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Diastereoselective allylation and crotylation of *N*-*tert*-butanesulfinyl imines with allylic alcohols

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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 imines 1:

To a solution of (R_S)-*tert*-butanesulfinamide (0.605 g, 5 mmol) and the corresponding carbonyl compound (4.5 mmol) in dry THF (20 mL) under argon at 23 °C was slowly added titanium tetraethoxide (2.005 g, 1.885 mL, 9 mmol). The reaction mixture was stirred for 12 h at the same temperature for aldehydes and at 76 ºC for 5 h for butanone. The resulting mixture was hydrolyzed with brine (30 mL), extracted with ethyl acetate (3 × 15 mL), dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure compounds **1**. Imines **1a** (derived from 3-phenylpropanal),[1] **1b** (derived from nonanal),[2] **1c** (derived from isobutyraldehyde),[3] **1d** (derived from benzaldehyde),[3] **1e** (derived from 4-methylbenzaldehyde),[4] **1f** (derived from 4-methoxybenzaldehyde),[4] **1g** (derived from 2-bromobenzaldehyde),[5] **1h** (derived from 4-cyanobenzaldehyde),[6] **1i** (derived from 3-chlorobenzaldehyde)[7] and **1j** (derived from butanone)[8] were characterized by comparison of their physical and spectroscopic data with those reported in the literature.

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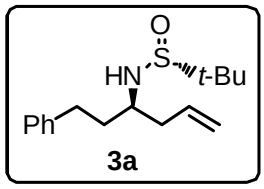
2. R. Almansa, D. Guijarro and M. Yus, *Tetrahedron: Asymmetry*, 2008, **19**, 2484.
3. G. Liu, D. A. Cogan, T. D. Owens, T. P. Tang and J. A. Ellman, *J. Org. Chem.*, 1999, **64**, 1278.
4. K. W. Kells and J. M. Chong, *J. Am. Chem. Soc.*, 2004, **126**, 15666.
5. L. Cheng, L. Liu, Y. Sui, D. Wang and Y.-J. Chen, *Tetrahedron: Asymmetry*, 2007, **18**, 1833.
6. L. Nielsen, K. B. Lindsay, J. Faber, N. C. Nielsen and T. Skrydstrup, *J. Org. Chem.*, 2007, **72**, 10035.
7. A. W. Buesking, T. D. Baguley and J. A. Ellman, *Organic Lett.*, 2011, **13**, 964.
8. F. A. Davis, S. Lee, H. Zhang and D. L. Fanelli, *J. Org. Chem.*, 2000, **65**, 8704.

General procedure for the stereoselective allylation and crotylation of *N-tert*-butanesulfinyl imines 1 with homoallylic alcohols 2:

To a flask containing dry THF (1.0 mL) was successively added homoallylic alcohol **2** (0.8 mmol), the corresponding *N-tert*-butanesulfinyl imine **1** (0.2 mmol), InI (96 mg, 0.4 mmol) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol). The reaction mixture was stirred for 14 h at 23 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 products **3**. Yields are given on Tables 1 and 3. Physical and spectroscopic data follow.

Characterization data of the obtained homoallylic amine derivatives 3

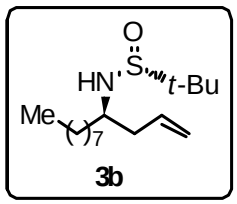
(3*R*,*R*$_S$)-*N*-*tert*-Bututanesulfinyl-1-phenylhex-5-en-3-amine (3a):[9]



3a

Colourless oil; $[\alpha]^{20}_D$ -46 (*c* 0.87, CH_2Cl_2); R_f 0.35 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.77-1.86 (m, 2H), 2.38-2.46 (m, 2H), 2.63-2.73 (m, 2H), 3.30-3.41 (m, 2H), 5.14-5.19 (m, 2H), 5.72-5.86 (m, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (CH_3), 32.0 (CH_2), 37.0 (CH_2), 40.6 (CH_2), 54.7 (CH), 56.0 (C), 119.3 (CH_2), 126.1 (CH), 128.5 (CH), 128.6 (CH), 134.0 (CH), 141.9 (C); IR (film) 3237, 3062, 3025, 2926, 2863, 1454, 1363, 1052 cm^{-1}; MS (EI) *m/z* 223 (M^+-56, 4%), 181 (12), 118 (11), 117 (67), 102 (14), 91 (100), 70 (22), 65 (18).

(4*R*,*R*$_S$)-*N*-*tert*-Butanesulfinyldodec-1-en-4-amine (3b):[9]



3b

Colourless oil; $[\alpha]^{20}_D$ -54 (*c* 0.83, CH_2Cl_2); R_f 0.52 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.0 Hz), 1.20 (s, 9H), 1.27-1.37 (m, 12H), 1.45-1.49 (m, 2H), 2.26-2.45 (m, 2H), 3.20-3.36 (m, 2H), 5.12-5.17 (m, 2H), 5.72-5.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.8 (CH_3), 25.6 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 35.1 (CH_2), 40.6 (CH_2), 55.0 (CH), 55.9 (C), 119.0 (CH_2), 134.4 (CH); IR (film) 3220, 2925, 2854, 1456, 1362, 1056 cm^{-1}; MS (EI) *m/z* 231 (M^+-56, 12%), 189 (21), 118 (17), 102 (34), 84 (28), 77 (19), 70 (78), 69 (19), 55 (43), 43 (84), 42 (19), 41 (100).

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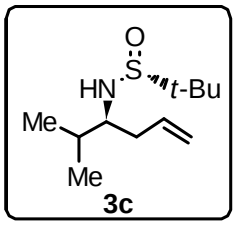
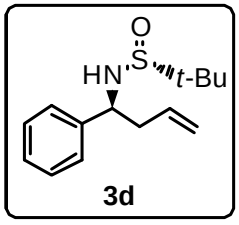
9. J. C. González-Gómez, M. Medjahdi, F. Foubelo and M. Yus, *J. Org. Chem.*, 2010, **75**, 6308.

(3*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-2-methylhex-5-en-3-amine (3c):[9]



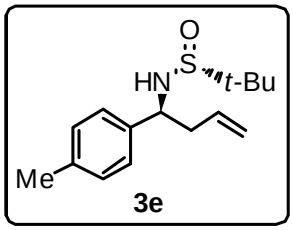
Colourless oil; $[\alpha]^{20}_D$ -65 (*c* 0.59, CH_2Cl_2); R_f 0.31 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, 6H, *J* = 8.8 Hz), 1.22 (s, 9H), 1.82-1.93 (m, 1H), 2.23-2.43 (m, 2H), 3.11-3.20 (m, 2H), 5.13-5.18 (m, 2H), 5.72-5.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0 (CH_3), 18.5 (CH_3), 22.9 (CH_3), 31.1 (CH_2), 37.1 (CH_2), 56.0 (C), 60.0 (CH), 118.8 (CH_2), 134.9 (CH); IR (film) 3239, 2957, 2871, 1466, 1388, 1364, 1055 cm^{-1}; MS (EI) *m/z* 161 (M^+-56, 15%), 120 (52), 119 (78), 118 (12), 62 (15), 57 (90), 56 (19), 55 (72), 43 (24), 41 (100).

(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-phenylbut-3-en-1-amine (3d):[9]



Colourless oil; $[\alpha]^{20}_D$ -146 (*c* 0.92, CH_2Cl_2); R_f 0.35 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9H), 2.42-2.64 (m, 2H), 3.67 (br s, 1H), 4.45-4.49 (m, 1H), 5.15-5.22 (m, 2H), 5.67-5.80 (m, 1H), 7.26-7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7 (CH_3), 43.6 (CH_2), 55.8 (C), 57.2 (CH), 119.4 (CH_2), 127.6 (CH), 127.8 (CH), 128.6 (CH), 134.3 (CH), 141.8 (C); IR (film) 3223, 3064, 3030, 1454, 1363, 1055 cm^{-1}; MS (EI) *m/z* 195 (M^+-56, 12%), 154 (22), 153 (71), 135 (13), 131 (100), 105 (16), 104 (27), 91 (25), 77 (18), 57 (63), 51 (16), 41 (66).

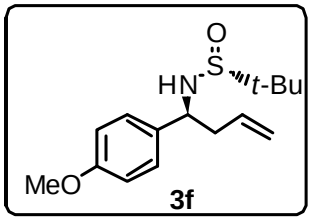
(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(4-methylphenyl)but-3-en-1-amine (3e):[10]



White solid; mp 79-81 ºC (pentane/CH_2Cl_2); $[\alpha]_D^{22}$ = -130 (*c* 0.94, CH_2Cl_2); R_f 0.34 (hexane/EtOAc: 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9H), 2.34 (s, 3H), 2.39-2.52 (m, 1H), 2.52-2.63 (m, 1H), 3.66 (d, 1H, *J* = 1.3 Hz), 4.43 (ddd, 1H, *J* = 7.9, 5.4, 2.1 Hz), 5.12-5.23 (m, 2H), 5.73 (dddd, 1H, *J* = 17.0, 10.2, 8.5, 5.8 Hz), 7.14 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 22.7 (CH_3), 43.6 (CH_2), 55.7 (C), 56.9 (CH), 119.3 (CH_2), 127.5 (CH), 129.3 (CH), 134.5 (CH), 137.4 (C), 138.8 (C); IR (KBr) 3200, 3060, 3032, 1455, 1049, 815 cm^{-1}; MS (EI) *m/z* 209 (M^+-56, 7%), 168 (12), 167 (100), 160 (12), 145 (22), 131 (18), 119 (51), 118 (41), 91 (24).

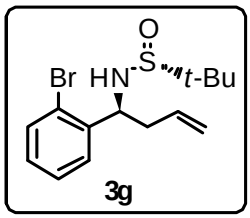
10. X.-W. Sun, M. Liu, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2008, **10**, 1259.

(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(4-methoxyphenyl)but-3-en-1-amine (3f):[10]



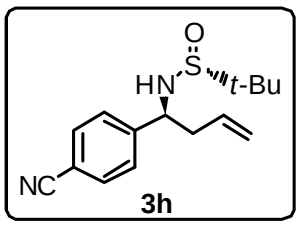
White solid; mp 75-78 ºC (pentane/CH_2Cl_2); $[\alpha]_D^{22}$ = -128 (*c* 1.10, CH_2Cl_2); R_f 0.28 (hexane/EtOAc: 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 9H), 2.38-2.51 (m, 1H), 2.51-2.62 (m, 1H), 3.65 (d, 1H, *J* = 1.5 Hz), 3.80 (s, 3H), 4.42 (ddd, 1H, *J* = 7.9, 5.5, 2.0 Hz), 5.11-5.23 (m, 2H), 5.65-5.81 (m, 1H), 6.87 (d, 2H, *J* = 8.8 Hz), 7.24 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 43.6 (CH_2), 55.3 (CH_3), 55.6 (C), 56.6 (CH), 113.9 (CH), 119.2 (CH_2), 128.8 (CH), 133.7 (C), 134.5 (CH), 159.2 (C); IR (KBr) 3198, 3063, 3031, 1612, 1509, 1241, 1051, 1039 cm^{-1}; MS (EI) *m/z* 281 (M^+, 1%), 225 (26), 207 (16), 183 (61), 176 (26), 162 (18), 161 (21), 147 (39), 136 (11), 135 (100), 134 (56), 91 (17), 77 (10).

(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(2-bromophenyl)but-3-en-1-amine (3g):[11]



Colourless oil; $[\alpha]^{20}_D$ -114 (*c* 0.98, CH_2Cl_2); R_f 0.48 (hexane/EtOAc 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.39-2.50 (m, 1H), 2.65-2.75 (m, 1H), 3.72 (d, 1H, *J* = 2.4 Hz), 4.98 (ddd, 1H, *J* = 8.1, 4.9, 3.1 Hz), 5.16-5.24 (m, 2H), 5.70-5.83 (m, 1H), 7.13 (td, 1H, *J* = 7.7, 1.7 Hz), 7.31 (td, 1H, *J* = 7.5, 1.0 Hz), 7.39 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.55 (dd, 1H, *J* = 8.0, 1.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7 (CH_3), 41.7 (CH_2), 56.0 (CH), 56.1 (C), 119.7 (CH_2), 123.6 (C), 127.5 (CH), 128.8 (CH), 129.0 (CH), 133.2 (CH), 133.9 (CH), 140.9 (C); IR (film) 3213, 1470, 1438, 1054, 1022, 913, 754 cm^{-1}; MS (EI) *m/z* 233 (M^+-98, 4%), 231 (54), 194 (17), 184 (17), 182 (17), 152 (100), 134 (16), 130 (18), 129 (10), 116 (11), 115 (10), 103 (10), 102 (13), 91 (14), 77 (16).

(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(4-cyanophenyl)but-3-en-1-amine (3h):

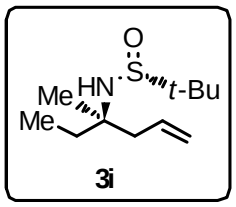


White solid; mp 144-147 ºC (pentane/CH_2Cl_2); $[\alpha]_D^{22}$ = -129 (*c* 0.90, CH_2Cl_2); R_f 0.21 (hexane/EtOAc: 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.40-2.51 (m, 1H), 2.54-2.63 (m, 1H), 3.72 (br s, 1H), 4.47-4.60 (m, 1H), 5.14-5.25 (m, 2H), 5.65-5.71 (m, 1H), 7.44 (d, 2H, *J* = 8.2 Hz), 7.64 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 43.2 (CH_2), 56.1 (C), 56.7 (CH), 111.8 (C), 118.8 (C), 120.3

11. J. A. Sirvent, F. Foubelo and M. Yus, *Eur. J. Org. Chem.*, 2013, 2461.

(CH_2), 128.4 (CH), 132.5 (CH), 133.3 (CH), 147.4 (C); IR (KBr) 3193, 3055, 3026, 2231, 1052 cm^{-1}; MS (EI) *m/z* 220 (M^+-56, 5%), 179 (12), 178 (100), 161 (11), 130 (22), 129 (35); HRMS: Calculated for $C_{15}H_{21}N_2OS$ (M^++1): 277.1375; found: 277.1373.

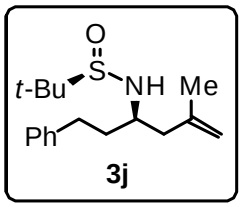
(3*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-3-methylhex-5-en-3-amine (3i):[12]



3i

Colourless oil; $[\alpha]^{20}_D$ -54 (*c* 0.88, CH_2Cl_2); R_f 0.56 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 7.5 Hz), 1.20 (s, 9H), 1.26 (s, 3H), 1.56 (q, 2H, *J* = 7.4 Hz), 2.30-2.34 (m, 2H), 3.20 (s, 1H), 5.11-5.17 (m, 2H), 5.76-5.91 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.9, 22.7, 25.6 (CH_3), 33.4, 45.7 (CH_2), 55.7, 57.5 (C), 119.2 (CH_2), 133.5 (CH); IR (film) 3179, 2962, 2915, 1641, 1456, 1362, 1183, 1157, 1035, 1001, 938, 922, 903, 675 cm^{-1}; MS (EI) *m/z* 161 (M^+-56, 31%), 161 (31), 160 (14), 143 (12), 120 (88), 119 (40), 110 (18), 104 (40), 97 (62), 96 (23), 81 (13), 74 (36), 73 (26), 72 (11), 71 (13), 70 (10), 69 (10), 57 (68), 56 (25), 55 (100).

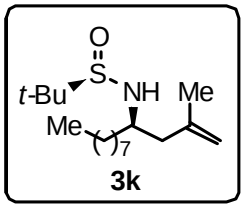
(3*R*,*R*$_S$)-*N*-*tert*-Bututanesulfinyl-5-methyl-1-phenylhex-5-en-3-amine (3j):[9]



3j

Colourless oil; $[\alpha]^{20}_D$ -71 (*c* 0.72, CH_2Cl_2); R_f 0.26 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 9H), 1.65 (s, 3H), 1.75-1.82 (m, 2H), 2.18-2.33 (m, 2H), 2.53-2.72 (m, 2H), 3.24 (d, 1H, *J* = 3.9 Hz), 3.33-3.43 (m, 1H), 4.72 (br s, 1H), 4.81 (br s, 1H), 7.08-7.23 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1 (CH_3), 22.8 (CH_3), 31.6 (CH_2), 37.2 (CH_2), 44.5 (CH_2), 51.5 (CH), 55.9 (C), 114.5 (CH_2), 126.1 (CH), 128.5 (CH), 128.6 (CH), 142.0 (C), 142.4 (C); IR (film) 3220, 3065, 3023, 2928, 2862, 1456, 1361, 1050 cm^{-1}; MS (EI) *m/z* 181 (M^+-112, 18%), 132 (11), 117 (78), 91 (100), 77 (13), 65 (14), 41 (29).

(4*R*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-2-methyldodec-1-en-4-amine (3k):[13]



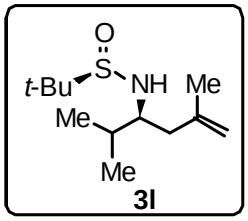
3k

Colourless oil; $[\alpha]^{20}_D$ -61 (*c* 1.32, CH_2Cl_2); R_f 0.39 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.1 Hz), 1.20 (s, 9H), 1.21-1.33 (m, 12H), 1.44-1.51 (m, 2H), 1.74 (s, 3H), 2.15-2.34 (m, 2H), 3.24 (br s, 1H), 3.33-3.34 (m, 1H), 4.79 (br s, 1H), 4.87 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.1 (CH_2), 22.7 (CH_3), 22.8 (CH_2), 25.2 (CH_2), 29.4

12. J. A. Sirvent, F. Foubelo and M. Yus, *Chem. Commun.*, 2012, **48**, 2543.
13. F. Foubelo and M. Yus, *Tetrahedron: Asymmetry*, 2004, **15**, 3823.

(CH_2), 29.6 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 35.4 (CH_2), 44.5 (CH_2), 51.5 (CH), 55.7 (C), 114.2 (CH_2), 142.7 (C); IR (film) 3220, 2925, 2854, 1456, 1362, 1056 cm^{-1}; MS (EI) *m/z* 245 (M^+-56, 3%), 189 (48), 116 (10), 84 (36), 77 (28), 70 (85), 69 (31), 55 (44), 41 (100).

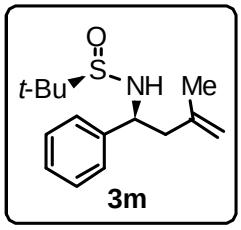
(3*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-2,5-dimethylhex-5-en-3-amine (3l):[13]



3l

Colourless oil; $[\alpha]^{20}_D$ -92 (*c* 1.05, CH_2Cl_2); R_f 0.36 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, 3H, *J* = 5.7 Hz), 0.91 (d, 3H, *J* = 5.7 Hz), 1.21 (s, 9H), 1.76 (s, 3H), 1.95-1.99 (m, 1H), 2.10 (dd, 1H, *J* = 13.7, 9.7 Hz), 2.24 (dd, 1H, *J* = 13.7, 5.0 Hz), 3.18 (br s, 1H), 3.27-3.34 (m, 1H), 4.80 (br s, 1H), 4.88 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4 (CH_3), 17.7 (CH_3), 21.8 (CH_3), 22.8 (CH_3), 30.7 (CH), 39.9 (CH_2), 55.8 (CH), 60.5 (C), 114.3 (CH_2), 142.9 (C); IR (film) 3230, 2962, 2876, 1469, 1383, 1360, 1054 cm^{-1}; MS (EI) *m/z* 176 (M^+-56, 4%), 119 (100), 69 (17), 57 (61), 56 (55), 55 (31), 41 (65).

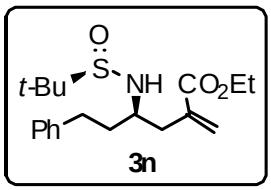
(1*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-3-methyl-1-phenylbut-3-en-1-amine (3m):[13]



3m

White solid; mp 77-78 ºC (pentane/CH_2Cl_2); $[\alpha]^{20}_D$ -149 (*c* 0.76, CH_2Cl_2); R_f 0.29 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.79 (s, 3H), 2.40-2.44 (m, 2H), 3.71 (s, 1H), 4.49-4.54 (m, 1H), 4.87 (br s, 1H), 4.94 (br s, 1H), 7.26-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9 (CH_3), 22.7 (CH_3), 48.0 (CH_2), 54.6 (CH), 55.7 (C), 115.1 (CH_2), 127.6 (CH), 127.7 (CH), 128.6 (CH), 142.2 (C), 142.4 (C); IR (KBr) 3240, 3060, 3031, 1462, 1352, 1054 cm^{-1}; MS (EI) *m/z* 209 (M^+-56, 3%), 153 (100), 145 (23), 136 (13), 105 (19), 104 (27), 77 (14), 57 (34), 41 (48).

(4*R*,*R*$_S$)-Ethyl *N*-(*tert*-butanesulfinyl)-4-amino-2-methylene-6-phenylhexanoate (3n):[14]



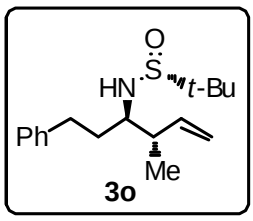
3n

Colourless oil; $[\alpha]^{20}_D$ -35 (*c* 0.89, CH_2Cl_2); R_f 0.34 (hexane/EtOAc 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.29 (t, 3H, *J* = 7.2 Hz), 1.71-1.88 (m, 2H), 2.61-2.80 (m, 4H), 3.47-3.54 (m, 1H), 3.67 (d, 1H, *J* = 5.5 Hz), 4.20 (q, 2H, *J* = 7.2 Hz), 5.68 (br s, 1H), 6.30 (br s, 1H), 7.15-7.30 (5H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.9 (CH_3), 32.0, 37.5, 38.5 (CH_2), 55.2 (CH), 56.0 (C), 61.2 (CH_2), 126.0, 128.4 (CH), 128.5 (CH_2), 128.6 (CH), 137.2, 141.8 (C), 167.6 (CO); IR (film) 3222, 3061, 3026, 2951, 1712, 1454, 1176, 1052, 699

14. H. K. Dema, F. Foubelo and M. Yus, *Heterocycles*, 2011, **82**, 1411.

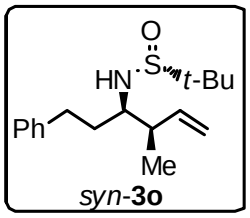
cm^{-1}; MS (EI) *m/z* 295 (M^+-56, 4%), 277 (27), 204 (100), 181 (18), 117 (62), 91 (87), 65 (14).

(3*R*,4*S*,*R*$_S$)-*N*-*tert*-Bututanesulfinyl-4-methyl-1-phenylhex-5-en-3-amine (3o):



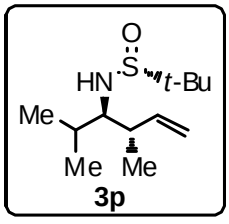
Light yellow solid; mp 46-48 ºC (pentane/CH_2Cl_2); $[\alpha]^{20}_D$ = -23 (*c* 0.49, CH_2Cl_2); R_f 0.23 (hexane/EtOAc: 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (d, 3H, *J* = 6.9 Hz), 1.25 (s, 9H), 1.49-1.63 (m, 1H), 1.87 (dddd, 1H, *J* = 13.7, 10.2, 6.7, 3.4 Hz), 2.56 (ddd, 1H, *J* = 13.7, 10.0, 6.7 Hz), 2.63-2.74 (m, 1H), 2.75-2.87 (m, 1H), 3.14-3.23 (m, 1H), 3.44 (d, 1H, *J* = 8.3 Hz), 5.13-5.25 (m, 2H), 5.68 (ddd, 1H, *J* = 17.2, 10.2, 8.6 Hz), 7.13-7.23 (m, 3H), 7.23-7.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.5 (CH_3), 22.8 (CH_3), 32.5 (CH_2), 33.0 (CH_2), 43.2 (CH), 56.1 (C), 60.1 (CH), 117.8 (CH_2), 125.9 (CH), 128.3 (CH), 128.4 (CH), 139.2 (CH), 141.8 (C); IR (KBr) 3295, 3065, 3034, 1458, 1057 cm^{-1}; MS (EI) *m/z* 237 (M^+-56, 3%), 181 (36), 133 (13), 132 (13), 118 (12), 117 (86), 116 (11), 91 (100); HRMS: Calculated for $C_{17}H_{28}NOS$ (M^++1): 294.1892; found: 294.1891.

(3*R*,4*R*,*R*$_S$)-*N*-*tert*-Bututanesulfinyl-4-methyl-1-phenylhex-5-en-3-amine (*syn*-3o):



Colourless oil; $[\alpha]^{20}_D$ = -44 (*c* 0.58, CH_2Cl_2); R_f 0.19 (hexane/EtOAc: 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, 3H, *J* = 6.9 Hz), 1.25 (s, 9H), 1.69-1.82 (m, 3H), 1.92 (dddd, 1H, *J* = 14.5, 10.4, 6.1, 4.0 Hz), 2.45-2.57 (m, 1H), 2.59-2.77 (m, 2H), 3.21 (dtd, 1H, *J* = 7.2, 5.8, 4.1 Hz), 3.39 (d, 1H, *J* = 5.9 Hz), 3.35-3.47 (m, 1H), 5.05-5.20 (m, 2H), 5.77 (ddd, 1H, *J* = 17.0, 10.6, 7.5 Hz), 7.13-7.23 (m, 3H), 7.24-7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.6 (CH_3), 22.8 (CH_3), 31.5 (CH_2), 34.4 (CH_2), 41.7 (CH), 56.0 (C), 58.7 (CH), 116.5 (CH_2), 125.9 (CH), 128.3 (CH), 128.4 (CH), 140.2 (CH), 142.0 (C); IR (film) 3290, 3064, 3033, 1460, 1055 cm^{-1}; MS (EI) *m/z* 237 (M^+-56, 10%), 133 (21), 132 (22), 118 (11), 117 (74), 92 (10), 91 (100), 84 (40); HRMS: Calculated for $C_{17}H_{28}NOS$ (M^++1): 294.1892; found: 294.1882.

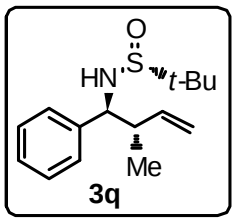
(3*R*,4*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-2,4-dimethylhex-5-en-3-amine (3p):



Colourless oil; $[\alpha]^{20}_D$ = +24 (*c* 0.89, CH_2Cl_2); R_f 0.57 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, 3H, *J* = 6.7 Hz), 0.97 (d, 3H, *J* = 6.8 Hz), 1.13 (d, 3H, *J* = 6.8 Hz), 1.23 (s, 9H), 1.82 (dtd, 1H, *J* = 13.5, 6.8, 5.4 Hz), 2.41-2.55 (m, 1H), 2.88 (dd, 1H, *J* = 11.4, 5.8 Hz),

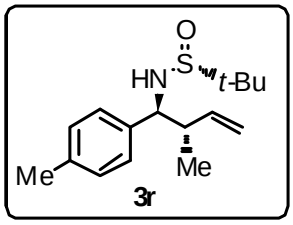
3.27 (br s, 1H), 5.05-5.19 (m, 2H), 5.86 (ddd, 1H, *J* = 17.2, 10.4, 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9 (CH_3), 18.0 (CH_3), 21.0 (CH_3), 23.2 (CH_3), 31.5 (CH), 40.1 (CH), 56.5 (C), 64.7 (CH), 116.6 (CH_2), 140.9 (CH); IR (film) 3245, 1457, 1363, 1057 cm^{-1}; MS (EI) *m/z* 175 (M^+-56, 20%), 176 (11), 120 (100), 119 (23), 104 (10), 69 (11), 57 (33), 56 (12), 55 (19); HRMS: Calculated for $C_{12}H_{26}NOS$ (M^++1): 232.1735; found: 232.1724.

(1*S*,2*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-phenyl-2-methylbut-3-en-1-amine (3q):



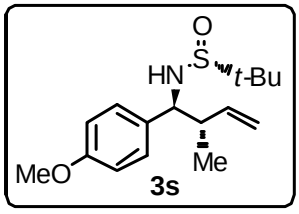
White solid; mp 70-72 ºC (pentane/CH_2Cl_2); $[\alpha]^{20}_D$ = -124 (*c* 0.95, CH_2Cl_2); R_f 0.30 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, 3H, *J* = 6.7 Hz), 1.16 (s, 9H), 2.32-2.49 (m, 1H), 3.93 (br s, 1H), 4.04 (d, 1H, *J* = 9.3 Hz), 5.19-5.30 (m, 2H), 5.74 (ddd, 1H, *J* = 17.1, 10.0, 9.3 Hz), 7.25-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (CH_3), 22.7 (CH_3), 46.6 (CH), 55.6 (C), 61.5 (CH), 117.8 (CH_2), 127.9 (CH), 128.4 (CH), 128.8 (CH), 140.3 (C), 141.7 (CH); IR (KBr) 3296, 3062, 3030, 1456, 1059 cm^{-1}; MS (EI) *m/z* 209 (M^+-56, 24%), 155 (13), 154 (92), 153 (100), 146 (12), 145 (73), 136 (28), 131 (12), 117 (17), 105 (25), 104 (34), 91 (22), 77 (16), 57 (17); HRMS: Calculated for $C_{15}H_{24}NOS$ (M^++1): 266.1579; found: 266.1592.

(1*S*,2*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-2-methyl-1-(4-methylphenyl)but-3-en-1-amine (3r):



Colorless oil; $[\alpha]^{20}_D$ = -138 (*c* 0.96, CH_2Cl_2); R_f 0.48 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, 3H, *J* = 6.7 Hz), 1.15 (s, 9H), 2.32-2.42 (m, 1H), 2.35 (s, 3H), 3.91 (br s, 1H), 4.00 (d, 1H, *J* = 9.4 Hz), 5.19-5.27 (m, 2H), 5.65-5.80 (m, 1H), 7.14 (d, 2H, *J* = 8.2 Hz), 7.18 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (CH_3), 21.3 (CH_3), 22.7 (CH_3), 46.7 (CH), 55.5 (C), 61.2 (CH). 117.6 (CH_2), 128.6 (CH), 129.2 (CH), 137.2 (C), 137.5 (C), 141.9 (CH); IR (film) 3281, 3070, 3034, 1456, 1060 cm^{-1}; MS (EI) *m/z* 221 (M^+-56, 6%), 205 (18), 168 (12), 167 (100), 151 (11), 150 (26), 149 (16), 145 (15), 119 (41), 118 (31), 117 (12), 91 (25); HRMS: Calculated for $C_{16}H_{26}NOS$ (M^++1): 280.1735; found: 280.1737.

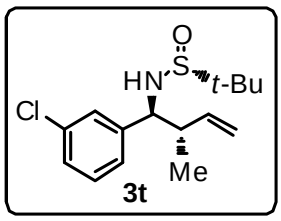
(1*S*,2*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(4-methoxyphenyl)-2-methylbut-3-en-1-amine (3s):



Colorless oil; $[\alpha]^{20}_D$ = -140 (*c* 1.22, CH_2Cl_2); R_f 0.38 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (d, 3H, *J*

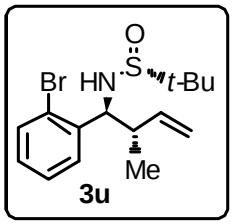
= 6.7 Hz), 1.15 (9H, s), 2.28-2.44 (m, 1H), 3.81 (s, 3H), 3.92 (br s, 1H), 3.98 (d, 1H, *J* = 9.5 Hz), 5.18-5.28 (m, 2H, m), 5.73 (ddd, 1H, *J* = 17.1, 10.0, 9.4 Hz), 6.87 (d, 2H, *J* = 8.7 Hz), 7.22 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (CH_3), 22.8 (CH_3), 46.8 (CH), 55.3 (CH_3), 55.5 (C), 60.9 (CH), 113.8 (CH), 117.6 (CH_2), 129.8 (CH), 132.1 (C), 141.9 (CH), 159.3 (C); IR (film) 3280, 1612, 1512, 1249, 1060, 1033 cm^{-1}; MS (EI) *m/z* 239 (M^+-56, 16%), 223 (11), 221 (51), 184 (10), 183 (96), 167 (25), 166 (38), 165 (54), 161 (27), 150 (12), 136 (12), 135 (100), 134 (46), 133 (28), 91 (15), 77.1 (11); HRMS: Calculated for $C_{16}H_{26}NO_2S$ (M^++1): 296.1684; found: 296.1678.

(1*S*,2*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(3-chlorophenyl)-2-methylbut-3-en-1-amine (3t):



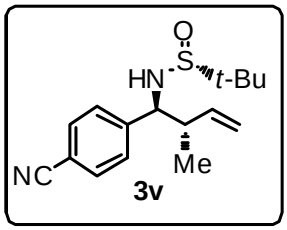
Colorless oil; $[\alpha]^{20}_D$ = -136 (*c* 1.02, CH_2Cl_2); R_f 0.48 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, 3H, *J* = 6.7 Hz), 1.17 (s, 9H), 2.32-2.45 (m, 1H), 3.94 (br s, 1H), 4.04 (d, 1H, *J* = 9.3 Hz), 5.22-5.29 (m, 2H, m), 5.67-5.79 (m, 1H), 7.17-7.22 (m, 1H), 7.25-7.29 (m, 2H), 7.29-7.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.6 (CH_3), 22.7 (CH_3), 46.5 (CH), 55.8 (C), 61.1 (CH), 118.1 (CH_2), 127.2 (CH), 128.1 (CH), 128.6 (CH), 129.7 (CH), 134.4 (C), 141.2 (CH), 142.6 (C); IR (film) 3282, 1473, 1062 cm^{-1}; MS (EI) *m/z* 243 (M^+-56, 9%), 227 (17), 225 (27), 189 (38), 188 (12), 187 (100), 172 (18), 171 (20), 170 (44), 169 (17), 141 (12), 140 (16), 139 (38), 138 (29), 137 (13), 111 (10), 91 (15), 75 (12), 55 (10); HRMS: Calculated for $C_{15}H_{23}{}^{35}ClNOS$ (M^++1): 300.1189; found: 300.1191.

(1*S*,2*S*,*R*$_S$)-*N*-*tert*-Butanesulfinyl-1-(2-bromophenyl)-2-methylbut-3-en-1-amine (3u):



Colorless oil; $[\alpha]^{20}_D$ = -124 (*c* 1.03, CH_2Cl_2); R_f 0.55 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, 3H, *J* = 6.8 Hz), 1.15 (s, 9H), 2.54 (m, 1H), 3.84 (br s, 1H), 4.62-4.83 (m, 1H), 5.19-5.29 (m, 2H), 5.73-5.85 (m, 1H), 7.13 (ddd, 1H, *J* = 8.0, 6.9, 2.2 Hz), 7.28-7.36 (m, 2H), 7.56 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0 (CH_3), 22.7 (CH_3), 45.7 (CH), 55.8 (C), 59.9 (CH), 118.0 (CH_2), 125.1 (C), 127.5 (CH), 129.0 (CH), 129.7 (CH), 133.0 (CH), 140.4 (C), 140.5 (CH); IR (film) 3278, 1471, 1062 cm^{-1}; MS (EI) *m/z* 289 (M^+-56, 3%), 287 (2), 271 (19), 269 (14), 233 (57), 231 (55), 215 (12), 208 (24), 184 (19), 182 (16), 183 (12), 152 (100), 144 (11), 136 (43), 134 (21), 130 (20), 129 (16), 115 (14), 103 (10), 102 (17), 91 (29), 88 (15), 77 (18), 75 (10); HRMS: Calculated for $C_{15}H_{23}{}^{79}BrNOS$ (M^++1): 344.0684; found: 344.0668.

(1*S*,2*S*,R_S)-*N*-*tert*-Butanesulfinyl-1-(4-cyanophenyl)-2-methylbut-3-en-1-amine (3v):



Colorless oil; $[\alpha]^{20}_D$ = -140 (*c* 0.99, CH_2Cl_2); R_f 0.34 (hexane/EtOAc: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (d, 3H, *J* = 6.7 Hz), 1.17 (s, 9H), 2.32-2.47 (m, 1H), 3.96 (br s, 1H), 4.12 (d, 1H, *J* = 9.2 Hz), 5.21-5.32 (m, 2H), 5.64-5.79 (m, 1H), 7.43 (d, 2H, *J* = 8.3 Hz), 7.56 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5 (CH_3), 22.7 (CH_3), 46.3 (CH), 55.9 (C), 61.2 (CH). 111.9 (C), 118.6 (CH_2), 118.8 (CN), 129.5 (CH), 132.3 (CH), 140.7 (CH), 146.1 (C); IR (film) 3280, 1608, 1457, 1062 cm^{-1}; MS (EI) *m/z* 234 (M^+-56, 9%), 179 (14), 178 (100), 161 (20), 156 (12), 130 (19), 129 (31); HRMS: Calculated for $C_{16}H_{23}N_2OS$ (M^++1): 291.1531; found: 291.1528.

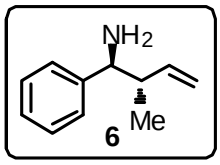
General procedure for the stereoselective crotylation of *N*-*tert*-butanesulfinyl imines 1 with crotyl bromide 5:

A mixture of *N*-*tert*-butanesulfinyl imine **1** (0.5 mmol), crotyl bromide (135 mg, 85%, 0.85 mmol) and indium (87 mg, 0.75 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 products **3o**-**v**. Yields are given on Table 3. Physical and spectroscopic are given above.

Desulfinylation of (1*S*,2*S*,R_S)-*N*-*tert*-Butanesulfinyl-1-phenyl-2-methylbut-3-en-1-amine (3q). Synthesis of (*S*)-2-Methyl-1-phenylbut-3-en-1-amine (6).

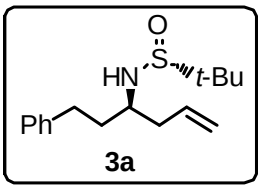
To a stirred solution of *N*-*tert*-butanesulfinyl amine **3q** (40 mg, 0.15 mmol) in THF (0.5 mL) was added a 6M HCl aqueous solution (0.39 mL) at 23 ºC. After 1 h stirring at this temperature, the resulting mixture was basified with a 1M NaOH aqueous solution (5 mL). The reaction mixture was extracted with EtOAc (2 × 10 mL), the organic layer was washed firs with 1M NaOH aqueous solution (5 mL) and then with H_2O (5 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr) to yield pure amine **6** (22.2 mg, 0.138 mmol, 92%). Physical and spectroscopic data follow.

(*S*)-2-Methyl-1-phenylbut-3-en-1-amine (6):[15]



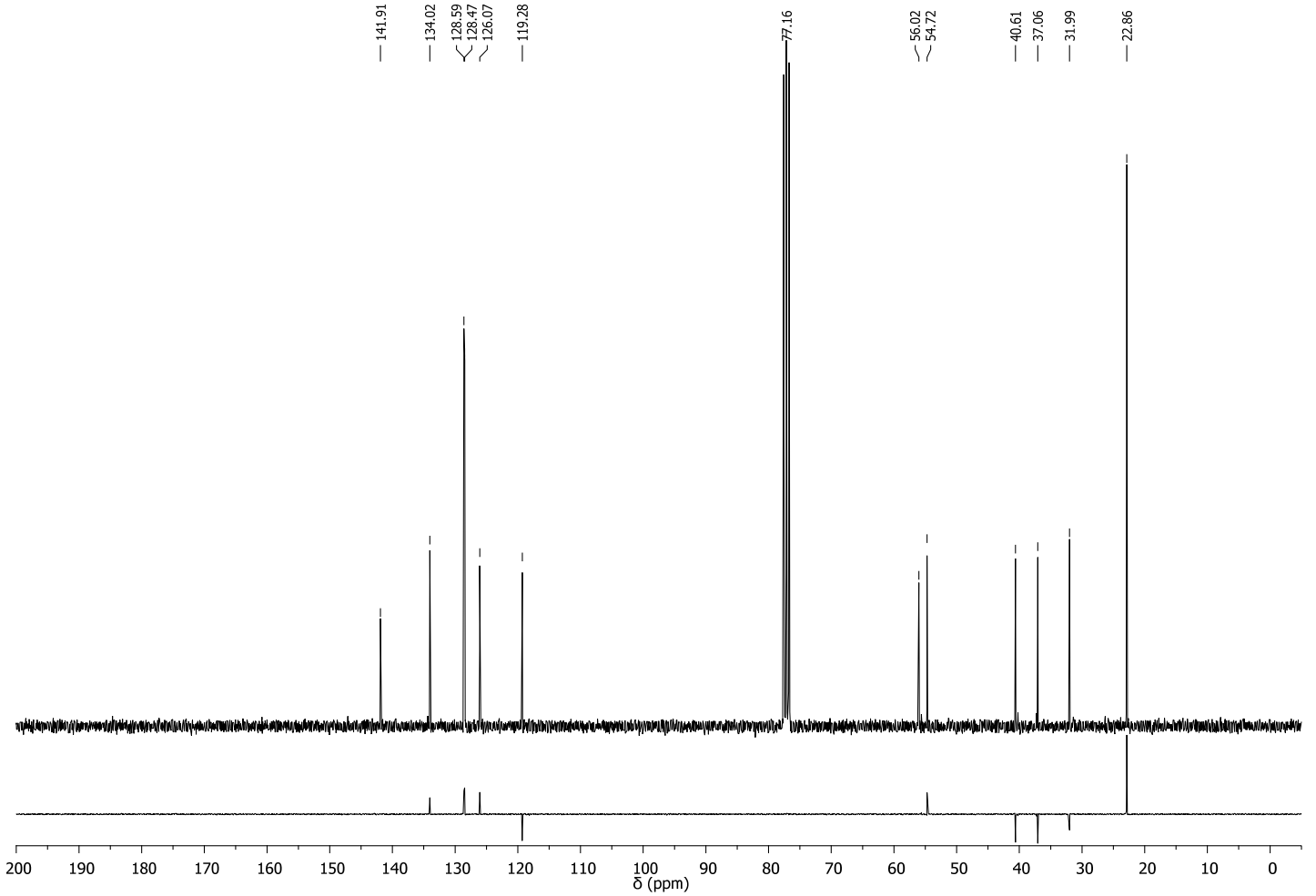
Colourless oil; $[\alpha]^{20}_D$ = +73 (*c* 0.50, $CHCl_3$) {lit. $[\alpha]^{20}_D$ = +76 (*c* 0.92, $CHCl_3$)};[15] R_f 0.23 (CH_2Cl_2/MeOH: 9/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, 3H, *J* = 6.8 Hz), 2.02 (br s, 2H), 2.21-2.56 (m, 1H), 3.65 (d, 1H, *J* = 7.9 Hz), 5.08-5.25 (m, 2H), 5.66-5.82 (m, 1H), 7.22-7.28 (m, 1H), 7.29-7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8 (CH_3), 46.4 (CH), 60.8 (CH), 116.2 (CH_2), 127.3 (CH), 127.5 (CH), 128.4 (CH), 141.7 (CH), 144.3 (C); IR (film) 3290, 3060, 2915, 1455, 915 cm^{-1}; MS (EI) *m/z* 106 (M^+-55, 100%), 79 (19), 77 (11).

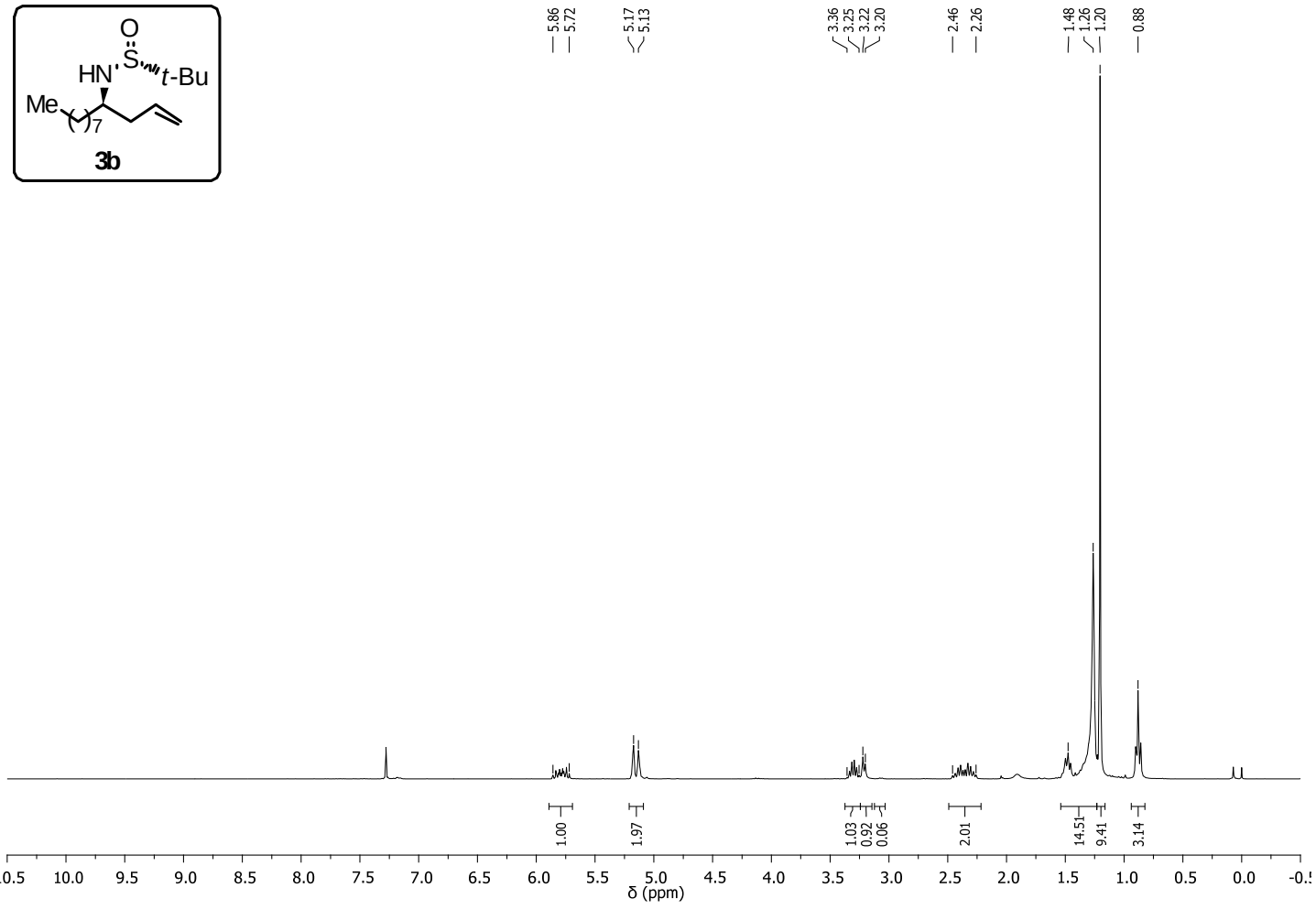
15. P. V. Ramachandran, T. E. Burghardt and L. Bland-Berry, *J. Org. Chem.*, 2005, **70**, 7911.

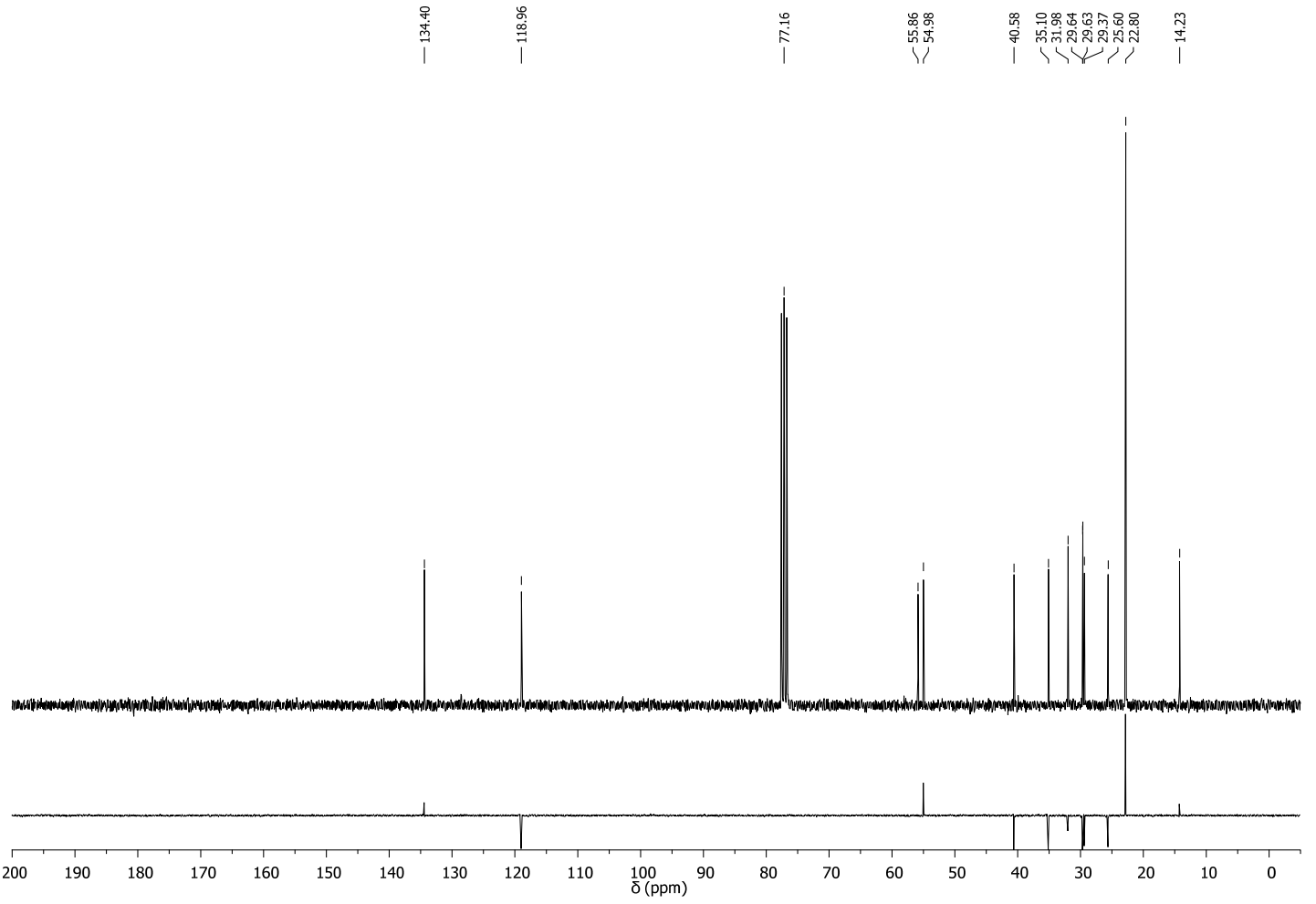

O
S
HN
t-Bu
Ph

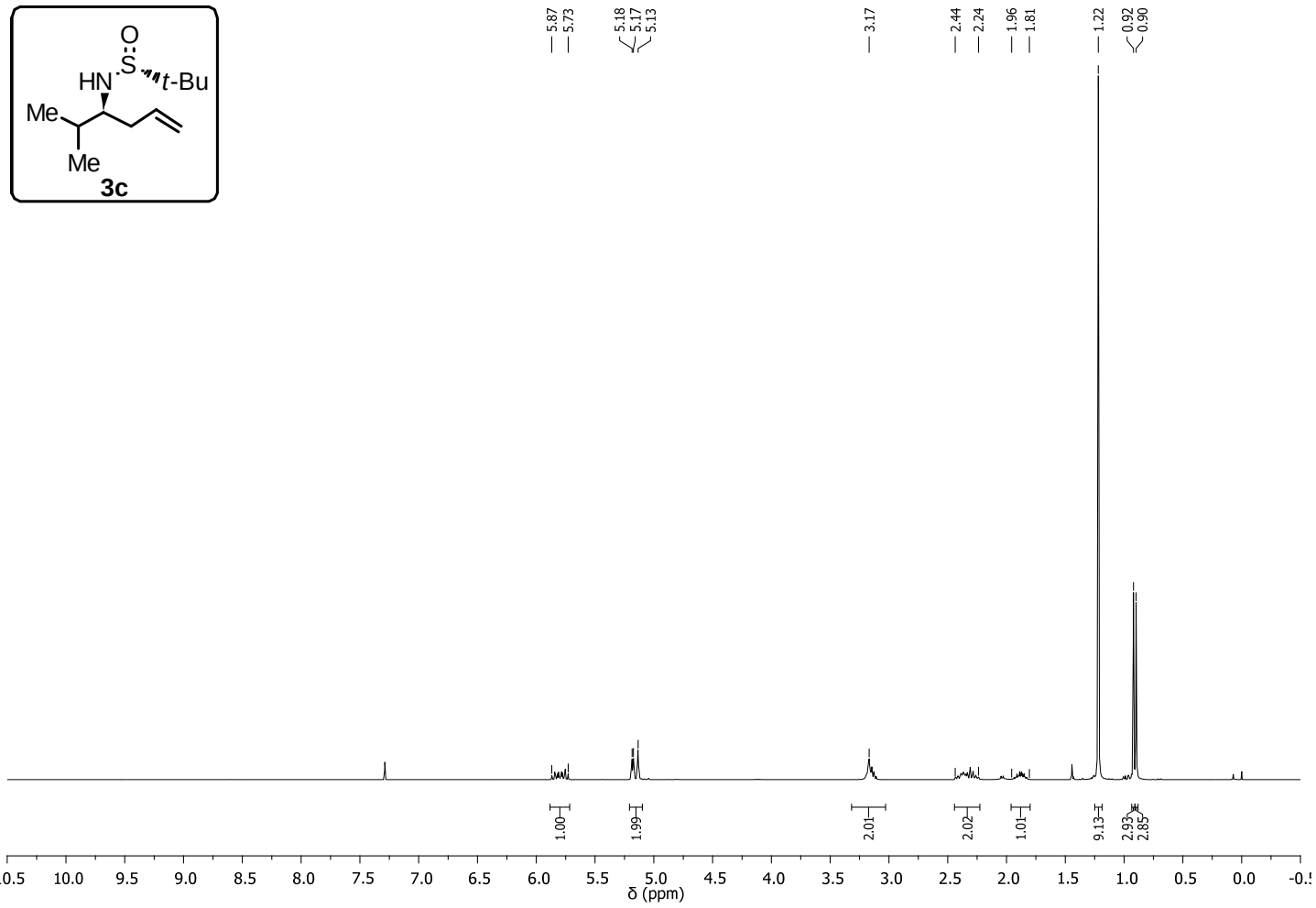
3a

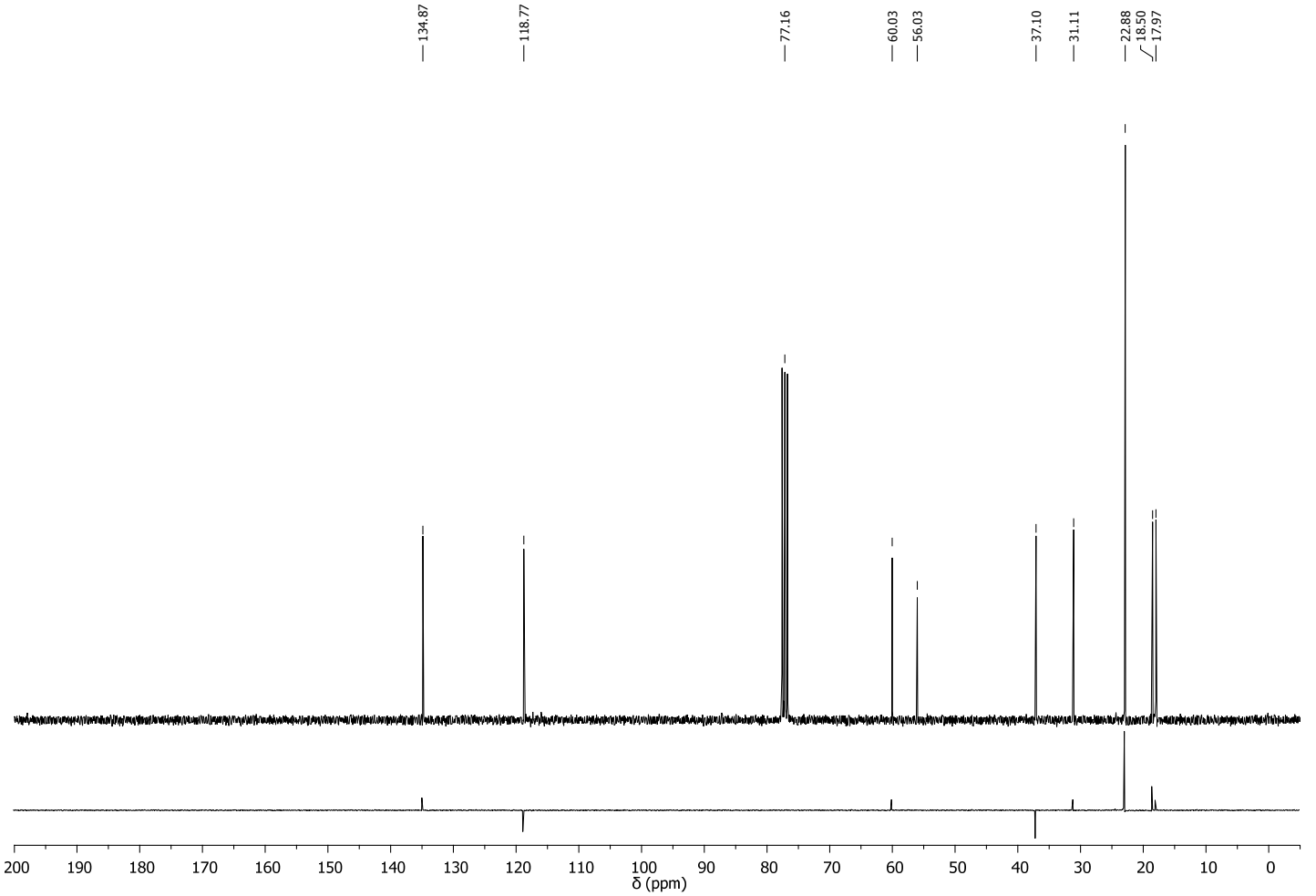
7.31
7.29
7.21
7.21
7.19
7.18
7.16
7.16
5.86
5.72
5.19
5.15
3.43
3.39
3.37
3.33
3.30
3.28
3.15
3.13
2.79
2.69
2.59
2.51
2.43
2.32
1.93
1.73
1.23
2.26
3.02
1.00
2.02
1.04
0.89
0.06
2.01
2.01
2.57
9.32
δ (ppm)

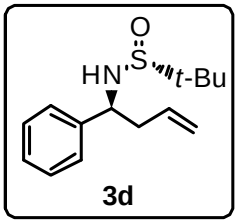

141.91
134.02
128.59
128.47
126.07
119.28
77.16
56.02
54.72
40.61
37.06
31.99
22.86
δ (ppm)


O
S
HN
t-Bu
Me
7
3b
5.86
5.72
5.17
5.13
3.36
3.25
3.22
3.20
2.46
2.26
1.48
1.26
1.20
0.88
1.00
1.97
1.03
0.92
0.06
2.01
14.51
9.41
3.14
δ (ppm)


134.40
118.96
77.16
55.86
54.98
40.58
35.10
31.98
29.64
29.63
29.37
25.60
22.80
14.23
δ (ppm)

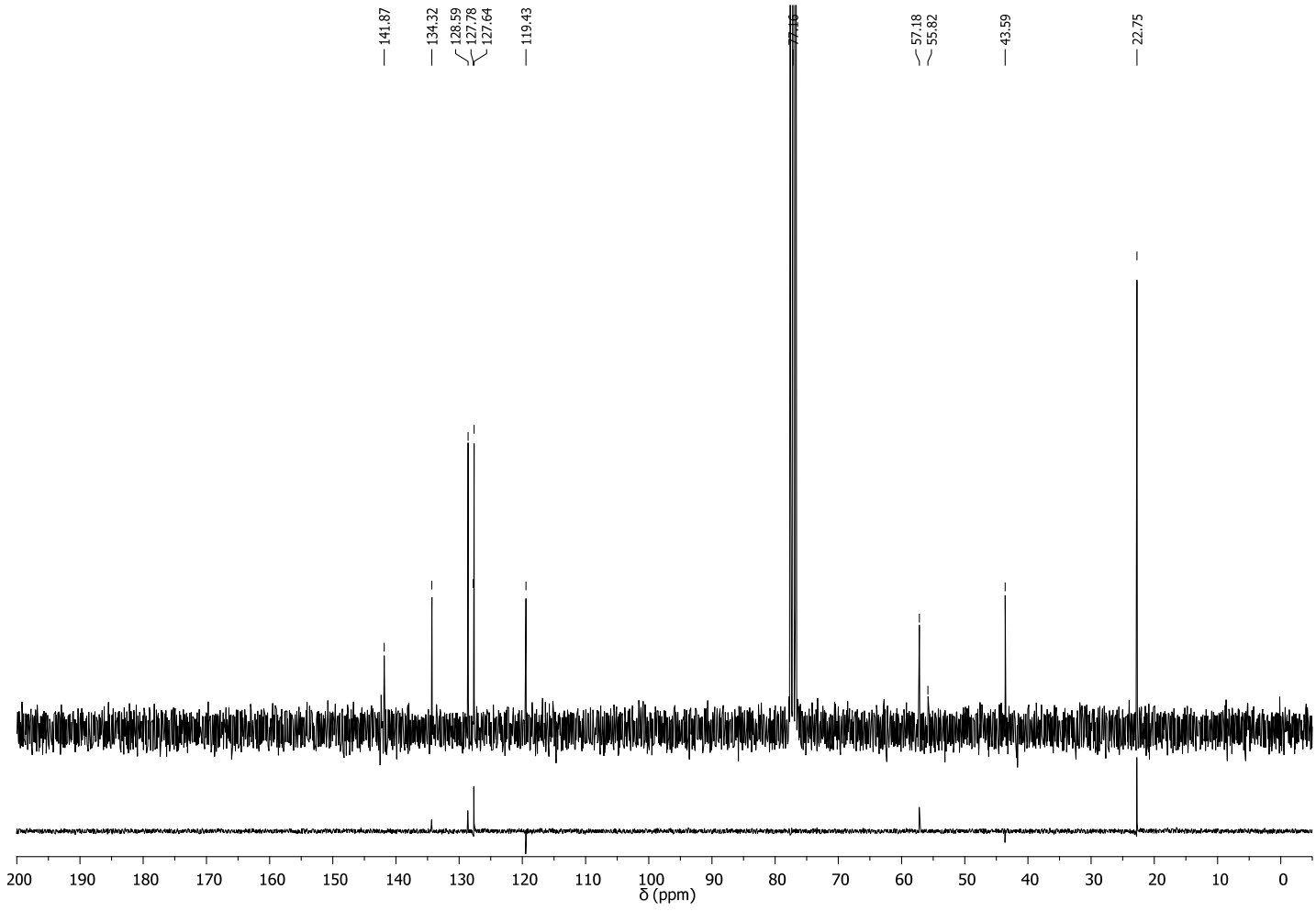

O
S
HN
t-Bu
Me
Me
3c
5.87
5.73
5.18
5.17
5.13
3.17
2.44
2.24
1.96
1.81
1.22
0.92
0.90
1.00
1.99
2.01
2.02
1.01
9.13
2.93
2.89
δ (ppm)

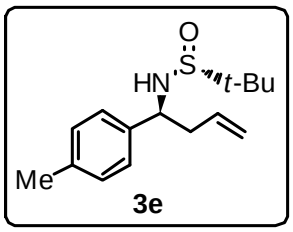

134.87
118.77
77.16
60.03
56.03
37.10
31.11
22.88
18.50
17.97
δ (ppm)


O
HN
S
t-Bu

3d

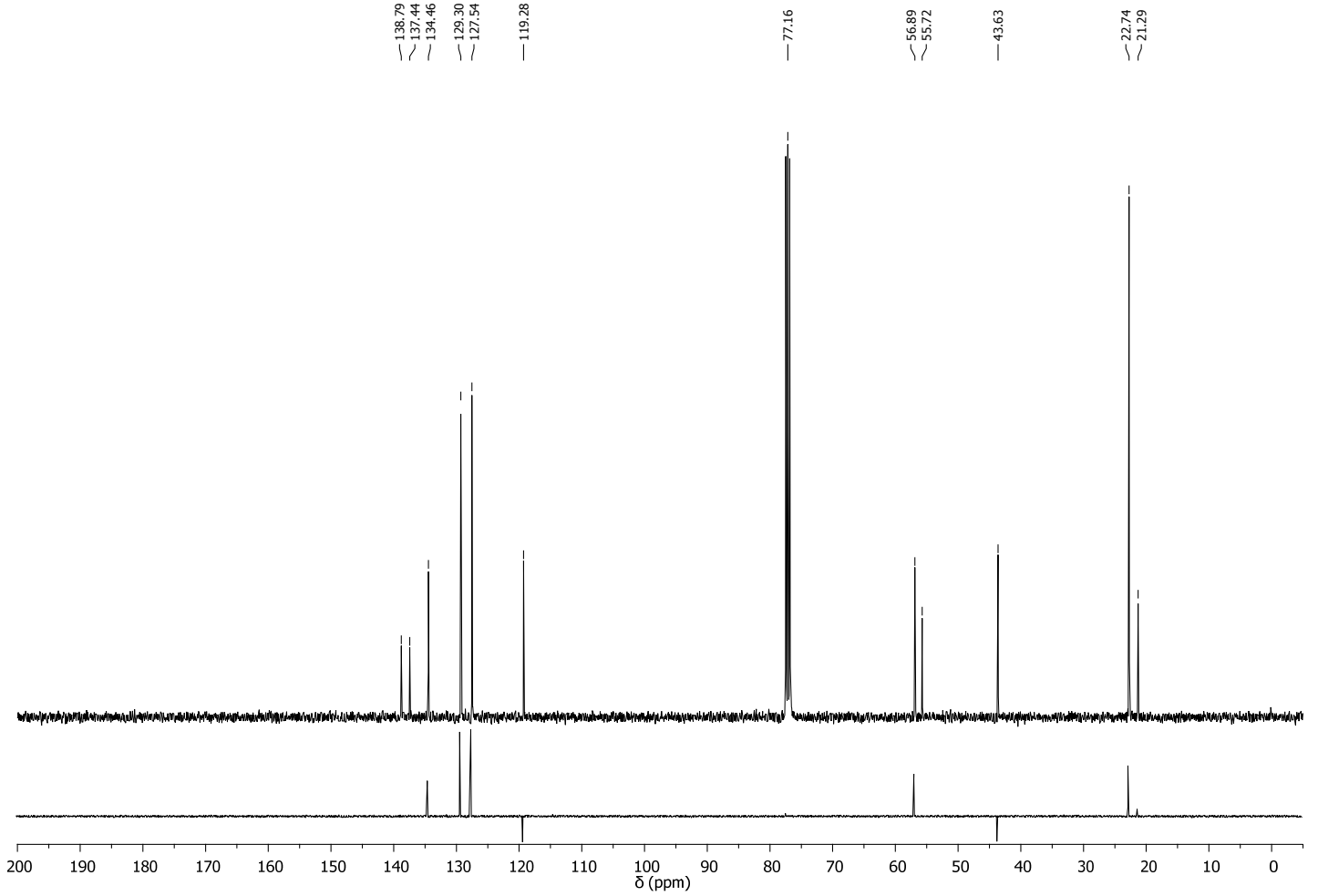
7.36
7.27
5.80
5.67
5.22
5.13
4.47
3.67
2.58
2.50
1.20
5.02
1.00
2.01
1.00
0.92
1.00
1.00
8.91
δ (ppm)

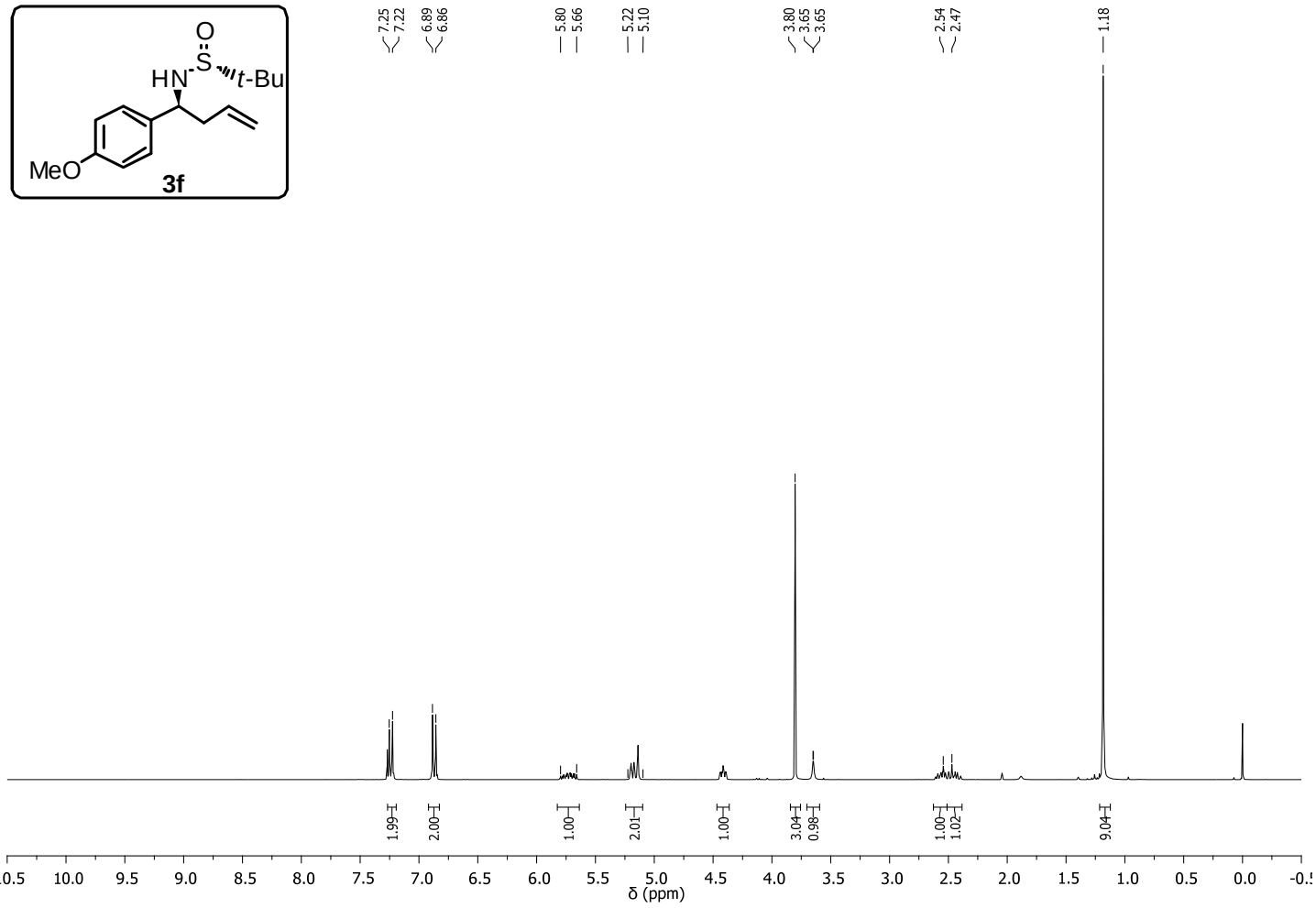

141.87
134.32
128.59
127.78
127.64
119.43
77.16
57.18
55.82
43.59
22.75
δ (ppm)

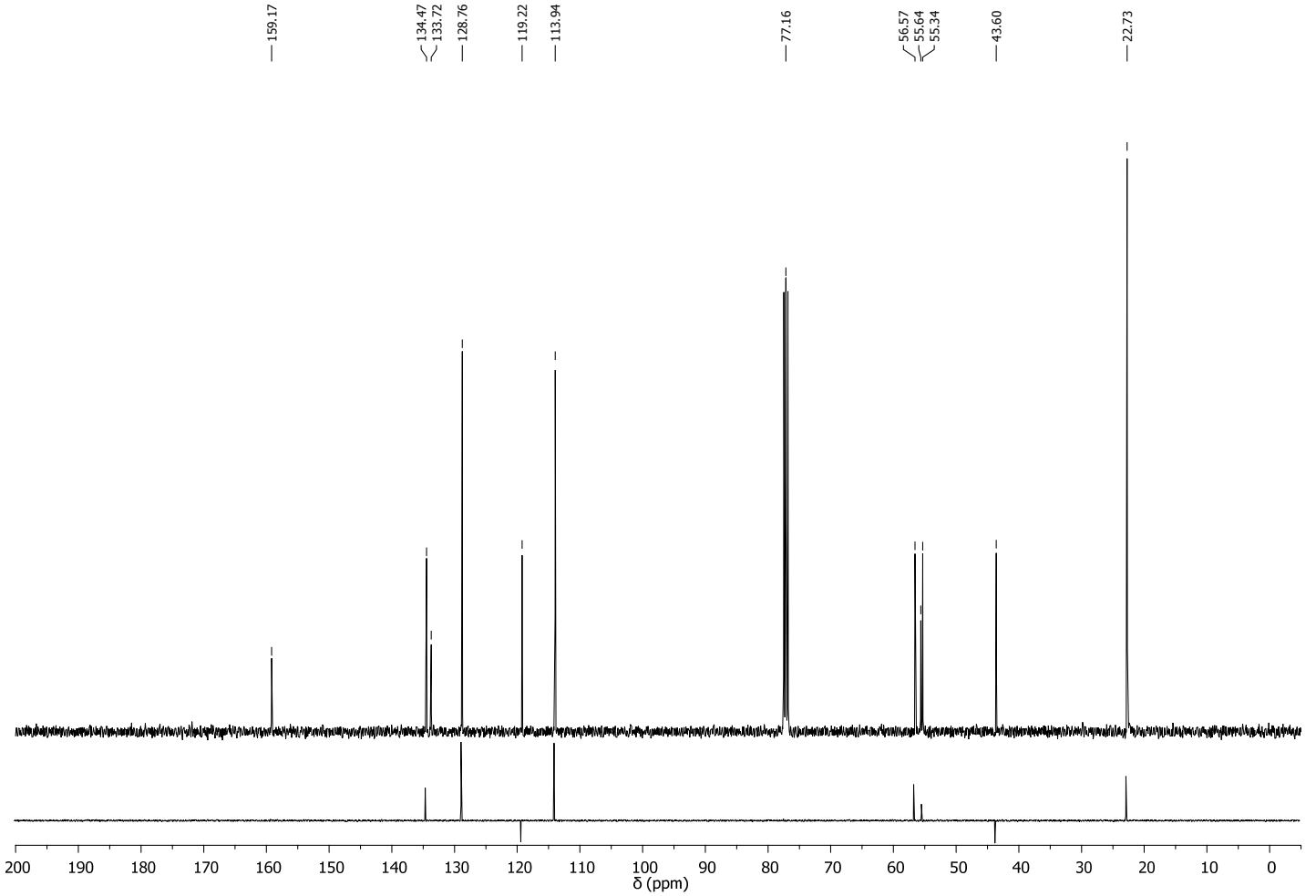

O
S
HN
t-Bu
Me

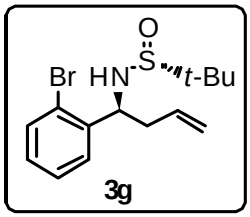
3e

7.22
7.20
7.16
7.13
5.80
5.66
5.21
5.12
4.43
3.66
3.66
2.56
2.47
2.34
1.19
2.02
2.00
0.98
2.03
1.00
0.97
1.00
1.03
3.00
8.98
δ (ppm)

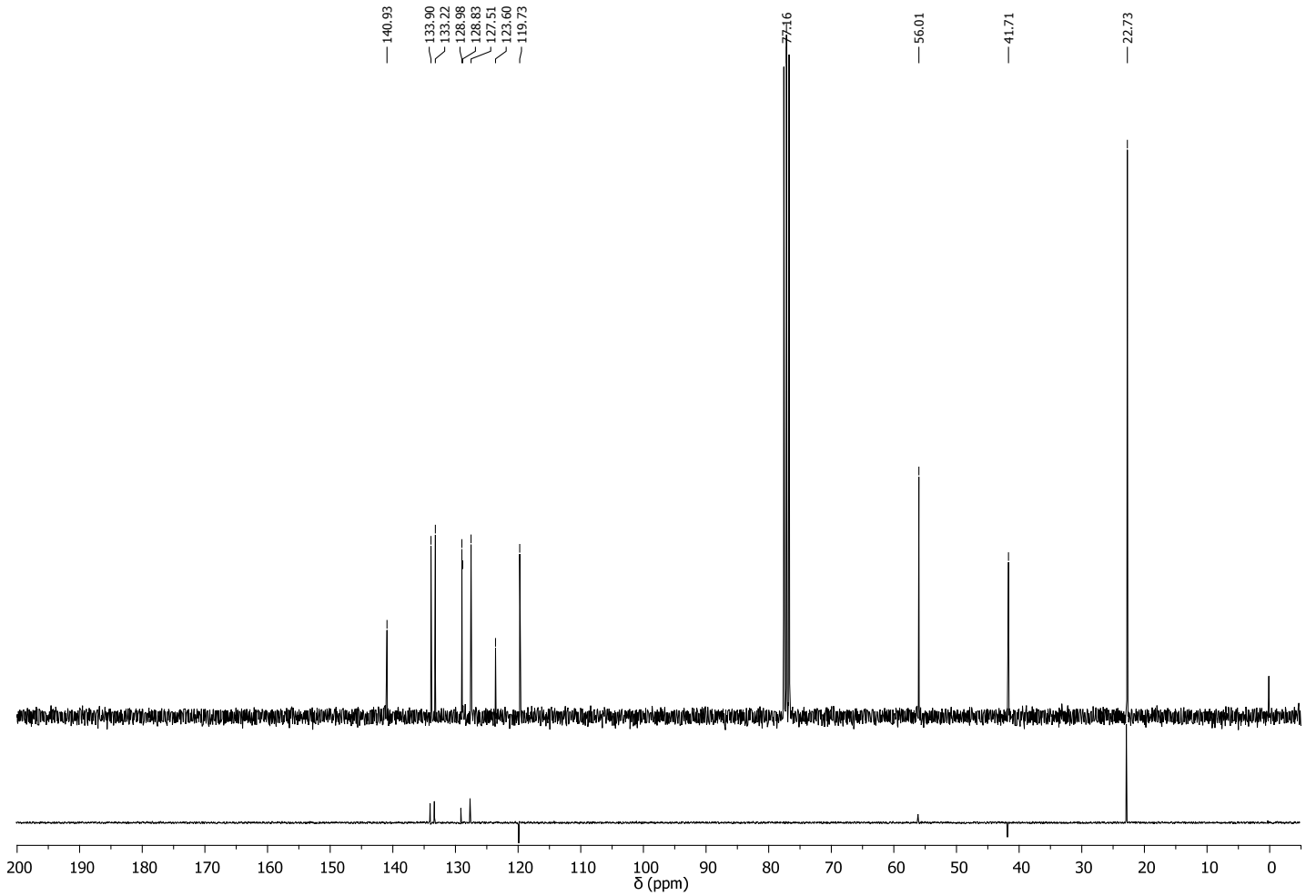

138.79
137.44
134.46
129.30
127.54
119.28
77.16
56.89
55.72
43.63
22.74
21.29
δ (ppm)

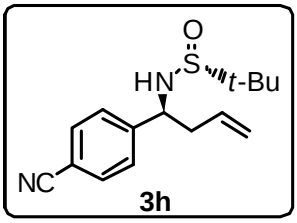

O
S
HN
t-Bu
MeO
3f
7.25
7.22
6.89
6.86
5.80
5.66
5.22
5.10
3.80
3.65
3.65
2.54
2.47
1.18
1.99
2.00
1.00
2.01
1.00
3.04
0.98
1.00
1.02
9.04
δ (ppm)


159.17
134.47
133.72
128.76
119.22
113.94
77.16
56.57
55.64
55.34
43.60
22.73
δ (ppm)


O
S
Br HN
t-Bu
3g

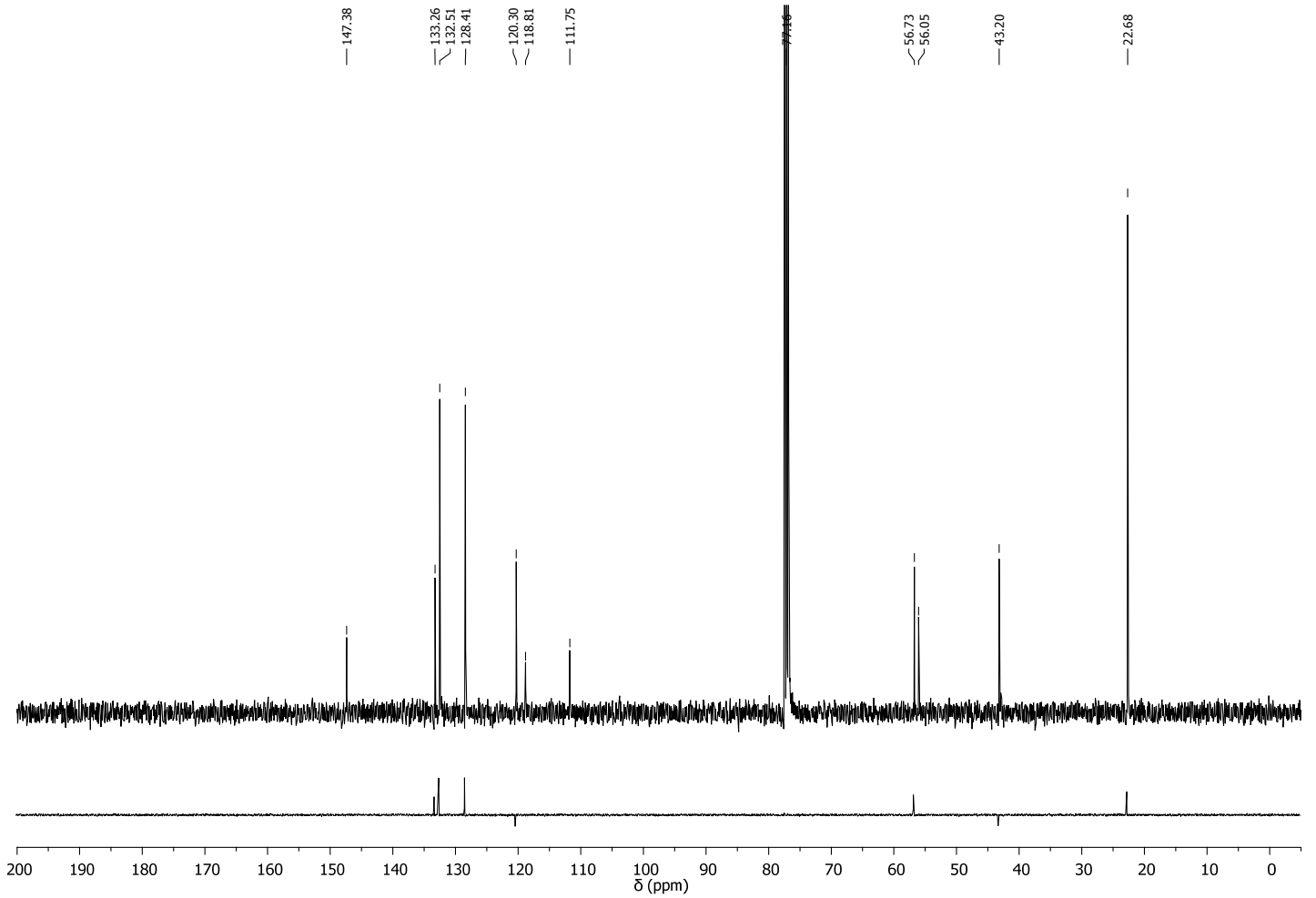
7.57
7.56
7.54
7.54
5.18
5.17
4.98
3.72
3.71
2.68
2.68
2.47
1.21
0.95
0.95
1.33
0.96
1.00
1.94
1.00
0.94
0.99
0.97
9.04
δ (ppm)

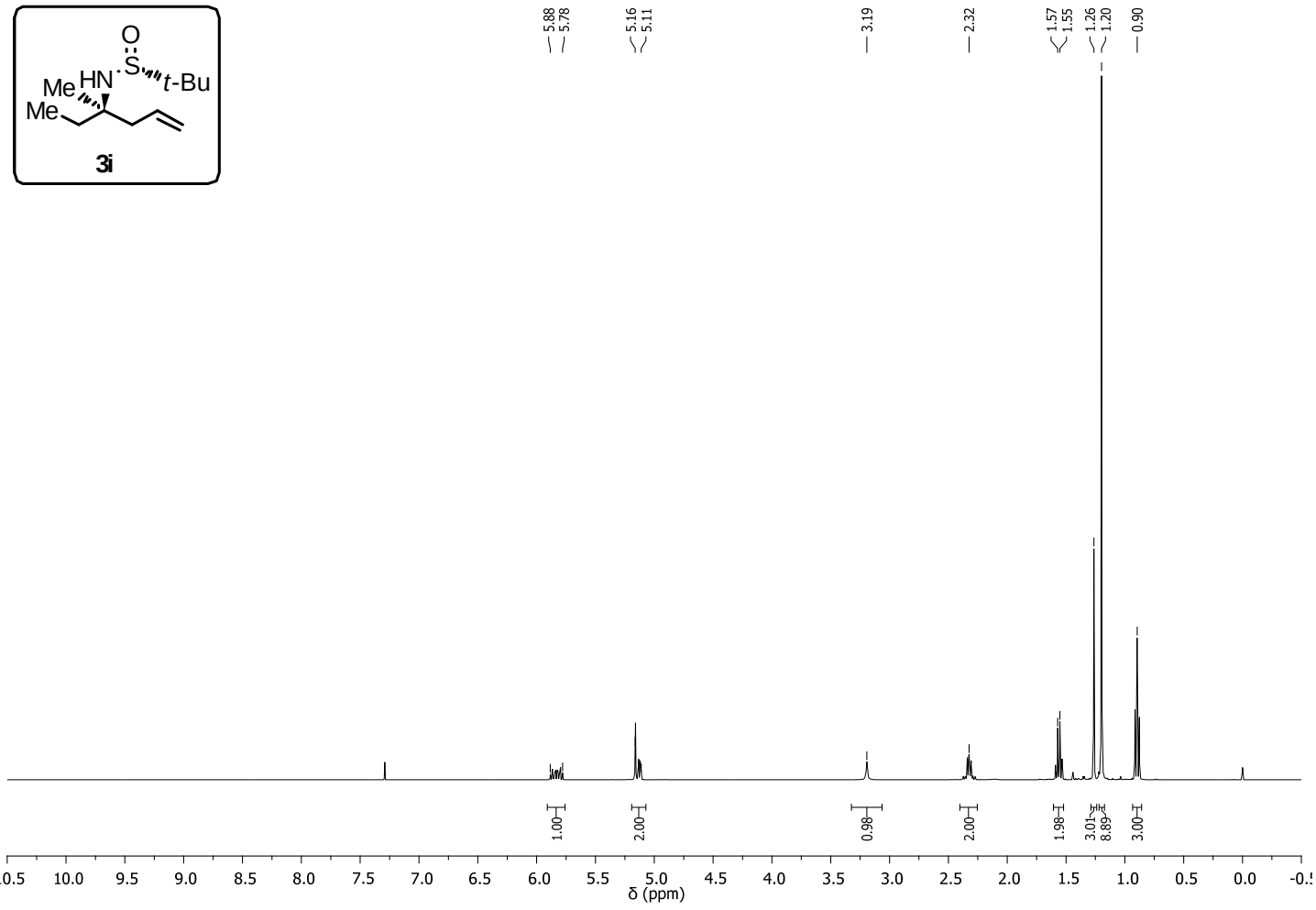

140.93
133.90
133.22
128.98
128.83
127.51
123.60
119.73
77.16
56.01
41.71
22.73
δ (ppm)

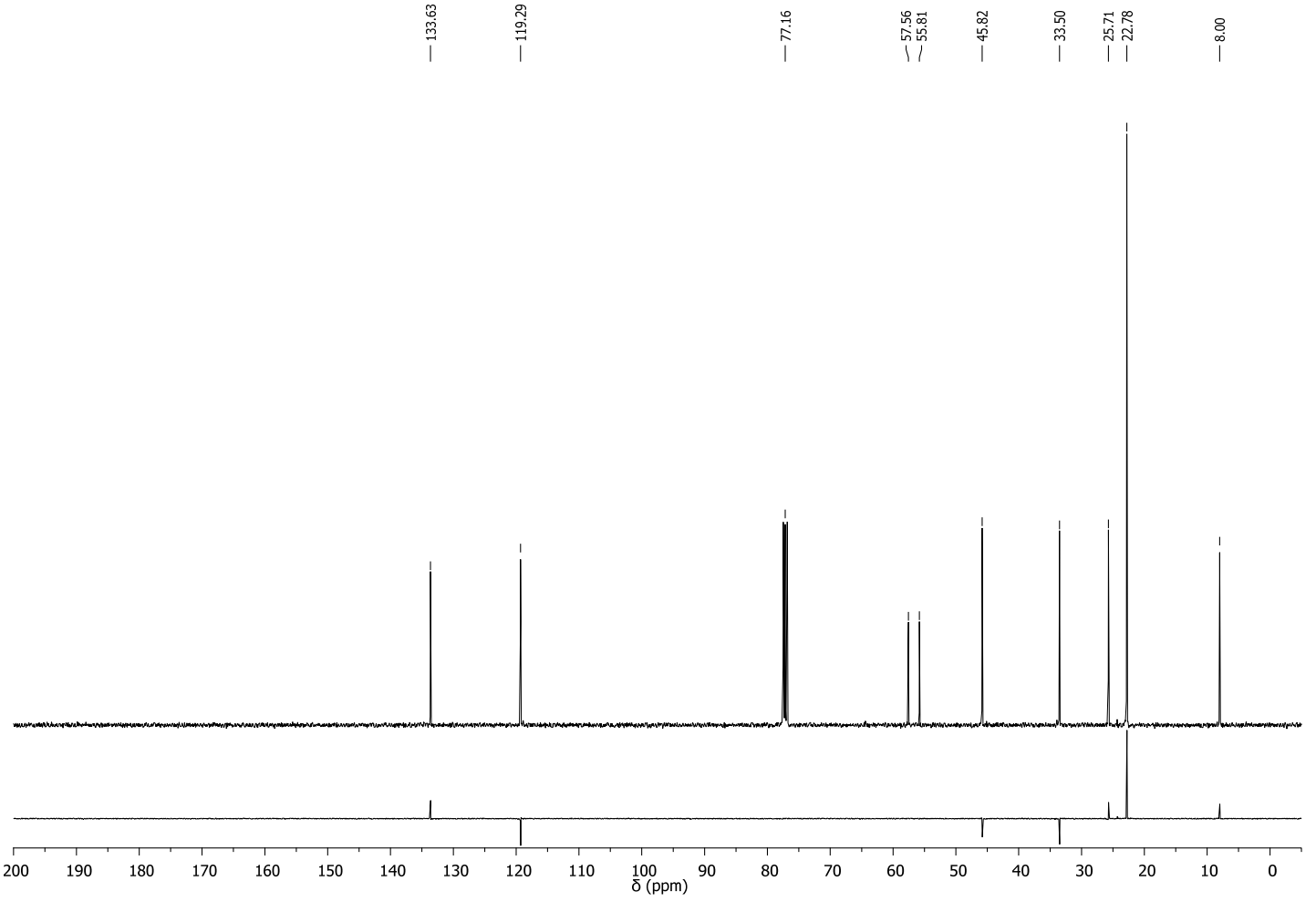

O
S
HN
t-Bu
NC

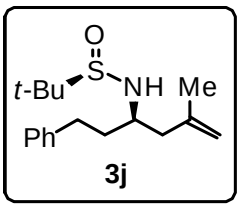
3h

7.65
7.63
7.45
7.43
5.68
5.23
5.15
4.54
3.72
2.57
2.47
1.21
2.00
2.00
0.99
2.02
1.00
0.96
2.02
8.93
δ (ppm)


147.38
133.26
132.51
128.41
120.30
118.81
111.75
77.16
56.73
56.05
43.20
22.68
δ (ppm)

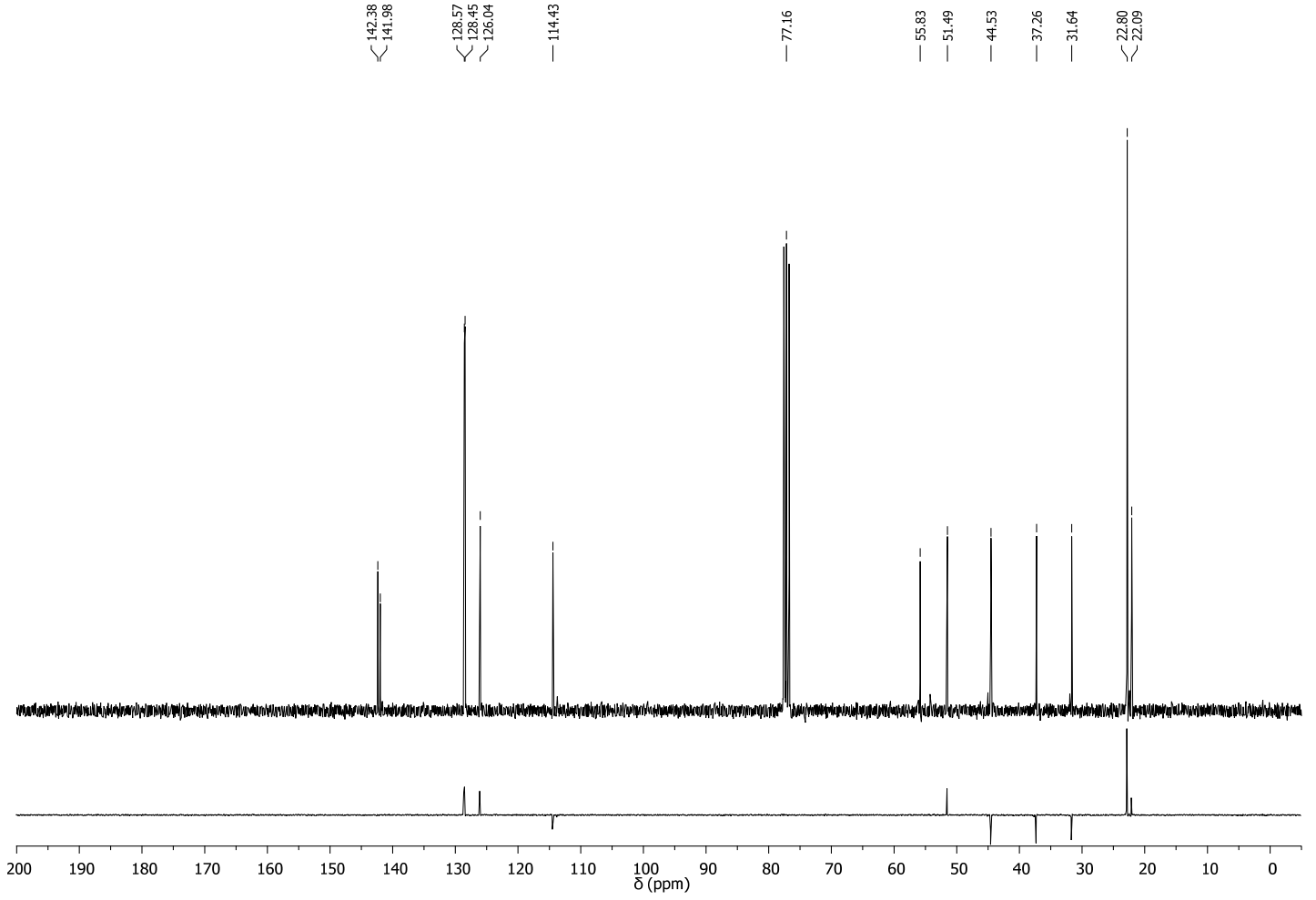

O
S
t-Bu
Me
HN
Me
3i
5.88
5.78
5.16
5.11
3.19
2.32
1.57
1.55
1.26
1.20
0.90
1.00
2.00
0.98
2.00
1.98
3.01
8.89
3.00
δ (ppm)

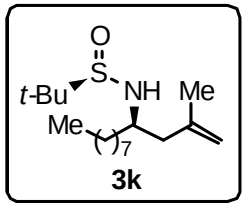

133.63
119.29
77.16
57.56
55.81
45.82
33.50
25.71
22.78
8.00
δ (ppm)


O
S
t-Bu
NH
Me
Ph

3j

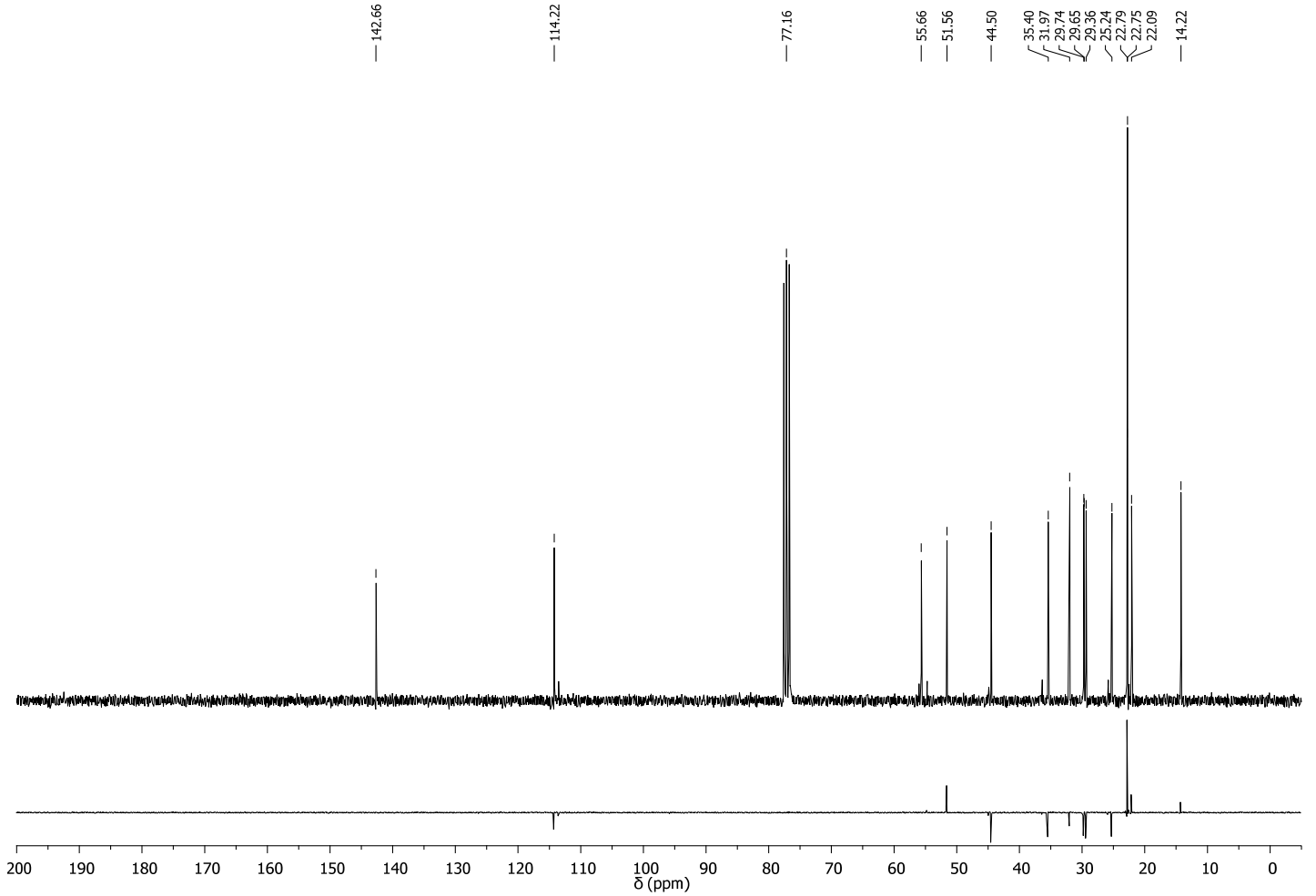
7.23
7.21
7.18
7.13
7.11
7.08
4.81
4.72
3.43
3.33
3.24
3.23
2.72
2.53
2.33
2.18
1.81
1.65
1.15
2.48
3.17
1.00
1.10
1.09
0.96
0.11
2.22
2.29
2.09
3.02
0.35
8.97
δ (ppm)

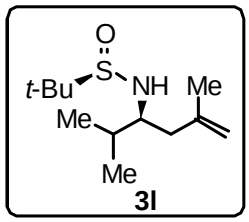

142.38
141.98
128.57
128.45
126.04
114.43
77.16
55.83
51.49
44.53
37.26
31.64
22.80
22.09
δ (ppm)


O
S
NH
Me
t-Bu
Me
7

3k

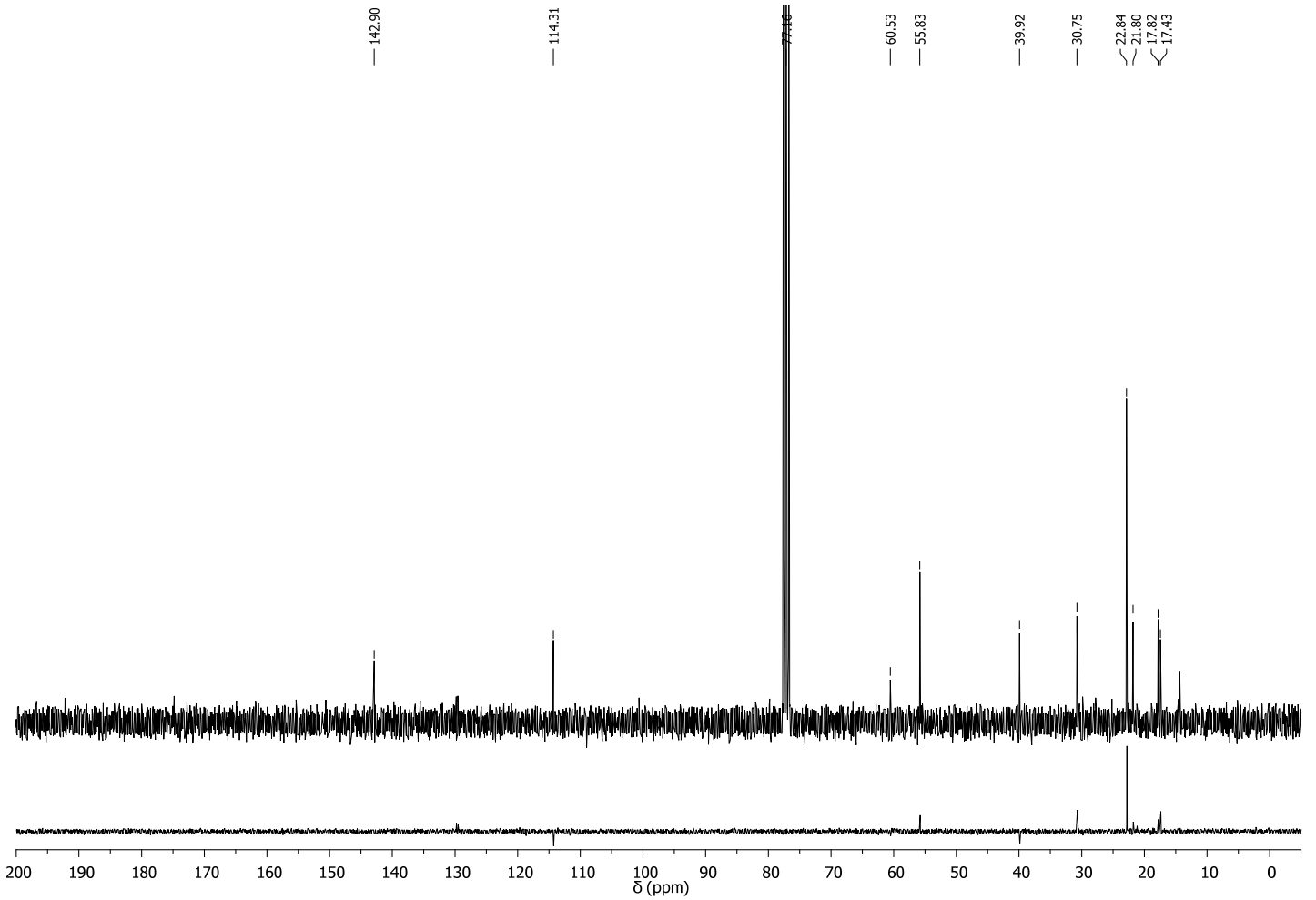
4.87
4.79
3.43
3.38
3.33
3.25
3.24
2.34
2.15
1.74
1.56
1.27
1.20
0.88
1.00
1.04
1.11
1.00
0.11
2.26
2.93
15.63
9.51
3.41
δ (ppm)

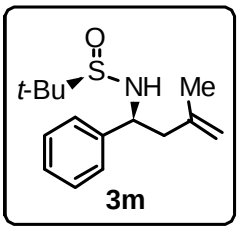

142.66
114.22
77.16
55.66
51.56
44.50
35.40
31.97
29.74
29.65
29.36
25.24
22.79
22.75
22.09
14.22
δ (ppm)


O
S
NH
Me
t-Bu
Me
Me

3l

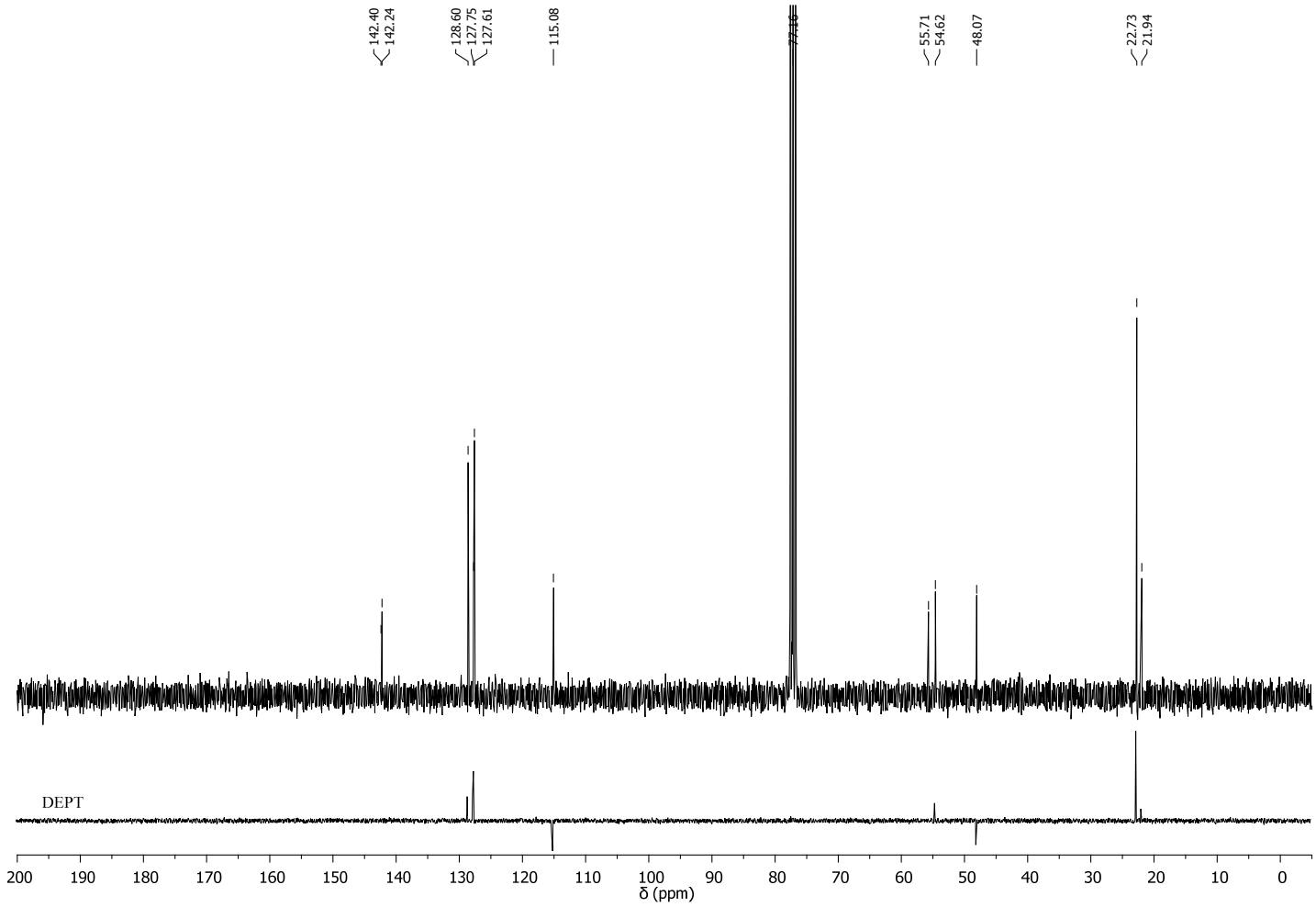
4.88
4.80
3.34
3.27
3.19
3.18
2.28
2.08
2.03
1.93
1.76
1.21
0.92
0.90
0.90
0.88
1.00
1.05
0.05
1.07
0.98
2.17
1.10
0.50
3.12
8.85
2.98
3.13
δ (ppm)

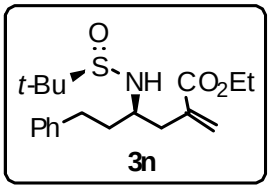

142.90
114.31
77.16
60.53
55.83
39.92
30.75
22.84
21.80
17.82
17.43
δ (ppm)


O
S
t-Bu
NH
Me

3m

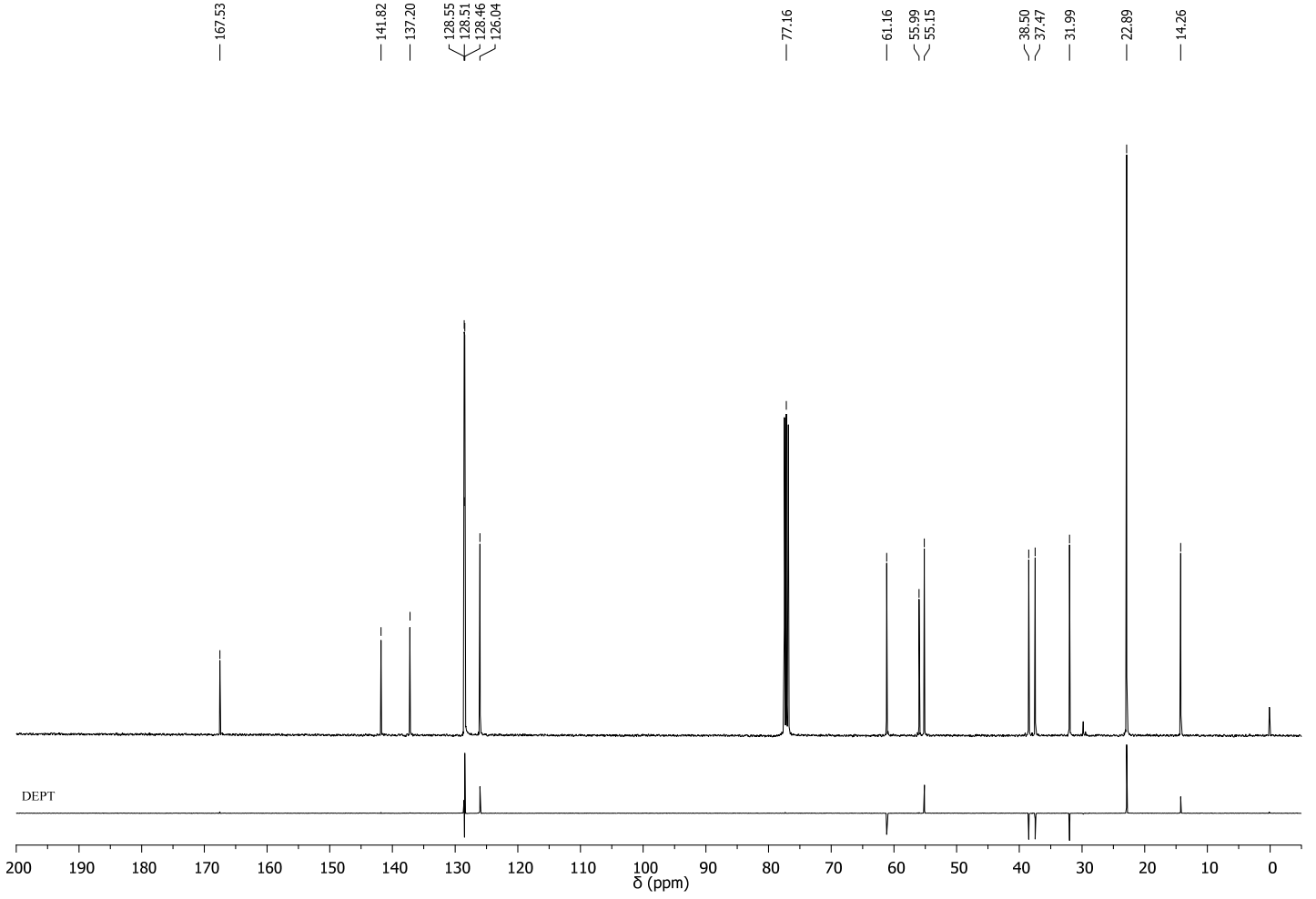
7.36
7.35
7.33
7.27
4.94
4.87
4.51
3.71
2.49
2.36
1.79
1.19
4.89
0.99
1.00
0.98
0.93
2.01
3.00
9.06
δ (ppm)

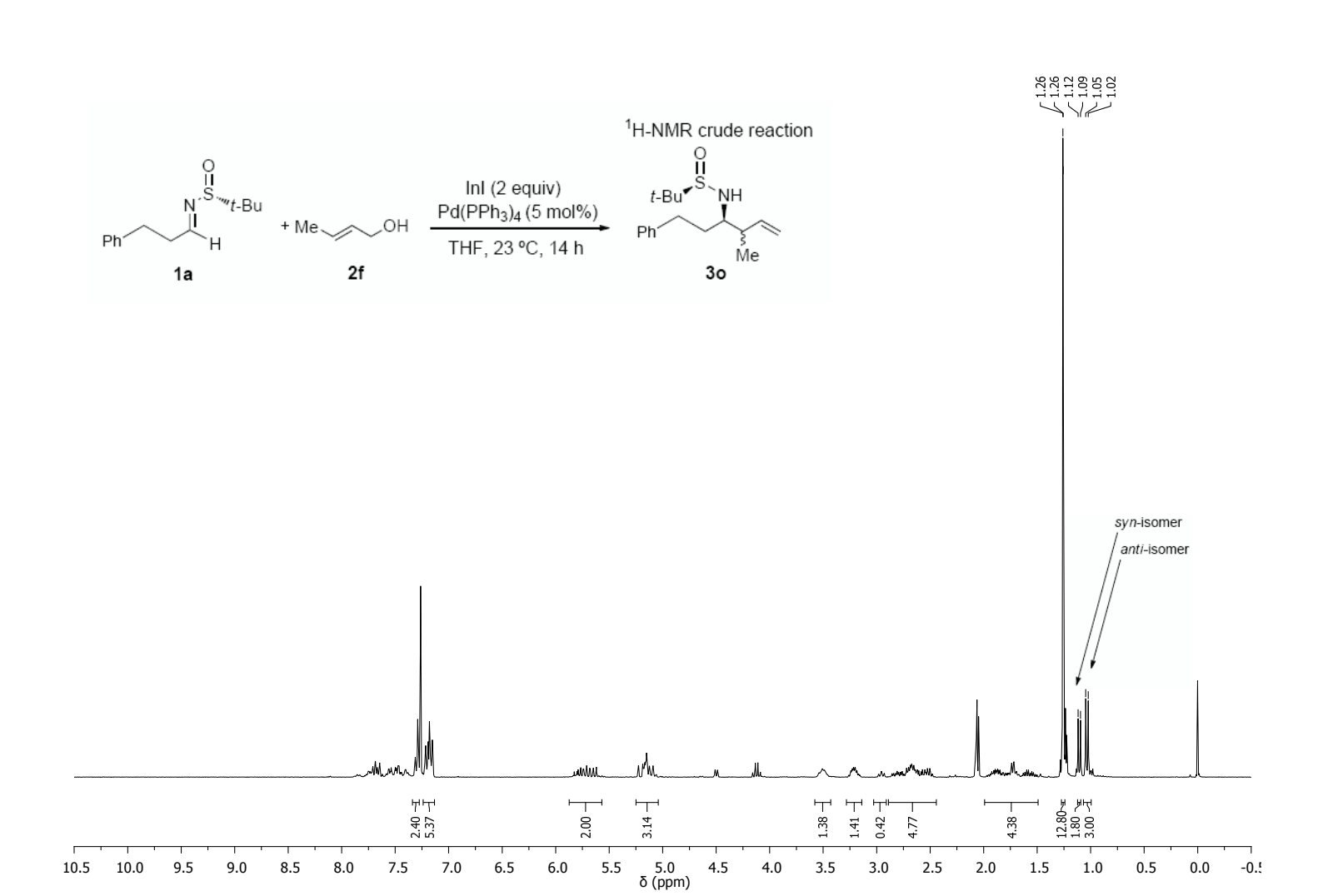

142.40
142.24
128.60
127.75
127.61
115.08
77.16
55.71
54.62
48.07
22.73
21.94
DEPT
δ (ppm)

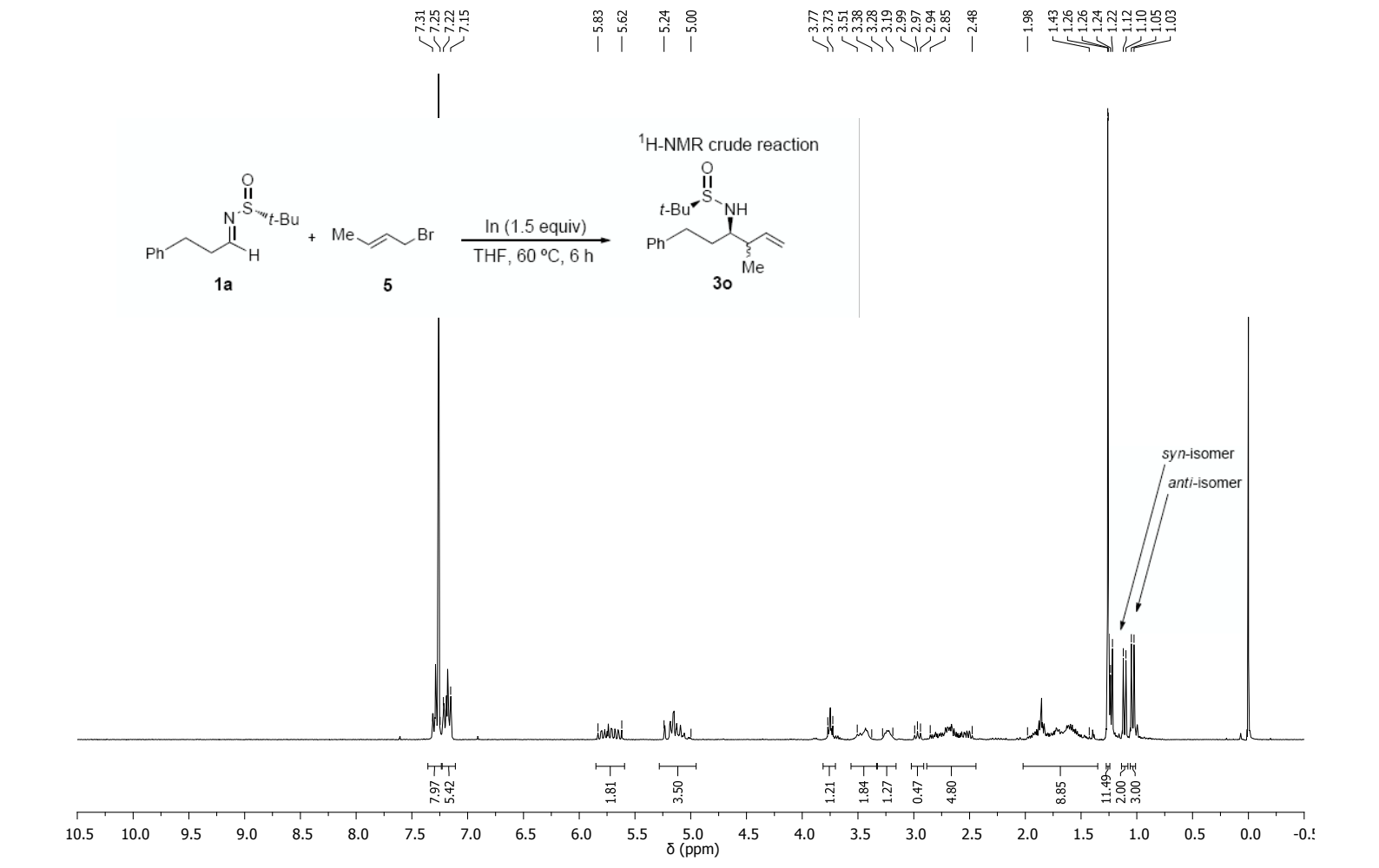

O
S
t-Bu
NH
CO2Et
Ph

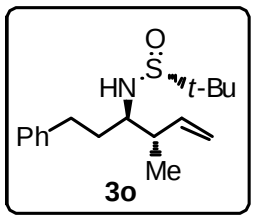
3n

7.30
7.28
7.26
7.20
7.18
7.15
6.31
6.30
5.69
5.68
4.23
4.21
4.19
4.17
3.67
3.66
3.54
3.52
3.50
3.49
3.47
2.80
2.70
2.67
2.61
1.88
1.71
1.29
1.23
2.18
2.97
0.98
0.98
2.00
0.97
1.00
4.04
1.95
3.17
8.92
δ (ppm)

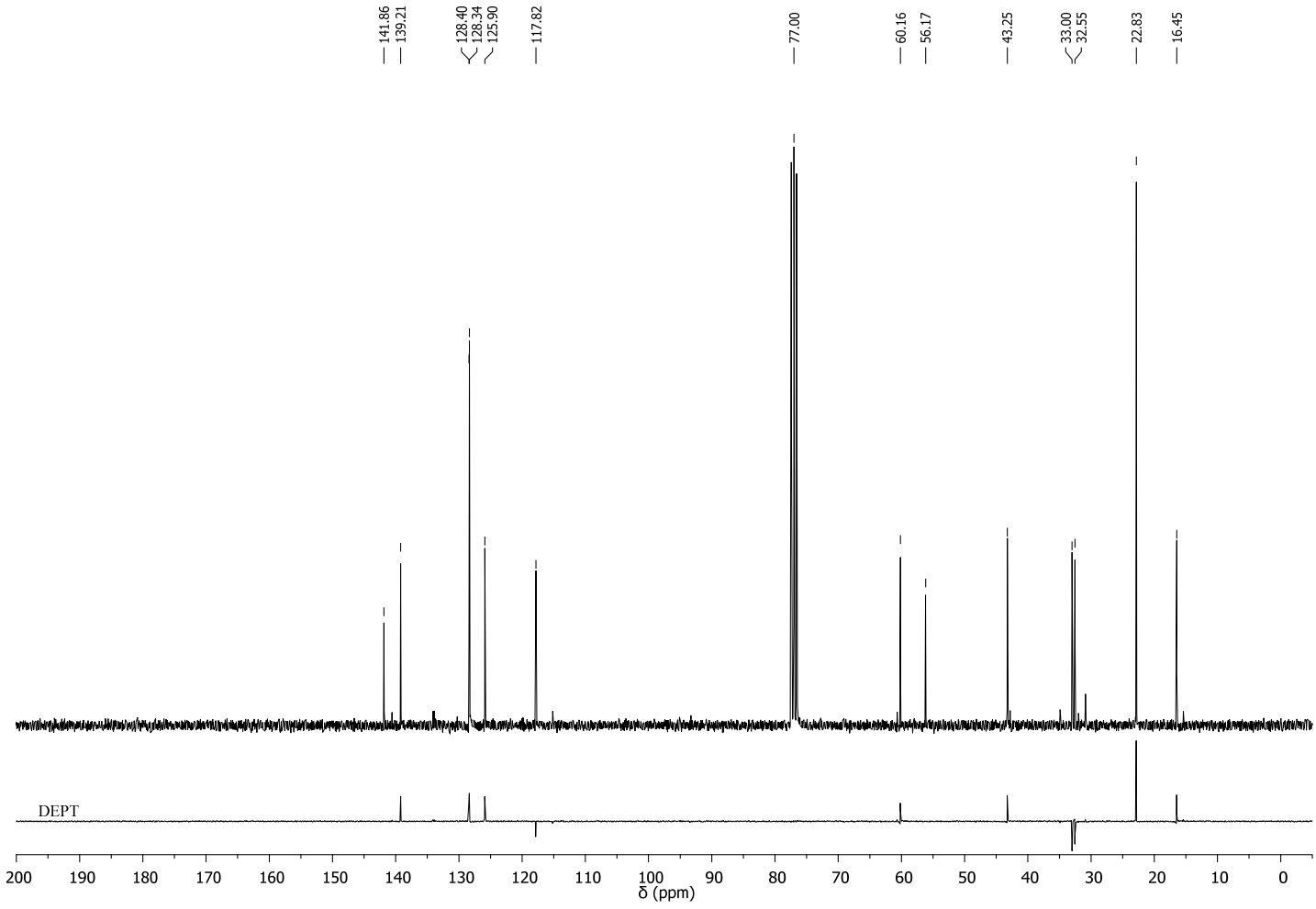

167.53
141.82
137.20
128.55
128.51
128.46
126.04
77.16
61.16
55.99
55.15
38.50
37.47
31.99
22.89
14.26
DEPT
δ (ppm)

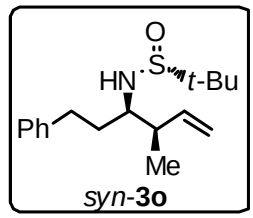

1H-NMR crude reaction
InI (2 equiv)
Pd(PPh3)4 (5 mol%)
THF, 23 ºC, 14 h
1a
2f
3o
syn-isomer
anti-isomer
δ (ppm)


1H-NMR crude reaction
In (1.5 equiv)
THF, 60 ºC, 6 h
1a
5
3o
syn-isomer
anti-isomer
δ (ppm)

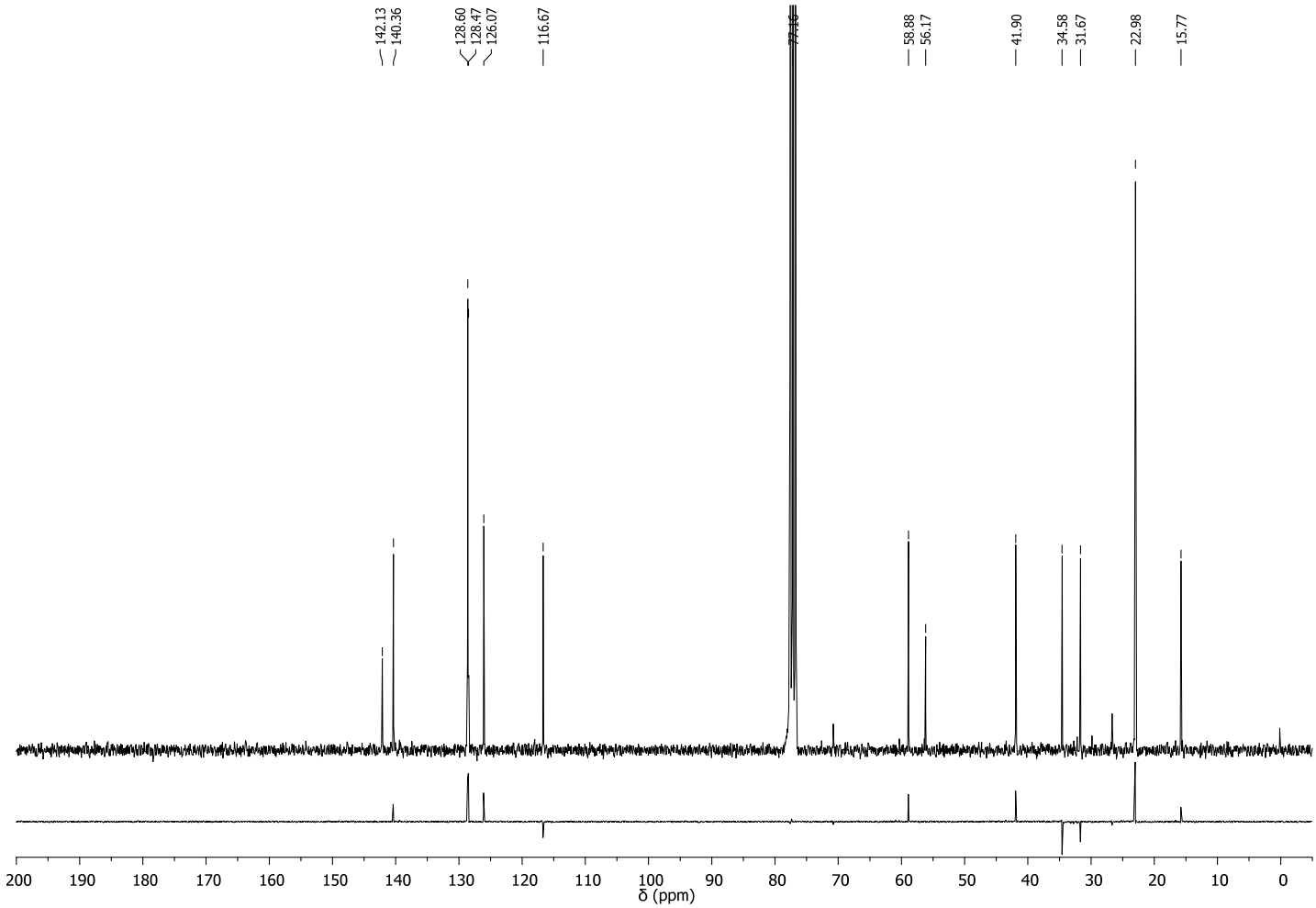

O
S
HN
t-Bu
Ph
Me
3o

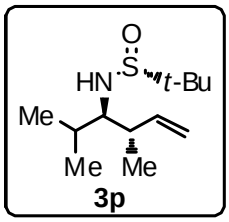
1.25
1.04
1.02
5.74
5.62
5.25
5.13
4.76
3.45
3.42
3.25
3.14
2.86
2.74
2.68
2.61
2.51
1.93
1.81
1.63
1.48
1.00
1.92
0.92
1.02
1.04
1.05
0.97
1.08
0.93
5.42
1.00
1.92
0.92
1.02
1.04
1.05
0.97
1.08
0.93
8.61
2.99
δ (ppm)


141.86
139.21
128.40
128.34
125.90
117.82
77.00
60.16
56.17
43.25
33.00
32.55
22.83
16.45
DEPT
δ (ppm)


O
S
HN
t-Bu
Ph
Me
syn-3o

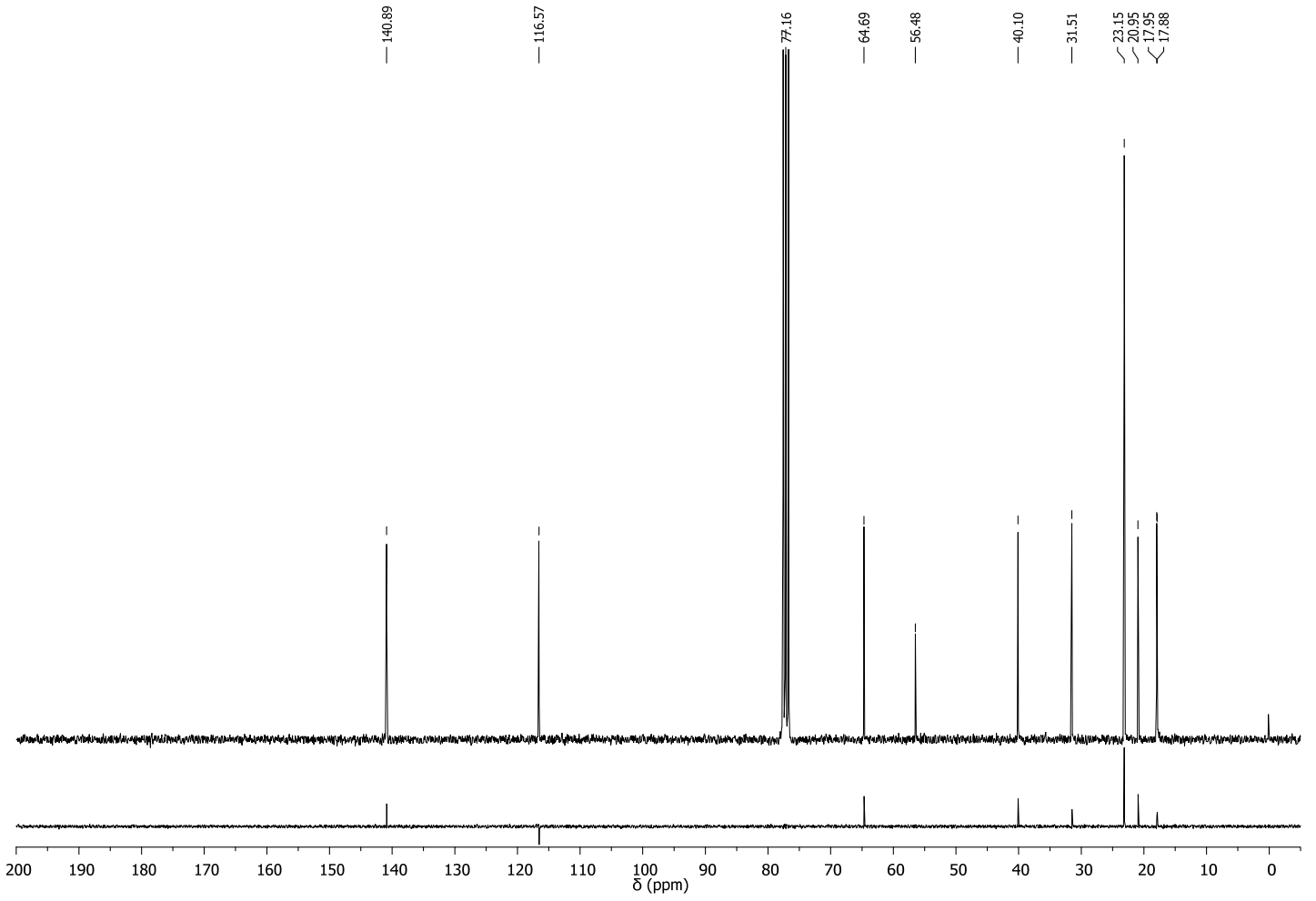
7.28
7.18
7.10
1.25
1.12
1.10
5.83
5.71
5.18
5.17
5.09
5.07
3.40
3.38
3.25
3.22
3.17
2.76
2.68
2.57
2.54
2.52
2.45
1.97
1.92
1.86
1.82
1.75
1.60
6.92
1.17
2.41
1.56
1.08
2.17
1.17
1.10
3.97
9.56
3.00
δ (ppm)

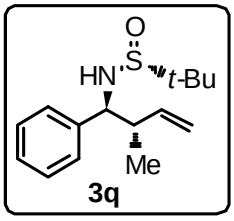

142.13
140.36
128.60
128.47
126.07
116.67
77.16
58.88
56.17
41.90
34.58
31.67
22.98
15.77
δ (ppm)


O
S
HN
t-Bu
Me
Me
Me

3p

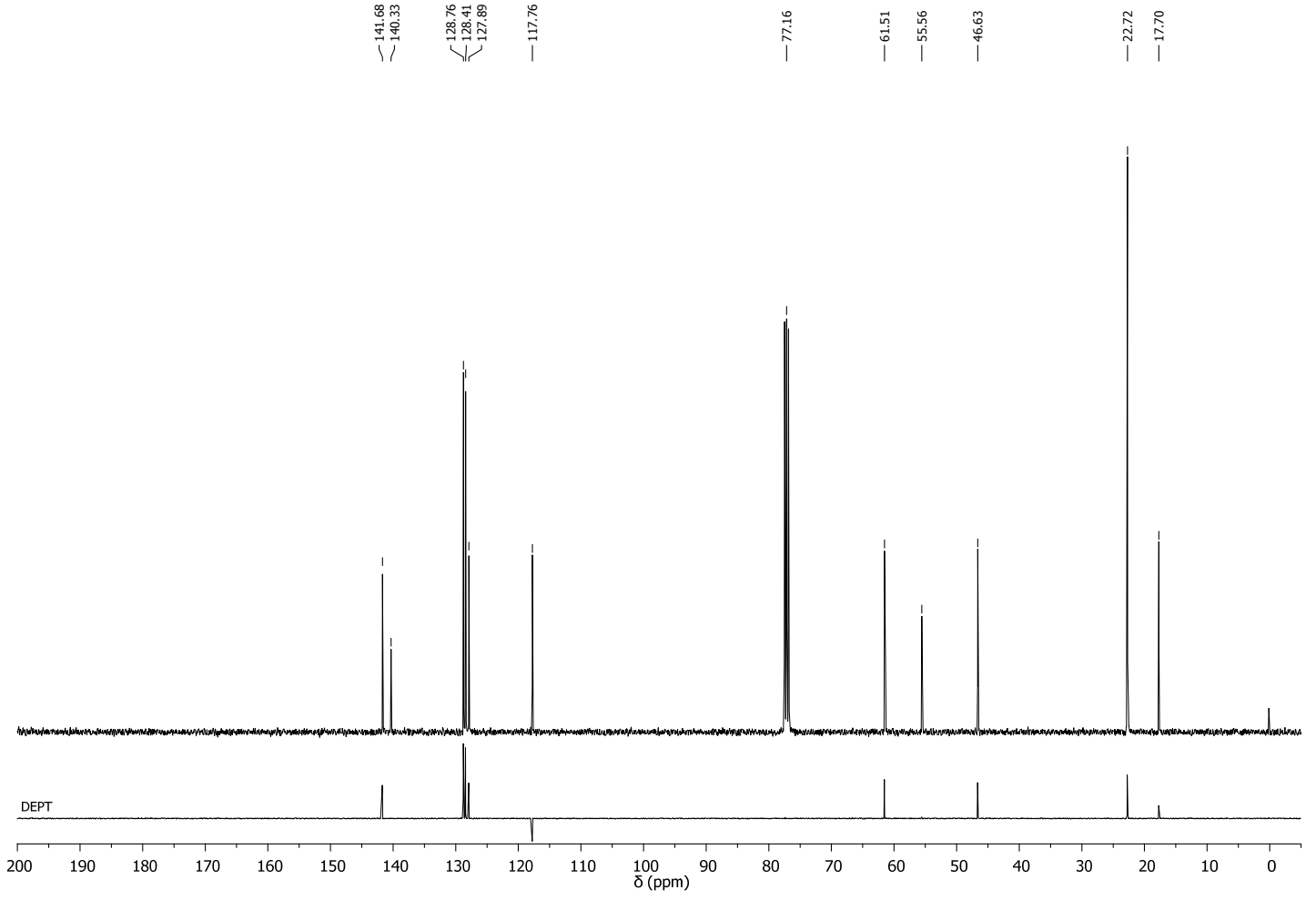
1.23
1.14
1.12
0.98
0.96
0.90
0.88
5.92
5.89
5.88
5.86
5.86
5.84
5.83
5.80
5.18
5.13
5.12
5.06
3.28
3.26
2.91
2.89
2.87
2.85
2.51
2.49
2.47
2.44
1.88
1.86
1.83
1.81
1.79
1.77
1.00
2.03
0.92
1.00
1.02
1.02
8.95
3.02
3.03
3.03
δ (ppm)

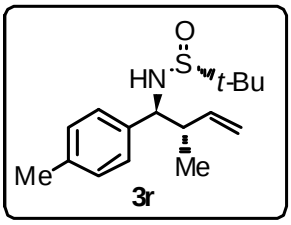

140.89
116.57
77.16
64.69
56.48
40.10
31.51
23.15
20.95
17.95
17.88
δ (ppm)


O
S
HN
t-Bu
Me

3q

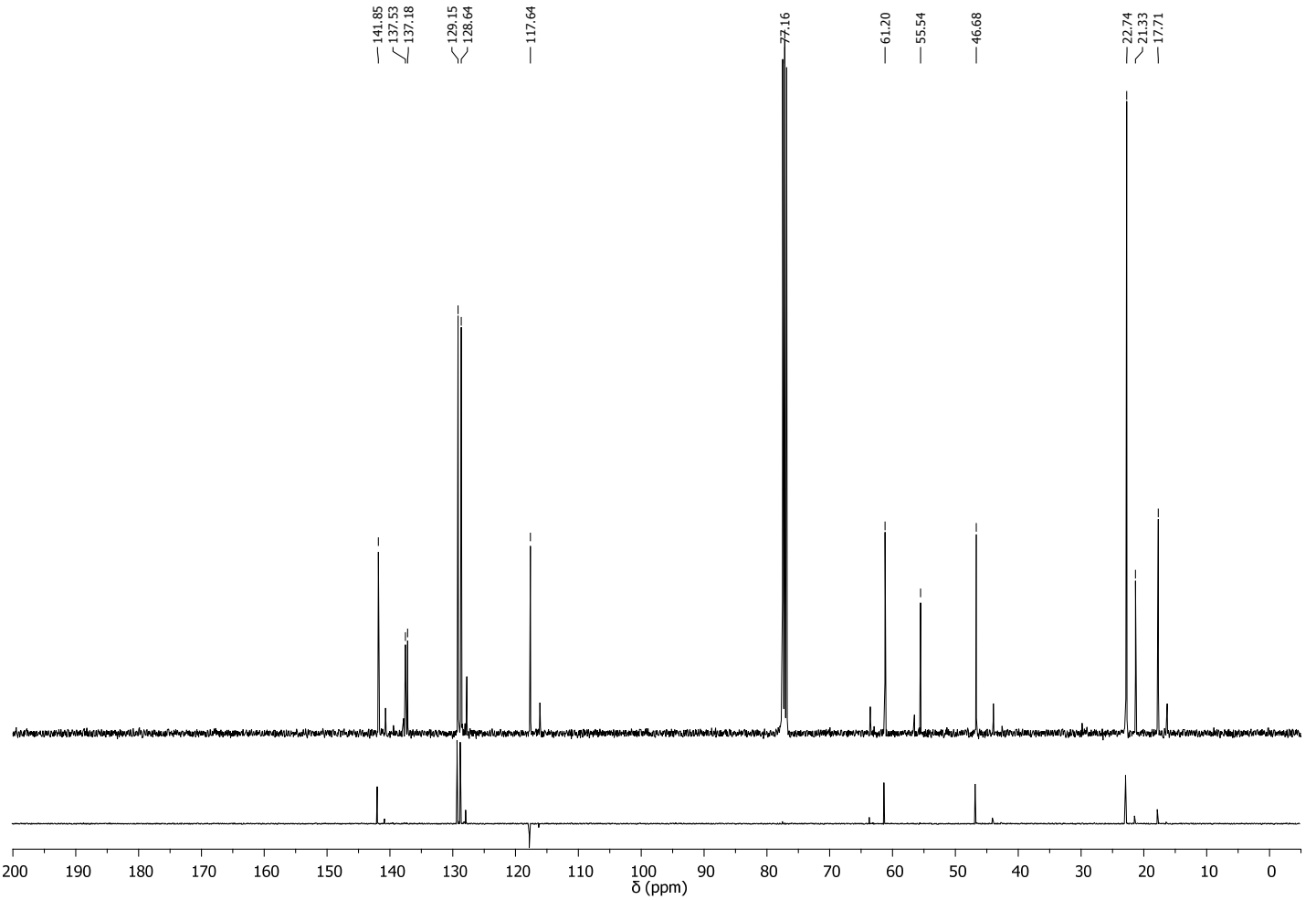
1.16
0.83
0.81
7.36
7.26
5.80
5.77
5.77
5.75
5.74
5.72
5.71
5.68
5.28
5.21
4.05
4.02
3.93
2.44
2.42
2.41
2.39
2.38
2.36
5.39
1.02
2.02
0.99
0.95
1.00
9.05
3.00
δ (ppm)

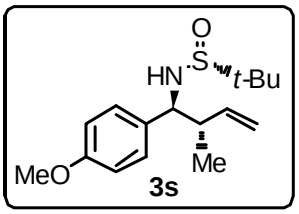

141.68
140.33
128.76
128.41
127.89
117.76
77.16
61.51
55.56
46.63
22.72
17.70
DEPT
δ (ppm)


O
S
HN
t-Bu
Me
Me

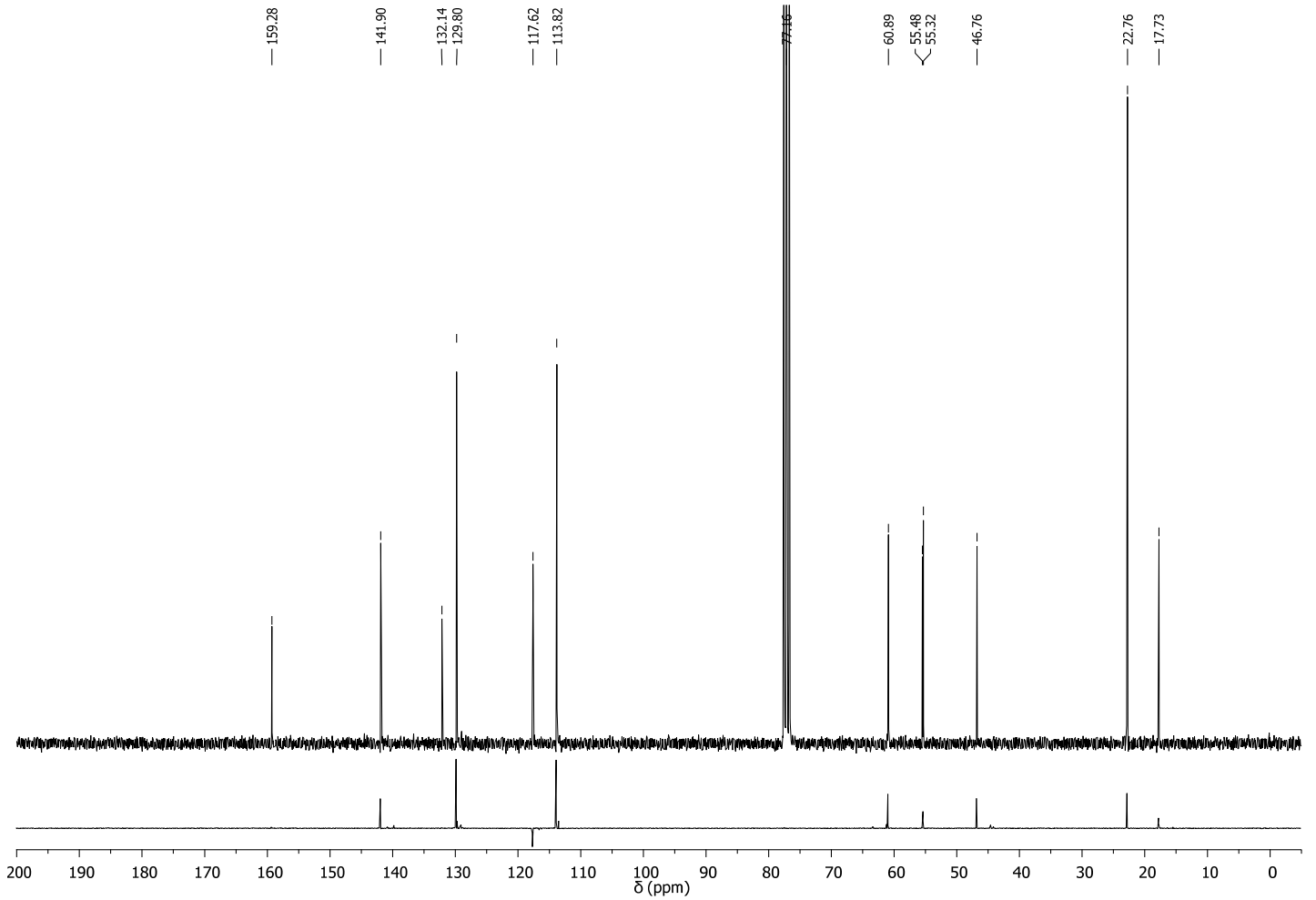
3r

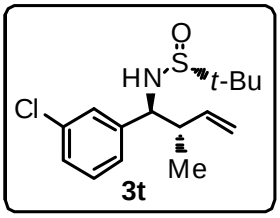
7.19
7.17
7.15
7.13
5.78
5.66
5.26
5.20
4.01
3.99
3.91
2.35
1.15
0.82
0.80
4.86
1.20
2.00
0.36
0.15
1.01
0.97
0.15
4.56
3.11
1.56
8.87
0.51
3.00
δ (ppm)


141.85
137.53
137.18
129.15
128.64
117.64
77.16
61.20
55.54
46.68
22.74
21.33
17.71
δ (ppm)

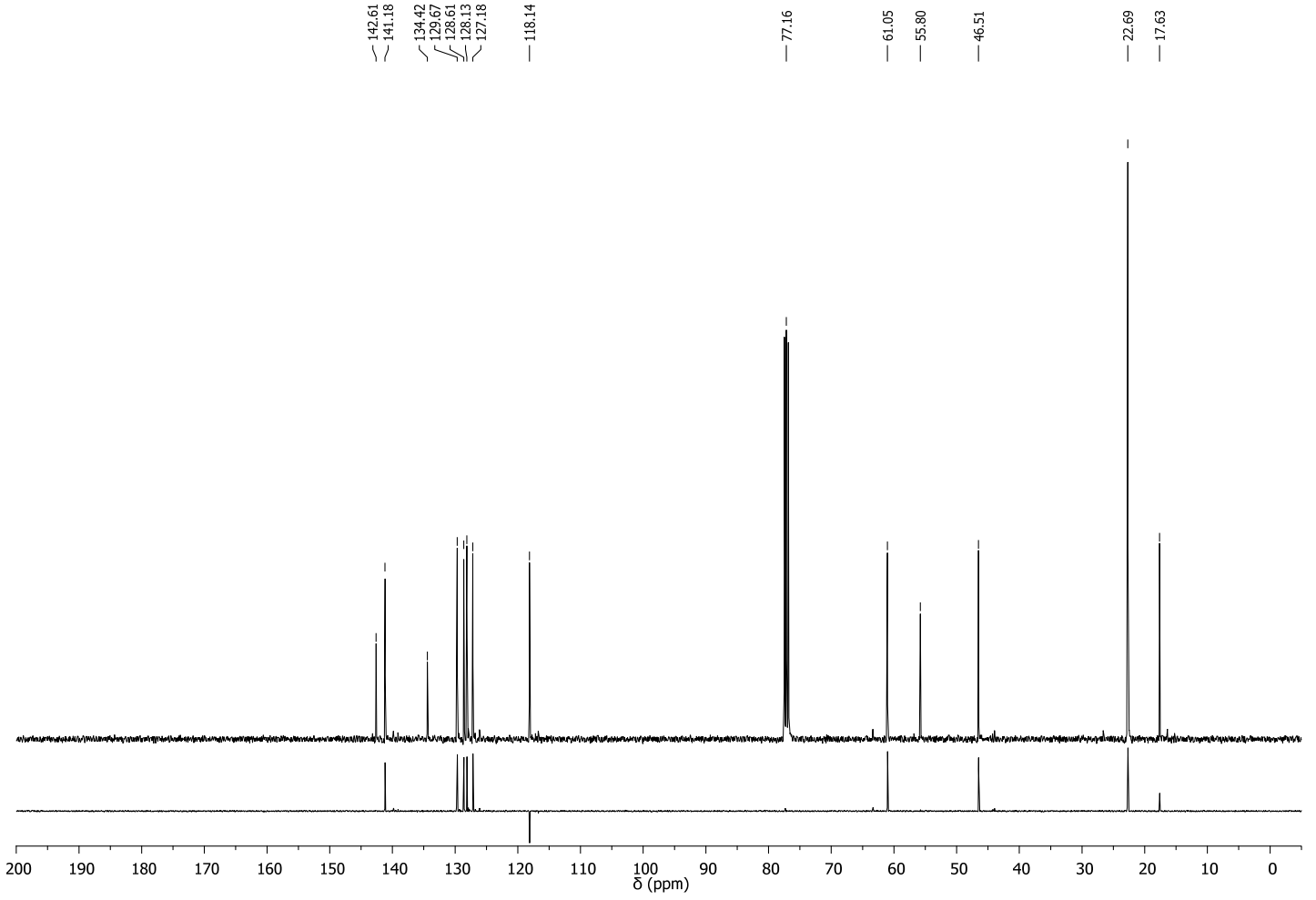

O
S
HN
t-Bu
Me
MeO
3s

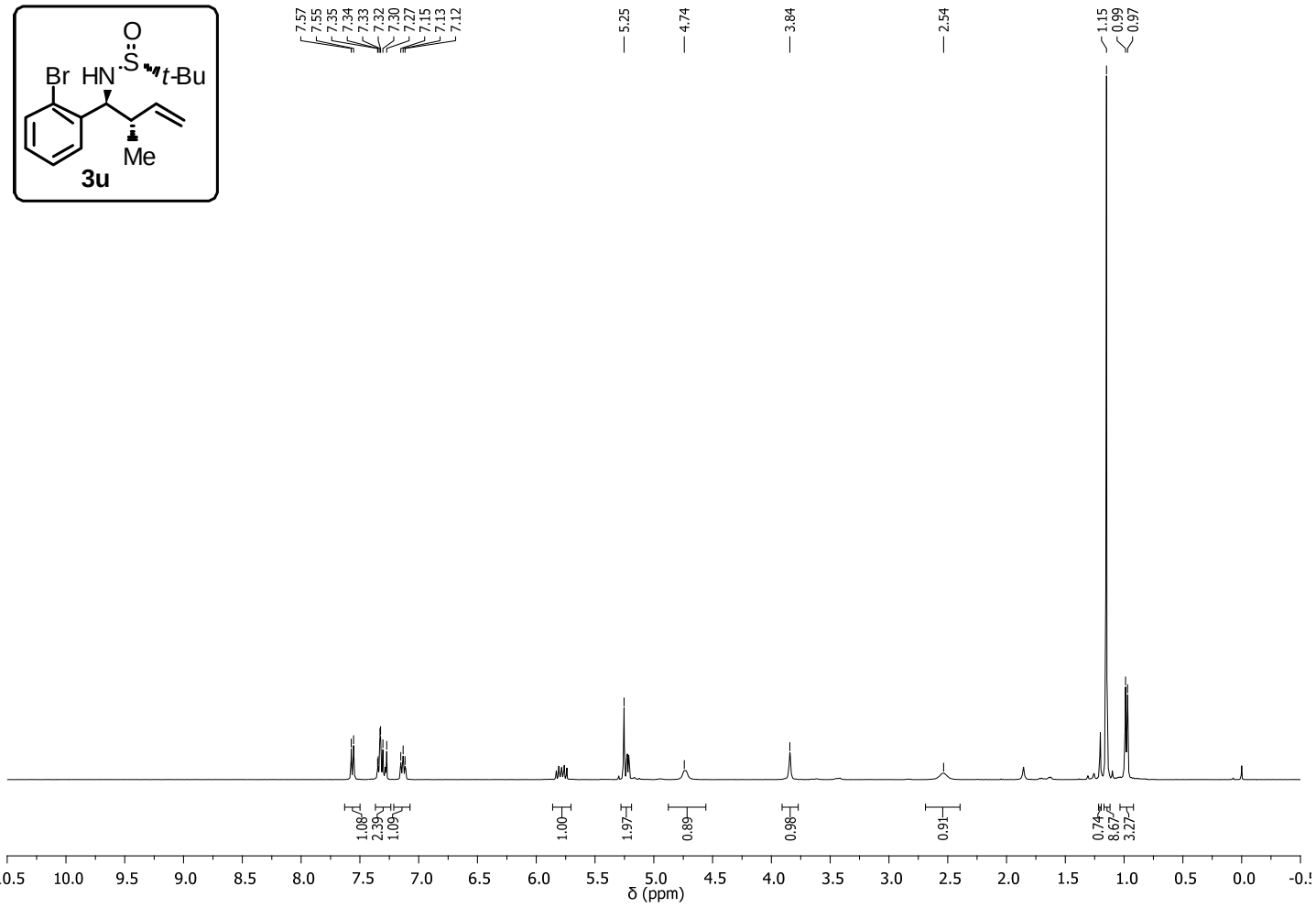
7.23
7.20
6.89
6.86
5.79
5.67
5.66
5.26
5.23
5.20
4.00
3.97
3.92
3.81
2.43
2.30
1.15
0.81
0.79
2.03
2.05
1.02
1.98
0.98
0.92
3.11
1.00
0.33
8.90
3.00
δ (ppm)

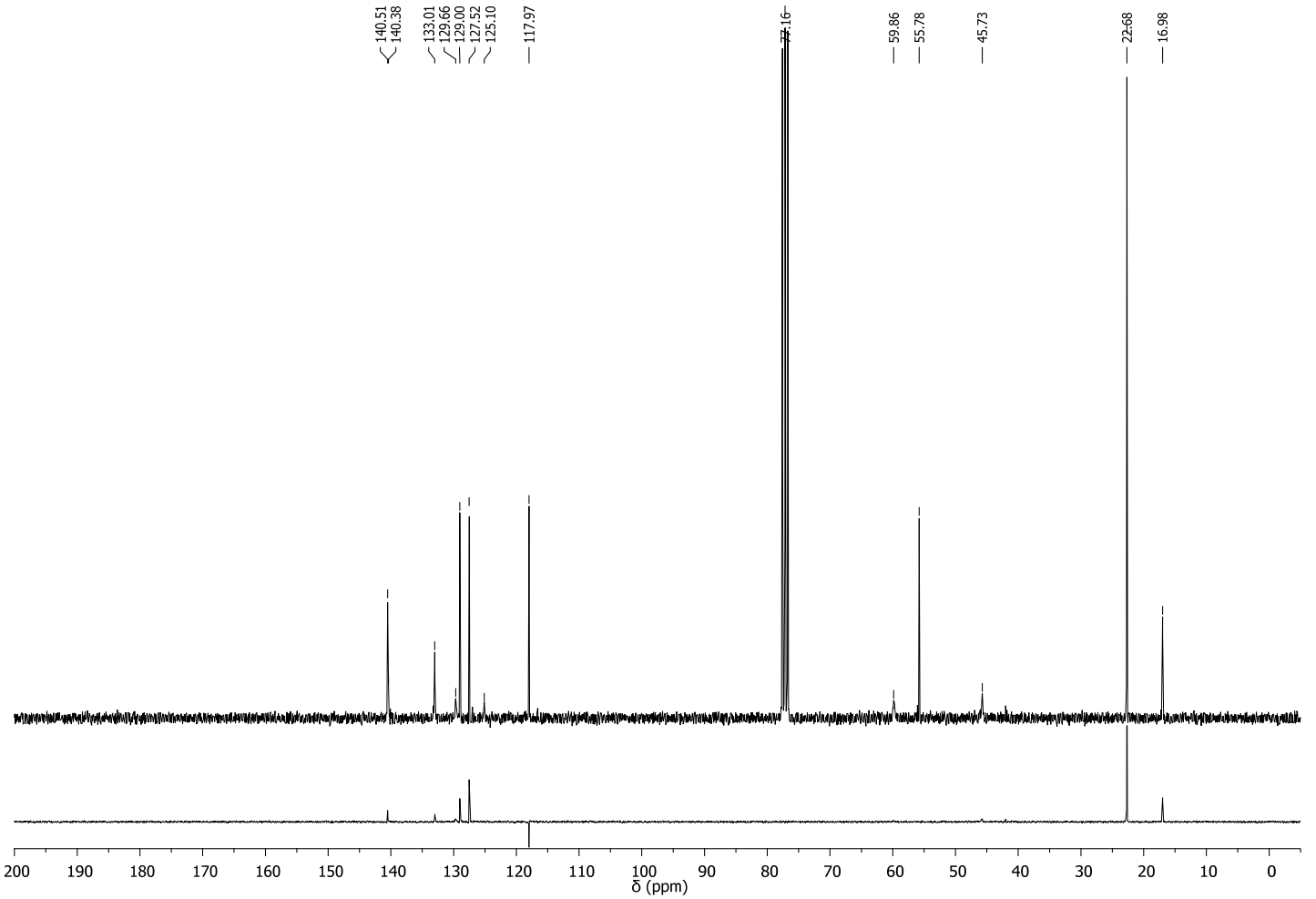

159.28
141.90
132.14
129.80
117.62
113.82
77.16
60.89
55.48
55.32
46.76
22.76
17.73
δ (ppm)

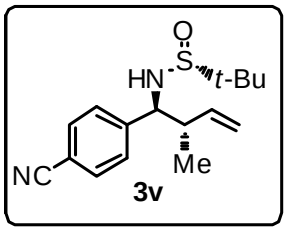

O
S
HN
t-Bu
Cl
Me
3t

7.27
7.19
5.77
5.68
5.27
5.27
5.26
5.23
4.06
4.03
3.94
1.17
0.85
0.83
0.94
2.30
1.08
1.11
2.02
0.99
0.95
1.00
0.95
2.30
1.08
1.11
2.02
0.99
0.95
1.00
8.88
0.24
3.03
δ (ppm)

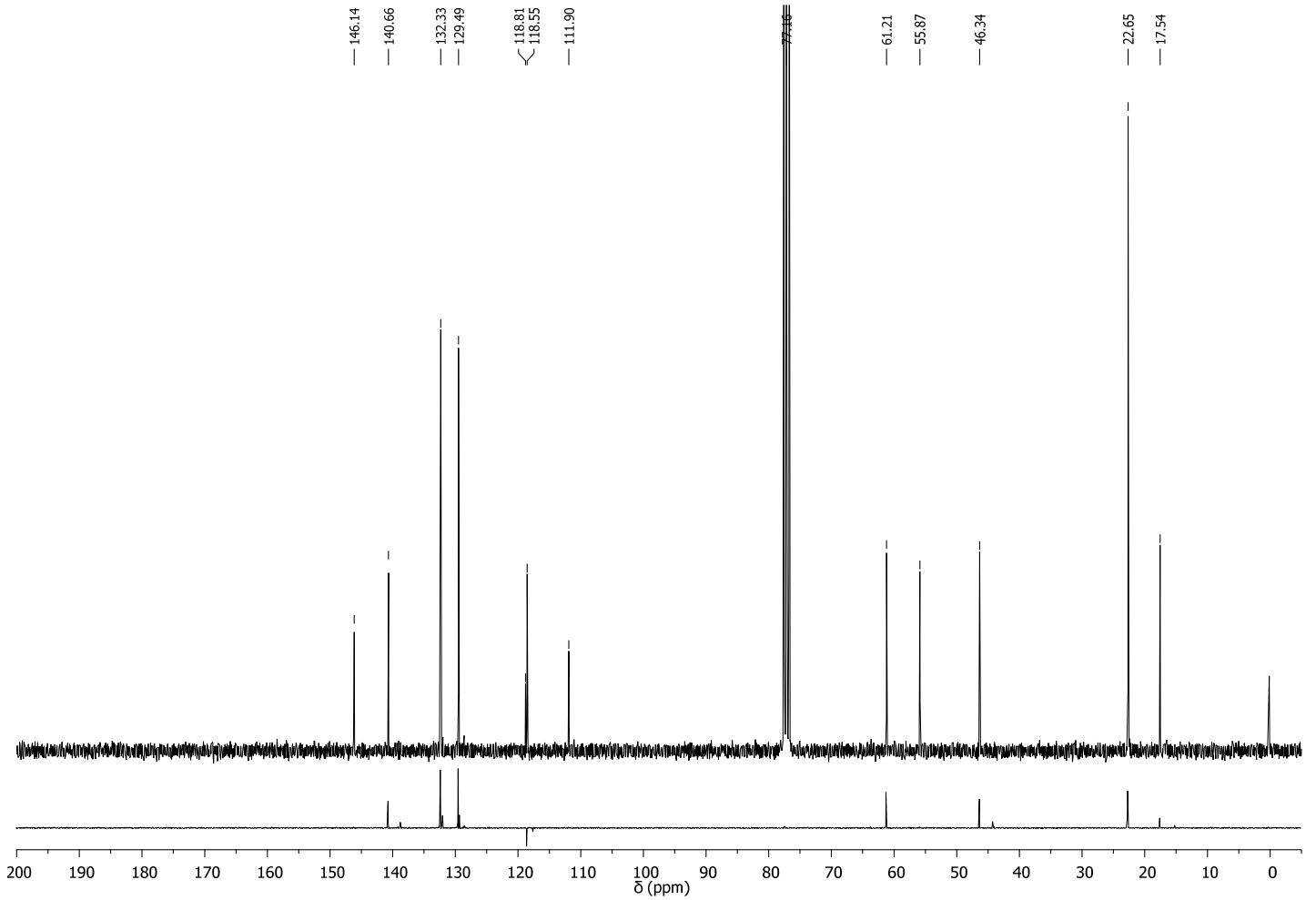

142.61
141.18
134.42
129.67
128.61
128.13
127.18
118.14
77.16
61.05
55.80
46.51
22.69
17.63
δ (ppm)

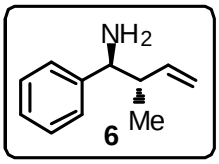

Br HN
O
S
t-Bu
Me
3u
7.57
7.55
7.35
7.34
7.33
7.32
7.30
7.27
7.15
7.13
7.12
5.25
4.74
3.84
2.54
1.15
0.99
0.97
1.08
2.39
1.09
1.00
1.97
0.89
0.98
0.91
0.74
8.67
3.27
δ (ppm)


140.51
140.38
133.01
129.66
129.00
127.52
125.10
117.97
77.16
59.86
55.78
45.73
22.68
16.98
δ (ppm)

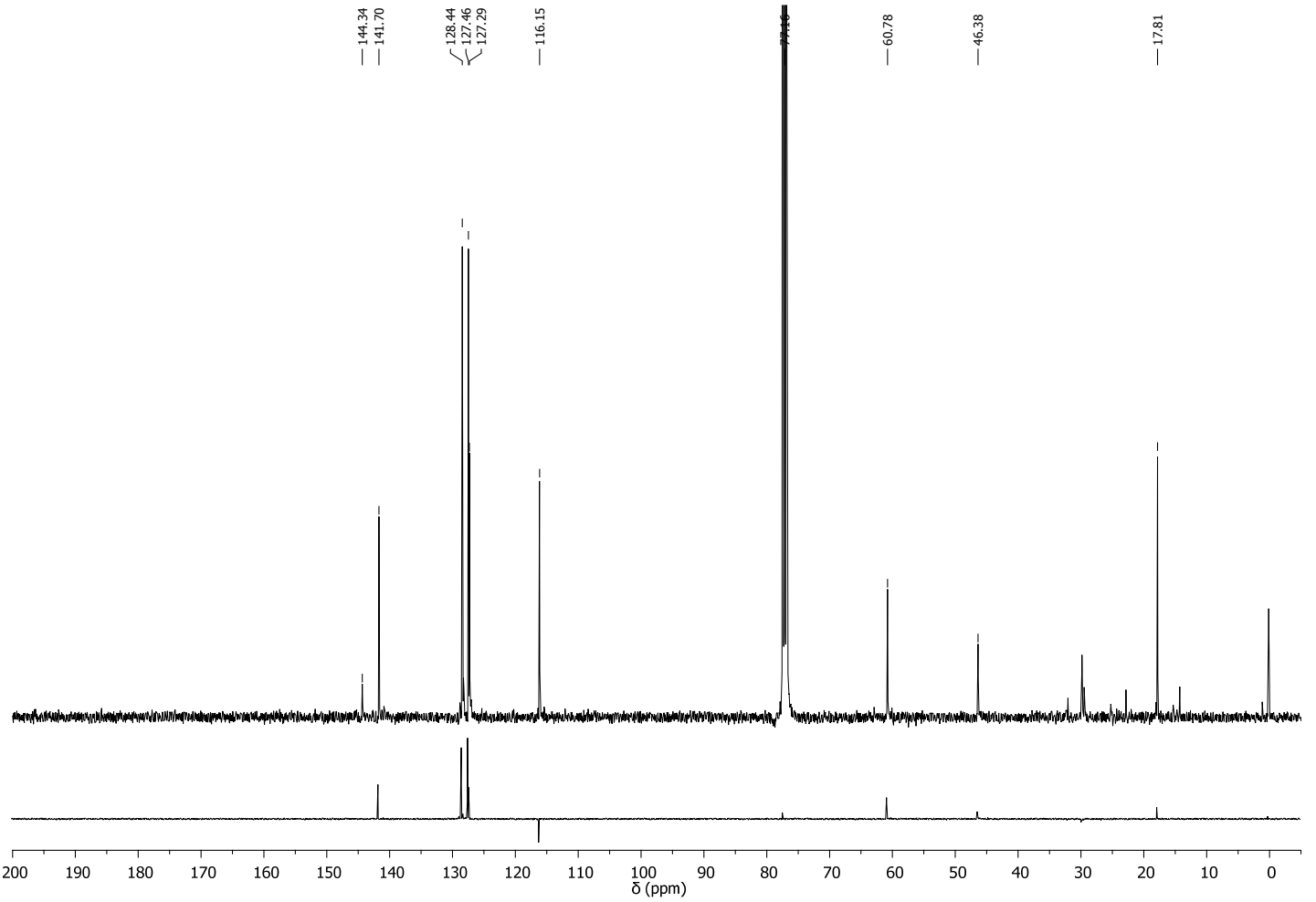

O
HN
S
t-Bu
Me
NC
3v

1.17
0.84
0.82
7.66
7.64
7.45
7.42
5.78
5.75
5.72
5.71
5.69
5.66
5.29
5.25
5.25
5.24
4.13
4.10
3.96
2.46
2.40
2.38
2.33
2.13
2.09
1.03
2.00
1.07
0.94
0.99
8.95
0.22
3.02
δ (ppm)


146.14
140.66
132.33
129.49
118.81
118.55
111.90
77.16
61.21
55.87
46.34
22.65
17.54
δ (ppm)


NH2
Me
6

7.36
7.22
5.81
5.66
5.20
5.14
5.11
3.66
3.64
2.53
2.40
2.38
2.24
2.02
0.99
0.97
0.83
0.81
4.27
2.07
1.00
1.93
0.99
1.03
2.73
2.86
δ (ppm)


144.34
141.70
128.44
127.46
127.29
116.15
60.78
46.38
17.81
δ (ppm)