Electronic Supplementary Material (ESI) for ChemComm.

In Situ Silane Activation Enables Catalytic Reduction of Carboxylic Acids

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Supporting Information

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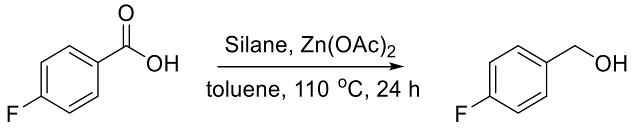
1 General Experimental

Reagents were purchased from commercial suppliers and used directly without further purification. Solvents were dried according to published methods and distilled before use;[1] except for toluene which was pre-dried over sodium wire and obtained from a solvent tower where degassed solvent was passed through two columns of activated alumina and 7-micron filter under a 4-bar pressure. Petroleum ether, boiling between 40-60 °C is referred to as petrol. All water was deionised before use, and unless specified, all experiments were carried out in oven dried glassware with an argon balloon atmosphere.

Analytical Thin Layer Chromatography (TLC) was performed on aluminium plates and visualized by ultraviolet (UV) irradiation (254 nm). Column chromatography was carried out using Fluorochem silica gel 60A (40-63 mesh). Melting points were calculated using a Stuart SMP3 and Fourier Transform Infrared Spectrometry (IR) was carried out using a Bruker Tensor 27 using an Attenuated Total Reflection (ATR) attachment. High Resolution Mass Spectrometry (HRMS) were measured on a Bruker microTOF II with Electron Spray Ionisation (ESI). Gas Chromatography Mass Spectrometry (GCMS) were measured on an Agilent 7890B Gas Chromatograph (GC) with a JEOL AccuTOF GCX Mass Spectrometer (MS) with Electron Ionisation (EI).

^{1}H NMR spectra were recorded on either a Bruker AV 400 in $CDCl_3$ or MeOD. ^{1}H NMR chemical shifts (δ) were reported in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz), with residual protic solvent as the internal reference ($CDCl_3$ $\delta = 7.26$ ppm, MeOD $\delta = 3.31$ ppm). Abbreviations used include s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad, app. – apparent. ^{13}C NMR were recorded on a 400 MHz spectrometer and chemical shifts (δ) were reported in ppm relative to the ^{13}C signals in the solvent (central peak of $CDCl_3$ $\delta = 77.16$ ppm). All ^{13}C NMR are reported as decoupled spectra.

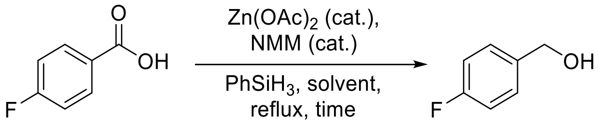
2 Reaction Optimisation



Entry	Silane	Silane equiv.	$Zn(OAc)_2$ mol%	Yield[a] / %
1	diethylsilane	5	10	1
2	diphenylsilane	5	10	6
3	phenylsilane	5	10	95
4	triethylsilane	5	10	0
5	triethoxysilane	5	10	22
6	triphenylsilane	5	10	0
7	PMHS	5	10	0
8	PMHS	10	10	0

[a] Yield determined by ^{19}F NMR analysis using α,α,α-trifluorotoluene as an internal standard.

To a solution of 4-fluorobenzoic acid (140 mg, 1.00 mmol) and zinc acetate (18.4 mg, 0.1 mmol) in toluene (1.2 mL) at reflux was added silane (see table) dropwise. The reaction mixture was stirred at reflux for 24 hours before NaOH (2 mL of a 2 M aqueous solution) was added to the reaction mixture dropwise and it was stirred for a further 30 mins. The pH was adjusted to pH 5 using HCl (1 M aqueous solution), and the product was extracted using EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. α,α,α-Trifluorotoluene (146 mg, 1.00 mmol) was added to the crude product and the yield was calculated using ^{19}F NMR.



Entry	**PhSiH$_3$ / equiv.**	**Solvent**	**Temperature / °C**	**Time / h**	**Zn(OAc)$_2$ / mol%**	**NMM / mol%**	**Yield[a] / %**
1	5	Toluene	110	24	0	0	0
2	5	Toluene	110	24	10	0	95
3	3	Toluene	110	24	10	0	82[b]
4	2	Toluene	110	24	10	0	90
5	1	Toluene	110	24	10	0	10
6	2	2-Me THF	80	24	10	0	91
7	**2**	**2-Me THF**	**80**	**16**	**10**	**0**	**53**
8	2	2-Me THF	80	6	10	0	2
9	2	2-Me THF	80	24	5	0	8
10	2	2-Me THF	80	24	0	20	0
11	**2**	**2-Me THF**	**80**	**16**	**10**	**20**	**99**
12	**2**	**2-Me THF**	**80**	**16**	**10**	**10**	**87**
13	2	2-Me THF	80	16	10	5	83
14	2	2-Me THF	80	16	5	10	49
15	2	2-Me THF	80	6	10	20	72

[a]Yield determined by ^{19}F NMR analysis using α,α,α-trifluorotoluene as an internal standard.

[b]Isolated yield

To a solution of 4-fluorobenzoic acid (140 mg, 1.00 mmol) and zinc acetate (mol% as table) in solvent (see table, 1.2 mL) at reflux was added phenylsilane (equiv. as table) and *N*-methyl morpholine (mol% as table) dropwise. The reaction mixture was stirred at reflux for time (see table) before NaOH (2 mL of a 2 M aqueous solution) was added to the reaction mixture dropwise and it was stirred for a further

30 mins. The pH was adjusted to pH 5 using HCl (1 M aqueous solution), and the product was extracted using EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. α,α,α-Trifluorotoluene (146 mg, 1.00 mmol) was added to the crude product and the yield was calculated using ^{19}F NMR.

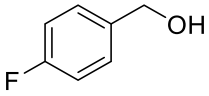
3 Experimental Procedures and Characterisation of Compounds

3.1 General Procedure 1 – Reduction of Carboxylic Acids

To a solution of carboxylic acid (1.00 mmol) and zinc acetate (18.3 mg, 0.1 mmol) in 2-Me THF (1.2 mL) at reflux was added phenylsilane (247 µL, 2.00 mmol) dropwise, followed by *N*-Me morpholine (11.0 µL, 0.1 mmol). The reaction mixture was stirred at reflux for 16 h, after which it was allowed to cool. NaOH (2 mL of a 2 M aqueous solution) was added to the reaction mixture dropwise and it was stirred for a further 30 mins. The pH was adjusted to pH 5 using HCl (1 M aqueous solution), and the product was extracted using EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography to give the desired product.

3.2 Synthesis of Alcohols

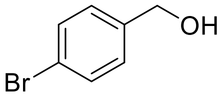
(4-Fluorophenyl)methanol **1**



Prepared according to general procedure 1, using 4-fluorobenzoic acid (140 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 2:3, $R_f = 0.24$) to afford the desired product as a colourless oil (114 mg, 0.900 mmol, 90%).

IR (ATR) ν_{max}/cm^{-1} 3311, 1604, 1509, 1429, 1221, 1131; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.07 – 7.00 (m, 2H), 4.63 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.6 Hz), 136.7 (d, *J* = 3.5 Hz), 128.9 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.6 Hz), 64.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.91; GCMS [EI (M + H^+)] m/z calculated for C_7H_7OF 126.0475, found 126.0474. The data matches those found in the literature.[2]

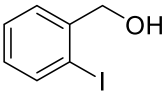
(4-Bromophenyl)methanol **2**



Prepared according to general procedure 1, using 4-bromobenzoic acid (201 mg, 1.00 mmol), and the crude product was purified by column chromatography (pure petrol to EtOAc / petrol 1:1 (EtOAc / petrol 2:3 R_f = 0.23)) to afford the desired product as a colourless solid (173 mg, 0.930 mmol, 93%), mp 76-77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.57 (s, 2H) 2.40 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 131.5, 128.5, 121.3, 64.3. The data matches those found in the literature.[3]

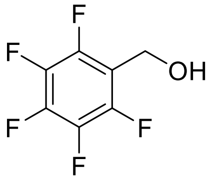
(2-Iodophenyl)methanol **3**



Prepared according to general procedure 1, using 2-iodobenzoic acid (248 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:4, R_f = 0.14) to afford the desired product as a colourless solid (172 mg, 0.730 mmol, 73%), mp 90 - 91 °C.

IR (ATR) ν_{max}/cm^{-1} 3229, 2395, 1445, 1433, 1362, 1196, 1051, 1034, 1010; **^{1}H NMR** (400 MHz, MeOD) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.99 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.59 (s, 2H); **^{13}C NMR** (101 MHz, MeOD) δ 144.3, 140.1, 129.8, 129.3, 128.8, 97.5, 69.3; **HRMS** [ESI (M + Na$^+$)] m/z calculated for C_7H_7INaO 256.9434, found 256.9429. The data matches those found in the literature.[4]

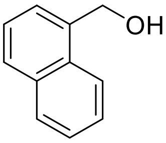
(Perfluorophenyl)methanol **4**



Prepared according to general procedure 1, using pentafluorobenzoic acid (212 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (EtOAc / petrol 1:4) to afford the desired product as a colourless oil (88.0 mg, 0.440 mmol, 44%).

IR (ATR) ν_{max}/cm^{-1} 3317, 1522, 1505, 1430, 1306, 1121, 1062, 1022; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 3.12 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.7, 144.2, 134.2, 128.0, 52.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.73 (ddd, *J* = 22.5, 9.0, 1.9 Hz), -154.42 (app. t, *J* = 20.5 Hz), -161.75 – -162.49 (m); **GCMS** [EI] m/z calculated for $C_7H_3OF_5$ 198.0099, found 198.0102. The data matches those found in the literature.[5]

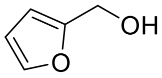
Naphthalen-1-ylmethanol **5**



Prepared according to general procedure 1, using 2-naphthoic acid (172 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:9, R_f = 0.25) to afford the desired product as a colourless solid (137 mg, 0.870 mmol, 87%), mp 61-63 °C.

IR (ATR) ν_{max}/cm^{-1} 3315, 3047, 2876, 1510, 1392, 1329, 1141, 1067; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (m, 1H), 7.94 – 7.86 (m, 1H), 7.82 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.47 – 7.40 (m, 2H), 5.01 (s, 2H), 2.91 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 133.7, 131.2, 128.6, 128.4, 126.2, 125.8, 125.4, 125.2, 123.6, 63.2; **HRMS** [ESI (M + H$^+$)] m/z calculated for $C_{11}H_{10}O$ 158.0726, found 158.0732. The data matches those found in the literature.[2]

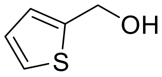
Furan-2-ylmethanol **6**



Prepared according to general procedure 1, using furan-2-carboxylic acid (112 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (pure petrol to EtOAc / petrol 2:3, $R_f = 0.29$) to afford the desired product as a colourless oil (83.0 mg, 0.850 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 1H), 6.35 – 6.29 (m, 1H), 6.29 – 6.24 (m, 1H), 4.56 (s, 2H), 2.52 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 142.4, 110.3, 107.6, 57.2. The data matches those found in the literature.[6]

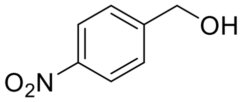
Thiophen-2-ylmethanol **7**



Prepared according to general procedure 1, using 2-thiophene carboxylic acid (128 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:4, $R_f = 0.19$) to afford the desired product as a colourless oil (82.0 mg, 0.720 mmol, 72%).

IR (ATR) ν_{max}/cm^{-1} 3288, 2870, 1432, 1374, 1210, 1153, 1133, 1077, 1002; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.04 – 6.96 (m, 2H), 4.78 (s, 2H), 2.60 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 126.9, 125.6, 125.5, 59.9; GCMS [EI] m/z calculated for $C_7H_{14}O$ 114.1039, found 114.1041. The data matches those found in the literature.[7]

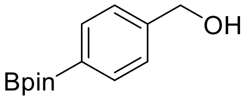
(4-Nitrophenyl)methanol **8**



Prepared according to general procedure 1, using 4-nitrobenzoic acid (167 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (EtOAc / petrol 2:3, $R_f = 0.17$) to afford the desired product as a pale yellow solid (105 mg, 0.690 mmol, 69%), mp 91-93 °C.

IR (ATR) ν_{max}/cm^{-1} 3507, 1600, 1504, 1457, 1333, 1196, 1055; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.15 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 4.83 (s, 1H), 1.98 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 147.4, 127.1, 123.9, 64.2; **HRMS** [ESI (M + H$^+$)] m/z calculated for $C_7H_8NO_3$ 154.0499, found 154.0501 (σ = 0.0174). The data matches those found in the literature.[8]

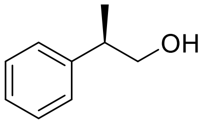
(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **9**



Prepared according to general procedure 1, using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (248 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (EtOAc / petrol 1:4) to afford the desired product as a colourless oil (208 mg, 0.640 mmol, 64%).

IR (ATR) ν_{max}/cm^{-1}3389, 2977, 2927, 1613, 1517, 1398, 1356, 1141, 1085, 1017; **^{1}H NMR** (400 MHz, $CDCl_3$) 7.80 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.69 (s, 2H), 1.35 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ144.1, 135.2, 126.2, 83.9, 65.3, 25.0; **^{11}B NMR** (128 MHz, CDCl3) δ 30.88. Quaternary carbon next to B is not observed; **HRMS** [ESI (M + Na$^+$)] m/z calculated for $C_{13}H_{19}BNaO_3$ 252.1766, found 252.1762. The data matches those found in the literature.[9]

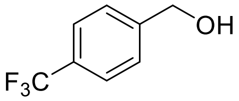
(*R*)-2-Phenylpropan-1-ol **10**



Prepared according to general procedure 1, using (*R*)-(-)-2-phenylpropionic acid (150 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:4, R_f = 0.17) to afford the desired product as a colourless oil (108 mg, 0.790 mmol, 79%).

IR (ATR) ν_{max}/cm^{-1} 3342, 2961, 2927, 2874, 1493, 1383, 1130; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.28 – 7.23 (m, 3H), 3.69 (d, *J* = 6.9 Hz, 2H), 2.95 (h, *J* = 6.9 Hz, 1H), 1.82 – 1.76 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 128.7, 127.6, 126.7, 68.7, 42.5, 17.7. Enantiomeric excess was determined by chiral HPLC with a AMY-C column (CO_2 / MeOH 85:15), 4.0 mL/min, 210-400 nm, 125 BarG, 40 °C, t_r (minor) = 1.72 min, t_r (major) = 1.96 min, 97% *e.e.*. The data matches those found in the literature.[10]

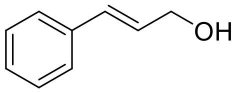
(4-(Trifluoromethyl)phenyl)methanol **11**



Prepared according to general procedure 1, using 4-(trifluoromethyl)benzoic acid (190 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 3:7, R_f = 0.12) to afford the desired product as a colourless oil (115 mg, 0.650 mmol, 65%).

IR (ATR) ν_{max}/cm^{-1} 3298, 1324, 1108, 1064, 1015; **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 2.86 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 129.8 (q, *J* = 32.3 Hz), 126.9, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 64.3; **^{19}F NMR** (376 MHz, CDCl3) δ -62.46; **GCMS** [EI (M + H$^+$)] m/z calculated for $C_8H_7OF_3$ 176.0444, found 176.0449. The data matches those found in the literature.[11]

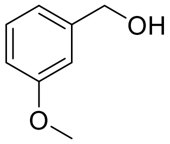
(*E*)-3-Phenylprop-2-en-1-ol **12**



Prepared according to general procedure 1, using *E*-cinnamic acid (148 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (EtOAc / petrol 1:4, R_f = 0.15) to afford the desired product as a colourless oil (117 mg, 0.870 mmol, 87%).

IR (ATR) ν_{max}/cm^{-1} 3319, 2916, 2849, 1493, 1449, 1265, 1131, 1090, 1069; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.25 (m, 5H), 6.65 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.39 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.34 (dd, *J* = 5.6, 1.6 Hz, 2H), 3.11 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 130.8, 128.6, 128.5, 127.6, 126.5, 63.4; GCMS [EI] m/z calculated for $C_9H_{10}O$ 134.0726, found 134.0729. The data matches those found in the literature.[12]

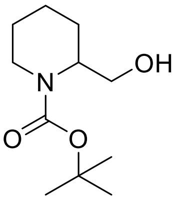
(3-Methoxyphenyl)methanol **13**



Prepared according to general procedure 1, using 3-methoxybenzoic acid (152 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:9, R_f = 0.23) to afford the desired product as a colourless oil (129 mg, 0.930 mmol, 93%).

IR (ATR) ν_{max}/cm^{-1} 3317, 2937, 2836, 1596, 1488, 1454, 1434, 1284, 1151, 1036; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 6.94 – 6.89 (m, 2H), 6.84 – 6.80 (m, 1H), 4.62 (s, 2H), 3.79 (s, 3H), 2.23 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 142.7, 129.7, 119.2, 113.3, 112.3, 65.2, 55.3; **HRMS** [ESI (M + H$^+$)] m/z calculated for $C_8H_{10}NaO_2$ 161.0573, found 161.0565 (σ = 0.0176). The data matches those found in the literature.[13]

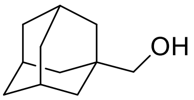
tert-Butyl 2-(hydroxymethyl)piperidine-1-carboxylate **14**



Prepared according to general procedure 1, using *N*-boc-2-piperidine carboxylic acid (229 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 3:17) to afford the desired product as a colourless solid (142 mg, 0.660 mmol, 66%).

IR (ATR) ν_{max}/cm^{-1} 2932, 1661, 1447, 1312, 1247; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.26 – 4.32 (m, 1H), 3.94 (d, *J* = 13.6 Hz, 1H), 3.78 – 3.85 (m, 1H), 3.57 – 3.63 (m, 1H), 2.80 – 2.93 (app. t, *J* = 12.6 Hz, 1H), 2.04 (br. s, 1H, **OH**), 1.63 – 1.69 (m, 1H), 1.56 – 1.63 (m, 3H), 1.46 (s, 9H), 1.39 – 1.45 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.5, 80.0, 62.0, 52.7, 40.1, 28.6, 25.5, 25.4, 19.8; **HRMS** [ESI (M + H$^+$)] m/z calculated for $C_{11}H_{22}NO_3$ 216.1594, found 216.1583. The data matches those found in the literature..[14]

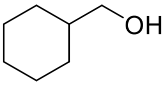
1-Adamantanemethanol **15**



Prepared according to general procedure 1, using 1-adamantane carboxylic acid (180 mg, 1.00 mmol) in toluene, and the crude product was purified by column chromatography (EtOAc / petrol 1:4, R_f = 0.17) to afford the desired product as a colourless solid (133 mg, 0.800 mmol, 80%), mp 113-115 °C.

IR (ATR) ν_{max}/cm^{-1} 2895, 2844, 2404, 1430, 1132, 1040; **^{1}H NMR** (400 MHz, MeOD) δ 3.10 (s, 2H), 1.97 (p, *J* = 2.9 Hz, 3H), 1.82 – 1.64 (m, 6H), 1.53 (d, *J* = 3.1 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 73.9, 40.2, 38.3, 35.5, 29.7; **HRMS** [ESI (M + H$^+$)] m/z calculated for $C_{11}H_{18}O$ 166.1352, found 166.1360. The data matches those found in the literature.[15]

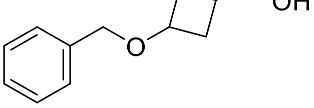
Cyclohexylmethanol **16**



Prepared according to general procedure 1, using cyclohexane carboxylic acid (128 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:4, R_f = 0.23) to afford the desired product as a colourless oil (90.0 mg, 0.790 mmol, 79%).

IR (ATR) ν_{max}/cm^{-1} 3313, 2919, 2850, 1448, 1133, 1090, 1023; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.42 (d, *J* = 6.3 Hz, 2H), 1.82 – 1.61 (m, 4H), 1.53 – 1.40 (m, 1H), 1.27 – 1.18 (m, 2H), 1.18 – 1.12 (m, 1H), 0.98 – 0.86 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 68.9, 40.6, 29.7, 26.7, 26.0. The data matches those found in the literature.[7]

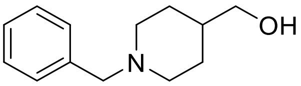
(3-(Benzyloxy)cyclobutyl)methanol **17**



Prepared according to general procedure 1, using 3-(benzyloxy)cyclobutane-1-carboxylic acid as a mixture of diastereoisomers (206 mg, 1.00 mmol) and the crude product was purified by column chromatography (pure petrol to EtOAc / petrol 1:1, R_f = 0.31) to afford the desired product as a colourless oil (144 mg, 0.750 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 - 7.32 (m, 5 H), 4.38 (d, *J* = 5.38 Hz, 2 H), 3.86 - 4.11 (m, 1 H) 3.51 (d, *J* = 6.85 Hz, 2 H) 2.60 (s, 1 H) 2.26 - 2.37 (m, 1 H) 1.94 - 2.16 (m, 3 H) 1.65 - 1.73 (m, 1 H); **^{13}C NMR** (101 MHz, $CDCl_3$) mixture of diastereomers: δ 138.1 (major), 138.0 (minor), 128.2, 127.7 (minor), 127.7 (major), 127.4 (minor), 127.4 (major), 71.7, 69.8 (major), 69.3 (minor), 66.7 (minor), 66.2 (major), 32.8 (minor), 31.5 (major), 29.5 (major), 28.0 (minor). The data matches those found in the literature.[16]

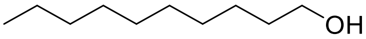
(1-Benzylpiperidin-4-yl)methanol **18**



Prepared according to general procedure 1, using 1-benzylpiperidine-4-carboxylic acid (219 mg, 1.0 mmol) in toluene, and the crude product was purified by column chromatography (KPNH column) (pure petrol to EtOAc / petrol 3:2 (EtOAc / petrol 1:1, R_f = 0.16)) to give the desired product as a colourless oil (161 mg, 0.784 mmol, 78 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.34 (m, 4 H), 7.24 - 7.26 (m, 1 H), 3.51 (s, 2 H), 3.46 (d, *J* = 6.36 Hz, 2H), 2.89 - 2.94 (m, 2 H), 2.49 - 2.58 (m, 1 H), 1.97 (ddd, *J* = 11.7, 11.7, 2.5 Hz, 2 H), 1.68 - 1.74 (m, 2 H), 1.44 - 1.52 (m, 1 H), 1.28 (qd, *J* = 11.5, 3.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 129.2, 128.1, 126.9, 67.6, 63.4, 53.3, 38.4, 28.7; **HRMS** [ESI (M + H^+)] m/z calculated for $C_{13}H_{19}NO$ 206.1539, found 206.1539. The data matches those found in the literature. [17]

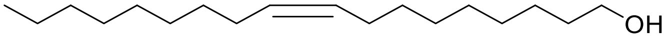
Decan-1-ol **20**



Prepared according to general procedure 1, using decanoic acid (172 mg, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:4, $R_f = 0.21$) to afford the desired product as a colourless oil (126 mg, 0.800 mmol, 80%).

IR (ATR) ν_{max}/cm^{-1} 2922, 2853, 1464, 1430, 1130, 1055; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.60 (t, *J* = 6.7 Hz, 2H), 2.00 (s, 1H), 1.59 – 1.47 (m, 2H), 1.34 – 1.19 (m, 14H), 0.92 – 0.81 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 63.0, 32.9, 32.0, 29.7, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2. The data matches those found in the literature.[15]

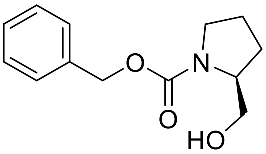
(*Z*)-Octadec-9-en-1-ol **21**



Prepared according to general procedure 1, using oleic acid (317 µL, 1.00 mmol), and the crude product was purified by column chromatography (EtOAc / petrol 1:9) to afford the desired product as a colourless oil (206 mg, 0.770 mmol, 77%).

IR (ATR) ν_{max}/cm^{-1} 3319, 2922, 2853, 1462, 1133, 1056; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.35 – 5.31 (m, 2H), 3.60 (t, *J* = 6.7 Hz, 2H), 1.99 (m, 4H), 1.54 (p, *J* = 6.8 Hz, 2H), 1.37 – 1.19 (m, 22H), 0.90 – 0.83 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.0, 129.9, 63.0, 32.9, 32.0, 29.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 27.3, 27.3, 25.9, 22.8, 14.2. The data matches those found in the literature.[18]

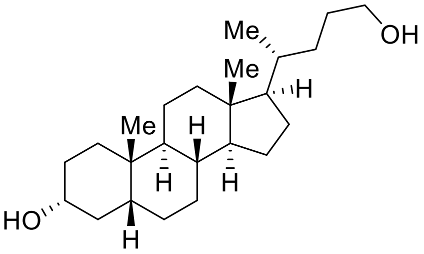
Benzyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate **22**



Prepared according to general procedure 1, using ((benzyloxy)carbonyl)-L-proline (249 mg, 1.00 mmol) and the crude product was purified by column chromatography (pure petrol to EtOAc / petrol 2:3, $R_f = 0.21$) to afford the desired product as a colourless oil (173 mg, 0.740 mmol, 74 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.38 (m, 5 H), 5.11 – 5.18 (m, 2 H), 4.31 – 4.40 (m, 1 H), 3.90 – 4.05 (m, 1 H), 3.59 – 3.72 (m, 2 H), 3.51 – 3.58 (m, 1 H), 3.36 – 3.43 (m, 1H), 1.98 – 2.07 (m, 1H), 1.76 – 1.91 (m, 2H), 1.55 – 1.70 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4, 136.6, 128.7, 128.2, 128.1, 67.4, 67.3, 60.9, 47.5, 28.8, 24.2, 23.0. Enantiomeric excess was determined by chiral HPLC with a Chiralpak IG5 column (MeOH), 1.0 mL/min, 215 nm, 25 °C, t_r (minor) = 4.75 min, t_r (major) = 5.32 min, >99% *e.e.*. The data matches those found in the literature.[19]

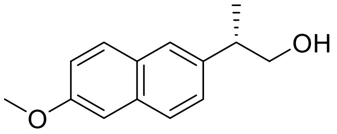
(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-hydroxypentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol **23**



(4*R*)-4-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]-phenanthren-17-yl)pentanoic acid (337 mg, 1.00 mmol) and zinc acetate (18.3 mg, 0.1 mmol) were dissolved in 2-Me THF (1.2 mL) and heated to reflux. Phenylsilane (370 µL, 3.00 mmol) was added to the reaction mixture dropwise, followed by *N*-Me morpholine (11.0 µL, 0.1 mmol). The reaction mixture was stirred at reflux for 16 h, after which it was allowed to cool. Aqueous 2 M NaOH (2 mL) was added to the reaction mixture dropwise and it was stirred for a further 30 mins. Aqueous 1 M HCl was then added to the reaction mixture until pH 5 was reached, and the product was extracted using EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (pure petrol to EtOAc / petrol 3:2) to afford the desired product as a colourless solid (317 mg, 0.87 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 - 3.58 (m, 3 H), 1.91 - 1.72 (m, 4 H), 1.69 - 1.51 (m, 6 H), 1.46 - 1.36 (m, 8 H), 1.29 - 1.21 (m, 4 H), 1.55 - 0.99 (m, 7 H), 0.94 - 0.91 (m, 6 H), 0.65 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 71.9, 63.6, 56.5, 56.2, 42.7, 42.1, 40.5, 40.2, 36.5, 35.9, 35.6, 35.4, 34.6, 31.8, 30.6, 29.5, 28.3, 27.2, 26.4, 24.2, 23.4, 20.9, 18.6, 12.1. The data matches those found in the literature.[20]

(*S*)-2-(6-Methoxynaphthalen-2-yl)propan-1-ol **23**

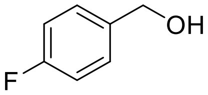


Prepared according to general procedure 1, using (*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (230 mg, 1.00 mmol), and the crude product was purified by column chromatography (pure petrol to EtOAc / petrol 2:3, $R_f = 0.22$) to afford the desired product as a colourless solid (188 mg, 0.870 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.73 (dd, *J* = 8.56, 2.69 Hz, 2 H), 7.62 - 7.64 (m, 1 H), 7.36 (dd, *J* = 8.56, 1.71 Hz, 1 H), 7.15 - 7.22 (m, 2 H), 3.93 (s, 3 H), 3.71 - 3.80 (m, 2 H), 3.03 - 3.12 (m, 1 H), 1.38 (d, *J* = 6.85 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4, 138.7, 133.5, 129.1, 129.1, 127.2, 126.3, 125.9, 118.9, 105.6, 68.6, 55.3, 42.4, 17.6. Enantiomeric excess was determined by chiral HPLC with an (*R*, *R*) Whelk-O1 column (Heptane / EtOH 60:40), 1.0 mL/min, 230 nm, 25 °C, t_r (minor) = 8.01 min, t_r (major) = 7.15 min, 97% *e.e.*. The data matches those found in the literature.[6]

3.3 Large Scale Synthesis

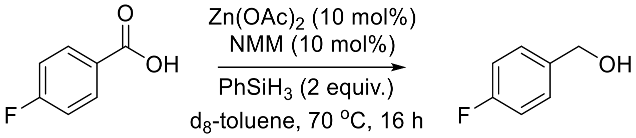
(4-Fluorophenyl)methanol **1**



4-Fluorobenzoic acid (1.00 g, 7.14 mmol) and zinc acetate (131 mg, 0.71 mmol) were dissolved in 2-Me THF (8.5 mL) and heated to reflux. Phenylsilane (1.76 mL, 14.28 mmol) was added to the reaction mixture dropwise, followed by *N*-Me morpholine (78.8 µL, 0.71 mmol). The reaction mixture was stirred at reflux for 18 h, before it was allowed to cool. 2M NaOH (5 mL) was added dropwise to the reaction mixture and it was stirred at room temperature for a further 1 h. 1M HCl was added to the reaction mixture until pH 7 was reached, and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (EtOAc / petrol 1:4) to give the product as a colourless oil (657 mg, 5.21 mmol, 73%).

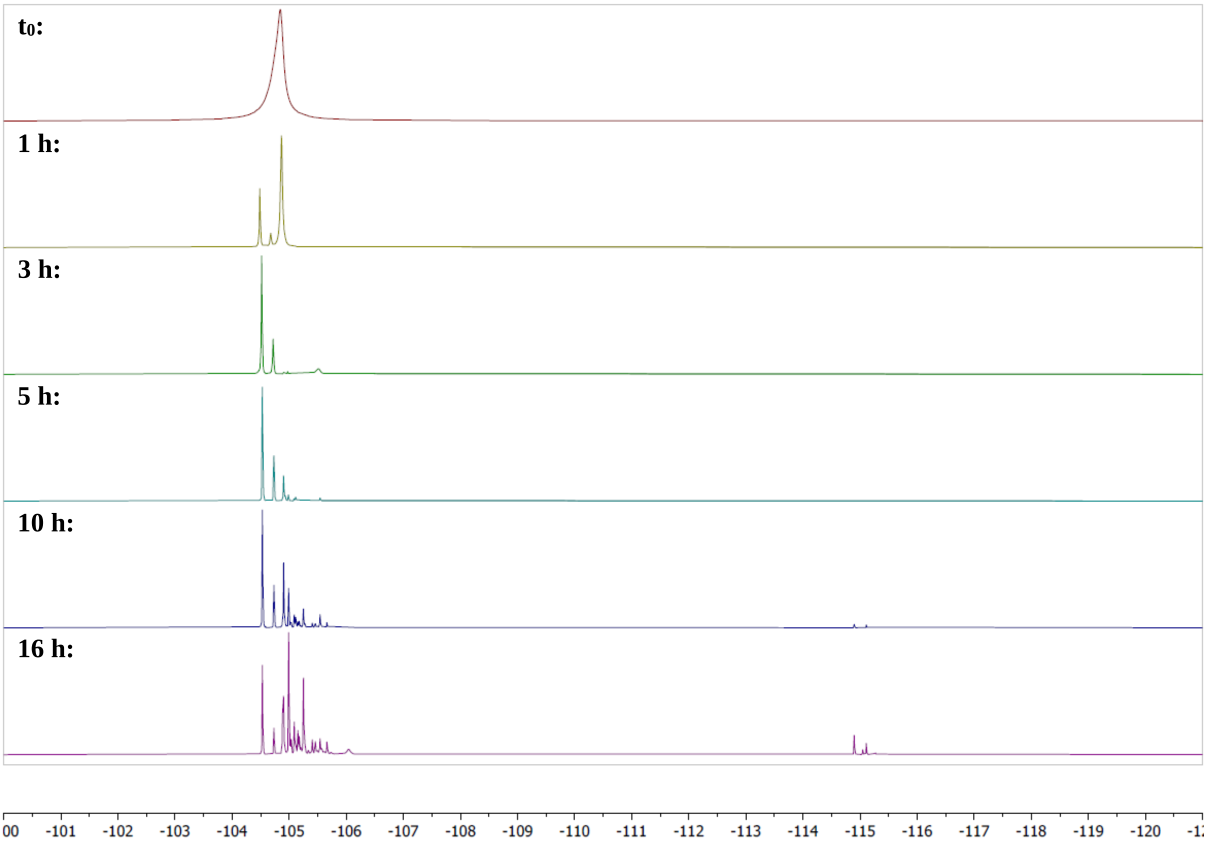
IR (ATR) ν_{max}/cm^{-1} 3311, 1604, 1509, 1429, 1221, 1131; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.07 – 7.00 (m, 2H), 4.63 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.6 Hz), 136.7 (d, *J* = 3.5 Hz), 128.9 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.6 Hz), 64.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.91; GCMS [EI (M + H^+)] m/z calculated for C_7H_7OF 126.0475, found 126.0474. The data matches those found in the literature.[2]

3.4 ^{19}F NMR Studies



Without the addition of NMM:

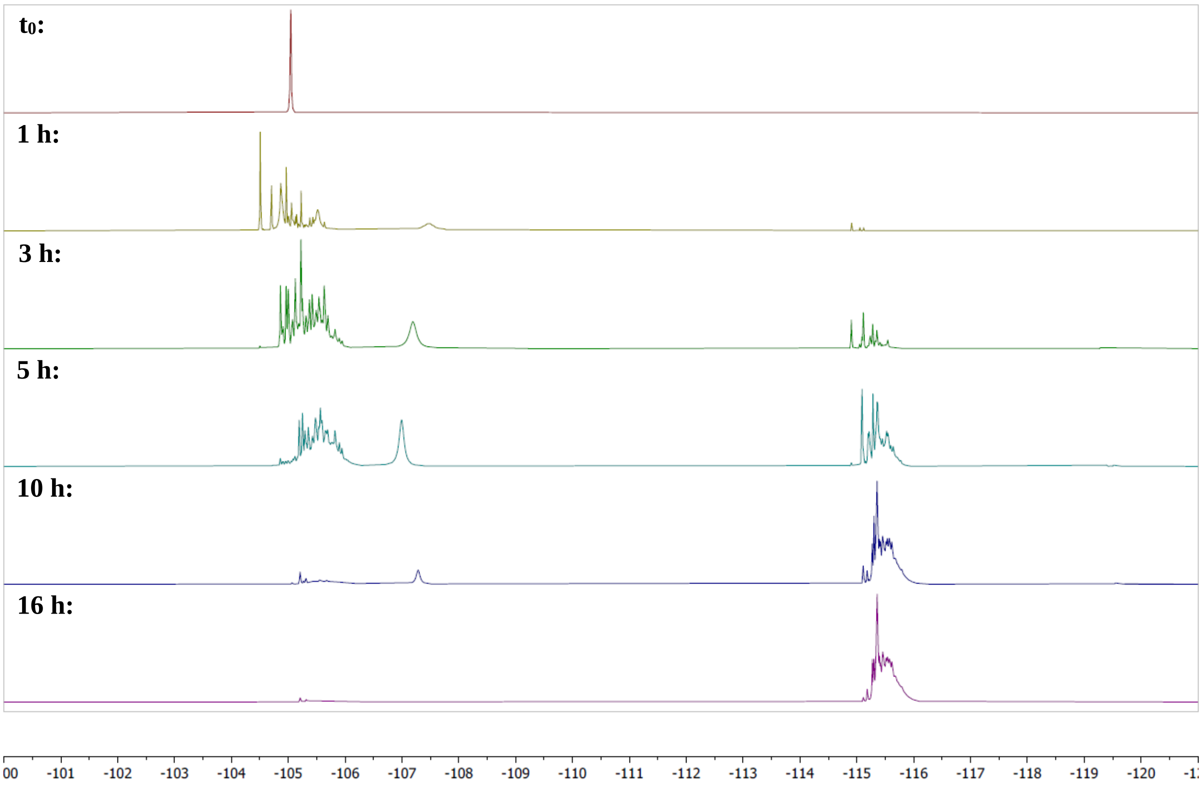
4-Fluorobenzoic acid (70.0 mg, 0.50 mmol) and zinc acetate (9.17 mg, 0.05 mmol) were added to an NMR tube, with trifluorotoluene (61.4 µL, 0.50 mmol) and d_8-toluene (0.5 mL). A ^{19}F NMR spectrum was acquired at 70 ˚C (t_0 below). Phenylsilane (123 µL, 1.00 mmol) was then added to the NMR tube and ^{19}F NMR spectra were acquired at 70 °C at 15 min intervals for 16 h.



With the addition of NMM:

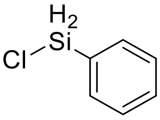
4-Fluorobenzoic acid (70.0 mg, 0.50 mmol) and zinc acetate (9.17 mg, 0.05 mmol) were added to an NMR tube, with trifluorotoluene (61.4 µL, 0.50 mmol) and d_8-toluene (0.5 mL). A ^{19}F NMR spectrum acquired at 70 ˚C (t_0 below). Phenylsilane (123 µL, 1.00 mmol) and *N*-Me morpholine (5.50 µL, 0.05

mmol) were then added to the NMR tube and ^{19}F NMR spectra were acquired at 70 °C at 15 min intervals for 16 h.



3.5 Independent Synthesis of Silyl Esters

Phenylchlorosilane



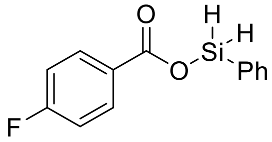
Phenylchlorosilane was synthesised using an adapted literature procedure.[21]

A mixture of phenylsilane (10.8 g, 100 mmol), anhydrous copper(II) chloride (26.9 g, 200 mmol), anhydrous copper(I) iodide (0.760 g, 4.00 mmol), and 4 Å molecular sieves (80 g) in a dry 500 mL round-bottomed flask was evacuated and backfilled with anhydrous dinitrogen (3 ×). 50 mL of Et_2O was added, and the mixture was stirred with a large magnetic stir bar at 250 rpm at room temperature for 2 h. The resulting mixture was filtered through a cannula to remove the copper salts and molecular sieves, and the solid was washed with diethyl ether (3 × 10 mL). The solution was then distilled, initially under a flow of N_2 to remove Et_2O, and then under reduced pressure (8 mbar) to give phenylchlorosilane (3.93 g, 27.5 mmol, 28%) contaminated with with *ca* 3% phenylsilane and *ca* 4% Et_2O (see ^{1}H NMR spectrum) as a colourless liquid.

^{1}H and ^{29}Si NMR spectra are consistent with the literature.[22]

^{1}H NMR (400 MHz, C_6D_6): δ 7.40-7.35 (m, 2H), 7.14-7.09 (m, 1H), 7.08-7.03 (m, 2H), 5.06 (s, 2H, Si–H). **^{13}C NMR (101 MHz, C_6D_6):** δ 134.7, 131.5, 130.3, 128.6. **^{29}Si NMR (79 MHz, C_6D_6):** δ -17.91.

Phenylsilyl 4-fluorobenzoate **SI-1**



Sodium 4-fluorobenzoate* (81.1 mg, 0.500 mmol) was added to a microwave tube. The tube was capped and evacuated and backfilled with anhydrous dinitrogen (3 ×). Dry, degassed benzene-*d*$_6$ (1.00 mL) was then added, and to the resulting stirred suspension was added phenyl chlorosilane (61.0 μL, 0.500 mmol). The mixture was stirred for 2 hours at room temperature. After allowing the suspension to settle (1 minute), A sample (*ca* 0.2 mL) was removed and diluted with dry, degassed benzene-*d*$_6$ in a dry NMR tube under a flow of anhydrous dinitrogen. The main component of the resulting mixture was phenylsilyl 4-fluorobenzoate (SI-1).

Assignments confirmed by ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC spectra. A key observation is the ^{1}H-^{13}C HMBC cross-peak between H-6 (the Si–H) and C-5 (the C=O). Despite a poor signal to noise ratio in the ^{29}Si{^{1}H} NMR spectrum, the unchanged phenylsilane is still observed (δ -60.32 ppm).

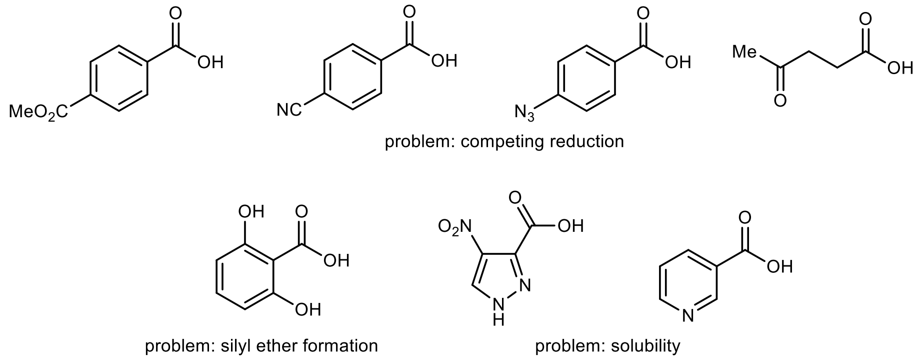
^{1}H NMR (400 MHz, C_6D_6): δ 7.84-7.79 (m, 2H, H-3), 7.71-7.67 (m, 2H, H-8), 7.15-7.05 (m**, H-9 and H-10), 6.58-6.52 (m, 2H, H-2), 5.33 (s, 2H, H-6). **^{13}C NMR (101 MHz, C_6D_6):** δ 166.26 (d, *J* = 253.9 Hz, C-1), 166.24 (C-5), 135.8 (C-8), 133.3 (d, *J* = 9.5 Hz, C-3), 131.4 (C-10), 130.6 (C-7), 128.5 (C-9), 126.8 (d, *J* = 3.0 Hz, C-4), 115.6 (d, *J* = 22.0 Hz, C-2). **^{19}F NMR (376 MHz, C_6D_6):** δ -105.09. **^{29}Si NMR (79 MHz, C_6D_6):** δ -19.72.

*Sodium 4-fluorobenzoate was prepared by deprotonation of 4-fluorobenzoic acid (280 mg, 2.00 mmol) with sodium hydride (60% in mineral oil, 80.0 mg, 2.00 mmol) in anhydrous THF (10 mL), followed by washing the precipitated salt with pentane (3 x 5 mL) to remove mineral oil. The salt (320 mg, 1.97 mmol, 99%) was used without further purification.

**Overlapped with peaks from $PhSiH_3$ impurity. Integral expected = 3H, measured ~ 4H.

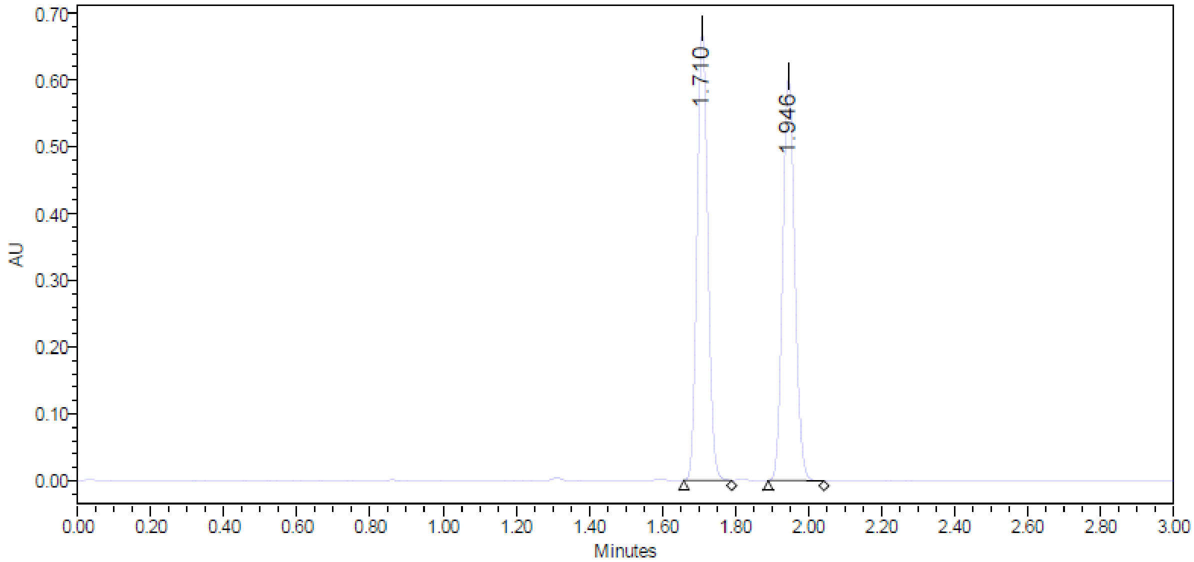
4 Problematic Substrates

While we have not carried out an exhaustive survey in terms of substrate scope some problematic examples are depicted below. We note that we have not made any attempt to optimise the reduction reaction on substrate by substrate basis so, with optimisation, reduction of these (and other) substrates may well be possible.



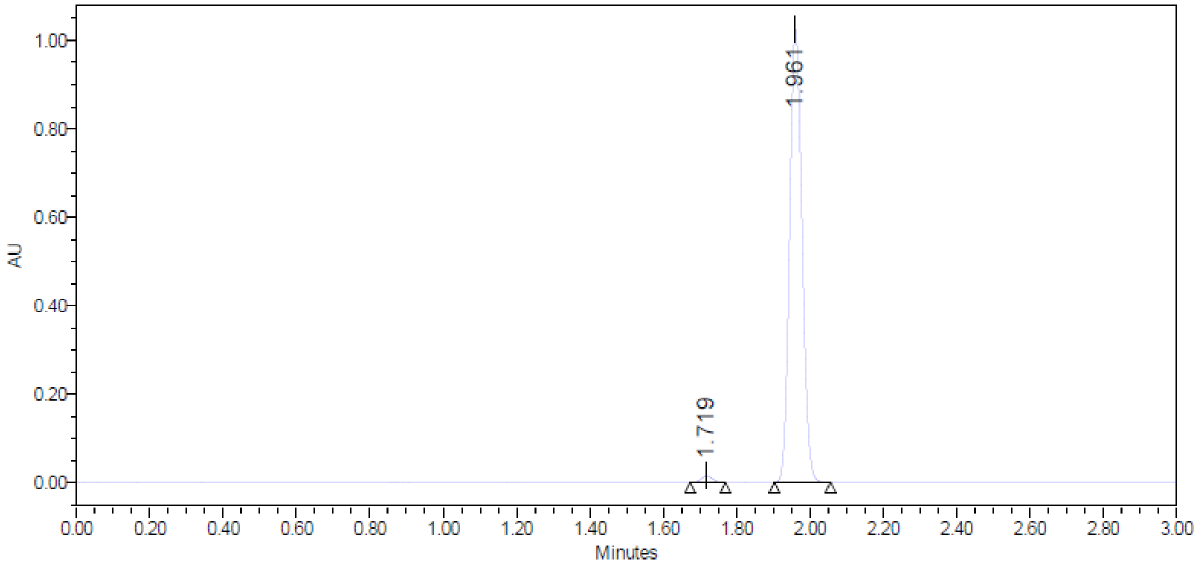
5 HPLC Traces

(*R*)-2-Phenylpropan-1-ol **10** (racemate trace followed by reduction product)



Peak Results

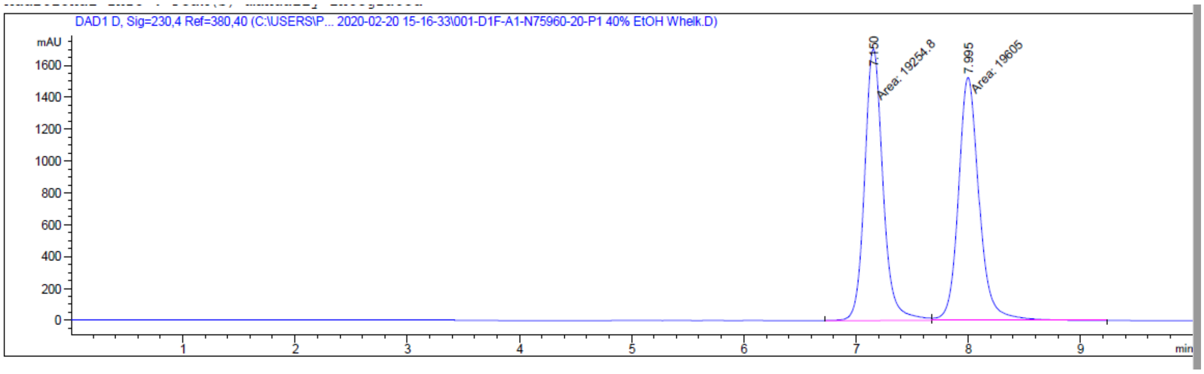
	Retention Time (min)	Area (µV*sec)	% Area	Width @ 50%
1	1.71	1394172	50.0	
2	1.95	1395963	50.0	



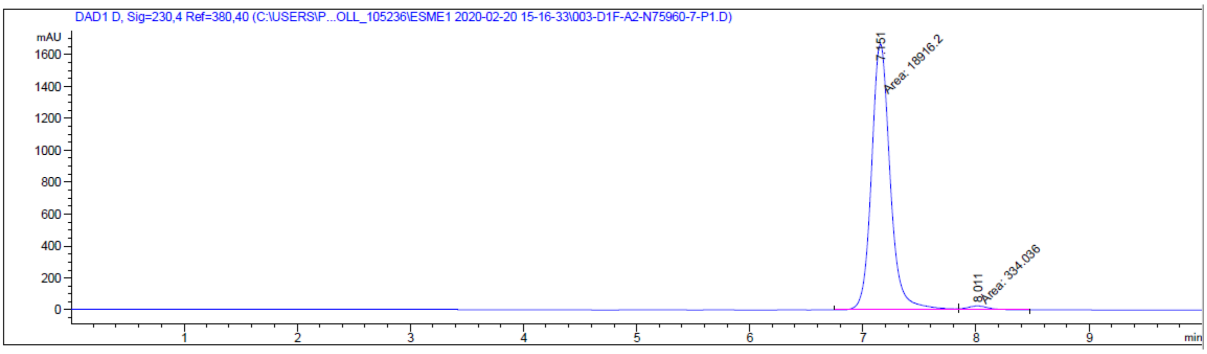
Peak Results

	Retention Time (min)	Area (µV*sec)	% Area	Width @ 50%
1	1.72	31338	1.3	
2	1.96	2392093	98.7	

<u>Benzyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate **22**</u> (racemate trace followed by reduction product)



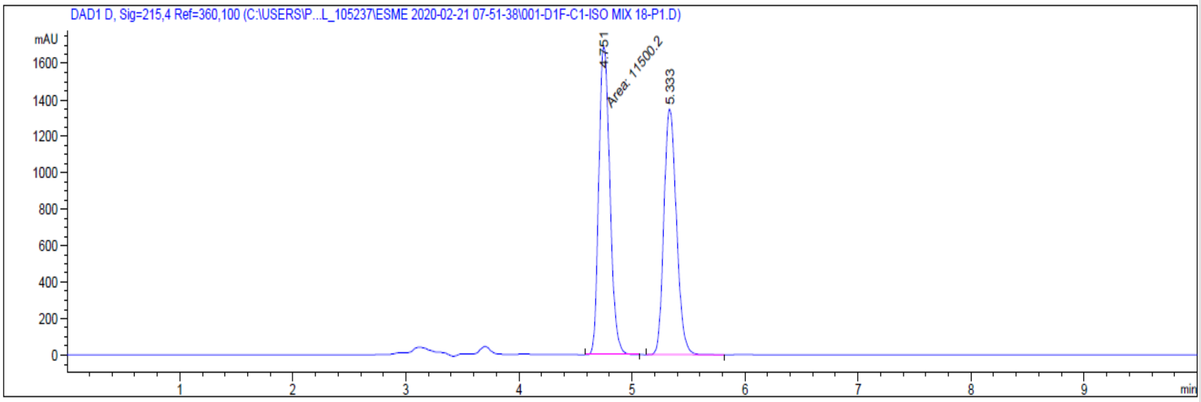
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.150 MM    0.1882 1.92548e4  1705.31201  49.5495
   2   7.995 MM    0.2142 1.96050e4  1525.42236  50.4505
```



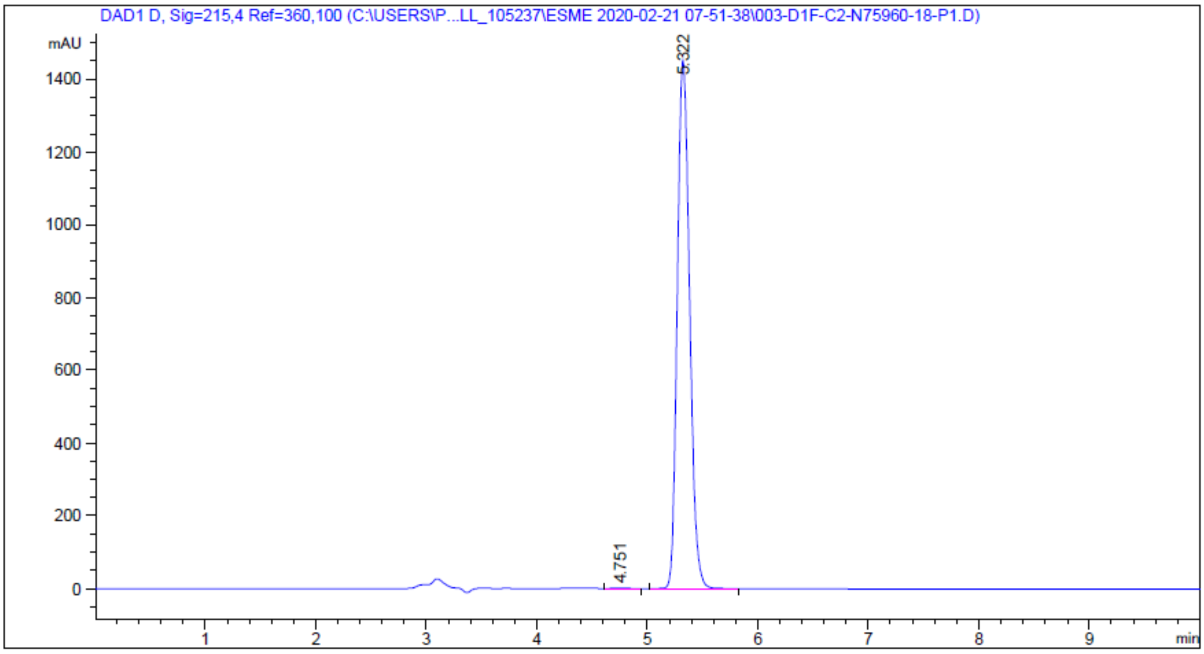
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.151 MM    0.1891 1.89162e4 1667.55676 98.2648
   2   8.011 MM    0.2279  334.03561   24.43273  1.7352

Totals :                  1.92502e4 1691.98949
```

(*S*)-2-(6-Methoxynaphthalen-2-yl)propan-1-ol **19** (racemate trace followed by reduction product)

The racemate was prepared from a 1:1 mixture of enantiomers.



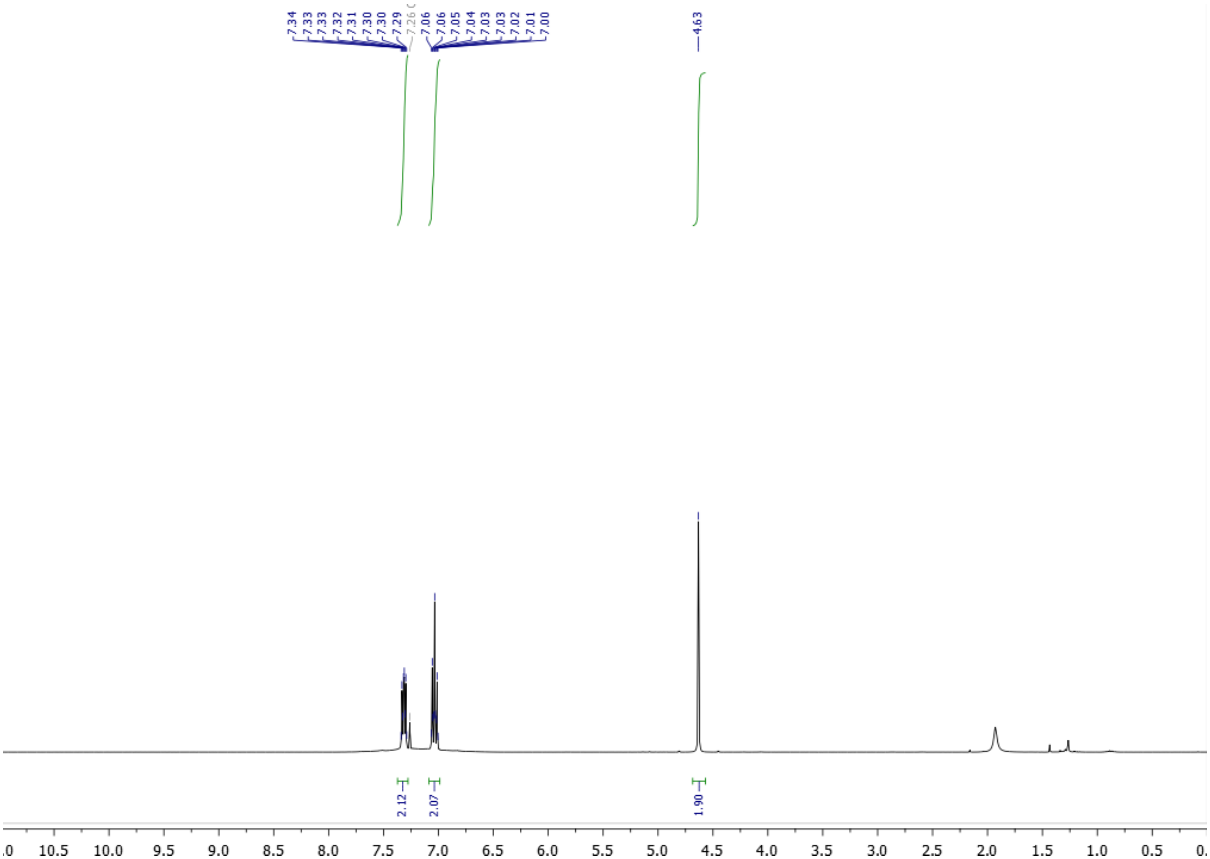
```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.751 MM     0.1134 1.15002e4  1690.81543  52.4646
   2   5.333 BB     0.1222 1.04197e4  1348.02344  47.5354
```

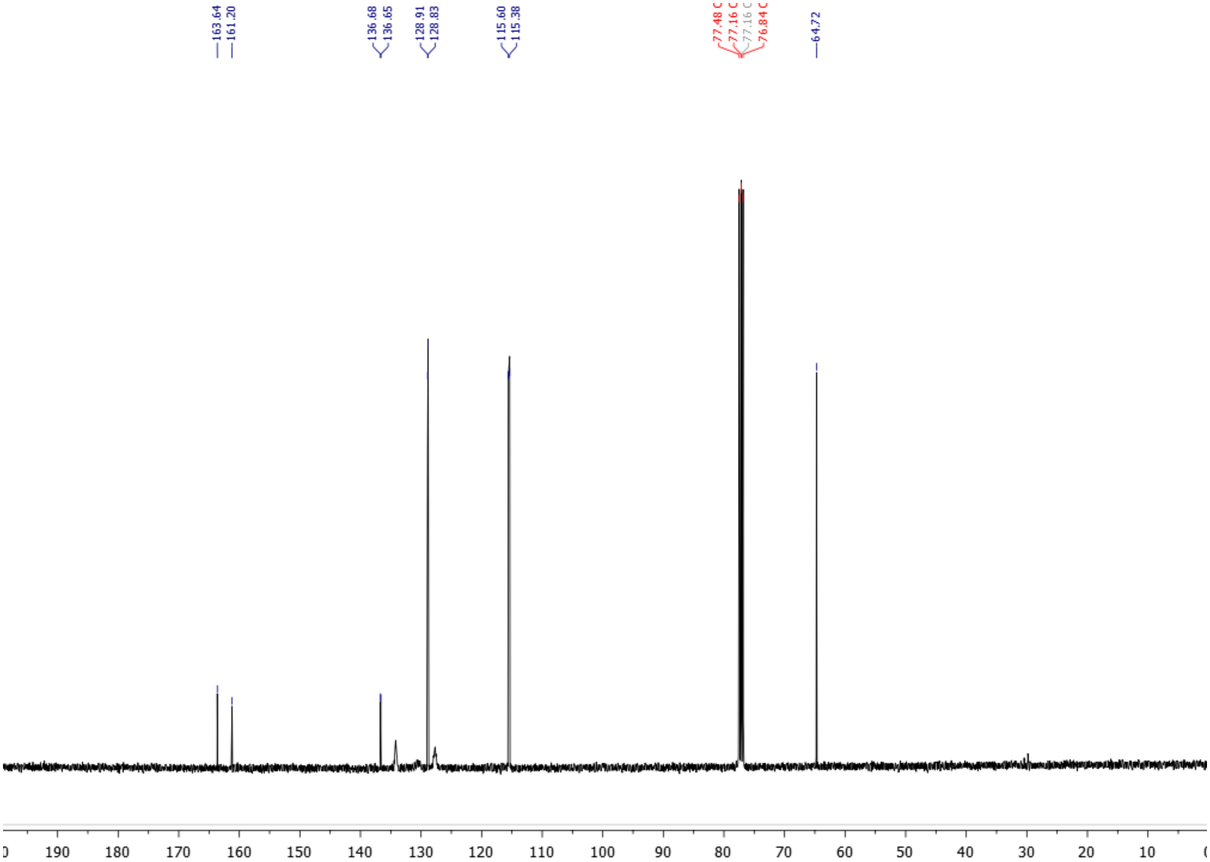


```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.751 BB     0.0889    7.54379    1.31643    0.0672
   2   5.322 BB     0.1201 1.12115e4  1451.31787   99.9328
```

6 NMR Spectra

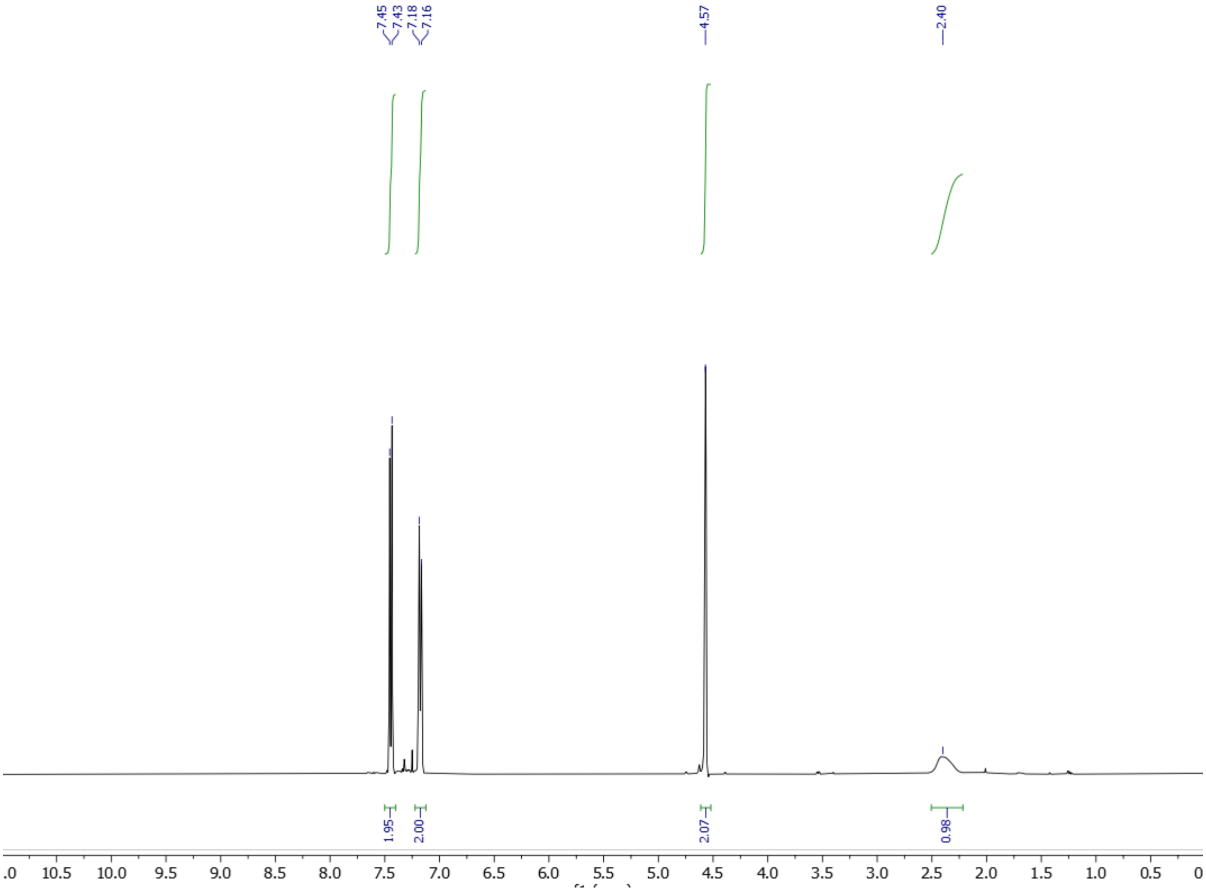
(4-Fluorophenyl)methanol **1**

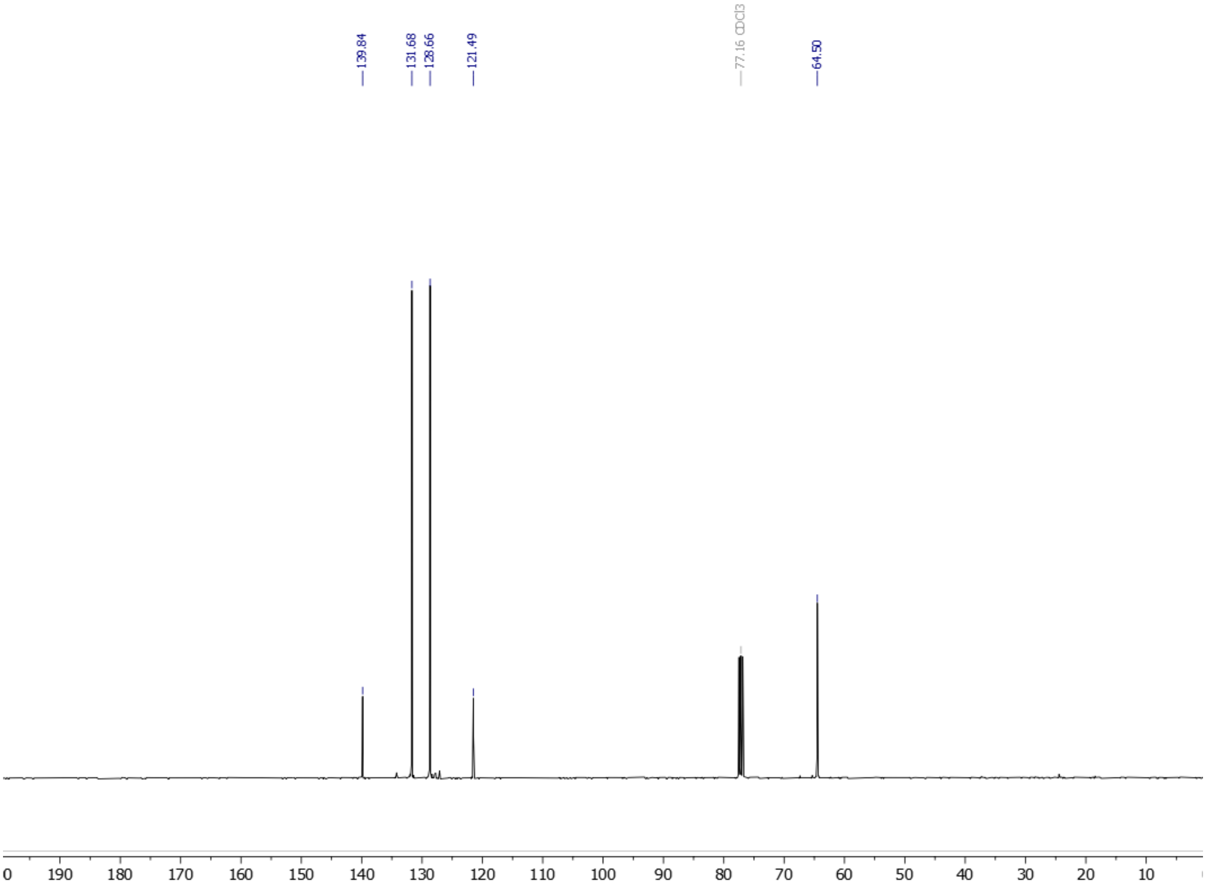




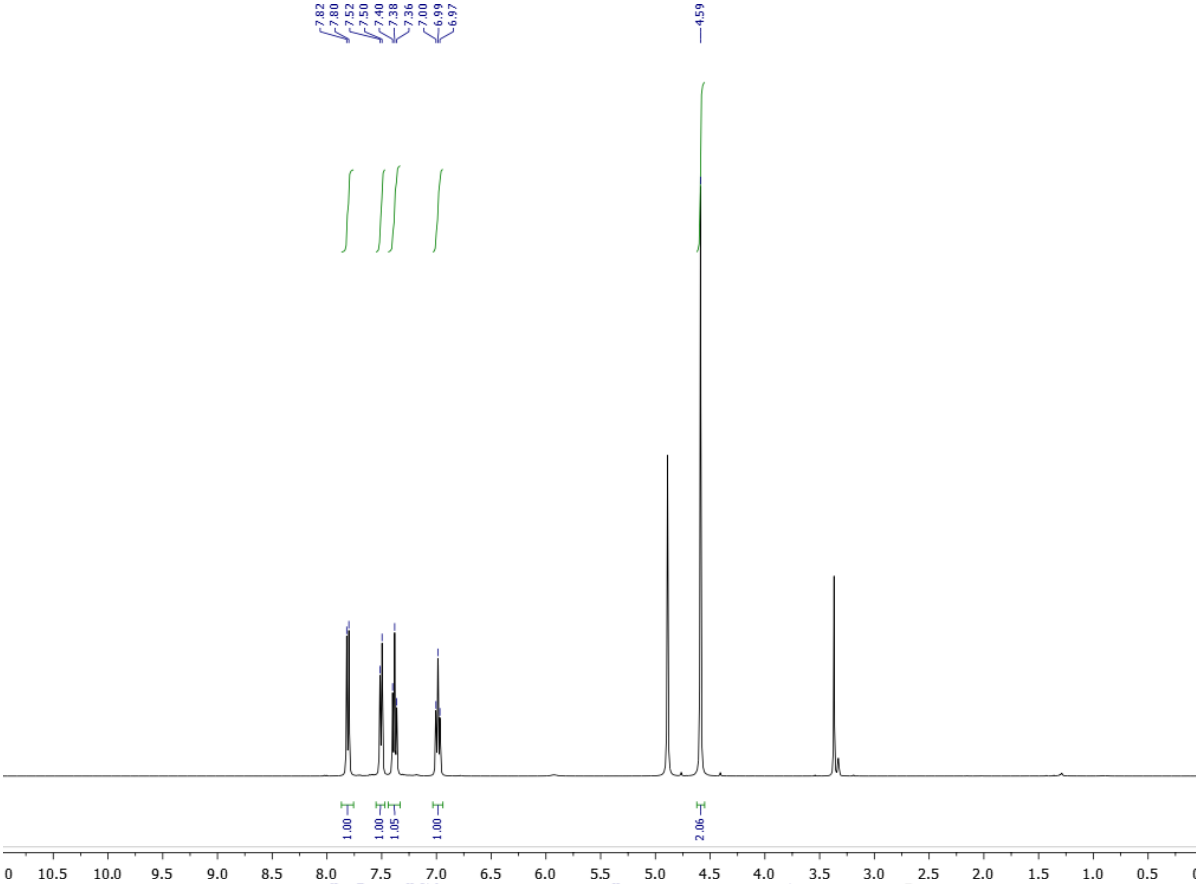

-114.91
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170

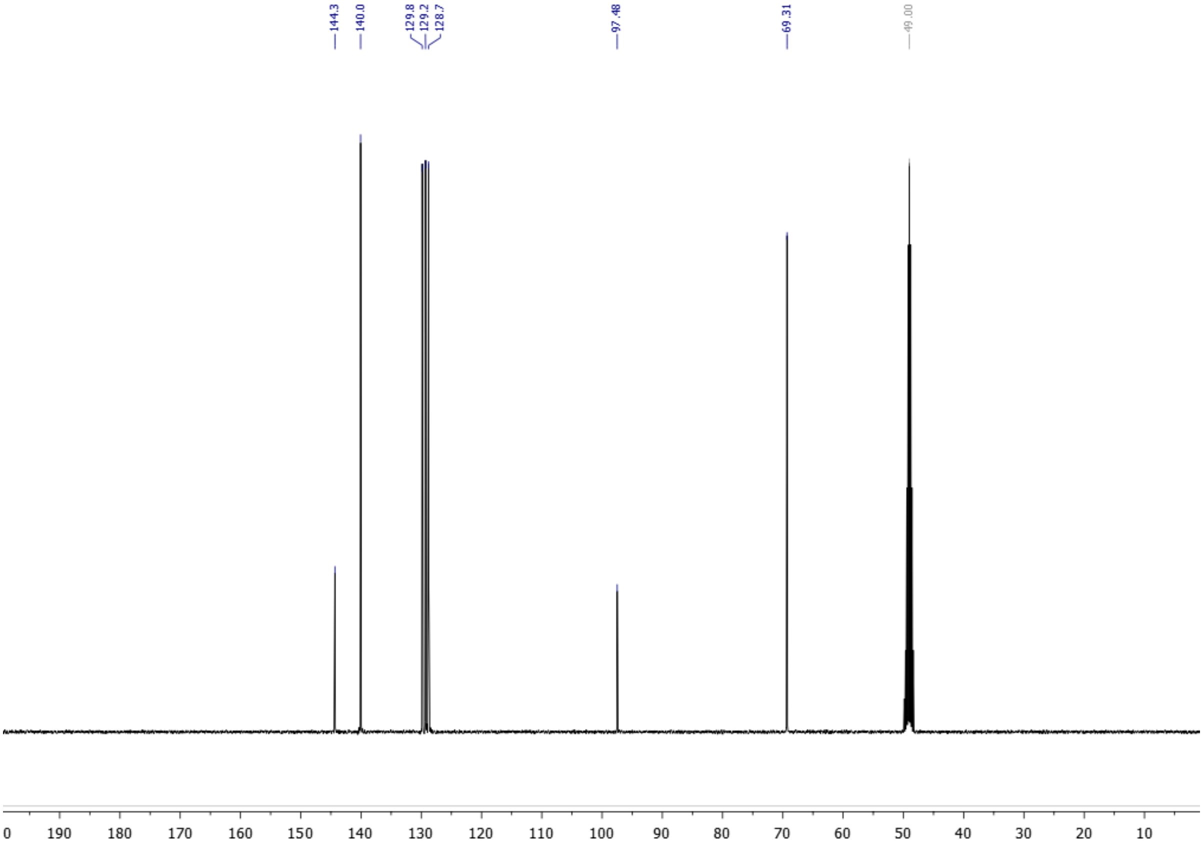
(4-Bromophenyl)methanol **2**



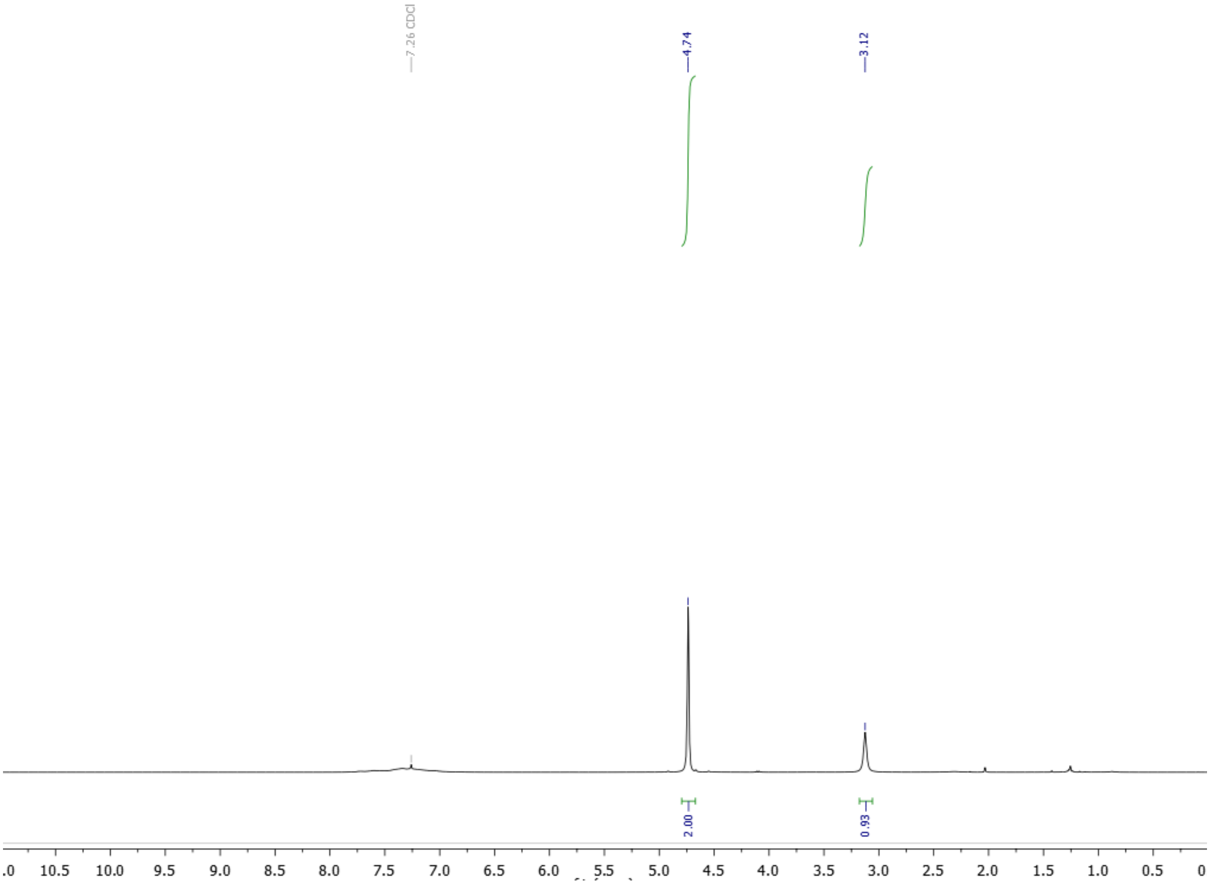


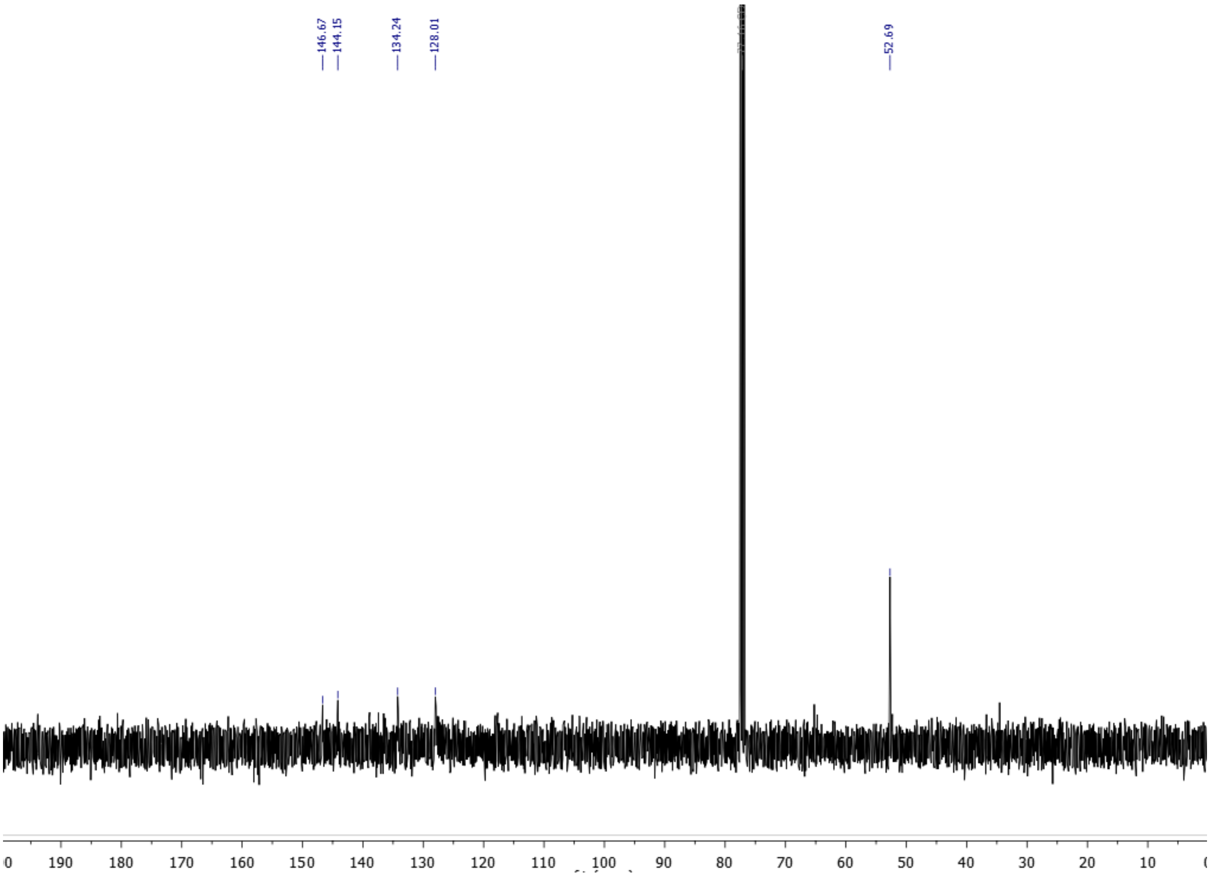
(2-Iodophenyl)methanol **3**

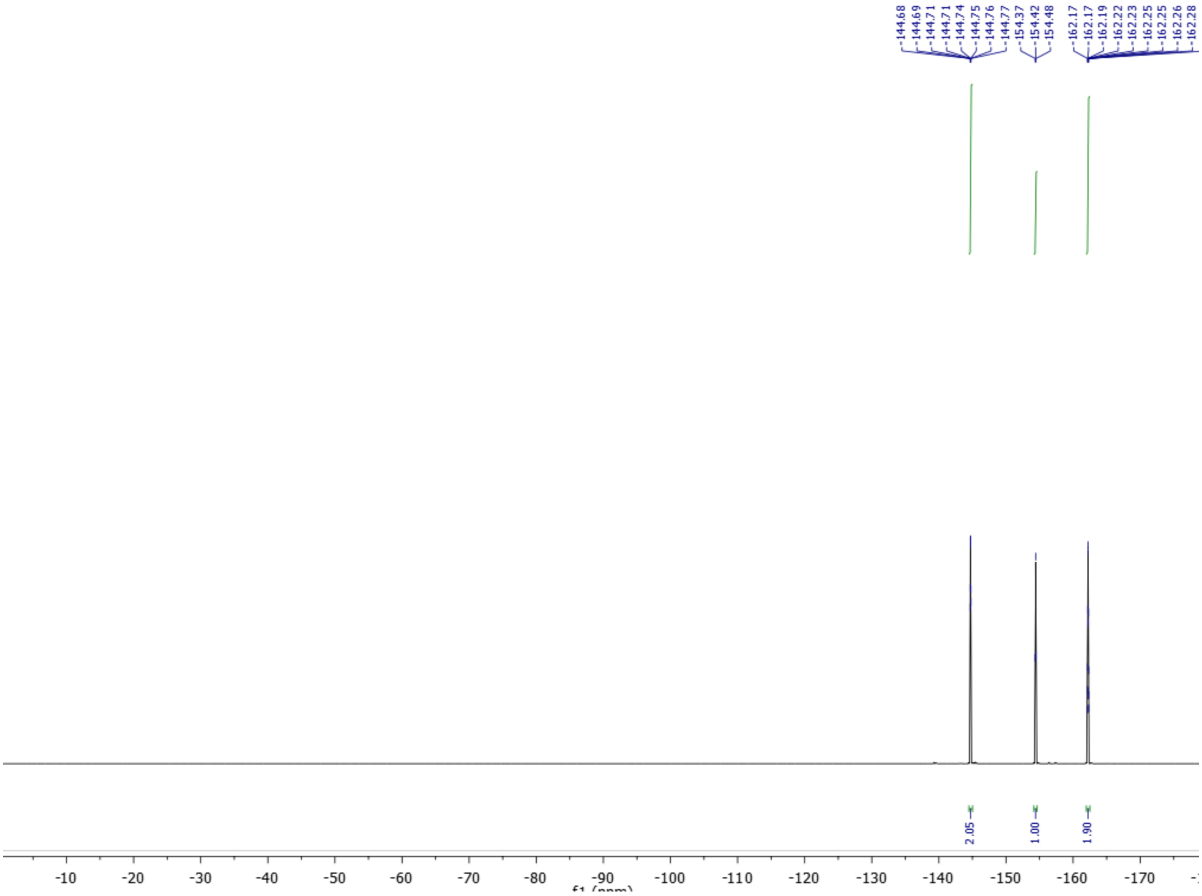




(Perfluorophenyl)methanol **4**



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-144.71
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-144.76
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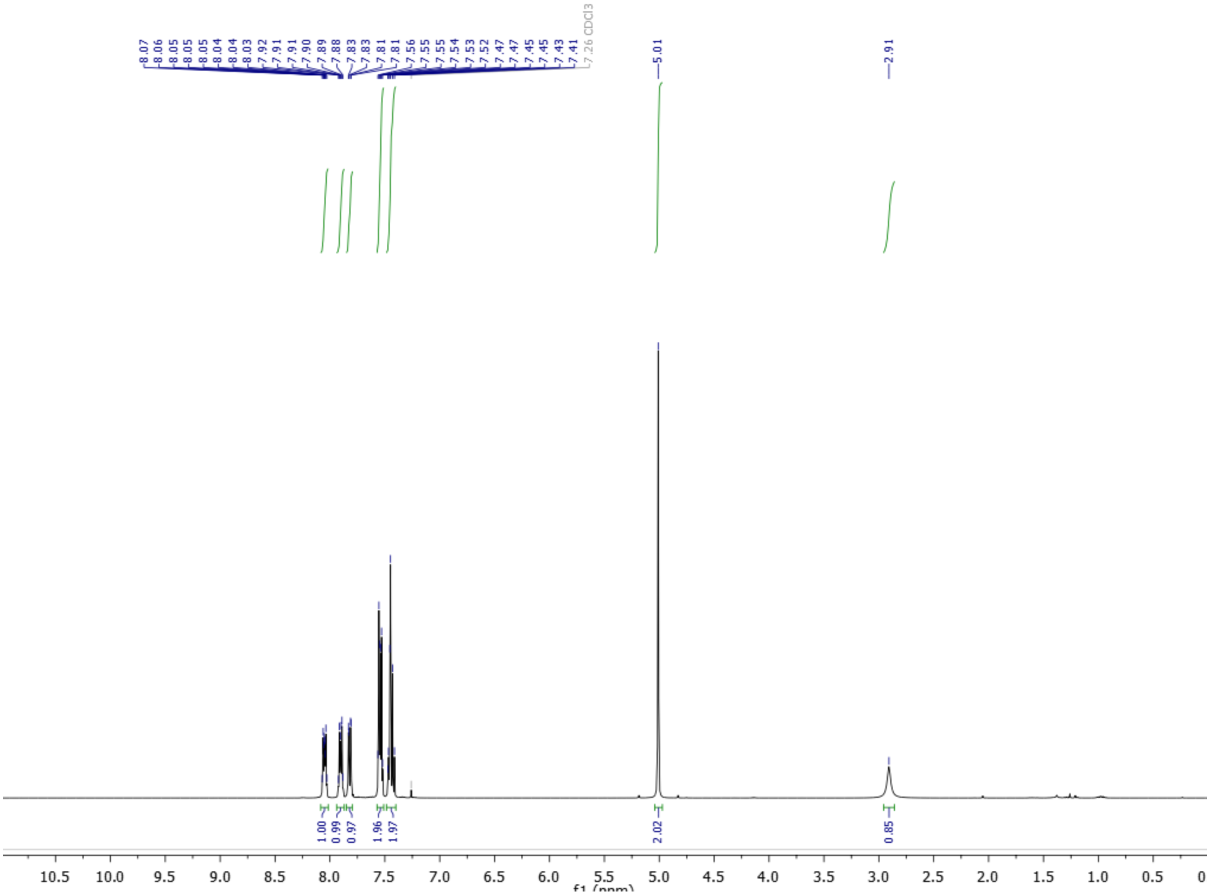
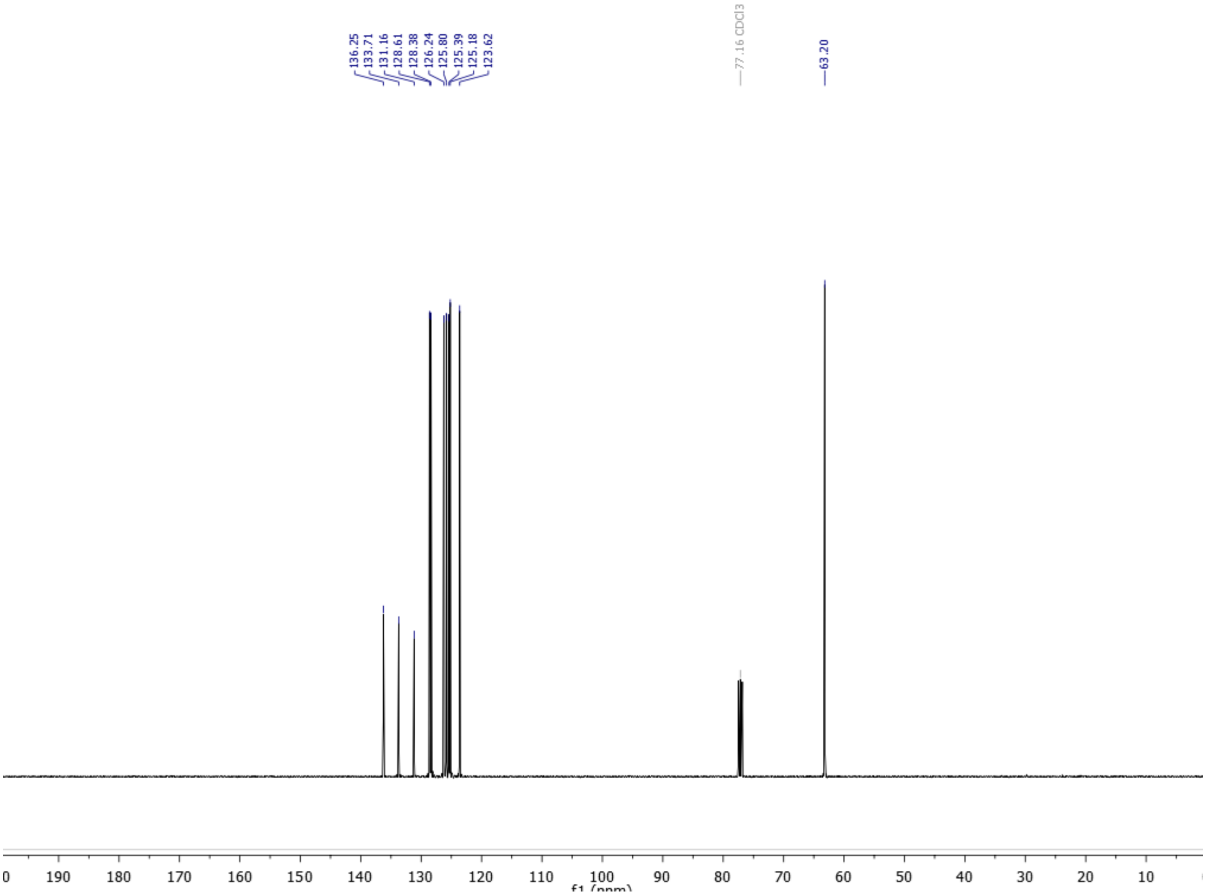
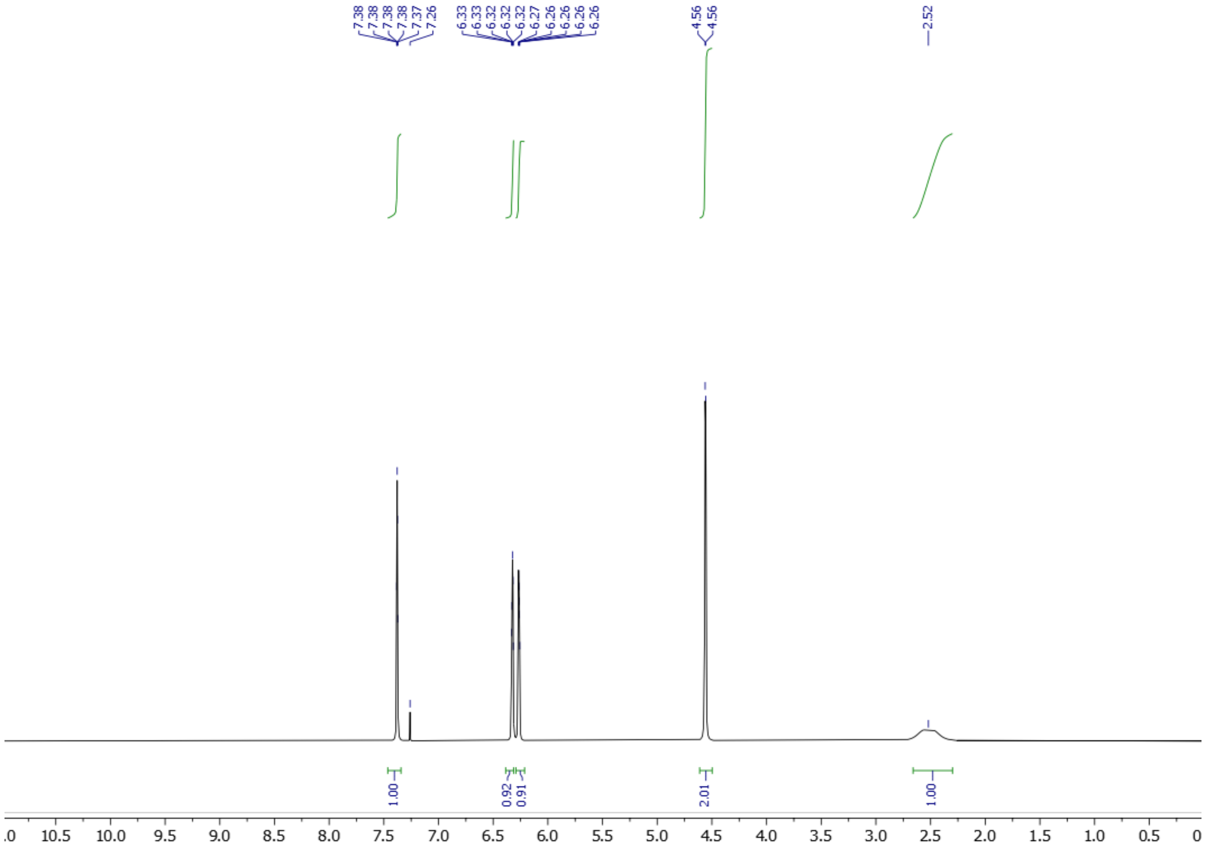
-154.42
-154.48
-162.17
-162.17
-162.19
-162.22
-162.23
-162.25
-162.25
-162.26
-162.28
2.05
1.00
1.90
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

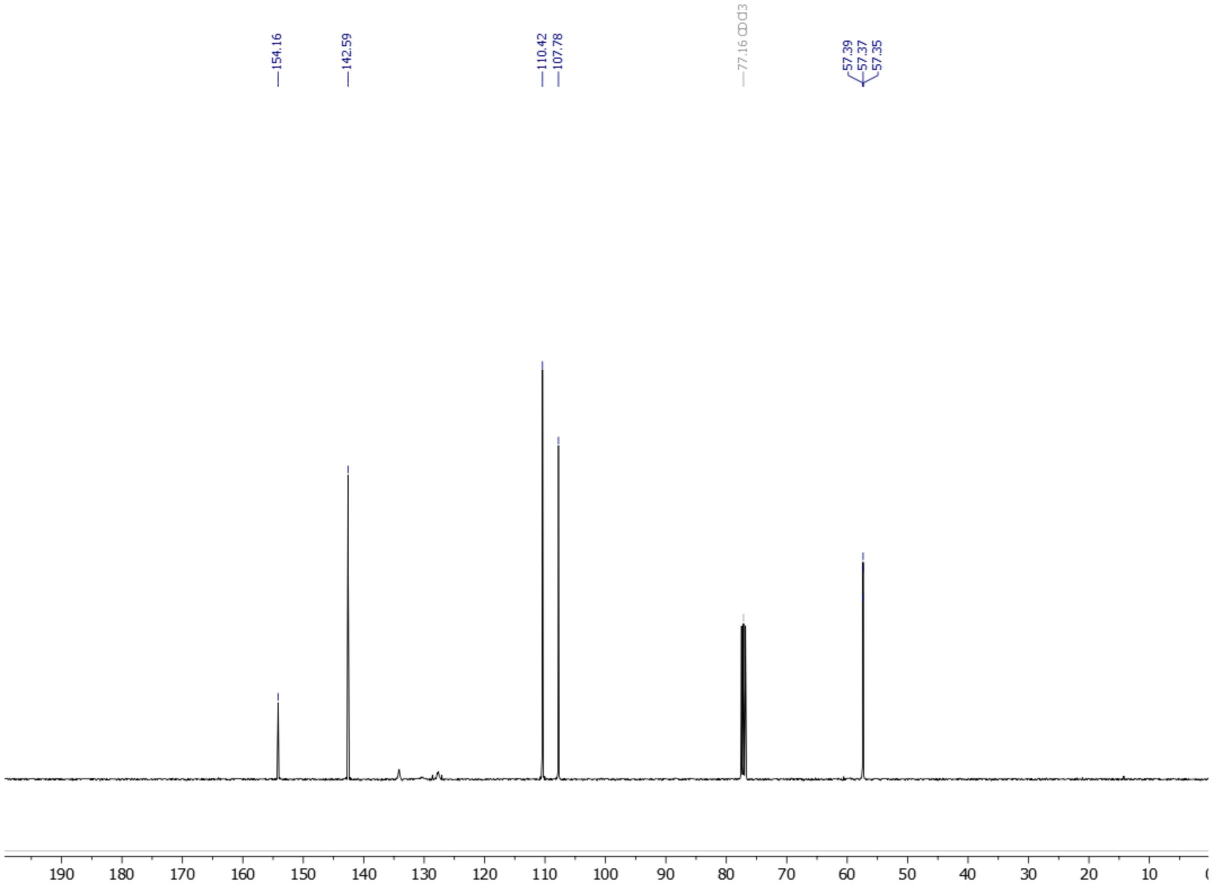
Naphthalen-1-ylmethanol **5**



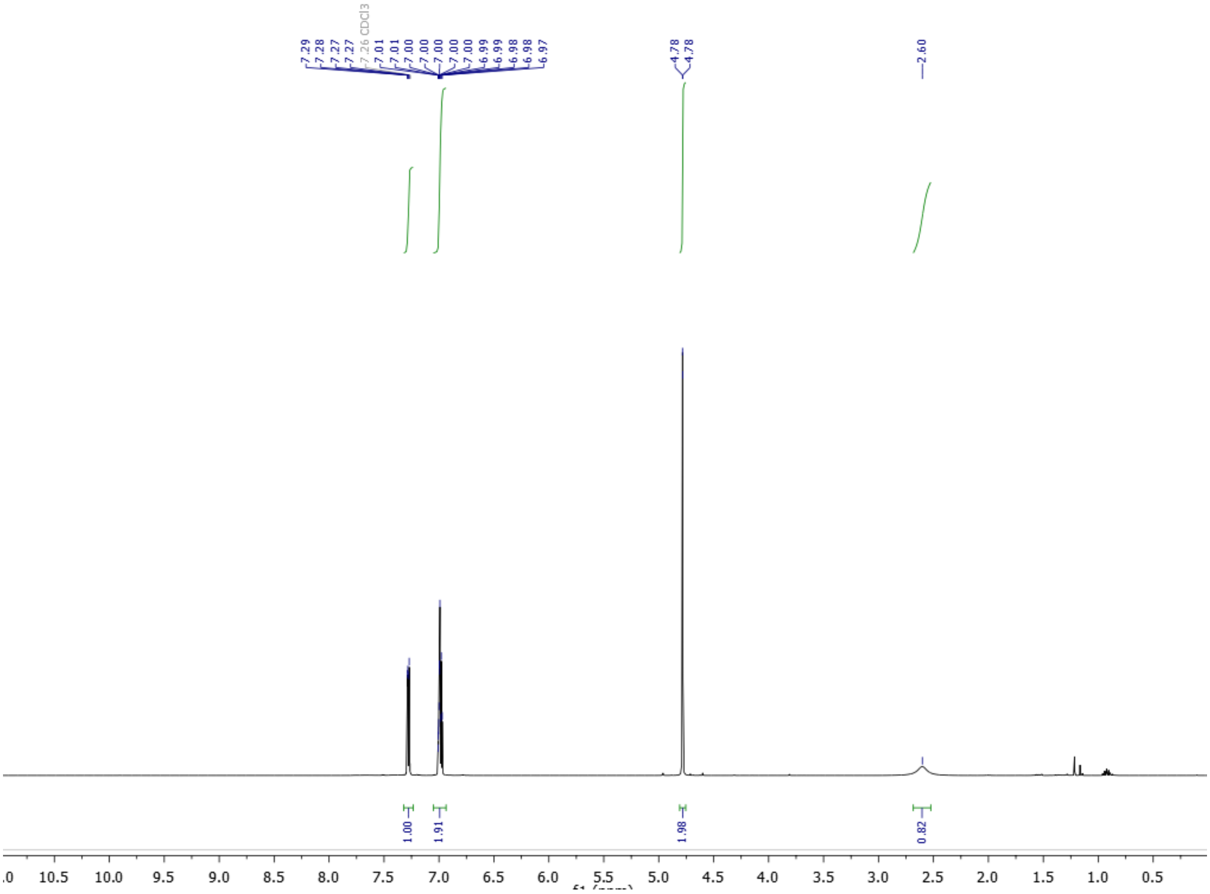


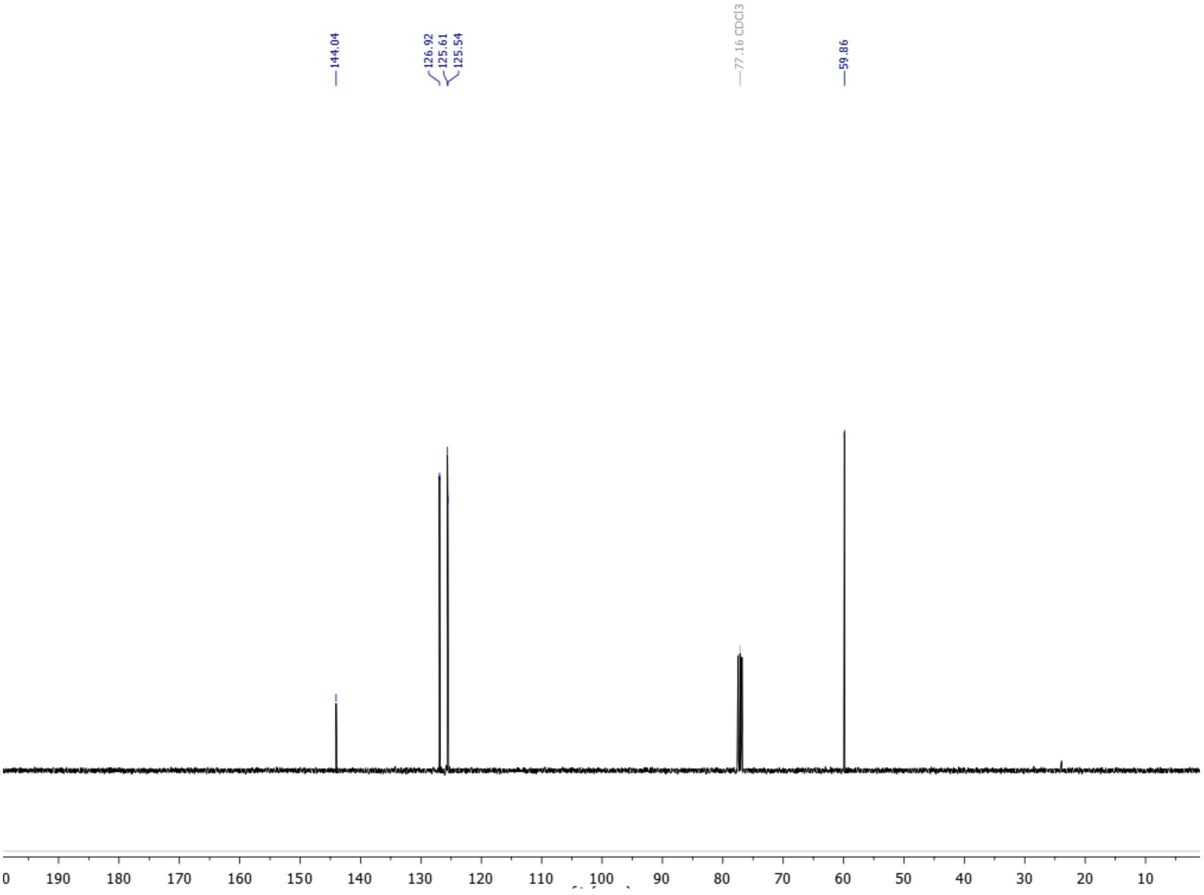
Furan-2-ylmethanol **6**



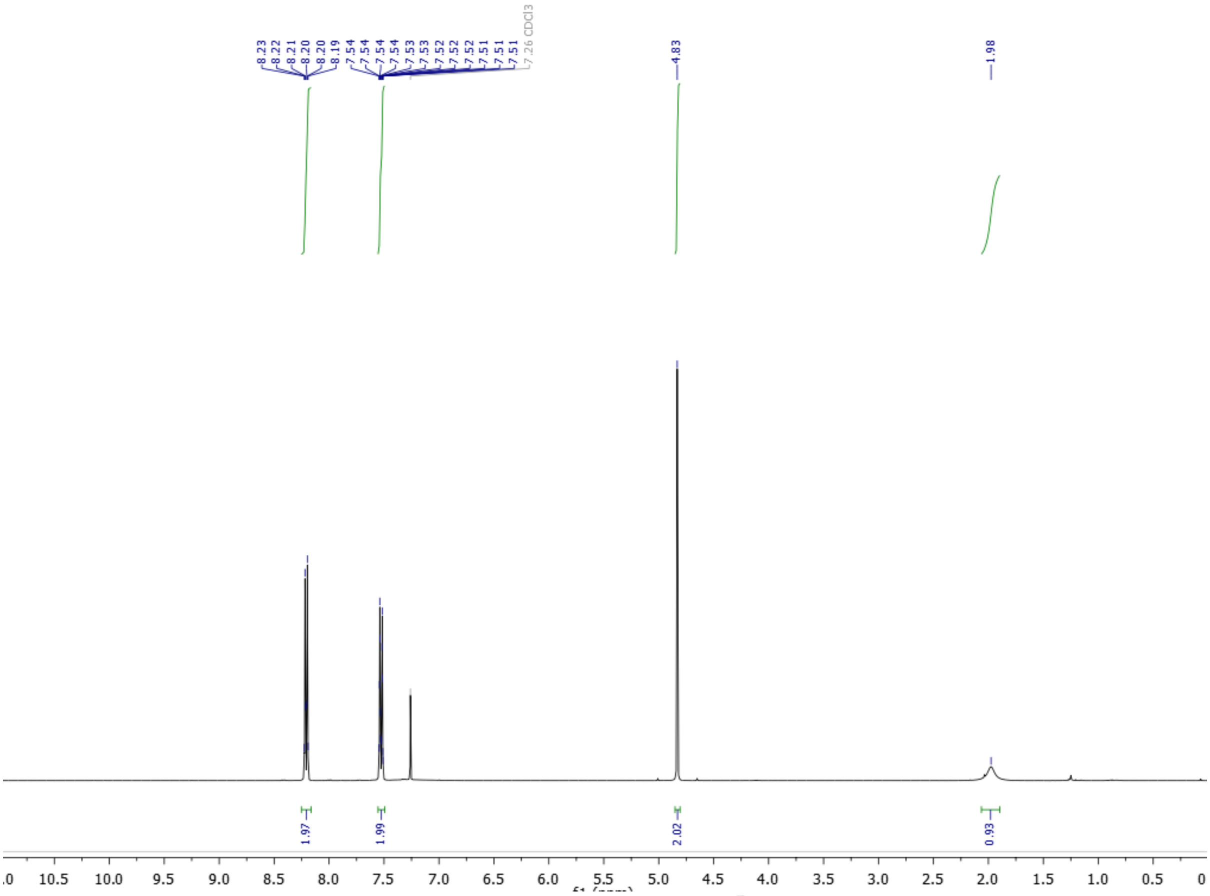


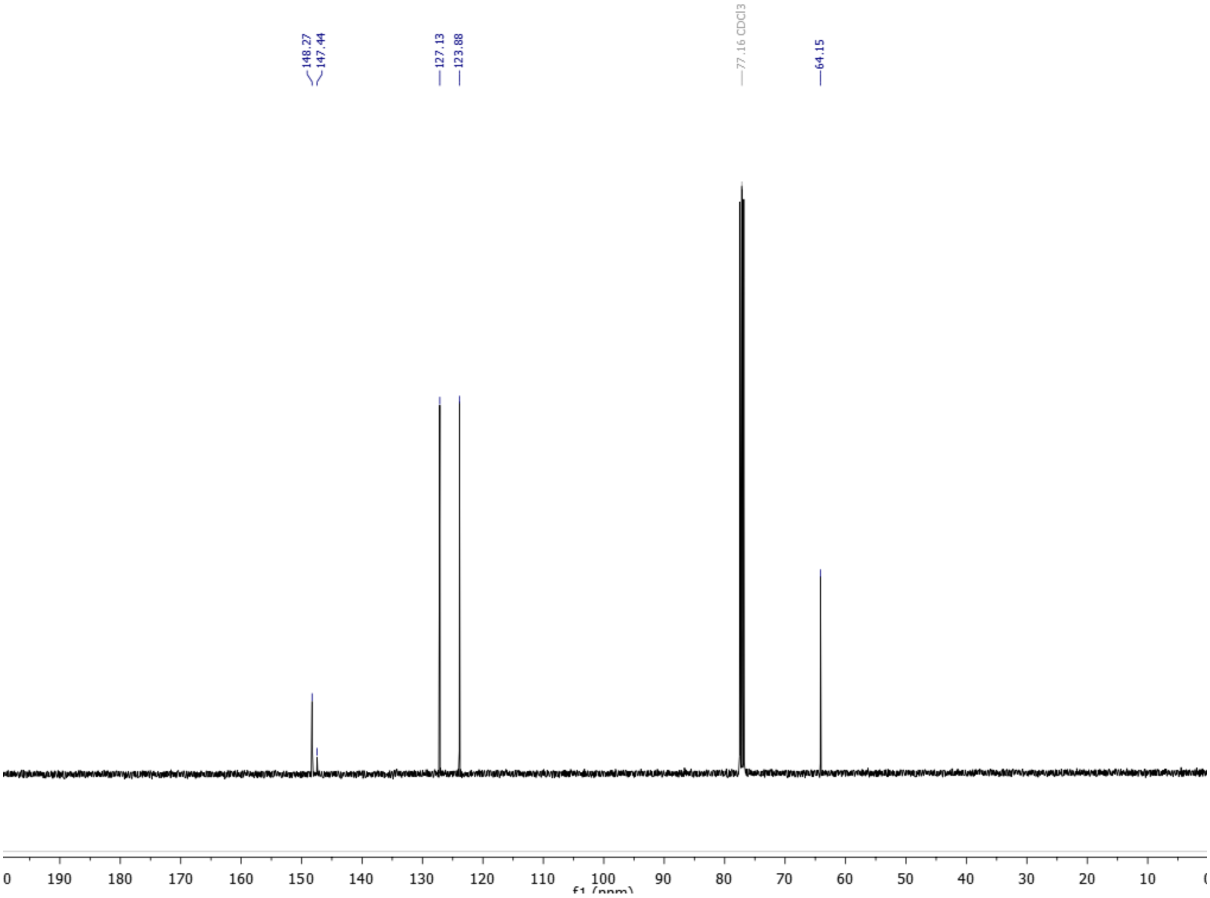
Thiophen-2-ylmethanol **7**



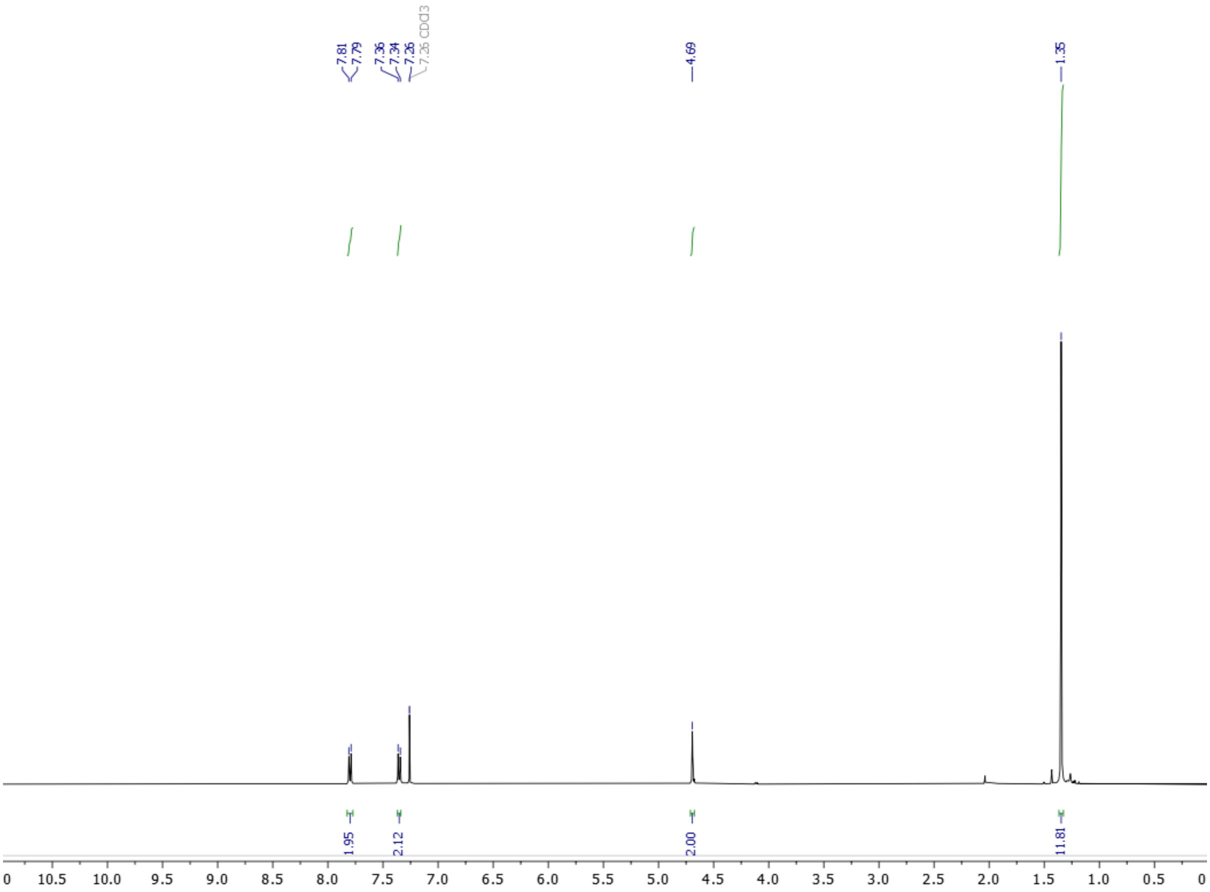


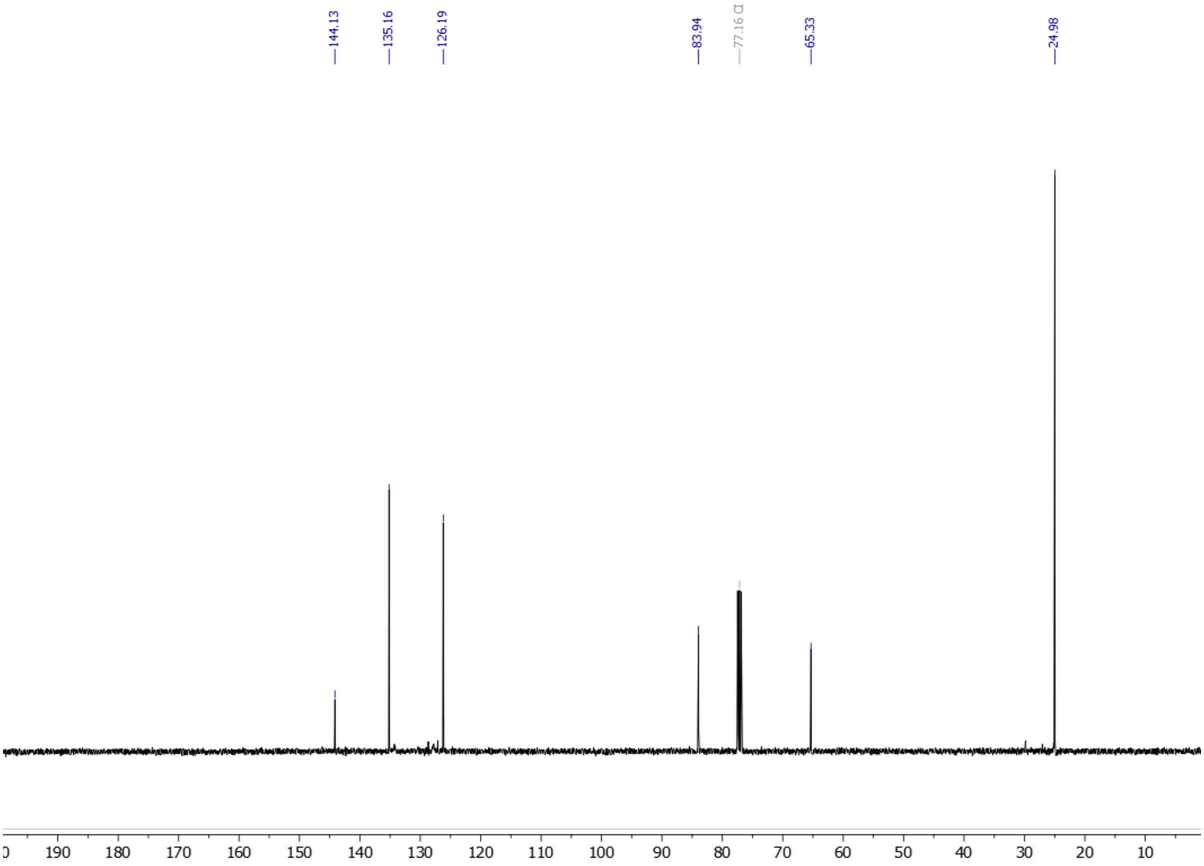
(4-Nitrophenyl)methanol **8**



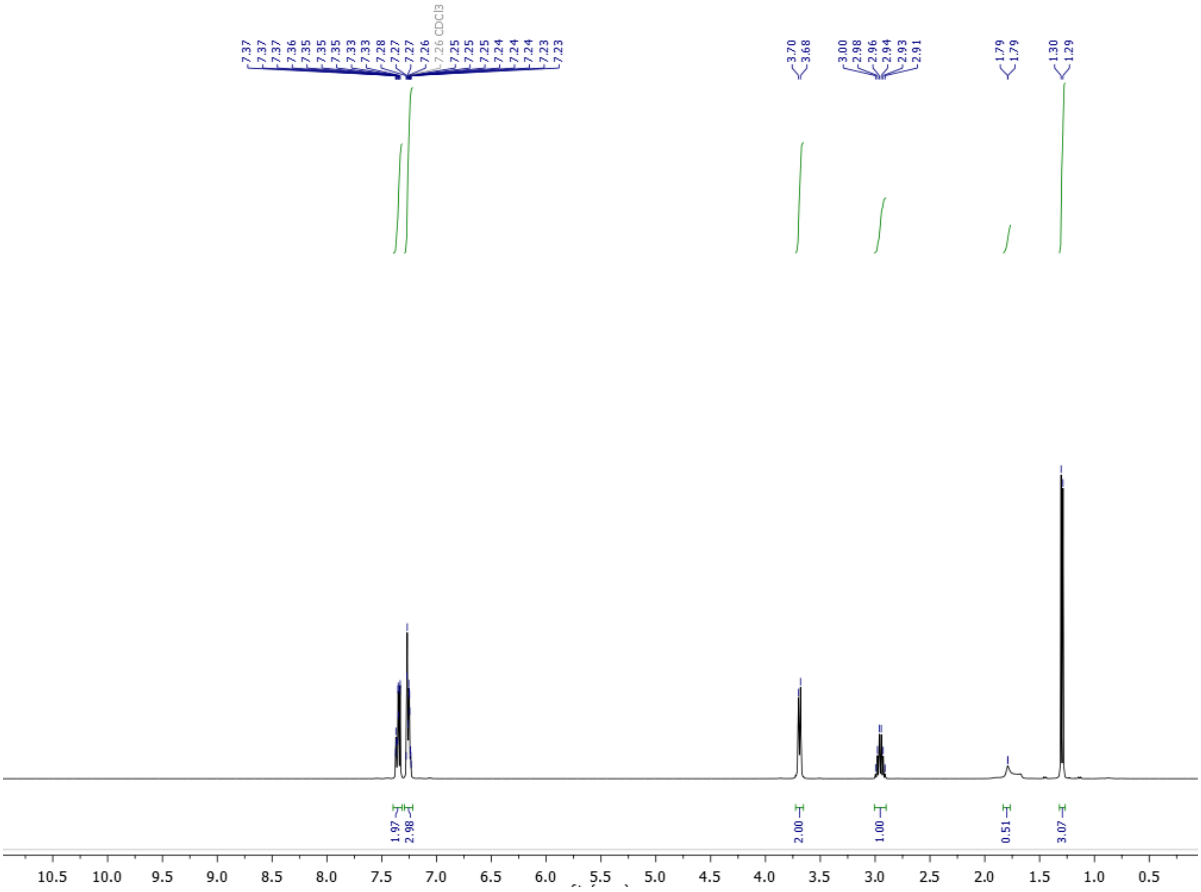


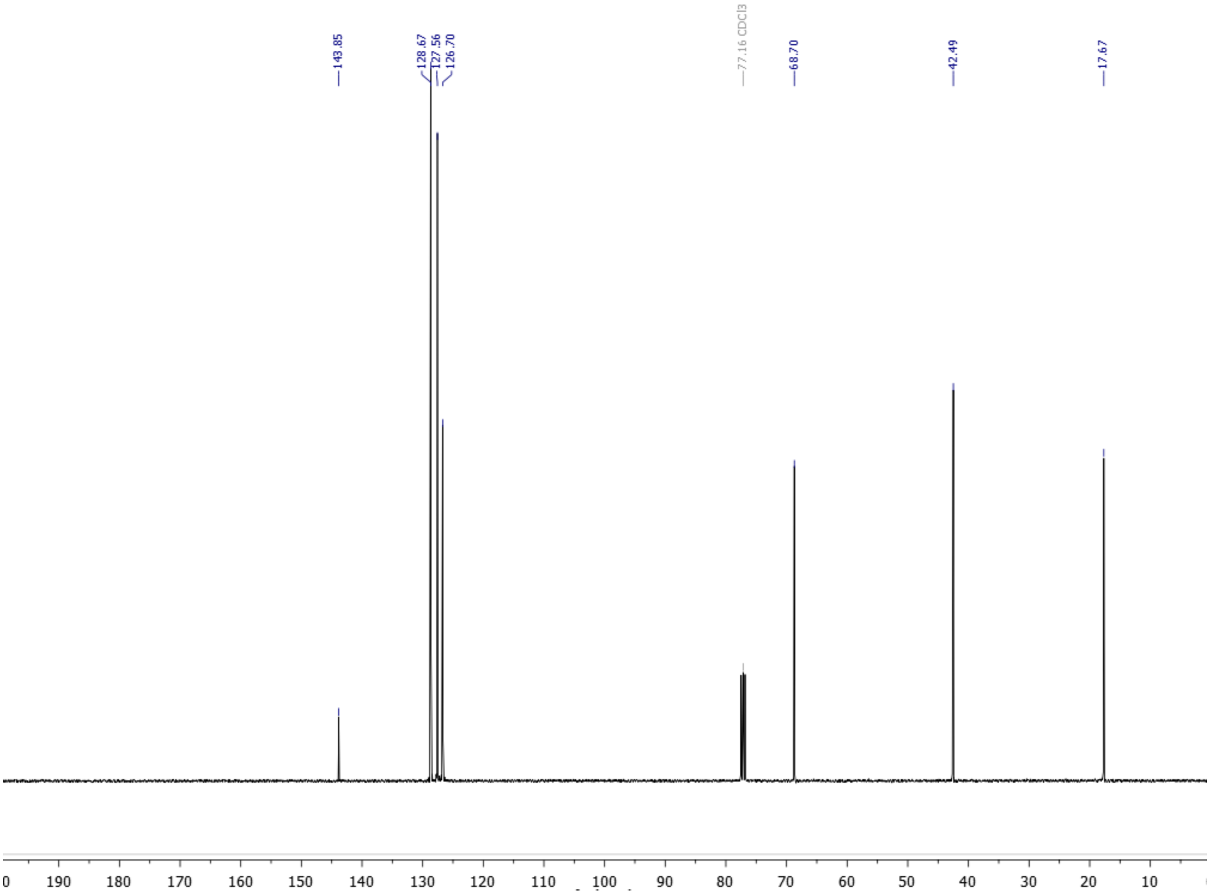
(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **9**



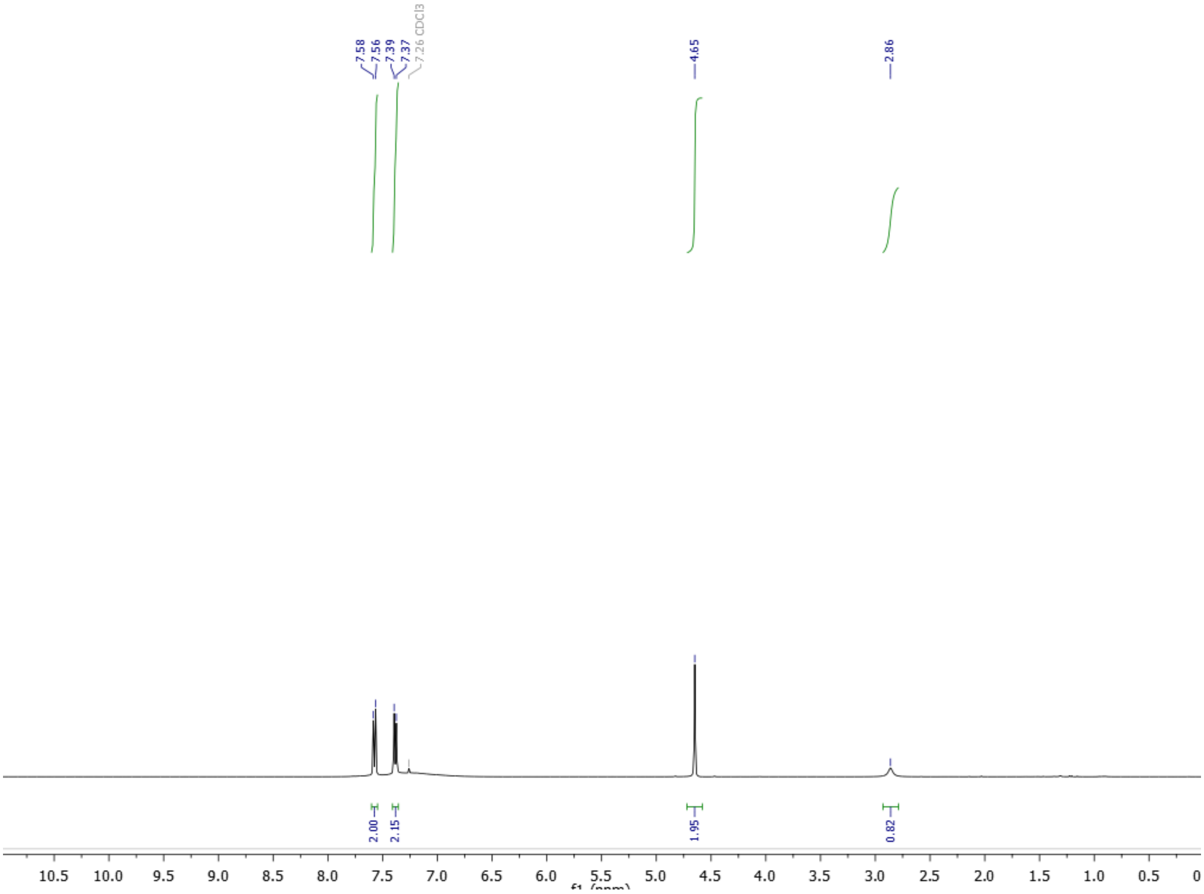


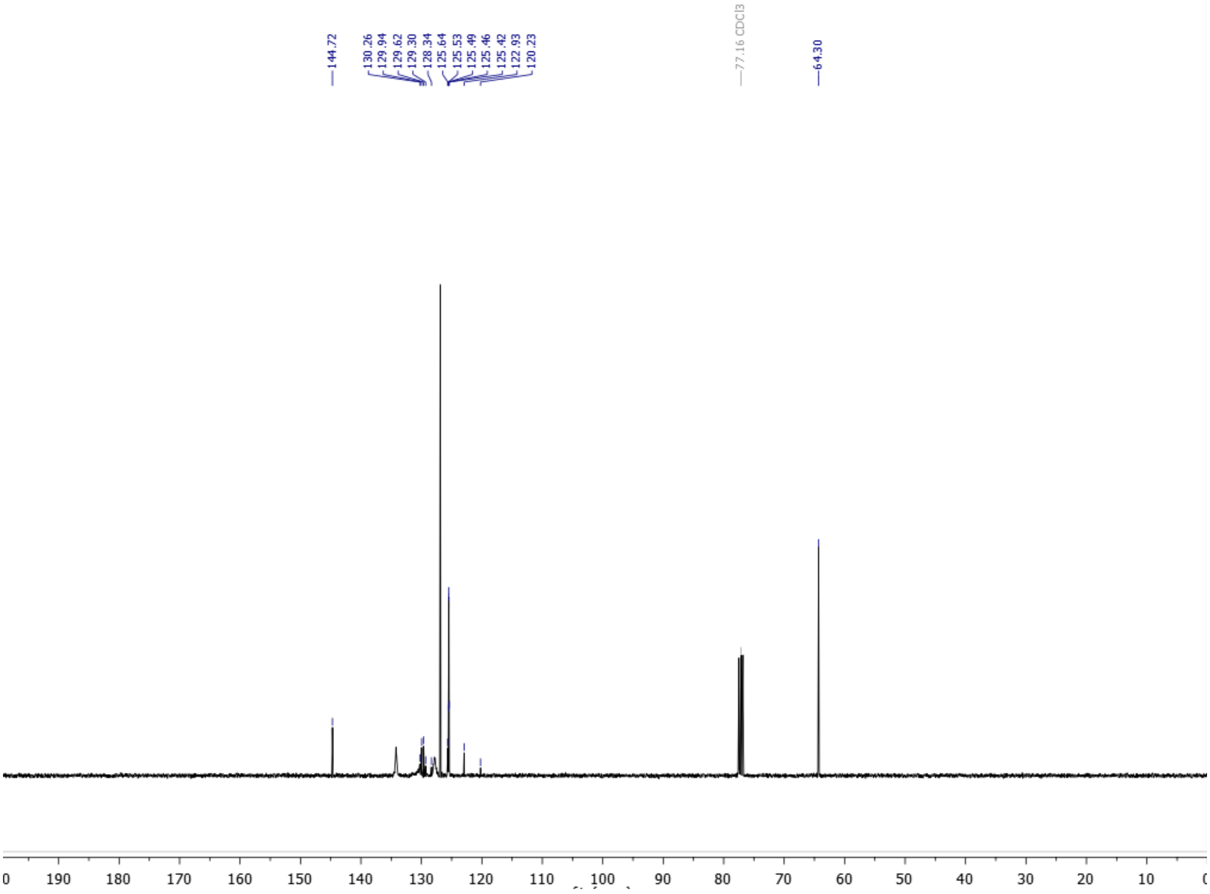
(*R*)-2-phenylpropan-1-ol **10**



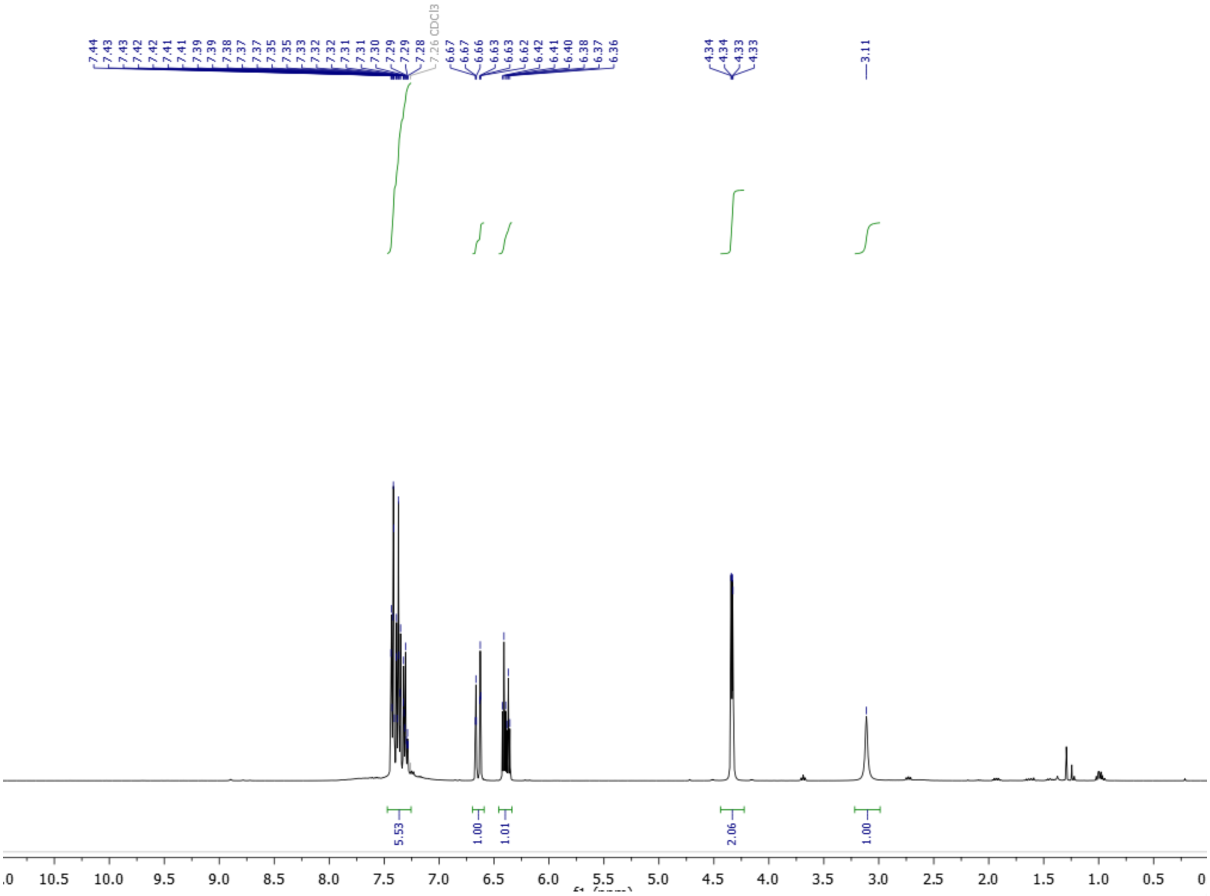


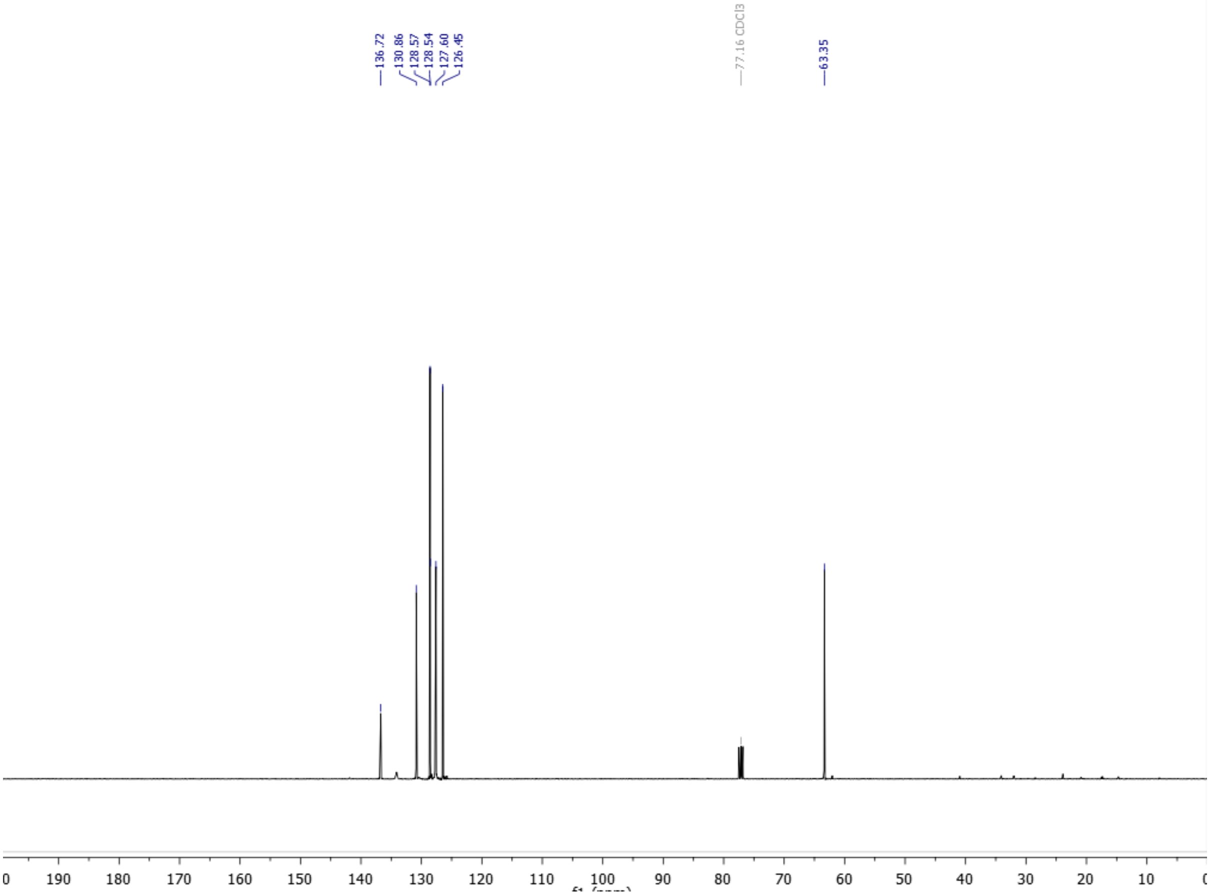
(4-(Trifluoromethyl)phenyl)methanol **11**



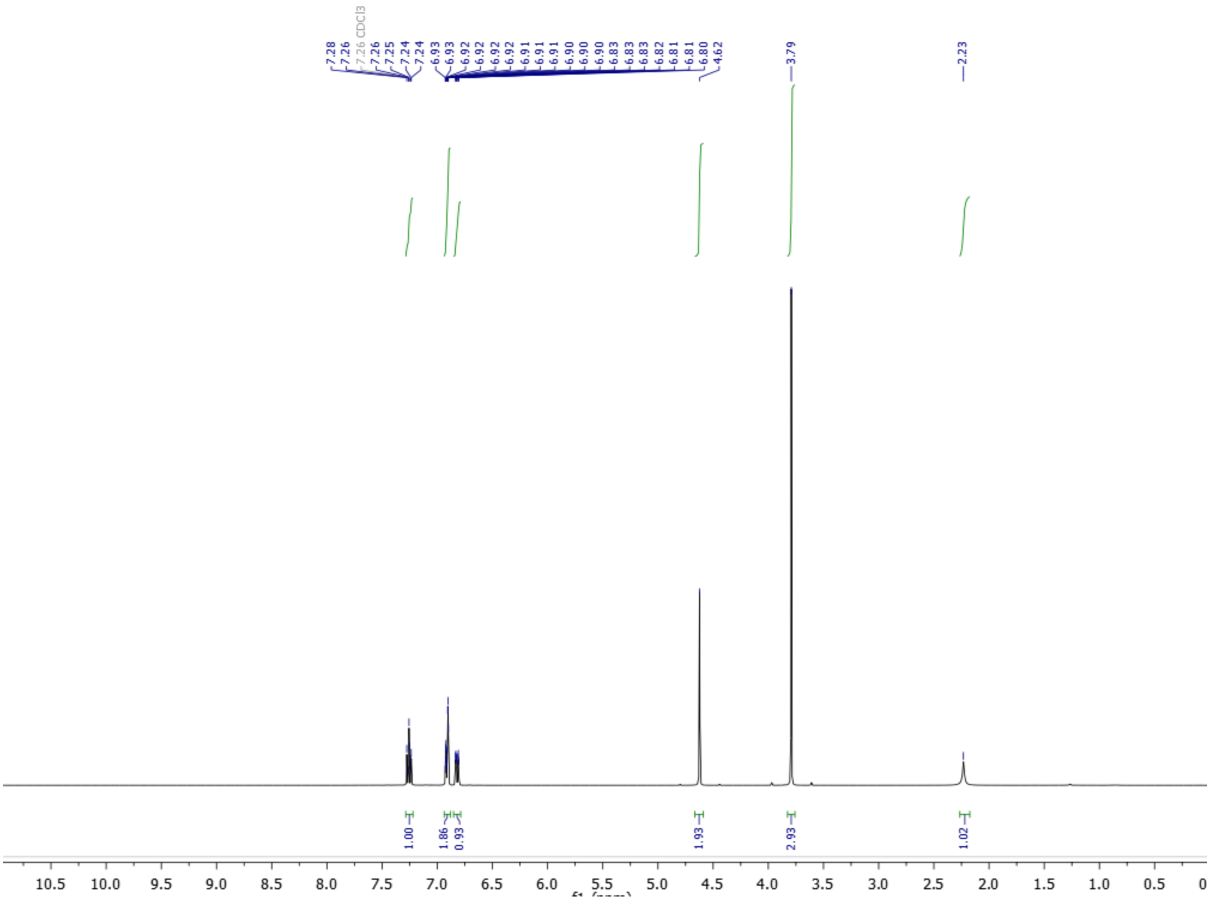


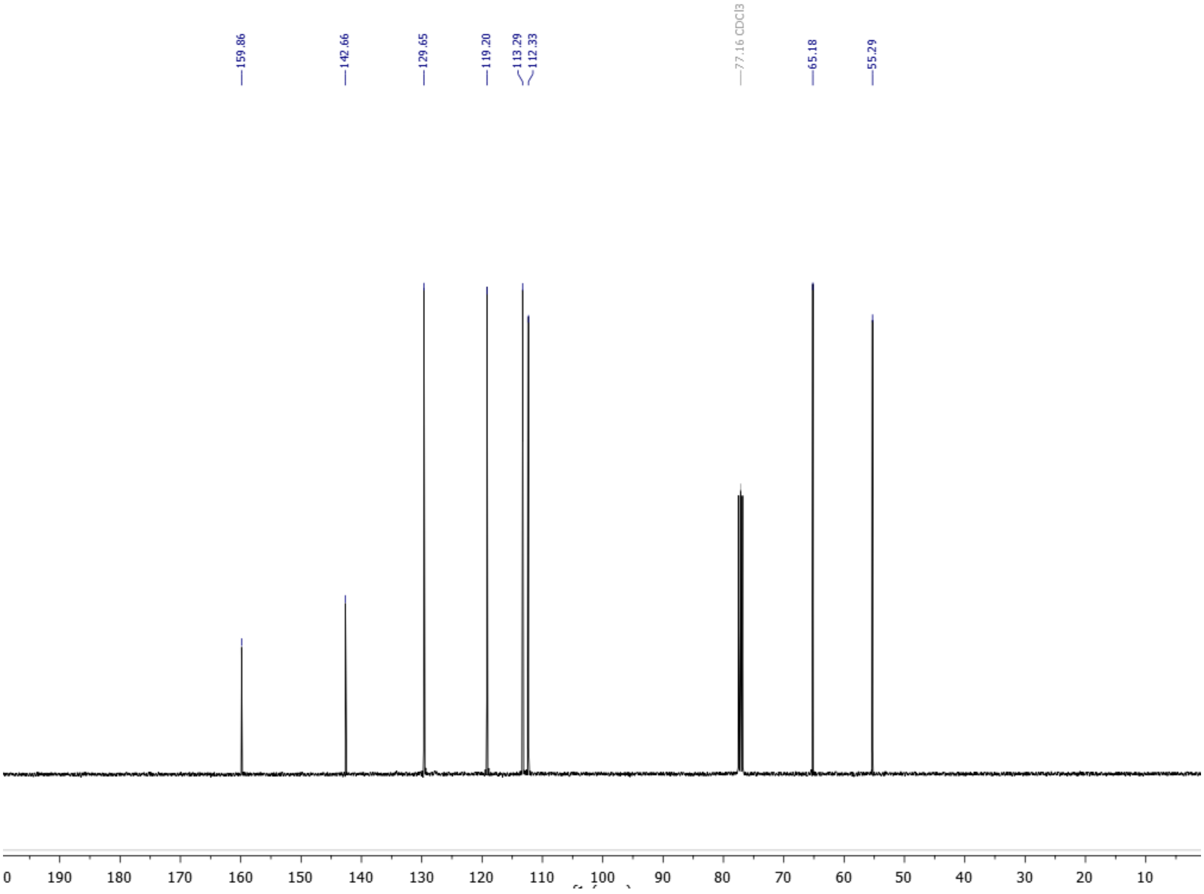
(*E*)-3-Phenylprop-2-en-1-ol **12**



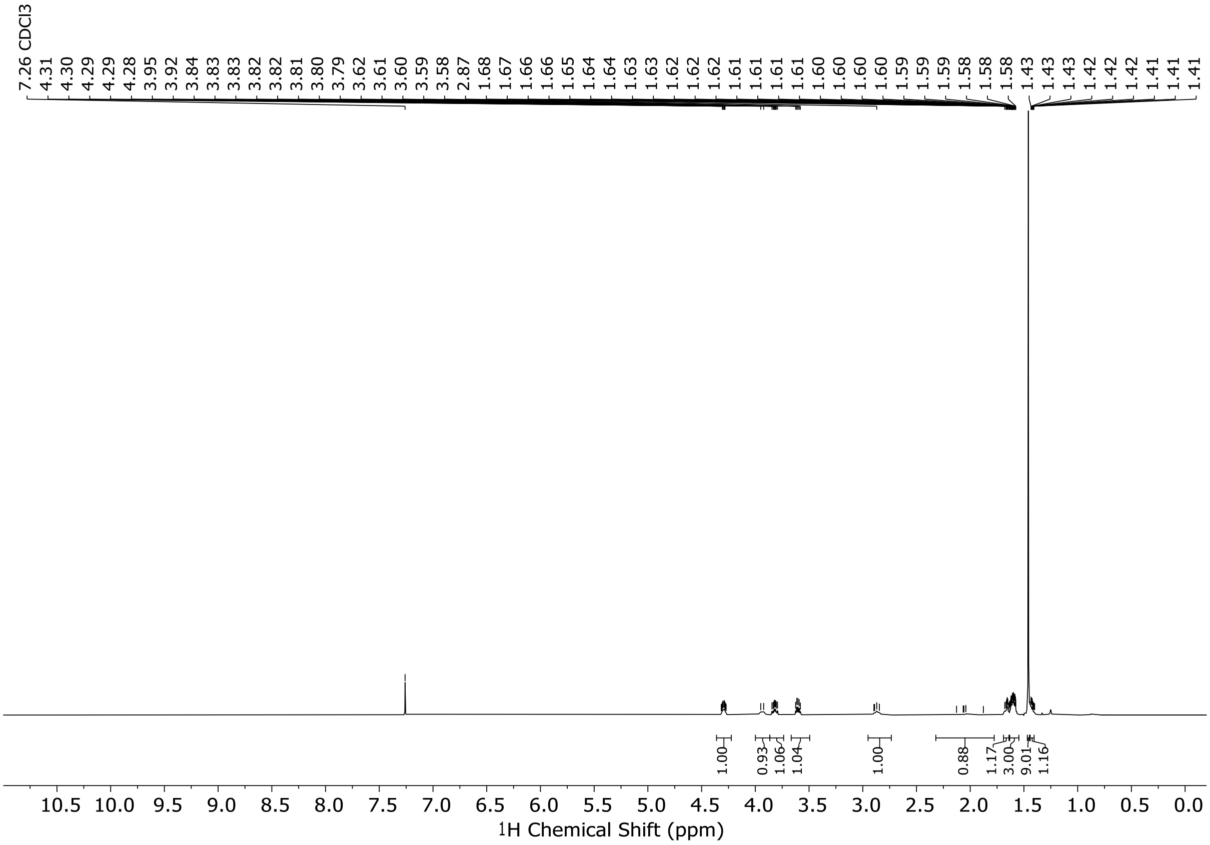


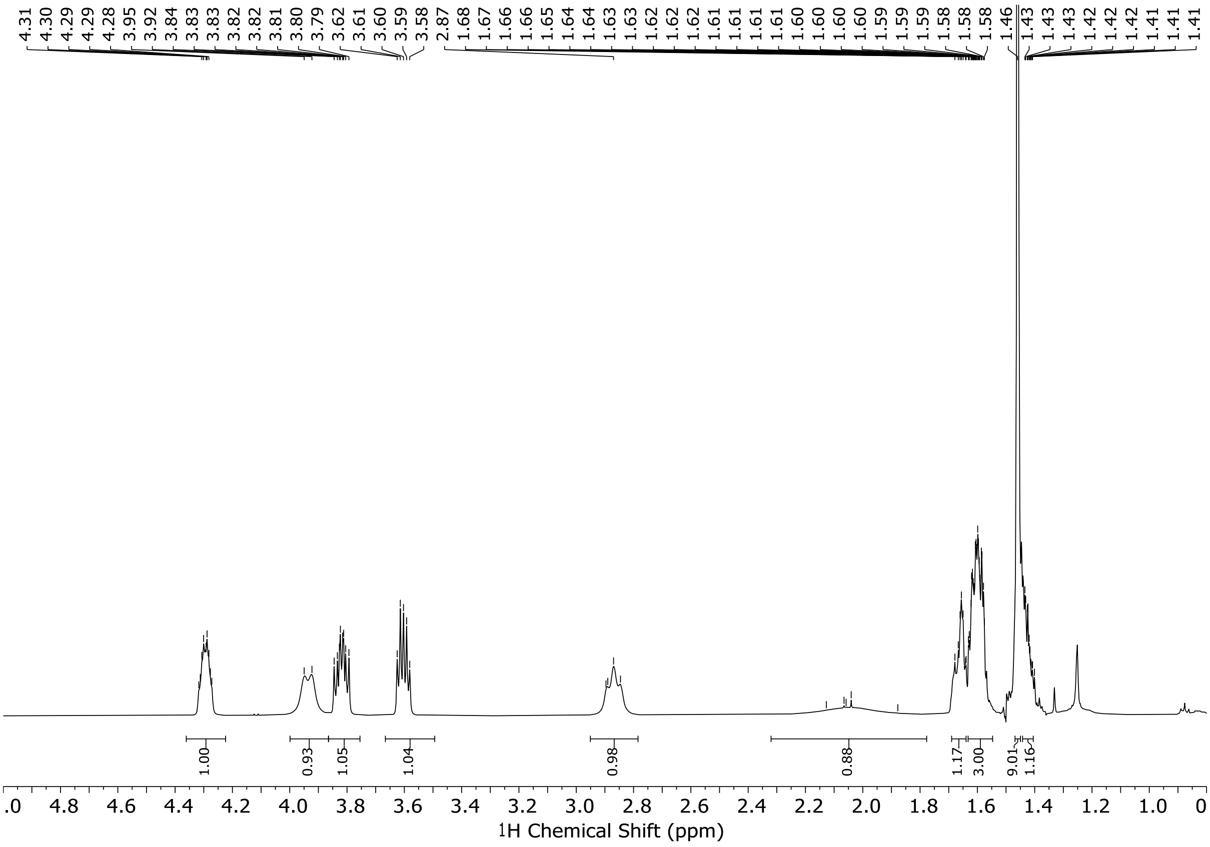
<u>(3-Methoxyphenyl)methanol **13**</u>

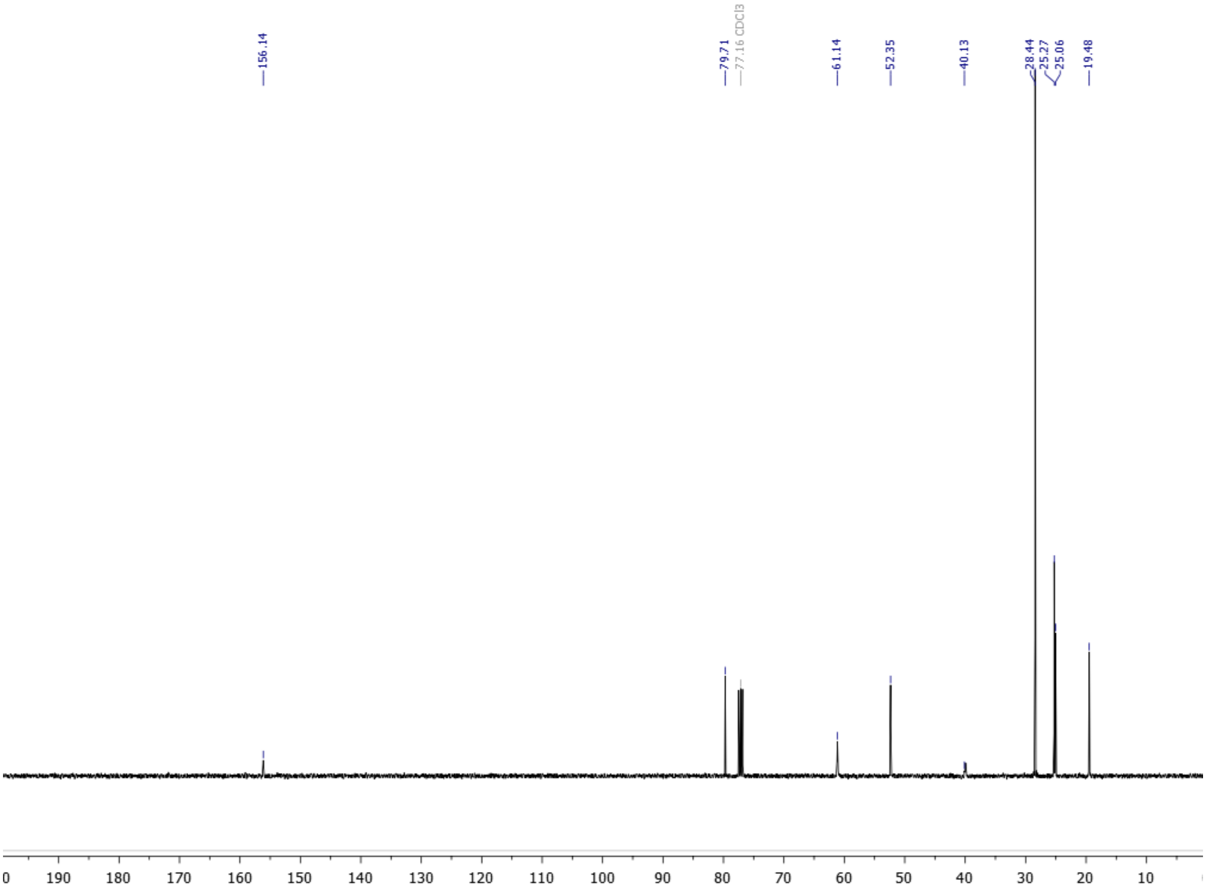




tert-Butyl 2-(hydroxymethyl)piperidine-1-carboxylate **14**



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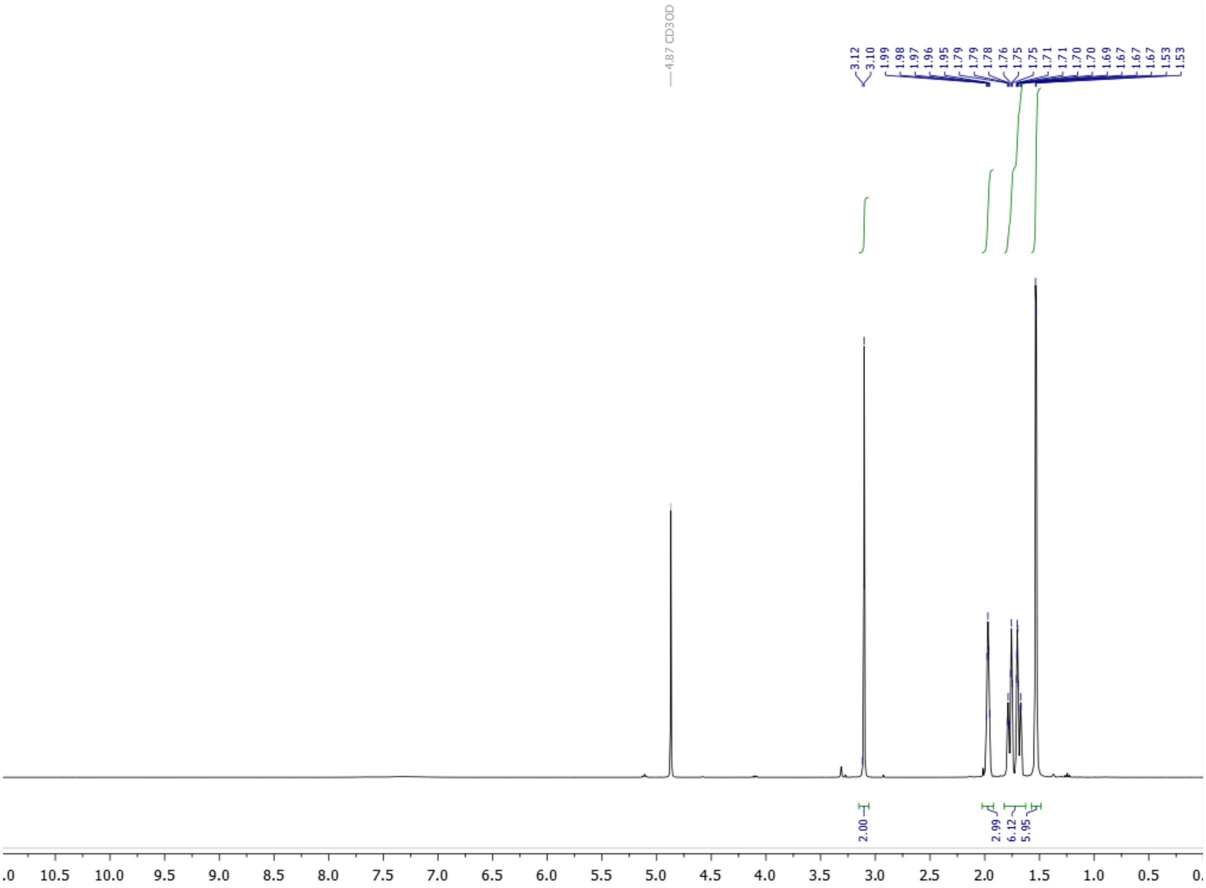
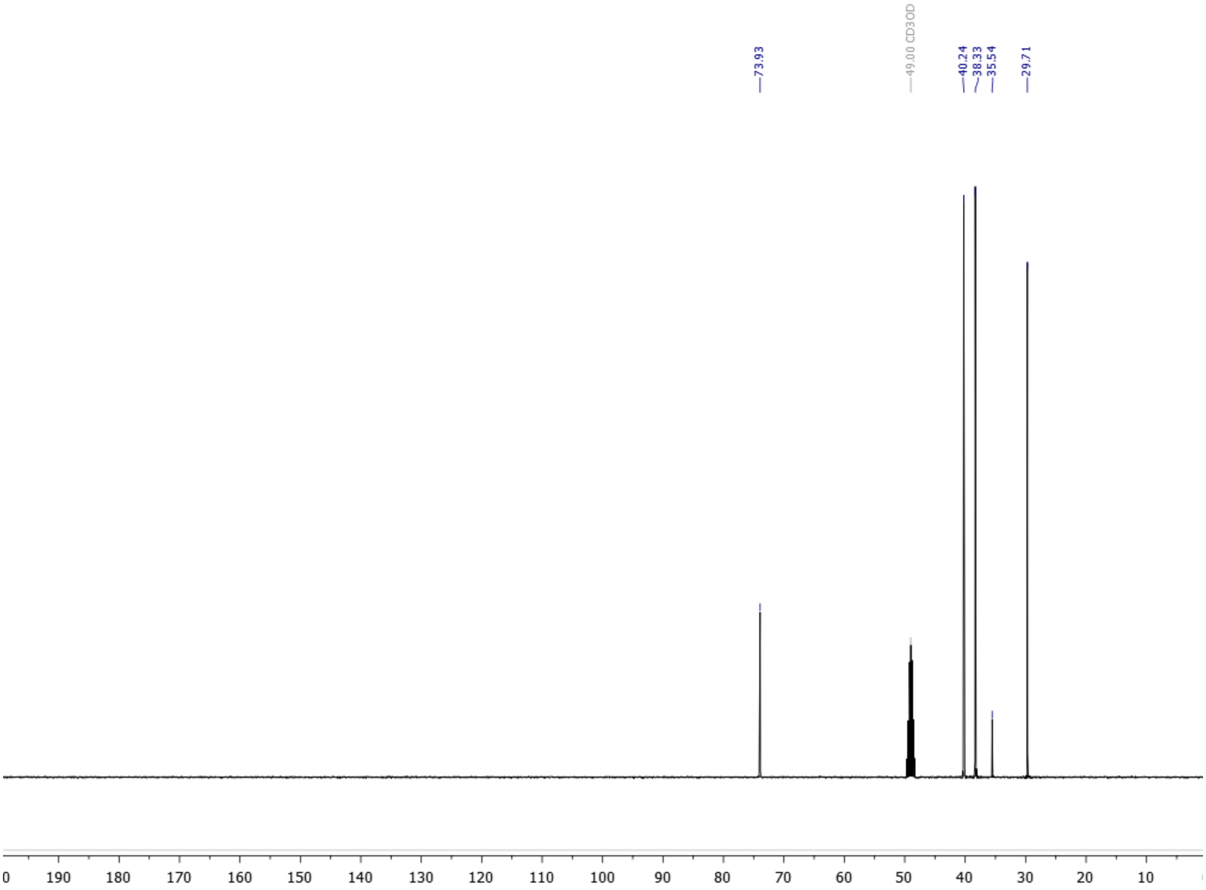
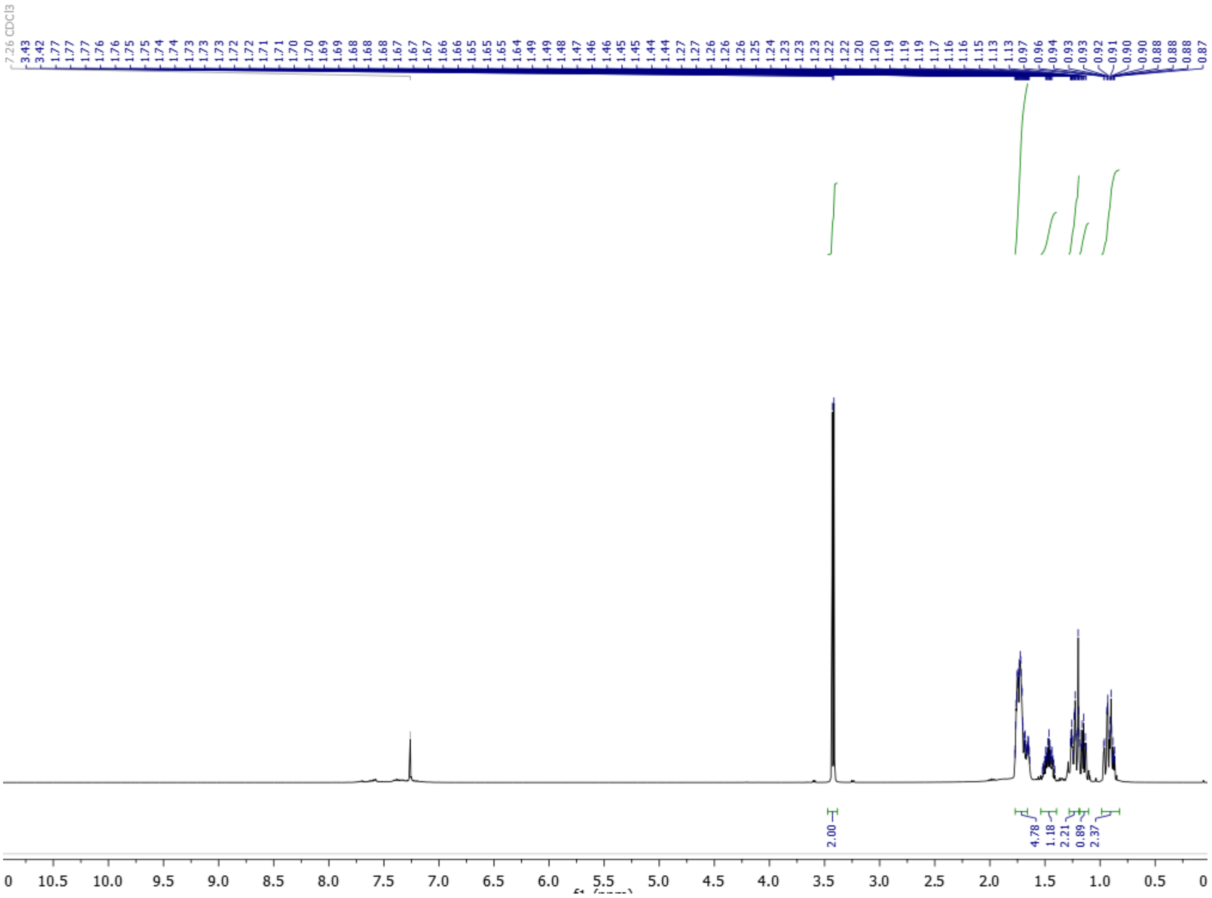
79.71
77.16 CDCl3
61.14
52.35
40.13
28.44
25.27
25.06
19.48
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

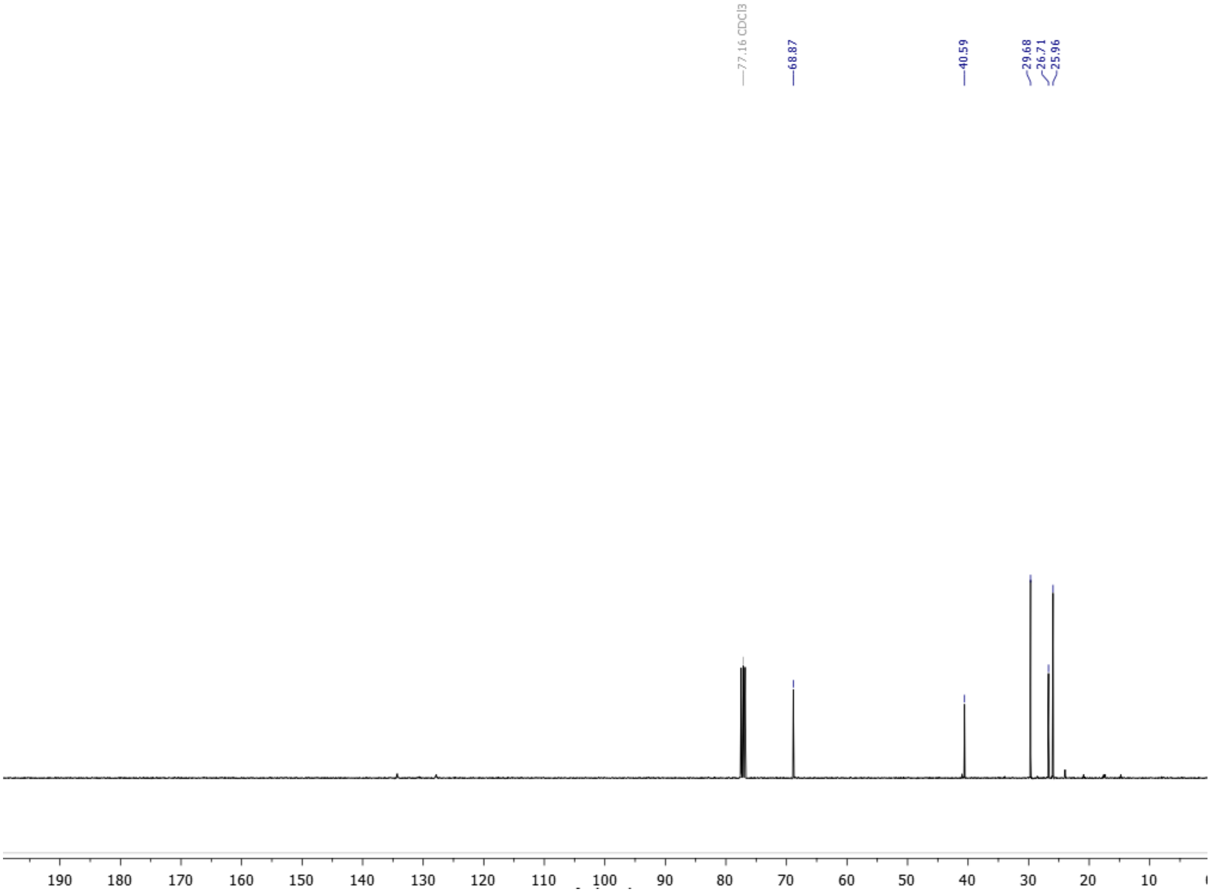
((3*R*,5*R*,7*R*)-Adamantan-1-yl)methanol **15**



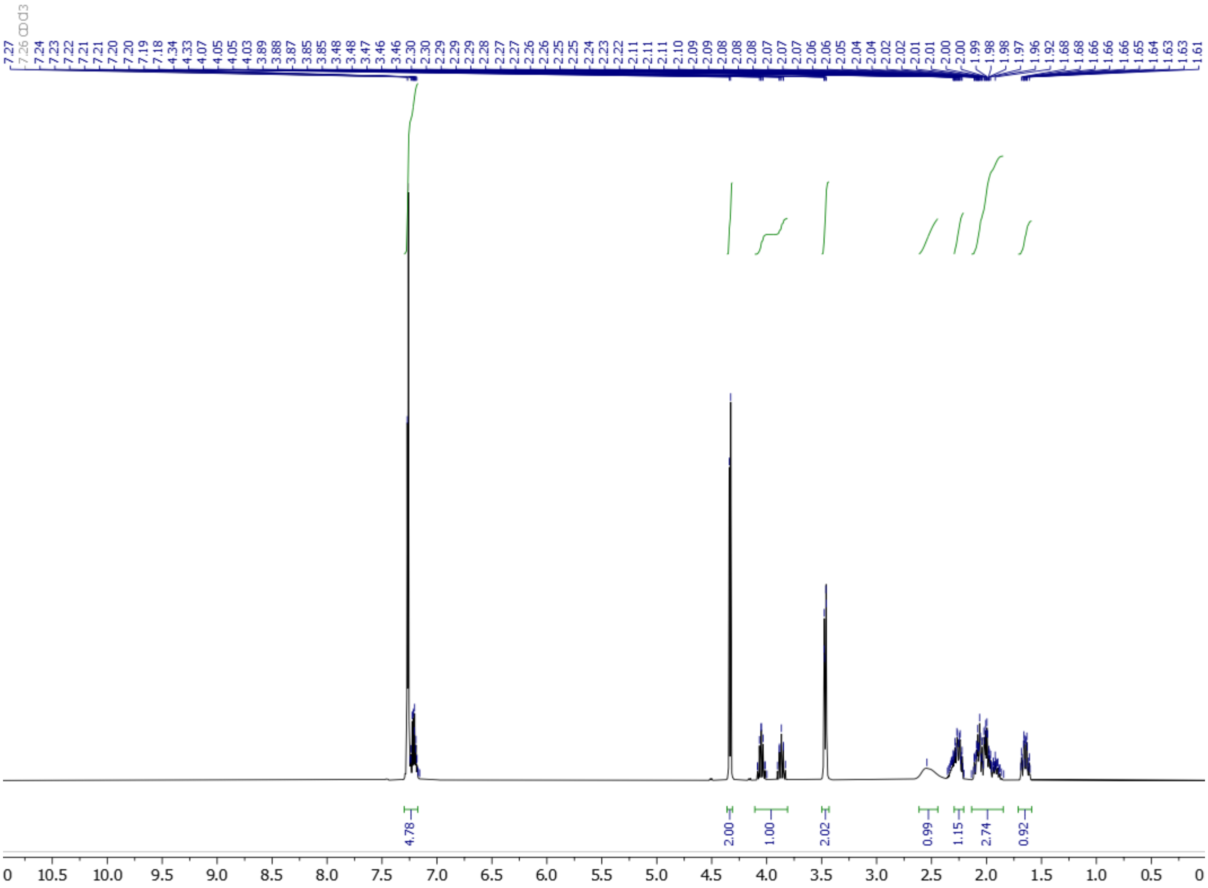


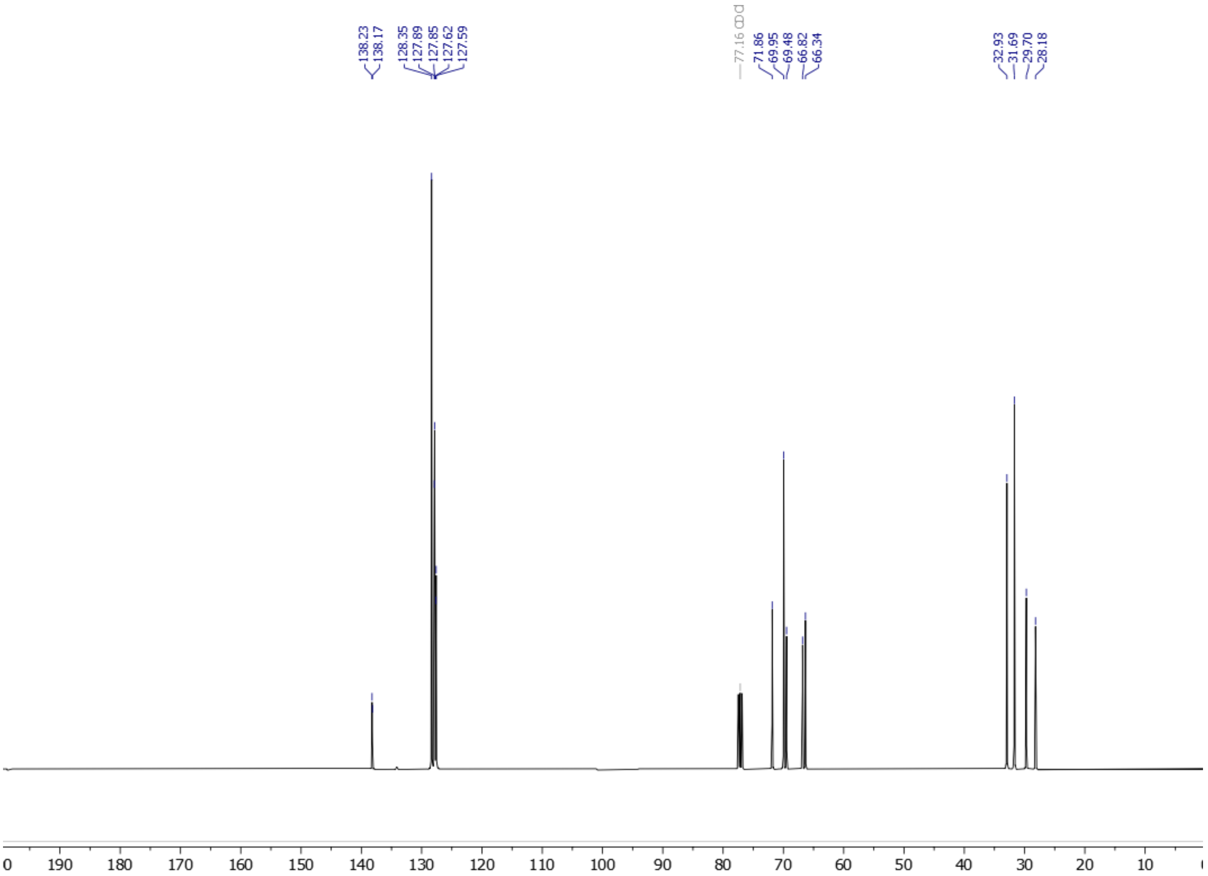
Cyclohexylmethanol **16**



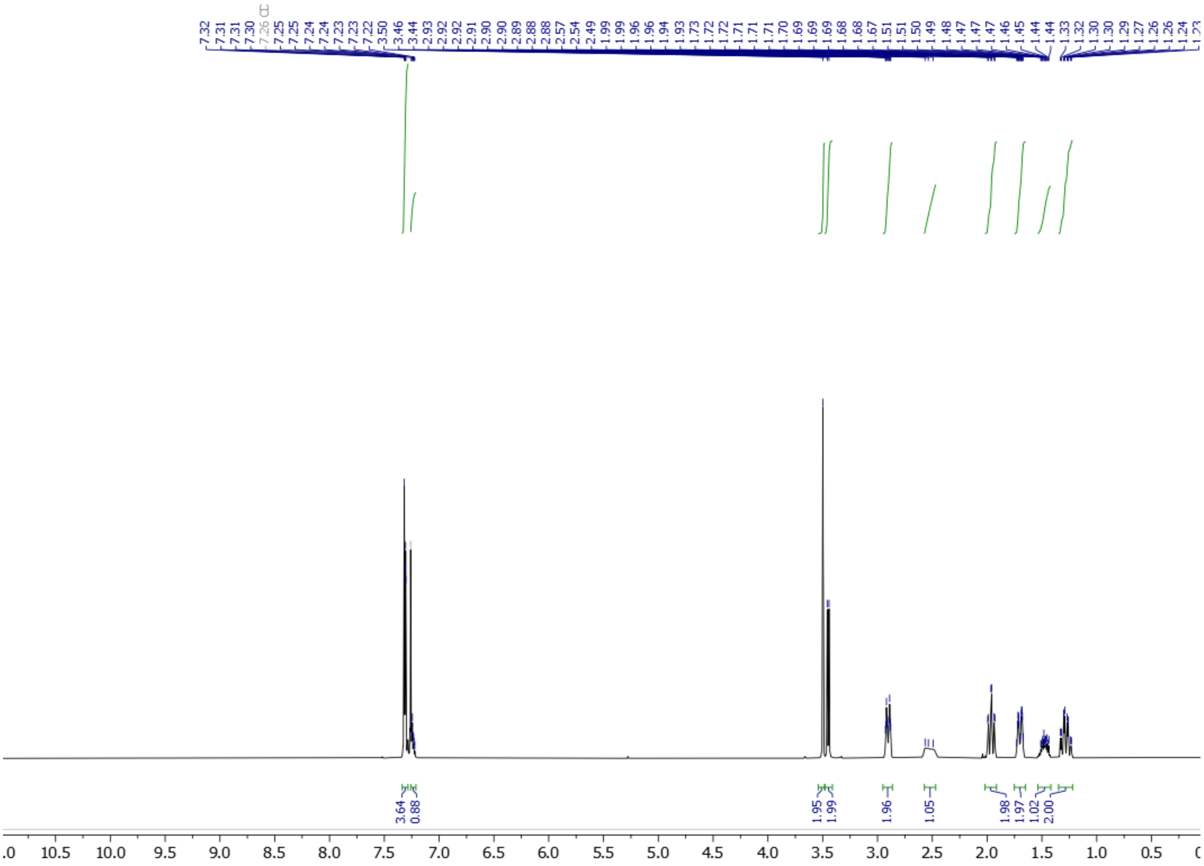


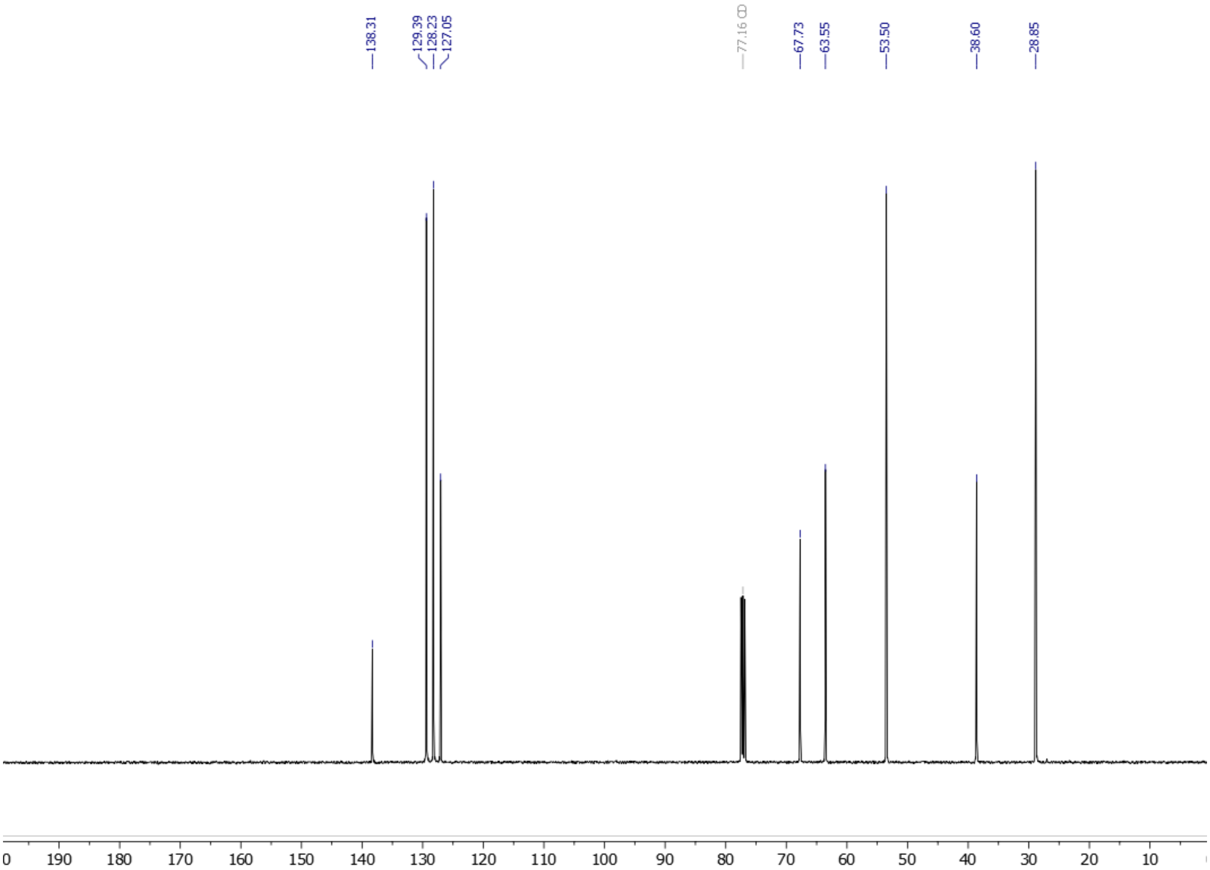
(3-(Benzyloxy)cyclobutyl)methanol **17**



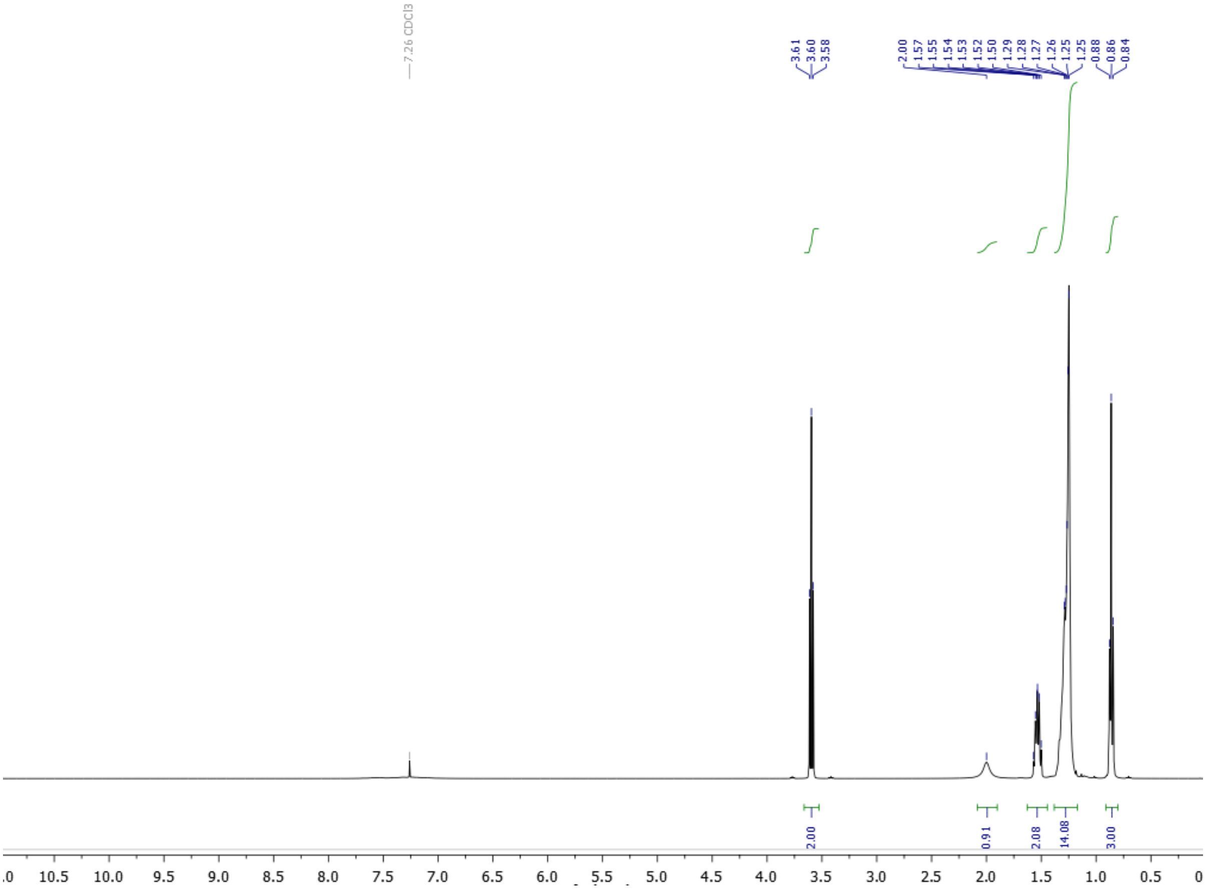


(1-Benzylpiperidin-4-yl)methanol **18**





Decan-1-ol **20**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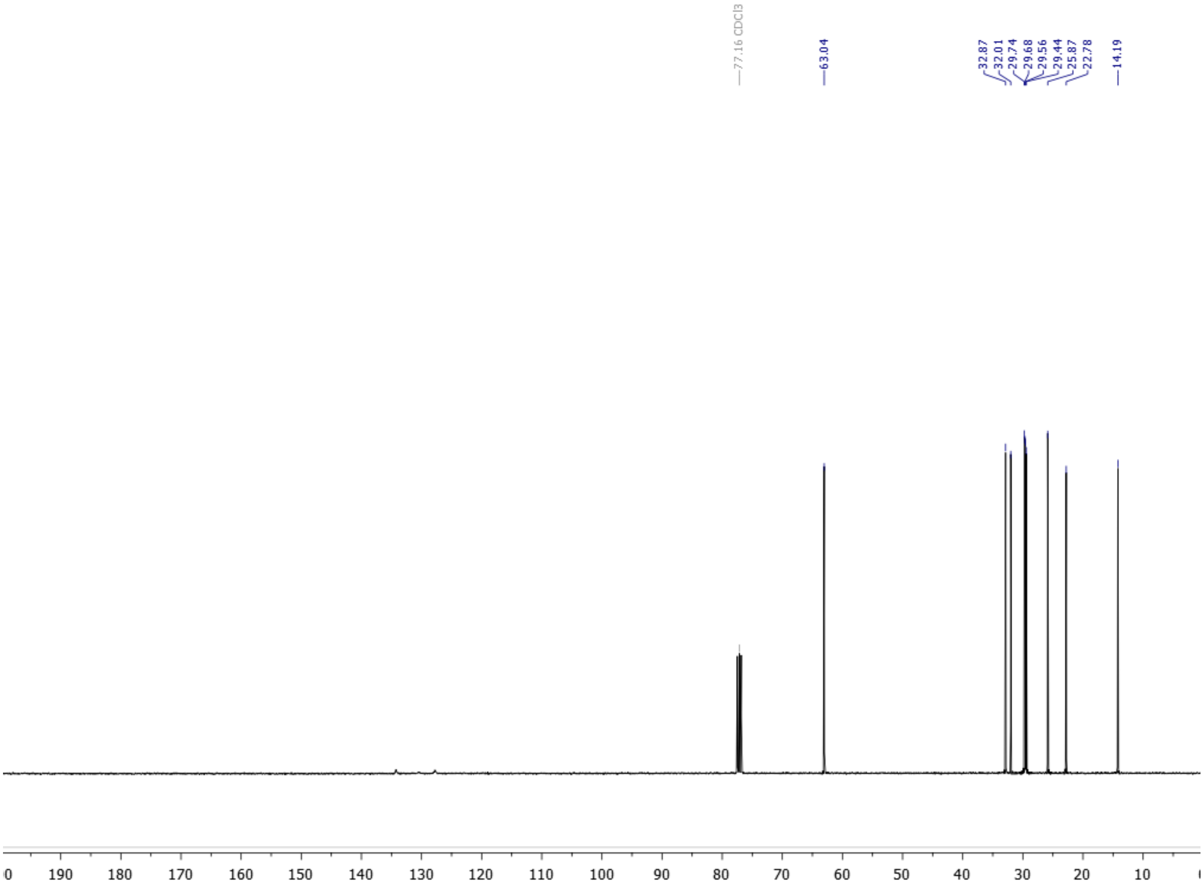
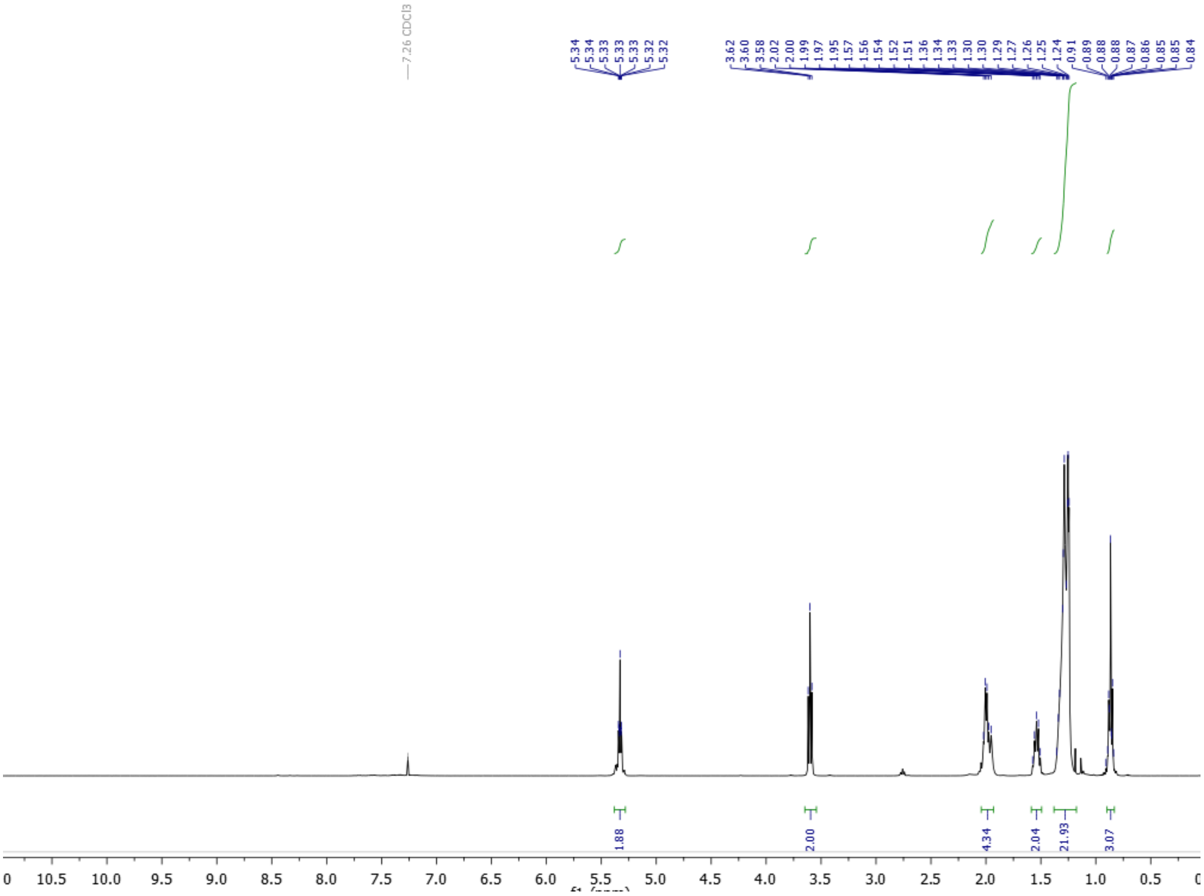
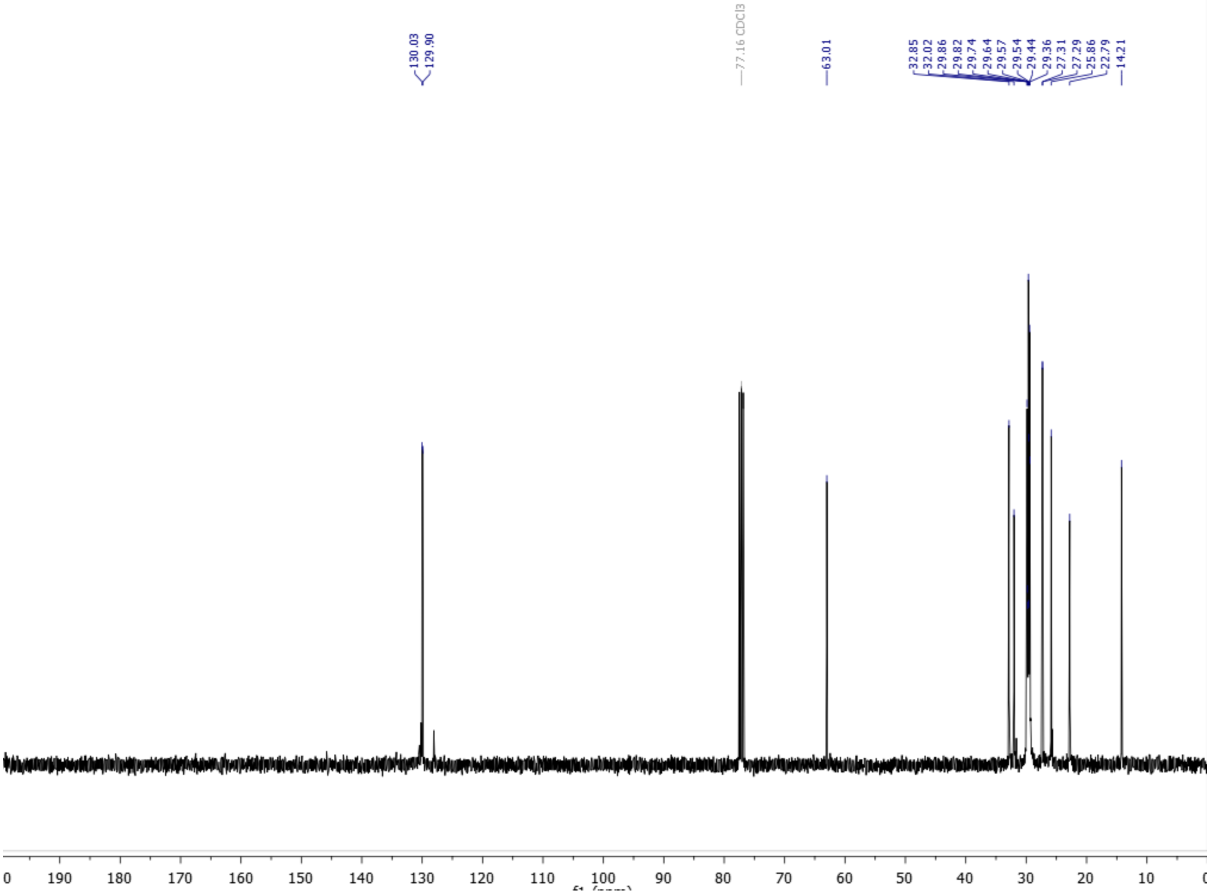
3.61
3.60
3.58
2.00
1.57
1.55
1.54
1.53
1.52
1.50
1.29
1.28
1.27
1.26
1.25
1.25
0.88
0.86
0.84
2.00
0.91
2.08
14.08
3.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

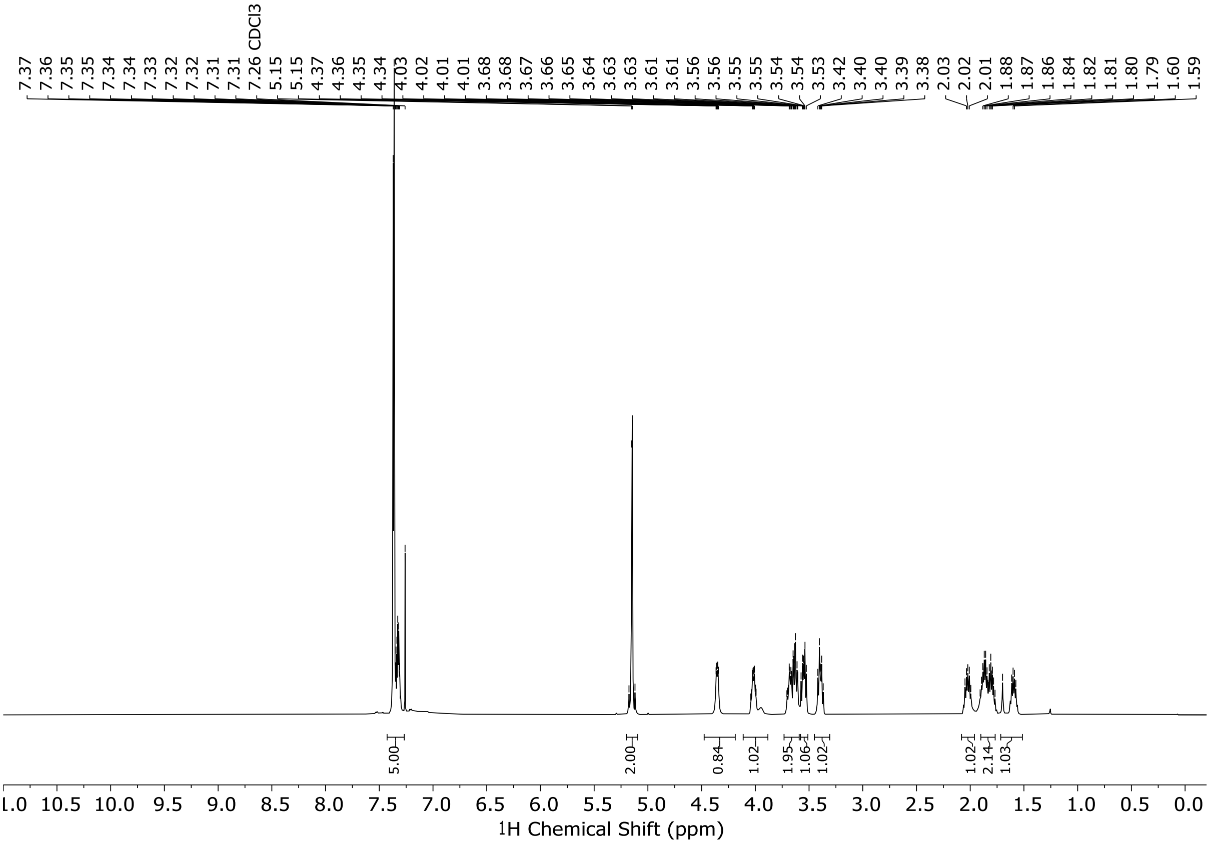

77.16 CDCl3
63.04
32.87
32.01
29.74
29.68
29.56
29.44
25.87
22.78
14.19
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

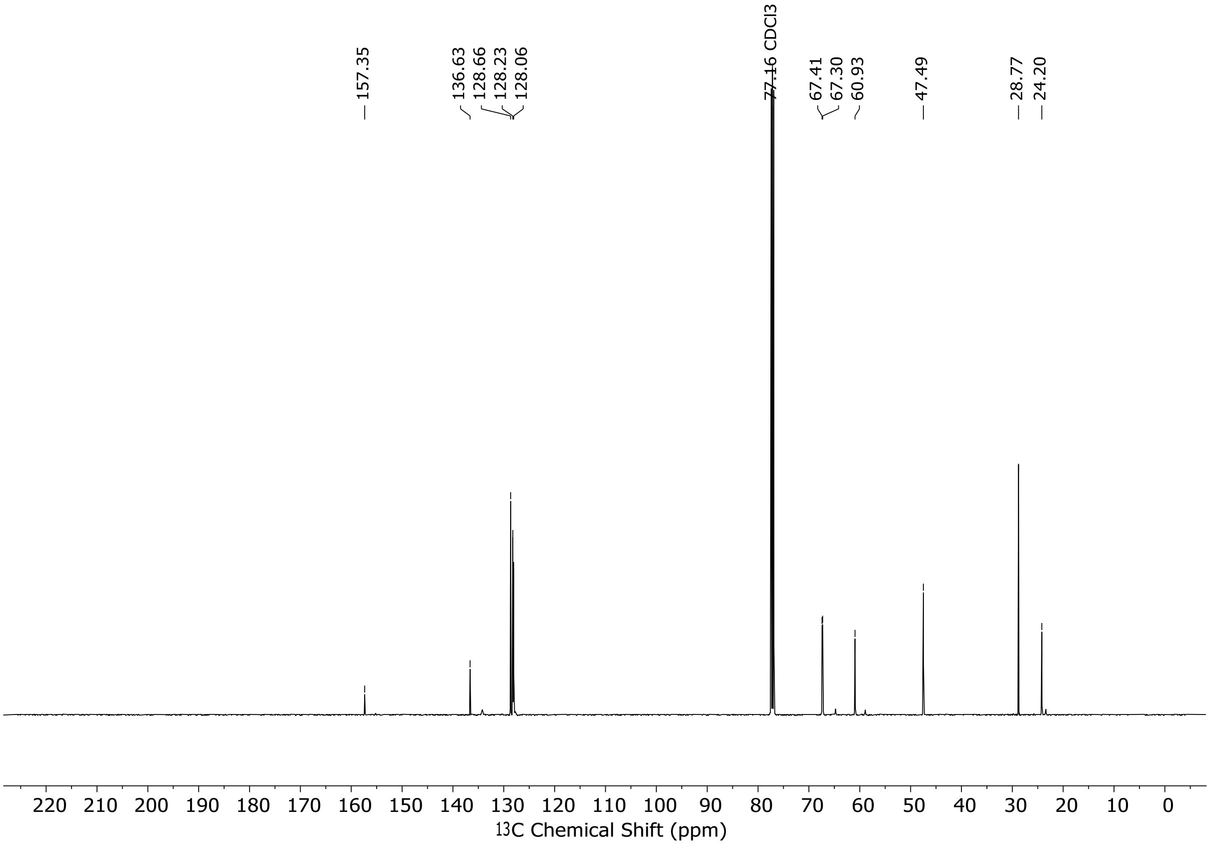
(*Z*)-Octadec-9-en-1-ol **21**



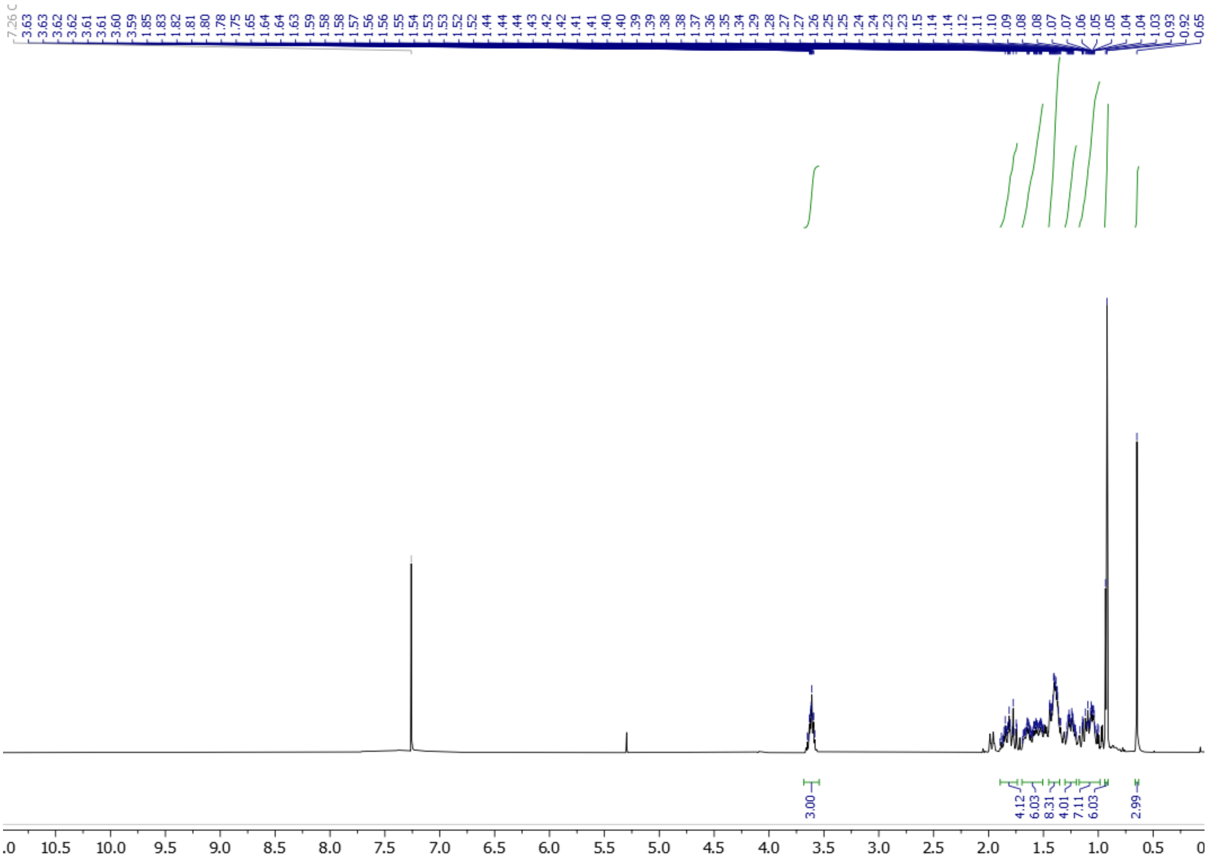


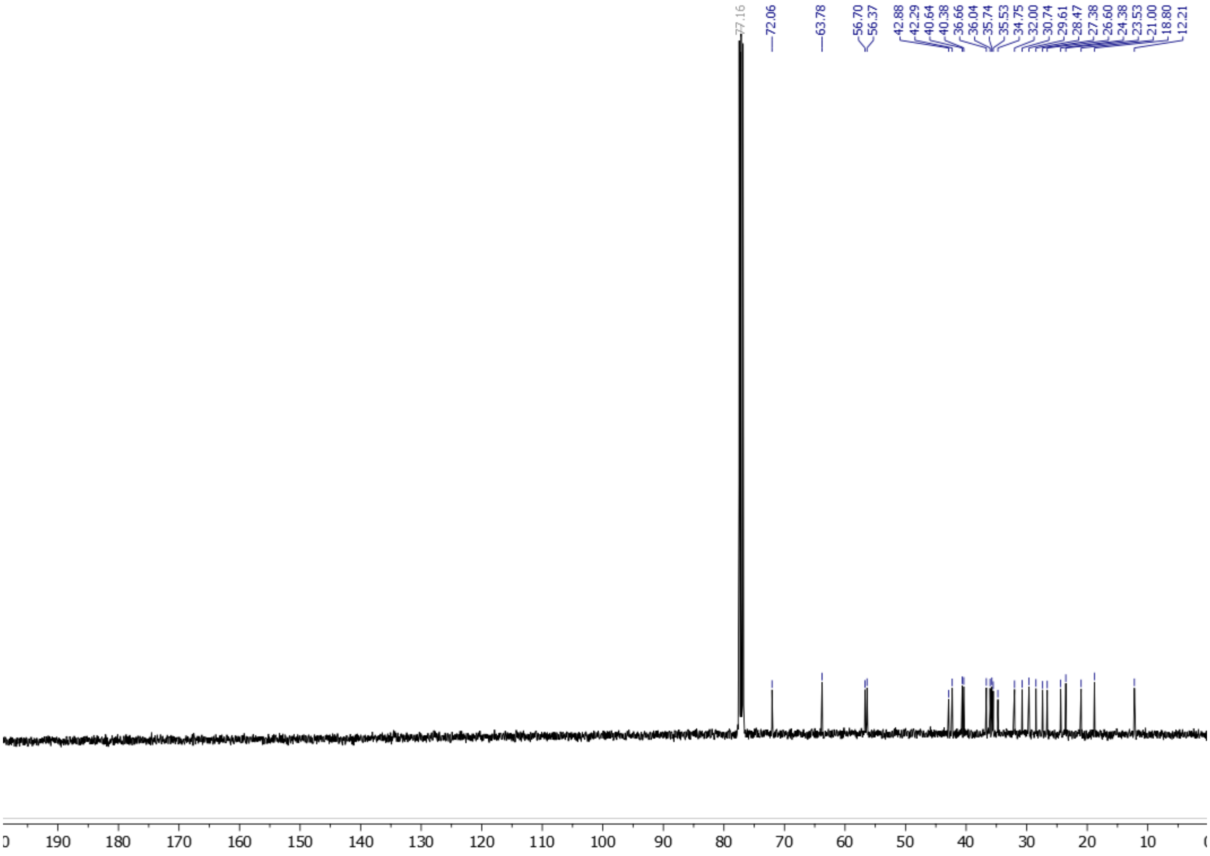
Benzyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate **22**



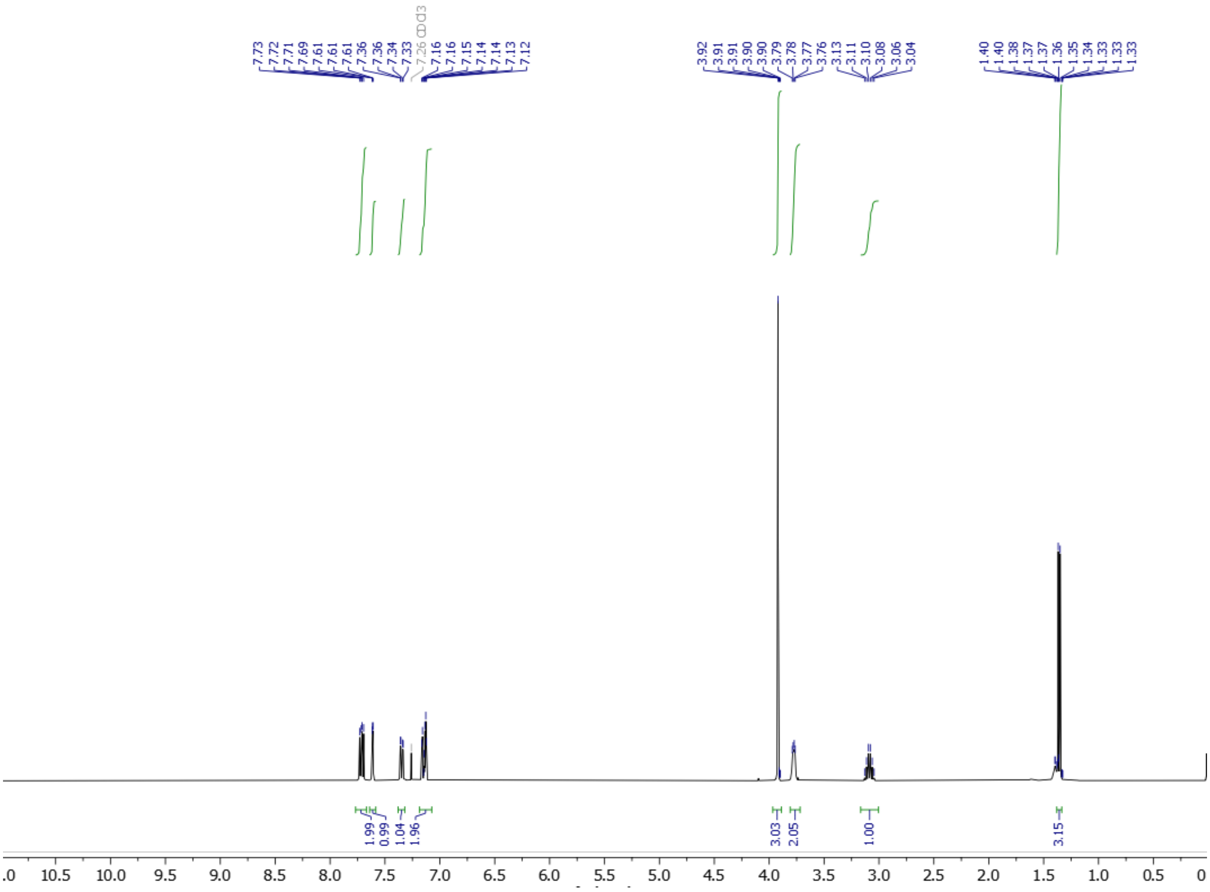


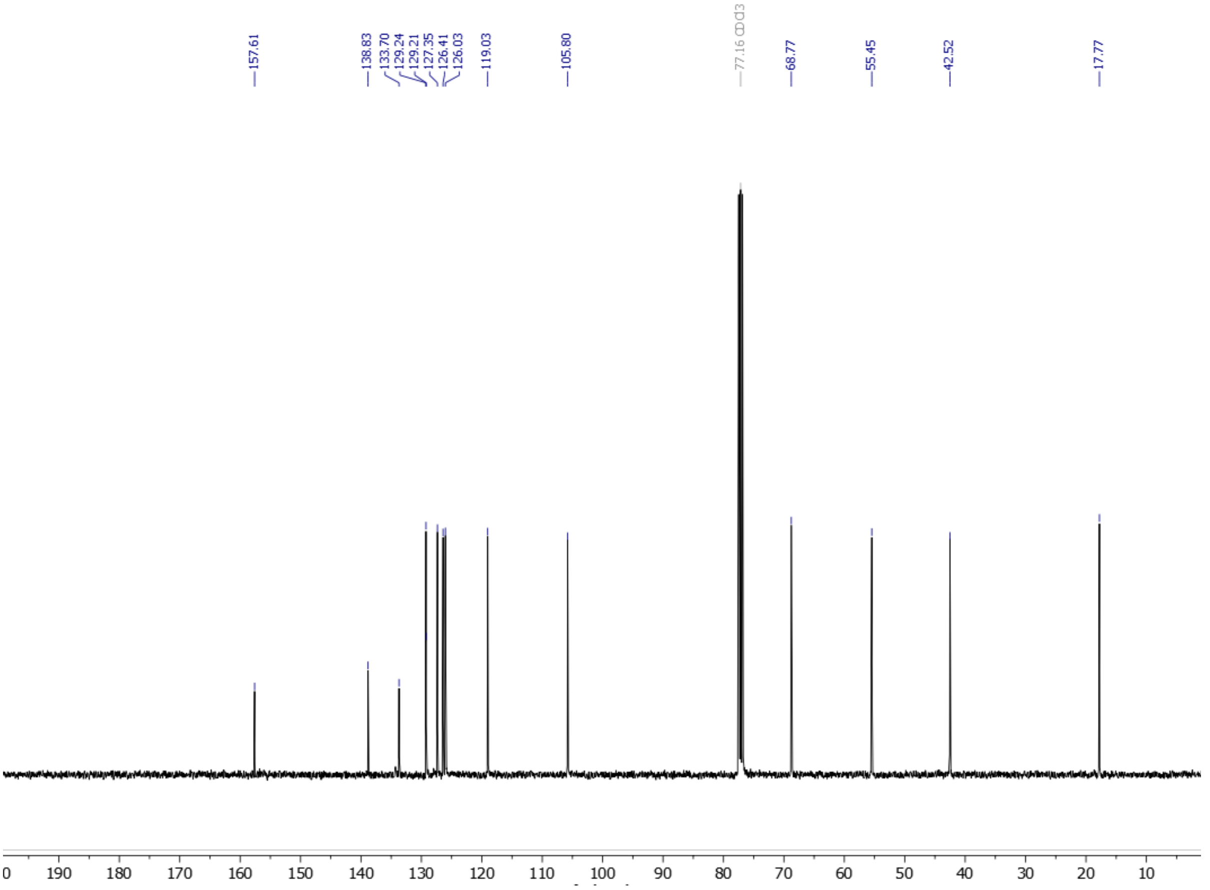
(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-hydroxypentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol **23**



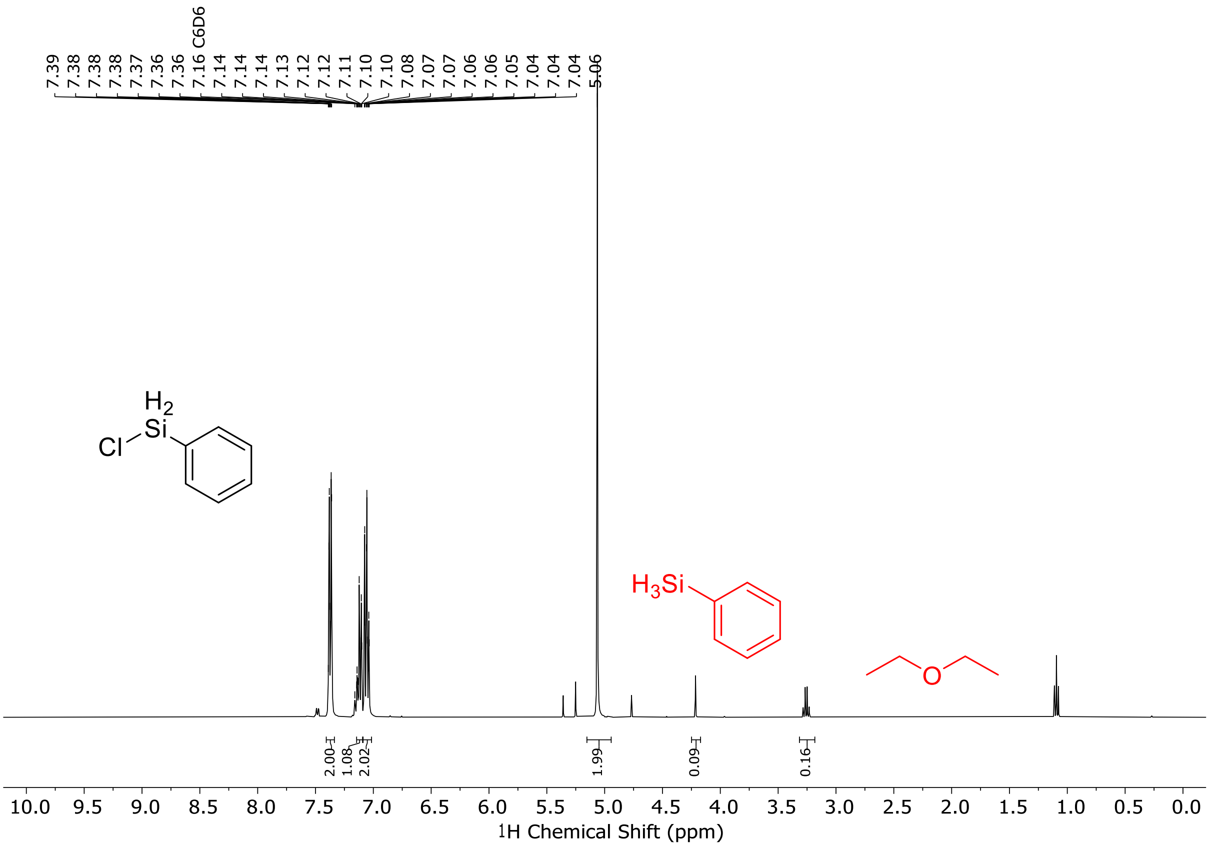


(*S*)-2-(6-Methoxynaphthalen-2-yl)propan-1-ol **19**

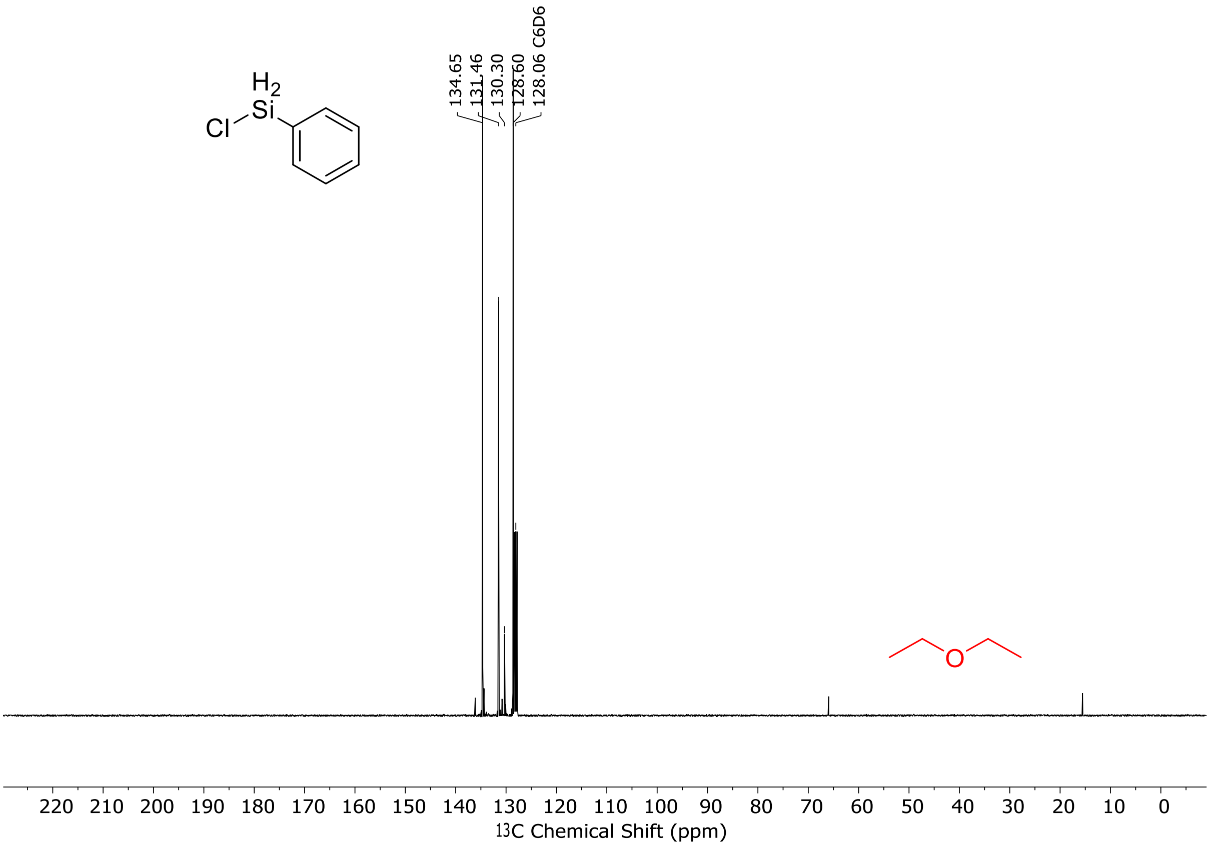




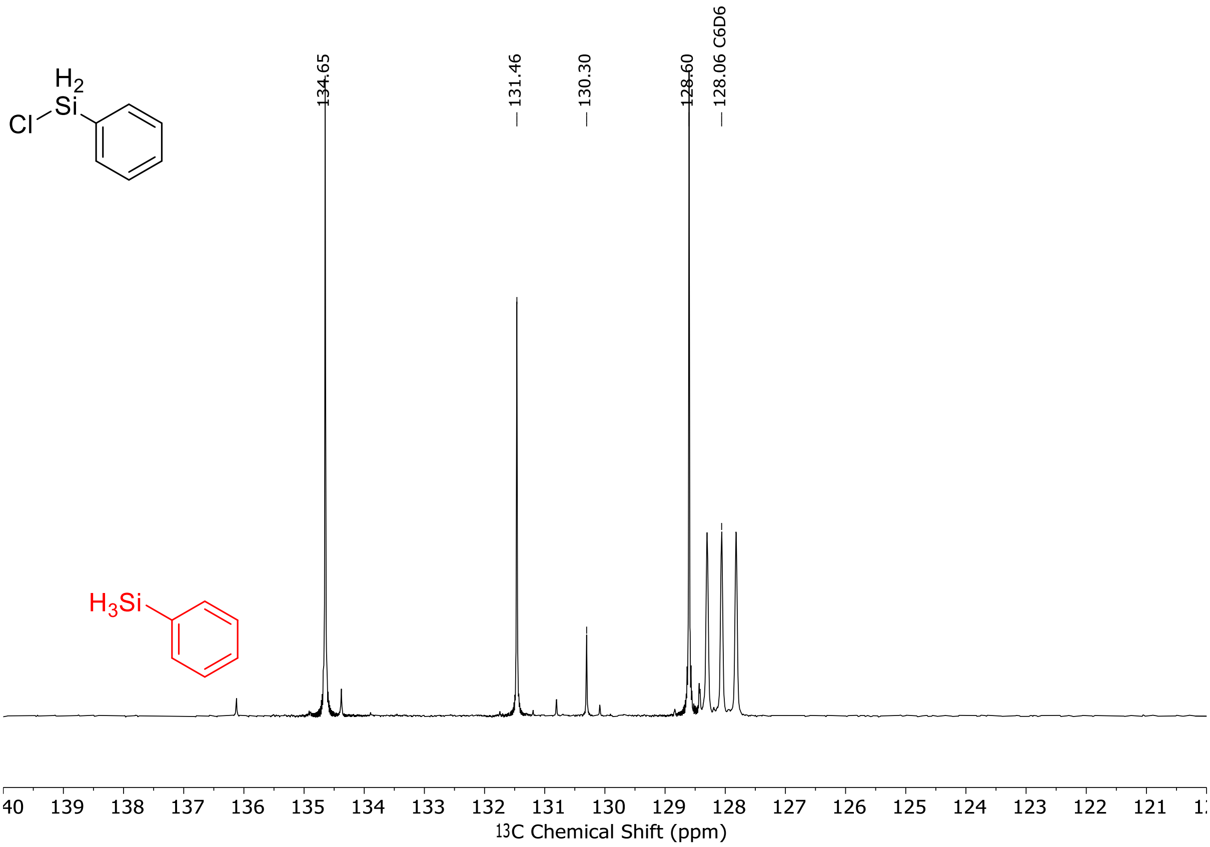
Phenylchlorosilane – ^{1}H NMR (400 MHz, C_6D_6)



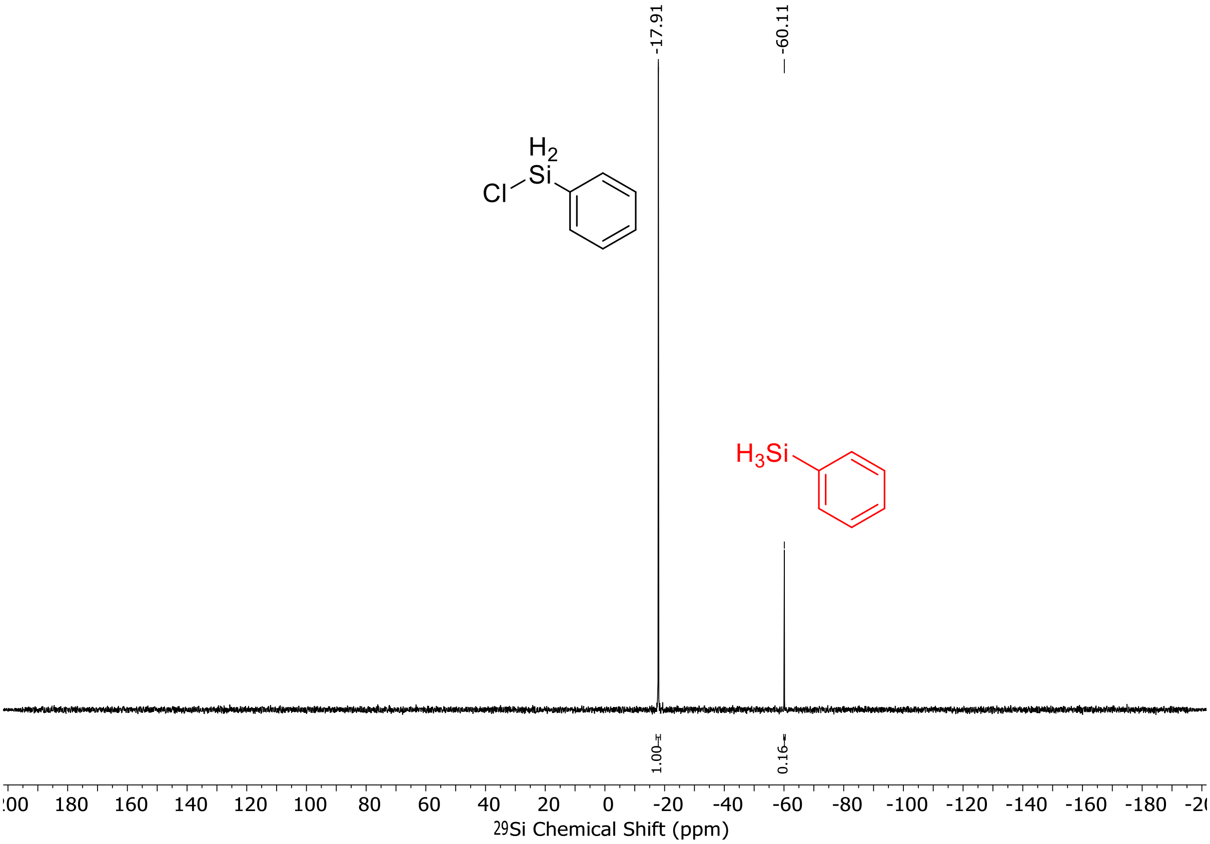
Phenylchlorosilane – $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6)



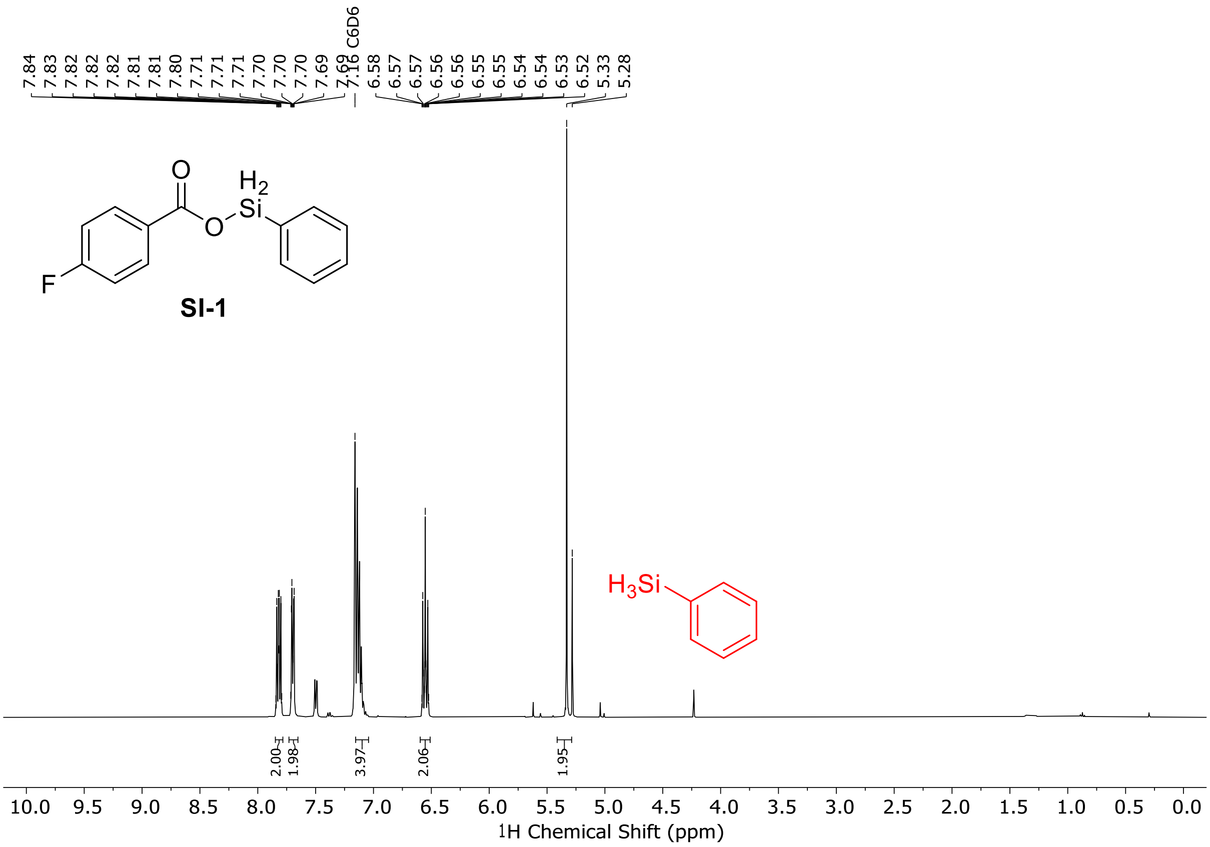
Phenylchlorosilane – $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) Expansion



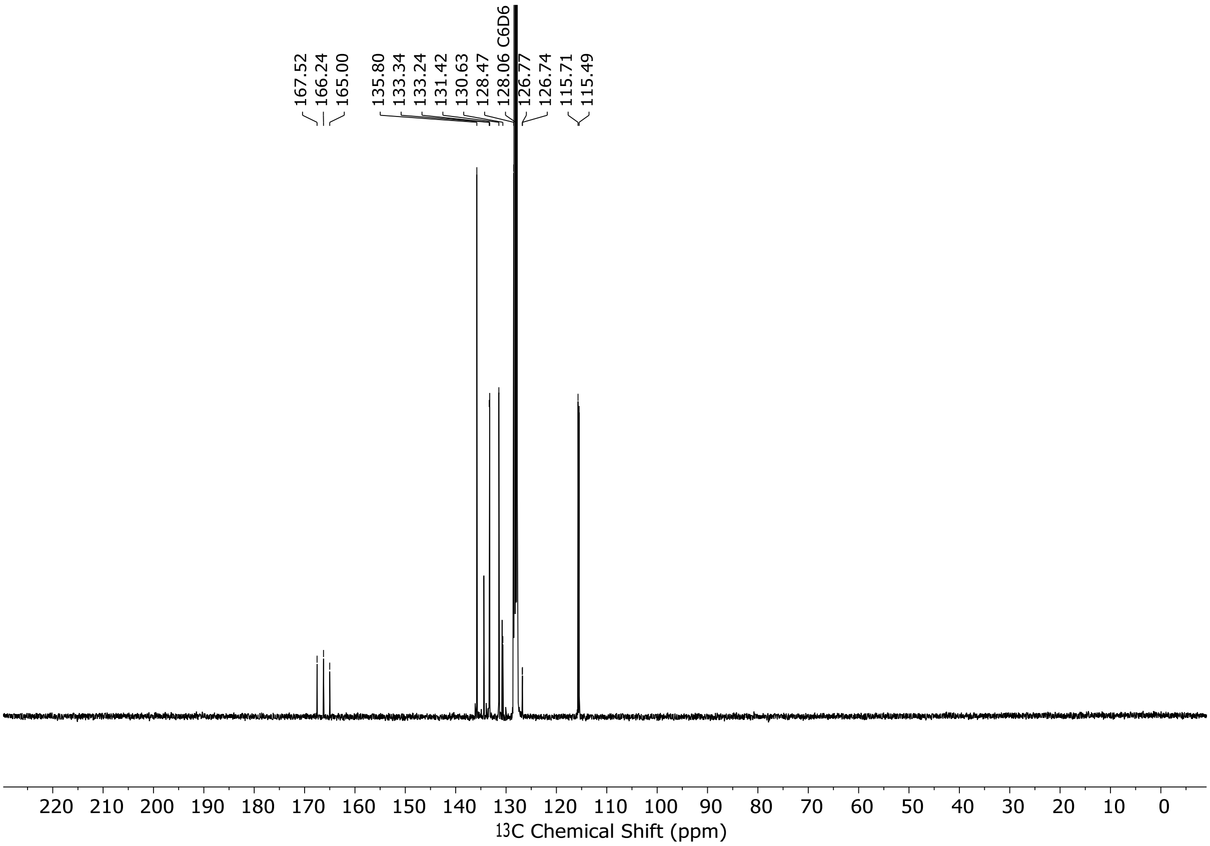
Phenylchlorosilane – $^{29}Si\{^1H\}$ NMR (79 MHz, C_6D_6) (Note: non-quantitative)



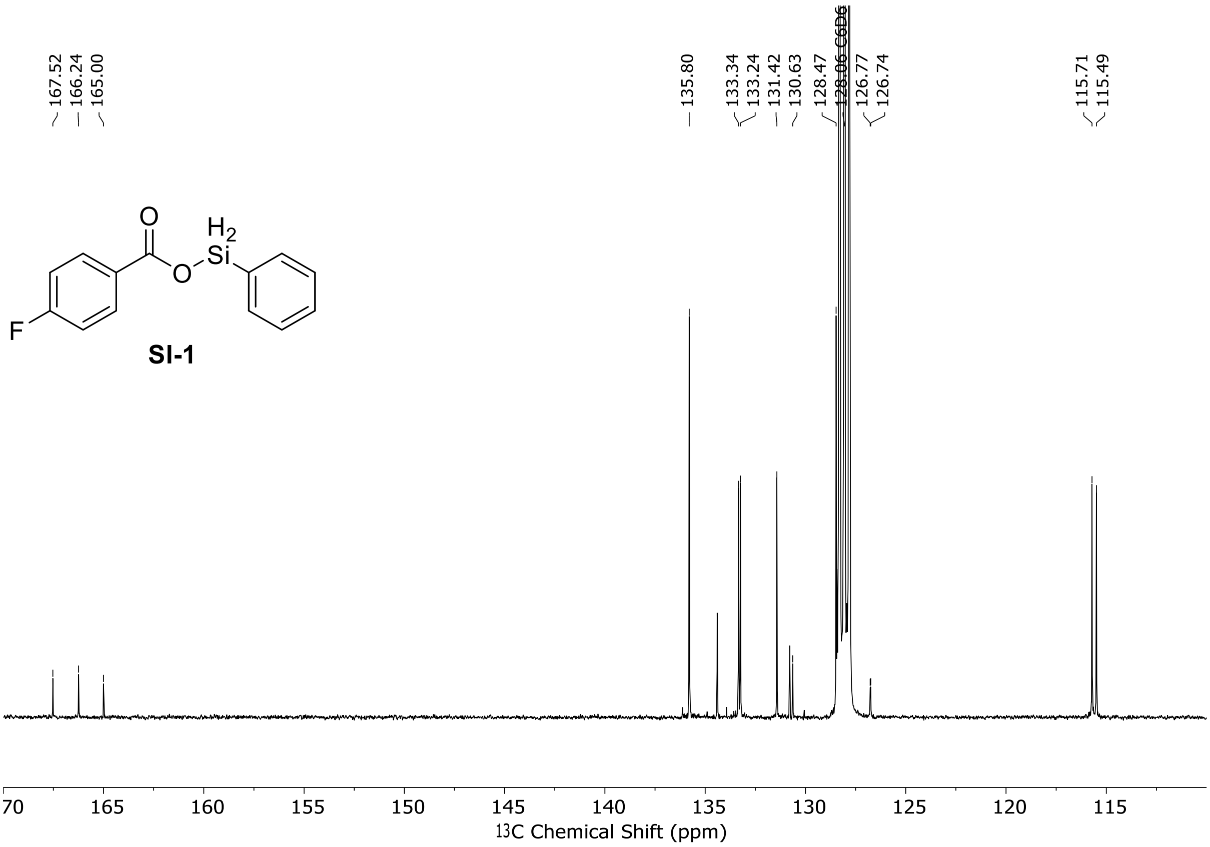
Phenylsilyl 4-fluorobenzoate (SI-1) – ^{1}H NMR (400 MHz, C_6D_6)



Phenylsilyl 4-fluorobenzoate (SI-1) – $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6)



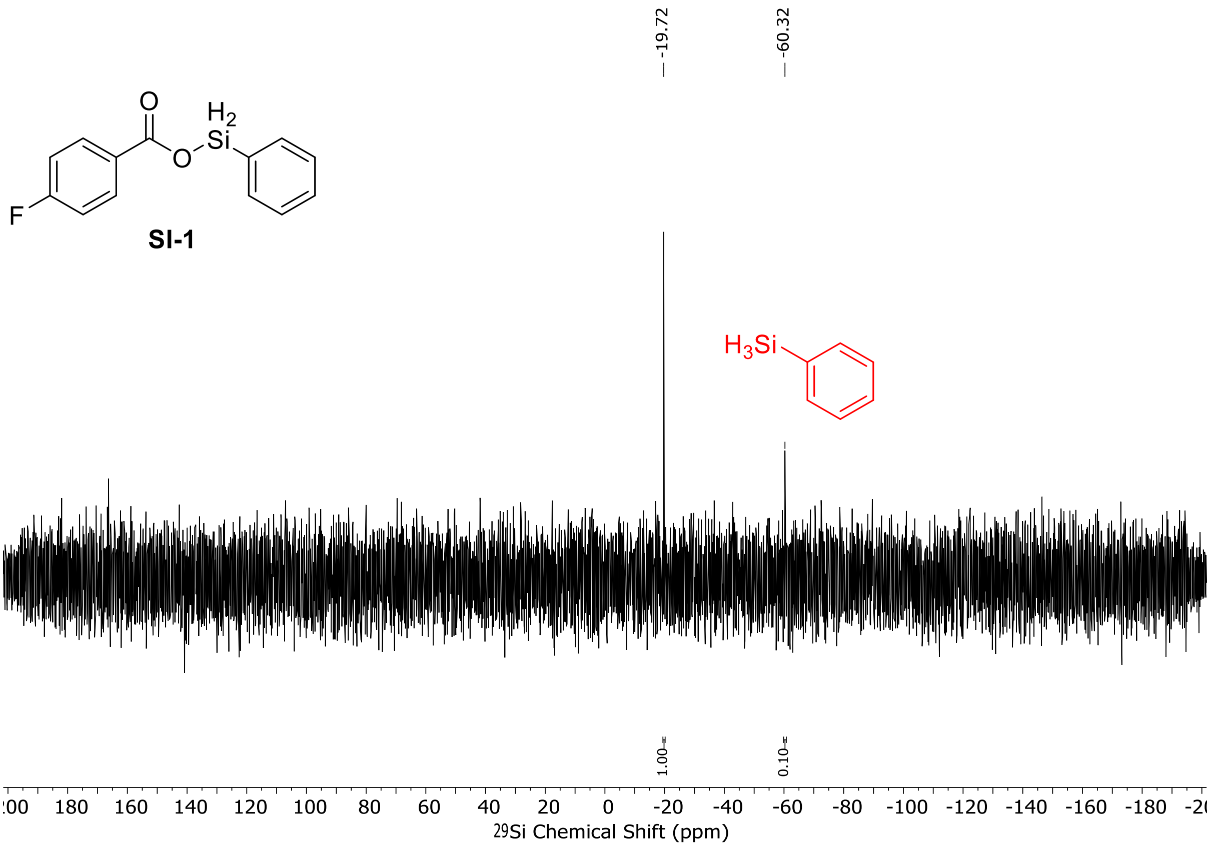
Phenylsilyl 4-fluorobenzoate (SI-1) – $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) Expansion



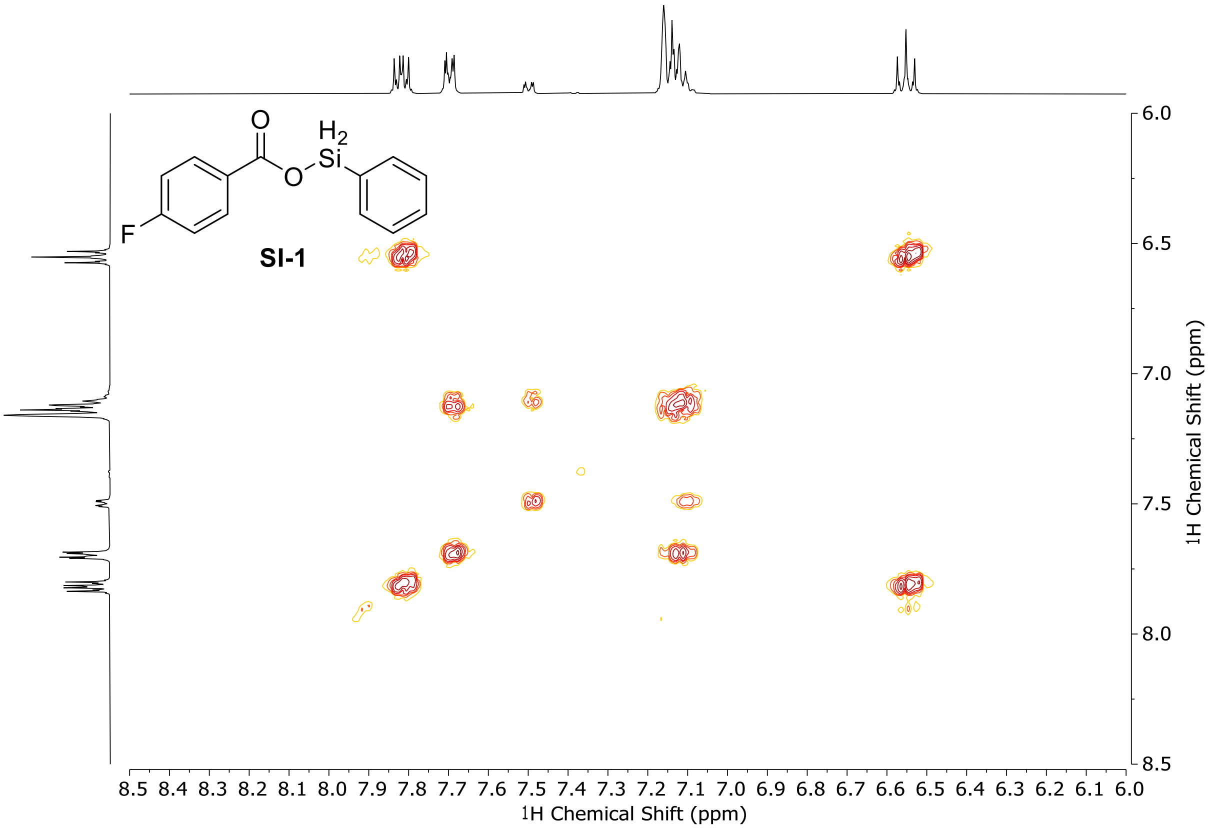
Phenylsilyl 4-fluorobenzoate (SI-1) – $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6)

Phenylsilyl 4-fluorobenzoate (SI-1) – $^{29}Si\{^{1}H\}$ NMR (79 MHz, C_6D_6)

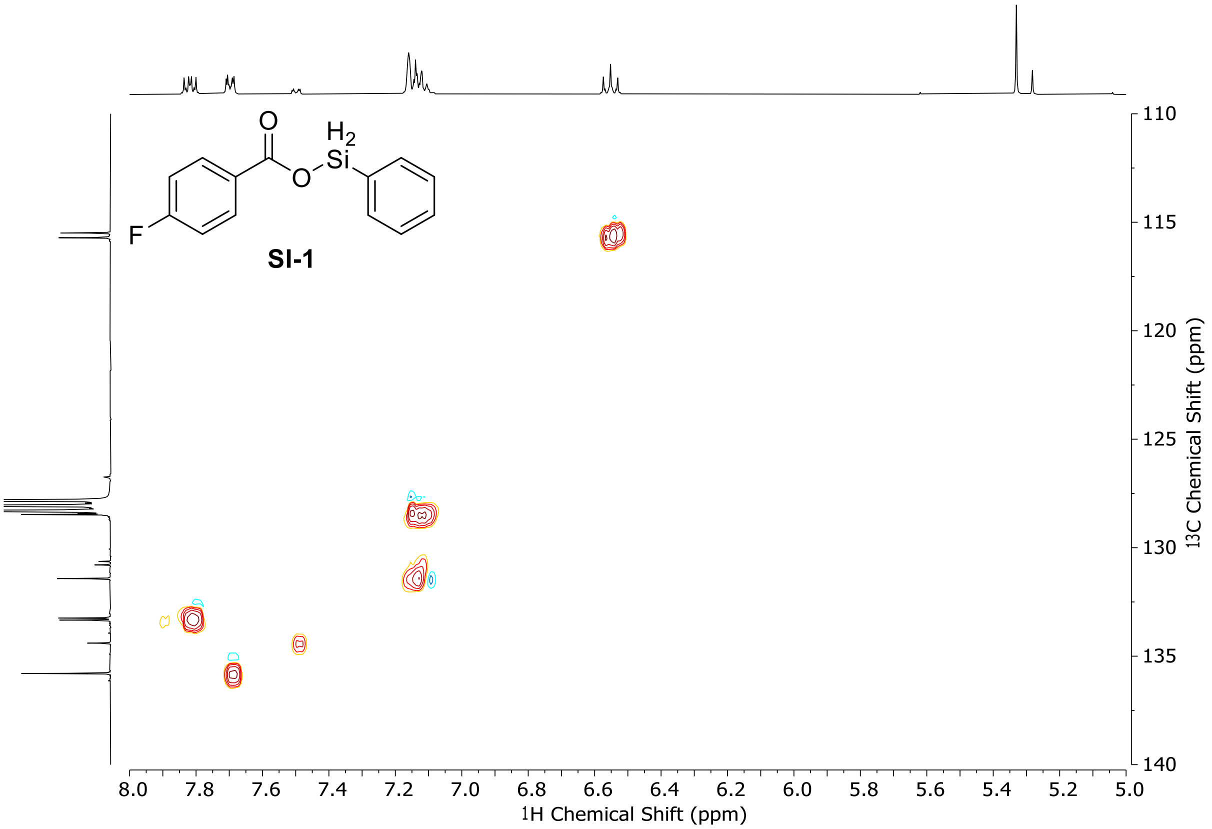
SI-1



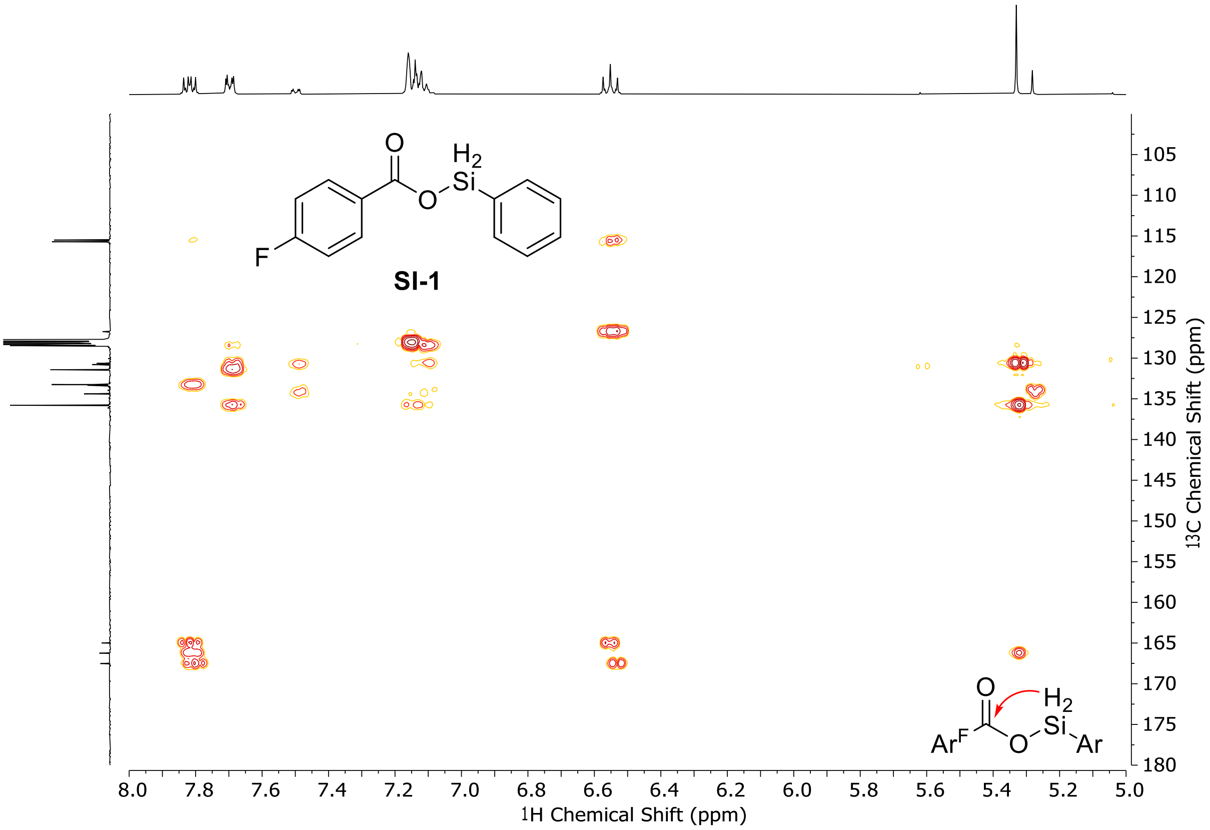
Phenylsilyl 4-fluorobenzoate (SI-1) – ^{1}H-^{1}H COSY NMR (C_6D_6)



Phenylsilyl 4-fluorobenzoate (SI-1) – ^{1}H-^{13}C HSQC NMR (C_6D_6)



Phenylsilyl 4-fluorobenzoate (SI-1) – ^{1}H-^{13}C HMBC NMR (C_6D_6)



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