

Supporting information

Rhodium(III)-Catalyzed C(sp³)-H Amination. Synthesis of Cyclic Amines from ω -Unsaturated N-Sulfonylamines.

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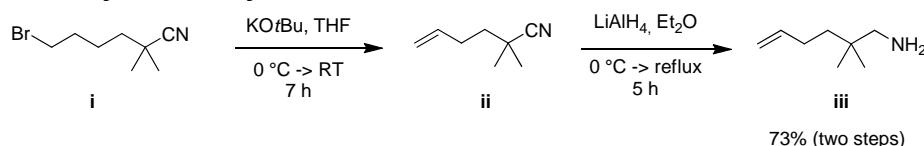
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I. General remarks

Infrared (IR) spectra were recorded on a Bruker TENSOR™ 27 (IRFT) on an ATR plate, wave numbers are indicated in cm⁻¹. NMR was performed on a Bruker Avance-1 400 instrument. ¹H NMR spectra were recorded at 400 MHz in CDCl₃ and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sext = sextuplet, m = multiplet or overlap of non-equivalent resonances, br = broad), integration. ¹³C NMR spectra were recorded at 100 MHz in CDCl₃ and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CDCl₃, 77.16 ppm), multiplicity, with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH₂, q = CH₃). High resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris-France). Optical rotations were measured with a Perkin Elmer model 343 polarimeter with a 1 dm path length. TLC was performed on Merck 60F254 silica gel plates with UV and Hanessian stain or *para*-anisaldehyde. CH₂Cl₂ was distilled from CaH₂, Et₂O and THF were distilled from sodium/benzophenone. Other reagents were obtained from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (230-400 mesh). Diastereomeric ratios were measured by examination of the ¹H NMR spectrum of the crude material.

II. Synthesis of substrates

1. Synthesis of 1 and 4a-f



2,2-Dimethylhex-5-enenitrile (**ii**):^[1]

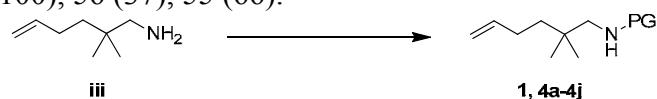
To a solution of 6-bromo-2,2-dimethylhexanenitrile (2.040 g, 10 mmol, 1 equiv) in THF (20 mL) at 0 °C was added KOtBu (1.232 g, 11 mmol, 1.1 equiv) and the reaction was allowed to warm to room temperature. After 7 h, volatiles are evaporated, the crude material retaken in Et₂O (40 mL). The organic phase was washed with H₂O (4 mL), dried over MgSO₄, filtrated and evaporated under *vacuum* to afford compound **ii** as a colourless oil which was used without further purification. Spectral data for **ii** match those previously described in the literature.

IR (film): ν 3081, 2979, 2939, 2876, 2234, 1710, 1643, 1472, 1456, 1392, 1371, 1207, 997, 914 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 5.79 (ddt, 1H, J = 16.8, 10.4, 6.6 Hz), 5.05 (dq, 1H, J = 16.8, 1.6 Hz), 4.98 (dq, 1H, J = 10.4, 1.4 Hz), 2.21 (m, 2H), 1.59 (m, 2H), 1.33 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 137.2 (d), 125.0 (s), 115.6 (t), 40.3 (t), 32.4 (s), 29.7 (t), 26.8 (q, 2CH₃).

2,2-Dimethylhex-5-en-1-amine (**iii**):^[2]

To a solution of 2,2-dimethylhex-5-enenitrile (~ 10 mmol, 1 equiv) in Et₂O (20 mL) at 0 °C was added portionwise LiAlH₄ (418 mg, 11 mmol, 1.1 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature, then refluxed 5 h and finally let at room temperature overnight. After 16 h, the reaction was quenched by consecutive additions of H₂O (418 μ L), NaOH_{aq} (15%) (418 μ L) and H₂O (1.254 mL). The resulting mixture was filtrated through Celite® and concentrated under *vacuum* to afford compound **iii** (934 mg, 7.3 mmol, 73%) as slightly yellow oil which was used without further purification. Spectral data for **iii** match those previously described in the literature.

IR (film): ν 3306, 3077, 2955, 2933, 2868, 1640, 1471, 1388, 1364, 1305, 1063, 994, 907 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 5.79 (ddt, 1H, J = 17.2, 10.4, 6.4 Hz), 4.98 (dq, 1H, J = 17.2, 2.0 Hz), 4.89 (br d, 1H, J = 10.2 Hz), 2.42 (s, 2H), 1.96 (m, 2H), 1.25 (m, 2H), 1.15 (br s, 2H, NH₂), 0.82 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.7 (d), 114.1 (t), 53.0 (t), 38.8 (t), 34.7 (s), 28.6 (t), 24.8 (q, 2CH₃). **SM (EI) m/z** (abundance): 128 (M⁺, 7), 115 (7), 97 (41), 69 (40), 57 (100), 56 (37), 55 (66).



N-(2,2-Dimethylhex-5-en-1-yl)-4-methylbenzenesulfonamide (**1**):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (~10 mmol, 1 equiv) in CH₂Cl₂ (20 mL) at 0 °C were added Et₃N (2.020 g, 20 mmol, 2 equiv) followed by TsCl (1.900 g, 10 mmol, 1 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (10 mL), extracted with Et₂O (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 90/10) compound **1** (1.518 g, 5.4 mmol, 54% over three steps) as a white solid.

mp: 68 °C. **IR** (film): ν 3268, 2960, 2918, 2875, 1640, 1598, 1474, 1423, 1321, 1157, 1095, 1071, 997, 901 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.73 (br d, 2H, J = 8.0 Hz), 7.28 (br d, 2H, J = 8.0 Hz), 5.71 (ddt, 1H, J = 16.8, 10.0, 6.8 Hz), 4.93 (br d, 1H, J = 17.2 Hz), 4.87 (br d, 1H, J = 10.0 Hz), 4.77 (br s, 1H, NH), 2.65 (br d, 2H, J = 6.8 Hz), 2.40 (s, 3H), 1.89 (m, 2H), 1.24 (m, 2H), 0.82 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.5 (d), 139.0 (s), 137.1

(s), 129.9 (d, 2CH), 127.3 (d, 2CH), 114.4 (t), 53.1 (t), 38.7 (t), 33.9 (s), 28.3 (t), 25.0 (q, 2CH₃), 21.7 (q). **SM** (EI) *m/z* (abundance) : 184 (TsNHCH₃⁺, 27), 155 (55), 126 (22), 112 (22), 110 (11), 97 (13), 92 (15), 91 (100), 81 (12), 65 (40), 56 (16), 55 (97). **HRMS** (ESI): Calculated for C₁₅H₂₃NO₂SNa: 304.1342. Found: 304.1341.

N-(2,2-Dimethylhex-5-en-1-yl)-4-methoxybenzenesulfonamide (4a):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (190 mg, 1.5 mmol, 1 equiv) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (454 g, 4.5 mmol, 3 equiv) followed by 4-methoxybenzenesulfonyl chloride (323 mg, 1.57 mmol, 1.05 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (10 mL), extracted with Et₂O (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 95/5) compound **4a** (347 mg, 1.17 mmol, 78%) as a white solid.

mp: 39 °C. **IR** (film): ν 3315, 2967, 2936, 1704, 1642, 1558, 1471, 1370, 1207, 1156, 993, 910 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.18 (br d, 2H, *J* = 8.8 Hz), 6.33 (br d, 2H, *J* = 8.8 Hz), 5.09 (ddt, 1H, *J* = 17.0, 10.2, 6.4 Hz), 4.52 (br s, 1H), 4.31 (br d, 1H, *J* = 17.2 Hz), 4.24 (br d, 1H, *J* = 10.2 Hz), 3.21 (s, 3H), 2.01 (d, 2H, *J* = 6.8 Hz), 1.27 (m, 2H), 0.63 (m, 2H), 0.20 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 162.7 (s), 139.0 (d), 131.6 (s), 129.2 (d, 2CH), 114.2 (d, 2CH), 114.2 (t), 55.6 (q), 52.9 (t), 38.6 (t), 33.8 (s), 28.1 (t), 24.9 (q, 2CH₃). **SM** (EI) *m/z* (abundance) : 282 ((M - Me)⁺, 1), 200 (26), 172 (10), 171 (100), 126 (22), 123 (13), 112 (33), 107 (23), 92 (11), 77 (22), 55 (37). **HRMS** (ESI): Calculated for C₁₅H₂₃NO₃SNa [M + Na]⁺: 320.1291. Found: 320.1286.

N-(2,2-Dimethylhex-5-en-1-yl)benzenesulfonamide (4b):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (171 mg, 1.35 mmol, 1 equiv) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (409 mg, 4.05 mmol, 3 equiv) followed by PhSO₂Cl (249 mg, 1.4 mmol, 1.05 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (10 mL), extracted into ether (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 9/1) compound **4b** as a white solid (232 mg, 0.87 mmol, 64%).

mp: 63 °C. **IR** (film): ν 3274, 2975, 2930, 2872, 1639, 1467, 1449, 1432, 1418, 1322, 1157, 1094, 1067, 912 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.88-7.84 (m, 2H), 7.58-7.46 (m, 3H), 5.71 (ddt, 1H, *J* = 17.0, 10.2, 6.6 Hz), 4.99-4.89 (m, 2H), 4.87 (br d, 1H, *J* = 10.0 Hz) 2.67 (d, 2H, *J* = 6.4 Hz), 1.89 (m, 2H), 1.25 (m, 2H), 0.82 (m, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 140.1 (s), 139.0 (d), 132.7 (d), 129.3 (d, 2CH), 127.2 (d, 2CH), 114.5 (t), 53.1 (t), 38.7 (t), 34.0 (s), 28.3 (t), 25.0 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 252 ((M-Me)⁺, 1), 170 (55), 141 (62), 126 (29), 112 (22), 110 (15), 109 (12), 97 (24), 96 (14), 81 (16), 77 (72), 56 (12), 55 (100), 51 (14). **HRMS** (ESI): calculated for C₁₄H₂₁NO₂SNa [M + Na]⁺: 290.1185. Found: 290.1187.

N-(2,2-Dimethylhex-5-en-1-yl)-4-bromobenzenesulfonamide (4c):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (190 mg, 1.5 mmol, 1 equiv) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (454 g, 4.5 mmol, 3 equiv) followed by 4-bromobenzenesulfonyl chloride (400 mg, 1.57 mmol, 1.05 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (10 mL), extracted into ether (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 98/8) compound **4c** (441 mg, 1.27 mmol, 85%) as a

white solid.

mp : 74 °C. **IR** (film) : ν 3271, 3076, 2969, 1640, 1574, 1472, 1454, 1428, 1389, 1327, 1273, 1154, 1089, 1066, 1055, 1010, 993, 911 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz) : δ 7.73 (dt_{app.}, 2H, J = 8.7, 2.1 Hz), 7.66 (dt_{app.}, 2H, J = 8.7, 2.1 Hz), 5.74 (ddt, 1H, J = 17.2, 10.0, 6.6 Hz), 4.97 (dq, 1H, J = 17.2, 1.6 Hz), 4.92 (br d, 1H, J = 10.0 Hz), 4.71 (t, 1H, J = 6.8 Hz, NH), 2.7 (d, 2H, J = 6.8 Hz), 1.93 (m, 2H), 1.27 (m, 2H), 0.86 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz) : δ 139.2 (s), 138.9 (d), 132.6 (d, 2CH), 128.8 (d, 2CH), 127.7 (s), 114.6 (t), 53.2 (t), 38.7 (t), 34.0 (s), 28.3 (t), 25.0 (q, 2CH₃). **SM** (EI) *m/z* (abundance) : 292 ((M(⁸¹Br) - butenyl)⁺, 1), 290 ((M(⁷⁹Br) - butenyl)⁺, 1), 250 (18), 248 (16), 221 (18), 219 (18), 157 (12), 155 (12), 126 (25), 112 (25), 110 (13), 109 (14), 97 (30), 96 (14), 95 (10), 81 (17), 76 (11), 69 (10), 56 (15), 55 (100). **HRMS** (ESI): Calculated for C₁₄H₂₀(⁷⁹Br)NO₂SNa [M + Na]⁺: 368.0290. Found: 368.0295.

N-(2,2-Dimethylhex-5-en-1-yl)-4-nitrobenzenesulfonamide (4d):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (127 mg, 1 mmol, 1 equiv) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (303 mg, 3 mmol, 3 equiv) followed by 4-NsCl (232 g, 1.05 mmol, 1.05 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (5 mL), extracted with Et₂O (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 90/10) compound **4d** (270 mg, 0.86 mmol, 86%) as a yellow solid.

mp: 66 °C. **IR** (film): ν 3289, 3101, 2965, 2934, 1641, 1607, 1532, 1423, 1350, 1310, 1159, 1090, 1064, 1026, 1012, 991, 906 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 8.32 (br d, 2H, J = 8.7 Hz), 8.04 (br d, 2H, J = 9.2 Hz), 5.68 (ddt, 1H, J = 17.0, 10.2, 6.4 Hz), 5.37 (br s, 1H, NH), 4.91 (dq_{app.}, 1H, J = 17.2, 1.6 Hz), 4.94 (br d, 1H, J = 10.4 Hz), 2.71 (s, 2H), 1.89 (m, 2H), 1.23 (m, 2H), 0.82 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 150.1 (s), 146.0 (s), 138.7 (d), 128.4 (d, 2CH), 124.6 (d, 2CH), 114.5 (t), 53.2 (t), 38.5 (t), 34.0 (s), 28.2 (t), 24.8 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 257 ((M-butenyl)⁺, 1), 156 (28), 126 (12), 112 (17), 97 (36), 92 (11), 69 (11), 57 (17), 56 (12), 55 (100). **HRMS** (ESI): Calculated for C₁₅H₂₃NO₂SNa: 335.1036. Found: 335.1038.

N-(2,2-Dimethylhex-5-en-1-yl)-2-nitrobenzenesulfonamide (4e):

To a solution of 2,2-dimethylhex-5-en-1-amine (**iii**) (127 mg, 1 mmol, 1 equiv) in CH₂Cl₂ (5 mL) at 0 °C was added Et₃N (303 mg, 3 mmol, 3 equiv) followed by 2-NsCl (232 g, 1.05 mmol, 1.05 equiv). After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by addition of water (5 mL), extracted with Et₂O (20 mL), washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 90/10) compound **4e** (274 mg, 0.88 mmol, 88%) as a yellow oil.

IR (film): ν 3354, 3079, 2963, 2932, 1640, 1594, 1538, 1469, 1441, 1416, 1344, 1164, 1125, 1063, 911 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz) : δ 8.10 (m, 1H), 7.84 (m, 1H), 7.76-7.69 (m, 2H), 5.73 (ddt, 1H, J = 17.0, 10.2, 6.4 Hz), 5.25 (br t, 1H, J = 6.4 Hz, NH), 4.96 (dq_{app.}, 1H, J = 17.1, 1.6 Hz), 4.90 (ddt, 1H, J = 10.1, 1.7, 1.3 Hz), 2.82 (d, 2H, J = 6.8 Hz), 1.95 (m, 2H), 1.30 (m, 2H), 0.89 (s, 6H). **¹³C NMR** (CDCl₃, 100 MHz): δ 148.3 (s), 138.8 (d), 133.8 (s), 133.7, 133.0, 131.4, 125.6 (d, 4CH_{ar}), 114.7 (t), 53.7 (t), 38.8 (t), 34.1 (s), 28.4 (t), 25.1 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 215 (NsNHCH₂⁺, 5), 186 (27), 156 (12), 126 (18), 112 (15), 97 (32), 96 (10), 95 (12), 93 (11), 92 (16), 81 (15), 69 (14), 57 (10), 56 (13), 55 (100). **HRMS** (ESI): Calculated for C₁₅H₂₃NO₂SNa: 335.1036. Found: 335.1038.

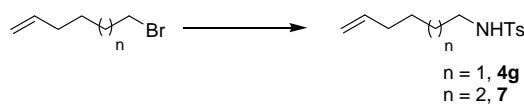
N-(2,2-Dimethylhex-5-en-1-yl)methanesulfonamide (4f):

To a solution of amine (63 mg, 0.5 mmol, 1 equiv) and Et₃N (151 g, 1.5 mmol, 3 equiv) in

CH_2Cl_2 (5 mL) cooled to 0 °C was added MsCl (60 mg, 0.525 mmol, 1.05 equiv). After 15 min the reaction was allowed to warm to room temperature and stirred 1 h. The reaction was then quenched with water (10 mL) and the phases separated. The organic phase was washed with brine (5mL), dried over MgSO_4 , filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc : 70/30) compound **4f** (67 mg, 0.33 mmol, 66%) as a colourless solid.

mp: 35 °C. **IR** (film): ν 3291, 2963, 2932, 1640, 1413, 1369, 1314, 1174, 1150, 1068, 995, 972, 910 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 5.81 (ddt, 1H, $J = 17.0, 10.2, 6.4$ Hz), 5.02 (dq, 1H, $J = 17.1, 1.6$ Hz), 4.94 (br d, 1H, $J = 10.1$ Hz), 4.88 (t, 1H, $J = 6.7$ Hz), 2.95 (s, 3H), 2.90 (d, 2H, $J = 6.8$ Hz), 2.02 (m, 2H), 1.34 (m, 2H), 0.93 (s, 6H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 138.9 (d), 114.4 (t), 53.1 (t), 39.9 (q), 38.6 (t), 33.9 (s), 28.2 (t), 24.8 (q, 2 CH_3). **SM (EI) m/z (abundance):** 150 ((M-but enyl) $^+$, 1), 108 (16), 97 (31), 96 (14), 81 (16), 56 (11), 55 (100). **HRMS (ESI):** Calculated for $\text{C}_9\text{H}_{19}\text{NO}_2\text{SNa}$ [$\text{M} + \text{Na}^+$]: 228.1029. Found: 228.1028.

2. Synthesis of **4g** and **7**



N-(Hex-5-en-1-yl)-4-methylbenzenesulfonamide (4g):^[3]

To a solution of 6-bromohex-1-ene (815 mg, 5 mmol, 1 equiv) in MeCN (20 mL) were added K_2CO_3 (1.38 g, 10 mmol, 2 equiv) and TsNH_2 (1.171 g, 10 mmol, 2 equiv), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and evaporated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 90/10) product **7a** as a colourless oil (1.265 g, 4.99 mmol, 99%). Spectral data for **4g** match those previously described in the literature.

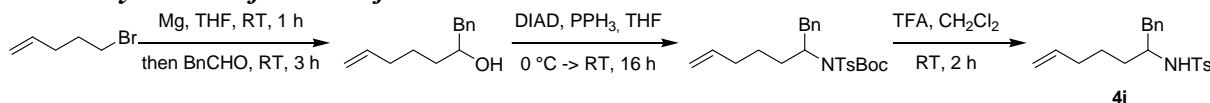
IR (film): ν 3280, 2930, 2862, 1640, 1599, 1424, 1322, 1306, 1156, 1093, 909, 814, 661 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 7.75 (dt_{app.}, 2H, $J = 8.4, 2.2$ Hz), 7.31 (br d, 2H, $J = 8.0$ Hz), 5.71 (ddt, 1H, $J = 16.8, 10.3, 6.8$ Hz), 4.99-4.89 (m, 2H), 4.63 (br s, 1H, NH), 2.93 (q_{app.}, 2H, $J = 6.8$ Hz), 2.43 (s, 3H), 1.98 (q_{app.}, 2H, $J = 7.1$ Hz), 1.51-1.42 (m, 2H), 1.41-1.31 (m, 2H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 143.5 (s), 138.3 (d), 137.1 (s), 129.9 (d, 2 CH), 127.3 (d, 2 CH), 115.1 (t), 43.2 (t), 33.3 (t), 29.1 (t), 25.9 (t), 21.7 (q). **SM (EI) m/z (abundance):** 184 ((M-pentenyl) $^+$, 5), 155 (40), 98 (24), 92 (13), 91 (100), 89 (11), 84 (27), 82 (12), 81 (25), 65 (45), 56 (12).

N-(hept-6-en-1-yl)-4-methylbenzenesulfonamide (7):

To a solution of 7-bromohept-1-ene (885 mg, 5 mmol, 1 equiv) in MeCN (20 mL) were added K_2CO_3 (1.38 g, 10 mmol, 2 equiv) and TsNH_2 (1.171 g, 10 mmol, 2 equiv), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and evaporated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 90/10) product **7** as a colourless oil (958 mg, 3.8 mmol, 72%).

IR (film): ν 3281, 2929, 2858, 1640, 1599, 1424, 1322, 1306, 1290, 1156, 1093, 908 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 7.73 (br d, 2H, $J = 8.4$ Hz), 7.28 (br d, 2H, $J = 8.0$ Hz), 5.72 (ddt, 1H, $J = 17.2, 10.4, 6.4$ Hz), 4.93 (br d, 1H, $J = 17.2$ Hz), 4.90 (br d, 1H, $J = 10.4$ Hz), 4.49 (br s, 1H, NH), 2.90 (q_{app.}, 2H, $J = 6.8$ Hz), 2.40 (s, 3H), 1.96 (q_{app.}, 2H, $J = 7.0$ Hz), 1.43 (quint_{app.}, 2H, $J = 7.2$ Hz), 1.34-1.20 (m, 4H). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 143.5 (d), 138.8 (s), 137.2 (s), 129.9 (d, 2 CH), 127.3 (d, 2 CH), 114.8 (t), 42.4 (t), 33.7 (t), 29.6 (t), 28.5 (t), 26.2 (t), 21.7 (q). **SM (EI) m/z (abundance):** 267 (M^+ , 1), 184 (12), 155 (48), 112 (21), 95 (19), 92 (11), 91 (100), 67 (12), 55 (14). **HRMS (ESI):** Calculated for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{SNa}$: 290.1185. Found: 290.1186.

3. Synthesis of **4i** and **4j**.



1-Phenylhept-6-en-2-ol:^[4]

To a suspension of mg turnings (115 mg, 4.8 mmol, 1 equiv) in a minimum of THF was added dropwise a solution of 5-bromopent-1-ene (715 mg, 4.8 mmol, 1 equiv) in THF (20 mL). After complete dissolution of mg turnings (~ 2 h), the reaction mixture was cooled to 0 °C and phenylacetaldehyde (601 mg, 5 mmol, 1.05 equiv) was added dropwise. The reaction was warmed to room temperature. After 5 h, the reaction was quenched by addition of a saturated aqueous NH₄Cl solution (10 mL) and diluted with EtOAc (20 mL). The phases were separated and the aqueous phase extracted with EtOAc (2 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 90/10) the title compound (155 mg, 0.82 mmol, 17%) as a colourless oil. Spectral data match those previously described in the literature.

IR (film): ν 3381, 3028, 2933, 1640, 1495, 1454, 1081, 1031, 996, 909 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.34-7.28 (m, 2H), 7.26-7.18 (m, 3H), 5.81 (ddt, 1H, *J* = 17.2, 10.2, 6.8 Hz), 5.01 (br d, 1H, *J* = 17.2 Hz), 4.96 (br d, 1H, *J* = 10.2 Hz), 3.81 (m, 1H), 2.82 (dd_{systAB}, 1H, *J* = 13.6, 4.3 Hz), 2.64 (dd_{systAB}, 1H, *J* = 13.6, 8.4 Hz), 2.16-2.01 (m, 2H), 1.67-1.42 (m, 5H). **¹³C NMR** (CDCl₃, 100 MHz): δ 138.7 (d), 138.6 (s), 129.4 (d, 2CH), 128.6 (d, 2CH), 126.5 (d), 114.7 (t), 72.6 (d), 44.1 (t), 36.3 (t), 33.7 (t) 25.1 (t). **SM** (EI) *m/z* (abundance) : 190 (M⁺, 1), 92 (100), 91 (30), 81 (15), 55 (13).

tert-Butyl N-(1-phenylhept-6-en-2-yl)-N-(tosyl)carbamate:

To a stirred solution of 1-phenylhept-6-en-2-ol (115 mg, 0.82 mmol, 1 equiv), PPh₃ (629 mg, 2.4 mmol, 3 equiv) and *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide (542 mg, 2 mmol, 2.5 equiv) in THF (10 mL) at 0 °C was added dropwise DIAD (404 mg, 2 mmol, 2.5 equiv). After 15 min, the reaction was allowed to warm to room temperature and stirred overnight. After 16 h, the volatiles were evaporated to afford after purification on silica gel (PE/EtOAc: 98/2) the title compound as a colourless oil (151 mg, 0.34 mmol, 41%).

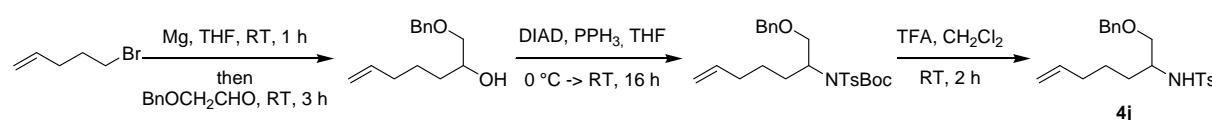
IR (film): ν 2979, 2931, 1723, 1598, 1456, 1347, 1279, 1255, 1149, 1087, 910 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.31-7.19 (m, 5H), 7.13-6.99 (m, 4H), 5.79 (ddt, 1H, *J* = 16.8, 10.4, 6.8 Hz), 5.00 (br d, 1H, *J* = 17.2 Hz), 4.95 (br d, 1H, *J* = 10.4 Hz), 4.73 (m, 1H), 3.31 (dd_{systAB}, 1H, *J* = 13.6, 9.4 Hz), 3.00 (dd_{systAB}, 1H, *J* = 13.6, 6.4 Hz), 2.34 (s, 3H), 2.16-2.02 (m, 3H), 1.75 (m, 1H), 1.58-1.44 (m, 2H), 1.35 (s, 9H). **¹³C NMR** (CDCl₃, 100 MHz): δ 150.8 (s), 143.3 (s), 139.1 (s), 138.4 (d), 137.6 (s), 129.6 (d, 2CH), 128.9 (d, 2CH), 128.7 (d, 2CH), 127.9 (d, 2CH), 126.5 (d), 114.8 (t), 84.0 (s), 61.2 (t), 39.7 (t), 33.5 (t), 32.8 (t), 28.0 (q, 3CH₃), 26.1 (t), 21.5 (q). **SM** (EI) *m/z* (abundance): 274 (2), 252 (39), 172 (17), 155 (45), 92 (11), 91 (100), 81 (25), 65 (15). **HRMS** (ESI): Calculated for C₂₅H₃₃NO₄SNa: 466.2022. Found: 466.2021.

4-Methyl-N-(1-phenylhept-6-en-2-yl)benzenesulfonamide (**4i**):

To a stirred solution of *tert*-butyl *N*-(1-phenylhept-6-en-2-yl)-*N*-(tosyl)carbamate (151 mg, 0.34 mmol, 1 equiv) in CH₂Cl₂ (10 mL) was added dropwise TFA (300 μL). After 2 h at RT, the reaction was quenched by addition of a saturated aqueous NaHCO₃ solution (10 mL). The phases were separated and the organic phase was washed with brine (10 mL), dried over MgSO₄, filtrated and evaporated to afford compound **4i** (98 mg, 0.29 mmol, 85%) as a colourless oil. The product was sufficiently pure to be used without further purification.

IR (film): ν 3280, 2925, 1640, 1599, 1495, 1454, 1423, 1322, 1155, 1091, 1031, 994, 909 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.66 (br d, 2H, *J* = 8.4 Hz), 7.26-7.14 (m, 5H), 7.05-6.98 (m, 2H), 5.64 (m, 1H), 4.91-4.83 (m, 2H), 4.68 (d, 1H, *J* = 8.4 Hz, NH), 3.42

(*sext*_{app.}, 1H, *J* = 6.6 Hz), 2.72-2.61 (m, 2H), 2.40 (s, 3H), 1.94-1.82 (m, 2H), 1.51-1.18 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 143.1 (s), 138.2 (d), 137.9 (s), 137.3 (s), 129.6 (d, 2CH), 129.5 (d, 2CH), 128.4 (d, 2CH), 127.0 (d, 2CH), 126.5 (d), 114.7 (t), 55.0 (d), 41.4 (t), 33.8 (t), 33.2 (t), 24.6 (t), 21.5 (q). SM (EI) *m/z* (abundance): 252 ((M-benzyl)⁺, 34), 172 (19), 155 (45), 92 (10), 91 (100), 81 (24), 65 (16). HRMS (ESI): Calculated for C₂₀H₂₅NO₂SNa: 366.1498. Found: 366.1502.



1-(Benzyl)hept-6-en-2-ol:^[5]

To a suspension of mg turnings (115 mg, 4.8 mmol, 1 equiv) in a minimum of THF was added dropwise a solution of 5-bromopent-1-ene (715 mg, 4.8 mmol, 1 equiv) in THF (20 mL). After complete dissolution of mg turnings (\sim 2 h), the reaction mixture was cooled to 0 °C and benzyloxyacetaldehyde (720 mg, 4.8 mmol, 1 equiv) was added dropwise. The reaction was warmed to room temperature. After 5 h, the reaction was quenched by addition of a saturated aqueous NH₄Cl solution (10 mL) and diluted with EtOAc (20 mL). The phases were separated and the aqueous phase extracted with EtOAc (2 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 85/15) the title compound (781 mg, 3.5 mmol, 74%) as a colourless oil. Spectral data match those previously described in the literature.

IR (film): ν 3441, 3065, 3031, 2927, 2860, 1640, 1454, 1364, 1254, 1206, 1093, 996, 909 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.25 (m, 5H), 5.78 (ddt, 1H, *J* = 17.0, 10.2, 6.8 Hz), 4.99 (dq, 1H, *J* = 17.1, 1.9 Hz), 4.93 (m, 1H), 4.54 (s, 2H), 3.80 (m, 1H), 3.49 (dd_{systAB}, 1H, *J* = 9.4, 3.0 Hz), 3.31 (dd_{systAB}, 1H, *J* = 9.4, 7.8 Hz), 2.36 (br d, 1H, *J* = 3.6 Hz), 2.09-2.00 (m, 2H), 1.56 (m, 1H), 1.50-1.35 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 138.8 (d), 138.2 (s), 128.7 (d, 2CH), 128.0 (d), 127.9 (d, 2CH), 114.9 (t), 74.8 (t), 73.5 (t), 70.5 (d), 33.9 (t), 32.7 (t), 25.0 (t). SM (EI) *m/z* (abundance): 220 (M⁺, 1), 107 (16), 92 (55), 91 (100), 81 (64), 65 (14), 57 (12), 55 (26). HRMS (ESI): Calculated for C₁₄H₂₀O₂Na: 243.1356. Found: 243.1350.

tert-Butyl [1-(benzyloxy)hept-6-en-2-yl]-N-(tosyl)carbamate:

To a stirred solution of 1-(benzyloxy)hept-6-en-2-ol (202 mg, 1 mmol, 1 equiv), PPh₃ (776 mg, 3 mmol, 3 equiv) and *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide (677 mg, 2.5 mmol, 2.5 equiv) in THF (14 mL) at 0 °C was added dropwise DIAD (505 mg, 2.5 mmol, 2.5 equiv). After 15 min, the reaction was allowed to warm to room temperature and stirred overnight. After 16 h, the volatiles were evaporated to afford after purification on silica gel (PE/EtOAc: 95/5) the title compound as a colourless oil (315 mg, 0.66 mmol, 67%).

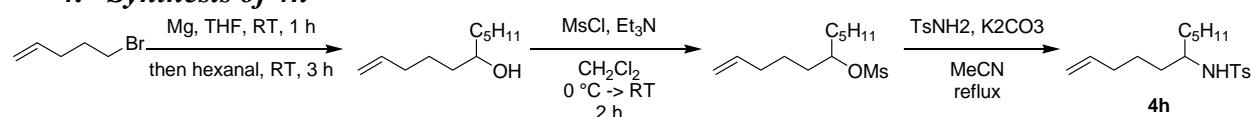
IR (film): ν 2980, 2930, 2865, 1723, 1640, 1598, 1455, 1348, 1282, 1255, 1151, 1087, 993, 911 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.33-7.22 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.79 (ddt, *J* = 17.2, 10.2, 6.6 Hz, 1H), 5.02 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.96 (m, 1H), 4.79 (m, 1H), 4.56 (d_{systAB}, *J* = 11.6 Hz, 1H), 4.44 (d_{systAB}, *J* = 11.6 Hz, 1H), 3.99 (dd_{systAB}, *J* = 9.6, 9.6 Hz, 1H), 3.58 (dd_{systAB}, *J* = 10.0, 5.2 Hz, 1H), 2.34 (s, 3H), 2.12 (m, 2H), 1.94 (m, 1H), 1.69-1.44 (m, 3H), 1.30 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 150.7 (s), 143.6 (s), 138.4 (d), 138.1 (s, C_{qar}), 137.9 (s), 128.9 (d, 2CH), 128.5 (d, 2CH), 128.4 (d, 2CH), 127.9 (d, 2CH), 127.6 (d), 115.0 (t), 84.0 (s), 73.1 (t), 70.8 (t), 58.6 (d), 33.5 (t), 29.9 (t), 28.0 (q, 3CH₃), 25.8 (t), 21.6 (q). SM (EI) *m/z* (abundance): 343 (1), 252 (30), 172 (17), 155 (34), 91 (100), 81 (19), 65 (11). HRMS (ESI): Calculated for C₂₆H₃₅NO₅SNa [M + Na]⁺: 496.2128. Found: 496.2129.

N-[1-(Benzyl)hept-6-en-2-yl]-4-methylbenzenesulfonamide (4j):^[6]

To a stirred solution of *tert*-butyl [1-(benzyloxy)hept-6-en-2-yl]-*N*-(tosyl)carbamate (315 mg, 0.67 mmol, 1 equiv) in CH₂Cl₂ (10 mL) was added dropwise TFA (600 µL). After 2 h at RT, the reaction was quenched by addition of a saturated aqueous NaHCO₃ solution (10 mL). The phases were separated and the organic phase was washed with brine (10 mL), dried over MgSO₄, filtrated and evaporated to afford compound **4j** (116 mg, 0.31 mmol, 46%) as a slightly yellow oil. The product was sufficiently pure to be used without further purification. Spectral data for **4j** match those previously described in the literature.

IR (film): ν 3276, 3064, 2924, 2861, 1746, 1640, 1598, 1496, 1454, 1417, 1325, 1158, 1091, 1022, 996, 909 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.71 (br d, 2H, J = 8.4 Hz), 7.36-7.18 (m, 7H), 5.68 (ddt, 1H, J = 16.8, 10.4, 6.6 Hz), 4.97-4.88 (m, 3H), 4.34 (s, 2H), 3.38-3.28 (m, 2H), 3.24 (m, 1H), 2.39 (s, 3H), 1.93 (q_{app} , 2H, J = 7.2 Hz), 1.59-1.53 (m, 2H), 1.40-1.17 (m, 2H). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.3 (s), 138.4 (d), 138.3 (s), 137.9 (s), 129.7 (d, 2CH), 128.5 (d, 2CH), 127.9 (d), 127.7 (d, 2CH), 127.2 (d, 2CH), 114.8 (t), 73.3 (t), 71.4 (t), 53.7 (d), 33.4 (t), 32.1 (t), 24.9 (t), 21.7 (q). **SM** (EI) m/z (abundance): 252 ((M-BnOCH₂)⁺, 27), 218 (10), 172 (19), 155 (37), 92 (12) 91 (100), 81 (20), 65 (13).

4. Synthesis of **4h**



Undec-1-en-6-ol:^[7]

To a suspension of mg turnings (115 mg, 4.8 mmol, 1.2 equiv) in a minimum of anhydrous THF was added dropwise a solution of 5-bromopent-1-ene (715 mg, 4.8 mmol, 1.2 equiv) in anhydrous THF (20 mL). After complete dissolution of mg turnings (~ 2 h), the reaction mixture was cooled to 0 °C and hexanal (400 mg, 4 mmol, 1 equiv) was added dropwise. The reaction was warmed to room temperature. After 5 h, the reaction was quenched by addition of a saturated aqueous NH₄Cl solution (10 mL) and diluted with EtOAc (20 mL). The phases were separated and the aqueous phase extracted with EtOAc (2 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 9/1) the title compound (395 mg, 2.3mmol, 58%) as a colourless oil. Spectral data match those previously described in the literature.

IR (film): ν 3334, 2929, 2859, 1641, 1459, 1378, 1126, 994, 909 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 5.81 (ddt, 1H, J = 17.0, 10.2, 6.8 Hz), 5.01 (q_{app} , 1H, J = 17.1, 1.8 Hz), 4.95 (br d, 1H, J = 10.2 Hz), 3.60 (m, 1H), 2.12-2.04 (m, 2H), 1.63-1.22 (m, 13H), 0.89 (t, 3H, J = 7.0 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.0 (d), 114.8 (t), 72.0 (d), 37.7, 37.1, 34.0, 32.1, 25.6, 25.2, 22.9 (t, 7CH₂), 14.3 (q). **SM** (EI) m/z (abundance): 152 ((M-H₂O)⁺, 1), 83 (34), 82 (14), 81 (69), 68 (10), 67 (15), 57 (32), 55 (100), 54 (24).

Undec-1-en-6-yl methanesulfonate:

To a solution of undec-1-en-6-ol (391 mg, 2.3 mmol, 1 equiv) and Et₃N (353 mg, 3.5 mmol, 1.5 equiv) in CH₂Cl₂ (7 mL) cooled to 0 °C was added MsCl (285 mg, 2.5 mmol, 1.1 equiv). After 15 min the reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was then quenched with water (5 mL) and the phases separated. The organic phase was washed with brine (7 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford the title compound (470 mg, 1.89 mmol, 82%) as a colourless oil. The product was used without further purification.

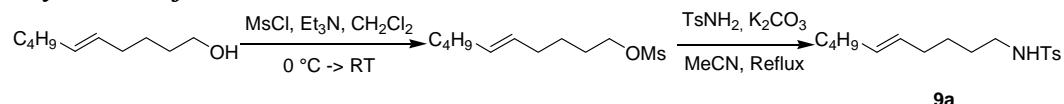
IR (film): ν 2933, 2862, 1641, 1460, 1333, 1172, 970, 901. **^1H NMR** (CDCl_3 , 400 MHz): δ 5.79 (ddt, 1H, J = 17.1, 10.2, 6.8 Hz), 5.06-4.95 (m, 2H), 4.72 (quint_{app.}, 1H, J = 6.0 Hz), 3.00 (s, 3H), 2.09 (q_{app.}, 2H, J = 7.2 Hz), 1.77-1.24 (m, 12H), 0.90 (t, 3H, J = 6.8 Hz). **^{13}C NMR** (CDCl_3 , 100 MHz): δ 138.2 (d), 115.3 (t), 84.2 (d), 38.9 (q), 34.6, 34.0, 33.5, 31.7, 24.8, 24.3, 22.6 (d, 7CH₂), 14.2 (q). **SM** (EI) m/z (abundance): 152 ((M-MsOH)⁺, 1), 97 (16), 96 (20), 95 (15), 83 (22), 82 (37), 81 (64), 69 (38), 68 (36), 67 (52), 57 (12), 56 (15), 55 (100), 54 (96), 53 (16). **HRMS (ESI)**: Calculated for $\text{C}_{12}\text{H}_{24}\text{O}_3\text{SNa}$: 271.1338. Found: 271.1340.

4-Methyl-N-(undec-1-en-6-yl)benzenesulfonamide (4h):^[8]

To a solution of undec-1-en-6-yl methanesulfonate (470 mg, 1.9 mmol, 1 equiv) in CH_3CN (7 mL) was added K_2CO_3 (552 mg, 4 mmol, 2.1 equiv) followed by TsNH_2 (684 mg, 4 mmol, 2.1 equiv). The reaction mixture was refluxed overnight. After 16 h, the mixture was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 95/5) compound **4h** (182 mg, 0.56 mmol, 30%) as a colourless oil. Spectral data for **4h** match those previously described in the literature.

IR (film): ν 3278, 2930, 2859, 1641, 1599, 1496, 1425, 1322, 1158, 1094, 1038, 993, 908 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz): δ 7.76 (br d, 2H, J = 8.3 Hz), 7.29 (br d, 2H, J = 8.2 Hz), 5.67 (ddt, 1H, J = 16.8, 10.4, 6.8 Hz), 4.95-4.87 (m, 2H), 4.43 (br s, 1H, NH), 3.20 (sext_{app.}, 1H), 2.42 (s, 3H), 1.91 (q_{app.}, 2H, J = 6.9 Hz), 1.47-1.02 (m, 12H), 0.81 (t, 3H, J = 7.2 Hz). **^{13}C NMR** (CDCl_3 , 100 MHz): δ 143.3 (s), 138.6 (s), 138.5 (d), 129.7 (d, 2CH), 127.2 (d, 2CH), 114.8 (t), 54.2 (d), 35.2 (t), 34.7 (t), 33.6, 31.7, 25.1, 24.6, 22.7 (t, 5CH₂), 21.7 (q), 14.1 (q). **SM** (EI) m/z (abundance): 254 ((M-pentenyl)⁺, 16), 155 (33), 92 (10), 91 (100), 81 (13), 65 (23), 55 (15).

5. Synthesis of 9a, 9b and 12



9a

(E)-Dec-5-en-1-yl methanesulfonate:

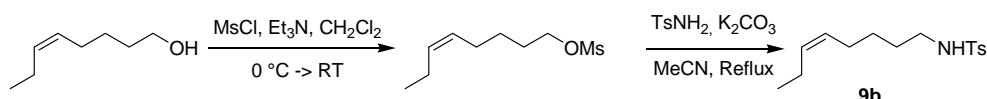
To a solution of (*E*)-dec-5-en-1-ol (472 mg, 2.7 mmol, 1 equiv) and Et_3N (372 mg, 3.7 mmol, 1.4 equiv) in CH_2Cl_2 (10 mL) cooled to 0 °C was added MsCl (370 mg, 2.5 mmol, 1.2 equiv). After 15 min the reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was then quenched with water (5 mL) and the two phases were separated. The organic phase was washed with brine (10 mL), dried over MgSO_4 , filtrated and concentrated under *vacuum* to afford the title compound (630 mg, 2.7 mmol, quant) as a yellow oil. The product was engaged in the next step without further purification.

IR (film): ν 2929, 2859, 1725, 1459, 1352, 1172, 969, 929 cm^{-1} . **^1H NMR** (CDCl_3 , 400 MHz): δ 5.44-5.28 (m, 2H), 4.20 (t, 2H, J = 6.6 Hz), 2.98 (s, 3H), 2.00 (q_{app.}, 2H, J = 7.0 Hz), 1.95 (q_{app.}, 2H, J = 7.0 Hz), 1.72 (m, 2H), 1.44 (m, 2H), 1.32-1.23 (m, 4H), 0.86 (t, 3H, J = 7.0 Hz). **^{13}C NMR** (CDCl_3 , 100 MHz): δ 131.7 (d), 129.2 (d), 70.3 (t), 37.6 (q), 32.4 (t), 32.0 (t), 31.9 (t), 28.7 (t), 25.5 (t), 22.4 (t), 14.2 (q). **SM** (EI) m/z (abundance): 138 ((M-MsOH)⁺, 20), 110 (23), 109 (12), 96 (28), 95 (51), 83 (10), 82 (57), 81 (80), 69 (18), 68 (70), 67 (100), 55 (68), 54 (68), 53 (11). **HRMS (ESI)**: Calculated for $\text{C}_{11}\text{H}_{22}\text{O}_3\text{SNa}$: 257.1182. Found: 257.1185.

(E)-N-(Dec-5-en-1-yl)-4-methylbenzenesulfonamide (9a):

To a solution of (*E*)-dec-5-en-1-yl methanesulfonate (~2.7 mmol, 1 equiv) in MeCN (10 mL) were added K_2CO_3 (745 mg, 5.4 mmol, 2 equiv) and TsNH_2 (923 mg, 5.4 mmol, 2 equiv), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and evaporated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 90/10) product **9a** as a colourless oil (172 mg, 0.55 mmol, 20% (over two steps)).

IR (film): ν 3281, 2926, 2858, 1599, 1434, 1325, 1158, 1094, 968, 920 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.75 (br d, 2H, J = 8.4 Hz), 7.31 (br d, 2H, J = 8.0 Hz), 5.39-5.24 (m, 2H), 4.46 (br s, 1H, NH), 2.93 (q_{app.}, 2H, J = 6.8 Hz), 2.43 (s, 3H), 1.98-1.88 (m, 4H), 1.45 (m, 2H), 1.35-1.25 (m, 6H), 0.88 (t, 3H, J = 6.9 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.3 (s), 137.0 (s), 131.2 (d), 129.7 (d, 2CH), 129.3 (d), 127.1 (d, 2CH), 43.1 (t, C), 32.2, 31.9, 31.8, 29.0, 26.4, 22.2 (t, 6CH₂), 21.5 (q), 14.0 (q). **SM** (EI) *m/z* (abundance): 309 (M⁺, 4), 210 (16), 184 (15), 155 (57), 154 (44), 138 (17), 96 (14), 95 (47), 92 (12), 91 (100), 84 (18), 82 (14), 81 (57), 69 (15), 68 (11), 67 (53), 56 (11), 55 (27). **HRMS** (ESI): Calculated for C₁₇H₂₇NO₂SNa: 332.1655. Found: 332.1654.



(Z)-Oct-5-en-1-yl methanesulfonate:

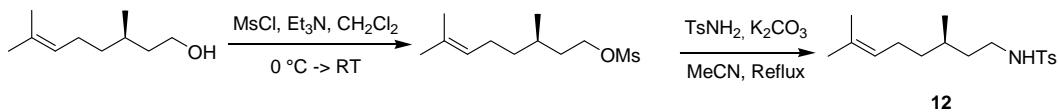
To a solution of (Z)-oct-5-en-1-ol (640 mg, 5 mmol, 1 equiv) and Et₃N (725 mg, 7.5 mmol, 1.5 equiv) in CH₂Cl₂ (10 mL) cooled to 0 °C was added MsCl (626 mg, 5.5 mmol, 1.1 equiv). After 15 min the reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was then quenched with water (10 mL) and the two phases were separated. The organic phase was washed with brine, dried over MgSO₄, filtrated and concentrated under *vacuum* to afford the title compound (1.031 g, 5 mmol, quant) as a colourless oil. The product was used without further purification.

IR (film): ν 2937, 1460, 1351, 1171, 972, 931 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 5.38 (dtt, 1H, J = 10.9, 7.1, 1.5 Hz), 5.26 (dtt, 1H, J = 10.9, 7.2, 1.5 Hz), 4.20 (t, 2H, J = 6.6 Hz), 2.98 (s, 3H), 2.04 (quint_{app.}, 2H, J = 7.5 Hz), 2.01 (quint_{app.}, 2H, J = 7.7 Hz), 1.73 (tt, 2H, J = 7.7, 6.8 Hz), 1.44 (quint_{app.}, 2H, J = 7.5 Hz), 0.93 (t, 3H, J = 7.6 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 132.8 (d), 128.2 (d), 70.2 (t), 37.6 (q), 28.8 (t), 26.5 (t), 25.7 (t), 20.7 (t), 14.5 (q). **SM** (EI) *m/z* (abundance): 110 ((M-MsOH)⁺, 22), 95 (19), 82 (63), 81 (51), 79 (23), 69 (21), 68 (67), 67 (100), 55 (28), 54 (17), 53 (11). **HRMS** (ESI): Calculated for C₉H₁₈O₃SNa: 229.0869. Found: 229.0870.

(Z)-4-Methyl-N-(oct-5-en-1-yl)benzenesulfonamide (9b):

To a solution of (Z)-oct-5-en-1-yl methanesulfonate (~ 5 mmol, 1 equiv) in MeCN (10 mL) were added K₂CO₃ (1.38 g, 10 mmol, 2 equiv) and TsNH₂ (1.78 g, 10 mmol, 2 equiv), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and evaporated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 95/5) product **9b** as a colourless oil (624 mg, 2.2 mmol, 44% over two steps).

IR (film): ν 3280, 2961, 2933, 2869, 1599, 1455, 1425, 1323, 1156, 1093 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.75 (br d, 2H, J = 8.4 Hz), 7.31 (br d, 2H, J = 8.4 Hz), 5.44-5.16 (m, 2H), 4.50 (m, 1H, NH), 2.93 (q_{app.}, 2H, J = 6.8 Hz), 2.43 (s, 3H), 2.02-1.88 (m, 4H), 1.46 (m, 2H), 1.31 (m, 2H), 0.92 (t, 3H, J = 7.5 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.3 (s), 137.0 (s), 132.3 (d) 129.7 (d, 2CH), 128.2 (d), 127.1 (d, 2CH), 43.1 (t), 29.1 (t), 26.6 (t), 26.4 (t), 21.5 (q), 20.5 (t), 14.3 (q). **SM** (EI) *m/z* (abundance): 281 (M⁺, 5), 210 (17), 184 (14), 155 (56), 126 (42), 110 (22), 109 (37), 92 (12), 91 (100), 84 (14), 81 (13), 68 (12), 67 (79), 65 (25), 55 (20). **HRMS** (ESI): Calculated for C₁₅H₂₈NO₂SNa: 304.1342. Found: 304.1343.



(R)-3,7-Dimethyloct-6-en-1-yl methanesulfonate:

To a solution of (*R*)-3,7-dimethyloct-6-en-1-ol (391 mg, 2.5 mmol, 1 equiv) and Et₃N (757 mg, 7.5 mmol, 3 equiv) in CH₂Cl₂ (5 mL) cooled to 0 °C was added MsCl (300 mg,

2.625 mmol, 1.05 equiv). After 15 min the reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was then quenched with water (10 mL) and the phases separated. The organic phase was washed with brine (10 mL), dried over MgSO₄, filtrated and concentrated under *vacuum* to afford the title compound (553 mg, 2.36 mmol, 95%) as a colourless oil. The product was used without further purification.

[α]_D²⁰ : + 3.1 (*c* 1.09, CHCl₃). **IR** (film): ν 2964, 2915, 1455, 1351, 1172, 973, 938 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 5.08 (br t, 1H, *J* = 7.0 Hz), 4.32-4.20 (m, 2H), 3.00 (s, 3H), 2.07-1.91 (m, 2H), 1.80 (m, 1H), 1.68 (s, 3H), 1.65-1.50 (m, 2H), 1.60 (s, 3H), 1.37 (m, 1H, H₄), 1.20 (m, 1H), 0.94 (d, 3H, *J* = 6.4 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 131.6 (s), 124.3 (d), 68.6 (t), 37.4 (q), 36.8 (t), 35.9 (t), 29.0 (d), 25.7 (q), 25.3 (t), 19.2 (q), 17.7 (q). **SM** (EI) *m/z* (abundance): 234 (M⁺, 1), 138 (21), 123 (34), 123 (34), 109 (31), 96 (16), 95 (70), 83 (17), 82 (72), 81 (79), 79 (20), 70 (15), 69 (100), 68 (42), 67 (10), 57 (10), 56 (20), 55 (67), 53 (12). **HRMS** (ESI): Calculated for C₁₁H₂₂O₃Na: 257.1182. Found: 257.1184.

(R)-N-(3,7-Dimethyloct-6-en-1-yl)-4-methylbenzenesulfonamide (12):

To a solution of (*R*)-3,7-dimethyloct-6-en-1-yl methanesulfonate (553 mg, 2.36 mmol, 1 equiv) in MeCN (10 mL) were added K₂CO₃ (657 mg, 4.76 mmol, 2 equiv) and TsNH₂ (814 g, 4.76 mmol, 2 equiv), and the reaction was heated to reflux. After 5 h, the reaction mixture was filtrated through Celite® and evaporated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 95/5 to 90/10) product **12** as a very low melting point solid (mp < 25 °C) (560 mg, 1.81 mmol, 78%).

IR (film): ν 3281, 2962, 2922, 1599, 1450, 1324, 1158, 1094 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.75 (br d, 2H, *J* = 8.4 Hz), 7.31 (br d, 2H, *J* = 8.2 Hz), 5.02 (br t, 1H, *J* = 7.0 Hz), 4.48 (m, 1H, NH), 3.02-2.88 (m, 2H), 2.43 (s, 3H), 1.98-1.80 (m, 2H), 1.67 (s, 3H), 1.57 (s, 3H), 1.51-1.36 (m, 2H), 1.31-1.03 (m, 3H), 0.81 (d, 3H, *J* = 6.6 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.3 (s), 137.0 (s), 131.4 (s), 129.7 (d, 2CH), 127.1 (d, 2CH), 124.4 (d), 41.3 (t), 36.8, 36.5 (t, 2C), 29.8 (d), 25.7 (q), 25.3 (t), 21.5 (q), 19.2 (q), 17.1 (q). **SM** (EI) *m/z* (abundance): 309 (M⁺, 1), 224 (34), 184 (12), 155 (47), 154 (44), 138 (27), 137 (11), 95 (42), 92 (10), 91 (84), 82 (18), 81 (100), 70 (10), 69 (43), 67 (20), 65 (19), 55 (20). **HRMS** (ESI): Calculated for C₁₇H₂₇NO₂Na: 332.1655. Found: 332.1656.

III. Cyclisation products

4,4-Dimethyl-1-tosyl-2-vinylpyrrolidine (2):^[9] and

3,3,6-trimethyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydropyridine (3)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **1** (28 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature and filtered through Celite® to afford after purification on silica gel (PE/EtOAc: 98/2) compound **2** as a white solid and compound **3** as a colourless oil (21.6 mg, 0.077 mmol, 77%) in a 5/1 ratio in favour of **2**. Spectral data for **2** match those previously described in the literature.

4,4-Dimethyl-1-tosyl-2-vinylpyrrolidine (2):^[9]

mp: 65 °C. **IR** (film): ν 2959, 2873, 1644, 1598, 1467, 1345, 1214, 1158, 1093, 1056, 1029, 1017, 984, 922 cm⁻¹. **¹H NMR** (CDCl₃, 100 MHz): δ 7.68 (d, 2H, *J* = 8.2 Hz), 7.28 (d, 2H, *J* = 8.2 Hz), 5.84 (ddd, 1H, *J* = 17.2, 10.4, 7.6 Hz), 5.15 (br d, 1H, *J* = 17.2 Hz), 5.05 (br d, 1H, *J* = 10.4 Hz), 3.99 (dt, 1H, *J* = 8.4, 7.4 Hz), 3.17 (d_{systAB}, 1H, *J* = 10.4 Hz), 3.12 (dd_{systAB}, 1H, *J* = 10.1, 0.9 Hz), 2.41 (s, 3H), 1.71 (ddd_{systAB}, 1H, *J* = 12.4, 7.4, 0.9 Hz), 1.55 (dd_{systAB}, 1H, *J* = 12.7, 8.4 Hz), 1.03 (s, 3H, H₆), 0.67 (s, 3H). **¹³C NMR** (CDCl₃, 400 MHz): δ 143.4 (s), 140.0 (d), 135.6 (s), 129.7 (d, 2CH), 127.8 (d, 2CH), 115.4 (d), 62.7 (d), 61.7 (d), 47.7 (t), 37.7 (s), 26.7 (q), 26.3 (q), 21.8 (q). **SM** (EI) *m/z* (abundance): 279 (M⁺, 3), 252 (21), 215 (20), 214 (33), 200 (16), 155 (23), 124 (28), 119 (21), 91 (64), 81 (21), 68 (100), 67 (13), 65 (18), 55

(13).

3,3,6-Trimethyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydropyridine (3):

¹H NMR (CDCl_3 , 400 MHz): δ 7.72 (br d, 2H, $J = 8.4$ Hz), 7.29-7.23 (br d, 2H, $J = 8.4$ Hz), 5.47 (br d, 1H, $J = 10.0$ Hz), 5.44 (dd, 1H, $J = 10.0, 3.2$ Hz), 4.36 (qd, 1H, $J = 6.7, 3.1$ Hz), 3.42 (d_{systAB} , 1H, $J = 12.8$ Hz), 2.83 (d_{systAB} , 1H, $J = 12.8$ Hz), 2.41 (s, 3H), 1.04 (d, 3H, $J = 6.7$ Hz), 0.96 (s, 3H), 0.93 (s, 3H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 142.9 (s), 138.5 (s), 135.1 (d), 129.5 (d, 2CH), 127.1 (d, 2CH), 126.9 (d), 50.2 (t), 49.3 (d), 33.0 (s), 26.6, 26.4 (q, 2CH₃), 21.5 (q), 18.1 (q). **SM** (EI) m/z (abundance): 264 ((M - Me)⁺, 100), 155 (21), 108 (37), 96 (76), 91 (61), 81 (43), 67 (11), 65 (18), 55 (14). **HRMS** (ESI): Calculated for $\text{C}_{15}\text{H}_{21}\text{NO}_2\text{SNa}$ [M + Na]⁺: 302.2285. Found: 302.1188.

1-[(4-Methoxyphenyl)sulfonyl]-4,4-dimethyl-2-vinylpyrrolidine (5a) and

N-(4-methoxyphenyl)sulfonyl-3,3,6-trimethyl-1,2,3,6-tetrahydropyridine (6a)

[(MeCN)₃RhCp^{*}] (SbF_6)₂ (4.2 mg, 0.005 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4a** (30 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5a** and **6a** as colourless oils (18.4 mg, 0.061 mmol, 61%) in a 15/1 ratio in favour of **5a**.

1-[(4-Methoxyphenyl)sulfonyl]-4,4-dimethyl-2-vinylpyrrolidine (5a):

IR (film): ν 3080, 2960, 2873, 1597, 1578, 1497, 1466, 1344, 1259, 1156, 1094, 1055, 1026, 923 cm^{-1} . **¹H NMR** (CDCl_3 , 400 MHz): δ 7.76 (br d, 2H, $J = 8.8$ Hz), 6.98 (br d, 2H, $J = 8.8$ Hz), 5.87 (ddd, 1H, $J = 17.2, 10.0, 7.6$ Hz), 5.17 (br d, 1H, $J = 17.2$ Hz), 5.07 (br d, 1H, $J = 10.0$ Hz), 4.00 (q_{app.}, 1H, $J = 7.6$ Hz), 3.87 (s, 3H), 3.19 (d_{systAB} , 1H, $J = 10.4$ Hz), 3.13 (d_{systAB} , 1H, $J = 10.4$ Hz), 1.74 (dd_{systAB}, 1H, $J = 12.8, 7.6$ Hz), 1.58 (dd_{systAB}, 1H, $J = 12.8, 8.4$ Hz), 1.06 (s, 3H), 0.71 (s, 3H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 163.0 (s), 140.1 (d), 130.3 (s), 129.8 (d, 2CH), 115.3 (t), 114.2 (d, 2CH), 62.6 (d), 61.7 (t), 55.8 (q), 47.7 (t), 37.7 (s), 26.8, 26.3 (q, 2CH₃). **SM** (EI) m/z (abundance): 295 (M⁺, 5), 268 (15), 231 (15), 230 (20), 216 (15), 171 (35), 135 (18), 108 (12), 107 (21), 92 (14), 81 (16), 77 (26), 68 (100), 55 (11). **HRMS** (ESI): Calculated for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{SNa}$: 318.1134. Found 318.1127.

N-(4-Methoxyphenyl)sulfonyl-3,3,6-trimethyl-1,2,3,6-tetrahydropyridine (6a):

IR (film): ν 2960, 2923, 2868, 1597, 1579, 1498, 1461, 1335, 1303, 1259, 1156, 1096, 1026, 1000, 912 cm^{-1} . **¹H NMR** (CDCl_3 , 400 MHz): δ 7.77 (br d, 2H, $J = 9.2$ Hz), 6.95 (br d, 2H, $J = 9.2$ Hz), 5.49-5.42 (m, 2H), 4.35 (qd, 1H, $J = 6.8, 2.8$ Hz), 3.86 (s, 3H), 3.38 (d_{systAB} , 1H, $J = 12.8$ Hz), 2.82 (d_{systAB} , 1H, $J = 12.4$ Hz), 1.06 (d, 3H, $J = 6.4$ Hz), 0.96 (s, 3H), 0.92 (s, 3H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 162.5 (s), 135.0 (d), 133.2 (s), 129.2 (d, 2CH), 127.0 (d), 114.0 (d, 2CH), 55.6 (d), 50.1 (t), 49.3 (q), 33.0 (s), 26.6, 26.4 (q, 2CH₃), 18.1 (q). **SM** (EI) m/z (abundance): 282 ((M - Me)⁺, 6), 281 (19), 280 (100), 171 (62), 123 (15), 108 (24), 107 (32), 96 (91), 92 (14), 81 (50), 79 (11), 77 (29), 67 (12), 55 (20). **HRMS** (ESI): Calculated for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{SNa}$: 318.1134. Found 318.1132.

4,4-Dimethyl-1-(phenylsulfonyl)-2-vinylpyrrolidine (5b) and

3,3,6-trimethyl-1-(phenylsulfonyl)-1,2,3,6-tetrahydropyridine (6b)

[(MeCN)₃RhCp^{*}] (SbF_6)₂ (4.2 mg, 0.005 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4b** (27 mg, 0.1 mmol, 1 equiv)

in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered on Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5b** and **6b** as colourless oils (8.5 mg, 0.032 mmol, 32%) in a 7/1 ratio in favour of **5b**.

4,4-Dimethyl-1-(phenylsulfonyl)-2-vinylpyrrolidine (5b):

IR (film): ν 2959, 2926, 2872, 1468, 1447, 1344, 1161, 1094, 1057, 923 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.85-7.81 (m, 2H), 7.58-7.49 (m, 3H), 5.86 (ddd, 1H, J = 17.2, 10.2, 7.6 Hz), 5.19 (dt, 1H, J = 17.2, 1.0 Hz), 5.08 (dt, 1H, J = 10.4, 1.0 Hz), 4.06 (br q_{app.}, 1H, J = 7.7 Hz), 3.20 (d_{systAB}, 1H, J = 10.4 Hz), 3.17 (br d_{systAB}, 1H, J = 10.4 Hz), 1.75 (ddd_{systAB}, 1H, J = 12.4, 7.4, 0.8 Hz), 1.58 (dd_{systAB}, 1H, J = 12.6, 8.4 Hz), 1.06 (s, 3H), 0.68 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.6 (d), 138.4 (s), 132.5 (d), 128.9 (d, 2CH), 127.5 (d, 2CH), 115.3 (t), 62.6 (d), 61.4 (t), 47.6 (t), 37.5 (s), 26.4, 25.9 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 265 (M⁺, 2), 238 (25), 201 (17), 200 (40), 186 (17), 141 (21), 124 (28), 105 (20), 96 (11), 81 (27), 77 (69), 69 (10), 68 (100), 67 (14), 55 (17), 51 (15). **HRMS** (ESI): Calculated for C₁₄H₁₉NO₂SNa: 288.1029. Found 288.1029.

3,3,6-Trimethyl-1-(phenylsulfonyl)-1,2,3,6-tetrahydropyridine (6b):

IR (film): ν 2960, 2927, 2868, 1714, 1447, 1333, 1160, 1095, 1002, 913 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.87-7.82 (m, 2H), 7.58-7.46 (m, 3H), 5.48 (br d, 1H, J = 10.4 Hz), 5.44 (dd, 1H, J = 10.4, 3.0 Hz), 4.39 (qd, 1H, J = 6.6, 3.0 Hz), 3.45 (d_{systAB}, 1H, J = 12.8 Hz), 2.85 (d_{systAB}, 1H, J = 12.7 Hz), 1.04 (d, 3H, J = 6.6 Hz), 0.96 (s, 3H), 0.92 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.6 (s), 135.1 (d), 132.2 (d), 128.9 (d, 2CH), 127.1 (d, 2CH), 126.8 (d), 50.2 (t), 49.4 (d), 33.0 (s), 26.6, 26.4 (q, 2CH₃), 18.2 (q). **SM** (EI) *m/z* (abundance): 250 ((M - Me)⁺, 100), 141 (16), 109 (10), 108 (53), 96 (64), 81 (47), 77 (51), 67 (12), 55 (18), 51 (11). **HRMS** (ESI): Calculated for C₁₄H₁₉NO₂SNa: 288.1029. Found 288.1033.

1-[(4-Bromophenyl)sulfonyl]-4,4-dimethyl-2-vinylpyrrolidine (5c) and

N-(4-bromophenyl)sulfonyl-3,3,6-trimethyl-1,2,3,6-tetrahydropyridine (6c)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4c** (35 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5c** and **6c** as colourless oils (8.7 mg, 0.025 mmol, 25%) in a 3/1 ratio in favour of **5c**.

1-[(4-Bromophenyl)sulfonyl]-4,4-dimethyl-2-vinylpyrrolidine (5c):

IR (film): ν 3087, 2960, 2872, 1574, 1470, 1389, 1350, 1164, 1092, 1067, 1008, 923 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.72-7.61 (m, 4H), 5.79 (ddd, 1H, J = 17.2, 10.2, 7.8 Hz), 5.18 (br d, 1H, J = 17.2 Hz), 5.08 (br d, 1H, J = 10.1 Hz), 4.06 (q_{app.}, 1H, J = 7.8 Hz), 3.18 (s, 2H), 1.79 (dd_{systAB}, 1H, J = 12.8, 7.6 Hz), 1.58 (dd_{systAB}, 1H, J = 12.8, 8.4 Hz), 1.07 (s, 3H), 0.77 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.2 (d), 137.9 (s), 132.1 (d, 2CH), 129.0 (d, 2CH), 127.4 (s), 115.8 (t), 62.6 (d), 61.4 (t), 47.5 (t), 37.6 (s), 26.3, 26.1 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 345 (M(⁸¹Br)⁺, 1), 343 (M(⁷⁹Br)⁺, 1), 318 (10), 280 (13), 278 (13), 157 (13), 155 (13), 124 (27), 108 (10), 96 (12), 81 (30), 76 (13), 75 (11), 68 (100), 67 (16), 55 (18). **HRMS** (ESI): Calculated for C₁₄H₁₈(⁷⁹Br)NO₂SNa: 366.0134. Found 366.0136.

N-(4-Bromophenyl)sulfonyl-3,3,6-trimethyl-1,2,3,6-tetrahydropyridine (6c):

IR (film): ν 2959, 2925, 2868, 1714, 1575, 1470, 1389, 1340, 1162, 1094, 1069, 1001, 913 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.73-7.60 (m, 4H), 5.49 (br d, 1H, J = 10.4 Hz), 5.44 (dd, 1H, J = 10.0, 3.6 Hz), 4.37 (m, 1H), 3.43 (br d_{systAB}, 1H, J = 12.8 Hz), 2.84 (d_{systAB}, 1H, J = 12.8 Hz), 1.05 (d, 3H, J = 6.7 Hz), 0.97 (s, 3H), 0.93 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 140.6 (s), 139.7 (s), 135.1 (d), 132.2 (d, 2CH), 128.6 (d, 2CH), 126.7 (d), 50.2 (t), 49.5 (d), 33.0 (s), 26.5, 26.4 (q, 2CH₃), 18.2 (q). **SM** (EI) *m/z* (abundance): 330 ((M(⁸¹Br)

- Me)⁺, 68), 328 (M(⁷⁹Br) - Me)⁺, 65), 221 (11), 219 (11), 157 (15), 155 (14), 109 (16), 108 (73), 96 (100), 94 (10), 82 (11), 81 (67), 79 (14), 76 (14), 75 (12), 55 (27), 53 (13). **HRMS** (ESI): Calculated for C₁₄H₁₈(⁷⁹Br)NO₂SNa: 366.0134. Found 366.0135.

4,4-Dimethyl-1-[(4-nitrophenyl)sulfonyl]-2-vinylpyrrolidine (**5d**) and 3,3,6-trimethyl-1-[(4-nitrophenyl)sulfonyl]-1,2,3,6-tetrahydropyridine (**6d**)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4d** (31 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5d** and **6d** as colourless oils (4.5 mg, 0.014 mmol, 14%) in a 4/1 ratio in favour of **5d**.

4,4-Dimethyl-1-[(4-nitrophenyl)sulfonyl]-2-vinylpyrrolidine (**5d**):

IR (film): ν 3105, 2961, 2872, 1720, 1605, 1528, 1348, 1306, 1161, 1092, 1058, 925 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 8.36-8.30 (m, 2H), 8.00-7.95 (m, 2H), 5.67 (ddd, 1H, *J* = 17.2, 10.0, 7.6 Hz), 5.19 (br d, 1H, *J* = 17.2 Hz), 5.07 (br d, 1H, *J* = 10.0 Hz), 4.16 (q, 1H, *J* = 8.0 Hz), 3.28 (dd_{systAB}, 1H, *J* = 10.0, 1.6 Hz), 3.15 (d_{systAB}, 1H, *J* = 10.0 Hz), 1.82 (ddd_{systAB}, 1H, *J* = 12.8, 7.4, 1.6 Hz), 1.56 (dd_{systAB}, 1H, *J* = 12.8, 8.2 Hz), 1.06 (s, 3H), 0.80 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 150.1 (s), 145.4 (s), 138.7 (d), 128.7 (d, 2CH), 124.3 (d, 2CH), 116.8 (t), 63.1 (d), 61.5 (t), 47.7 (t), 38.0 (s), 26.3, 26.1 (q, 2CH₃). **SM** (EI) *m/z* (abundance): 295 ((M-Me)⁺, 2), 283 (14), 246 (12), 245 (33), 231 (17), 156 (12), 124 (25), 122 (14), 108 (14), 96 (12), 93 (10), 92 (14), 82 (13), 81 (30), 76 (12), 69 (13), 68 (100), 67 (19), 65 (11), 55 (24). **HRMS** (ESI): Calculated for C₁₄H₁₈N₂O₄SNa: 333.0880. Found: 333.0879.

3,3,6-Trimethyl-1-[(4-nitrophenyl)sulfonyl]-1,2,3,6-tetrahydropyridine (**6d**):

IR (film): ν 2958, 2925, 2854, 1735, 1606, 1530, 1464, 1349, 1162, 1095, 1001, 914 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 8.38-8.32 (m, 2H), 8.05-7.99 (m, 2H), 5.51 (br d, 1H, *J* = 10.2 Hz), 4.45 (dd_{app}, 1H, *J* = 10.2, 3.8 Hz), 4.43 (m, 1H), 3.51 (d_{systAB}, 1H, *J* = 12.8 Hz), 2.89 (d_{systAB}, 1H, *J* = 12.8 Hz), 1.05 (d, 3H, *J* = 6.8 Hz), 0.99 (s, 3H), 0.93 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 149.8 (s), 147.5 (s), 135.2 (d), 128.2 (d, 2CH), 126.3 (d), 124.3 (d, 2CH), 50.4 (t), 49.7 (d), 33.1 (s), 26.4 (q, 2CH₃), 18.5 (q). **SM** (EI) *m/z* (abundance): 295 ((M-Me)⁺, 100), 207 (20), 108 (66), 96 (72), 81 (54), 55 (22).

4,4-Dimethyl-1-(methylsulfonyl)-2-vinylpyrrolidine (**5f**) and

3,3,6-trimethyl-1-(methylsulfonyl)-1,2,3,6-tetrahydropyridine (**6f**)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4f** (21 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5f** and **6f** as an inseparable mixture (8.2 mg, 0.040 mmol, 40%) in a 8/2 ratio in favour of **5f**.

4,4-Dimethyl-1-(methylsulfonyl)-2-vinylpyrrolidine (**5f**):

¹H NMR (CDCl₃, 400 MHz): δ 5.78 (ddd, 1H, *J* = 17.2, 10.0, 8.0 Hz), 5.25 (dt_{app}, 1H, *J* = 17.2, 1.0 Hz), 5.13 (br d, 1H, *J* = 10.1 Hz), 4.30 (q_{app}, 1H, *J* = 8.0 Hz), 3.38 (dd_{systAB}, 1H, *J* = 9.9, 1.5 Hz), 3.06 (dd_{systAB}, 1H, *J* = 10.0, 1.4 Hz), 2.85 (s, 3H, H₉), 1.95 (ddd_{systAB}, 1H, *J* = 12.8, 7.6, 1.2 Hz), 1.59 (dd_{systAB}, 1H, *J* = 12.8, 8.4 Hz), 1.10 (s, 3H), 1.08 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 139.0 (d), 116.9 (t), 62.2 (d), 60.7 (t), 47.7 (t), 40.1 (q), 37.9 (s), 26.1 (d, 2CH₃). **SM** (EI) *m/z* (abundance): 203 (M⁺, 13), 188 (22), 176 (22), 124 (81), 108 (25), 98

(27), 96 (14), 82 (11), 81 (42), 79 (13), 69 (15), 68 (100), 67 (22), 55 (27), 54 (11).

3,3,6-Trimethyl-1-(methylsulfonyl)-1,2,3,6-tetrahydropyridine (6f):

¹H NMR (CDCl_3 , 400 MHz): δ 5.51 (dt_{app.}, 1H, J = 10.2, 1.4 Hz), 5.46 (dd, 1H, J = 10.2, 3.8 Hz), 4.30 (m, 1H), 3.33 (br d_{systAB}, 1H, J = 12.7 Hz), 2.87 (s, 3H), 2.82 (br d_{systAB}, 1H, J = 12.5 Hz), 1.24 (d, 3H, J = 6.8 Hz), 1.07 (s, 3H), 0.98 (s, 3H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 135.3 (d), 126.7 (d), 49.9 (t), 49.2 (d), 40.2 (q), 29.8 (s), 26.5, 26.4 (q, 2CH₃), 18.3 (q). **SM (EI) *m/z* (abundance):** 188 ((M - Me)⁺, 100), 110 (14), 109 (15), 108 (75), 96 (60), 94 (13), 82 (12), 81 (65), 79 (14), 68 (19), 67 (16), 55 (19), 53 (11).

1-Tosyl-2-vinylpyrrolidine (5g):^[10]

$[(\text{MeCN})_3\text{RhCp}^*](\text{SbF}_6)_2$ (4.2 mg, 0.005 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **7a** (26 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compound **8a** (12.6 mg, 0.050 mmol, 50%) as a white solid. Spectral data for **8a** match those previously described in the literature.

mp: 70 °C (litt:^[12] mp 65-66 °C). **IR** (film): ν 2920, 1597, 1449, 1404, 1344, 1196, 1158, 1093, 1055, 1010, 920 cm^{-1} . **¹H NMR** (CDCl_3 , 400 MHz): δ 7.72 (d_{app.}, 2H, J = 8.0 Hz), 7.31 (d_{app.}, 2H, J = 8.0 Hz), 5.81 (ddd, 1H, J = 16.8, 10.4, 6.0 Hz), 5.28 (dt_{app.}, 1H, J = 16.8, 1.4 Hz), 5.12 (dt_{app.}, 1H, J = 10.4, 1.3 Hz), 4.14 (m, 1H), 3.45 (ddd_{systAB}, 1H, J = 11.6, 7.2, 4.2 Hz), 3.23 (dt_{systAB}, 1H, J = 9.6, 7.4 Hz), 2.43 (s, 3H), 1.87-1.58 (m, 4H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 143.4 (s), 138.9 (d), 135.3 (s), 129.8 (d, 2CH), 127.7 (d, 2CH), 115.5 (t), 62.1 (d), 49.0 (t), 32.5 (t), 23.9 (t), 21.7 (q). **SM (EI) *m/z* (abundance):** 251 (M⁺, 9), 224 (30), 187 (15), 186 (30), 155 (36), 96 (63), 92 (14), 91 (100), 69 (21), 68 (41), 67 (14), 65 (30), 54 (16).

2-Pentyl-1-tosyl-5-vinylpyrrolidine (5h) and

6-methyl-2-pentyl-1-tosyl-1,2,3,6-tetrahydropyridine (6h):

$[(\text{MeCN})_3\text{RhCp}^*](\text{SbF}_6)_2$ (2.5 mg, 0.003 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.13 mmol, 2.1 equiv) were added to a solution of sulfonamide **4h** (19 mg, 0.060 mmol, 1 equiv) in DCE (0.6 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5h** and **6h** (8.7 mg, 0.030 mmol, 50%) in a 90/10 ratio in favour of **5h**.

IR (film): ν 2955, 2927, 2859, 1599, 1494, 1460, 1347, 1203, 1160, 1094, 1040, 986 cm^{-1} .

2-Pentyl-1-tosyl-5-vinylpyrrolidine (5h)

cis-2-Pentyl-1-tosyl-5-vinylpyrrolidine (major diastereoisomer):

¹H NMR (CDCl_3 , 400 MHz): δ 7.65 (br d, 2H, J = 8.0 Hz), 7.23 (br d, 2H, J = 8.0 Hz), 5.76 (ddd, 1H, J = 17.0, 10.4, 5.8 Hz), 5.22 (dt, 1H, J = 17.0, 1.4 Hz), 5.04 (dt, 1H, J = 10.4, 1.4 Hz), 4.04 (m, 1H), 3.55 (m, 1H), 2.36 (s, 3H), 1.86 (m, 1H), 1.74-1.10 (m, 11H), 0.82 (m, 3H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 143.2 (s), 139.6 (d), 135.5 (s), 129.6 (d, 2CH), 127.6 (d, 2CH), 115.2 (t), 62.9 (d), 62.1 (d), 36.9, 31.7, 31.0, 29.7, 22.6, 21.6 (t, 6CH₂), 21.5 (q), 14.1 (q). **SM (EI) *m/z* (abundance):** 294 ((M - vinyl)⁺, 1), 251 (15), 250 (100), 155 (32), 94 (42), 91 (70), 65 (11).

trans-2-Pentyl-1-tosyl-5-vinylpyrrolidine (minor diastereoisomer, only the following signals of the ¹H NMR and ¹³C NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl₃, 400 MHz): δ 5.48 (m, 1H), 5.10 (d, 1H, J = 16.8 Hz), 4.91 (br d, 1H, J = 10.4 Hz), 4.26 (t_{app} , 1H, J = 7.6 Hz), 3.74 (m, 1H), 2.34 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 137.9 (d), 129.1 (d, 2CH), 126.7 (d, 2CH), 116.1 (t), 63.2 (d), 60.6 (d). **SM (EI) m/z** (abundance): 250 ((M - pentyl)⁺, 100), 155 (31), 94 (48), 91 (69), 65 (11).

6-Methyl-2-pentyl-1-tosyl-1,2,3,6-tetrahydropyridine (6h) (only the following signals of the ¹H NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl₃, 400 MHz): δ 5.55-5.46 (m, 2H), 4.26 (m, 1H), 3.91 (m, 1H), 2.33 (s, 3H), 1.31 (d, 3H, J = 7.2 Hz). **SM (EI) m/z** (abundance): 306 ((M - methyl)⁺, 16), 251 (14), 250 (31), 155 (33), 94 (23), 91 (74).

HRMS (ESI): Calculated for C₁₈H₂₇NO₂SnA: 344.1655. Found 344.1659.

2-Benzyl-1-tosyl-5-vinylpyrrolidine (5i) and

2-benzyl-6-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6i)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4i** (31 mg, 0.09 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered on Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **5i** and **6i** as a colourless oil (7.5 mg, 0.022 mmol, 25%) in a 15/1 ratio in favour of **5i**.

IR: ν 2926, 1726, 1598, 1495, 1453, 1342, 1157, 1092, 1030, 986, 921 cm⁻¹.

2-Benzyl-1-tosyl-5-vinylpyrrolidine (5i):

cis-2-Benzyl-1-tosyl-5-vinylpyrrolidine (major diastereoisomer):

¹H NMR (CDCl₃, 400 MHz): δ 7.76 (br d, 2H, J = 8.4 Hz), 7.34-7.19 (m, 7H), 5.80 (ddd, 1H, J = 16.8, 10.4, 6.0 Hz), 5.28 (dt, 1H, J = 17.2, 1.3 Hz), 5.12 (dt, 1H, J = 10.4, 1.2 Hz), 4.08 (m, 1H), 3.84 (m, 1H), 3.38 (d_{systAB}, 1H, J = 13.2, 3.6 Hz), 2.72 (dd_{systAB}, 1H, J = 13.2, 10.0 Hz), 2.42 (s, 3H), 1.66-1.36 (m, 4H). **¹³C NMR** (CDCl₃, 100 MHz): δ 143.4 (s), 139.4 (d), 138.5 (s), 135.1 (s), 129.7, 129.6, 128.5, 127.7, 126.5 (d, 9CH), 115.4 (t), 63.5 (d), 63.3 (d), 43.2 (t), 30.9, 28.9 (t, 2CH₂), 21.6 (q). **SM (EI) m/z** (abundance): 250 ((M - benzyl)⁺, 63), 155 (26), 94 (44), 91 (100), 65 (18).

trans-2-Benzyl-1-tosyl-5-vinylpyrrolidine (minor diastereoisomer, only the following signals of the ¹H NMR and ¹³C NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl₃, 400 MHz): δ 5.48 (ddd, 1H, J = 17.0, 10.2, 8.8 Hz), 5.18 (d, 1H, J = 16.8 Hz), 4.97 (d, 1H, J = 10.0 Hz), 4.36 (t_{app} , 1H, J = 8.2 Hz), 4.07 (m, 1H), 3.42 (dd_{systAB}, 1H, J = 13.2, 3.2 Hz), 2.63 (dd_{systAB}, 1H, J = 13.2, 10.1 Hz), 2.41 (s, 3H). **¹³C NMR** (CDCl₃, 100 MHz): δ 137.7 (d), 129.3, 128.5, 127.7, 127.1, 126.8 (d, 9CH), 116.5 (t), 61.8 (d), 59.9 (d), 41.3 (t), 30.6, 27.6 (t, 2CH₂), 21.3 (q).

2-Benzyl-6-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6i) (only the following signals of the ¹H NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl₃, 400 MHz): δ 5.68-5.61 (m, 2H), 0.81 (d, 3H, J = 6.4 Hz).

2-[(Benzyl)oxy]methyl-1-tosyl-5-vinylpyrrolidine (5j) and

2-[(benzyl)oxy]methyl-6-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6j)

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **4j** (37 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (EP/AcOEt: 98/2) compounds **5j** and **6j** as a colourless oil (11.1 mg, 0.030 mmol, 30%) in a 7/1 ratio in favour of **5j**.

2-[(Benzyl)oxy]methyl-1-tosyl-5-vinylpyrrolidine (5j):

cis-2-[(Benzylxy)methyl]-1-tosyl-5-vinylpyrrolidine (major diastereoisomer):

¹H NMR (CDCl_3 , 400 MHz): δ 7.71 (br d, 2H, $J = 8.4$ Hz), 7.38-7.18 (m, 7H), 5.83 (ddd, 1H, $J = 17.1, 10.4, 6.3$ Hz), 5.23 (dt, 1H, $J = 17.1, 1.3$ Hz), 5.09 (dt, 1H, $J = 10.4, 1.3$ Hz), 4.55 (d_{systAB}, 2H), 4.02 (q_{app.}, 1H, $J = 6.6$ Hz), 3.85 (m, 1H), 3.82 (m, 1H), 3.46 (m, 1H), 2.43 (s, 3H), 1.89-1.54 (m, 4H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 143.5 (s), 139.4 (d), 138.3 (s), 134.9 (s), 129.7, 128.4, 127.7 (d, 9CH), 115.4 (t), 73.5, 73.4 (t, 2CH₂), 63.5 (d), 60.6 (d), 31.2, 27.8 (t, 2CH₂), 21.6 (q, C₁₀). **SM** (EI) *m/z* (abundance): 250 ((M - CH₂OBn)⁺, 81), 155 (28), 110 (10), 94 (34), 91 (100), 65 (15).

trans-2-[(Benzylxy)methyl]-1-tosyl-5-vinylpyrrolidine (minor diastereoisomer, only the following signals of the ¹H NMR and ¹³C NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl_3 , 400 MHz): δ 5.50 (m, 1H), 5.18 (d, 1H, $J = 16.8$ Hz), 4.99 (d, 1H, $J = 10.0$ Hz), 4.48 (d_{systAB}, 1H, $J = 11.8$ Hz), 4.43 (d_{systAB}, 1H, $J = 11.8$ Hz), 4.36 (m, 1H), 3.99 (m, 1H), 3.82 (m, 1H), 3.46 (m, 1H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 134.9 (d), 116.5 (t), 73.3, 73.0 (t, 2CH₂), 63.8 (d), 59.1 (d), 31.0, 27.3 (t, 2CH₂).

2-[(Benzylxy)methyl]-6-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6j) (only the following signals of the ¹H NMR and ¹³C NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl_3 , 400 MHz): δ 5.59-5.51 (m, 2H), 4.35 (m, 1H), 4.23 (q_{app.}, 1H, $J = 7.2$ Hz), 3.82 (m, 1H), 3.46 (m, 1H), 1.30 (d, 3H, $J = 7.2$ Hz). **¹³C NMR** (CDCl_3 , 100 MHz): δ 128.0, 121.6 (d, 2CH), 71.7, 71.3 (t, 2CH₂), 49.2 (d), 48.8 (d), 24.2 (q), 23.4 (t).

(E)-2-(Prop-1-en-1-yl)-1-tosylpyrrolidine (8a):^[11] and 1-tosyl-2-vinylpiperidine (8b):^[8]

[(MeCN)₃RhCp^{*}] (SbF_6)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide 7 (27 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **8a** and **8b** (8.2 mg, 0.031 mmol, 31%) in a 45/55 ratio in favour of **8b**. Spectral data for **8a** and **8b** match those previously described in the literature.

(E)-2-(Prop-1-en-1-yl)-1-tosylpyrrolidine (8a):^[11]

IR (film): ν 2919, 2873, 1598, 1449, 1345, 1196, 1158, 1094, 988, 965 cm⁻¹. **¹H NMR** (CDCl_3 , 400 MHz): δ 7.68 (br d, 2H, $J = 8.0$ Hz), 7.27 (br d, 2H, $J = 8.4$ Hz), 5.64 (dq, 1H, $J = 15.2, 6.6, 1.0$ Hz), 5.34 (ddq, 1H, $J = 15.2, 6.8, 1.6$ Hz), 4.09 (m, 1H), 3.39 (m, 1H), 3.23 (m, 1H), 2.40 (s, 3H), 1.84-1.54 (m, 4H), 1.64 (br d, 3H, $J = 6.5$ Hz). **¹³C NMR** (CDCl_3 , 100 MHz): δ 143.3 (s), 135.8 (s), 131.7 (d), 129.7 (d, 2CH), 127.8 (d, 2CH), 126.8 (d), 61.8 (d), 48.8 (t), 32.9 (t), 24.1 (t), 21.7 (q), 17.8 (q). **SM** (EI) *m/z* (abundance): 265 (M⁺, 11), 250 (12), 283 (18), 224 (10), 186 (27), 184 (13), 173 (13), 155 (40), 110 (91), 108 (11), 92 (13), 91 (100), 83 (11), 82 (34), 81 (12), 80 (10), 68 (24), 67 (15), 65 (31), 55 (28), 54 (10).

1-Tosyl-2-vinylpiperidine (8b):^[8]

IR (film): ν 2937, 2860, 1598, 1453, 1337, 1156, 1111, 1093, 1054, 963, 918 cm⁻¹. **¹H NMR** (CDCl_3 , 400 MHz): δ 7.69 (br d, 2H, $J = 8.0$ Hz), 7.27 (br d, 2H, $J = 8.0$ Hz), 5.70 (ddd, 1H, $J = 17.2, 10.8, 5.2$ Hz), 5.18-5.10 (m, 2H), 4.59 (br s, 1H), 3.67 (br d, 1H, $J = 13.2$ Hz), 2.99 (td_{app.}, 1H, $J = 13.2, 3.2$ Hz), 2.42 (s, 3H), 1.75-1.34 (m, 6H). **¹³C NMR** (CDCl_3 , 100 MHz): δ 143.1 (s), 138.1 (s), 135.7 (d), 129.7 (d, 2CH), 127.5 (d, 2CH), 117.4 (t), 55.2 (d), 41.9 (t), 29.9 (t), 21.7 (q), 21.7 (t), 19.3 (t). **SM** (EI) *m/z* (abundance): 265 (M⁺, 12), 239 (10), 238 (56), 155 (34), 110 (100), 108 (11), 91 (85), 83 (11), 82 (11), 68 (11), 65 (23), 55 (32), 54 (21).

(E)-2-(Hex-1-en-1-yl)-1-tosylpyrrolidine (11a):^[12] and (E)-2-(pent-1-en-1-yl)-1-

tosylpiperidine (10a):

$[(\text{MeCN})_3\text{RhCp}^*](\text{SbF}_6)_2$ (4.2 mg, 0.005 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **9a** (31 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **10a** and **11a** (9.5 mg, 0.031 mmol, 50%) in a 1/1 ratio. Spectral data for **11a** match those previously described in the literature.

(E)-2-(Hex-1-en-1-yl)-1-tosylpyrrolidine (11a):^[12]

IR (film): ν 2955, 2927, 2857, 1694, 1598, 1460, 1347, 1196, 1160, 1094, 970 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 7.71 (br d, 2H, $J = 8.0$ Hz), 7.29 (br d, 2H, $J = 8.4$ Hz), 5.63 (dtd, 1H, $J = 15.2, 6.7, 1.0$ Hz), 5.33 (ddt, 1H, $J = 15.2, 6.8, 1.6$ Hz), 4.12 (m, 1H), 3.41 (m, 1H), 3.27 (m, 1H), 2.42 (s, 3H), 2.00 (br q_{app.}, 2H, $J = 6.6$ Hz), 1.87-1.56 (m, 4H), 1.35-1.24 (m, 4H), 0.89 (t, 3H, $J = 7.0$ Hz). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 143.2 (s), 135.9 (s), 132.2 (d), 130.3 (d), 129.6 (d, 2CH), 127.7 (d, 2CH), 61.8 (d), 48.8 (t), 33.0 (t), 32.0, 31.4, 24.1, 22.5 (t, 4CH₂), 21.7 (q), 14.2 (q). **SM (EI) *m/z* (abundance):** 264 ((M-propyl)⁺, 6), 250 (39), 225 (19), 224 (20), 186 (14), 173 (14), 155 (52), 152 (59), 136 (30), 124 (15), 110 (10), 108 (10), 96 (15), 92 (12), 91 (100), 81 (13), 80 (14), 68 (12), 67 (14), 65 (22), 55 (14), 54 (10).

(E)-2-(Pent-1-en-1-yl)-1-tosylpiperidine (10a):

IR (film): ν 2956, 2852, 1712, 1598, 1454, 1336, 1255, 1181, 1154, 1095, 1025 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 7.64 (br d, 2H, $J = 8.0$ Hz), 7.23 (br d, 2H, $J = 8.0$ Hz), 5.50 (dtd, 1H, $J = 15.6, 6.6, 1.2$ Hz), 5.29 (ddt, 1H, $J = 15.6, 6.0, 1.3$ Hz), 4.54 (br s, 1H), 3.66 (dt, 1H, $J = 13.2, 4.0$ Hz), 2.92 (td, 1H, $J = 12.4, 3.2$ Hz), 2.39 (s, 3H), 1.87 (m, 2H), 1.71-1.38 (m, 6H), 1.32-1.22 (m, 2H), 0.82 (t, 3H, $J = 7.4$ Hz). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 142.9 (s), 138.1 (s), 133.6 (d), 129.5 (d, 2CH), 127.6 (d, 2CH), 126.6 (t), 54.9 (d), 41.8 (t), 34.6 (t), 22.3 (t), 21.7 (q), 30.7, 25.4, 19.3 (t, 3CH₂), 13.9 (q, C₁₁). **SM (EI) *m/z* (abundance):** 238 ((M-pentenyl)⁺, 44), 225 (14), 155 (49), 152 (99), 136 (67), 108 (33), 96 (20), 91 (100), 65 (36), 55 (35).

(E)-2-(But-1-en-1-yl)-1-tosylpyrrolidine (11b) and

(E)-2-(prop-1-en-1-yl)-1-tosylpiperidine (10b):^[8]

$[(\text{MeCN})_3\text{RhCp}^*](\text{SbF}_6)_2$ (4.2 mg, 0.005 mmol, 5 mol %) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **9b** (25 mg, 0.09 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® and concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) compounds **11b** and **10b** as colourless oils (9.5 mg, 0.034 mmol, 38%) in a 1/1 ratio. Spectral data for **10b** match those previously described in the literature.

(E)-2-(But-1-en-1-yl)-1-tosylpyrrolidine (11b):

IR (film): ν 2956, 2923, 1736, 1670, 1599, 1459, 1344, 1160, 1095, 1009, 969, 913 cm^{-1} . **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 7.71 (br d, 2H, $J = 8.4$ Hz), 7.29 (br d, 2H, $J = 8.4$ Hz), 5.68 (dtd, 1H, $J = 15.2, 6.2, 1.0$ Hz), 5.32 (ddt, 1H, $J = 15.2, 6.8, 1.6$ Hz), 4.14 (m, 1H), 3.44-3.38 (m, 1H), 3.31-3.24 (m, 1H), 2.42 (s, 3H), 2.02 (quint_{app.}, 2H, $J = 7.2$ Hz), 1.87-1.54 (m, 4H), 0.96 (t, 3H, $J = 7.4$ Hz). **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 144.3 (s), 135.7 (s), 133.5 (d), 129.5 (d, 2CH), 129.2 (d), 127.6 (d, 2CH), 61.6 (d), 48.6 (t), 32.8 (t), 25.2 (t), 23.9 (t), 21.5 (q), 13.3 (q). **SM (EI) *m/z* (abundance):** 279 (M⁺, 8), 250 (31), 224 (15), 186 (14), 155 (51), 124 (81), 108 (25), 96 (25), 95 (14), 94 (12), 92 (10), 91 (100), 82 (16), 81 (11), 79 (10), 68 (10), 67 (13), 65 (26), 55 (16).

(E)-2-(Prop-1-en-1-yl)-1-tosylpiperidine (10b):^[6]

IR (film): ν 2936, 2863, 1734, 1598, 1451, 1337, 1159, 1093, 1057, 965, 934 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.65 (br d, 2H, J = 8.4 Hz), 7.29-7.22 (m, 2H), 5.59-5.51 (m, 1H), 5.34 (ddq, 1H, J = 15.2, 6.4, 1.6 Hz), 4.54 (m, 1H), 3.67 (m, 1H), 2.92 (m, 1H), 2.41 (s, 3H), 1.78-1.37 (m, 6H), 1.57 (dt, 3H, J = 6.8, 1.4 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 142.7 (s), 138.2 (s), 129.3 (d, 2CH), 128.3 (d), 127.5 (d, 2CH), 127.3 (d), 54.8 (d), 41.7, 30.4, 25.2 (d, 3CH₂), 21.5 (q), 19.0 (d), 17.8 (q). **SM** (EI) m/z (abundance): 128 ((M - propenyl)⁺, 12), 155 (15), 124 (100), 108 (19), 91 (73), 82 (19), 68 (38), 65 (13), 55 (39).

4-Methyl-2-(2-methylprop-1-en-1-yl)-1-tosylpiperidine (13):

[(MeCN)₃RhCp^{*}](SbF₆)₂ (4.2 mg, 0.005 mmol, 5 mol %) and Cu(OAc)₂.H₂O (42 mg, 0.21 mmol, 2.1 equiv) were added to a solution of sulfonamide **13** (31 mg, 0.1 mmol, 1 equiv) in DCE (1 mL) and the reaction mixture was heated to reflux. After 16 h, the reaction was cooled to room temperature, filtered through Celite® concentrated under *vacuum* to afford after purification on silica gel (PE/EtOAc: 98/2) the title compound **13** as a colourless oil (8.4 mg, 0.027 mmol, 27%) in a 9/1 ratio in favour of the *cis* compound.

cis-(2R,4S)-4-methyl-2-(2-methylprop-1-en-1-yl)-1-tosylpiperidine (13):

IR (film): ν 2926, 2870, 1598, 1445, 1338, 1306, 1261, 1154, 1097, 1083, 1049, 921 cm⁻¹. **¹H NMR** (CDCl₃, 400 MHz): δ 7.57 (br d, 2H, J = 8.3 Hz), 7.22 (br d, 2H, J = 8.1 Hz), 5.01 (m, 1H), 4.84 (m, 1H), 3.73 (m, 1H), 2.83 (td, 1H, J = 12.7, 2.6 Hz), 2.40 (s, 3H), 1.66 (s, 3H), 1.68-1.55 (m, 2H, H₄), 1.48 (s, 3H), 1.53-1.35 (m, 2H), 1.21 (m, 1H), 0.85 (d, 3H, J = 6.3 Hz). **¹³C NMR** (CDCl₃, 100 MHz): δ 142.6 (s), 137.1 (s, C_{qar}), 133.9 (s, C_{qar}), 129.0 (d, 2CH_{ar}), 127.5 (d, 2CH_{ar}), 120.1 (d, C₇), 51.6 (d, C₂), 41.4 (t), 39.9 (t), 33.7 (t), 25.7 (d), 25.2 (q), 22.1 (q), 21.5 (q), 18.0 (q). **SM** (EI) m/z (abundance): 252 ((M - isopropenyl)⁺, 20), 153 (10), 152 (100), 136 (44), 123 (21), 96 (19), 91 (56), 82 (22), 81 (11), 69 (17), 67 (17), 65 (15), 55 (21). **HRMS** (ESI): Calculated for C₁₇H₂₅NO₂SnA: 330.1498. Found: 330.1496.

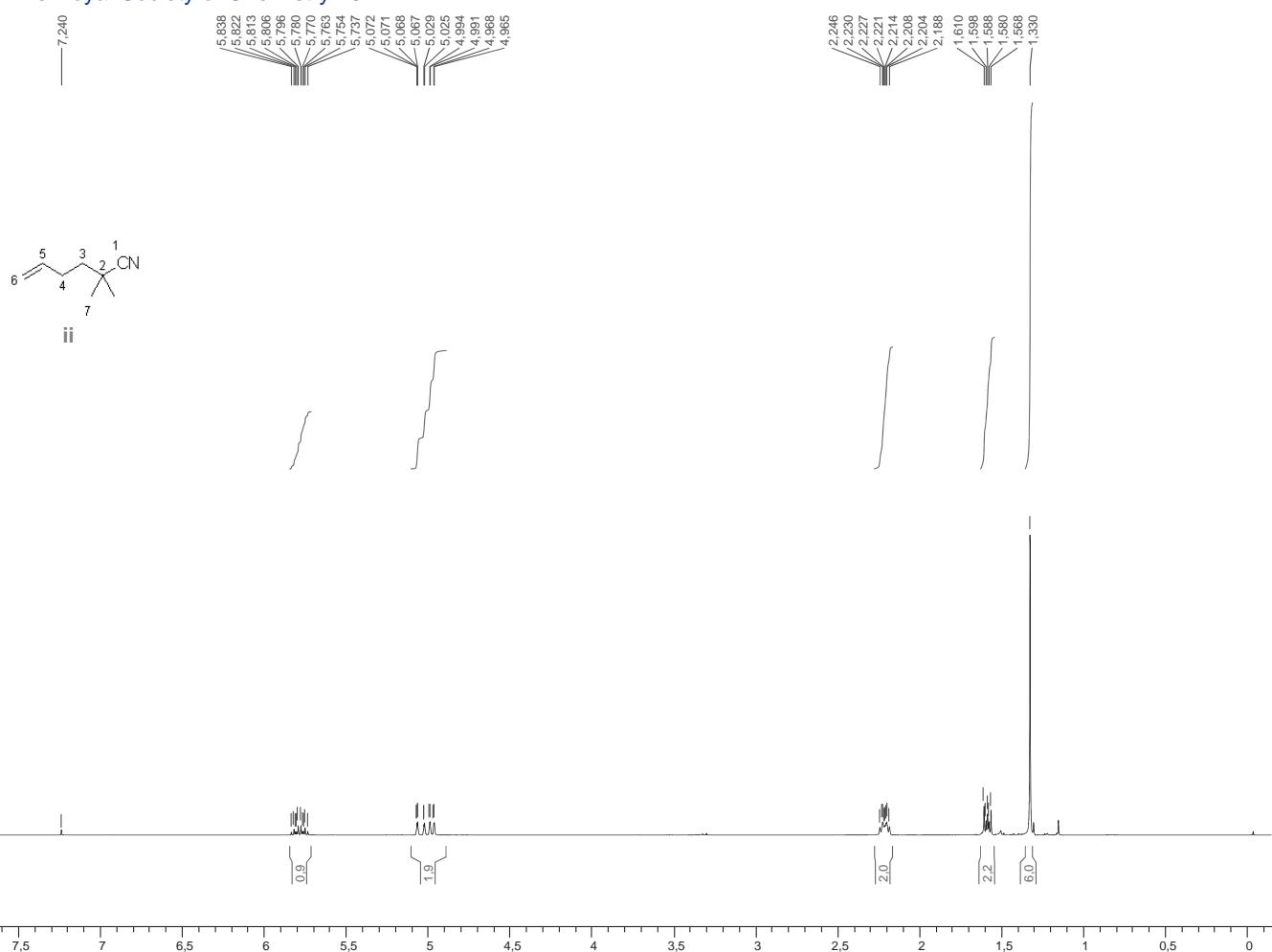
trans-(2S,4S)-4-methyl-2-(2-methylprop-1-en-1-yl)-1-tosylpiperidine (13') (only the following signals of the ¹H NMR spectroscopic data were assigned unambiguously):

¹H NMR (CDCl₃, 400 MHz): δ 5.29 (dquint, 1H, J = 9.3, 1.3 Hz), 4.00 (dt, 1H, J = 12.1, 4.1 Hz), (3.36, m, 1H), 2.62 (ddd, 1H, J = 12.1, 11.2, 2.9 Hz), 2.41 (s, 3H), 1.66 (s, 3H), 1.48 (s, 3H), 0.90 (d, 3H, J = 6.4 Hz).

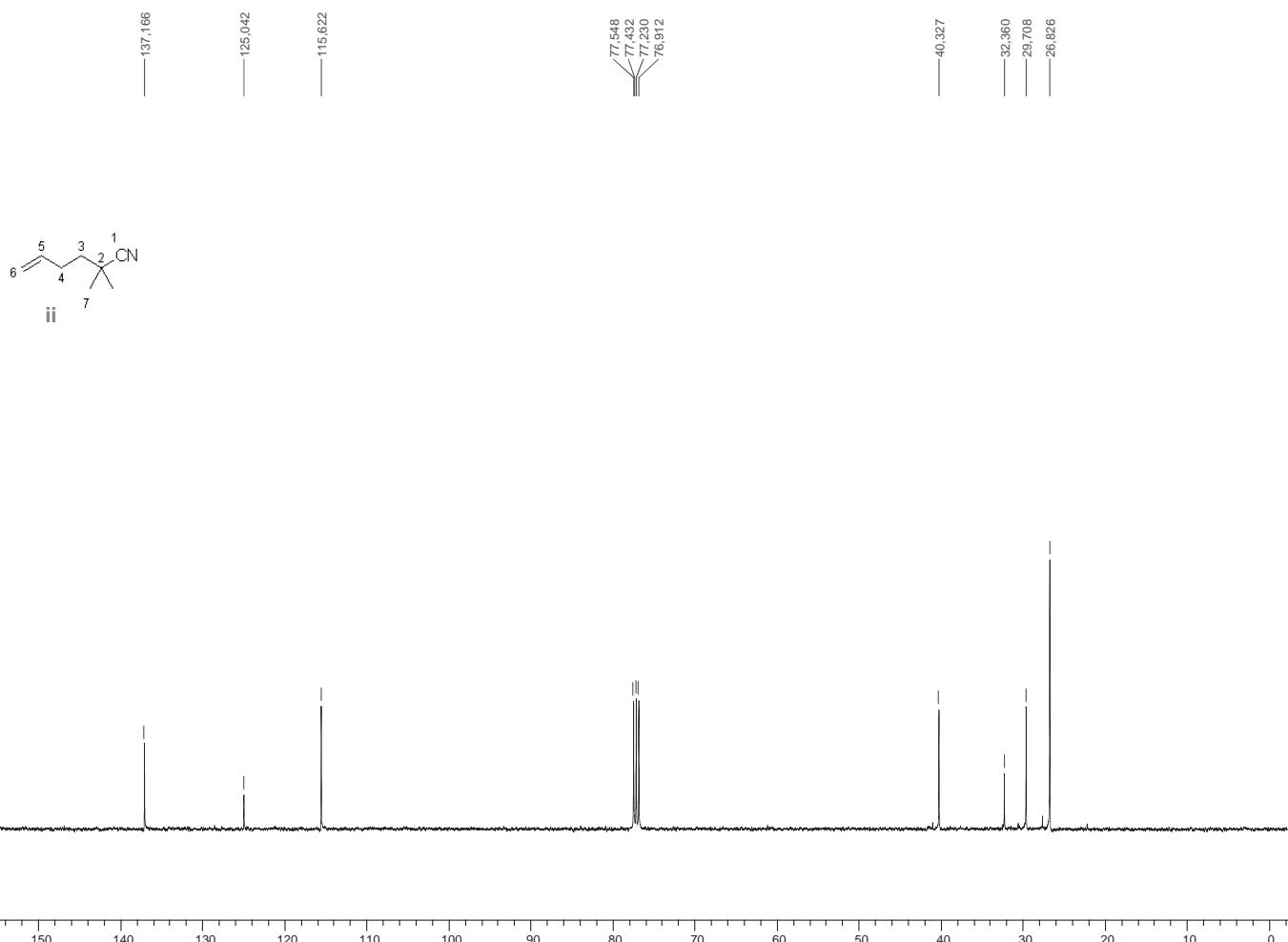
- [1] A. J. M. Burrell, I. Coldham, L. Watson, N. Oram, C. D. Pilgram, N. G. Martin, *J. Org. Chem.* **2008**, *74*, 2290-2300.
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IV. ^1H NMR and ^{13}C NMR spectra for all the compounds.

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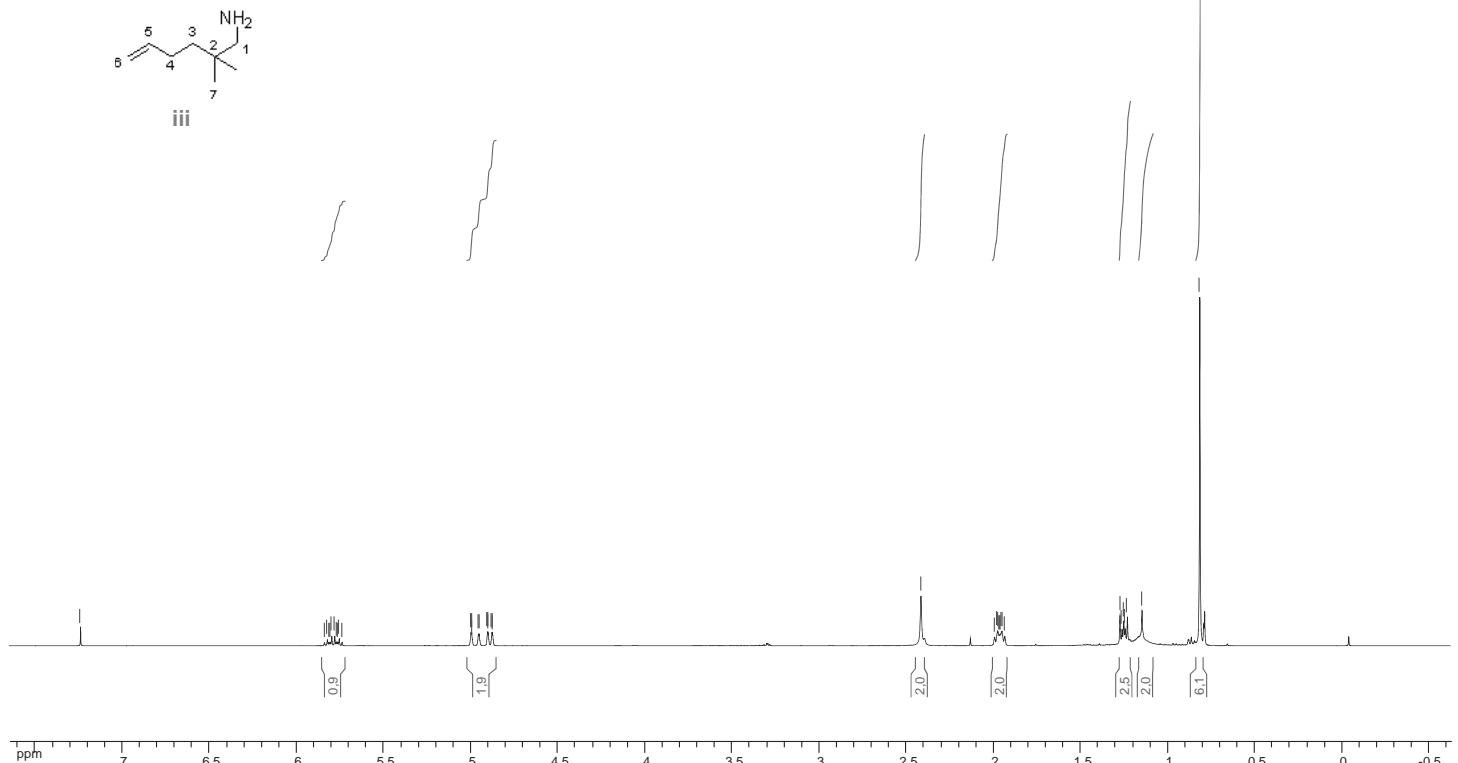
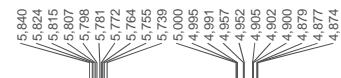


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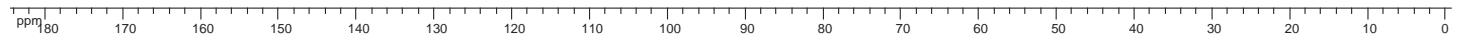
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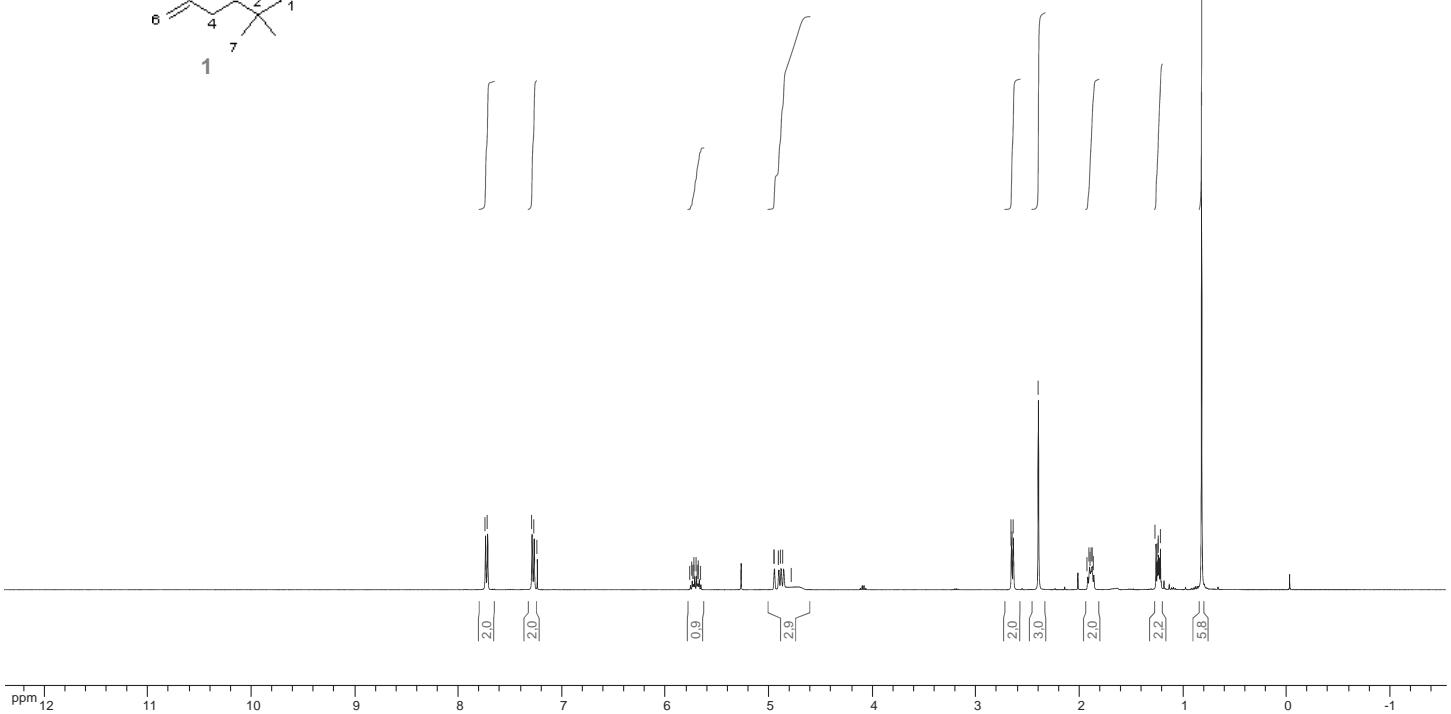
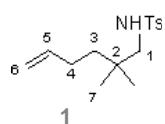
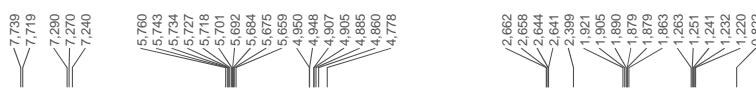
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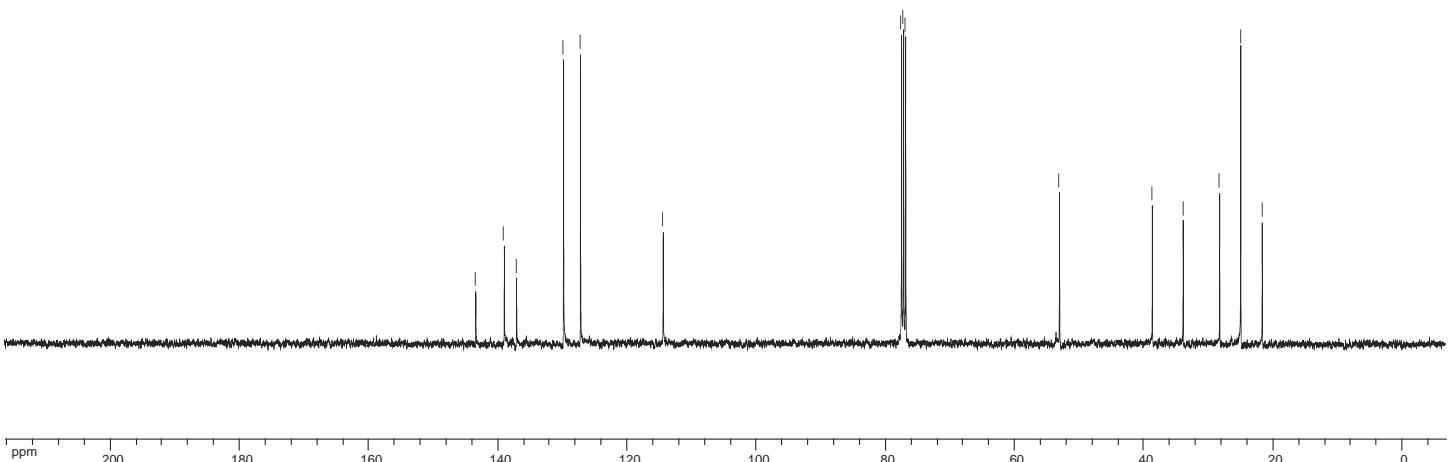
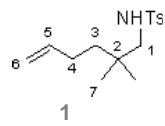
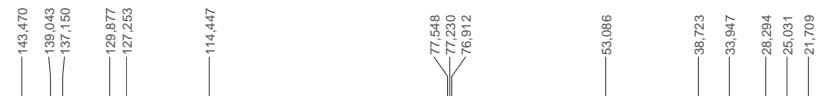
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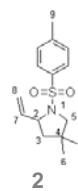
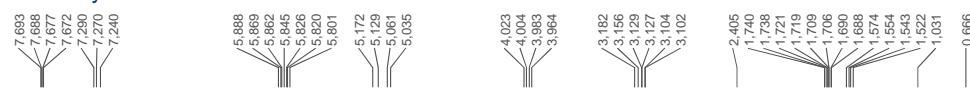
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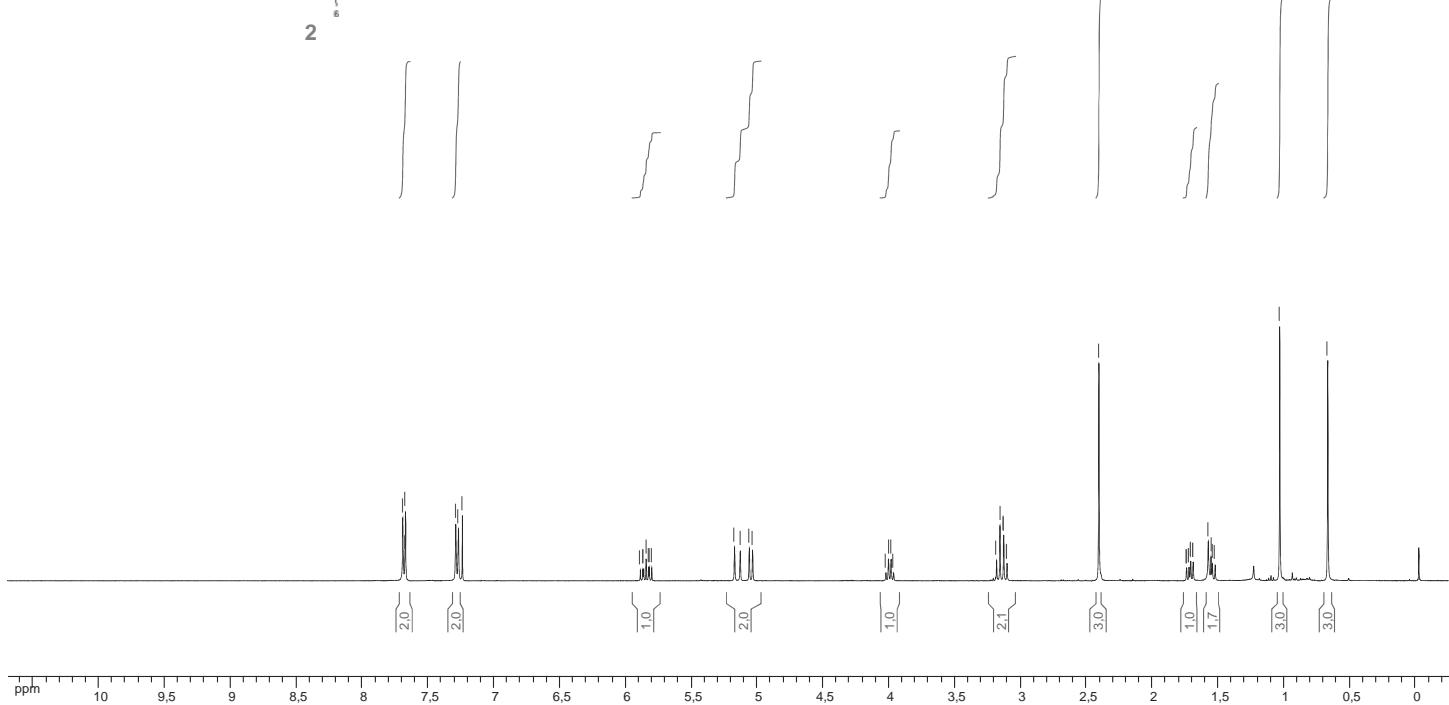
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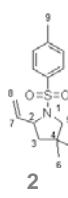
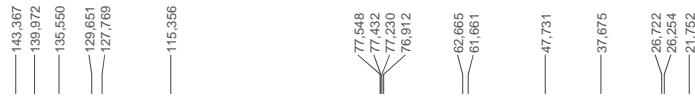
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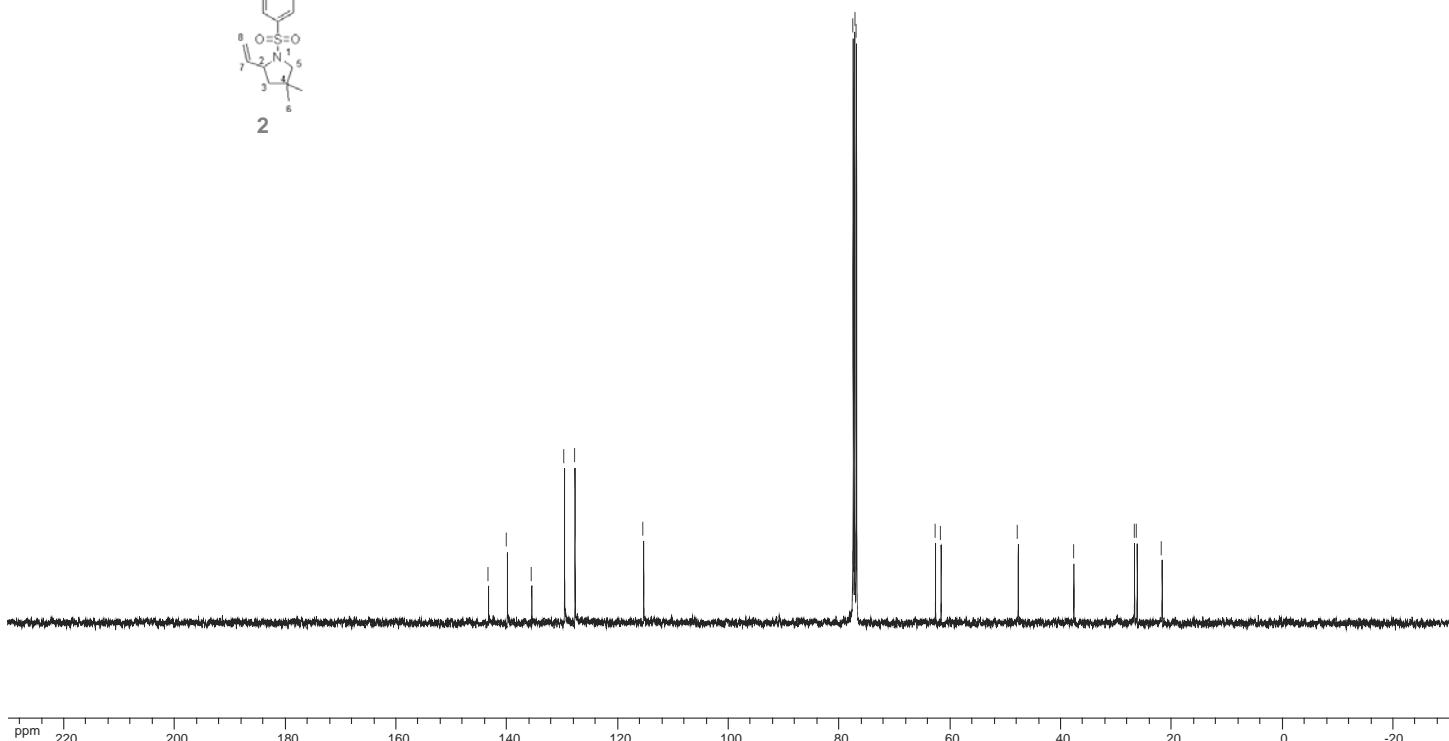
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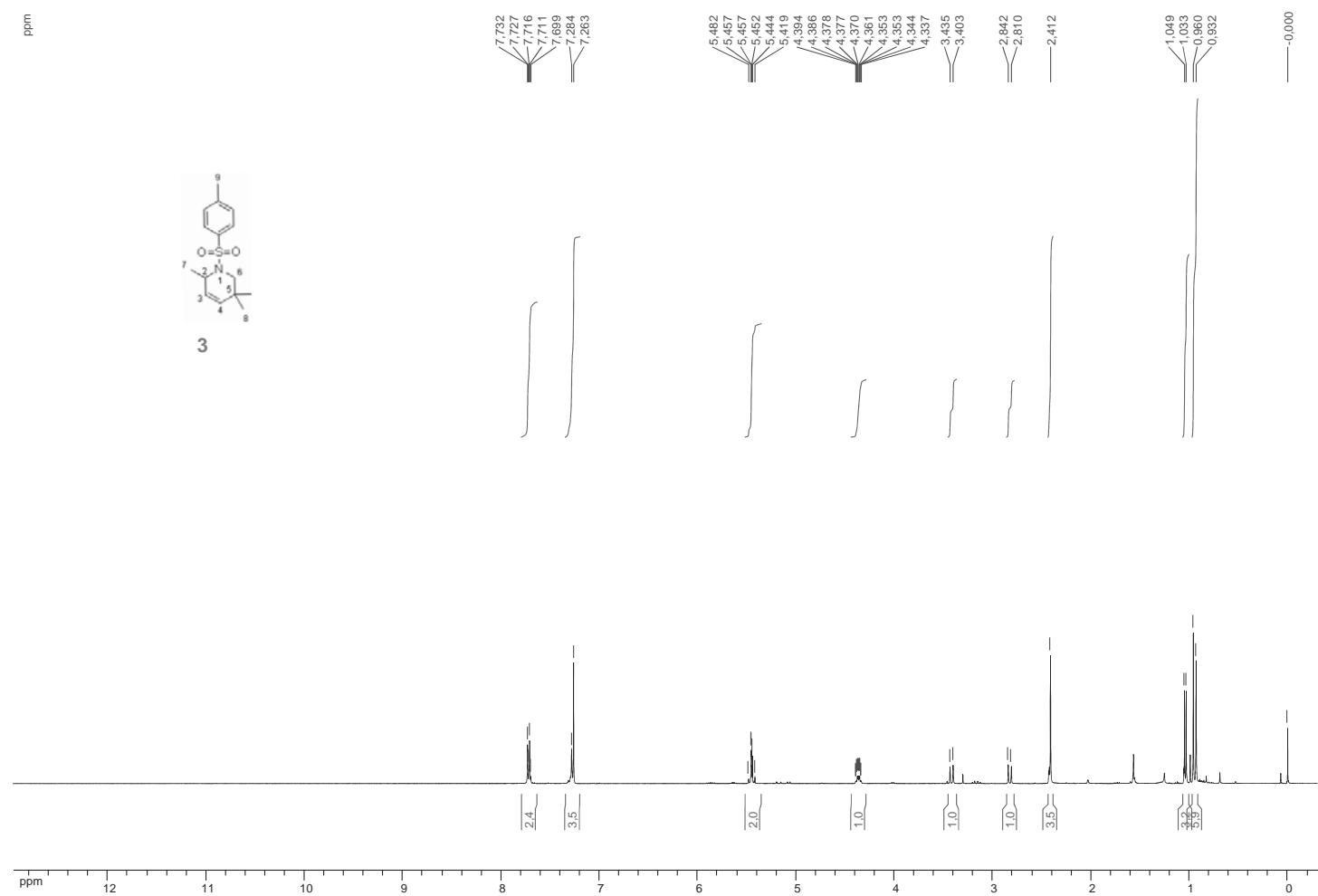
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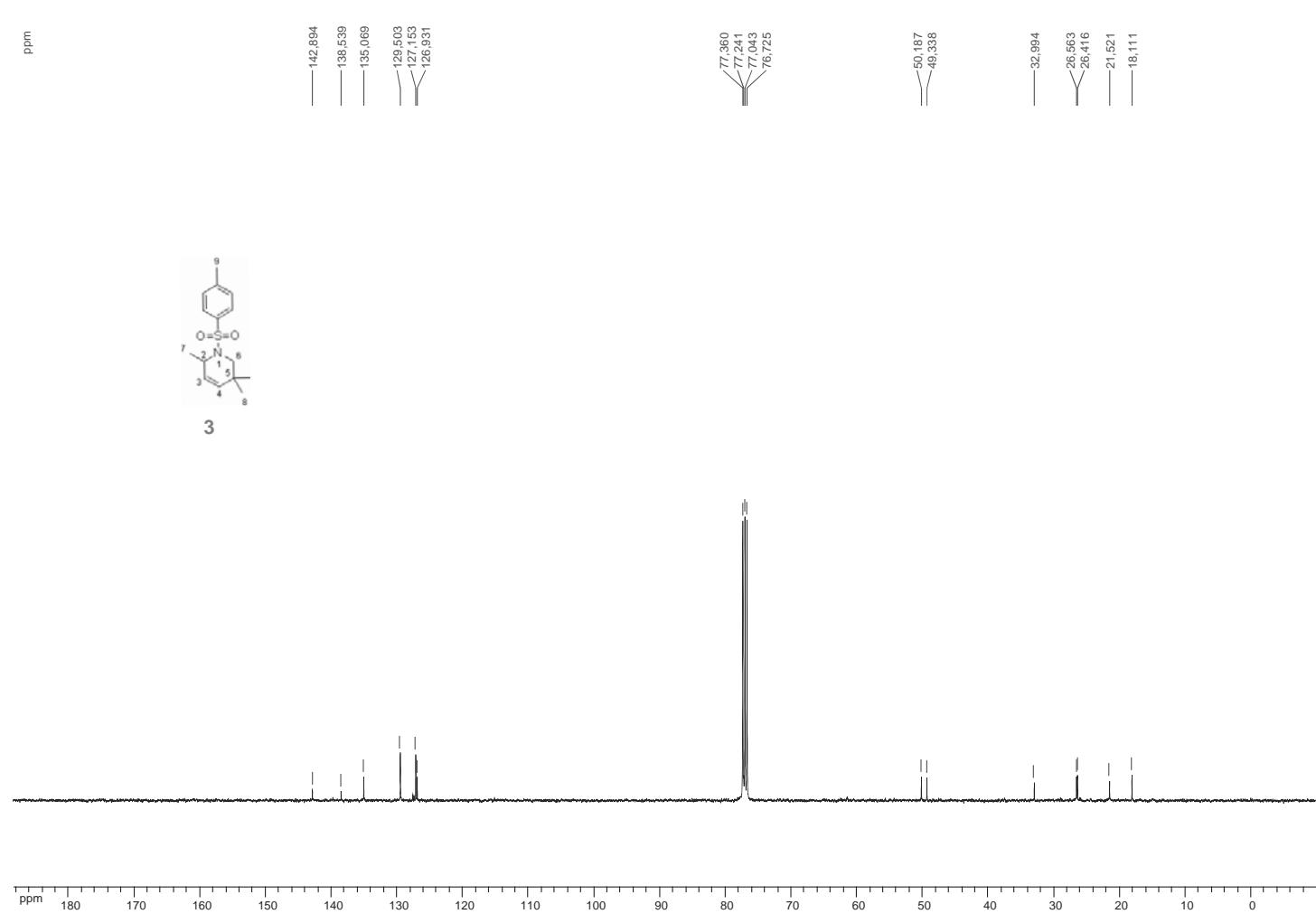
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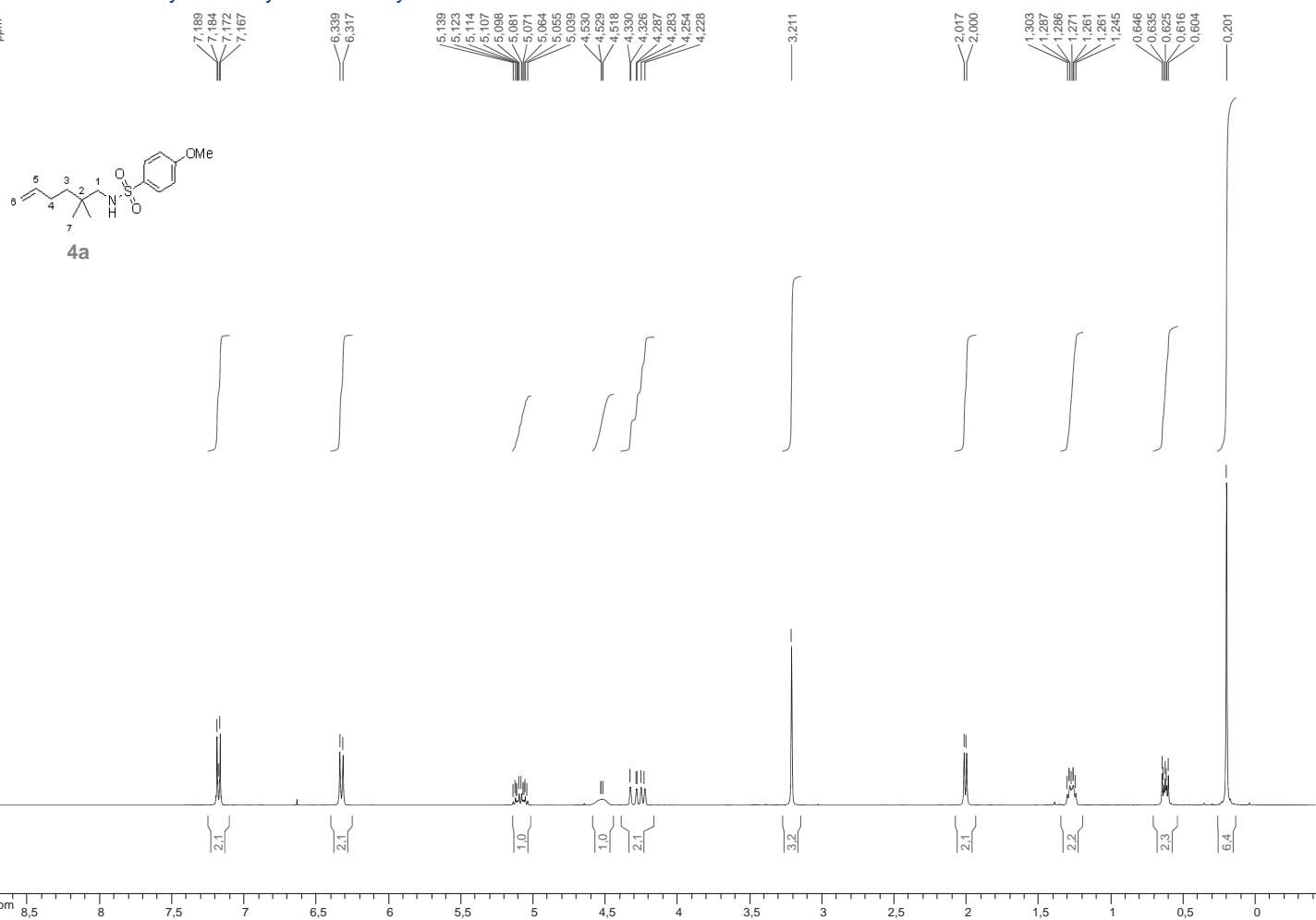
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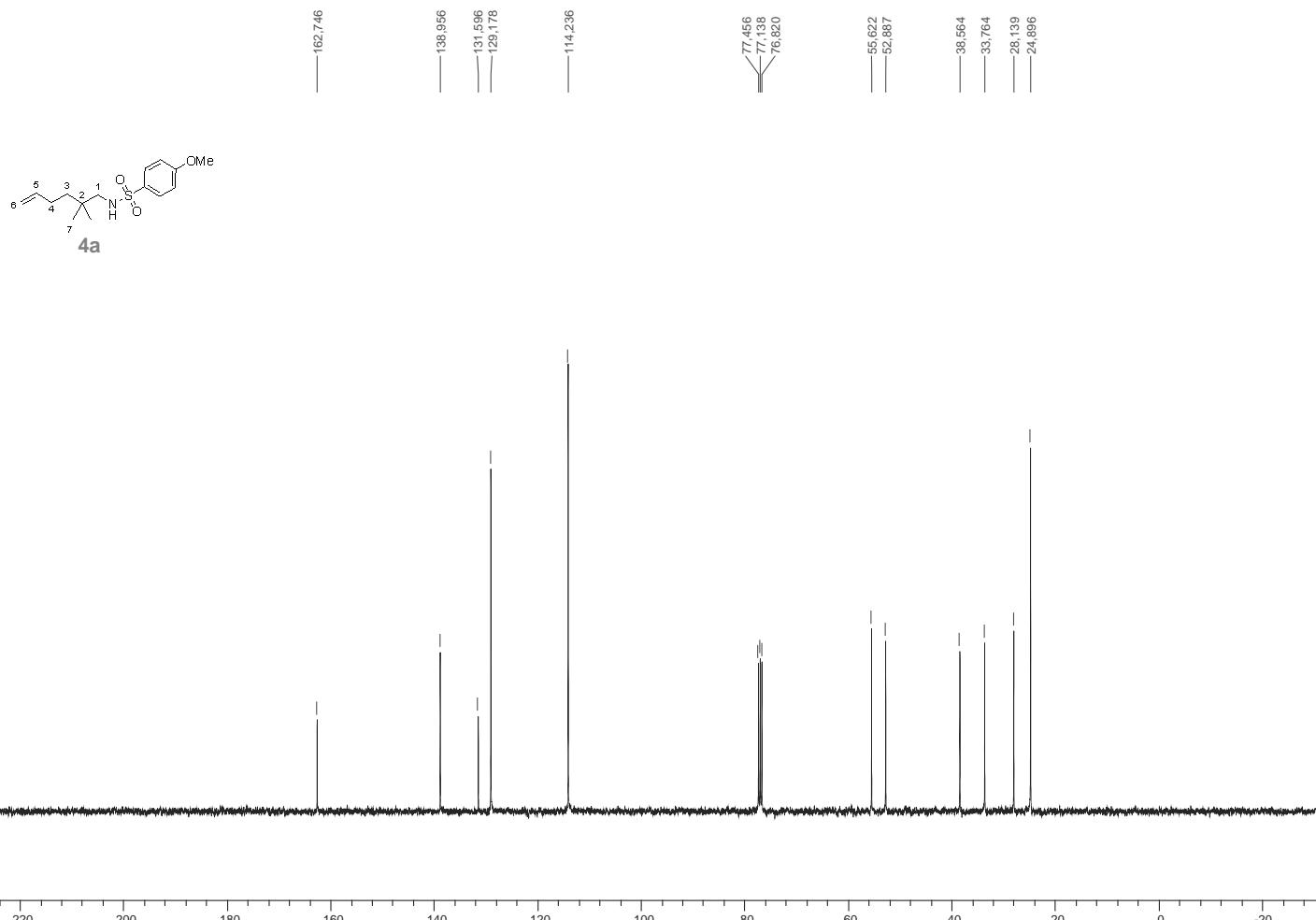
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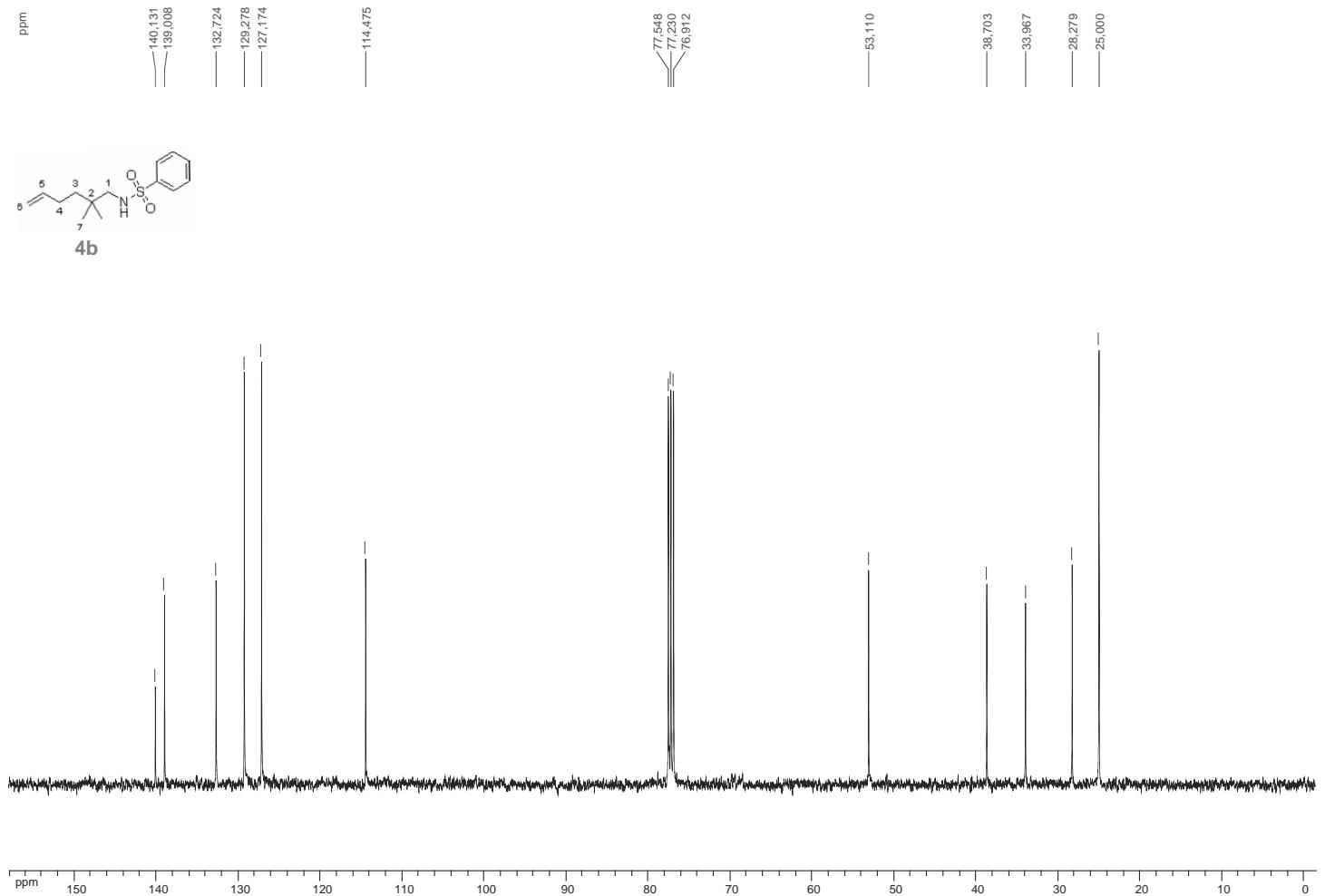
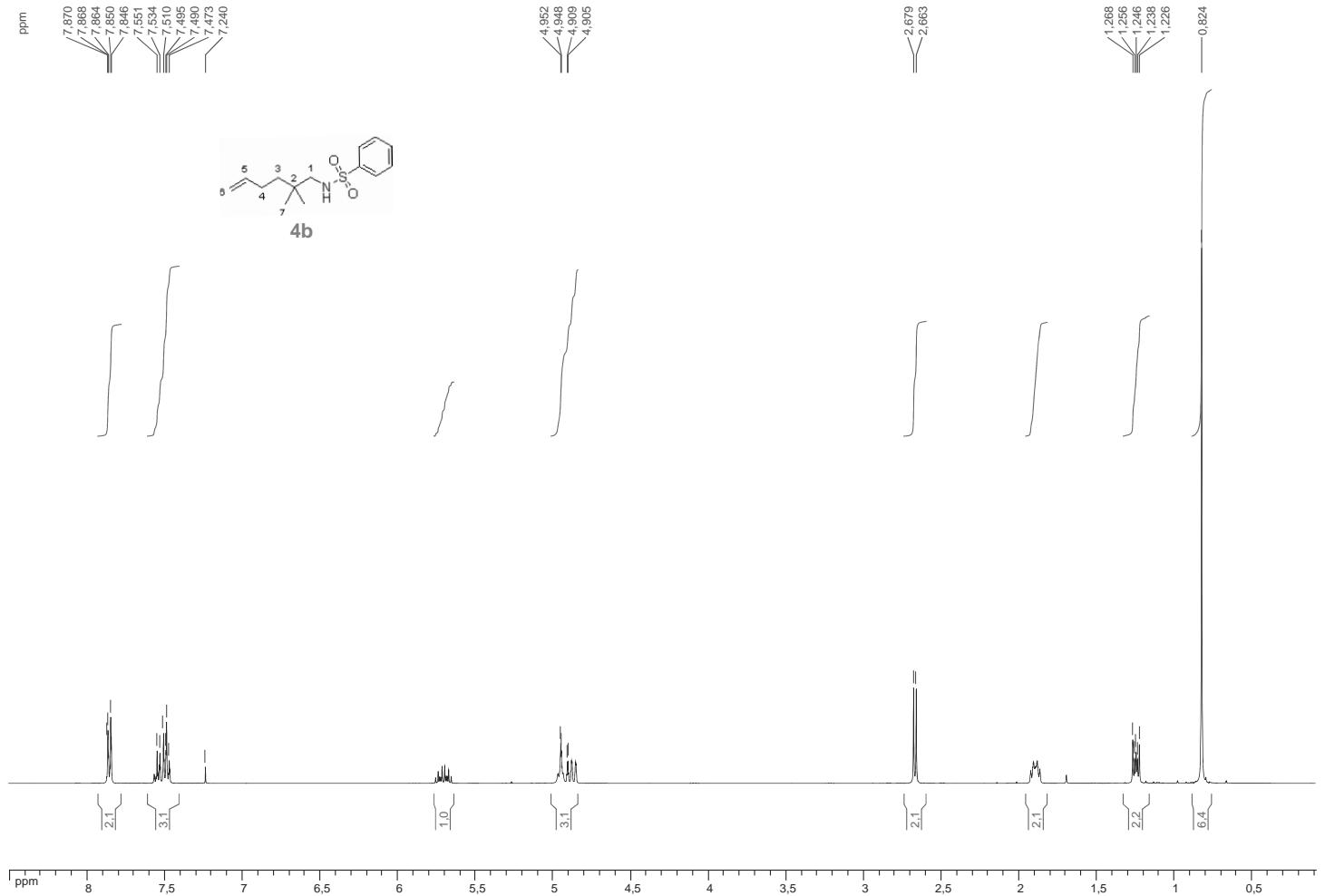


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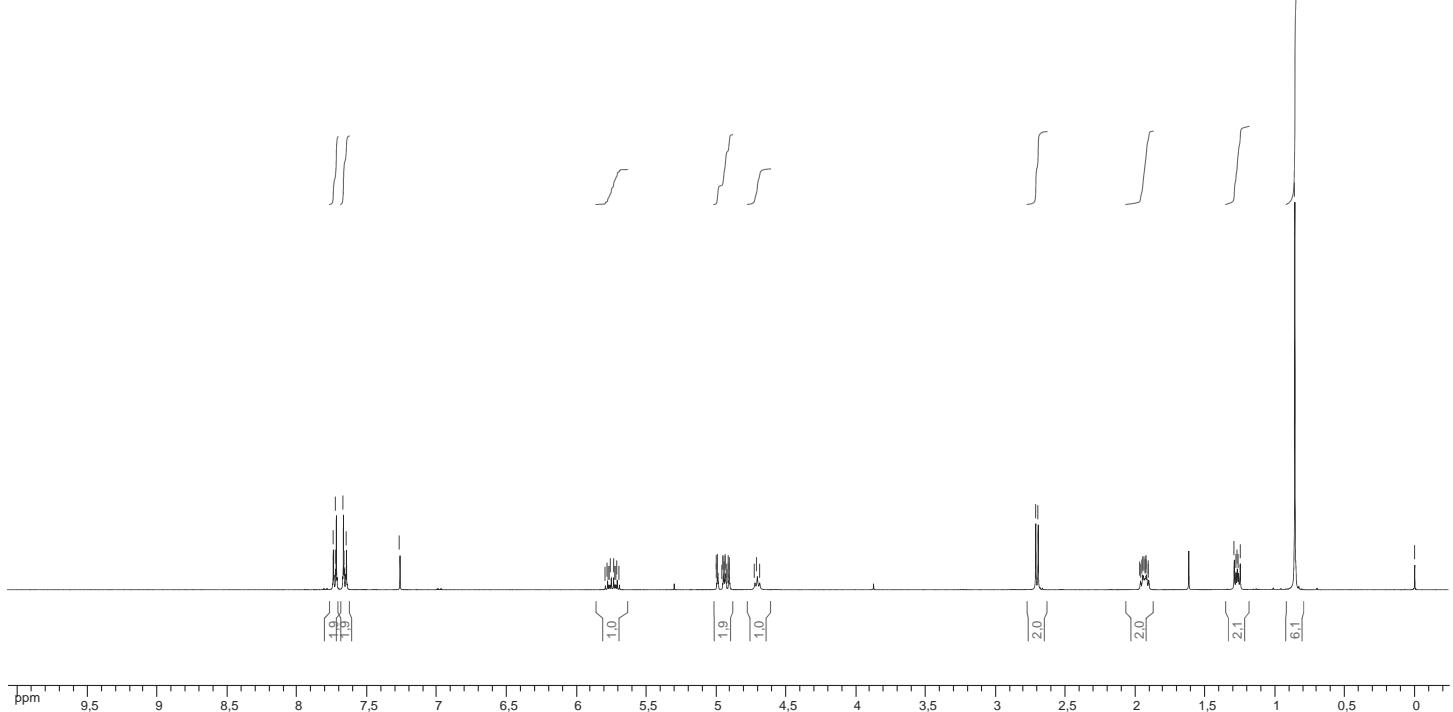
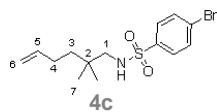
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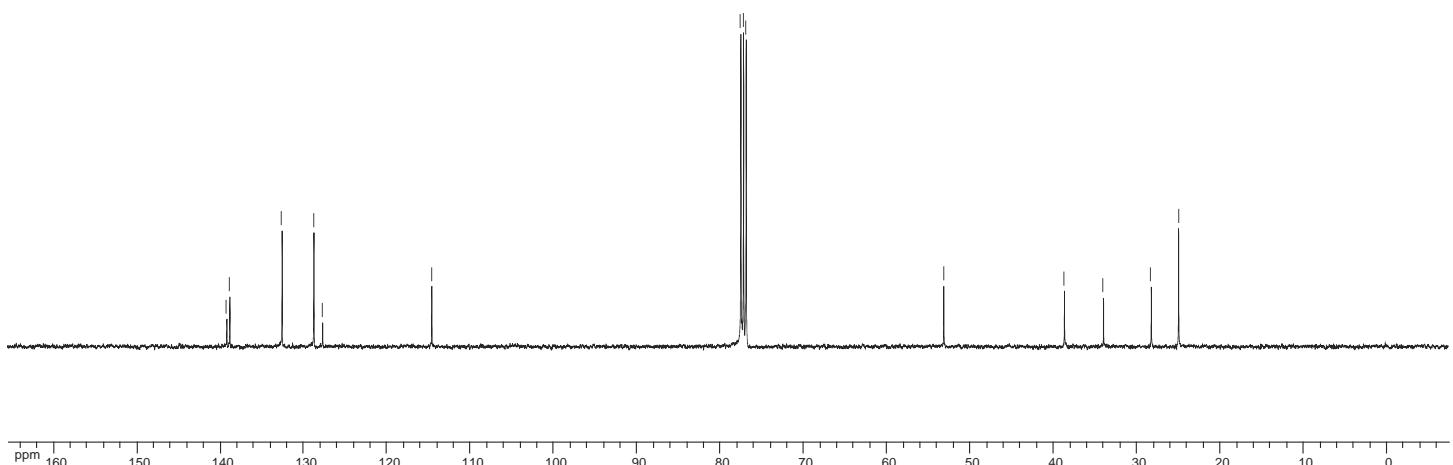
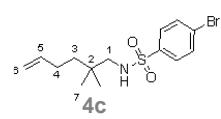
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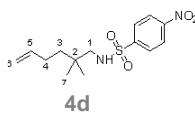
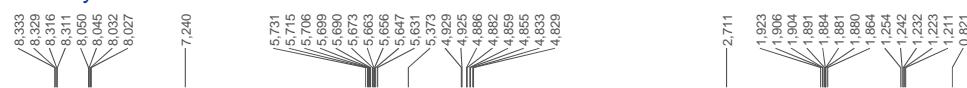
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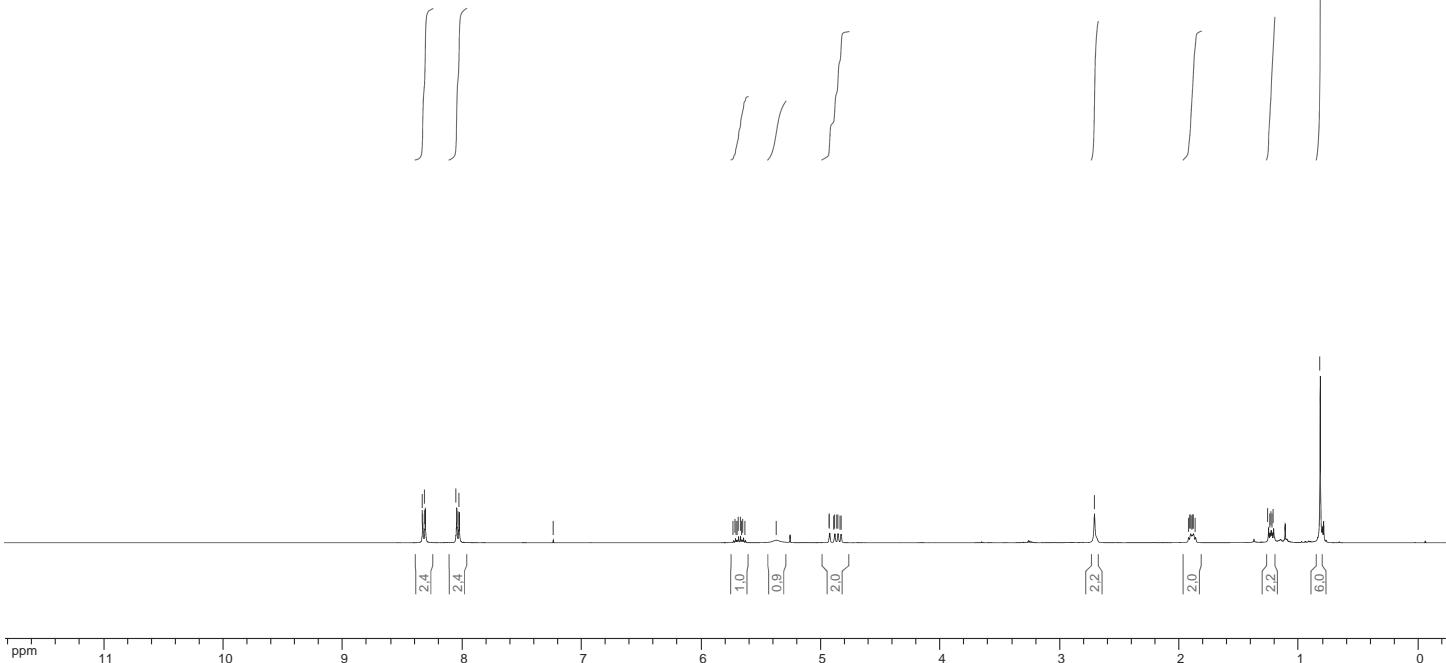
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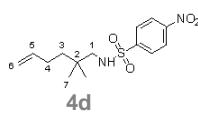
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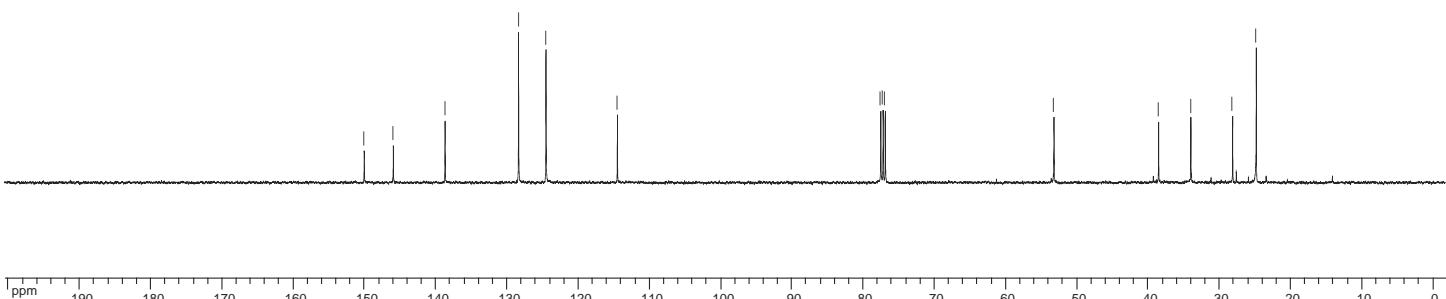
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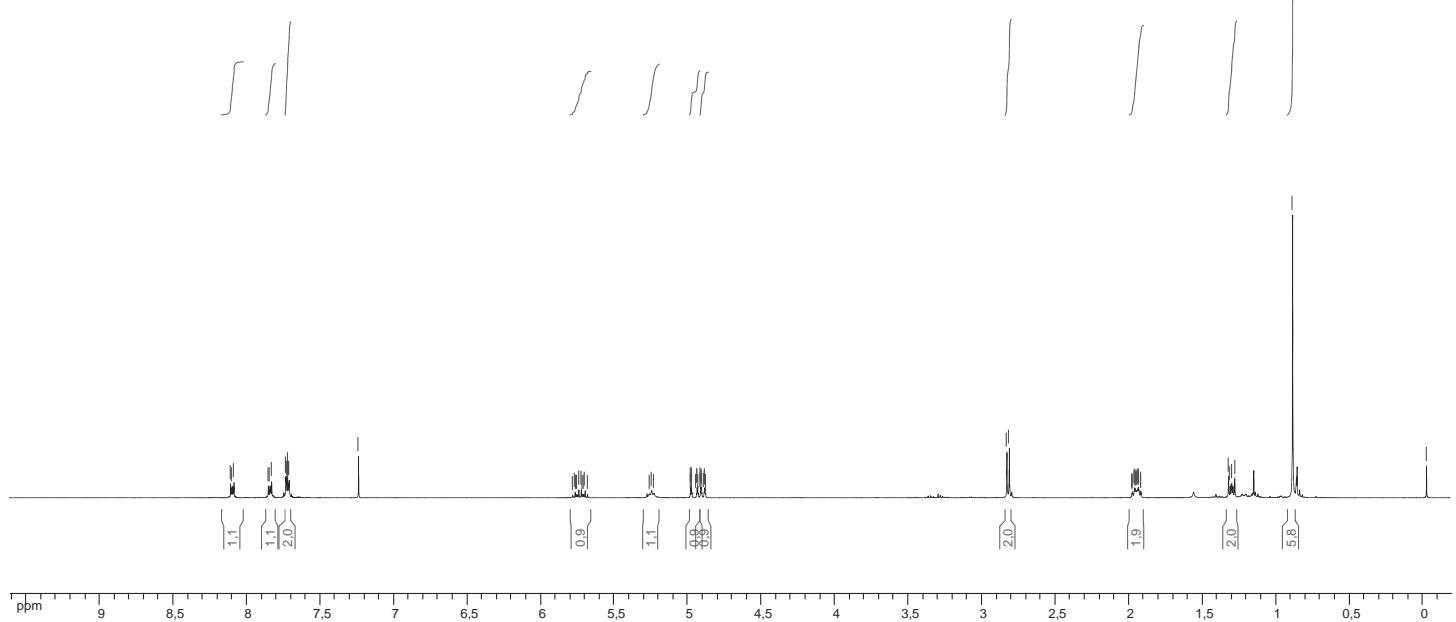
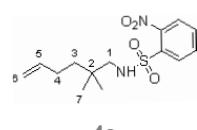
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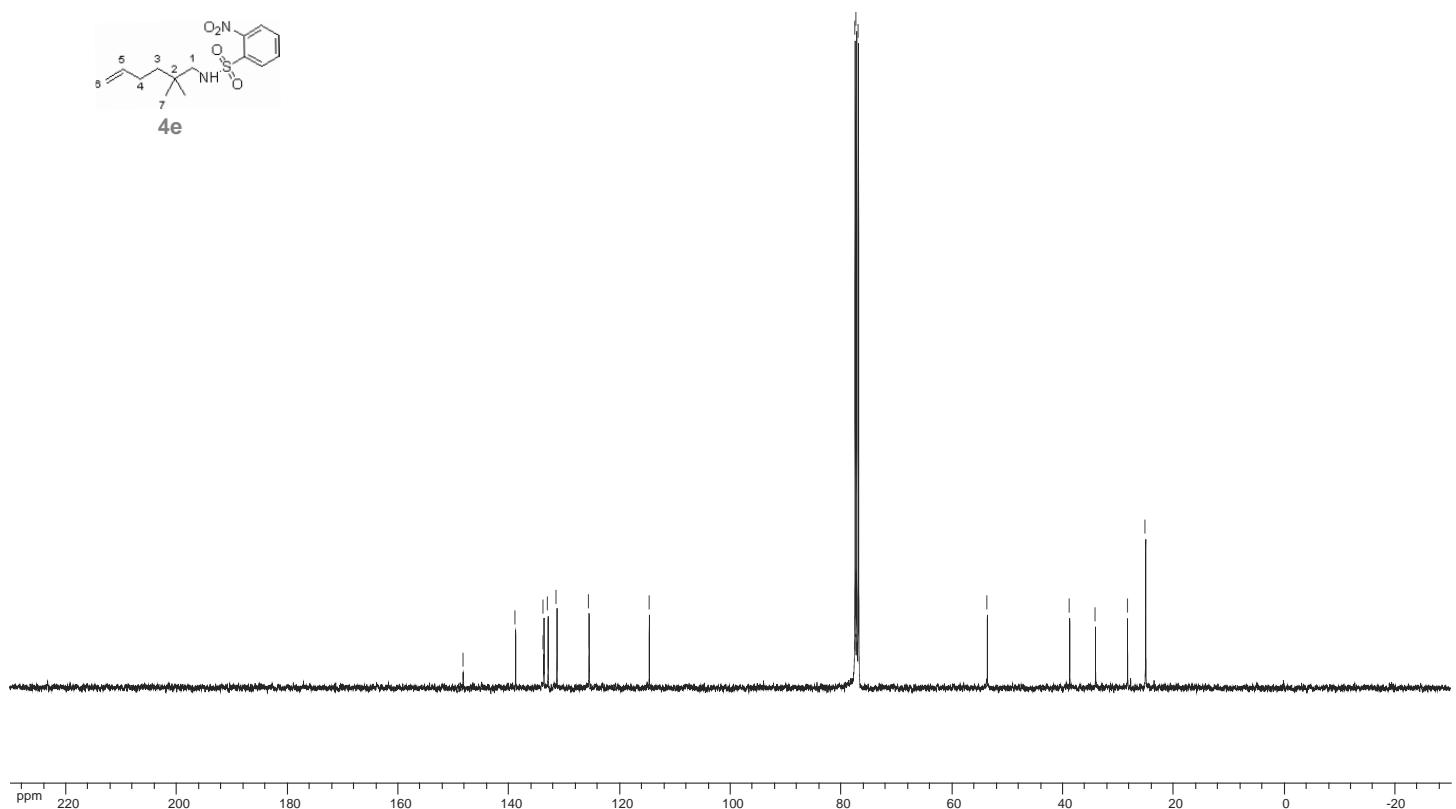
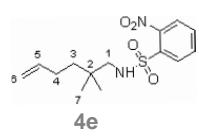
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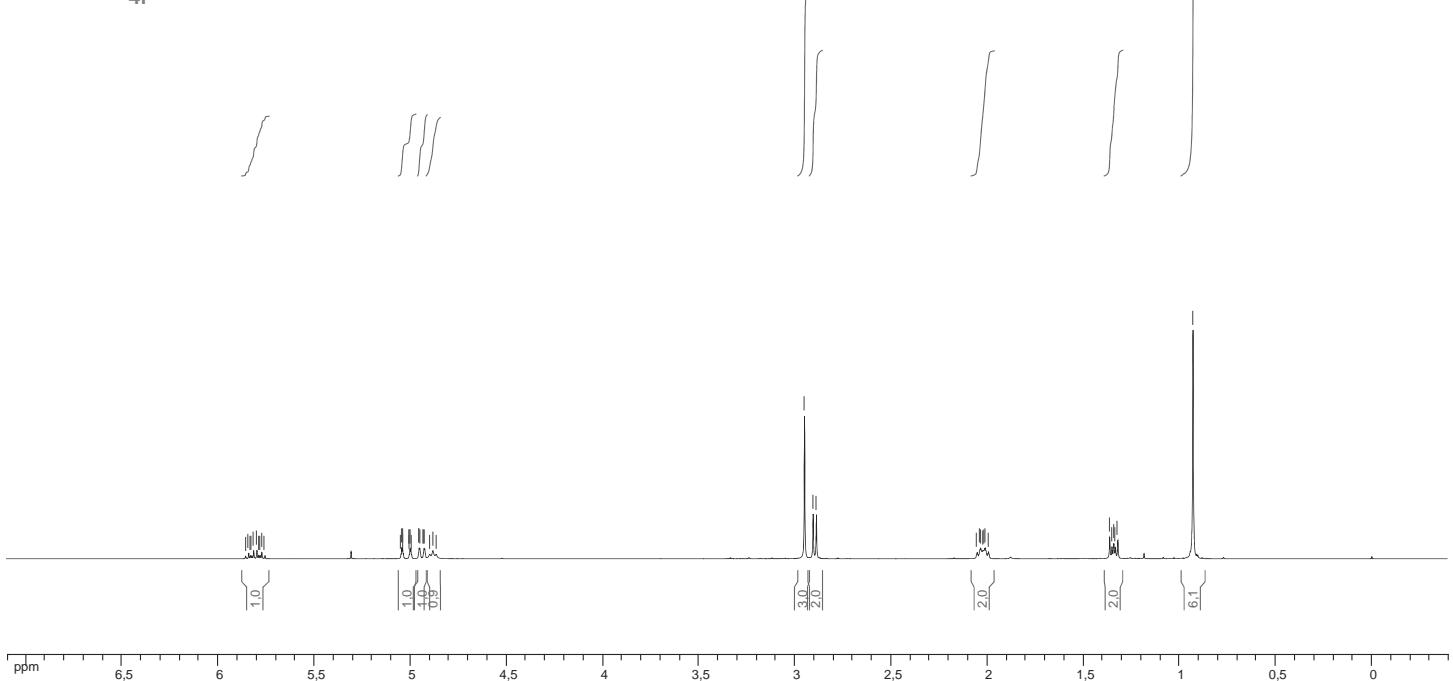
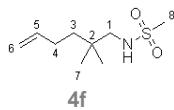


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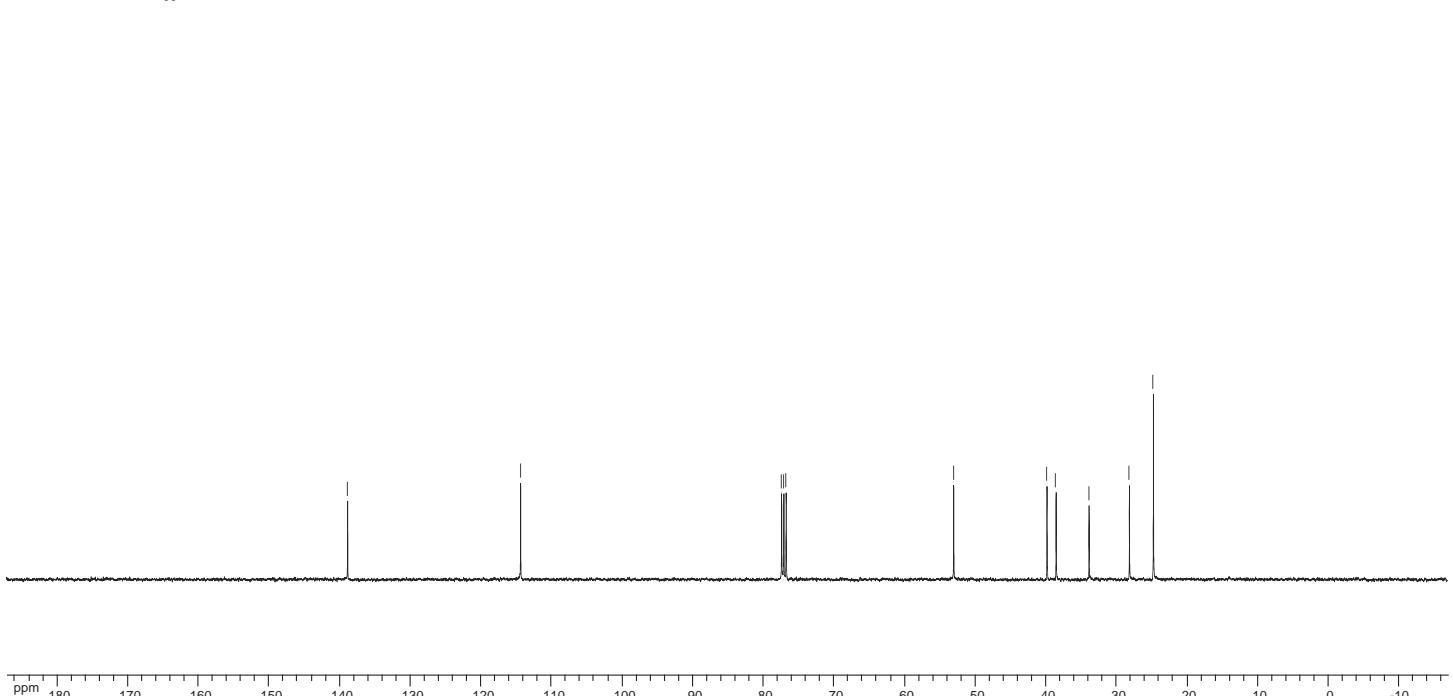
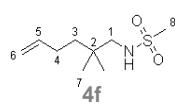


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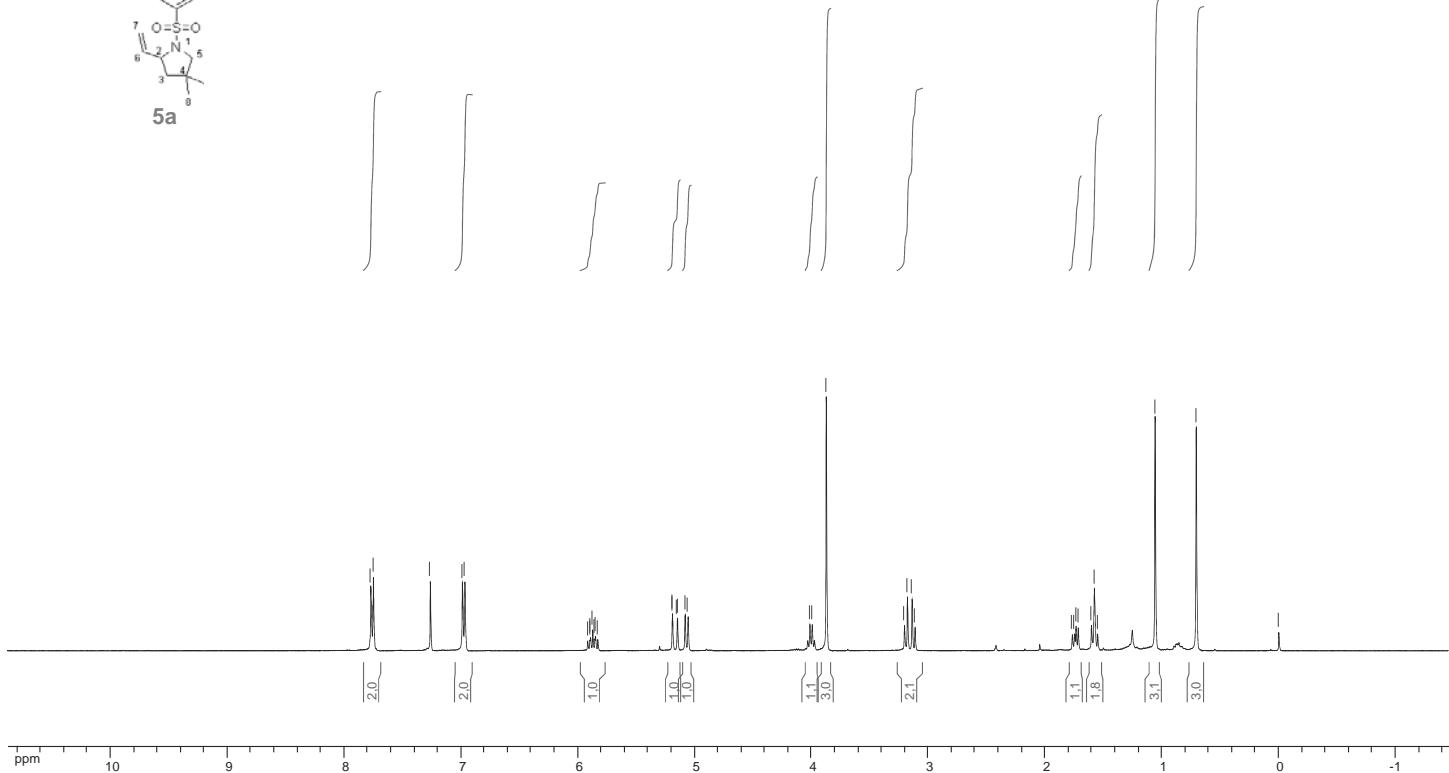
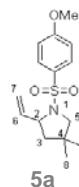
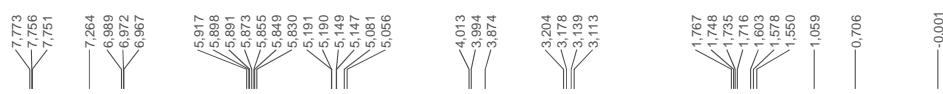
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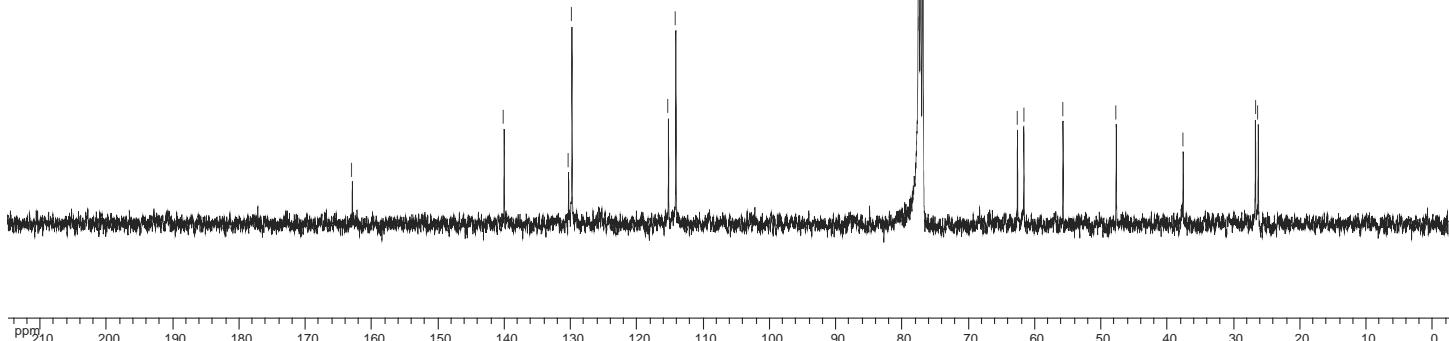
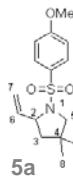
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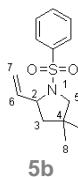
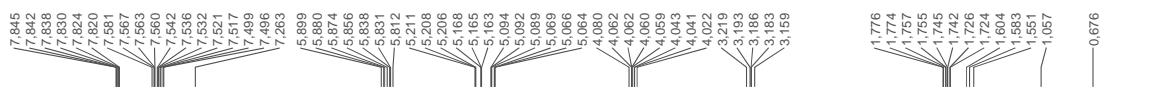
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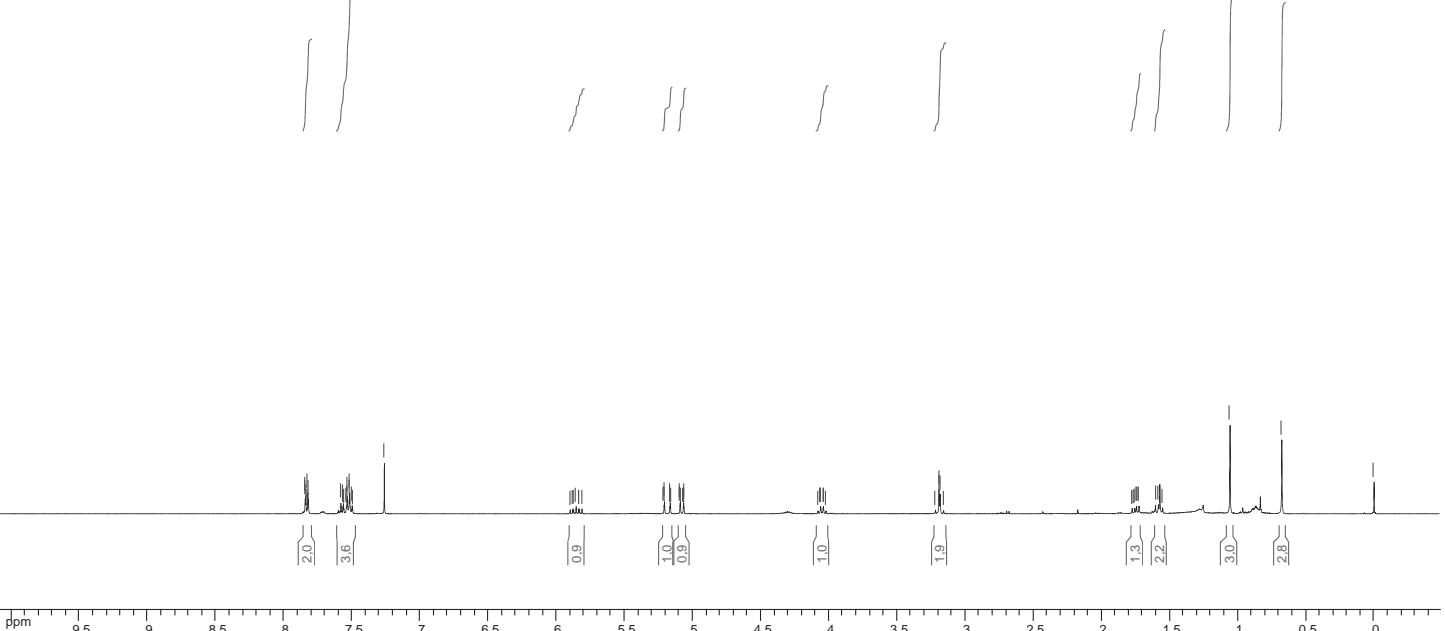
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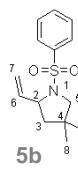
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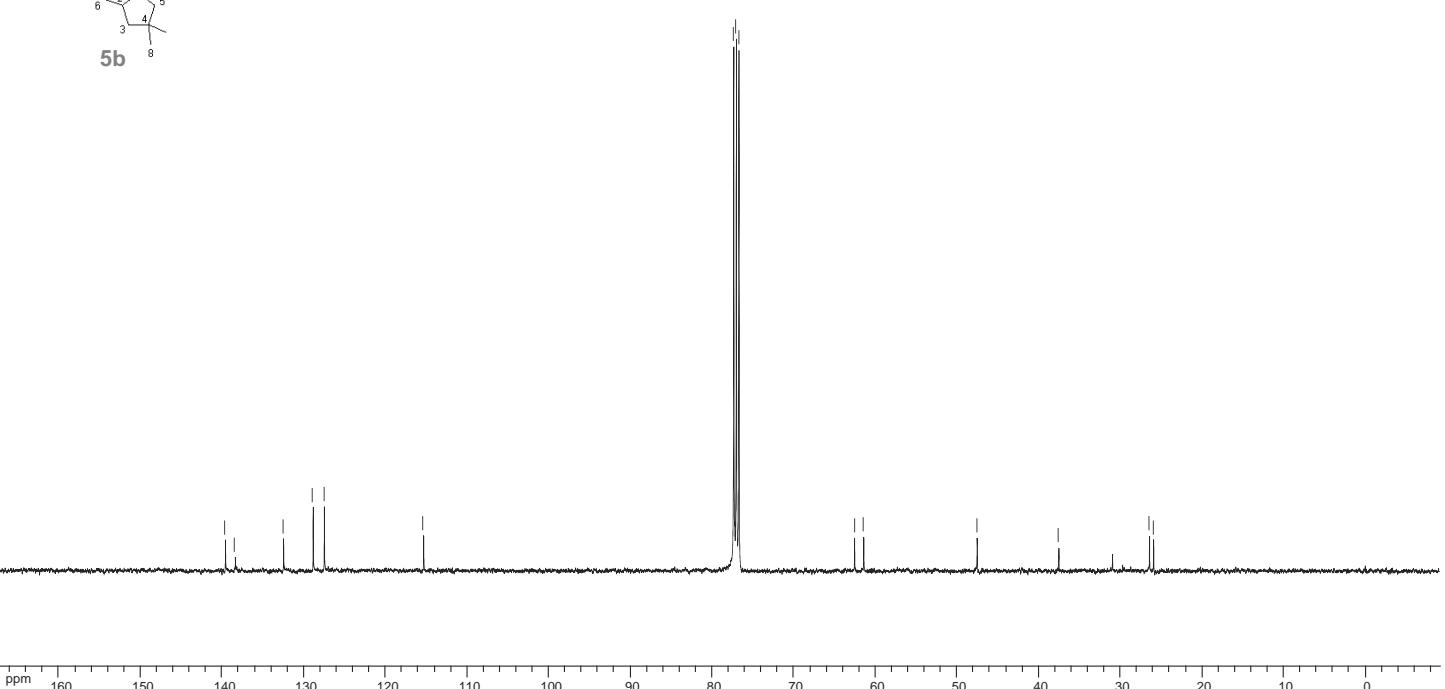
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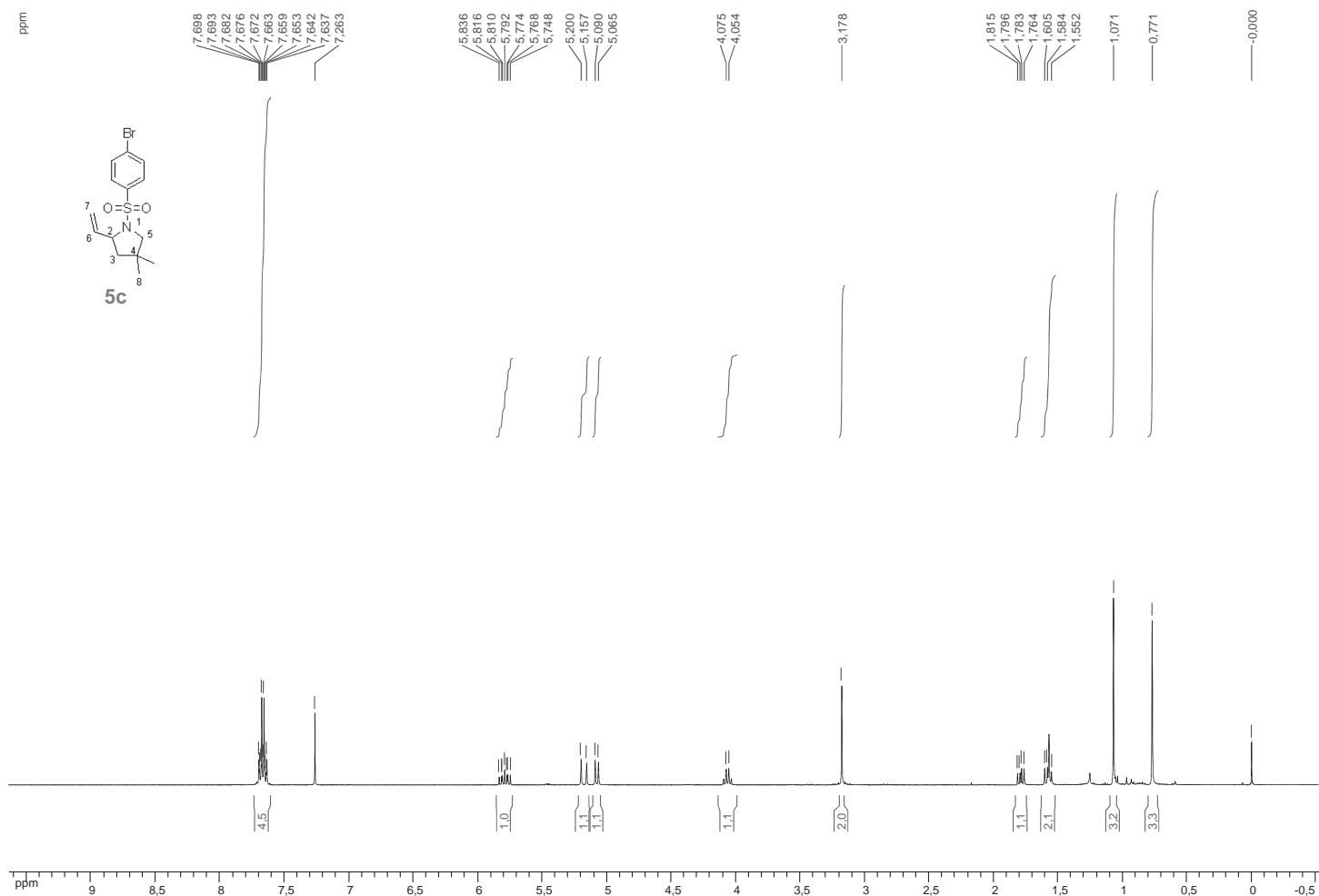
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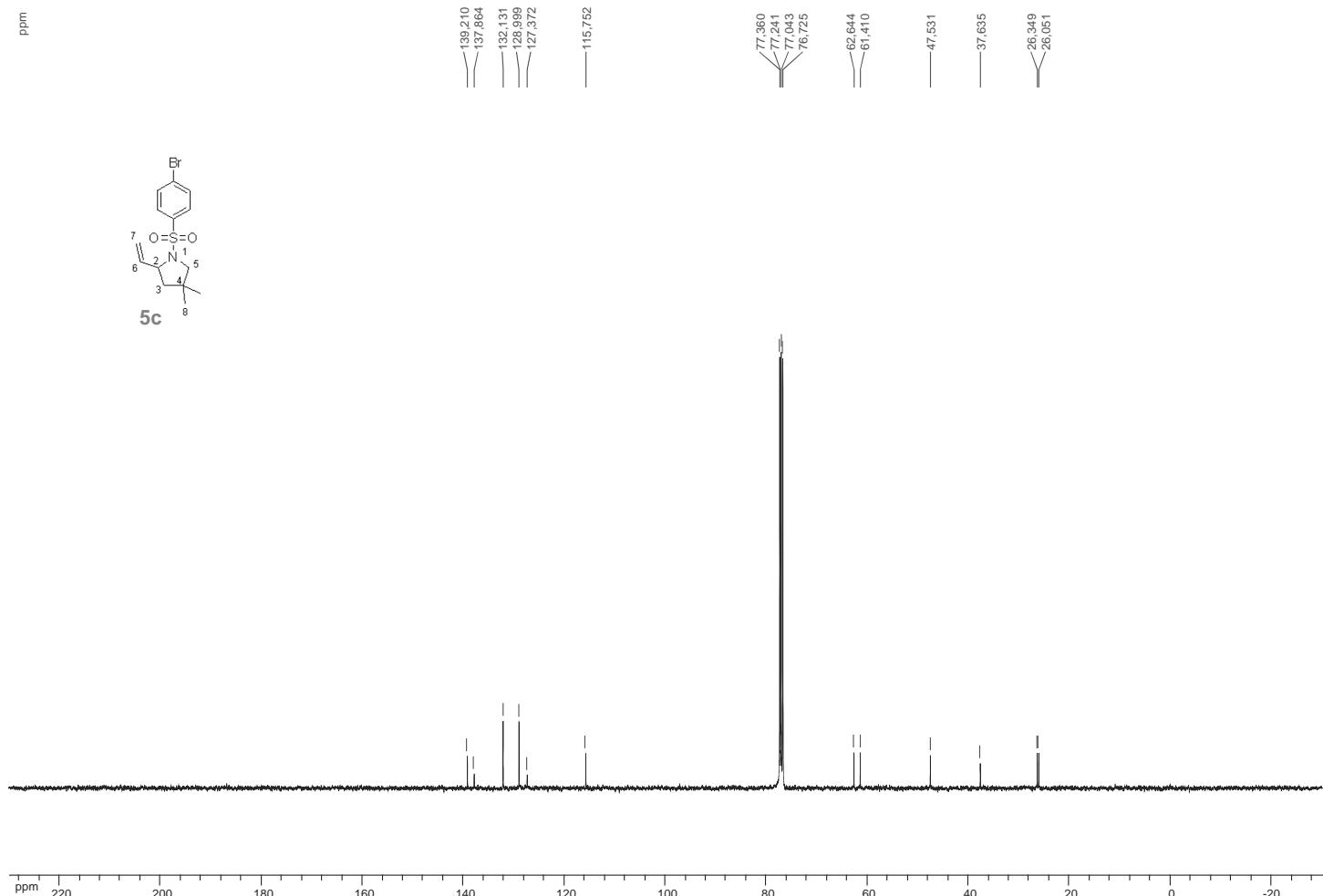
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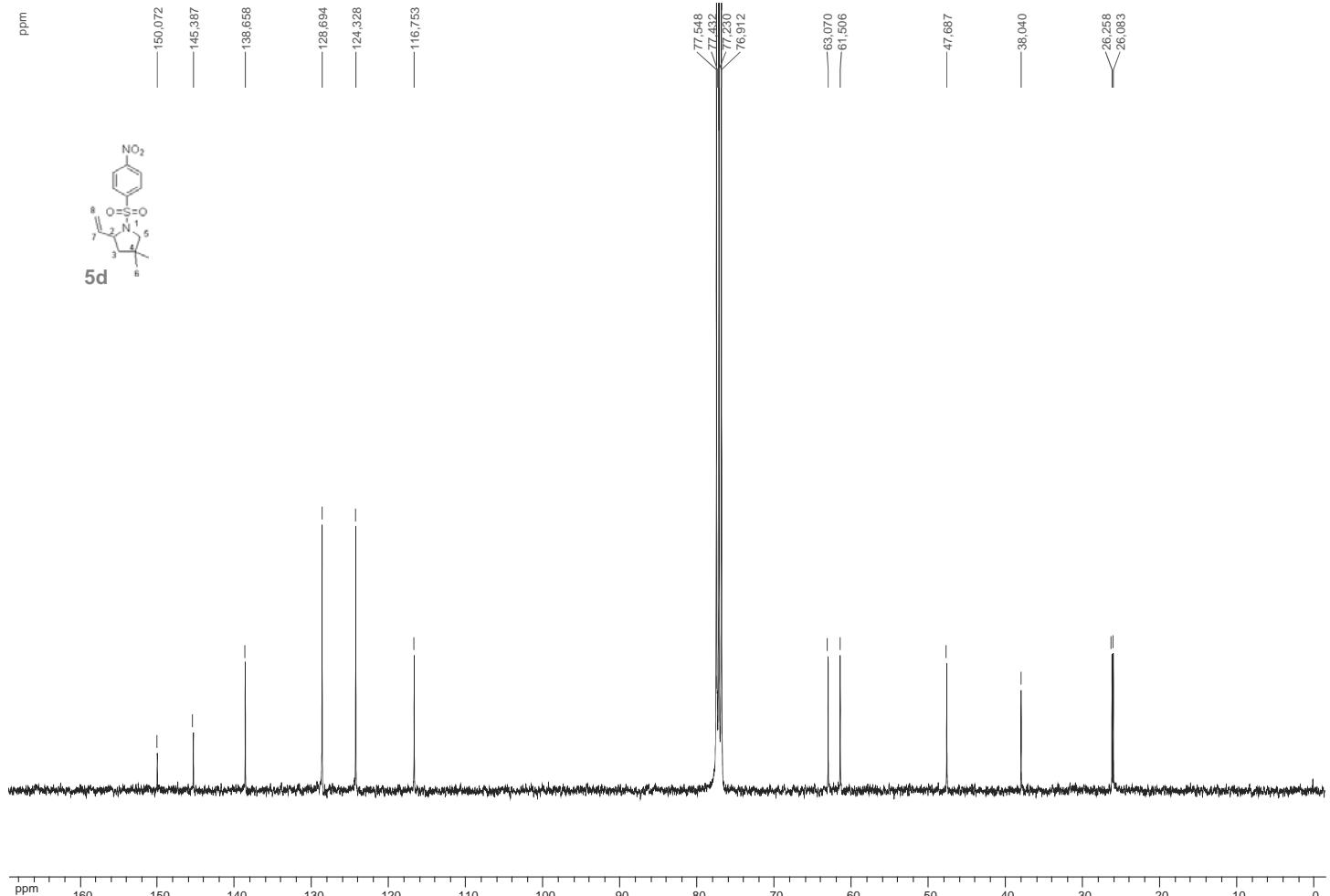
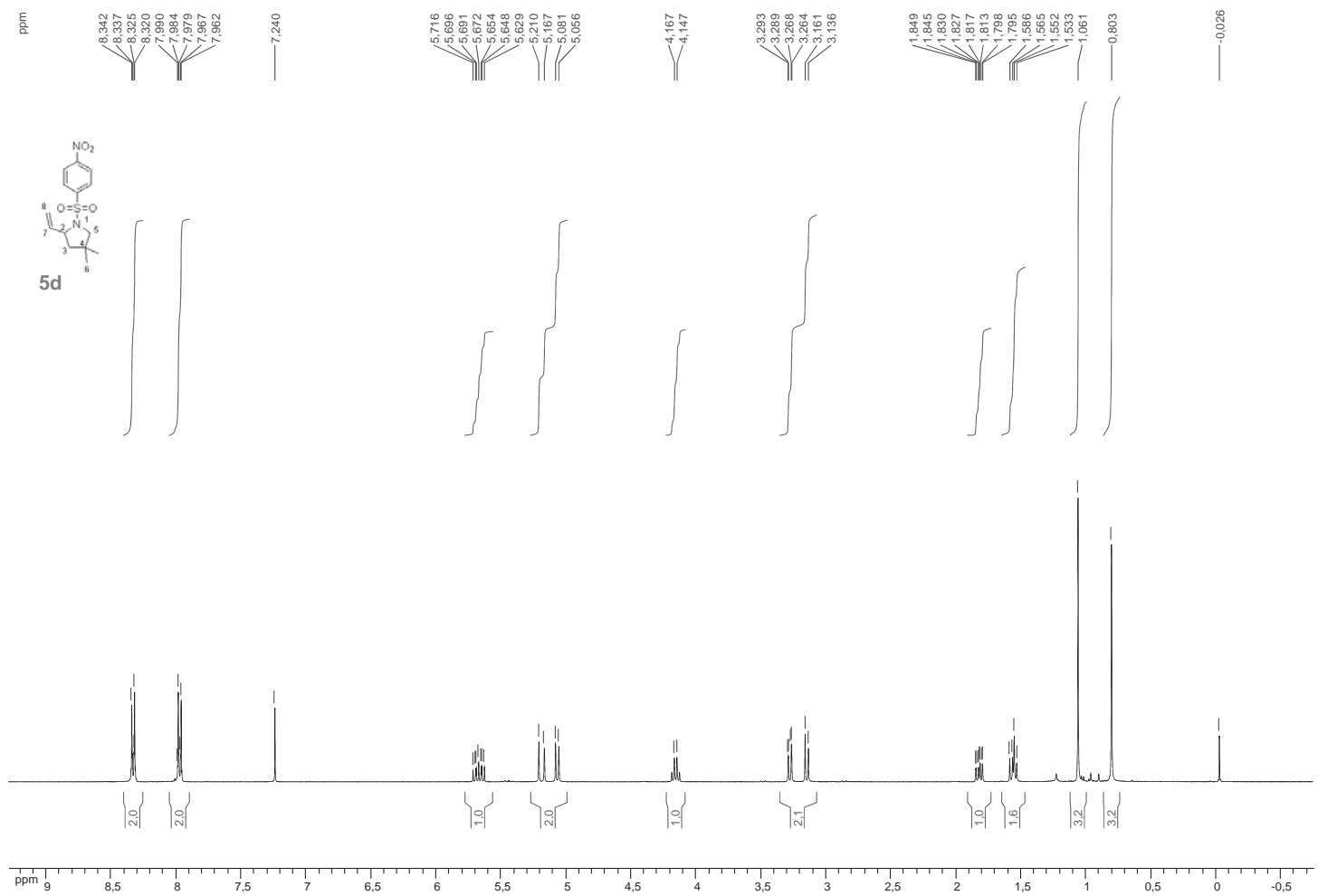


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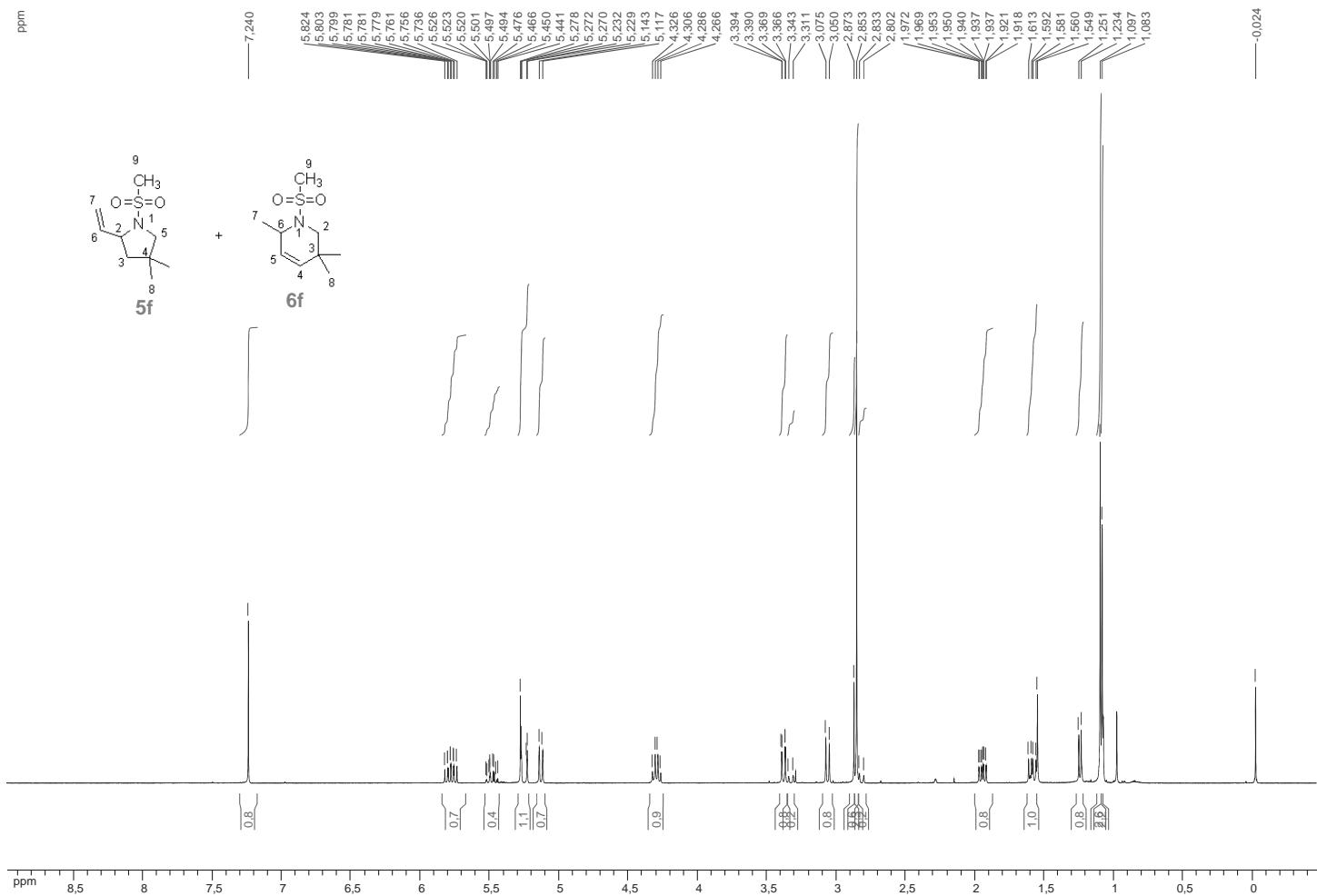


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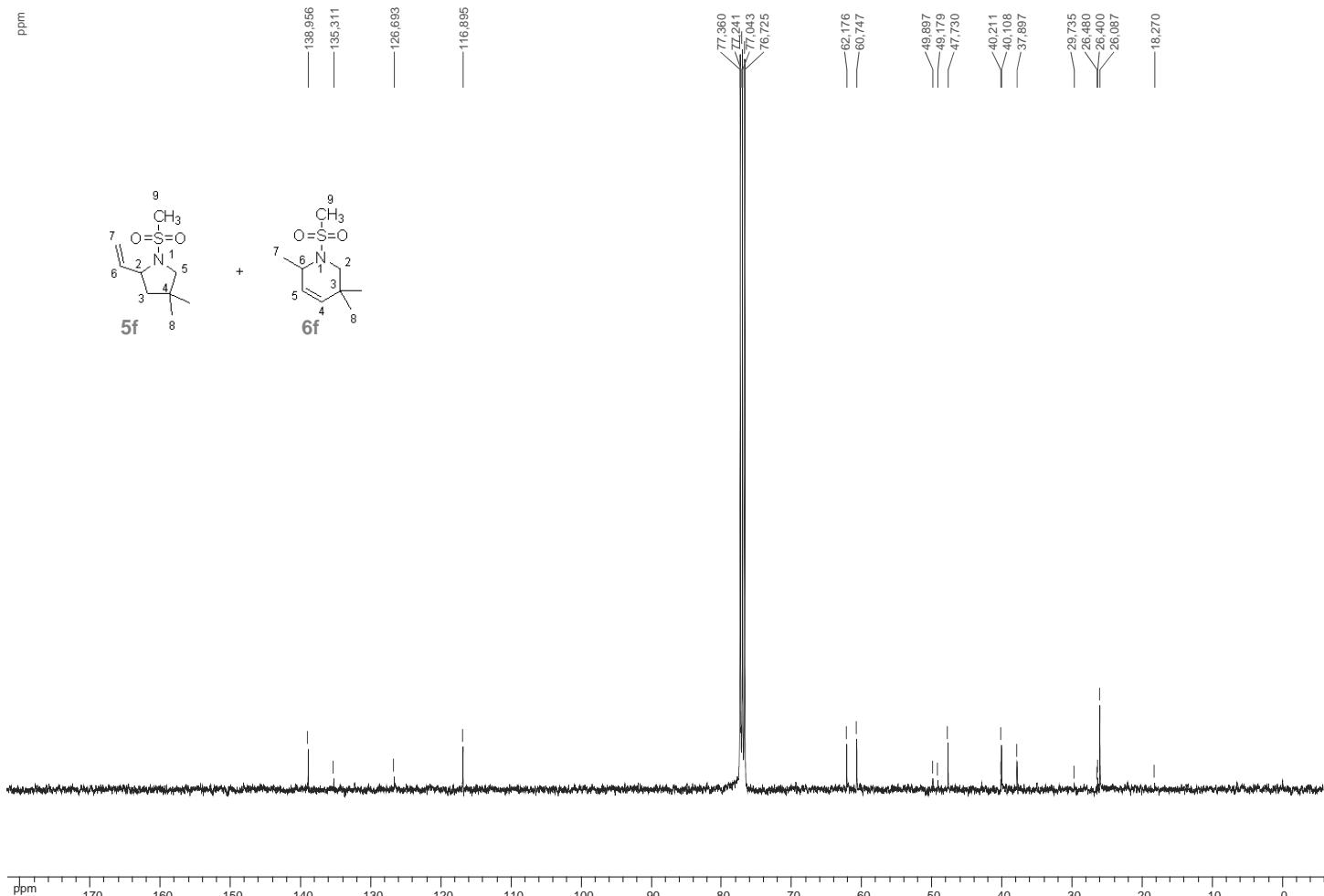




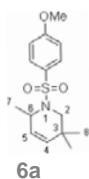
ppm



ppm



ppm



5.454
5.446

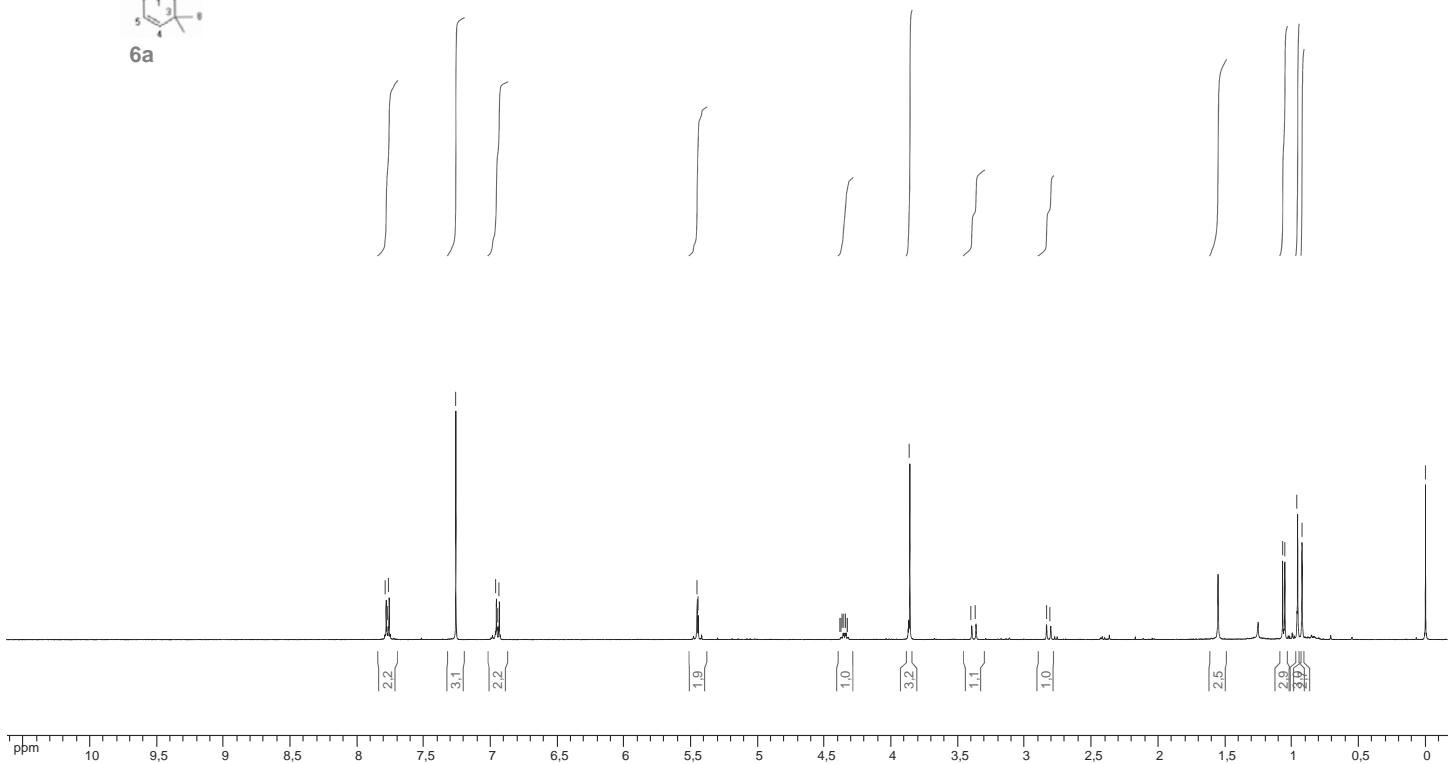
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4.372
4.362
4.361
4.355
4.346
4.338
4.328
4.322
3.861

3.398
3.366

2.837
2.306

1.069
1.053
0.957
0.924

-0.000



ppm

162.532

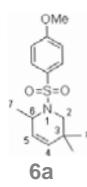
135.049
133.160
129.249
126.959

114.005

77.352
77.336
76.717

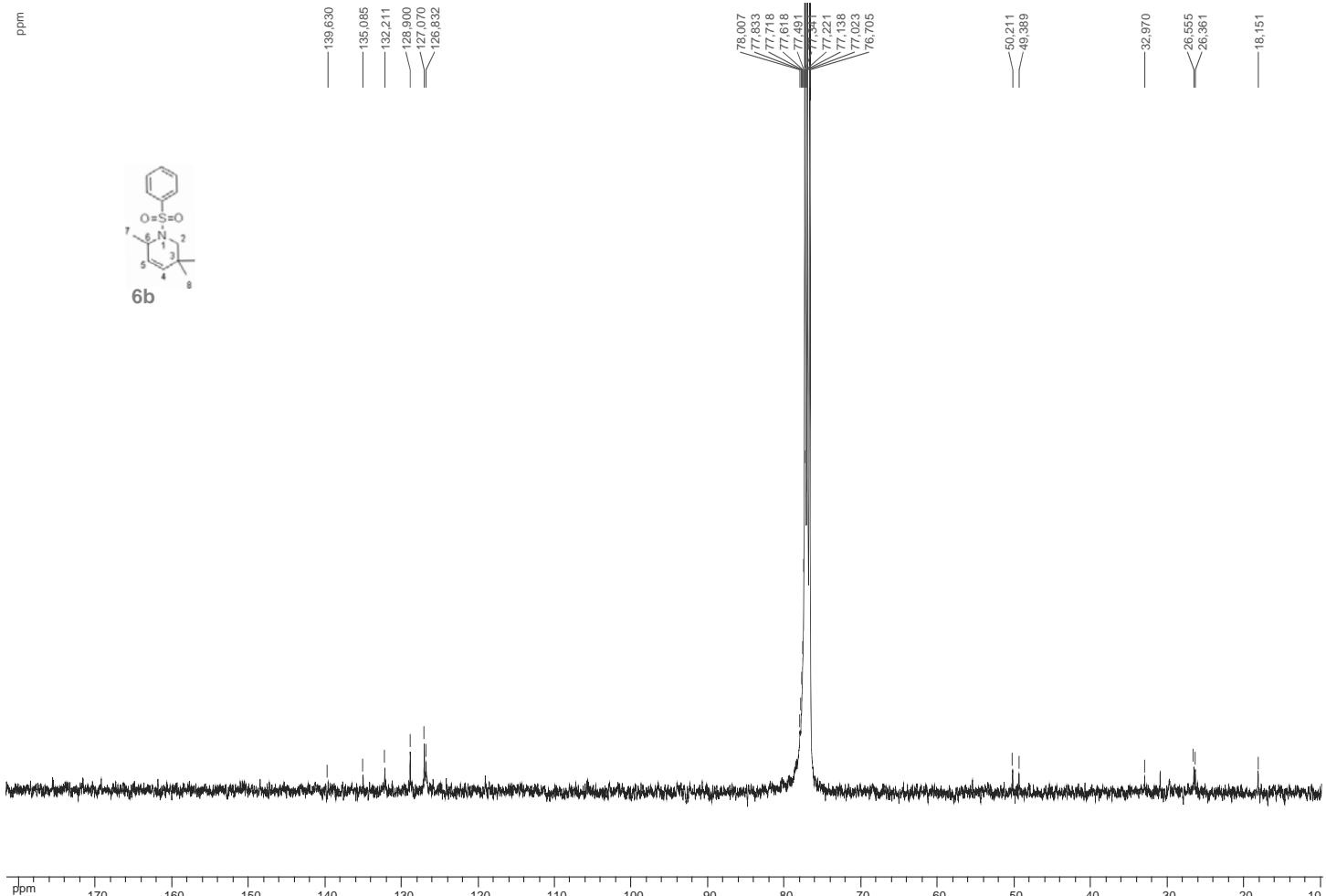
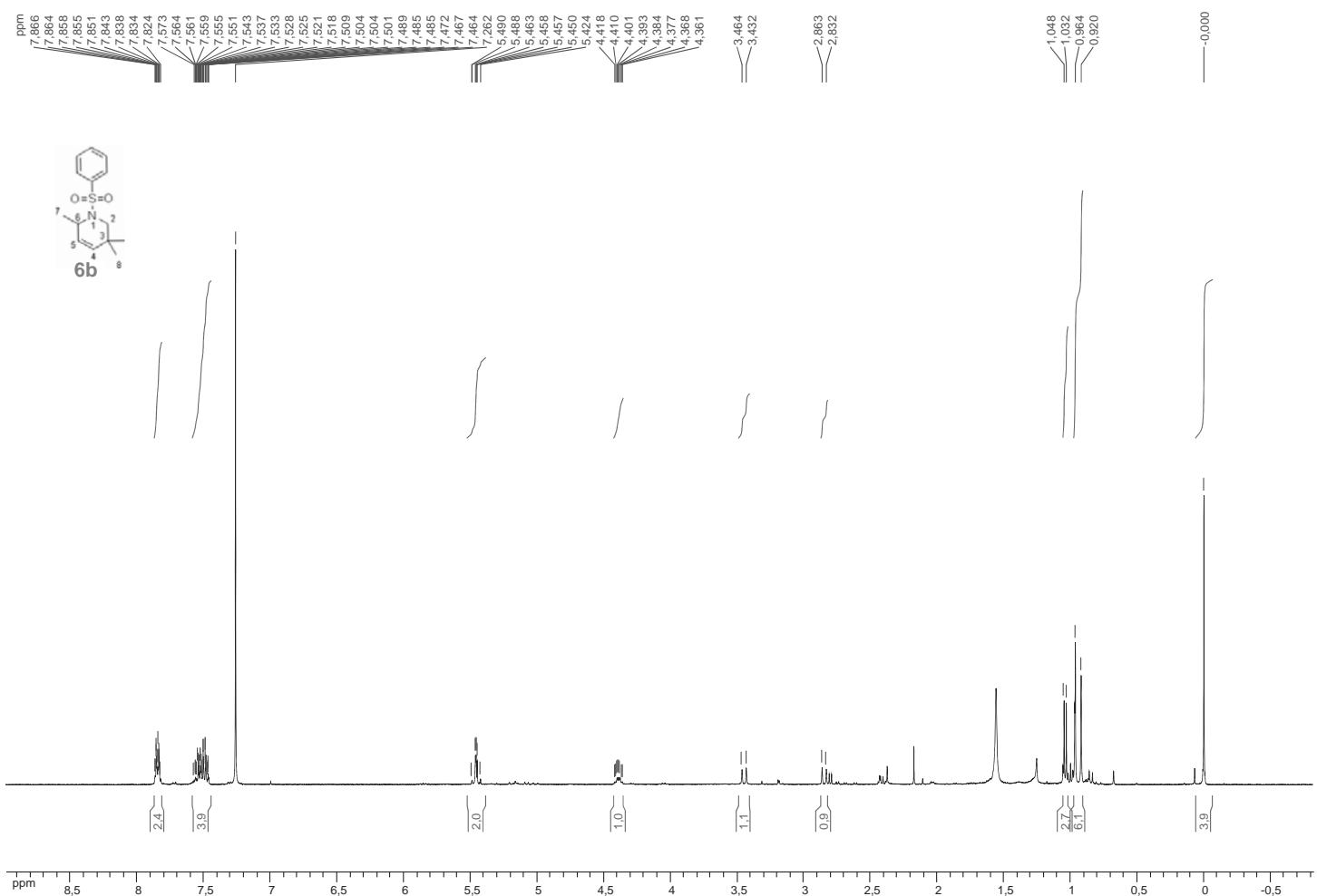
55.574
50.132
49.314

32.998
26.575
26.440
18.147

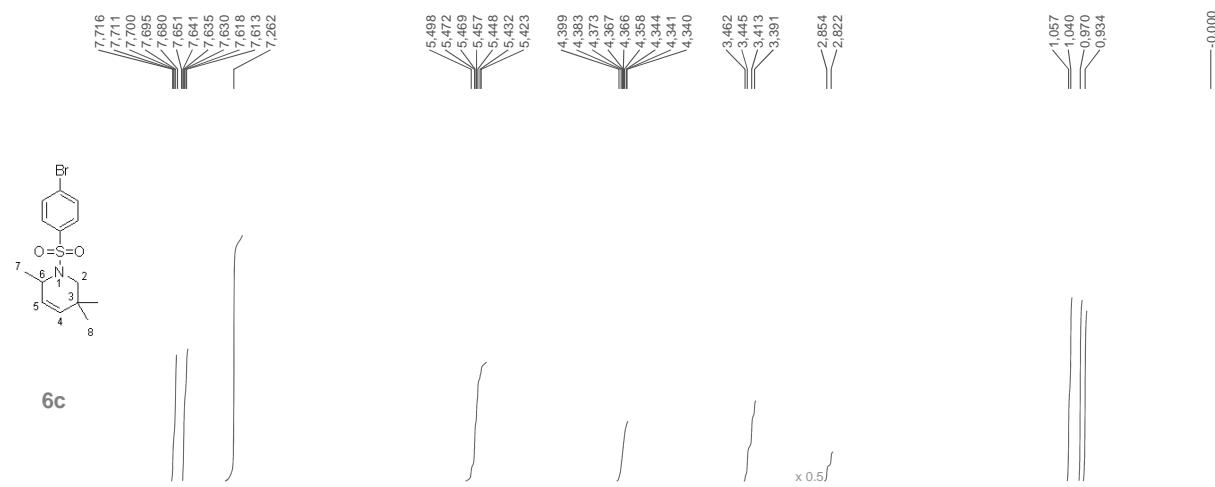


6a

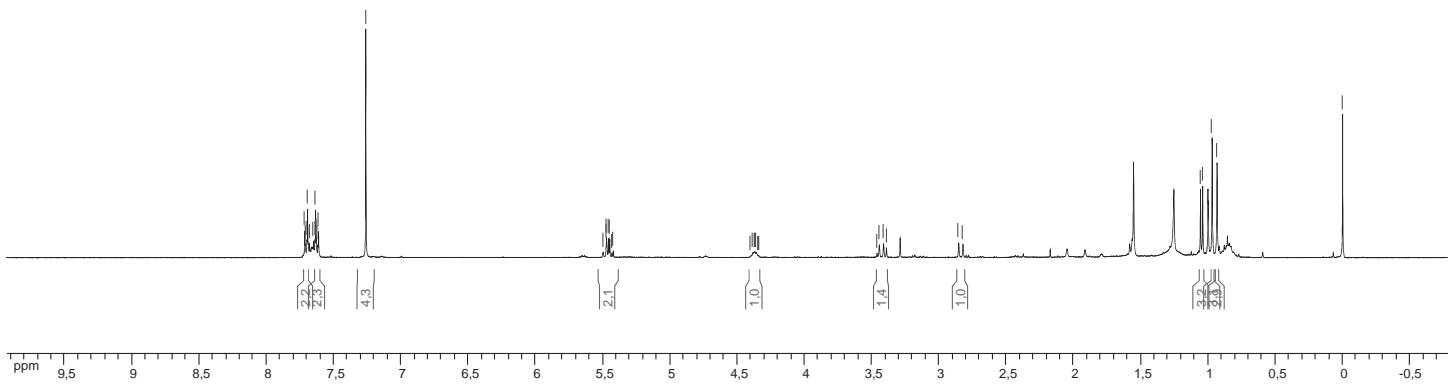




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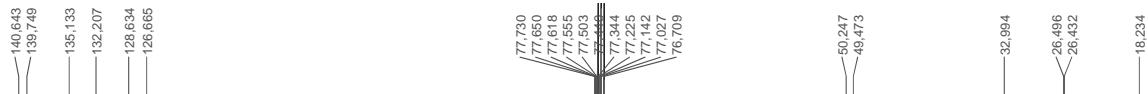


6c



ppm 9.5 8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0 -0.5

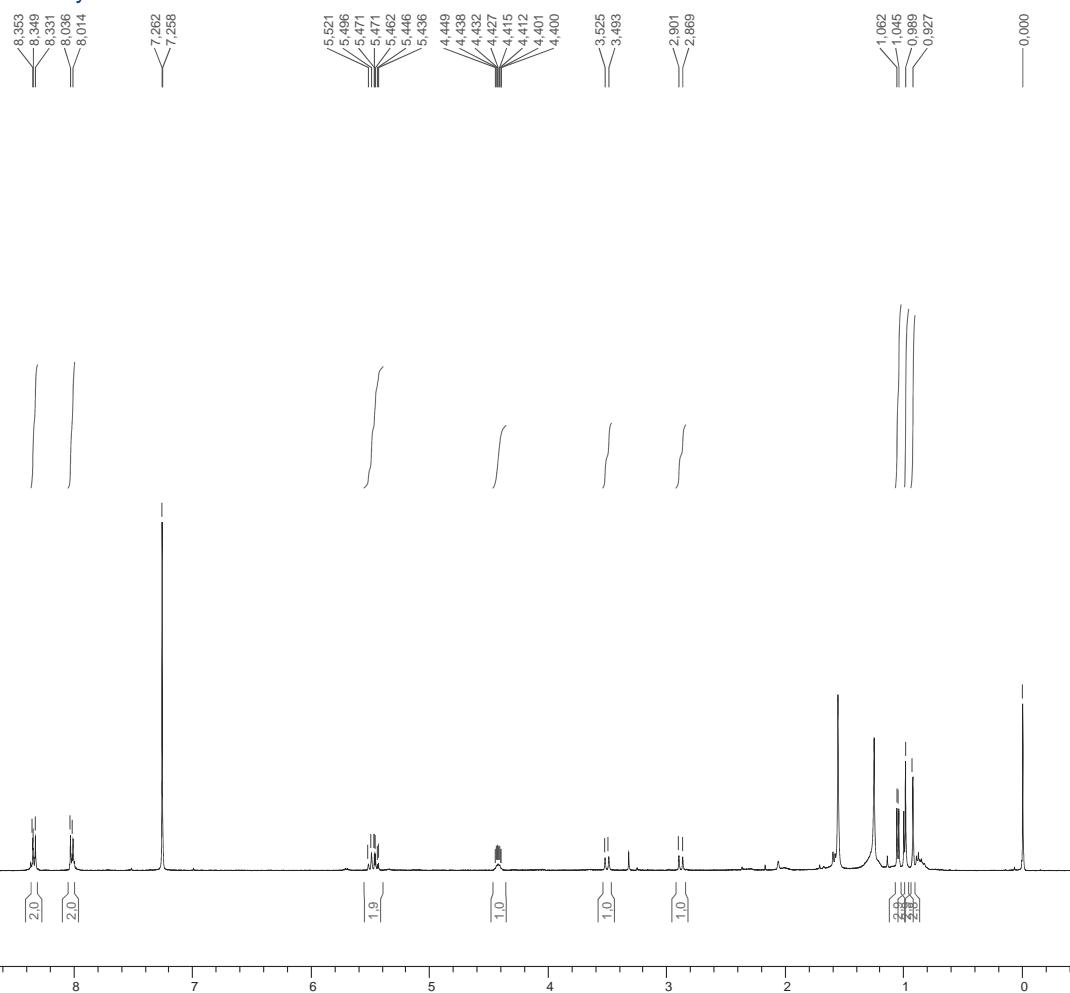
ppm



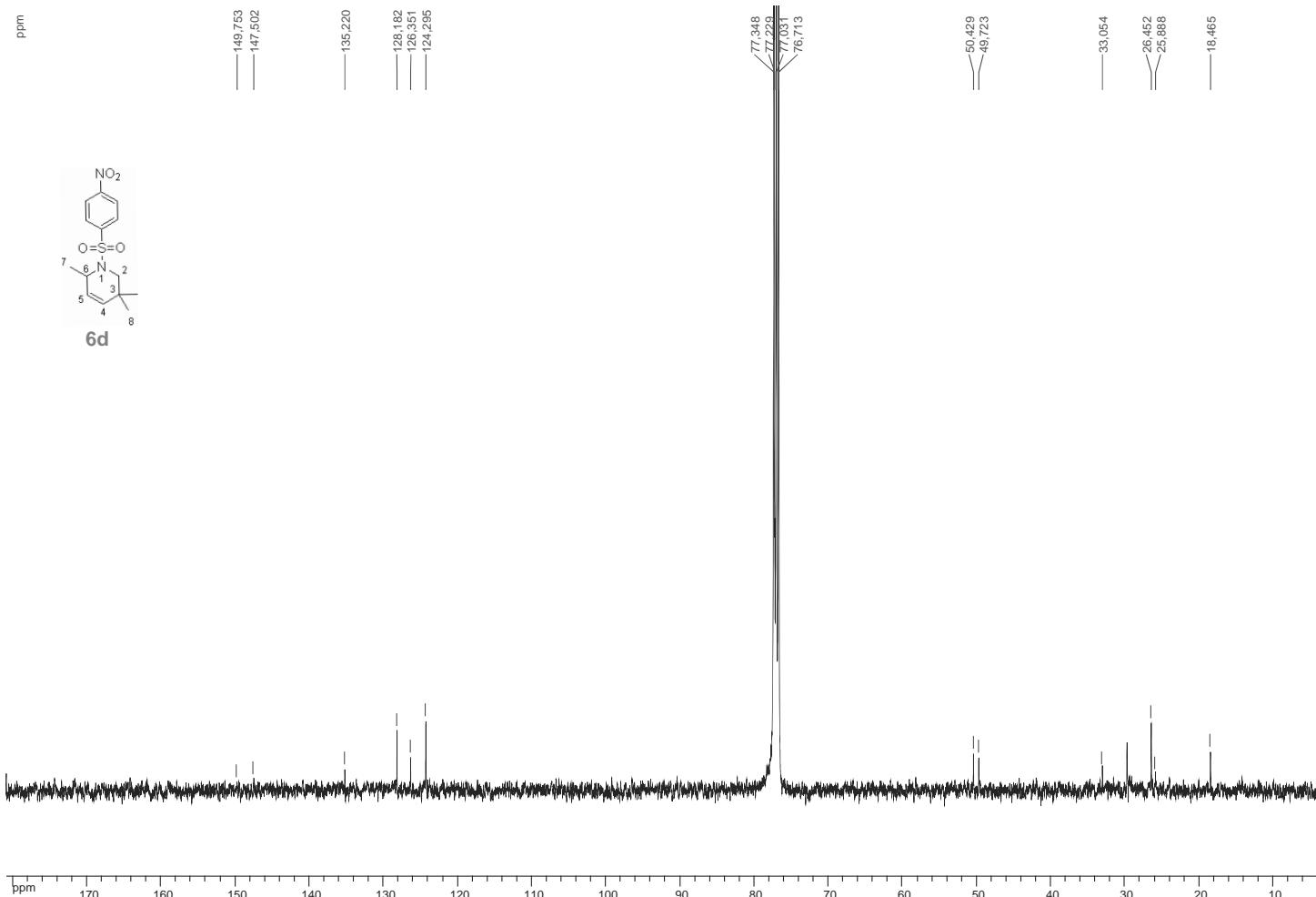
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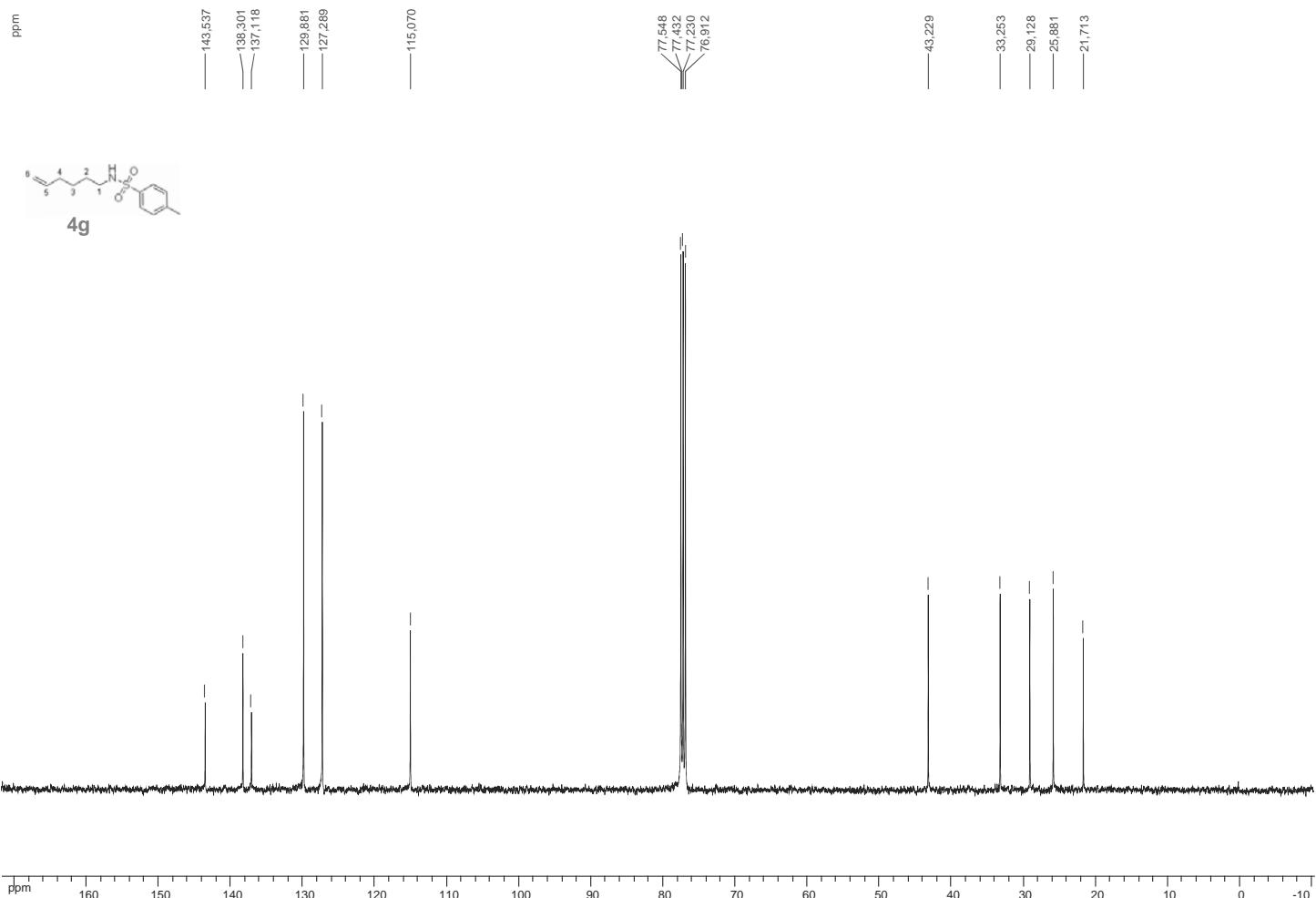
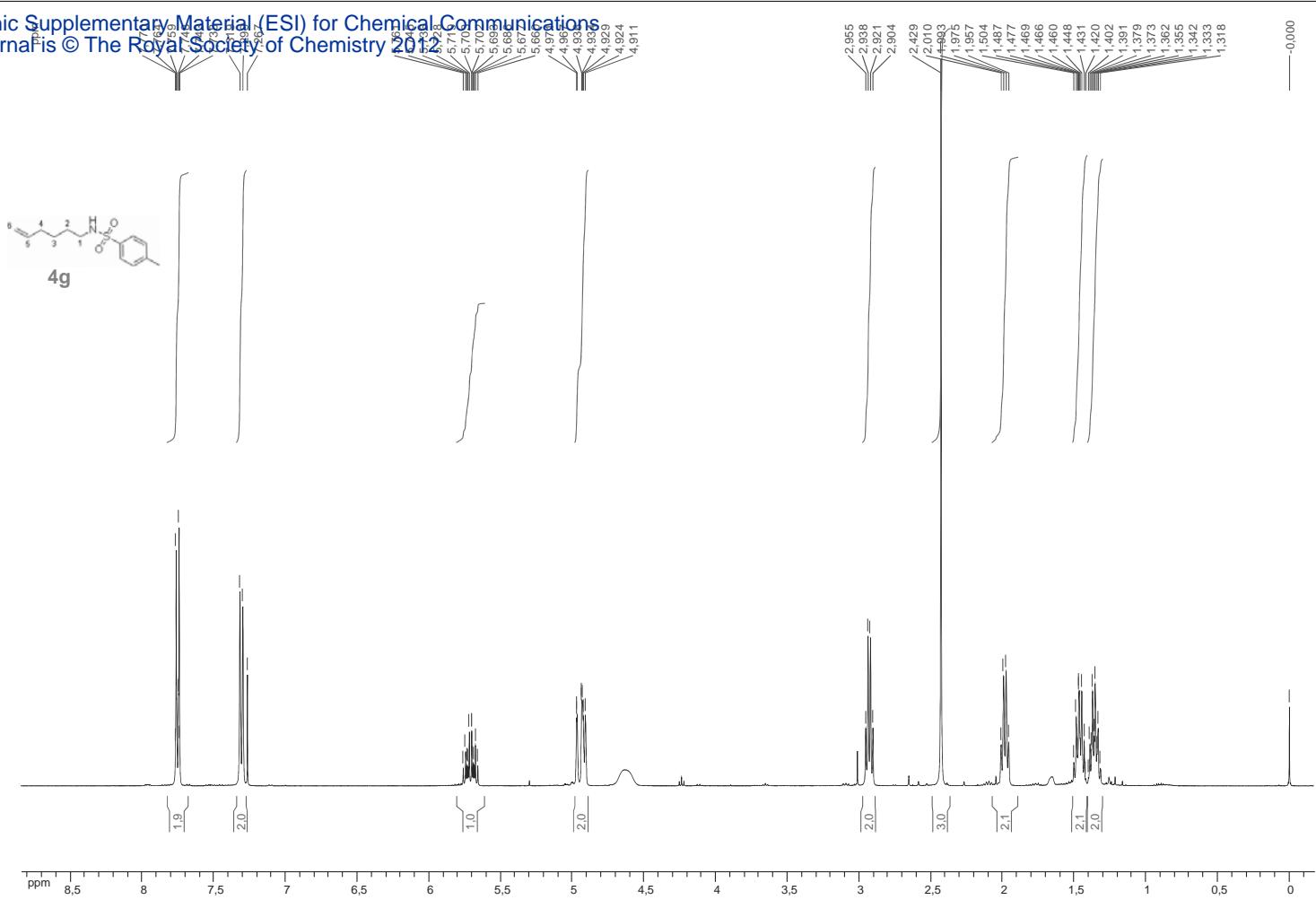
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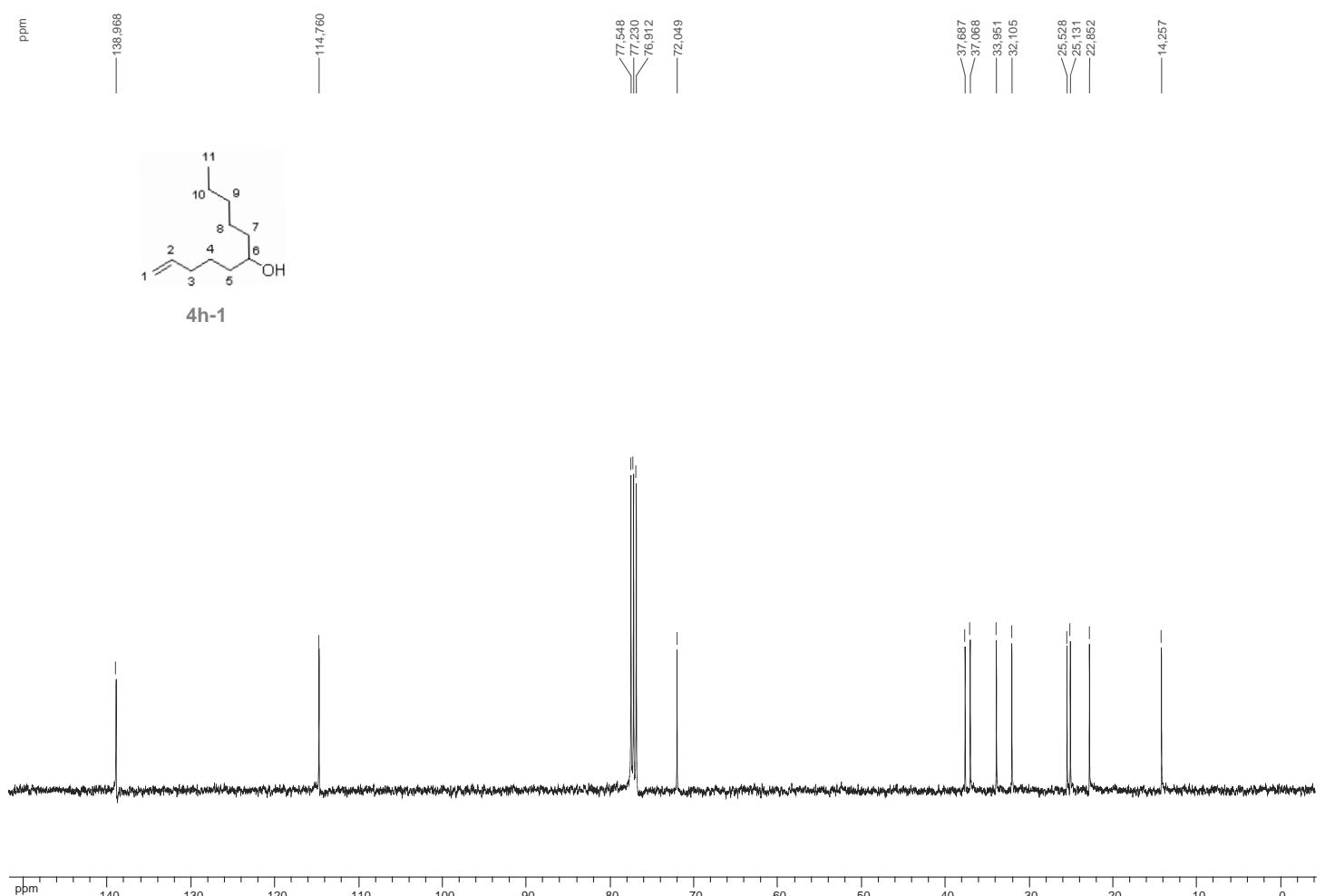
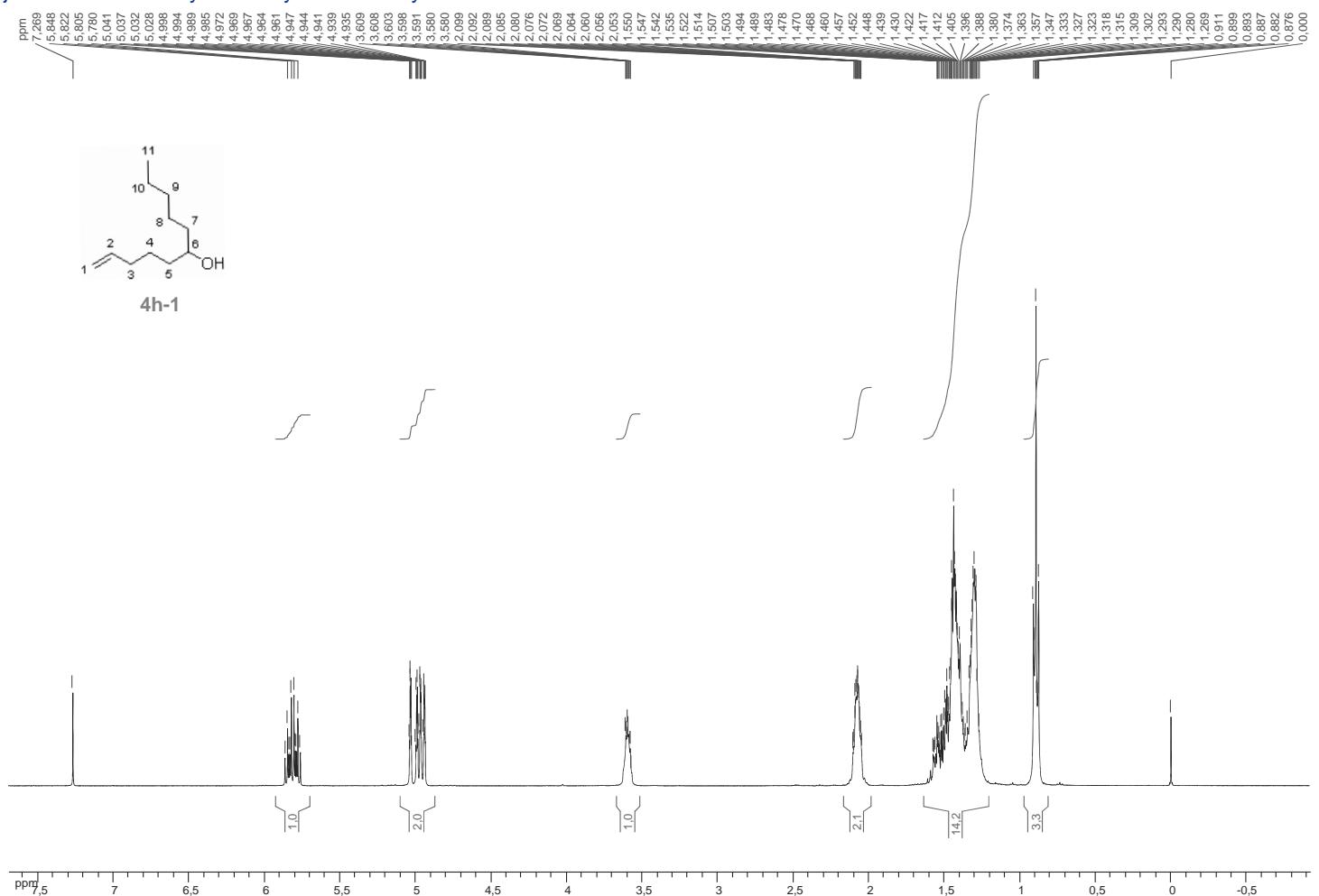
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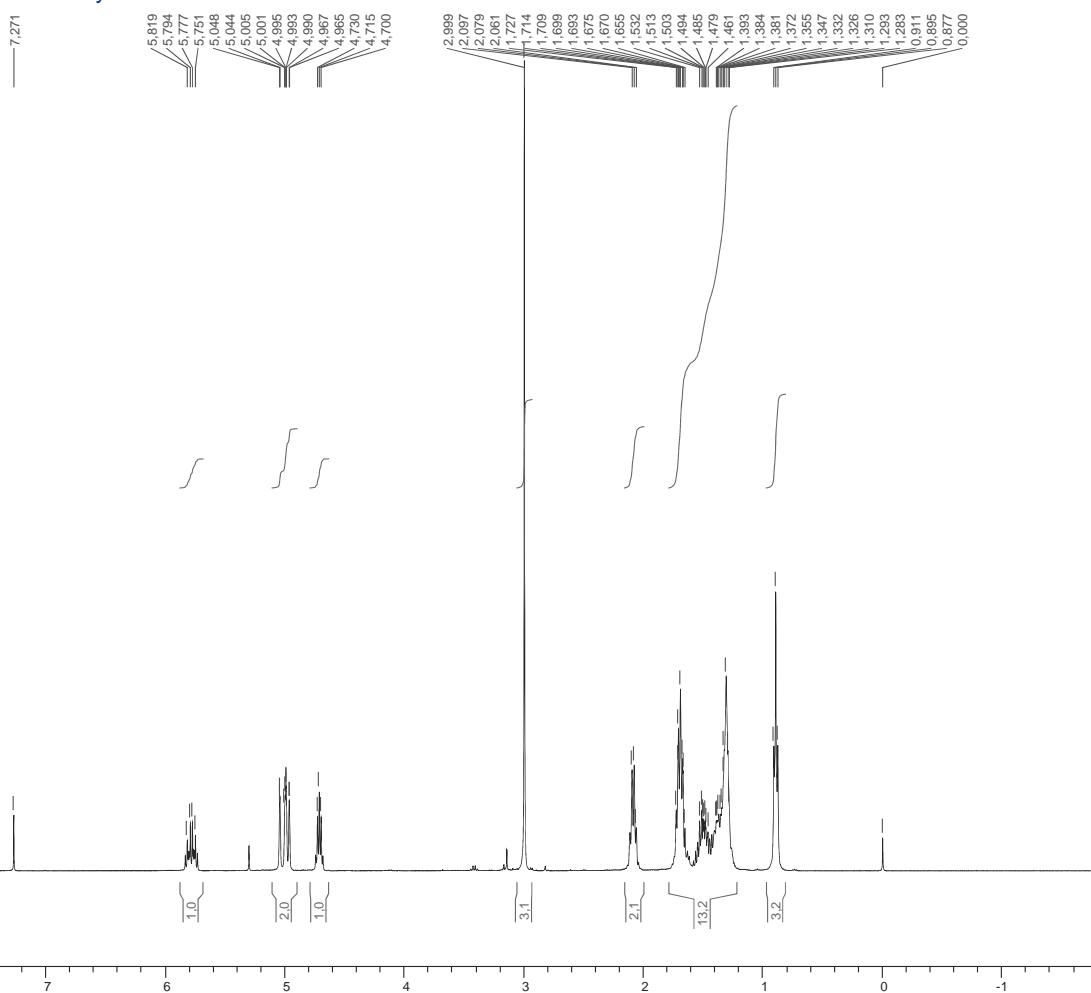
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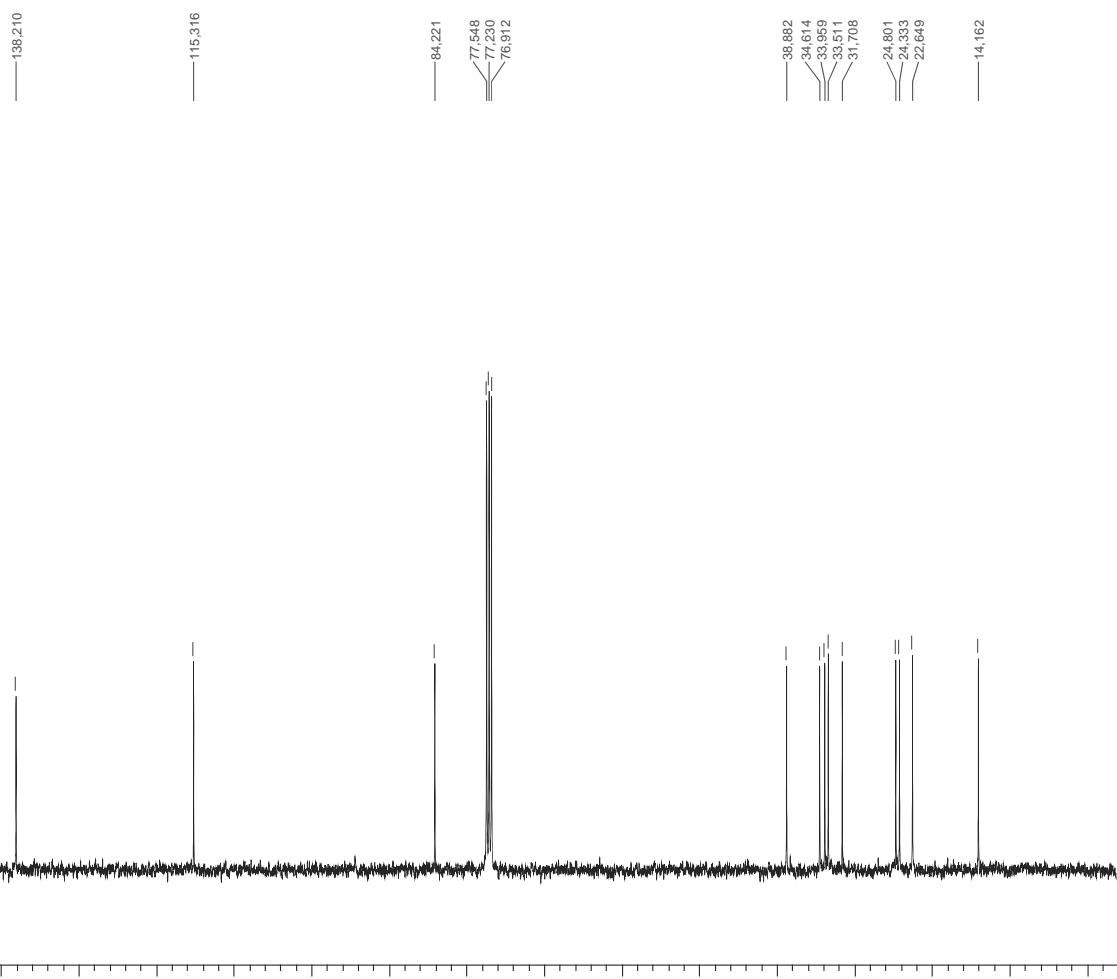




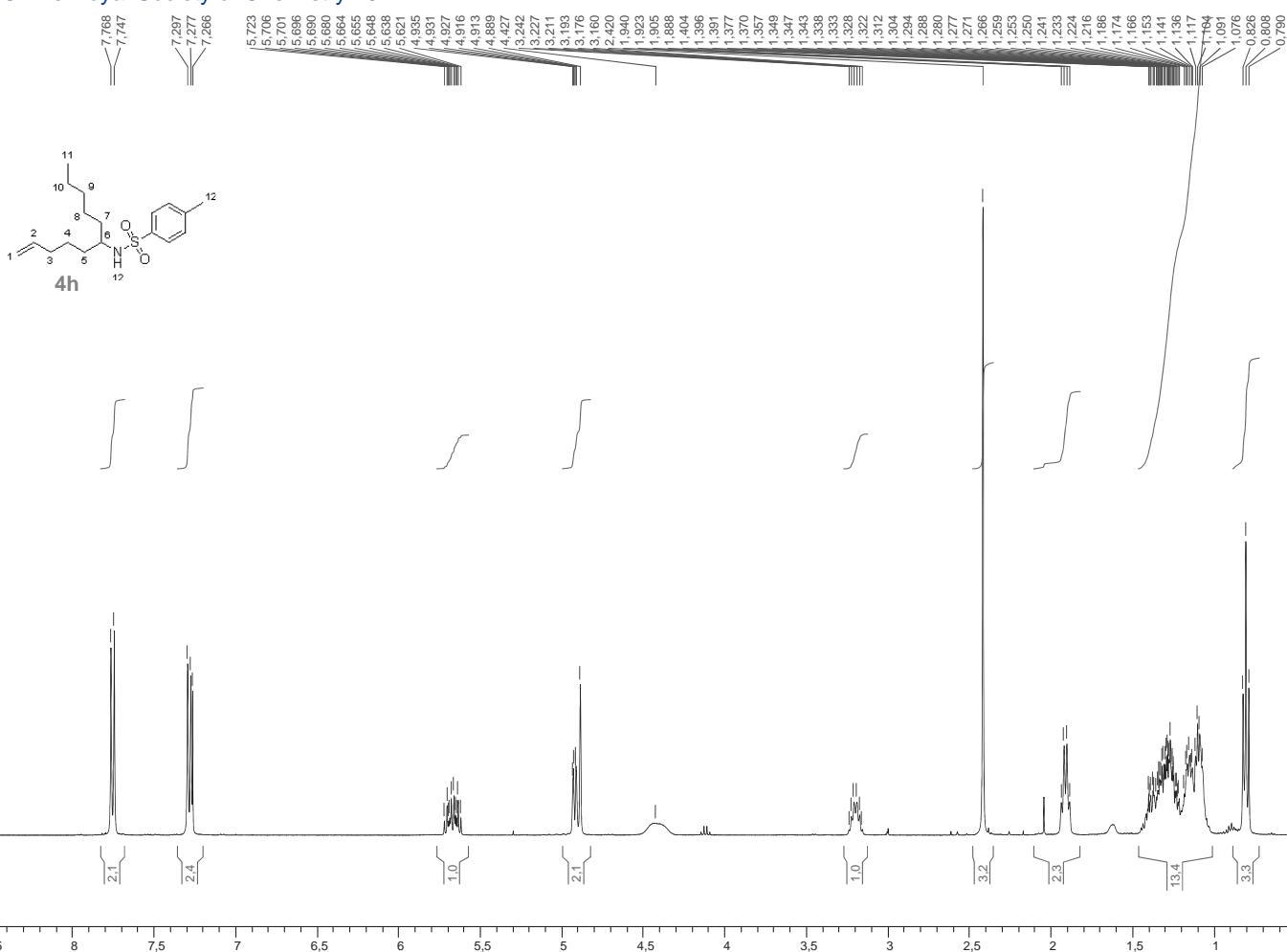
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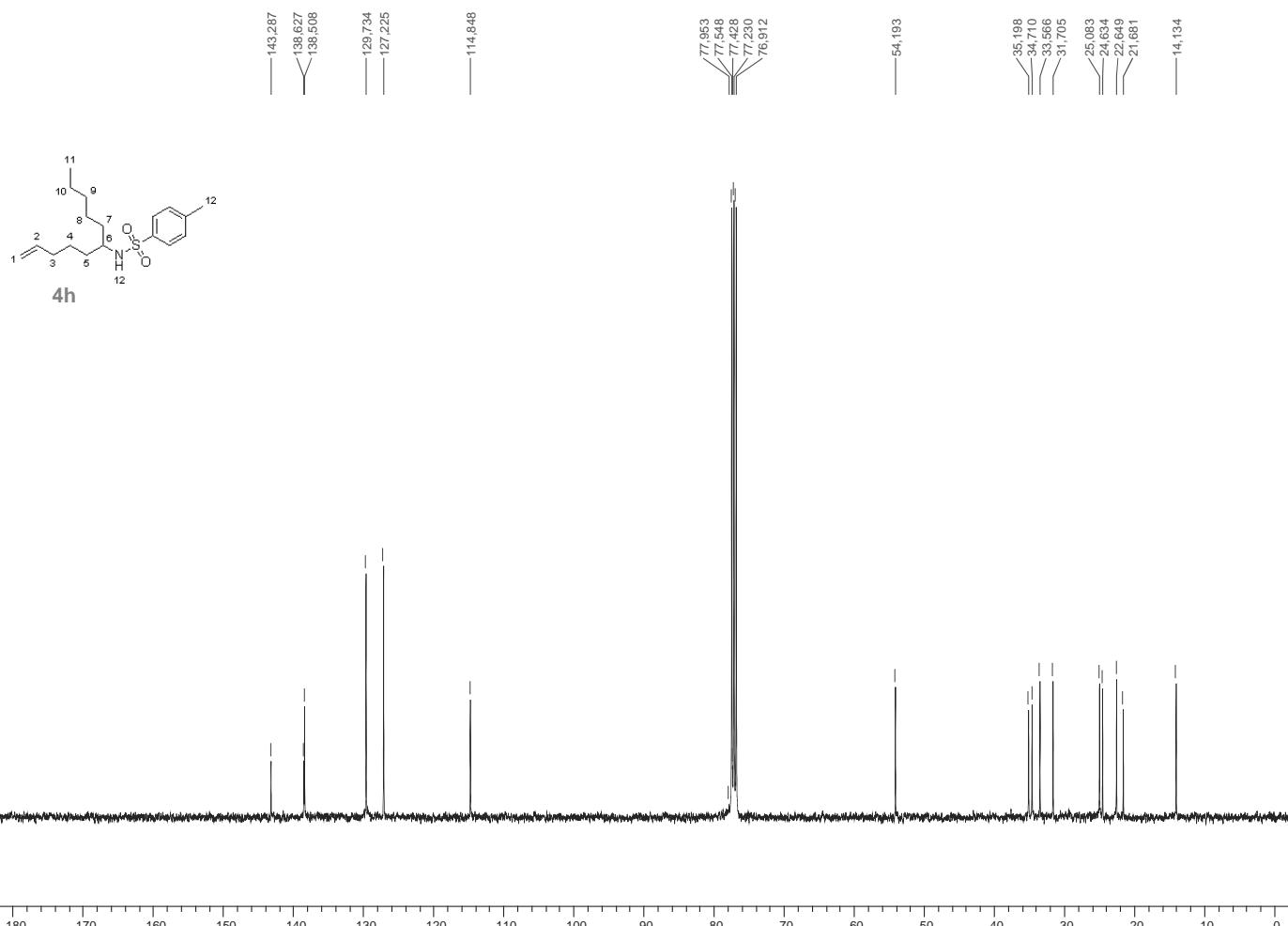
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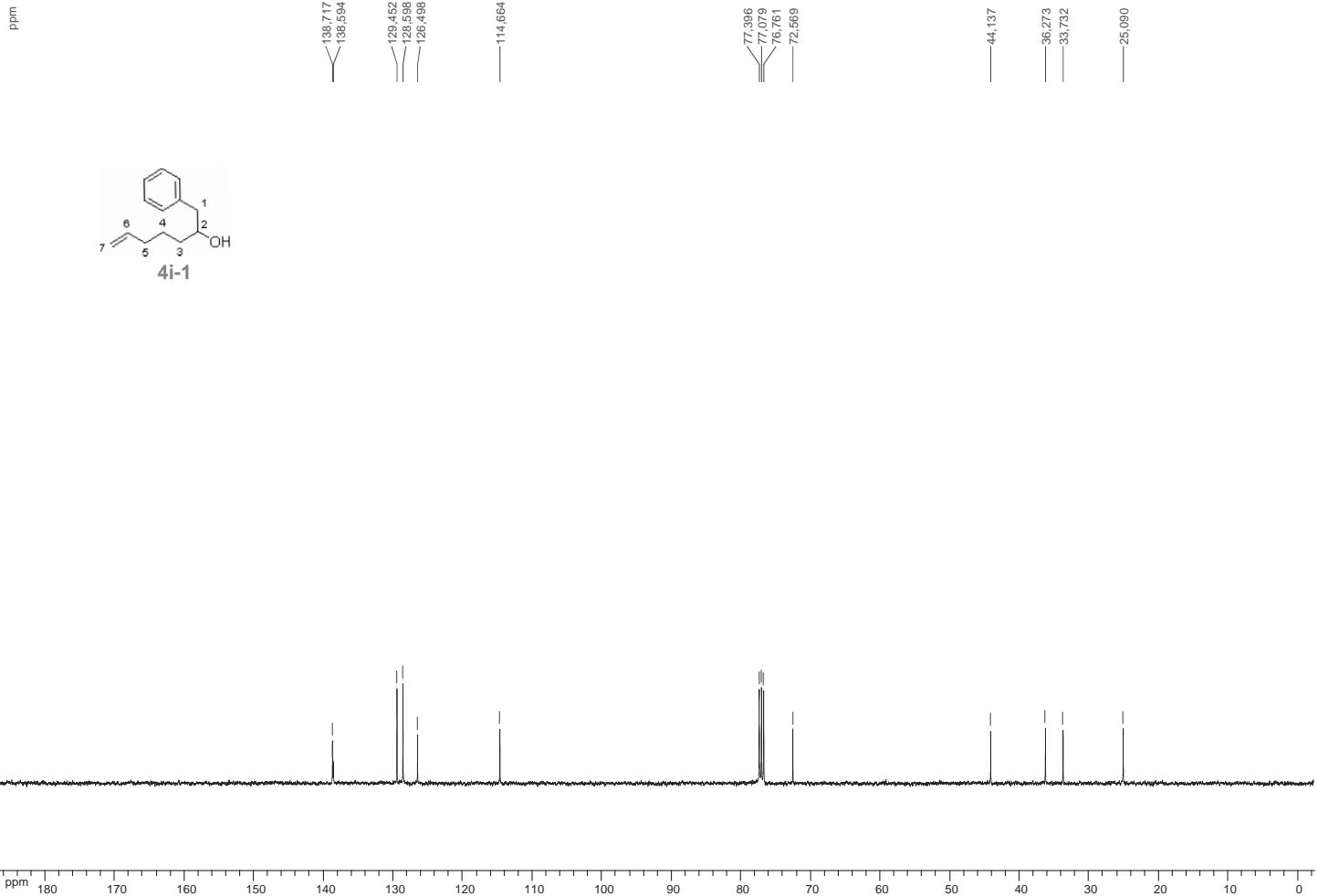
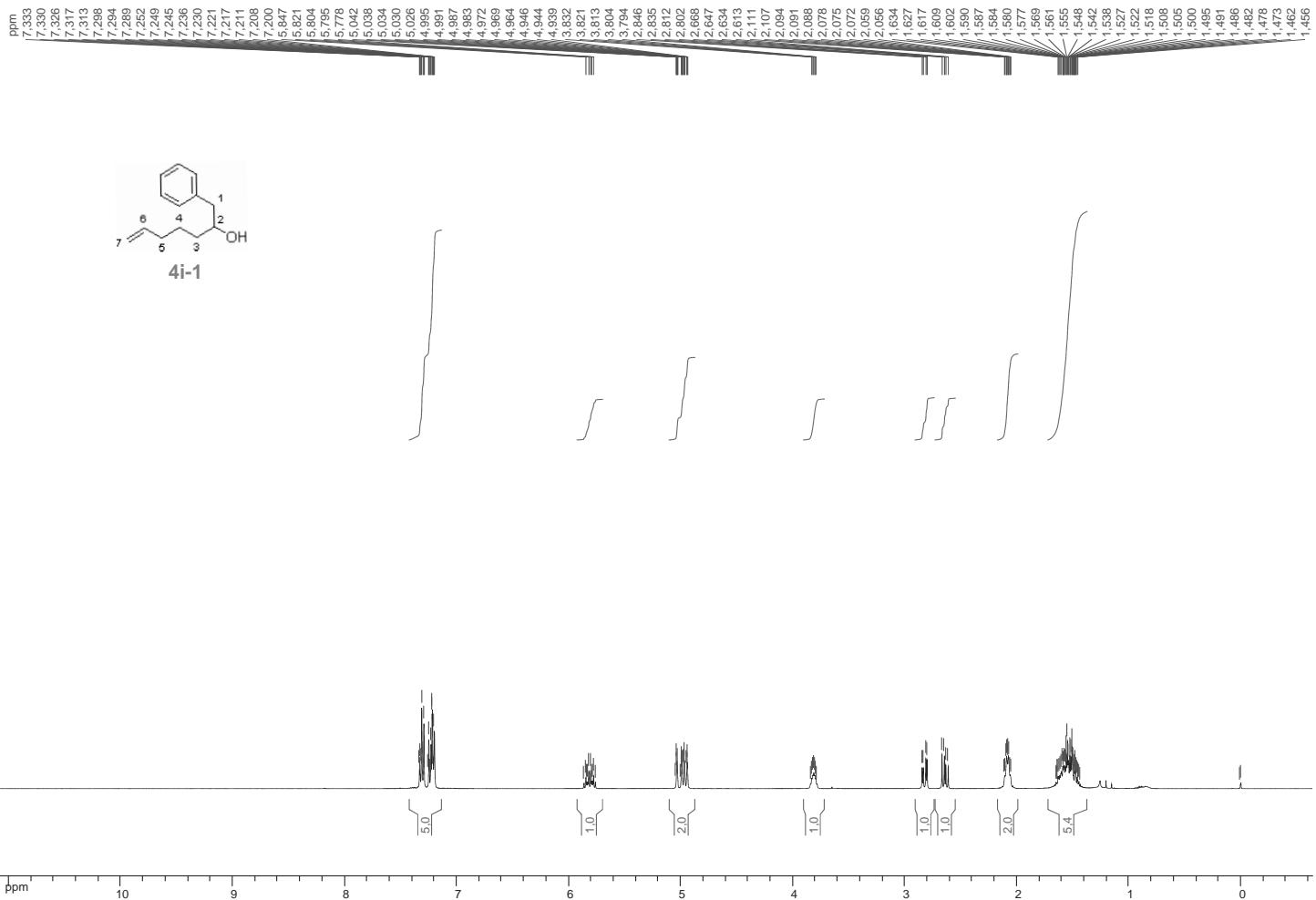


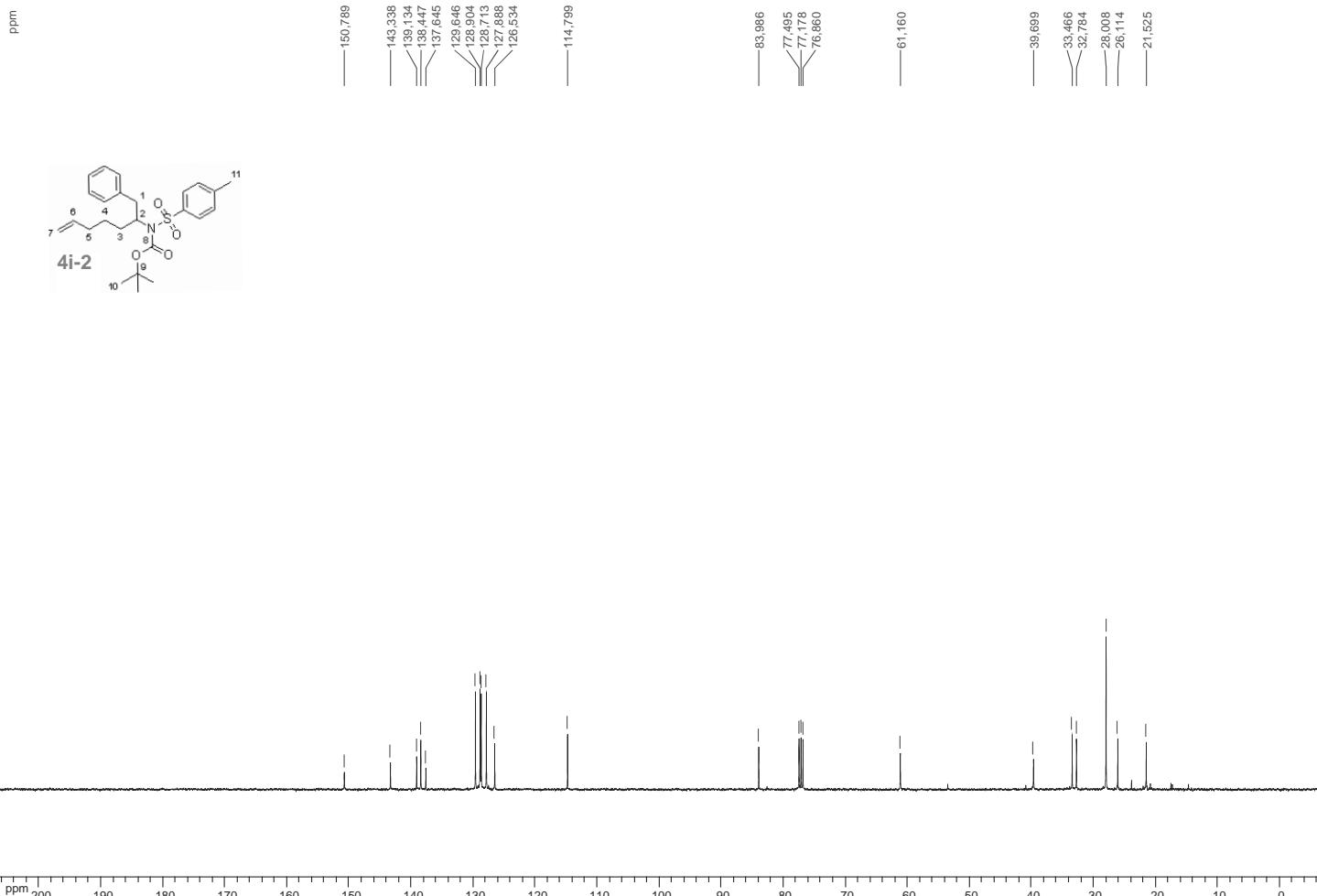
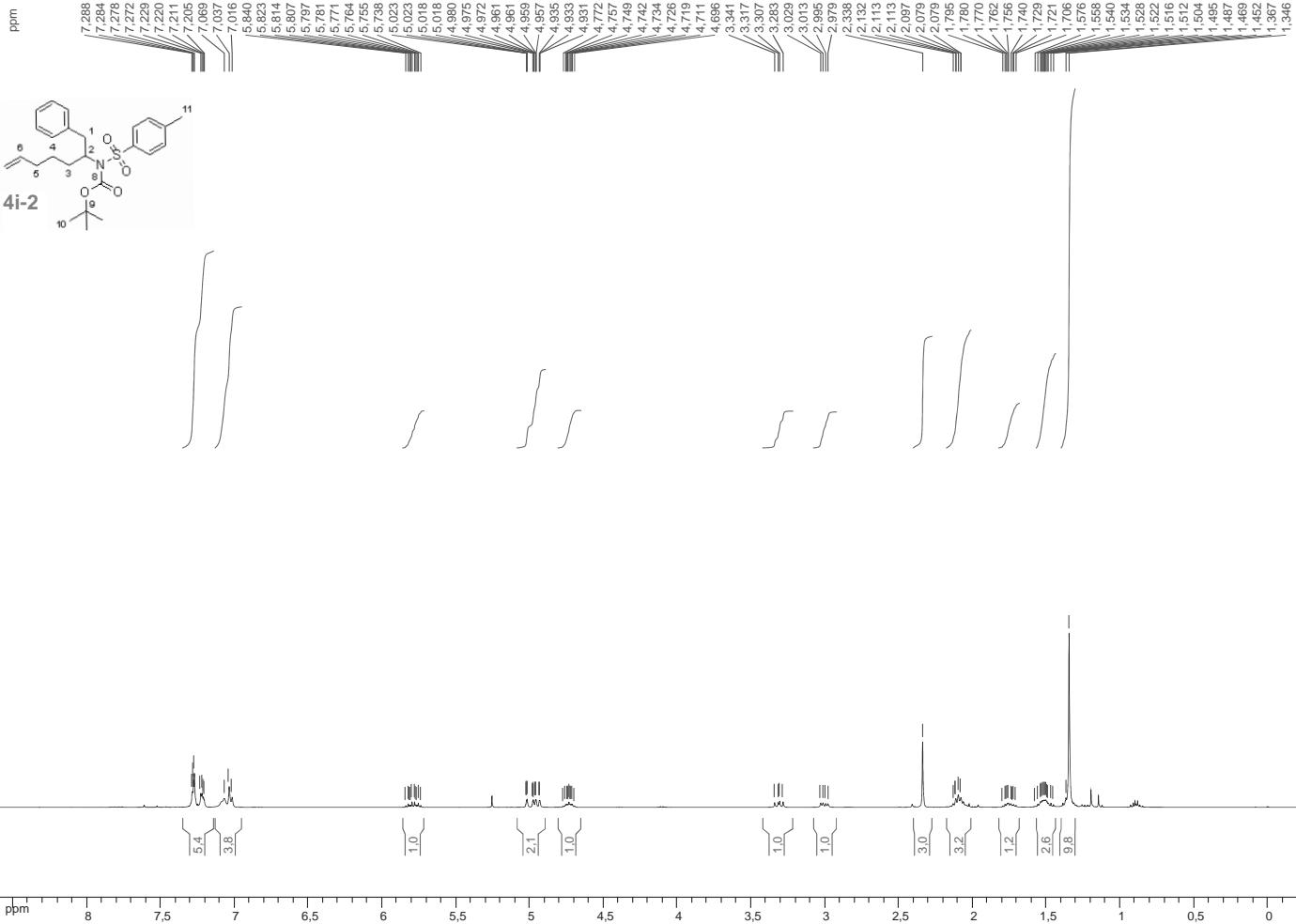
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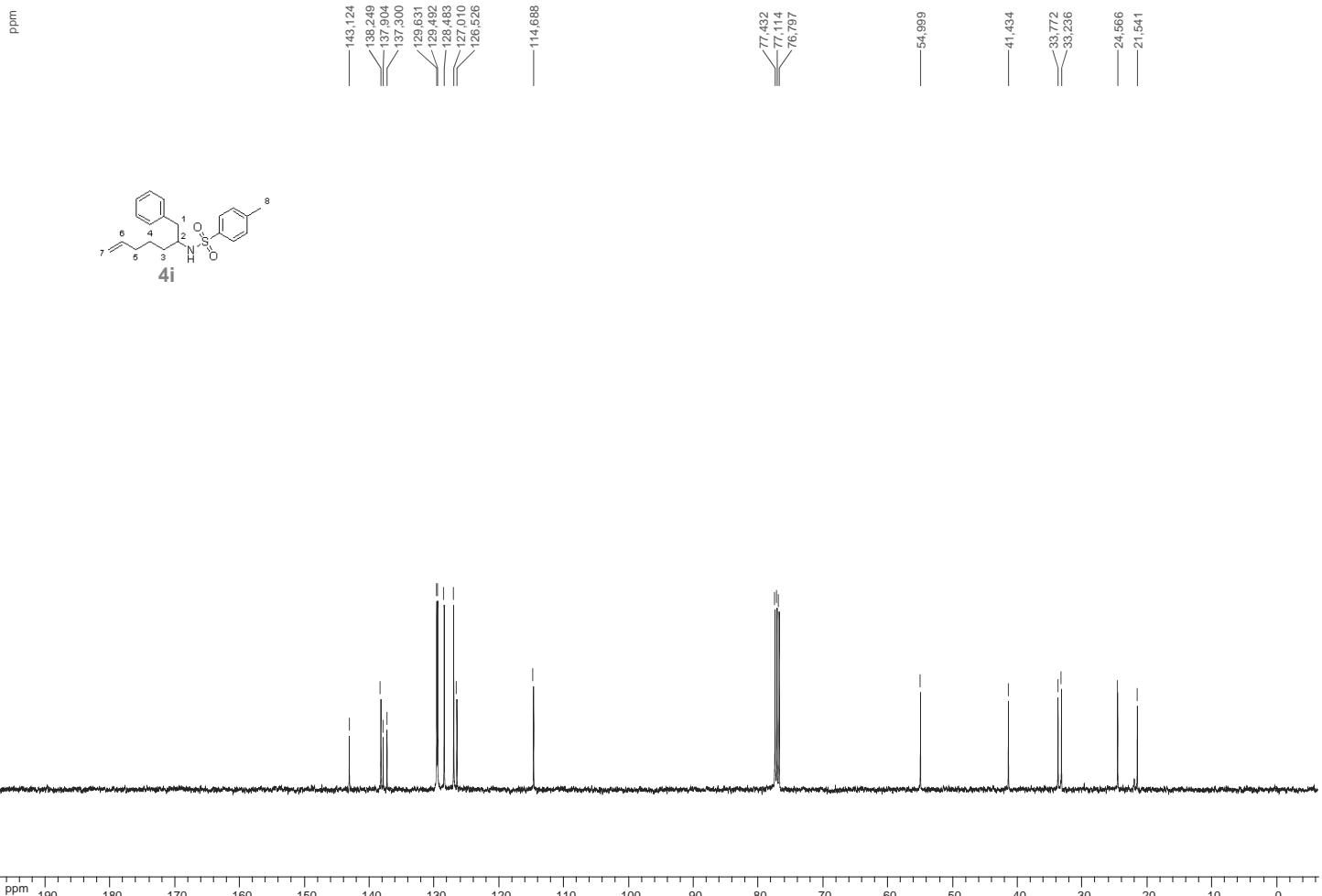
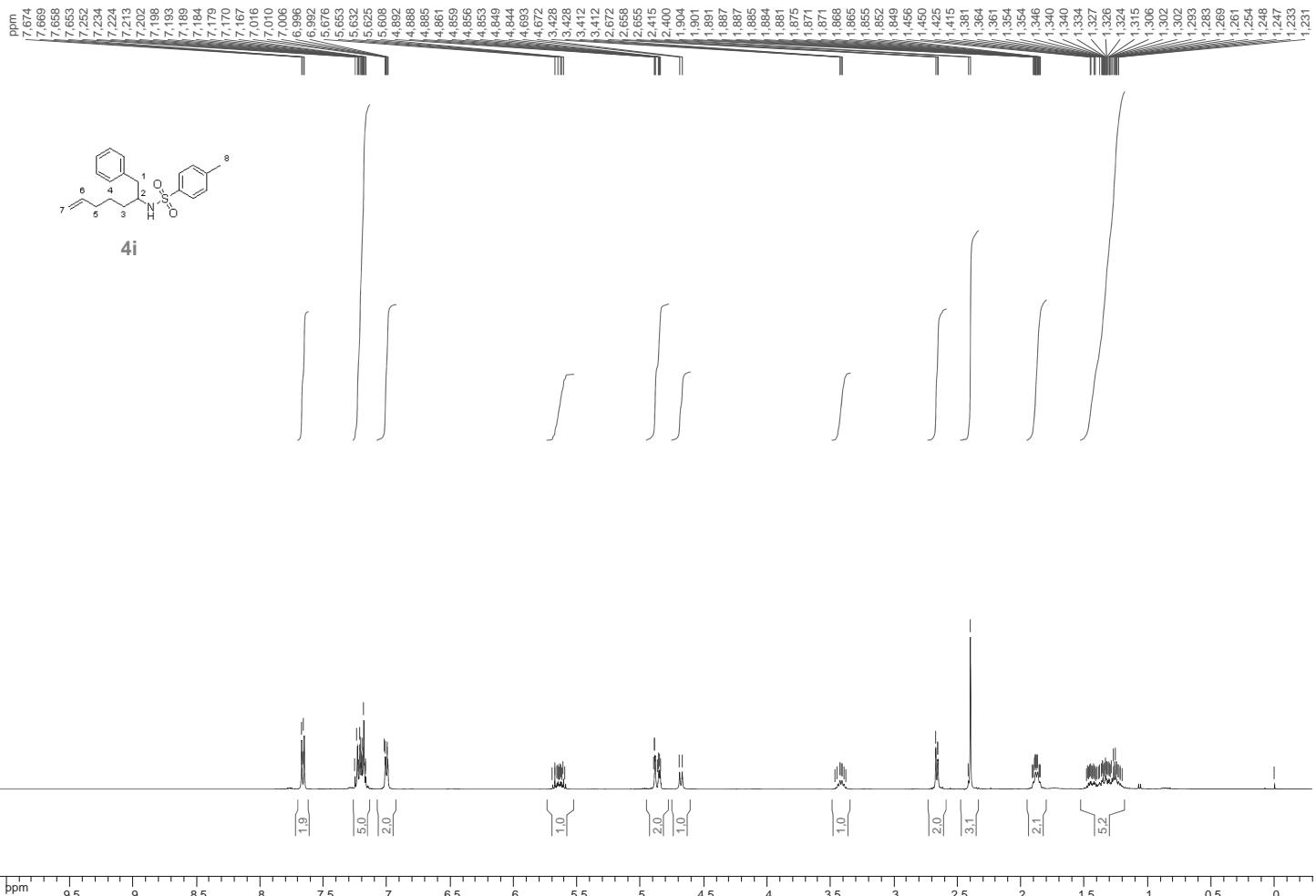


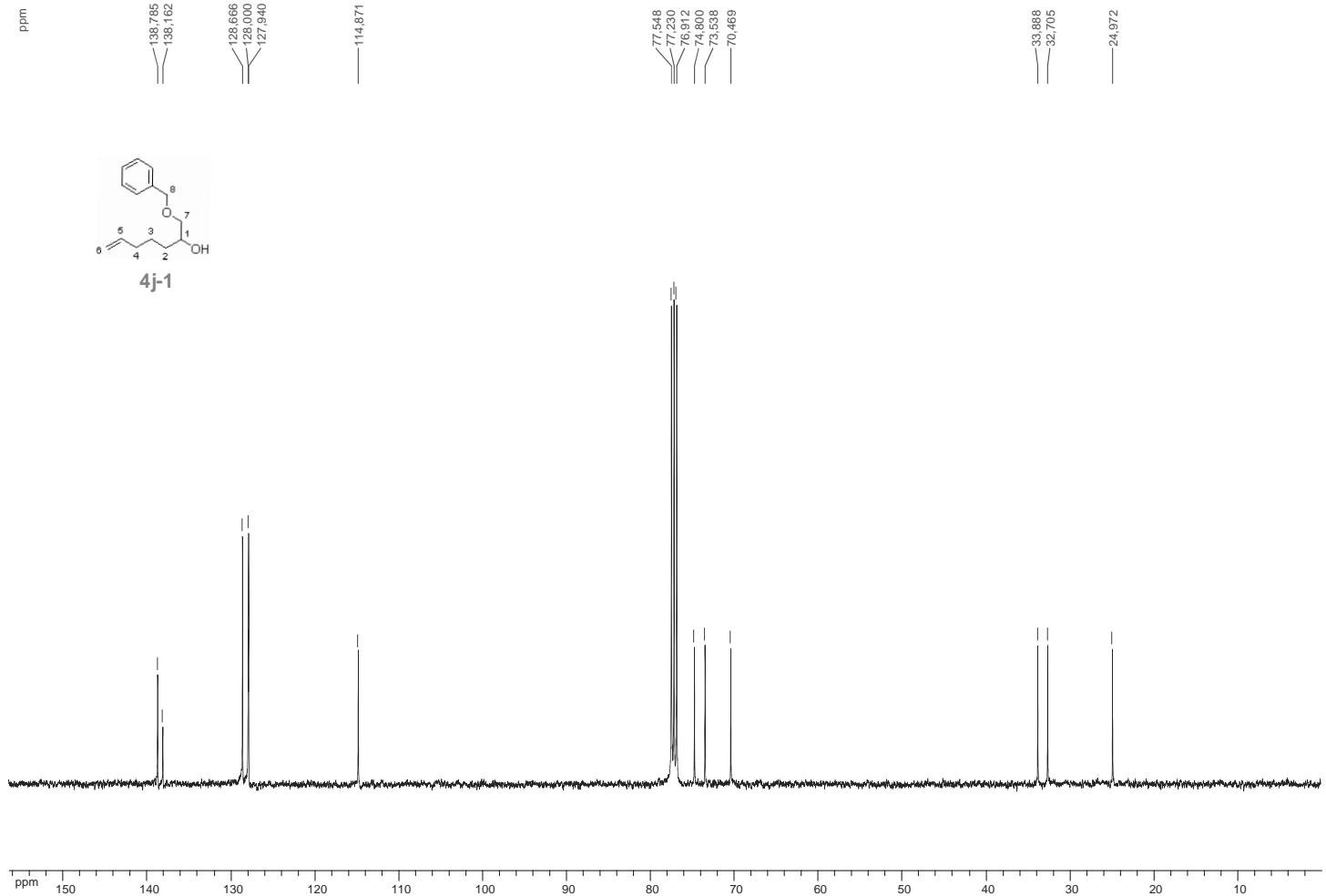
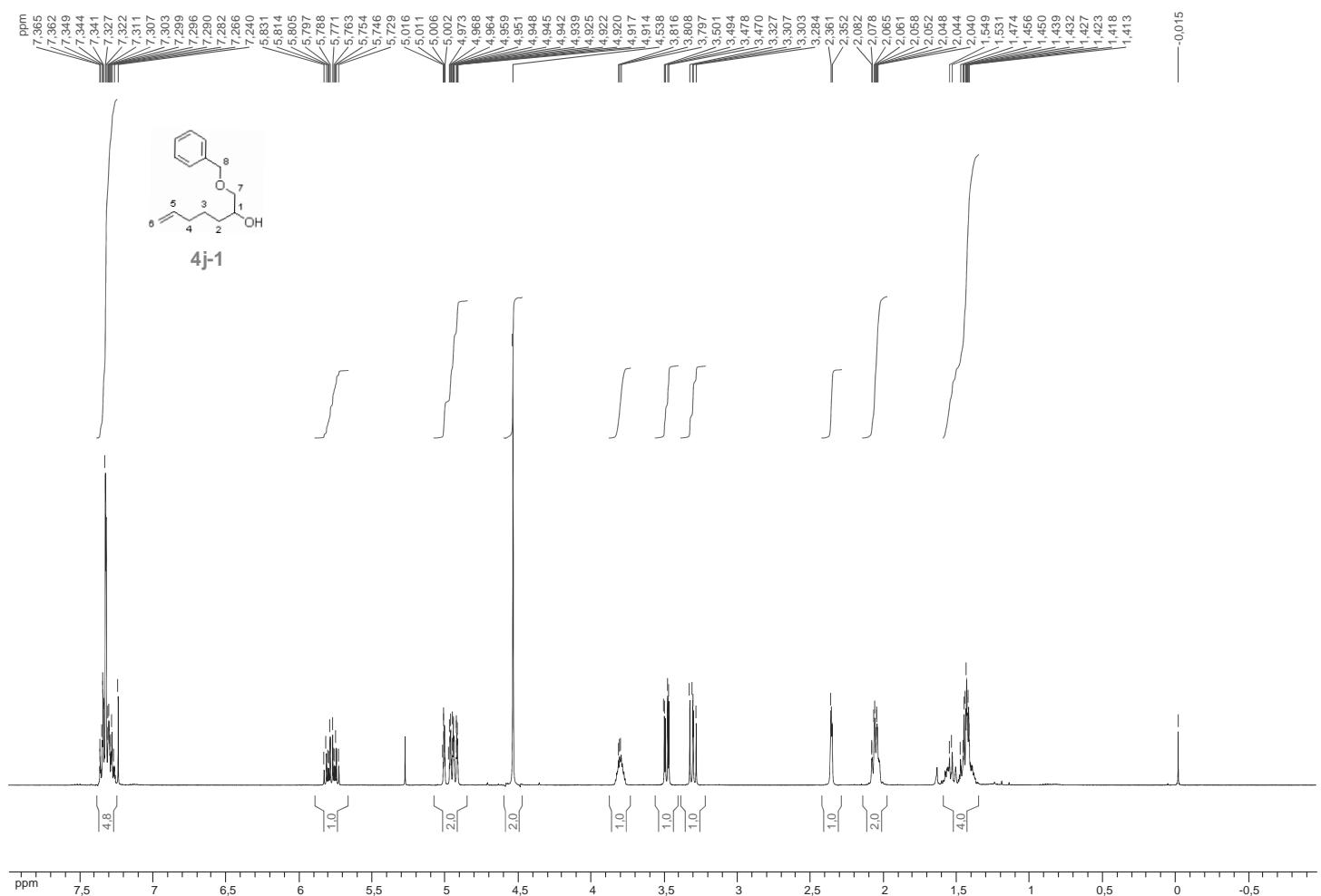
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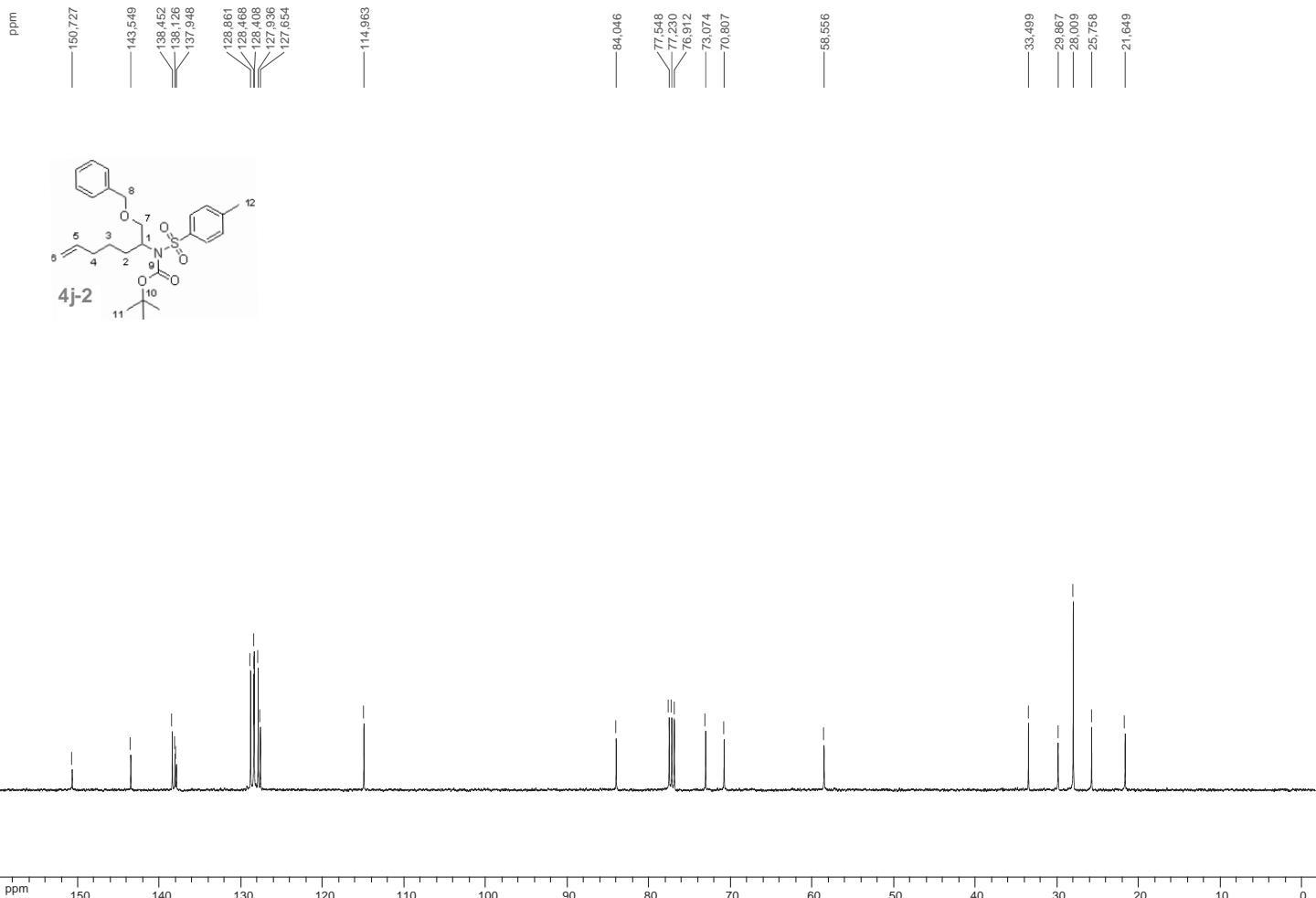
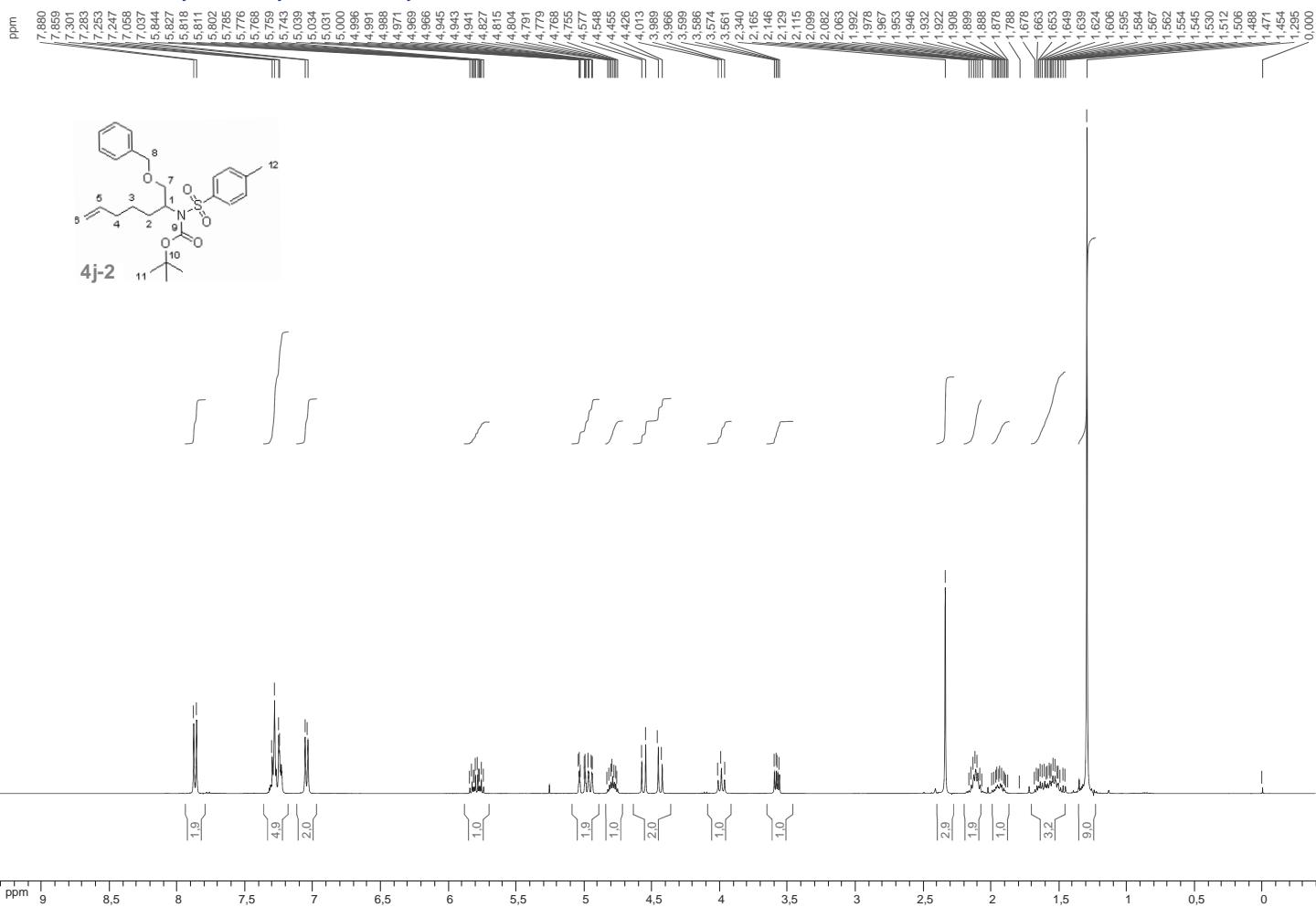




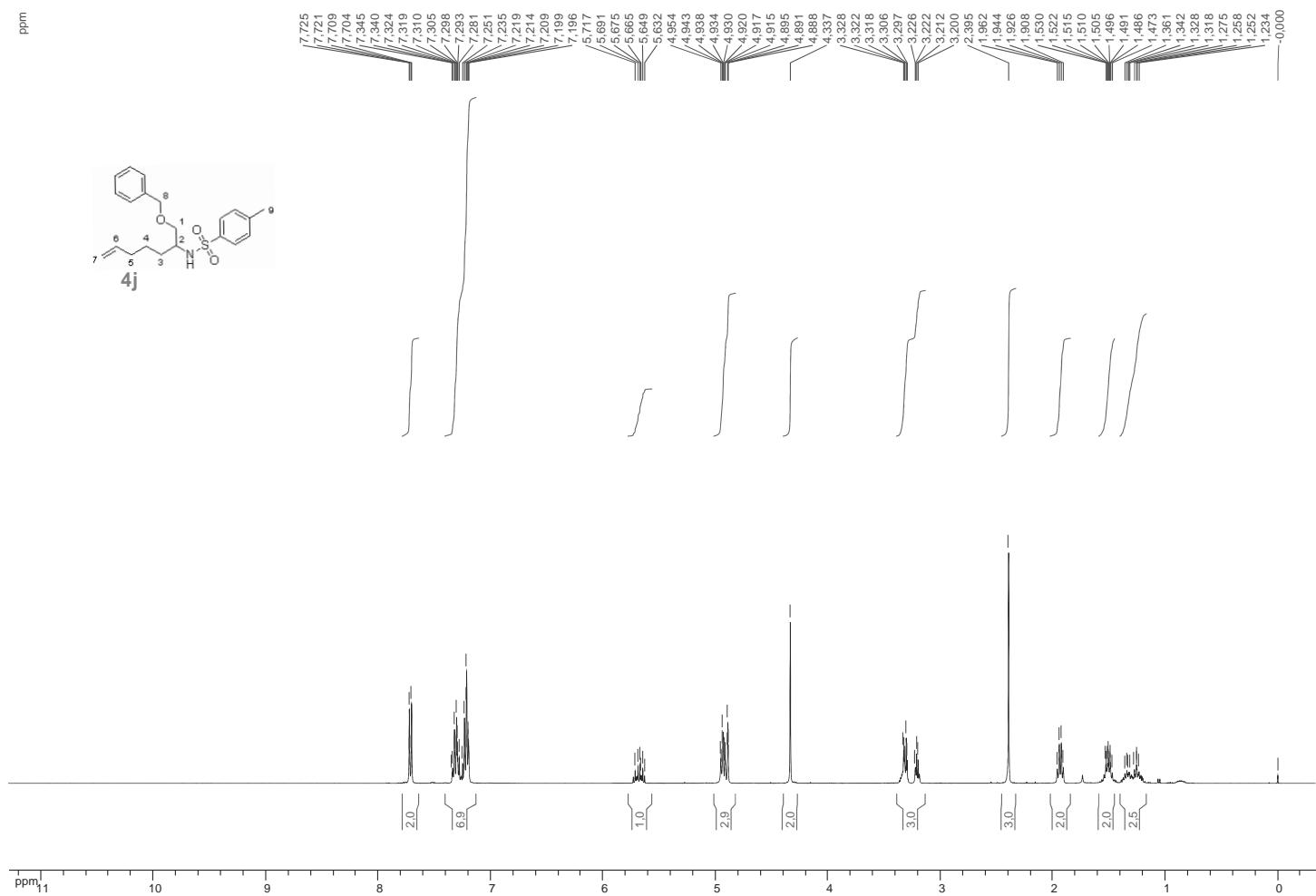




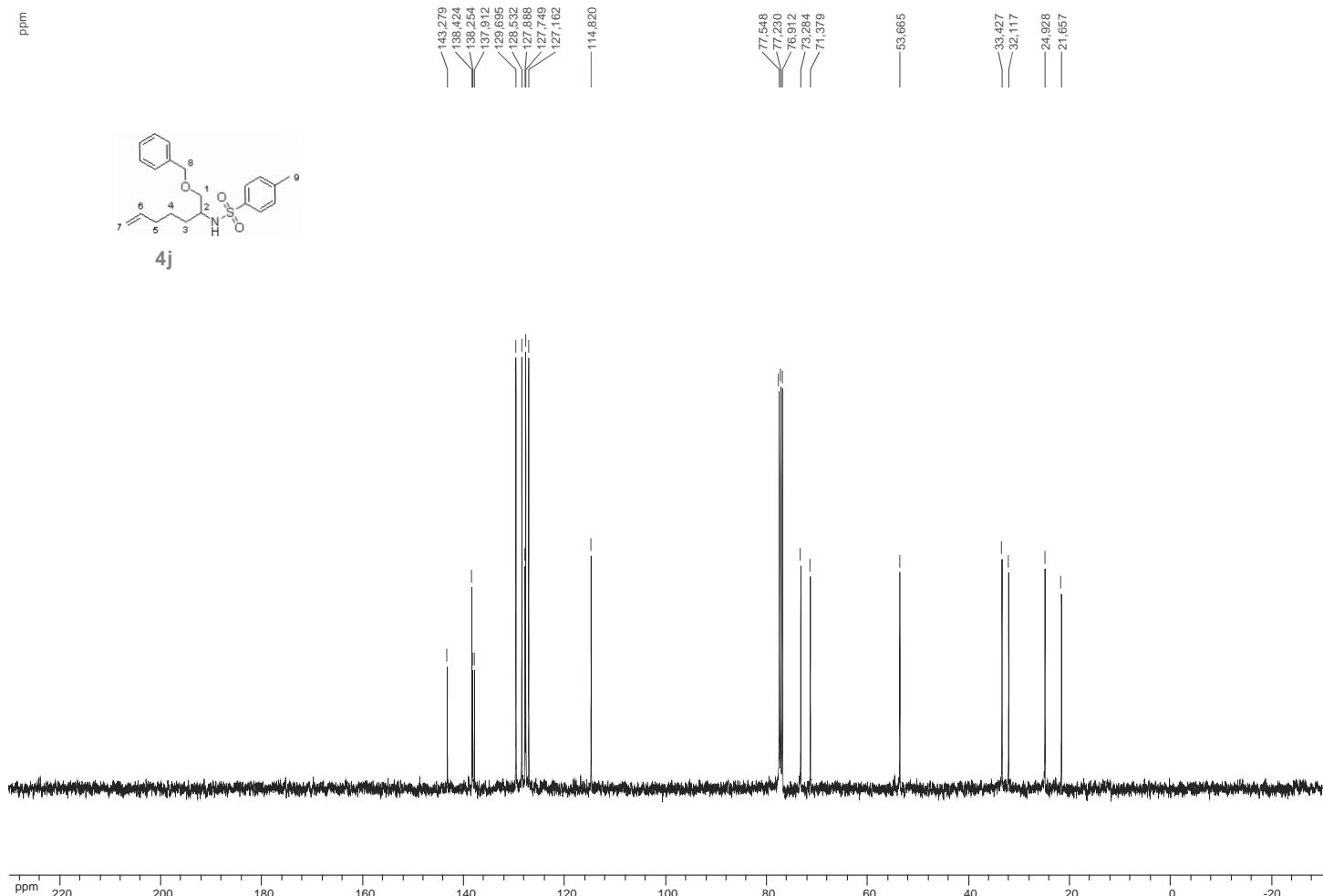




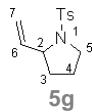
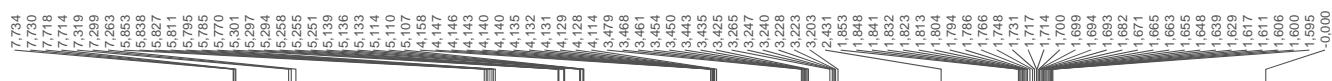
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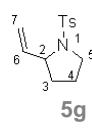
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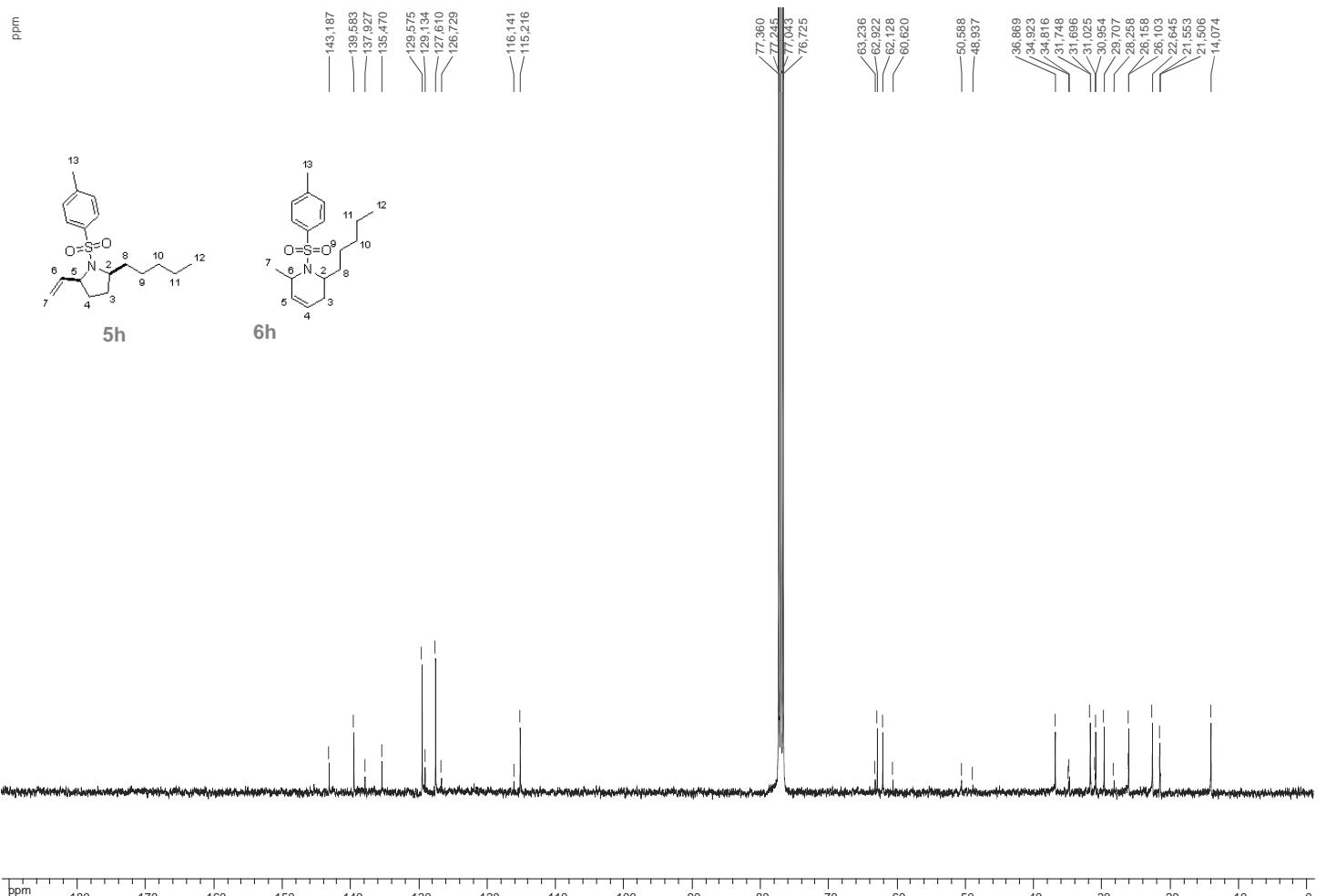
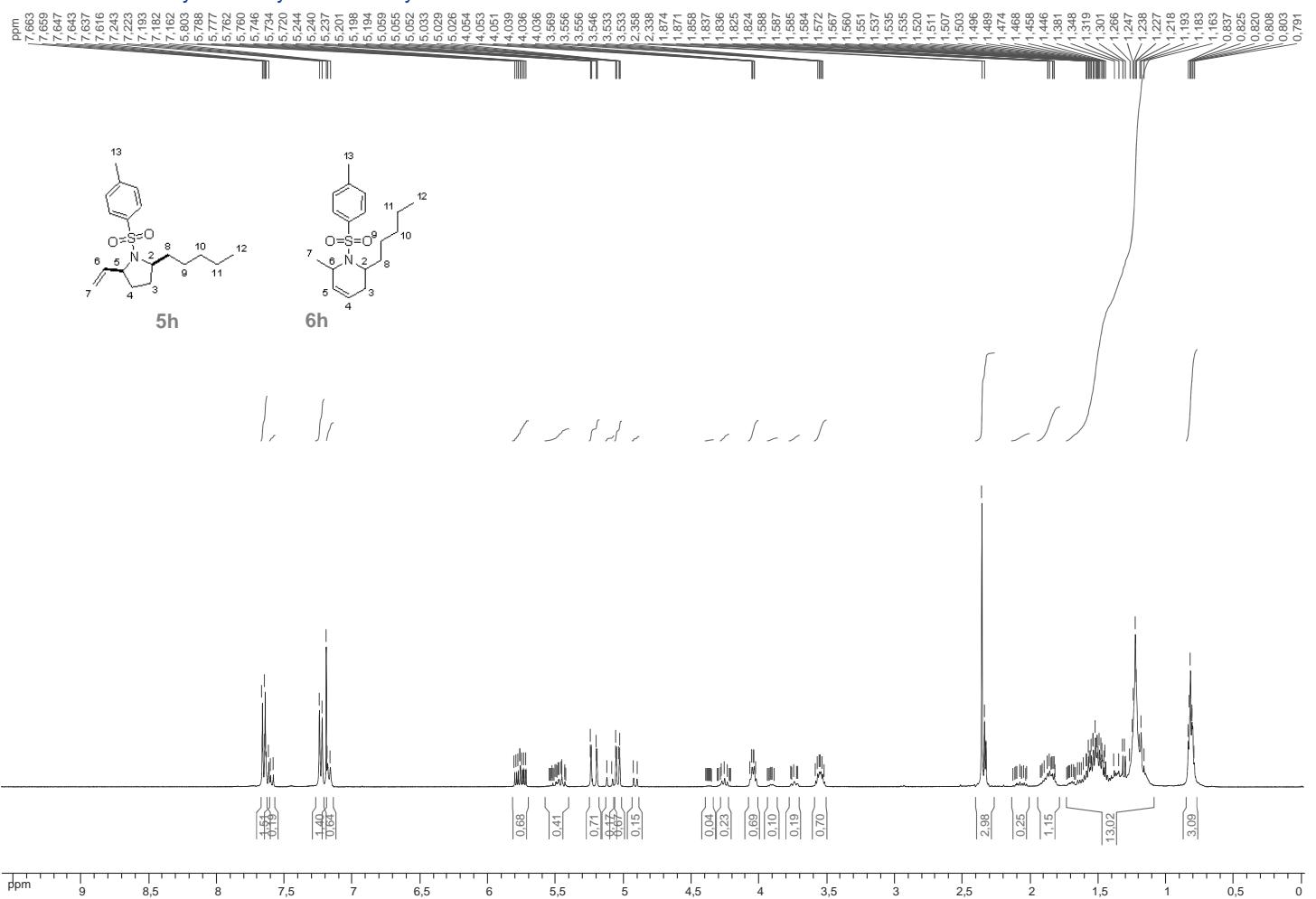


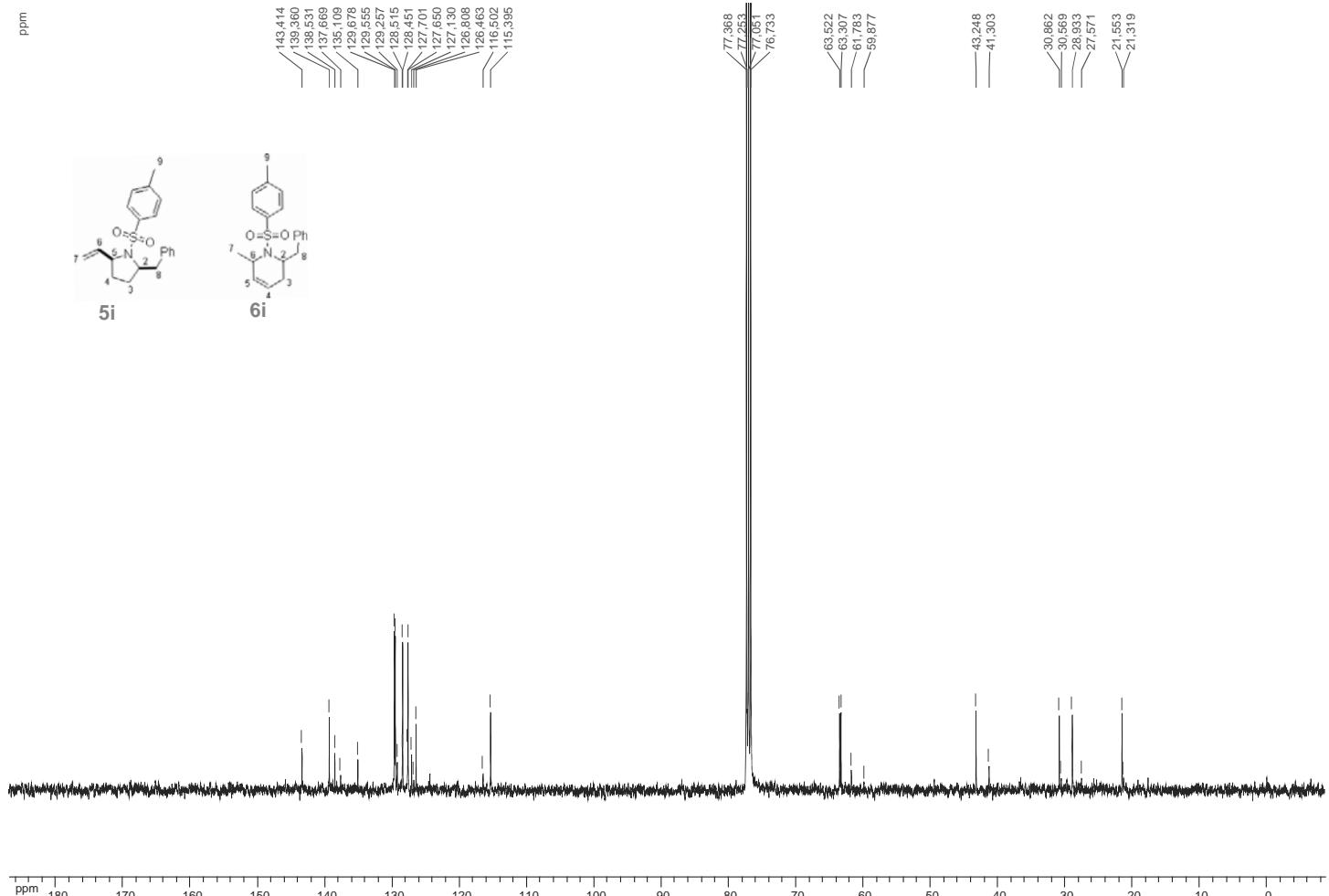
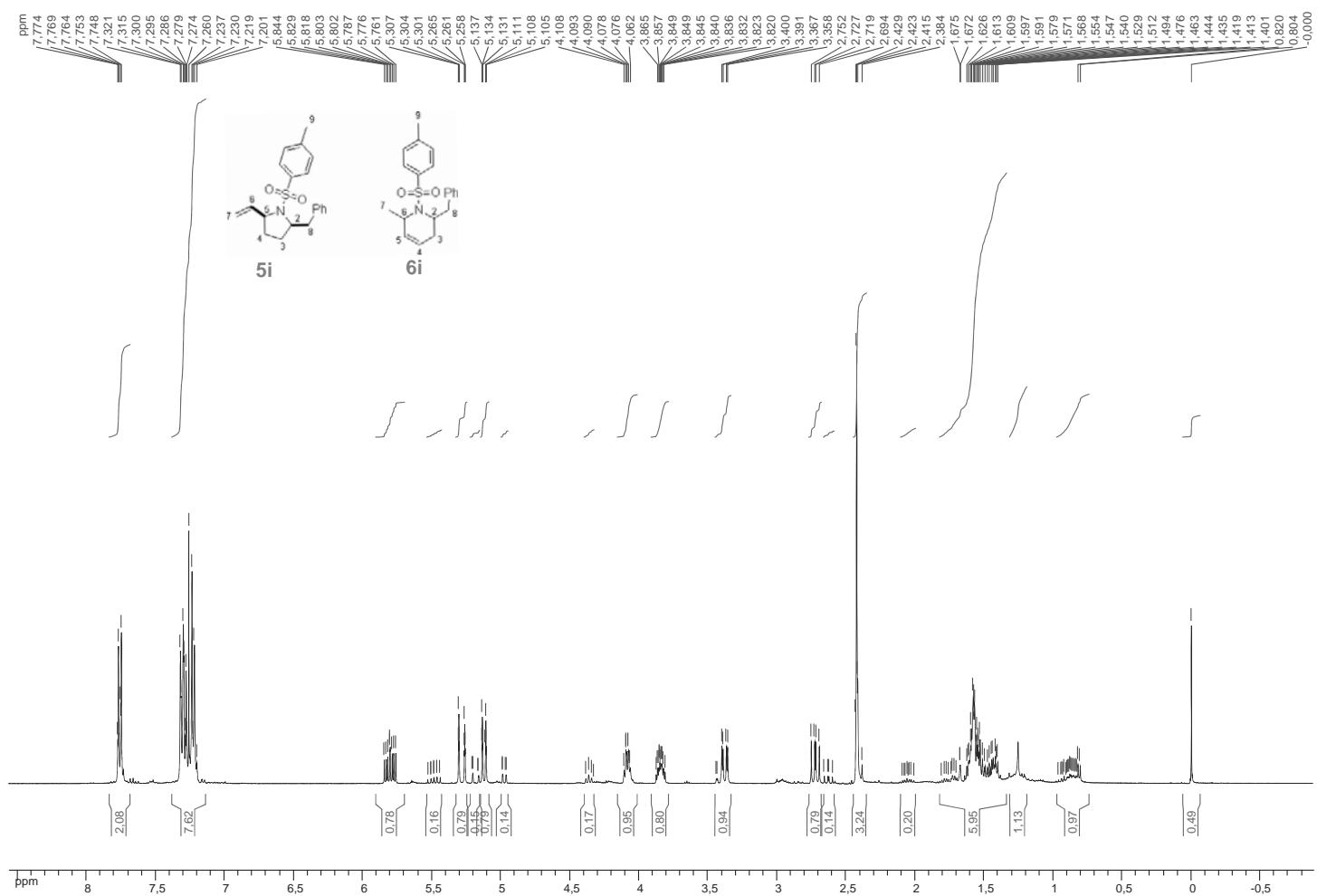
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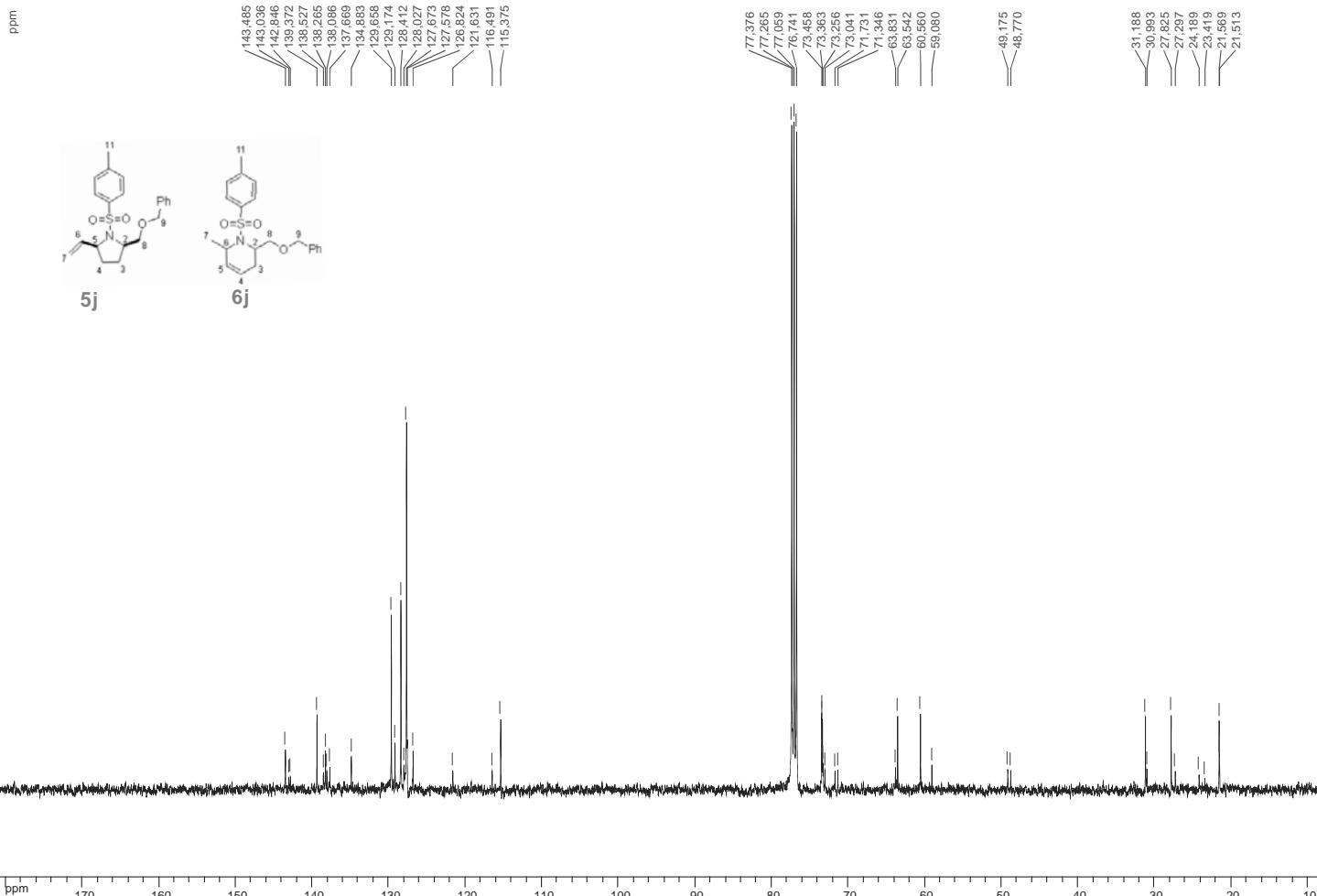
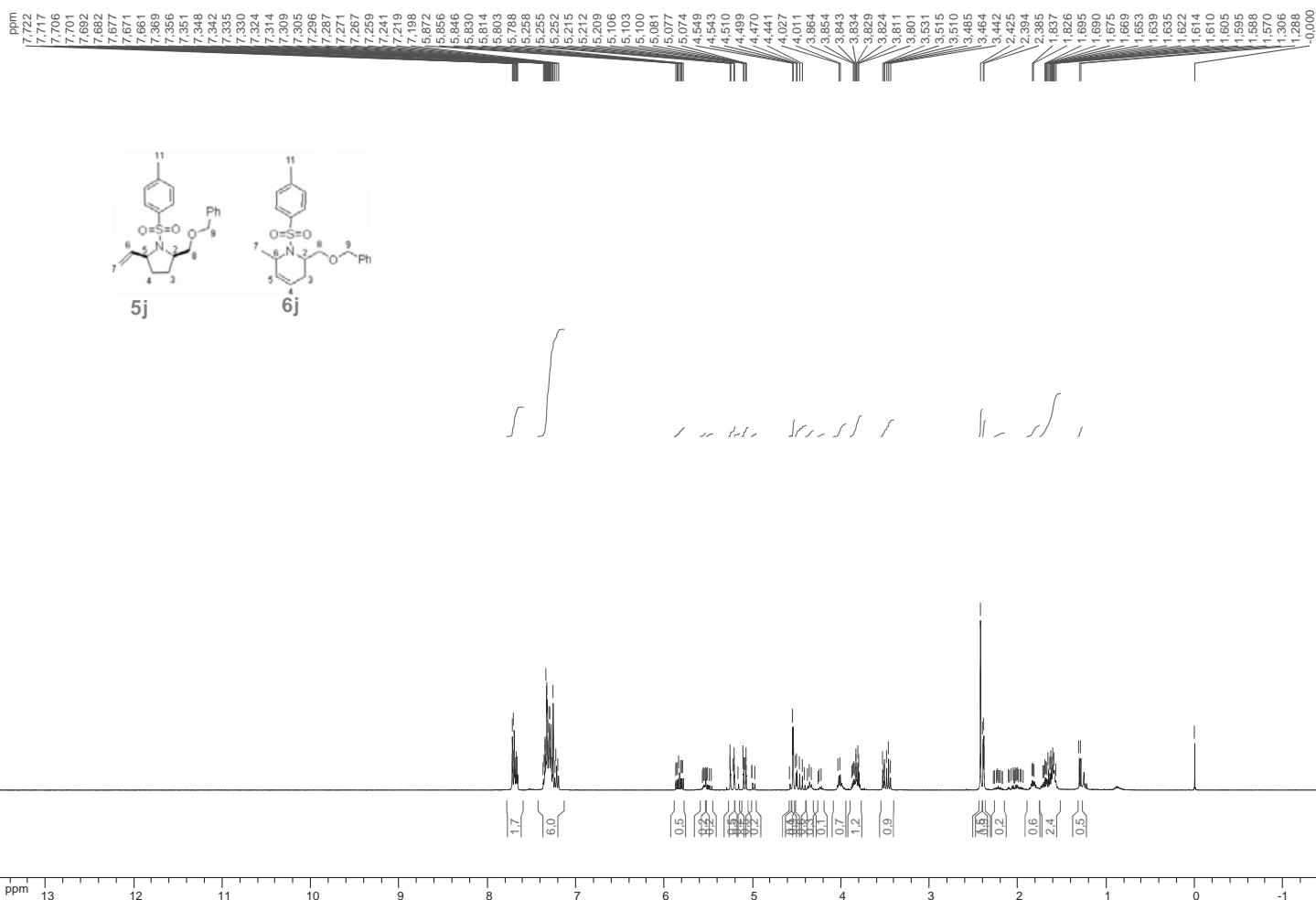


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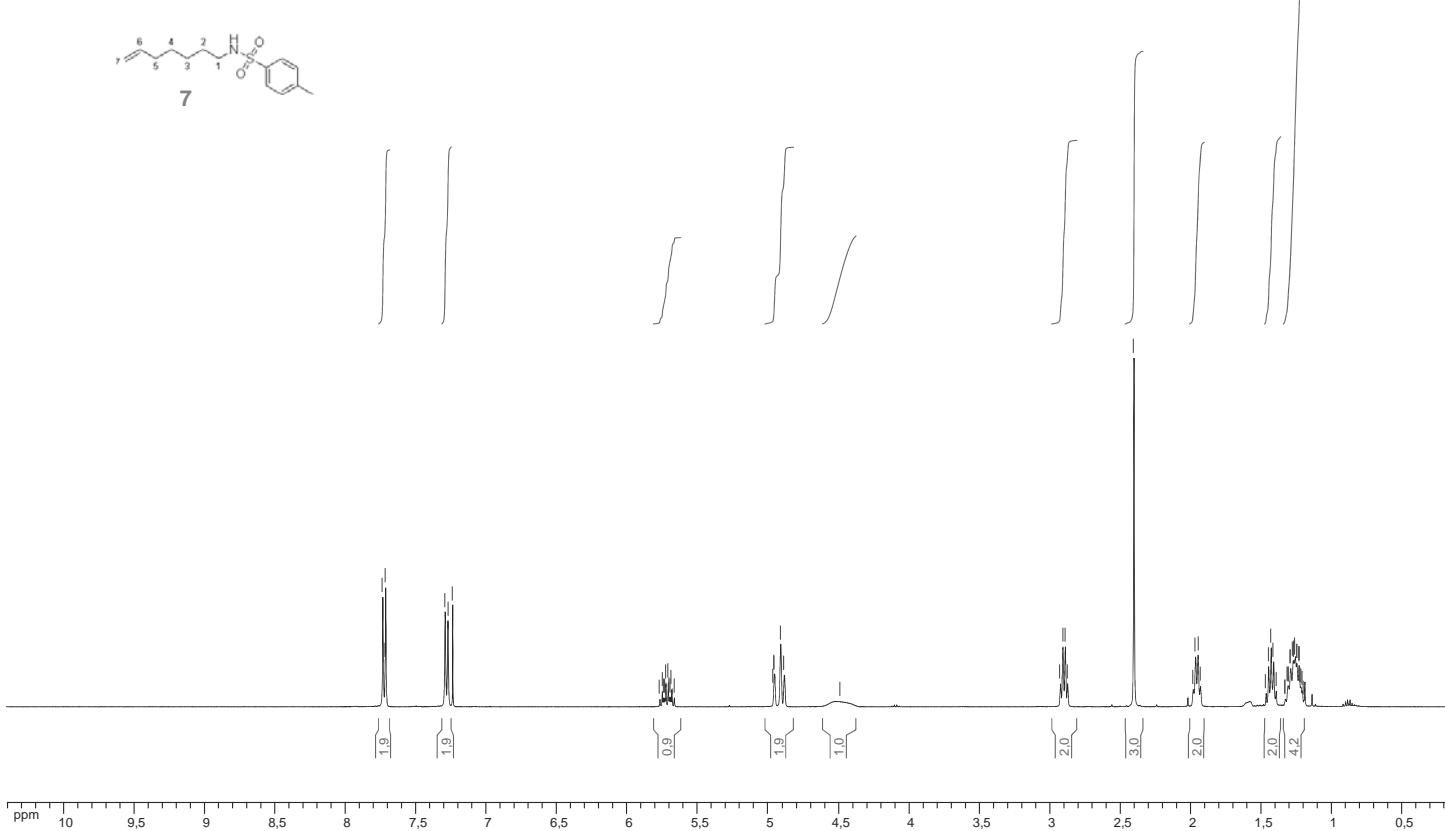
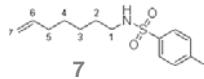




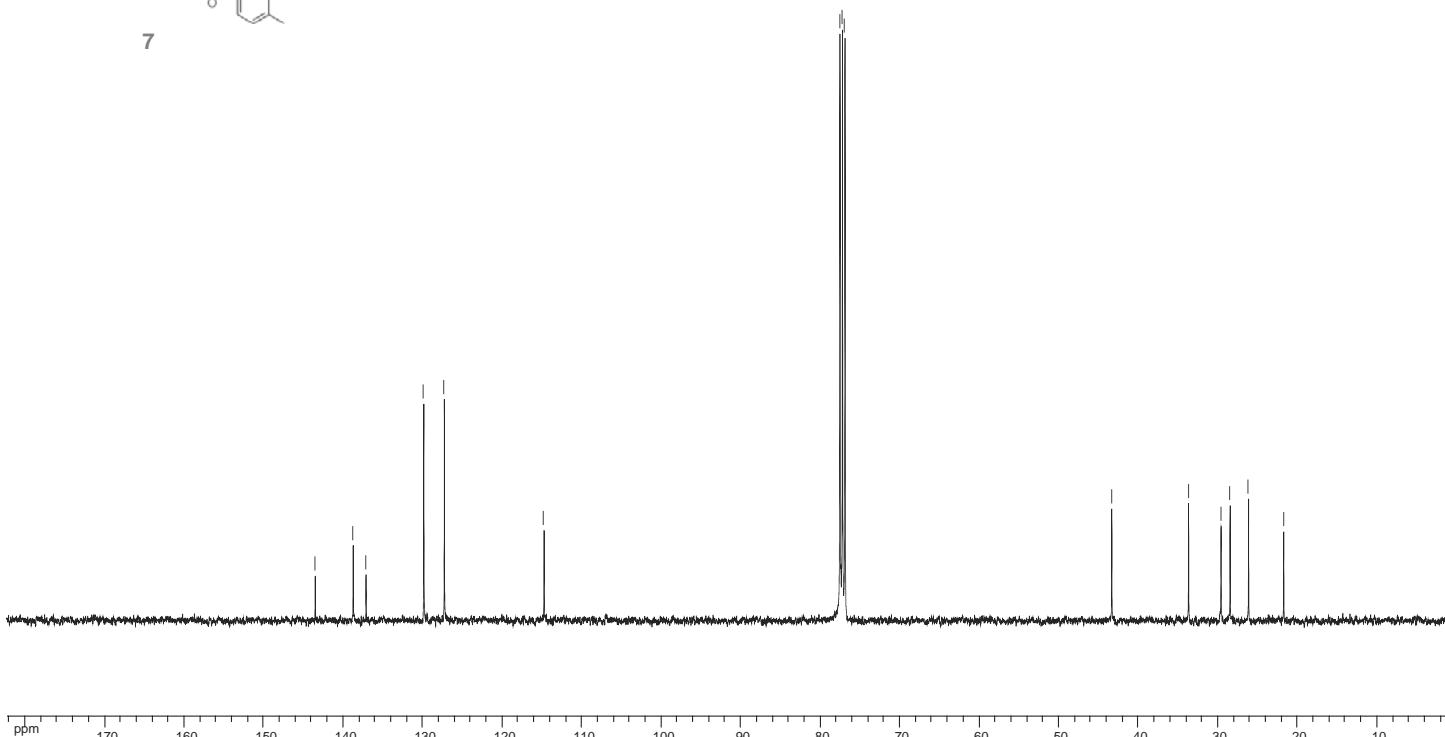
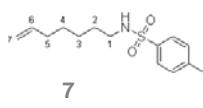




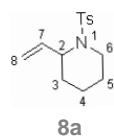
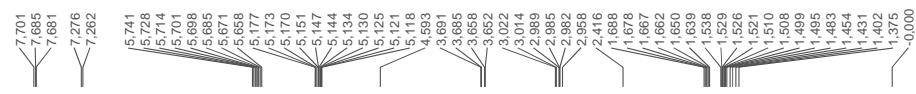
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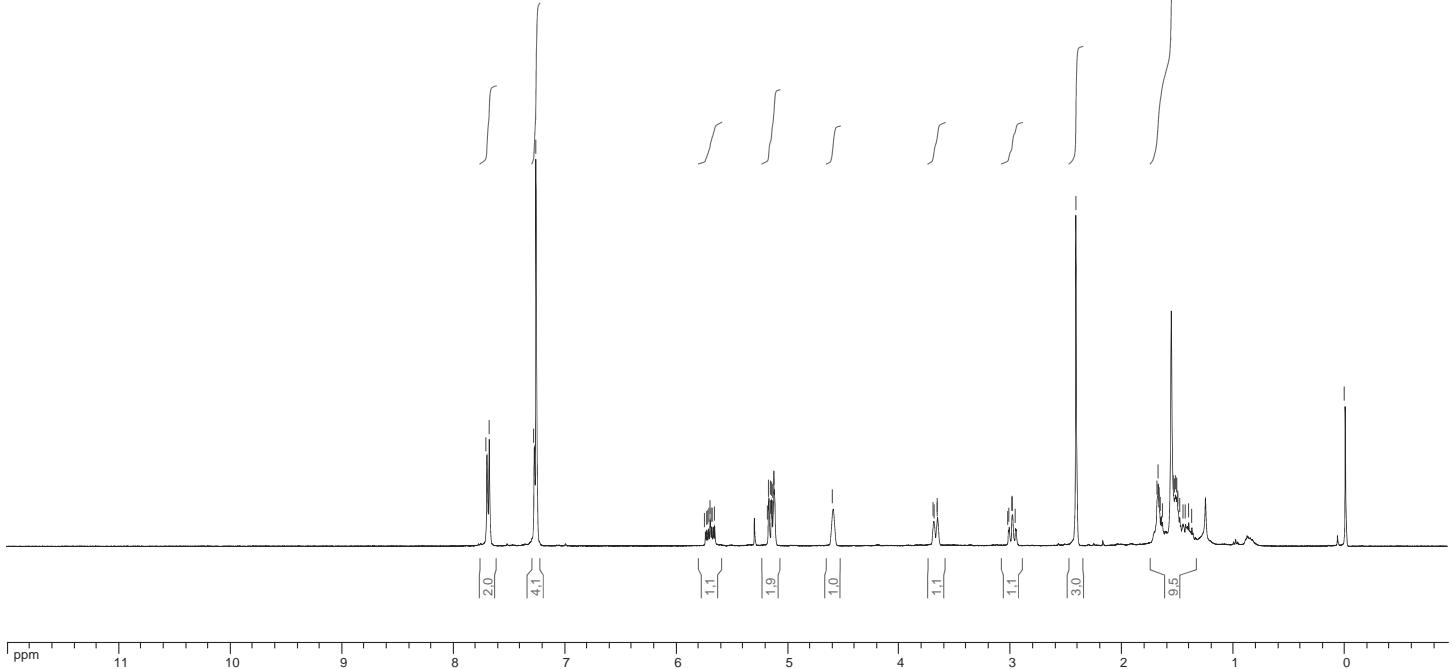
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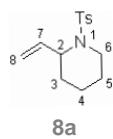


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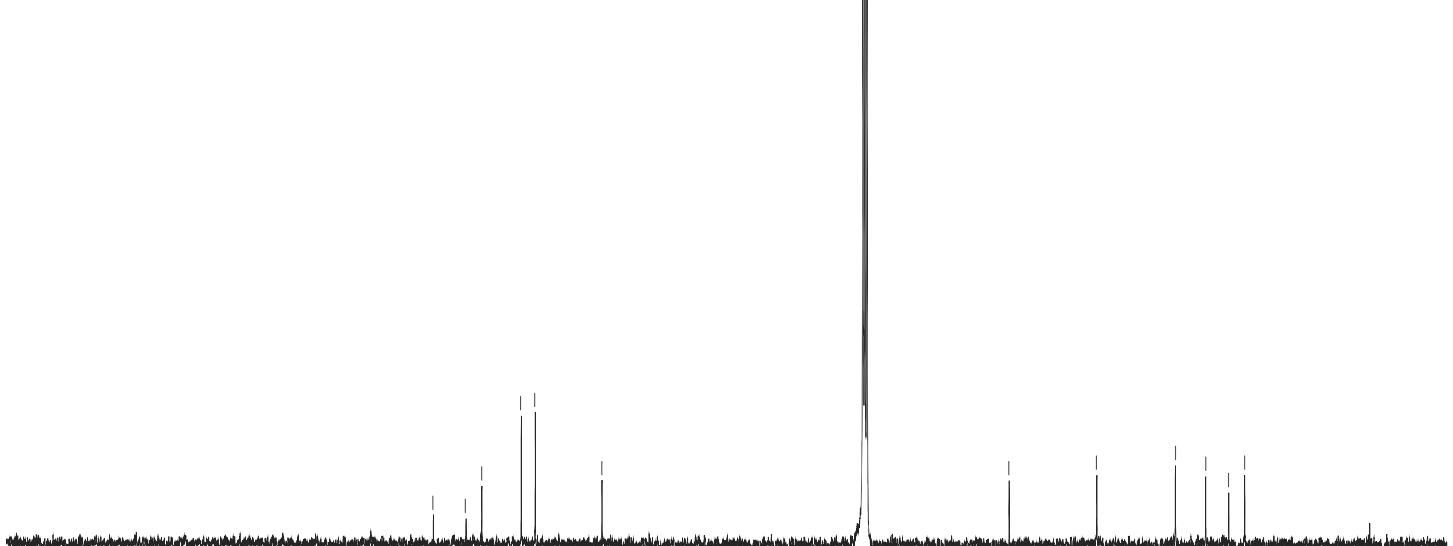


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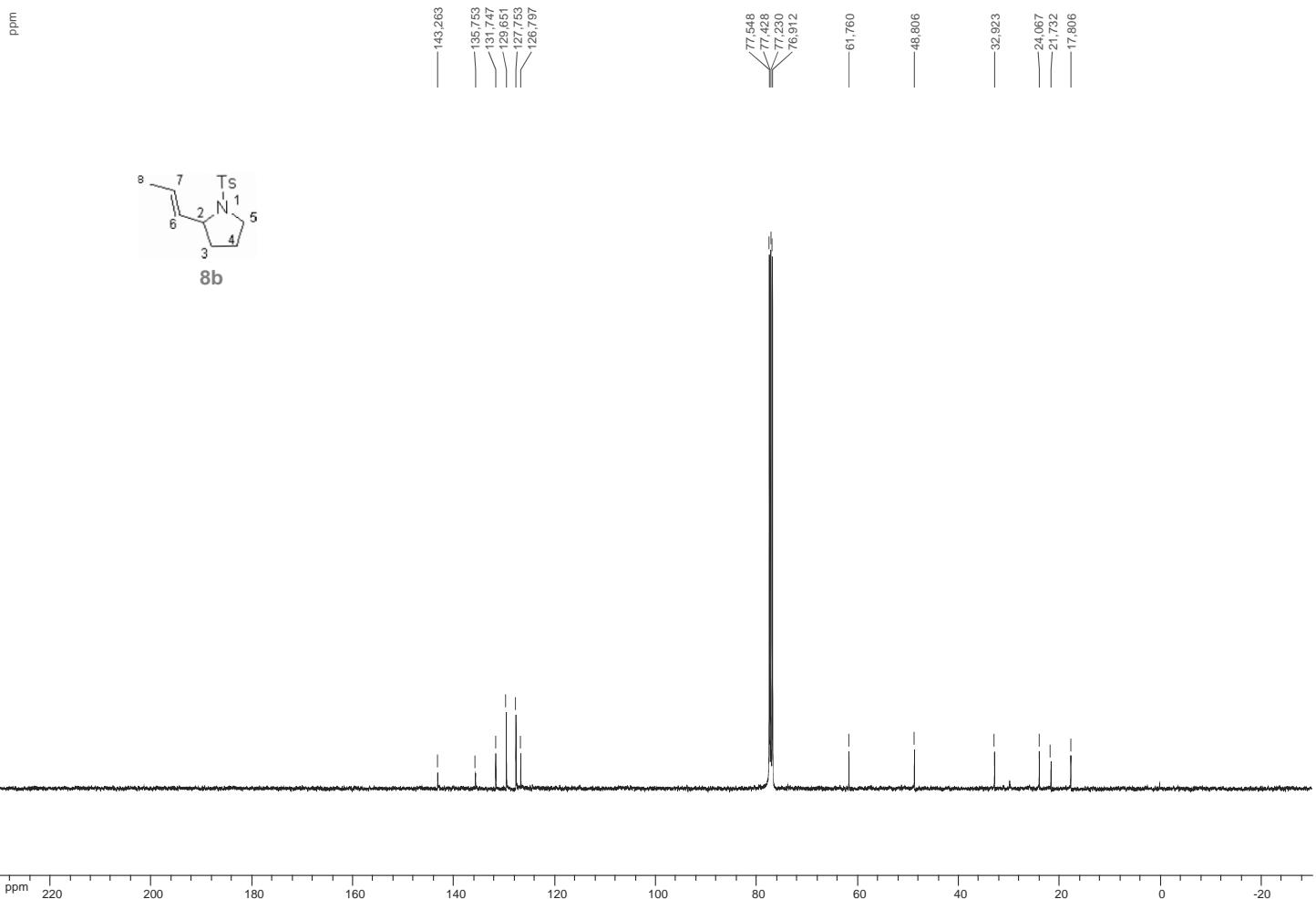
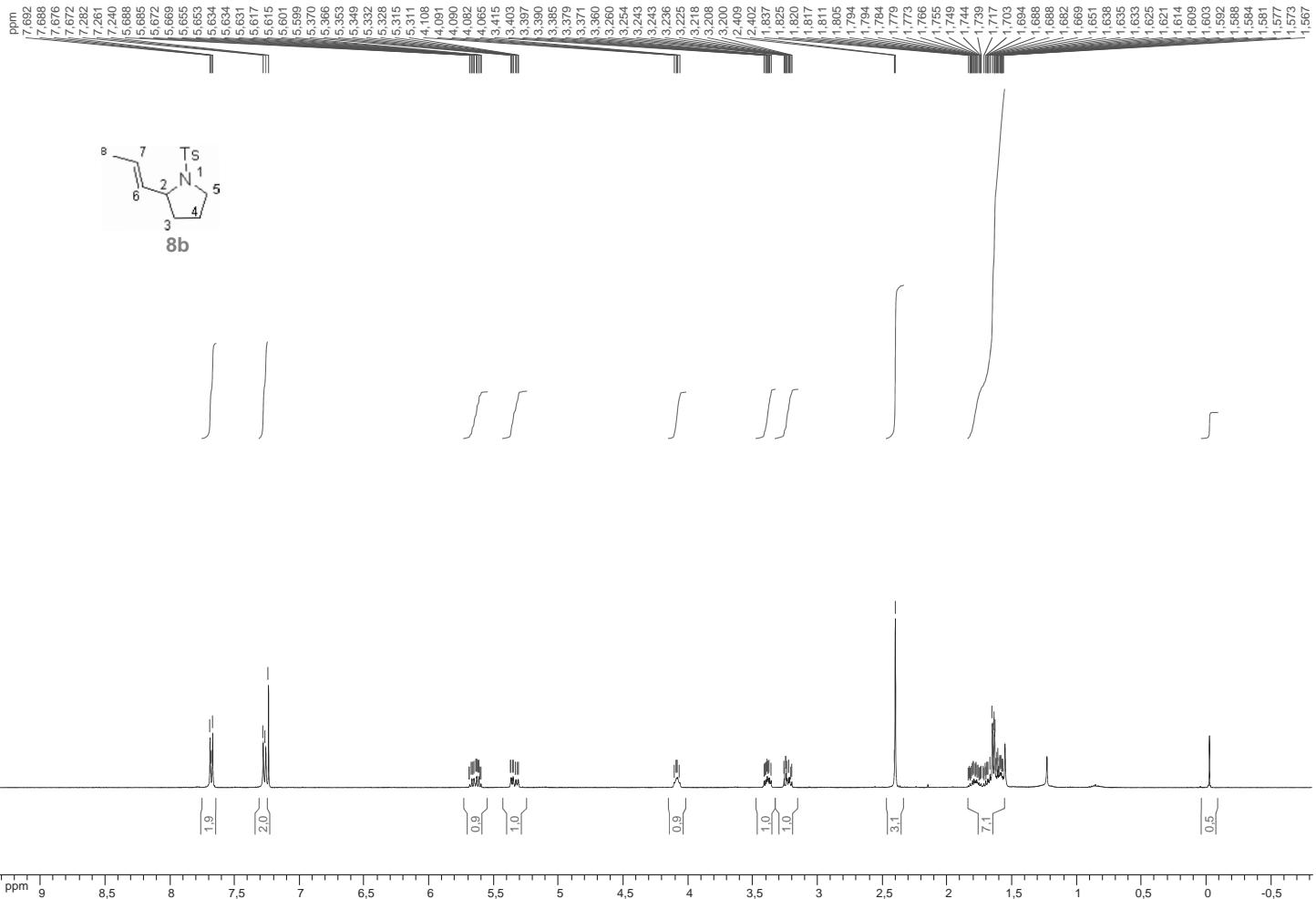
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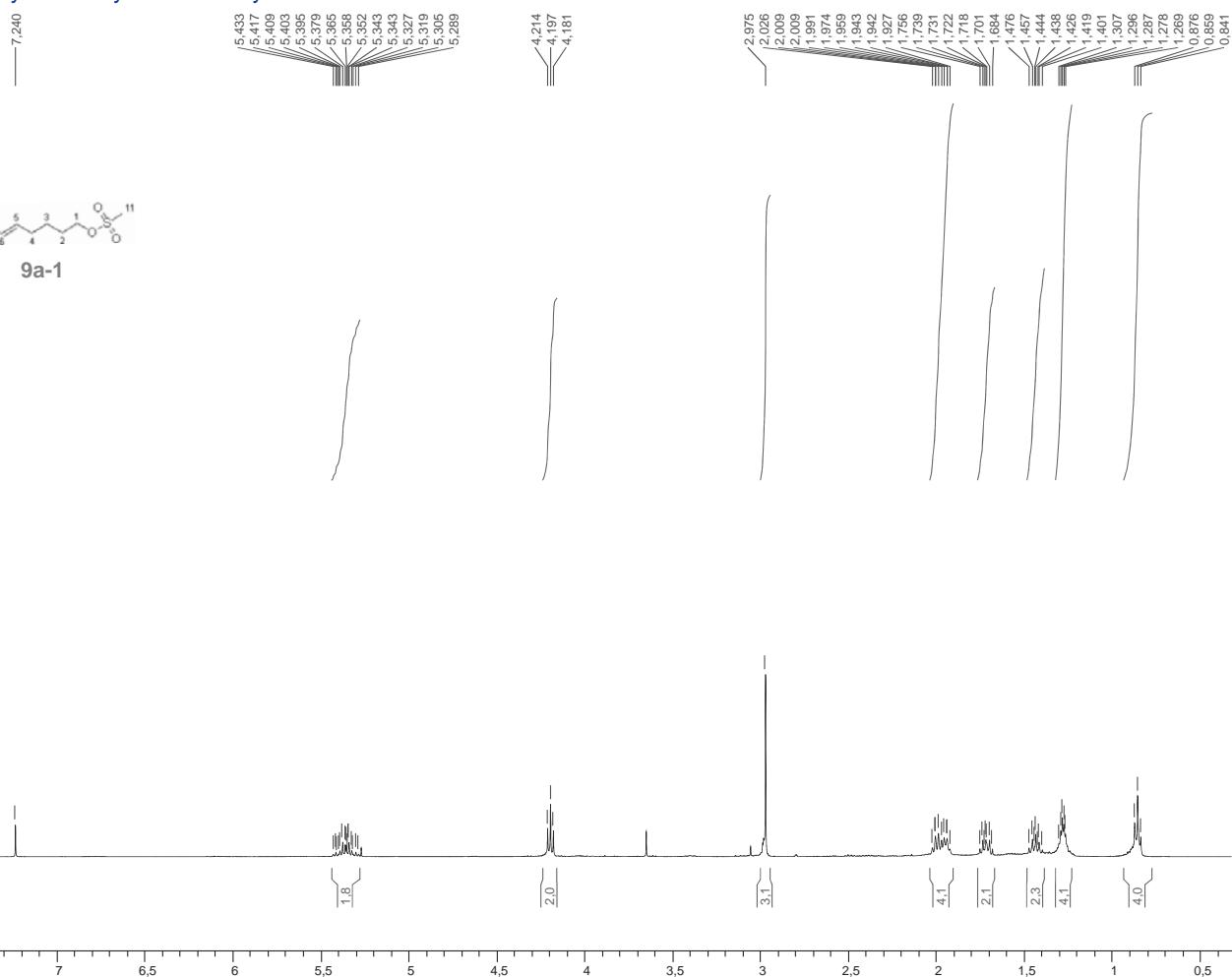
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ppm



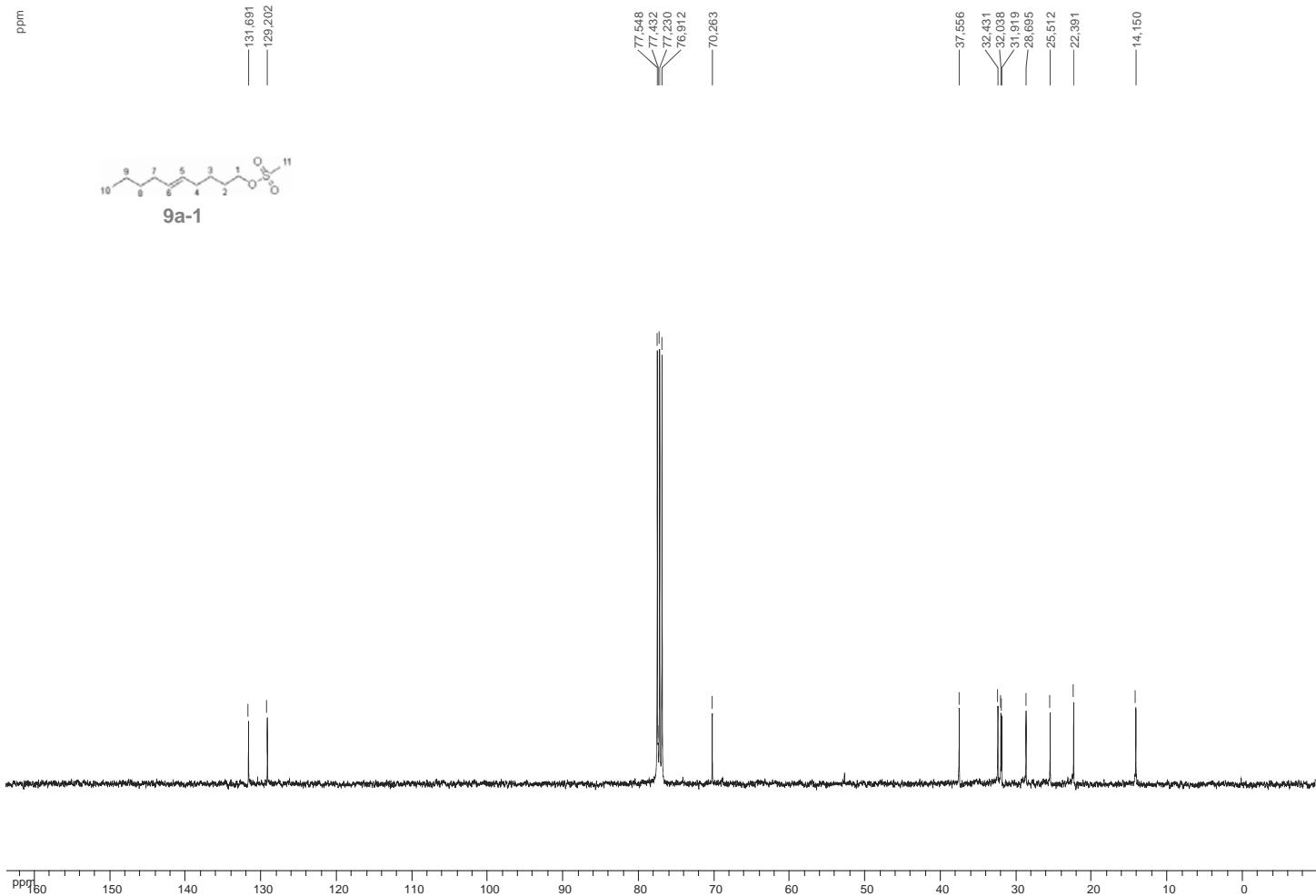
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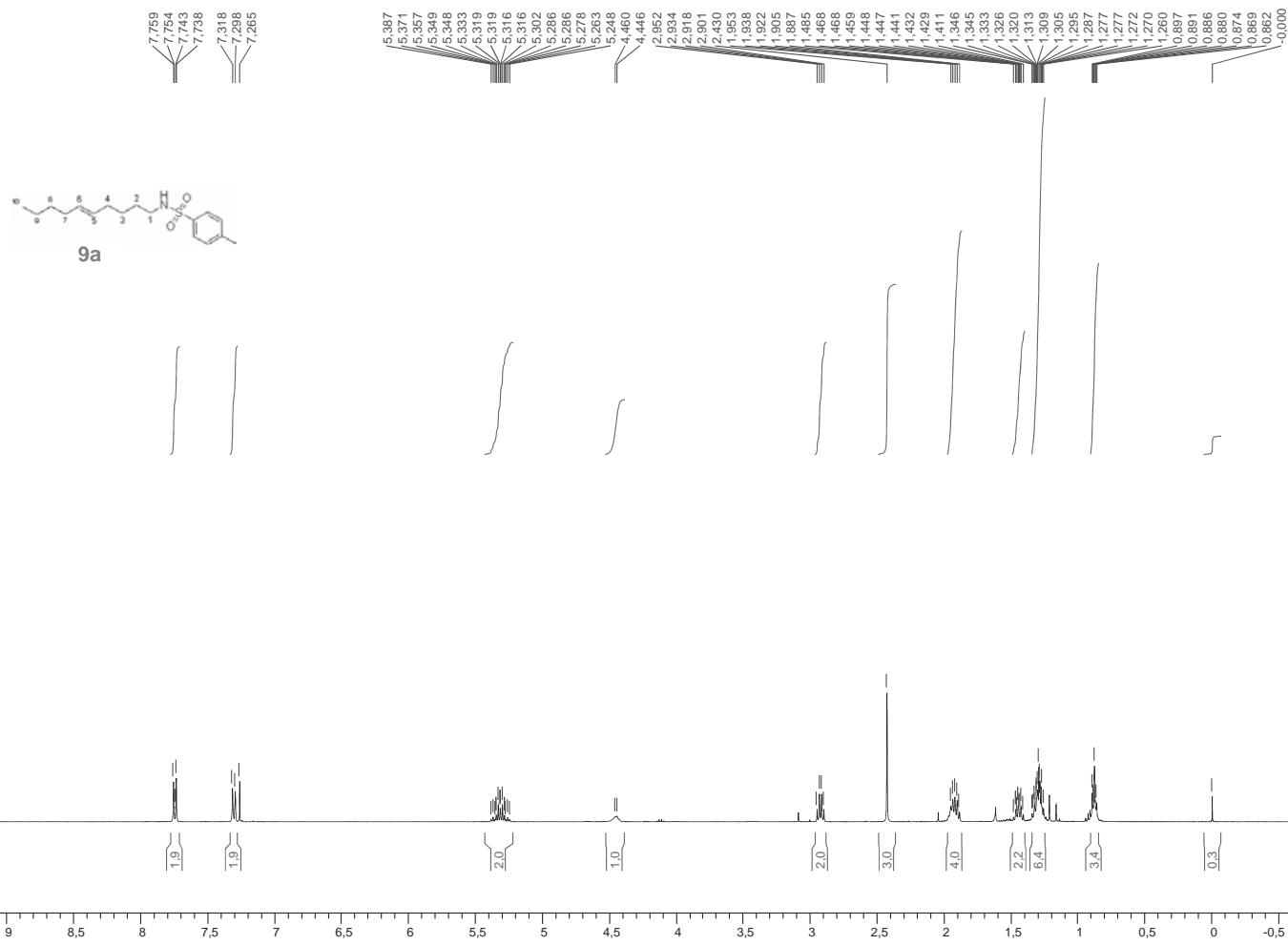
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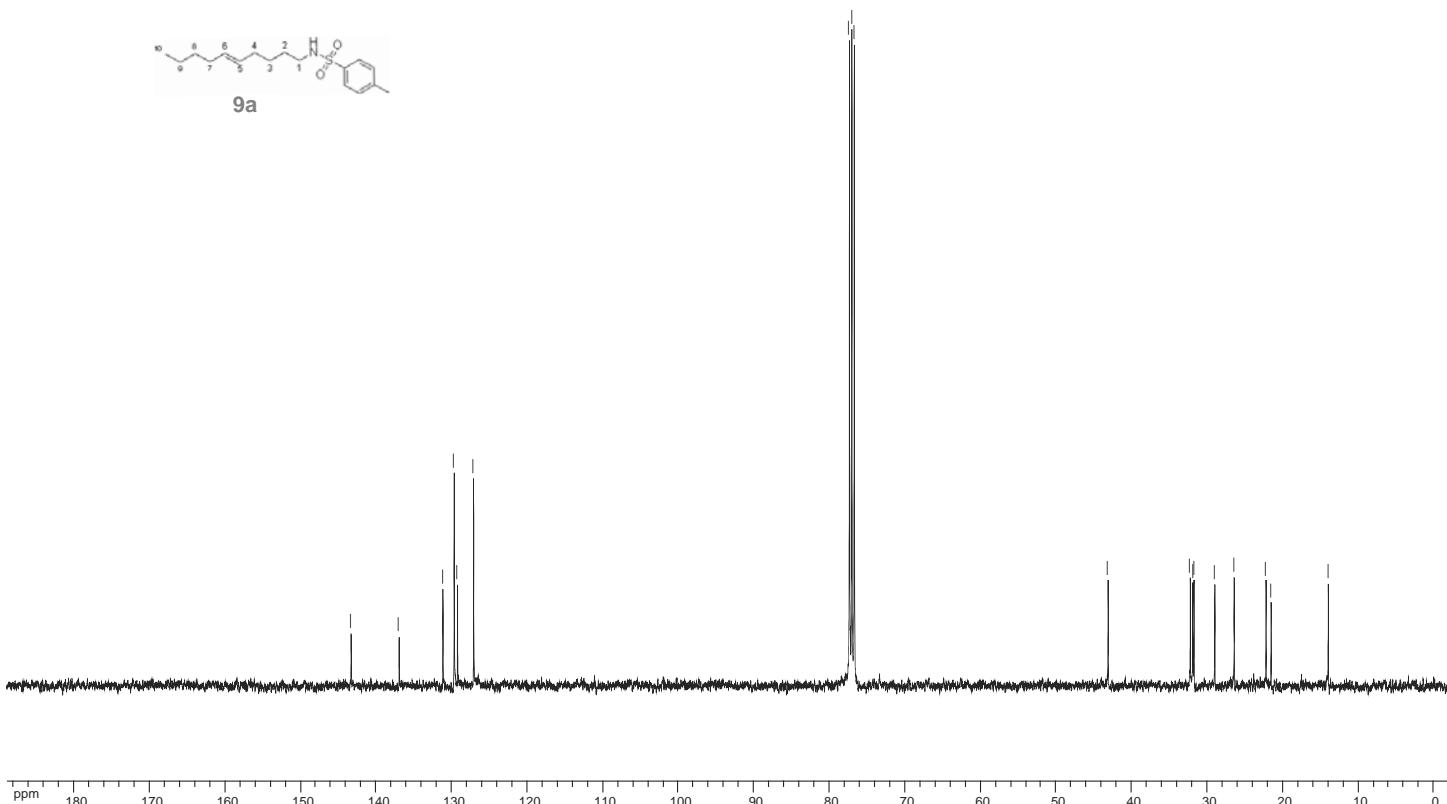
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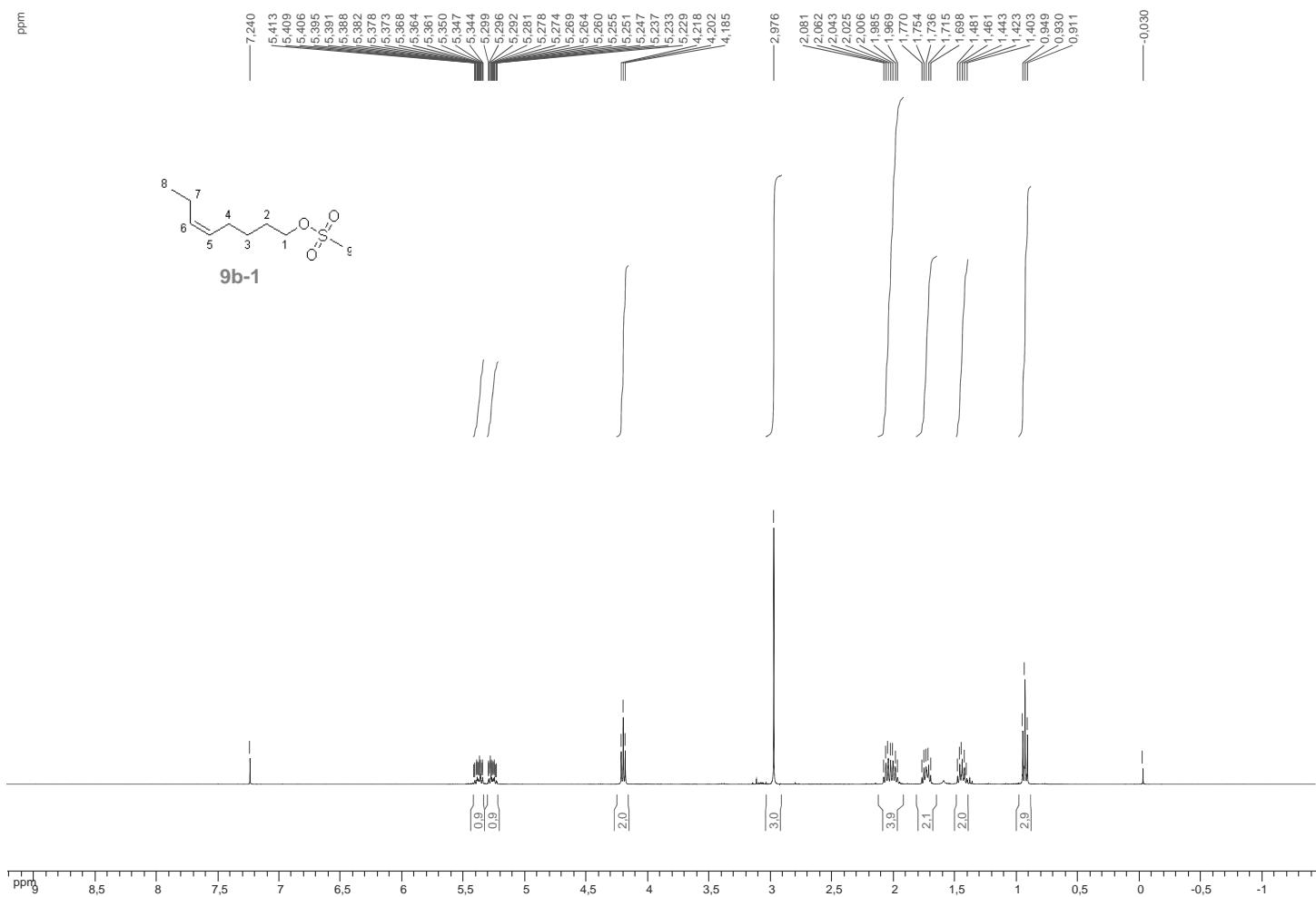
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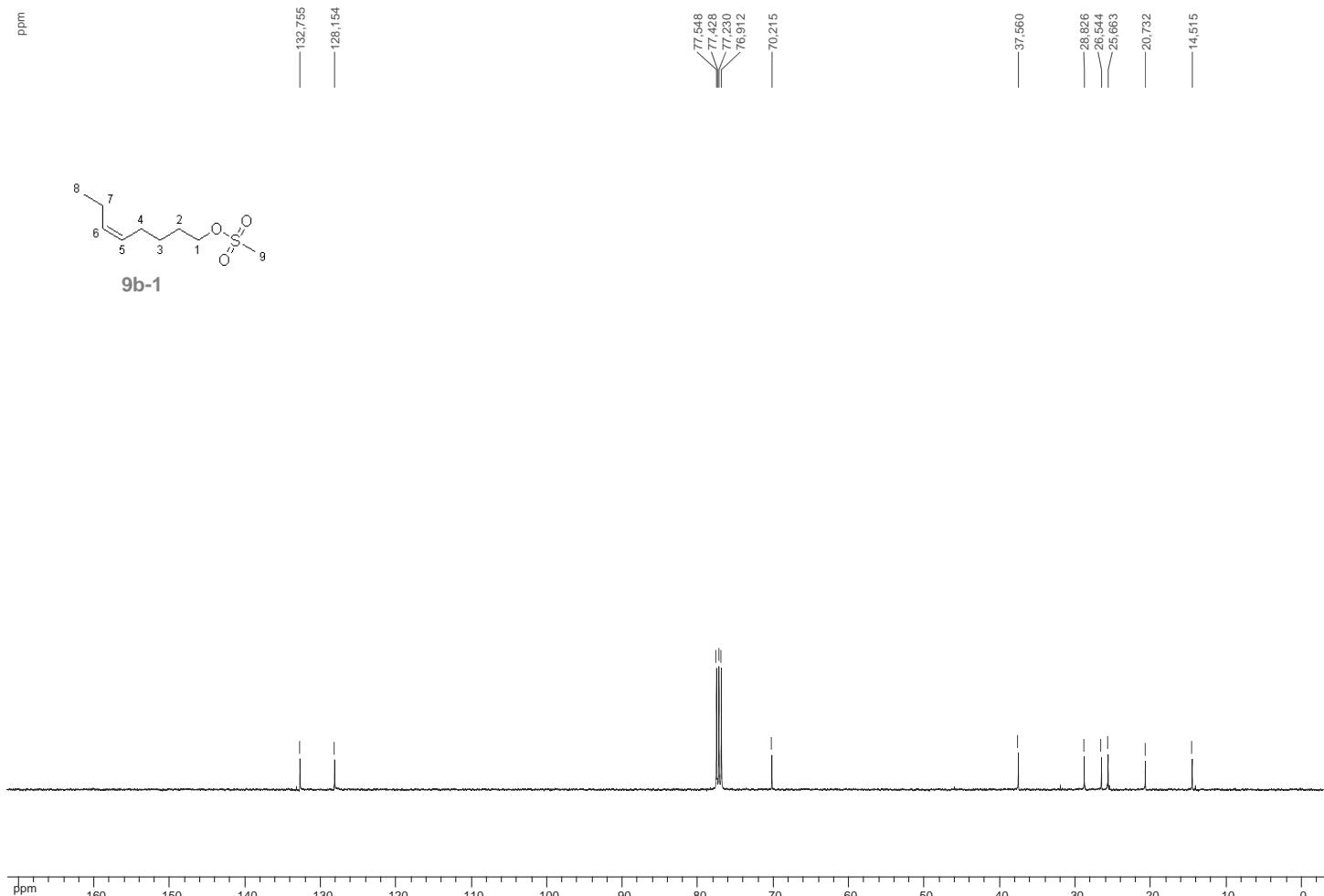
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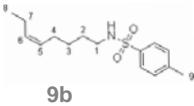
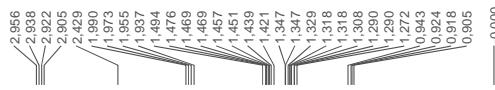
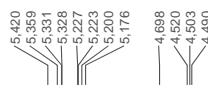
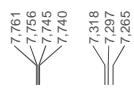
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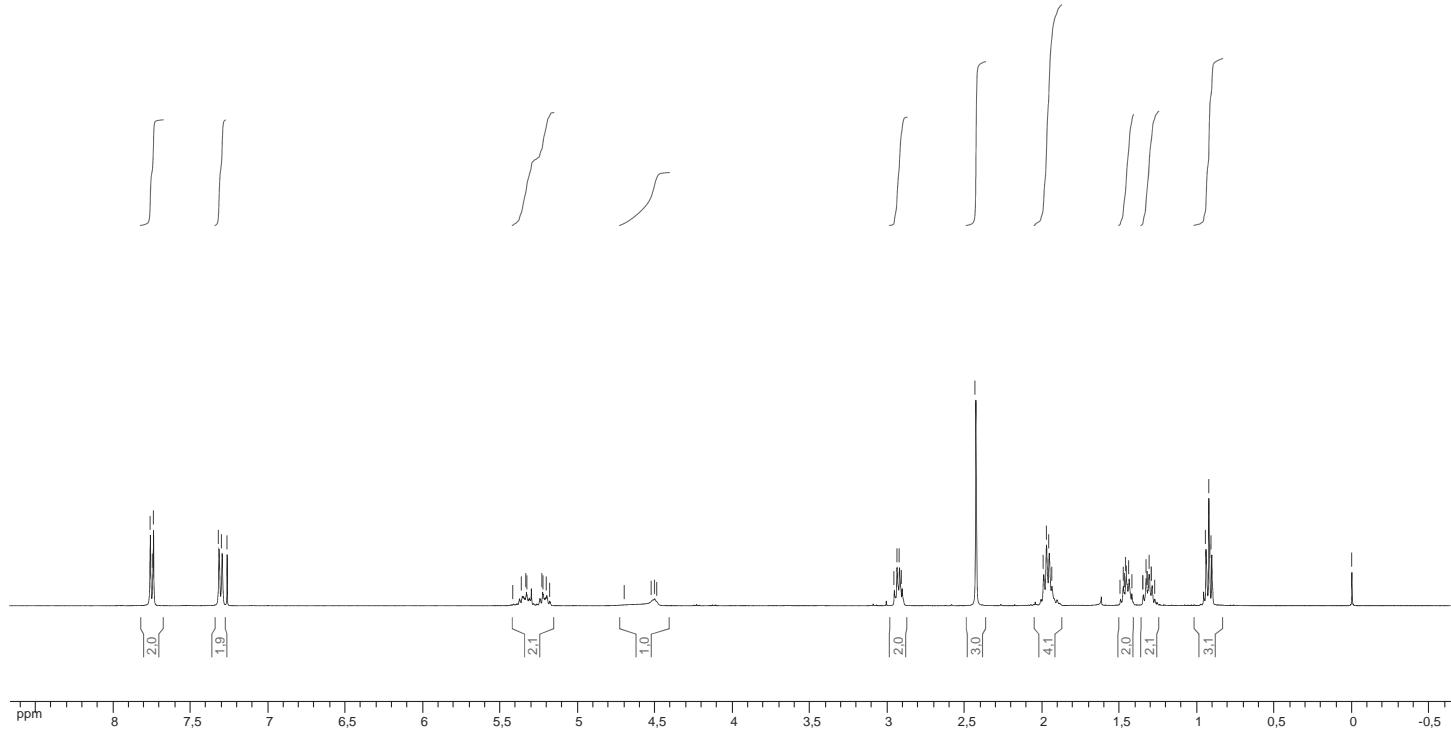
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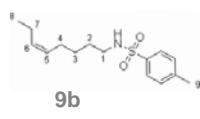
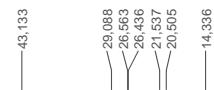
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9b



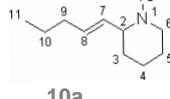
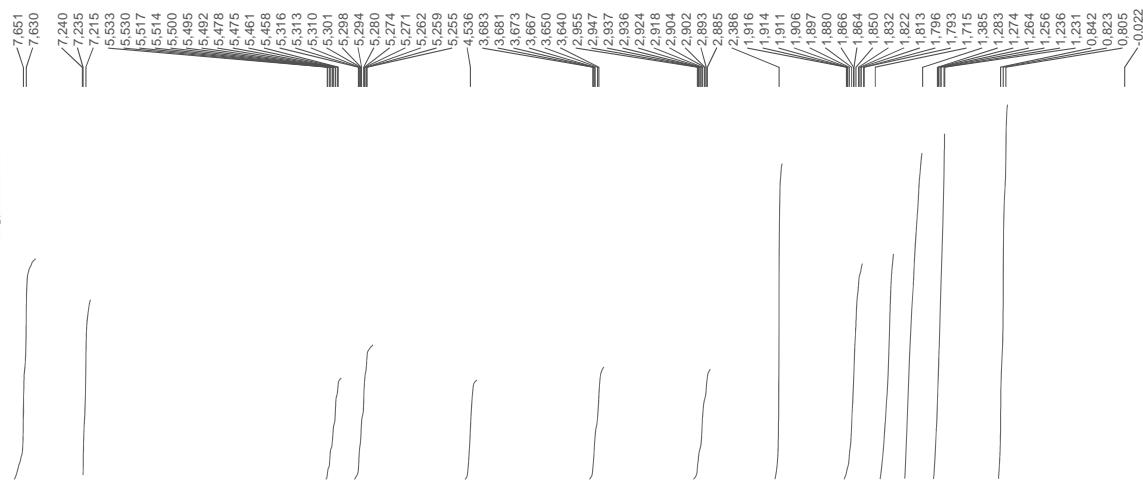
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9b

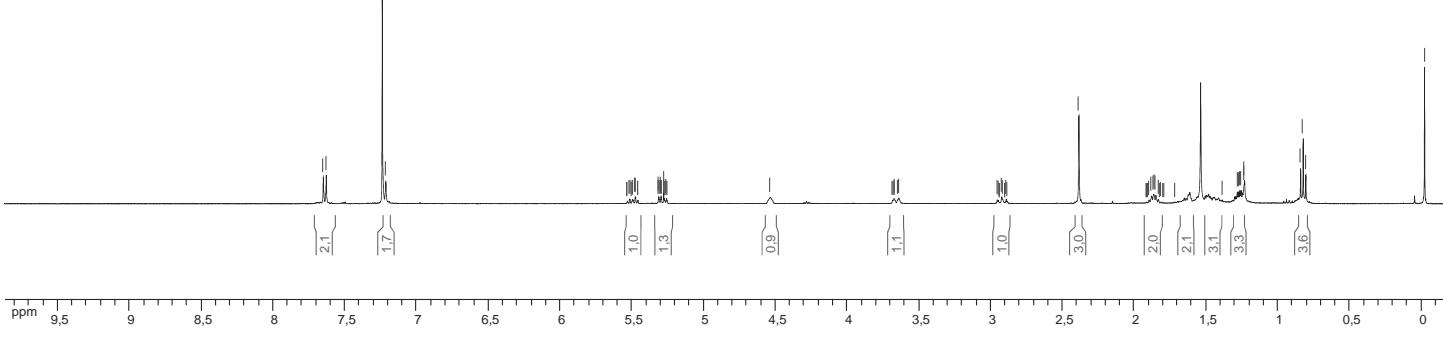


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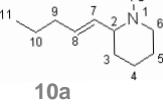
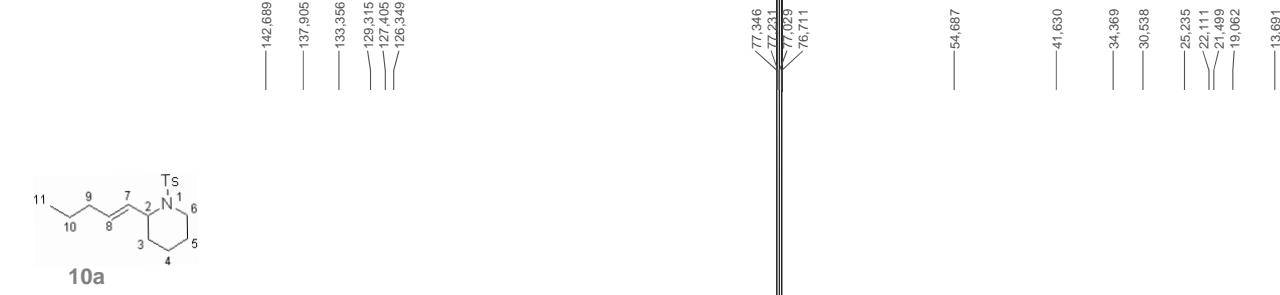


10a

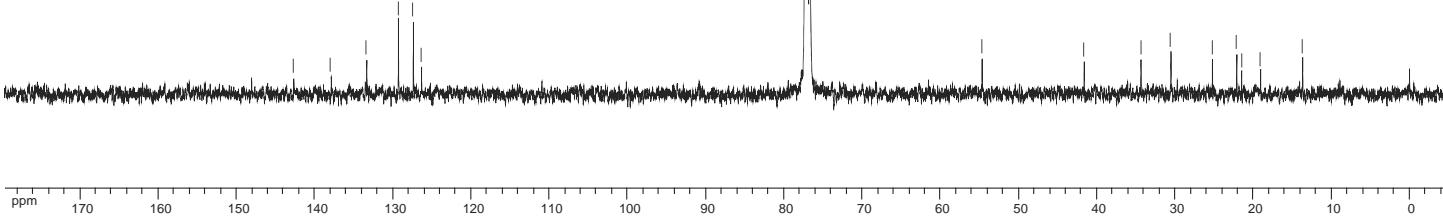
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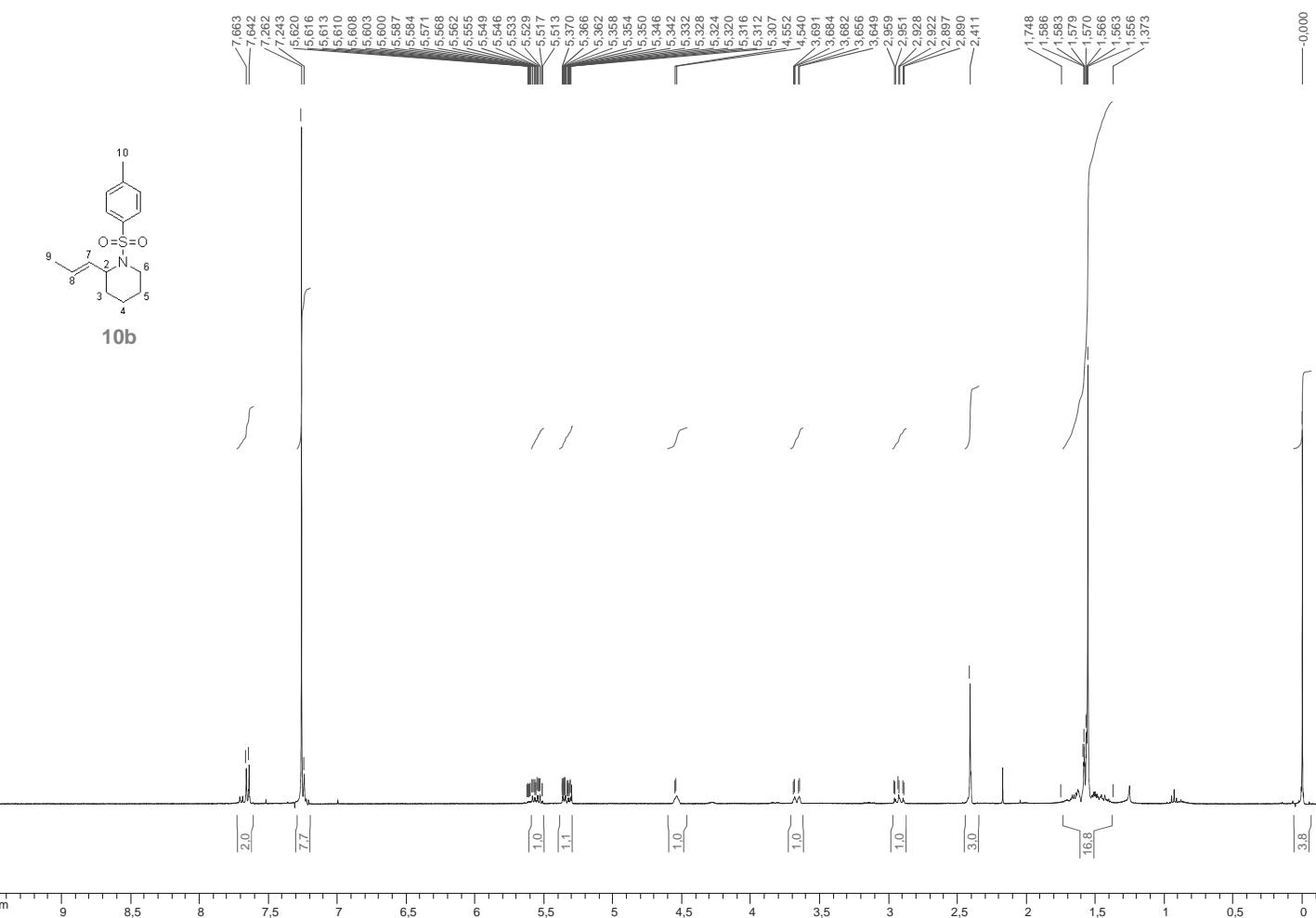
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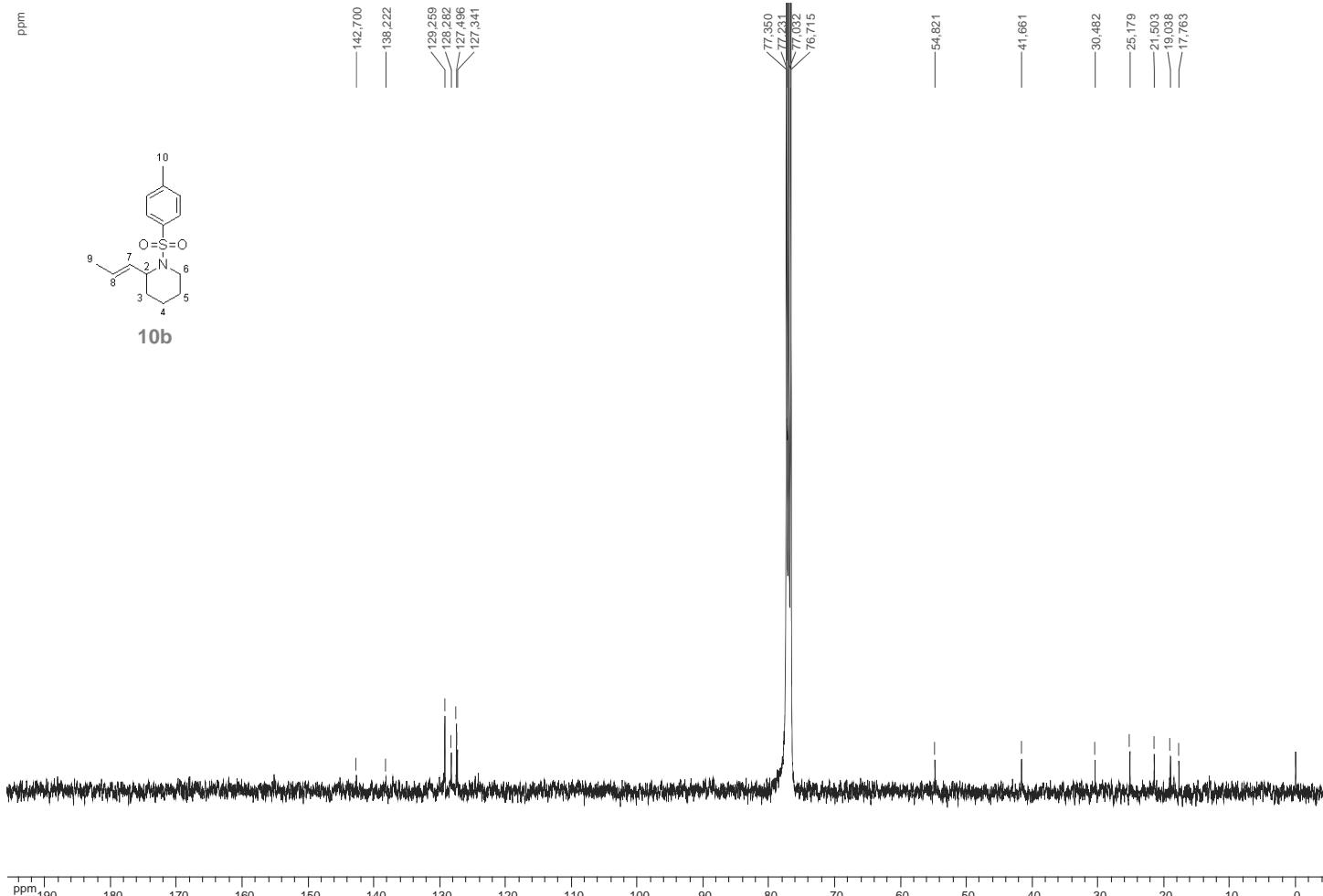
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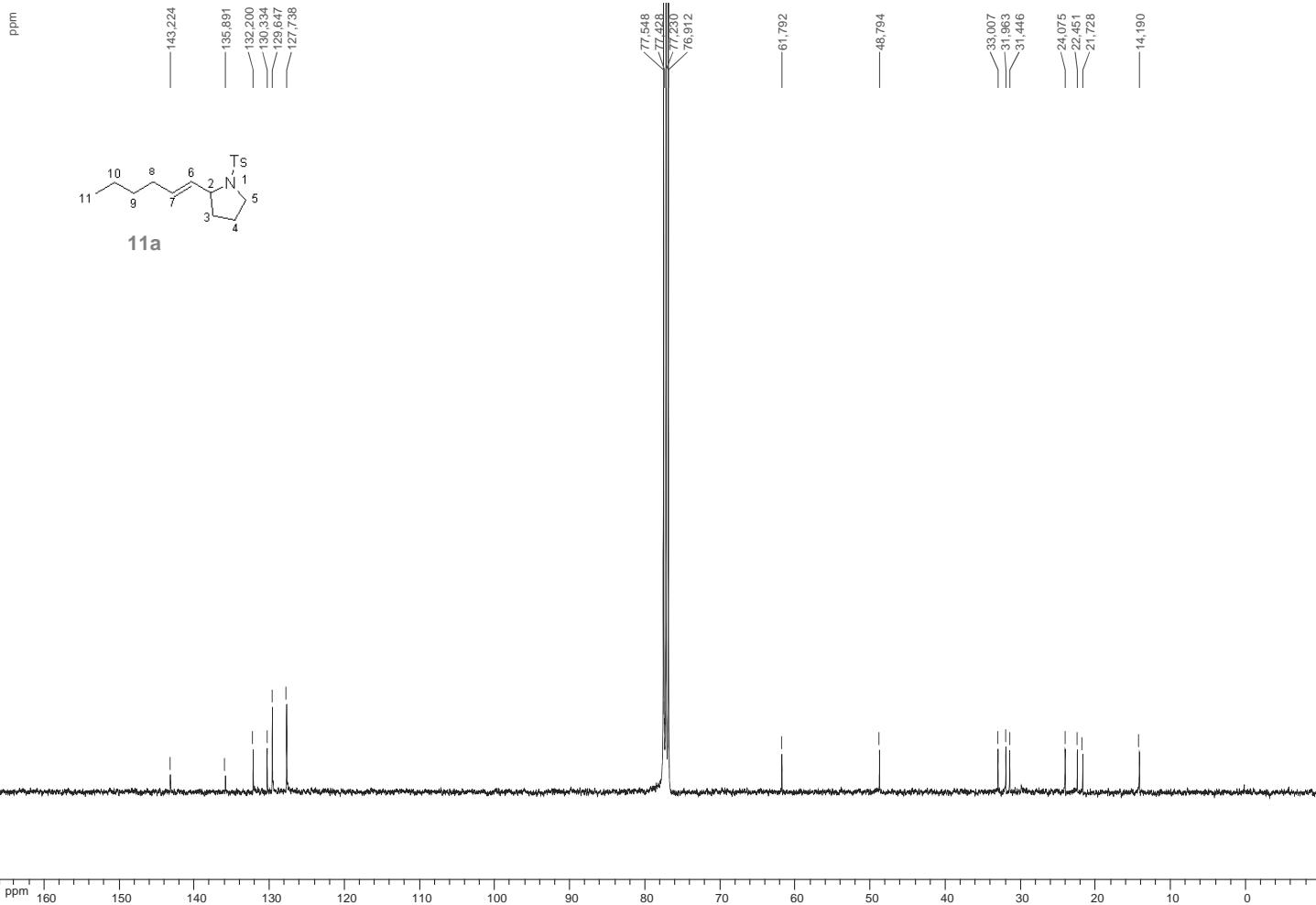
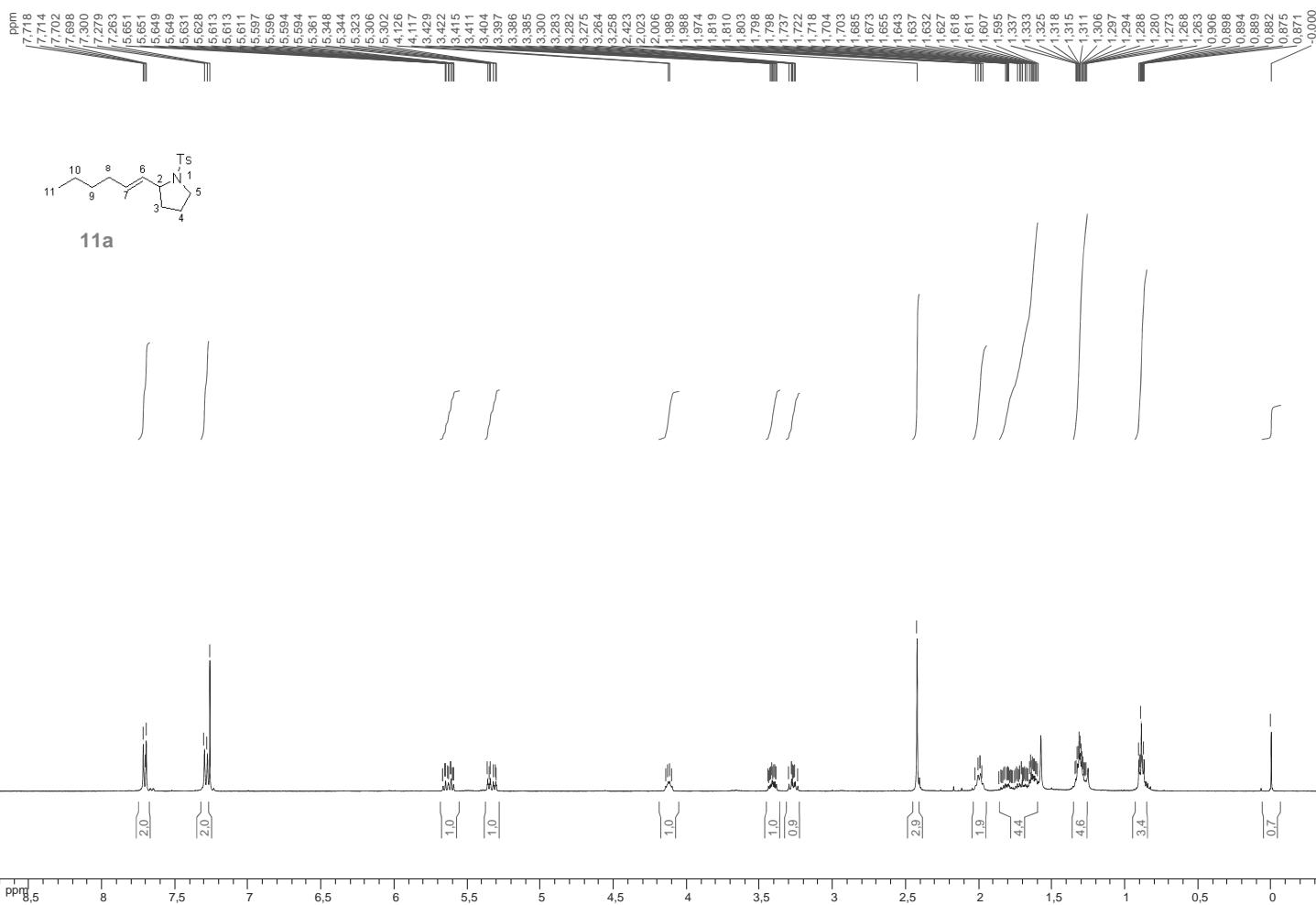


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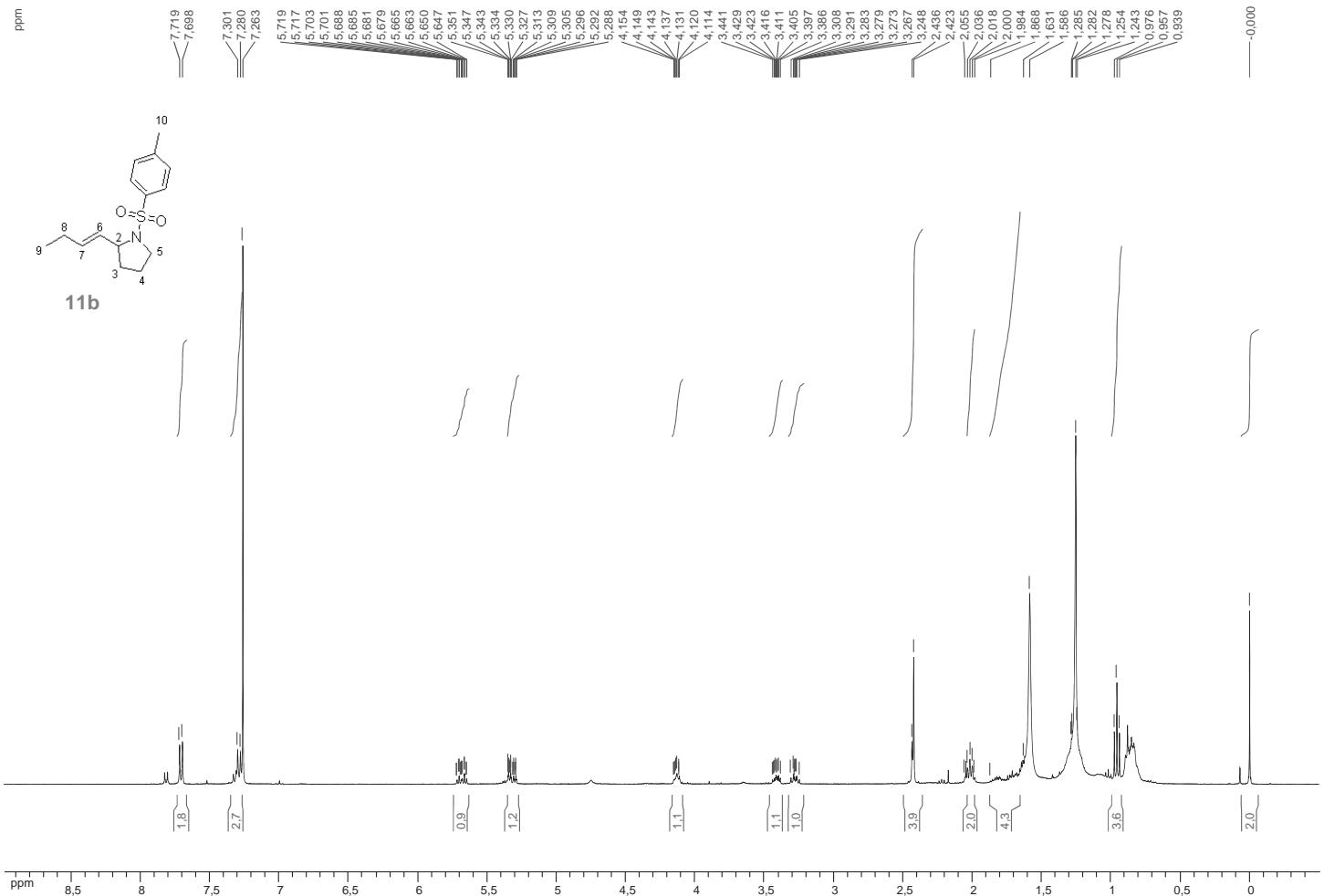


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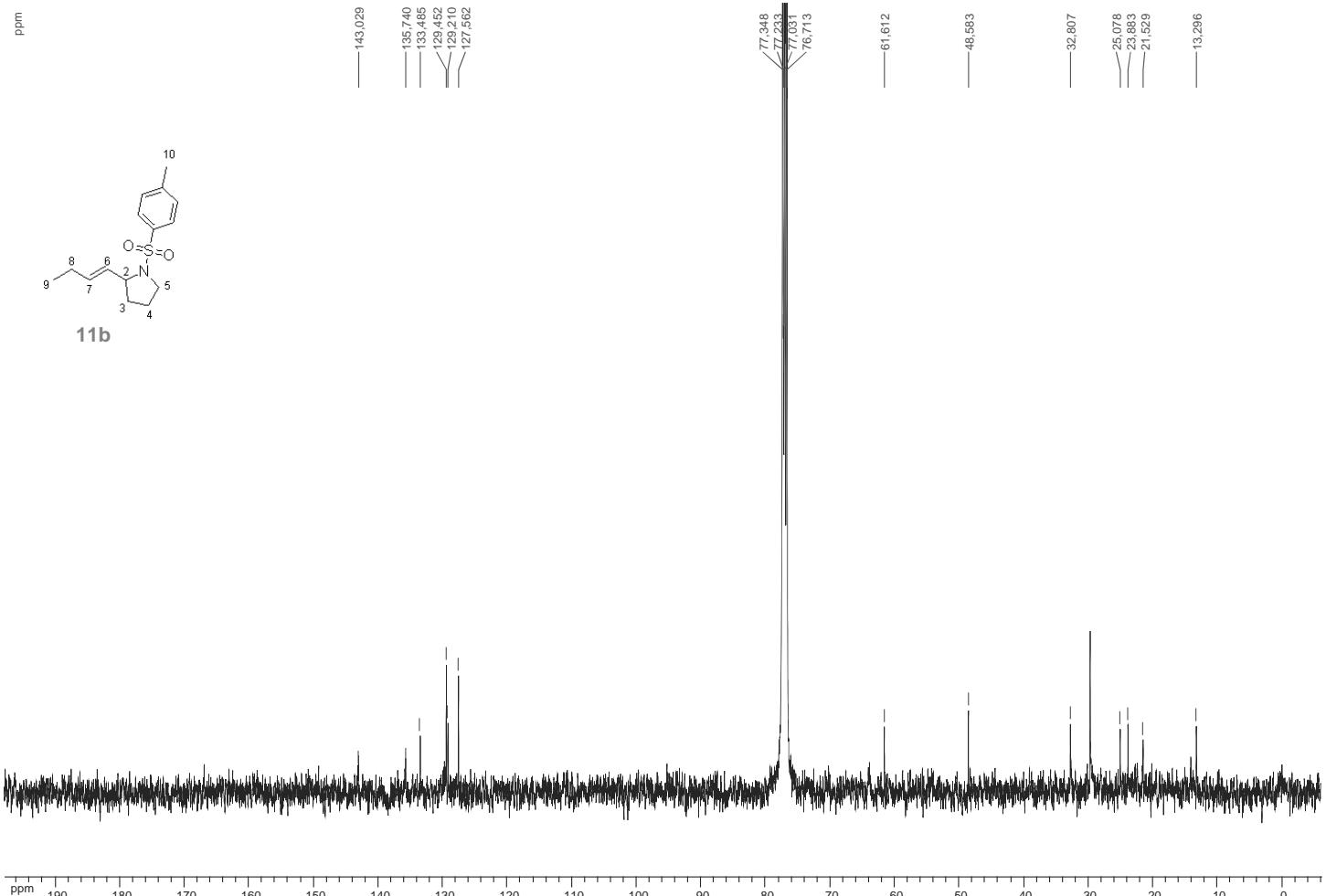




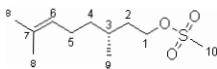
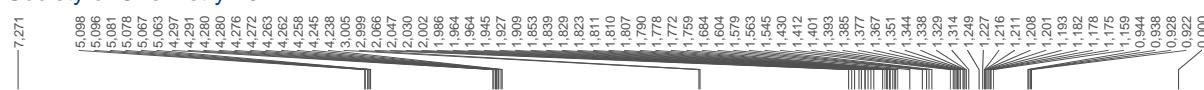
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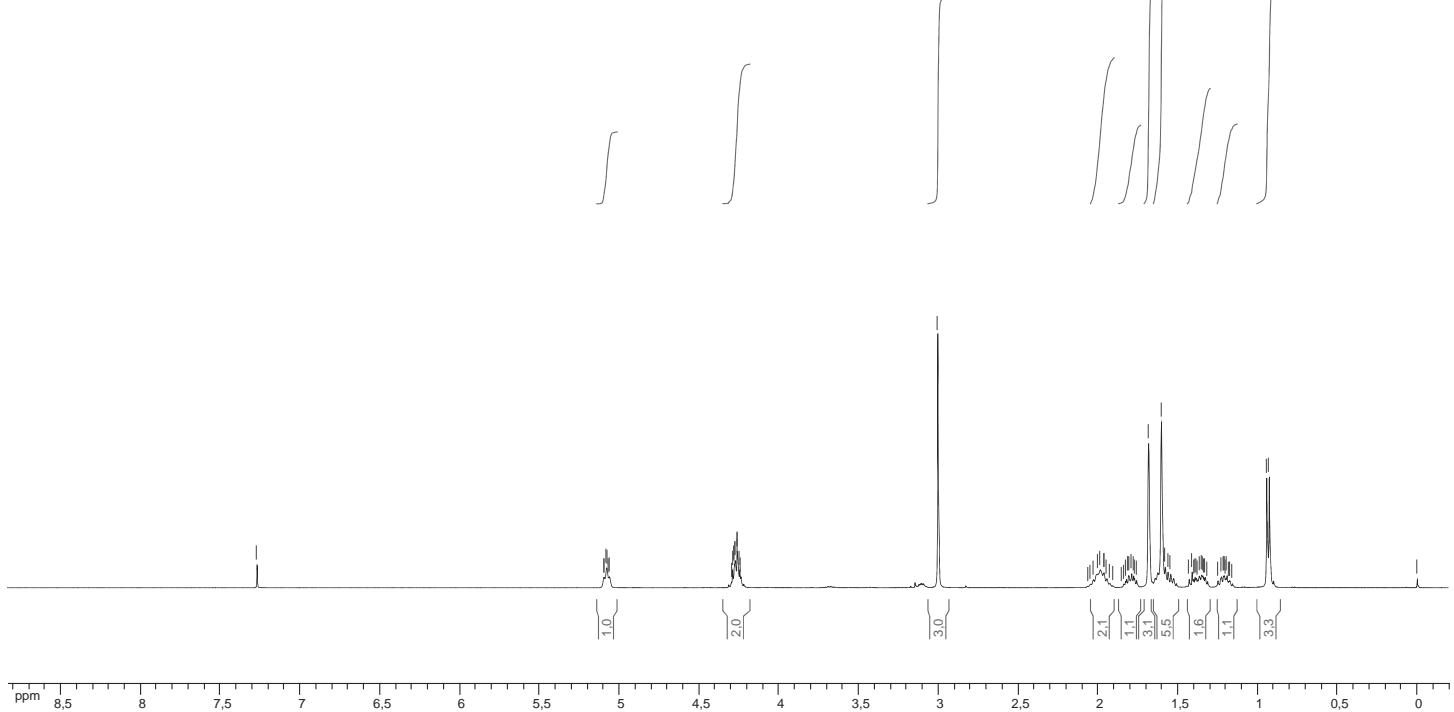
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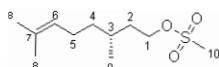
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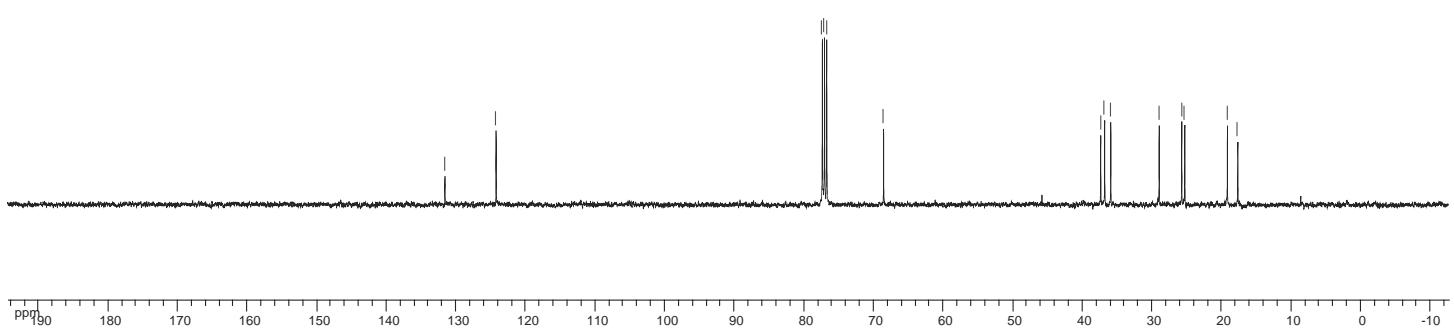
12-1



ppm



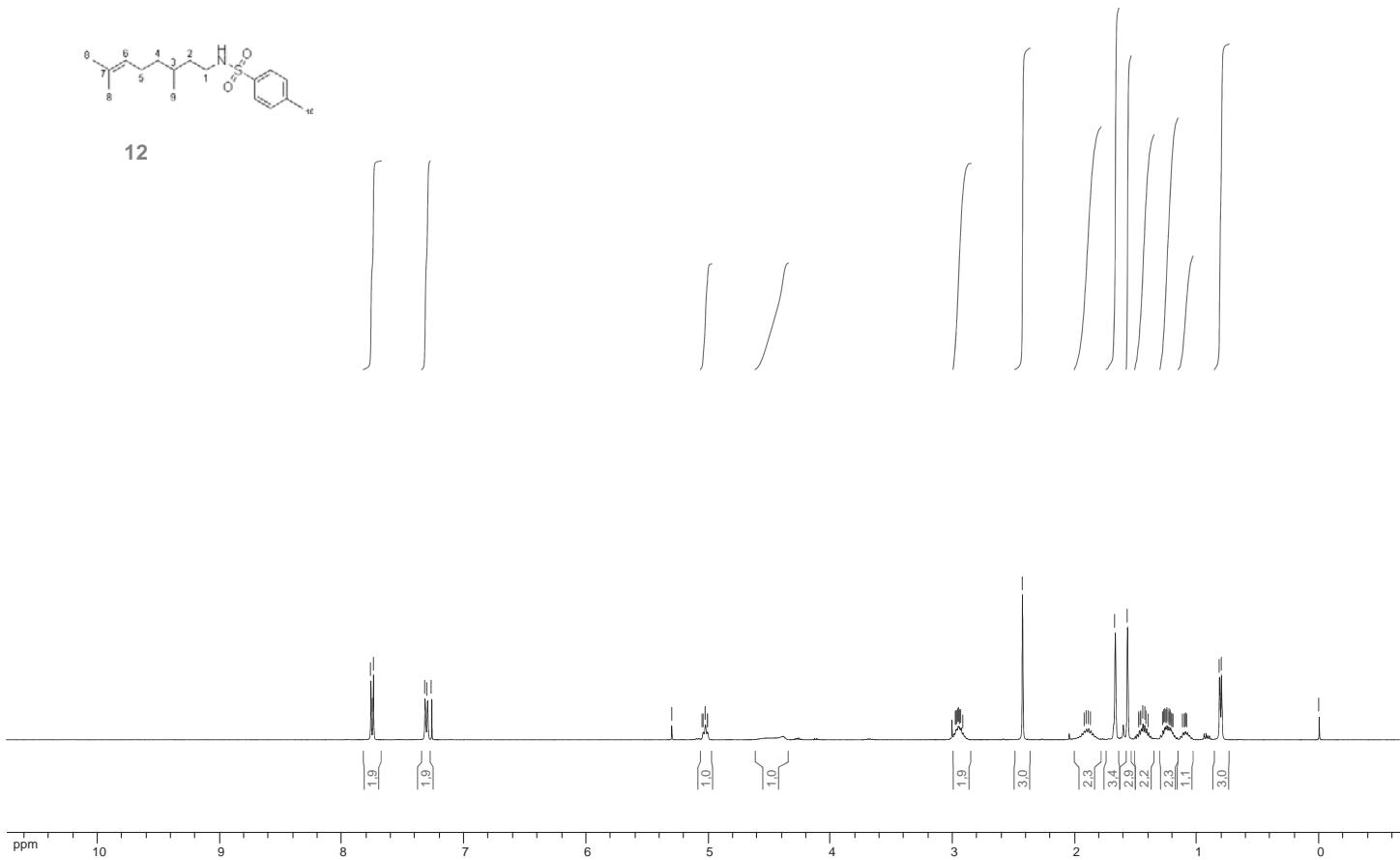
12-1



ppm



12



ppm

