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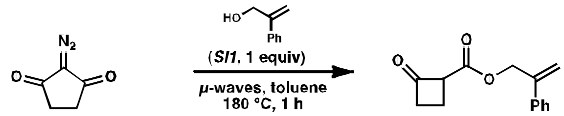
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an inert atmosphere of argon or nitrogen using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). THF, Et_2O, CH_2Cl_2, toluene, benzene, CH_3CN, and dioxane were dried by passage through an activated alumina column under argon. Triethylamine was distilled over CaH_2 prior to use. Brine solutions are saturated aqueous solutions of sodium chloride. 1,3-Cyclopentanedione was purchased from AK Scientific, Inc., reagent grade acetone was purchased from Aldrich and distilled from anhydrous Ca_2SO_4 and stored over molecular sieves (3 Å) under an atmosphere of argon. *para*-Acetamidobenzenesulfonyl azide (*p*-ABSA) was prepared following a procedure by Davies *et al*.[1] 2-Phenylprop-2-en-1-ol, 2-(4-methoxyphenyl)prop-2-en-1-ol and 2-(3-fluorophenyl)prop-2-en-1-ol were prepared according to the method by Gouverneur and Brown.[2] 2-Diazocyclopentane-1,3-dione was prepared through diazotization of 1,3-cyclopentanedione with *p*-ABSA following a procedure by Coquerel and Rodriguez.[3] Phosphinooxazoline (PHOX) ligands were prepared by methods described in our previous work.[4] Tris(4,4'-methoxydibenzylideneacetone)dipalladium(0) ($Pd_2(pmdba)_3$) was prepared according to the method of Ibers[5] or Fairlamb.[6] All other reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator unless otherwise indicated. Stirring was accomplished with Teflon® coated magnetic stir bars. Microwave-assisted reactions were performed in a Biotage Initiator 2.5 microwave reactor. Glove box manipulations were performed under a N_2 atmosphere. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash column chromatography. ^1H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), C_6H_6 (δ 7.16 ppm), or CH_2Cl_2 (δ 5.32 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz (126 MHz) or Varian Mercury 300 MHz (75 MHz) spectrometer and are reported relative to $CHCl_3$ (δ 77.16 ppm) or C_6H_6 (δ 128.06 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = heptet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent, ee). Analytical UHPLC-LCMS was performed with an Agilent 1290 Infinity Series UHPLC/Agilent 6140 Quadrupole LCMS utilizing an Agilent Eclipse Plus C18 RRHD 1.8 μm column (2.1 x 50 mm), part number 959757-902. High-resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility (EI+ or FAB+) or on an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), or mixed (MM: ESI-APCI) ionization mode.

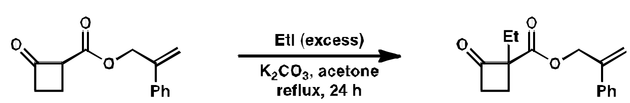
Representative Procedure for the Preparation of 2-Oxocyclobutanecarboxylates



2-Phenylallyl 2-oxocyclobutanecarboxylate. To a 20 mL microwave vial charged with a magnetic stir bar were added 2-diazocyclopentane-1,3-dione (**2**, 500 mg, 4.03 mmol), toluene (13.5 mL) and 2-phenylprop-2-en-1-ol (**SI1**, 540 mg, 4.03 mmol). The vial was sealed with a microwave crimp cap and heated to 180 °C for one hour using a Biotage Initiator microwave reactor (sensitivity set to low; reaction mixture heated gradually over first 2 minutes by increasing the temperature in 20 °C increments). After 30 minutes of stirring, the mixture was cooled to ambient temperature and the pressure was released by puncture of the crimp cap with a needle. The reaction vessel was then subsequently irradiated at 180 °C for an additional 30 minutes. The vessel was then cooled to ambient temperature, the vial uncapped and mixture directly loaded onto a silica gel column followed by elution with hexanes to 20% EtOAc in hexanes to afford of **SI2** (635 mg, 68% yield) as a colorless oil. R_f = 0.2 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.30 (m, 5H), 5.57–5.55 (m, 1H), 5.40–5.39 (m, 1H), 5.06–5.05 (m, 2H), 4.26–4.20 (m, 1H), 3.20–3.15 (m, 2H), 2.48–2.34 (m, 1H), 2.29–2.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 166.5, 142.0, 137.8, 128.5, 128.1, 126.0, 115.4, 66.5, 64.5, 47.1, 13.6; IR (Neat Film, NaCl) 3448, 3084, 3057, 3024, 2970, 1956, 1790, 1732, 1633, 1600, 1574, 1497, 1445, 1387, 1310, 1177, 1046, 915, 780 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{15}O_3$ [M+H]$^+$: 231.1016; found 231.1018.

*With the exception of compound **SI2**, all 2-carboxyallylcyclobutanone derivatives were directly used in the following steps without rigorous characterization due to their instability.*

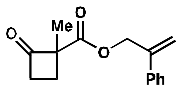
Representative Procedure for the Alkylation of 2-Oxocyclobutanecarboxylates



2-Phenylallyl 1-ethyl-2-oxocyclobutanecarboxylate (4a). To a solution of **SI2** (233 mg, 1.01 mmol) in acetone (14 mL) were added K_2CO_3 (224 mg, 1.62 mmol) and freshly distilled EtI (787 mg, 5.05 mmol). The mixture was heated to reflux until full consumption of the starting material was indicated by TLC analysis (alkylation reaction times typically ranged from 12 to 24 hours). Upon completion, the mixture was cooled to 25 °C, the solids were removed by filtration through filter paper and the mixture was concentrated *in vacuo*. The crude material was purified by flash column chromatography (SiO_2, hexanes to 10% EtOAc in hexanes to 20% EtOAc in hexanes) to provide **4a** (105 mg, 40% yield) as a colorless oil. R_f = 0.3 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 5.55 (s, 1H), 5.38 (s, 1H), 5.06 (dd, J = 9.0, 1.0 Hz, 2H), 2.56–2.17 (m, 3H), 1.88-1.63 (m, 3H), 0.69 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)

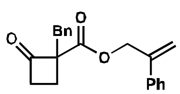
δ 209.4, 171.5, 142.2, 137.8, 128.5, 128.1, 126.1, 116.5, 66.5, 63.7, 35.5, 30.4, 27.1, 8.6; IR (Neat Film, NaCl) 3084, 2972, 2880, 1738, 1709, 1460, 1444, 1231, 1207, 1138 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1334; found 259.1326.

2-Phenylallyl 1-methyl-2-oxocyclobutanecarboxylate (4b)



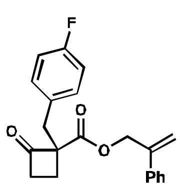
Compound **4b** was isolated by flash column chromatography (SiO_2, hexanes to 10% EtOAc in hexanes) as a colorless oil. 32% yield. R_f = 0.5 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 5.54–553 (m, 1H), 5.35–5.34 (m, 1H), 5.06 (dq, *J* = 11.2, 1.0 Hz, 1H), 3.20 (ddd, *J* = 18.3, 11.3, 7.6 Hz, 1H), 3.10 (ddd, *J* = 18.3, 9.9, 6.3 Hz, 1H), 2.53 (td, *J* = 11.3, 6.3 Hz, 1H), 1.84 (ddd, *J* = 11.5, 9.9, 7.6 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 170.0, 142.3, 137.9, 128.5, 128.1, 126.0, 115.2, 69.4, 66.5, 45.3, 23.1, 18.4; IR (Neat Film, NaCl) 2970, 2930, 1788, 1729, 1452, 1274, 1145, 1049 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1100; found 244.1103.

2-Phenylallyl 1-benzyl-2-oxocyclobutanecarboxylate (4c)



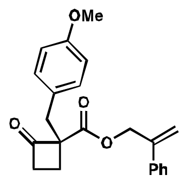
Compound **4c** was isolated by flash column chromatography (SiO_2, hexanes to 10% EtOAc in hexanes) as a colorless oil. 37% yield. R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.33–7.14 (m, 8H), 7.04–7.02 (m, 2H), 5.47 (s, 1H), 5.28–5.27 (m, 1H), 5.01–4.95 (m, 2H), 3.12, 3.10 (AB system, J_{AB} = 14.2 Hz, 2H), 2.95 (ddd, *J* = 18.3, 11.1, 7.3 Hz, 1H), 2.62 (ddd, *J* = 18.3, 10.3, 6.3 Hz, 1H), 2.39 (ddd, *J* = 11.9, 11.1, 6.3 Hz, 1H), 1.93 (ddd, *J* = 11.9, 10.3, 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 168.7, 142.1, 137.8, 135.9, 129.7, 128.51, 128.49, 128.1, 126.9, 126.0, 115.5, 75.0, 66.7, 45.2, 37.9, 19.2; IR (Neat Film, NaCl) 3029, 2924, 1788, 1725, 1496, 1270, 1191, 1046 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{42}H_{40}NaO_6$ $[2M+Na]^+$: 663.2717; found 663.2692.

2-Phenylallyl 1-(4-fluorobenzyl)-2-oxocyclobutanecarboxylate (4d)



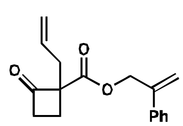
Compound **4d** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 6% EtOAc in hexanes) as a colorless oil. 22% yield. R_f = 0.4 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 7.08–7.04 (m, 2H), 6.95–6.91 (m, 2H), 5.54 (s, 1H), 5.34 (d, *J* = 0.9 Hz, 1H), 5.05 (s, 2H), 3.18, 3.16 (AB system, J_{AB} = 14.3 Hz, 2H), 3.05 (ddd, *J* = 18.4, 11.2, 7.4 Hz, 1H), 2.73 (ddd, *J* = 18.4, 10.2, 6.2 Hz, 1H), 2.46 (ddd, *J* = 11.8, 11.2, 6.2 Hz, 1H), 1.97 (ddd, *J* = 11.8, 10.2, 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 168.6, 161.9 (d, $^1J_{CF}$ = 245.6 Hz), 142.1, 137.8, 131.6 (d, $^4J_{CF}$ = 3.7 Hz), 131.2 (d, $^3J_{CF}$ = 8.0 Hz), 128.5, 128.1, 126.0, 115.7, 115.3 (d, $^2J_{CF}$ = 21.2 Hz), 75.0, 66.8, 45.2, 37.0, 19.3; IR (Neat Film, NaCl) 3052, 2968, 2928, 1784, 1717, 1506, 1219, 1186, 1042, 912 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{20}{}^{19}FO_3$ $[M+H]^+$: 339.1391; found 339.1387.

2-Phenylallyl 1-(4-methoxybenzyl)-2-oxocyclobutanecarboxylate (4e)



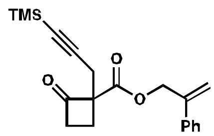
To a solution of NaI (1.88 g, 12.54 mmol) in acetone (20 mL) was added 4-methoxybenzyl chloride (1.55 mL, 11.38 mmol). The mixture was stirred at 25 °C for 2 hours before K_2CO_3 (504 mg, 3.65 mmol) and **SI2** (524 mg, 2.28 mmol) were added. The resulting mixture was heated to reflux for 16 hours until full conversion of the starting material was indicated by TLC analysis. The mixture was cooled to room temperature, the solids removed by filtration and concentrated *in vacuo*. The crude material was purified by flash column chromatography (SiO_2, hexanes to 10% EtOAc in hexanes to 20% EtOAc in hexanes) to provide **4e** (506 mg, 63% yield) as a colorless oil. R_f = 0.5 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.36–7.29 (m, 3H), 7.04–7.01 (m, 2H), 6.80–6.77 (m, 2H), 5.54 (s, 1H), 5.36–5.35 (m, 1H), 5.08–5.02 (m, 2H), 3.77 (s, 3H), 3.13 (s, 2H), 3.00 (ddd, *J* = 18.3, 11.1, 7.2 Hz, 1H), 2.68 (ddd, *J* = 18.3, 10.3, 6.4 Hz, 1H), 2.45 (ddd, *J* = 11.8, 11.1, 6.4 Hz, 1H), 2.00 (ddd, *J* = 11.8, 10.3, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 168.8, 158.5, 142.1, 137.8, 130.7, 128.5, 128.1, 127.8, 126.0, 115.5, 113.9, 75.2, 66.7, 55.2, 45.0, 37.1, 19.1; IR (Neat Film, NaCl) 2957, 2933, 2836, 1788, 1725, 1513, 1248, 1179, 1037 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{22}H_{23}O_4$ $[M+H]^+$: 351.1596; found 351.1601.

2-Phenylallyl 1-allyl-2-oxocyclobutanecarboxylate (4f)



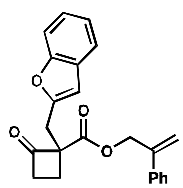
Compound **4f** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 4% EtOAc in hexanes) as a colorless oil. 68% yield. R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.27 (m, 5H), 5.64 (ddt, *J* = 17.5, 9.7, 7.1 Hz, 1H), 5.56 (q, *J* = 0.8 Hz, 1H), 5.38 (q, *J* = 1.2 Hz, 1H), 5.12–5.08 (m, 2H), 5.07 (dd, *J* = 1.4, 0.7 Hz, 2H), 3.14 (ddd, *J* = 18.4, 11.0, 7.4 Hz, 1H), 3.02 (ddd, *J* = 18.4, 10.1, 6.4 Hz, 1H), 2.70 (ddt, *J* = 14.3, 7.1, 1.2 Hz, 1H), 2.59–2.44 (m, 2H), 1.99 (ddd, *J* = 11.9, 10.1, 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 168.6, 142.3, 137.9, 131.9, 128.5, 128.1, 126.1, 119.2, 115.5, 73.6, 66.6, 45.0, 36.7, 19.5; IR (Neat Film, NaCl) 3072, 2967, 1786, 1725, 1638, 1497, 1440, 1387, 1193, 1142, 1043, 919, 779 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1329; found 271.1330.

2-Phenylallyl 2-oxo-1-(3-(trimethylsilyl)prop-2-yn-1-yl)cyclobutanecarboxylate (4g)



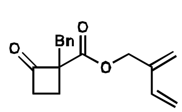
Compound **4g** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 7% EtOAc in hexanes) as a colorless oil. 63% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.27 (m, 5H), 5.54 (q, *J* = 0.7 Hz, 1H), 5.35 (td, *J* = 1.3, 0.7 Hz, 1H), 5.10–4.98 (m, 2H), 3.18 (ddd, *J* = 18.4, 11.0, 7.4 Hz, 1H), 3.06 (ddd, *J* = 18.4, 10.4, 6.5 Hz, 1H), 2.82 (d, *J* = 17.3 Hz, 1H), 2.69 (d, *J* = 17.3 Hz, 1H), 2.48 (ddd, *J* = 11.8, 11.0, 6.5 Hz, 1H), 2.27 (ddd, *J* = 11.8, 10.4, 7.4 Hz, 1H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.9, 168.1, 142.1, 137.8, 128.5, 128.1, 126.0, 115.4, 100.9, 87.9, 72.1, 66.8, 46.3, 22.8, 19.7, -0.1; IR (Neat Film, NaCl) 3058, 2959, 2177, 1949, 1794, 1732, 1634, 1575, 1496, 1444, 1422, 1315, 1250, 1194, 1161, 1116, 1028, 906, 843, 778, 760, 708 cm^{-1}; HRMS (APCI) *m/z* calc'd for $C_{20}H_{25}O_3Si$ [M+H]$^+$: 341.1567; found 341.1582.

2-Phenylallyl 1-(benzofuran-2-ylmethyl)-2-oxocyclobutanecarboxylate (4h)



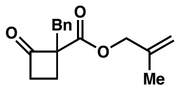
Compound **4h** was isolated by flash column chromatography (SiO_2, 5% EtOAc in hexanes to 10% EtOAc in hexanes) as a colorless oil. 27% yield. R_f = 0.6 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.46 (m, 1H), 7.40–7.38 (m, 3H), 7.33–7.29 (m, 3H), 7.25–7.18 (m, 2H), 6.37 (d, *J* = 0.8 Hz, 1H), 5.55 (m, 1H), 5.37 (m, 1H), 5.09 (s, 2H), 3.43 (d, *J* = 15.6 Hz, 1H), 3.28 (dd, *J* = 15.6, 0.8 Hz, 1H), 3.18 (ddd, *J* = 18.4, 11.2, 7.6 Hz, 1H), 2.97 (ddd, *J* = 18.4, 10.2, 6.1 Hz, 1H), 2.58 (ddd, *J* = 11.9, 11.2, 6.1 Hz, 1H), 2.11 (ddd, *J* = 11.9, 10.2, 7.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 168.1, 154.8, 153.6, 142.1, 137.7, 128.5, 128.4, 128.1, 126.0, 123.8, 122.7, 120.6, 115.7, 110.9, 104.9, 73.1, 67.0, 45.8, 30.9, 19.9; IR (Neat Film, NaCl) 3582, 3056, 3033, 2963, 2928, 1790, 1726, 1601, 1586, 1455, 1253, 1193, 1045 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{21}O_4$ [M+H]$^+$: 361.1434; found 361.1427.

2-Methylenebut-3-en-1-yl 1-benzyl-2-oxocyclobutanecarboxylate (4i)



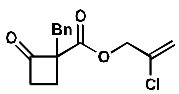
Compound **4i** was isolated by flash column chromatography (SiO_2, 1% EtOAc in hexanes to 8% EtOAc in hexanes) as a colorless oil. 51% yield. R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.20 (m, 3H), 7.19–7.05 (m, 2H), 6.36 (ddd, *J* = 17.9, 11.1, 0.8 Hz, 1H), 5.28–5.09 (m, 4H), 4.89–4.78 (m, 2H), 3.24 (dd, *J* = 18.6, 14.2 Hz, 2H), 3.14 (ddd, *J* = 18.3, 11.0, 7.2 Hz, 1H), 2.75 (ddd, *J* = 18.3, 10.3, 6.4 Hz, 1H), 2.58 (ddd, *J* = 11.8, 11.0, 6.4 Hz, 1H), 2.06 (ddd, *J* = 11.8, 10.3, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 168.7, 140.0, 136.0, 135.9, 129.7, 128.5, 127.0, 118.4, 114.8, 75.1, 64.6, 45.2, 38.0, 19.2; IR (Neat Film, NaCl) 3987, 3027, 2929, 1789, 1725, 1598, 1495, 1454, 1393, 1266, 1192, 1044, 909, 743 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1329; found 271.1330.

2-Methylallyl 1-benzyl-2-oxocyclobutanecarboxylate (4j)



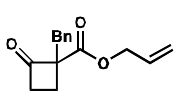
Compound **4j** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes) as a colorless oil. 44% yield. R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.24 (m, 3H), 7.19–7.17 (m, 2H), 4.97 (d, J = 15.1 Hz, 2H), 4.60, 4.56 (AB system, J_{AB} = 13.1 Hz, 2H), 3.28, 3.26 (AB system, J_{AB} = 14.2 Hz, 2H), 3.16 (ddd, J = 18.3, 11.0, 7.2 Hz, 1H), 2.77 (ddd, J = 18.3, 10.4, 6.5 Hz, 1H), 2.61 (ddd, J = 11.8, 11.0, 6.5 Hz, 1H), 2.09 (ddd, J = 11.8, 10.4, 7.2 Hz, 1H) 1.70 (d, J = 0.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 168.7, 139.3, 134.0, 129.7, 128.5, 127.0, 113.4, 75.1, 68.7, 45.2, 38.0, 19.4, 19.2; IR (Neat Film, NaCl) 3030, 2974, 2925, 1790, 1727, 1454, 1271, 1193, 1047, 907 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{19}O_3$ $[M+H]^+$ 259.1329; found 259.1340.

2-Chloroallyl 1-benzyl-2-oxocyclobutanecarboxylate (4k)



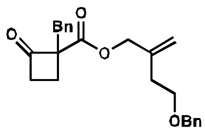
Compound **4k** was isolated by flash column chromatography (SiO_2, 2% EtOAc in hexanes to 5% EtOAc in hexanes) as a colorless oil. 63% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 3H), 7.18–7.16 (m, 2H), 5.44–5.40 (m, 2H), 4.71 (m, 2H), 3.26 (s, 2H), 3.17 (ddd, J = 18.3, 11.0, 7.2 Hz, 1H), 2.77 (ddd, J = 18.3, 10.3, 6.5 Hz, 1H), 2.61 (ddd, J = 11.8, 11.0, 6.5 Hz, 1H), 2.01 (ddd, J = 11.8, 10.3, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 168.2, 135.7, 135.2, 129.7, 128.6, 127.1, 115.3, 74.9, 66.7, 45.3, 38.0, 19.2; IR (Neat Film, NaCl) 3578, 2918, 1792, 1734, 1637, 1439, 1268, 1191, 1045 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{15}H_{15}ClO_3$ $[M]^+$: 278.0710; found 278.0714.

Allyl 1-benzyl-2-oxocyclobutanecarboxylate (4l)



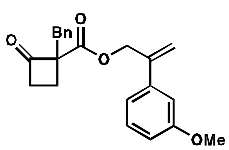
Compound **4l** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 6% EtOAc in hexanes) as a colorless oil. 87% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.30–7.27 (m, 2H), 7.25–7.22 (m, 1H), 7.17–7.14 (m, 2H), 5.88 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.31 (dq, J = 17.2, 1.4 Hz, 1H), 5.24 (dq, J = 10.5, 1.4 Hz, 1H), 4.64 (dq, J = 5.7, 1.4 Hz, 2H), 3.26, 3.22 (AB system, J_{AB} = 14.2 Hz, 2H), 3.14 (ddd, J = 18.3, 11.0, 7.2 Hz, 1H), 2.75 (ddd, J = 18.3, 10.3, 6.5 Hz, 1H), 2.59 (ddd, J = 11.8, 11.0, 6.5 Hz, 1H), 2.07 (ddd, J = 11.8, 10.3, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 168.6, 136.0, 131.5, 129.7, 128.5, 127.0, 118.7, 75.1, 66.1, 45.1, 38.1, 19.3; IR (Neat Film, NaCl) 2916, 2848, 1781, 1715, 1438, 1181, 1040 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1172; found 245.1178.

4-(Benzyloxy)-2-methylenebutyl 1-benzyl-2-oxocyclobutanecarboxylate (4m)



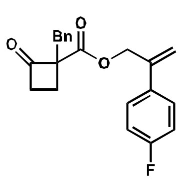
Compound **4m** was isolated by flash column chromatography (SiO_2, 1% EtOAc in Hexanes to 3% EtOAc in hexanes) as a colorless oil. 51% yield. R_f = 0.5 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.12 (m, 10H), 5.11 (q, *J* = 1.0 Hz, 1H), 5.04 (h, *J* = 1.1 Hz, 1H), 4.67, 4.61 (AB system, J_{AB} = 13.3 Hz, 2H), 4.53 (s, 2H), 3.60 (t, *J* = 6.6, 2H), 3.26 (s, 2H), 3.14 (ddd, *J* = 18.2, 11.0, 7.2 Hz, 1H), 2.76 (ddd, *J*=18.3, 10.3, 6.4 Hz, 1H), 2.60 (ddd, *J* = 11.8, 11.0, 6.5 Hz, 1H), 2.42–2.33 (m, 2H), 2.08 (ddd, *J* = 11.8, 10.3, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 168.7, 140.7, 138.2, 136.0, 129.7, 128.6, 128.4, 127.7, 127.6, 127.0, 114.4, 75.1, 73.0, 68.5, 68.0, 45.2, 38.1, 33.5, 19.3; IR (Neat Film, NaCl) 3029, 2920, 2849, 1784, 1717, 1495, 1451, 1360, 1268, 1187, 1095, 904, 732 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{24}H_{27}O_4$ $[M+H]^+$: 379.1904; found 379.1926.

2-(3-Methoxyphenyl)allyl 1-benzyl-2-oxocyclobutanecarboxylate (4n)



Compound **4n** was isolated by flash column chromatography (SiO_2, 3% EtOAc in Hexanes to 7% EtOAc in Hexanes) as a colorless oil. 79% yield. R_f = 0.35 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.16 (m, 4H), 7.16–7.09 (m, 2H), 7.05–6.90 (m, 2H), 6.91–6.82 (m, 1H), 5.60–5.53 (m, 1H), 5.37 (q, *J* = 1.2 Hz, 1H), 5.12–5.01 (m, 2H), 3.84 (s, 3H), 3.24, 3.21 (AB system, J_{AB} = 14.13 Hz, 2H), 3.06 (ddd, *J* = 18.3, 11.1, 7.3 Hz, 1H), 2.72 (ddd, *J* = 18.3, 10.2, 6.3 Hz, 1H), 2.51 (ddd, *J* = 11.9, 11.1, 6.3 Hz, 1H), 2.04 (ddd, *J* = 11.8, 10.2, 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 168.7, 159.7, 142.1, 139.4, 136.0, 129.7, 129.5, 128.5, 126.9, 118.5, 115.8, 113.6, 111.8, 75.1, 66.8, 55.3, 45.2, 37.9, 19.2; IR (Neat Film, NaCl) 2957, 2833, 1786, 1720, 1575, 1494, 1453, 1387, 1221, 1180, 1039, 783 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{23}O_4$ $[M+H]^+$: 351.1591; found 351.1582.

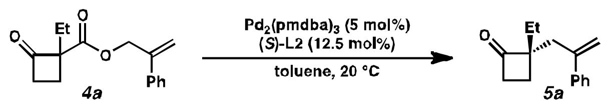
2-(4-Fluorophenyl)allyl 1-benzyl-2-oxocyclobutanecarboxylate (4o)



Compound **4o** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 6% EtOAc in hexanes) as a colorless oil. 93% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.30–7.23 (m, 3H), 7.14–7.11 (m, 2H), 7.07–7.02 (m, 2H), 5.51 (s, 1H), 5.36 (s, 1H), 5.07–5.01 (m, 2H), 3.23, 3.20 (AB system, J_{AB} = 14.2 Hz, 2H), 3.06 (ddd, J = 18.3, 11.0, 7.3 Hz, 1H), 2.74 (ddd, J = 18.3, 10.3, 6.4 Hz, 1H), 2.51 (ddd, J = 11.9, 11.0, 6.4 Hz, 1H), 2.05 (ddd, J = 11.9, 10.3, 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.5, 168.6, 162.7 (d, $^1J_{CF}$ = 247.5 Hz), 141.1, 135.9, 133.9 (d, $^4J_{CF}$ = 3.9 Hz), 129.6, 128.5, 127.7 (d, $^3J_{CF}$ = 8.6 Hz), 126.9, 115.7, 115.4 (d, $^2J_{CF}$ = 21.4 Hz), 75.0, 66.7, 45.1, 37.8, 19.2; IR (Neat Film, NaCl) 3060, 3029, 2967, 2928, 1790, 1728, 1634, 1602, 1511, 1454, 1386, 1233, 1193, 1162, 1047, 917, 840, 744 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{21}H_{20}{}^{19}FO_3$ $[M+H]^+$: 339.1391; found 339.1397.

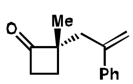
Representative Procedure for the Asymmetric Decarboxylative Allylic Alkylation of 2-Carboxallylcyclobutanones

(*S*)-2-Ethyl-2-(2-phenylallyl)cyclobutanone (5a)



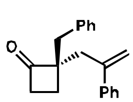
To a 20 mL scintillation vial with a stir bar were added $Pd_2(pmdba)_3$ (16.4 mg, 0.015 mmol), **L2** (21.9 mg, 0.037 mmol) and toluene (9 mL) in a nitrogen−filled glove box. The dark purple mixture was stirred at ambient glove box temperature (ca. 30 °C) for 35 minutes at which point the mixture had become red-orange. 2-Carboxyallylcyclobutanone **4a** (80.0 mg, 0.31 mmol) was then added. The resulting yellow-greenish reaction mixture was stirred at 20 °C until full conversion of the starting material was indicated by TLC analysis (reaction times typically ranged 18 to 36 hours). The vial was removed from the glove box, uncapped and directly purified by flash column chromatography (SiO_2, pentane to 15% Et_2O in pentane) afforded **5a** (41 mg, 62% yield) as colorless oil. R_f = 0.3 (15% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.25 (m, 5H), 5.55 (d, *J* = 0.9 Hz, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.16–4.92 (m, 2H), 2.51 (ddd, *J* = 14.7, 10.5, 2.0 Hz, 1H), 2.42–2.30 (m, 1H), 2.29–2.14 (m, 1H), 1.93–1.77 (m, 2H), 1.73–1.59 (m, 1H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.1, 145.2, 141.9, 128.3, 127.6, 126.5, 116.5, 63.8, 42.8, 40.6, 23.5, 21.6, 8.4; IR (Neat Film, NaCl) 3078, 2966, 1699, 1464, 1443, 905 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{17}O$ [(M+H)–H_2]$^+$: 213.1279; found 213.1274; $[\alpha]_D^{26.0}$ +8.50 (*c* 1.00, $CHCl_3$, 99% ee).

(*S*)-2-Methyl-2-(2-phenylallyl)cyclobutanone (5b)



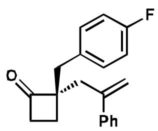
Cyclobutanone **5b** was isolated by flash column chromatography (SiO_2, 10% Et_2O in pentane) as a colorless oil. 92% yield. R_f = 0.3 (10% Et_2O in pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.19 (m, 5H), 5.25 (d, *J* = 1.5 Hz, 1H), 5.04–5.03 (m, 1H), 2.93–2.66 (m, 3 H), 2.56 (d, *J* = 14.1 Hz, 1H), 1.82 (ddd, *J* = 11.4, 10.5, 6.9 Hz, 1H), 1.47 (ddd, *J* = 11.4, 10.2, 6.6 Hz, 1H), 1.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 145.2, 141.9, 128.3, 127.6, 126.5, 116.5, 63.8, 42.8, 40.6, 23.5, 21.6; IR (Neat Film, NaCl) 2080, 2865, 1774, 1443, 1059 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{17}O$ [M+H]$^+$: 201.1279; found 201.1286; $[\alpha]_D^{26.0}$ −83.9 (*c* 1.00, $CHCl_3$, 90% ee).

(*R*)-2-Benzyl-2-(2-phenylallyl)cyclobutanone (5c)



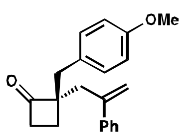
Cyclobutanone **5c** was isolated by flash column chromatography (SiO_2, 5% Et_2O in petroleum ether) as a colorless oil. 81% yield. R_f = 0.6 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.26 (m, 8H), 7.13–7.11 (m, 2H), 5.37 (d, *J* = 1.4 Hz, 1H), 5.15–5.14 (m, 1H), 2.94 (t, *J* = 14.9 Hz, 2H), 2.72 (t, *J* = 14.2 Hz, 2H), 2.61 (ddd, *J* = 18.1, 9.6, 7.2 Hz, 1H), 2.32 (ddd, *J* = 18.1, 10.0, 7.5 Hz, 1H), 1.86–1.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214, 145.0, 141.8, 137.3, 130.0, 128.4, 128.3, 127.7, 126.5, 126.4, 116.9, 68.8, 43.7, 41.2, 39.9, 20.0; IR (Neat Film, NaCl) 3028, 2918, 1770, 1494, 1453, 1074, 905 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{20}H_{21}O$ $[M+H]^+$: 277.1587; found 277.1587; $[\alpha]_D^{26.0}$ –2.91 (*c* 1.14, $CHCl_3$, 95% ee).

(*R*)-2-(4-Fluorobenzyl)-2-(2-phenylallyl)cyclobutanone (5d)



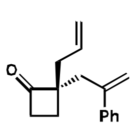
Cyclobutanone **5d** was isolated by flash column chromatography (SiO_2, hexanes to 3% Et_2O in hexanes) as a colorless oil. 71% yield. R_f = 0.3 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.36–7.26 (m, 5H), 7.09–7.05 (m, 2H), 6.97–6.93 (m, 2H), 5.37 (d, *J* = 1.4 Hz, 1H), 5.14 (d, *J* = 0.9 Hz, 1H), 2.93–2.89 (m, 2H), 2.74–2.67 (m, 2H), 2.33 (ddd, *J* = 18.1, 10.7, 6.9 Hz, 1H), 2.62 (ddd, *J* = 18.1, 10.4, 6.5 Hz, 1H), 1.83 (ddd, *J* = 11.7, 10.4, 6.9 Hz, 1H), 1.75 (ddd, *J* = 11.7, 10.7, 6.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.7, 161.7 (d, $^1J_{CF}$ = 244.8 Hz), 144.9, 141.8, 132.9 (d, $^4J_{CF}$ = 3.8 Hz), 131.5 (d, $^3J_{CF}$ = 8.3 Hz), 128.8, 127.2, 126.4, 117.0, 115.1 (d, $^2J_{CF}$ = 21.1 Hz), 68.7, 43.7, 40.2, 39.9, 19.9; IR (Neat Film, NaCl) 3047, 2918, 2848, 1772, 1599, 1508, 1221, 1158, 1060 836 cm^{-1}; HRMS (MM: ESI-APCI) m/z calc'd for $C_{20}H_{20}{}^{19}FO$ $[M+H]^+$: 294.1420; found 294.1408; $[\alpha]_D^{26.0}$ –9.9 (*c* 0.59, $CHCl_3$, 94% ee).

(*R*)-2-(4-Methoxybenzyl)-2-(2-phenylallyl)cyclobutanone (5e)



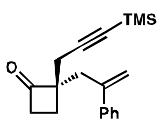
Cyclobutanone **5e** was isolated by flash column chromatography (SiO_2, 10% EtOAc in hexanes) as a colorless oil. 83% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.37–7.26 (m, 5H), 7.06–7.01 (m, 2H), 6.83–6.78 (m, 2H), 5.37 (d, *J* = 1.2 Hz, 1H), 5.14 (s, 1H), 3.78 (s, 3H), 2.91 (dd, *J* = 14.5, 3.1 Hz, 2H), 2.69 (dd, *J* = 14.5, 1.9 Hz, 2H), 2.64–2.53 (m, 1H), 2.37-2.26 (m, 1H) 1.78 (ddd, *J* = 10.1, 7.2, 2.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ215.1, 158.2, 145.0, 141.8, 131.0, 129.2, 128.3, 127.6, 126.4, 116.8, 113.6, 68.9, 55.1, 43.6, 40.3, 39.8; IR (Neat Film, NaCl) 3080, 2913, 2835, 1770, 1611, 1513, 1248, 1179, 1035, 907 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{21}H_{22}O_2$ $[M]^+$: 306.1620; found 306.1614; $[\alpha]_D^{26.0}$ –0.60 (*c* 1.00, $CHCl_3$, 95% ee).

(*R*)-2-Allyl-2-(2-phenylallyl)cyclobutanone (5f)



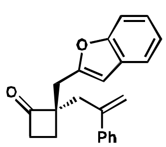
Cyclobutanone **5f** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 4% EtOAc in hexanes) as a colorless oil. 86% yield. R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.25 (m, 5H), 5.84–5.71 (m, 1H), 5.37 (d, *J* = 1.5 Hz, 1H), 5.14 (d, *J* = 1.0 Hz, 1H), 5.15–5.05 (m, 2H), 2.91, 2.70 (AB system, J_{AB} = 14.4 Hz, 2H), 2.87–2.65 (m, 2H), 2.36 (ddt, *J* = 13.9, 7.1, 1.2 Hz, 1H), 2.27 (ddt, *J* = 13.9, 7.6, 1.1 Hz, 1H), 1.85 (ddd, *J* = 11.7, 10.4, 6.8 Hz, 1H), 1.77–1.64 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.5, 145.1, 141.8, 133.3, 128.3, 128.3, 126.5, 118.7, 116.9, 67.5, 43.3, 39.7, 39.1, 20.3; IR (Neat Film, NaCl) 3078, 2921, 1774, 1625, 1493, 1443, 1387, 1059, 1000, 908, 779 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{19}O$ [M+H]$^+$: 227.1430; found 227.1418; α_D^{25} –13.98 (*c* 0.51, $CHCl_3$, 92% ee).

(*S*)-2-(2-Phenylallyl)-2-[3-(trimethylsilyl)prop-2-yn-1-yl]cyclobutanone (5g)



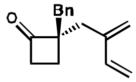
Cyclobutanone **5g** was isolated by flash column chromatography (SiO_2, 1% EtOAc in hexanes to 3% EtOAc in hexanes) as a colorless oil. 90% yield. R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.08 (m, 5H), 5.37 (d, *J* = 1.4 Hz, 1H), 5.13 (d, *J* = 1.1 Hz, 1H), 2.93–2.86 (m, 2H), 2.82–2.75 (m, 2H), 2.42, 2.37 (AB system, J_{AB} = 17.0 Hz, 2H), 1.96–1.85 (m, 2H) 0.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.6, 144.5, 141.4, 128.4, 127.7, 126.4, 116.9, 102.7, 87.2, 66.6, 43.9, 38.9, 25.8, 20.9, 0.0; IR (Neat Film, NaCl) 2957, 2169, 1776, 1713, 1444, 1249, 1177, 1061, 1031, 834, 760 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{25}OSi$ [M+H]$^+$: 297.1681; found 297.1683; $[\alpha]_D^{25}$ +10.76 (*c* 0.29, $CHCl_3$, 93% ee).

(S)-2-(Benzofuran-2-ylmethyl)-2-(2-phenylallyl)cyclobutanone (5h)



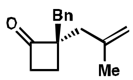
Cyclobutanone **5h** was isolated by flash column chromatography (SiO_2, hexanes to 10% EtOAc in hexanes) as a colorless oil. 82% yield. R_f = 0.5 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.42–7.40 (m, 1H), 7.38–7.36 (m, 2H), 7.33–7.28 (m, 3H), 7.25–7.18 (m, 2H), 6.44 (s, 1H), 5.40 (d, *J* = 1.34 Hz, 1H), 5.17 (m, 1H), 3.07 (d, *J* = 15.2 Hz, 1H), 2.98 (dd, *J* = 14.3, 0.9 Hz, 1H), 2.96 (d, *J* = 15.0 Hz, 1H), 2.82 (d, *J* = 14.3 Hz, 1H), 2.79–2.64 (m, 2H), 1.96–1.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.2, 155.0, 154.7, 144.7, 141.6, 128.5, 128.4, 127.8, 126.4, 123.6, 122.6, 120.5, 117.2, 110.9, 105.0, 67.2, 43.8, 39.6, 33.7, 20.9; IR (Neat Film, NaCl) 3054, 2917, 2849, 1770, 1598, 1585, 1453, 1251, 1104, 1061, 905 cm^{-1}; HRMS (MM ESI-APCI) *m/z* calc'd for $C_{22}H_{21}O_2$ [M+H]$^+$: 317.1536; found 317.1530; $[\alpha]_D^{26}$ +56.4 (*c* 1.00, $CHCl_3$, 92% ee).

(*S*)-2-Benzyl-2-(2-methylenebut-3-en-1-yl)cyclobutanone (5i)



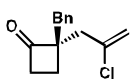
Cyclobutanone **5i** was isolated by flash column chromatography (SiO_2, hexanes to 5% Et_2O in hexanes) as a colorless oil. 92% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 7.25–7.20 (m, 2H), 7.19–7.12 (m, 1H), 6.59–6.19 (m, 1H), 5.24–5.06 (m, 2H), 5.05 (s, 2H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.80 (d, *J* = 13.6 Hz, 1H), 2.68 (ddd, *J* = 18.1, 10.3, 6.8 Hz, 1H), 2.57 (dd, *J* = 14.4, 1.0 Hz, 1H), 2.45 (ddd, *J* = 18.1, 10.3, 6.9 Hz, 1H), 2.40 (d, *J* = 14.4 Hz, 1H), 1.95 (qdd, *J* = 11.6, 10.2, 6.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 142.4, 139.4, 137.3, 130.1, 128.3, 126.6, 119.2, 114.5, 68.6, 43.9, 41.4, 35.5, 20.2; IR (Neat Film, NaCl) 3022, 2921, 2843, 1768, 1590, 1493, 1452, 1384, 1065, 989, 898, 755 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{18}O$ $[M+H]^+$: 227.1430; found 227.1433; $[\alpha]_D^{25}$ +0.44 (*c* 1.60, $CHCl_3$, 91% ee).

(*S*)-2-Benzyl-2-(2-methylallyl)cyclobutanone (5j)



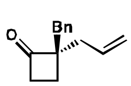
Cyclobutanone **5j** was isolated by flash column chromatography (SiO_2, 2% Et_2O in hexanes to 5% Et_2O in hexanes) as a colorless oil. 82% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.12 (m, 5H), 4.91 (t, *J* = 1.7 Hz, 1H), 4.78 (dd, *J* = 2.0 Hz, 1.0, 1H), 2.88, 2.65 (AB system, J_{AB} = 13.7 Hz, 2H), 2.77 (ddd, *J* = 18.1, 9.6, 6.9 Hz, 1H), 2.43–2.33 (m, 1H), 2.33, 2.22 (AB system, J_{AB} = 14.2 Hz, 2H), 1.97 (ddd, *J* = 9.4, 7.2, 3.1, 2H), 1.80–1.72 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.3, 141.8, 137.4, 130.1, 128.3, 126.5, 114.8, 68.2, 43.6, 43.2, 40.6, 24.0, 20.7; IR (Neat Film, NaCl) 3072, 3027, 2964, 2919, 1772, 1322, 1131, 1062, 894 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{18}O$ $[M]^+$: 214.1358, found 214.1346; $[\alpha]_D^{26}$ –2.4° (*c* 0.48, $CHCl_3$, 90% ee).

(*R*)-2-Benzyl-2-(2-chloroallyl)cyclobutanone (5k)



Cyclobutanone **5k** was isolated by flash column chromatography (SiO_2, hexanes to 3% EtOAc in hexanes) as a colorless oil. 67% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.21 (m, 3H), 7.18–7.15 (m, 2H), 5.33 (d, *J* = 1.3 Hz, 1H), 5.22–5.21 (m, 1H), 2.97 (d, *J* = 13.7 Hz, 1H), 2.90–2.76 (m, 1H), 2.82 (d, *J* = 13.7 Hz, 1H), 2.74 (dd, *J* = 14.7, 1.0 Hz, 1H), 2.59 (d, *J* = 14.7 Hz, 1H), 2.43 (ddd, *J* = 18.1, 10.8, 7.3 Hz, 1H), 2.19 (ddd, *J* = 11.8, 10.2, 7.2 Hz, 1H), 2.04 (ddd, *J* = 11.8, 10.8, 6.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.7, 138.4, 136.7, 130.1, 128.4, 126.8, 116.4, 67.5, 44.1, 43.8, 40.5, 20.7; IR (Neat Film, NaCl) 3028, 2919, 2848, 1772, 1631, 1494, 1453, 1063, 888 cm^{-1}; HRMS (MM ESI-APCI) *m/z* calc'd for $C_{14}H_{16}{}^{35}ClO$ $[M+H]^+$: 235.0884; found 235.0883; $[\alpha]_D^{26}$ +1.51 (*c* 0.56, $CHCl_3$, 94% ee).

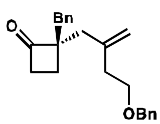
(*S*)-2-Allyl-2-benzylcyclobutanone (5l)



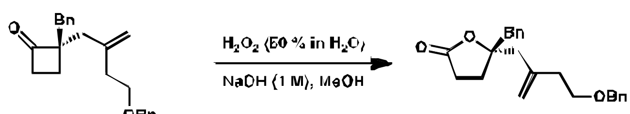
Cyclobutanone **5l** was isolated by flash column chromatography (SiO_2, 2% Et_2O in hexanes to 5% Et_2O in hexanes) as a colorless oil. 82% yield. R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR

(500 MHz, $CDCl_3$) δ7.30–7.27 (m, 2H), 7.24–7.21 (m, 1H), 7.16–7.15 (m, 2H), 5.81 (ddt, *J* = 17.2, 10.0, 7.4 Hz, 1H), 5.16–5.10 (m, 2H), 2.97 (d, *J* = 13.7 Hz, 1H), 2.78 (ddd, *J* = 18.2, 10.3, 6.5 Hz, 1H), 2.72 (d, *J* = 13.7 Hz, 1H), 2.49 (ddd, *J* = 18.2, 10.6, 6.8 Hz, 1H), 2.39 (ddt, *J* = 13.9, 7.4, 1.1 Hz, 1H), 2.67 (ddt, *J* = 13.9, 7.4, 1.1 Hz, 1H), 1.94 (ddd, *J* = 11.5, 10.6, 6.5 Hz, 1H), 1.86 (ddd, *J* = 11.5, 10.3, 6.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ214.9, 137.3, 133.2, 130.0, 128.3, 126.5, 118.7, 68.4, 42.9, 40.3, 39.5, 19.8; IR (Neat Film, NaCl) 3029, 2918, 1771, 1495, 1437, 1454, 1076, 920 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{16}O$ [M]$^+$: 200.1201; found 200.1199; $[\alpha]_D^{26}$ +4.69 (*c* 0.55, $CHCl_3$, 88% ee).

(*S*)-2-Benzyl-2-[4-(benzyloxy)-2-methylenebutyl]cyclobutanone (5m)



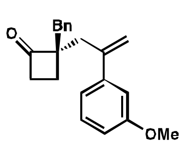
Cyclobutanone **5m** was isolated by flash column chromatography (SiO_2, 1% EtOAc in hexanes to 3% EtOAc in hexanes) as a colorless oil (95% yield). R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.12 (m, 10H), 5.01 (q, *J* = 1.4 Hz, 1H), 4.93–4.92 (m, 1H), 4.54 (s, 2H), 3.59 (td, *J* = 6.8, 0.7, 2H), 2.95, 2.73 (AB system, J_{AB} = 13.7, 2H), 2.83–2.71 (m, 1H), 2.51–2.27 (m, 5H), 2.04–1.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 142.6, 138.4, 137.4, 130.1, 128.4, 128.3, 127.7, 127.6, 126.5, 115.1, 72.9, 68.7, 68.3, 43.6, 41.5, 40.6, 37.0, 20.7; IR (Neat Film, NaCl) 3022, 2923, 2853, 1768, 1641, 1494, 1452, 1360, 1099, 899, 735 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{27}O_2$ [M+H]$^+$: 335.2006; found 335.2020;



5m *SI3*

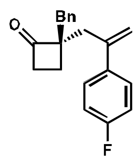
Enantiomeric excess determined for the corresponding Baeyer-Villiger product, which was obtained by general procedure below. Lactone **SI3** was isolated by flash column chromatography (SiO_2, 4% EtOAc in hexanes) as a colorless oil (93% yield). R_f = 0.2 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.18 (m, 10H), 5.09 (q, *J* = 1.5 Hz, 1H), 4.98 (dd, *J* = 1.7, 0.9 Hz, 1H), 4.51 (s, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 3.09 (d, *J* = 14.1 Hz, 1H), 2.75 (d, *J* = 14.1 Hz, 1H), 2.61–2.38 (m, 4H), 2.23 (ddd, *J* = 17.6, 9.4, 5.9 Hz, 1H), 2.17–2.03 (m, 2H), 1.68 (ddd, *J* = 17.6, 10.0, 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 141.8, 138.4, 135.5, 130.5, 128.5, 128.3, 127.7, 127.5, 127.1, 117.1, 87.8, 72.8, 68.5, 46.7, 45.6, 37.0, 29.3, 29.2; IR (Neat Film, NaCl) 3524, 3062, 3029, 2919, 2855, 1958, 1770, 1642, 1603, 1495, 1454, 1416, 1361, 1271, 1232, 1177, 1101, 1080, 1029, 932, 741 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{27}O_3$ [M+H]$^+$: 351.1955; found 351.1951; α_D^{25} +21.17 (*c* 0.44, $CHCl_3$, 89% ee).

(*R*)-2-Benzyl-2-(2-[3-methoxyphenyl]allyl)cyclobutanone (5n)



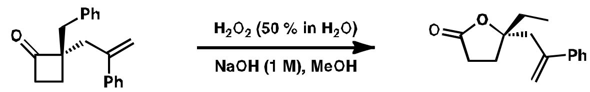
Cyclobutanone **5n** was isolated by flash column chromatography (SiO_2, 1% EtOAc in hexanes to 3% EtOAc in hexanes) as a colorless oil. 91% yield. R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.19 (m, 4H), 7.19–7.10 (m, 2H), 6.98 (ddd, *J* = 7.7, 1.7, 0.9 Hz, 1H), 6.91 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.85 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.17 (q, *J* = 1.1 Hz, 1H), 3.83 (s, 3H), 3.03–2.86 (m, 2H), 2.86–2.68 (m, 2H), 2.63 (ddd, *J* = 18.1, 9.7, 7.1 Hz, 1H), 2.35 (ddd, *J* = 18.1, 10.1, 7.4 Hz, 1H), 1.96–1.72 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.0, 159.6, 144.9, 143.5, 137.3, 130.1, 129.4, 128.4, 126.6, 119.0, 117.1, 112.9, 112.4, 68.9, 55.3, 43.8, 41.2, 40.0, 20.0; IR (Neat Film, NaCl) 2913, 2829, 1766, 1595, 1572, 1488, 1451, 1286, 1221, 1170, 1039, 898, 873, 779 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{23}O_2$ $[M+H]^+$: 307.1693; found 307.1693; α_D^{25} –4.78 (*c* 0.45, $CHCl_3$, 92% ee).

(*R*)-2-Benzyl-2-(2-(4-fluorophenyl)allyl)cyclobutanone (5o)



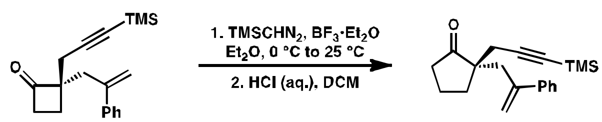
Cyclobutanone **5o** was isolated by flash column chromatography (SiO_2, 3% EtOAc in hexanes to 7% EtOAc in hexanes) as a colorless oil. 94% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.12 (m, 5H), 7.05–7.03 (m, 2H), 6.95–6.90 (m, 2H), 5.25 (d, *J* = 1.3 Hz, 1H), 5.05 (s, 1H), 2.88 (d, *J* = 13.7 Hz, 1H), 2.82 (dd, *J* = 14.4, 1.0 Hz, 1H), 2.66 (d, *J* = 13.7 Hz, 1H), 2.59 (d, *J* = 14.4 Hz, 1H), 2.54–2.47 (m, 1H), 2.29–2.22 (m, 1H), 1.73 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.6, 162.3 (d, $^1J_{CF}$ = 246.8 Hz), 144.0, 137.8 (d, $^4J_{CF}$ = 3.3 Hz), 137.1, 130.0, 128.3, 128.0 (d, $^3J_{CF}$ = 7.9 Hz), 126.6, 116.9, 115.2 (d, $^2J_{CF}$ = 21.3 Hz), 68.6, 43.7, 41.2, 40.5, 20.0; IR (Neat Film, NaCl) 2913, 1766, 1597, 1505, 1219, 1055, 837 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{20}{}^{19}FO$ $[M+H]^+$: 295.1493; found 295.1502; $[\alpha]_D^{25}$ +3.53 (*c* 0.16, $CHCl_3$, 94% ee).

Procedures for Derivatization of α-Quaternary Cyclobutanones and Absolute Configuration Determination



5c *6*

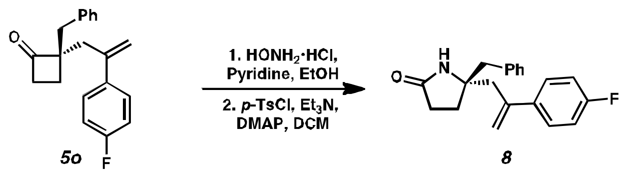
(*R*)-5-Benzyl-5-(2-phenylallyl)dihydrofuran-2(3*H*)-one (6). To a stirred solution of cyclobutanone **5c** (43 mg, 0.23 mmol) in MeOH (4.6 mL) was added NaOH (1 M in H_2O, 0.23 μL, 0.23 mmol) followed by H_2O_2 (50 wt% in H_2O, 17 mg, 0.46 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was then acidified to pH 7 with 1 N aqueous HCl and extracted with dichloromethane (2 mL x 5). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (SiO_2, 15% EtOAc in hexanes) to afford lactone **6** (37 mg, 0.17 mmol, 80% yield) as a colorless oil. R_f = 0.2 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.41–7.18 (m, 10H), 5.46 (d, *J* = 1.4 Hz, 1H), 5.27 (s, 1H), 3.08–2.92 (m, 3H), 2.79 (d, *J* = 14.1 Hz, 1H), 2.17 (ddd, *J* = 17.4, 9.8, 6.4 Hz, 1H), 2.04–1.86 (m, 2H), 1.76–1.62 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ176.7, 143.4, 141.7, 135.4, 130.6, 128.6, 128.5, 127.8, 127.0, 126.3, 119.2, 87.7, 46.1, 45.3, 29.3, 28.8; IR (Neat Film, NaCl) 3029, 2918, 1771, 1495, 1437, 1454, 1076, 920 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{21}O_2$ $[M+H]^+$: 293.1536; found 293.1536; $[\alpha]_D^{26}$ –0.60 (*c* 1.00, $CHCl_3$, 89% ee).



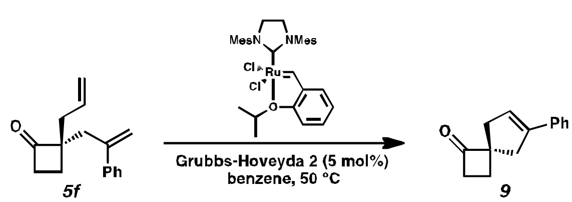
5g *7*

(*S*)-2-(2-Phenylallyl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)cyclopentanone (7). To a solution of **5g** (0.1023 g, 0.345 mmol) in Et_2O (3.5 mL), cooled to 0 °C with a water/ice bath, under an atmosphere of N_2, was added BF_3 etherate (0.112 mL, 0.379 mmol) dropwise followed by trimethylsilyldiazomethane (0.345 mL, 2 M solution in hexane) dropwise. The mixture was allowed to warm to 25 °C and stirred for 18 hours, at which point the reaction was determined to be complete by TLC analysis. To the mixture was added 3 mL of saturated aqueous $NaHCO_3$. After stirring for 30 minutes, this mixture was extracted with Et_2O (5 mL x 3), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 1% EtOAc in hexanes to 5% EtOAc in hexanes) to afford trimethylsilylcyclopentanone **SI4** as a colorless oil. The identity of the α-trimethylsilylcyclopentanone **SI4** was confirmed by NMR analysis; the product was taken on without further characterization. R_f = 0.3 (10% EtOAc in hexanes); To a solution of trimethylsilylcyclopentanone **SI4** (61 mg, 0.159 mmol) in 2 ml dichloromethane was added 2 mL of 1 N aqueous HCl in H_2O at 25 °C. The mixture was stirred for 24 hours at which point the reaction was determined to be complete by TLC analysis. The mixture was diluted with dichloromethane (2 ml) and then extracted with dichloromethane (5 mL x 3). The collected organic layers were then washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (SiO_2, hexanes to 1% EtOAc in hexanes) to afford cyclopentanone **7** (47 mg, 0.153 mmol, 69% yield over two steps) as a colorless oil. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.12 (m, 5H), 5.32 (d, *J* = 1.6 Hz, 1H), 5.14–4.97 (m, 1H), 2.83–2.73 (m, 2H), 2.22 (dd, *J* = 16.9, 38.9 Hz, 2H), 2.16–2.08 (m, 1H), 2.03–1.91 (m, 2H), 1.89–1.71 (m, 3H), 0.14

(s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 145.1, 141.6, 128.3, 127.6, 126.5, 117.4, 103.7, 87.1, 52.2, 39.8, 38.4, 31.4, 27.4, 18.7, 0.0; IR (Neat Film, NaCl) 3080, 2958, 1738, 1623, 1494, 1447, 1404, 1308, 1249, 1154, 1046, 1029, 973, 904, 841, 778, 759 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{20}H_{26}OSi$ $[M]^+$: 310.1753; found 310.1765; $[\alpha]_D^{25}$ +4.13 (*c* 0.50, $CHCl_3$, 93% ee).

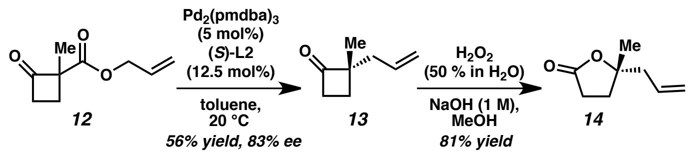


(*R*)-5-Allyl-5-(2-phenylallyl)pyrrolidin-2-one (8). To a solution of cyclobutanone **5o** (65 mg, 0.221 mmol) in 7 mL absolute ethanol was added hydroxylamine hydrochloride (76 mg, 1.104 mmol), followed by pyridine (0.27 ml, 3.31 mmol) and the mixture was stirred at 25 °C for 24 hours. The crude mixture was concentrated *in vacuo* and loaded directly onto a flash column. Flash column chromatography (SiO_2, 8% EtOAc in hexanes to 11% EtOAc in hexanes) afforded the corresponding oxime **SI5**, whose identity was confirmed by ^{1}H NMR and which was taken on without further characterization; R_f = 0.2 (25% EtOAc in hexanes); To a mixture of 4-toluenesulfonyl chloride (83 mg, 0.43 mmol), triethylamine (0.06 mL, 0.43 mmol) and catalytic 4-dimethylaminopyridine in 2.5 mL of dichloromethane under an atmosphere of N_2 was added dropwise a solution of oxime **SI4** (54 mg, 0.175 mmol) in 1 mL of dichloromethane. The mixture was stirred at 25 °C for 4 hours. The crude mixture was washed with H_2O (5 mL), washed with brine (5 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (SiO_2, 3% EtOAc in hexanes to EtOAc) to afford lactam **8** (16 mg, 0.05 mmol, 22% yield over two steps) as a pale yellow oil. R_f = 0.4 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.07 (m, 7H), 7.07–6.96 (m, 2H), 5.35 (d, *J* = 1.3 Hz, 1H), 5.26 (s, 1H), 5.15 (q, *J* = 1.0 Hz, 1H), 2.87–2.63 (m, 4H), 2.06–1.85 (m, 3H), 1.69–1.55 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 176.9, 162.4 (d, $^1J_{CF}$ = 247.4 Hz), 143.7, 138.0 (d, $^4J_{CF}$ = 3.4 Hz), 136.1, 130.3, 128.5, 127.8 (d, $^3J_{CF}$ = 8.0 Hz), 127.0, 118.6, 115.7 (d, $^2J_{CF}$ = 21.4 Hz), 62.0, 47.0, 46.5, 30.9, 30.1; IR (Neat Film, NaCl) 3196, 3081, 2927, 1690, 1601, 1507, 1452, 1260, 1224, 1159, 1087, 906, 842, 750 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{20}H_{20}ONF$ $[M]^+$: 309.1529; found 309.1517; $[\alpha]_D^{25}$ +53.19 (*c* 0.08, $CHCl_3$, 94% ee).



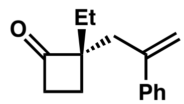
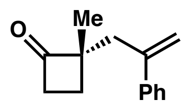
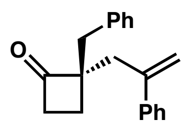
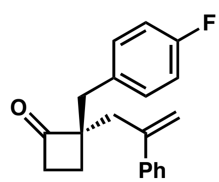
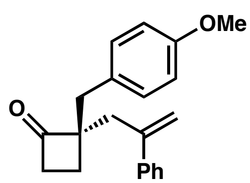
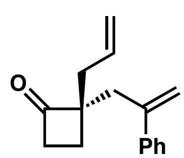
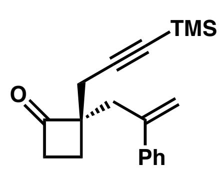
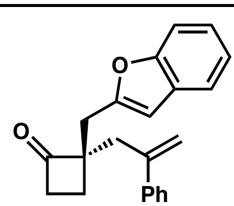
(*R*)-6-phenylspiro[3.4]oct-6-en-1-one (9). To a flask charged with Grubbs-Hoveyda an atmosphere of argon was added a solution of cyclobutanone **5f** (50 mg, 0.221 mmol) in 5 mL benzene. The reaction mixture was heated to 50 °C and stirred for one hour, at which point the reaction was determined to be complete by TLC analysis. The reaction vessel was cooled to 25 °C and 1 mL of ethyl vinyl ether was added. After 30 minutes of stirring, the crude mixture was purified directly by flash column chromatography (SiO_2, hexanes to 3% EtOAc in hexanes) to afford spirocycle **9** (43 mg, 0.215 mmol, 97% yield) as a colorless oil. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.32–7.21 (m, 2H), 7.24–7.15 (m, 1H), 5.97 (p, *J* = 2.4 Hz, 1H), 3.19 (dq, *J* = 16.0, 2.2 Hz, 1H), 3.04 (t, *J* = 8.61 Hz, 2H), 3.04–

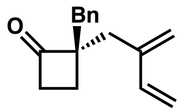
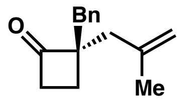
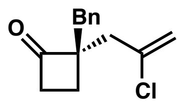
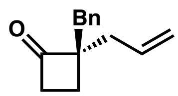
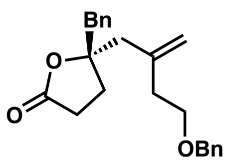
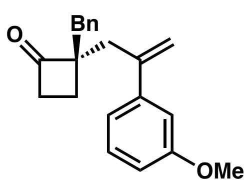
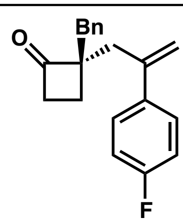
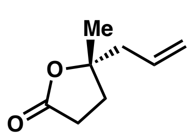
2.97 (m, 1H), 2.81 (dq, *J* = 16.0, 1.7 Hz, 1H), 2.63 (dtd, *J* = 17.5, 2.5, 1.4 Hz, 1H), 2.09 (td, *J* = 8.9, 2.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.1, 140.0, 135.6, 128.4, 127.3, 125.6, 122.9, 67.9, 43.6, 43.1, 42.8, 28.3; IR (Neat Film, NaCl) 2890, 2924, 1765, 1595, 1491, 1385, 1298, 1241, 1056, 747 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{14}H_{15}O$ $[M+H]^+$: 199.1117; found 199.1120; $[\alpha]_D^{25}$ –41.23 (*c* 0.30, $CHCl_3$, 92% ee).



(*S*)-5-allyl-5-methyldihydrofuran-2(3*H*)-one (14). Dihydrofuranone **14** was generated from 2-Carboxyallylcyclobutanone **12**, via cyclobutanone **13**, following the general procedures described above (see SI 3, SI 10 and SI 16). When compared with known compound (5*S*)-(+)-5-allyl-5-methyldihydrofuran-2(3*H*)-one, the optical rotation value for **14** was found to be of the same sign and of nearly identical magnitude ($[\alpha]_D^{25}$ +2.96 (c 1.5, CH_3OH), literature value: $[\alpha]_D^{17}$ +3.33 (c 1.27, CH_3OH)).[7] The absolute configurations of all other compounds described herein were established by analogy to **13**. Cyclobutanone **12** was isolated by flash column chromatography (SiO_2, 3% Et_2O in pentane to 7% Et_2O in pentane) as a colorless oil. 84% yield. R_f = 0.4 (15% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.38–5.14 (m, 2H), 4.63 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.42–3.06 (m, 2H), 2.65 (td, *J* = 11.3, 6.3 Hz, 1H), 1.88 (ddd, *J* = 11.6, 9.9, 7.5 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 169.8, 131.6, 118.4, 65.9, 45.2, 23.1, 18.6; IR (Neat Film, NaCl) 2933, 1792, 1730, 1457, 1376, 1274, 1193, 1147, 1050, 983 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_9H_{12}O_2$ $[M+H]^+$: 153.0910; found 153.0905. Cyclobutanone **13** was isolated by flash column chromatography (SiO_2, 1% Et_2O in pentane to 5% Et_2O in pentane) as a colorless oil. 56% yield. R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.6, 10.5, 7.3 Hz, 1H), 5.14–5.05 (m, 2H), 3.08–2.89 (m, 2H), 2.31 (ddt, *J* = 13.8, 7.2, 1.2 Hz, 1H), 2.21 (ddt, *J* = 13.8, 7.5, 1.1 Hz, 1H), 1.98 (ddd, *J* = 11.3, 10.3, 6.7 Hz, 1H), 1.73 (ddd, *J* = 11.3, 10.1, 6.9 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.1, 140.0, 135.6, 128.4, 127.3, 125.6, 122.9, 67.9, 43.6, 43.1, 42.8, 28.3; IR (Neat Film, NaCl) 2929, 2854, 1728, 1323, 1261, 1170, 1129, 1060, 1019, 799 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_8H_{12}O$ $[M+H]^+$: 125.0961; found 125.0955. Enantiomeric excess was determined for the corresponding Baeyer-Villiger product **14**, which was isolated as by flash column chromatography (SiO_2, 10% Et_2O in pentane) as a colorless oil (81% yield). Spectroscopic and physical data for **14** were identical to those reported in the literature.[7] ($[\alpha]_D^{25}$ +2.96 (c 1.5, CH_3OH), 83% ee).

Determination of Enantiomeric Excess

entry	compound	assay method and conditions	retention time of major isomer (min)	retention time of minor isomer (min)	%ee
1		SFC, 10% MeOH in CO_2, 2.5 mL/min, AS-H col.	5.31	6.02	*99*
2		SFC, 3% MeOH in CO_2, 2.5 mL/min, AS-H col.	2.68	3.08	*90*
3		SFC, 3% MeOH in CO_2, 3 mL/min, OJ-H col.	8.91	7.93	*95*
4		SFC, 2% MeOH in CO_2, 3 mL/min, OJ-H col.	10.43	11.45	*93*
5		SFC, 2% MeOH in CO_2, 2.5 mL/min, AS-H col.	8.82	8.38	*97*
6		SFC, 1% MeOH in CO_2 2.5 mL/min, AS-H col.	3.37	3.15	*92*
7		SFC, 2% MeOH in CO_2 3.0 mL/min, OJ-H col.	2.68	4.32	*93*
8		HPLC, 2% *i*PrOH in hexanes, 0.6 mL/min, AD col.	9.74	8.94	*92*

entry	compound	assay method and conditions	retention time of major isomer (min)	retention time of minor isomer (min)	%ee
9		SFC, 1% MeOH in CO_2 2.5 mL/min, OB-H col.	3.40	2.83	*91*
10		SFC, 1% MeOH in CO_2, 3 mL/min, OB-H col.	2.76	2.53	*90*
11		GC, 110 °C, isotherm 1 mL/min, GTA col.	10.41	11.34	*93*
12		SFC, 1% MeOH in CO_2, 2.5 mL/min, OB-H col.	3.38	2.93	*86*
13		SFC, 10% MeOH in CO_2, 3.0 mL/min, AD-H col.	6.09	7.29	*89*
14		SFC, 1% MeOH in CO_2, 2.5 mL/min, AS-H col.	16.17	14.84	*92*
15		SFC, 1% MeOH in CO_2, 3 mL/min, AS-H col.	7.29	6.78	*94*
16		GC, 130 °C, isotherm 1 mL/min, GTA col.	10.15	13.32	*83*

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[i] H. M. L. Davies, W. R. Cantrell, Jr., K. R. Romines, J. S. Baum, *Org. Syn.* **1992***, 70, 93–97*.

[2] C. Hollingworth, A. Hazari, M. N. Hopkinson, M. Tredwell, E. Benedetto, M. Huiban, A. D. Gee, J. M. Brown, V. Gouverneur, *Angew. Chem. Int. Ed.* **2011**, *50*, 2613–2617.

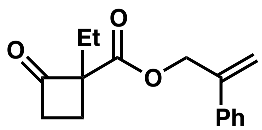
[3] M. Presset, D. Mailhol, Y. Coquerel, J. Rodriguez, *Synthesis* **2011**, 2549–2552.

[4] (a) D. C. Behenna, B. M. Stoltz, *J. Am. Chem. Soc.* **2004**, *126*, 15044–15045. (b) K. Tani, D. C. Behenna, R. M. McFadden, B. M. Stoltz, *Org. Lett.* **2007**, *9*, 2529–2531. (c) Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 181–193.

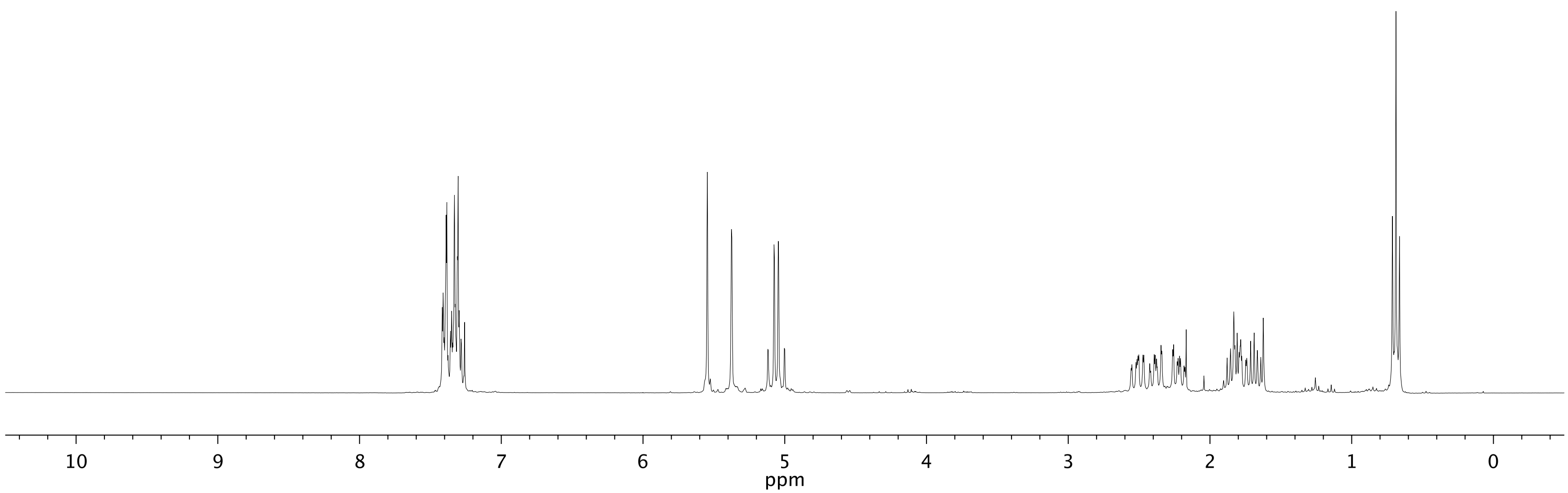
[5] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organometallic Chem.* **1999**, *65*, 253–266.

[6] I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, *Org. Lett.* **2004**, *6*, 4435–4438.

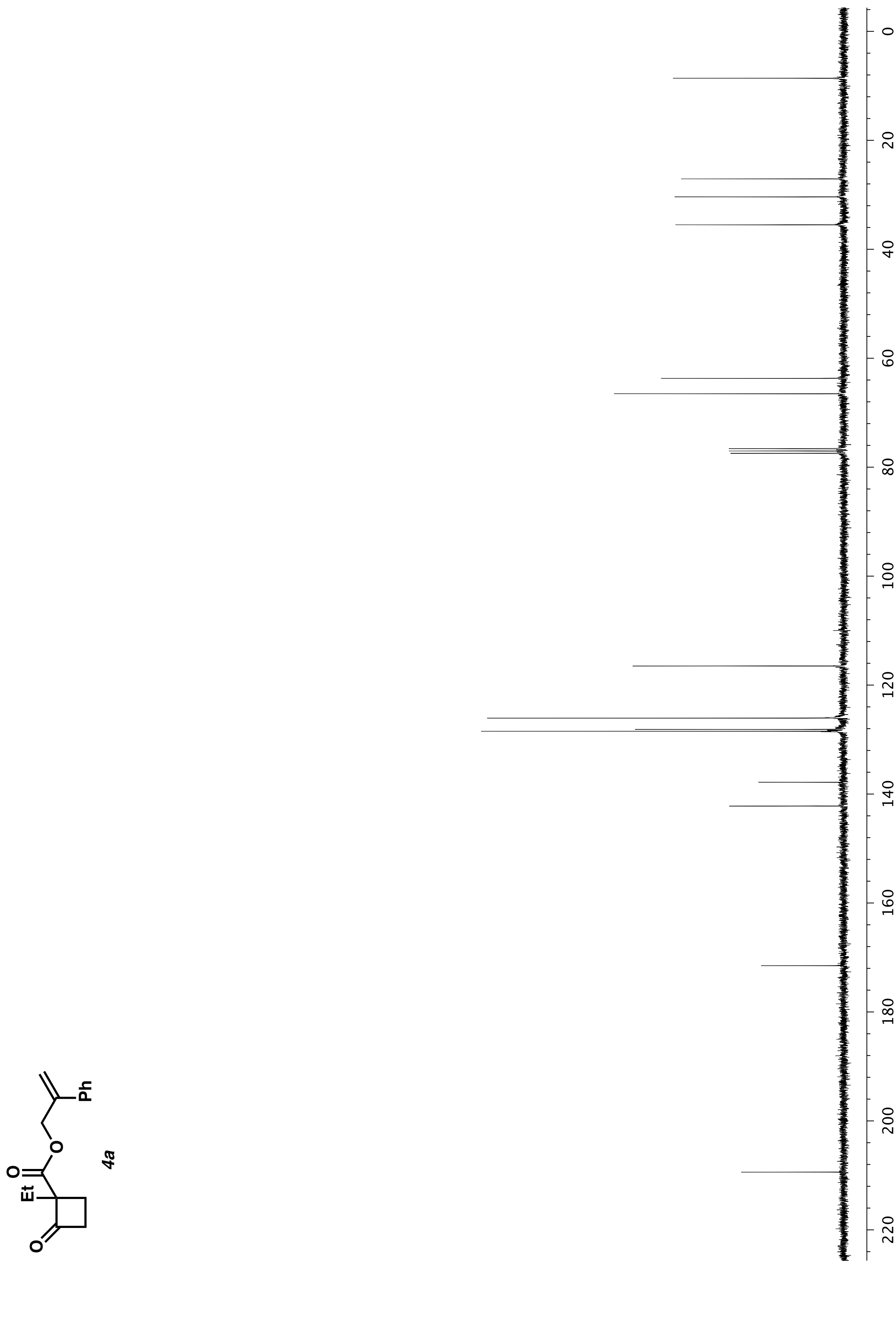
[7] K. Matsuo, T. Arase, S. Ishida, Y Sakaguchi, *Heterocycles*, **1996**, *43*, 1287–1300.



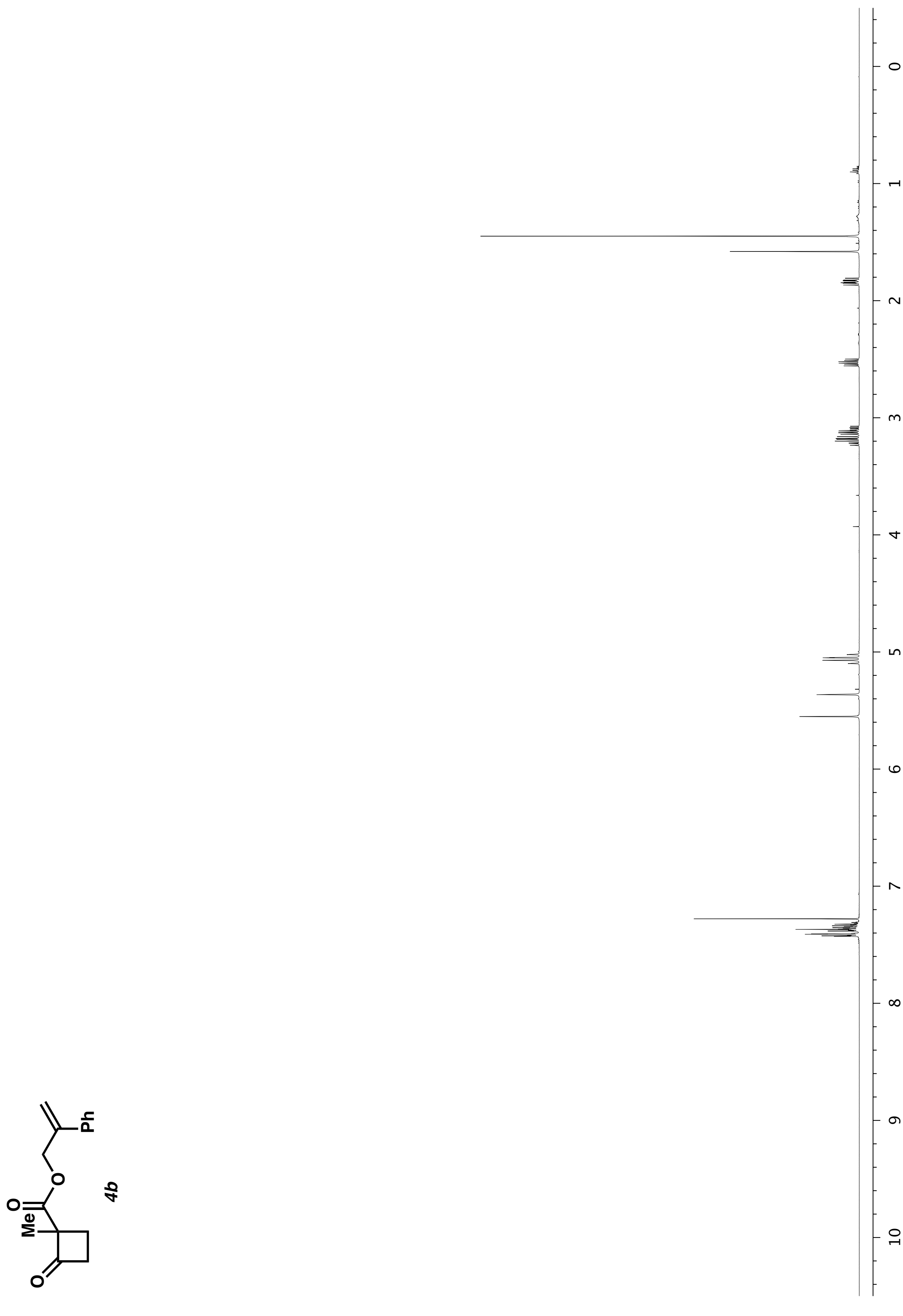
4a



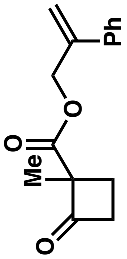
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**.



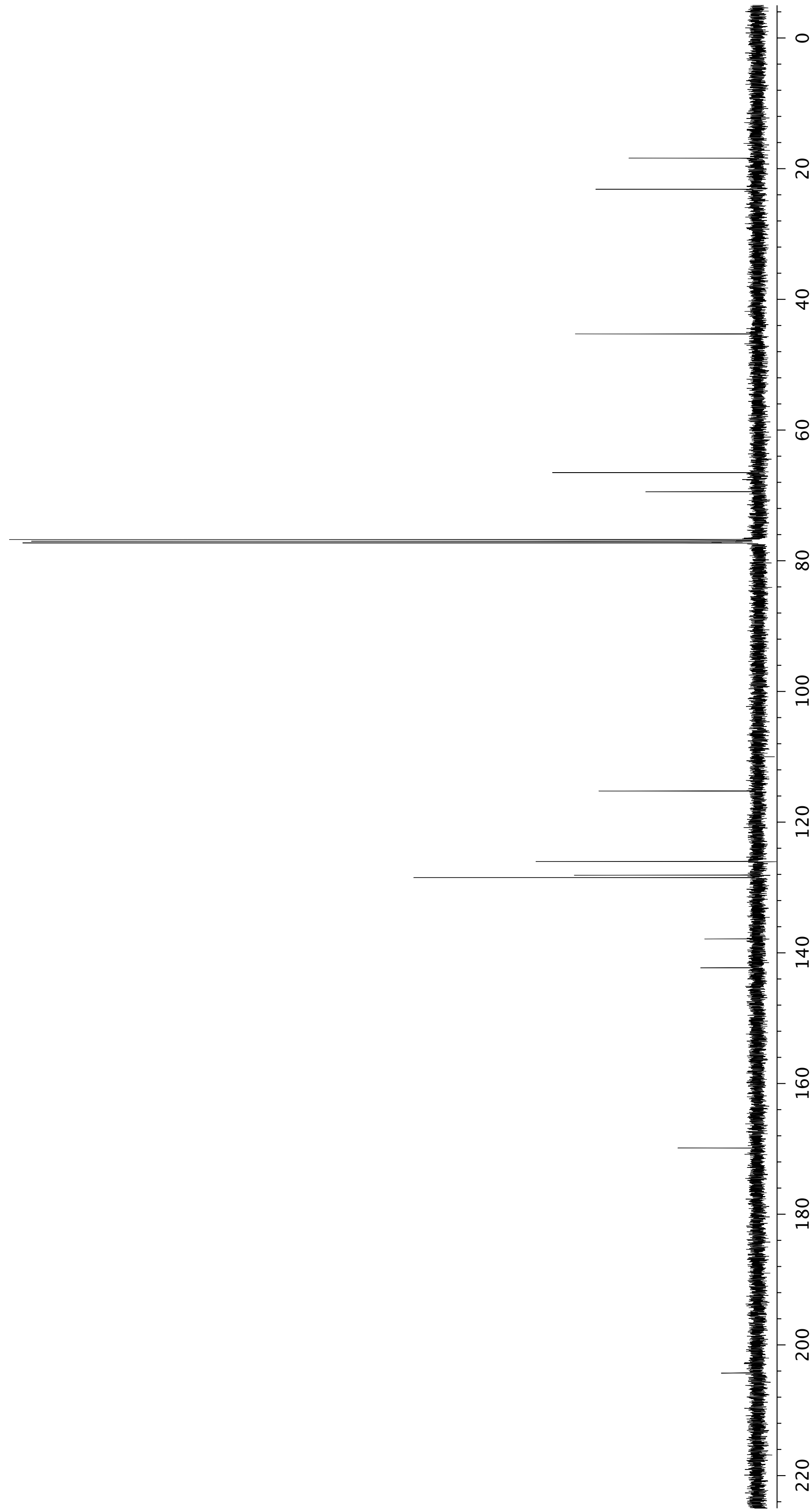
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a**.



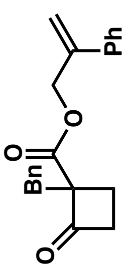
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**.



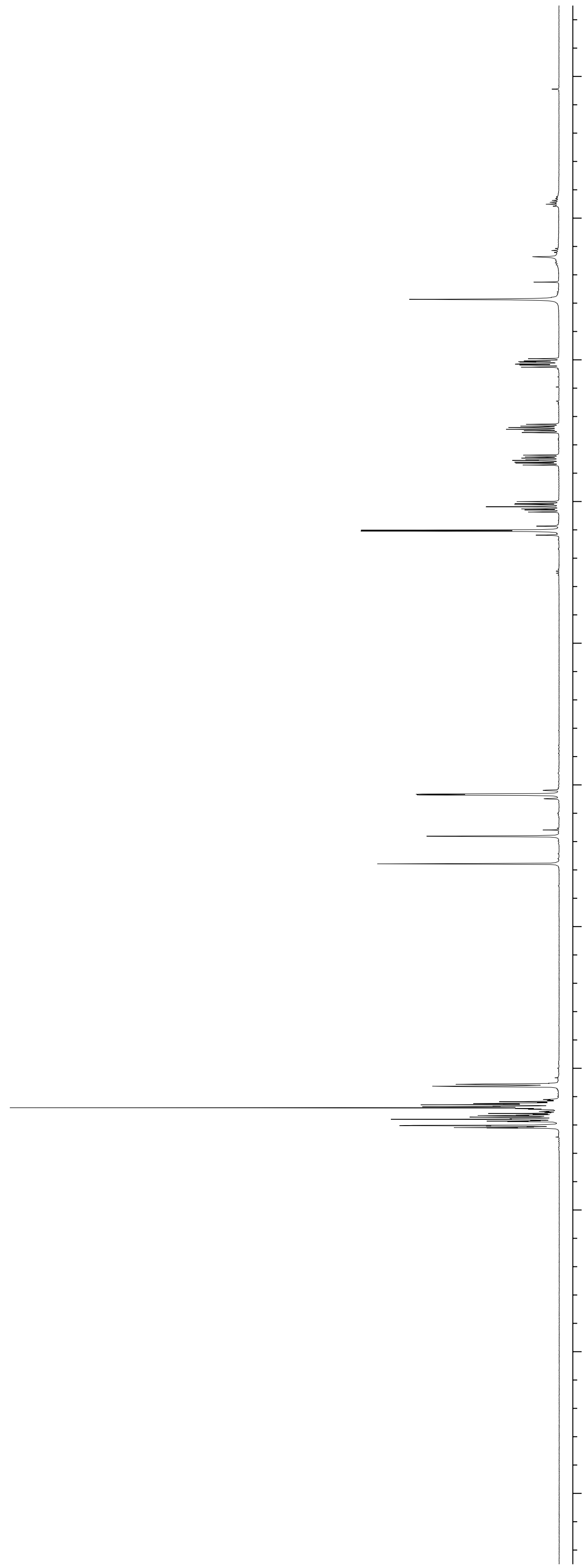
4b



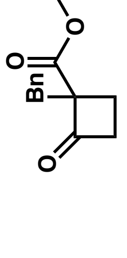
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4b**.



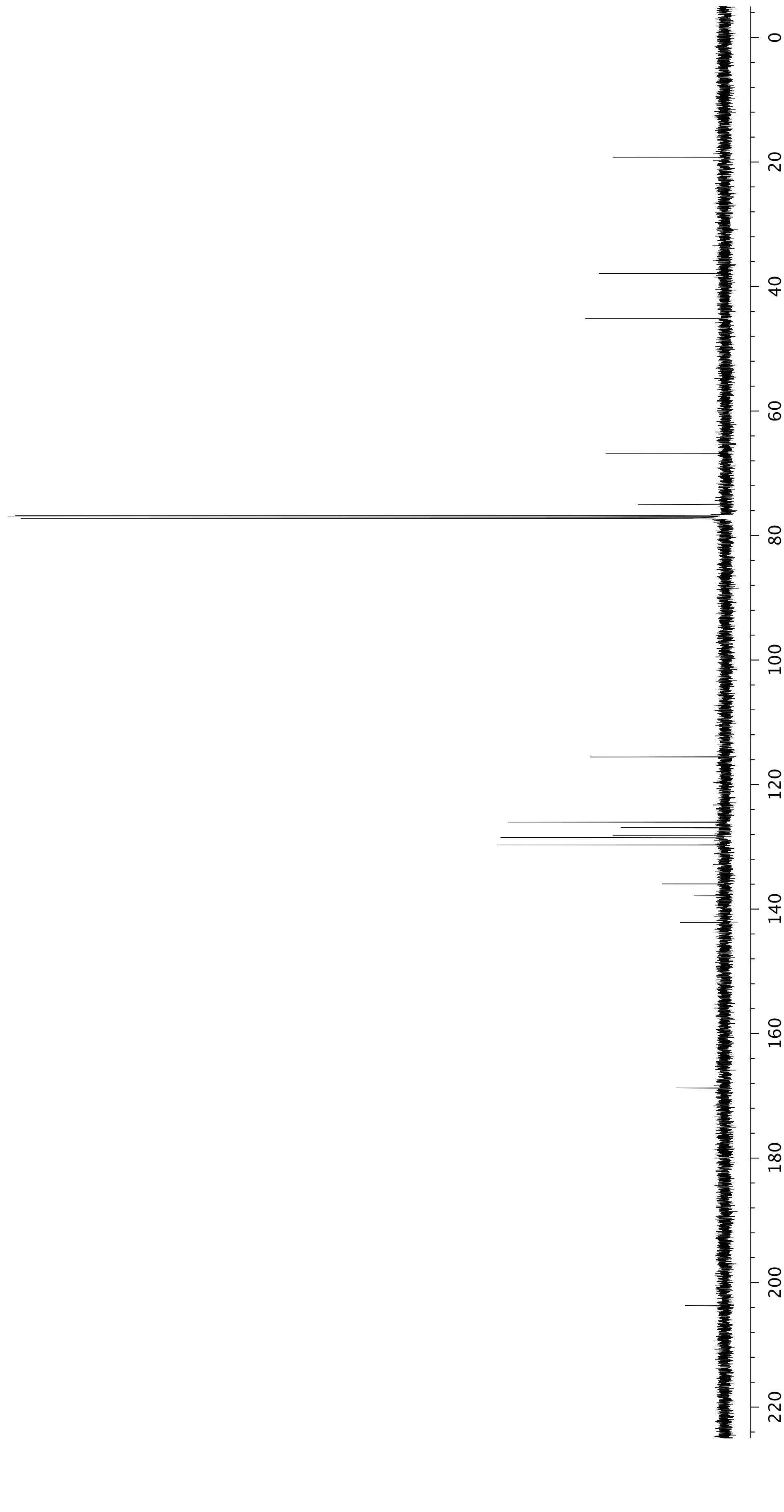
4c



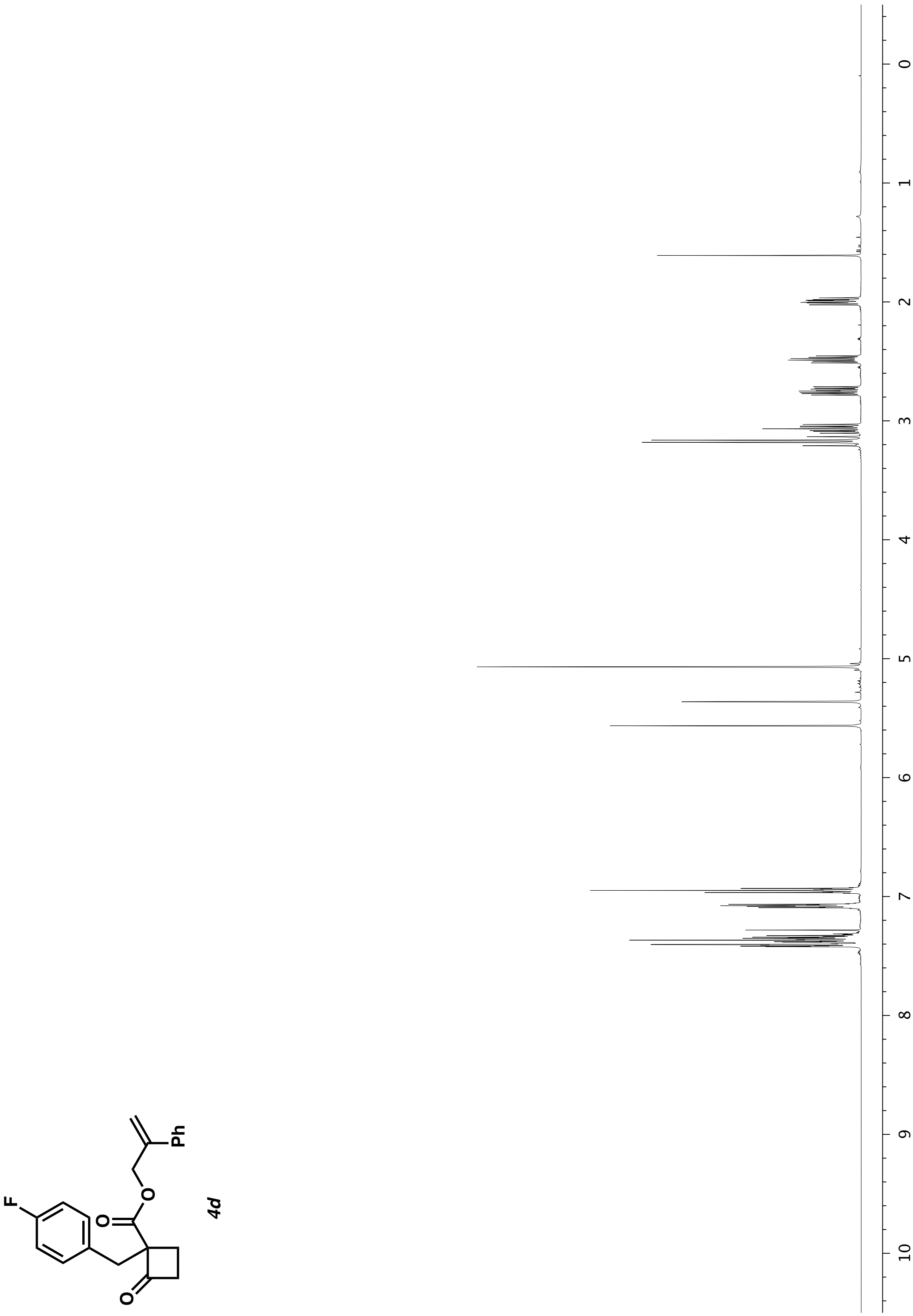
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**.



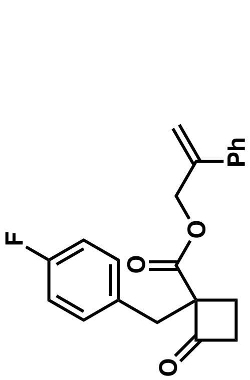
4c



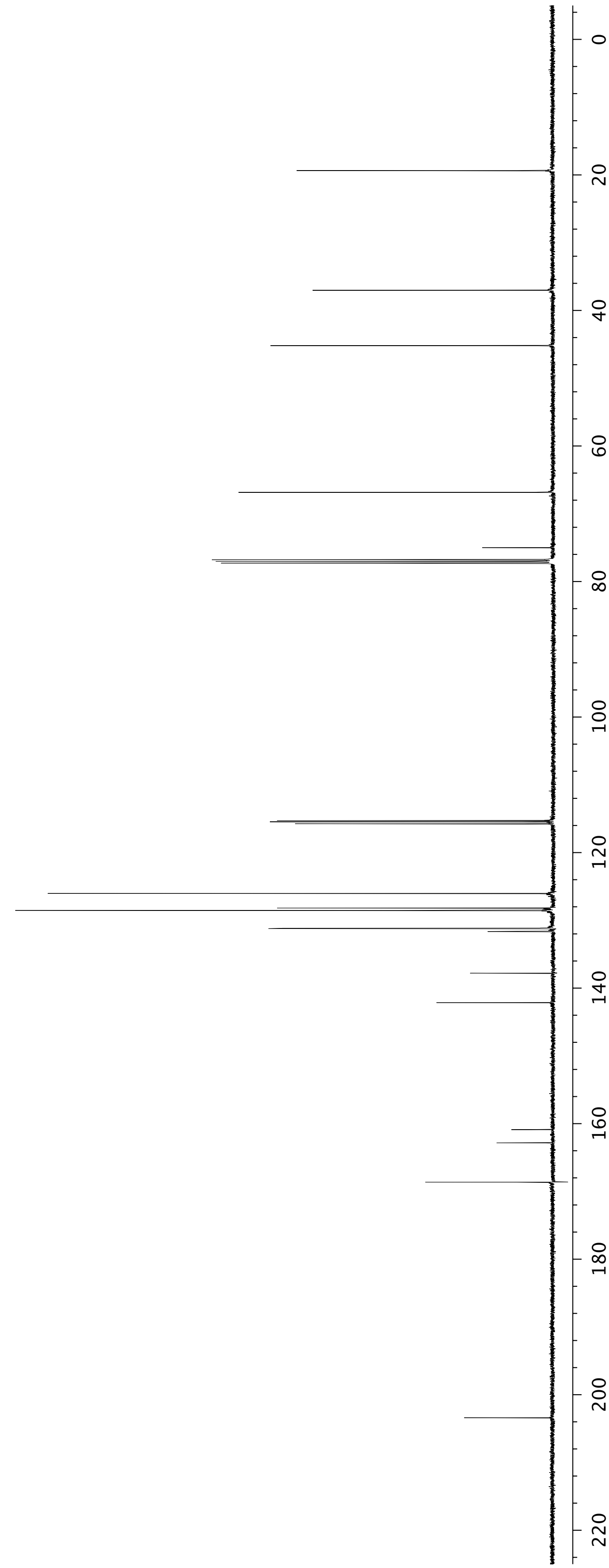
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4c**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**.



4d



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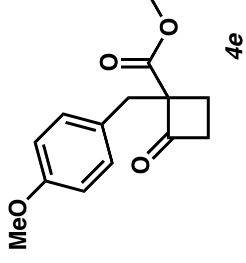
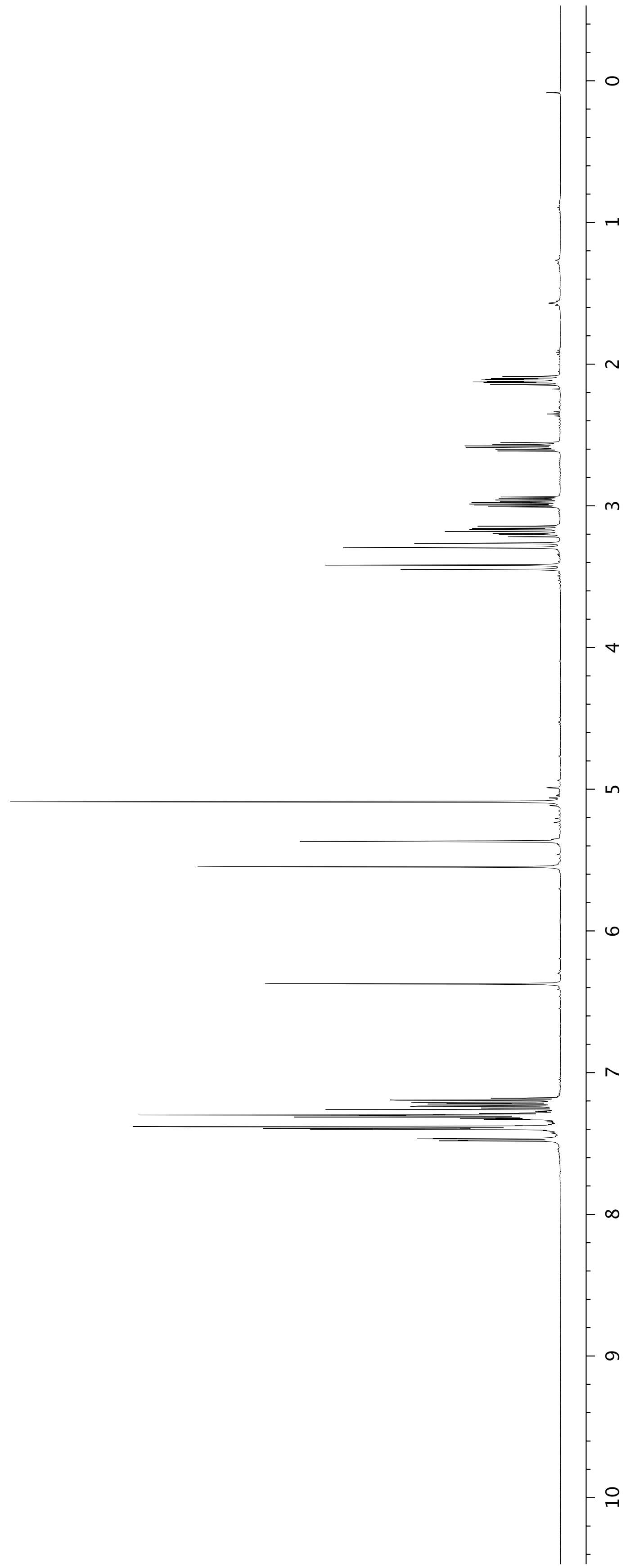
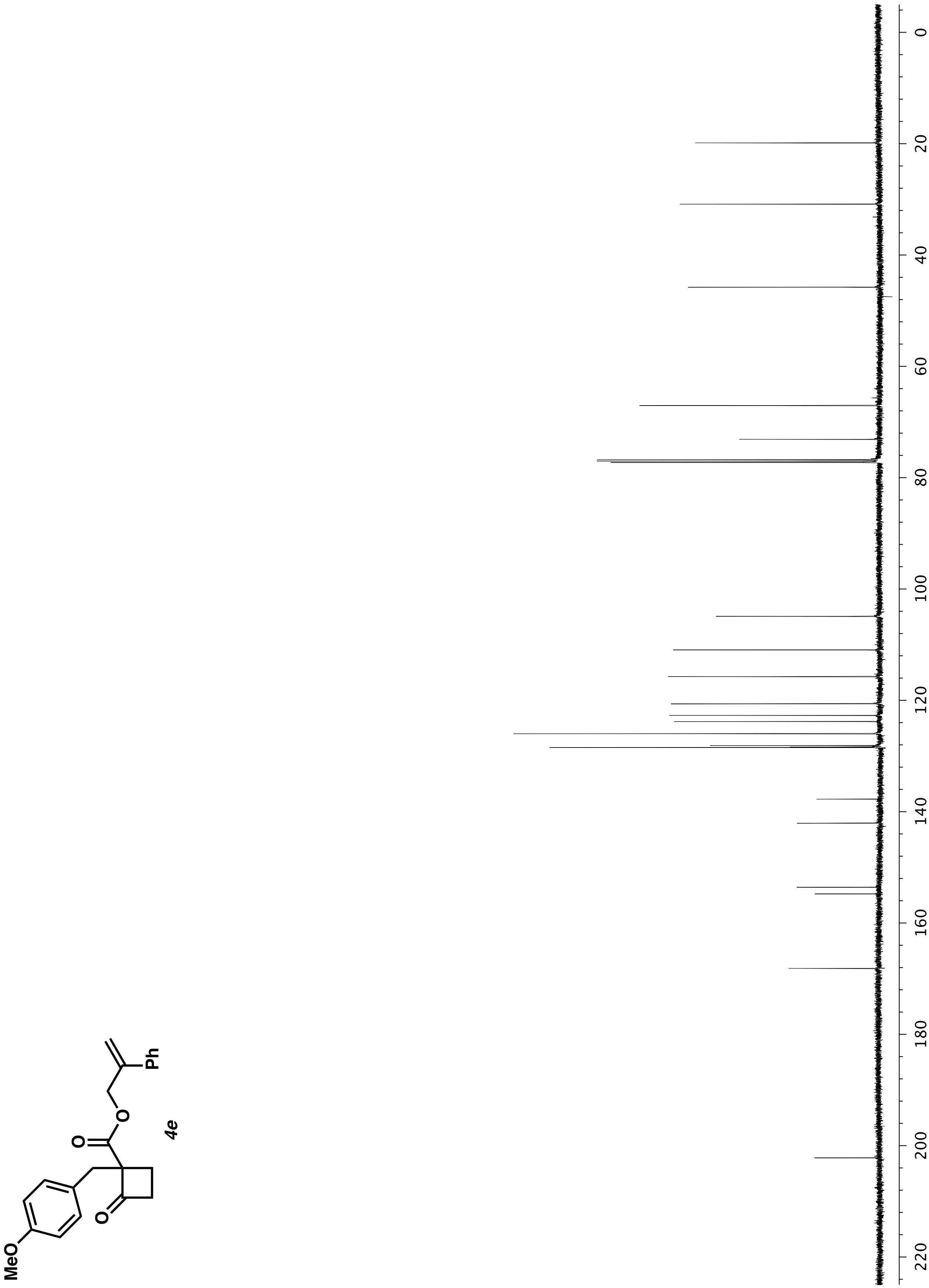




^{1}H NMR (500 MHz, $CDCl_3$) of compound **4e**.



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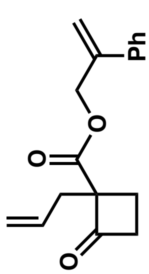
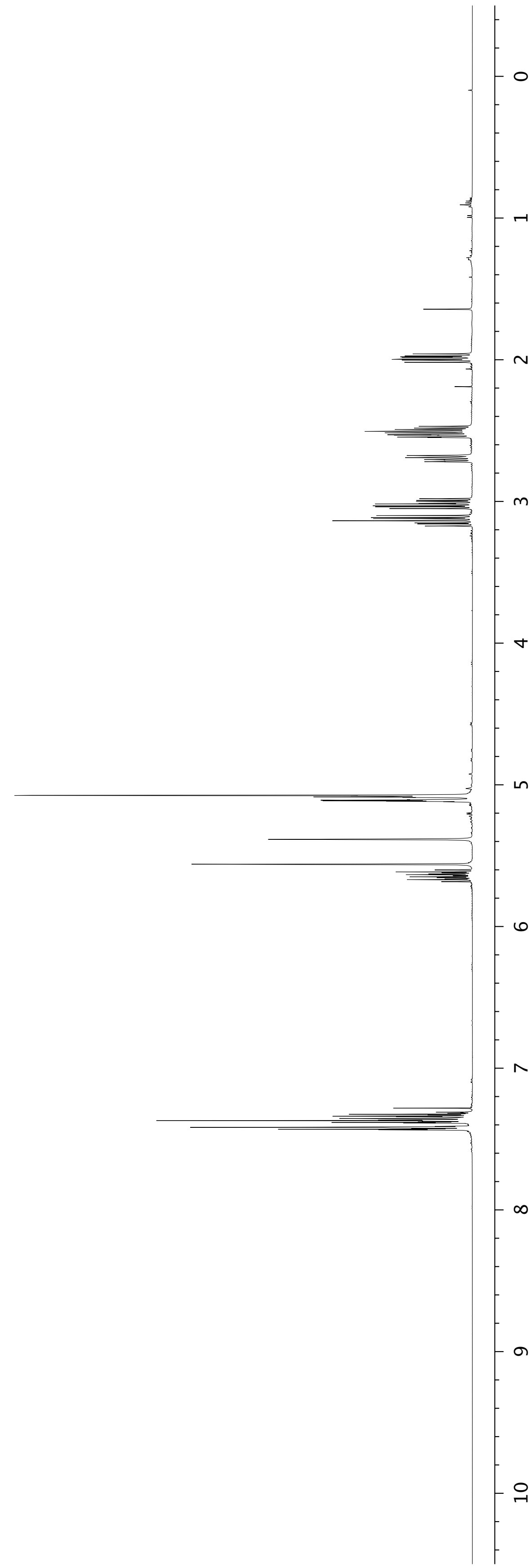


4f



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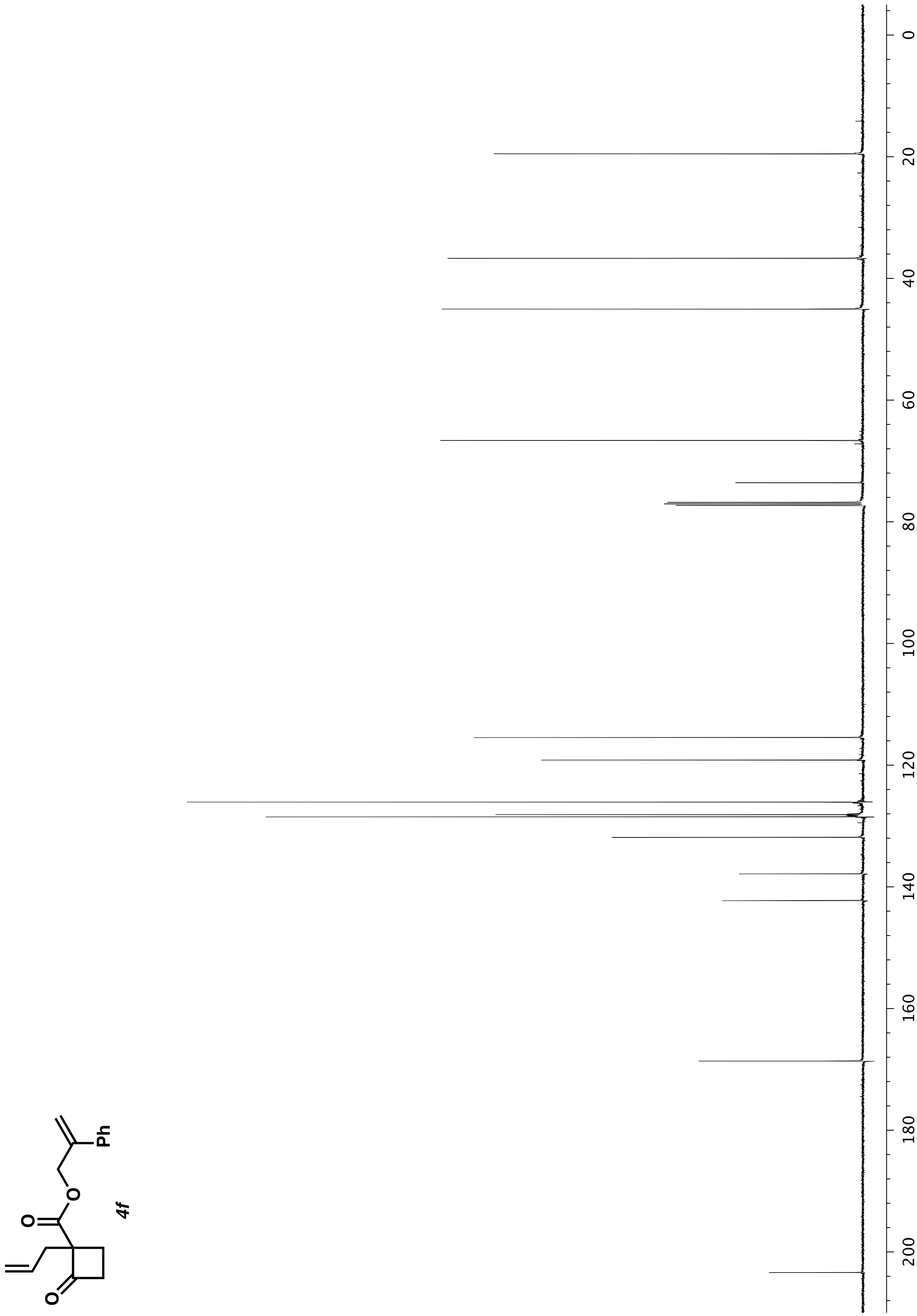

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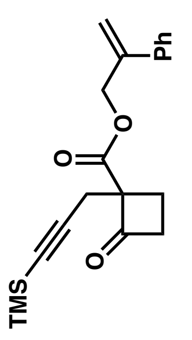
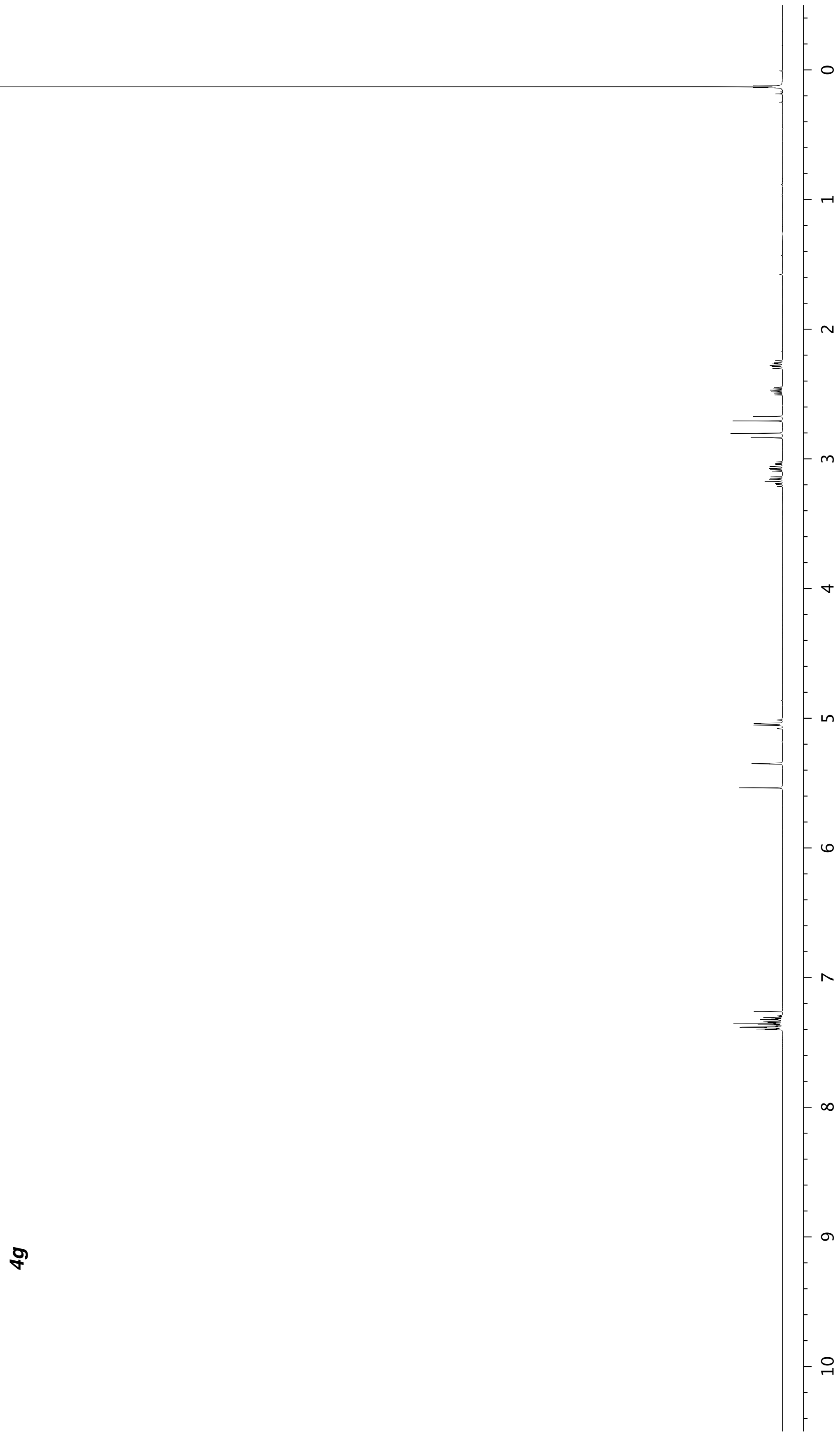
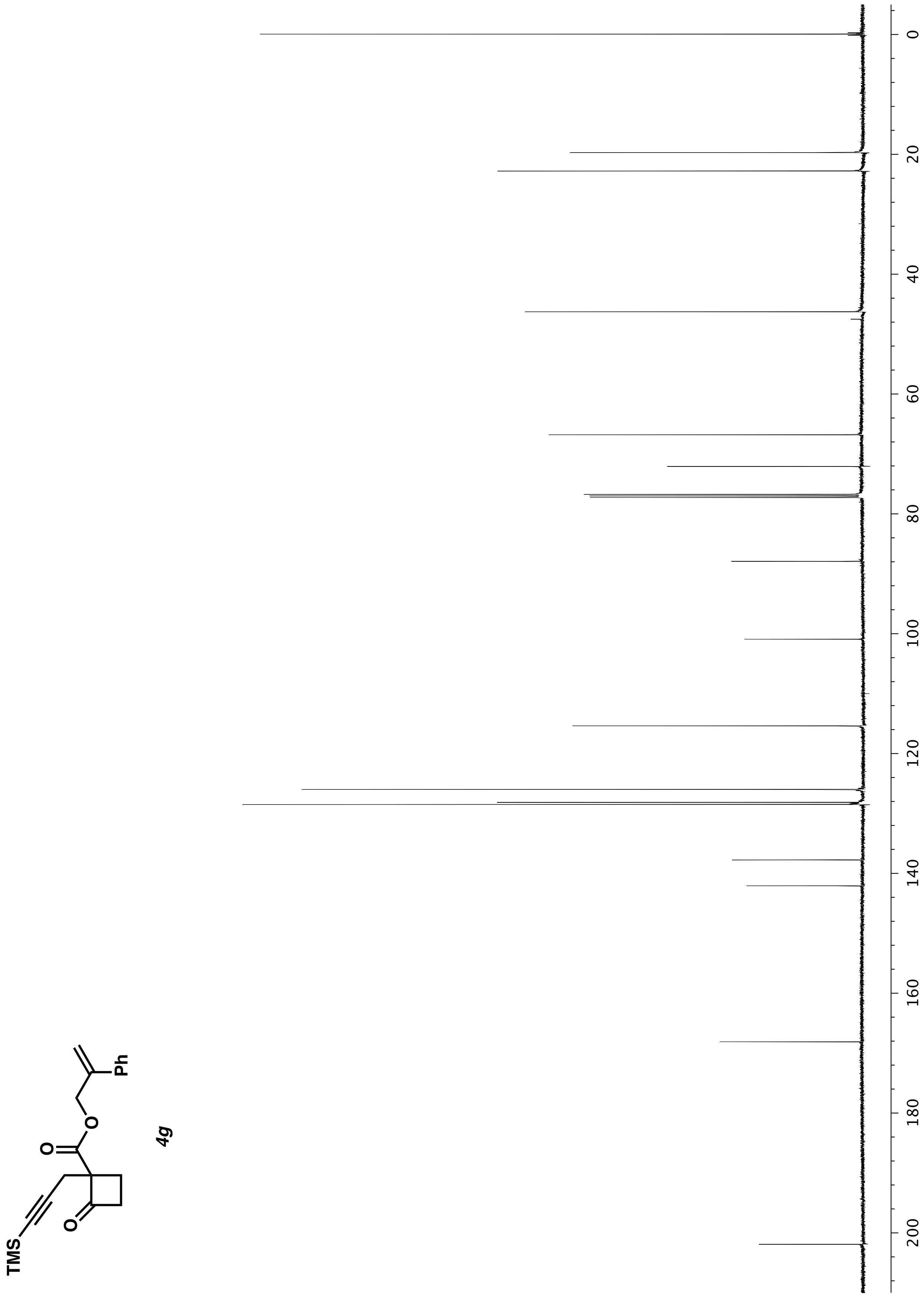


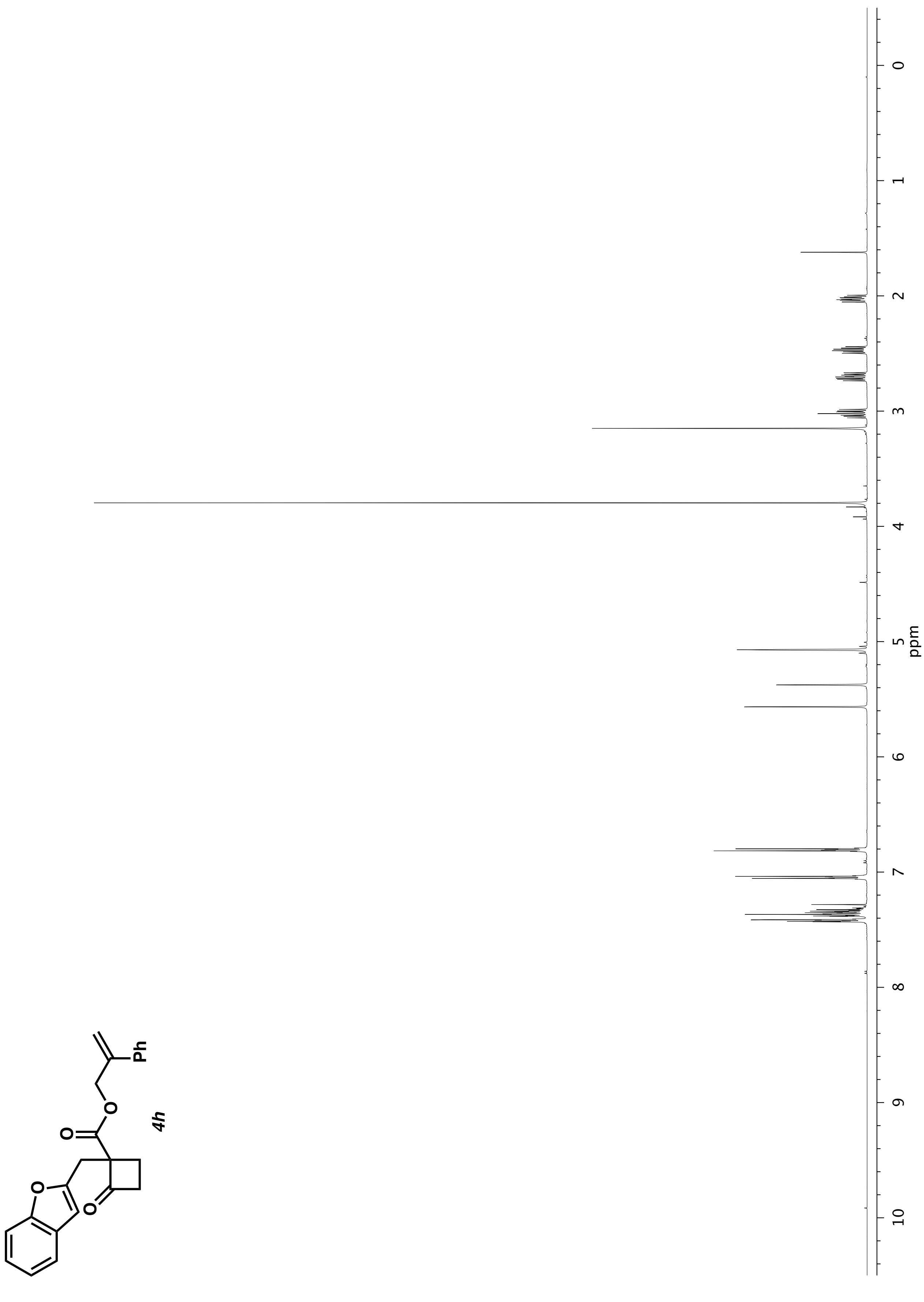
4g



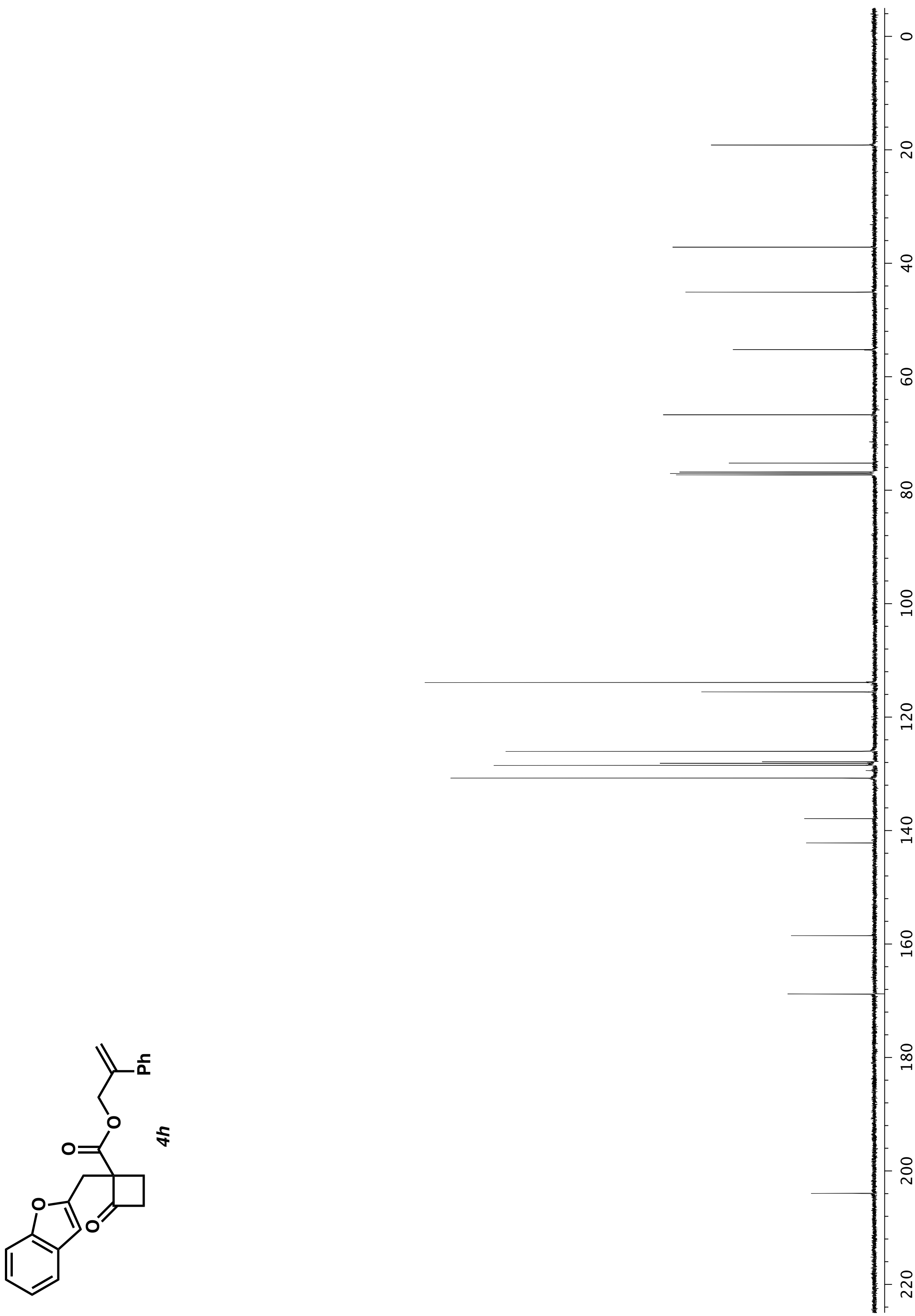
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**.



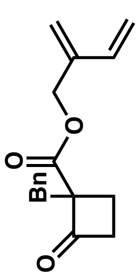
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4g**.



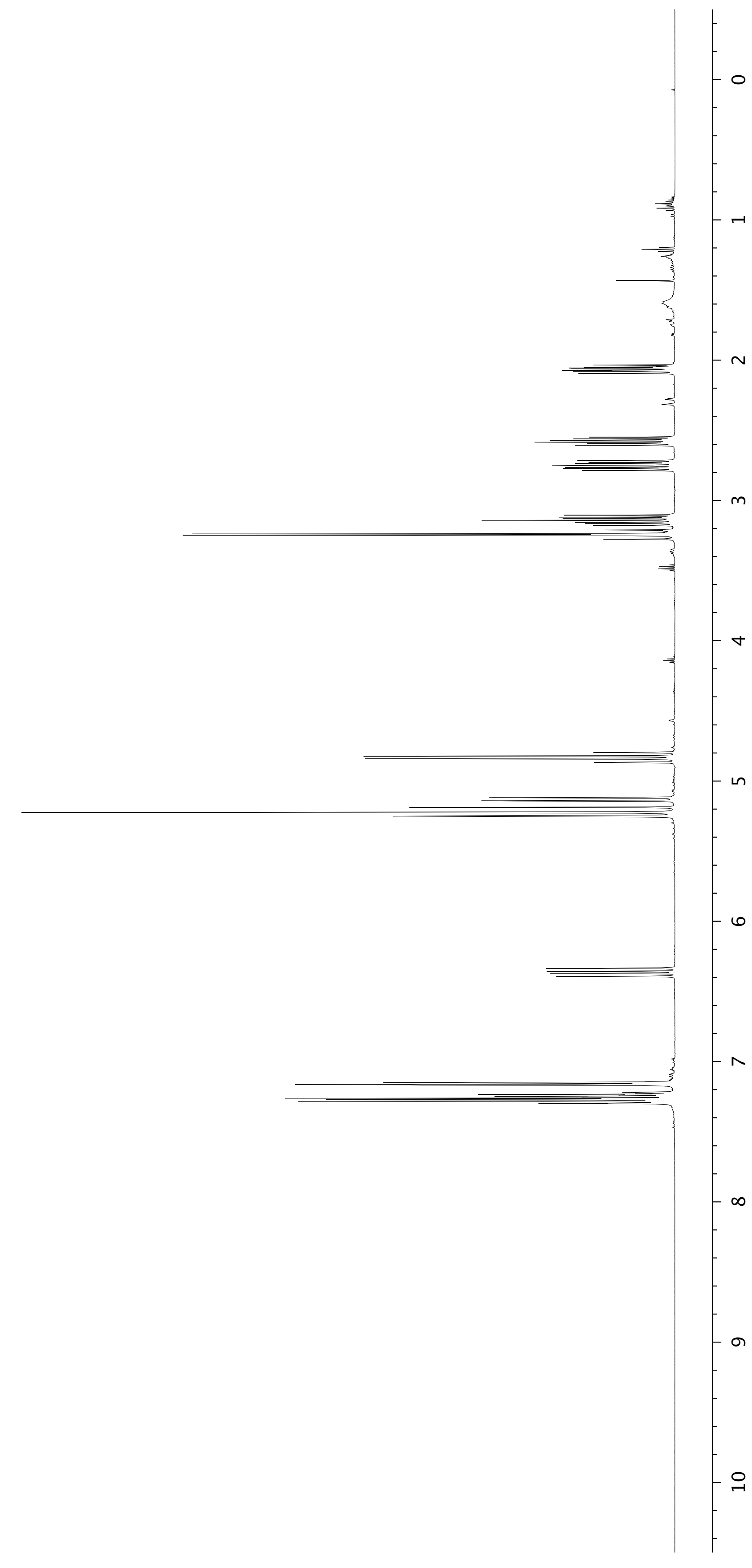
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**.



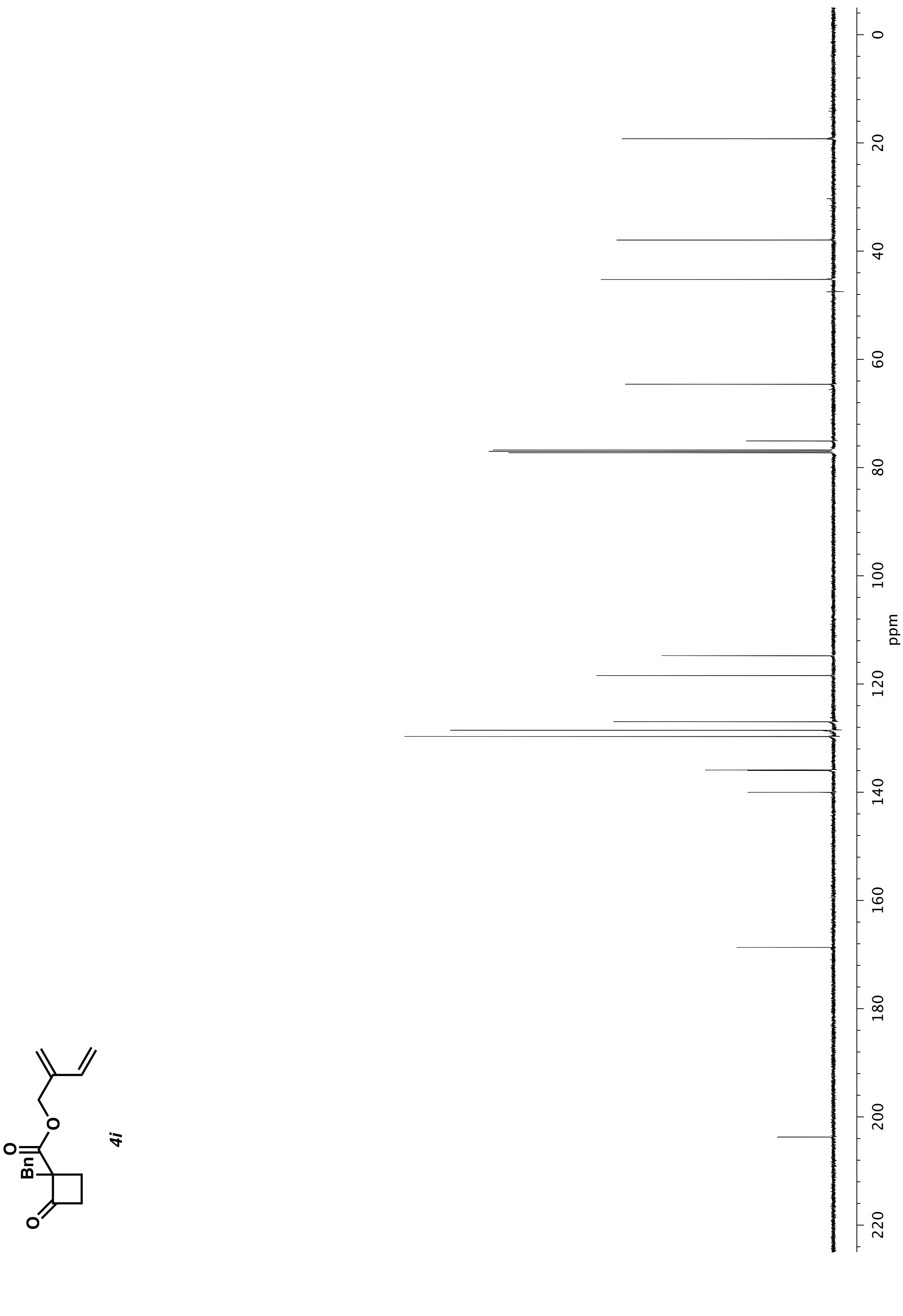
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**.



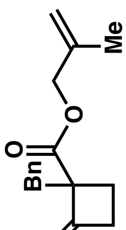
4i



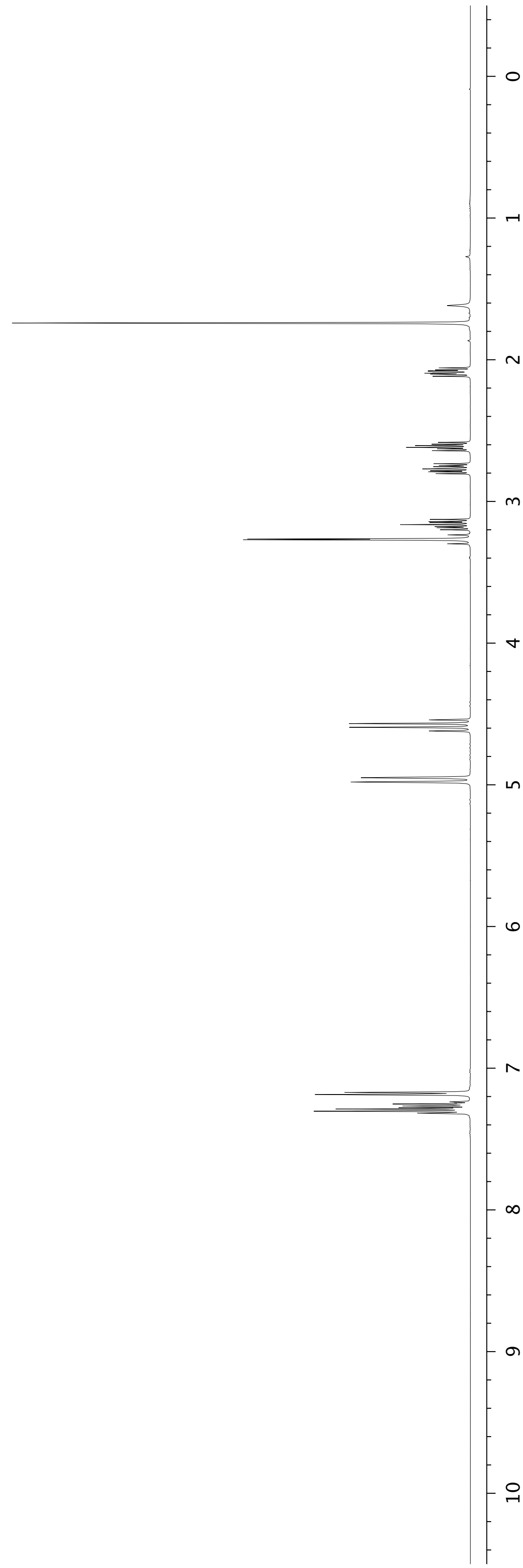
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4i**.



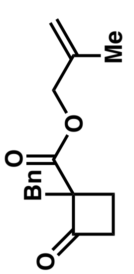
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4i**.



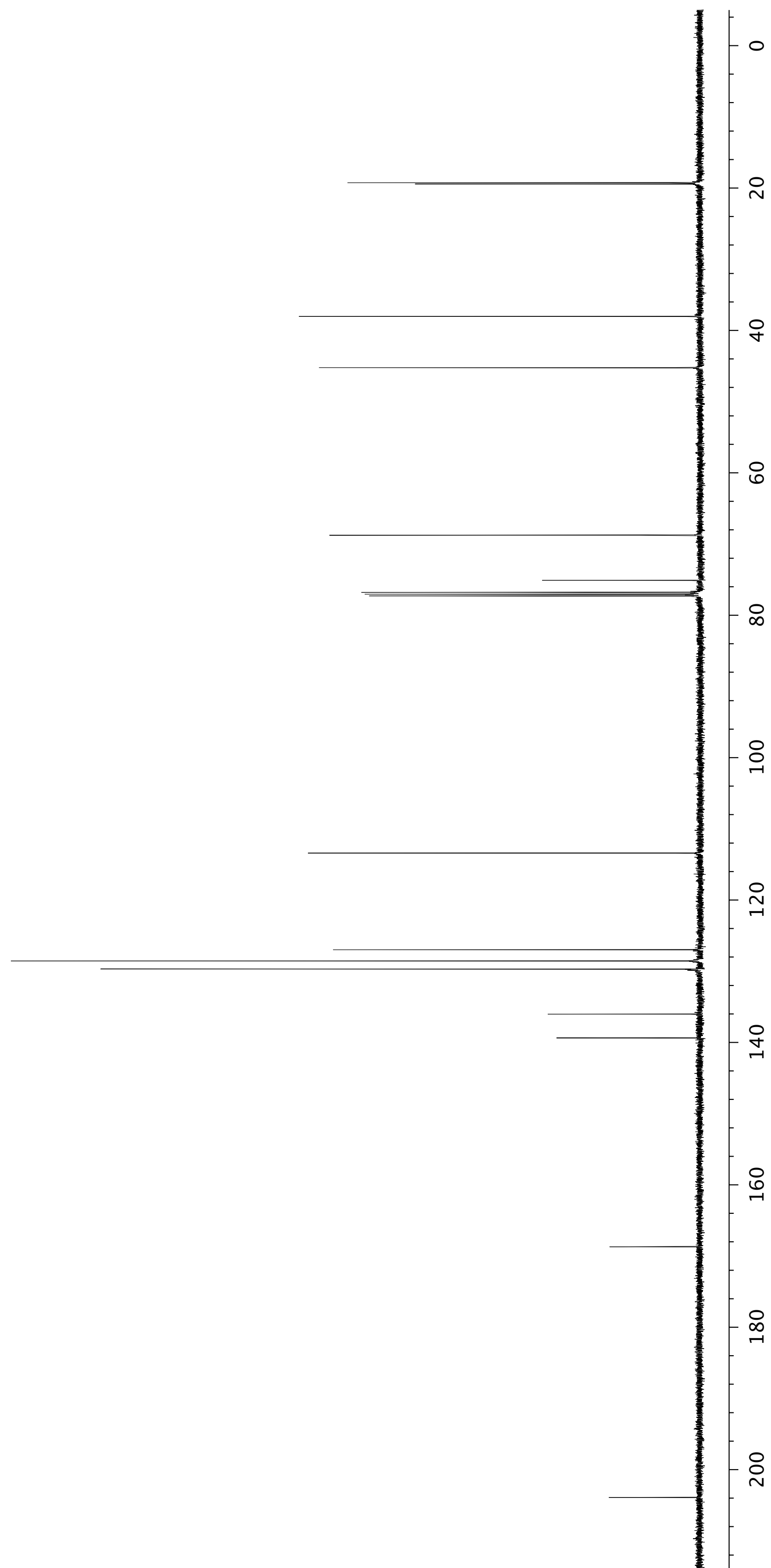
4j



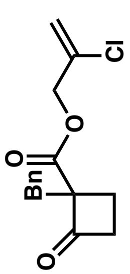
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j**.



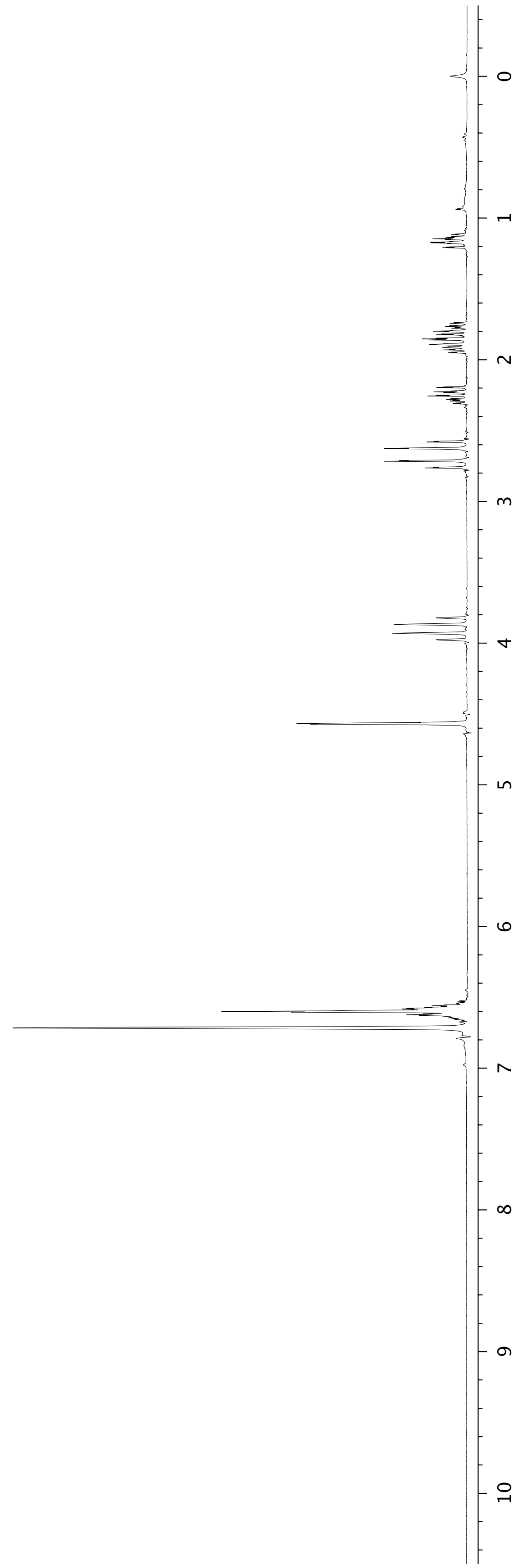
4j



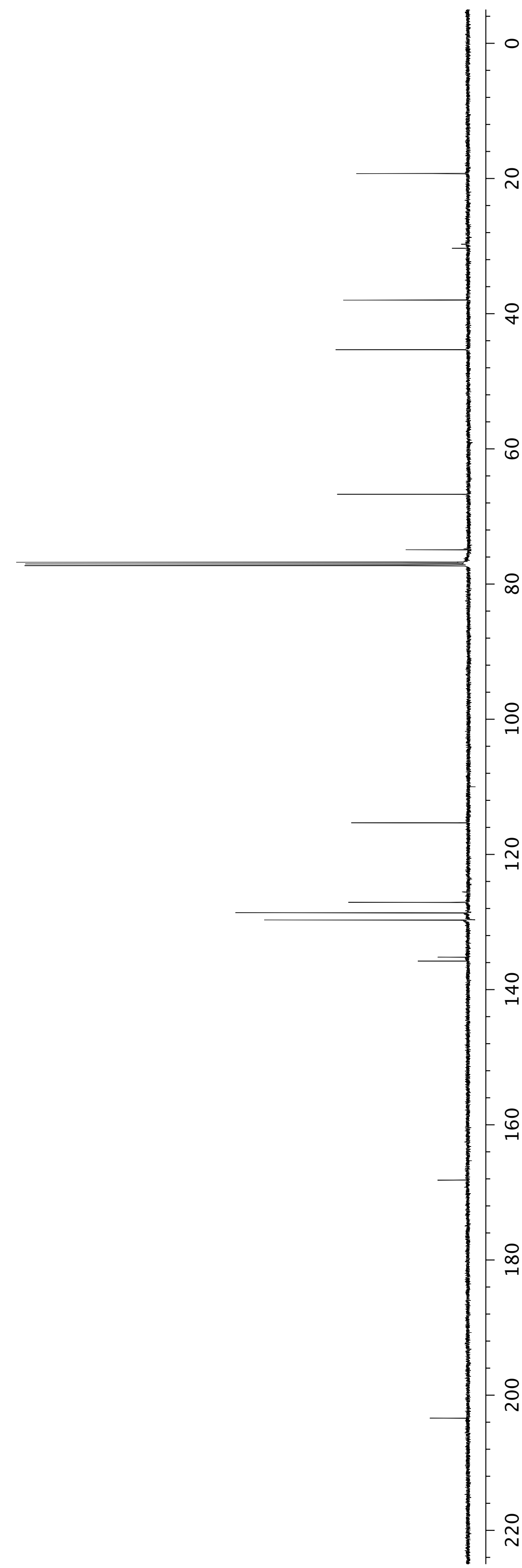
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4j**.

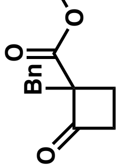


4k



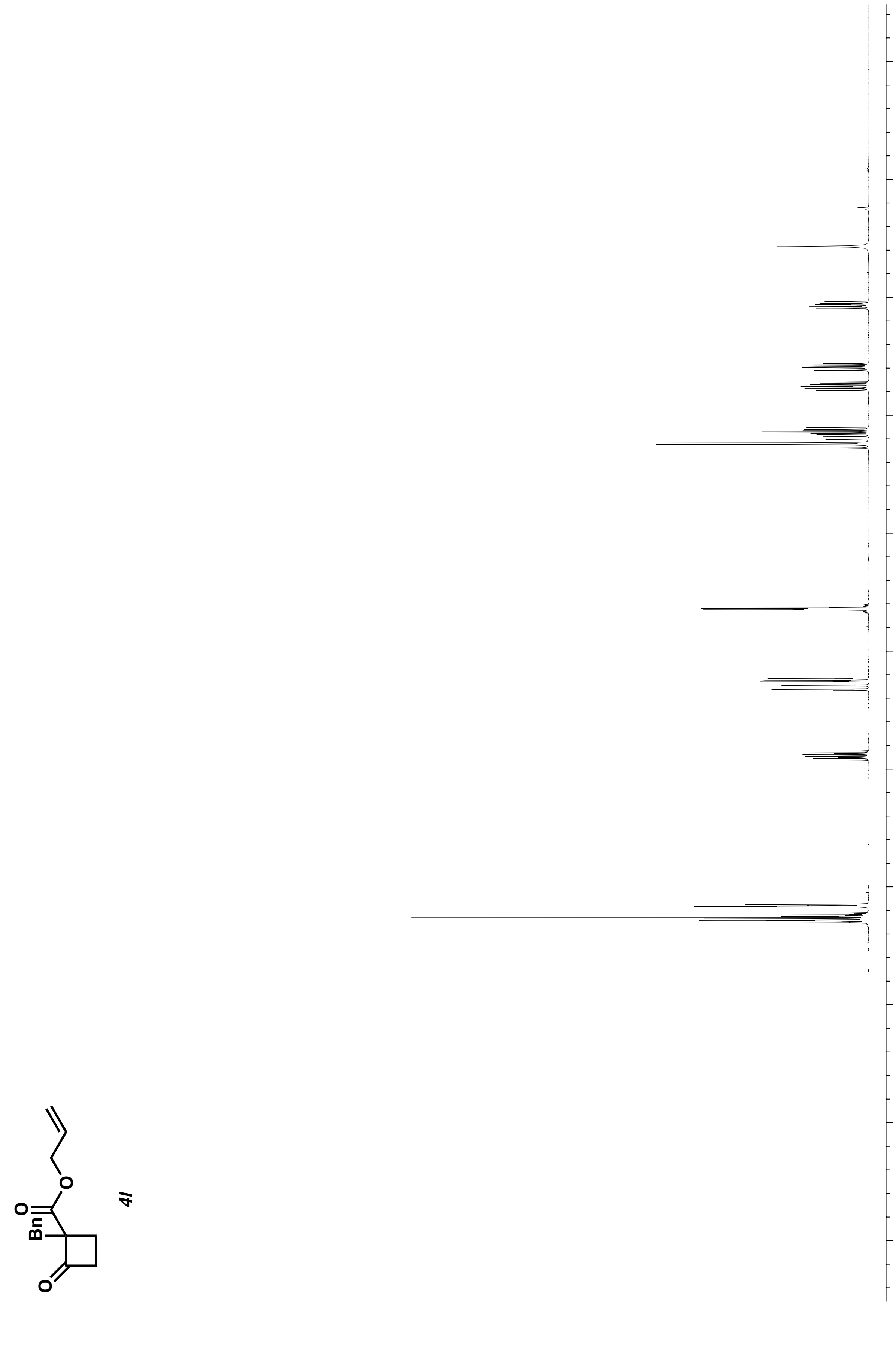
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4k**.





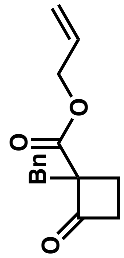
4k

^{13}C NMR (126 MHz, $CDCl_3$) of compound **4k**.

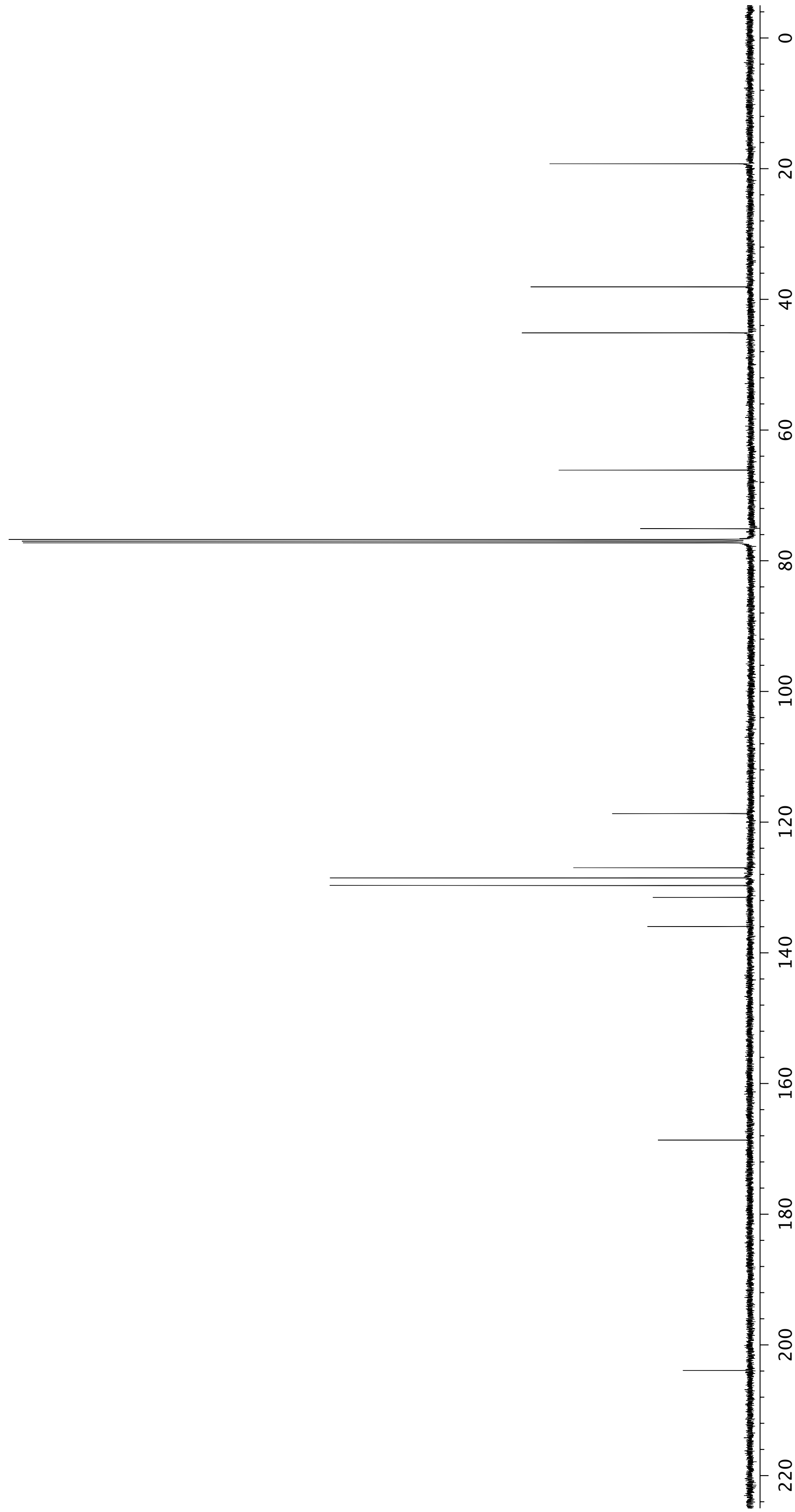


4l

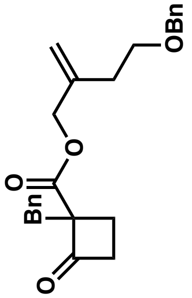
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4l**.



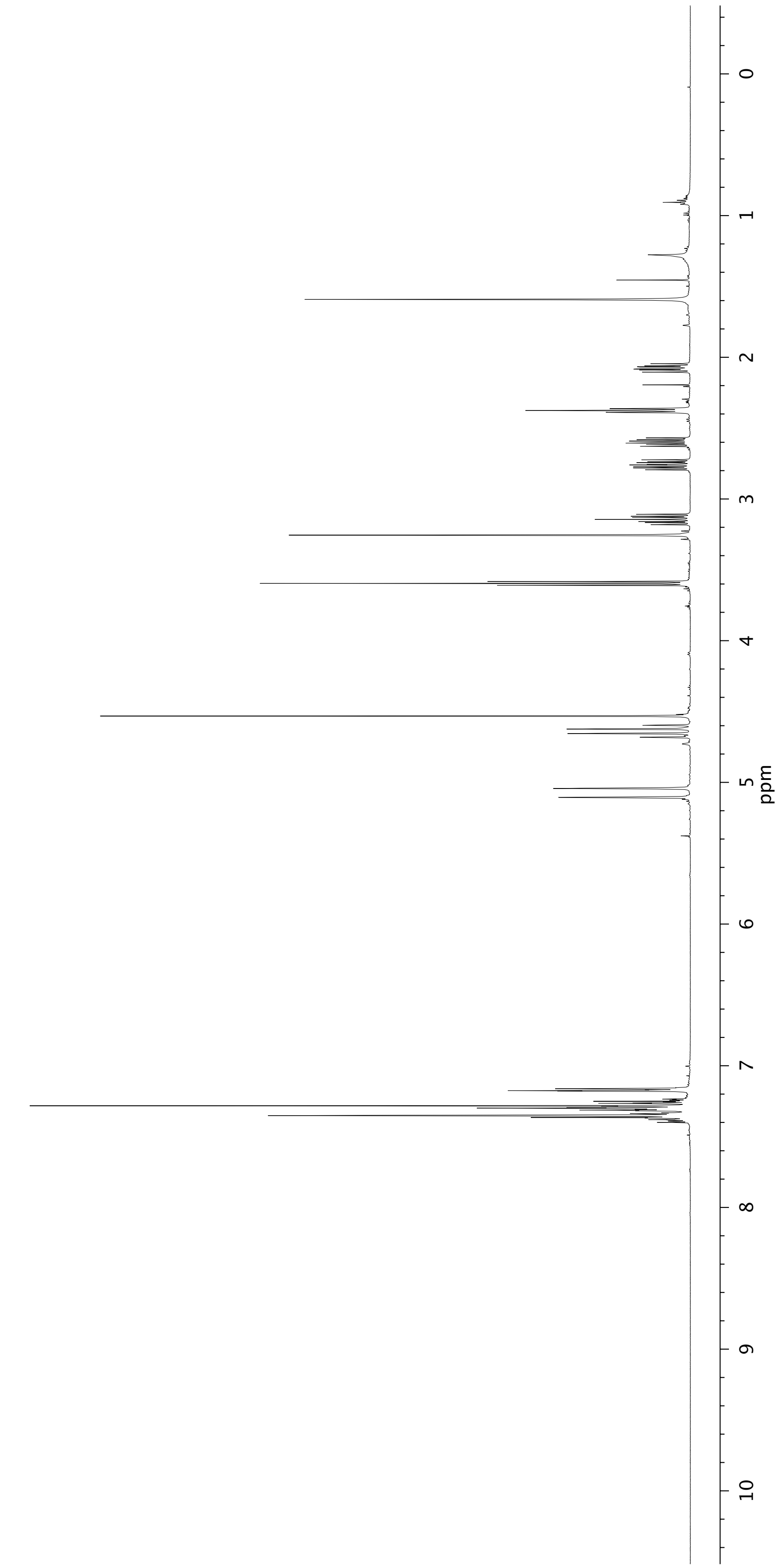
4l



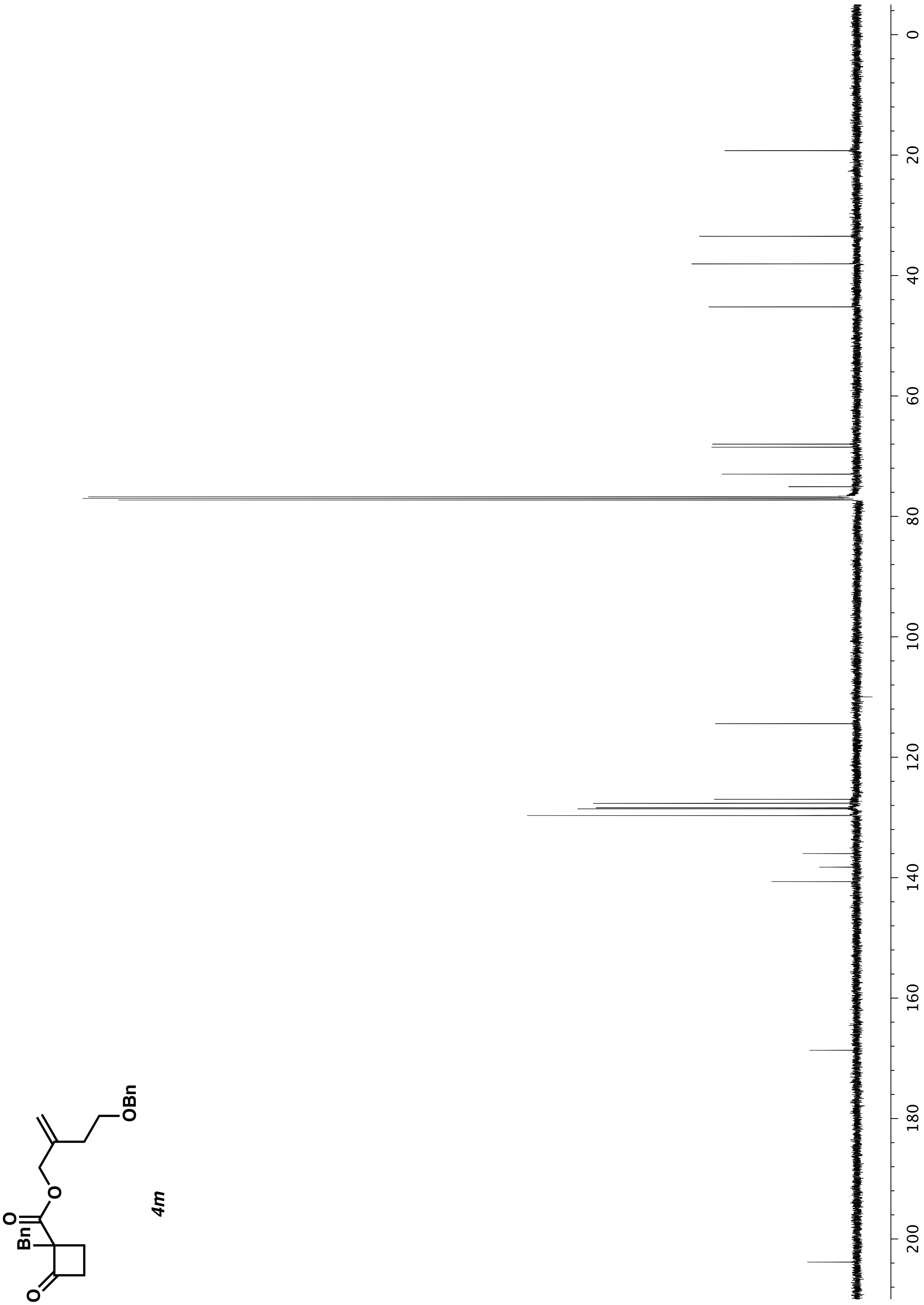
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4l**.



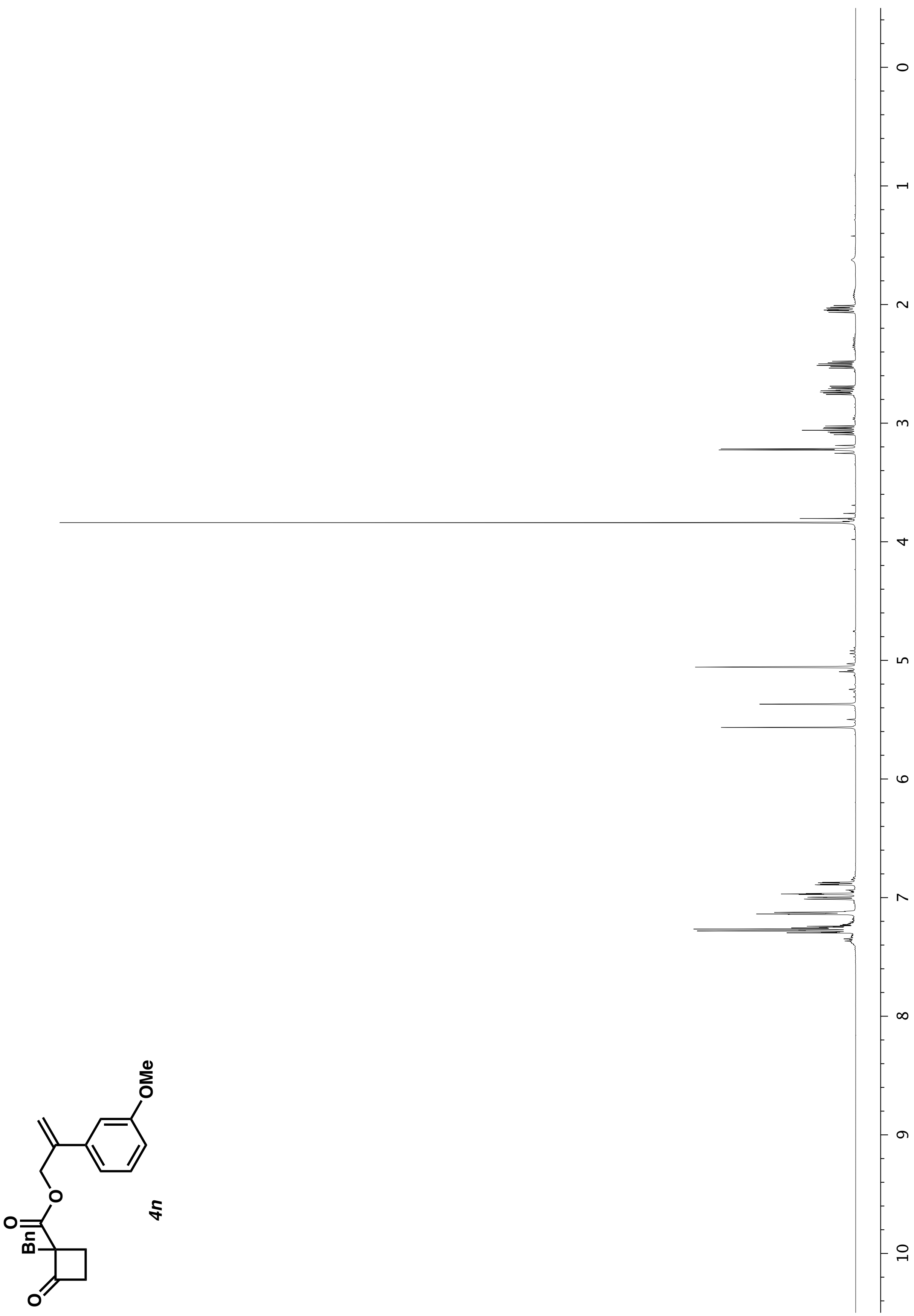
4m



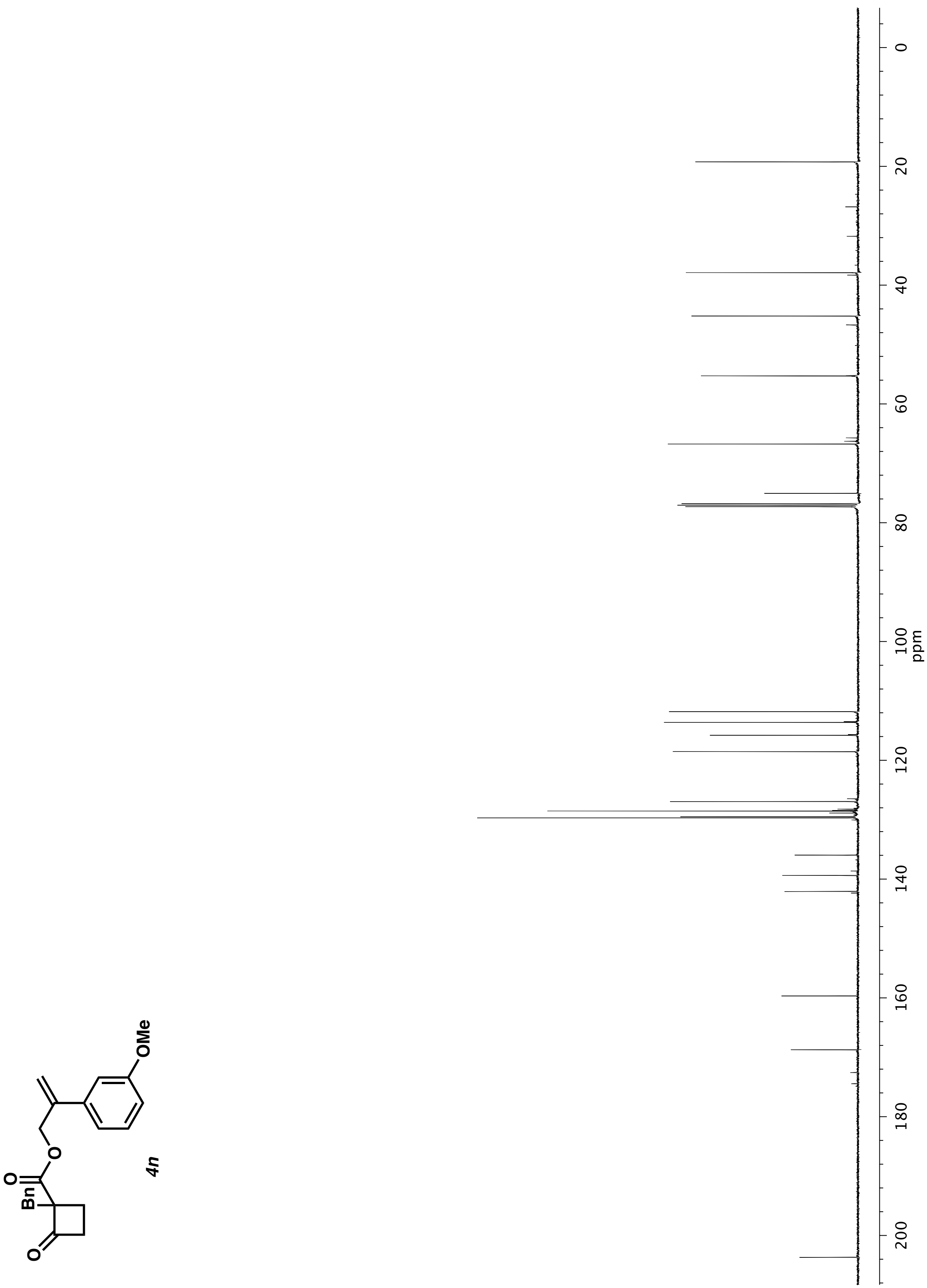
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4m**.



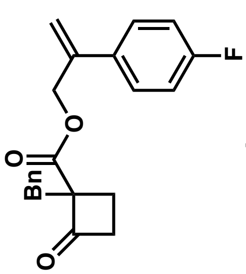
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4m**.



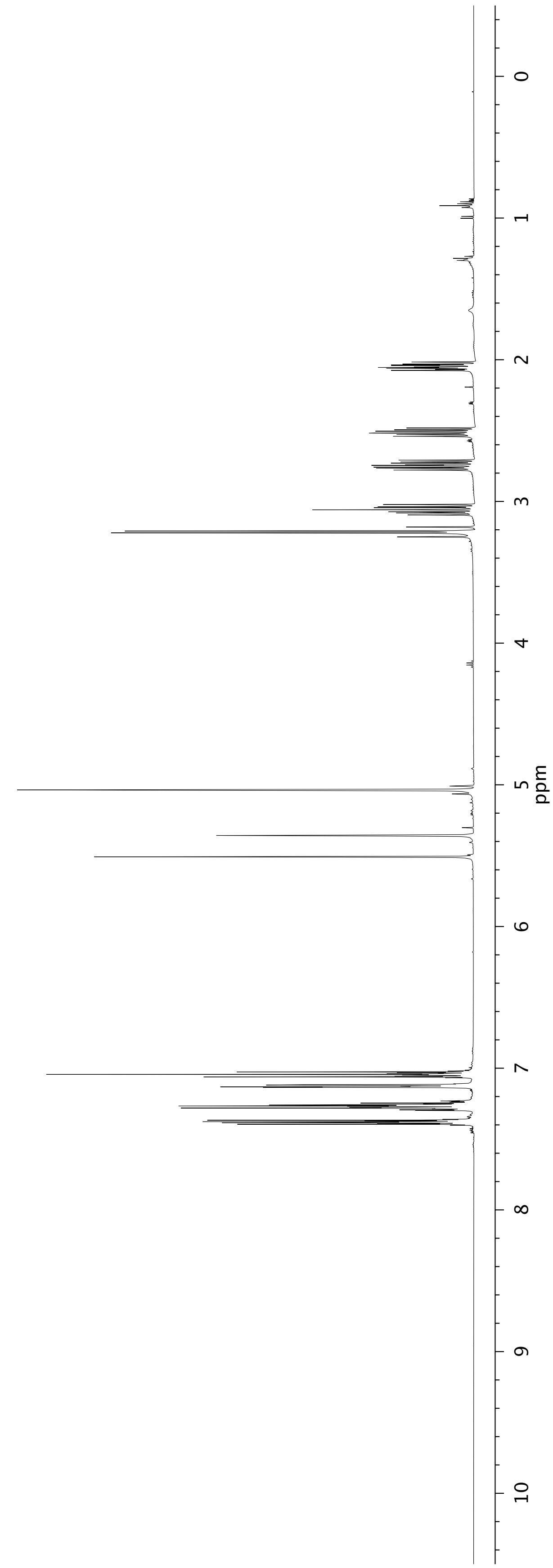
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4n**.



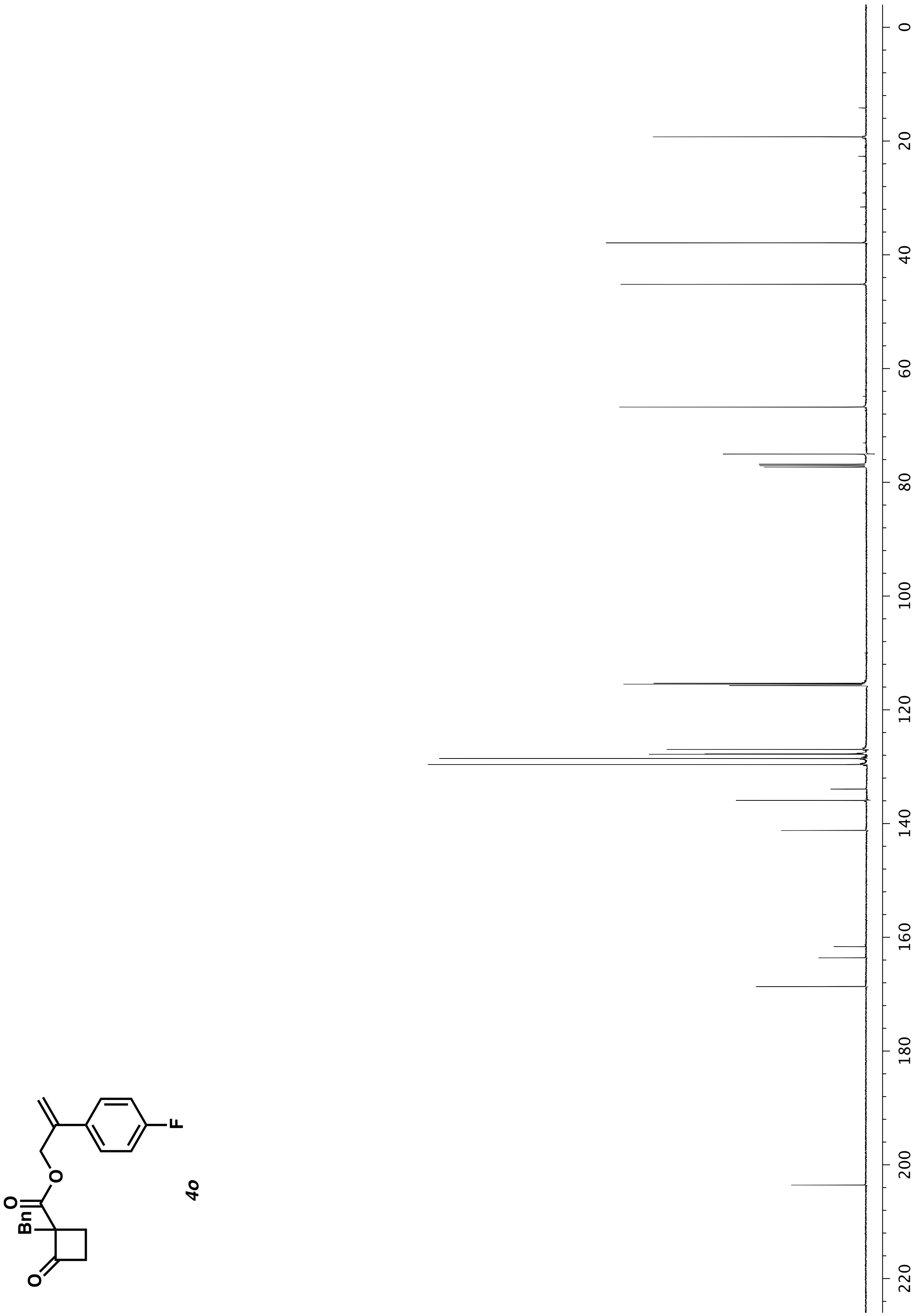
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4n**.



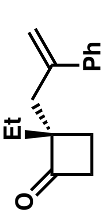
4o



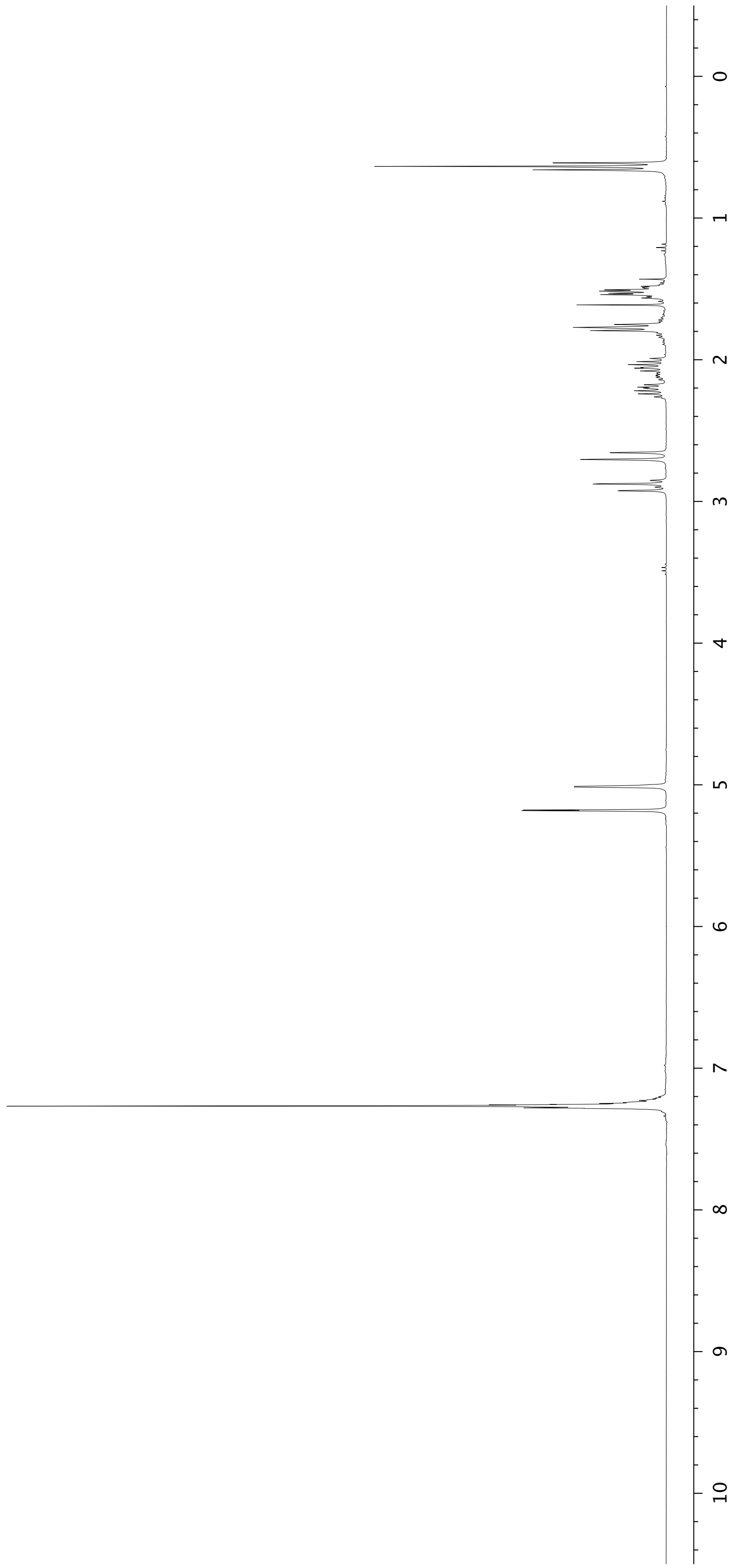
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4o**.



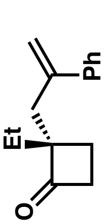
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4o**.



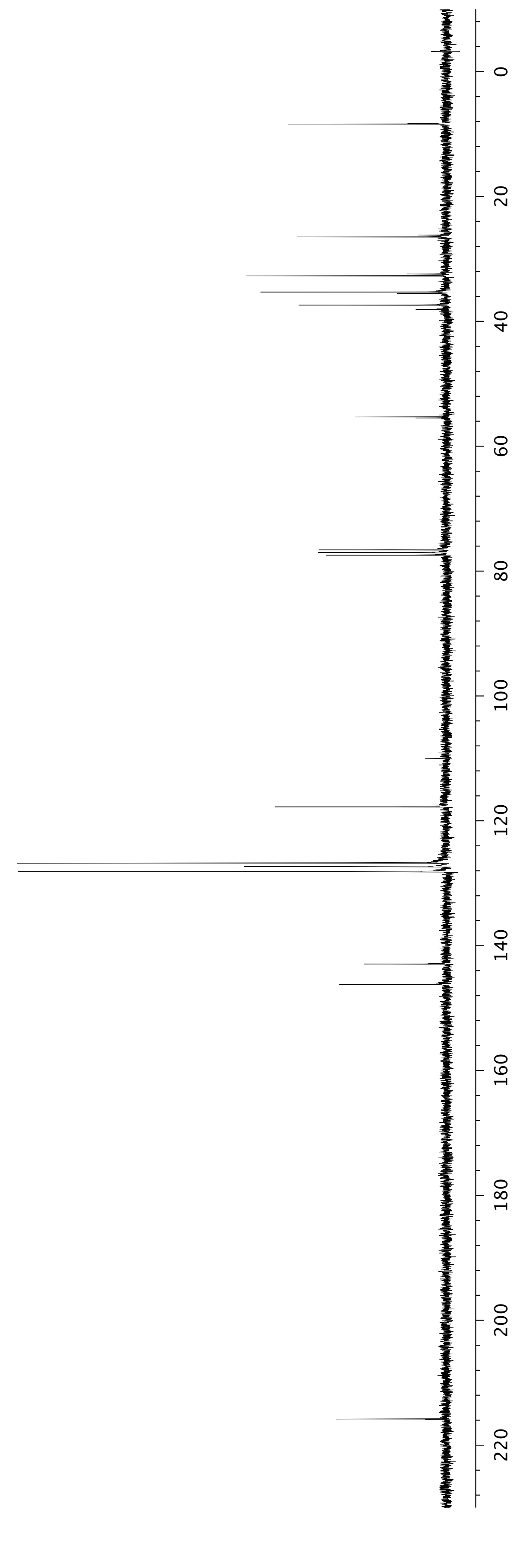
5a



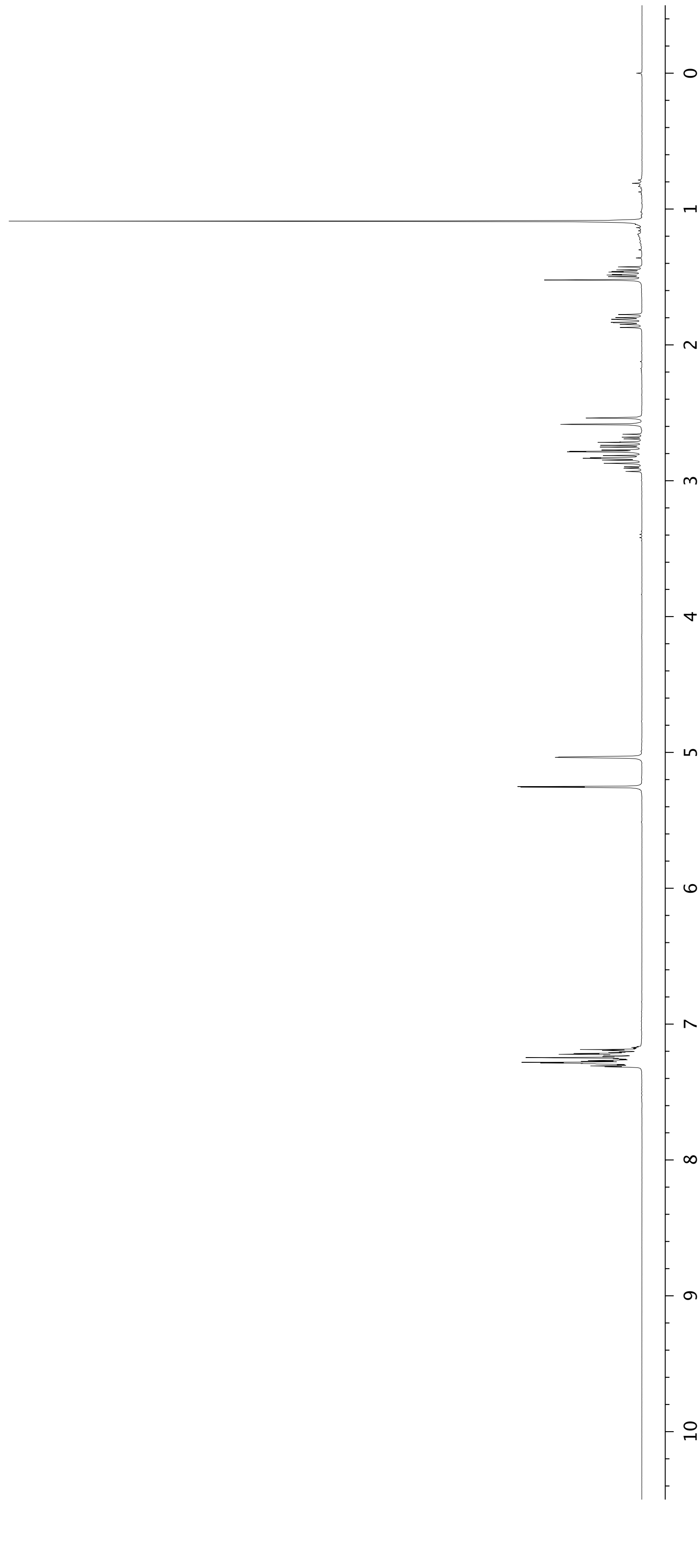
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5a**.

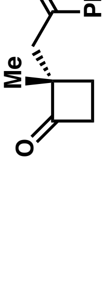


5a



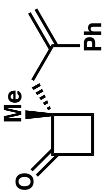
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5a**.



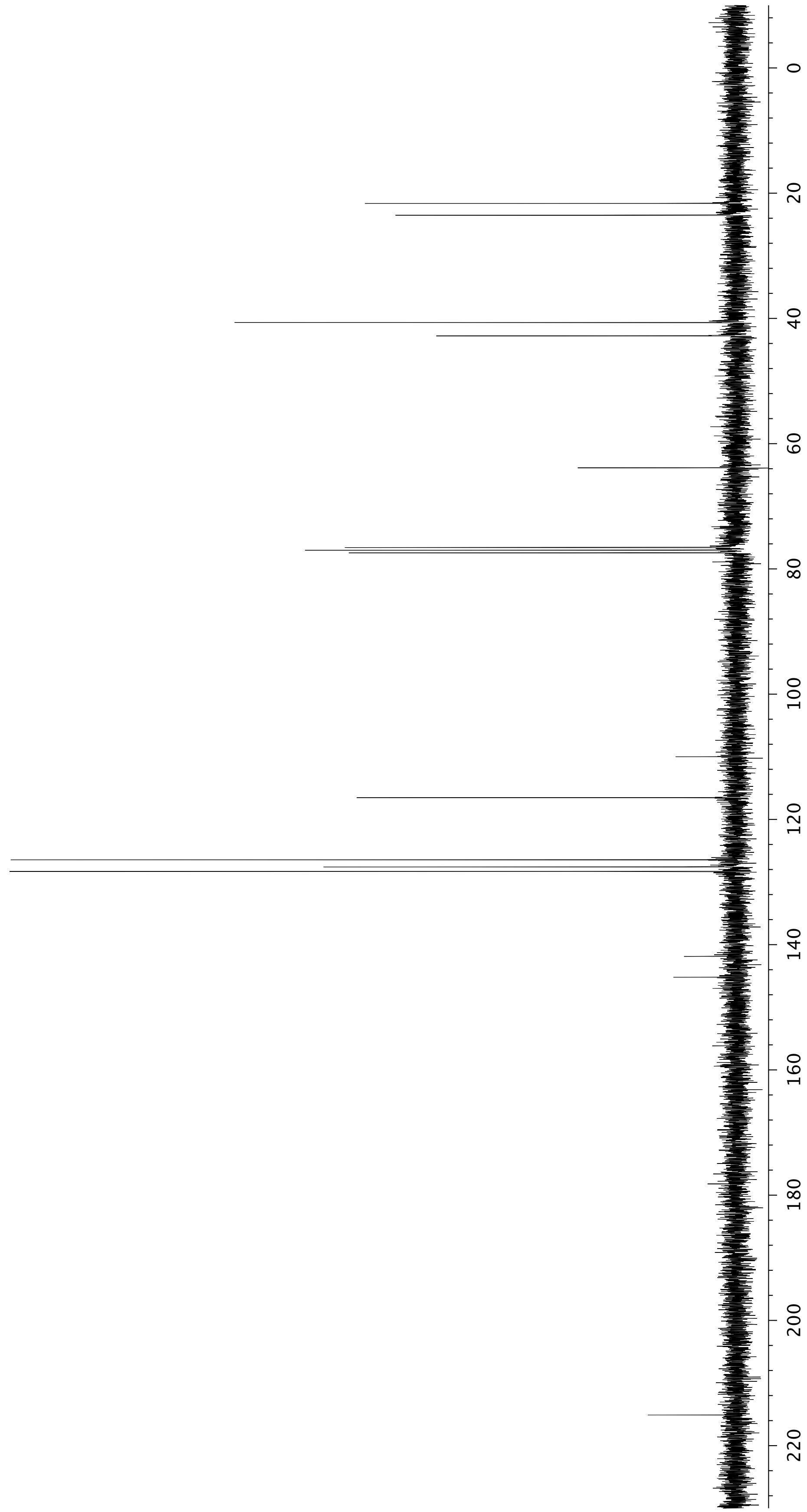


5b

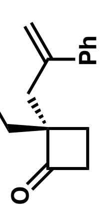
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b**.



5b



^{13}C NMR (126 MHz, $CDCl_3$) of compound **5b**.



5c

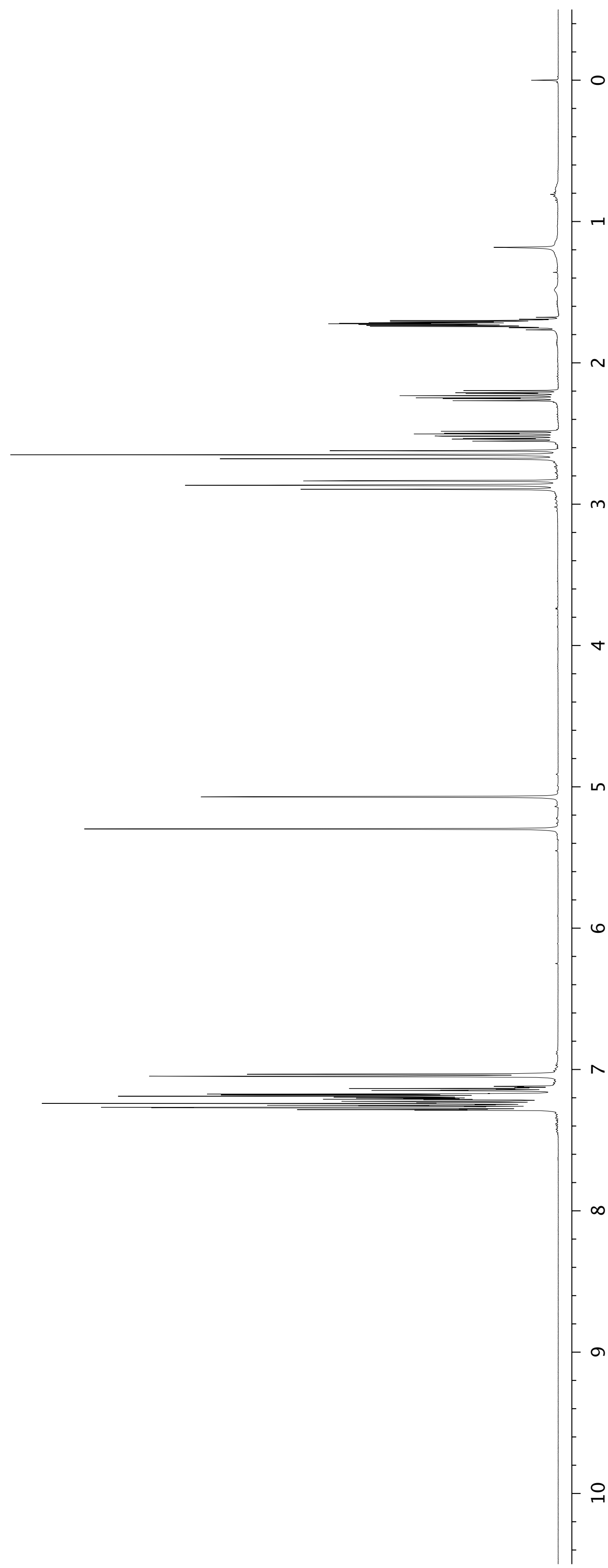


Figure SI-18A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **5c**.

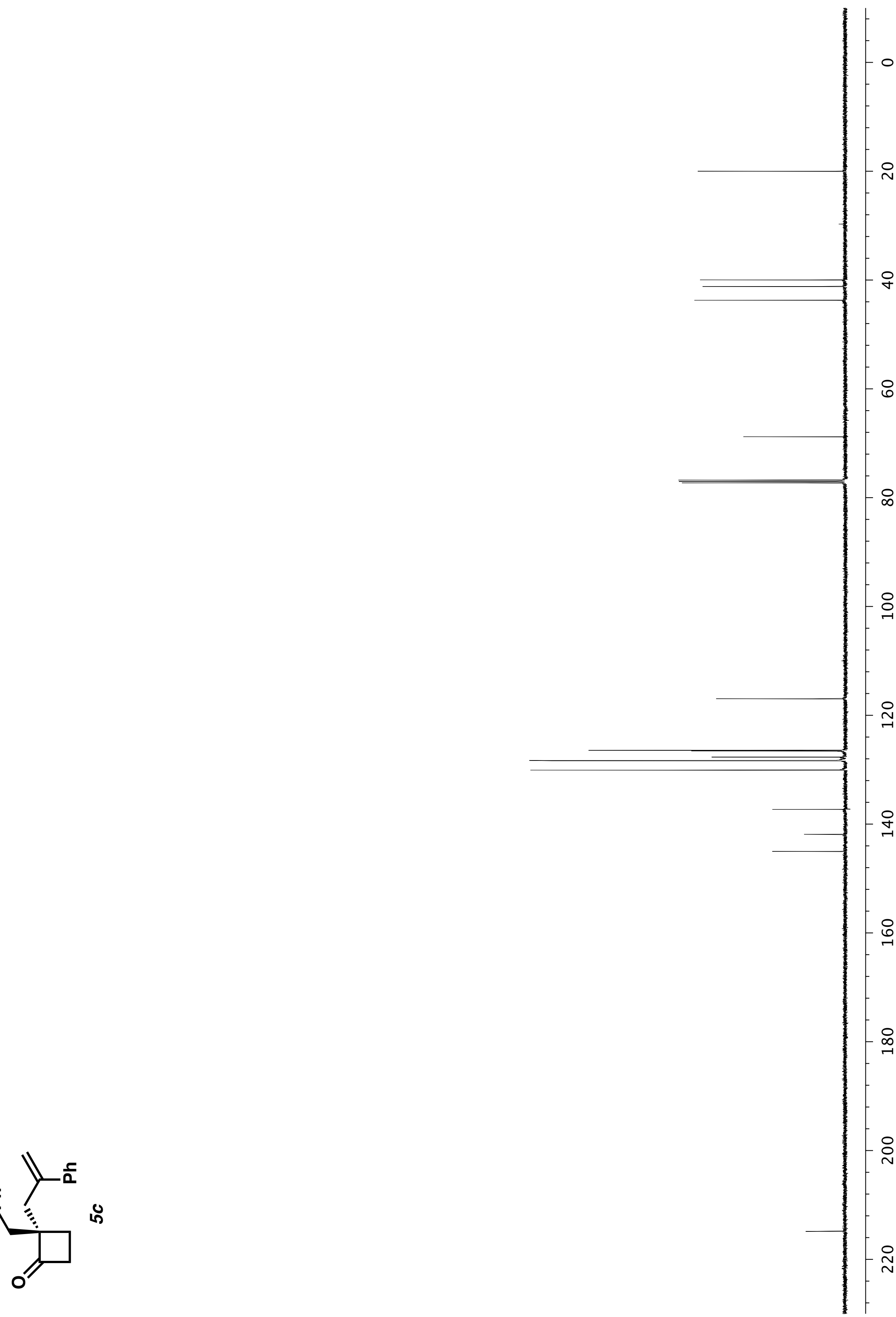
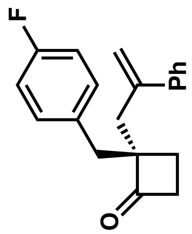
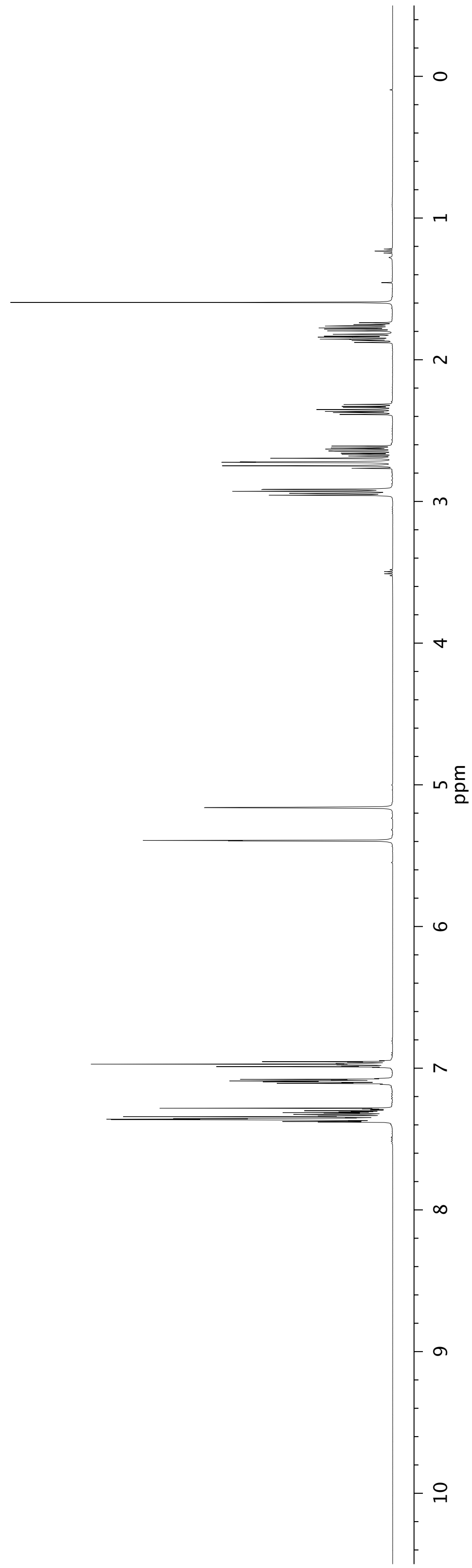


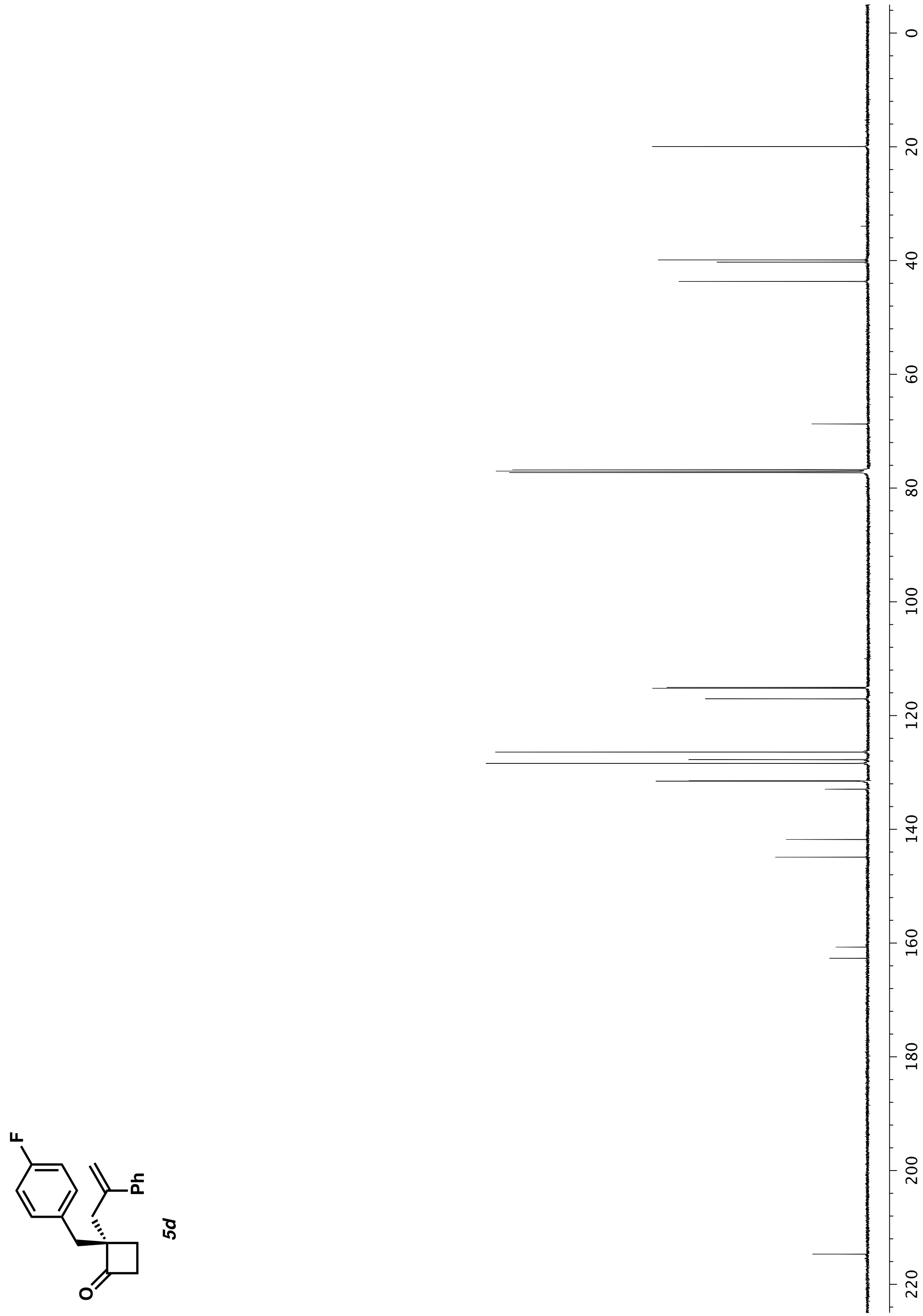
Figure SI-18B. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **5c**.



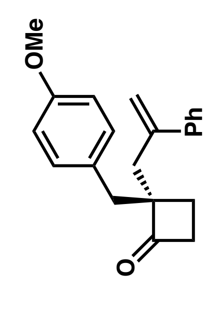
5d



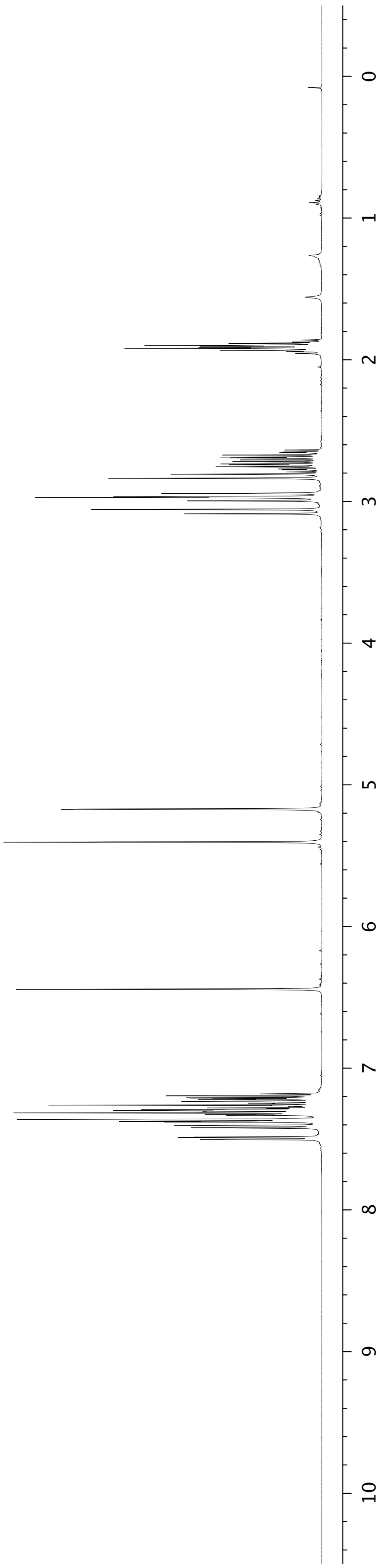
^{1}H NMR (500 MHz, CDCl$_3$) of compound **5d**.



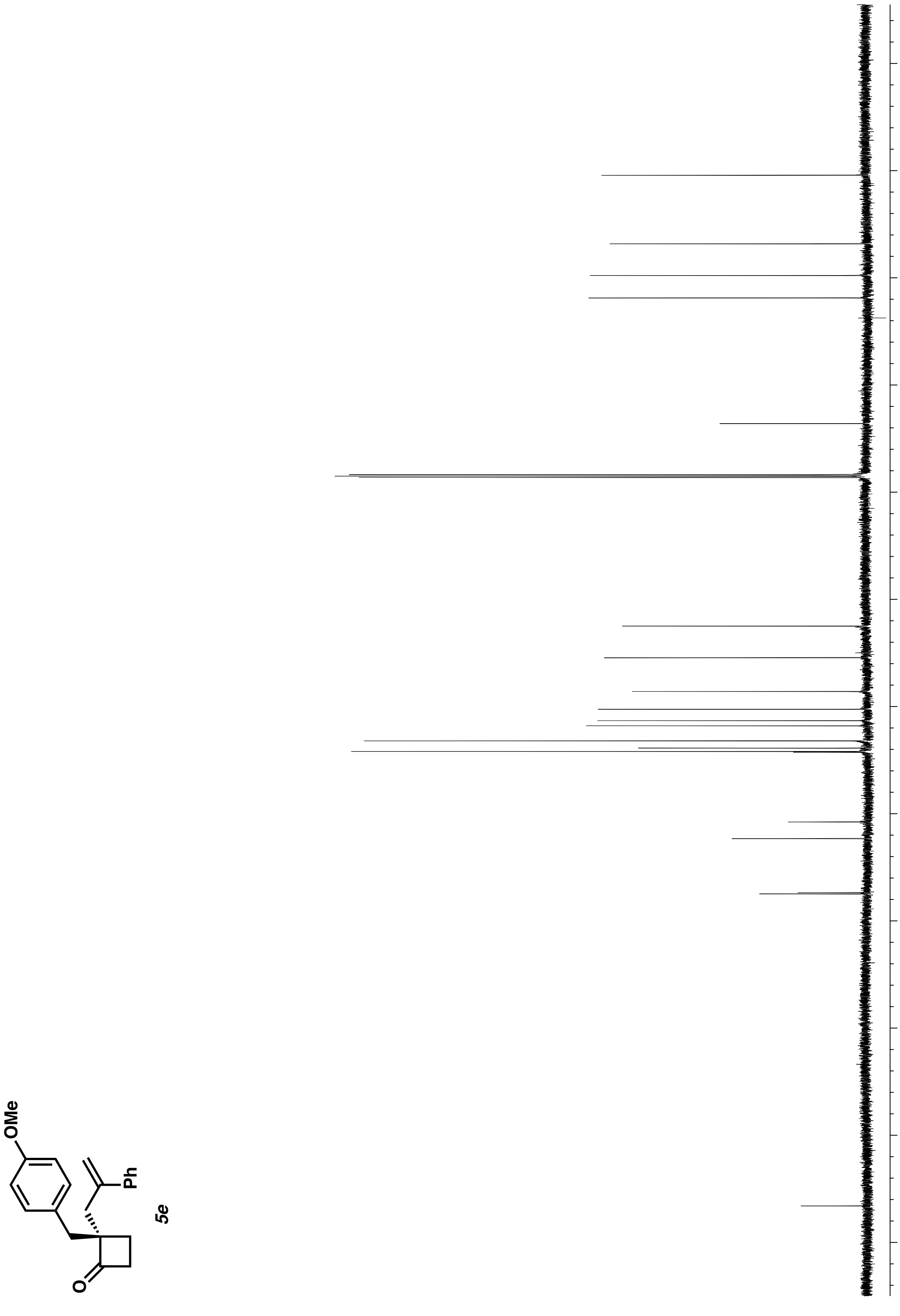
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5d**.



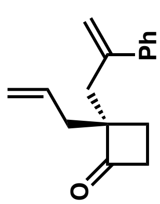
5e



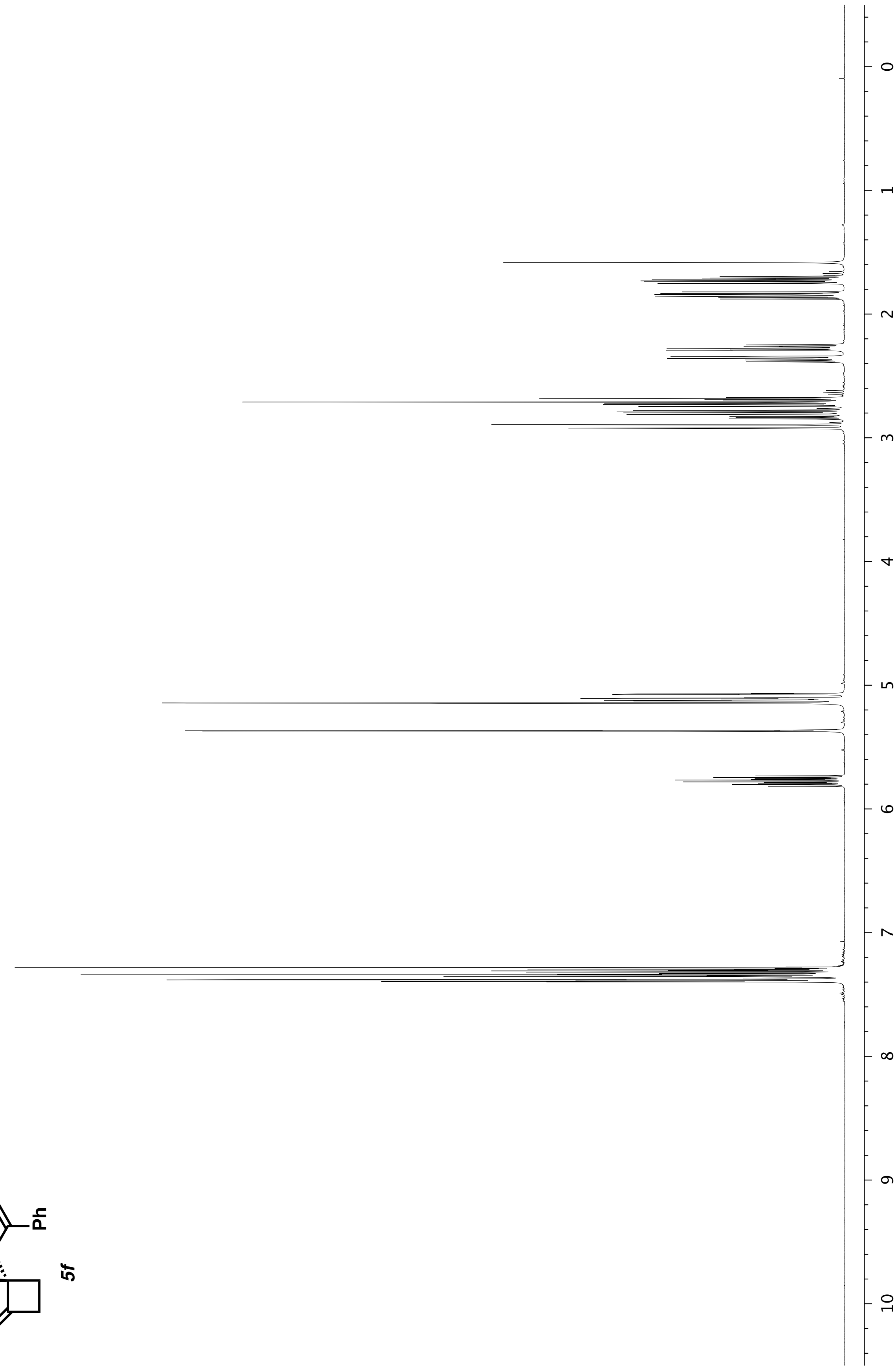
[1]H NMR (500 MHz, $CDCl_3$) of compound **5e**.



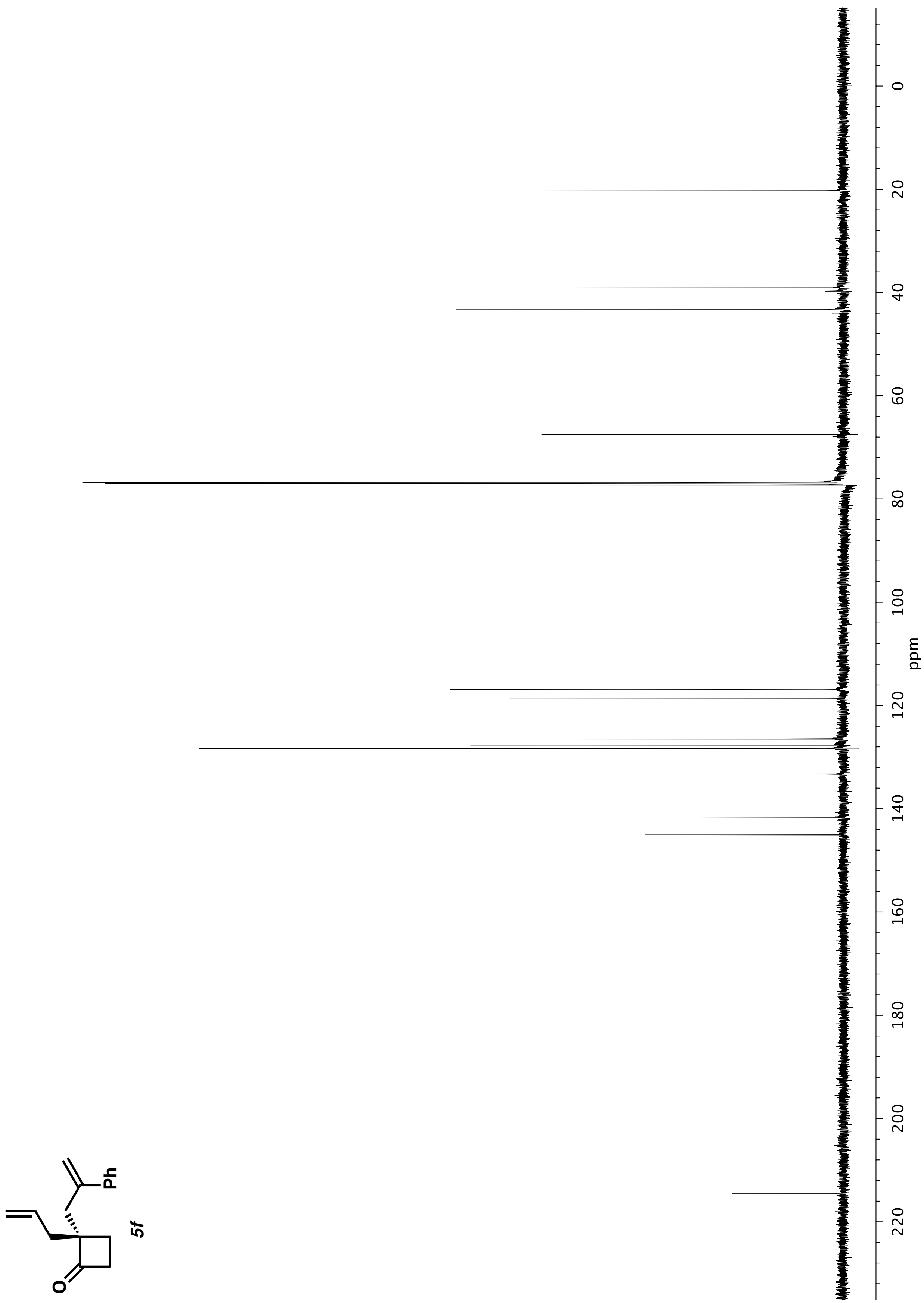
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5e**.



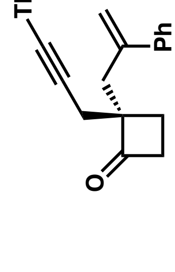
5f



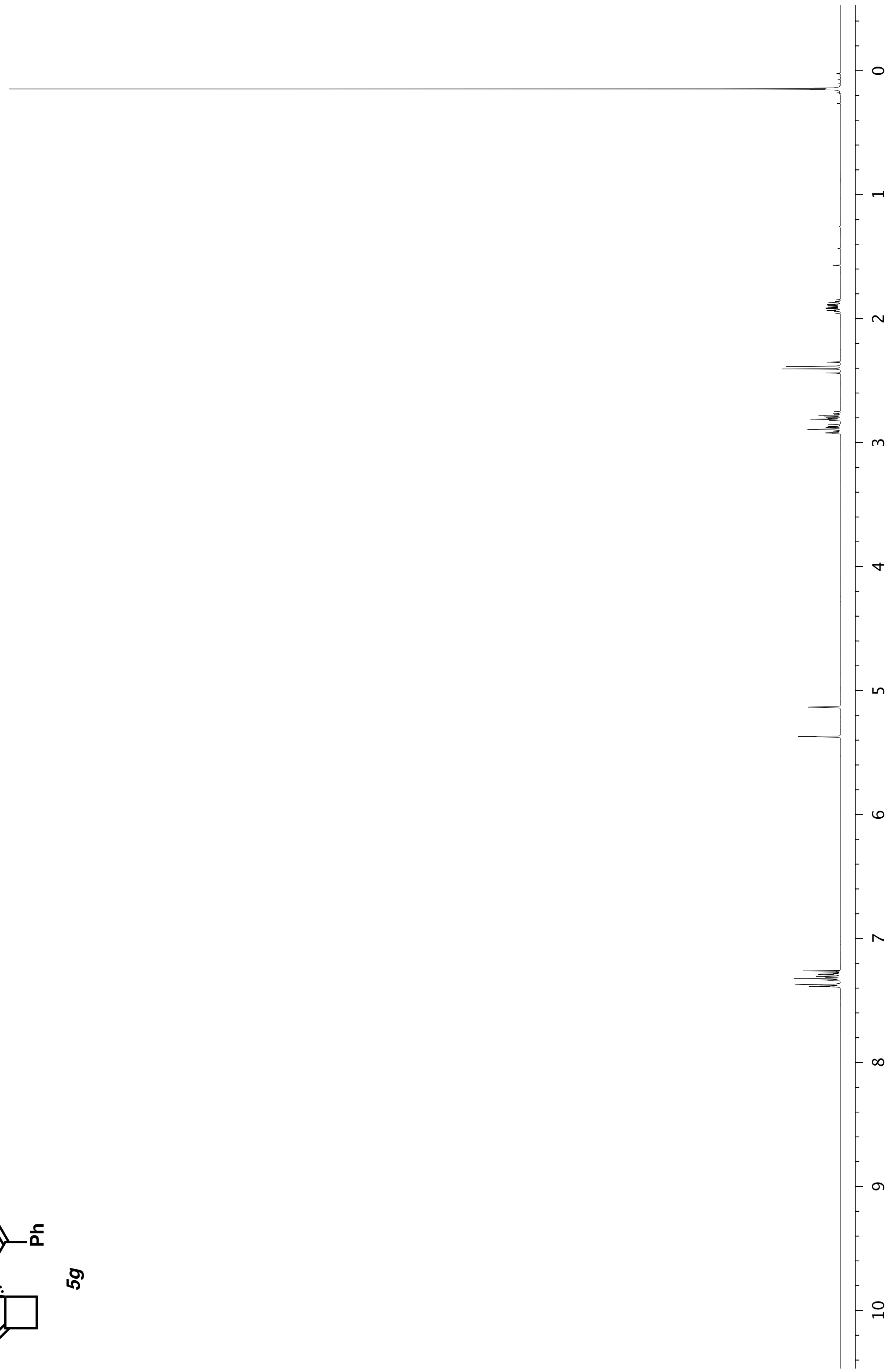
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5f**.



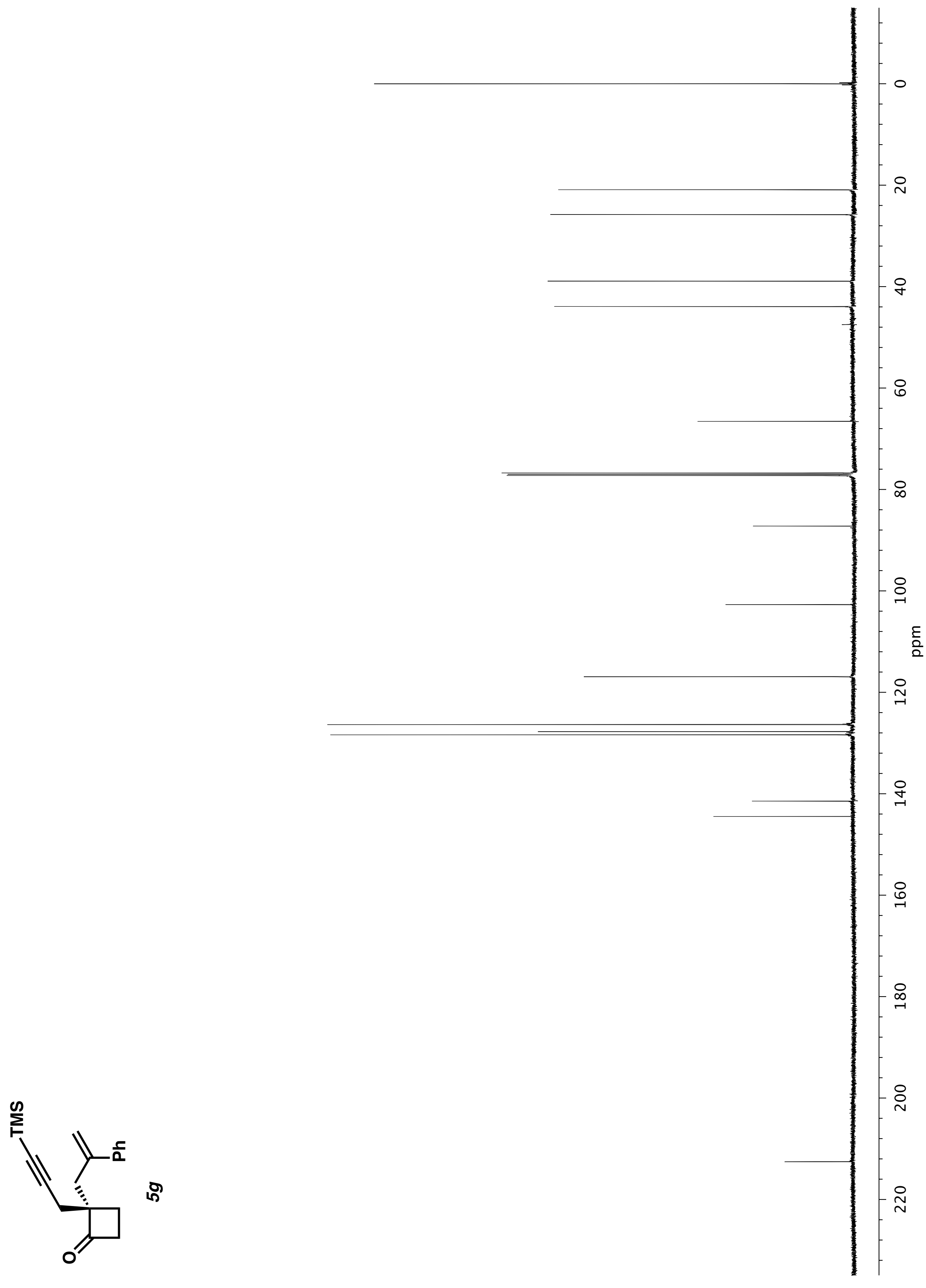
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5f**.



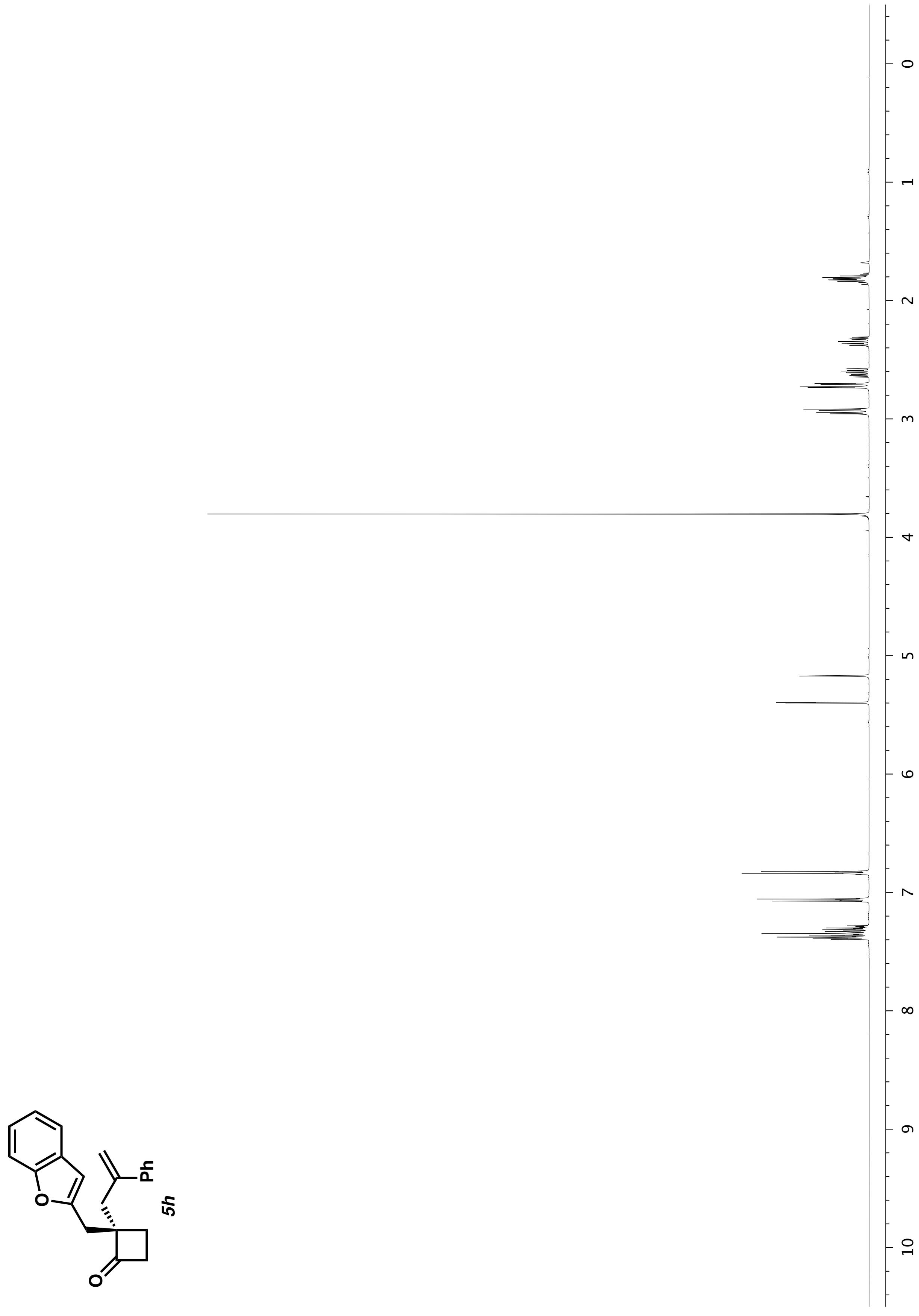
5g



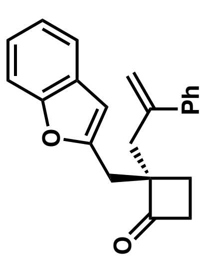
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5g**.



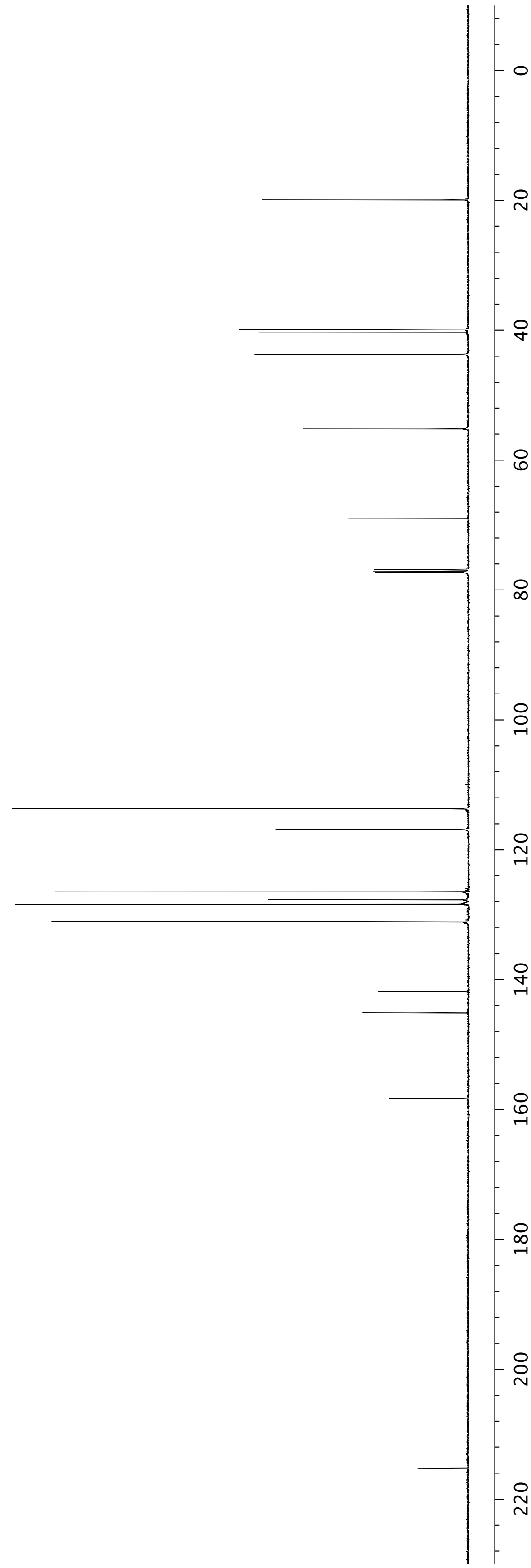
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5g**.



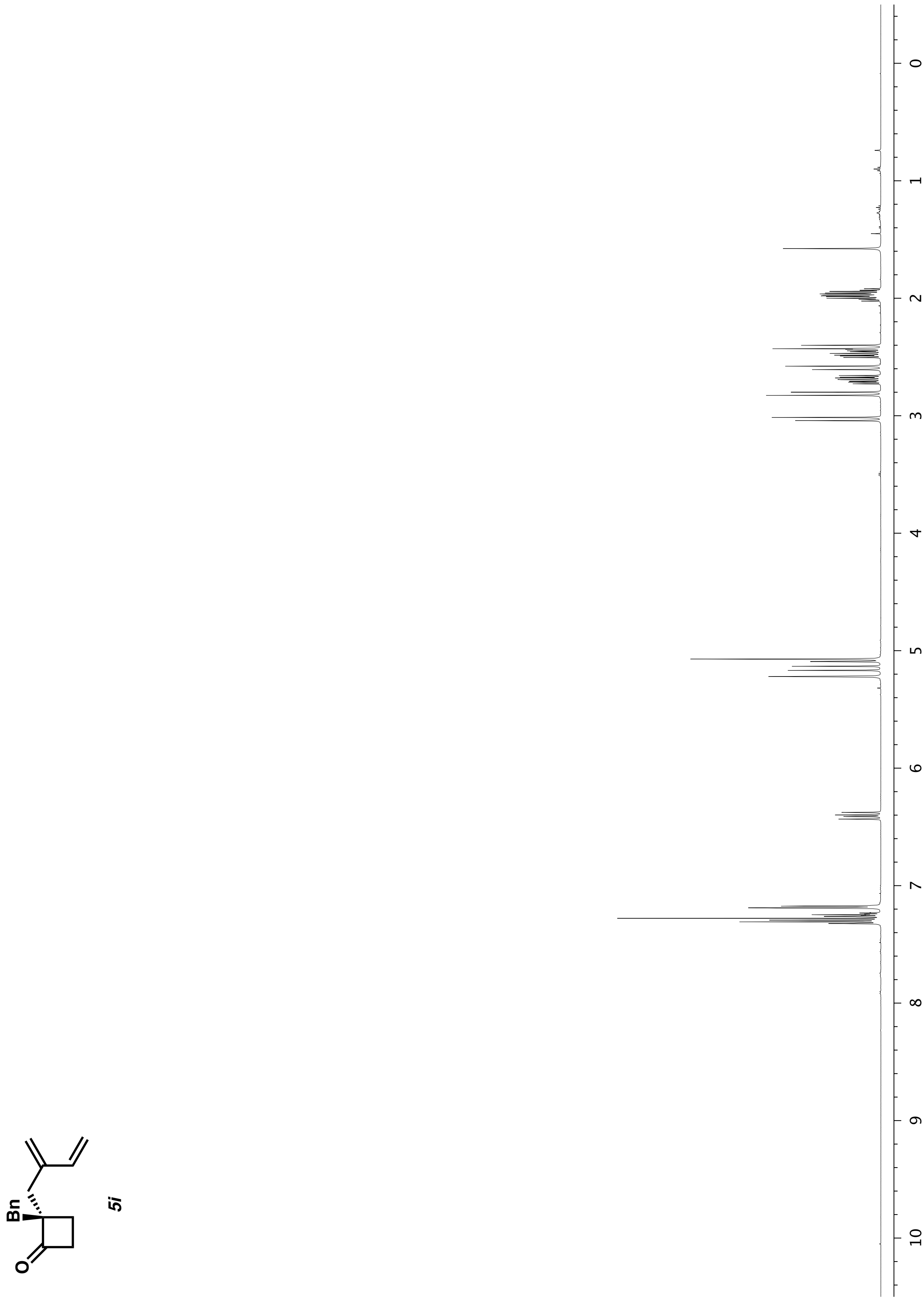
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**.



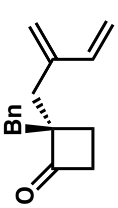
5h



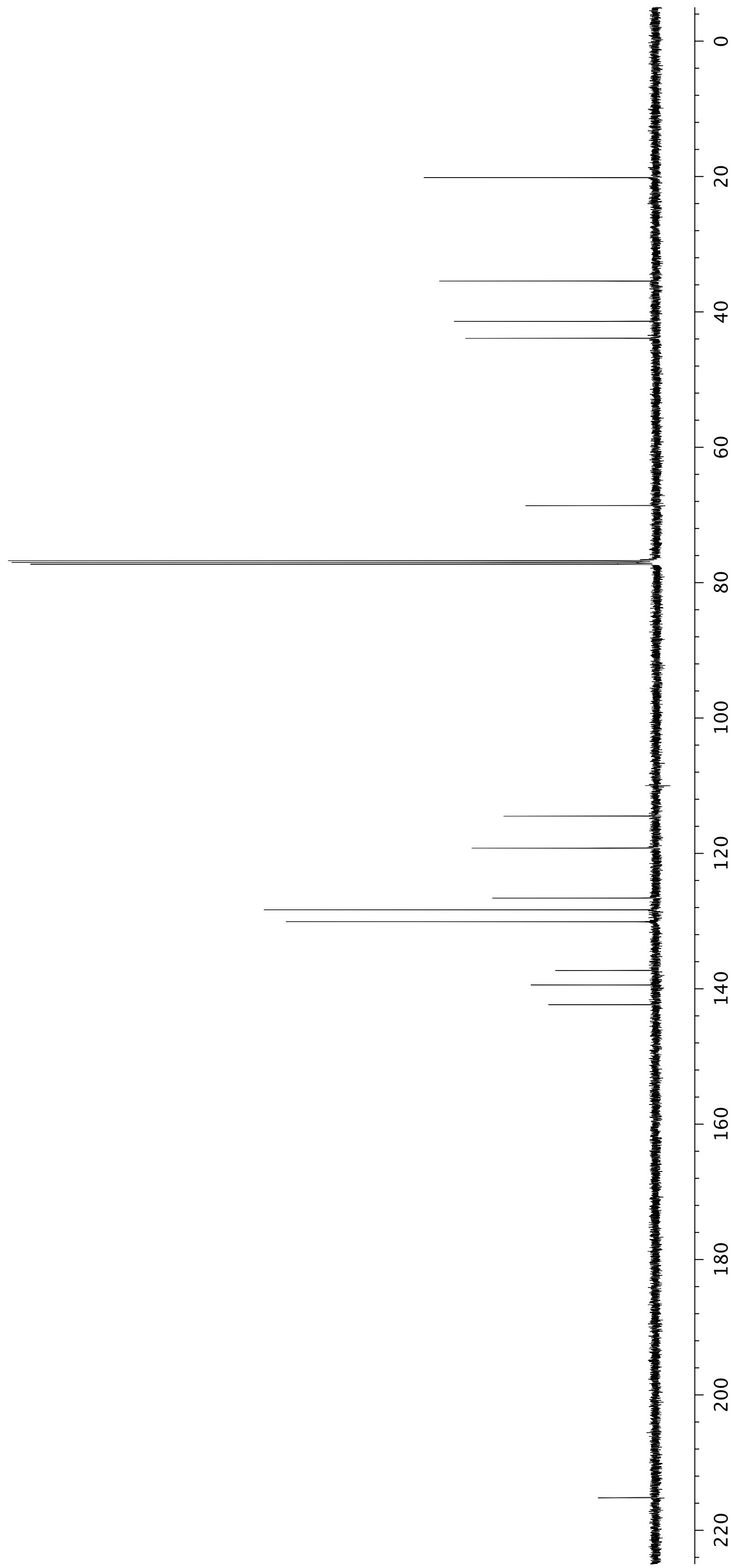
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5h**.



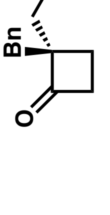
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5i**.



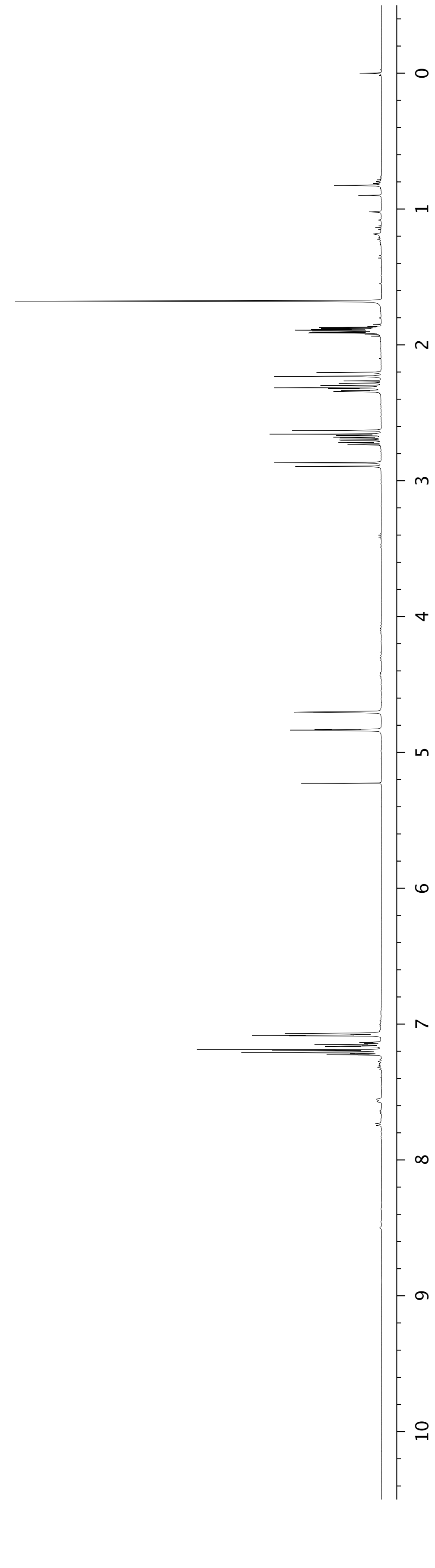
5i



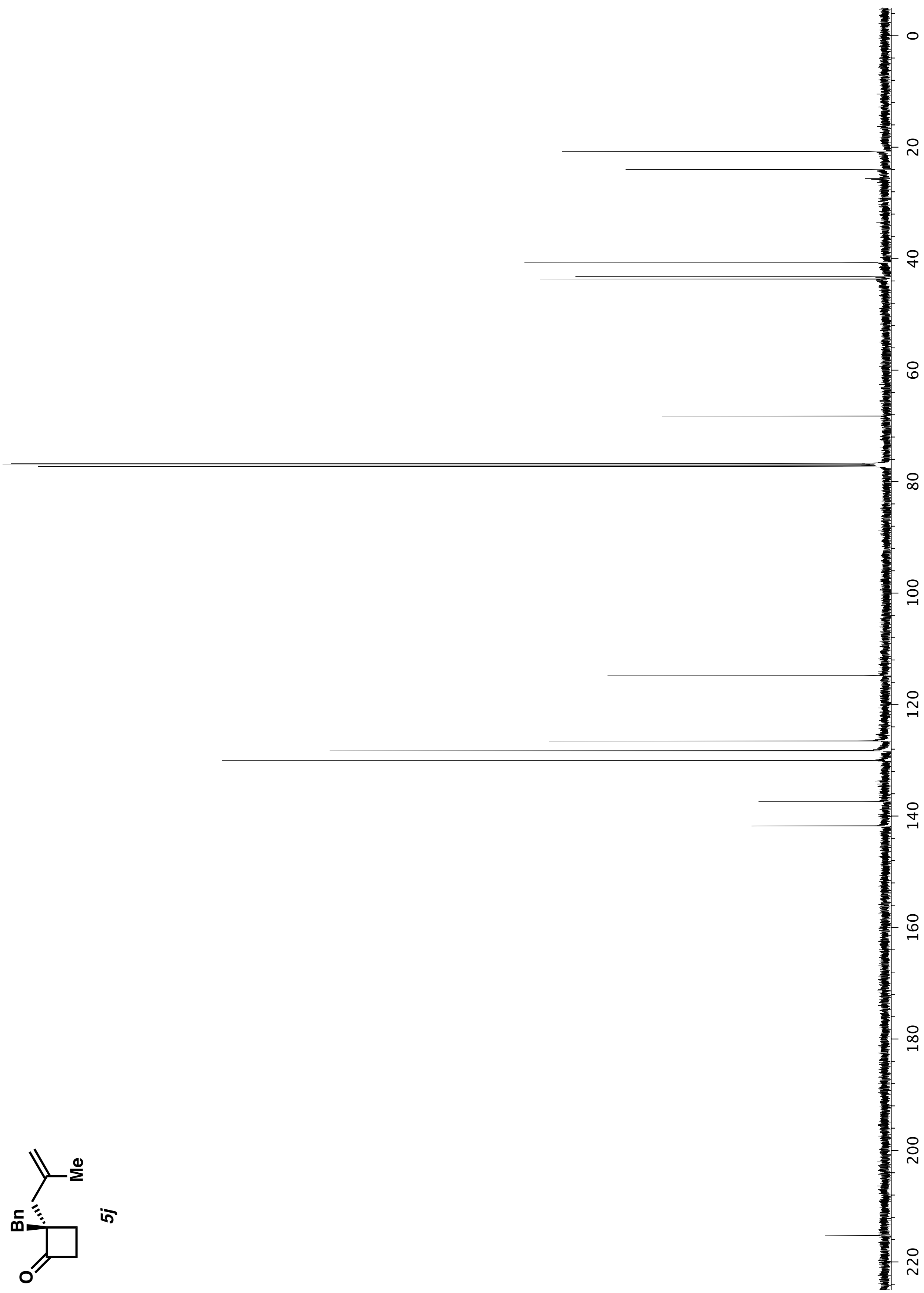
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5i**.



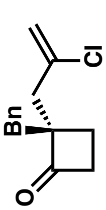
5j



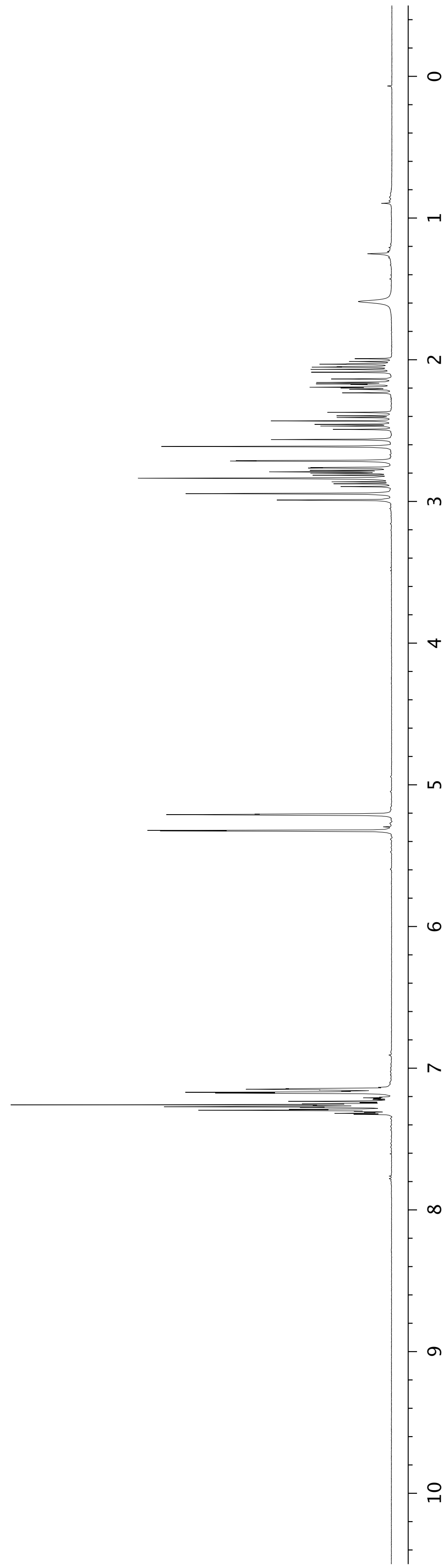
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5j**.



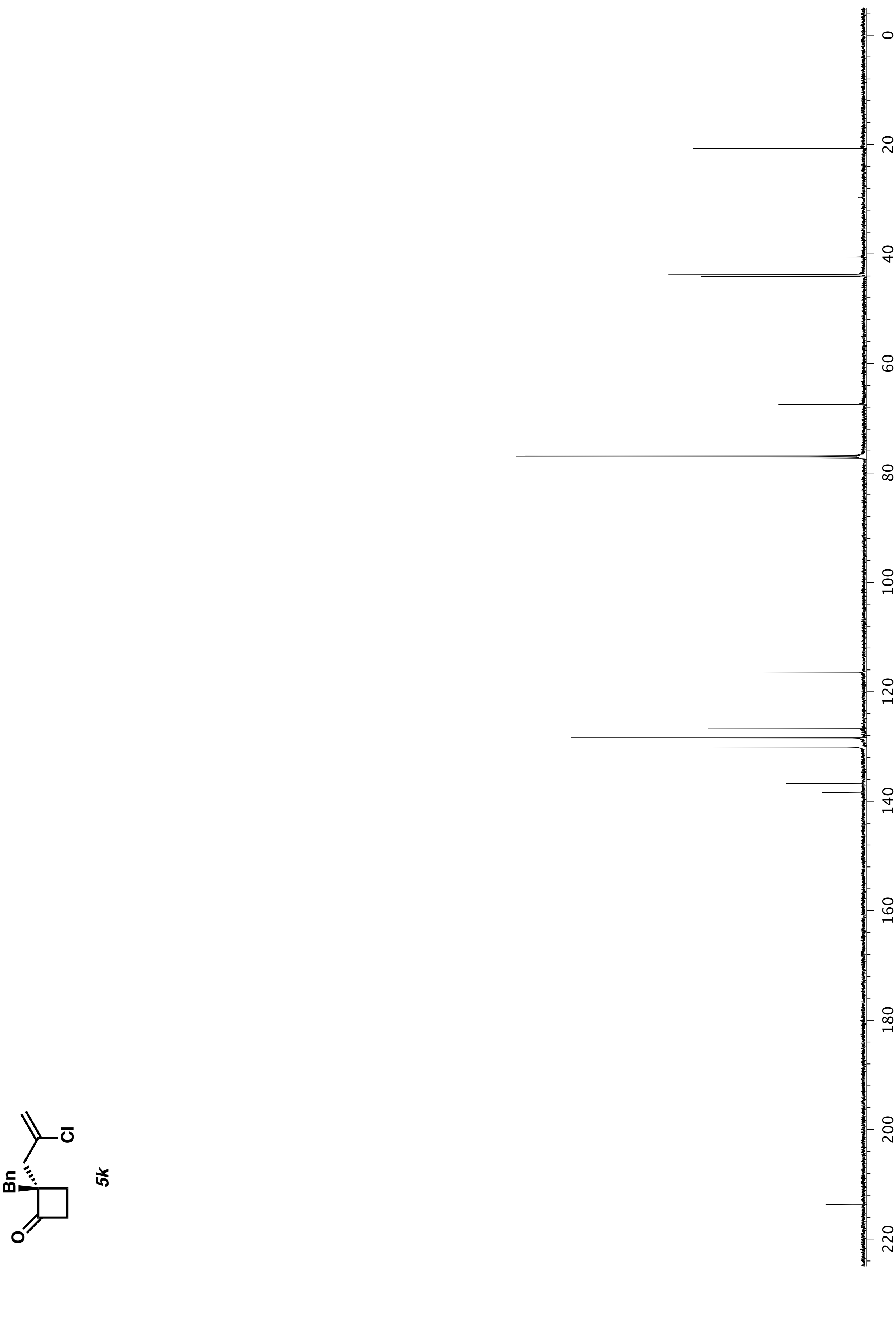
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5j**.



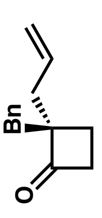
5k



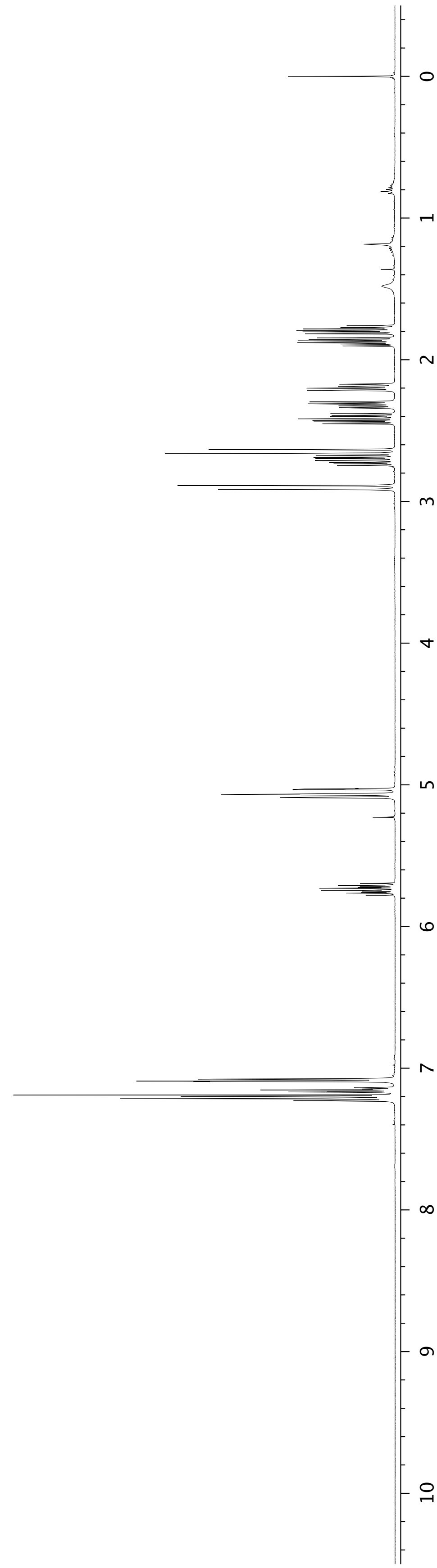
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5k**.



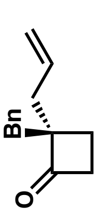
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5k**.



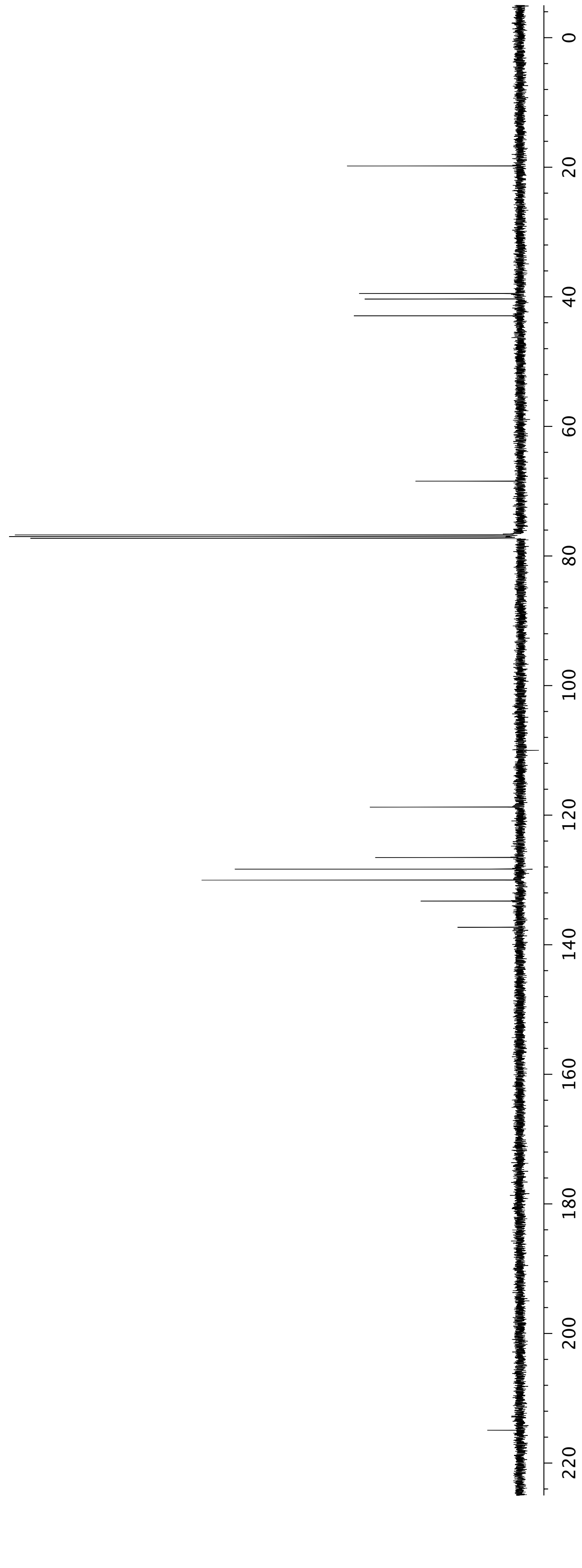
5l



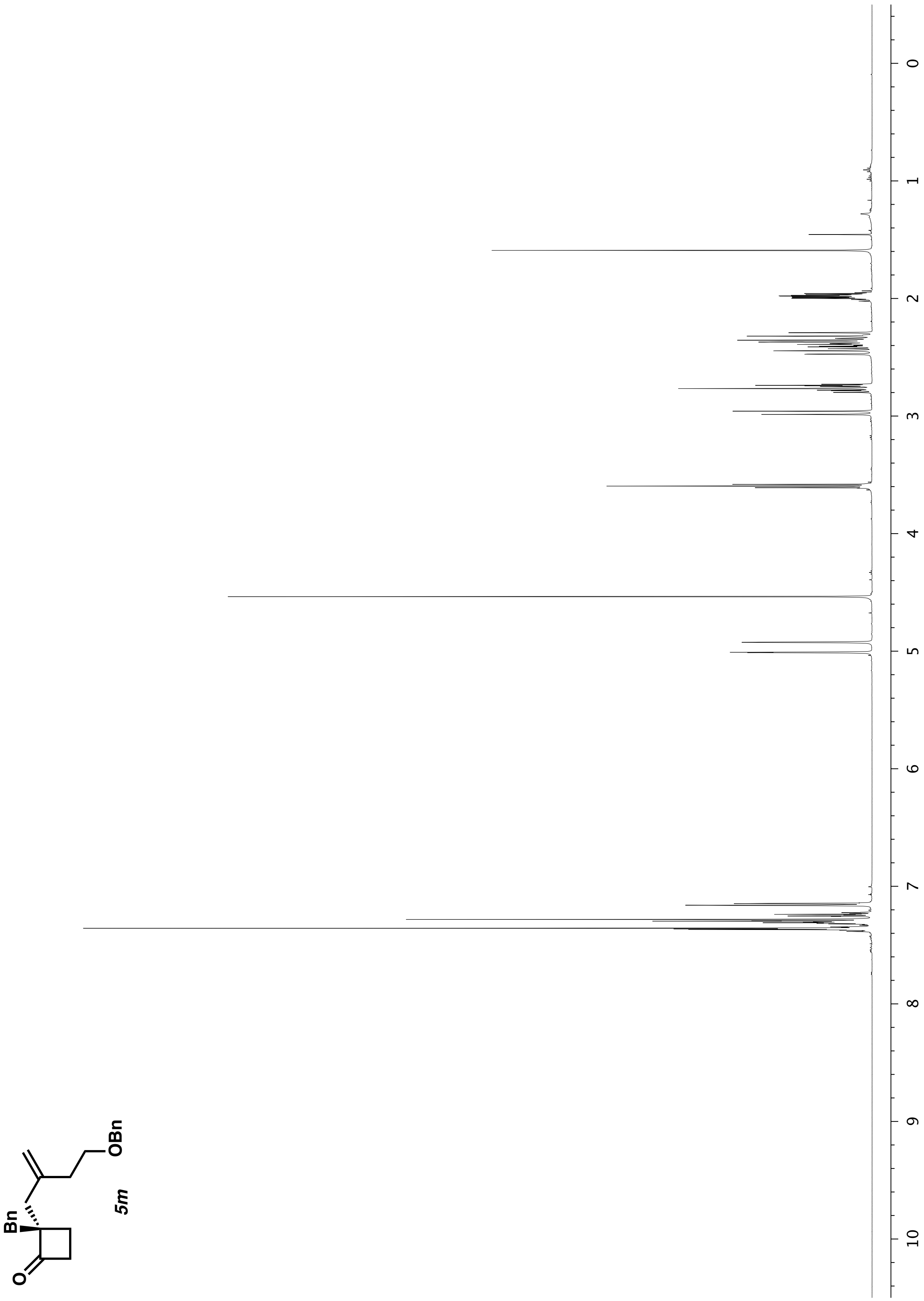
^1H NMR (500 MHz, $CDCl_3$) of compound **5l**.



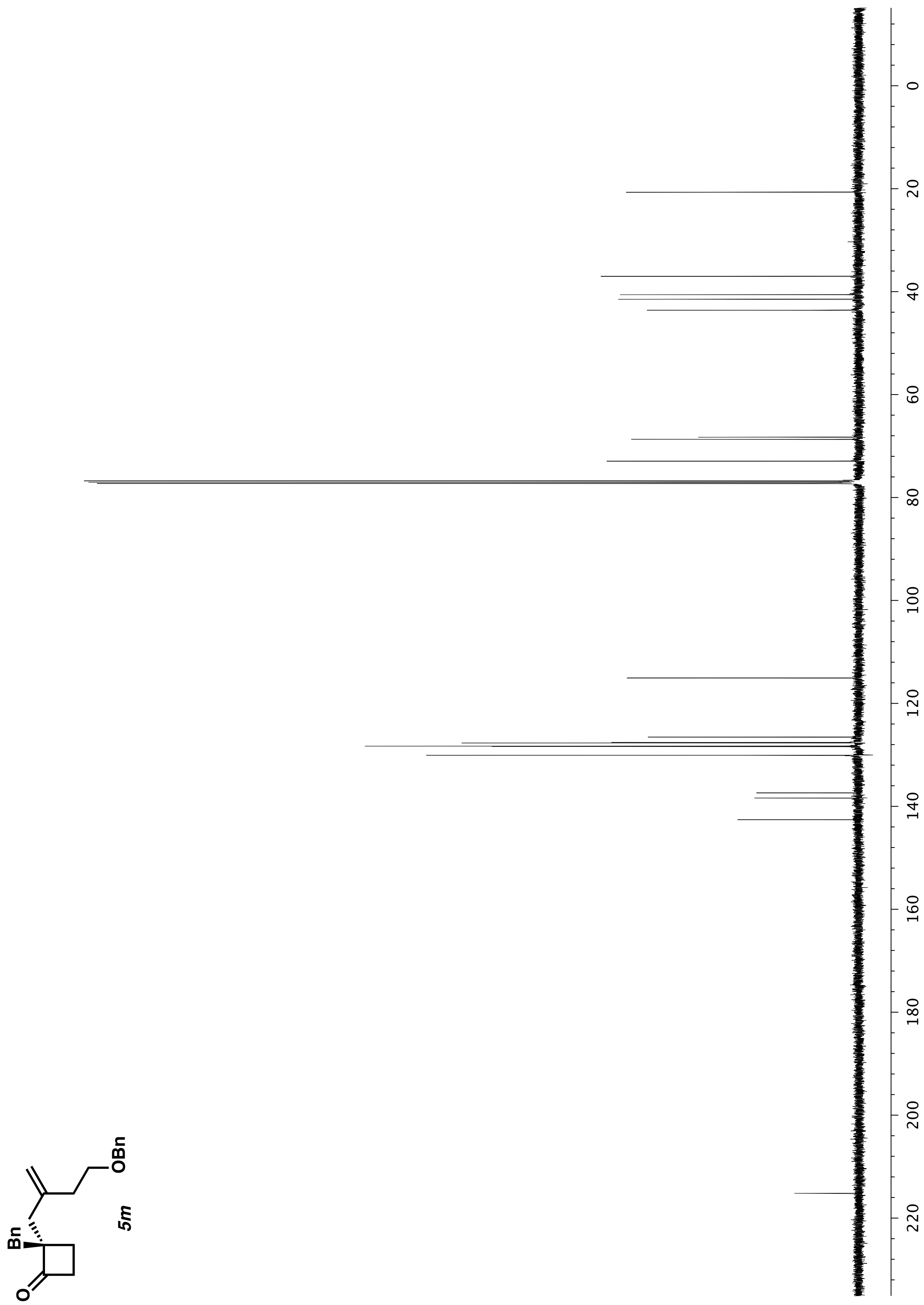
5l



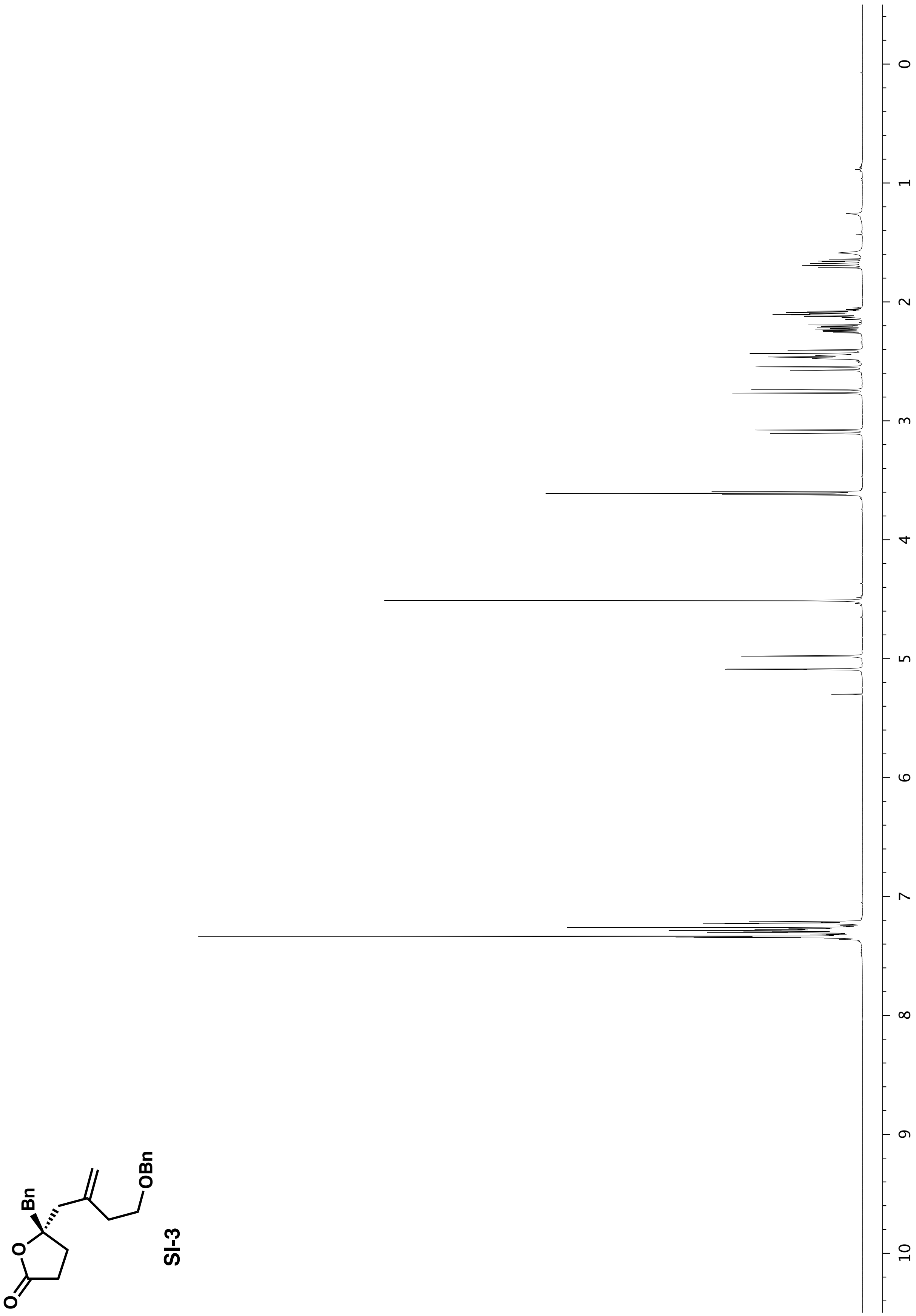
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5l**.



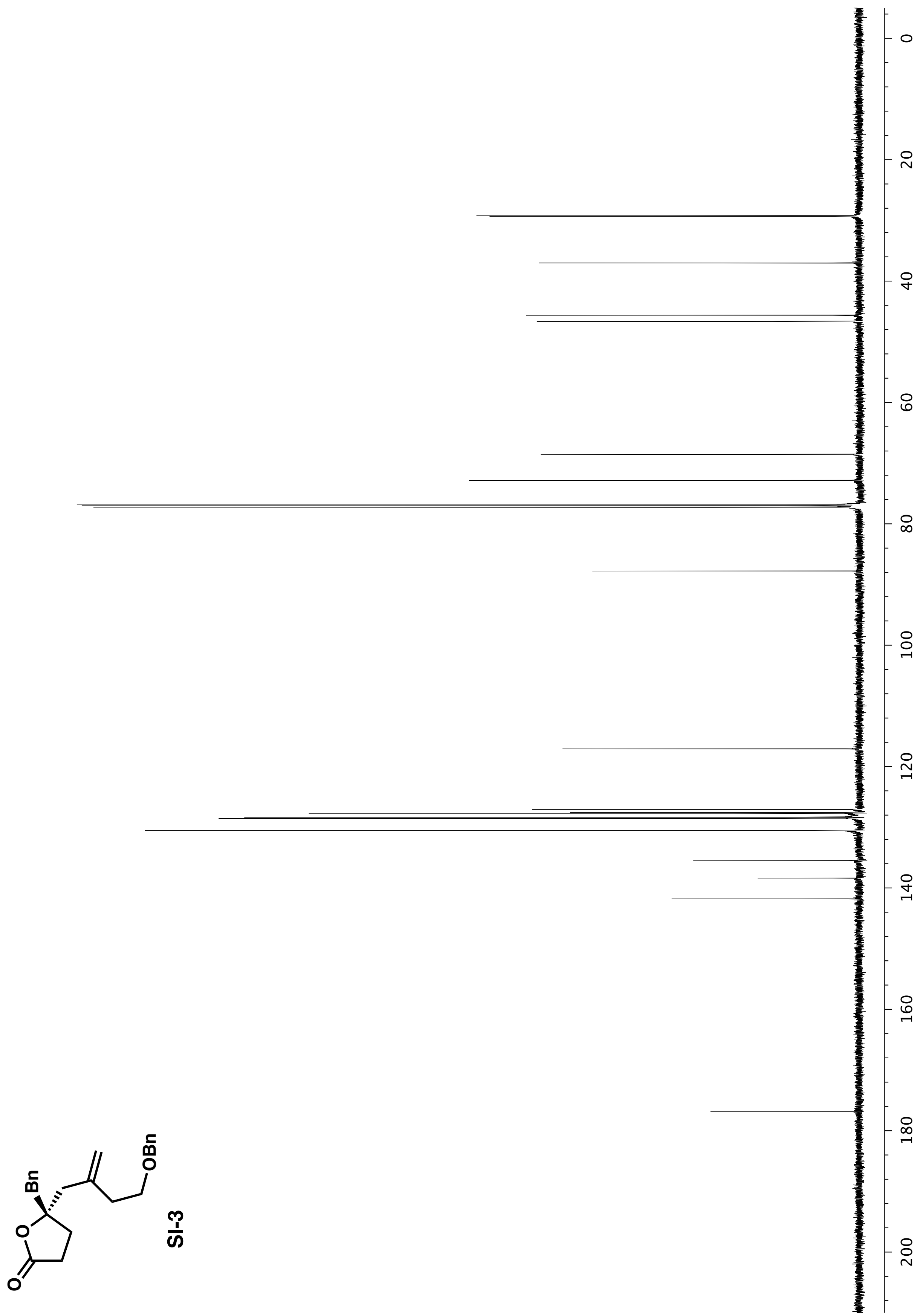
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5m**.



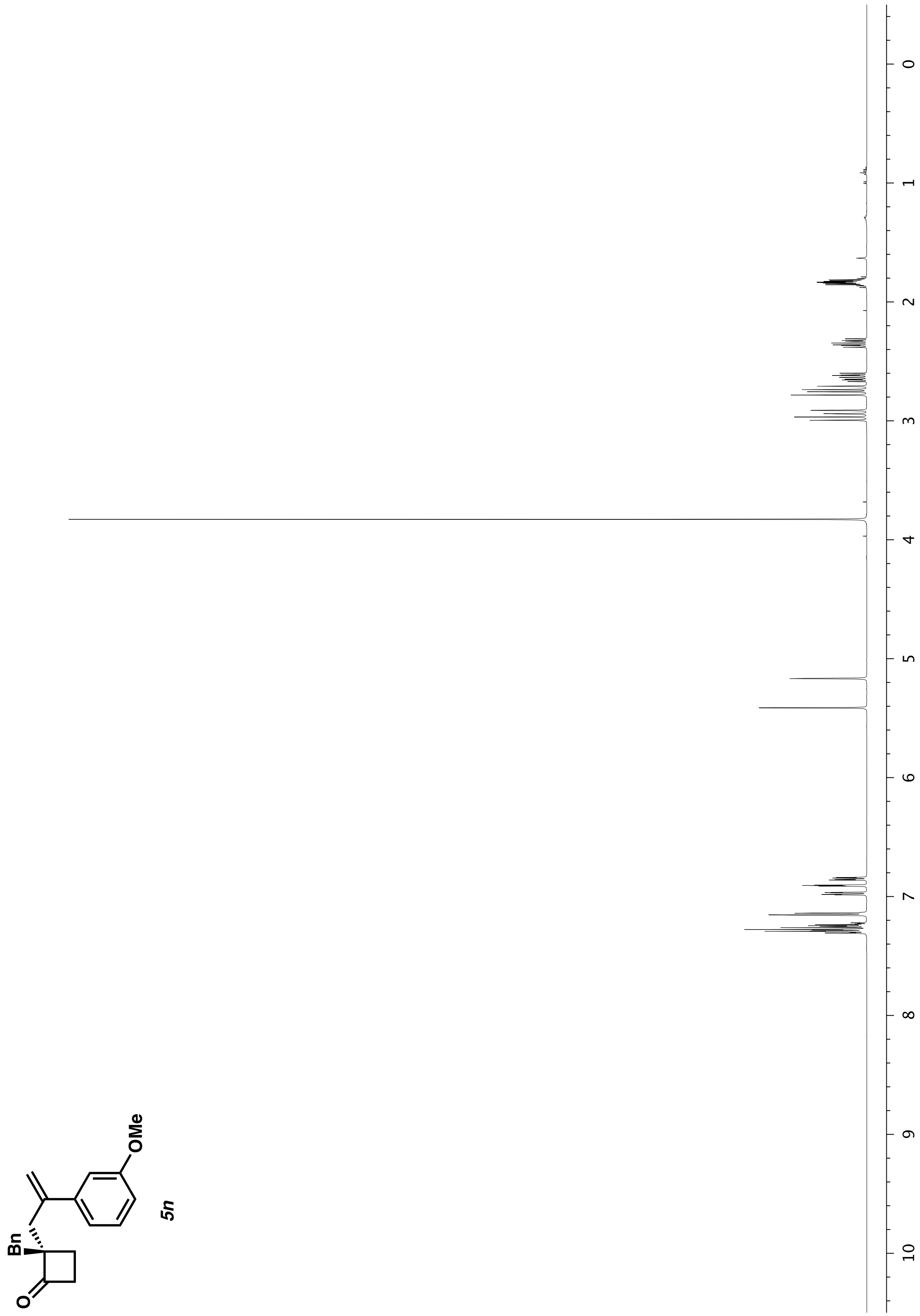
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5m**.



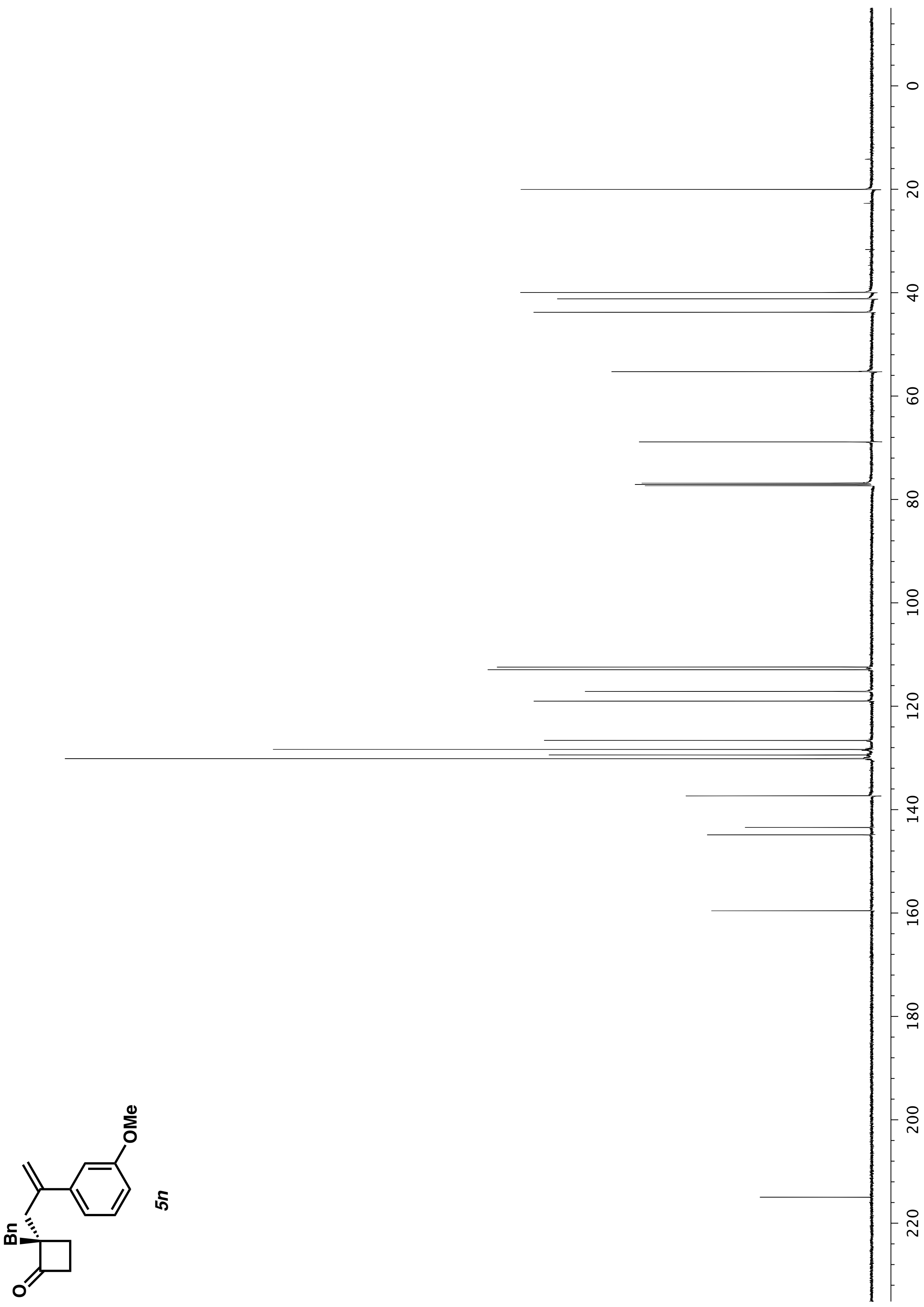
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-3**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-3**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5n**.



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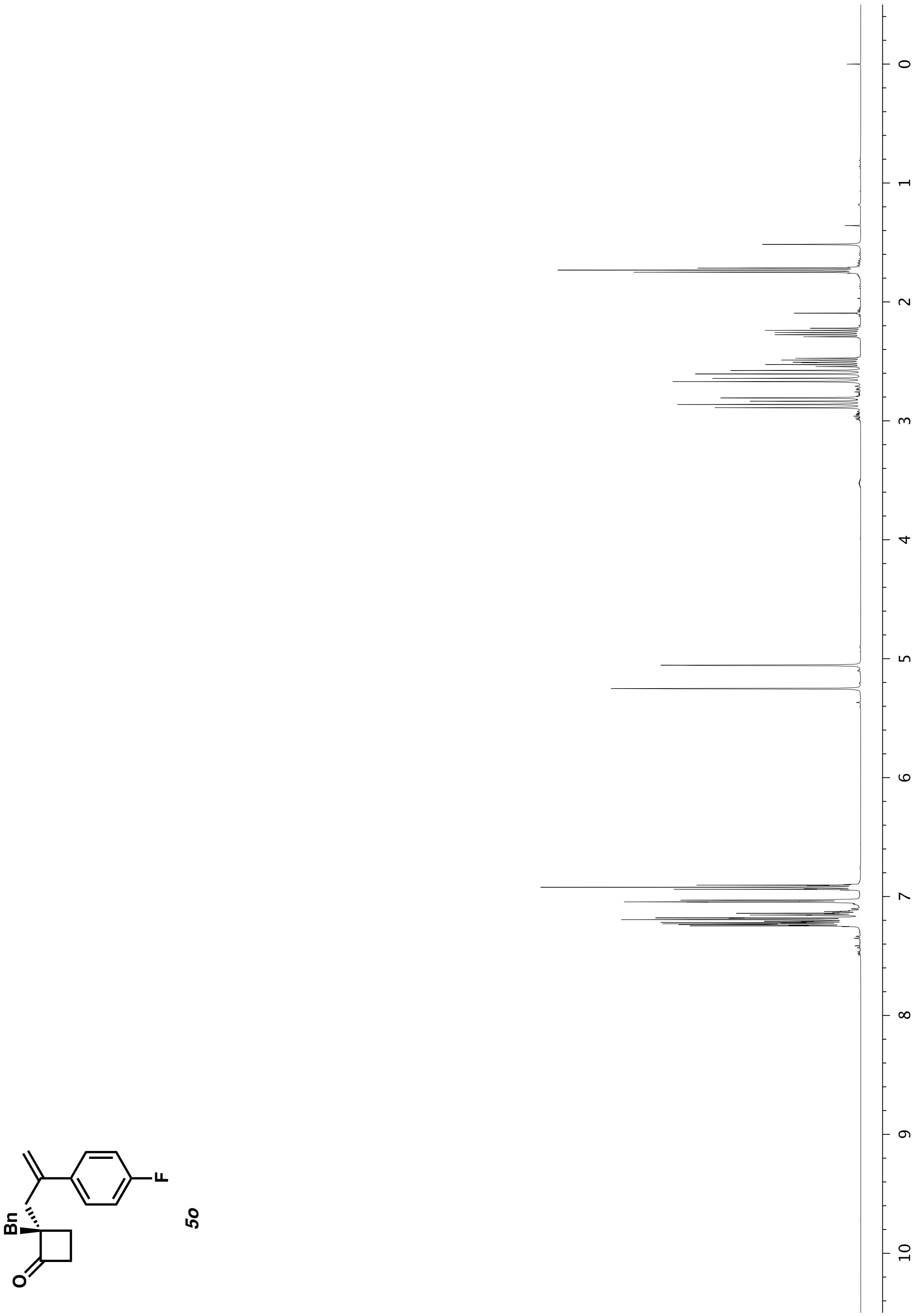
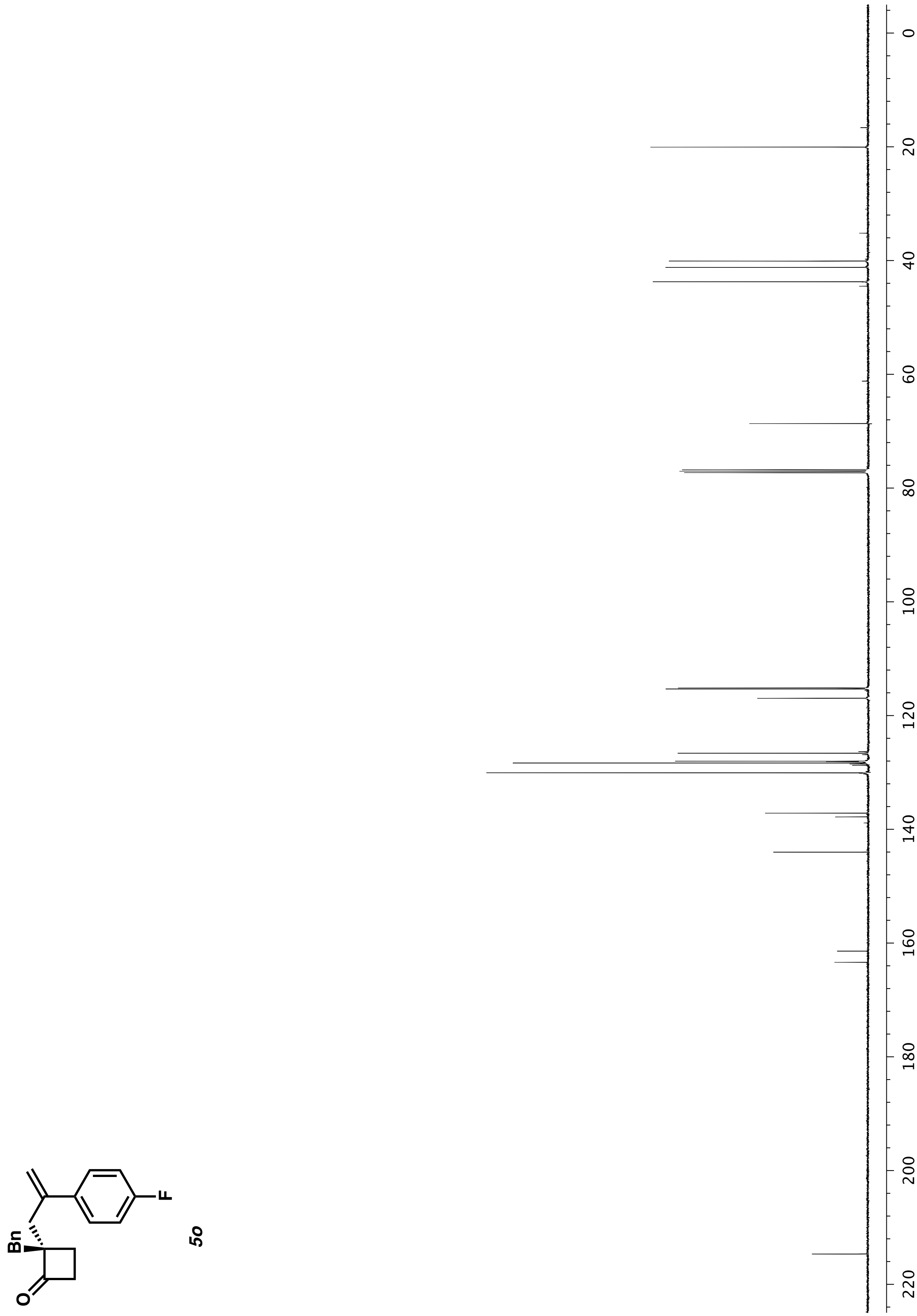
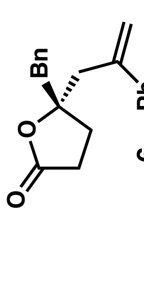


^{1}H NMR (500 MHz, $CDCl_3$) of compound **5o**.

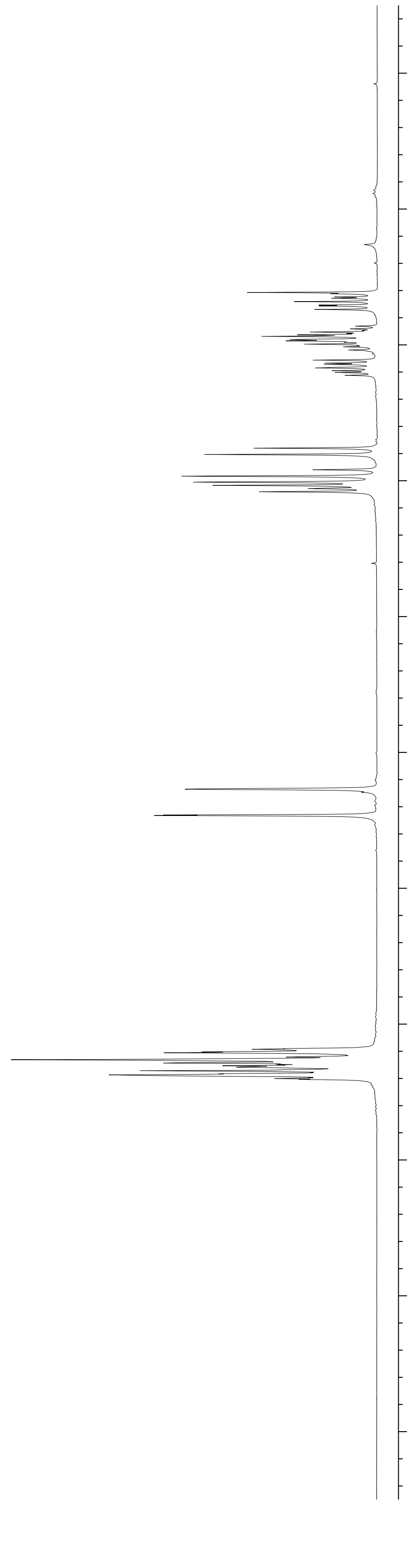


5o

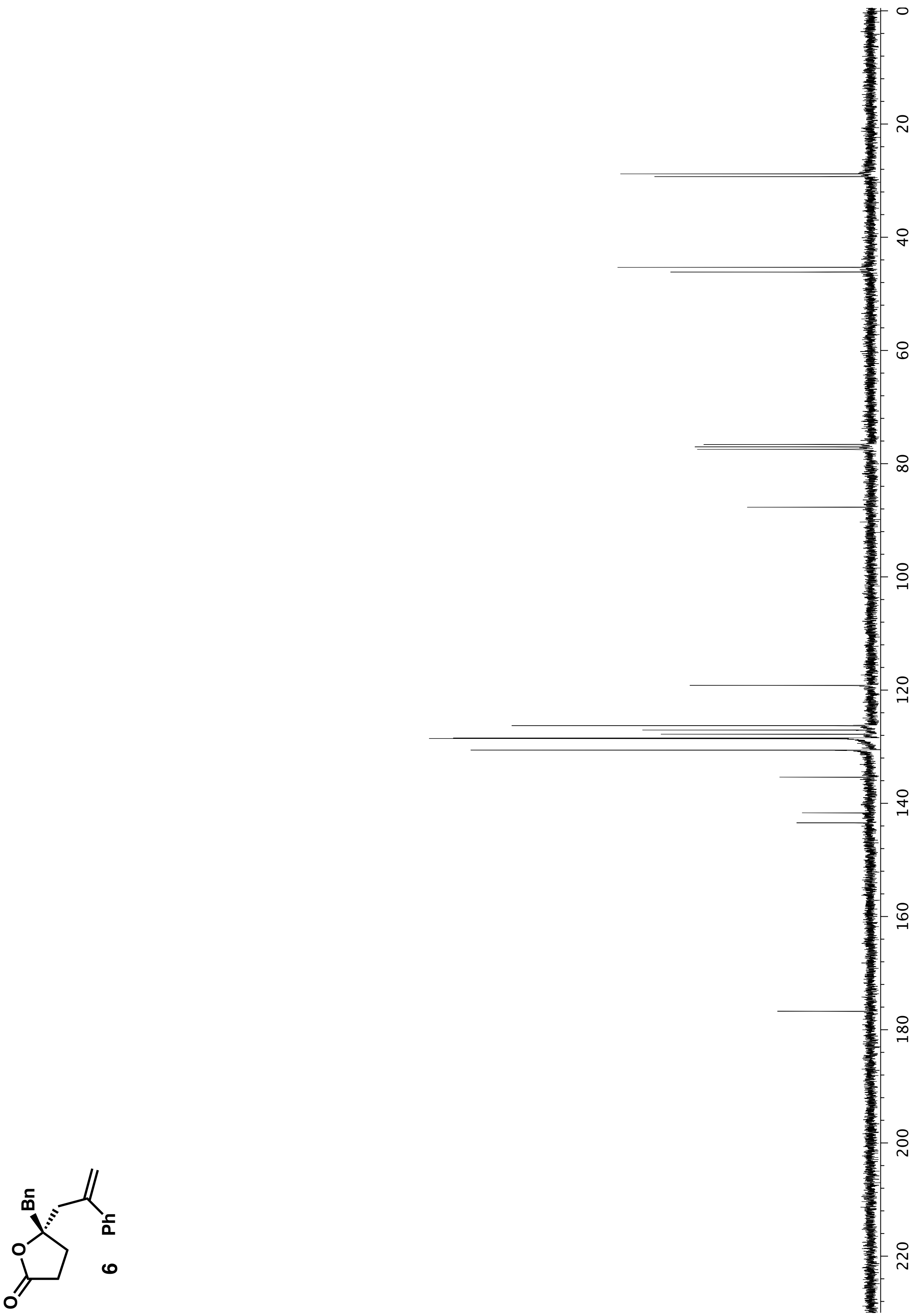
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5o**.



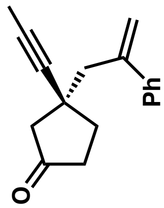
6



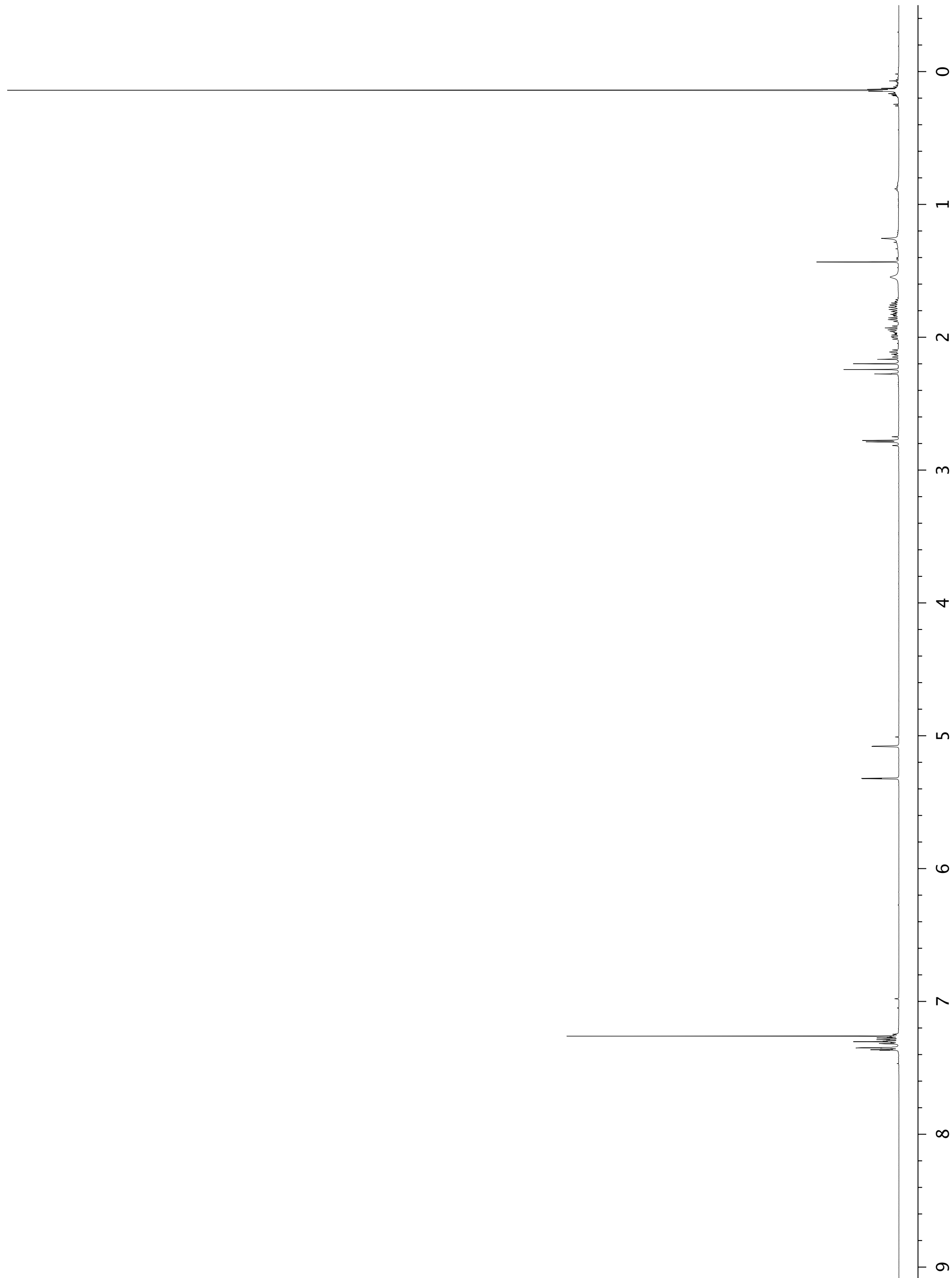
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



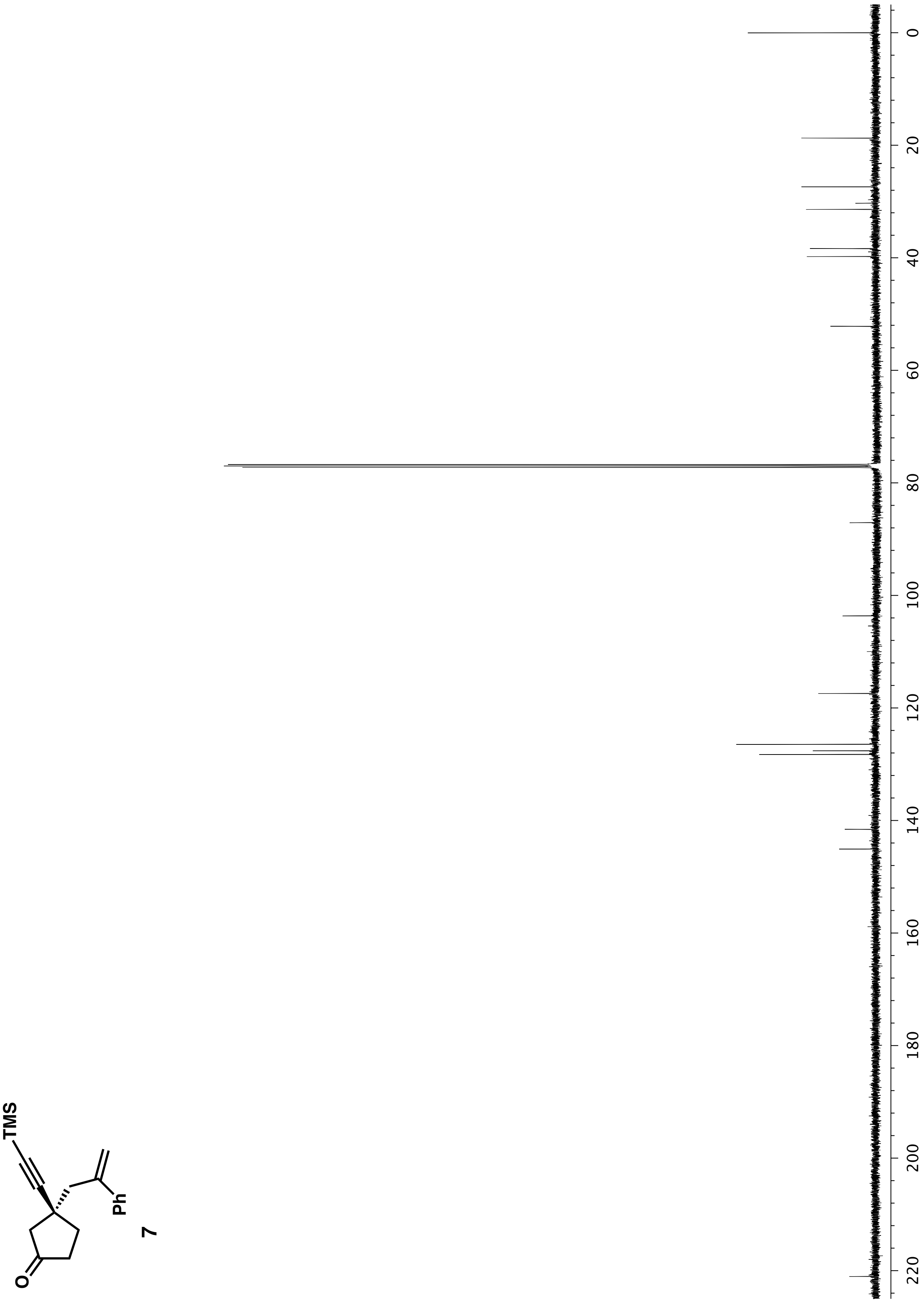
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**.



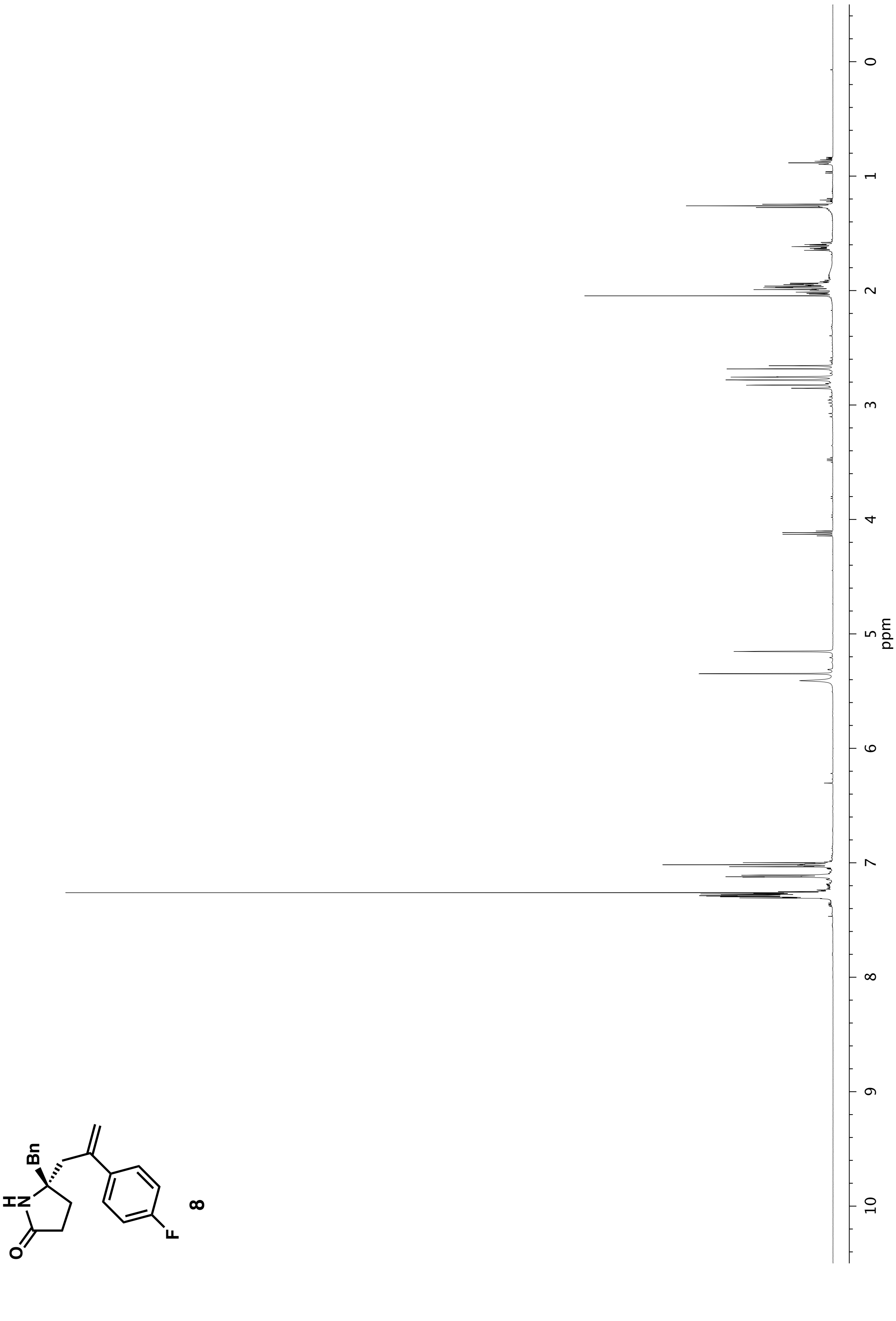
7



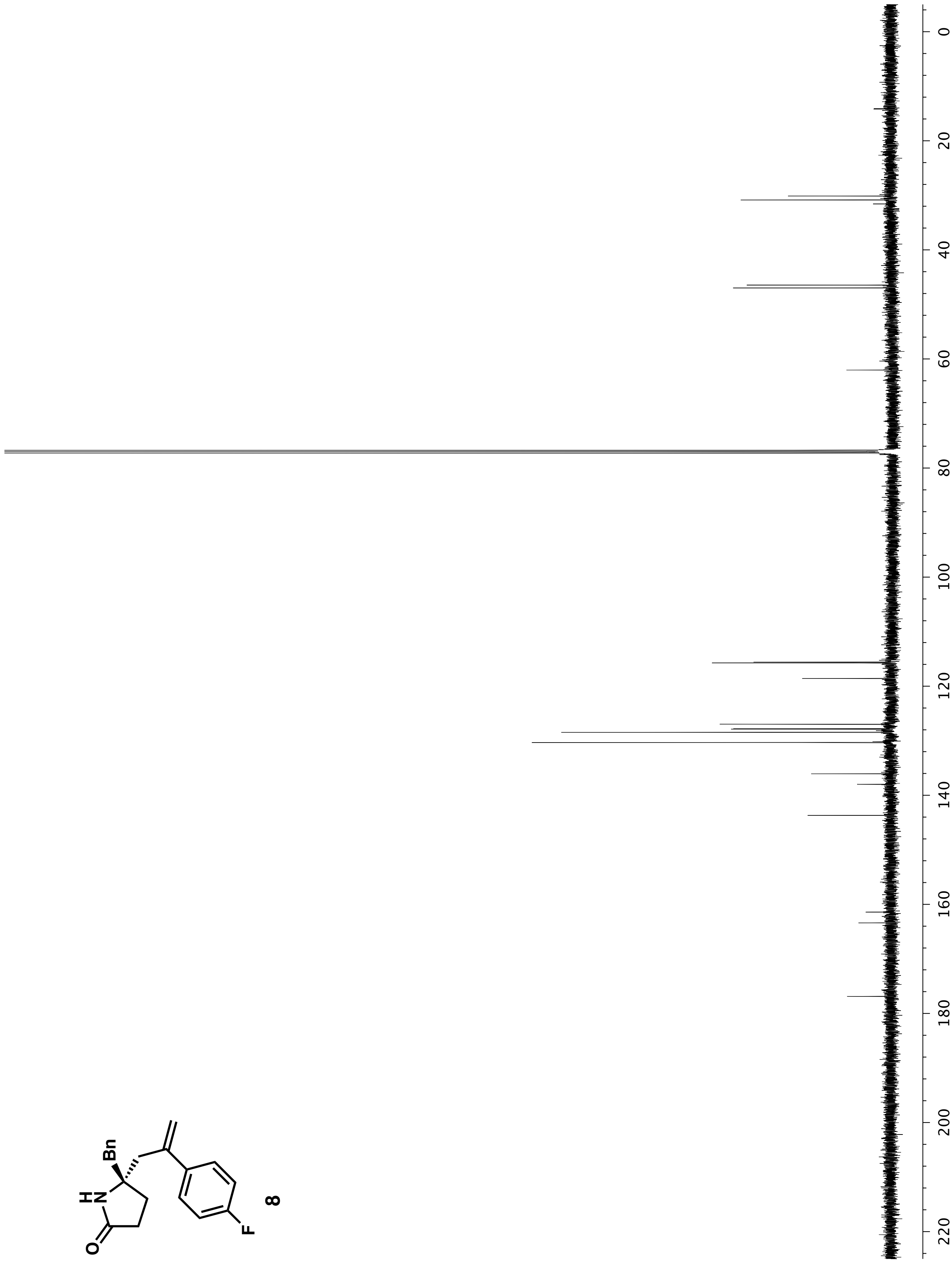
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.



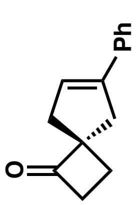
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**.



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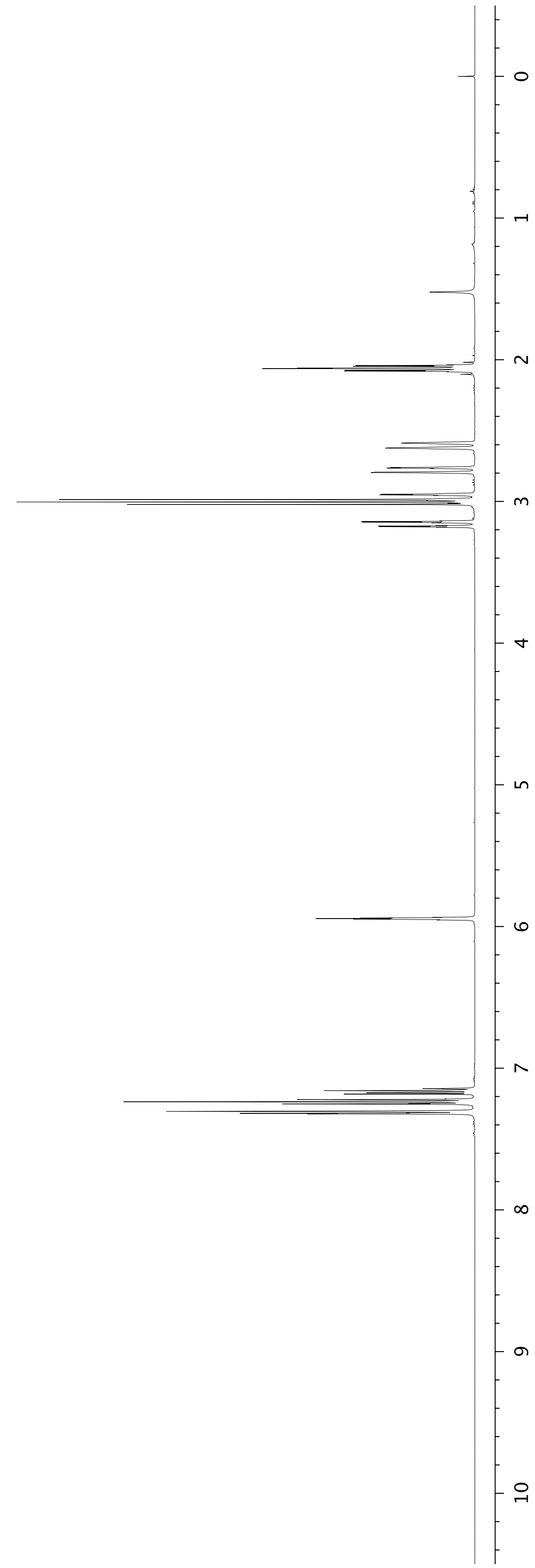
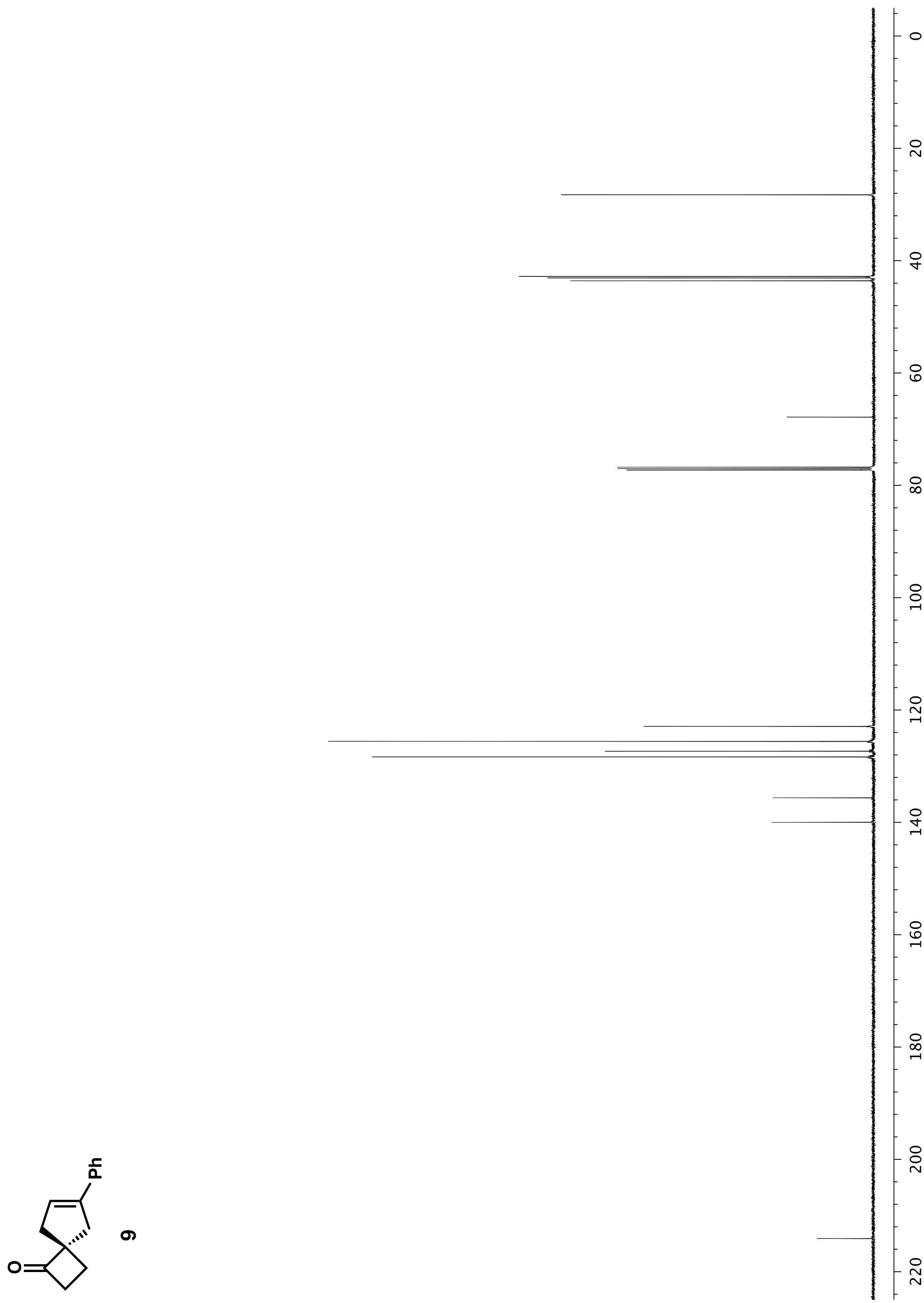
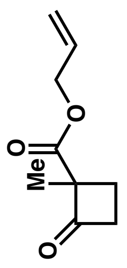


^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **9**.



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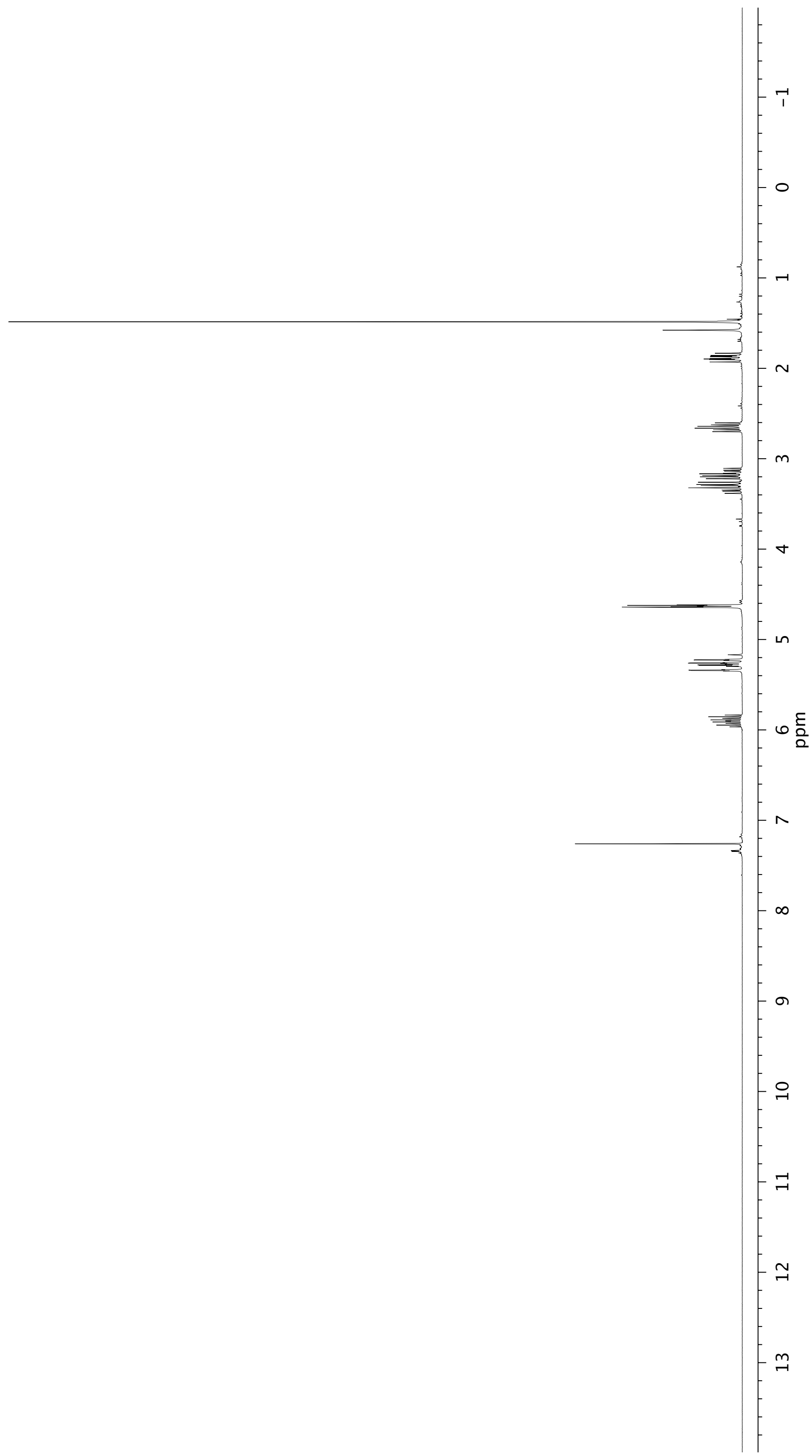
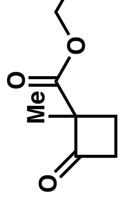


^{1}H NMR (300 MHz, $CDCl_3$) of compound **12**.



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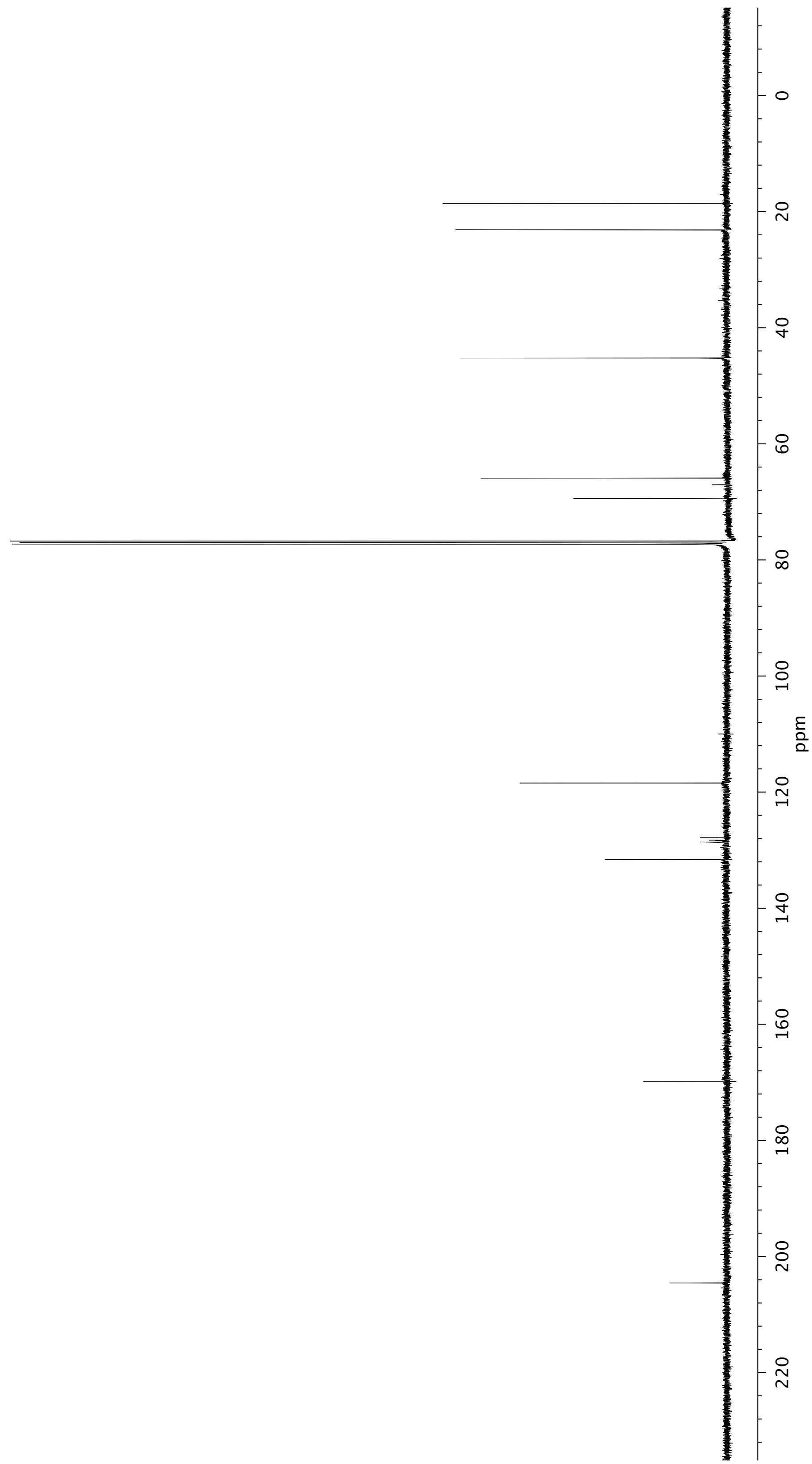
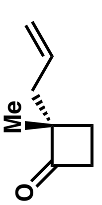


^{13}C NMR (126 MHz, $CDCl_3$) of compound **12**.



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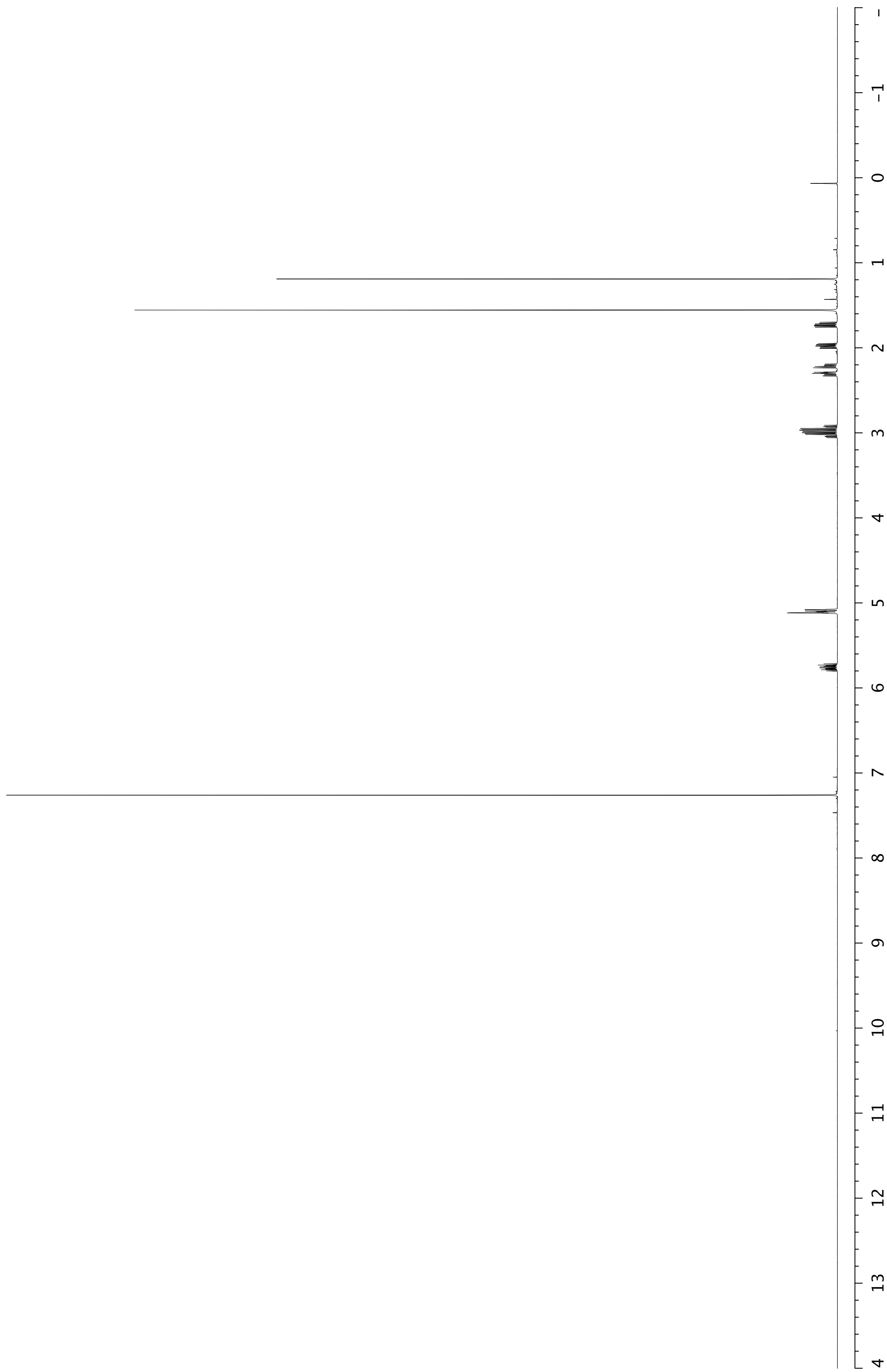
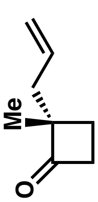


^{1}H NMR (500 MHz, $CDCl_3$) of compound **13.**



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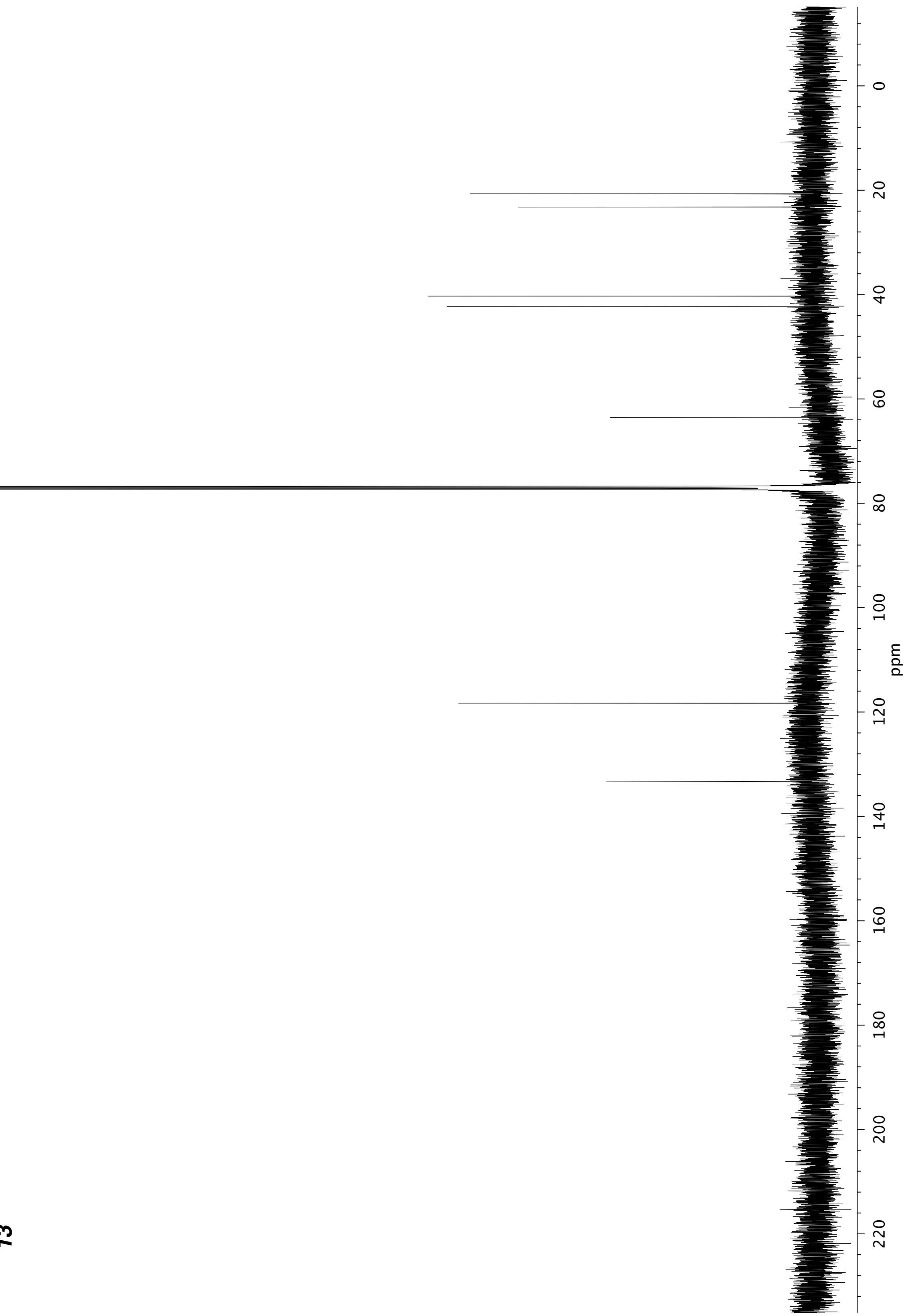

^{13}C NMR (126 MHz, $CDCl_3$) of compound **13**.