

## Supporting Information

### Stereoselective Additions of Thiyl Radicals to Terminal Ynamides

Biplab Banerjee, Dmitry N. Litvinov, Junghoon Kang, Jennifer D. Bettale, and Steven L.

Castle\*

*Department of Chemistry and Biochemistry*

*Brigham Young University, Provo, Utah, 84602*

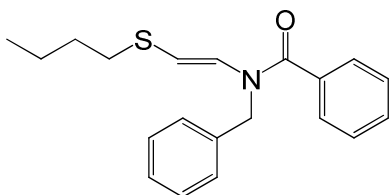
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## General Experimental Details

Flash chromatography was carried out using 60–230 mesh silica gel.  $^1\text{H}$  NMR spectra were acquired on a 500 MHz spectrometer with chloroform (7.27 ppm) as internal reference. Signals are reported as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), br s (broad singlet), m (multiplet). Coupling constants are reported in hertz (Hz).  $^{13}\text{C}$  NMR spectra were acquired on a spectrometer operating at 125 MHz with chloroform (77.23 ppm) as internal reference. Infrared spectra were obtained on an FT-IR spectrometer. Mass spectral data were obtained using ESI techniques.

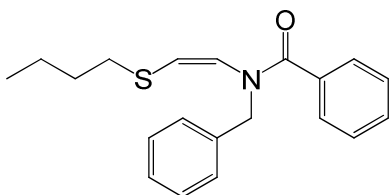
**General Procedure for Thiyl Radical Additions to Ynamides.** A solution of the ynamide (1 equiv) and thiol (1–4 equiv) in dry *t*-BuOH (stored over 4 Å MS) at rt under Ar was treated with AIBN (0.5–2 equiv). The resulting mixture was stirred at 85 °C for the appropriate length of time (10–360 min), then concentrated in vacuo. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (1 mL) and stirred with sat aq  $\text{NaHCO}_3$  for 2 h. The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 1$  mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  ( $2 \times 1$  mL) and brine (1 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated in vacuo. Flash chromatography ( $\text{SiO}_2$ ) afforded the  $\beta$ -thioenamide adducts in diastereomerically pure form.



**(*E*)-*N*-Benzyl-*N*-(2-(butylthio)vinyl)benzamide (*E*-3a).**

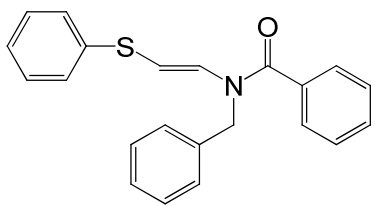
Prepared from **1** (10 mg, 0.043 mmol), *n*-butyl thiol (18  $\mu\text{L}$ , 0.17 mmol, 4 equiv), *t*-BuOH (300  $\mu\text{L}$ ), and AIBN (14 mg, 0.085 mmol, 2 equiv) according to the General

Procedure with a 3 h reaction time. The crude product (*E*:*Z* = 15:1) was purified by flash chromatography (SiO<sub>2</sub>, 15% EtOAc in hexanes elution) to afford *E*-**3a** (10 mg, 0.031 mmol, 72%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.50–7.42 (m, 3H), 7.40–7.35 (m, 2H), 7.32–7.27 (m, 4H), 5.48 (d, *J* = 13.5 Hz, 1H), 5.02 (br s, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.40–1.34 (m, 2H), 1.31–1.24 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 170.4, 136.8, 134.4, 130.9 (2C), 129.1 (2C), 129.0 (3C), 128.8, 127.5 (2C), 126.9, 105.5, 47.8, 34.3, 31.6, 21.9, 13.8; IR (film) ν<sub>max</sub> 3054, 3045, 2926, 1659, 1604, 1495, 1446, 1375, 1315, 1245, 1137, 1076, 982, 935 cm<sup>-1</sup>; HRMS (ESI) *m/z* 326.1581 (MH<sup>+</sup>, C<sub>20</sub>H<sub>23</sub>NOSH<sup>+</sup> requires 326.1573).



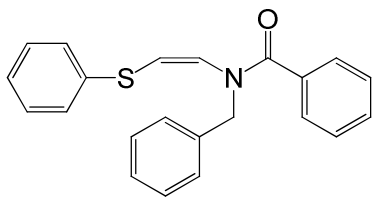
**(Z)-N-Benzyl-N-(2-(butylthio)vinyl)benzamide (Z-3a).**

Prepared from **1** (10 mg, 0.043 mmol), *n*-butyl thiol (4.6 μL, 0.043 mmol, 1 equiv), *t*-BuOH (300 μL), and AIBN (3.5 mg, 0.021 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E*:*Z* = 1:11) was purified by flash chromatography (SiO<sub>2</sub>, 15% EtOAc in hexanes elution) to afford *Z*-**3a** (10.5 mg, 0.032 mmol, 76%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.58 (d, *J* = 7.0 Hz, 2H), 7.43–7.30 (m, 6H), 7.28–7.25 (m, 2H), 6.07 (br s, 1H), 5.59 (br s, 1H), 5.00 (s, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.55–1.45 (m, 2H), 1.38–1.28 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 171.1, 137.7, 136.1, 130.6 (2C), 128.6 (4C), 128.1 (2C), 127.5 (2C), 126.9, 122.2, 49.0, 34.5, 32.6, 21.8, 13.9; IR (film) ν<sub>max</sub> 3030, 2956, 2928, 1651, 1602, 1495, 1446, 1376, 1274, 1138, 1074, 982 cm<sup>-1</sup>; HRMS (ESI) *m/z* 326.1573 (MH<sup>+</sup>, C<sub>20</sub>H<sub>23</sub>NOSH<sup>+</sup> requires 326.1573).



**(E)-N-Benzyl-N-(2-(phenylthio)vinyl)benzamide (E-3b).**

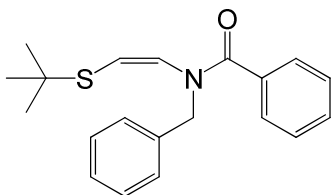
Prepared from **1** (10 mg, 0.043 mmol), thiophenol (17  $\mu$ L, 0.17 mmol, 4 equiv), *t*-BuOH (300  $\mu$ L), and AIBN (14 mg, 0.085 mmol, 2 equiv) according to the General Procedure with a 5 h reaction time. The crude product (*E*:*Z* = 33:1) was purified by flash chromatography (SiO<sub>2</sub>, 15% EtOAc in hexanes elution) to afford *E*-**3b** (14.3 mg, 0.041 mmol, 97%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.57 (d, *J* = 7.5 Hz, 2H), 7.50–7.42 (m, 3H), 7.41–7.38 (m, 2H), 7.35–7.30 (m, 4H), 7.14–7.06 (m, 3H), 6.84 (d, *J* = 7.0 Hz, 2H), 5.58 (d, *J* = 13.5 Hz, 1H), 5.14 (br s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.4, 138.0, 137.0, 136.2, 134.4, 130.9 (2C), 129.0 (3C), 128.8 (2C), 128.3, 127.5 (2C), 127.2, 126.9 (2C), 125.8 (2C), 102.0, 48.0; IR (film)  $\nu_{\max}$  3060, 2899, 1662, 1604, 1495, 1478, 1439, 1371, 1315, 1243, 1207, 1135, 1076, 1024, 980 cm<sup>-1</sup>; HRMS (ESI) *m/z* 346.1267 (MH<sup>+</sup>, C<sub>22</sub>H<sub>19</sub>NOSH<sup>+</sup> requires 346.1260).



**(Z)-N-Benzyl-N-(2-(phenylthio)vinyl)benzamide (Z-3b).**

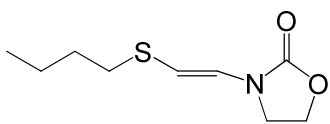
Prepared from **1** (10 mg, 0.043 mmol), thiophenol (4.5  $\mu$ L, 0.045 mmol, 1 equiv), *t*-BuOH (300  $\mu$ L), and AIBN (3.5 mg, 0.021 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E*:*Z* = 1:4.3) was purified by flash chromatography (SiO<sub>2</sub>, 15% EtOAc in hexanes elution) to afford *Z*-**3b** (4.9 mg, 0.014 mmol, 33%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.62 (d, *J* = 7.0 Hz, 2H), 7.45–7.36 (m, 5H), 7.34–7.32 (m, 2H), 7.30–7.19 (m, 4H), 7.09 (d, *J* = 7.5 Hz, 2H),

6.31 (br s, 1H), 5.80 (d,  $J = 6.5$  Hz, 1H), 5.07 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  171.1, 137.4, 135.9, 135.2, 130.7 (2C), 129.8 (2C), 129.3 (2C), 128.7 (4C), 128.2 (2C), 127.6 (2C), 127.3 (2C), 119.4, 49.9; IR (film)  $\nu_{\text{max}}$  3068, 3058, 2991, 1644, 1601, 1494, 1477, 1439, 1368, 1340, 1274, 1178, 1138, 1074, 1025, 981  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  346.1259 ( $\text{MH}^+$ ,  $\text{C}_{22}\text{H}_{19}\text{NOSH}^+$  requires 346.1260).



**(Z)-N-Benzyl-N-(2-(tert-butylthio)vinyl)benzamide (Z-3c).**

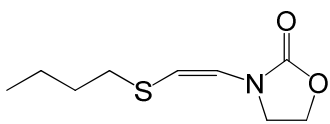
Prepared from **1** (10 mg, 0.043 mmol), *tert*-butyl thiol (19  $\mu\text{L}$ , 0.17 mmol, 4 equiv), *t*-BuOH (300  $\mu\text{L}$ ), and AIBN (14 mg, 0.085 mmol, 2 equiv) according to the General Procedure with a 6 h reaction time. The crude product (only *Z* isomer detected) was purified by flash chromatography ( $\text{SiO}_2$ , 15% EtOAc in hexanes elution) to afford **Z-3c** (5.7 mg, 0.017 mmol, 41%) as a colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.57 (d,  $J = 7.0$  Hz, 2H), 7.45–7.29 (m, 8H), 6.12 (br s, 1H), 5.79 (br s, 1H), 5.01 (s, 2H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  171.0, 137.6, 136.0, 130.3, 130.0, 128.3 (5C), 127.8 (2C), 127.2 (2C), 118.1, 48.8, 44.5, 30.8 (3C); IR (film)  $\nu_{\text{max}}$  3030, 2960, 1741, 1652, 1600, 1494, 1455, 1367, 1260, 1141, 1075, 1027, 983  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  326.1573 ( $\text{MH}^+$ ,  $\text{C}_{20}\text{H}_{23}\text{NOSH}^+$  requires 326.1573).



**(E)-3-(2-(butylthio)vinyl)oxazolidin-2-one (E-4a).** Prepared

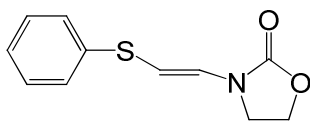
from **2** (30 mg, 0.27 mmol), *n*-butyl thiol (115  $\mu\text{L}$ , 96.2 mg, 1.07 mmol, 4 equiv), *t*-BuOH (300  $\mu\text{L}$ ), and AIBN (88.7 mg, 0.54 mmol, 2 equiv) according to the General Procedure with a 3 h reaction time. The crude product (*E*:*Z* = 8.4:1) was purified by flash

chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford *E*-**4a** (39.6 mg, 0.197 mmol, 73%) as an oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.97 (d, *J* = 13.5 Hz, 1H), 5.35 (d, *J* = 14.0 Hz, 1H), 4.46 (dd, *J* = 8.2, 8.0 Hz, 2H), 3.75 (dd, *J* = 9.0, 7.0 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.61–1.56 (m, 2H), 1.44–1.40 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 154.7, 127.6, 103.6, 62.1, 42.5, 34.2, 31.3, 21.8, 13.6; IR (film) ν<sub>max</sub> 3058, 2956, 2923, 2871, 1996, 1755, 1628, 1558, 1506, 1479, 1399, 1371, 1332, 1274, 1231, 1070, 1035, 977 cm<sup>-1</sup>; HRMS (ESI) *m/z* 202.0899 (MH<sup>+</sup>, C<sub>9</sub>H<sub>15</sub>NO<sub>2</sub>SH<sup>+</sup> requires 202.0896).

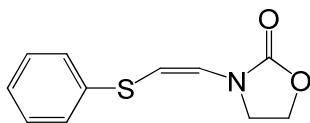


**(Z)-3-(2-(butylthio)vinyl)oxazolidin-2-one (Z-4a).** Prepared

from **2** (24.0 mg, 0.216 mmol), *n*-butyl thiol (23 μL, 19.2 mg, 0.213 mmol, 1 equiv), *t*-BuOH (300 μL), and AIBN (17.7 mg, 0.108 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E*:*Z* = 1:6.0) was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford *Z*-**4a** (31.3 mg, 0.155 mmol, 72%) as an oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.59 (d, *J* = 8.5 Hz, 1H), 5.27 (d, *J* = 9.0 Hz, 1H), 4.41 (dd, *J* = 8.7, 6.7 Hz, 2H), 4.23 (dd, *J* = 8.7, 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.63–1.59 (m, 2H), 1.44–1.40 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 156.5, 123.2, 106.5, 62.6, 44.9, 35.1, 31.9, 21.6, 13.6; IR (film) ν<sub>max</sub> 3027, 2956, 2925, 2871, 1760, 1653, 1617, 1558, 1540, 1506, 1479, 1407, 1326, 1267, 1205, 1078, 1031, 976 cm<sup>-1</sup>; HRMS (ESI) *m/z* 202.0901 (MH<sup>+</sup>, C<sub>9</sub>H<sub>15</sub>NO<sub>2</sub>SH<sup>+</sup> requires 202.0896).

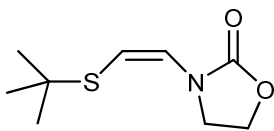


**(E)-3-(2-(phenylthio)vinyl)oxazolidin-2-one (E-4b).** Prepared from **2** (23.0 mg, 0.207 mmol), thiophenol (85  $\mu$ L, 91.5 mg, 0.830 mmol, 4 equiv), *t*-BuOH (300  $\mu$ L), and AIBN (68.0 mg, 0.414 mmol, 2 equiv) according to the General Procedure with a 5 h reaction time. The crude product (*E:Z* = 8.5:1) was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford **E-4b** (33.4 mg, 0.151 mmol, 73%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.32–7.24 (m, 5H), 7.20–7.17 (m, 1H), 5.52 (d, *J* = 13.5 Hz, 1H), 4.50 (t, *J* = 8.0 Hz, 2H), 3.81 (t, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  154.6, 137.0, 132.0, 129.0 (2C), 127.7 (2C), 126.1, 100.6, 62.2, 42.5; IR (film)  $\nu_{\text{max}}$  3068, 2922, 1748, 1623, 1582, 1510, 1479, 1439, 1418, 1329, 1279, 1210, 1085, 1031, 976 cm<sup>-1</sup>; HRMS (ESI) *m/z* 222.0592 (MH<sup>+</sup>, C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>SH<sup>+</sup> requires 222.0583).



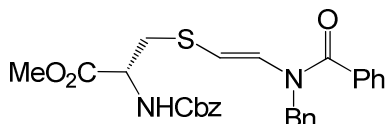
**(Z)-3-(2-(phenylthio)vinyl)oxazolidin-2-one (Z-4b).** Prepared from **2** (30 mg, 0.27 mmol), thiophenol (28  $\mu$ L, 30.1 mg, 0.273 mmol, 1 equiv), *t*-BuOH (300  $\mu$ L), and AIBN (22.2 mg, 0.135 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E:Z* = 1:5.1) was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford **Z-4b** (44.2 mg, 0.200 mmol, 74%) as a colorless oil: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.34–7.29 (m, 4H), 7.23–7.19 (m, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 4.41 (t, *J* = 8.5 Hz, 2H), 4.29 (t, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  156.4, 136.6, 129.2 (2C), 128.3, 127.5 (2C), 126.2, 100.8, 62.7, 44.8; IR (film)  $\nu_{\text{max}}$  3068, 3044, 2998, 1746, 1625,

1578, 1475, 1437, 1402, 1235, 1180, 1083, 1034, 980  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  222.05867 ( $\text{MH}^+$ ,  $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{SH}^+$  requires 222.05833).



**(Z)-3-(2-(tert-butylthio)vinyl)oxazolidin-2-one (Z-4c).** Prepared from **2** (30 mg, 0.27 mmol), *tert*-butyl thiol (121  $\mu\text{L}$ , 96.8 mg, 1.07 mmol, 4 equiv), *t*-BuOH (300  $\mu\text{L}$ ), and AIBN (88.7 mg, 0.54 mmol, 2 equiv) according to the General Procedure with a 6 h reaction time. The crude product ( $E:Z = 1:5.2$ ) was purified by flash chromatography ( $\text{SiO}_2$ , 20% acetone in hexanes elution) to afford **Z-4c** (39.1 mg, 0.194 mmol, 72%) and **E-4c** (7.6 mg, 0.038 mmol, 14%), both as colorless oils. For **Z-4c**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.72 (d,  $J = 9.0$  Hz, 1H), 5.42 (d,  $J = 9.0$  Hz, 1H), 4.39 (t,  $J = 8.5$  Hz, 2H), 4.23 (t,  $J = 8.5$  Hz, 2H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  156.6, 125.6, 101.8, 62.6, 45.4, 44.8, 30.3 (3C); IR (film)  $\nu_{\text{max}}$  2963, 2239, 1755, 1623, 1582, 1480, 1402, 1234, 1079, 1037  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  202.0891 ( $\text{MH}^+$ ,  $\text{C}_9\text{H}_{15}\text{NO}_2\text{SH}^+$  requires 202.0896).

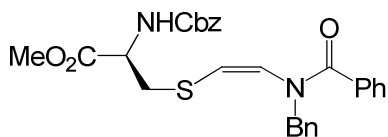
For **E-4c**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.12 (d,  $J = 14.0$  Hz, 1H), 5.41 (d,  $J = 13.5$  Hz, 1H), 4.46 (t,  $J = 8.0$  Hz, 2H), 3.77 (t,  $J = 8.0$  Hz, 2H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  154.6, 132.6, 99.8, 62.1, 44.2, 42.5, 30.4 (3C); IR (film)  $\nu_{\text{max}}$  2963, 1745, 1614, 1481, 1416, 1363, 1286, 1213, 1090, 1032  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  202.0884 ( $\text{MH}^+$ ,  $\text{C}_9\text{H}_{15}\text{NO}_2\text{SH}^+$  requires 202.0896).



**(E)-Methyl 3-(2-(N-benzylbenzamido)vinylthio)-2-(benzyloxycarbonylamino)propanoate (E-6).** Prepared from **1** (10.0 mg, 0.042 mmol),



**5**<sup>1</sup> (22.9 mg, 0.085 mmol, 2 equiv), *t*-BuOH (300 μL), and AIBN (14.0 mg, 0.085 mmol, 2 equiv) according to the General Procedure with a 3 h reaction time. The crude product (*E*:*Z* = 8.5:1) was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford *E*-**6** (14.6 mg, 0.029 mmol, 68%) as an oil:  $[\alpha]_D^{25} -4.7$  (*c* 0.15, EtOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.56–7.50 (m, 2H), 7.49–7.41 (m, 3H), 7.38–7.30 (m, 7H), 7.27–7.20 (m, 4H), 5.43–5.40 (m, 1H), 5.42 (d, *J* = 14.0 Hz, 1H), 5.12 (d, *J* = 11.5 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.96 (br s, 2H), 4.50–4.46 (m, 1H), 3.60 (s, 3H), 2.92–2.83 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 170.9, 170.4, 155.5, 136.2, 136.0, 134.4, 130.9, 128.9 (3C), 128.7 (2C), 128.6 (3C), 128.3 (2C), 128.2 (3C), 127.4 (2C), 126.6, 67.1, 53.4, 52.5, 47.3, 37.2; IR (film)  $\nu_{\max}$  3352, 3022, 2992, 2981, 1717, 1653, 1507, 1423, 1207, 1110, 1008, 950 cm<sup>-1</sup>; HRMS (ESI) *m/z* 505.1795 (MH<sup>+</sup>, C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>SH<sup>+</sup> requires 505.1792).

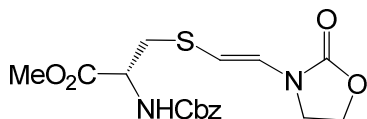


**(Z)-Methyl 3-(2-(N-benzylbenzamido)vinylthio)-2-**

**(benzyloxycarbonylamino)propanoate (Z-6).** Prepared from **1** (10.0 mg, 0.042 mmol), **5**<sup>1</sup> (11.4 mg, 0.042 mmol, 1 equiv), *t*-BuOH (300 μL), and AIBN (3.5 mg, 0.021 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E*:*Z* = 1:6.1) was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes elution) to afford *Z*-**6** (14.4 mg, 0.029 mmol, 67%) as an oil:  $[\alpha]_D^{25} -30$  (*c* 0.5, EtOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.42–7.38 (m, 1H), 7.36–7.29 (m, 11H), 7.27–7.23 (m, 1H), 6.01 (br s, 1H), 5.42 (d, *J* = 7.0 Hz, 1H), 5.33 (d, *J* = 5.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 15.0 Hz,

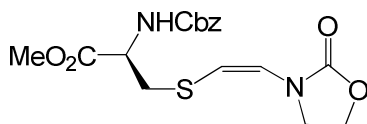
<sup>1</sup> Tao, F.; Luo, Y.; Huang, Q.; Liu, Y.; Li, B.; Zhang, G. *Amino Acids* **2009**, *37*, 603.

1H), 4.90 (d,  $J = 15.0$  Hz, 1H), 4.57–4.53 (m, 1H), 3.72 (s, 3H), 3.13–3.06 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  170.9, 170.4, 155.7, 137.5, 136.3, 135.9, 130.7, 128.8 (2C), 128.7 (3C), 128.5 (2C), 128.4 (3C), 128.2 (3C), 127.6 (2C), 120.3, 67.4, 54.4, 53.0, 50.0, 37.0; IR (film)  $\nu_{\text{max}}$  3334, 3032, 2953, 1718, 1652, 1517, 1437, 1343, 1214, 1055  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  505.1798 ( $\text{MH}^+$ ,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_5\text{SH}^+$  requires 505.1792).



**(E)-Methyl 2-(benzyloxycarbonylamino)-3-(2-(2-**

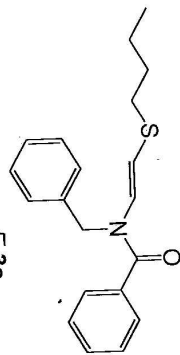
**oxooxazolidin-3-yl)vinylthio)propanoate (E-7).** Prepared from **2** (10.0 mg, 0.090 mmol), **5**<sup>1</sup> (48.4 mg, 0.18 mmol, 2 equiv), *t*-BuOH (300  $\mu\text{L}$ ), and AIBN (14.8 mg, 0.090 mmol, 1 equiv) according to the General Procedure with a 2.5 h reaction time. The crude product ( $E:Z = 10:1$ ) was purified by flash chromatography ( $\text{SiO}_2$ , 20–30% acetone in hexanes gradient elution) to afford *E-7* (24.3 mg, 0.064 mmol, 71%) as a colorless oil:  $[\alpha]_{\text{D}}^{25} +11$  ( $c$  0.18,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.37–7.31 (m, 5H), 7.07 (d,  $J = 13.5$  Hz, 1H), 5.56 (d,  $J = 8.0$  Hz, 1H), 5.27 (d,  $J = 14.0$  Hz, 1H), 5.16 (d,  $J = 12.0$  Hz, 1H), 5.09 (d,  $J = 12.5$  Hz, 1H), 4.65–4.61 (m, 1H), 4.40–4.33 (m, 2H), 3.76 (s, 3H), 3.63–3.55 (m, 2H), 3.08 (dd,  $J = 14.0, 5.0$  Hz, 1H), 3.01 (dd,  $J = 14.0, 5.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  170.9, 155.5, 154.4, 136.1, 130.5, 128.5 (2C), 128.2, 128.1 (2C), 101.3, 67.1, 62.1, 53.7, 52.7, 42.2, 37.3; IR (film)  $\nu_{\text{max}}$  3333, 3032, 2953, 1746, 1620, 1524, 1409, 1329, 1210, 1085, 1036  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  398.1362 ( $\text{MNH}_4^+$ ,  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_6\text{SNH}_4^+$  requires 398.1380).



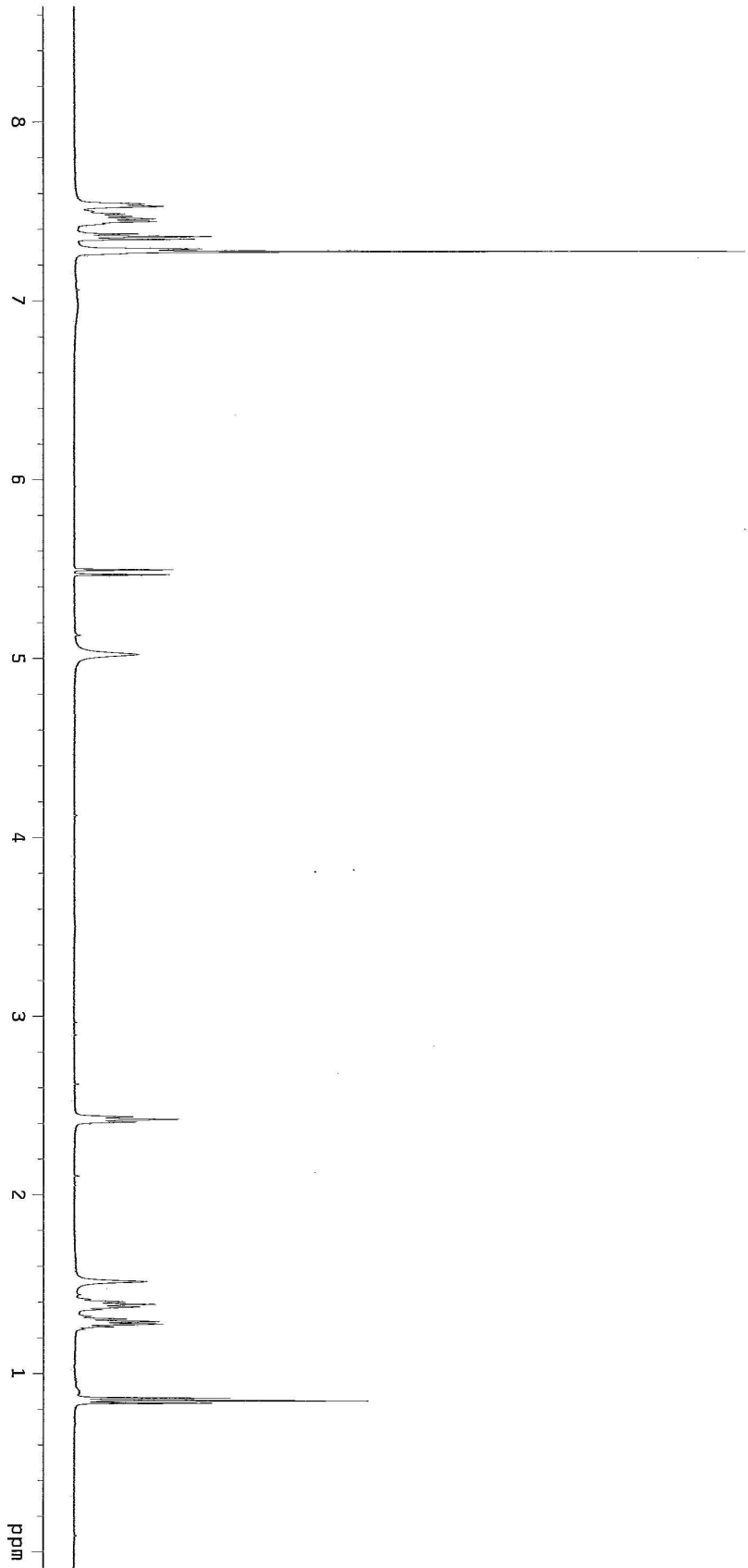
**(Z)-Methyl 2-(benzyloxycarbonylamino)-3-(2-(2-**

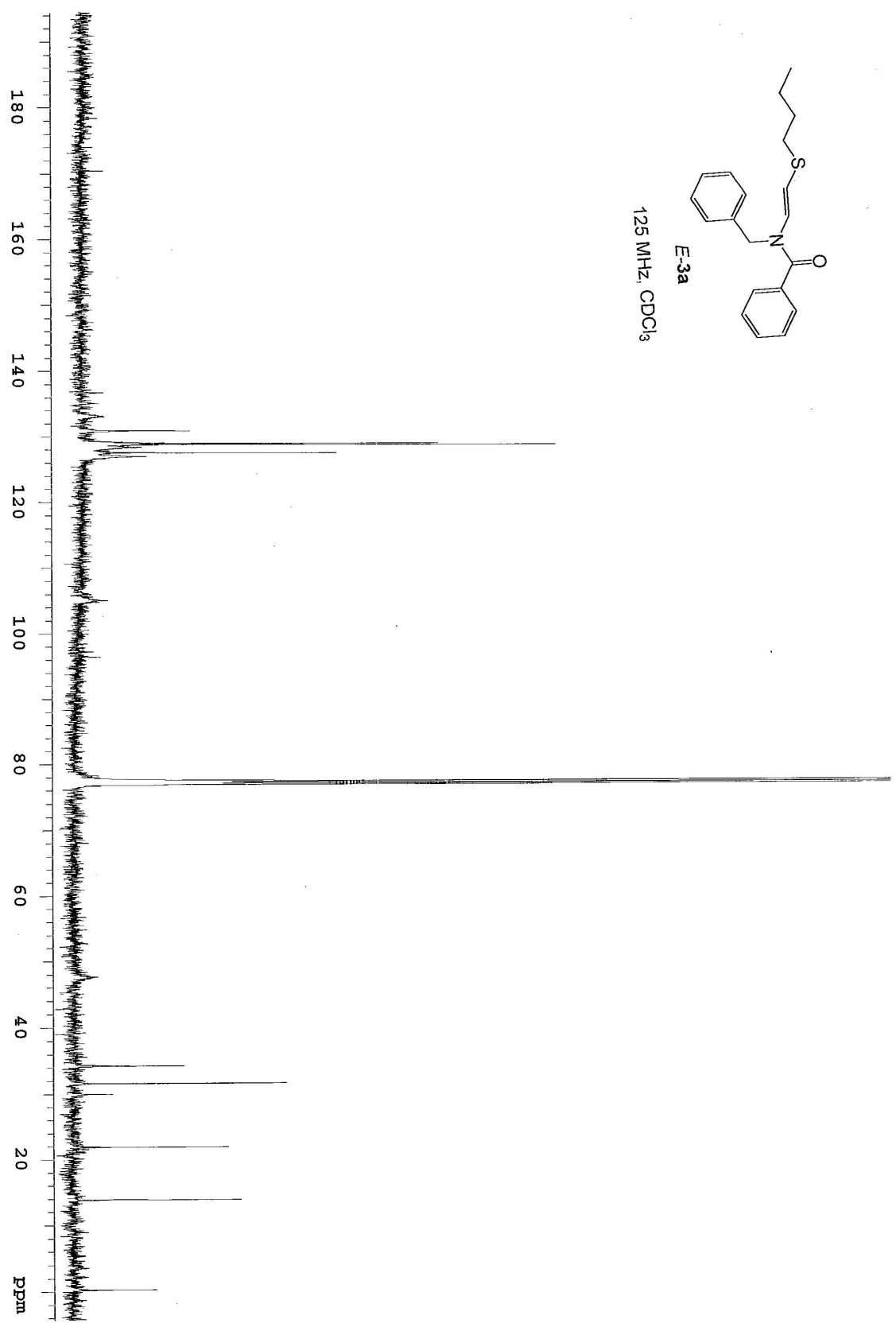
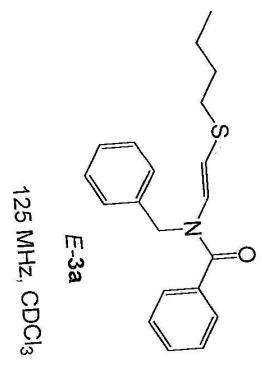
**oxooxazolidin-3-yl)vinylthio)propanoate (Z-7).** Prepared from **2** (10.0 mg, 0.090

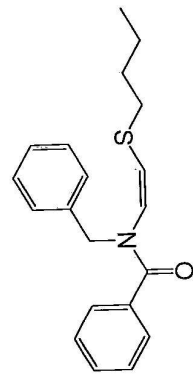
mmol), **5**<sup>1</sup> (24.2 mg, 0.090 mmol, 1 equiv), *t*-BuOH (300  $\mu$ L), and AIBN (7.4 mg, 0.045 mmol, 0.5 equiv) according to the General Procedure with a 10 min reaction time. The crude product (*E*:*Z* = 1:2.9) was purified by flash chromatography (SiO<sub>2</sub>, 20–30% acetone in hexanes gradient elution) to afford **Z-7** (20.5 mg, 0.054 mmol, 60%) as a colorless oil:  $[\alpha]_{\text{D}}^{25} +22$  (*c* 0.15, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.39–7.33 (m, 5H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.57 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 8.5 Hz, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 4.68–4.63 (m, 1H), 4.38–4.31 (m, 2H), 4.15 (t, *J* = 7.8 Hz, 2H), 3.75 (s, 3H), 3.18 (dd, *J* = 14.5, 4.0 Hz, 1H), 3.06 (dd, *J* = 14.2, 4.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.6, 156.4, 155.5, 136.0, 128.6 (2C), 128.4, 128.2 (2C), 125.2, 103.7, 67.2, 62.6, 54.0, 52.7, 44.7, 38.0; IR (film)  $\nu_{\text{max}}$  3337, 2954, 1748, 1630, 1519, 1403, 1341, 1237, 1039 cm<sup>-1</sup>; HRMS (ESI) *m/z* 398.1377 (MNH<sub>4</sub><sup>+</sup>, C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>SNH<sub>4</sub><sup>+</sup> requires 398.1380).



500 MHz, CDCl<sub>3</sub>

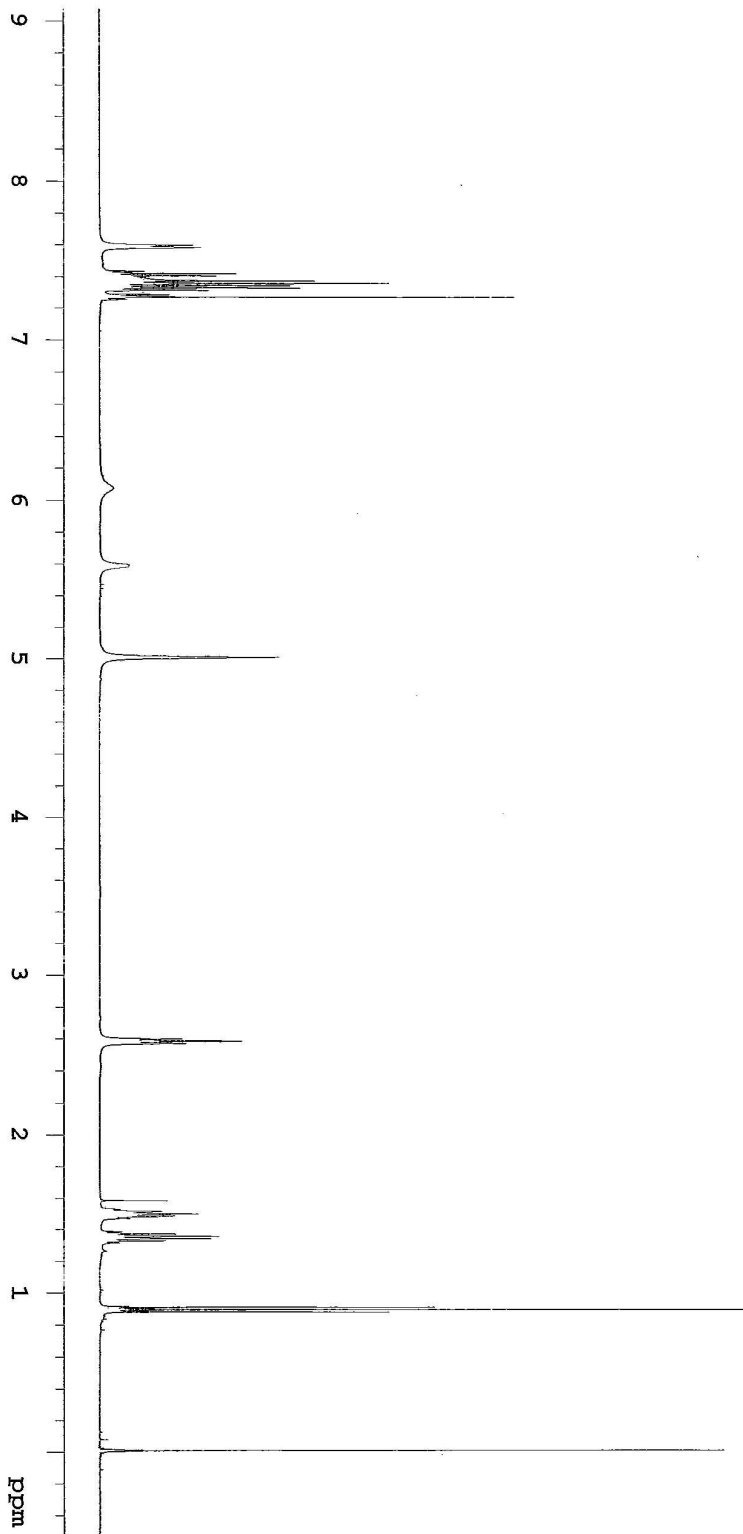


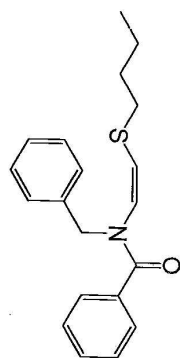




Z-3a

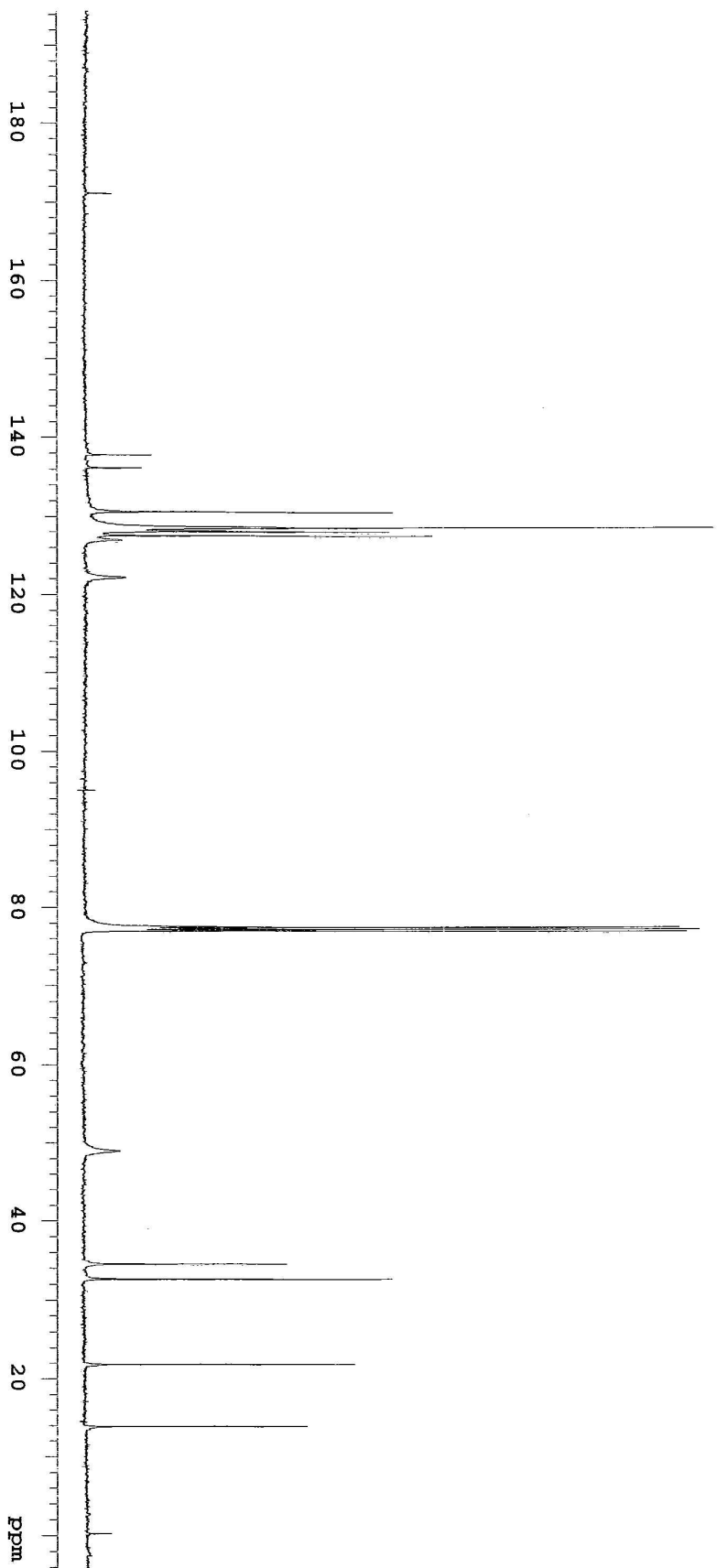
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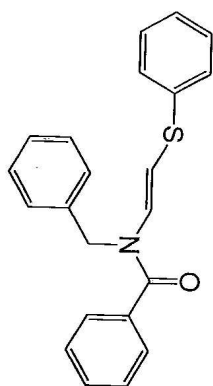




Z-3a

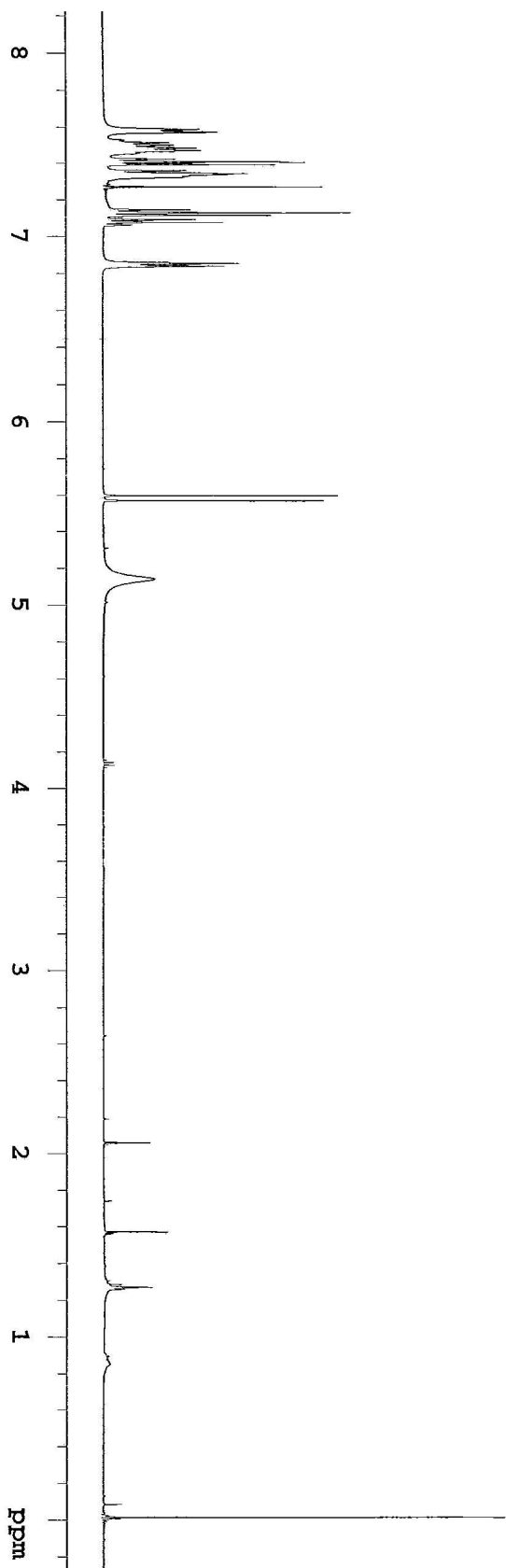
125 MHz, CDCl<sub>3</sub>



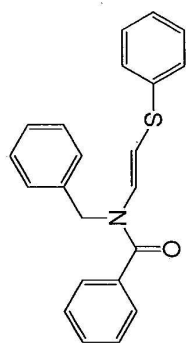


*E-3b*

500 MHz, CDCl<sub>3</sub>

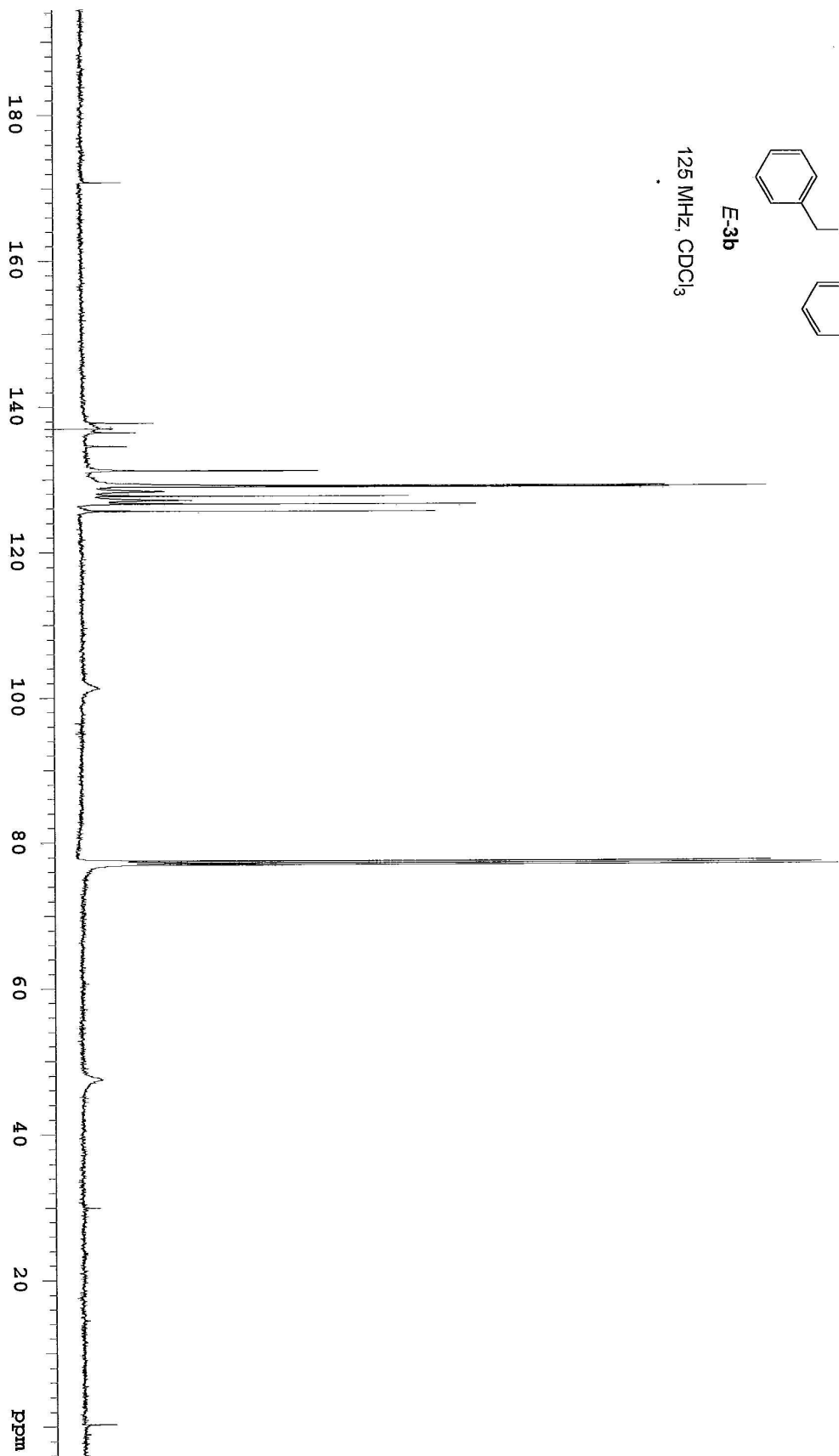


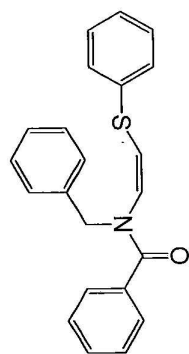




*E*-3b

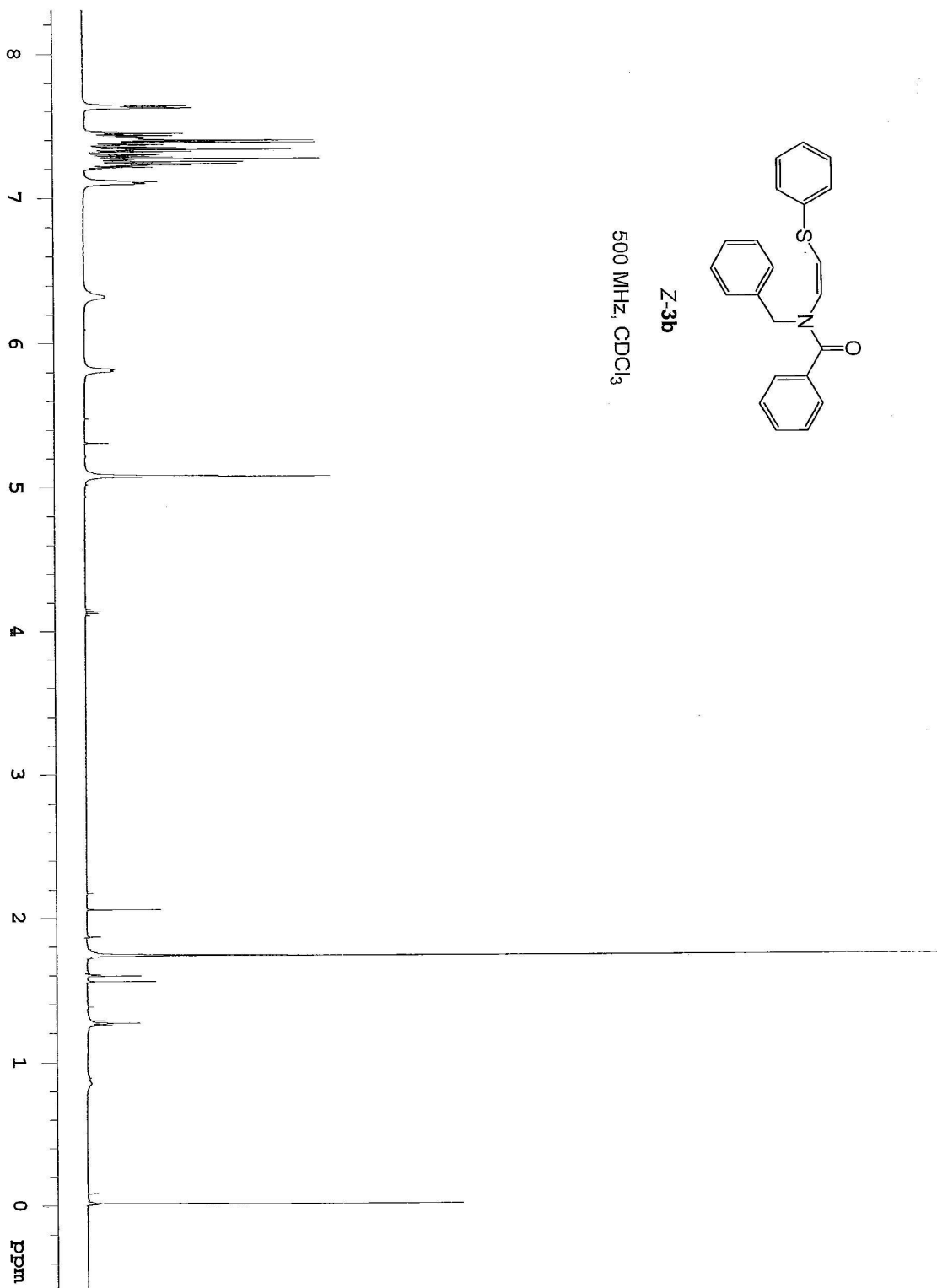
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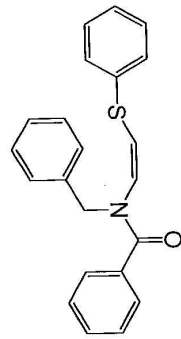




**Z-3b**

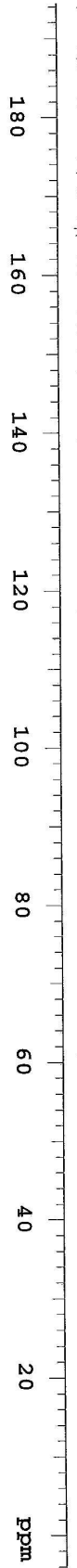
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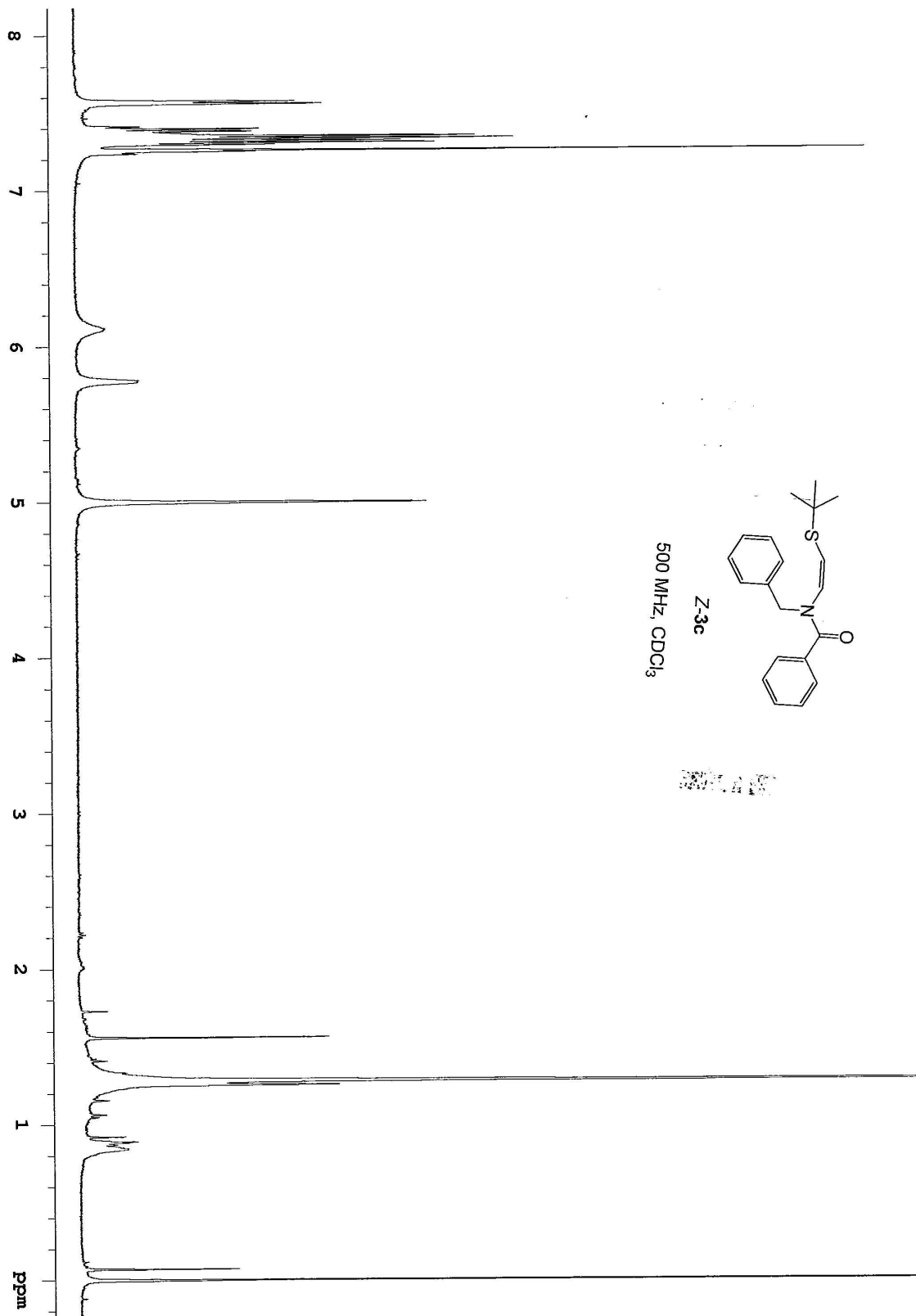


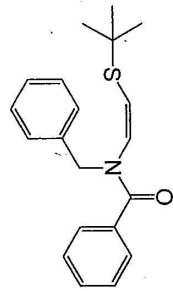


Z-3b

125 MHz, CDCl<sub>3</sub>

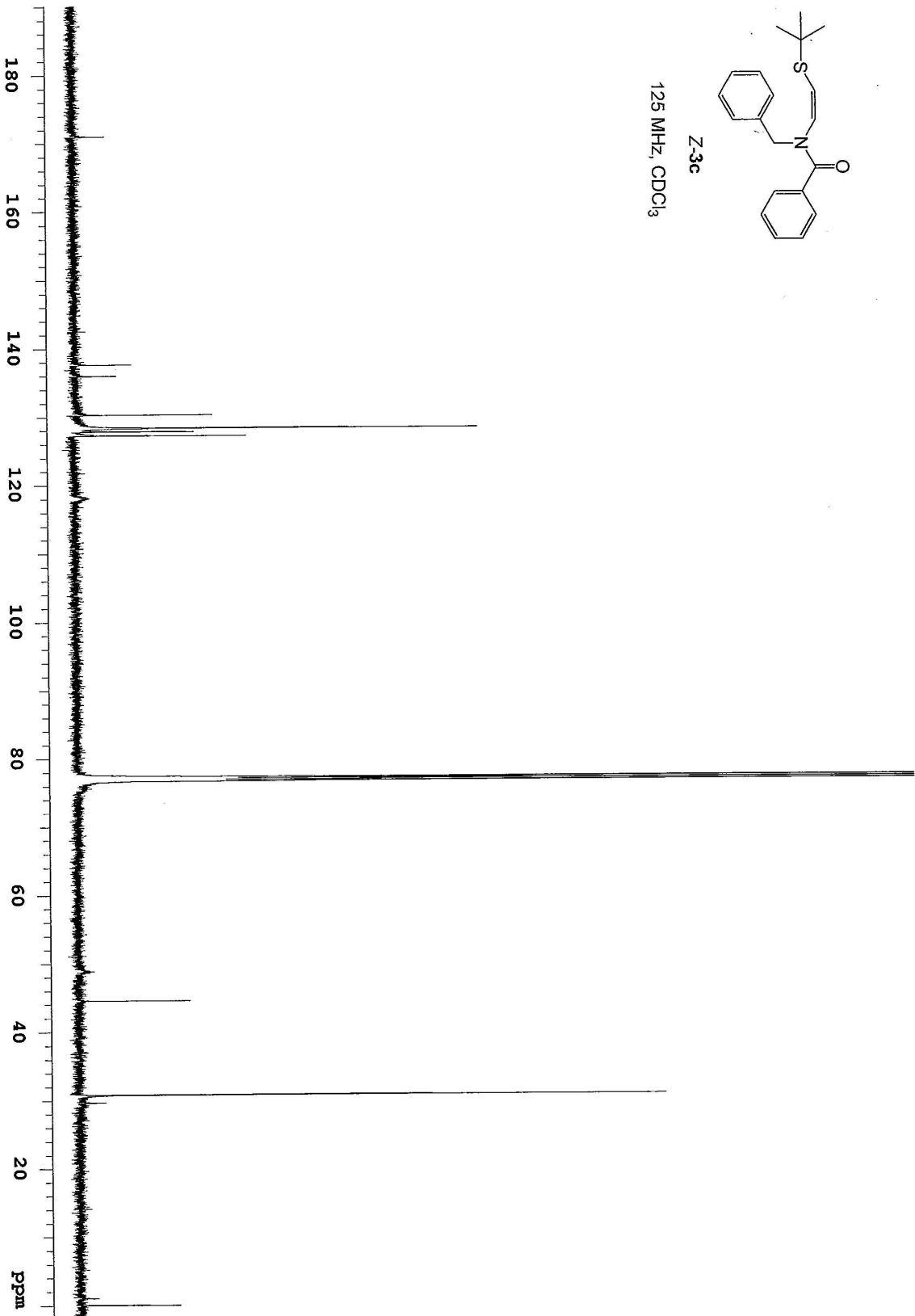


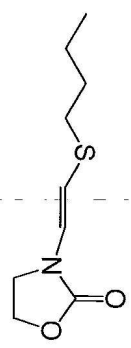




Z-3c

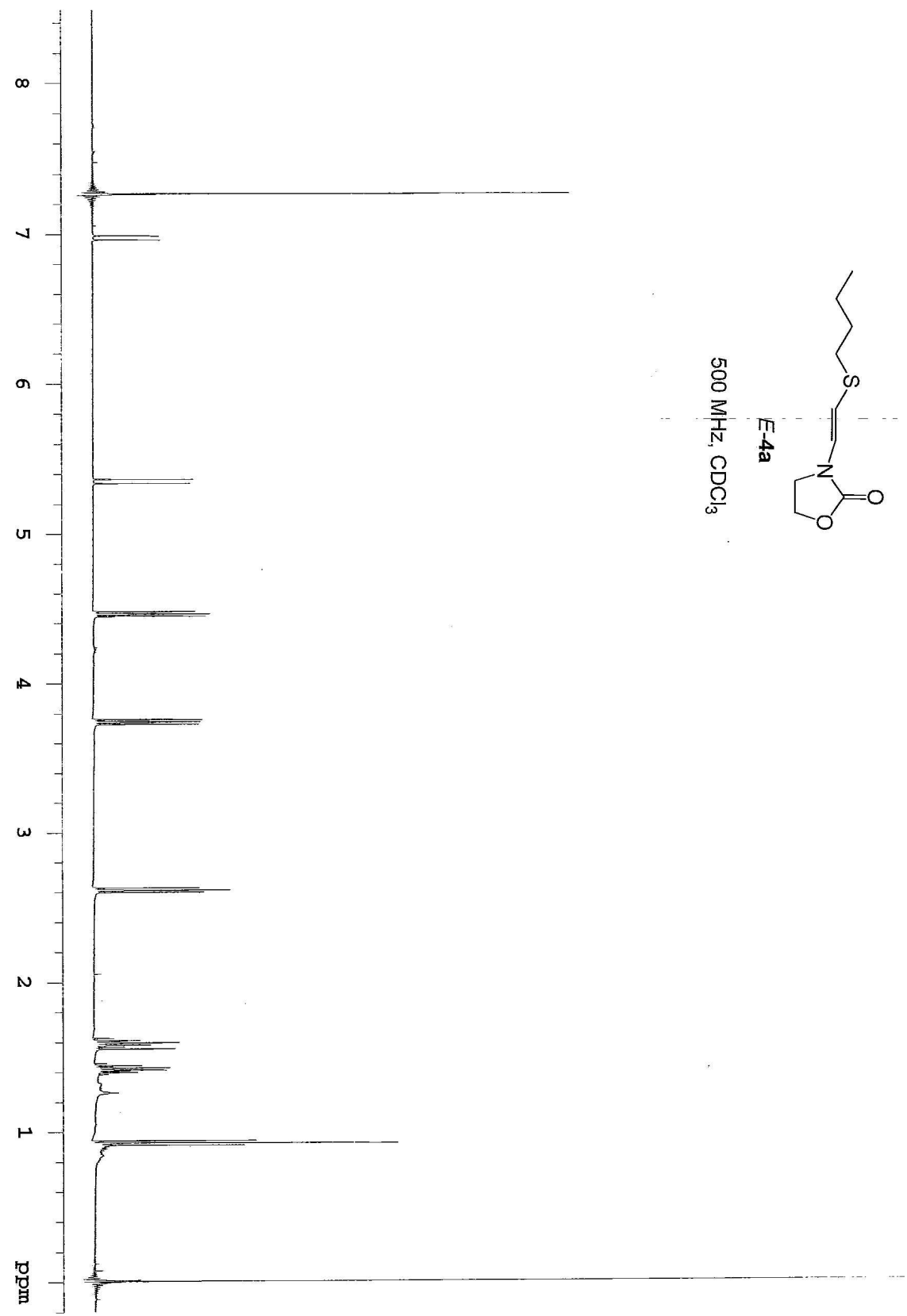
125 MHz, CDCl<sub>3</sub>

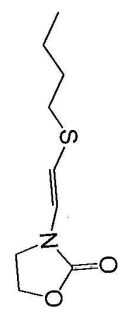




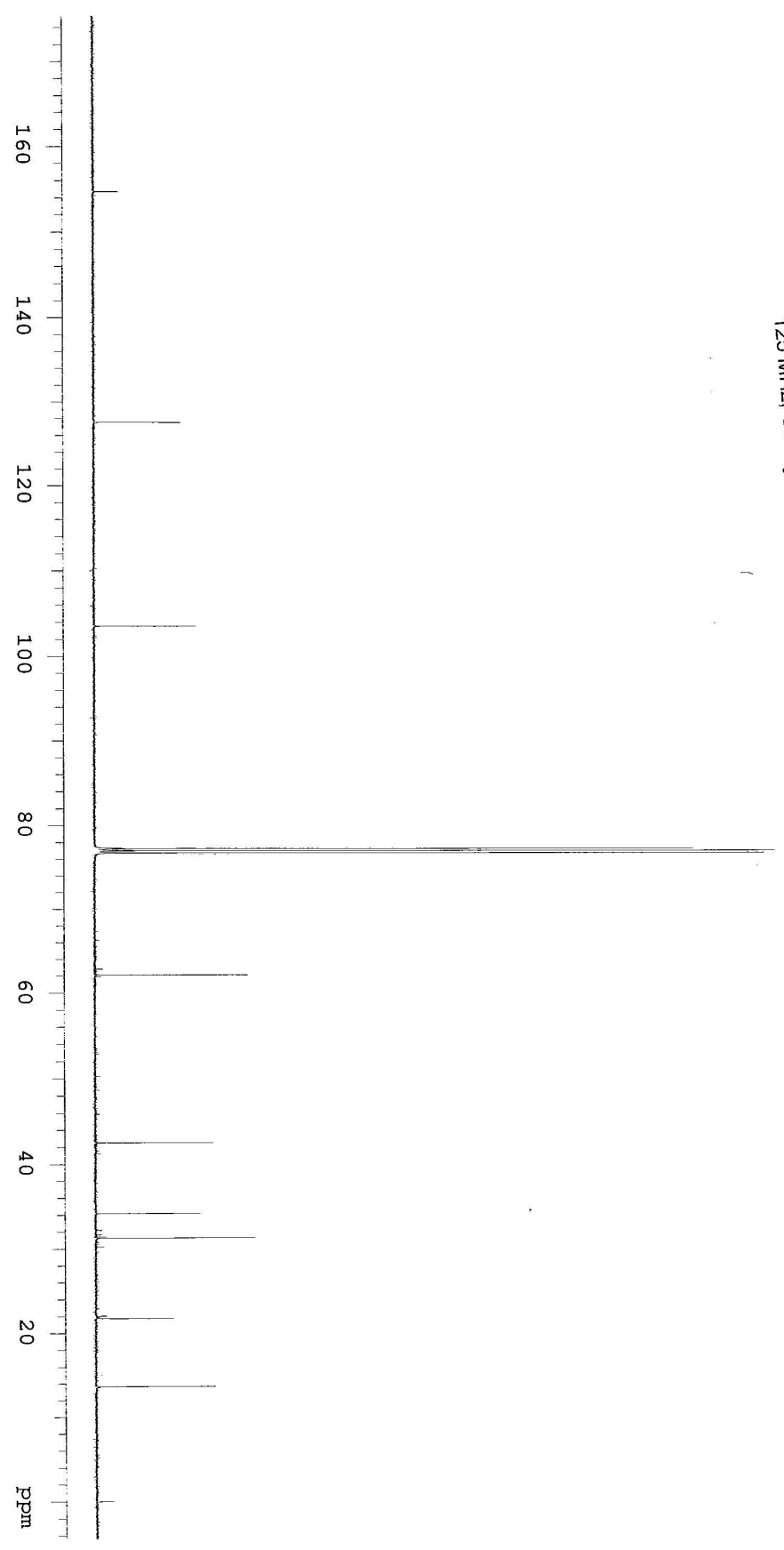
*E*-4a

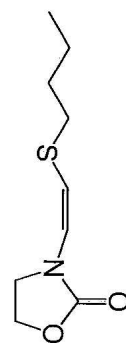
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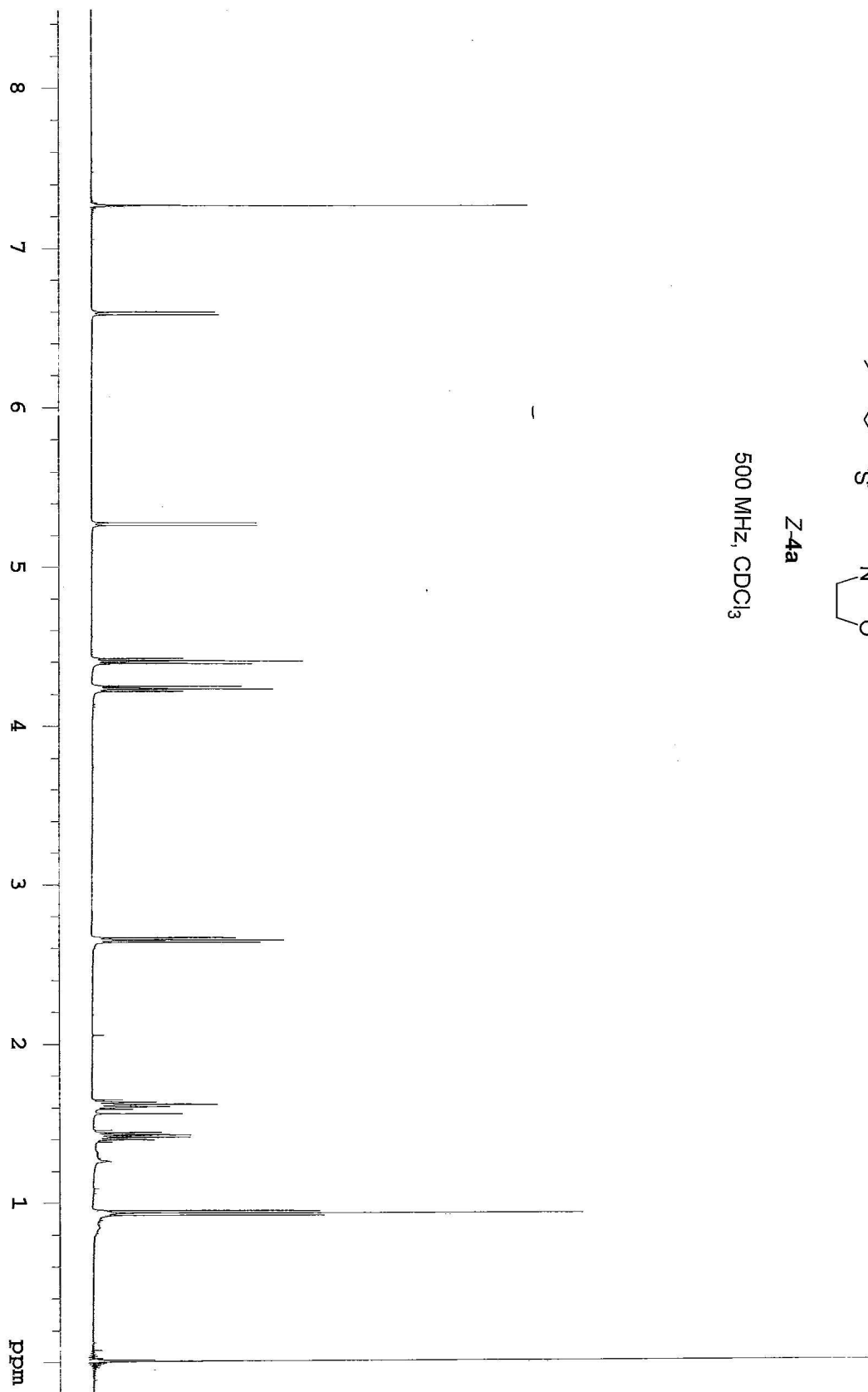
125 MHz, CDCl<sub>3</sub>





Z-4a

500 MHz, CDCl<sub>3</sub>

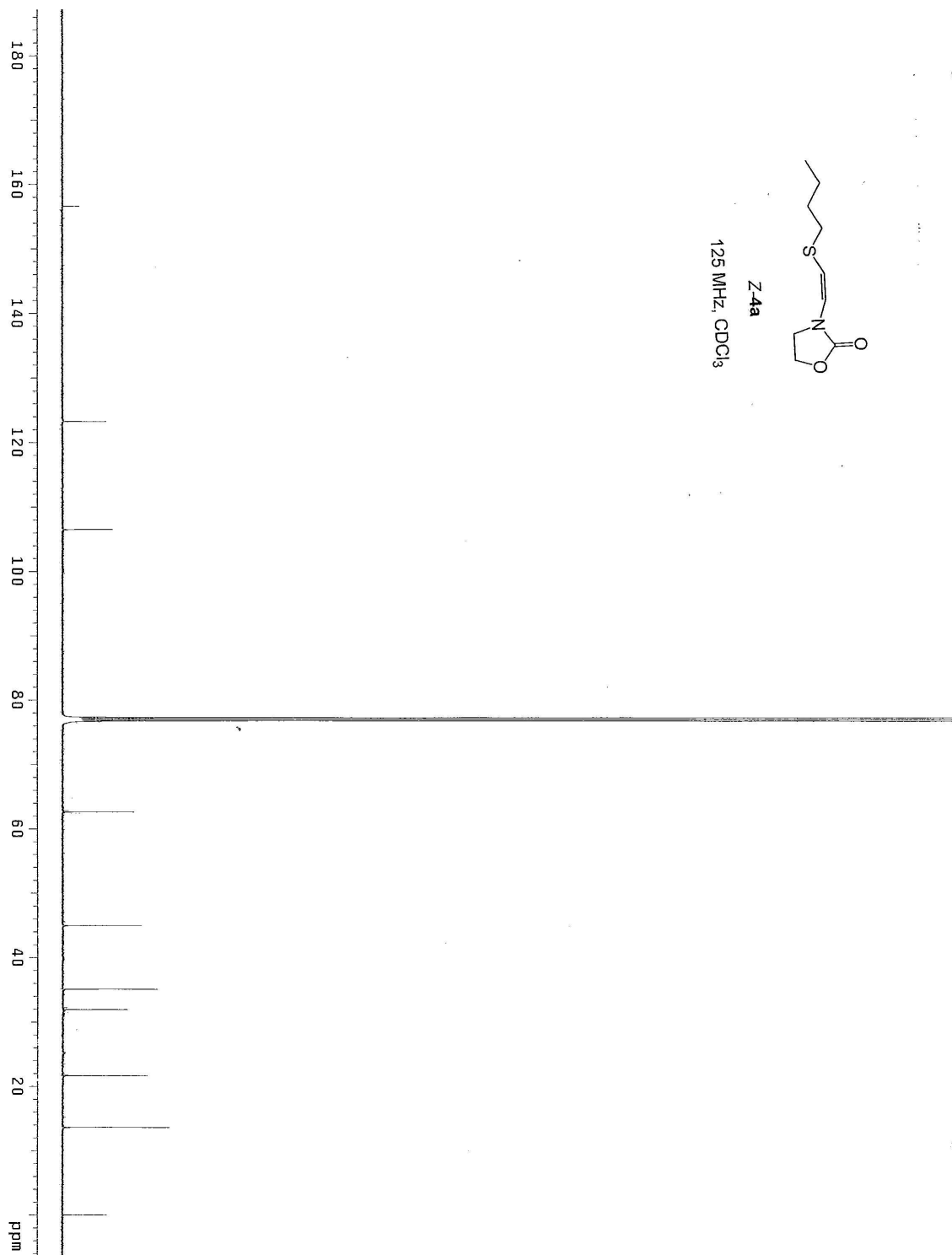


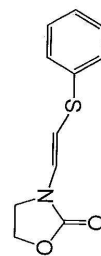




Z-4a

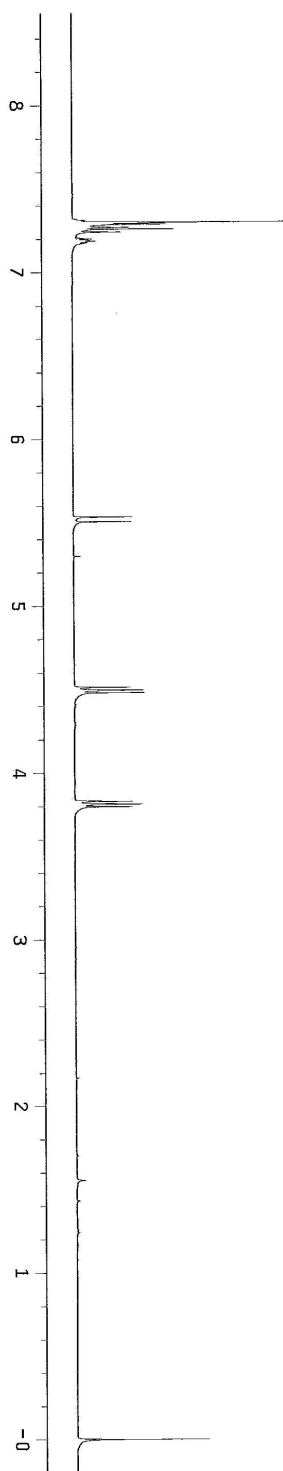
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**E-4b**

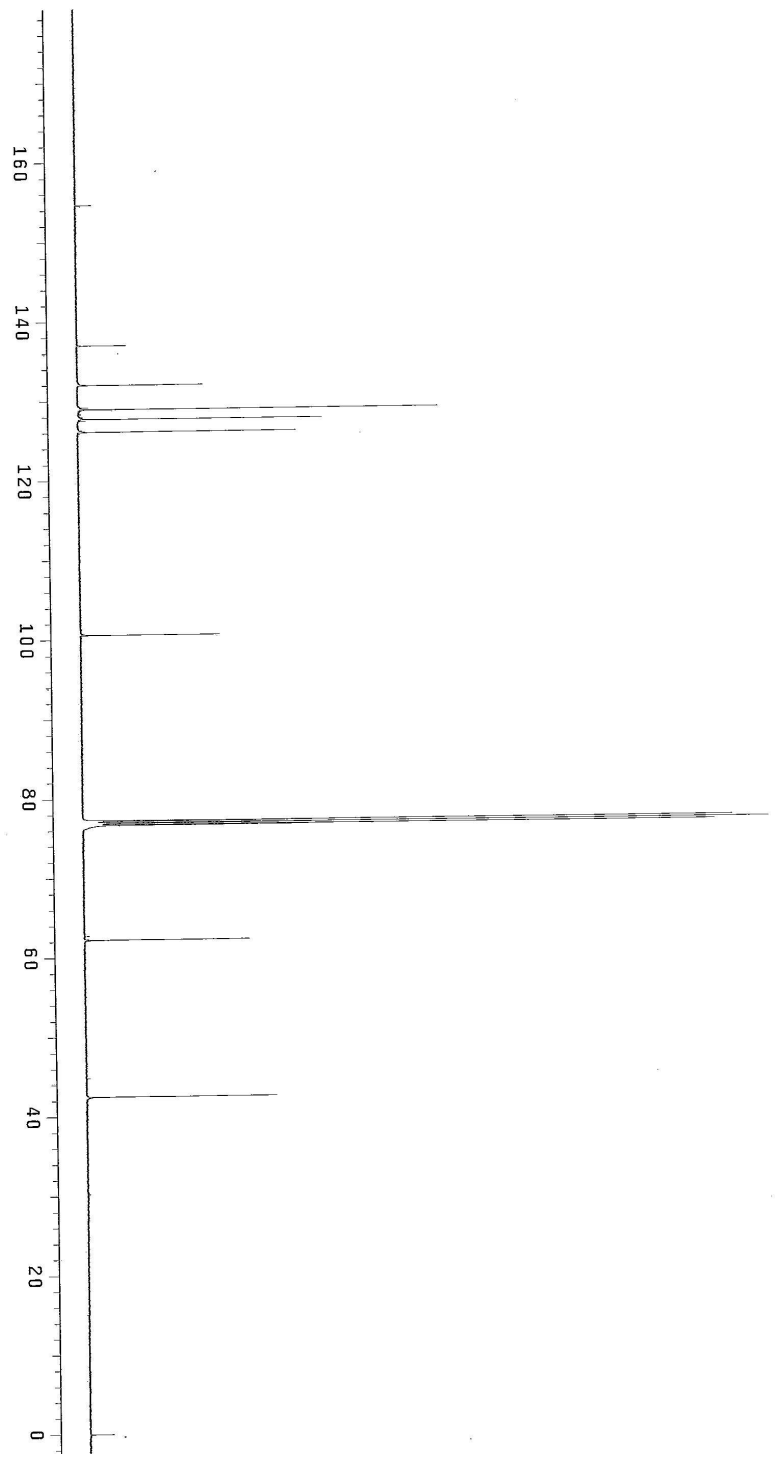
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**E-4b**

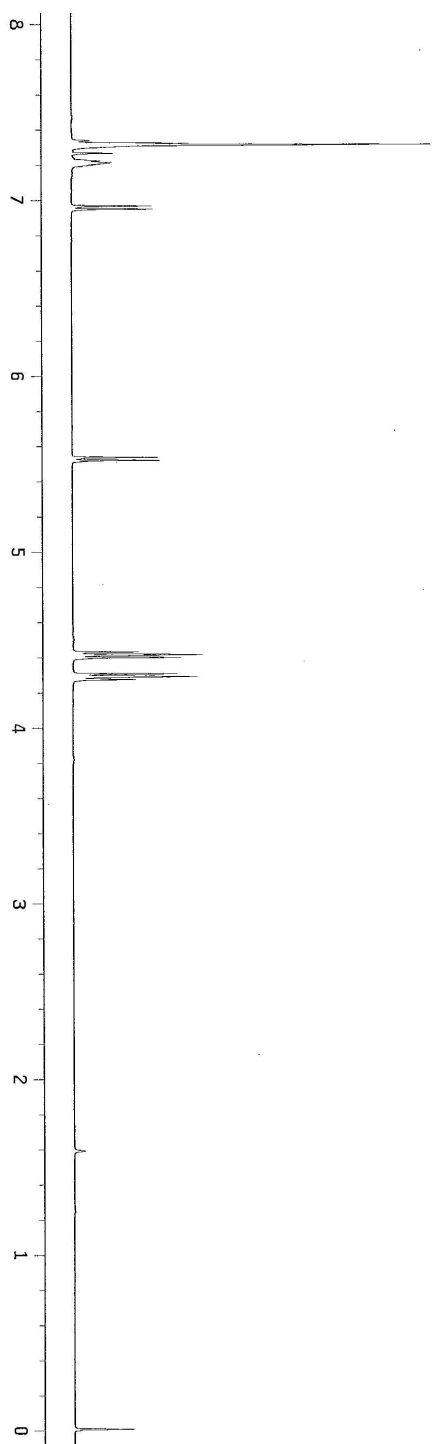
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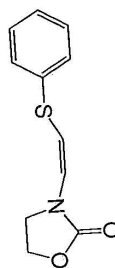




Z-4b

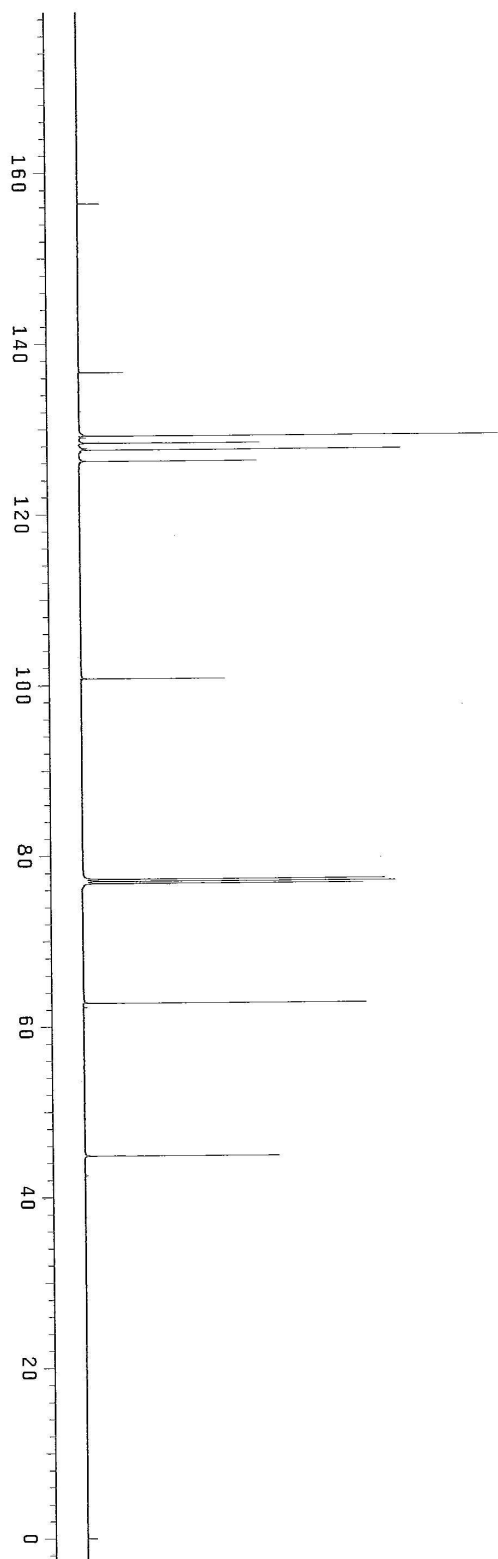
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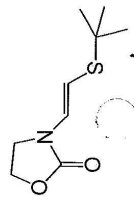




Z-4b

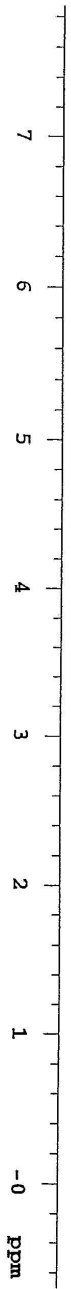
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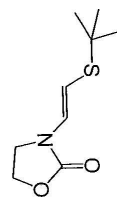




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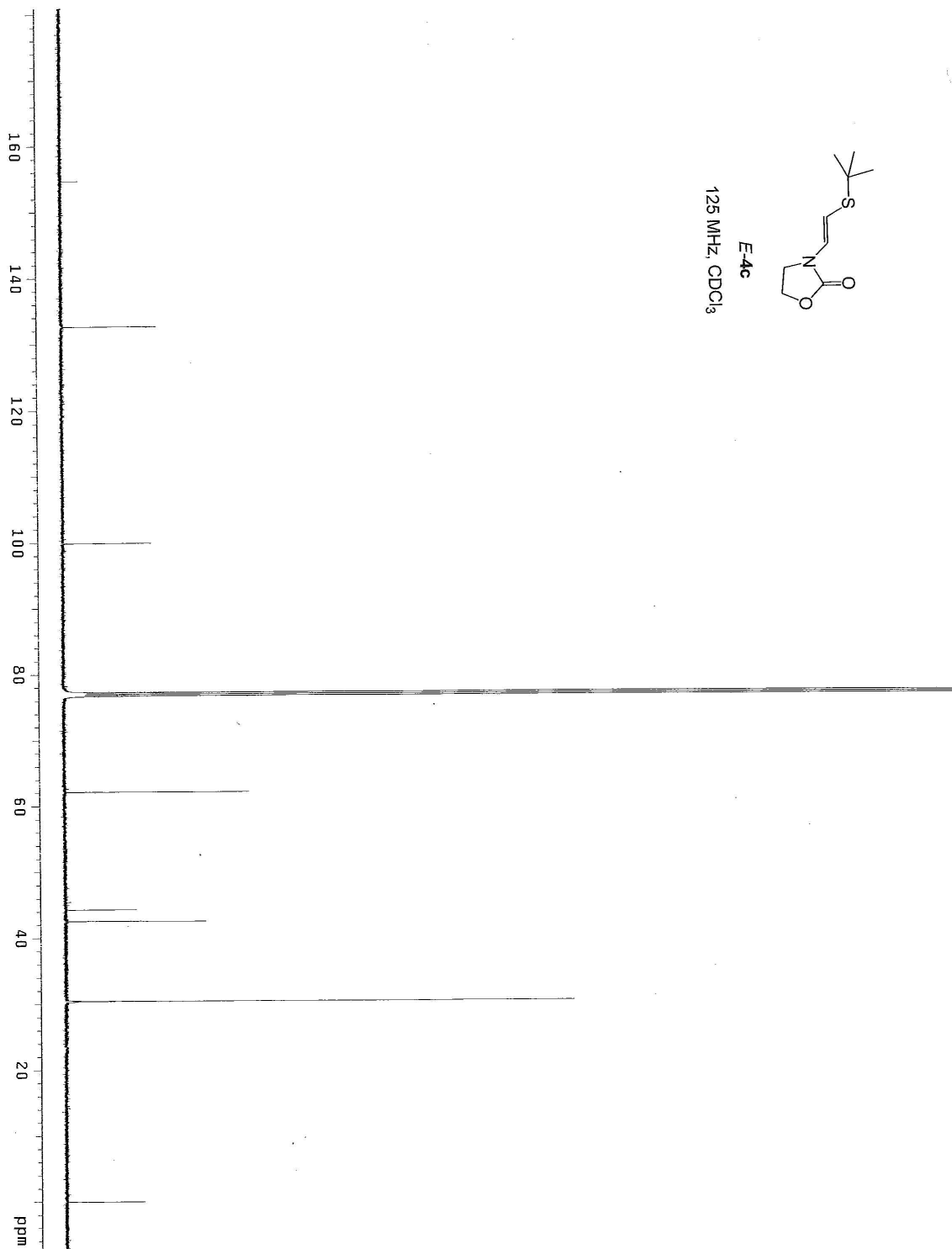
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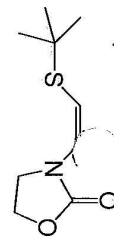




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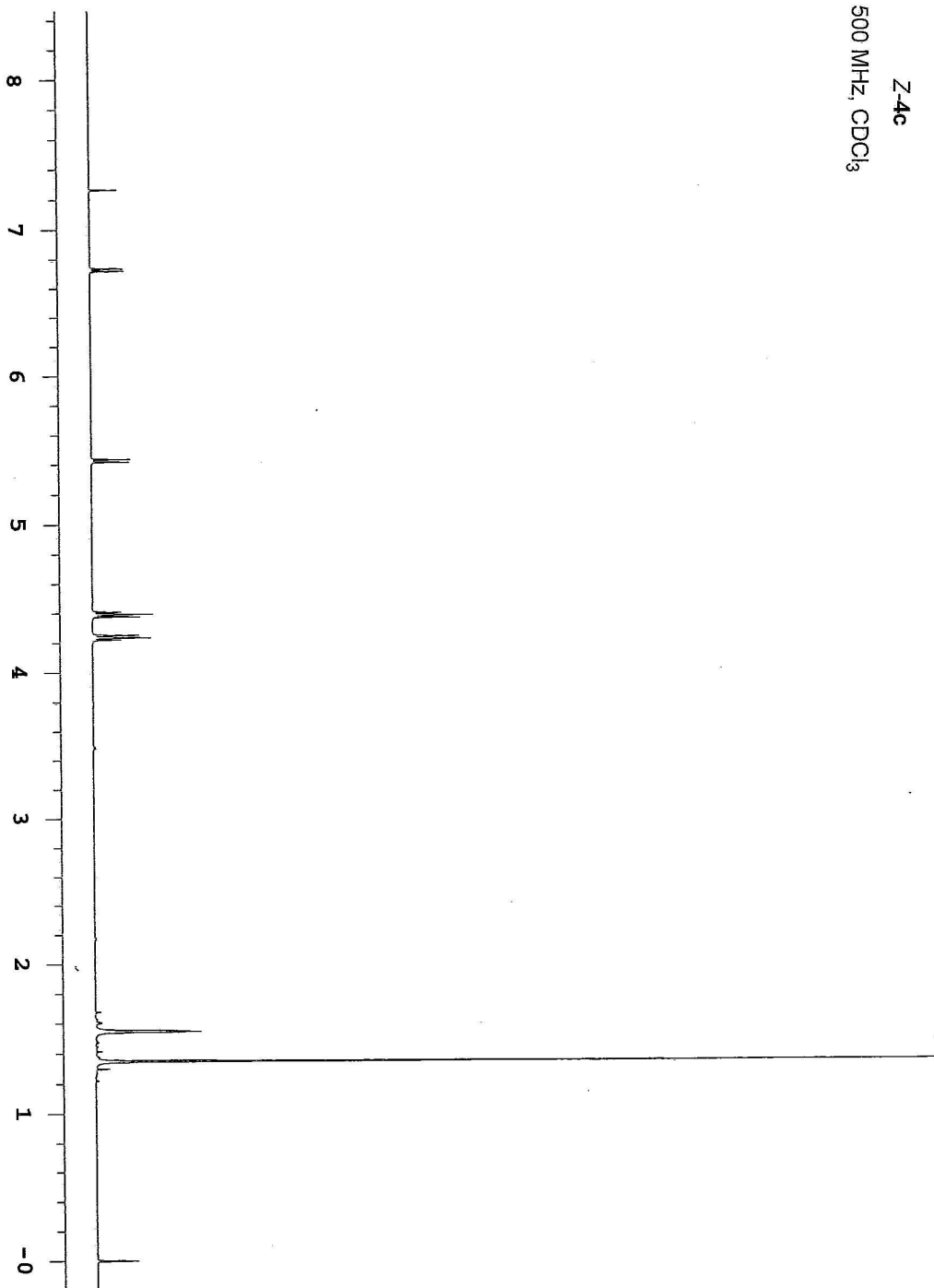
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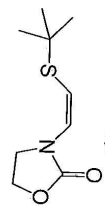


Z-4c

500 MHz, CDCl<sub>3</sub>

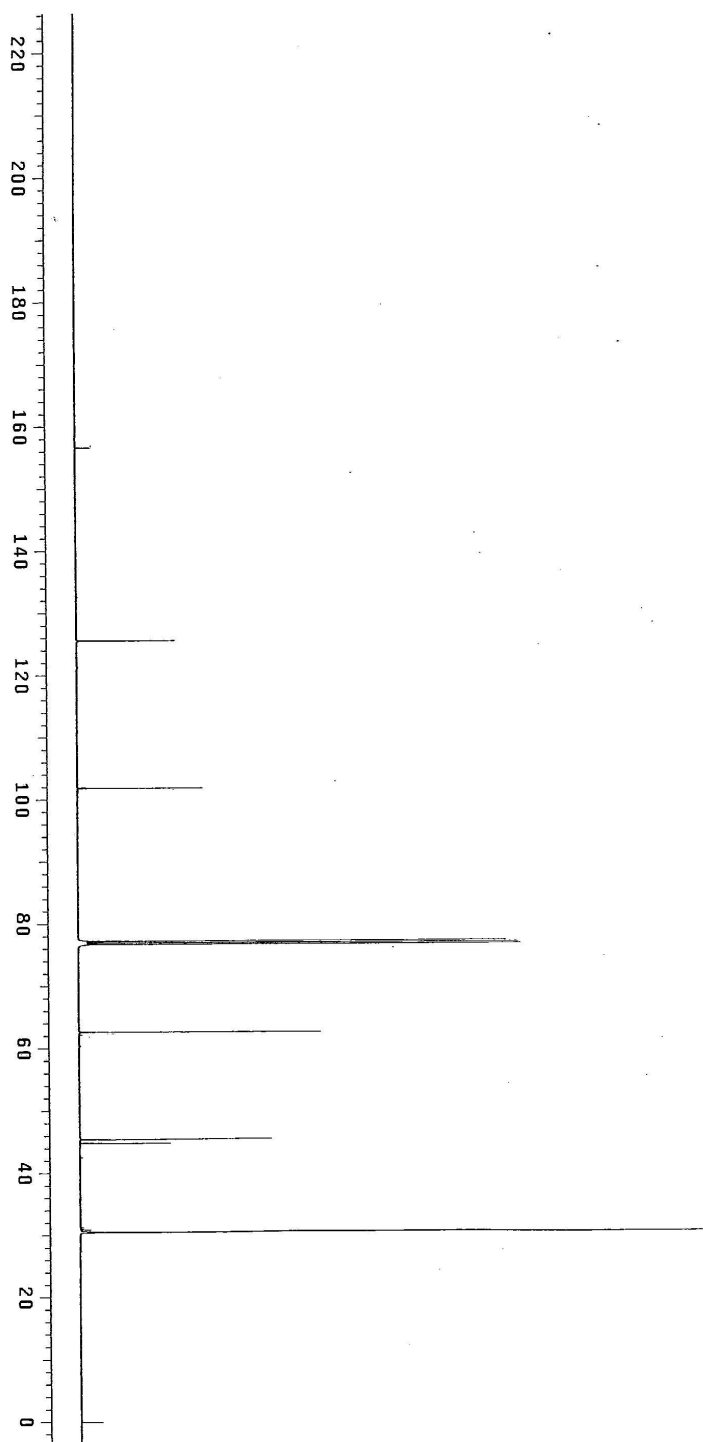


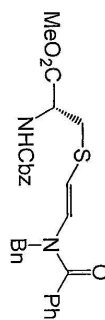




Z-4c

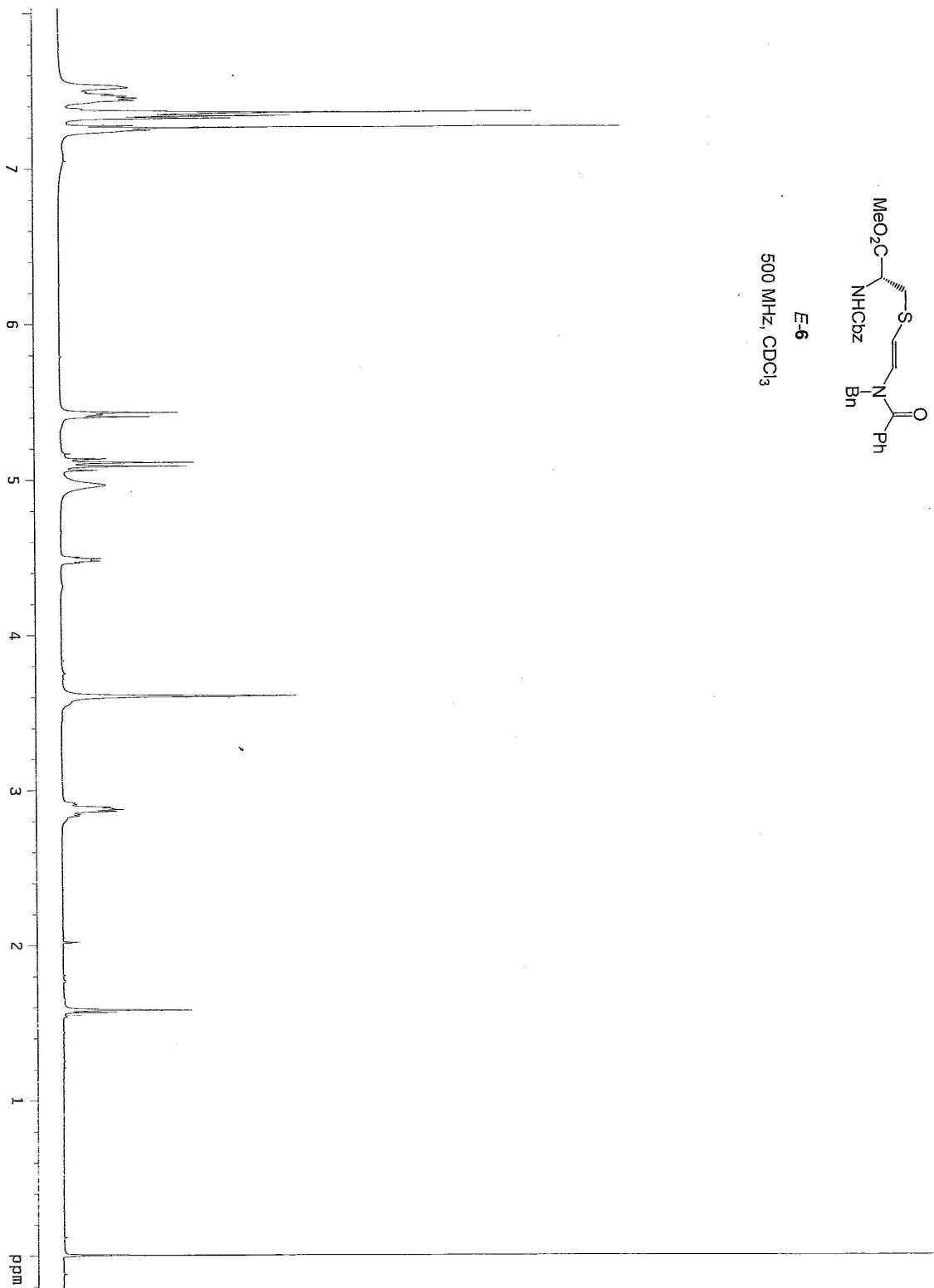
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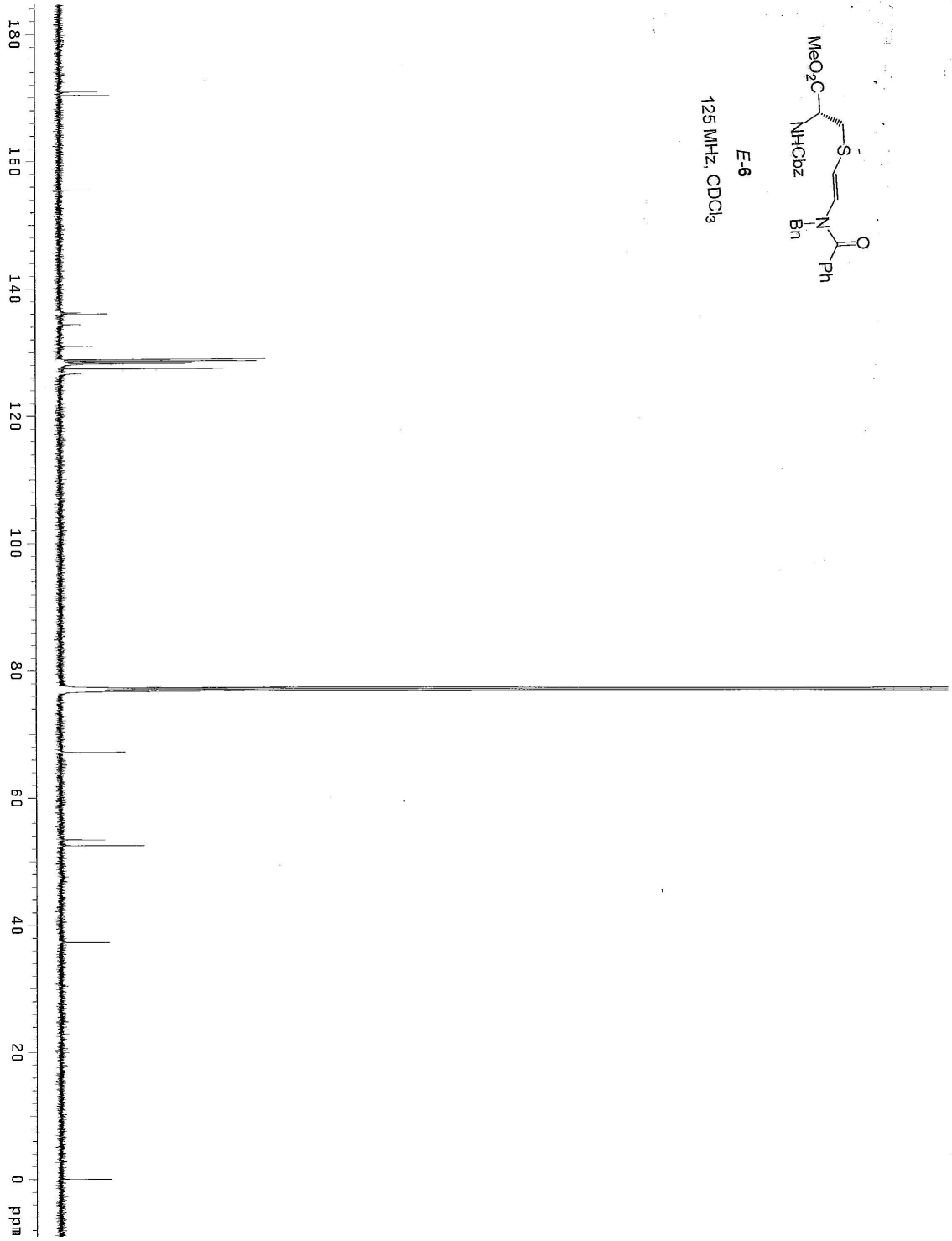
E-6

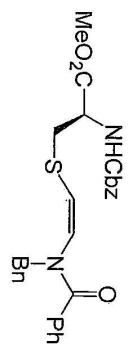
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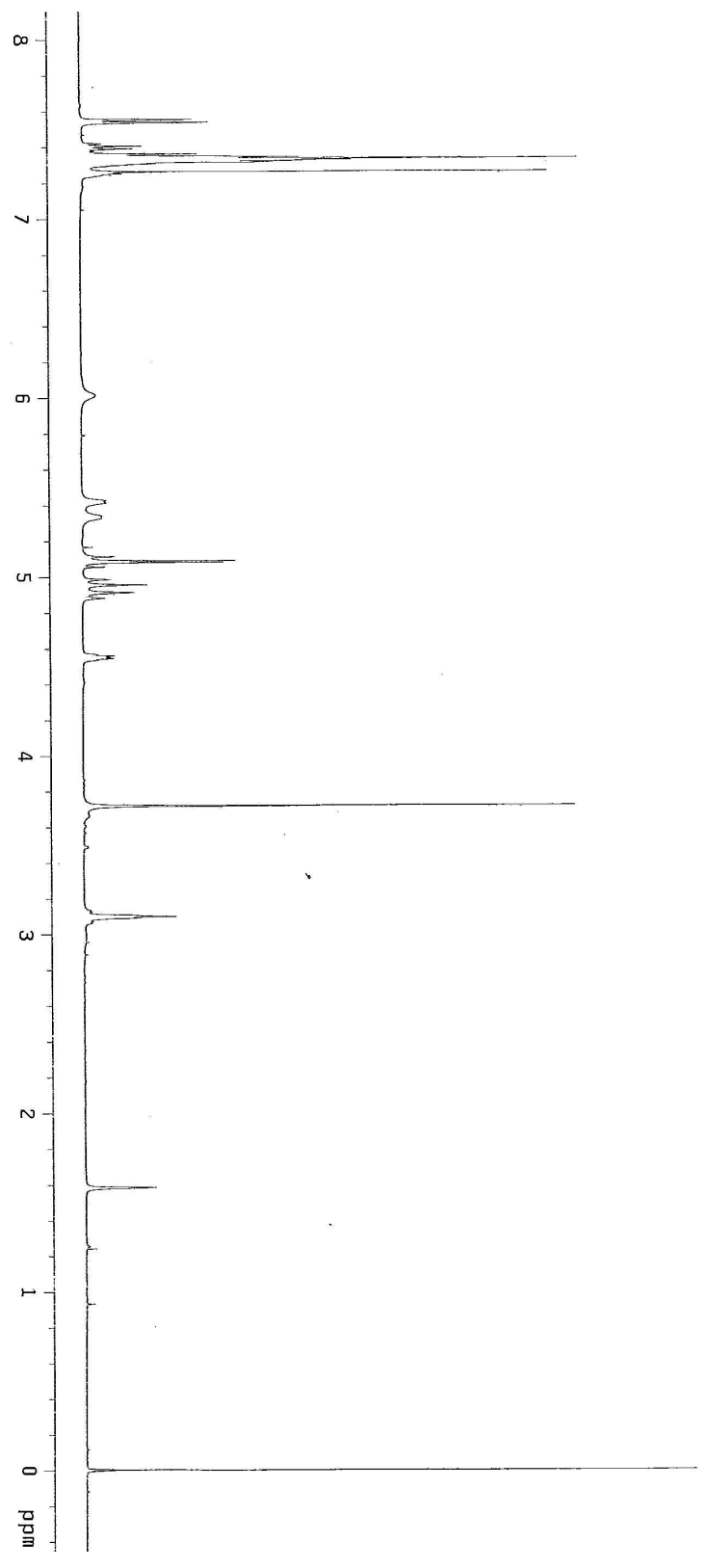
E-6  
125 MHz, CDCl<sub>3</sub>

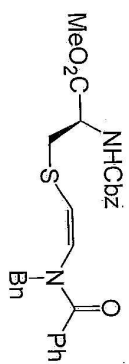




Z-6

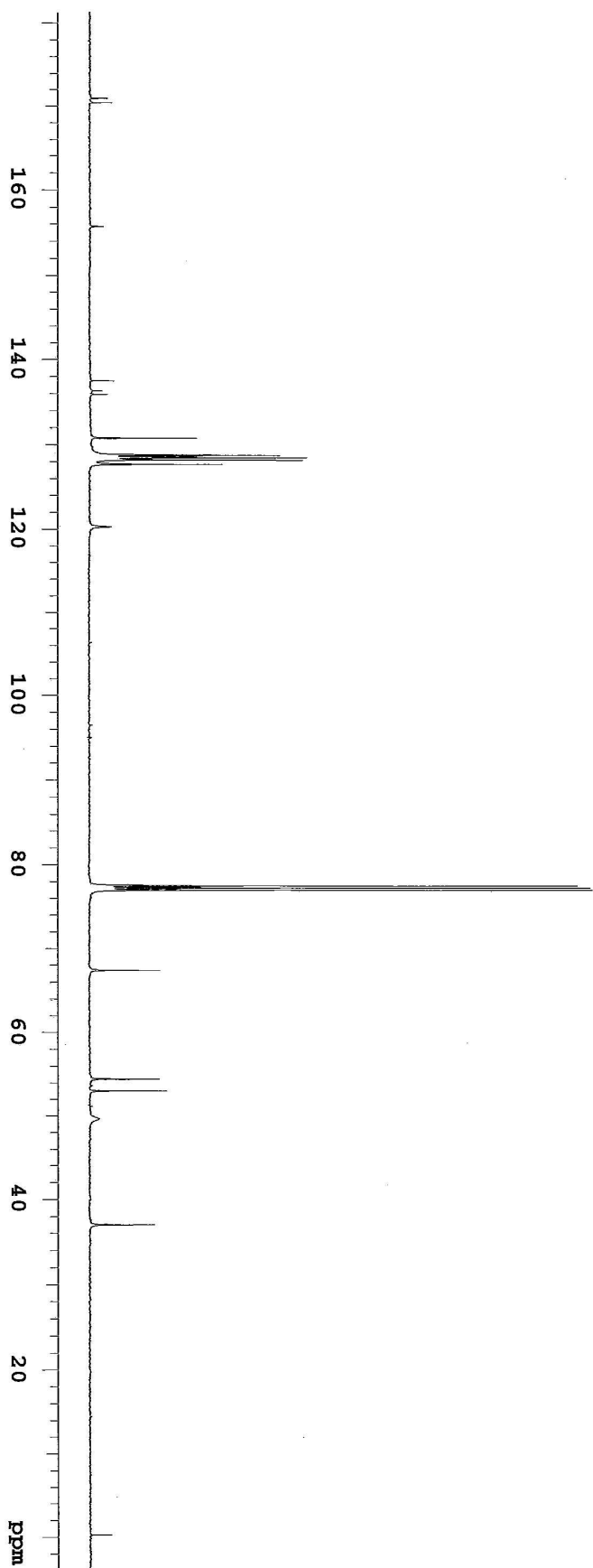
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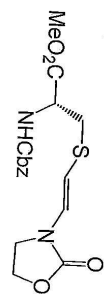




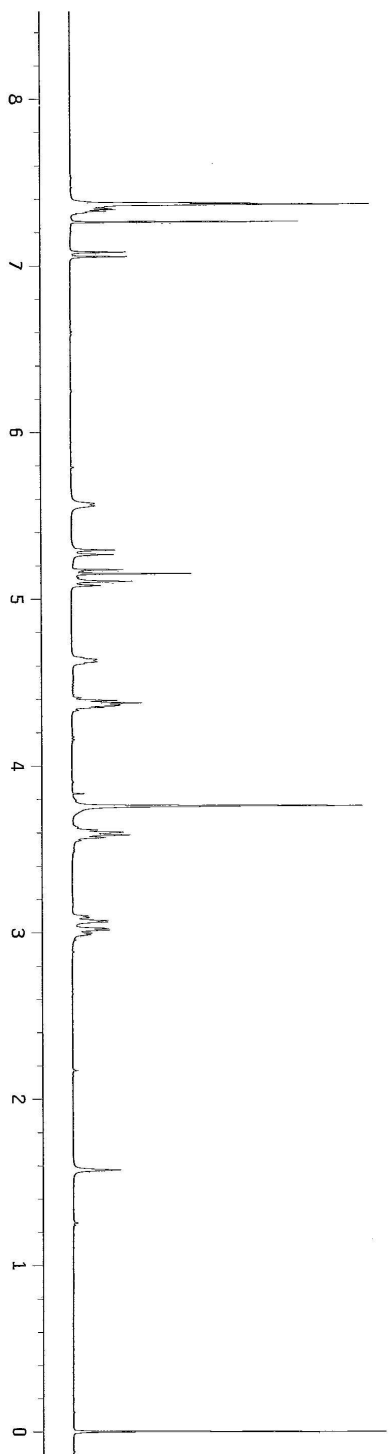
Z-6

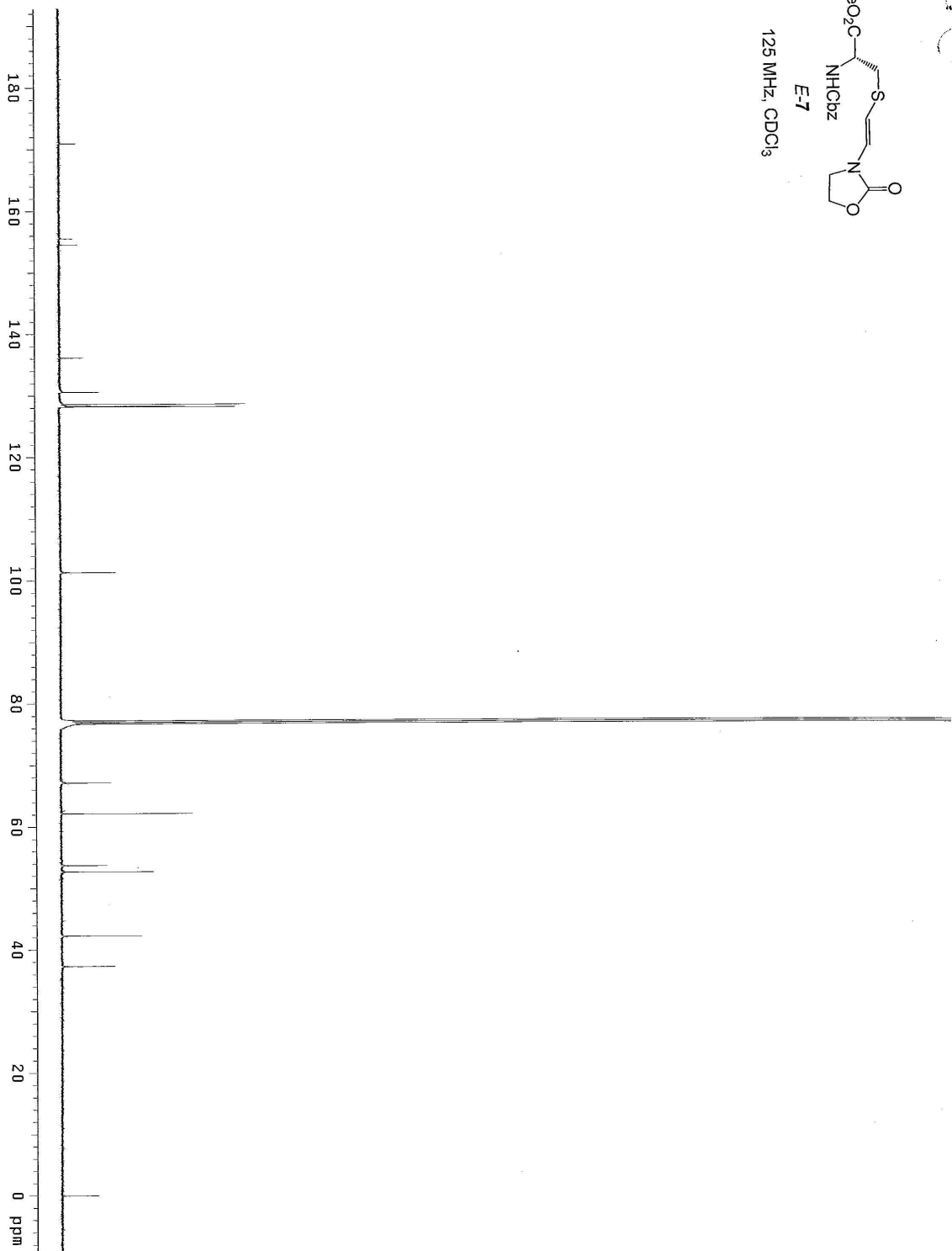
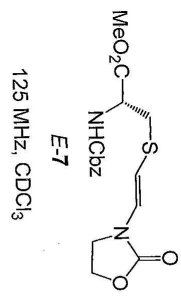
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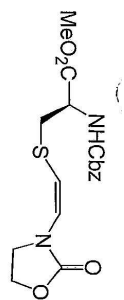




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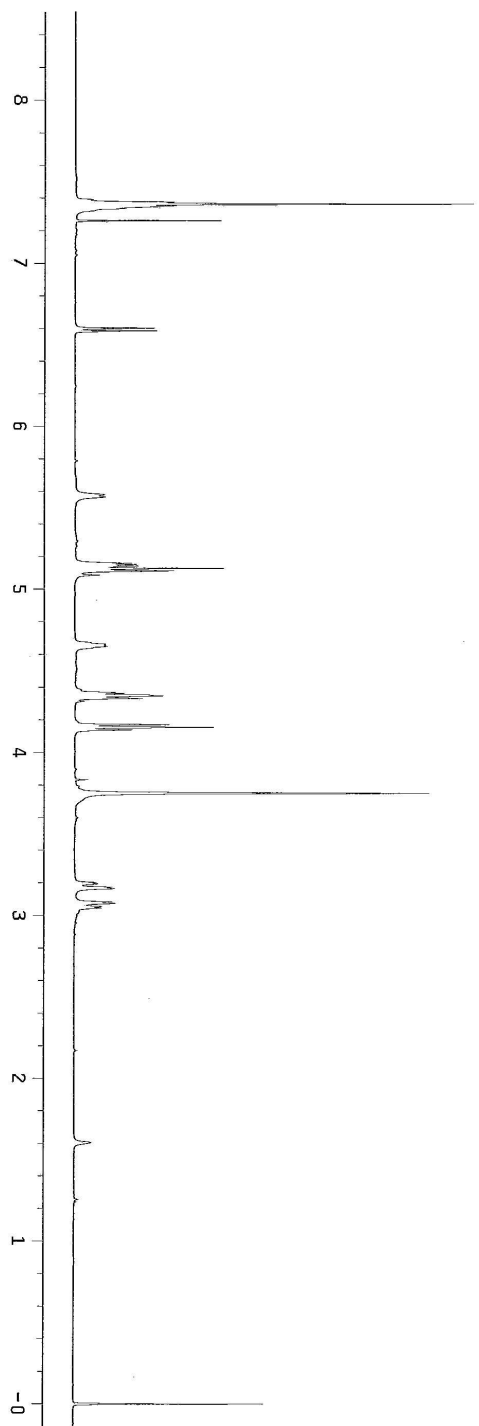




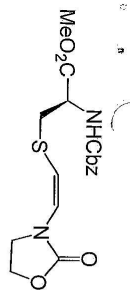


Z-7

500 MHz, CDCl<sub>3</sub>







Z-7

125 MHz, CDCl<sub>3</sub>

