Intermolecular Hydroamination of Ethylene and 1-Alkenes with Cyclic Ureas Catalyzed by Achiral and Chiral Gold(I) Complexes

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Experimental procedures, spectroscopic and analytical data, and scans of ^{1}H and ^{13}C NMR spectra for new compounds and scans of HPLC traces for enantiomerically enriched cyclic ureas (65 pages).

General Methods

Reactions were performed under a nitrogen atmosphere employing standard Schlenk and/or drybox techniques unless specified otherwise. NMR spectra were obtained on Varian spectrometers operating at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR in $CDCl_3$ at 25 °C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatography equipped with a 15 m or 25 m polydimethylsiloxane capillary column and FID detector. Chiral HPLC was performed on a Hewlett-Parkard chromatograph equipped with a 0.46 cm × 25 cm Chiralpak AD-H column. Column chromatography was performed employing 230-400 mesh silica gel (Silicycle). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (EMD Chemicals Inc.). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Room temperature is 23 °C. Catalytic reactions were performed in sealed heavy-walled pressure tubes under an atmosphere of dry nitrogen unless noted otherwise. Pressurized reactions were performed behind a blast shield in a heavy-walled pressure tube equipped with a pressure gauge and a valve that allowed the pressure of the tube to be controlled throughout the transformation.

All solvents were purchased from Aldrich or Acros in anhydrous form and used as received. All reagents and ligands, and gold salts were purchased from major suppliers and used as received. Gold complexes (**2a**)AuCl, (**2b**)AuCl, and (**L1**)AuCl-(**L3**)AuCl were prepared employing published procedures.[S1] Chiral bis(gold) phosphine complexes [(*S*)-**4**](AuCl)$_2$ and [(*S*)-**L3**](AuCl)$_2$ - [(*S*)-**L7**](AuCl)$_2$ were synthesized employing the method of Echavarren.[S2]

Part I: Hydroamination Employing Achiral Catalysts

Gold Complex (2b)AuCl. ^{1}H NMR: δ 8.21 (d, *J* = 8.4 Hz, 1 H), 8.02-7.95 (m, 3 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.57 (dd, *J* = 6.8, 8.4 Hz, 1 H), 7.52 (dt, *J* = 0.8, 6.8 Hz, 1 H), 7.45 (dt, *J* = 1.2, 6.8 Hz, 1 H), 7.31 (dd, *J* = 0.8, 6.8 Hz, 1 H), 7.23-7.18 (m, 2 H), 6.96 (d, *J* = 8.4 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 1

H), 1.44 (d, *J* = 15.6 Hz, 9 H), 1.41 (d, *J* = 15.6 Hz, 9 H). ^{31}P NMR: δ 63.1. ^{13}C{^{1}H} NMR: δ 148.0, 147.8, 136.35, 136.27, 134.8, 134.7, 134.4, 134.2, 134.1, 133.6, 129.7, 129.5, 129.4, 128.91, 128.88, 128.7, 128.6, 128.3, 127.8, 127.5, 127.4, 127.21, 127.19, 126.3, 126.2, 126.1, 125.7, 125.3, 125.0, 38.4, 38.19, 38.16, 37.9, 31.9, 31.8, 31.0, 30.9. HRMS calcd (found) for $C_{28}H_{31}AuClP$ (M^+): 630.1517 (630.1514).

Hydroamination with gaseous alkenes

1-Ethyl-3-methylimidazolidin-2-one (3). A suspension of (**2b**)AuCl (6.3 mg, 0.010 mmol), $AgSbF_6$ (3.4 mg, 0.010 mmol), and **1** (20.0 mg, 0.20 mmol) in dioxane (0.5 mL) in a pressure tube was evacuated via a freeze-pump-thaw cycle, pressurized with ethylene (60 psi), and heated at 60 °C for 24 h at constant ethylene pressure. The tube was cooled to room temperature, depressurized, and the crude reaction mixture was chromatographed (hexanes–EtOAc = 1:1 → 1:5) to give **3** (25.2 mg, 99%) as a colorless oil. TLC (EtOAc): R_f = 0.23. ^{1}H NMR (Figure S1): δ 3.19 (s, 4 H), 3.15 (q, *J* = 7.2 Hz, 2 H), 2.69 (s, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S2): δ 161.8, 45.3, 42.0, 38.9, 31.5, 12.8. IR (neat, cm^{-1}): 2978, 2861, 1679, 1499, 1439, 1404, 1277, 1256, 760. HRMS calcd (found) for $C_6H_{12}N_2O$ (M^+): 128.0950 (128.0948).

All remaining intermolecular hydroamination reactions employing gaseous alkenes were performed employing a procedure analogous to that used to synthesize **3** employing the catalyst mixture and conditions outlined in Tables 1 or 2.

1-*tert*-Butyl-3-ethylimidazolidin-2-one (Table 1, entry 5). Colorless oil, 80%. TLC (hexane–EtOAc = 1:1): R_f = 0.47. ^{1}H NMR: δ 3.26-3.22 (m, 2 H), 3.14-3.10 (m, 2 H), 3.13 (q, *J* = 7.2 Hz, 2 H), 1.29 (s, 9 H), 1.03 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 161.7, 53.1, 41.9, 40.9, 38.8, 27.6, 12.8. IR (neat, cm^{-1}): 2973, 2869, 1685, 1485, 1419, 1269, 1249, 1227, 765. HRMS calcd (found) for $C_9H_{18}N_2O$ (M^+): 170.1419 (170.1421).

3-Ethyloxazolidin-2-one (Table 1, entry 6).[S3] Colorless oil, 75%. TLC (EtOAc): R_f = 0.38. ^{1}H NMR (Figure S3): δ 4.27-4.23 (m, 2 H), 3.52-3.48 (m, 2 H), 3.26 (q, *J* = 7.2 Hz, 2 H), 1.10 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S4): δ 158.4, 61.8, 44.1, 39.0, 12.7. IR (neat, cm^{-1}): 2983, 2833, 1754, 1489, 1385, 1278, 1221, 1103, 699. HRMS calcd (found) for $C_5H_9NO_2$ (M^+): 115.0633 (115.0634).

1,3-Diethylimidazolidin-2-one (Table 1, entry 7).[S4] Colorless oil, 95%. TLC (hexanes–EtOAc = 1:1): R_f = 0.23. ^{1}H NMR (Figure S5): δ 3.23 (s, 4 H), 3.19 (q, *J* = 7.2 Hz, 4 H), 1.05 (t, *J* = 7.2 Hz, 6 H). ^{13}C{^{1}H} NMR (Figure S6): δ 161.3, 42.3, 38.9, 12.9. IR (neat, cm^{-1}): 2973, 2933, 1677, 1492, 1433, 1379, 1356, 1259, 759, 644. HRMS calcd (found) for $C_7H_{14}N_2O$ (M^+): 142.1106 (142.1107).

1,3-Diisopropylimidazolidin-2-one (Table 1, entry 8). Colorless oil, 85%. TLC (hexanes–EtOAc = 1:1): R_f = 0.30. ^{1}H NMR (Figure S7): δ 4.08 (septet, *J* = 6.8 Hz, 2 H), 3.16 (s, 4 H), 1.05 (d, *J* = 6.8 Hz, 12 H). ^{13}C{^{1}H} NMR (Figure S8): δ 160.3, 43.5, 37.4, 19.6. IR (neat, cm^{-1}): 2974, 2934, 1664, 1491, 1439, 1274, 1222, 1124, 1100, 761. HRMS calcd (found) for $C_9H_{18}N_2O$ (M^+): 170.1419 (170.1419).

1,3-di-*sec*-Butylimidazolidin-2-one (Table 1, entry 9). Colorless oil, 86%, dr = 1:1. TLC (hexanes–EtOAc = 5:1): R_f = 0.14. ^{1}H NMR (Figure S9): δ 3.83-3.73 (m, 2 H), 3.16-3.05 (m, 4 H), 1.43-1.27 (m, 4 H), 0.99-0.96 (m, 6 H), 0.80-0.75 (m, 6 H). ^{13}C{^{1}H} NMR (Figure S10): δ 160.9, 160.8, 49.1, 49.0, 37.3, 37.2, 27.1, 27.0, 17.6, 17.3, 11.1, 11.0. IR (neat, cm^{-1}): 3199, 2965, 2874, 1669, 1489, 1429, 1260, 1212, 757. HRMS calcd (found) for $C_{11}H_{22}N_2O$ (M^+): 198.1732 (198.1734).

1,3-Diethyl-tetrahydropyrimidin-2(1*H*)-one (Table 1, entry 10). Colorless oil, 98%. TLC (EtOAc): R_f = 0.23. ^{1}H NMR (Figure S11): δ 3.29 (q, *J* = 7.2 Hz, 4 H), 3.15 (t, *J* = 6.0 Hz, 4 H), 1.86 (quintet, *J* = 6.0 Hz, 2 H), 1.01 (t, *J* = 7.2 Hz, 6 H). ^{13}C{^{1}H} NMR (Figure S12): δ 155.6, 45.1, 42.6, 22.5, 13.0. IR (neat, cm^{-1}): 2971, 2932, 2869, 1609, 1511, 1441, 1290, 1213, 1081, 753. HRMS calcd (found) for $C_8H_{16}N_2O$ (M^+): 156.1263 (156.1260).

1,3-Diisopropyl-tetrahydropyrimidin-2(1*H*)-one (Table 1, entry 11). Colorless oil, 86%. TLC (hexanes–EtOAc = 1:1): R_f = 0.27. ^{1}H NMR (Figure S13): δ 4.69 (septet, *J* = 6.8 Hz, 2 H), 3.02 (t, *J* = 6.0 Hz, 4 H), 1.79 (quintet, *J* = 6.0 Hz, 2 H), 1.00 (d, *J* = 6.8 Hz, 12 H). ^{13}C{^{1}H} NMR (Figure S14): δ 155.2, 44.7, 38.3, 22.8, 19.8. IR (neat, cm^{-1}): 2956, 2871, 1603, 1497, 1439, 1303, 1207, 1091, 669. HRMS calcd (found) for $C_{10}H_{20}N_2O$ (M^+): 184.1576 (184.1573).

1-Isopropyl-3-methylimidazolidin-2-one (Table 2, entry 2). Colorless oil, 98%. TLC (EtOAc): R_f = 0.23. ^{1}H NMR (Figure S15): δ 4.05 (septet, *J* = 6.8 Hz, 1 H), 3.18-3.16 (m, 4 H), 2.69 (s, 3 H), 1.03 (d, *J* = 6.8 Hz, 6 H). ^{13}C{^{1}H} NMR (Figure S16): δ 161.2, 45.5, 43.7, 37.1, 31.5, 19.6. IR (neat, cm^{-1}): 2970, 2873, 1678, 1496, 1436, 1402, 1365, 1280, 1257, 760. HRMS calcd (found) for $C_7H_{14}N_2O$ (M^+): 142.1106 (142.1102).

1-*sec*-Butyl-3-methylimidazolidin-2-one (Table 2, entry 3). Colorless oil, 96%. TLC (hexane-EtOAc = 1:1): R_f = 0.16. ^{1}H NMR (Figure S17): δ 3.79 (sextet, *J* = 6.8 Hz, 1 H), 3.22-3.07 (m, 4 H), 2.70 (s, 3 H), 1.45-1.30 (m, 2 H), 1.01 (d, *J* = 6.8 Hz, 3 H), 0.80 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S18): δ 161.6, 49.4, 45.6, 37.1, 31.6, 27.1, 17.6, 11.2. IR (neat, cm^{-1}): 2965, 2874, 1680, 1496, 1436, 1402, 1353, 1279, 1255, 761. HRMS calcd (found) for $C_8H_{16}N_2O$ (M^+): 156.1263 (156.1265).

1-*tert*-Butyl-3-methylimidazolidin-2-one (Table 2, entry 10). Colorless oil, 72%. TLC (hexanes–EtOAc = 1:1): R_f = 0.28. ^{1}H NMR (Figure S19): δ 3.28-3.24 (m, 2 H), 3.16-3.12 (m, 2 H), 2.70 (s, 3 H), 1.31 (s, 9 H). ^{13}C{^{1}H} NMR (Figure S20): δ 162.2, 53.2, 45.1, 40.8, 31.6, 27.6. IR (neat, cm^{-1}): 2960, 2865, 1682, 1492, 1427, 1392, 1360, 1244, 765. HRMS calcd (found) for $C_8H_{16}N_2O$ (M^+): 156.1263 (156.1264). Anal. calcd (found) for $C_8H_{16}N_2O$: C, 61.50 (61.44); H, 10.32 (10.16); N, 17.93 (17.99).

Hydroamination of liquid alkenes

1-Methyl-3-(octan-2-yl)imidazolidin-2-one (S1; Table 2, entry 4). A suspension of (**2b**)AuCl (6.3 mg, 0.010 mmol), $AgSbF_6$ (3.4 mg, 0.010 mmol), 1-octene (224 mg, 2.00 mmol), and **1** (20.0 mg, 0.20 mmol) in dioxane (0.5 mL) in a pressure tube was heated at 100 °C for 24 h. The crude reaction mixture was chromatographed (hexanes–EtOAc = 5:1 → 1:1) to give **S1** (40.7 mg, 96%) as a colorless oil. TLC (hexanes–EtOAc = 1:1): R_f = 0.24. ^{1}H NMR (Figure S21): δ 3.88 (qt, *J* = 6.4, 8.8 Hz, 1 H), 3.23-3.08 (m, 4 H), 2.71 (s, 3 H), 1.43-1.27 (m, 2 H), 1.26-1.13 (m, 8 H), 1.01 (d, *J* = 6.8 Hz, 3 H), 0.81 (t, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S22): δ 161.5, 47.9, 45.6, 37.2, 34.2, 31.9, 31.7, 29.3, 26.6, 22.7, 17.9, 14.2. IR (neat, cm^{-1}): 2954, 2855, 1688, 1493, 1434, 1401, 1277, 1253, 760, 725. HRMS calcd (found) for $C_{12}H_{24}N_2O$ (M^+): 212.1889 (212.1889).

All remaining intermolecular hydroamination reactions employing liquid alkenes were performed employing a procedure analogous to that used to synthesize **S1** employing the catalyst mixture and conditions outlined in Tables 1 or 2.

1-(5-Hydroxypentan-2-yl)-3-methylimidazolidin-2-one (Table 2, entry 5). Pale yellow oil, 98%. TLC (EtOAc–MeOH = 15:1): R_f = 0.17. ^{1}H NMR (Figure S23): δ 3.93-3.85 (m, 1 H), 3.54-3.51 (m, 2 H), 3.22-3.09 (m, 5 H), 2.67 (s, 3 H), 1.48-1.36 (m, 4 H), 1.01 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S24): δ 161.6, 62.2, 47.6, 45.5, 37.1, 31.5, 30.5, 29.4, 18.1. IR (neat, cm^{-1}): 2938, 2867, 1670, 1500, 1442, 1405, 1280, 1058, 760, 729. HRMS calcd (found) for $C_9H_{18}N_2O_2$ (M^+): 186.1368 (186.1373). Anal. calcd (found) for $C_9H_{18}N_2O_2$: C, 58.04 (57.95); H, 9.74 (9.75); N, 15.04 (14.96).

1-(5-Benzyloxypentan-2-yl)-3-methylimidazolidin-2-one (Table 2, entry 6). Pale yellow oil, 95%. TLC (hexanes–EtOAc = 1:1): R_f = 0.14. ^{1}H NMR (Figure S25): δ 7.34-7.20 (m. 5 H), 4.44 (s, 2 H), 3.92 (sextet, *J* = 7.2 Hz, 1 H), 3.44 (t, *J* = 6.0 Hz, 2 H), 3.24 - 3.11 (m, 4 H), 2.72 (s, 3 H), 1.60-1.52 (m, 2 H), 1.51-1.45 (m, 2 H), 1.04 (d, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S26): δ 161.4, 138.7, 128.4, 127.6, 127.5, 72.9, 70.0, 47.6, 45.5, 37.1, 31.6, 30.7, 26.8, 18.0. IR (neat, cm^{-1}): 2937, 2856,

1682, 1494, 1435, 1278, 1255, 1096, 737. HRMS calcd (found) for $C_{16}H_{24}N_2O_2$ (M^+): 276.1838 (276.1837).

4-(3-Methyl-2-oxoimidazolidin-1-yl)pentanoic acid (Table 2, entry 7). Pale yellow oil, 98%. TLC (EtOAc–MeOH = 10:1): R_f = 0.25. ^{1}H NMR (Figure S27): δ 9.80 (br s, 1 H), 3.91 (qt, *J* = 6.4, 8.8 Hz, 1 H), 3.28-3.12 (m, 4 H), 2.69 (s, 3 H), 2.25 (t, *J* = 7.6 Hz, 2 H), 1.76-1.62 (m, 2 H), 1.04 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S28): δ 177.0, 161.7, 47.6, 45.4, 37.2, 31.5, 31.4, 29.2, 17.9. IR (neat, cm^{-1}): 3389, 2938, 1721, 1651, 1503, 1447, 1406, 1281, 1258, 1188, 915, 759, 729. HRMS calcd (found) for $C_9H_{16}N_2O_3$ (M^+): 200.1161 (200.1156). Anal. calcd (found) for $C_9H_{16}N_2O_3$: C, 53.98 (53.81); H, 8.05 (8.02); N, 13.99 (13.88).

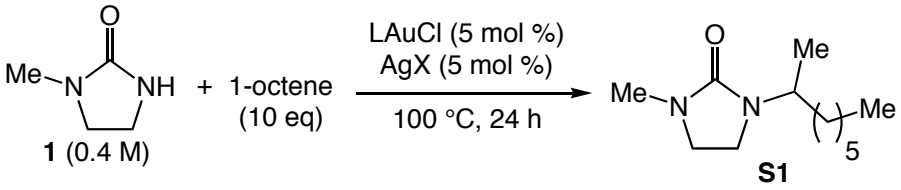
Ethyl 6-(3-methyl-2-oxoimidazolidin-1-yl)heptanoate (Table 2, entry 8). Pale yellow oil, 90%. TLC (EtOAc): R_f = 0.40. ^{1}H NMR (Figure S29): δ 4.03 (q, *J* = 7.2 Hz, 2 H), 3.86 (qt, *J* = 6.4, 8.8 Hz, 1 H), 3.21-3.05 (m, 4 H), 2.68 (s, 3 H), 2.20 (t, *J* = 7.2 Hz, 2 H), 1.63-1.09 (m, 6 H), 1.16 (t, *J* = 7.2 Hz, 3 H), 1.00 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S30): δ 173.7, 161.5, 60.2, 47.7, 45.5, 37.1, 34.3, 33.8, 31.6, 26.1, 24.9, 17.9, 14.3. IR (neat, cm^{-1}): 2936, 2865, 1730, 1687, 1495, 1437, 1402, 1373, 1278, 1252, 1178, 1035, 761. HRMS calcd (found) for $C_{13}H_{24}N_2O_3$ (M^+): 256.1787 (256.1789). Anal. calcd (found) for $C_{13}H_{24}N_2O_3$: C, 60.91 (60.75); H, 9.44 (9.24); N, 10.93 (10.87).

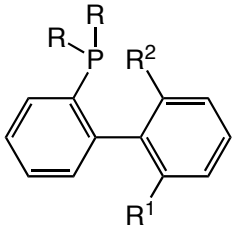
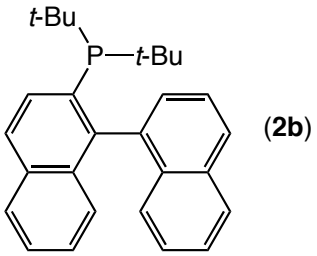
1-Methyl-3-(1-phenylethyl)imidazolidin-2-one (Table 2, entry 9). Colorless oil, 75%. TLC (hexanes–EtOAc = 1:1): R_f = 0.23. ^{1}H NMR (Figure S31): δ 7.36-7.21 (m, 5 H), 5.25 (q, *J* = 7.2 Hz, 1 H), 3.26-3.14 (m, 3 H), 2.94-2.84 (m, 1 H), 2.77 (s, 3 H), 1.49 (d, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S32): δ 161.3, 141.0, 128.6, 127.4, 50.6, 45.4, 37.7, 31.6, 16.3. IR (neat, cm^{-1}): 2936, 2872, 1686, 1494, 1436, 1401, 1278, 1253, 759, 701. HRMS calcd (found) for $C_{12}H_{16}N_2O$ (M^+): 204.1263 (204.1262). Anal. calcd (found) for $C_{12}H_{16}N_2O$: C, 70.56 (70.49); H, 7.90 (7.74); N, 13.71 (13.65).

1-(Bicyclo[2.2.1]heptan-2-yl)-3-methylimidazolidin-2-one (Table 2, entry 11). Colorless oil that solidified on standing, 86%. TLC (hexane–EtOAc = 1:1): R_f = 0.15. ^{1}H NMR (Figure S33): δ 3.77 (dd, *J* = 4.8, 8.4 Hz, 1 H), 3.31-3.12 (m, 4 H), 2.71 (s, 3 H), 2.24 (s, br, 1 H), 2.16 (s, br, 1 H), 1.61 (ddd, *J* =

2.4, 8.4, 12.4 Hz, 1 H), 1.49-1.39 (m, 3 H), 1.38-1.34 (m, 1 H), 1.29-1.21 (m, 1 H), 1.14-1.08 (m, 2 H). $^{13}C\{^1H\}$ NMR (Figure S34): δ 161.6, 55.8, 45.7, 40.5, 39.8, 36.9, 36.7, 36.2, 31.7, 28.4, 27.9. IR (neat, cm^{-1}): 2951, 2853, 1687, 1491, 1278, 760, 699. HRMS calcd (found) for $C_{11}H_{18}N_2O$ (M^+): 194.1419 (194.1418).

Table S1. Effect of Ligand, Silver Salt, and Solvent on the Gold(I)-Catalyzed Hydroamination of 1-octene with **1**.



entry	L	solvent	X	yield (%)[a]
				
1	R = *t*-Bu, R_1 = R_2 = H (**2a**)	dioxane	OTf	38
2	**2a**	dioxane	SbF_6	96
3	R = *t*-Bu, R_1 = NMe_2, R_2 = H (**L1**)	dioxane	OTf	34
4	R = Cy, R_1 = R_2 = H (**L2**)	dioxane	OTf	16
5	R = Cy, R_1 = R_2 = OMe (**L3**)	dioxane	OTf	33
6	 (**2b**)	dioxane	OTf	44
7		dioxane	AsF_6	26
8		dioxane	BF_4	12
9		dioxane	ClO_4	6
10		dioxane	SbF_6	99 (96)
11		toluene	SbF_6	39
12		MeOH	SbF_6	80
13		diglyme[b]	SbF_6	97 (95)
14		diglyme[c]	SbF_6	40

[a]Yield determined by ^1H NMR analysis of the crude reaction mixture; isolated yields in parentheses. [b]Five equivalents 1-octene employed. [c]One and a half equivalents 1-octene employed.

Control Reactions

1) Gold/ligand only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (220 mg, 2.0 mmol), and (**2b**)AuCl (12.6 mg, 0.020 mmol) in diglyme (0.5 mL) in a pressure tube was stirred at 100 °C for 24 h and then cooled to room temperature. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **S1**.

2) Silver only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (220 mg, 2.0 mmol), and $AgSbF_6$ (6.9 mg, 0.020 mmol) in diglyme (0.5 mL) in a pressure tube was stirred at 100 °C for 24 h and then cooled to room temperature. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **S1**.

3) Silver/ligand only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (220 mg, 2.0 mmol), $AgSbF_6$ (6.9 mg, 0.020 mmol), and **2b** (8.0 mg, 0.020 mmol) in diglyme (0.5 mL) in a pressure tube was stirred at 100 °C for 24 h and then cooled to room temperature. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **S1**.

4) HOTf only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (220 mg, 2.0 mmol), and HOTf (3.0 mg, 0.020 mmol) in diglyme (0.5 mL) in a pressure tube was stirred at 100 °C for 24 h and then cooled to room temperature. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **S1**.

A suspension of HOTf (4.5 mg, 0.030 mmol), and **1** (25.8 mg, 0.30 mmol) in dioxane (0.5 mL) in a pressure tube was evacuated via a freeze-pump-thaw cycle, pressurized with ethylene (120 psi), and heated at 100 °C for 48 h at constant ethylene pressure. The tube was cooled to room temperature and depressurized. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **3**.

5) HOTf/ligand only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (220 mg, 2.0 mmol), HOTf (3.0 mg, 0.020 mmol), and **2b** (8.0 mg, 0.020 mmol) in diglyme (0.5 mL) in a pressure tube was stirred at 100 °C for 24 h and then cooled to room temperature. GC analysis of the crude reaction mixture revealed no detectable consumption of **1** and no detectable formation of **S1**.

Part II: Enantioselective Hydroamination.

1-Methyl-3-(octan-2-yl)imidazolidin-2-one (S1; Table 3, entry 1). A suspension of **1** (20 mg, 0.20 mmol), 1-octene (1.3 g, 12 mmol), [(*S*)-**4**]$(AuCl)_2$ (8.0 mg, 5.0×10^{-3} mmol), and AgOTf (2.6 mg, 1.0×10^{-2} mmol) in *m*-xylene (0.5 mL) was stirred at 100 °C for 48 h. The crude mixture was filtered through plug of silica gel, concentrated, and chromatographed (hexanes–EtOAc = 5:1 → 1:1) to give **S1** (37 mg, 86%) as a colorless oil. Enantiopurity of **S1** (76% ee) was determined by HPLC analysis (95:5 hexanes/isopropanol, 0.5 mL/min; Figure S35).

All remaining enantiomericially enriched cyclic ureas were synthesized employing a procedure similar to that used to synthesize enantiomerically enriched **S1**.

1-(Octan-2-yl)-3-phenylimidazolidin-2-one (Table 3, entry 2). Colorless oil, 80% yield. TLC (hexanes–EtOAc = 5:1): R_f = 0.43. ^{1}H NMR (Figure S36): δ 7.57-7.55 (m, 2 H), 7.34-7.30 (m, 2 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 4.08 (qt, *J* = 6.4, 8.8 Hz, 1 H), 3.82-3.78 (m, 2 H), 3.50-3.33 (m, 2 H), 1.52-1.21 (m, 10 H), 1.15 (d, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S37): δ 157.38, 140.76, 128.70, 122.0, 117.17, 47.67, 42.53, 36.37, 34.0, 31.73, 29.12, 26.46, 22.59, 17.87, 14.05. IR (neat, cm^{-1}): 2924, 2855, 1697, 1600, 1503, 1481, 1456, 1417, 1391, 1259, 1145, 1095, 752. HRMS calcd (found) for $C_{17}H_{26}N_2O$ (M^+): 274.2045 (274.2050). Enantiopurity (71% ee) was determined by HPLC analysis (99:1 hexanes/isopropanol, 0.5 mL/min; Figure S38).

1-(4-Fluorophenyl)-3-(octan-2-yl)imidazolidin-2-one (Table 3, entry 3). Colorless oil, 81% yield. TLC (hexanes–EtOAc = 5:1): R_f = 0.37. ^{1}H NMR (Figure S39): δ 7.45-7.41 (m, 2 H), 6.97-6.92 (m, 2 H), 4.06 (qt. *J* = 7.2, 8.4 Hz, 1H), 3.73-3.68 (m, 2 H), 3.38-3.26 (m, 2 H), 1.49-1.33 (m, 2 H), 1.32-

1.14 (m, 8 H), 1.08 (d, J = 6.8 Hz, 3 H), 0.80 (t, J = 6.4 Hz, 3 H). $^{13}C\{^1H\}$ NMR (Figure S40): δ 159.4, 157.4, 136.9, 118.8, 118.7, 115.4, 115.1, 47.8, 42.8, 36.4, 34.0, 31.7, 29.1, 26.5, 22.6, 17.8, 14.0. IR (neat, cm^{-1}): 2926, 2856, 1693, 1510, 1482, 1424, 1392, 1259, 1224, 1160, 1144, 828, 750. HRMS calcd (found) for $C_{17}H_{25}FN_2O$ (M^+): 292.1951 (292.1954). Enantiopurity (74% ee) was determined by HPLC analysis (95:5 hexanes/isopropanol, 0.5 mL/min; Figure S41).

1-*tert*-Butyl-3-(octan-2-yl)imidazolidin-2-one (Table 3, entry 4). Colorless oil, 89% yield. TLC (hexanes–EtOAc = 2:1): R_f = 0.70. ^1H NMR (Figure S42): δ 3.90 (sextet, J = 6.8 Hz, 1 H), 3.30-3.21 (m, 2 H), 3.14-3.03 (m, 2H), 1.33 (s, 9 H), 1.32-1.19 (m, 10 H), 1.04 (d, J = 6.8 Hz, 3 H), 0.85 (t, J = 7.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR (Figure S43): δ 161.4, 53.09, 47.44, 41.16, 36.92, 34.28, 32.0, 29.4, 27.6, 26.7, 22.8, 17.8, 14.3. IR (neat, cm^{-1}): 2958, 2925, 2855, 1683, 1482, 1455, 1414, 1392, 1361, 1267, 1249, 1227, 1144, 1102, 765, 745. HRMS calcd (found) for $C_{15}H_{30}N_2O$ (M^+): 254.2358 (254.2357). Enantiopurity (78% ee) was determined by HPLC analysis (97:3 hexanes/isopropanol, 0.5 mL/min; Figure S44).

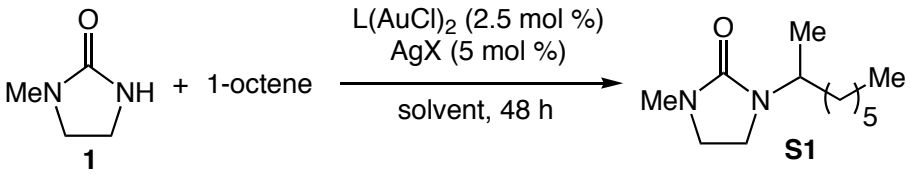
1-(Decan-2-yl)-3-methylimidazolidin-2-one (Table 3, entry 5). Colorless oil. 83% yield. TLC (hexanes–EtOAc = 1:1): R_f = 0.33. ^1H NMR (Figure S45): δ 3.92 (qt, J = 6.4, 8.8 Hz, 1 H), 3.24-3.10 (m, 4 H), 2.73 (s, 3 H), 1.45-1.33 (m, 2 H), 1.32-1.17 (m, 12 H), 1.03 (d, J = 6.8 Hz, 3 H), 0.83 (t, J = 7.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR (Figure S46): δ 161.9, 48.3, 46.0, 37.5, 34.6, 32.4, 32.0, 30.0, 29.9, 29.8, 27.0, 23.1, 18.3, 14.6. IR (neat, cm^{-1}): 2923, 2853, 1690, 1493, 1433, 1401, 1277, 1253, 1048, 760. HRMS calcd (found) for $C_{14}H_{28}N_2O$ (M^+): 240.2202 (240.2207). Enantiopurity (73% ee) was determined by HPLC analysis (98:2 hexanes/isopropanol, 0.5 mL/min; Figure S47).

1-(Dodecan-2-yl)-3-methylimidazolidin-2-one (Table 3, entry 6). Colorless oil, 76% yield. TLC (hexanes–EtOAc = 1:1): R_f = 0.36. ^1H NMR (Figure S48): δ 3.87 (qt, J = 7, 8.5 Hz, 1 H), 3.21-3.08 (m, 4 H), 2.71 (s, 3 H), 1.39-1.27 (m, 2 H), 1.26-1.13 (m, 16 H), 1.05 (d, J = 7.0 Hz, 3 H), 0.81 (t, J = 7.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR (Figure S49): δ 161.7, 48.0, 45.8, 37.3, 34.3, 32.1, 31.8, 29.8, 29.8, 29.8, 29.6, 26.7, 22.9, 18.0, 14.3. IR (neat, cm^{-1}): 2922, 2852, 2922, 2852, 1693, 1493, 1433, 1401, 1277, 1254,

1046, 760. HRMS calcd (found) for $C_{16}H_{32}N_2O$ (M^+): 268.2515 (268.2511). Enantiopurity (75% ee) was determined by HPLC analysis (97:3 hexanes/isopropanol, 0.5 mL/min; Figure S50).

Optimization of Enantioselective Hydroamination

Table S2. Effect of Silver Salt and Solvent on the Enantioselectivity of the Gold(I)-Catalyzed Hydroamination of 1-Octene with **1** Catalyzed by Bis(gold) Phosphine Complexes.



1 **S1**

entry	L	X	solvent	1-octene amount (equiv)	temp (°C)	ee (%)[a]
1	(*S*)-**4**	BF_4	dioxane	15	80	46
2	(*S*)-**4**	OTs	dioxane	15	80	—
3	(*S*)-**4**	PF_6	dioxane	15	80	47
4	(*S*)-**4**	OTf	dioxane	15	80	62
5	(*S*)-**4**	ClO_4	dioxane	15	80	47
6	(*S*)-**4**	AsF_6	dioxane	15	80	45
7	(*S*)-**4**	SbF_6	dioxane	6	60	38
8	(*S*)-**4**	OTf	MeOH	6	60	38
9	(*S*)-**4**	OTf	DMSO	6	60	—
10	(*S*)-**4**	OTf	toluene	6	60	54
11	(*S*)-**4**	OTf	dioxane	6	60	48
12	(*S*)-**4**	OTf	CH_3NO_2	6	60	—
13	(*S*)-**4**	OTf	MeCN	6	60	34
14	(*S*)-**4**	OTf	THF	6	60	46
15	(*S*)-**4**	OTf	toluene	15	60	66
16	(*S*)-**4**	OTf	dioxane	15	60	61
17	(*S*)-**L4**	OTf	toluene	15	60	50
18	(*S*)-**L4**	OTf	dioxane	15	60	56
19	(*S*)-**L5**	OTf	toluene	15	60	—
20	(*S*)-**L5**	OTf	dioxane	15	60	7
21	(*S*)-**L6**	OTf	toluene	15	60	—
22	(*S*)-**L6**	OTf	dioxane	15	60	—
23	(*S*)-**L7**	OTf	toluene	15	60	68
24	(*S*)-**L7**	OTf	dioxane	15	60	57
25	(*S*)-**L7**	OTf	toluene	30	60	69
26	(*S*)-**L7**	OTf	*m*-xylene	30	60	70
27	(*S*)-**4**	OTf	toluene	30	60	71
28	(*S*)-**4**	OTf	*m*-xylene	30	60	74

[a]Enantiomeric purity determined by HPLC analysis on a chiral stationary phase.

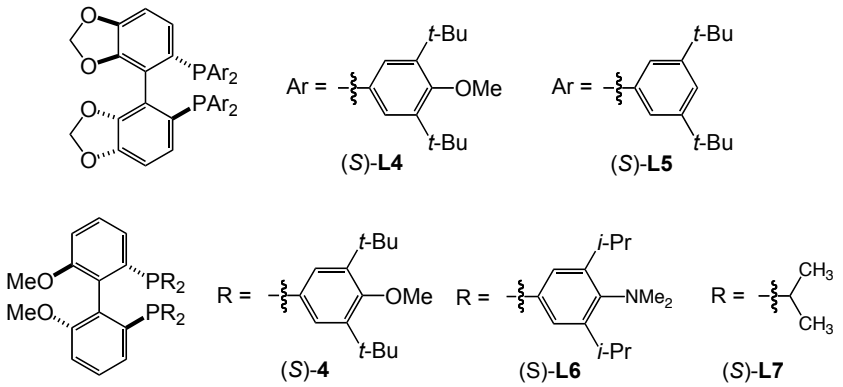
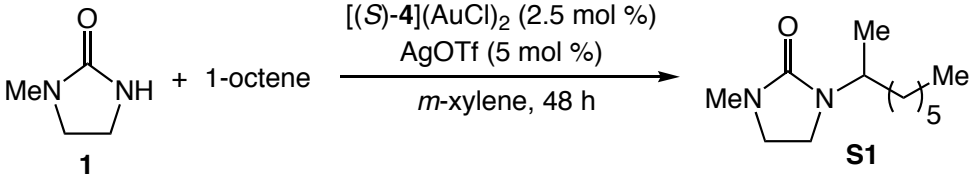


Table S3. Effect of Temperature and Alkene Loading on the Conversion and Enantioselectivity of the Hydroamination of 1-Octene with **1** catalyzed by [(*S*)-**4**](AuCl)$_2$ (2.5 mol %) and AgOTf (5 mol %) in *m*-xylene.



entry	1-octene amount	temp (°C)	conversion (%)[a]	ee (%)[b]
1	30 equiv	60	38	74
2	30 equiv	100	100	73
3	60 equiv	100	100	76
4	30 equiv	120	100	73
5	60 equiv	120	100	75

[a]Determined by ^{1}H NMR analysis of the crude reaction mixture. [b]Enantiomeric purity determined by HPLC analysis on a chiral stationary phase.

Control reactions

(1) Silver/ligand only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (1.92 mL, 12.0 mmol), AgOTf (5.1 mg, 0.020 mmol), and (*S*)-**4** (23.0 mg, 0.020 mmol) in *m*-xylene (0.5 mL) in a pressure tube was stirred at 100 °C for 48 h. The crude mixture was then filtered through a silica gel

plug and concentrated. NMR analysis of the crude reaction mixture revealed no detectable formation of **S1**.

(2) HOTf/ligand only. A suspension of **1** (20.0 mg, 0.20 mmol), 1-octene (1.92 mL, 12.0 mmol), HOTf (3.0 mg, 0.020 mmol), and (*S*)-**4** (23.0 mg, 0.020 mmol) in *m*-xylene (0.5 mL) in a pressure tube was stirred at 100 °C for 48 h. The crude mixture was then filtered through a silica gel plug and concentrated. NMR analysis of the crude reaction mixture revealed no detectable formation of **S1**.

Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$.

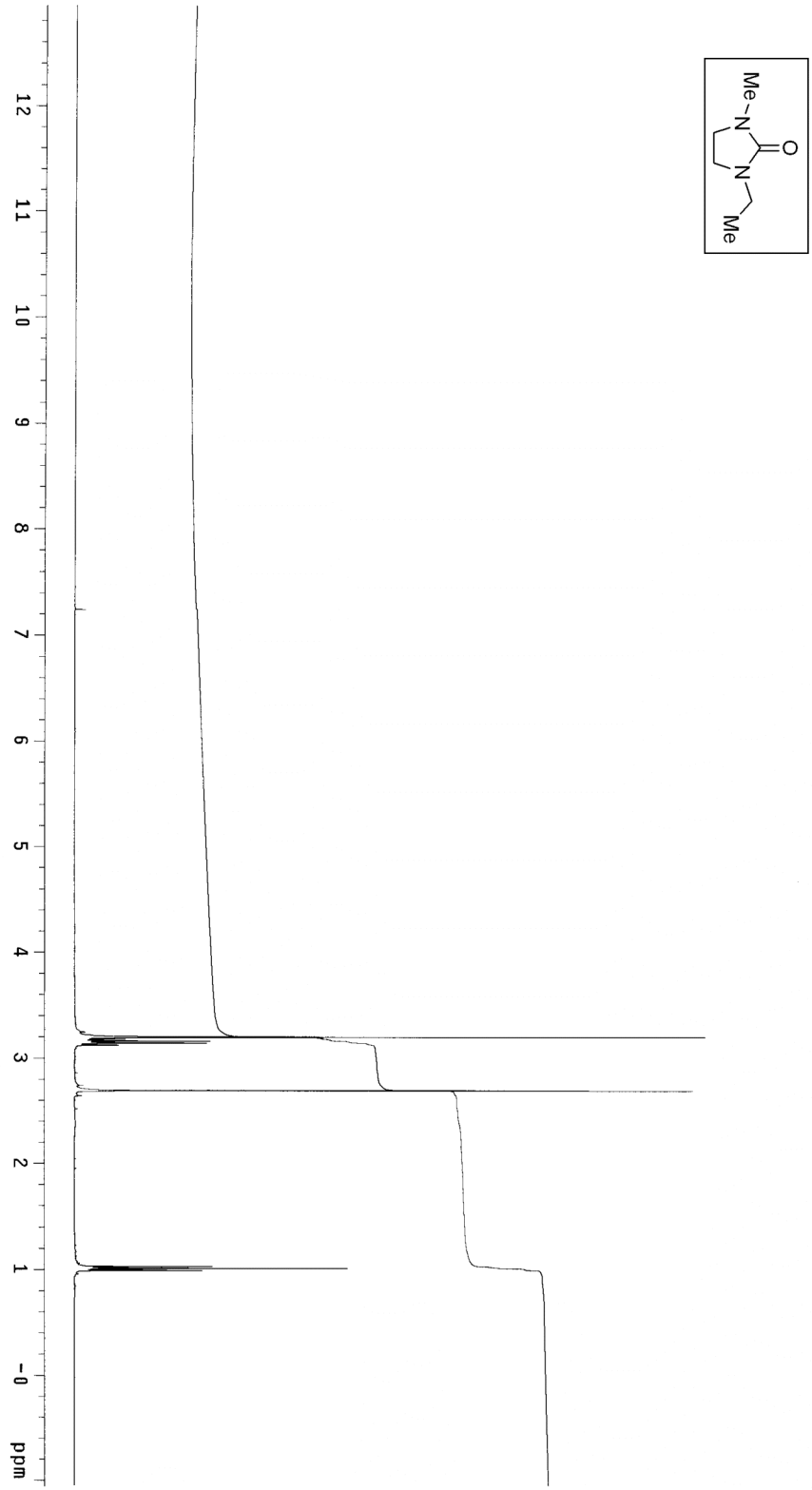


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

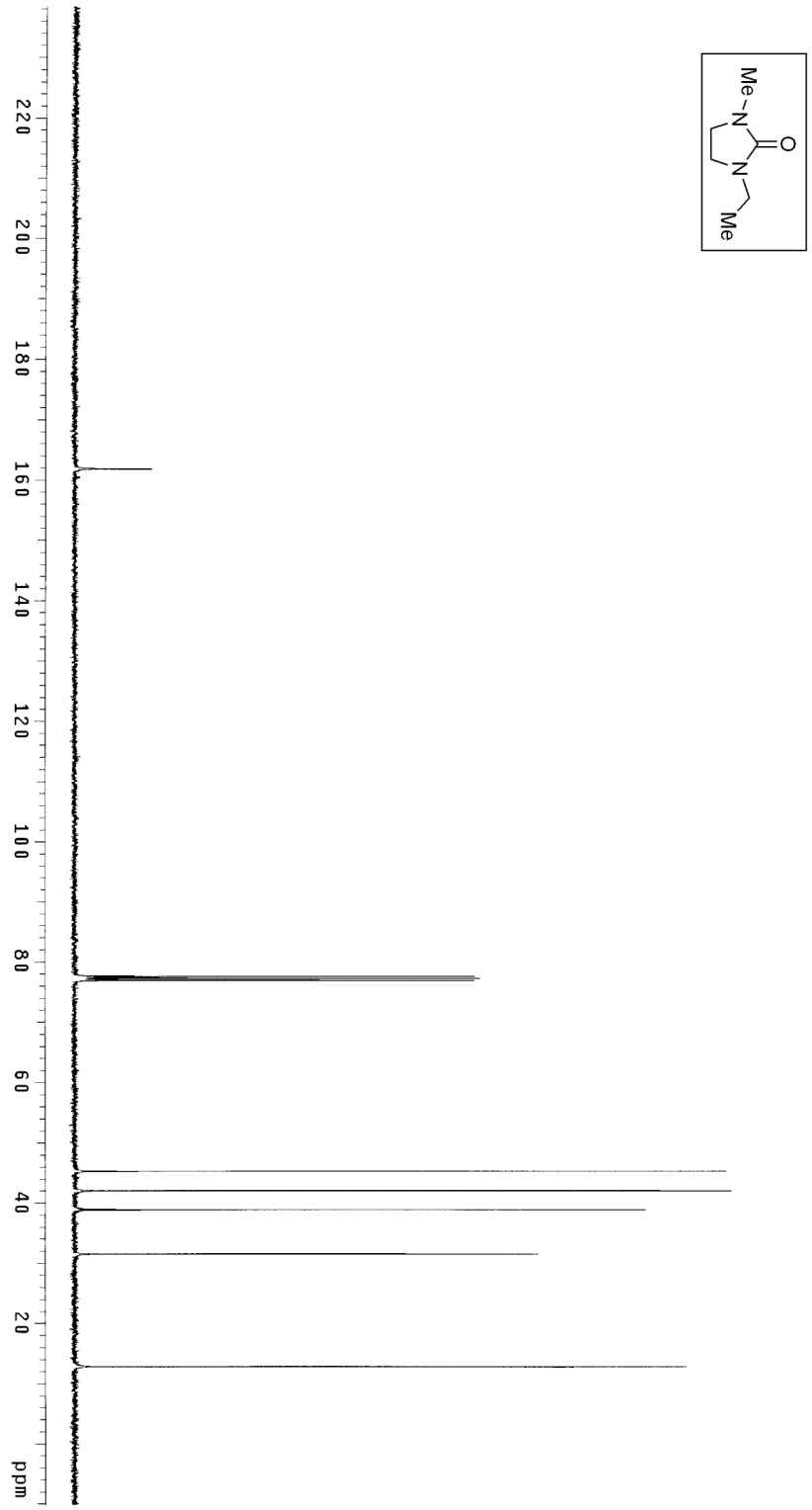


Figure S3. ^{1}H NMR spectrum of 3-ethyloxazolidin-2-one in $CDCl_3$.

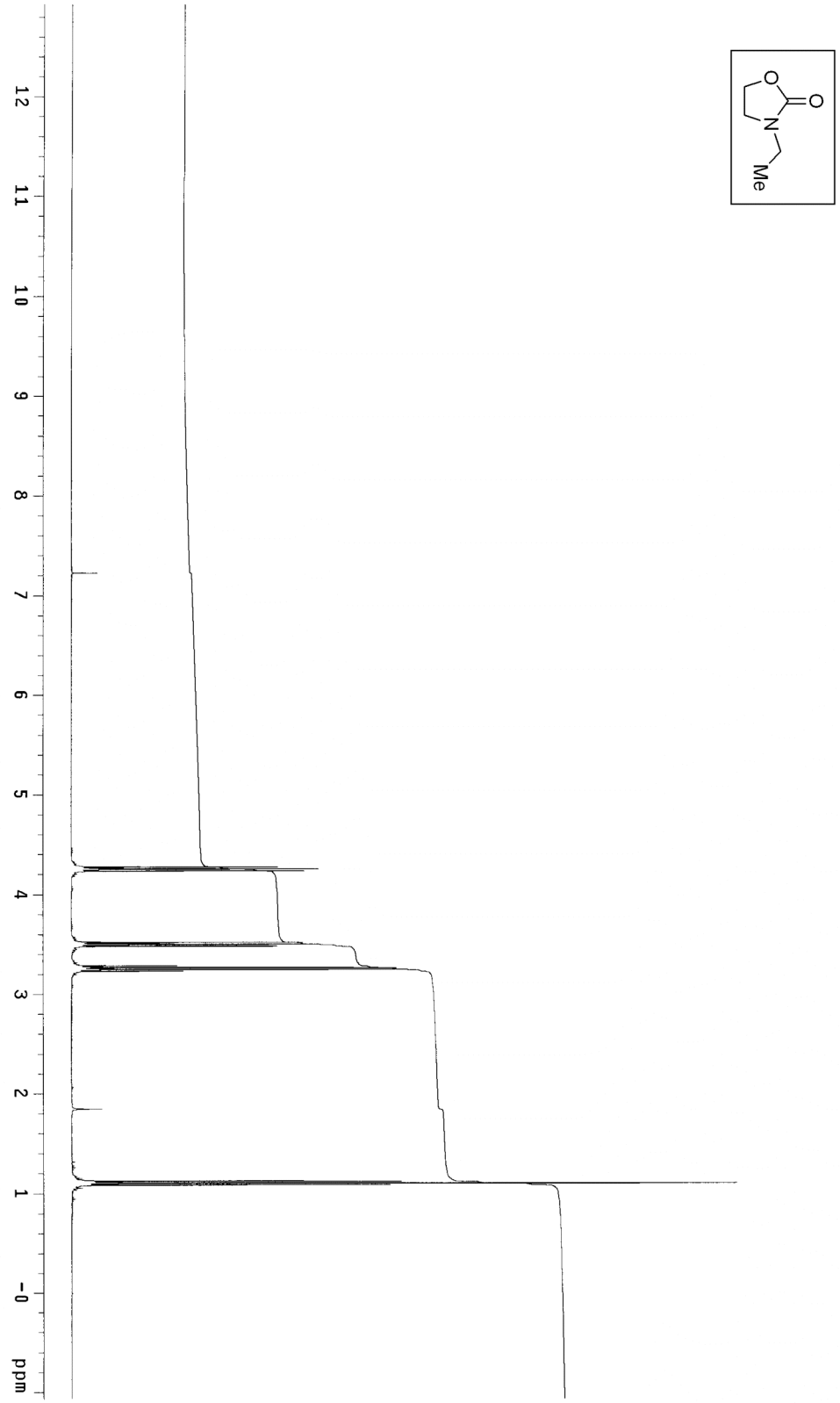


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of 3-ethyloxazolidin-2-one in $CDCl_3$.

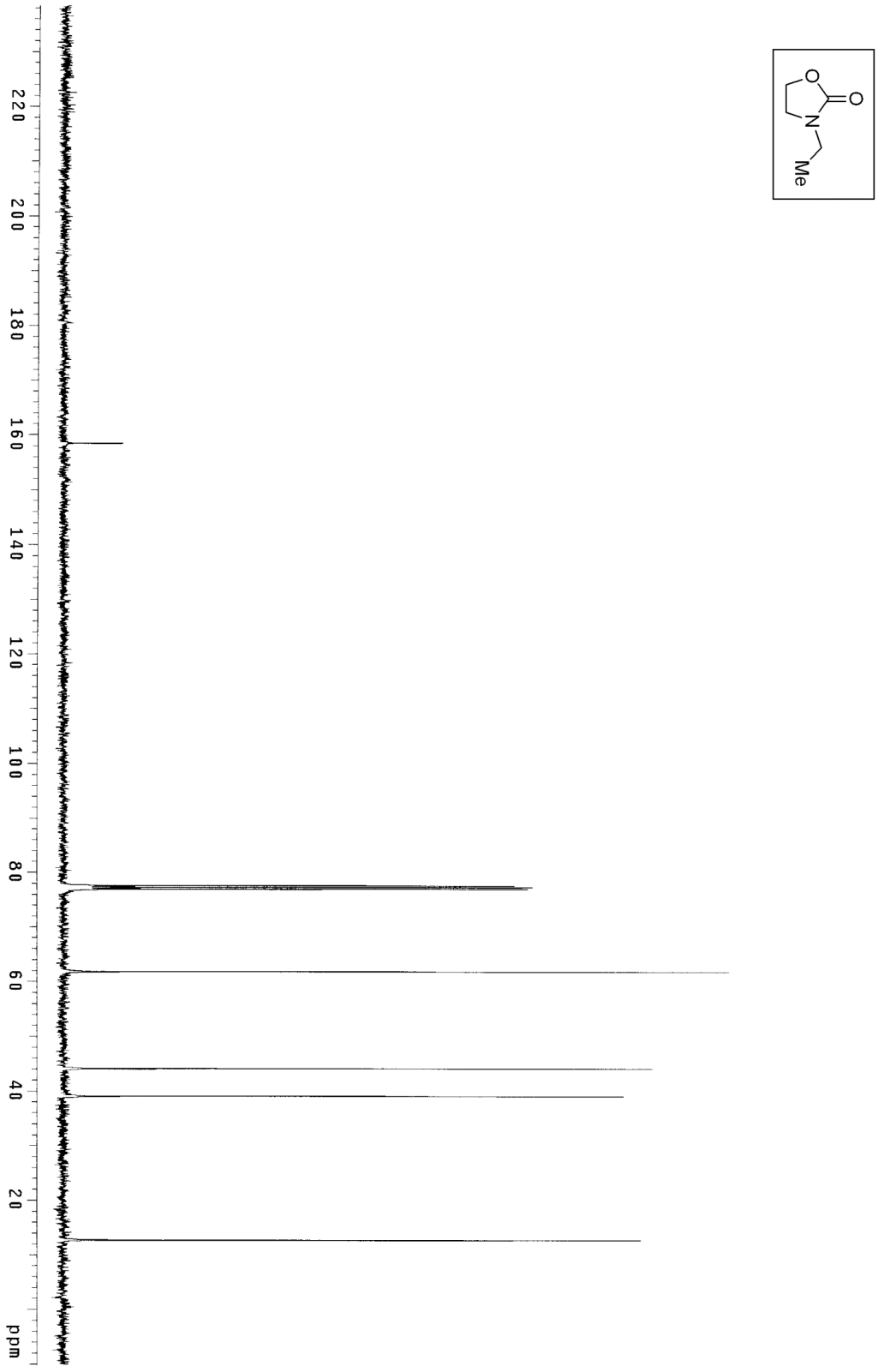


Figure S5. ^{1}H NMR spectrum of 1,3-diethylimidazolidin-2-one in $CDCl_3$.

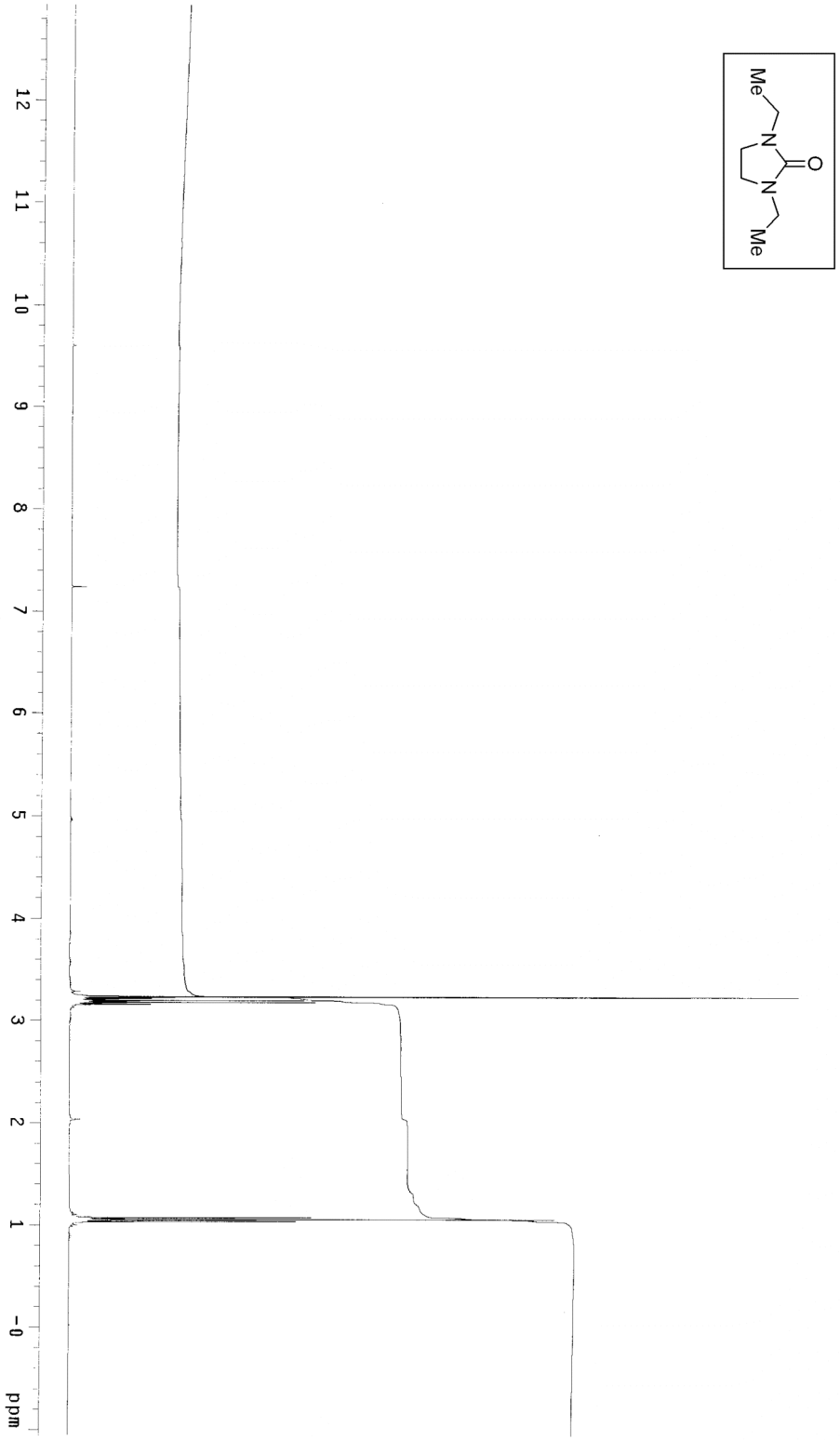


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-diethylimidazolidin-2-one in $CDCl_3$.

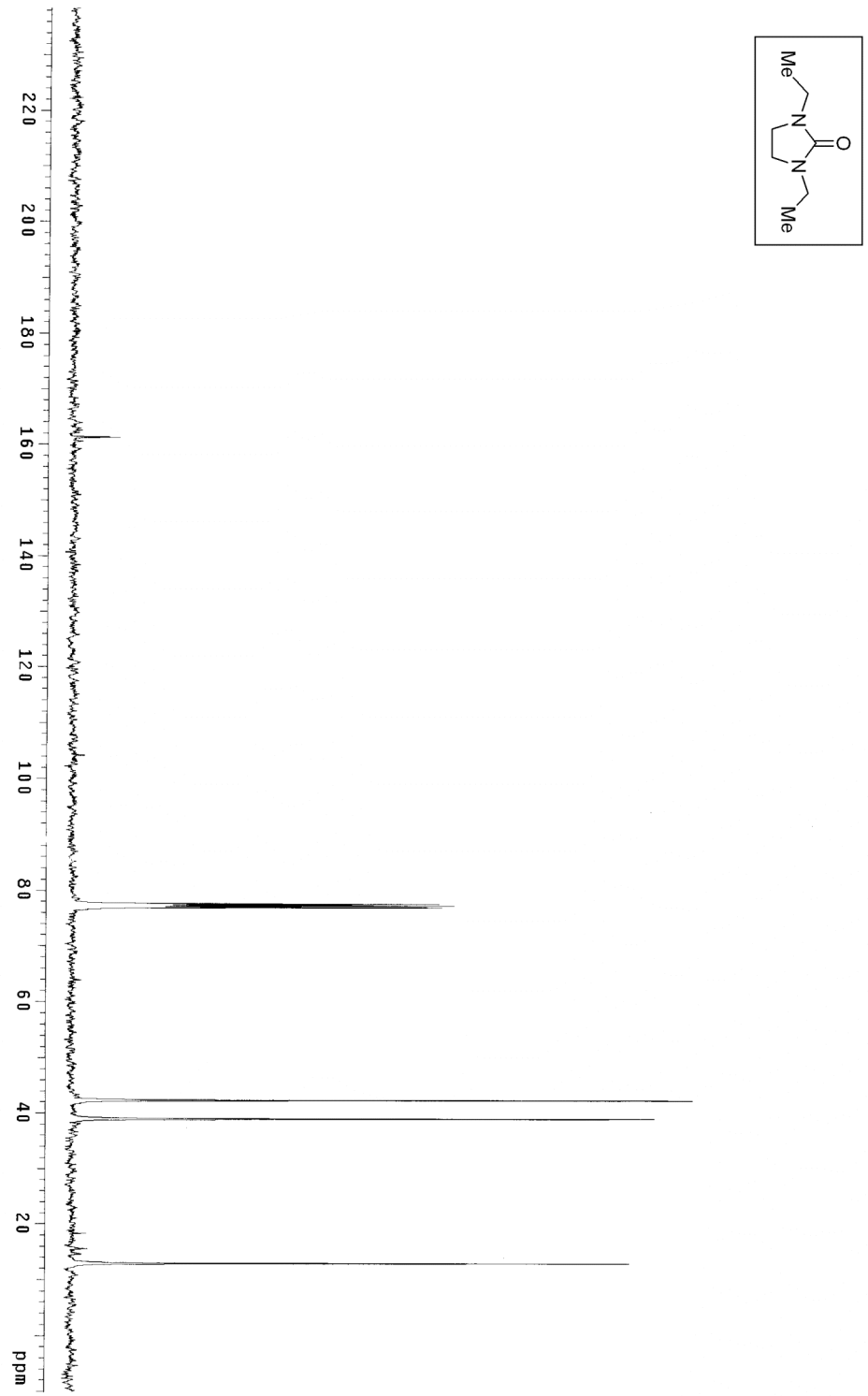


Figure S7. ^{1}H NMR spectrum of 1,3-diisopropylimidazolidin-2-one in $CDCl_3$.

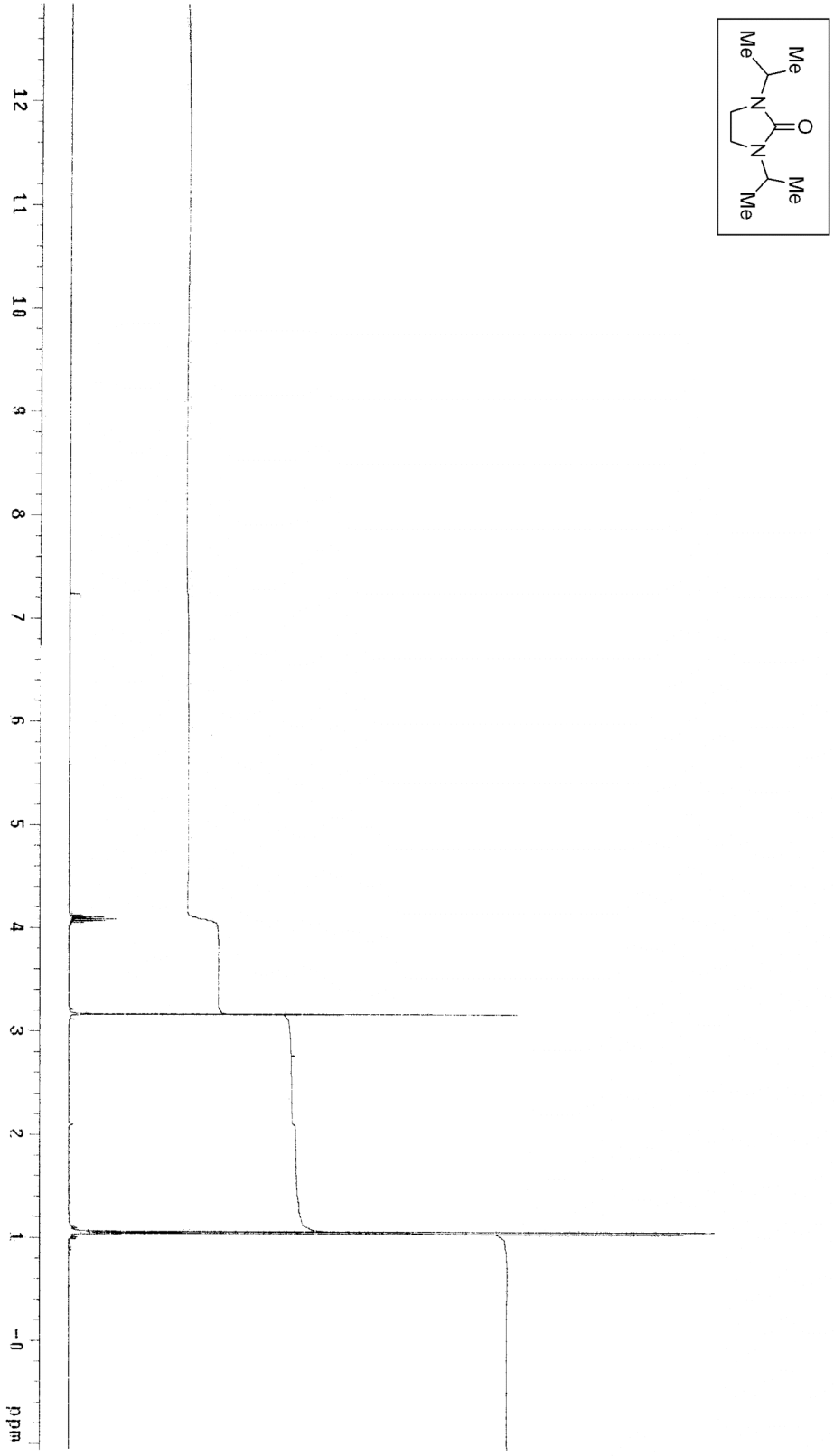


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-diisopropylimidazolidin-2-one in $CDCl_3$.

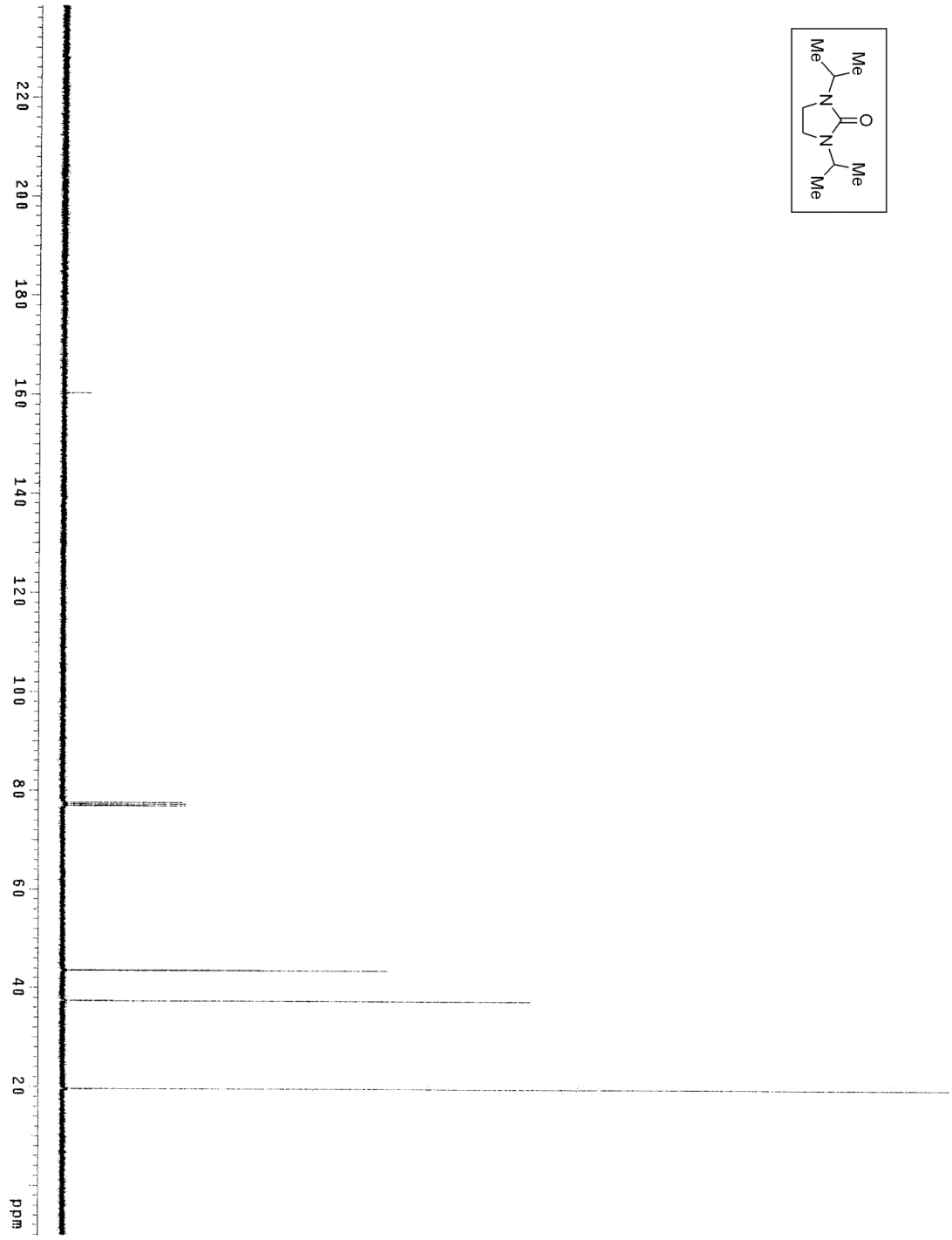


Figure S9. ^{1}H NMR spectrum of 1,3-di-*sec*-butylimidazolidin-2-one in $CDCl_3$.

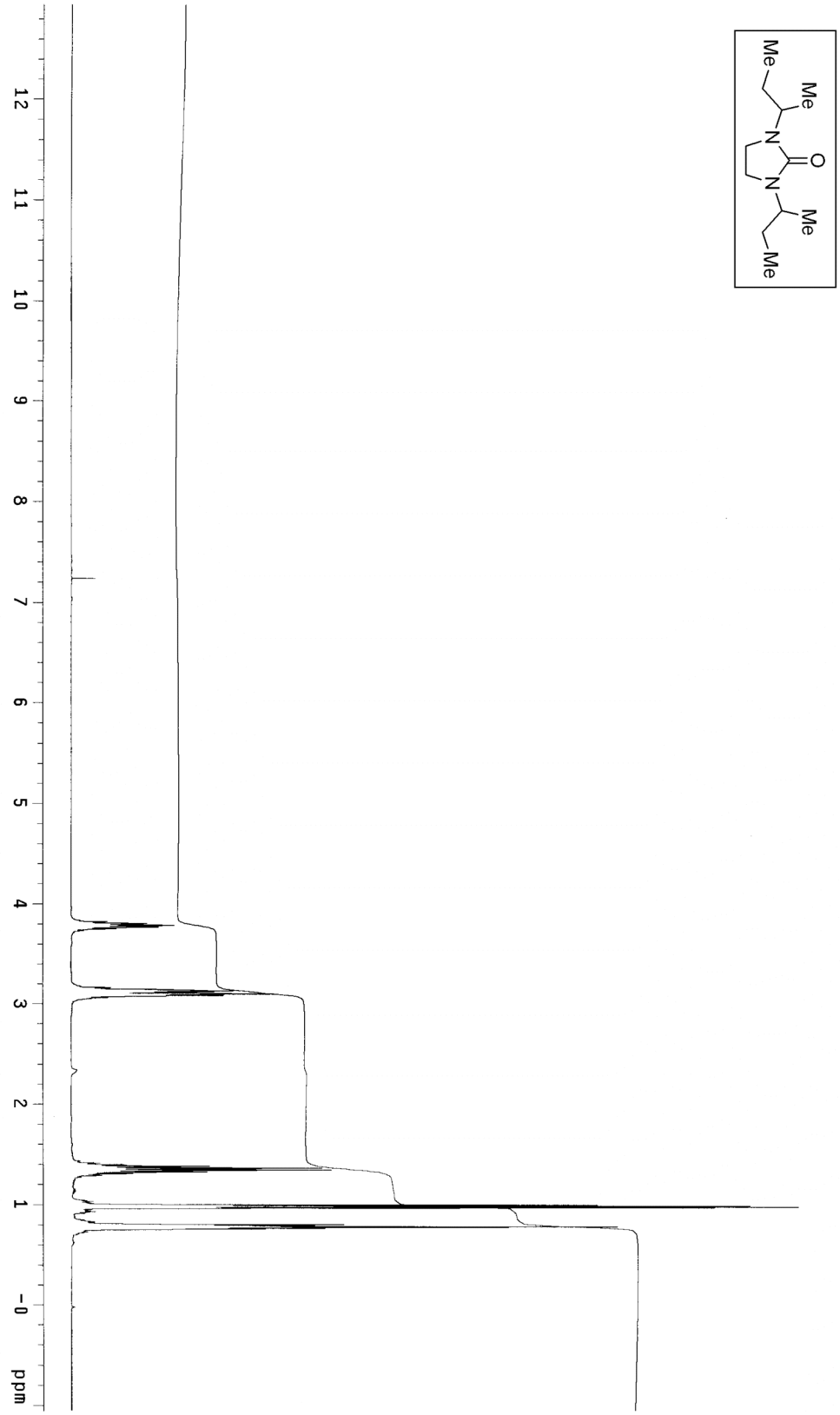


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-di-*sec*-butylimidazolidin-2-one in $CDCl_3$.

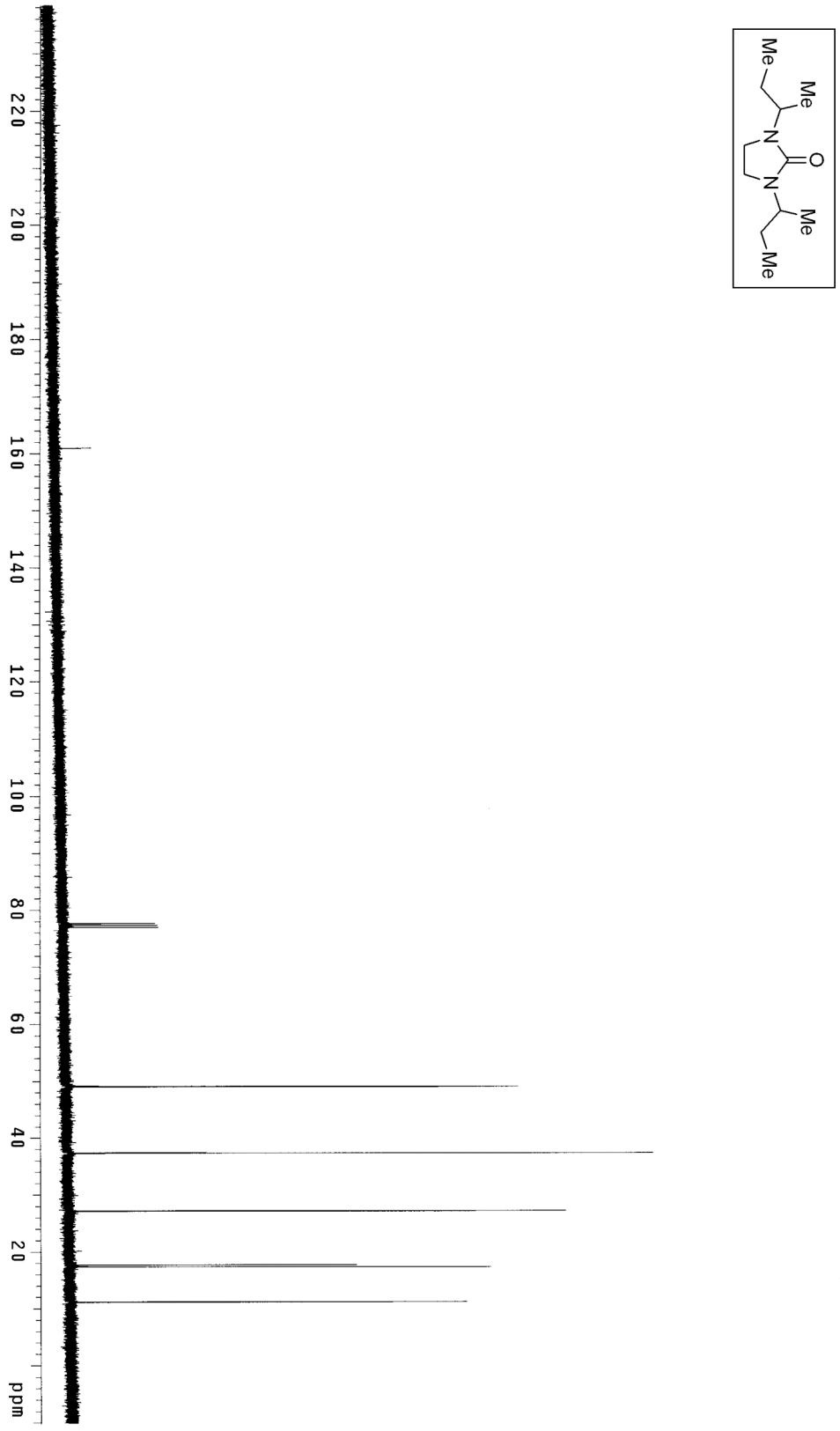


Figure S11. ^{1}H NMR spectrum of 1,3-diethyl-tetrahydropyrimidin-2(1*H*)-one in $CDCl_3$.

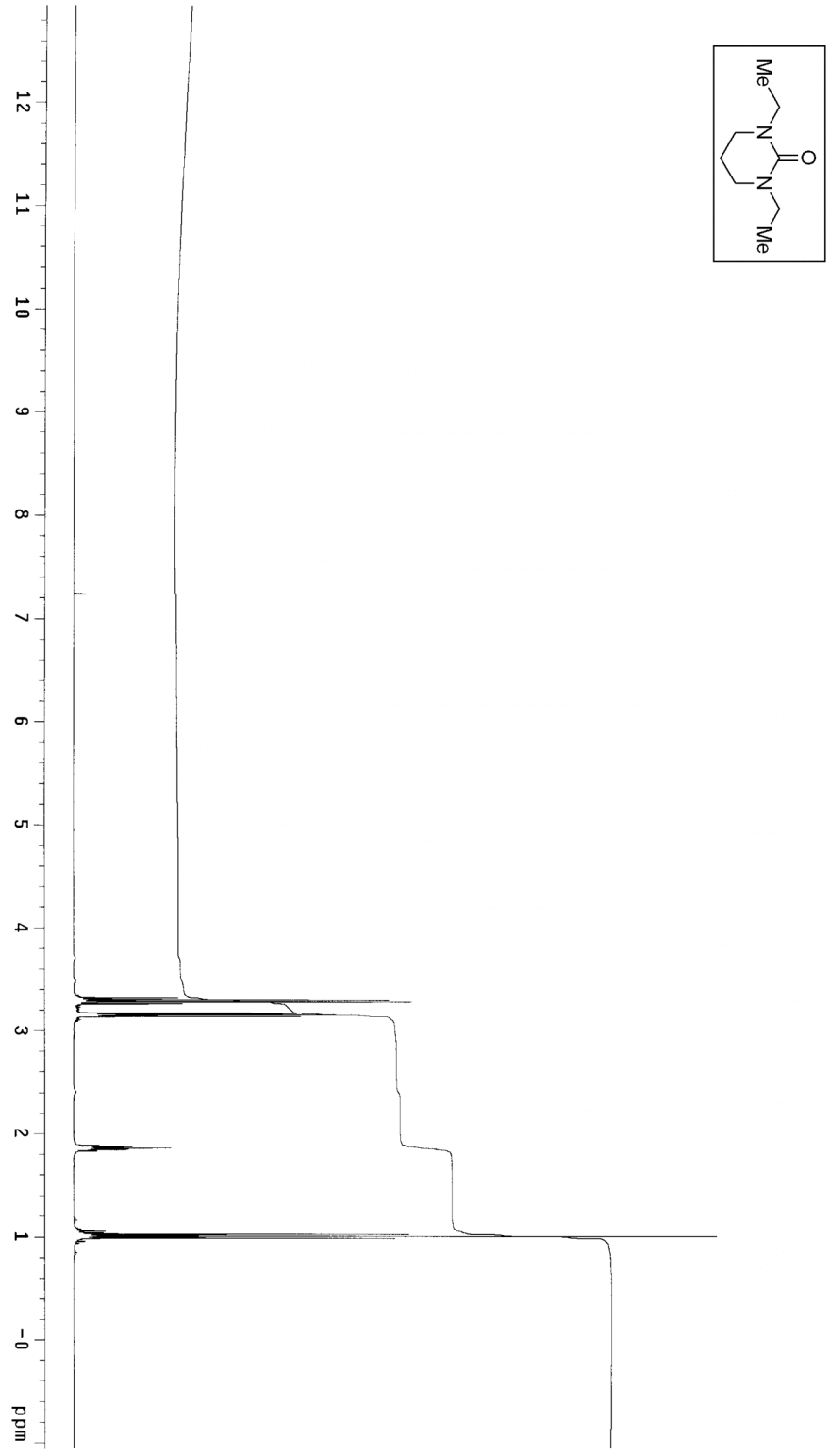


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-diethyl-tetrahydropyrimidin-2(1*H*)-one in $CDCl_3$.

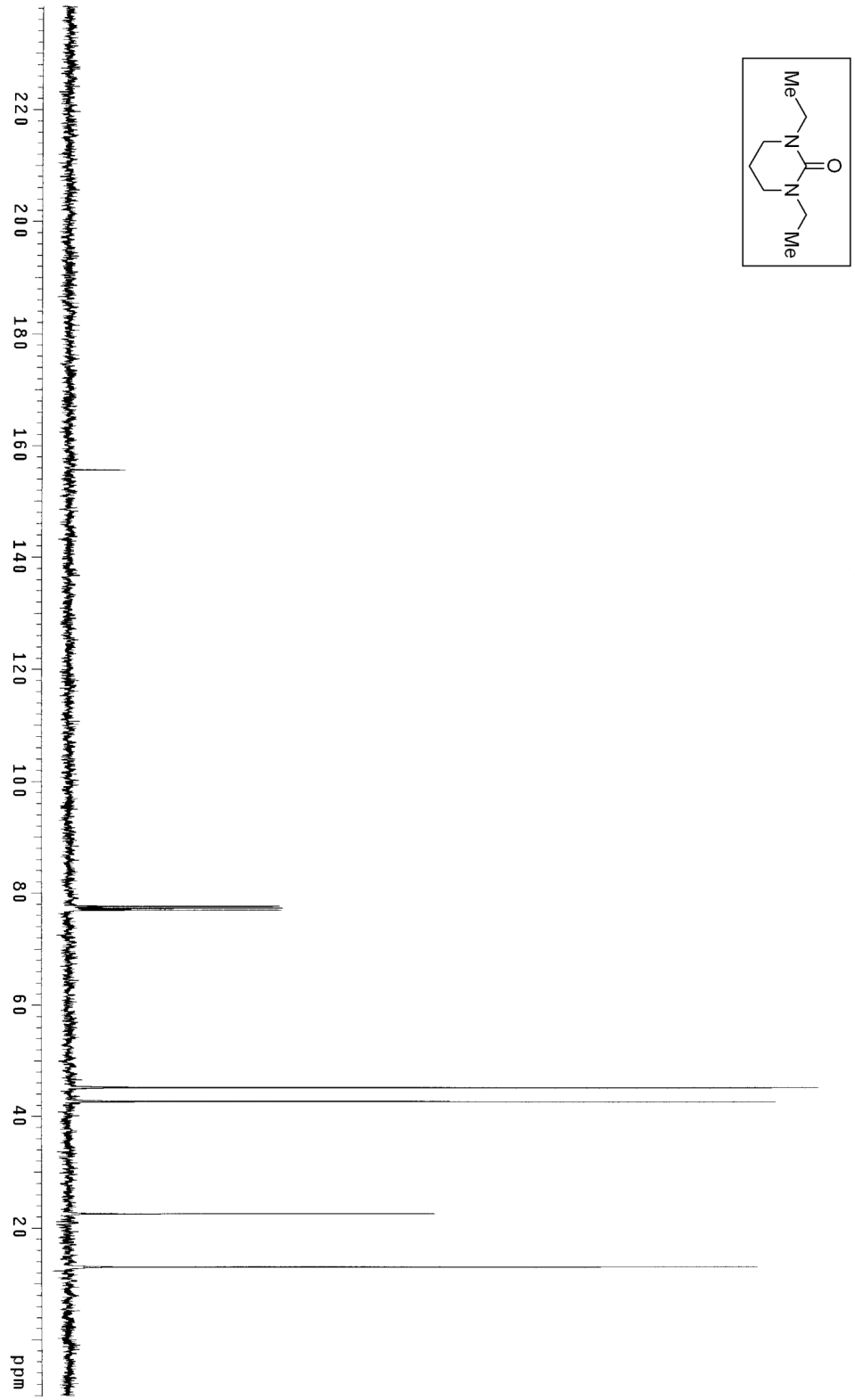


Figure S13. ^{1}H NMR spectrum of 1,3-diisopropyl-tetrahydropyrimidin-2(1*H*)-one in $CDCl_3$.

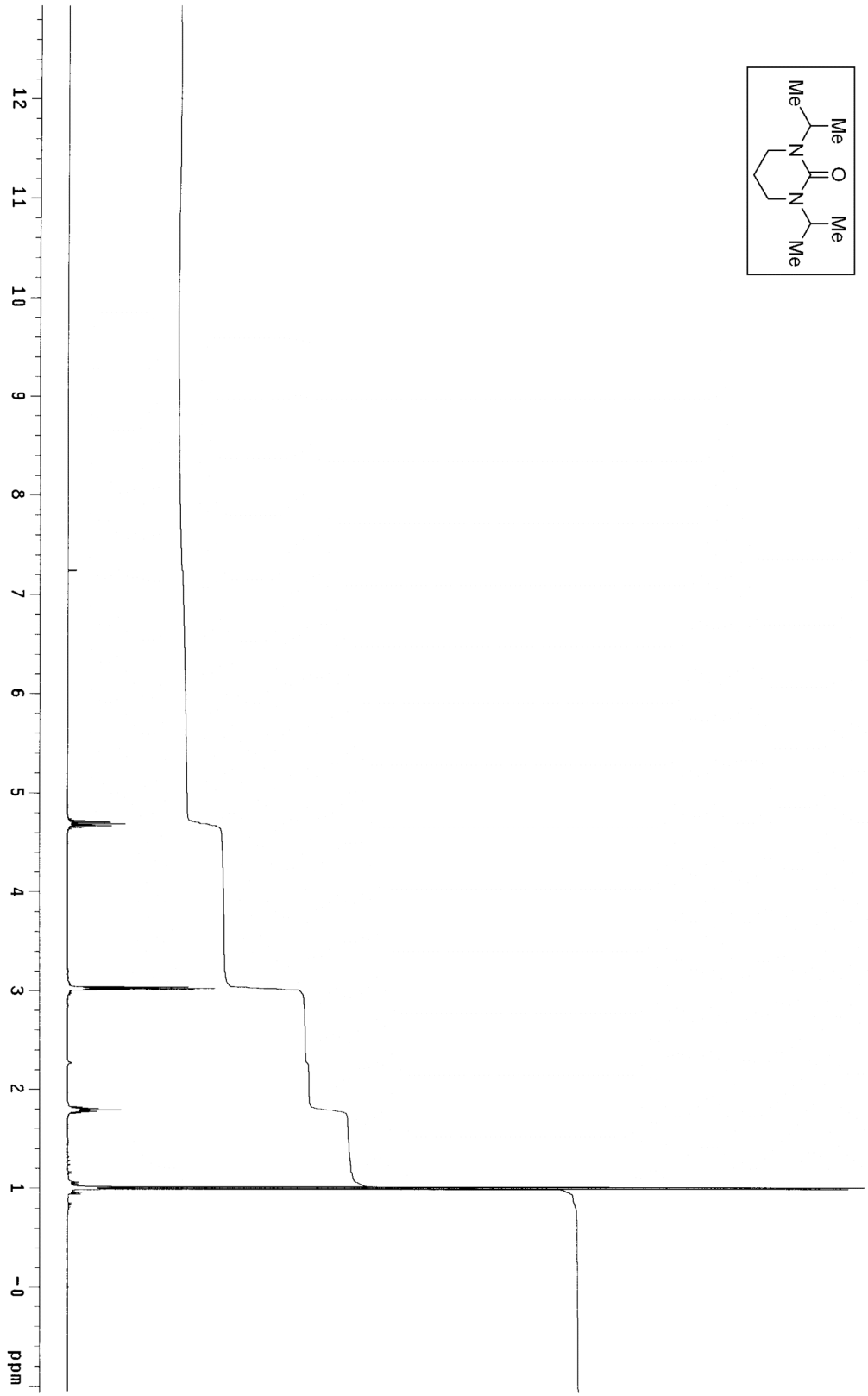


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-diisopropyl-tetrahydropyrimidin-2(1*H*)-one in $CDCl_3$.

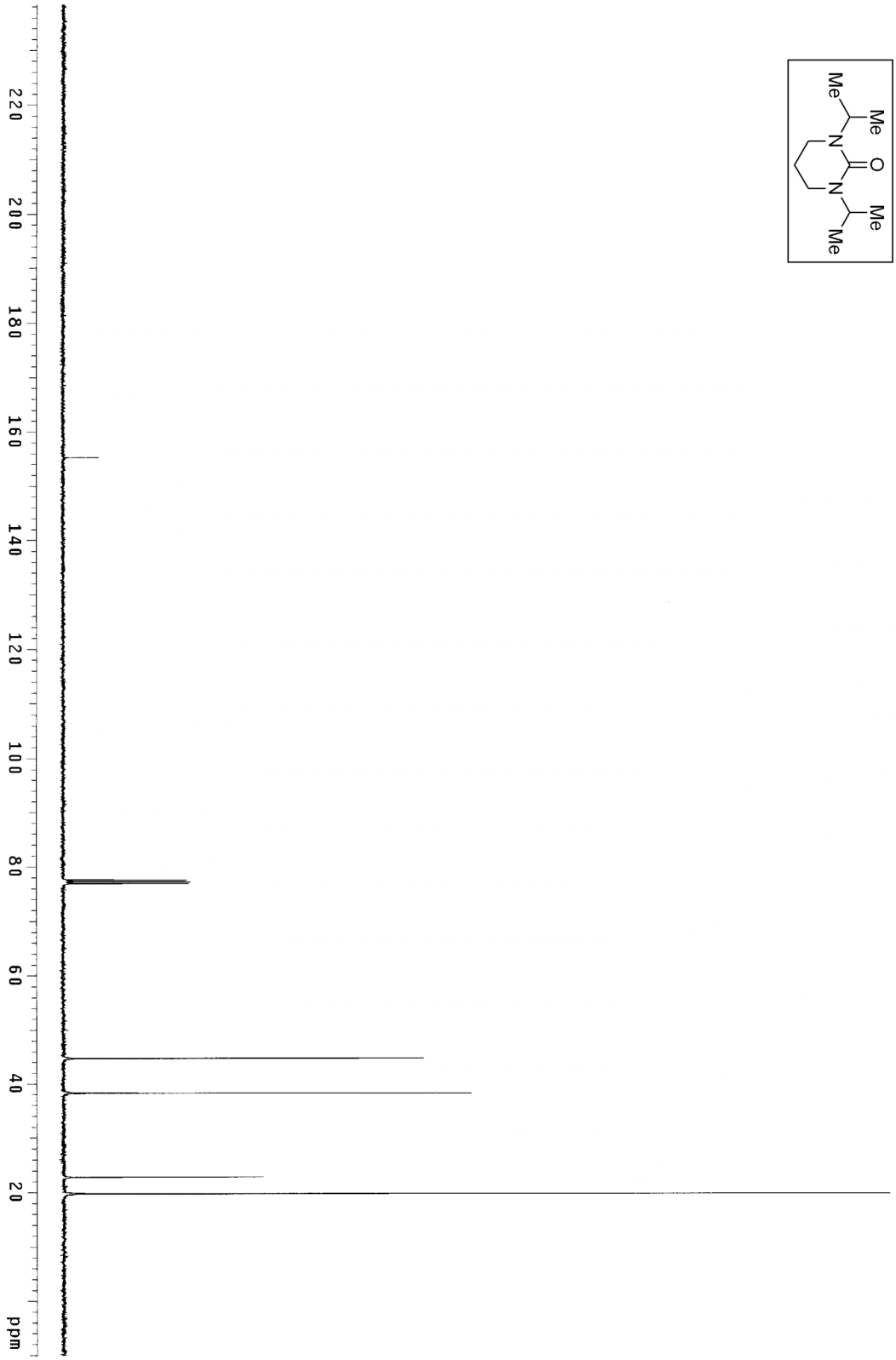


Figure S15. ^{1}H NMR spectrum of 1-isopropyl-3-methylimidazolidin-2-one in $CDCl_3$.

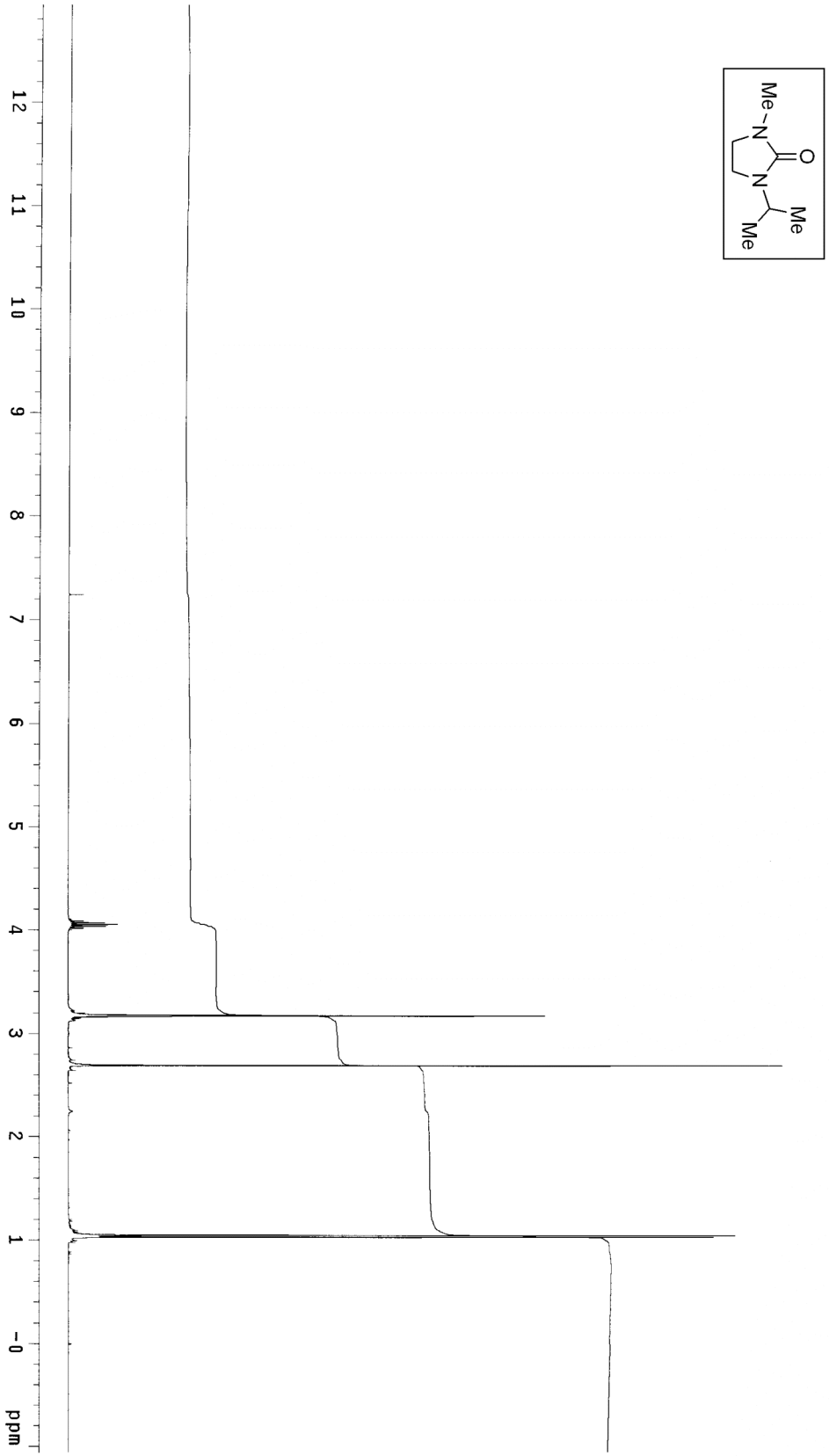


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of 1-isopropyl-3-methylimidazolidin-2-one in $CDCl_3$.

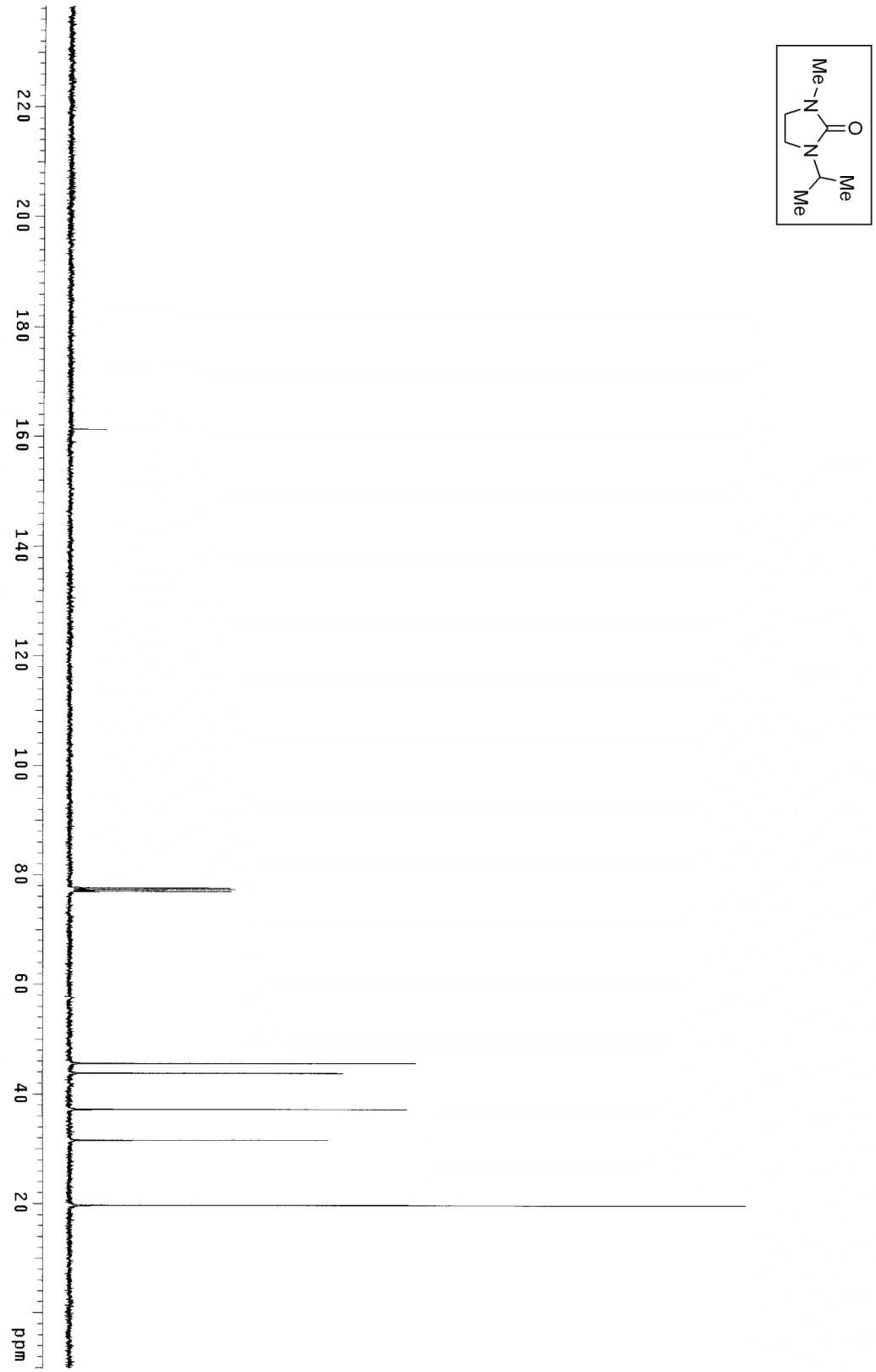


Figure S17. ^{1}H NMR spectrum of 1-*sec*-butyl-3-methylimidazolidin-2-one in $CDCl_3$.

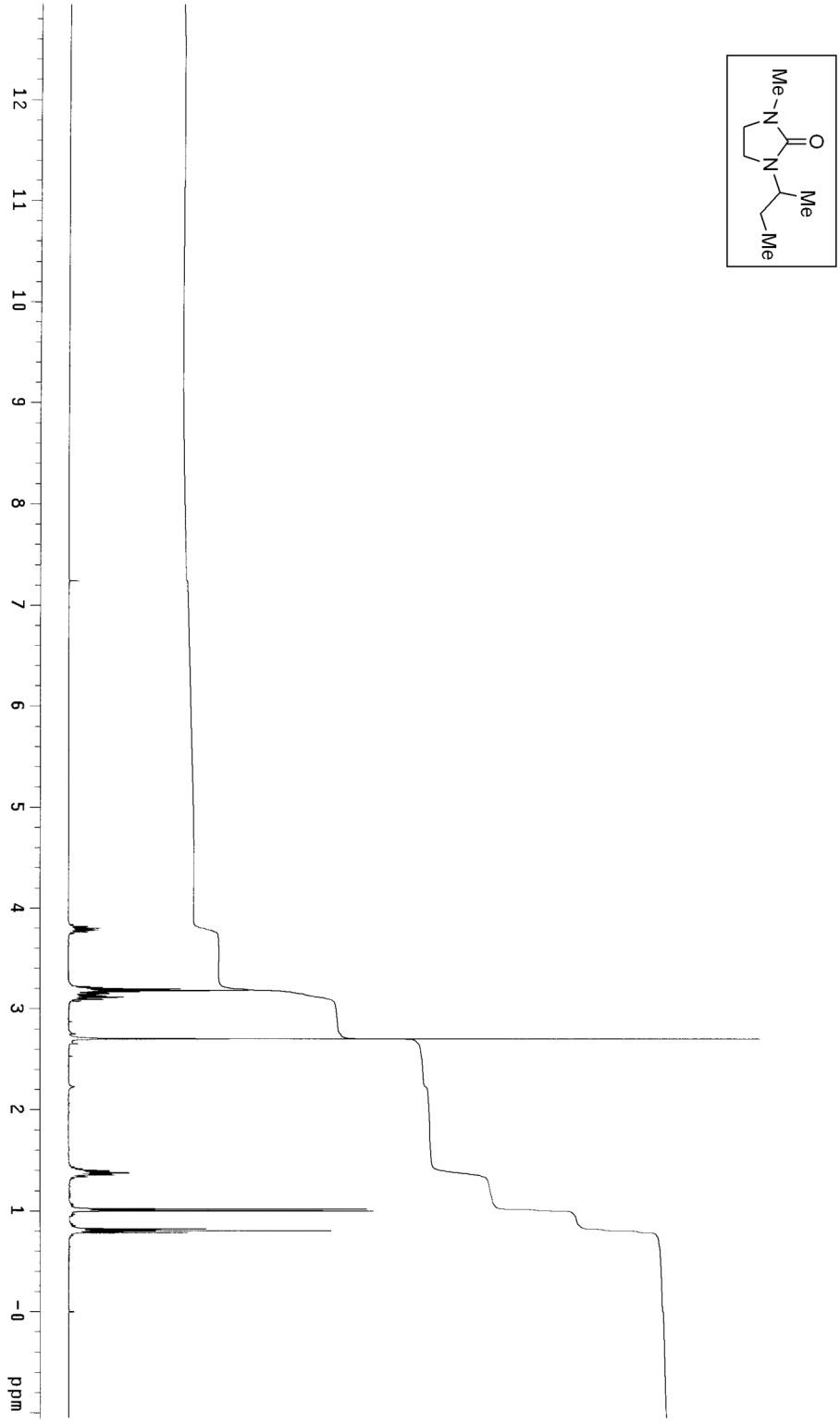


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of 1-*sec*-butyl-3-methylimidazolidin-2-one in $CDCl_3$.

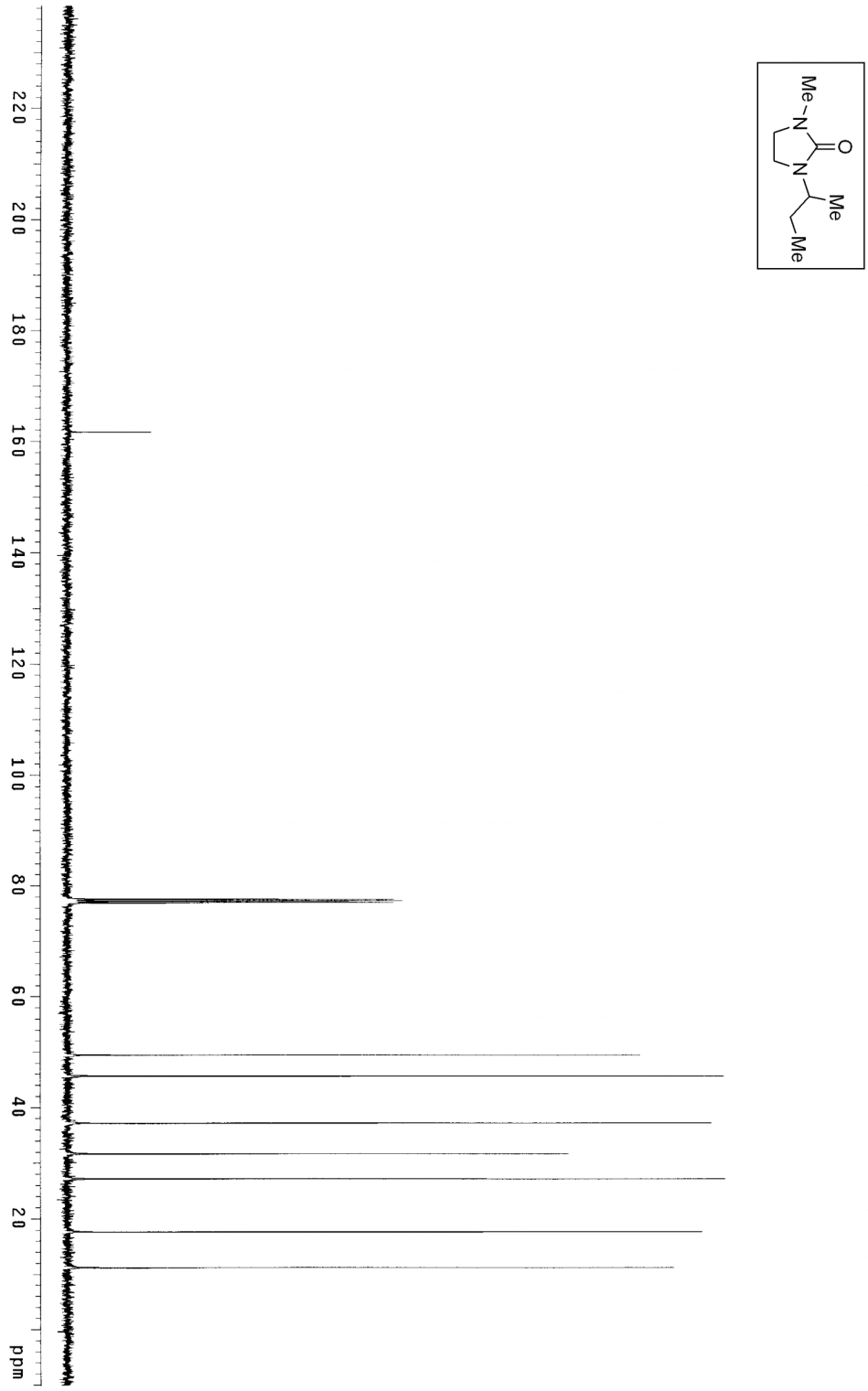


Figure S19. ^{1}H NMR spectrum of 1-*tert*-butyl-3-methylimidazolidin-2-one in $CDCl_3$.

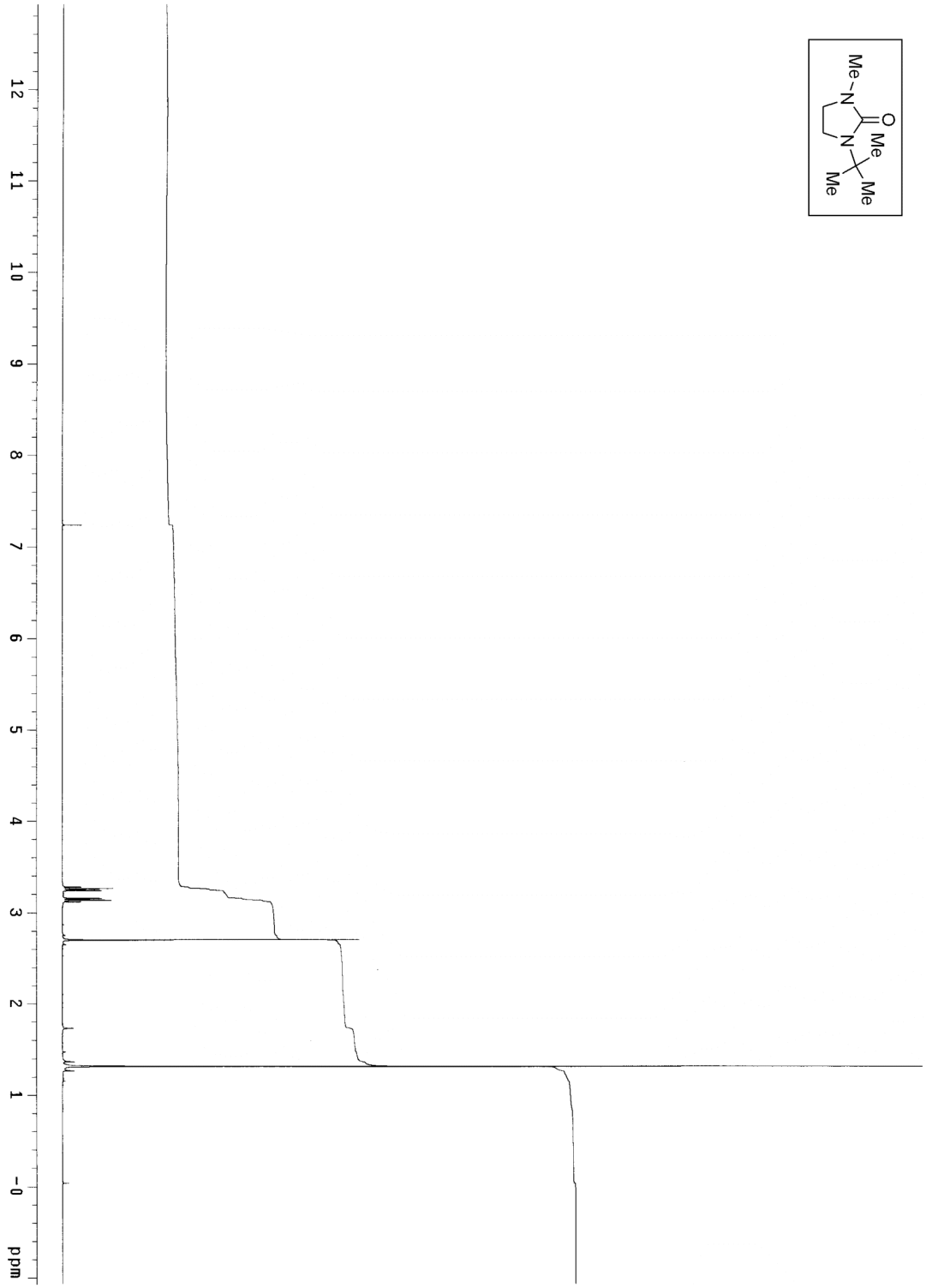


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of 1-*tert*-butyl-3-methylimidazolidin-2-one in $CDCl_3$.

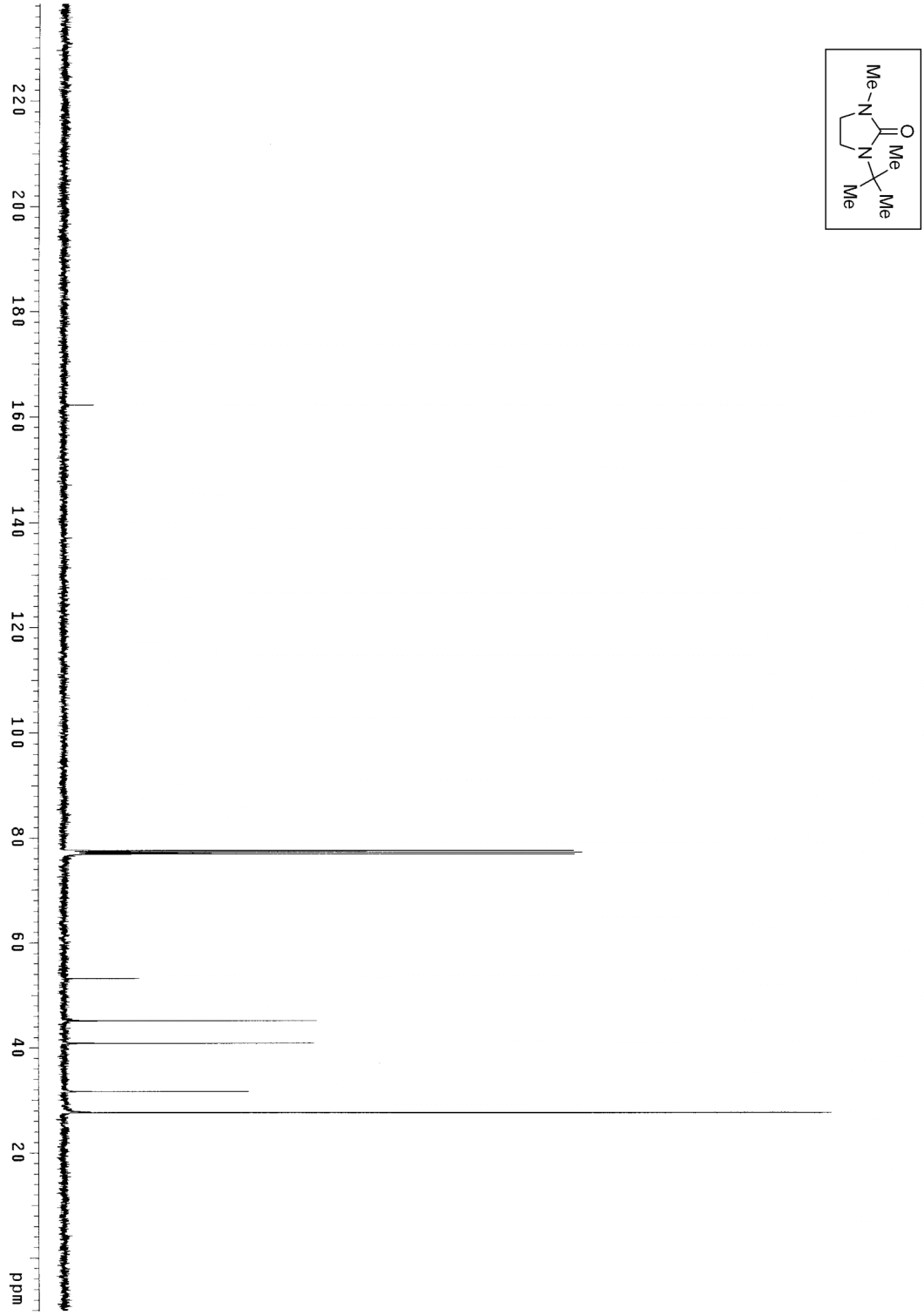


Figure S21. ^{1}H NMR spectrum of 1-methyl-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

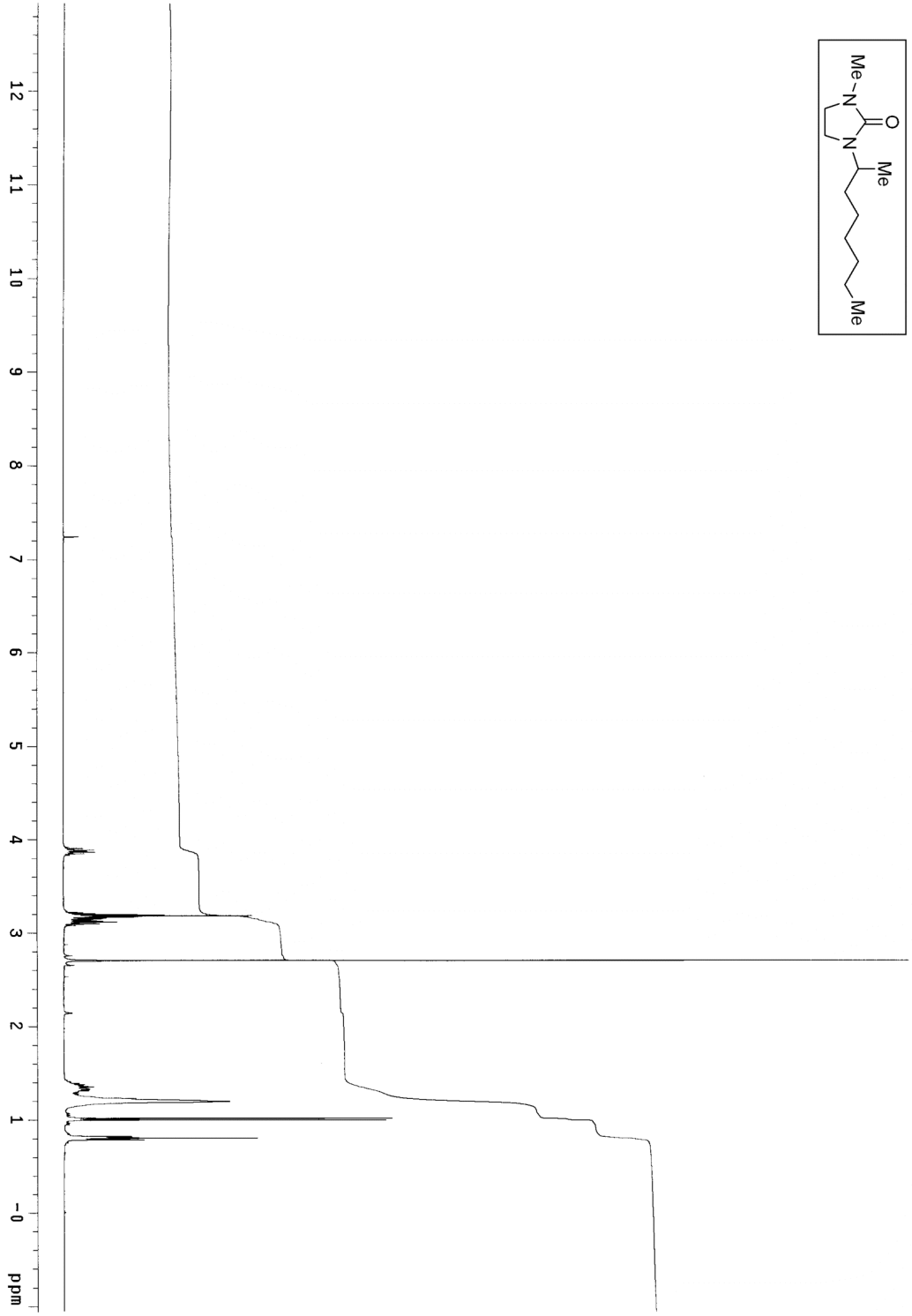


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of 1-methyl-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

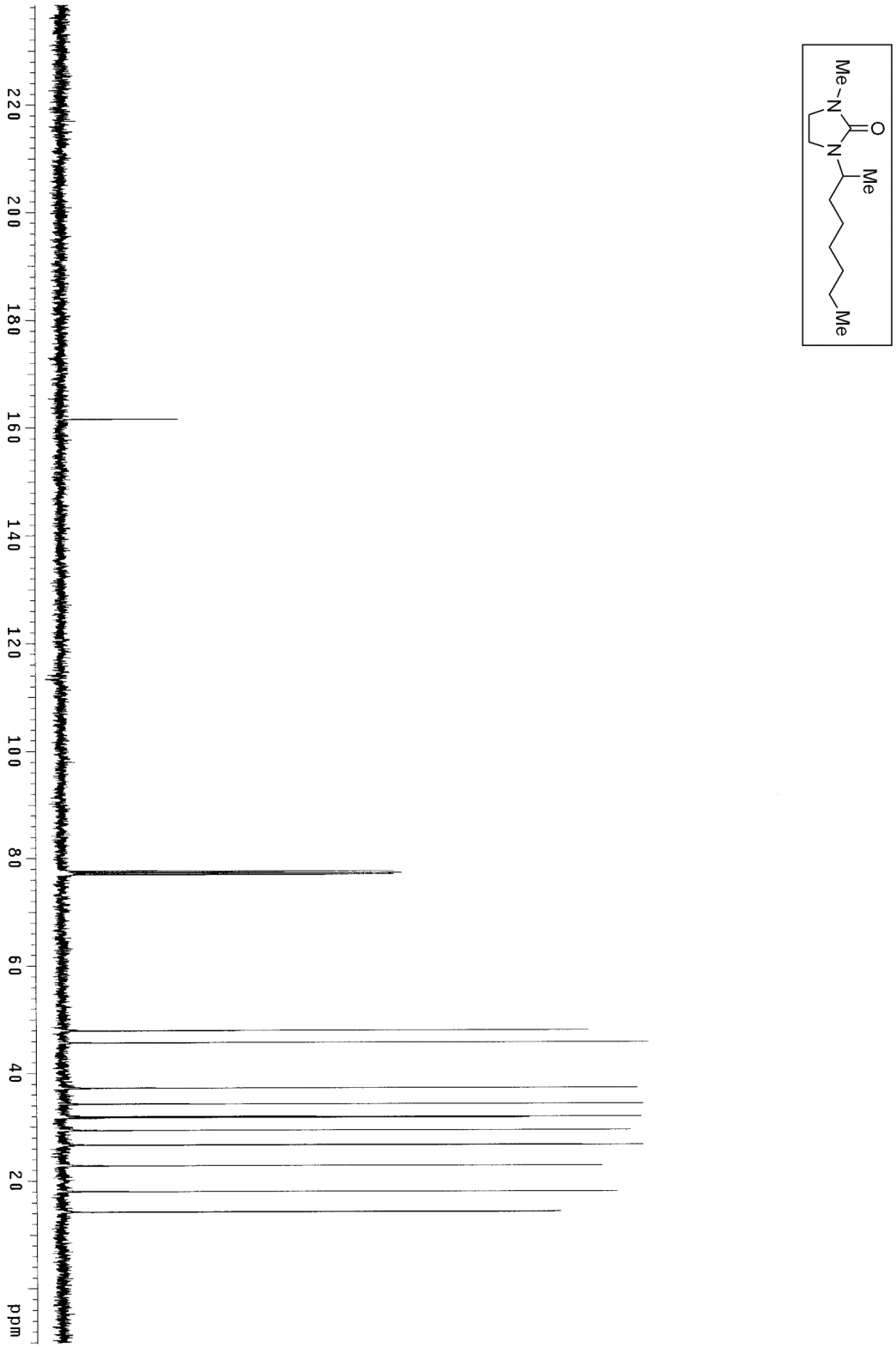


Figure S23. ^{1}H NMR spectrum of 1-(5-hydroxypentan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

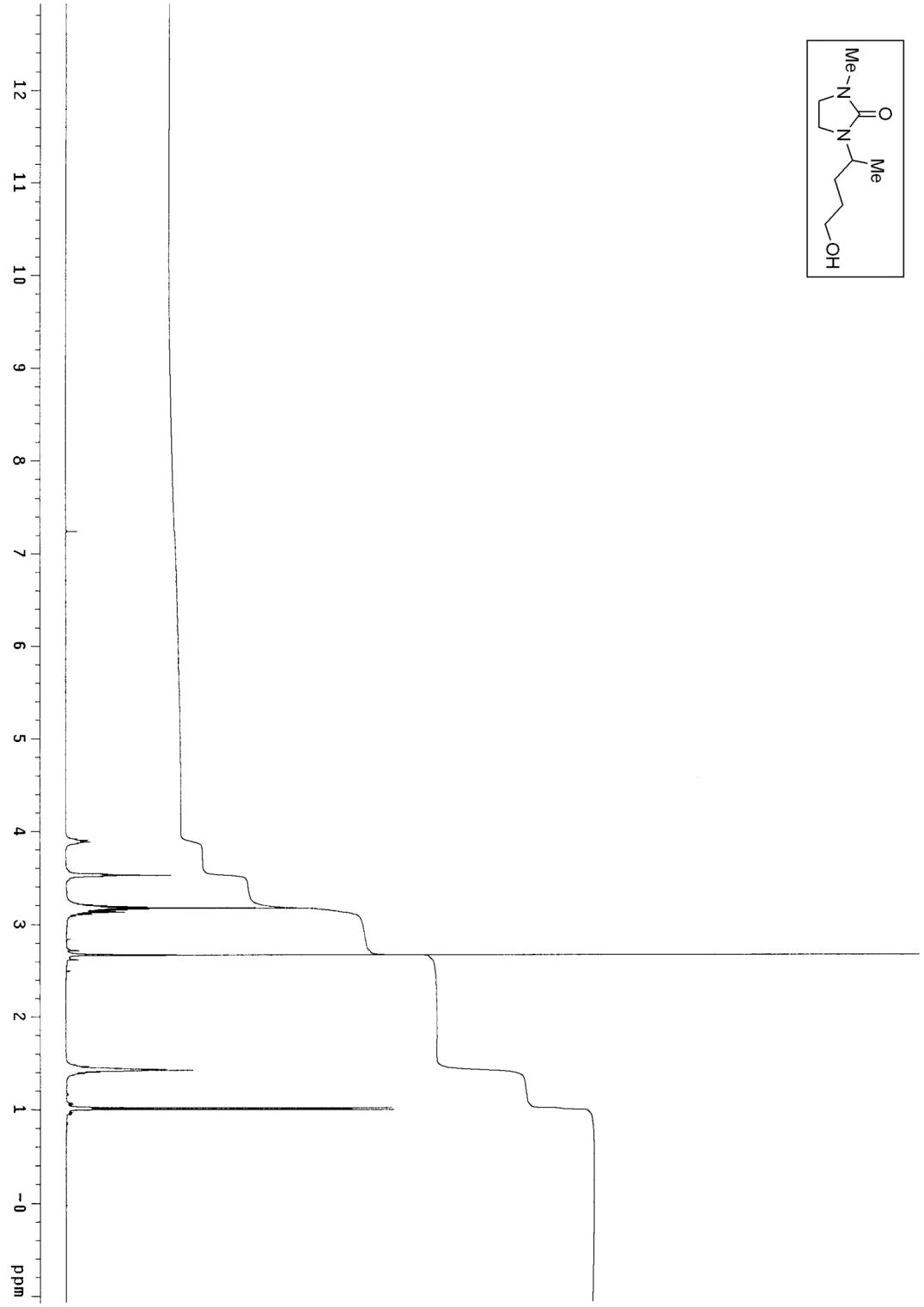


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(5-hydroxypentan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

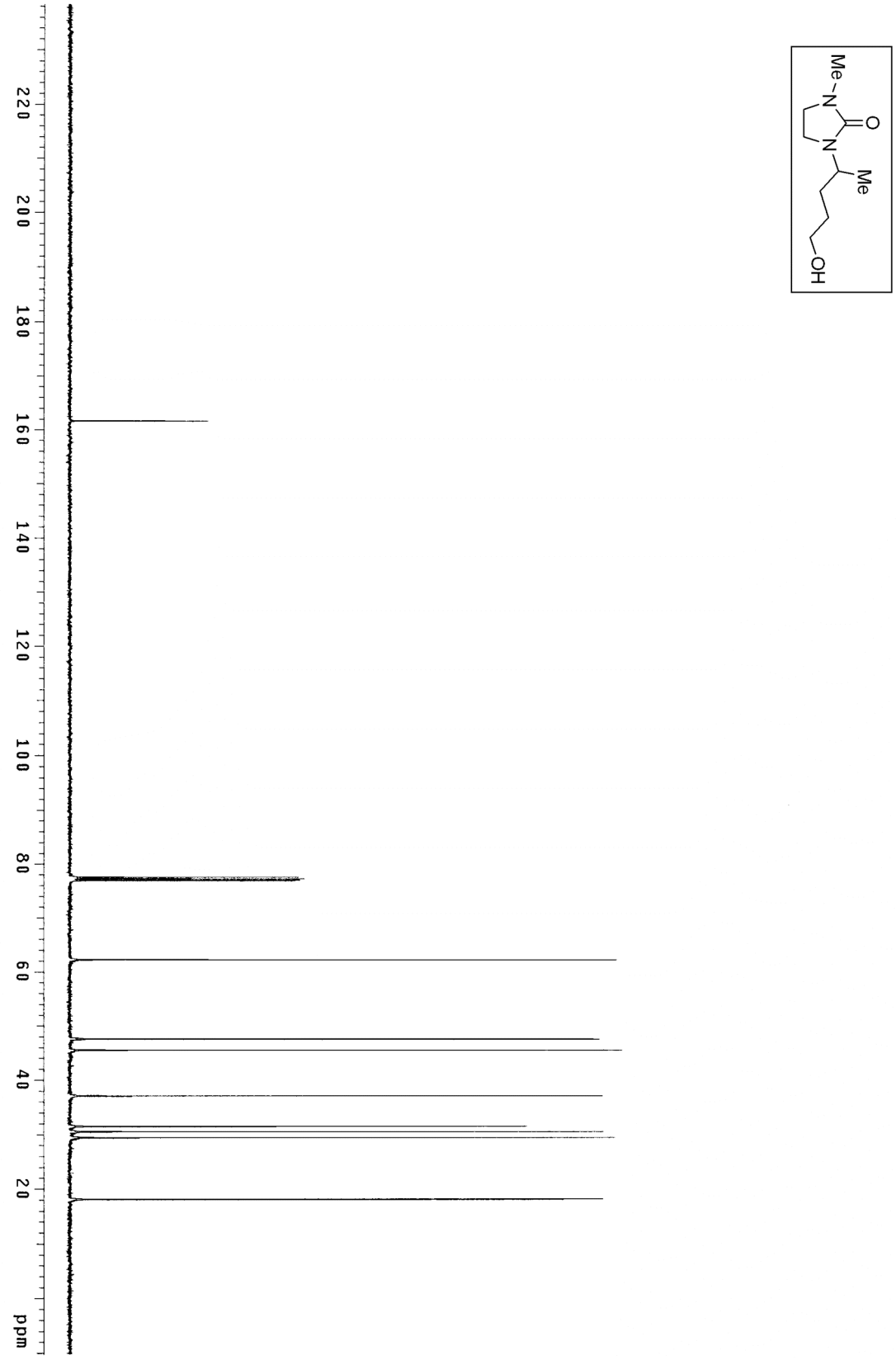


Figure S25. ^{1}H NMR spectrum of 1-(5-benzyloxypentan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

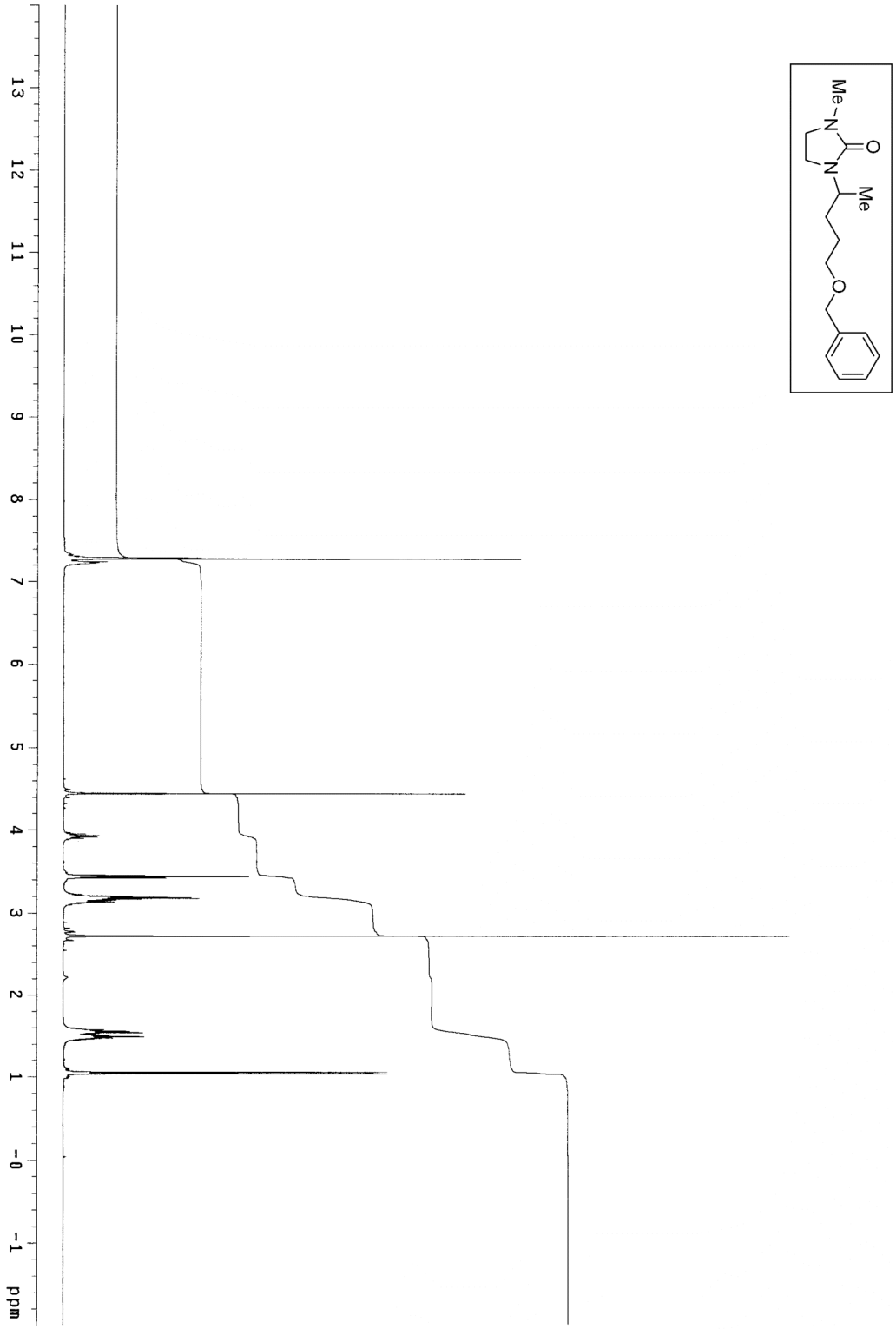


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(5-benzyloxypentan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

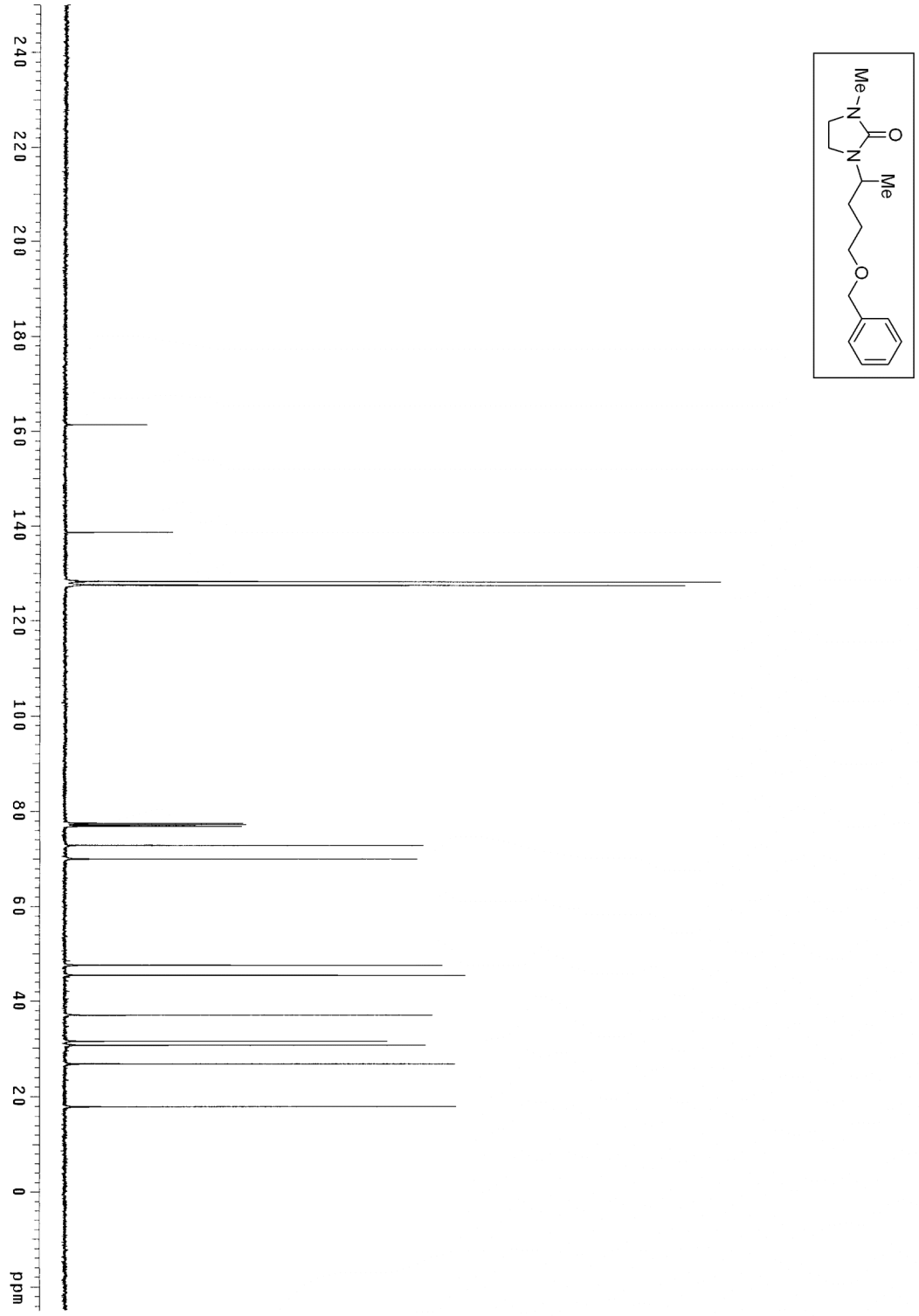


Figure S27. ^{1}H NMR spectrum of 4-(3-methyl-2-oxoimidazolidin-1-yl)pentanoic acid in $CDCl_3$.

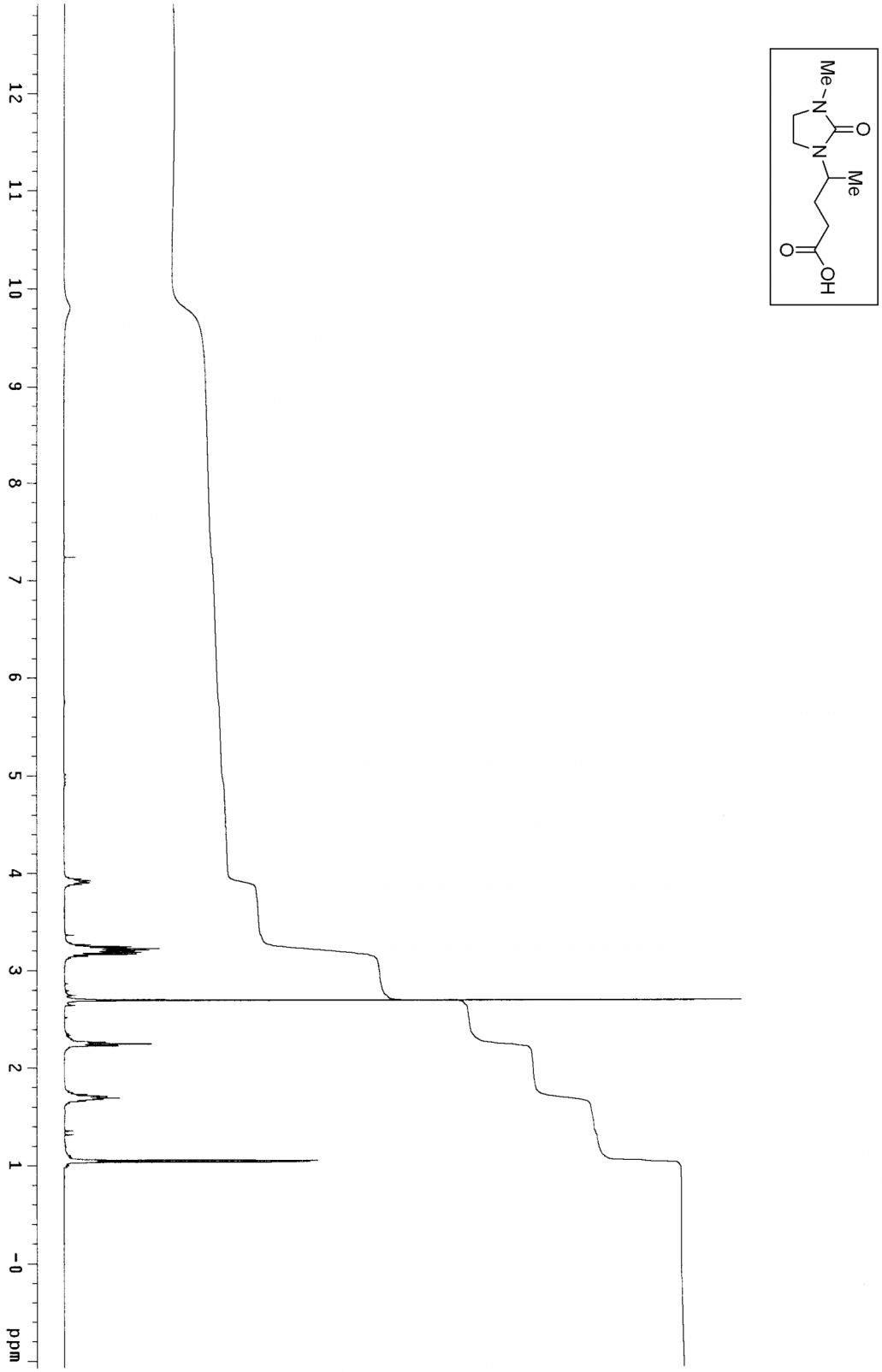
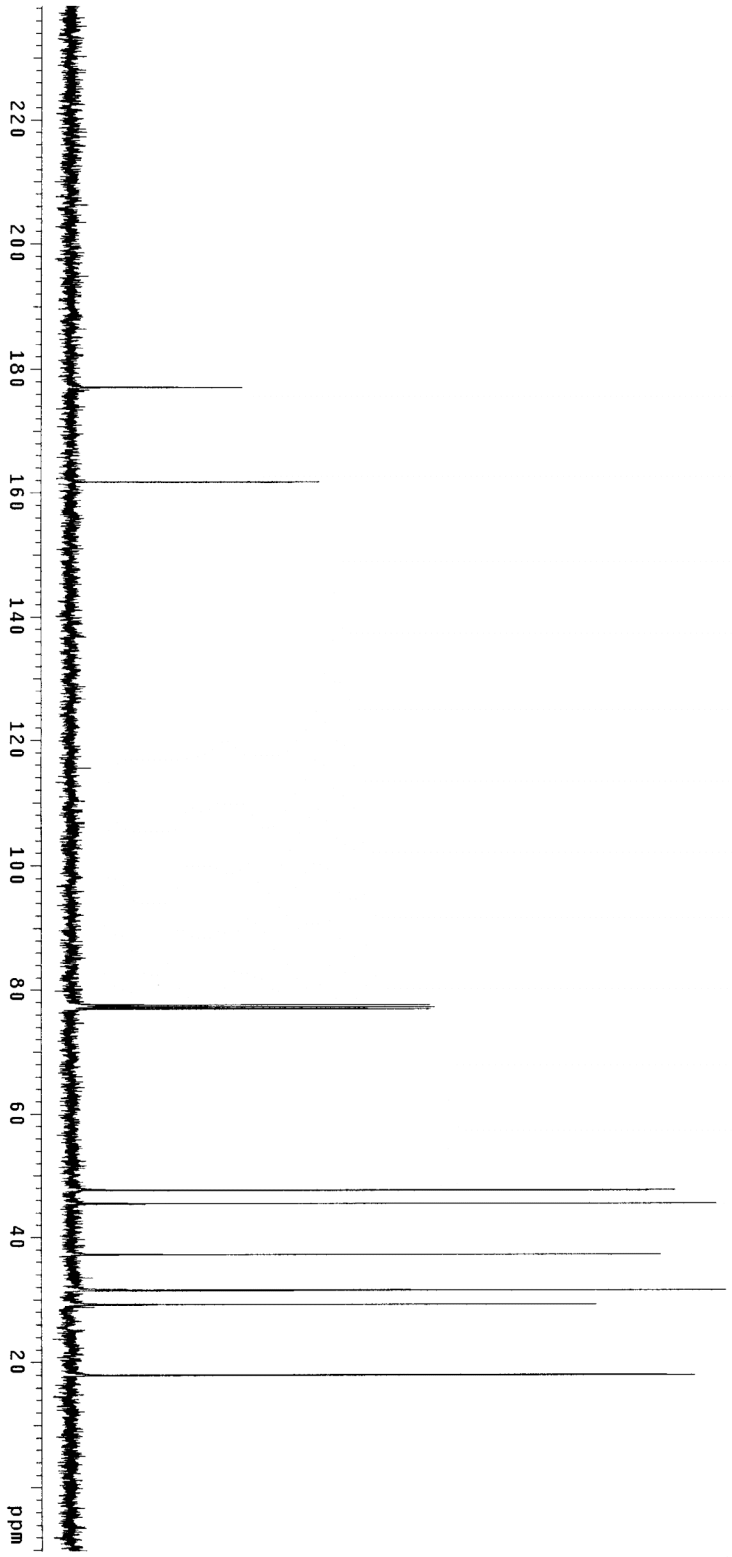


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(3-methyl-2-oxoimidazolidin-1-yl)pentanoic acid in $CDCl_3$.



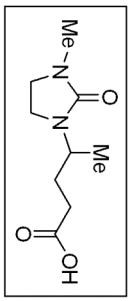


Figure S29. ^{1}H NMR spectrum of ethyl 6-(3-methyl-2-oxoimidazolidin-1-yl)heptanoate in $CDCl_3$.

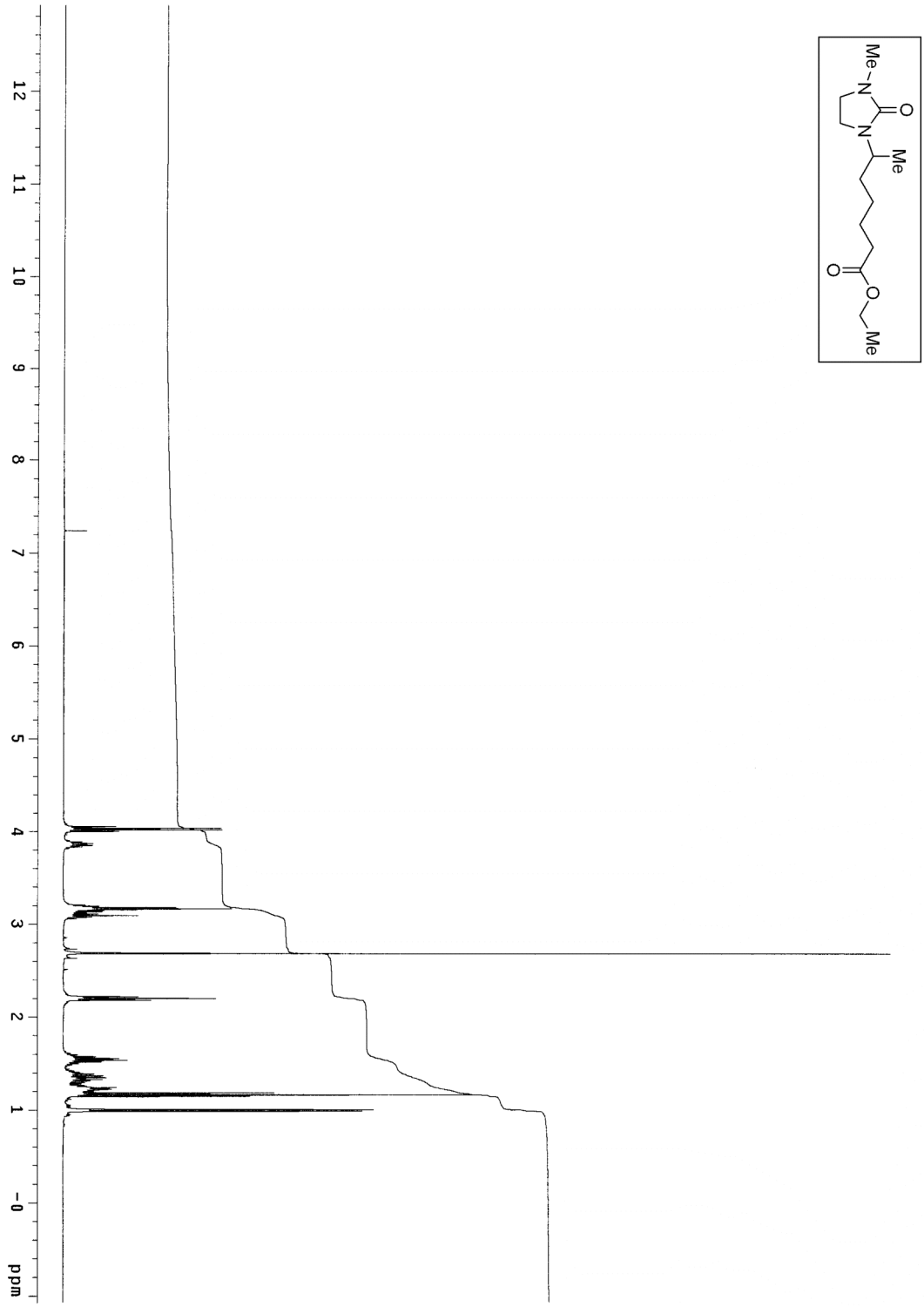


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 6-(3-methyl-2-oxoimidazolidin-1-yl)heptanoate in $CDCl_3$.

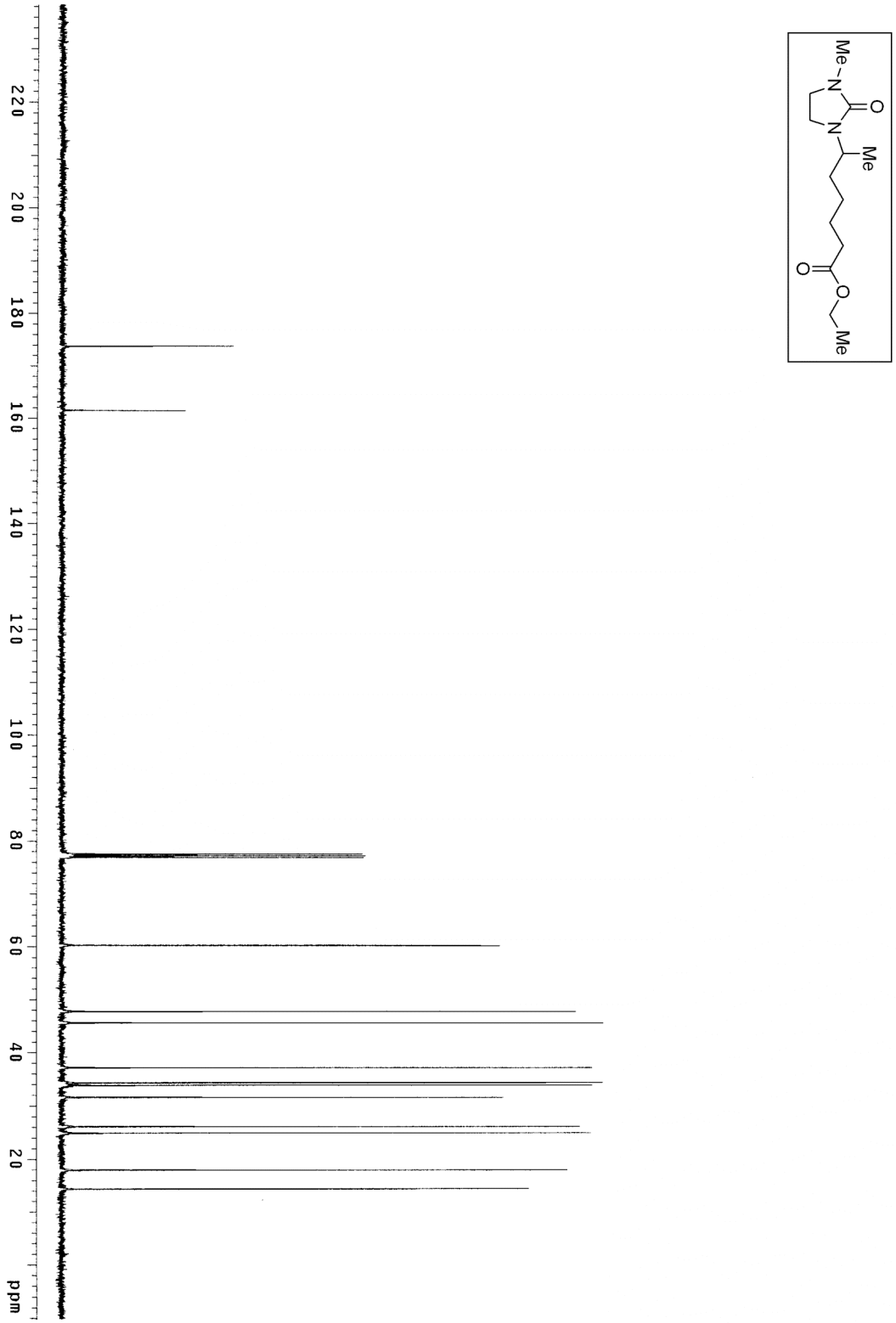


Figure S31. ^{1}H NMR spectrum of 1-methyl-3-(1-phenylethyl)imidazolidin-2-one in $CDCl_3$.

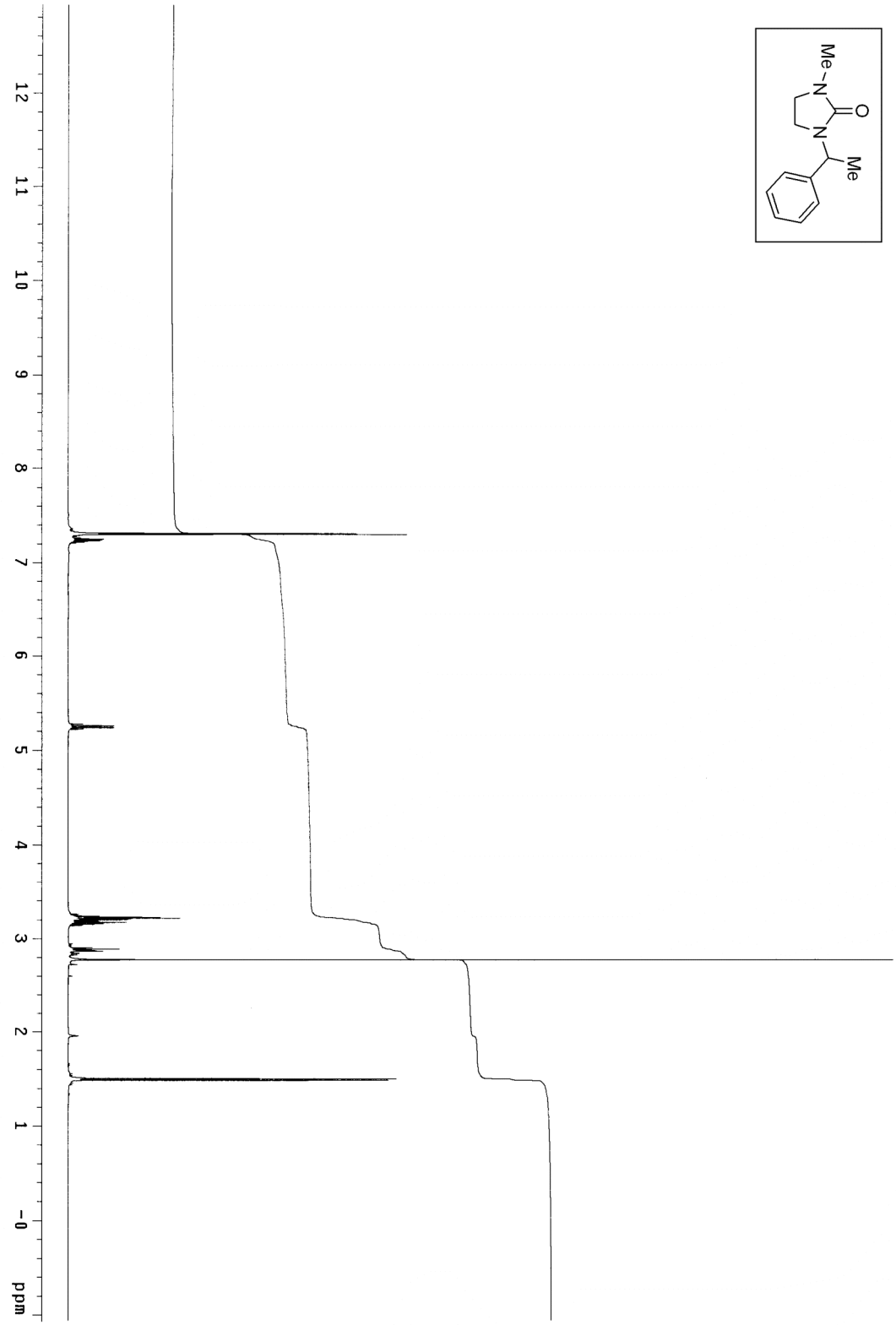


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of 1-methyl-3-(1-phenylethyl)imidazolidin-2-one in $CDCl_3$.

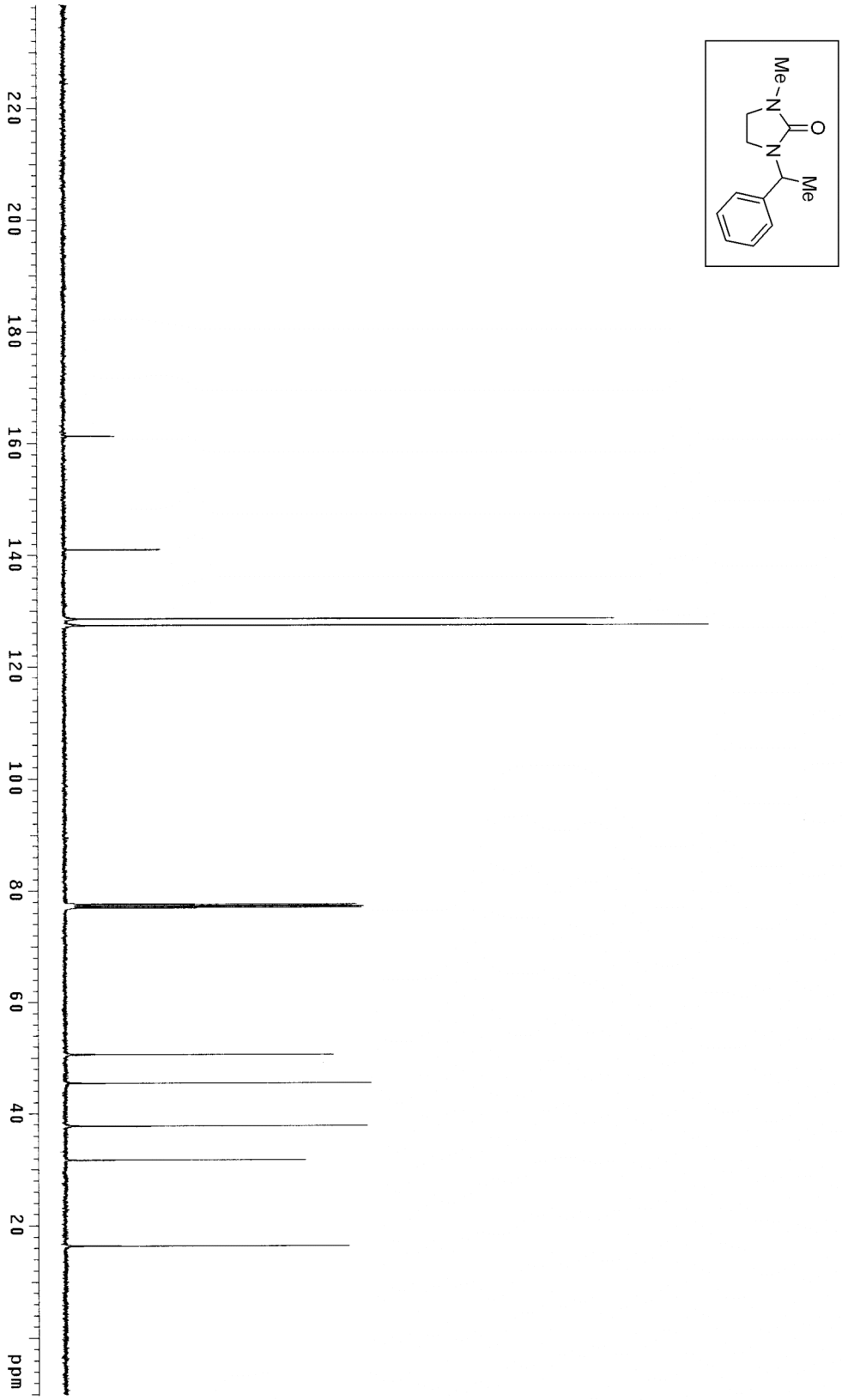


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(bicyclo[2.2.1]heptan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

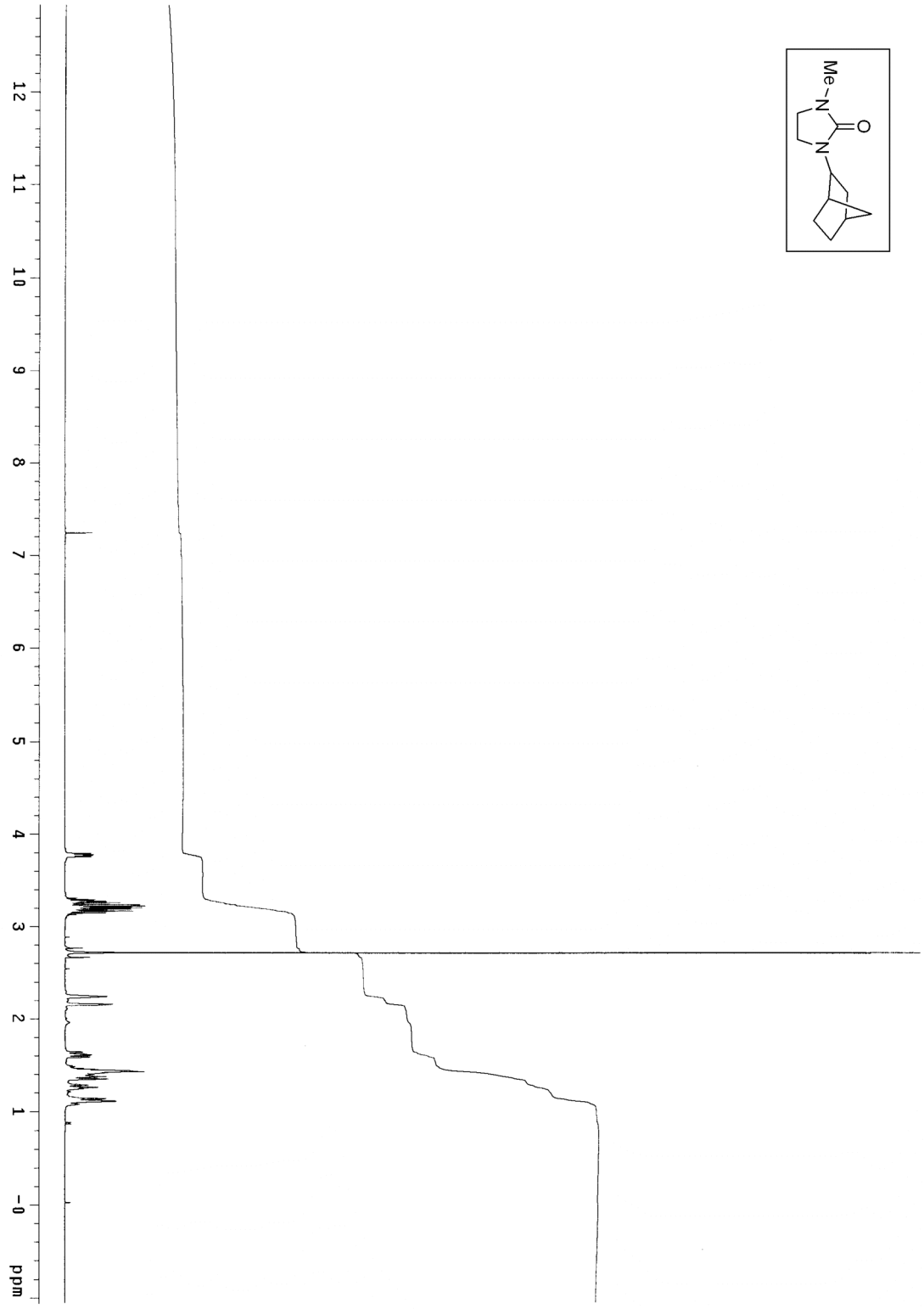


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(bicyclo[2.2.1]heptan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

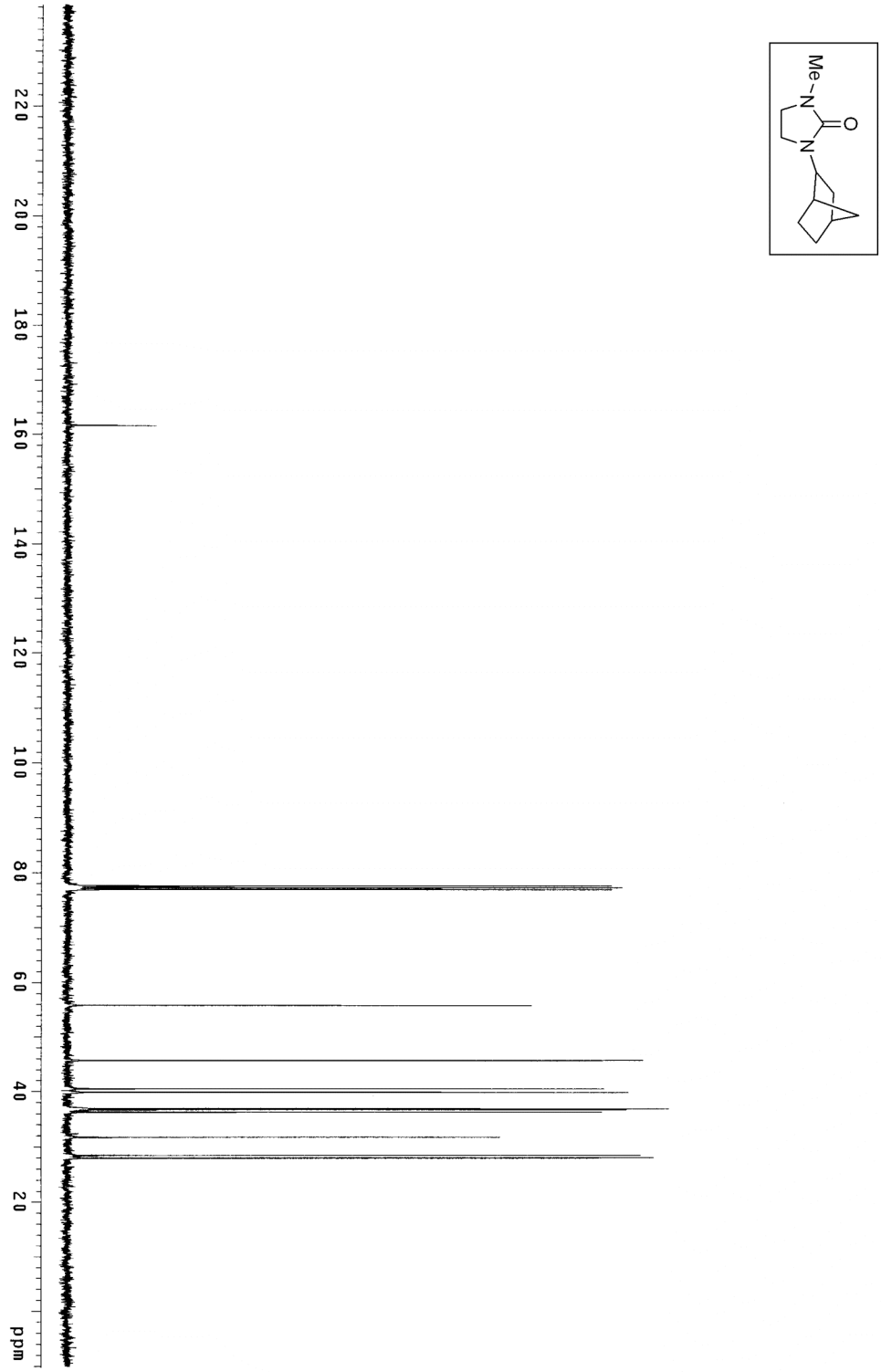
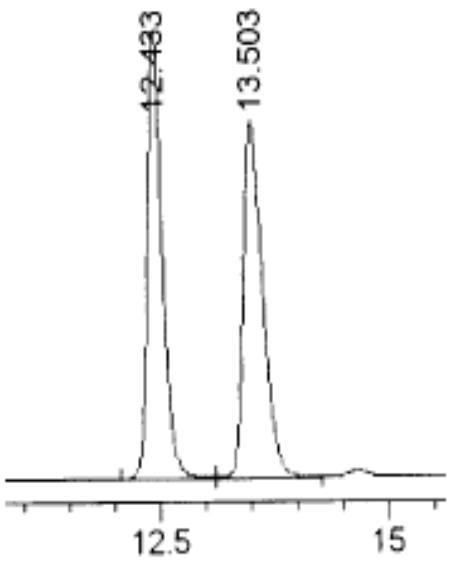


Figure S35. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 76 % ee) methyl-3-(octan-2-yl)imidazolidin-2-one.



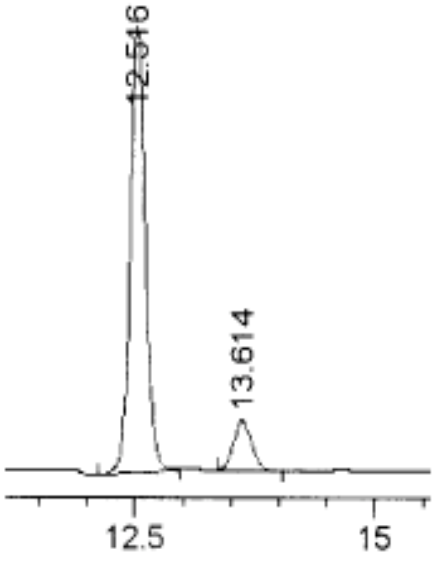


Figure S36. ^{1}H NMR spectrum of 1-(octan-2-yl)-3-phenylimidazolidin-2-one in $CDCl_3$.

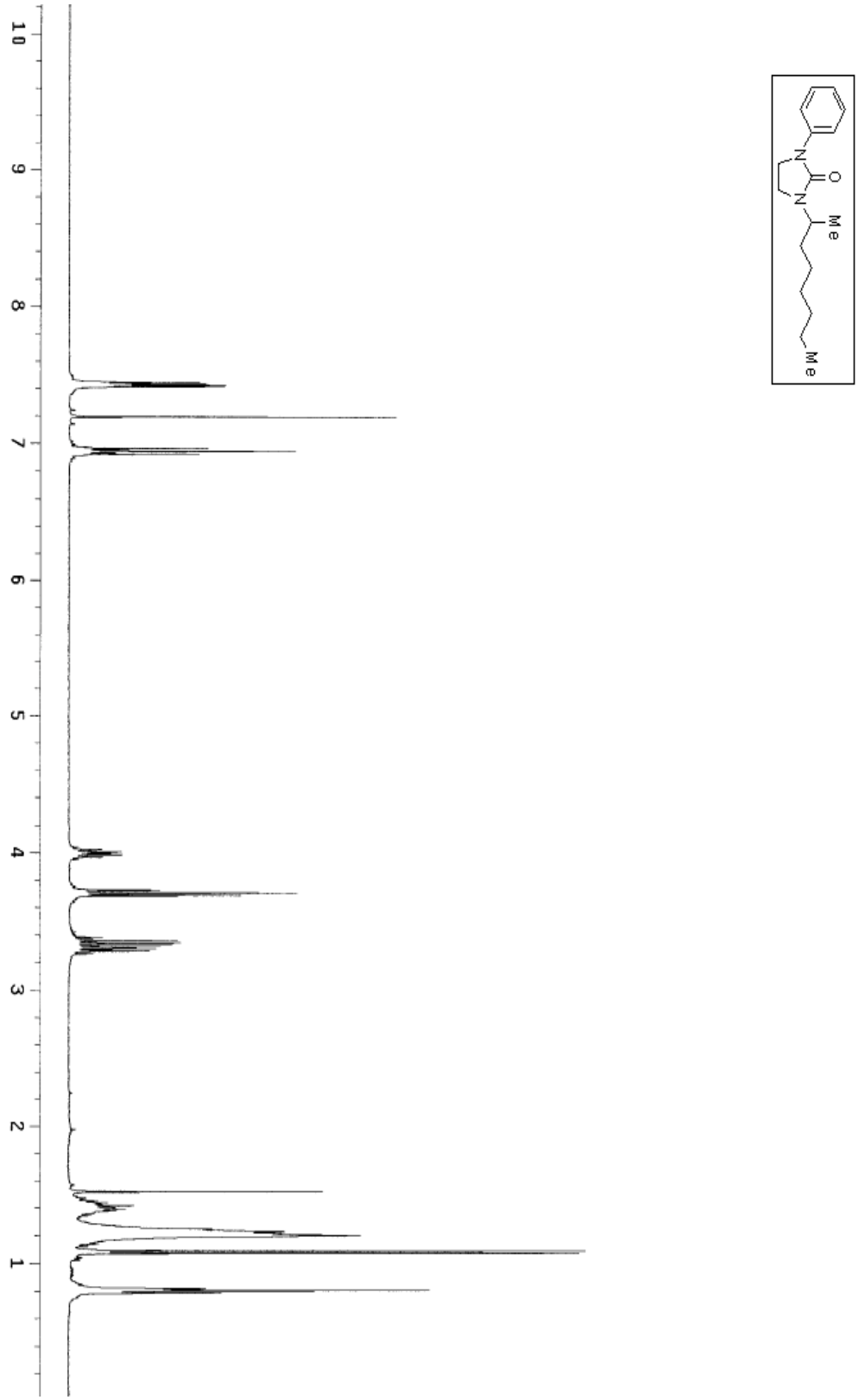


Figure S37. ^{13}C NMR spectrum of 1-(octan-2-yl)-3-phenylimidazolidin-2-one in $CDCl_3$.

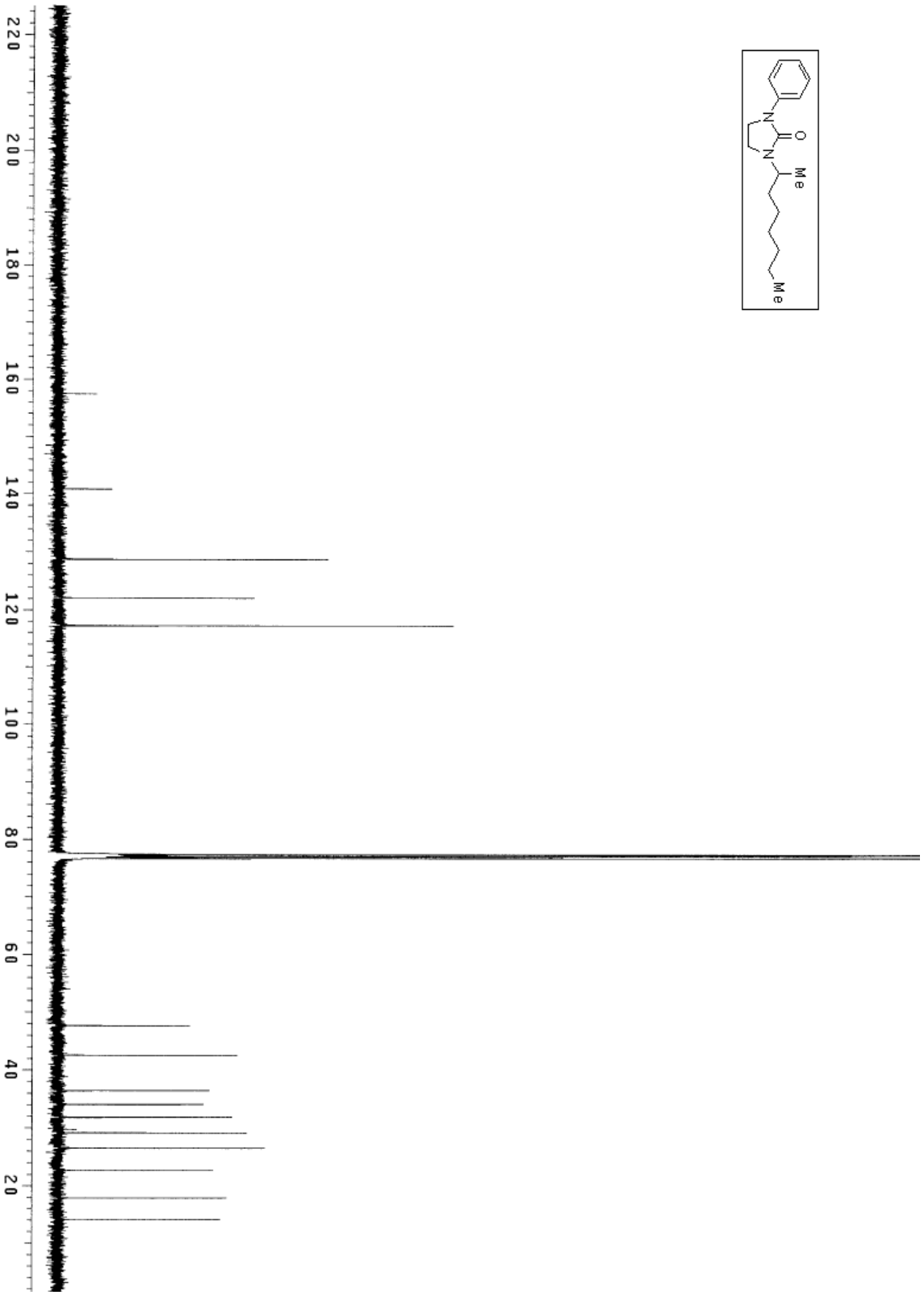


Figure S38. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 71 % ee) 1-(octan-2-yl)-3-phenylimidazolidin-2-one.

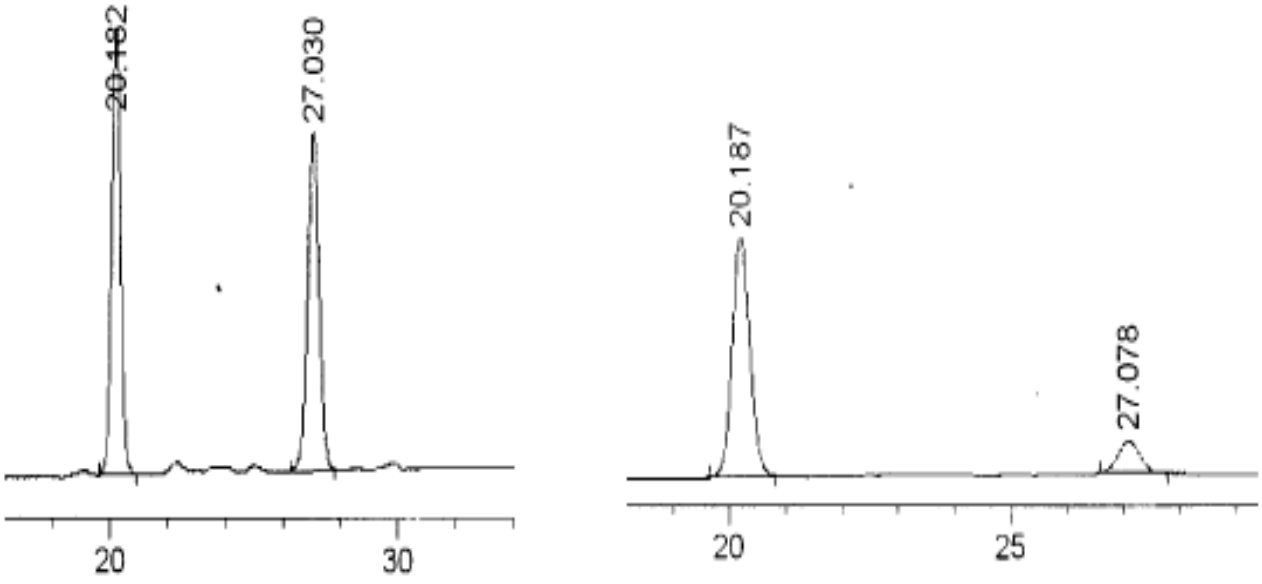


Figure S39. ^{1}H NMR spectrum of 1-(4-fluorophenyl)-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

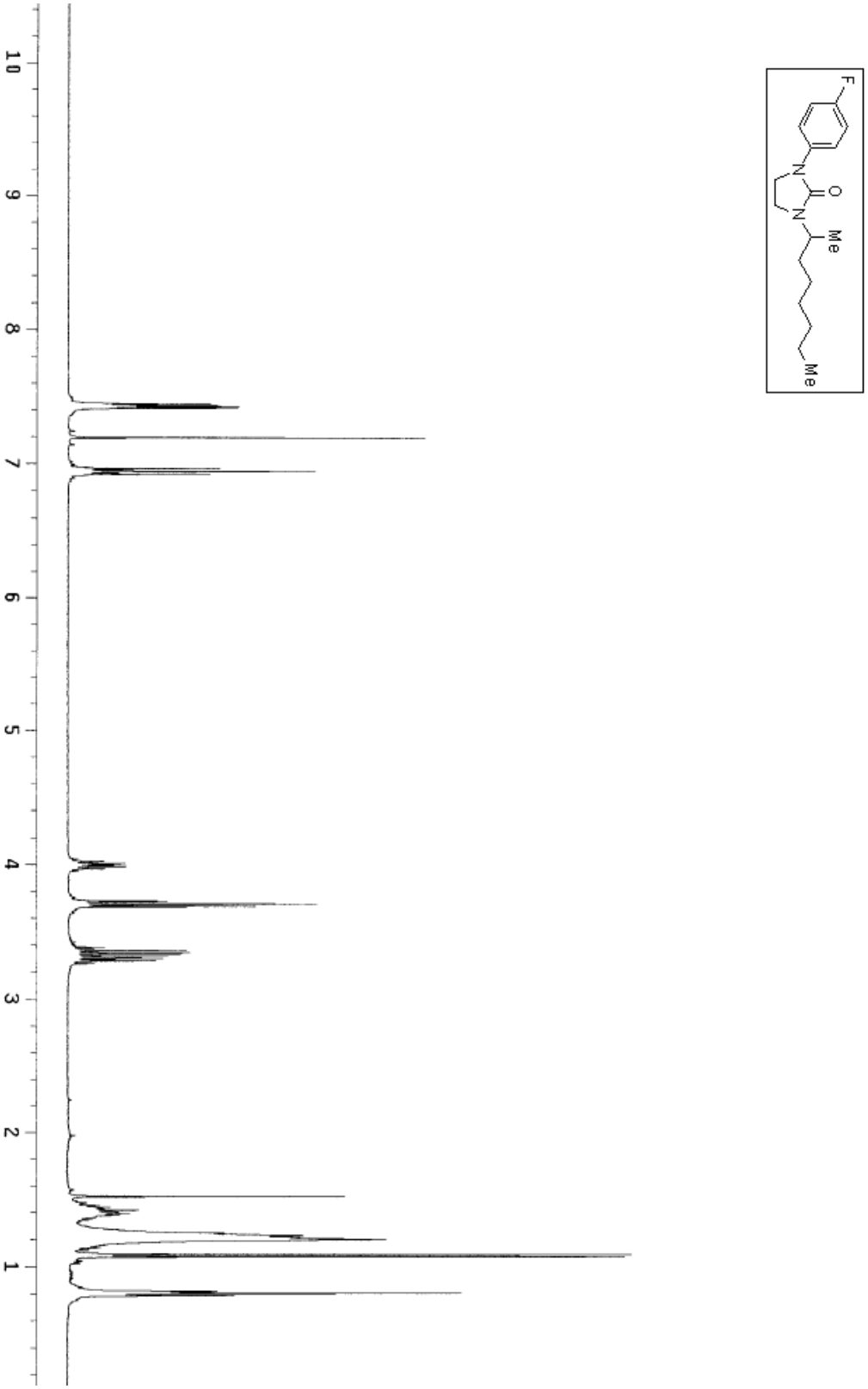


Figure S40. ^{13}C NMR spectrum of 1-(4-fluorophenyl)-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

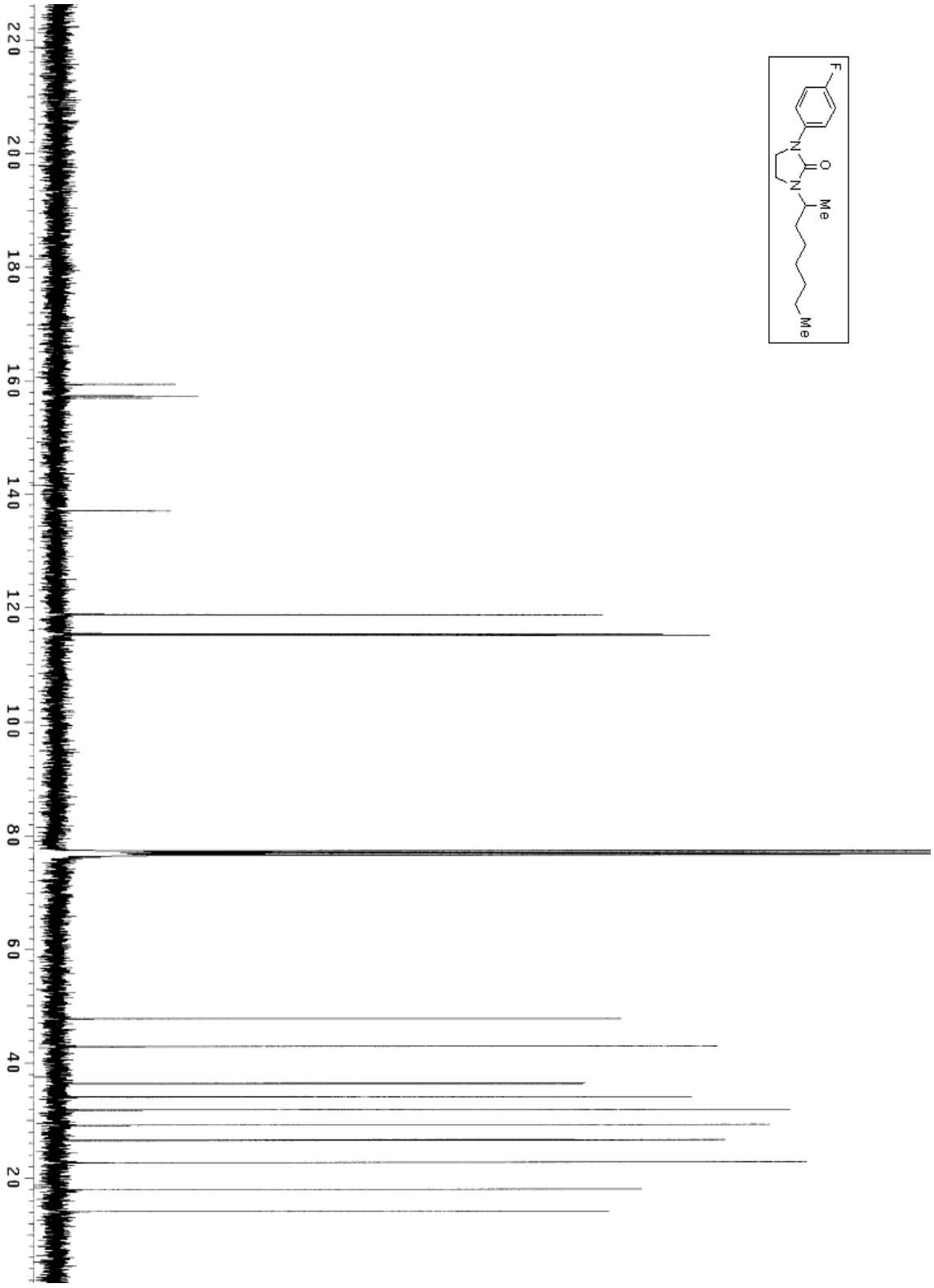


Figure S41. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 74 % ee) 1-(4-fluorophenyl)-3-(octan-2-yl)imidazolidin-2-one.

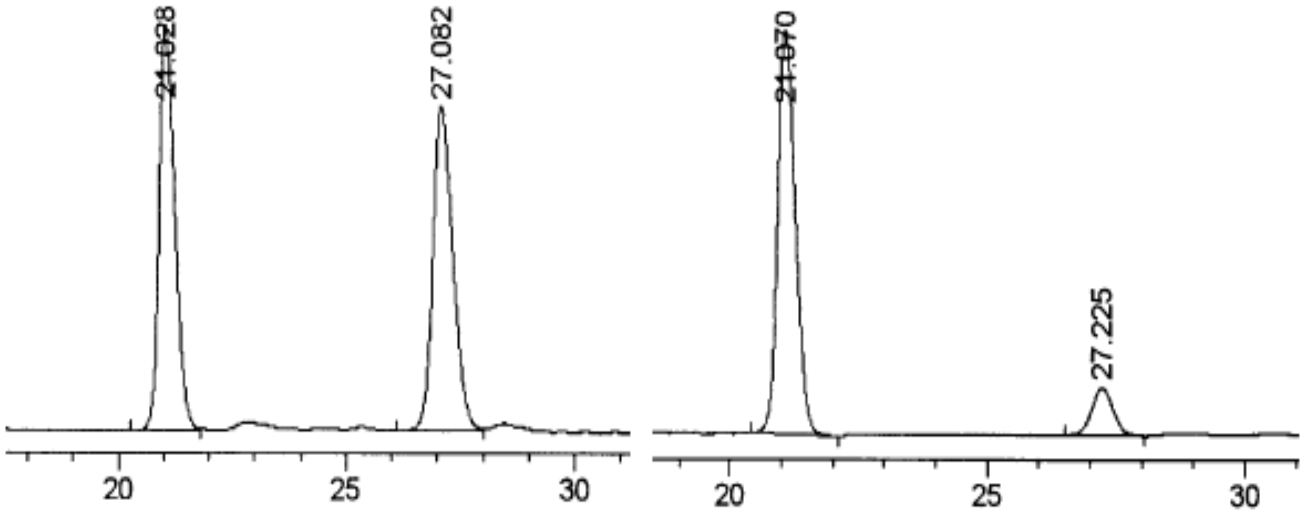


Figure S42. ^{1}H NMR spectrum of 1-*tert*-butyl-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

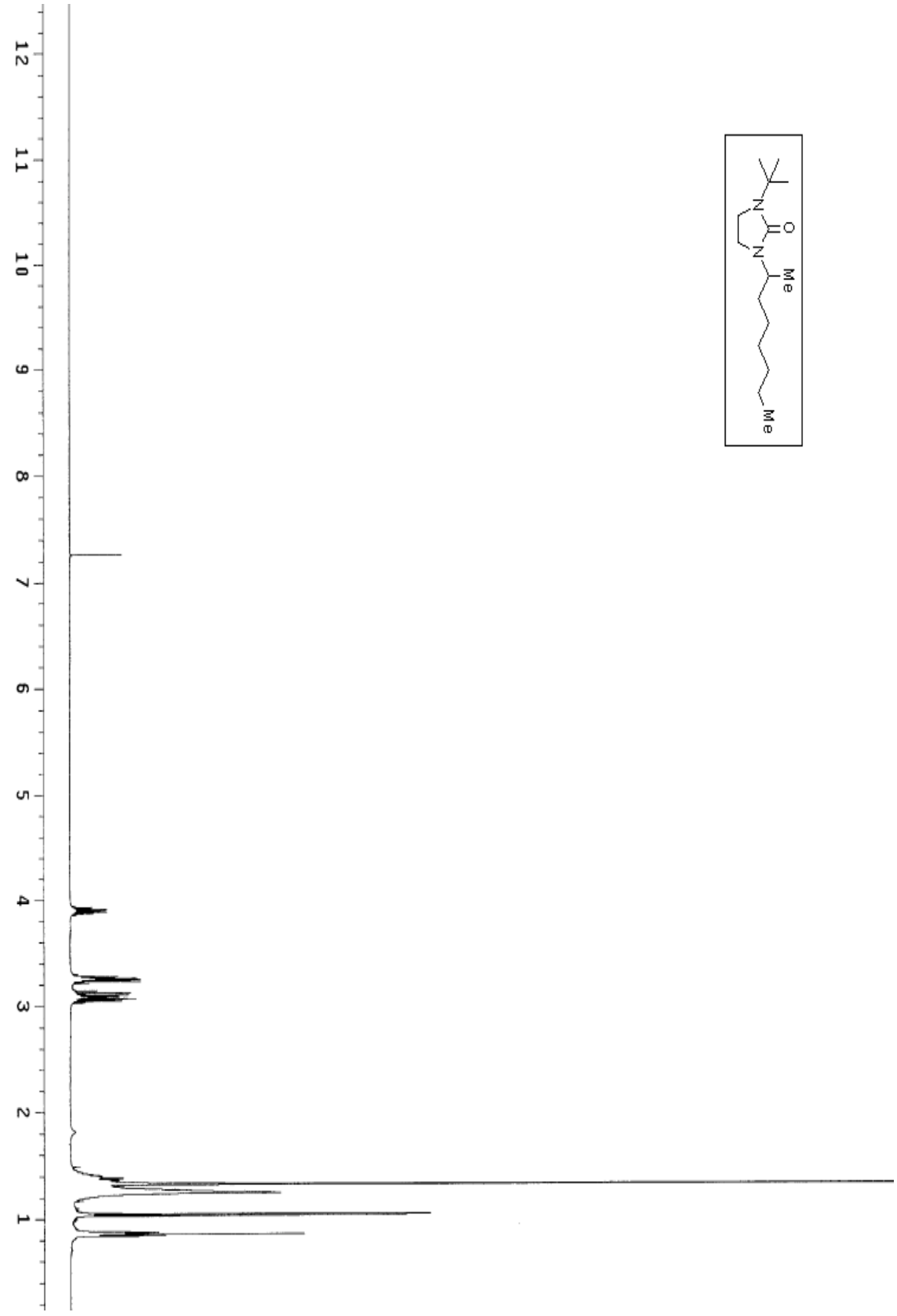


Figure S43. ^{13}C NMR spectrum of 1-*tert*-butyl-3-(octan-2-yl)imidazolidin-2-one in $CDCl_3$.

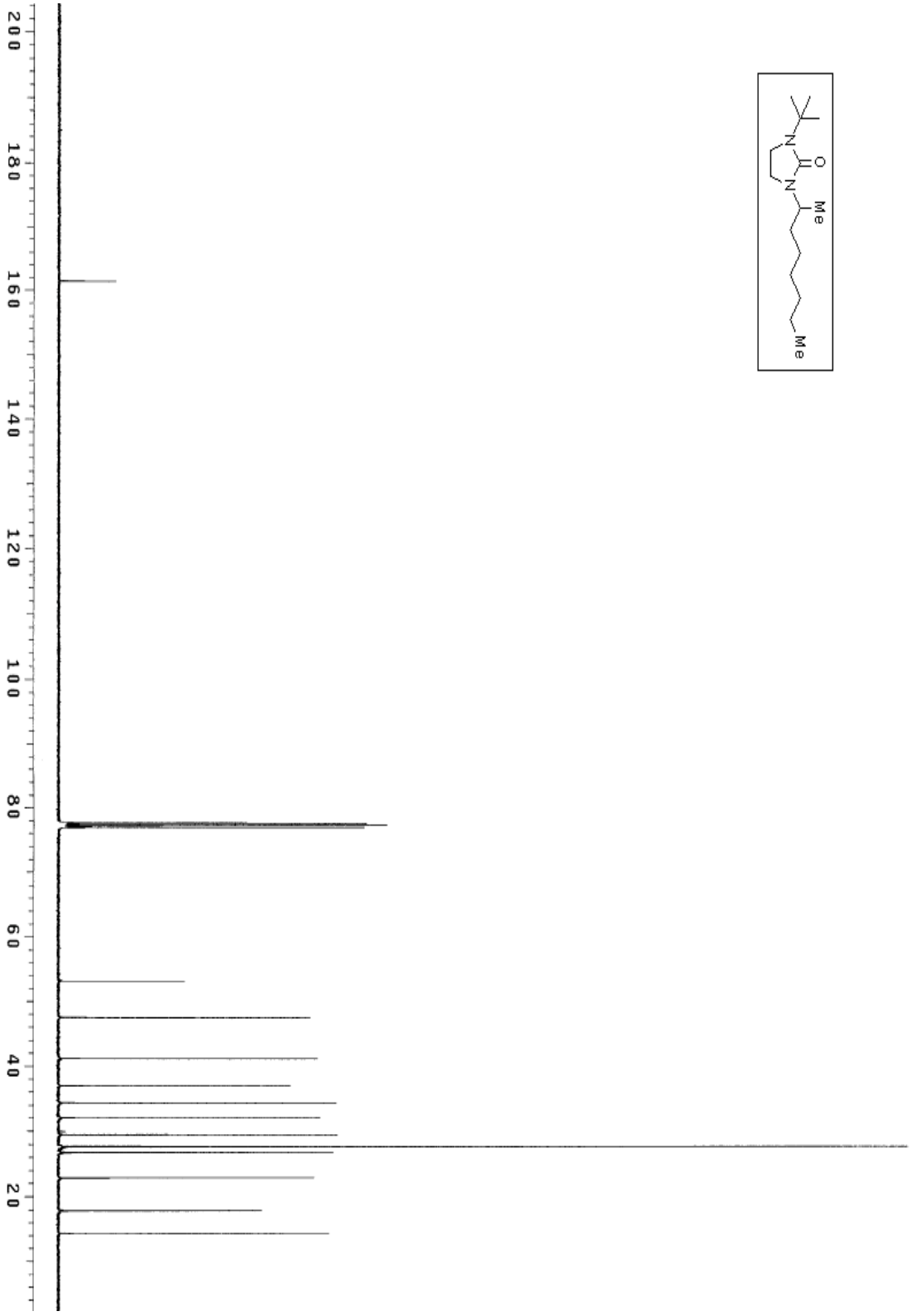


Figure S44. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 78 % ee) 1-*tert*-butyl-3-(octan-2-yl)imidazolidin-2-one.

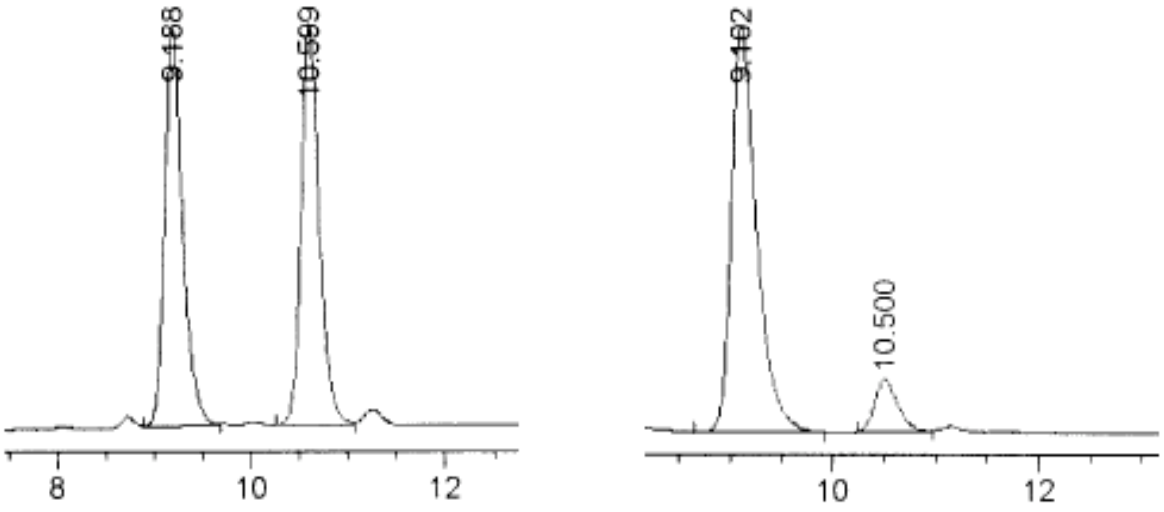


Figure S45. ^{1}H NMR spectrum of 1-(decan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

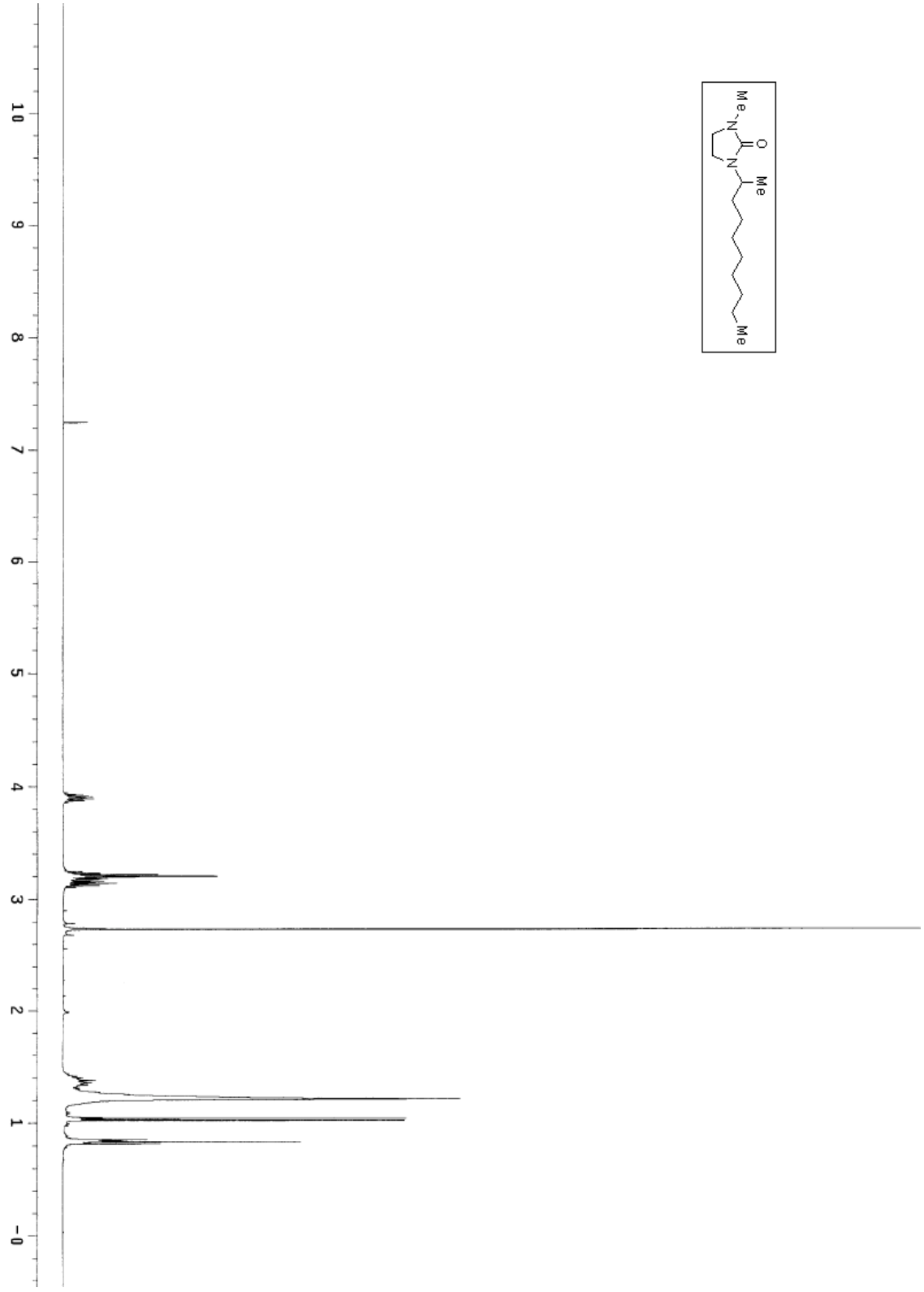


Figure S46. ^{13}C NMR spectrum of 1-(decan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

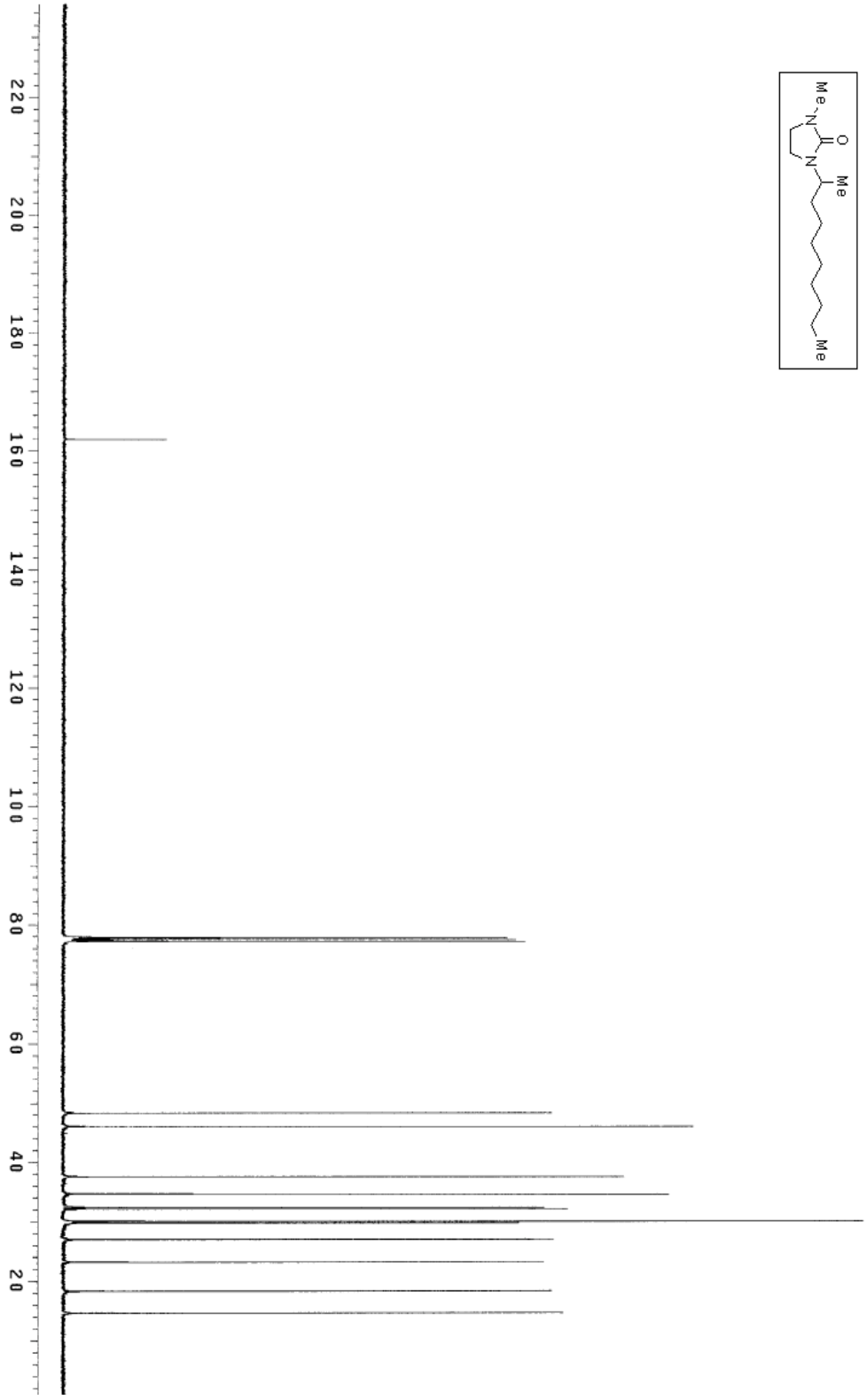
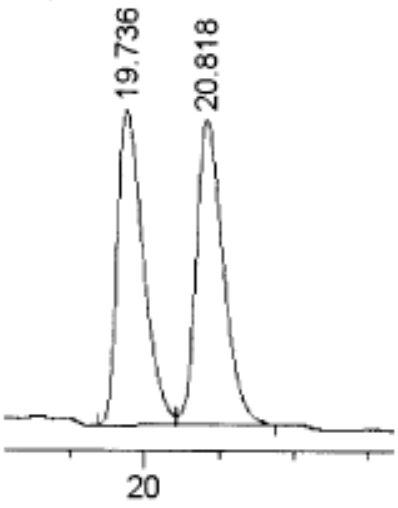


Figure S47. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 73 % ee) 1-(decan-2-yl)-3-methylimidazolidin-2-one.



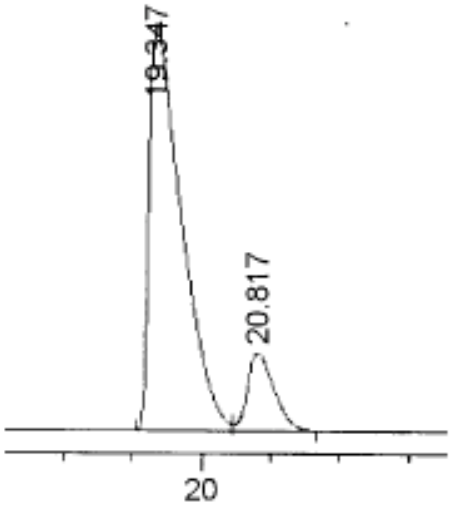


Figure S48. ^{1}H NMR spectrum of 1-(dodecan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

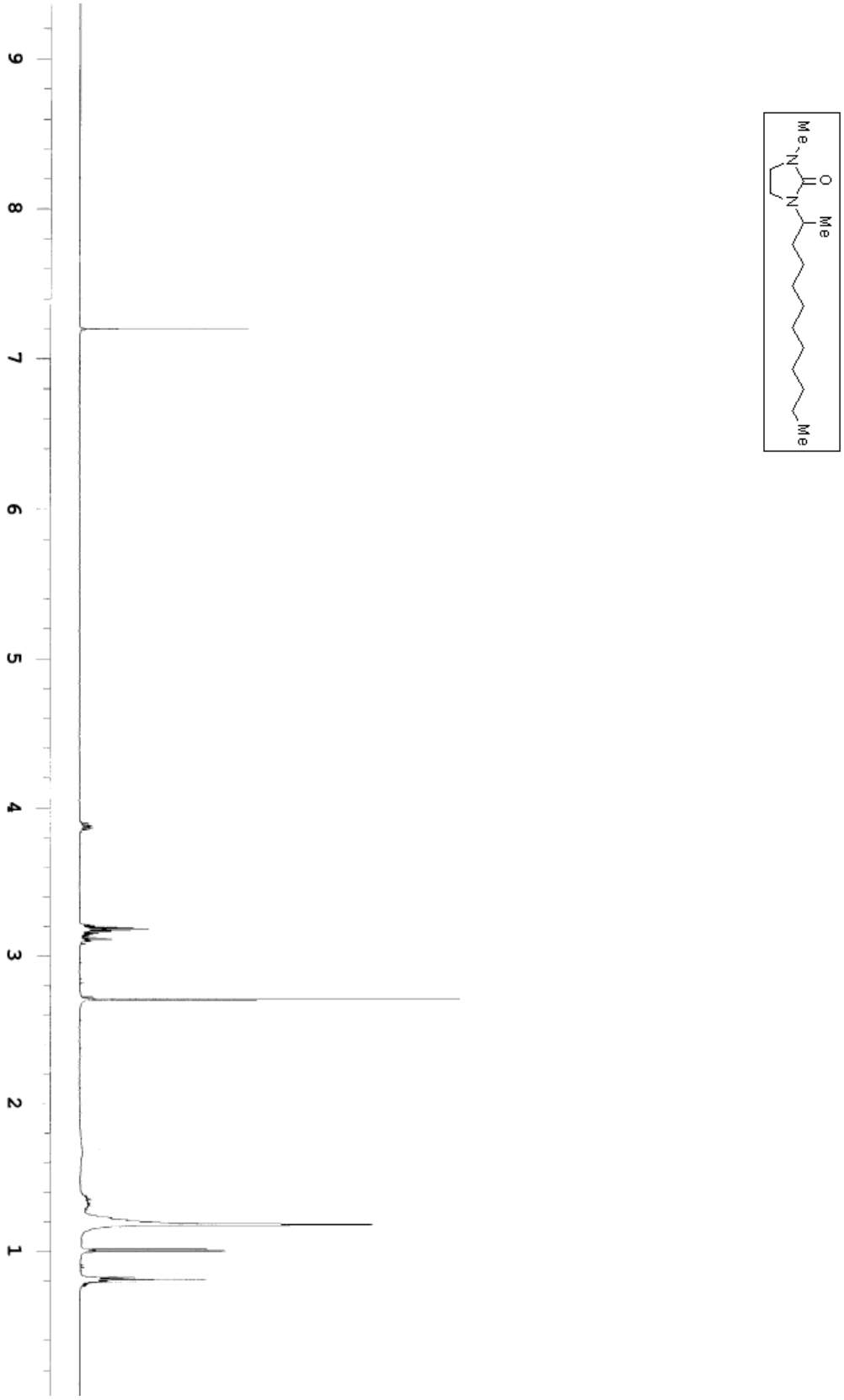


Figure S49. ^{13}C NMR spectrum of 1-(dodecan-2-yl)-3-methylimidazolidin-2-one in $CDCl_3$.

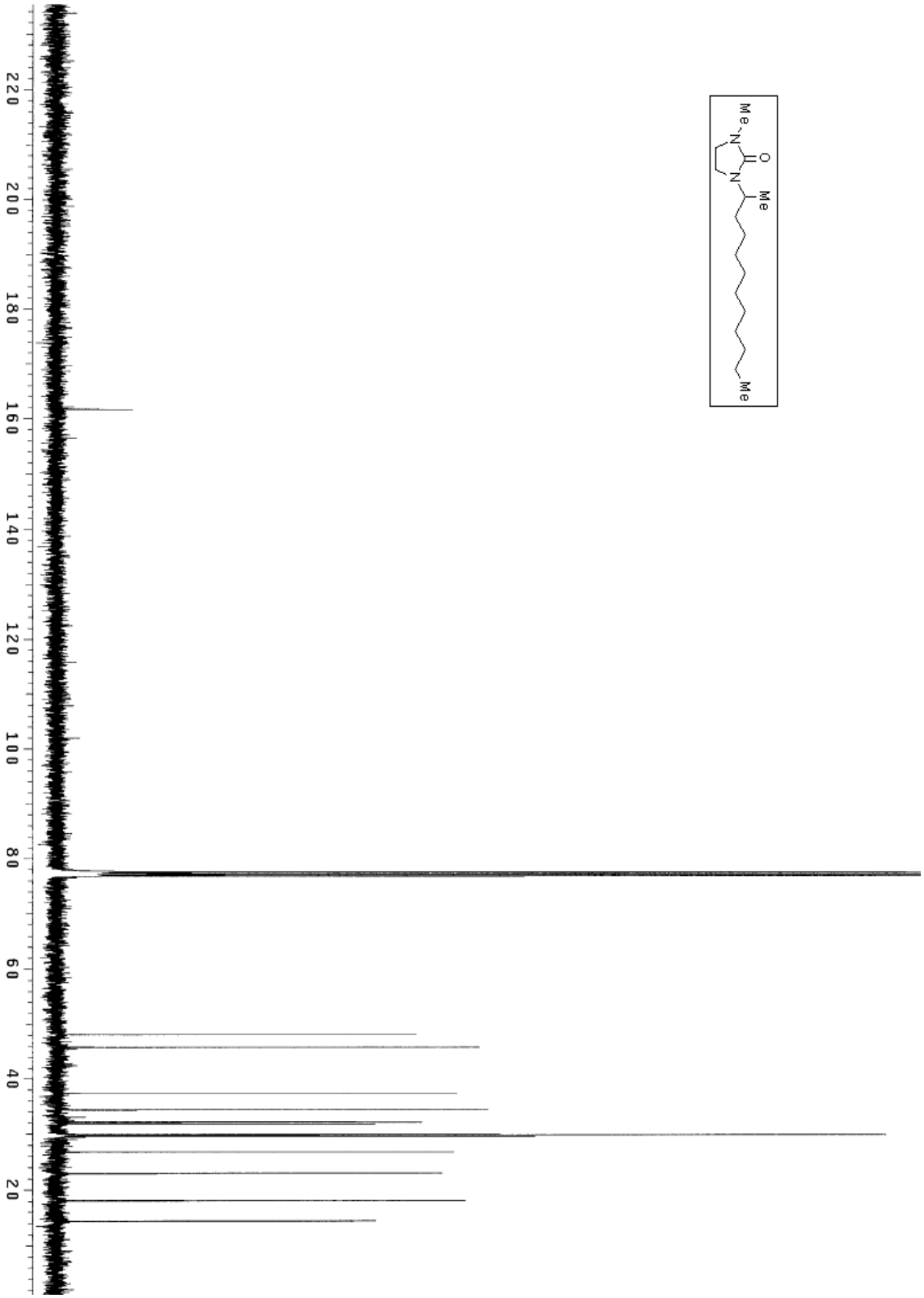
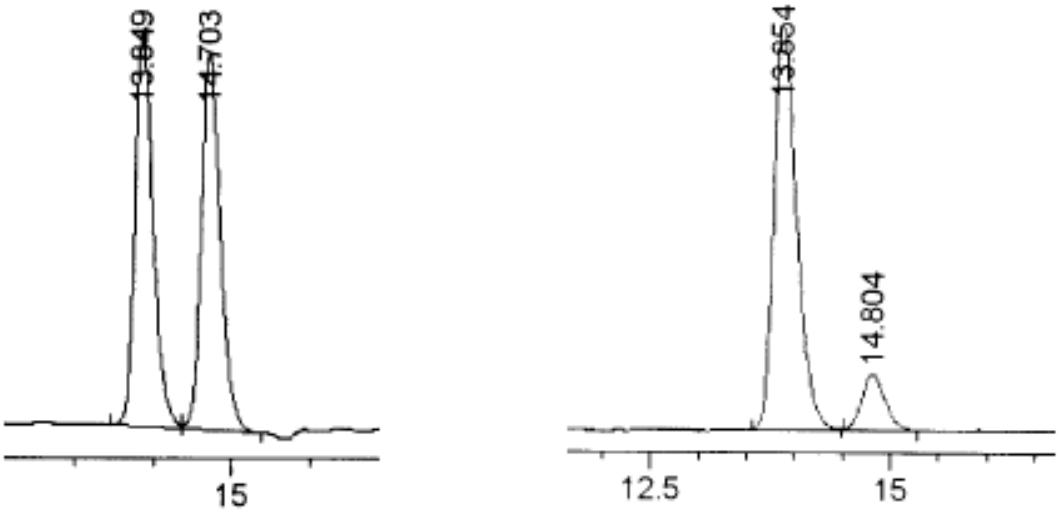


Figure S50. Chiral HPLC traces of racemic (left trace) and enantiomerically enriched (right trace, 75 % ee) 1-(dodecan-2-yl)-3-methylimidazolidin-2-one.



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S1) (a) Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc*. **2005**, *127*, 6178. (b) Bender, C. F.; Widenhoefer, R. A. *Chem. Commun*. **2008**, 2741.

S2) Munoz, M. P.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics* **2005**, *24*, 1293.

S3) Peet, N. P.; Sunder, S. *J. Org. Chem*. **1980**, *45*, 536.

S4) (a) Bogatsky, A. V.; Lukyanenko, N. G.; Kirichenko, T. I. *Synthesis* **1982**, *6*, 464. (b) Cerioni, G. *Spectrochimica Acta* **1983**, *39A*, 929.