

Supporting Information

KMnO₄-catalyzed chemoselective deprotection of acetate and controllable deacetylation-oxidation in one-pot

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Abstract: A novel and efficient protocol for chemoselective deacetylation under ambient conditions has been developed by using catalytic KMnO₄. The stoichiometric use of KMnO₄ highlights the dual-role of heterogeneous oxidant enabling the direct access to aromatic aldehydes in one-pot sequential deacetylation-oxidation. Switching to alternative solvent system allows the clean transformation of benzyl acetate to sensitive aldehyde in a single step besides preventing the over-oxidation to acids. Use of inexpensive and readily accessible KMnO₄ as environmentally benign reagent and ease of reaction operation is particularly attractive, performing the controlled oxidation as well facile cleavage of acetate in preceding step.

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Supporting Material

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A. General Experimental Information:

General Synthesis Information:

Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Experiments were monitored by thin layer chromatography (TLC).

Materials:

Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mm Hg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg).

Chromatography:

Analytical TLC was performed using Whatman 250-micron aluminum backed UV F254 pre-coated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with *p*-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization.

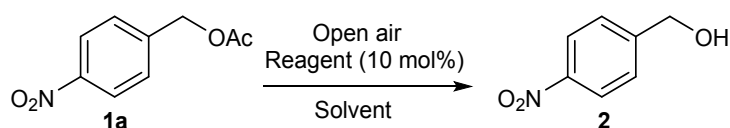
Physical Data:

Proton and Carbon nuclear magnetic resonance spectra (¹H, ¹³C NMR) were recorded on Avance 300, 400 or 500 MHz and ECS 4000 MHz (JEOL) NMR spectrometers. The proton resonances are annotated as: chemical shift (δ) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (*J*, Hz), and number of protons for a given resonance is indicated by nH.

Abbreviations used:

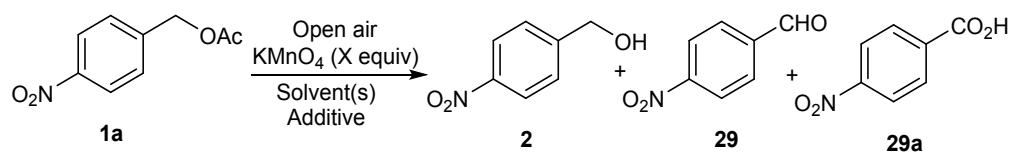
MeCN: Acetonitrile, DCE: Dichloroethane, DCM: Dichloromethane, MeOH: Methanol, THF: Tetrahydrofuran, TLC: Thin layer chromatography, EtOAc: Ethylacetate, *m*-CPBA: *meta*-Chloroperbenzoic acid; KMnO₄: Potassium permanganate; TBHP: *tert*-Butyl hydroperoxide; PCC: Pyridinium chlorochromate; PDC: Pyridiniumdichromate; CAN: Ceric ammonium nitrate; DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone.

B. Optimizations Studies:

Table S1. Screening and evaluation of reaction condition.^[a]

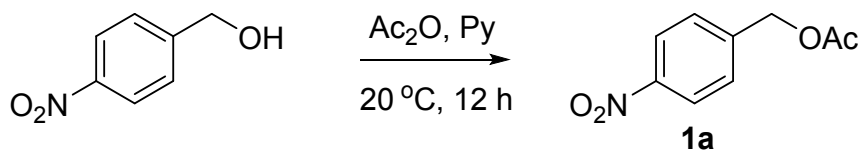
Entry	Reagent	Solvent	Time	Conv. (%) ^[b]
1	MnO ₂	EtOH	24 h	10%
2	MnO ₂	MeOH	24 h	30%
3	KMnO ₄	EtOH	4 h	70%
4	KMnO₄	MeOH	1 h	100%
5	KMnO ₄	Toluene	24 h	NR
6	KMnO ₄	DCM	24 h	NR
7	KMnO ₄	THF	24 h	NR
8	KMnO ₄	DMF	24 h	NR
9	KMnO ₄	1,4-Dioxane	24 h	NR
10	KMnO ₄	H ₂ O	24 h	NR
11 ^[c]	KMnO ₄	CH ₃ CN	1 h	ND
12	NaBO ₃ ·H ₂ O	MeOH	24 h	30%
13	NaBO ₃ ·5H ₂ O	MeOH	24 h	30%
14	NaIO ₄	MeOH	24 h	Traces
15	Oxone	MeOH	24 h	Traces
16	(NH ₄) ₂ S ₂ O ₈	MeOH	24 h	Traces
17	<i>m</i> -CPBA	MeOH	24 h	Traces
18	PhI(OAc) ₂	MeOH	24 h	NR
19	H ₂ O ₂ (35%)	MeOH	24 h	Traces
20	TBHP (70%)	MeOH	24 h	>20%
21	PCC or PDC	MeOH	24 h	NR
22	CAN	MeOH	24 h	30%
23	DDQ	MeOH	24 h	>5%
24 ^[d]	KMnO ₄	MeOH	12 h	>15%

^[a]Reaction conditions: **1a** (50 mg, 0.25 mmol, 1.0 equiv.), solvent (1 mL), 25 °C under atmospheric pressure of air. Oxone: (2KHSO₅·KHSO₄·K₂SO₄); *m*-CPBA: *meta*-Chloroperbenzoic acid; TBHP: *tert*-Butyl hydroperoxide; PCC: Pyridinium chlorochromate; PDC: Pyridinium dichromate; CAN: Ceric ammonium nitrate; DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone; NR = No reaction. ^[b]The conversion based on the starting material **1a**. ^[c]ND = Not detected, decomposition of starting material. ^[d]The reaction was performed under nitrogen or argon atmosphere.

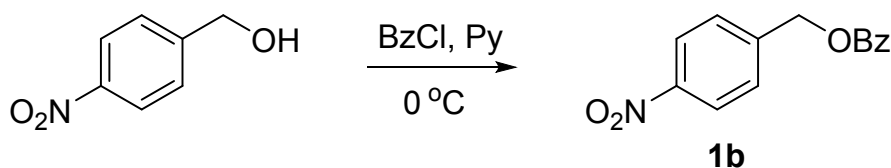
Table S2. Optimization of reaction condition for one-pot deacetylation-oxidation.^[a]

Entry	Solvent	Time	Selectivities ^[b] 2/29/29a
1 ^[c]	MeOH	24 h	30/70/0
2	MeOH	6 h	25/75/0
3	MeOH	12 h	10/85/5
4 ^[d]	MeOH	6 h	0/0/100
5	DCE:MeOH (1:1)	16 h	50/50/0
6	DCE: MeOH (1:9)	16 h	0/100/0
7	Toluene: MeOH (1:9)	20 h	20/80/0
8	DCM: MeOH (1:9)	20 h	20/80/0
9	1,4-Dioxane:MeOH (1:9)	24 h	30/70/0
10	EtOAc: MeOH (1:9)	16 h	0/100/0
11	H ₂ O: MeOH (1:9)	24 h	30/50/20
12	PEG: MeOH (1:9)	24 h	20/70/10

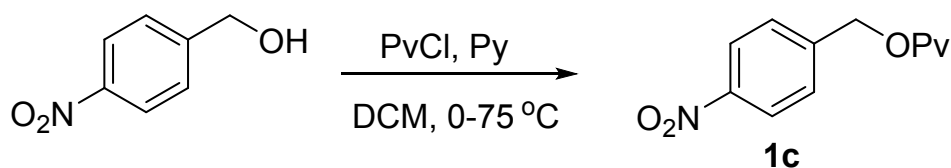
^[a]Reaction conditions: **1a** (50 mg, 0.25 mmol, 1.0 equiv.), KMnO_4 (1.0 equiv.), solvent (2 mL), 25 °C under atmospheric pressure of air; NR = No reaction. ^[b]The selectivities is based on the conversion of starting material **1a**. ^[c]The reaction was performed with 0.1 equiv. of KMnO_4 . ^[d]2.0 equiv. of KMnO_4 was used. PEG: Polyethylene glycol (PEG 400).

C. Synthesis and Spectroscopic Characterization Data.

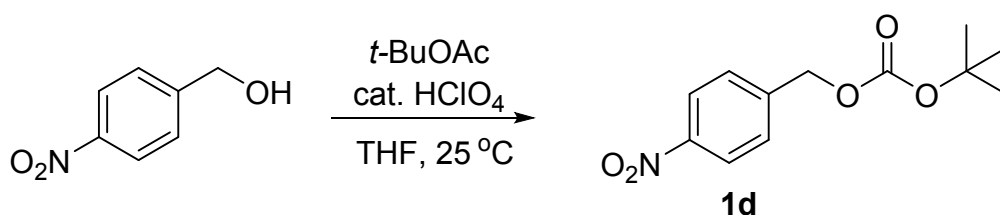
4-Nitrobenzyl acetate (1a): Following the slightly modified procedure,^[1,2] a preformed solution of (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in dry pyridine (5 mL) was treated with acetic anhydride (92 μL , 100 mg, 0.979 mmol, 1.5 equiv.), and the mixture was stirred for 12 h at 20 $^\circ\text{C}$ and adjudged by TLC. The resultant filtrate was treated with saturated aqueous NaHCO_3 (5 mL), and aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to obtain the analytical pure product 4-nitrobenzyl acetate (**1a**) (117 mg, 0.60 mmol, 92%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.7$ Hz, 2H), 7.52 (d, $J = 8.6$ Hz, 2H), 5.21 (s, 2H), 2.16 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



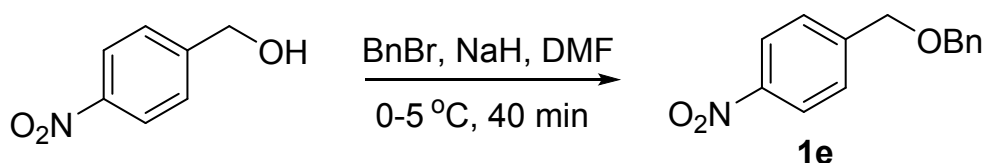
4-Nitrobenzyl benzoate (1b): Following the slightly modified procedure,^[3] a preformed solution of (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in dry pyridine and DCM as cosolvent was treated with benzyl chloride (112 μL , 123 mg, 0.979 mmol, 1.5 equiv.) at 0 $^\circ\text{C}$, and the mixture was stirred till completion of starting material as adjudged by TLC. The resultant filtrate was treated with saturated aqueous NaHCO_3 (5 mL), and aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to obtain the analytical pure product 4-nitrobenzyl benzoate (**1b**) (149 mg, 0.581 mmol, 89%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.23-8.22 (m, 1H), 8.17-8.15 (m, 2H), 7.70-7.66 (m, 1H), 7.58-7.52 (m, 5H), 4.65 (s, 2H); the overall spectroscopic data are in complete agreement with assigned structure.



4-Nitrobenzyl pivalate (1c): Following the slightly modified procedure,^[4,5] a stirred solution of (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in dry pyridine cooled to 0 °C, was treated with pivalic acid chloride (119 μ L, 117 mg, 0.979 mmol, 1.5 equiv.), and stored at 5 °C for 2.5 days. Ice chips were added, and the mixture was stirred for 1 h at 5 °C and evaporated. After completion of the reaction, the reaction mixture was dissolved in DCM and washed with distilled water, then the organic layer was dried with Na₂SO₄ and solvent was evaporated under vacuum to yield the corresponding product 4-nitrobenzyl pivalate (**1c**) (144 mg, 0.607 mmol, 93%). ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, J = 5.3 Hz, 2H), 7.51 (d, J = 5.9 Hz, 2H), 5.21 (s, 2H), 1.27 (s, 3H), 1.26 (s, 6H); the overall spectroscopic data are in complete agreement with assigned structure.

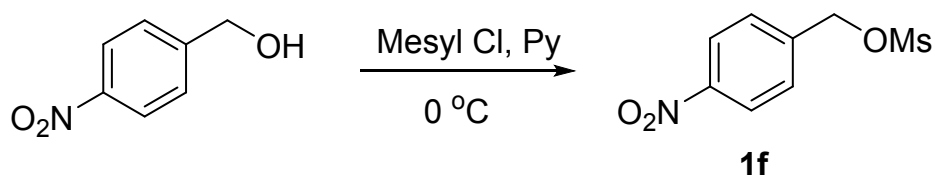


4-Nitro benzyl tert-butyl carbonate (1d): Following the slightly modified procedure,^[6] a preformed solution of the (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in *t*-BuOAc, was treated with HClO₄ (8 μ L, 13 mg, 0.136 mmol, 0.2 equiv.), and the mixture was stirred at 25 °C until the reaction was complete (reaction monitored by TLC). Na₂CO₃ (2.0 equiv.) was added and the mixture was stirred for 40 min. After filtration, the solvent was removed under vacuum (for the re-use of *t*-BuOAc, this was washed with a saturated solution of NaHCO₃, then with H₂O and finally dried over Na₂SO₄). The *tert*-butyl ether was separated from the residual alcohol by flash chromatography on silica gel (petroleum ether-Et₂O or *n*-hexane-EtOAc) to yield the corresponding product *tert*-butyl (4-nitrobenzyl) carbonate (**1d**) (143 mg, 0.568 mmol, 87%). ¹H NMR (500 MHz, CDCl₃) δ 8.27-8.18 (m, 2H), 7.52 (d, J = 8.2 Hz, 2H), 5.18 (s, 2H), 1.53 (s, 3H), 1.50 (s, 6H); the overall spectroscopic data are in complete agreement with assigned structure.

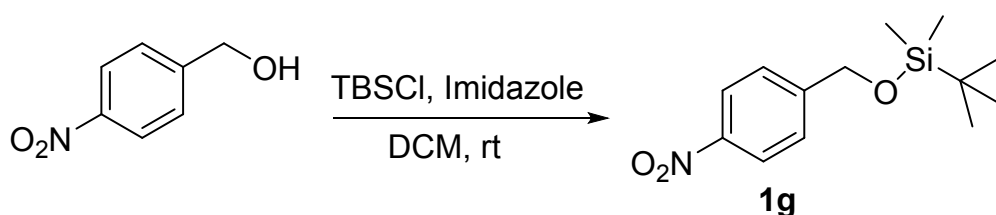


4-Nitrobenzyl phenyl ether (1e): Following the slightly modified procedure,^[7] a preformed solution of (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in anhydrous N,N-dimethylformamide at 0 °C was treated with sodium hydride (30 mg, 1.306 mmol, 2.0 equiv.) and stirred at room temperature

for 30 min. The resulting dark brown solution was cooled to 0 °C and was followed by dropwise addition of benzyl bromide (155 μ L, 223 mg, 1.306 mmol, 2.0 equiv.) under nitrogen atmosphere, stirred at room temperature for 1-15 h. At the end of the reaction (judged by TLC), excess of NaH was quenched by the addition of 10 mL methanol. The reaction mixture was diluted with water and extracted with ethyl acetate (3 x 20 mL), combined organic layers were dried over anhydrous sodium sulphate, concentrated *in vacuo* and the crude residue was purified by silica gel column chromatography to yield the corresponding product 1-((benzyloxy)methyl)-4-nitrobenzene (**1e**) (150 mg, 0.620 mmol, 95%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.20 (dd, $J = 12.6, 9.1$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.38-7.32 (m, 5H), 4.65 (s, 2H), 4.62 (s, 2H); the overall spectroscopic data are in complete agreement with assigned structure.

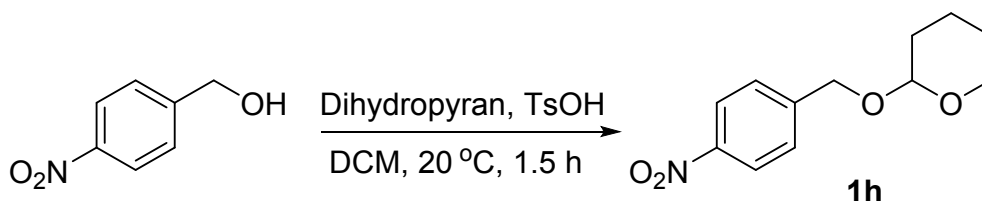


4-Nitrobenzyl methanesulfonate (1f): Following the slightly modified procedure,^[4] a stirred solution of (4-nitrophenyl)methanol (100 mg, 0.653 mmol, 1.0 equiv.) in dry pyridine was cooled to 0 °C, and treated with mesyl chloride (75 μ L, 111 mg, 0.979 mmol, 1.5 equiv.) and stored at 5 °C for 2.5 days. Ice chips were added, and the mixture was stirred for 1 h and evaporated. A solution of this residue in DCM was washed with saturated NaHCO_3 and H_2O , dried (Na_2SO_4), and evaporated under vacuum to yield the corresponding product 4-nitrobenzyl methanesulfonate (**1f**) (131 mg, 0.568 mmol, 87%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.22 (d, $J = 2.0$ Hz, 2H), 7.58 (d, $J = 2.0$ Hz, 2H), 4.66 (s, 2H), 3.69 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

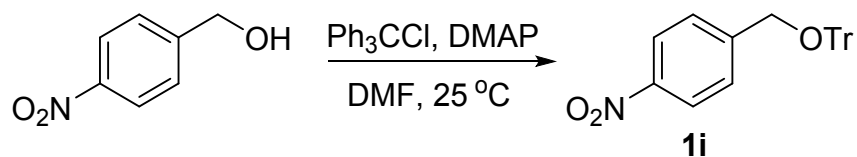


4-Nitrobenzyl oxy tert-butyl dimethylsilane (1g): Following the slightly modified procedure,^[8] a preformed solution of (4-nitrophenyl) methanol (100 mg, 0.653 mmol, 1.0 equiv.) and imidazole (100 mg, 0.653 mmol, 1.0 equiv.) in dry DCM was treated with TBSCl (168 μ L, 147 mg, 0.979 mmol, 1.5 equiv.) and the resulting mixture was stirred at rt for 18 h. The resultant mixture was diluted with DCM and H_2O was added. The mixture was extracted with DCM and the combined organic layers were dried

(Na₂SO₄), filtered and concentrated *in vacuo*. The resultant oil was purified *via* column chromatography (4:1 hexane:ethyl acetate) to yield the corresponding product *tert*-butyldimethyl((4-nitrobenzyl)oxy)silane (**1g**) (150 mg, 0.561 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.19 (m, 2H), 7.50-7.47 (m, 2H), 4.83 (s, 2H), 0.96 (s, 9H), 0.12 (s, 6H); the overall spectroscopic data are in complete agreement with assigned structure.

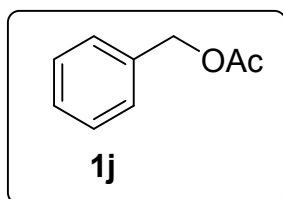


2-((4-Nitrobenzyl)oxy)tetrahydro-2H-pyran (1h): Following the slightly modified procedure,^[9] a preformed solution of (4-nitrophenyl) methanol (100 mg, 0.653 mmol, 1.0 equiv.) and DHP (71 μL, 65 mg, 0.783 mmol, 1.2 equiv.) in dry DCM was treated with p-PTSA (11 mg, 0.065 mmol, 0.10 equiv.) and the resulting mixture was stirred at room temperature for 1-3 h. The resultant mixture was diluted with DCM and H₂O was added. A solution of this residue in DCM was washed with saturated NaHCO₃ and H₂O, dried (Na₂SO₄), and evaporated under vacuum to yield the corresponding product 2-((4-nitrobenzyl)oxy)-3,4-dihydro-2H-pyran (**1h**) (131 mg, 0.548 mmol, 84%). ¹H NMR (500 MHz, CDCl₃) δ 8.29-8.11 (m, 2H), 7.54 (m, 2H), 4.89 (d, *J* = 13.5 Hz, 1H), 4.74 (t, *J* = 3.5 Hz, 1H), 4.61 (d, *J* = 13.5 Hz, 1H), 3.91-3.86 (m, 1H), 3.59-3.54 (m, 1H), 1.92-1.84 (m, 1H), 1.83-1.76 (m, 1H), 1.72-1.55 (m, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

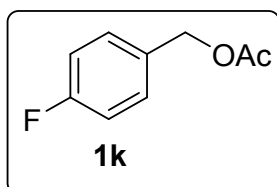


4-Nitrobenzyl trityl ether (1i): Following the slightly modified procedure,^[10] a preformed solution of (4-nitrophenyl) methanol (100 mg, 0.653 mmol, 1.0 equiv.) in DMF was treated with tritylchloride (272 mg, 0.979 mol, 1.5 equiv.), triethylamine (109 μL, 79 mg, 0.783 mmol, 1.2 equiv.) and DMAP (8 mg, 0.065 mmol, 0.1 equiv.), and stirred overnight at room temperature under nitrogen. After 12 h stirring, the yellow cloudy solution was poured into ice-water and extracted with dichloromethane. The organic extracts were washed with saturated ammonium chloride solution, water, and dried with sodium sulfate. After removal of the solvents, the yellowish solid was recrystallized from ethanol to give (((4nitrobenzyl)oxy)methanetriyl)tribenzene (**1i**) (226 mg, 0.574 mmol, 88%). ¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.51-7.47 (m, 5H), 7.36-7.30 (m, 5H), 7.30-

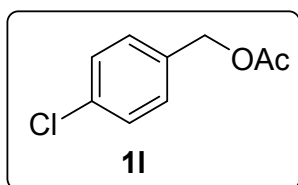
7.24 (m, 5H), 4.31 (s, 2H); the overall spectroscopic data are in complete agreement with assigned structure.



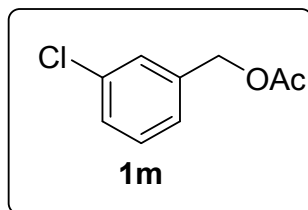
Benzyl acetate (1j): Following general acetylation procedure using benzyl alcohol (100 μ L, 104 mg, 0.962 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (124 mg, 0.827 mmol, 86%). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.29 (m, 5H), 5.09 (s, 2H), 2.08 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



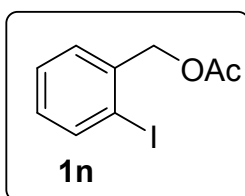
4-Fluorobenzyl acetate (1k): Following general acetylation procedure using 4-fluoro-benzyl alcohol (100 μ L, 115 mg, 0.912 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (137 mg, 0.820 mmol, 90%). ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.32 (m, 2H), 7.07-7.03 (m, 2H), 5.07 (s, 2H), 2.09 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



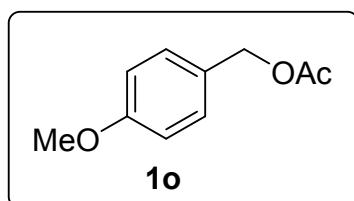
4-Chlorobenzyl acetate (1l): Following general acetylation procedure using 4-chloro-benzyl alcohol (100 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (110 mg, 0.598 mmol, 85%). ^1H NMR (500 MHz, CDCl_3) δ 7.33 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 2H), 5.07 (s, 2H), 2.10 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



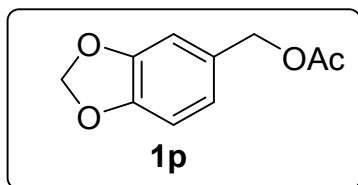
3-Chlorobenzyl acetate (1m): Following general acetylation procedure using 3-chloro-benzyl alcohol (100 μ L, 121 mg, 0.852 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (144 mg, 0.783 mmol, 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (s, 1H), 7.30-7.25 (m, 2H), 7.24-7.20 (m, 1H), 5.06 (s, 2H), 2.10 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



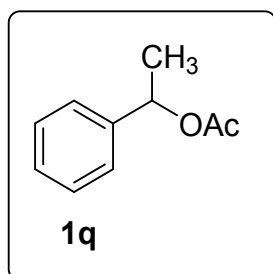
2-Iodobenzyl acetate (1n): Following general acetylation procedure **1a** using 2-iodo-benzyl alcohol (100 mg, 0.427 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (99 mg, 0.362 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.86-7.84 (m, 1H), 7.39-7.33 (m, 2H), 7.04-7.00 (m, 2H), 5.12 (s, 2H), 2.14 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



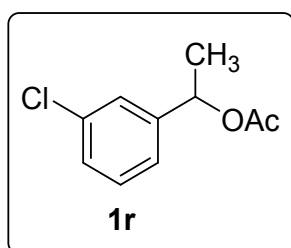
4-Methoxybenzyl acetate (1o): Following general acetylation procedure **1a** using 4-methoxy benzyl alcohol (100 μ L, 111 mg, 0.804 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (118 mg, 0.659 mmol, 82%). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.04 (s, 2H), 3.81 (s, 3H), 2.07 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



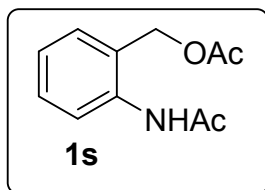
Piperonyl acetate (1p): Following general acetylation procedure using Piperonyl alcohol (100 mg, 0.657 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (108 mg, 0.558 mmol, 85%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.85-6.81 (m, 2H), 6.77 (d, $J = 7.9$ Hz, 1H), 5.95 (s, 2H), 4.99 (s, 2H), 2.07 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



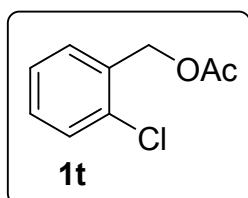
1-Penylethyl acetate (1q): Following general acetylation procedure using α -methyl benzyl alcohol (100 μL , 101 mg, 0.827 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (119 mg, 0.727 mmol, 88%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37-7.34 (m, 4H), 7.31-7.26 (m, 1H), 5.88 (q, $J = 6.6$ Hz, 1H), 2.07 (s, 3H), 1.53 (d, $J = 6.6$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



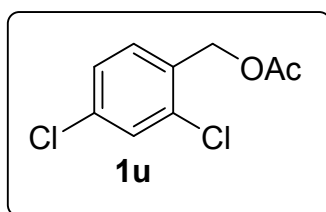
1-(3-Chlorophenyl)ethyl acetate (1r): Following general acetylation procedure using 3-chloro- α -methyl benzyl alcohol (100 μL , 117 mg, 0.75 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (123 mg, 0.622 mmol, 83%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 (s, 1H), 7.27 (m, 2H), 7.24-7.19 (m, 1H), 5.83 (q, $J = 6.6$ Hz, 1H), 2.08 (s, 3H), 1.52 (d, $J = 6.6$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



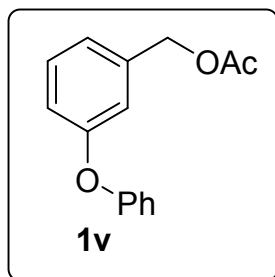
2-Acetamidobenzyl acetate (1s): Following general acetylation procedure using benzyl alcohol (100 mg, 0.606 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (110 mg, 0.533 mmol, 88%). ^1H NMR (500 MHz, CDCl_3) δ 8.77 (s, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.44-7.26 (m, 2H), 7.26 (s, 1H), 7.14 (t, $J = 7.4$ Hz, 1H), 5.12 (s, 2H), 2.23 (s, 3H), 2.10 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



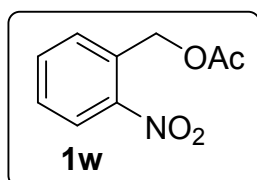
2-Chlorobenzyl acetate (1t): Following general acetylation procedure using 2-chloro-benzyl alcohol (100 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (117 mg, 0.640 mmol, 91%). ^1H NMR (500 MHz, CDCl_3) δ 7.41 (dd, $J = 5.5, 3.8$ Hz, 1H), 7.40-7.36 (m, 1H), 7.26 (m, 2H), 5.21 (s, 2H), 2.12 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



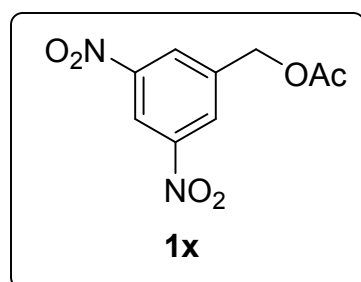
2,4-Dichlorobenzyl acetate (1u): Following general acetylation procedure using 2,4-dichloro benzyl alcohol (100 mg, 0.564 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (101 mg, 0.468 mmol, 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 2.1$ Hz, 1H), 7.36 (d, $J = 8.3$ Hz, 1H), 7.27 (s, 1H), 5.17 (s, 2H), 2.13 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



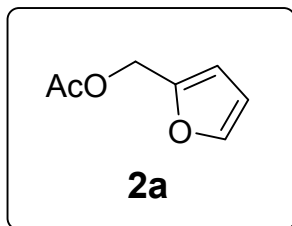
3-Phenoxybenzyl acetate (1v): Following general acetylation procedure using 3-phenoxy benzyl alcohol (100 μ L, 114 mg, 0.57 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (118 mg, 0.490 mmol, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.30 (m, 3H), 7.12-7.10 (m, 1H), 7.09-7.07 (m, 1H), 7.02-6.99 (m, 2H), 6.95-6.92 (m, 1H), 5.06 (s, 2H), 2.08 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



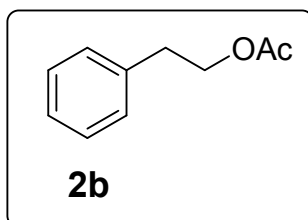
2-Nitrobenzyl acetate (1w): Following general acetylation procedure using 2-nitro-benzyl alcohol (100 mg, 0.653 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (103 mg, 0.528 mmol, 81%). ^1H NMR (500 MHz, CDCl_3) δ 8.11 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.66 (td, $J = 7.6, 1.2$ Hz, 1H), 7.60 (d, $J = 7.6$ Hz, 1H), 7.53-7.46 (m, 1H), 5.52 (s, 2H), 2.17 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



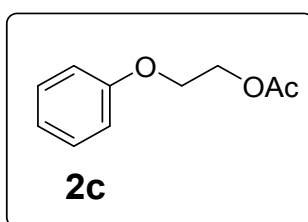
3,5-Dinitrobenzyl Acetate (1x): Following general acetylation procedure using 3,5-dinitro benzyl alcohol (100 mg, 0.505 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (109 mg, 0.454 mmol, 90%). ^1H NMR (500 MHz, CDCl_3) δ 9.01 (s, 1H), 8.56 (d, $J = 2.0$ Hz, 2H), 5.30 (s, 2H), 2.20 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



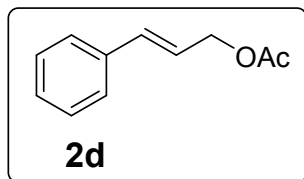
Furfuryl acetate (2a): Following general acetylation procedure using furfuryl alcohol (100 mg, 0.505 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (109 mg, 0.454 mmol, 90%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45-7.39 (m, 1H), 6.41 (d, $J = 3.2$ Hz, 1H), 6.36 (d, $J = 1.8$ Hz, 1H), 5.05 (s, 2H), 2.07 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



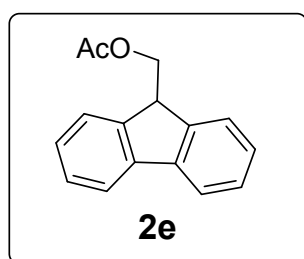
Phenethyl acetate (2b): Following general acetylation procedure using phenethyl alcohol (100 μL , 98 mg, 0.803 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (110 mg, 0.674 mmol, 84%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (ddd, $J = 6.7, 4.1, 1.4$ Hz, 2H), 7.26-7.19 (m, 3H), 4.28 (t, $J = 7.1$ Hz, 2H), 2.93 (t, $J = 7.1$ Hz, 2H), 2.03 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



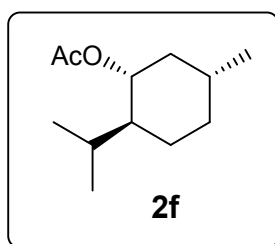
2-Phenoxyethyl acetate (2c): Following general acetylation procedure using 2-phenoxyethanol (100 μL , 90 mg, 0.652 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (102 mg, 0.567 mmol, 87%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30-7.25 (m, 2H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.93-6.87 (m, 2H), 4.42-4.38 (m, 2H), 4.14 (dt, $J = 5.1, 3.7$ Hz, 2H), 2.07 (d, $J = 1.7$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



Cinnamyl acetate (2d): Following general acetylation procedure using cinnamyl alcohol (100 μ L, 96 mg, 0.717 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (104 mg, 0.595 mmol, 83%). ^1H NMR (500 MHz, CDCl_3) δ 7.41 - 7.37 (m, 2H), 7.32 (dd, J = 8.2, 6.8 Hz, 2H), 7.26 (d, J = 7.7 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H), 4.73 (d, J = 1.3 Hz, 1H), 4.72 (d, J = 1.3 Hz, 1H), 2.10 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

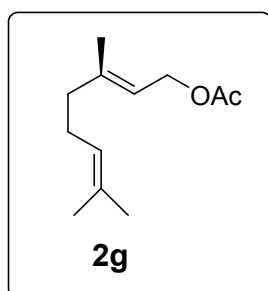


9-Fluorenylmethyl acetate (2e): Following general acetylation procedure using 9-fluorenylmethanol (100 mg, 0.510 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (104 mg, 0.438 mmol, 86%). ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.31 (td, J = 7.5, 1.0 Hz, 2H), 4.36 (d, J = 7.3 Hz, 2H), 4.21 (t, J = 7.3 Hz, 1H), 2.14 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

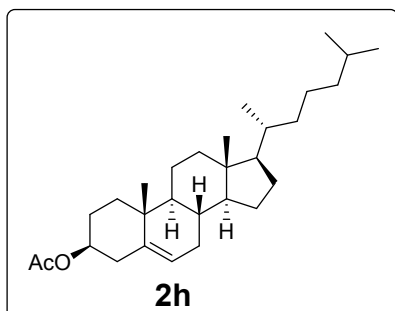


Menthyl acetate (2f): Following general acetylation procedure using menthol (100 mg, 0.641 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (111 mg, 0.564 mmol, 88%). ^1H NMR (500 MHz, CDCl_3) δ 4.68 (td, J = 10.9, 4.4 Hz, 1H), 2.03 (s, 3H), 2.02-1.96 (m, 1H), 1.91-1.82 (m, 1H), 1.68 (dtt, J = 12.9, 6.5, 3.2 Hz, 2H), 1.54-1.44 (m, 1H), 1.36 (ddt, J = 14.2, 10.9, 3.1 Hz, 1H), 1.11-1.01 (m, 1H), 1.01-0.92 (m, 1H), 0.92-0.87

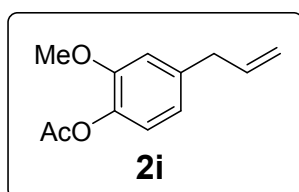
(m, 7H), 0.87-0.82 (m, 1H), 0.77 (d, $J = 7.0$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



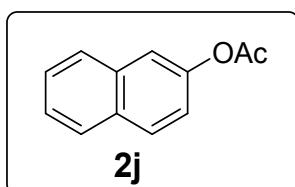
Geranyl acetate (2g): Following general acetylation procedure using geraniol (100 μ L, 112 mg, 0.727 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (116 mg, 0.596 mmol, 82%). ^1H NMR (400 MHz, CDCl_3) δ 5.34 (td, $J = 7.1, 1.0$ Hz, 1H), 5.11-5.05 (m, 1H), 4.59 (d, $J = 7.1$ Hz, 2H), 2.06 (m, 4H), 2.05 (s, 3H), 1.69 (d, $J = 8.0$ Hz, 6H), 1.60 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



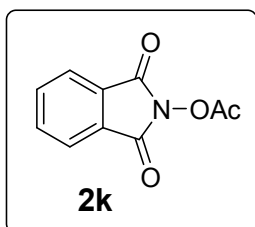
Cholesteryl acetate (2h): Following general acetylation procedure using cholesterol (104 mg, 0.368 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (143 mg, 0.334 mmol, 91%). ^1H NMR (500 MHz, CDCl_3) δ 5.37 (d, $J = 4.8$ Hz, 1H), 4.65 - 4.55 (m, 1H), 2.32 (d, $J = 7.0$ Hz, 2H), 2.03 (s, 3H), 1.85 (dd, $J = 8.2, 6.5$ Hz, 4H), 1.71-1.42 (m, 10H), 1.34 (d, $J = 8.3$ Hz, 6H), 1.18-1.08 (m, 6H), 1.02 (s, 3H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 2.3$ Hz, 3H), 0.86 (d, $J = 2.2$ Hz, 3H), 0.68 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



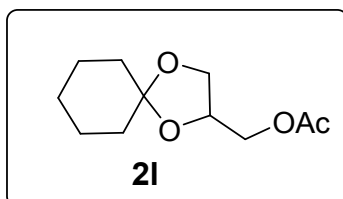
Eugenyl acetate (2i): Following general acetylation procedure using eugenol (100 μ L, 94 mg, 0.575 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (100 mg, 0.488 mmol, 85%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.93 (d, $J = 8.0$ Hz, 1H), 6.80-6.73 (m, 2H), 5.99-5.90 (m, 1H), 5.13-5.06 (m, 2H), 3.79 (s, 3H), 3.36 (d, $J = 6.8$ Hz, 2H), 2.28 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



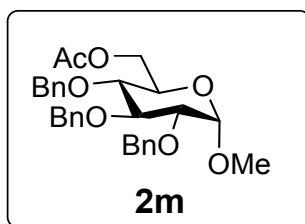
β -Naphthyl acetate (2j): Following general acetylation procedure using β -naphthol (100 mg, 0.694 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (112 mg, 0.603 mmol, 87%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90-7.85 (m, 2H), 7.84-7.79 (m, 1H), 7.58 (d, $J = 2.2$ Hz, 1H), 7.50 (ddd, $J = 7.7, 5.6, 1.6$ Hz, 2H), 7.25 (dd, $J = 8.9, 2.3$ Hz, 1H), 2.38 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



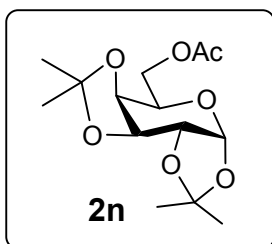
N-(acetoxy)phthalimide (2k): Following general acetylation procedure using N-hydroxyphthalimide (100 mg, 0.613 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (110 mg, 0.537 mmol, 79%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.88 (dd, $J = 5.5, 3.2$ Hz, 2H), 7.79 (ddd, $J = 5.8, 3.2, 2.6$ Hz, 2H), 2.40 (d, $J = 5.6$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



1,4-Dioxaspiro [4,5] decan acetate (2l): Following general acetylation procedure using 1,4-dioxaspiro [4,5] decanol (100 mg, 0.581 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (109 mg, 0.511 mmol, 88%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.34-4.27 (m, 1H), 4.14 (dd, $J = 11.5, 5.0$ Hz, 1H), 4.09 (dd, $J = 7.6, 3.8$ Hz, 1H), 4.07-4.04 (m, 1H), 2.09 (s, 3H), 1.67-1.51 (m, 9H), 1.48-1.30 (m, 2H); the overall spectroscopic data are in complete agreement with assigned structure.

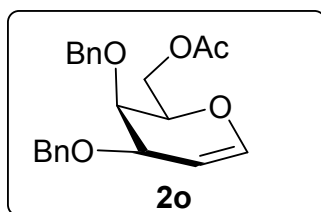


Methyl 2,3,4-tri-O-benzyl-6-O-acetyl- α -D-glucopyranoside (2m): Following general acetylation procedure using methyl 2,3,4-tri-O-benzyl-6-hydroxy- α -D-glucopyranoside (104 mg, 0.215 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (96 mg, 0.191 mmol, 89%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.38-7.28 (m, 15H), 5.01 (d, $J = 10.8$ Hz, 1H), 4.91-4.84 (m, 2H), 4.83-4.78 (m, 1H), 4.67 (d, $J = 12.1$ Hz, 1H), 4.59 (dd, $J = 17.3, 7.2$ Hz, 2H), 4.26 (t, $J = 3.4$ Hz, 2H), 4.02 (s, 1H), 3.85-3.80 (m, 1H), 3.55 (dd, $J = 9.6, 3.5$ Hz, 1H), 3.48 (m, 1H), 3.38 (s, 3H), 2.03 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

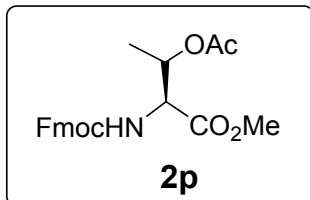


1,2,3,4-di-O-isopropylidene-6-O-acetyl- α -D-galactopyranoside (2n): Following general acetylation procedure using 1,2,3,4-di-O-isopropylidene-6-hydroxy- α -D-galactopyranoside (100 mg, 0.384 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (102 mg, 0.337 mmol, 88%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.54 (d, $J = 5.0$ Hz, 1H), 4.62 (dd, $J = 7.9, 2.5$ Hz, 1H), 4.33 (dd, $J = 5.0, 2.5$ Hz, 1H), 4.29 (dd, $J = 11.6, 4.7$ Hz, 1H), 4.24 (dd, $J = 7.9, 1.8$ Hz, 1H), 4.19 (dd, $J = 11.6, 7.7$ Hz, 1H), 4.06-3.99 (m, 1H), 2.09 (s, 3H), 1.52 (s, 3H), 1.45

(s, 3H), 1.34 (d, $J = 2.6$ Hz, 6H); the overall spectroscopic data are in complete agreement with assigned structure.



6-O-Acetyl-3,4-di-O-benzyl-D-lyxo-hexapyranose (2o): Following general acetylation procedure using 3,4-di-O-benzyl-D-lyxo-hexapyranose (100 mg, 0.306 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (100 mg, 0.272 mmol, 89%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41-7.28 (m, 10H), 6.34 (dd, $J = 6.2, 1.1$ Hz, 1H), 4.91 (ddd, $J = 6.2, 3.6, 0.7$ Hz, 1H), 4.84 (d, $J = 11.9$ Hz, 1H), 4.75-4.62 (m, 3H), 4.47 (dd, $J = 12.0, 8.5$ Hz, 1H), 4.31 (dd, $J = 12.1, 3.4$ Hz, 1H), 4.25 (dd, $J = 7.7, 3.9$ Hz, 1H), 4.15 (t, $J = 3.8$ Hz, 1H), 3.91 (t, $J = 3.3$ Hz, 1H), 2.04 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



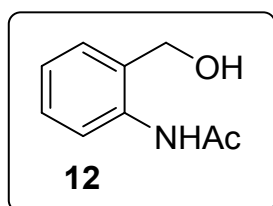
Fluorenylmethoxycarbonyl-Methyl-L-threonine acetate (2p): Following general acetylation procedure using fluorenylmethoxycarbonyl-methyl-L-threonine (100 mg, 0.281 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (99 mg, 0.250 mmol, 89%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.4$ Hz, 2H), 7.62 (t, $J = 6.8$ Hz, 2H), 7.40 (dd, $J = 7.4, 3.6$ Hz, 2H), 7.36-7.30 (m, 2H), 7.26 (s, 1H), 5.48-5.39 (m, 2H), 4.50 (dd, $J = 9.7, 2.5$ Hz, 1H), 4.45 (d, $J = 7.0$ Hz, 2H), 4.26 (s, 1H), 3.75 (s, 3H), 2.04 (s, 3H), 1.30 (d, $J = 6.5$ Hz, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

(A) Representative Procedure for the chemoselective deacetylation:

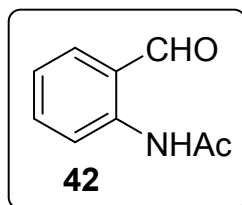
To a preformed solution of benzyl acetate **1a** (50 mg, 1.0 equiv.) in MeOH (1 mL) was added KMnO_4 (0.1 equiv.) at room temperature. The mixture was stirred at room temperature in open air environment and the reaction progress was monitored by TLC. After the complete consumption of starting material was observed, typically 1-12 h for deacetylation, the reaction mixture was filtered and washed with EtOAc (10 mL). The resultant filtrate was treated with saturated aqueous NaHCO_3 (5 mL), and aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to obtain the analytical pure products **3-11** and **13-28**. For 2-acetamidobenzyl acetate, the crude residues were purified by silica gel column chromatography using EtOAc/Hexane to obtain the desired 2-acetamido benzyl alcohol (**12**).

(B) Representative Procedure for the one-pot deacetylation oxidation:

To a preformed solution of benzyl acetate **1a** (50 mg, 1.0 equiv.) in MeOH:EtOAc (9:1; 2 mL) was added KMnO_4 (1.0 equiv.) at room temperature. The mixture was stirred at room temperature in open air environment and the reaction progress was monitored by TLC. After the complete consumption of starting material was observed, typically 10-32 h for deacetylation-oxidation, the reaction mixture was diluted with EtOAc (10 mL). The resultant mixture was treated with saturated aqueous NaHCO_3 (5 mL), and aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to obtain the analytical pure products **29-41**. For 2-acetamidobenzyl acetate, the crude residues were purified by silica gel column chromatography using EtOAc/Hexane to obtain the desired 2-acetamido benzaldehyde (**42**).



2-Acetamido benzyl alcohol (12): Following chemoselective deacetylation procedure using **1s** (100 mg, 0.483 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (62 mg, 0.376 mmol, 78%). ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.37-7.31 (m, 1H), 7.20 (d, $J = 6.7$ Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 5.10 (s, 1H), 4.71 (s, 2H), 2.20 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.



2-Acetamido benzaldehyde (42): Following one-pot deacetylation oxidation procedure **B** using **1s** (100 mg, 0.483 mmol) and purified by silica gel column chromatography, eluting with hexanes-ethyl acetate gradient afforded the title compound (66 mg, 0.405 mmol, 84%). ¹H NMR (500 MHz, CDCl₃) δ 11.13 (s, 1H), 9.92 (s, 1H), 8.74 (d, *J* = 8.5 Hz, 2H), 7.68-7.66 (m, 1H), 7.63-7.60 (m, 1H), 7.25-7.20 (m, 1H), 2.26 (s, 3H); the overall spectroscopic data are in complete agreement with assigned structure.

(C) General Procedure for Gram-Scale one-pot deacetylation oxidation:

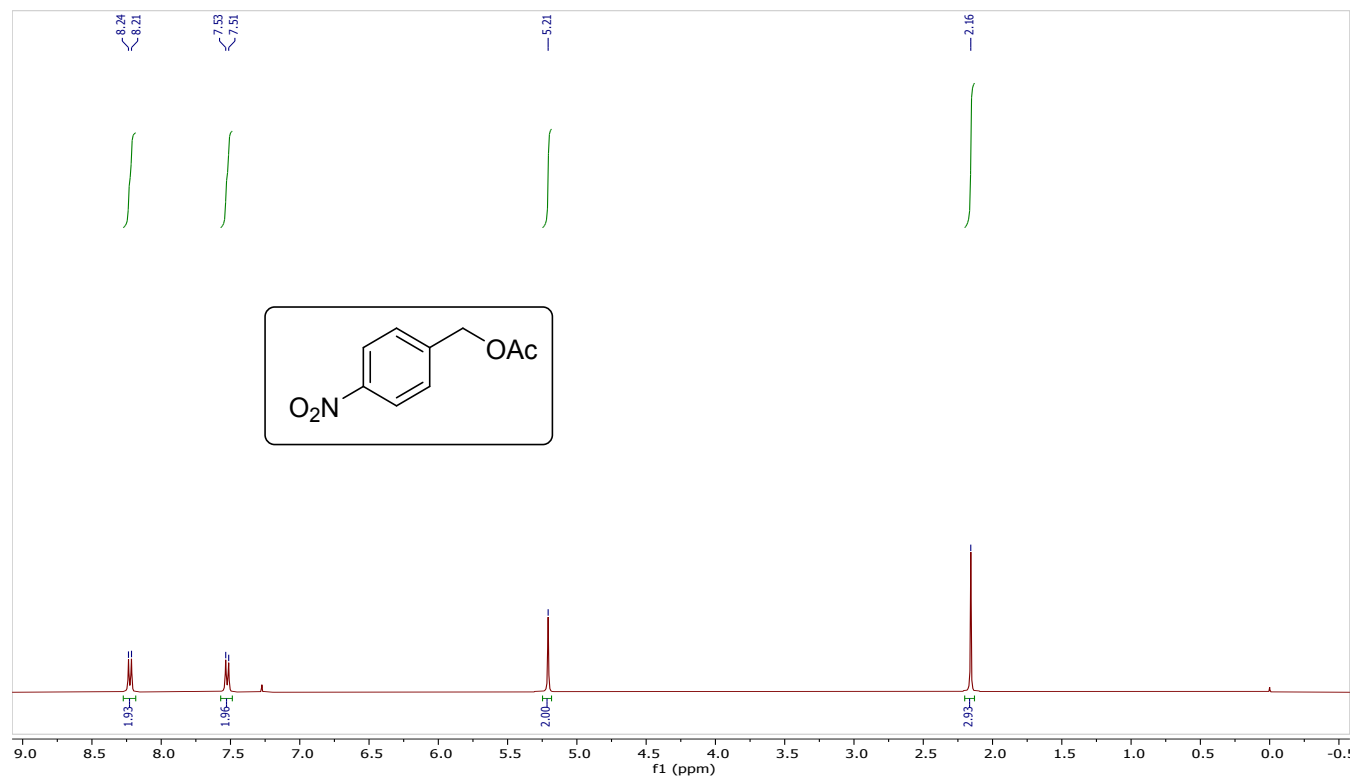
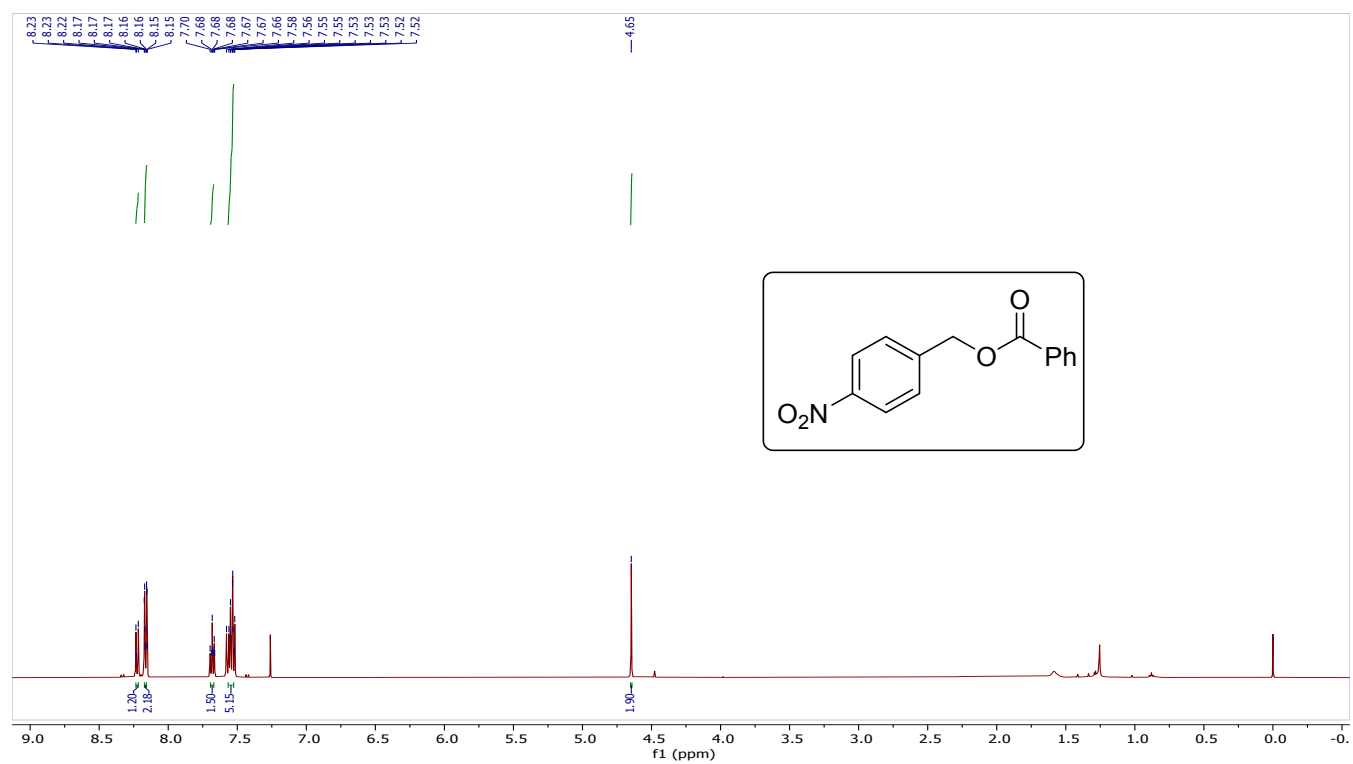
2-Iodobenzylaldehyde (35): Following general procedure **B** using 2-Iodobenzyl acetate (**1n**, 1.84 g, 6.667 mmol), KMnO₄ (1.0 g, 1.0 equiv.) in MeOH:EtOAc (9:1; 10 mL) solvent system, and following usual work-up, afforded the analytically pure product as crystalline solid (1.52 g, 6.534 mmol, 98%).

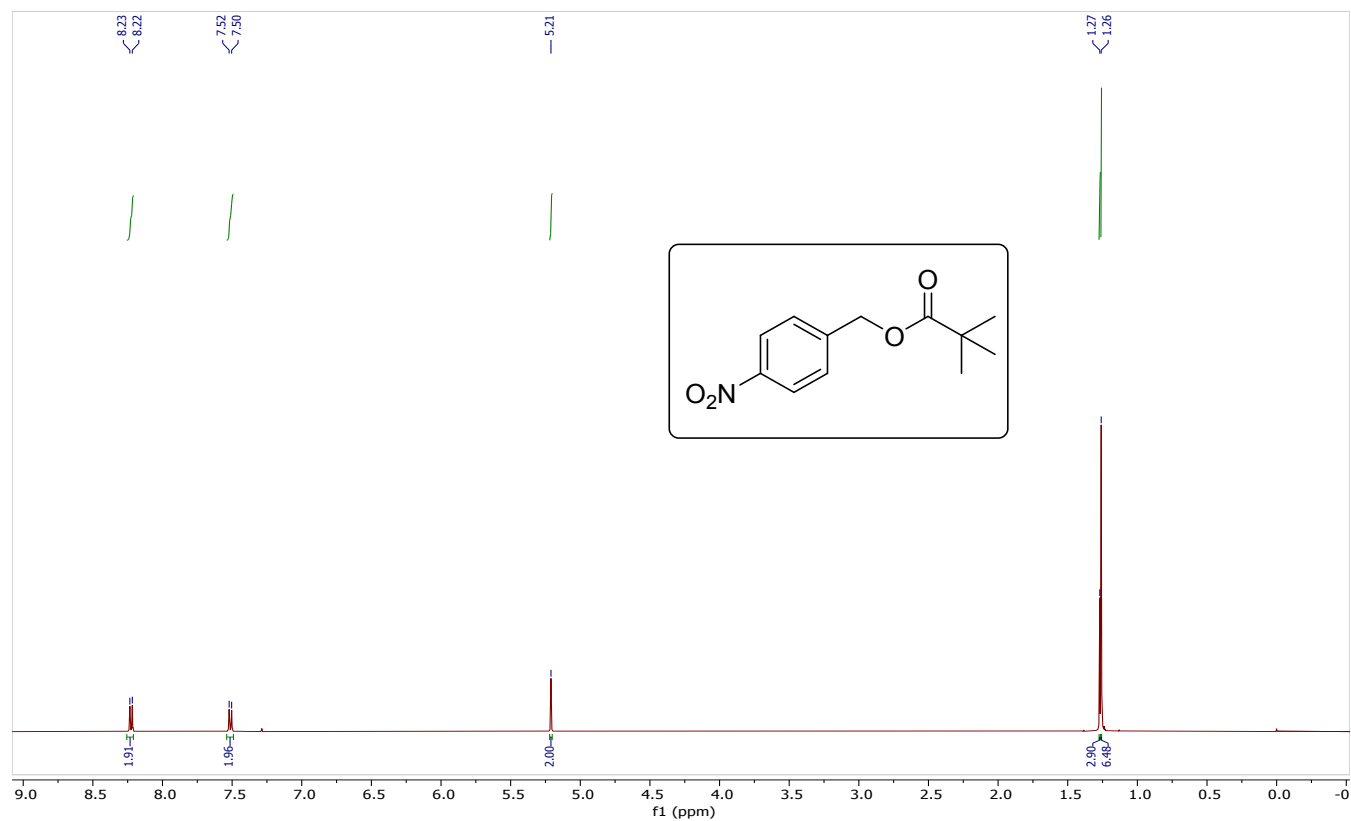
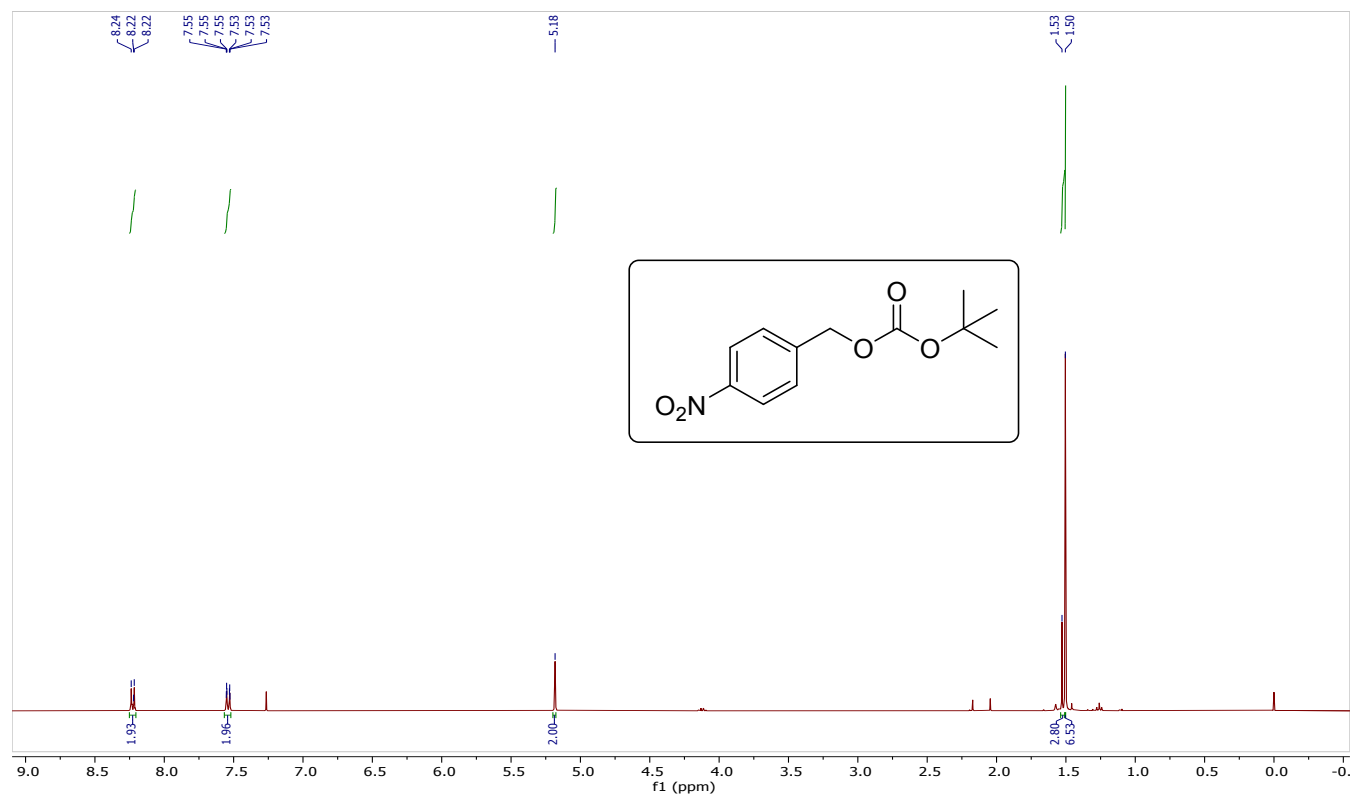
Piperonal (41): Following general procedure **B** using Piperonyl acetate (**1p**, 2.12 g, 10.928 mmol), KMnO₄ (1.73 g, 1.0 equiv.) in MeOH:EtOAc (9:1; 10 mL) solvent system, and following usual work-up, afforded the analytically pure product as pale yellow solid (1.51 g, 10.054 mmol, 92%).

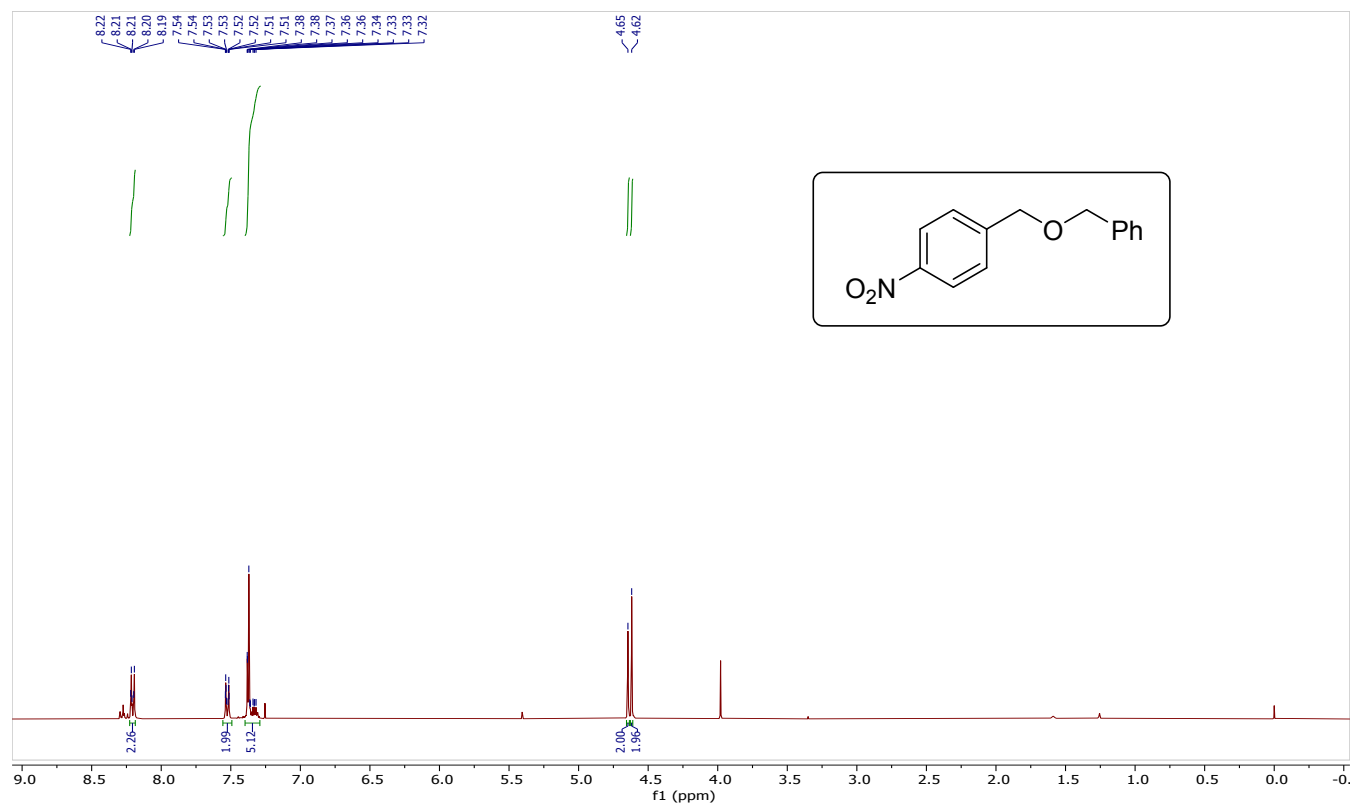
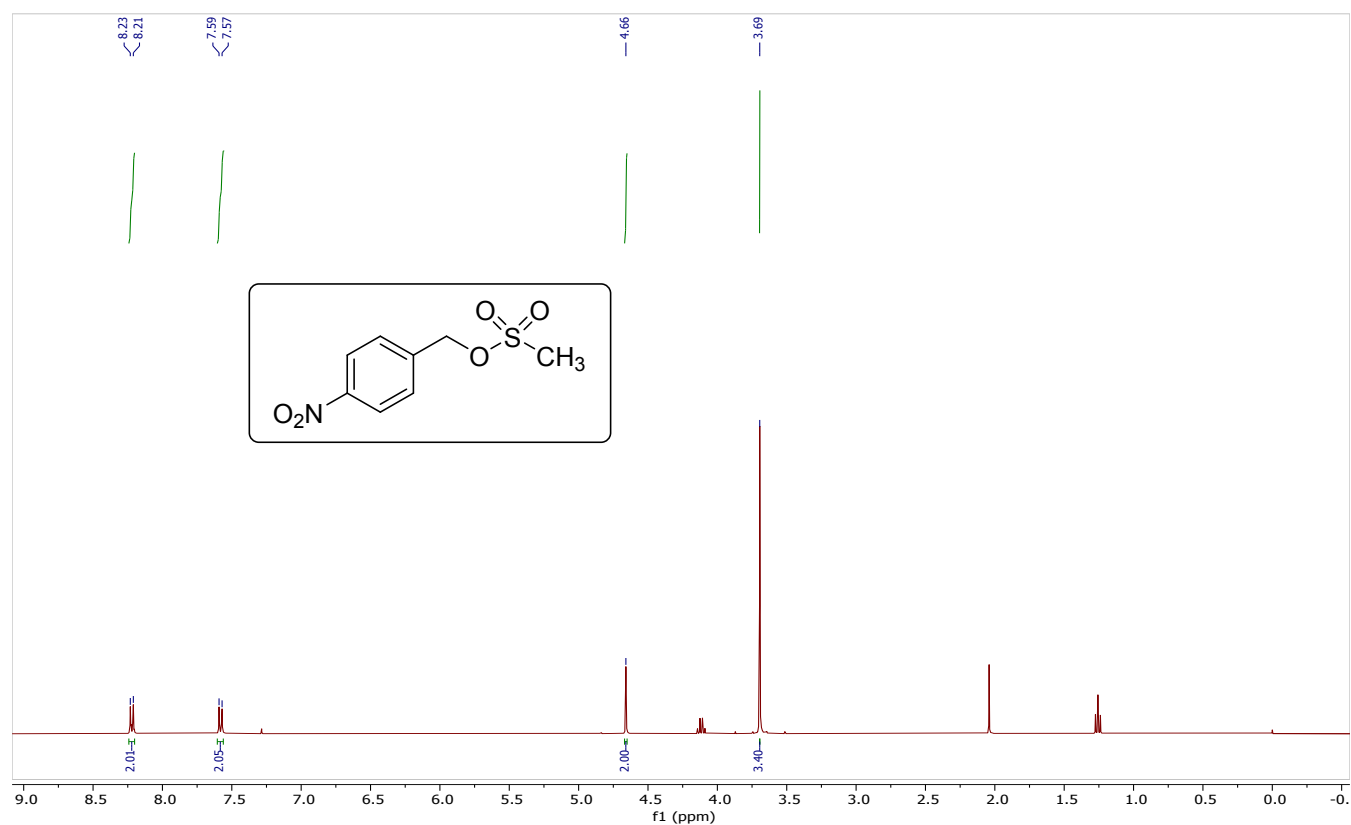
D. References for Supporting Information

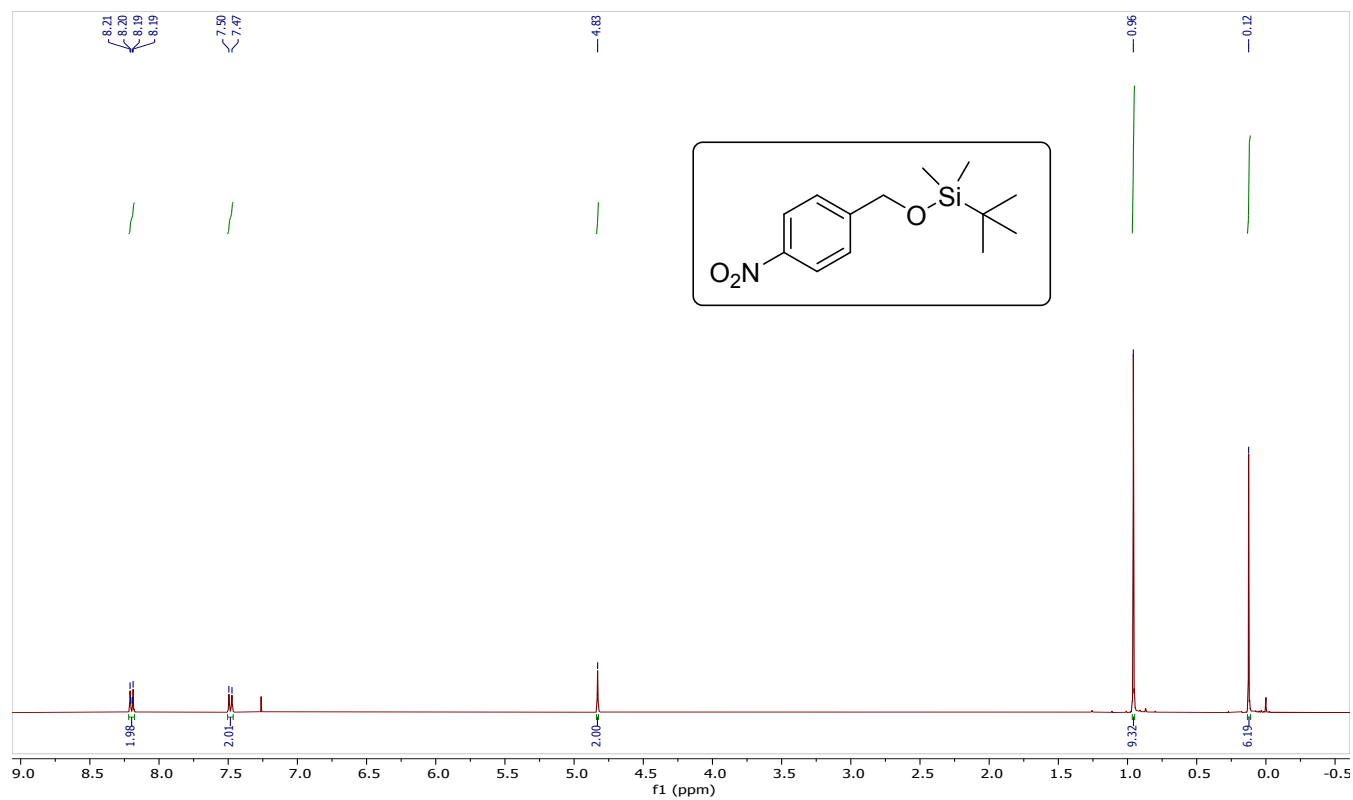
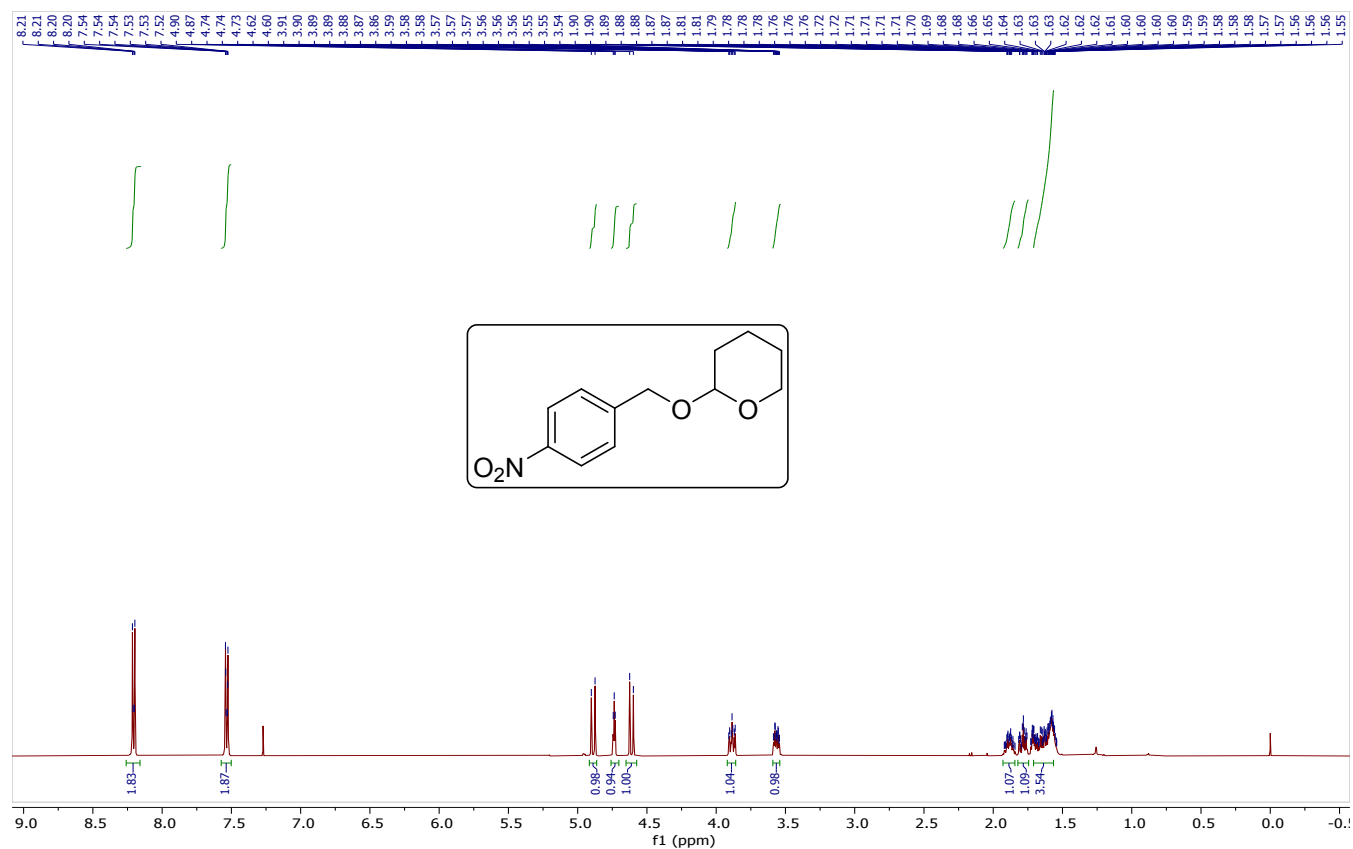
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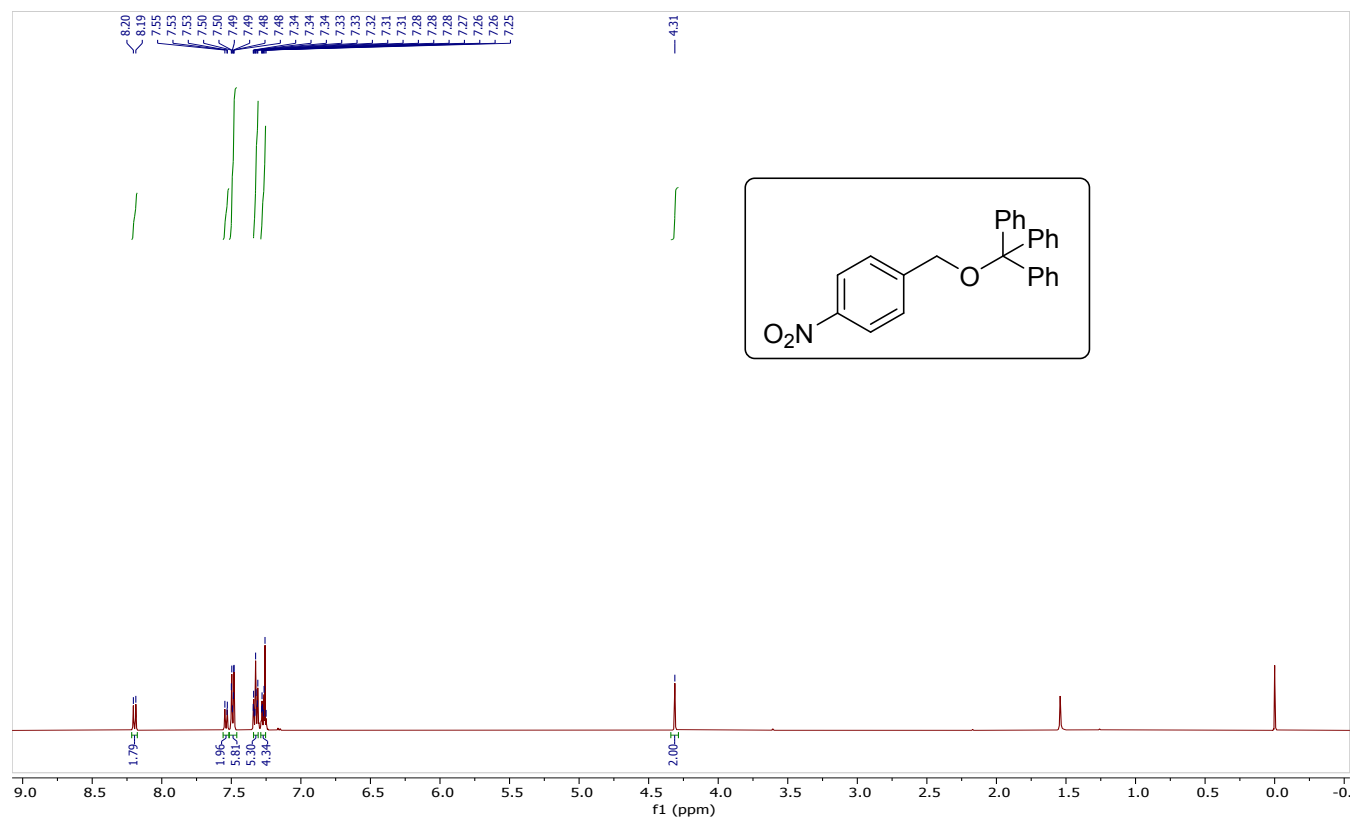
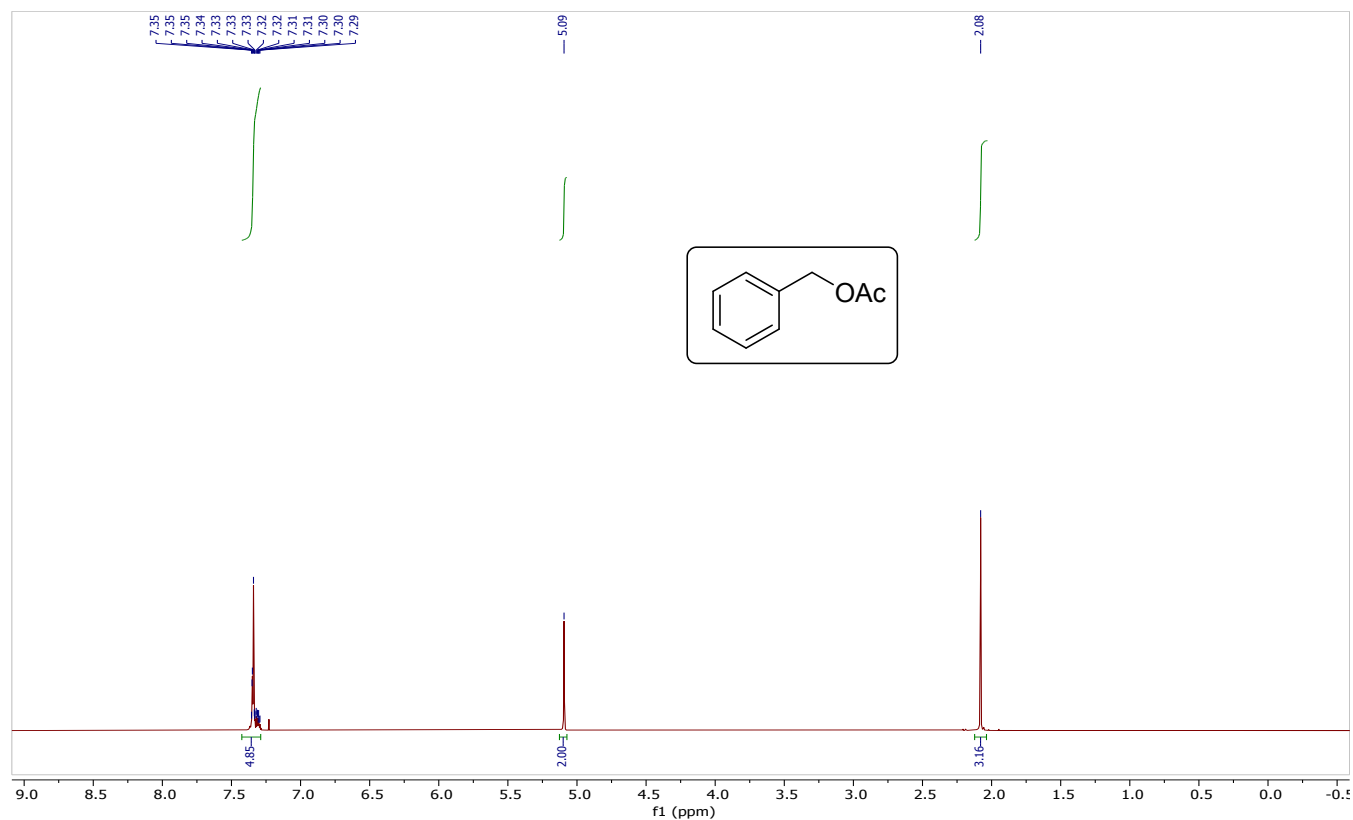
E. NMR Spectra:

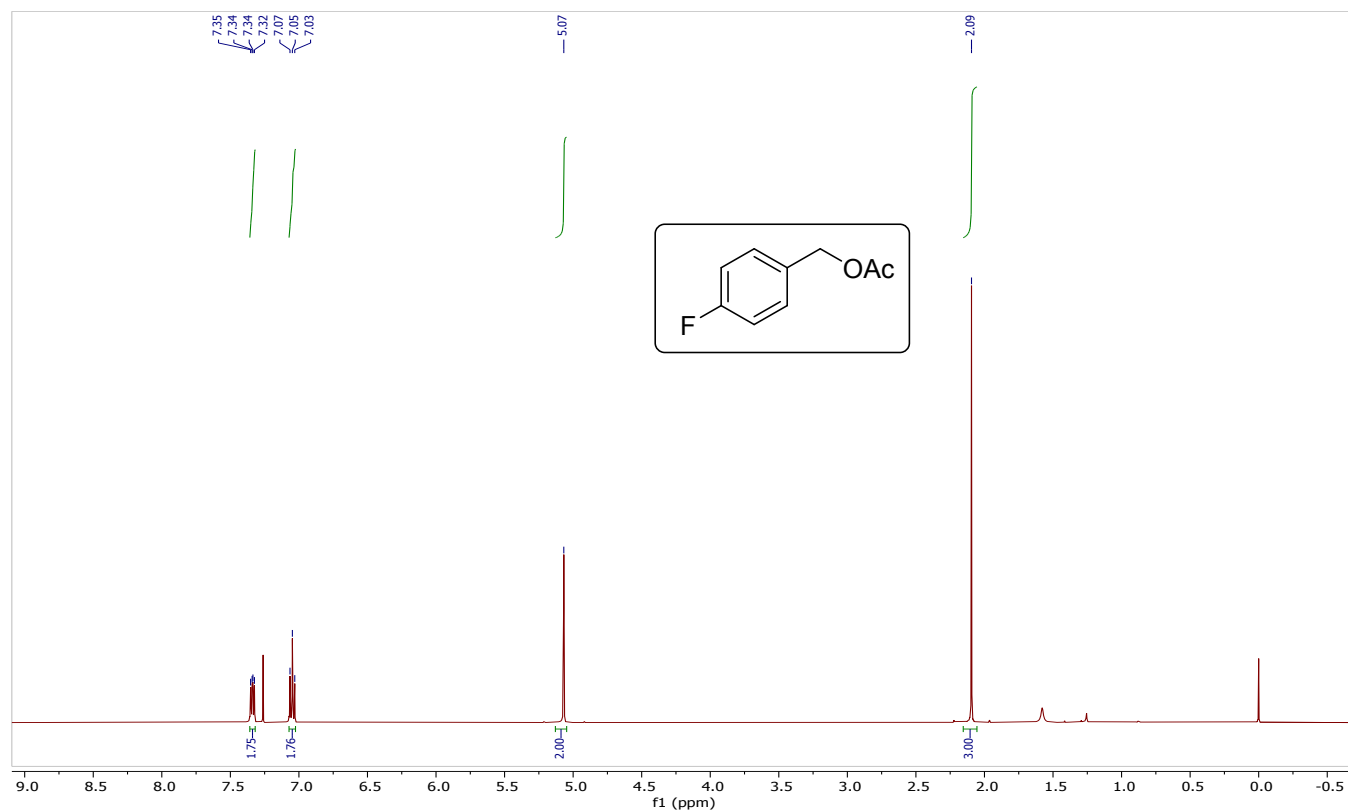
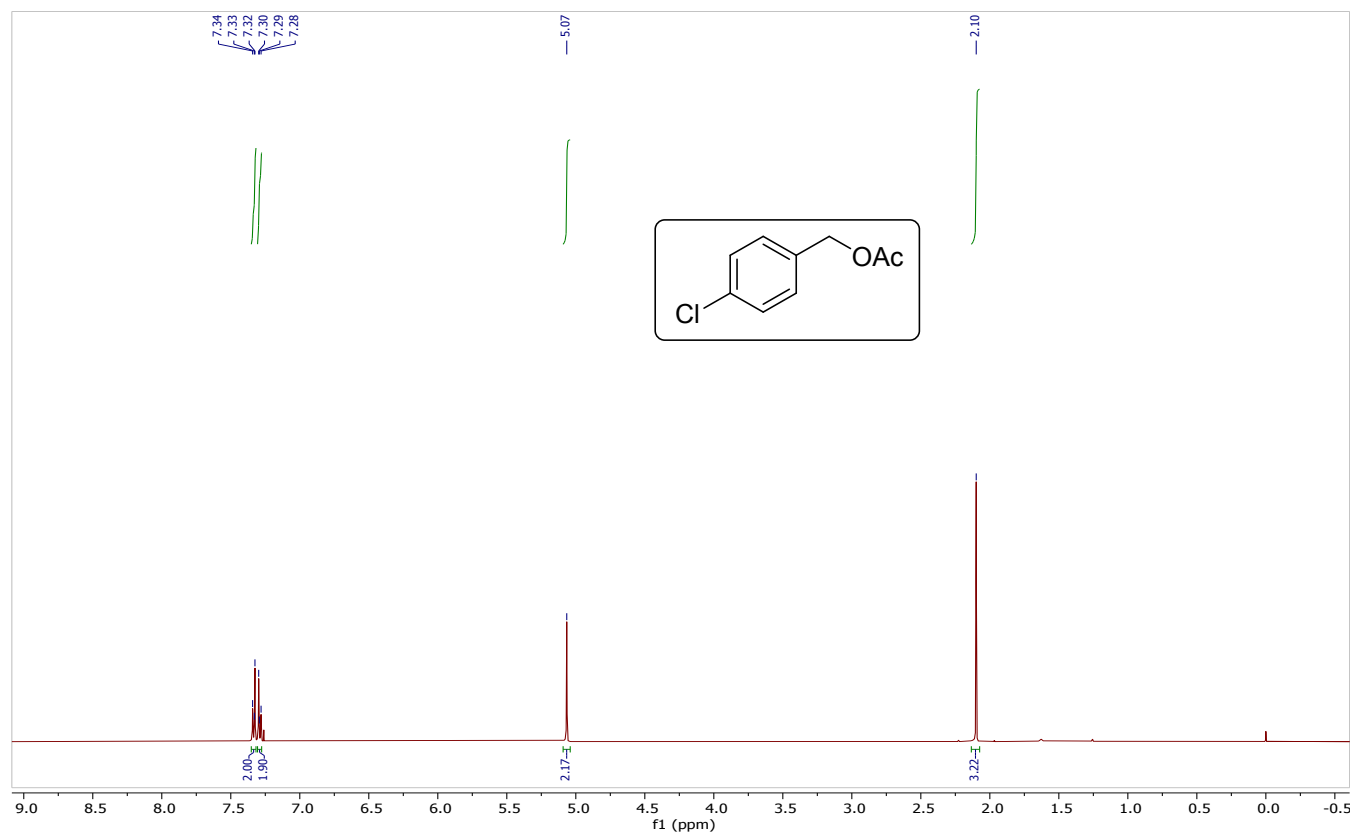
 ^1H NMR spectrum of compound **1a** in CDCl_3  ^1H NMR spectrum of compound **1b** in CDCl_3 

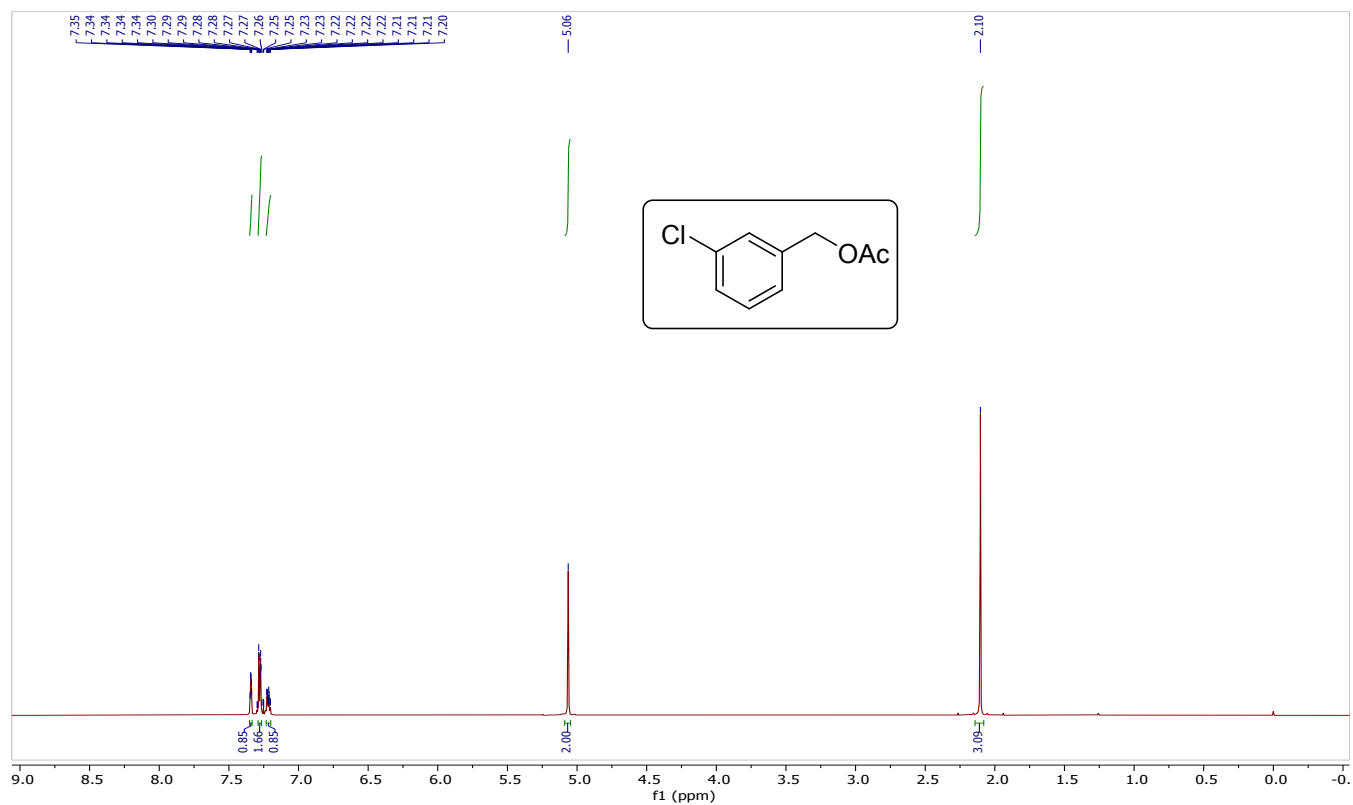
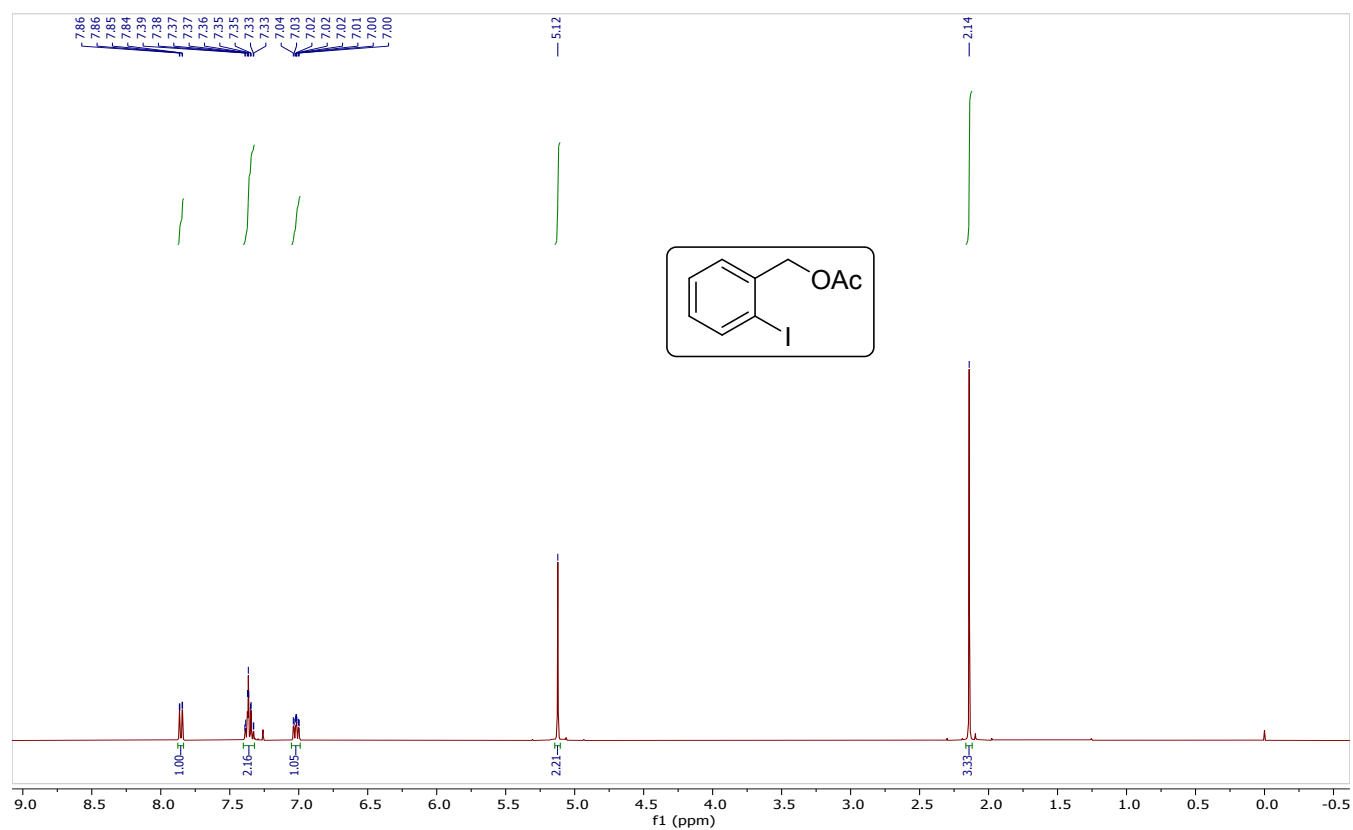
^1H NMR spectrum of compound **1c** in CDCl_3  ^1H NMR spectrum of compound **1d** in CDCl_3 

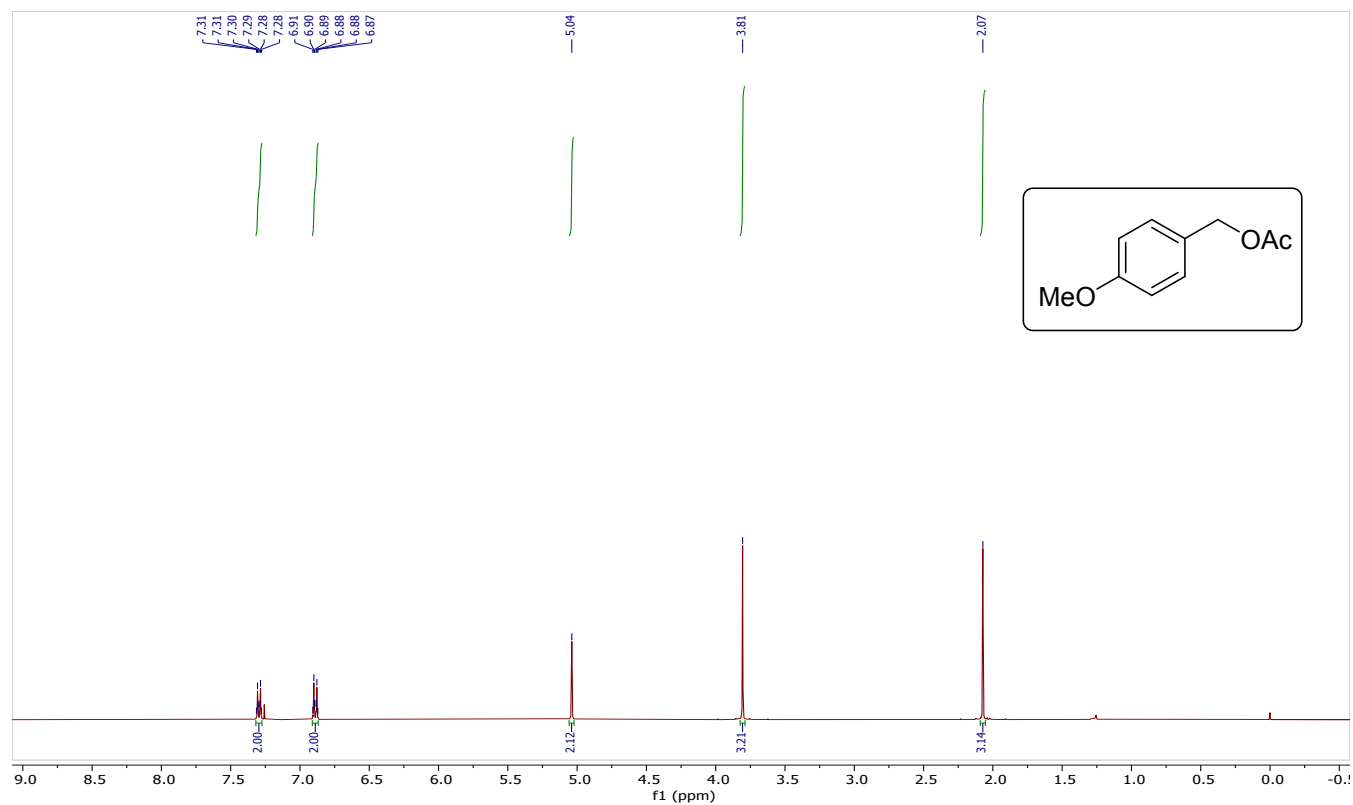
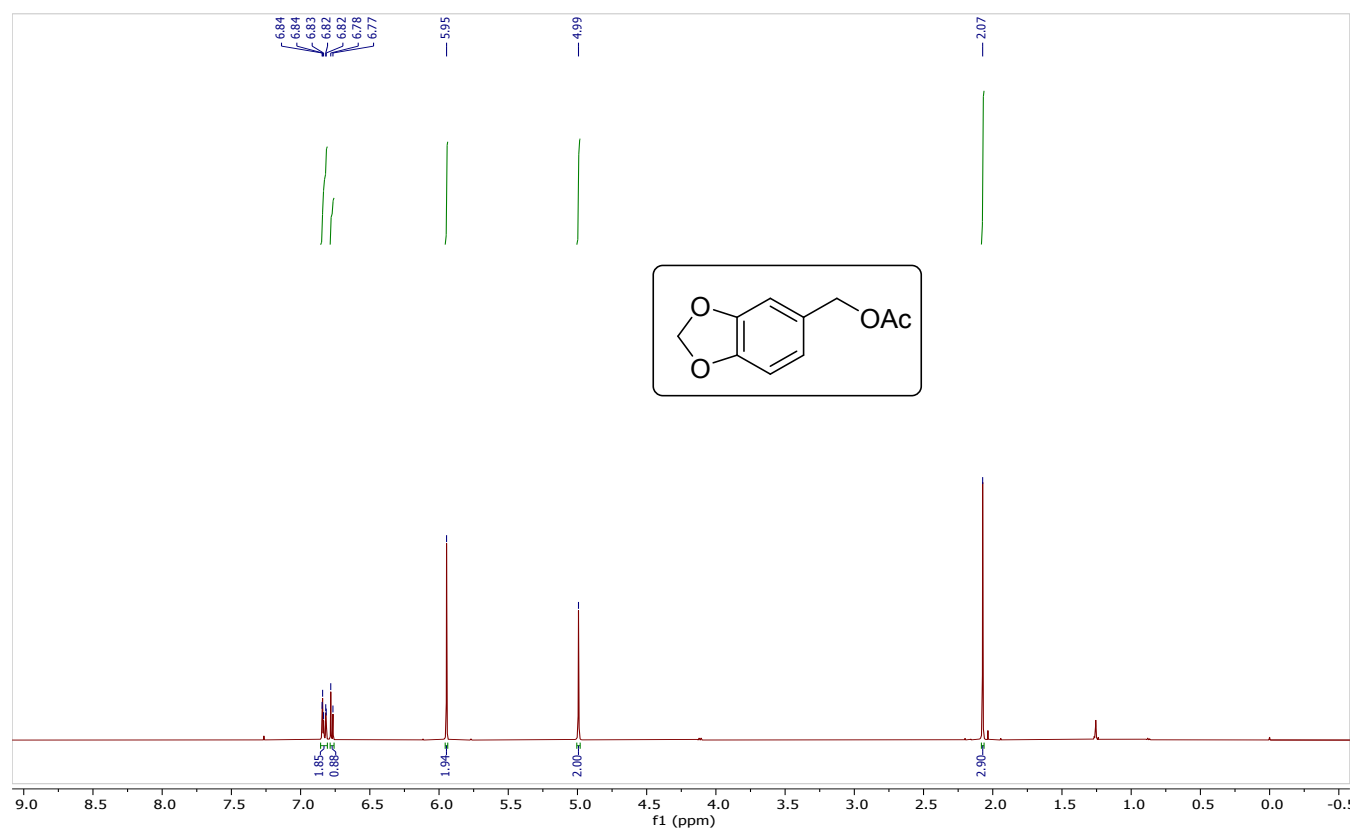
^1H NMR spectrum of compound **1e** in CDCl_3  ^1H NMR spectrum of compound **1f** in CDCl_3 

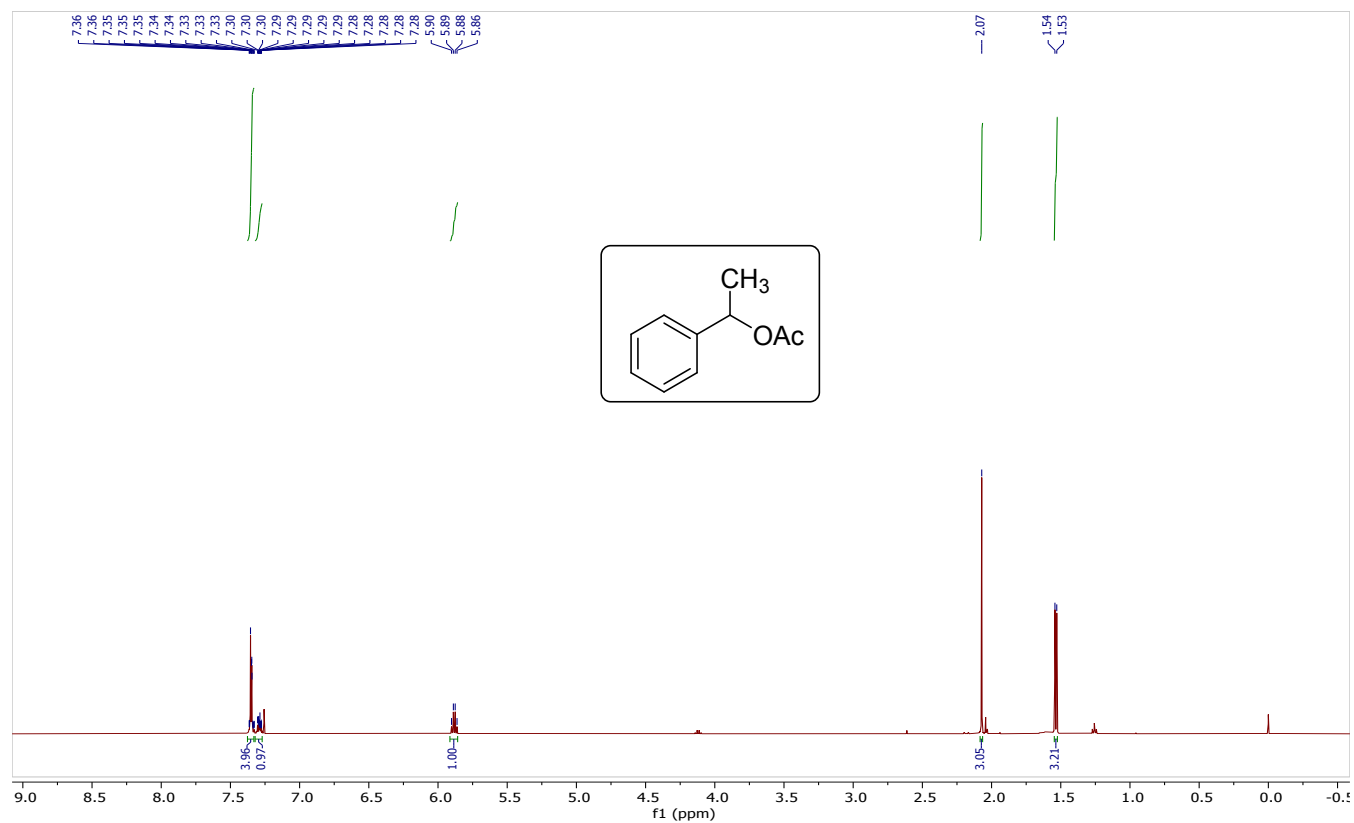
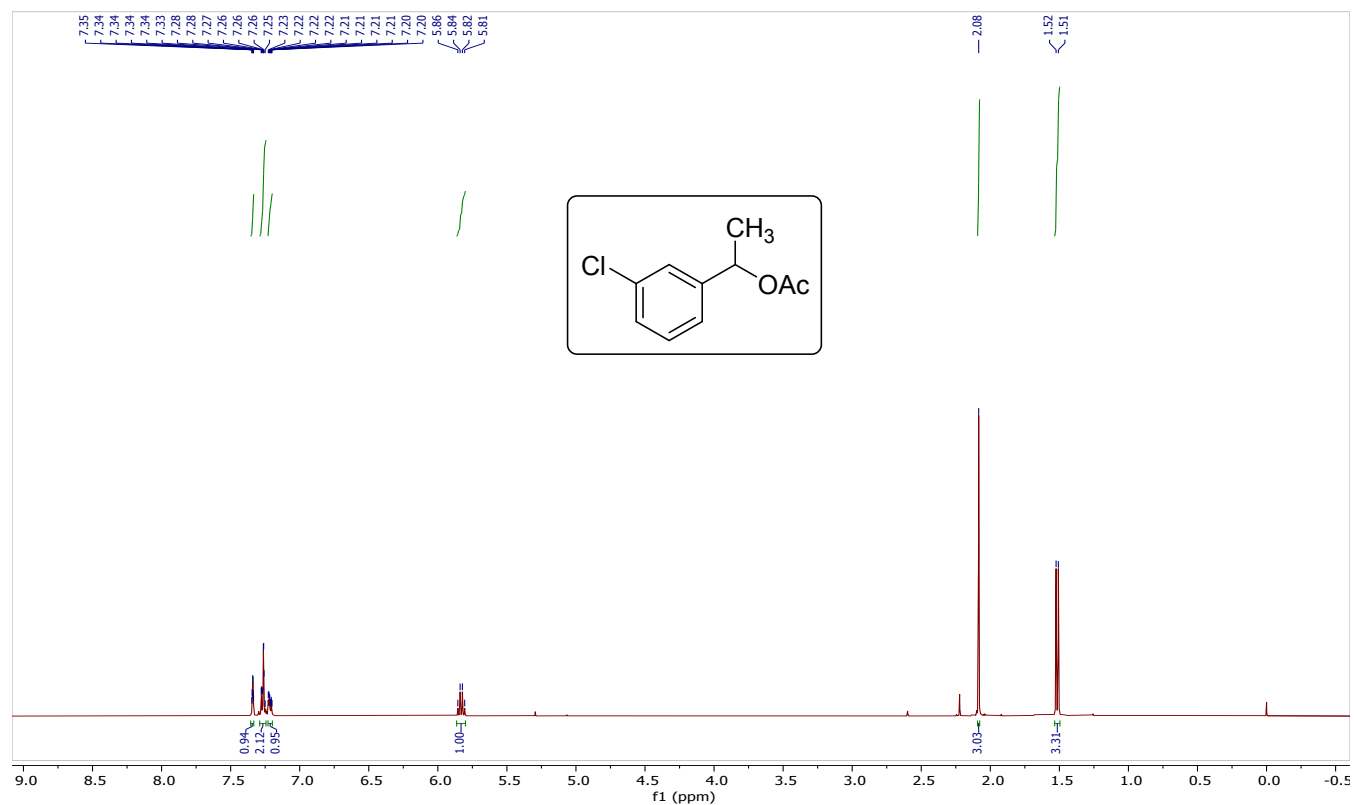
^1H NMR spectrum of compound **1g** in CDCl_3  ^1H NMR spectrum of compound **1h** in CDCl_3 

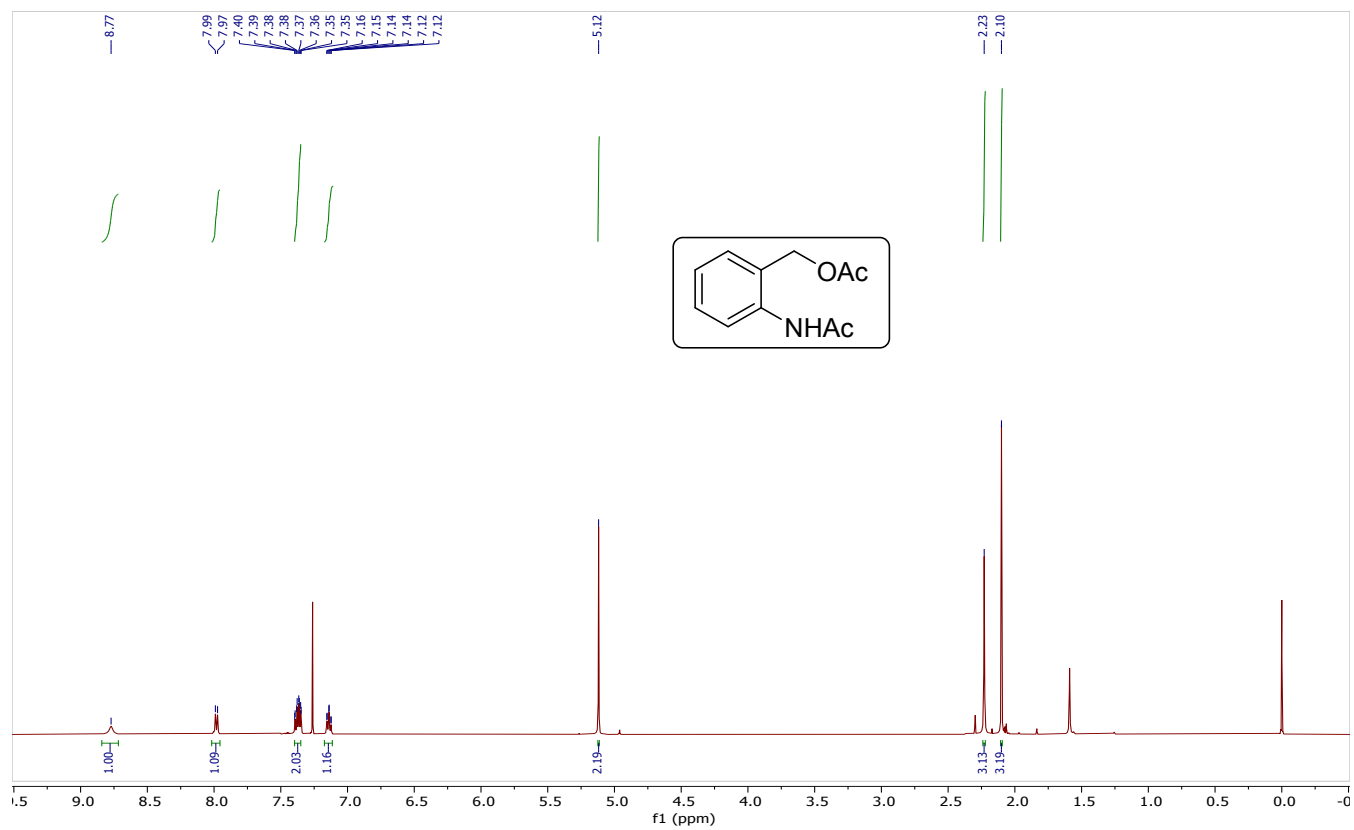
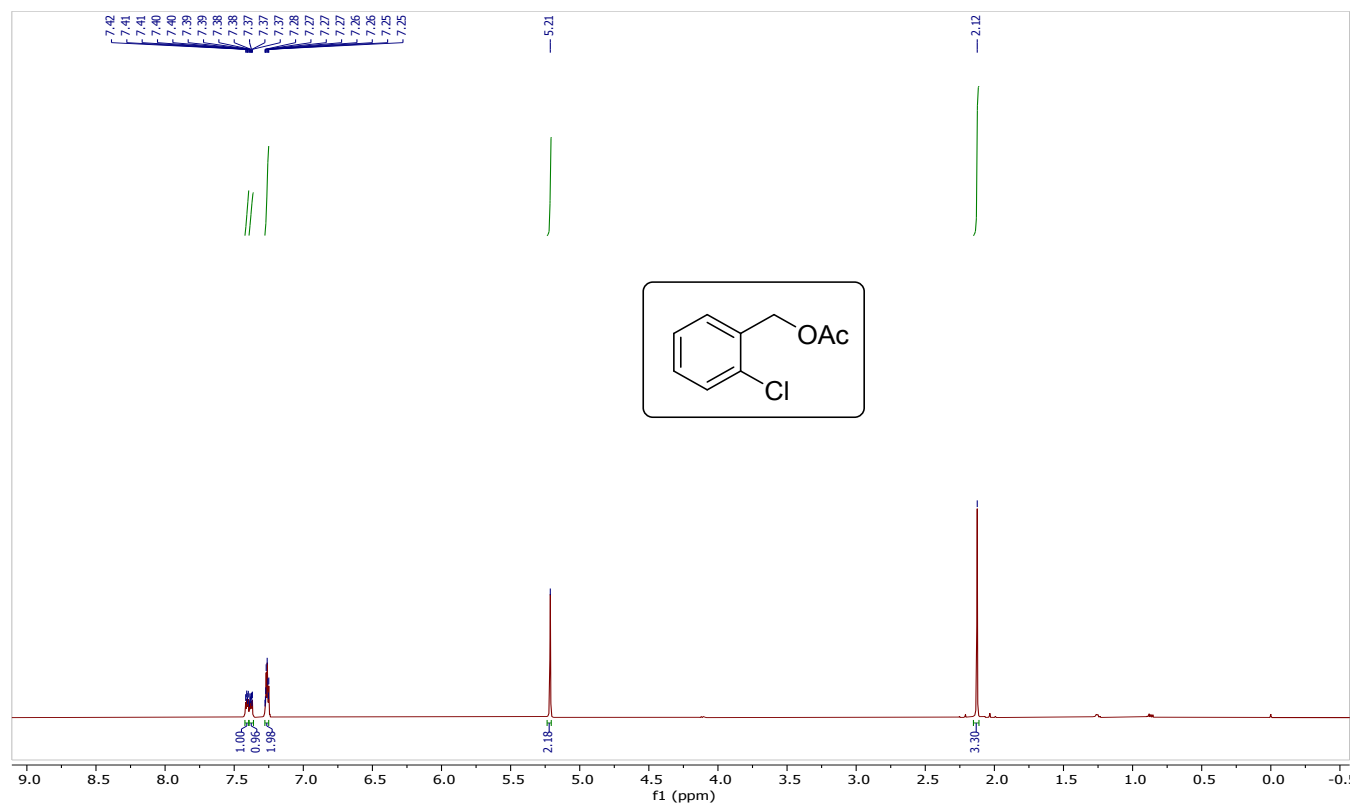
^1H NMR spectrum of compound **1i** in CDCl_3  ^1H NMR spectrum of compound **1j** in CDCl_3 

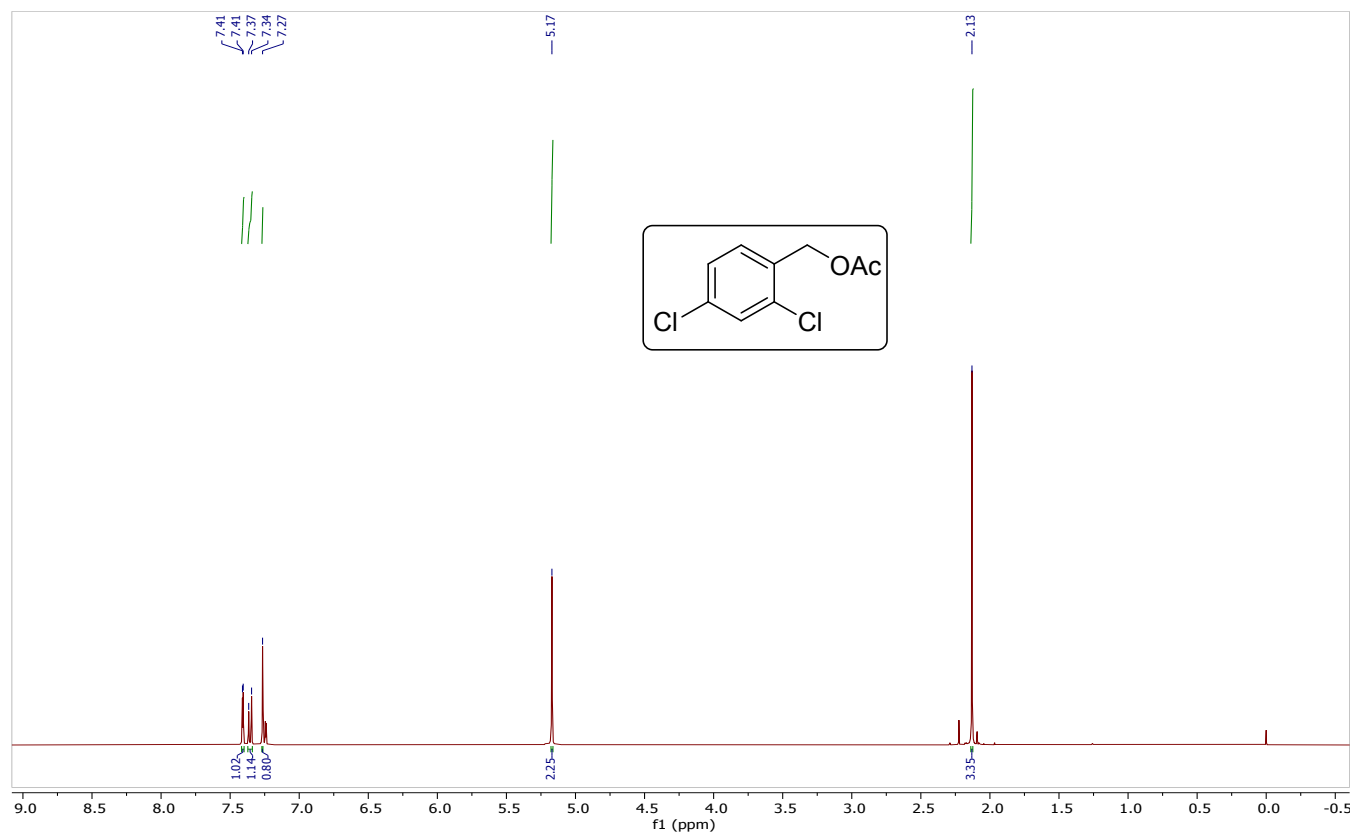
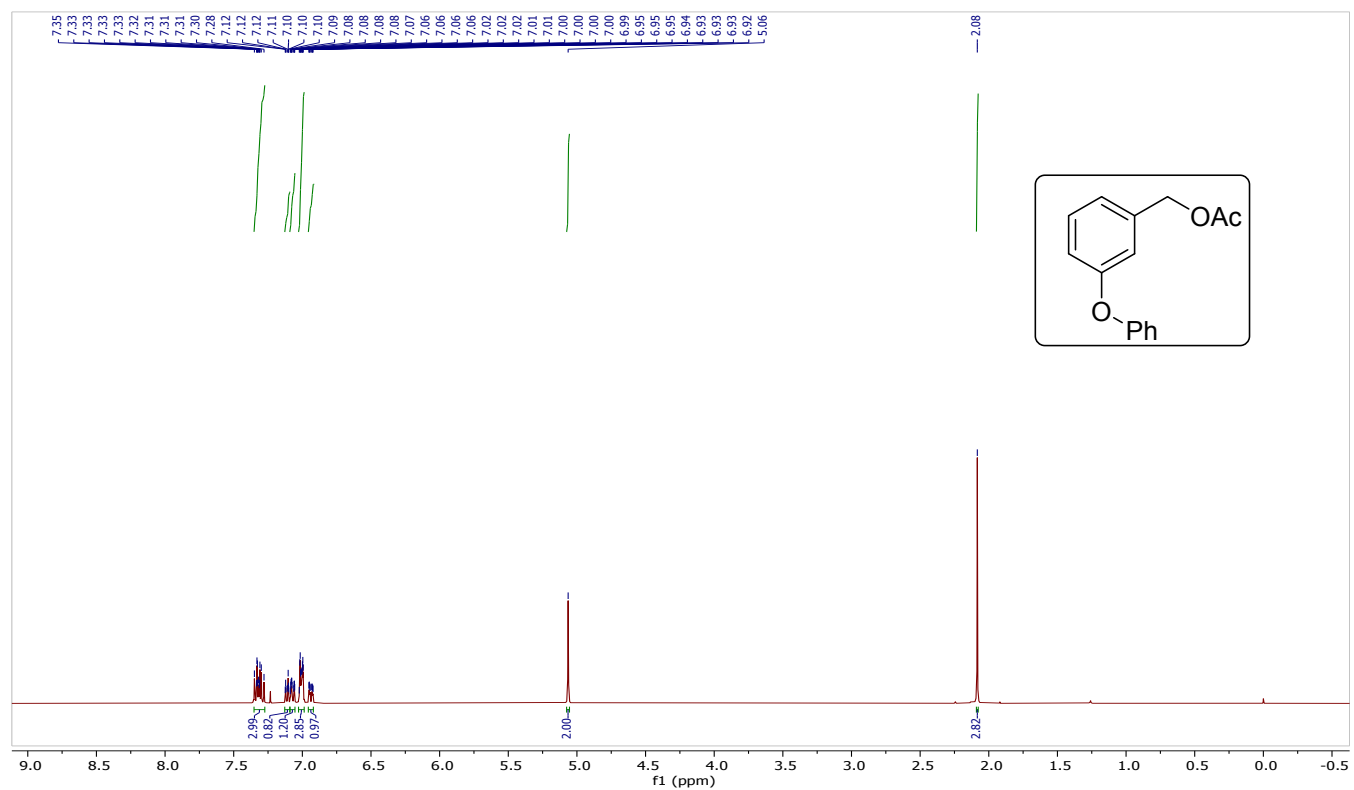
^1H NMR spectrum of compound **1k** in CDCl_3  ^1H NMR spectrum of compound **1l** in CDCl_3 

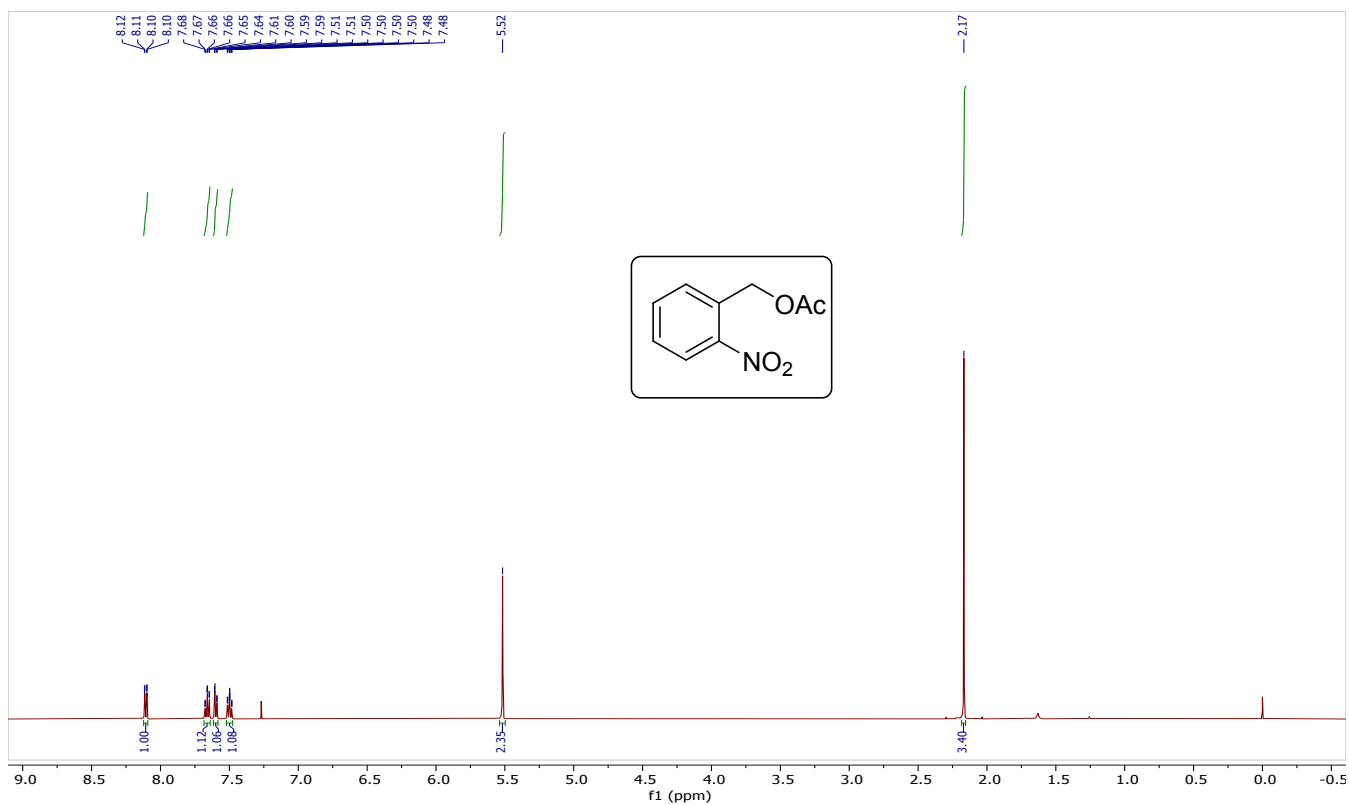
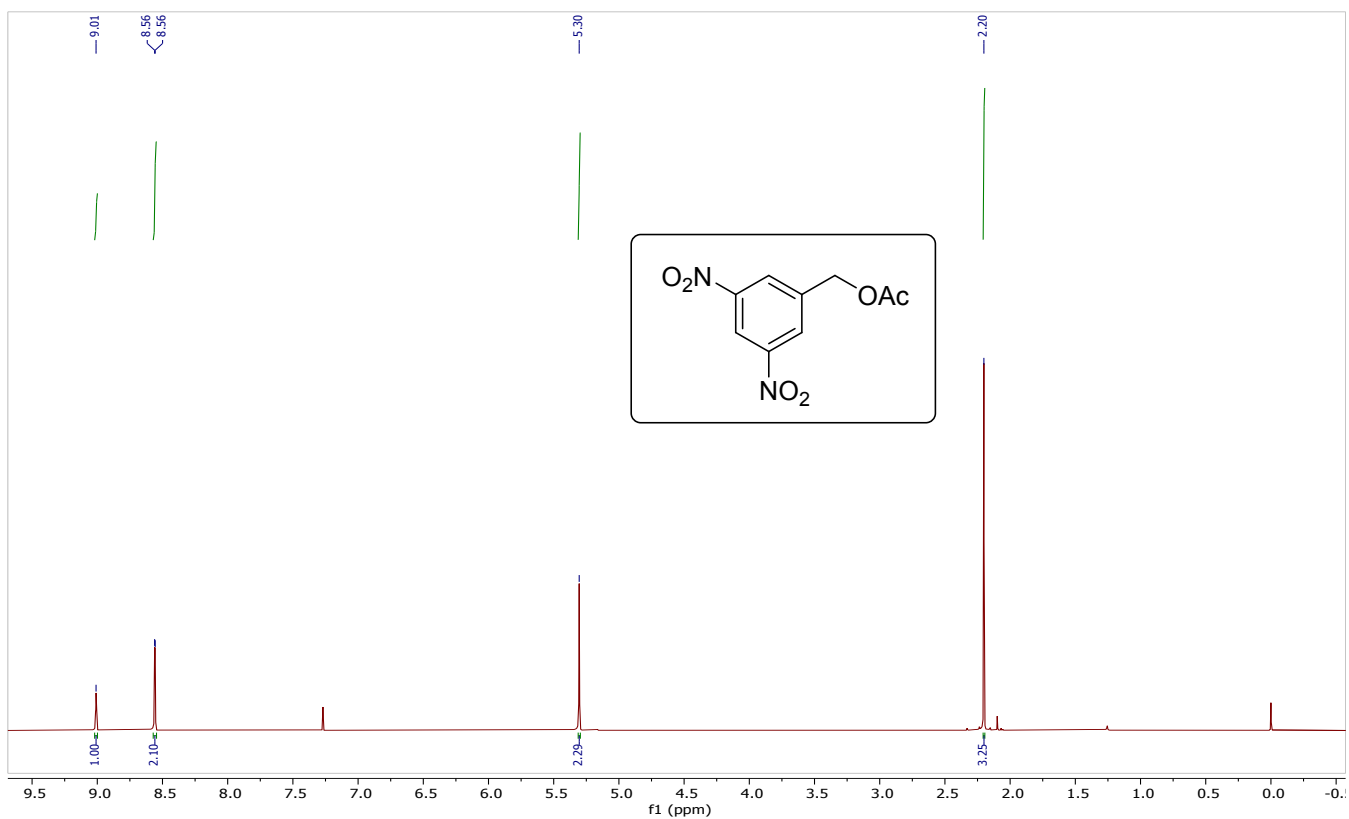
^1H NMR spectrum of compound **1m** in CDCl_3  ^1H NMR spectrum of compound **1n** in CDCl_3 

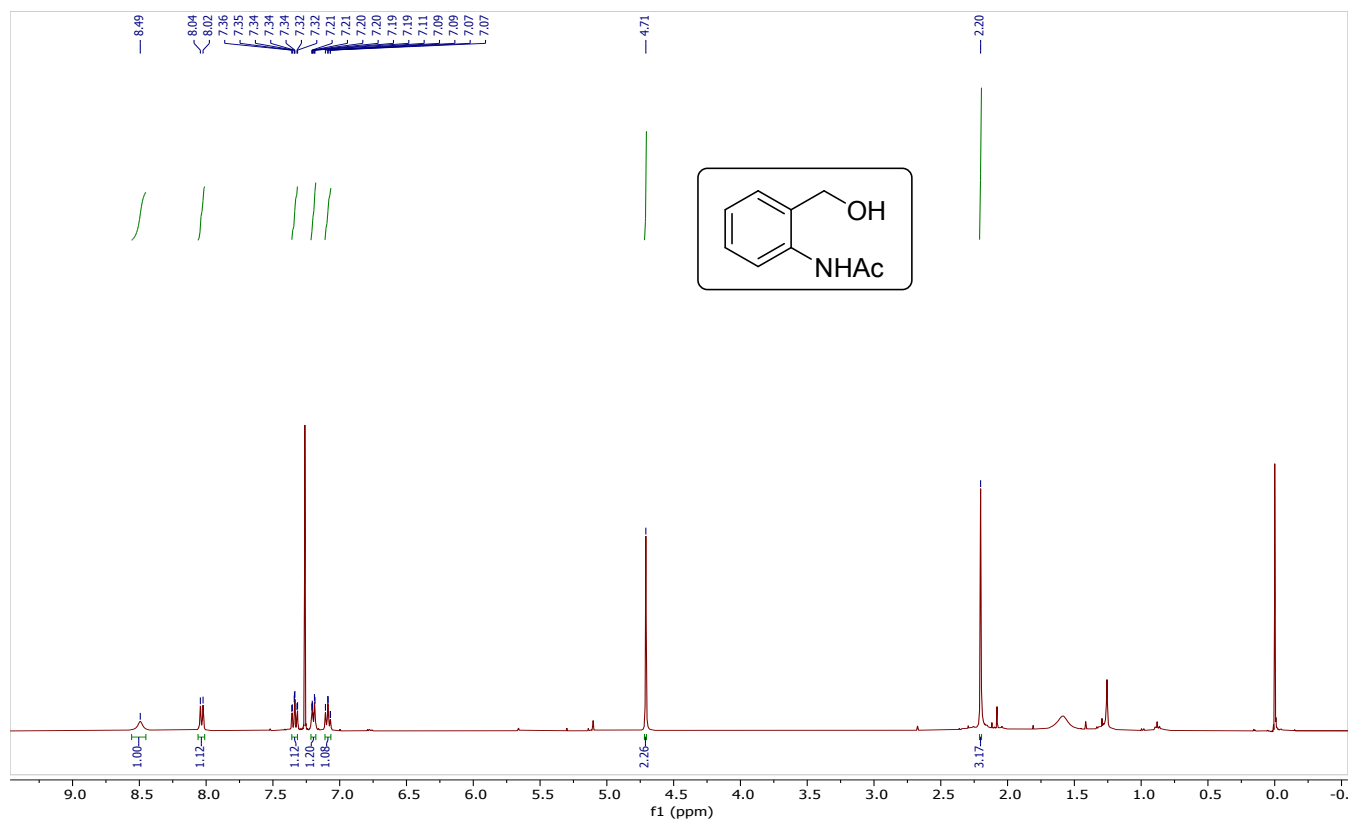
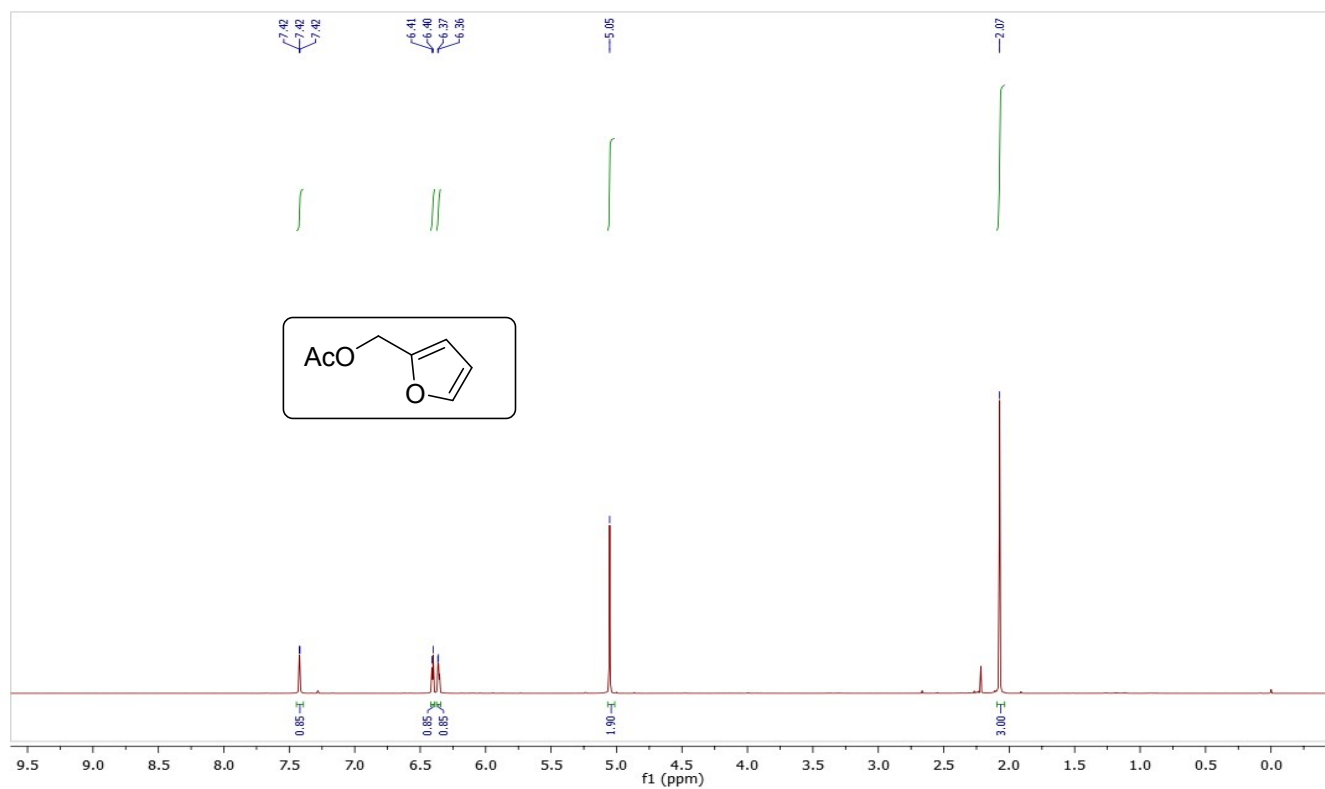
^1H NMR spectrum of compound **1o** in CDCl_3  ^1H NMR spectrum of compound **1p** in CDCl_3 

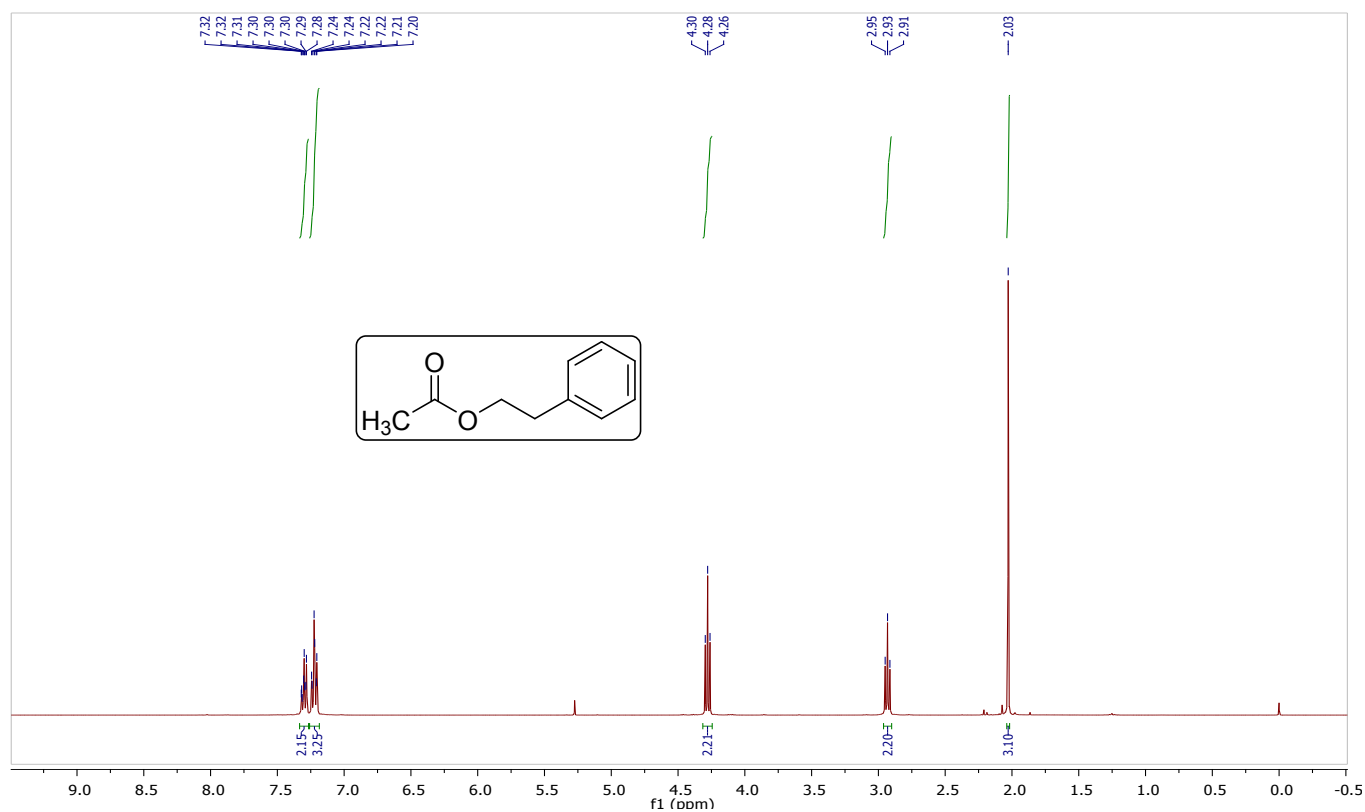
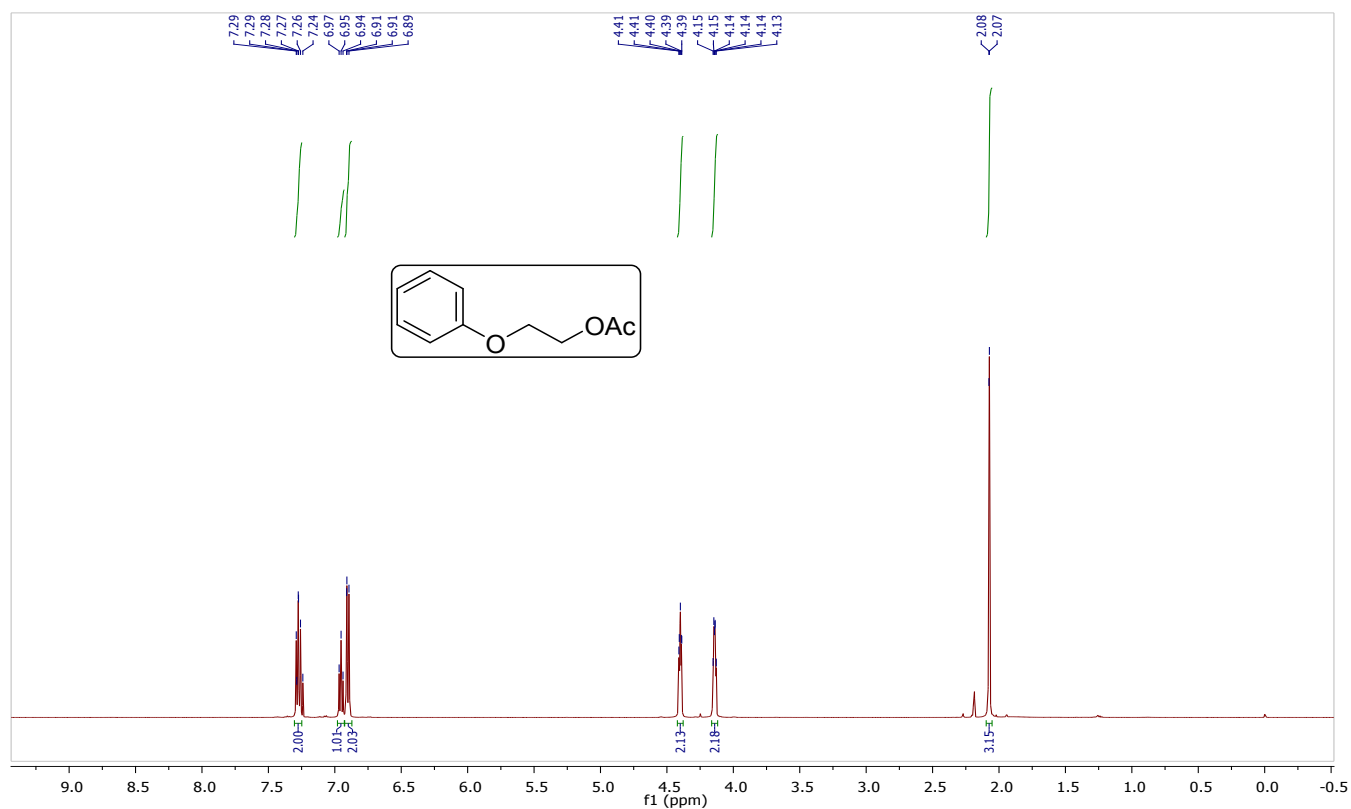
^1H NMR spectrum of compound **1q** in CDCl_3  ^1H NMR spectrum of compound **1r** in CDCl_3 

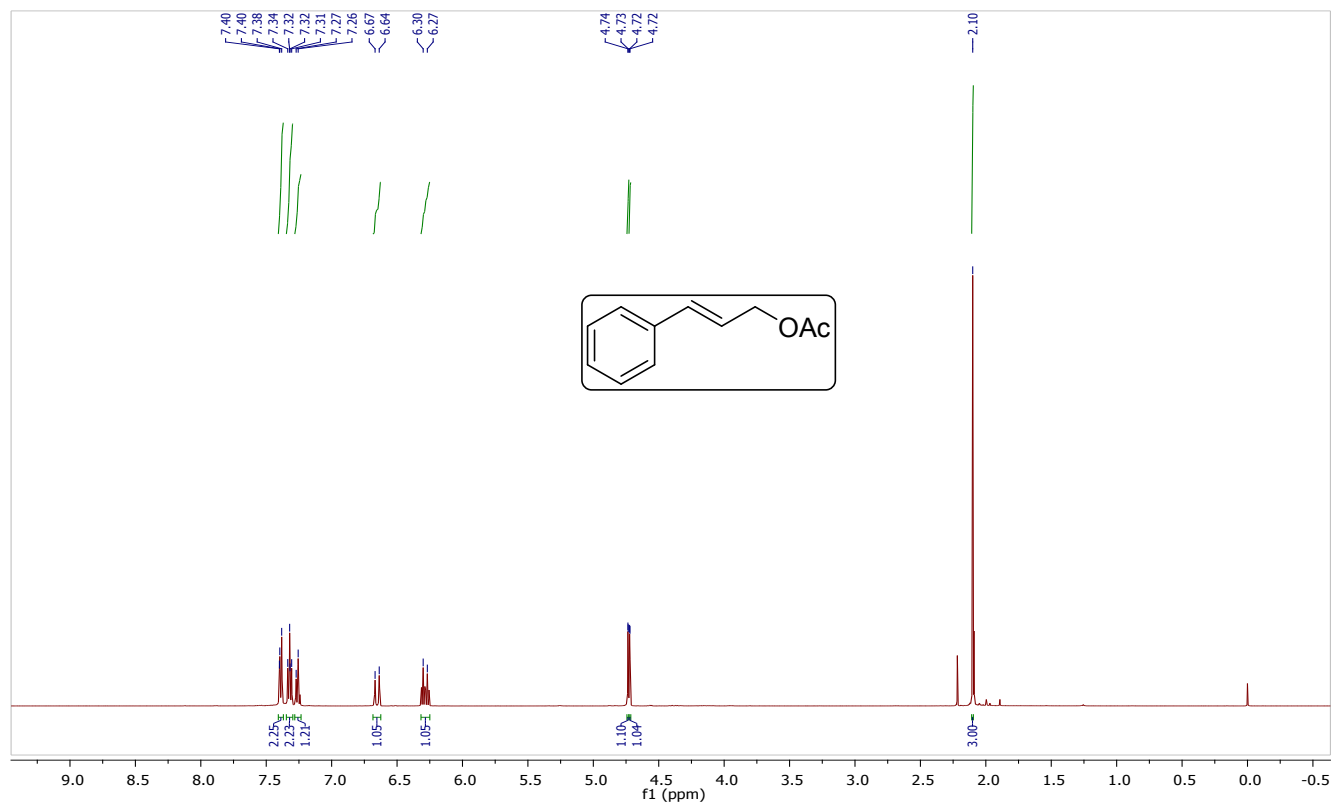
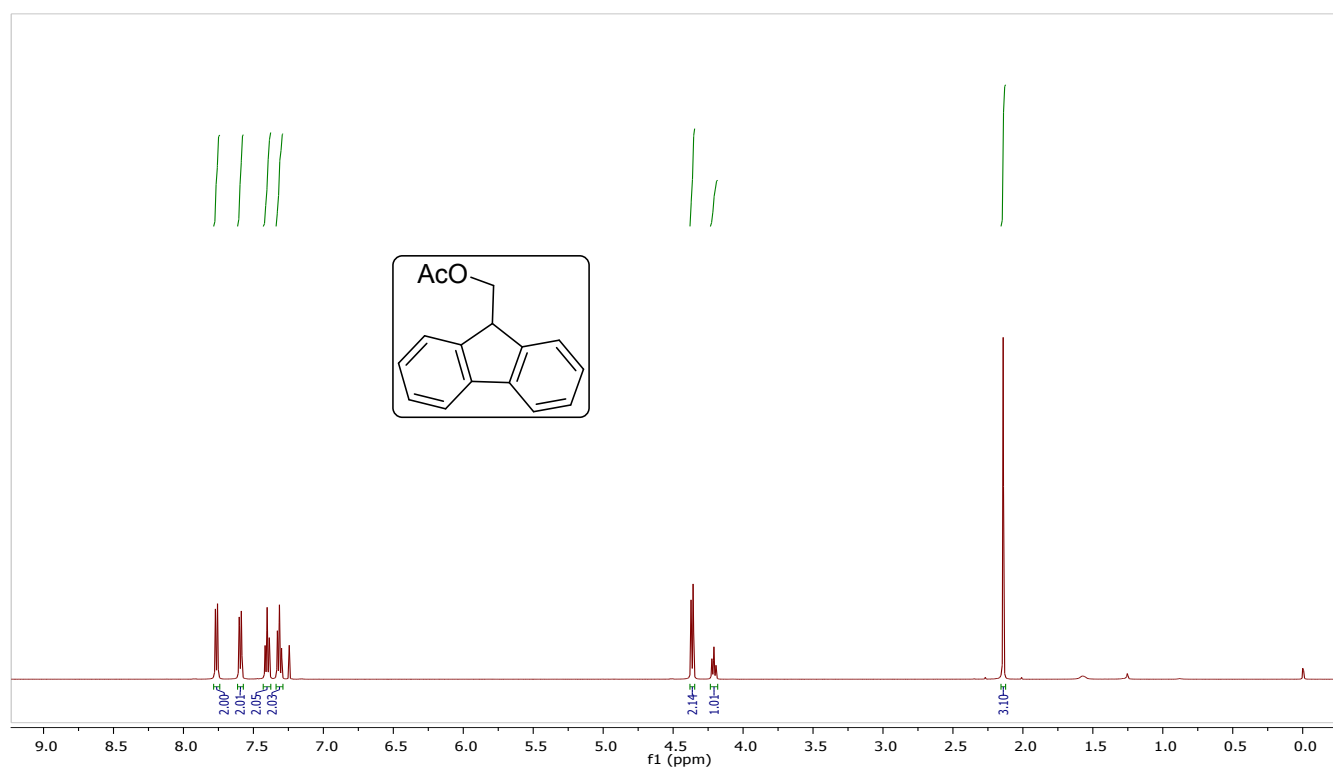
^1H NMR spectrum of compound **1s** in CDCl_3  ^1H NMR spectrum of compound **1t** in CDCl_3 

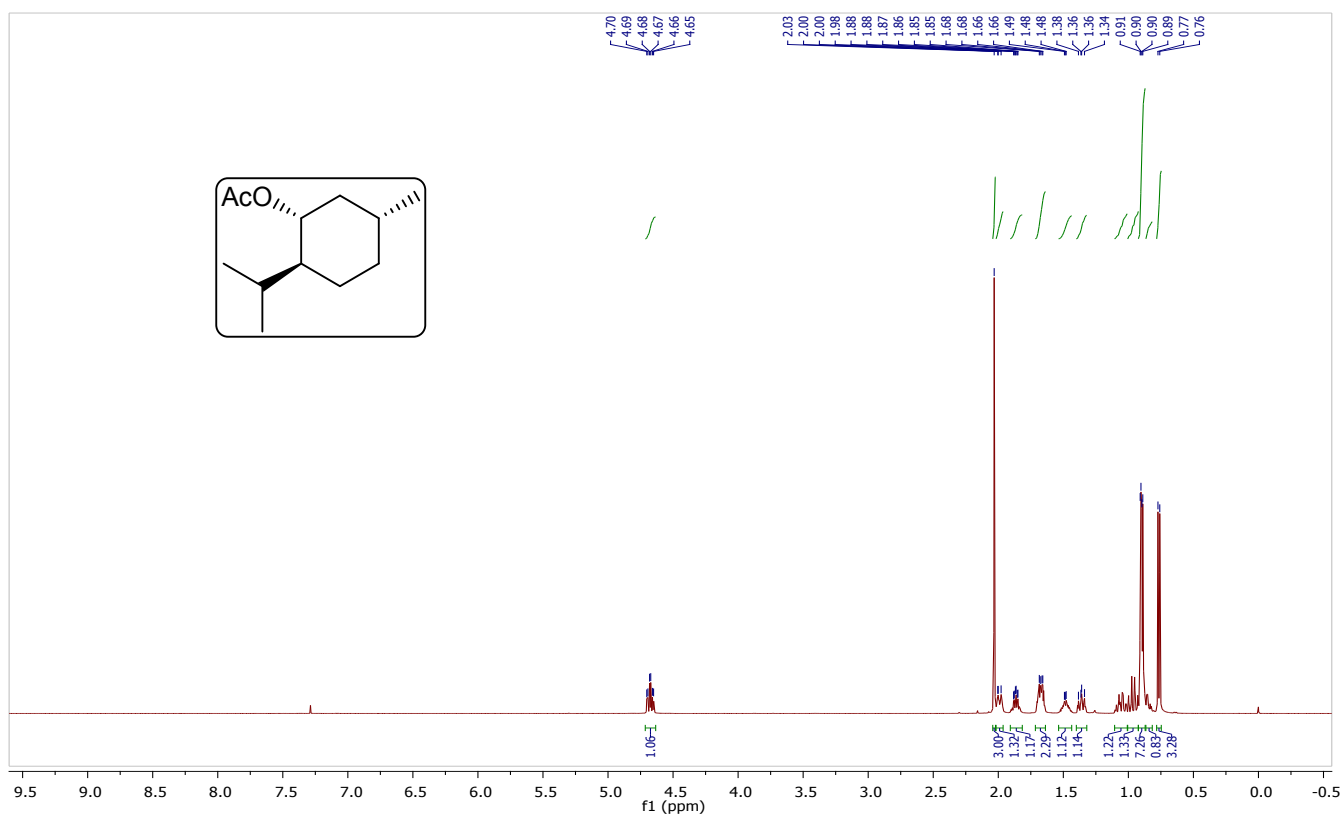
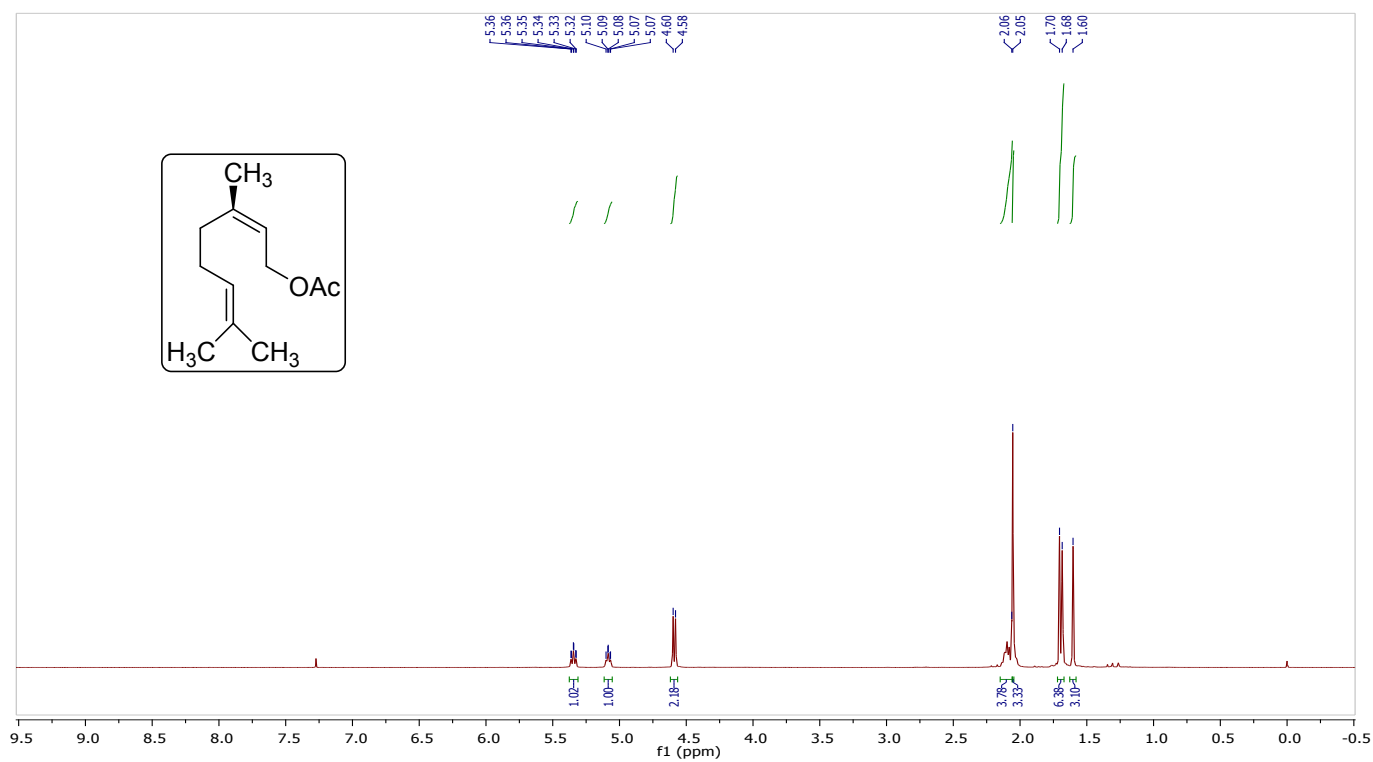
^1H NMR spectrum of compound **1u** in CDCl_3  ^1H NMR spectrum of compound **1v** in CDCl_3 

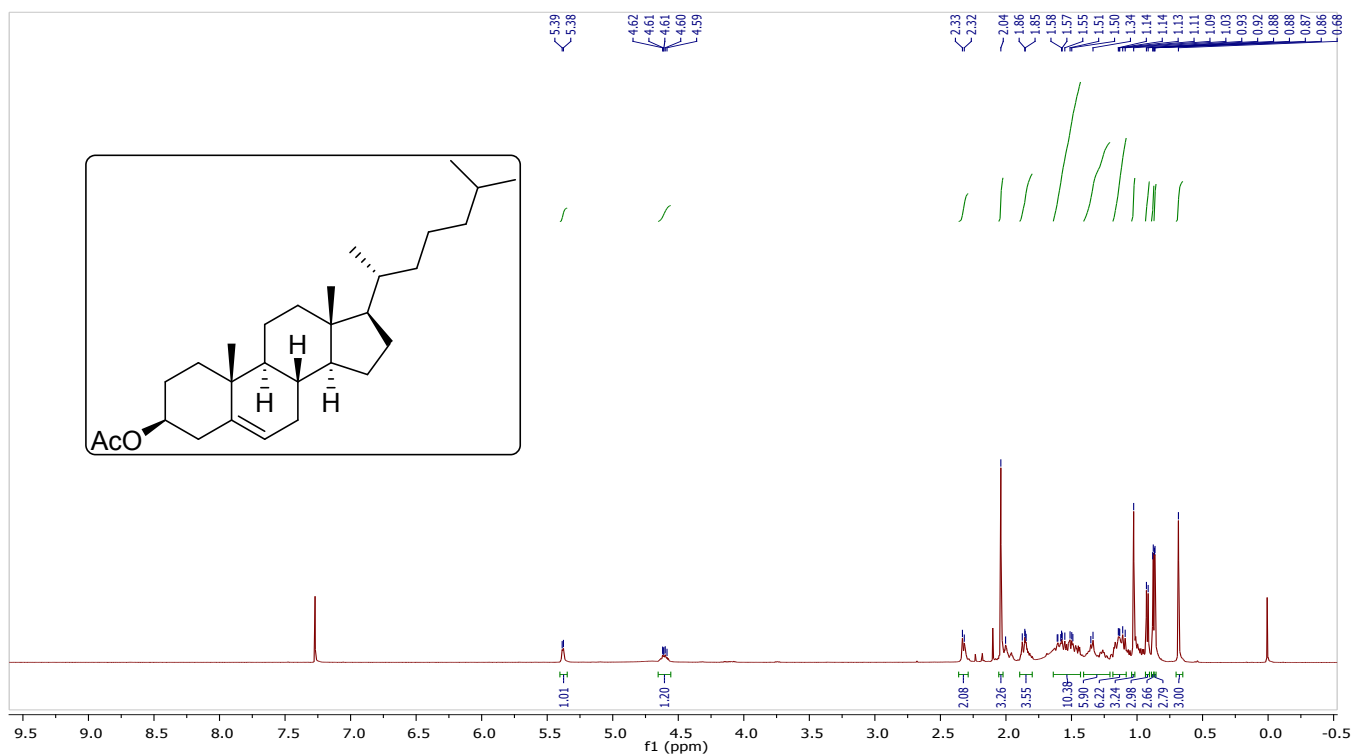
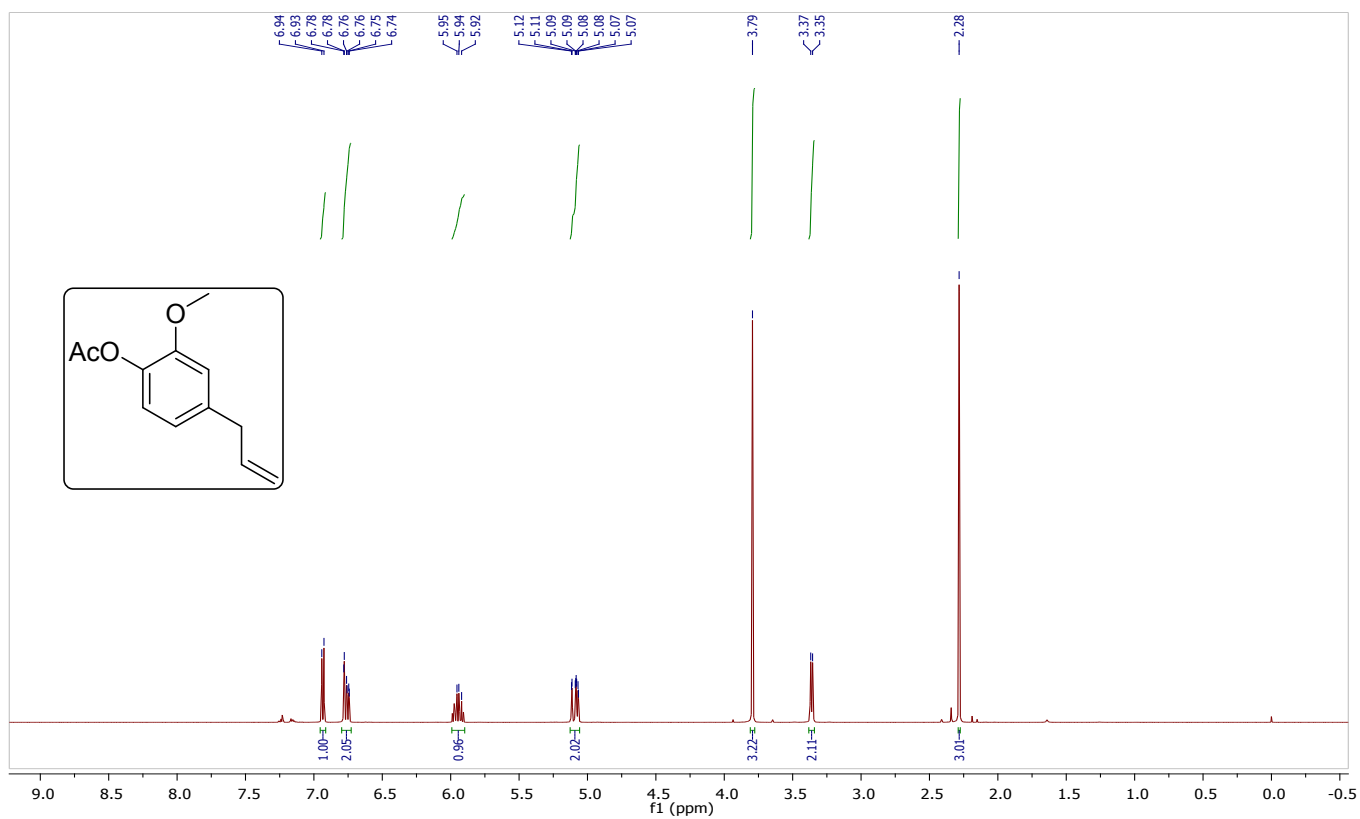
^1H NMR spectrum of compound **1w** in CDCl_3  ^1H NMR spectrum of compound **1x** in CDCl_3 

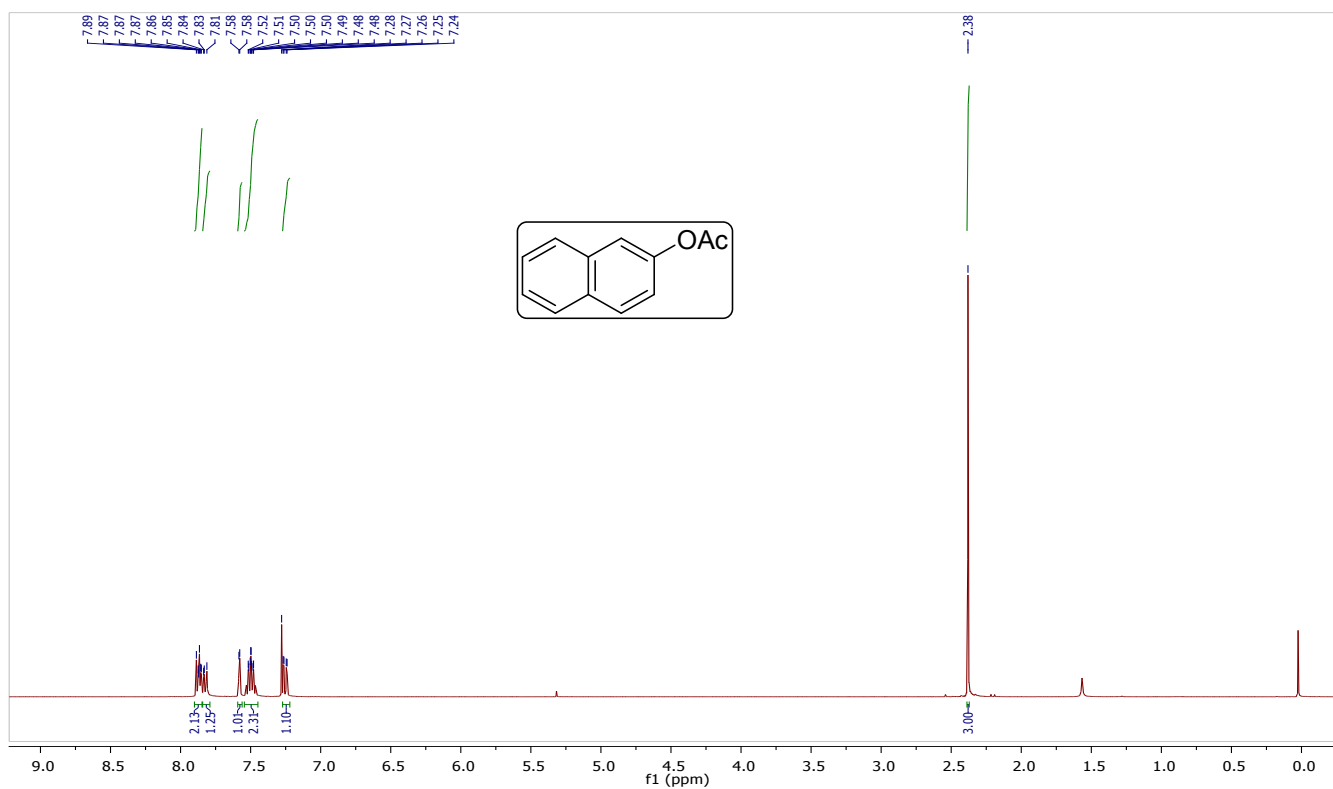
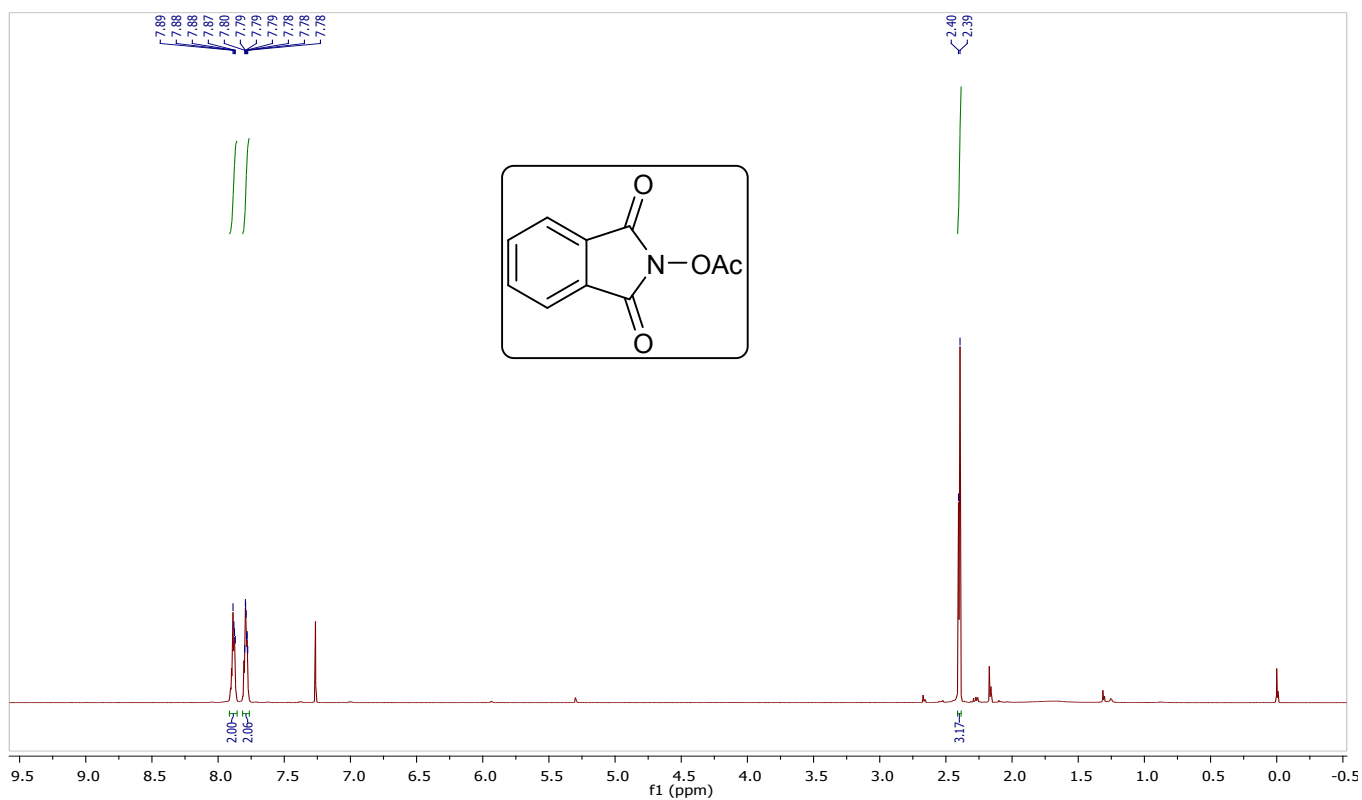
^1H NMR spectrum of compound **12** in CDCl_3  ^1H NMR spectrum of compound **2a** in CDCl_3 

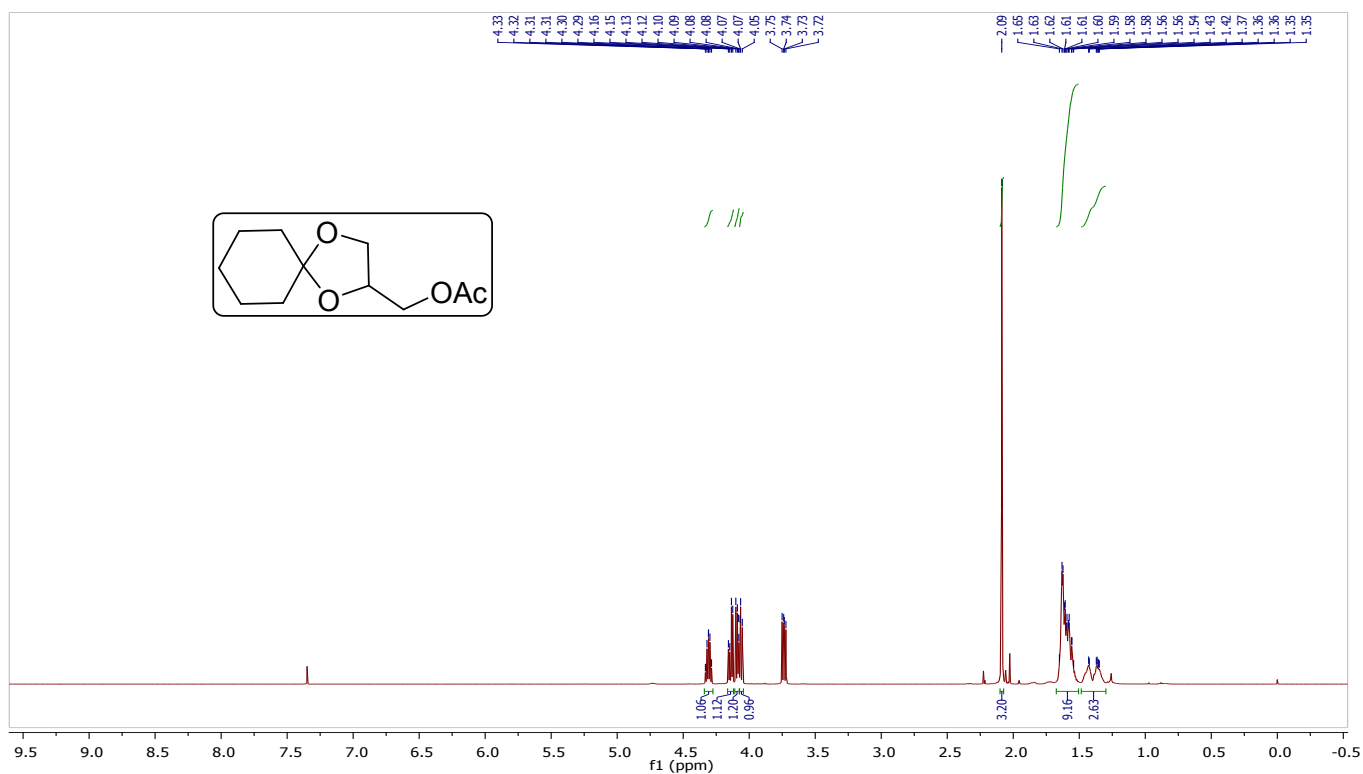
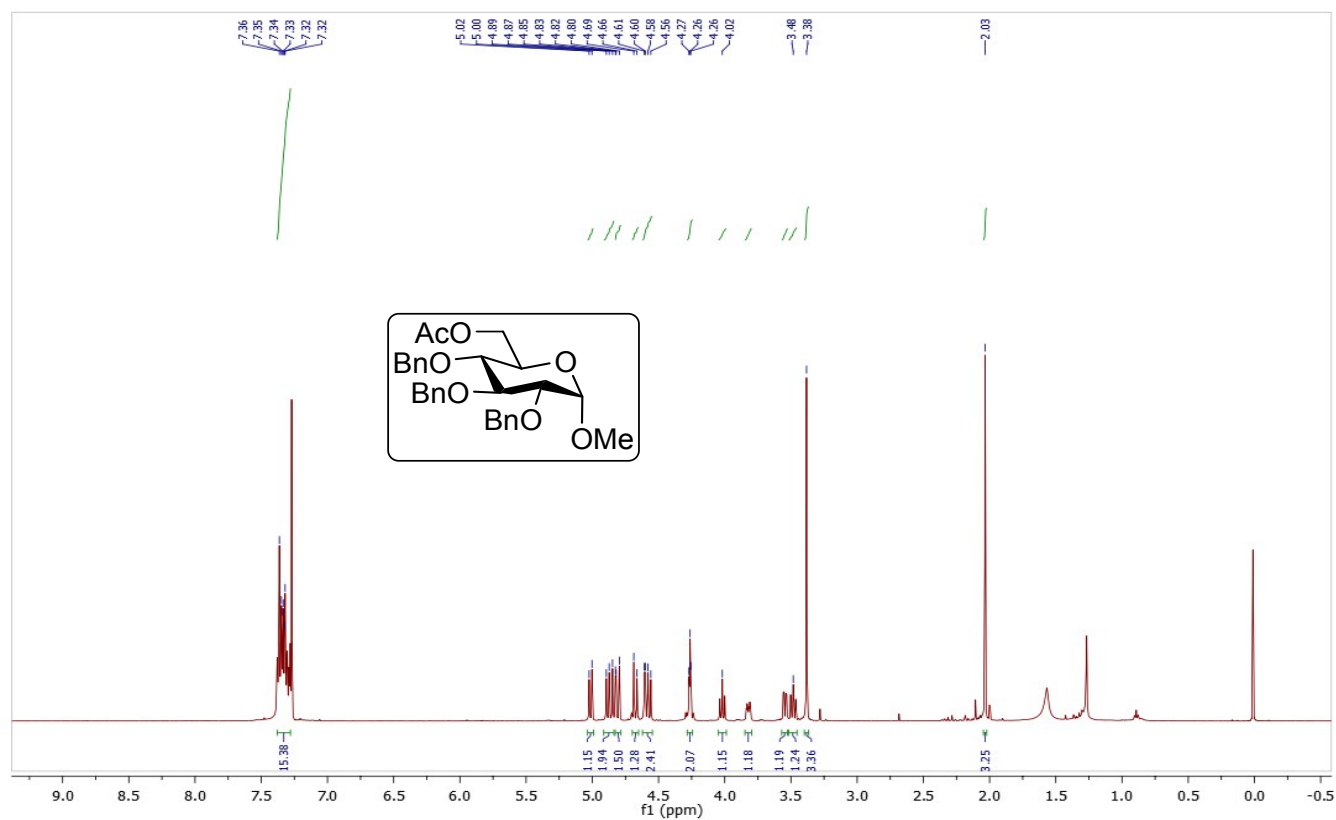
^1H NMR spectrum of compound **2b** in CDCl_3  ^1H NMR spectrum of compound **2c** in CDCl_3 

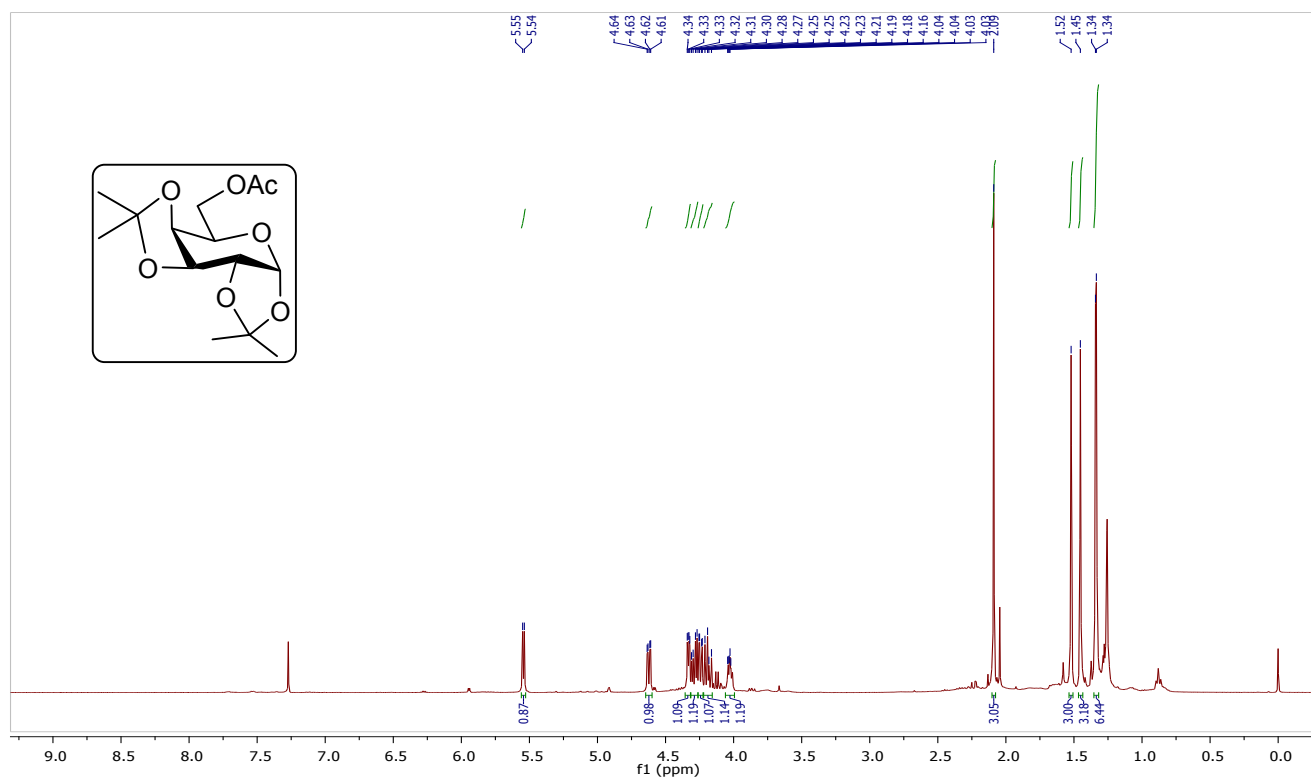
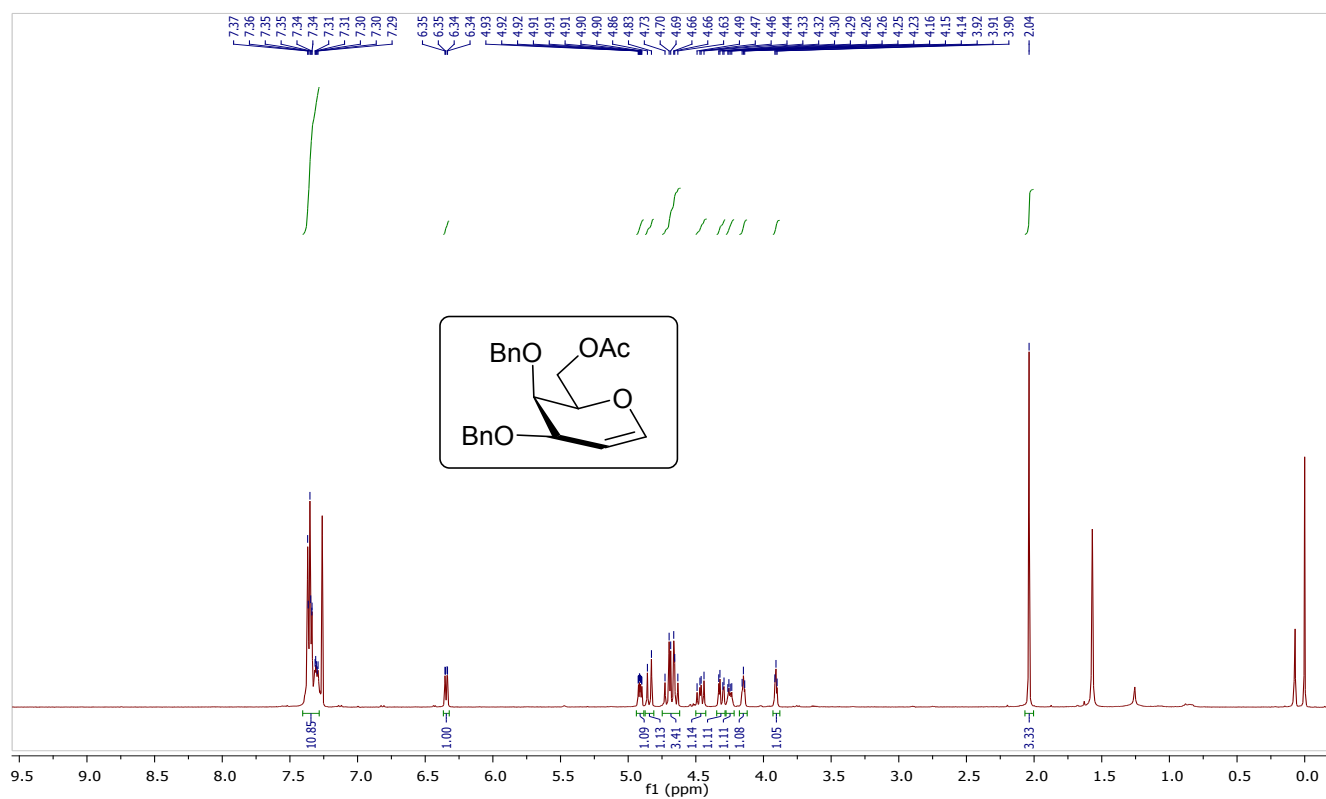
^1H NMR spectrum of compound **2d** in CDCl_3  ^1H NMR spectrum of compound **2e** in CDCl_3 

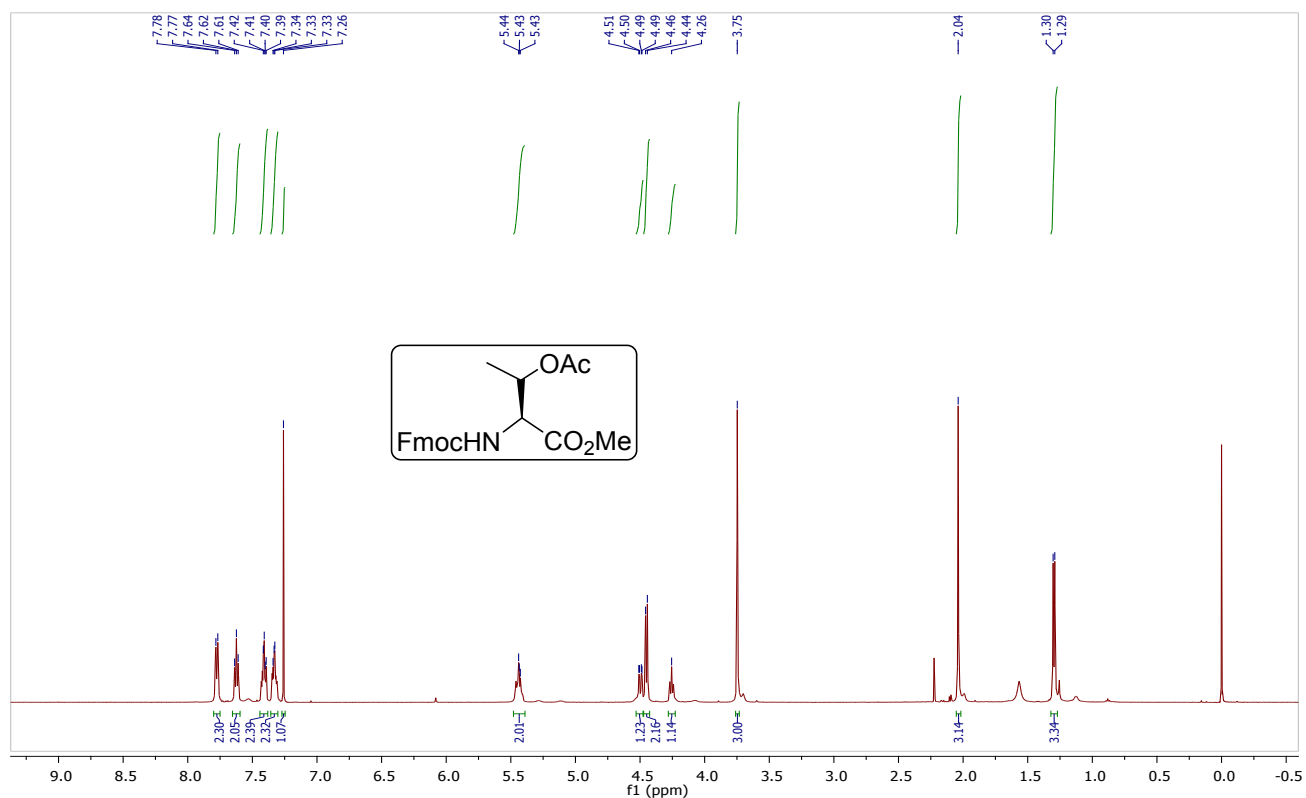
^1H NMR spectrum of compound **2f** in CDCl_3  ^1H NMR spectrum of compound **2g** in CDCl_3 

^1H NMR spectrum of compound **2h** in CDCl_3  ^1H NMR spectrum of compound **2i** in CDCl_3 

^1H NMR spectrum of compound **2j** in CDCl_3  ^1H NMR spectrum of compound **2k** in CDCl_3 

^1H NMR spectrum of compound **2l** in CDCl_3  ^1H NMR spectrum of compound **2m** in CDCl_3 

^1H NMR spectrum of compound **2n** in CDCl_3  ^1H NMR spectrum of compound **2o** in CDCl_3 

^1H NMR spectrum of compound **2p** in CDCl_3  ^1H NMR spectrum of compound **42** in CDCl_3 