Supporting Information

General Information

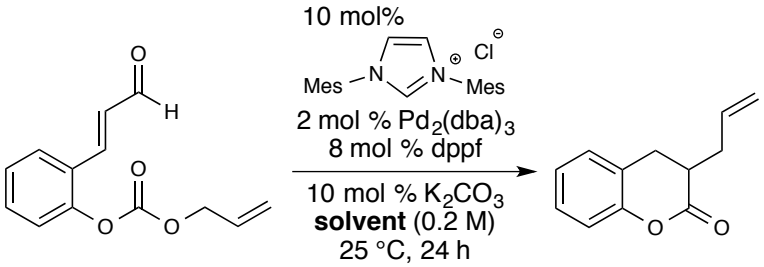
All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. CH_2Cl_2, THF, and toluene were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent or Silicycle silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and potassium permanganate stain followed by heating. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 500 MHz w/ direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, d_6-DMSO at 2.50 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker Avance 500 MHz w/ direct cryoprobe (126 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm, d_6-DMSO at 39.5 ppm). ^{31}P-NMR spectra were recorded on a 400 MHz Agilent 400MR-DD2 spectrometer equipped with an OneNMR probe and a 7600AS autosampler. Mass spectra data were obtained on a Gas Chromatography Mass Spectrometer (Agilent 7890A/5975C GCMS System).

(E)-3-(2-hydroxyphenyl)acrylaldehyde derivatives were prepared according to reported protocol.[3]

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.
[2] D. D. Perrin, W. L. Armarego, *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.
[3] L. Zu, S. Zhang, H. Xie, W. Wang, *Org. Lett.* **2009**, *11*, 1627.
[4] A. M. Sawayama, H. Tanaka, T. J. Wandless, *J. Org. Chem.* **2004**, *69*, 8810.
[5] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Pure. Appl. Chem.* **1999**, *71*, 1443.
[6] M. Murakata, T. Jono, T. Shoji, A. Moriya, Y. Shirai, *Tetrahedron Asymmetry* **2008**, *19*, 2479.
[7] Y. Kuang, X. Liu, L. Chang, Min. Wang, L. Lin, X. Feng, *Org. Lett.* **2011**, *13*, 3814.

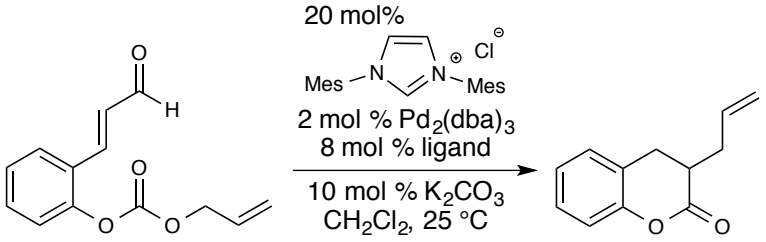
Optimization of reaction conditions

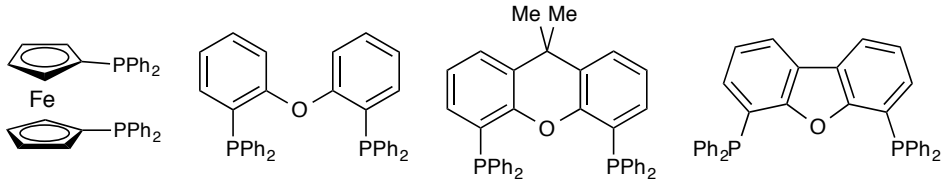
Selected examples of solvents:



entry	solvent	yield
1	THF	29%
2	CH_2ClCH_2Cl	44%
3	benzene	28%
4	toluene	47%
5	PhCl	56%
6	**CH_2Cl_2**	**56%**

Selected examples of ligand optimization:[5]

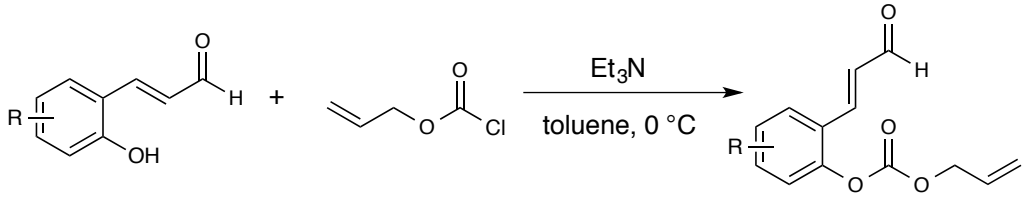




natural bite angle	99°	102°	110°	131°
yield	61%	55%	62%	8%

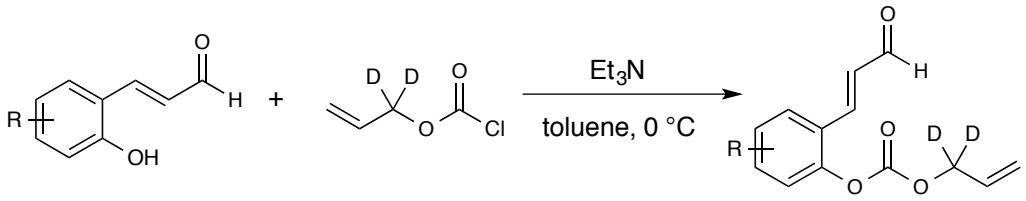
General Procedure for Synthesis of *(E)*-3-(2-hydroxyphenyl)acrylaldehyde derivatives

Method A:

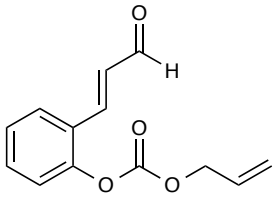


To a solution of the (*E*)-3-(2-hydroxyphenyl)acrylaldehyde derivative (1.0 equiv) in toluene (0.2 M) was added Et_3N (1.3 equiv) at 0 ºC. Then allyl chloroformate (1.2 equiv) was added slowly. The reaction mixture was stirred for 2 h at room temperature. Then water was added to quench the reaction and organic phase was separated. The aqueous solution was extracted with EtOAc for three times. The combined organic phase was washed with brine and dried over Na_2SO_4. After evaporation of the volatile, the residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the products as colorless oil/solid.

Method B:

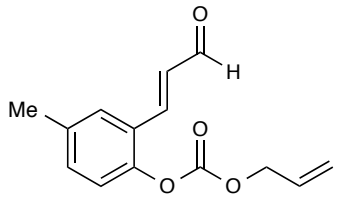


Freshly prepared d_2-allyl chloroformate[4] derivative (1.5 equiv) was added slowly to a solution of (*E*)-3-(2-hydroxyphenyl)acrylaldehyde (1.0 equiv) and Et_3N (2.0 equiv) in toluene (0.2 M) at 0 ºC. The reaction mixture was stirred for 2 h at room temperature. Then water was added to quench the reaction and organic phase was separated. The aqueous solution was extracted with EtOAc for three times. The combined organic phase was washed with brine and dried over Na_2SO_4. After evaporation of the volatile, the residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the product as colorless oil.

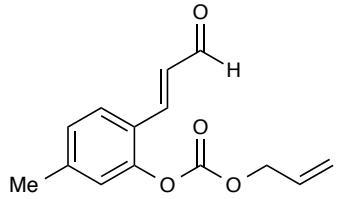


(*E*)-allyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1a): Prepared according to Method A using (*E*)-3-(2-hydroxyphenyl)acrylaldehyde (1.48 g, 10.00 mmol). The residue was purified using column chromatography to afford **1a** as colorless oil (2.05 g, 88%). Analytical data for **1a**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.74 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 7.8 1.6 Hz, 1H), 7.68 (d, *J* = 16.1 Hz, 1H), 7.51 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1 H), 7.37 – 7.29 (m, 2H), 6.78 (dd, *J* = 16.1, 7.7

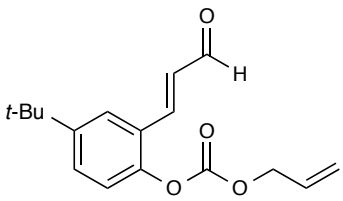
Hz, 1H), 6.07 – 6.02 (m, 1H), 5.49 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.40 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.81 (dt, *J* = 5.9, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 152.9, 149.5, 145.3, 132.2, 130.8, 130.5, 128.0, 126.7, 126.5, 122.7, 120.0, 69.6; IR (film) cm^{-1} 3067, 1750, 1706, 1682, 1606, 1487, 1457, 1418, 1263, 1218, 1175, 1124, 1079, 984, 964, 766; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{12}O_4$: 232.1; found 232.1.



(*E*)-allyl (4-methyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1b): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-methylphenyl)acrylaldehyde (0.81 g, 5.00 mmol). The residue was purified using column chromatography to afford **1b** as colorless oil (0.77 g, 63%). Analytical data for **1b**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.73 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 8.4, 2.2 Hz, 1 H), 7.19 (d, *J* = 8.3, 1H), 6.75 (dd, *J* = 16.1, 7.7 Hz, 1H), 6.16 – 6.01 (m, 1H), 5.48 (dq, *J* = 16.9, 1.3 Hz, 1H), 5.39 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.86 – 4.74 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 153.2, 147.5, 145.6, 136.6, 133.0, 130.8, 130.3, 128.3, 126.1, 122.4, 120.0, 69.6, 20.9; IR (film) cm^{-1} 2954, 1740, 1665, 1629, 1490, 1363, 1297, 1211, 1128, 1108, 979, 952, 778; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{14}O_4$: 246.1; found 246.0.

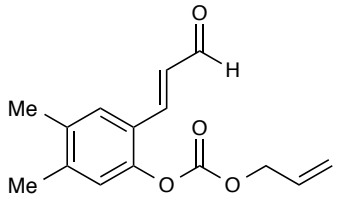


(*E*)-allyl (4-methyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1c): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-methylphenyl)acrylaldehyde (0.35 g, 2.00 mmol). The residue was purified using column chromatography to afford **1c** as colorless oil (0.39 g, 75%). Analytical data for **1c**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.71 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.12 – 7.10 (m, 2H), 6.73 (dd, *J* = 16.1, 7.7 Hz, 1H), 6.07 – 6.01 (m, 1H), 5.49 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.40 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.80 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.9, 153.1, 149.4, 145.6, 143.6, 130.8, 129.6, 127.8, 127.7, 123.7, 123.2, 120.1, 69.7, 21.6; IR (film) cm^{-1} 2980, 1751, 1681, 1614, 1460, 1399, 1361, 1264, 25, 1188, 1109, 972, 779; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{14}O_4$: 246.1; found 246.1.

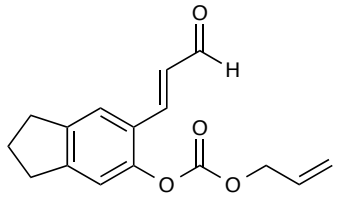


(*E*)-allyl (2-(4-*tert*-butyl-3-oxoprop-1-en-1-yl)phenyl) carbonate (1d): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-*tert*-butylphenyl)acrylaldehyde (0.41 g, 2.00 mmol). The

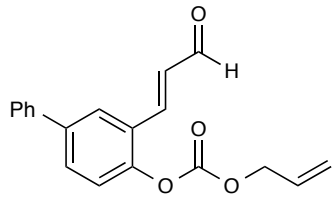
residue was purified using column chromatography to afford **1d** as colorless solid (0.43 g, 75%). Analytical data for **1d**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.73 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.79 (dd, *J* = 16.0, 7.7 Hz, 1H), 6.06–6.00 (m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.38 (d, *J* = 10.4, 1H), 4.79 (d, *J* = 6.0, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 153.1, 149.7, 147.4, 146.1, 130.8, 130.2, 129.7, 125.7, 124.8, 122.2, 120.0, 69.6, 34.68, 31.3; IR (film) cm^{-1} 2954, 1755, 1676, 1629, 1604, 1493, 1381, 1259, 1205, 1132, 1048, 975, 777; LRMS (EI): Mass calcd for $[M]^+$ $C_{17}H_{20}O_4$: 288.1; found 288.1.



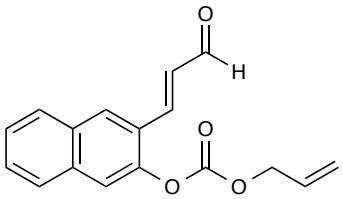
(*E*)-allyl (4,5-dimethyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1e): Prepared according to Method A using (*E*)-3-(2-hydroxy-4,5-dimethylphenyl)acrylaldehyde (0.35 g, 2.00 mmol). The residue was purified using column chromatography to afford **1e** as colorless oil (0.39 g, 75%). Analytical data for **1e**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.69 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.43 (s, 1H), 7.07 (s, 1H), 6.72 (dd, *J* = 16.0, 7.7 Hz, 1H), 6.07 – 5.99 (m, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 4.79 (d, *J* = 5.8 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 153.3, 147.6, 145.8, 142.2, 135.4, 130.9, 129.4, 128.7, 123.7, 123.5, 120.0, 69.6, 20.2, 19.3; IR (film) cm^{-1} 2980, 1774, 1744, 1676, 1616, 1362, 1295, 1258, 1236, 1182, 1123, 1035, 990, 780; LRMS (EI): Mass calcd for $[M]^+$ $C_{15}H_{16}O_4$: 260.1; found 260.1.



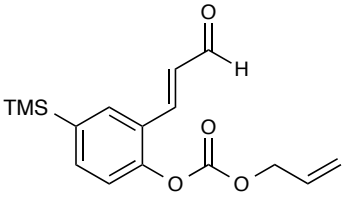
(*E*)-allyl (6-(3-oxoprop-1-en-1-yl)-2,3-dihydro-1*H*-inden-5-yl) carbonate (1f): Prepared according to Method A using (*E*)-3-(6-hydroxy-2,3-dihydro-1*H*-inden-5-yl)acrylaldehyde (0.37 g, 2.00 mmol). The residue was purified using column chromatography to afford **1f** as colorless oil (0.47 g, 86%). Analytical data for **1f**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.69 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 15.9 Hz, 1H), 7.51 (s, 1H), 7.13 (s, 1H), 6.71 (dd, *J* = 15.9, 7.7 Hz, 1H), 6.07 – 5.99 (m, 1H), 5.47 (d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 4.78 (d, *J* = 5.8 Hz, 2H), 2.98 – 2.92 (m, 4H), 2.17 – 2.11 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.9, 153.3, 150.0, 148.4, 146.2, 143.0, 130.9, 129.2, 124.2, 123.0, 119.9, 118.5, 69.6, 33.3, 32.2, 25.6; IR (film) cm^{-1} 2980, 1774, 1743, 1674, 1616, 1363, 1295, 1256, 1234, 1189, 1122, 1029, 978, 780; LRMS (EI): Mass calcd for $[M]^+$ $C_{16}H_{16}O_4$: 272.1; found 272.1.



(*E*)-allyl (4-phenyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1g): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-phenylphenyl)acrylaldehyde (0.45 g, 2.00 mmol). The residue was purified using column chromatography to afford **1g** as colorless oil (0.57 g, 93%). Analytical data for **1g**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.74 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 16.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.58 – 7.56 (m, 2H), 7.49 – 7.46 (m, 2H), 7.42 – 7.37 (m, 2H), 6.83 (dd, *J* = 16.1, 7.6 Hz, 1H), 6.10 – 6.02 (m, 1H), 5.50 (dd, *J* = 17.2, 2.6 Hz, 1H), 5.41 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.8, 153.2, 149.0, 145.5, 140.2, 139.6, 131.1, 130.9, 129.2, 128.2, 127.3, 126.9, 126.8, 123.2, 120.3, 69.9; IR (film) cm^{-1} 2980, 1795, 1744, 1670, 1524, 1364, 1321, 1255, 1210, 1187, 1123, 1030, 977, 768; LRMS (EI): Mass calcd for $[M]^+$ $C_{19}H_{16}O_4$: 308.1; found 308.1.

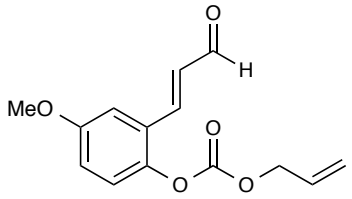


(*E*)-allyl (3-(3-oxoprop-1-en-1-yl)naphthalen-2-yl) carbonate (1h): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-phenylphenyl)acrylaldehyde (0.50 g, 2.50 mmol). The residue was purified using column chromatography to afford **1h** as colorless solid (0.55 g, 78%). Analytical data for **1h**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.73 (d, *J* = 7.7 Hz, 1H), 78.14 (s, 1H), 7.88 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.73 – 7.70 (m, 2H), 7.55 – 7.51 (m, 2H), 6.89 (dd, *J* = 16.1, 7.7 Hz, 1H), 6.06 – 5.98 (m, 1H), 5.48 – 5.44 (m, 1H), 5.38 – 5.35 (m, 1H), 4.79 – 4.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.8, 153.2, 146.5, 146.3, 134.7, 131.2, 130.8, 129.4, 128.6, 128.4, 127.6, 126.9, 125.8, 120.1, 120.0, 69.7; IR (film) cm^{-1} 2983, 1797, 1740, 1673, 1525, 1365, 1321, 1255, 1211, 1190, 1125, 1032, 978, 768; LRMS (EI): Mass calcd for $[M]^+$ $C_{17}H_{14}O_4$: 282.1; found 282.1.

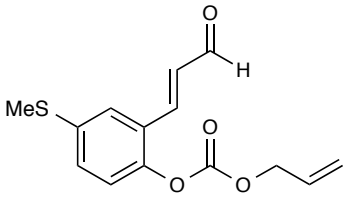


(*E*)-allyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1i): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-(trimethylsilyl)phenyl)acrylaldehyde (0.44 g, 2.00 mmol). The residue was purified using column chromatography to afford **1i** as colorless oil (0.53 g, 86%). Analytical data for **1i**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.54 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 16.1 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.61 (dd, *J* = 16.1, 7.7

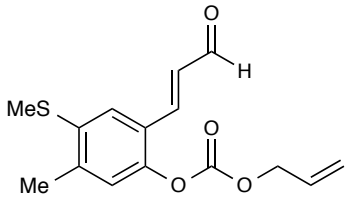
Hz, 1H), 5.87 – 5.82 (m, 1H), 5.29 (d, *J* = 17.2, 1.4 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.66 – 4.65 (m, 2H), 0.12 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.79, 152.89, 149.99, 145.80, 139.48, 137.25, 133.12, 130.72, 130.41, 125.65, 121.83, 120.05, 69.64, -1.24; IR (film) cm^{-1} 2981, 1740, 1666, 1630, 1489, 1381, 1297, 1259, 1233, 1211, 1108, 1050, 994, 779; LRMS (EI): Mass calcd for $[M]^+$ $C_{16}H_{20}O_4Si$: 304.1; found 304.1.



(*E*)-allyl (2-(4-methoxy-3-oxoprop-1-en-1-yl)phenyl) carbonate (1j): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-methoxyphenyl)acrylaldehyde (0.35 g, 2.00 mmol). The residue was purified using column chromatography to afford **1j** as colorless solid (0.45 g, 86%). Analytical data for **1j**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.72 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 16.1 Hz, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 7.13 (s, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.73 (dd, *J* = 15.8, 7.7 Hz, 1H), 6.05 – 5.99 (m, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.5, 1H), 4.78 (d, *J* = 6.2, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 157.6, 153.3, 145.3, 143.3, 130.8, 130.5, 127.2, 123.6, 120.0, 118.1, 111.7, 69.6, 55.7; IR (film) cm^{-1} 2980, 1744, 1673, 1495, 1443, 1420, 1282, 1246, 1205, 1146, 975, 936, 780; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{14}O_5$: 262.2; found 262.0.

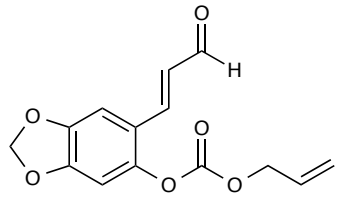


(*E*)-allyl (4-(methylthio)-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1k): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-(methylthio)phenyl)acrylaldehyde (0.44 g, 2.00 mmol). The residue was purified using column chromatography to afford **1k** as colorless solid (0.53 g, 86%). Analytical data for **1k**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.70 (d, *J* = 7.6 Hz, 1H), 9.59 (d, *J* = 16.1, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.03 – 5.97 (m, 1H), 5.47 – 5.43 (m, 1H), 5.36 (d, *J* = 10.3 Hz, 1H), 4.76 (d, *J* = 6.0, 2H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.6, 153.0, 147.0, 144.8, 137.4, 130.8, 130.7, 130.2, 126.9, 125.5, 123.1, 120.2, 69.8, 16.2; IR (film) cm^{-1} 2954, 1786, 1744, 1673, 1618, 1524, 1461, 1363, 1293, 1255, 1212, 1186, 1125, 978, 777; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{14}O_4S$: 278.1; found 278.0.

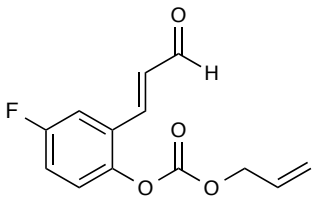


(*E*)-allyl (5-methyl-4-(methylthio)-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1l): Prepared according to Method A using (*E*)-3-(2-hydroxy-4-methyl-5-(methylthio)phenyl)acrylaldehyde

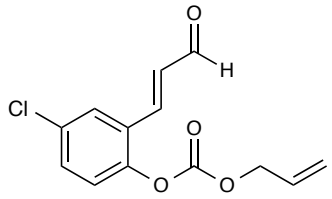
(0.42 g, 2.00 mmol). The residue was purified using column chromatography to afford **1l** as colorless solid (0.57 g, 97%). Analytical data for **1l**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.70 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 16.1 Hz, 1H), 7.36 (s, 1H), 7.09 (s, 1H), 6.73 (dd, J = 15.3, 7.9 Hz, 1H), 6.06 – 5.98 (m, 1H), 5.47 (d, J = 17.3 Hz, 1H), 5.38 (d, J = 10.6 Hz, 1H), 4.78 (d, J = 6.7, 2H), 2.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.7, 153.1, 146.7, 145.2, 141.0, 137.0, 130.8, 129.8, 124.5, 123.8, 123.3, 120.1, 69.7, 20.3, 15.5; IR (film) cm^{-1} 2990, 1745, 1677, 1635, 1517, 1382, 1287, 1270, 1210, 1180, 1121, 1051, 939, 887; LRMS (EI): Mass calcd for $[M]^+$ $C_{15}H_{16}O_4S$: 292.1; found 292.0.



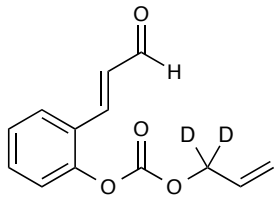
(*E*)-allyl (6-(3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxol-5-yl) carbonate (1m): Prepared according to Method A using (*E*)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)acrylaldehyde (0.33 g, 1.70 mmol) **1m** as colorless solid (0.43 g, 90%). Analytical data for **1m**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.59 (d, J = 7.7, 1H), 7.49 (d, J = 15.9 Hz, 1H), 6.98 (s, 1H)，6.70 (s, 1H), 6.50 (dd, J = 15.9, 7.7 Hz, 1H), 6.00 (s, 2H), 5.97 – 5.91 (m, 1H), 5.42– 5.41 (m, 1H), 5.32 – 5.29 (m, 1H), 4.70 (dt, J = 6.0, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.6, 153.1, 150.9, 146.5, 145.2, 145.0, 130.7, 128.4, 120.2, 119.9, 105.1, 104.0, 102.6, 69.8; IR (film) cm^{-1} 2981, 1754, 1666, 1626, 1606, 1503, 1492, 1375, 1293, 1248, 1221, 1163, 1121, 1034, 991, 772; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{12}O_6$: 276.0; found 276.0.



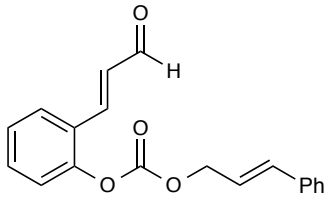
(*E*)-allyl (4-fluoro-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1n): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-fluorophenyl)acrylaldehyde (0.17 g, 1.00 mmol). The residue was purified using column chromatography to afford **1n** as colorless solid (0.23 g, 94%). Analytical data for **1n**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.71 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.7, 3.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.19 – 7.11 (m, 1H), 6.69 (dd, J = 16.1, 7.6 Hz, 1H), 6.03 – 5.96 (m, 1H), 5.45 (d, J = 17.2, 1.4 Hz, 1H), 5.37 (d, J = 10.4, 1.2 Hz, 1H), 4.76 (dt, J = 5.8, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.3, 161.3, 159.3, 153.0, 145.4 (d, $J_{C\text{-}F}$ = 2.8 Hz), 143.9 (d, $J_{C\text{-}F}$ = 2.3 Hz), 131.0 (d, $J_{C\text{-}F}$ = 79.4 Hz), 128.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.3 (d, $J_{C\text{-}F}$ = 8.6 Hz), 120.2, 119.0 (d, $J_{C\text{-}F}$ = 23.8 Hz), 113.9 (d, $J_{C\text{-}F}$ = 24.2 Hz), 69.8; IR (film) cm^{-1} 3028, 1751, 1683, 1632, 1516, 1460, 1262, 1254, 1185, 1177, 1044, 972, 735; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{11}FO_4$: 250.1; found 250.1.



(*E*)-allyl (4-chloro-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1o): Prepared according to Method A using (*E*)-3-(2-hydroxy-5-fchlorophenyl)acrylaldehyde (0.18 g, 1.00 mmol). The residue was purified using column chromatography to afford **1o** as colorless solid (0.24 g, 88%). Analytical data for **1o**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.73 (d, J = 7.6 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.45 – 7.43 (m, 1H), 7.29 – 7.26 (m, 1H), 6.73 (dd, J = 16.6, 7.7 Hz, 1H), 6.05 – 5.99 (m, 1H), 5.50– 5.46 (m, 1H), 5.41– 5.38 (m, 1H), 4.79 (dt, J = 5.8, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.2, 152.7, 147.8, 143.7, 132.3, 131.9, 131.3, 130.6, 128.0, 127.6, 124.1, 120.3, 69.9; IR (film) cm^{-1} 3064, 1752, 1675, 1634, 1520, 1360, 1256, 1211, 1179, 1122, 1051, 979, 772; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{11}ClO_4$: 266.0; found 266.0.

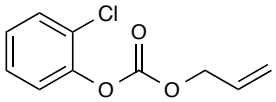


(*E*)-allyl-1,1-d_2 (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (8): Prepared according to Method B using (*E*)-3-(2-hydroxyphenyl)acrylaldehyde (0.59 g, 4.00 mmol) and allyl-1,1-d_2 carbonochloridate. The residue was purified using column chromatography to afford **8** as colorless oil (0.34 g, 36%). Analytical data for **6**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.74 (d, J = 7.6 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.53 – 7.49 (m, 1H), 7.37 – 7.29 (m, 2H), 6.77 (dd, J = 16.1, 7.6 Hz, 1H), 6.72 (dd, J = 17.2, 10.4 Hz, 1H), 5.49 (dd, J = 17.2, 1.2 Hz, 1H), 5.04 (dd, J = 10.4, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.7, 152.9, 149.5, 145.4, 132.3, 130.7, 130.5, 128.0, 126.8, 126.5, 122.7, 120.3, 69.1 (p, J = 22.6, 22.2 Hz); IR (film) cm^{-1} 2982, 1751, 1667, 1625, 1375, 1248, 1162, 1123, 1025, 991, 772; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{10}D_2O_4$: 234.1; found 234.0.

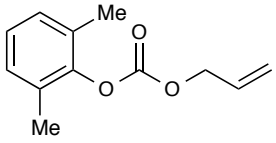


(*E*)-cinnamyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (11): Prepared according to Method B using (*E*)-3-(2-hydroxyphenyl)acrylaldehyde (0.29 g, 2.00 mmol) and cinnamyl carbonochloridate. The residue was purified using column chromatography to afford **11** as colorless oil (0.25 g, 40%). Analytical data for **9**: ^{1}H NMR (500 MHz, $CDCl_3$) 9.72 (d, J = 7.7 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.52 – 7.49 (m, 1H), 7.47 – 7.44 (m, 2H), 7.41 – 7.29 (m, 5H), 6.80 – 6.77 (m, 2H), 6.40 (dt, J = 15.9, 6.6 Hz, 1H), 4.97 (dd, J = 6.8, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 193.7, 153.0, 149.5, 145.35, 136.2, 135.7, 132.3, 130.5, 128.7, 128.6, 128.0,

126.8, 126.8, 126.5, 122.7, 121.4, 69.8; IR (film) cm^{-1} 2980, 1754, 1669, 1626, 1485, 1396, 1245, 1217, 1163, 1122, 1096, 1025, 972, 771; LRMS (EI): Mass calcd for $[M]^+$ $C_{19}H_{16}O_4$: 308.1; found 308.1.



Allyl (2-chlorophenyl) carbonate (14): Prepared according to Method A using 2-chlorophenol (1.29 g, 10.00 mmol) and allyl carbonochloridate. The residue was purified using column chromatography to afford **12** as colorless oil (2.09 g, 98%). Analytical data for **12**: ^{1}H NMR (500 MHz, $CDCl_3$) 7.48 (d, J = 7.9, 1.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 6.06 – 6.00 (m, 1H), 5.47 (dq, J = 17.2, 1.4 Hz, 1H), 5.37 (dq, J = 10.3, 1.1 Hz, 1H), 4.80 (dt, J = 5.7, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 152.6, 147.1, 130.9, 130.5, 127.9, 127.4, 126.9, 123.3, 119.6, 69.6; IR (film) cm^{-1} 2991, 1764, 1689, 1636, 1517, 1477, 1277, 1242, 1211, 1105, 983, 940, 794; LRMS (EI): Mass calcd for $[M]^+$ $C_{10}H_9ClO_3$: 212.0; found 212.1.

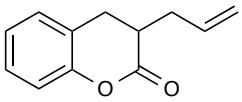


Allyl (2,6-dimethylphenyl) carbonate(6): Prepared according to Method A using 2,6-dimethylphenol (2.44 g, 20.00 mmol) and allyl carbonochloridate. colorless oil (3.80 g, 92%). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) 7.09 (br, 3H), 6.05 – 6.00 (m, 1H), 5.46 (dt, J = 17.1, 1.4 Hz, 1H), 5.36 (dd, J = 10.4, 1.3 Hz, 1H), 4.78 (d, J = 5.6 Hz, 2H), 2.24 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) 152.8, 148.3, 131.3, 130.2, 128.7, 126.1, 119.4, 69.1, 16.1; IR (film) cm^{-1} 2981, 1756, 1691, 1652, 1637, 1381, 1236, 1178, 1143, 1047, 984, 767; LRMS (EI): Mass calcd for $[M]^+$ $C_{12}H_{14}O_3$: 206.1; found 206.0.

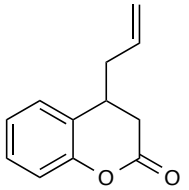
General procedure for NHC-catalyzed reaction

Into an oven-dried, screw-capped vial equipped with a magnetic stirbar was weighed $Pd_2(dba)_3$ (0.016 mmol, 0.04 equiv) and dppf (0.064 mmol, 0.16 equiv) in a nitrogen-filled drybox. The vial was capped with a septum cap and degassed CH_2Cl_2 (0.6 mL) was added into the vial, and the solution was stirred for 10 min.

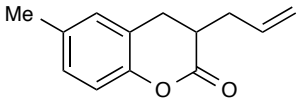
Into another oven-dried, screw-capped vial equipped with a magnetic stirbar was weighed aldehyde **1** (0.400 mmol, 1 equiv). The vial was taken into a nitrogen-filled drybox at which time azolium salt **A** (0.08 mmol, 0.20 equiv) was added. Into the vial were then successively added CH_2Cl_2 (1.0 mL) and the premixed Pd-dppf solution via cannula (washed with 2×0.2 mL degassed CH_2Cl_2). Then allyl 2-chlorophenylcarbonate **12** (0.400 mmol, 1.0 equiv) was added via a syringe. The reaction was stirred at room temperature in drybox for 24 h (all reactions were completed within 24 h). The reaction mixture was filtered over a short pad of silica gel eluted with dichloromethane and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexanes afforded the corresponding 3-allyldihydrocoumarins.



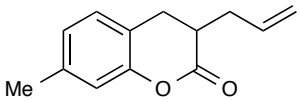
3-allyl-dihydrocoumarin (2a):[6] Prepared according to the general procedure using **1a**. The NMR yield was determined using Me_3SiPh as internal standard. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2a** as a colorless oil. Analytical data for **2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H), 7.17 – 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 5.88 – 5.77 (m, 1H), 5.14 – 5.10 (m, 2H), 2.98 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.81 – 2.65 (m, 3H), 2.37 – 2.29 (m, 1H); LRMS (EI): Mass calcd for $[M]^+$ $C_{12}H_{12}O_2$: 188.1; found 188.1.



4-allyl-dihydrocoumarin (3a):[7] Prepared according to the general procedure using **1a**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **3a** as a colorless oil. Analytical data for **3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 1H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.11 – 7.09 (m, 1H), 7.05 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.77 – 5.67 (m, 1H), 5.12 – 5.06 (m, 2H), 3.19 – 3.04 (m, 1H), 2.78 (dd, *J* = 5.2, 2.8 Hz, 2H), 2.46 – 2.39 (m, 1H), 2.32 – 2.25 (m, 1H); (EI): Mass calcd for $[M]^+$ $C_{12}H_{12}O_2$: 188.1; found 188.0.

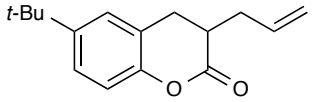


3-allyl-6-methyldihydrocoumarin (2b): Prepared according to the general procedure using **1b**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2b** as a colorless oil. Analytical data for **2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.80 – 5.73 (m, 1H), 5.08 – 5.04 (m, 2H), 2.87 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.74 – 2.59 (m, 3H), 2.29 – 2.22 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.7, 149.5, 134.4, 133.9, 128.7, 128.6, 122.2, 118.2, 116.3, 38.8, 33.9, 28.6, 20.8; IR (film) cm^{-1} 2980, 1739, 1642, 1625, 1499, 1454, 1379, 1268, 1258, 1210, 1159, 1103, 1025, 886, 775; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{14}O_2$: 202.1; found 202.1.

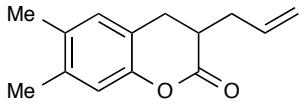


3-allyl-7-methyldihydrocoumarin (2c): Prepared according to the general procedure using **1c**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2c** as a colorless oil. Analytical data for **2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.6 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.84 (d, *J* = 1.4 Hz, 1H), 5.87 – 5.79 (m, 1H), 5.13 – 5.10 (m, 2H), 2.96 – 2.92 (m, 1H), 2.81 – 2.66 (m, 3H), 2.36 – 2.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.7, 151.4, 138.5, 134.4, 127.8, 125.1, 119.3, 118.2, 117.0, 38.9, 34.0, 28.3, 21.2; IR (film)

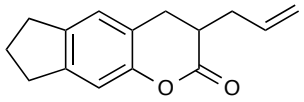
cm^{-1} 2978, 1740, 1642, 1625, 1583, 1491, 1437, 1358, 1249, 1218, 1196, 1143, 1105, 1026, 896, 764; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{14}O_2$: 202.1; found 202.1.



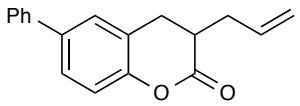
3-allyl-6-*tert*-butyldihydrocoumarin (2d): Prepared according to the general procedure using **1d**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2d** as a colorless oil. Analytical data for **2d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.17 (m, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.82 – 5.73 (m, 1H), 5.08 – 5.08 (m, 2H), 2.90 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.76 – 2.62 (m, 3H), 2.31 – 2.24 (m, 1H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.7, 149.3, 147.4, 134.5, 125.1, 125.0, 121.9, 118.2, 116.0, 38.8, 34.4, 34.0, 31.5, 29.0; IR (film) cm^{-1} 2979, 1763, 1707, 1642, 1613, 1498, 1462, 1365, 1272, 1232, 1145, 1125, 1027, 887, 768; LRMS (EI): Mass calcd for $[M]^+$ $C_{16}H_{20}O_2$: 244.1; found 244.0.



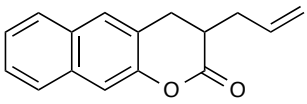
3-allyl-6,7-dimethyldihydrocoumarin (2e): Prepared according to the general procedure using **1e**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2e** as a colorless oil. Analytical data for **2e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.81 (s, 1H), 5.87 – 5.78 (m, 1H), 5.14 – 5.10 (m, 2H), 2.93 – 2.87 (m, 1H), 2.78 – 2.65 (m, 3H), 2.35 – 2.28 (m, 1H), 2.23 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.9, 149.5, 136.7, 134.5, 132.5, 128.9, 119.3, 118.1, 117.4, 39.0, 34.0, 28.2, 19.6, 19.1; IR (film) cm^{-1} 2975, 1759, 1641, 1627, 1503, 1455, 1409, 1275, 1174, 1102, 1021, 866, 771; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{16}O_2$: 216.1; found 216.1.



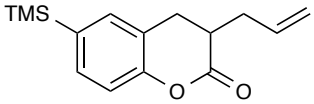
3-allyl-4,6,7,8-tetrahydrocyclopenta[g]chromen-2(3H)-one (2f): Prepared according to the general procedure using **1h**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2f** as a colorless oil. Analytical data for **2f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ .99 (s, 1H), 6.89 (s, 1H), 5.87 – 5.79 (m, 1H), 5.14 – 5.10 (m, 2H), 2.95 – 2.78 (m, 5H), 2.75 – 2.66 (m, 3H), 2.31 – 2.30 (m, 1H), 2.11– 2.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.0, 150.2, 144.5, 140.2, 134.5, 123.5, 120.0, 118.1, 112.5, 38.9, 33.9, 32.8, 32.2, 28.7, 25.8; IR (film) cm^{-1} 3002, 1750, 1640, 1622, 1477, 1426, 1356, 1263, 1258, 1204, 1148, 1107, 998, 870, 751; LRMS (EI): Mass calcd for $[M]^+$ $C_{15}H_{16}O_2$: 228.1; found 228.1.



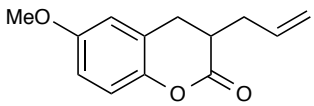
3-allyl-6-phenyldihydrocoumarin (2g): Prepared according to the general procedure using **1g**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2g** as a colorless solid. Analytical data for **2g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.51 – 7.45 (m, 3H), 7.42 – 7.36 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 5.93 – 5.85 (m, 1H), 5.21 – 5.17 (m, 2H), 3.09 (dd, *J* = 15.5, 5.6 Hz, 1H), 2.93 – 2.74 (m, 3H), 2.44– 2.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.4, 151.0, 140.1, 137.6, 134.3, 128.9, 127.4, 127.0, 126.9, 126.8, 122.9, 118.4, 116.9, 38.8, 34.0, 28.8; IR (film) cm^{-1} 2980, 1762, 1706, 1641, 1601, 1507, 1481, 1453, 1354, 1226, 1142, 1120, 1024, 893, 760; LRMS (EI): Mass calcd for $[M]^+$ $C_{18}H_{16}O_2$: 264.1; found 264.1.



3-allyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-one (2h): Prepared according to the general procedure using **1h**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2h** as a colorless solid. Analytical data for **2h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.65 (br, 1H), 7.48 – 7.41 (m, 3H), 5.90 – 5.81 (m, 1H), 5.17 – 5.13 (m, 2H), 3.21 – 3.16 (m, 1H), 3.01– 2.95 (m, 1H), 2.82– 2.81 (m, 1H), 2.73– 2.70 (m, 1H), 2.39– 2.33 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.5, 149.7, 134.2, 133.1, 130.56, 127.4, 127.3, 127.0, 126.5, 125.5, 123.1, 118.41, 112.8, 39.1, 34.0, 29.1; IR (film) cm^{-1} 2982, 1764, 1708, 1640, 1603, 1508, 1483, 1455, 1357, 1227, 1142, 1121, 1026, 897, 760; LRMS (EI): Mass calcd for $[M]^+$ $C_{16}H_{14}O_2$: 238.1; found 238.1.

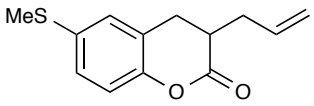


3-allyl-6-trimethylsilyldihydrocoumarin (2i): Prepared according to the general procedure using **1i**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2i** as a colorless oil. Analytical data for **2i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 1H), 7.28 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 5.87 – 5.79 (m, 1H), 5.15 – 5.11 (m, 2H), 2.99 (dd, *J* = 15.1, 5.1 Hz, 1H), 2.83 – 2.66 (m, 3H), 2.37 – 2.31 (m, 1H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.5, 152.2, 136.5, 134.4, 133.3, 133.2, 121.9, 118.2, 116.0, 38.9, 34.0, 28.7, -1.0; IR (film) cm^{-1} 2980, 1767, 1707, 1642, 1600, 1487, 1440, 1352, 1232, 1143, 1094, 1025, 929, 820; LRMS (EI): Mass calcd for $[M]^+$ $C_{15}H_{20}O_2Si$: 260.1; found 260.1.

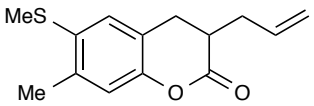


3-allyl-6-methoxydihydrocoumarin (2j): Prepared according to the general procedure using **1j**. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford **2j** as a colorless solid. Analytical data for **2j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.71 (d, *J* = 2.9 Hz 1H), 5.90 – 5.82 (m, 1H), 5.17 – 5.14 (m, 2H), 3.81 (s, 3H), 2.97 (dd, *J* = 15.1, 5.1 Hz, 1H), 2.84 – 2.70 (m, 3H), 2.39 – 2.32 (m,

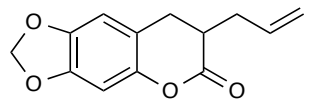
1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.6, 156.1, 145.5, 134.3, 123.5, 118.3, 117.3, 113.2, 113.2, 55.7, 38.7, 33.9, 28.9; IR (film) cm^{-1} 2980, 1757, 1641, 1593, 1493, 1428, 1354, 1277, 1202, 1147, 1030, 885; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{14}O_3$: 218.1; found 218.1.



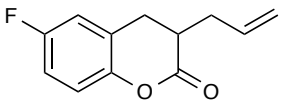
3-allyl-6-methylthioldihydrocoumarin (2k): Prepared according to the general procedure using **1k**. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford **2k** as a colorless solid. Analytical data for **2k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4, 2.3, Hz, 1H), 7.08 – 7.07 (m, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.86 – 5.79 (m, 1H), 5.15 – 5.11 (m, 2H), 2.96 (dd, *J* = 14.9, 4.8 Hz, 1H), 2.81 – 2.62 (m, 3H), 2.46 (s, 3H), 2.35 – 2.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.2, 149.5, 134.2, 133.9, 127.0, 126.8, 123.3, 118.4, 117.1, 38.6, 33.9, 28.6, 16.7; IR (film) cm^{-1} 3078, 1750, 1641, 1622, 1479, 1427, 1355, 1263, 1263, 1200, 1148, 1106, 1032, 860, 766; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{14}O_2S$: 234.1; found 234.1.



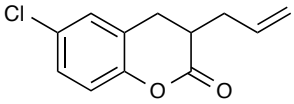
3-allyl-7-methyl-6-methylthioldihydrocoumarin (2l): Prepared according to the general procedure using **1l**. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford **2l** as a colorless solid. Analytical data for **2l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.84 (s, 1H), 5.86 – 5.78 (m, 1H), 5.14 – 5.10 (m, 2H), 2.96 (dd, *J* = 14.5, 4.6 Hz, 1H), 2.79 – 2.66 (m, 3H), 2.43 (s, 3H), 2.37 – 2.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.5, 149.2, 136.6, 134.32 133.1, 125.2, 120.5, 118.3, 117.9, 38.9, 33.9, 28.4, 19.9, 16.1; IR (film) cm^{-1} 3078, 1748, 1640, 1501, 1476, 1436, 1397, 1356, 1244, 1157, 1104, 1034, 885, 781; LRMS (EI): Mass calcd for $[M]^+$ $C_{14}H_{16}O_2S$: 248.1; found 248.1.



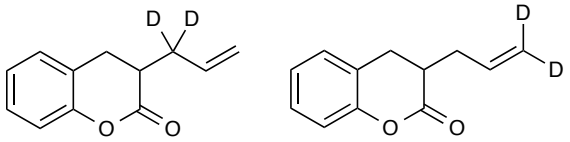
7-allyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromen-6-one (2m): Prepared according to the general procedure using **1m**. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford **2m** as solid. Analytical data for **2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.57 (s, 1H), 5. 95 (s, 2H), 5.86 – 5.77 (m, 1H), 5.14 – 5.10 (m, 2H), 2.89 – 2.82 (m, 1H), 2.72 – 2.65 (m, 3H), 2.34 – 2.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.4, 147.1, 145.9, 144.1, 134.3, 118.3, 114.5, 107.2, 101.6, 98.9, 38.6, 33.8, 28.4; IR (film) cm^{-1} 2980, 1745, 1641, 1616, 1501, 1474, 1355, 1298, 1260, 1233, 1197, 1105, 1033, 887, 781; LRMS (EI): Mass calcd for $[M]^+$ $C_{13}H_{12}O_4$: 232.1; found 232.0.



3-allyl-6-fluorodihydrocoumarin (2n): Prepared according to the general procedure using **1n**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2n** as a colorless solid. Analytical data for **2n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 – 6.98 (m, 1H), 6.95 – 6.91 (m, 1H), 6.89 – 6.87 (m, 1H), 5.84 – 5.78 (m, 1H), 5.15 – 5.11 (m, 2H), 2.96 (dd, J = 15.4, 5.4 Hz, 1H), 2.83 – 2.67 (m, 3H), 2.37 – 2.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.0, 159.9, 158.0, 147.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 134.0, 124.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 118.5, 117.8 (d, $J_{C\text{-}F}$ = 8.5 Hz), 114.8 (d, $J_{C\text{-}F}$ = 23.7, 18.2 Hz), 38.3, 33.9, 28.6; IR (film) cm^{-1} 2980, 1739, 1642, 1597, 1491, 1435, 1270, 1257, 1218, 1196, 1164, 1104, 1025, 894, 776; LRMS (EI): Mass calcd for $[M]^+$ $C_{12}H_{11}FO_2$: 206.1; found 206.1.



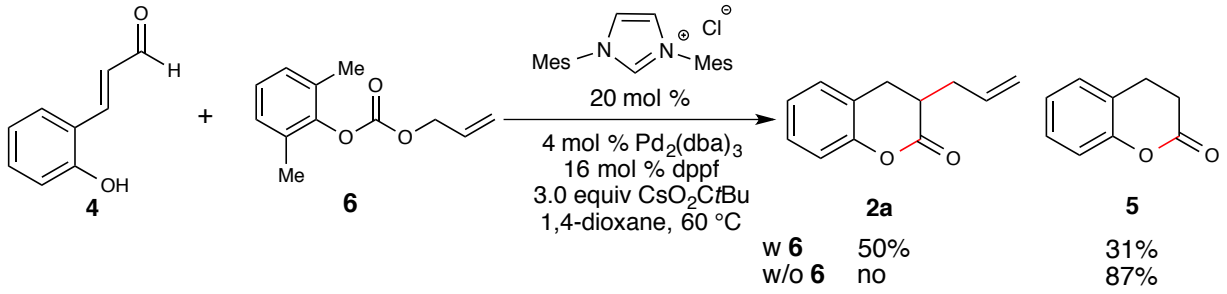
3-allyl-6-chlorodihydrocoumarin (2o): Prepared according to the general procedure using **1o**. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **2o** as colorless solid. Analytical data for **2o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 2H), 6.91 (d, J = 8.6 Hz, 1H), 5.79 – 5.71 (m, 1H), 5.10 – 5.06 (m, 2H), 2.92 – 2.88 (m, 1H), 2.76 – 2.61 (m, 3H), 2.30 – 2.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.7, 150.1, 133.9, 129.4, 128.3, 128.0, 124.2, 118.6, 117.9, 38.4, 33.8, 28.4; IR (film) cm^{-1} 2980, 1747, 1642, 1479, 1439, 1356, 1233, 1152, 1104, 1026, 896, 767; LRMS (EI): Mass calcd for $[M]^+$ $C_{12}H_{11}ClO_2$: 222.0; found 222.0.



1:1 ratio of 3-*d2*-allyl-drocoumarins (9) and (10): Prepared according to the general procedure using **8**. The NMR yield was determined using Me_3SiPh as internal standard. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford **9** and **10** as a colorless oil. Analytical data for **9** and **10** (1:1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 1H), 7.11 – 7.09 (m, 1H), 7.03 – 7.00 (m, 1H), 6.97 – 6.95 (m, 1H), 5.79 – 5.73 (m, 1H), 5.09 – 5.04 (m, 1H), 2.94 – 2.89 (m, 1H), 2.79 – 2.60 (m, 2.5H), 2.30 – 2.24 (m, 0.5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.5, 151.6, 134.2, 134.1, 128.3, 128.2, 124.4, 122.6, 118.3, 116.6, 38.74, 38.59, 33.8, 28.6, 28.5; IR (film) cm^{-1} 2980, 1739, 1642, 1625, 1499, 1454, 1379, 1268, 1258, 1210, 1159, 1103, 1025, 886, 775; LRMS (EI): Mass calcd for $[M]^+$ $C_{12}H_{10}D_2O_2$: 190.1; found 190.1.

Mechanistic Studies

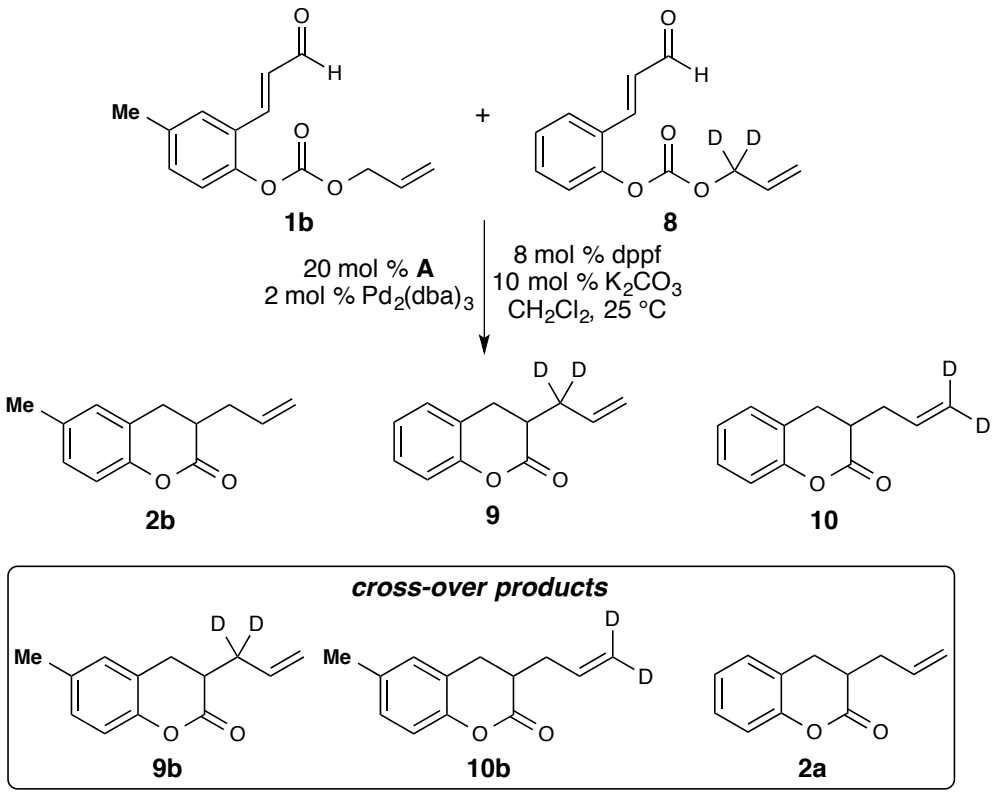
Two component reaction of 2-(2-hydroxyphenyl)acrylaldehyde with allyl (2,6-dimethylphenyl)carbonate: [a]



[a] Follow the General procedure of NHC-catalyzed reaction and yield was determined by ^{1}H NMR (500 MHz).

Cross over reaction of 1b and 6:

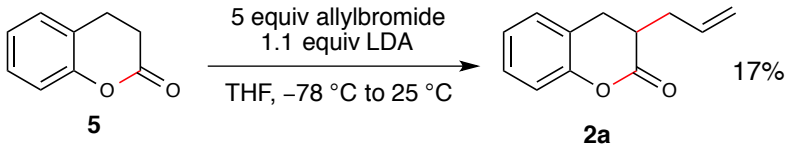
The non cross-over (**2b**, **9**, **10**) and cross-over products (**9b**, **10b**, **2a**) were observed by ^{1}H NMR in 45% combined yield. However, the chemical shifts of these products were too close to each other to accurately calculate the ratio of products using ^{1}H NMR. Instead, an alternative cross-over experiment was conducted, which is discussed in the manuscript text.



Procedure for monitoring aldehyde 7 using GC-MS:

The reaction was set up under the standard reaction condition (0.2 mmol scale, 0.2 M). Aliquot (5 μL) was taken from the reaction vial using syringe at indicated time and mixed with dodecane (10 μL, 0.1 M in CH_2Cl_2). The mixture was subjected to GC-MS analysis. The conversion of **1a** and yield of **2a** and **7** was calculated based on the ratio of integrated area relative to dodecane.

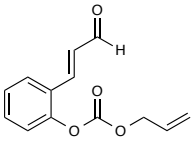
Procedure for allylation of dihydrocoumarin 5:

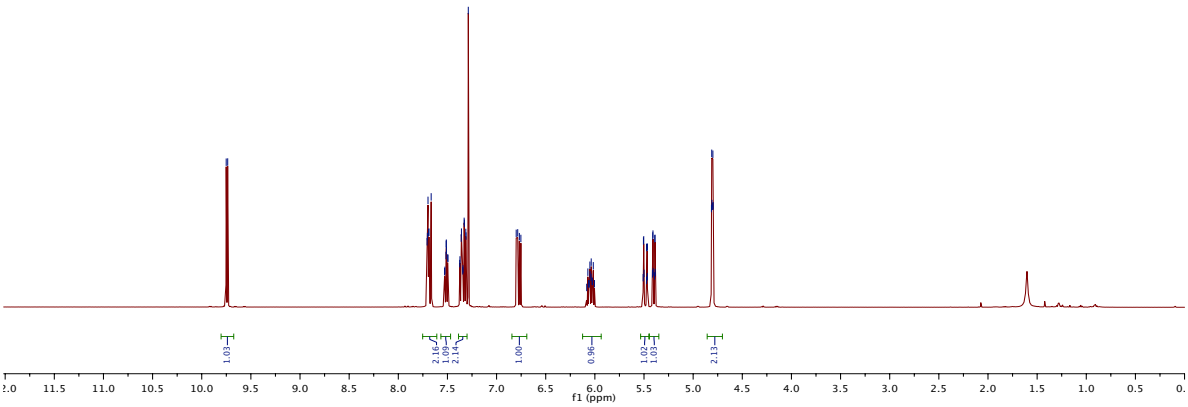


Dihydrocoumarin **5** (1 mmol, 1.0 equiv) was added to freshly prepared LDA in THF (5 mL) at –78 ºC. After 30 min, freshly distilled allylbromide (5.0 equiv) was added dropwise. The reaction mixture was stirred at –78 ºC for 5 h and then allowed to slowly warm to room temperature overnight. Ammonium chloride (5 mL, sat. aqueous) was added to quench the reaction, followed by extraction with Et_2O (3 x 10 mL). The combined organic fractions were washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation of the volatiles, the crude residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the product, **2a** (17%, 31.5 mg).

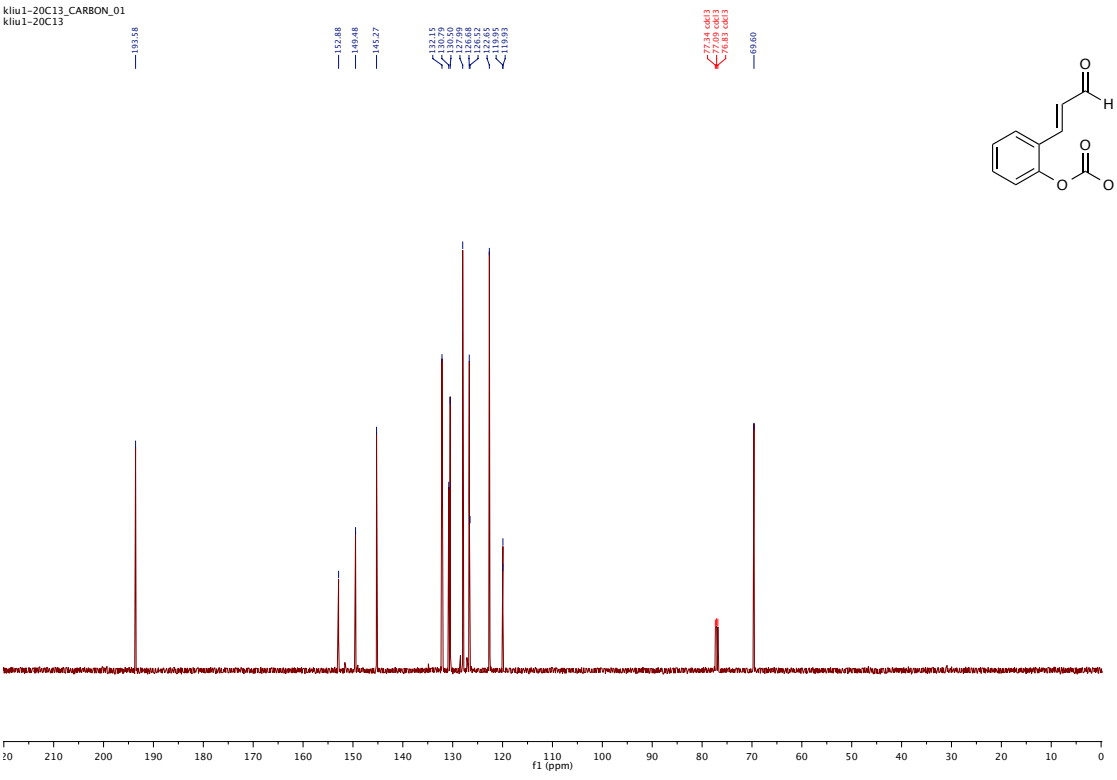
Selected NMR Spectra:

^{1}H NMR Spectra of **1a** (500 MHz, $CDCl_3$):

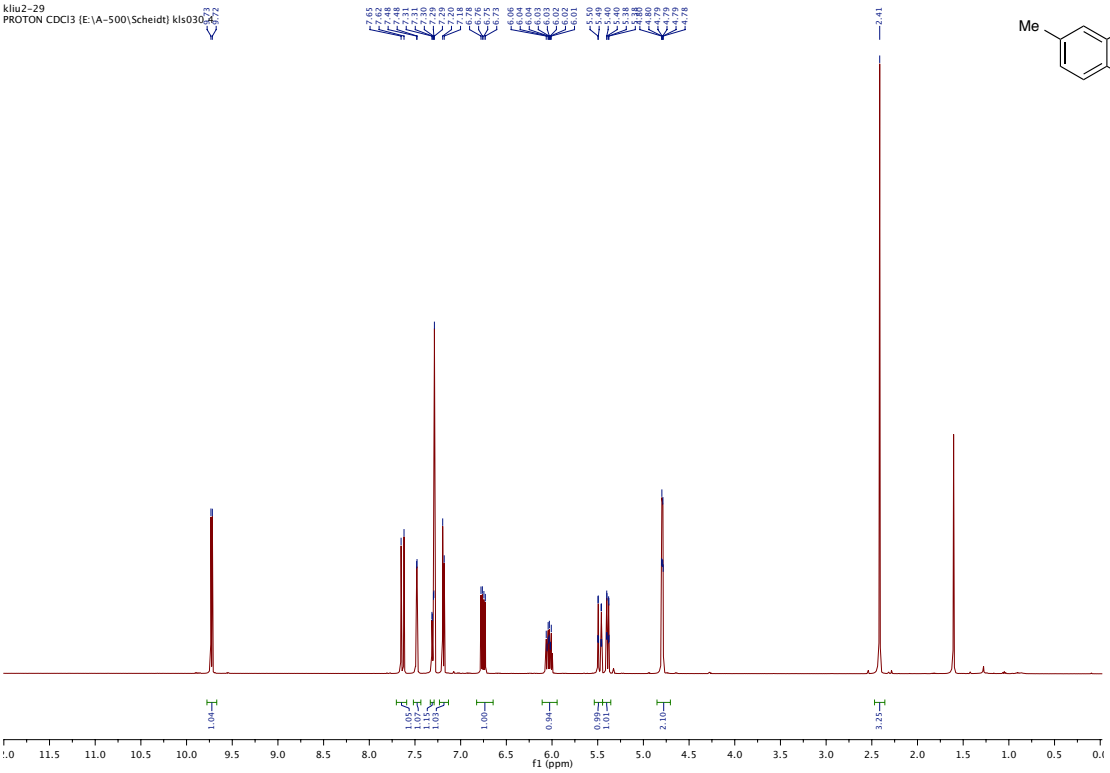


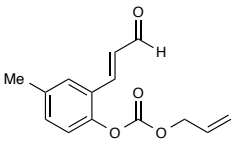


^{13}C NMR Spectra of **1a** (126 MHz, $CDCl_3$):

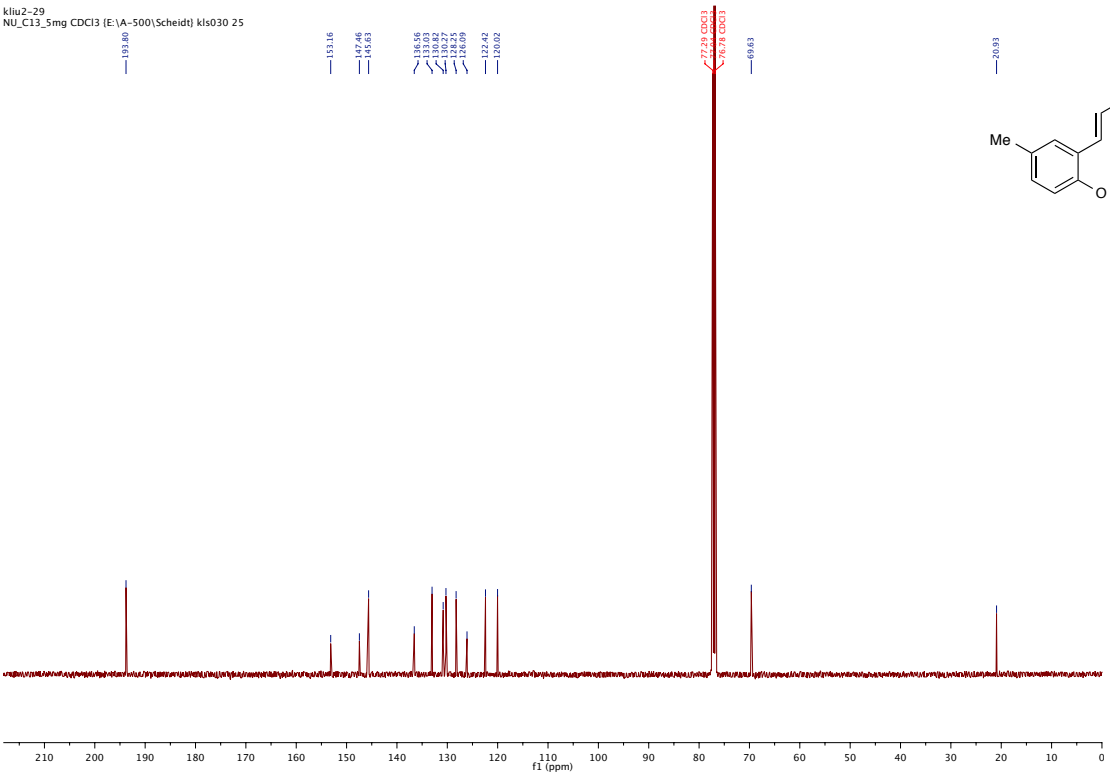


^{1}H NMR Spectra of **1b** (500 MHz, $CDCl_3$):

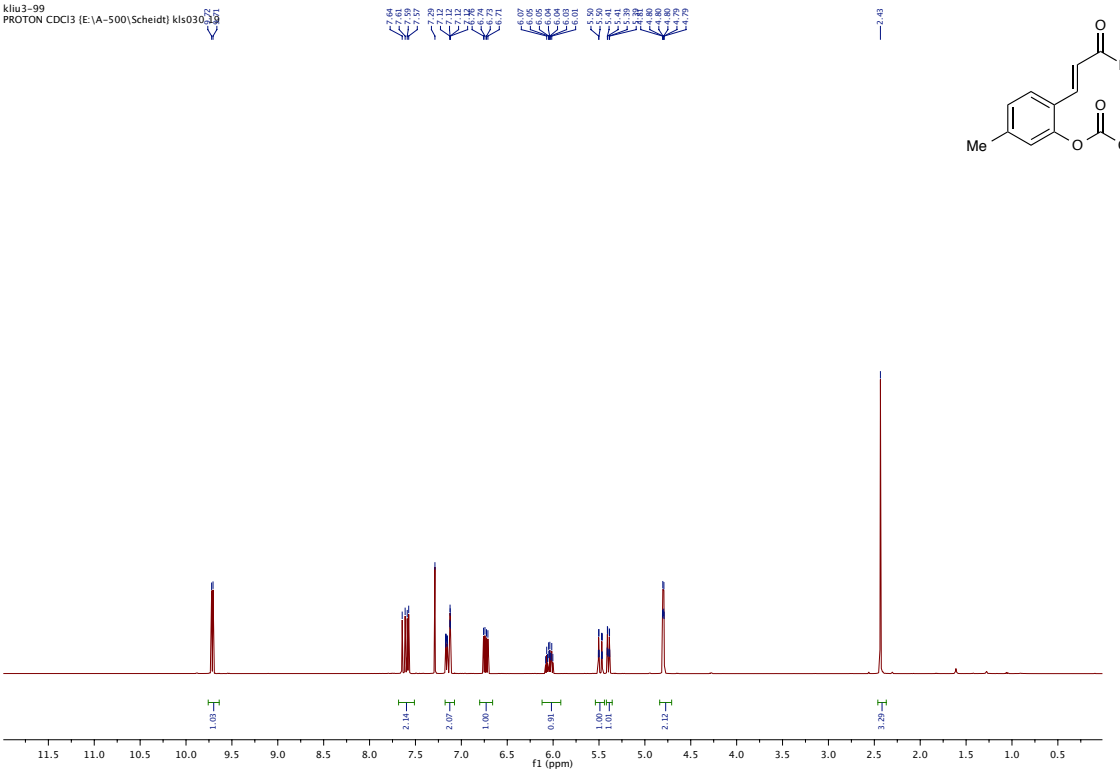




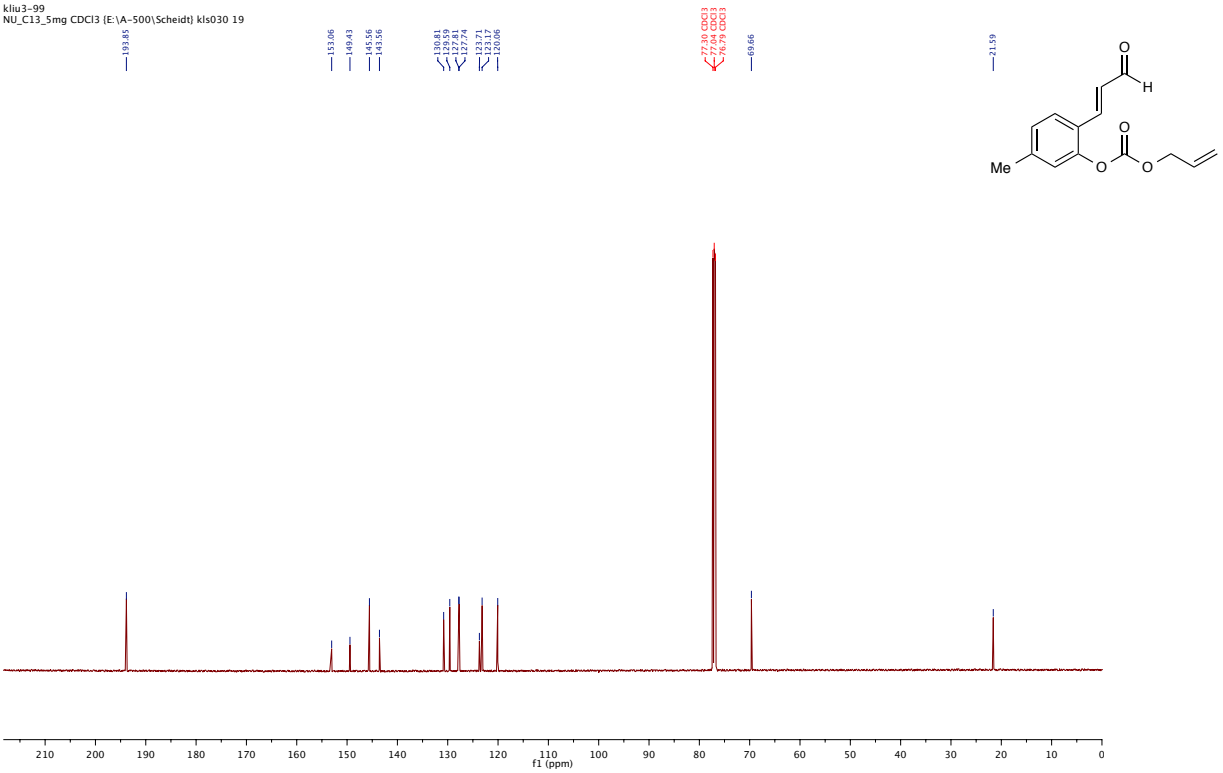
^{13}C NMR Spectra of **1b** (126 MHz, $CDCl_3$):



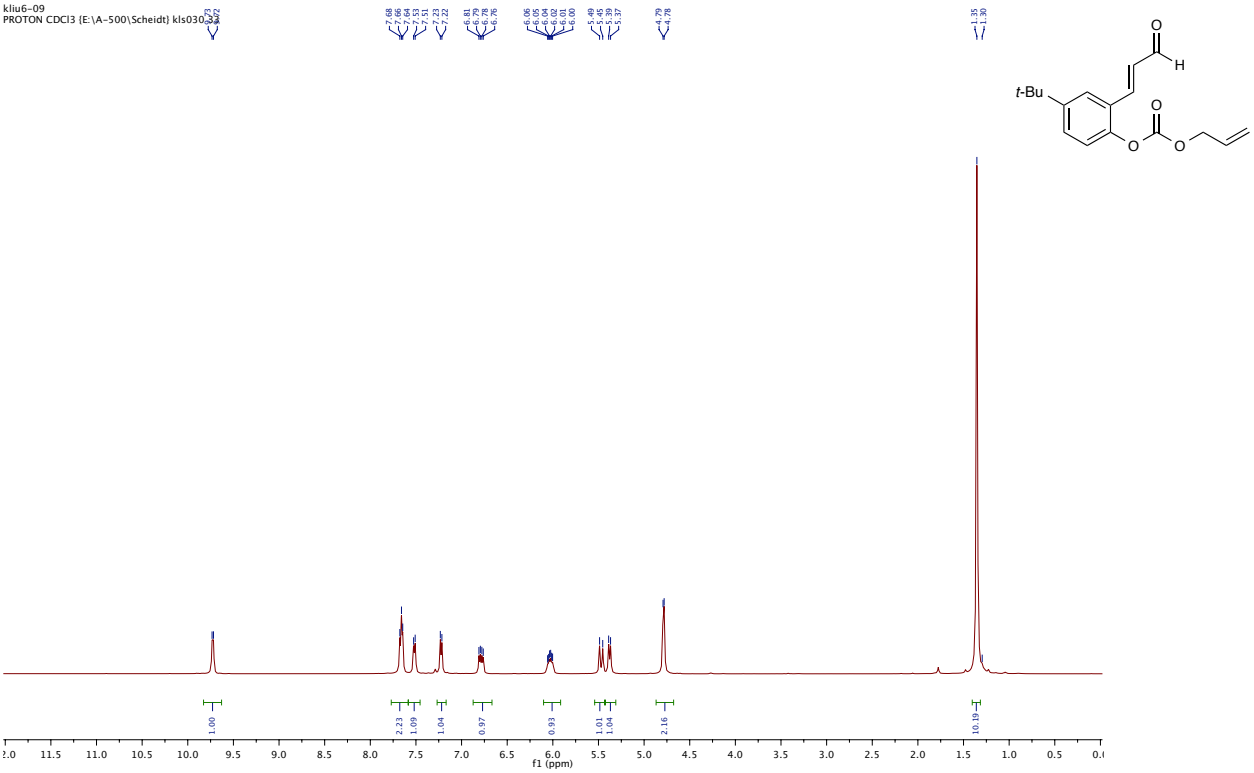
^{1}H NMR Spectra of **1c** (126 MHz, $CDCl_3$):



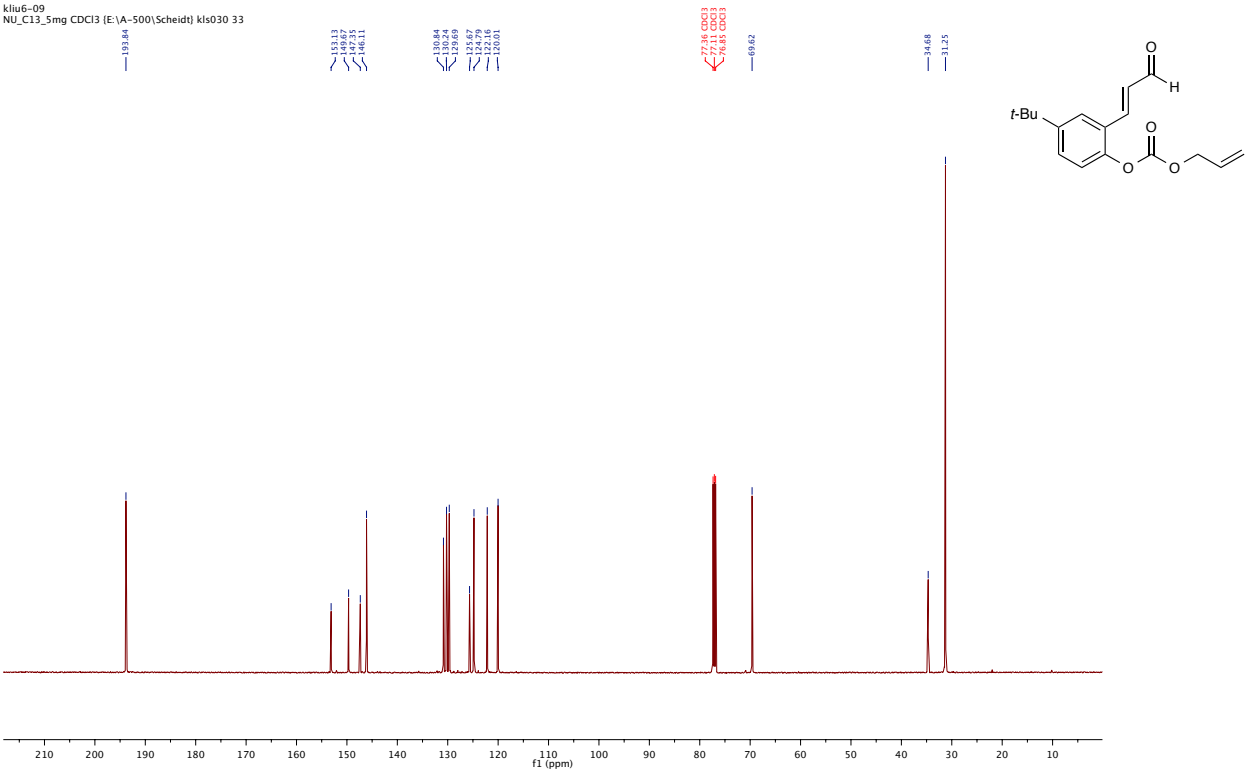
^{13}C NMR Spectra of **1c** (126 MHz, $CDCl_3$):



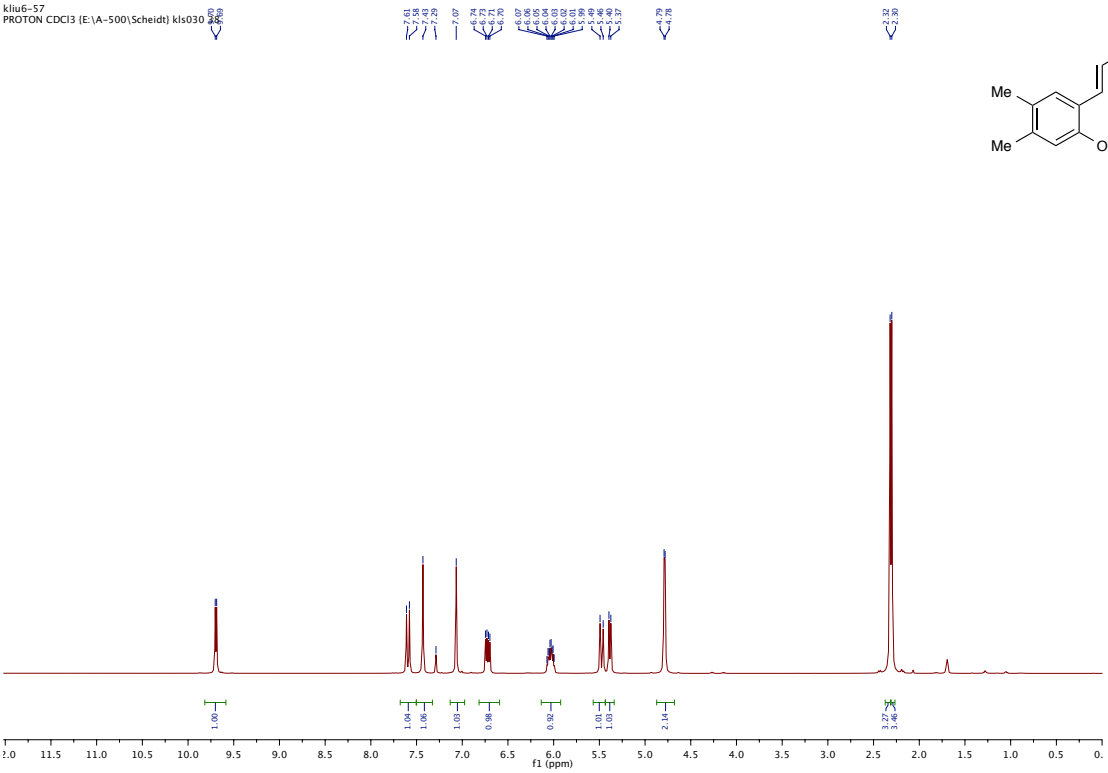
^{1}H NMR Spectra of **1d** (126 MHz, $CDCl_3$):



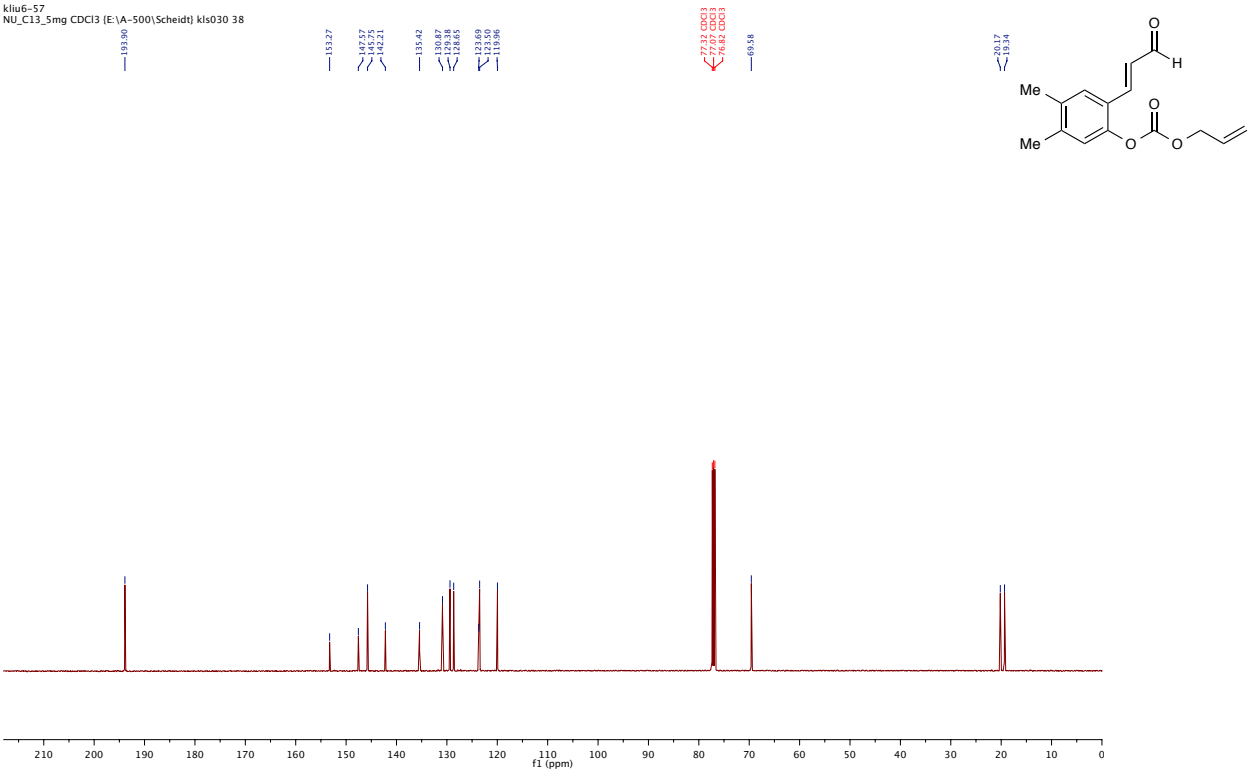
^{13}C NMR Spectra of **1d** (126 MHz, $CDCl_3$):



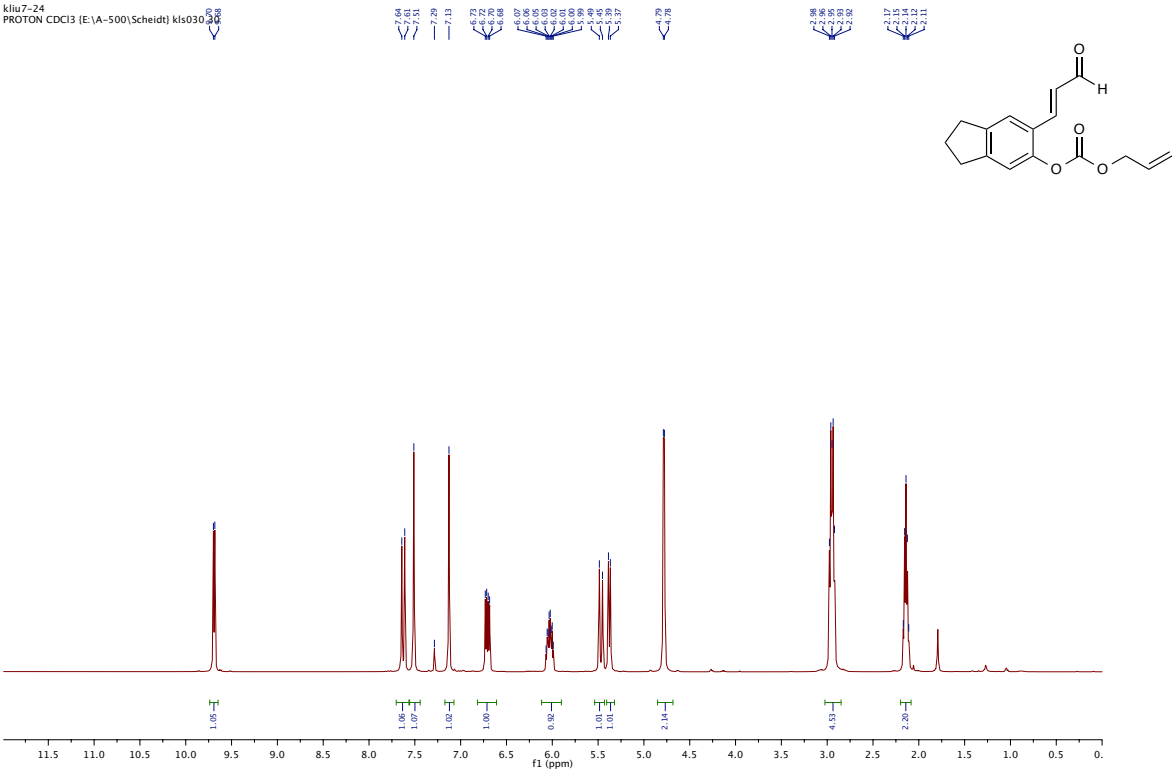
^{1}H NMR Spectra of **1e** (126 MHz, $CDCl_3$):



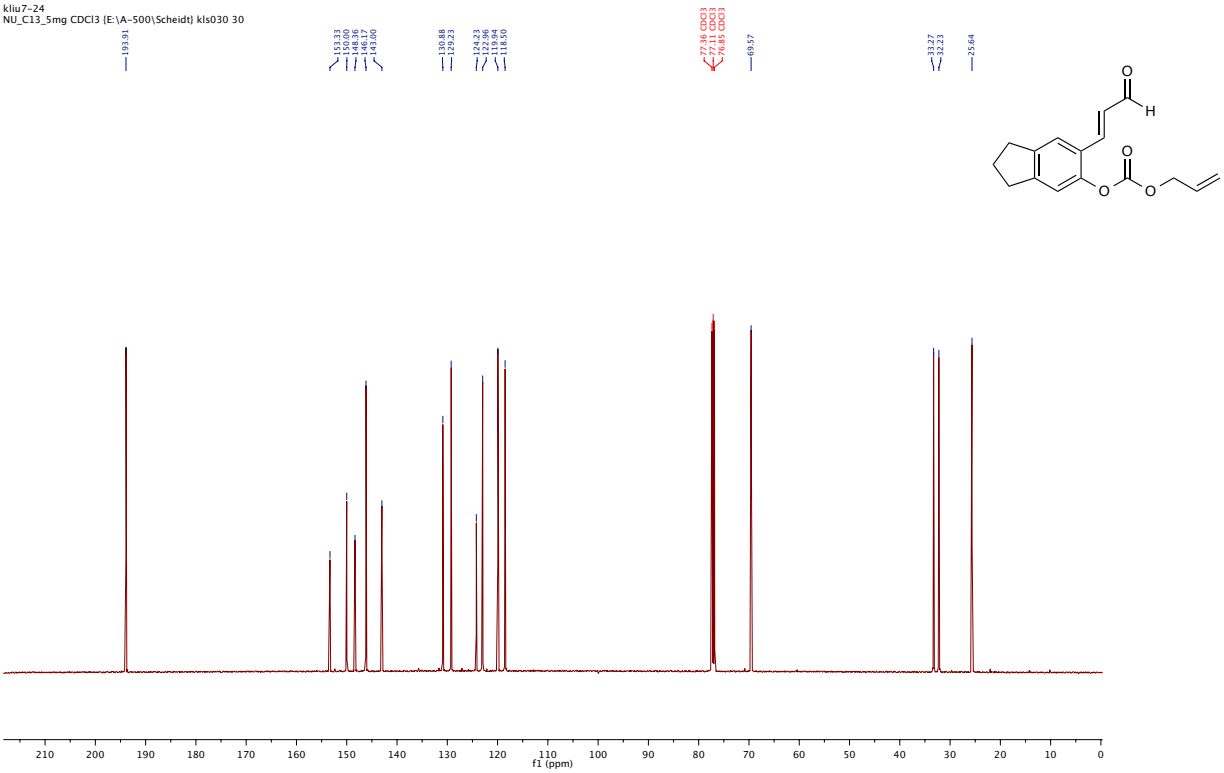
^{13}C NMR Spectra of **1e** (126 MHz, $CDCl_3$):



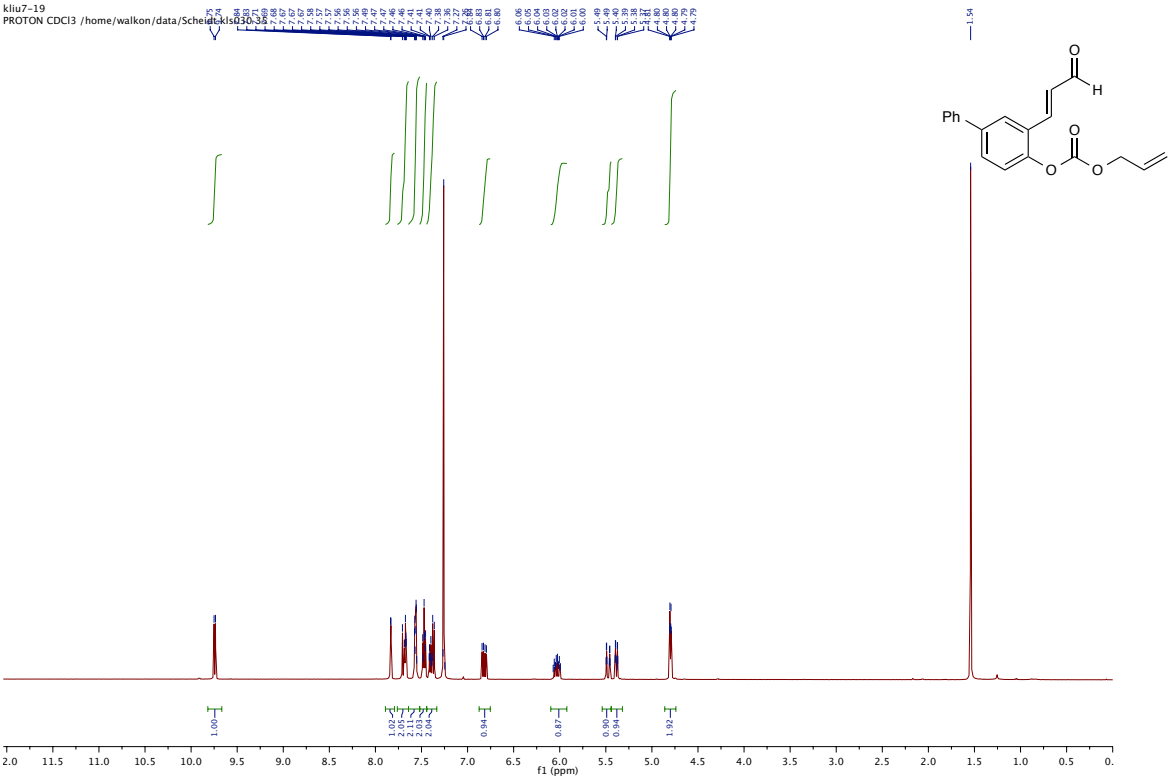
^{1}H NMR Spectra of **1f** (500 MHz, $CDCl_3$):



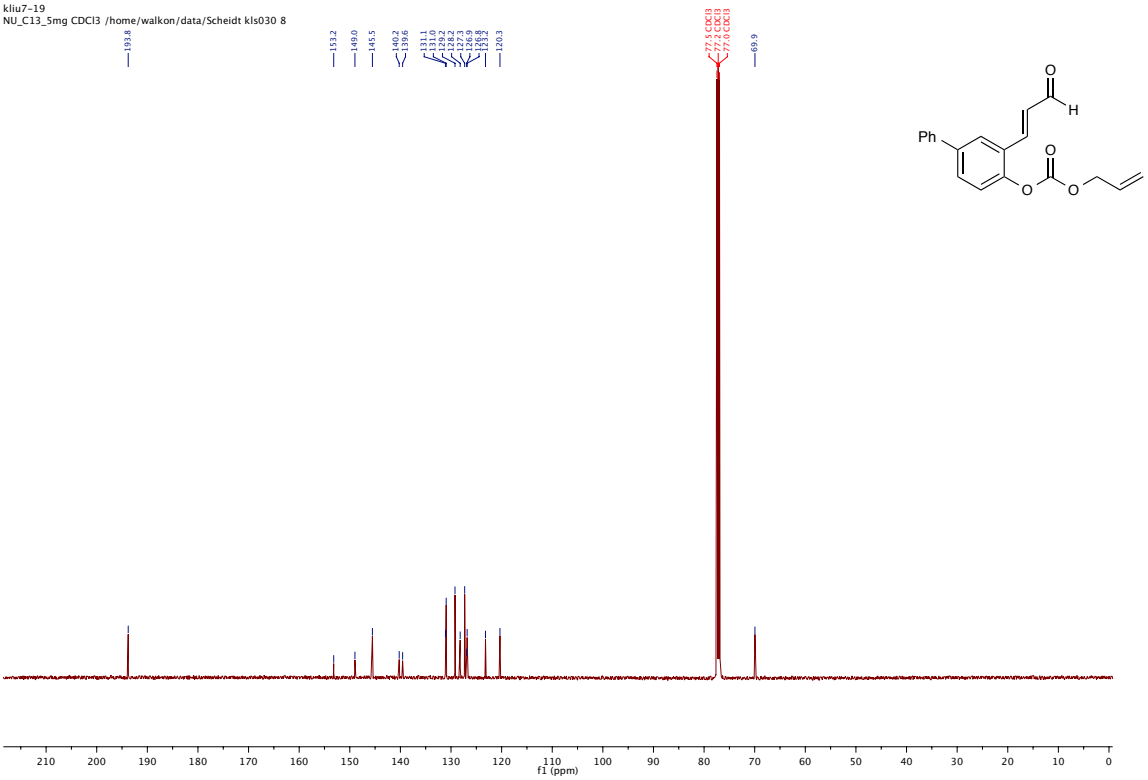
^{13}C NMR Spectra of **1f** (126 MHz, $CDCl_3$):



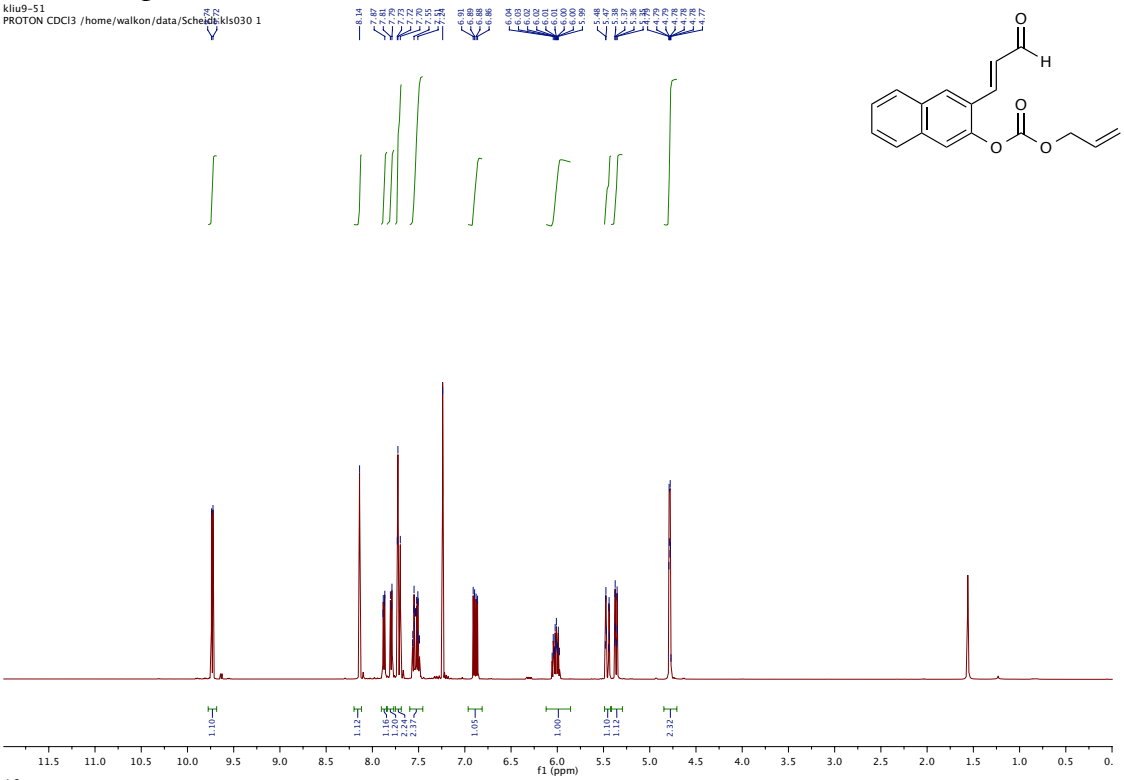
^{1}H NMR Spectra of **1g** (500 MHz, $CDCl_3$):



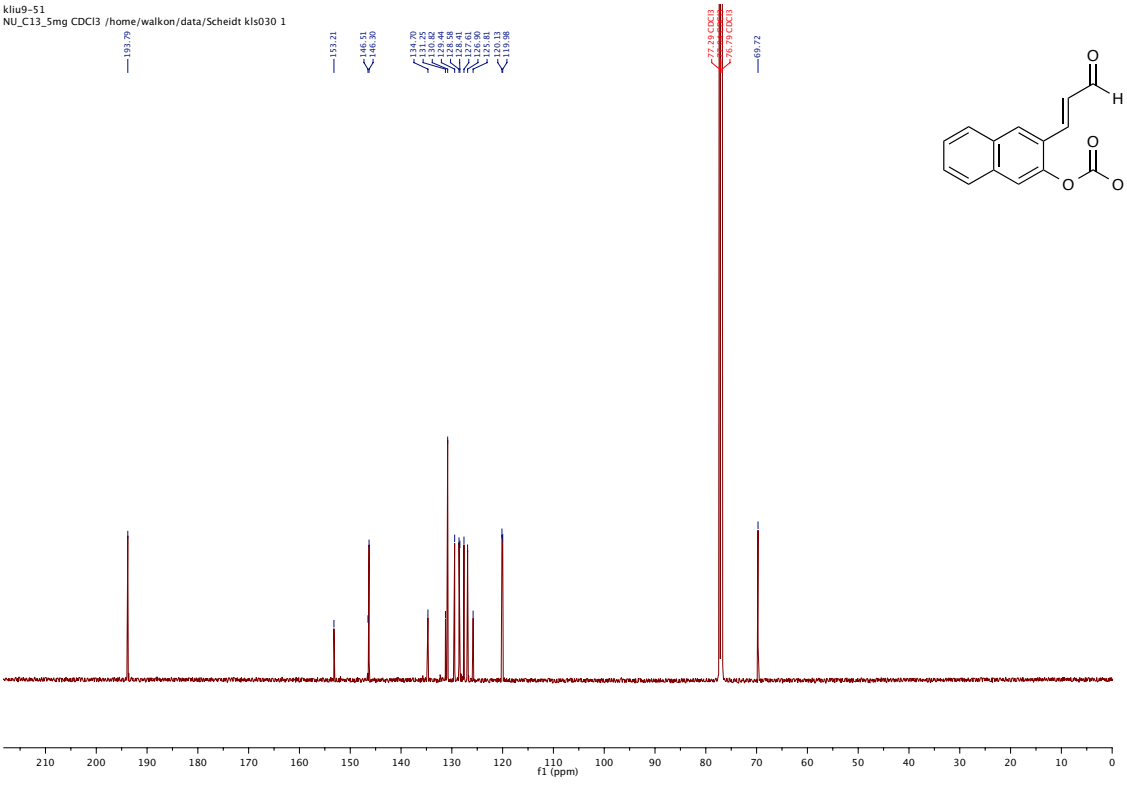
^{13}C NMR Spectra of **1g** (126 MHz, $CDCl_3$):



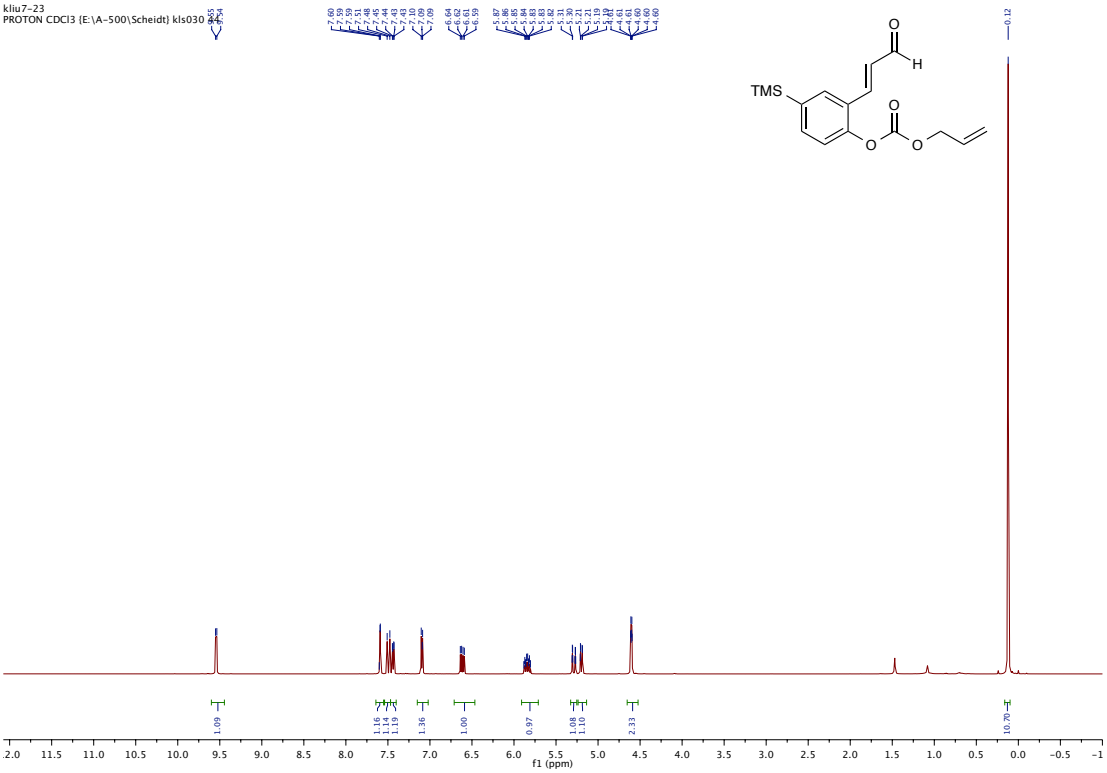
^{1}H NMR Spectra of **1h** (500 MHz, $CDCl_3$):



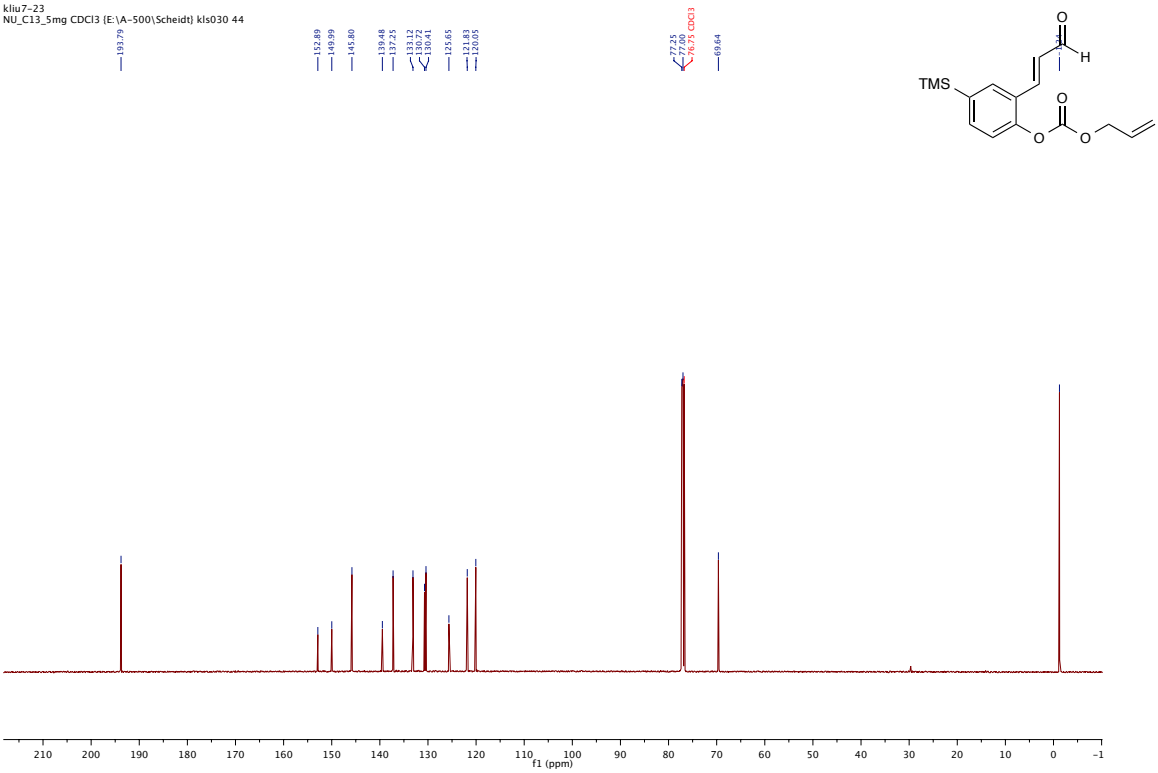
^{13}C NMR Spectra of **1g** (126 MHz, $CDCl_3$):



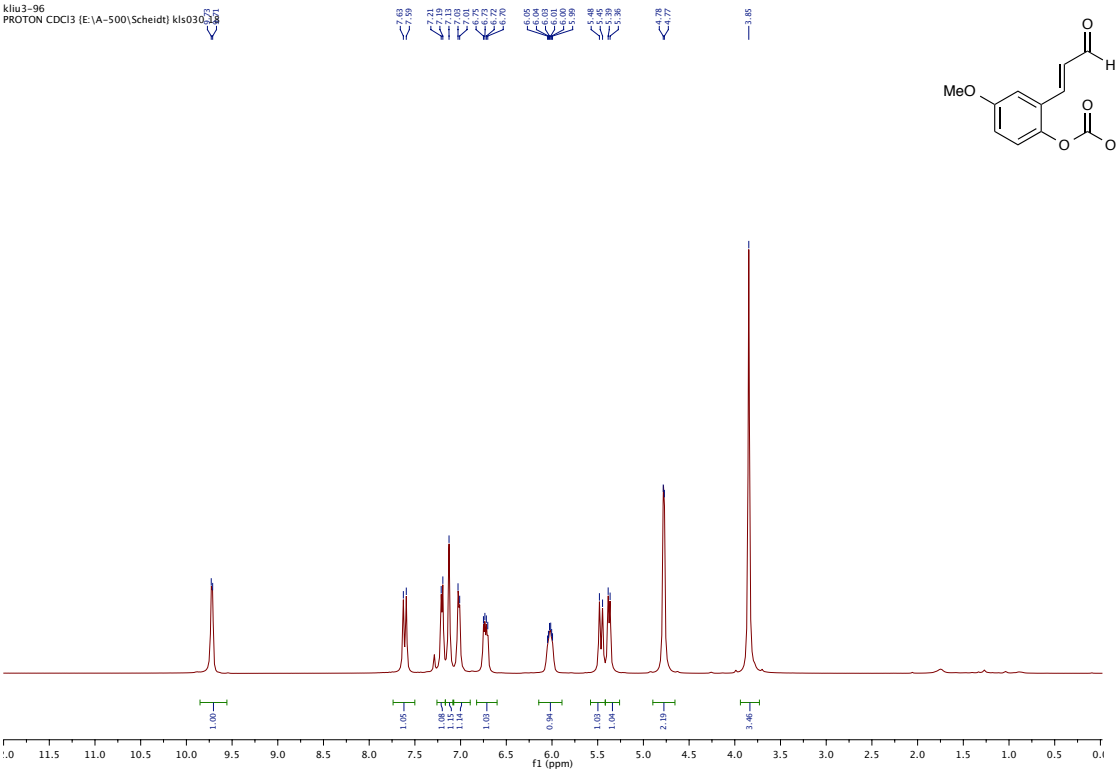
^{1}H NMR Spectra of **1i** (500 MHz, $CDCl_3$):



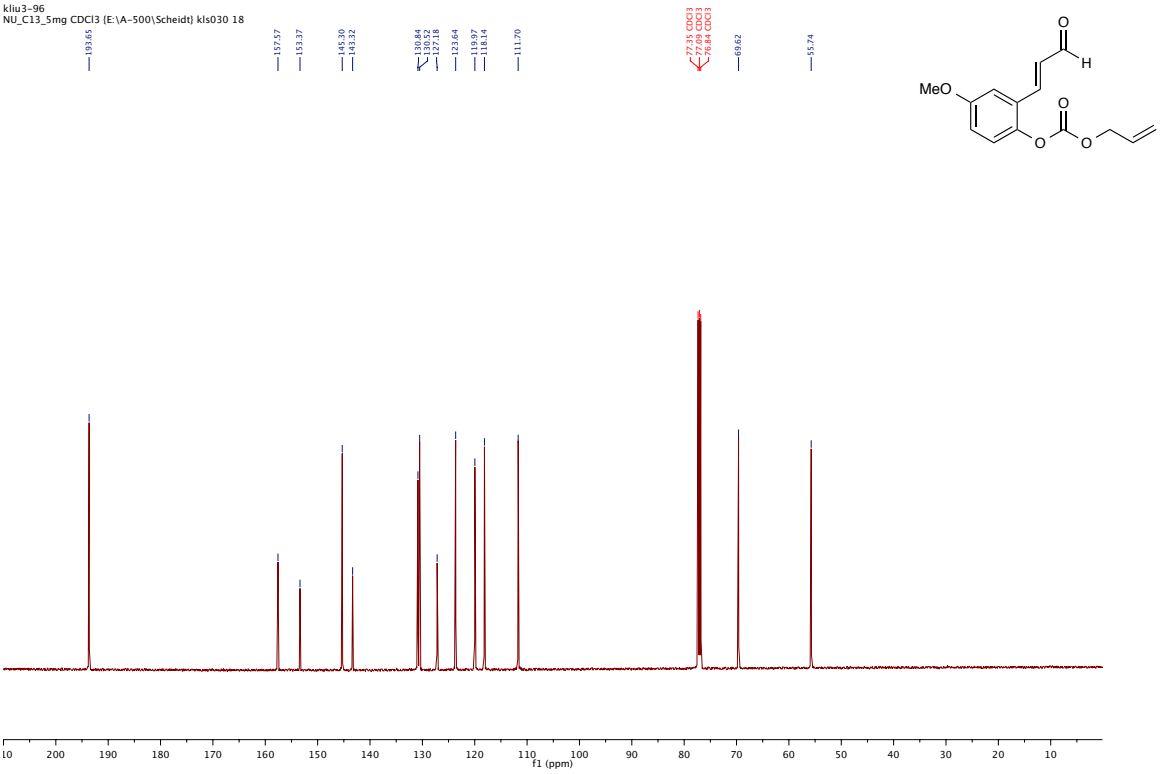
^{13}C NMR Spectra of **1i** (126 MHz, $CDCl_3$):



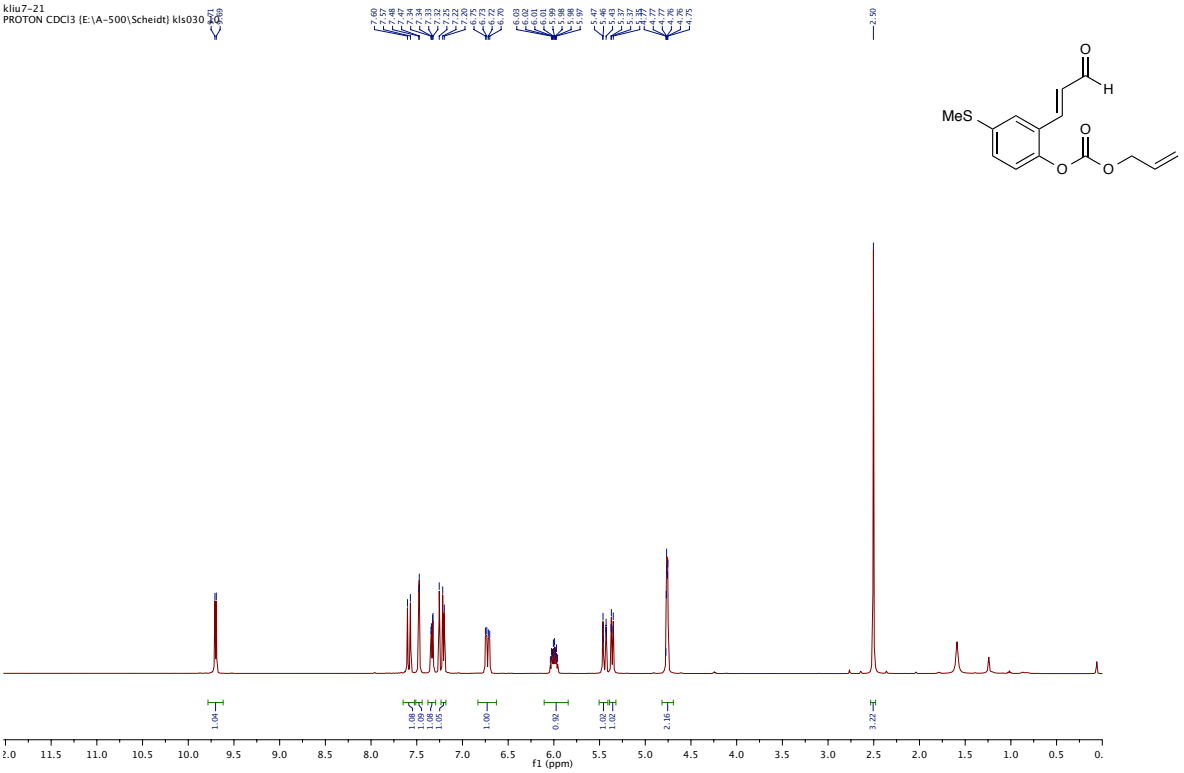
^{1}H NMR Spectra of **1j** (500 MHz, $CDCl_3$):



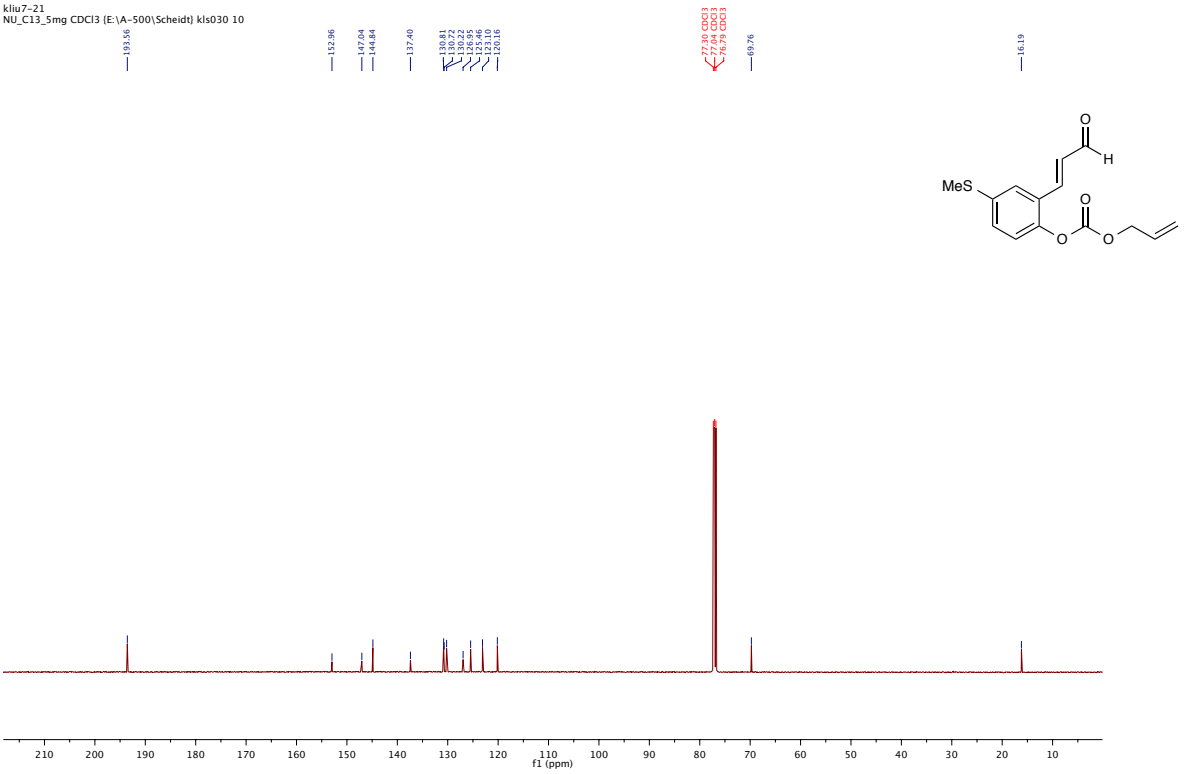
^{13}C NMR Spectra of **1j** (126 MHz, $CDCl_3$):



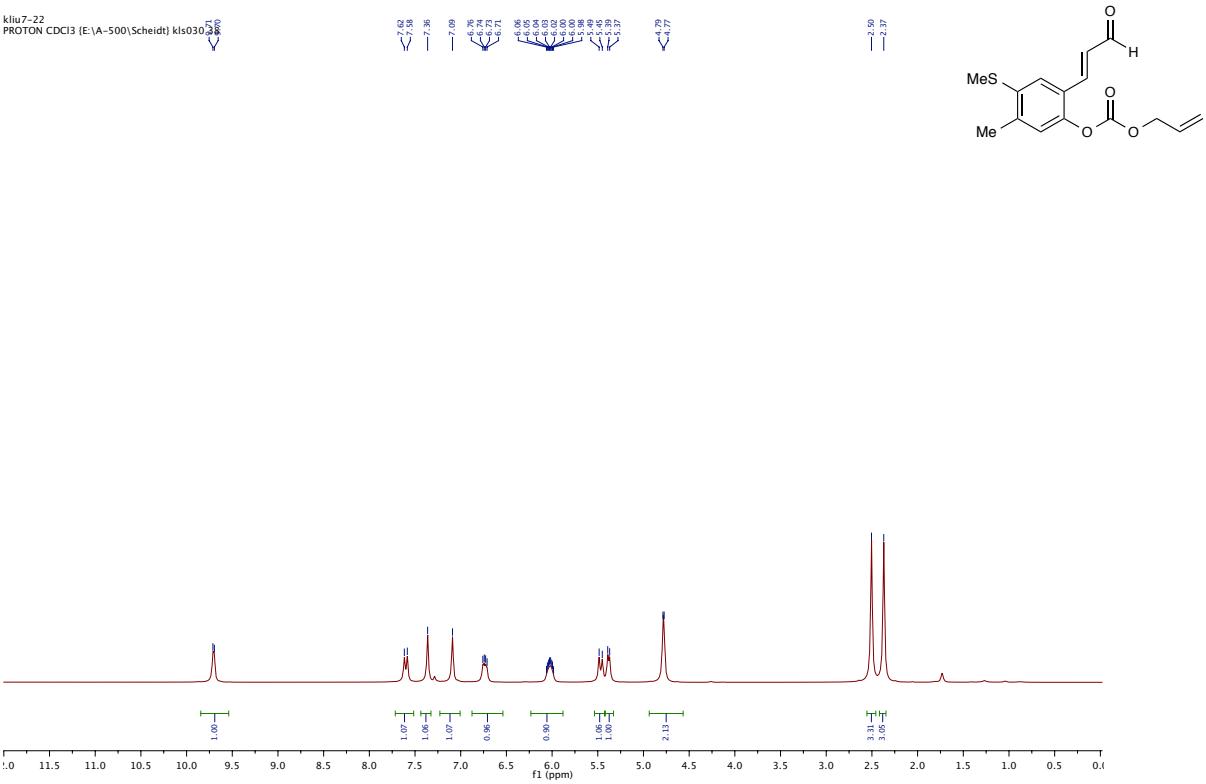
^{1}H NMR Spectra of **1k** (500 MHz, $CDCl_3$):



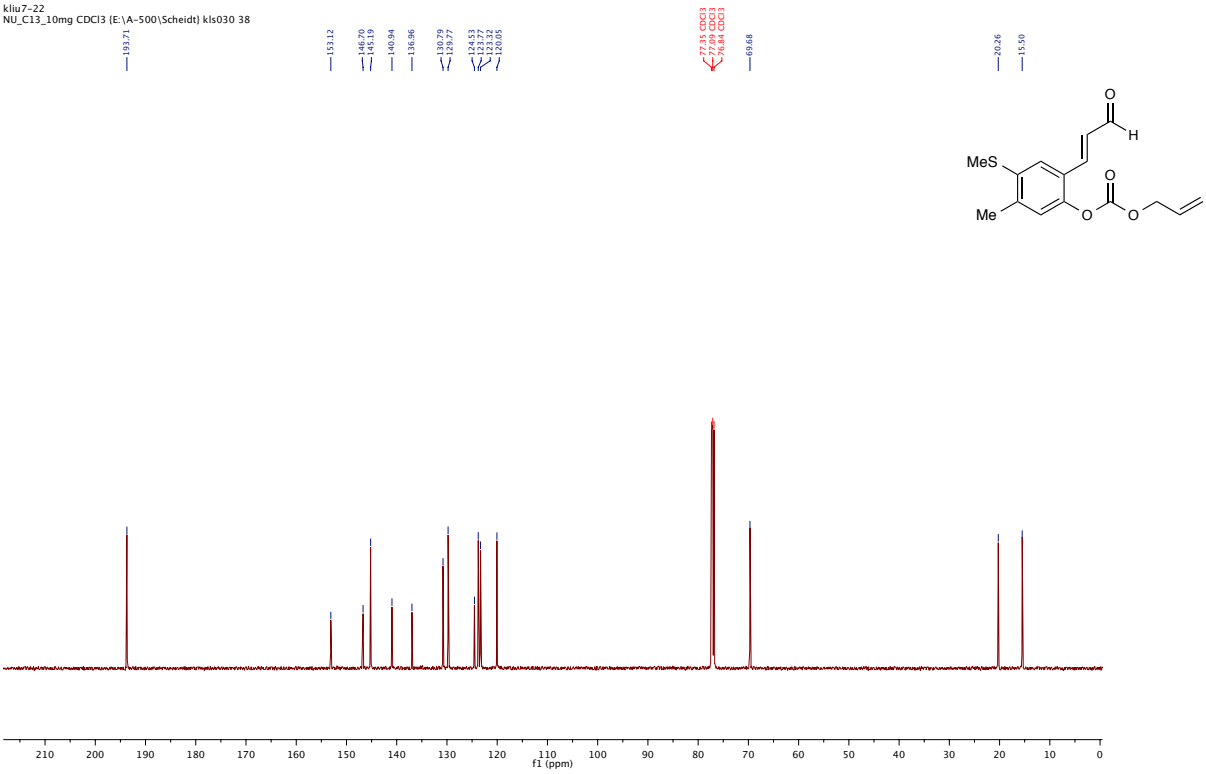
^{13}C NMR Spectra of **1k** (126 MHz, $CDCl_3$):



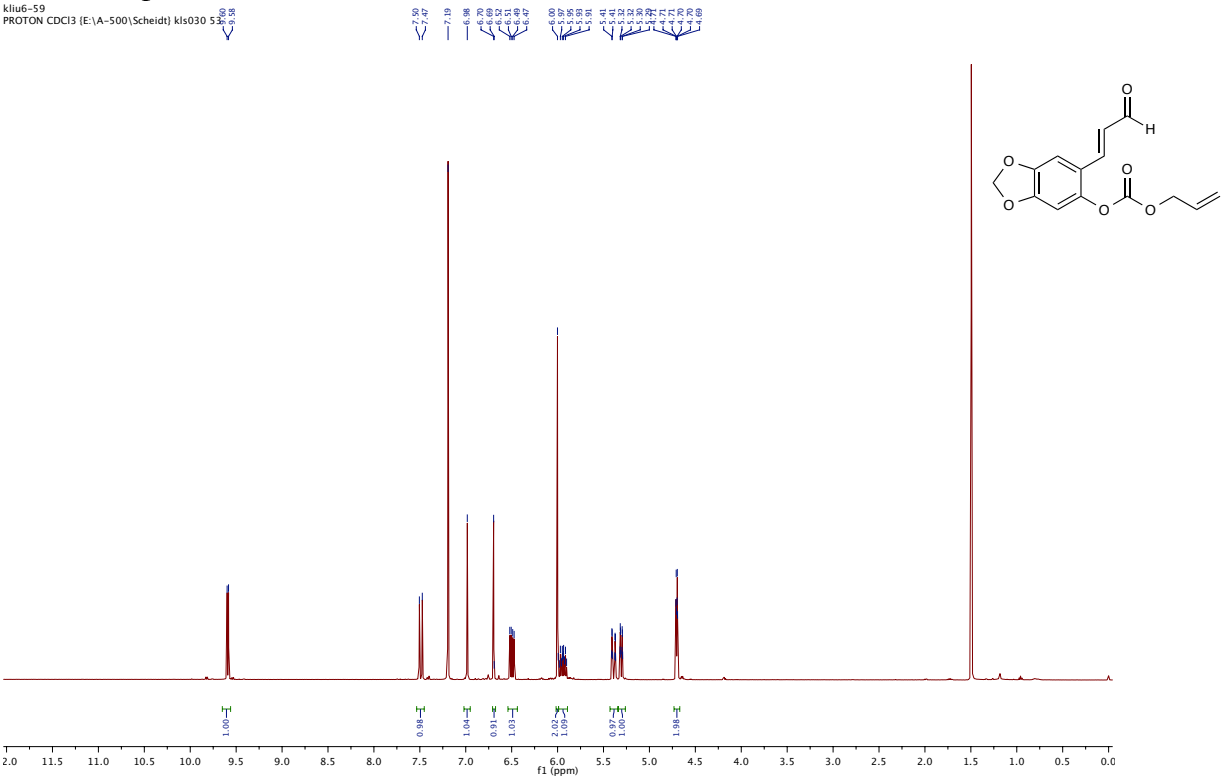
^{1}H NMR Spectra of **1l** (500 MHz, $CDCl_3$):



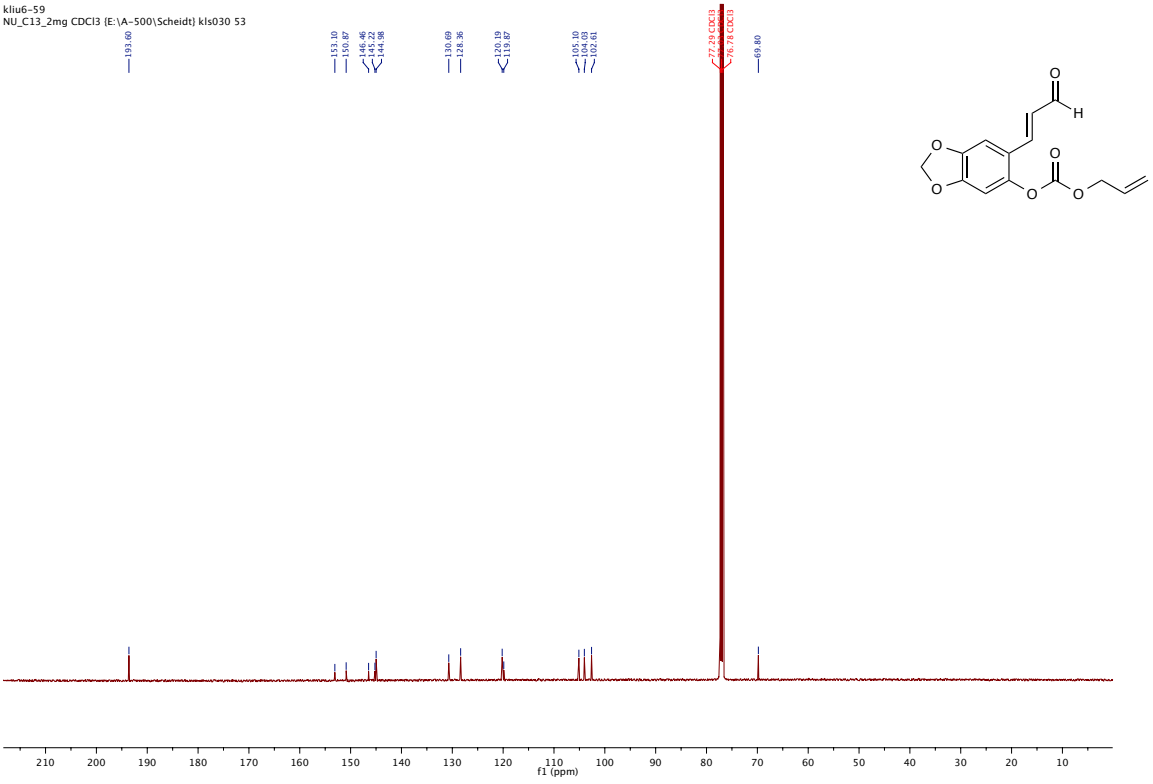
^{13}C NMR Spectra of **1l** (126 MHz, $CDCl_3$):



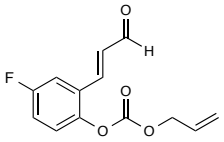
^{1}H NMR Spectra of **1m** (500 MHz, $CDCl_3$):

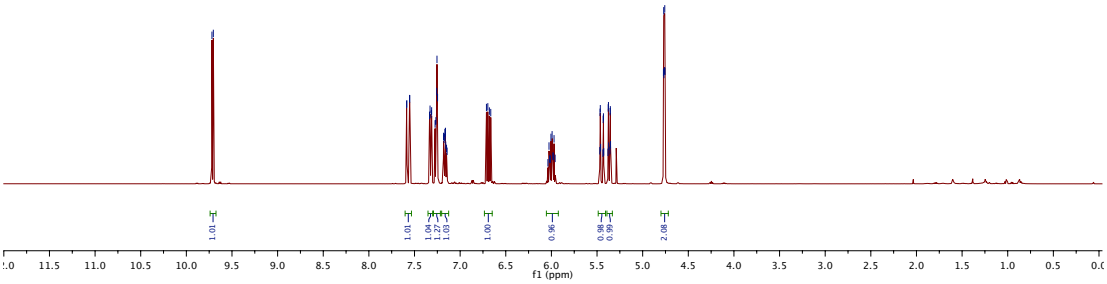


^{13}C NMR Spectra of **1m** (126 MHz, $CDCl_3$):

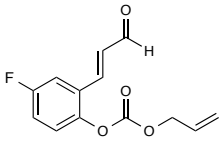


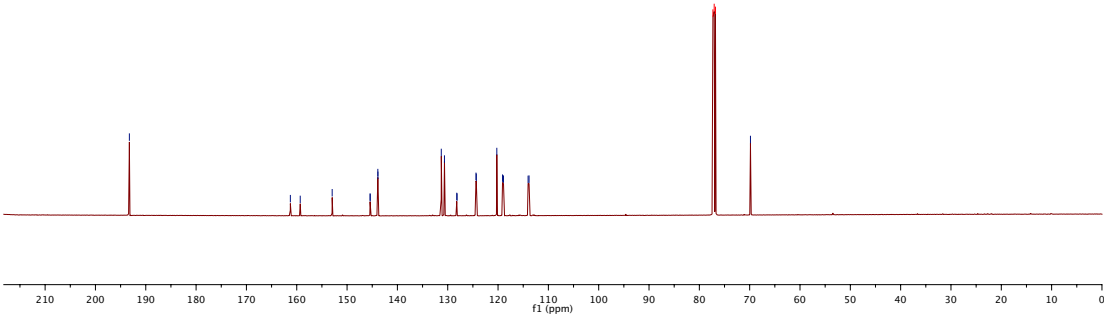
^{1}H NMR Spectra of **1n** (500 MHz, $CDCl_3$):



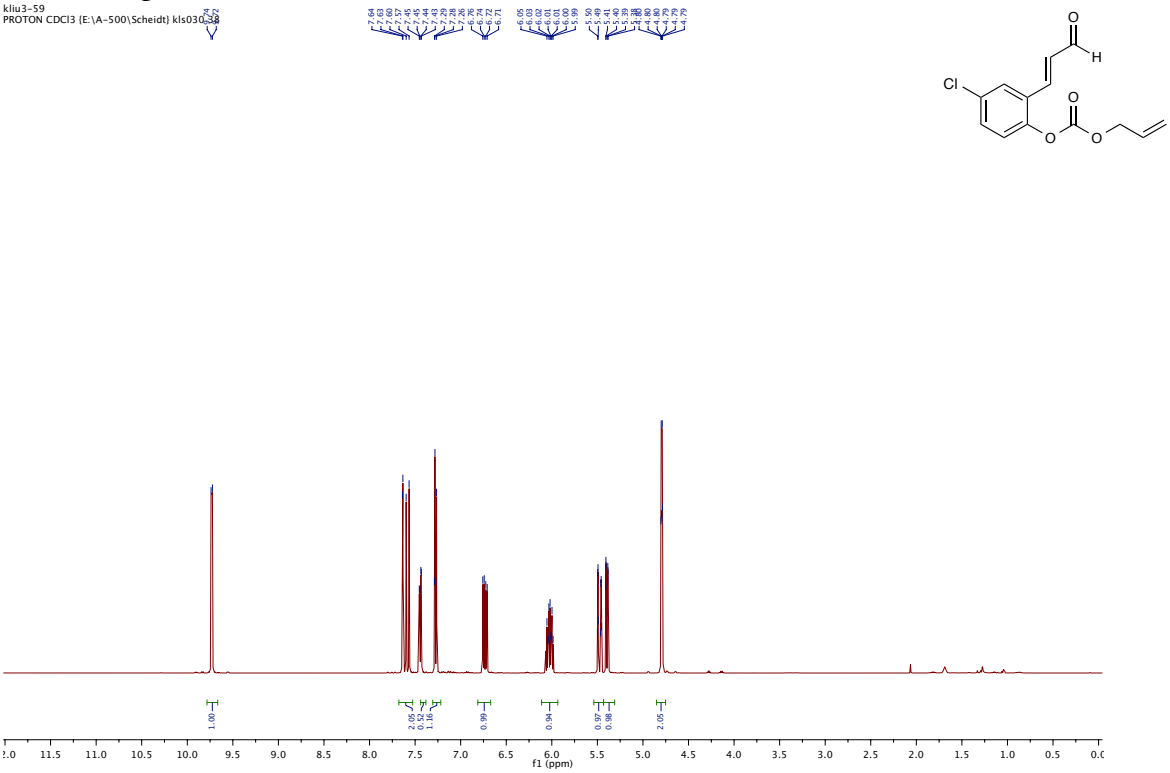


^{13}C NMR Spectra of **1n** (126 MHz, $CDCl_3$):

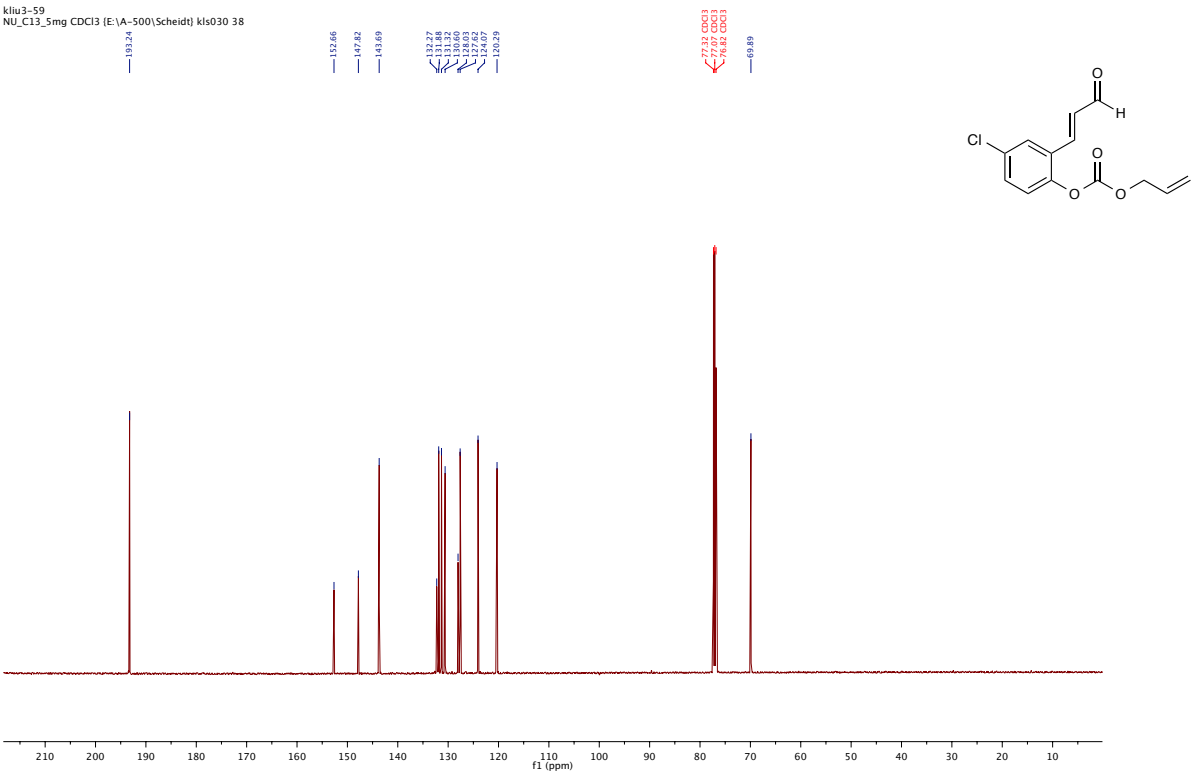




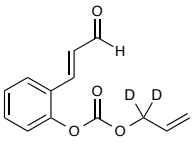
^{1}H NMR Spectra of **1o** (500 MHz, $CDCl_3$):

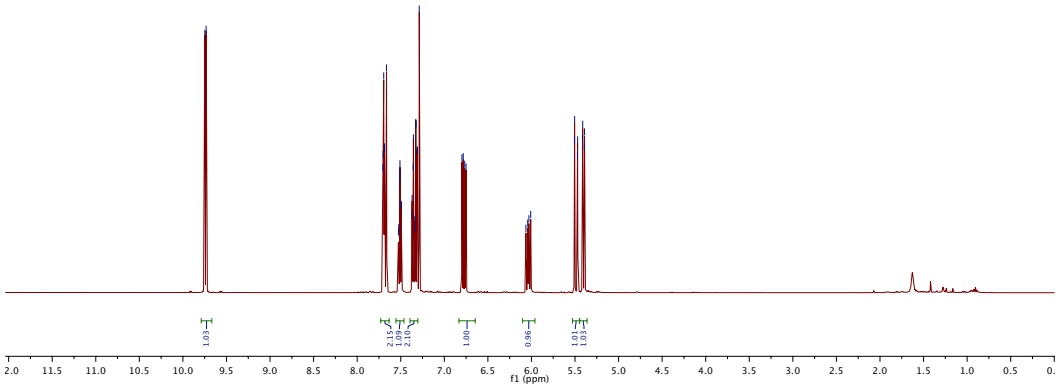


^{13}C NMR Spectra of **1o** (126 MHz, $CDCl_3$):

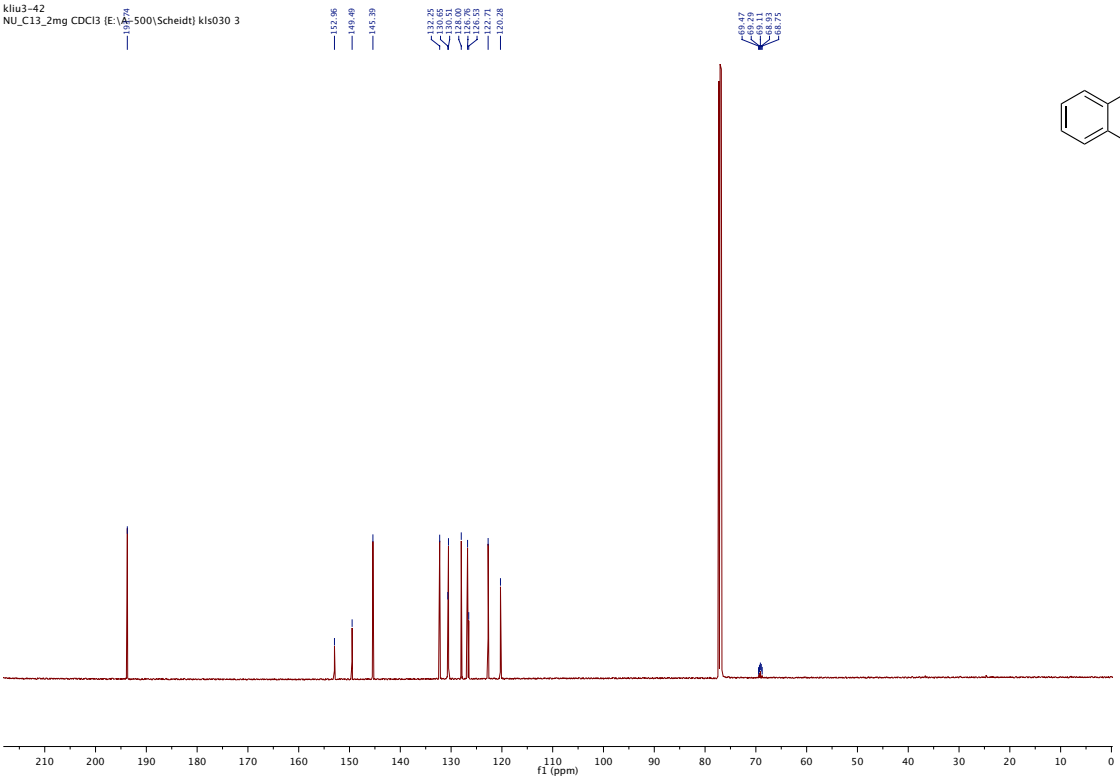


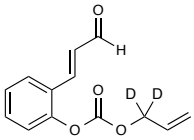
^{1}H NMR Spectra of **8** (500 MHz, $CDCl_3$):



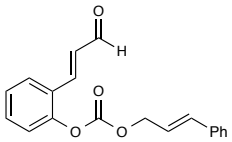


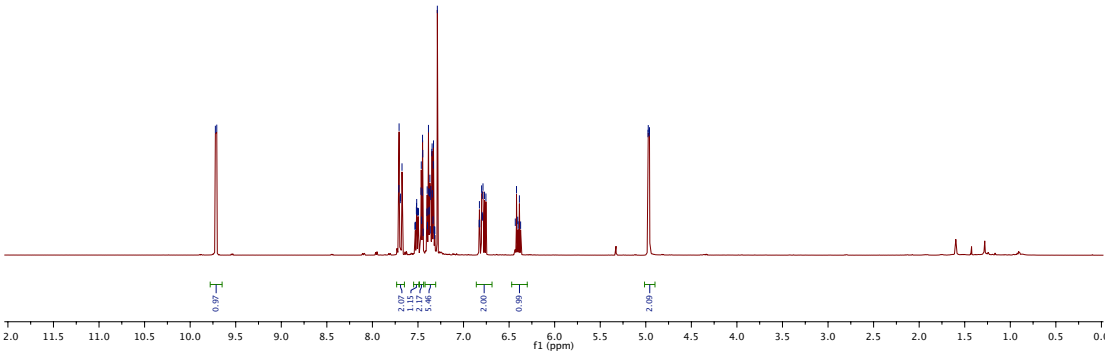
^{13}C NMR Spectra of **8** (126 MHz, $CDCl_3$):



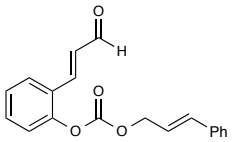


^{1}H NMR Spectra of **11** (500 MHz, $CDCl_3$):

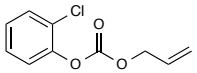


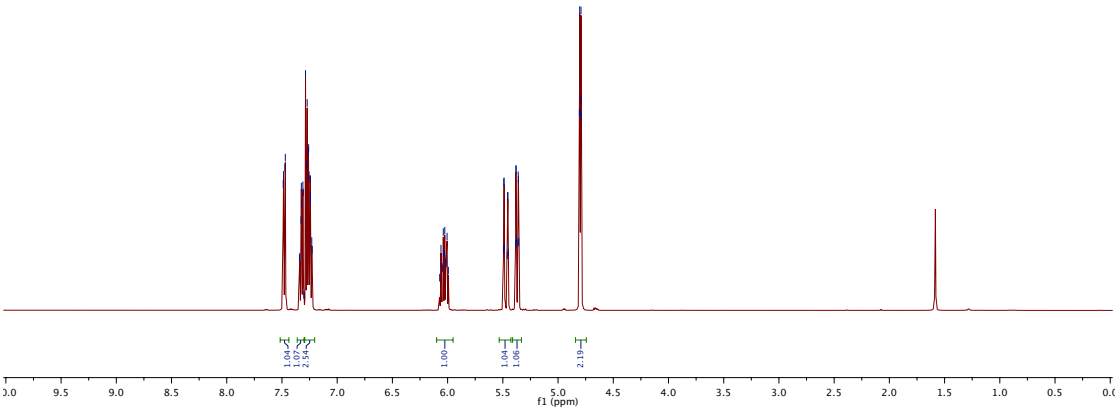


^{13}C NMR Spectra of **11** (126 MHz, $CDCl_3$):

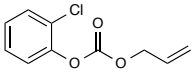


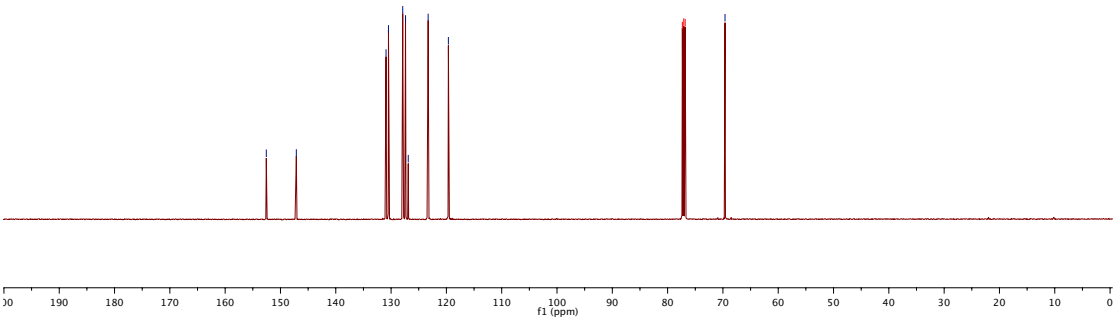
^{1}H NMR Spectra of **14** (500 MHz, $CDCl_3$):



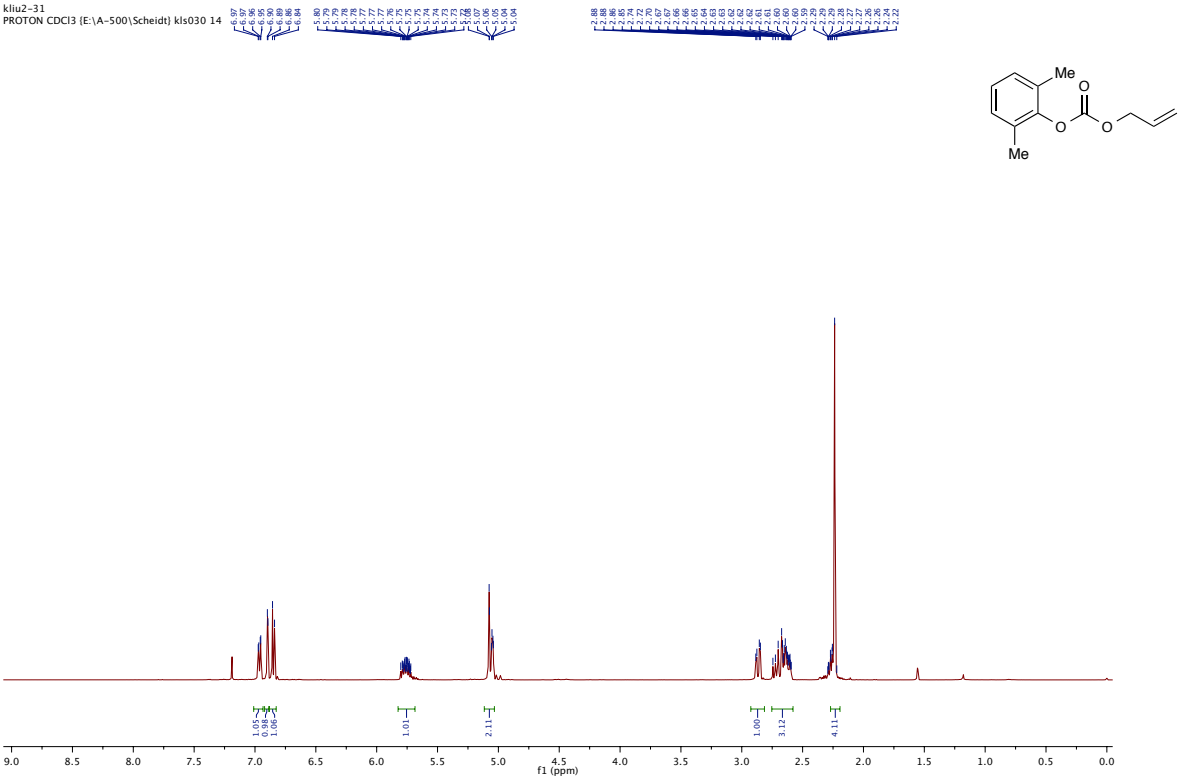


^{13}C NMR Spectra of **14** (126 MHz, $CDCl_3$):

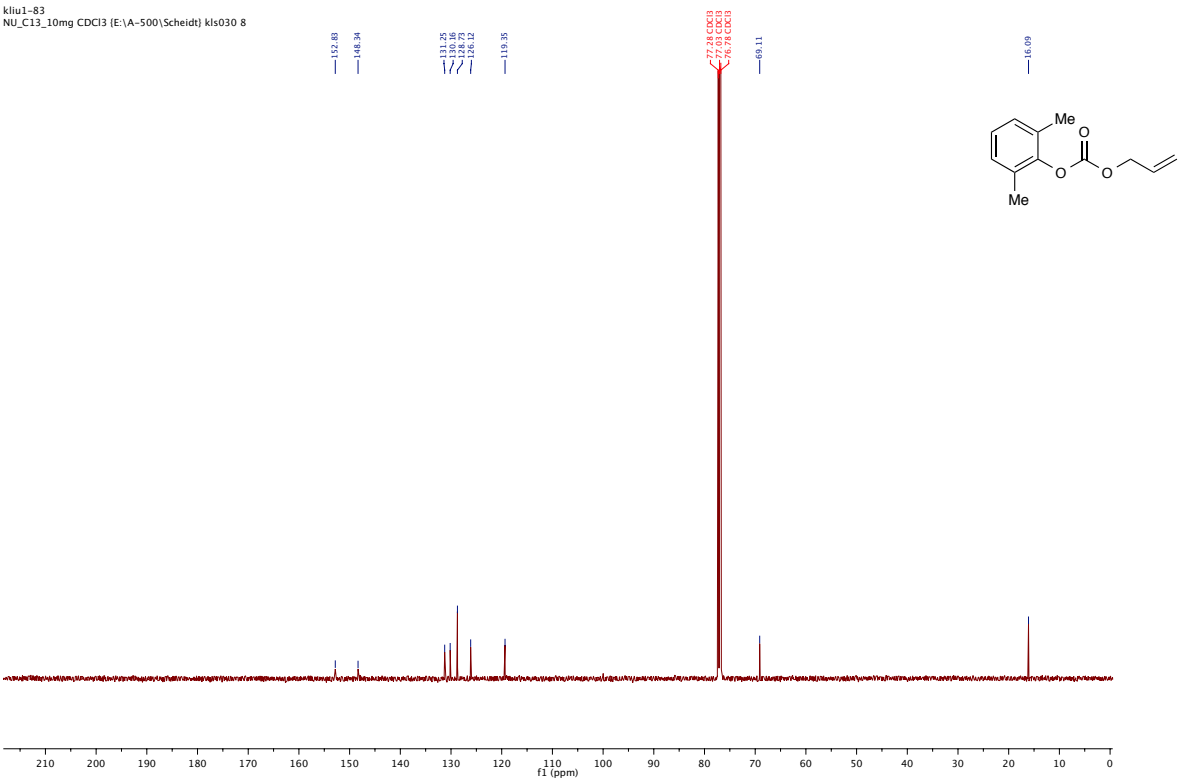




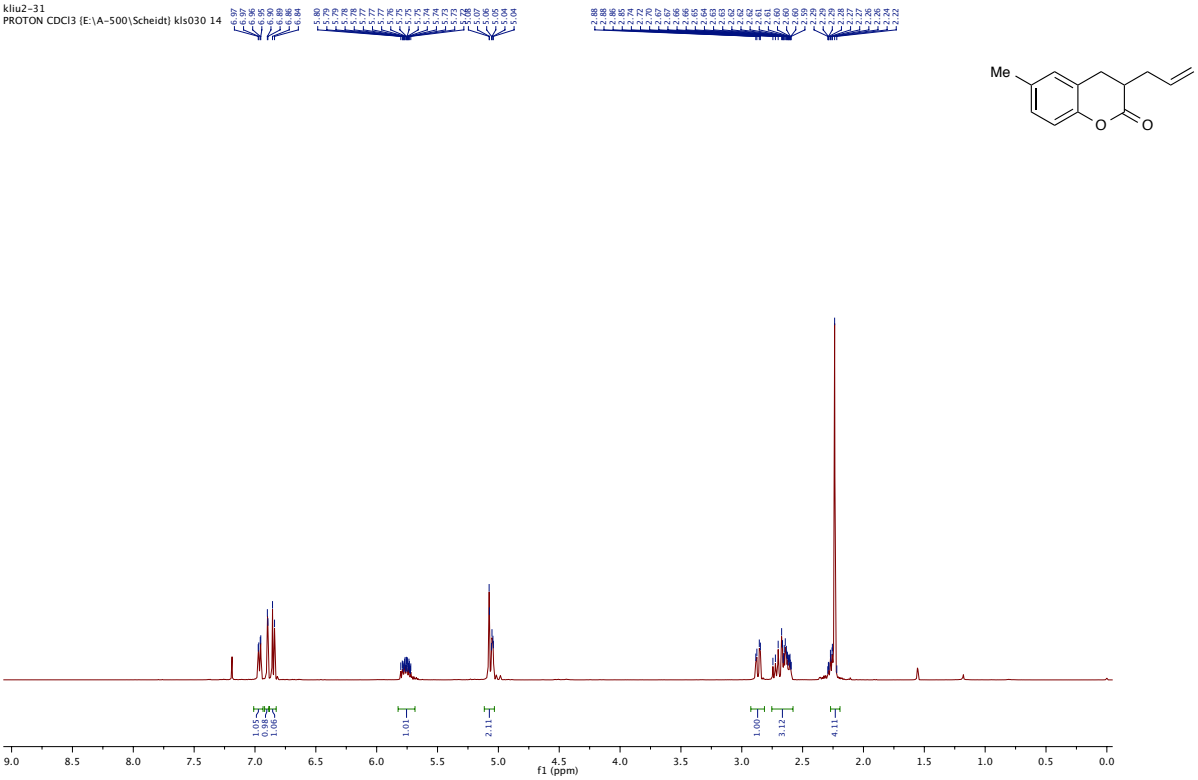
^{1}H NMR Spectra of **6** (500 MHz, $CDCl_3$):



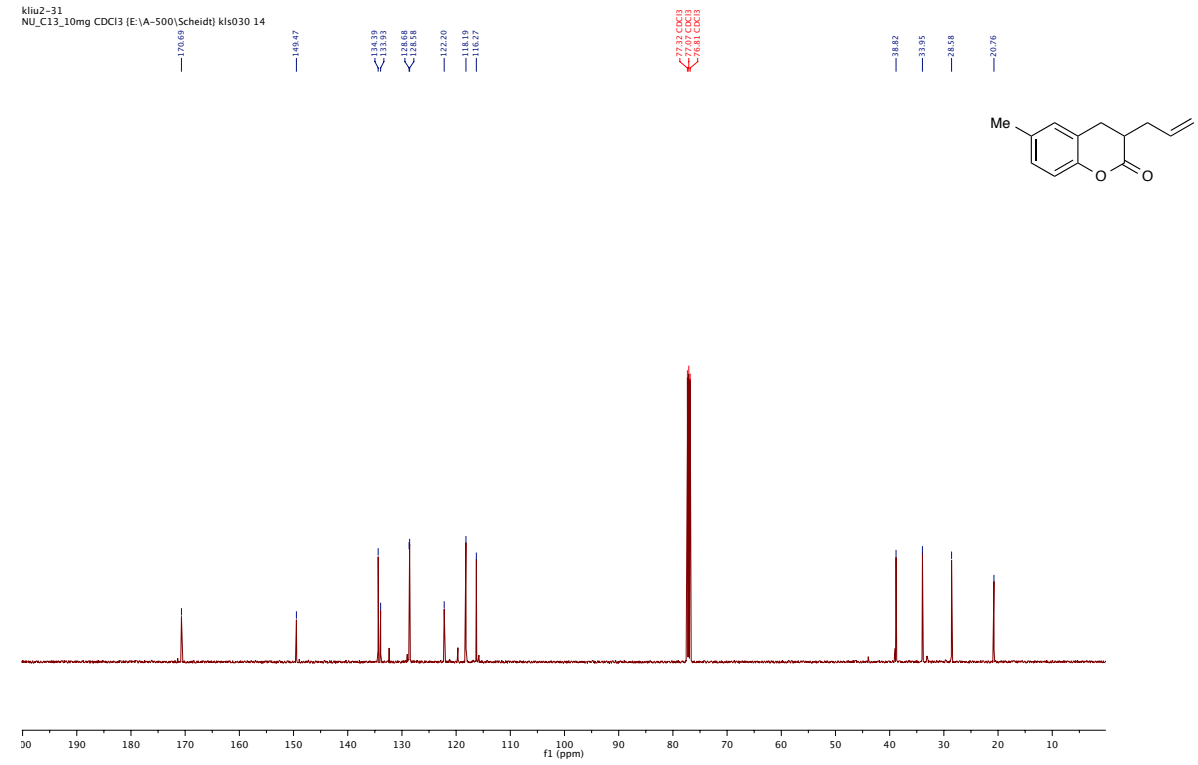
^{13}C NMR Spectra of **6** (126 MHz, $CDCl_3$



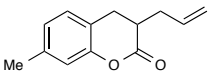
^{1}H NMR Spectra of **2b** (500 MHz, $CDCl_3$):

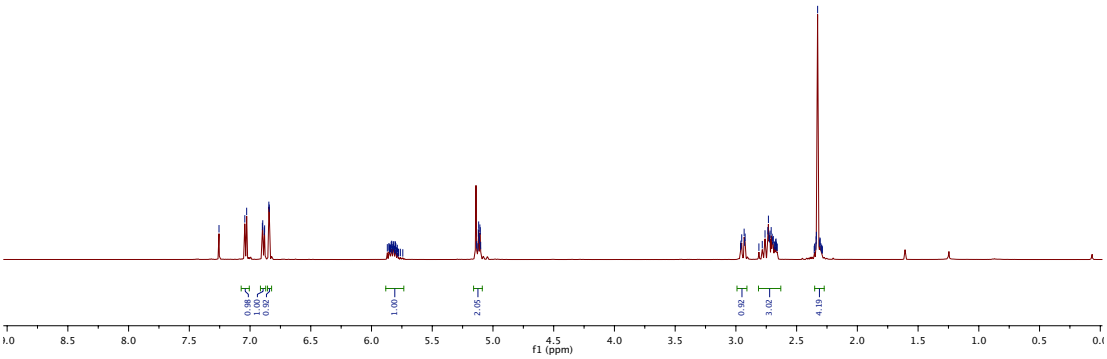


^{13}C NMR Spectra of **2b** (126 MHz, $CDCl_3$):

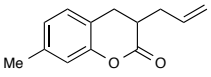


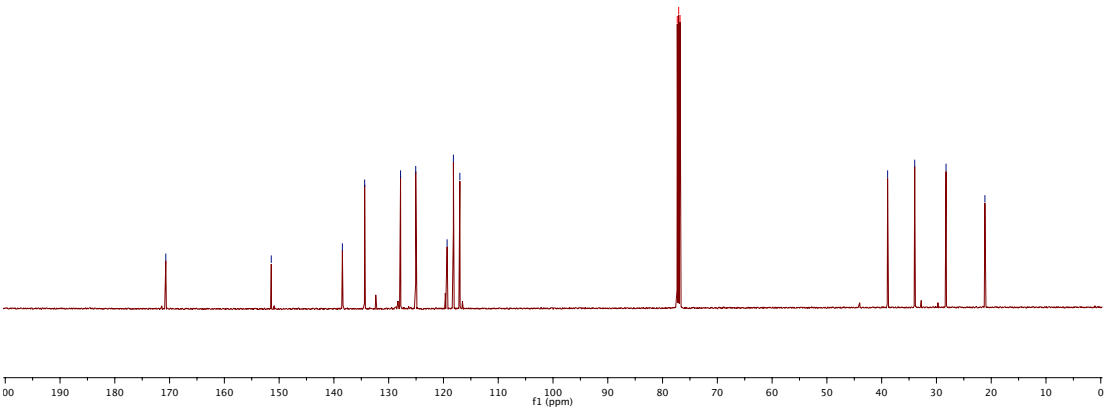
^{1}H NMR Spectra of **2c** (500 MHz, $CDCl_3$):



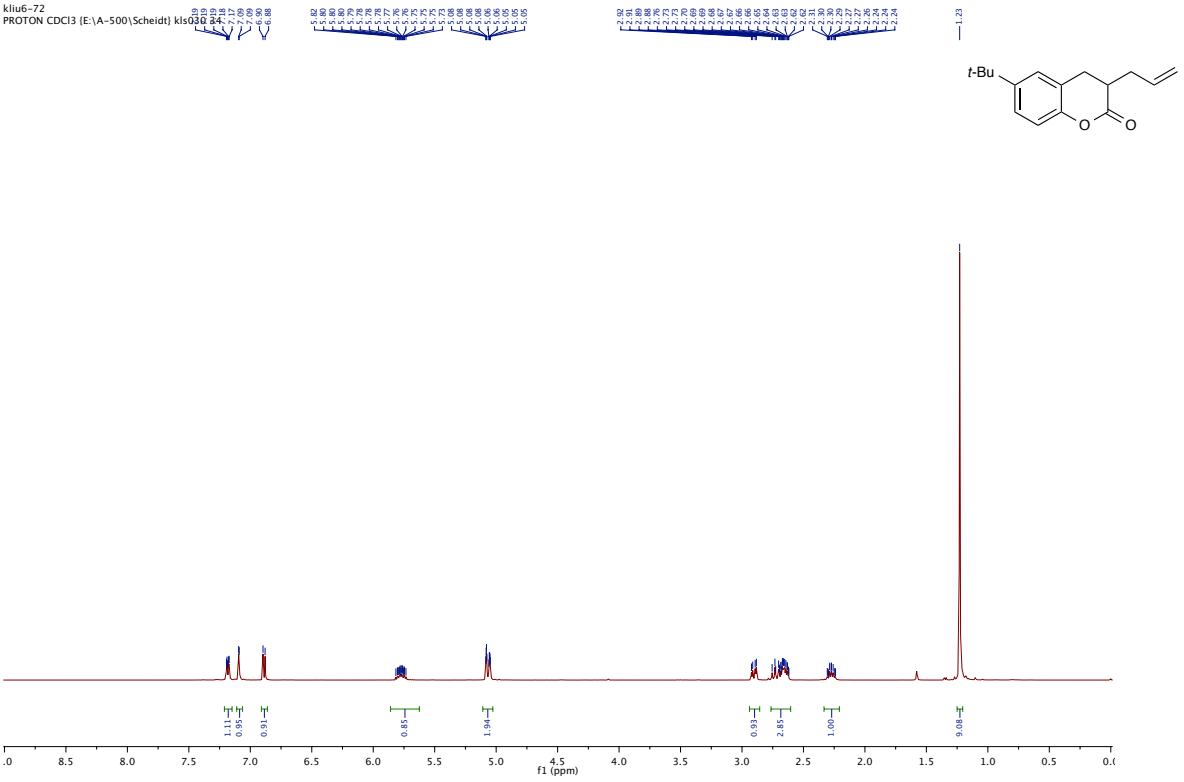


^{13}C NMR Spectra of **2c** (126 MHz, $CDCl_3$):

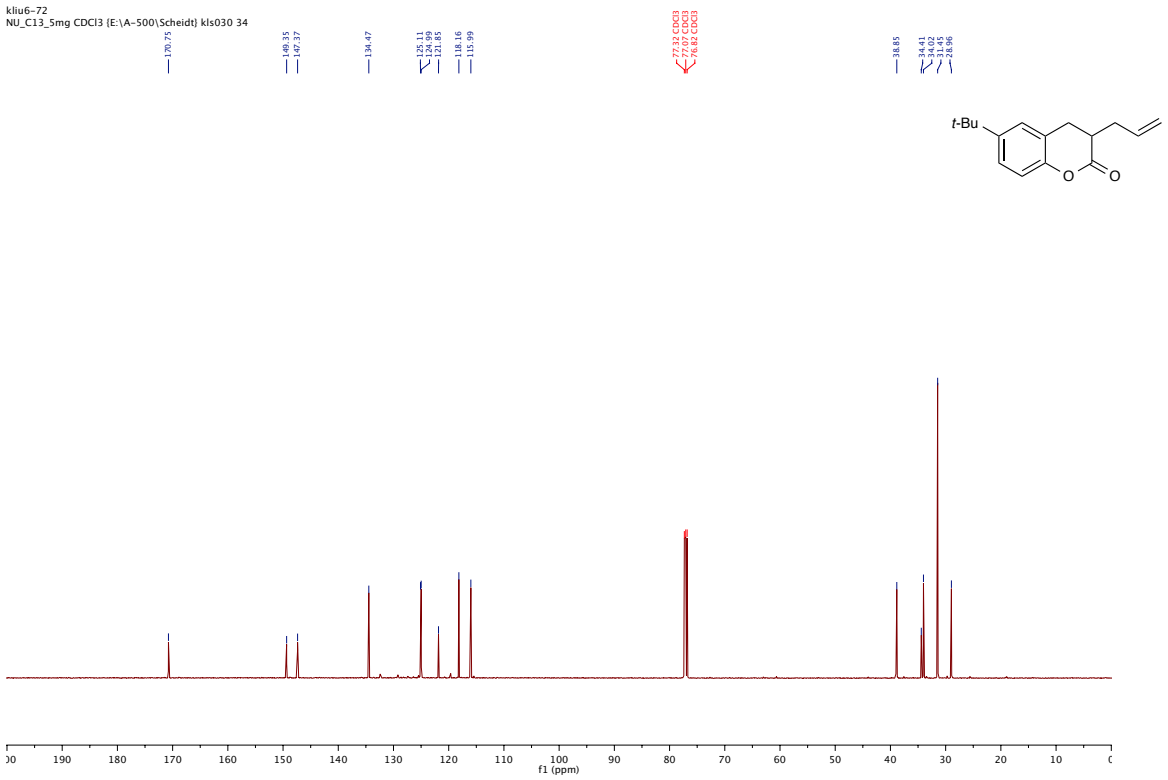




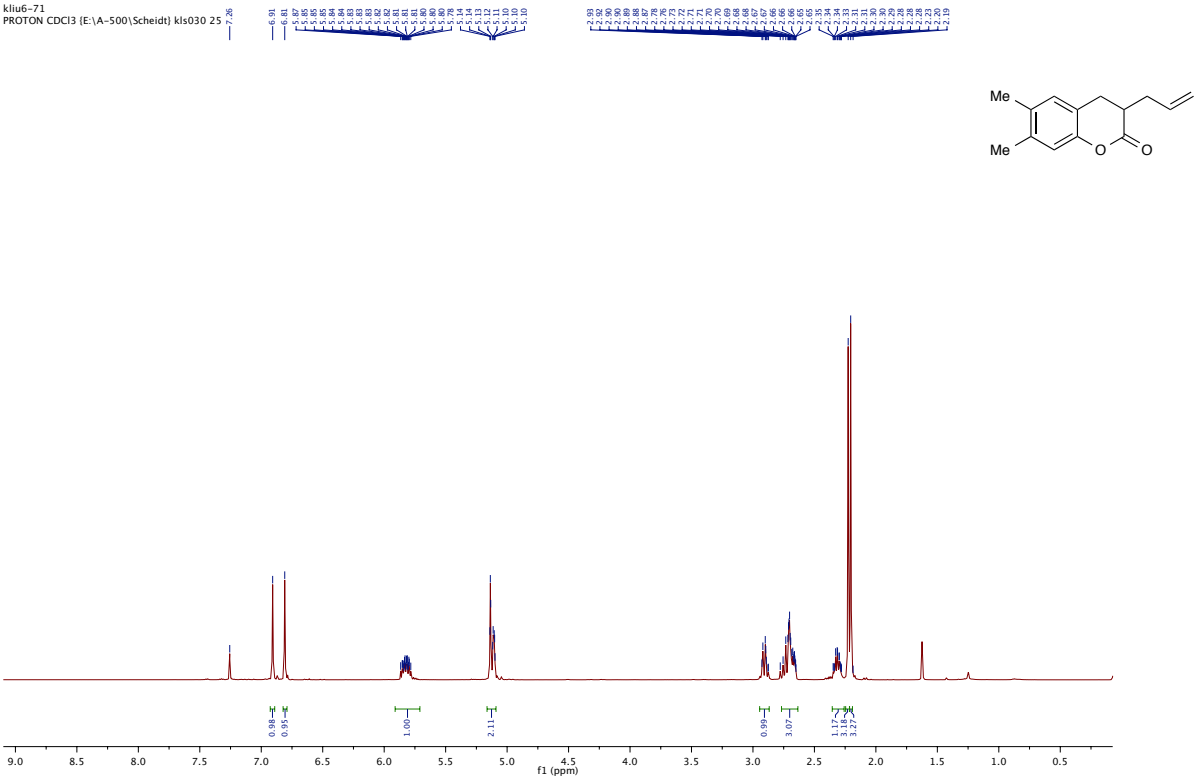
^{1}H NMR Spectra of **2d** (500 MHz, $CDCl_3$):



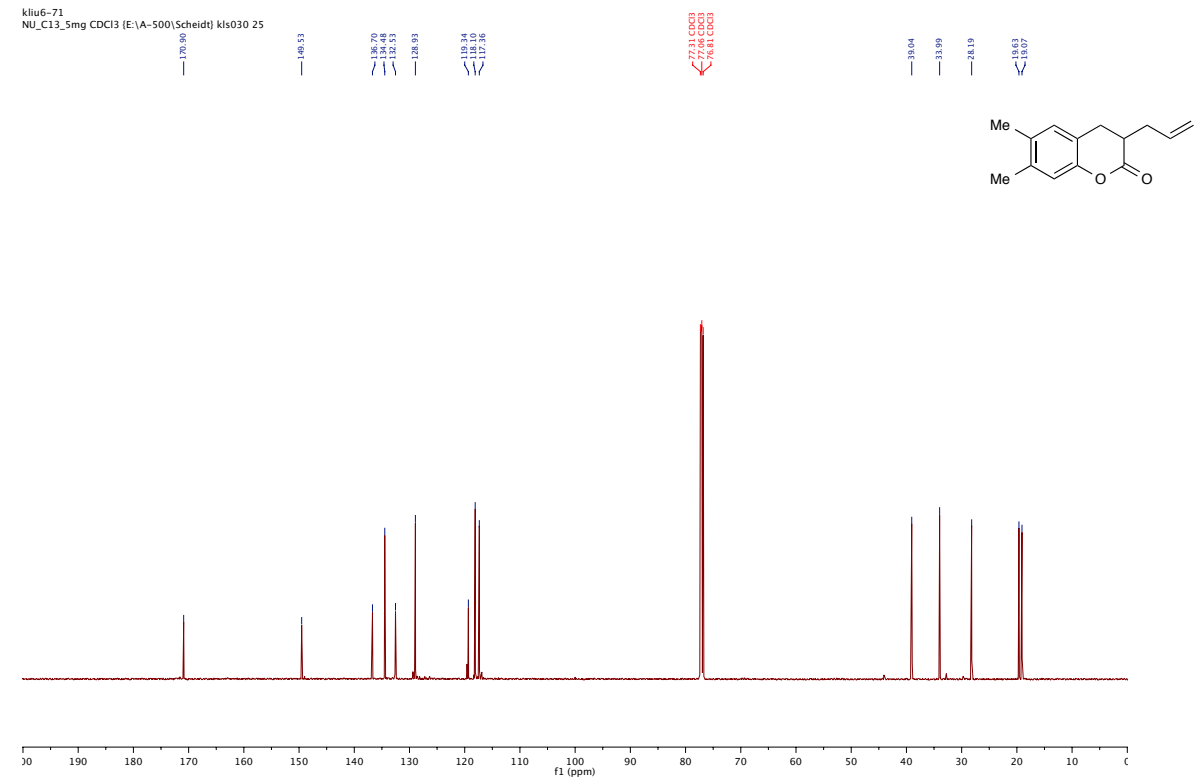
^{13}C NMR Spectra of **2d** (126 MHz, $CDCl_3$):



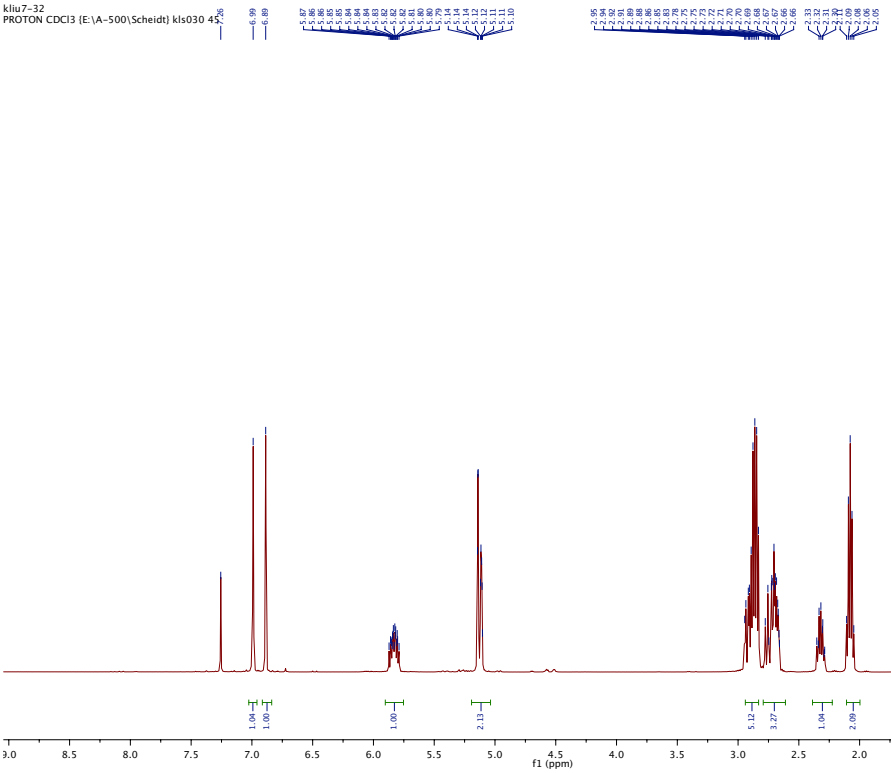
^{1}H NMR Spectra of **2e** (500 MHz, $CDCl_3$):



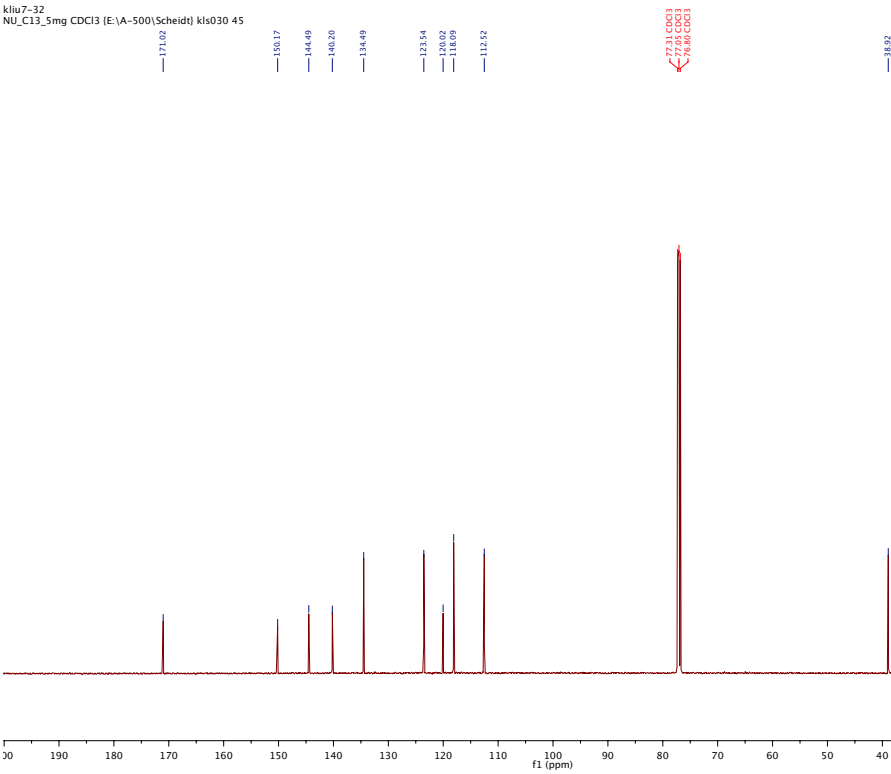
^{13}C NMR Spectra of **2e** (126 MHz, $CDCl_3$):



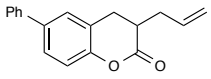
^{1}H NMR Spectra of **2f** (500 MHz, $CDCl_3$):

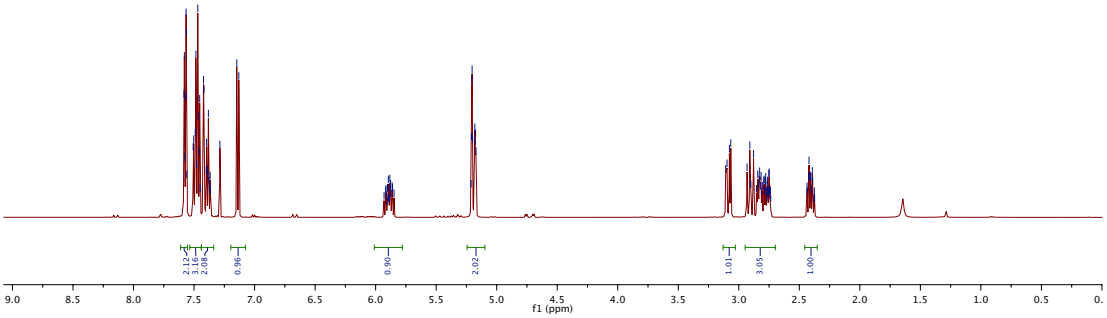


^{13}C NMR Spectra of **2f** (126 MHz, $CDCl_3$):

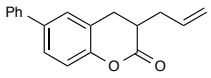


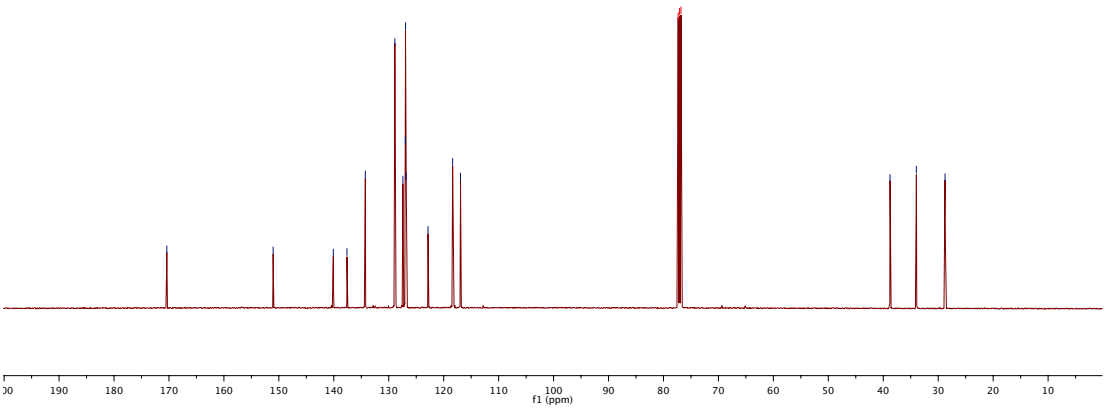
^{1}H NMR Spectra of **2g** (500 MHz, $CDCl_3$):



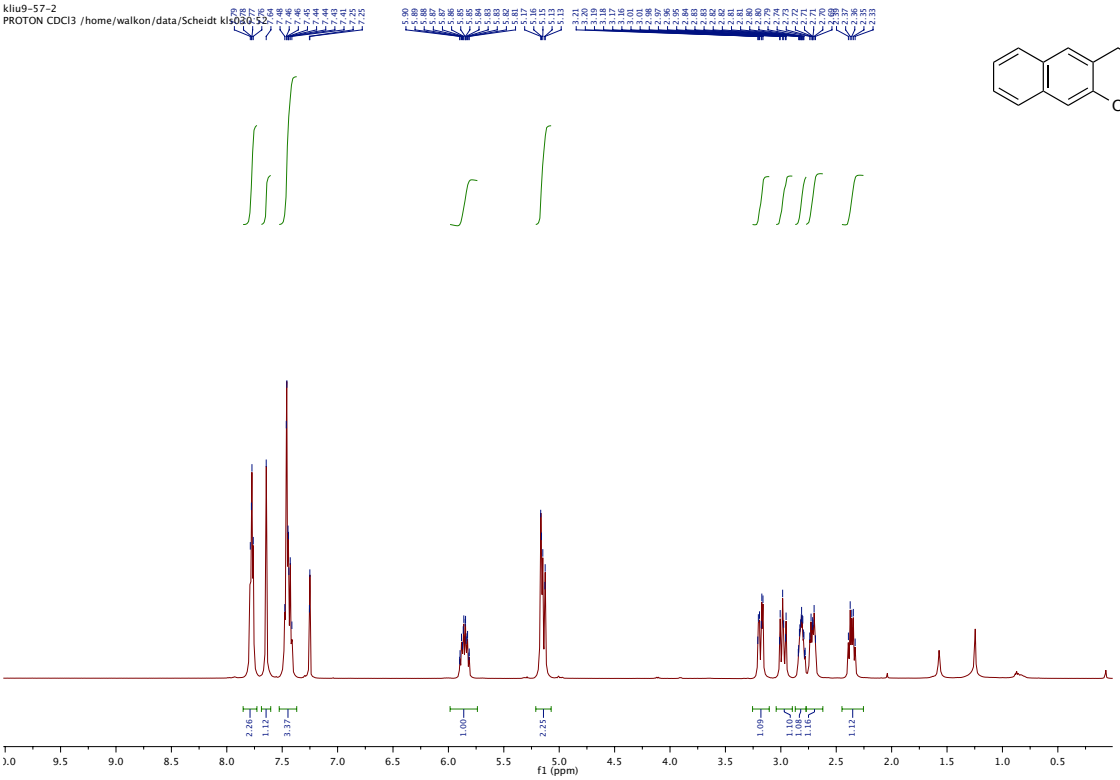


^{13}C NMR Spectra of **2g** (126 MHz, $CDCl_3$):

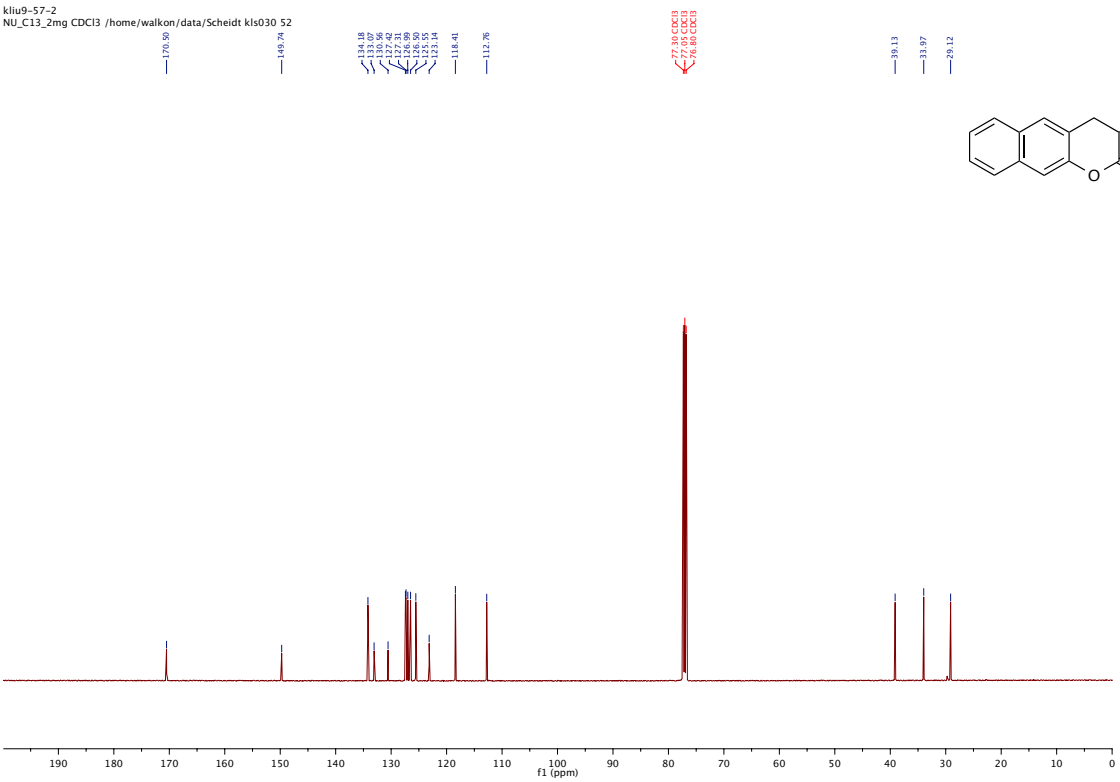




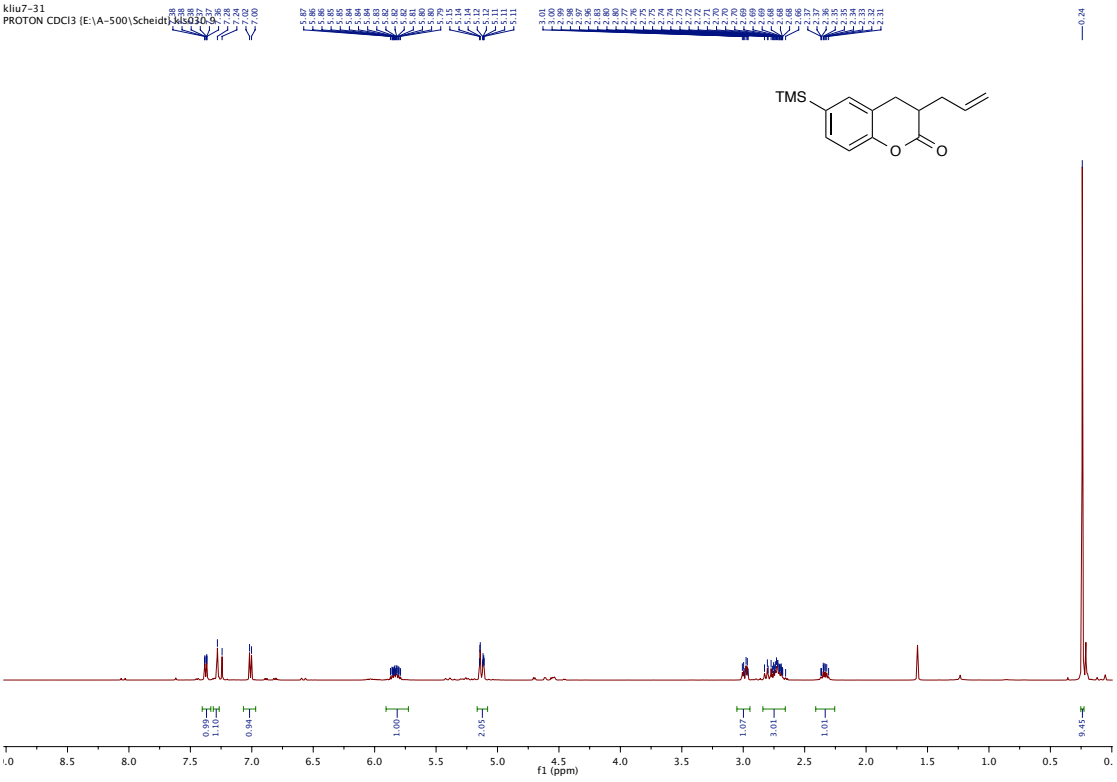
^{1}H NMR Spectra of **2h** (500 MHz, $CDCl_3$):



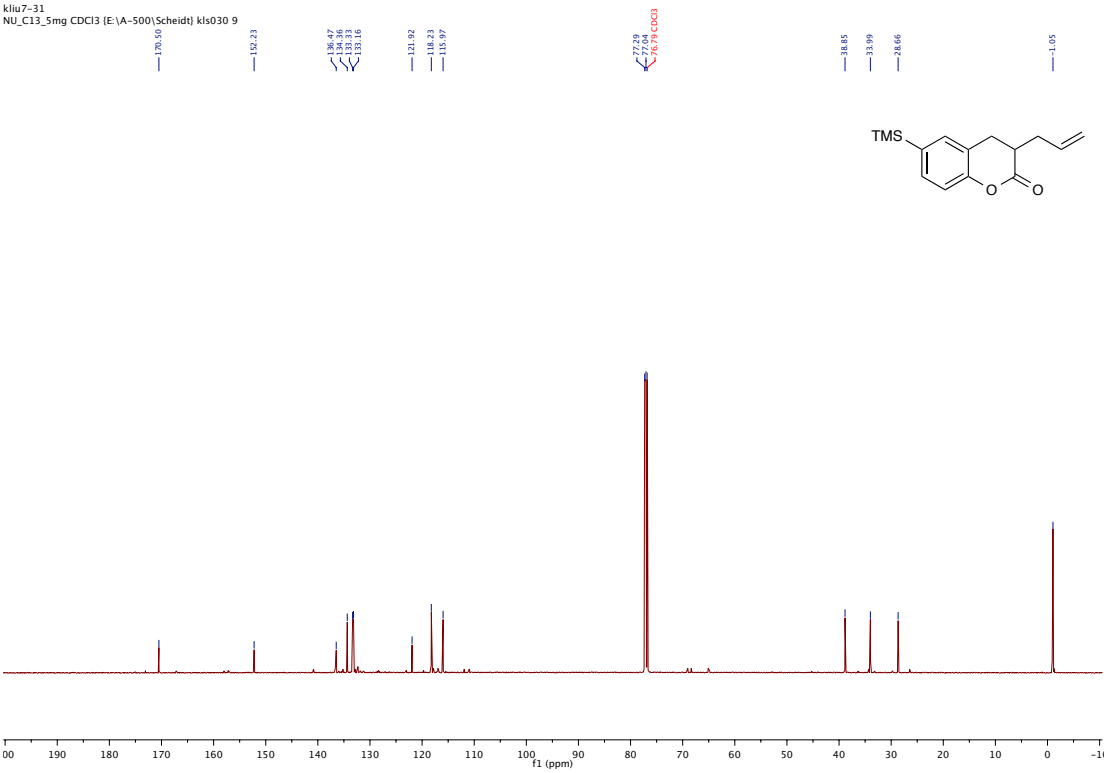
^{13}C NMR Spectra of **2h** (126 MHz, $CDCl_3$):



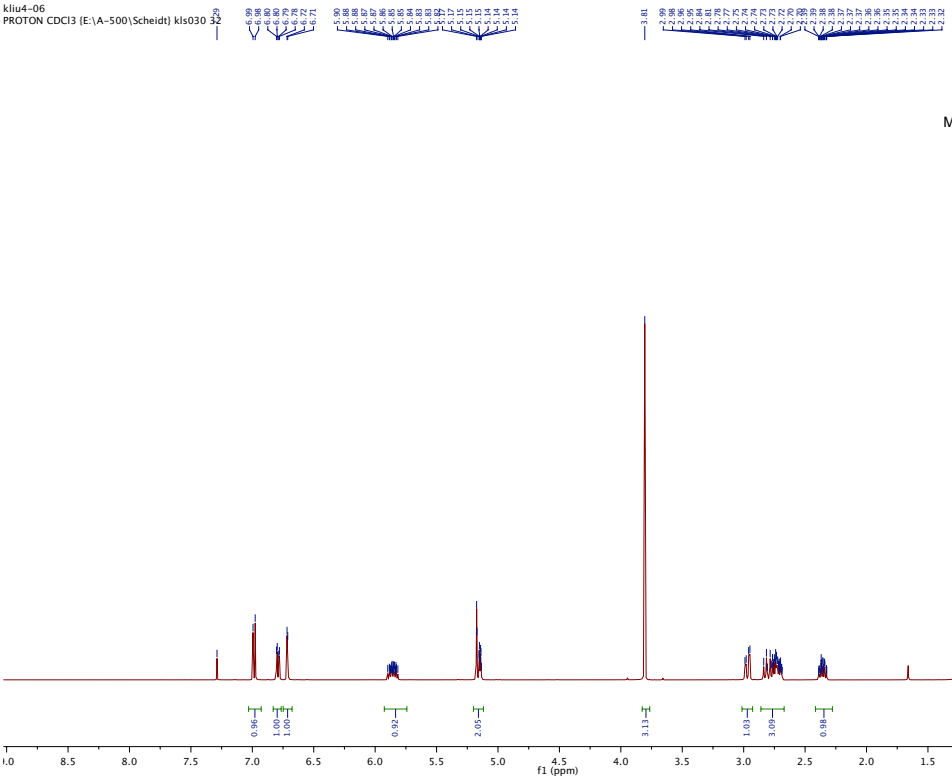
^{1}H NMR Spectra of **2h** (500 MHz, $CDCl_3$):



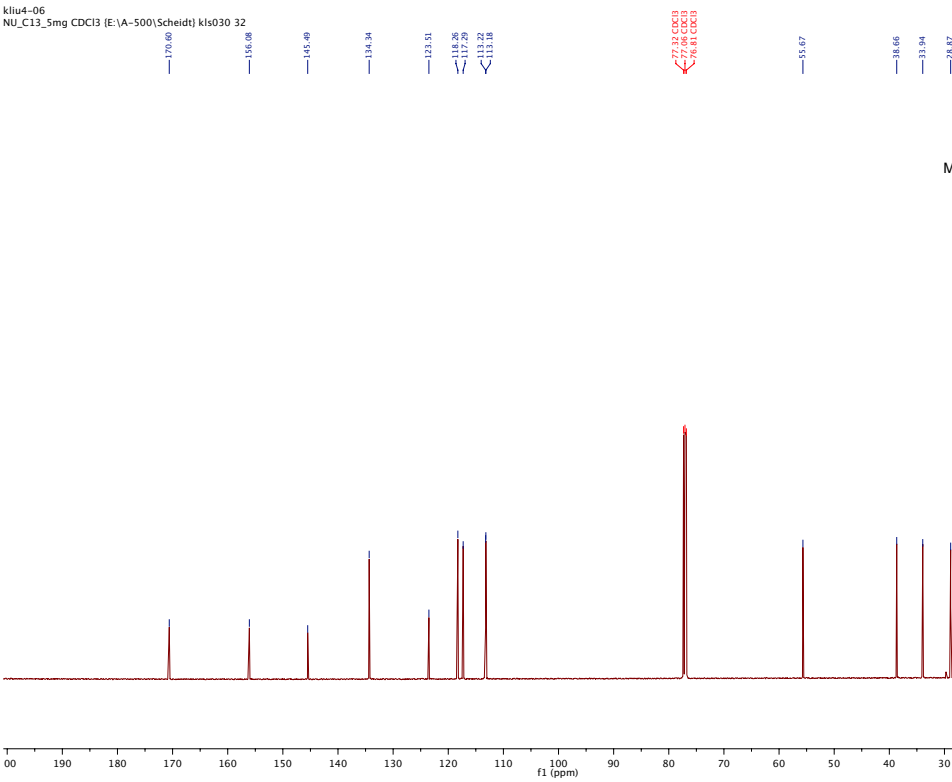
^{13}C NMR Spectra of **2i** (126 MHz, $CDCl_3$):



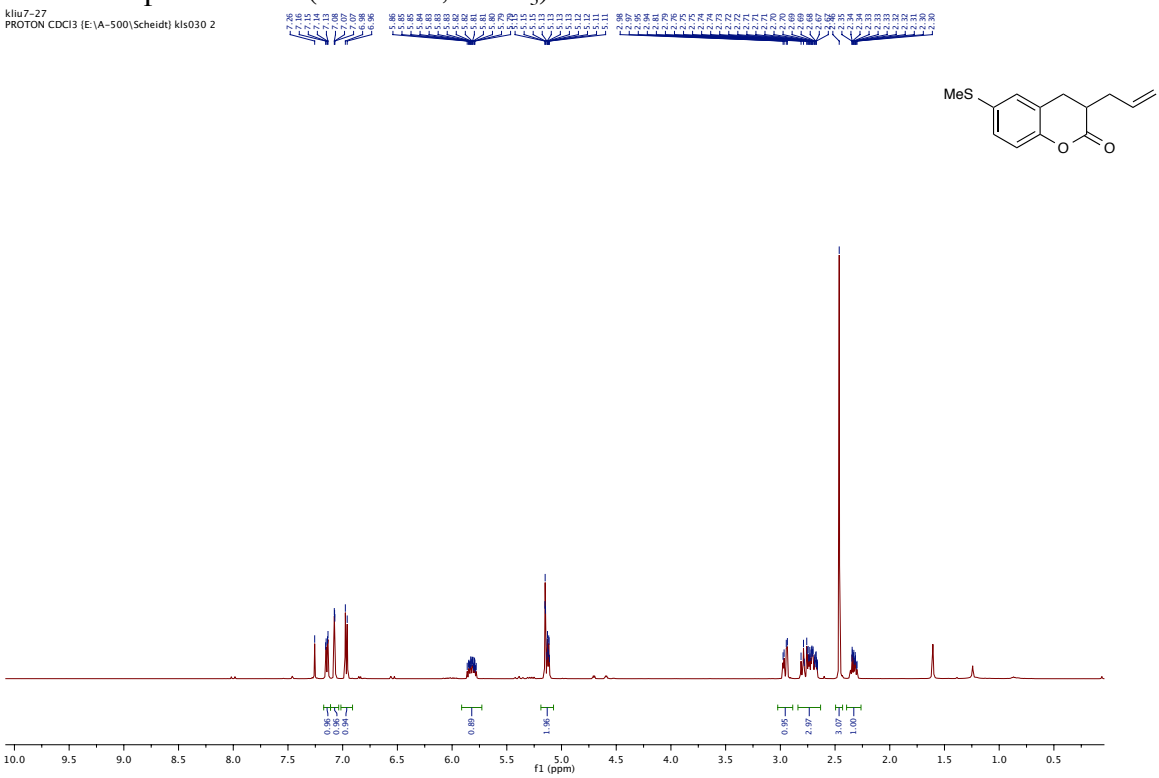
^{1}H NMR Spectra of **2j** (500 MHz, $CDCl_3$):



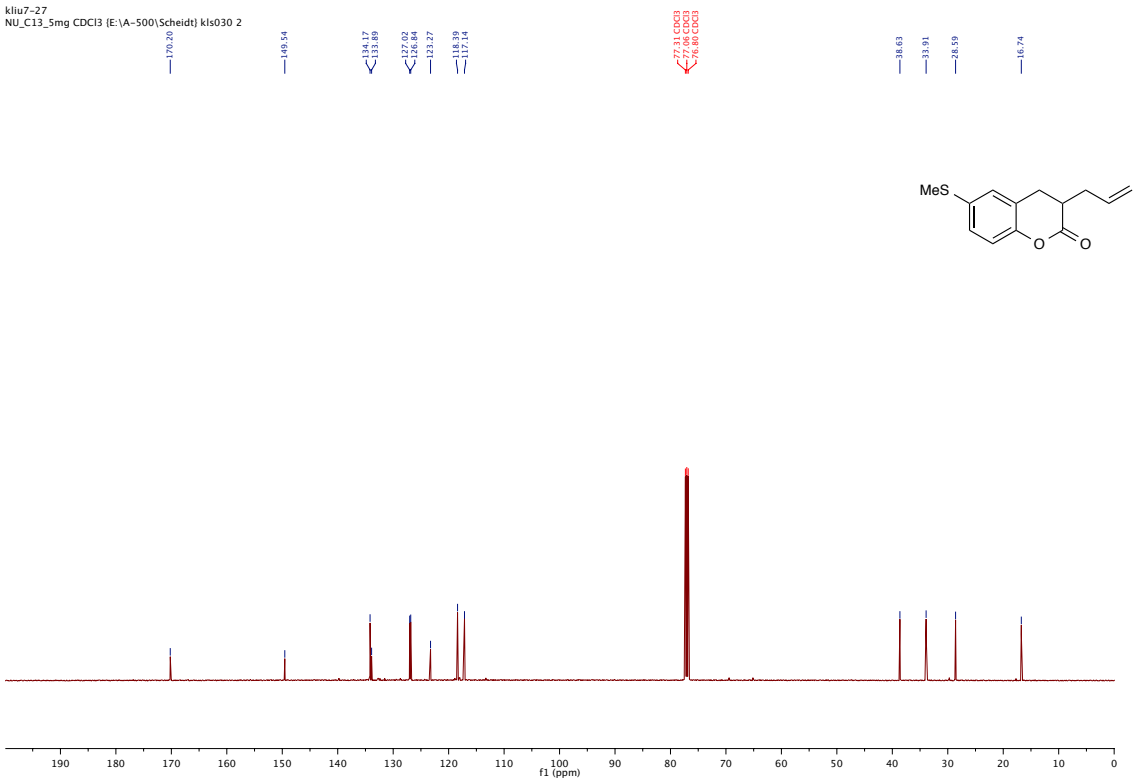
^{13}C NMR Spectra of **2j** (126 MHz, $CDCl_3$):



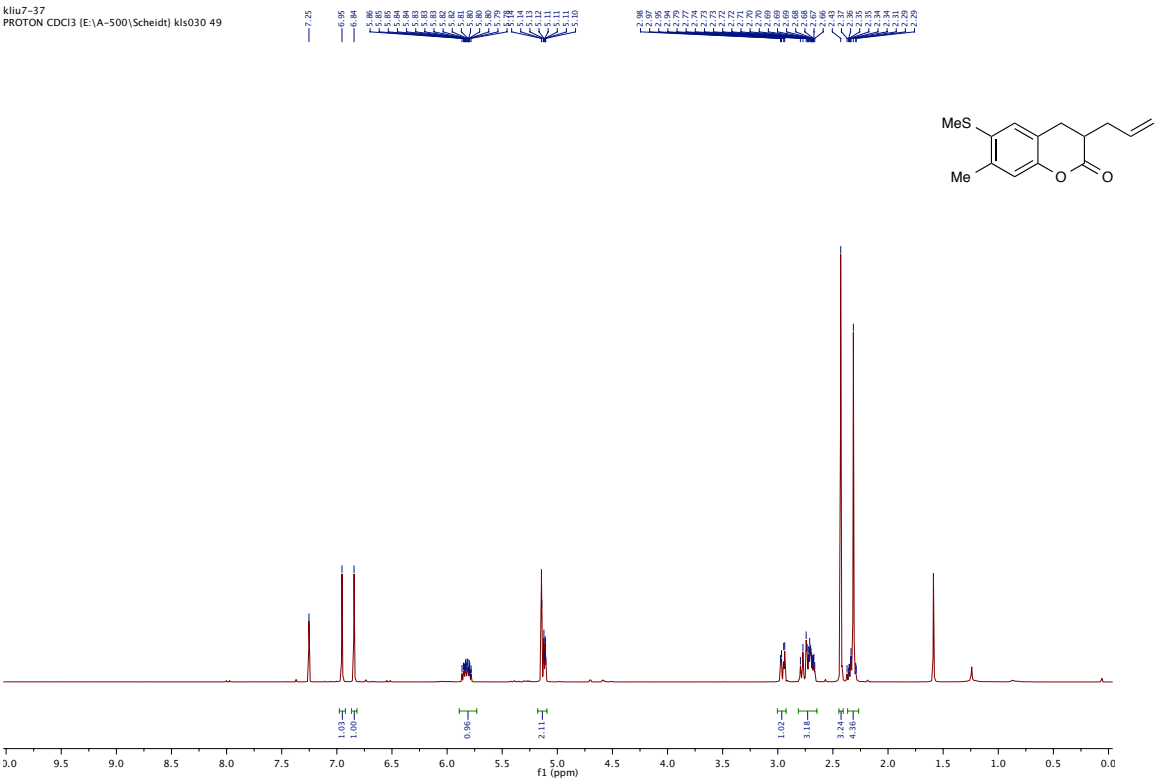
^{1}H NMR Spectra of **2k** (500 MHz, $CDCl_3$):



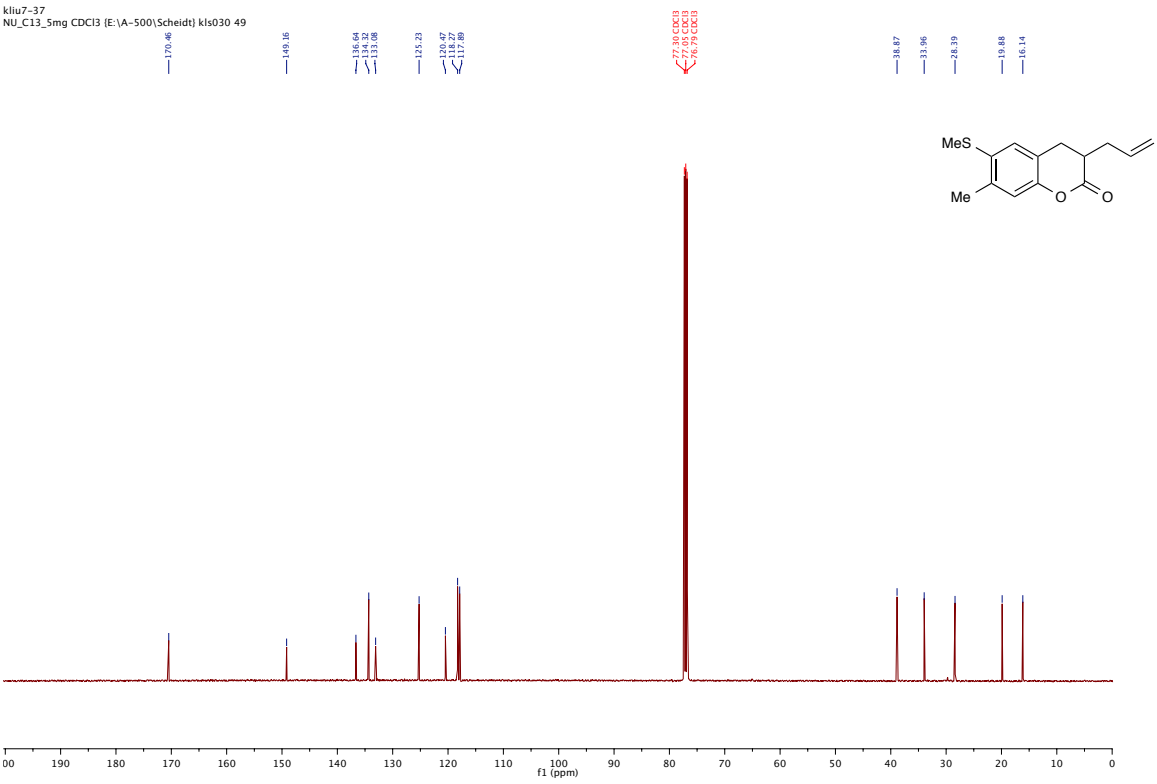
^{13}C NMR Spectra of **2k** (126 MHz, $CDCl_3$):



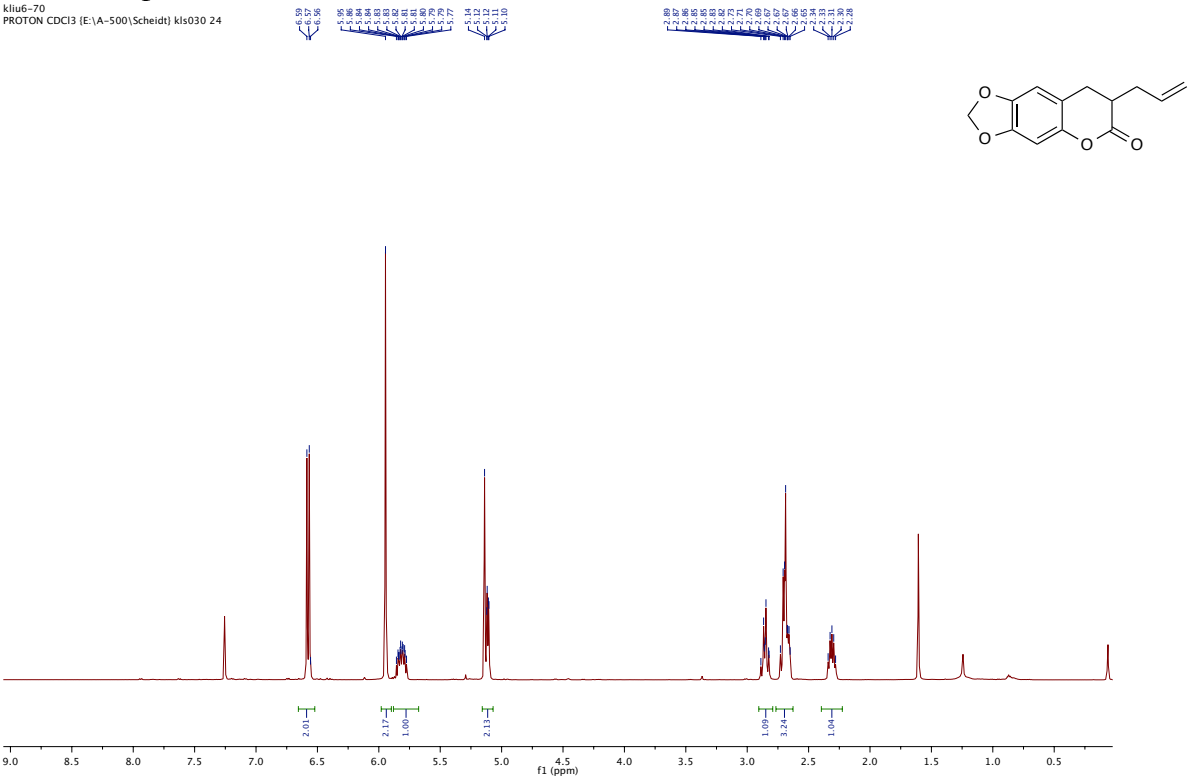
^{1}H NMR Spectra of **2l** (500 MHz, $CDCl_3$):



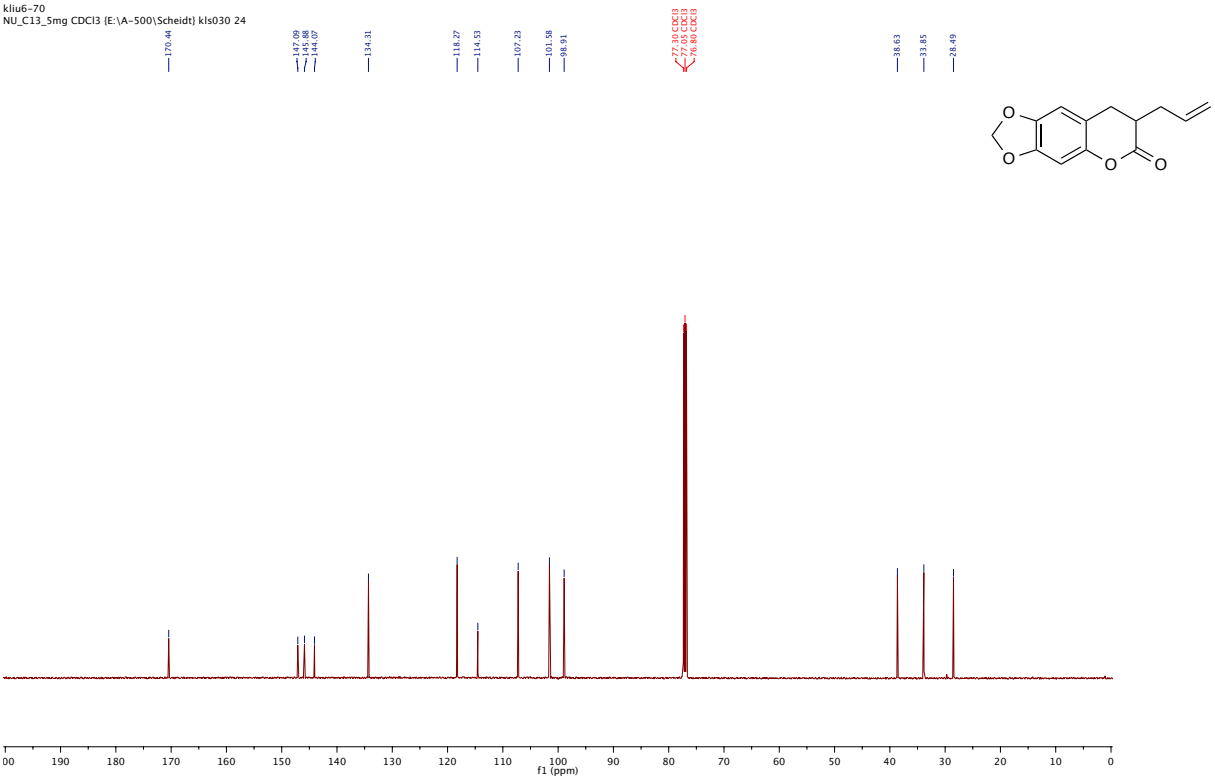
^{13}C NMR Spectra of **2l** (126 MHz, $CDCl_3$):



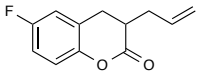
^{1}H NMR Spectra of **2m** (500 MHz, $CDCl_3$):

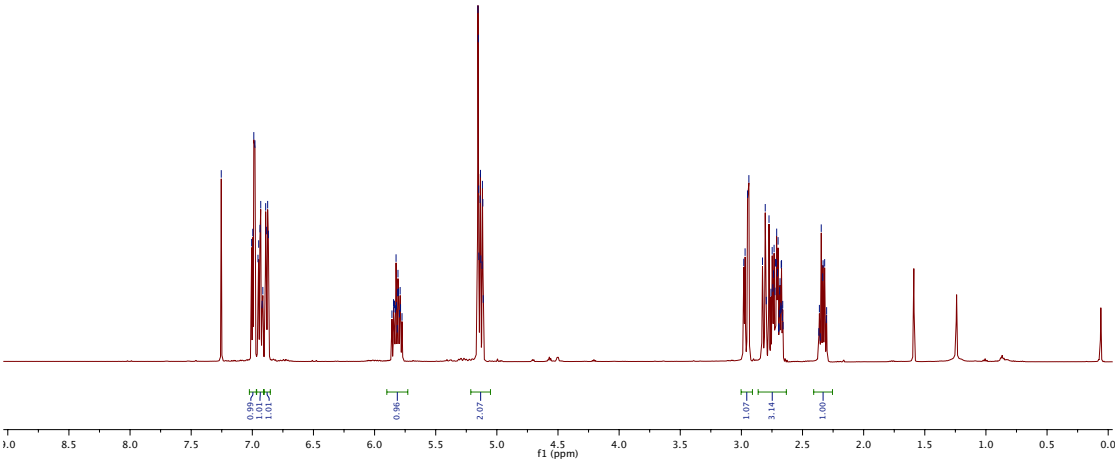


^{13}C NMR Spectra of **2m** (126 MHz, $CDCl_3$):

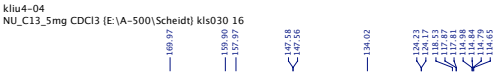


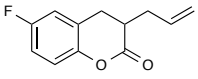
^{1}H NMR Spectra of **2n** (500 MHz, $CDCl_3$):

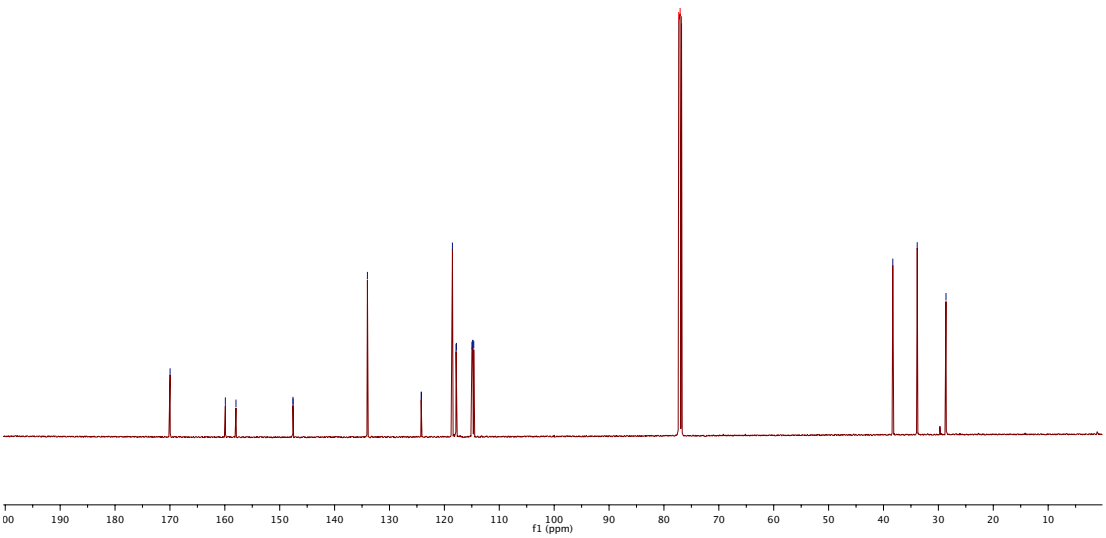




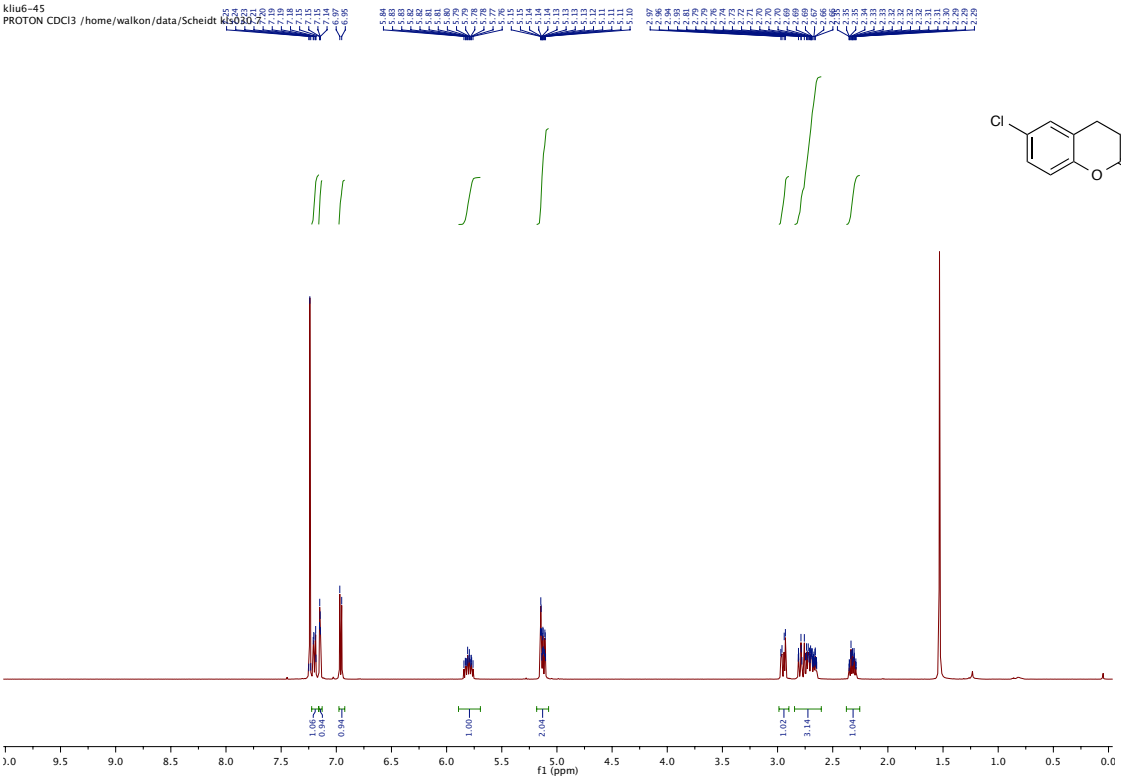
^{13}C NMR Spectra of **2n** (126 MHz, $CDCl_3$):



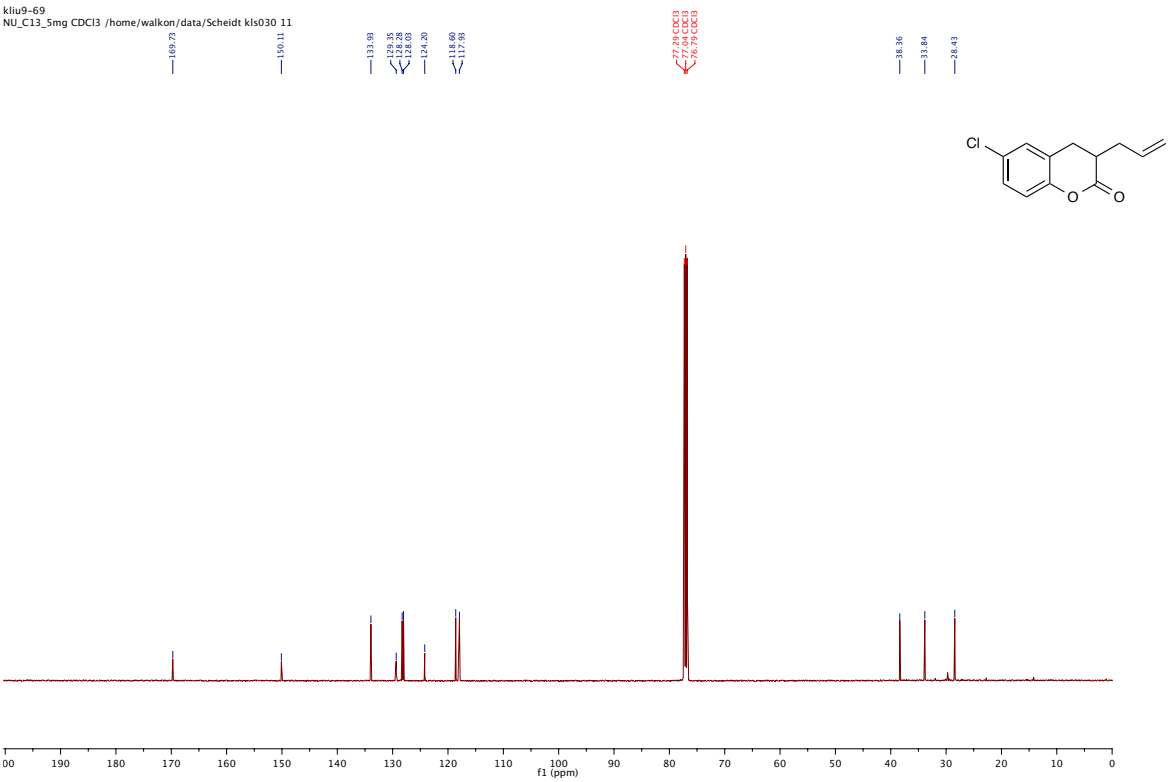




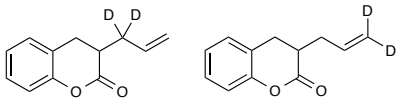
^{1}H NMR Spectra of **2o** (500 MHz, $CDCl_3$):

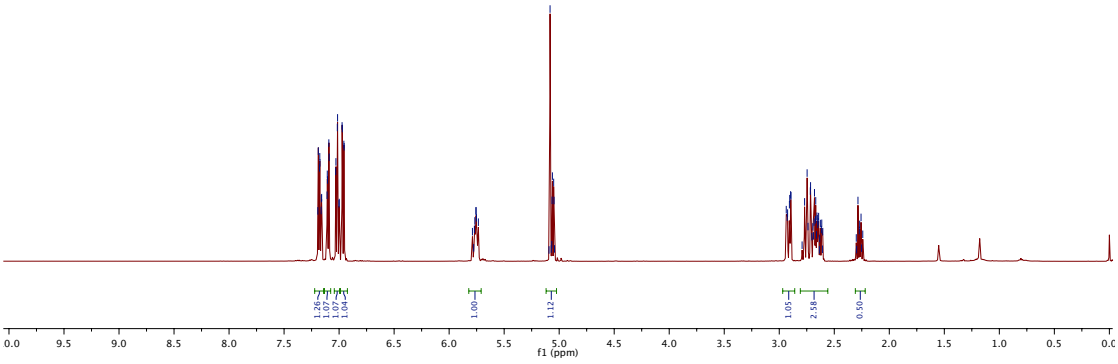


^{13}C NMR Spectra of **2o** (126 MHz, $CDCl_3$):

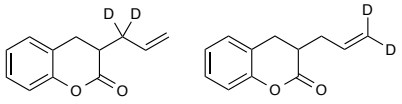


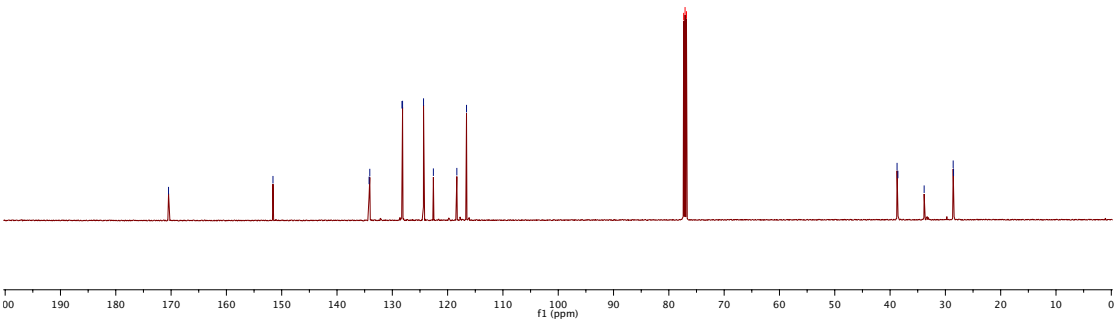
^{1}H NMR Spectra of **9** and **10** (500 MHz, $CDCl_3$):





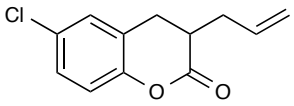
^{13}C NMR Spectra of **9** and **10** (126 MHz, $CDCl_3$):





Structure Determination of the dihydrocoumarin by X-ray analysis for 2o:

The relative stereochemistry was determined by the X-ray diffraction. The dihydrocoumarin was recrystallized from CH_2Cl_2 and hexane.



X-ray crystal structure of 3-allyl-6-chlorodihydrocoumarin:

X-ray diffraction was performed at 100 K and raw frame data were processed using SAINT. Molecular structures was solved using direct methods and refined on F2 by full-matrix least-square techniques. The GOF = 1.084 for 136 variables refined to R1 = 0.0267 for 1613 reflections with I>2α(I). A SADABS-2012/1 multi-scan absorption correction was performed. Further information can be found in the CIF file. This crystal structure was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 969294.