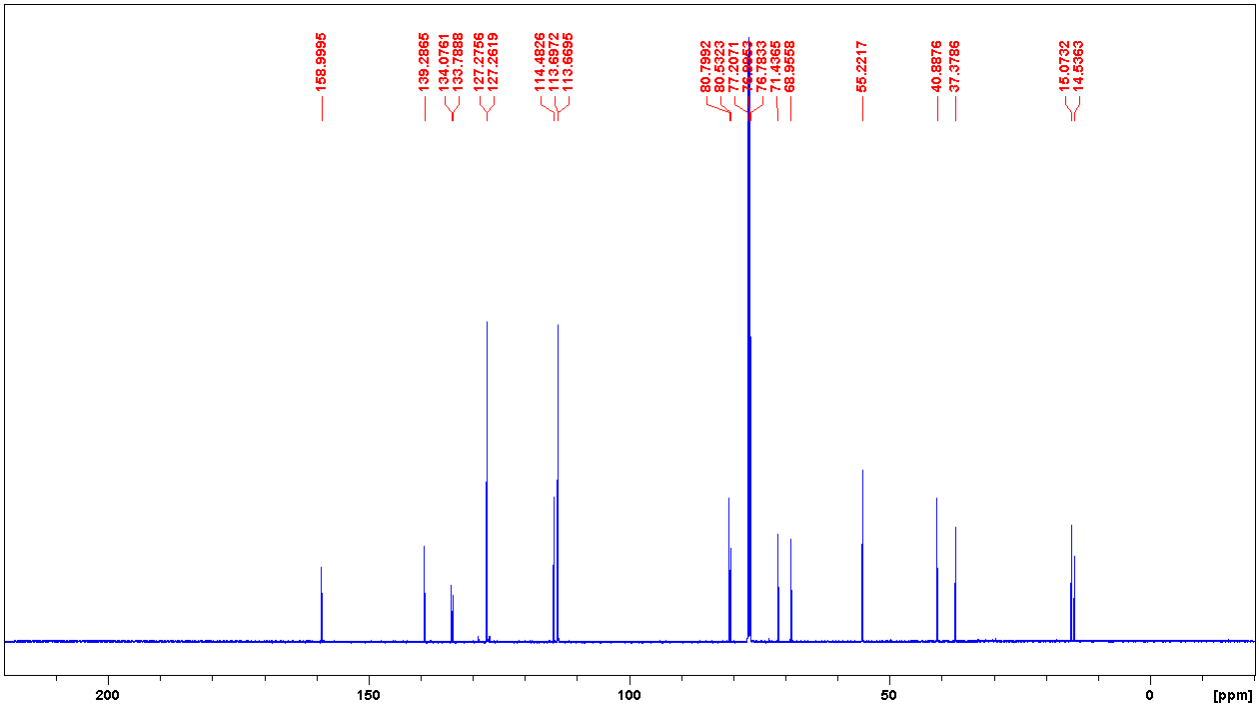

MeO2C
Ph
Br
7.386
7.374
7.361
7.298
7.252
7.240
5.619
5.608
5.591
5.316
5.173
5.171
5.148
5.146
5.143
5.133
3.708
3.244
3.240
3.236
3.232
3.224
3.216
3.151
3.143
3.131
3.127
3.123
2.903
2.890
2.879
2.867
2.775
2.763
2.751
2.739
2.656
2.651
2.649
2.636
2.558
2.550
2.538
2.536
2.530
2.527
9
8
7
6
5
4
3
2
1
0 ppm
1.981
1.009
2.017
0.969
2.001
2.967
1.000
1.013
1.024
1.018
1.014
1.031

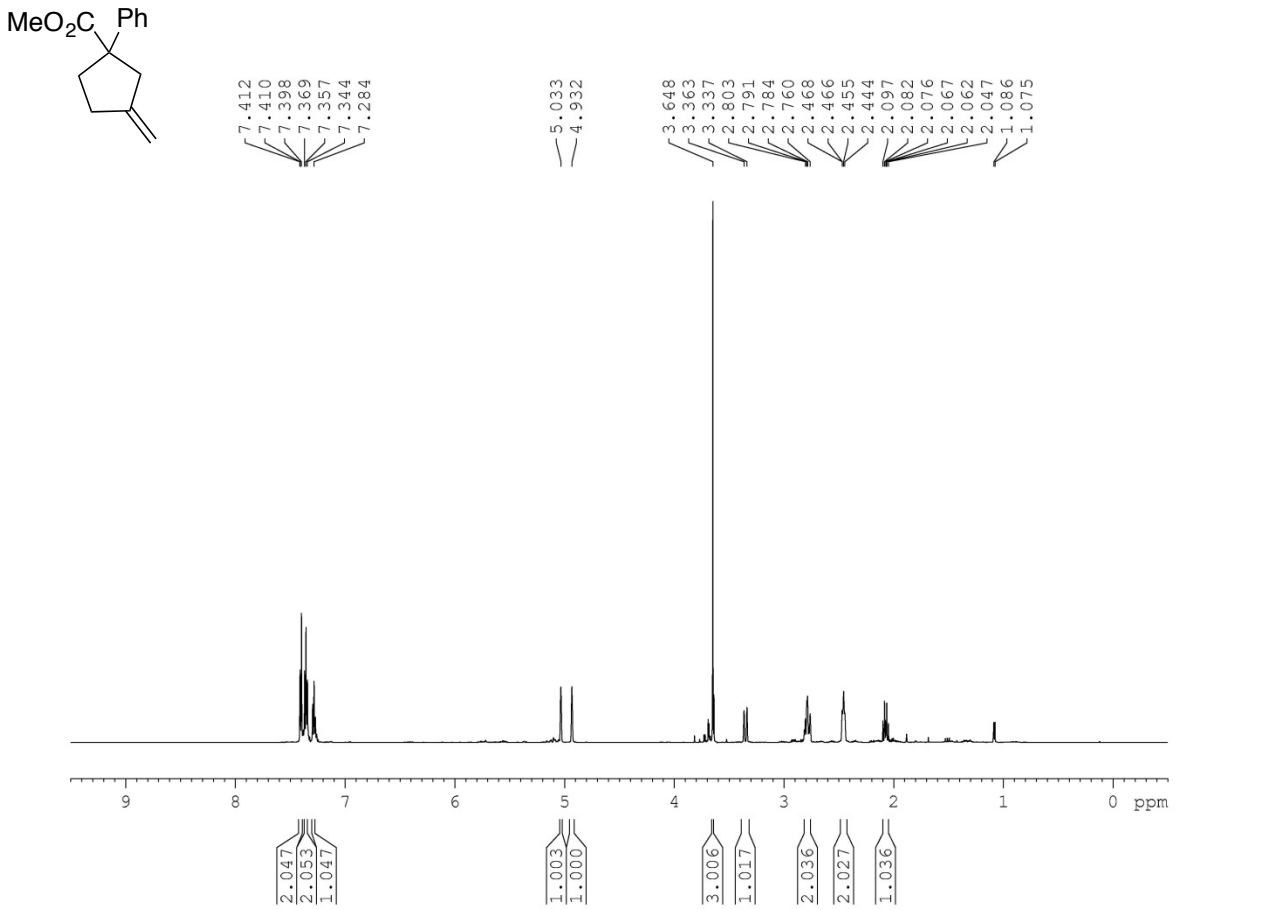

174.6706
140.5062
132.7766
128.6981
127.2932
126.1630
119.1689
77.2138
77.0020
76.7903
54.4992
52.2873
39.9809
38.8332
27.8587
200
150
100
50
0
[ppm]

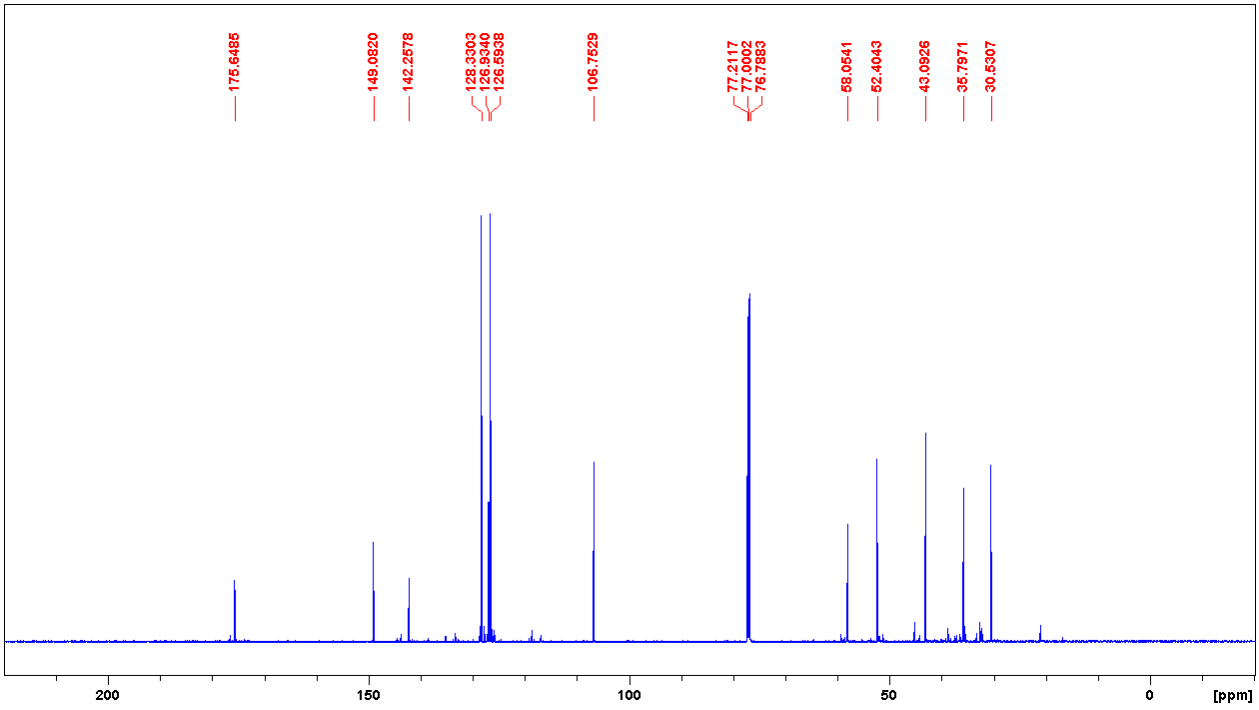

7.73
7.72
7.36
7.34
7.29
4.97
4.96
4.92
4.91
4.91
3.71
3.45
3.45
3.44
3.44
3.44
3.43
3.43
3.41
3.41
3.40
3.40
3.39
3.39
2.46
1.76
1.76
1.76
1.60
TsN
Br
2.06
2.00
2.00
1.06
1.01
2.10
2.07
2.02
3.08
3.02
f1 (ppm)

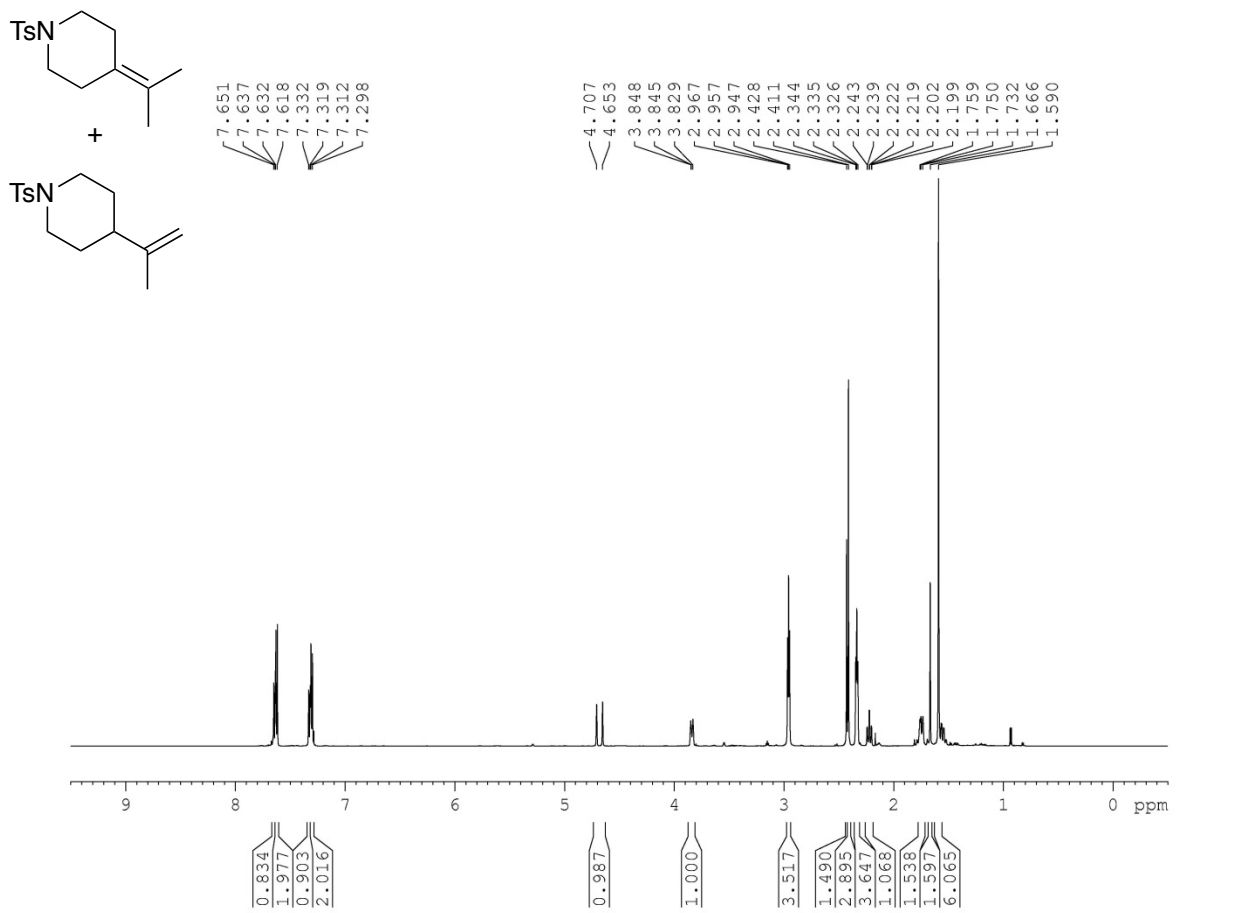

143.72
140.48
136.04
129.86
127.19
115.45
77.26
77.04
76.83
55.92
49.55
28.99
21.59
19.78
f1 (ppm)

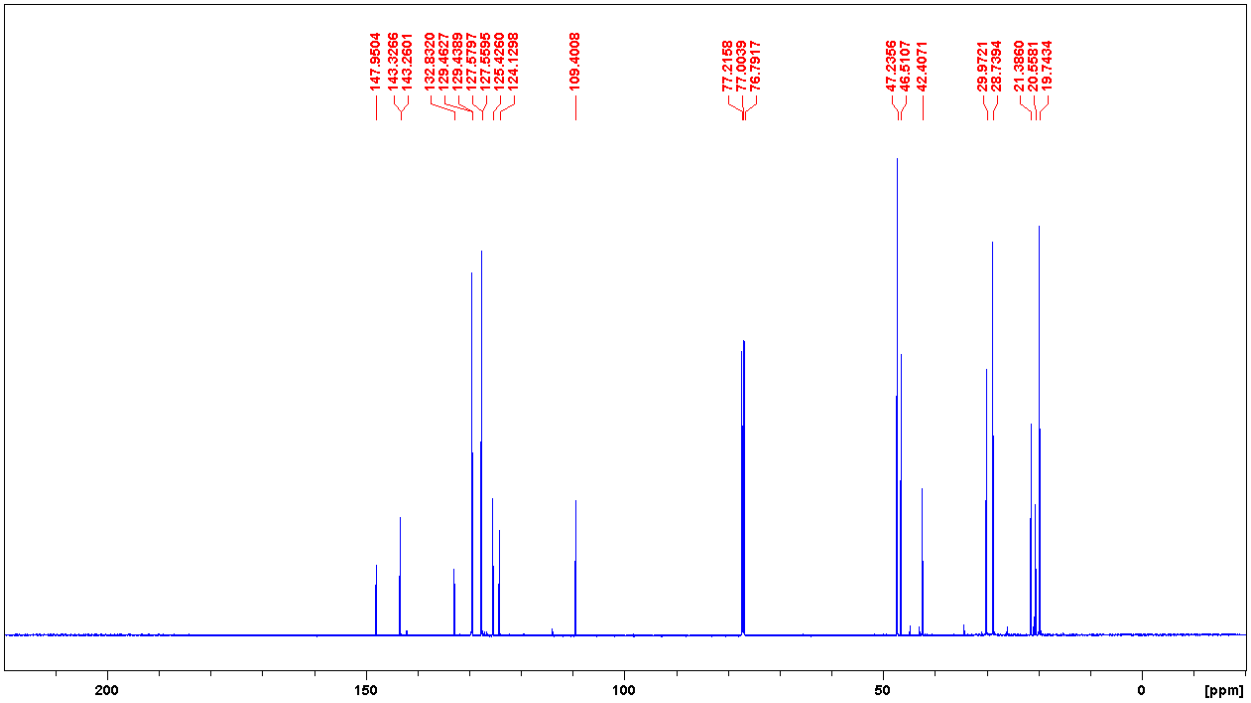

7.327
7.314
7.286
6.920
6.917
6.914
6.910
6.906
6.899
5.435
5.434
5.431
5.427
5.423
5.423
4.934
4.923
4.920
4.909
4.894
4.884
4.880
4.869
4.619
4.617
4.597
4.595
4.558
4.537
4.431
4.429
4.427
4.409
4.407
4.382
4.380
4.378
4.376
3.831
3.827
1.689
1.686
1.683
1.678
1.675
1.672
1.625
1.622
1.621
1.618
1.613
1.611
1.609
1.607
PMP
O
Me
9
8
7
6
5
4
3
2
1
0
ppm
2.031
2.039
1.000
0.996
1.035
1.034
3.011
1.041
0.537
0.512
1.501
1.533

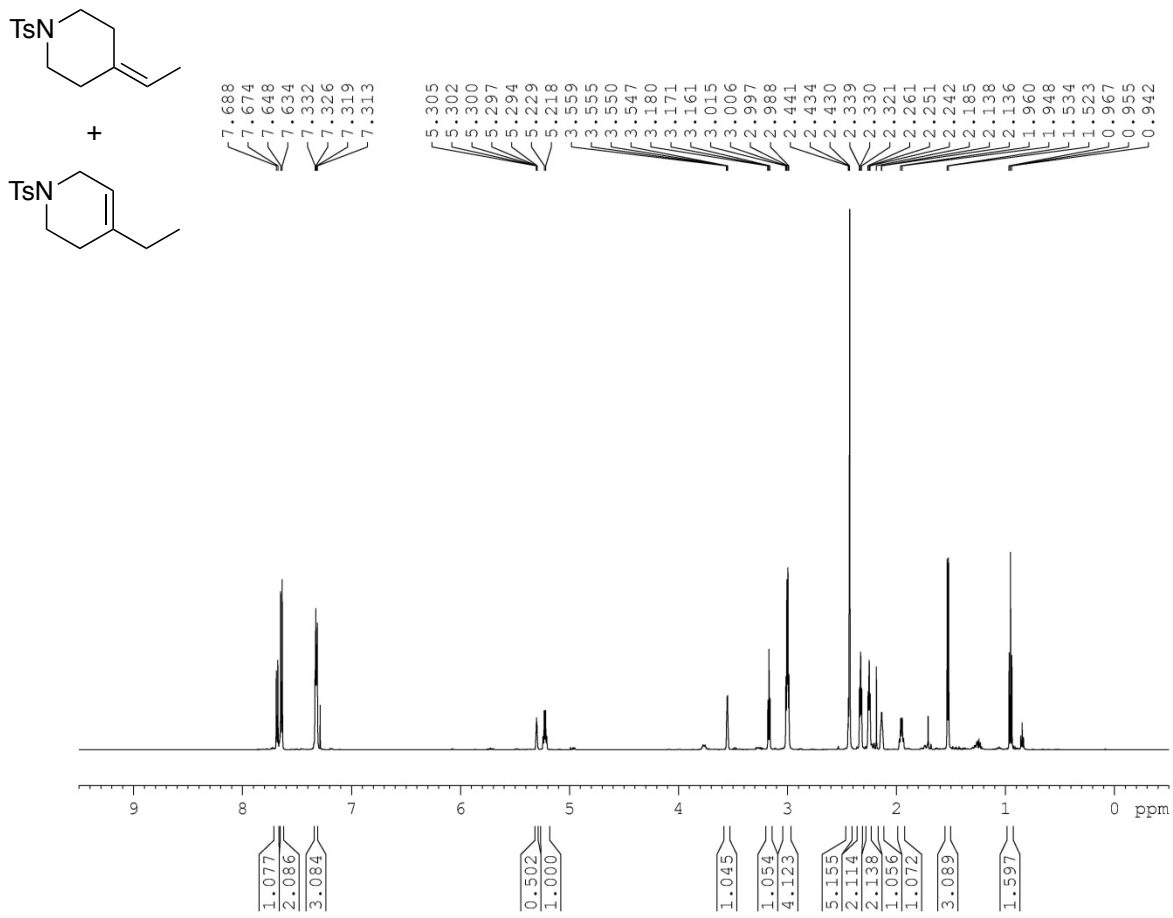

158.9995
139.2865
134.0761
133.7888
127.2756
127.2619
114.4826
113.8972
113.8695
80.7982
80.5323
77.2071
76.7833
71.4365
68.9558
55.2217
40.8876
37.3786
15.0732
14.5363
200
150
100
50
0
[ppm]

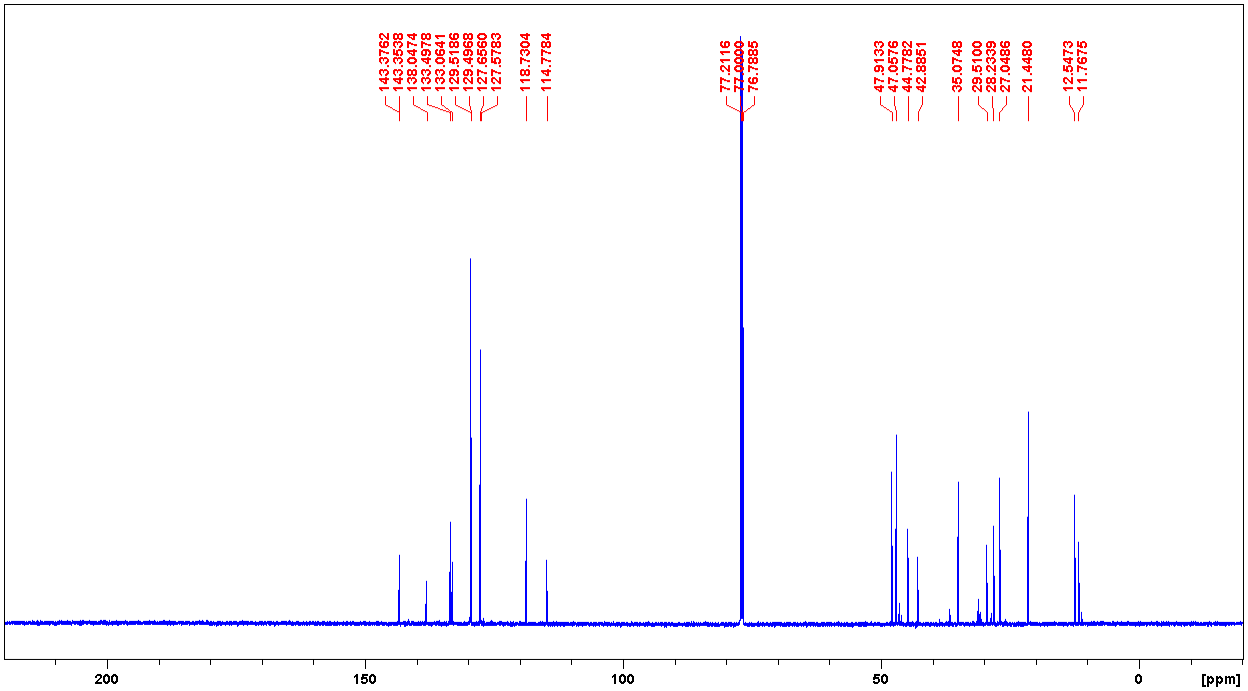

MeO2C
Ph
7.412
7.410
7.398
7.369
7.357
7.344
7.284
5.033
4.932
3.648
3.363
3.337
2.803
2.791
2.784
2.760
2.468
2.466
2.455
2.444
2.097
2.082
2.076
2.067
2.062
2.047
1.086
1.075
9
8
7
6
5
4
3
2
1
0 ppm
2.047
2.053
1.047
1.003
1.000
3.006
1.017
2.036
2.027
1.036

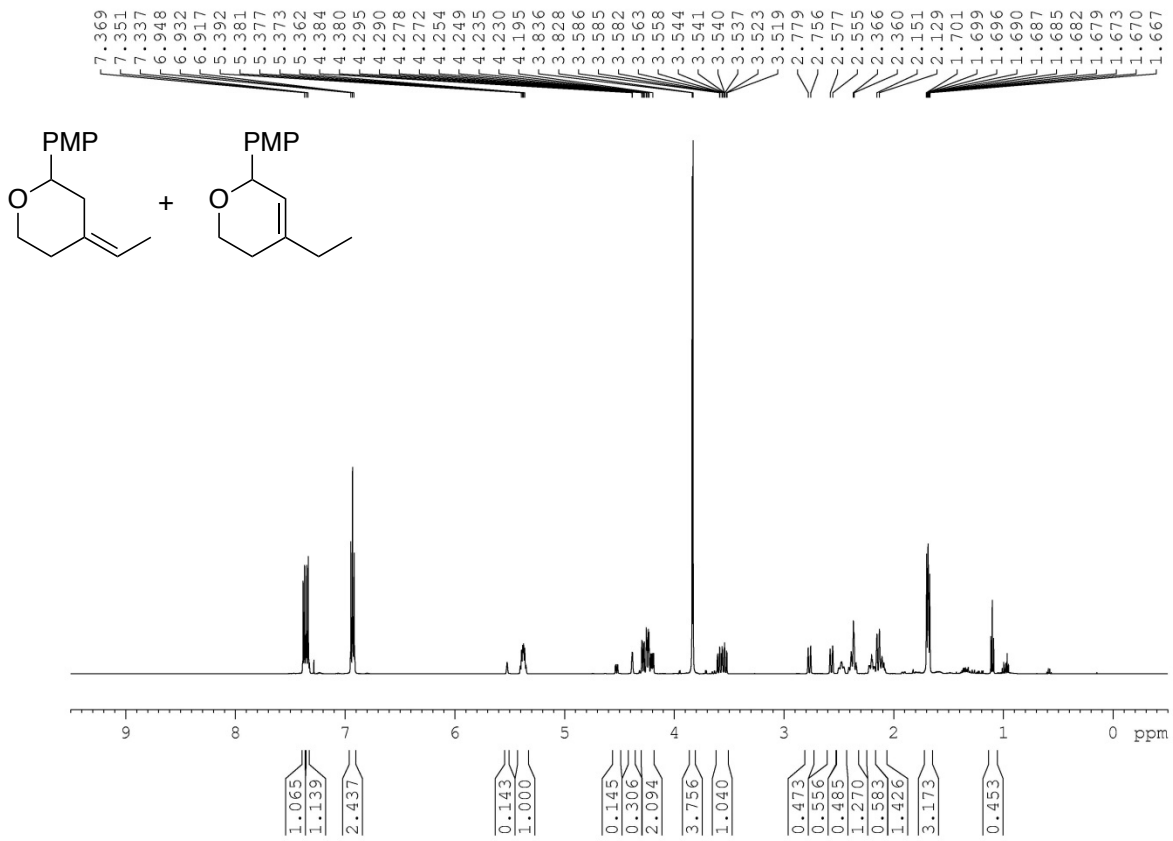

175.6485
149.0820
142.2578
128.3303
126.9340
126.5938
106.7529
77.2117
77.0002
76.7883
58.0541
52.4043
43.0926
35.7971
30.5307
200
150
100
50
0
[ppm]

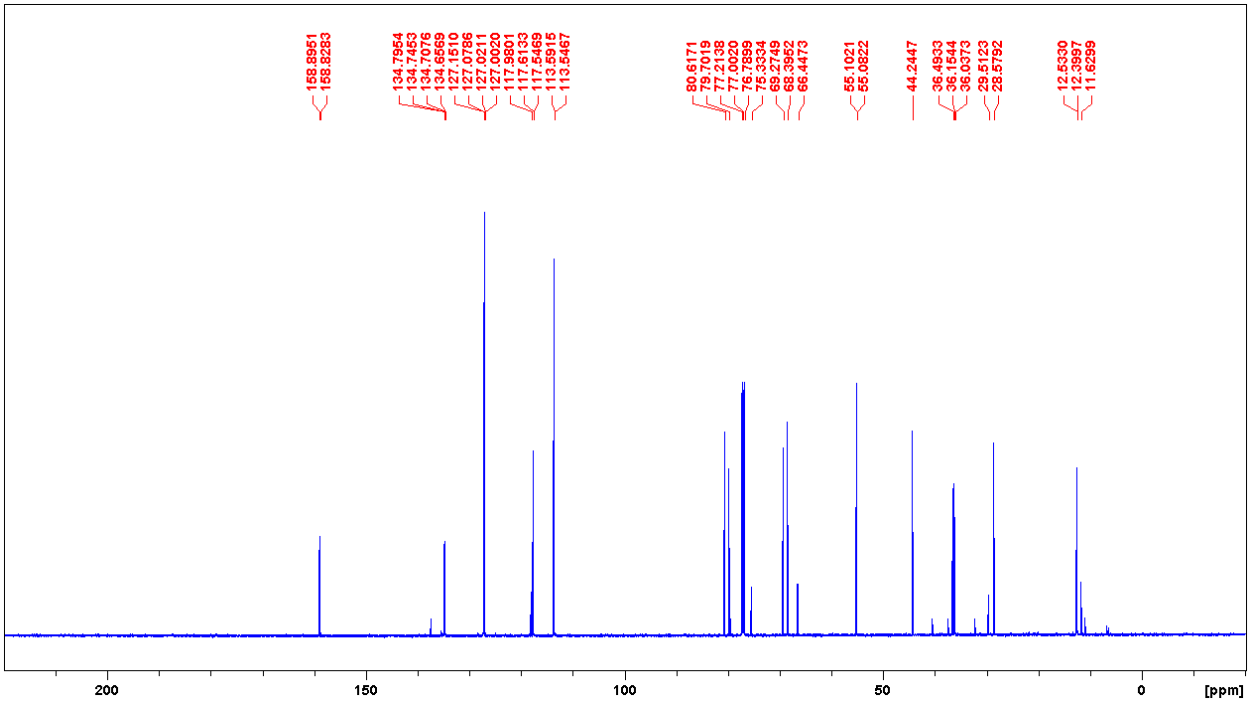

TsN
+
TsN
7.651
7.637
7.632
7.618
7.332
7.319
7.312
7.298
4.707
4.653
3.848
3.845
3.829
2.967
2.957
2.947
2.428
2.411
2.344
2.335
2.326
2.243
2.239
2.222
2.219
2.202
2.199
1.759
1.750
1.732
1.666
1.590
9
8
7
6
5
4
3
2
1
0 ppm
0.834
1.977
0.903
2.016
0.987
1.000
3.517
1.490
2.895
3.647
1.068
1.538
1.597
6.065


147.5504
143.3266
143.2601
132.8320
129.4627
129.4389
127.5797
127.5595
125.4260
124.1298
109.4008
77.2158
77.0039
76.7917
47.2356
46.5107
42.4071
29.9721
28.7394
21.3860
20.5581
19.7434
200
150
100
50
0
[ppm]


TsN
+
TsN
7.688
7.674
7.648
7.634
7.332
7.326
7.319
7.313
5.305
5.302
5.300
5.297
5.294
5.229
5.218
3.559
3.555
3.550
3.547
3.180
3.171
3.161
3.015
3.006
2.997
2.988
2.441
2.434
2.430
2.339
2.330
2.321
2.261
2.251
2.242
2.185
2.138
2.136
1.960
1.948
1.534
1.523
0.967
0.955
0.942
9
8
7
6
5
4
3
2
1
0 ppm
1.077
2.086
3.084
0.502
1.000
1.045
1.054
4.123
5.155
2.114
2.138
1.056
1.072
3.089
1.597


143.3762
143.3538
138.0474
133.4878
133.3641
129.5186
129.4968
127.6560
127.5783
118.7304
114.7784
77.2116
77.0000
76.7885
47.9133
47.0576
44.7782
42.8851
35.0748
29.5100
28.2339
27.0486
21.4480
12.5473
11.7675
200
150
100
50
0
[ppm]


7.369
7.351
7.337
6.948
6.932
6.917
5.392
5.381
5.377
5.373
5.362
4.384
4.380
4.295
4.290
4.278
4.272
4.254
4.249
4.235
4.230
4.195
3.836
3.828
3.586
3.585
3.582
3.563
3.558
3.544
3.541
3.540
3.537
3.523
3.519
2.779
2.756
2.577
2.555
2.366
2.360
2.151
2.129
1.701
1.699
1.696
1.690
1.687
1.685
1.682
1.679
1.673
1.670
1.667
PMP
O
+
PMP
O
9
8
7
6
5
4
3
2
1
0
ppm
1.065
1.139
2.437
0.143
1.000
0.145
0.306
2.094
3.756
1.040
0.473
0.556
0.485
1.270
0.583
1.426
3.173
0.453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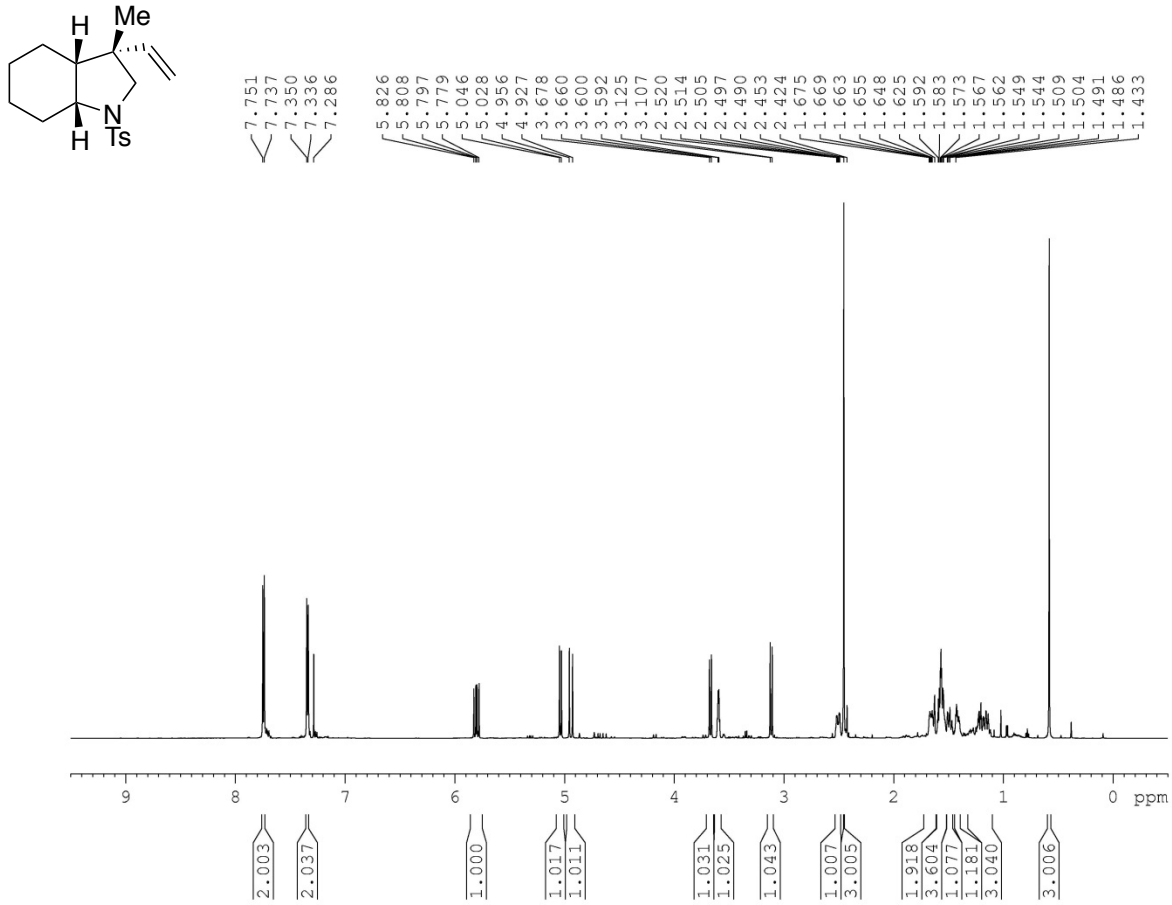
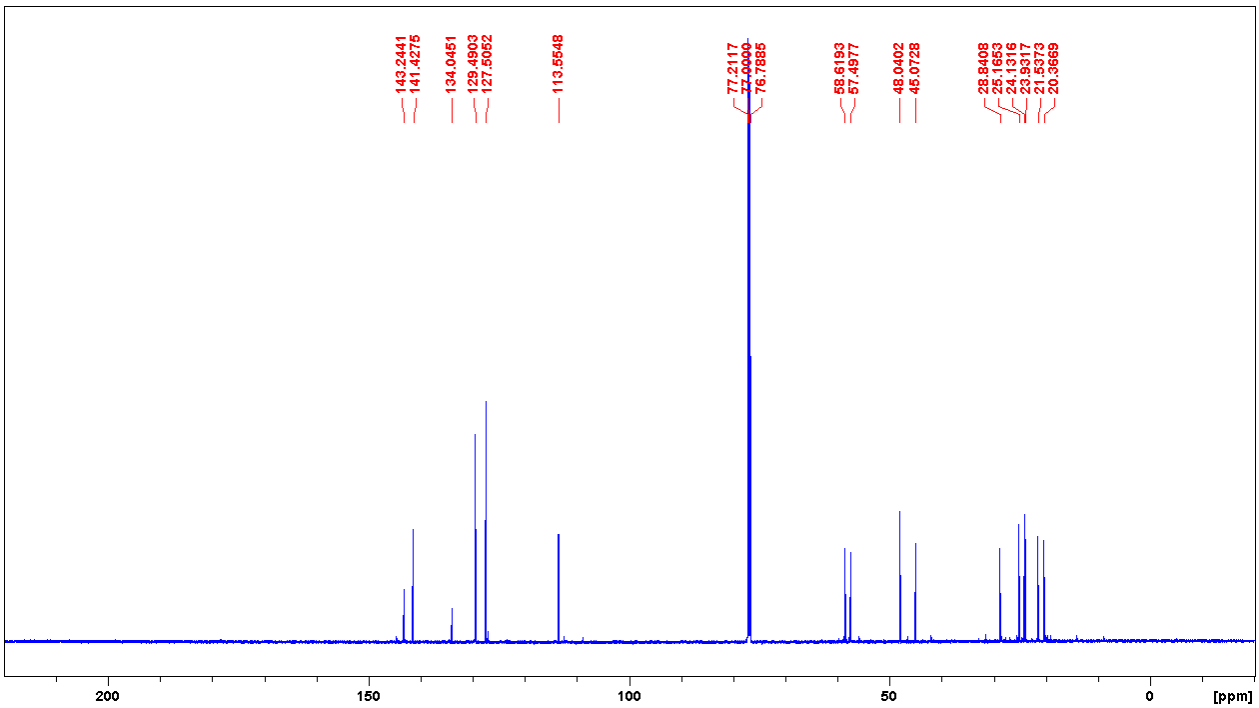
158.8283
134.7954
134.7453
134.7076
134.6669
134.4510
127.1786
127.0786
127.0211
127.0020
117.9801
117.6133
117.5469
113.5915
113.5467
80.6171
79.7019
77.2138
77.0020
76.7899
75.3334
69.2749
68.3962
66.4473
55.1021
55.0822
44.2447
36.4933
36.1544
36.0373
29.5123
28.5792
12.5330
12.3997
11.6299
200
150
100
50
0
[ppm]


H
Me
N
Ts
H
7.751
7.737
7.350
7.336
7.286
5.826
5.808
5.797
5.779
5.046
5.028
4.956
4.927
3.678
3.660
3.600
3.592
3.125
3.107
2.520
2.514
2.505
2.497
2.490
2.453
2.424
1.675
1.669
1.663
1.655
1.648
1.625
1.592
1.583
1.573
1.567
1.562
1.549
1.544
1.509
1.504
1.491
1.486
1.433
9
8
7
6
5
4
3
2
1
0 ppm
2.003
2.037
1.000
1.017
1.011
1.031
1.025
1.043
1.007
3.005
1.918
3.604
1.077
1.181
3.040
3.006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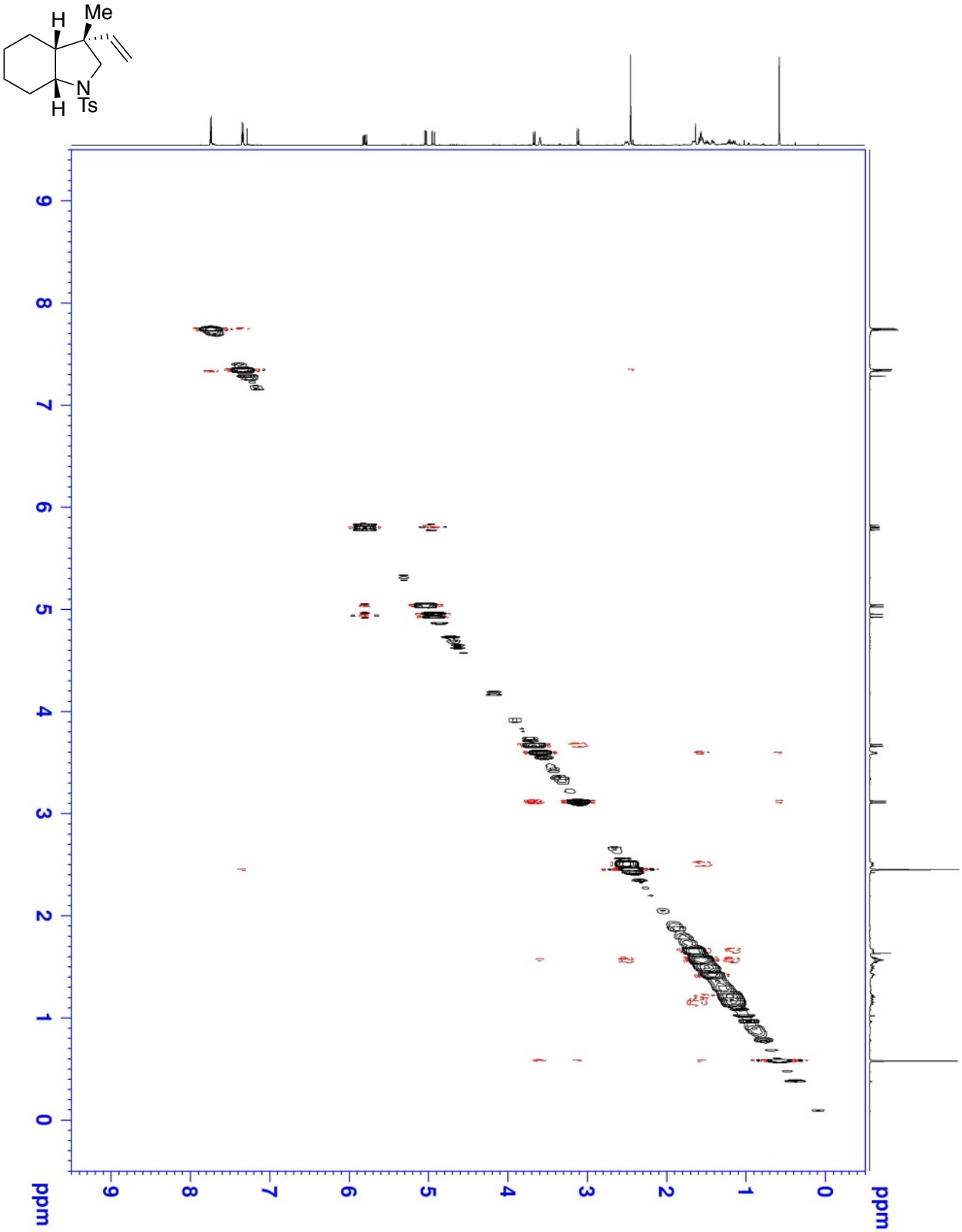
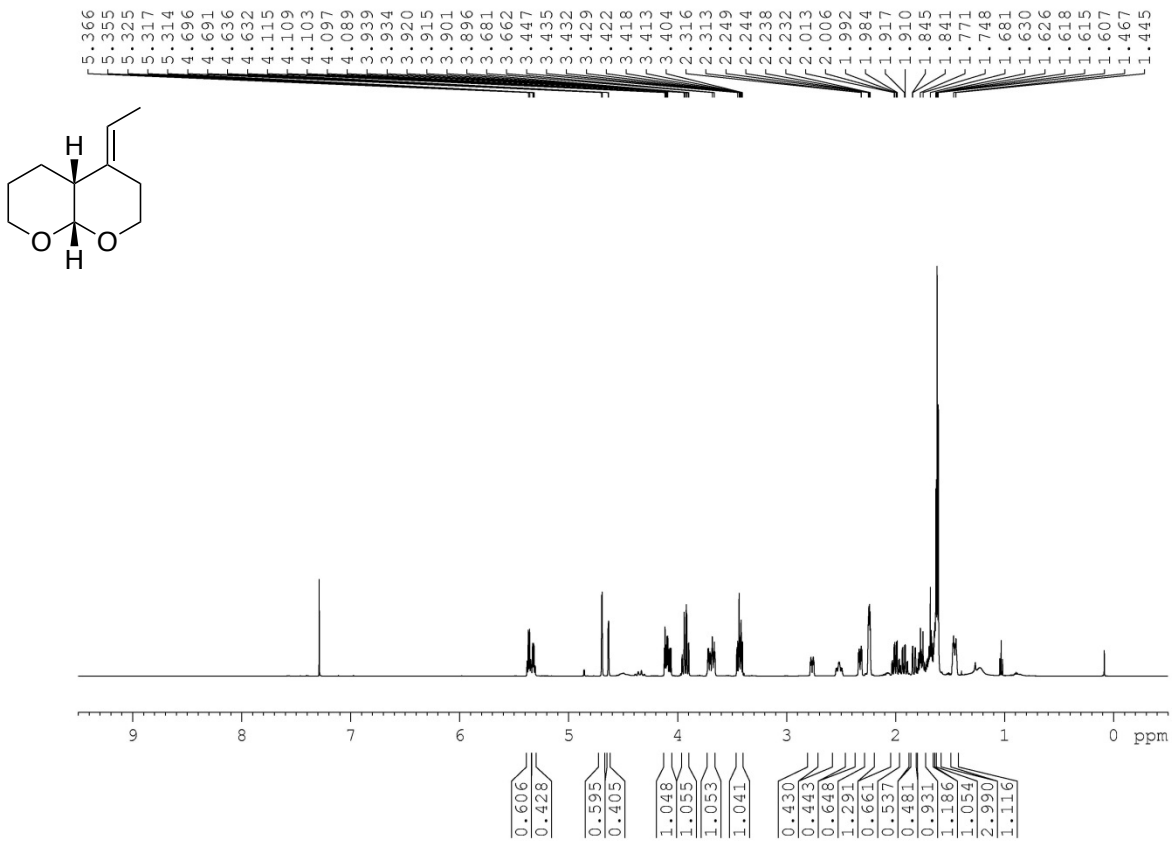
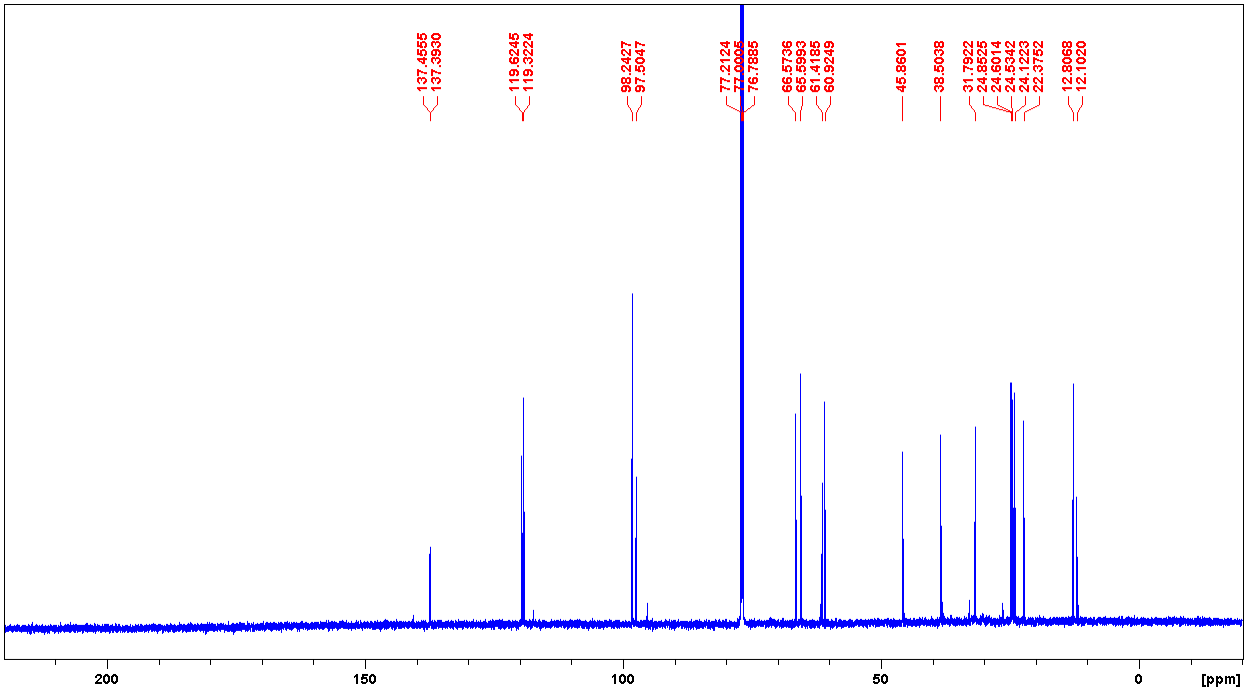
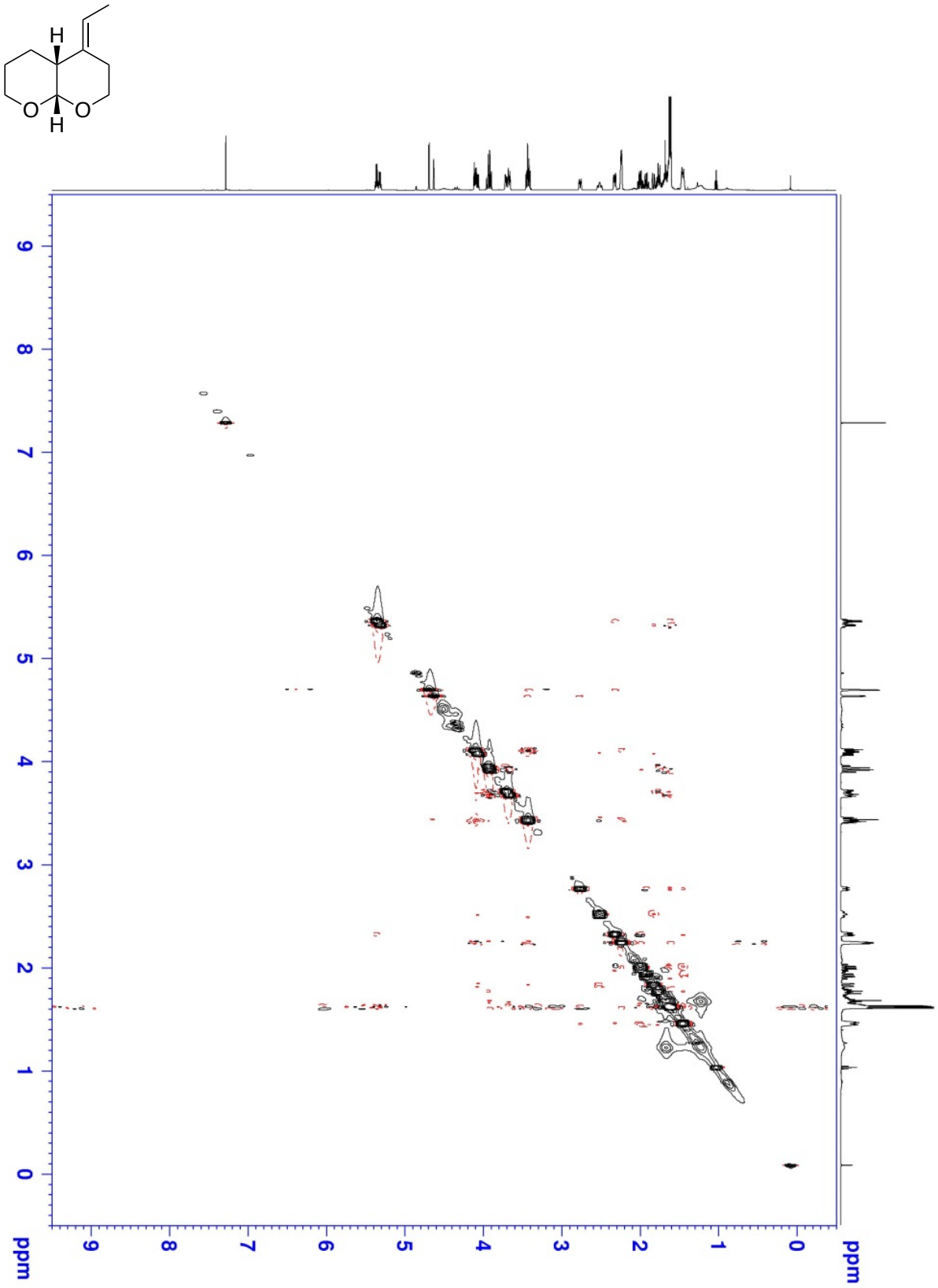
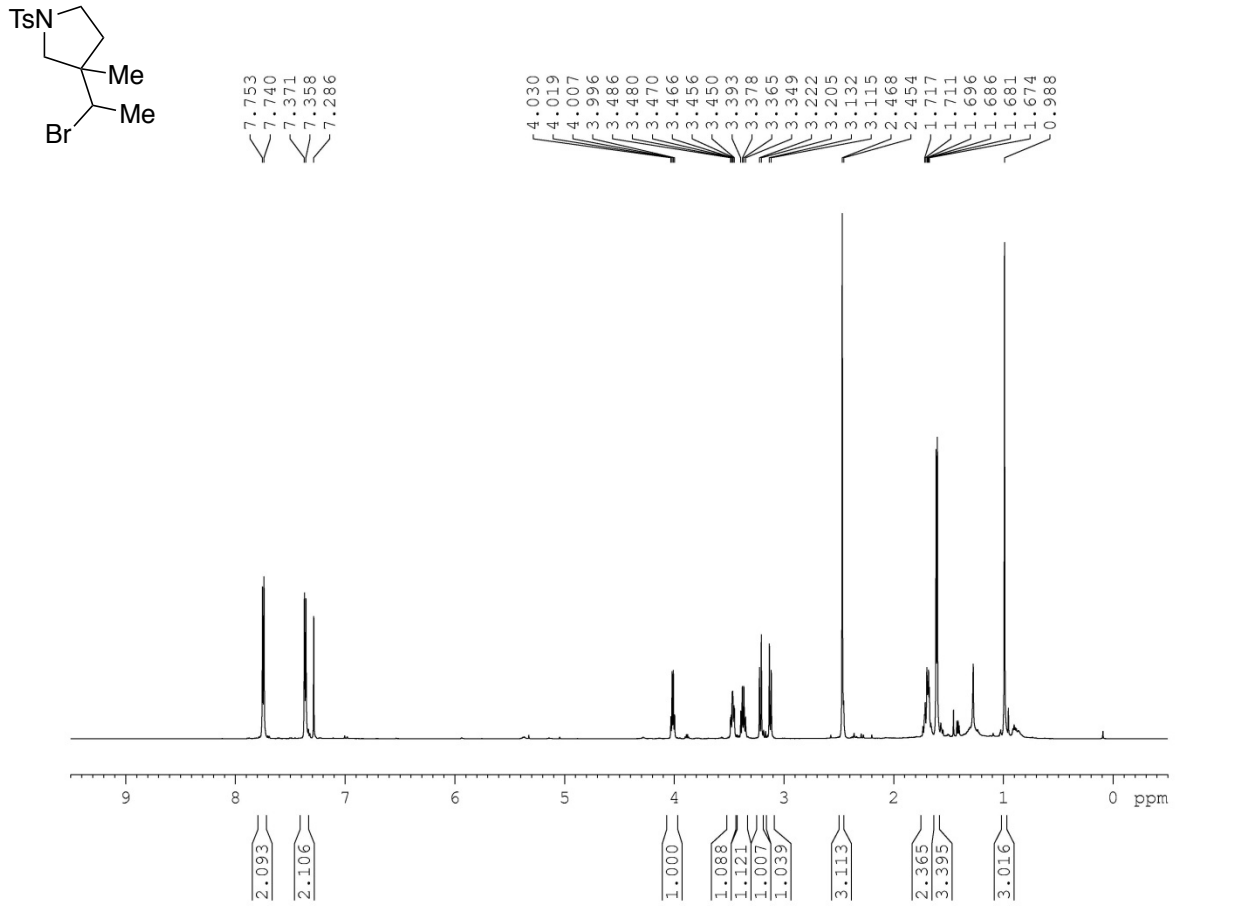
141.4275
134.0451
129.4903
127.5052
113.5548
77.2117
77.0000
76.7885
58.6193
57.4977
48.0402
45.0728
28.8408
25.1653
24.1316
23.9317
21.5373
20.3669
200
150
100
50
0
[ppm]


H
Me
N
Ts
H
ppm
ppm


5.366
5.355
5.325
5.317
5.314
4.696
4.691
4.636
4.632
4.115
4.109
4.103
4.097
4.089
3.939
3.934
3.920
3.915
3.901
3.896
3.681
3.662
3.447
3.435
3.432
3.429
3.422
3.418
3.413
3.404
2.316
2.313
2.249
2.244
2.238
2.232
2.013
2.006
1.992
1.984
1.917
1.910
1.845
1.841
1.771
1.748
1.681
1.630
1.626
1.618
1.615
1.607
1.467
1.445
H
O
O
H
9
8
7
6
5
4
3
2
1
0 ppm
0.606
0.428
0.595
0.405
1.048
1.055
1.053
1.041
0.430
0.443
0.648
1.291
0.661
0.537
0.481
0.931
1.186
1.054
2.990
1.116


137.4555
137.3930
119.6245
119.3224
98.2427
97.5047
77.2124
77.0005
76.7885
66.5736
65.5993
61.4185
60.9249
45.8601
38.5038
31.7922
24.8525
24.6014
24.5342
24.1223
22.3752
12.8068
12.1020
200
150
100
50
0
[ppm]


H
O
O
H
ppm
ppm


TsN
Me
Me
Br
7.753
7.740
7.371
7.358
7.286
4.030
4.019
4.007
3.996
3.486
3.480
3.470
3.466
3.456
3.450
3.393
3.378
3.365
3.349
3.222
3.205
3.132
3.115
2.468
2.454
1.717
1.711
1.696
1.686
1.681
1.674
0.988
9
8
7
6
5
4
3
2
1
0
ppm
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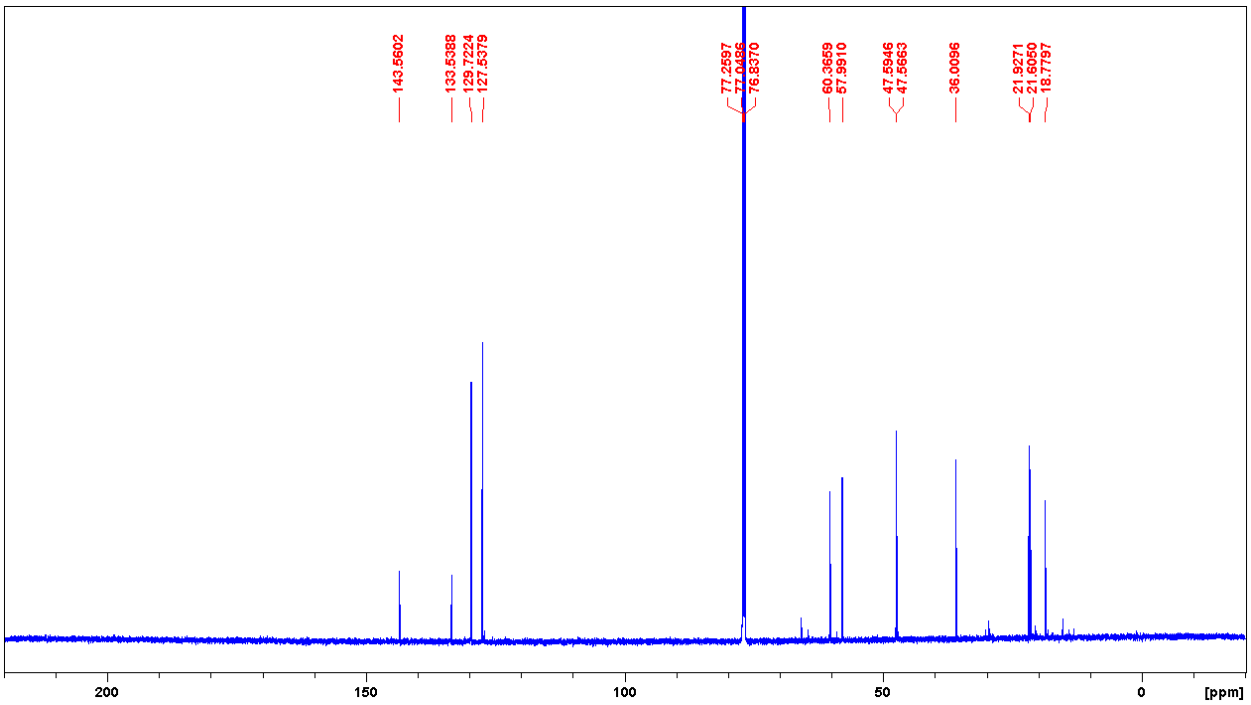
1.000
1.088
1.121
1.007
1.039
3.113
2.365
3.395
3.016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129.7224
127.5579
77.2597
77.0486
76.8370
60.3659
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47.5663
36.0096
21.9271
21.6050
18.7797
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100
50
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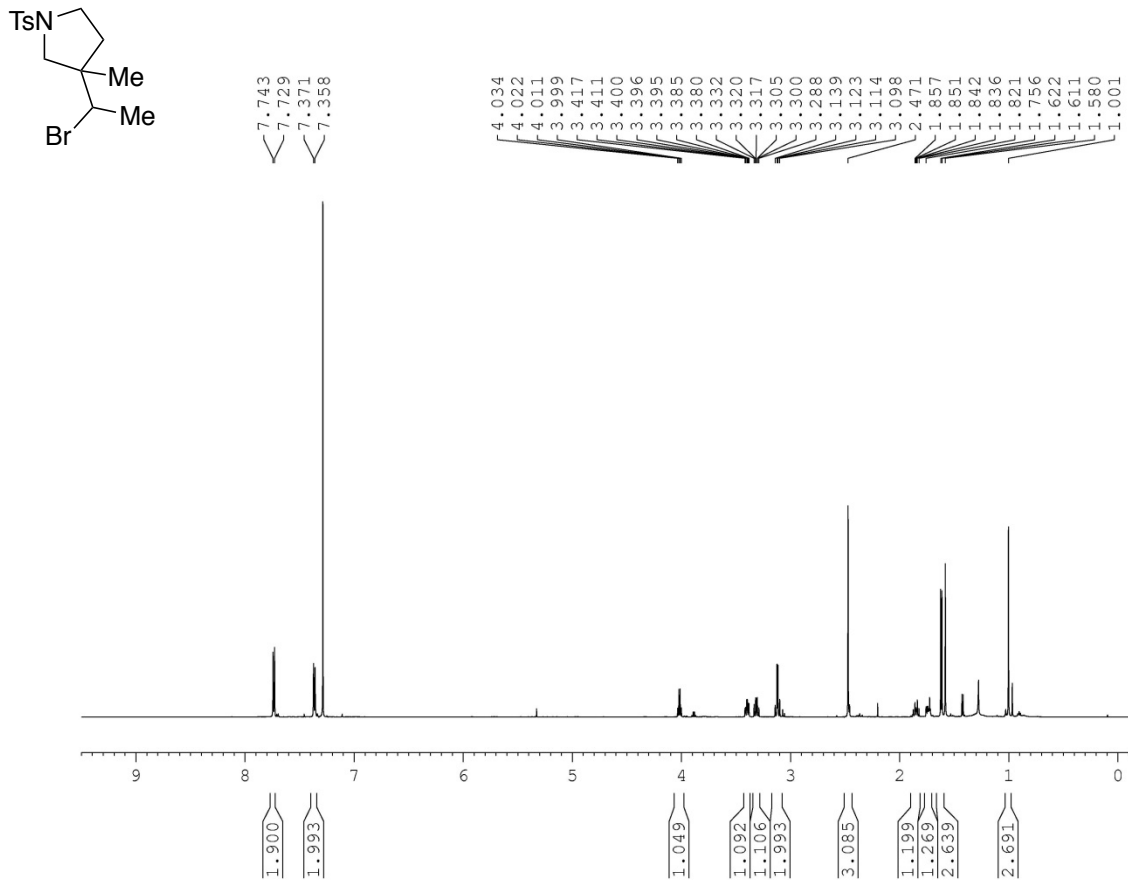
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Me
Me
Br
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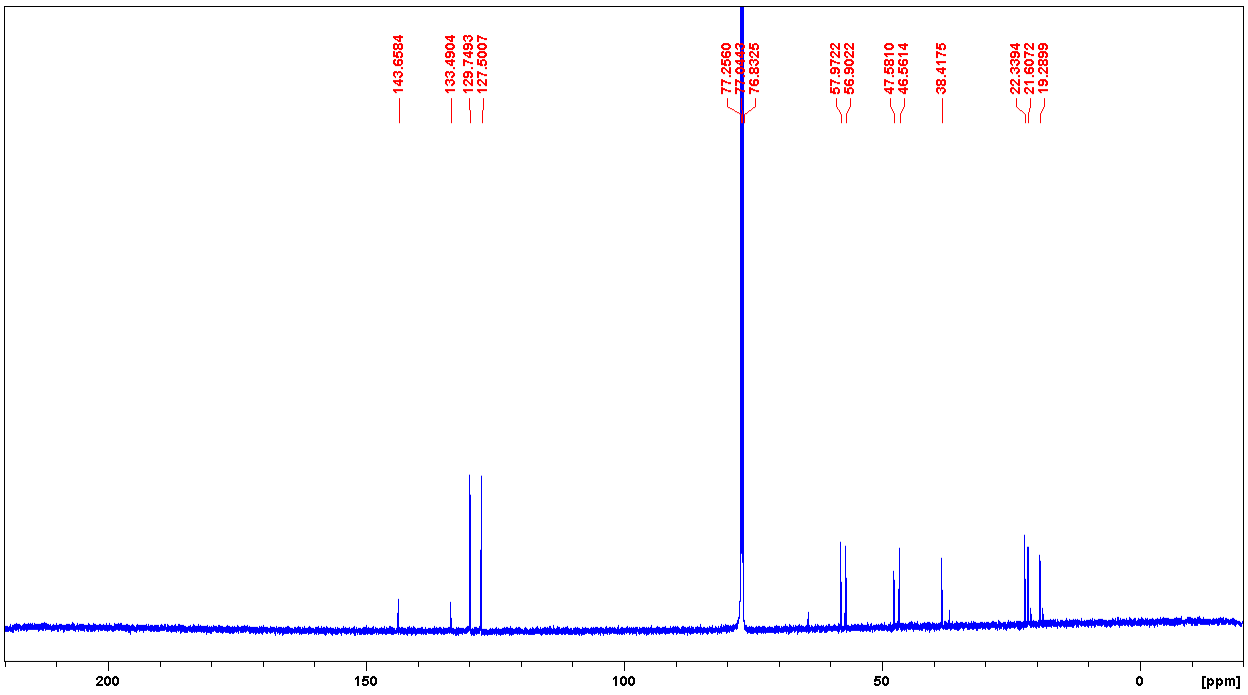
7.729
7.371
7.358
4.034
4.022
4.011
3.999
3.417
3.411
3.400
3.396
3.395
3.385
3.380
3.332
3.320
3.317
3.305
3.300
3.288
3.139
3.123
3.114
3.098
2.471
1.857
1.851
1.842
1.836
1.821
1.756
1.622
1.611
1.580
1.001
9
8
7
6
5
4
3
2
1
0 ppm
1.900
1.993
1.049
1.092
1.106
1.993
3.085
1.199
1.269
2.639
2.691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129.7493
127.5007
77.2560
77.0443
76.8325
57.9722
56.9022
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46.5614
38.4175
22.3394
21.6072
19.2899
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100
50
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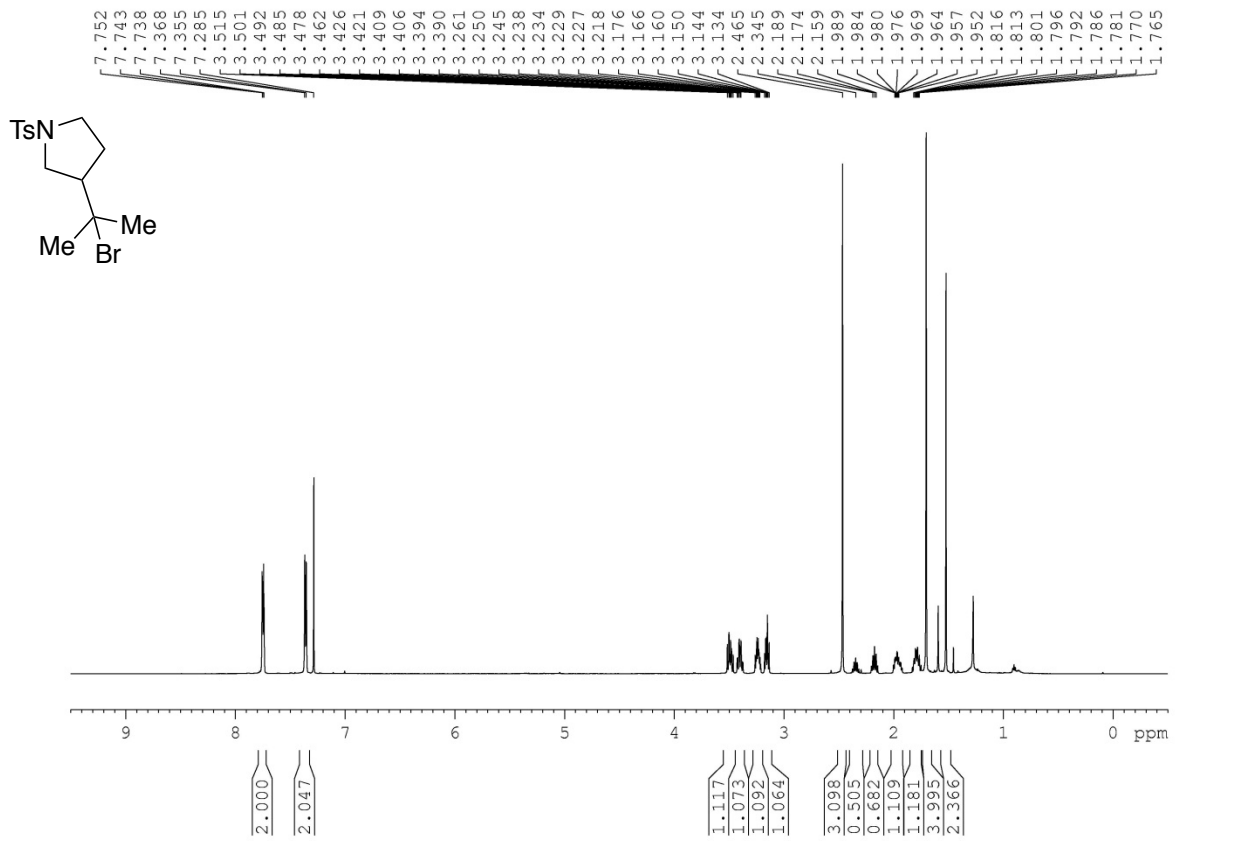
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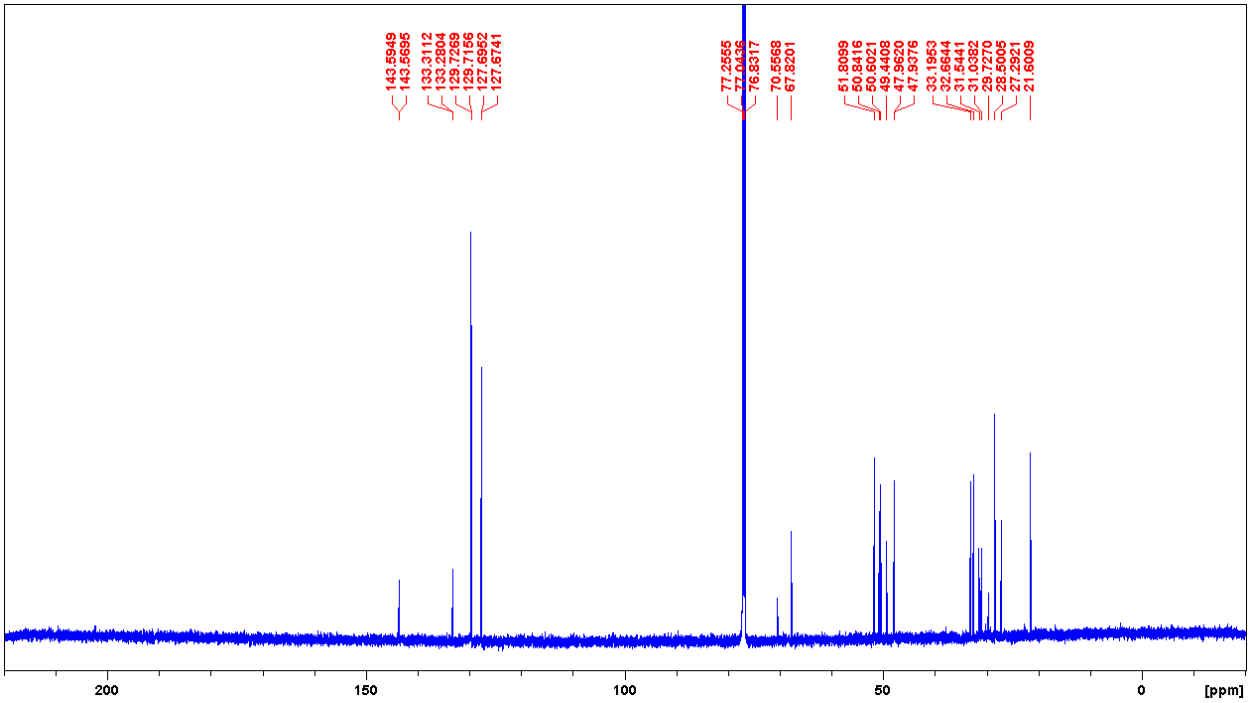
7.743
7.738
7.368
7.355
7.285
3.515
3.501
3.492
3.485
3.478
3.462
3.426
3.421
3.409
3.406
3.394
3.390
3.261
3.250
3.245
3.238
3.234
3.229
3.227
3.218
3.176
3.166
3.160
3.150
3.144
3.134
2.465
2.345
2.189
2.174
2.159
1.989
1.984
1.980
1.976
1.969
1.964
1.957
1.952
1.816
1.813
1.801
1.796
1.792
1.786
1.781
1.770
1.765
TsN
Me
Me
Br
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.047
1.117
1.073
1.092
1.064
3.098
0.505
0.682
1.109
1.181
3.995
2.366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143.5695
133.3112
133.2804
129.7269
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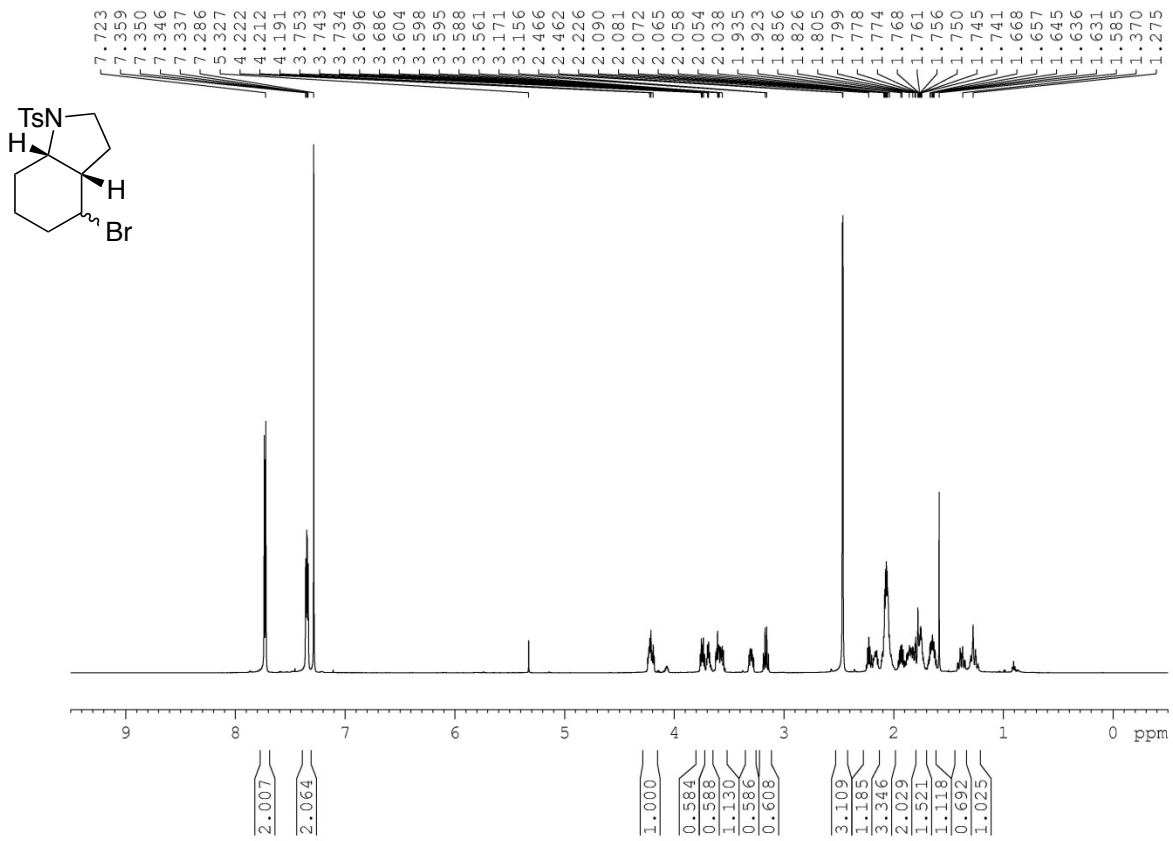
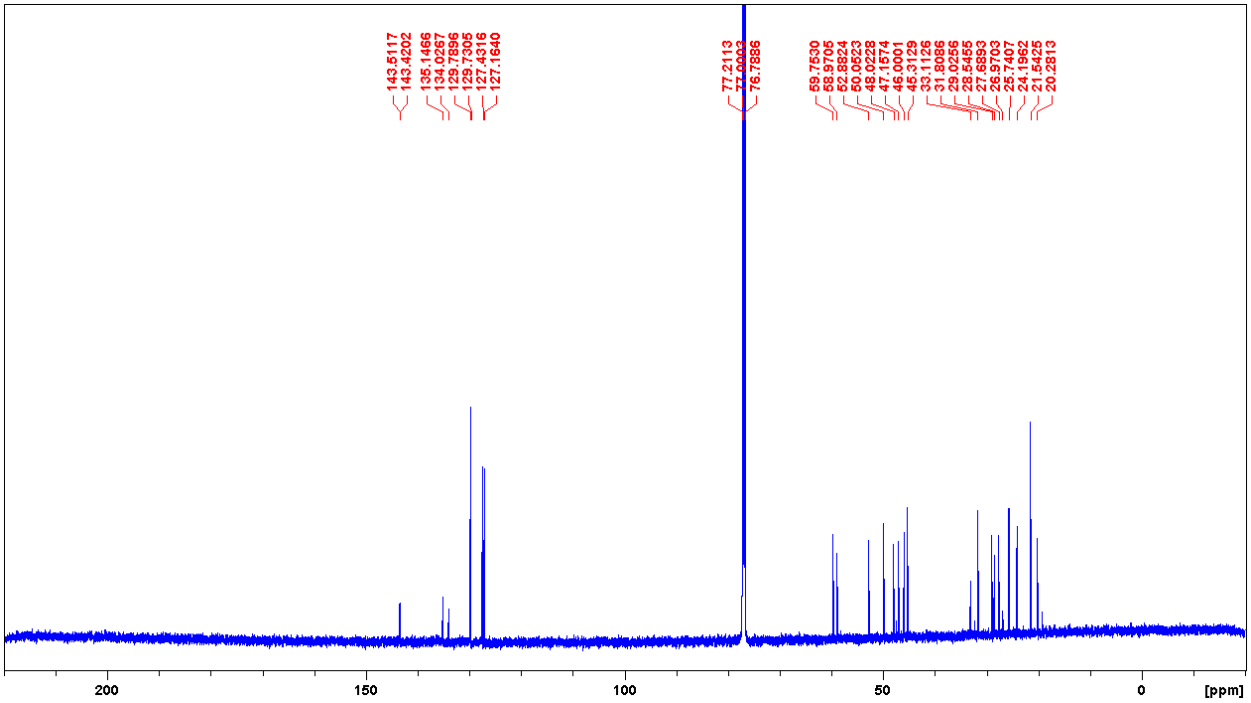
127.6952
127.5741
77.2565
77.0436
76.8317
70.5568
67.8201
51.8099
50.8416
50.6021
49.4408
47.9620
47.5376
33.1953
32.6644
31.5441
31.0382
29.7270
28.5005
27.2921
21.6009
200
150
100
50
0
[ppm]


7.723
7.359
7.350
7.346
7.337
7.286
5.327
4.222
4.212
4.191
3.753
3.743
3.734
3.696
3.686
3.604
3.598
3.595
3.588
3.561
3.171
3.156
2.466
2.462
2.226
2.090
2.081
2.072
2.065
2.058
2.054
2.038
1.935
1.923
1.856
1.826
1.805
1.799
1.778
1.774
1.768
1.761
1.756
1.750
1.745
1.741
1.668
1.657
1.645
1.636
1.631
1.585
1.370
1.275
TsN
H
H
Br
9
8
7
6
5
4
3
2
1
0 ppm
2.007
2.064
1.000
0.584
0.588
1.130
0.586
0.608
3.109
1.185
3.346
2.029
1.521
1.118
0.692
1.025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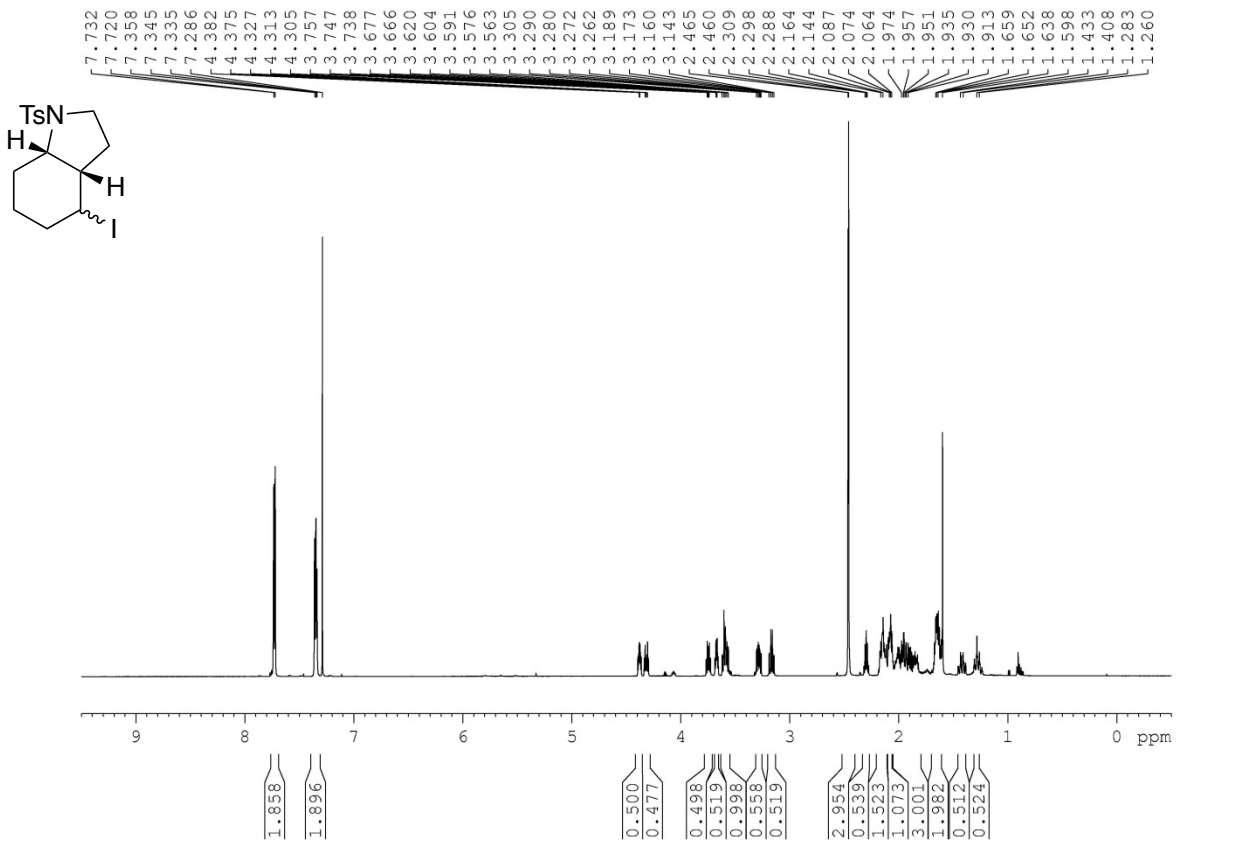
143.4202
135.1466
134.0267
129.7896
129.7306
127.4316
127.1640
77.2113
77.0003
76.7886
59.7530
58.9705
52.8824
50.0523
48.0228
47.1574
46.0001
45.3129
33.1126
31.8086
29.0256
28.5455
27.6893
26.9703
25.7407
24.1962
21.5425
20.2813
200
150
100
50
0
[ppm]


TsN
H
H
I
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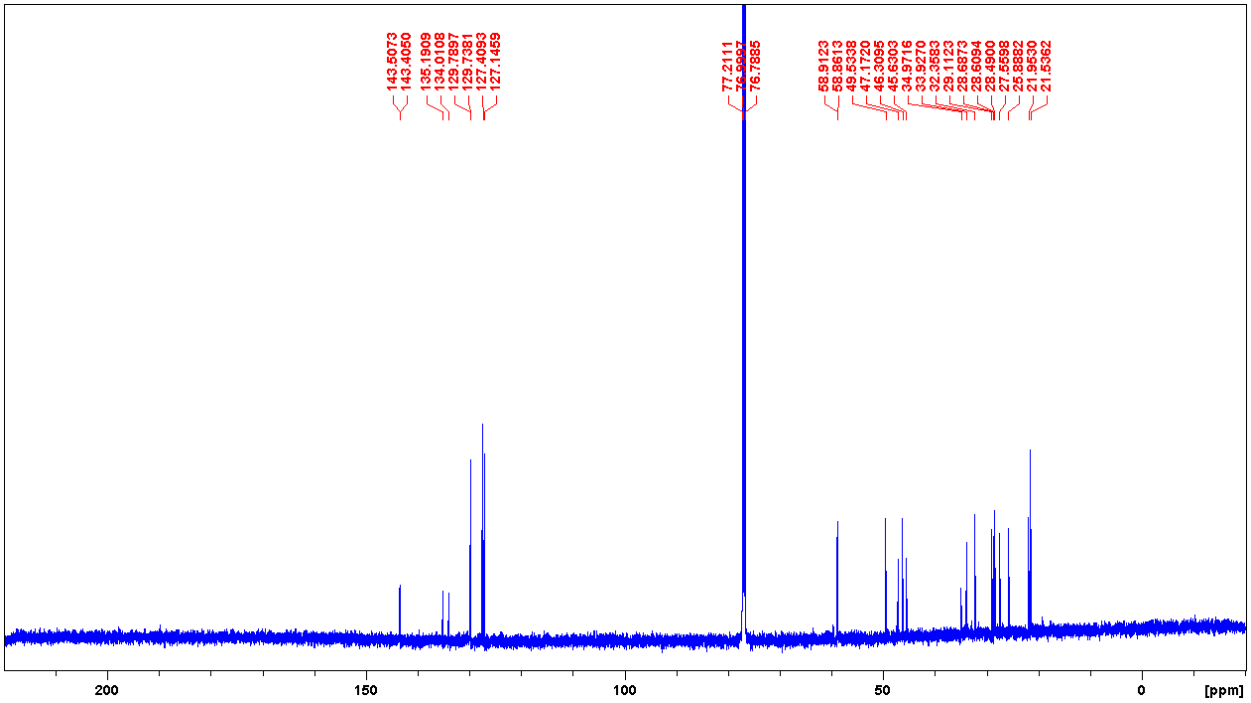
7.720
7.358
7.345
7.335
7.286
4.382
4.375
4.327
4.313
4.305
3.757
3.747
3.738
3.677
3.666
3.620
3.604
3.591
3.576
3.563
3.305
3.290
3.280
3.272
3.262
3.189
3.173
3.160
3.143
2.465
2.460
2.309
2.298
2.288
2.164
2.144
2.087
2.074
2.064
1.974
1.957
1.951
1.935
1.930
1.913
1.659
1.652
1.638
1.598
1.433
1.408
1.283
1.260
9
8
7
6
5
4
3
2
1
0 ppm
1.858
1.896
0.500
0.477
0.498
0.519
0.998
0.558
0.519
2.954
0.539
1.523
1.073
3.001
1.982
0.512
0.524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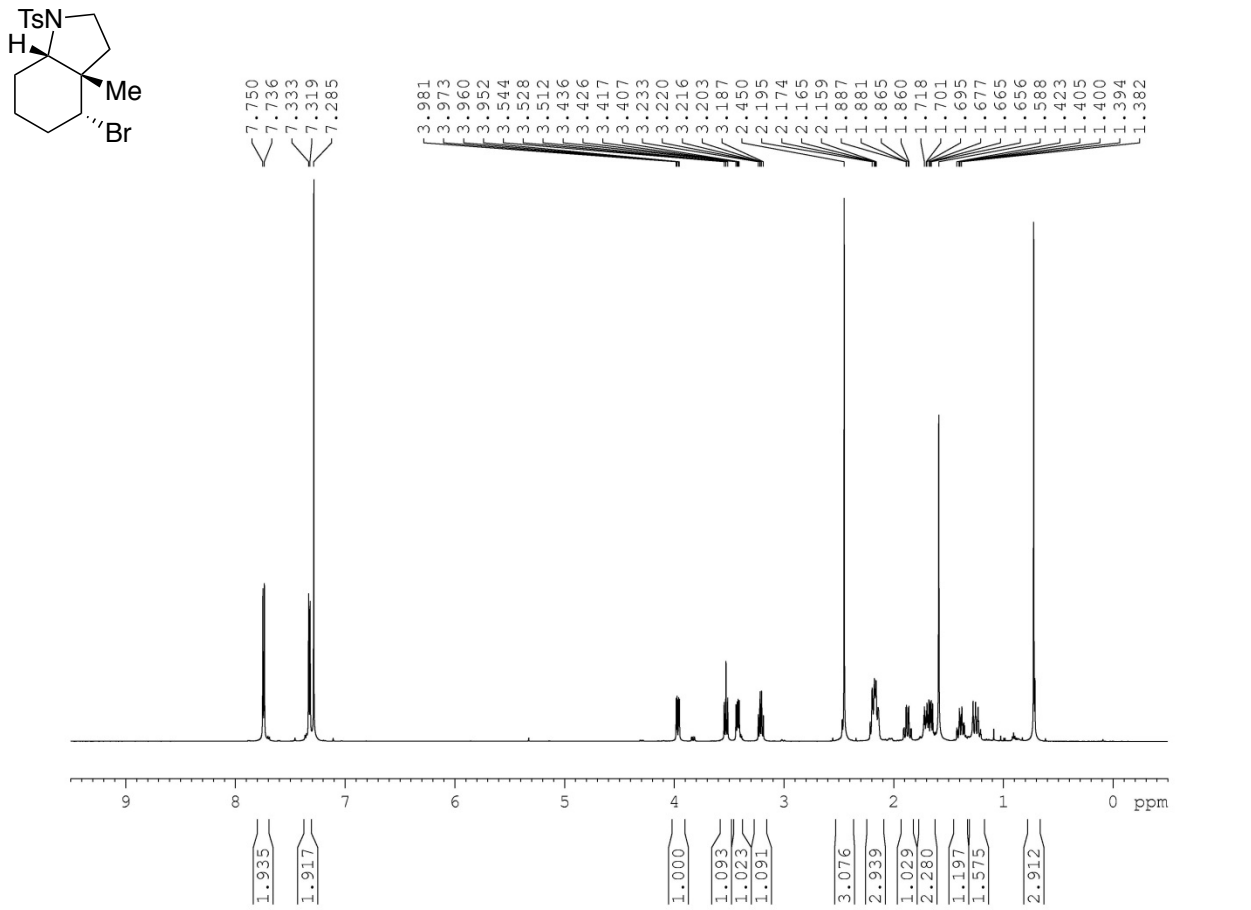
143.4050
135.1909
134.0108
129.7397
127.4083
127.1459
77.2111
76.9997
76.7885
58.9123
58.8613
49.5338
47.1720
46.3095
45.6303
34.9716
33.9270
32.3583
29.1123
28.6873
28.6094
28.4900
27.5598
25.8882
21.9530
21.5362
200
150
100
50
0
[ppm]


TsN
H
Me
Br
7.750
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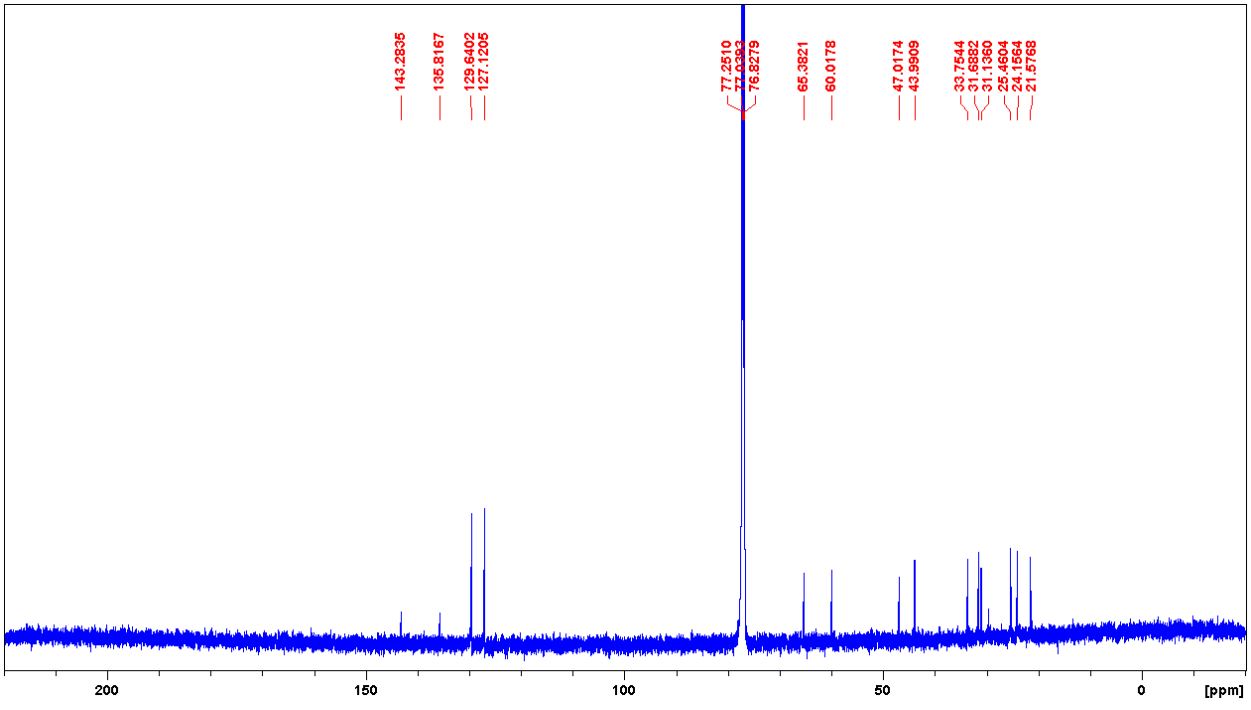
7.333
7.319
7.285
3.981
3.973
3.960
3.952
3.544
3.528
3.512
3.436
3.426
3.417
3.407
3.233
3.220
3.216
3.203
3.187
2.450
2.195
2.174
2.165
2.159
1.887
1.881
1.865
1.860
1.718
1.701
1.695
1.677
1.665
1.656
1.588
1.423
1.405
1.400
1.394
1.382
9
8
7
6
5
4
3
2
1
0 ppm
1.935
1.917
1.000
1.093
1.023
1.091
3.076
2.939
1.029
2.280
1.197
1.575
2.912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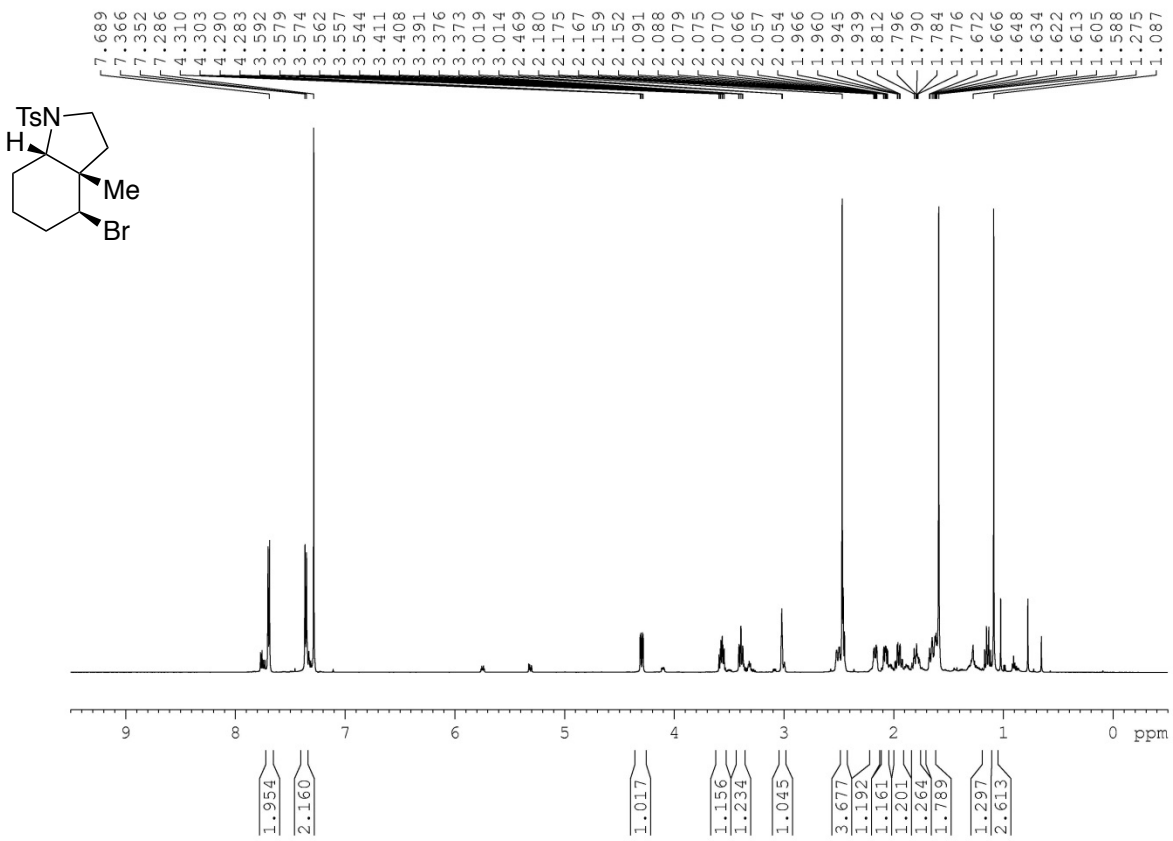
135.8167
129.6402
127.1205
77.2510
77.0383
76.8279
65.3821
60.0178
47.0174
43.9909
33.7544
31.6882
31.1360
25.4604
24.1564
21.5768
200
150
100
50
0
[ppm]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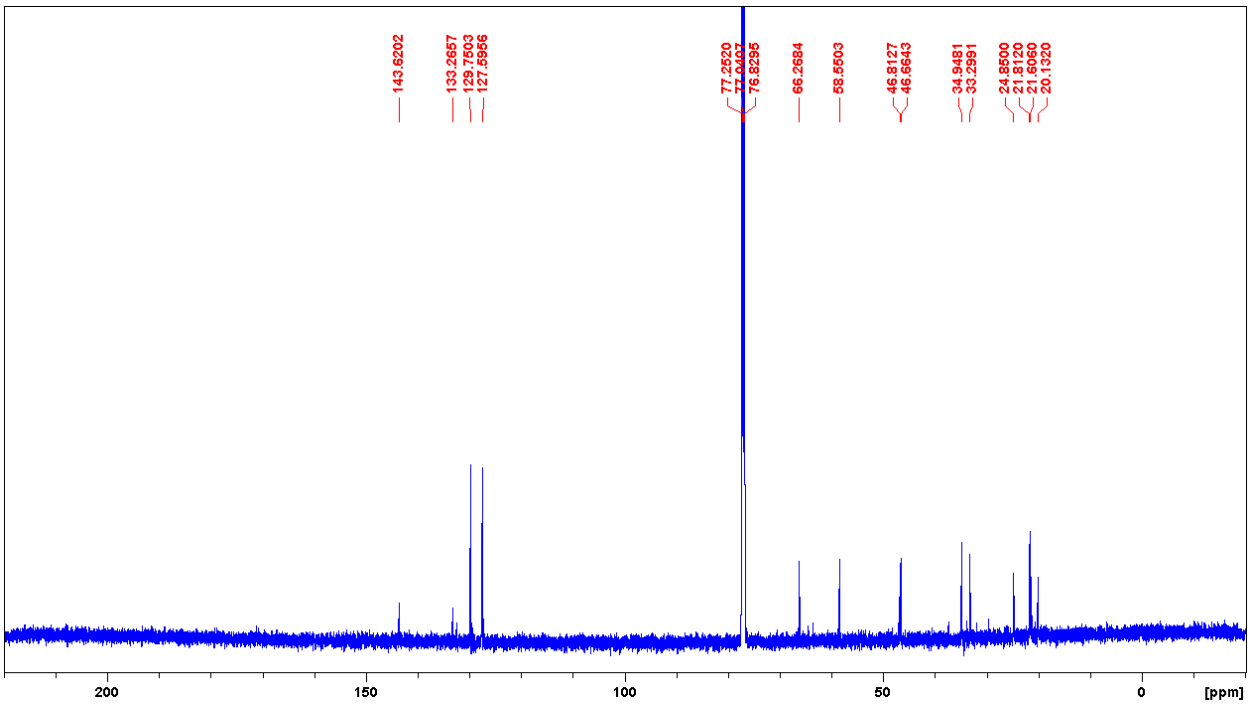
7.286
4.310
4.303
4.290
4.283
3.592
3.579
3.574
3.562
3.557
3.544
3.411
3.408
3.391
3.376
3.373
3.019
3.014
2.469
2.180
2.175
2.167
2.159
2.152
2.091
2.088
2.079
2.075
2.070
2.066
2.057
2.054
1.966
1.960
1.945
1.939
1.812
1.796
1.790
1.784
1.776
1.672
1.666
1.648
1.634
1.622
1.613
1.605
1.588
1.275
1.087
TsN
H
Me
Br
9
8
7
6
5
4
3
2
1
0
ppm
1.954
2.160
1.017
1.156
1.234
1.045
3.677
1.192
1.161
1.201
1.264
1.789
1.297
2.613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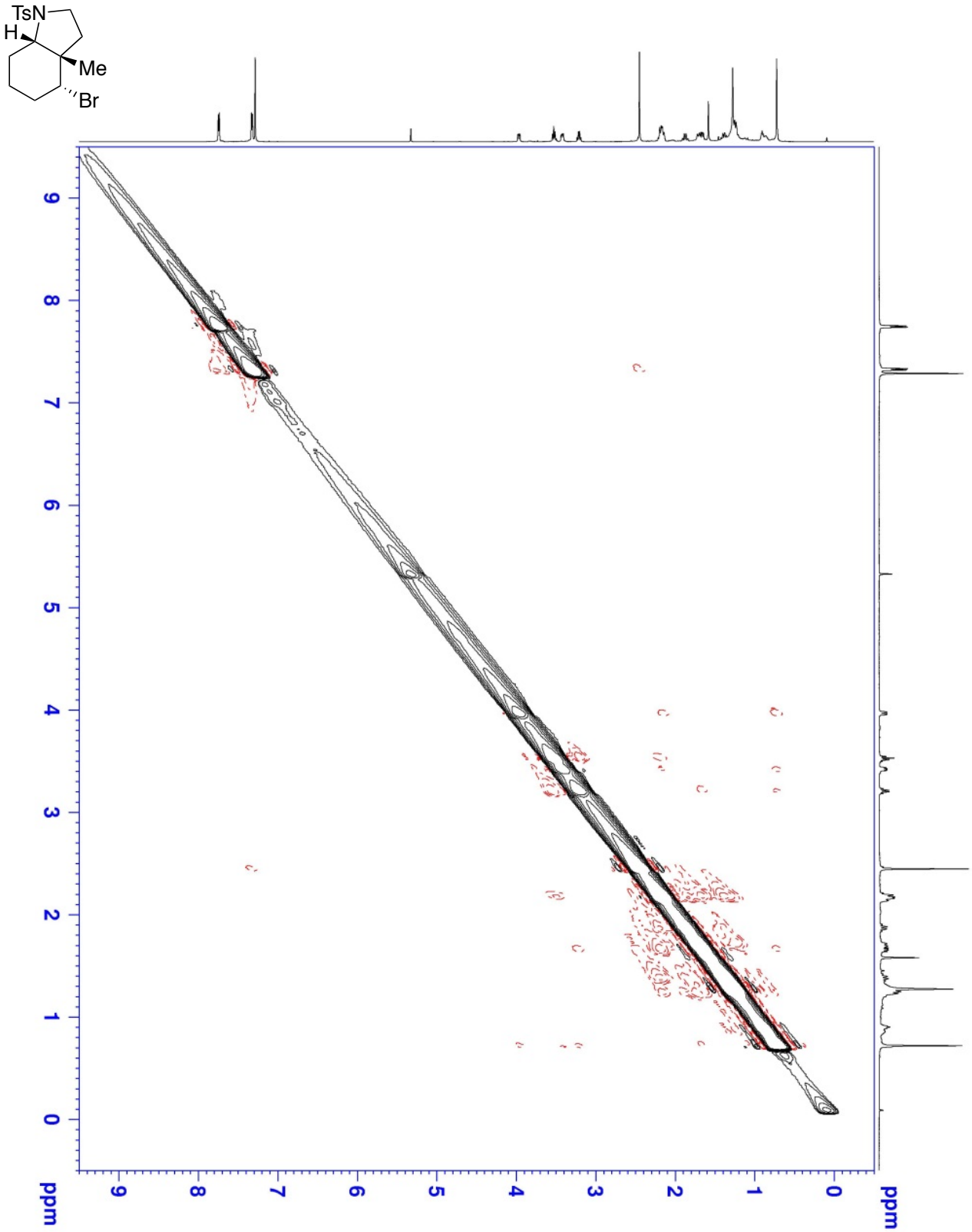
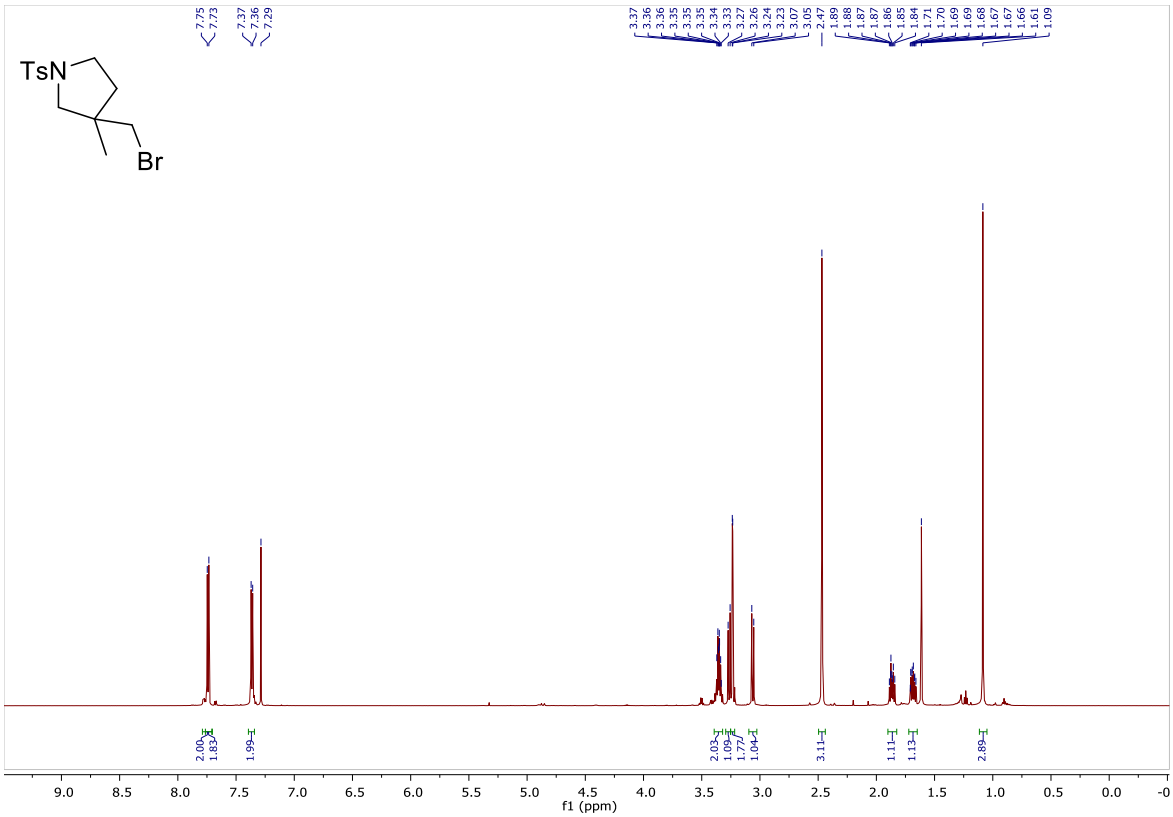
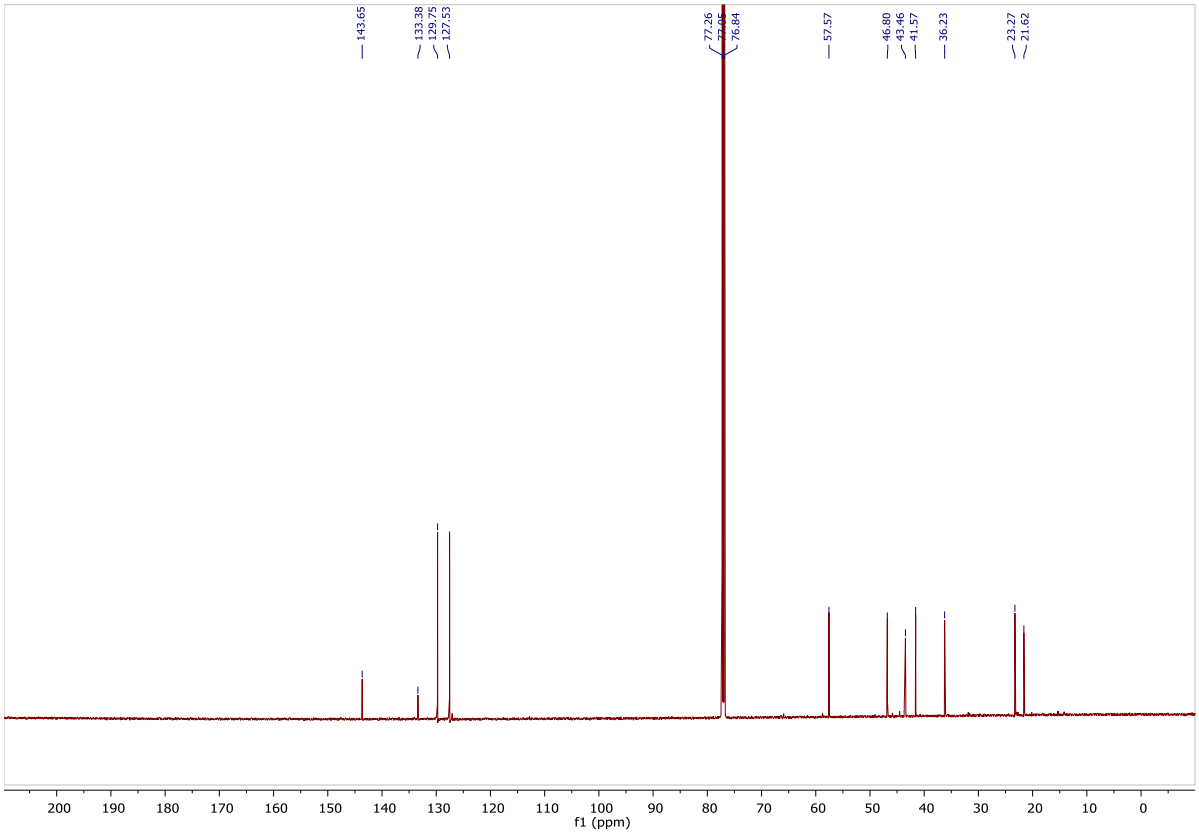
77.2520
77.0407
76.8295
66.2684
58.5503
46.8127
46.6643
34.9481
33.2991
24.8500
21.8120
21.6060
20.1320
200
150
100
50
0
[ppm]

.


TsN
H
Me
Br
ppm
ppm


TsN
Br
f1 (ppm)


f1 (ppm)