Electronic Supplementary Information:

Vanadium-catalysed regioselective hydroboration of epoxides for synthesis of secondary alcohols

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General Considerations. Unless specified otherwise, all reactions were carried out under a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Anhydrous grade solvents (stored over 4 Å molecular sieves) and epoxide substrates were purchased from Sigma-Aldrich, Fisher Scientific and TCI America. 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine was purchased from TCI America. Pinacolborane was purchased from Acros or Alfa Aesar and used as received. FT-IR spectra were recorded on a Shimadzu 8400S instrument with solid samples under N_2 using a Golden Gate ATR accessory. ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature on a Bruker AV 500 or 600 MHz NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. GC-MS analysis was obtained using a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer. Vanadium complexes **1** and **2** were prepared according to published procedures.[1]

Synthesis of vanadium complex 3. In a glovebox under N_2, In a 20 mL scintillation vial, 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (301 mg, 1.00 mmol) and vanadium(III) trichloride (156 mg, 1.00 mmol) were added to THF (10 mL). The solution was allowed to stir at room temperature for 24 h, during which time orange-brown suspension had formed. The precipitate was filtered and washed with THF (3 × 1 mL), dried in vacuo to give a brownish solid. Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a dilute solution of **3** in THF. Yield: 375 mg (82%). FT-IR (solid, cm^{-1}): 3068w, 2961w, 1637w, 1618s, 1577s, 1489m, 1403s, 1389s, 1283s, 1260m, 1206s, 1080m, 961s, 924s, 757m. Anal. Calc. for $C_{17}H_{23}Cl_3N_3O_2V$, C 44.52, H 5.05, N 9.16%; Found C 44.36, H 4.98, N 9.10%.

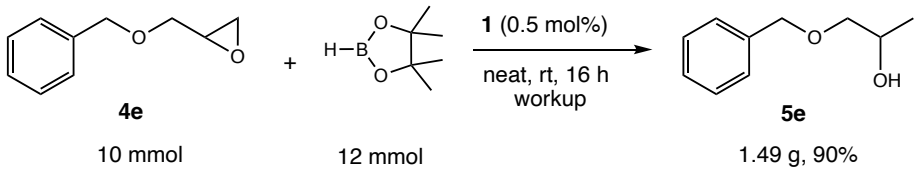
X-ray Crystallography. X-ray diffraction data for **3** were collected on a Bruker X8 Kappa Apex II diffractometer using Mo Kα radiation. Crystal data, data collection and refinement parameters are summarized in **Error! Reference source not found.**. The structure was solved using a dual-space method and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2017/1).[2] All hydrogen atoms were placed in calculated positions and refined with a riding model [U_{iso}(H) = 1.2–1.5U_{eq}(C)]. CCDC No. 2267023 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S1. X-ray crystallographic refinements for 3.

	3•THF
lattice	Orthorhombic
formula	$C_{21}H_{31}Cl_3N_3O_3V$
formula weight	530.78
space group	$P2_12_12_1$
a/Å	12.4989(5)
b/Å	12.5715(5)
c/Å	15.7661(6)
α/°	90
β/°	90
γ/°	90
V/Å^3	2477.33(17)
Z	4
temperature (K)	130(2)
radiation (λ, Å)	0.71073
ρ (calcd.) g cm^{-3}	1.423
μ (Mo Kα), mm^{-1}	0.751
θ max, deg.	34.302
no. of data collected	80912
no. of data	10059
no. of parameters	285
R_1 [$I > 2\sigma(I)$]	0.0359
wR_2 [$I > 2\sigma(I)$]	0.0800
R_1 [all data]	0.0522
wR_2 [all data]	0.0867
GOF	1.053
R_{int}	0.0474

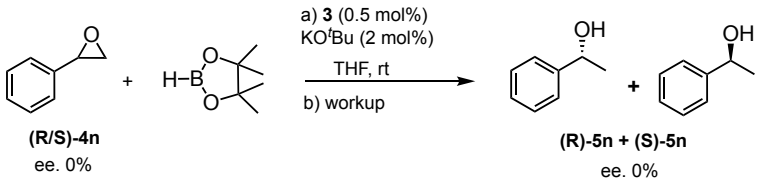
General Procedure for 1-Catalysed Hydroboration of Epoxides. In a glovebox under N_2 atmosphere, catalyst **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. Epoxide (1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added and the reaction mixture was allowed to stir at room temperature for 16 h. After completion of the reaction, the reaction mixture was first analyzed by GC-MS to determine the regioselectivity of desired boronate esters. The reaction mixture was quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture then subject to a flash column chromatography on silica using ethyl acetate/hexane as an eluent. The pure products of alcohols were obtained and characterized by ^1H and ^{13}C NMR spectroscopies.

Gram-Scale Experiment for synthesis of 5e. In a glovebox under N_2 atmosphere, catalyst **1** (26.7 mg, 0.5 mol%) was placed in a 20 mL glass vial equipped with a tiny stir bar. 2-((Benzyloxyl)methyl)oxirane (1.64 g, 10 mmol) and pinacolborane (1.54 g, 12 mmol, 1.2 eq) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS (95% GC yield) and then the product was isolated (1.49 g, 90%) by column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. The product was characterized by ^1H and ^{13}C NMR spectroscopies.



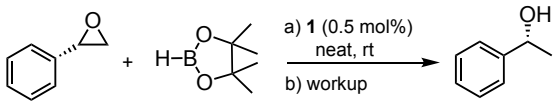
Scheme S1. Gram-scale synthesis of 5e.

Determination of Enantiomeric Excess (ee) of Alcohol Product Catalysed by 3.



In a glovebox under N_2 atmosphere, complex **3** (2.29 mg, 0.5 mol%) and potassium *tert*-butoxide (2.2 mg, 2 mol%) were dissolved in THF (0.5 mL) in a 1.5 mL glass vial equipped with a stir bar. Racemic styrene oxide (120 mg, 1.0 mmol, 0% ee) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated (52%). The product was subject to the reaction with (*R*)-(-)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride to give Mosher ester for determination of enatiomeric excess by ^1H NMR spectroscopy (0% ee was detected).[3]

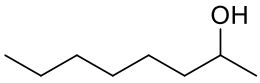
Hydroboration of Enantiopure 4n Catalysed by 1:



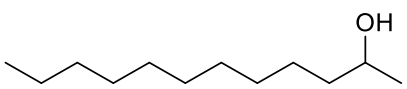
(S)-4n ee. 98% **(R)-5n** ee. 98%

In a glovebox under N_2 atmosphere, catalyst **1** (2.67 mg, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a stir bar. (*S*)-(-)-Styrene oxide (120 mg, 1.0 mmol, 98% ee) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated (82%). The product was subject to the reaction with (*R*)-(-)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride to give the desired Mosher ester for determination of enatiomeric excess by ^{1}H NMR (in comparison with the ^{1}H NMR spectroscopy of the diastereomeric mixture made from racemic 1-phenylethanol and (*R*)-(-)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride).[3]

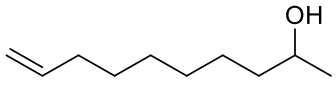
Catalytic details and characterization data



2-Octanol (5a):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 1,2-Epoxyoctane (128 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 117 mg (90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 – 3.72 (m, 1H), 1.58 (s, 1H), 1.47 – 1.35 (m, 3H), 1.32 – 1.24 (m, 7H), 1.16 (d, J = 6.3 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 68.3, 39.5, 32.0, 29.4, 25.9, 23.6, 22.7, 14.2 ppm.

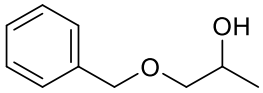


2-Dodecanol (5b):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 1,2-Epoxydodecane (184 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil was isolated. Yield: 175 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (h, J = 6.1 Hz, 1H), 1.76 (s, 1H), 1.52 – 1.36 (m, 3H), 1.34 – 1.24 (m, 15H), 1.18 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.2, 39.5, 32.0, 29.8, 29.8, 29.7, 29.5, 25.9, 23.5, 22.8, 14.2 ppm.

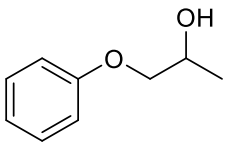


Dec-9-en-2-ol (5c):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-(Oct-7-en-1-yl)oxirane (154 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched

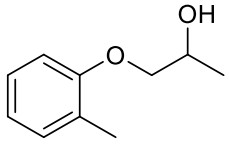
with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil was isolated. Yield: 136 mg (91%). ^1H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02 – 4.85 (m, 2H), 3.76 (tdd, J = 6.1, 4.9, 1.2 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.56 (s, 1H), 1.45 – 1.26 (m, 10H), 1.16 (d, J = 6.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 114.3, 68.2, 39.4, 33.9, 29.6, 29.2, 29.0, 25.8, 23.6 ppm.



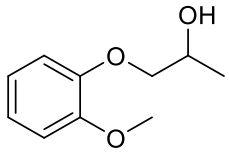
1-(Benzyloxy)propan-2-ol (5e):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-((Benzyloxyl)methyl)oxirane (164 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 158 mg (95%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 5H), 4.48 (s, 2H), 3.98 – 3.87 (m, 1H), 3.39 (dd, J = 9.4, 3.1 Hz, 1H), 3.21 (dd, J = 9.5, 8.1 Hz, 1H), 2.24 (s, 1H), 1.07 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 128.5, 127.8, 127.8, 75.9, 73.3, 66.5, 18.7 ppm.



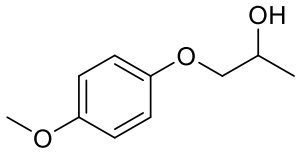
1-Phenoxypropan-2-ol (5f):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-(Phenoxymethyl)oxirane (150 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 143 mg (94%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 2H), 6.83 – 6.74 (m, 1H), 6.74 – 6.68 (m, 2H), 4.04 – 3.93 (m, 1H), 3.72 (dd, J = 9.2, 3.3 Hz, 1H), 3.61 (dd, J = 9.3, 7.6 Hz, 1H), 2.60 – 2.41 (m, 1H), 1.09 (d, J = 6.4 Hz, 4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 129.6, 121.1, 114.6, 73.3, 66.3, 18.9 ppm.



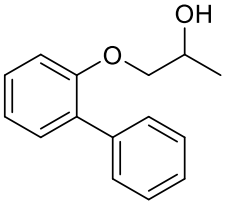
1-(2-Methylphenoxy)propan-2-ol (5g):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-(2-Methylphenoxymethyl)oxirane (164 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 139 mg (84%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 2H), 6.90 (td, J = 7.4, 1.2 Hz, 1H), 6.87 – 6.78 (m, 1H), 4.28 – 4.15 (m, 1H), 3.95 (dd, J = 9.2, 3.4 Hz, 1H), 3.83 (dd, J = 9.2, 7.4 Hz, 1H), 2.37 (s, 1H), 2.27 (s, 3H), 1.32 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.8, 126.9, 120.9, 111.3, 73.3, 66.5, 18.9, 16.3 ppm.



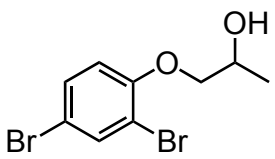
1-(2-Methoxyphenoxy)propan-2-ol (5h):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-(2-Methoxyphenoxymethyl)oxirane (180 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White gel was isolated. Yield: 158 mg (87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 – 6.86 (m, 4H), 4.23 – 4.14 (m, 1H), 4.00 (dd, J = 9.7, 3.0 Hz, 1H), 3.85 (s, 3H), 3.79 (dd, J = 9.7, 8.3 Hz, 1H), 3.15 (s, 1H), 1.24 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 148.3, 122.2, 121.1, 115.6, 112.1, 76.0, 66.1, 55.9, 18.4 ppm.



1-(4-Methoxyphenoxy)propan-2-ol (5i):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-(4-Methoxyphenoxymethyl)oxirane (180 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White gel was isolated. Yield: 155 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 – 6.76 (m, 4H), 4.20 – 4.09 (m, 1H), 3.86 (dd, J = 9.3, 3.3 Hz, 1H), 3.75 (d, J = 1.9 Hz, 3H), 3.74 – 3.70 (m, 1H), 2.72 (s, 1H), 1.25 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 152.8, 115.6, 114.7, 74.1, 66.3, 55.7, 18.8 ppm.

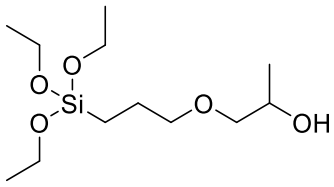


1-([1,1'-Biphenyl]-2-yloxy)propan-2-ol (5j):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. THF (1 mL) was added and then added and 2-([1,1'-Biphenyl]-2-yloxy methyl)oxirane (226 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were added later. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid was isolated. Yield: 187 mg (82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 2H), 7.32 (dd, J = 8.5, 6.9 Hz, 2H), 7.27 – 7.17 (m, 3H), 6.97 (td, J = 7.5, 1.1 Hz, 1H), 6.89 (dd, J = 8.2, 1.1 Hz, 1H), 3.95 (ddd, J = 7.7, 6.4, 3.4 Hz, 1H), 3.86 (dd, J = 9.1, 3.2 Hz, 1H), 3.65 (dd, J = 9.2, 7.6 Hz, 1H), 2.03 (s, 1H), 1.08 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 138.4, 131.5, 130.9, 129.5, 128.7, 128.1, 127.1, 121.7, 113.4, 74.3, 66.2, 18.6 ppm.

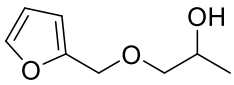


1-([1,1'-Biphenyl]-2-yloxy)propan-2-ol (5k):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 3.8 mL glass vial equipped with a tiny stir bar. THF (1 mL) was added and then 2-(2,4-dibromophenoxymethyl)oxirane (308 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched

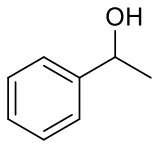
with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White gel was isolated. Yield: 291 mg (94%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 2.4 Hz, 1H), 7.35 (dd, J = 8.7, 2.4 Hz, 1H), 6.75 (d, J = 8.7 Hz, 1H), 4.22 (td, J = 6.9, 3.2 Hz, 1H), 3.97 (dd, J = 9.1, 3.3 Hz, 1H), 3.80 (dd, J = 9.1, 7.3 Hz, 1H), 2.61 (s, 1H), 1.30 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 135.5, 131.3, 114.8, 113.5, 74.8, 66.0, 18.7 ppm.



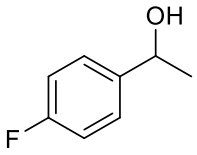
1-(3-(Triethoxysilyl)propoxy)propan-2-ol (5l):[5] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. Triethoxy(3-glycidyloxypropyl)silane (278 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 238 mg (85%). ^1H NMR (500 MHz, $CDCl_3$) δ 3.97 – 3.91 (m, 1H), 3.82 (q, J = 7.0 Hz, 6H), 3.49 – 3.44 (m, 1H), 3.42 (ddd, J = 9.2, 4.8, 1.7 Hz, 2H), 3.21 (dd, J = 9.5, 8.3 Hz, 1H), 2.57 (s, 1H), 1.74 – 1.66 (m, 2H), 1.23 (t, J = 7.0 Hz, 9H), 1.14 (d, J = 6.4 Hz, 3H), 0.69 – 0.63 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 76.3, 73.4, 66.4, 58.4, 23.0, 18.6, 18.3, 6.7 ppm.



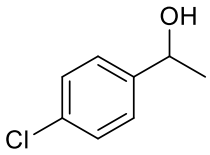
1-(Furan-2-methoxy)propan-2-ol (5m):[5] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 2-((Furan-2-methoxy)methyl)oxirane (156 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 133 mg (84%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, J = 1.8, 0.9 Hz, 1H), 6.40 – 6.26 (m, 2H), 4.55 – 4.42 (m, 2H), 3.96 (tdd, J = 6.4, 3.1, 1.8 Hz, 1H), 3.47 (dd, J = 9.5, 3.1 Hz, 1H), 3.27 (dd, J = 9.5, 8.2 Hz, 1H), 2.45 (s, 1H), 1.13 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 142.8, 110.4, 109.3, 75.6, 66.5, 65.1, 18.5 ppm.



1-Phenylethanol (5n):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. Styrene oxide (120 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 111 mg (91%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 5H), 4.80 (q, J = 6.5 Hz, 1H), 2.48 (s, 1H), 1.43 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 128.4, 127.4, 125.4, 70.2, 25.1 ppm.

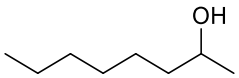


1-(4-Fluorophenyl)ethanol (5o):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 4-Fluorostyrene oxide (138 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated. Yield: 125 mg (89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 2H), 7.08 – 6.95 (m, 2H), 4.87 (q, J = 6.5 Hz, 1H), 1.98 (s, 1H), 1.47 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 162.1 (d, J = 245.3 Hz), 141.5, 141.5, 127.1 (d, J = 8.0 Hz), 127.0, 115.3 (d, J = 21.2 Hz), 115.2, 69.8, 25.3 ppm.



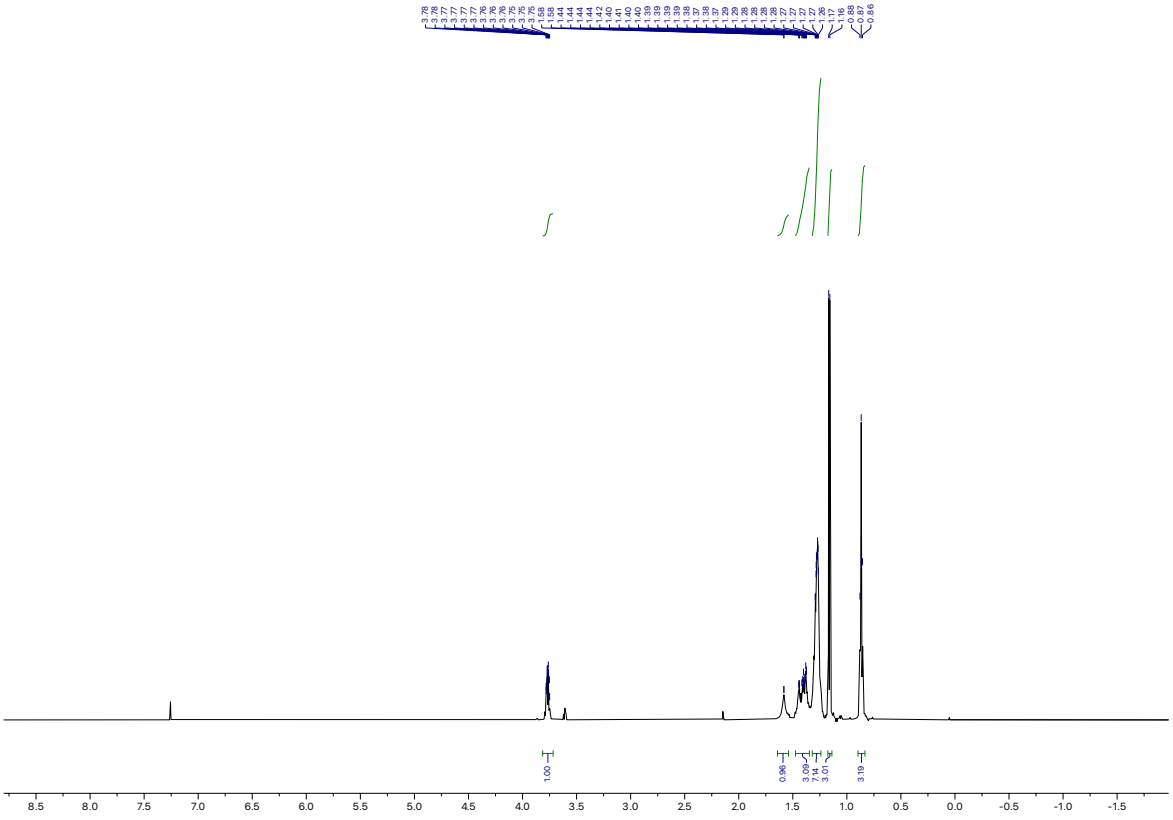
1-(4-Chlorophenyl)ethanol (5p):[4] In a glovebox under N_2 atmosphere, **1** (2.67 mg, 5.0 μmol, 0.5 mol%) was placed in a 1.5 mL glass vial equipped with a tiny stir bar. 4-Chlorostyrene oxide (156 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at 70 ºC for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid was isolated. Yield: 136 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (q, J = 8.5 Hz, 4H), 4.79 (q, J = 6.5 Hz, 1H), 2.63 (s, 1H), 1.41 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 133.1, 128.6, 126.9, 69.7, 25.3 ppm.

Copies of ^{1}H and ^{13}C NMR spectra for compounds 5a-p.



5a

^{1}H NMR spectrum:



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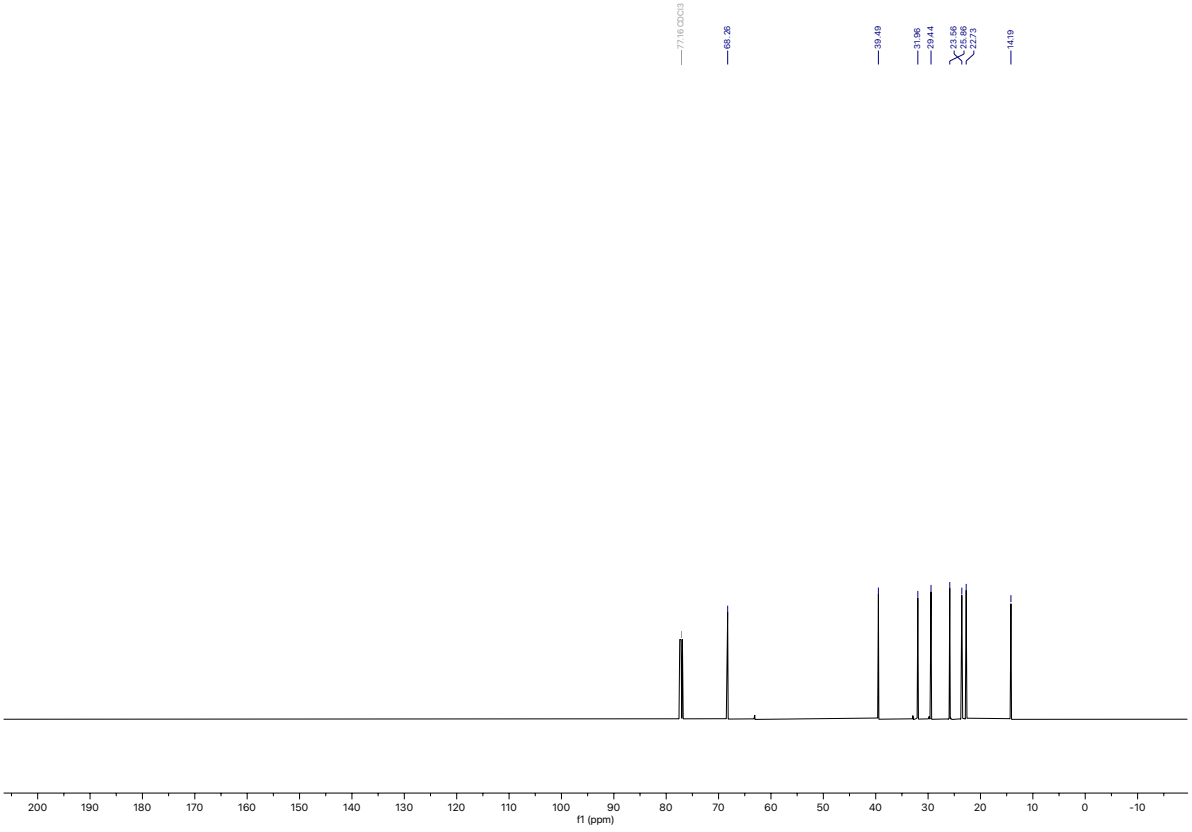
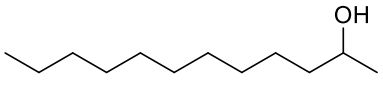
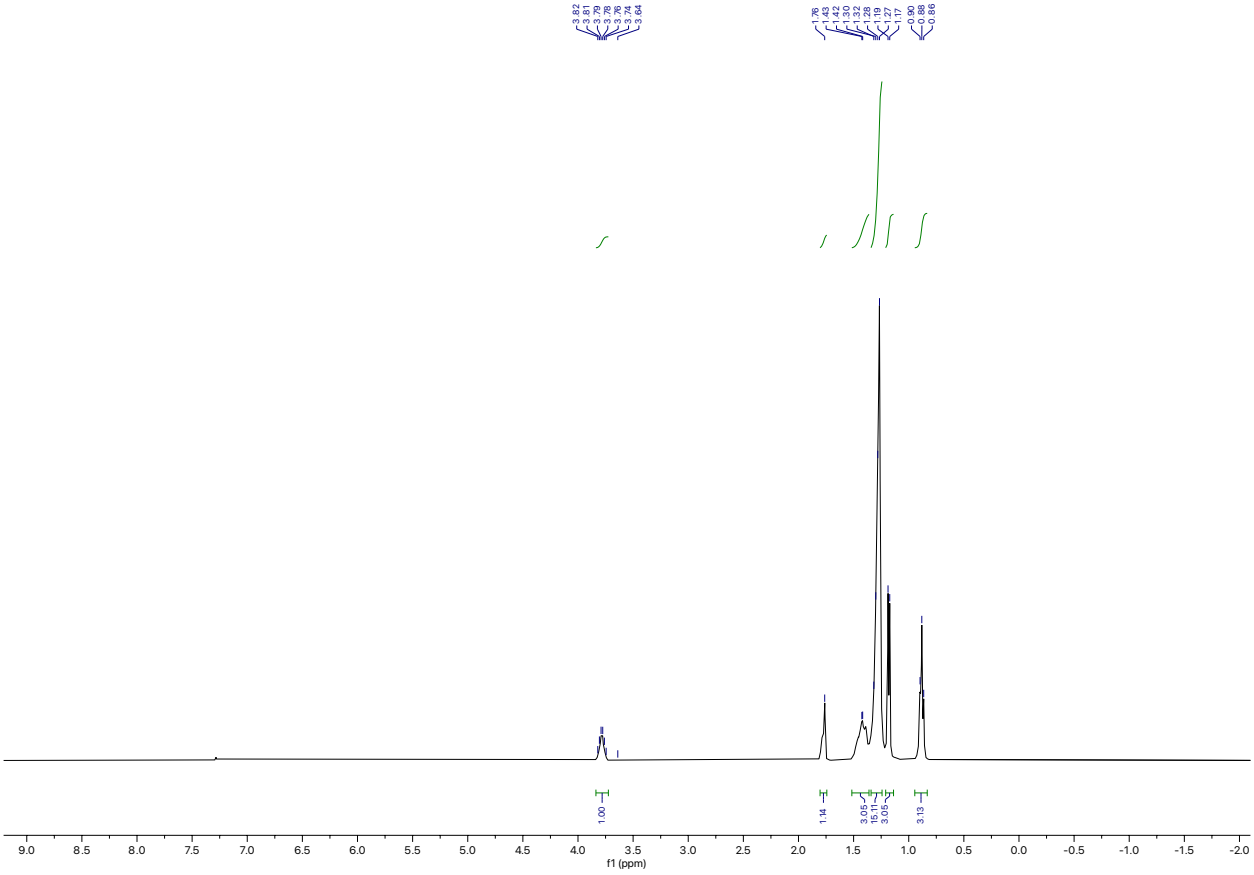


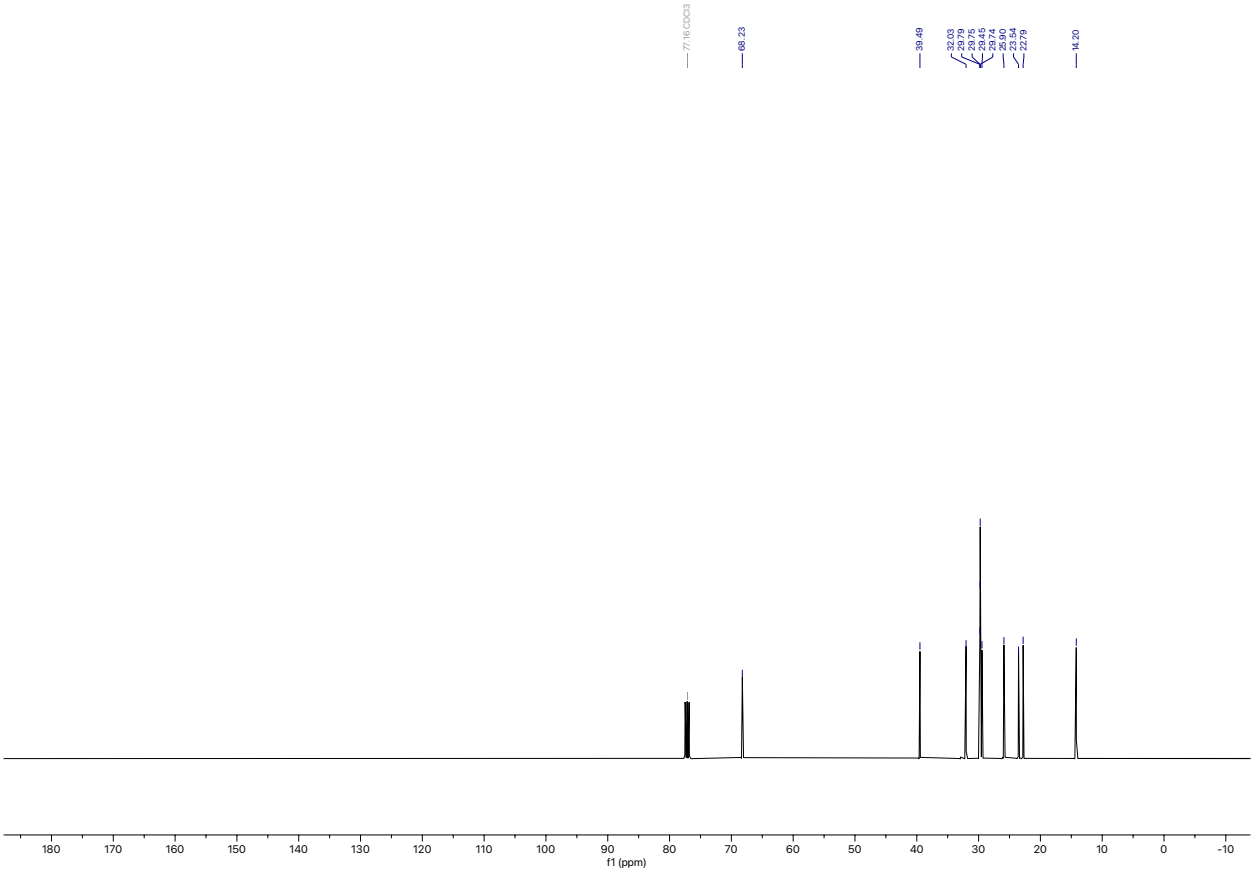


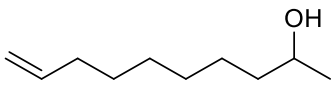
5b

^{1}H NMR spectrum:



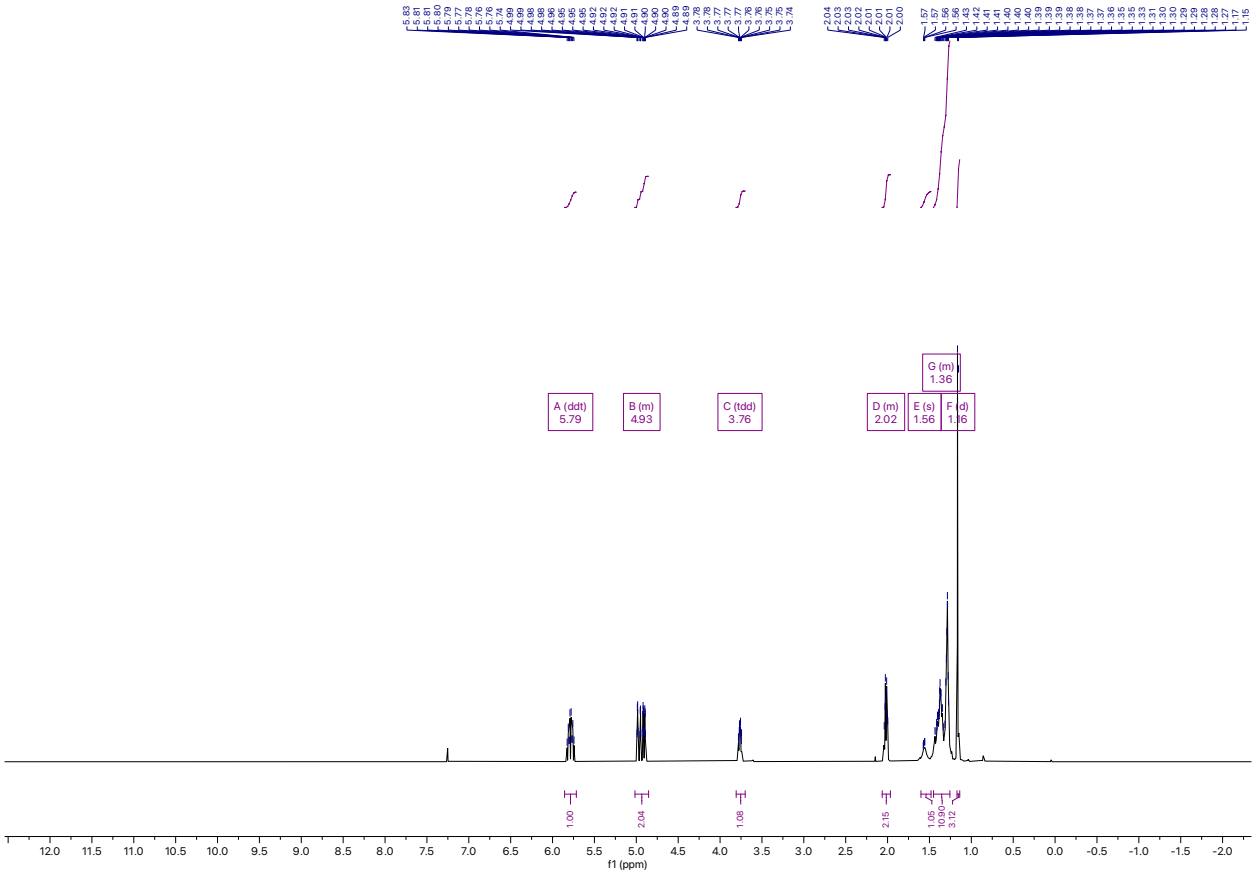
^{13}C NMR spectrum:



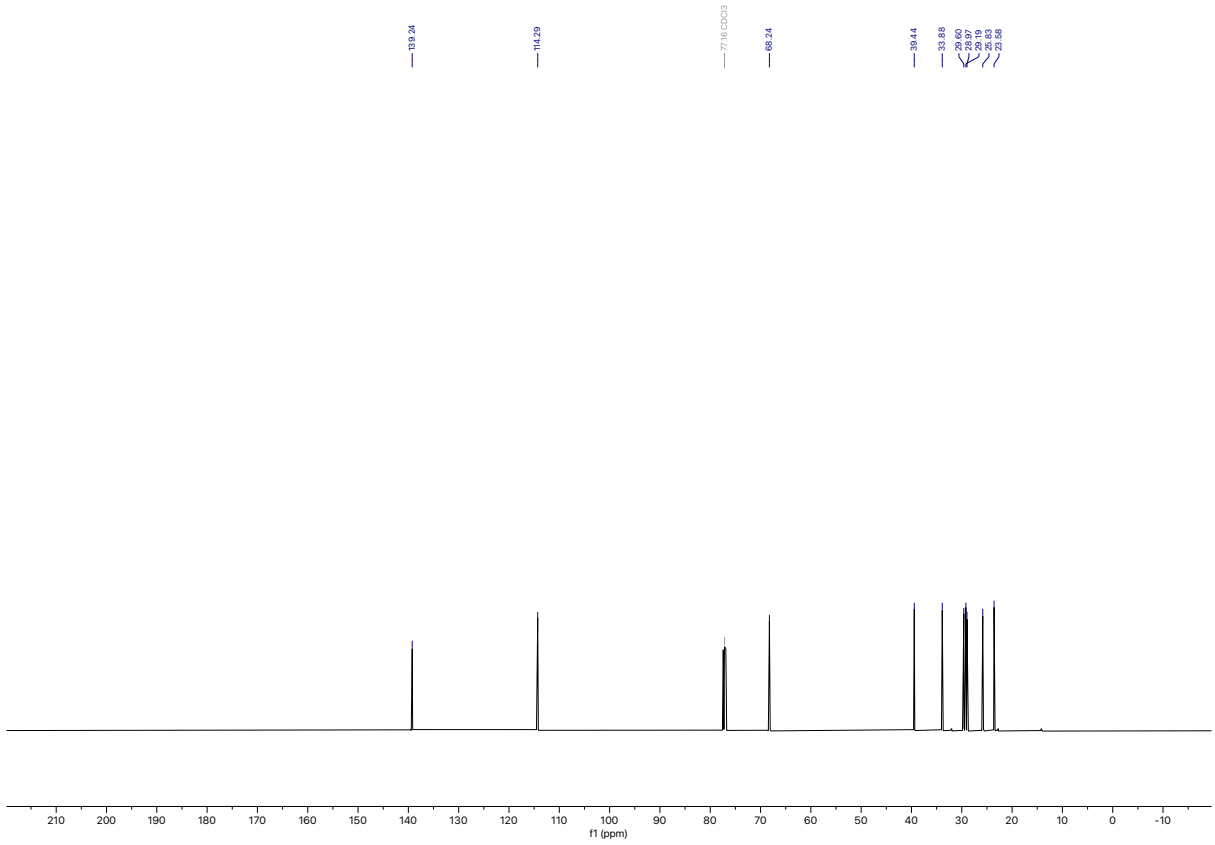


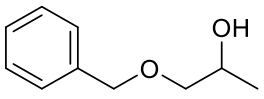
5c

^{1}H NMR spectrum:



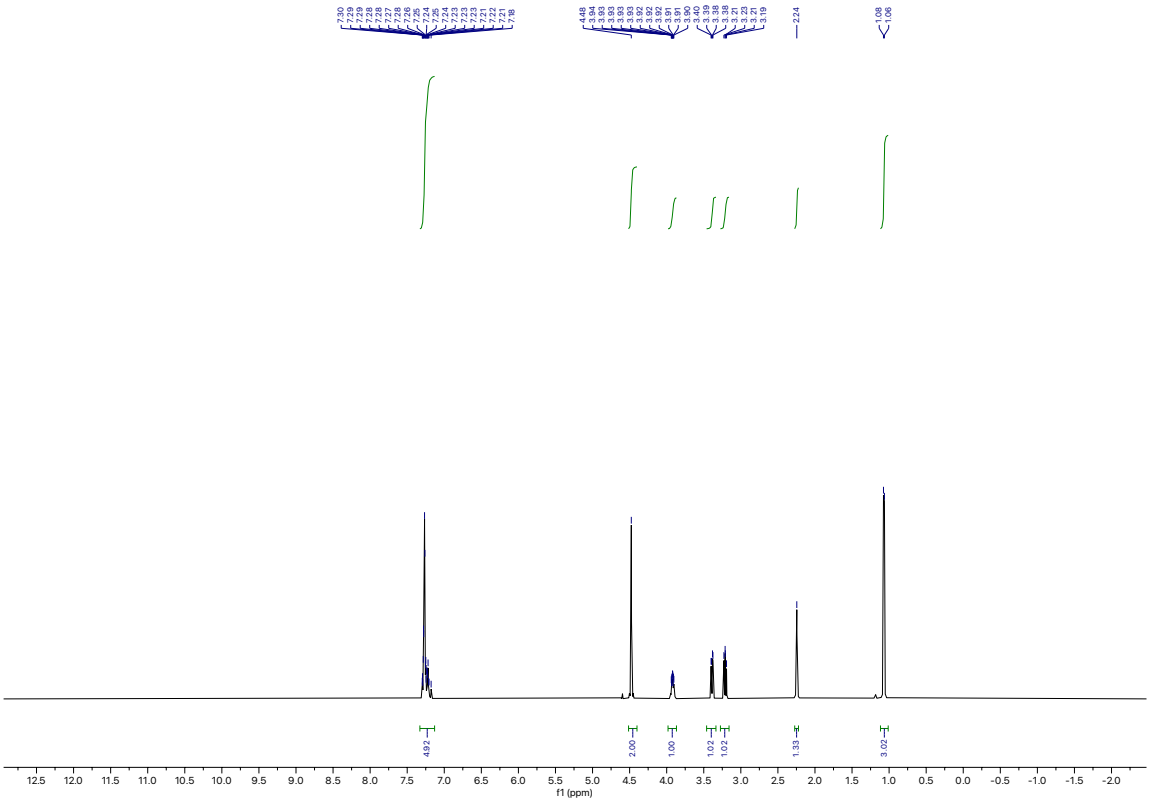
^{13}C NMR spectrum:



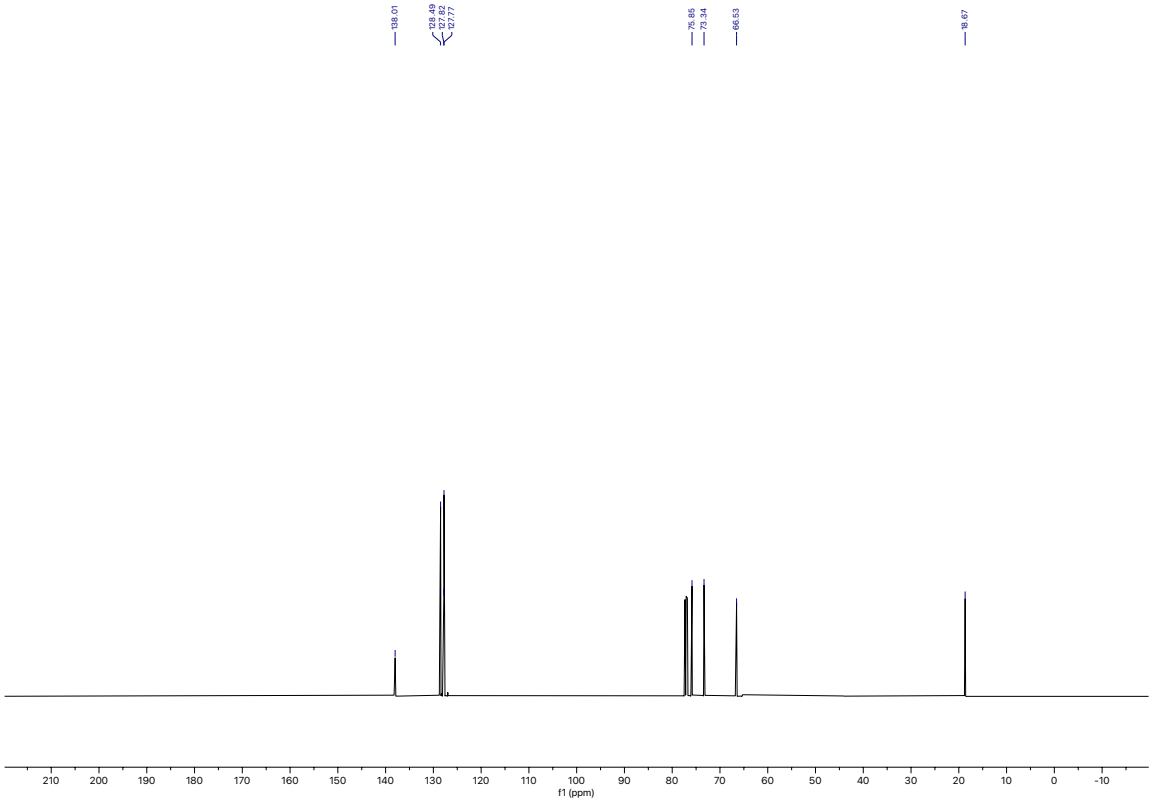


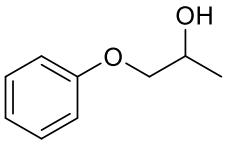
5e

^{1}H NMR spectrum:



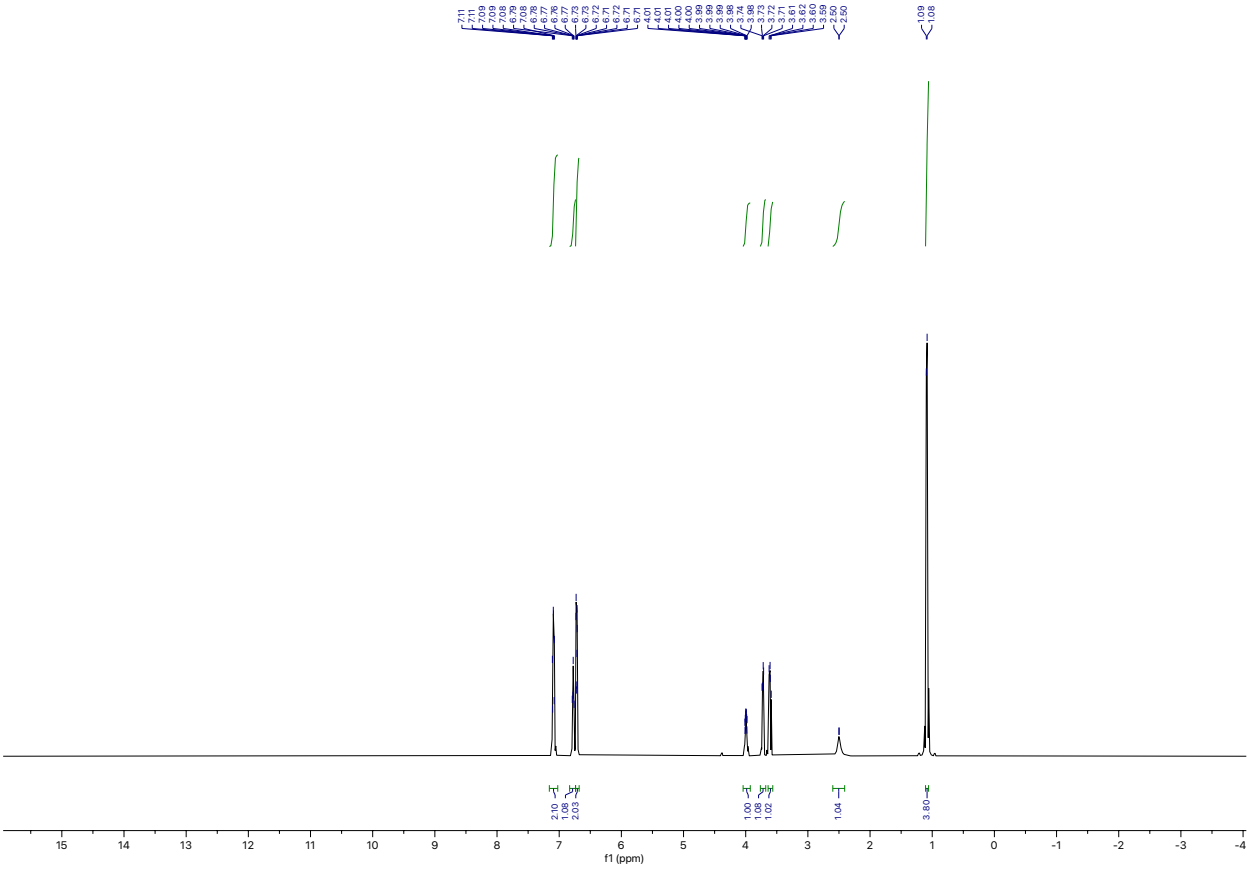
^{13}C NMR spectrum:



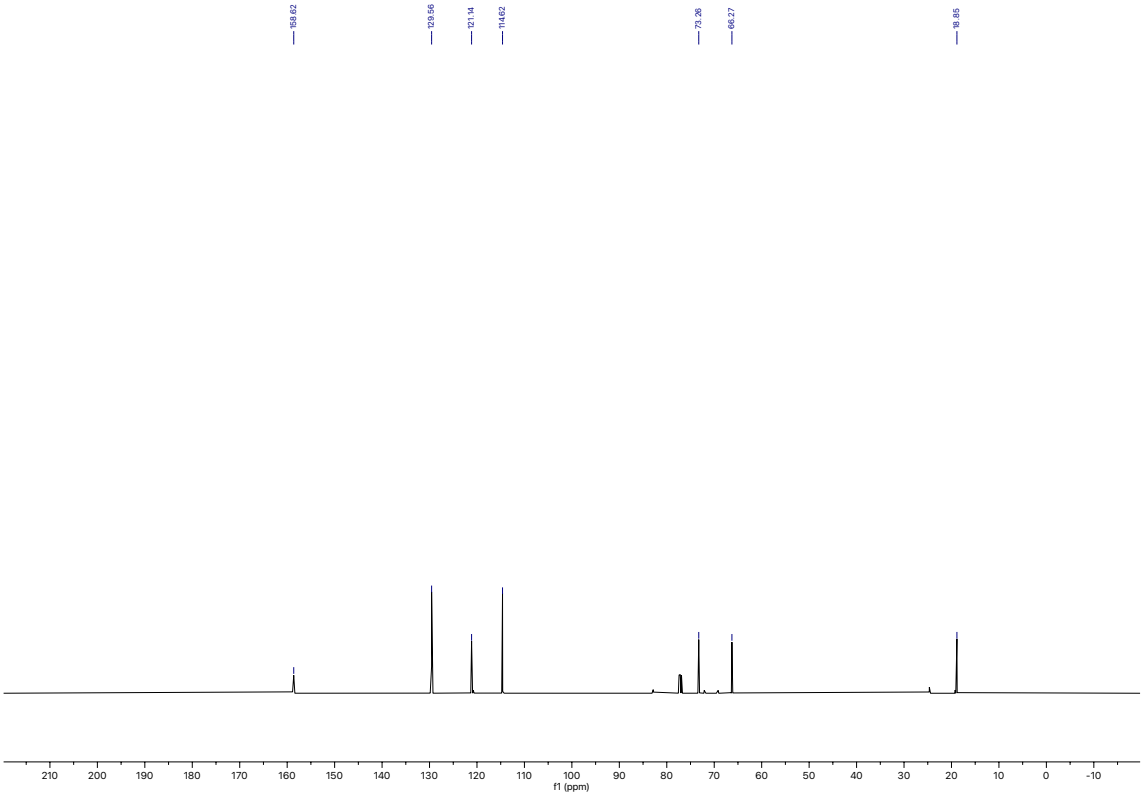


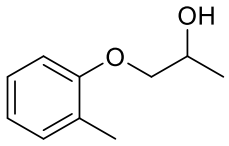
5f

^{1}H NMR spectrum:



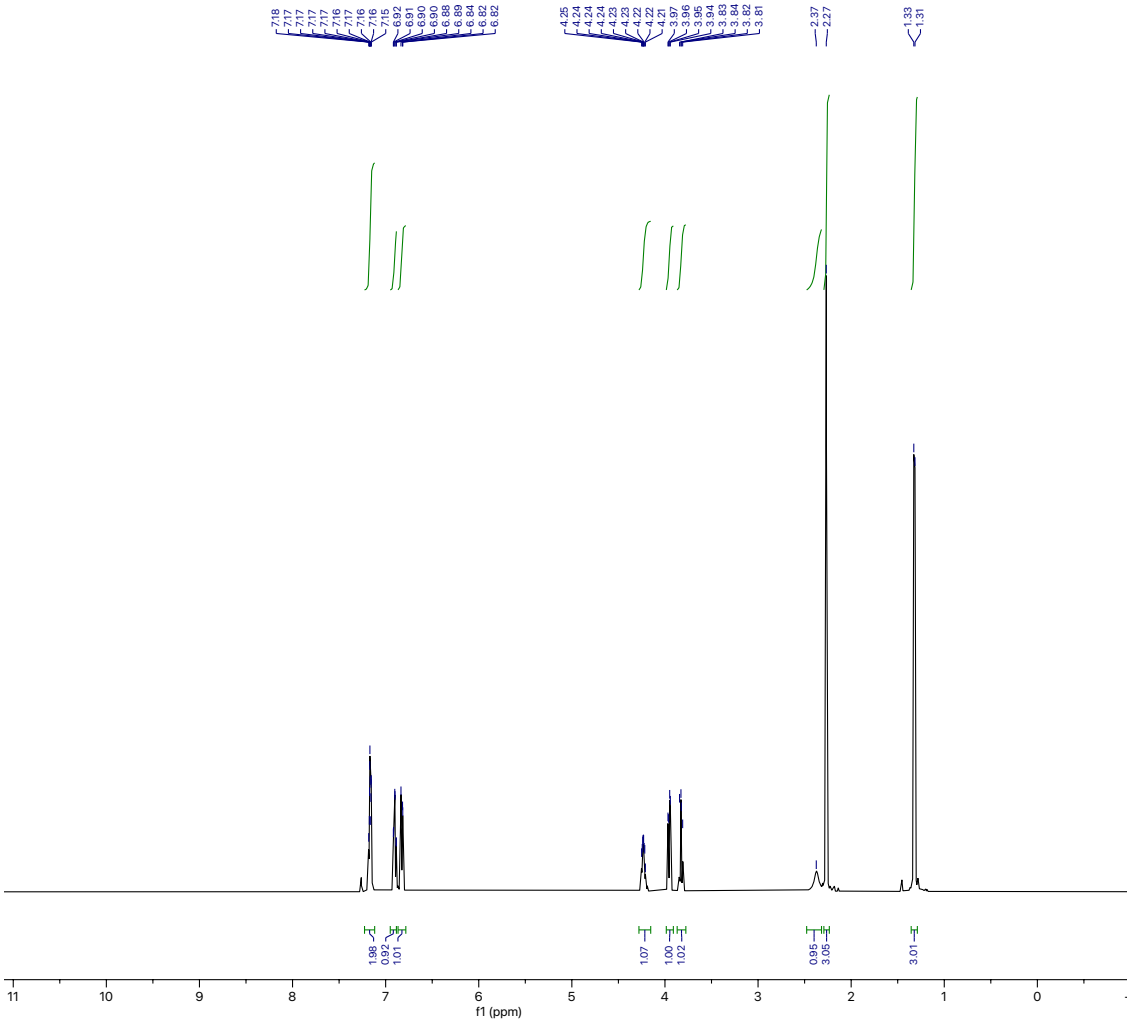
^{13}C NMR spectrum:



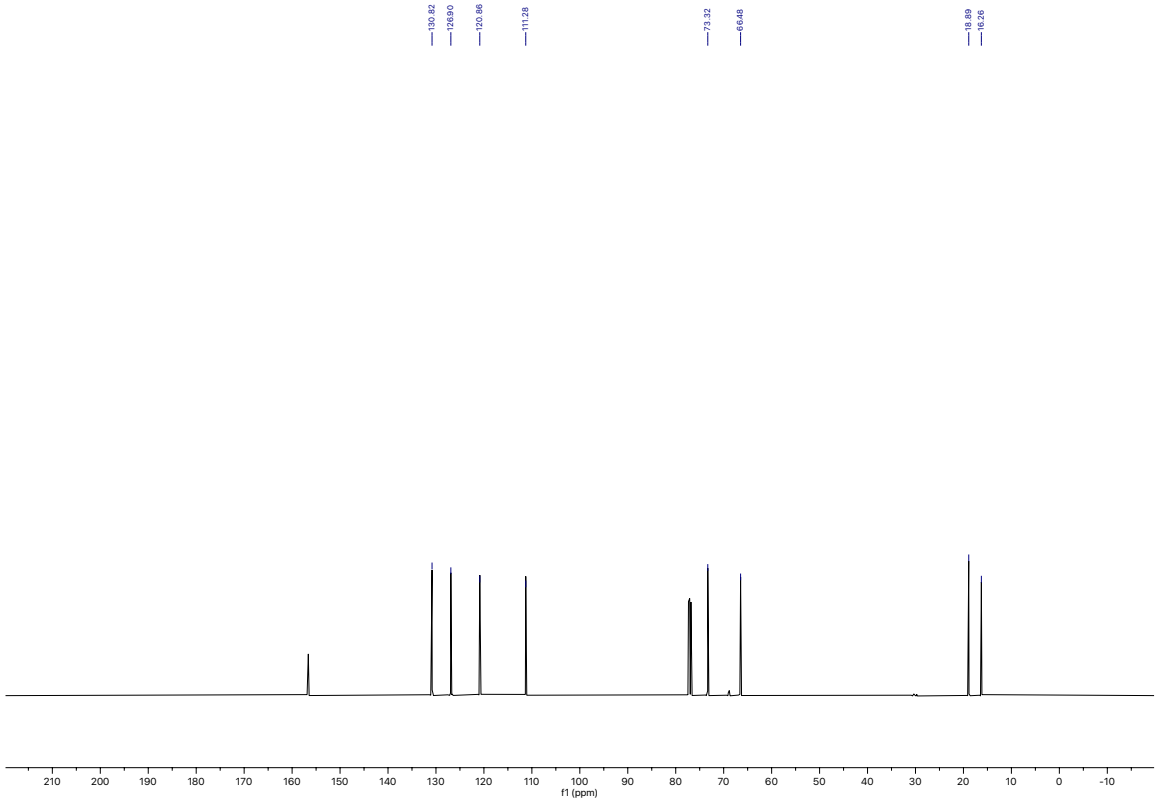


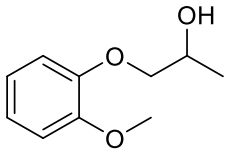
5g

^{1}H NMR spectrum:



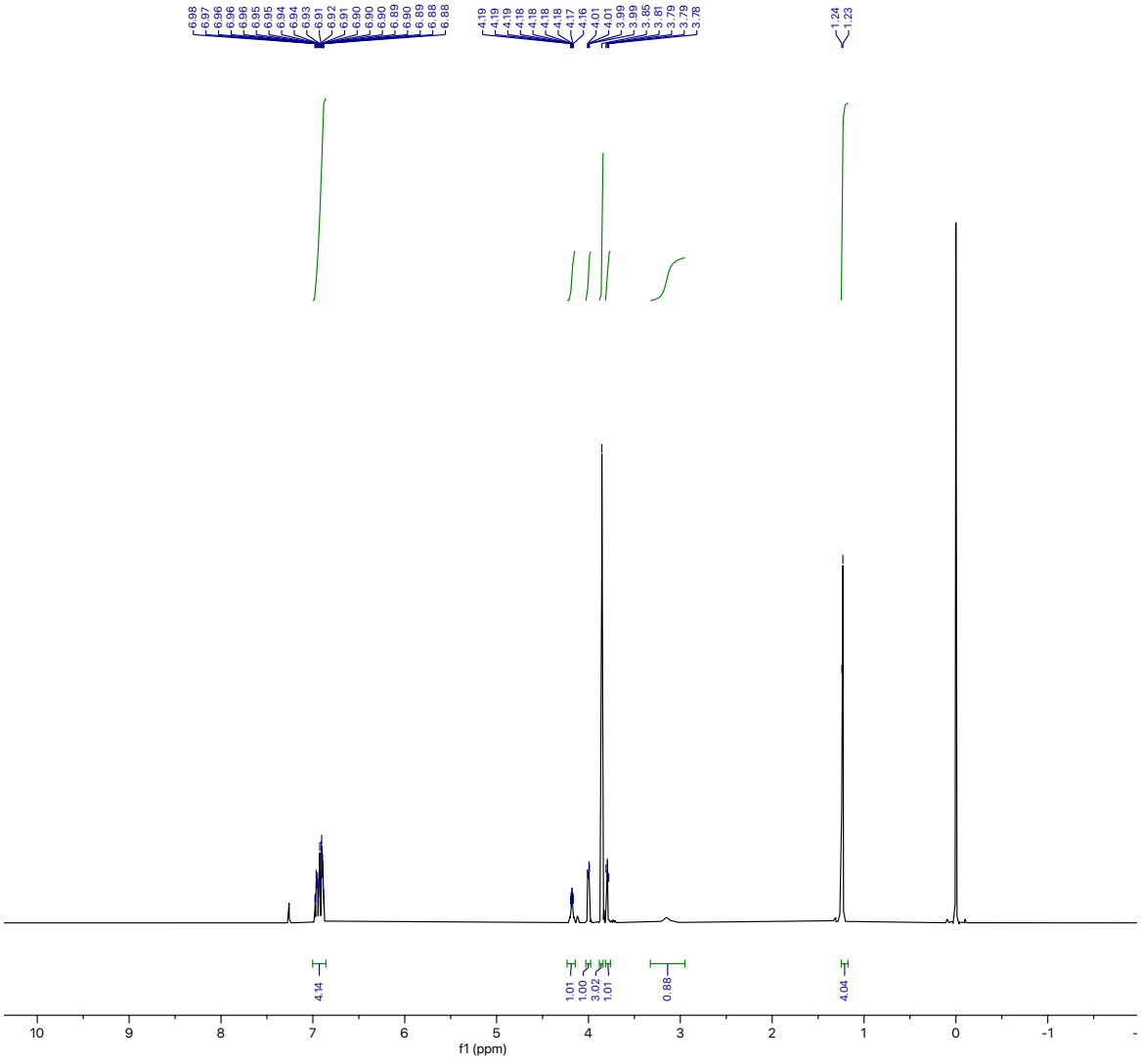
^{13}C NMR spectrum:



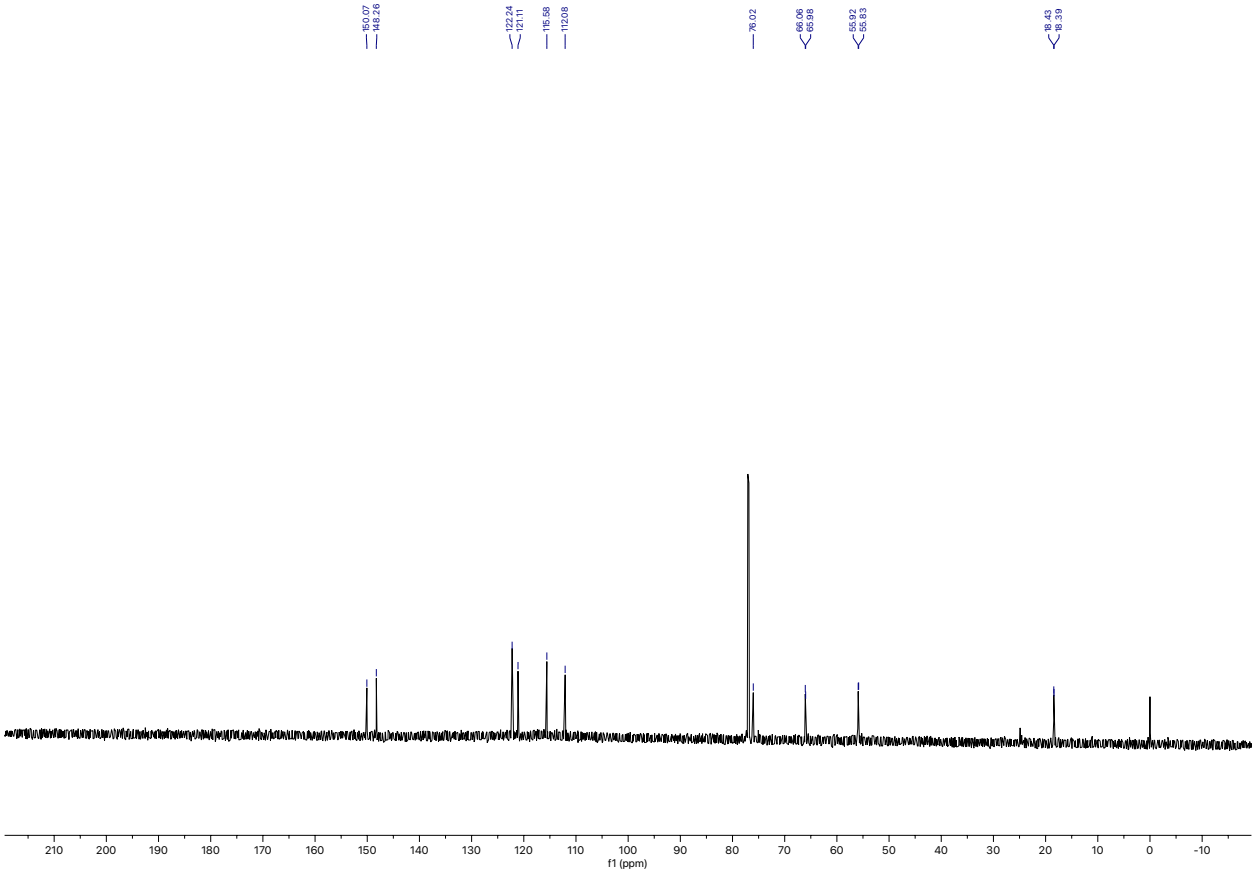


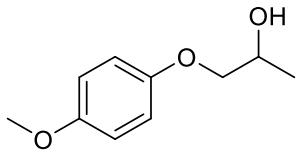
5h

^{1}H NMR spectrum:



^{13}C NMR spectrum:





5i

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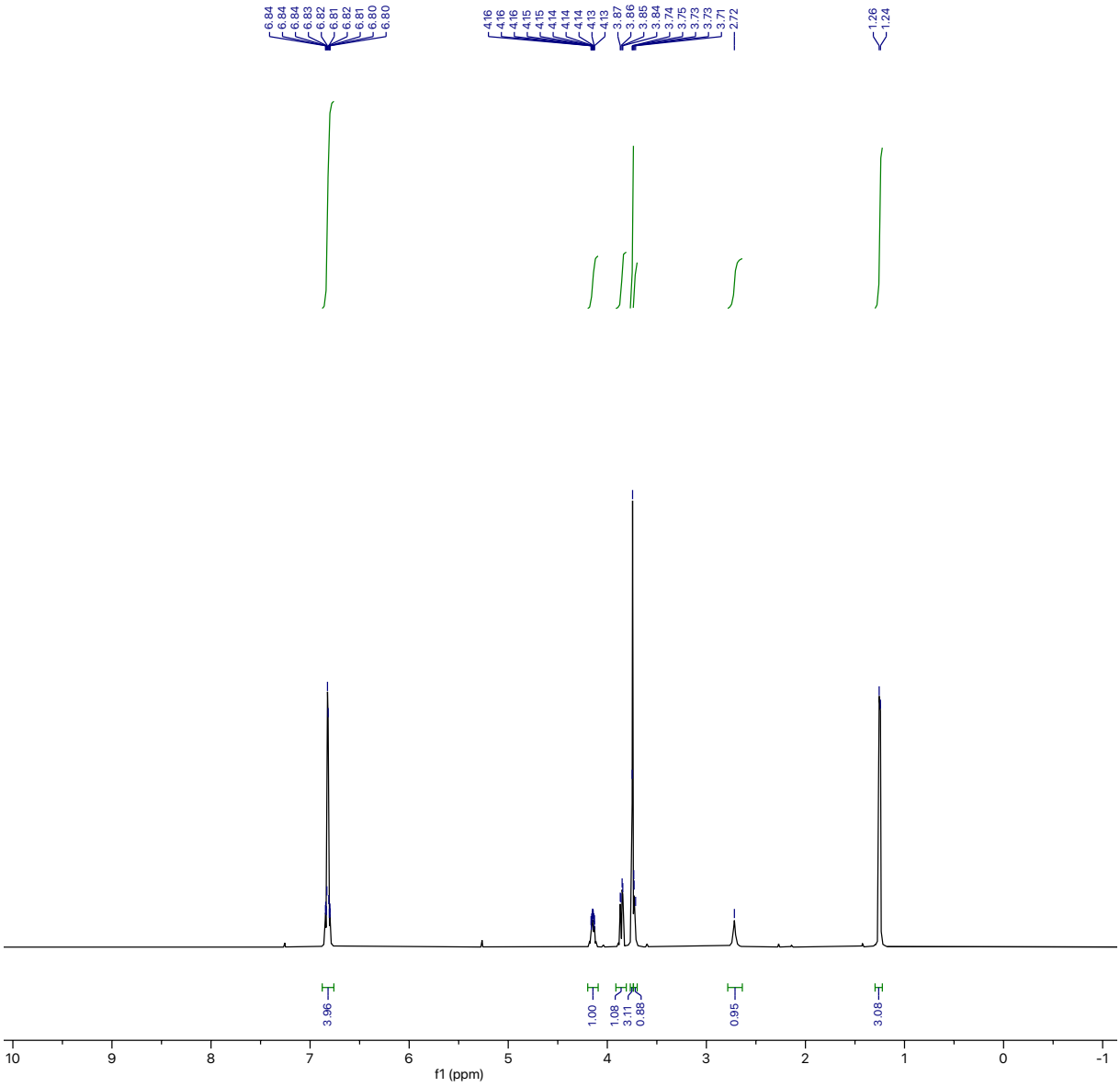
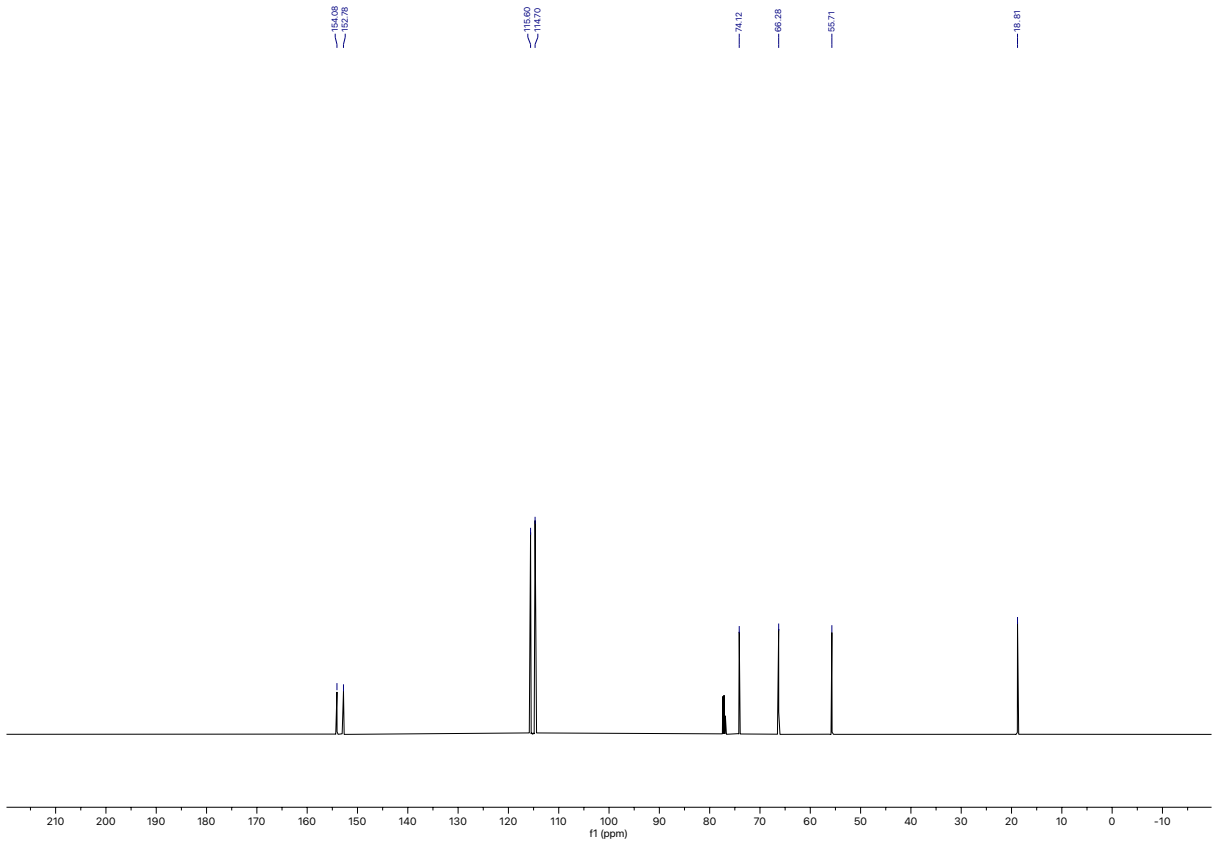
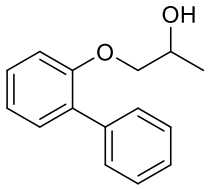


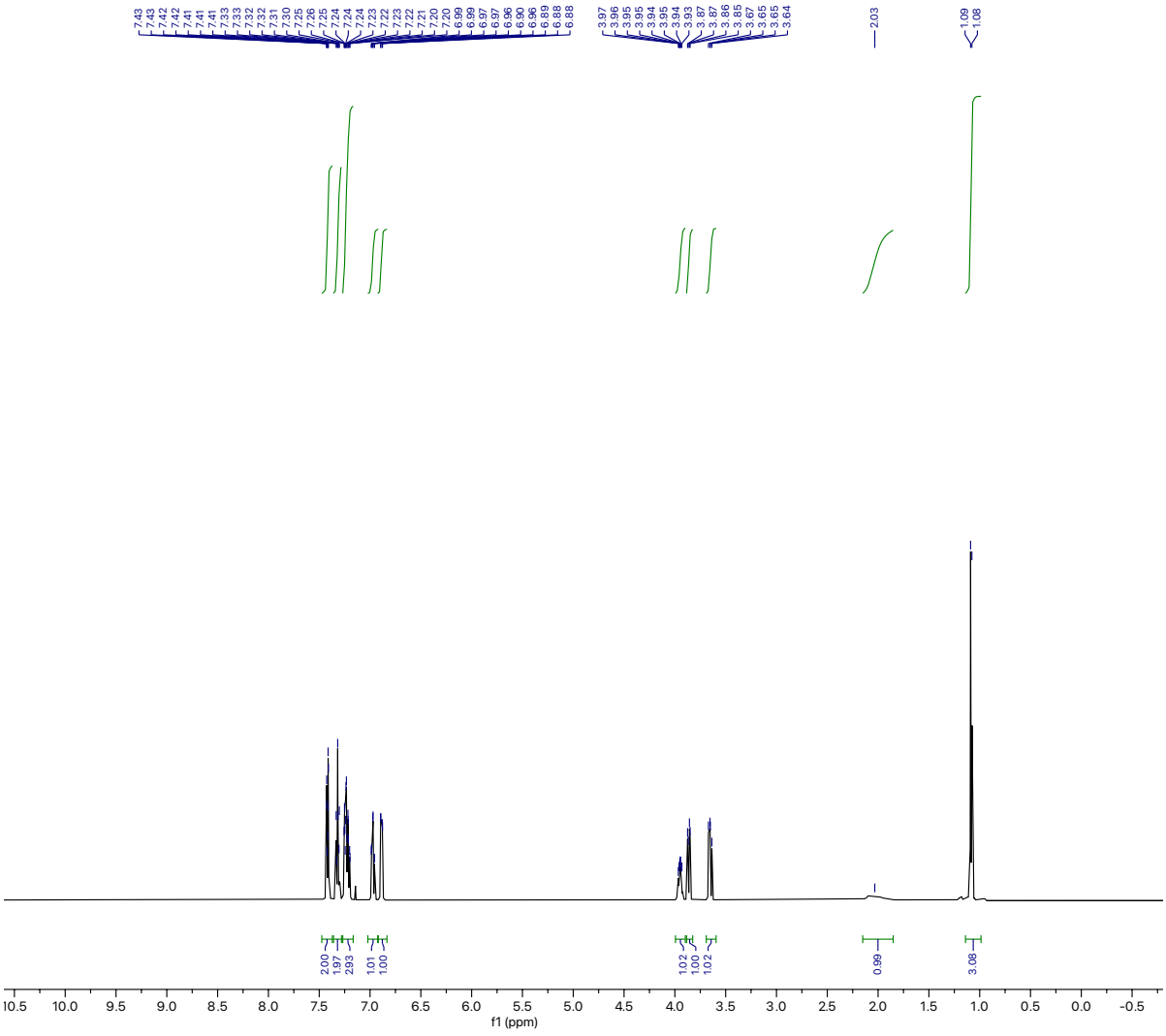
^{13}C NMR spectrum:



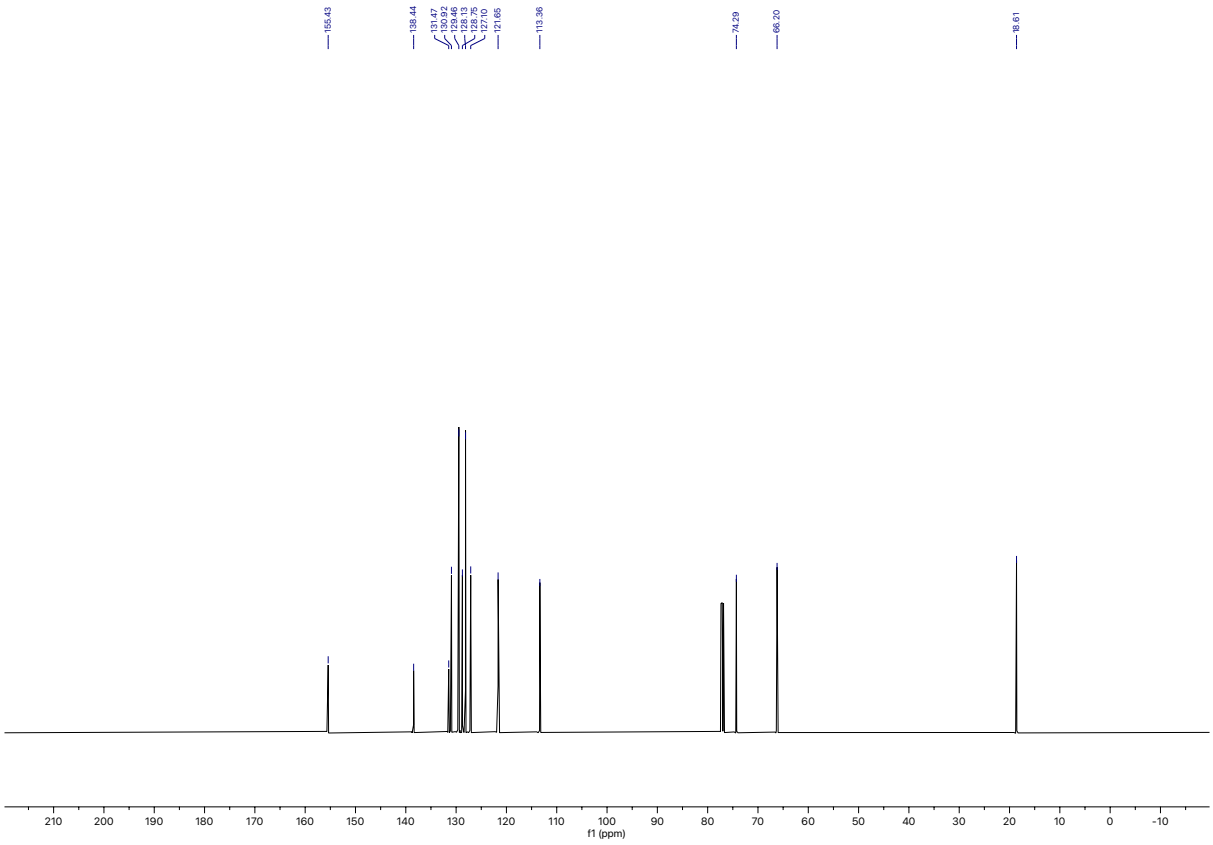


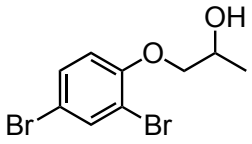
5j

^{1}H NMR spectrum:



^{13}C NMR spectrum:





5k

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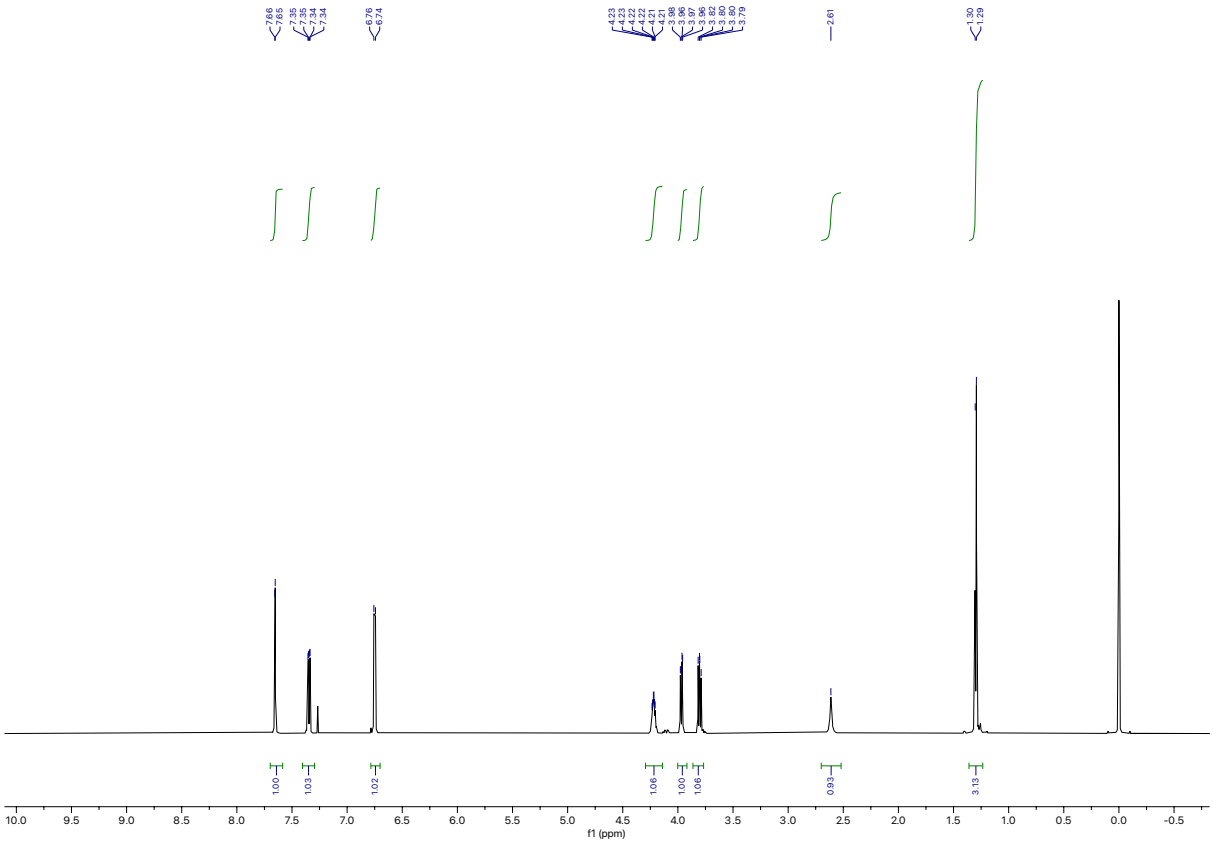

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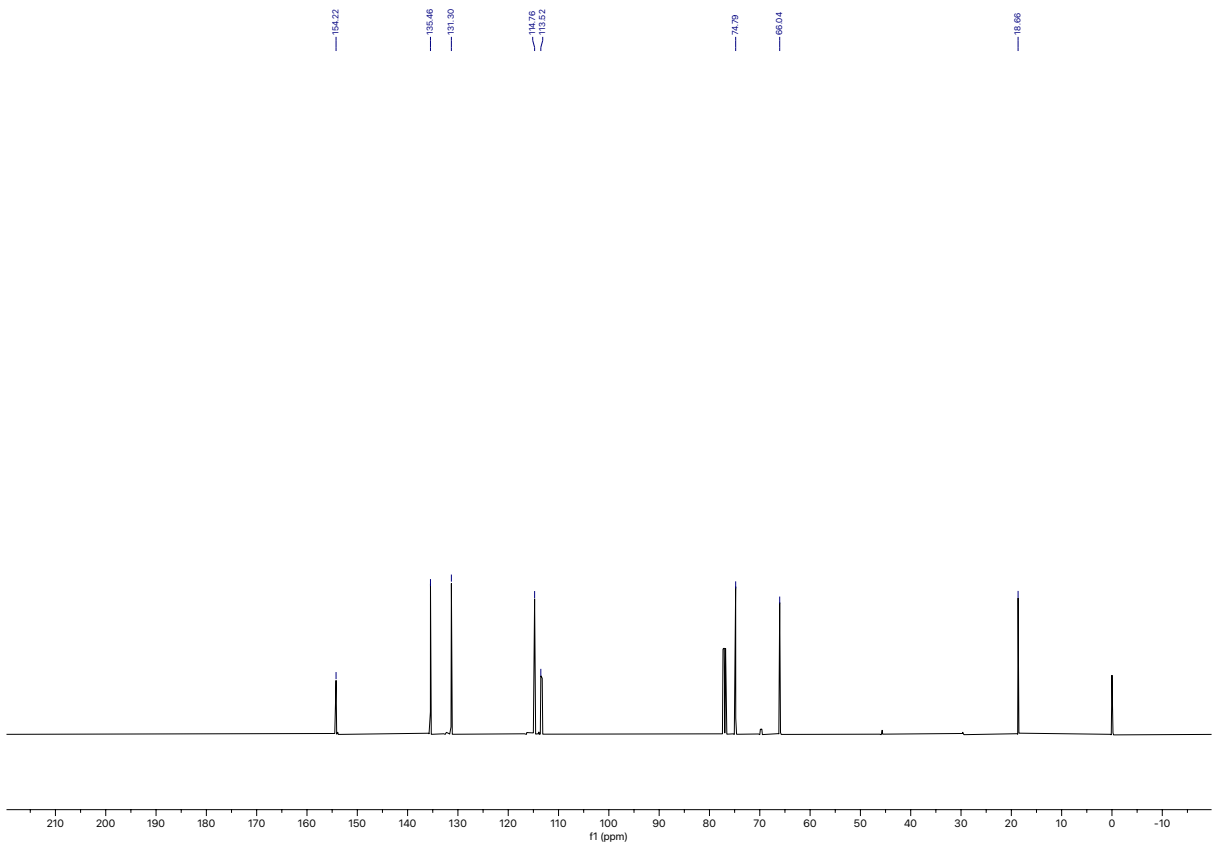

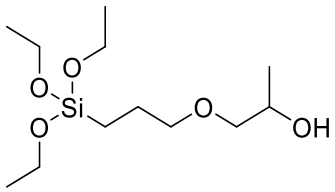

5l

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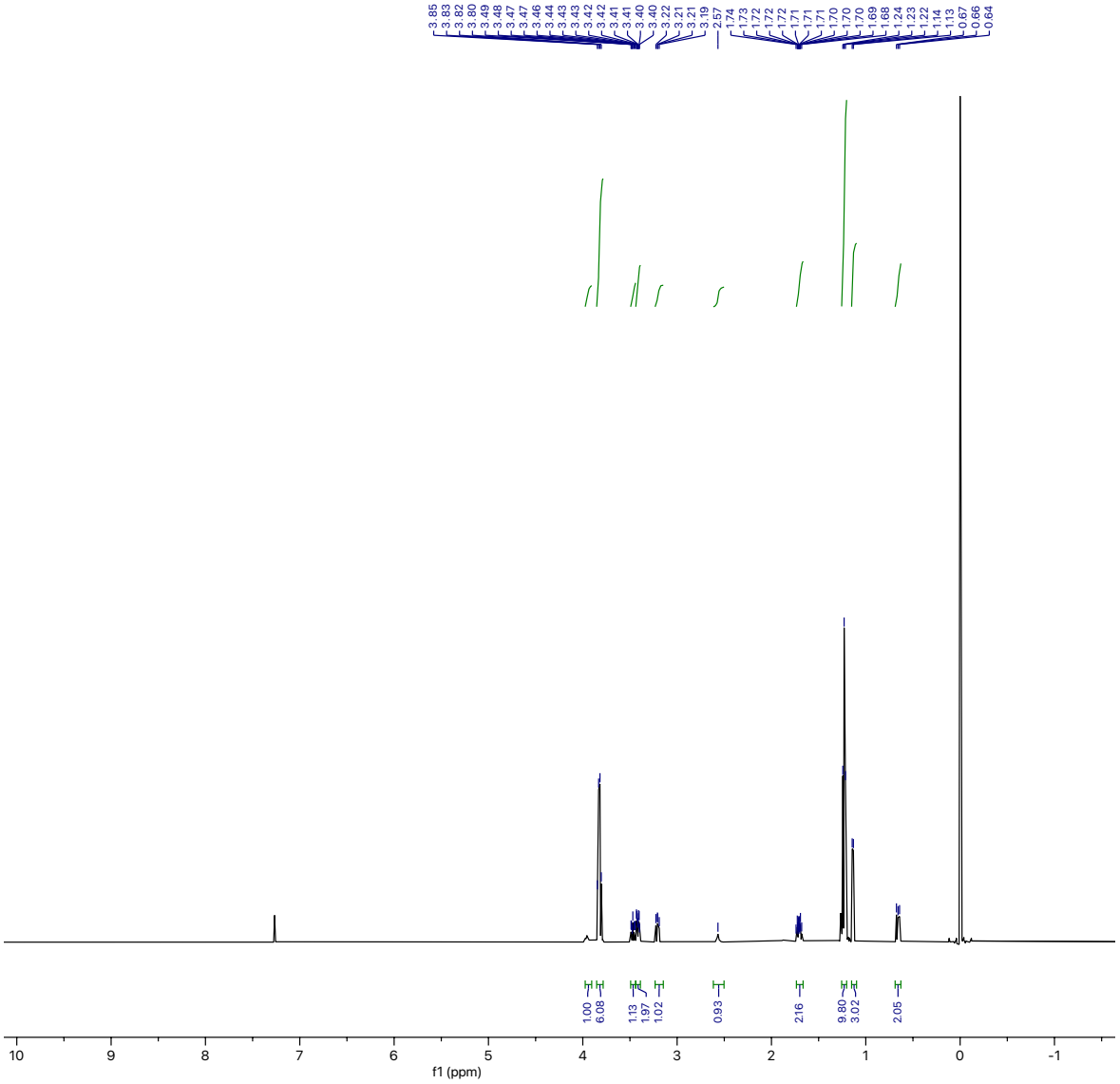
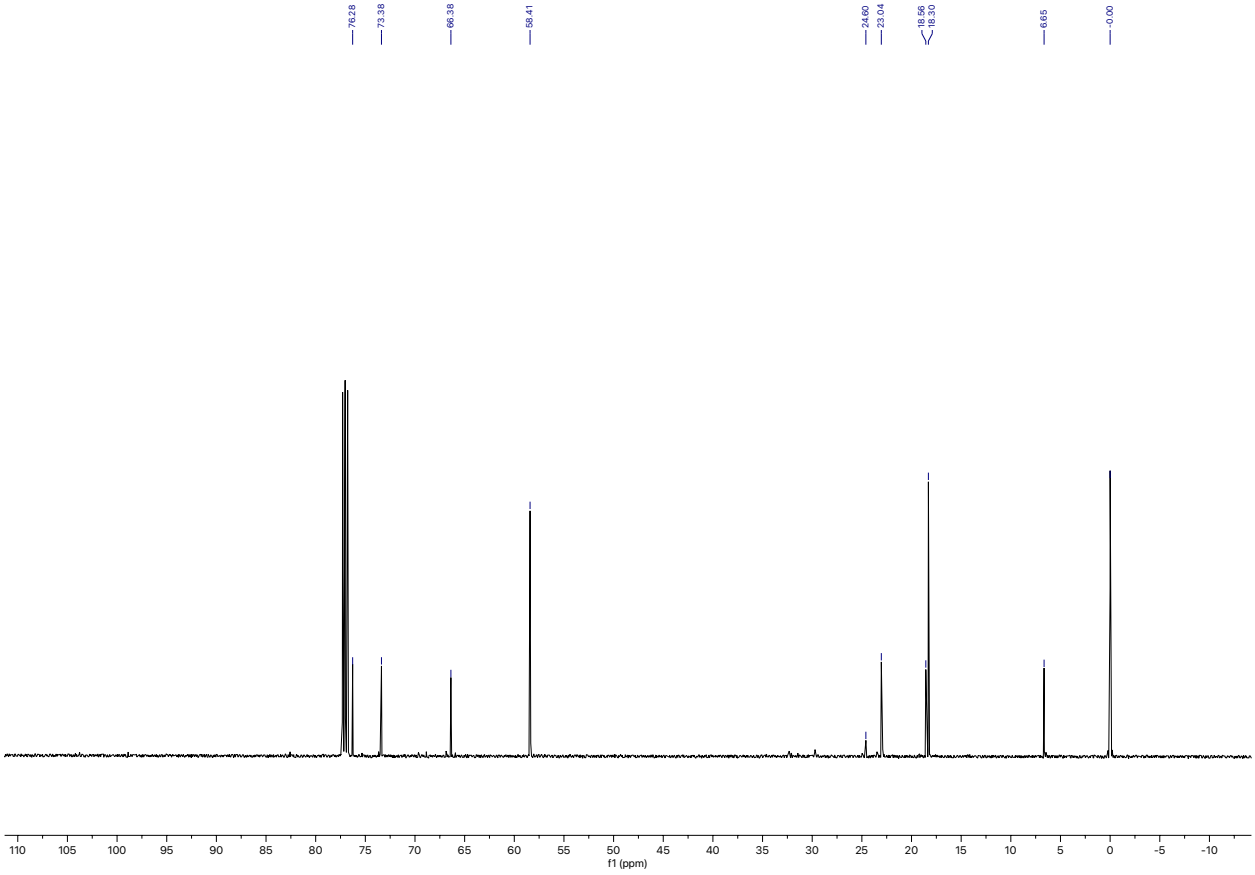
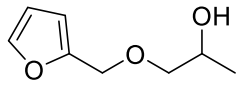


^{13}C NMR spectrum:





5m

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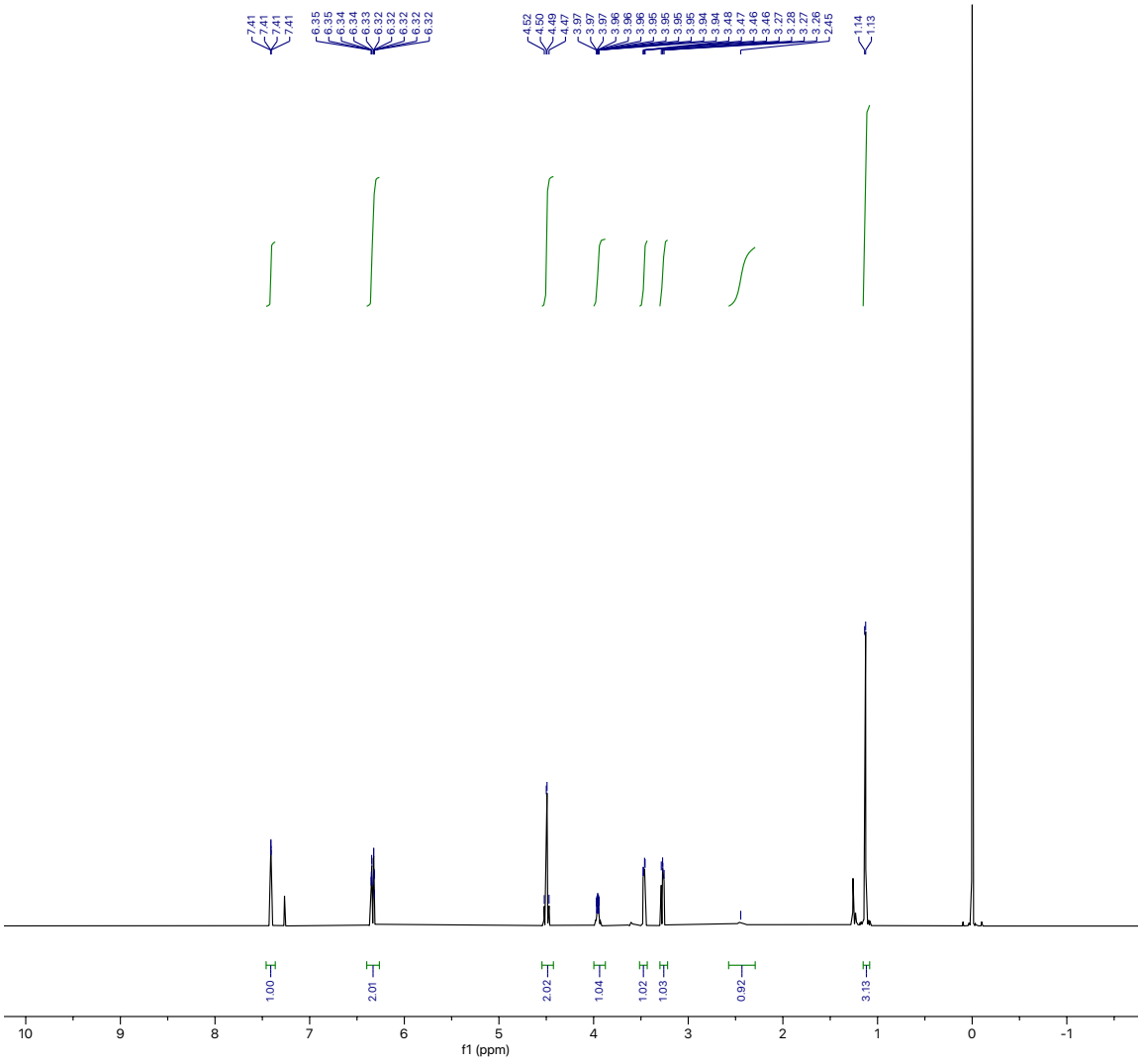
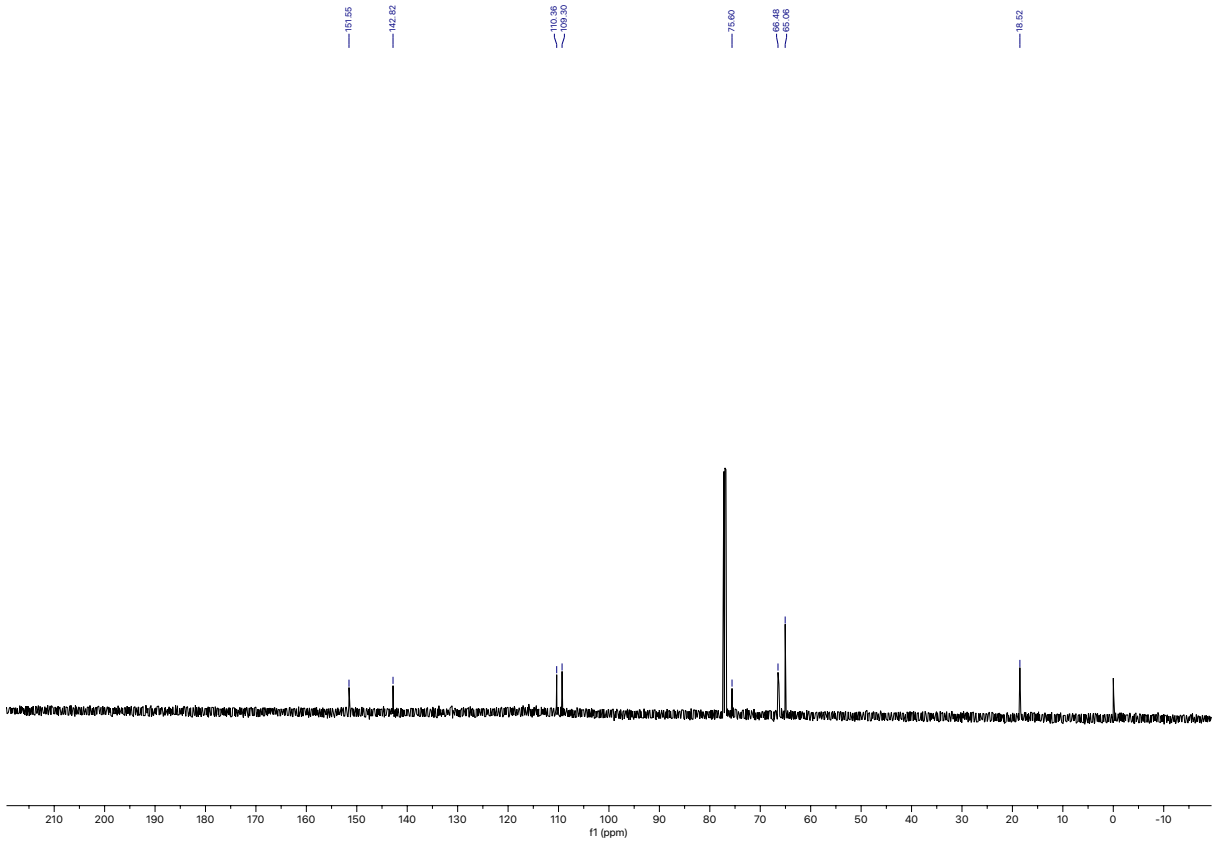
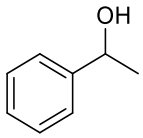


^{13}C NMR spectrum:





5n

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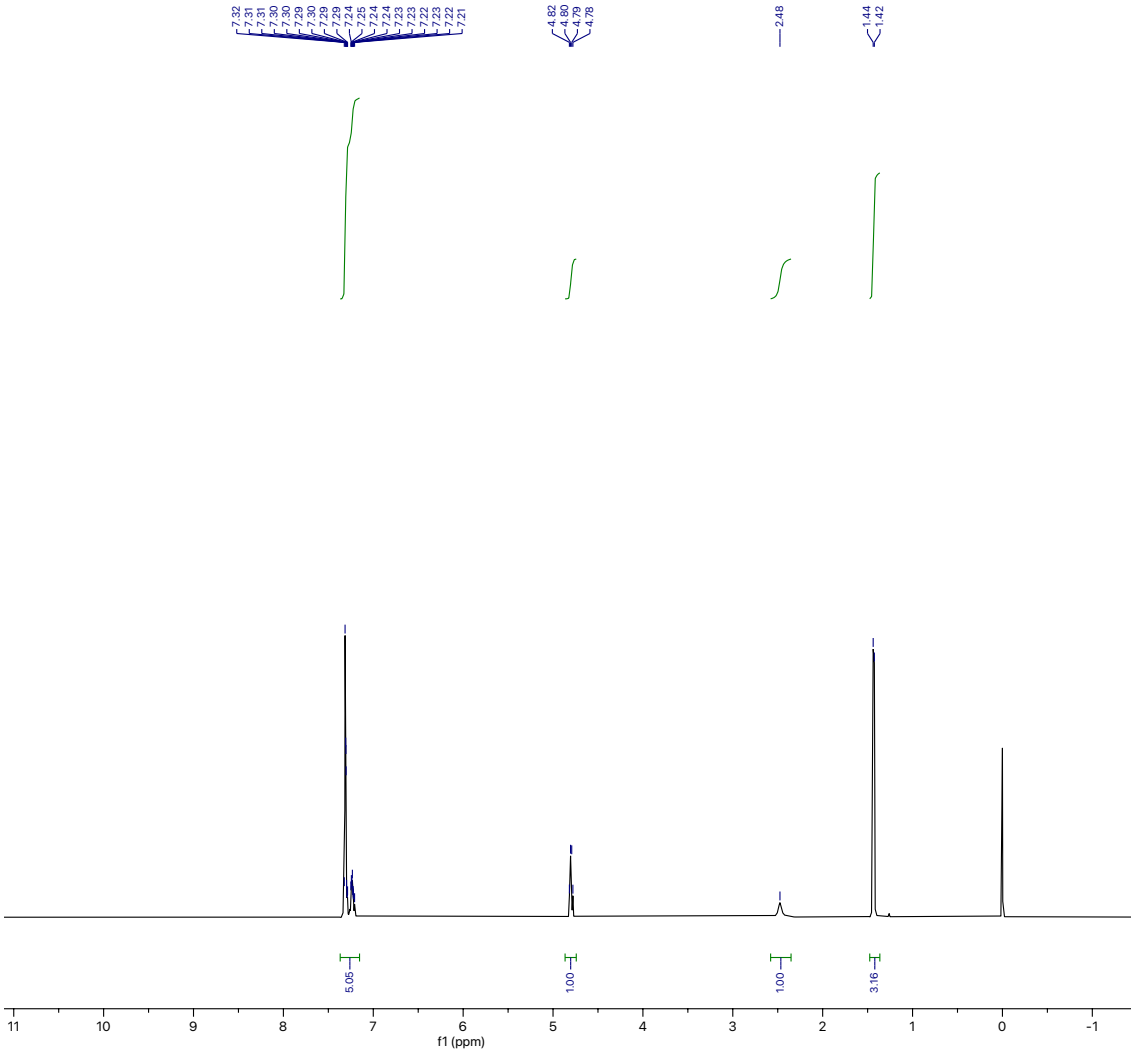
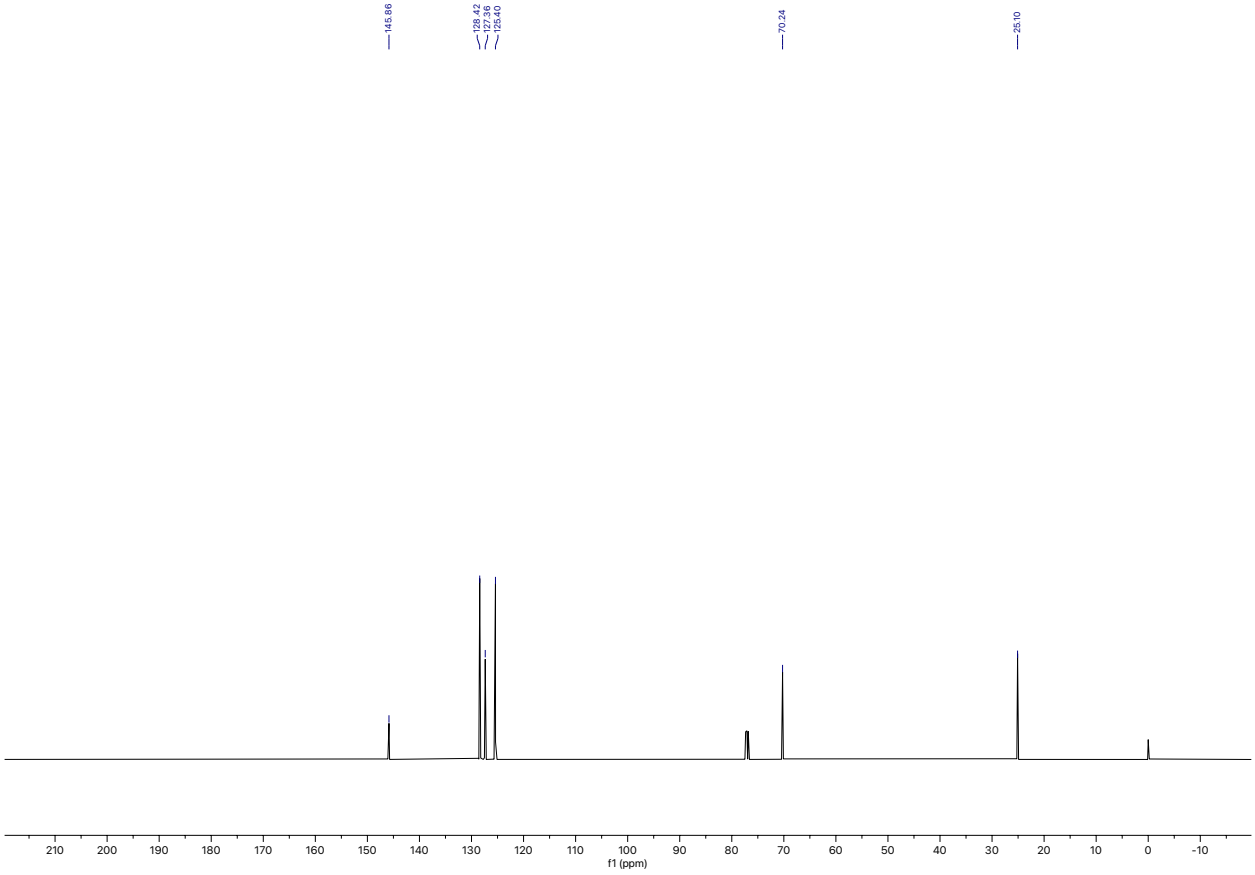
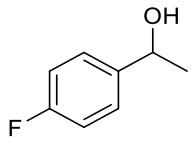


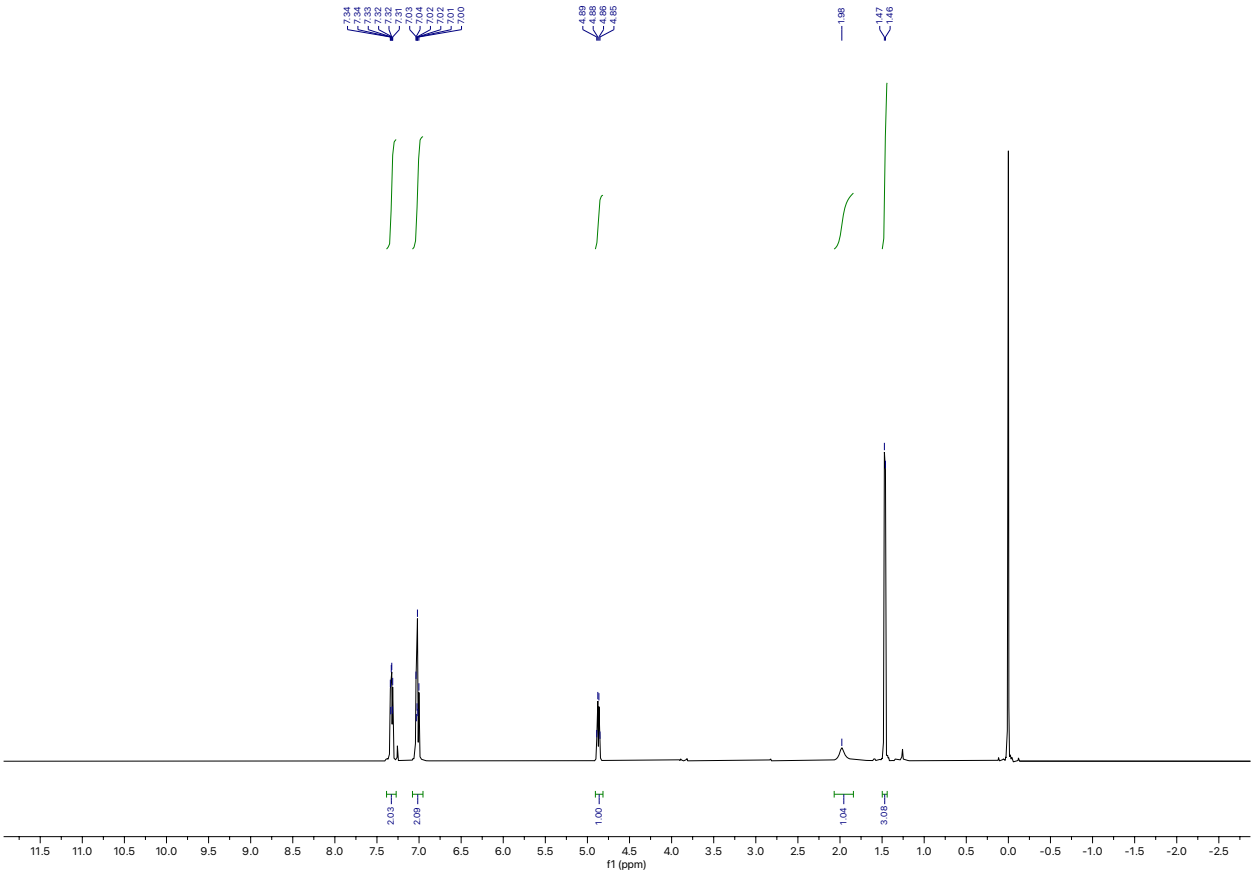
^{13}C NMR spectrum:





5o

^{1}H NMR spectrum:



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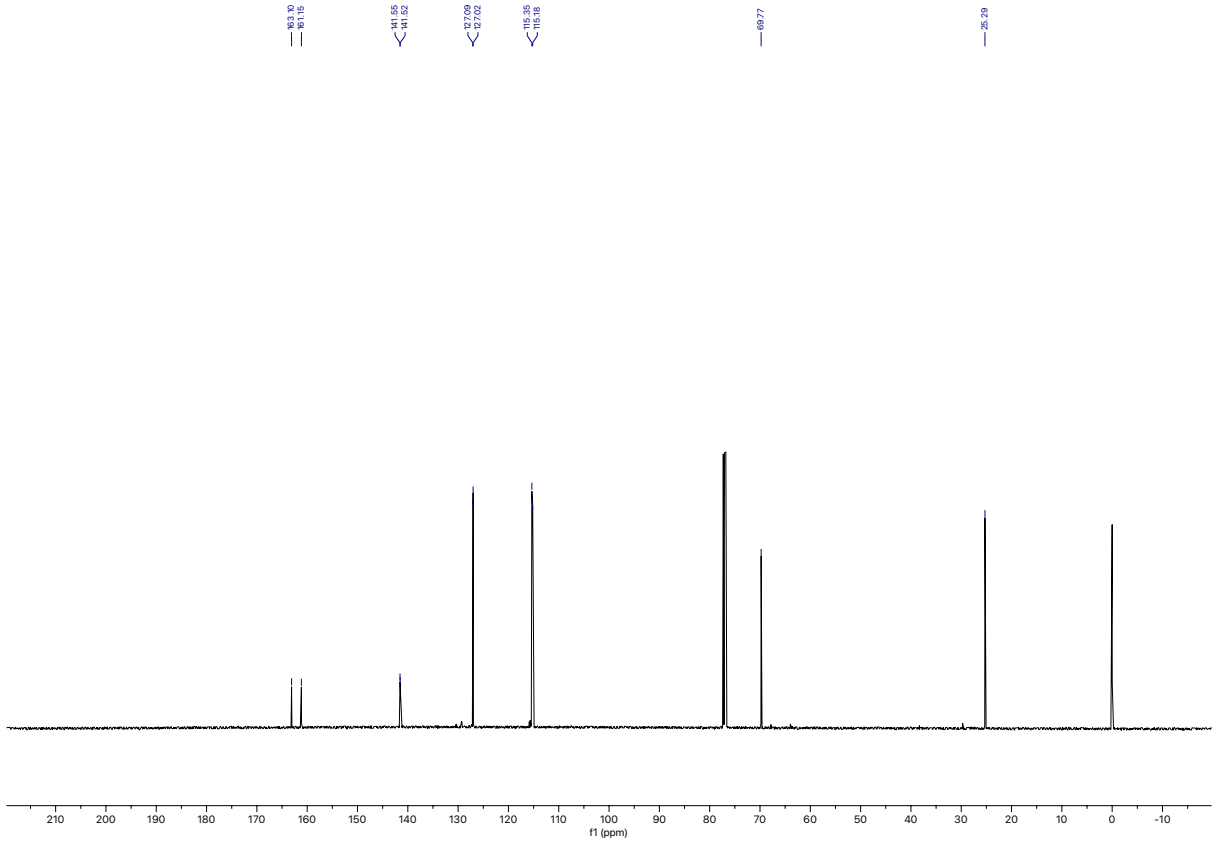
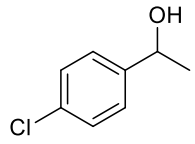
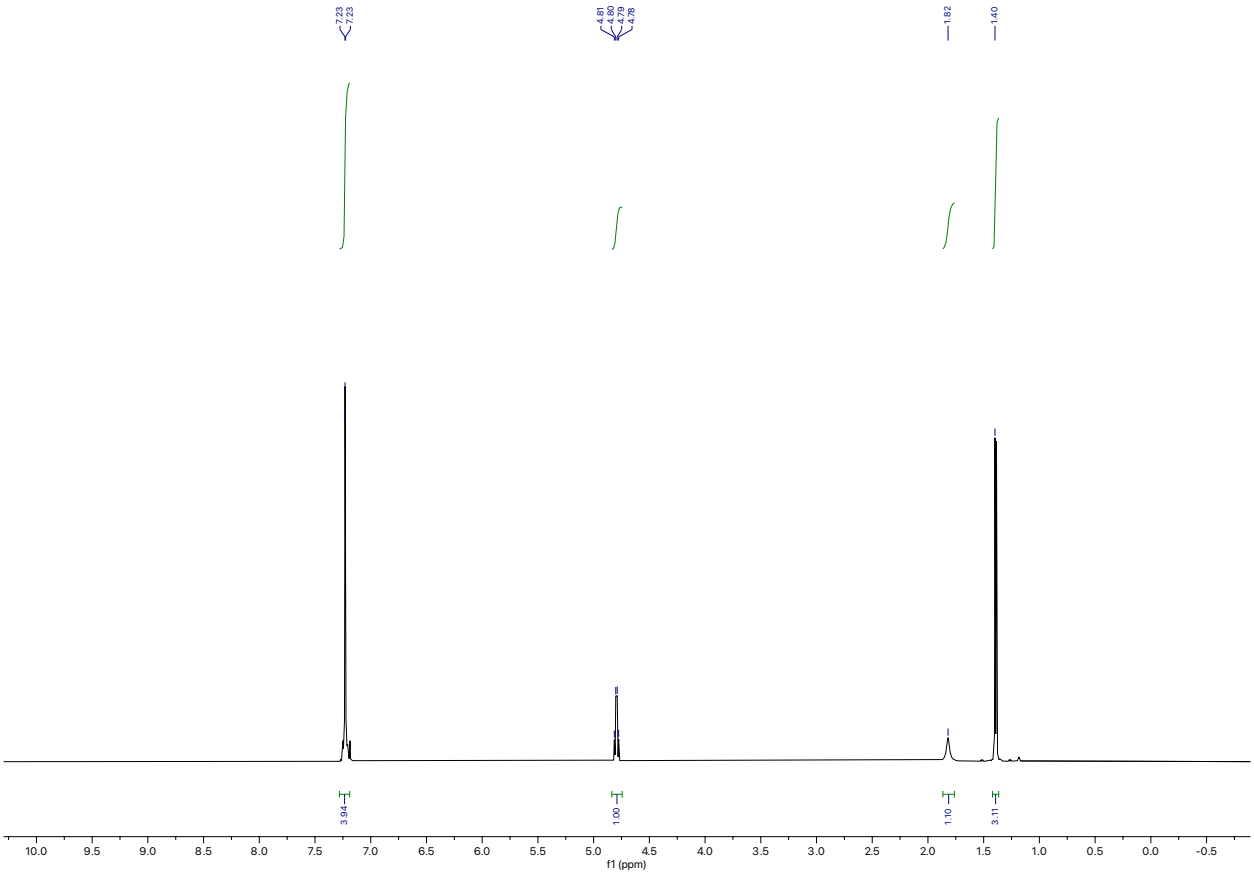




5p

^{1}H NMR spectrum:



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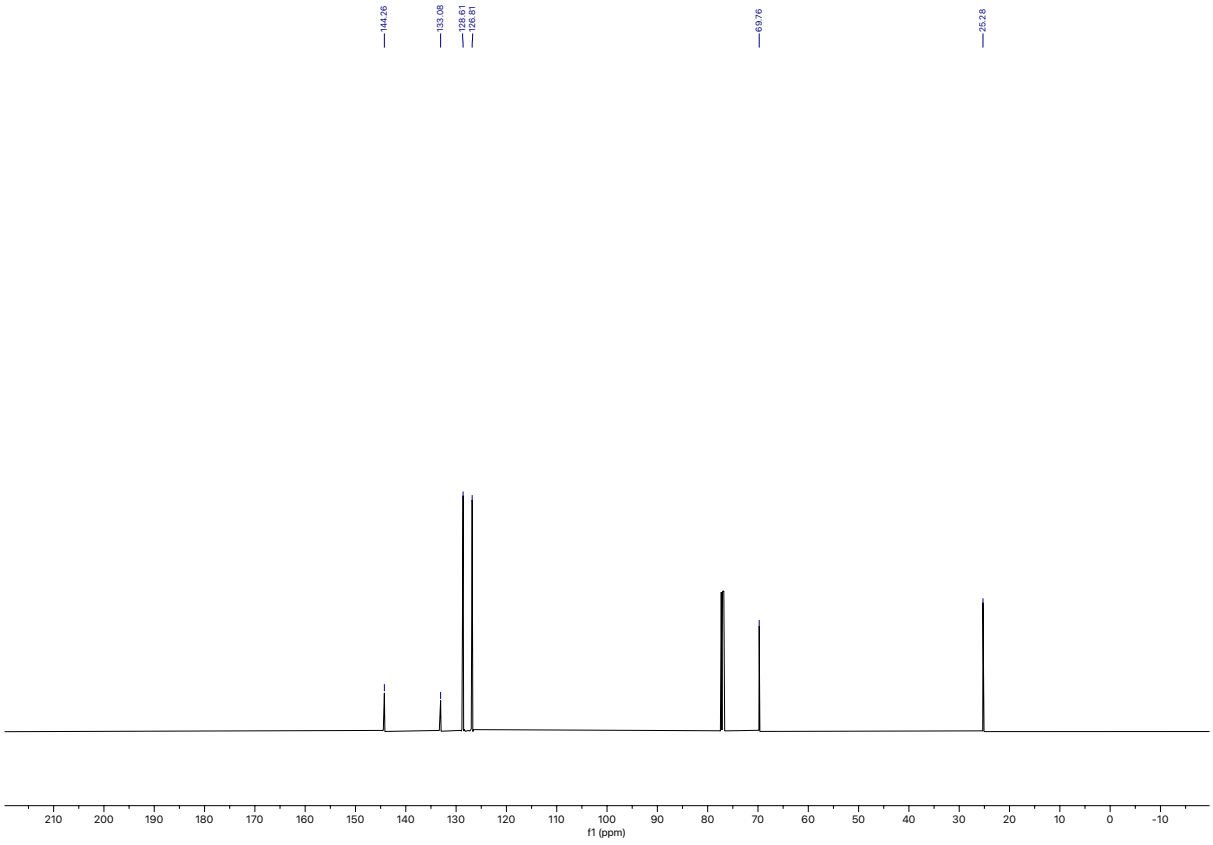

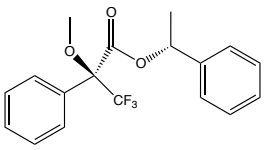

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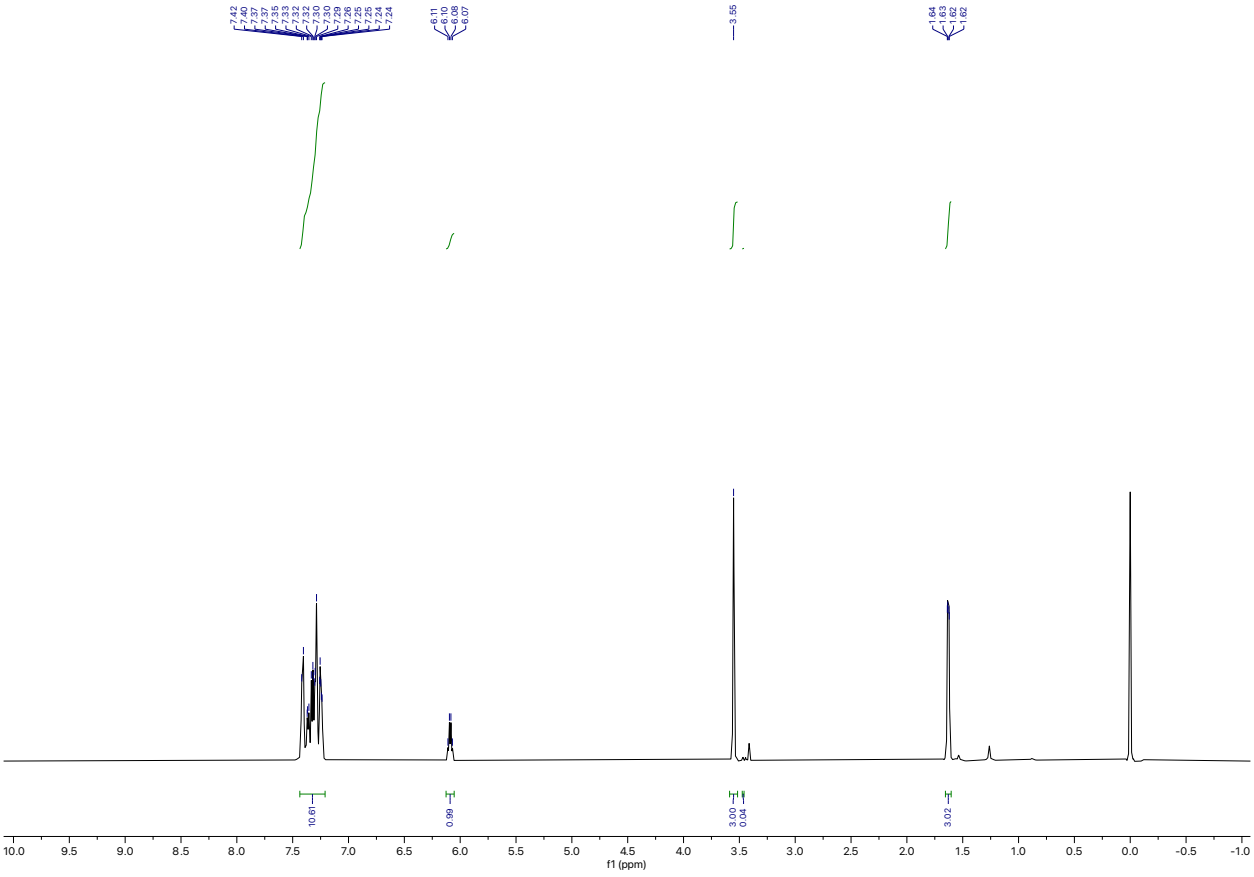

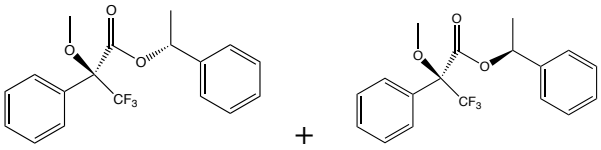

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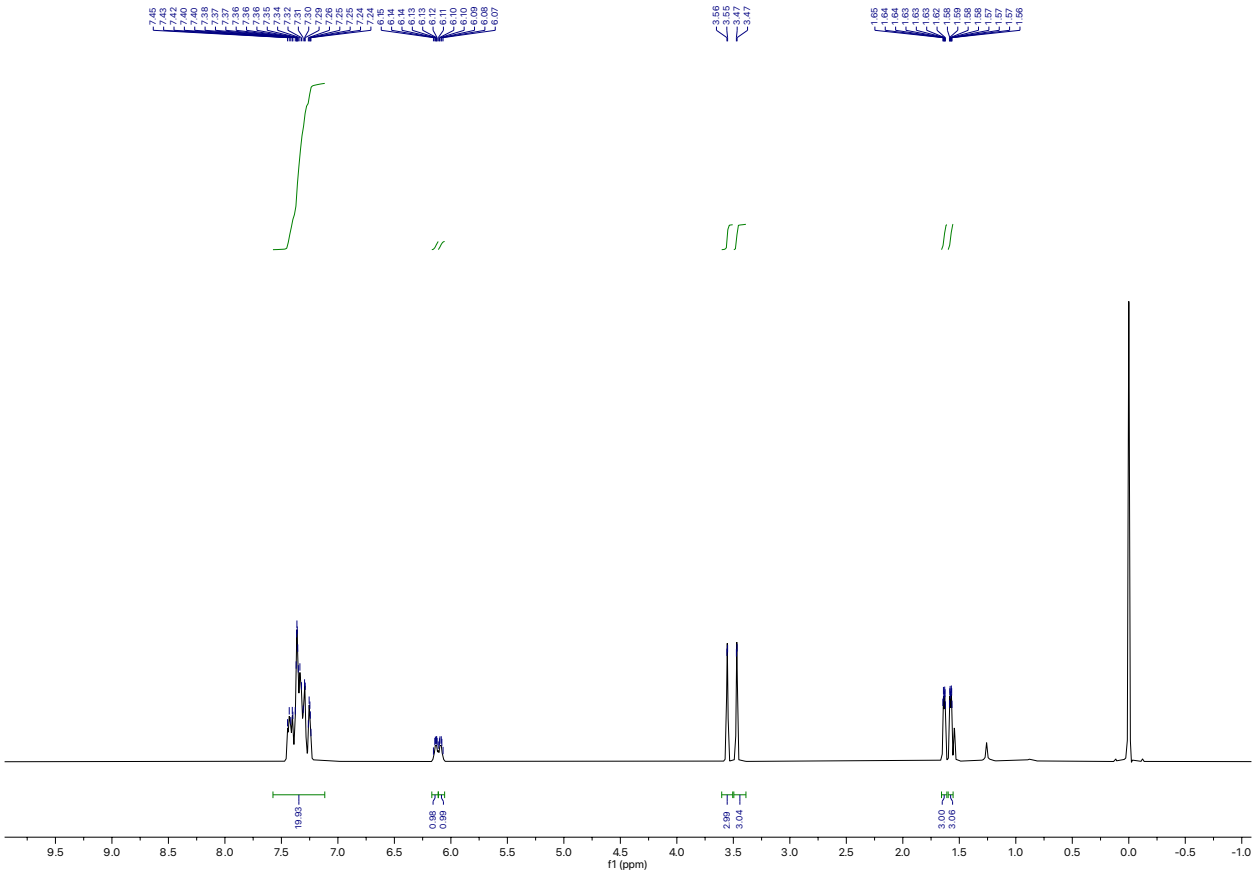

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