

Electronic Supplementary Information

Stereoselective synthesis of (Z)- α -haloacrylic acid derivatives, and (Z)-haloallylic alcohols from aldehydes and trihaloesters or amides promoted by Rieke

Manganese

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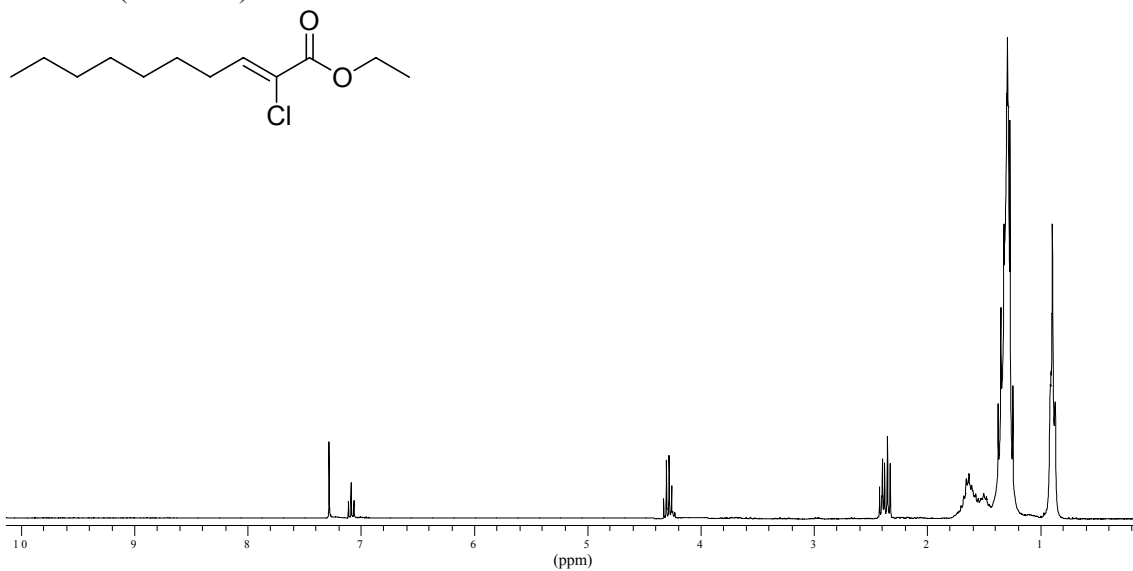
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GENERAL

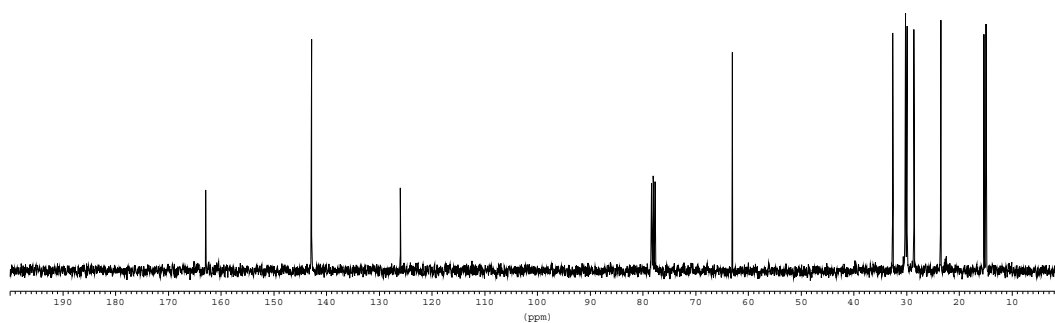
All reactions involving organometallic or other moisture-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard vacuum-line techniques and glassware that was flame dried and cooled under nitrogen before use. THF was distilled from sodium/benzophenone ketyl immediately prior to use. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. All reagents were purchased in the highest quality available and were used without further purification. Organic layers were dried over Na₂SO₄. Thin layer chromatography was performed on aluminium plates coated with 60 F254 silica. Plates were visualised using UV light (254 nm), iodine, 1% aq. KMnO₄, or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed on Kieselgel 60 silica. NMR spectra were recorded in the deuterated solvent stated and the field was locked by external referencing to the relevant deuterium resonance. ¹H NMR spectra were recorded on spectrometers at 300 or 400 MHz. ¹³C NMR spectra and DEPT experiments were determined at 75 or 100 MHz. Unless otherwise noted NMR spectra are recorded at room temperature. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard. GC-MS and HRMS were measured at 70 eV. Only the most important IR absorptions (in cm⁻¹) and the molecular ions and/or base peaks in MS are given.

Ethyl (Z)-2-Chlorodec-2-enoate (3a): ^1H NMR (300 MHz, CDCl_3): δ 7.08 (t, $J = 6.8$ Hz, 1 H), 4.29 (q, $J = 7.0$ Hz, 2 H), 2.42-2.32 (m, 2 H), 1.69-1.48 (m, 2 H), 1.37-1.24 (m, 11 H), 0.89 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.8 (C), 142.8 (CH), 125.9 (C), 63.0 (CH_2), 32.6 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 28.6 (CH_2), 23.5 (CH_2), 15.3 (CH_3), 14.9 (CH_3); MS (70 eV, EI) m/z (%) 232 [M^+ , 5], 137 (32), 135 (100), 122 (58), 107 (73); HRMS (70 eV) calc. for $\text{C}_{12}\text{H}_{21}\text{ClO}_2$ 232.1230, found 232.1227; IR (neat): 2928, 1750, 1267 cm^{-1} ; $R_f = 0.5$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

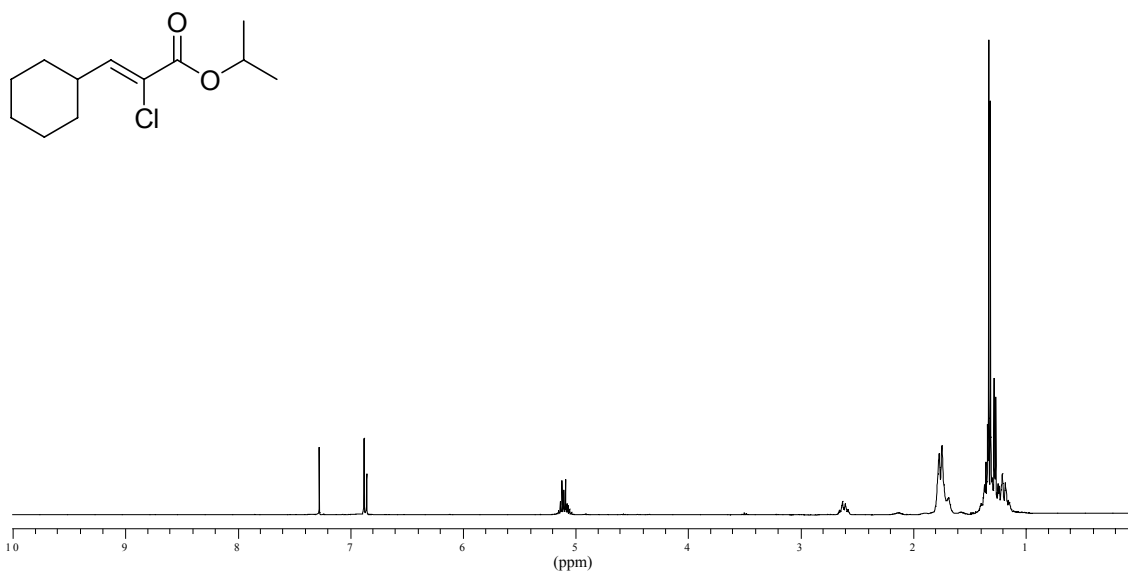


^{13}C NMR (100 MHz)

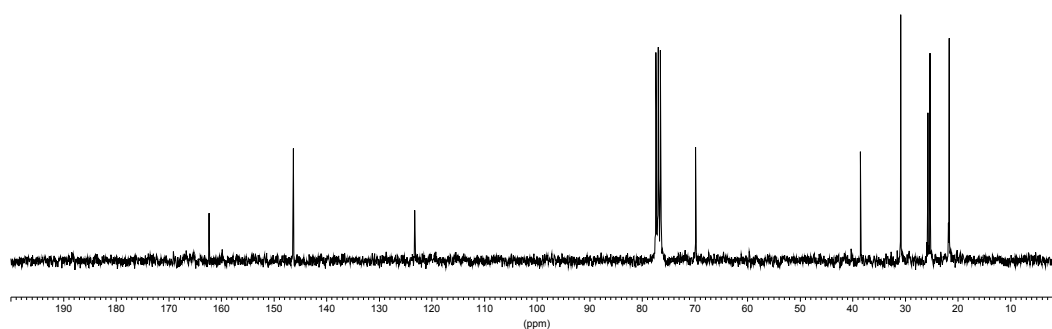


Isopropyl (Z)-2-Chloro-3-cyclohexylacrylate (3d): ^1H NMR (400 MHz, CDCl_3): δ 6.86 (d, $J = 9.3$ Hz, 1 H), 5.18-5.02 (m, 1 H), 2.69-2.52 (m, 1 H), 1.81-1.72 (m, 2 H), 1.39-1.18 (m, 8 H), 1.31 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.3 (C), 146.3 (CH), 123.2 (C), 69.8 (CH), 38.5 (CH), 30.9 (2 x CH_2), 25.7 (CH_2), 25.3 (2 x CH_2), 21.7 (2 x CH_3); MS (70 eV, EI) m/z (%) 230 [M^+ , 2], 188 (64), 82 (100), 67 (66), 55 (16); HRMS (70 eV) calc. for $\text{C}_{12}\text{H}_{19}\text{ClO}_2$ 230.1074, found 230.1084; IR (neat): 2982, 1729, 1628, 1145 cm^{-1} ; $R_f = 0.39$ (Hexane: EtOAc 20:1).

^1H NMR (400 MHz)

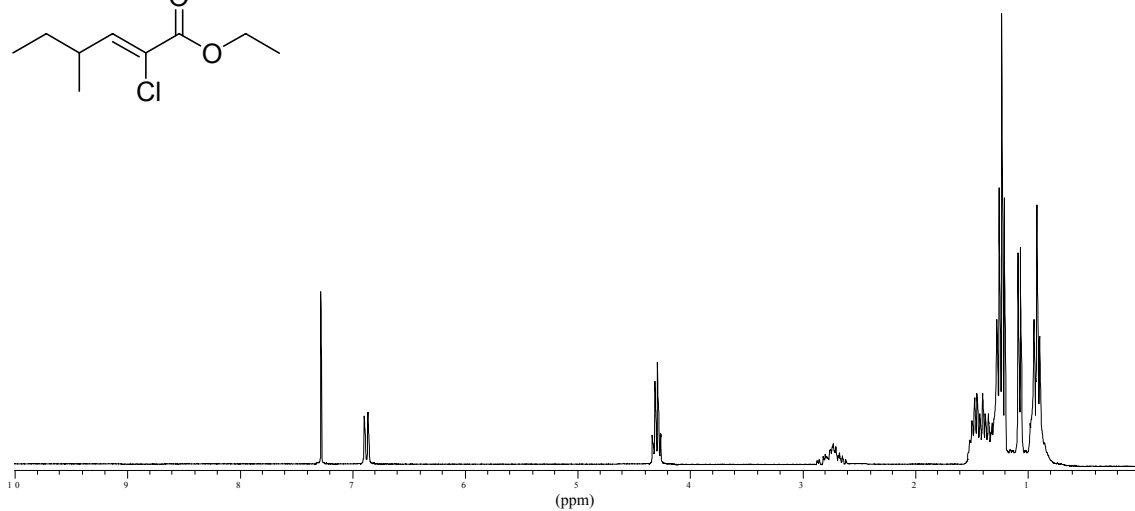
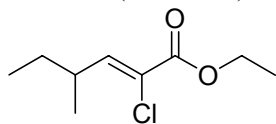


^{13}C NMR (100 MHz)

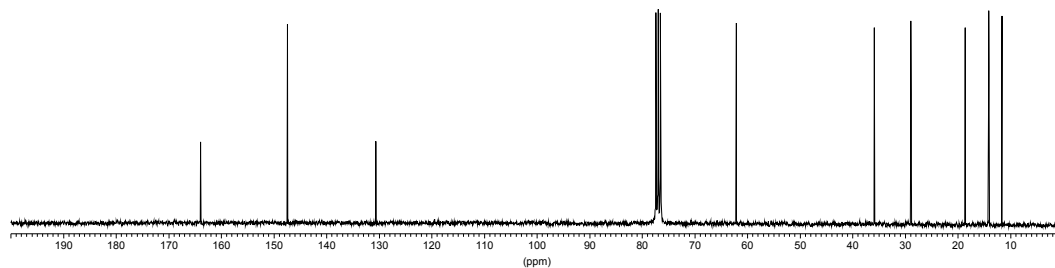


Ehtyl (Z)-2-Chloro-4-methylhex-2-enoate (3f): ^1H NMR (300 MHz, CDCl_3): δ 6.87 (d, $J = 9.6$ Hz, 1 H), 4.29 (q, $J = 7.1$ Hz, 2 H), 2.87-2.59 (m, 1 H), 1.49-1.33 (m, 2 H), 1.23 (t, $J = 7.0$ Hz, 3 H), 1.07 (d, $J = 6.8$ Hz, 3 H), 0.91 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 163.9 (C), 147.4 (CH), 130.6 (C), 62.1 (CH_2), 35.9 (CH), 28.9 (CH_2), 18.6 (CH_3), 14.1 (CH_3), 11.6 (CH_3); MS (70 eV, EI) m/z (%) 190 [M^+ , 8], 225 (36), 179 (28), 69 (100); HRMS (70 eV) calc. for $\text{C}_9\text{H}_{15}\text{ClO}_2$ 190.0761, found 190.0769; IR (neat): 3415, 1645, 1263 cm^{-1} ; $R_f = 0.37$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

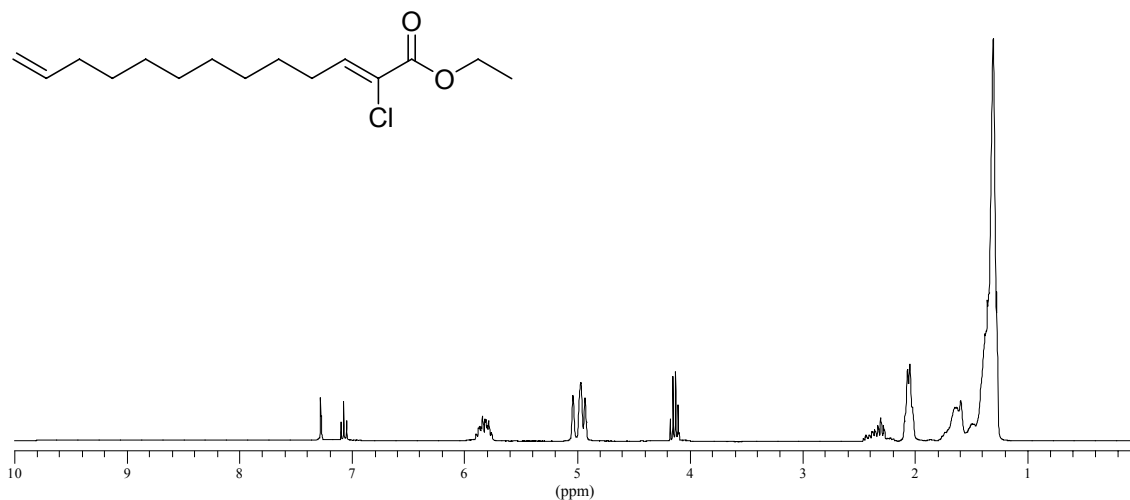


^{13}C NMR (75 MHz)

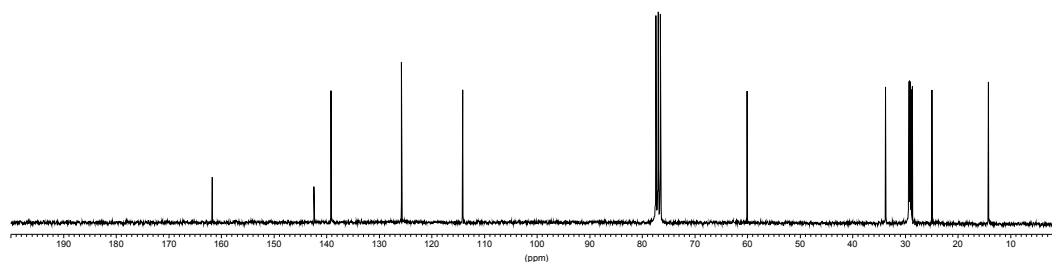


Ethyl (Z)-2-Chlorotrideca-2,12-dienoate (3g): ^1H NMR (300 MHz, CDCl_3): δ 7.07 (t, $J = 7.5$ Hz, 1 H), 5.97-5.74 (m, 1 H), 5.04-4.93 (m, 2 H), 4.14 (q, $J = 6.9$ Hz, 2 H), 2.43-2.24 (m, 2 H), 2.10-2.00 (m, 2 H), 1.70-1.55 (m, 2 H), 1.44-1.25 (m, 13 H); ^{13}C NMR (75 MHz, CDCl_3): δ 161.7 (C), 142.4 (C), 139.1 (CH), 126.7 (CH), 114.1 (CH_2), 60.1 (CH_2), 33.7 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 28.6 (CH_2), 24.9 (CH_2), 14.2 (CH_3); MS (70 eV, EI) m/z (%) 272 [M^+ , 8], 135 (100), 107 (66), 69 (86); HRMS (70 eV) calc. for $\text{C}_{15}\text{H}_{25}\text{ClO}_2$ 272.1543, found 272.1524; IR (neat): 2928, 2853, 1737, 1641 cm^{-1} ; $R_f = 0.42$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

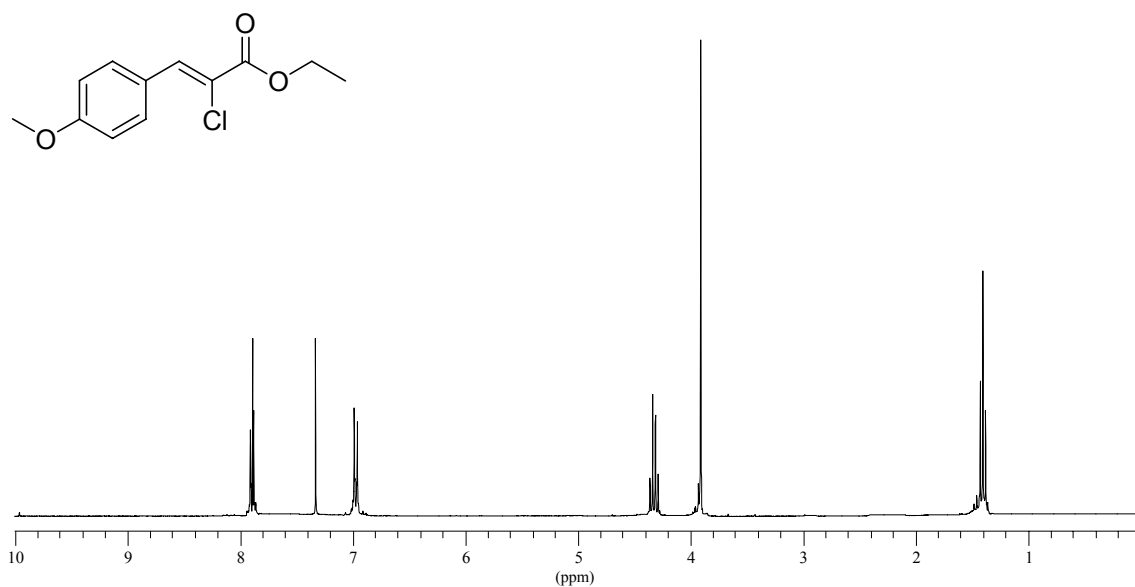


^{13}C NMR (75 MHz)

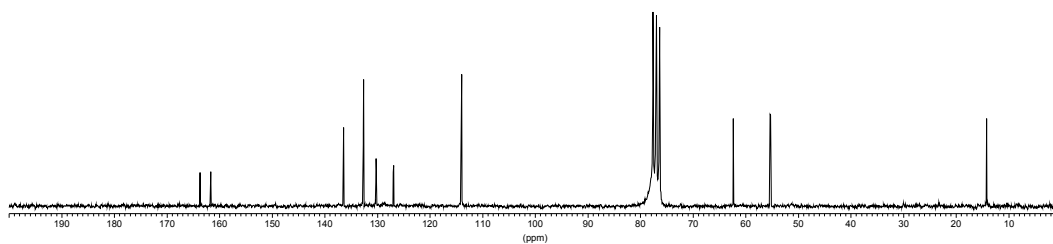


Ethyl (Z)-2-Chloro-3-(4-methoxyphenyl)acrylate (3h): ^1H NMR (300 MHz, CDCl_3): δ 7.89 (d, $J = 8.6$ Hz, 2 H), 7.89 (s, 1 H), 6.96 (d, $J = 8.7$ Hz, 2 H), 4.36 (q, $J = 7.1$ Hz, 2 H), 3.90 (s, 3 H), 1.40 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 163.7 (C), 161.6 (C), 136.4 (CH), 132.6 (2 x CH), 130.2 (C), 126.9 (C), 113.9 (2 x CH), 62.3 (CH_2), 55.3 (CH_3), 14.2 (CH_3); MS (70 eV, EI) m/z (%) 240 [M^+ , 100], 177 (20), 132 (70), 89 (10); HRMS (70 eV) calc. for $\text{C}_{12}\text{H}_{13}\text{ClO}_3$ 240.0553, found 240.0505; IR (neat): 3055, 1717, 1603, 738 cm^{-1} ; $R_f = 0.32$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

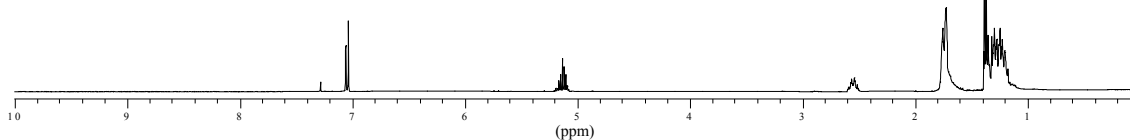
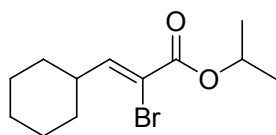


^{13}C NMR (75 MHz)

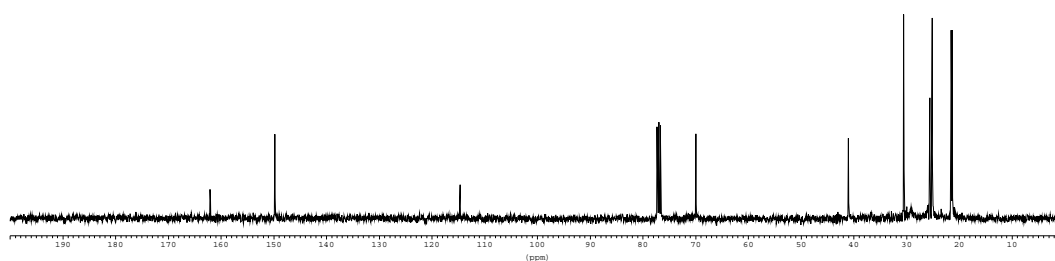


Isopropyl (Z)-2-Bromo-3-cyclohexylacrylate (3j): ^1H NMR (400 MHz, CDCl_3): δ 7.04 (d, $J = 7.8$ Hz, 1 H), 5.17-5.09 (m, 1 H), 2.60-2.51 (m, 1 H), 1.75-1.66 (m, 2 H), 1.37 (d, $J = 6.0$ Hz, 6 H), 1.35-1.14 (m, 8 H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.0 (C), 149.7 (CH), 114.6 (C), 70.0 (CH), 40.9 (CH), 30.5 (2 x CH_2), 25.6 (CH_2), 25.1 (2 x CH_2), 21.5 (CH_3), 21.3 (CH_3); MS (70 eV, EI) m/z (%) 274 [M^+ , < 1], 225 (42), 183 (100), 165 (68), 101 (27); HRMS (70 eV) calc. for $\text{C}_{12}\text{H}_{19}\text{BrO}_2$ 274.0568, found 274.0659; IR (neat): 2929, 1726, 1450, 1264 cm^{-1} ; $R_f = 0.62$ (Cyclohexane: EtOAc 30:1).

^1H NMR (400 MHz)

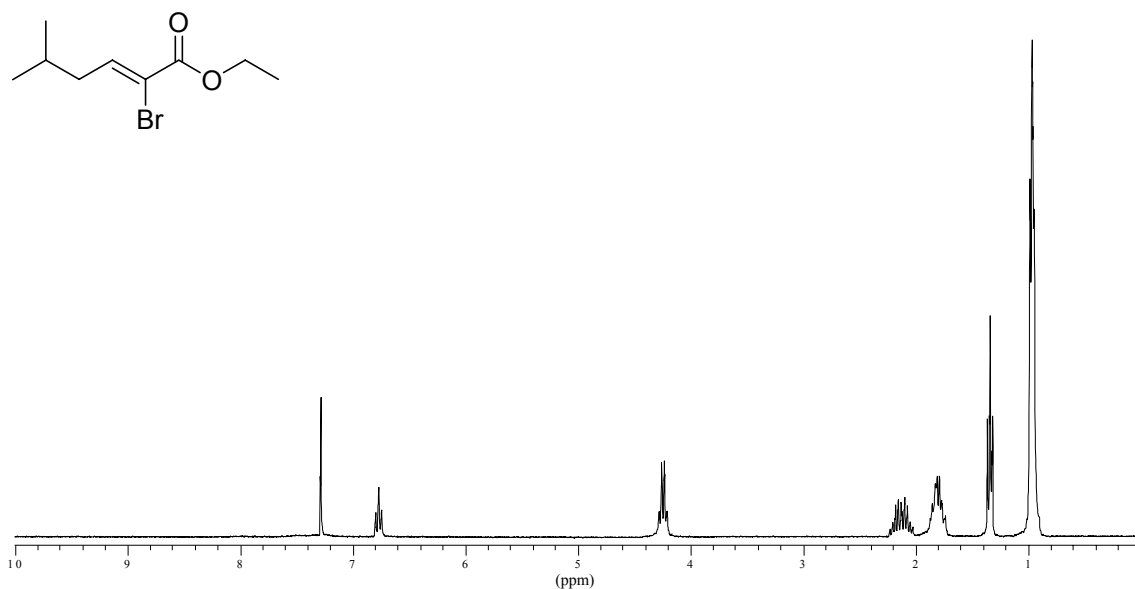


^{13}C NMR (100 MHz)

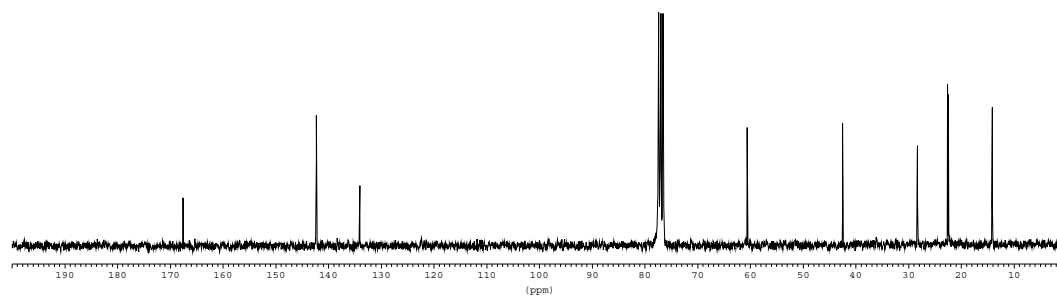


Ethyl (Z)-2-Bromo-5-methylhex-2-enoate (3k): ^1H NMR (300 MHz, CDCl_3): δ 6.77 (t, $J = 7.5$ Hz, 1 H), 4.24 (q, $J = 7.2$ Hz, 2 H), 2.22-2.02 (m, 1 H), 1.87-1.72 (m, 2 H), 1.33 (t, $J = 7.2$ Hz, 3 H), 0.97 (d, $J = 5.7$ Hz, 3 H), 0.95 (d, $J = 5.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.6 (C), 142.2 (CH), 134.0 (C), 60.5 (CH_2), 42.5 (CH_2), 28.3 (CH), 22.6 (CH_3), 22.4 (CH_3), 14.1 (CH_3); MS (70 eV, EI) m/z (%) 205 [M^+ - Et, 10], 139 (77), 118 (72), 69 (100), 55 (32); HRMS (70 eV) calc. for [$\text{C}_9\text{H}_{15}\text{BrO}_2$ - Et] 204.9864, found 204.9888; IR (neat): 2995, 1745, 1472 cm^{-1} ; $R_f = 0.55$ (Cyclohexane: EtOAc 30:1).

^1H NMR (300 MHz)

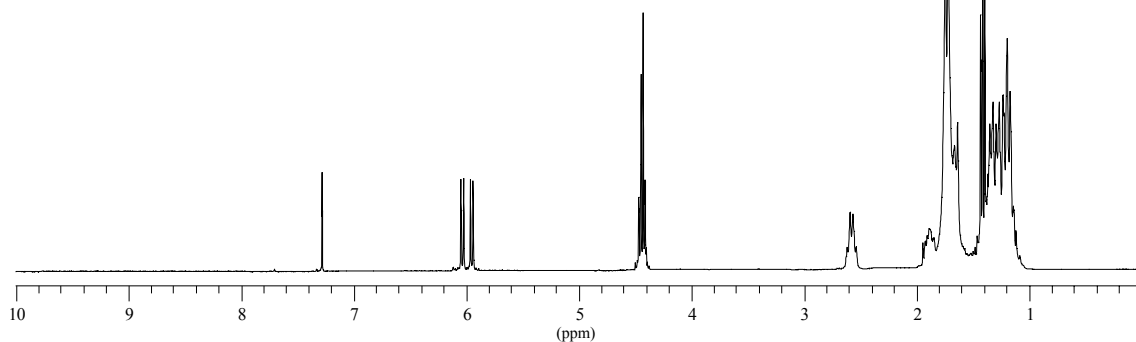
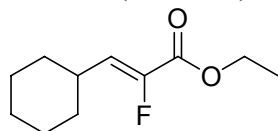


^{13}C NMR (100 MHz)

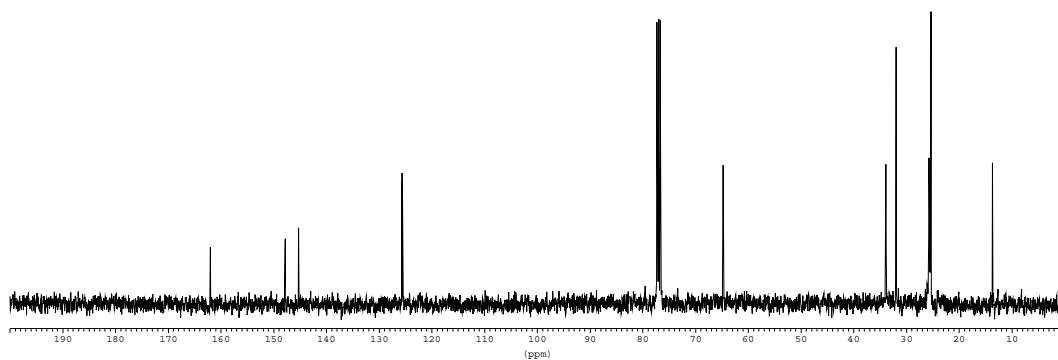


Ethyl (Z)-2-Fluorocyclohexyl-2-enoate (3l): ^1H NMR (400 MHz, CDCl_3): δ 6.01 (dd, $J = 34.2, 9.6$ Hz, 1 H), 4.43 (q, $J = 6.8$ Hz, 2 H), 2.61-2.53 (m, 1 H), 1.94-1.84 (m, 2 H), 1.74-1.63 (m, 4 H), 1.41 (t, $J = 6.8$ Hz, 3 H), 1.34-1.11 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.9 (C), 146.5 (d, $J = 253.5$ Hz, C), 125.5 (d, $J = 11.7$ Hz, CH), 64.7 (CH_2), 33.9 (CH), 31.9 (2 x CH_2), 25.7 (CH_2), 25.3 (2 x CH_2), 13.6 (CH_3); MS (70 eV, EI) m/z (%) 200 [M^+ , 28], 81 (100), 67 (83), 55 (59); HRMS (70 eV) calc. for $\text{C}_{11}\text{H}_{17}\text{FO}_2$ 200.1213, found 200.1223; IR (neat): 1729, 1265, 740 cm^{-1} ; $R_f = 0.20$ (Hexane: EtOAc 20:1).

^1H NMR (400 MHz)

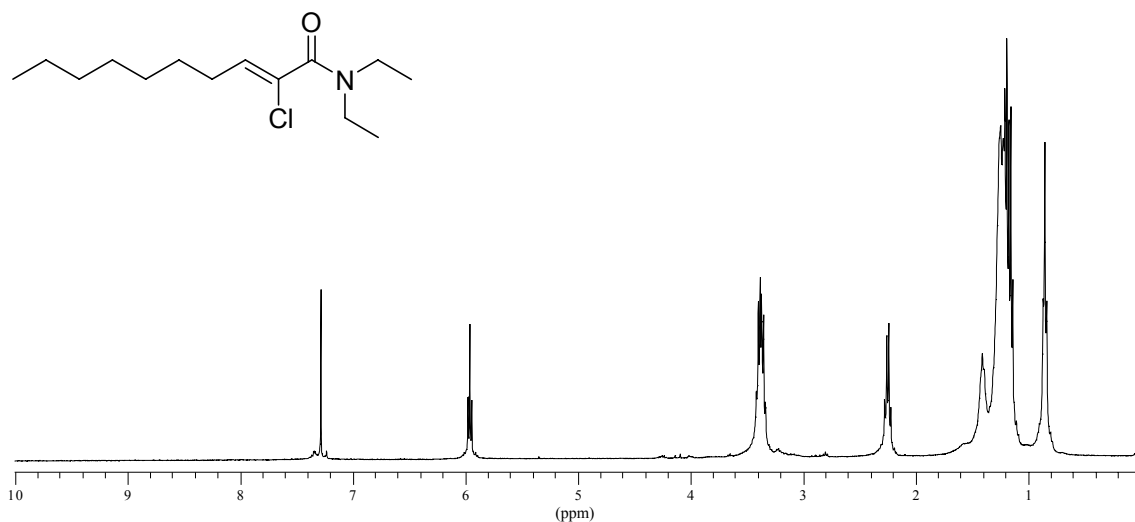


^{13}C NMR (100 MHz)

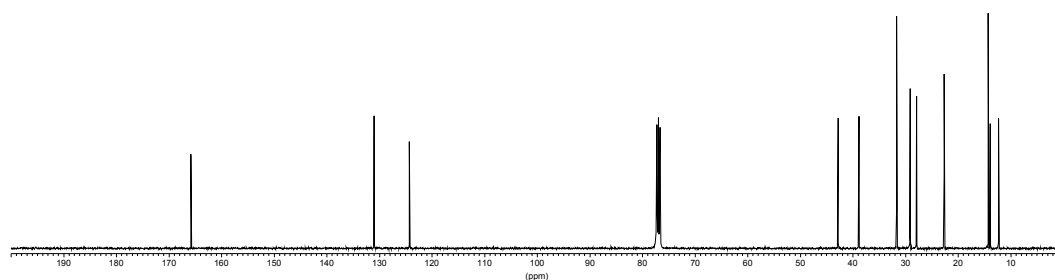


(Z)-2-Chloro-N,N-diethyldec-2-enamide (5a): ^1H NMR (400 MHz, CDCl_3): δ 5.96 (t, $J = 7.1$ Hz, 1 H), 3.41-3.33 (m, 4 H), 2.24 (apparent q, $J = 7.2$ Hz, 2 H), 1.41-1.39 (m, 2 H), 1.25-1.15 (m, 8 H), 1.19 (t, $J = 7.1$ Hz, 3 H), 1.15 (t, $J = 7.1$ Hz, 3 H), 0.85 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 165.8 (C), 131.0 (CH), 124.3 (C), 42.8 (CH_2), 38.8 (CH_2), 31.7 (2 x CH_2), 29.1 (CH_2), 27.8 (CH_2), 22.6 (2 x CH_2), 14.2 (CH_3), 13.9 (CH_3), 12.3 (CH_3); MS (70 eV, EI) m/z (%) 259 [M^+ , 15], 224 (100), 187 (32), 160 (79); HRMS (70 eV) calc. for $\text{C}_{14}\text{H}_{26}\text{ClNO}$ 259.1703, found 259.1727; IR (neat): 3451, 2974, 1642, 1460 cm^{-1} ; $R_f = 0.52$ (Hexane: EtOAc 3:1).

^1H NMR (400 MHz)

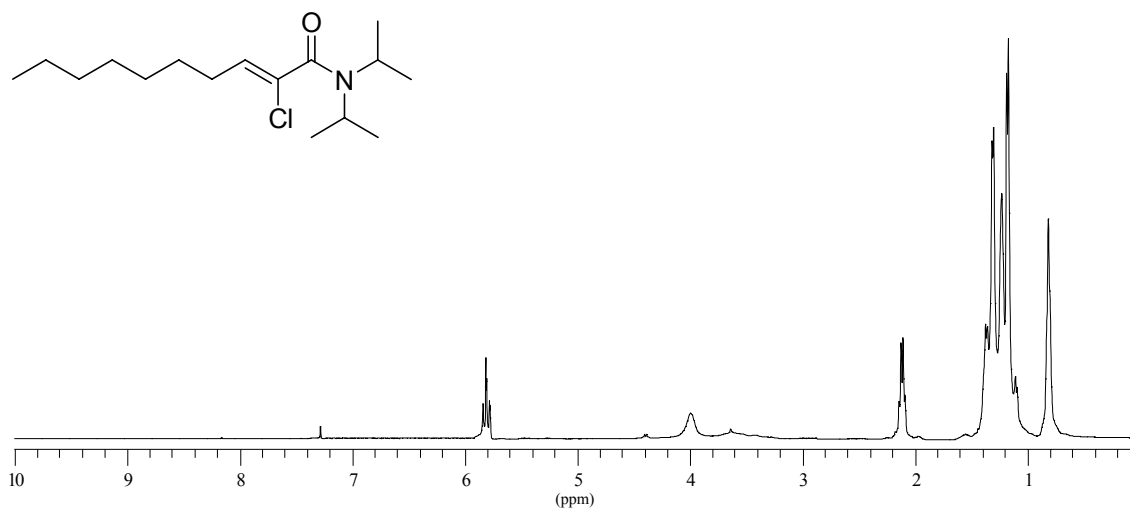


^{13}C NMR (100 MHz, 233 K)

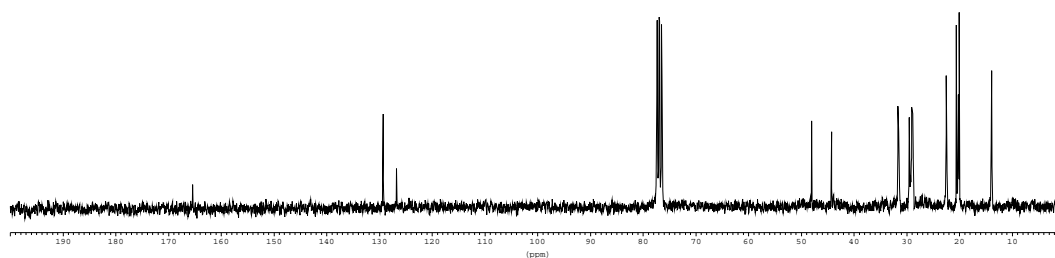


(Z)-2-Chloro-N,N-diisopropyldec-2-enamide (5b): ^1H NMR (400 MHz, CDCl_3 , 233 K): δ 5.81 (t, $J = 7.2$ Hz, 1 H), 4.02-3.95 (m, 1 H), 3.80-3.40 (m, 1 H), 2.11 (apparente q, $J = 6.8$ Hz, 2 H), 1.40-1.09 (m, 10 H), 1.30 (d, $J = 5.8$ Hz, 6 H), 1.17 (d, $J = 6.0$ Hz, 6 H), 0.81 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 165.4 (C), 129.3 (CH), 126.7 (C), 48.0 (CH), 44.2 (CH), 31.6 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 22.5 (CH_2), 20.5 (2 x CH_3), 20.2 (CH_2), 20.0 (2 x CH_3), 13.9 (CH_3); MS (70 eV, EI) m/z (%) 287 [M^+ , 8], 252 (100), 201 (41); HRMS (70 eV) calc. for $\text{C}_{16}\text{H}_{30}\text{ClNO}$ 287.2016, found 287.2025; IR (neat): 3444, 2927, 1643, 1431 cm^{-1} ; $R_f = 0.55$ (Hexane: EtOAc 10:1).

^1H NMR (400 MHz, 233 K)

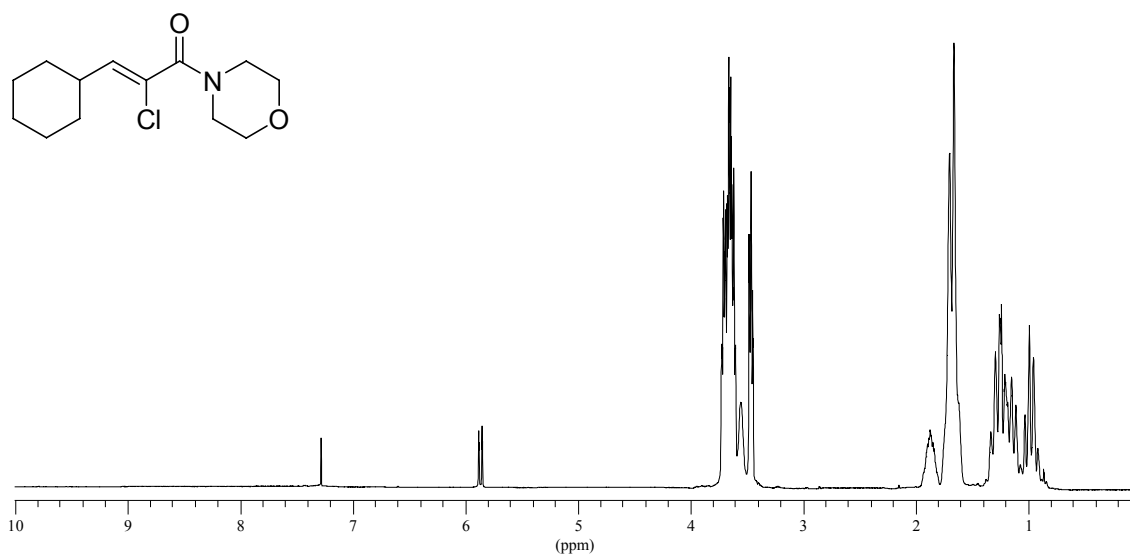


^{13}C NMR (100 MHz, 233 K)

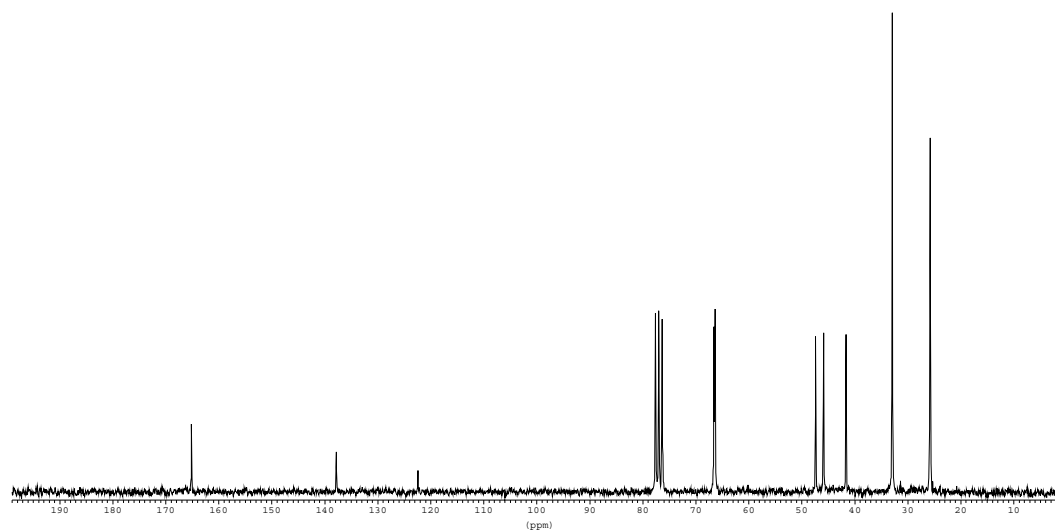


4-[(Z)-(1-Chlorocyclohex-1-en-1-yl)carbonyl]morpholine (5e): ^1H NMR (300 MHz, CDCl_3): δ 5.86 (d, $J = 9.0$ Hz, 1 H), 3.72-3.60 (m, 4 H), 3.54-3.44 (m, 4 H), 1.91-1.81 (m, 1 H), 1.71-1.60 (m, 2 H), 1.33-1.11 (m, 4 H), 1.03-0.91 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3): δ 165.1 (C), 137.8 (CH), 122.4 (C), 66.6 (CH_2), 66.4 (CH_2), 47.4 (CH_2), 45.9 (CH_2), 41.6 (CH), 32.9 (4 x CH_2), 25.7 (CH_2); MS (70 eV, EI) m/z (%) 257 [M^+ , 14], 135 (26), 86 (50), 56 (88), 41 (100); HRMS (70 eV) calc. for $\text{C}_{13}\text{H}_{20}\text{ClNO}_2$ 257.1183, found 257.1139; IR (neat): 2926, 1712, 1642, 1448 cm^{-1} ; $R_f = 0.57$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

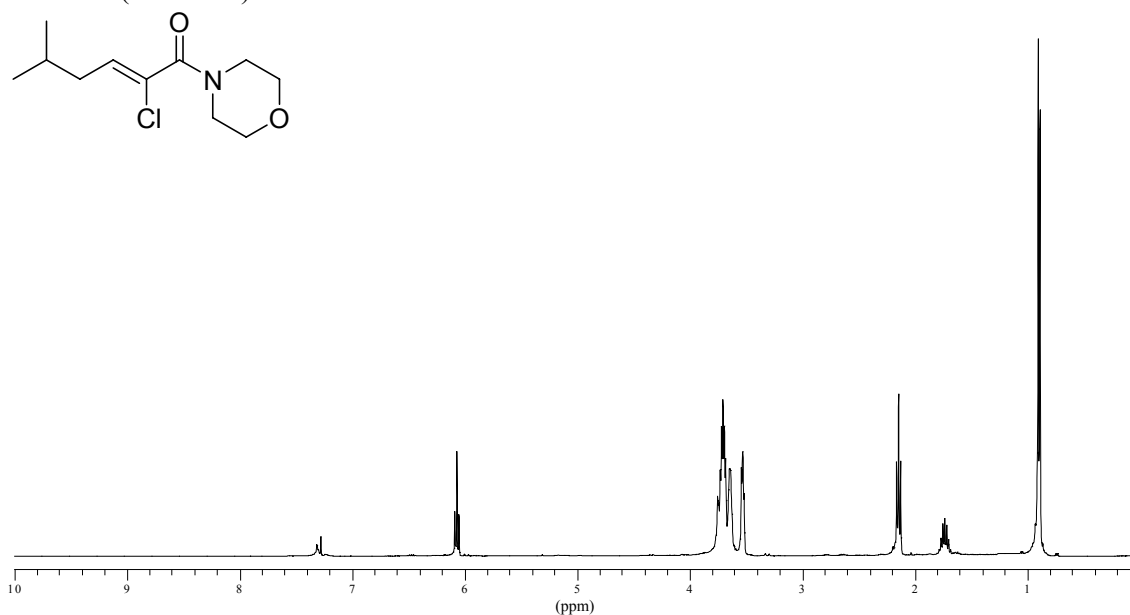


^{13}C NMR (75 MHz)

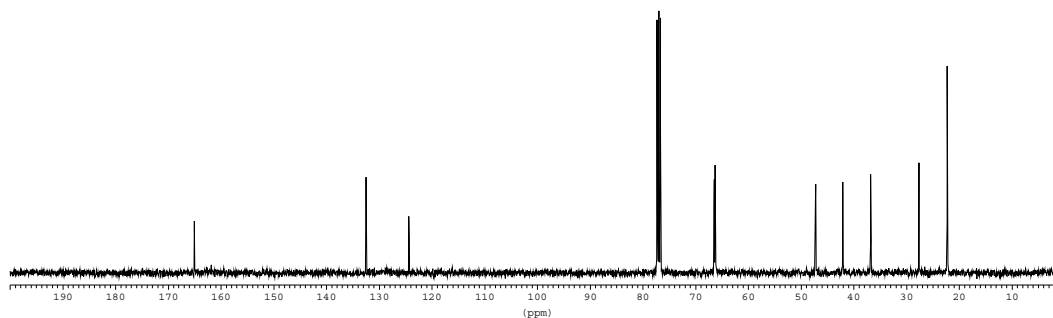


4-[(Z)-(1-Chloro-5-methylhex-1-en-1-yl)carbonyl]morpholine (5g): ^1H NMR (400 MHz, CDCl_3): δ 6.07 (t, $J = 7.4$ Hz, 1 H), 3.72-3.53 (m, 8 H), 2.14 (apparent t, $J = 7.2$ Hz, 2 H), 1.78-1.68 (m, 1 H), 0.89 (d, $J = 6.6$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 165.0 (C), 132.5 (CH), 124.3 (C), 66.5 (CH_2), 66.3 (CH_2), 47.2 (CH), 42.1 (CH_2), 36.7 (CH_2), 27.6 (CH_2), 22.3 (2 x CH_3); MS (70 eV, EI) m/z (%) 231 [M^+ , 20], 216 (32), 196 (36), 174 (86), 86 (100); HRMS (70 eV) calc. for $\text{C}_{11}\text{H}_{18}\text{ClNO}_2$ 231.1020, found 231.1021; IR (neat): 2959, 1641, 1439, 1116 cm^{-1} ; $R_f = 0.25$ (Hexane: EtOAc 3:1).

^1H NMR (400 MHz)

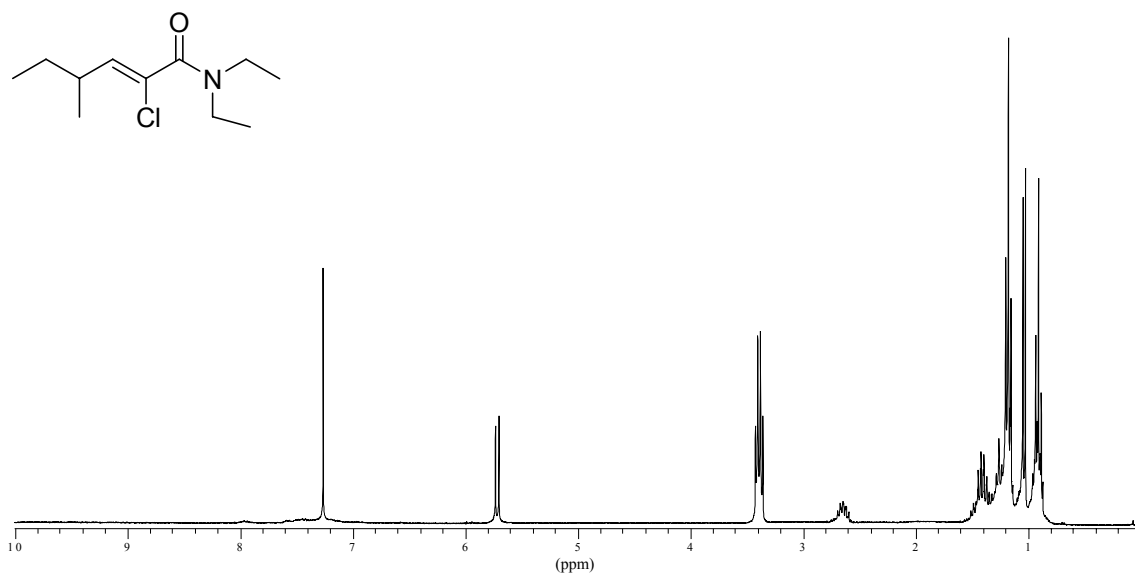


^{13}C NMR (100 MHz, 233 K)

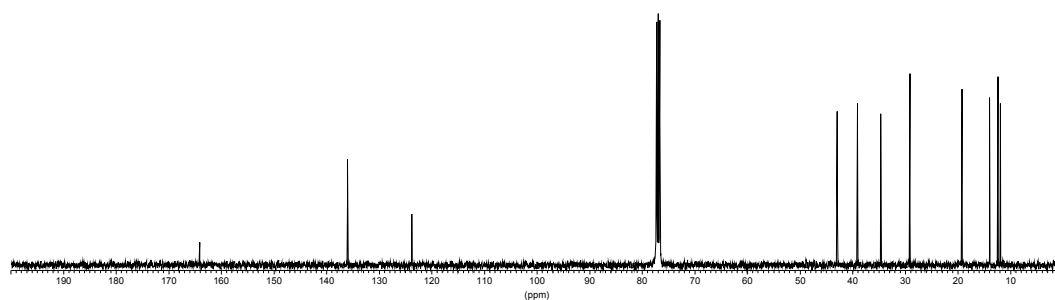


(Z)-2-Chloro-N,N-diethyl-4-methylhex-2-enamide (5h): ^1H NMR (300 MHz, CDCl_3): δ 5.73 (d, $J = 9.4$ Hz, 1 H), 3.41 (q, $J = 7.1$ Hz, 4 H), 2.71-2.61 (m, 1 H), 1.48-1.39 (m, 2 H), 1.19 (t, $J = 7.1$ Hz, 6 H), 1.05 (d, $J = 6.7$ Hz, 3 H), 0.93 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 164.1 (C), 136.0 (CH), 123.8 (C), 42.9 (CH_2), 39.1 (CH_2), 34.6 (CH), 29.1 (CH_2), 19.2 (CH_3), 14.0 (CH_3), 12.4 (CH_3), 11.9 (CH_3); MS (70 eV, EI) m/z (%) 217 [M^+ , 50], 182 (99), 160 (100), 145 (68); HRMS (70 eV) calc. for $\text{C}_{11}\text{H}_{20}\text{ClNO}$ 217.1233, found 217.1222; IR (neat): 3511, 2949, 1643, 1458 cm^{-1} ; $R_f = 0.41$ (Hexane: EtOAc 3:1).

^1H NMR (300 MHz)

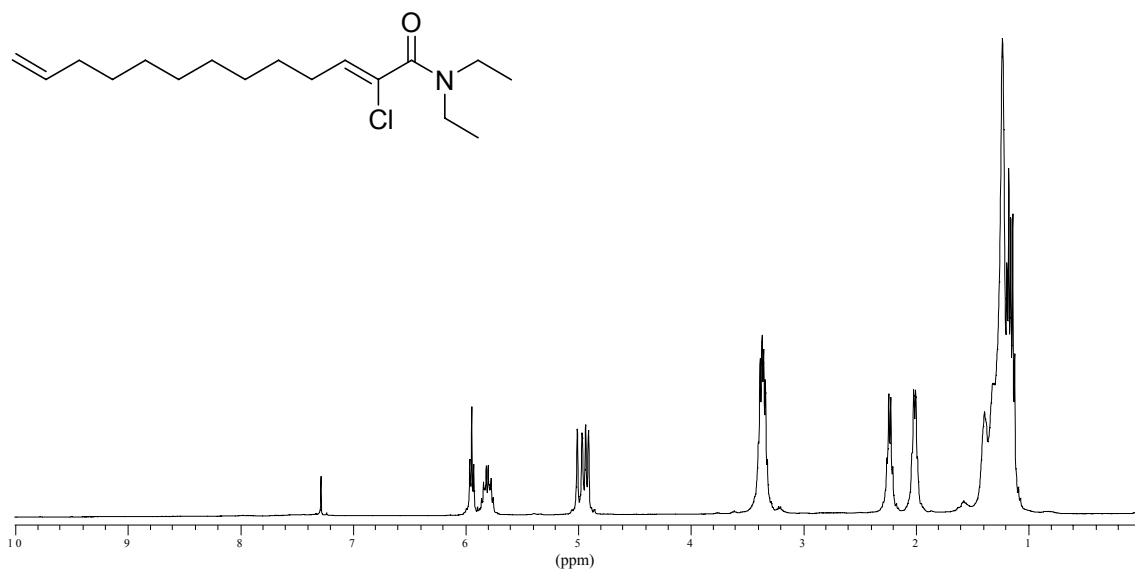


^{13}C NMR (100 MHz, 233 K)

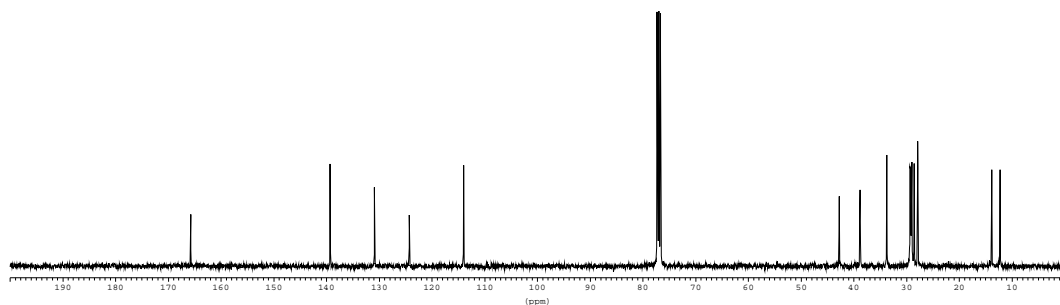


(Z)-2-Chloro-N,N-diethyltrideca-2,12-dienamide (5i): ^1H NMR (400 MHz, CDCl_3): δ 5.94 (t, $J = 7.1$ Hz, 1 H), 5.84-5.75 (m, 1 H), 5.01-4.89 (m, 2 H), 3.42-3.30 (m, 4 H), 2.25-2.20 (m, 2 H), 2.04-1.96 (m, 2 H), 1.42-1.10 (m, 12 H), 1.17 (t, $J = 6.9$ Hz, 3 H), 1.13 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 166.2 (C), 139.8 (CH), 131.3 (CH), 124.7 (C), 114.4 (CH_2), 43.2 (CH_2), 39.2 (CH_2), 34.2 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 28.3 (2 x CH_2), 14.3 (CH_3), 12.7 (CH_3); MS (70 eV, EI) m/z (%) 299 [M^+ , 6], 264 (100), 160 (94), 41 (72); HRMS (70 eV) calc. for $\text{C}_{17}\text{H}_{30}\text{ClNO}$ 299.2016, found 299.2022; IR (neat): 3440, 2927, 1659, 1462 cm^{-1} ; $R_f = 0.42$ (Hexane: EtOAc 3:1).

^1H NMR (400 MHz)

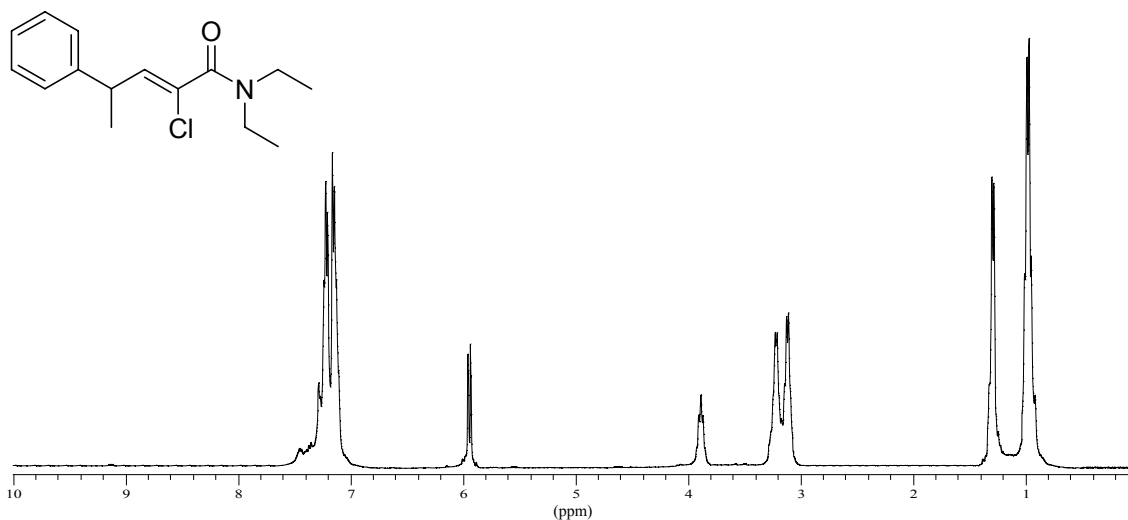


^{13}C NMR (100 MHz, 233 K)

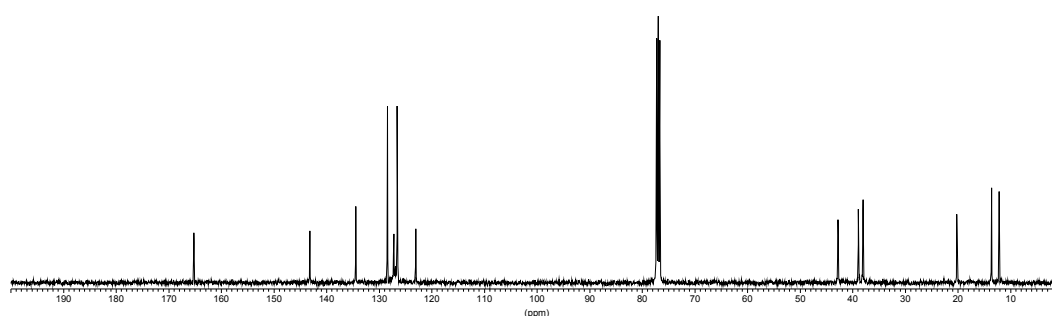


(Z)-2-Chloro-N,N-diethyl-4-phenylpent-2-enamide (5j): ^1H NMR (400 MHz, CDCl_3 , 233 K): δ 7.42-7.10 (m, 5 H), 5.94 (d, $J = 9.2$ Hz, 1 H), 3.93-3.84 (m, 1 H), 3.28-3.19 (m, 2 H), 3.15-3.06 (m, 2 H), 1.29 (d, $J = 6.8$ Hz, 3 H), 0.98 (t, $J = 6.8$ Hz, 3 H), 0.96 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 233 K): δ 165.2 (C), 143.1 (C), 134.4 (CH), 128.4 (2 x CH), 127.2 (C), 126.5 (2 x CH), 123.0 (CH), 42.7 (CH), 38.9 (CH_2), 38.0 (CH_2), 20.2 (CH_3), 13.6 (CH_3), 12.1 (CH_3); MS (70 eV, EI) m/z (%) 265 [M^+ , 47], 230 (100), 158 (98), 129 (89), 72 (71); HRMS (70 eV) calc. for $\text{C}_{15}\text{H}_{20}\text{ClNO}$ 265.1233, found 265.1191; IR (neat): 3425, 1615, 1451, 701cm^{-1} ; $R_f = 0.35$ (Hexane: EtOAc 3:1).

^1H NMR (400 MHz, 233 K)

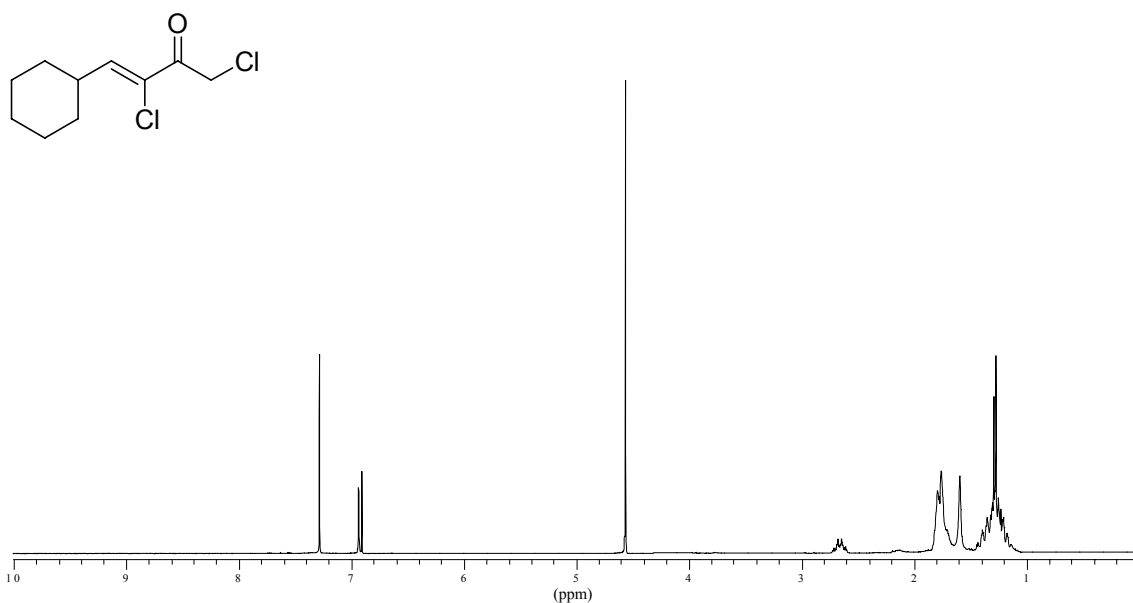


^{13}C NMR (100 MHz, 233 K)

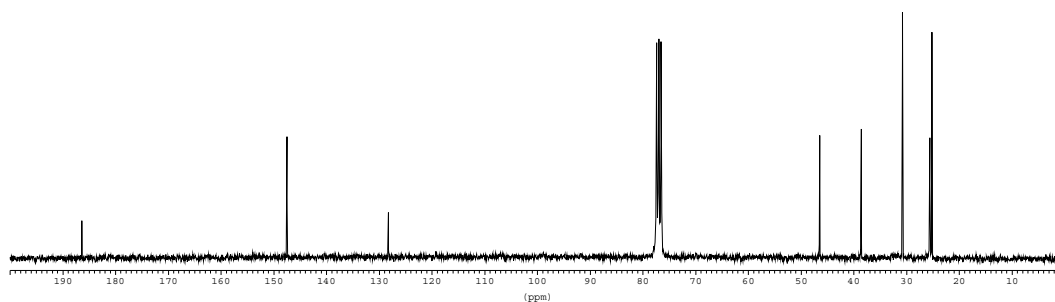


(Z)-1,3-Dichloro-4-cyclohexylbut-3-en-2-one (9c): ^1H NMR (300 MHz, CDCl_3): δ 6.92 (d, J = 9.3 Hz, 1 H), 4.56 (s, 2 H), 2.71-2.59 (m, 1 H), 1.79-1.59 (m, 4 H), 1.43-1.17 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 186.4 (C), 147.5 (CH), 128.2 (C), 46.4 (CH_2), 38.6 (CH), 30.7 (2 x CH_2), 25.6 (CH_2), 25.1 (2 x CH_2); MS (70 eV, EI) m/z (%) 220 [M^+ , 18], 151 (10), 89 (15), 81 (100); HRMS (70 eV) calc. for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}$ 220.0422, found 220.0413; IR (neat): 2932, 1711, 1266, 739 cm^{-1} ; R_f = 0.22 (Hexane: EtOAc 20:1).

^1H NMR (300 MHz)

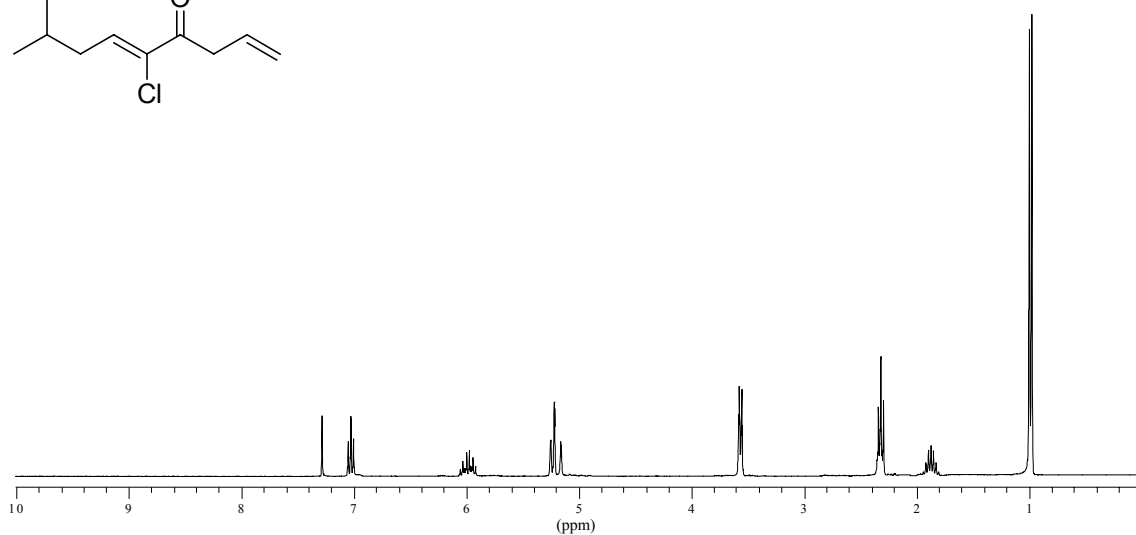
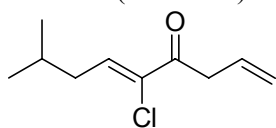


^{13}C NMR (75 MHz)

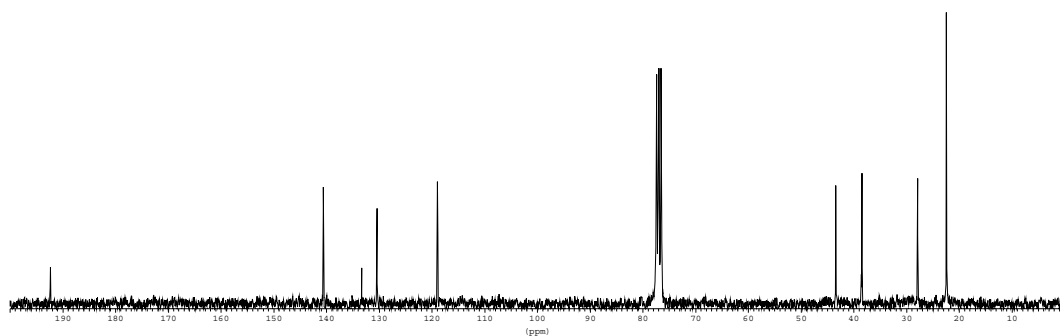


(Z)-5-Chloro-8-methylnona-1,5-dien-4-one (9d): ^1H NMR (300 MHz, CDCl_3): δ 7.02 (t, $J = 7.2$ Hz, 1 H), 6.05-5.91 (m, 1 H), 5.25-5.15 (m, 2 H), 3.56 (d, $J = 7.2$ Hz, 2 H), 2.31 (apparent t, $J = 7.2$ Hz, 2 H), 1.92-1.82 (m, 1 H), 0.98 (d, $J = 6.9$ Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 192.3 (C), 140.6 (CH), 133.3 (C), 130.4 (CH), 118.9 (CH_2), 43.4 (CH), 38.4 (CH_2), 27.9 (CH_2), 22.4 (2 x CH_3); IR (neat): 3055, 1726, 1266, 739 cm^{-1} ; $R_f = 0.42$ (Hexane: EtOAc 10:1).

^1H NMR (300 MHz)

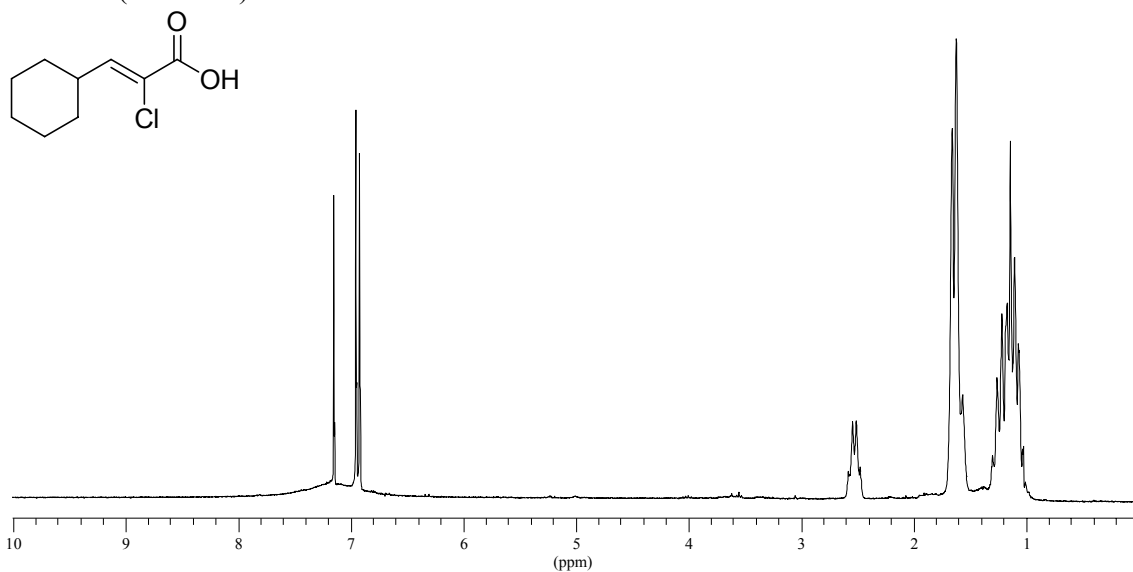


^{13}C NMR (75 MHz)

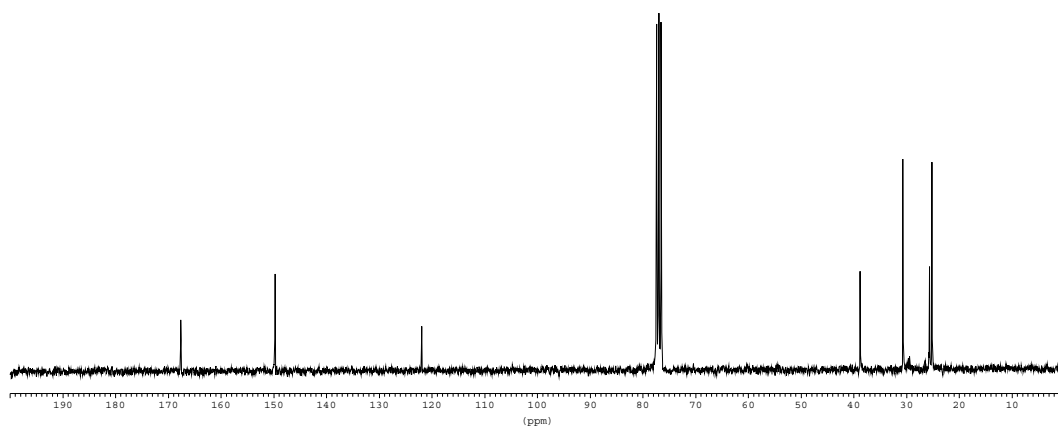


(Z)-2-Chloro-3-cyclohexylacrylic acid (10a): ^1H NMR (300 MHz, CDCl_3): δ 7.26 (br s, 1 H), 7.07 (d, $J = 9.3$ Hz, 1 H), 2.66 (m, 1 H), 1.79-1.66 (m, 4 H), 1.43-1.15 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.6 (C), 149.8 (CH), 122.0 (C), 38.8 (CH), 30.7 (2 x CH_2), 25.7 (CH_2), 25.2 (2 x CH_2); MS (70 eV, EI) m/z (%) 188 [M^+ , 11], 107 (17), 82 (100), 67 (74), 41 (22); HRMS (70 eV) calc. for $\text{C}_9\text{H}_{13}\text{ClO}_2$ 188.0604, found 188.0608; IR (neat): 3430, 2925, 1692, 1624 cm^{-1} ; $R_f = 0.17$ (Hexane: EtOAc 1:1).

^1H NMR (300 MHz)

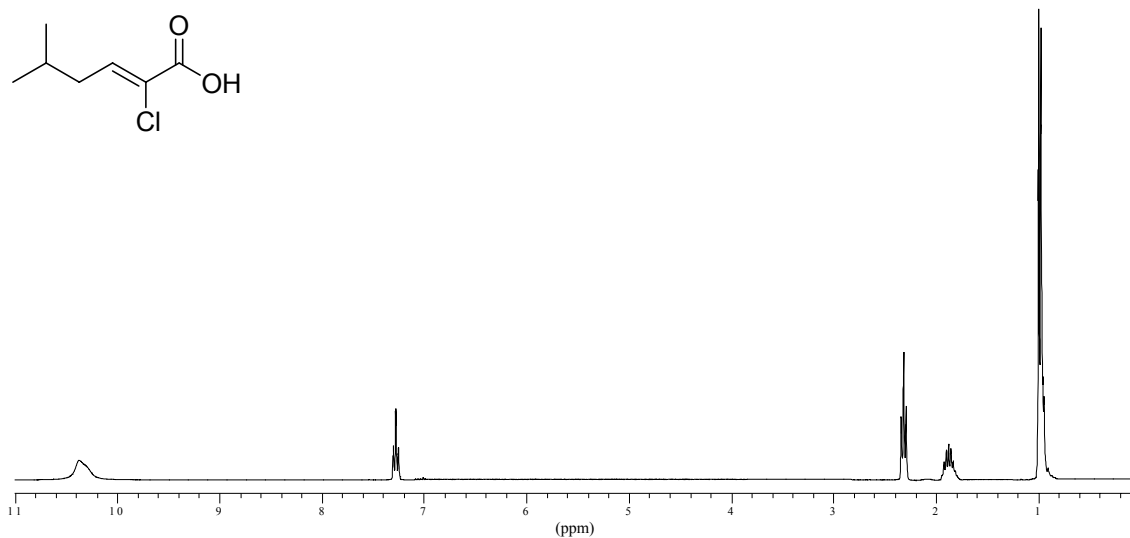


^{13}C NMR (75 MHz)

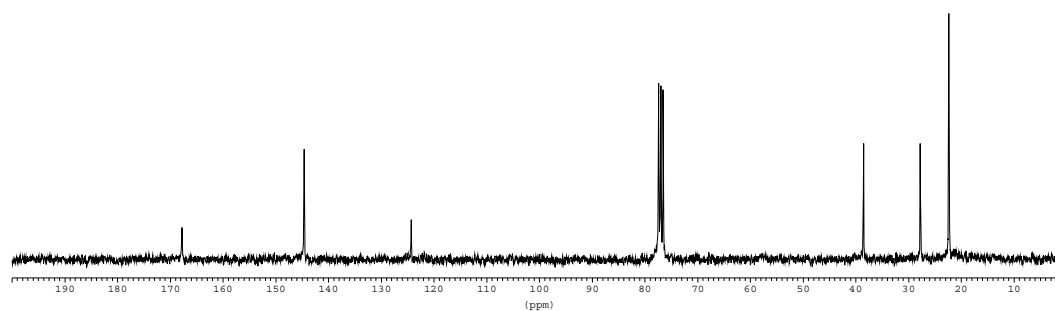


(Z)-2-Chloro-5-methylhex-2-enoic acid (10b): ^1H NMR (300 MHz, CDCl_3): δ 10.37 (br s, 1 H), 7.27 (t, $J = 7.4$ Hz, 1 H), 2.31 (t, $J = 7.2$ Hz, 2 H), 1.94-1.81 (m, 1 H), 0.98 (d, $J = 6.6$ Hz, 3 H), 0.97 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.7 (C), 144.6 (CH), 124.3 (C), 38.5 (CH), 27.7 (CH_2), 22.3 (2 x CH_3); MS (70 eV, EI) m/z (%) 162 [M^+ , 8], 120 (100), 69 (15), 56 (25); HRMS (70 eV) calc. for $\text{C}_7\text{H}_{11}\text{ClO}_2$ 162.0448, found 162.0450; IR (neat): 3426, 1630, 1466, 1266 cm^{-1} ; $R_f = 0.17$ (Hexane: EtOAc 3:1).

^1H NMR (300 MHz)

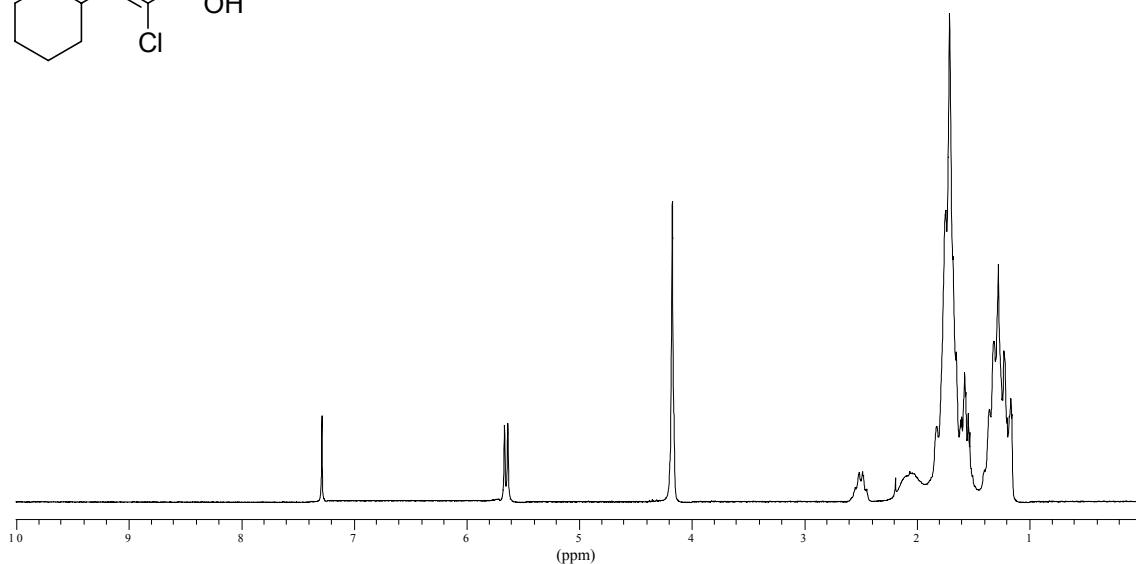
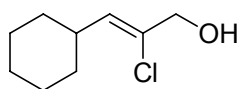


^{13}C NMR (75 MHz)



(Z)-2-Chloro-3-cyclohexylprop-2-en-1-ol (11b): ^1H NMR (300 MHz, CDCl_3): δ 5.64 (d, $J = 9.0$ Hz, 1 H), 4.17 (s, 2 H), 2.54-2.44 (m, 1 H), 2.08 (br s, 1 H), 1.82-1.52 (m, 6 H), 1.35-1.16 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3): δ 132.5 (CH), 131.1 (C), 67.4 (CH_2), 34.3 (CH), 33.6 (2 x CH_2), 32.1 (2 x CH_2), 31.8 (CH_2); MS (70 eV, EI) m/z (%) 174 [M^+ , 4], 159 (59), 123 (100), 81 (85), 55 (55); HRMS (70 eV) calc. for $\text{C}_9\text{H}_{15}\text{ClO}$ 174.0811, found 174.0817; IR (neat): 3357, 2924, 1449 cm^{-1} ; $R_f = 0.46$ (Hexane: EtOAc 5:1).

^1H NMR (300 MHz)



^{13}C NMR (75 MHz)

