Supporting Information

Palladium Catalyzed Tandem Bis-allylation of Isocyanates

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The starting materials were purchased from Aldrich or Lancaster. The substituted-allyl chlorides and 2-methyl-allyltributyltin were prepared using standard procedures reported in the literature.[1-5] The solvents were freshly distilled prior to use. All reactions were conducted under argon atmosphere by employing standard manifold techniques. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions by either Varian 300 or Varian 400 spectrometer at room temperature. The chemical shifts (ppm) are obtained using $CDCl_3$ as an internal standard (7.26 ppm, ^{1}H; 77.36 ppm, ^{13}C). Mass spectra were recorded on a Finnigan Thermoquest 2000A spectrometer. Merck silica gel 60 (230-400 mesh) was used for the chromatography.

Spectra data obtained for products **4-9**

N-But-3-enoyl-(N-prop-2-en)-tolylsulfonamide (4). ^{1}H NMR: δ 7.82 (d, 8.5 Hz, 2H), 7.33 (d, 8.5 Hz, 2H), 5.86 (m, 2H), 5.27 (dq, 17.1 Hz, 1.1 Hz, 1H), 5.24 (dq, 10.2 Hz, 1.1 Hz, 1H), 5.14 (dd, 10.3 Hz, 1.3 Hz, 1H), 5.04 (dd, 17.2, 1.5 Hz, 1H), 4.46 (dt, 5.5 Hz, 1.5 Hz, 2H), 3.36 (dt, 6.7, 1.5 Hz, 2H), 2.43 (s, 3H).^{13}C NMR: 171.3, 145.3, 136.9, 133.0, 130.2, 130.0, 128.4, 119.3 118.6, 48.9, 41.0, 22.0. MS (EI): *m/z* (rel intens) 279 (M^+, 1), 155 (37), 124 (3), 108 (32), 91 (100).

N-But-3-enoyl-(N-1-methyl-but-2-enyl)-tolylsulfonamide (5). Formed as a 1:5 mixture of *cis* and *trans* isomers. ^{1}H NMR: δ 7.78 (d, 7.9 Hz, 2H), 7.33 (d, 7.9 Hz, 2H), 5.84 (m, 2H), 5.52 (ddd, 15Hz, 6.6 Hz, 1.1 Hz, 1H), 5.12 (dt, 10.1 Hz, 1.3 Hz, 1H), 5.02 (dd, 17.1 Hz, 1.4 Hz, 1H), 4.90 (quintet, 1H), 3.34 (m, 2H), 2.45 (s, 3H), 1.63 (m, 3H), 1.50 (d, 6.7 Hz, 3H). ^{13}C NMR: 171.5, 144.8, 137.4, 131.0, 130.6, 130.3, 130.2, 130.1, 130.0, 128.8, 127.8, 127.5 127.5, 118.8, 58.3, 53.0, 42.7, 42.5, 22.0, 21.0, 20.2, 18.0, 13.5. MS (EI): *m/z* (rel intens) 307 (M^+, 5), 242 (37), 155(48), 152 (100), 124 (32), 91 (68), 85 (61), 70 (34).

N-But-3-enoyl-(N-1,4-dimethyl-pent-2-enyl)-tolylsulfonamide (6). ^{1}H NMR: δ 7.79 (d, 8.3 Hz, 2H), 7.32 (d, 8.3 Hz, 2H), 5.87 (m, 1H), 6.78 (ddd, 14.2 Hz, 7.3 Hz, 1.3 Hz, 1H) 5.41 (ddd, 15.4, 6.9 Hz, 1.1 Hz, 1H), 5.12 (dd, 10.2 Hz, 1.3 Hz, 1H), 5.03 (dd, 17.2 Hz, 1.5 Hz, 1H), 4.91 (q, 7.1 Hz, 1H), 3.41 (m, 2H), 2.44 (s, 3H), 2.22 (septet, 6.9 Hz, 1H), 1.52 (d, 6.9

Hz, 3H), 0.93 (d, 6.7 Hz, 3H), 0.91 (d, 6.7 Hz, 3H). ^{13}C NMR: 171.7, 145.0, 141.3, 137.6, 130.8, 130.1, 128.0, 127.0, 118.9, 58.5, 42.7, 31.1, 22.6, 22.4, 21.9, 20.4. MS (EI): *m/z* (rel intens) 335 (M^+, 3)320 (6), 252 (10), 224 (10), 180 (100), 155 (16), 112 (95), 91 (29).

N-But-3-enoyl-(N-1-methyl-3-cyclohexanyl-prop-2-enyl)-tolylsulfonamide (7). ^{1}H NMR: δ 7.78 (d, 8.4 Hz, 2H), 7.31 (d, 8.4 Hz, 2H), 5.86 (m, 1H), 5.77 (dd, 15.4 Hz, 7.3 Hz, 1H), 5.38 (ddd, 15.9, 6.8, 1.0 Hz, 1H), 5.12 (dq, 10.1 Hz, 1.4 Hz, 1H), 5.01 (dq, 17.1 Hz, 1.6 Hz, 1H), 4.90 (quintet, 6.9 Hz, 1H), 3.39 (m, 2H), 2.43 (s, 3H), 1.89 (m, 1H), 1.65 (m, 5H), 1.51 (d, 6.9 Hz, 3H), 1.20 (m, 3H), 0.98 (m, 2H). ^{13}C NMR: 171.7, 144.9, 140.1, 137.6, 130.8, 130.0, 127.9, 127.4, 118.8, 58.5, 42.7, 40.6, 33.0, 32.9, 26.4, 26.2, 21.9, 20.4. (EI): *m/z* (rel intens) 375 (M^+, 1), 292 (4), 224 (40), 220 (98), 155 (17), 135 (100), 91 (28).

N-2-Methyl-but-3-enoyl-(N-2-methyl-prop-2-enyl)-tolylsulfonamide (8). ^{1}H NMR: δ 7.85 (d, 8.4 Hz, 2H), 7.31 (d, 8.4 Hz, 2H), 4.97 (s, 1H), 4.88 (s, 2H), 4.62 (s, 1H), 4.41 (s, 2H), 3.18 (s, 2H), 2.43 (s, 3H), 1.79 (s, 3H), 1.66 (s, 3H). ^{13}C NMR: 171.1, 145.1, 140.6, 138.6, 136.7, 129.7, 128.8, 115.1, 112.1, 51.7, 44.9, 22.7, 21.9, 20.5. MS (EI): *m/z* (rel intens) 307 (M^+, 2), 155 (35), 152 (44), 91 (100).

N-2-Methyl-but-3-enoyl-(N-1-methyl-but-2-enyl)-tolylsulfonamide (9). Spectra data obtained for the *trans* isomer: ^{1}H NMR: δ 7.78 (d, 8.4 Hz, 2H), 7.32 (d, 8.4 Hz, 2H), 5.84 (ddq, 15.5 Hz, 7.1 Hz, 1.4 Hz, 1H), 5.52 (ddq, 14.9 Hz, 6.3 Hz, 1.0 Hz, 1H), 4.87 (m, 2H), 4.66 (br. s, 1H), 3.32 (m, 2H), 2.43 (s, 3H), 1.66 (br. s, 3H), 1.64 (br. d, 6.5 Hz, 3H), 1.51 (d, 6.8 Hz, 3H). ^{13}C NMR: 171.4, 144.9, 139.3, 137.6, 131.2, 130.0, 128.8, 128.0, 115.1, 58.2, 46.5, 22.8, 21.9, 20.2, 17.9. MS (EI): *m/z* (rel intens) 321 (M^+, 10), 253 (100), 238 (47), 224 (32), 198 (44), 155 (81), 110 (88), 91 (92).

References:

1) Brooks, L. A.; Snyder, H. R. *Org. Synth.* **1955**, *Coll. Vol.*, *3*, 698.

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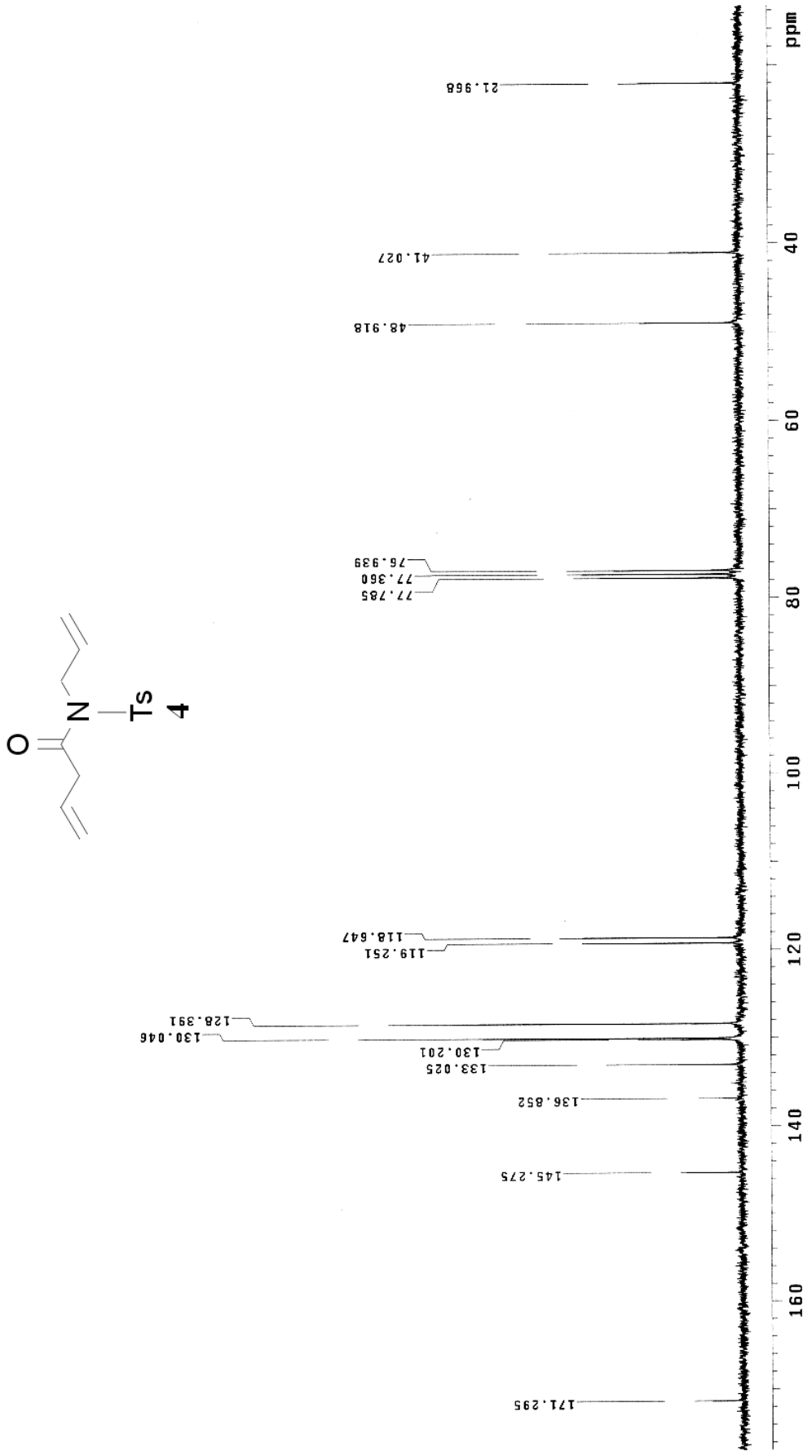
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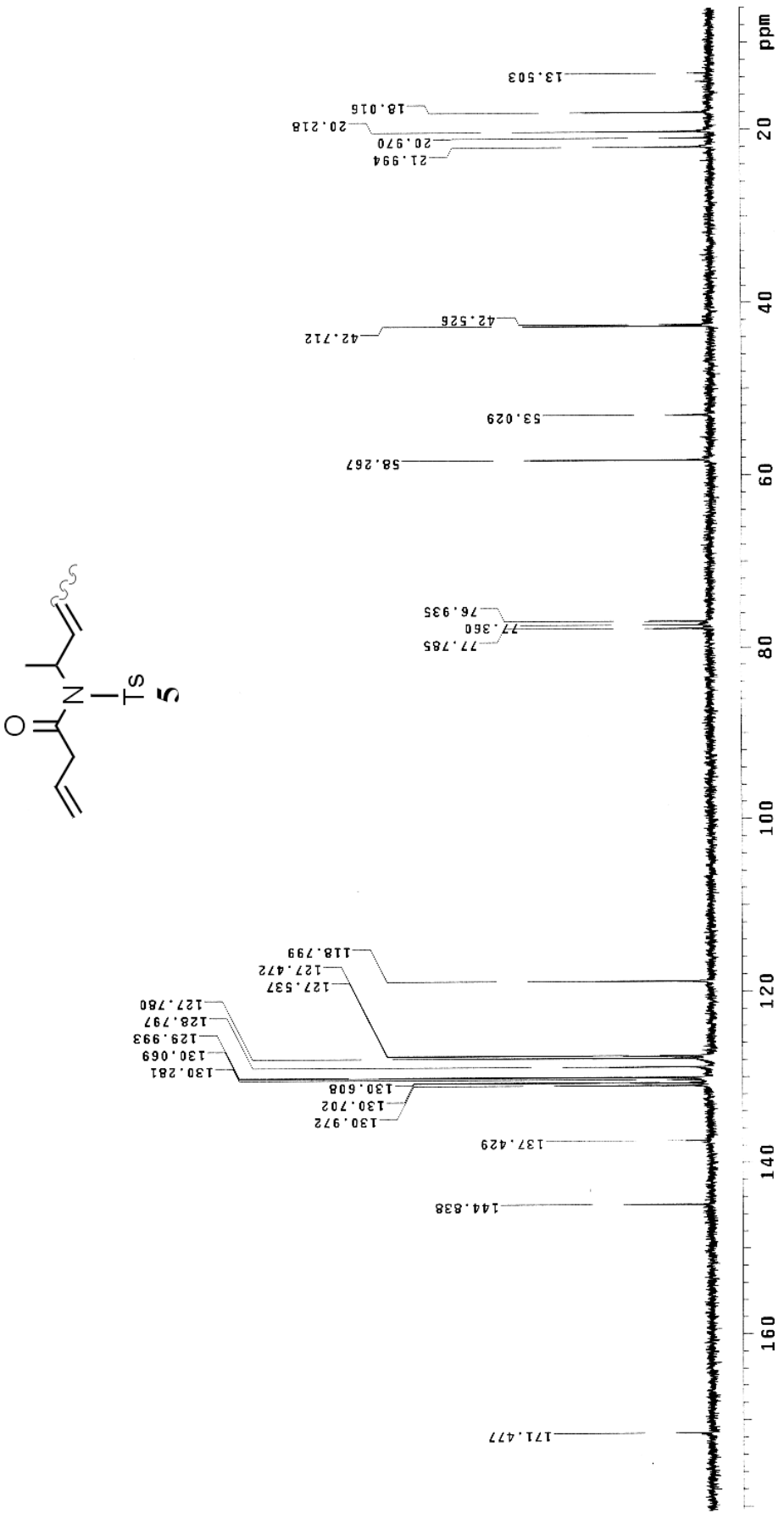
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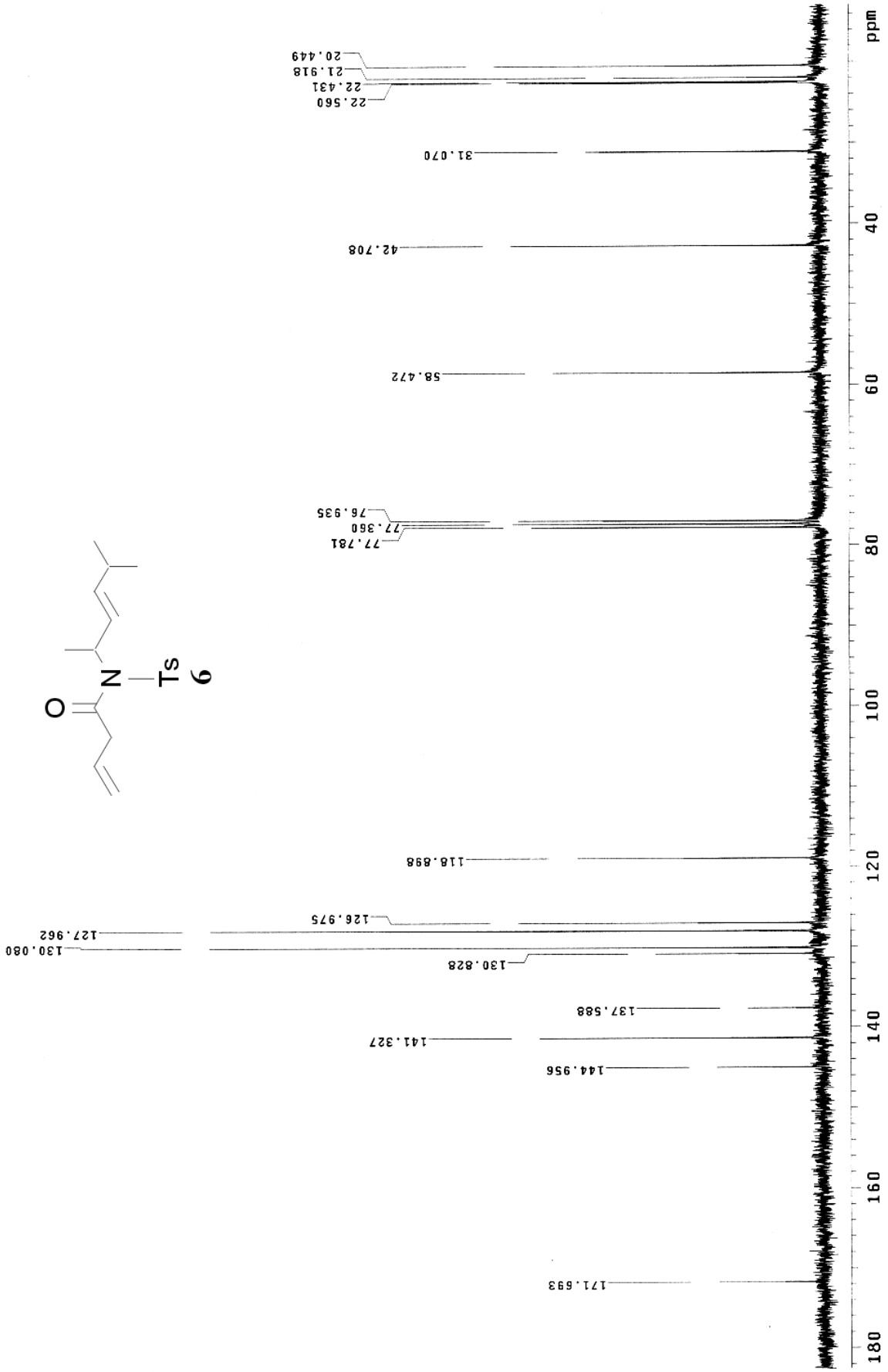
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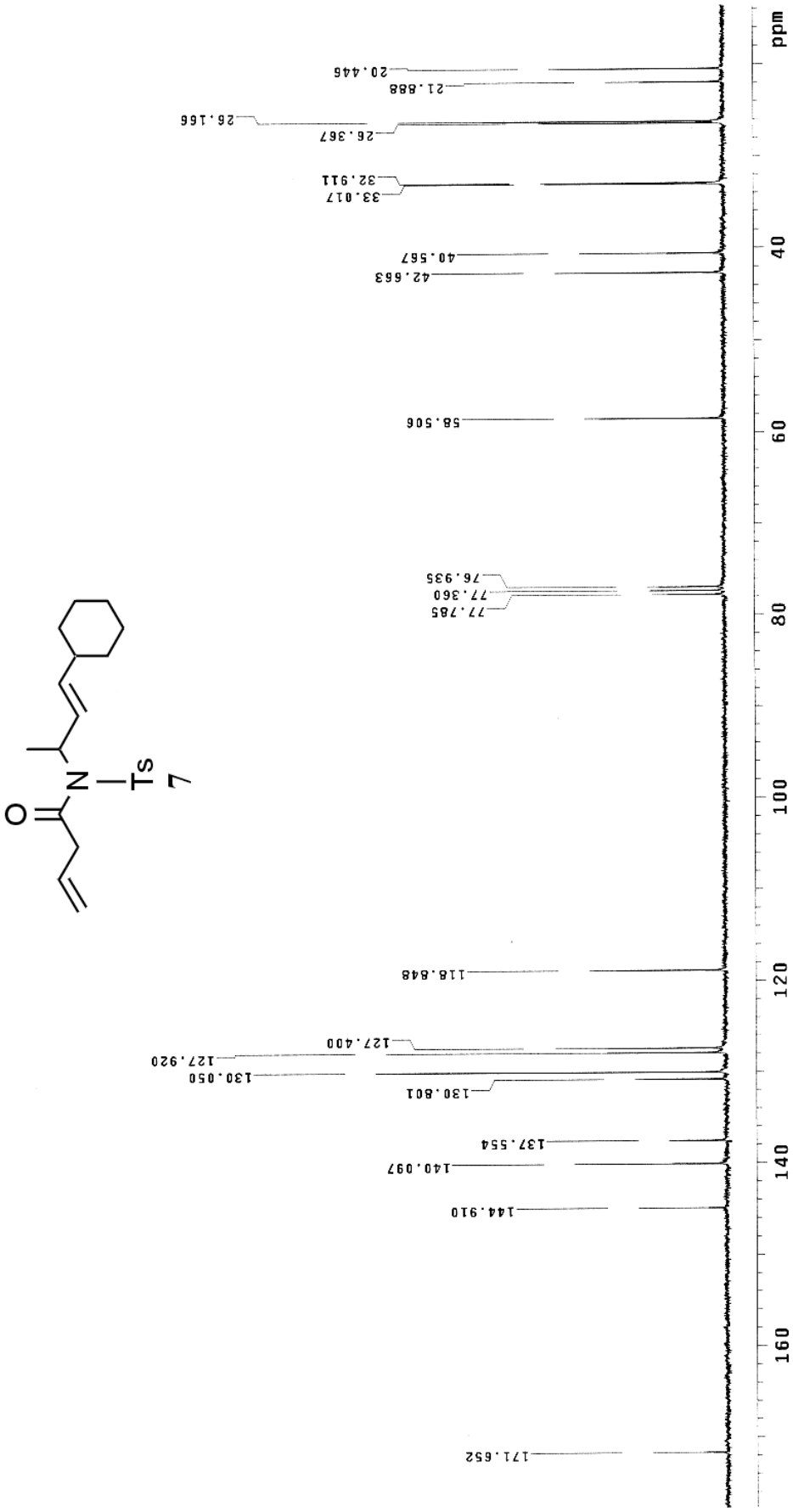
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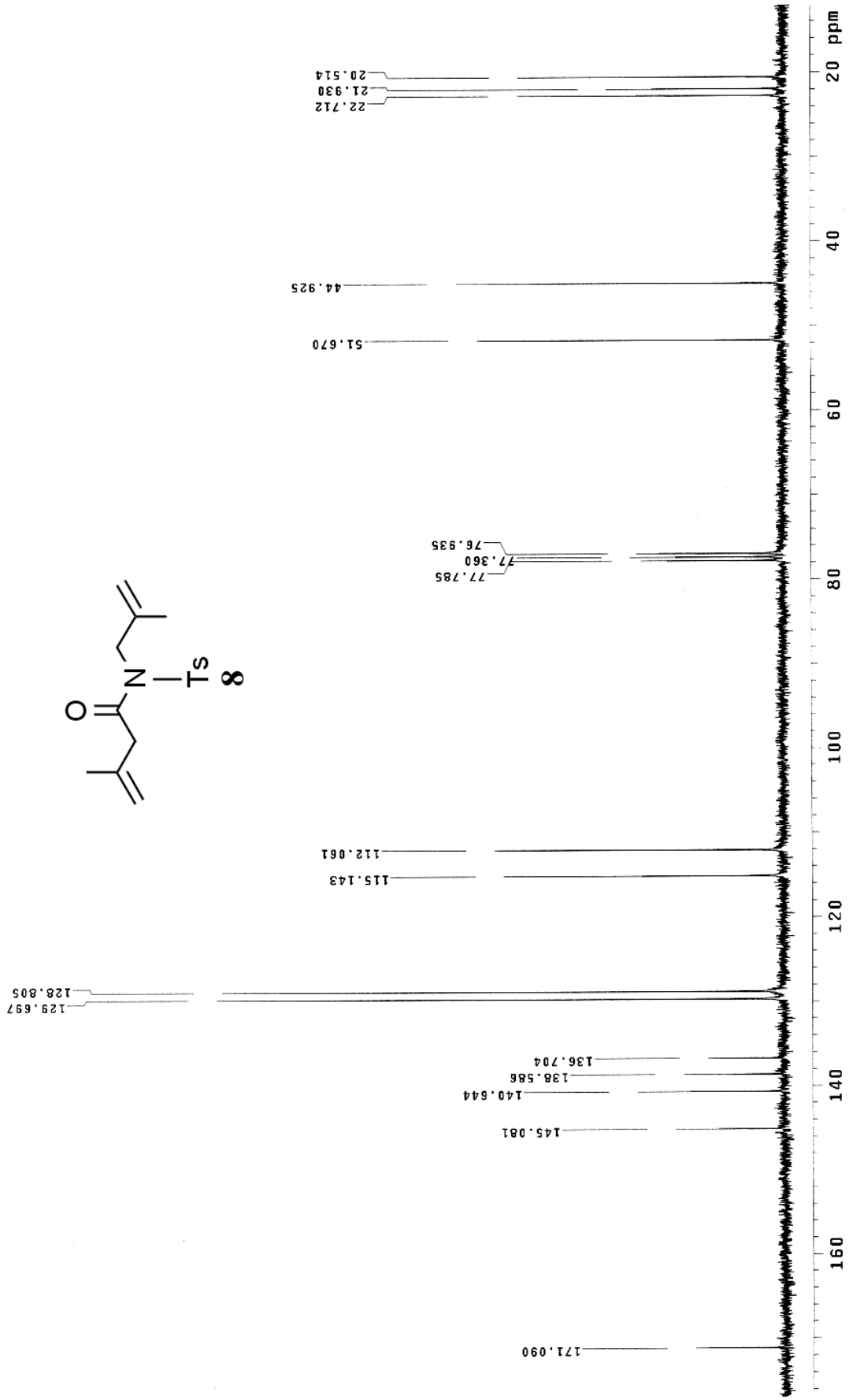
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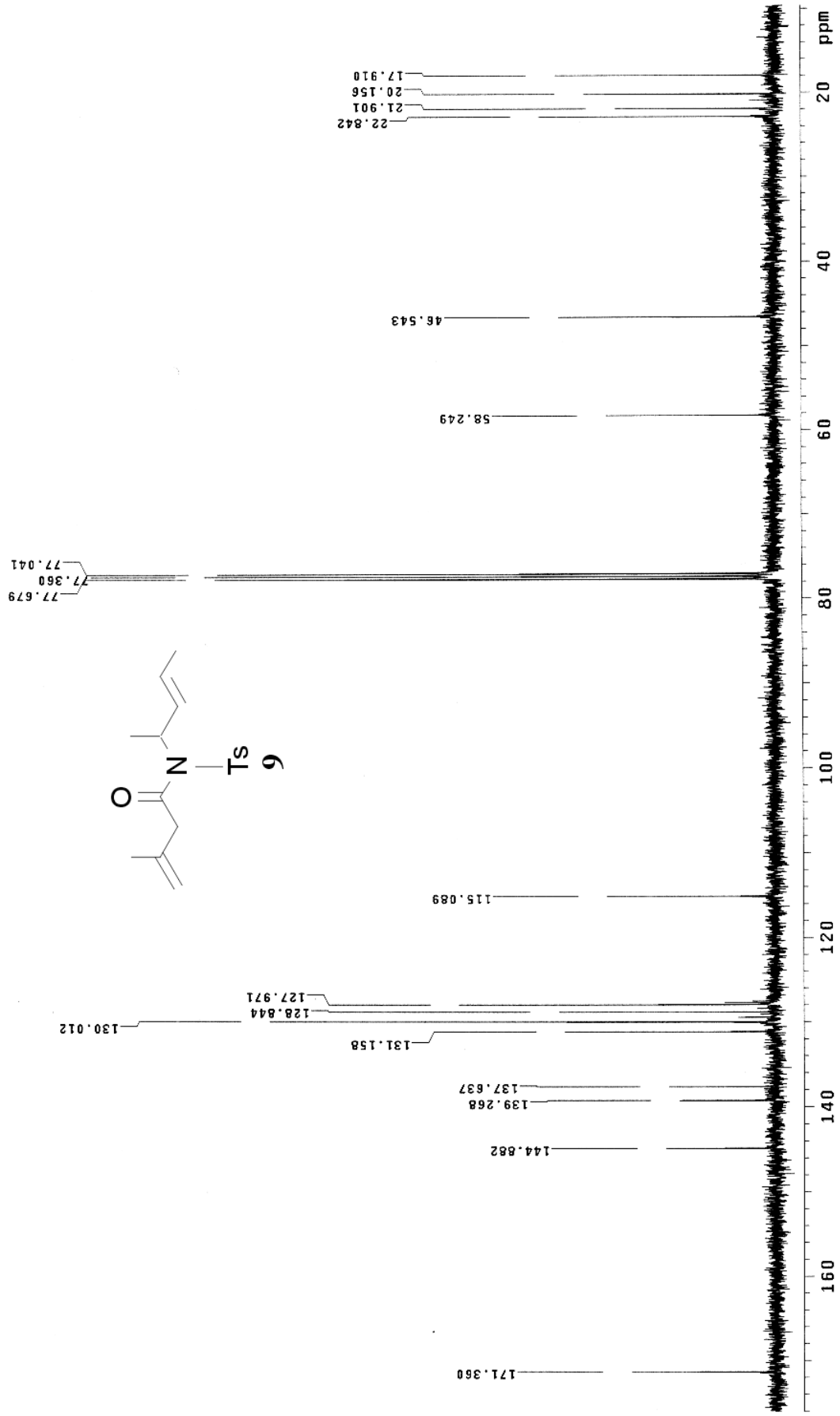
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