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Diastereoselective palladium(II)-mediated oxydation of homoallylic *N*-*tert*-butanesulfinyl amine derivatives

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Contents

General Methods ……page 2
General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 2……page 3
General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 4……page 4
General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 4d and 10……page 6
Tandem desulfinylation-*N*-Boc protection of 4a. Synthesis of compound 6……Page 7
General procedure for the synthesis of *N*-*tert*-butanesulfinyl allyl amine derivatives 8……Page 8
General procedure for the regioselective palladium(II)-catalyzed oxidation of *N*-*tert*-butanesulfinyl homoallyl amines 2. Characterization of compounds 3……Page 9
General procedure for the regio- and stereoselective palladium(II)-catalyzed oxidation of *N*-*tert*-butanesulfinyl substituted aminoalkenes 4, 6, 8 and 10……Page11
of *N*-*tert*-butanesulfinyl imines 1 with homoallylic X-Ray structure of compound 5f ……page 17
^{1}H-NMR and ^{13}C-NMR spectra of compounds 3 and 6……pages 18-46

General Methods: (R_S)-*N*-*tert*-butanesulfinamide was a gift of Medalchemy (>99% ee by chiral HPLC on a Chiracel AS column, 90:10 *n*-hexane/*i*-PrOH, 1.2 mL/min, λ=222 nm). All other commercially available reagents were used as received.

TLC was performed on silica gel 60 F_{254}, using aluminum plates and visualized with phosphomolybdic acid (PMA) stain. Flash chromatography was carried out on handpacked columns of silica gel 60 (230-400 mesh). Melting points are uncorrected. IR spectra were recorded as a film deposited from $CDCl_3$ or CH_2Cl_2 on NaCl plates followed by solvent evaporation and all absorptions are reported in cm^{-1}.

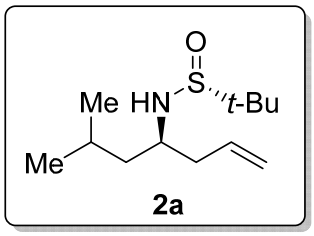
Mass spectra (EI) were obtained at 70 eV; fragment ions are given in m/z with relative intensities (%) in parentheses. HRMS analyses were also carried out in the electron impact mode (EI) at 70 eV using a quadrupole mass analyzer or in the electrospray ionization mode (ESI) using a TOF analyzer.

^{1}H NMR spectra were recorded at 300 MHz using $CDCl_3$ or CD_3OD as the solvent and TMS as internal standard (0.00 ppm). The data is being reported as [s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad signal, integration, coupling constant(s) in Hz]. ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.16 ppm. DEPT-135 experiments were performed to assign CH, CH_2 and CH_3.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 2:

A mixture of the corresponding *N*-*tert*-butanesulfinyl imine (0.5 mmol), allyl bromide (121.0 mg, 0.086 mL, 1.0 mmol) and indium (115 mg, 1.0 mmol) in dry THF (2 mL) was stirred for 6 h at 66 ºC. Then, the resulting mixture was hydrolyzed with H_2O (5 mL), extracted with EtOAc (3 × 10 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compounds **3**. Homoallyl imine derivatives **2a** (derived from the imine of isovaleraldehyde), **2b** (derived from the imine of 3-phenylpropanal),[1] **2c** (derived from the imine of benzaldehyde)[1] and **2d** (derived from the imine of butanone)[2] were characterized by comparison of their physical and spectroscopic data with those reported in the literature. Yield, physical and spectroscopic data for new compound **2a** follow.

(4*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-6-methylhept-1-en-4-amine (2a):



2a

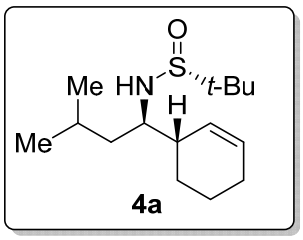
Following the general procedure, 82 mg of **2a** (71%) was obtained after column chromatography as a yellow oil; R_F 0.55 (hexane/AcOEt 1:1); $[\alpha]_D^{20}$ -39.8 (*c* 1.3, CH_2Cl_2); IR (film) ν 3070, 2956, 2927, 1638, 1467, 1364, 1199, 1051, 910, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, d, *J* = 6.7 Hz, CH_3), 0.91 (3H, d, *J* = 6.7 Hz, CH_3), 1.21 [9H, s, $C(CH_3)_3$], 1.34-1.46 (2H, m, CH_2), 1.66-1.84 (1H, m, CH), 2.28-2.48 (2H, m, CH_2), 3.20 (1H, d, *J* = 7.4 Hz, NH), 3.32-3.46 (1H, m, CH), 5.11-5.20 (2H, m, CH_2=CH), 5.71-5.88 (1H, m, CH_2=*CH*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1 (CH_3), 22.7 (CH_3), 23.1 (CH_3), 24.5 (CH), 41.1 (CH_2), 44.6 (CH_2), 53.7 (CH_2); 56.0 (C), 119.0 (CH_2), 134.1 (CH_2); LRMS (EI) *m/z* 175 (M^+-C_4H_8, 23%), 174 (22), 134 (100), 133 (82), 118 (61), 78 (17), 69 (32), 57 (65); HRMS (ESI-TOF) Calcd for $C_{12}H_{26}NOS$ $[M+H]^+$ 232.1735, found 232.1728.

1. J. C. González-Gómez, M. Medjahdi, F. Foubelo and M. Yus, *J. Org. Chem.*, 2010, **75**, 6308-6311.
2. J. A. Sirvent, F. Foubelo and M. Yus, *Chem. Commun.*, 2012, **48**, 2543-2545.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 4:

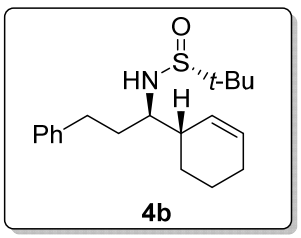
A mixture of indium powder (173 mg, 1.50 mmol), (S_S)-*N*-*tert*-butanesulfinamide (121 mg, 1.00 mmol), the corresponding aldehyde (1.15 mmol), and Ti(OEt)4 (450 μL, 2.00 mmol) in THF (2 mL) was stirred under argon for 1 h at 23 ºC. At this time, 3-bromocyclohexene (241 mg, 0.172 mL, 1.50 mmol) was added and the reaction mixture heated for 5 h at 60 ºC. The mixture was allowed to cool down to room temperature, quenched with brine (2 mL), and diluted with EtOAc (20 mL). The resulting suspension was filtered through a short pad of Celite and concentrated in vacuo (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compounds **4**. Yields, physical and spectroscopic data for compounds **4a**, **4b**, **4c**, **4e** and **4f** follow.

(1*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl]-3-methylbutan-1-amine (4a):



Following the general procedure, 200.5 mg of **4a** (74%) was obtained after column chromatography as a yellow oil; R_F 0.3 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -33.4 (*c* 0.26, CH_2Cl_2); IR (film) ν 3255, 2946, 2927, 2863, 1509, 1465, 1383, 1235, 1018, 814, 738 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 6.6 Hz, CH_3), 0.90 (3H, d, *J* = 6.6 Hz, CH_3), 1.21 [9H, s, $C(CH_3)_3$], 1.40-1.54 (2H, m, CH_2), 1.65-1.75 [1H, m, $(CH_3)_2CH$], 1.75-1.84 (2H, m, CH_2), 1.94-2.02 (2H, m, CH_2), 2.50-2.58 (1H, m, HNCHC*H*), 3.17 (1H, d, *J* = 8.1 Hz, NH), 3.17-3.32 (1H, m, HNC*H*), 5.52 (1H, dt, *J* = 10.2, 1.7 Hz, CH), 5.80-5.89 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8 (CH_3), 22.1 (CH_2), 22.9 (CH_3), 23.6 (CH_3), 24.8 (CH), 24.8 (CH_2), 25.4 (CH_2), 41.1 (CH), 42.8 (CH_2), 56.2 (C), 58.5 (CH), 127.4 (CH), 130.7 (CH); LRMS (EI) *m/z* 215 (M^+-C_4H_8, 10%), 142 (29), 134 (31), 133 (100), 109 (13), 95 (38), 91 (29), 81 (24), 77 (32); HRMS (ESI-TOF) Calcd for $C_{15}H_{30}NOS$ $[M+H]^+$ 272.2048, found 272.2044.

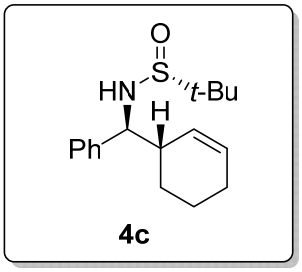
(1*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl]-3-phenylpropan-1-amine (4b):[1]



Following the general procedure, 134 mg of **4b** (42%) was obtained after column chromatography as a white solid; mp 73-74 ^oC; R_F 0.34 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -69.1 (*c* 0.78, CH_2Cl_2); IR (film) ν 2927, 2894, 1453, 1364, 1044, 951, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 [9H, s, $C(CH_3)_3$], 1.50-1.55 (2H, m, CH_2), 1.74-1.85 (2H, m,

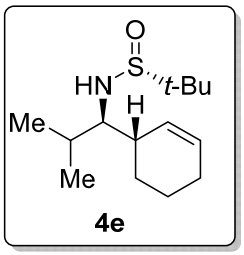
CH_2), 1.87-2.02 (2H, m, CH_2), 2.56-2.70 (3H, m, HNCHC*H*, C*H*$_2$), 2.77-2.85 (2H, m, CH_2), 3.32-3.34 (1H, m, HNC*H*), 3.31 (1H, d, *J* = 7.6 Hz, NH), 5.51-5.58 (1H, m, CH), 5.81-5.91 (1H, m, CH), 7.16-7.34 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0 (CH_2), 23.0 (CH_3), 25.0 (CH_2), 25.4 (CH_2), 32.9 (CH_2), 35.8 (CH_2), 40.8 (CH), 56.2 (C), 60.1 (CH), 126.0 (CH), 127.0 (CH), 128.5 (CH), 128.5 (CH), 130.9 (CH), 142.0 (C); LRMS (EI) *m/z* 263 (M^+-C_4H_8, 7.3%), 247 (12), 181 (17), 142 (36), 117 (78), 91 (100), 81 (10), 79 (14), 77 (12), 67 (13).

(1*S*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl](phenyl)methanamine (4c):



Following the general procedure, 105 mg of **4c** (36%) was obtained after column chromatography as a white solid; mp 82-83 °C; R_F 0.23 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -129 (*c* 0.6, CH_2Cl_2); IR (film) ν 3201, 2952, 2911, 2857, 2836, 1455, 1035, 876, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $C(CH_3)_3$], 1.34-1.77 (4H, m, 2 × CH_2), 1.94-2.01 (2H, m, CH_2), 2.51 (1H, m, HNCHC*H*), 3.60 (1H, d, *J* = 3.5 Hz, NH), 4.33 (1H, m, HNC*H*), 5.63-5.75 (1H, dd, *J* = 11.0, 2.0 Hz, CH), 5.88 (1H, m, CH), 7.27-7.38 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_2), 22.7 (CH_3), 25.3 (CH_2), 26.6 (CH_2), 42.7 (CH), 55.8 (C), 62.8 (CH), 125.8 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 131.5 (CH), 141.6 (C); LRMS (EI) *m/z* 235 (M^+-C_4H_8, 1.7%), 154 (20), 153 (100), 137 (13), 136 (36), 105 (17), 104 (33), 91 (17), 81 (11), 77 (16); HRMS (ESI-TOF) Calcd for $C_{17}H_{26}NOS$ $[M+H]^+$ 292.1735, found 292.1734.

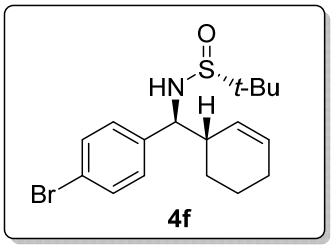
(1*S*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl]-2-methylpropan-1-amine (4e):



Following the general procedure, 56.5 mg of **4e** (22%) was obtained after column chromatography as a white solid; mp 57-58 °C; R_F 0.39 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -97.0 (*c* 0.2, CH_2Cl_2); IR (film) ν 3203, 2946, 2908, 2868, 1460, 1362, 1037, 1008, 861 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (3H, d, *J* = 6.7 Hz, CH_3), 0.93 (3H, d, *J* = 6.7 Hz, CH_3), 1.24 [9H, s, $C(CH_3)_3$], 1.36-1.60 (2H, m, CH_2), 1.63-1.88 (2H, m, CH_2), 1.98-1.99 (2H, m, CH_2), 2.44-2.48 (1H, m, HNCHC*H*), 2.79-2.83 (1H, m, HNC*H*), 3.23 (1H, d, *J* = 6.2 Hz, NH), 5.69-5.73 (1H, m, CH), 5.88-5.93 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9 (CH_3), 20.4 (CH_3), 22.1 (CH_2), 23.2 (CH_3), 25.3 (CH_2), 27.3 (CH_2), 31.9 (CH), 38.1 (CH), 56.4 (C), 65.2 (CH), 126.6 (CH), 131.7 (CH); LRMS (EI) *m/z* 201 (M^+-C_4H_8, 14.9%), 158

(54), 142 (40), 137 (18), 120 (22), 119 (100), 110 (11), 95 (46), 82 (13), 81 (46), 79 (20), 67 (22), 56 (65); HRMS (ESI-TOF) Calcd for $C_{14}H_{28}NOS$ $[M+H]^+$ 258.1892, found 258.1887.

(1*S*,*R*$_S$)-1-(4-Bromophenyl)-*N*-(*tert*-butanesulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl]methanamine (4f):

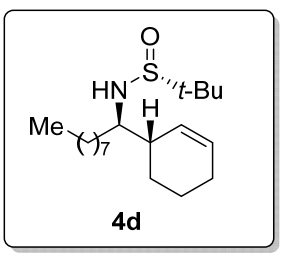


Following the general procedure, 180 mg of **4f** (49%) was obtained after column chromatography as a white solid; mp 86-87 ^oC; R_F 0.2 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -146.1 (*c* 0.6, CH_2Cl_2); IR (film) ν 2925, 2863, 1484, 1406, 1224, 1176, 1051, 1009, 829 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $C(CH_3)_3$], 1.30-1.52 (2H, m, CH_2), 1.59-1.73 (2H, m, CH_2), 1.94-1.99 (2H, m, CH_2), 2.45-2.50 (1H, m, HNCHC*H*), 3.59 (1H, d, *J* = 3.1 Hz, NH), 4.28-4.31 (1H, m, HNC*H*), 5.92-5.67 (1H, m, CH), 5.85-5.90 (1H, m, CH), 7.16-7.19 (2H, m, ArH), 7.44-7.47 (2H, d, *J* = 8.3 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2 (CH_2), 22.7 (CH_3), 25.2 (CH_2), 26.4 (CH_2), 42.6 (CH), 55.8 (C), 62.2 (CH), 121.3 (C), 125.4 (CH), 129.6 (CH), 131.4 (CH), 131.7 (CH), 140.6 (C); LRMS (EI) *m/z* 314 (M^+-C_4H_8, 0.4%), 297 (10), 234 (20), 233 (100), 232 (19), 231 (96), 217 (14), 216 (23), 215 (17), 214 (20), 185 (30), 184 (36), 183 (32), 182 (30), 171 (15), 170 (18), 169 (15), 81 (19), 77 (18); HRMS (ESI-TOF) Calcd for $C_{17}H_{25}NOSBr$ $[M+H]^+$ 370.0840, found 370.0834.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl homoallyl amine derivatives 4d and 10:

A mixture of the corresponding *N*-*tert*-butanesulfinyl imine (0.5 mmol), 3-bromocyclohexene for compound **4d** (161 mg, 0.115 mL, 1.0 mmol) or 3-bromocycloheptene for compound **10** (175.0 mg, 0.156 mL, 1.0 mmol), and indium (115 mg, 1.0 mmol) in dry THF (2 mL) was stirred for 6 h at 66 ºC. Then, the resulting mixture was hydrolyzed with H_2O (5 mL), extracted with EtOAc (3 × 10 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compounds **4d** or **10**. Yields, physical and spectroscopic data for these compounds follow.

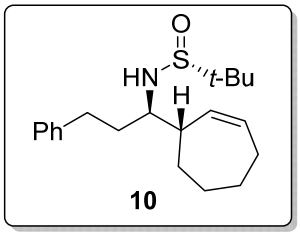
(1*R*,*R*$_S$)-*N*-(*tert*-Butenosulfinyl)-1-[(*S*)-cyclohex-2-en-1-yl]nonan-1-amine (4d):



Following the general procedure, 123 mg of **4d** (75%) was obtained after column chromatography as a yellow oil; R_F 0.37 (hexane/AcOEt

2:1); $[\alpha]^{20}_D$ -53.3 (*c* 1.0, CH_2Cl_2); IR (film) ν 2957, 2927, 2848, 1460, 1352, 1175, 1067, 880, 713 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85-0.92 (3H, m, CH_3), 1.21 [9H, s, $C(CH_3)_3$], 1.26 [10H, s, $(CH_2)_5$], 1.36-1.58 (6H, m, 3 × CH_2), 1.71-1.86 (3H, m, CH, CH_2), 1.99 (2H, m, CH_2), 2.50 (1H, m, HNCHC*H*), 3.18 (1H, m, HNC*H*), 3.20 (1H, m, CH), 5.55 (1H, dt, *J* = 10.3, 1.8 Hz, CH), 5.80-5.89 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.0 (CH_2), 22.8 (CH_2), 22.9 (CH_3), 25.2 (CH_2), 25.4 (CH_2), 26.5 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 33.7 (CH_2), 40.6 (CH), 56.1 (C), 60.5 (CH), 127.1 (CH), 130.7 (CH); LRMS (EI) *m/z* 271 (M^+-C_4H_8, 10%), 255 (14), 190 (33), 189 (68), 153 (11), 142 (100), 140 (18), 109 (12), 95 (23), 81 (32), 67 (29), 55 (22); HRMS (ESI-TOF) Calcd for $C_{19}H_{38}NOS$ $[M+H]^+$ 328.2674, found 328.2672.

(1*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-[(*S*)-cyclohept-2-en-1-yl]3-phenylpropan-1-amine (10):



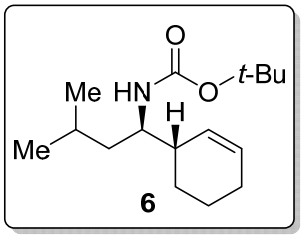
Following the general procedure, 140 mg of **10** (84%) was obtained after column chromatography as a yellow solid; mp 85-86 ºC; R_F 0.39 (hexano/AcOEt 2:1); $[\alpha]^{20}_D$ -42.1 (*c* 0.69, CH_2Cl_2); IR (film) ν 3373, 3025, 2924, 2848, 1453, 1412, 1362, 1165, 1048, 944, 739, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 [9H, s, $C(CH_3)_3$], 1.66-1.86 (5H, m, 2 × CH_2, CH), 1.96-2.21 (4H, m, 2 × CH_2), 2.60-2.66 (3H, m, CH_2, CH), 2.71-2.76 (2H, m, CH_2), 3.23-3.29 (2H, m, NH, HNC*H*), 5.49-5.55 (1H, m, CH), 5.82-5.91 (1H, m, CH), 7.15-7.21 (4H, m, ArH), 7.26-7.28 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9 (CH_3), 26.6 (CH_2), 28.5 (CH_2), 29.4 (CH_2), 30.3 (CH_2), 32.7 (CH_2), 35.0 (CH_2), 44.5 (CH), 56.2 (C), 60.8 (CH), 126.0 (CH), 128.5 (CH), 128.6 (CH), 132.7 (CH), 133.6 (CH), 142.0 (C); LRMS (EI) *m/z* 261 (M^+-C_4H_8, 25%), 181 (22), 156 (44), 134 (16), 124 (14), 117 (92), 91 (100), 81 (12), 67 (13); HRMS (ESI-TOF) Calcd for $C_{20}H_{32}NOS$ $[M+H]^+$ 334.2205, found 334.2196.

Tandem desulfinylation-*N*-Boc protection of 4a. Synthesis of (1*R*)-*N*-(*tert*-Butoxycarbonyl)-1-[(*S*)-cyclohex-2-en-1-yl]-3-methylbutan-1-amine (6):

To a stirred solution of **4a** (400 mg, 1.48 mmol) in methanol (15 mL) was added drop wise a 4M HCl solution in dioxane (2.6 mL, 10.5 mmol) at 23 ºC. After 2 h stirring at this temperature, the resulting mixture was hydrolyzed with water (30 mL) and extracted with EtOAc (3 × 15 mL). The aqueous layer was basified with a 2M NaOH aqueous solution (15 mL), extracted with EtOAc (3 × 15 mL), dried over anhydrous $MgSO_4$ and evaporated (15

Torr). The resulting white solid was dissolved in methanol (7.0 mL) and to this methanolic solution was successively added sodium carbonate (0.5 g, 4.7 mmol), di-*tert*-butyl dicarbonate (0.98 g, 4.5 mmol) and triethylamine (0.727 g, 1.0 mL, 7.3 mmol). After refluxing for 1 h, the reaction mixture was allowed to cool down to room temperature and after that EtOAc was added (15 mL). The solid was filtered off and the filtrate evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield 241 mg of pure compound **6** (61%). Physical and spectroscopic data follow.

(1*R*)-*N*-(*tert*-Butoxycarbonyl)-1-[(*S*)-cyclohex-2-en-1-yl]-3-methylbutan-1-amine (6):

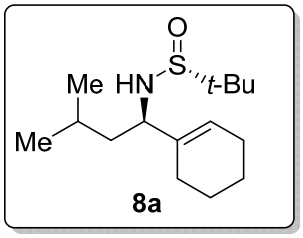


White solid; mp 67-68 ^{o}C; R_F 0.55 (hexane/AcOEt 20:1); $[\alpha]^{20}_{D}$ -4.5 (*c* 0.54, CH_2Cl_2); IR (film) ν 3373, 3013, 2977, 2929, 2866, 1681, 1518, 1362, 1268, 1173, 1012 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.6 Hz, CH_3), 0.92 (3H, d, *J* = 6.6 Hz, CH_3), 1.26-1.32 (2H, m, CH_2), 1.44 [9H, s, $C(CH_3)_3$], 1.50-1.82 (5H, m, 2 × CH_2, CH), 1.96-2.00 (2H, m, CH_2), 2.21-2.33 (1H, m, CH), 3.58-3.70 (1H, m, HNC*H*), 4.29-4.33 (1H, m, NH), 5.51-5.56 (1H, m, CH), 5.81-5.85 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0 (CH_2), 22.3 (CH_3), 23.5 (CH_3), 25.1 (CH_3), 25.4 (CH_2), 26.1 (CH_2), 28.6 (CH_3), 40.0 (CH), 42.2 (CH_2), 52.3 (CH), 78.9 (C), 127.0 (CH), 130.5 (CH), 156.0 (C); LRMS (EI) *m/z* 211 (M^+-C_4H_8, 0.5%), 186 (27), 130 (100), 86 (96), 81 (20); HRMS (ESI-TOF) Calcd for $C_{16}H_{30}NO_2$ $[M+H]^+$ 268.2277, found 268.2264.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl allyl amine derivatives 8:

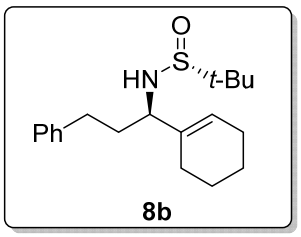
To a solution of the (R_S)-*N*-*tert*-butanesulfinyl imine derived from cyclohexene-1-carbaldehyde (213 mg, 1.0 mmol) in THF (4.0 mL) was added dropwise a 0.8M solution of isopentenylmagnesium bromide in THF for compound **8a** (2.0 mL, 1.6 mmol) or 3-phenylpropylmagnesium bromide for compound **8b** (2.0 mL, 1.6 mmol) at -78 ºC. The reaction was allowed to reach room temperature and after 4 h, it was cooled down to 0 ºC, hydrolyzed with water (5 mL) and extracted with EtOAc (4 × 15 mL). The organic layers were successively washed with water (15 mL), brine (10 mL) and then dried over anhydrous $MgSO_4$and concentrate under vacuum (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compounds **8**. Yields, physical and spectroscopic data for these compounds follow.

(1*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-(cyclohexen-1-yl)-3-methylbutan-1-amine (8a):



Following the general procedure, 173 mg of **8a** (64%) was obtained after column chromatography as a white solid; mp 72-73 ^{o}C; R_F 0.34 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -92.3 (*c* 0.57, CH_2Cl_2); IR (film) ν 3235, 2955, 2932, 2864, 1468, 1451, 1363, 1170, 1049, 1006, 917, 802 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.4 Hz, CH_3), 0.91 (3H, d, *J* = 6.4 Hz, CH_3), 1.20 [9H, s, $C(CH_3)_3$], 1.50-1.62 (4H, m, 2 × CH_2), 1.91-2.07 (4H, m, 2 × CH_2), 2.95 (1H, d, *J* = 2.3 Hz, NH), 3.82 (1H, m, HNC*H*), 5.72-5.73 (1H, t, *J* = 1.8 Hz, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (CH_3), 22.7 (CH_2), 22.75 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 23.3 (CH_2), 25.0 (CH_2), 25.3 (CH), 43.3 (CH_2), 55.0 (C), 59.6 (CH), 126.93 (CH), 136.2 (C); LRMS (EI) *m/z* 215 (M^+-C_4H_8, 23%), 151 (35), 140 (10), 110 (25), 109 (16), 95 (100), 81 (23), 79 (14), 67 (12), 57 (25); HRMS (ESI-TOF) Calcd for $C_{17}H_{30}NOS$ $[M+H]^+$ 272.2048, found 272.2045.

(1*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-(cyclohexen-1-yl)-3-phenylpropan-1-amine (8b):



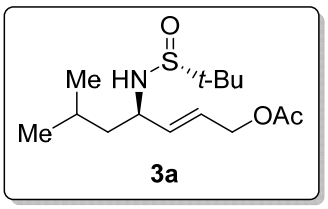
Following the general procedure, 268 mg of **8b** (84%) was obtained after column chromatography as a white solid; mp 88-89 ^{o}C; R_F 0.26 (hexane/AcOEt 2:1); $[\alpha]^{20}_D$ -65.2 (*c* 0.62, CH_2Cl_2); IR (film) ν 3215, 2941, 2925, 2857, 1455, 1294, 1181, 1051, 884, 751, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 [9H, s, $C(CH_3)_3$], 1.56-1.66 (4H, m, 2 × CH_2), 1.80-1.95 (4H, m, 2 × CH_2), 2.06-2.08 (2H, m, CH_2), 2.55-2.60 (2H, m, CH_2), 3.01 (1H, d, *J* = 2.8 Hz, NH), 3.73-3.78 (1H, m, HNC*H*), 5.73-5.74 (1H, m, CH), 7.17-7.19 (4H, m, ArH), 7.25-7.28 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_2), 22.8 (CH_3), 22.9 (CH_2), 23.1 (CH_2), 25.3 (CH_2), 29.8 (CH_2), 32.6 (CH_2), 35.9 (CH_2), 55.1 (C), 61.3 (CH), 126.1 (CH), 127.5 (CH), 128.5 (CH), 128.5 (CH), 135.7 (C), 141.6 (C); LRMS (EI) *m/z* 261 (M^+-C_4H_8, 38%), 213 (22), 212 (30), 198 (13), 184 (11), 157 (30), 153 (11), 109 (20), 107 (35), 106 (15), 105 (100), 104 (35), 94 (23), 91 (99), 81 (18), 79 (53), 77 (36), 65 (19); HRMS (ESI-TOF) Calcd for $C_{19}H_{30}NOS$ $[M+H]^+$ 320.2048, found 320.2045.

General procedure for the regioselective palladium(II)-catalyzed oxidation of *N*-*tert*-butanesulfinyl homoallyl amines 2. Characterization of compounds 3:

To a flask containing the corresponding homoallyl amine derivative **2** (0.2 mmol), 3Å molecular sieves (44 mg), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and freshly distilled *p*-

benzoquinone (43.2 mg, 0.4 mmol), was successively added acetic acid (0.63 g, 0.6 mL, 10.5 mmol) and DMSO (0.66 g, 0.6 mL, 8.5 mmol). The reaction mixture was stirred for 48 h at 40 ºC. Then, the resulting mixture was hydrolyzed with an aqueous NH_4Cl saturated solution (10 mL), extracted with EtOAc (3 × 15 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield products **3**. Yields are given on Table 2. Physical and spectroscopic data follow.

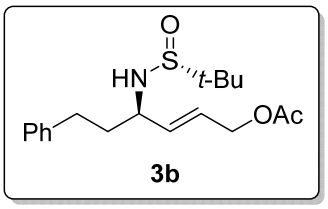
***E*-(4*R*,*R*$_S$)-1-Acetoxy-*N*-(*tert*-butanesulfinyl)-6-methylhept-2-en-4-amine (3a)**:



3a

Brown oil; R_F 0.46 (hexane/AcOEt 1:2); $[\alpha]^{20}_D$ -14.5 (*c* 1.0, CH_2Cl_2); IR (film) ν 2959, 2938, 2868, 1737, 1456, 1364, 1229 1027, 971, 797, 733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, d, *J* = 6.6 Hz, CH_3), 0.91 (3H, d, *J* = 6.6 Hz, CH_3), 1.22 [9H, s, $C(CH_3)_3$], 1.51-1.63 (1H, m, CH), 1.66-1.73 (2H, m, CH_2), 2.07 (3H, s, $COCH_3$), 3.18 (1H, d, *J* = 7.4 Hz, NH), 3.77-3.88 (1H, m, HNC*H*), 4.56 (2H, d, *J* = 4.3 Hz, CH_2O), 5.77-5.80 (2H, m, 2 x CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_3), 22.5 (CH_3), 22.8 (CH_3), 24.6 (CH_3), 45.0 (CH_2), 56.2 (C), 56.5 (CH), 64.4 (CH_2), 125.8 (CH), 136.6 (CH), 171.0 (C); LRMS (EI) *m/z* 233 (M^+-C_4H_8, 0.9%), 167 (33), 150 (11), 149 (100), 71 (14), 70 (13), 57 (20); HRMS (ESI-TOF) Calcd for $C_{14}H_{28}NO_3S$ $[M+H]^+$ 290.1790, found 290.1776.

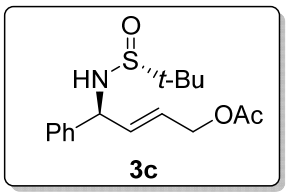
***E*-(3*R*,*R*$_S$)-3-Acetoxy-*N*-(*tert*-butanesulfinyl)-1-phenylhex-4-en-3-amine (3b)**:



3b

Orange oil; R_F 0.44 (hexane/AcOEt 1:2); $[\alpha]^{20}_D$ -18.0 (*c* 0.3, CH_2Cl_2); IR (film) ν 2957, 2927, 1736, 1455, 1364, 1227, 1181, 1025, 969, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.22 [9H, s, $C(CH_3)_3$], 1.85-2.08 (4H, m, 2 × CH_2), 2.08 (3H, s, $COCH_3$), 3.27 (1H, d, *J* = 6.5 Hz, NH), 3.81-3.85 (1H, m, HNC*H*), 4.55-4.59 (2H, m, CH_2O), 5.80-5.82 (2H, m, 2 × CH), 7.15-7.19 (3H, m, ArH), 7.26-7.29 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8 (CH_3), 25.3 (CH_3), 29.8 (CH_2), 37.3 (CH_2), 56.2 (C), 57.5 (CH), 64.3 (CH_2), 126.2 (CH), 128.6 (CH), 128.7 (CH), 130.8 (CH), 135.7 (CH), 141.5 (C), 170.9 (C); LRMS (EI) *m/z* 281 (M^+-C_4H_8, 1%), 279 (10), 167 (32), 149 (100), 71 (15), 70 (13), 57 (22); HRMS (ESI-TOF) Calcd for $C_{18}H_{28}NO_3S$ $[M+H]^+$ 338.1790, found 338.1784.

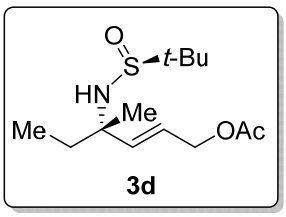
***E*-(1*R*,*R*$_S$)-4-Acetoxy-*N*-(*tert*-butanesulfinyl)-1-phenylbut-2-en-1-amine 3c)**:



3c

Orange oil; R_F 0.25 (hexane/AcOEt 1:2); $[\alpha]^{20}_D$ -36.9 (*c* 0.25, CH_2Cl_2); IR (film) ν 3031, 2955, 2926, 2871, 1735, 1647, 1455, 1232, 1026, 967, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $C(CH_3)_3$], 2.06 (3H, s, $COCH_3$), 3.53 (1H, d, *J* = 3.8 Hz, NH), 4.55 (2H, d, *J* = 5.6 Hz, CH_2O), 4.98-5.01 (1H, m, HNC*H*), 5.78-5.85 (1H, m, CH), 5.94-6.02 (1H, m, CH), 7.28-7.37 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_3), 22.7 (CH_3), 56.0 (C), 60.8 (CH), 64.1 (CH_2), 126.7 (CH), 127.9 (CH), 128.1 (CH), 128.9 (CH), 129.3 (CH), 135.2 (CH), 140.3 (C), 170.8 (C); LRMS (EI) *m/z* 279 (M^+-2 CH_3, 11.6%), 253 (0.05), 167 (34), 150 (12), 149 (100), 71 (15), 70 (13), 57 (21); HRMS (ESI-TOF) Calcd for $C_{16}H_{24}NO_3S$ $[M+H]^+$ 310.1477, found 310.1465.

***E*-(3*S*,*S*$_S$)-6-Acetoxy-*N*-(*tert*-butanesulfinyl)-3-methylhex-4-en-3-amine (3d)**:



3d

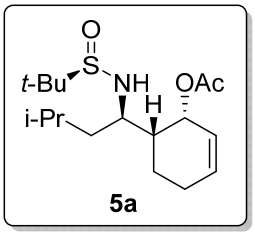
Brown oil; R_F 0.38 (hexane/AcOEt 1:2); $[\alpha]^{20}_D$ +18.3 (*c* 0.13, CH_2Cl_2); IR (film) ν 2972, 2963, 2938, 2911, 1735, 1457, 1363, 1229, 1026, 969, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (3H, t, *J* = 7.4 Hz, CH_3), 1.21 [9H, s, $C(CH_3)_3$], 1.35 (3H, s, CH_3), 1.55-1.70 (2H, m, CH_2), 2.08 (3H, s, $COCH_3$), 3.21 (1H, br s, NH), 4.59 (2H, d, *J* = 5.5 Hz, CH_2O), 5.74 (1H, dt, *J* = 15.7, 5.5 Hz, CH), 5.80 (1H, d, *J* = 15.9 Hz, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_3), 22.8 (CH_3), 25.6 (CH_3), 29.8 (CH_3), 34.4 (CH_2), 56.0 (C), 58.9 (C), 64.8 (CH_2), 123.6 (CH), 140.8 (CH), 171.0 (C); LRMS (EI) *m/z* 275 (M^+, 0.2%), 219 (0.6), 167 (33), 150 (12), 149 (100), 71 (13), 70 (13), 57 (21); HRMS (ESI-TOF) Calcd for $C_{13}H_{26}NO_3S$ $[M+H]^+$ 276.1633, found 276.1622.

General procedure for the regio- and stereoselective palladium(II)-catalyzed oxidation of *N*-*tert*-butanesulfinyl substituted aminoalkenes 4, 6, 8 and 10:

To a flask containing the corresponding *N*-*tert*-butanesulfinyl substituted aminoalkene **4**, **6**, **8** or **10** (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and freshly distilled *p*-benzoquinone (43.2 mg, 0.4 mmol), was successively added 1,4 dioxane (0.62 g, 0.6 mL, 7.0 mmol) and acetic acid (0.48 g, 0.46 mL, 8.0 mmol). The reaction mixture was stirred for 48 h at 50 ºC. Then, the resulting mixture was hydrolyzed with an aqueous NH_4Cl saturated solution (10 mL), extracted with EtOAc (3 × 15 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield

products **5**, **7**, **9** and **11**. Yields are given on Table 3 and Schemes 2 and 3. Physical and spectroscopic data follow.

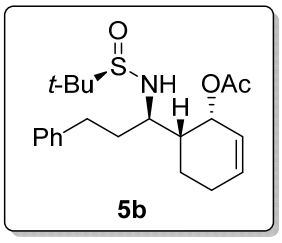
(1*R*,*R*$_S$)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butanesulfinyl)-3-methylbutan-1-amine (5a):



5a

Yellow oil; R_F 0.35 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -158.5 (*c* 0.2, CH_2Cl_2); IR (film) ν 2954, 2927, 2867, 1734, 1466, 1366, 1234, 1056, 1013, 894 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.6 Hz), 0.91 (3H, d, *J* = 6.6 Hz), 1.22 [9H, s, $C(CH_3)_3$], 1.65-1.74 (2H, m, CH_2), 1.85-1.89 (1H, m, HNCHC*H*), 2.07 (3H, s, COC*H*$_3$), 2.10-2.41 (2H, m, CH_2), 3.38 (1H, m, HN*CH*), 3.91 (1H, d, *J* = 7.5 Hz, NH), 5-29-5.31 (1H, m, OCH), 5.85-5.94 (2H, m, 2 × CH), 5.96-6.03 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (CH_3), 22.0 (CH_3), 22.1 (CH_2), 23.1 (CH_3), 23.5 (CH), 24.5 (CH), 26.2 (CH_2), 41.5 (CH), 44.5 (CH_2), 56.1 (C), 57.8 (CH), 68.3 (CH), 124.3 (CH), 134.0 (CH), 170.1 (C); LRMS (EI) *m/z* 273 (M^+-C_4H_8, 6.7%), 258 (11), 257 (53), 255 (20), 213 (49), 201 (12), 200 (64), 168 (14), 133 (40), 129 (22), 113 (100), 112 (27), 79 (88); HRMS (ESI-TOF) Calcd for $C_{17}H_{32}NO_3S$ $[M+H]^+$ 330.2103, found 330.2093.

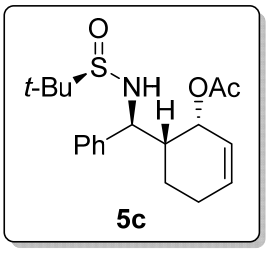
(1*R*,*R*$_S$)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butanesulfinyl)-3-phenylpropan-1-amine (5b):



5b

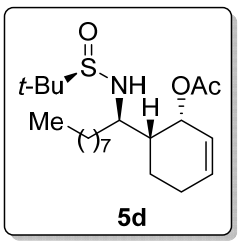
Orange oil; R_F 0.32 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -180 (*c* 0.22, CH_2Cl_2); IR (film) ν 2927, 1726, 1454, 1367, 1234, 1053, 909, 729, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 [9H, s, $C(CH_3)_3$], 1.75-2.00 (5H, m, CH, 2 × CH_2), 2.06 (3H, s, $COCH_3$), 2.60-2.67 (2H, m, CH_2), 2.72-2.81 (2H, m, CH_2), 3.33-3.42 (1H, m, HNCH), 3.99 (1H, d, *J* = 6.7 Hz, NH), 5.33-5.35 (1H, m, OCH), 5.89-5.93 (1H, m, CH), 5.97-6.02 (1H, m, CH), 7.16-7.23 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (CH_3), 21.8 (CH_2), 23.1 (CH_3), 26.1 (CH_2), 32.0 (CH_2), 36.4 (CH_2), 41.2 (CH), 56.2 (C), 58.3 (CH), 67.6 (CH), 124.3 (CH), 126.1 (CH), 128.5 (CH), 128.6 (CH), 133.9 (CH), 141.8 (C), 170.3 (C); LRMS (EI) *m/z* 321 (M^+-C_4H_8, 0.12%), 155 (22), 132 (11), 127 (24), 117 (38), 105 (18), 92 (12), 91 (100), 80 (14), 79 (57), 78 (24), 77 (32), 65 (11); HRMS (ESI-TOF) Calcd for $C_{21}H_{32}NO_3S$ $[M+H]^+$ 378.2103, found 378.2102.

(1*S*,*R*$_S$)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butanosulfinyl)-1-phenylmethanamine (5c):



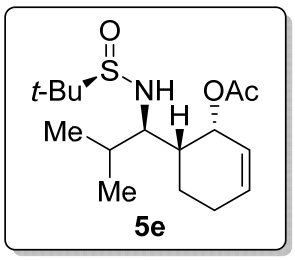
Brown oil; R_F 0.28 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -61.9 (*c* 0.4, CH_2Cl_2); IR (film) ν 2957, 2926, 2873, 1725, 1522, 1455, 1455, 1237, 1180, 1025, 735, 700, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 [9H, s, $C(CH_3)_3$], 1.99-2.12 (5H, m, CH, 2 × CH_2), 2.18 (3H, s, $COCH_3$), 4.17 (1H, d, *J* = 3.0 Hz, NH), 4.28 (1H, dd, *J* = 9.6, 3.0 Hz, HNCH), 5.42-5.45 (1H, m, OCH), 5.83.6.05 (2H, m, 2 × CH), 7.27-7.40 (5H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_2), 21.5 (CH_3), 22.8 (CH_3), 25.7 (CH_2), 29.8 (CH_2), 44.3 (CH), 55.6 (C), 60.3 (CH), 65.6 (CH), 124.1 (CH), 127.9 (CH), 128.6 (CH), 129.3 (CH), 133.9 (CH), 140.8 (C), 171.4 (C) LRMS (EI) *m/z* 293 (M^+-C_4H_8, 0.4%), 203 (12), 182 (14), 155 (14), 154 (12), 153 (100), 152 (30), 139 (33), 117 (12), 115 (12), 106 (19), 105 (17), 104 (30), 103 (17), 97 (26), 91 (18), 80 (24), 79 (83), 78 (16), 77 (38), 61 (13), 51 (11); HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3S$ $[M+H]^+$ 350.1790, found 350.1787.

(1*R*,*R*$_S$)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butanesulfinyl)nonan-1-amine (5d):



Orange oil; R_F 0.46 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -150.3 (*c* 1.0, CH_2Cl_2); IR (film) ν 2917, 2858, 1726, 1451, 1362, 1244, 1057, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.84-0.92 (3H, t, *J* = 5.6 Hz, CH_3), 1.23 [9H, s, $C(CH_3)_3$], 1.26-1.33 (12H, br s , 6 × CH_2), 1.53-2.05 (6H, m, 3 × CH_2), 2.07 (3H, s, $COCH_3$), 2.20-2.28 (1H, m, HNCHC*H*), 3.29-3.33 (1H, m, HNC*H*), 3.88 (1H, d, *J* = 6.6 Hz, NH), 5.29-5.31 (1H, m, OCH*),* 5.90-6.01 (2H, m, 2 × CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (CH_3), 21.6 (CH_3), 21.8 (CH_2), 22.8 (CH_2), 23.0 (CH_3), 25.7 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 34.4 (CH_2), 40.9 (CH), 56.0 (C), 58.9 (CH), 67.7 (CH), 124.3 (CH), 133.9 (CH), 170.3 (C); LRMS (EI) *m/z* 329 (M^+-C_4H_8, 0.5%), 189 (9), 139 (26), 97 (20), 91 (33), 80 (20), 79 (100), 78 (30), 77 (27), 61 (15), 55 (14); HRMS (ESI-TOF) Calcd for $C_{21}H_{39}NO_3S$ $[M+H]^+$ 386.2729, found 386.2724.

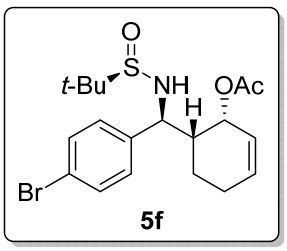
(1*S*,R_S)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butanesulfinyl)-2-methylpropan-1-amine (5e):



5e

Yellow oil; R_F 0.36 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -357.5 (*c* 0.15, CH_2Cl_2); IR (film) ν 2959, 2927, 2870, 1740, 1472, 1365, 1230, 1054, 1013, 908, 728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (3H, d, *J* = 6.7 Hz, CH_3), 0.95 (3H, d, *J* = 6.7 Hz, CH_3), 1.26 [9H, s, $C(CH_3)_3$], 1.70-2.05 (6H, m, 2 × CH, 2 × CH_2), 2.08 (3H, s, $COCH_3$), 3.05 (1H, q, *J* = 6.9 Hz, HNCH), 3.89 (1H, d, *J* = 7.1 Hz, NH), 5.25-5.28 (1H, m, OCH), 5.97-5.99 (2H, m, 2 × CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8 (CH_3), 20.7 (CH_3), 21.7 (CH_3), 22.4 (CH_2), 23.4 (CH_3), 26.3 (CH_2), 31.6 (CH), 39.4 (CH), 56.6 (C), 64.6 (CH), 68.0 (CH), 124.6 (CH), 133.7 (CH), 170.0 (C); LRMS (EI) *m/z* 259 (M^+-C_4H_8, 6%), 200 (17), 199 (10), 156 (24), 152 (32), 151 (16), 150 (16), 140 (12), 135 (14), 119 (47), 109 (15), 108 (17), 107 (100), 81 (20), 79 (46), 77 (20), 57 (43), 56 (27); HRMS (ESI-TOF) Calcd for $C_{16}H_{30}NO_3S$ $[M+H]^+$ 316.1946, found 316.1938.

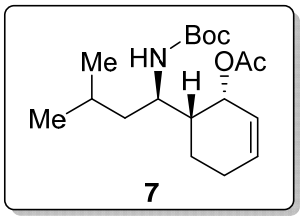
(1*S*,R_S)-1-[(1*S*,2*S*)-2-Acetoxycyclohex-3-en-1-yl]-1-(4-bromophenyl)-*N*-(*tert*-butanesulfinyl)methanamine (5f):



5f

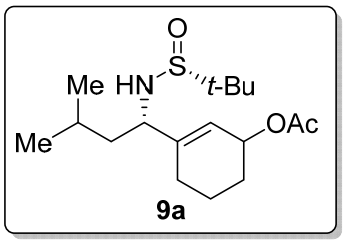
White soli; mp 140-141 °C; R_F 0.31 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -202 (*c* 0.12, CH_2Cl_2); IR (film) ν 3242, 2957, 2917, 1714, 1486, 1363, 1256, 1069, 1010, 888 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 [9H, s, $C(CH_3)_3$], 1.49-2.01 (5H, m, CH, 2 × CH_2), 2.17 (3H, s, $COCH_3$), 4.07 (1H, br s, NH), 4.22-4.26 (1H, dd, *J* = 9.0, 2.2 Hz, HNCH), 5.43-5.46 (1H, m, OCH), 5.80-5.87 (1H, m, CH), 5.99-6.05 (1H, m, CH), 7.19 (2H, d, *J* = 8.4 Hz, ArH), 7.48 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (CH_2), 21.4 (CH_3), 22.7 (CH_3), 25.6 (CH_2), 44.3 (CH), 55.6 (C), 59.4 (CH), 65.3 (CH), 121.8 (C), 123.9 (CH), 130.3 (CH), 131.8 (CH), 133.8 (CH), 139.9 (C), 171.3 (C); LRMS (EI) *m/z* 372 (M^+-C_4H_8, 1%), 283 (12), 281 (12), 262 (13), 260 (12), 233 (40), 232 (16), 231 (30), 230 (14), 185 (20), 184 (28), 183 (33), 182 (21), 167 (12), 155 (11), 139 (13), 116 (14), 115 (12), 102 (21), 97 (28), 80 (34), 79 (100), 78 (41), 77 (41); HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3SBr$ $[M+H]^+$ 428.0895, found 428.0883.

(1*R*,*R*$_S$)-1-[(1*R*,2*R*)-2-Acetoxycyclohex-3-en-1-yl]-*N*-(*tert*-butoxycarbonyl)-3-methylbutan-1-amine (7):



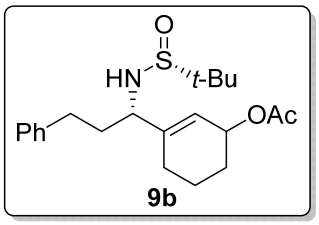
Yellow wax; R_F 0.36 (hexane/AcOEt 9:1); $[\alpha]^{20}_D$ -21.1 (*c* 0.51, CH_2Cl_2); IR (film) ν 2957, 2928, 2858, 1706, 1507, 1264, 1160, 733, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (3H, d, *J* = 6.4 Hz, CH_3), 0.94 (3H, d, *J* = 6.4 Hz, CH_3), 1.42 [9H, s, $C(CH_3)_3$], 1.55-1.71 (6H, m, 3 × CH_2), 2.06 (3H, s, OCH_3), 3.72-3.88 (1H, m, HNCH), 4.39 (1H, d, *J* = 10.2 Hz, NH), 5.22-5.27 (1H, m, OCH), 5.85-6.03 (2H, m, 2 × CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2 (CH_3), 23.8 (CH), 25.0 (CH_3), 26.1 (CH_2), 29.8 (CH_2), 42.6 (CH), 43.4 (CH_2), 50.0 (CH), 67.1 (CH), 72.9 (C), 124.8 (CH), 133.4 (CH), 155.7 (C), 170.7 (C); LRMS (EI) *m/z* 268 (M^+-C_4H_8, 2%), 186 (18), 152 (37), 130 (100), 108 (14), 97 (18), 80 (83), 79 (34), 57 (95); HRMS (ESI-TOF) Calcd for $C_{18}H_{31}NO_4Na$ $[M+Na]^+$ 348.2151, found 348.2139.

(1*R*,*R*$_S$)-1-(3-Acetoxycyclohexen-1-yl)-*N*-(*tert*-butanesulfinyl)-3-methylbutan-1-amine (9a):



Yellow oil; R_F 0.26 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -60.4 (*c* 0.34, CH_2Cl_2); IR (film) ν 2953, 2925, 2863, 1734, 1457, 1368, 1238, 1161, 1051, 1024, 913 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (3H, d, *J* = 6.5 Hz, CH_3), 0.93 (3H, d, *J* = 6.5 Hz, CH_3), 1.19 [9H, s, $C(CH_3)_3$], 1.46-1.64 (7H, m, 3 × CH_2, CH), 1.94-1.96 (2H, m, CH_2), 2.04 (3H, s, $COCH_3$), 3.02 (1H, d, *J* = 2.8 Hz, NH), 3.84 (2H, td, *J* = 7.3, 2.7 Hz, HNCH), 5.29-5.33 (1H, m, OCH), 5.70-5.74 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 22.7 (CH_3), 22.9 (CH_3), 23.6 (CH_2), 24.9 (CH_3), 28.6 (CH_2), 29.6 (CH_2), 43.6 (CH_2), 55.4 (C), 59.0 (CH), 68.9 (CH), 124.6 (CH), 143.0 (C), 170.9 (C); LRMS (EI) *m/z* 209 (M^+-$HNSOC_4H_9$, 1.3%), 166 (16), 150 (11), 125 (22), 107 (25), 98 (20), 97 (100), 96 (17), 85 (28), 83 (82), 82 (24), 79 (24), 71 (47), 70 (40), 69 (69), 67 (18), 57 (77), 56 (41), 55 (84); HRMS (ESI-TOF) Calcd for $C_{17}H_{32}NO_3S$ $[M+H]^+$ 330.2103, found 330.2091.

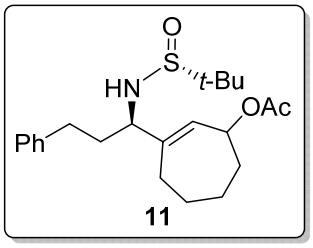
(1*R*,*R*$_S$)-1-(3-Acetoxycyclohexen-1-yl)-*N*-(*tert*-butanesulfinyl)-3-phenylpropan-1-amine (9b):



Orange oil; R_F 0.26 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -97.0 (*c* 0.39, CH_2Cl_2); IR (film) ν 3205, 2950, 2934, 2880, 1735, 1455, 1367, 1237, 1052, 1020, 751, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ

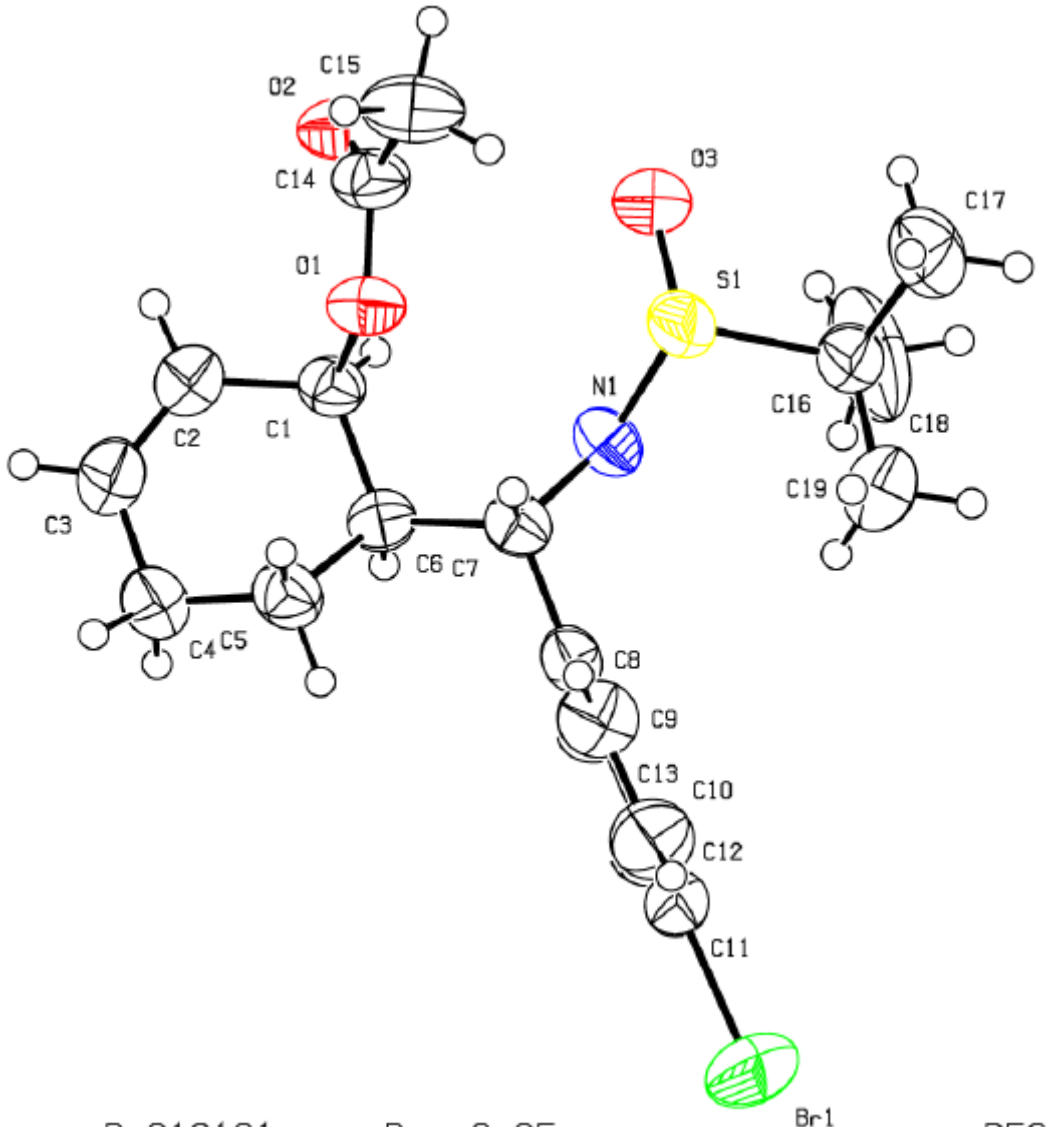
1.17 [9H, s, $C(CH_3)_3$], 1.62-1.68 (2H, m, CH_2), 1.89-1.99 (7H, m, 3 × CH_2, CH), 2.06 (3H, s, $COCH_3$), 2.57-2.66 (2H, m, CH_2), 3.08 (1H, d, *J* = 3.2 Hz, NH), 3.81 (1H, td, *J* = 7.1, 3.1 Hz, HNC*H*), 5.29-5.36 (1H, m, OCH), 5.71-5.75 (1H, m, CH), 7.14-7.23 (4H, m, ArH), 7.25-7.33 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5 (CH_2), 22.7 (CH_3), 23.8 (CH_2), 28.6 (CH_2), 32.4 (CH_2), 36.0 (CH_2), 55.5 (C), 60.7 (CH), 68.7 (CH), 125.1 (CH), 126.2 (CH), 128.6 (CH), 128.6 (CH), 141.2 (C), 142.4 (C), 170.8 (C); LRMS (EI) *m/z* 257 (M^+-$HNSOC_4H_9$, 3%), 256 (14), 214 (21), 210 (16), 155 (28), 117 (21), 106 (23), 105 (60), 104 (18), 91 (100), 79 (29); HRMS (ESI-TOF) Calcd for $C_{21}H_{32}NO_3S$ $[M+H]^+$ 378.2103, found 378.2092.

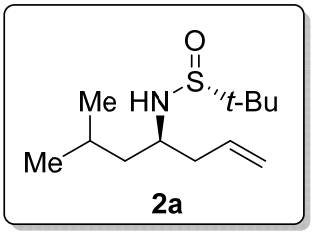
(1*R*,*R*$_S$)-1-(3-Acetoxycyclohepten-1-yl)-*N*-(*tert*-butanesulfinyl)-3-phenylpropan-1-amine (11):



Orange wax; R_F 0.43 (hexane/AcOEt 1:1); $[\alpha]^{20}_D$ -32.5 (*c* 0.26, CH_2Cl_2); IR (film) ν 3025, 2925, 2857, 1732, 1454, 1366, 1240, 1025, 748, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 [9H, s, $C(CH_3)_3$], 1.68-1.73 (8H, m, 4 × CH_2), 1.93-2.00 (2H, m, CH_2), 2.07 (3H, s, $COCH_3$), 2.53-2.60 (2H, m, CH_2), 3.22 (1H, d, *J* = 7.1 Hz, NH), 3.66-3.77 (1H, m, HNC*H*), 5.35-5.47 (1H, m, OCH), 5.64-5.69 (1H, m, CH), 7.10-7.21 (4H, m, ArH), 7.26-7.29 (1H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 27.5 (CH_2), 28.0 (CH_2), 29.8 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 34.8 (CH_2), 56.0 (C), 63.2 (CH), 73.9 (CH), 126.1 (CH), 128.5 (CH), 128.6 (CH), 132.3 (CH), 141.6 (C), 142.2 (C), 170.6 (C); LRMS (EI) *m/z* 271 (M^+-$HNSOC_4H_9$, 2%), 210 (19), 207 (31), 186 (16), 169 (18), 137 (20), 121 (20), 119 (26), 117 (18), 105 (36), 94 (43), 91 (100), 77 (27), 65 (24); HRMS (ESI-TOF) Calcd for $C_{22}H_{34}NO_3S$ $[M+H]^+$ 392.2259, found 392.2254.

X-Ray structure of compound 5f




O
S
Me HN
t-Bu
Me

2a

5.84
5.81
5.78
5.78
5.75
5.19
5.19
5.18
5.18
5.18
5.14
5.14
5.13
5.13
5.12
5.11
5.11
3.42
3.41
3.40
3.39
3.38
3.37
3.37
3.36
3.35
3.21
3.19
2.42
2.40
2.38
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2.36
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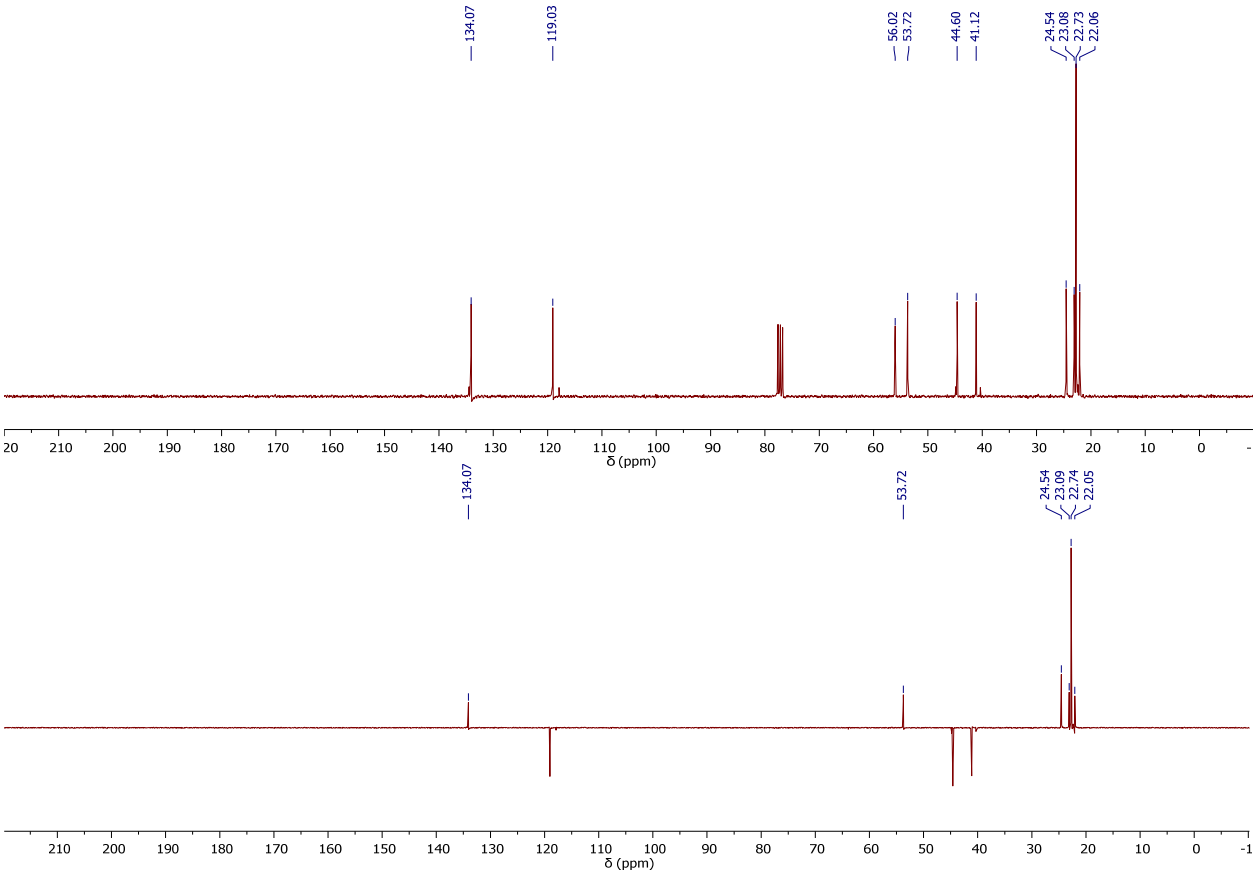
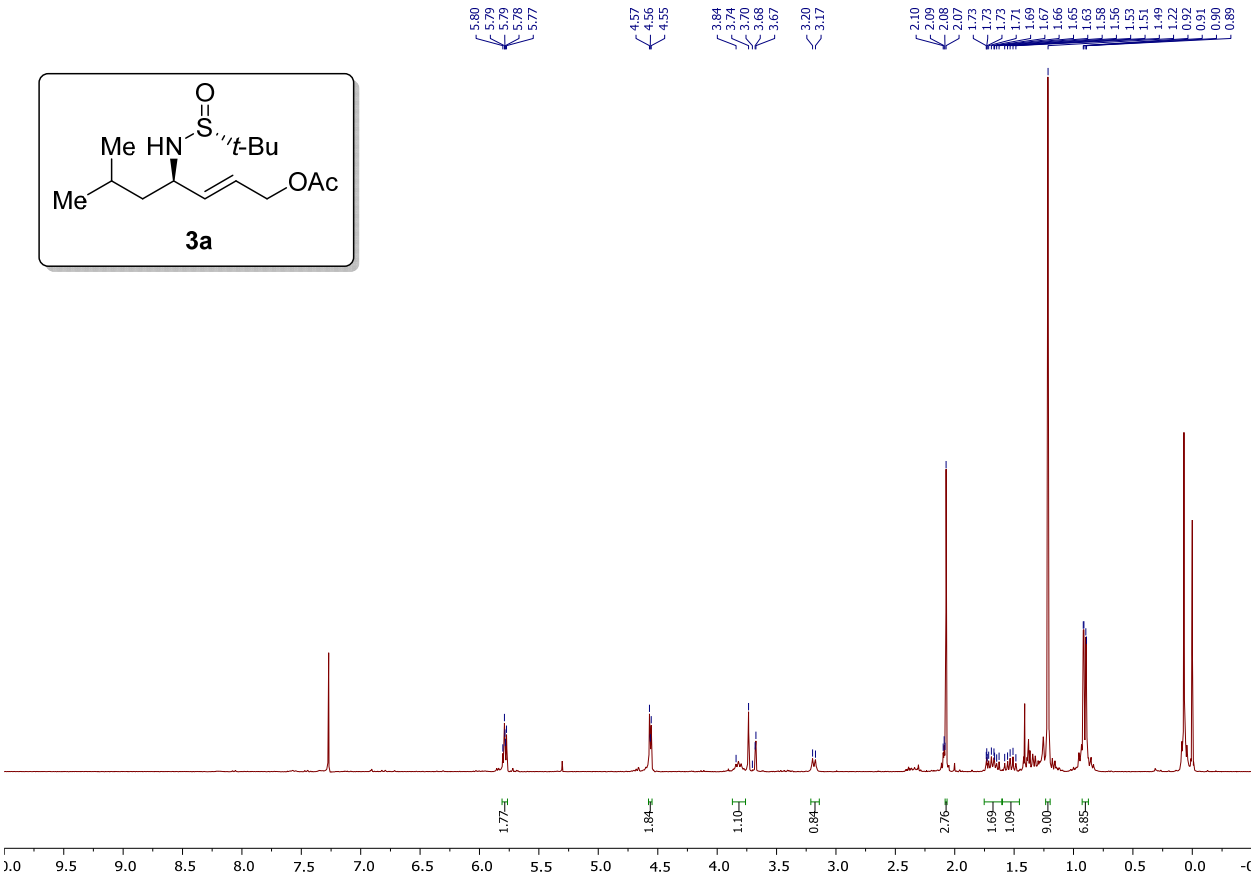
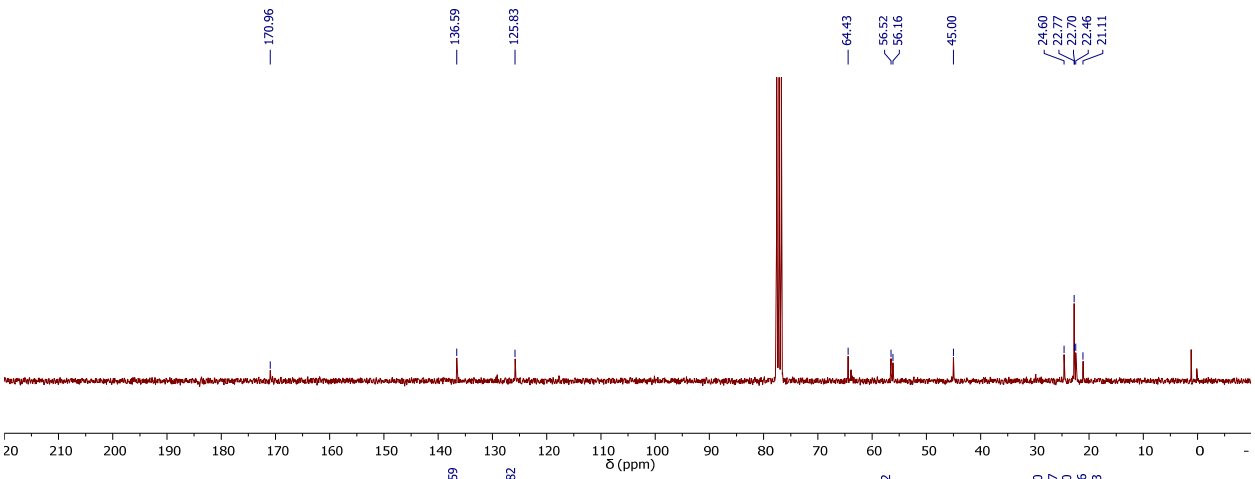
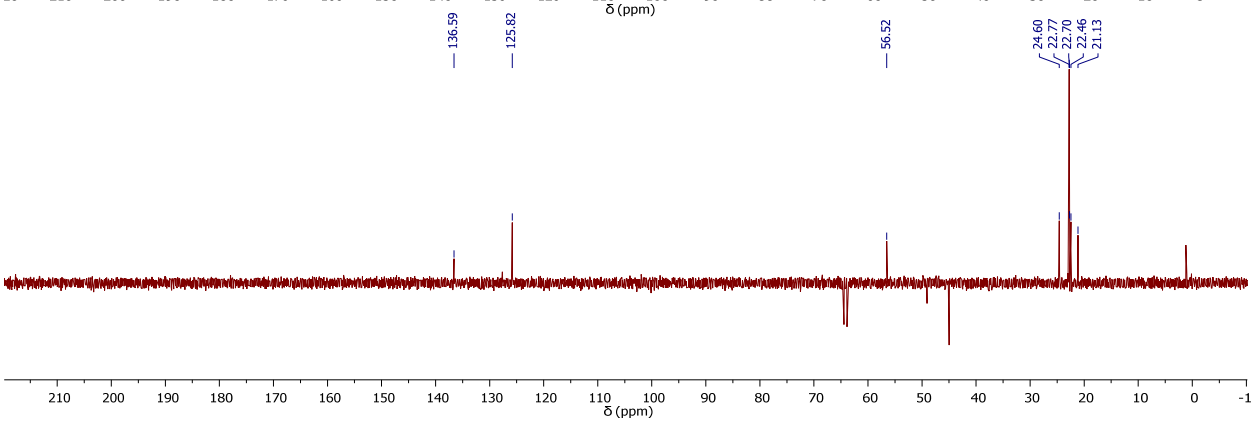
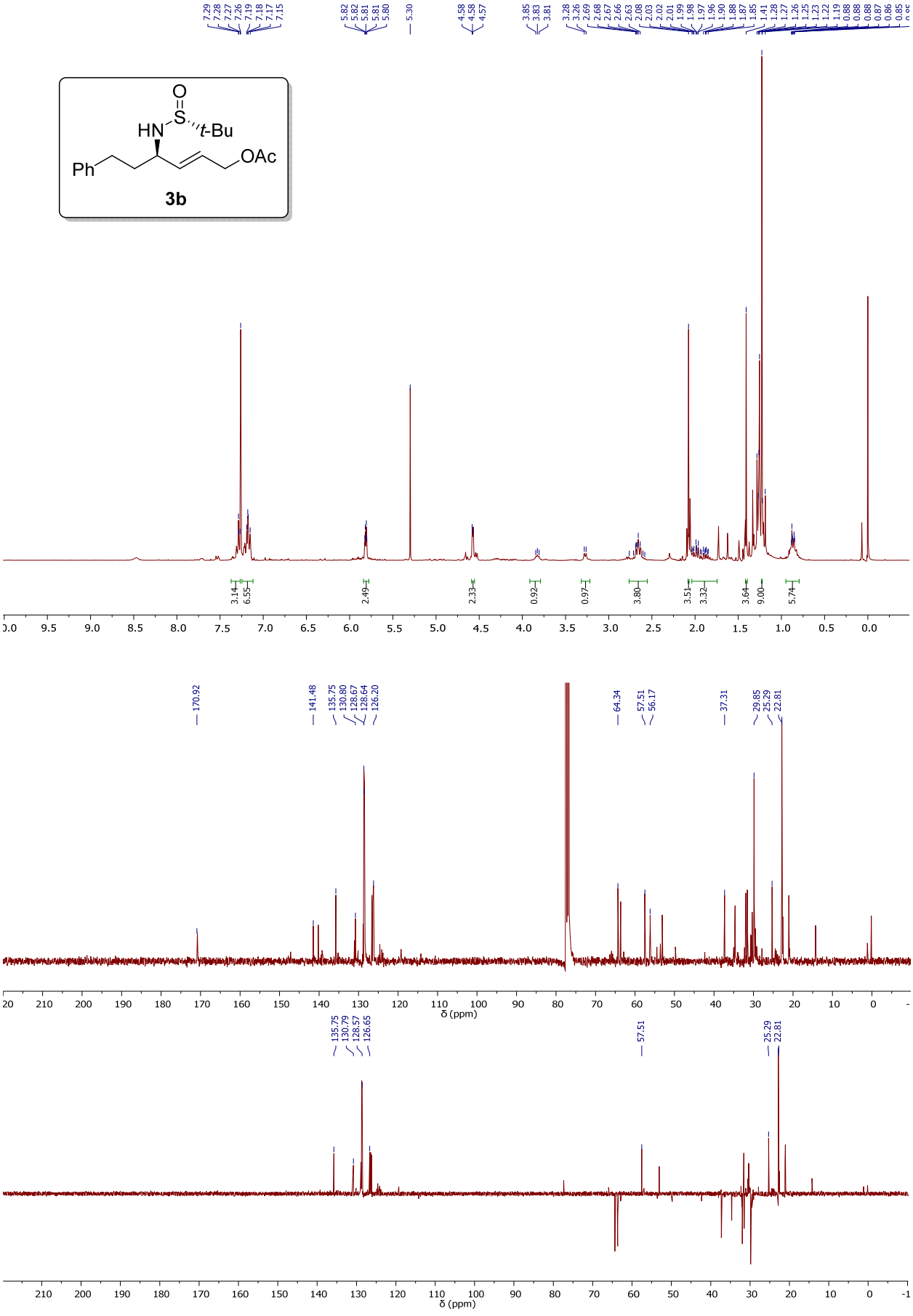
1.76
1.76
1.74
1.74
1.73
1.73
1.72
1.72
1.69
1.63
1.21
0.92
0.90
0.88
1.17
1.92
1.09
0.72
2.17
1.65
7.93
5.20

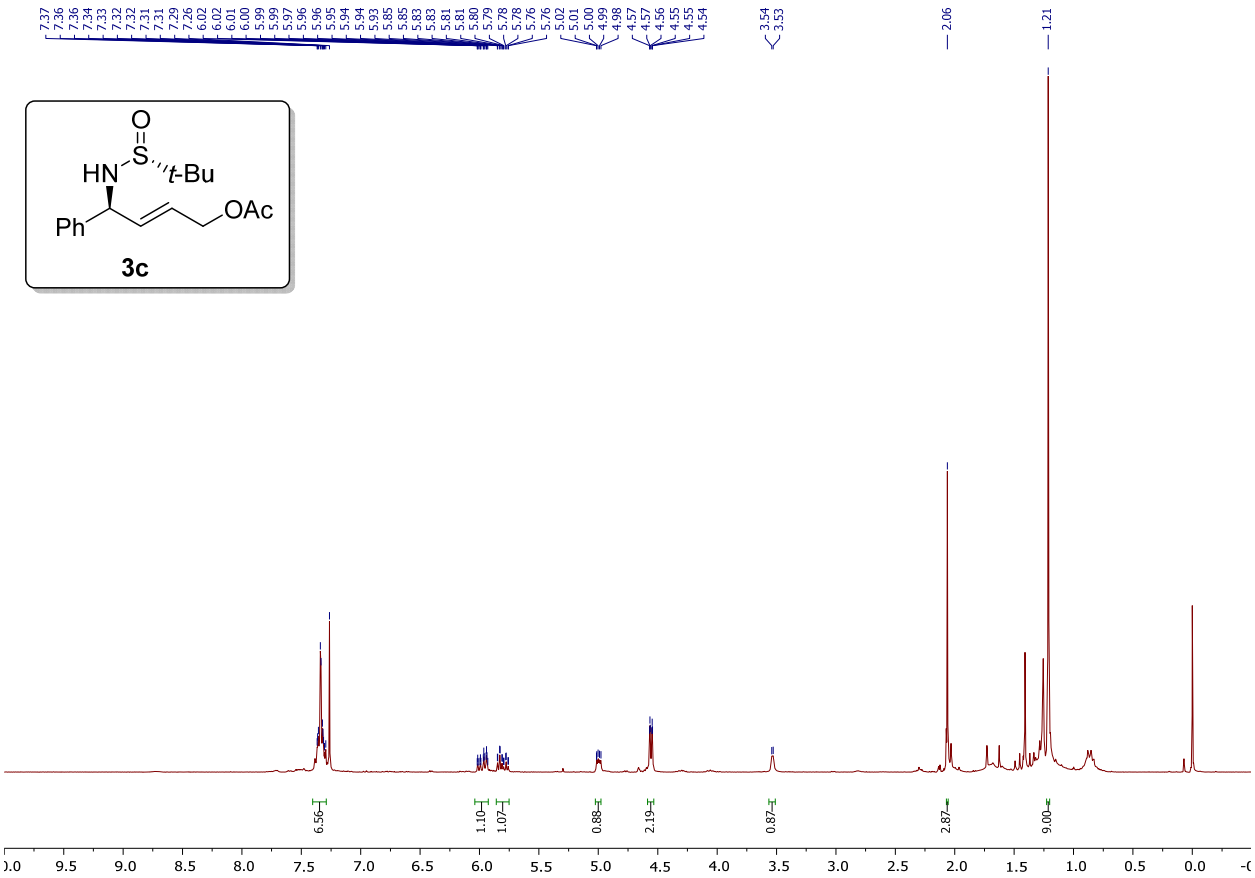

134.07
119.03
56.02
53.72
44.60
41.12
24.54
23.08
22.73
22.06
δ (ppm)
134.07
53.72
24.54
23.09
22.74
22.05
δ (ppm)


Me HN
S
O
t-Bu
OAc
Me
3a






O
HN
S
t-Bu
Ph
OAc
3b
δ (ppm)


7.37
7.36
7.36
7.34
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7.32
7.32
7.31
7.31
7.29
7.26
6.02
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6.00
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5.96
5.96
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4.57
4.57
4.56
4.55
4.55
4.54
3.54
3.53
2.06
1.21
O
S
HN
t-Bu
Ph
OAc
3c
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1.10
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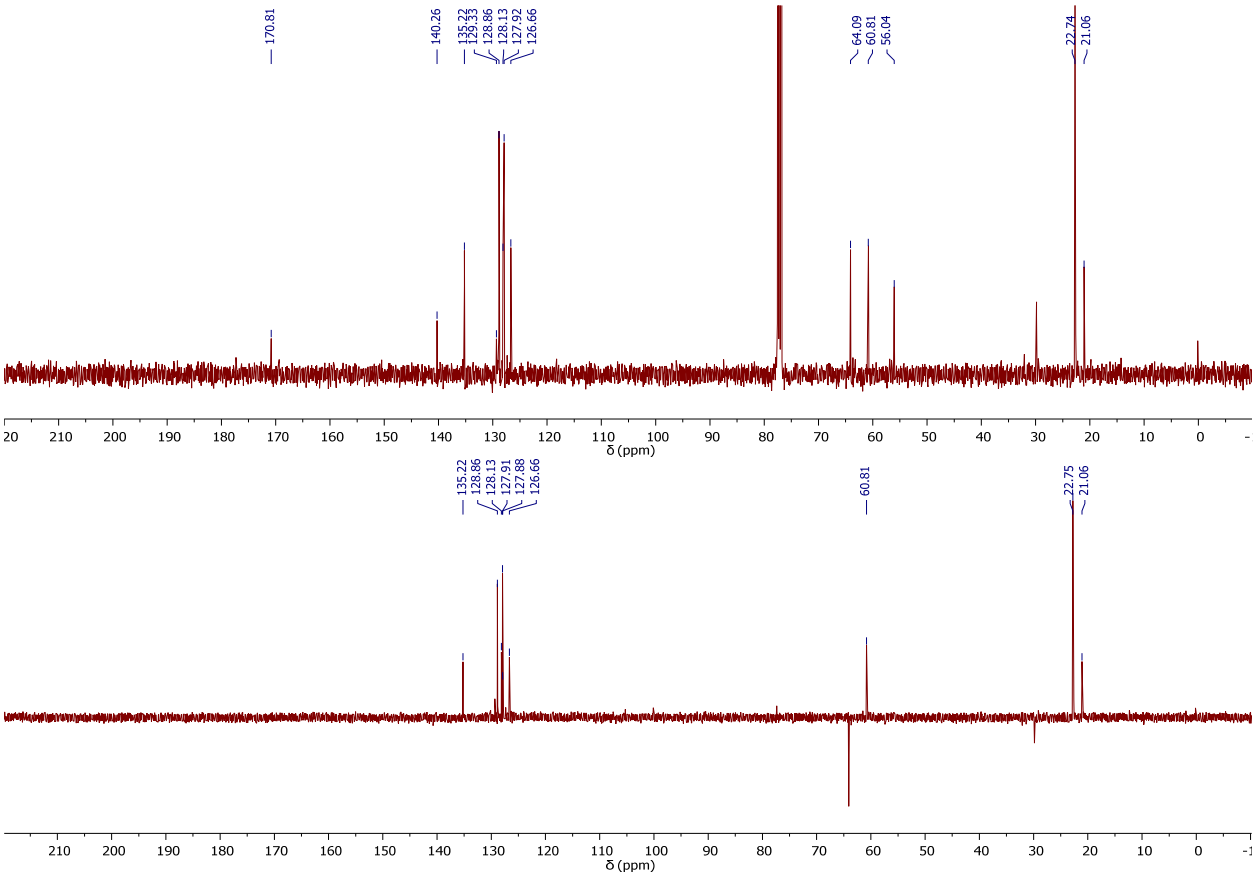
0.88
2.19
0.87
2.87
9.00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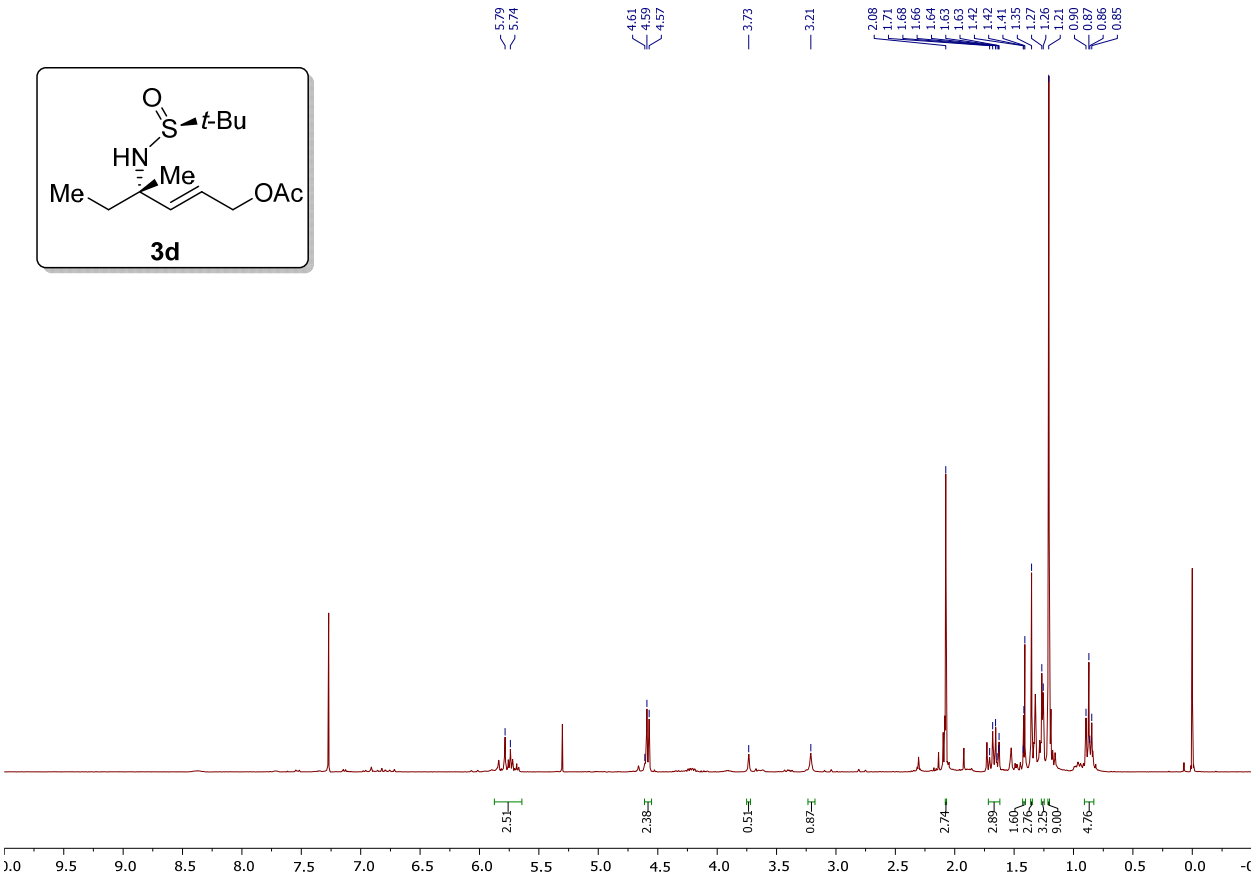
128.86
128.13
127.92
126.66
64.09
60.81
56.04
22.74
21.06
δ (ppm)
135.22
128.86
128.13
127.91
127.88
126.66
60.81
22.75
21.06
δ (ppm)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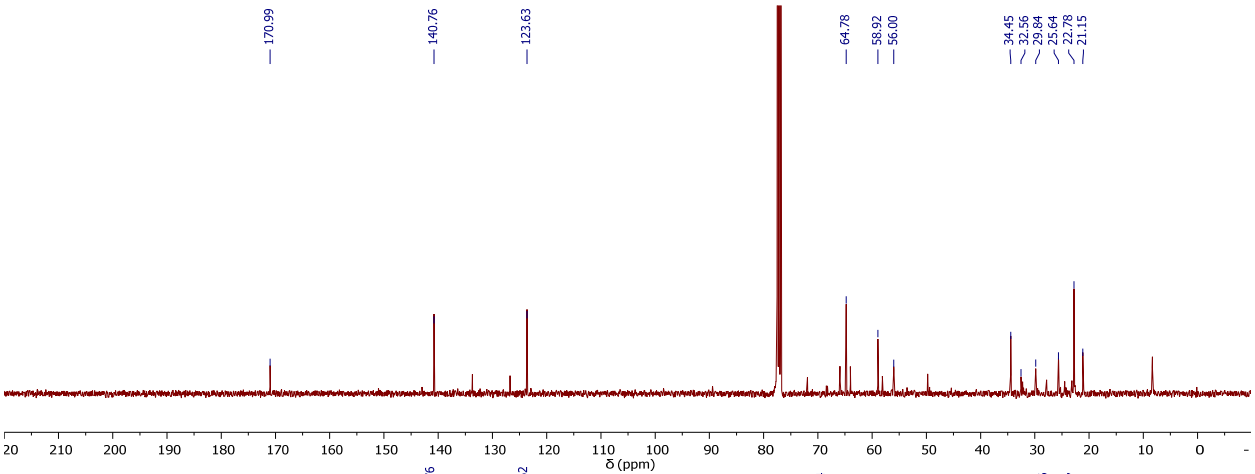
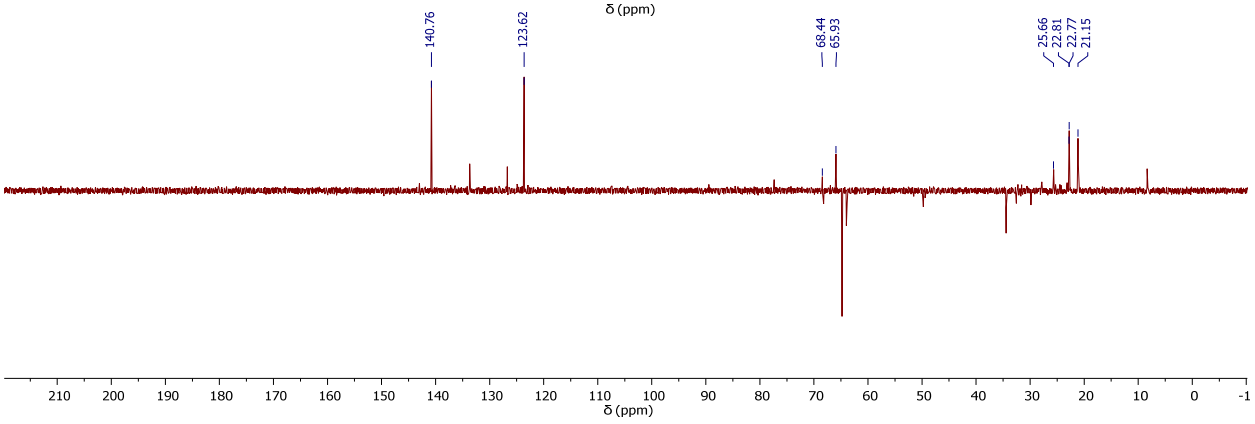
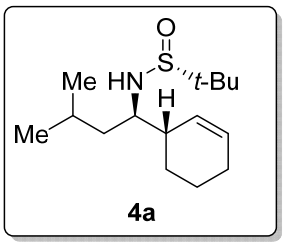
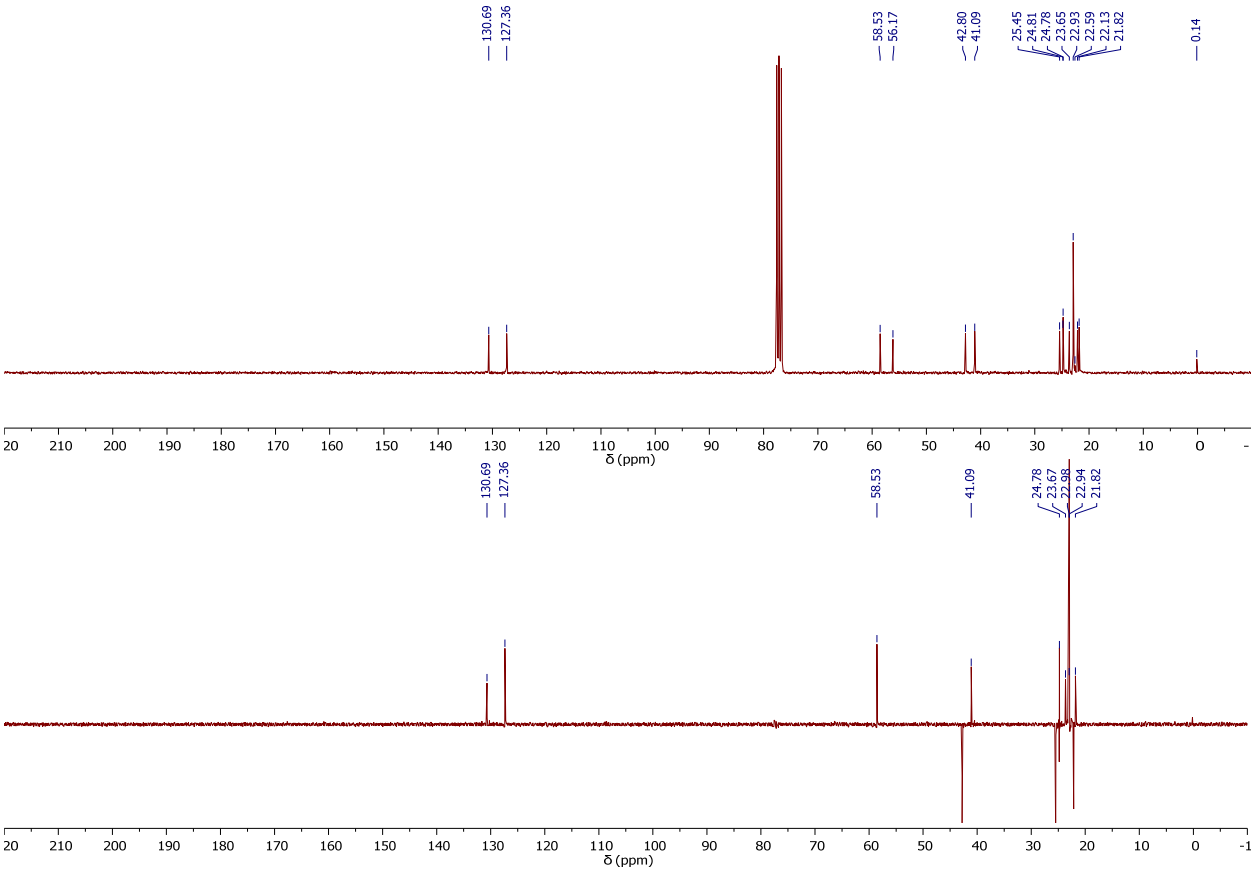
4.61
4.59
4.57
3.73
3.21
2.08
1.71
1.68
1.66
1.64
1.63
1.63
1.42
1.42
1.41
1.35
1.27
1.26
1.21
0.90
0.87
0.86
0.85
2.51
2.38
0.51
0.87
2.74
2.89
1.60
2.76
3.25
9.00
4.76
O
S
t-Bu
HN
Me
Me
OAc
3d

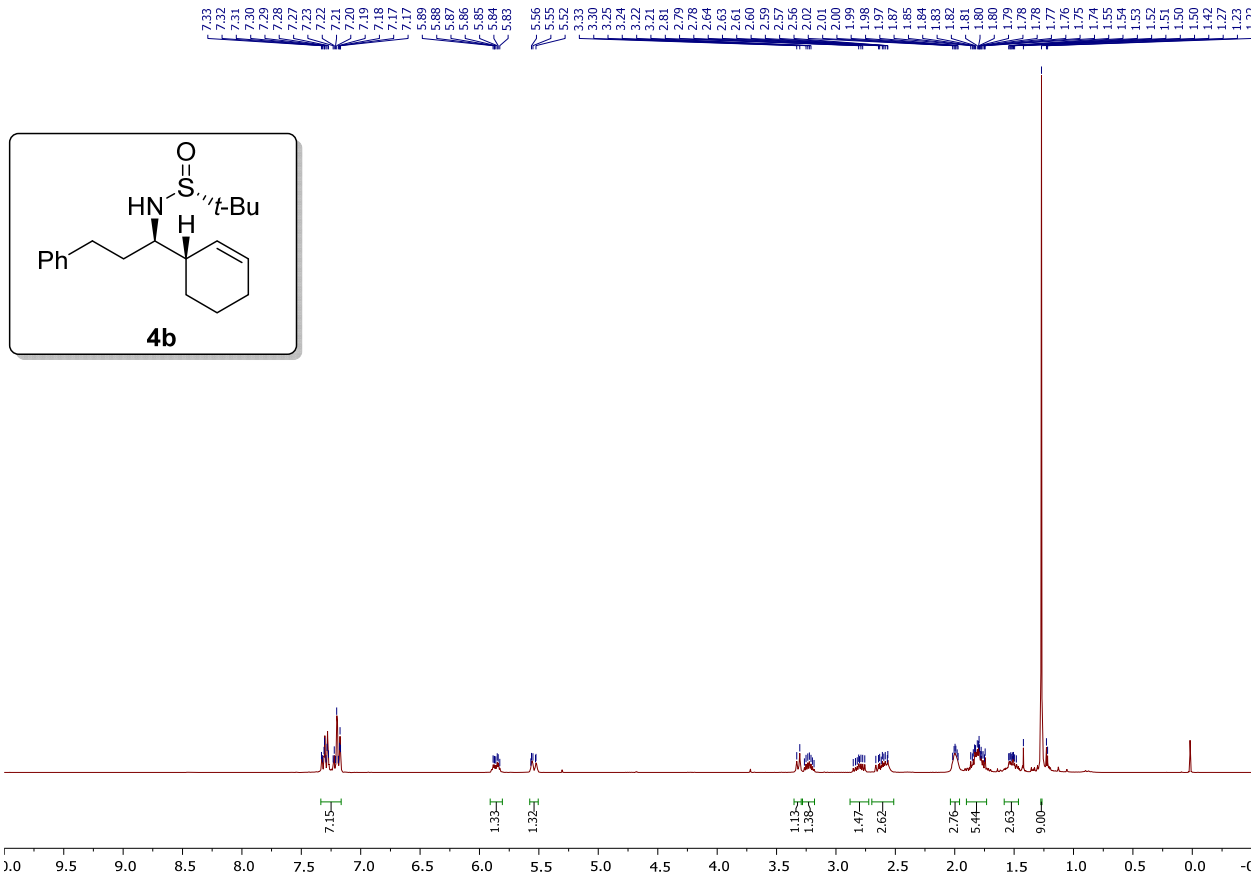

170.99
140.76
123.63
64.78
58.92
56.00
34.45
32.56
29.84
25.64
22.78
21.15
δ (ppm)

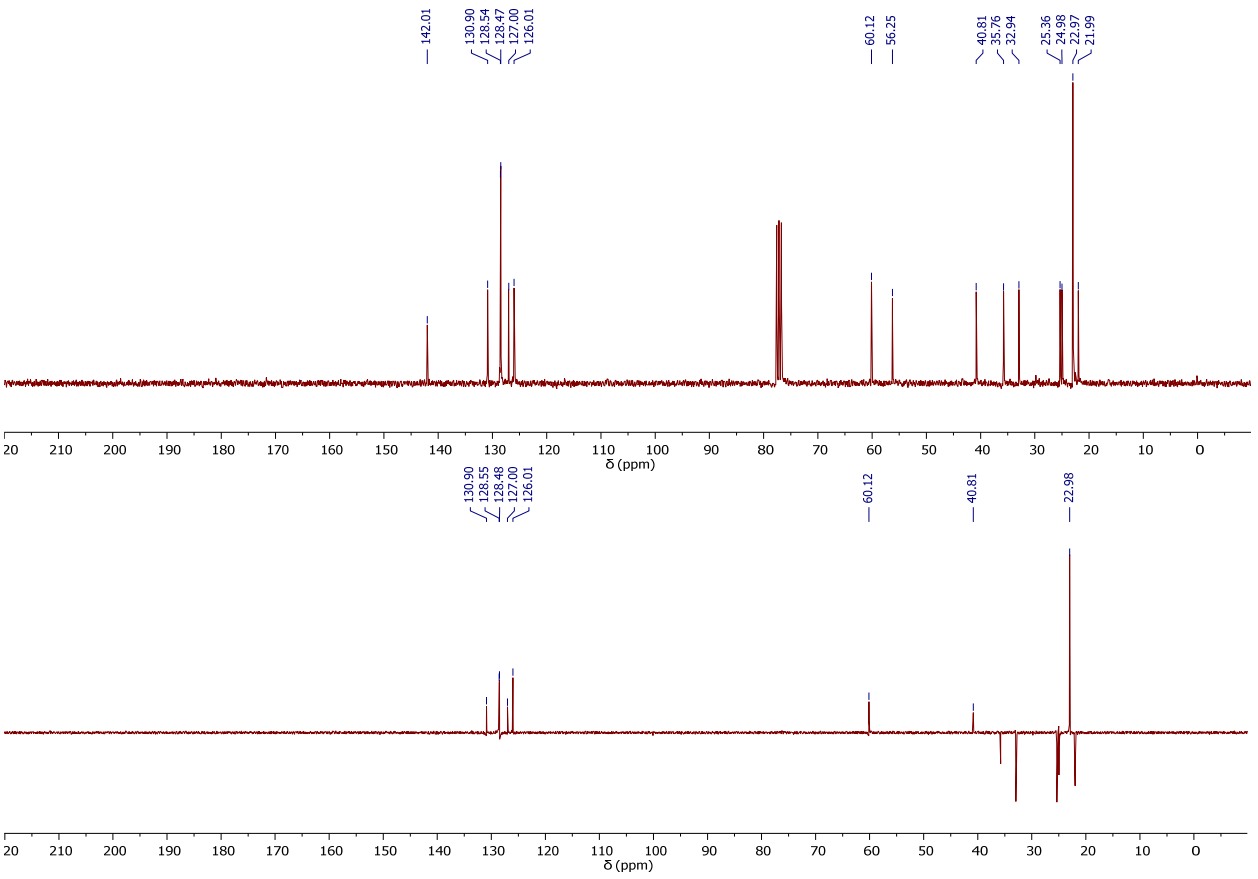

140.76
123.62
68.44
65.93
25.66
22.81
22.77
21.15
δ (ppm)



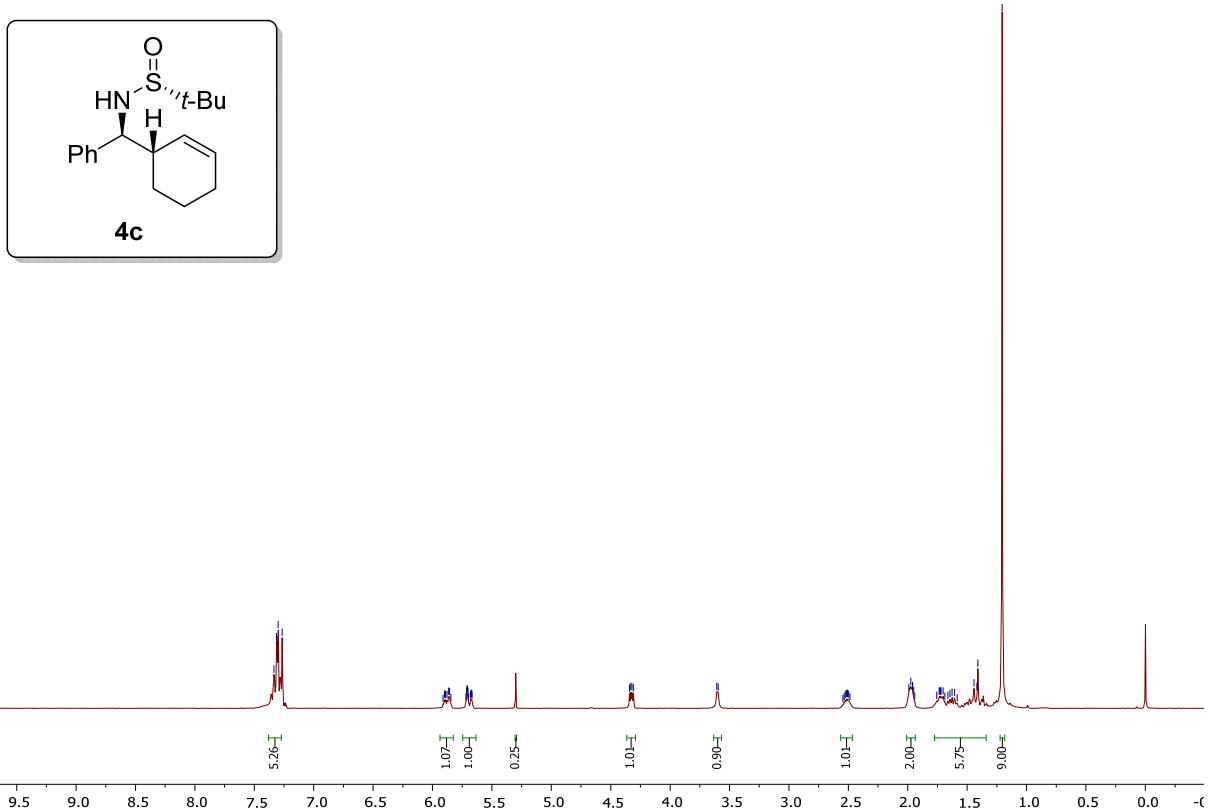
4a

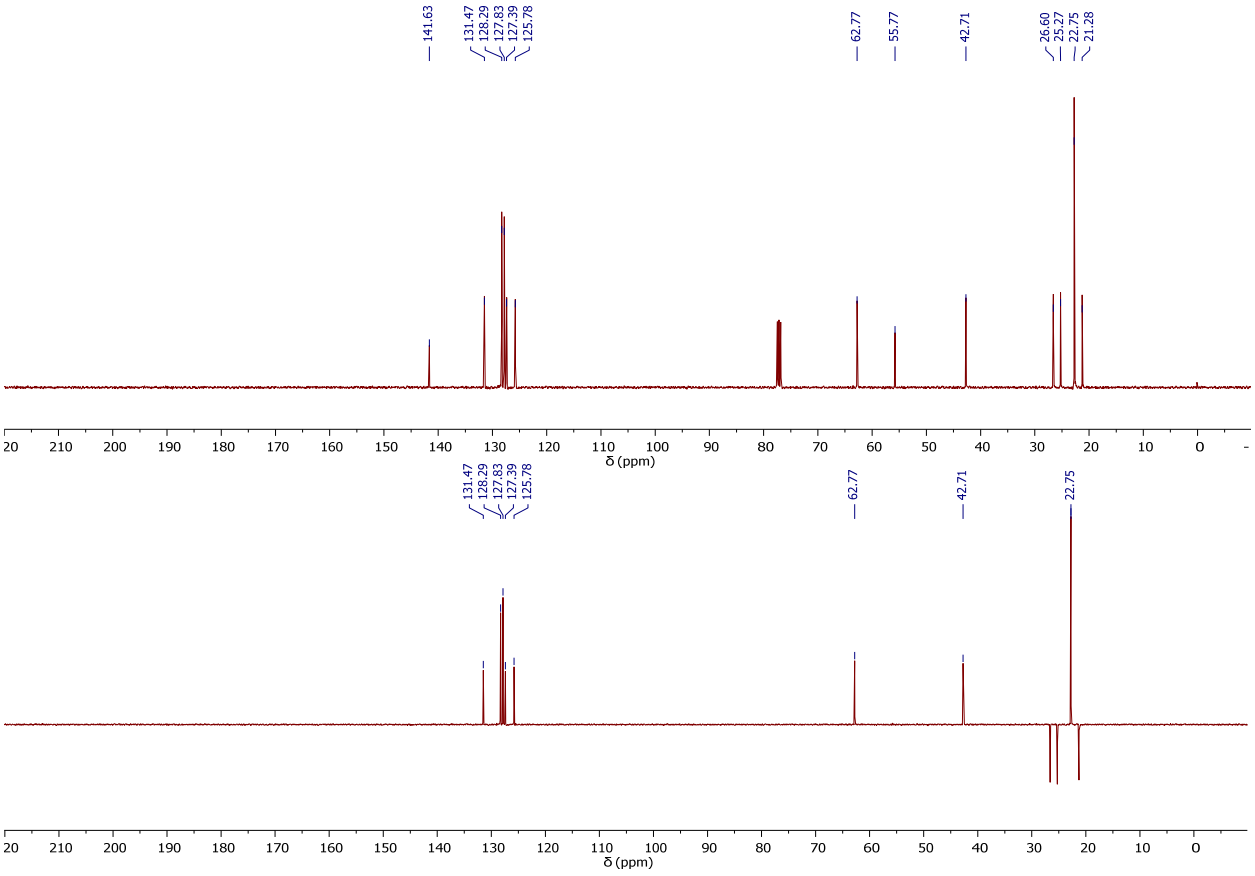



O
S
HN
H
t-Bu
Ph
4b

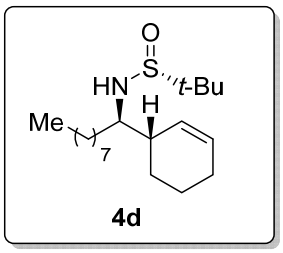

δ (ppm)

δ (ppm)


O
S
HN
t-Bu
H
Ph
4c

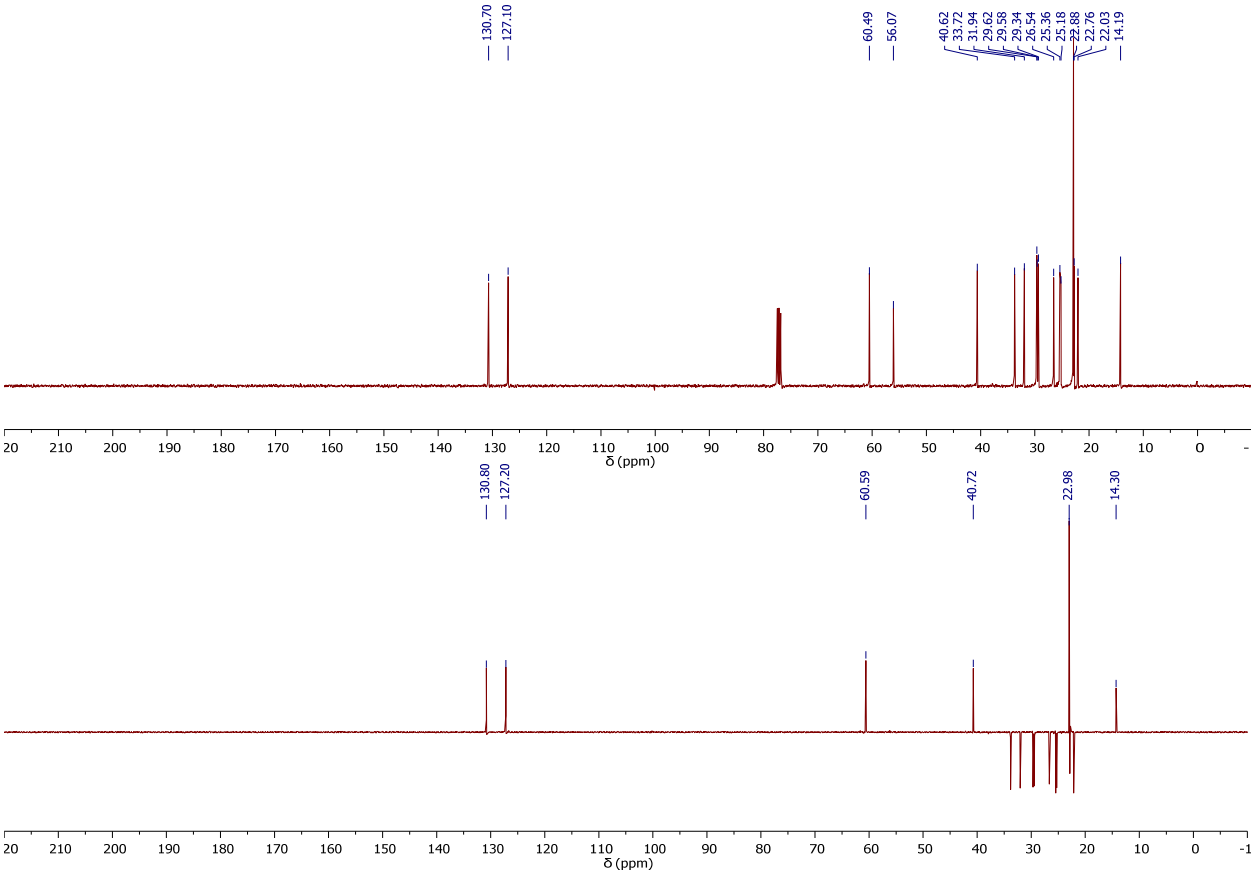

δ (ppm)

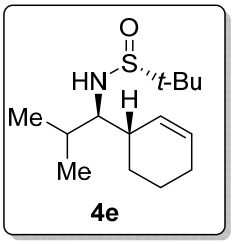
δ (ppm)


O
S
HN
t-Bu
H
Me
7

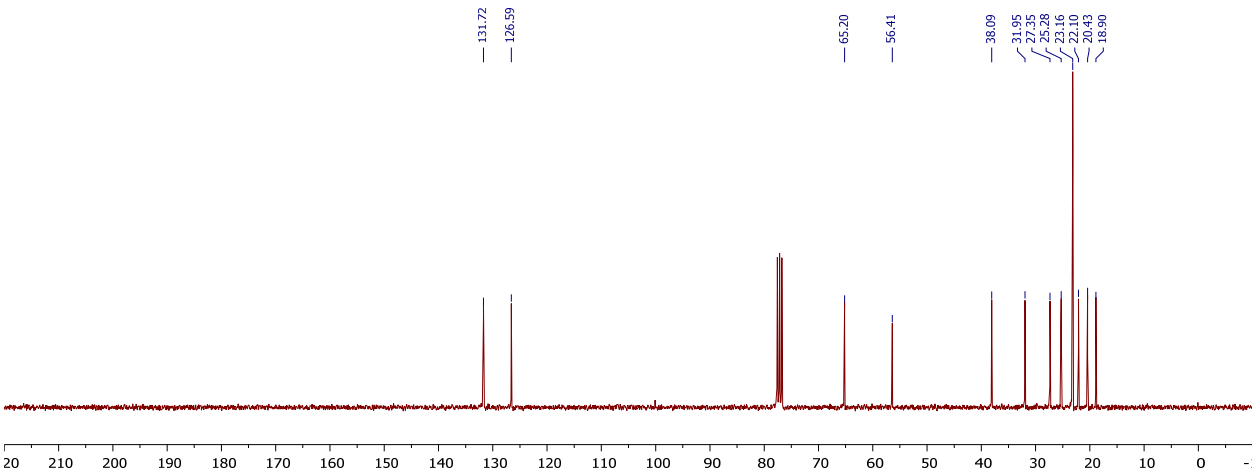
4d

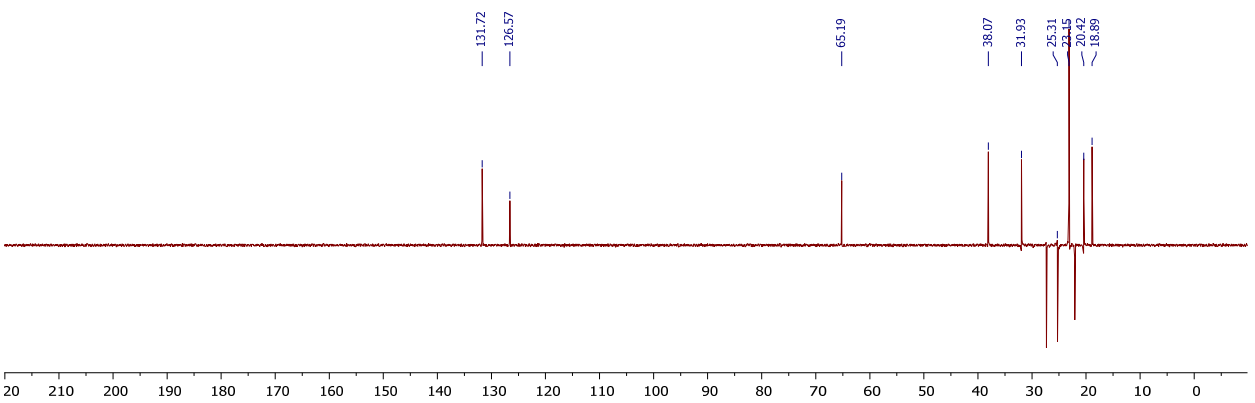
5.88
5.87
5.86
5.85
5.83
5.82
5.81
5.81
5.58
5.57
5.57
5.54
5.54
5.53
3.20
3.18
3.15
3.14
3.13
2.50
1.99
1.83
1.81
1.80
1.78
1.76
1.74
1.73
1.73
1.73
1.49
1.42
1.41
1.30
1.26
1.21
0.90
0.88
0.88
0.86
0.99
0.97
0.25
1.94
0.96
1.92
2.62
5.69
10.03
9.00
3.28

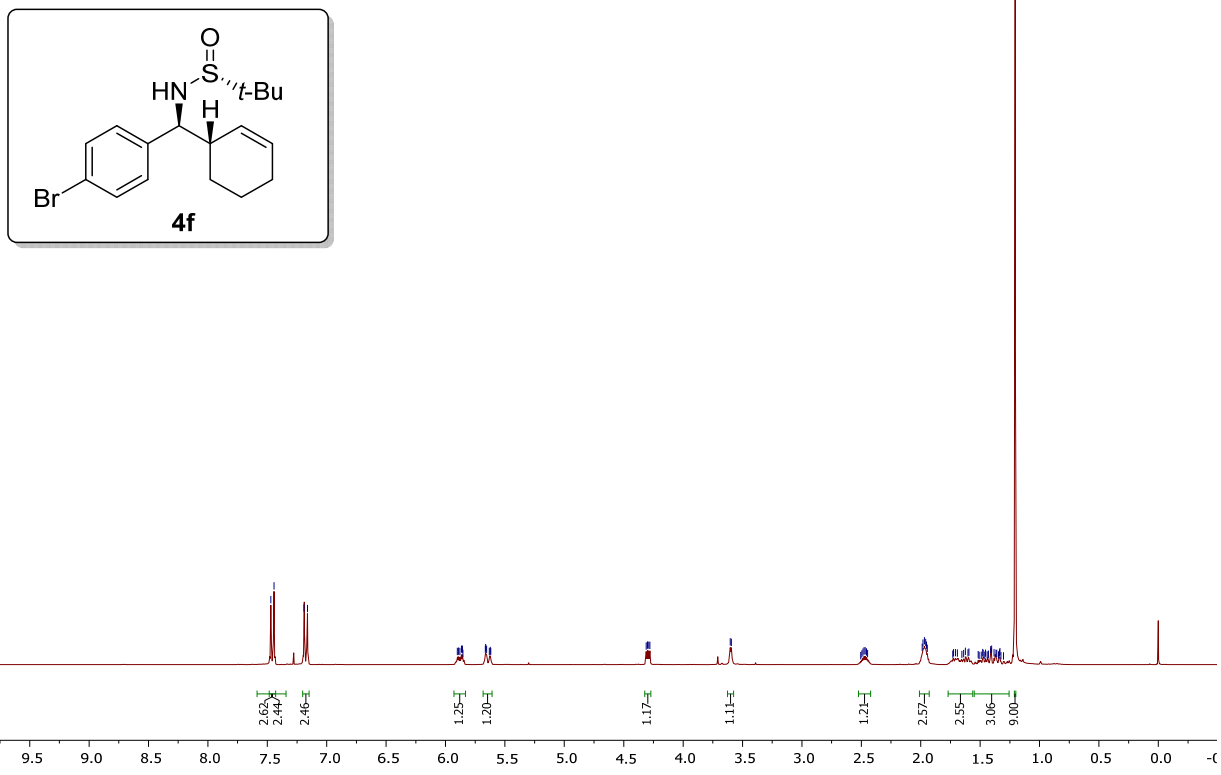

130.70
127.10
60.49
56.07
40.62
33.72
31.94
29.62
29.58
29.34
26.54
25.36
25.18
22.88
22.76
22.03
14.19
δ (ppm)
130.80
127.20
60.59
40.72
22.98
14.30
δ (ppm)

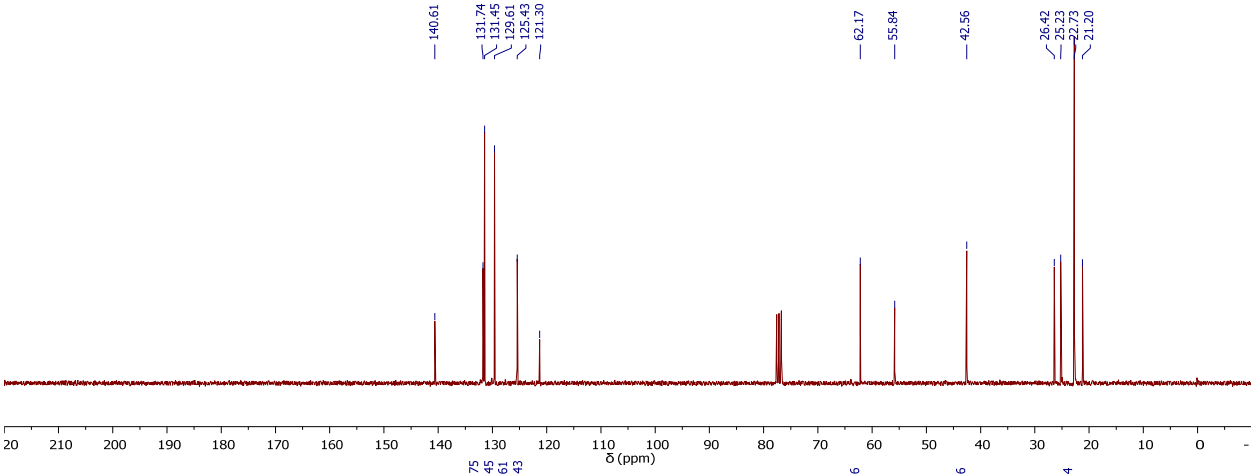


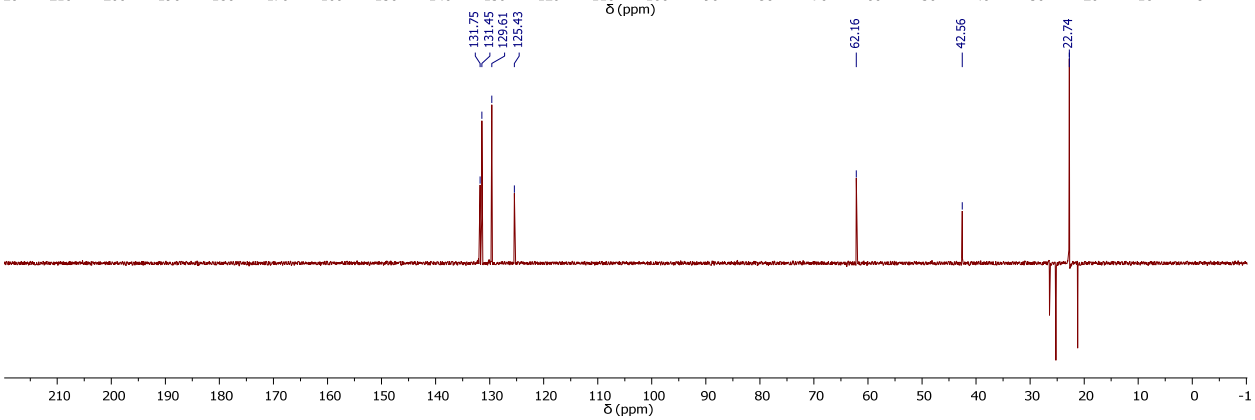
4e

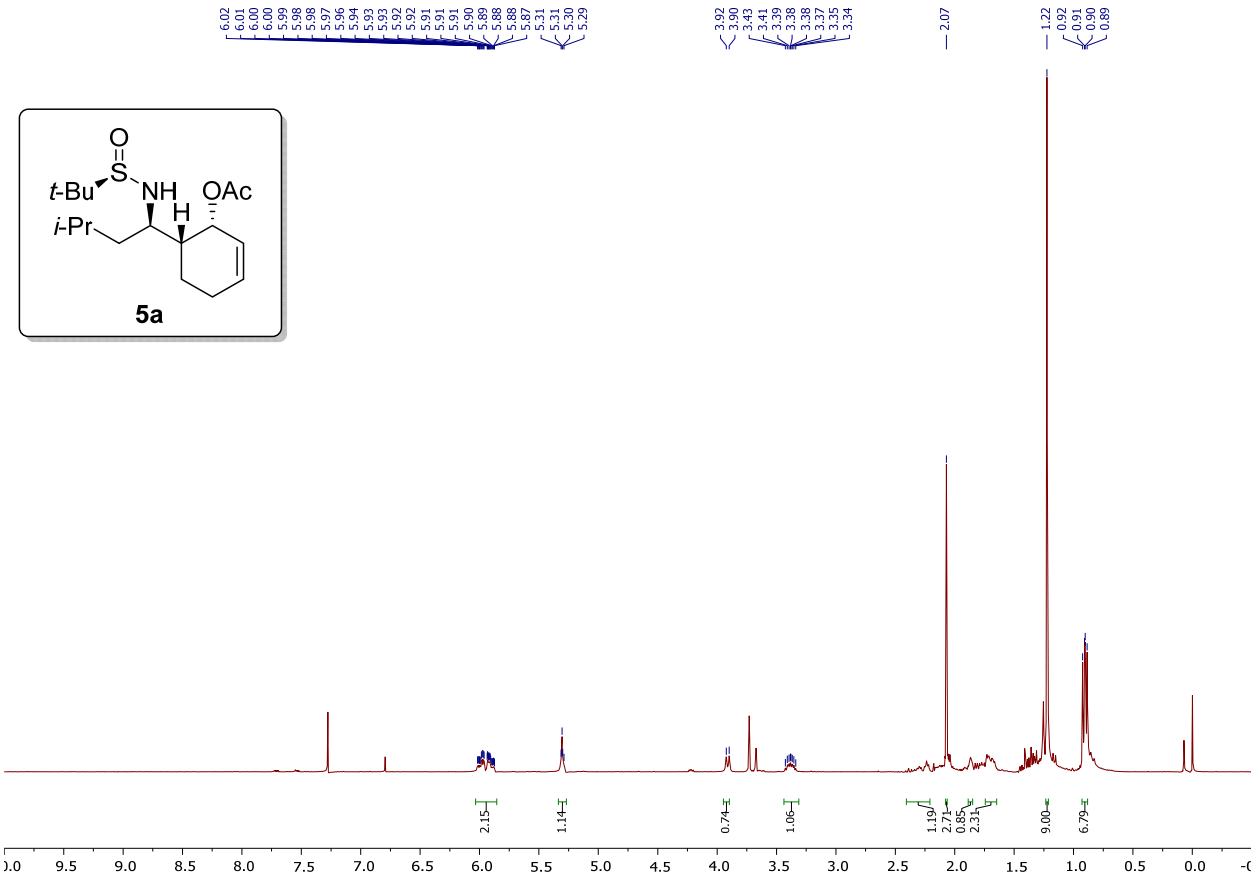


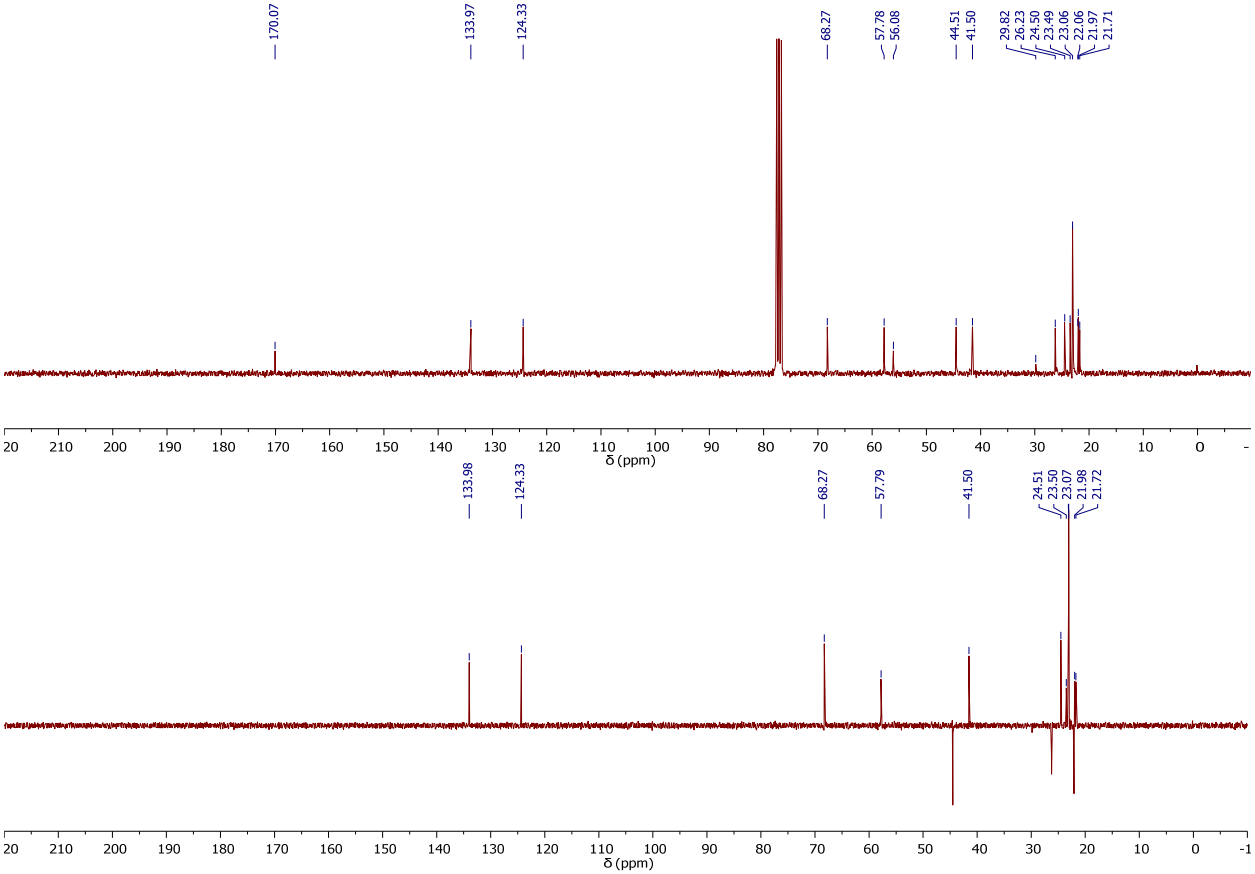



7.47
7.44
7.19
7.16
5.90
5.89
5.88
5.87
5.86
5.85
5.67
5.66
5.65
5.63
5.62
5.62
4.31
4.30
4.29
4.28
3.60
3.59
2.50
2.49
2.48
2.47
2.46
2.45
1.99
1.98
1.97
1.96
1.95
1.94
1.73
1.72
1.71
1.69
1.65
1.64
1.62
1.60
1.59
1.52
1.48
1.47
1.45
1.44
1.43
1.41
1.40
1.38
1.37
1.36
1.34
1.33
O
S
HN
t-Bu
H
Br
4f
2.62
2.44
2.46
1.25
1.20
1.17
1.11
1.21
2.57
2.55
3.06
9.00
δ (ppm)

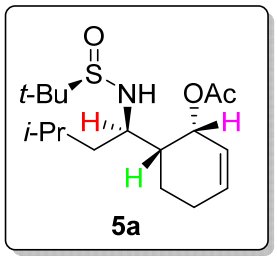

140.61
131.74
131.45
129.61
125.43
121.30
62.17
55.84
42.56
26.42
25.23
22.73
21.20
δ (ppm)


131.75
131.45
129.61
125.43
62.16
42.56
22.74
δ (ppm)

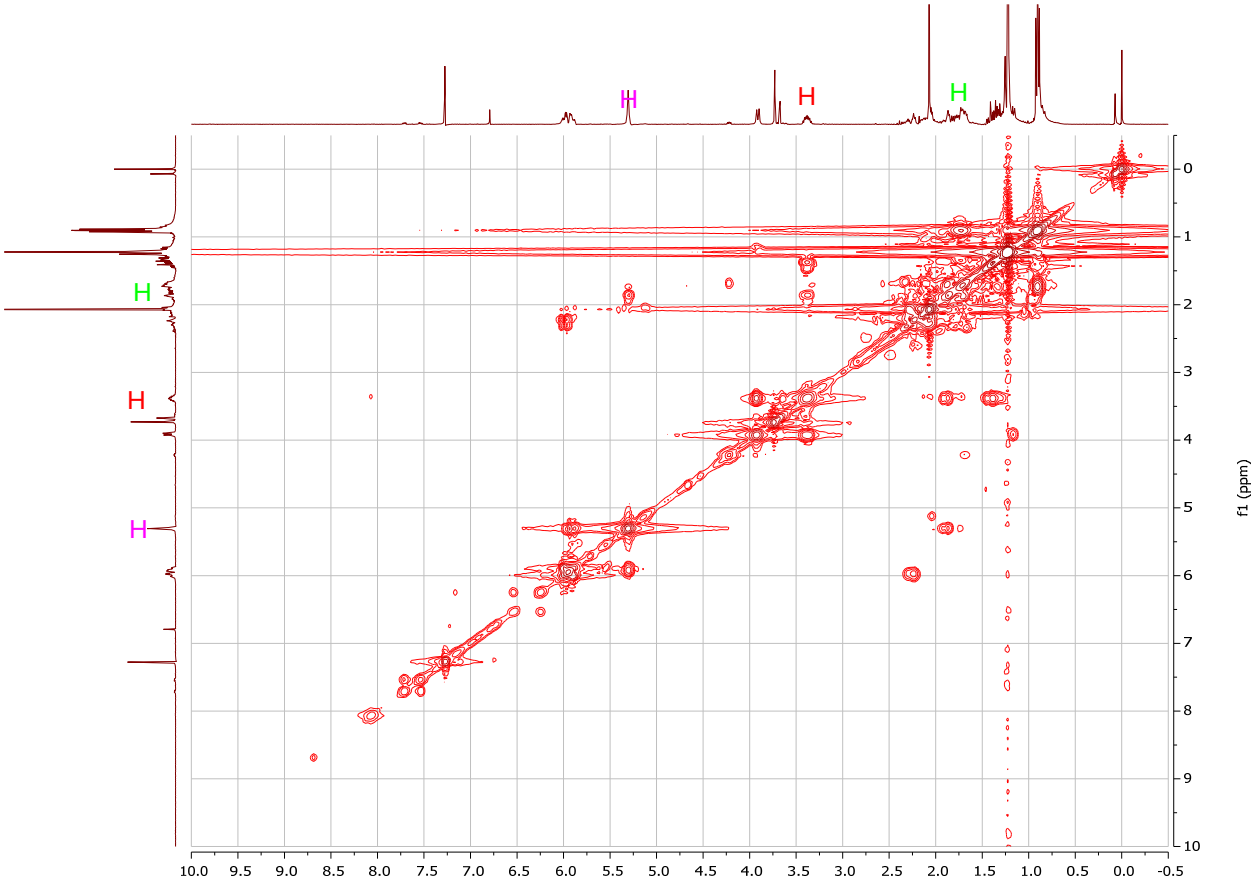

6.02
6.01
6.00
6.00
5.99
5.98
5.98
5.97
5.96
5.94
5.93
5.93
5.92
5.92
5.91
5.91
5.91
5.90
5.89
5.88
5.88
5.87
5.31
5.31
5.30
5.29
3.92
3.90
3.43
3.41
3.39
3.38
3.38
3.37
3.35
3.34
2.07
1.22
0.92
0.91
0.90
0.89
O
S
t-Bu
NH
H
OAc
i-Pr
5a
2.15
1.14
0.74
1.06
1.19
2.71
0.85
2.31
9.00
6.79

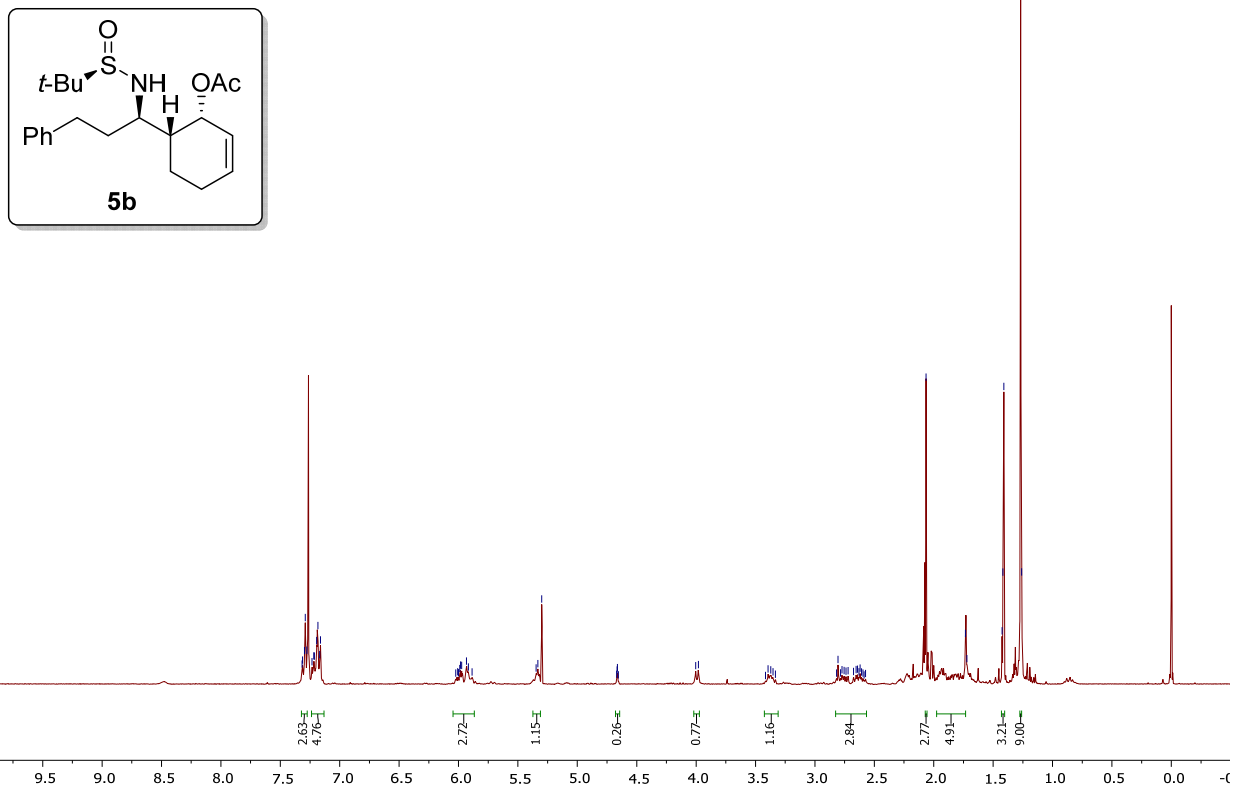

170.07
133.97
124.33
68.27
57.78
56.08
44.51
41.50
29.82
26.23
24.50
23.49
23.06
22.06
21.97
21.71
δ (ppm)

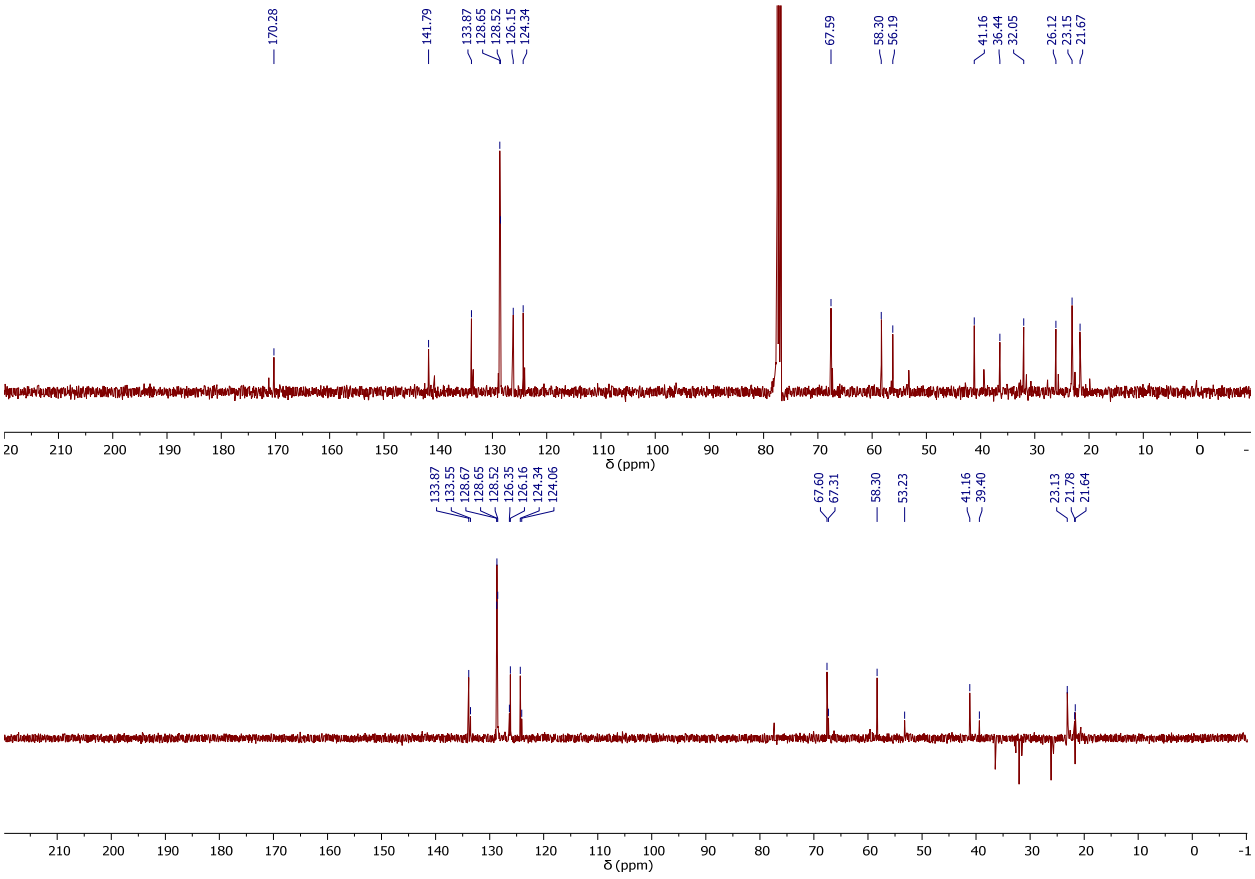
133.98
124.33
68.27
57.79
41.50
24.51
23.50
23.07
21.98
21.72
δ (ppm)

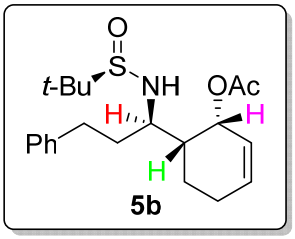

O
S
t-Bu
NH
OAc
i-Pr
H
H
H

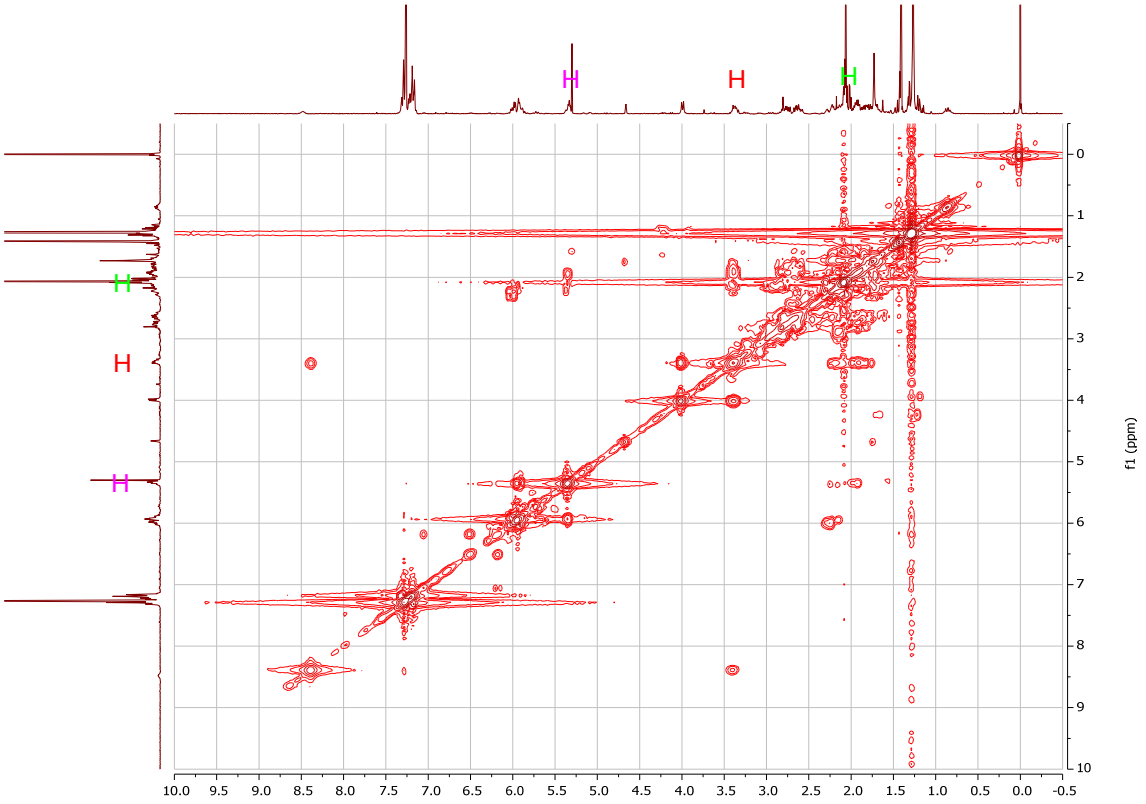
5a

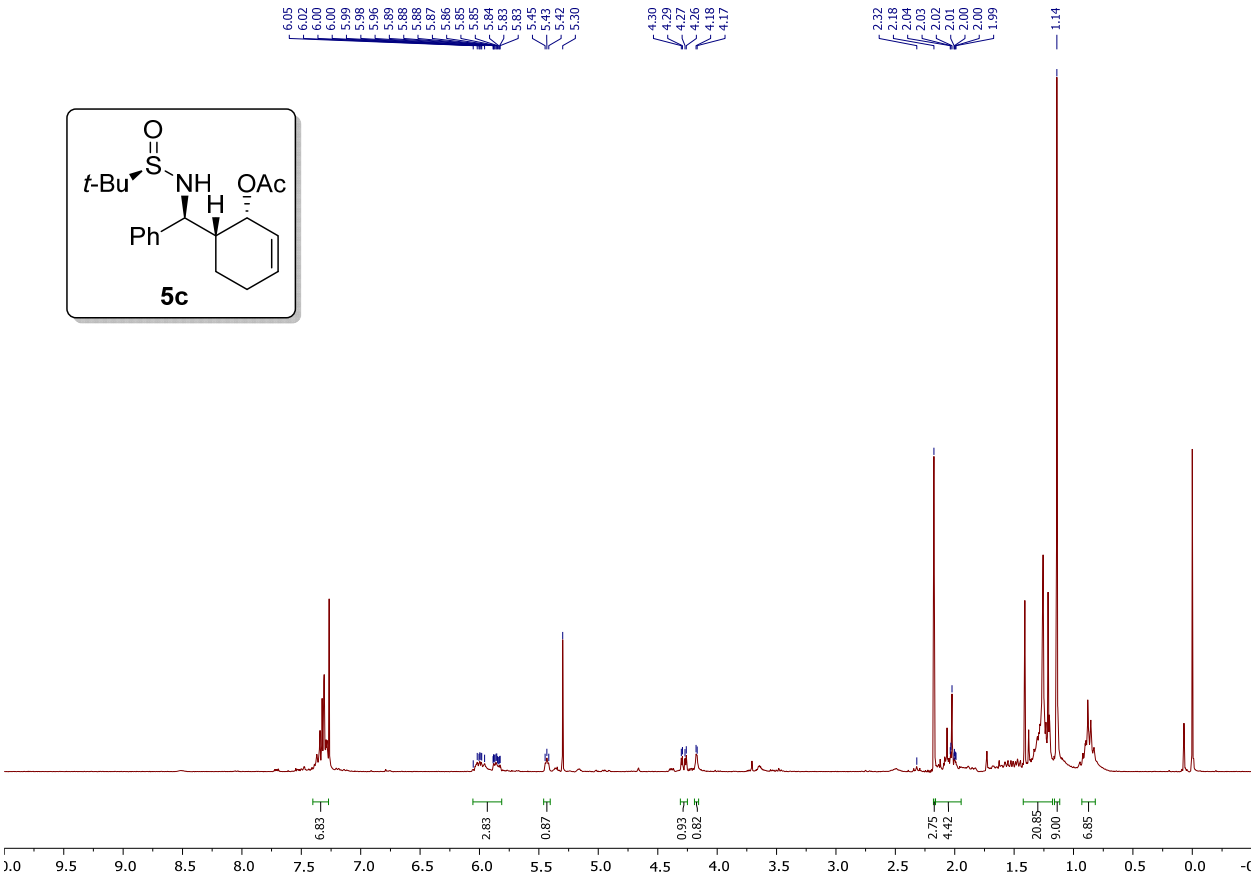

H
H
H
H
H
H
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7 8 9 10

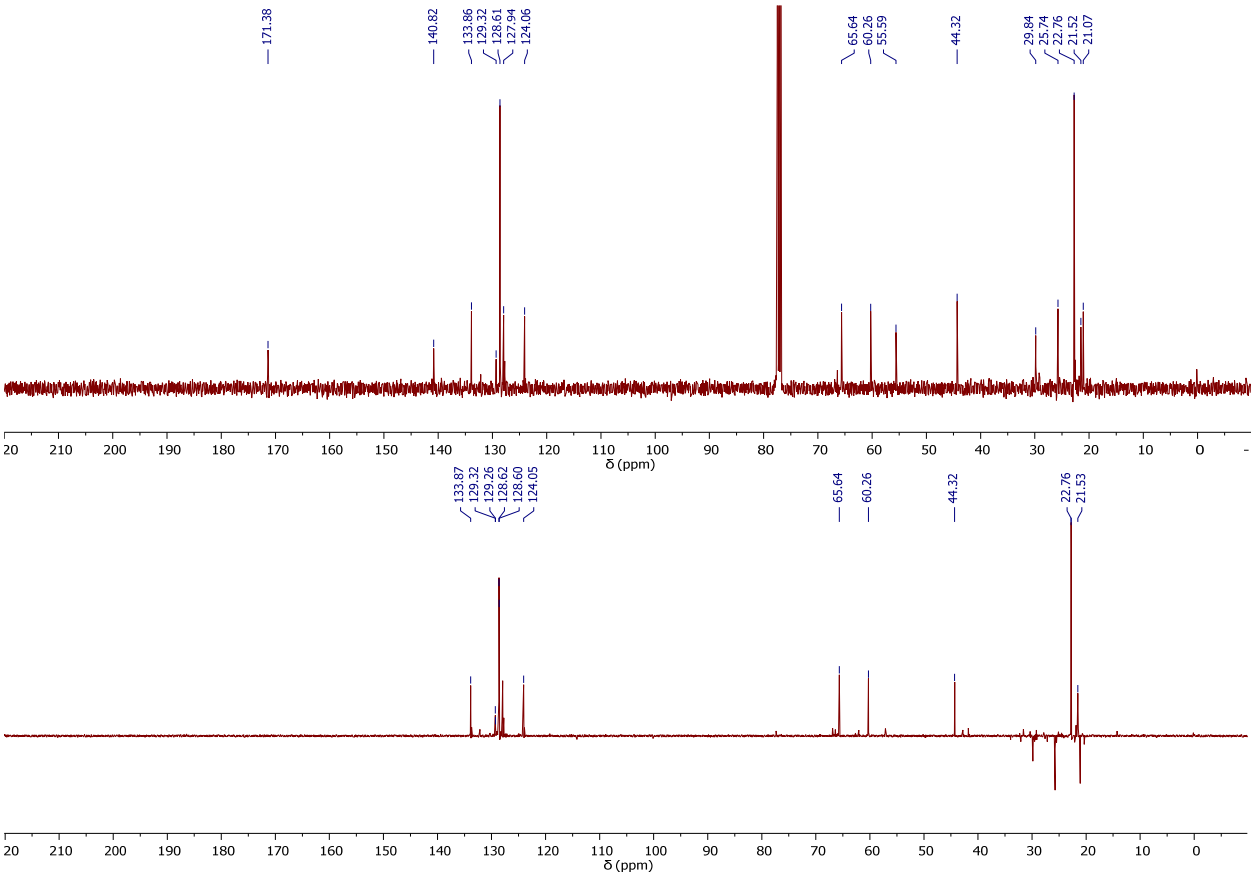

5b

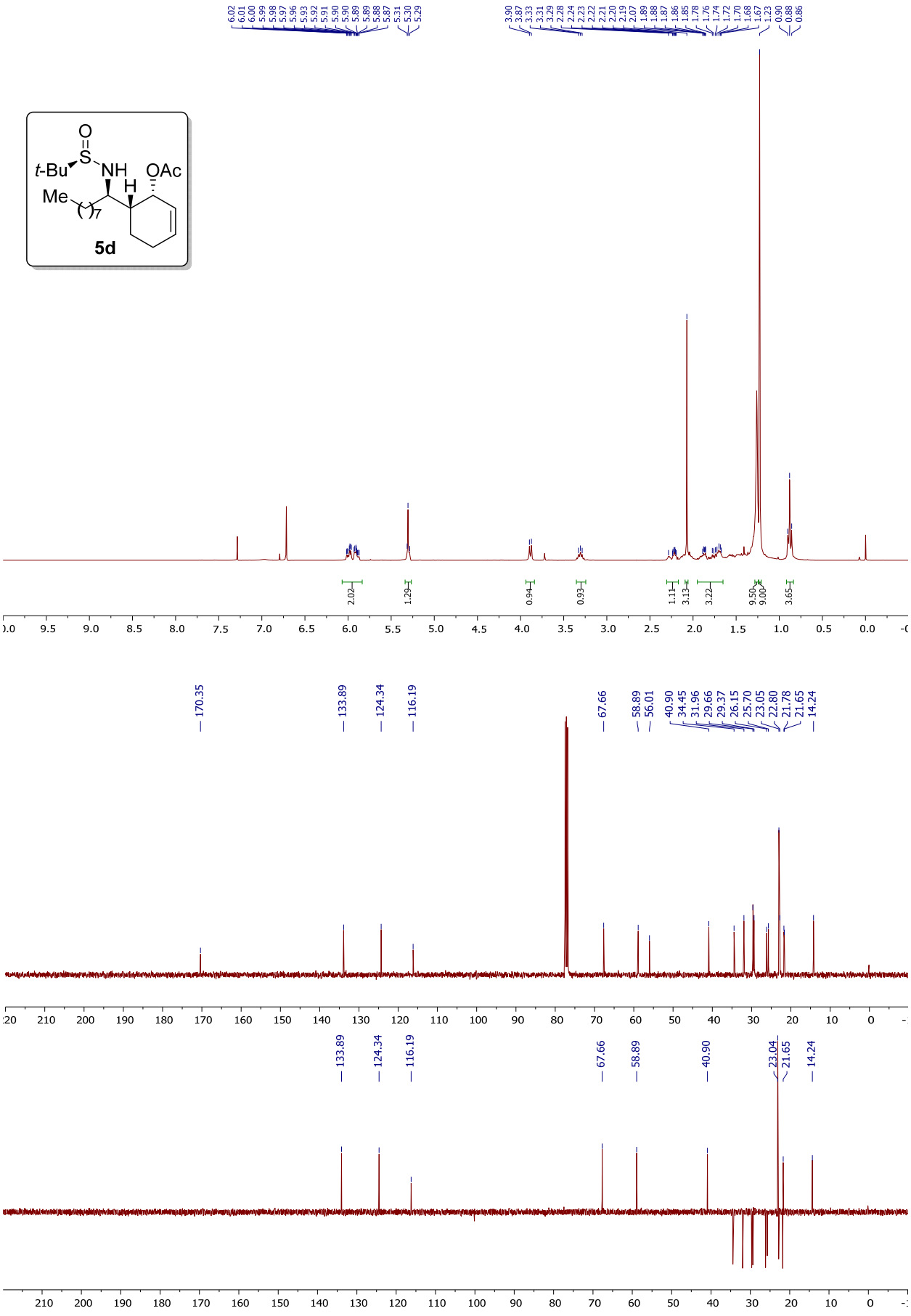

δ (ppm)

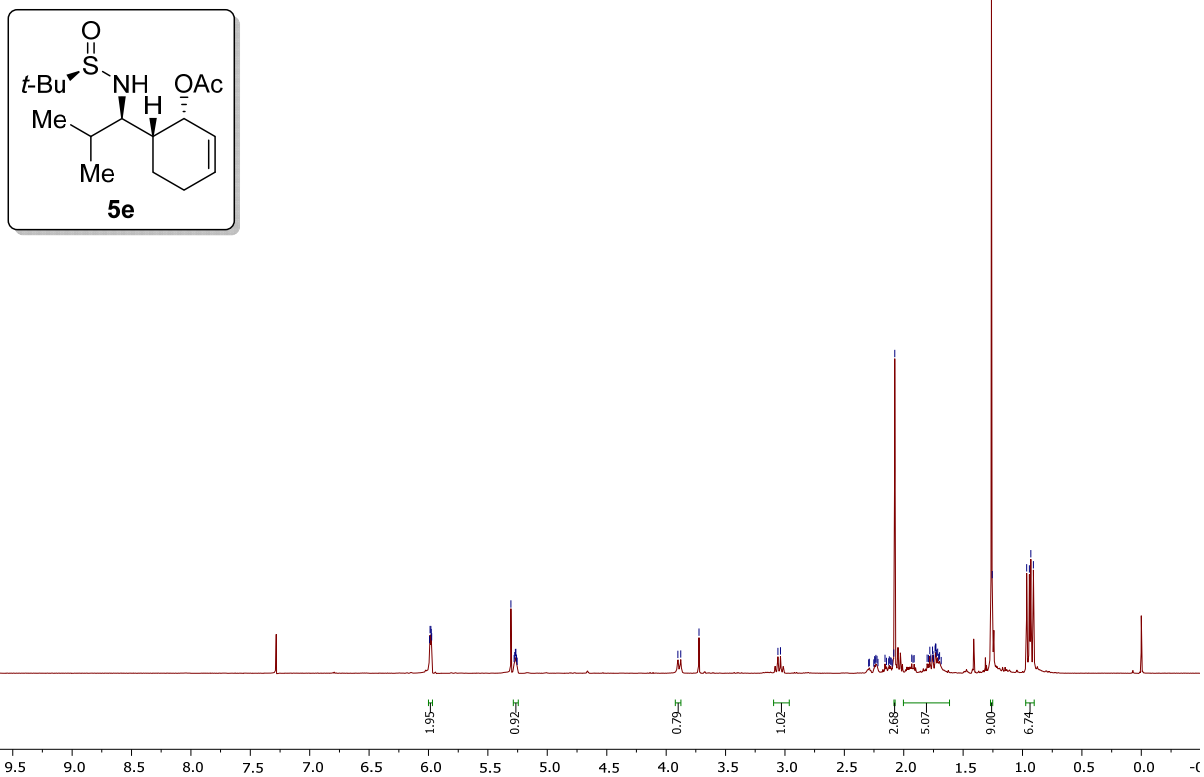

O
S
t-Bu
NH
OAc
H
H
Ph
H
5b


H
H
H
H
H
H
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

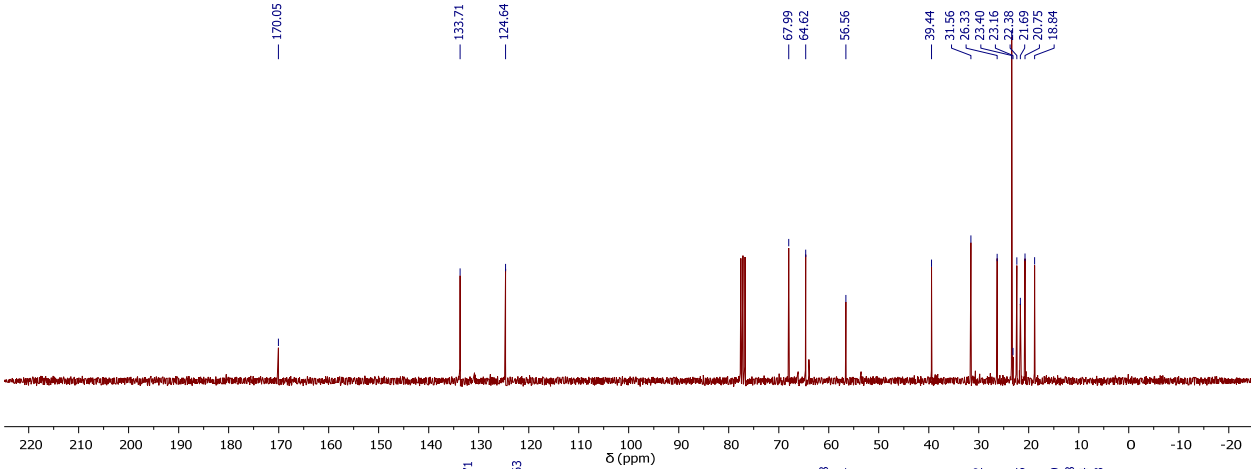

6.05
6.02
6.00
6.00
5.99
5.98
5.96
5.89
5.88
5.88
5.87
5.86
5.85
5.85
5.84
5.83
5.83
5.45
5.43
5.42
5.30
4.30
4.29
4.27
4.26
4.18
4.17
2.32
2.18
2.04
2.03
2.02
2.01
2.00
2.00
1.99
1.14
O
S
NH
H
t-Bu
OAc
Ph
5c
6.83
2.83
0.87
0.93
0.82
2.75
4.42
20.85
9.00
6.85

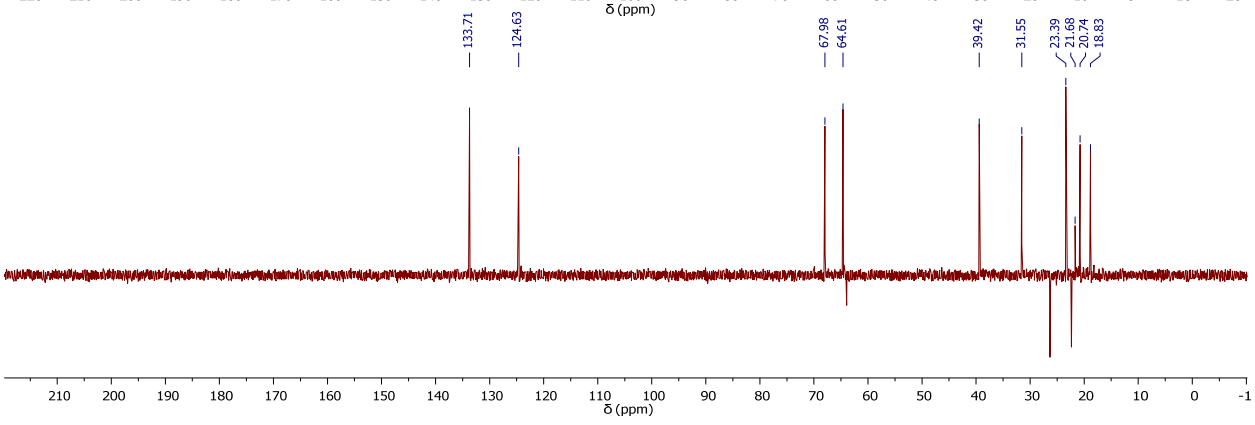

171.38
140.82
133.86
129.32
128.61
127.94
124.06
65.64
60.26
55.59
44.32
29.84
25.74
22.76
21.52
21.07
δ (ppm)
133.87
129.32
129.26
128.62
128.60
124.05
65.64
60.26
44.32
22.76
21.53
δ (ppm)

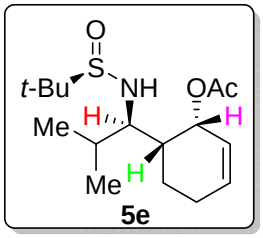

O
S
NH
H
OAc
t-Bu
Me
5d

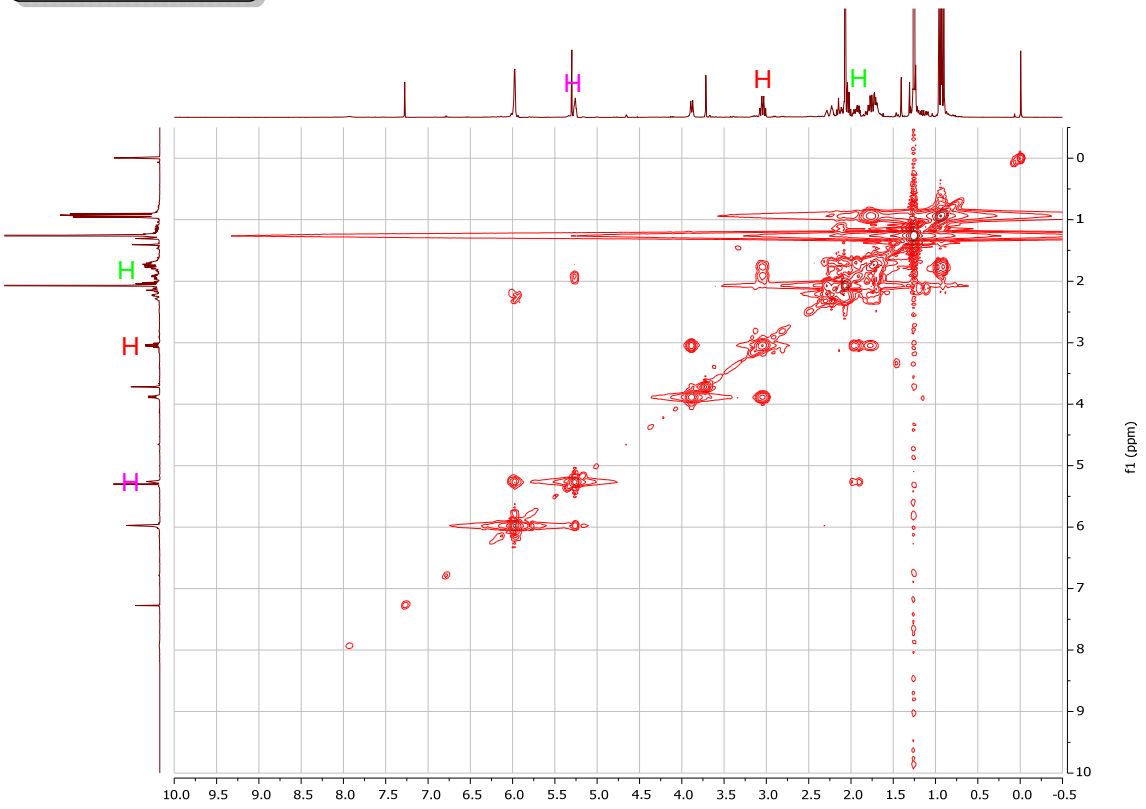

O
S
t-Bu
NH
H
OAc
Me
Me
5e

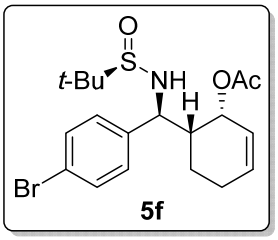
1.95
0.92
0.79
1.02
2.68
5.07
9.00
6.74

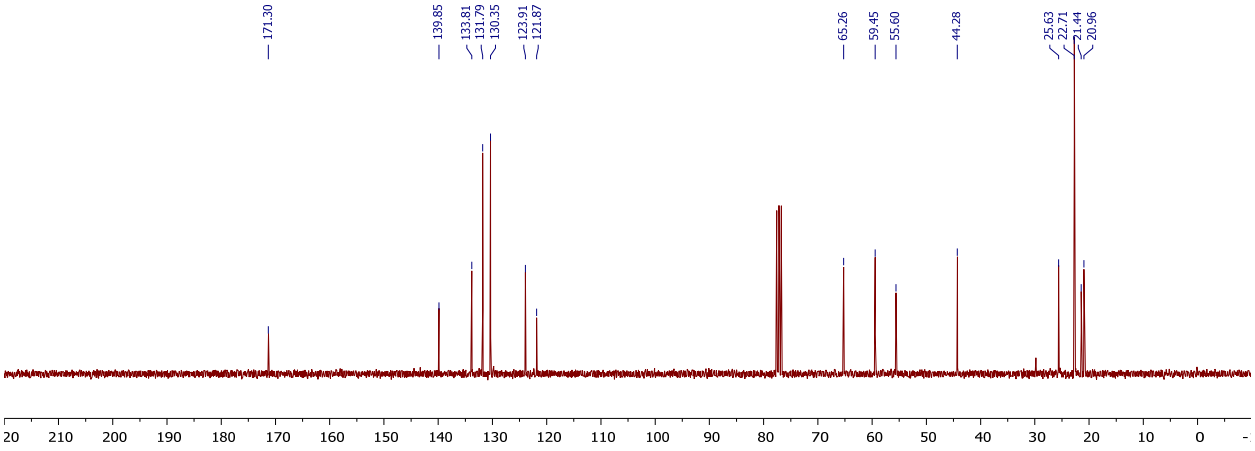

δ (ppm)

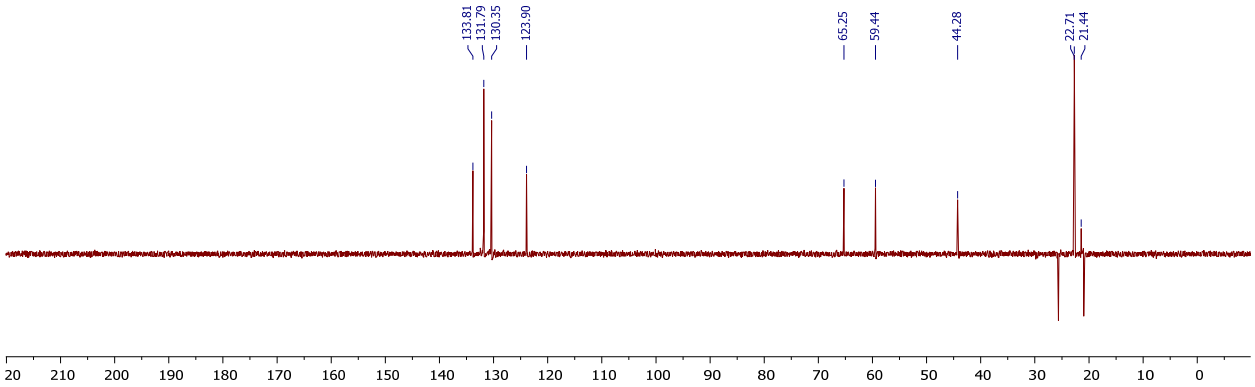

δ (ppm)

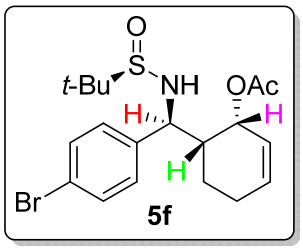

O
S
t-Bu
NH
OAc
Me
H
H
Me
H
5e

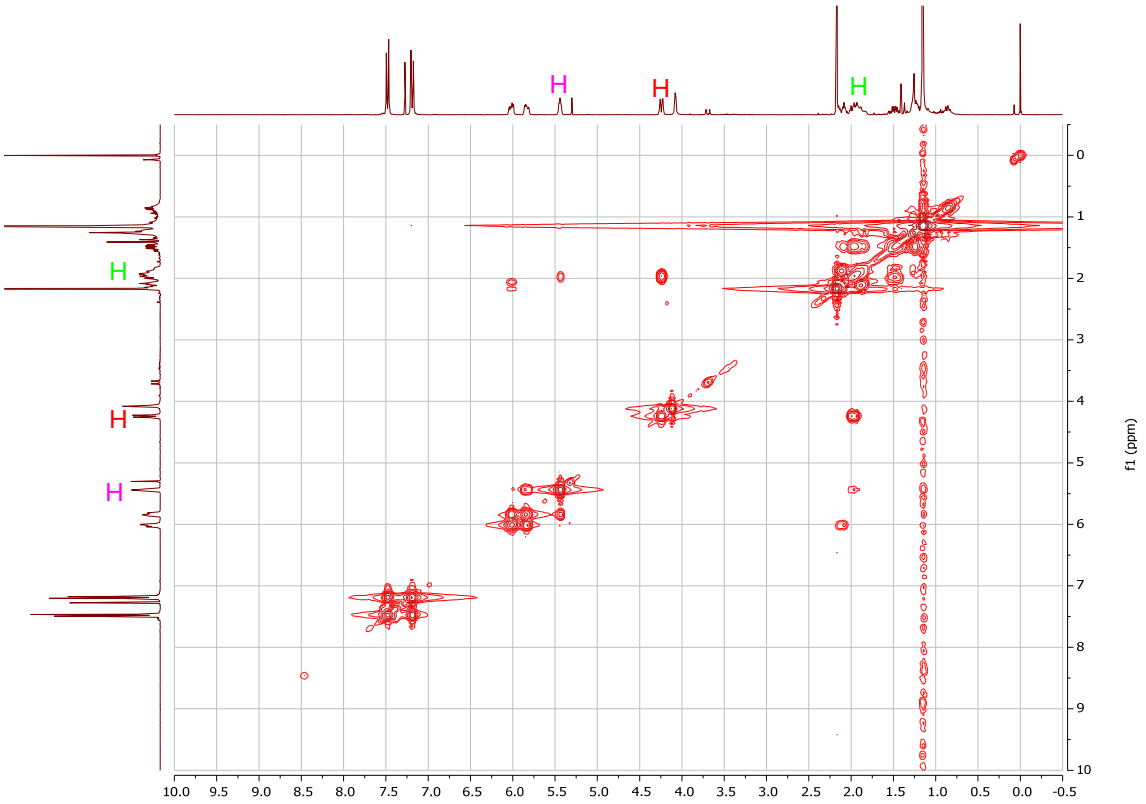

H
H
H
H
H
H
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7 8 9 10

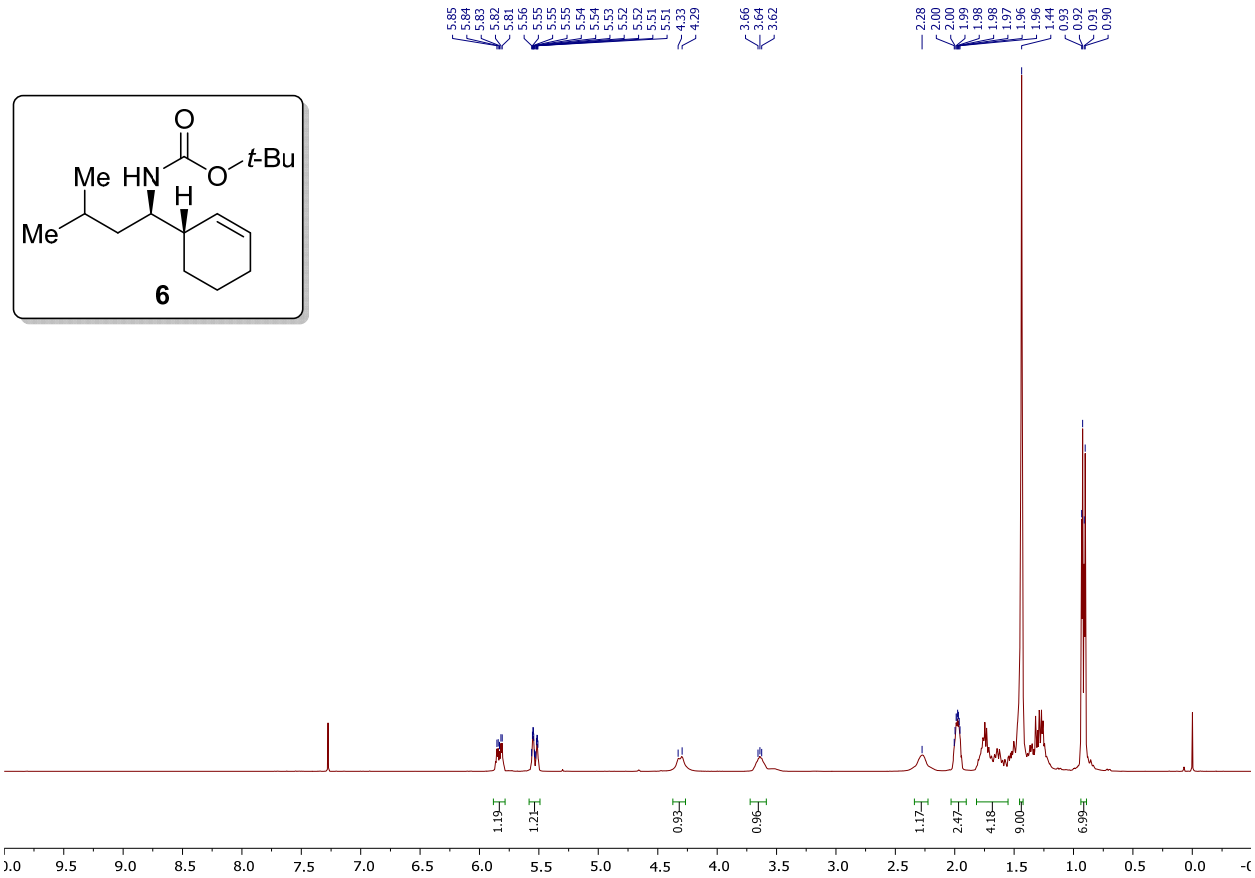

O
S
t-Bu
NH
H
OAc
Br
5f

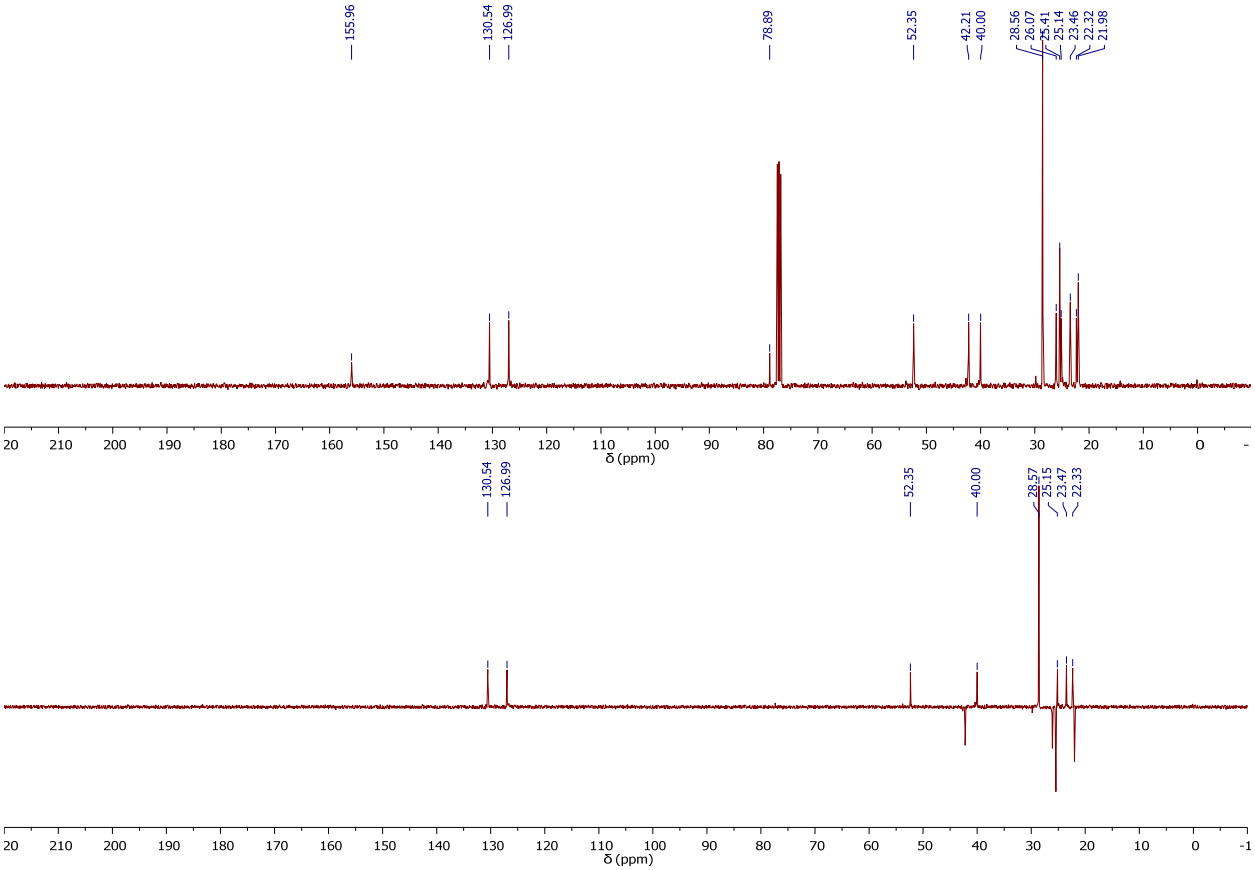


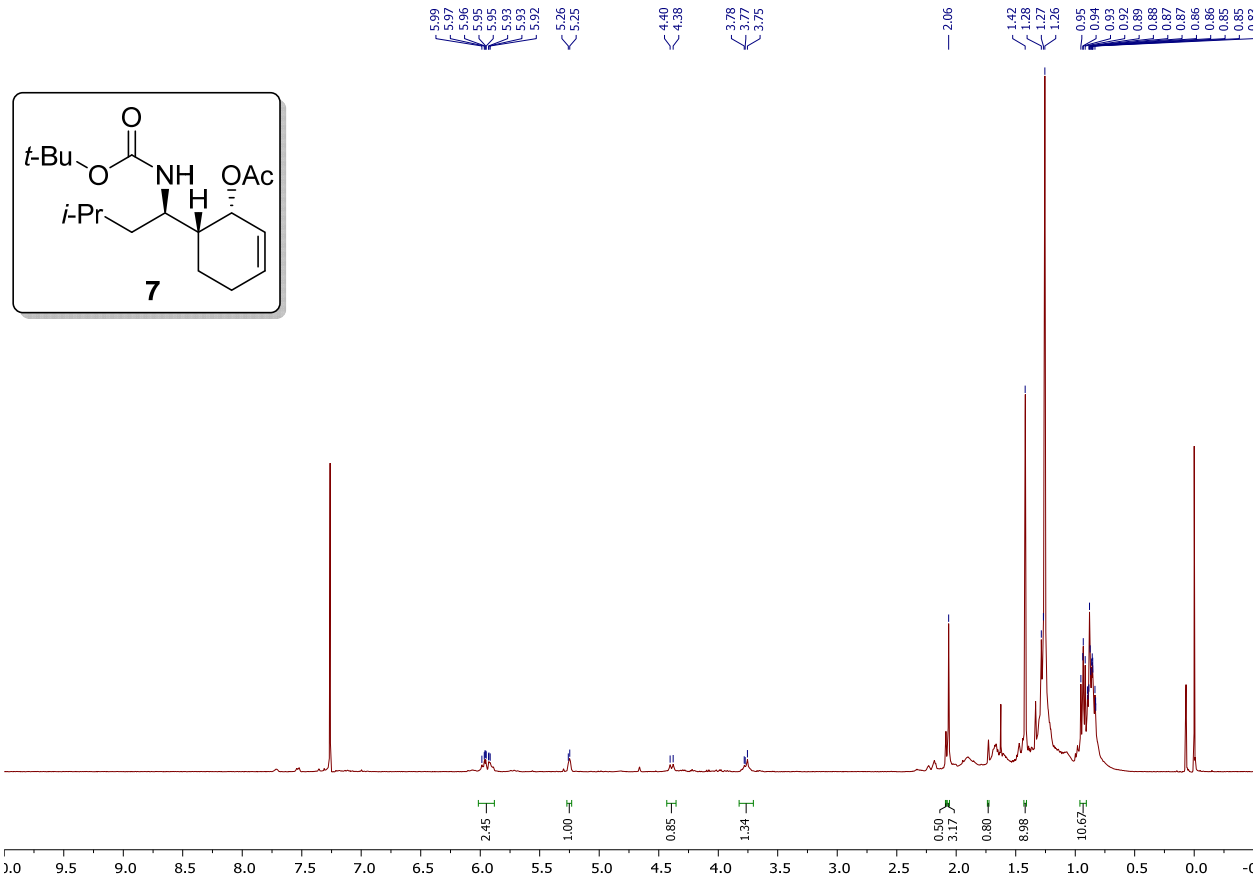


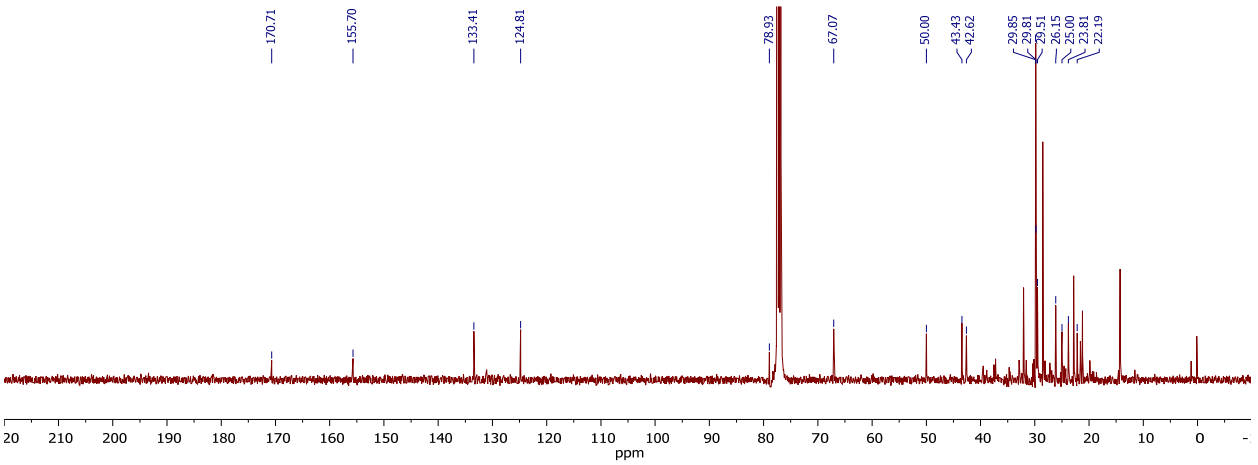

O
S
t-Bu
NH
OAc
H
H
H
Br
5f

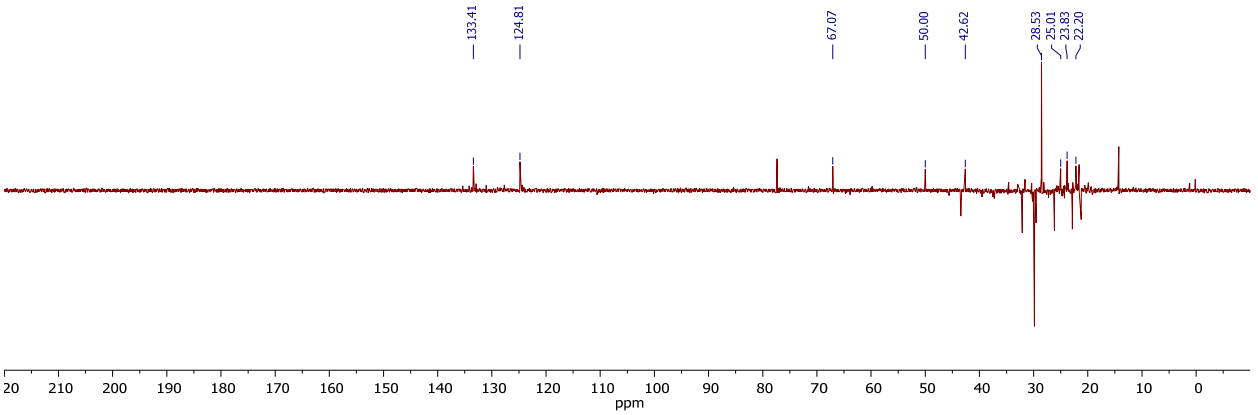

H
H
H
H
H
H
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7 8 9 10

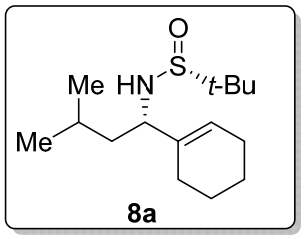

5.85 5.84 5.83 5.82 5.81 5.56 5.55 5.55 5.55 5.54 5.54 5.53 5.52 5.52 5.51 5.51 4.33 4.29
3.66 3.64 3.62
2.28 2.00 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.44 0.93 0.92 0.91 0.90
O
Me HN
O
t-Bu
H
Me
6
1.19 1.21 0.93 0.96 1.17 2.47 4.18 9.00 6.99
δ (ppm)


155.96
130.54 126.99
78.89
52.35
42.21 40.00
28.56 26.07 25.41 25.14 23.46 22.32 21.98
δ (ppm)
130.54 126.99
52.35
40.00
28.57 25.15 23.47 22.33
δ (ppm)


t-Bu
O
NH
OAc
i-Pr
H
7


ppm


ppm


O
S
Me HN
t-Bu
Me

8a

5.73
5.72
5.72
3.84
3.84
3.82
3.81
3.79
3.79
2.95
2.95
2.07
2.06
2.05
2.04
2.03
1.94
1.93
1.92
1.84
1.83
1.65
1.64
1.63
1.62
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.20
0.93
0.91
1.16
1.20
0.98
2.17
3.53
0.17
9.01
9.00
7.78
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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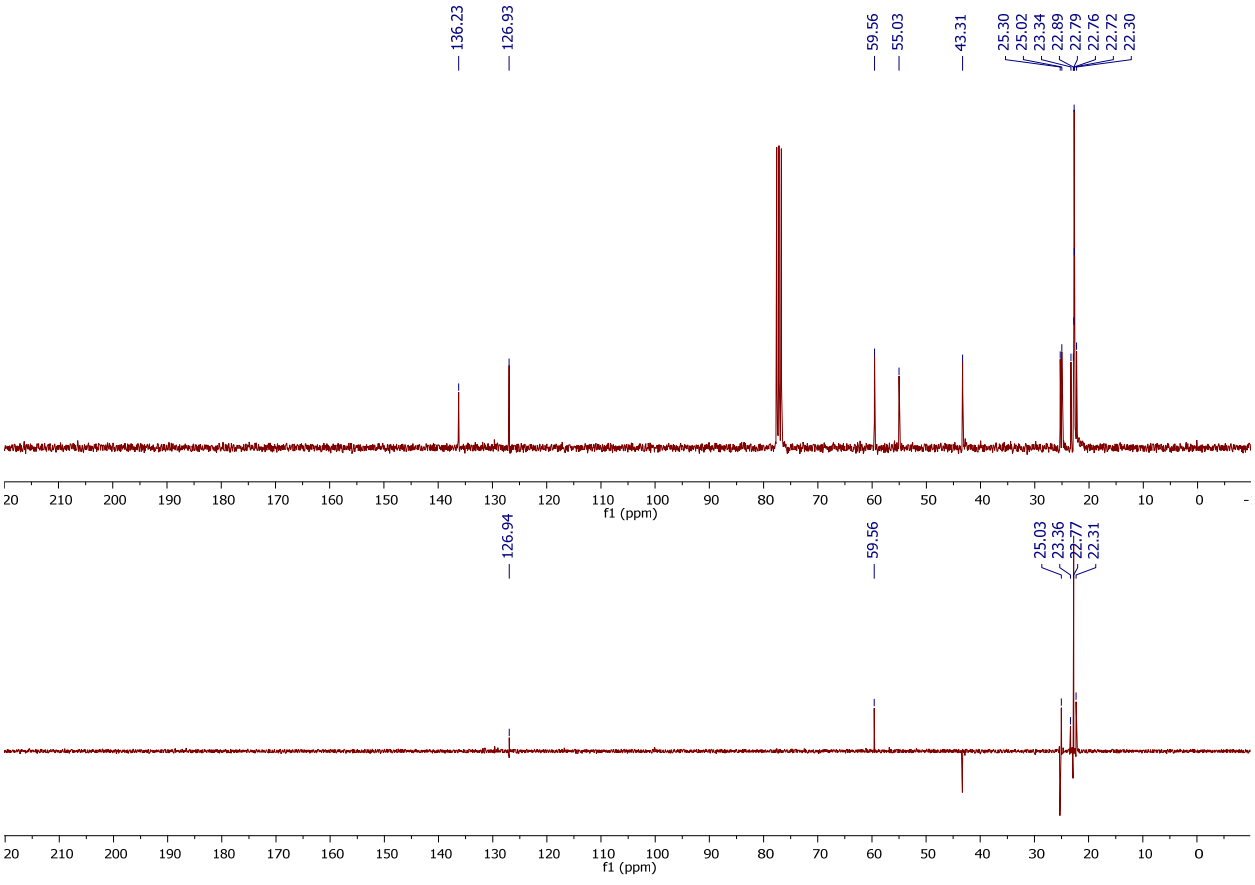
136.23
126.93
59.56
55.03
43.31
25.30
25.02
23.34
22.89
22.79
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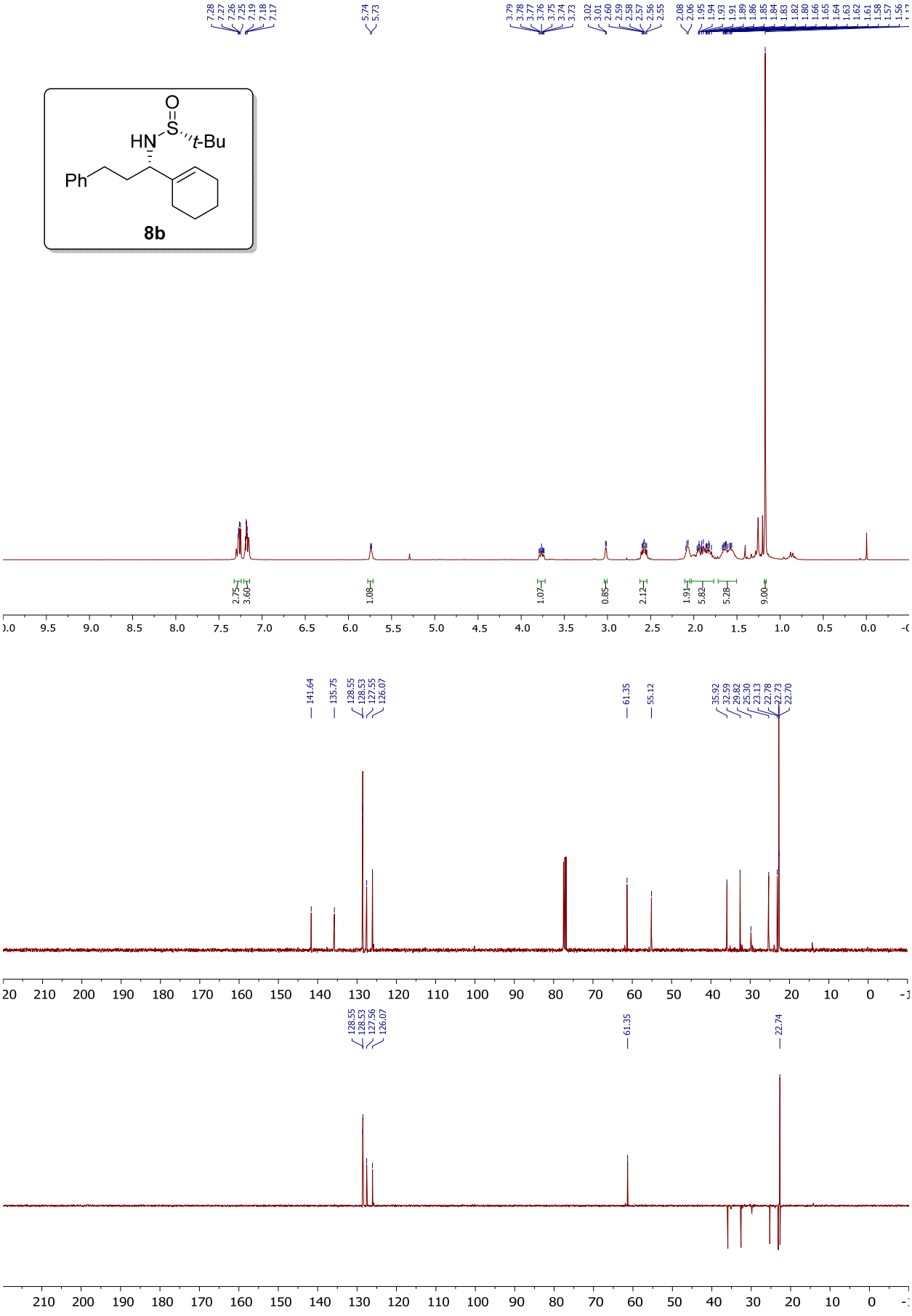
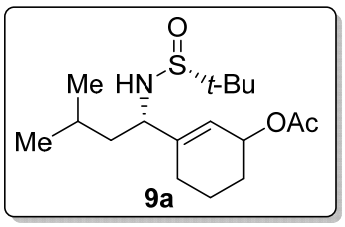
22.30
f1 (ppm)
126.94
59.56
25.03
23.36
22.77
22.31
f1 (ppm)


O
S
HN
t-Bu
Ph
8b


O
S
Me HN
t-Bu
OAc
Me
9a

5.72
5.72
5.71
5.33
5.31
5.31
5.30
5.29
3.87
3.86
3.84
3.83
3.82
3.82
3.81
3.02
3.01
2.04
1.19
0.94
0.93
0.92
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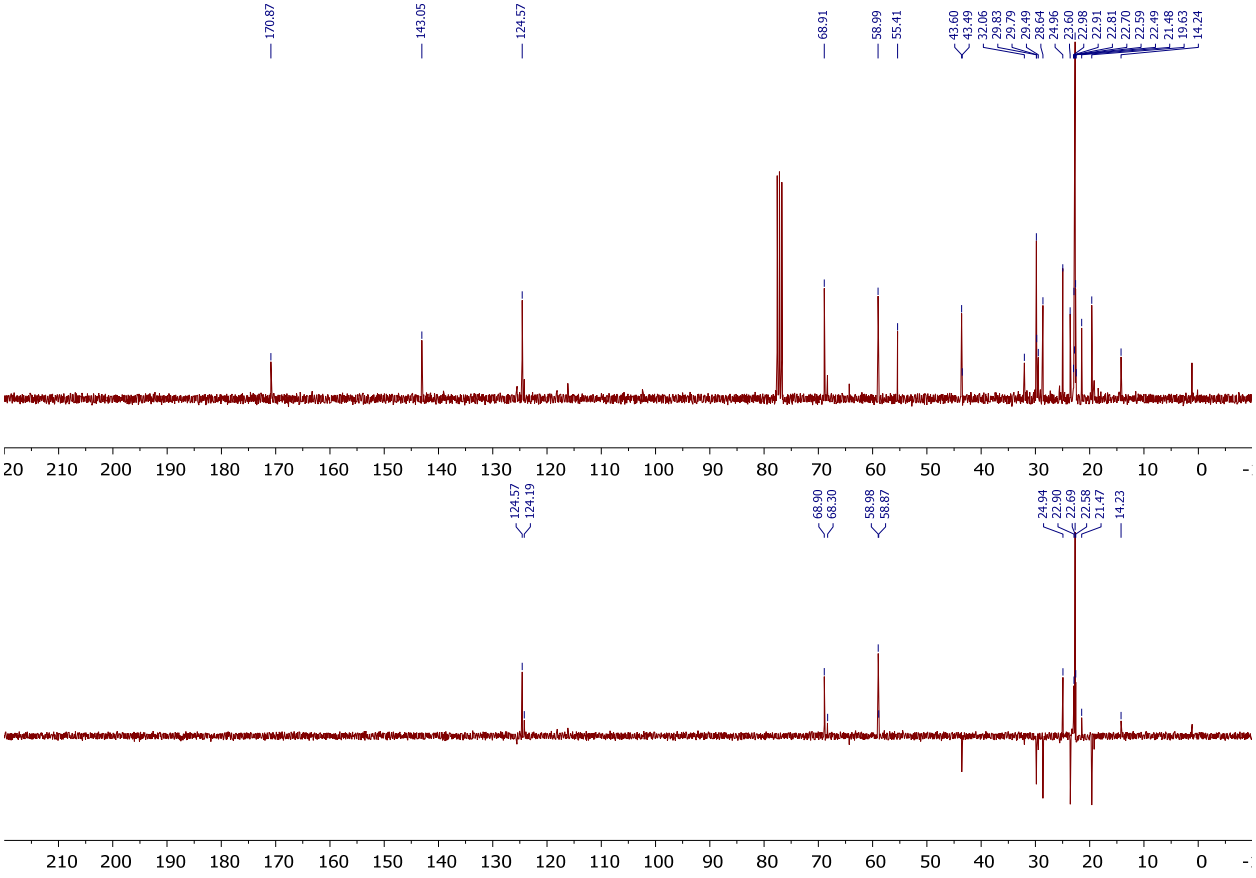
0.88
1.04
1.06
1.18
0.91
2.34
9.00
9.33


170.87
143.05
124.57
68.91
58.99
55.41
43.60
43.49
32.06
29.83
29.79
29.49
28.64
24.96
23.60
22.98
22.91
22.81
22.70
22.59
22.49
21.48
19.63
14.24
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58.98
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24.94
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22.69
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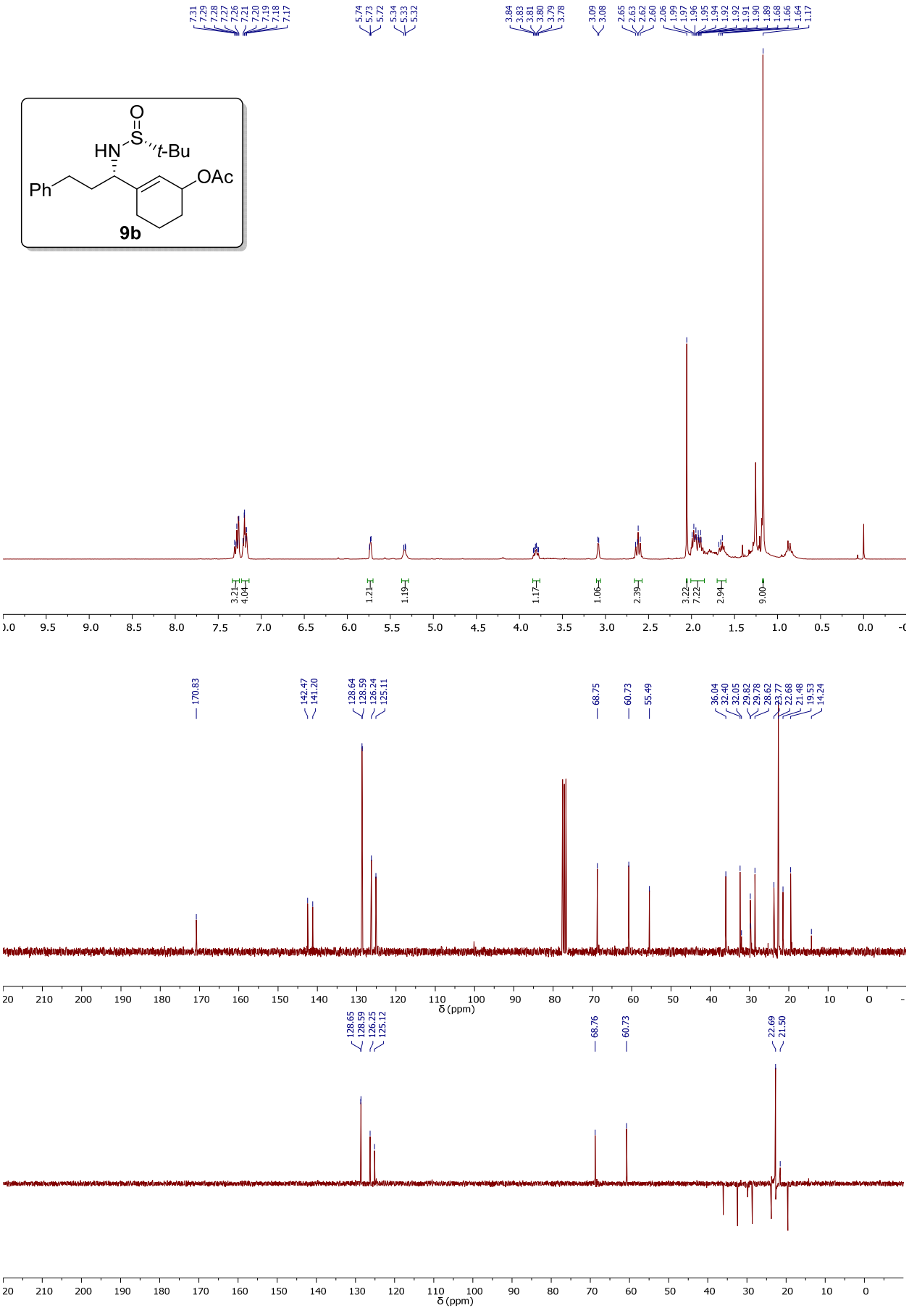
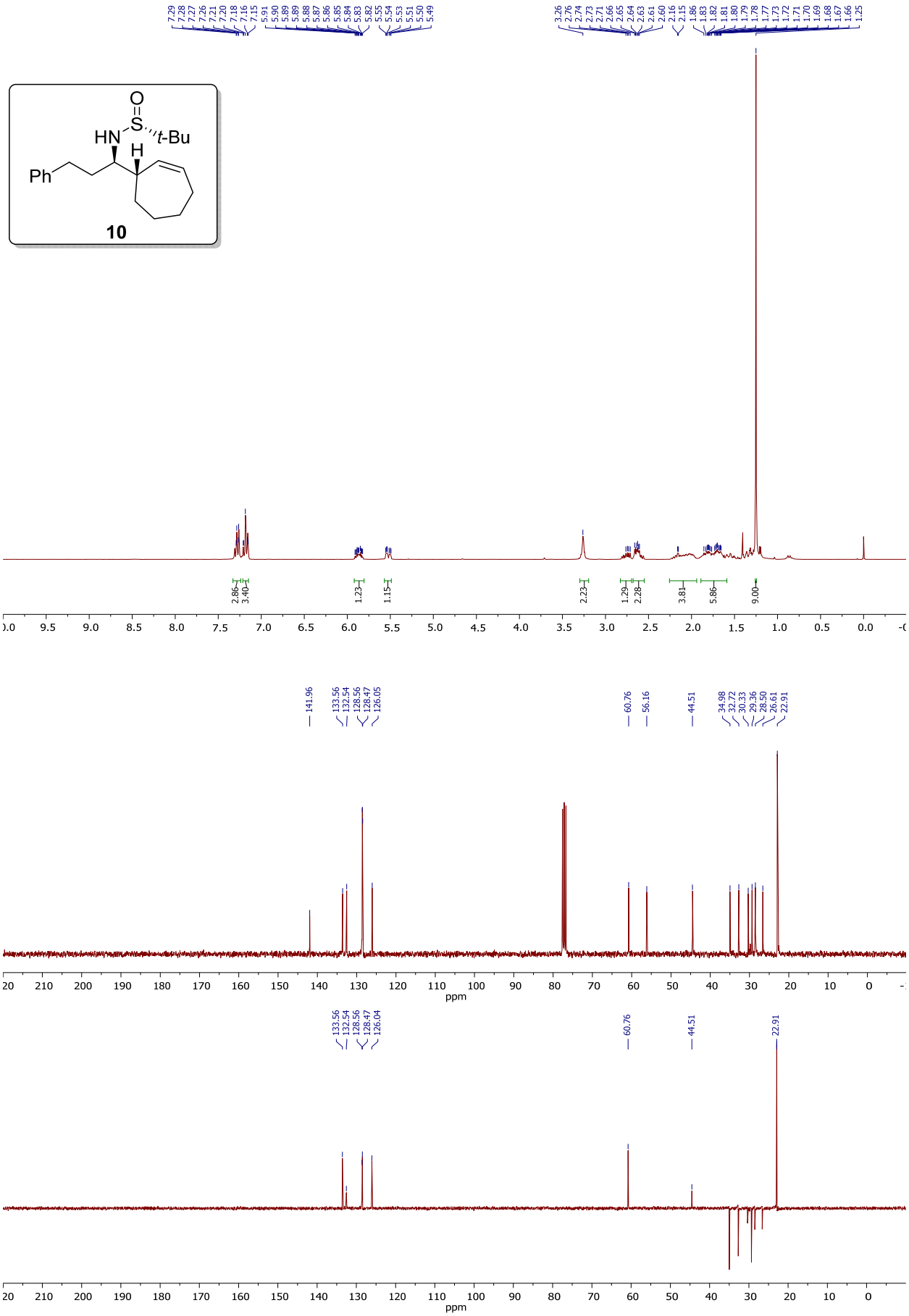
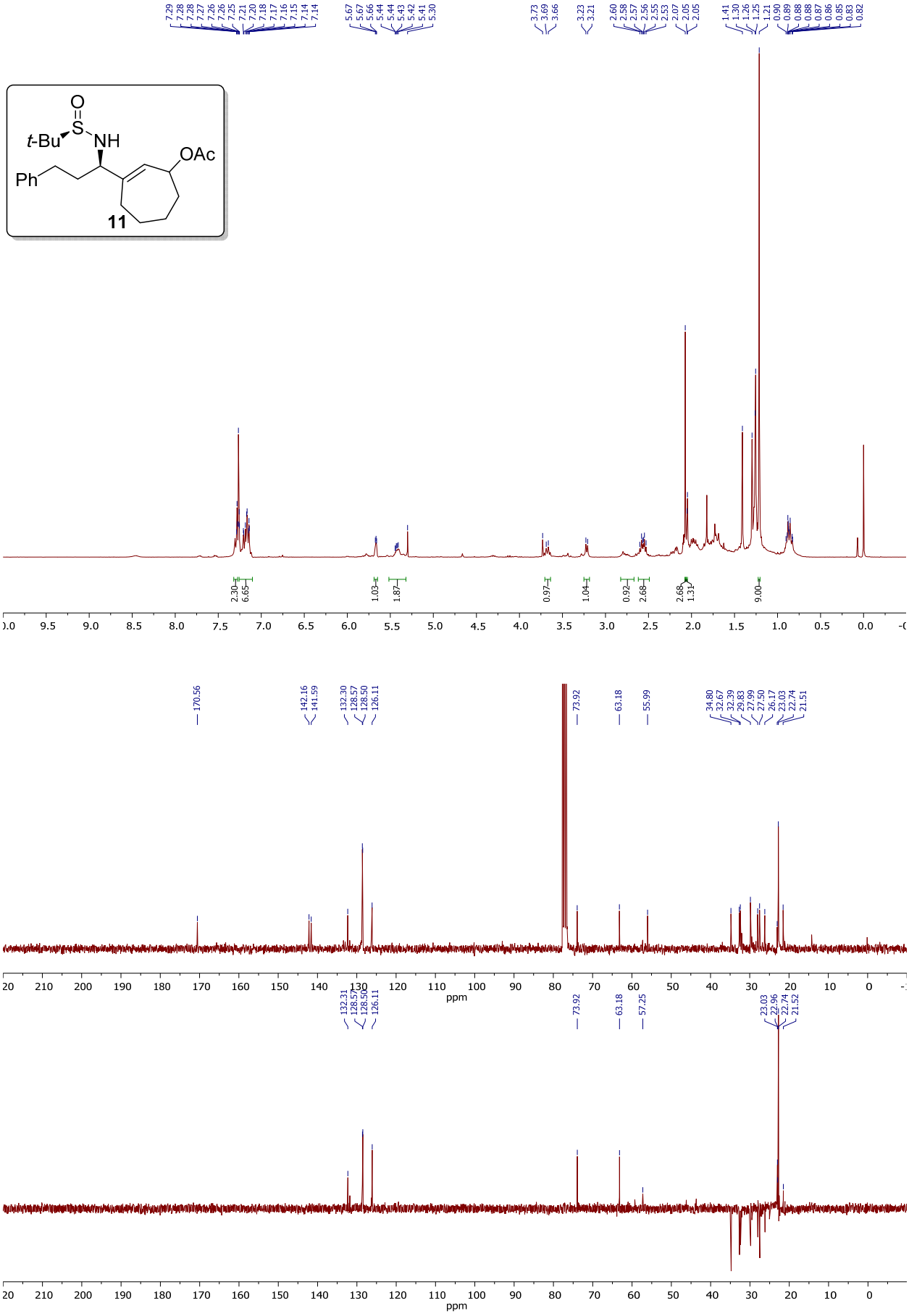
21.47
14.23


O
S
HN
t-Bu
Ph
OAc
9b
δ (ppm)


O
S
HN
H
t-Bu
Ph
10
ppm


t-Bu
NH
OAc
Ph
11
ppm
ppm