Electronic Supplementary Material (ESI) for Chemical Communications

Diastereoselective indium-mediated allylation of *N-tert*-butanesulfinyl ketimines: Easy access to asymmetric quaternary stereocenters bearing nitrogen atoms

Juan Alberto Sirvent, Francisco Foubelo,* and Miguel Yus*

Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain. E-mail: foubelo@ua.es; yus@ua.es

Contents

General Methods: *N*-*tert*-butanesulfinamides (S_S and R_S) were 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}.

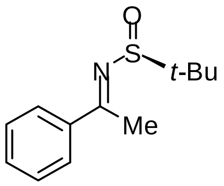
^{1}H NMR spectra were recorded at 400 MHz using $CDCl_3$ or CD_3OD as the solvent and TMS as internal standard (0.00 ppm). The data is being reported as [s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br s = broad signal, integration, coupling constant(s) in Hz]. ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.15 ppm. DEPT-135 experiments were performed to assign CH, CH_2 and CH_3.

General procedure for the synthesis of *N*-*tert*-butanesulfinyl ketimines 1:

A mixture of *N*-*tert*-butanesulfinamide (242 mg, 2.0 mmol), the corresponding ketone (2.0 mmol) and $Ti(OEt)_4$ (912 mg, 0.900 mL, 4.0 mmol) in THF (8 mL) was stirred for 12 h at 66 ºC. Then, the resulting mixture was hydrolyzed with brine (8 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 **1**. Yields, physical and spectroscopic data follow.

Characterization data of the obtained *N*-*tert*-butanesulfinyl ketimines 1

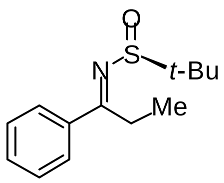
(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-1-phenylethanimine (1a):



1a

86% Yield; white solid; mp 36-40 ºC; $[\alpha]^{20}_D$ +13 (*c* 1.03, CH_2Cl_2); R_f 0.54 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.77 (s, 3H, s), 7.40-7.51 (m, 3H), 7.89 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7 (CH_3), 43.40 (CH_2), 55.8 (C), 56.5 (CH), 119.75 (CH_2), 121.6 (C), 129.35 (CH), 131.75 (CH), 133.8 (CH), 140.9 (C); IR (KBr) 1604, 1591, 1573, 1361, 1275, 1082, 1064, 768, 692, 680, 628 cm^{-1}; MS (EI) *m/z* 167 (M^+-56, 22%), 207 (13), 151 (34), 150 (50), 136 (11), 119 (55), 105 (13), 104 (100), 103 (41), 78 (12), 77 (51), 76.

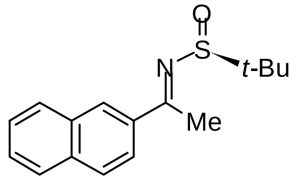
(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-1-phenylpropanimine (1b):



1b

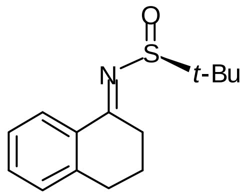
63% Yield; yellow oil; $[\alpha]^{20}_D$ +9 (*c* 1.06, CH_2Cl_2); R_f 0.67 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J* = 7.7 Hz), 1.33 (s, 9H), 3.16-3.34 (m, 2H), 7.39-7.52 (m, 3H), 7.80-7.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3 (CH_3), 22.8 (CH_3), 26.0 (CH_2), 57.5 (C), 127.6, 128.7, 131.7 (CH), 137.6 (C), 181.3 (C=N); IR (film) 2977, 2359, 1592, 1569, 1071, 693 cm^{-1}; MS (EI) *m/z* 132 (M^+-105, 46%), 105 (12), 104 (100), 103 (36), 77 (34), 76 (16), 64 (11), 56 (12), 51 (16), 50 (10).

(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-1-(2-naphthyl)ethanimine (1c):


1c

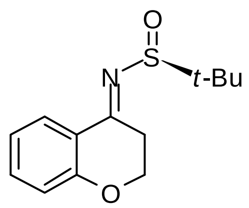
76% Yield; yellow solid; mp 118-121 ºC; $[\alpha]^{20}_{D}$ +6 (*c* 0.98, CH_2Cl_2); R_f 0.56 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 2.88 (s, 3H), 7.50-7.58 (m, 2H), 7.82-7.87 (m, 2H), 7.91 (dd, 1H, *J* = 8.1, 6.5 Hz), 8.07 (dd, 1H, *J* = 8.7, 1.4 Hz), 8.28-8.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9 (CH_3), 22.7 (CH_3), 57.7 (C), 124.0, 126.8, 127.8, 128.0, 128.3, 128.3, 129.3 (ArCH), 132.8, 135.0, 136.2 (C), 176.2 (C=N); IR (KBr) 2360, 1587, 1571, 1289, 1075 cm^{-1}; MS (EI) *m/z* 169 (M^+-104, 56%), 199 (29), 170 (11), 155 (21), 154 (100), 153 (40), 128 (15), 127 (48), 126 (21), 77 (16), 63 (10).

(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-3,4-dihydronaphthalen-1(2*H*)-imine (1d):


1d

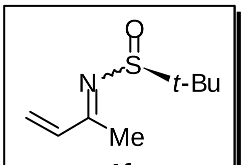
39% Yield; yellow solid; mp 40 ºC (CH_2Cl_2); $[\alpha]^{20}_{D}$ +27 (*c* 0.84, CH_2Cl_2); R_f 0.52 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 1.88-2.13 (m, 2H), 2.88 (t, 2H,, *J* = 6.2 Hz), 3.06 (ddd, 1H, *J* = 17.5, 7.2, 4.8 Hz), 3.29 (ddd, 1H, *J* = 17.5, 8.9, 5.1 Hz), 7.20 (t, 1H, *J* = 8.1 Hz), 7.24-7.29 (m, 1H), 7.39 (td, 1H, *J* = 7.4, 1.4 Hz), 8.17 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5 (CH_3), 22.7, 29.5, 32.4 (CH_2), 57.2 (C), 126.5, 127.0 128.9, 132.0 (CH), 133.0, 142.2 (C), 177.0 (C=N); IR (KBr) 2945, 2161, 1609, 1578, 1563, 1451, 1359, 1293, 1192, 1077, 1061, 1027, 903, 774, 731, 672 cm^{-1}; MS (EI) *m/z* 177 (M^+-72, 22%), 191 (13), 145 (63), 144 (34), 143 (89), 142 (19), 130 (18), 129 (19), 128 (28), 118 (13), 117 (100), 116 (47), 115 (57), 90 (21), 89 (27), 64 (15), 63 (12), 56 (12), 51 (11).

(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)chroman-4-imine (1e):


1e

90% Yield; yellow oil; $[\alpha]^{20}_{D}$ +98 (*c* 1.03, CH_2Cl_2); R_f 0.52 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 3.27 (ddd, 1H, *J* = 17.4, 7.3, 4.3 Hz), 3.51 (ddd, 1H, *J* = 17.4, 8.6, 4.8 Hz), 4.24-4.44 (m, 2H), 6.92 (dd, 1H, *J* = 8.3, 0.9 Hz), 6.97 (ddd, 1H, *J* = 8.1, 7.2, 1.1 Hz), 7.38 (ddd, 1H, *J* = 8.4, 7.2, 1.7 Hz), 8.00 (dd, 1H, *J* = 8.0, 1.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6 (CH_3), 30.7 (CH_2), 58.0 (C), 65.5 (CH_2), 118.0 (CH), 121.1 (ArC), 121.3, 126.9, 134.2 (ArCH), 159.2, 169.6 (C); IR (film) 2958, 1588, 1478, 1454, 1307, 1258, 1215, 1078, 1056, 1041, 877, 827, 761 cm^{-1}; MS (EI) *m/z* 147 (M^+-104, 63%), 146 (15), 145 (28), 120 (11), 119 (100), 118 (12), 91 (48), 80 (13), 64 (26), 63 (14), 56 (17).

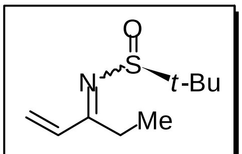
(S_S)-*N*-(*tert*-Butanesulfinyl)but-3-en-2-imine (1f, 3:1 diastereomeric mixture):



1f

43% Yield; yellow oil; R_f 0.51 (hexane/EtOAc 1:1); major diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 9H), 2.45 (s, 3H), 5.72 (d, 1H, J = 10.8 Hz), 5.96 (d, 1H, J = 17.7 Hz), 6.46 (dd, 1H, J = 17.7, 10.8 Hz); minor diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 9H), 2.32 (s, 3H), 5.78 (d, 1H, J = 10.9 Hz), 5.90 (d, 1H, J = 17.3 Hz), 7.43 (dd, 1H, J = 17.3, 10.9 Hz); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 22.3 (CH_3), 57.1 (C), 124.5 (CH_2), 139.5 (CH), 176.5 (C=N); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 22.3 (CH_3), 57.1 (C), 124.5 (CH_2), 139.5 (CH), 176.5 (C=N); IR (film) 2958, 1588, 1478, 1454, 1307, 1258, 1215, 1078, 1056, 1041, 877, 827, 761 cm^{-1}; MS (EI) *m/z* 117 (M^+-56, 100%), 102 (11), 101 (18), 100 (29), 99 (36), 73 (10), 69 (43), 64 (19), 58 (15), 57 (76), 56 (33), 55 (17), 54 (27), 53 (16); HRMS: Calculated for C_4H_7NOS (M^+-C_4H_8): 117.0248; found: 117.0249.

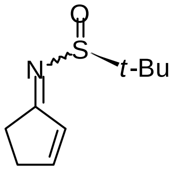
(S_S)-*N*-(*tert*-Butanesulfinyl)pent-1-en-3-imine (1g, 63:37 diastereomeric mixture):



1g

44% Yield; yellow oil; R_f 0.64 (hexane/EtOAc 1:1); major diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 6.9 Hz,), 1.26 (s, 9H), 2.57-2.77 (m, 2H), 5.73 (d, 1H, J = 11.2 Hz), 5.88 (d, 1H, J = 17.6 Hz), 7.40 (dd, 1H, J = 17.4, 11.3 Hz); minor diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 6.9 Hz), 1.26 (s, 9H), 2.80-2.98 (m, 2H), 5.68 (d, 1H, J = 11.6 Hz), 5.99 (d, 1H, J = 17.9 Hz), 6.36 (dd, 1H, J = 16.9, 11.0 Hz); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5, 22.5 (CH_3), 29.4 (CH_2), 57.7 (C), 125.2 (CH_2), 131.4 (CH), 181.0 (C=N); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 22.5 (CH_3), 25.2 (CH_2), 57.1 (C), 124.1 (CH_2), 137.7 (CH), 178.0 (C=N); IR (film) 2976, 1575, 1361, 1072, 942 cm^{-1}; MS (EI) *m/z* 131 (M^+-56, 100%), 115 (14), 114 (31), 113 (29), 112 (47), 86 (17), 83 (75), 82 (60), 67 (10), 64 (12), 59 (10), 58 (12), 57 (88), 56 (37), 55 (26), 54 (51), 53 (12); HRMS: Calculated for C_5H_9NOS (M^+-C_4H_8): 131.0405; found: 131.0409.

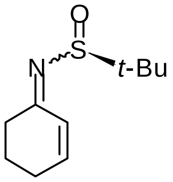
(S_S)-*N*-(*tert*-Butanesulfinyl)cyclopent-2-enimine (1h, 65:35 diastereomeric mixture):



1h

38% Yield; orange oil; R_f 0.30 (hexane/EtOAc 1:1); diastereomeric mixture ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 and 1.26 (2s, 9H), 2.55-2.60 (m, 0.65H), 2.69-2.75 (m, 2H), 2.75-2.80 (m, 0.35H), 3.11-3.22 (m, 1H), 6.32-6.38 (m, 1H), 7.11-7.18 (m, 0.65H), 7.18-7.24 (m, 0.35); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4 (CH_3), 30.3, 32.5 (CH_2), 56.7 (C), 135.5, 156.1 (CH), 189.4 (C=N); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5 (CH_3), 29.1, 34.5 (CH_2), 57.1 (C), 128.9 (CH), 158.3 (CH), 186.8 (C=N); IR (film) 2957, 1600, 1360, 1201, 1068, 754, 722 cm^{-1}; MS (EI) *m/z* 129 (M^+-56, 100%), 113 (18), 81 (24), 80 (30), 66 (33), 57 (32), 53 (16); HRMS: Calculated for C_5H_7NOS (M^+-C_4H_8): 129.0248; found: 129.0247.

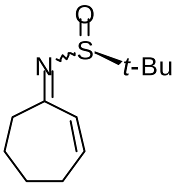
(S_S)-*N*-(*tert*-Butanesulfinyl)cyclohex-2-enimine (1i, 3:2 diastereomeric mixture):



1i

76% Yield; yellow oil; R_f 0.41 (hexane/EtOAc 1:1); diastereomeric mixture ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 1.79-2.01 (m, 2H, m), 2.25-2.34 (m, 2H), 2.57 (dd, 08H, *J* = 7.8, 5.3 Hz), 2.83 (ddd, 0.6H, *J* = 17.0, 7.5, 5.0 Hz), 3.05 (ddd, 0.6H, *J* = 17.0, 9.0, 5.0 Hz), 6.21 (dt, 0.6H, *J* = 10.3, 1.8 Hz), 6.61-6.72 (m, 1H), 7.10 (dt, 0.4H, *J* = 10.2, 2.3 Hz); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9 (CH_2), 22.2 (CH_3), 25.2, 30.9 (CH_2), 56.5 (C), 130.4, 144.8 (CH), 177.9 (C=N); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_3), 22.5, 26.0, 36.1 (CH_2), 56.9 (C), 123.1, 146.0 (CH), 175.7 (C=N); IR (film) 2924, 2359, 1620, 1568, 1361, 1071, 869, 736 cm^{-1}; MS (EI) *m/z* 143 (M^+-56, 100%), 127 (26), 95 (48), 94 (28), 93 (27), 80 (13), 79 (11), 67 (47), 66 (25), 65 (15), 64 (25), 57 (35), 56 (25), 55 (13).

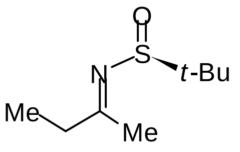
(S_S)-*N*-(*tert*-Butanesulfinyl)cyclohept-2-enimine (1j, 53:47 diastereomeric mixture):



1j

48% Yield; yellow oil; R_f 0.51 (hexane/EtOAc 1:1); major diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.67-1.97 (m, 4H), 2.29-2.49 (m, 2H), 2.65-2.75 (m, 1H), 2.83-2.96 (m, 1H), 6.42 (ddd, 1H, *J* = 17.7, 11.4, 5.6 Hz), 6.89 (d, 1H, *J* = 11.7 Hz); minor diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 1.67-1.97 (m, 4H), 2.29-2.49 (m, 2H), 2.65-2.75 (m, 1H), 3.10-3.22 (m, 1H), 6.22 (d, 1H, *J* = 11.7 Hz), 6.42 (ddd, 1H, *J* = 17.7, 11.4, 5.6 Hz); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_3), 24.8, 26.0, 28.9, 40.8 (CH_2), 57 (C), 127.1, 144.4 (CH), 180.2 (C=N); minor diastereoisomer [13]C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_3), 24.3, 26.5, 29.1, 35.4 (CH_2), 56.4 (C), 133.6, 143.8 (CH), 182.7 (C=N); IR (film) 2928, 1622, 1570, 1454, 1360, 1173, 1071, 744 cm^{-1}; MS (EI) *m/z* 157 (M^+-56, 58%), 197 (37), 157 (58), 142 (11), 141 (100), 140 (26), 139 (13), 126 (11), 113 (11), 112 (16), 109 (36), 108 (36), 107 (15), 106 (30), 99 (12), 95 (11), 94 (39), 93 (20), 92 (13), 91 (17), 81 (34), 80 (51), 79 (39), 78 (14), 77 (21), 67 (38), 66 (17), 65 (13), 64 (27), 57 (82), 55 (27), 54 (22), 53 (28), 52 (14), 51 (17), 50 (11); HRMS: Calculated for $C_7H_{11}NOS$ (M^+-C_4H_8): 157.0561; found: 157.0557.

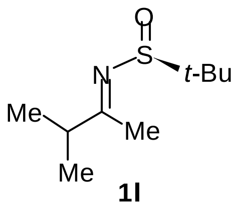
(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)butan-2-imine (1k):



1k

60% Yield; yellow oil; $[\alpha]^{20}_D$ +98 (*c* 1.2, CH_2Cl_2); R_f 0.45 (hexane/EtOAc 1:1); [1]H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, 3H, *J* = 7.3 Hz), 1.24 (s, 9H), 2.32 (s, 3H), 2.39-2.49 (m, 2H); [13]C NMR (75 MHz, $CDCl_3$) δ 9.9, 22.1 (CH_3), 22.8, 36.6 (CH_2), 56.3 (C), 186.1 (C=N); IR (film) 3237, 2977, 2959, 2359, 1621, 1458, 1362, 1192, 1053 cm^{-1}; MS (EI) *m/z* 119 (M^+-56, 100%), 74 (10), 71 (81), 70 (20), 57 (67), 56 (20), 55 (13).

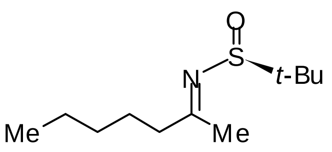
(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-3-methylbutan-2-imine (1l):



1l

73% Yield; yellow oil; $[\alpha]^{20}_D$ +198 (*c* 1.2, CH_2Cl_2); R_f 0.51 (hexane/EtOAc 1:1); [1]H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, 3H, *J* = 6.8 Hz), 1.14 (d,3H, *J* = 6.8 Hz), 1.24 (s, 9H), 2.32 (s, 3H), 2.49-2.64 (m, 1H); [13]C NMR (75 MHz, $CDCl_3$) δ 19.6, 19.8 (CH_3), 21.1 (CH), 22.2, 41.3 (CH_3), 56.4 (C), 189.2 (C=N); IR (film) 2967, 2928, 2871, 1623, 1459, 1362, 1094, 1072, 792, 671 cm^{-1}; MS (EI) *m/z* 133 (M^+-56, 84%), 85 (39), 84 (12), 74 (14), 70 (100), 69 (11), 57 (65), 55 (10).

(S_S,*E*)-*N*-(*tert*-Butanesulfinyl)heptan-2-imine (1m):

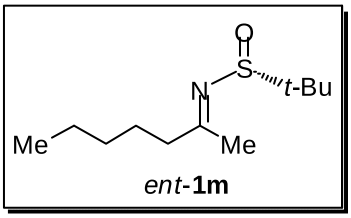


1m

75% Yield; yellow oil; $[\alpha]^{20}_D$ +144 (*c* 1.07, CH_2Cl_2); R_f 0.59 (hexane/EtOAc 1:1); [1]H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.9 Hz), 1.24 (s, 9H), 1.26-1.38 (m, 4H), 1.53-1.69 (m, 2H), 2.31 (s, 3H), 2.35-2.44 (m, 2H); [13]C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.1 (CH_3), 22.4 (CH_2), 23.0 (CH_3), 25.2, 31.3, 43.4 (CH_2), 56.2 (C), 185.6 (C); IR (film) 2955, 2928, 2862, 1622, 1457, 1362, 1187, 1074, 669 cm^{-1}; MS (EI) *m/z* 161 (M^+-56, 58%), 112 (15), 105

(56), 97 (26), 96 (20), 89 (43), 82 (10), 70 (17), 64 (60), 58 (11), 57 (100), 56 (71), 55 (54), 54 (12), 53 (15), 50 (11); HRMS: Calculated for $C_7H_{15}NOS$ (M^+-C_4H_8): 161.0874; found: 161.0870.

(R_S,*E*)-*N*-(*tert*-Butanesulfinyl)heptan-2-imine (*ent*-1m):



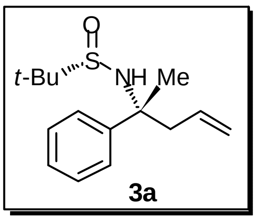
73% Yield; physical and spectroscopic dada were found to be same than for **1m**. $[\alpha]^{20}_D$ -156 (*c* 1.07, CH_2Cl_2).

General procedure for the stereoselective allylation of *N*-*tert*-butanesulfinyl ketimines 1:

A mixture of *N*-*tert*-butanesulfinyl ketimine **1** (0.5 mmol), the corresponding allylic bromide (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 products **3**. Yields are given on Table 1. Physical and spectroscopic data follow.

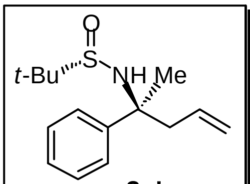
Characterization data of the obtained homoallylic amine derivatives 3

(2*R*,S_S)-*N*-(*tert*-Butanesulfinyl)-2-phenylpent-4-en-2-amine (3a):



White solid; mp 38-41 ºC (CH_2Cl_2); R_f 0.57 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.77 (s, 3H), 2.69 (d, 2H, J = 7.4 Hz), 3.77 (s, 1H), 5.01-5.24 (m, 2H), 5.42-5.65 (m, 1H), 7.21-7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 27.8 (CH_3), 49.1 (CH_2), 56.2 (C), 59.9 (C), 120.4 (CH_2), 126.3, 127.0, 128.2, 133.1 (CH), 145.4 (C); IR (KBr) 3364, 3183, 2160, 1676, 1450, 996, 933, 777, 706 cm^{-1}; MS (EI) *m/z* 209 (M^+-56, 6%), 194 (18), 189 (21), 188 (13), 175 (13), 168 (10), 167 (100), 150 (22), 145 (16), 131 (29), 129 (11), 128 (10), 119 (37), 117 (11), 104 (52), 103 (19), 91 (24), 77 (32), 51 (14).

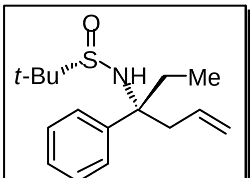
(2*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-2-phenylpent-4-en-2-amine (3a'):



3a'

R$_f$ 0.57 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 1.71 (s, 3H), 2.59-2.84 (m, 2H), 3.65 (s, 1H), 5.01-5.24 (m, 2H), 5.42-5.65 (m, 1H), 7.21-7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 28.3 (CH_3), 47.8 (CH_2), 56.2, 60.4 (C), 119.1 (CH_2), 126.3, 127.1, 128.2, 133.4 (CH), 145.5 (C).

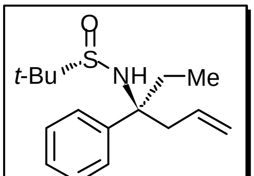
(3*R*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-3-phenylhex-5-en-3-amine (3b):



3b

Yellow oil; R$_f$ 0.63 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76 (t, 3H, *J* = 7.3 Hz), 1.26 (s, 9H), 1.95-2.11 (m, 2H), 2.74-2.90 (m, 2H), 3.75 (s, 1H), 5.04-5.15 (m, 2H), 5.61 (ddt, 1H, *J* = 17.1, 10.2, 7.2 Hz), 7.21-7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.0, 22.9 (CH_3), 33.3, 43.8 (CH_2), 56.4, 63.6 (C), 119.2 (CH_2), 126.8, 127.0, 128.2, 133.2 (CH), 143.4 (C); IR (film) 2926, 1738, 1446, 1063, 912, 761, 731, 700 cm^{-1}; MS (EI) *m/z* 235 (M+-44, 18%), 194 (12), 193 (100), 171 (12), 157 (14), 145 (34), 144 (43), 143 (15), 141 (12), 130 (20), 129 (41), 128 (25), 117 (33), 116 (16), 115 (23), 91 (13); HRMS: Calculated for $C_{13}H_{17}NOS$ [M^+-(Et,Me)] 235.1031; found: 235.1030.

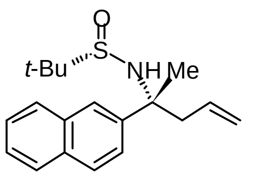
(3*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-3-phenylhex-5-en-3-amine (3b'):



3b'

R$_f$ 0.63 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71 (t, 3H, *J* = 7.3 Hz), 1.30 (s, 9H), 2.30 (dq, 2H, *J* = 14.4, 7.2 Hz), 2.74-2.90 (m, 2H), 3.91 (s, 1H), 5.09-5.26 (m, 2H), 5.34-5.52 (m, 1H) , 7.21-7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 23.0 (CH_3), 32.5, 45.8 (CH_2), 56.4, 63.4 (C), 121.1 (CH_2), 126.4, 126.7, 128.2, 132.9 (CH), 143.8 (C).

(2*R*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-2-(2-naphthyl)pent-4-en-2-amine (3c):

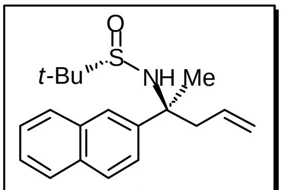


3c

White solid; mp 43-46 ºC; $[\alpha]^{20}_D$ +46 (*c* 0.65, CH_2Cl_2); R$_f$ 0.55 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 1.89 (s, 3H), 2.75 (d, 2H, *J* = 7.3 Hz), 3.83 (br s, 1H), 5.08-5.24 (m, 2H), 5.58 (ddt, 1H, *J* = 17.3, 10.1, 7.3 Hz), 7.42-7.52 (m, 2H), 7.57 (dd, 1H, *J* = 8.8, 1.7 Hz), 7.77-7.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 27.7 (CH_3), 49.2 (CH_2), 56.4, 60.2 (C), 120.5

(CH_2), 125.0, 125.5, 126.2, 126.3, 127.5, 128.1, 128.4 (ArCH), 132.5, 133.1 (C), 133.2 (CH), 142.6 (C); IR (KBr) 3214, 2977, 2359, 1381, 1364, 1047, 961, 819, 748 cm^{-1}; MS (EI) *m/z* 259 (M^+-56, 32%), 244 (46), 243 (11), 239 (14), 228 (11), 226 (28), 225 (35), 224 (12), 217 (56), 200 (13), 195 (27), 194 (11), 181 (44), 180 (12), 179 (16), 178 (17), 170 (14), 169 (100), 168 (12), 167 (13), 166 (19), 165 (34), 155 (11), 154 (64), 153 (34), 152 (24), 141 (11), 128 (22), 127 (45), 126 (16), 115 (14), 77 (11); HRMS: Calculated for $C_{15}H_{17}NOS$ (M^+-C_4H_8) 259.1031; found: 259.1027.

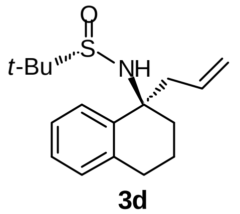
(2*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-2-(2-naphthyl)pent-4-en-2-amine (3c'):



3c'

Yellow oil; $[\alpha]^{20}_D$ +4.2 (*c* 0.73, CH_2Cl_2); R_f 0.55 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.79 (s, 3H), 2.76 (dd, 1H, *J* = 13.6, 7.4 Hz), 2.92 (dd, 1H, *J* = 13.6, 7.0 Hz), 3.73 (br s, 1H), 5.02-5.15 (m, 2H), 5.53 (ddt, 1H, *J* = 17.3, 10.1, 7.2 Hz), 7.44-7.51 (m, 2H), 7.59 (dd, 1H, *J* = 8.7, 1.9 Hz), 7.78-7.89 (m, 3H), 7.92 (dd, 1H, *J* = 8.7, 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 28.5 (CH_3), 47.6 (CH_2), 56.4, 60.6 (C), 119.5 (CH_2), 124.9, 125.3, 126.3, 127.5, 128.2, 128.5 (CH), 132.6, 133.1 (C), 133.5 (CH), 142.8 (C).

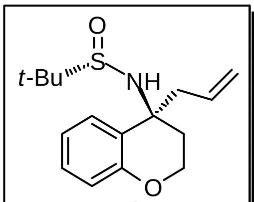
(1*R*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-allyl-1,2,3,4-tetrahydronaphthalen-1-amine (3d):



3d

Orange oil; R_f 0.49 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.75-1.98 (m, 2H), 2.01-2.21 (m, 2H), 2.67-2.69 (m, 4H), 3.62 (s, 1H), 4.98-5.21 (m, 2H), 5.50-5.63 (m, 1H), 7.06-7.14, (m, 1H), 7.15-7.24 (m, 2H), 7.46-7.50 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8 (CH_2), 22.7 (CH_3), 29.9, 36.4, 46.6 (CH_2), 56.0, 58.7 (C), 118.9 (CH_2), 125.9, 127.3, 128.0, 129.3, 133.8 (CH), 137.8 (C), 139.0 (C); IR (film) 2938, 2364, 2323, 1448, 1046, 912, 760, 731 cm^{-1}; MS (EI) *m/z* 235 (M^+-56, 18%), 194 (12), 193 (100), 171 (12), 157 (14), 145 (34), 144 (43), 143 (15), 141 (12), 130 (20), 129 (41), 128 (25), 117 (33), 116 (16), 115 (23), 91 (13); HRMS: Calculated for $C_{13}H_{17}NOS$ (M^+-C_4H_8) 235.1031; found: 235.1035.

(4*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-4-allylchroman-4-amine (3e):

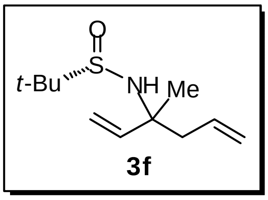


3e

Yellow oil; $[\alpha]^{20}_D$ +61 (*c* 0.87, CH_2Cl_2); R_f 0.40 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9H), 2.09-2.30 (m, 2H), 2.86 (ddd, 2H, *J* = 19.9, 13.9, 7.3 Hz), 3.70 (s, 1H), 4.26

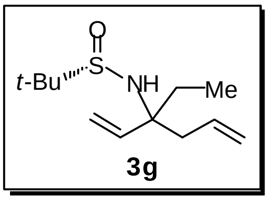
(dd, 2H, J = 8.9, 3.4 Hz), 5.15 (d, 1H, J = 17.2 Hz), 5.18 (d, 1H, J = 24.1 Hz), 5.62 (dddd, 1H, J = 14.5, 10.0, 8.4, 6.1 Hz), 6.84 (dd, 1H, J = 8.2, 1.1 Hz), 6.90-6.99 (m, 1H), 7.16-7.23 (m, 1H), 7.47 (dd, 1H, J = 7.9, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7 (CH_3), 35.0, 45.6 (CH_2), 55.0, 56.1 (C), 62.2 (CH_2), 117.4 (CH), 120.1 (CH_2), 120.3 (CH), 123.9 (C), 128.5, 129.4, 132.9 (CH), 154.8 (C); IR (film) 3208, 2957, 1608, 1579, 1488, 1451, 1223, 1055, 754 cm^{-1}; MS (EI) *m/z* 237 (M^+-56, 55%), 207 (19), 195 (45), 175 (14), 174 (100), 173 (31), 172 (14), 171 (17), 160 (15), 159 (83), 158 (11), 157 (21), 147 (85), 146 (39), 145 (26), 144 (18), 132 (11), 131 (52), 129 (11), 128 (18), 120 (11), 119 (64), 115 (22), 103 (11), 91 (36), 89 (10), 77 (21), 65 (12), 64 (21), 63 (21), 51 (12); HRMS: Calculated for $C_{12}H_{15}NO_2S$ (M^+-C_4H_8) 237.0823; found: 237.0831.

(S_S)-*N*-(*tert*-Butanesulfinyl)-3-methylhexa-1,5-dien-3-amine (3f, 3:2 diastereomeric mixture):



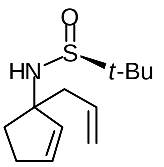
Yellow oil; R_f 0.43 (hexane/EtOAc 1:2); major diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.36 (s, 3H), 2.27-2.48 (m, 2H), 3.32 (s, 1H), 5.08-5.32 (m, 4H), 5.72-5.89 (m, 1H), 5.96 (dd, 1H, J = 17.4, 10.8 Hz); minor diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.44 (s, 3H), 2.27-2.48 (m, 2H), 3.35 (s, 1H), 5.08-5.32 (m, 4H), 5.72-5.89 (m, 1H), 5.85 (dd, 1H, J = 17.4, 10.7 Hz); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 25.9 (CH_3), 46.3 (CH_2), 55.8 (C), 58.4 (C), 114.0, 119.3 (CH_2), 133.2, 143.8 (CH); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 25.7 (CH_3), 47.1 (CH_2), 55.9 (C), 58.4 (C), 114.1, 119.7 (CH_2), 133.1, 143.5 (CH); IR (film) 3208, 2956, 2359, 2323, 1363, 1052, 996, 915 cm^{-1}; MS (EI) *m/z* 159 (M^+-56, 6%), 141 (13), 118 (33), 117 (16), 116 (100), 110 (16), 102 (12), 101 (14), 100 (71), 99 (34), 96 (11), 95 (91), 94 (29), 93 (16), 91 (16), 79 (44), 77 (33), 74 (14), 73 (16), 70 (12), 68 (12), 67 (38), 65 (11), 64 (21), 59 (38), 58 (15), 57 (63), 56 (79), 55 (48), 54 (25), 53 (45), 51 (17), 50 (15); HRMS: Calculated for $C_7H_{13}NOS$ (M^+-C_4H_8) 159.0718; found: 159.0720.

(S_S)-*N*-(*tert*-Butanesulfinyl)-3-ethylhexa-1,5-dien-3-amine (3g):



Orange oil; $[\alpha]^{20}_D$ +42 (c 1.03, CH_2Cl_2); R_f 0.55 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.4 Hz), 1.22 (s, 9H), 1.55-1.77 (m, 3H), 2.43-2.54 (m, 2H), 3.41 (s, 1H), 5.12-5.27 (m, 4H), 5.71-5.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.8, 22.8 (CH_3), 31.8, 42.0 (CH_3), 56.1, 61.4 (C), 115.0, 119.3 (CH_2), 133.1, 142.3 (CH); IR (film) 3230, 2962, 2360, 2326, 1637, 1457, 1363, 1052, 996, 915 cm^{-1}; MS (EI) *m/z* 173 (M^+-56, 5%), 155 (16), 132 (29), 131 (11), 130 (41), 124 (21), 116 (13), 115 (14), 114 (74), 113 (18), 112 (22), 109 (44), 108 (11), 99 (18), 93 (14), 91 (11), 86 (86), 84 (12), 82 (16), 81 (16), 80 (10), 79 (28), 19 (77), 73 (18), 67 (100), 65 (10), 59 (18), 57 (61), 56 (51), 55 (40), 54 (39), 53 (15); HRMS: Calculated for $C_8H_{15}NOS$ (M^+-C_4H_8) 173.0874; found: 173.0877.

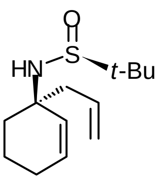
(S_S)-*N*-(*tert*-Butanesulfinyl)-1-allylcyclopent-2-enamine (3h, 4:1 diastereomeric mixture):



3h

Yellow oil; R_f 0.55 (hexane/EtOAc 1:2); major diastereoisomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.92-2.20 (m, 2H), 2.22-2.64 (m, 4H), 3.42 (s, 1H), 5.09-5.20 (m, 2H), 5.71-5.90 (m, 2H), 5.92-5.97 (m, 1H); major diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6 (CH_3), 31.3, 36.7, 45.5 (CH_2), 55.5 (C), 70.1 (C), 119.0 (CH_2), 133.7 (CH), 133.8 (CH), 135.8 (CH); minor diastereoisomer ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7 (CH_3), 31.5, 36.7, 45.8 (CH_2), 55.7, 70.5 (C), 118.9 (CH_2), 133.7, 134.3, 134.9 (CH); IR (film) 3207, 2953, 2359, 1456, 1362, 1047, 911, 756 cm^{-1}; MS (EI) *m/z* 171 (M^+-56, 2%), 107 (52), 106 (55), 105 (34), 104 (20), 103 (26), 91 (100), 79 (54), 78 (65), 77 (40), 65 (15), 63 (24), 57 (20), 56 (23), 55 (10), 53 (11), 52 (11), 51 (21), 50 (12); HRMS: Calculated for $C_8H_{13}NOS$ (M^+-C_4H_8) 171.0718; found: 171.0731.

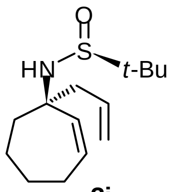
(1*S*,S_S)-*N*-(*tert*-Butanesulfinyl)-1-allylcyclohex-2-enamine (3i):



3i

White solid; mp 94-98 ºC (CH_2Cl_2); $[\alpha]^{20}_D$ +162 (*c* 0.6, CH_2Cl_2); R_f 0.57 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.54-2.15 (m, 6H), 2.32-2.52 (m, 2H), 3.42 (br s, 1H), 5.16-5.20 (m, 2H), 5.67-5.74 (m, 1H), 5.74-5.87 (m, 1H), 5.91 (dt, 1H, *J* = 10.1, 3.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4 (CH_2), 22.8 (CH_3), 25.1, 35.6, 46.9 (CH_2), 55.9, 55.9 (C), 119.5 (CH_2), 131.0 (CH), 131.3 (CH), 133.5 (CH); IR (KBr) 3195, 2936, 1362, 1176, 1038, 994, 904 cm^{-1}; MS (EI) *m/z* 200 (M^+-41, 3%), 185 (10), 144 (16), 121 (100), 93 (21), 79 (30), 67 (30), 57 (23); HRMS: Calculated for $C_9H_{15}NOS$ (M^+-C_4H_8) 185.0874; found: 185.0885.

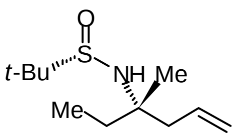
(1*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-1-allylcyclohept-2-enamine (3j):



3j

White solid; mp 90-96 ºC (CH_2Cl_2); $[\alpha]^{20}_D$ +80 (*c* 1.2, CH_2Cl_2); R_f 0.61 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.50-1.77 (m, 4H), 1.79-1.92 (m, 2H.), 2.12-2.19 (m, 2H), 2.40-2.56 (m, 2H), 3.41 (s, 1H), 5.13-5.20 (m, 2H), 5.69-5.91 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (CH_3), 24.1, 27.2, 28.0, 38.4, 47.0 (CH_2), 55.8, 61.6 (C), 119.5 (CH_2), 132.9, 133.5, 136.1 (CH); IR (KBr) 3191, 2928, 1639, 1065, 1034, 994, 952, 904, 679 cm^{-1}; MS (EI) *m/z* 199 (M^+-41, 29%), 183 (12), 181 (15), 166 (15), 158 (24), 157 (52), 152 (10), 151 (14), 150 (21), 149 (11), 148 (14), 140 (15), 136 (17), 135 (74), 134 (34), 121 (11), 120 (13), 119 (18), 117 (12), 115 (11), 109 (24), 108 (24), 107 (31), 106 (24), 105 (33), 94 (41), 93 (81), 92 (26), 91 (100), 81 (48), 80 (34), 79 (73), 78 (21), 77 (56), 73 (10), 69 (10), 68 (18), 67 (49), 66 (14), 65 (25), 63 (10), 59 (11), 57 (47), 56 (20), 55 (28), 54 (17), 53 (29), 51 (17); HRMS: Calculated for $C_{10}H_{17}NOS$ (M^+-C_4H_8) 199.1031; found: 199.1034.

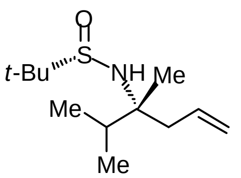
(3*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-3-methylhex-5-en-3-amine (3k):



3k

Colourless oil; $[\alpha]^{20}_D$ +52 (*c* 0.77, CH_2Cl_2); R_f 0.56 (hexane/EtOAc 1:2); ^1H 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); HRMS: Calculated for $C_7H_{15}NOS$ (M^+-C_4H_8) 161.0874; found: 161.0868.

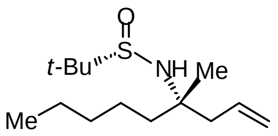
(3*R*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-2,3-dimethylhex-5-en-3-amine (3l):



3l

Yellow oil; $[\alpha]^{20}_D$ +50 (*c* 0.99, CH_2Cl_2); R_f 0.62 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 6H, *J* = 6.6 Hz), 1.21 (s, 9H), 1.24 (s, 3H), 1.71-1.82 (m, 1H), 2.34-2.47 (m, 2H), 3.29 (s, 1H), 5.16-5.21 (m, 2H), 5.78-5.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.9, 17.0, 21.7, 22.8 (CH_3), 35.6 (CH), 44.2 (CH_2), 56.0, 59.9 (C), 119.6 (CH_2), 133.4 (CH); IR (film) 3240, 2959, 2874, 2360, 1638, 1457, 1388, 1457, 1164, 1045, 910 cm^{-1}; MS (EI) *m/z* 175 (M^+-56, 26%), 190 (12), 134 (93), 133 (28), 132 (41), 118 (17) , 116 (26), 111 (31), 110 (30), 95 (15), 84 (10), 74 (24), 73 (21), 70 (22), 69 (100), 57 (72), 55 (40); HRMS: Calculated for $C_8H_{17}NOS$ (M^+-C_4H_8) 175.1031; found: 175.1029.

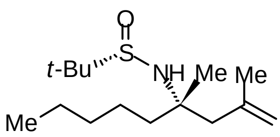
(4*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-4-methylnon-1-en-4-amine (3m):



3m

Yellow oil; $[\alpha]^{20}_D$ +53 (*c* 0.96, CH_2Cl_2); R_f 0.58 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 6.7 Hz, CH_3), 1.19 (s, 9H), 1.21-1.39 (m, 6H), 1.27 (s, 3H), 1.45-1.54 (m, 2H), 2.25-2.38 (m, 2H), 3.19 (s, 1H), 5.08-5.18 (m, 2H), 5.76-5.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 22.6 (CH_2), 22.7 (CH_3), 23.0 (CH_2), 26.2 (CH_3), 32.2, 40.9, 46.1 (CH_2), 55.7, 57.4 (C), 119.2 (CH_2), 133.6 (CH); IR (film) 3217, 2932, 2863, 1457, 1362, 1053, 912 cm^{-1}; MS (EI) *m/z* 203 (M^+-56, 22%), 163 (10), 162 (100), 161 (33), 146 (19), 138 (10), 132 (18), 114 (11), 97 (45), 96 (19), 83 (70), 82 (16), 74 (23), 73 (18), 70 (11), 69 (35), 57 (63), 56 (11), 55 (39); HRMS: Calculated for $C_{10}H_{21}NOS$ (M^+-C_4H_8) 203.1344; found: 203.1341.

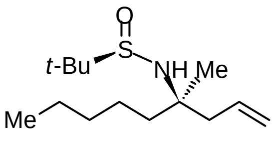
(4*S*,*S*$_S$)-*N*-(*tert*-Butanesulfinyl)-2,4-dimethylnon-1-en-4-amine (3n):



3n

Colourless oil; $[\alpha]^{20}_D$ +58 (*c* 1.0, CH_2Cl_2); R_f 0.66 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.8 Hz), 1.20 (s, 9H), 1.22-1.40 (m, 8H), 1.34 (s, 3H), 1.47-1.59 (m, 2H), 1.82 (s, 3H), 2.28 (s, 2H), 3.46 (s, 1H), 4.82-4.86 (m, 1H), 4.96-5.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.8 (CH_2), 22.9 (CH_3), 23.4 (CH_2), 25.5, 27.2 (CH_3), 32.4, 41.4, 49.7 (CH_2), 55.9, 57.5 (C), 116.5 (CH_2), 142.1 (C); IR (film) 3217, 2933, 2863, 1457, 1377, 1052, 930, 892 cm^{-1}; MS (EI) *m/z* 218 (M^+-55, 8%), 202 (12), 162 (56), 161 (100), 146 (37), 144 (15), 130 (24), 114 (22), 110 (30), 105 (20), 97 (45), 96 (32), 95 (13), 89 (21), 87 (41), 85 (11), 83 (21), 81 (11), 74 (37), 70 (19), 69 (26), 59 (13), 58 (11), 57 (85), 56 (32), 55 (71), 53 (18); HRMS: Calculated for $C_{11}H_{23}NOS$ (M^+-C_4H_8) 217.1500; found: 217.1498.

(4*R*,*R*$_S$)-*N*-(*tert*-Butanesulfinyl)-4-methylnon-1-en-4-amine (*ent*-3m):


ent-**3m**

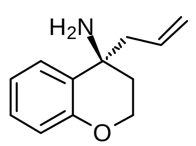
Physical and spectroscopic dada were found to be same than for **3m**. $[\alpha]^{20}_D$ -50 (*c* 1.03, CH_2Cl_2).

General procedure for the stereoselective allylation of *N*-*tert*-butanesulfinyl ketimines 1:

To a stirred solution of the corresponding *N*-*tert*-butanesulfinyl amine **3** (0.33 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. 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 the corresponding amines **4**. Yields are given on Figure 3. Physical and spectroscopic data follow.

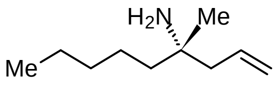
Characterization data of the obtained amines 4

(*S*)-4-Allylchroman-4-amine (4e):


4e

Yellow oil; $[\alpha]^{20}_D$ +9 (*c* 1.14, CH_2Cl_2); R_f 0.40 (CH_2Cl_2/MeOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (br s, 2H), 1.81 (ddd, 1H, *J* = 14.0, 6.4, 4.2 Hz), 2.13 (ddd, 1H, *J* = 14.0, 7.0, 4.5 Hz), 2.56 (d, 2H, d, *J* = 7.2 Hz), 4.21-4.27 (m, 2H), 5.10-5.15 (m, 1H), 5.15-5.20 (m, 1H), 5.66-5.85 (m, 1H), 6.81 (dd, 1H, *J* = 8.2, 1.2 Hz), 6.89-6.95 (m, 1H), 7.13 (ddd, 1H, *J* = 8.2, 7.2, 1.7 Hz), 7.40 (dd, 1H, *J* = 7.8, 1.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.1, 47.4 (CH_2), 49.5 (C), 63.0 (CH_2), 117.1 (CH), 119.2 (CH_2), 120.6, 126.6, 128.2, 133.5 (CH), 153.9 (C); IR (film) 3208, 2956, 2359, 2323, 1363, 1052, 996, 915 cm^{-1}; MS (EI) *m/z* 189 (M^+, 1%), 159 (100); HRMS: Calculated for $C_{12}H_{15}NOS$ 189.1154; found: 189.1155.

(*S*)-4-Methylnon-1-en-4-amine (4m):



4m

Yellow oil; $[\alpha]^{20}_{D}$ -0.5 (*c* 0.84, CH_2Cl_2); R_f 0.28 (CH_2Cl_2/MeOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.8 Hz), 1.07 (s, 3H), 1.18-1.41 (m, 8H), 2.13 (d, 2H, *J* = 7.5 Hz), 4.89-5.18 (m, 2H), 5.69-5.97 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6, 23.5 (CH_2), 27.4 (CH_3), 32.4, 42.4, 46.9 (CH_2), 51.9 (C), 118.2 (CH_2), 134.3 (CH); IR (film) 3354, 3279, 2927, 1639, 1458, 1377, 911 cm^{-1}; MS (EI) *m/z* 155 (M^+, 1%), 114 (100); HRMS: Calculated for $C_{10}H_{21}N$ 155.1674; found: 155.1663.

X-Ray structures of compounds 3i and 3j

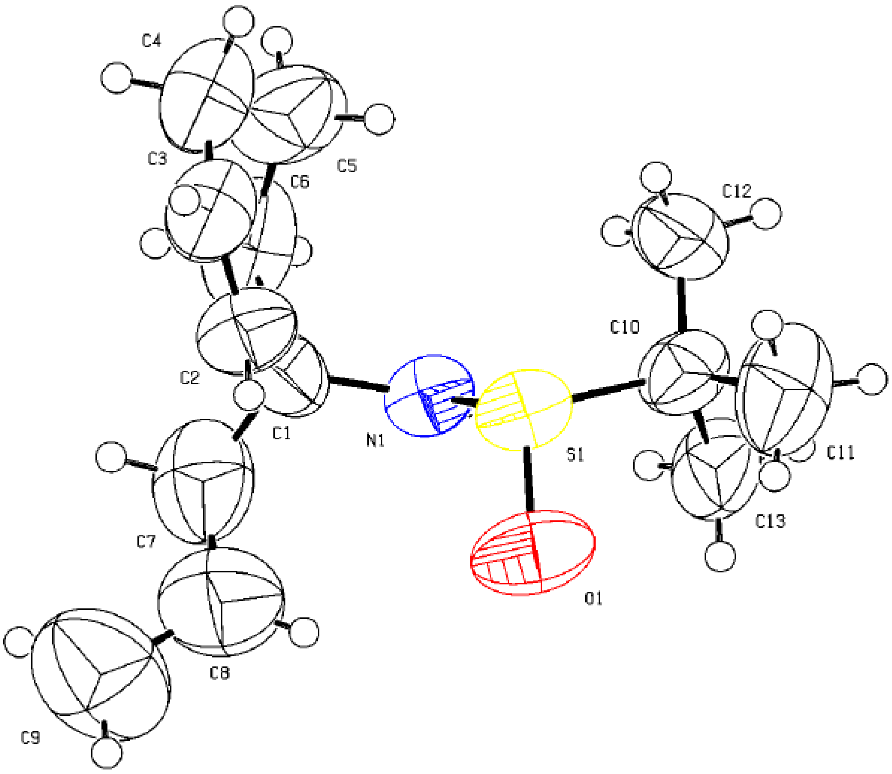


Figure 1. Molecular Structure for Product **3i** as Determined by X-ray Analysis

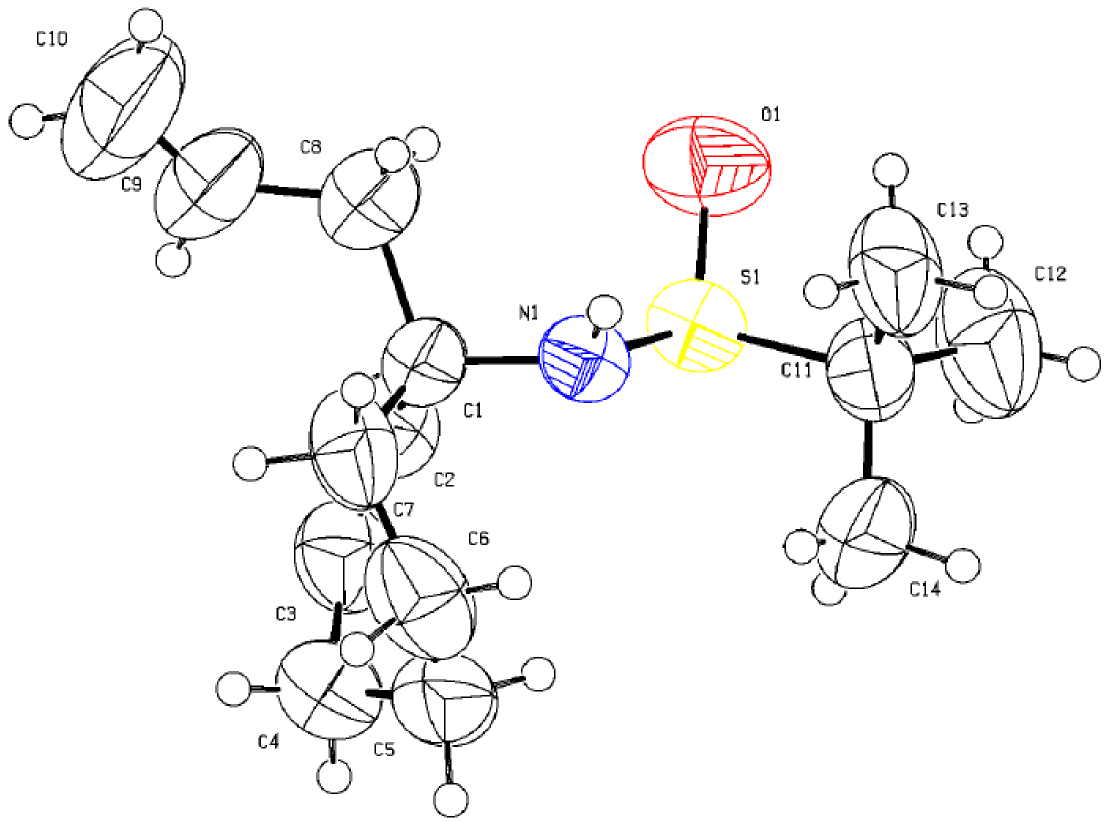
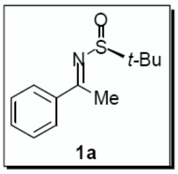
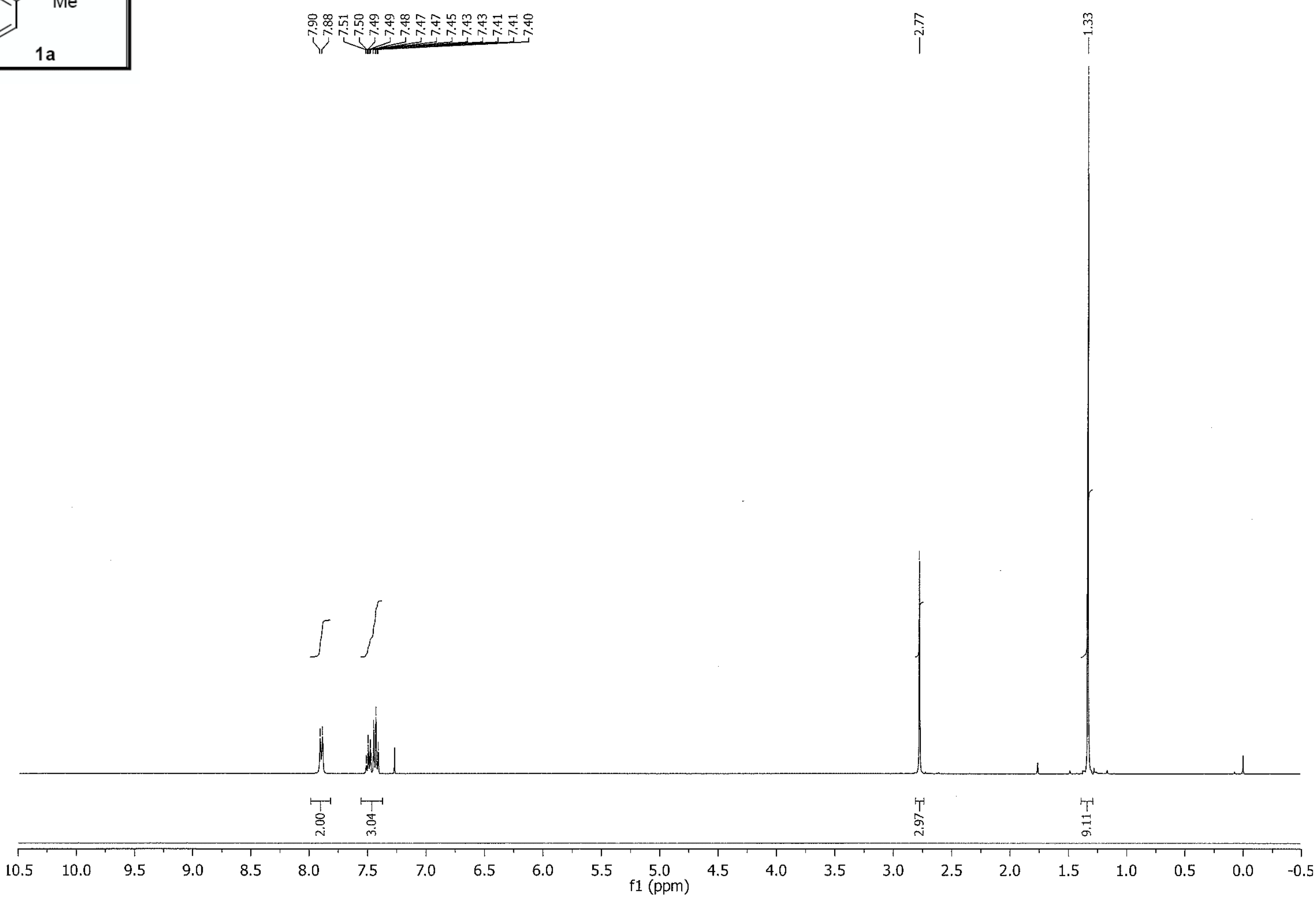
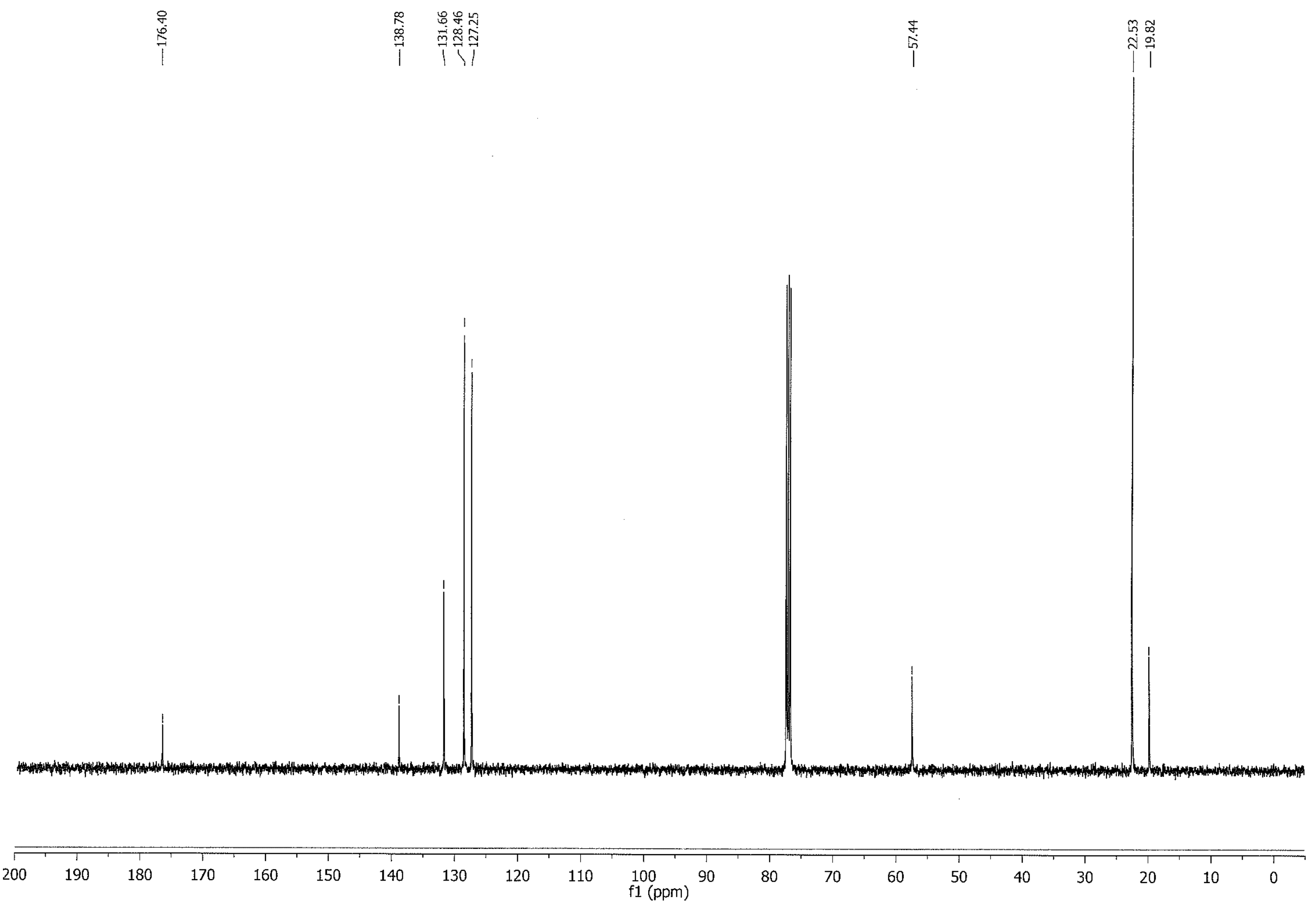
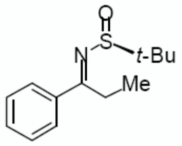


Figure 2. Molecular Structure for Product **3j** as Determined by X-ray Analysis

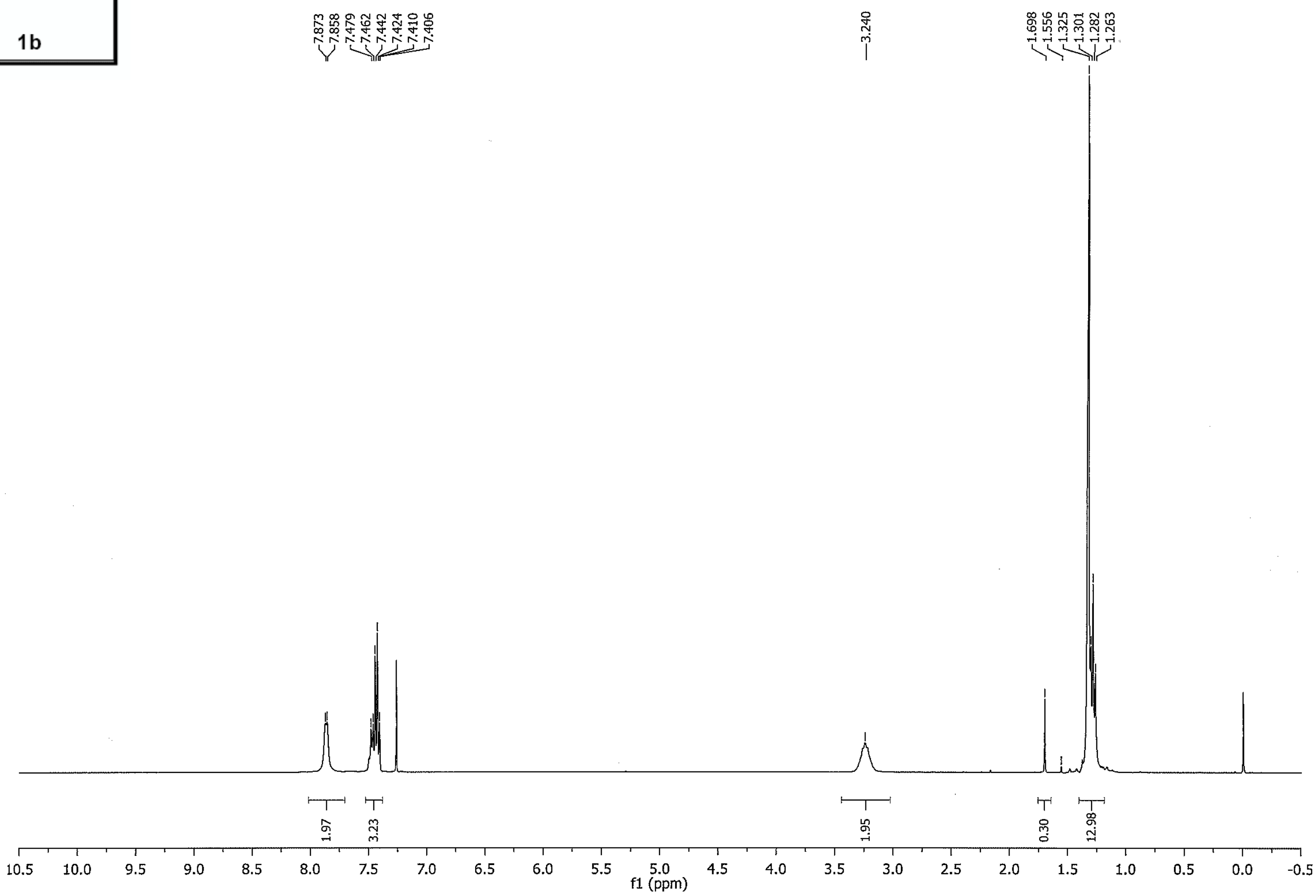

t-Bu
Me
1a

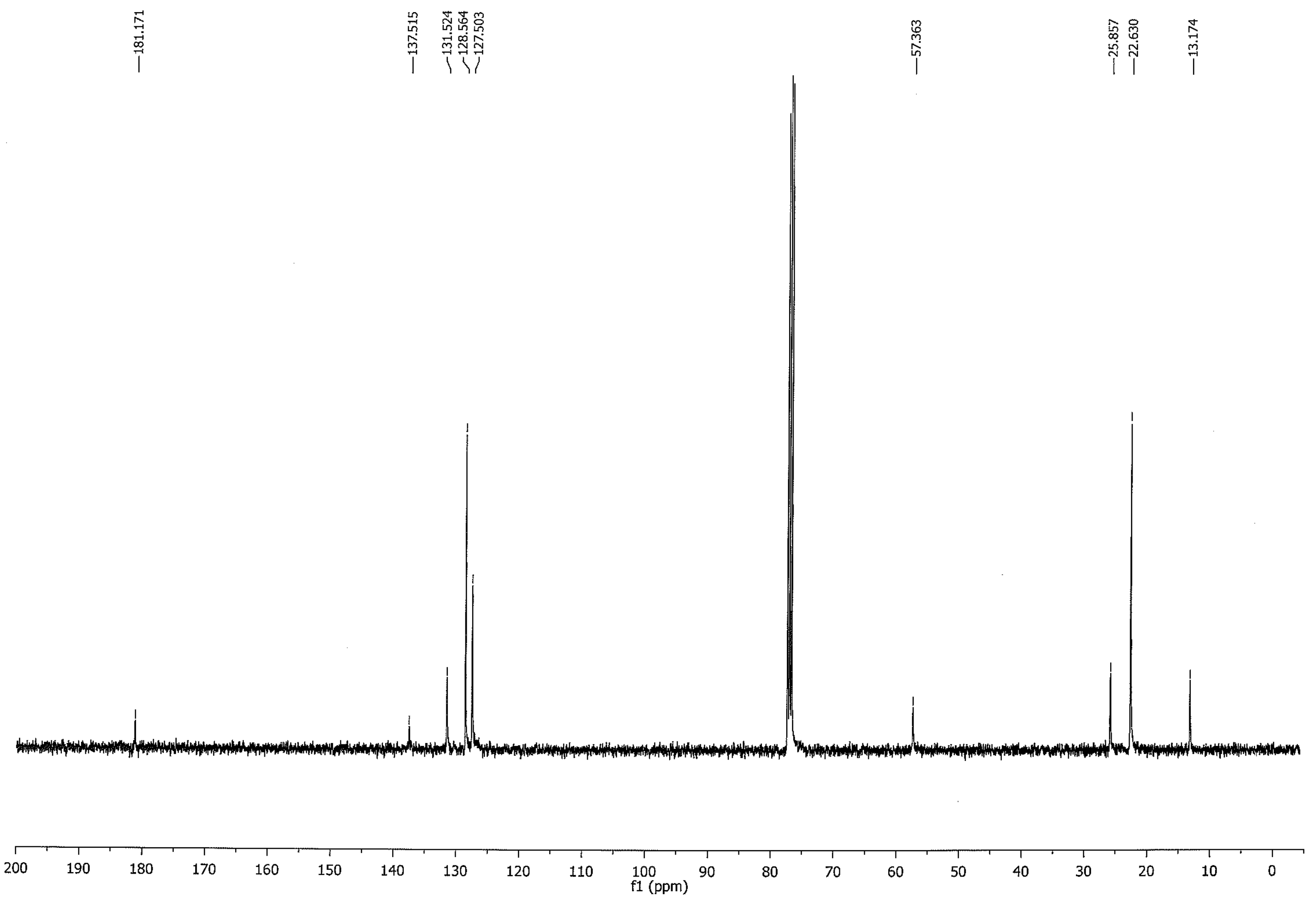

7.90
7.88
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.43
7.43
7.41
7.41
7.40
2.77
1.33
2.00
3.04
2.97
9.11
f1 (ppm)

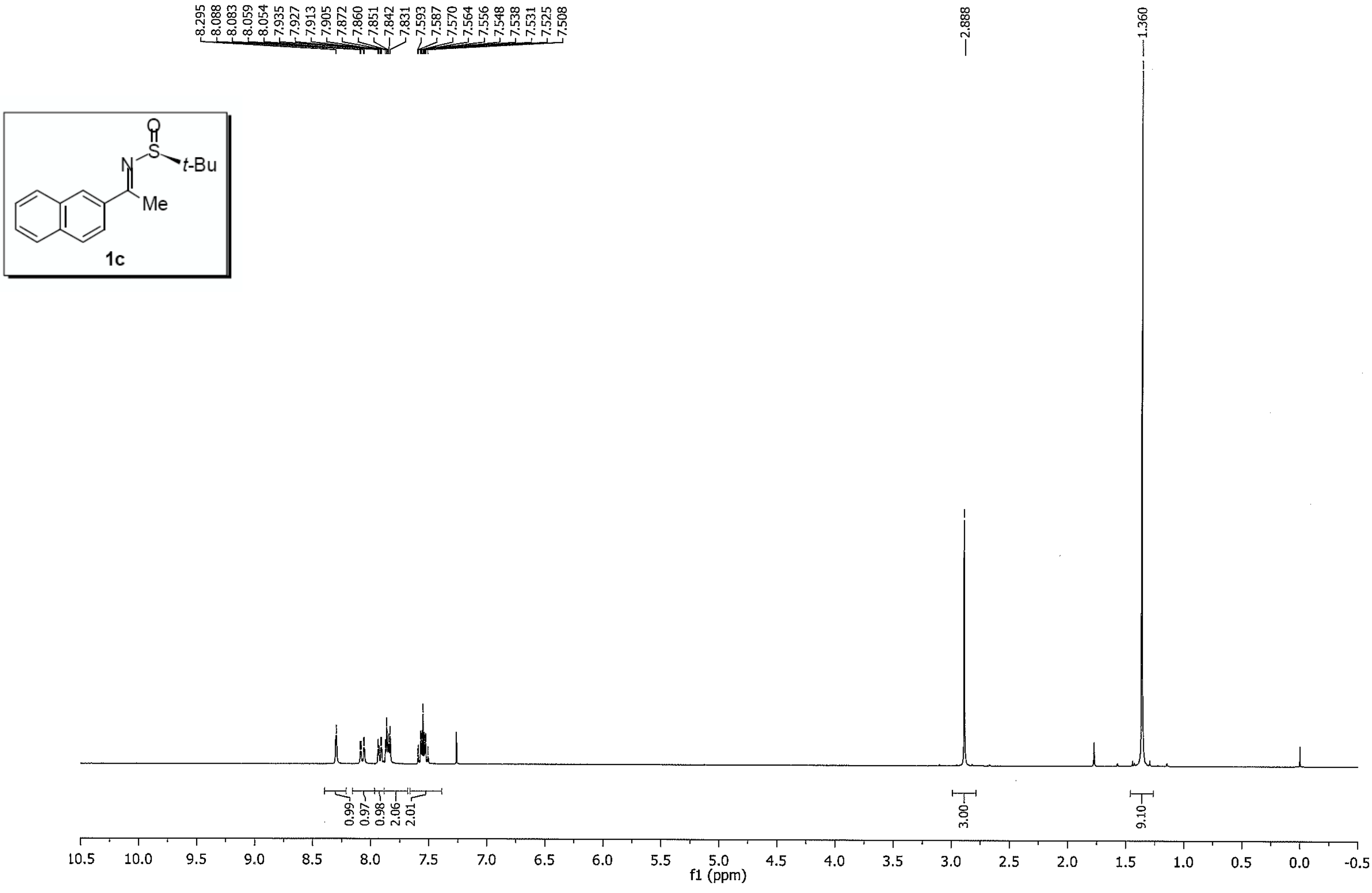

176.40
138.78
131.66
128.46
127.25
57.44
22.53
19.82
f1 (ppm)

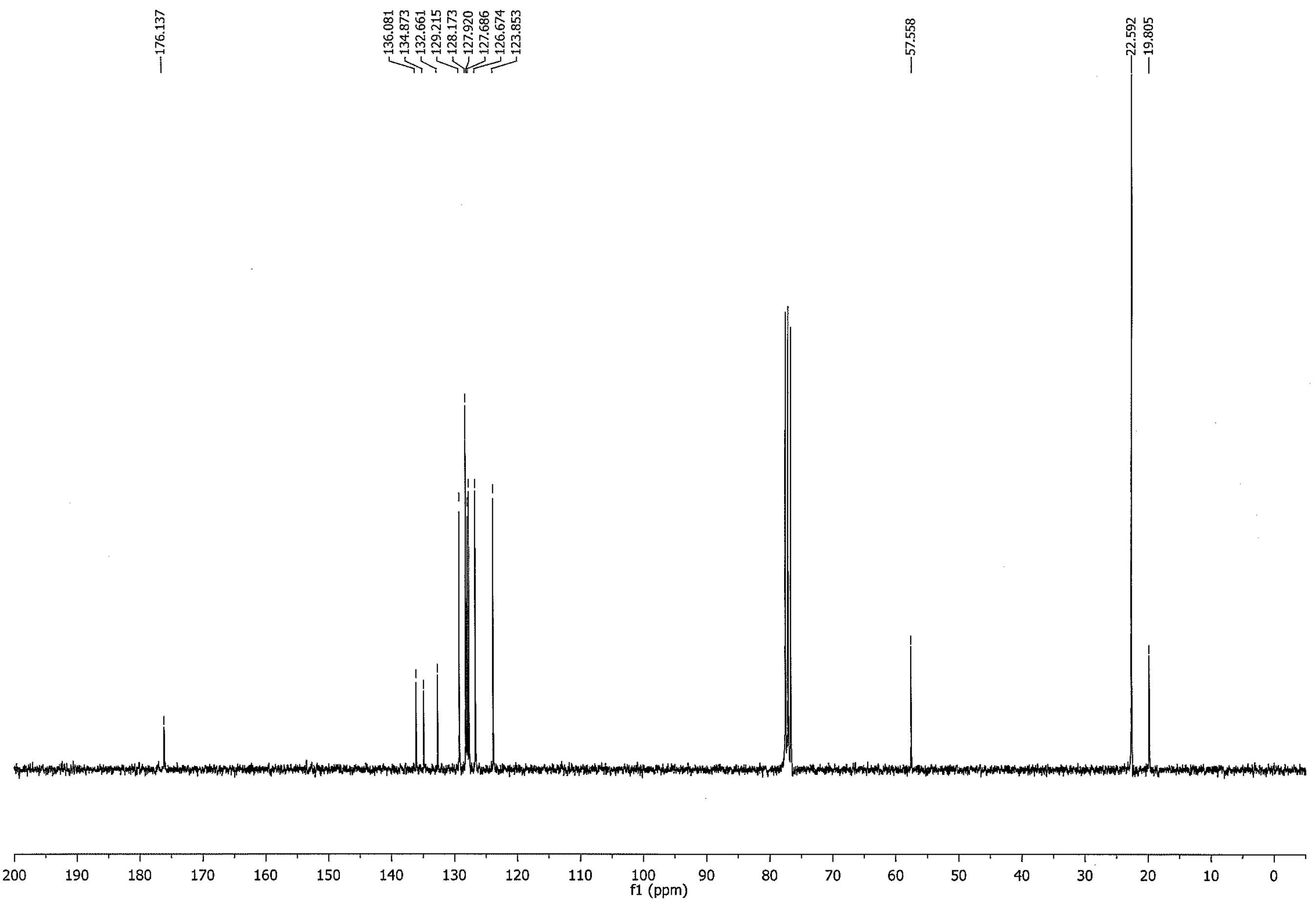

O
S
N
t-Bu
Me

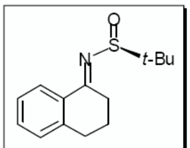
1b


7.873
7.858
7.479
7.462
7.442
7.424
7.410
7.406
3.240
1.698
1.556
1.325
1.301
1.282
1.263
1.97
3.23
1.95
0.30
12.98
f1 (ppm)

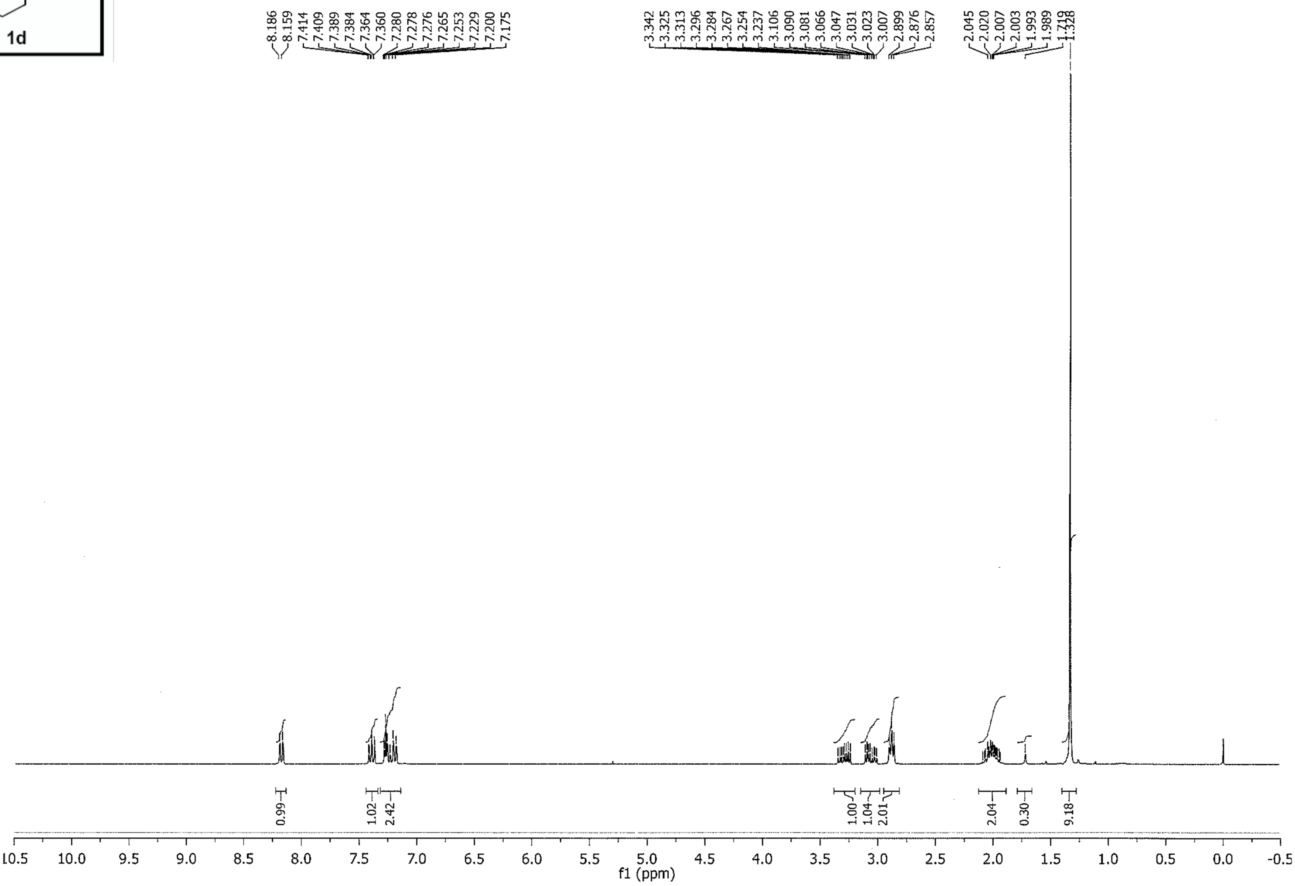

181.171
137.515
131.524
128.564
127.503
57.363
25.857
22.630
13.174
f1 (ppm)

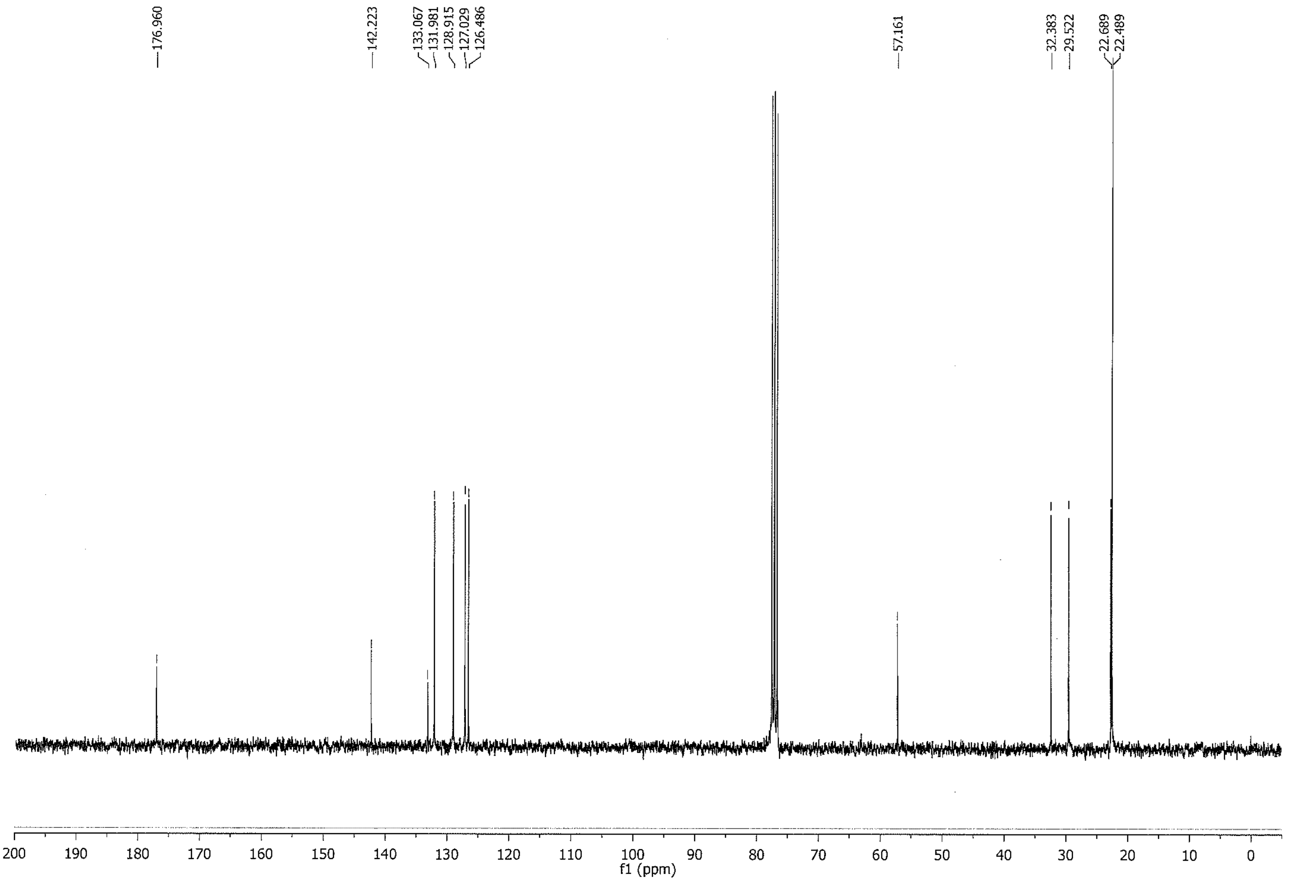

8.295
8.088
8.083
8.059
8.054
7.935
7.927
7.913
7.905
7.872
7.860
7.851
7.842
7.831
7.593
7.587
7.570
7.564
7.556
7.548
7.538
7.531
7.525
7.508
2.888
1.360
t-Bu
Me
1c
0.99
0.97
0.98
2.06
2.01
3.00
9.10
f1 (ppm)

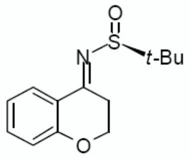

176.137
136.081
134.873
132.661
129.215
128.173
127.920
127.686
126.674
123.853
57.558
22.592
19.805
f1 (ppm)



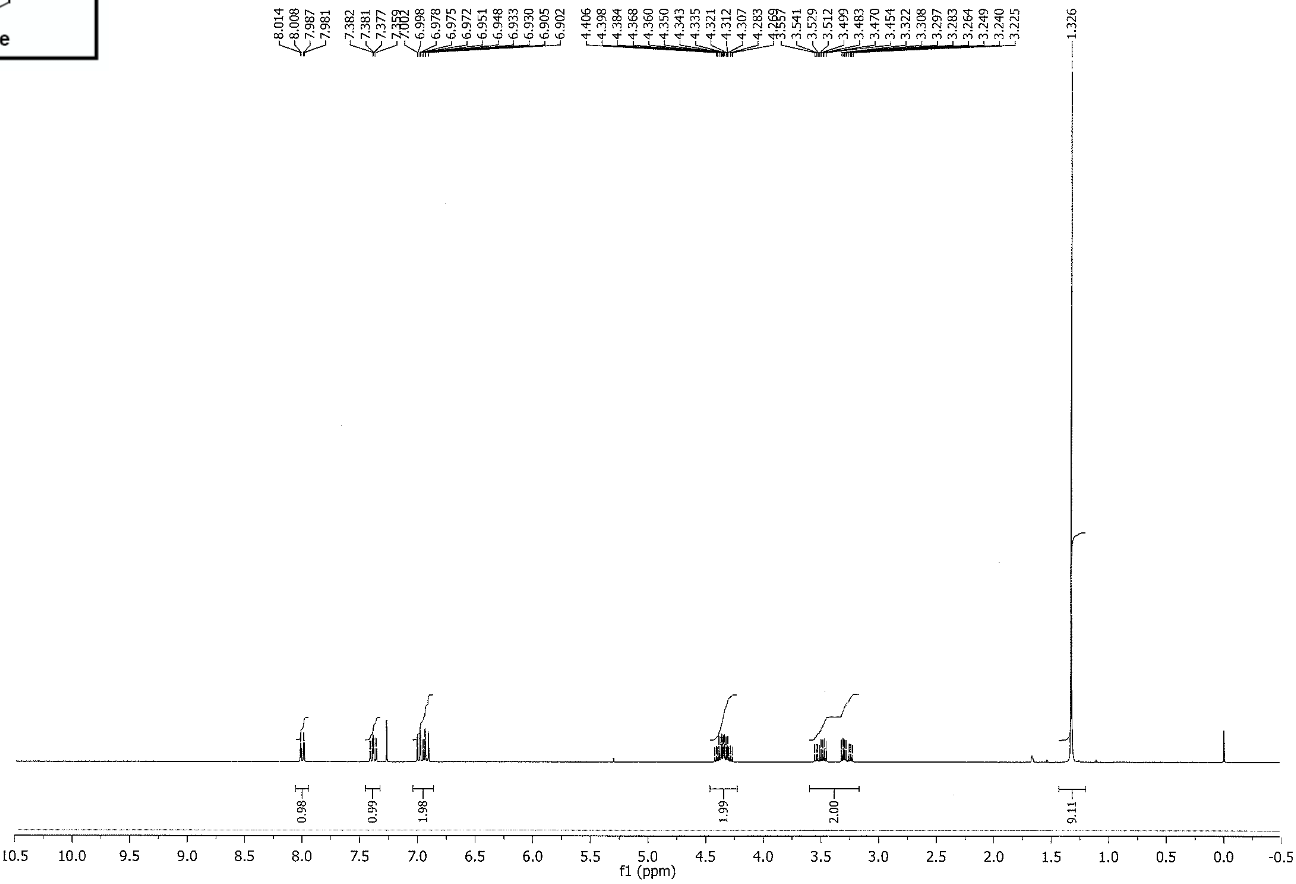
1d

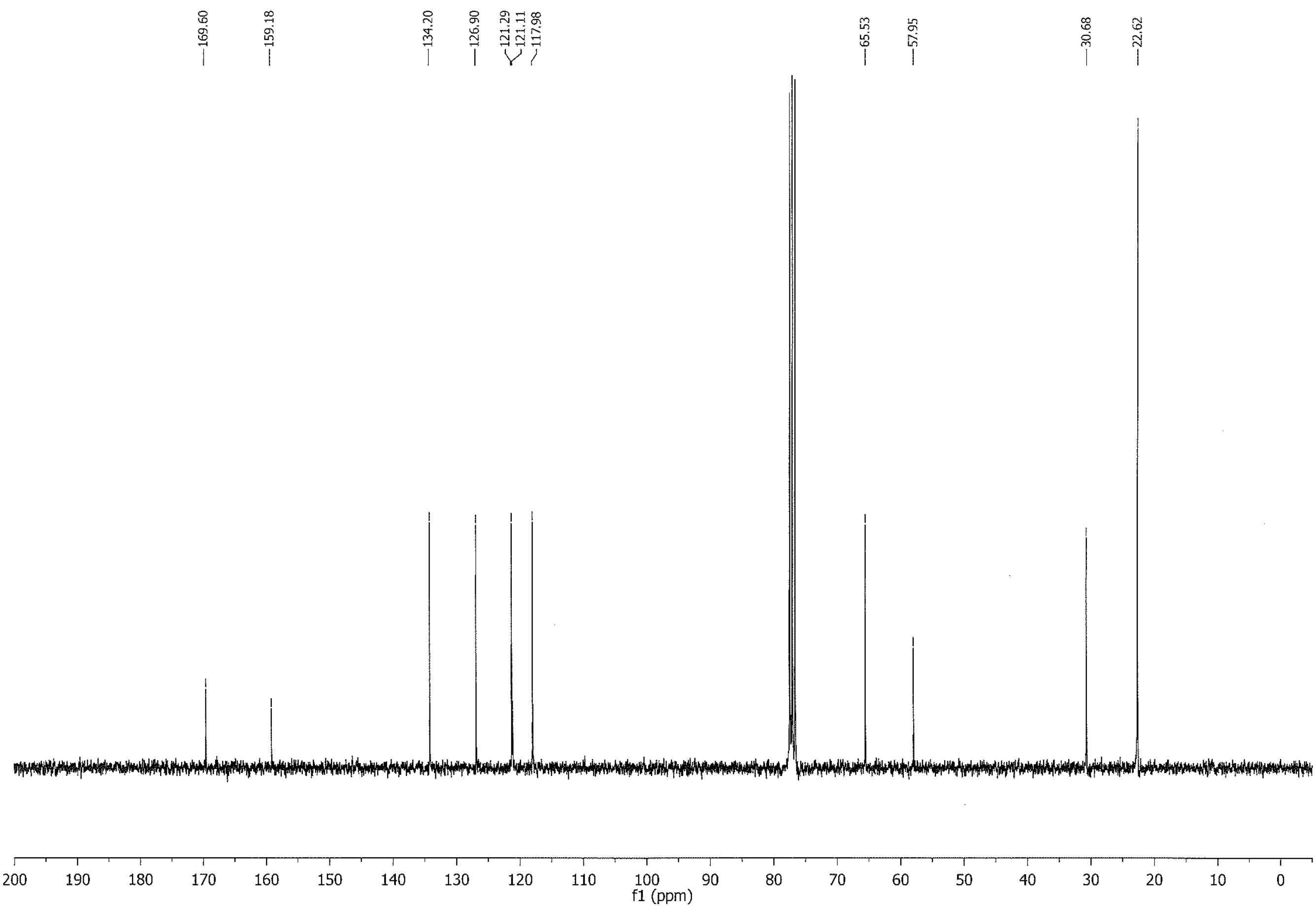


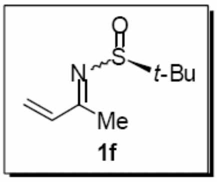



O
S
N
t-Bu
O

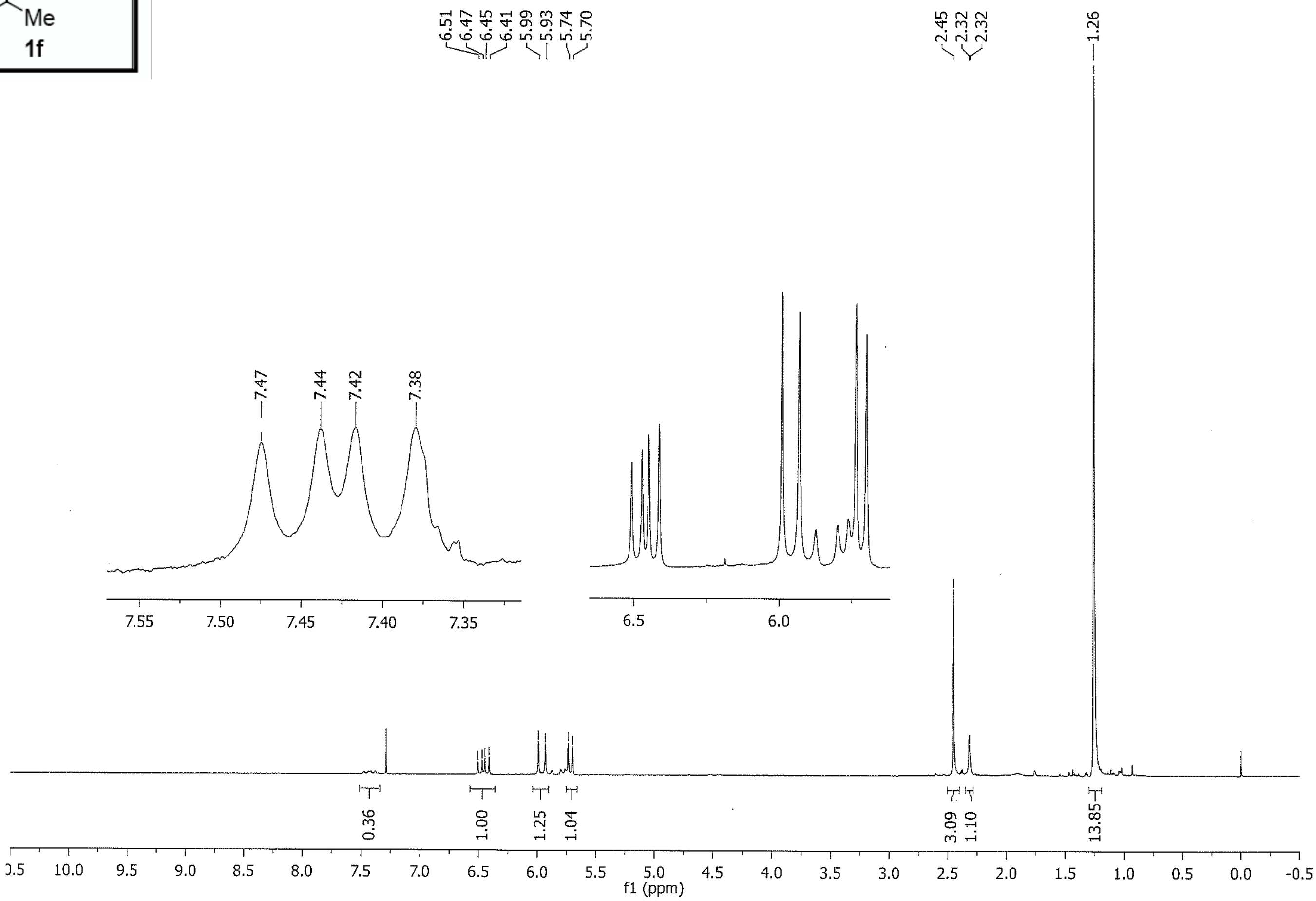
1e

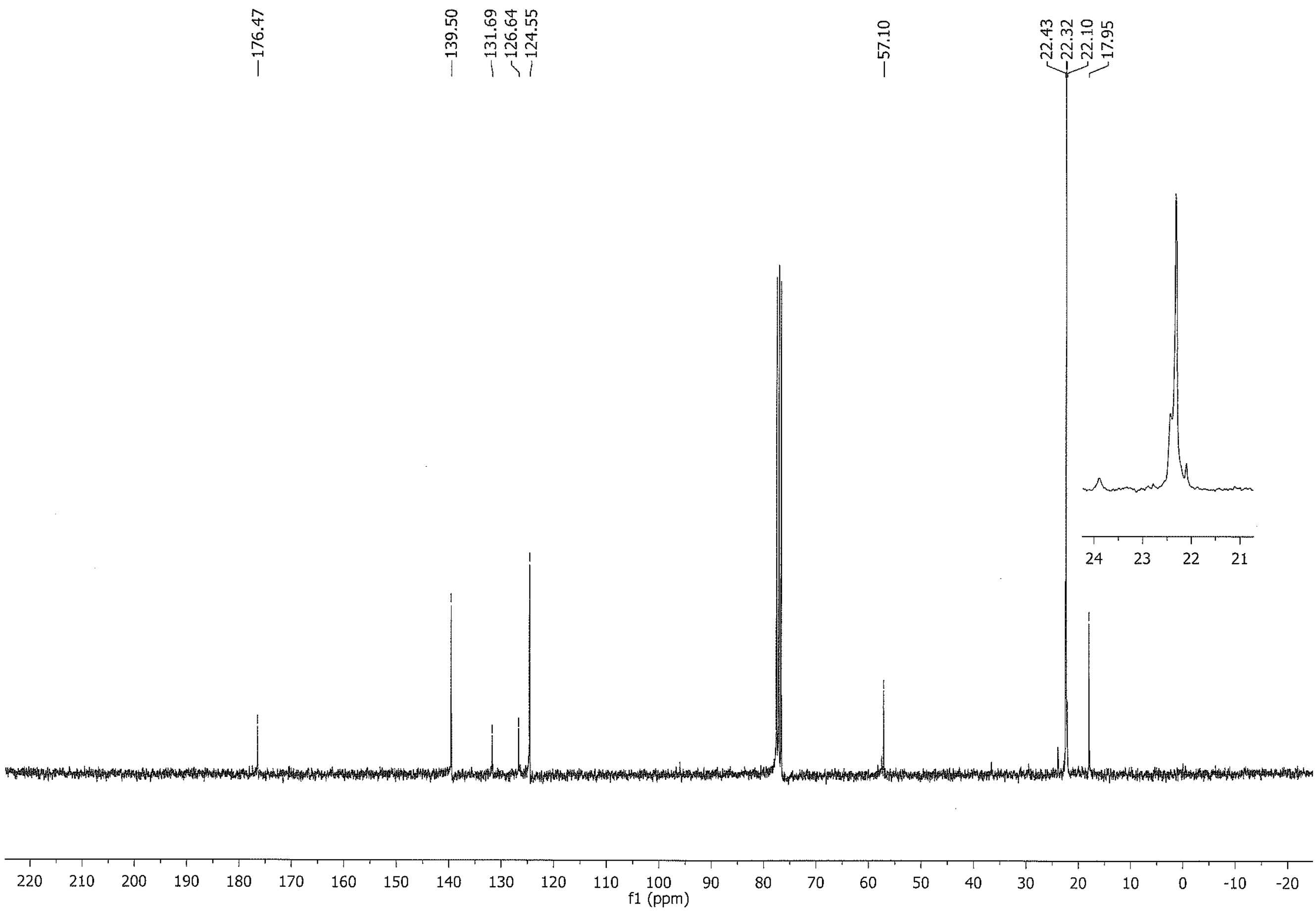

8.014
8.008
7.987
7.981
7.382
7.381
7.377
7.359
7.002
6.998
6.978
6.975
6.972
6.951
6.948
6.933
6.930
6.905
6.902
4.406
4.398
4.384
4.368
4.360
4.350
4.343
4.335
4.321
4.312
4.307
4.283
4.269
3.557
3.541
3.529
3.512
3.499
3.483
3.470
3.454
3.322
3.308
3.297
3.283
3.264
3.249
3.240
3.225
1.326
0.98
0.99
1.98
1.99
2.00
9.11
f1 (ppm)

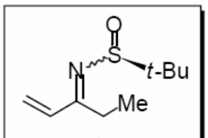

169.60
159.18
134.20
126.90
121.29
121.11
117.98
65.53
57.95
30.68
22.62
f1 (ppm)



(3:1 diastereomeric mixture)

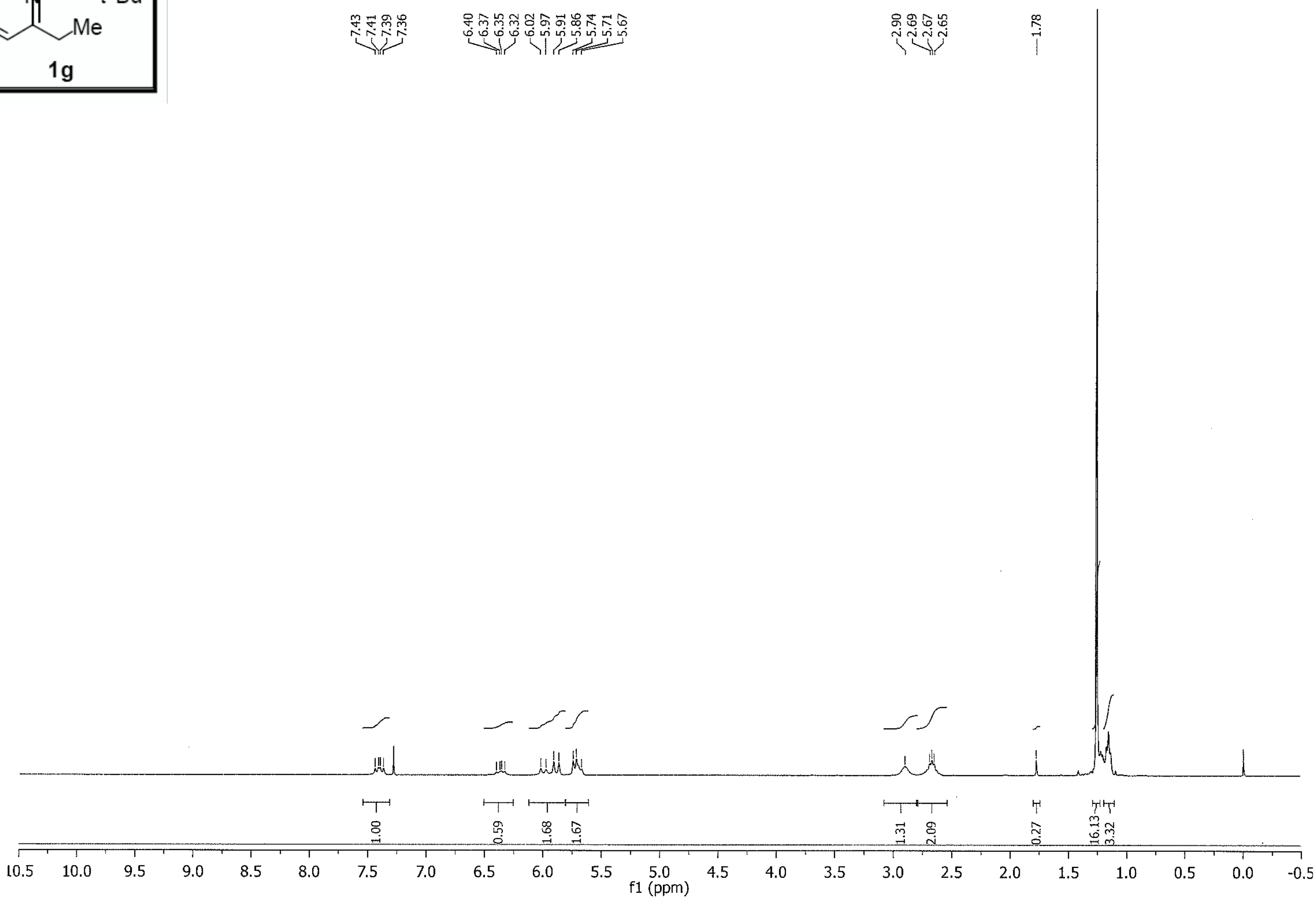


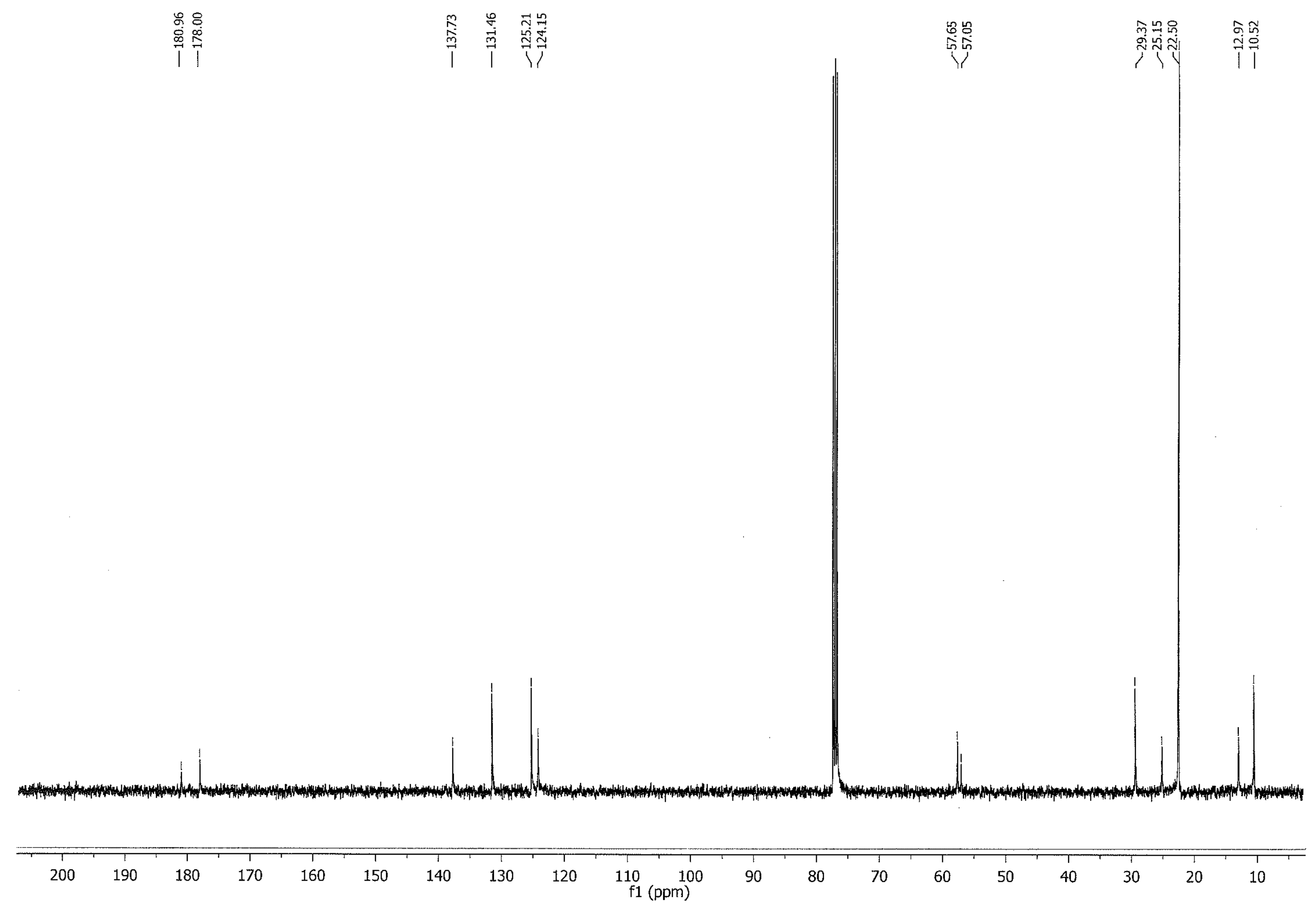


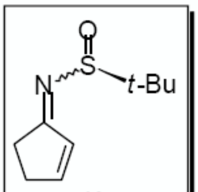


1g

(63:37 diastereomeric mixture)

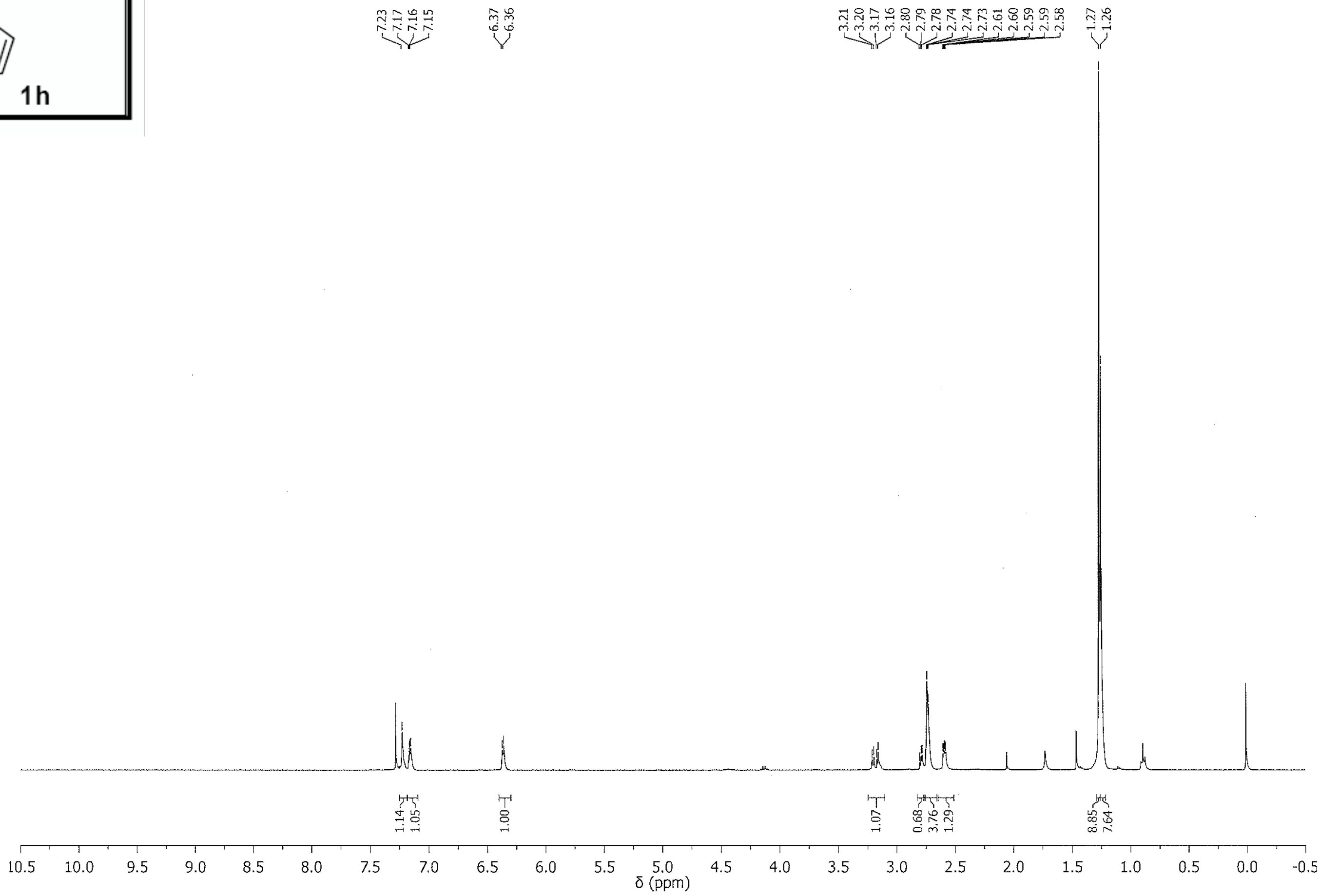


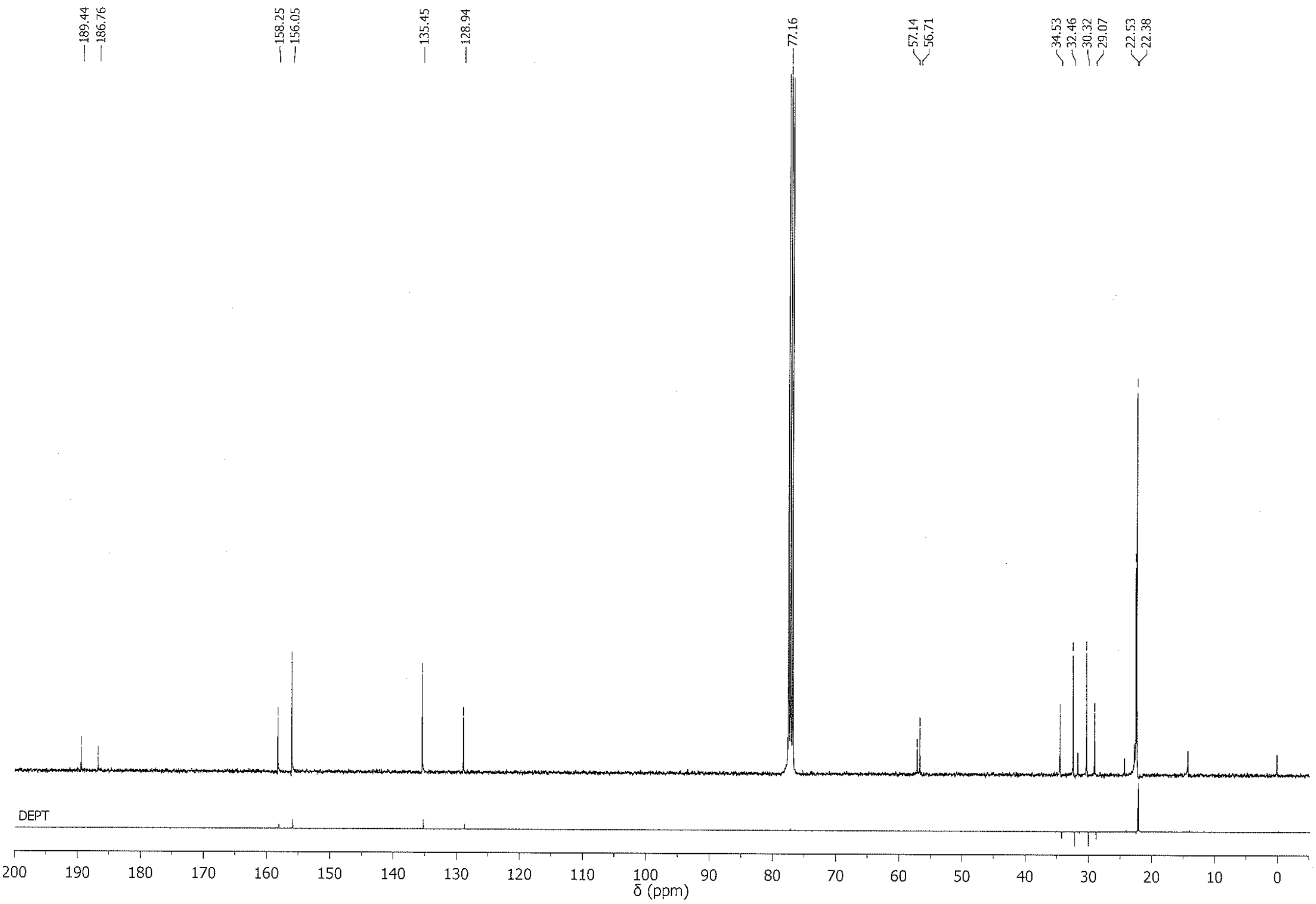


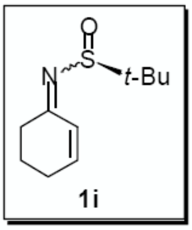


1h

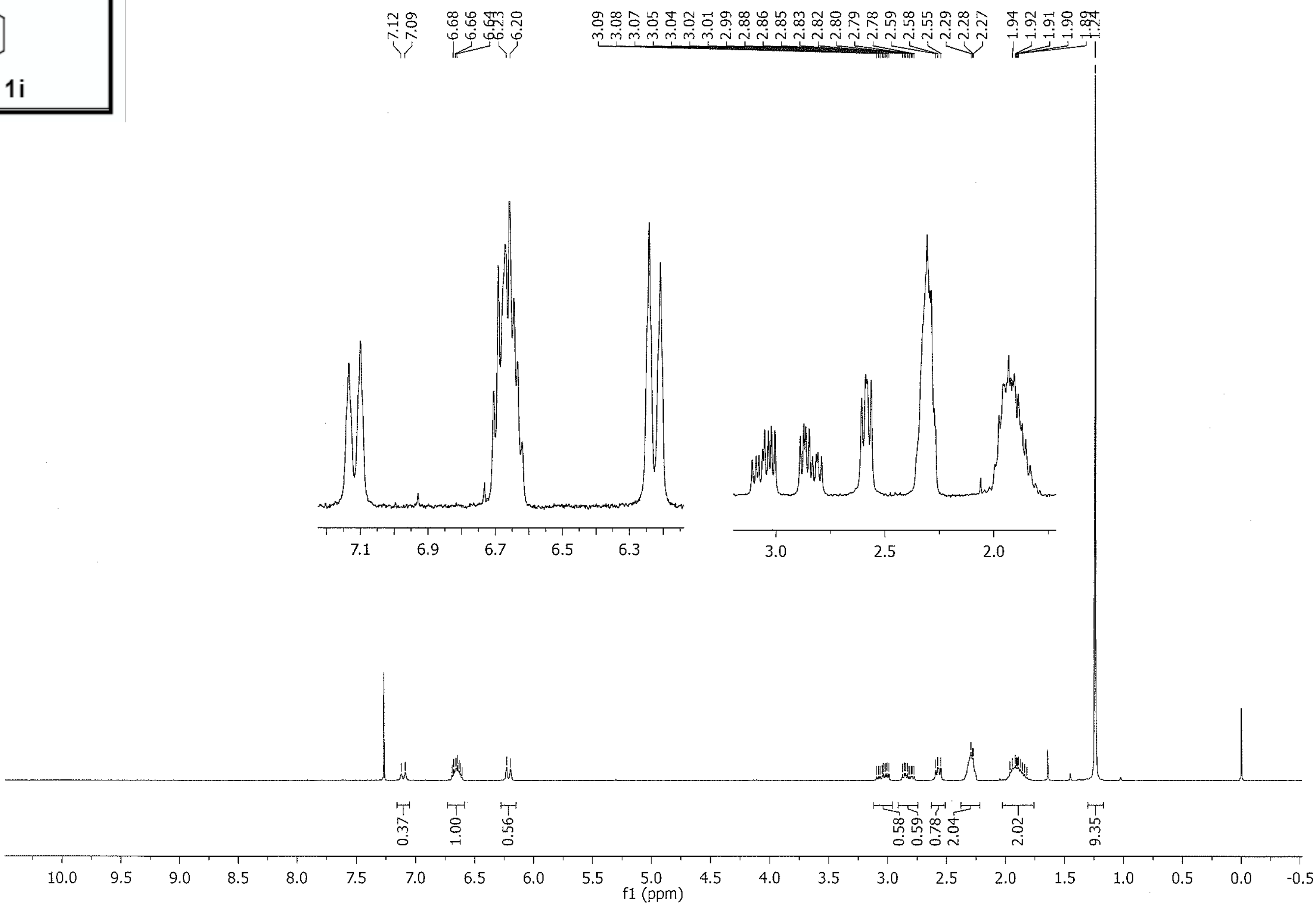
(65:35 diastereomeric mixture)

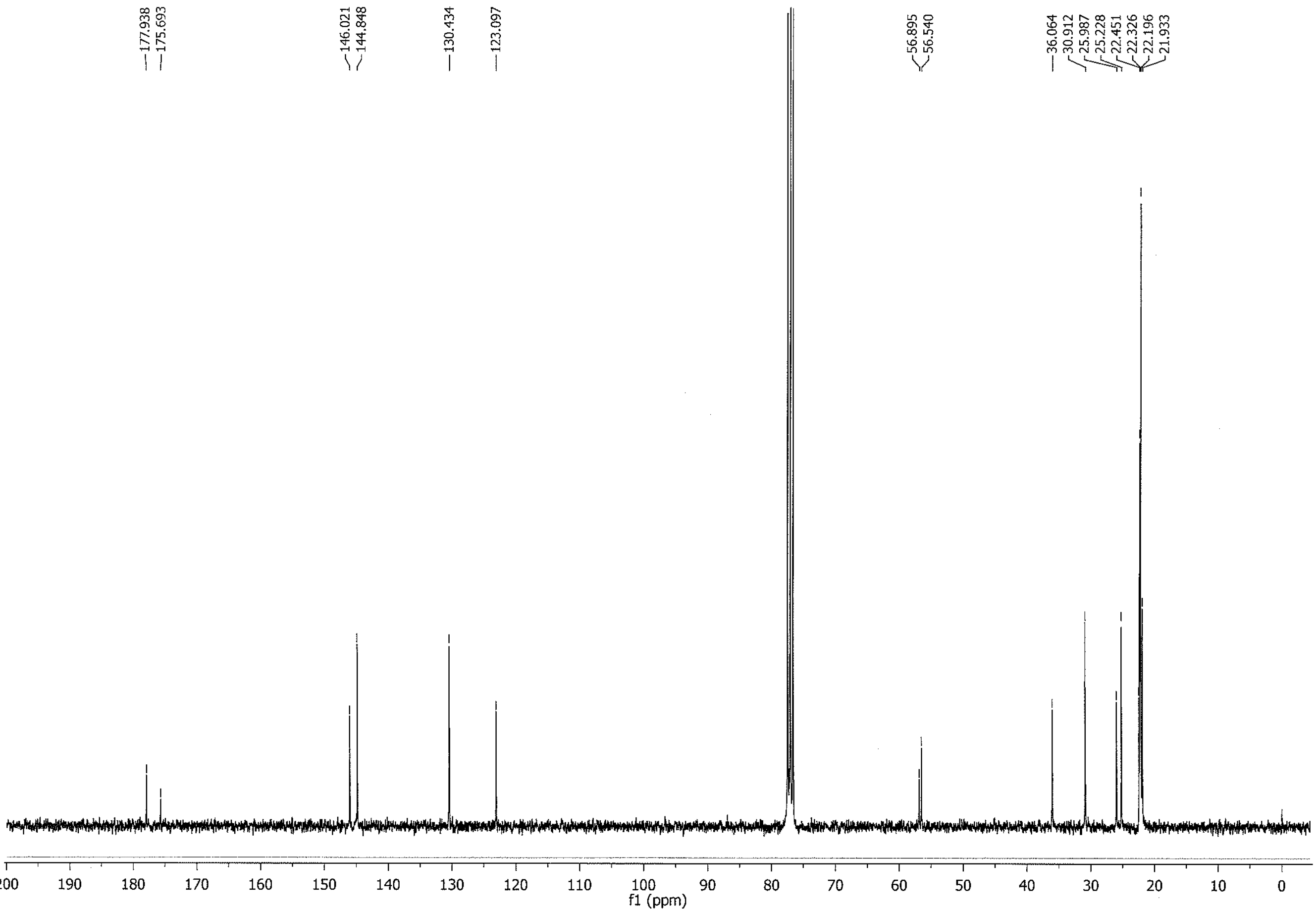




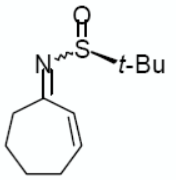


(60:40 diastereomeric mixture)

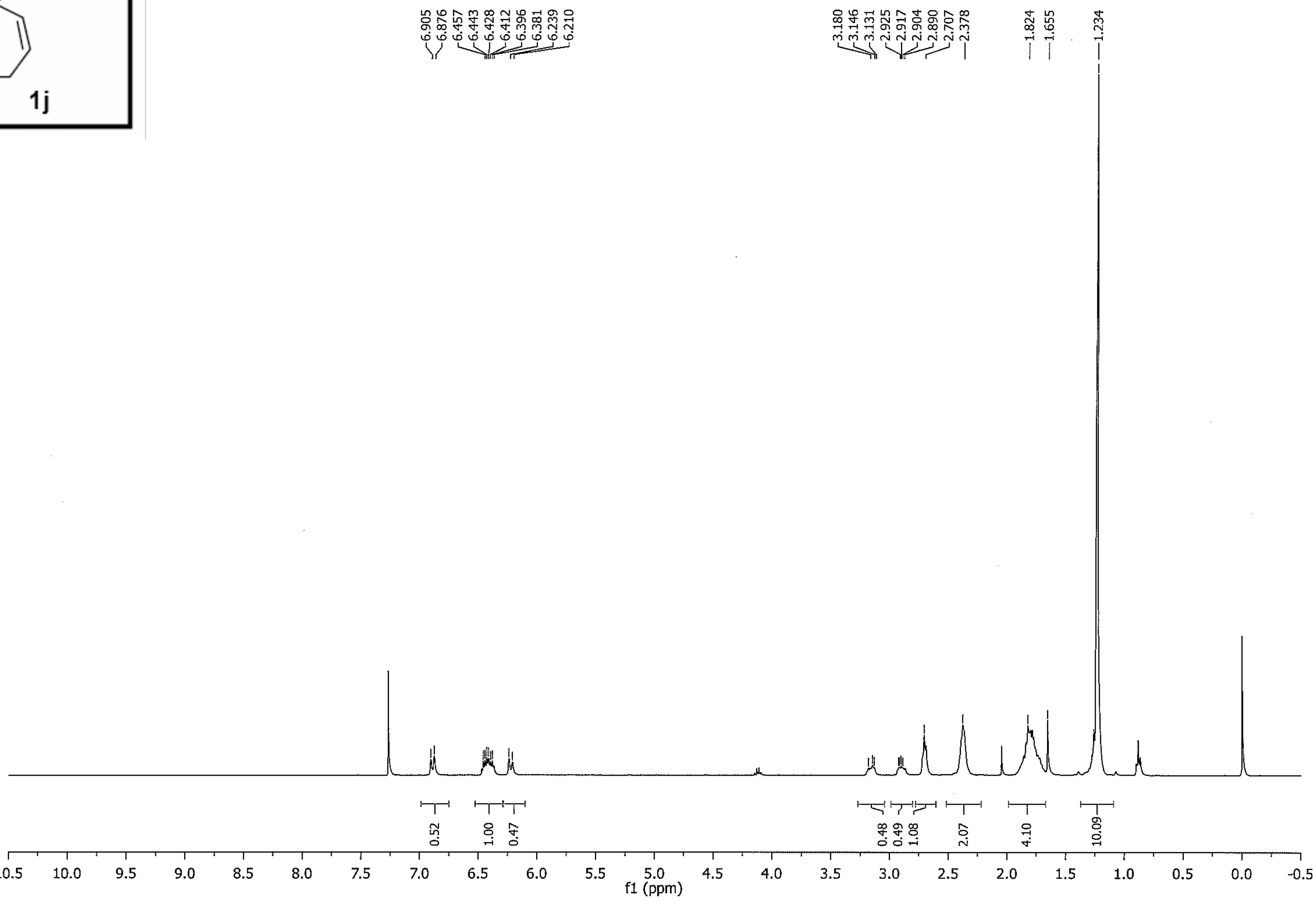


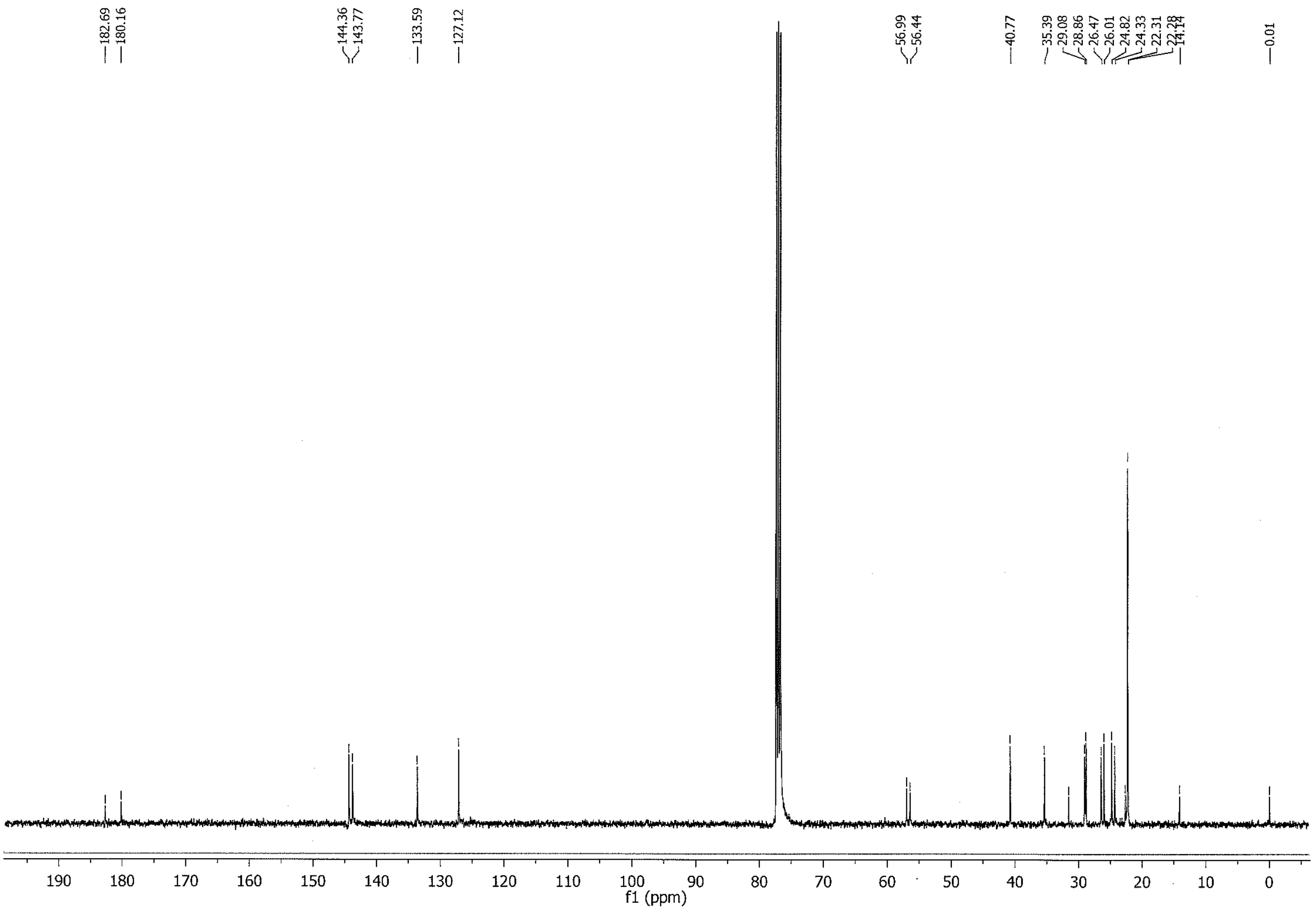


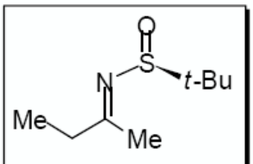
(53:47 diastereomeric mixture)



1j

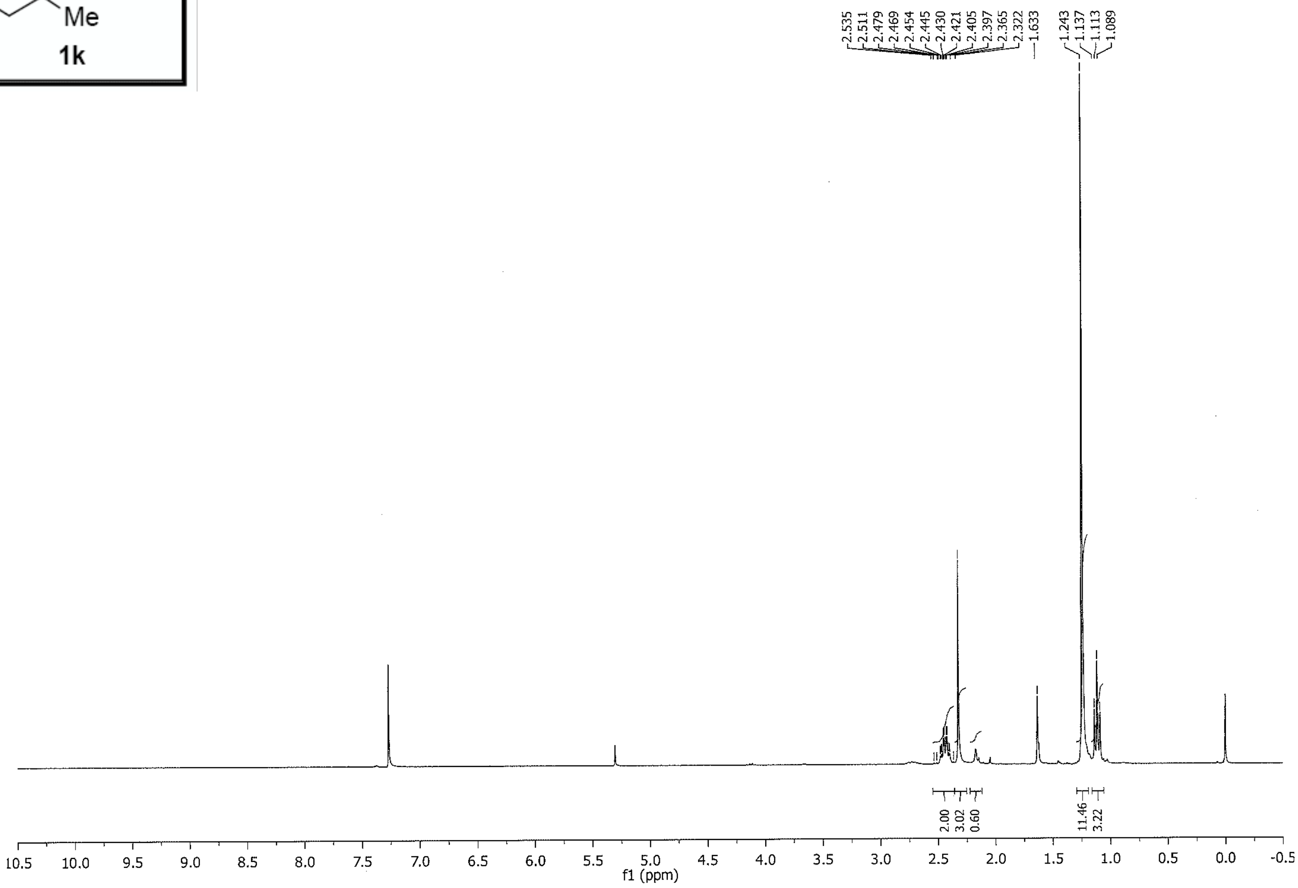


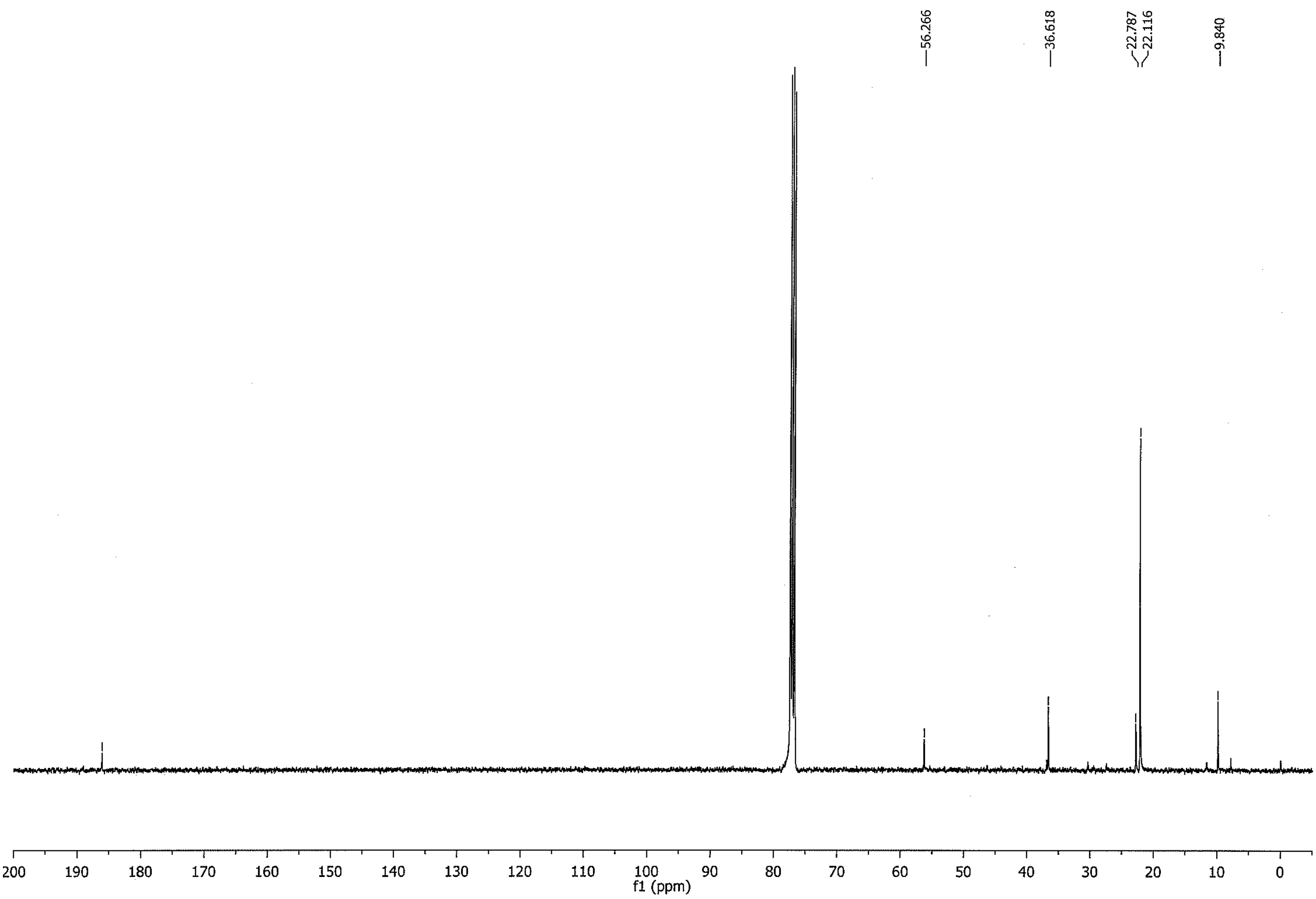


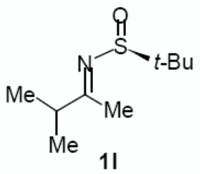


1k

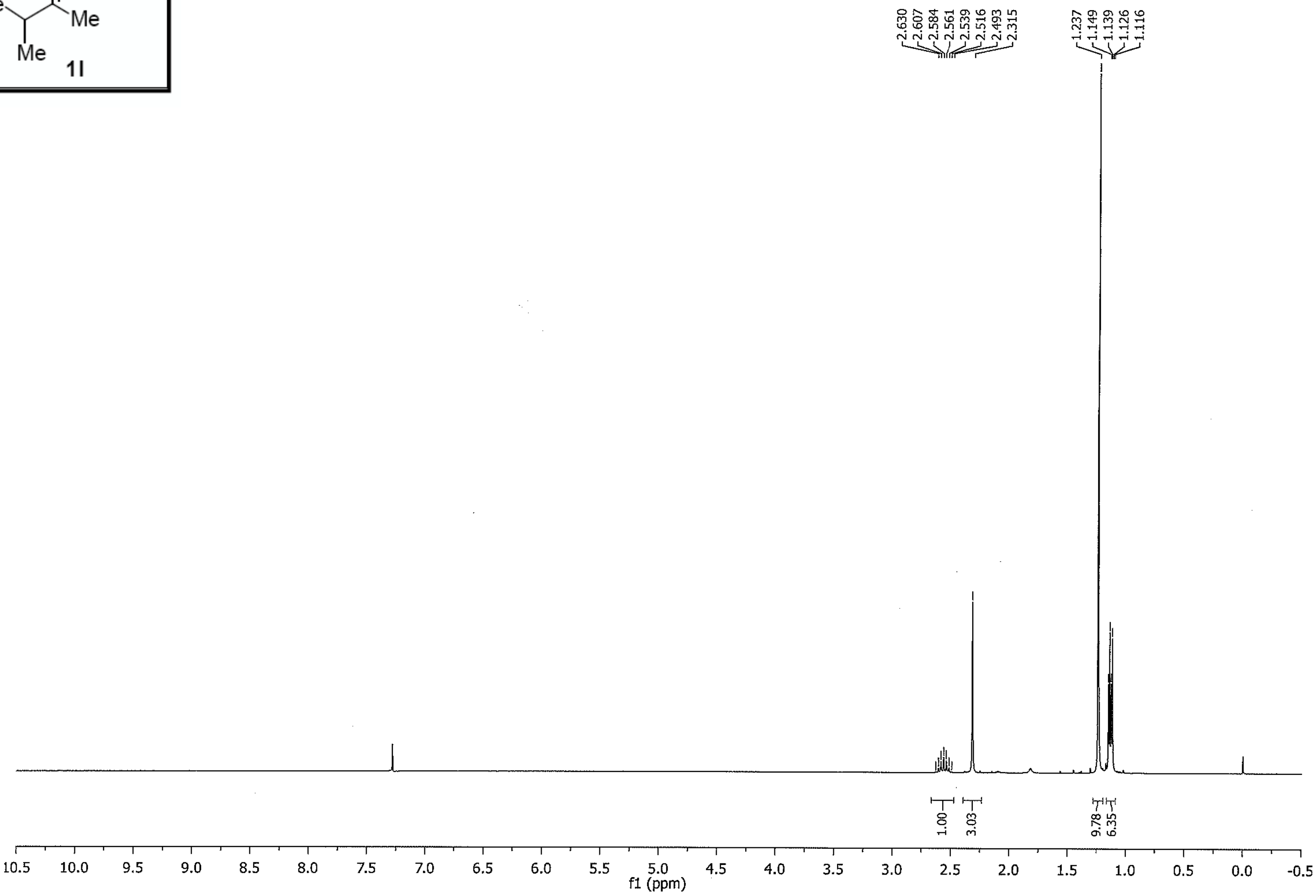
(5:1 diastereomeric mixture)

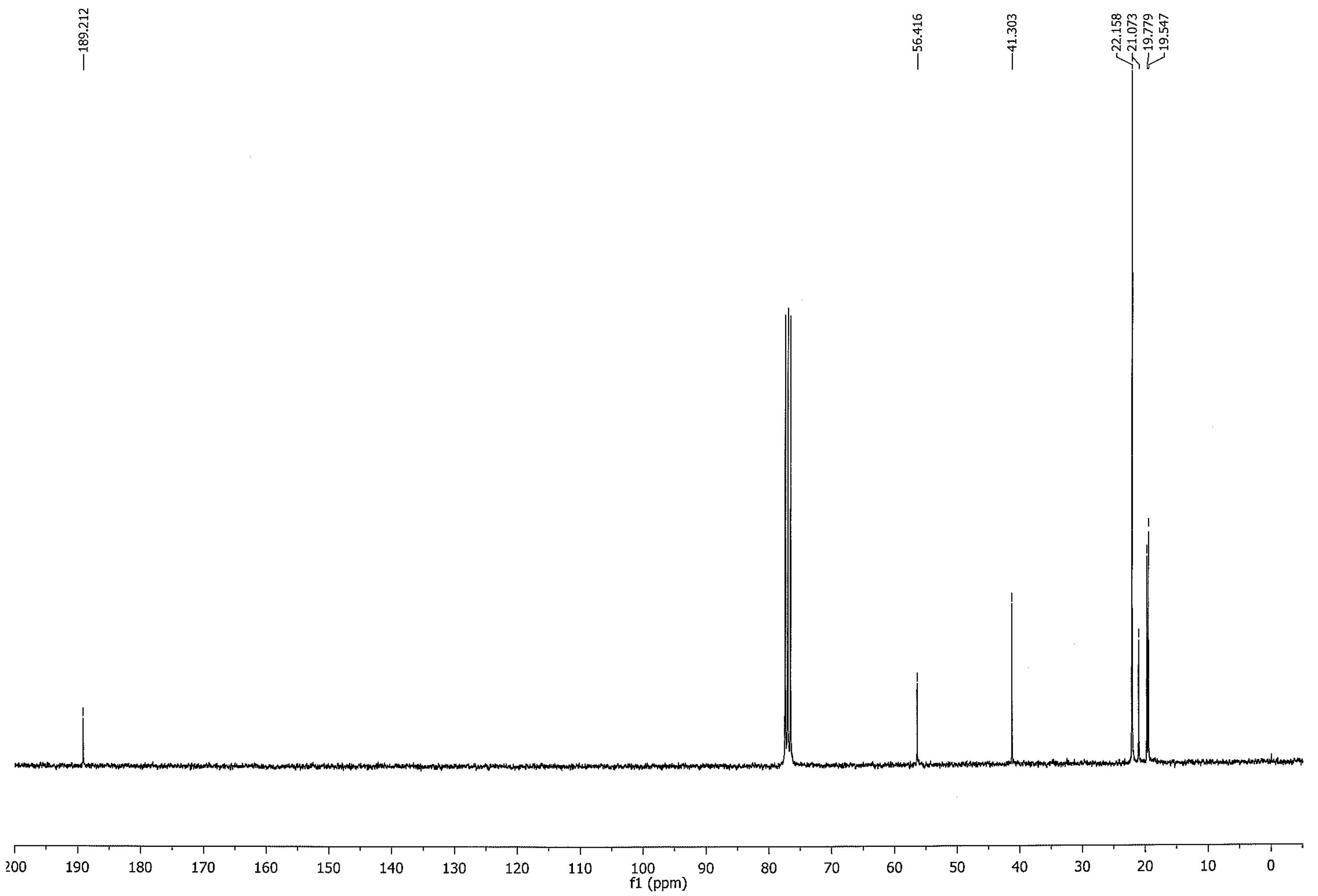




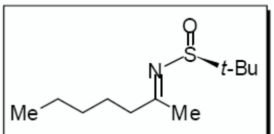

O
S
t-Bu
N
Me
Me
Me

1l

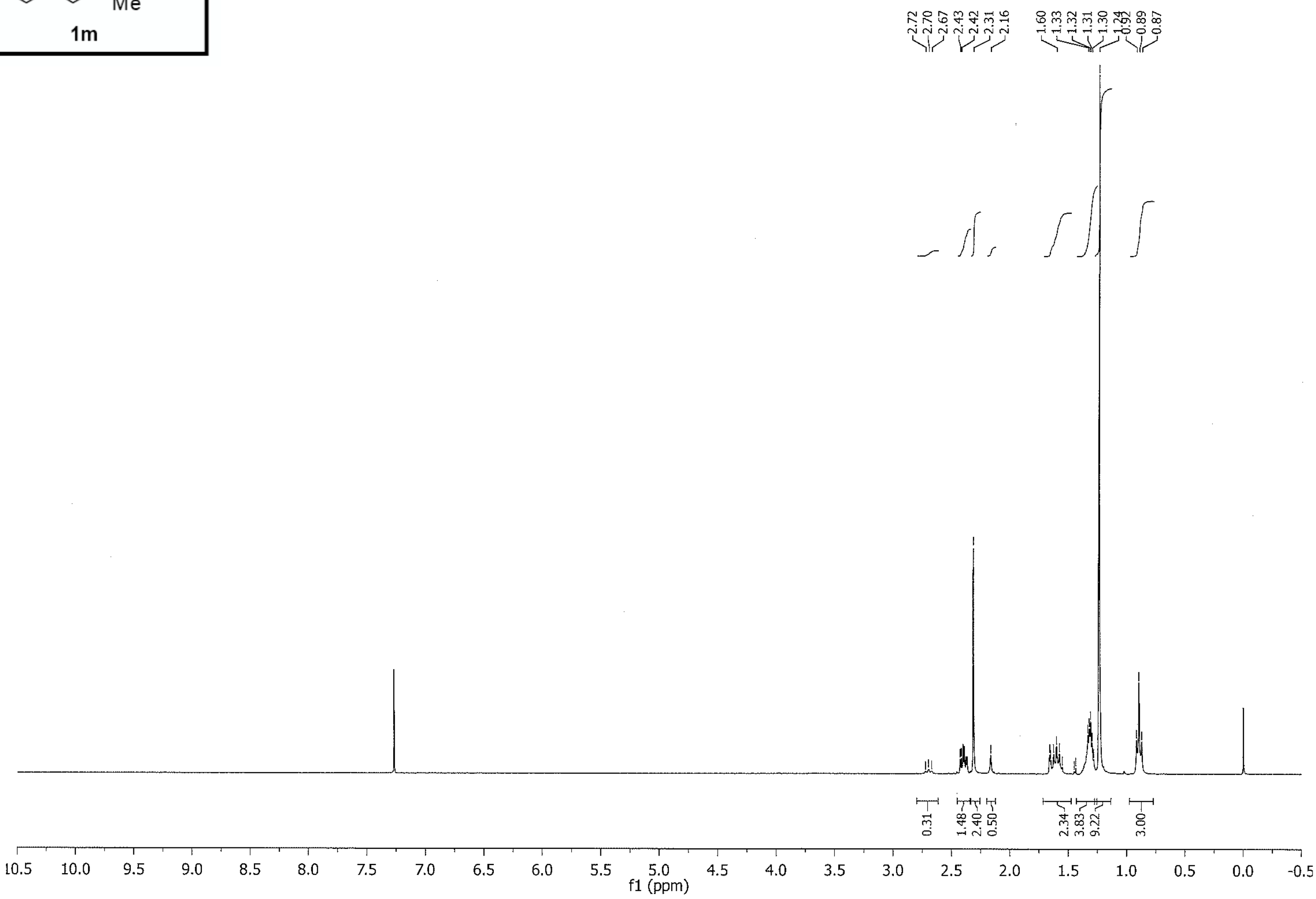

2.630
2.607
2.584
2.561
2.539
2.516
2.493
2.315
1.237
1.149
1.139
1.126
1.116
1.00
3.03
9.78
6.35
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

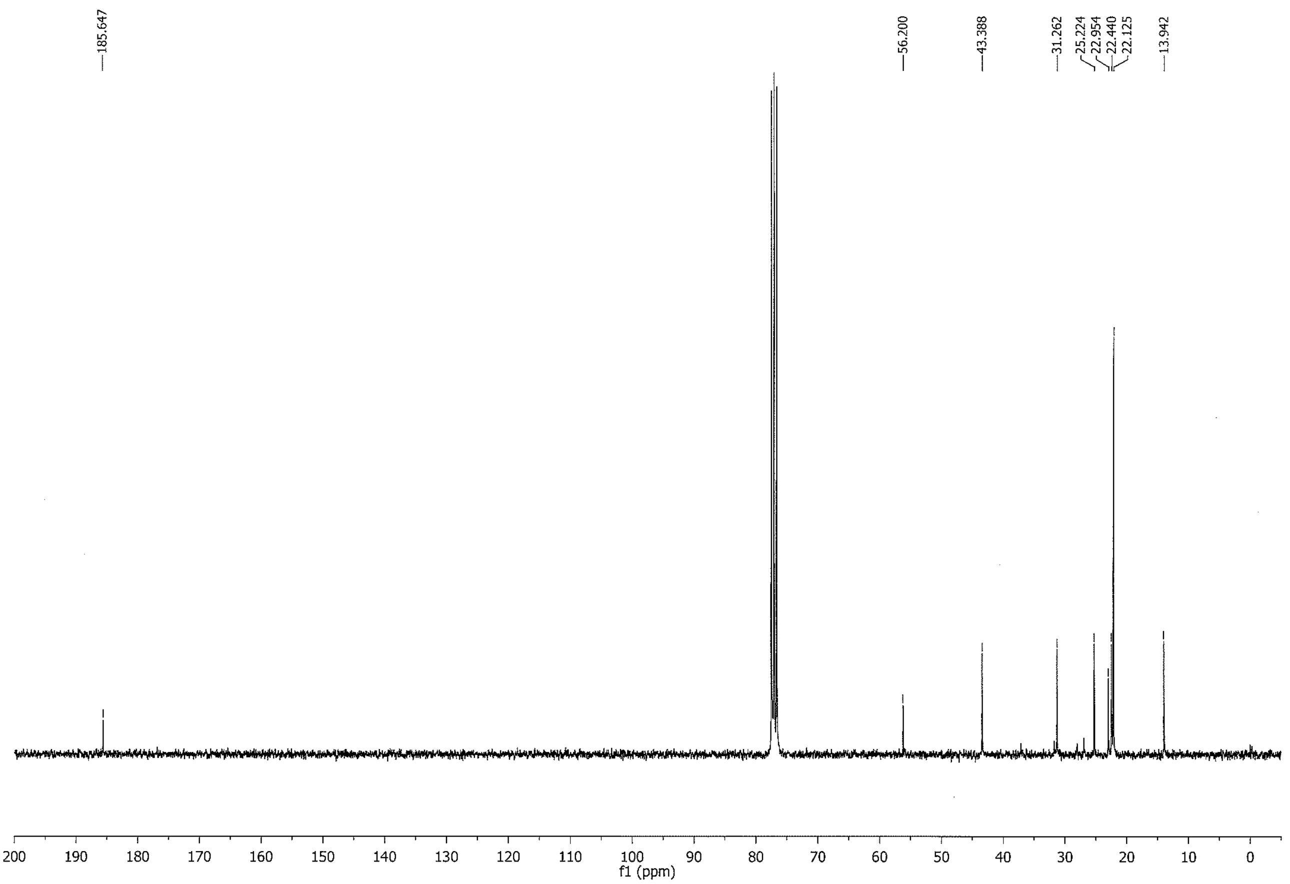

189.212
56.416
41.303
22.158
21.073
19.779
19.547
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

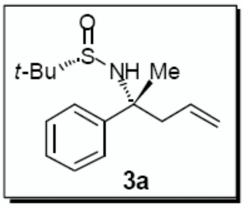
(5:1 diastereomeric mixture)



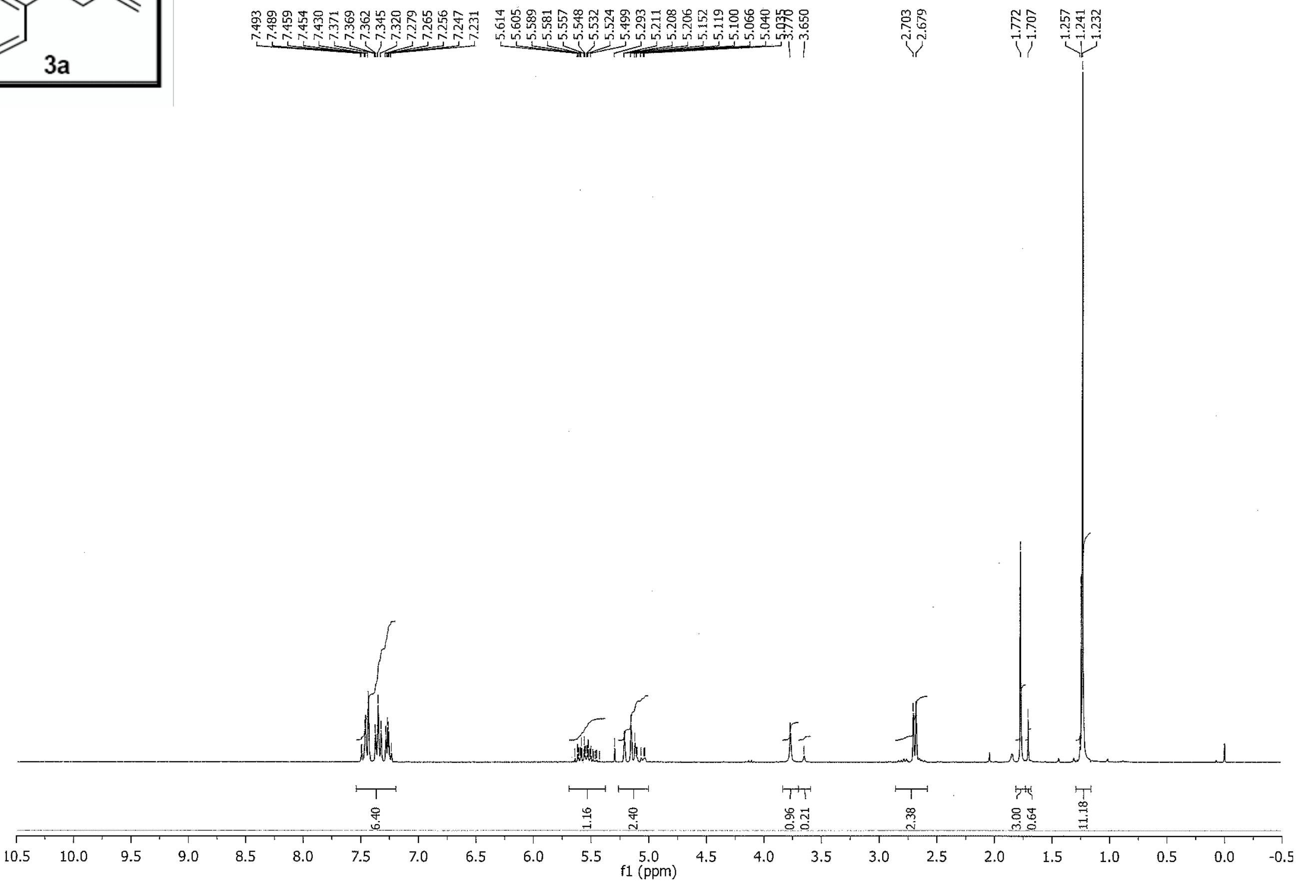
1m

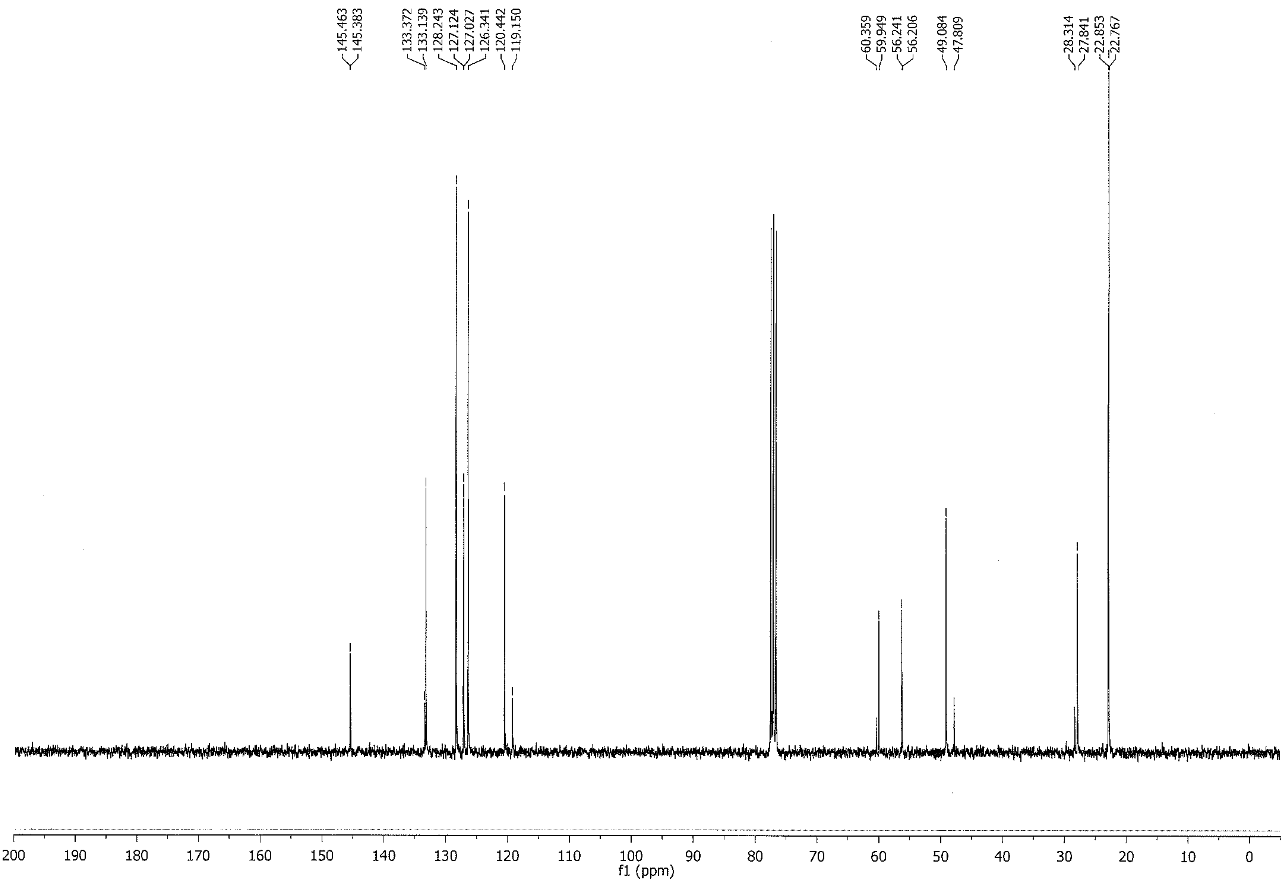


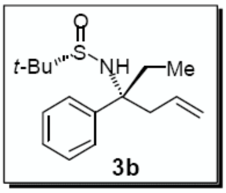




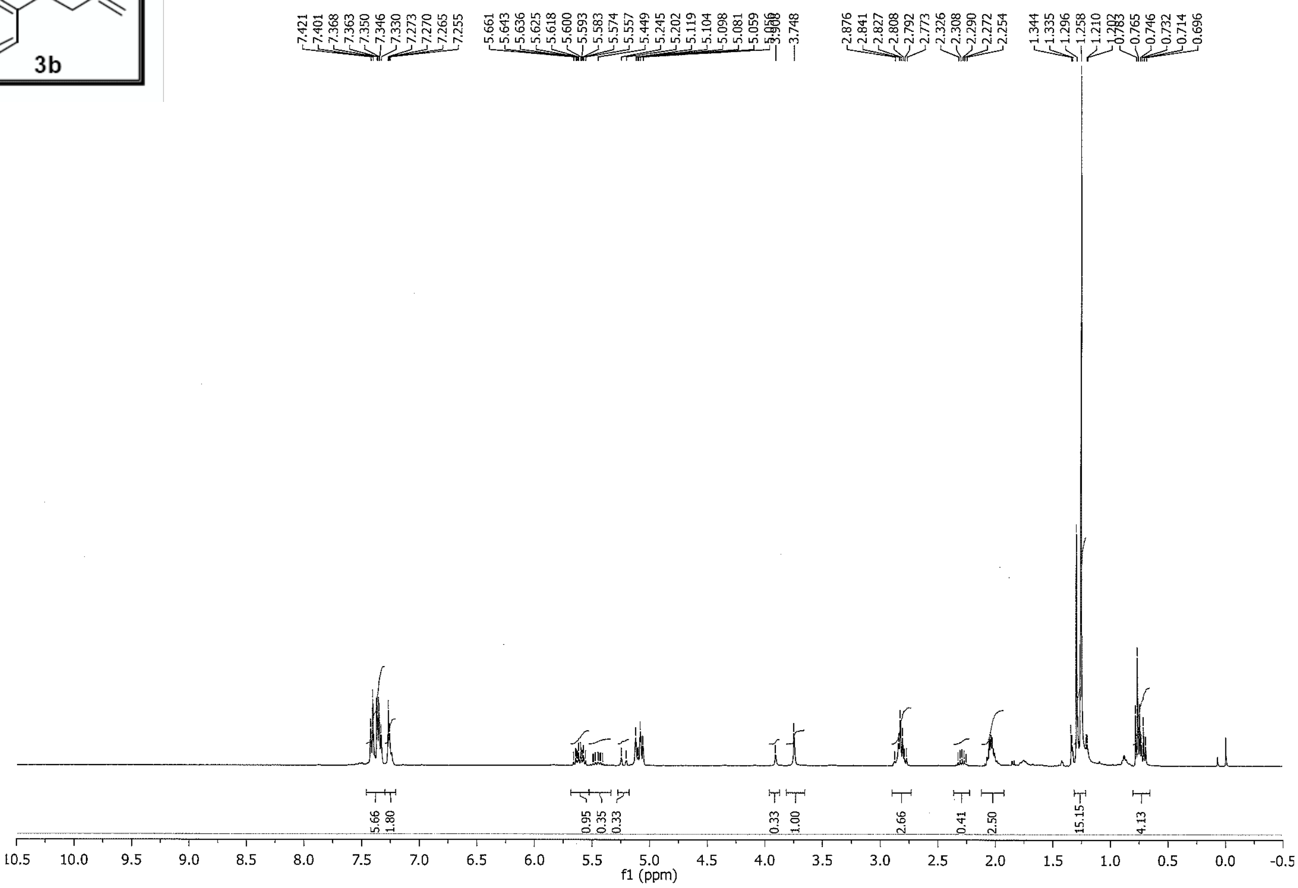
(82:18 diastereomeric mixture)

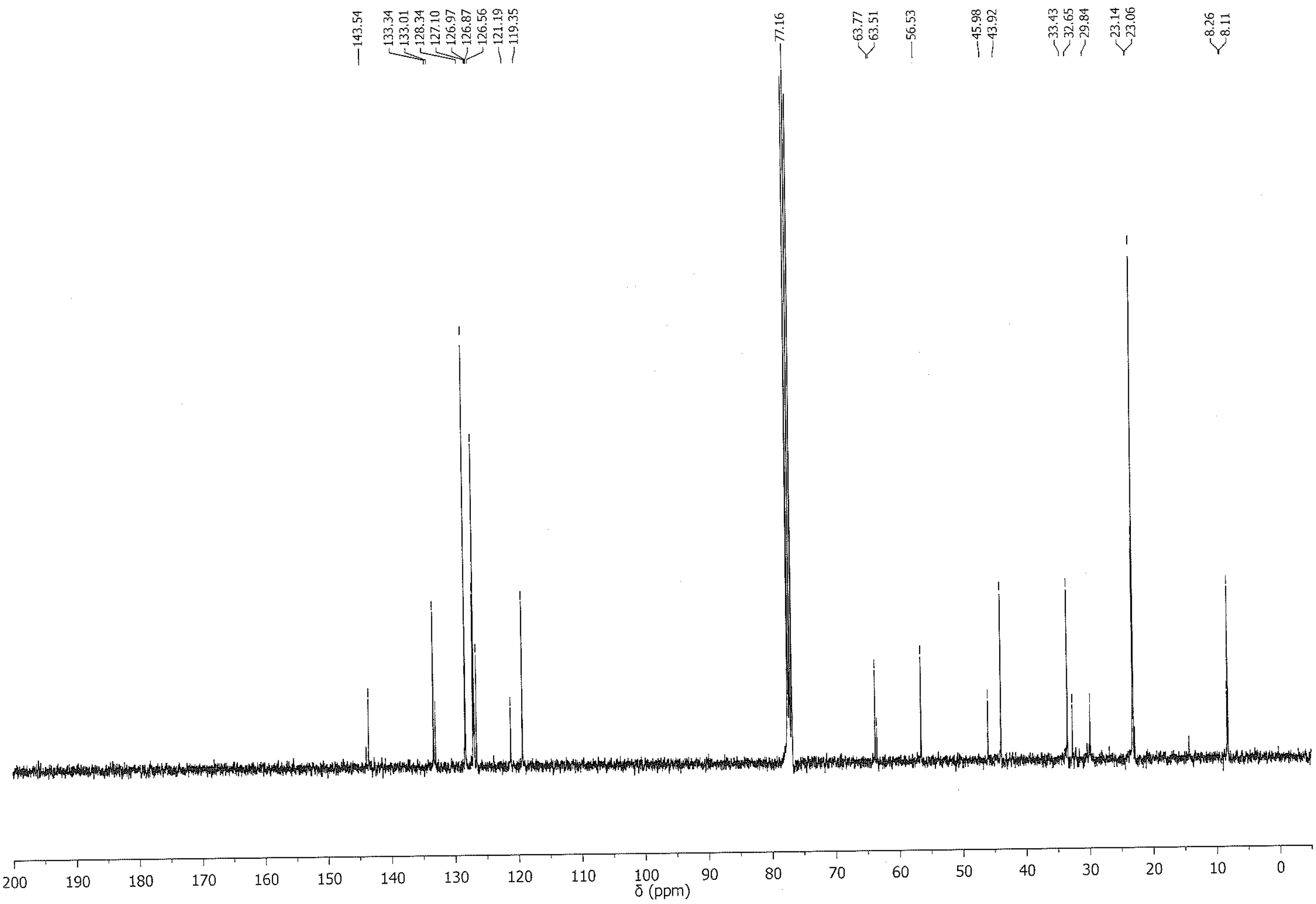


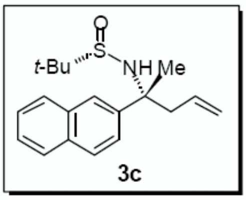


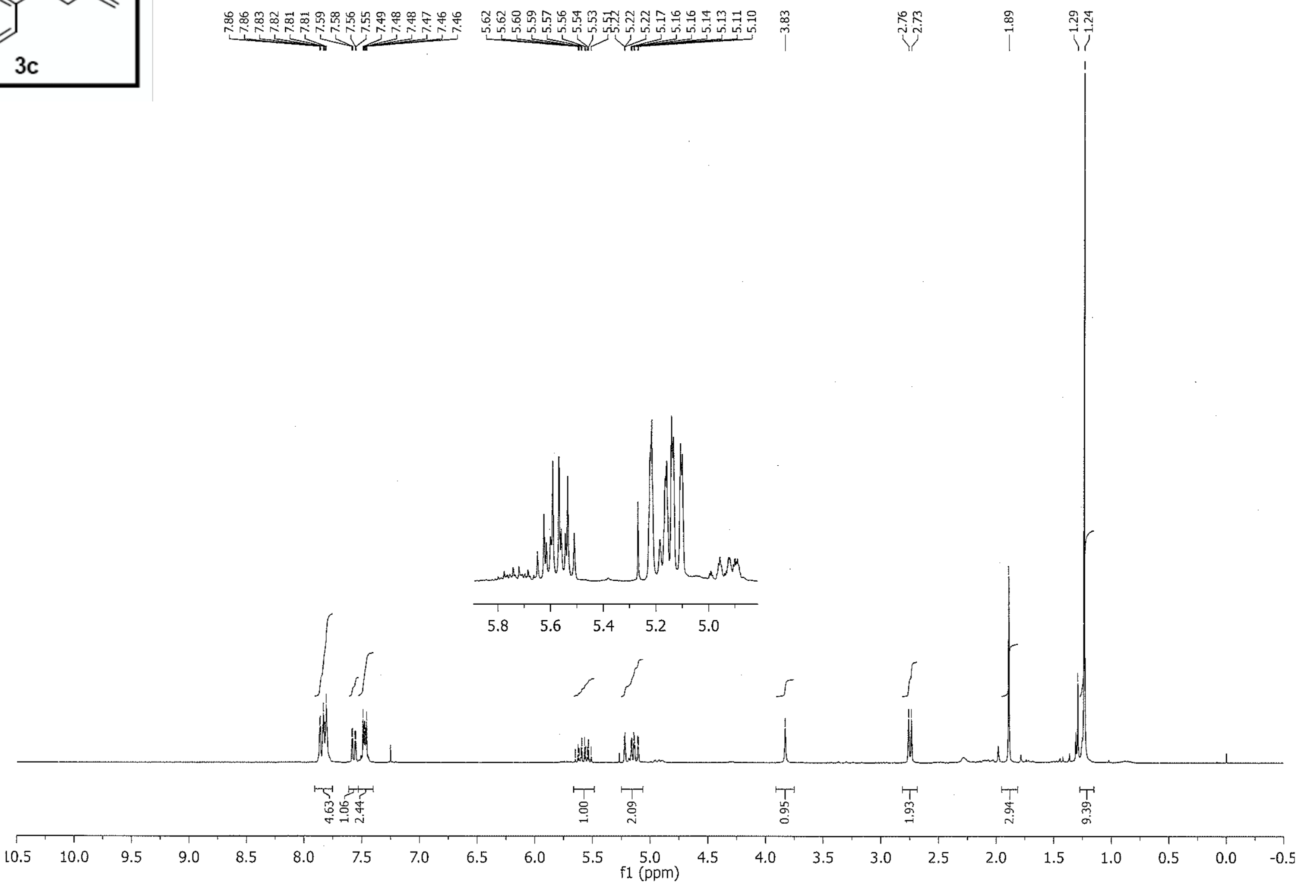


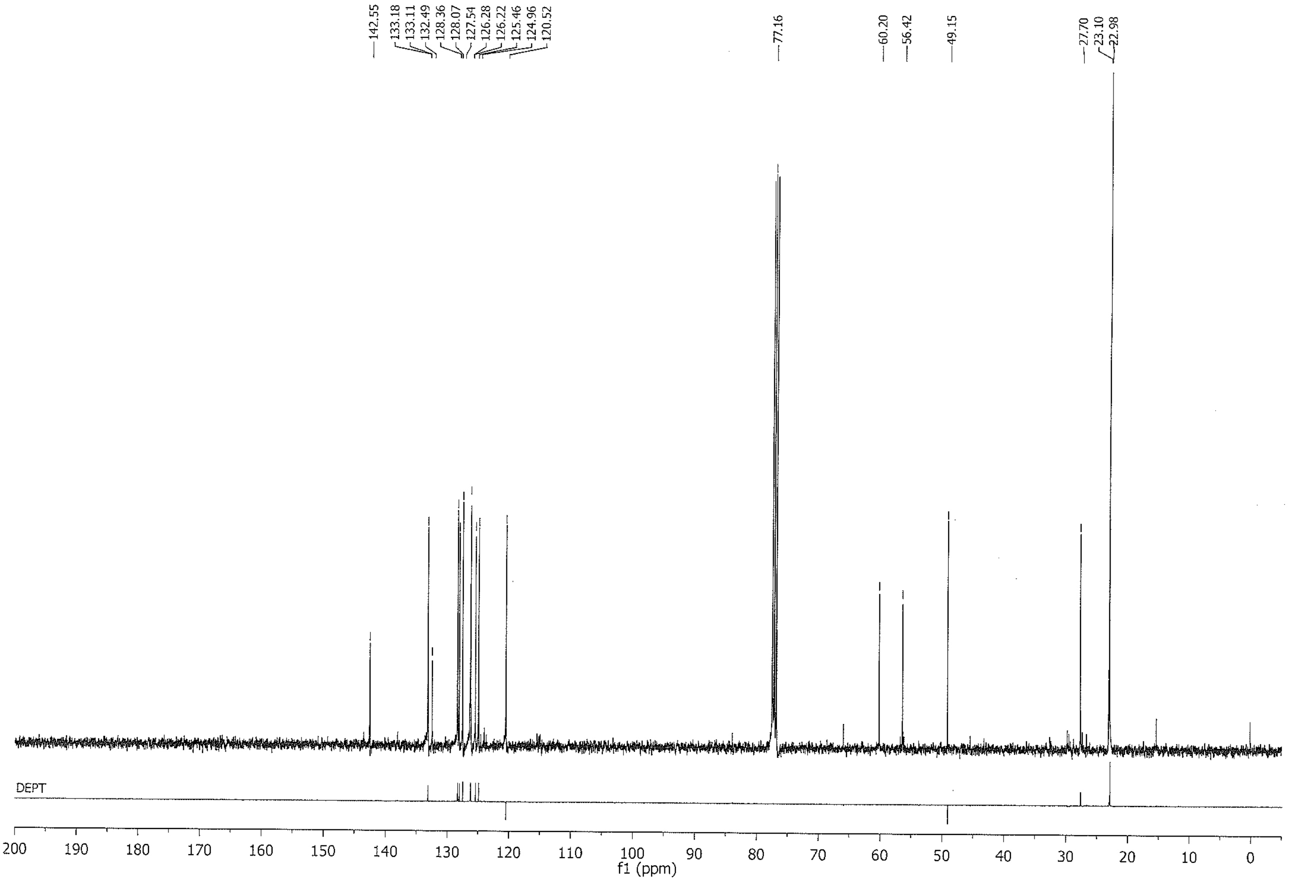
(75:25 diastereomeric mixture)

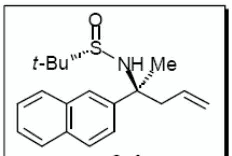




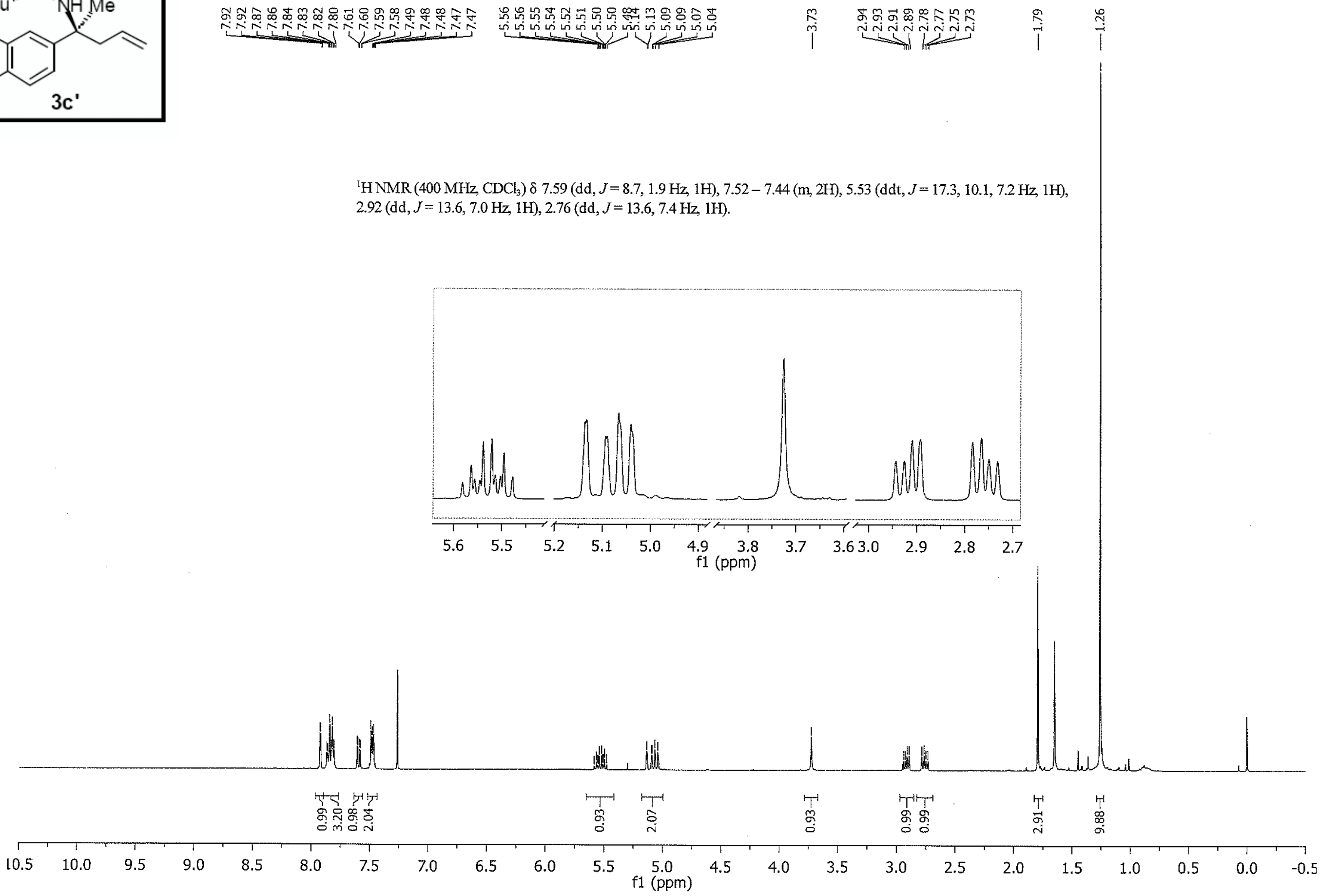

t-Bu
S
O
NH Me
3c


7.86
7.86
7.83
7.82
7.81
7.81
7.59
7.58
7.56
7.55
7.49
7.48
7.48
7.47
7.46
7.46
5.62
5.62
5.60
5.59
5.57
5.56
5.54
5.53
5.51
5.22
5.22
5.22
5.17
5.16
5.16
5.14
5.13
5.11
5.10
3.83
2.76
2.73
1.89
1.29
1.24
5.8 5.6 5.4 5.2 5.0
4.63
1.06
2.44
1.00
2.09
0.95
1.93
2.94
9.39
10.5 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
f1 (ppm)

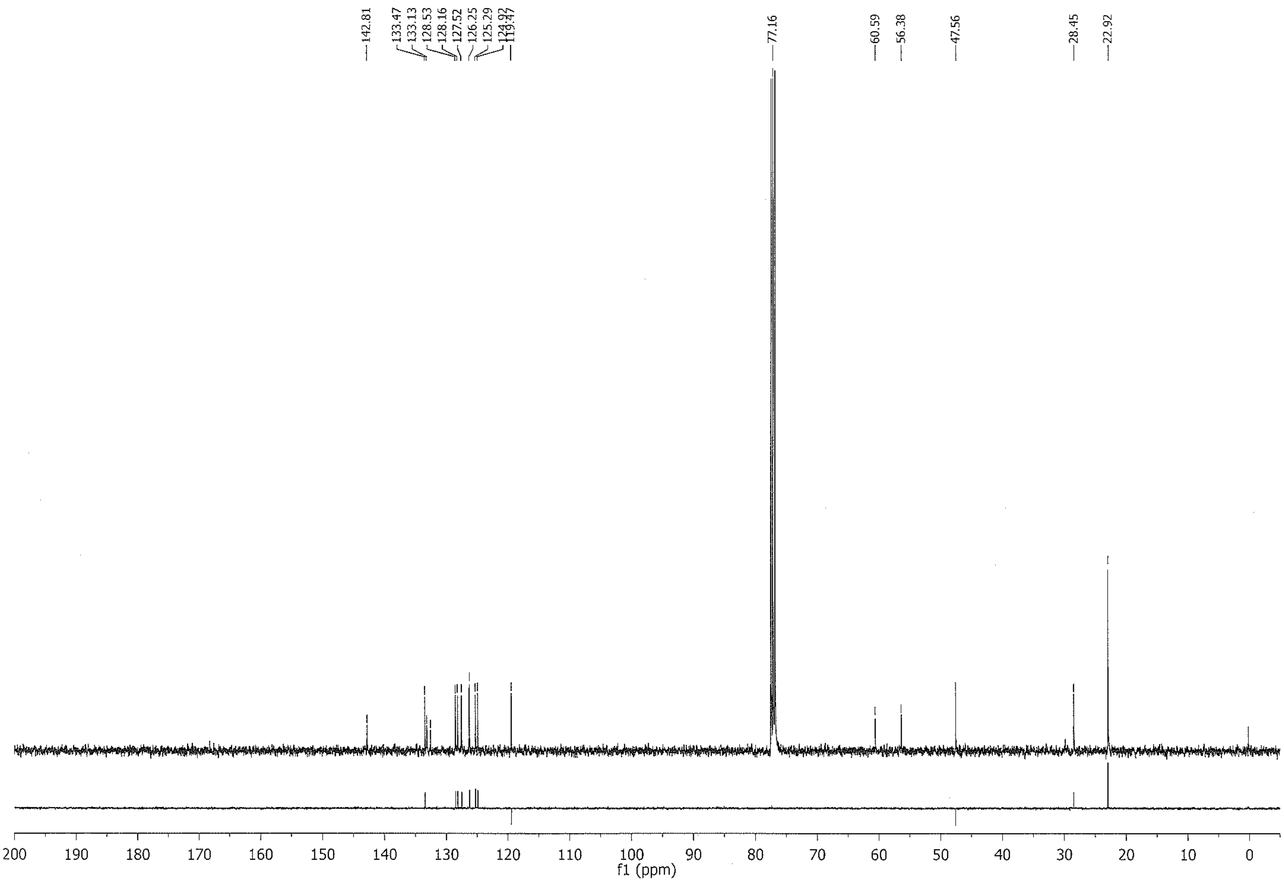

142.55
133.18
133.11
132.49
128.36
128.07
127.54
126.28
126.22
125.46
124.96
120.52
77.16
60.20
56.42
49.15
27.70
23.10
22.98
DEPT
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



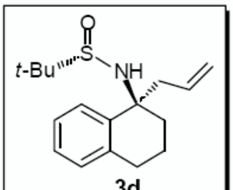
3c'



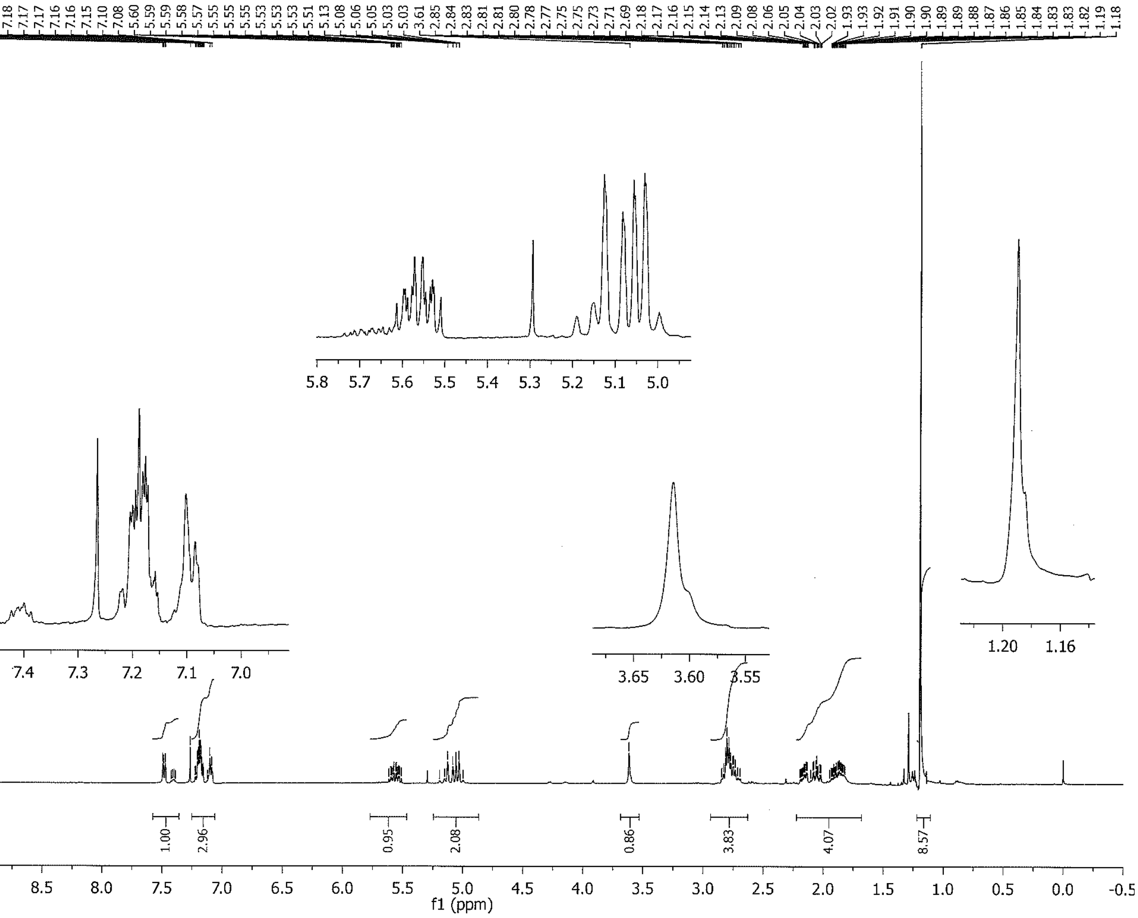
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.7, 1.9 Hz, 1H), 7.52 – 7.44 (m, 2H), 5.53 (ddt, J = 17.3, 10.1, 7.2 Hz, 1H), 2.92 (dd, J = 13.6, 7.0 Hz, 1H), 2.76 (dd, J = 13.6, 7.4 Hz, 1H).

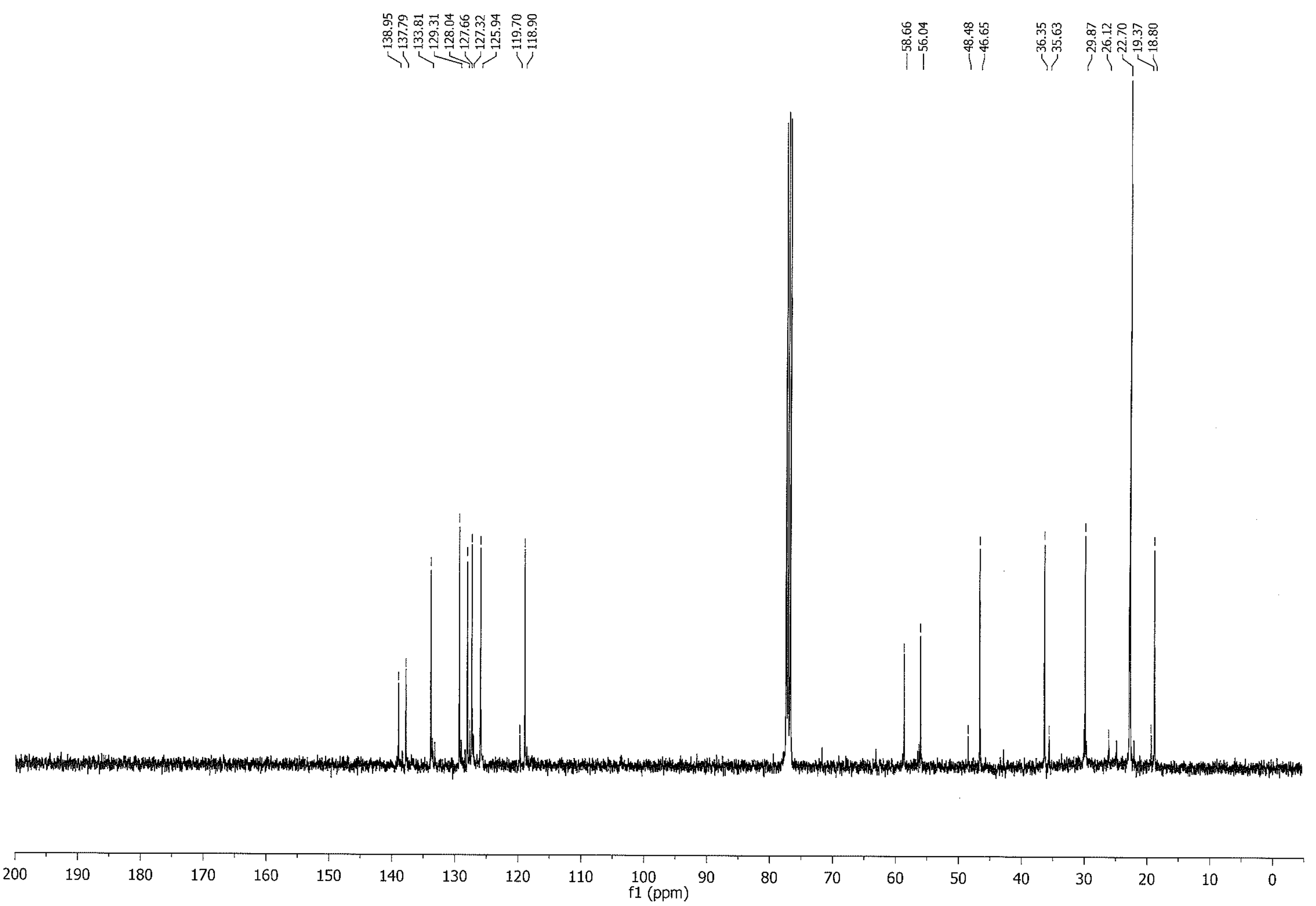


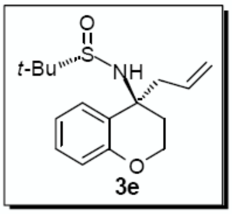
(80:20 diastereomeric mixture)



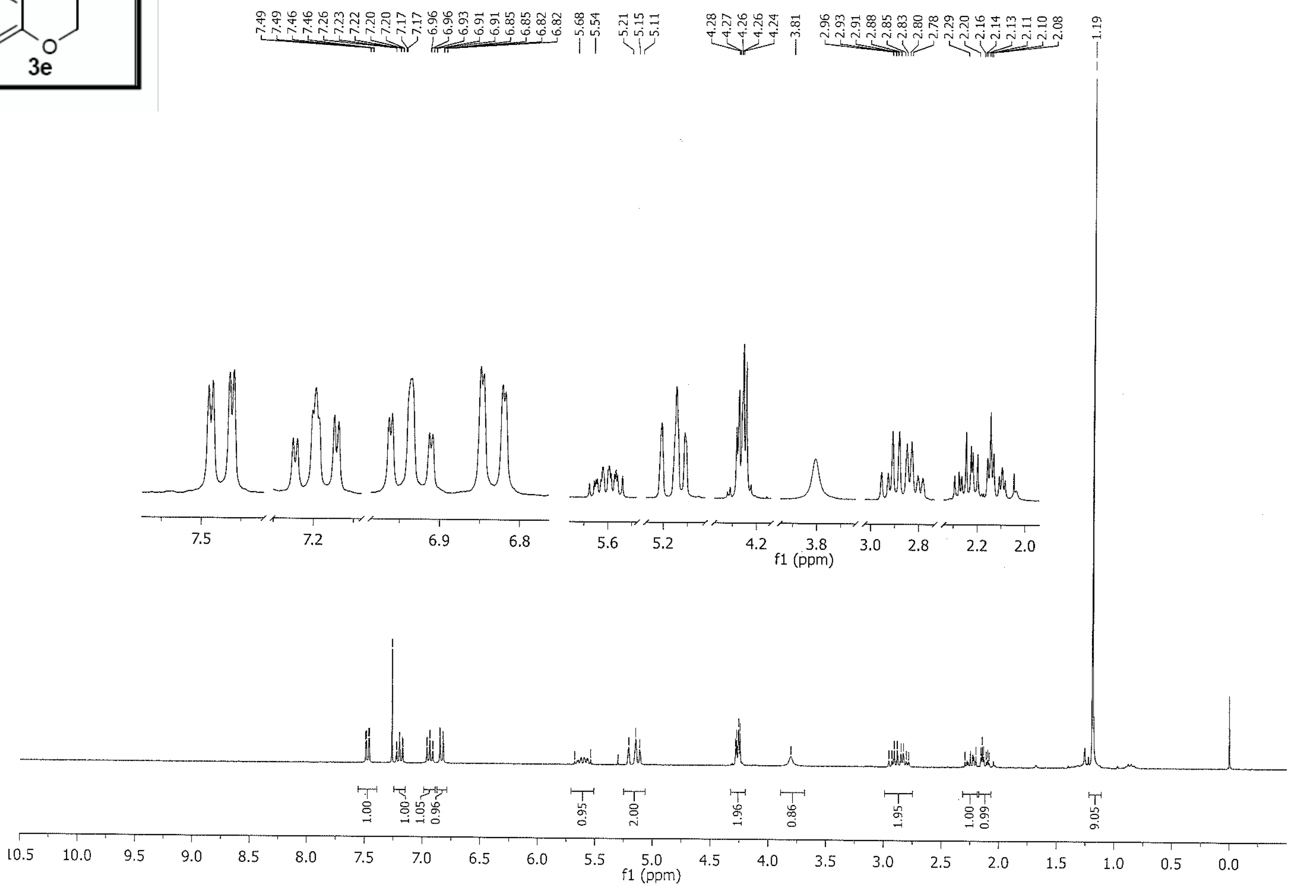
3d

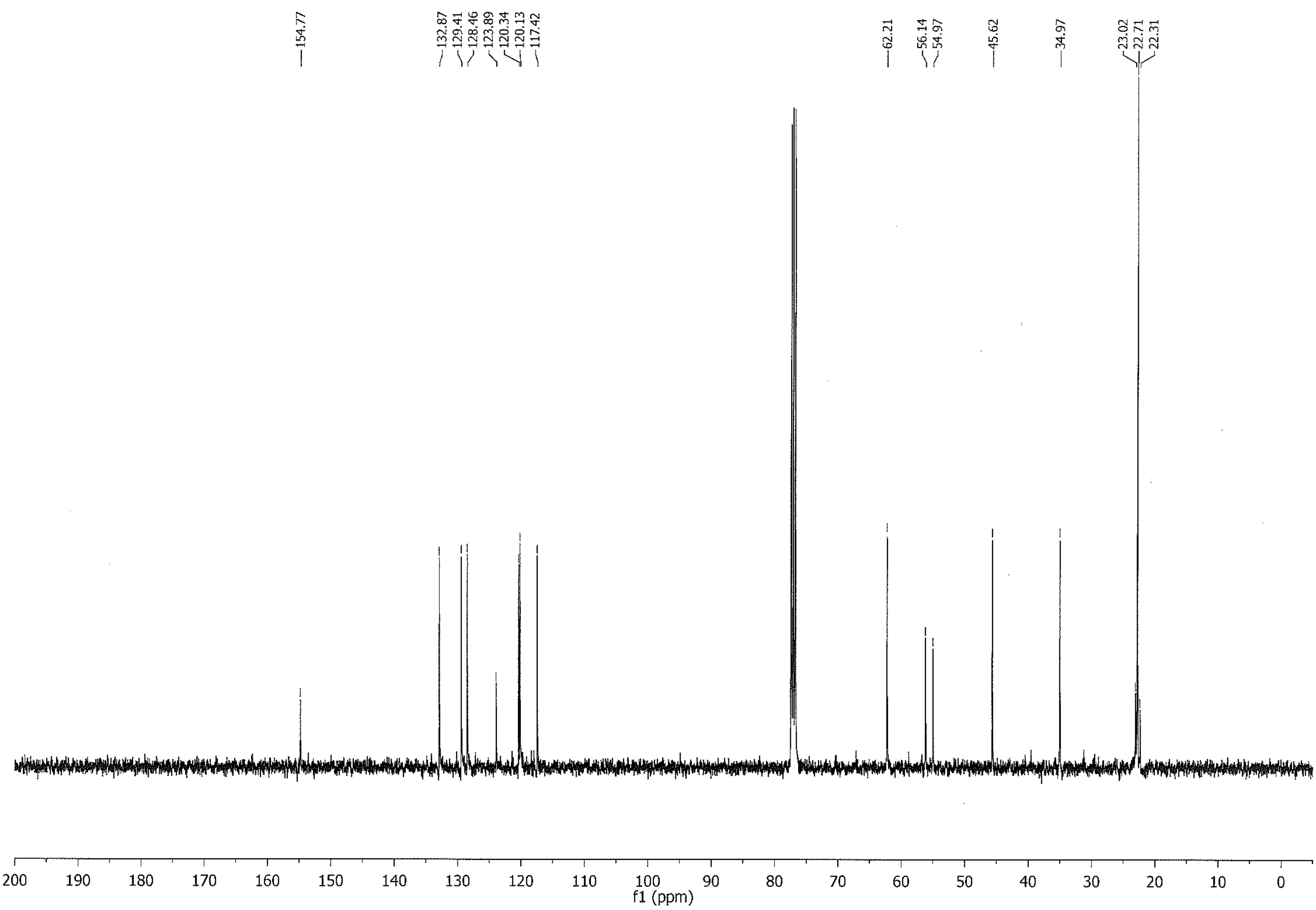


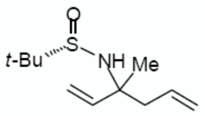




(85:15 diastereomeric mixture)

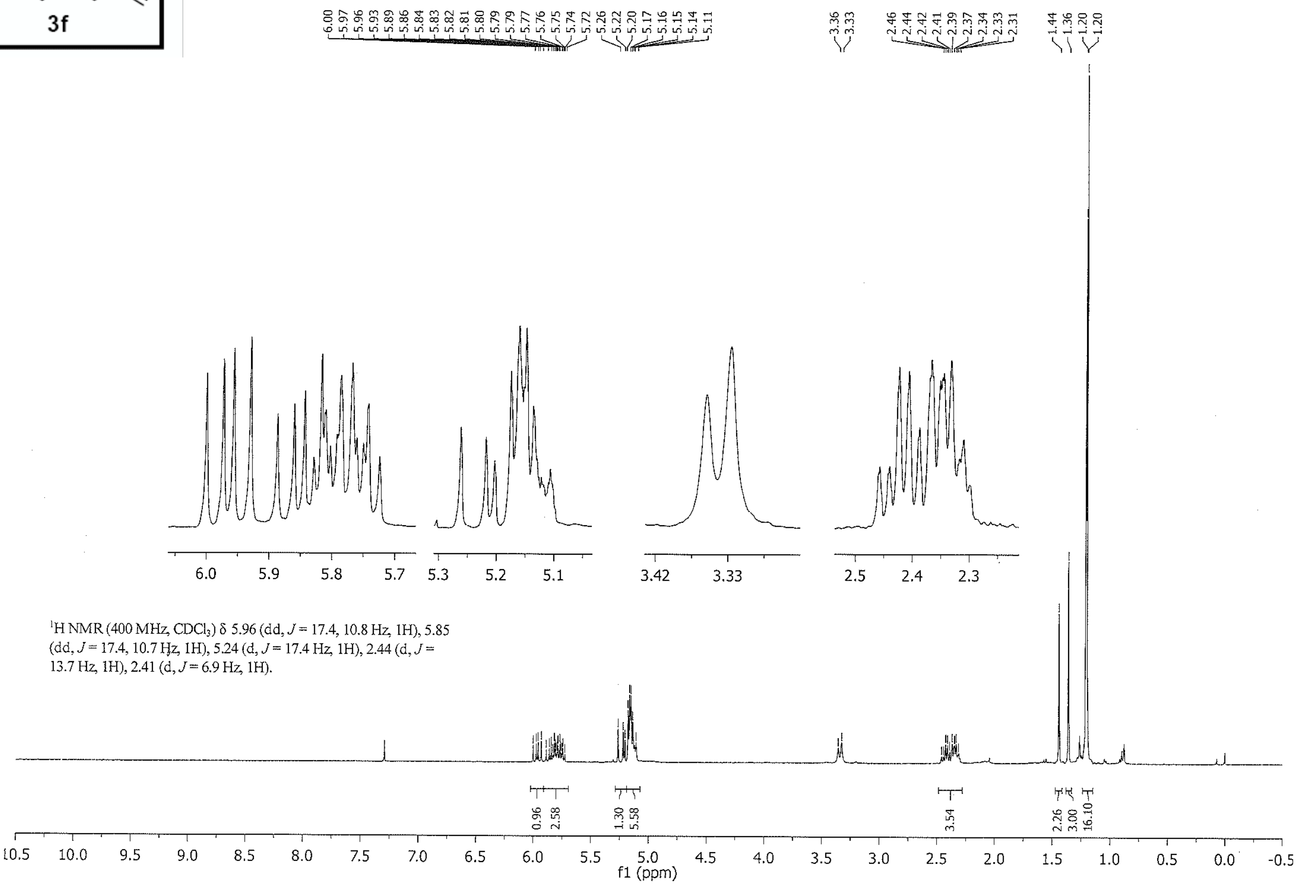




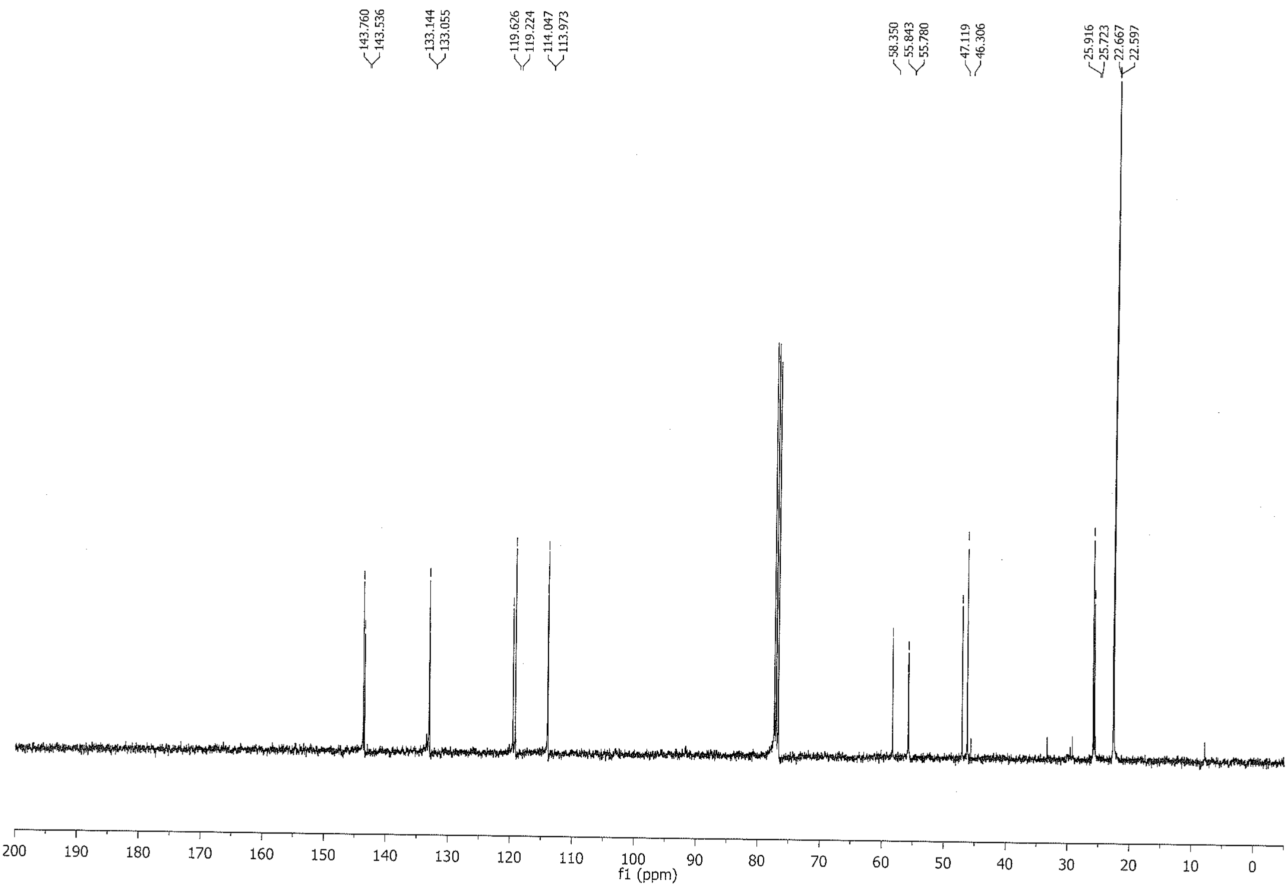


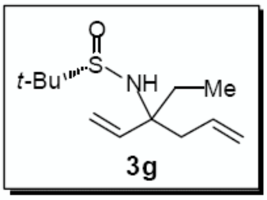
3f

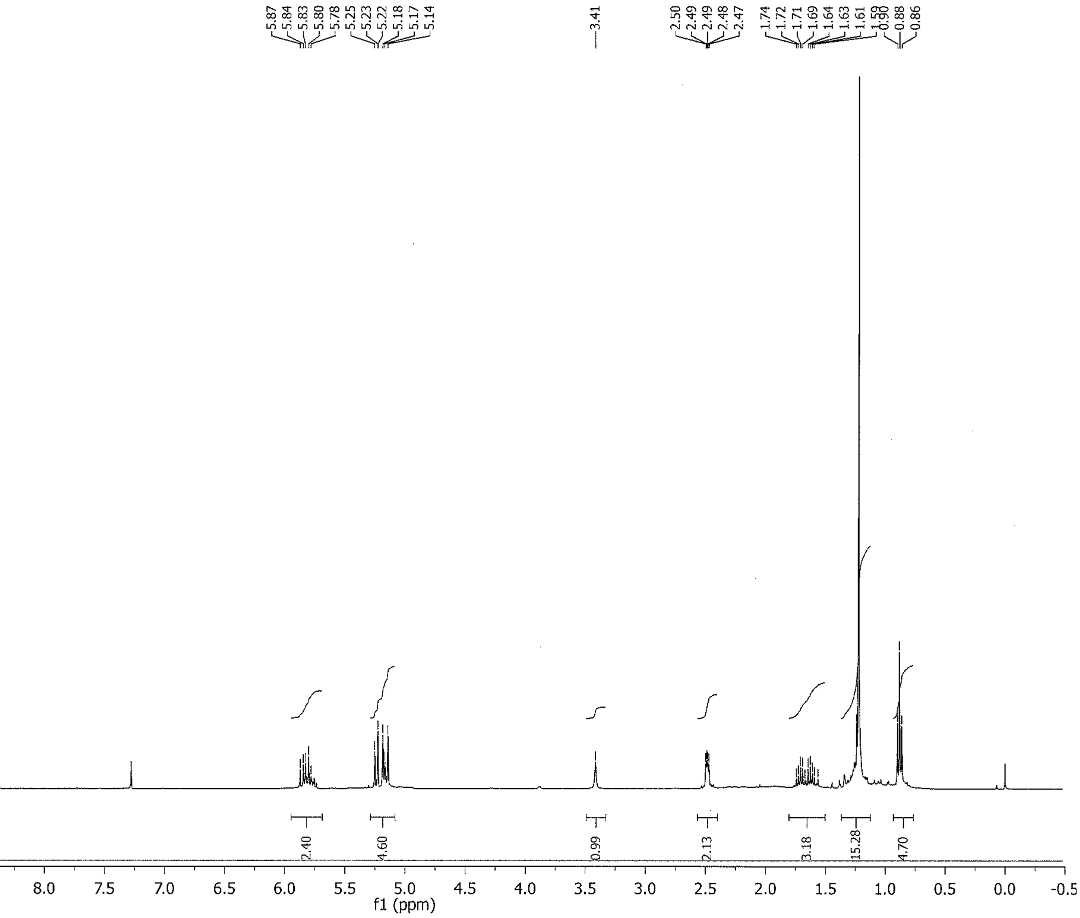
(59:41 diastereomeric mixture)

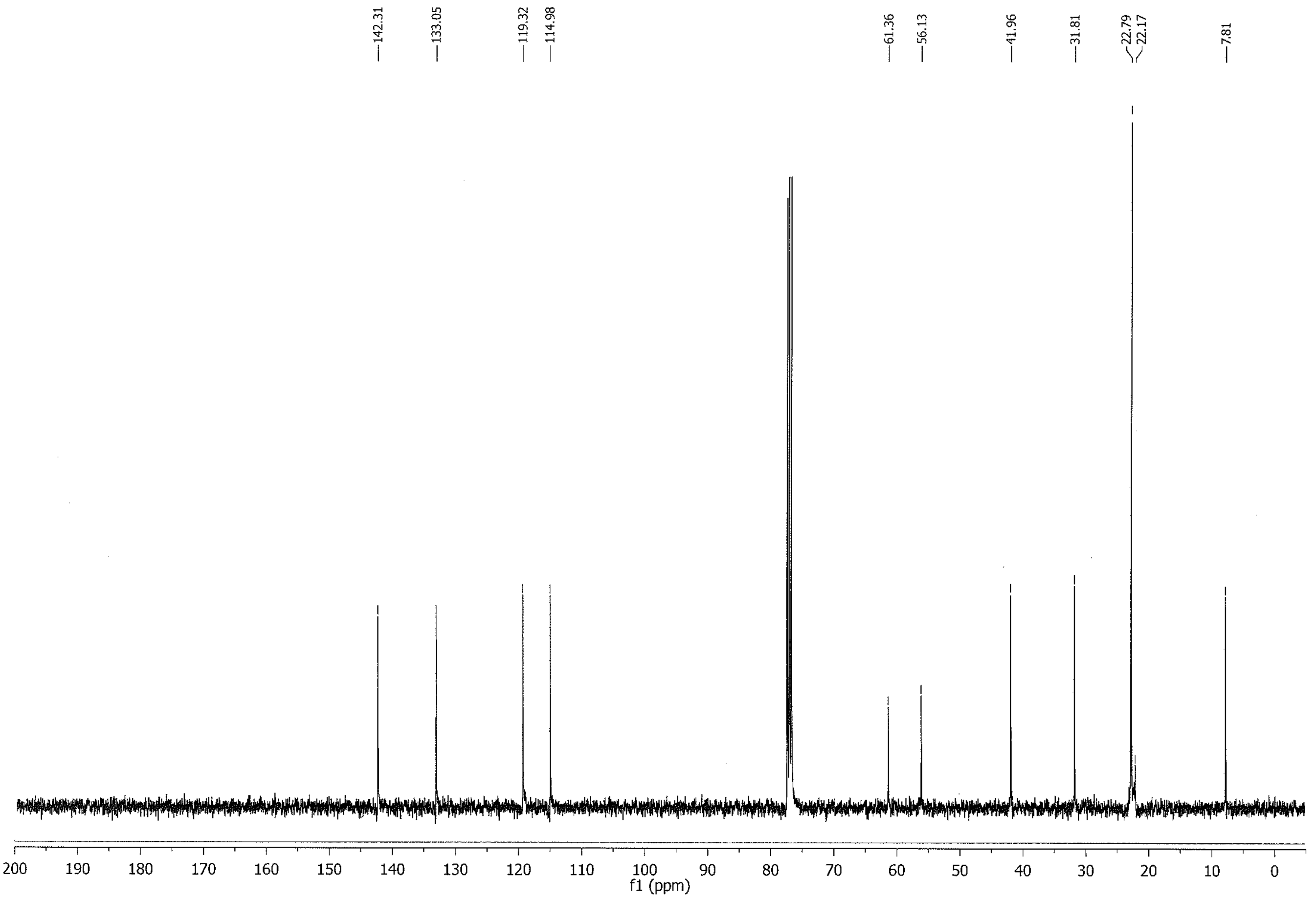


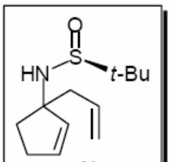
[1]H NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, J = 17.4, 10.8 Hz, 1H), 5.85 (dd, J = 17.4, 10.7 Hz, 1H), 5.24 (d, J = 17.4 Hz, 1H), 2.44 (d, J = 13.7 Hz, 1H), 2.41 (d, J = 6.9 Hz, 1H).




t-Bu
S
O
NH
Me
3g

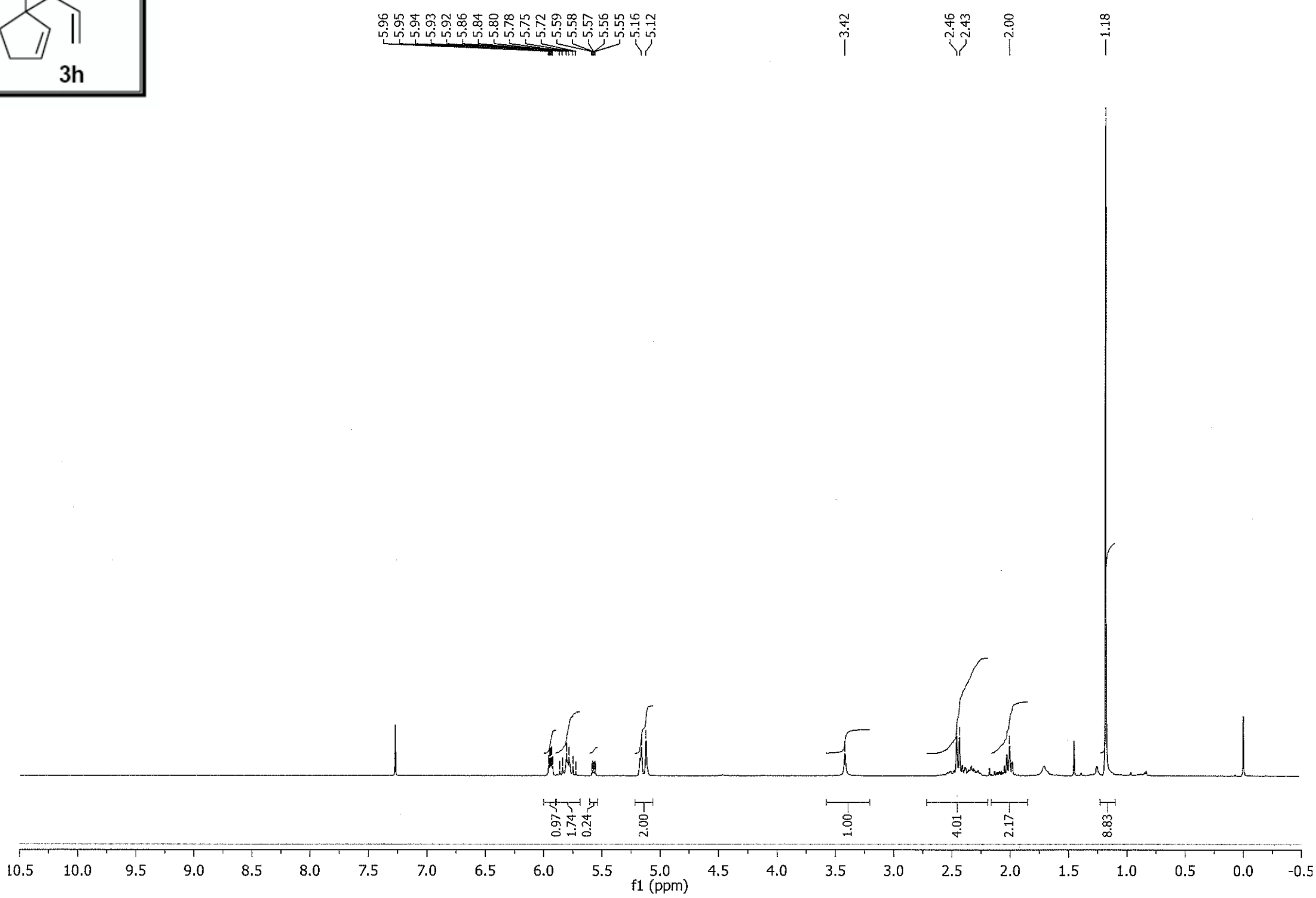

5.87
5.84
5.83
5.80
5.78
5.25
5.23
5.22
5.18
5.17
5.14
3.41
2.50
2.49
2.49
2.48
2.47
1.74
1.72
1.71
1.69
1.64
1.63
1.61
0.90
0.88
0.86
2.40
4.60
0.99
2.13
3.18
15.28
4.70
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

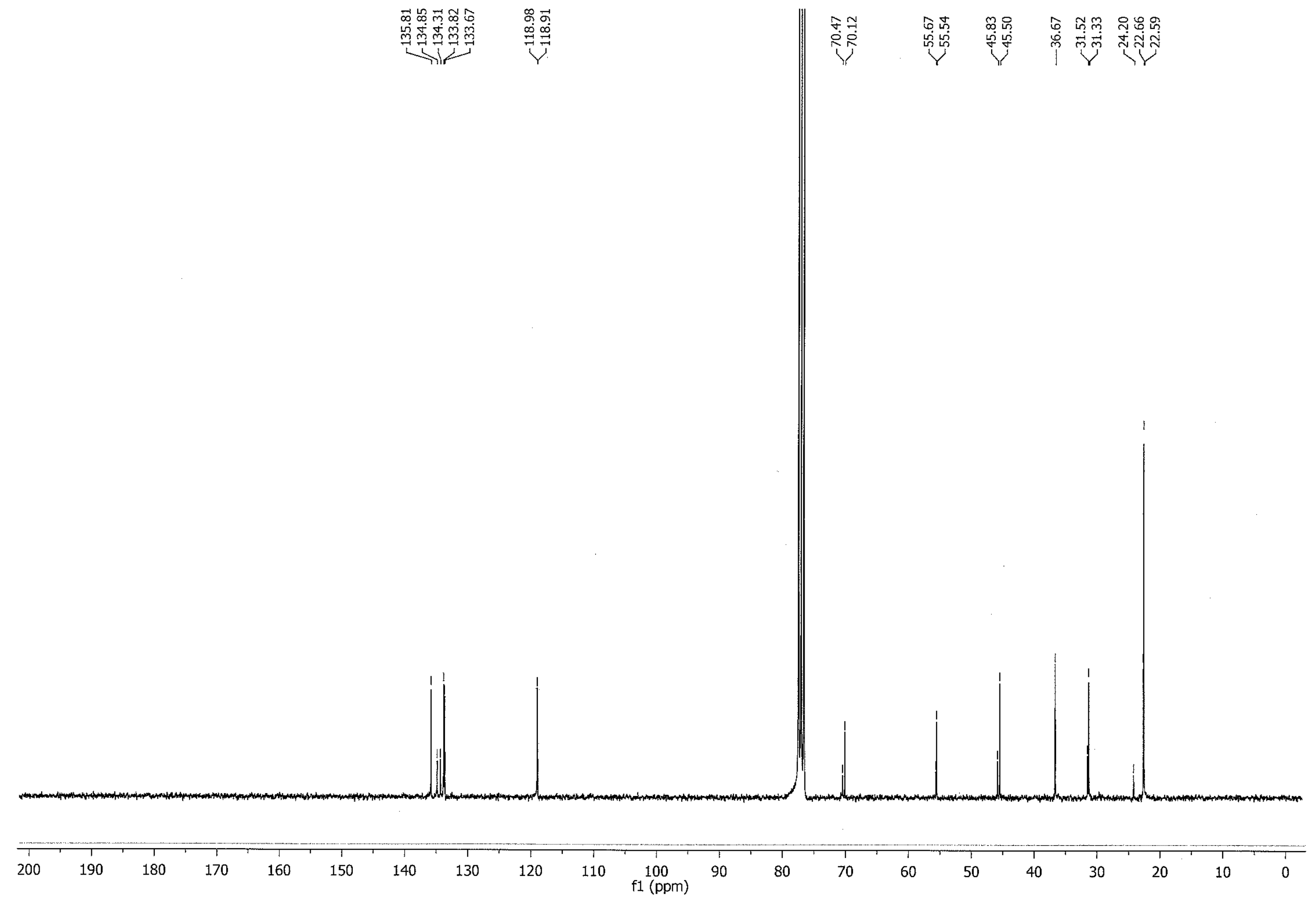

142.31
133.05
119.32
114.98
61.36
56.13
41.96
31.81
22.79
22.17
7.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

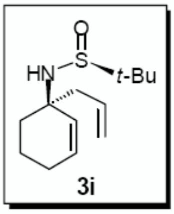


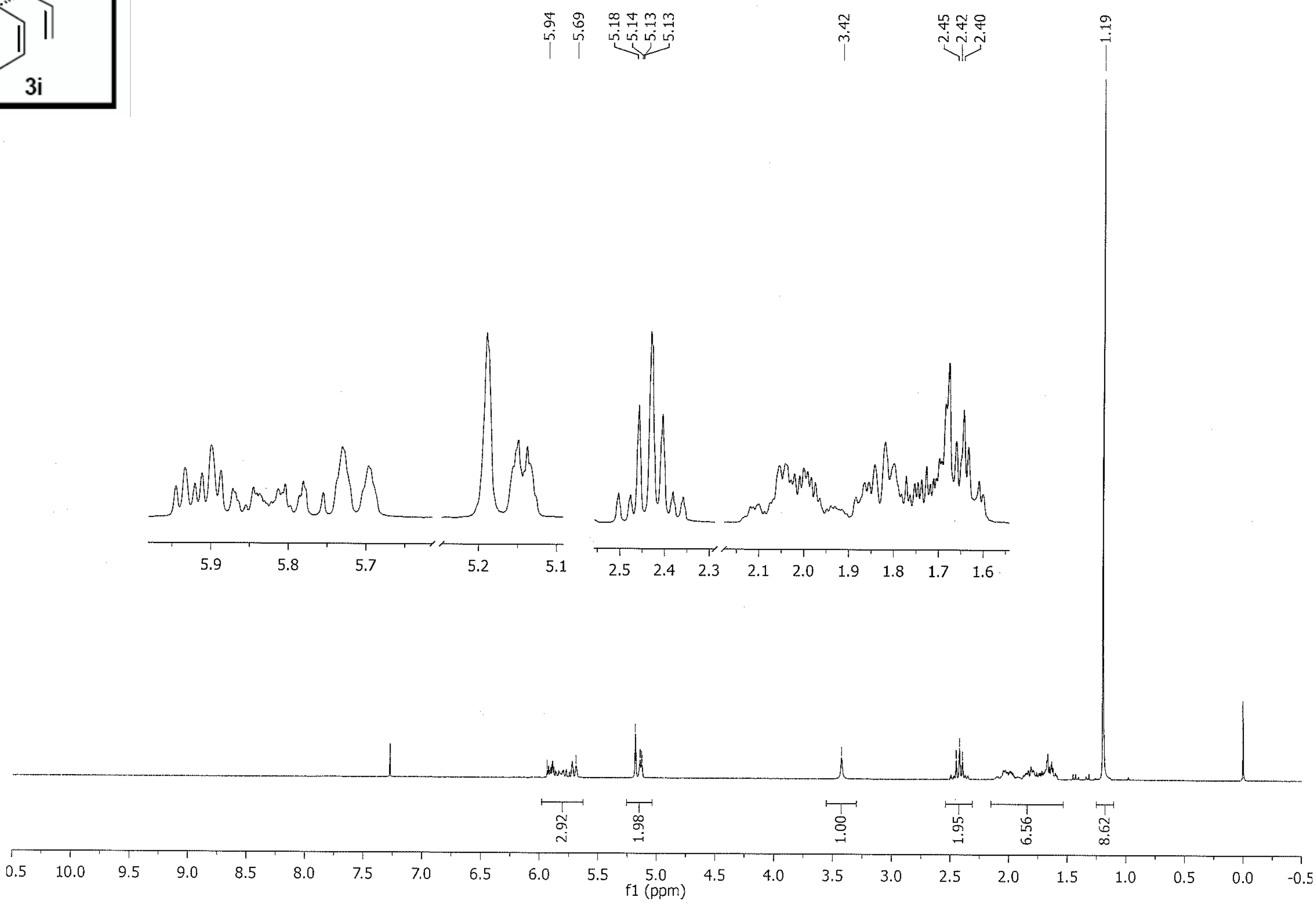
3h

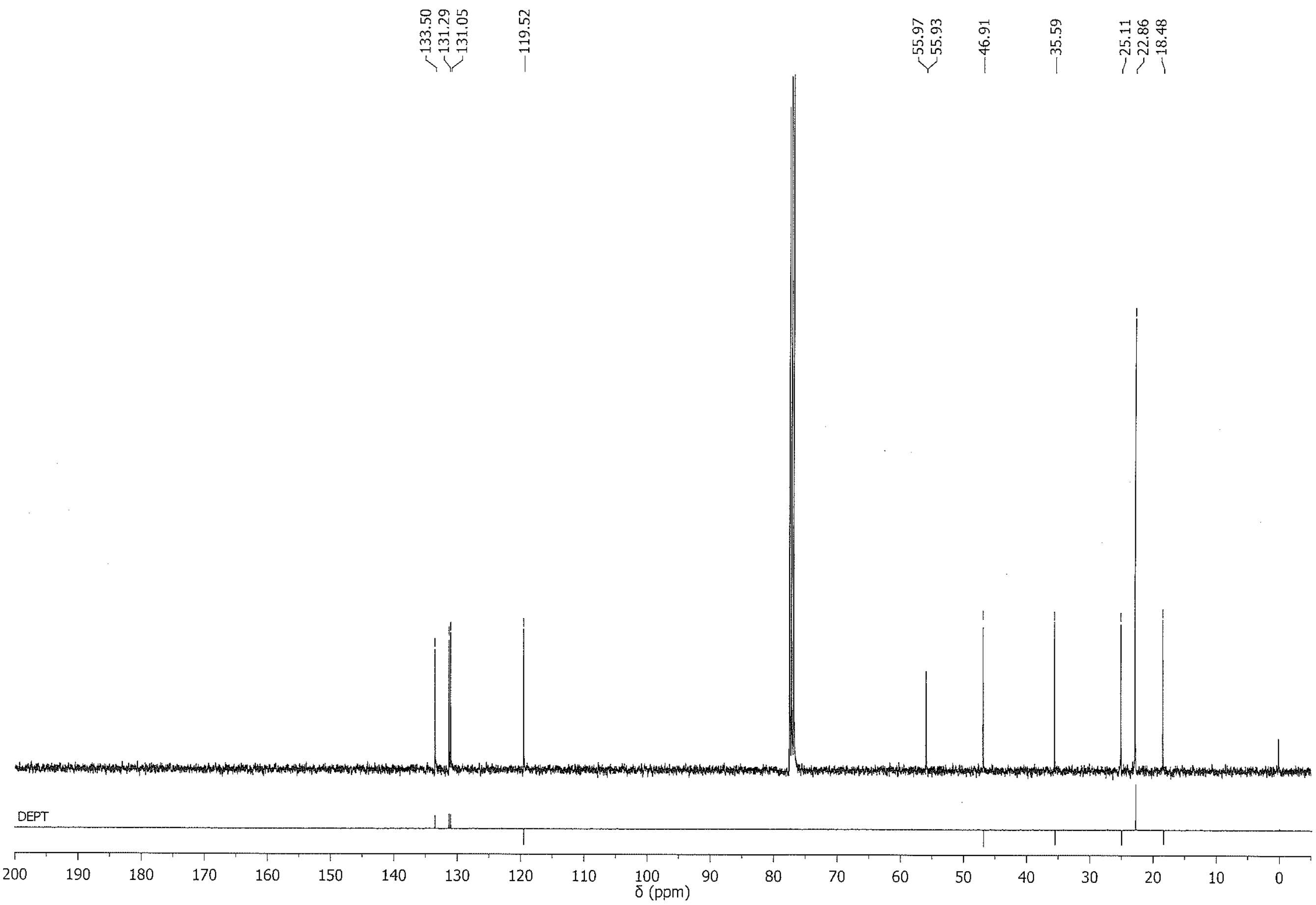
(80:20 diastereomeric mixture)

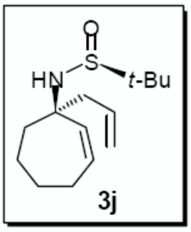


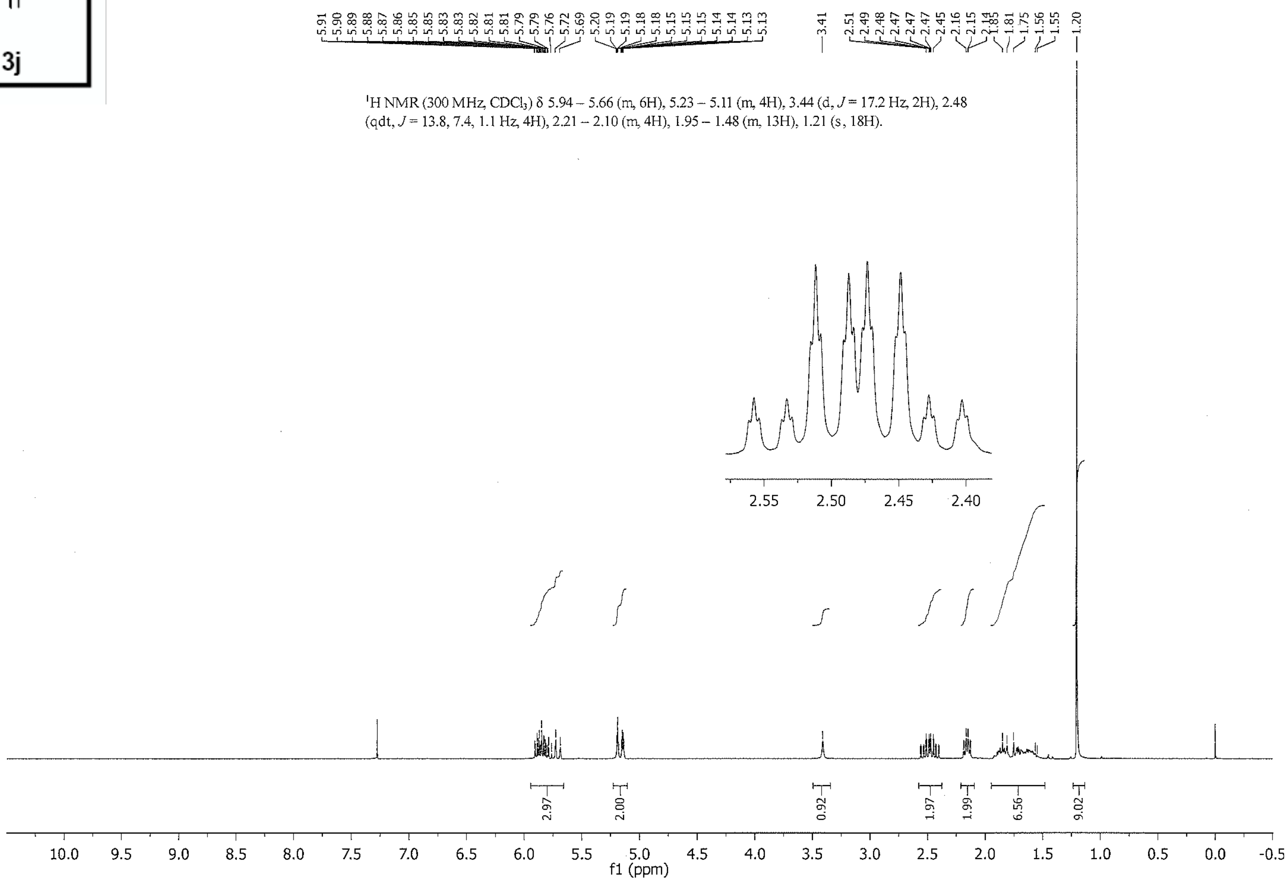


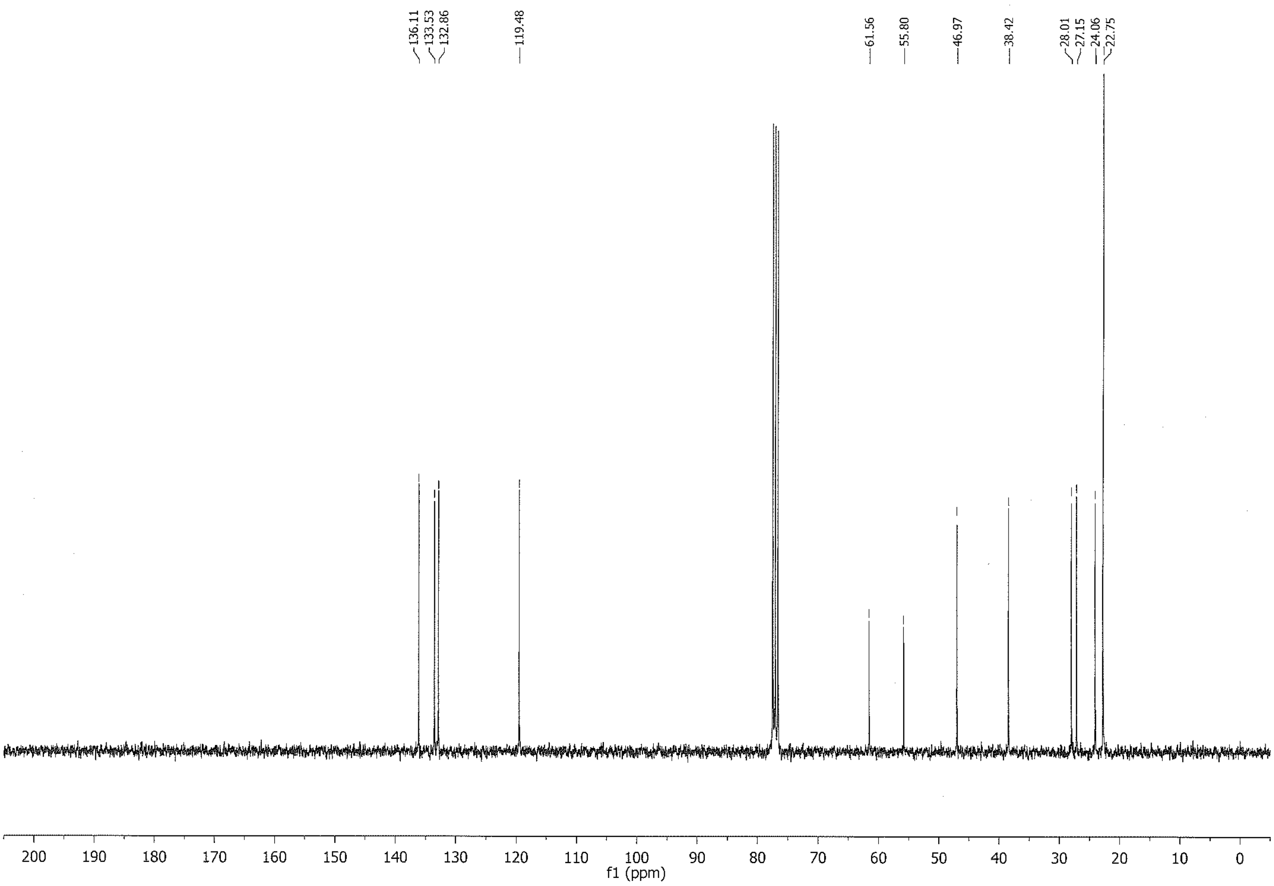

O
HN
S
t-Bu
3i

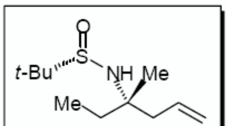

5.94
5.69
5.18
5.14
5.13
5.13
3.42
2.45
2.42
2.40
1.19
5.9
5.8
5.7
5.2
5.1
2.5
2.4
2.3
2.1
2.0
1.9
1.8
1.7
1.6
2.92
1.98
1.00
1.95
6.56
8.62
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


133.50
131.29
131.05
119.52
55.97
55.93
46.91
35.59
25.11
22.86
18.48
DEPT
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

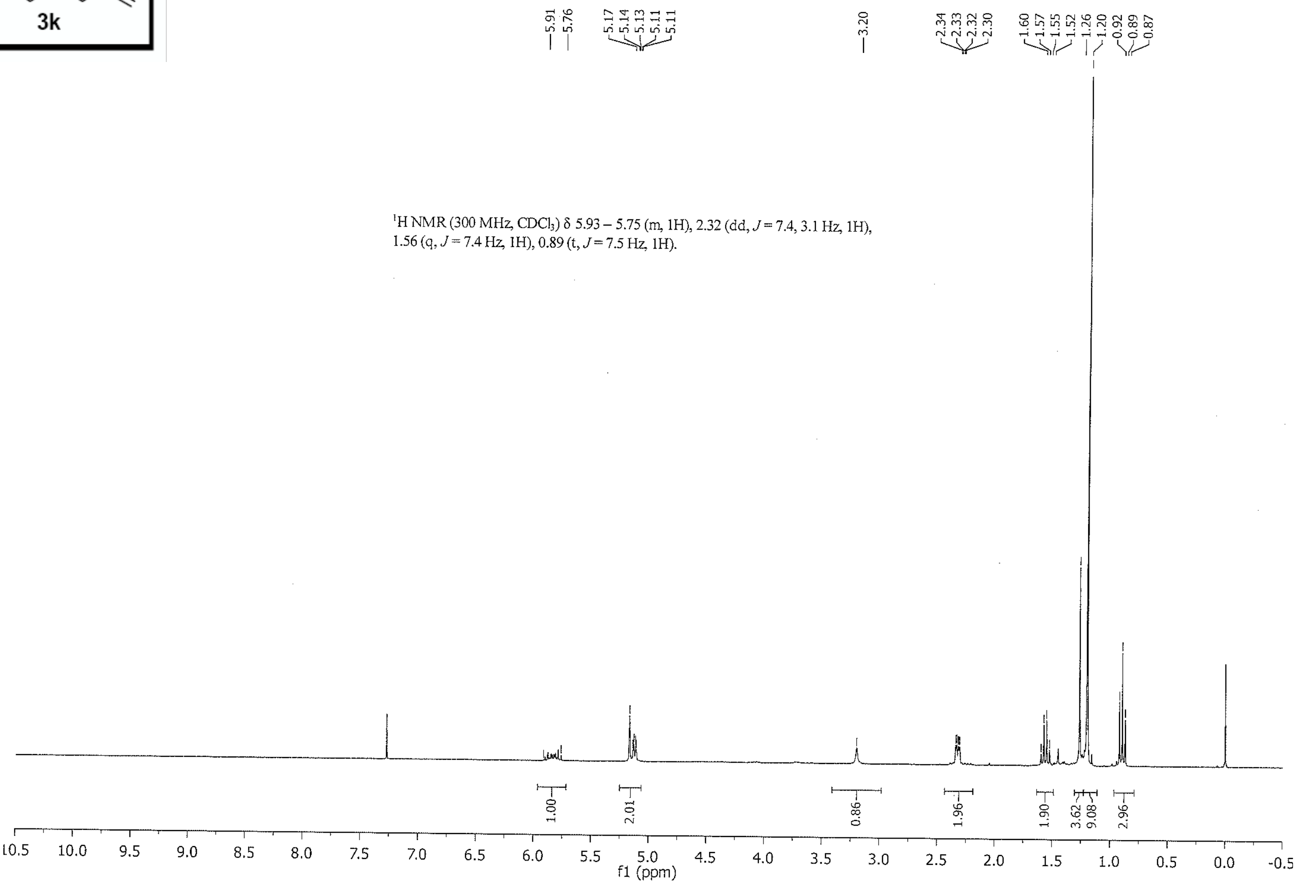

HN
S
O
t-Bu
3j

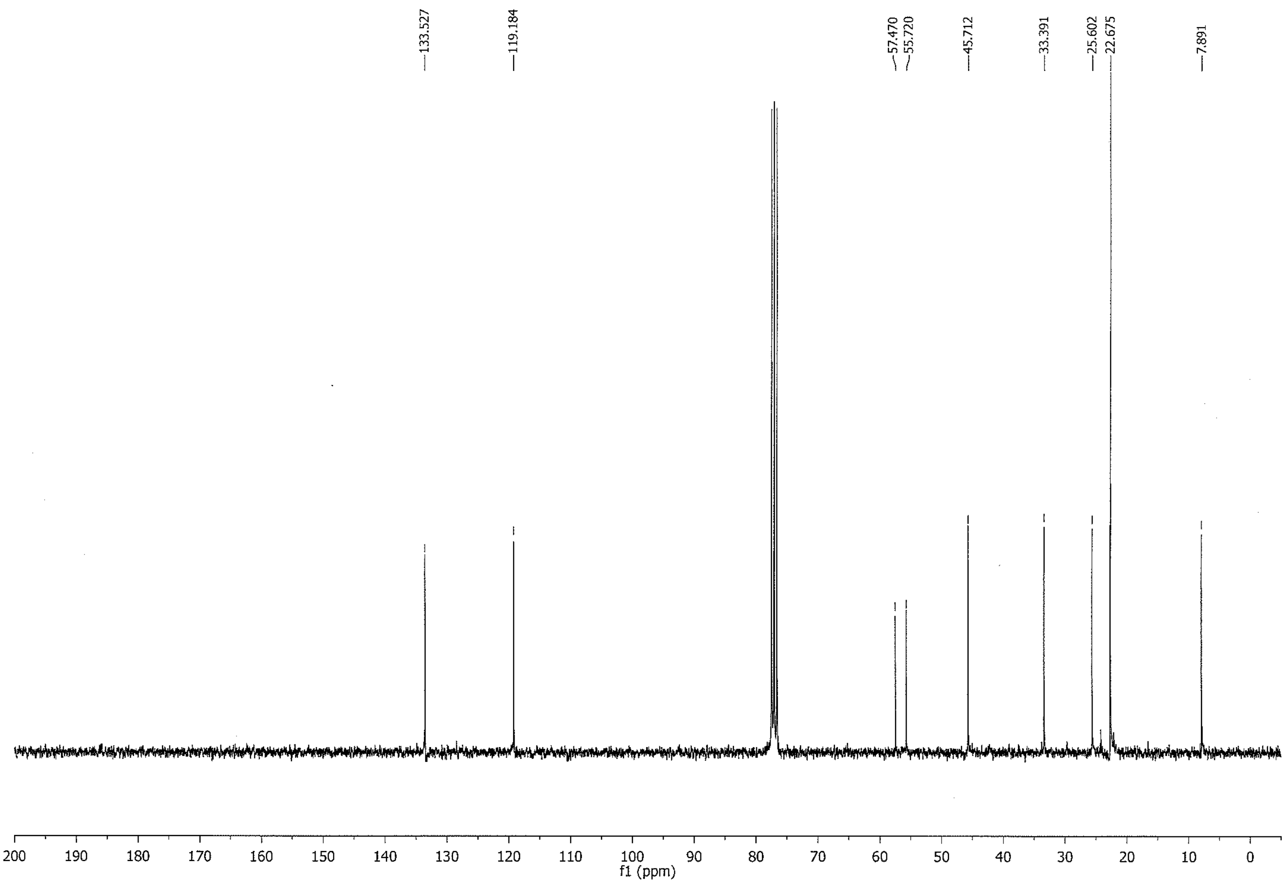

1H NMR (300 MHz, CDCl3) δ 5.94 – 5.66 (m, 6H), 5.23 – 5.11 (m, 4H), 3.44 (d, J = 17.2 Hz, 2H), 2.48 (qdt, J = 13.8, 7.4, 1.1 Hz, 4H), 2.21 – 2.10 (m, 4H), 1.95 – 1.48 (m, 13H), 1.21 (s, 18H).
2.97
2.00
0.92
1.97
1.99
6.56
9.02
f1 (ppm)

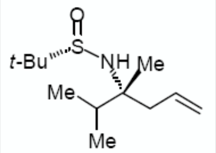

136.11
133.53
132.86
119.48
61.56
55.80
46.97
38.42
28.01
27.15
24.06
22.75
f1 (ppm)


t-Bu
S
O
NH
Me
Me

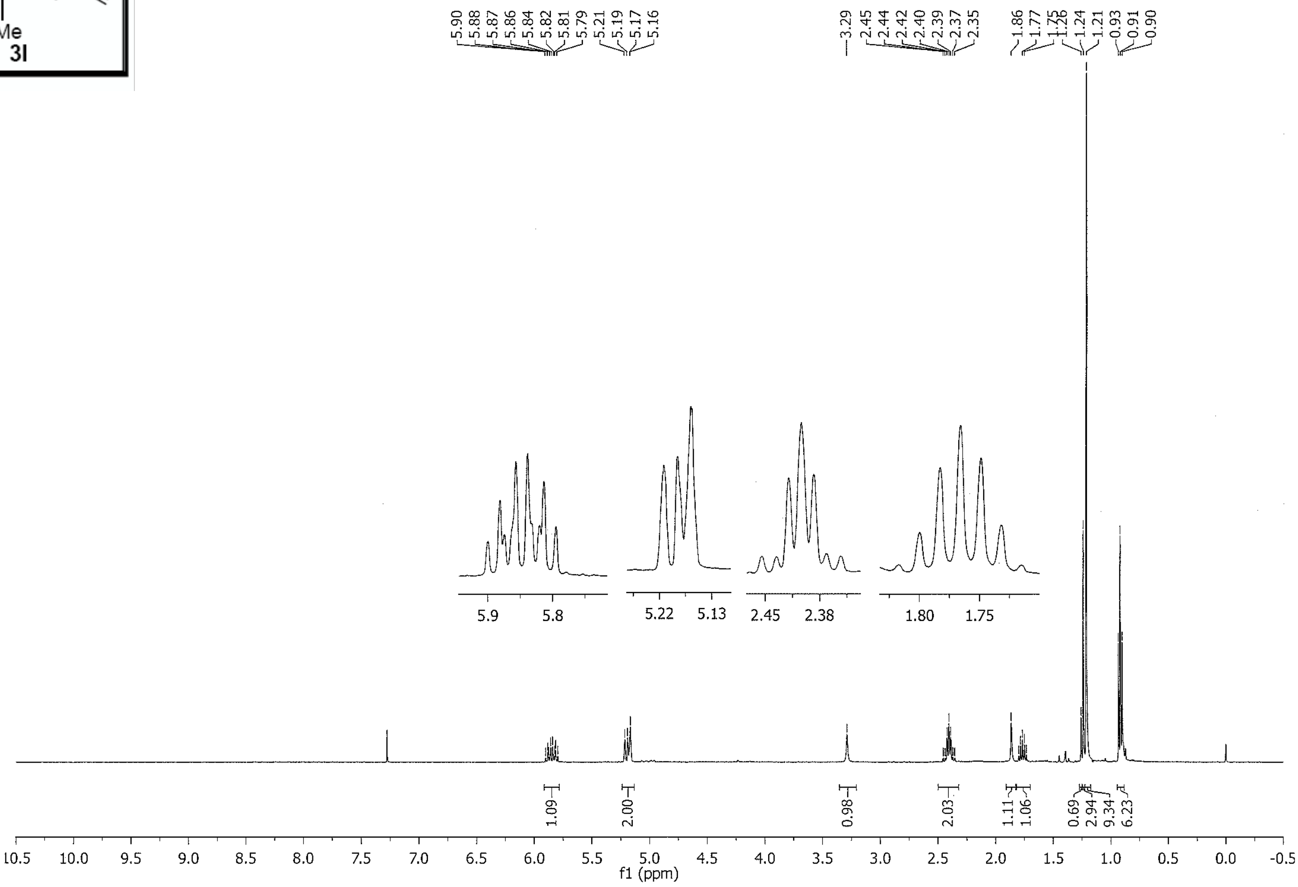
3k

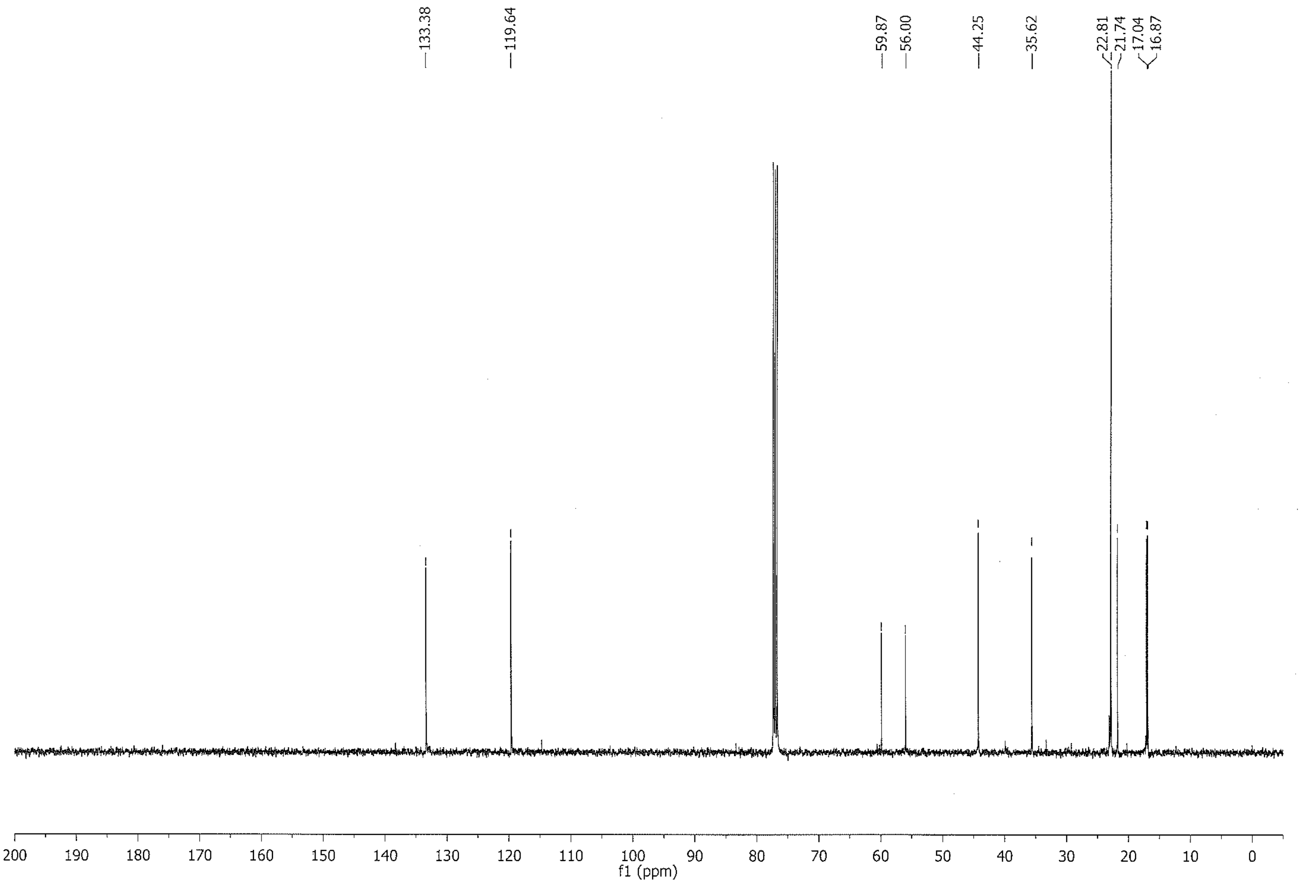

5.91
5.76
5.17
5.14
5.13
5.11
5.11
3.20
2.34
2.33
2.32
2.30
1.60
1.57
1.55
1.52
1.26
1.20
0.92
0.89
0.87
[1]H NMR (300 MHz, CDCl3) δ 5.93 – 5.75 (m, 1H), 2.32 (dd, J = 7.4, 3.1 Hz, 1H), 1.56 (q, J = 7.4 Hz, 1H), 0.89 (t, J = 7.5 Hz, 1H).
1.00
2.01
0.86
1.96
1.90
3.62
9.08
2.96
f1 (ppm)

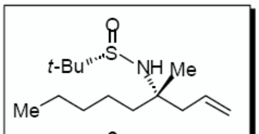

133.527
119.184
57.470
55.720
45.712
33.391
25.602
22.675
7.891
f1 (ppm)


t-Bu
S
O
NH
Me
Me
Me

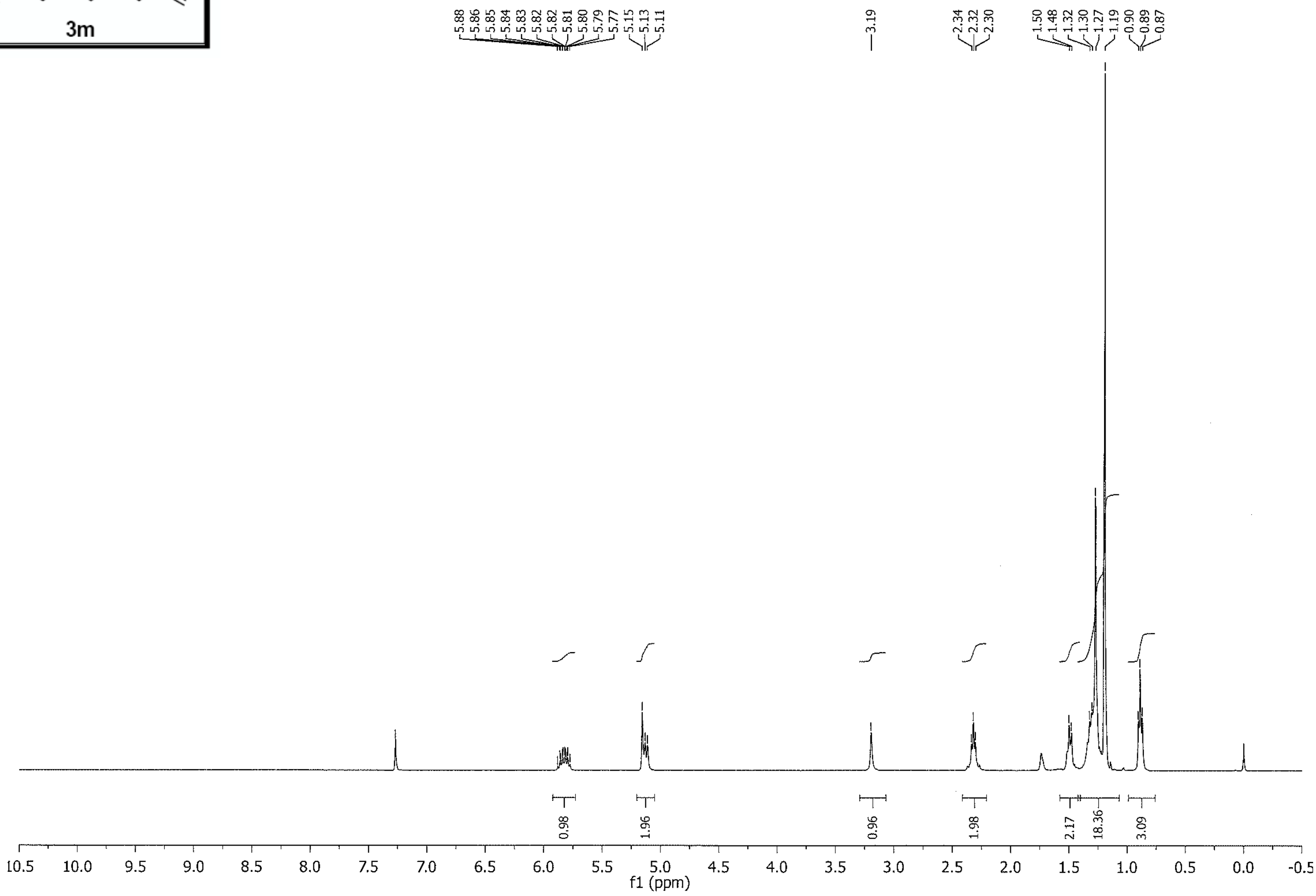
3l

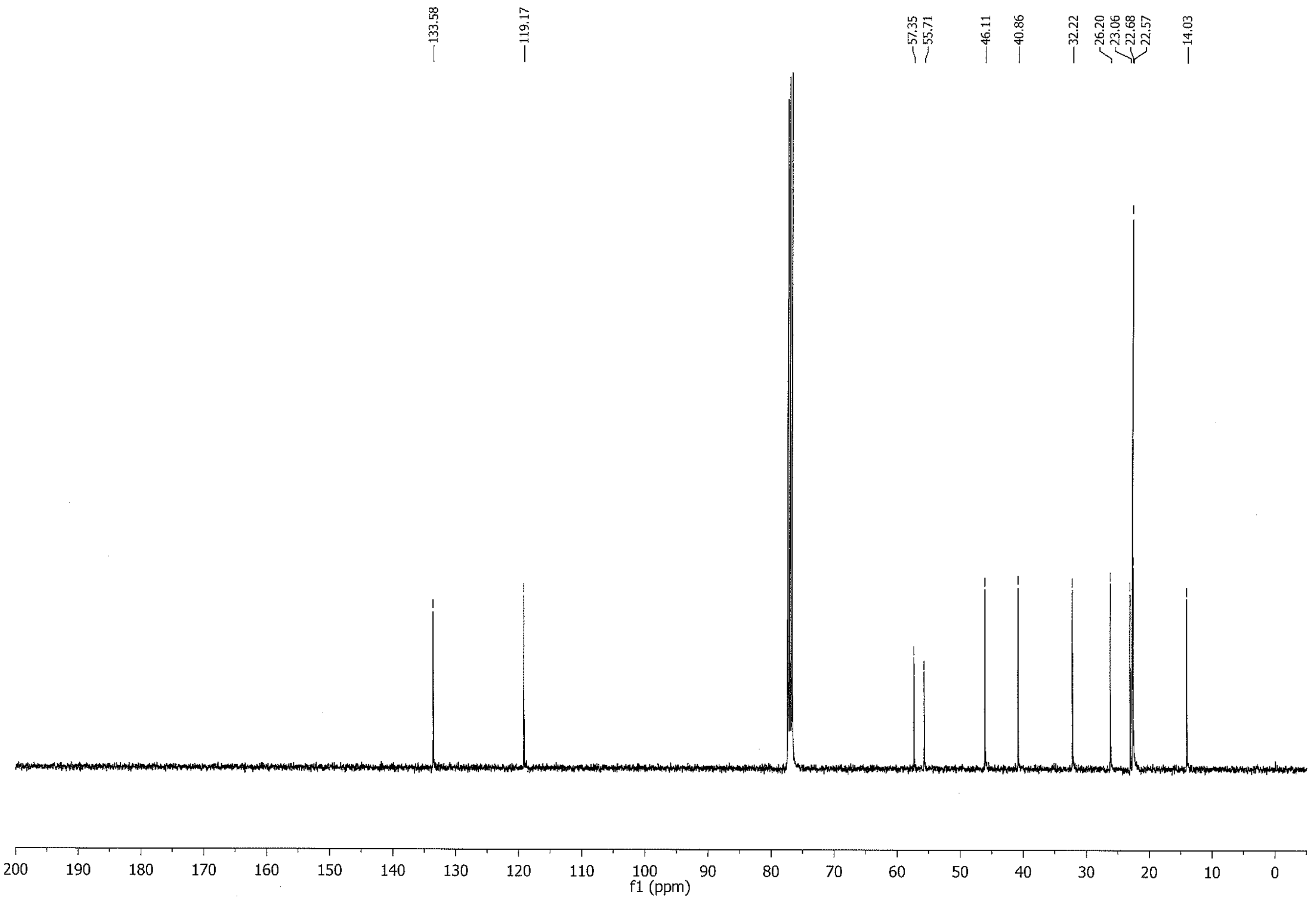

5.90 5.88 5.87 5.86 5.84 5.82 5.81 5.79 5.21 5.19 5.17 5.16
3.29 2.45 2.44 2.42 2.40 2.39 2.37 2.35
1.86 1.77 1.75 1.26 1.24 1.21 0.93 0.91 0.90
1.09 2.00 0.98 2.03 1.11 1.06 0.69 2.94 9.34 6.23
f1 (ppm)

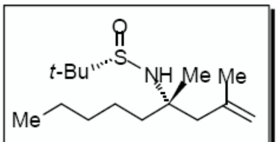

133.38
119.64
59.87 56.00
44.25
35.62
22.81 21.74 17.04 16.87
f1 (ppm)


t-Bu
S
O
NH
Me
Me

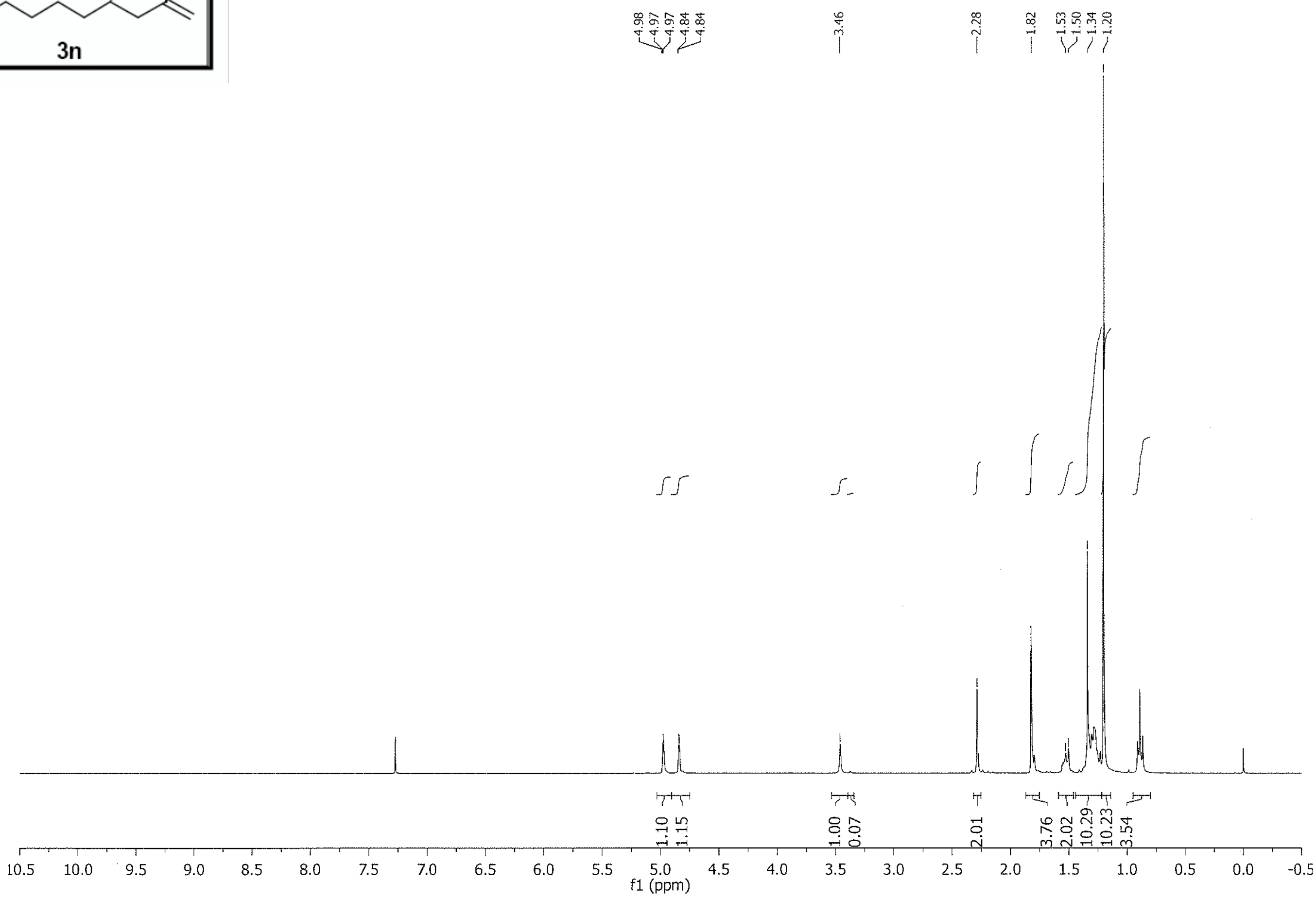
3m

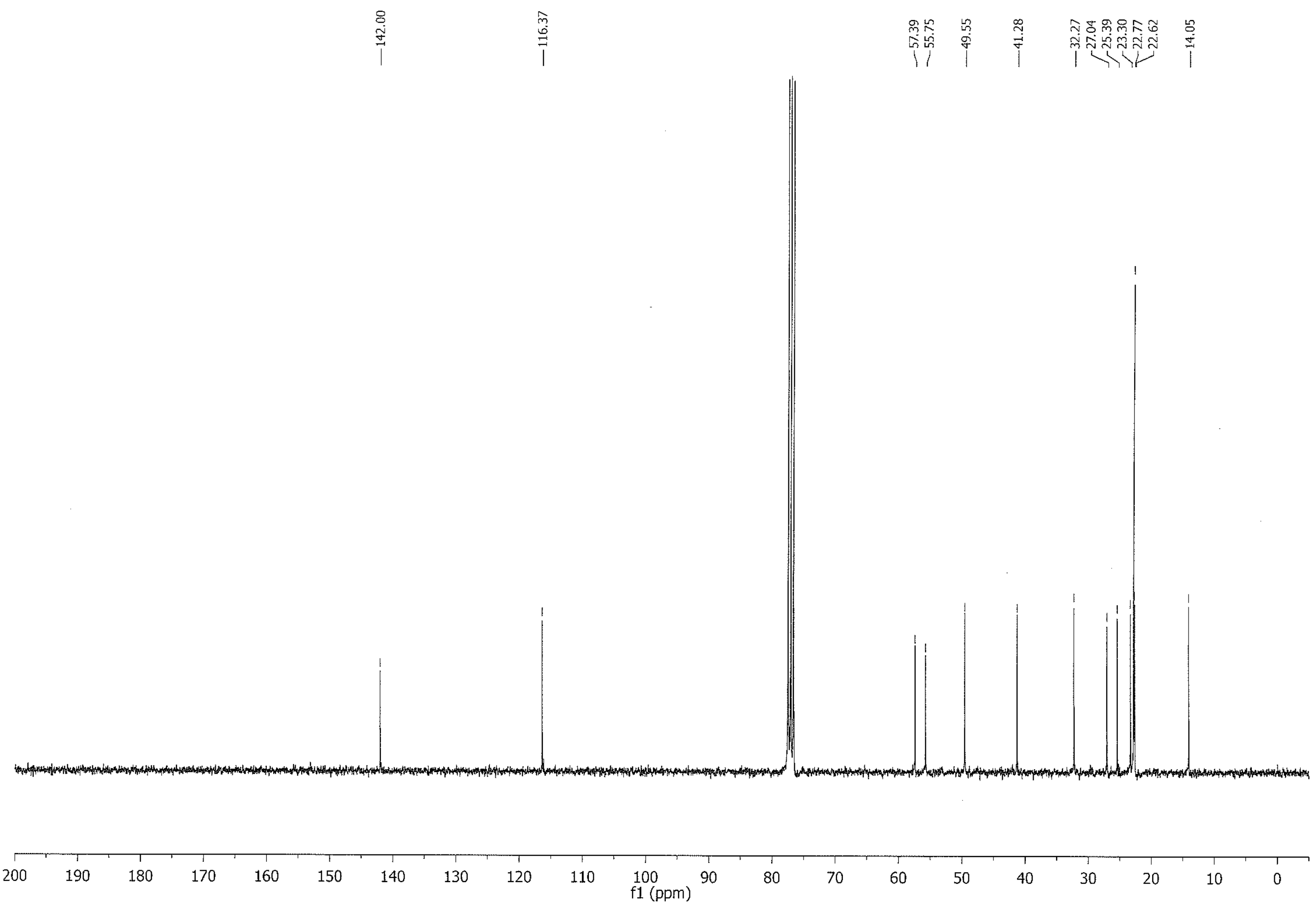

5.88
5.86
5.85
5.84
5.83
5.82
5.82
5.81
5.80
5.79
5.77
5.15
5.13
5.11
3.19
2.34
2.32
2.30
1.50
1.48
1.32
1.30
1.27
1.19
0.90
0.89
0.87
0.98
1.96
0.96
1.98
2.17
18.36
3.09
f1 (ppm)

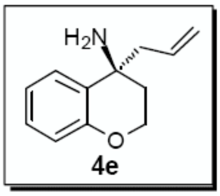

133.58
119.17
57.35
55.71
46.11
40.86
32.22
26.20
23.06
22.68
22.57
14.03
f1 (ppm)

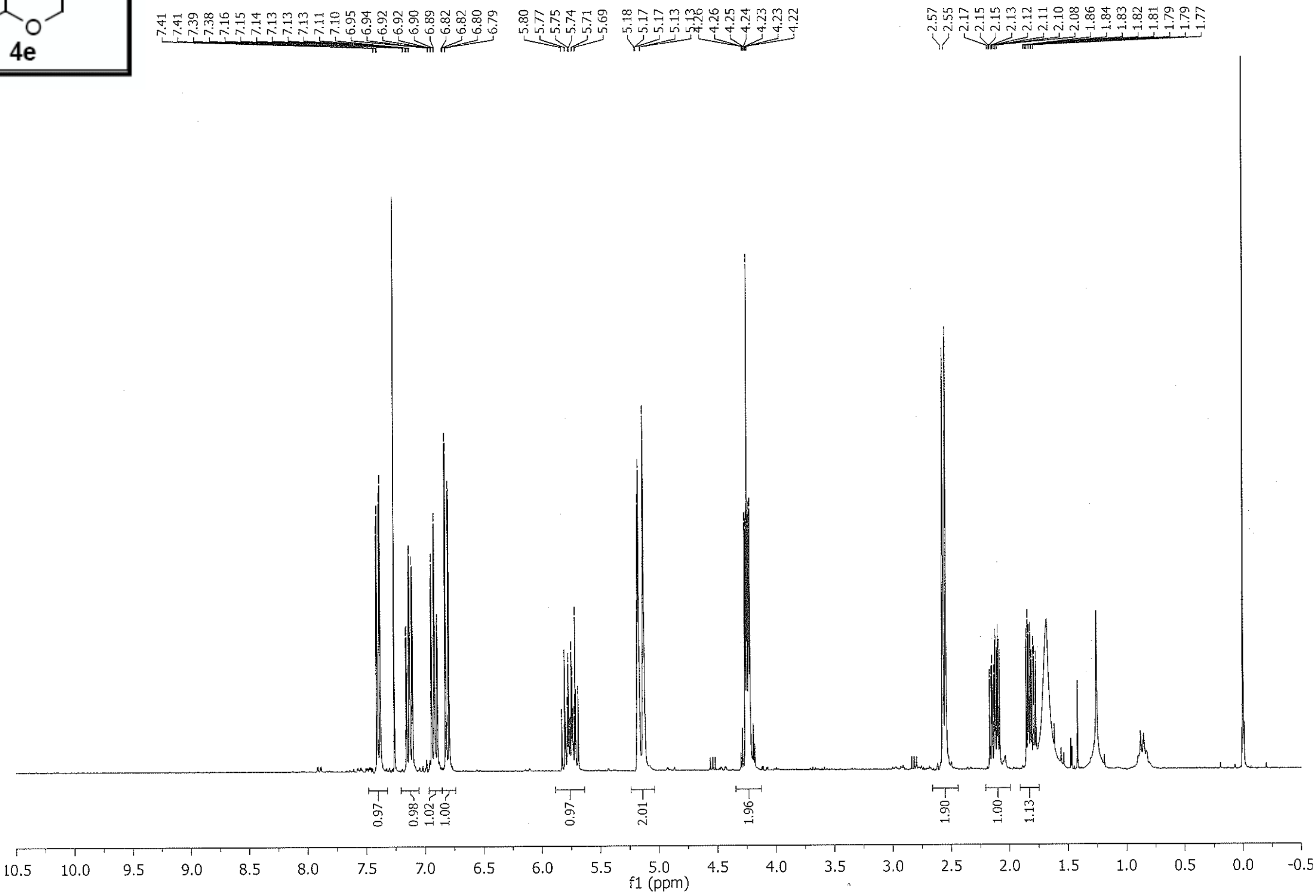

O
S
t-Bu
NH
Me
Me
Me

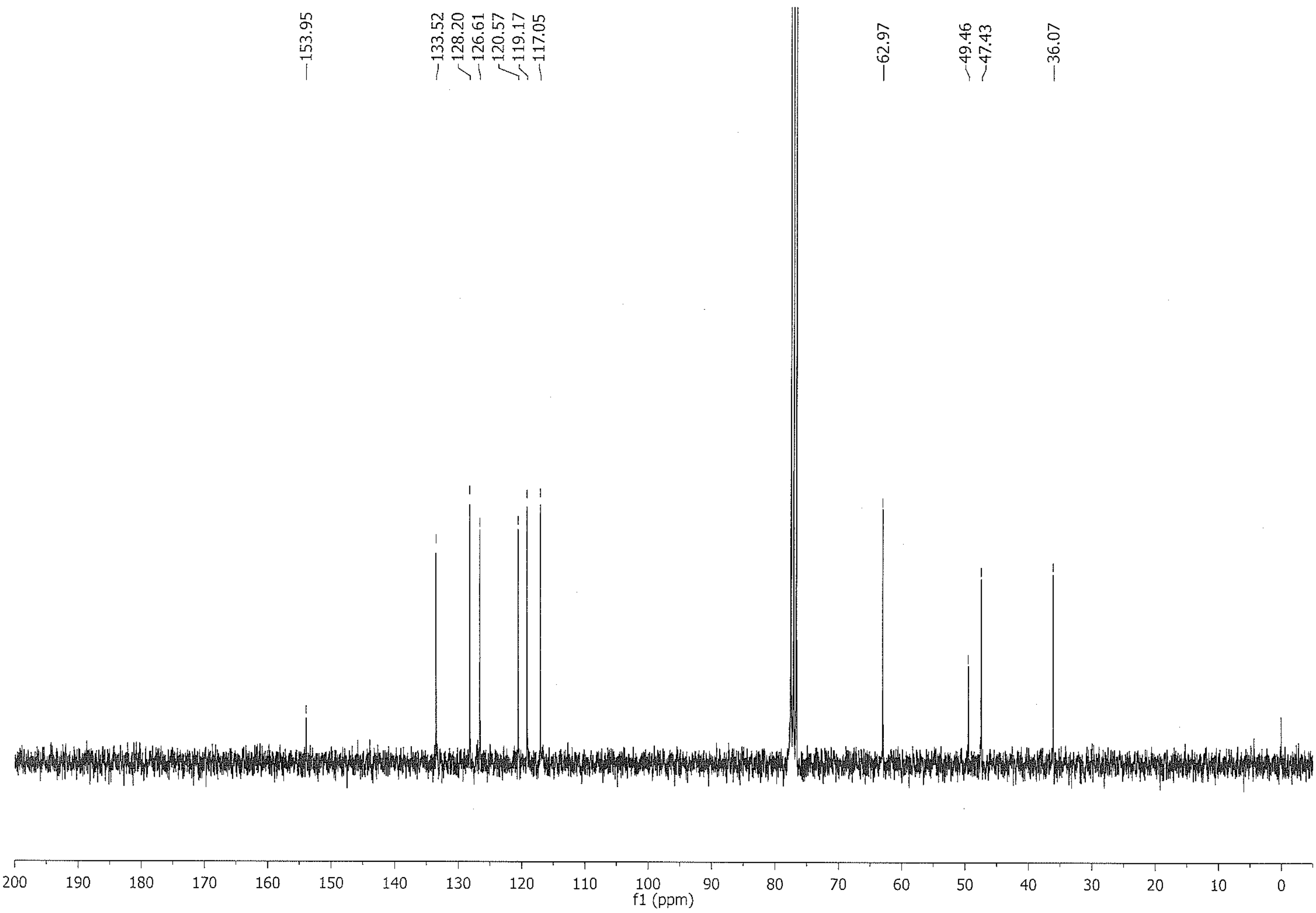
3n

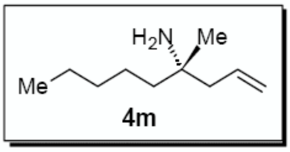

4.98
4.97
4.97
4.84
4.84
3.46
2.28
1.82
1.53
1.50
1.34
1.20
1.10
1.15
1.00
0.07
2.01
3.76
2.02
10.29
10.23
3.54
f1 (ppm)


142.00
116.37
57.39
55.75
49.55
41.28
32.27
27.04
25.39
23.30
22.77
22.62
14.05
f1 (ppm)


H2N
O
4e


7.41
7.41
7.39
7.38
7.16
7.15
7.14
7.13
7.13
7.13
7.11
7.10
6.95
6.94
6.92
6.92
6.90
6.89
6.82
6.82
6.80
6.79
5.80
5.77
5.75
5.74
5.71
5.69
5.18
5.17
5.17
5.13
5.13
4.26
4.25
4.24
4.23
4.23
4.22
2.57
2.55
2.17
2.15
2.15
2.13
2.12
2.11
2.10
2.08
1.86
1.84
1.83
1.82
1.81
1.79
1.79
1.77
0.97
0.98
1.02
1.00
0.97
2.01
1.96
1.90
1.00
1.13
f1 (ppm)


153.95
133.52
128.20
126.61
120.57
119.17
117.05
62.97
49.46
47.43
36.07
f1 (ppm)


H2N
Me
Me
4m