Supporting Information

Effective copper-iron-based sonocatalyst for the microwave-assisted acyloxylation of 1,4-dioxane and cyclohexene

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Contents

General

All reagents and solvents were purchased from commercial suppliers and used without further purification. Reactions were monitored through TLC on commercial silica gel plates precoated with silica gel F_{254}. Visualization was performed by fluorescence quenching and ethanolic solution of ceric ammonium molybdate or anysaldehyde as developing agents. GC analyses were performed in a Perkin-Elmer Clarus 400 chromatograph employing a DB-5 column. Column chromatography was performed employing 230-400 mesh silica gel. HPLC purification was carried out in a Merck-Hitachi L6270 chromatograph equipped with a silica gel column (LiChrosorb Si 60, 10 μm particle size).

^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectra were recorded on a Bruker Avance Neo 400 or Bruker Avance Neo 500 instruments and calibrated using residual undeuterated solvent as an internal reference for ^{1}H NMR and to the central peak of $CDCl_3$ for ^{13}C NMR. ^{19}F NMR spectra were referenced from 85% H_3PO_4 and $CFCl_3$ respectively.

IR spectra of the organic compounds were recorded as a film on a NaCl plate in a Perkin Elmer Spectrum BX spectrophotometer. IR spectra of the catalysts were recorded in attenuated total reflection mode (ATR).

Mass spectra were recorded employing a Bruker Scion CG-TQ gas chromatograph coupled to a Bruker TQ mass spectrometer. High resolution spectra were recorded on a HRMS SYNAPT G2 (Waters) with a APGC interface and a QTOF analyzer or in a XEVO QTOF for ESI ionization.

Microwave-promoted reactions were carried out in a SynthWave MA167 reactor pressurized with nitrogen limited to 45 bar of maximum pressure. The reactions were run on 50 mL glass vials immersed on 200 mL of water as charge solvent with magnetic stirring.

Ultrasound-assisted reactions were carried out with an ultrasonic generator BANDELIN SONOPULS HD 2200.2, operating at 20 kHz and providing a maximum power of 200 W, equipped with a 13 mm titanium tip. Size distribution studies with dynamic light scattering (DLS) technique were performed with a Microtrac Nanotrac Wave particle analyser equipped with a laser diode emitting at a wavelength of 780 nm, with a nominal power of 3 mW.

Transmission electron microscopy (TEM) and electron diffraction studies were carried out on a TALOS F200X microscope, equipped with a field emission gun, a scanning-transmission electron (STEM) module, a high angle annular dark field detector (HAADF) and an energy dispersive X-ray spectroscopy (EDS) microanalyzer. The microscope was operated at 200 kV with a structural resolution of 0.19 nm.

X-ray diffractogram (XRD) were recorded with a diffractometer D8 Advance A25 (Bruker, Billerica, Massachusetts, US) using as source Cu Kα λ = 0.1542 nm and operating with 40 kV and 30 mA.

The TGA curves were recorded in a Shimadzu T-50 thermobalance over 20 mg of sample with a 10 ^{0}C min^{-1} heating rate under an air flow (100 mL min^{-1}).

TPR profiles were obtained in an experimental device coupled to a TCD Autochem Micromeritics apparatus (Thermal conductivity detector). The amount of sample was 30 mg, the 5% H_2/Ar flow rate was 25 mL min^{-1}, and the heating ramp was 10 ^{0}C min^{-1}. Prior to the TPR, the sample was cleaned by heating it under flowing He at 25 mL min^{-1}, at a

rate of 10 ^{0}C min^{-1}, up to 150 ^{0}C; then, it was kept for 1 h at this temperature and cooled down to room temperature.

Temperature programmed reduction (CO_2-TPD) profiles were conducted by first submitting the sample (40 mg) to a treatment consisting of a cleaning in a flow of He (60 mL min^{-1}) at 150 ^{0}C for 1 h, with a heating rate of 10 ^{0}C min^{-1}. Subsequently, it was subjected to pure CO_2 (5 mL min^{-1}) for 1 h. Then the flow switched to He (60 mL min^{-1}) heating up with a 10 ^{0}C min^{-1} rate.

Nitrogen adsorption/desorption isotherms and pore size distribution were performed in a Micromeritics ASAP 2020 device. Prior to the analysis the samples were degassed for 2 h at 150 ^{0}C under vacuum. Specific surface area was calculated by the BET method, average pore diameter was determined by the BJH method using the desorption branch, and the total pore volume was determined from the amount adsorbed at $P/P_0 = 0.99$.

Compositional analysis of the copper−iron mixed oxide was studied by means of both inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF).

Catalyst characterization

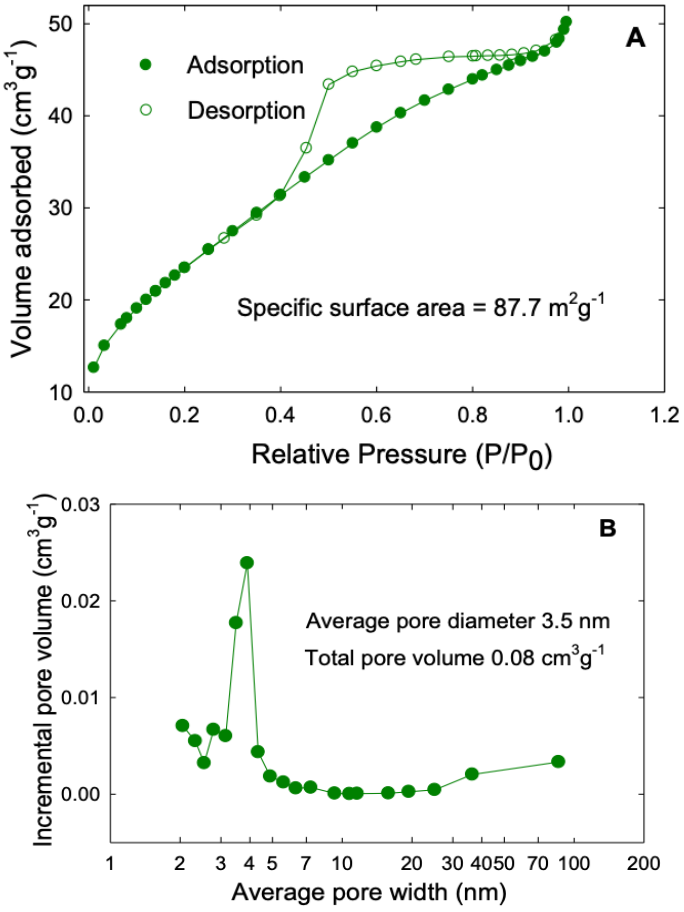


Figure S1. Nitrogen adsorption (●)/desorption (o) isotherm **(A)**, and pore size distribution curve obtained by means of BJH analysis of the desorption branch **(B)** corresponding to the *S*-CuFeOx catalyst.

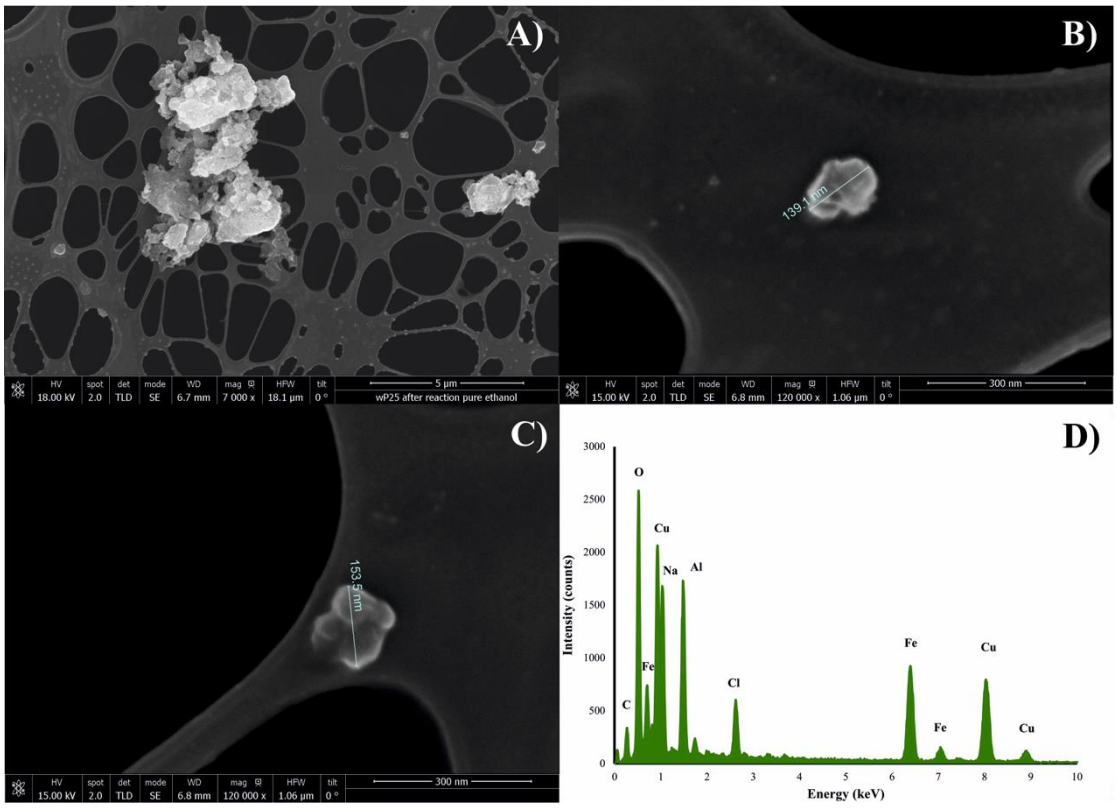


Figure S2. SEM micrographs (A,B,C) and EDS spectrum (D) corresponding to the *S*-CuFeOx catalyst. Micrograph (A) was taken with 7000x magnification, while (B,C) were taken with 120000x magnification, all of them in a Nova NanoSEM 450 microscope. Along with those of Cu and Fe elements, the peaks from O and C from the catalyst phases appear as well, while the Al peak is attributed to the equipment composition, and Cl and Na peaks can be due to residues from the synthesis process.

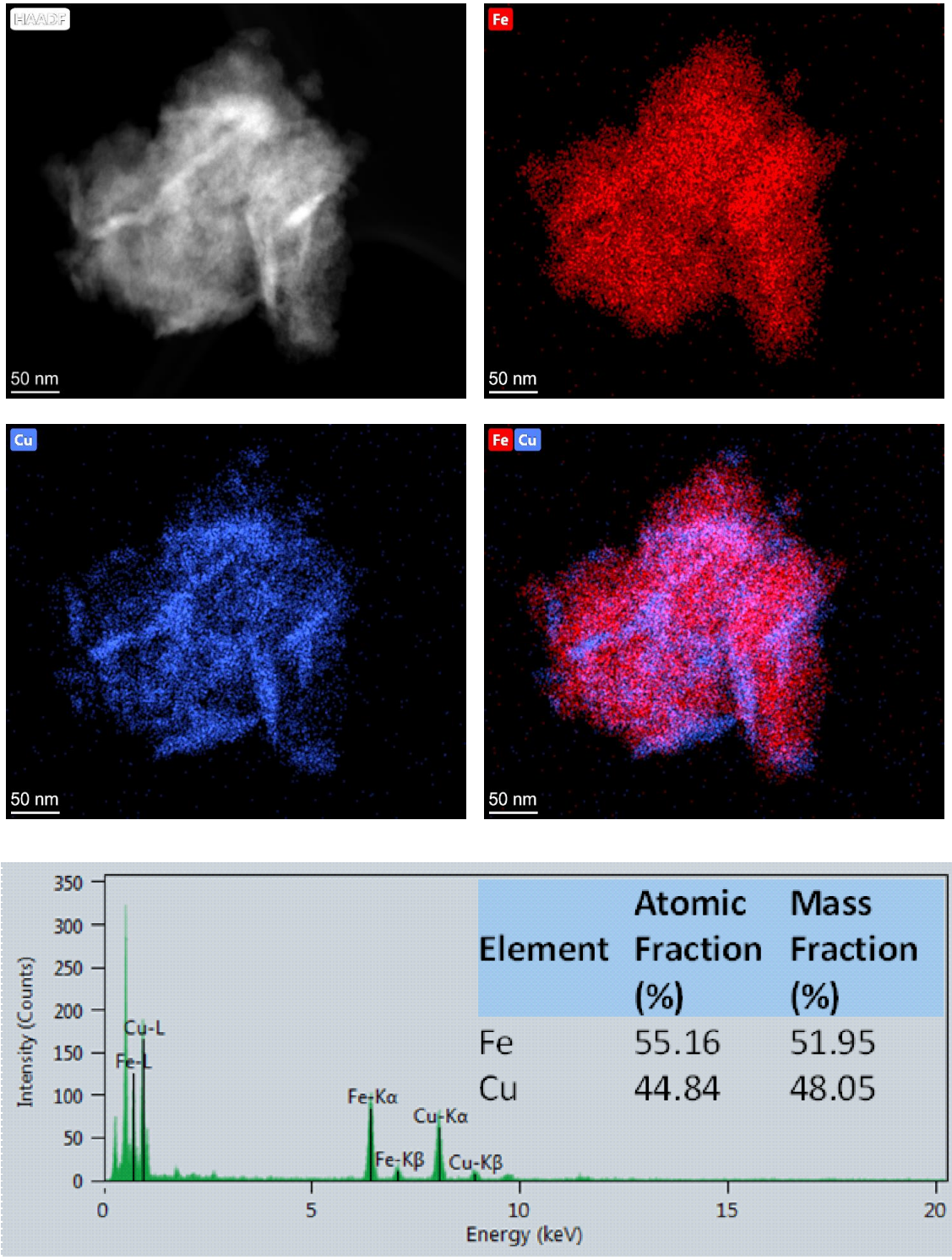


Figure S3. Scanning-Transmission Electron Microscopy in High angle-Annular Dark-Field mode (STEM-HAADF) image of the *S*-CuFeOx catalyst and the STEM-EDS analysis of this area. Both the individual maps and the map overlaying all the elemental signals in the catalyst sample analysed are shown. These data were recorded in a TALOS F200X microscope, operating at 200 kV, with a structural resolution of 0.19 nm.

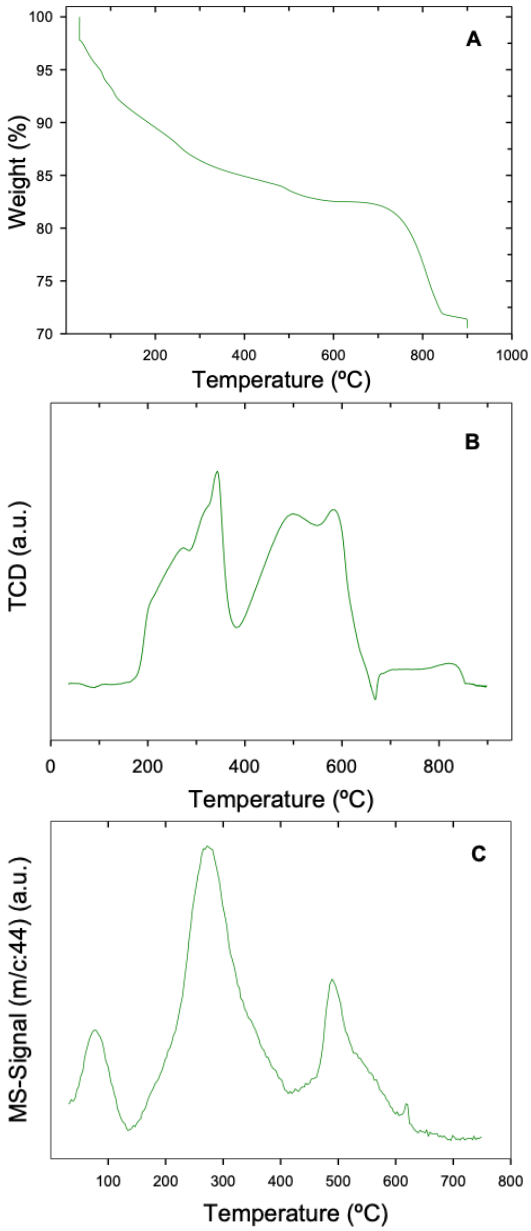
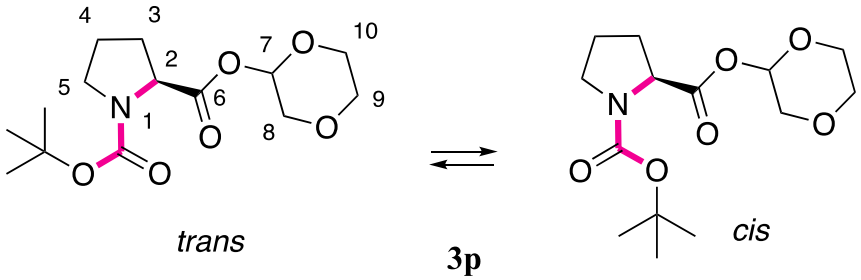


Figure S4. A: TGA curve recorded for *S*-CuFeOx. According to previous study of *T*-CuFeOx samples with different Cu/Fe ratio values and surface areas (M.P. Yeste et al., *Appl. Catal. A*, 2018, **552**, 58-69) the higher total weight loss and the intense drop above 700 ºC suggest carbonates decomposition processes beyond surface dehydroxylation. B: TPR profile obtained by Thermal Conductivity Detector (TCD) showing the H_2 consumption by the *S*-CuFeOx sample. The region between 200 and 400 ºC approx. and the second one at higher temperature (from 400 ºC) can be associated with consecutive reduction processes of copper and iron species, respectively (M.P. Yeste et al., *Appl. Catal. A*, 2018, **552**, 58-69 and references herein cited). C: CO_2-TPD profile of the *S*-CuFeOx catalyst by Mass Spectrometry. The peak at low temperature can be reasonably assigned to weakly adsorbed CO_2 while the most intense peak around 300 ºC is attributable to strongly chemisorbed CO_2. Finally, the peak at 500 ºC should be related to decomposition of massive carbonates, in good agreement with the TGA results.

Variable temperature NMR spectra of compounds 3p, 4p and 7r



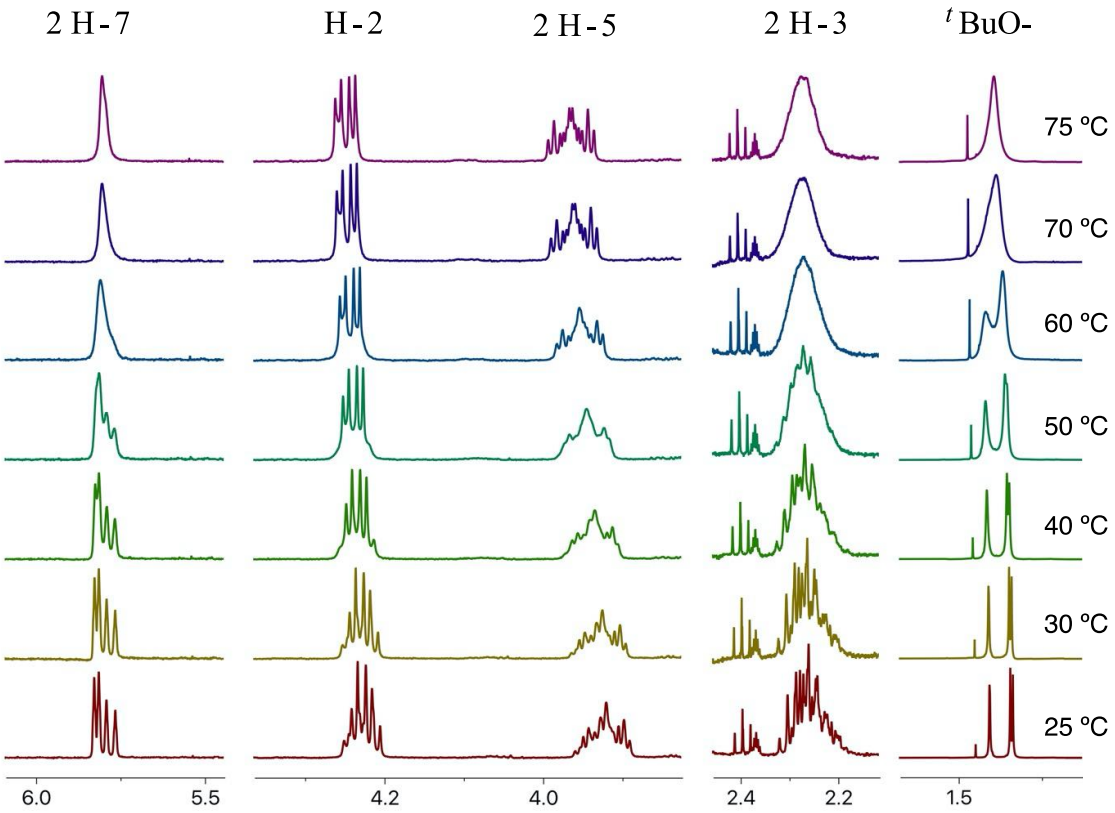


Figure S5. Variable temperature ^{1}H NMR spectra of compound **3p** (*trans:cis*, 60:40 at 25ºC, 500 MHz, DMSO-d_6).

Figure S6. Variable temperature ^{1}H NMR spectra of compound **3p** in DMSO-d_6.

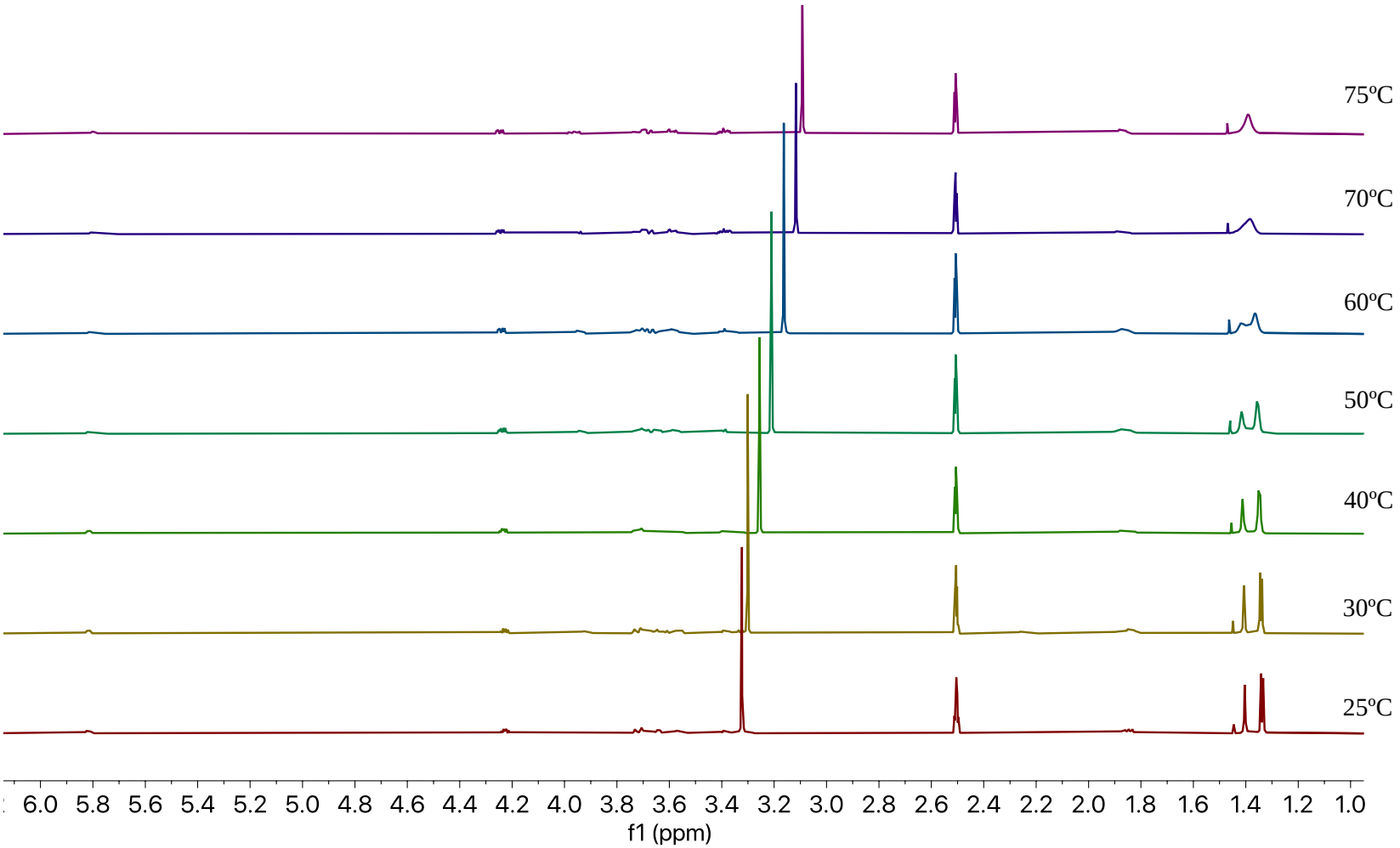
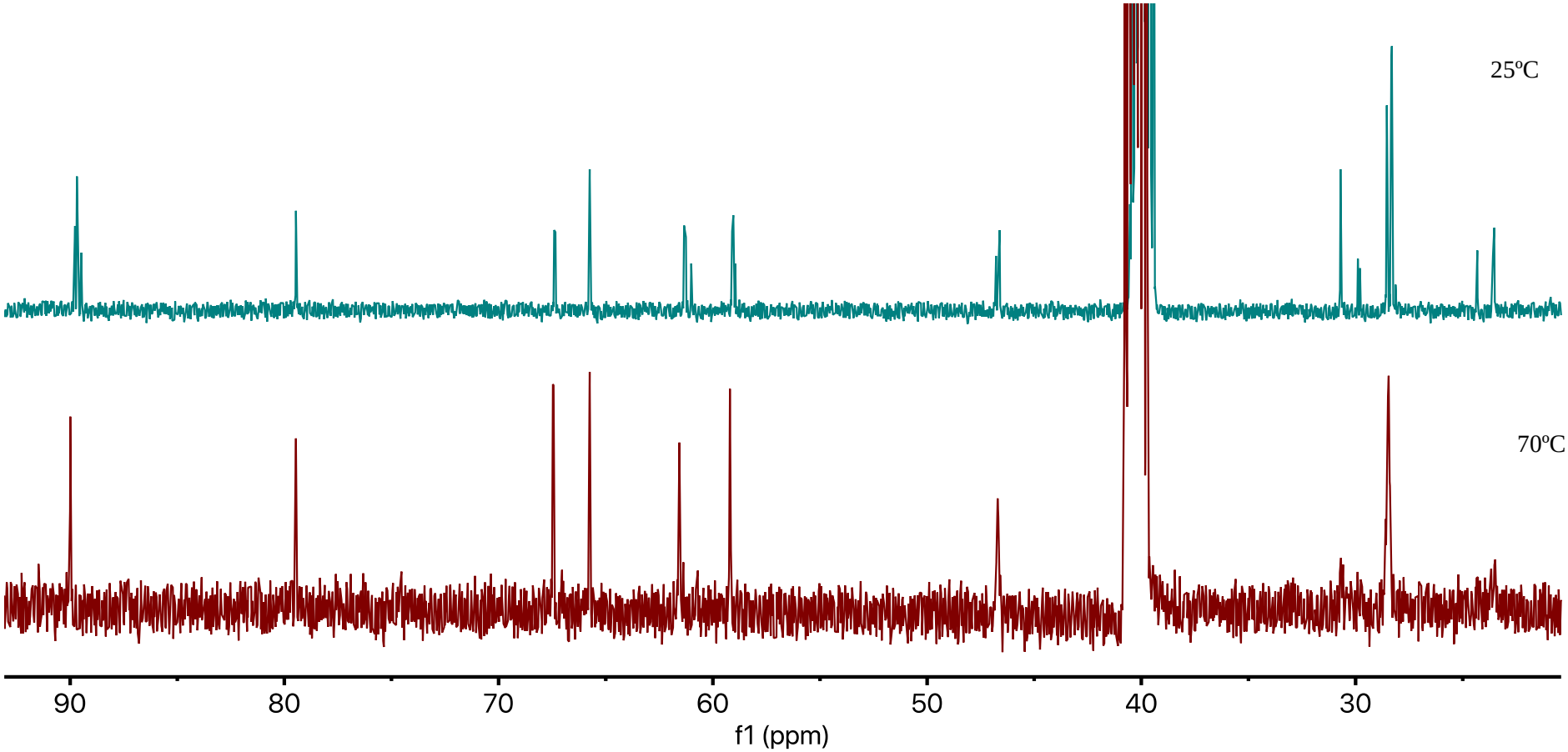
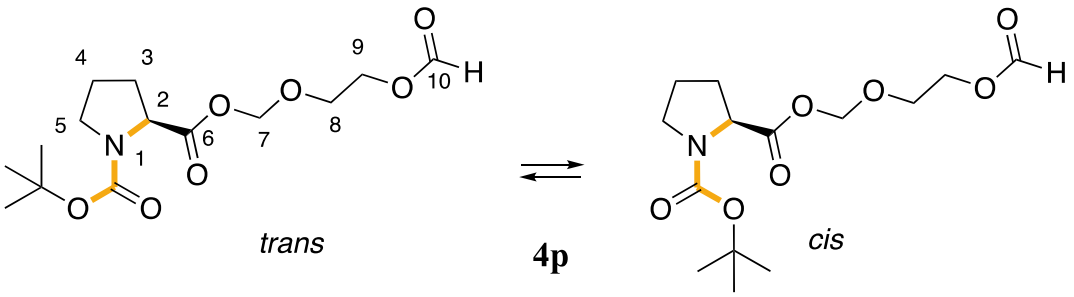


Figure S7. Variable temperature ^{13}C NMR spectra (125 MHz) of compound **3p** in DMSO-d_6.





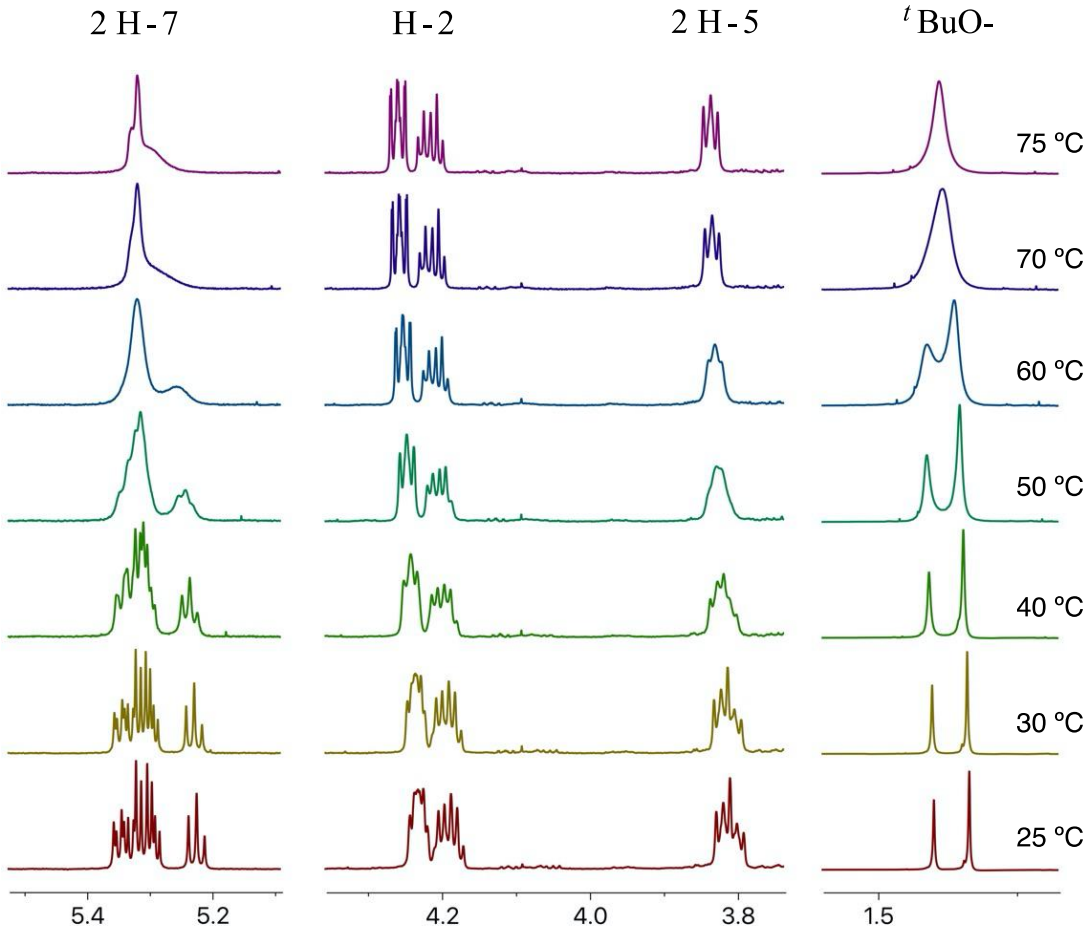
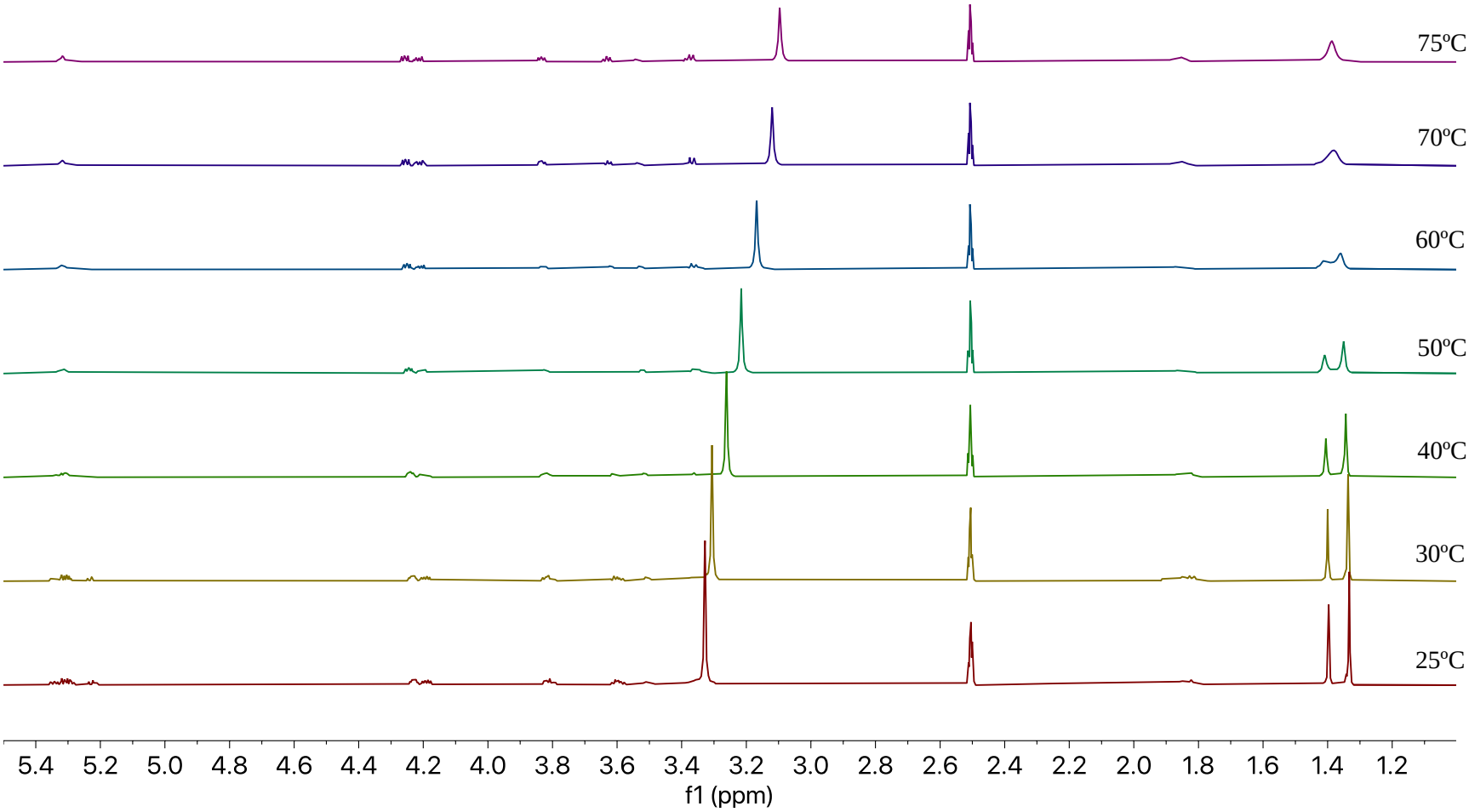


Figure S8. Variable temperature ^{1}H NMR spectra of compound **4p** (*trans:cis*, 58:42 at 25ºC, 500 MHz, DMSO-d_6).

Figure S9. Variable temperature ^{1}H NMR spectra of compound **4p** in DMSO-d_6.



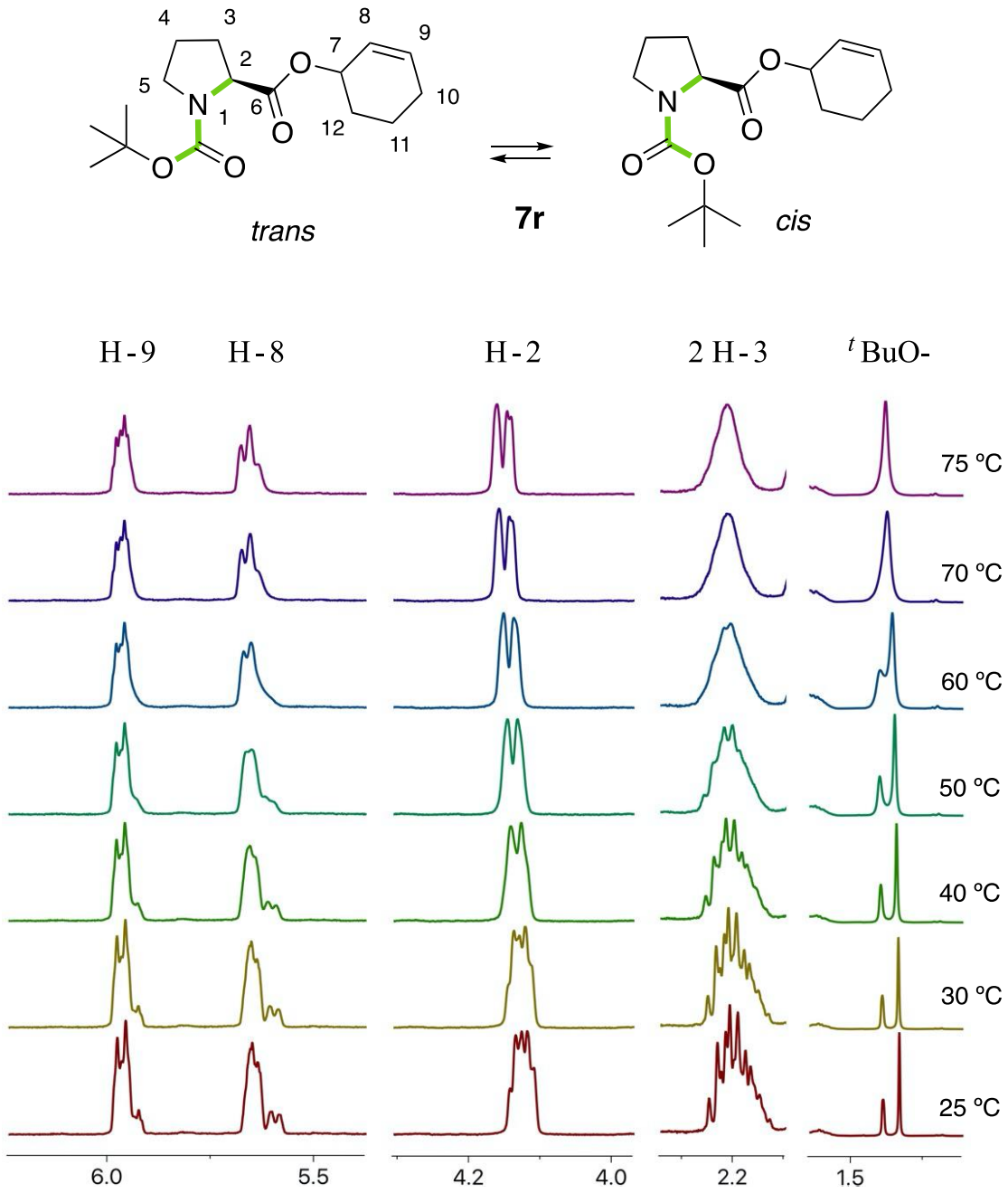
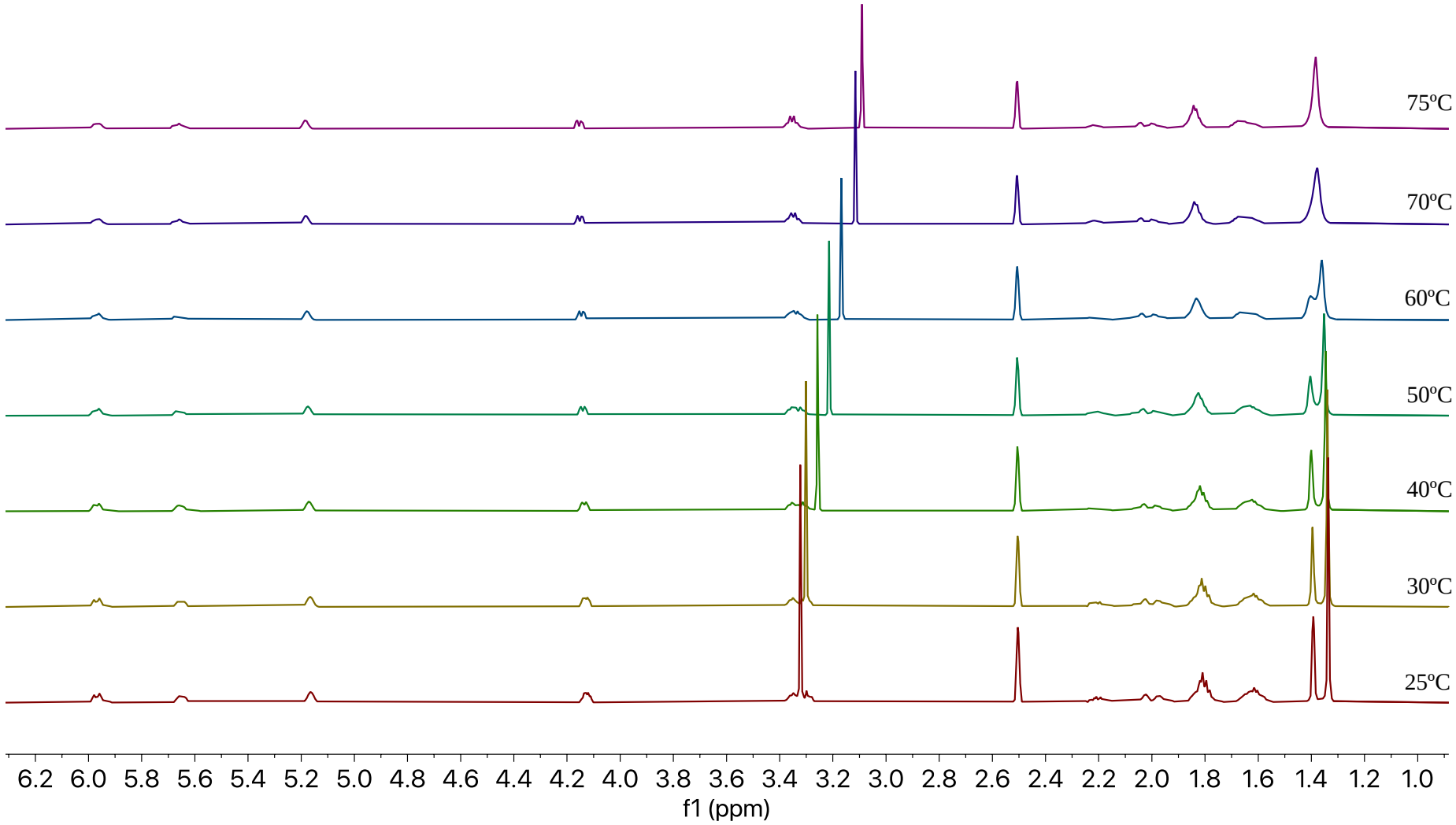


Figure S10. Variable temperature ^{1}H NMR spectra of compound **7r** (*trans:cis*, 63:37 at 25ºC, 500 MHz, DMSO-d_6).

Figure S11. Variable temperature ^{1}H NMR spectra of compound **7r** in DMSO-d_6.



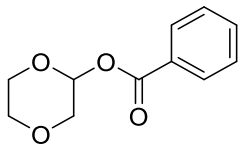
MW Methods

Table S1. Method A

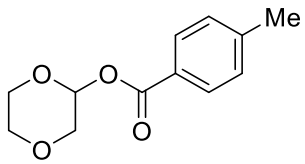
Nº	t	T_1 – vessel (ºC)	T_2 – system (ºC)	P (bar)	E (W)
1	00:00:10	120	50	35.0	1500
2	00:01:00	120	50	45.0	1500
3	00:09:00	120	50	45.0	1500

Analytical data

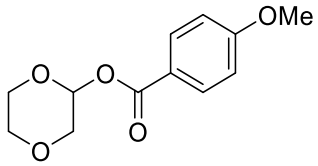
1,4-Dioxan-2-yl benzoate (3a): Colorless crystals (170.6 mg, 82%, table 3; 67 mg, 29%, table 4), mp 72.7-74.5 ºC. Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.10 (m, 2H), 7.60-7.55 (m, 1H), 7.48-7.43 (m, 2H), 6.09 (dd, J = 2.0, 2.0 Hz, 1H), 4.25-4.19 (m, 1H), 3.88 (d, J = 2.0 Hz, 2H), 3.82 (dd, J = 7.1, 2.8, 2H), 3.67 (ddd, J = 11.8, 2.6, 2.6, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.2, 133.4, 129.9, 129.7, 128.4, 89.8, 67.8, 66.1, 61.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{12}O_4Na$ 231.0633; Found 231.0633. IR (KBr, cm^{-1}) 1852, 1687, 1454, 1426, 1327, 1293, 1073, 1027, 935, 707.



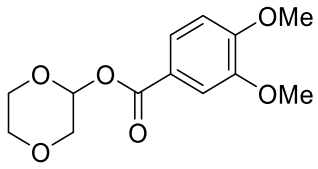
1,4-Dioxan-2-yl 4-methylbenzoate (3b): Colorless oil (100.2 mg, 45%, table 3; 112.7 mg, 46%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.09 (dd, J = 2.1, 2.1 Hz, 1H), 4.27-4.18 (m, 1H), 3.91-3.88 (m, 2H), 3.85-3.80 (m, 2H), 3.68 (ddd, J = 11.8, 2.7, 2.7 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.3, 144.2, 130.0, 129.2, 126.9, 89.6, 67.9, 66.1, 61.8, 21.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_4Na$ 245.0790; Found 245.0785. IR (KBr, cm^{-1}) 1972, 2856, 1723, 1612, 1276, 1259, 1233, 1178, 1154, 1086, 1066, 1014, 912, 881, 856, 753, 577.



1,4-Dioxan-2-yl 4-methoxybenzoate (3c): Colorless oil (171.4 mg, 72%, table 3; 133.1 mg, 51%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.05 (m, 2H), 6.96-6.91 (m, 2H), 6.07 (dd, J = 2.1, 2.1 Hz, 1H), 4.25-4.17 (m, 1H), 3.90-3.86 (m, 5H), 3.84-3.80 (m, 2H), 3.68 (ddd, J = 11.8, 2.7, 2.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.9, 163.7, 132.0, 122.0, 113.7, 89.5, 67.9, 66.1, 61.8, 55.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_5Na$ 261.0739; Found 261.0742. IR (KBr, cm^{-1}) 2969, 2856, 1718, 1607, 1512, 1257, 1234, 1170, 1155, 1115, 1088, 1066, 1020, 913, 883, 850.

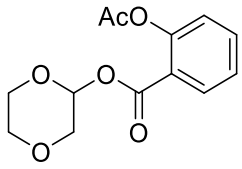


1,4-Dioxan-2-yl 3,4-dimethoxybenzoate (3d): Colorless crystals (136.9 mg, 51%, table 3; 145.5 mg, 50%, table 4), mp 98.0-99.5 ºC. Column chromatography eluent, petroleum

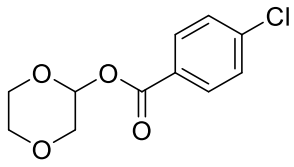


ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.4, 2.0 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.07 (dd, J = 2.0, 2.0 Hz, 1H), 4.22-4.14 (m, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.88-3.85 (m, 2H), 3.80 (dd, J = 6.7, 2.7 Hz, 2H), 3.66 (ddd, J = 11.7, 2.7, 2.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.9, 153.4, 148.7, 124.0, 122.0, 112.1, 110.2, 89.6, 67.8, 66.1, 61.8, 56.0, 56.0. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_6Na$ 291.0845; Found 291.0843. IR (KBr, cm^{-1}) 1717, 1602, 1515, 1416, 1271, 1221, 1020, 931, 907, 879, 763.

1,4-Dioxan-2-yl 2-acetoxybenzoate (3e): Colorless oil (130.3 mg, 49%, table 3; 109.8 mg, 38%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.7, 1.7 Hz, 1H), 7.60 (ddd, J = 8.1, 7.7, 1.7 Hz, 1H), 7.35 (ddd, J = 7.7, 7.7, 1.2 Hz, 1H), 7.12 (dd, J = 8.1, 1.1 Hz, 1H), 6.05 (dd, J = 1.7, 1.7 Hz, 1H), 4.26-4.12 (m, 1H), 3.87 (d, J = 1.9 Hz, 2H), 3.84-3.78 (m, 2H), 3.65 (ddd, J = 11.7, 2.4, 2.4 Hz, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 163.1, 150.9, 134.3, 132.1, 126.0, 123.9, 122.7, 89.9, 67.6, 66.0, 61.5, 20.9. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{13}H_{14}O_6Na$ 289.0688; Found 289.0685. IR (KBr, cm^{-1}) 2976, 2860, 1769, 1730, 1607, 1485, 1452, 1369, 1292, 1252, 1194, 1157, 1062, 1014, 912, 881, 854, 755, 705, 580.

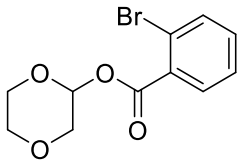


1,4-Dioxan-2-yl 4-chlorobenzoate (3f): Colorless crystals (184.5 mg, 76%), mp 121.0-122.0 ºC. Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 2H), 7.47-7.41 (m, 2H), 6.08 (dd, J = 2.0, 2.0 Hz, 1H), 4.24-4.16 (m, 1H), 3.89 (d, J = 1.9 Hz, 2H), 3.83 (dd, J = 6.9, 2.6 Hz, 2H), 3.68 (ddd, J = 11.7, 2.6, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 140.0, 131.3, 128.8, 128.2, 90.0, 67.8, 66.1, 61.8. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{11}H_{11}O_4ClNa$ 265.0244; Found 265.0236. IR (KBr, cm^{-1}) 2961, 2856, 1717, 1682, 1593, 1282, 1265, 1152, 1119, 1086, 1069, 1032, 1016, 938, 913, 881, 853.

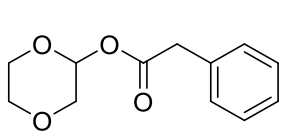


1,4-Dioxan-2-yl 2-iodobenzoate (3g): Colorless oil (157.0 mg, 47%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.8, 1.2 Hz, 1H), 7.94 (dd, J = 7.8, 1.7 Hz, 1H), 7.43 (ddd, J = 7.8, 7.4, 1.2 Hz, 1H), 7.18 (ddd, J = 7.8, 7.4, 1.7 Hz, 1H), 6.11 (dd, J = 1.9, 1.9 Hz, 1H), 4.31-4.22 (m, 1H), 3.97-3.80 (m, 4H), 3.70 (ddd, J = 11.8, 2.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.0, 141.6, 134.3, 133.0, 131.4, 128.0, 94.3, 90.7, 67.7, 66.1, 61.9. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{11}H_{11}IO_4Na$ 356.9600; Found 356.9611. IR (KBr, cm^{-1}) 2970, 2854, 1732, 1288, 1248, 1232, 1157, 1130, 1088, 1067, 1043, 1008, 910, 880, 740, 581.

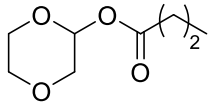
1,4-Dioxan-2-yl 2-bromobenzoate (3h): Colorless oil (169.5 mg, 59%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.89 (m, 1H), 7.71-7.66 (m, 1H), 7.43-7.33 (m, 2H), 6.12 (dd, J = 1.8, 1.8 Hz, 1H), 4.32-4.20 (m, 1H), 3.93-3.88 (m, 2H), 3.86-3.81 (m, 2H), 3.70 (ddd, J = 11.8, 2.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 134.5, 133.0, 131.8, 131.5, 127.2, 122.0, 90.6, 67.7, 66.1, 61.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}O_4Br$ 286.9919; Found 286.9924. IR (KBr, cm^{-1}) 2976, 2856, 1737, 1592, 1432, 1291, 1249, 1232, 1156, 1130, 1102, 1067, 1044, 1028, 1010, 911, 881, 853, 744, 582.



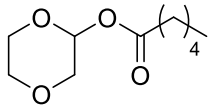
1,4-Dioxan-2-yl 2-phenylacetate (3i): Colorless oil (131.0 mg, 59%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 5.86 (dd, J = 1.9, 1.9 Hz, 1H), 4.07-3.98 (m, 1H), 3.81-3.73 (m, 4H), 3.71 (s, 2H), 3.58 (ddd, J = 11.7, 2.7, 2.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 133.5, 129.3, 128.6, 127.2, 89.6, 67.6, 66.0, 61.6, 41.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_4Na$ 245.0790; Found 245.0792. IR (KBr, cm^{-1}) 2974, 2859, 1743, 1498, 1455, 1252, 1233, 1139, 1109, 1068, 1018, 943, 899, 879, 698.



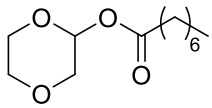
1,4-Dioxan-2-yl butyrate (3j): Yellow oil (148.1 mg, 80%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (dd, J = 2.2, 2.2 Hz, 1H), 4.16-4.08 (m, 1H), 3.82-3.70 (m, 4H), 3.63 (ddd, J = 11.8, 2.8, 2.8 Hz, 1H), 2.38 (td, J = 7.4, 1.5 Hz, 2H), 1.70 (tq, J = 7.4, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.4, 89.0, 67.8, 66.1, 61.7, 36.2, 18.3, 13.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{15}O_4$ 175.0970; Found 175.0981. IR (KBr, cm^{-1}) 2963, 1734, 1261, 1031, 877, 780.



1,4-Dioxan-2-yl hexanoate (3k): Colorless oil (145.5 mg, 72%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (br s, 1H), 4.17-4.05 (m, 1H), 3.83-3.68 (m, 4H), 3.63 (ddd, J = 11.9, 2.8, 2.8 Hz, 1H), 2.39 (t, J = 8.2 Hz, 2H), 1.67 (tt, J = 7.4, 7.4 Hz, 2H), 1.38-1.27 (m, 4H), 0.94-0.85 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.6, 89.0, 67.8, 66.1, 61.7, 34.3, 31.2, 24.5, 22.3, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{18}O_4Na$ 225.1103; Found 225.1106. IR (KBr, cm^{-1}) 2960, 2933, 2860, 1745, 1455, 1232, 1147, 1085, 1068, 1020, 943, 906, 879, 857.



1,4-Dioxan-2-yl octanoate (3l): Colorless oil (119.8 mg, 52%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd, J = 2.1, 2.1 Hz, 1H), 4.15-4.06 (m, 1H), 3.82-3.67 (m, 4H), 3.62 (ddd, J = 11.7, 2.8, 2.8 Hz, 1H), 2.42-2.35 (m, 2H), 1.66 (tt, J = 7.5, 7.5 Hz, 2H), 1.39-1.21 (m, 8H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 89.0, 67.8, 66.1, 61.7, 34.3, 31.6, 29.0, 28.9, 24.8, 22.6, 14.0.



HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{22}O_4Na$ 253.1416; Found 253.1424. IR (KBr, cm^{-1}) 2958, 2929, 2857, 1746, 1263, 1227, 1147, 1106, 1086, 1069, 1020, 930, 907, 880.

1,4-Dioxan-2-yl 3-methylbut-2-enoate (3m): Colorless oil (94.9 mg, 51%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (br s, 1H), 5.76 (br s, 1H), 4.17-4.02 (m, 1H), 3.84-3.67 (m, 4H), 3.61 (ddd, J = 11.7, 2.7, 2.7 Hz, 1H), 2.18 (s, 3H), 1.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.9, 159.1, 115.3, 88.4, 67.9, 66.0, 61.7, 27.5, 20.4. HRMS (APGC) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{14}O_4Na$ 209.0790; Found 209.0782. IR (KBr, cm^{-1}) 2943, 2917, 1727, 1650, 1450, 1379, 1351, 1226, 1122, 1064, 969, 852, 732, 606.

1,4-Dioxan-2-yl (E)-2-methylbut-2-enoate (3n): Colorless oil (120.9 mg, 65%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (qq, J = 7.0, 1.4 Hz, 1H), 5.89 (dd, J = 2.1, 2.1 Hz, 1H), 4.17-4.06 (m, 1H), 3.85-3.72 (m, 4H), 3.63 (ddd, J = 11.7, 2.8, 2.8 Hz, 1H), 1.86 (qd, J = 1.3, 1.3 Hz, 3H), 1.81 (dq, J = 7.0, 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 138.8, 128.2, 89.3, 67.9, 66.1, 61.8, 14.4, 11.9. HRMS (APGC) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{14}O_4Na$ 209.0790; Found 209.0790. IR (KBr, cm^{-1}) 2973, 2931, 2858, 1719, 1651, 1454, 1382, 1257, 1233, 1131, 1069, 1021, 954, 909, 883, 732, 581.

1,4-Dioxan-2-yl cyclohex-2-ene-1-carboxylate (3o): Mixture of diastereomers. Colorless oil (152.6 mg, 72%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (dd, J = 2.0, 2.0 Hz, 1H), 5.69 (br s, 2 H), 4.17-4.04 (m, 1H), 3.84-3.69 (m, 4H), 3.63 (ddd, J = 11.7, 2.4, 2.4 Hz, 1H), 2.72-2.60 (m, 1H), 2.37-2.25 (m, 2H), 2.18-1.98 (m, 3H), 1.82-1.66 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.5, 126.7, 126.6, 125.0, 89.1, 89.1, 67.8, 67.7, 66.1, 61.7, 61.7, 39.4, 27.3, 27.2, 25.1, 24.9, 24.4, 24.3. HRMS (APGC) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{16}O_4Na$ 235.0946; Found 235.0954. IR (KBr, cm^{-1}) 3027, 2971, 2925, 2852, 1741, 1454, 1438, 1301, 1265, 1222, 1146, 1111, 1087, 1068, 1021, 999, 954, , 905, 881, 856, 652, 580.

1-(tert-Butyl) 2-(1,4-dioxan-2-yl) (2S)-pyrrolidine-1,2-dicarboxylate (3p): Mixture of rotamers. Colorless oil (171.8 mg, 57%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.91-5.80 (m, 1H), 4.39-4.24 (m, 1H), 4.16-4.01 (m, 1H), 3.81-3.64 (m, 4H), 3.64-3.33 (m, 3H), 2.33-2.16 (m, 1H), 2.04-1.82 (m, 3H), 1.46-1.35 (m, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 171.6, 89.8, 89.6, 89.4, 80.0, 79.8, 79.7, 67.6, 67.5, 67.5, 65.9, 65.9, 61.6, 61.6, 61.4, 59.0, 58.9, 58.6, 46.5, 46.3, 46.3, 30.9, 30.8, 29.9, 28.4, 28.2, 24.3, 24.2, 23.5. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{23}NO_6Na$ 324.1423; Found 324.1428. IR

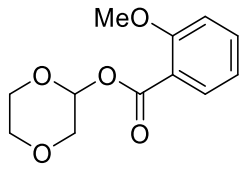
(KBr, cm^{-1}) 2976, 2933, 2882, 1754, 1700, 1482, 1456, 1398, 1367, 1260, 1161, 1147, 1089, 1067, 1017, 939, 906, 879, 851, 773. $[\alpha]_D^{25}$ = -63.0 (c=1.0, $CHCl_3$).

1,4-Dioxan-2-yl (tert-butoxycarbonyl)-L-alaninate (3q): Colorless oil (168.8 mg, 61%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (m, 1H), 5.09 (br s, 1H), 4.42-4.31 (m, 1H), 4.17-4.00 (m, 1H), 3.85-3.67 (m, 4H), 3.60 (ddd, *J* = 11.7, 2.3, 2.3 Hz, 1H), 1.42 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.2, 155.1, 90.1, 89.8, 79.9, 67.4, 67.4, 65.9, 65.9, 61.5, 49.3, 49.2, 28.3, 18.5. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{12}H_{21}NO_6Na$ 298.1267; Found 298.1272. IR (KBr, cm^{-1}) 3360, 2978, 2935, 2859, 1753, 1711, 1518, 1458, 1367, 1298, 1252, 1157, 1148, 1111, 1064, 1017, 914, 881, 856, 784, 759, 588. $[\alpha]_D^{25}$ = -20.8 (c =1, acetic acid).

1,4-Dioxan-2-yl 1H-indole-2-carboxylate (3r): Colorless crystals (155.8 mg, 63%), mp 161.5-162.3 ºC. Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (br s, 1H), 7.71 (ddd, *J* = 8.1, 2.0, 1.0 Hz, 1H), 7.44 (ddd, *J* = 8.4, 2.0, 1.0 Hz, 1H), 7.39 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.4, 6.9, 1.0 Hz, 1H), 7.17 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H), 6.13 (dd, *J* = 2.0, 2.0 Hz, 1H), 4.30-4.20 (m, 1H), 3.92 (d, *J* = 1.9 Hz, 2H), 3.88-3.83 (m, 4H), 3.69 (ddd, *J* = 11.8, 2.5, 2.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.6, 137.1, 127.4, 126.5, 125.8, 122.7, 120.9, 111.9, 110.0, 89.6, 67.8, 66.1, 61.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{13}H_{11}NO_4$ 248.0923; Found 248.0921. IR (KBr, cm^{-1}) 3333, 2974, 2858, 1710, 1530, 1383, 1341, 1308, 1247, 1232, 1194, 1144, 1112, 1066, 1018, 968, 910, 881, 852, 773, 749, 576.

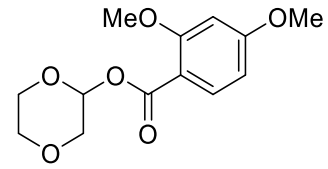
1,4-Dioxan-2-yl oleate (3s): Colorless oil (265.4 mg, 72%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^1H NMR (500 MHz, $CDCl_3$) δ 5.86 (dd, *J* = 2.2, 2.2 Hz, 1H), 5.39-5.29 (m, 2H), 4.14-4.06 (m, 1H), 3.82-3.68 (m, 4H), 3.63 (ddd, *J* = 11.6, 2.7, 2.7 Hz, 1H), 2.39 (td, *J* = 7.4, 1.2 Hz, 2H), 2.03-1.97 (m, 4H), 1.70-1.61 (m, 2H), 1.40-1.21 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 172.6, 130.0, 129.7, 89.0, 67.8, 66.1, 61.7, 34.3, 31.90, 29.8, 29.7, 29.5, 29.3, 29.3, 29.1, 29.1, 29.0, 27.2, 27.2, 24.8, 22.7, 14.1. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{22}H_{40}O_4Na$ 391.2824; Found 391.2820. IR (KBr, cm^{-1}) 2927, 2855, 1744, 1457, 1379, 1362, 1298, 1265, 1233, 1147, 1122, 1085, 1077, 1069, 1021, 938, 907, 880, 856, 724, 563.

1,4-Dioxan-2-yl 2-methoxybenzoate (3t): Colorless oil (138.2 mg, 58%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.02-6.95 (m, 2H), 6.08 (dd, *J* = 2.1, 2.1 Hz, 1H), 4.28-4.19 (m, 1H), 3.91 (s, 3H), 3.87 (d, *J* = 2.0 Hz, 2H), 3.83-

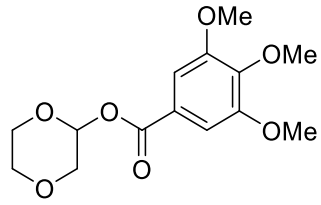


3.77 (m, 2H), 3.67 (ddd, J = 11.7, 2.6, 2.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.5, 159.6, 134.0, 131.9, 120.1, 119.3, 112.1, 89.6, 67.8, 66.1, 61.7, 56.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_5Na$ 261.0739; Found 261.0733. IR (KBr, cm^{-1}) 2972, 2927, 2856, 1731, 1601, 1582, 1491, 1464, 1438, 1351, 1298, 1250, 1232, 1156 1128, 1061, 1017, 913, 882, 867, 758, 705, 660, 691, 526.

1,4-Dioxan-2-yl 2,4-dimethoxybenzoate (3u): Yellow oil (118.0 mg, 44%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 6.54-6.45 (m, 2H), 6.05 (dd, J = 2.1, 2.1 Hz, 1H), 4.26-4.17 (m, 1H), 3.89 (s, 3H), 3.86-3.78 (m, 7H), 3.66 (ddd, J = 11.6, 2.7, 2.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 164.7, 163.8, 162.0, 134.2, 111.5, 104.6, 98.9, 89.3, 67.9, 66.1, 61.8, 56.0, 55.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_6Na$ 291.0845; Found 291.0849. IR (KBr, cm^{-1}) 2971, 2942, 2852, 1726, 1609, 1576, 1506, 1461,1419, 1331, 1297, 1249, 1233, 1213, 1161, 1136, 1113, 1062, 1019, 911, 882, 847, 836, 770, 608, 572, 522.



1,4-Dioxan-2-yl 3,4,5-trimethoxybenzoate (3v): Colorless crystals (125.3 mg, 42%), mp 104.5-105.3 ºC. Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 6.04 (dd, J = 2.0, 2.0 Hz, 1H), 4.21-4.11 (m, 1H), 3.88 (s, 6H), 3.88 (s, 3H), 3.86 (d, J = 2.0 Hz, 2H), 3.79 (dd, J = 6.5, 2.7 Hz, 2H), 3.66 (ddd, J = 11.8, 2.7, 2.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8, 152.9, 142.6, 124.5, 107.1, 89.9, 67.7, 66.0, 61.9, 60.8, 56.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}O_5$ 239.0919; Found 239.0913. IR (KBr, cm^{-1}) 2971, 2942, 2844, 1720, 1590, 1502, 1458, 1416, 1359, 1331, 1220, 1150, 1127, 1065, 1017, 948, 908, 882.



1,4-Dioxan-2-yl 2,3,4-trimethoxybenzoate (3w): Colorless oil (137.5 mg, 46%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.9 Hz, 1H), 6.06 (dd, J = 1.7, 1.7 Hz, 1H), 4.27-4.17 (m, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 3.88-3.84 (m, 5H), 3.83-3.78 (m, 2H), 3.66 (ddd, J = 11.7, 2.5, 2.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.9, 157.4, 154.9, 142.9, 127.2, 117.1, 106.7, 89.4, 67.7, 66.0, 61.7, 61.6, 60.8, 55.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}O_7Na$ 321.0950; Found 321.0942. IR (KBr, cm^{-1}) 2941, 1722, 1594, 1495, 1466, 1413, 1290, 1273, 1217, 1166, 1112, 1096, 1016, 945, 914, 798, 750.

1,4-Dioxan-2-yl 4-bromobenzoate (3x): Colorless oil (83.3 mg, 29%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.89 (m, 2H), 7.67-7.52 (m, 2H), 6.08 (dd, J = 1.9, 1.9 Hz, 1H), 4.28-4.11 (m, 1H), 3.89 (d, J = 1.9 Hz, 2H), 3.83 (dd, J = 6.8, 2.5 Hz, 2H), 3.68 (ddd, J = 11.7, 2.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 131.8, 131.4, 128.6, 128.6, 90.0, 67.7, 66.1, 61.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}O_4Br$ 286.9919; Found 286.9924. IR (KBr, cm^{-1}) 2974, 2932, 2857, 1728, 1590, 1485, 1454, 1398, 1356, 1274, 1259, 1233, 1155, 1116, 1089, 1068, 1009, 912, 882, 852, 757, 683, 581, 497.

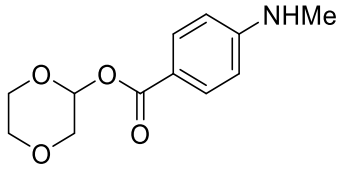
1,4-Dioxan-2-yl 4-fluorobenzoate (3y): Colorless crystals (110.8 mg, 49%), mp 48.9-49.8 ºC. Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.06 (m, 2H), 7.19-7.06 (m, 2H), 6.08 (dd, J = 1.9, 1.9 Hz, 1H), 4.29-4.12 (m, 1H), 3.89 (d, J = 2.0 Hz, 2H), 3.83 (dd, J = 6.9, 2.7 Hz, 2H), 3.68 (ddd, J = 11.7, 2.6, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0 (d, $^{1}J_{C\text{-}F}$ = 254.6 Hz), 164.2, 132.5 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 125.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 89.9, 67.8, 66.1, 61.8. ^{19}F{^{1}H} NMR (162 MHz, $CDCl_3$) δ -104.79. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}O_4F$ 227.0720; Found 227.0733. IR (KBr, cm^{-1}) 2974, 2929, 2859,1728, 1605, 1508, 1454, 1413, 1354, 1277, 1260, 1234, 1155, 1115, 1086, 1066, 1013, 912, 882, 855, 799, 767, 688, 606, 578.

1,4-Dioxan-2-yl 4-(trifluoromethyl)benzoate (3z): Colorless oil (129.7 mg, 47%). Column chromatography eluent, petroleum ether/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 6.12 (dd, J = 1.8, 1.8 Hz, 1H), 4.29-4.15 (m, 1H), 3.92 (d, J = 1.9 Hz, 2H), 3.85 (dd, J = 7.0, 2.5 Hz, 2H), 3.70 (ddd, J = 11.8, 2.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 134.9 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 133.0 (m), 130.3, 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $^{1}J_{C\text{-}F}$ = 272.9 Hz), 90.4, 67.7, 66.1, 61.8. ^{19}F{^{1}H} NMR (162 MHz, $CDCl_3$) δ -63.16. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}O_4F_3$ 277.0688; Found 277.0692. IR (KBr, cm^{-1}) 2977, 2934, 2860, 1732, 1587, 1514, 1456, 1413, 1327, 1278, 1262, 1235, 1164, 1131, 1093, 1067, 1013, 912, 883, 864, 776, 743, 704, 689, 580.

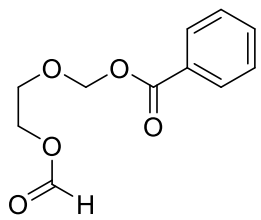
1,4-Dioxan-2-yl 1-naphthoate (3aa): Colorless amorphous solid (165.3 mg, 64%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (br d, J = 8.6 Hz, 1H), 8.36 (dd, J = 7.3, 1.3 Hz, 1H), 8.06 (br d, J = 8.2 Hz, 1H), 7.90 (br d, J = 8.1 Hz, 1H), 7.64 (ddd, J = 8.6, 6.8, 1.4 Hz, 1H), 7.58-7.51 (m, 2H), 6.22 (dd, J = 1.9, 1.9 Hz, 1H), 4.33-4.22 (m, 1H), 3.99-3.94 (m, 2H), 3.90-3.82 (m, 2H), 3.73 (ddd, J = 11.8, 2.6, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 134.0, 133.8, 131.5, 130.9, 128.6, 128.0, 126.3, 126.1, 125.7,

124.4, 89.83, 67.9, 66.1, 61.9. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{15}H_{14}O_4Na$ 281.0790; Found 281.0787. IR (KBr, cm^{-1}) 2973, 2928, 2856, 1720, 1594, 1576, 1510, 1453, 1248, 1278, 1243, 1232, 1195, 1156, 1130, 1109, 1067, 1019, 994, 911, 883, 856, 815, 783, 585.

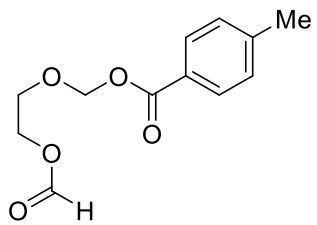
1,4-Dioxan-2-yl 4-(dimethylamino)benzoate (3ab): Brown crystals (105.5 mg, 42%), mp 94.7-95.5. Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.91 (m, 2H), 6.60-6.52 (m, 2H), 6.05 (dd, J = 2.2, 2.2 Hz, 1H), 4.27 (br s, 1H), 4.25-4.14 (m, 1H), 3.90-3.78 (m, 4H), 3.67 (ddd, J = 11.7, 2.8, 2.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.3, 153.3, 132.0, 117.4, 111.1, 89.0, 68.1, 66.2, 61.9, 30.1. HRMS (APGC) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{16}NO_4$ 238.1079; Found 238.1081. IR (KBr, cm^{-1}) 2975, 2932, 2857, 1704, 1606, 1534, 1351, 1277, 1261, 1176, 1151, 1116, 1087, 1064, 1020, 912, 880, 771, 702.



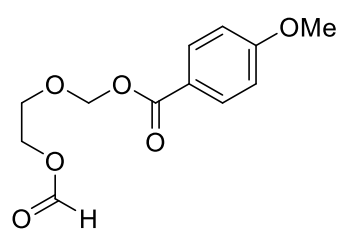
(2-(Formyloxy)ethoxy)methyl benzoate (4a): Colorless oil (38.1 mg, 17%, table 3; 20.3 mg, 9%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 8.04 (s, 1H), 7.62-7.57 (m, 1H), 7.50-7.44 (m, 2H), 5.57 (s, 2H), 4.39-4.34 (m, 2H), 4.01-3.96 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 160.7, 133.4, 129.8, 129.6, 128.5, 89.6, 68.1, 62.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_{13}O_5$ 225.0763; Found 225.0749. IR (KBr, cm^{-1}) 2963, 1726, 1261, 1059, 1024, 799, 773.



(2-(Formyloxy)ethoxy)methyl 4-methylbenzoate (4b): Colorless oil (28.6 mg, 12%, table 3; 52.6 mg, 22%, Table 4). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (br s, 1H), 7.99-7.94 (m, 2H), 7.29-7.23 (m, 2H), 5.56 (s, 2H), 4.38-4.33 (m, 2H), 4.00-3.95 (m, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.0, 160.7, 144.2, 129.9, 129.2, 126.8, 89.4, 68.0, 62.7, 21.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{15}O_5$ 239.0919; Found 239.0928. IR (KBr, cm^{-1}) 2925, 1722, 1611, 1271, 1180, 1165, 1144, 1060, 1018, 927, 753.



(2-(Formyloxy)ethoxy)methyl 4-methoxybenzoate (4c): Colorless oil (45.8 mg, 18%, table 3; 60.9 mg, 22%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 8.04-8.00 (m, 2H), 6.96-6.91 (m, 2H), 5.54 (s, 2H), 4.39-4.31 (m, 2H), 3.99-3.92 (m, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 163.7, 160.7, 131.9, 121.9, 113.7, 89.3, 67.9, 62.7, 55.5. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_6Na$ 277.0688; Found 277.0695. IR (KBr, cm-



[1]) 2958, 2842, 1724, 1607, 1581, 1512, 1458, 1422, 1318, 1258, 1170, 1062, 1027, 1007, 933, 850, 771, 698, 613, 511.

(2-(Formyloxy)ethoxy)methyl 3,4-dimethoxybenzoate (4d): Yellow oil (42.6 mg, 15%, table 3; 52.2 mg, 17%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 7.71 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 5.53 (s, 2H), 4.37-4.31 (m, 2H), 3.98-3.94 (m, 2H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 160.7, 153.4, 148.7, 123.9, 121.9, 112.1, 110.3, 89.3, 68.0, 62.7, 56.0, 56.0. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_7Na$ 307.0794; Found 307.0803. IR (KBr, cm^{-1}) 2940, 2841, 1720, 1600, 1516, 1465, 1420, 1347, 1293, 1272, 1223, 1178, 1132, 1072, 1024, 942, 876, 764, 729, 635.

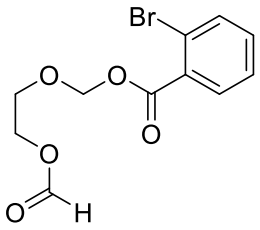
(2-(Formyloxy)ethoxy)methyl 2-acetoxybenzoate (4e): Colorless oil (33.8 mg, 12%, table 3; 64.1 mg, 21%, table 4). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 8.05 (dd, J = 7.8, 1.7 Hz, 1H), 7.59 (ddd, J = 8.1, 7.8, 1.7 Hz, 1H), 7.33 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.12 (dd, J = 8.1, 1.2 Hz, 1H), 5.51 (s, 2H), 4.40-4.29 (m, 2H), 3.98-3.90 (m, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 163.1, 150.9, 134.3, 132.1, 126.0, 123.9, 122.7, 89.9, 67.6, 66.0, 61.5, 20.9. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}O_7Na$ 305.0637; Found 305.0640. IR (KBr, cm^{-1}) 2958, 1766, 1724, 1607, 1486, 1553, 1370, 1293, 1255, 1194, 1121, 1070, 1038, 917, 834, 754, 705.

(2-(Formyloxy)ethoxy)methyl 4-chlorobenzoate (4f): Colorless oil (59.5 mg, 23%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.1Hz, 2H), 5.55 (s, 2H), 4.38-4.33 (m, 2H), 3.99-3.95 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 160.6, 139.9, 131.1, 128.8, 128.0, 89.7, 68.1, 62.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}O_5Cl$ 259.0373; Found 259.0377. IR (KBr, cm^{-1}) 2962, 1725, 1595, 1268, 1165, 1092, 1064, 1019, 925, 800, 760.

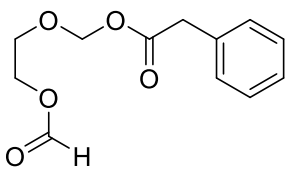
(2-(Formyloxy)ethoxy)methyl 2-iodobenzoate (4g): Colorless crystals (45.4 mg, 13%), mp 139.1-140.5. Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 8.02 (dd, J = 7.8, 1.2 Hz, 1H), 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.42 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.18 (ddd, J = 7.8, 7.8, 1.7 Hz, 1H), 5.57 (s, 2H), 4.40-4.34 (m, 2H), 4.04-3.98 (m, 2H). ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$) δ 165.7, 160.7, 141.6, 134.3, 133.1, 131.2, 128.0, 94.2, 90.2, 68.4, 62.6. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{11}O_5INa$ 372.9549; Found 372.9548. IR (KBr, cm^{-1}) 2943, 2882, 1723, 1700, 1582, 1561, 1466, 1429, 1404, 1292, 1268, 1251, 1167, 1142, 1122, 1072, 1037, 1014, 911, 736, 680, 637.

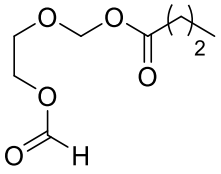
(2-(Formyloxy)ethoxy)methyl 2-bromobenzoate (4h): Colorless oil (42.4 mg, 14%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.87-7.83 (m, 1H), 7.72-7.66 (m, 1H), 7.42-7.33 (m, 2H), 5.57 (s, 2H), 4.43-4.31 (m, 2H), 4.06-3.96 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 160.7, 134.5, 133.0, 131.6, 131.4, 127.2, 121.9, 90.1, 68.3, 62.6. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{11}O_5BrNa$ 324.9688; Found 324.9683. IR (KBr, cm^{-1}) 2948, 1726, 1590, 1470, 1433, 1291, 1250, 1168, 1129, 1079, 1023, 918, 746, 644.



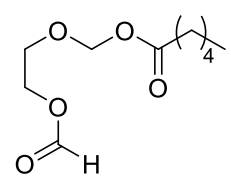
(2-(Formyloxy)ethoxy)methyl 2-phenylacetate (4i): Colorless oil (38.1 mg, 16%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 7.37-7.27 (m, 5H), 5.32 (s, 2H), 4.30-4.23 (m, 2H), 3.83-3.76 (m, 2H), 3.67 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 171.0, 160.7, 133.5, 129.2, 128.6, 127.3, 89.3, 67.9, 62.5, 41.4. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_5Na$ 261.0739; Found 261.0741. IR (KBr, cm^{-1}) 2951, 1726, 1497, 1455, 1248, 1168, 1120, 959, 856, 762, 711.



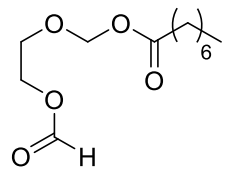
(2-(Formyloxy)ethoxy)methyl butyrate (4j): Colorless oil (19.0 mg, 10%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 5.31 (s, 2H), 4.39-4.23 (m, 2H), 3.93-3.80 (m, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.68 (tq, *J* = 7.4, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 160.7, 88.8, 67.8, 62.6, 36.1, 18.2, 13.6. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_{14}O_5Na$ 213.0739; Found 213.0736. IR (KBr, cm^{-1}) 2967, 2937, 2880, 1727, 1549, 1363, 1251, 1170, 1131, 1084, 1038, 955, 858.



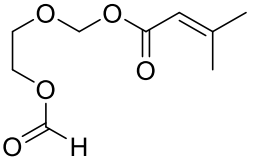
(2-(Formyloxy)ethoxy)methyl hexanoate (4k): Colorless oil (26.2 mg, 12%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09-8.08 (m, 1H), 5.31 (s, 2H), 4.35-4.31 (m, 2H), 3.90-3.86 (m, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.69-1.61 (m, 2H), 1.37-1.28 (m, 4H), 0.93-0.86 (m, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.3, 161.0, 88.8, 67.8, 62.6, 34.2, 31.2, 24.4, 22.3, 13.9. HRMS (APGC) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{19}O_5$ 219.1232; Found 219.1239. IR (KBr, cm^{-1}) 2958, 2933, 2873, 1728, 1168, 1132, 1087, 953.



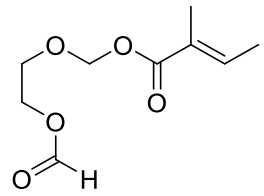
(2-(Formyloxy)ethoxy)methyl octanoate (4l): Colorless oil (29.7 mg, 12%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 5.31 (s, 2H), 4.35-4.31 (m, 2H), 3.89-3.85 (m, 2H), 2.35 (t, J = 7.5 Hz, 2H), 1.64 (tt, J = 7.2, 7.2 Hz, 2H), 1.37-1.21 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.4, 160.7, 88.8, 67.8, 62.6, 34.3, 31.6, 29.0, 28.9, 24.7, 22.6, 14.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{23}O_5$ 247.1545; Found 247.1568. IR (KBr, cm^{-1}) 2962, 2930, 2858, 1732, 1261, 1092, 1027, 800.



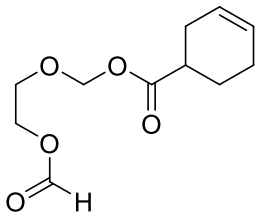
(2-(Formyloxy)ethoxy)methyl 3-methylbut-2-enoate (4m): Colorless oil (32.4 mg, 17%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 5.70 (qq, J = 1.1, 1.1 Hz, 1H), 5.33 (s, 2H), 4.36-4.27 (m, 2H), 3.93-3.82 (m, 2H), 2.18 (d, J = 1.1 Hz, 3H), 1.92 (d, J = 1.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 160.8, 159.0, 115.3, 88.2, 67.6, 62.7, 27.5, 20.4. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_9H_{14}O_5Na$ 225.0739; Found 225.0740. IR (KBr, cm^{-1}) 2975, 2916, 2857, 1727, 1649, 1452, 1381, 1359, 1265, 1224, 1158, 1138, 1068, 1023, 969, 907, 884, 865, 582.



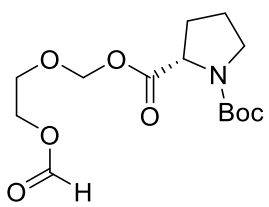
(2-(Formyloxy)ethoxy)methyl (E)-2-methylbut-2-enoate (4n): Colorless oil (26.3 mg, 13%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 6.94 (qq, J = 6.9, 1.3 Hz, 1H), 5.39 (s, 2H), 4.38-4.28 (m, 2H), 3.95-3.83 (m, 2H), 1.85 (qd, J = 1.0, 1.0 Hz, 3H), 1.82 (dq, J = 7.2, 1.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 167.3, 160.7, 138.7, 128.2, 89.1, 67.8, 62.7, 14.5, 11.9. HRMS (APGC) m/z: $[M+H]^+$ Calcd for $C_9H_{15}O_5$ 203.0919; Found 203.0928. IR (KBr, cm^{-1}) 2974, 2916, 1724, 1649, 1452, 1382, 1263, 1169, 1014, 957, 912, 734.



(2-(Formyloxy)ethoxy)methyl cyclohex-2-ene-1-carboxylate (4o): Colorless oil (52.4 mg, 23%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (br s, 1H), 5.75-5.64 (m, 2H), 5.36 (s, 2H), 4.42-4.31 (m, 2H), 3.95-3.84 (m, 2H), 2.70-2.56 (m, 1H), 2.36-2.24 (m, 2H), 2.16-2.02 (m, 3H), 1.81-1.68 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.2, 160.7, 126.7, 125.0, 88.9, 67.8, 62.6, 39.3, 27.2, 24.9, 24.3. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{16}O_5Na$ 251.0895; Found 251.0885. IR (KBr, cm^{-1}) 3028, 2931, 2845, 1728, 1455, 1437, 1375, 1223, 1167, 1127, 1061, 992, 957, 652.

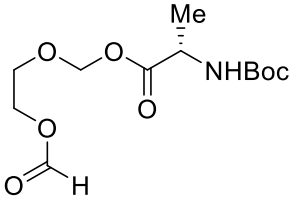


1-(tert-Butyl) 2-((2-(formyloxy)ethoxy)methyl) (S)-pyrrolidine-1,2-dicarboxylate (4p): Mixture of rotamers. Yellow oil (82.5 mg, 26%, 2 rotamers). Column chromatography eluent, petroleum ether/EtOAc 8.5:1.5. ^{1}H NMR (400 MHz, $CDCl_3$, 2 rotamers, 53:47 ratio): δ major rotamer: 8.07 (br s, 1H), 5.35 (d, J = 6.2 Hz, 1H), 5.33 (d, J = 6.2 Hz, 1H), 4.34-4.28 (m, 2H), 4.25 (dd, J = 8.7, 4.0 Hz, 1H), 3.90-3.84 (m, 2H), 3.60-3.34 (m, 2H), 2.32-2.15 (m, 1H), 2.05-1.81 (m, 3H), 1.40 (s, 9H); δ minor rotamer: 8.07 (br s, 1H), 5.44 (d, J = 6.2 Hz, 1H), 5.27 (d, J = 6.2 Hz, 1H), 4.35-4.28 (m, 3H), 3.90-3.84 (m, 2H), 3.60-3.34 (m, 2H), 2.32-2.15 (m, 1H), 2.05-1.81 (m, 3H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR

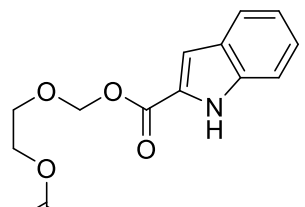


(100 MHz, $CDCl_3$): δ major rotamer: 172.6, 160.6, 153.7, 89.4, 80.0, 68.0, 62.5, 59.1, 46.3, 30.8, 28.3, 23.6; δ minor rotamer: 172.6, 160.8, 154.4, 89.3, 79.9, 67.7, 62.6, 58.9, 46.6, 29.9, 28.4, 24.4. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{23}NO_7Na$ 340.1372; Found 340.1379. IR (KBr, cm^{-1}) 2977, 2929, 2880, 1699, 1673, 1480, 1414, 1368, 1163, 1128, 1090, 978, 915, 888, 855, 773. $[\alpha]_D^{25}$ = -50.2 (c = 0.7, $CHCl_3$).

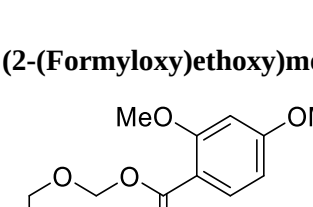
(2-(Formyloxy)ethoxy)methyl (tert-butoxycarbonyl)-L-alaninate (4q): Colorless oil (66.9 mg, 23%). Column chromatography eluent, petroleum ether/EtOAc 8.5:1.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 5.38 (d, *J* = 6.2 Hz, 1H), 5.32 (d, *J* = 6.2 Hz, 1H), 5.03 (br s, 1H), 4.38-4.23 (m, 3H), 3.96-3.80 (m, 2H), 1.43 (s, 9H), 1.40 (d, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.0, 160.7, 155.1, 89.6, 80.0, 68.0, 62.5, 49.3, 28.3, 18.4. HRMS (APGC) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{21}NO_7Na$ 314.1216; Found 314.1191. IR (KBr, cm^{-1}) 2980, 2937, 1724, 1516, 1455, 1368, 1298, 1251, 1168, 1131, 1063, 938, 861, 784. $[\alpha]_D^{25}$ = -24.3 (c =0.8, acetic acid).

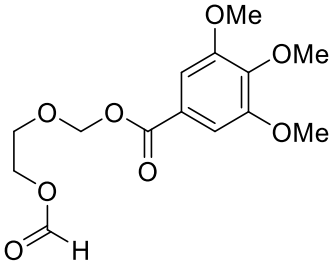


(2-(Formyloxy)ethoxy)methyl 1H-indole-2-carboxylate (4r): Yellow oil (55.3 mg, 21%). Column chromatography eluent, petroleum ether/EtOAc 8.5:1.5. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (br s, 1H), 8.06 (br s, 1H), 7.71 (ddd, *J* = 8.1, 1.0, 1.0 Hz, 1H), 7.44 (ddd, *J* = 8.3, 1.0, 1.0 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.0, 1.0 Hz, 1H), 7.30 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 5.59 (s, 2H), 4.41-4.34 (m, 2H), 4.04-3.97 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 160.8, 137.1, 127.4, 126.4, 125.8, 122.7, 121.0, 111.9, 109.7, 89.4, 68.2, 62.6. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{13}NO_5Na$ 286.0691; Found 286.0693. IR (KBr, cm^{-1}) 3341, 2952, 2880, 1712, 1620, 1575, 1530, 1430, 1365, 1341, 1247, 1194, 1165, 1135, 1076, 965, 916, 826, 773, 749.



(2-(Formyloxy)ethoxy)methyl 2,4-dimethoxybenzoate (4u): Colorless oil (56.8 mg, 20%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 6.53-6.46 (m, 2H), 5.51 (s, 2H), 4.42-4.27 (m, 2H), 4.02-3.93 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.7, 164.7, 161.8, 160.8, 134.1, 111.4, 104.6, 98.9, 89.0, 67.9, 62.7, 55.9, 55.5. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_7Na$ 307.0794; Found 307.0799. IR (KBr, cm^{-1}) 3517, 2945, 2842, 1723, 1610, 1575, 1506, 1465, 1421, 1331, 1270, 1251, 1214, 1166, 1130, 1053, 1027, 934, 837, 771, 699, 613.

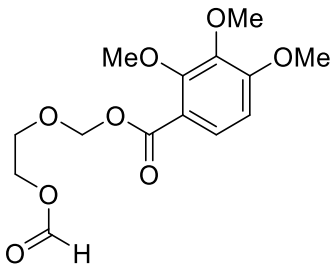




(2-(Formyloxy)ethoxy)methyl 3,4,5-trimethoxybenzoate (4v): Colorless oil (62.8 mg, 20%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.32 (s, 2H), 5.55 (s, 2H), 4.43-4.29 (m, 2H), 4.04-3.93 (m, 2H), 3.91 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 160.7, 153.0, 142.6, 124.4, 107.04, 107.02, 89.6, 71.8, 68.1, 62.6, 61.7, 60.9, 56.3. HRMS (APGC) *m/z*: $[M+Na]^+$ Calcd for

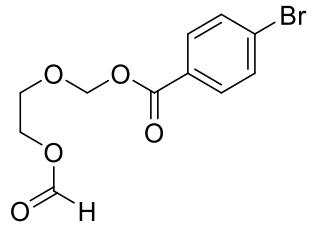
$C_{14}H_{18}O_8Na$ 337.0899; Found 337.0900. IR (KBr, cm^{-1}) 2944, 2838, 1722, 1590, 1504, 1461, 1416, 1337, 1225, 1128, 1002, 949, 766,

(2-(Formyloxy)ethoxy)methyl 2,3,4-trimethoxybenzoate (4w): Colorless oil (53.4 mg, 17%).

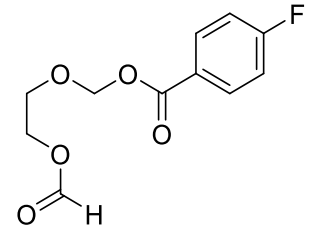


Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 7.67 (d, J = 8.9 Hz, 1H), 6.73 (d, J = 8.9 Hz, 1H), 5.55 (s, 2H), 4.44-4.30 (m, 2H), 4.02-3.98 (m, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 157.5, 155.1, 143.0, 127.3, 117.3, 106.9, 89.5, 67.9, 66.1, 61.8, 61.7, 60.9, 56.0. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}O_8Na$ 337.0899; Found 337.0901. IR (KBr, cm^{-1}) 2943, 1723, 1594, 1494, 1467, 1413, 1290, 1270, 1218, 1095, 1014, 944, 913, 881, 797.

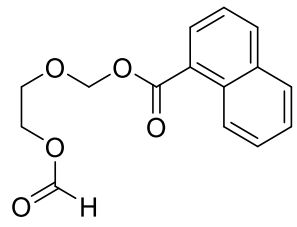
(2-(Formyloxy)ethoxy)methyl 4-bromobenzoate (4x): Colorless crystals (51.5 mg, 17%), mp 98.8-100.0 ºC. Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.95-7.90 (m, 2H), 7.63-7.58 (m, 2H), 5.56 (s, 2H), 4.41-4.28 (m, 2H), 4.05-3.91 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.2, 160.7, 131.9, 131.3, 128.7, 128.5, 89.8, 68.2, 62.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{11}O_5BrNa$ 324.9688; Found 324.9683. IR (KBr, cm^{-1}) 2934, 1723, 1590, 1484, 1453, 1398, 1268, 1165, 1146, 1069, 1010, 921, 848, 756, 708, 683.

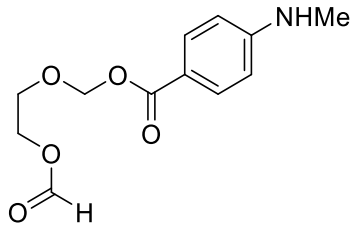


(2-(Formyloxy)ethoxy)methyl 4-fluorobenzoate (4y): Colorless oil (50.8 mg, 21%). Column chromatography eluent, petroleum ether/EtOAc 9.5:0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.07 (m, 2H), 8.05 (br s, 1H), 7.17-7.10 (m, 2H), 5.56 (s, 2H), 4.40-4.30 (m, 2H), 4.04-3.92 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7 (d, $^1J_{C\text{-}F}$ = 254.4 Hz), 165.0, 160.5, 132.4 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 125.8 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 89.7, 68.1, 62.6. ^{19}F{^{1}H} NMR (162 MHz, $CDCl_3$) δ -104.69. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{11}O_5FNa$ 265.0488; Found 265.0490. IR (KBr, cm^{-1}) 2917, 1726, 1603, 1508, 1270, 1154, 1061, 1015, 925, 856, 768, 689.

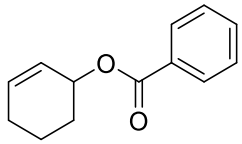


(2-(Formyloxy)ethoxy)methyl 1-naphthoate (4aa): Yellow oil (49.3 mg, 18%). Column chromatography eluent, petroleum ether/EtOAc 8.5:1.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (br d, J = 8.5 Hz, 1H), 8.27 (dd, J = 7.3, 1.3 Hz, 1H), 8.06 (br d, J = 8.5 Hz, 1H), 8.05 (br s, 1H), 7.90 (br d, J = 8.1 Hz, 1H), 7.64 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.59-7.49 (m, 2H), 5.66 (s, 2H), 4.48-4.31 (m, 2H), 4.13-3.94 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 160.7, 134.0, 133.8, 131.5, 130.7, 128.6, 128.0, 126.3, 126.1, 125.7, 124.4, 89.5, 68.1, 62.7. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{14}O_5Na$ 297.0739; Found 297.0741. IR (KBr, cm^{-1}) 2955, 1724, 1594, 1576, 1510, 1453, 1367, 1278, 1243, 1194, 1166, 1118, 1075, 1028, 987, 929, 816, 784.

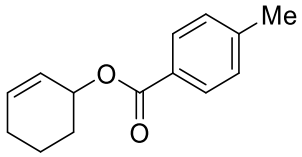


(2-(Formyloxy)ethoxy)methyl 4-(methylamino)benzoate (4ab): Yellow oil (20.2 mg, 8%). Column chromatography eluent, petroleum ether/EtOAc 8.5:1.5. 

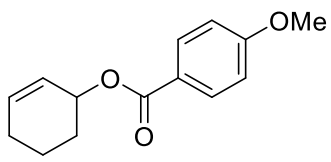
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.97-7.85 (m, 2H), 6.60-6.51 (m, 2H), 5.52 (s, 2H), 4.41-4.31 (m, 2H), 4.24 (br s, 1H), 3.99-3.90 (m, 2H), 2.90 (d, J = 4.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 160.8, 153.3, 131.9, 117.3, 111.1, 88.8, 67.8, 62.8, 30.1. HRMS (APGC) *m*/*z*: $[M+Na]^+$ Calcd for $C_{12}H_{15}NO_5Na$ 276.0848; Found 276.0853. IR (KBr, cm^{-1}) 3404, 2938, 1716, 1605, 1532, 1454, 1415, 1344, 1312, 1274, 1178, 1053, 938, 838, 771, 701.

Cyclohex-2-en-1-yl benzoate (7a): Colorless oil (188.1 mg, 93%). Column chromatography eluent, petroleum ether/EtOAc 8:2. 

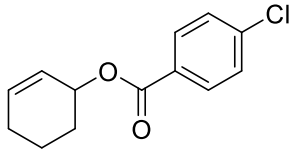
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-7.96 (m, 2H), 7.61-7.50 (m, 1H), 7.49-7.36 (m, 2H), 6.09-5.96 (m, 1H), 5.93-5.79 (m, 1H), 5.59-5.43 (m, 1H), 2.20-2.04 (m, 2H), 2.02-1.94 (m, 1H), 1.92-1.80 (m, 2H), 1.75-1.66 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 132.8, 132.7, 130.8, 129.6, 128.2, 125.7, 68.6, 28.4, 24.9, 18.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.1072; Found 203.1072. IR (KBr, cm^{-1}) 2930, 1715, 1456, 1314, 1271, 1110, 925, 710, 691.

Cyclohex-2-en-1-yl 4-methylbenzoate (7b): Colorless oil (166.3 mg, 77%). Column chromatography eluent, petroleum ether/EtOAc 8:2. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.25-7.20 (m, 2H), 6.03-5.95 (m, 1H), 5.87-5.79 (m, 1H), 5.54-5.45 (m, 1H), 2.40 (s, 3H), 2.19-2.10 (m, 1H), 2.09-1.93 (m, 2H), 1.91-1.79 (m, 2H), 1.75-1.65 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 143.3, 132.7, 129.6, 129.0, 128.0, 125.9, 68.4, 28.4, 25.0, 21.6, 19.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1229; Found 217.1209. IR (KBr, cm^{-1}) 3033, 2939, 2867, 1711, 1611, 1509, 1453, 1409, 1311, 1272, 1208, 1177, 1108, 1058, 1050, 1020, 918, 841, 755, 728, 691, 677.

Cyclohex-2-en-1-yl 4-methoxybenzoate (7c): Colorless oil (218.1 mg, 94%). Column chromatography eluent, petroleum ether/EtOAc 8:2. 

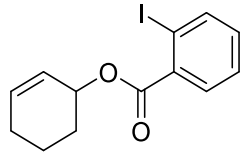
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.93 (m, 2H), 6.99-6.82 (m, 2H), 6.08-5.90 (m, 1H), 5.89-5.78 (m, 1H), 5.54-5.38 (m, 1H), 3.83 (s, 3H), 2.17-1.91 (m, 3H), 1.89-1.77 (m, 2H), 1.74-1.64 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 163.1, 132.5, 131.5, 125.9, 123.1, 113.4, 68.1, 55.3, 28.4, 24.9, 18.9. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{14}H_{17}O_3$ 233.1178; Found 233.1180. IR (KBr, cm^{-1}) 2938, 1706, 1607, 1511, 1257, 1168, 1102, 1030, 918, 847, 771.

Cyclohex-2-en-1-yl 4-chlorobenzoate (7d): Colorless oil (191.7 mg, 81%). Column chromatography eluent, petroleum ether/EtOAc 8:2. 

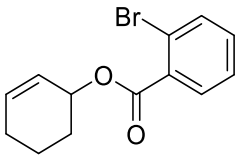
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.95 (m, 2H), 7.43-7.38 (m, 2H), 6.04-5.99 (m, 1H), 5.84-5.79 (m, 1H), 5.52-5.47 (m, 1H), 2.19-2.10 (m, 1H), 2.09-2.01 (m, 1H), 1.91-1.79 (m, 2H), 1.75-1.66 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.3, 139.1, 133.1, 131.0, 129.2, 128.6, 125.5,

68.9, 28.4, 24.9, 18.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}O_2Cl$ 237.0682; Found 237.0674. IR (KBr, cm^{-1}) 2941, 1717, 1594, 1270, 1092, 1015, 915, 760.

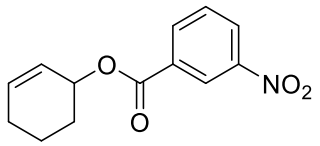
Cyclohex-2-en-1-yl 2-iodobenzoate (7e): Colorless oil (262.4 mg, 80%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42-7.35 (m, 1H), 7.13 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H), 6.07-5.98 (m, 1H), 5.91-5.82 (m, 1H), 5.56-5.48 (m, 1H), 2.19-2.09 (m, 1H), 2.09-2.03 (m, 1H), 2.01-1.80 (m, 3H), 1.75-1.65 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 140.9, 135.5, 133.0, 132.2, 130.6, 127.7, 125.1, 93.8, 69.4, 28.0, 24.7, 18.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}O_2I$ 329.0038; Found 329.0040. IR (KBr, cm^{-1}) 3033, 2940, 2867, 1722, 1584, 1562, 1467, 1430, 1287, 1250, 1133, 1100, 1043, 1015, 911, 743, 682, 639.



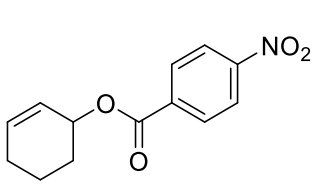
Cyclohex-2-en-1-yl 2-bromobenzoate (7f): Colorless oil (109.6 mg, 39%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.64-7.58 (m, 1H), 7.36-7.25 (m, 2H), 6.04-5.96 (m, 1H), 5.89-5.79 (m, 1H), 5.56-5.46 (m, 1H), 2.17-2.07 (m, 1H), 2.07-2.00 (m, 1H), 2.00-1.90 (m, 2H), 1.89-1.76 (m, 1H), 1.73-1.63 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.8, 134.1, 133.1, 132.8, 132.2, 131.1, 127.0, 125.1, 121.3, 69.4, 28.1, 24.8, 18.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}O_2Br$ 281.0177; Found 281.0168. IR (KBr, cm^{-1}) 2941, 2869, 1725, 1591, 1470, 1433, 1288, 1249, 1131, 1109, 1029, 1007, 912, 746, 642.



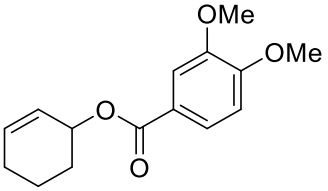
Cyclohex-2-en-1-yl 3-nitrobenzoate (7g): Yellow oil (163.0 mg, 66%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 1.9, 1.9 Hz, 1H), 8.42-8.31 (m, 2H), 7.63 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.06-5.97 (m, 1H), 5.86-5.77 (m, 1H), 5.57-5.48 (m, 1H), 2.21-2.09 (m, 1H), 2.09-2.00 (m, 1H), 1.98-1.79 (m, 3H), 1.75-1.66 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 148.1, 135.2, 133.5, 132.5, 129.5, 127.1, 124.9, 124.4, 69.7, 28.2, 24.8, 18.8. HRMS (APGC) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_4$ 248.0923; Found 248.0945. IR (KBr, cm^{-1}) 2937, 2869, 1719, 1616, 1533, 1409, 1437, 1351, 1292, 1264, 1136, 1068, 1006, 909, 814, 777, 718.



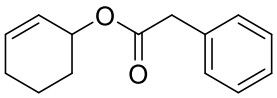
Cyclohex-2-en-1-yl 4-nitrobenzoate (7h): Colorless crystals (175.4 mg, 71%), mp 67.1-69.0 °C. Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31-8.24 (m, 2H), 8.24-8.18 (m, 2H), 6.10-6.02 (m, 1H), 5.87-5.80 (m, 1H), 5.57-5.49 (m, 1H), 2.22-2.11 (m, 1H), 2.12-2.05 (m, 1H), 2.01-1.96 (m, 1H), 1.95-1.90 (m, 1H), 1.89-1.81 (m, 1H), 1.77-1.70 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.3, 150.4, 136.2, 133.6, 130.7, 124.9, 123.4, 69.8, 28.3, 24.9, 18.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_4$ 248.0923; Found 248.0918. IR (KBr, cm^{-1}) 2939, 2867, 1720, 1605, 1528, 1346, 1272, 1165, 1116, 1103, 1050, 1013, 912, 874, 841, 785, 720.



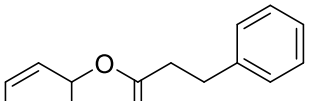
Cyclohex-2-en-1-yl 3,4-dimethoxybenzoate (7i): Colorless oil (149.3 mg, 57%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.60 (m, 1H), 7.54-7.47 (m, 1H), 6.82 (d, J = 8.5 Hz, 1H), 5.98-5.89 (m, 1H), 5.82-5.74 (m, 1H), 5.49-5.39 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.14-2.04 (m, 1H), 2.04-1.98 (m, 1H), 1.95-1.88 (m, 1H), 1.87-1.73 (m, 2H), 1.70-1.61 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 152.6, 148.3, 132.4, 125.7, 123.3, 123.1, 111.8, 110.0, 106.6, 68.3, 55.8, 28.2, 24.8, 18.9. HRMS (APGC) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}O_4$ 263.1283; Found 263.1273. IR (KBr, cm^{-1}) 2937, 2841, 1705, 1601, 1589, 1515, 1464, 1418, 1348, 1271, 1223, 1177, 1133, 1106, 1025, 764, 728.



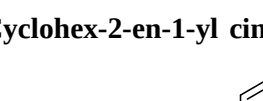
Cyclohex-2-en-1-yl 2-phenylacetate (7j): Yellow pale oil (146.9 mg, 68%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 5.99-5.91 (m, 1H), 5.73-5.66 (m, 1H), 5.31-5.24 (m, 1H), 3.61 (s, 2H), 2.13-1.92 (m, 2H), 1.90-1.80 (m, 1H), 1.77-1.66 (m, 2H), 1.66-1.56 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 134.2, 132.8, 129.2, 128.5, 126.9, 125.5, 68.5, 41.7, 28.2, 24.8, 18.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1229; Found 217.1232. IR (KBr, cm^{-1}) 3031, 2940, 1731, 1455, 1250, 1156, 1009, 908, 726.



Cyclohex-2-en-1-yl 3-phenylpropanoate (7k): Colorless oil (213.9 mg, 93%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.23-7.17 (m, 3H), 5.98-5.90 (m, 1H), 5.70-5.62 (m, 1H), 5.30-5.22 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.13-2.03 (m, 1H), 2.02-1.93 (m, 1H), 1.88-1.79 (m, 1H), 1.74-1.60 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 140.5, 132.6, 128.3, 128.2, 126.1, 125.6, 68.0, 36.1, 31.0, 28.2, 24.8, 18.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1385; Found 231.1377. IR (KBr, cm^{-1}) 3030, 2936, 2867, 1731, 1604, 1497, 1454, 1371, 1290, 1248, 1160, 1078, 1058, 1009, 914, 751, 730, 699.



Cyclohex-2-en-1-yl cinnamate (7l): Colorless oil (127.7 mg, 56%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 8.57-7.48 (m, 2H), 7.42-7.34 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 6.04-5.96 (m, 1H), 5.83-5.74 (m, 1H), 5.46-5.36 (m, 1H), 2.19-2.08 (m, 1H), 2.07-2.01 (m, 1H), 1.96-1.90 (m, 1H), 1.86-1.78 (m, 2H), 1.71-1.64 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 144.5, 134.5, 132.8, 130.1, 128.8, 128.0, 125.8, 118.6, 68.1, 28.4, 24.9, 18.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}O_2$ 229.1229; Found 229.1223. IR (KBr, cm^{-1}) 3034, 2937, 2867, 1709, 1638, 1496, 1450, 1332, 1304, 1281, 1255, 1202, 1172, 1058, 1011, 979, 919, 768, 710, 648.



Cyclohex-2-en-1-yl 3-methylbut-2-enoate (7m): Colorless oil (88.2 mg, 49%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98-5.91 (m, 1H), 5.75-5.70 (m, 1H), 5.68 (qq, J = 1.3, 1.3 Hz, 1H), 5.32-5.26 (m, 1H), 2.17 (d, J = 1.3, 1.3 Hz, 3H), 2.13-

1.85 (m, 3H), 1.88 (d, J = 1.3, 1.3 Hz, 3H), 1.81-1.70 (m, 2H), 1.68-1.60 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.2, 156.1, 132.2, 126.0, 116.4, 66.9, 28.4, 27.3, 24.8, 20.1, 18.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}O_2$ 181.1229; Found 181.1236. IR (KBr, cm^{-1}) 3033, 2937, 2867, 1716, 1653, 1445, 1379, 1355, 1271, 1228, 1148, 1076, 1059, 1011, 978, 925, 852, 724, 675.

Cyclohex-2-en-1-yl pent-4-enoate (7n): Colorless oil (88.1 mg, 49%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.98-5.90 (m, 1H), 5.88-5.75 (m, 1H), 5.72-5.64 (m, 1H), 5.30-5.23 (m, 1H), 5.05 (dd, J = 17.1, 1.6 Hz, 1H), 4.99 (dd, J = 10.4, 1.3 Hz, 1H), 2.45-2.31 (m, 4H), 2.14-2.02 (m, 1H), 2.02-1.92 (m, 1H), 1.90-1.81 (m, 1H), 1.76-1.61 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 136.7, 132.6, 125.7, 115.4, 68.0, 33.8, 29.0, 28.3, 24.8, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{16}O_2Na$ 203.1048; Found 203.1055. IR (KBr, cm^{-1}) 3398, 3082, 3034, 3002, 2938, 2868, 2838, 2036, 1705, 1601, 1590, 1515, 1464, 1454, 1417, 1348, 1271, 1223, 1177, 1133, 1107, 1058, 1026, 914, 878, 824, 765, 728, 680, 632, 611.

Cyclohex-2-en-1-yl hexanoate (7o): Colorless oil (137.2 mg, 70%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.98-5.91 (m, 1H), 5.72-5.66 (m, 1H), 5.29-5.23 (m, 1H), 2.28 (t, J = 7.6 Hz, 2H), 2.14-2.03 (m, 1H), 2.03-1.94 (m, 1H), 1.91-1.82 (m, 1H), 1.78-1.68 (m, 2H), 1.66-1.57 (m, 3H), 1.35-1.25 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 132.5, 125.8, 67.8, 34.7, 31.3, 28.3, 24.9, 24.7, 22.3, 18.9, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{20}O_2$ 219.1361; Found 219.1342. IR (KBr, cm^{-1}) 3034, 2934, 2871, 1732, 1456, 1372, 1245, 1175, 1097, 1058, 1011, 962, 915, 729.

Cyclohex-2-en-1-yl octanoate (7p): Yellow pale oil (181.4 mg, 81%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.92-5.77 (m, 1H), 5.67-5.58 (m, 1H), 5.23-5.13 (m, 1H), 2.26-2.15 (m, 2H), 2.03-1.87 (m, 2H), 1.84-1.74 (m, 1H), 1.70-1.61 (m, 2H), 1.60-1.47 (m, 3H), 1.30-1.13 (m, 8H), 0.87-0.74 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 132.5, 125.8, 67.8, 34.7, 31.7, 29.1, 28.9, 28.3, 25.1, 24.9, 22.6, 18.9, 14.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{24}O_2Na$ 247.1674; Found 247.1658. IR (KBr, cm^{-1}) 2931, 2858, 1732, 1456, 1377, 1161.

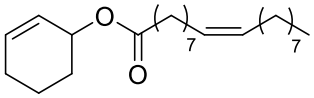
Cyclohex-2-en-1-yl heptadecanoate (7q): Colorless oil (252.4 mg, 72%). Column chromatography eluent, petroleum ether/EtOAc 8:2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.98-5.90 (m, 1H), 5.73-5.65 (m, 1H), 5.30-5.22 (m, 1H), 2.29 (t, J = 7.4 Hz, 2H), 2.14-1.93 (m, 3H), 1.92-1.82 (m, 1H), 1.79-1.67 (m, 3H), 1.66-1.57 (m, 3H), 1.31-1.22 (m, 24H), 0.87 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 132.3, 125.8, 67.6, 34.6, 31.9, 29.62, 29.60, 29.58, 29.57, 29.5, 29.4, 29.3, 29.2, 29.0, 28.3, 25.0, 24.8, 22.6, 18.8, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{42}O_2Na$ 373.3083; Found 373.3085. IR (KBr, cm^{-1}) 3033, 2925, 2854, 1734, 1466, 1376, 1332, 1246, 1175, 1161, 1115, 1097, 1058, 1011, 918, 723.

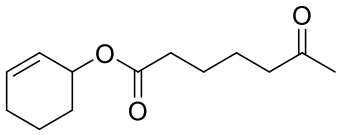
1-(tert-Butyl) 2-(cyclohex-2-en-1-yl) (2*R*)-pyrrolidine-1,2-dicarboxylate (7r): Mixture of rotamers, colorless oil (265.5 mg, 90%). Column chromatography eluent, petroleum ether/EtOAc 7.5:2.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03-5.82 (m, 1H), 5.74-5.57 (m, 1H), 5.36-5.15 (m, 1H), 4.32-4.13 (m, 1H), 3.60-3.26 (m, 2H), 2.28-2.09 (m, 1H), 2.06-1.78 (m, 6H), 1.77-1.53 (m, 3H), 1.48-1.34 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 172.4, 172.1, 172.1, 154.0, 153.5, 132.6, 132.3, 125.2, 125.1, 125.0, 125.0, 79.4, 79.3, 79.2, 68.2, 68.1, 68.0, 58.9, 58.9, 58.8, 58.7, 46.2, 46.0, 30.6, 30.6, 29.7, 29.6, 28.1, 28.0, 27.9, 27.8, 24.5, 23.9, 23.2, 23.2, 18.5, 18.4. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{16}H_{25}NO_4Na$ 318.1681; Found 318.1695. IR (KBr, cm^{-1}) 3033, 2976, 2937, 2878, 1743, 1702, 1479, 1454, 1396, 1366, 1323, 1276, 1257, 1188m 1161, 1121, 1088, 1057, 1010, 979, 952, 926, 888, 859, 797, 772, 729, 672, 549. $[\alpha]_D^{25}$ = -32.9 (c =1, $CHCl_3$).

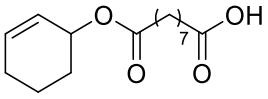
Cyclohex-2-en-1-yl (tert-butoxycarbonyl)-L-alaninate (7s): Colorless oil (223.3 mg, 83%). Column chromatography eluent, petroleum ether/EtOAc 7.5:2.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02-5.89 (m, 1H), 5.73-5.61 (m, 1H), 5.27 (br s, 1H), 5.07 (br s, 1H), 4.26 (br s, 1H), 2.13-1.91 (m, 2H), 1.87-1.56 (m, 4H), 1.42 (s, 9H), 1.39-1.32 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 155.0, 133.1, 125.1, 125.0, 79.6, 69.0, 68.9, 49.3, 28.3, 28.1, 24.8, 24.8, 18.7, 18.7, 18.7, 18.6. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{14}H_{23}NO_4Na$ 292.1525; Found 292.1529. IR (KBr, cm^{-1}) 3370, 3034, 2978, 2938, 2875, 1716, 1513, 1454, 1394, 1367, 1304, 1251, 1212, 1164, 1097, 1056, 1023, 915, 856, 782, 729. $[\alpha]_D^{25}$ = -17.6 (c =1, acetic acid).

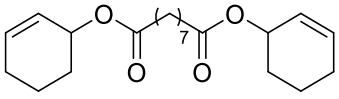
Cyclohex-2-en-1-yl 1H-indole-2-carboxylate (7t): Colorless oil (142.2 mg, 59%). Column chromatography eluent, petroleum ether/EtOAc 7:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (br s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.49-7.43 (m, 1H), 7.37-7.31 (m, 1H), 7.31-7.28 (m, 1H), 7.21-7.15 (m, 1H), 6.11-6.02 (m, 1H), 5.97-5.85 (m, 1H), 5.67-5.57 (m, 1H), 2.25-2.13 (m, 1H), 2.13-2.07 (m, 1H), 2.06-1.85 (m, 3H), 1.80-1.69 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 136.9, 133.1, 127.6, 127.4, 125.4, 125.2, 122.4, 120.6, 111.9, 108.7, 68.9, 28.4, 24.9, 18.8. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1167. IR (KBr, cm^{-1}) 3326, 2939, 1688, 1528, 1431, 1386, 1343, 1309, 1249, 1202, 1147, 1050, 1006, 976, 912, 817, 772, 746.

Cyclohex-2-en-1-yl 2-acetoxybenzoate (7u): Colorless crystals (205.4 mg, 79%), mp 102.1-103.5 ºC. Column chromatography eluent, petroleum ether/EtOAc 8:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H), 7.30 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.04-5.96 (m, 1H), 5.83-5.76 (m, 1H),5.52-5.45 (m, 1H), 2.33 (s, 3H), 2.17-2.00 (m, 2H), 2.00-1.92 (m, 1H), 1.88-1.74 (m, 2H), 1.73-1.63 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 164.2, 150.5, 133.6, 133.0, 131.9, 126.0, 125.6, 123.9, 123.7, 68.9, 28.3, 24.9, 21.1, 18.9. HRMS (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $C_{15}H_{16}O_4Na$ 283.0946; Found 283.0952. IR (KBr, cm^{-1}) 2940, 1771, 1715, 1607,1485, 1452, 1368, 1289, 1252, 1194, 1161, 1124, 1079, 1008, 914, 753, 704.

Cyclohex-2-en-1-yl oleate (7v): Colorless oil (333.6 mg, 92%). Column chromatography eluent, petroleum ether/EtOAc 8:2.  ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.77 (m, 1H), 5.73-5.55 (m, 1H), 5.33-5.22 (m, 1H), 5.21-5.10 (m, 1H), 2.19 (td, J = 7.6, 2.9 Hz, 2H), 2.04-1.83 (m, 6H), 1.82-1.72 (m, 1H), 1.72-1.47 (m, 6H), 1.35-1.07 (m, 20H), 0.80 (t, J = 5.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 131.9, 129.6, 129.4, 125.7, 67.4, 34.3, 31.7, 29.5, 29.4, 29.3, 29.1, 29.1, 28.94, 28.86, 28.1, 27.0, 26.9, 24.8, 24.6, 22.5, 18.7, 13.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{43}O_2$ 363.3263; Found 363.3250. IR (KBr, cm^{-1}) 3004, 2926, 2855, 1734, 1457, 1376, 1244, 1178, 1161, 1058, 1010, 917, 727.

Cyclohex-2-en-1-yl 6-oxoheptanoate (7w): Colorless oil (212.8 mg, 95%). Column chromatography eluent, petroleum ether/EtOAc 8:2.  ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99-5.89 (m, 1H), 5.71-5.64 (m, 1H), 5.29-5.21 (m, 1H), 2.44 (t, J = 6.8 Hz, 2H), 2.30 (t, J = 7.0 Hz, 2H), 2.12 (s, 3H), 2.08-1.92 (m, 2H), 1.90-1.81 (m, 1H), 1.77-1.63 (m, 3H), 1.62-1.56 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 208.5, 173.0, 132.6, 125.6, 67.9, 43.2, 34.3, 29.8, 28.3, 24.8, 24.4, 23.1, 18.8. HRMS (APGC) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{20}O_3Na$ 247.1310; Found 247.1318. IR (KBr, cm^{-1}) 2940, 2867, 1719, 1420, 1364, 1248, 1178, 1058, 1010, 914, 729.

9-(Cyclohex-2-en-1-yloxy)-9-oxononanoic acid (7xa): Yellow oil (59.0 mg, 22%). Column chromatography eluent, petroleum ether/EtOAc 7:3.  ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (br s, 1H), 6.02-5.78 (m, 1H), 5.72-5.50 (m, 1H), 5.27-5.10 (m, 1H), 2.27 (t, J = 7.5 Hz, 2H), 2.22 (t, J = 7.5 Hz, 2H), 2.08-1.97 (m, 1H), 1.96-1.86 (m, 1H), 1.84-1.75 (m, 1H), 1.72-1.60 (m, 2H), 1.59-1.47 (m, 5H), 1.31-1.19 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 179.6, 173.5, 132.5, 125.6, 67.8, 34.5, 33.9, 28.8, 28.2, 24.8, 24.8, 24.5, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{24}O_4Na$ 291.1572; Found 291.1573. IR (KBr, cm^{-1}) 2935, 2860, 1731, 1710, 1417, 1247, 1179, 1096, 1058, 1010, 914, 729.

Di(cyclohex-2-en-1-yl) nonanedioate (7xb): Colorless oil (149.8 mg, 43%). Column chromatography eluent, petroleum ether/EtOAc 8:2.  ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94-5.86 (m, 2H), 5.69-5.59 (m, 2H), 5.25-5.16 (m, 2H), 2.24 (t, J = 7.0 Hz, 4H), 2.08-1.89 (m, 4H), 1.86-1.76 (m, 2H), 1.74-1.63 (m, 4H), 1.61-1.52 (m, 6H), 1.30-1.23 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.3, 132.4, 125.7, 67.7, 51.3, 34.5, 33.9, 28.8, 28.8, 28.2, 24.8, 24.7, 24.7, 18.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{32}O_4Na$ 371.2198; Found 371.2208. IR (KBr, cm^{-1}) 3033, 2935, 2862, 1731, 1455, 1437, 1372, 1247, 1177, 1162, 1096, 1058, 1010, 916, 729.

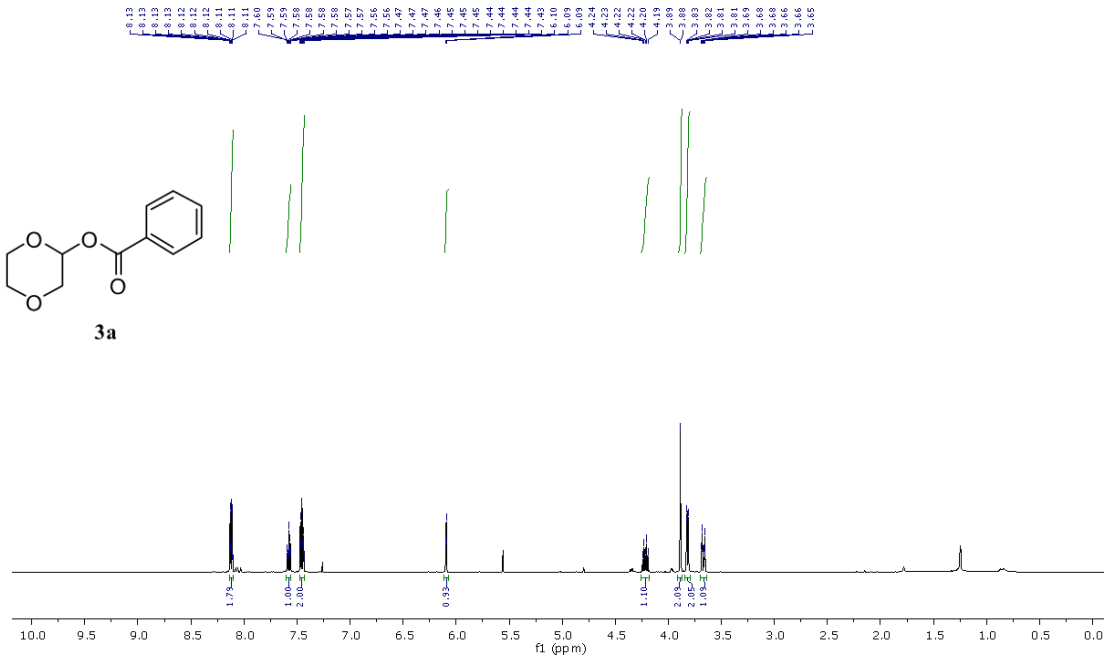


Figure S12. ^{1}H Spectrum of **3a** in $CDCl_3$ (400 MHz)

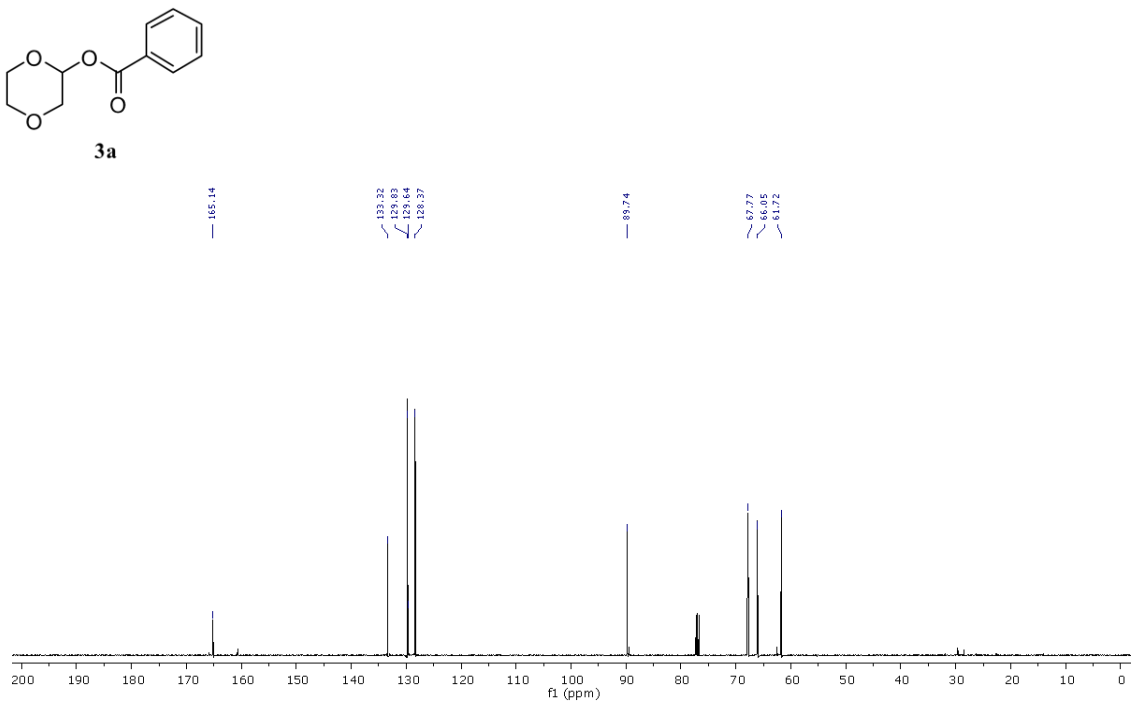


Figure S13. ^{13}C Spectrum of **3a** in $CDCl_3$ (100 MHz)

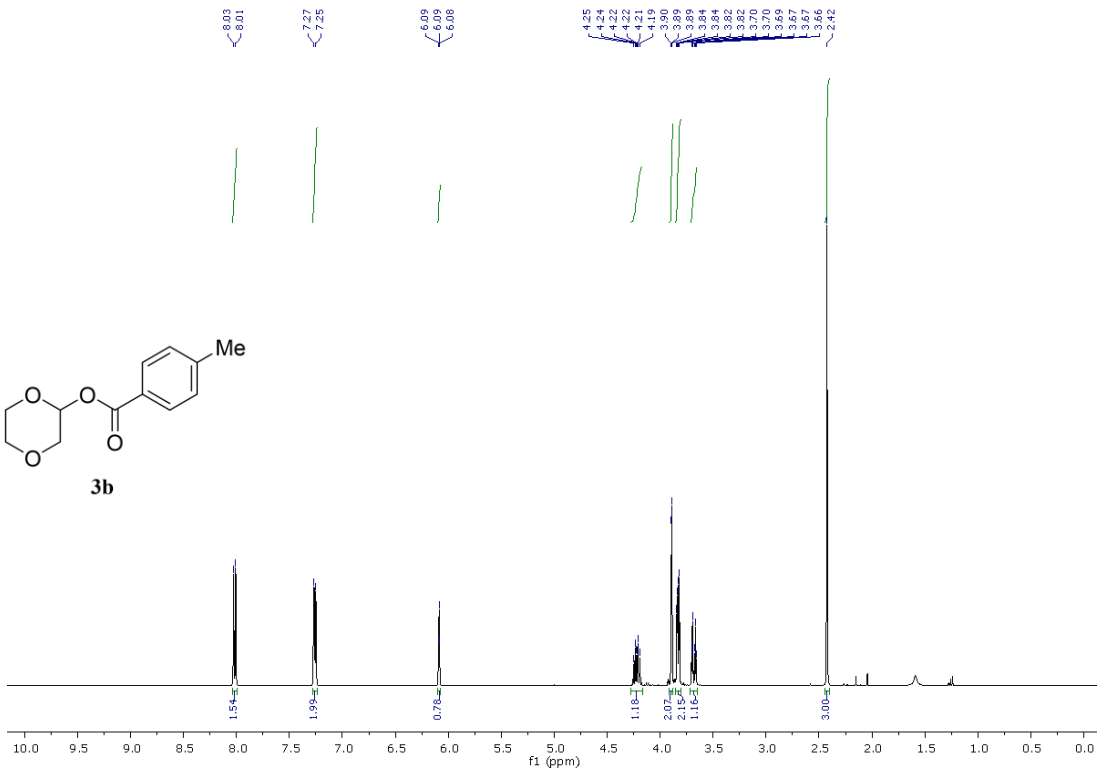


Figure S14. ^{1}H Spectrum of **3b** in $CDCl_3$ (400 MHz)

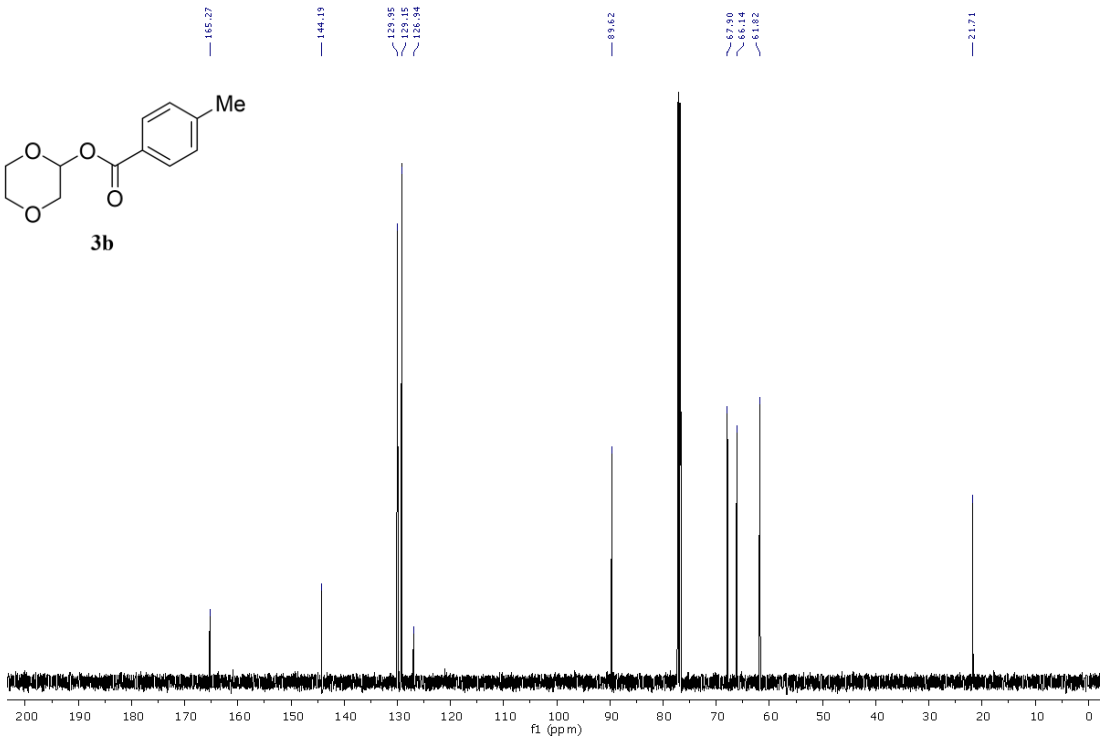


Figure S15. ^{13}C Spectrum of **3b** in $CDCl_3$ (100 MHz)

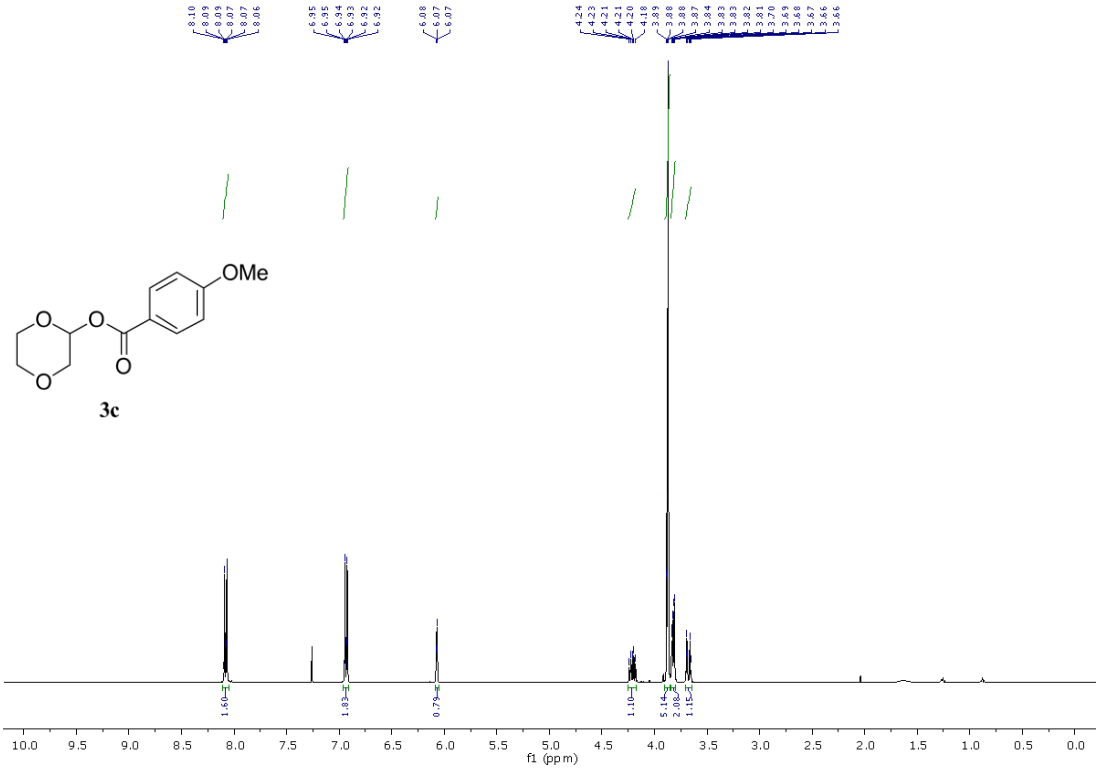


Figure S16. ^{1}H Spectrum of **3c** in $CDCl_3$ (400 MHz)

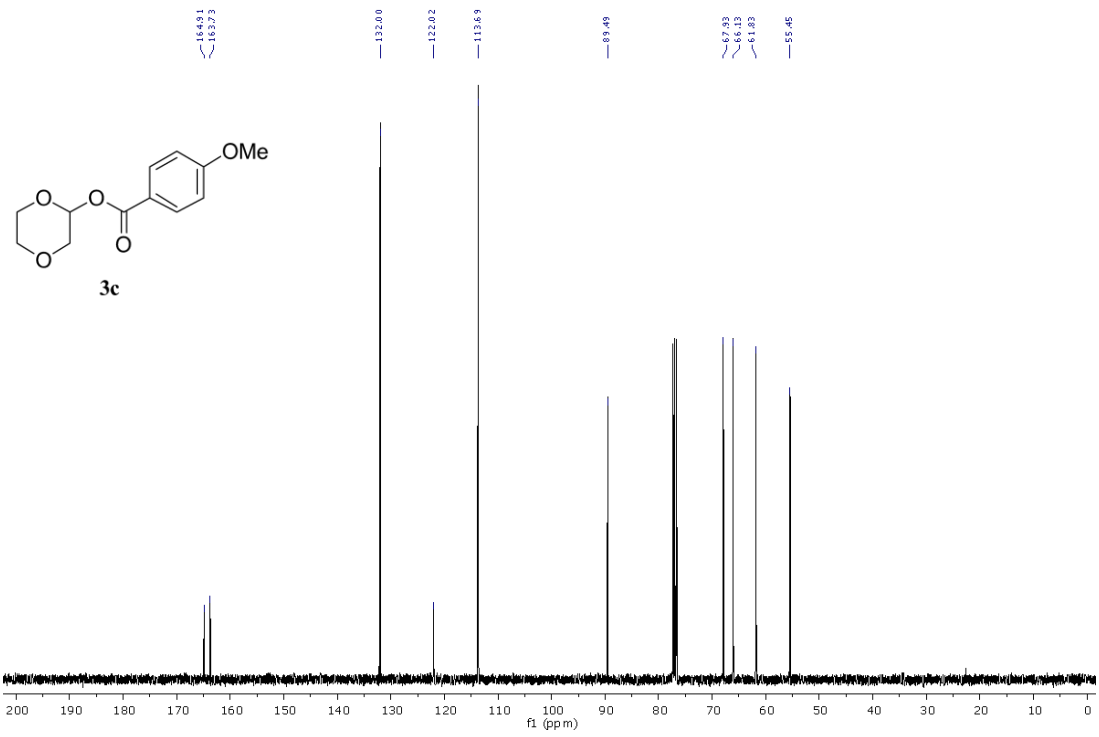


Figure S17. ^{13}C Spectrum of **3c** in $CDCl_3$ (100 MHz)

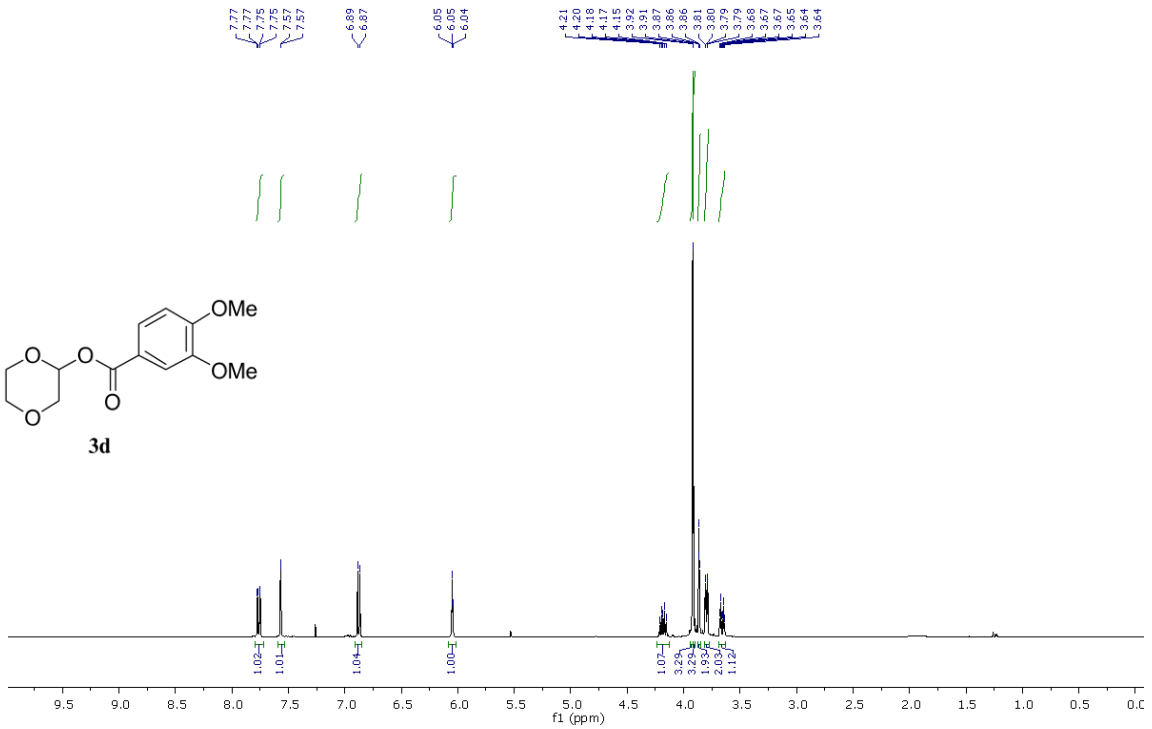


Figure S18. ^{1}H Spectrum of **3d** in $CDCl_3$ (400 MHz)

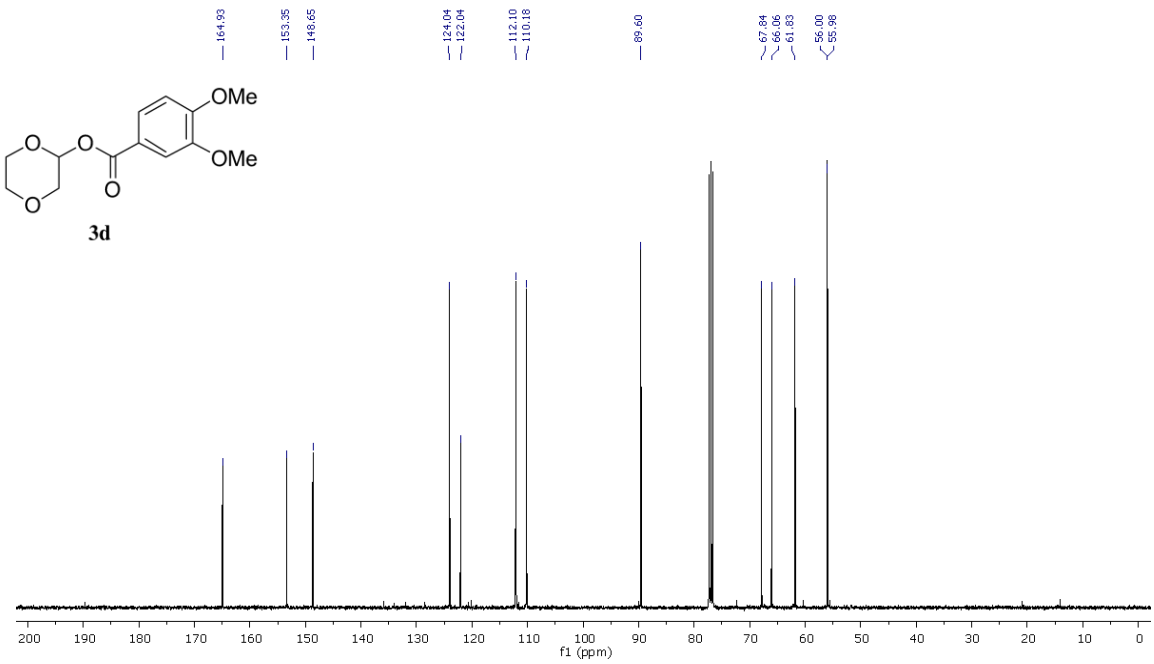


Figure S19. ^{13}C Spectrum of **3d** in $CDCl_3$ (100 MHz)

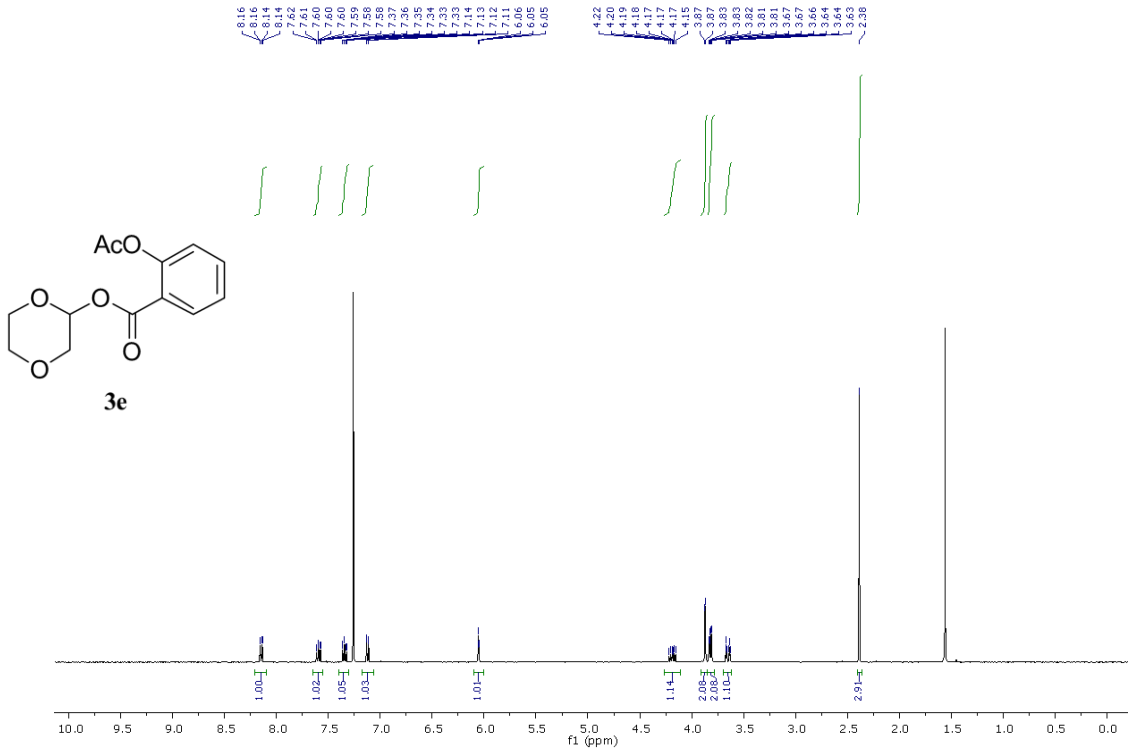


Figure S20. ^{1}H Spectrum of **3e** in $CDCl_3$ (400 MHz)

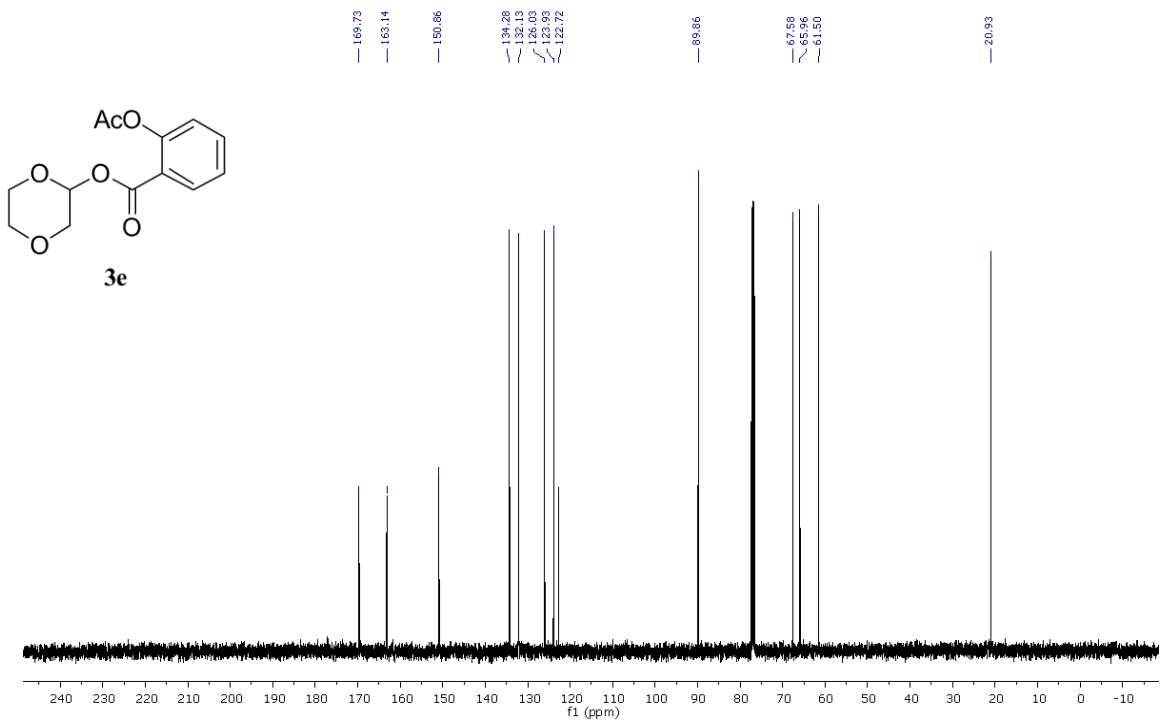


Figure S21. ^{13}C Spectrum of **3e** in $CDCl_3$ (100 MHz)

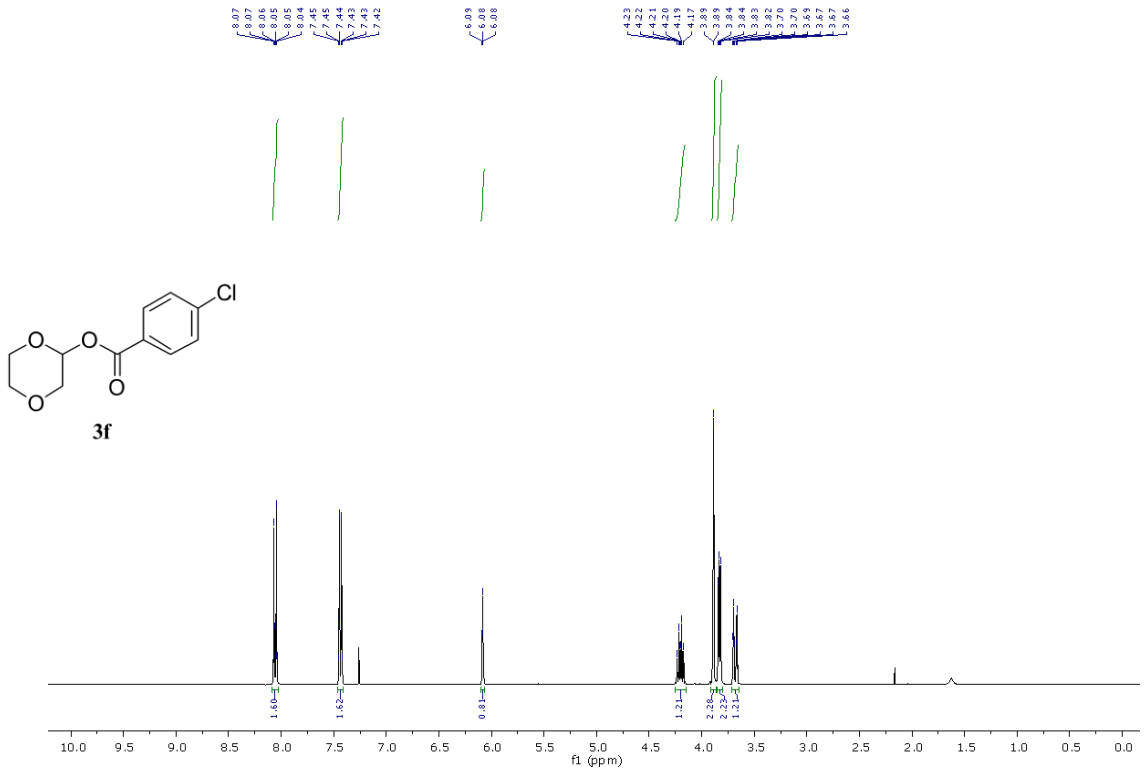


Figure S22. ^{1}H Spectrum of **3f** in $CDCl_3$ (400 MHz)

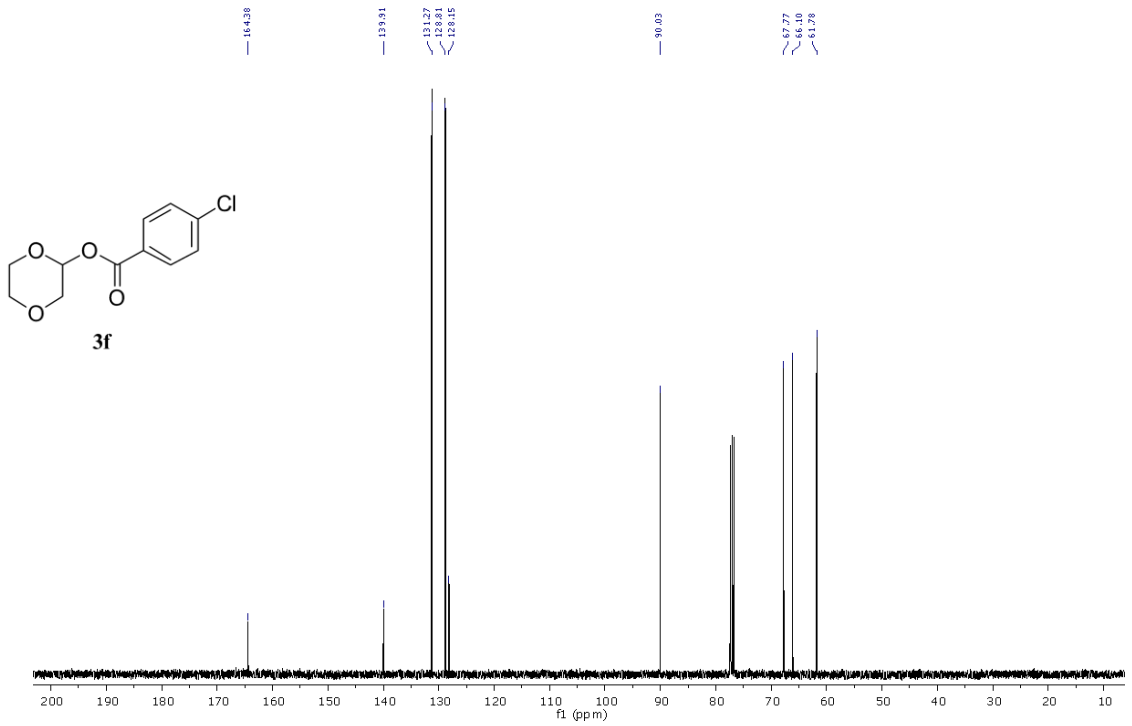


Figure S23. ^{13}C Spectrum of **3f** in $CDCl_3$ (100 MHz)

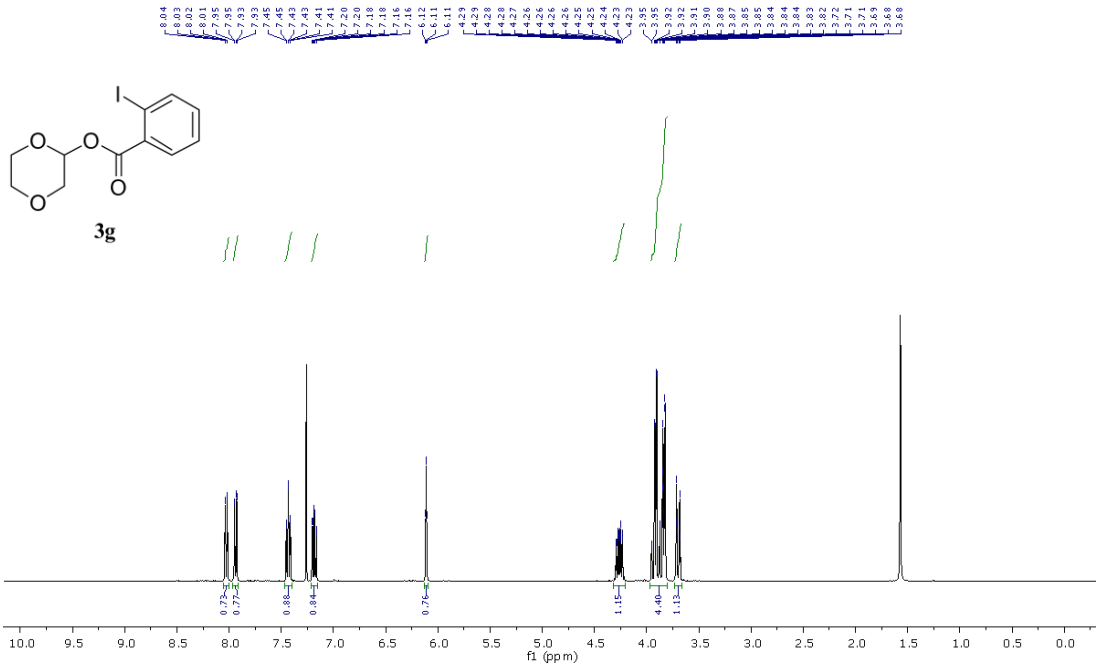


Figure S24. ^{1}H Spectrum of **3g** in $CDCl_3$ (400 MHz)

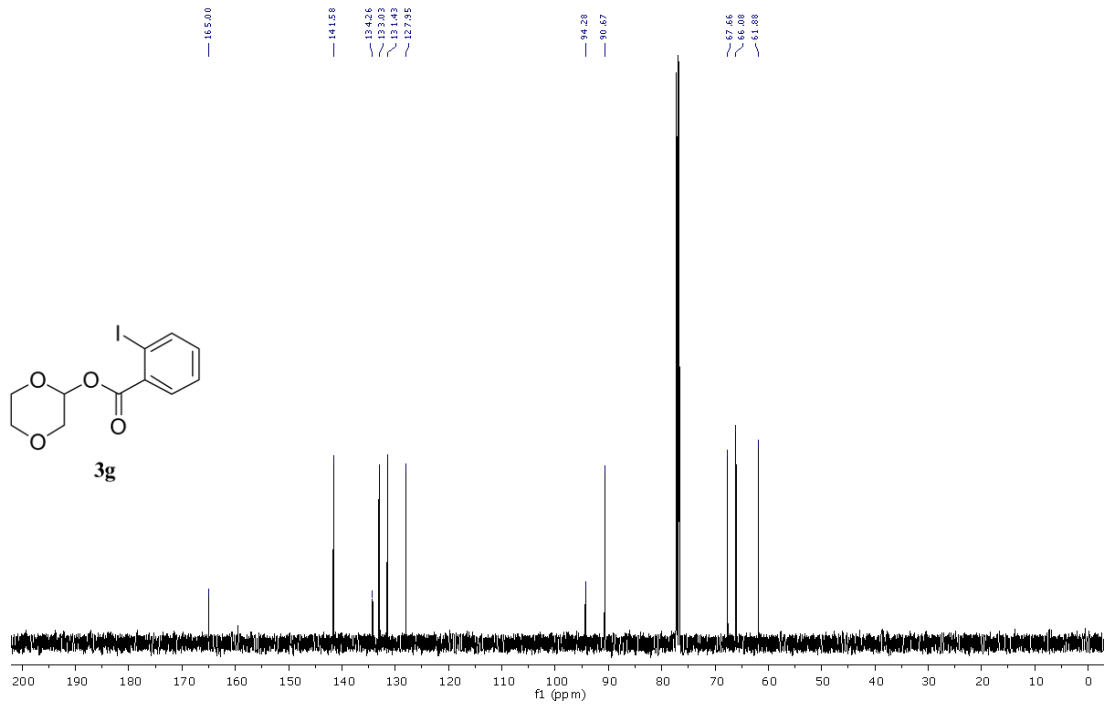


Figure S25. ^{13}C Spectrum of **3g** in $CDCl_3$ (100 MHz)

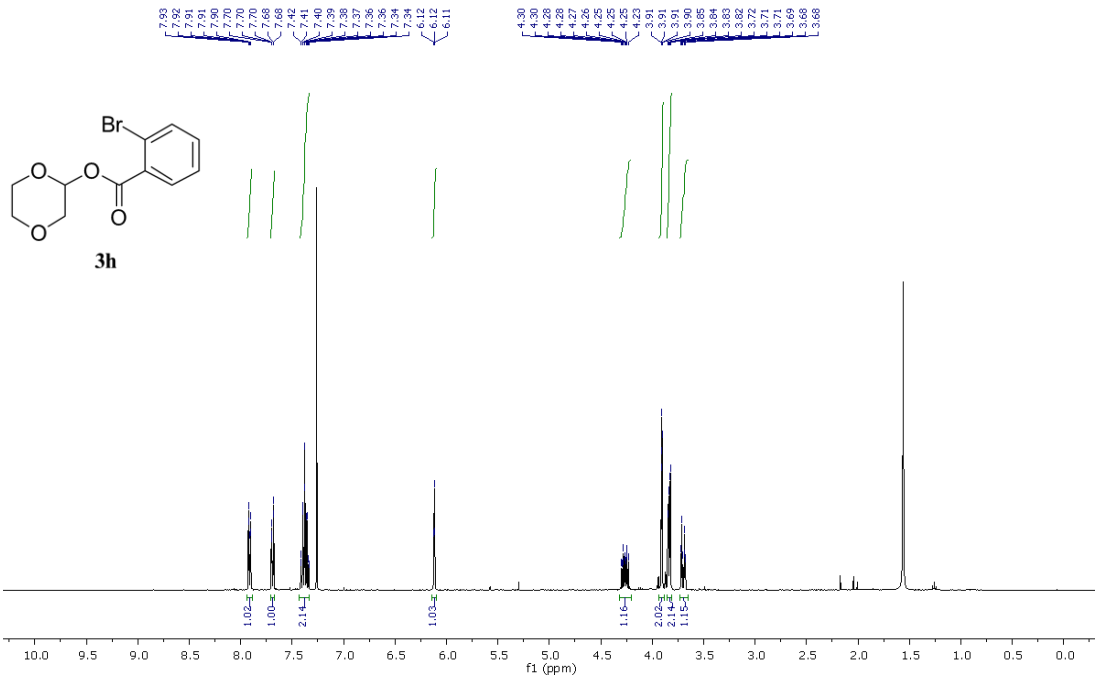


Figure S26. ^{1}H Spectrum of **3h** in $CDCl_3$ (400 MHz)

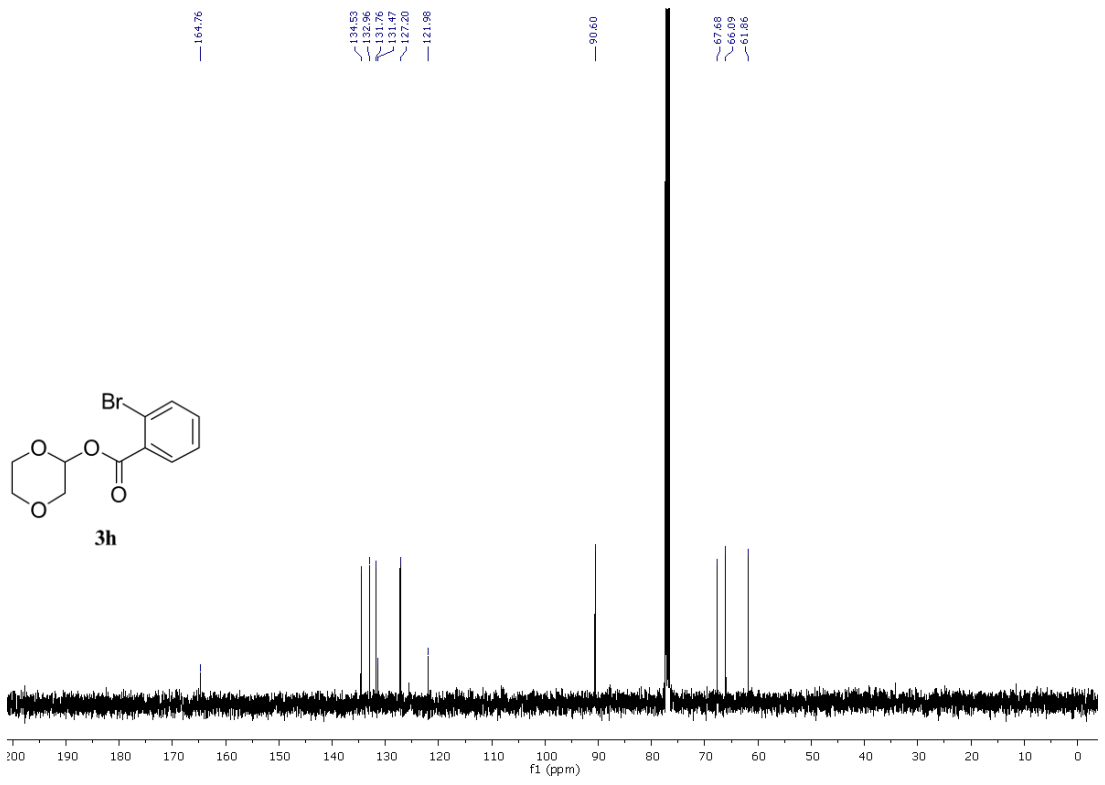


Figure S27. ^{13}C Spectrum of **3h** in $CDCl_3$ (100 MHz)

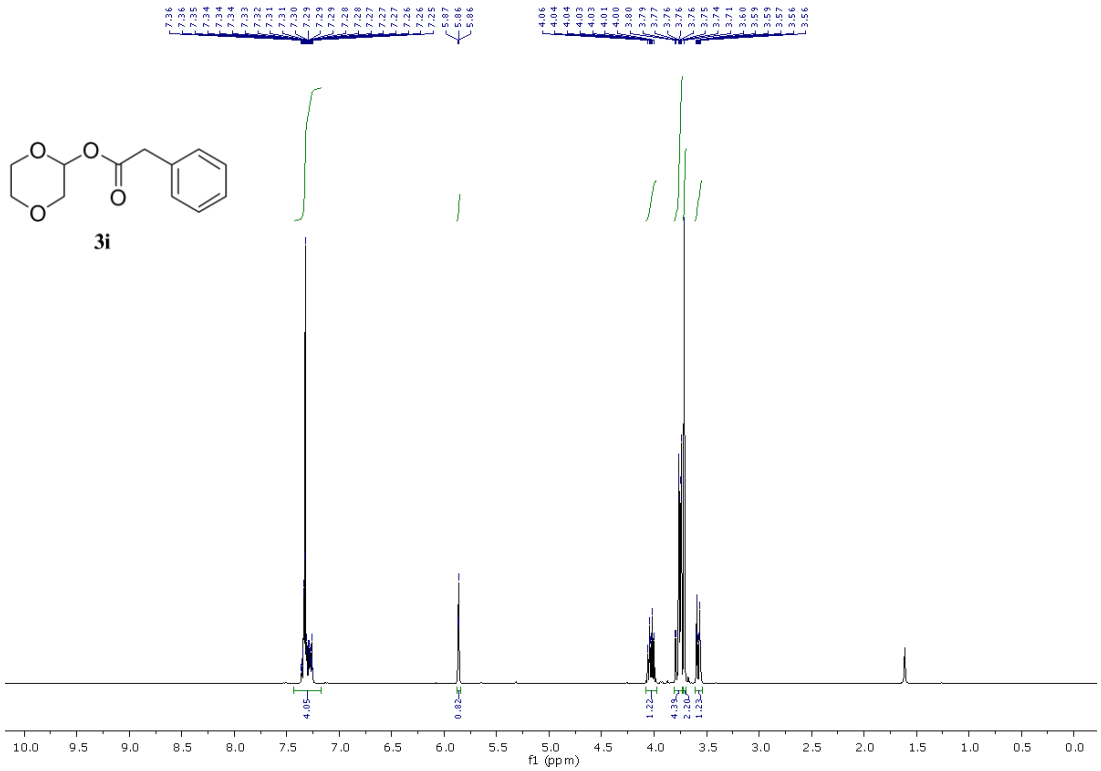


Figure S28. ^{1}H Spectrum of **3i** in $CDCl_3$ (400 MHz)

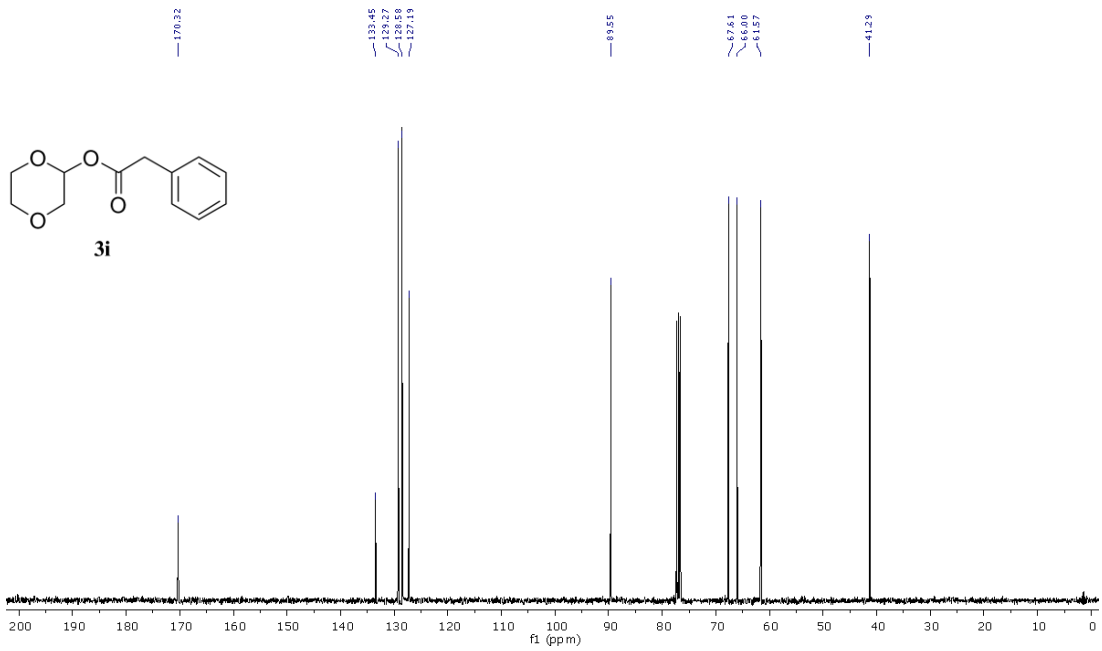


Figure S29. ^{13}C Spectrum of **3i** in $CDCl_3$ (100 MHz)

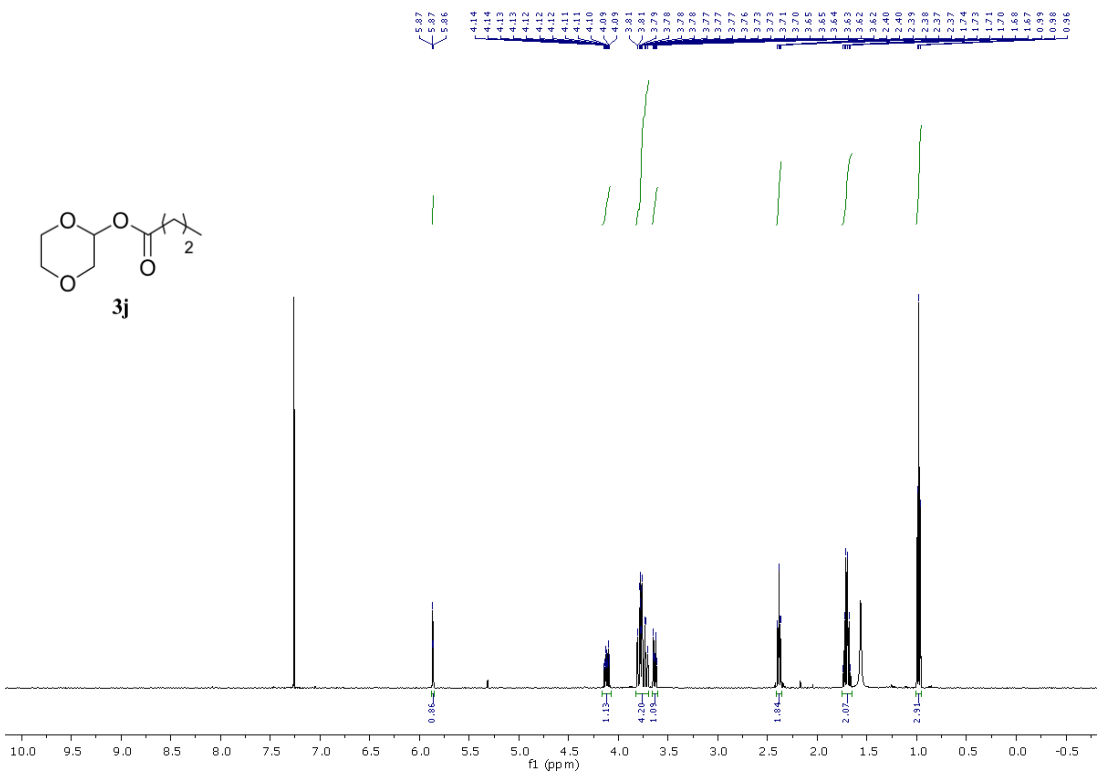


Figure S30. ^{1}H Spectrum of **3j** in $CDCl_3$ (400 MHz)

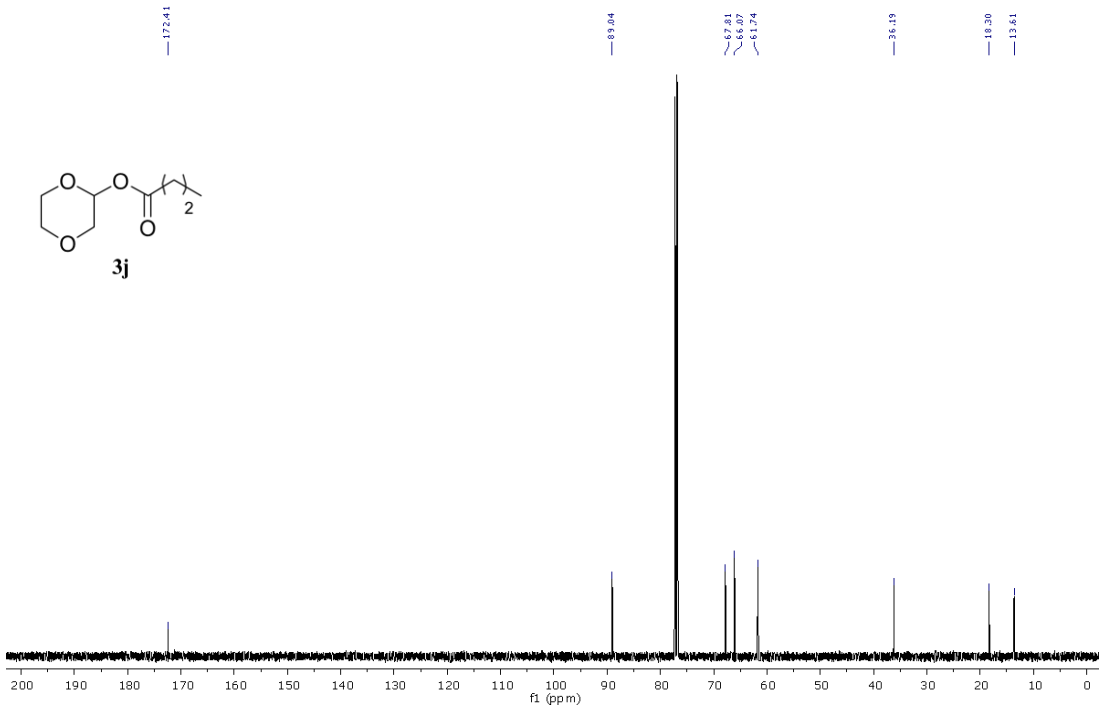


Figure S31. ^{13}C Spectrum of **3j** in $CDCl_3$ (100 MHz)

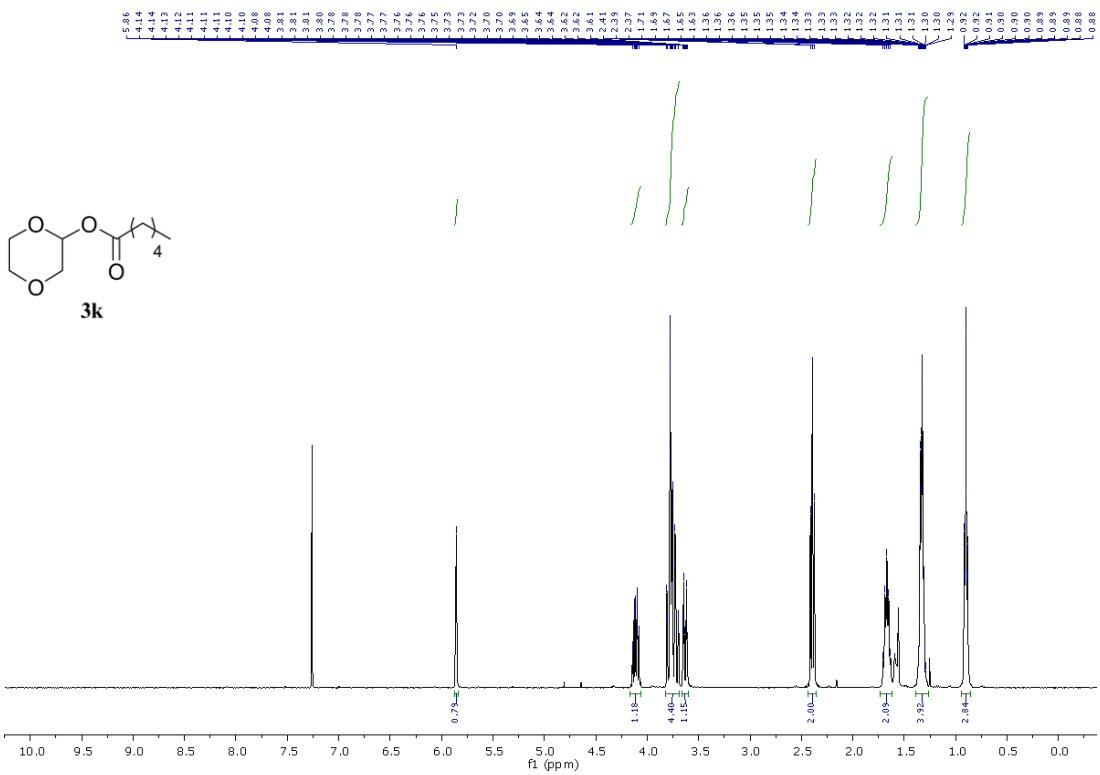


Figure S32. ^{1}H Spectrum of **3k** in $CDCl_3$ (400 MHz)

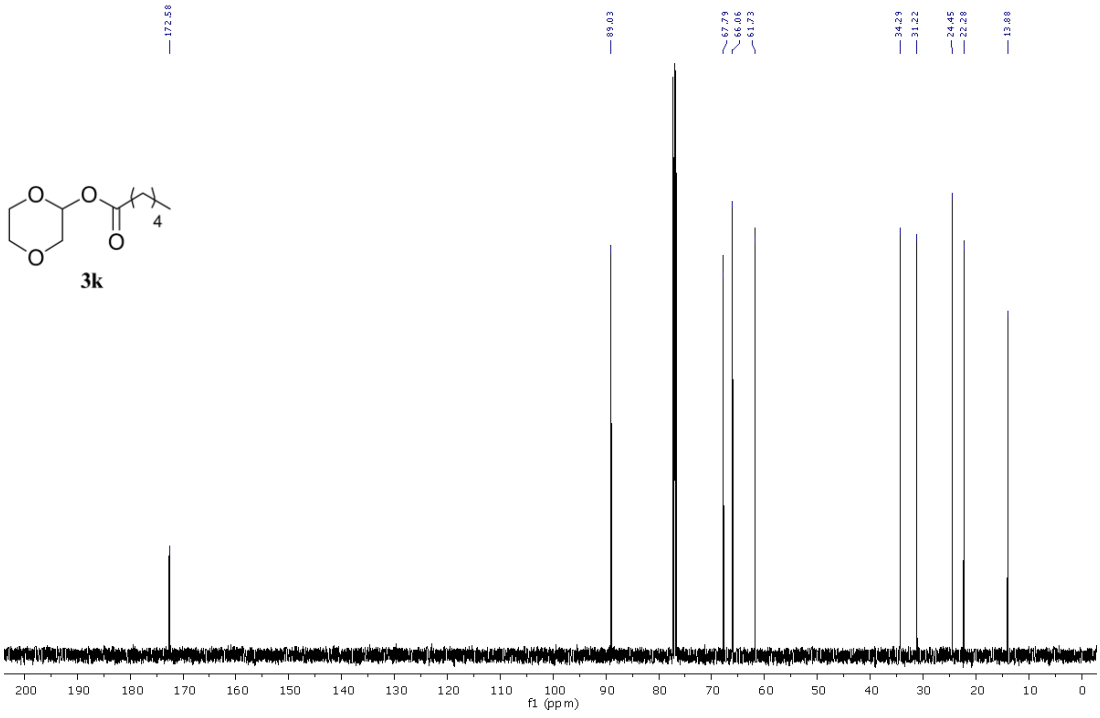


Figure S33. ^{13}C Spectrum of **3k** in $CDCl_3$ (100 MHz)

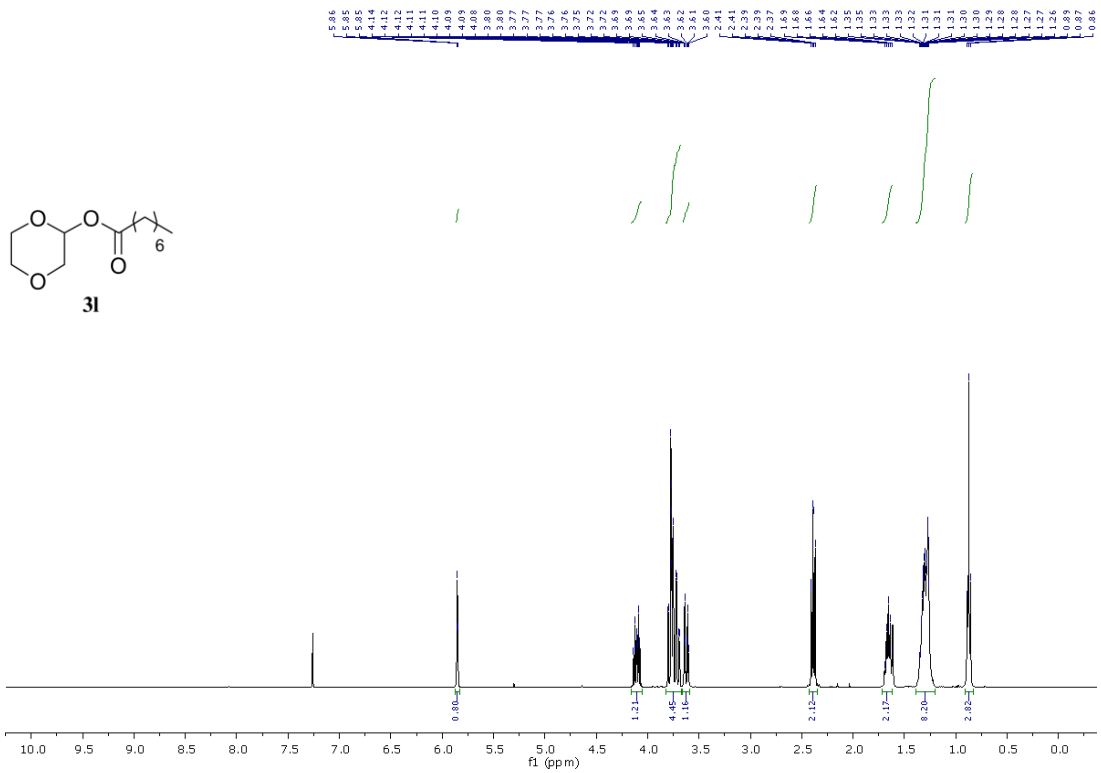


Figure S34. ^{1}H Spectrum of **3l** in $CDCl_3$ (400 MHz)

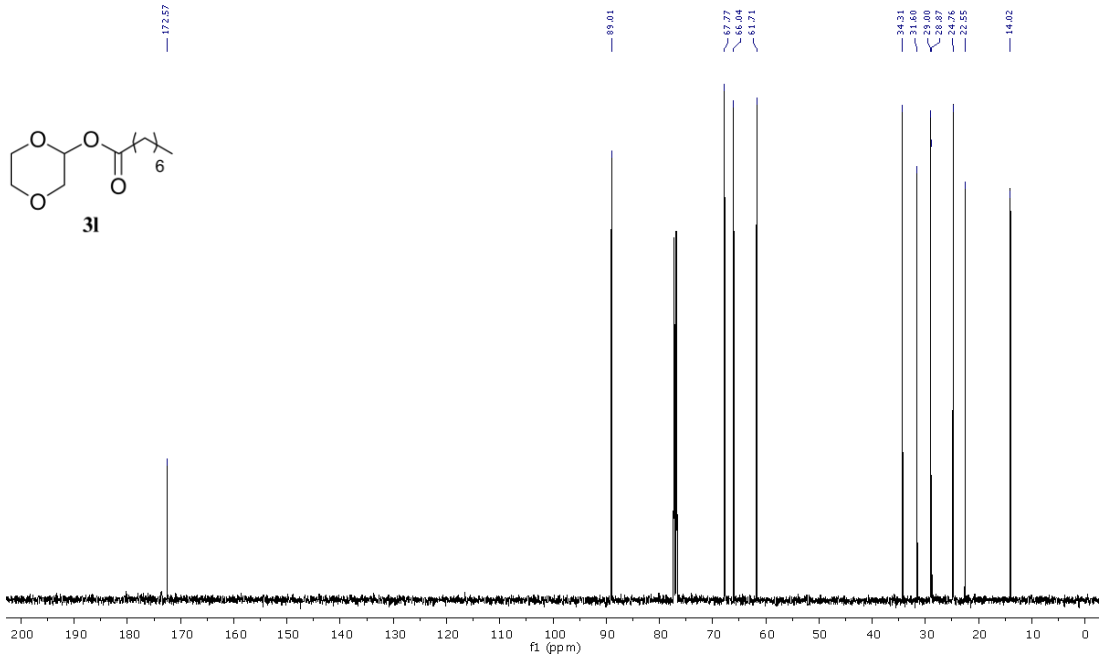


Figure S35. ^{13}C Spectrum of k**3l** in $CDCl_3$ (100 MHz)

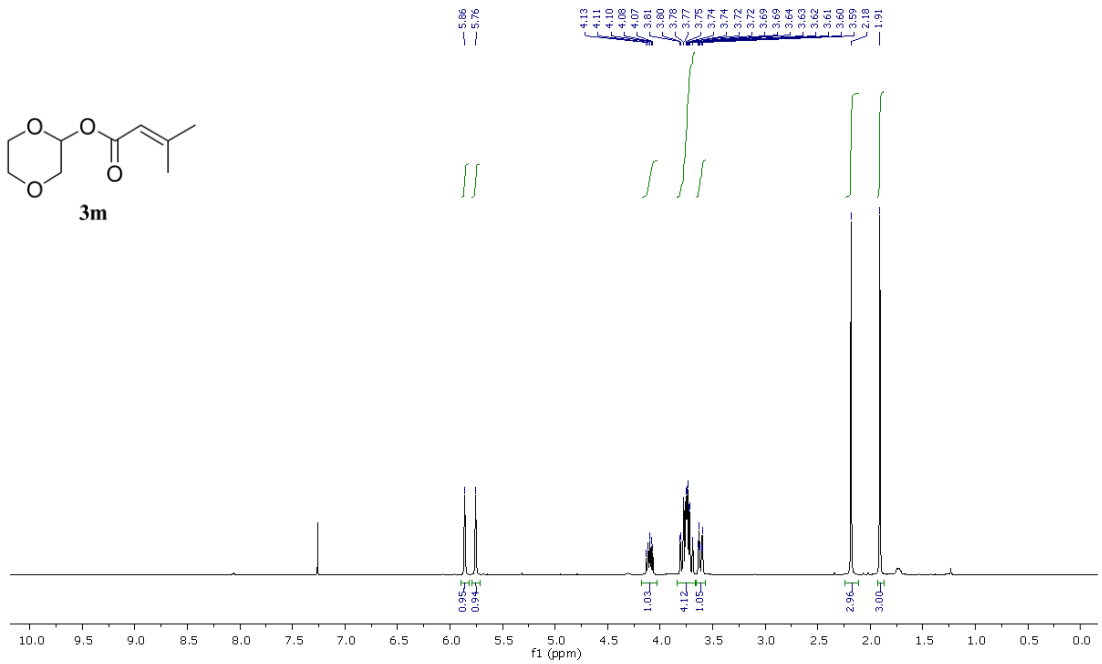


Figure S36. ^{1}H Spectrum of **3m** in $CDCl_3$ (400 MHz)

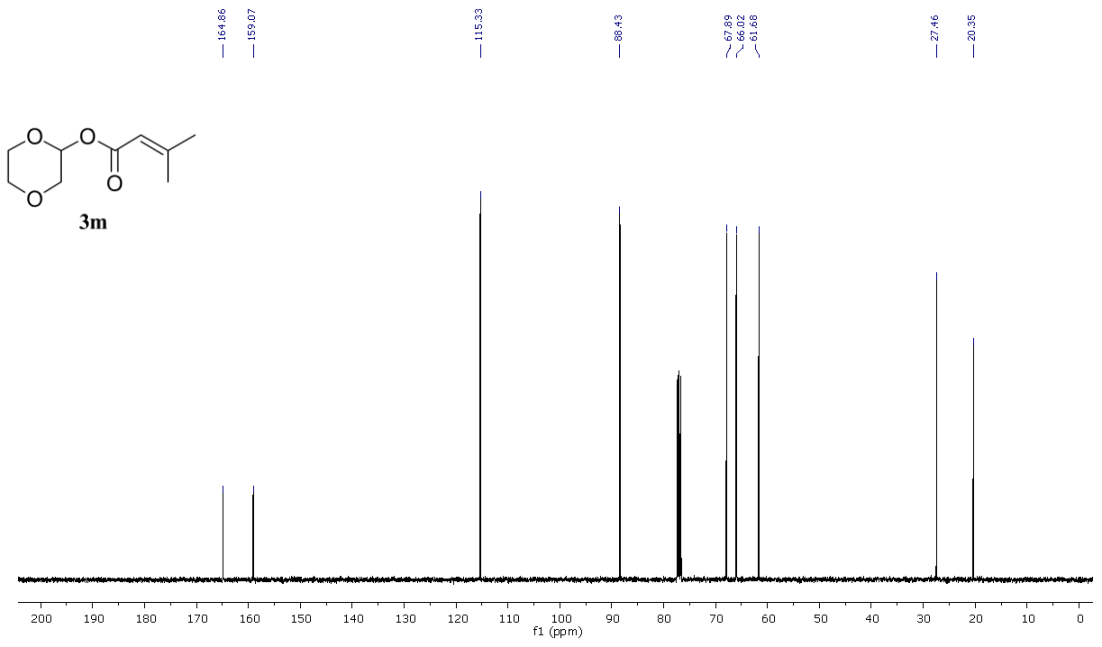


Figure S37. ^{13}C Spectrum of **3m** in $CDCl_3$ (100 MHz)

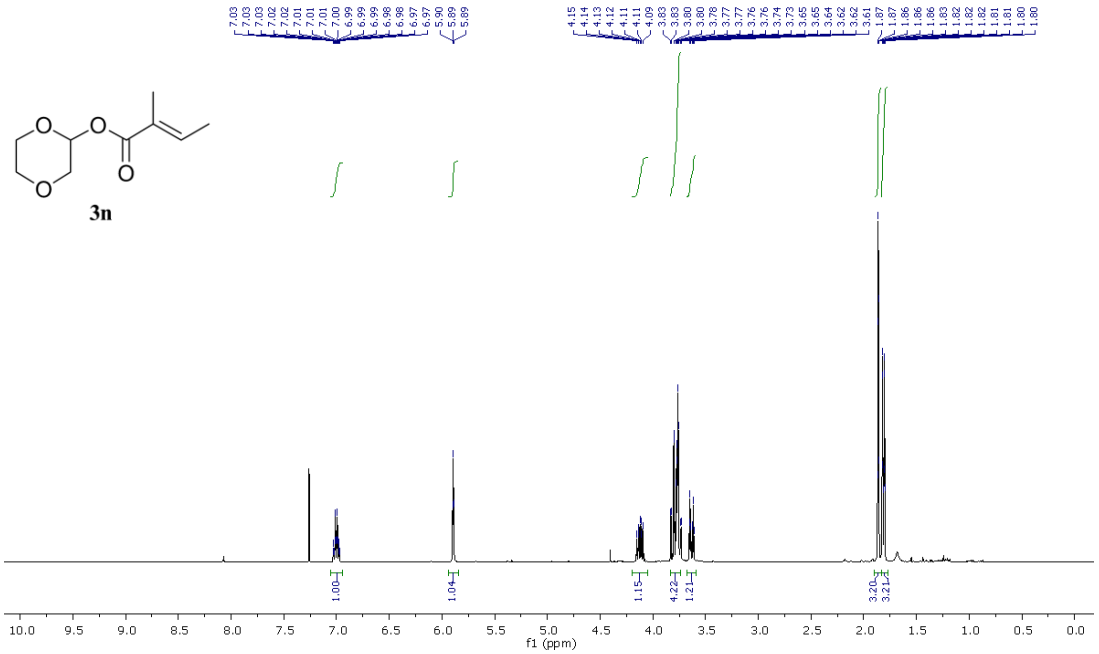


Figure S38. ^{1}H Spectrum of **3n** in $CDCl_3$ (400 MHz)

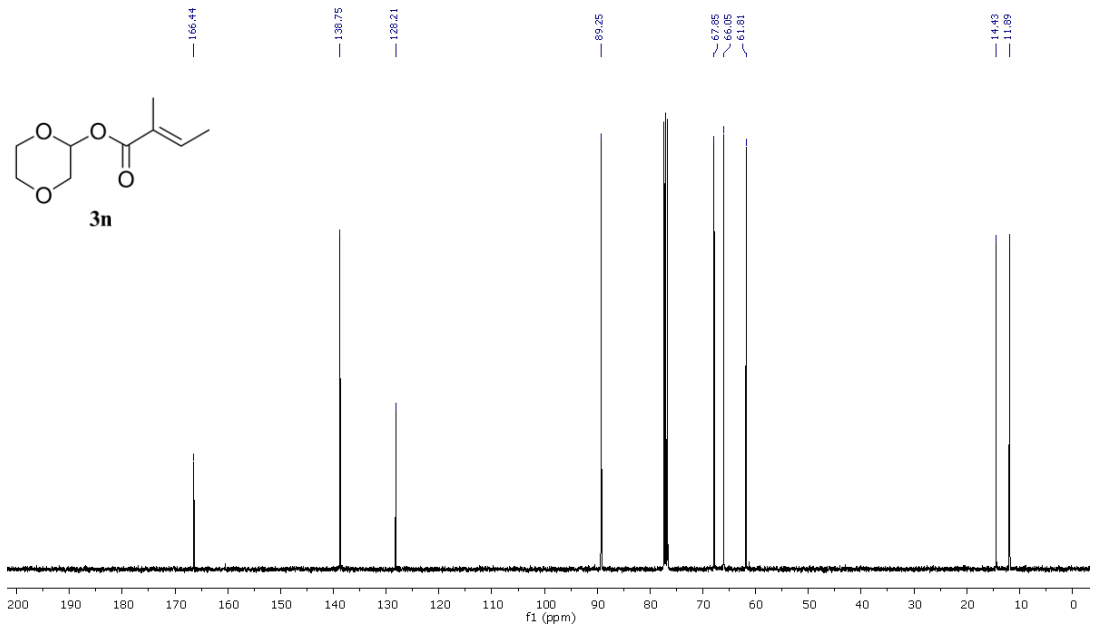


Figure S39. ^{13}C Spectrum of **3n** in $CDCl_3$ (100 MHz)

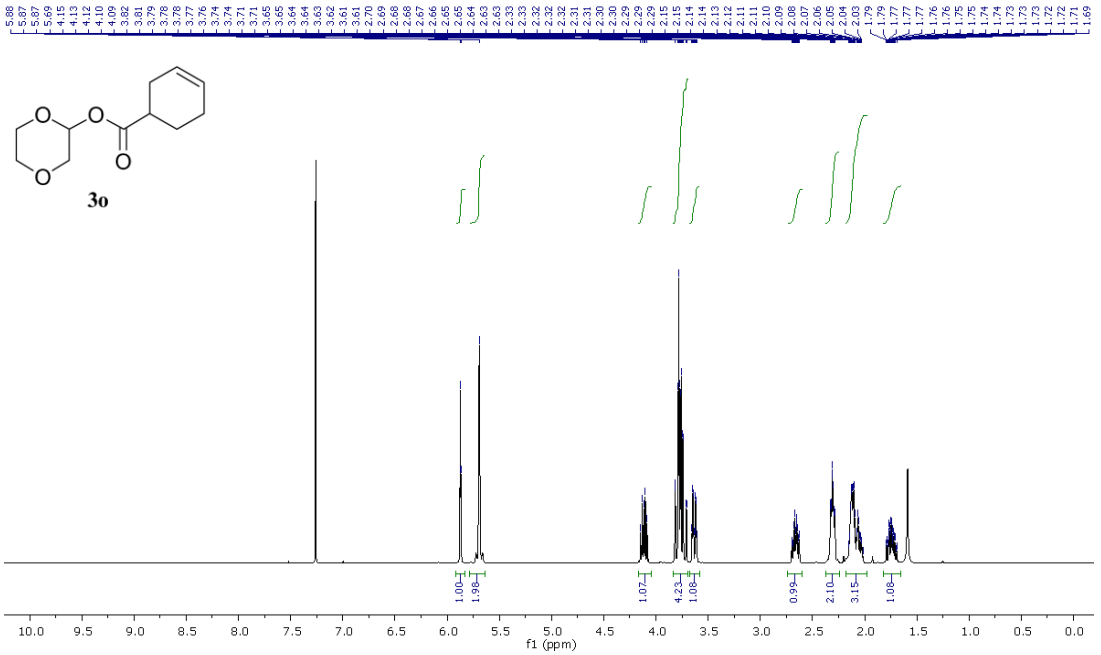


Figure S40. ^{1}H Spectrum of **3o** in $CDCl_3$ (400 MHz)

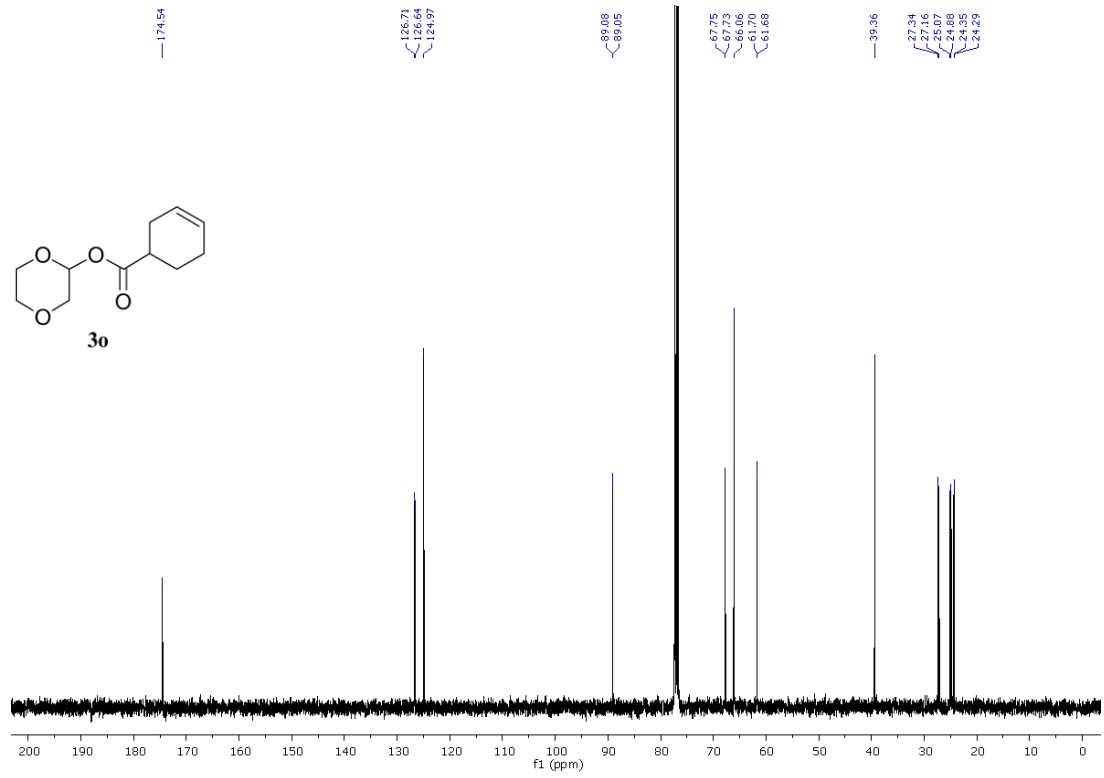


Figure S41. ^{13}C Spectrum of **3o** in $CDCl_3$ (100 MHz)

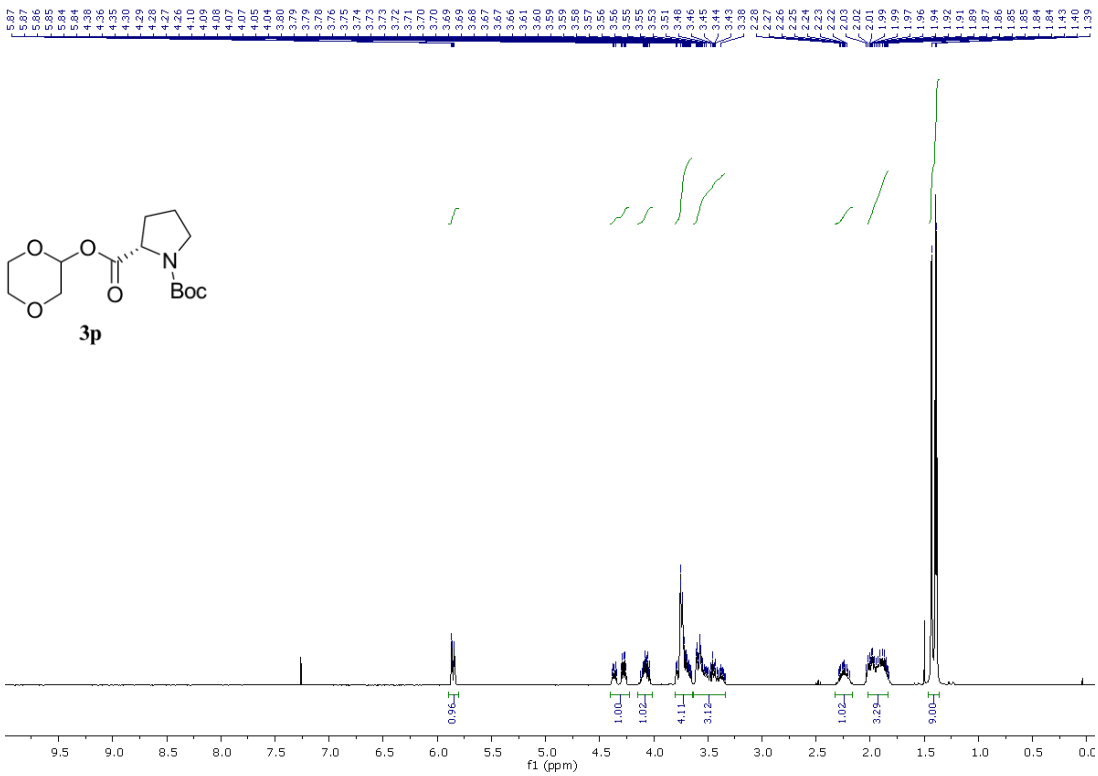


Figure S42. ^{1}H Spectrum of **3p** in $CDCl_3$ (500 MHz)

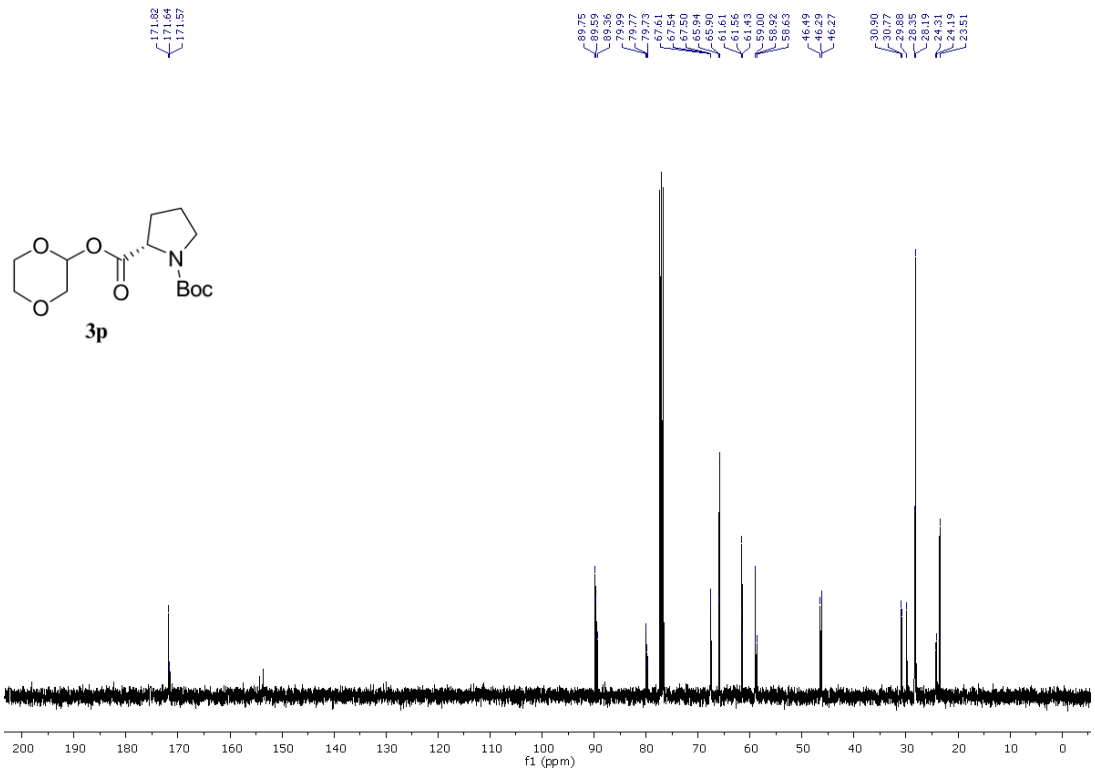


Figure S43. ^{13}C Spectrum of **3p** in $CDCl_3$ (125 MHz)

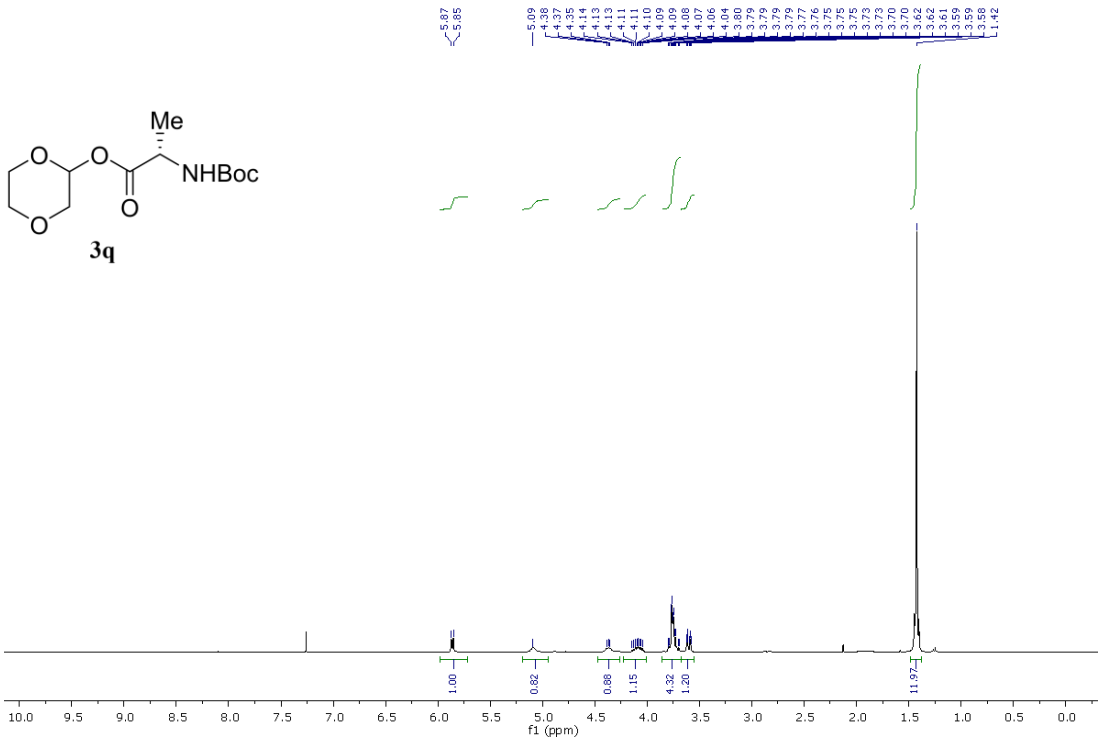


Figure S44. ^{1}H Spectrum of **3q** in $CDCl_3$ (400 MHz)

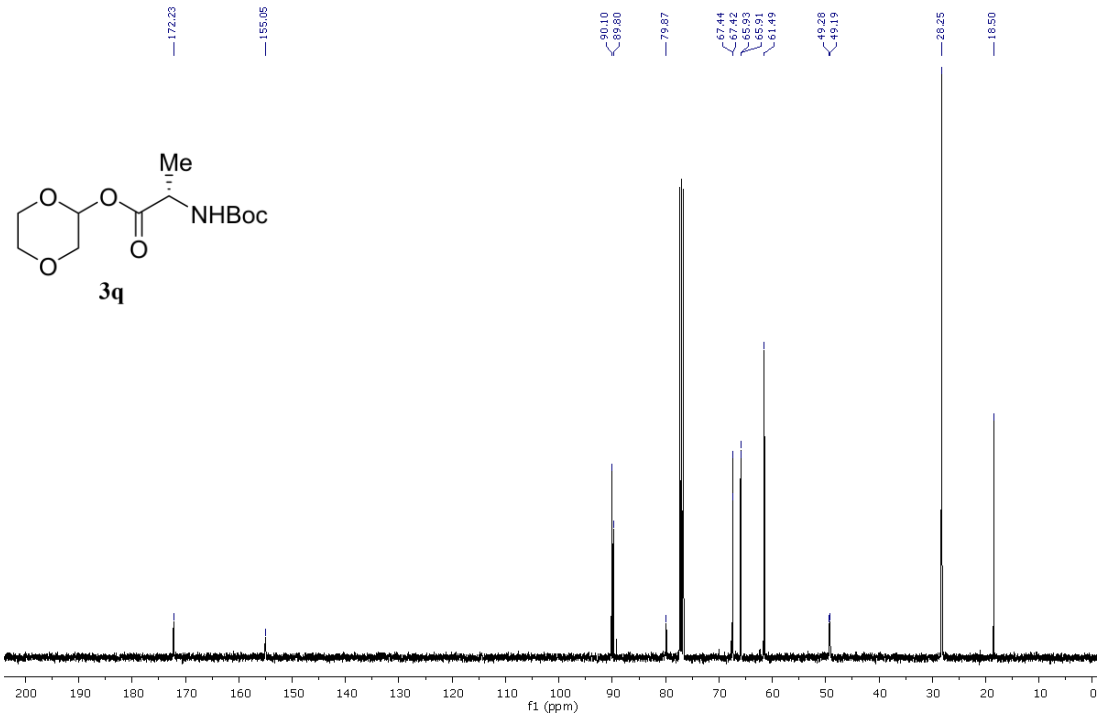


Figure S45. ^{13}C Spectrum of **3q** in $CDCl_3$ (100 MHz)

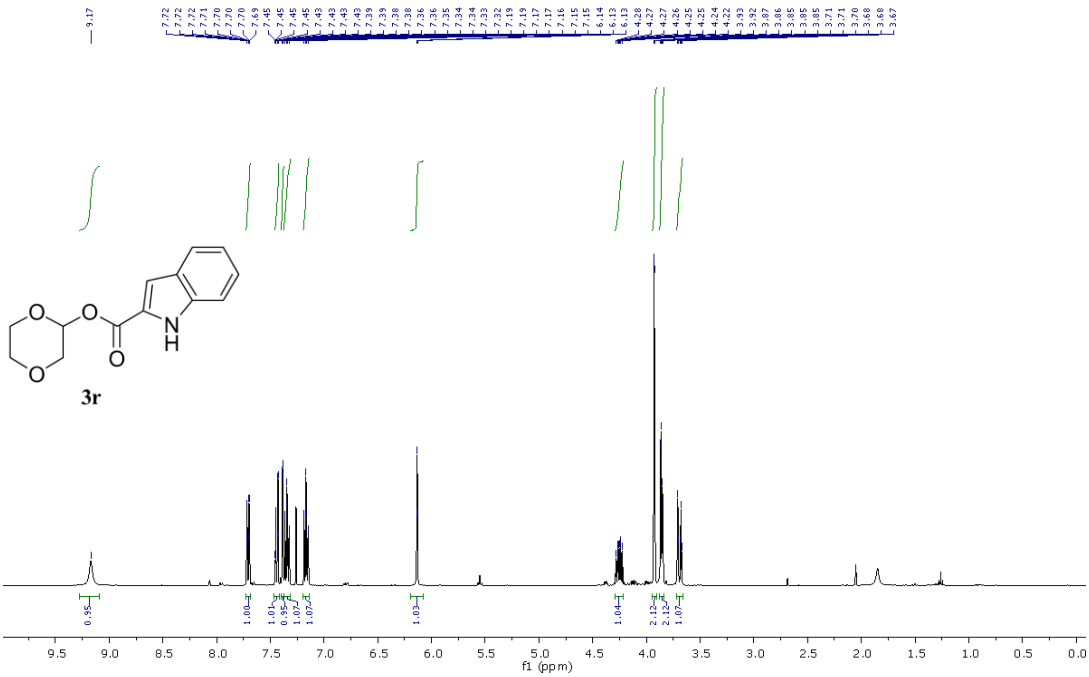


Figure S46. ^{1}H Spectrum of **3r** in $CDCl_3$ (400 MHz)

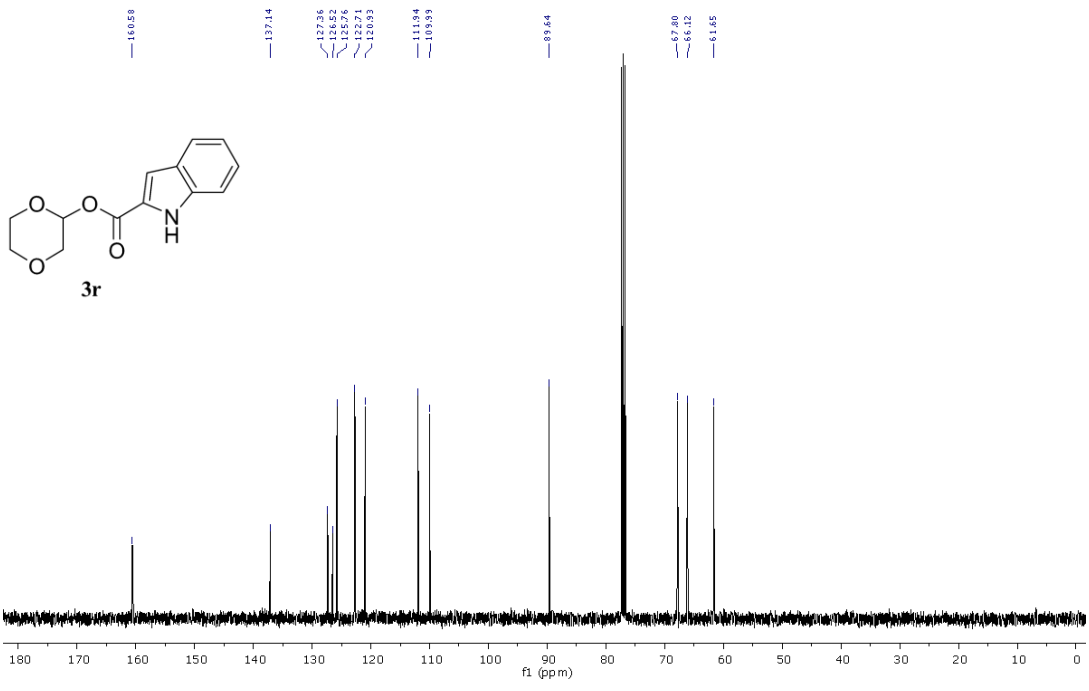


Figure S47. ^{13}C Spectrum of **3r** in $CDCl_3$ (100 MHz)

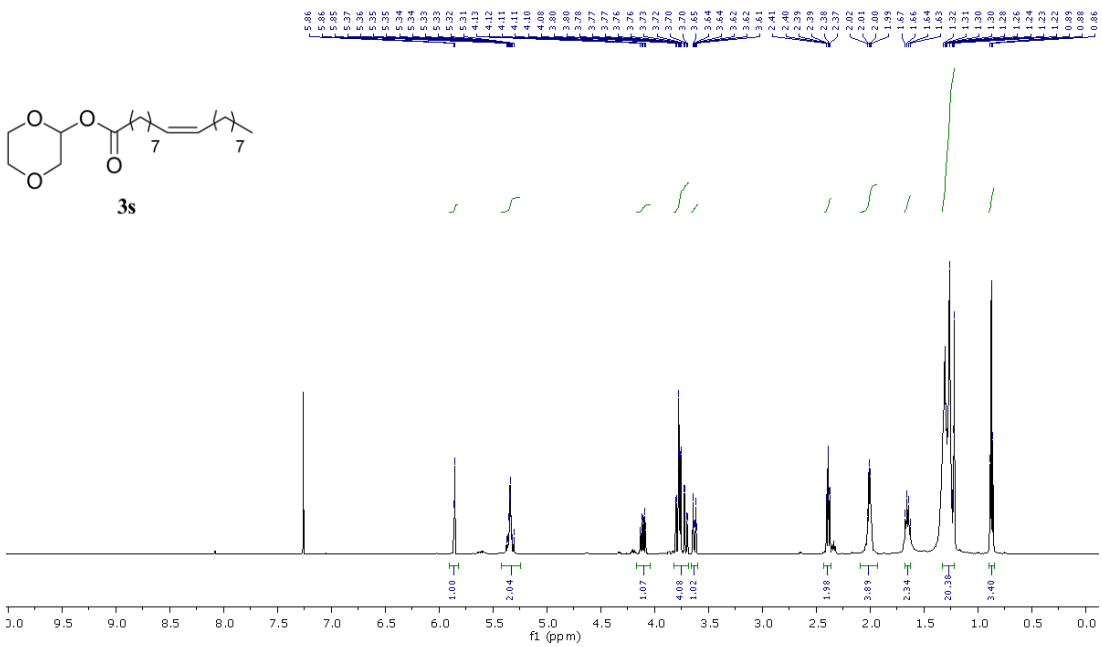


Figure S48. ^{1}H Spectrum of **3s** in $CDCl_3$ (500 MHz)

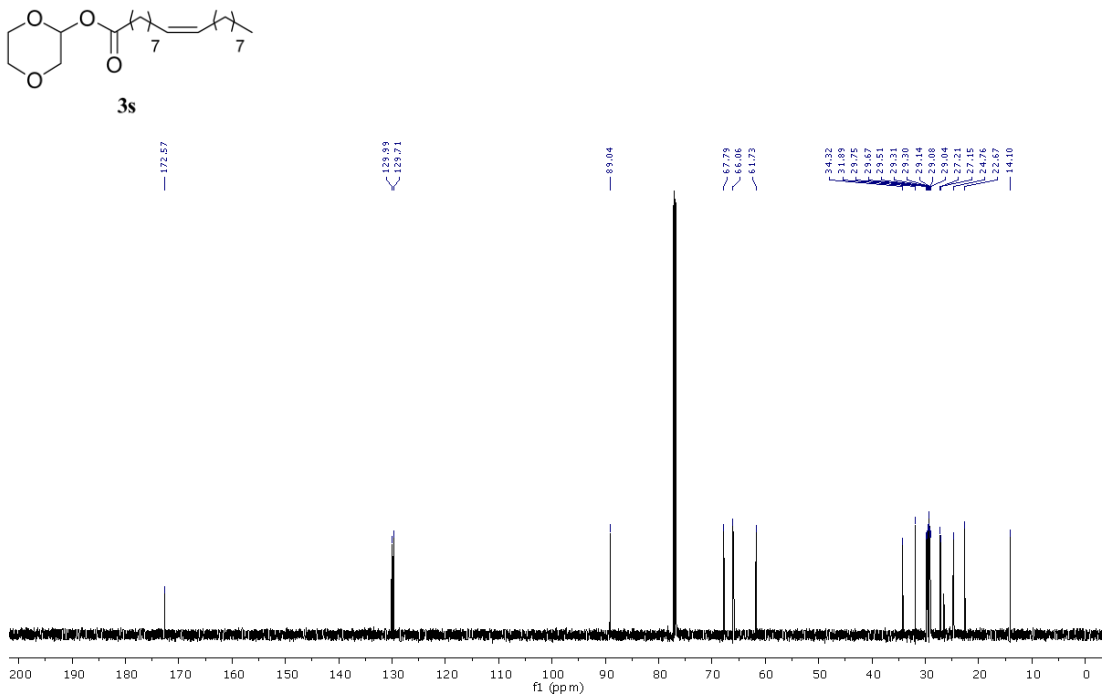


Figure S49. ^{13}C Spectrum of **3s** in $CDCl_3$ (125 MHz)

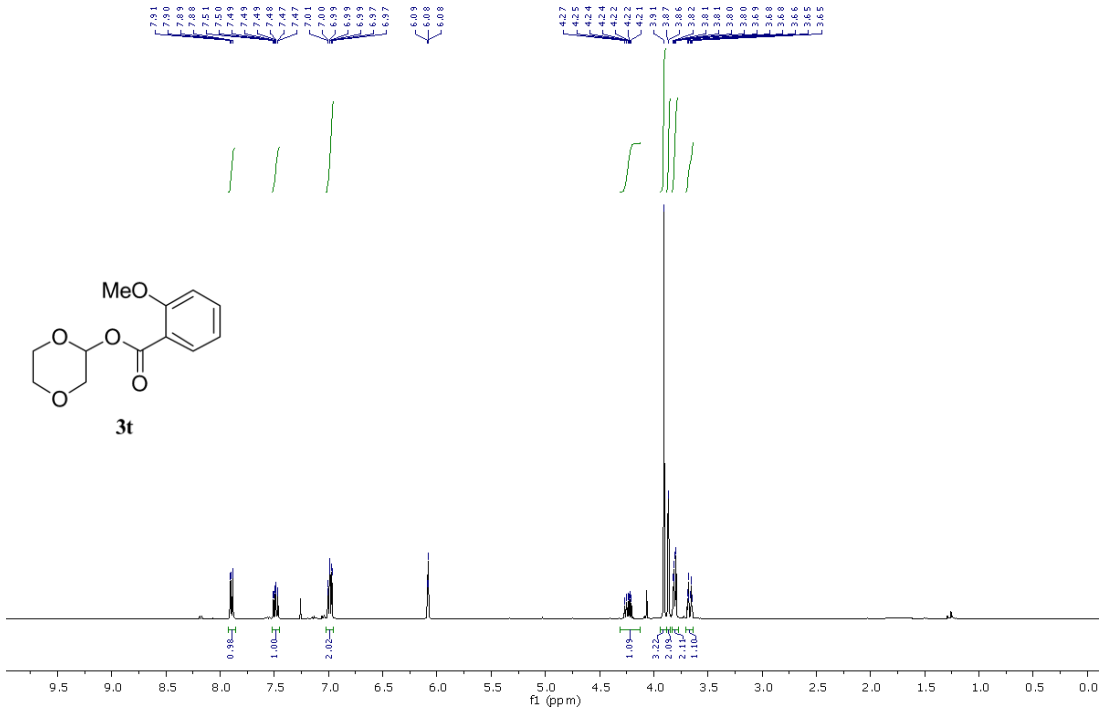


Figure S50. ^{1}H Spectrum of **3t** in $CDCl_3$ (400 MHz)

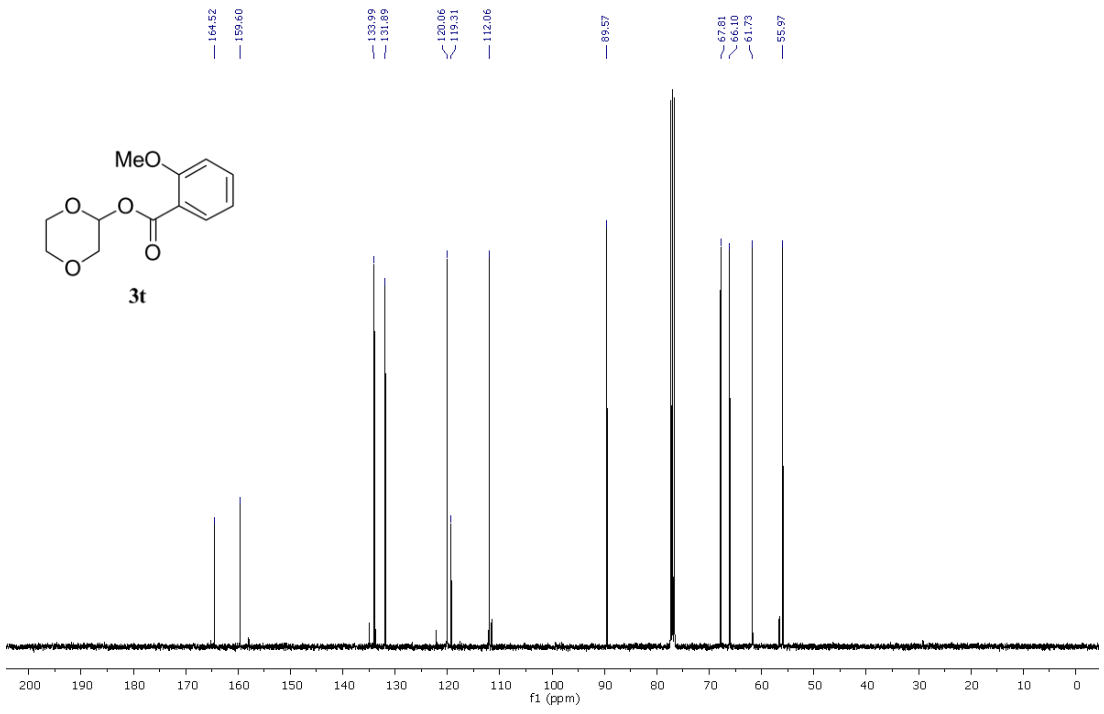


Figure S51. ^{13}C Spectrum of **3t** in $CDCl_3$ (100 MHz)

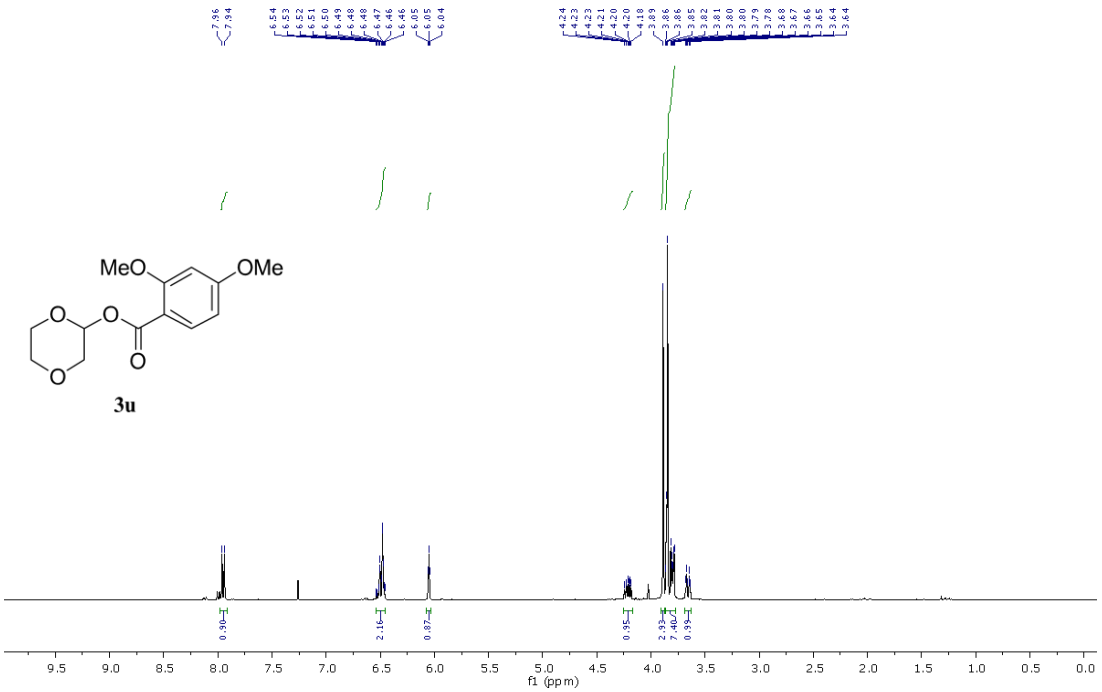


Figure S52. ^{1}H Spectrum of **3u** in $CDCl_3$ (500 MHz)

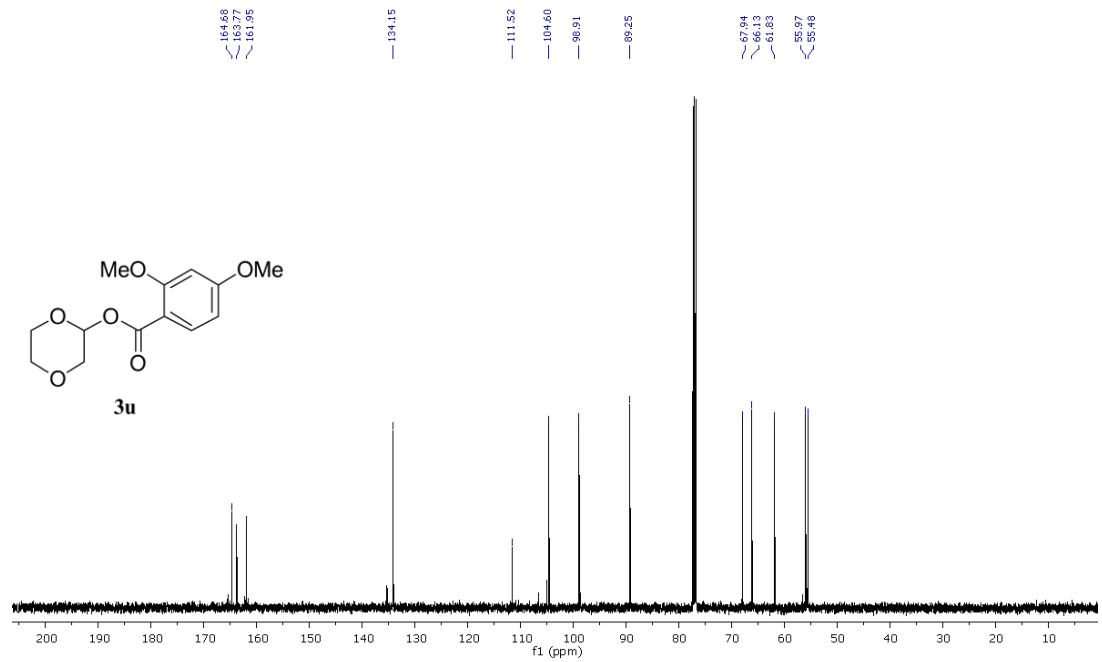


Figure S53. ^{13}C Spectrum of **3u** in $CDCl_3$ (125 MHz)

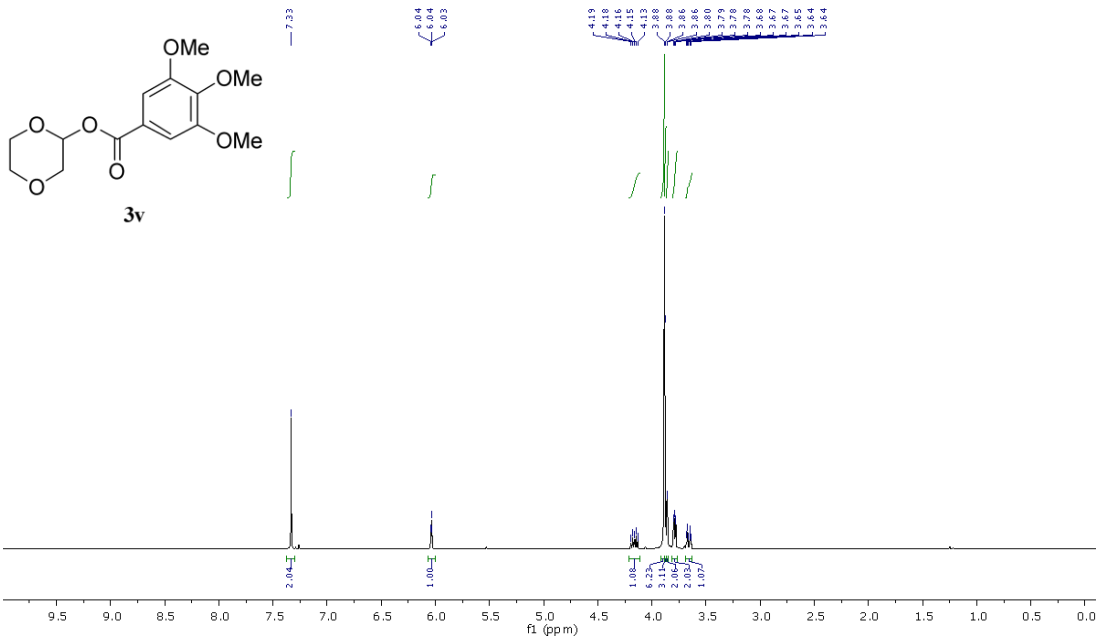


Figure S54. ^{1}H Spectrum of **3v** in $CDCl_3$ (400 MHz)

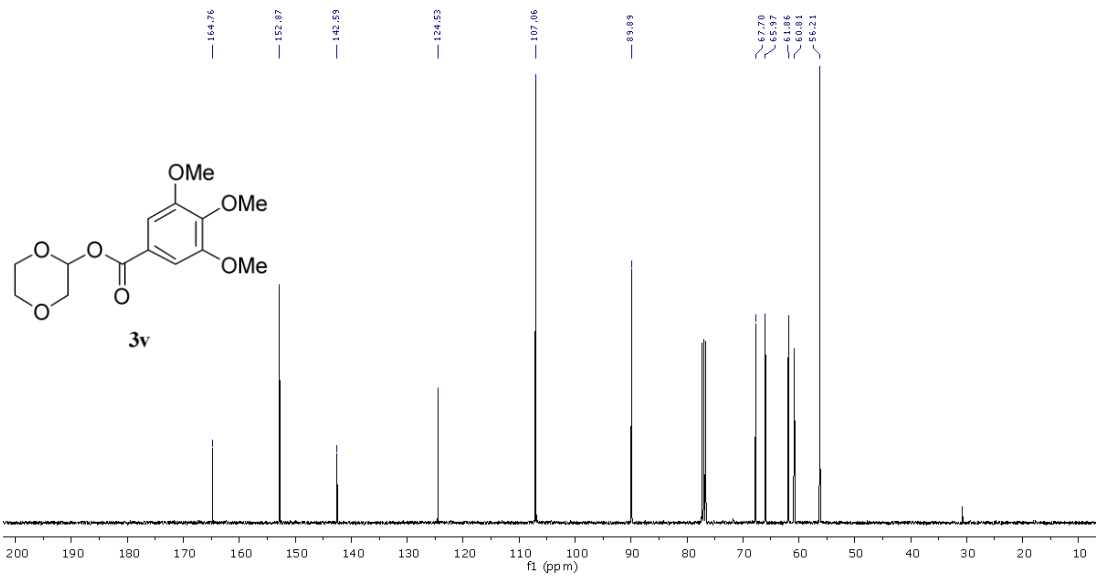


Figure S55. ^{13}C Spectrum of **3v** in $CDCl_3$ (100 MHz)

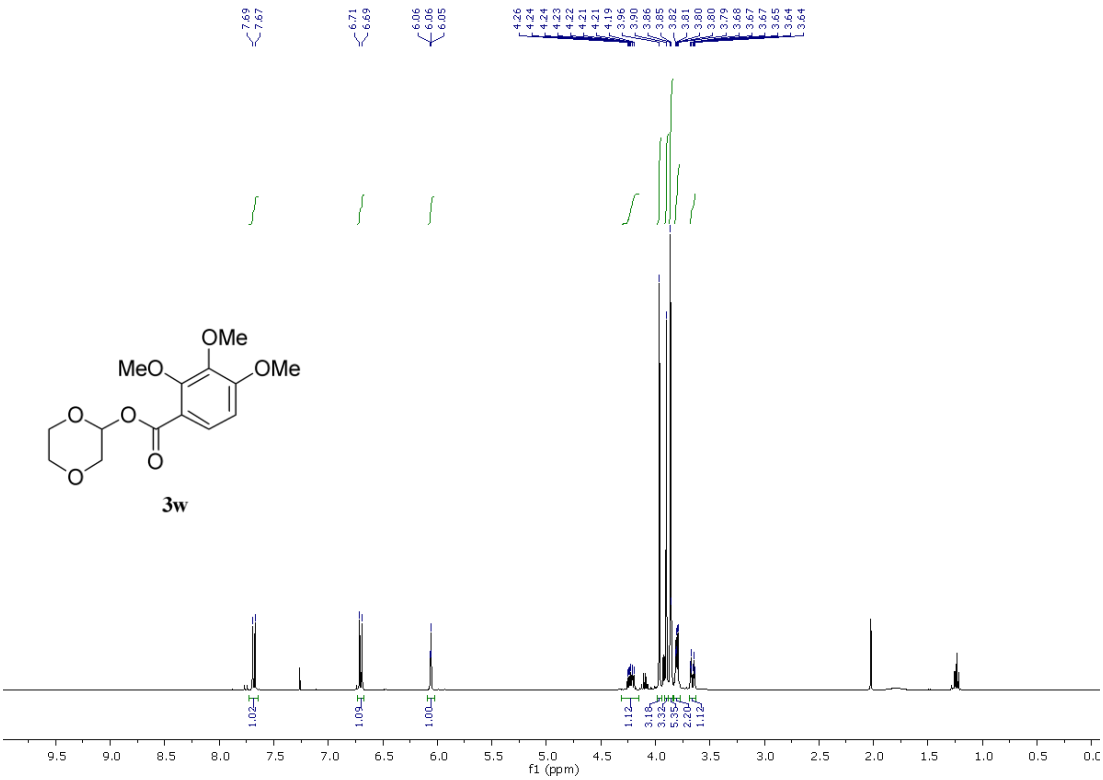


Figure S56. ^{1}H Spectrum of **3w** in $CDCl_3$ (400 MHz)

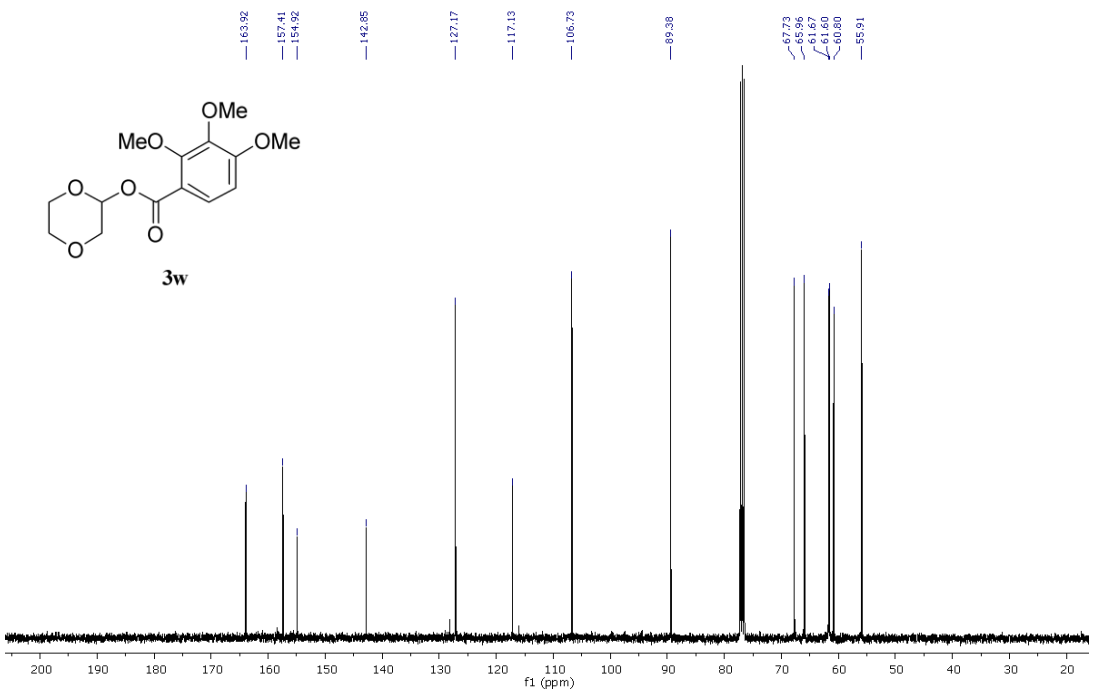


Figure S57. ^{13}C Spectrum of **3w** in $CDCl_3$ (100 MHz)

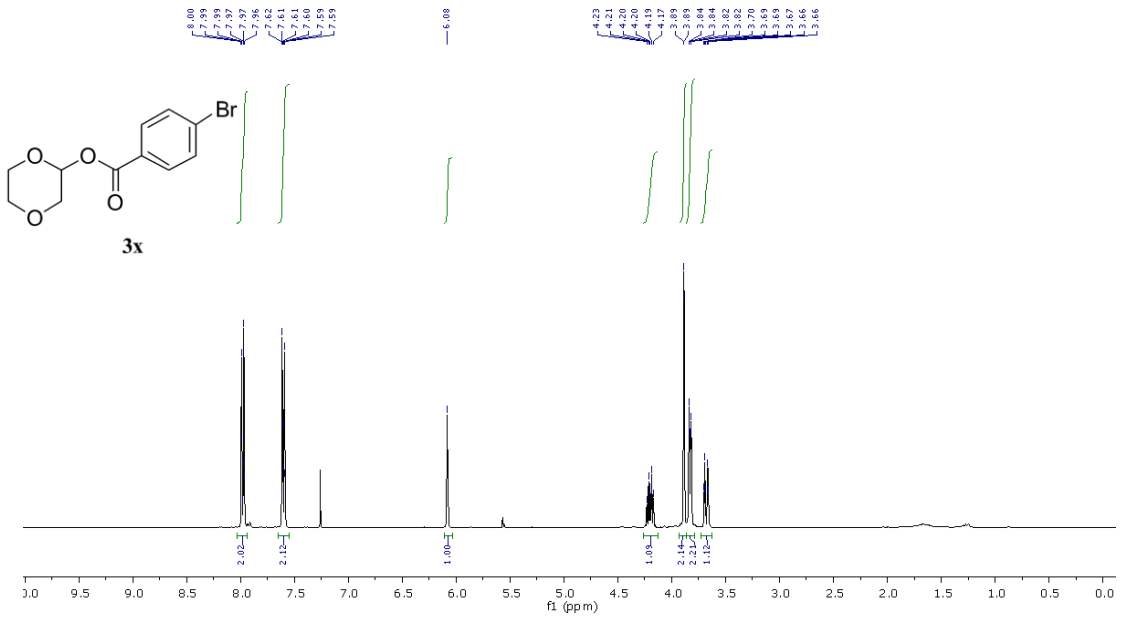


Figure S58. ^{1}H Spectrum of **3x** in $CDCl_3$ (400 MHz)

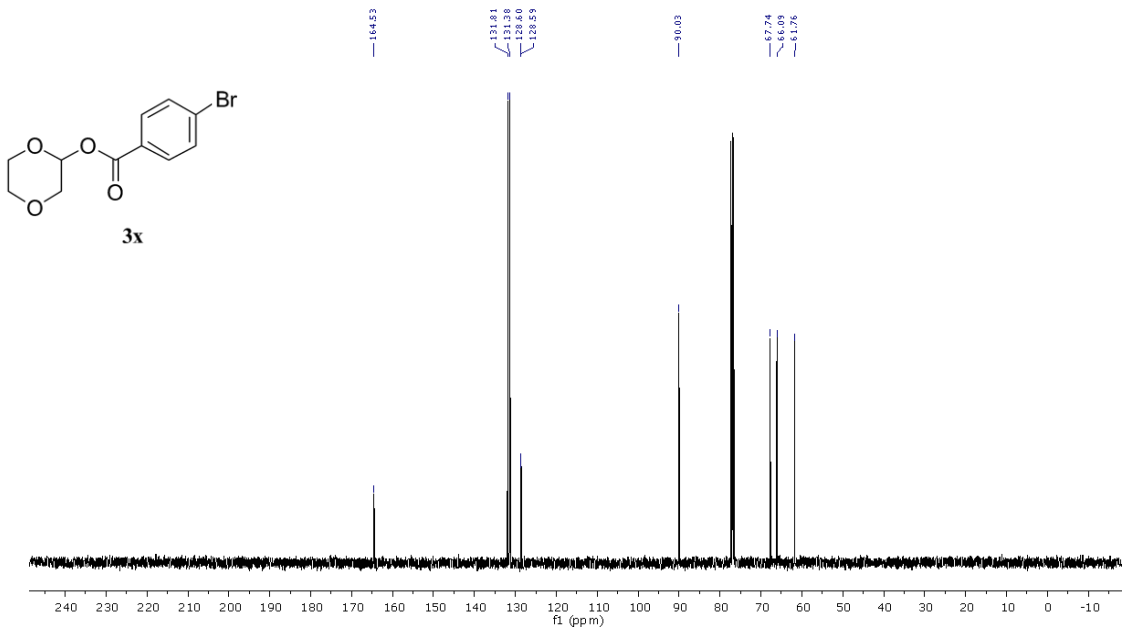


Figure S59. ^{13}C Spectrum of **3x** in $CDCl_3$ (100 MHz)

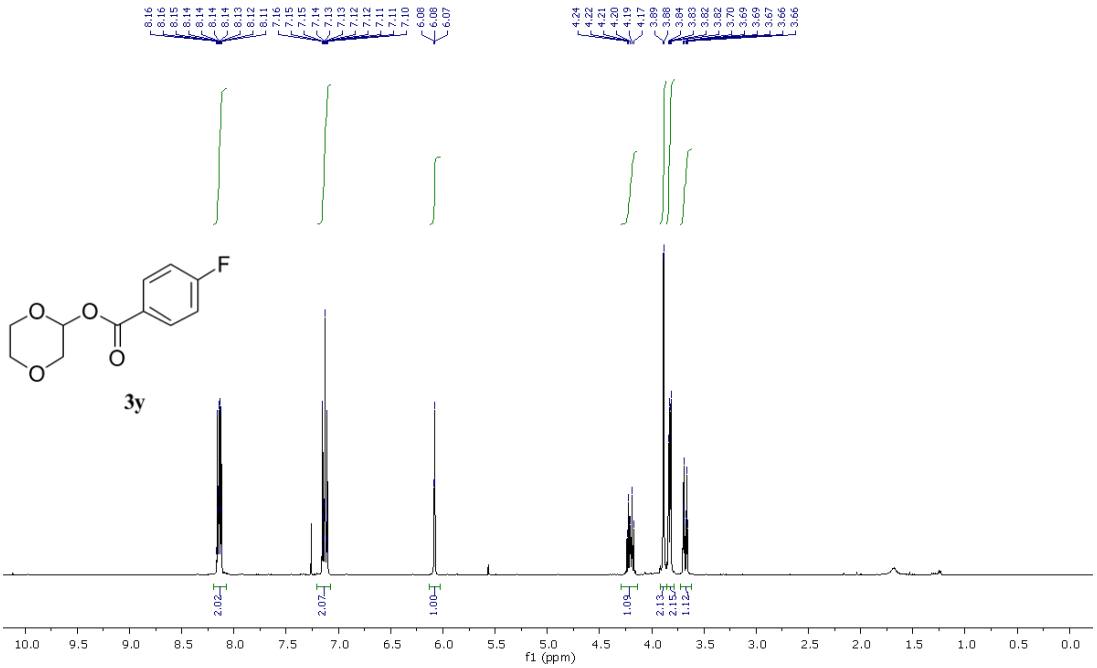


Figure S60. ^{1}H Spectrum of **3y** in $CDCl_3$ (400 MHz)

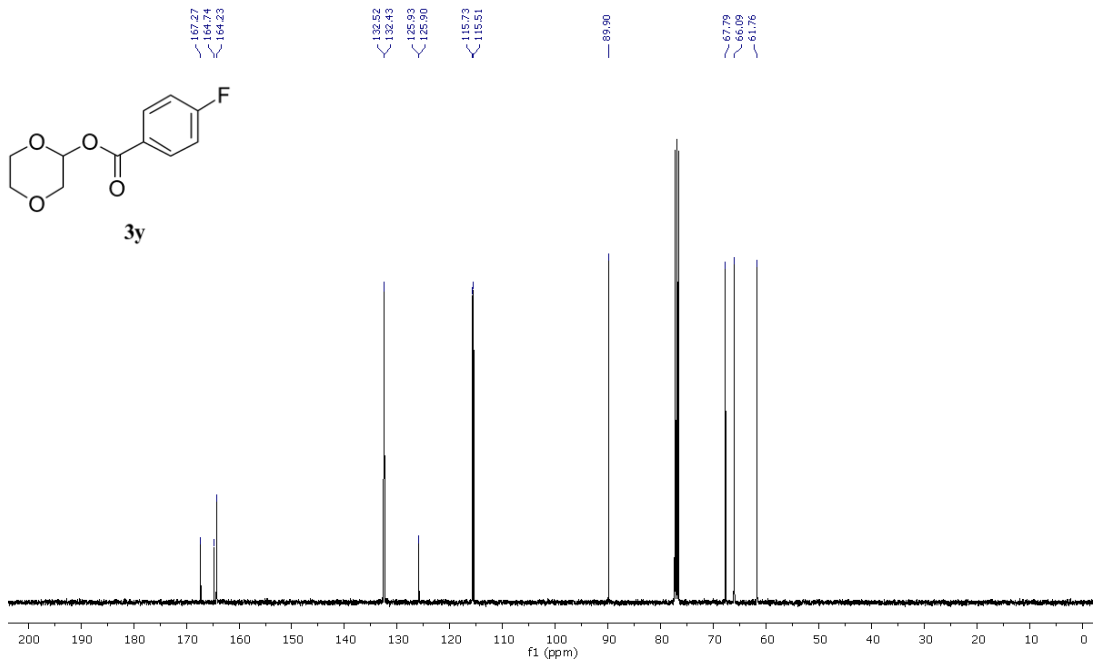


Figure S61. ^{13}C Spectrum of **3y** in $CDCl_3$ (100 MHz)

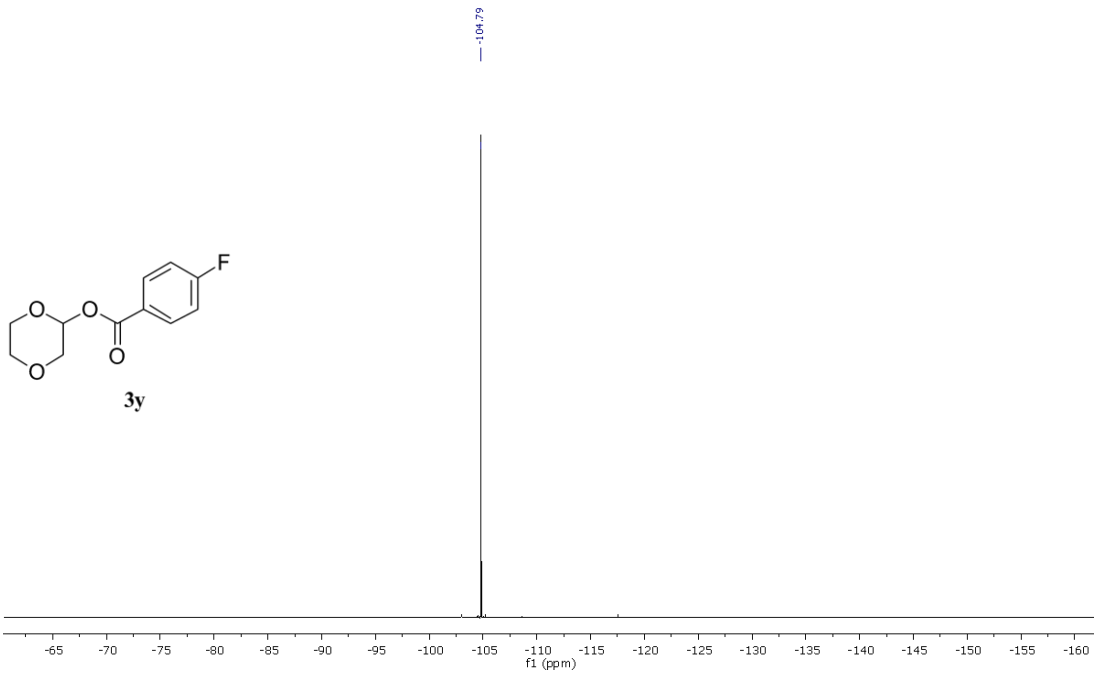


Figure S62. ^{19}F Spectrum of **3y** in $CDCl_3$ (376 MHz)

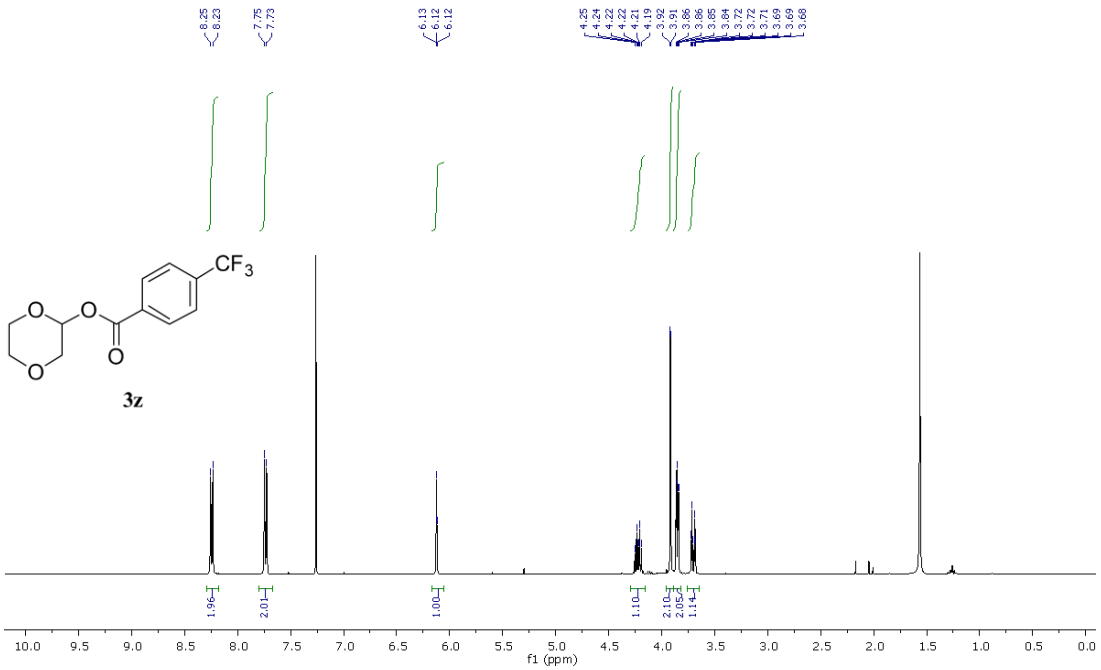


Figure S63. ^{1}H Spectrum of **3z** in $CDCl_3$ (400 MHz)

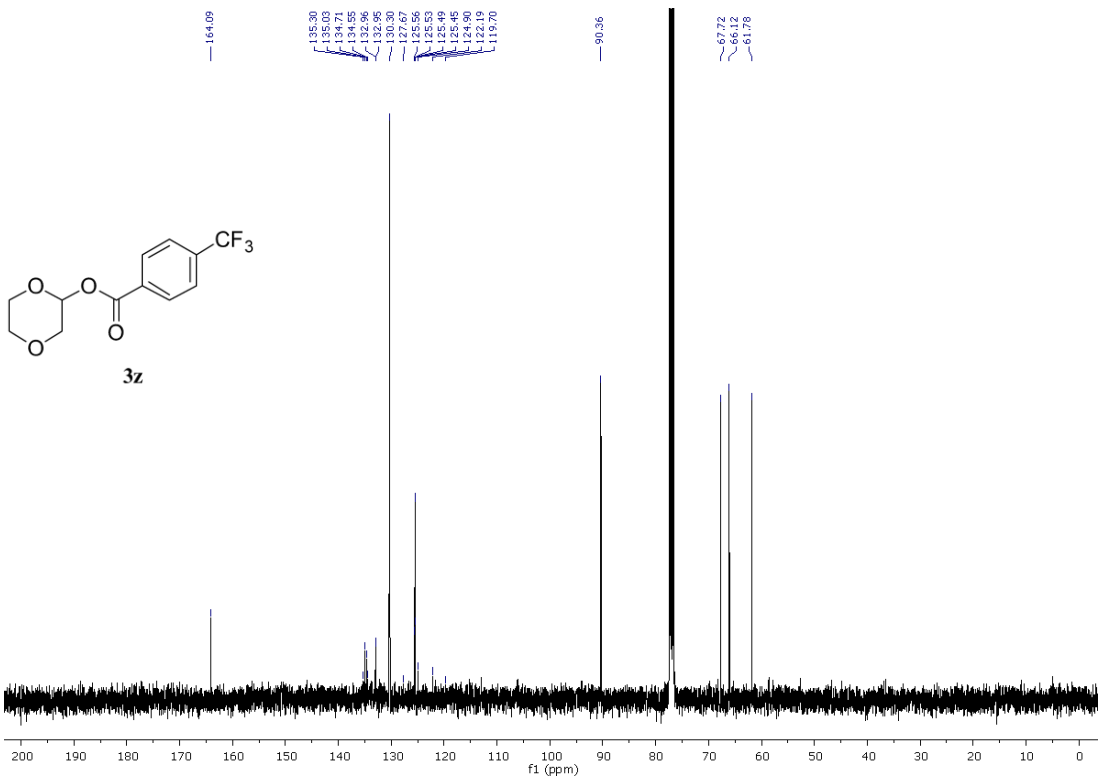


Figure S64. ^{13}C Spectrum of **3z** in $CDCl_3$ (100 MHz)

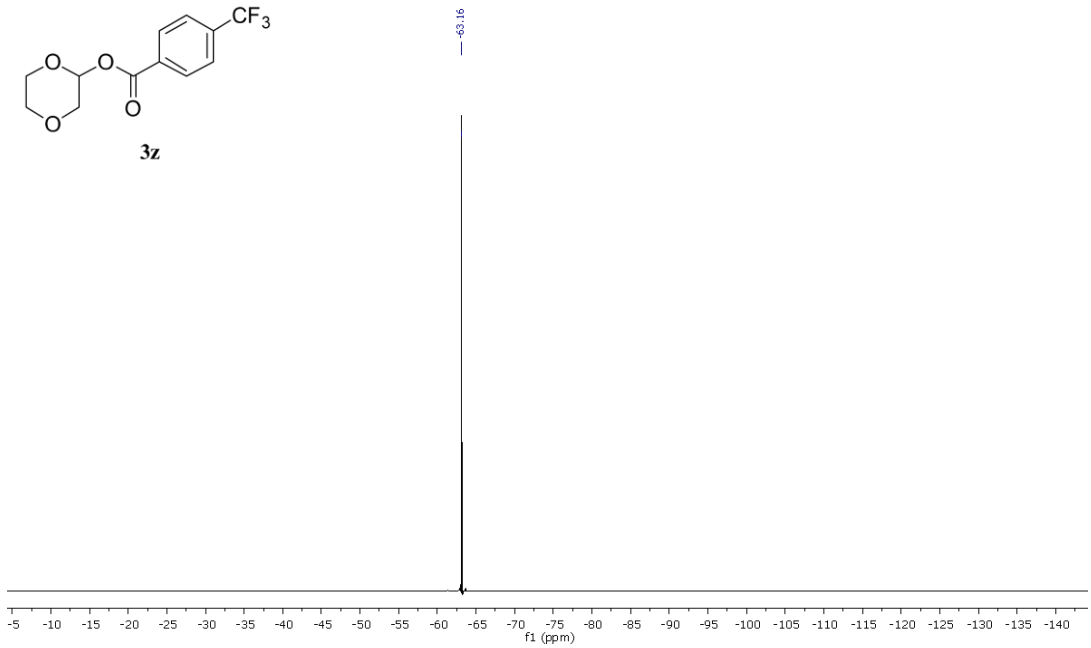


Figure S65. ^{19}F Spectrum of **3z** in $CDCl_3$ (376 MHz)

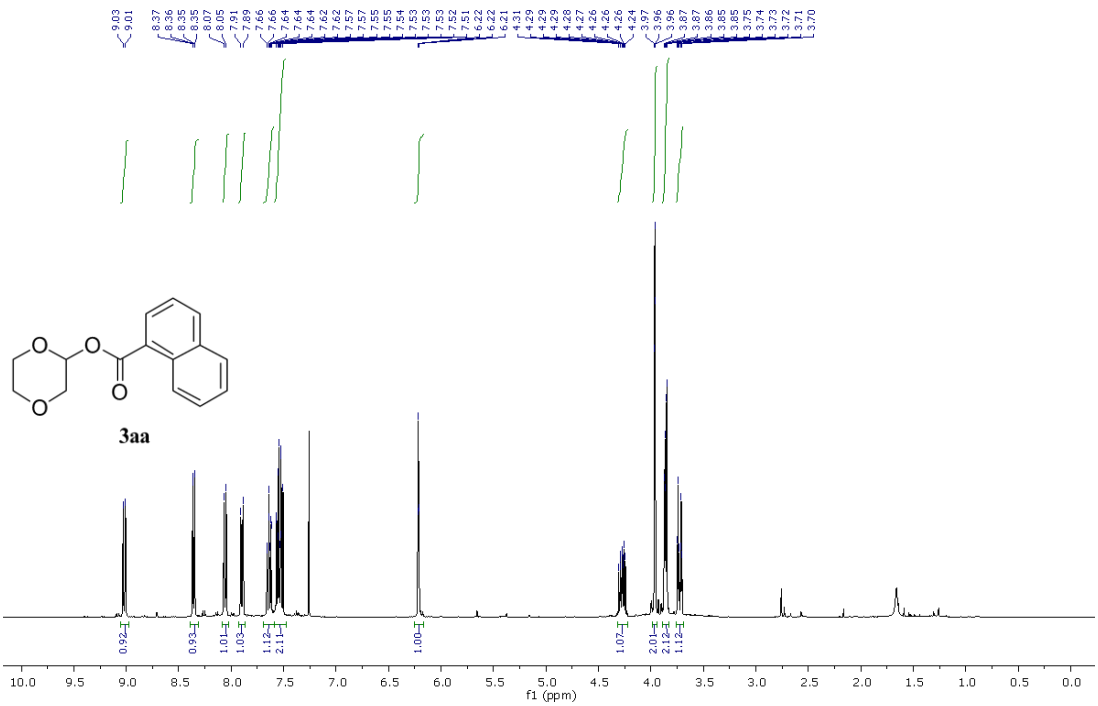


Figure S66. ^{1}H Spectrum of **3aa** in $CDCl_3$ (400 MHz)

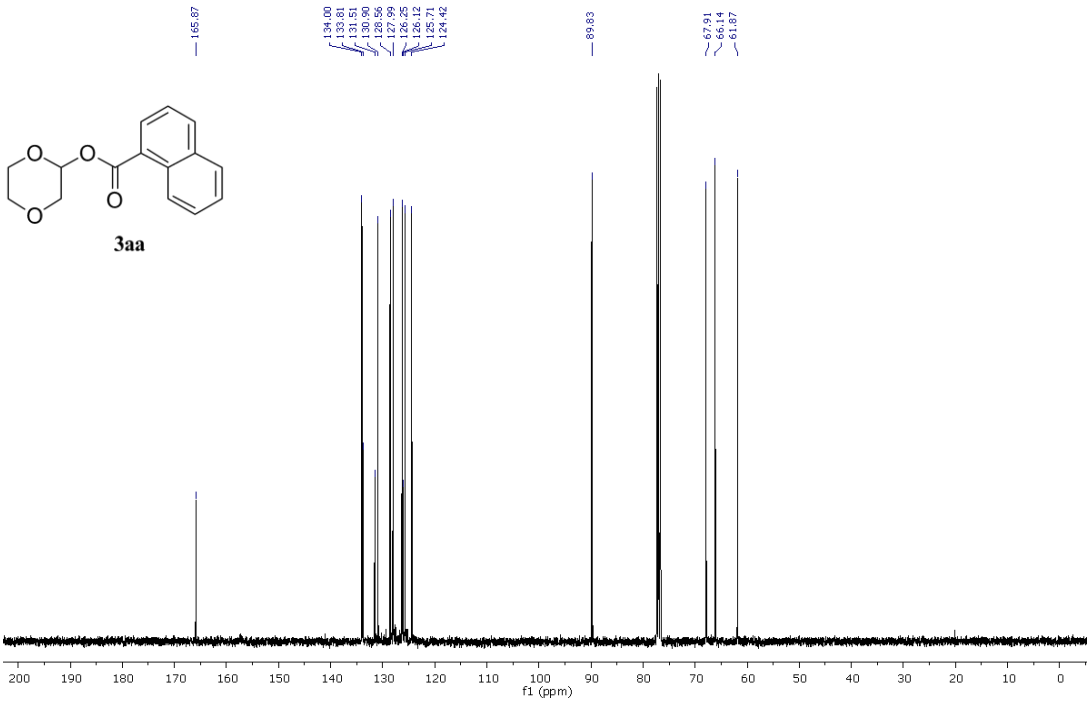


Figure S67. ^{13}C Spectrum of **3aa** in $CDCl_3$ (100 MHz)

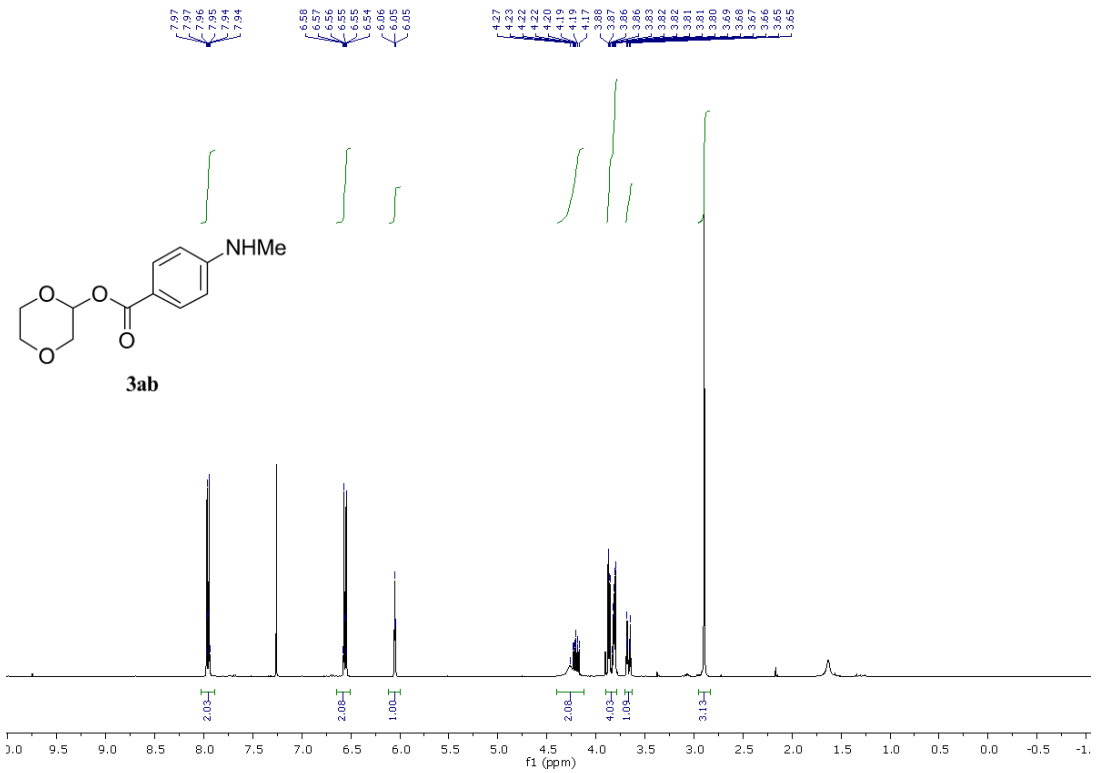


Figure S68. ^{1}H Spectrum of **3ab** in $CDCl_3$ (400 MHz)

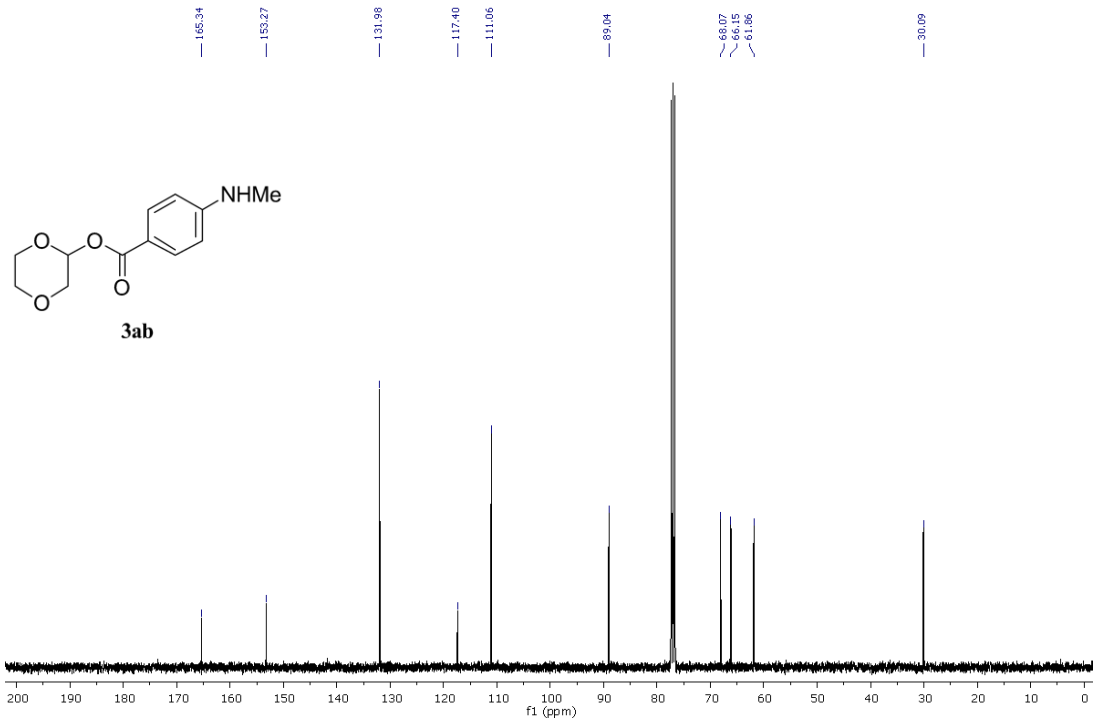


Figure S69. ^{13}C Spectrum of **3ab** in $CDCl_3$ (100 MHz)

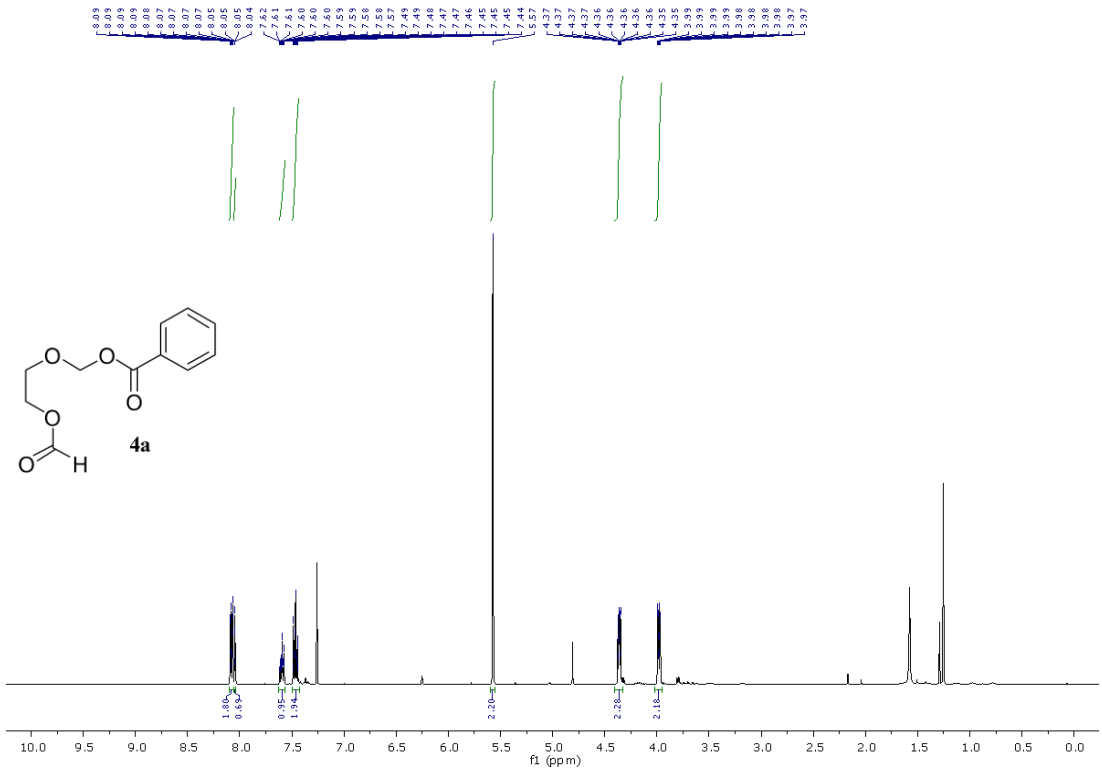


Figure S70. ^{1}H Spectrum of **4a** in $CDCl_3$ (400 MHz)

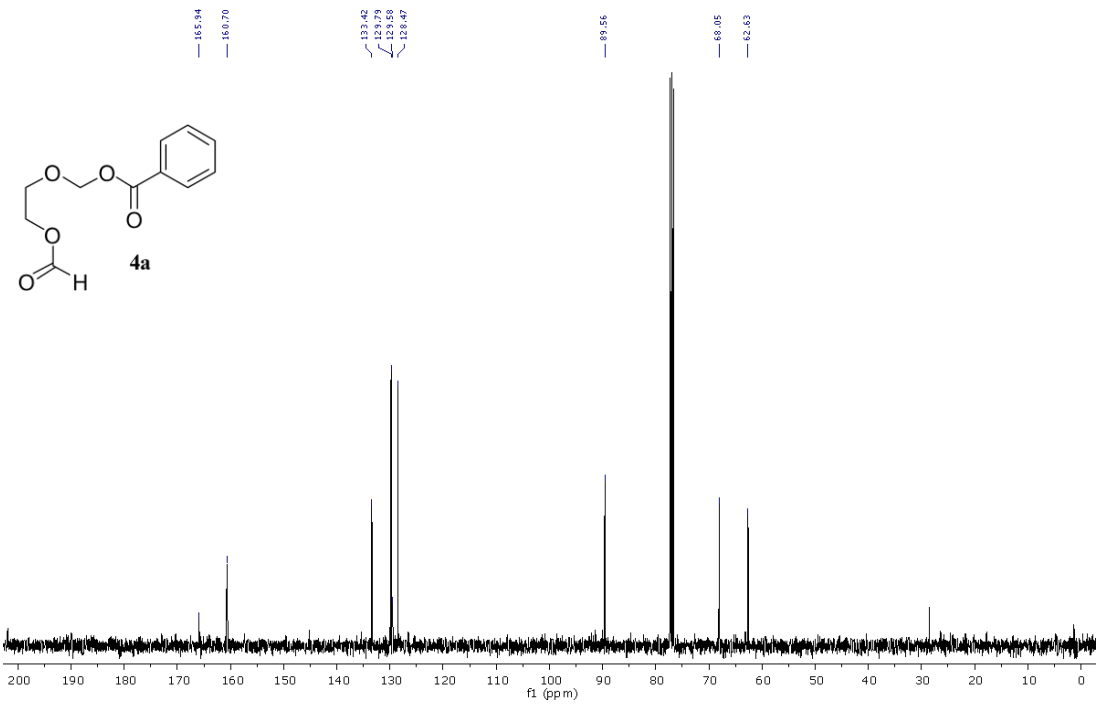


Figure S71. ^{13}C Spectrum of **4a** in $CDCl_3$ (100 MHz)

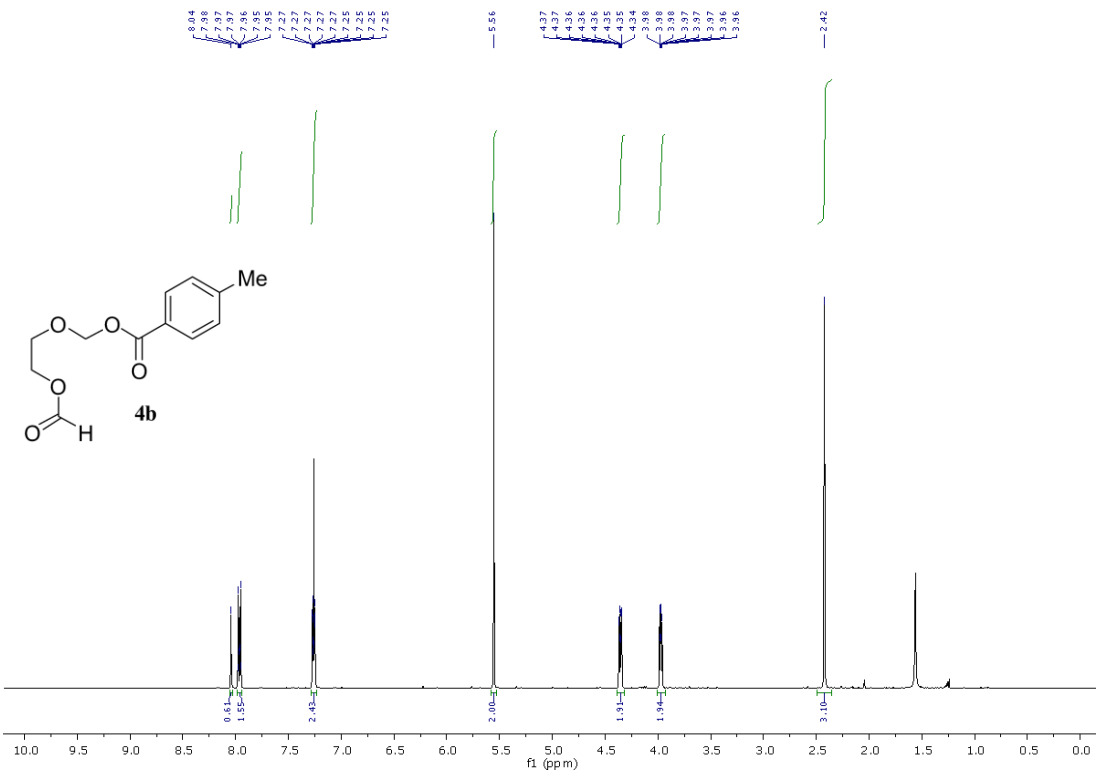


Figure S72. ^{1}H Spectrum of **4b** in $CDCl_3$ (400 MHz)

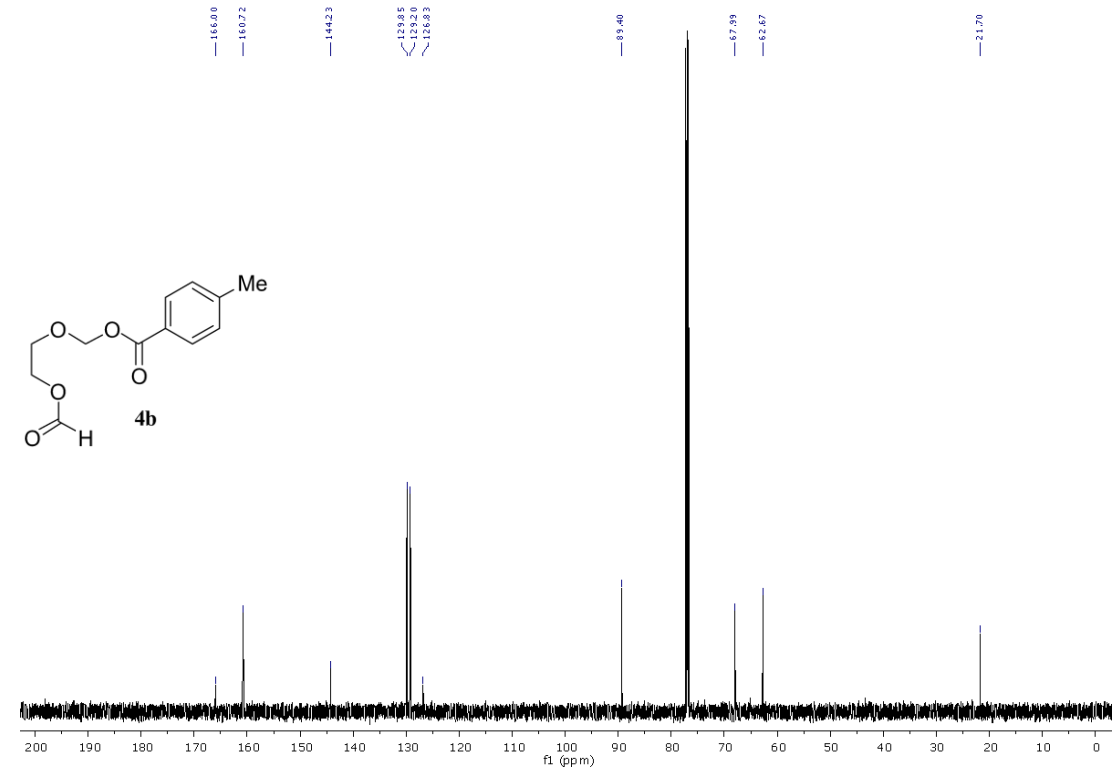


Figure S73. ^{13}C Spectrum of **4b** in $CDCl_3$ (100 MHz)

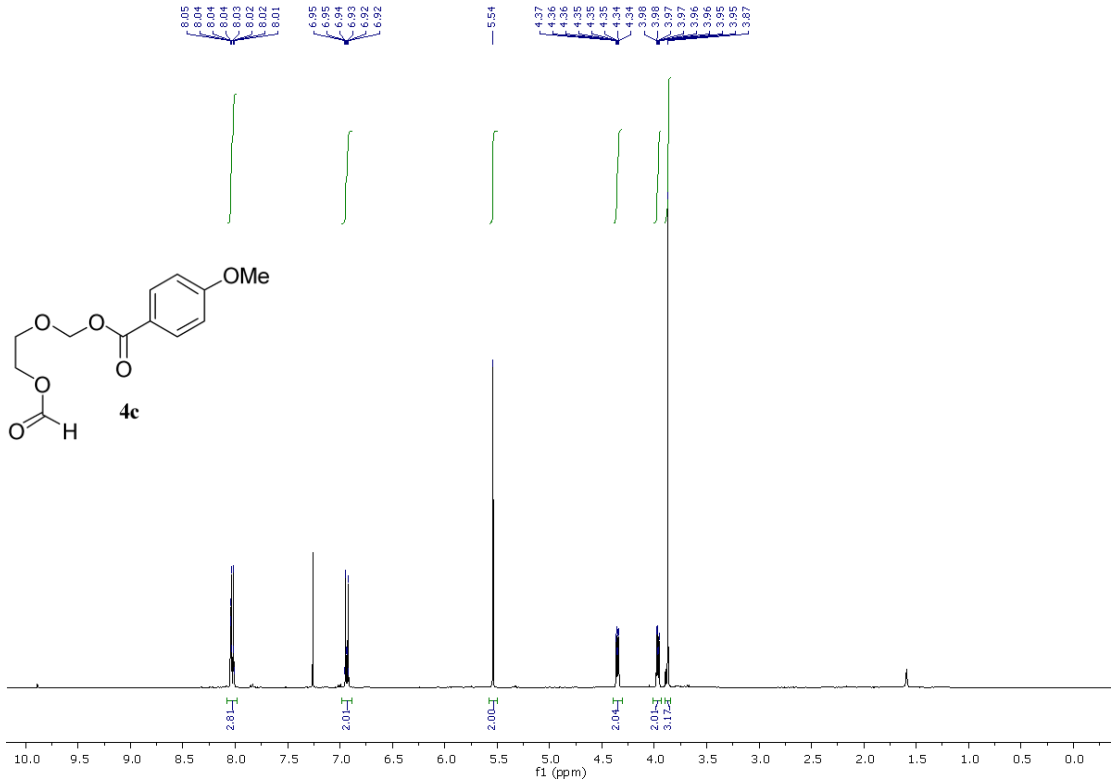


Figure S74. ^{1}H Spectrum of **4c** in $CDCl_3$ (400 MHz)

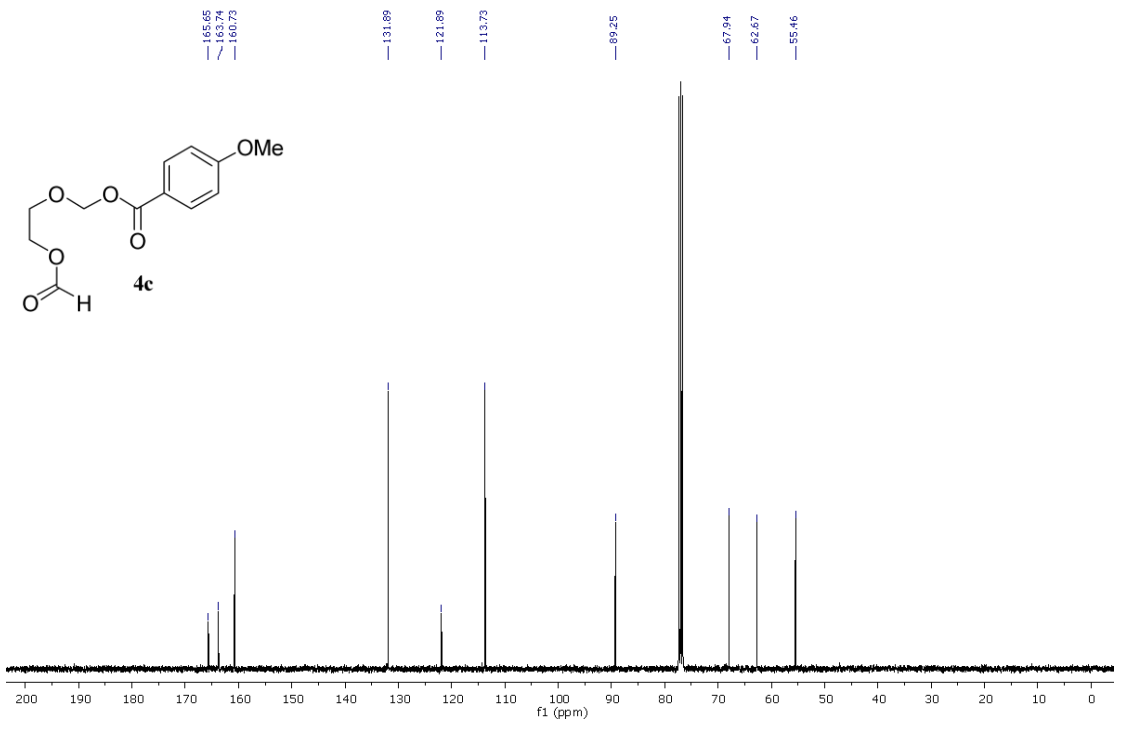


Figure S75. ^{13}C Spectrum of **4c** in $CDCl_3$ (100 MHz)

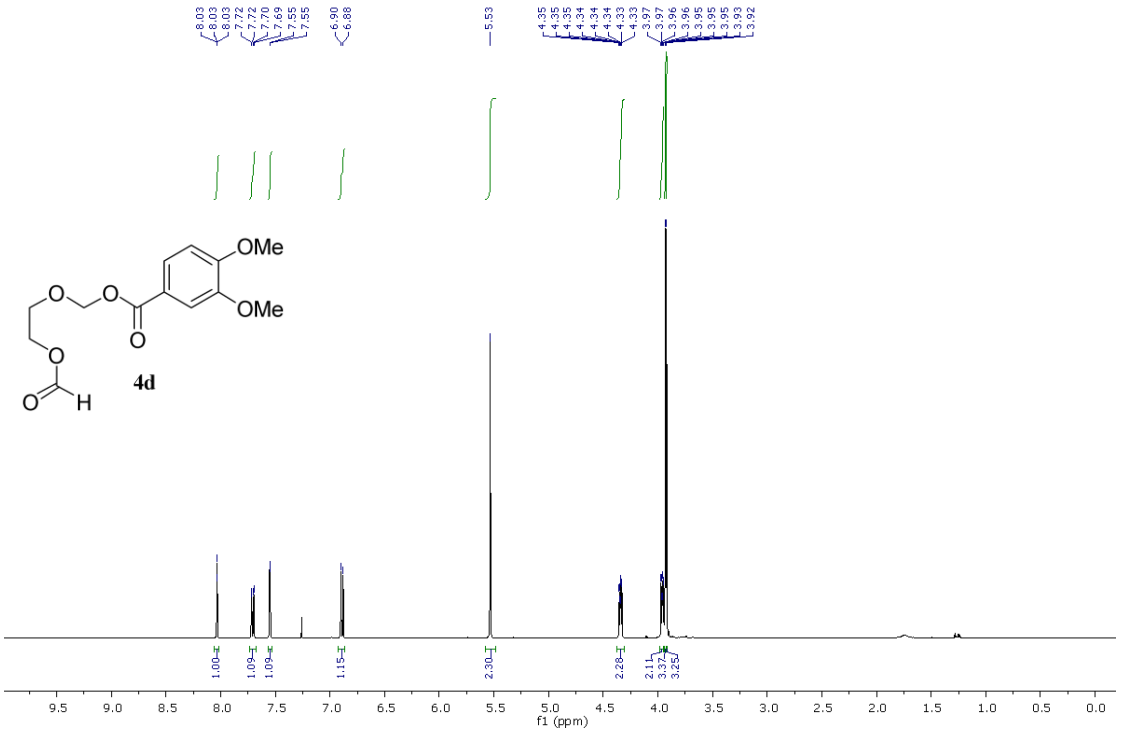


Figure S76. ^{1}H Spectrum of **4d** in $CDCl_3$ (400 MHz)

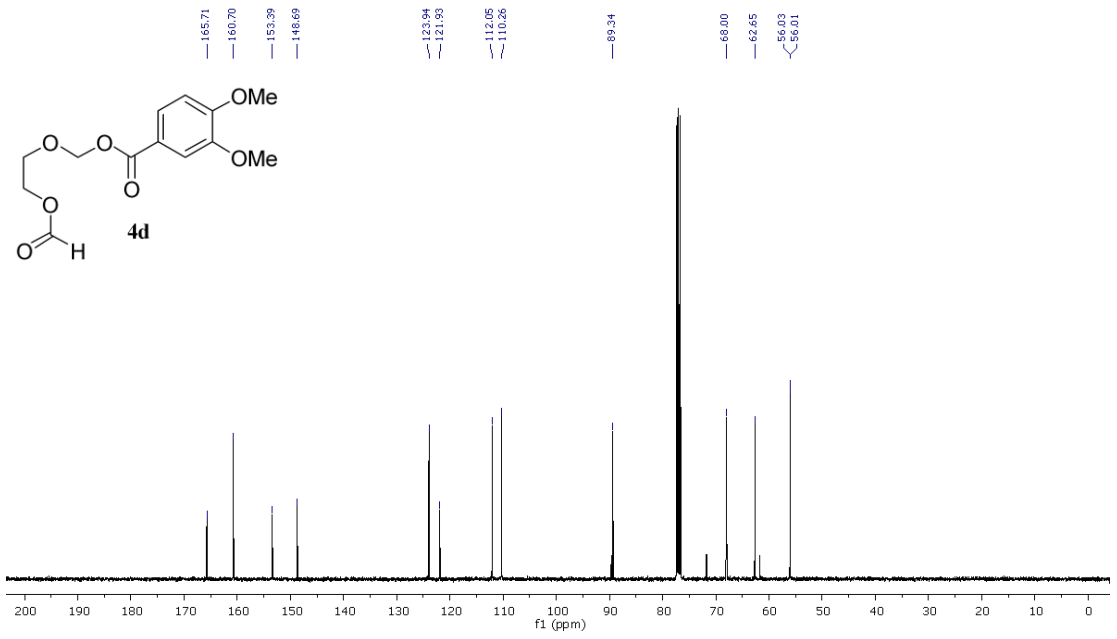


Figure S77. ^{13}C Spectrum of **4d** in $CDCl_3$ (100 MHz)

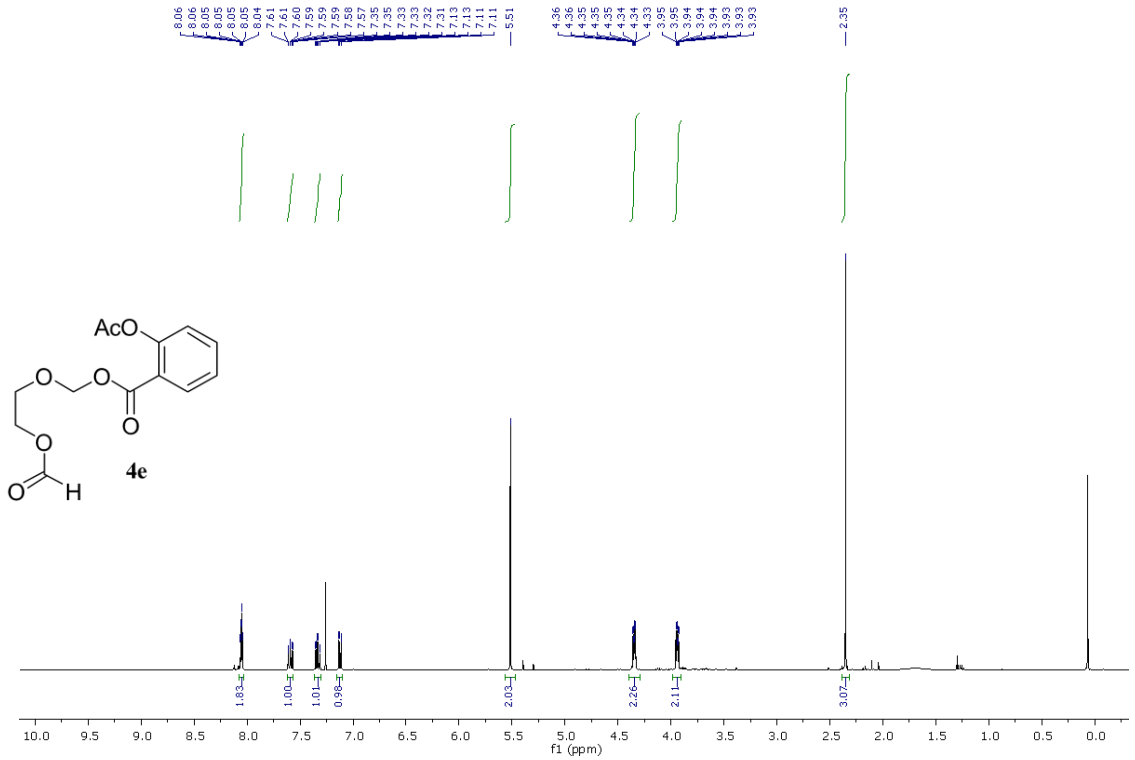


Figure S78. ^{1}H Spectrum of **4e** in $CDCl_3$ (400 MHz)

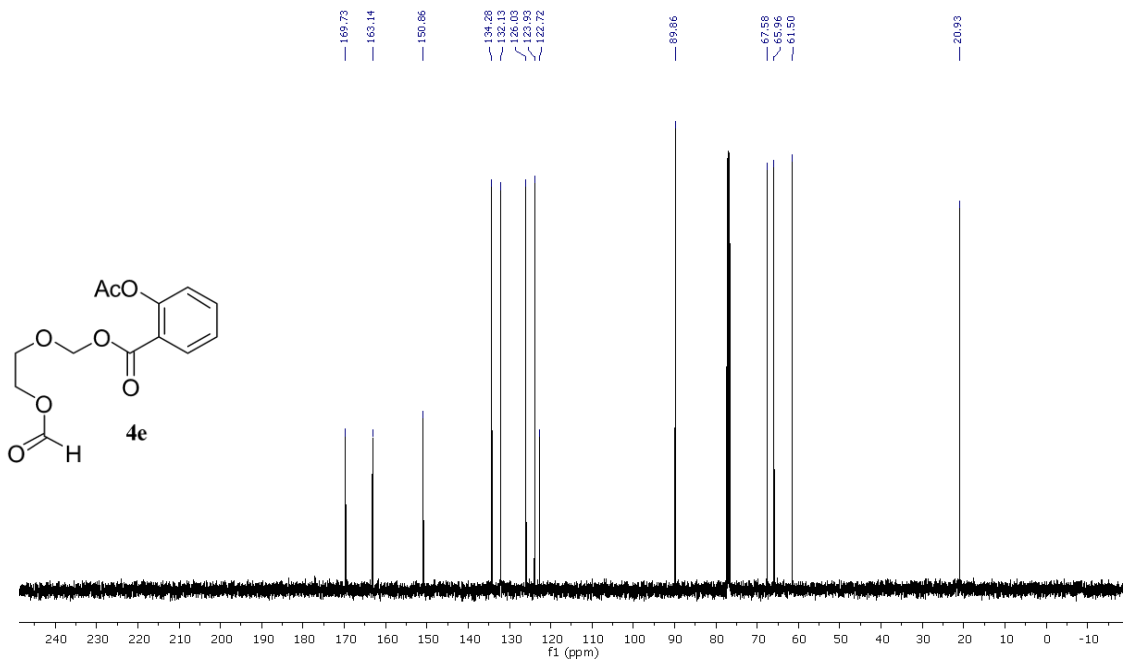


Figure S79. ^{13}C Spectrum of **4e** in $CDCl_3$ (100 MHz)

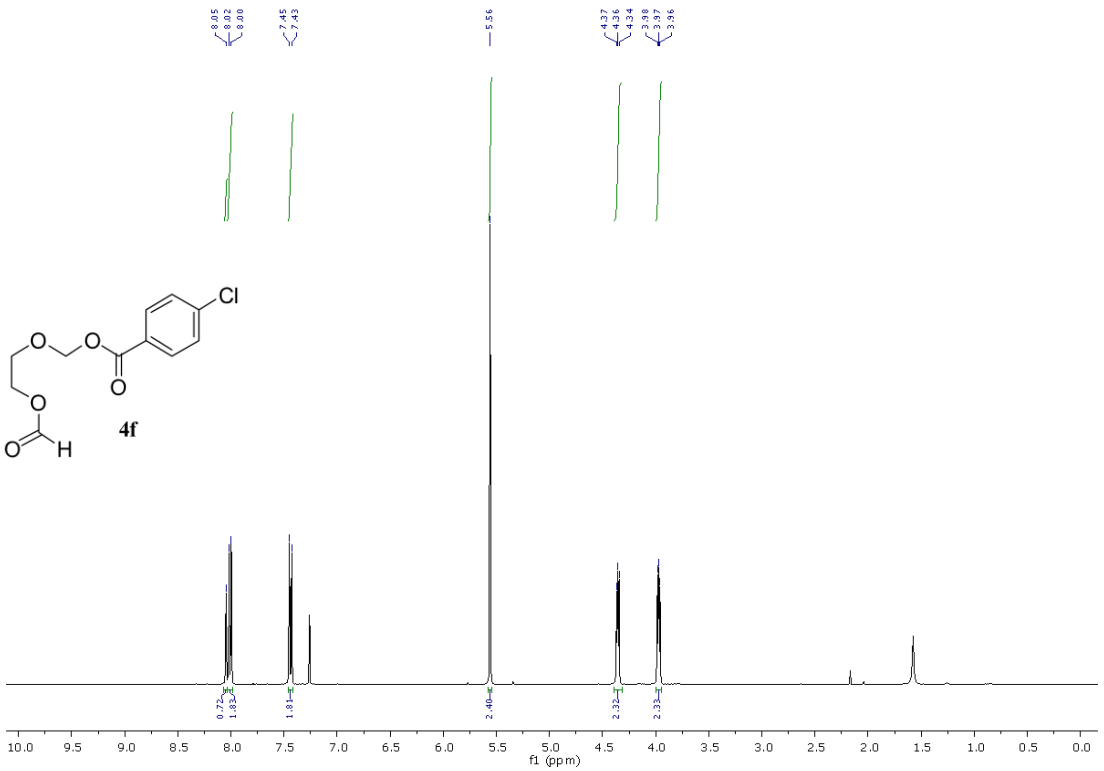


Figure S80. ^{1}H Spectrum of **4f** in $CDCl_3$ (400 MHz)

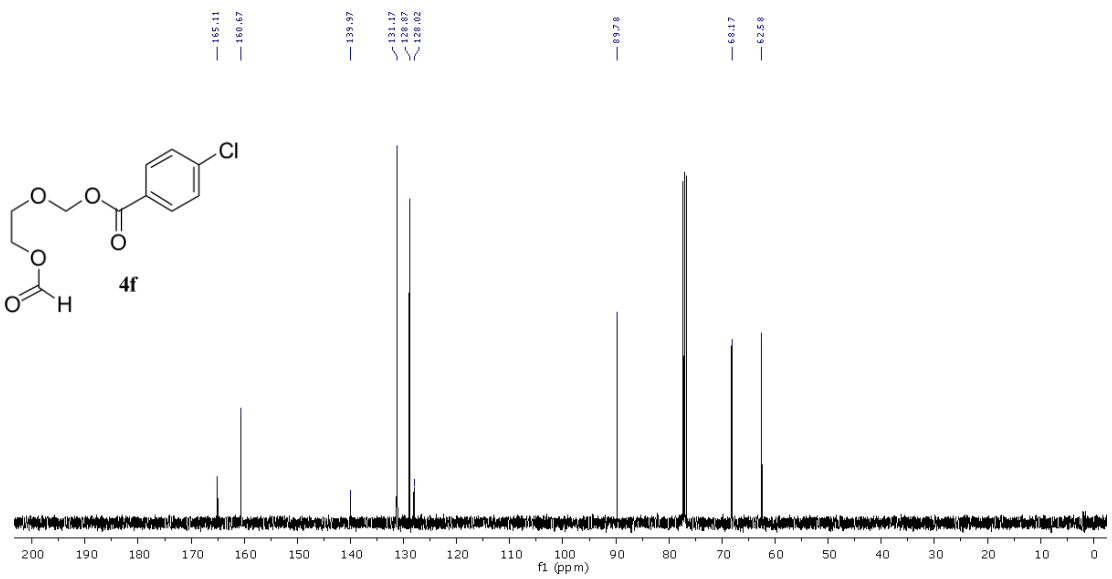


Figure S81. ^{13}C Spectrum of **4f** in $CDCl_3$ (100 MHz)

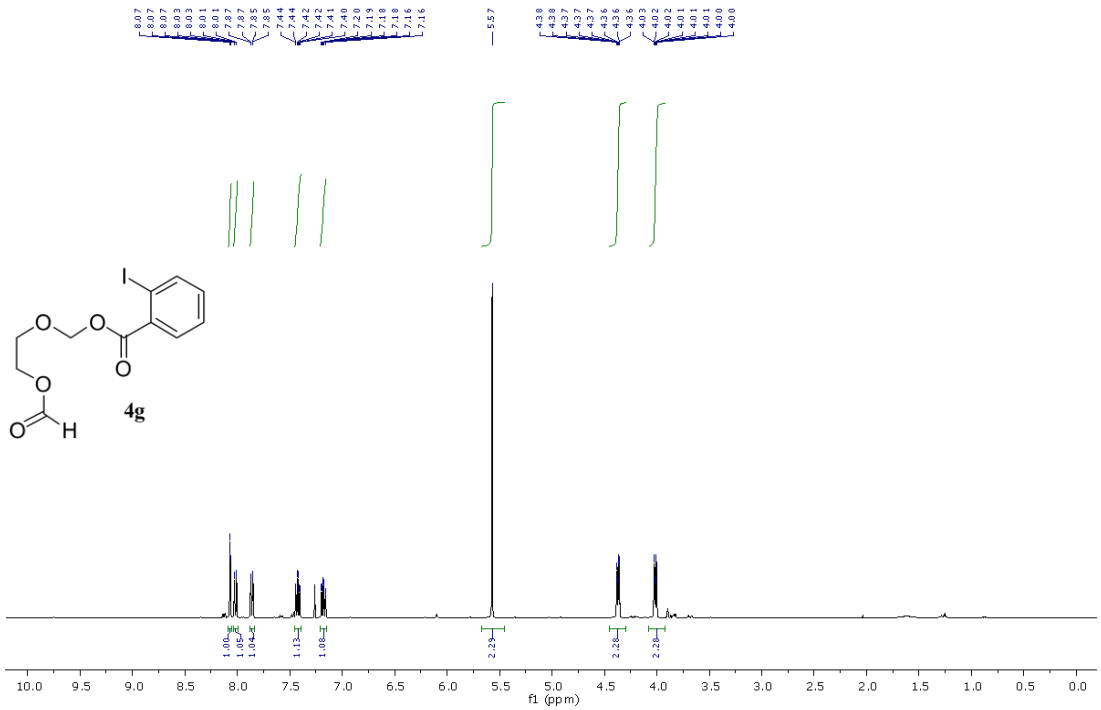


Figure S82. ^{1}H Spectrum of **4g** in $CDCl_3$ (500 MHz)

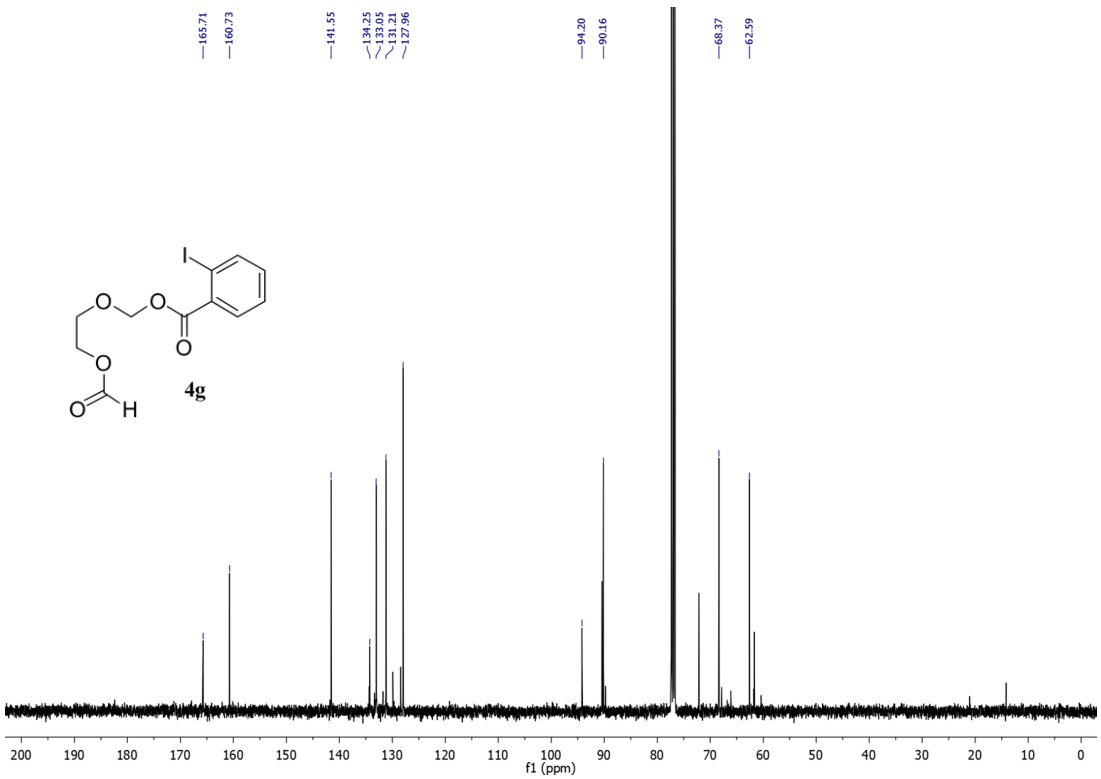


Figure S83. ^{13}C Spectrum of **4g** in $CDCl_3$ (125 MHz)

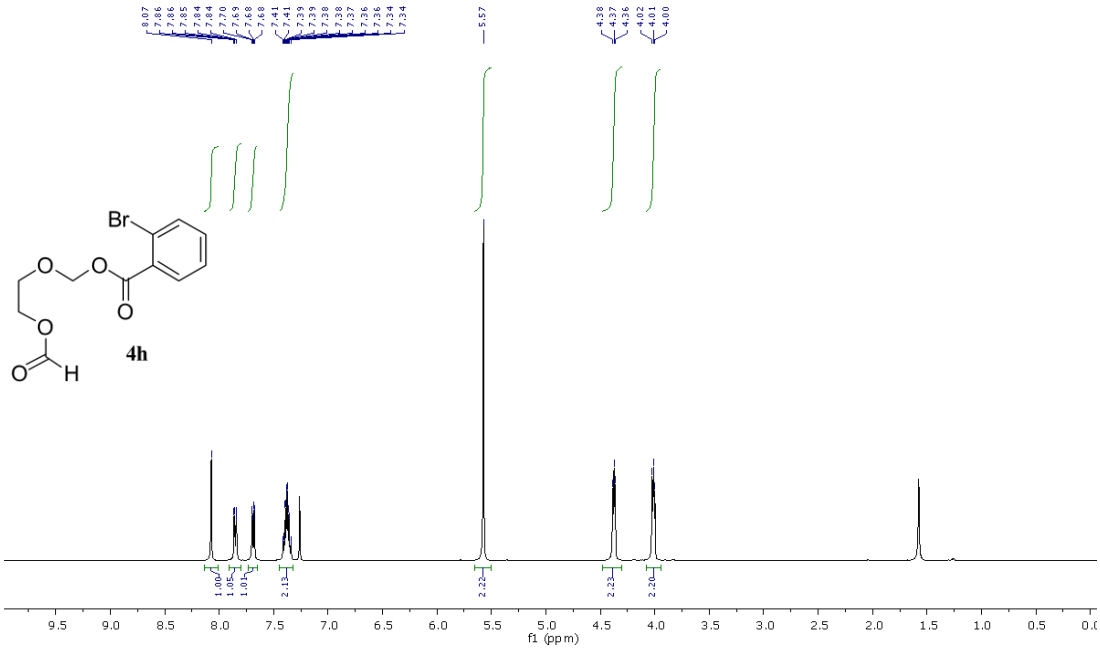


Figure S84. ^{1}H Spectrum of **4h** in $CDCl_3$ (400 MHz)

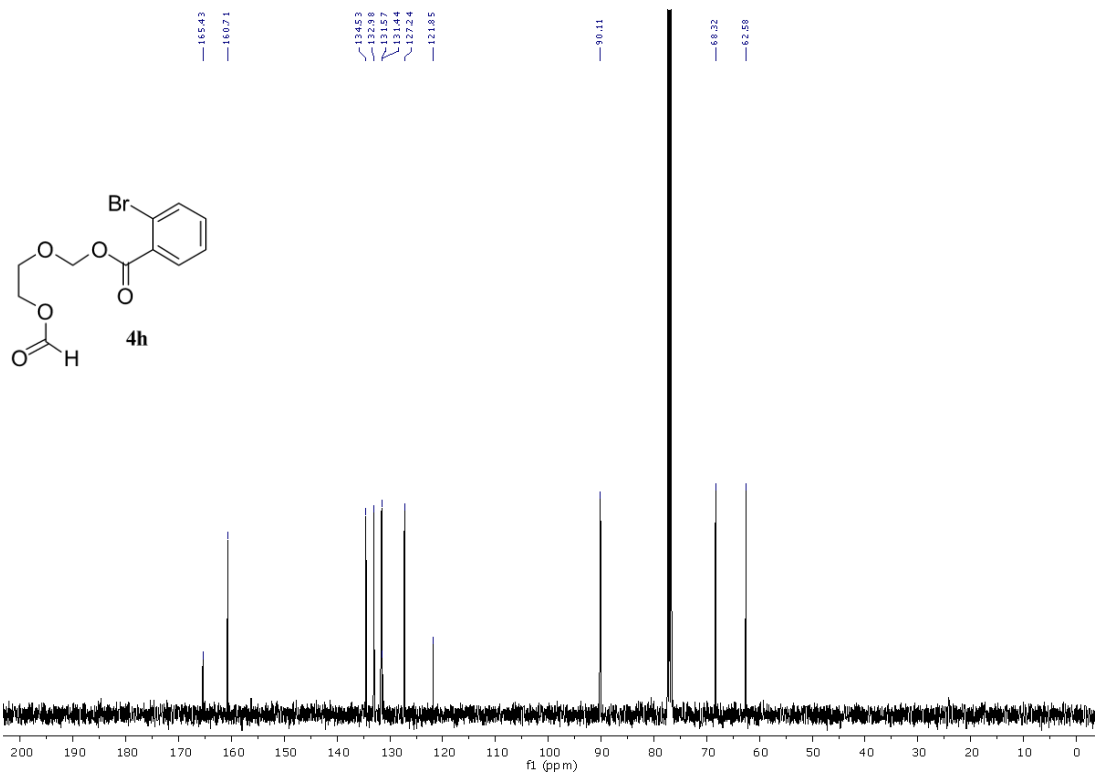


Figure S85. ^{13}C Spectrum of **4h** in $CDCl_3$ (100 MHz)

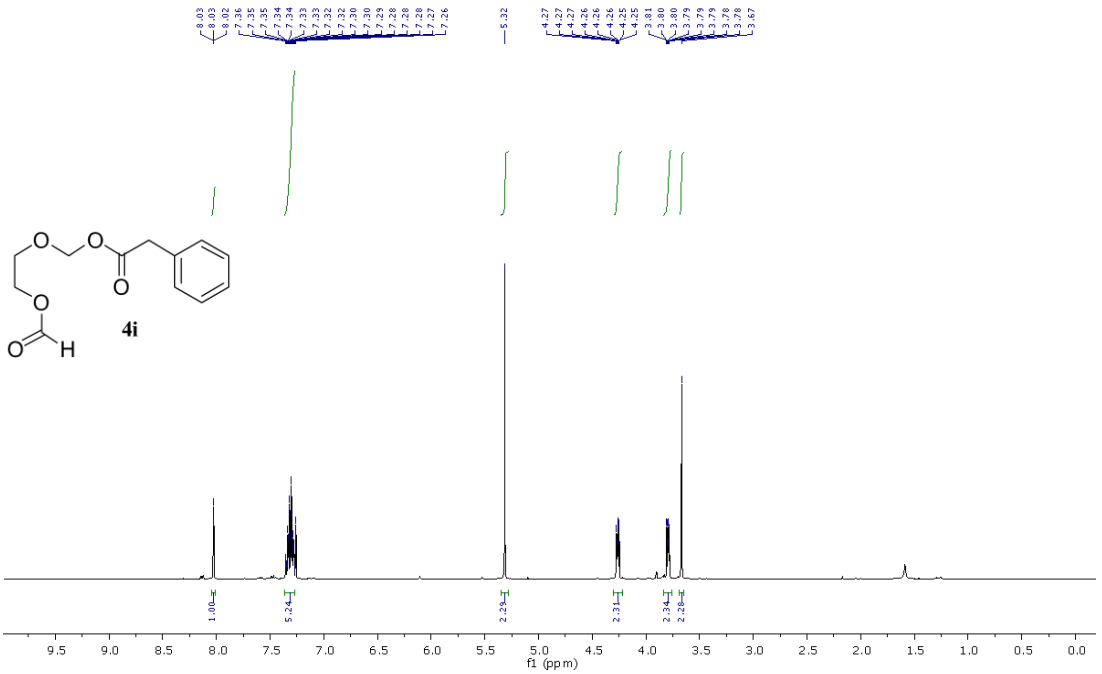


Figure S86. ^{1}H Spectrum of **4i** in $CDCl_3$ (500 MHz)

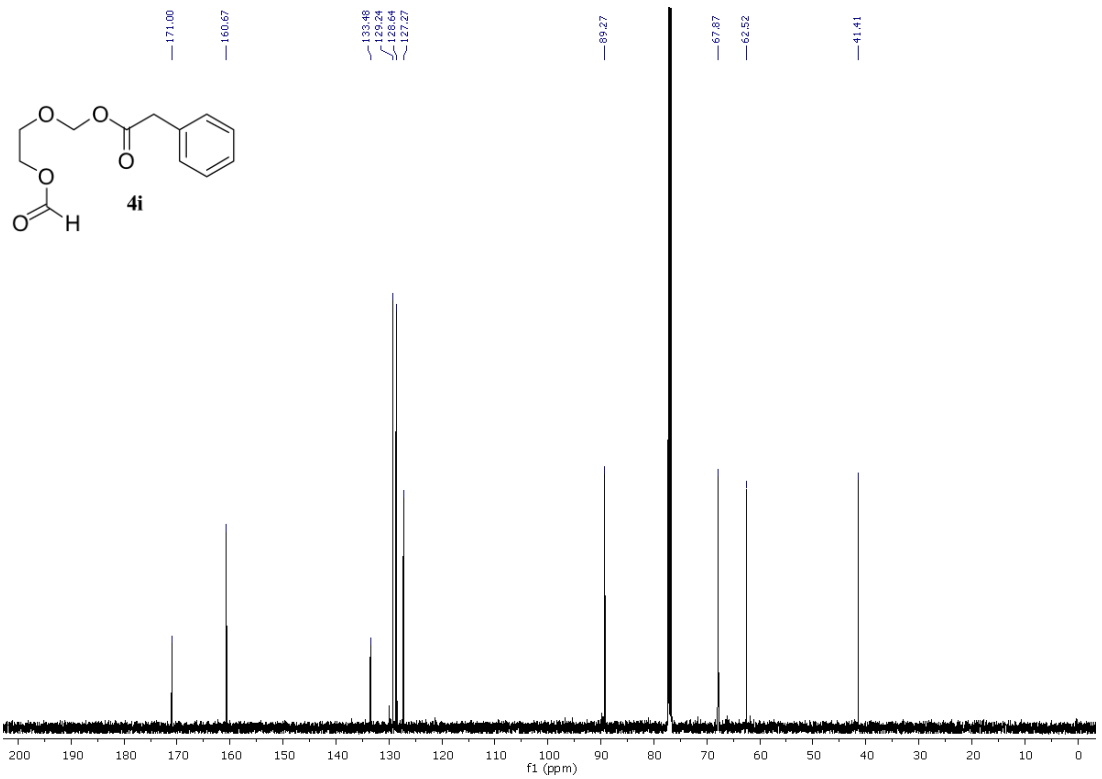


Figure S87. ^{13}C Spectrum of **4i** in $CDCl_3$ (125 MHz)

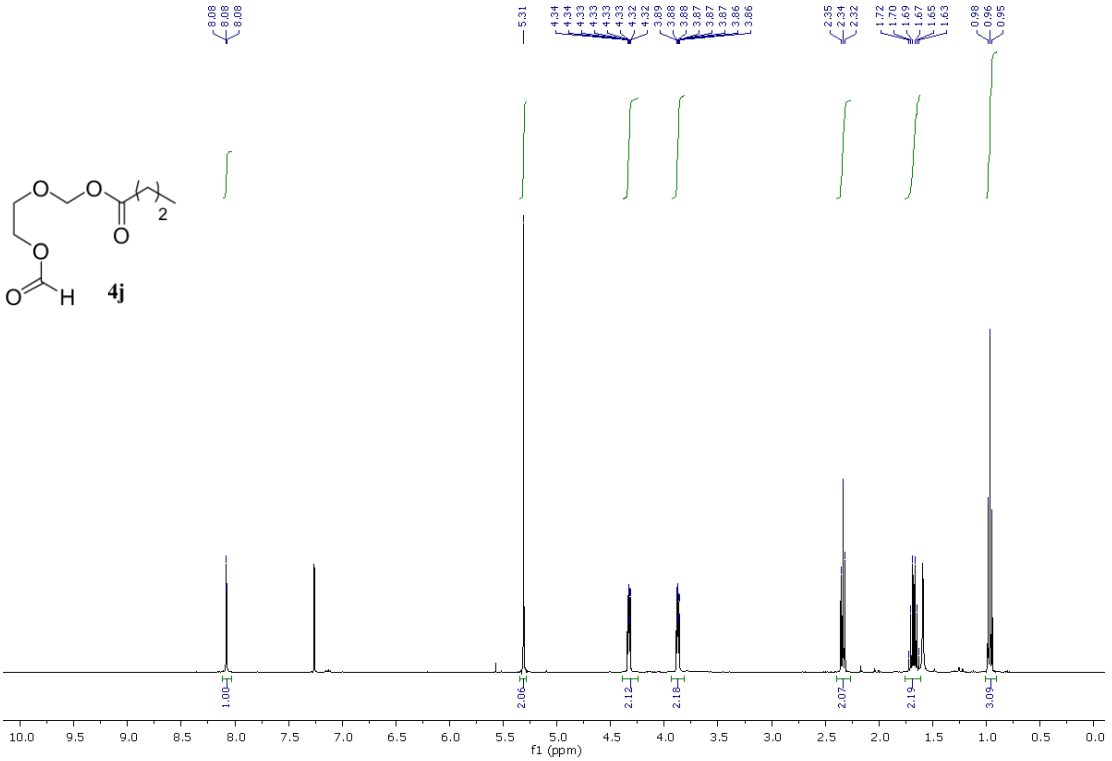


Figure S88. ^{1}H Spectrum of **4j** in $CDCl_3$ (400 MHz)

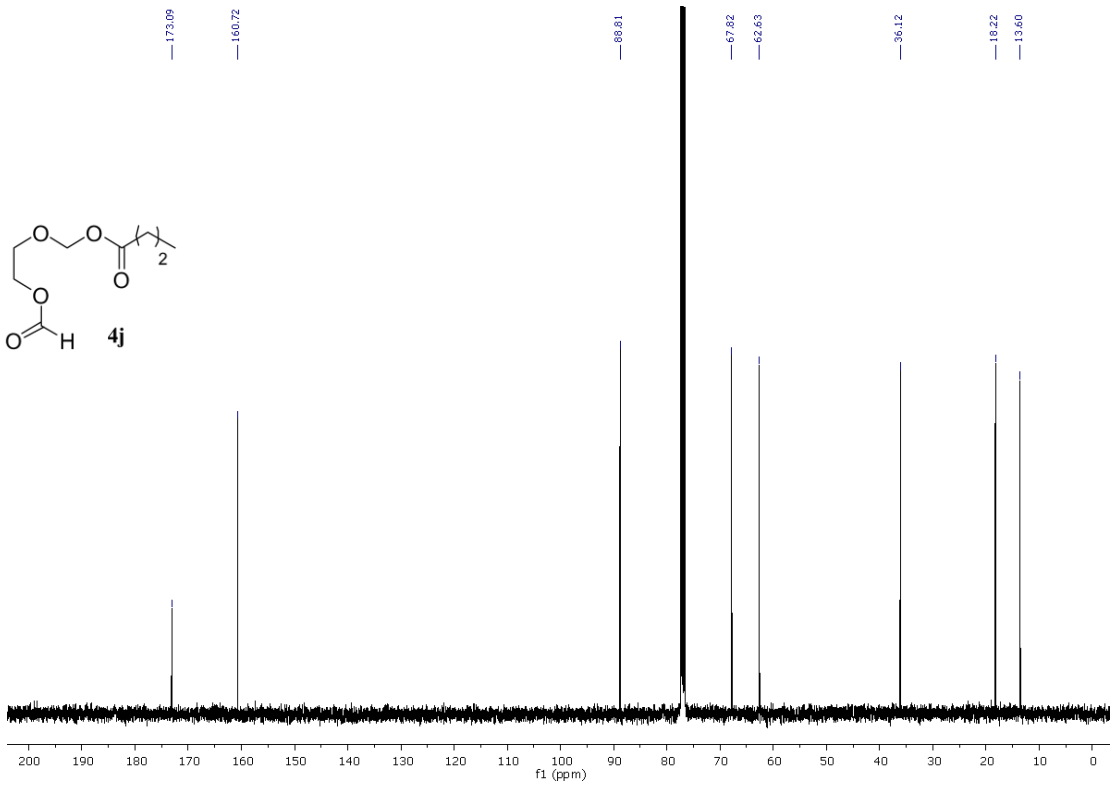


Figure S89. ^{13}C Spectrum of **4j** in $CDCl_3$ (100 MHz)

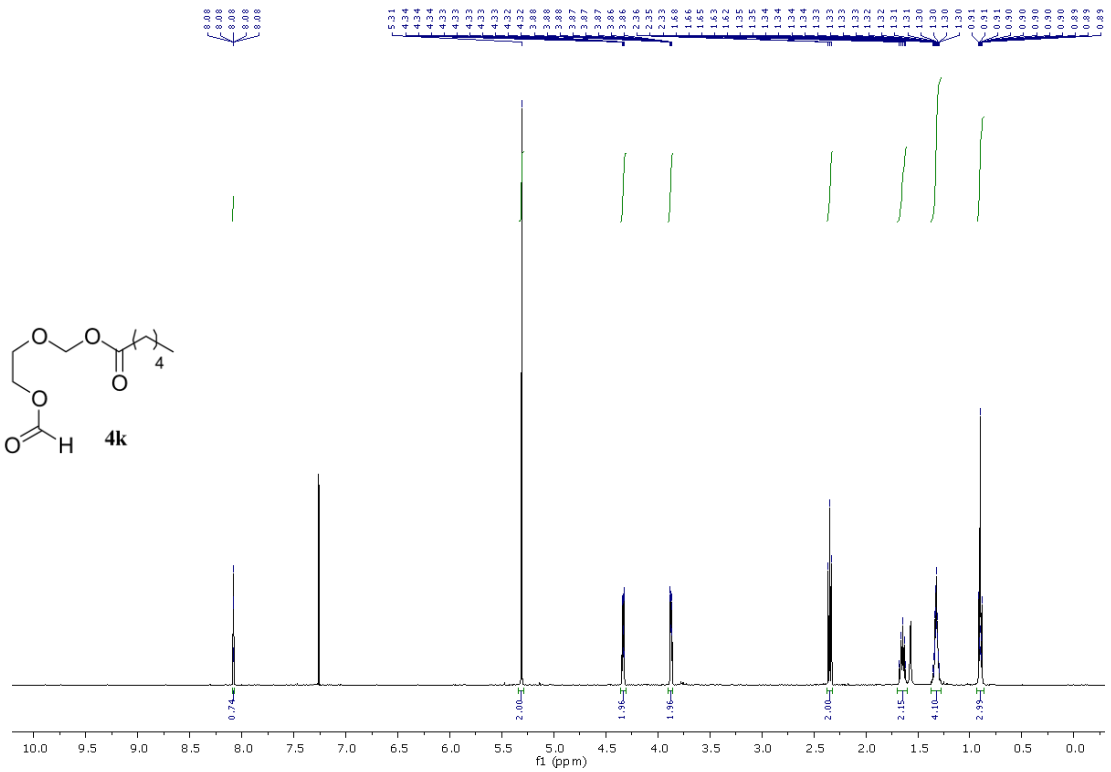


Figure S90. ^{1}H Spectrum of **4k** in $CDCl_3$ (400 MHz)

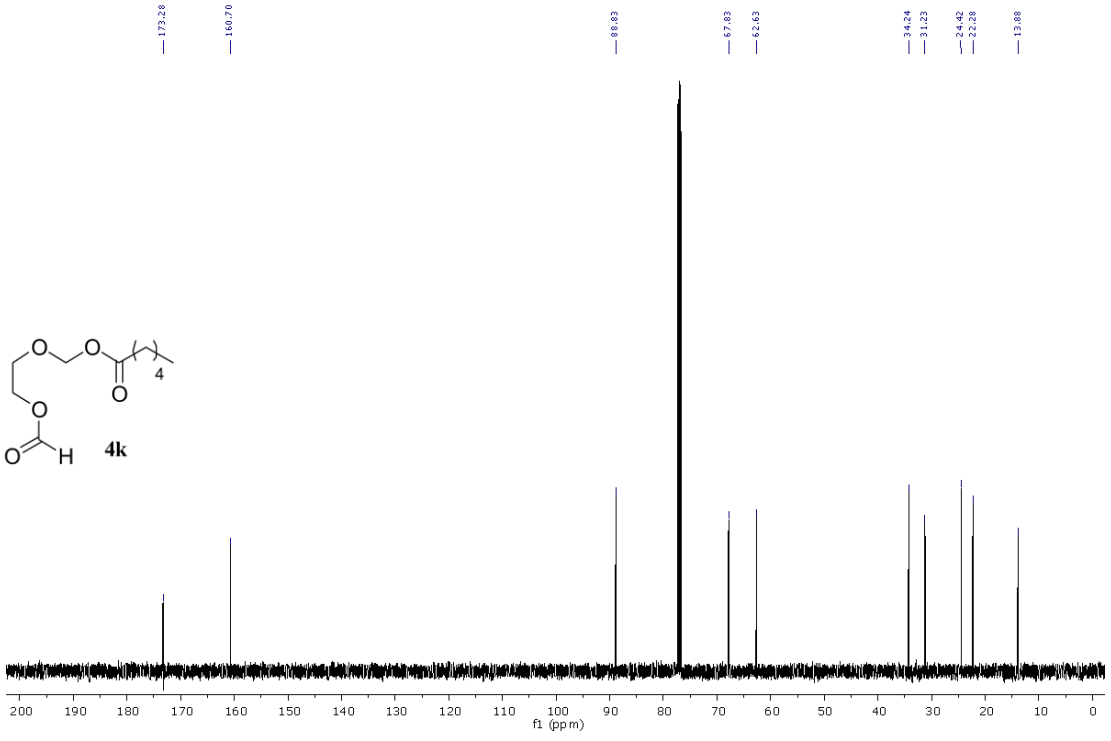


Figure S91. ^{13}C Spectrum of **4k** in $CDCl_3$ (100 MHz)

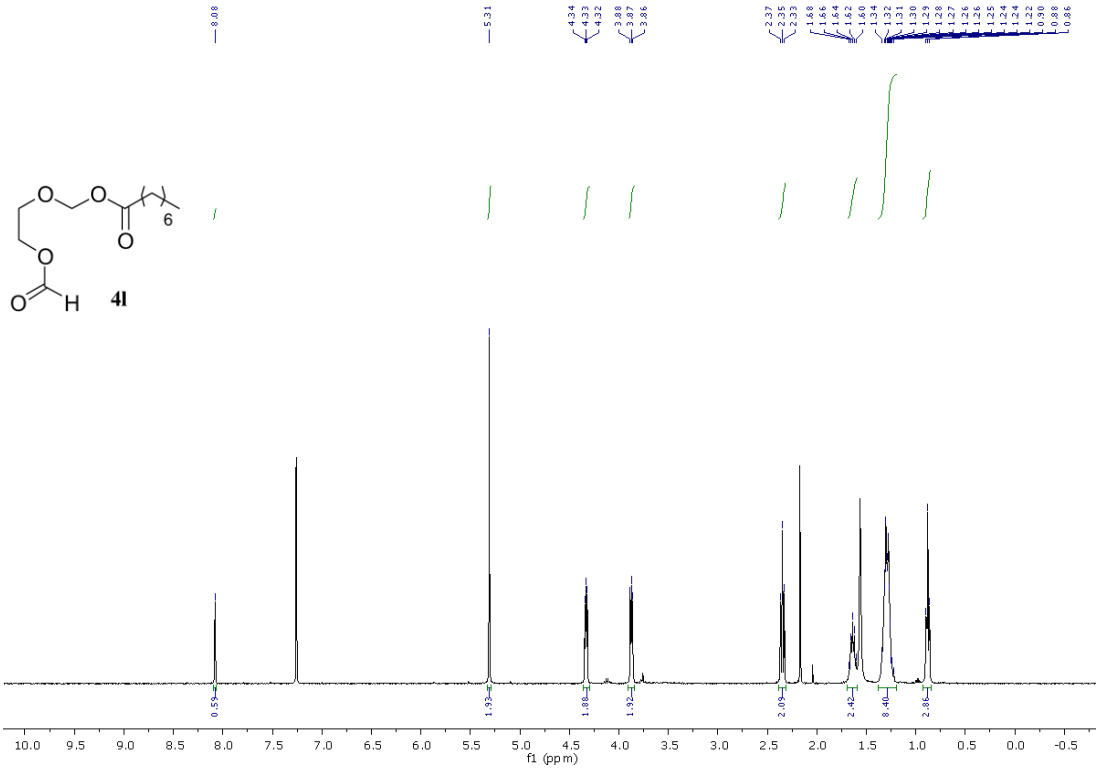


Figure S92. ^{1}H Spectrum of **4l** in $CDCl_3$ (400 MHz)

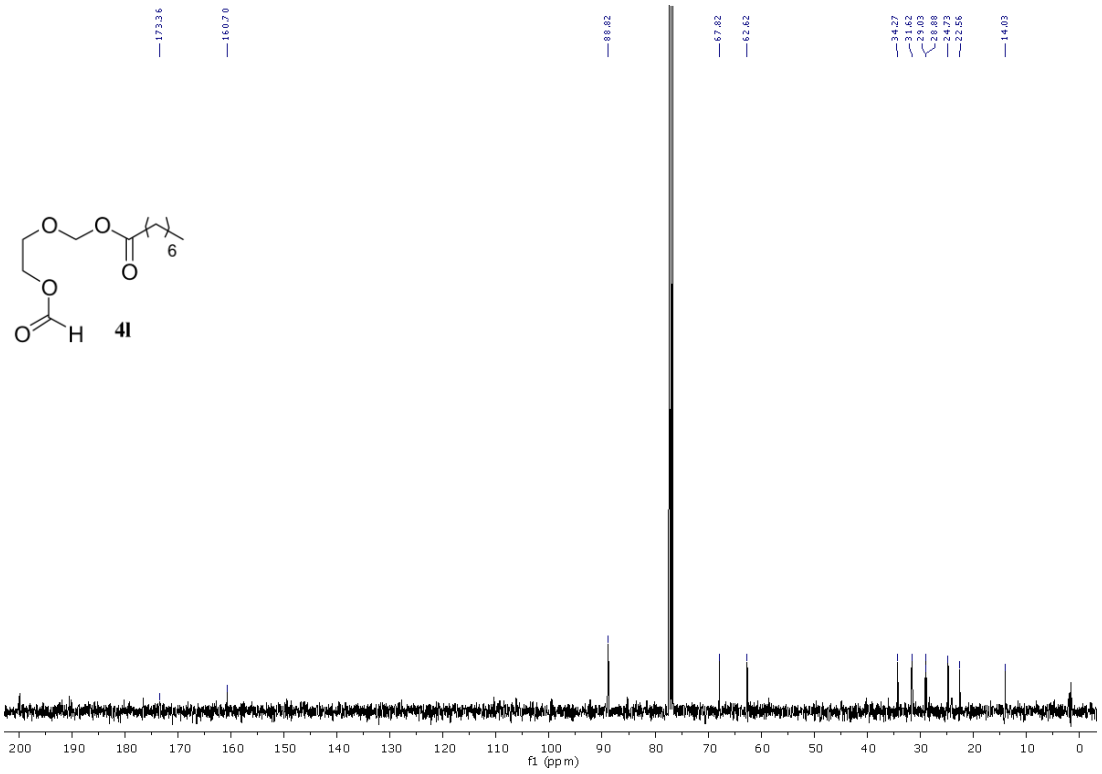


Figure S93. ^{13}C Spectrum of **4l** in $CDCl_3$ (100 MHz)

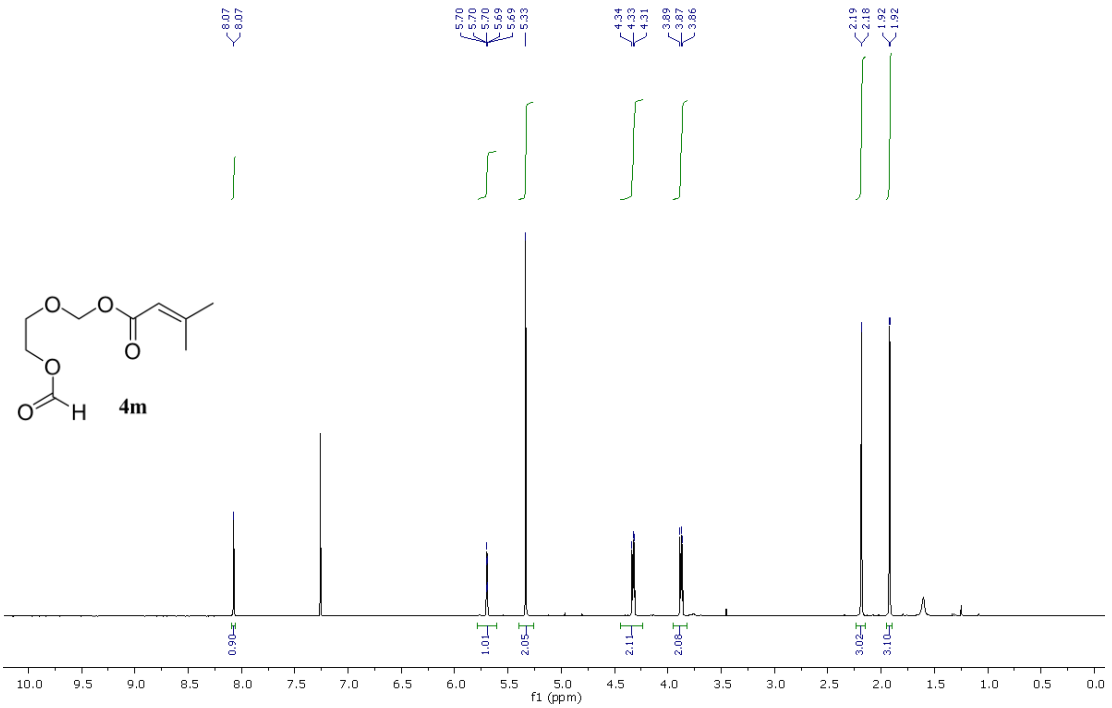


Figure S94. ^{1}H Spectrum of **4m** in $CDCl_3$ (400 MHz)

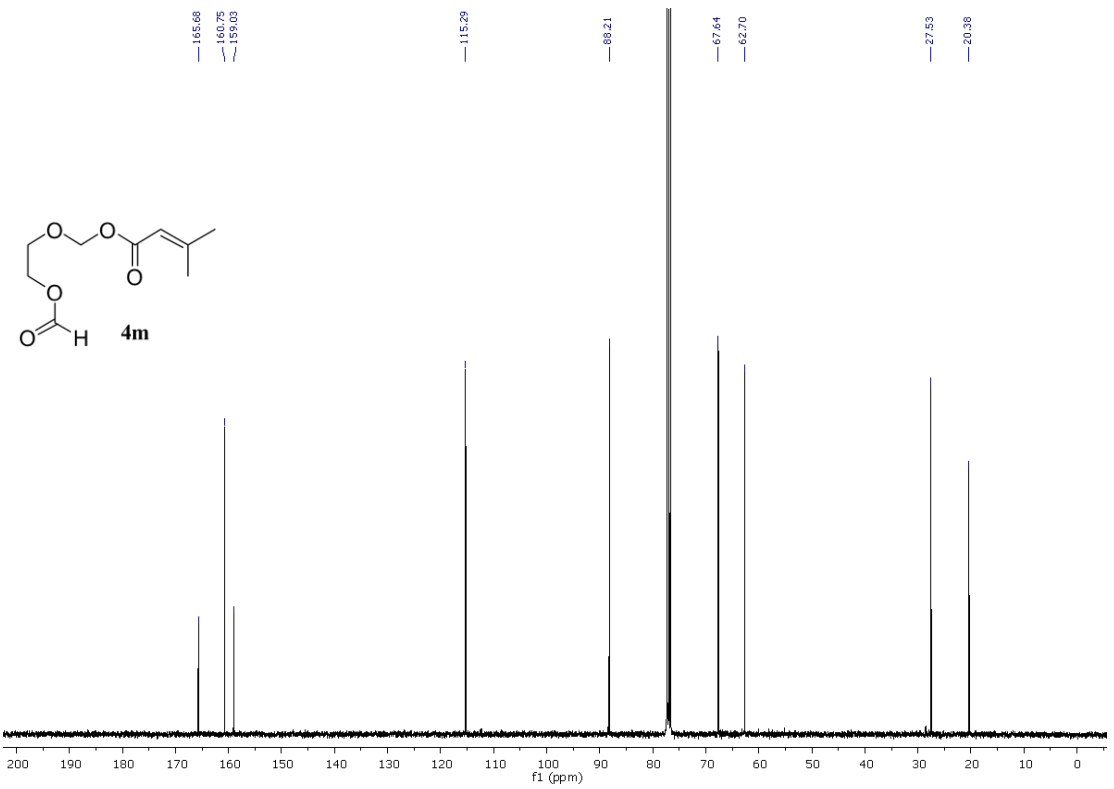


Figure S95. ^{13}C Spectrum of **4m** in $CDCl_3$ (100 MHz)

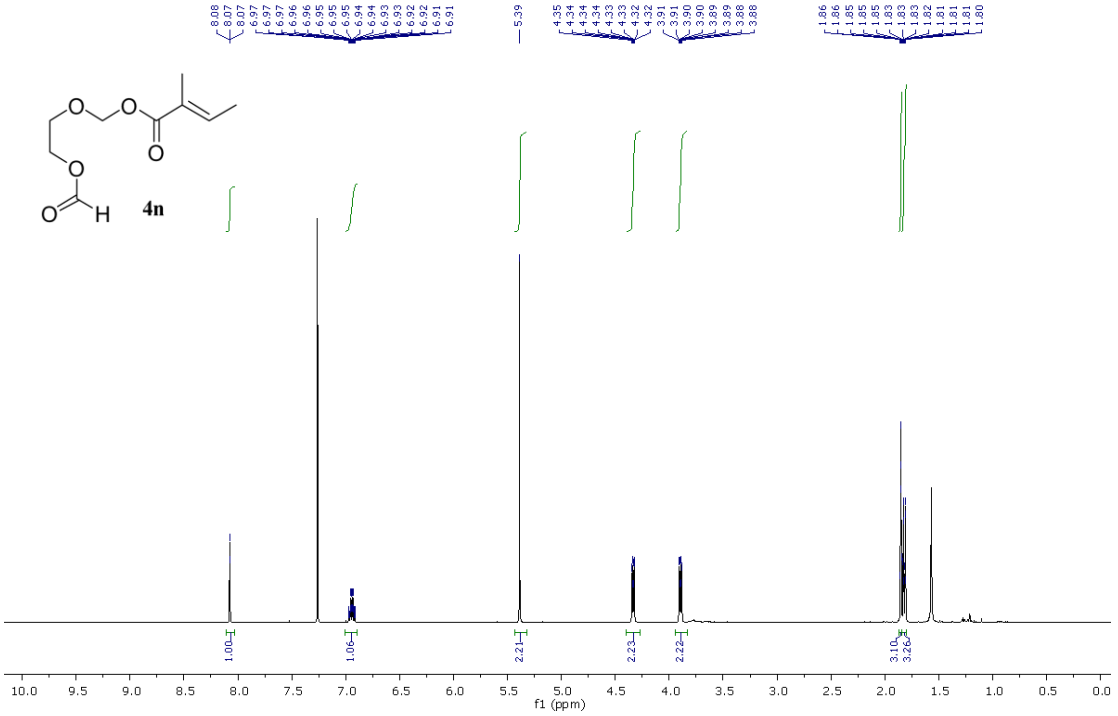


Figure S96. ^{1}H Spectrum of **4n** in $CDCl_3$ (400 MHz)

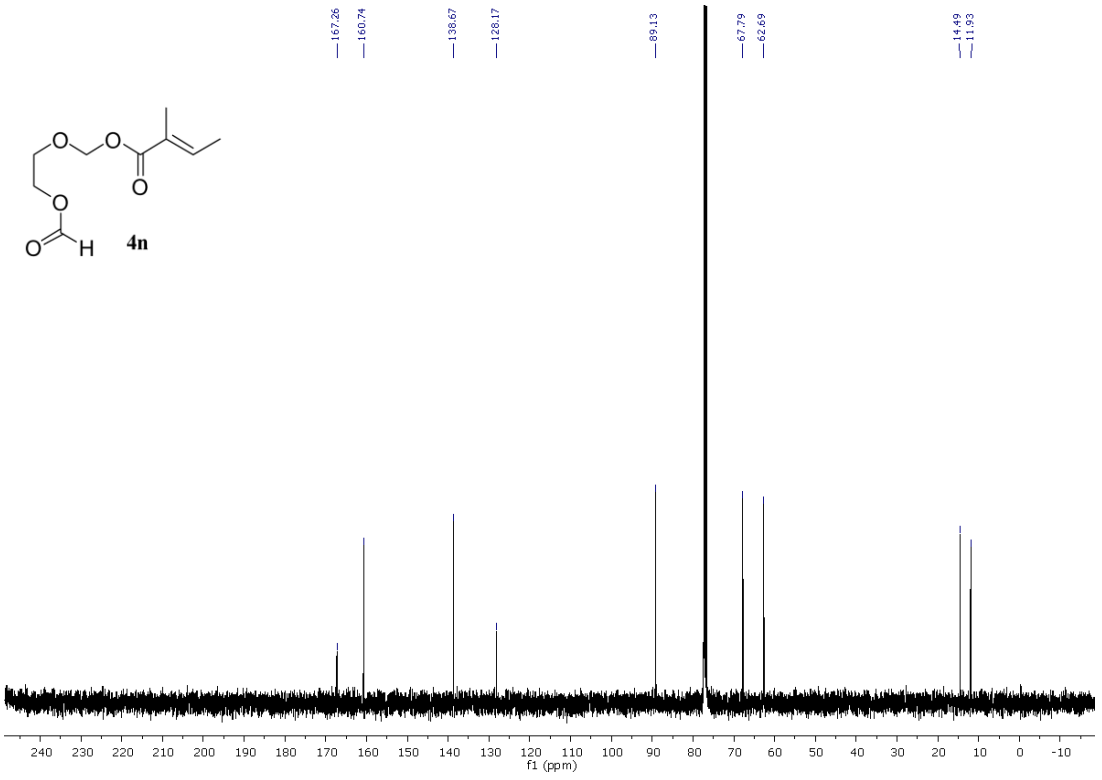


Figure S97. ^{13}C Spectrum of **4n** in $CDCl_3$ (100 MHz)

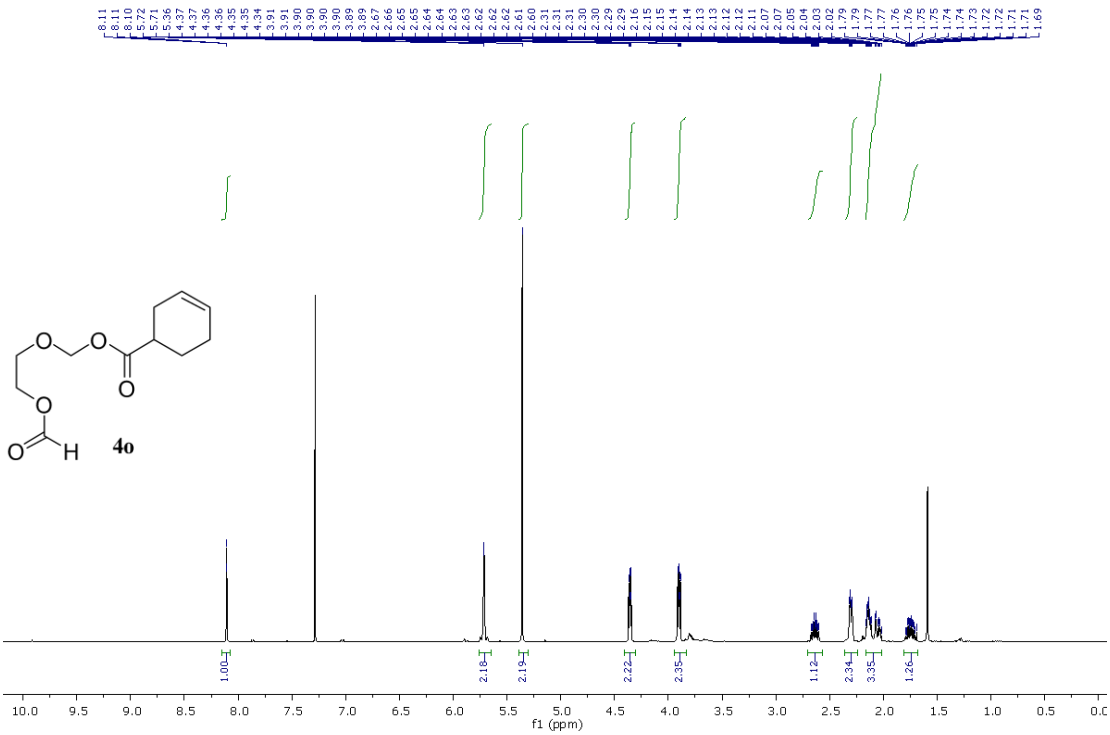


Figure S98. ^{1}H Spectrum of **4o** in $CDCl_3$ (400 MHz)

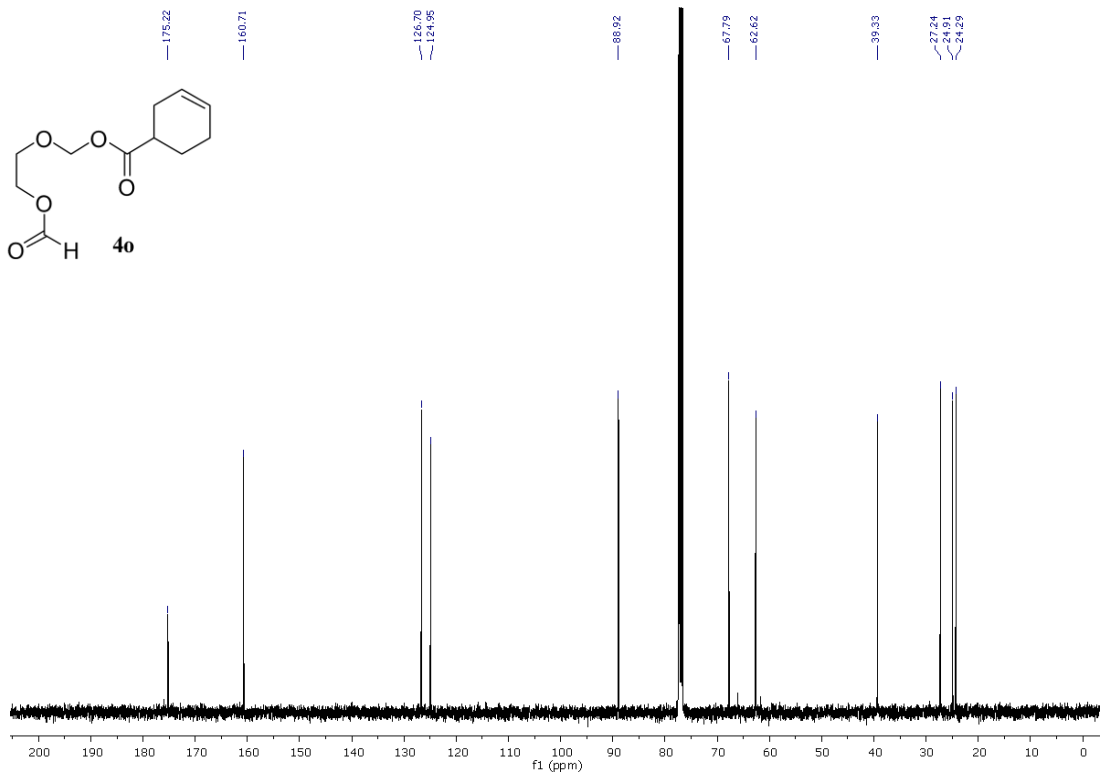


Figure S99. ^{13}C Spectrum of **4o** in $CDCl_3$ (100 MHz)

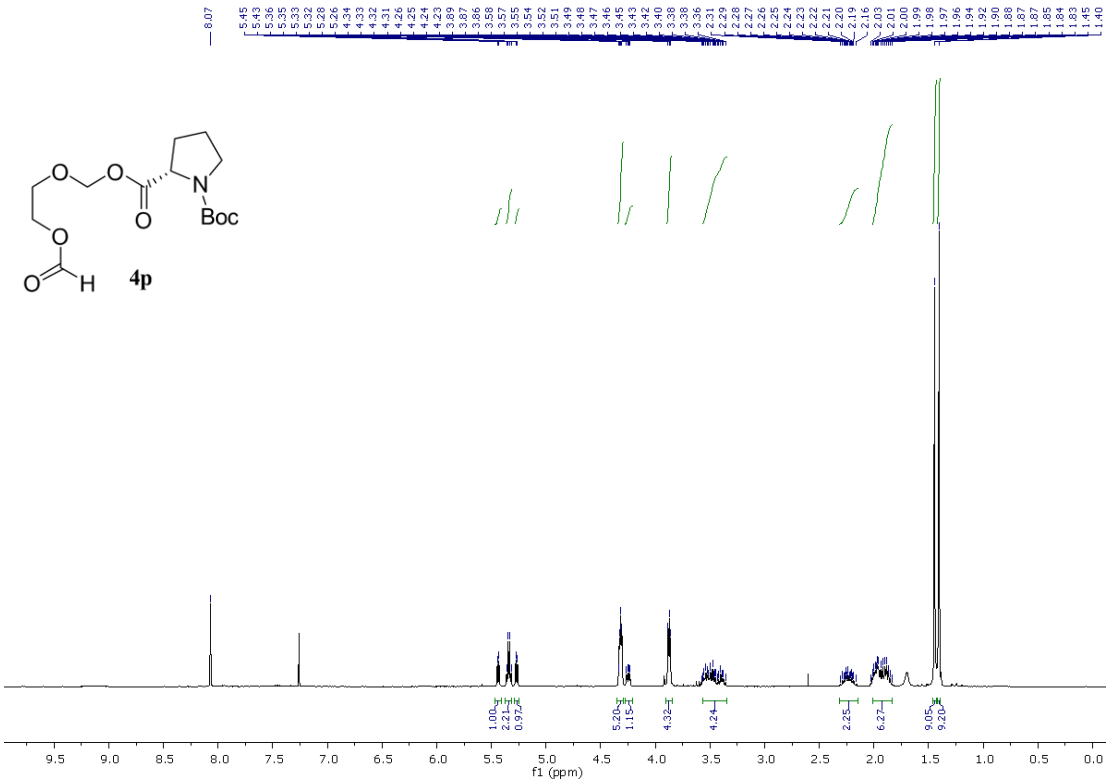


Figure S100. ^{1}H Spectrum of **4p** in $CDCl_3$ (500 MHz)

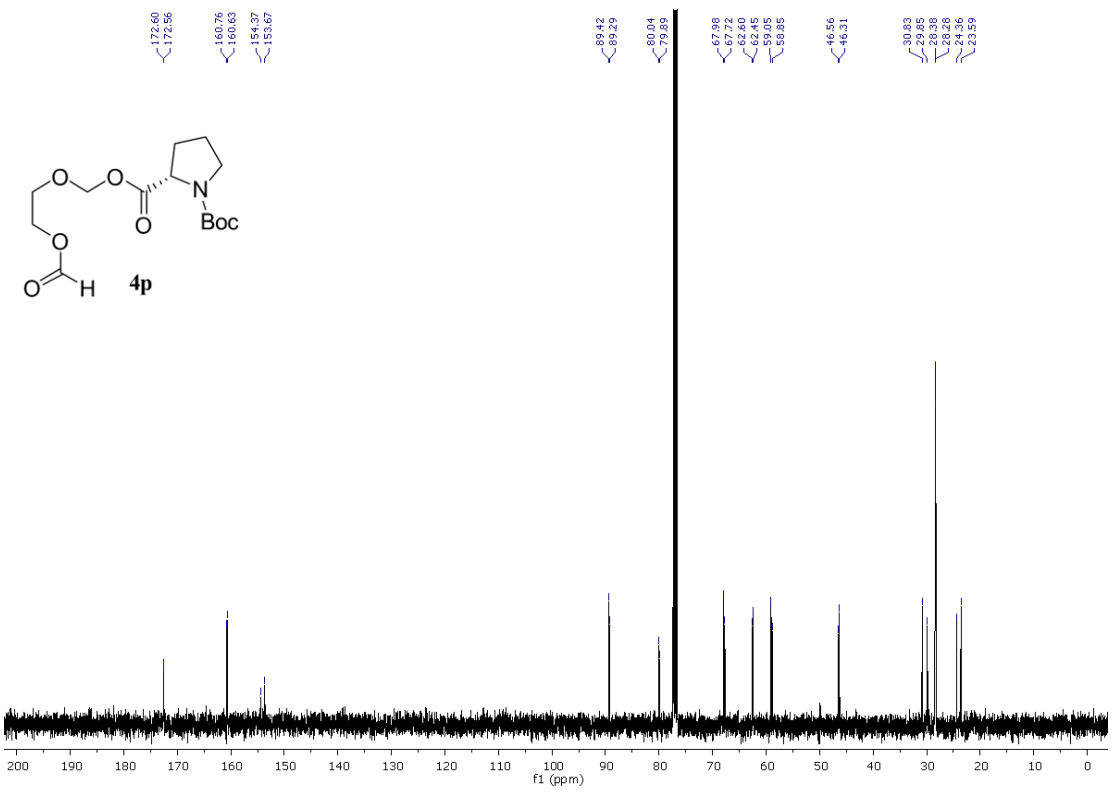


Figure S101. ^{13}C Spectrum of **4p** in $CDCl_3$ (124 MHz)

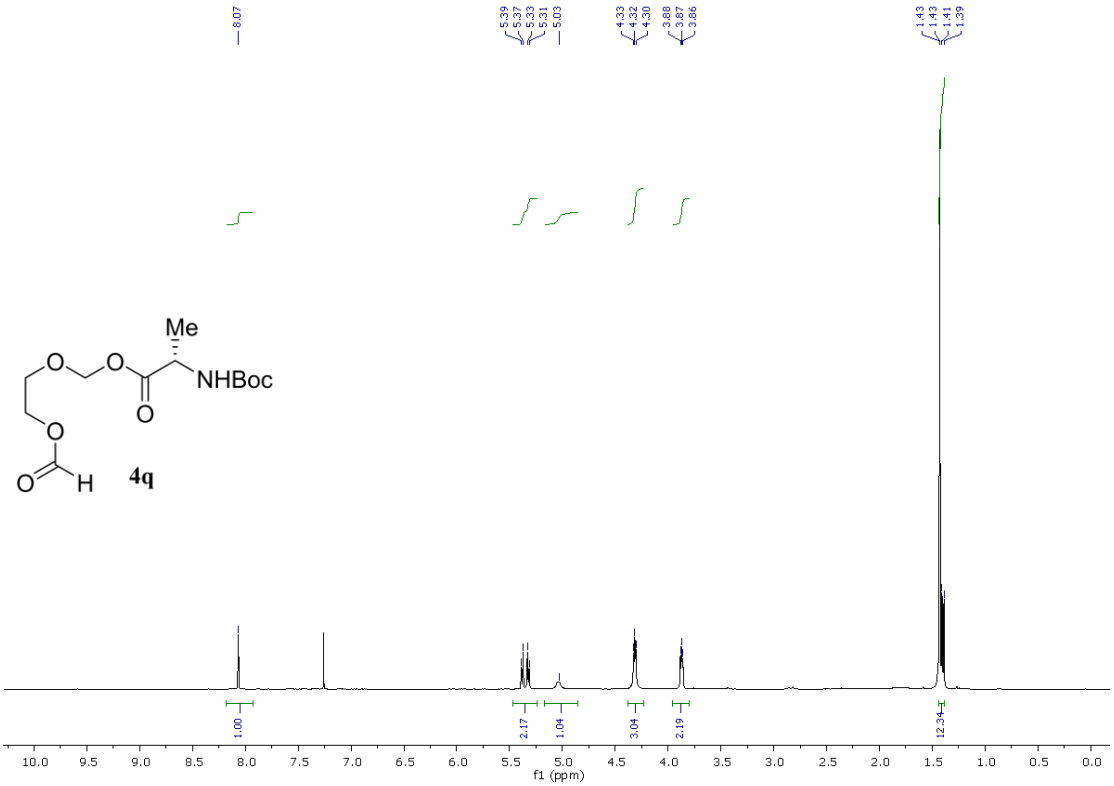


Figure S102. ^{1}H Spectrum of **4q** in $CDCl_3$ (400 MHz)

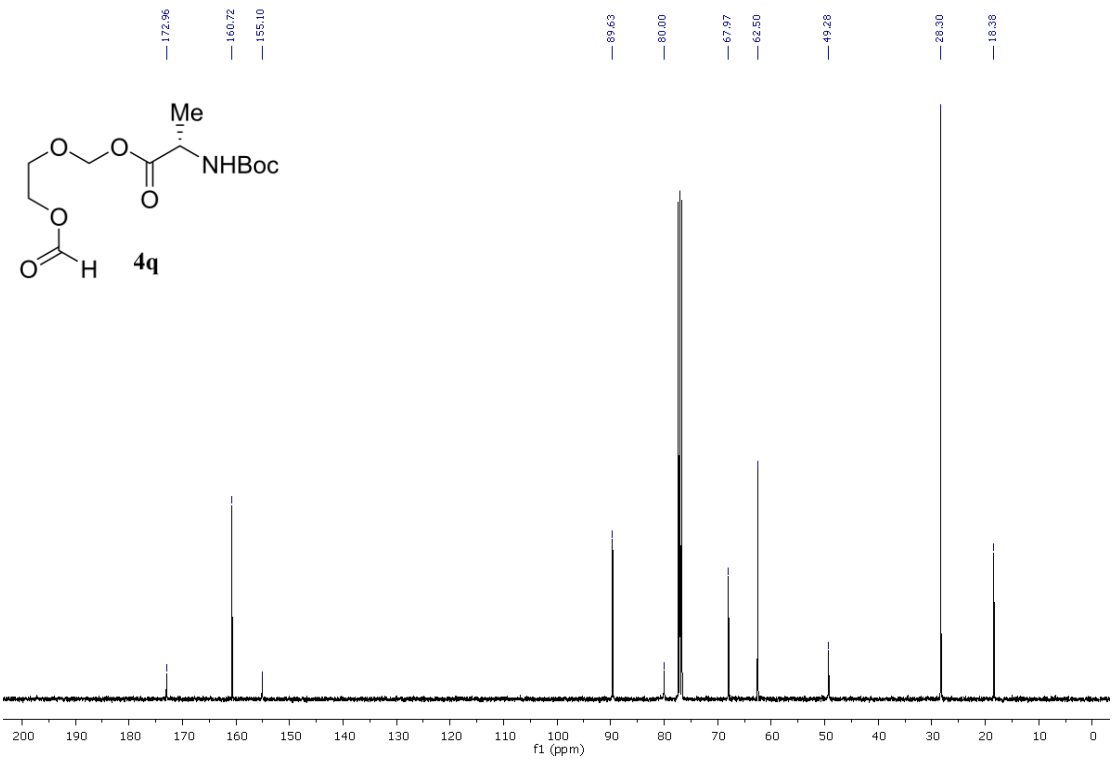


Figure S103. ^{13}C Spectrum of **4q** in $CDCl_3$ (100 MHz)

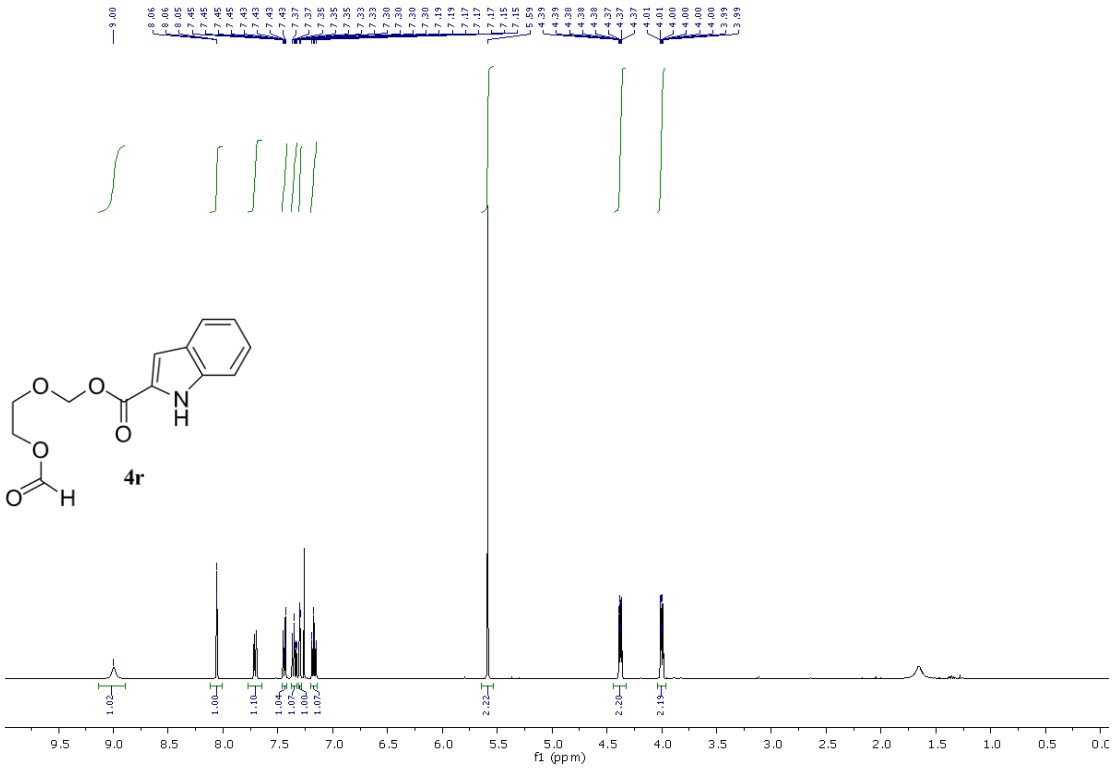


Figure S104. ^{1}H Spectrum of **4r** in $CDCl_3$ (400 MHz)

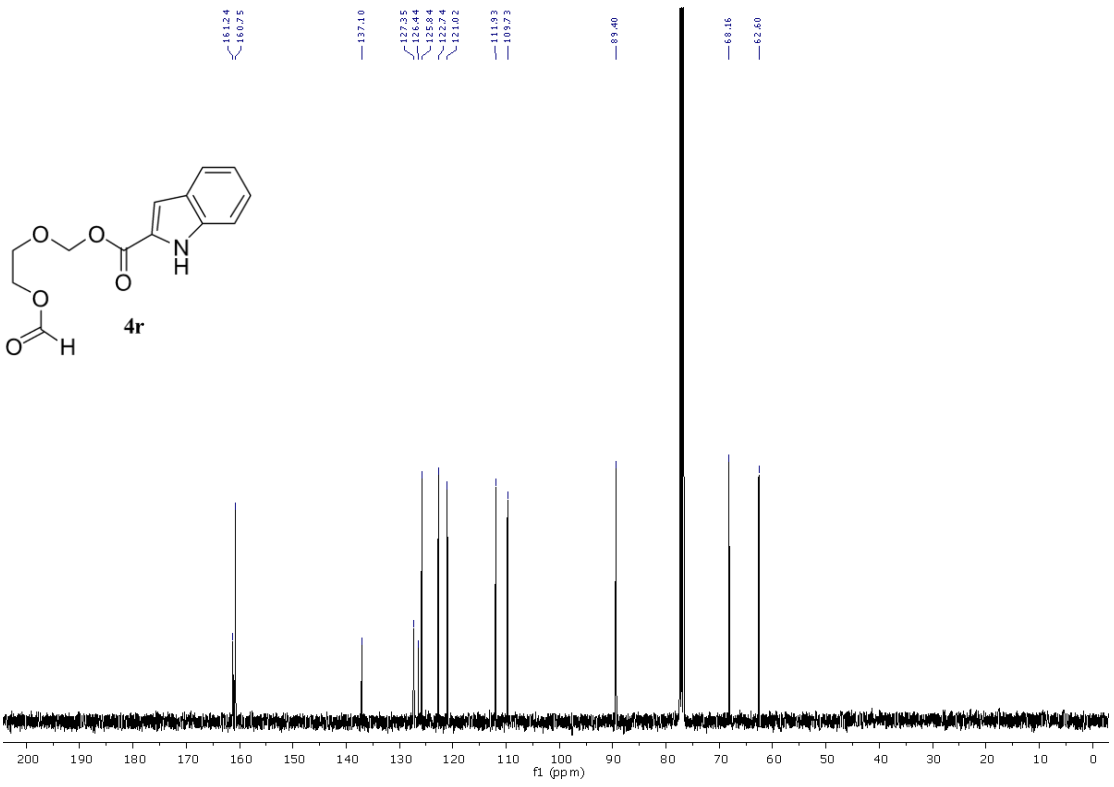


Figure S105. ^{13}C Spectrum of **4r** in $CDCl_3$ (100 MHz)

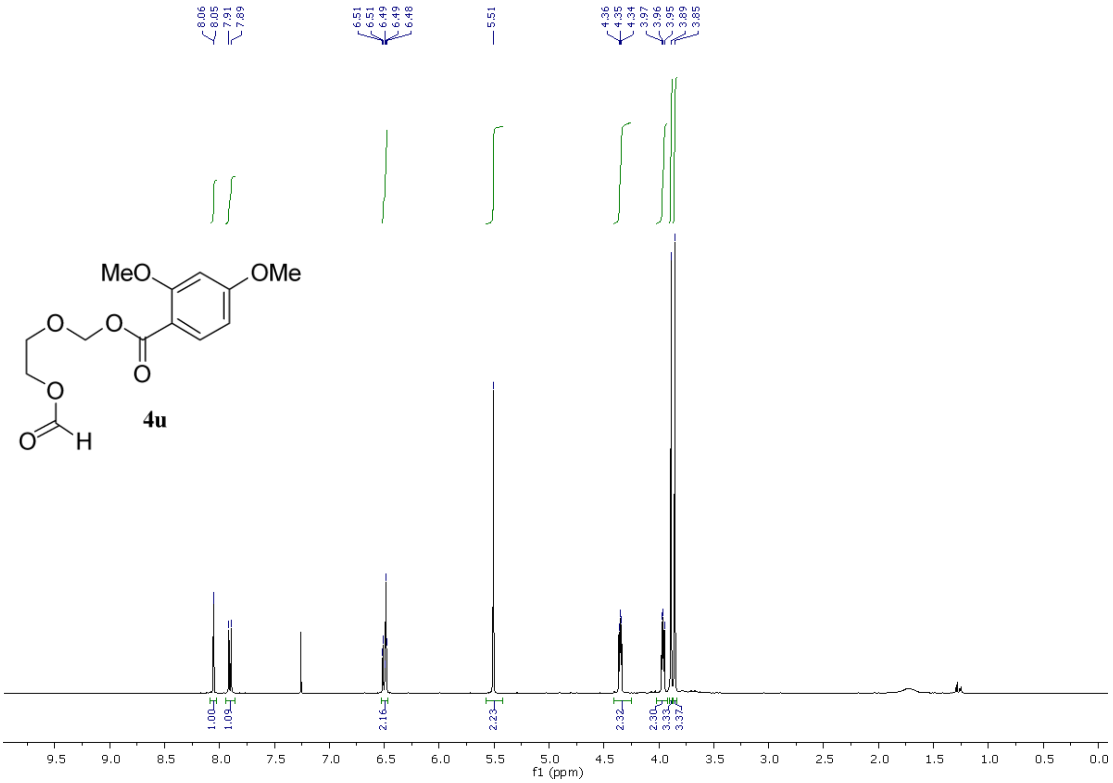


Figure S106. ^{1}H Spectrum of **4u** in $CDCl_3$ (400 MHz)

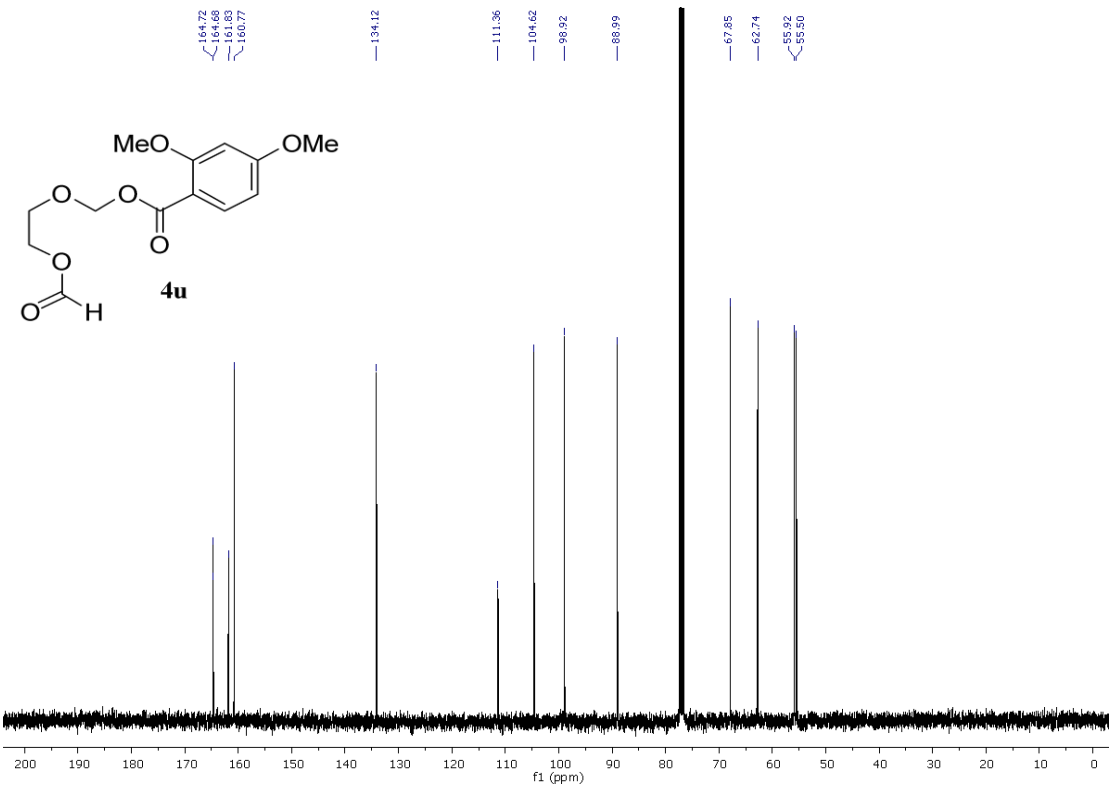


Figure S107. ^{13}C Spectrum of **4u** in $CDCl_3$ (100 MHz)

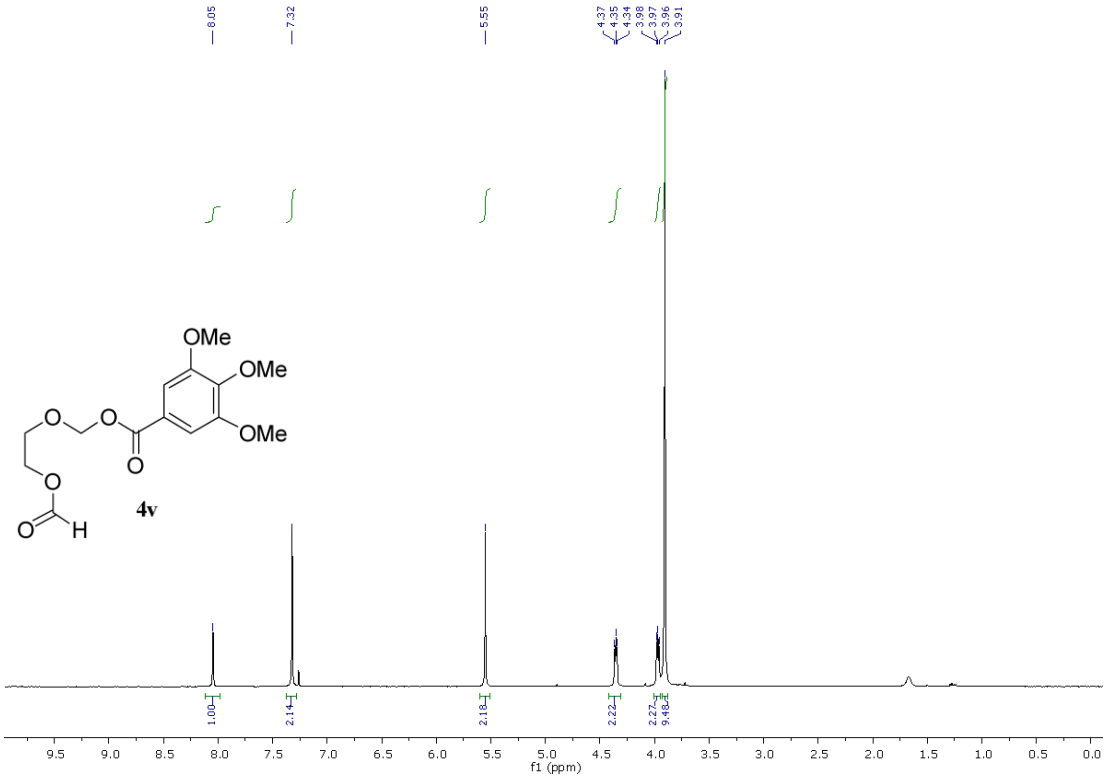


Figure S108. ^{1}H Spectrum of **4v** in $CDCl_3$ (400 MHz)

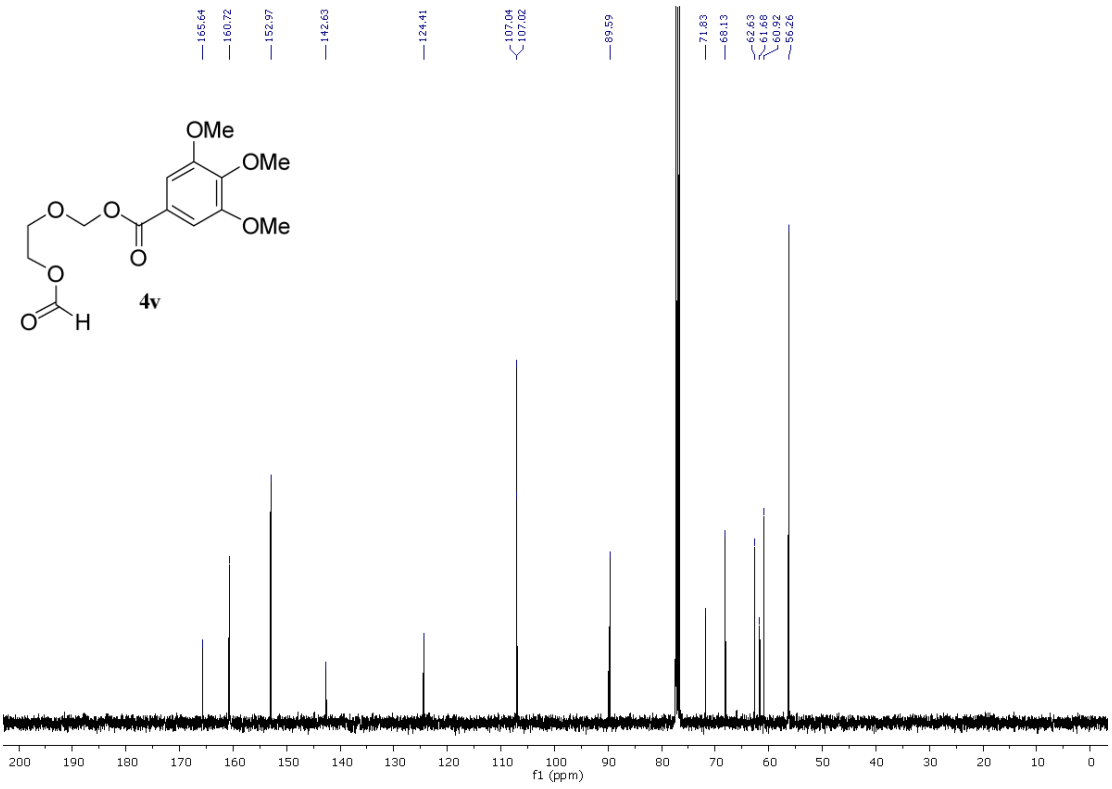


Figure S109. ^{13}C Spectrum of **4v** in $CDCl_3$ (100 MHz)

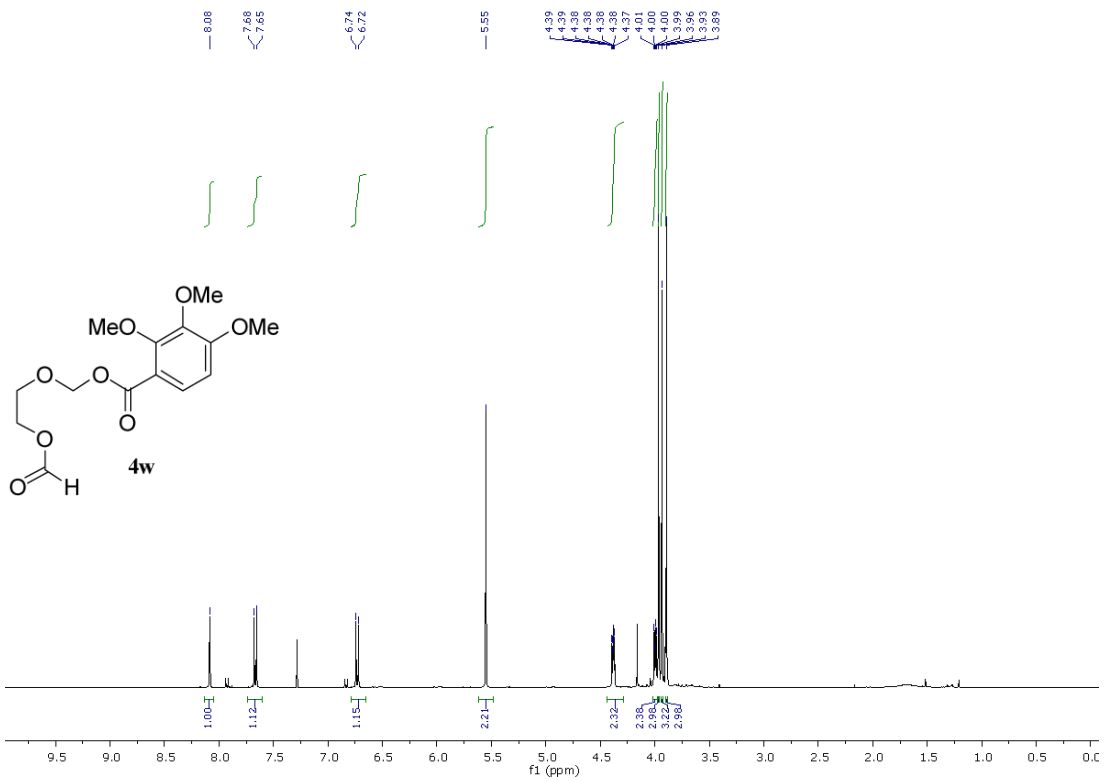


Figure S110. ^{1}H Spectrum of **4w** in $CDCl_3$ (400 MHz)

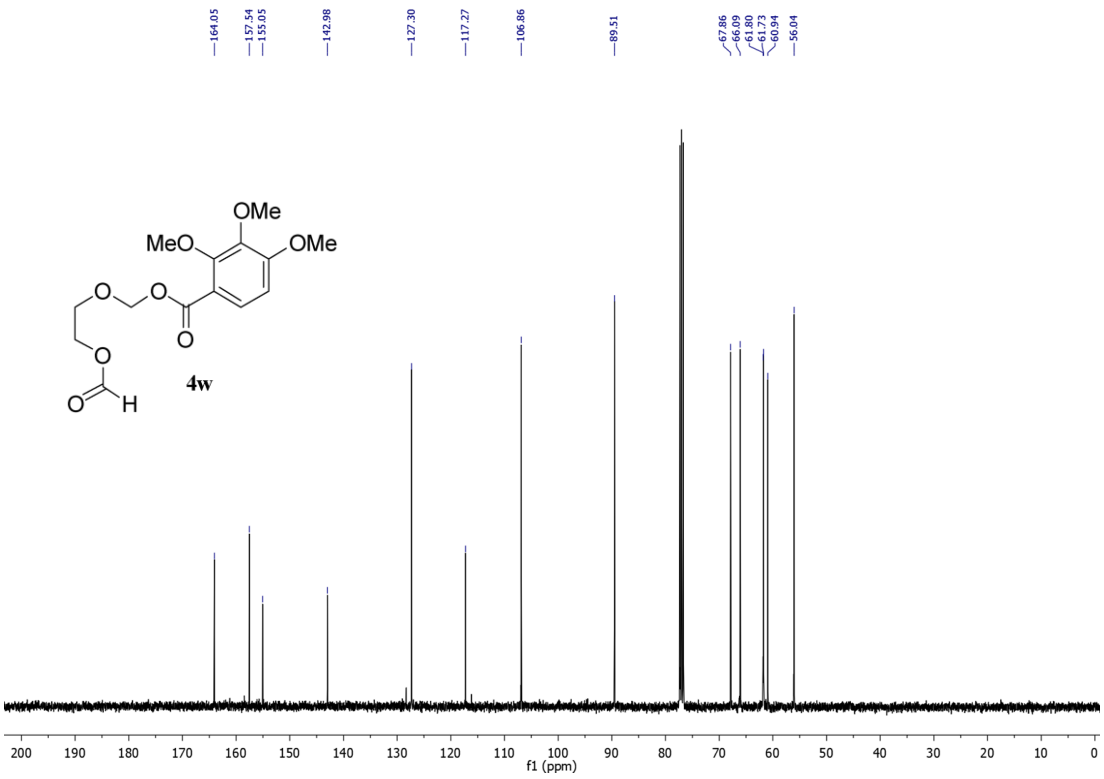


Figure S111. ^{13}C Spectrum of **4w** in $CDCl_3$ (100 MHz)

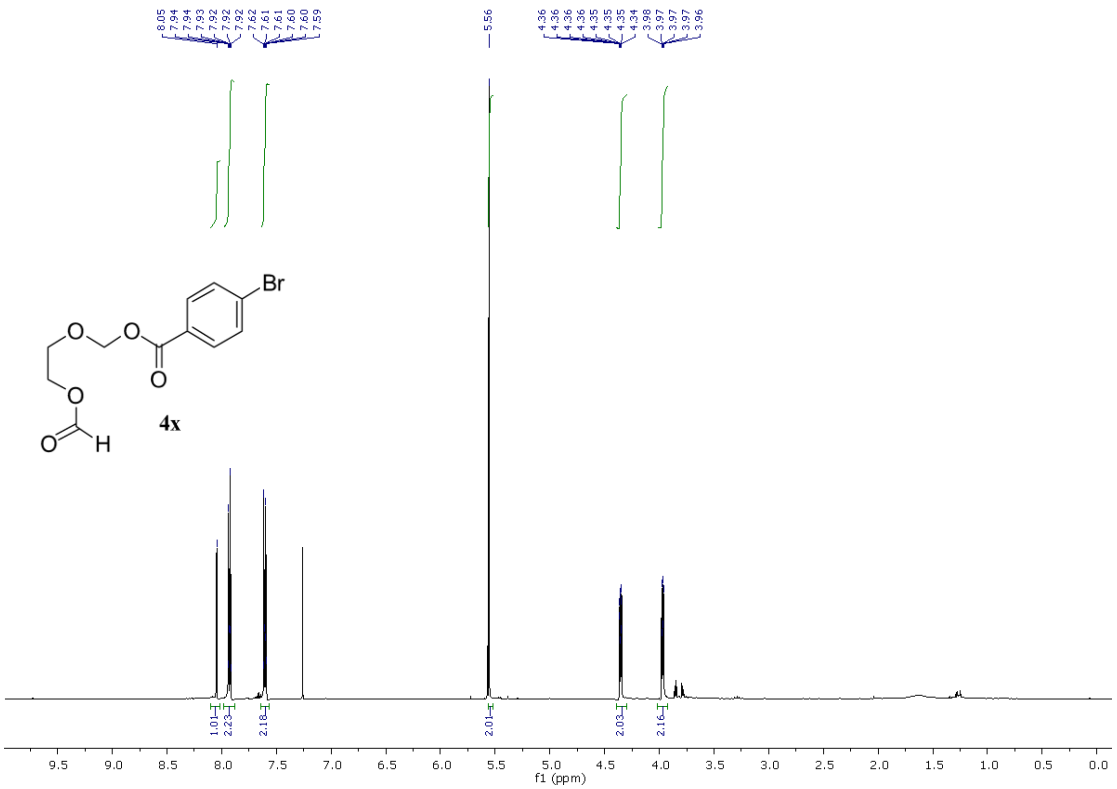


Figure S112. ^{1}H Spectrum of **4x** in $CDCl_3$ (500 MHz)

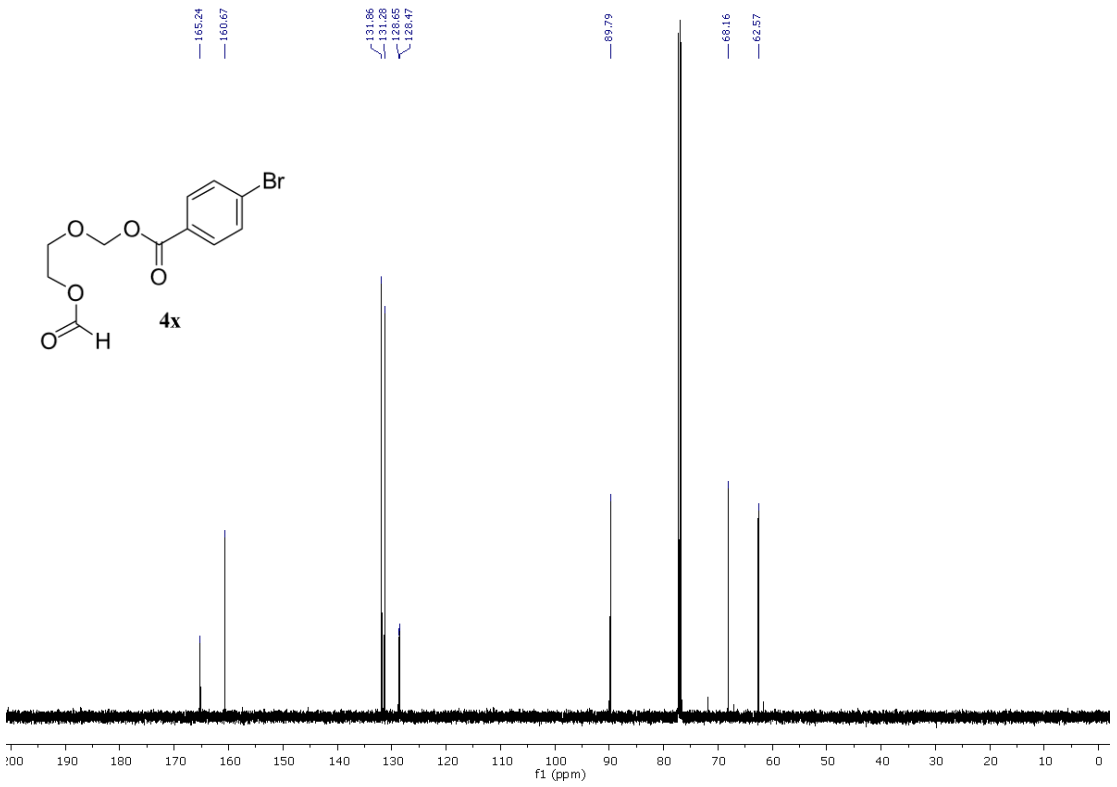


Figure S113. ^{13}C Spectrum of **4x** in $CDCl_3$ (125 MHz)

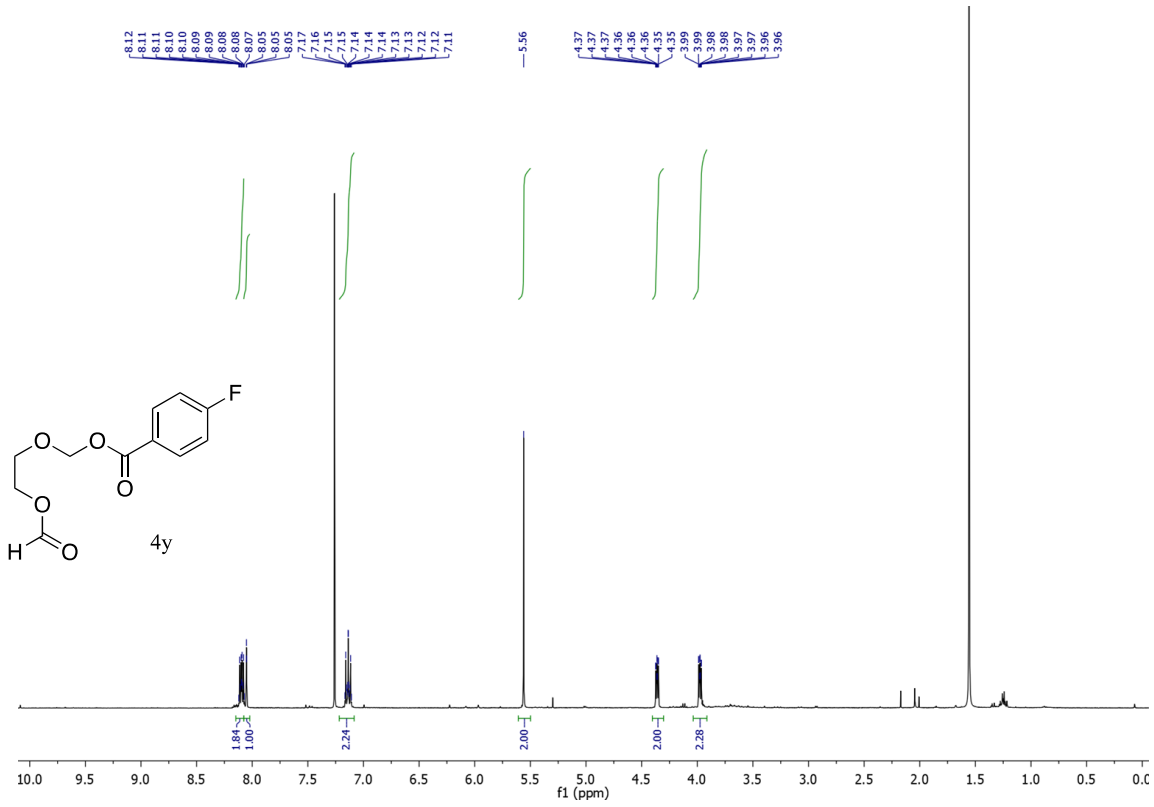


Figure S114. ^{1}H Spectrum of **4y** in $CDCl_3$ (500 MHz)

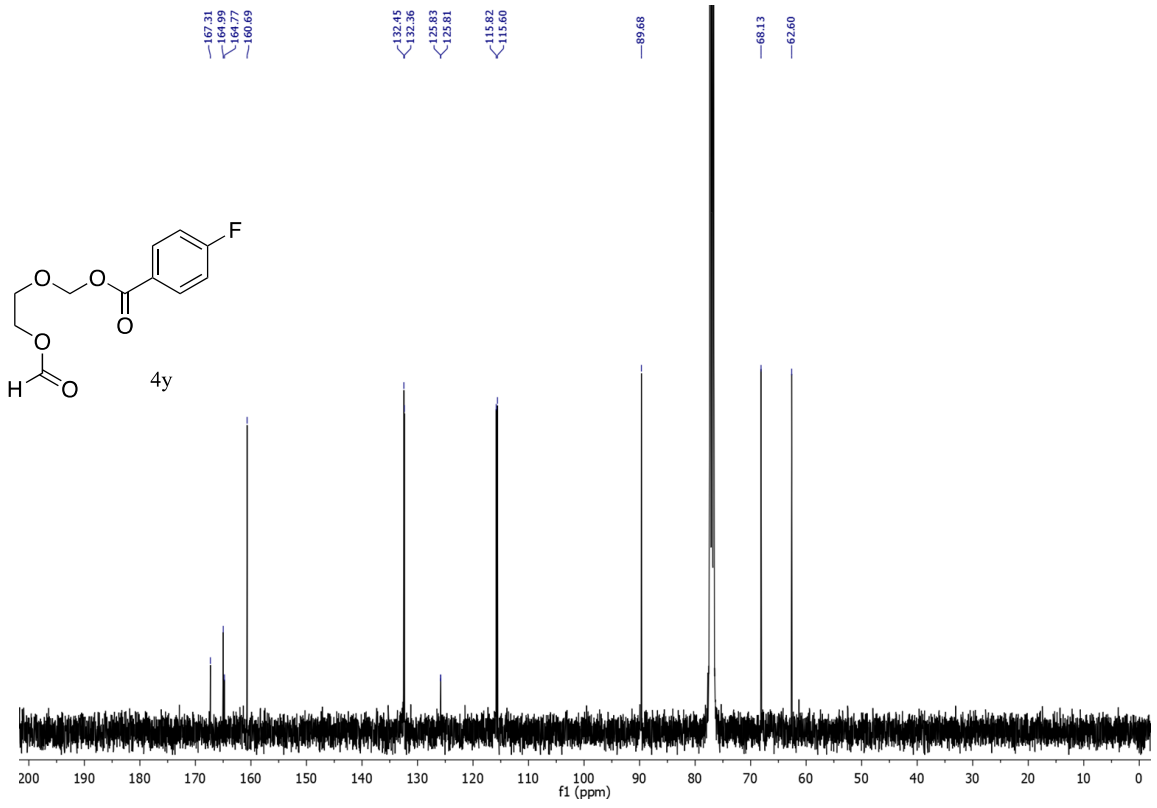


Figure S115. ^{13}C Spectrum of **4y** in $CDCl_3$ (125 MHz)

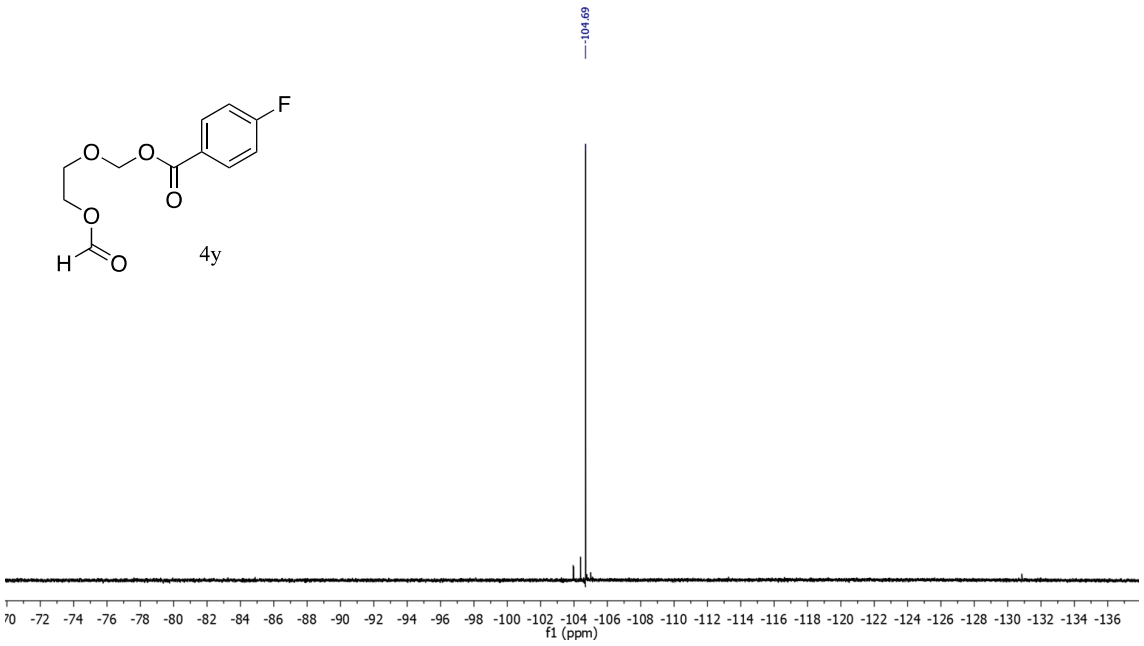


Figure S116. ^{19}F Spectrum of **4y** in $CDCl_3$ (376 MHz)

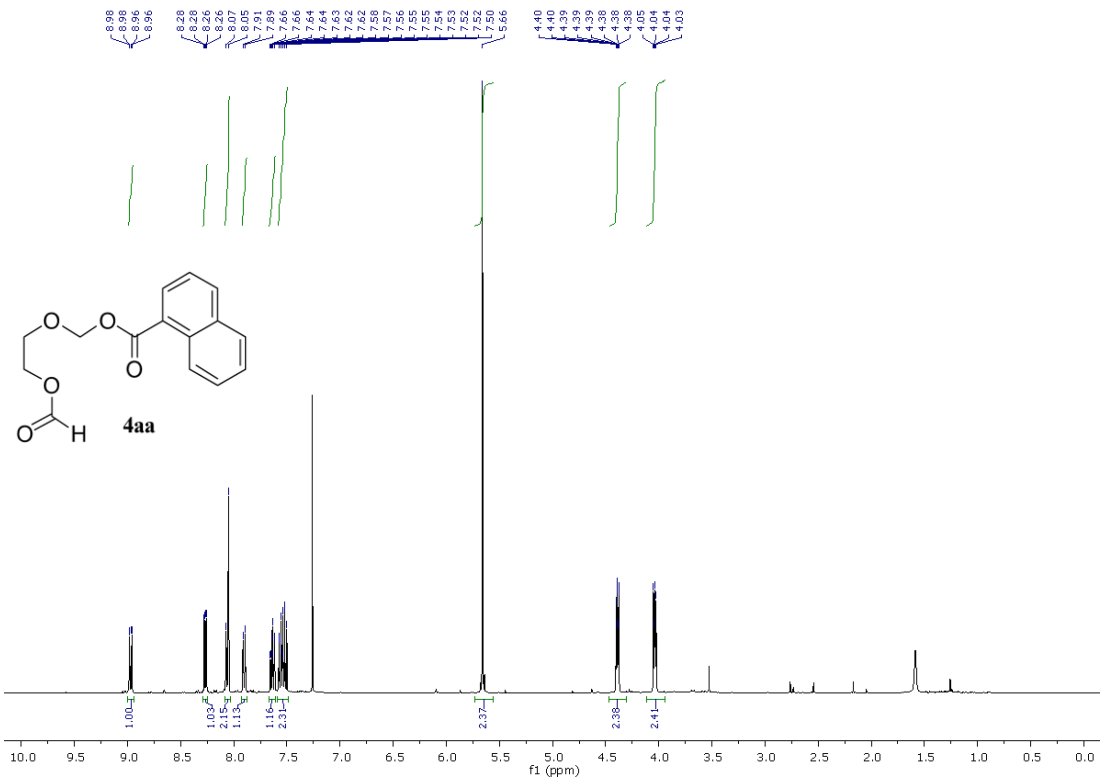


Figure S117. ^{1}H Spectrum of **4aa** in $CDCl_3$ (400 MHz)

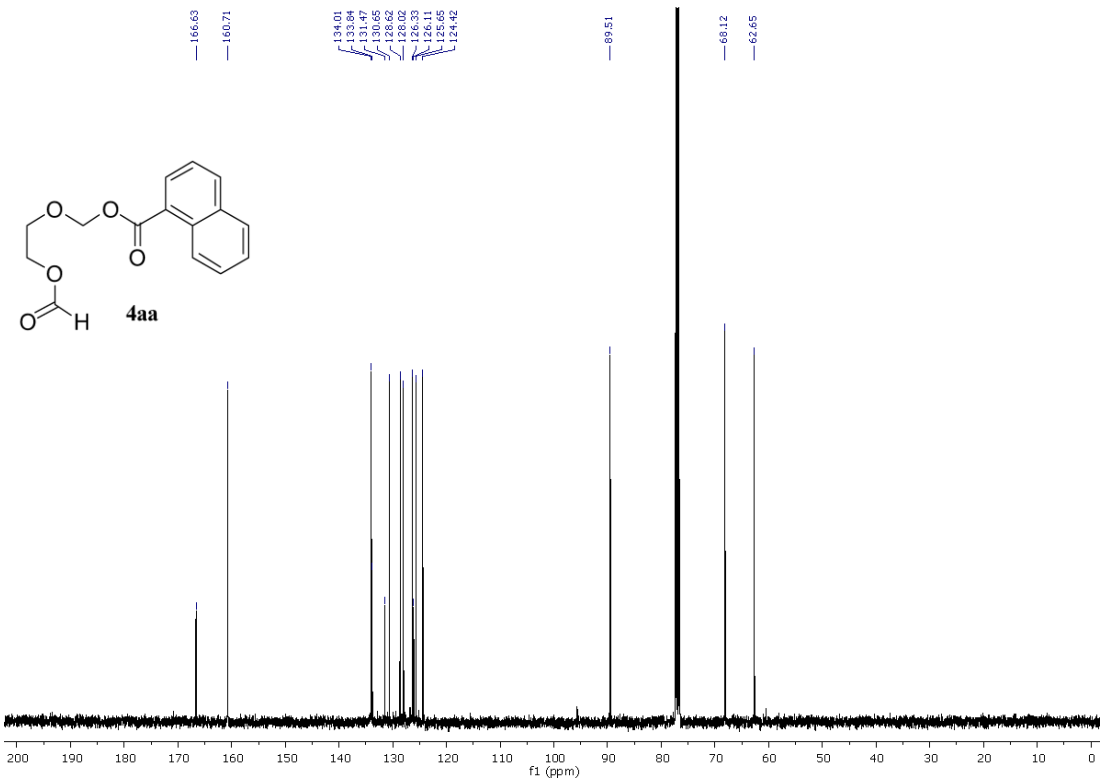


Figure S118. ^{13}C Spectrum of **4aa** in $CDCl_3$ (100 MHz)

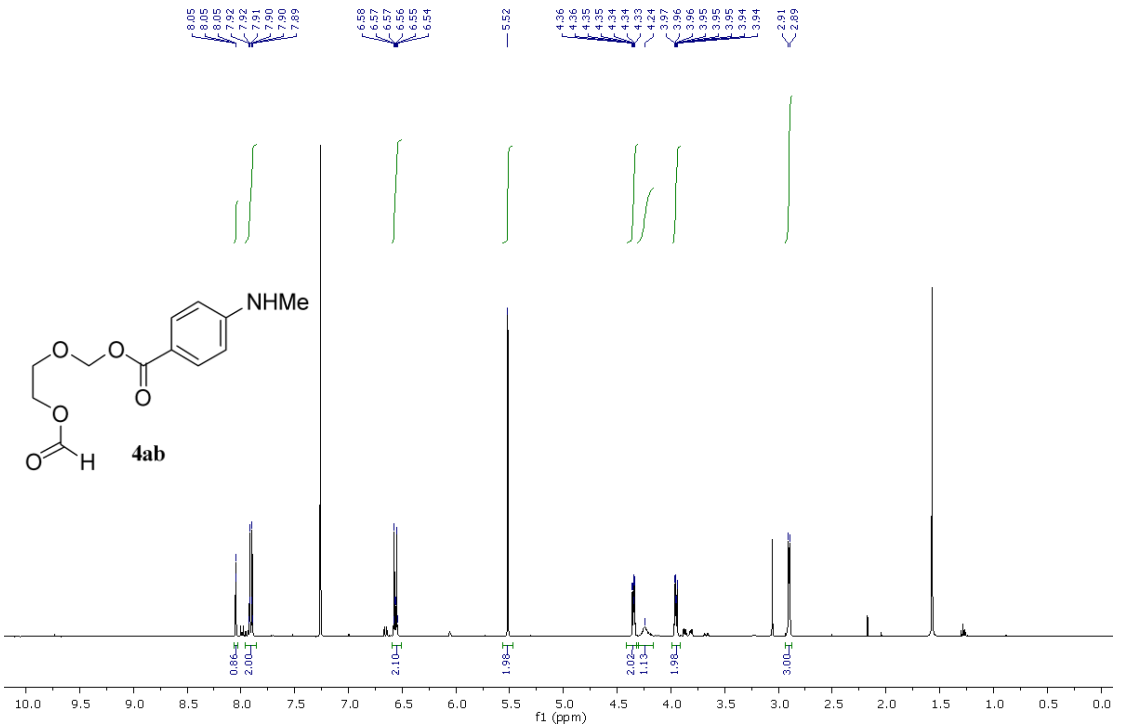


Figure S119. ^{1}H Spectrum of **4ab** in $CDCl_3$ (400 MHz)

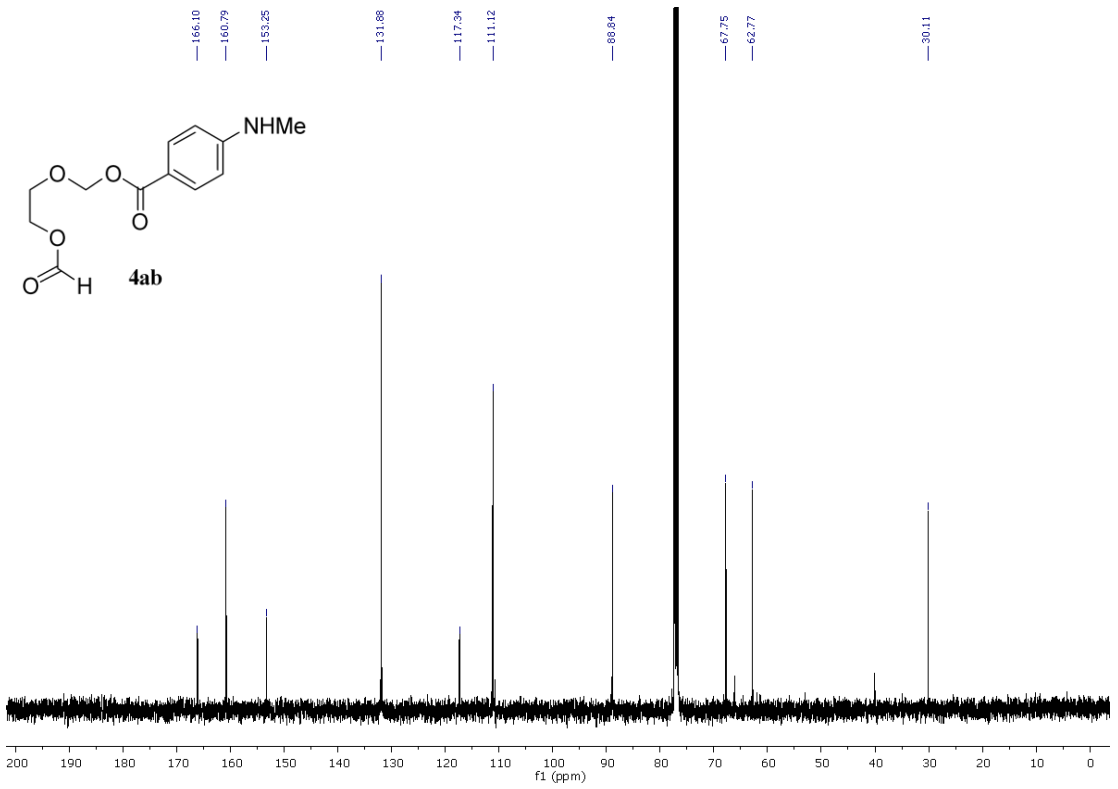


Figure S120. ^{13}C Spectrum of **4ab** in $CDCl_3$ (100 MHz)

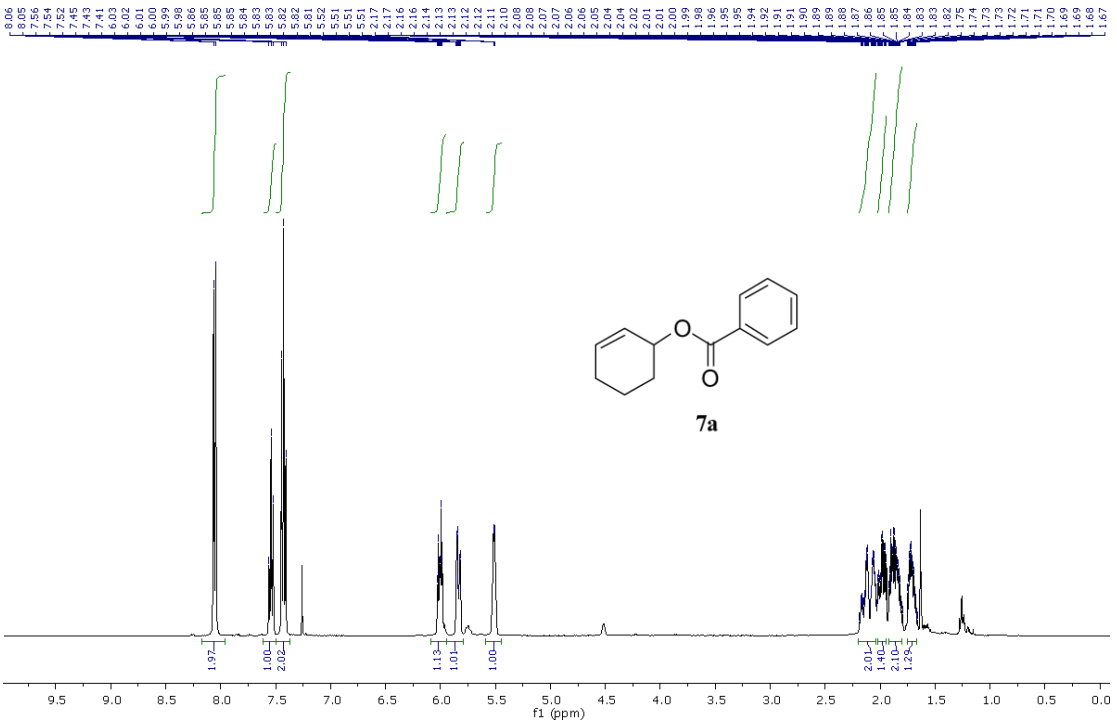


Figure S121. ^{1}H Spectrum of **7a** in $CDCl_3$ (400 MHz)

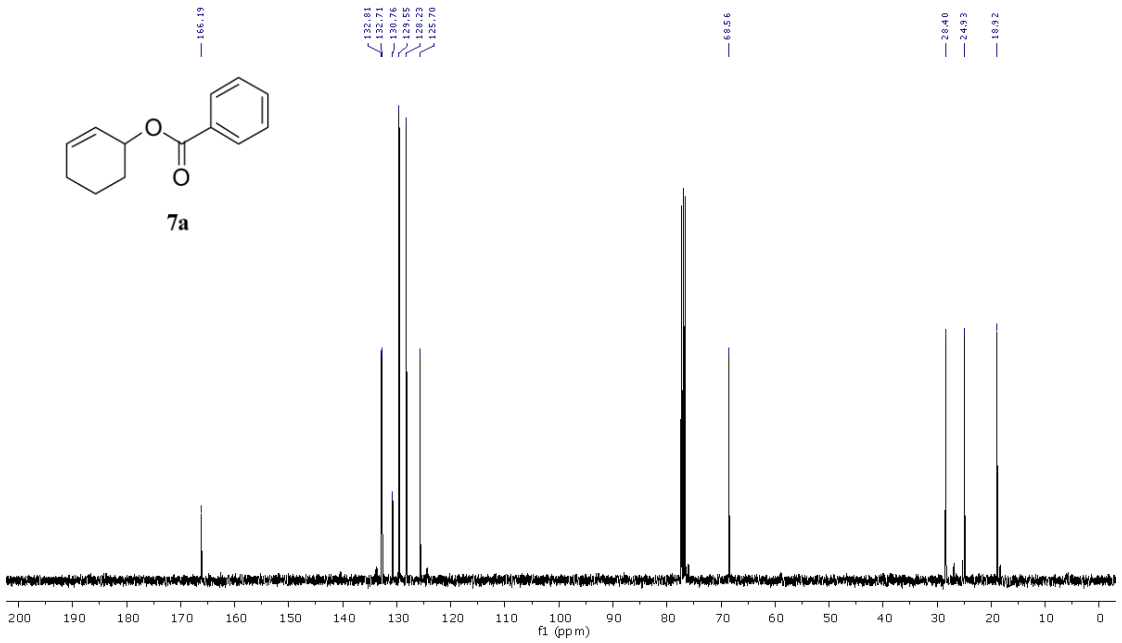


Figure S122. ^{13}C Spectrum of **7a** in $CDCl_3$ (100 MHz)

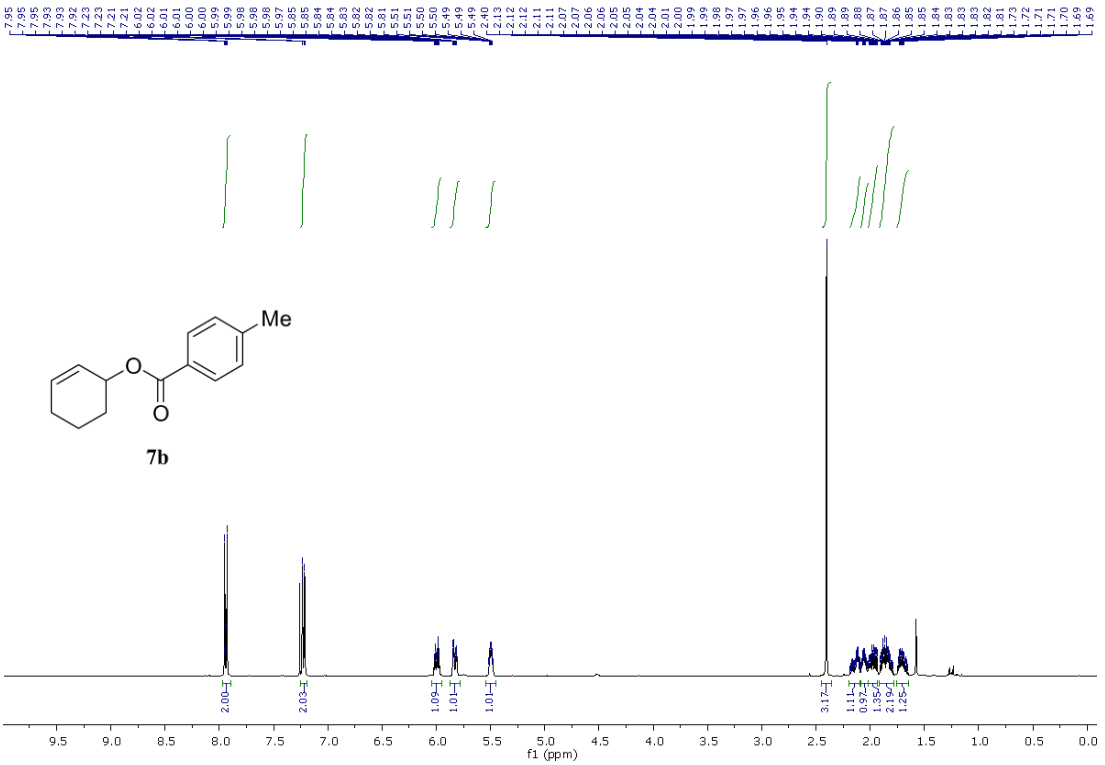


Figure S123. ^{1}H Spectrum of **7b** in $CDCl_3$ (400 MHz)

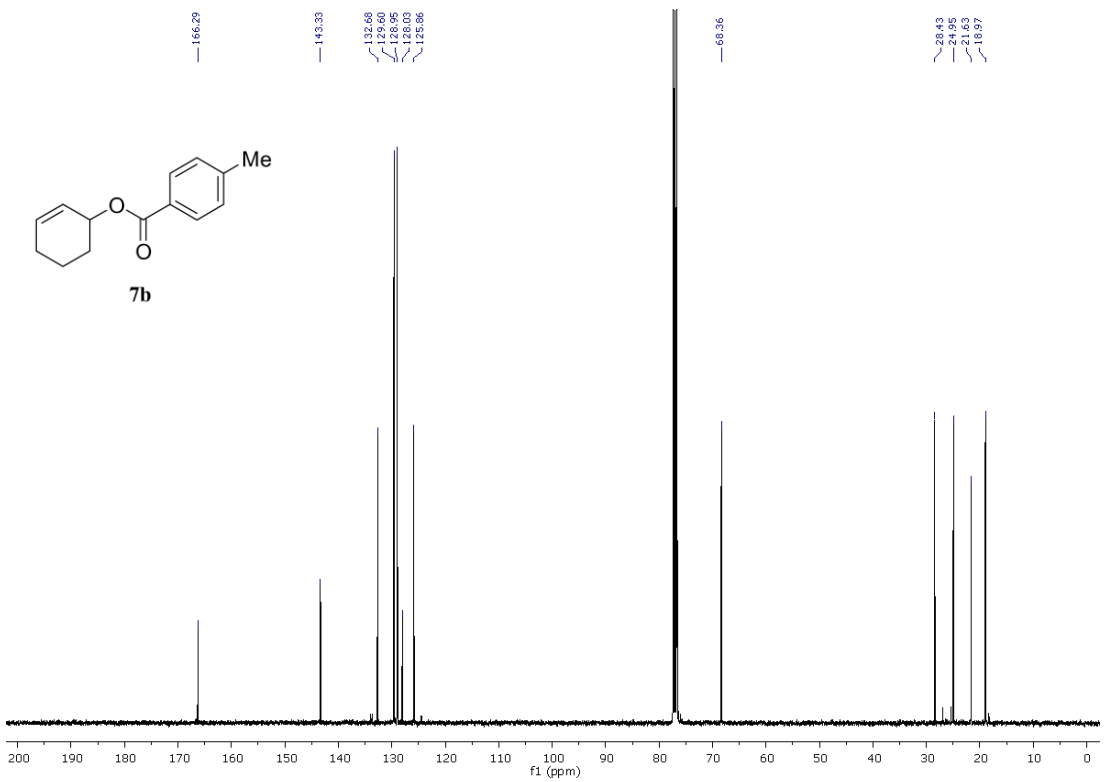


Figure S124. ^{13}C Spectrum of **7b** in $CDCl_3$ (100 MHz)

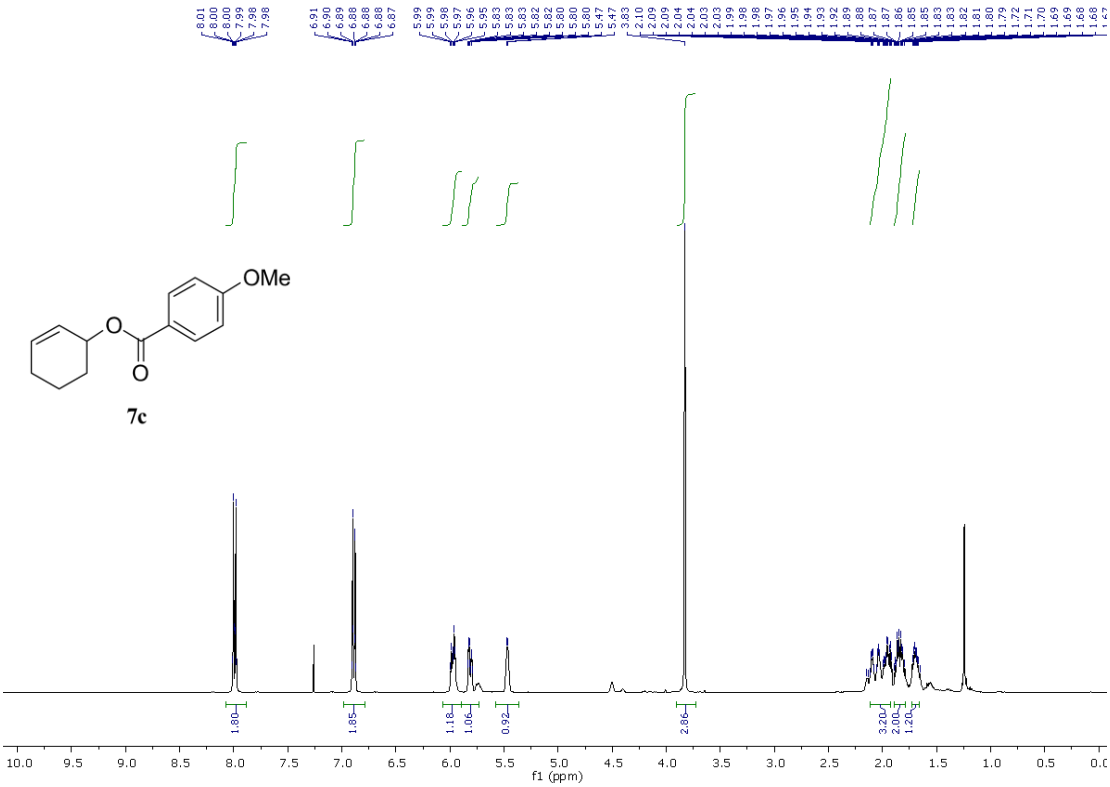


Figure S125. ^{1}H Spectrum of **7c** in $CDCl_3$ (400 MHz)

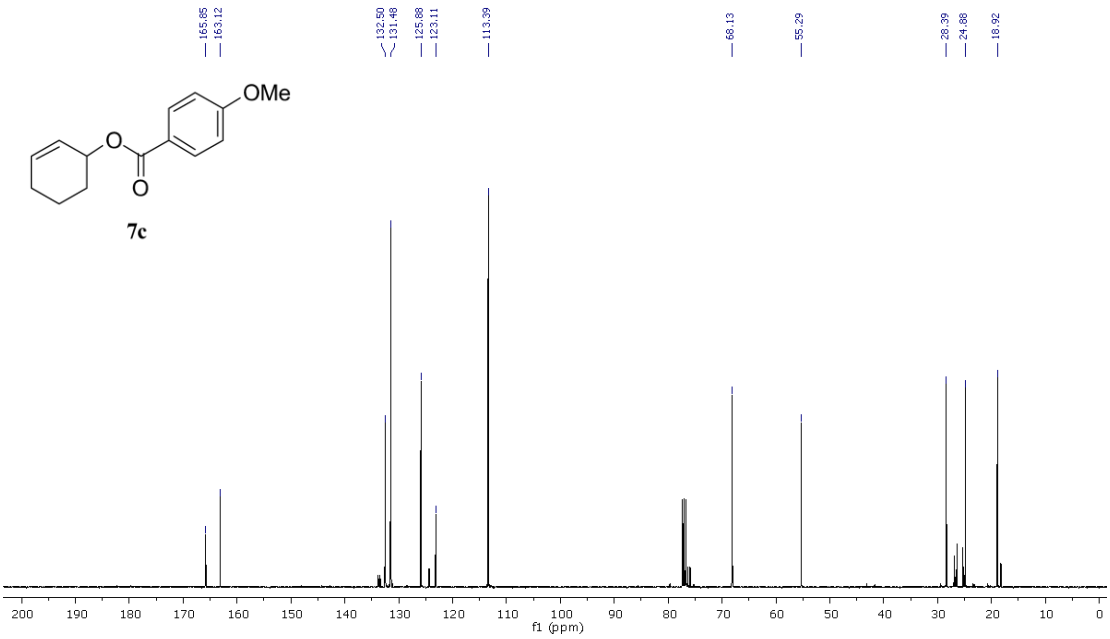


Figure S126. ^{13}C Spectrum of **7c** in $CDCl_3$ (100 MHz)

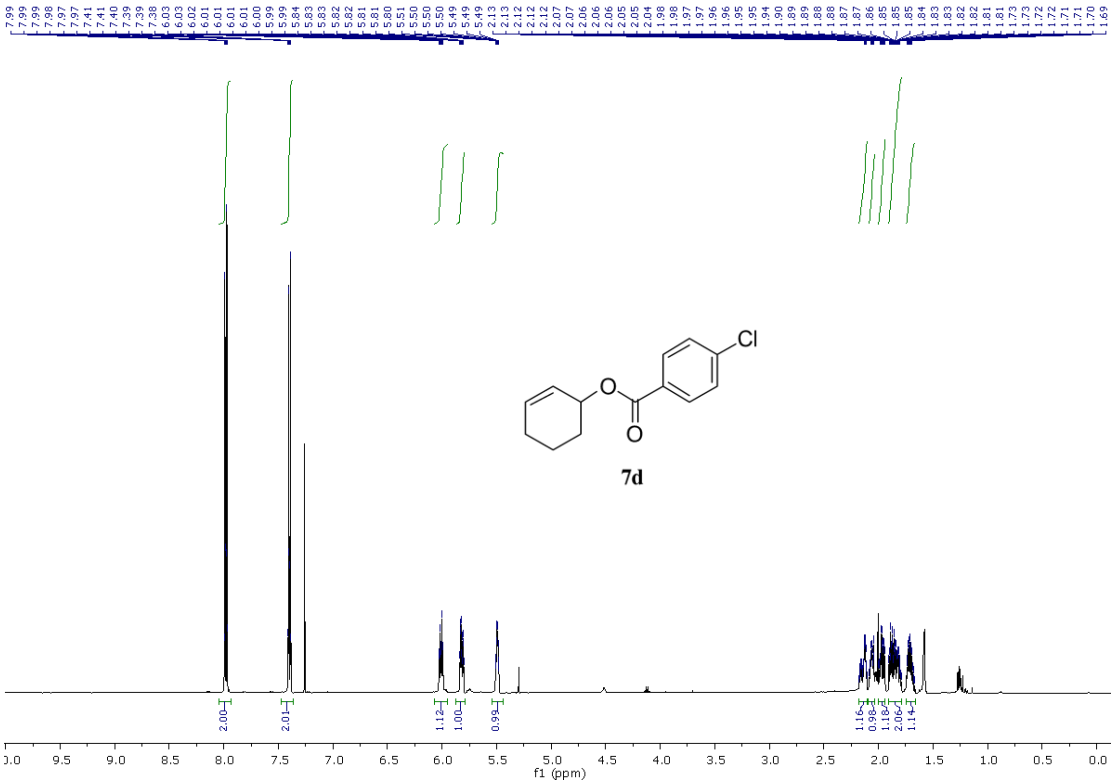


Figure S127. ^{1}H Spectrum of **7d** in $CDCl_3$ (500 MHz)

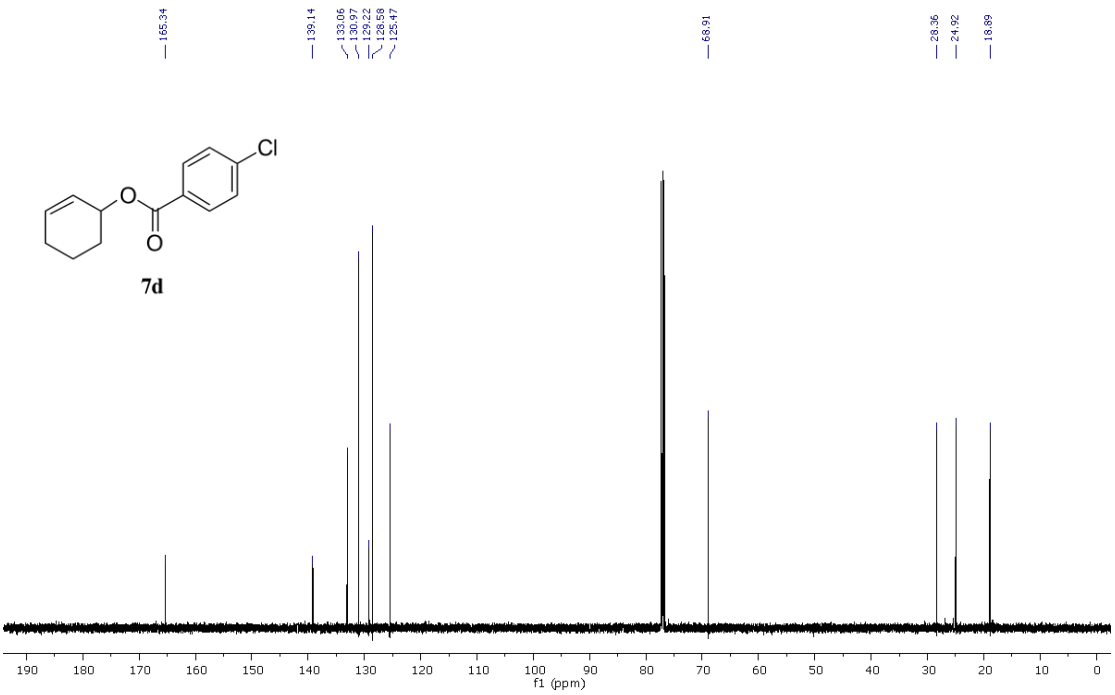


Figure S128. ^{13}C Spectrum of **7d** in $CDCl_3$ (125 MHz)

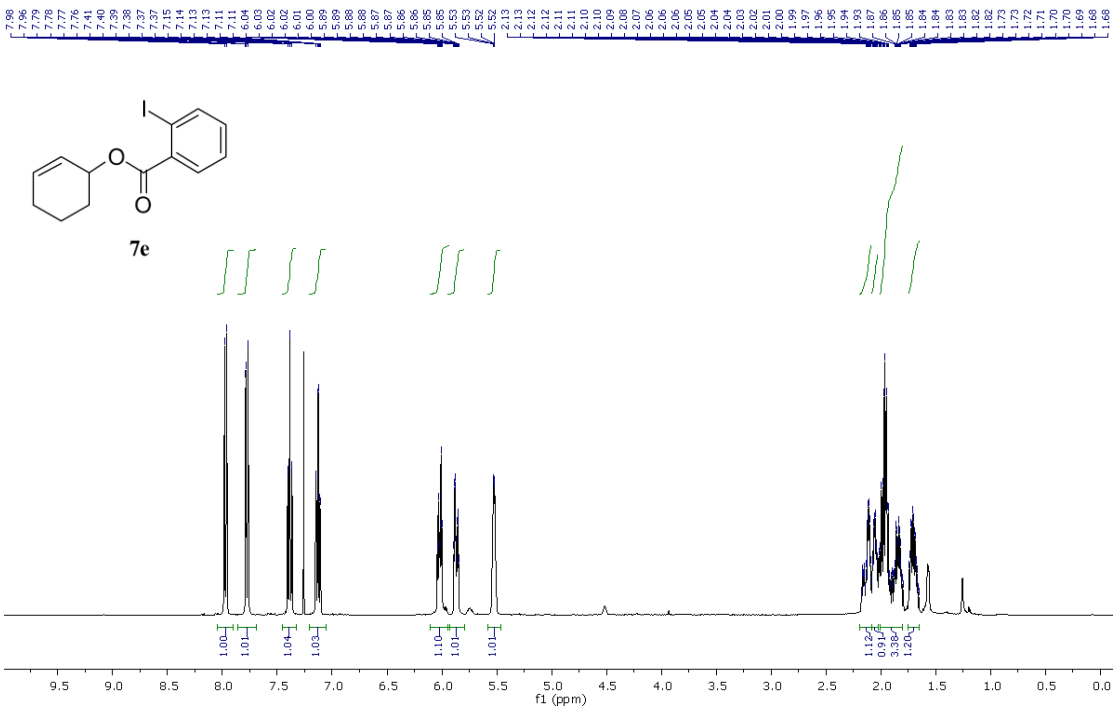


Figure S129. ^{1}H Spectrum of **7e** in $CDCl_3$ (400 MHz)

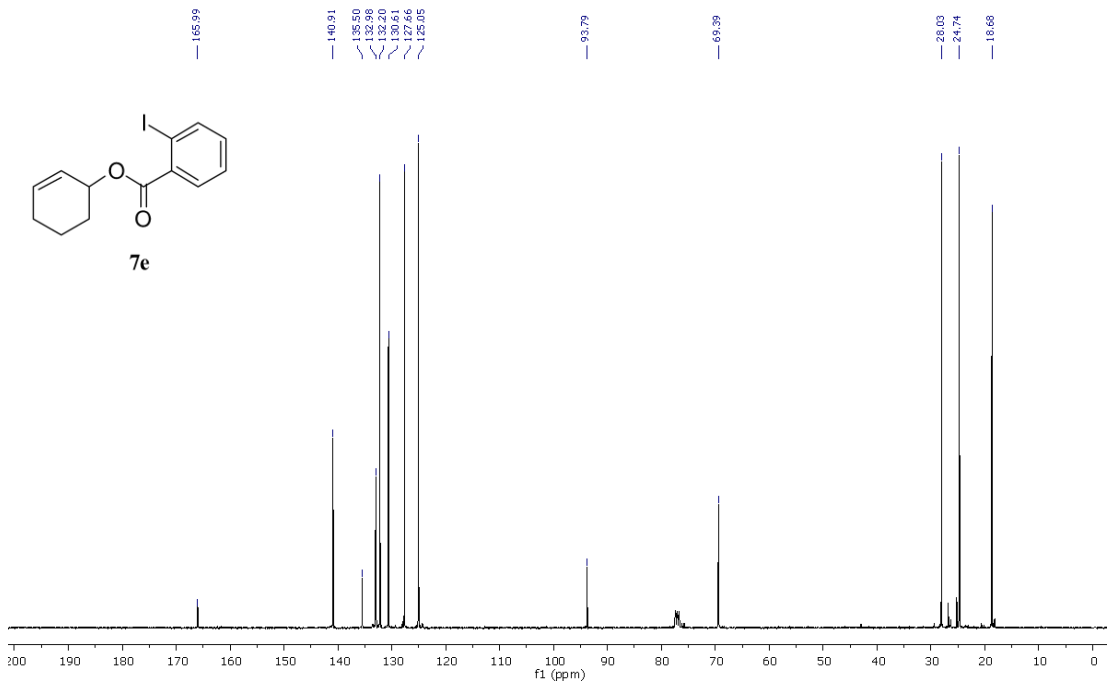


Figure S130. ^{13}C Spectrum of **7e** in $CDCl_3$ (100 MHz)

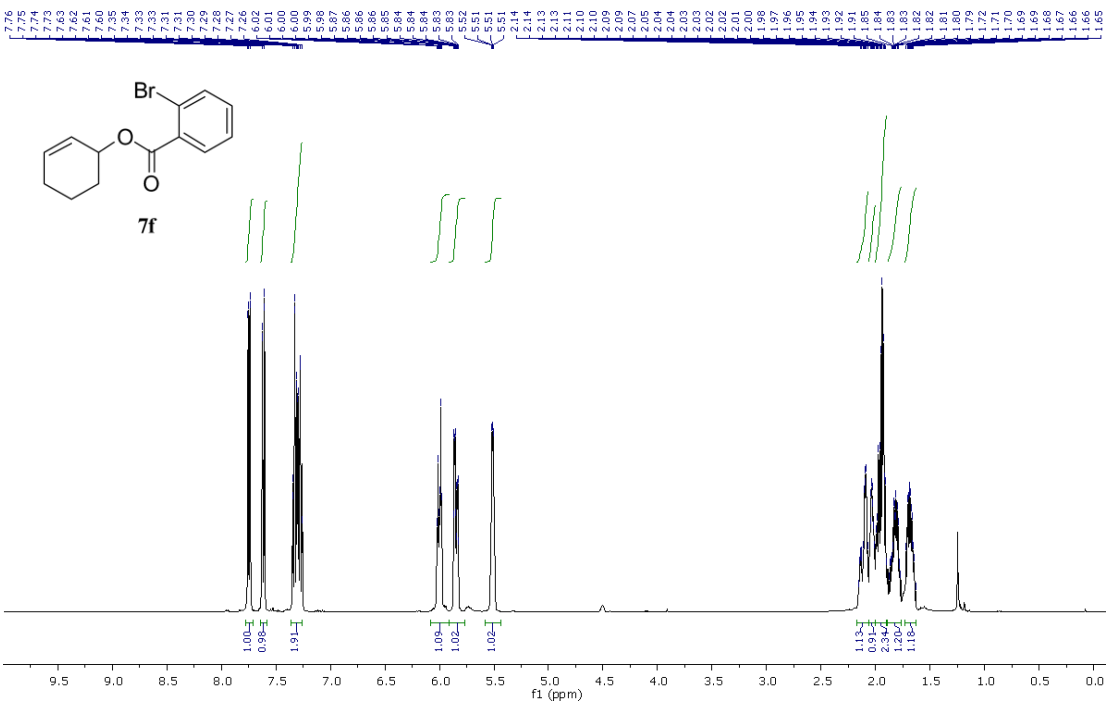


Figure S131. ^{1}H Spectrum of **7f** in $CDCl_3$ (400 MHz)

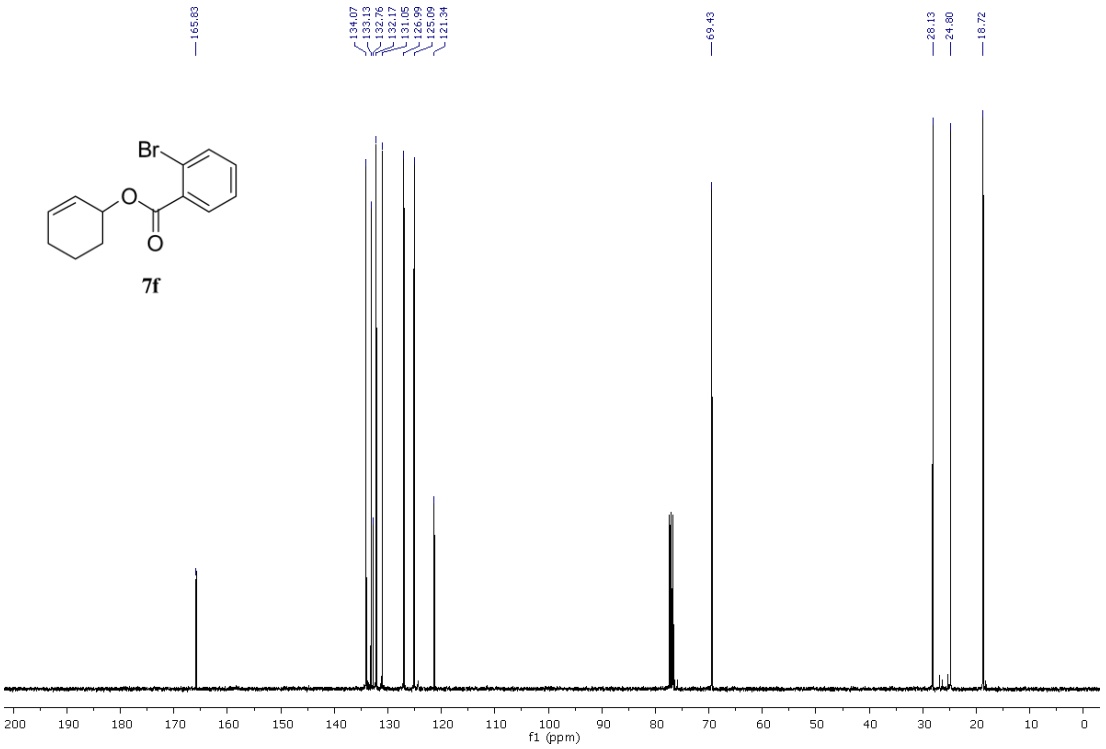


Figure S132. ^{13}C Spectrum of **7f** in $CDCl_3$ (100 MHz)

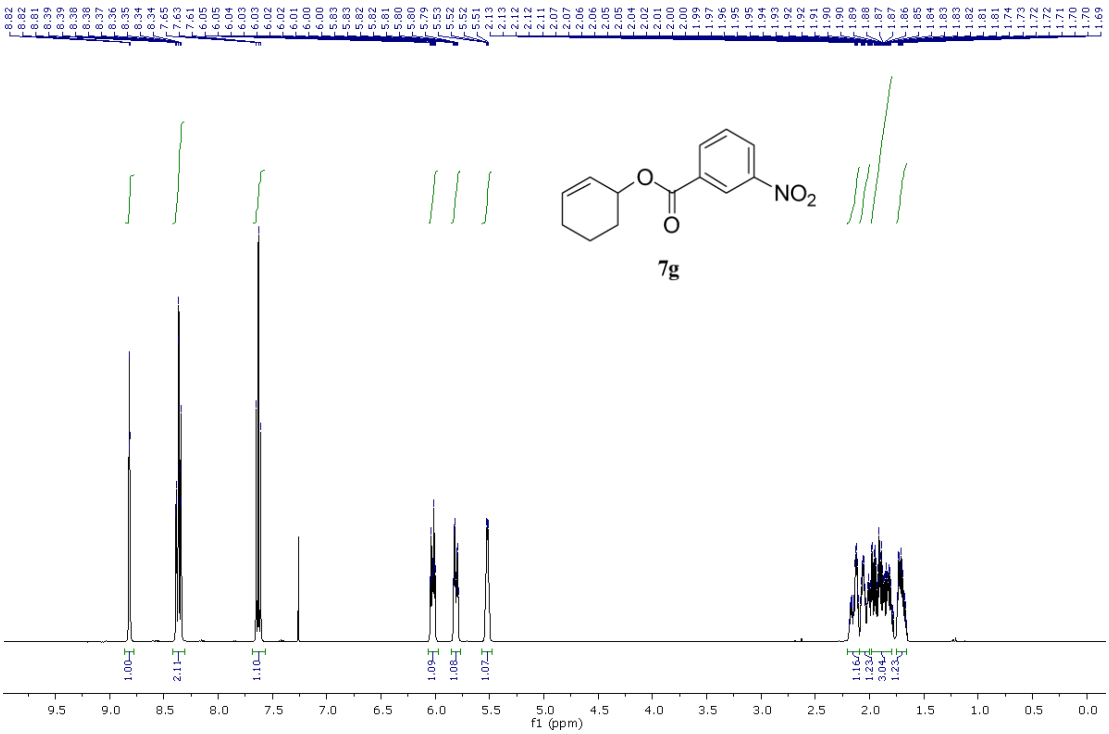


Figure S133. ^{1}H Spectrum of **7g** in $CDCl_3$ (400 MHz)

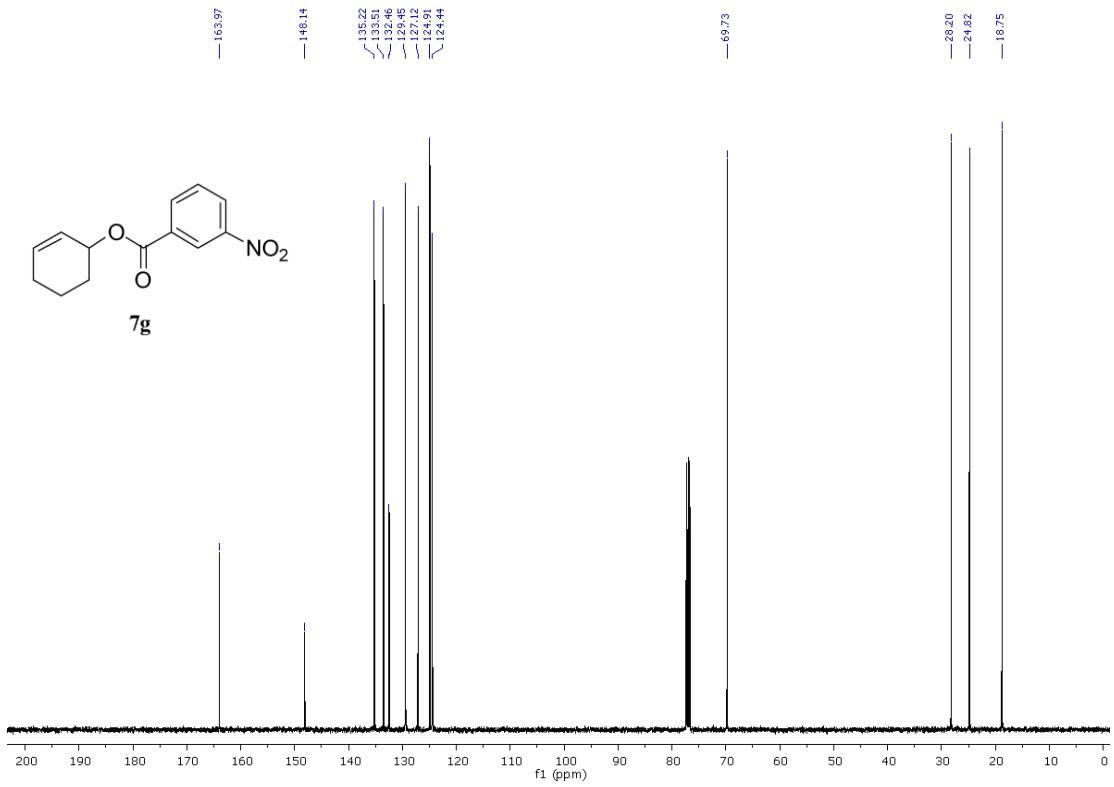


Figure S134. ^{13}C Spectrum of **7g** in $CDCl_3$ (100 MHz)

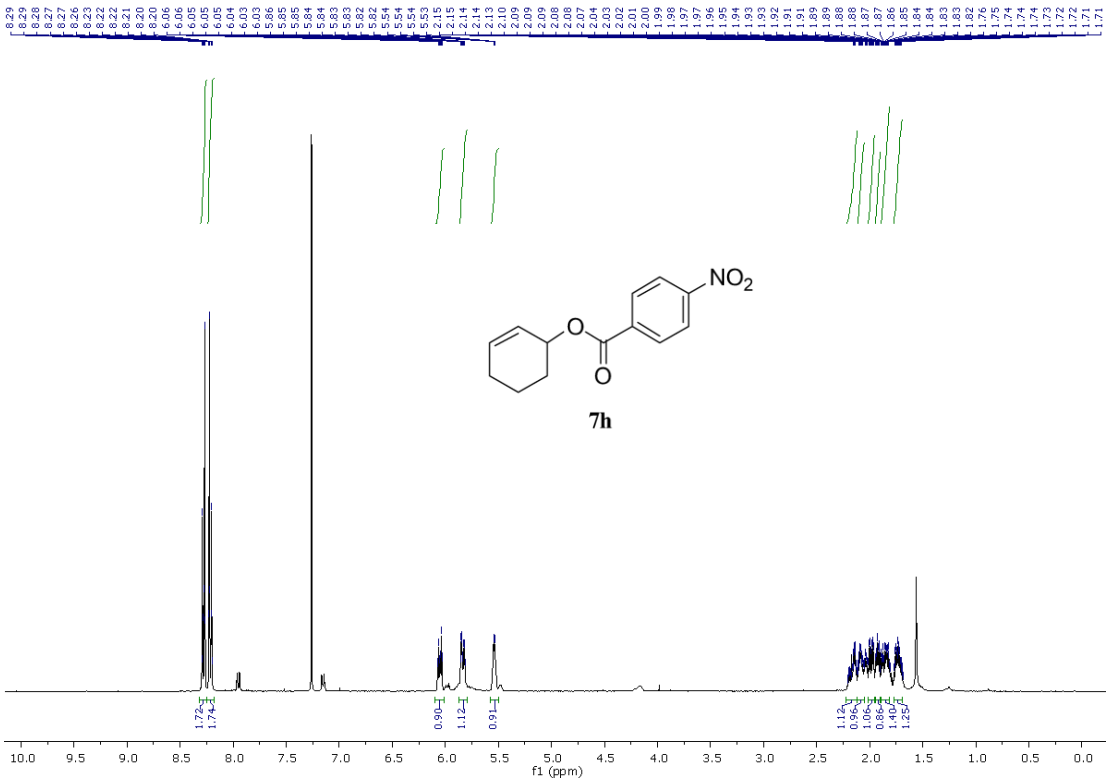


Figure S135. ^{1}H Spectrum of **7h** in $CDCl_3$ (400 MHz)

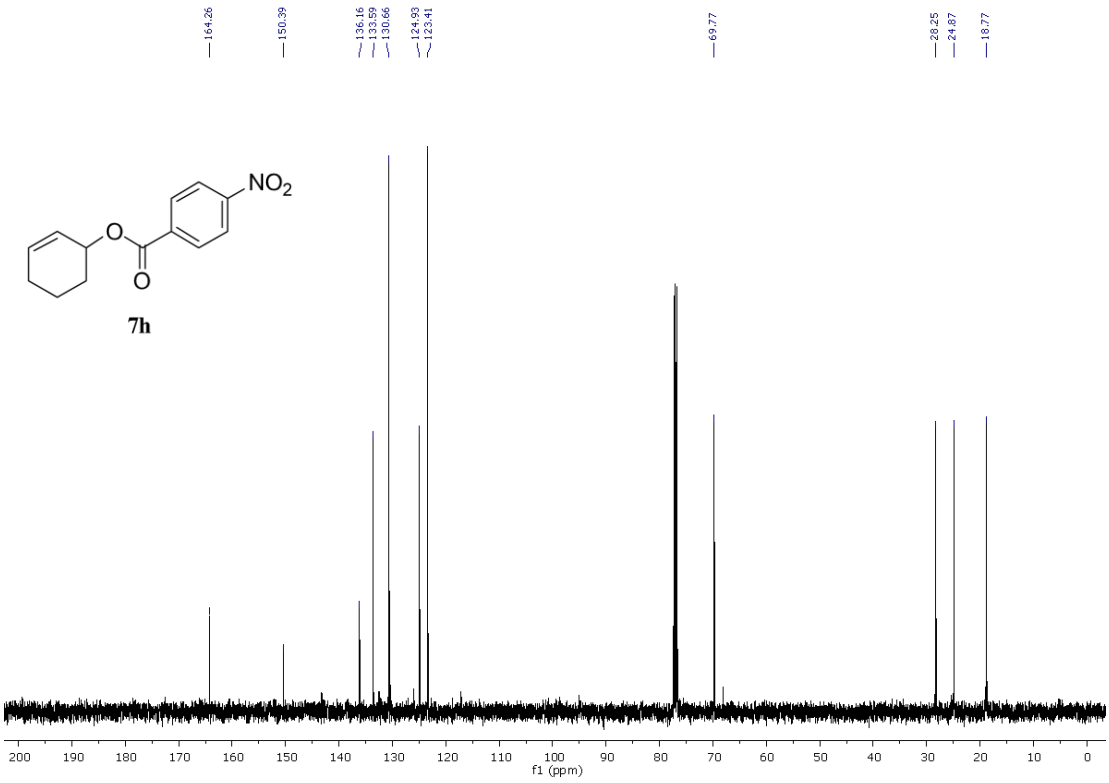


Figure S136. ^{13}C Spectrum of **7h** in $CDCl_3$ (100 MHz)

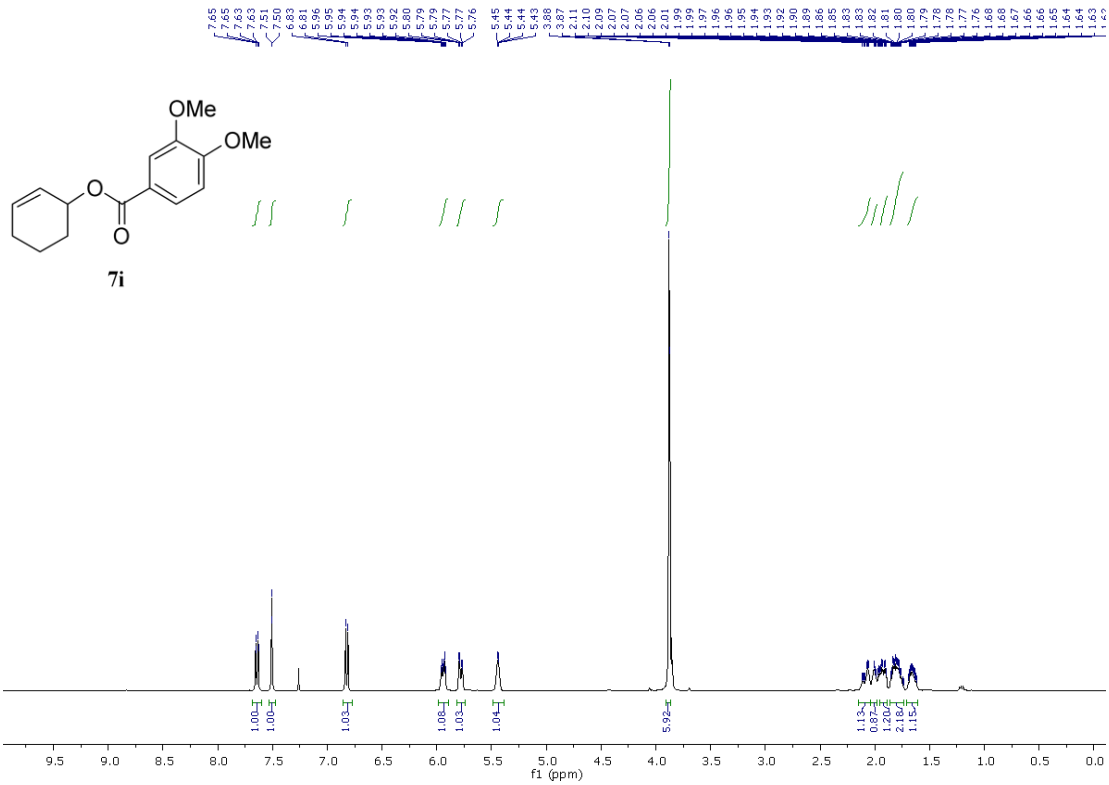


Figure S137. ^{1}H Spectrum of **7i** in $CDCl_3$ (400 MHz)

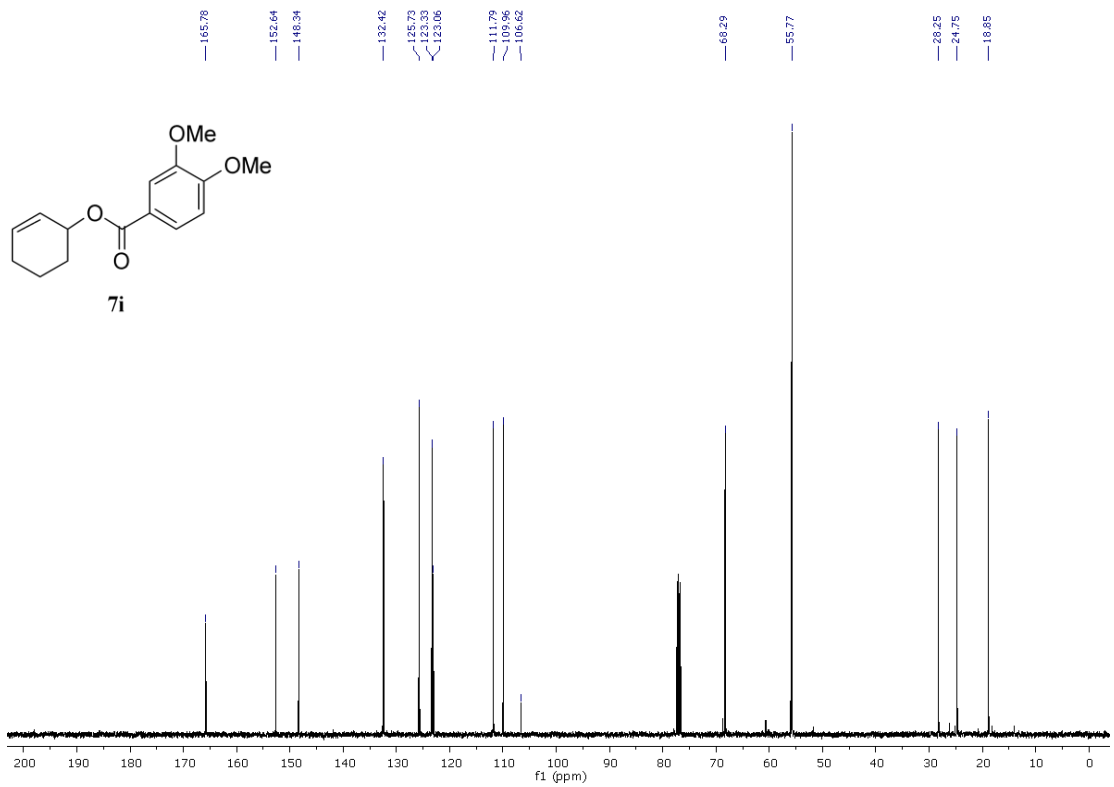


Figure S138. ^{13}C Spectrum of **7i** in $CDCl_3$ (100 MHz)

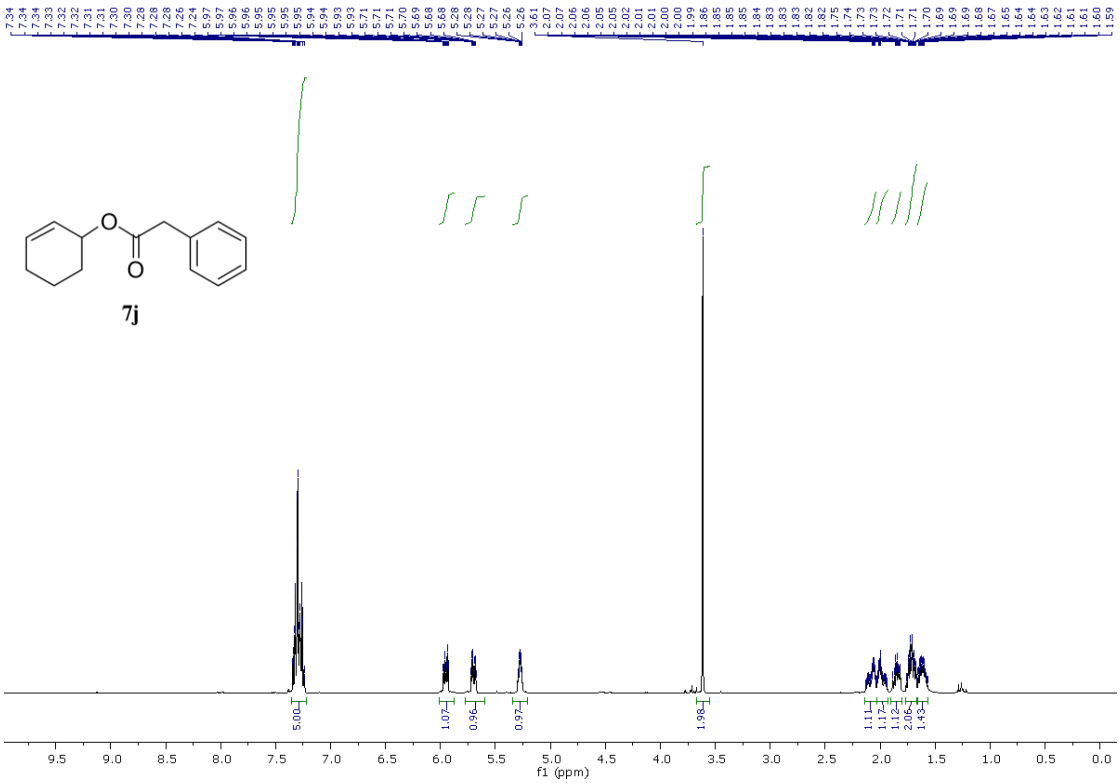


Figure S139. ^{1}H Spectrum of **7j** in $CDCl_3$ (400 MHz)

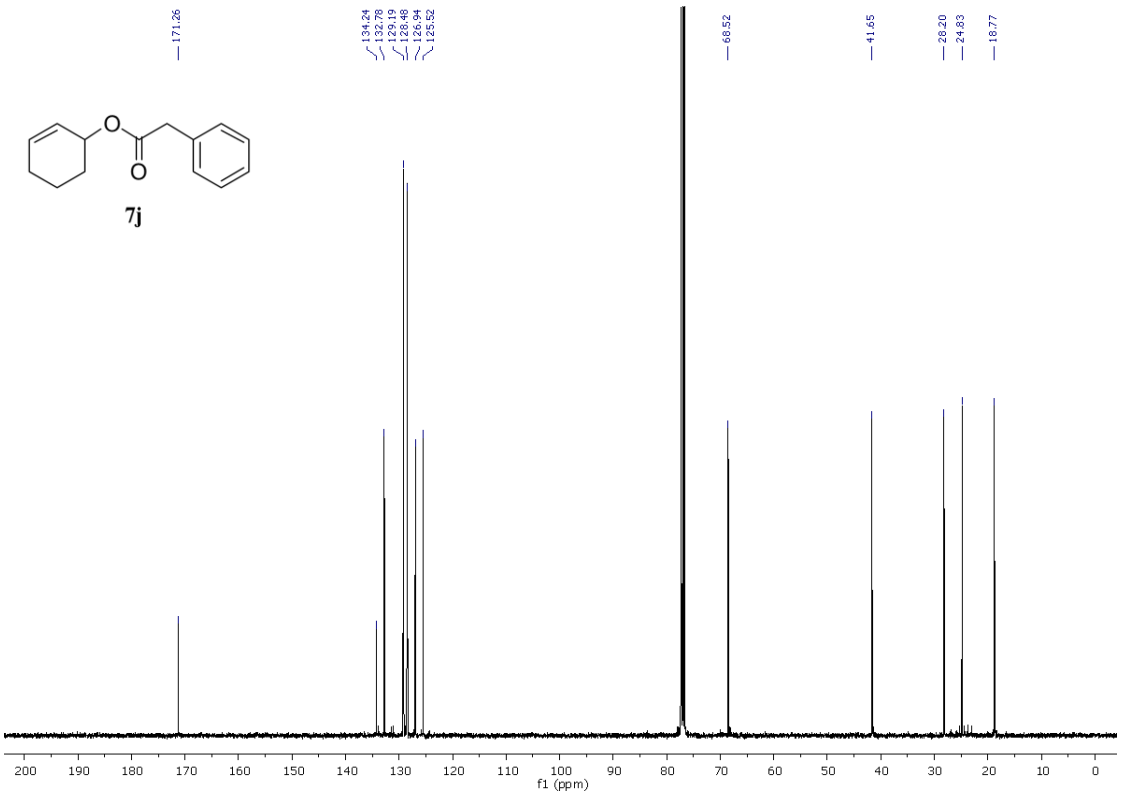


Figure S140. ^{13}C Spectrum of **7j** in $CDCl_3$ (100 MHz)

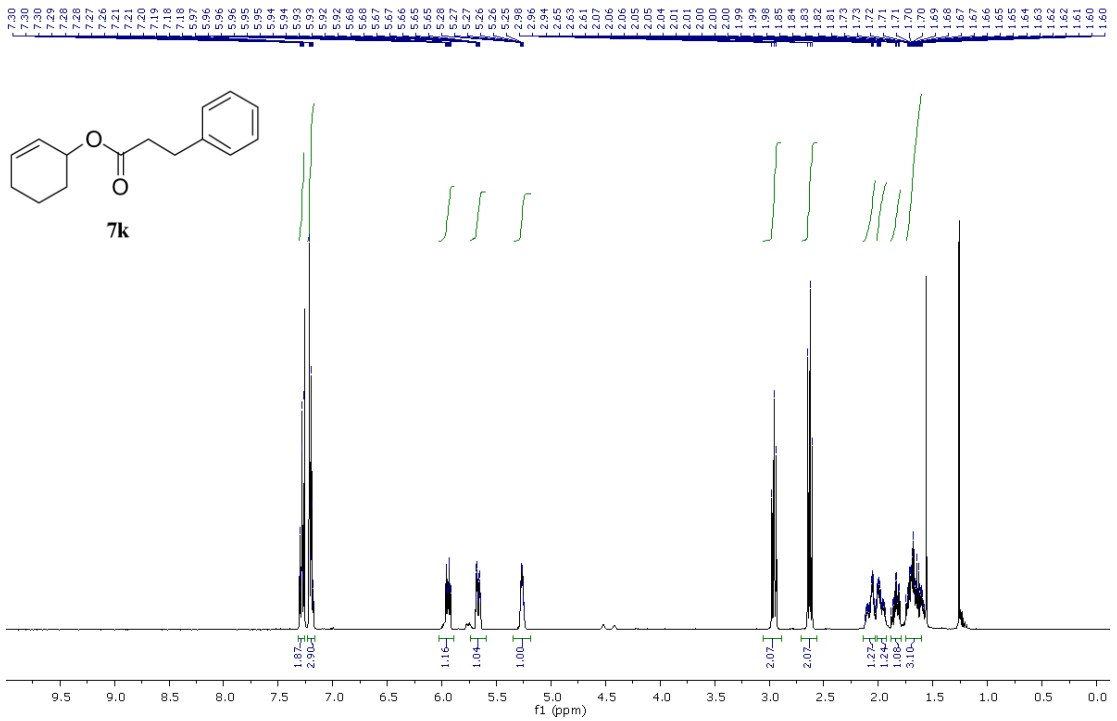


Figure S141. ^{1}H Spectrum of **7k** in $CDCl_3$ (400 MHz)

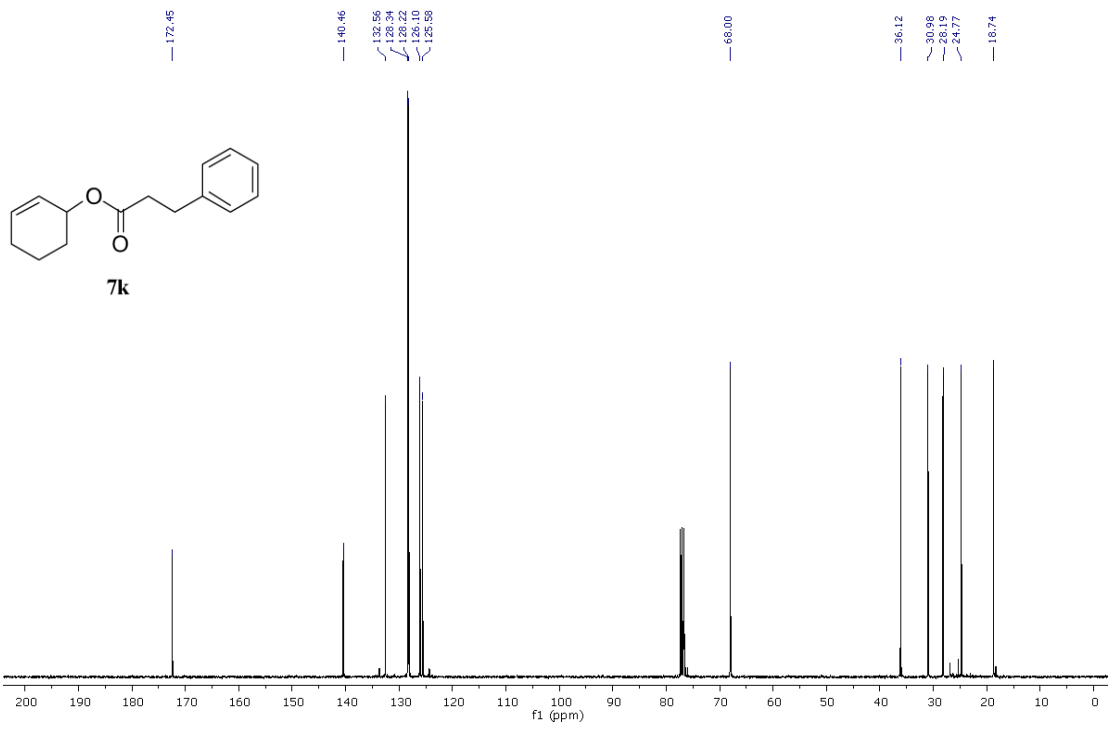


Figure S142. ^{13}C Spectrum of **7k** in $CDCl_3$ (100 MHz)

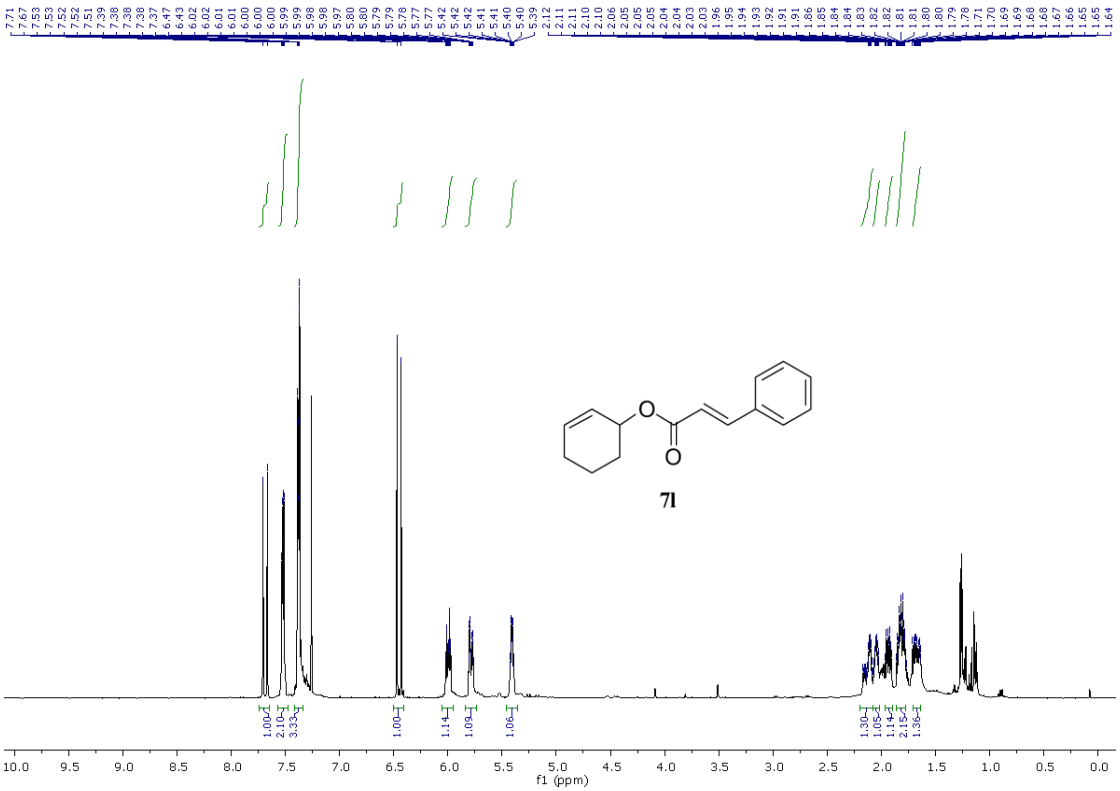


Figure S143. ^{1}H Spectrum of **7l** in $CDCl_3$ (400 MHz)

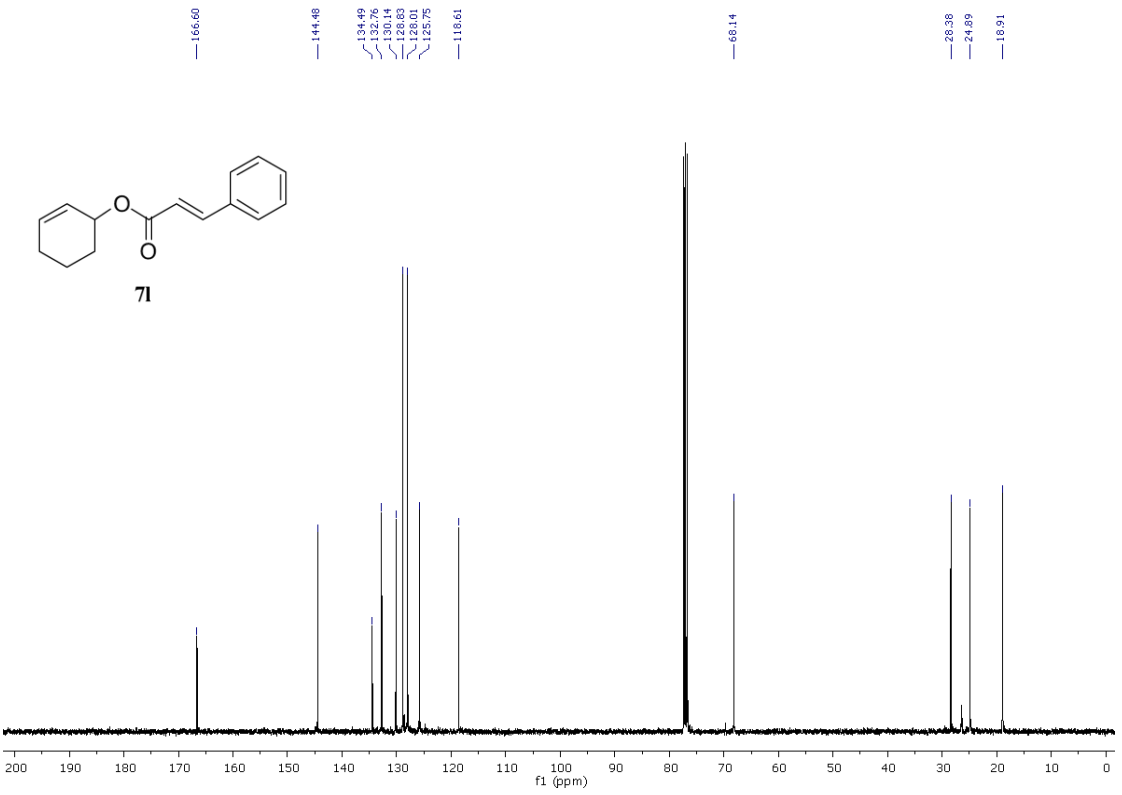


Figure S144. ^{13}C Spectrum of **7l** in $CDCl_3$ (100 MHz)

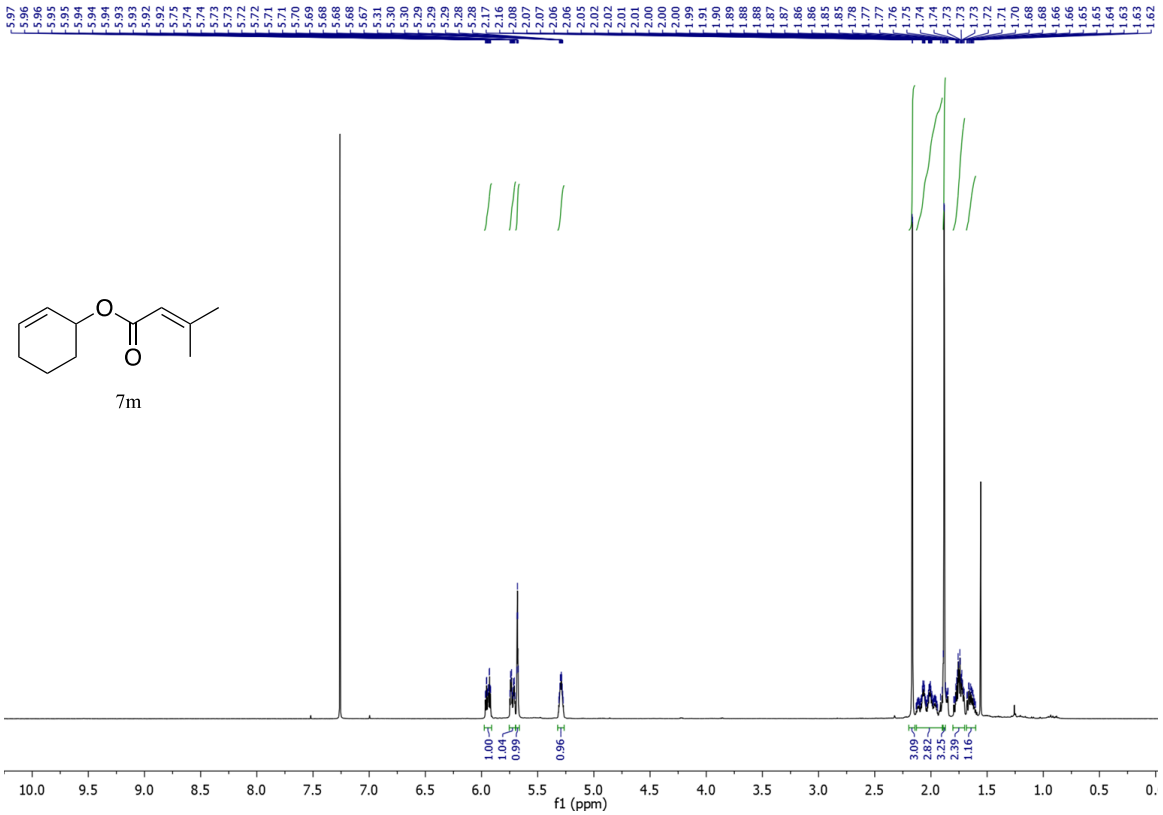


Figure S145. ^{1}H Spectrum of **7m** in $CDCl_3$ (500 MHz)

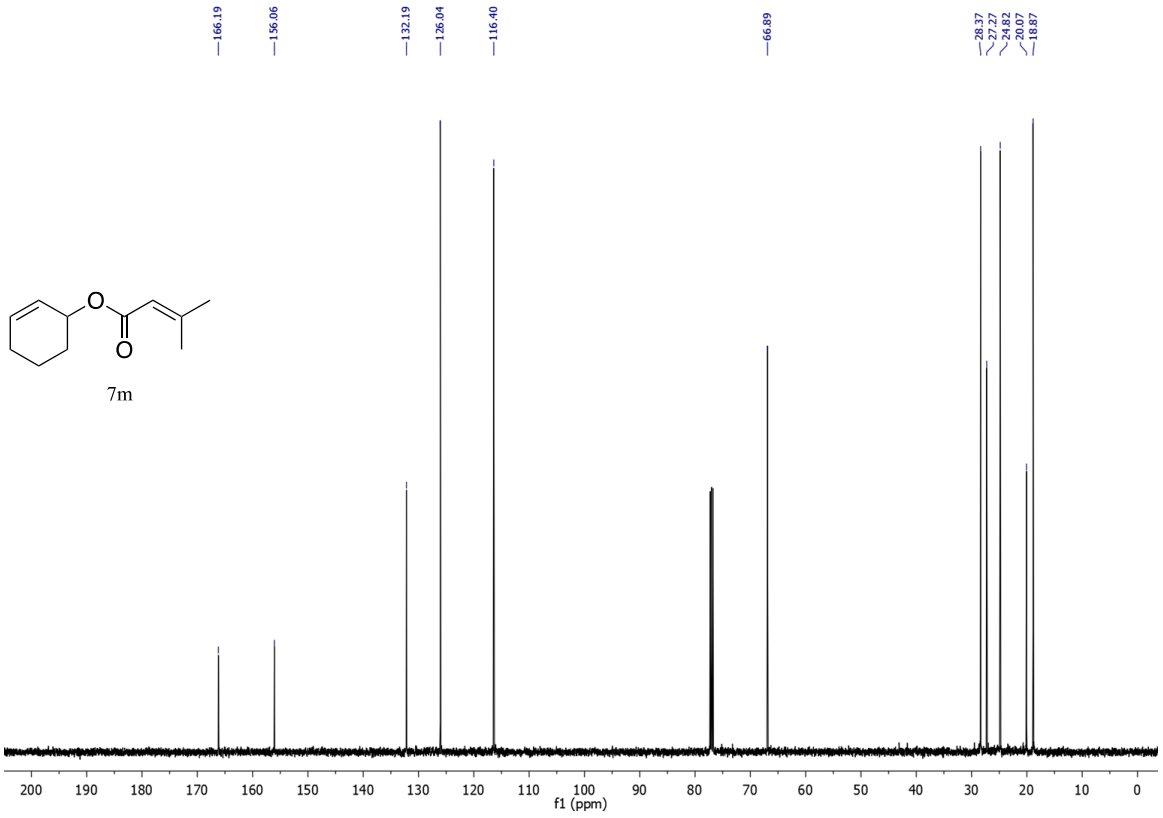


Figure S146. ^{13}C Spectrum of **7m** in $CDCl_3$ (125 MHz)

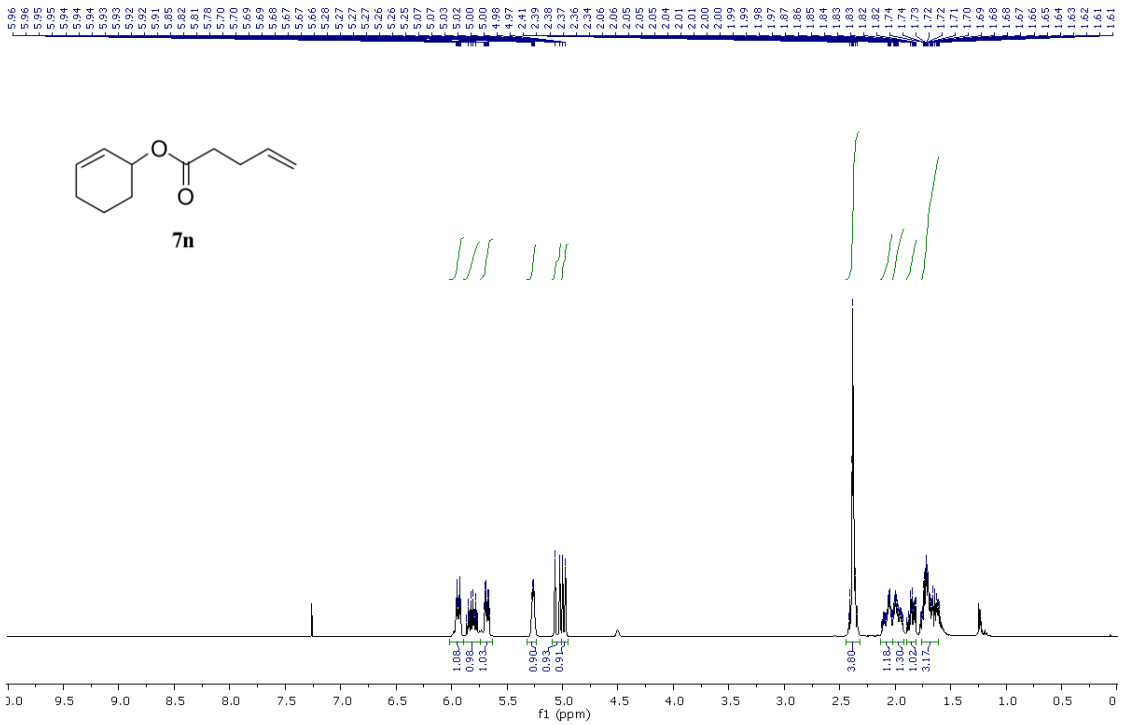


Figure S147. ^{1}H Spectrum of **7n** in $CDCl_3$ (400 MHz)

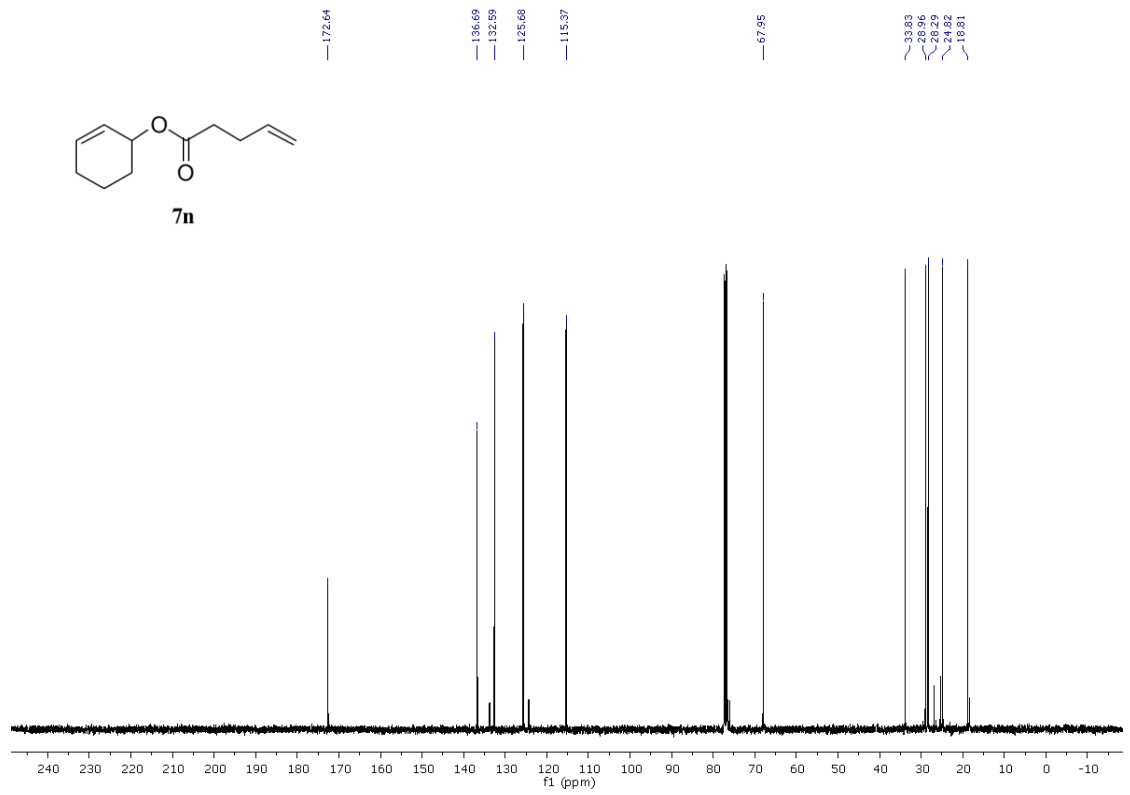


Figure S148. ^{13}C Spectrum of **7n** in $CDCl_3$ (100 MHz)

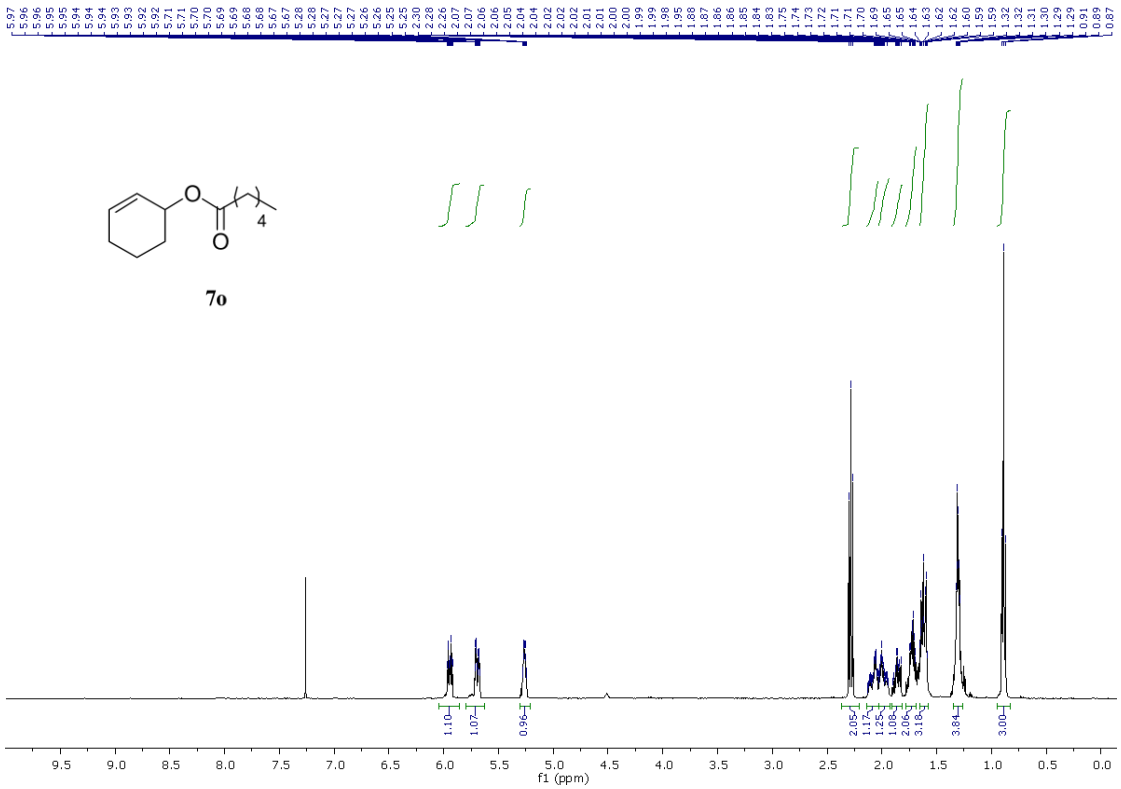


Figure S149. ^{1}H Spectrum of **7o** in $CDCl_3$ (400 MHz)

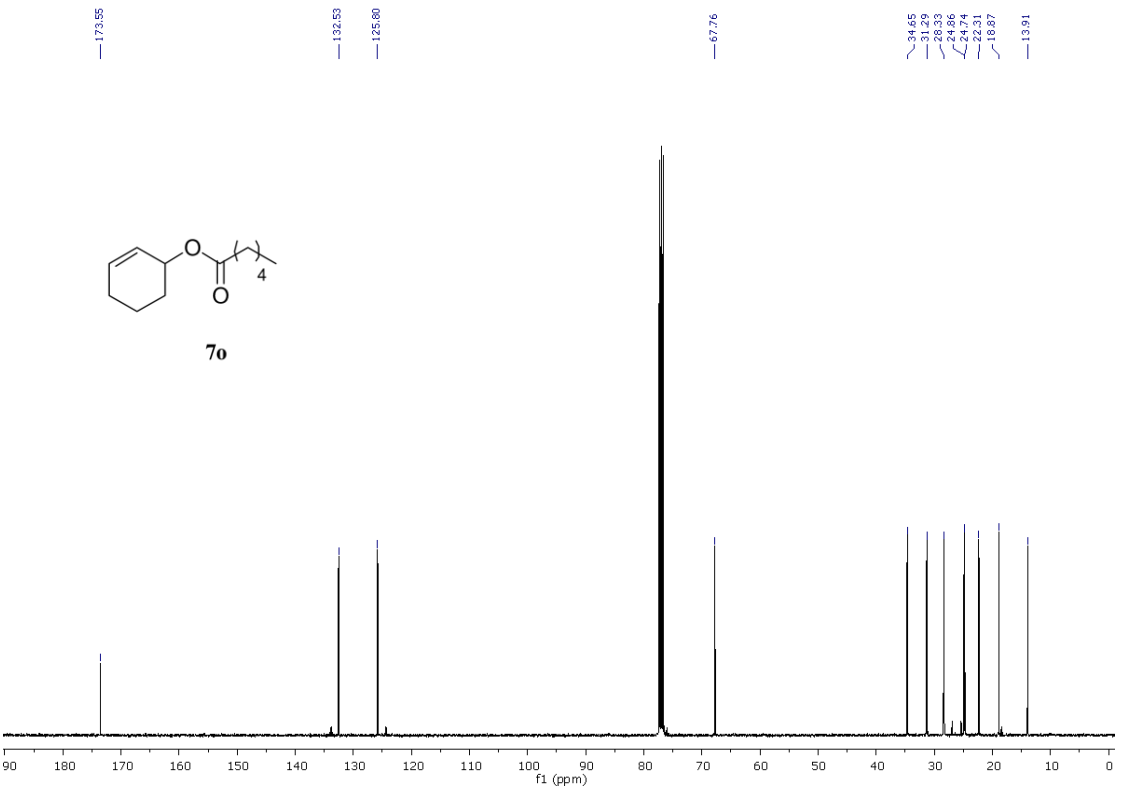


Figure S150. ^{13}C Spectrum of **7o** in $CDCl_3$ (100 MHz)

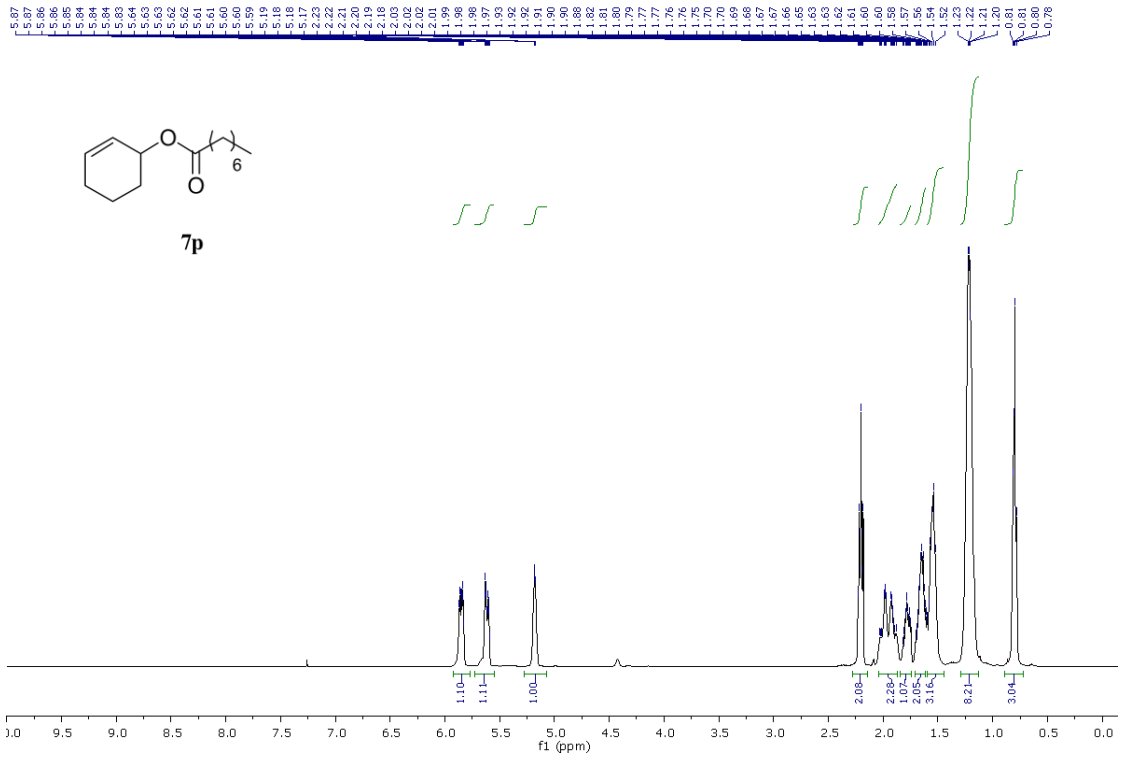


Figure S151. ^{1}H Spectrum of **7p** in $CDCl_3$ (400 MHz)

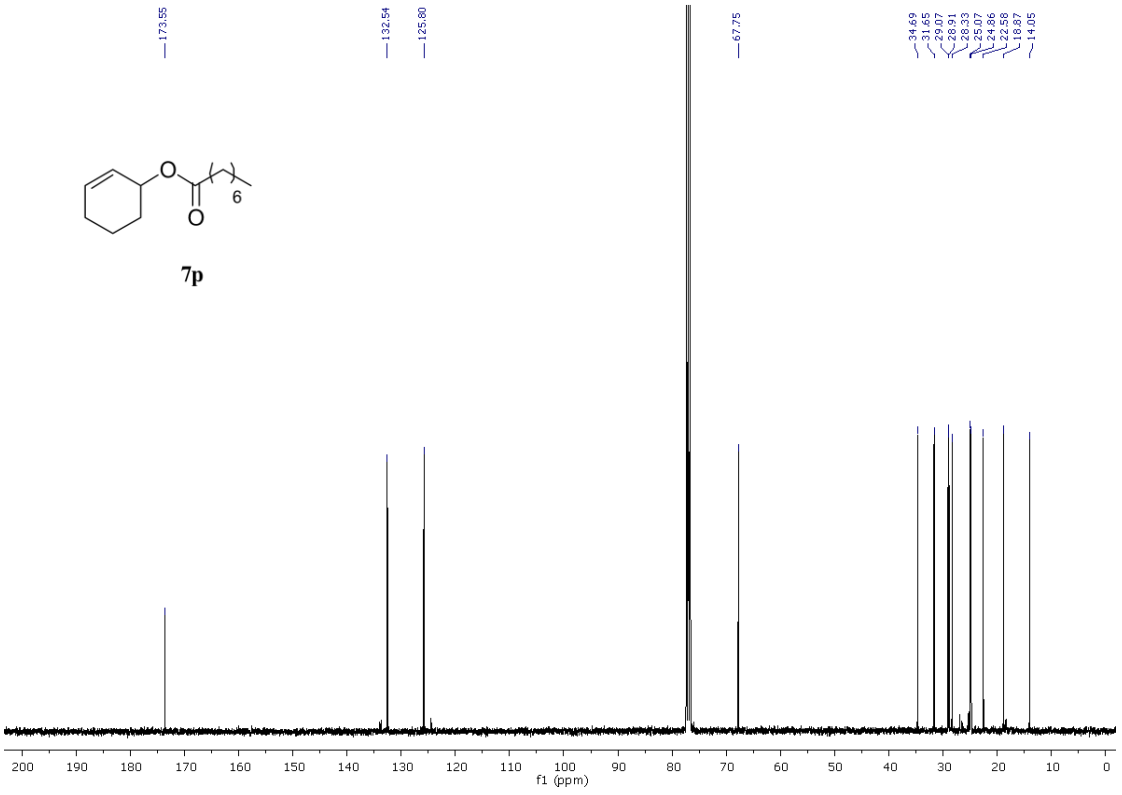


Figure S152. ^{13}C Spectrum of **7p** in $CDCl_3$ (100 MHz)

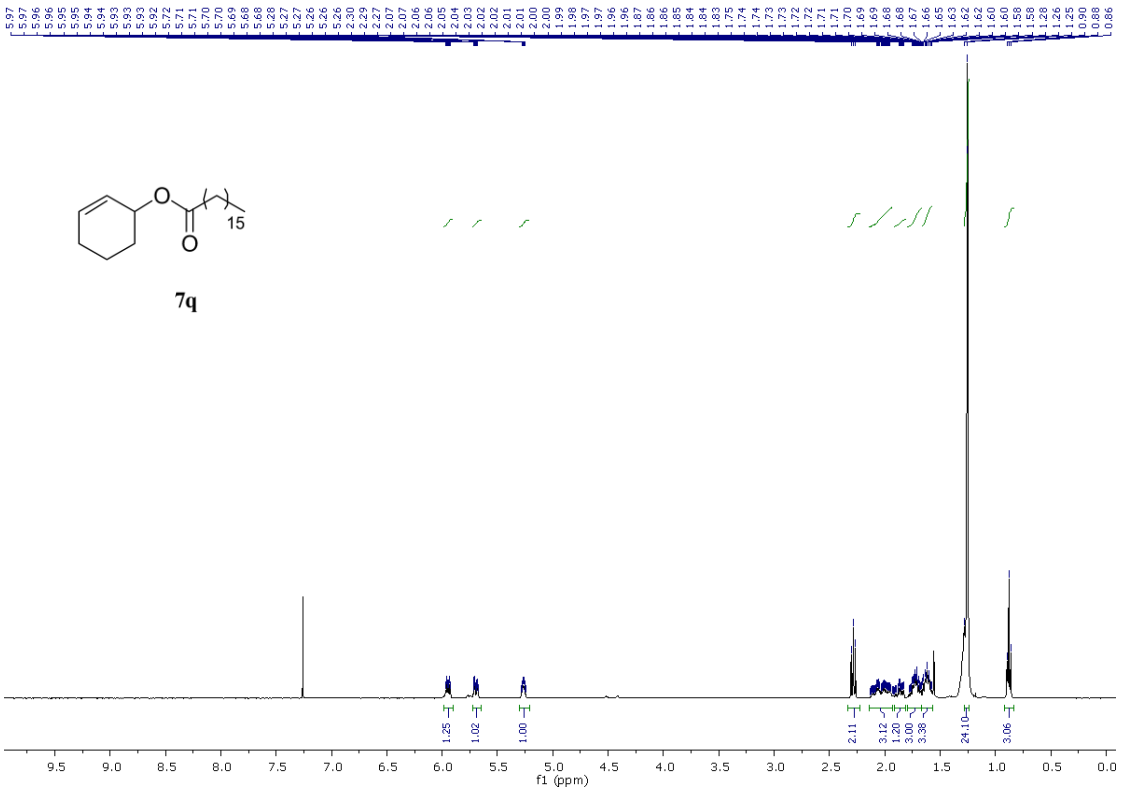


Figure S153. ^{1}H Spectrum of **7q** in $CDCl_3$ (400 MHz)

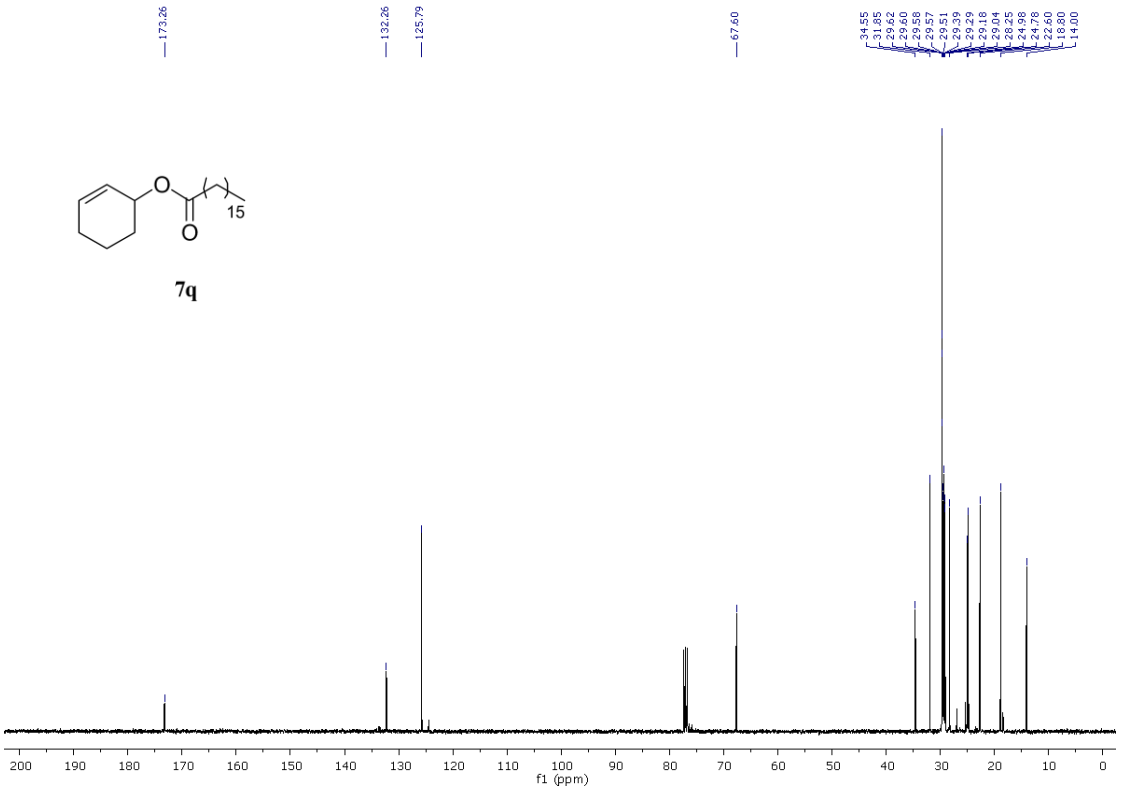


Figure S154. ^{13}C Spectrum of **7q** in $CDCl_3$ (100 MHz)

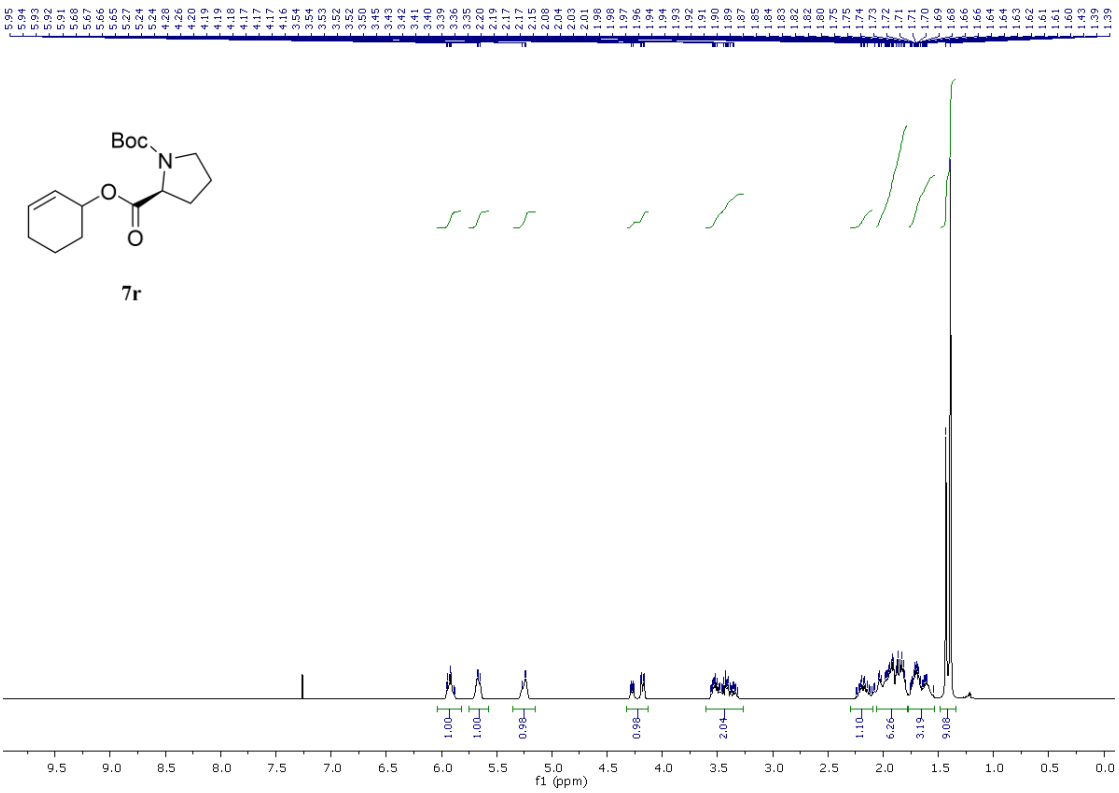


Figure S155. ^{1}H Spectrum of **7r** in $CDCl_3$ (500 MHz)

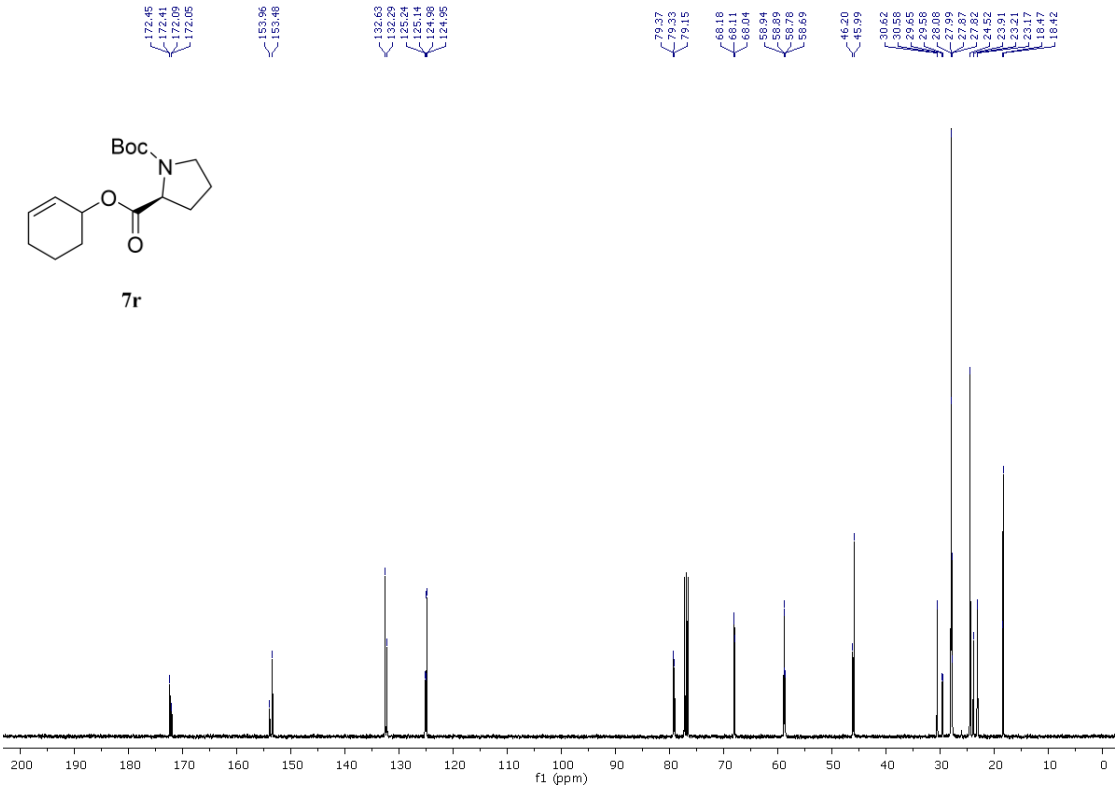


Figure S156. ^{13}C Spectrum of **7r** in $CDCl_3$ (125 MHz)

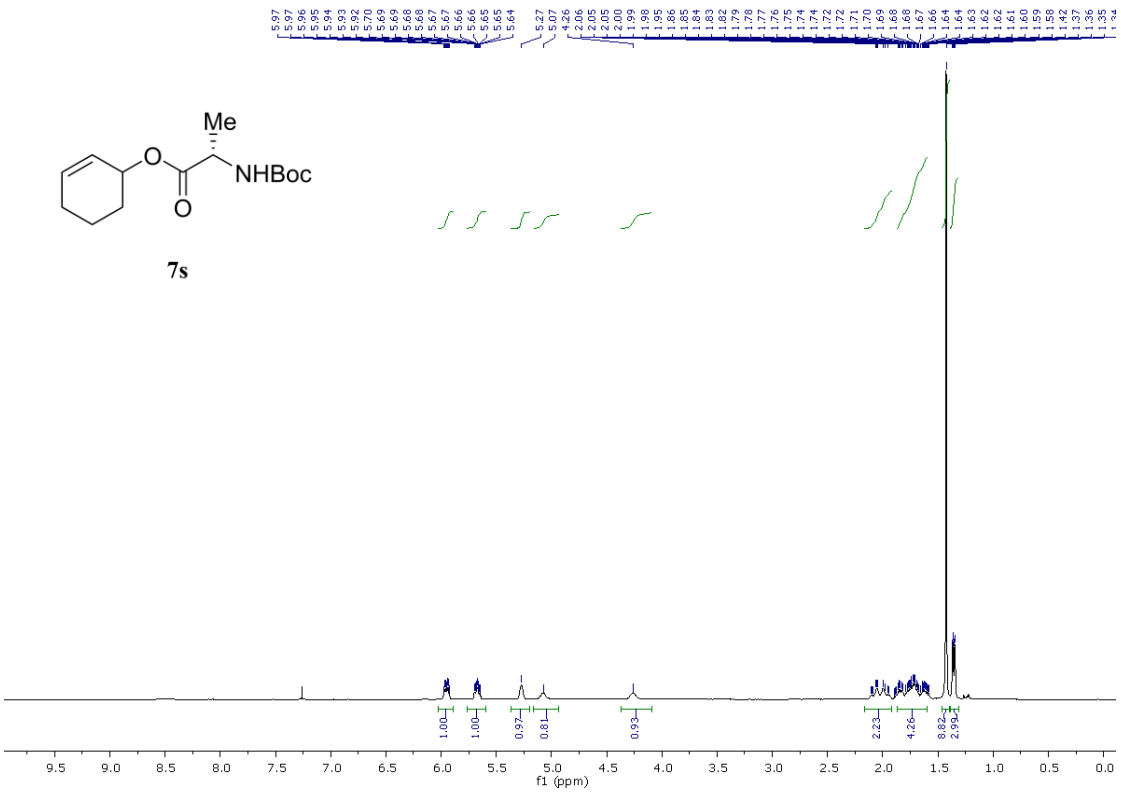


Figure S157. ^{1}H Spectrum of **7s** in $CDCl_3$ (400 MHz)

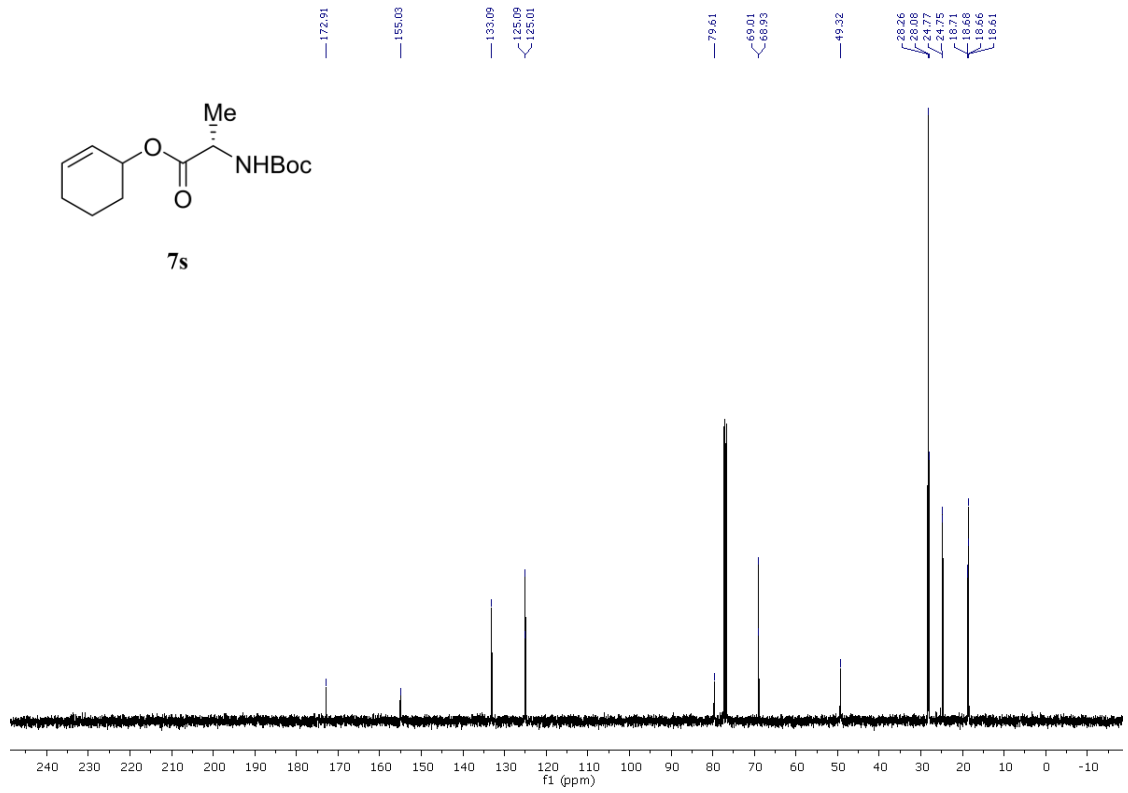


Figure S158. ^{13}C Spectrum of **7s** in $CDCl_3$ (100 MHz)

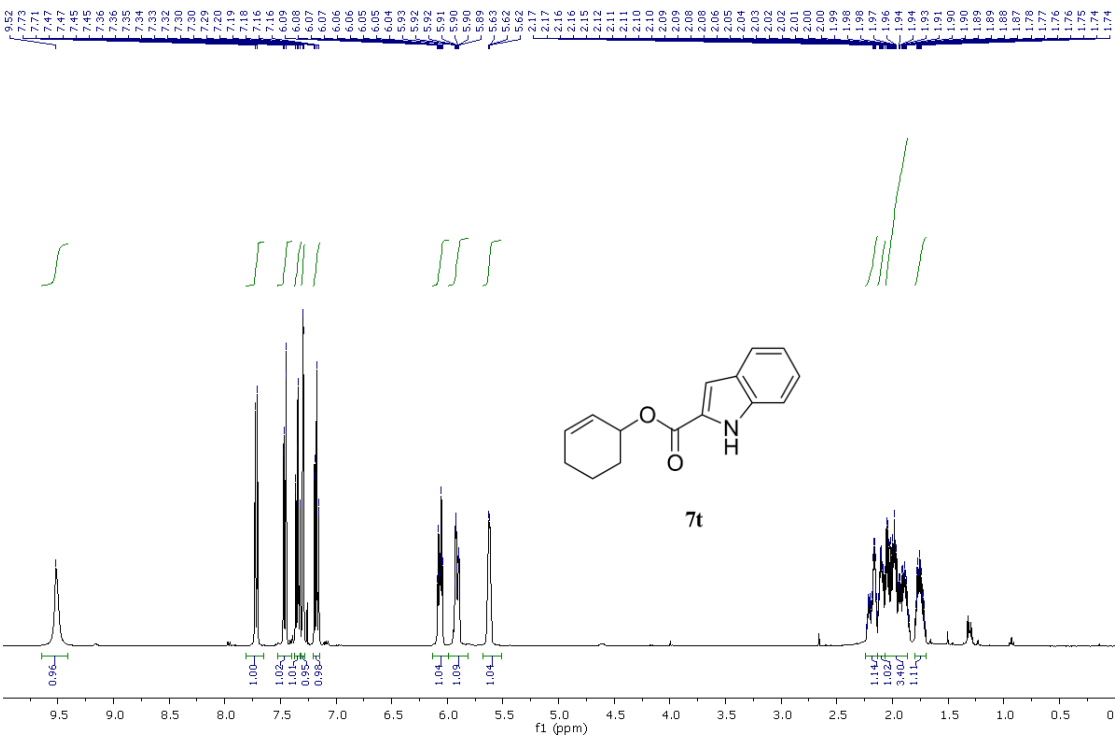


Figure S159. ^{1}H Spectrum of **7t** in $CDCl_3$ (400 MHz)

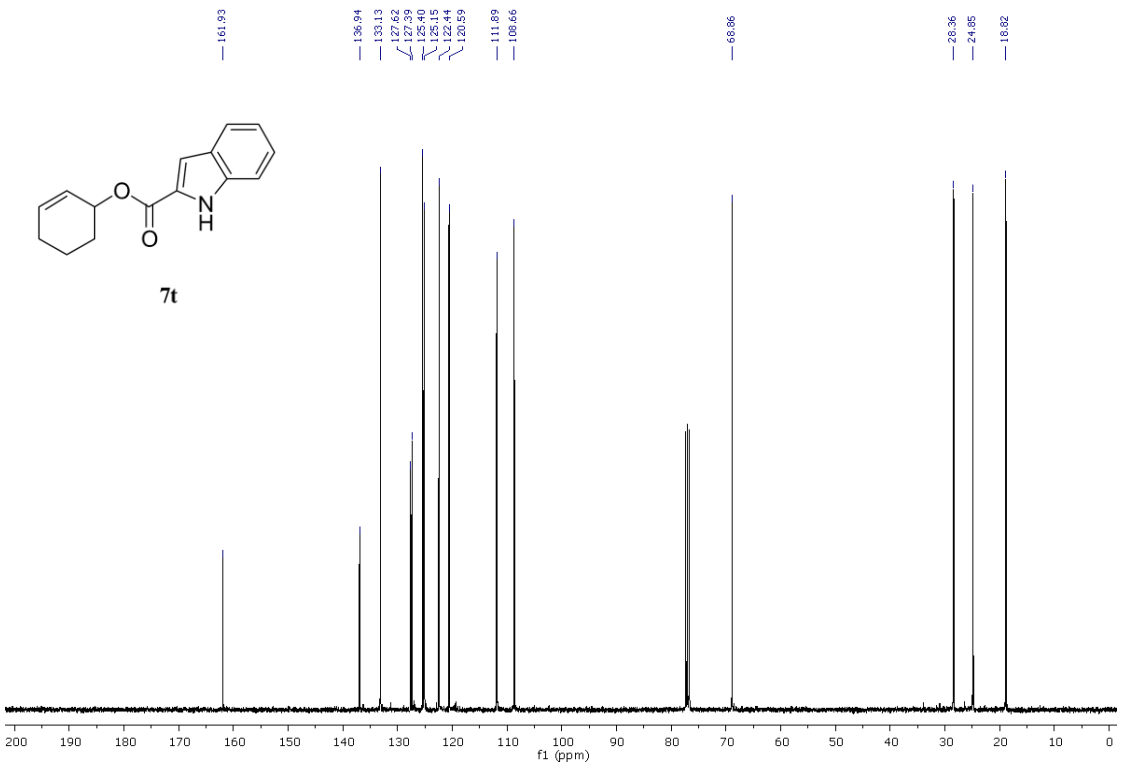


Figure S160. ^{13}C Spectrum of **7t** in $CDCl_3$ (100 MHz)

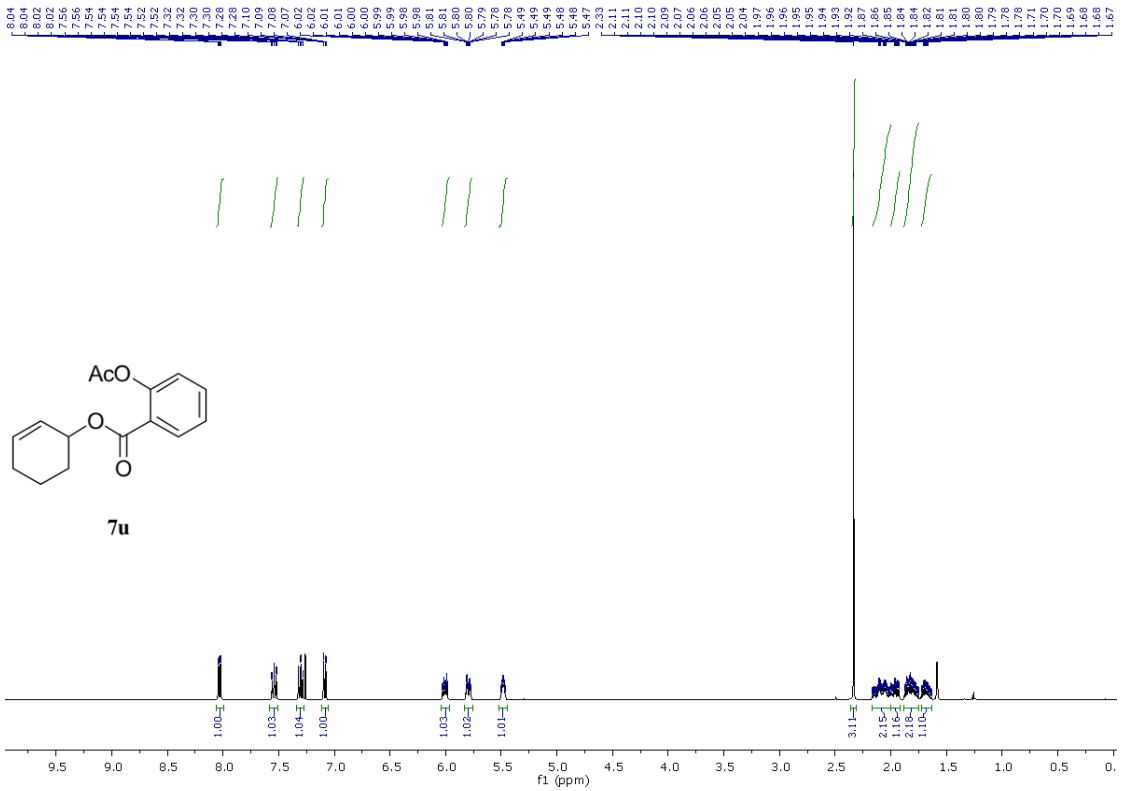


Figure S161. ^{1}H Spectrum of **7u** in $CDCl_3$ (400 MHz)

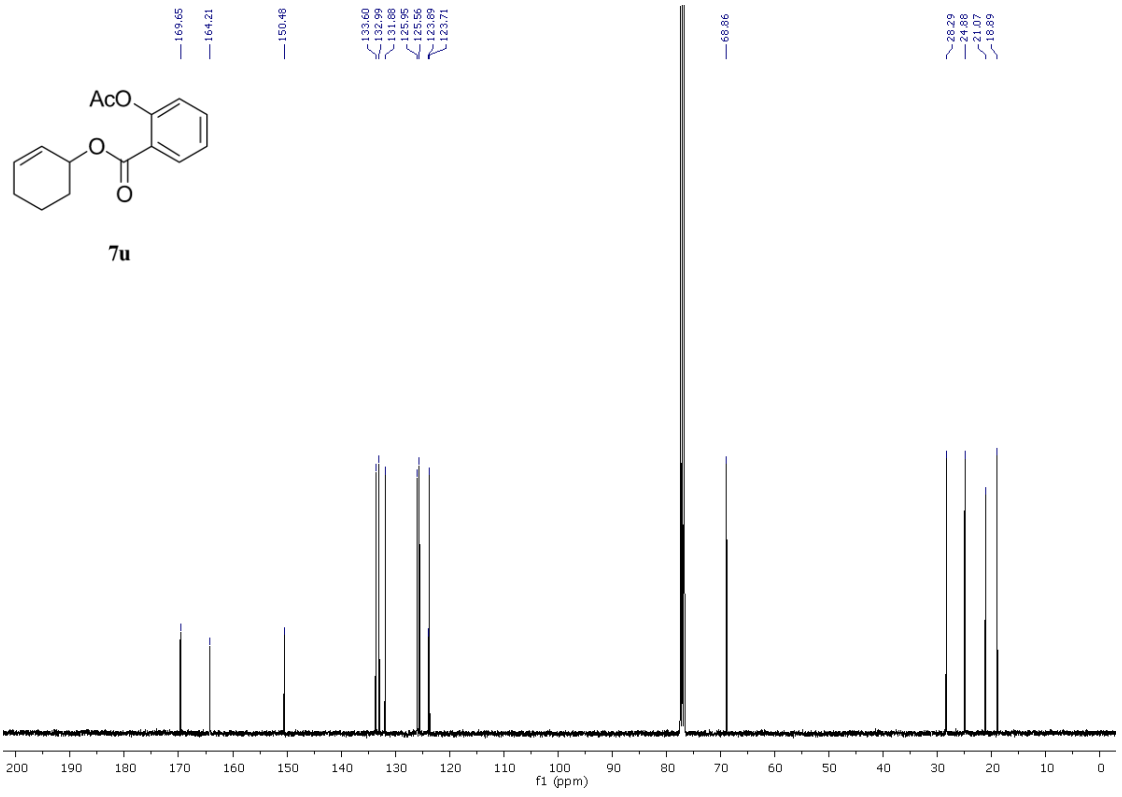


Figure S162. ^{13}C Spectrum of **7u** in $CDCl_3$ (100 MHz)

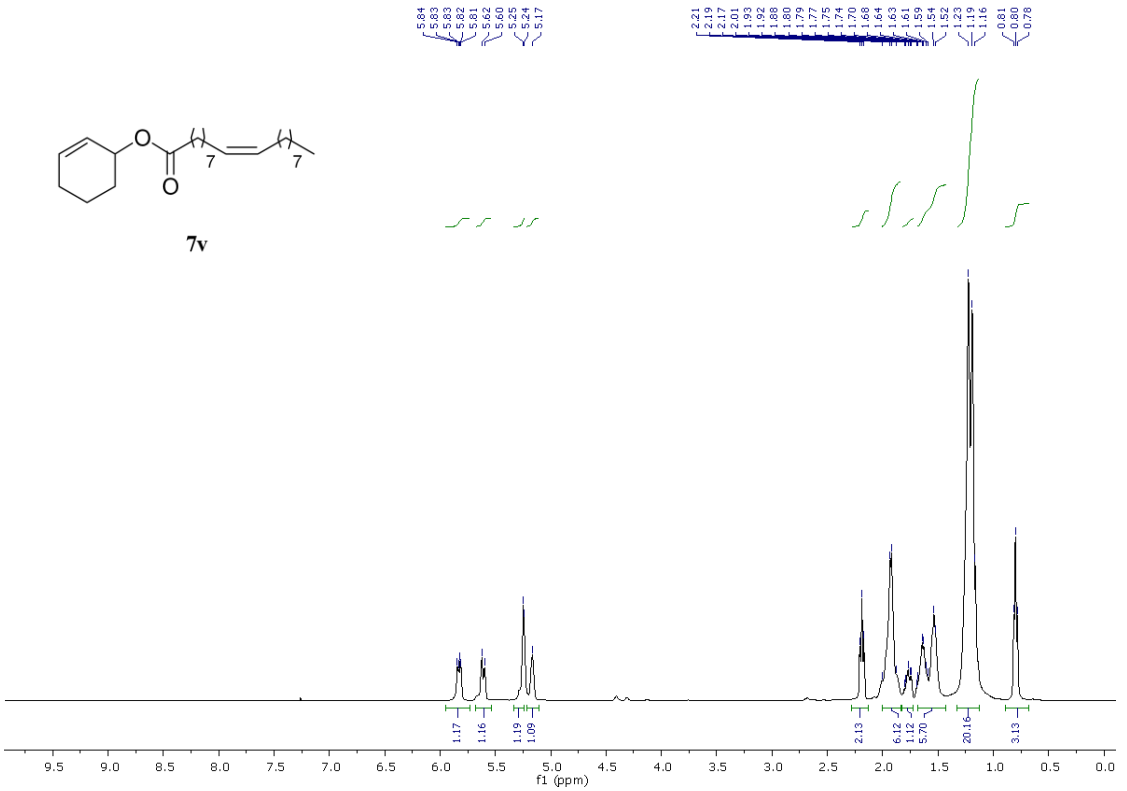


Figure S163. ^{1}H Spectrum of **7v** in $CDCl_3$ (400 MHz)

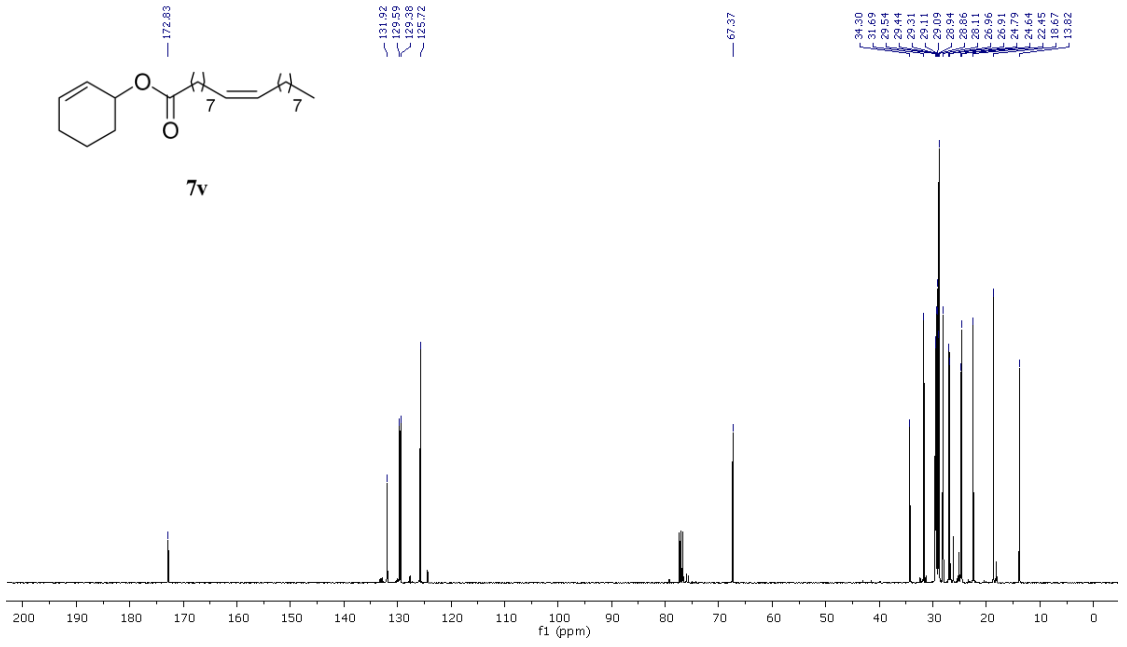


Figure S164. ^{13}C Spectrum of **7v** in $CDCl_3$ (100 MHz)

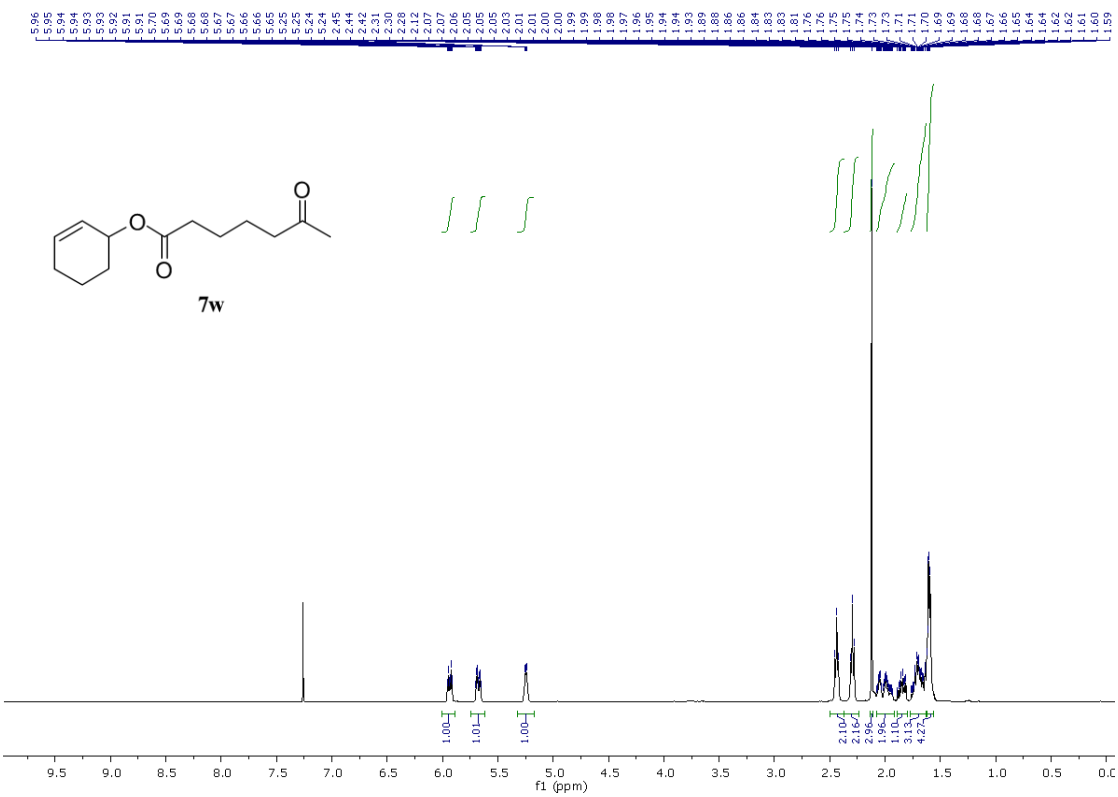


Figure S165. ^{1}H Spectrum of **7w** in $CDCl_3$ (400 MHz)

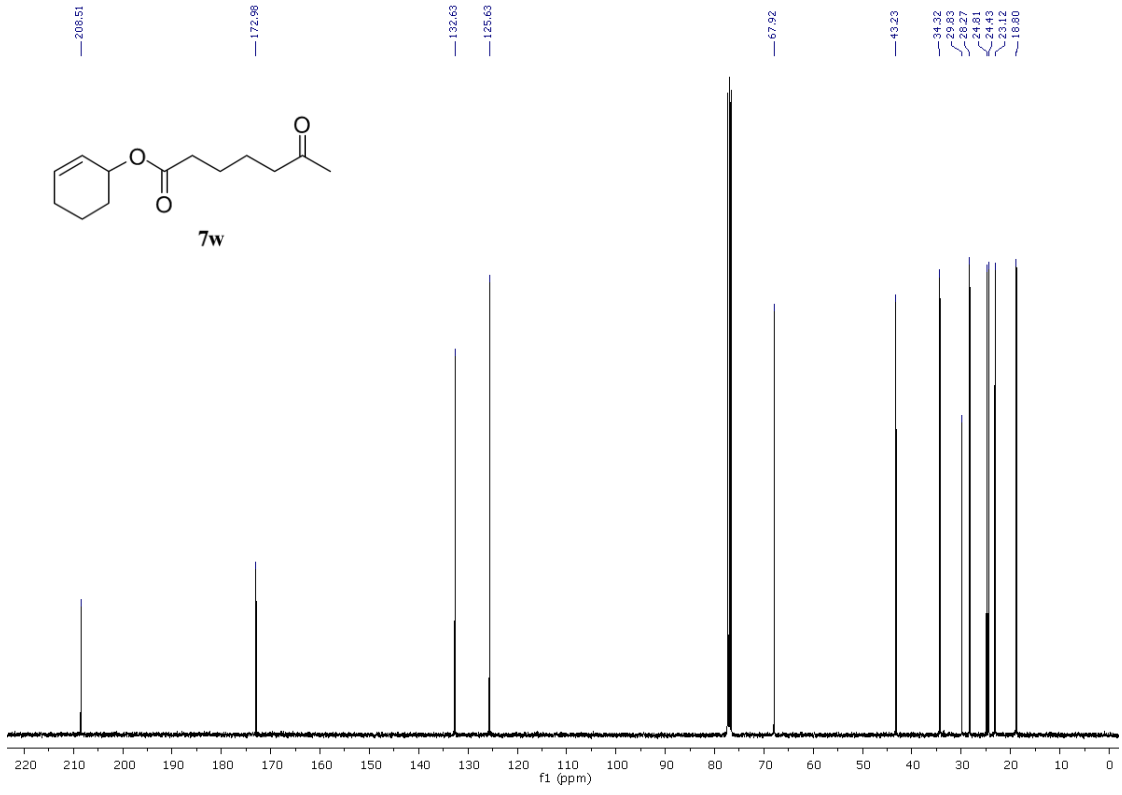


Figure S166. ^{13}C Spectrum of **7w** in $CDCl_3$ (100 MHz)

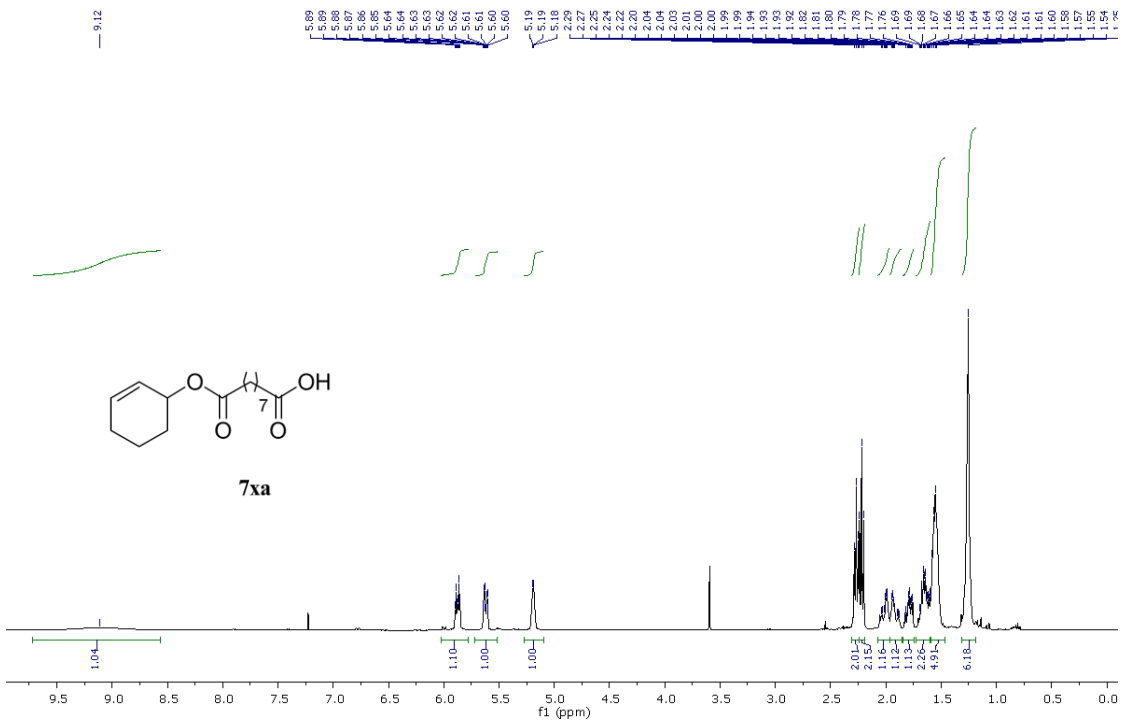


Figure S167. ^{1}H Spectrum of **7xa** in $CDCl_3$ (400 MHz)

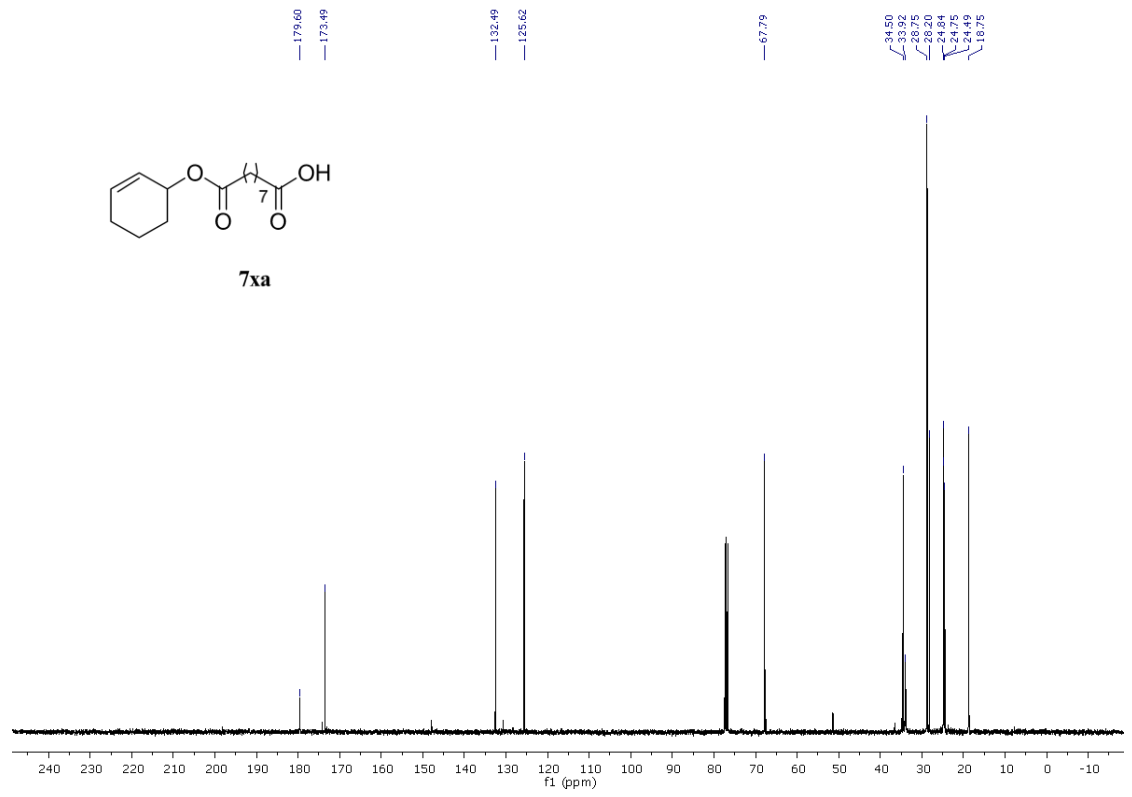


Figure S168. ^{13}C Spectrum of **7xa** in $CDCl_3$ (100 MHz)

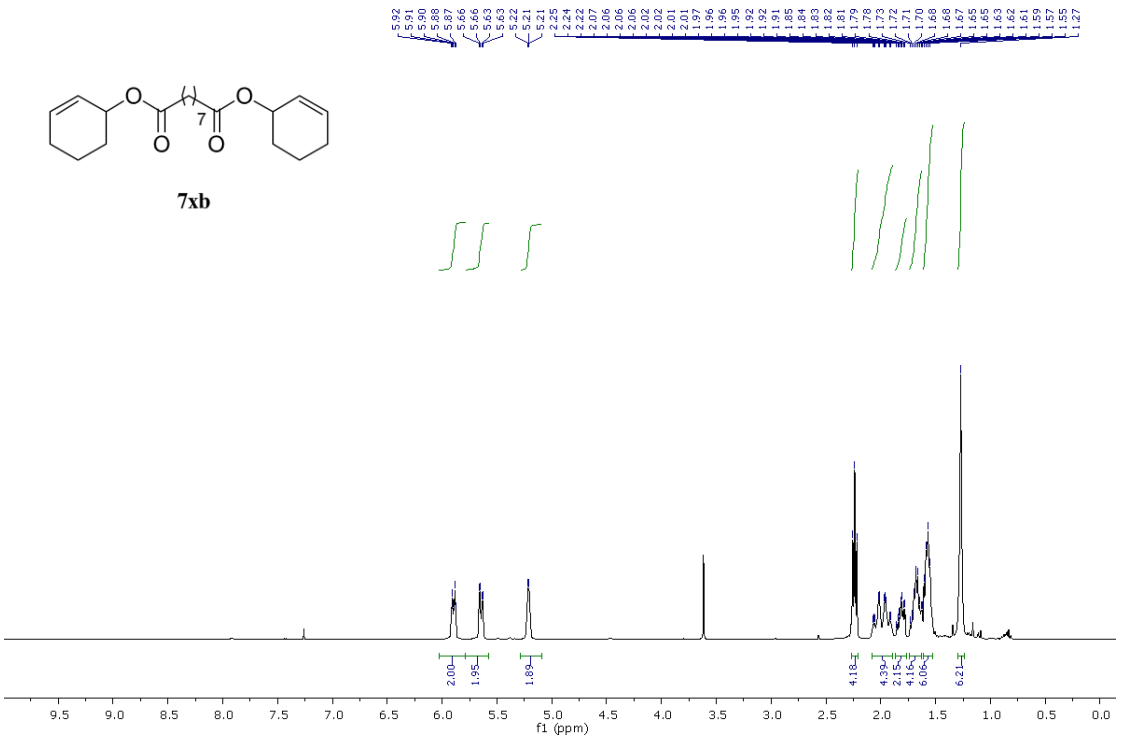


Figure S169. ^{1}H Spectrum of **7xb** in $CDCl_3$ (400 MHz)

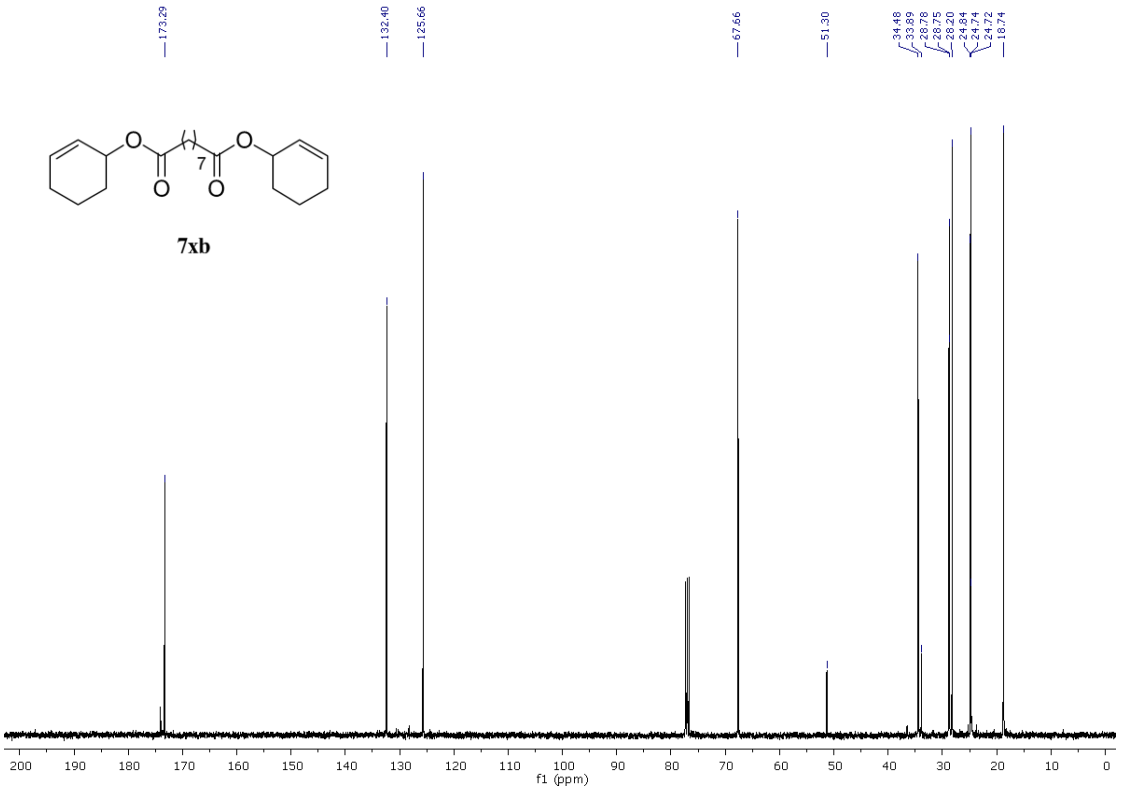


Figure S170. ^{13}C Spectrum of **7xb** in $CDCl_3$ (100 MHz)