Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Iron-Catalyzed Protodehalogenation of Alkyl and Aryl Halides Using Hydrosilanes

Ramadevi Pilli, Venkadesh Balakrishnan, Revathi Chandrasekaran, Ramesh Rasappan*

School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Vithura, Thiruvananthapuram, Kerala 695551, India.

E-mail: rr@iisertvm.ac.in (R. Rasappan)

Table of contents

1. GENERAL INFORMATION

1.1 Analysis and purification:

Reactions were monitored by single Quadrupole GC/MS-Agilent which has a silica capillary column (Cat. No. 19091S-433UI, HP-5MSUI, with dimensions 30 m X 0.25 mm) and thin layer chromatography (Merck, Cat. No. 1.05554.0007, aluminium sheets with TLC Silica gel 60 F_{254} coating). TLC analysis was done using shortwave UV-254 nm or I_2 as visualizing agents or the stain made out of phosphomolybdic acid, then heating as the developer. NMR spectra were recorded using 700 and 500 MHz Bruker avance spectrometer, with TMS as internal standard and ^{1}H and ^{13}C spectra were reported in δ (ppm) with respect to a reference. $CDCl_3$ from sigma Aldrich (Cat. No. 151823, 99.8 atom % D) was used for NMR analysis. 1,3,5-trimethoxybenzene from Alfa Aesar (Cat. No. A13981, 99%), was used as an internal standard to calculate the NMR yield. GC yield was taken by first calibrating the authentic sample (May it be the isolated one or the commercial one) with an internal standard and then analysing the yield using the calibrated values to find the relative yield of the product to that of the internal standard. IR Spectra were recorded on FT-IR Alpha E (Bruker) spectrometer. Solid and liquid compounds were measured by neat condition. The wave numbers are given in cm^{-1}. Q-Exactive benchtop HRMS was used for the high resolution analysis. Celite 545 (purchased from Merck) was used for filtration. The column chromatography was performed using Silica Gel 230-400 mesh from FINAR (CASR: 63231-67-4). Kugelrohr apparatus was used for distillation of the reaction crude using ice as the coolant.

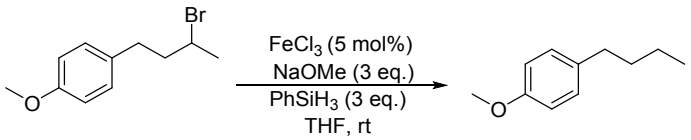
1.1.1 Solvents:

Tetrahydrofuran (THF), purchased from Spectrochem (anhydrous grade) was distilled over Sodium wire. Dichloromethane (DCM/CH_2Cl_2), purchased from Merck was stirred in CaH_2 for 2 h, refluxed and then distilled. Acetonitrile (CH_3CN), purchased from Spectrochem (HPLC grade), was passed through an activated alumina column. All the dry solvents were degassed for a minimum of 20 min. using nitrogen balloon and stored over 4Å molecular sieves.

1.1.2 Chemicals:

Iron (III) chloride, ($FeCl_3$, Cat. No. 12357, CAS 7705-08-0, 98%), Iron (II) chloride ($FeCl_2$, Cat. No. 35701, 99.5%), Phenylsilane ($PhSiH_3$, Cat. No. A17901, 97%) and Sodium methoxide (NaOMe, Cat. No. L05673, 98%) were purchased from Alfa Aesar.

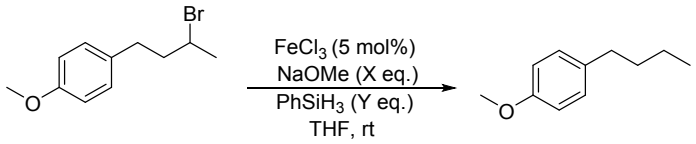
Table S1: Results of deviations from the optimized condition



Entry	Deviations from the optimized conditions	Time (h)	Conversion of SM (%)	Yield [a] (%)
1[b]	10 mol% $FeCl_2$, 1.8 eq. NaO^{t}Bu without $PhSiH_3$	15	55	24
2	10 mol% $FeCl_2$, 0.3 eq. EtMgBr without $PhSiH_3$	15	63	25
3[b]	10 mol% $FeCl_2$, 1.8eq. NaO^{t}Bu, 0.3 eq. B_2Pin_2 without $PhSiH_3$	15	72	21
4	10 mol% $FeCl_2$, 1.8 eq. NaO^{t}Bu, 0.2 eq. HBPin without $PhSiH_3$	15	64	15
5[b]	10 mol% $FeCl_2$, 1.8 eq. NaO^{t}Bu, 1.5eq. Si_2Me_6	15	2	ND
4[b]	2 eq. of MeOH as additive	15	100	19
5[b]	TBAF instead of NaOMe	15	70	ND
6	K_3PO_4 instead of NaOMe	15	10	ND
8	H_2O instead of THF	15	0	ND
9	20 mol% $FeCl_3$, 2 eq. $PhSiH_3$, 2 eq. NaOMe	15	100	95
10	None	5	100	99 (92)
11[b]	^{t}BuOH instead of $PhSiH_3$	32	10	ND
12[b]	Me_2PhSiH instead of $PhSiH_3$	15	32	ND
13	Ph_3SiH instead of $PhSiH_3$	15	22	5
14	10 mol% $FeCl_2$, 1.8 eq. NaO^{t}Bu	15	100	59
15	10 mol% $Fe(acac)_3$, 1.8 eq. NaO^{t}Bu	15	70	62
16	1.8 eq. NaO^{t}Bu instead of NaOMe, 1.5 eq. $PhSiH_3$	32	94	82
17[b]	1.8 eq. KO^{t}Bu instead of NaOMe, 1.5 eq. $PhSiH_3$	16	95	53
18	2 eq. $PhSiH_3$, 2 eq. NaOMe	15	98	83
19	1.8 eq. CsF instead of NaOMe	32	47	<5%
20	1.8 eq. KOMe instead of NaOMe	15	5	<5%
21	3 eq. K_2CO_3 instead of NaOMe, EtOH instead of THF	13	13	ND
22	3 eq. Lutidine instead of NaOMe	12	12	ND
23	Without $FeCl_3$	4	13	7
24	Without NaOMe	12	0	ND
25	Without $PhSiH_3$	12	5	ND
26[b]	CH_3CN as solvent	15	98	31
27	Et_2O as solvent	18	97	92

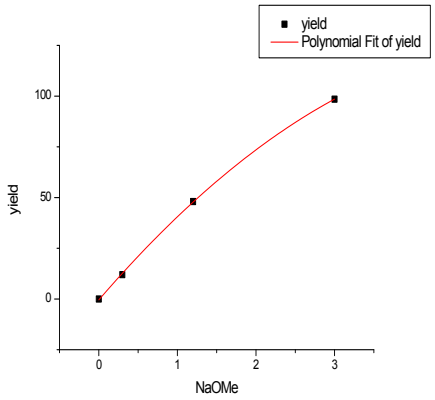
(a) determined by GC analysis using dodecane as an internal standard (b) elimination observed, values in parentheses are isolated yield, ND = not detected

Table S2. Influence of the varying amounts of phenyl silane and sodium methoxide in the optimized reaction condition



Entry	NaOMe (eq.)	$PhSiH_3$ (eq.)	Yield[a] (%)	
			5 h	15 h
1	0	3	0	0
2	0.3	3	12.2	12
3	1.2	3	38.4	48
4	3	3	99.2	98.5
5	3	0	0	<5%
6	3	1.2	53	77
7	3	2	55	87
8	2	2	82	83.3

(a) determined by GC analysis using dodecane as an internal standard



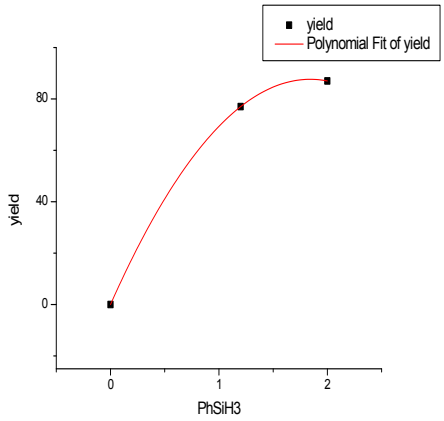
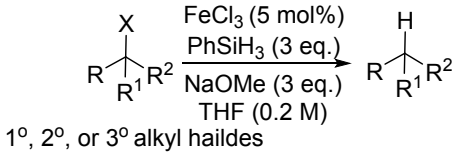


Fig. S1: Amount of NaOMe *vs.* yield **Fig. S2:** Amount of $PhSiH_3$ *vs.* yield

Increase in the concentration of NaOMe in the reaction mixture led to the increase in the yield of the protodehalogenated product. Also, increase in the amount of $PhSiH_3$ led to the increase in the yield.

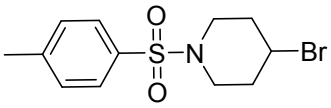
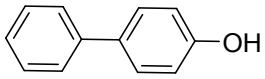
Table S3: Scope of other alkyl/aryl halides



1°, 2°, or 3° alkyl haildes

X = Br, Cl, I

Entry	**Substrate**	**Temp. (°C)**	**Time (h)**	**Yield (%)**

1	 **1q**	rt	24	61[b]
2	 **4k**	rt	2	33

[b]Isolated yield

1.1.3 General procedure for the Iron-Catalysed Protodehalogenation of Alkyl and Aryl Halides Using Hydrosilanes:

A flame dried Schlenk tube was evacuated and refilled with nitrogen. The Schlenk tube was taken inside the glove box and was charged with iron (III) chloride (5 mol%, 0.0302 mmol, 5 mg) and NaOMe (3 eq., 1.81 mmol, 100 mg). It was then removed from the glove box and was connected to the Schlenk line. Half of the required solvent (1.5 mL, fig. S3) was added into it (total conc. of the reaction is 0.2 M). Addition of Phenylsilane (3 eq., 1.81 mmol, and 231 µL) into the reaction tube gave a dark grey/black coloured solution from light yellow solution which indicates the formation of active catalyst (fig. S4). After few minutes of stirring, the substrate was added followed by the addition of remaining solvent (1.5 mL). Note: Phenylsilane must be added in the end as mentioned above, we noticed a spark when mixing phenylsilane and NaOMe alone in the absence of $FeCl_3$ and alkyl halides that may due to the formation of SiH_4, details are in page S16. The reaction was typically monitored using GC/MS or TLC. After the reaction was complete, the mixture was filtered through a celite plug using Et_2O/CH_2Cl_2/THF (based on the volatility and polarity of the material) to remove metal salts and the filtrate was concentrated under vacuum. The crude was taken for further purification step.

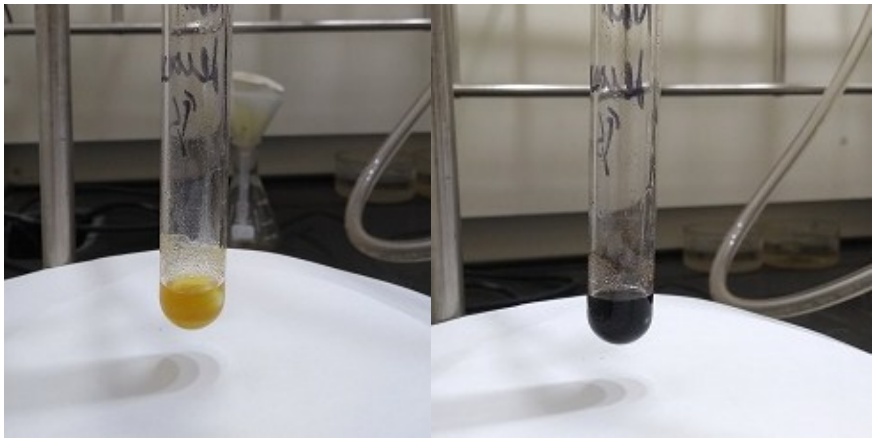
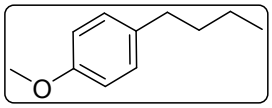


Fig. S3: Before the addition of silane **Fig. S4:** After the addition of silane

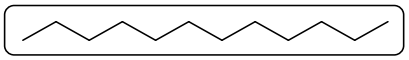
2. SCOPE OF HALIDES

4-*n*-butylanisole (1a-1c)



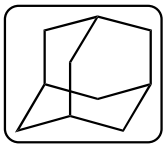
4-*n*-butylanisole was obtained as a colourless oil from 4-(*p*-methoxy)phenyl-2-bromobutane (0.604 mmol, 147 mg, 5 h) by following the general procedure. The crude was distilled slowly using Kugelrohr apparatus and the desired product was obtained at 100 ^{o}C with 4 mbar pressure in 92% yield (91 mg). Increasing the temperature leads to the distillation of diphenylsilane (by-product, at around 120 ^{o}C). 4-*n*-butylanisole from 4-(*p*-methoxy)phenyl-2-chlorobutane and 4-(*p*-methoxy)phenyl-2-iodobutane gave 63% and 92% yield respectively. **FT-IR** (neat) *v*: 2998, 2955, 2928, 2859, 1612, 1510, 1461, 1298, 1241, 1177, 1036, 825, 698, 556 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 4H), 2.66 (m, 2H), 1.80 – 1.68 (m, 2H), 1.46 – 1.43(m, 1H), 1.22 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 134.1, 129.3, 113.8, 67.5, 55.3, 41.1, 31.2, 23.6. **MS** (**m/z**): 164.1 $(C_{11}H_{16}O)^{+}$.

Dodecane (1d-1e)



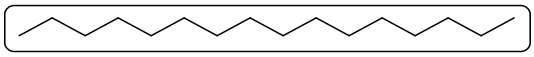
Dodecane was obtained from 1-bromododecane (**1d**, 0.604 mmol, 152 mg, 10 h), 1-chlorododecane (**1e**, 0.604, 124 mg, 75 ^{o}C, 19 h) in 90% and 95% GC yield respectively. **MS** (**m/z**): 170.2 $(C_{12}H_{26})^{+}$.

Adamantane (1f-1g)



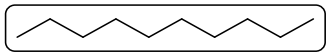
Adamantane was obtained as a colourless solid from 1-bromoadamantane (**1f**, 0.747 mmol, 160.8 mg), and 1-chloroadamantane (**1g**, 0.369 mmol, 63.1 mg) in 78% and 89% yield respectively, by following the general procedure. The crude was distilled to give the product at 300 mbar and 50 ^{o}C. **FT-IR** (neat) *v*: 2893, 2845, 2662, 1448, 1352, 1263, 1099, 1028, 802 cm^{-1}. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 1.87 (s, 4H), 1.75 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 37.8, 28.4. **MS** (**m/z**): 136.0 $(C_{10}H_{16})^{+}$.

Hexadecane (1h)



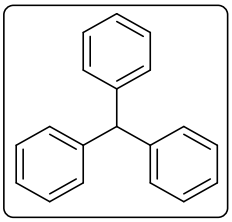
Hexadecane was obtained as a colourless oil from 1-bromohexadecane (0.363 mmol, 113 mg, 3 h) by following the general procedure. The crude was distilled and the product was obtained as first fraction at 110 °C and 2 mbar pressure in 94% yield. **FT-IR** (neat) *v*: 2957, 2921, 2853, 1463, 1260, 1096, 1019, 803, 726 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.26 (s, 28H), 0.89 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 31.9, 29.7, 29.7, 29.4, 22.7, 14.1. **MS** (**m/z**): 226.3 $(C_{16}H_{34})^+$.

Decane (1i-1k, 1n)



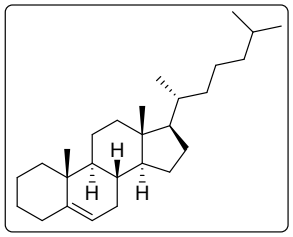
Decane was obtained from 1,10-dibromodecane (**1i**, 0.604 mmol, 187 mg, 2 h), 1-bromodecane (**1j**, 0.242 mmol, 54.5 mg, 4 h), 1-chlorodecane (**1k**, 0.242 mmol, 43.6 mg, 100 °C, 17 h), 1-iododecane (**1n**, 0.604 mmol, 165 mg, 2 h), in 61%, 80%, 62%, 89% of GC yield respectively. **MS** (**m/z**): 142.2 $(C_{10}H_{22})^+$.

Triphenylmethane (1l)



Triphenylmethane was obtained as a colourless solid from bromotriphenylmethane (0.363 mmol, 120 mg, 4 h) by following the general procedure. The crude was purified using column chromatography (has an R_f value of 0.6 in 98:2 of PET ether : Ethyl acetate) to give 60 mg of product in 54% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 6H), 7.22 (d, *J* = 7.2 Hz, 3H), 7.12 (d, *J* = 7.5 Hz, 6H), 5.56 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 129. 5, 128.3, 126.3, 56.9. **MS** (**m/z**): 244.1 $(C_{19}H_{16})^+$.

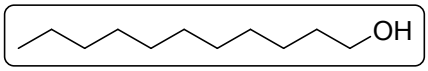
Cholest-5-ene (1m)



Cholest-5-ene was obtained as a colourless solid from Cholesteryl iodide (0.483 mmol, 240 mg, 2 h) by following the general procedure. The crude was purified using column chromatography (R_f = 0.8 in 100% PET ether) in 86% yield. **FT-IR** (neat) *v*: 2927, 2854, 1727, 1461, 1375, 1266, 1121, 1024, 987, 959, 832, 801, 734, 635, 555 cm^{-1}. **^{1}H NMR**

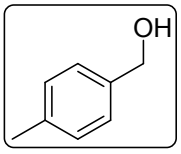
(500 MHz, $CDCl_3$) δ 5.27 (dd, *J* = 5.0, 2.3 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.04 – 1.91 (m, 3H), 1.87 – 1.78 (m, 2H), 1.76 – 1.70 (m, 1H), 1.62 – 1.30 (m, 12H), 1.26 (s, 2H), 1.19 – 1.03 (m, 7H), 1.00 (s, 6H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.7, 2.3 Hz, 6H), 0.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 119.0, 56.9, 56.2, 50.6, 42.3, 39.9, 39.9, 39.5, 36.2, 35.8, 32.9, 31.9, 31.9, 28.3, 28.1, 28.0, 24.3, 23.9, 22.8, 22.6, 20.8, 19.5, 18.7, 11.9. **HRMS (ESI, m/z):** Calculated for $C_{27}H_{46}$ $(M+H)^+$ 371.3672, found 371.3664.

1-undecanol (1o)



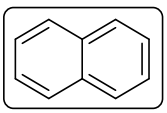
1-undecanol was obtained as a colorless liquid from 11-bromoundecan-1-ol (0.967 mmol, 243 mg, 1 h) by following the general procedure. The crude was distilled (110 °C, 4.7 mbar) to give pure product in 72% yield. **FT-IR** (neat) *v*: 3341, 2922, 2855, 1461, 1378, 1056, 722 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.63 (d, *J* = 6.3 Hz, 2H), 1.58 (d, *J* = 4.1 Hz, 4H), 1.27 (d, *J* = 11.8 Hz, 13H), 0.88 (s, 3H), 0.07 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 62.1, 31.8, 30.9, 28.6, 28.4, 28.3, 24.7, 21.7, 13.1. **MS** (**m/z**): 171.1 $(C_{11}H_{24}O)^+$.

4-methylbenzylalcohol (1p)



4-methylbenzylalcohol was obtained as white needles from methyl 4-(bromomethyl)benzoate (0.967 mmol, 221 mg) by following the general procedure. The product was purified by distillation (60 °C, 4.7 mbar) which gave the pure product in 63% yield. **FT-IR** (neat) *v*: 3360, 3277, 2971, 2916, 1514, 1444, 1344, 1015, 802, 628 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.58 (d, *J* = 3.6 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.9, 137.4, 129.3, 127.1, 65.3, 21.2. **MS** (**m/z**): 122.1 $(C_8H_{10}O)^+$.

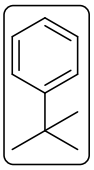
Naphthalene (4a- 4b)



Naphthalene was obtained as a colourless solid from 1-bromonaphthalene (**4a**, 0.363 mmol, 0 °C, 30 min.) and 1-chloronaphthalene (**4b**, 0.363 mmol, ambient temperature, 12 h) in 40% and 71% yield respectively. **FT-IR** (neat) *v*: 3047, 1586, 1498, 1383, 1265, 1118, 957, 767 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.2,

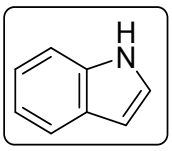
3.3 Hz, 4H), 7.53 (dd, *J* = 6.2, 3.2 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.5, 133.5, 128.0, 127.9, 125.9, 125.9. **MS** (**m/z**): 128.0 $(C_{10}H_8)^+$.

***tert*-butylbenzene (4c)**



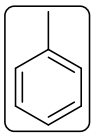
The *tert*-butyl benzene was obtained in 74% GC yield from 1-bromo-4-(tert-butyl) benzene (0.604 mmol, 133 mg, 1 h) by following the general procedure. **MS** (**m/z**): 134.1 $(C_{10}H_{14})^+$.

Indole (4d)



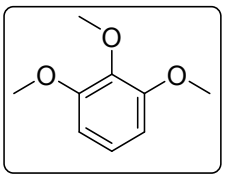
Indole was obtained as a colourless solid from 5-bromoindole (0.620 mmol, 118 mg) by following the general procedure with the exceptions that the reaction mixture was heated to 60 °C and 4 eq. silane was used. With 3 eq. of $PhSiH_3$ decrease in the yield was seen (probably due to the removal of acidic hydrogen by the *in-situ* generated hydride). The reaction crude was purified using column chromatography to give 40% of the desired product. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.68 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 6.58 (d, *J* = 2.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.8, 127.9, 124.1, 122.0, 120.8, 119.8, 111.0, 102.7. **MS** (**m/z**): 117.0 $(C_8H_7N)^+$.

Toluene (4e)



Toluene was obtained in 74% GC yield from 4-chlorotoluene (0.242 mmol, 31.2 mg) at 100 °C. **MS** (**m/z**): 91.0 $(C_7H_8)^+$.

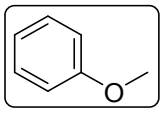
1,2,3-trimethoxybenzene (4f)



1,2,3-trimethoxybenzene was obtained as a colourless solid from 5-bromo-1,2,3-trimethoxybenzene (0.604 mmol, 154 mg) in 2 h by following the general procedure. The crude was purified by distillation (130 °C with 130 mbar) to obtain the desired product in 61% (62.2 mg) yield. **FT-IR** (neat) *v*: 3050, 2938, 2838, 1722, 1595, 1478, 1298, 1254, 1177, 1110, 1009, 778, 733, 696, 530 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.86 (d, *J* = 4.6 Hz,

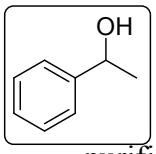
9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.5, 123.6, 105.3, 60.8, 56.1. **MS (m/z)**: 168.1 $(C_9H_{12}O_3)^+$.

Anisole (4g-4i)



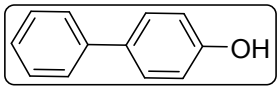
Anisole was obtained in 66%, 78%, 46% of GC yield from 4-bromoanisole (**4g**, 0 ^oC, 1h), 4-chloroanisole (**4h**,100 ^oC, 34 h) and 4-iodoanisole (**4i**, 0 ^oC, 0.5 h) respectively. **MS (m/z)**: 108.0 $(C_7H_8O)^+$.

1-Phenylethanol (4j)



1-phenylethanol was obtained as a colourless liquid in 50% yield from 4́-bromoacetophenone in 1 h by following the general procedure. The product was purified by column chromatography (95:5, PET ether: Ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.24 (d, *J* = 5.9 Hz, 2H), 4.80 (s, 1H), 4.76 (d, *J* = 6.5 Hz, 1H), 1.36 (dd, *J* = 6.5, 3.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.9, 128.5, 127.5, 125.4, 70.4, 25.2. **MS (m/z):** 122.1 $(C_8H_{10}O)^+$.

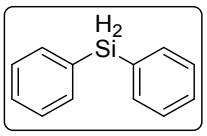
4-phenylphenol (4l):



4-phenylphenol was obtained from 4′-bromo-(1,1′-biphenyl)-4-ol by following the general procedure in 33% yield. The crude mixture was purified using column chromatography. **FT-IR** (neat) *v*: 3384, 3033, 1598, 1502, 1479, 1370, 1239, 1194, 1112, 825, 749, 677 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.9 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.02 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.1, 140.7, 134.1, 128.7, 128.4, 126.7, 115.7. **MS (m/z):** 170.1 $(C_{12}H_{10}O)^+$.

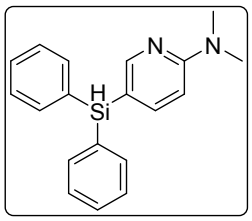
2.1 SIDE PRODUCTS:

Diphenylsilane:

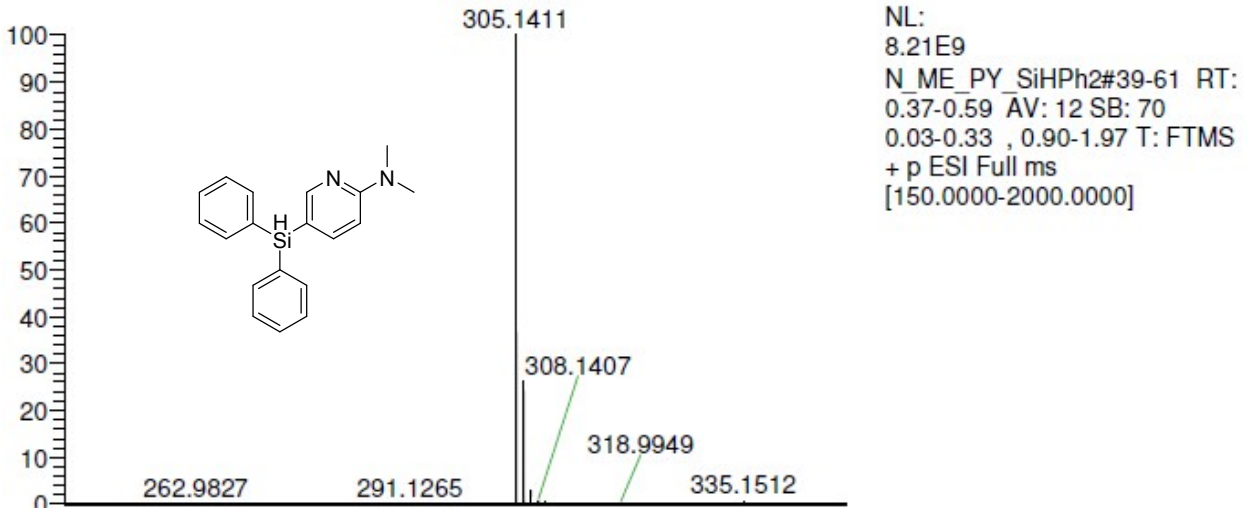


Diphenylsilane was obtained as a by-product in all the reactions done by using the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.46 – 7.37 (m, 6H), 4.95 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.7, 131.5, 129.9, 128.1. **MS (m/z)**: 184.1 $(C_{12}H_{12}Si)^+$.

5-(diphenylsilyl)-N, N-dimethylpyridin-2-amine:



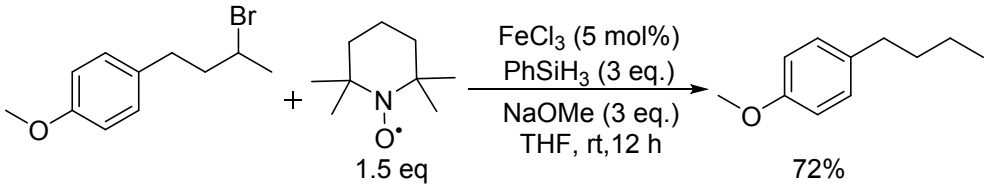
5-(diphenylsilyl)-N,N-dimethylpyridin-2-amine was obtained as a colourless liquid (by-product) along with 2-N,N-dimethyl amino pyridine from 2-dimethylamino-5-bromopyridine (0.604 mg, 121 mg), by following the general procedure, in 24% isolated yield. This has an R_f of 0.6 in 100% PET ether. **FT-IR** (neat) *v*: 3058, 3006, 2922, 2119, 1585, 1508, 1432, 1382, 1211, 1112, 1006, 798, 541 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.8 Hz, 1H), 7.59 (dt, *J* = 8.2, 2.4 Hz, 5H), 7.44 – 7.35 (m, 7H), 6.53 (d, *J* = 8.5 Hz, 1H), 5.44 (s, 1H), 3.11 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.1, 144.0, 135.7, 133.6, 129.7, 128.0, 112.4, 105.8, 37.9. **^{13}C NMR DEPT -135** (126 MHz, $CDCl_3$) δ 155.18, 144.02, 135.71, 129.75, 128.05, 105.77. **MS (m/z):** 304.1 $(C_{19}H_{20}N_2Si)^+$. **HRMS (ESI, m/z):** Calculated for $C_{19}H_{20}N_2Si$ $(M+H)^+$ 305.1469, Found: 305.1411.



3. MECHANISTIC STUDIES

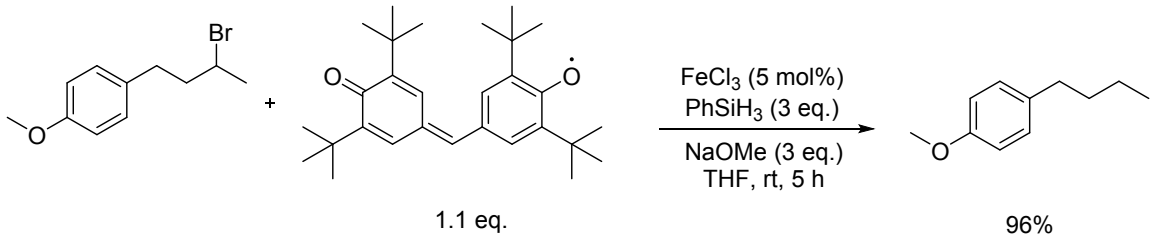
3.1 Treating the reaction mixture

3.1.1 With TEMPO:



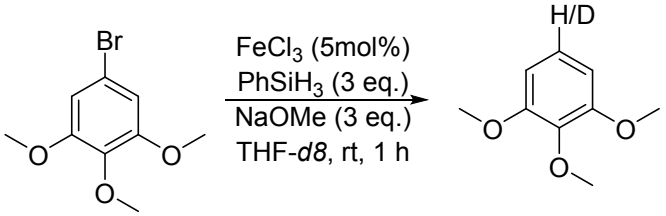
4-(*p*-methoxy)phenyl-2-bromobutane (0.60 mmol, 147 mg) was treated to the conditions as in the given procedure. TEMPO (0.906 mmol, 142 mg) was added additionally just before the addition of the substrate. When monitored using GC/MS, no new peak corresponding to TEMPO coupled substrate was seen. The reaction proceeded towards protodehalogenation to give 4-*n*-butylanisole in 72% yield.

3.1.2 With galvinoxyl:



4-(*p*-methoxy)phenyl-2-bromobutane (0.242 mmol, 58.8 mg) was treated to the conditions as in the given procedure. Galvinoxyl (0.266 mmol, 112 mg) was added additionally just before the addition of the substrate. When monitored using GC/MS, no new peak corresponding to the galvinoxyl adduct of the substrate was seen. The reaction proceeded towards protodehalogenation to give 4-*n*-butylanisole in 96% yield.

3.1.3 With THF-*d8*:

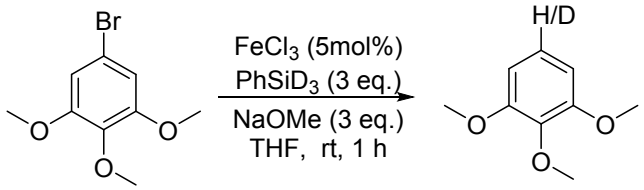


H= 100%

5-bromo-1,2,3-trimethoxybenzene (0.483mmol, 123 mg), was subjected to the reaction conditions as in the general procedure in THF-*d8* instead of normal THF. The reaction was monitored using GC/MS. After the completion of the reaction, the mixture was passed through celite, concentrated and distilled (130 ^{o}C and 130 mbar) to obtain 45 mg (55% yield) of the product.

NMR studies has proven that the material obtained was non-deuterated which implies that solvent doesn't act as the source of H-atom. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.86 (d, *J* = 4.6 Hz, 9H).

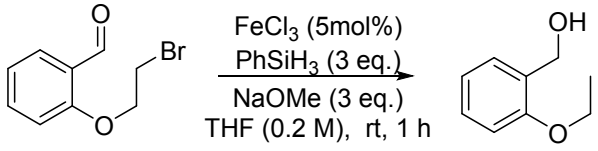
3.1.4 With $PhSiD_3$:



D= 72%

5-bromo-1,2,3-trimethoxybenzene (0.483 mmol, 123 mg), was subjected to the reaction conditions as in the general procedure with an exception that $PhSiD_3$ was taken. The reaction was monitored using GC/MS. After the completion of the reaction, the crude was purified using column chromatography. NMR shows 72% incorporation of the deuterium.

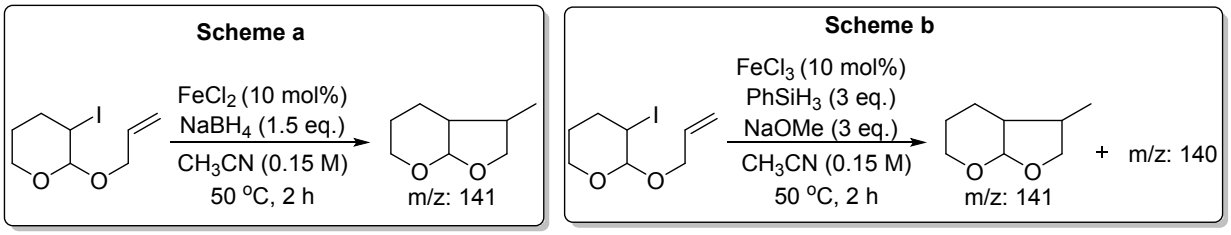
3.1.5 With 2-(2-bromoethoxy)benzaldehyde:



A carbonyl trap experiment was done using 2-(2-bromoethoxy)benzaldehyde as substrate. It also led to the uncyclized product. The crude was purified by column chromatography and was

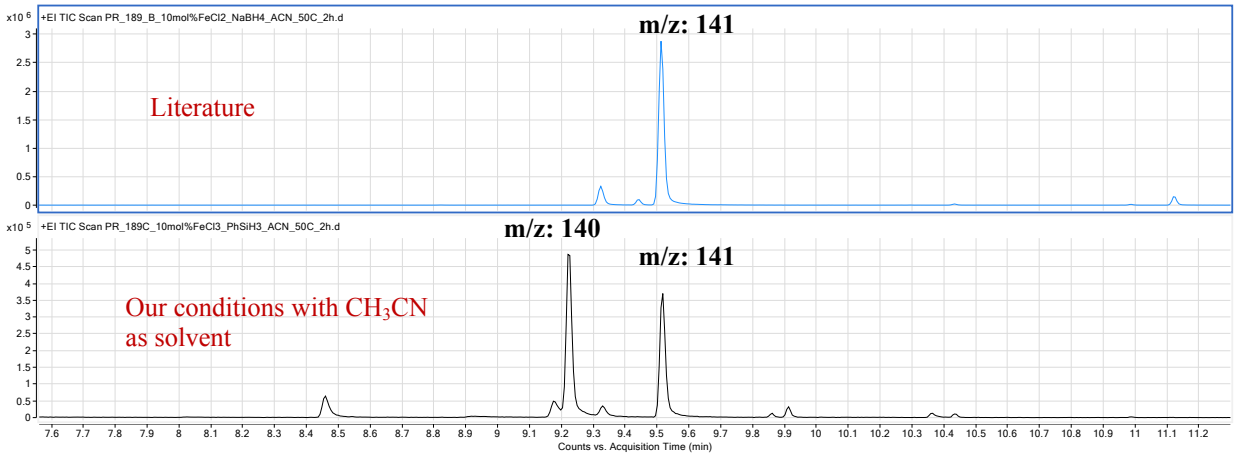
further confirmed by NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.26 (s, 1H), 6.93 (d, *J* = 1.0 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 4.70 (s, 2H), 4.10 (d, *J* = 7.0 Hz, 2H), 1.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 1567.0, 129.1, 128.9, 128.8, 120. 6, 111.1, 63.5, 62.5, 14.9. **MS (m/z)**: 152.1 $(C_9H_{12}O_2)^+$.

3.1.6 Protodehalogenation of an iodoalkene, comparison with literature[3]:



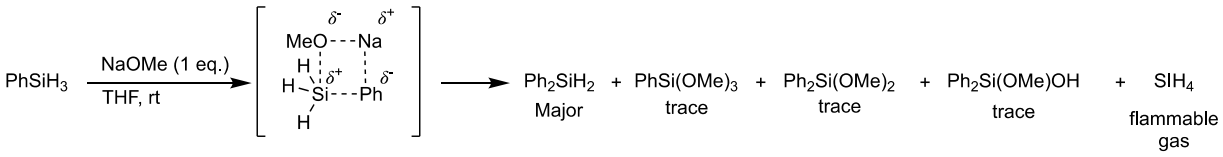
Scheme a: Literature (0.387 mmol of substrate, 0.0387 mmol of $FeCl_2$, 0.58 mmol of $NaBH_4$, 1 mL CH_3CN)
Scheme b: Optimised reaction conditions (0.387 mmol of substrate, 0.0387 mmol of $FeCl_3$, 1.16 mmol $PhSiH_3$, 1.16 mmol NaOMe, 1 mL CH_3CN)

As reported by Ollivier et. al., protodehalogenation *via* cyclization is the reaction pathway for 2-(allyloxy)-3-bromotetrahydro-2H-pyran. This substrate with the optimized reaction conditions always gave a product with the same mass but a different retention time in GC/MS. Efforts to obtain exclusively the cyclized product didn't go well, giving a mixture of products with the same mass, even with the usage of CH_3CN as solvent which promotes radical type reactions.

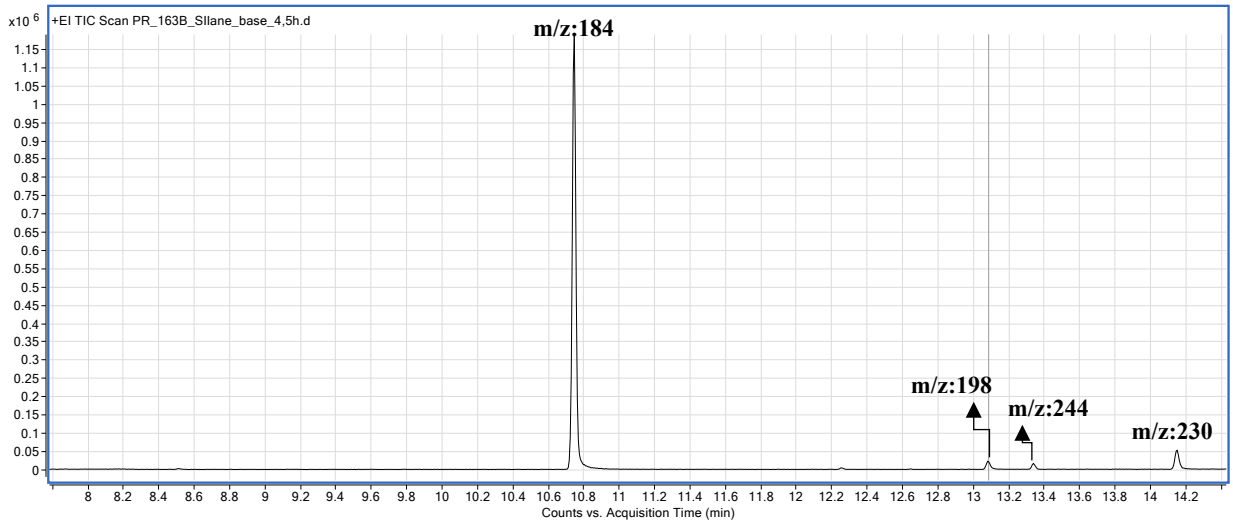


This information supports that the formation of cyclized product is not favoured with our reaction conditions thereby concluding that the reaction doesn't undergo radical pathway.

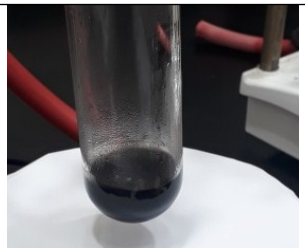
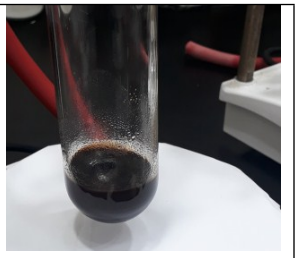
3.1.6 Disproportionation of $PhSiH_3$[9]



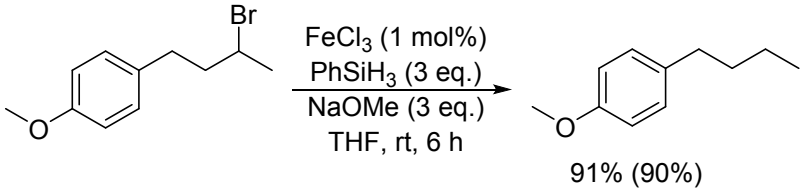
When $PhSiH_3$ was treated with NaOMe (1 eq.) in THF, we observed the formation of Ph_2SiH_2 (care must be taken as we noticed a spark when mixing phenylsilane and NaOMe alone in the absence of $FeCl_3$ and alkyl halides, the spark may due to the formation of flammable SiH_4, the spark was observed only in the initial stage of reaction but not during the course of reaction). GCMS analysis (shown below) indicates the $PhSiH_3$ converted into Ph_2SiH_2 in 1h and we also observed traces of $PhSi(OMe)_3$ (m/z: 198), $Ph_2Si(OMe)_2$ (m/z: 244), and $Ph_2Si(OMe)OH$ (m/z: 230).



4. LARGE SCALE SYNTHESIS

			
$FeCl_3$ +NaOMe	$FeCl_3$ +NaOMe+THF	$FeCl_3$+NaOMe+THF+$PhSiH_3$	$FeCl_3$+NaOMe+THF+$PhSiH_3$+ substrate

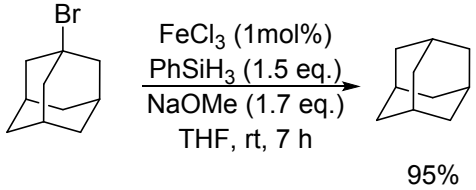
4.1 Reaction of 4-(*p*-methoxy)phenyl-2-bromobutane with 1 mol% catalyst loading:



4-(*p*-methoxy)phenyl-2-bromobutane (2.04 mmol, 500 mg) was subjected to the reaction conditions as in the general procedure with an exception that 1 mol% of $FeCl_3$ was taken. 4-bromoanisole was obtained by distillation in 90% isolated yield (91% GC yield).

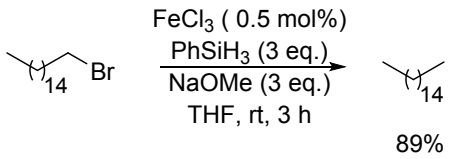
(Caution: Addition of $PhSiH_3$ into Schlenk tube may generate SiH_4 & NaH *in-situ* which are pyrophoric in nature).

4.2 Reaction of 1-bromoadamantane with 1 mol% catalyst, 1.5 eq. $PhSiH_3$ and 1.7 eq. NaOMe:



1-bromoadamantane (4.6 mmol, 1 g) was subjected to the reaction conditions as in the general procedure with the exception that 1 mol% of $FeCl_3$, 1.5 eq. $PhSiH_3$ and 1.7 eq. of NaOMe was taken. Adamantane was obtained in 95% GC yield.

4.3 Synthesis of hexadecane with 0.5 mol% of catalyst loading:

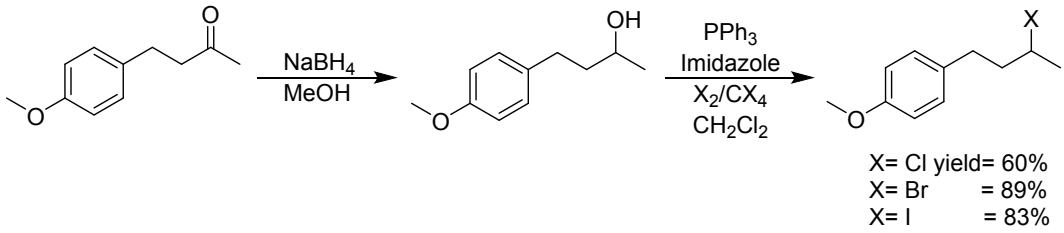


1-bromohexadecane (6.03 mmol, 1.86 mL) was subjected to the reaction conditions as in the general procedure with an exception that 0.5 mol% of $FeCl_3$ was taken. Hexadecane was distilled out from the crude after 3 h in 89% yield.

(Caution: Addition of $PhSiH_3$ into Schlenk tube may generate SiH_4 & NaH *insitu* which are pyrophoric in nature).

5. SYNTHESIS OF STARTING MATERIALS

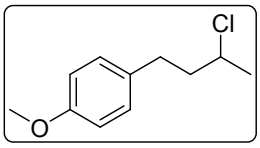
5.1 Synthesis of 4-(*p*-methoxy)phenyl-2-halobutane[1]:



A flame-dried two neck round bottomed flask equipped with a stir bar was fitted with a rubber septum and backfilled with N_2. The ketone (58.7 mmol, 10 mL) and dry MeOH (25 mL) were taken into the flask, then kept in an ice bath. $NaBH_4$ (88 mmol, 3.33 g) was added portionwise at 0 °C to control the evolution of gas from the reaction flask. The ice bath was removed after the addition and allowed to stir at room temperature for 1.5 h. The reaction was quenched with saturated $NaHCO_3$ solution (25 mL) and diluted with 15 mL water to dissolve the precipitated materials, extracted three times with CH_2Cl_2 (3 x 50 mL), dried with $MgSO_4$, and rotor evaporated to yield 89% alcohol as a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 4H), 2.73 – 2.58 (m, 2H), 1.80 – 1.68 (m, 2H), 1.44 (d, *J* = 4.3 Hz, 1H), 1.22 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 134.1, 129.3, 113.8, 67.5, 55.3, 41.1, 31.2, 23.6.

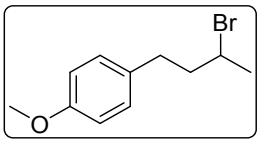
For halogenation, a round bottomed flask was equipped with a stir bar and flame dried, then PPh_3 (1.05 eq.), imidazole (1.05 eq.) and halogenating agent (1.05 eq.) were added to the flask under N_2. Dry CH_2Cl_2 (0.2 M) was added and then flask was cooled to 0 °C using an ice bath and stirred for 10 min. At 0 °C alcohol (0.555 mmol), diluted 5:1 in CH_2Cl_2, was added drop by drop. After complete addition of the alcohol the reaction was left to stir overnight at room temperature. After the reaction was complete (confirm by TLC), the mixture was concentrated under reduced pressure and was diluted with 25% EtOAc in hexanes and filtered through silica plug. The filtrate was concentrated again in rotor evaporator and pure desired compound was isolated by column chromatography (98:2, PET ether: Ethyl acetate) to yield the alkyl halide.

4-(*p*-methoxy)phenyl-2-chlorobutane:



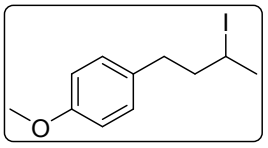
FT-IR (neat) *v*: 2934, 2837, 1612, 1510, 1452, 1242, 1177, 1035, 822, 609, 558 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.02 – 3.93 (m, 1H), 3.79 (s, 3H), 2.82 – 2.75 (m, 1H), 2.72 – 2.65 (m, 1H), 2.04 – 1.91 (m, 2H), 1.52 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 133.1, 129.4, 113.9, 57.9, 55.3, 42.2, 32.0, 25.4. **MS** (**m/z**): 198.1($C_{11}H_{15}ClO^+$)

4-(*p*-methoxy)phenyl-2-bromobutane:



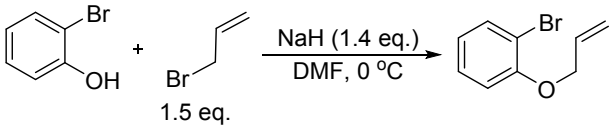
FT-IR (neat) *v*: 2926, 2835, 1611, 1510, 1451, 1297, 1241, 1176, 1035, 824, 749, 611, 527 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.02 – 3.93 (m, 1H), 3.79 (s, 3H), 2.84 – 2.64 (m, 2H), 2.04 – 1.91 (m, 2H), 1.52 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 132.9, 129.4, 113.9, 55.3, 50.9, 42.9, 33.0, 26.5. **MS** (**m/z**): 242.1($C_{11}H_{15}BrO^+$)

4-(*p*-methoxy)phenyl-2-iodobutane:



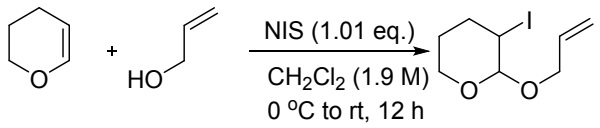
FT-IR (neat) *v*: 2918, 2835, 1611, 1509, 1449, 1296, 1242, 1179, 1034, 822, 749, 705, 568 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.15 – 4.05 (m, 1H), 3.79 (s, 3H), 2.83 – 2.73 (m, 1H), 2.68 – 2.59 (m, 1H), 2.18 – 2.07 (m, 1H), 1.94 (d, *J* = 6.8 Hz, 3H), 1.88 – 1.80 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 132.8, 129.4, 113.9, 55.3, 44.6, 34.9, 29.7, 29.0. **MS** (**m/z**): 290.1 ($C_{11}H_{15}IO^+$)

5.2 Synthesis of allyl-2-bromophenylether[2]:



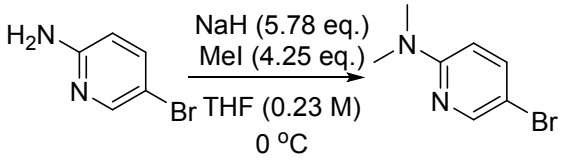
To 2-bromophenol (11.3 mmol, 1.34 mL) in 25 mL DMF, NaH (1.4 eq., 15.9 mmol, 60% suspension) was added at 0 °C and stirred for 10 min., later allylbromide (1.5 eq.) was added dropwise to the reaction mixture. After 1 h, the reaction mixture was quenched with water and the crude was extracted using diethylether. Allyl-2-bromophenylether was isolated using column chromatography (95:5 of PET ether: Ethyl acetate) in 82% yield.

5.3 Synthesis of 2-(allyloxy)-3-iodotetrahydro-2H-pyran[3]:



3,4-dihydro-2H-pyran (1 eq., 42.5 mmol, 3.62 g) was added dropwise to a mixture of N-iodosuccinimide (1.01 eq., 43.1 mmol, 10 g) and allyl alcohol (0.98 eq., 42 mmol, 2.49 g) in CH_2Cl_2 (23 mL) at -10 °C. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated sodium thiosulfate (3 × 20 mL). The combined aqueous phase was extracted using CH_2Cl_2 and the combined organic layers was washed with brine, dried over Na_2SO_4 and was concentrated under reduced pressure. The pure product was obtained as a pale yellow liquid (10.147 g, 89.5%) by column chromatography. **FT-IR** (neat) *v*: 3070, 2941, 2857, 1610, 1439, 1345, 1274, 1199, 1124, 1070, 1017, 928, 867, 694, 586 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 16.2, 10.9, 5.3 Hz, 1H), 5.32 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.24 – 5.14 (m, 1H), 4.67 (d, *J* = 5.4 Hz, 1H), 4.29 – 4.20 (m, 1H), 4.15 – 3.92 (m, 3H), 3.58 (td, *J* = 7.6, 3.7 Hz, 1H), 2.37 (dq, *J* = 11.5, 4.0 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.76 (dq, *J* = 10.5, 3.4 Hz, 1H), 1.62 – 1.51 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.9, 117.5, 101.6, 69.0, 63.5, 32.7, 29.2, 25.5. **MS** (**m/z**): 268.1 ($C_8H_{13}IO_2^+$)

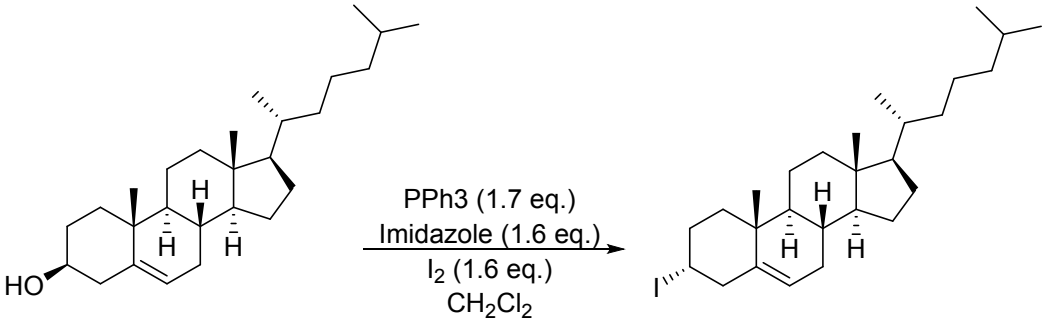
5.4 Synthesis of 5-Bromo-N,N-dimethylpyridin-2-amine[4]:



NaH (1.96 g, 49.1 mmol) was added to a solution of 5-bromopyridin-2-amine in THF (36 mL) at 0 °C and stirred for 20 min. The methyl iodide (2.26 mL, 36.1 mmol) was added to the solution and stirred overnight. The reaction mixture was quenched with water (50 mL) and was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The compound was purified by flash column chromatography on silica gel (Ethyl acetate: PET ether, 0.75:10) to give the pure compound (1.6

g, 94%). **FT-IR** (neat) *v*: 2892, 2845, 2661, 1588, 1501, 1448, 1352, 1264, 1099, 965, 802 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.40 (d, *J* = 9.0 Hz, 1H), 3.05 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 148.3, 139.3, 107.2, 106.0, 38.2, 30.9. **MS** (**m/z**): 200.0 ($C_7H_9BrN_2^+$).

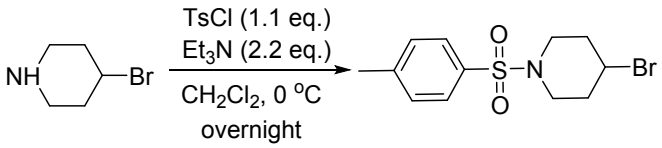
5.5 Synthesis of Cholesteryl Iodide[5]:



83%

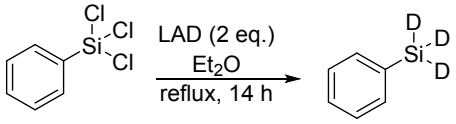
To a solution of PPh_3 (1.68 eq., 1.62 g, 6.19 mmol) and imidazole (1.58 eq., 0.396 g, 5.82 mmol) in 5 mL CH_2Cl_2 at 0 °C, I_2 (1.58 eq., 1.48 g, 5.82 mmol) was added and stirred for 30 min. Cholesterol (1 eq., 1.5 g, 3.69 mmol) in 5 mL CH_2Cl_2 was added dropwise to the reaction mixture and was left for stirring at room temperature overnight. Completion of the reaction was confirmed through TLC and then water (15 mL) was added to the reaction mixture followed by workup with CH_2Cl_2 (3 X 15 mL). The crude mixture was obtained by combining organic extracts, drying over Na_2SO_4, followed by concentration. Pure product was isolated using column chromatography (R_f = 0.8 in 100% PET ether) followed by recrystallization from acetone as colourless needles (83% yield). **FT-IR** (neat) *v*: 2939, 2868, 2360, 1667, 1530, 1461, 1374, 1179, 1122, 1027, 993, 958, 811, 671, 627, 586, 543 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.38 – 5.34 (m, 1H), 4.12 – 4.01 (m, 1H), 2.95 (td, *J* = 13.2, 2.6 Hz, 1H), 2.73 – 2.67 (m, 1H), 2.34 – 2.18 (m, 2H), 2.06 – 1.94 (m, 2H), 1.85 (dtd, *J* = 13.5, 9.4, 6.0 Hz, 1H), 1.75 (d, *J* = 13.5 Hz, 1H), 1.63 – 0.99 (m, 23H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.89 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 121.7, 56.7 , 56.2, 50.4, 46.4, 42.3, 41.9, 39.7, 39.5, 36.6, 36.5, 36.2, 35.8, 31.8, 31.7, 30.6, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 20.8, 19.2, 18.7, 11.9. **HRMS (ESI, m/z):** Calculated for $C_{27}H_{45}I$ $(M+Na)^+$ 519.2458, found 519.2345.

5.6 Synthesis of 4-Bromo-1-[(4-methylphenyl)sulfonyl]-piperidine[6]:



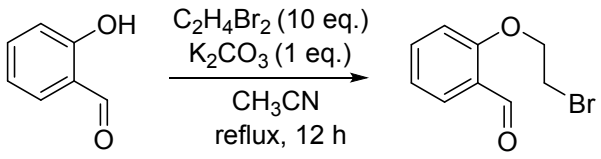
N-tosyl-4-bromopiperidine was synthesized according to the literature protocol[6]. To a mixture of 4-bromopiperidine hydrobromide (0.718 mmol) and tosyl chloride (0.789 mmol) in CH_2Cl_2 at 0 °C, triethylamine (1.58 mmol) was added dropwise and was left to stir overnight. Later, it was quenched with 2M HCl and was extracted using CH_2Cl_2. The organic portion was then dried over $MgSO_4$ and was concentrated. The crude was purified by column chromatography (80: 20 Ethyl acetate: PET ether) to give the compound as a white solid in 80% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 4.27 – 4.21 (m, 1H), 3.23 – 3.06 (m, 4H), 2.45 (s, 3H), 2.23 – 2.14 (m, 2H), 2.10 – 2.01 (m, 2H).

5.7 Synthesis of Deuterated phenylsilane[7]:



A flame dried Schlenk round bottom flask, that was evacuated and refilled with nitrogen, was charged with $LiAlD_4$ (2 eq., 7.15 mmol, 0.3 mg). Diethylether was added to it at 0 °C. Trichlorophenylsilane (3.57 mmol, 0.572 mL) was added dropwise. After the addition, the reaction mixture was brought to room temperature and refluxed for 20 h. The solvent was distilled out by fractional distillation and the product was distilled into a cold trap. NMR shows the presence of $PhSiD_3$, which agrees with the reported literature, along with Et_2O. **FT-IR** (neat) *v*: 3030, 2925, 2858, 1742, 1595, 1447, 1338, 1241, 1157, 1092, 1049, 925, 853, 807, 698, 647, 572, 545 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.41 – 7.31 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.8, 129.8, 128.1. **MS** (**m/z**): 111.0 ($C_6H_5D_3Si^+$).

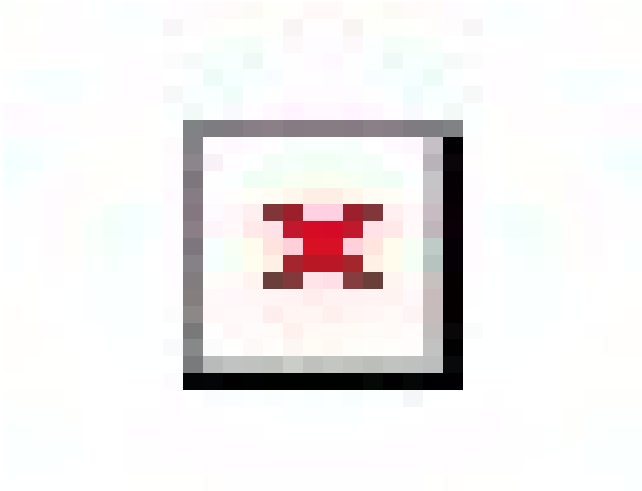
5.8 Synthesis of 2-(2-bromoethoxy)benzaldehyde[8]:



80%

A flame dried two neck round bottomed flask equipped with a stir bar was fitted with a rubber septum and backfilled with N_2. Salicylaldehyde (0.873 mL, 8.19 mmol) was taken and CH_3CN (2 mL) was added. Then K_2CO_3 (1.13 g, 8.19 mmol) was added into it. The solution was refluxed for 1 h, and then 1,2-dibromoethane (7.09 mL, 8.19 mmol) was added. Then the reaction mixture was refluxed for another 10 h under nitrogen. Later, the reaction mixture was cooled to room temperature, filtered through silica and was concentrated in vacuum. The resulting crude was purified by column chromatography to give a pure product with 80% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.54 (td, *J* = 8.1, 7.5, 2.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.41 (dd, *J* = 6.9, 5.0 Hz, 2H), 3.70 (td, *J* = 6.0, 1.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 189.6, 160.4, 135.9, 128.5, 125.2, 121.5, 112.7, 68.3, 28.8. **MS** (**m/z**): 230.0 ($C_9H_9BrO_2^+$)

Competitive experiments



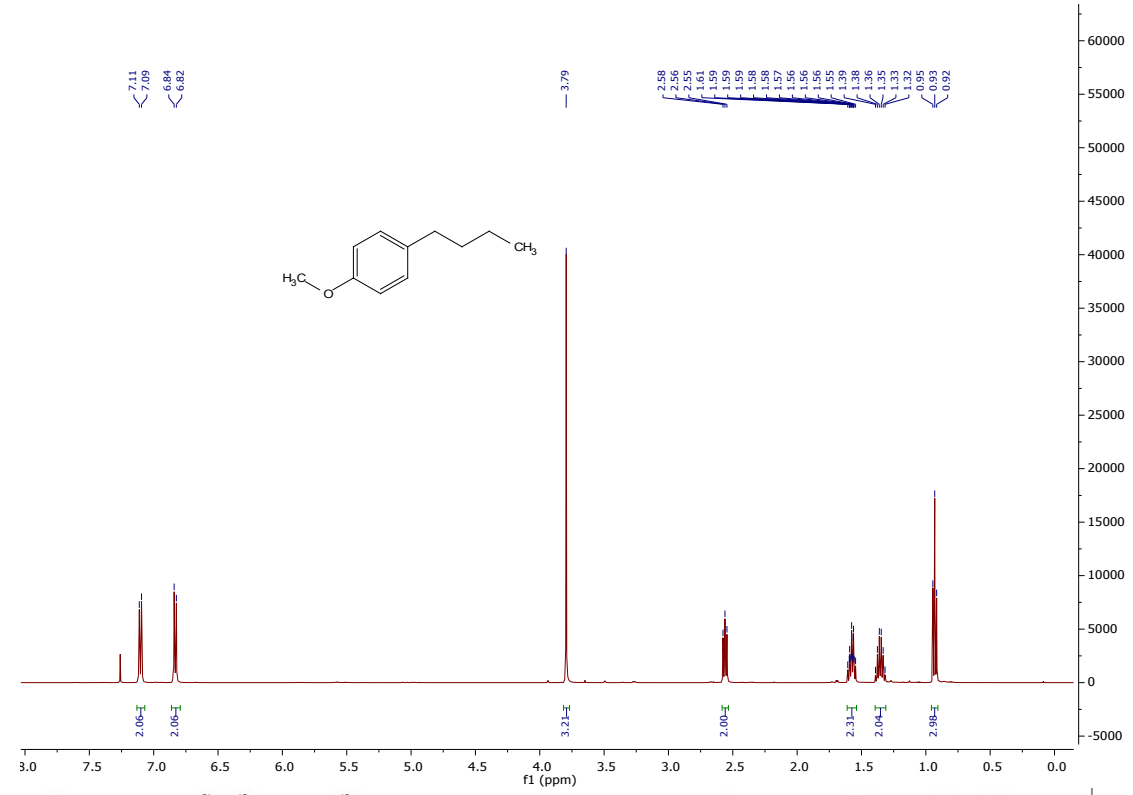
Competitive experiments were conducted to determine the order of reactivity, in one-pot chlorodecane **1j**, bromide **1k** and iodide were subjected to the standard reaction condition, the complete consumption of iodides occurred within 20 minutes and the bromide took 24 h to get completely consumed, however, the chloride was intact even after 48 h.

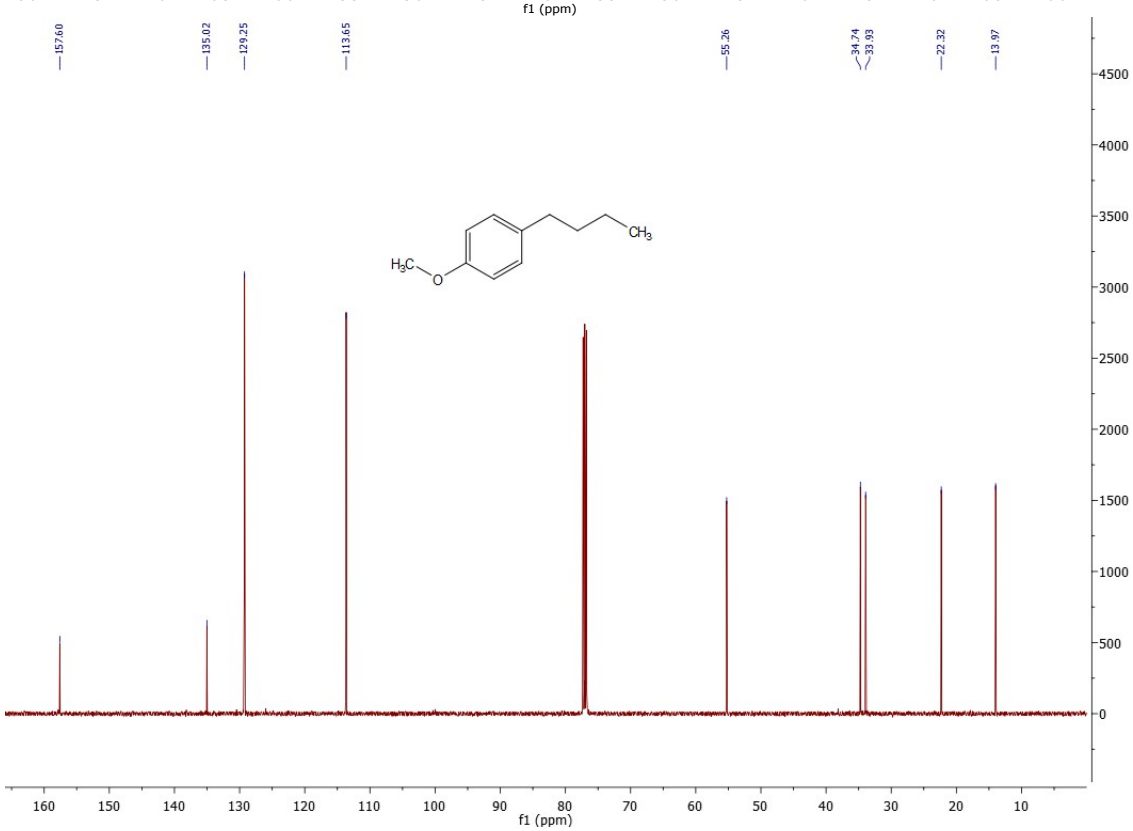
6. REFERENCES

1. Atack, T. C.; Lecker, R. M.; Cook, S. P. *J. Am. Chem. Soc.* **2014,** *136*, 9521-9523.
2. Ocasio, C. A.; Scanlan, T. S. *Bioorganic Med. Chem.* **2008,** *16*, 762-770.
3. Kyne, S. H.; Lévêque, C.; Zheng, S.; Fensterbank, L.; Jutand, A.; Ollivier, C. *Tetrahedron* **2016,** *72*, 7727-7737.
4. Bao, R.; Lai, C.; Qian, C. Treatment of Cancers Having K-Ras Mutations. WO2011/130628, **2011**.
5. Soulard, V.; Villa, G.; Vollmar, D. P.; Renaud, P. *J. Am. Chem. Soc.* **2018,** *140*, 155-158.
6. Bedford, R. B.; Brenner, P. B.; Carter, E.; Gallagher, T.; Murphy, D. M.; Pye, D. R. *Organometallics* **2014,** *33*, 5940-5943.
7. Kumar, A.; Pandiakumar, A. K.; Samuelson, A. G. *Tetrahedron* **2014,** *70*, 3185-3190.
8. Singh, A.; Singh, A.; Singh, N.; Jang, D. O. *Tetrahedron* **2016**, *72*, 3535-3541.
9. Becker, B.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L. *J. Organomet. Chem.* **1989**, *369*, 147.

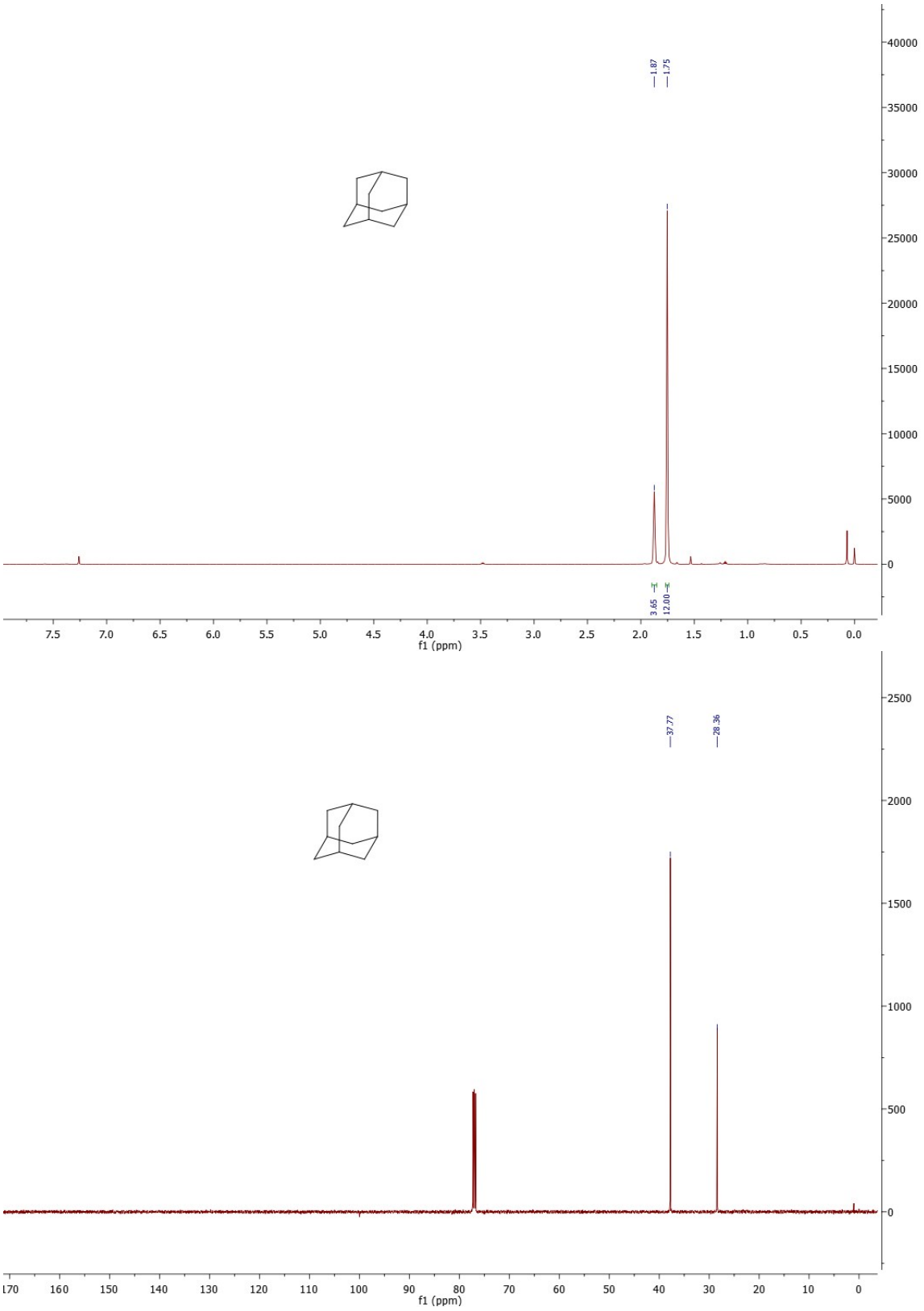
7. NMR SPECTRA

4-*n*-butylanisole (1a-1c)

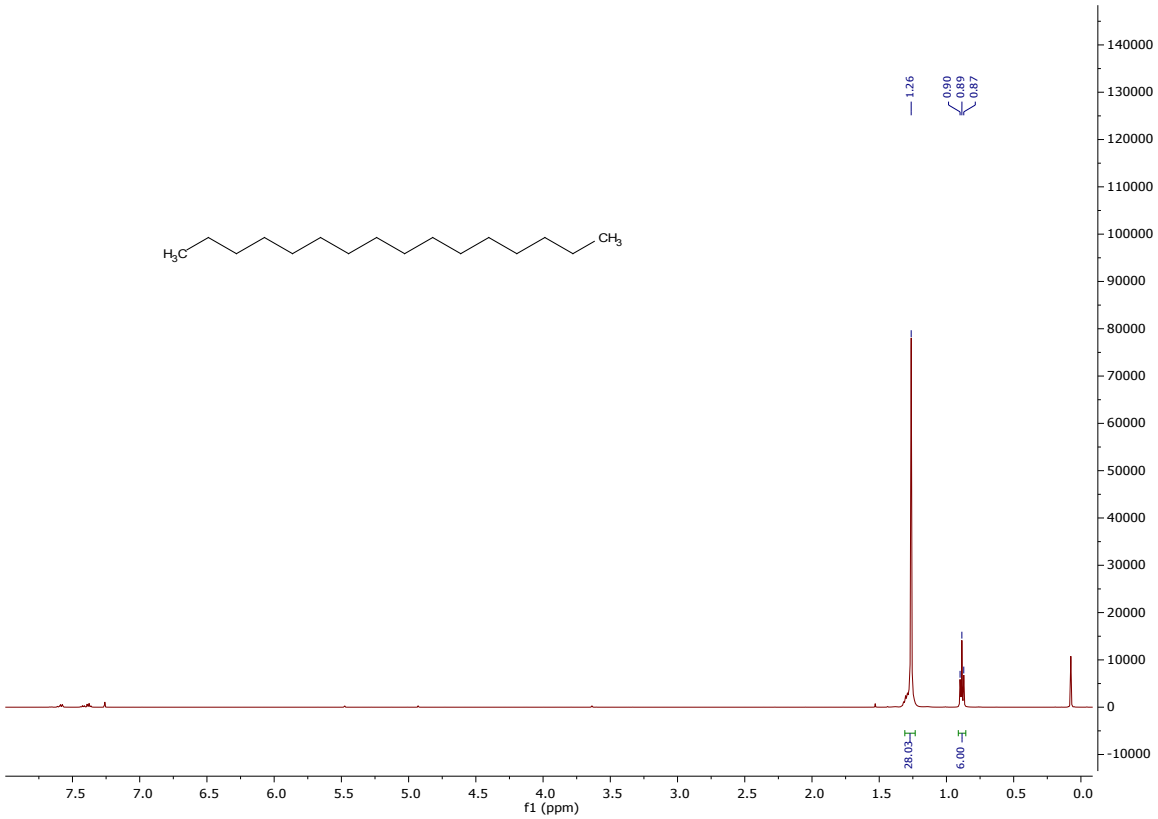


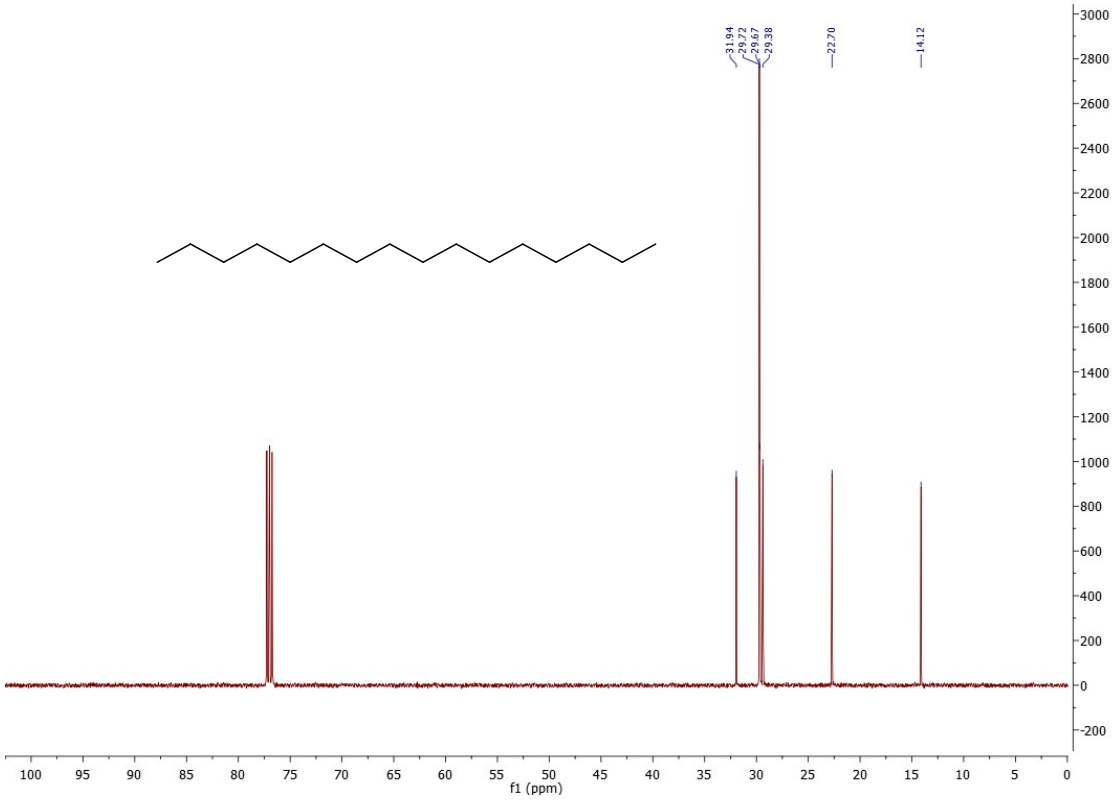


Adamantane (1f-1g)

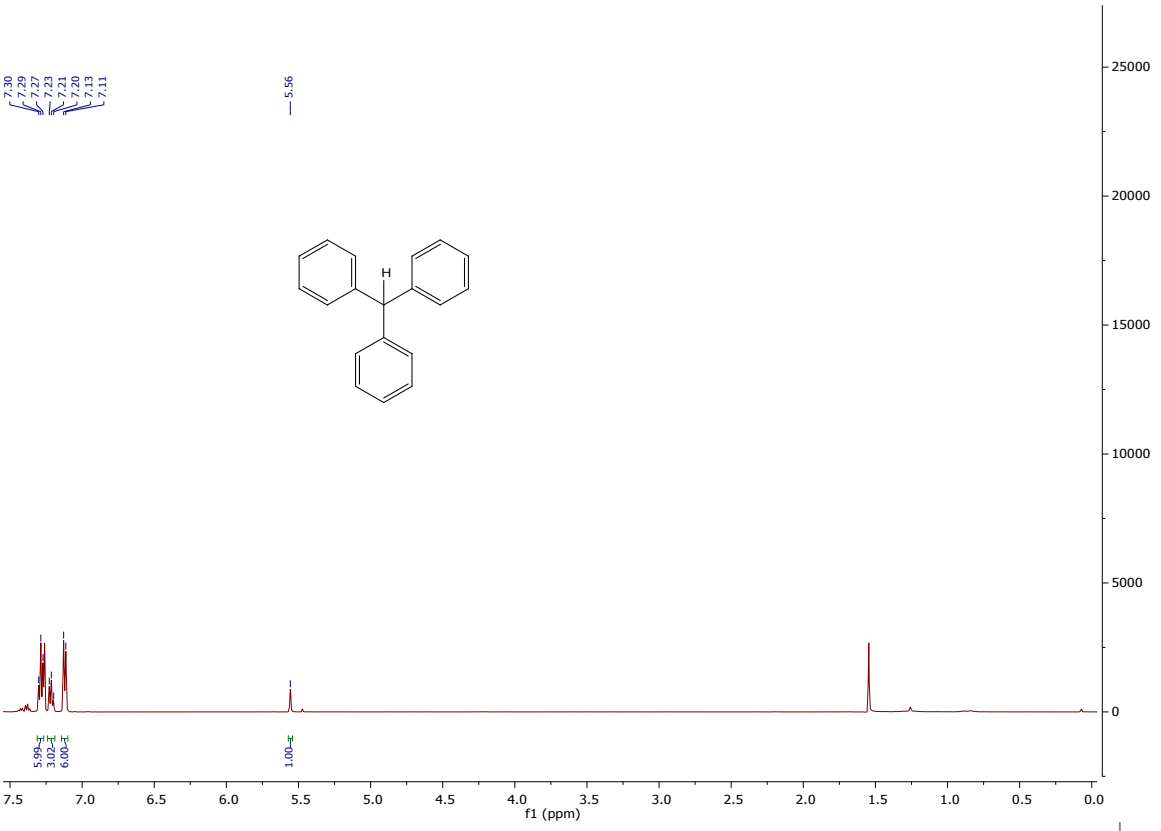


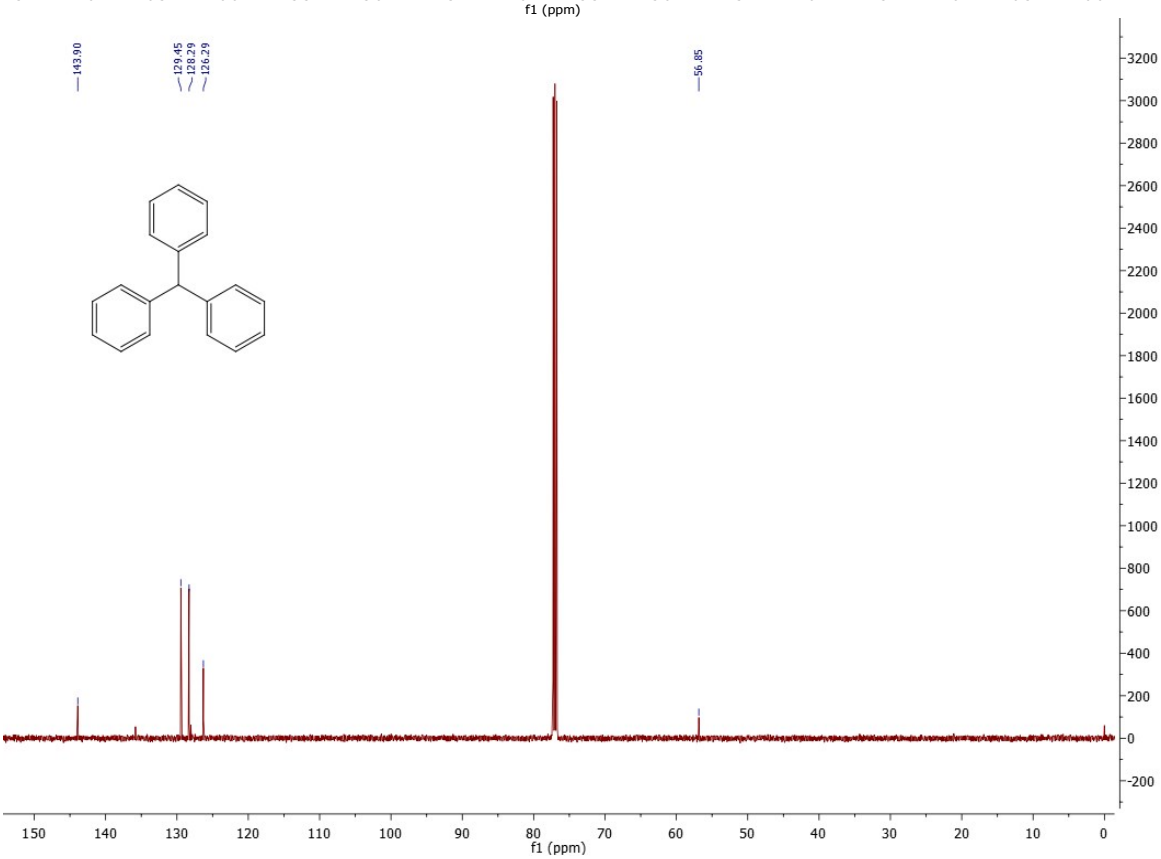
Hexadecane (1h)



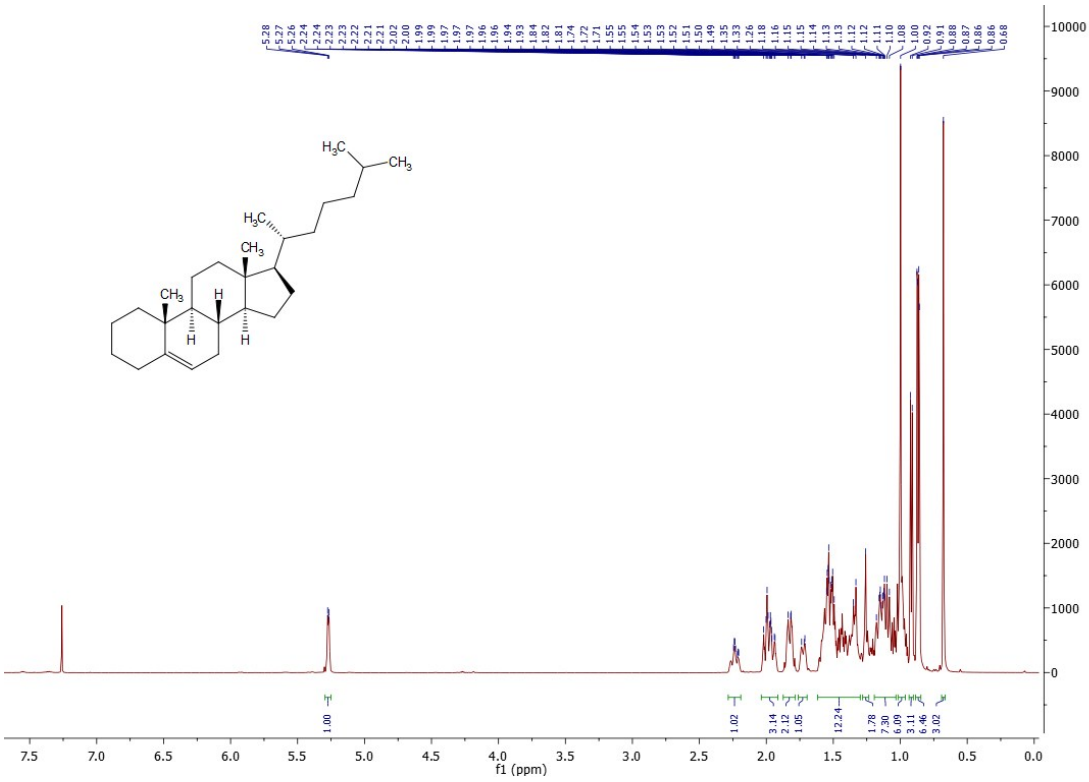


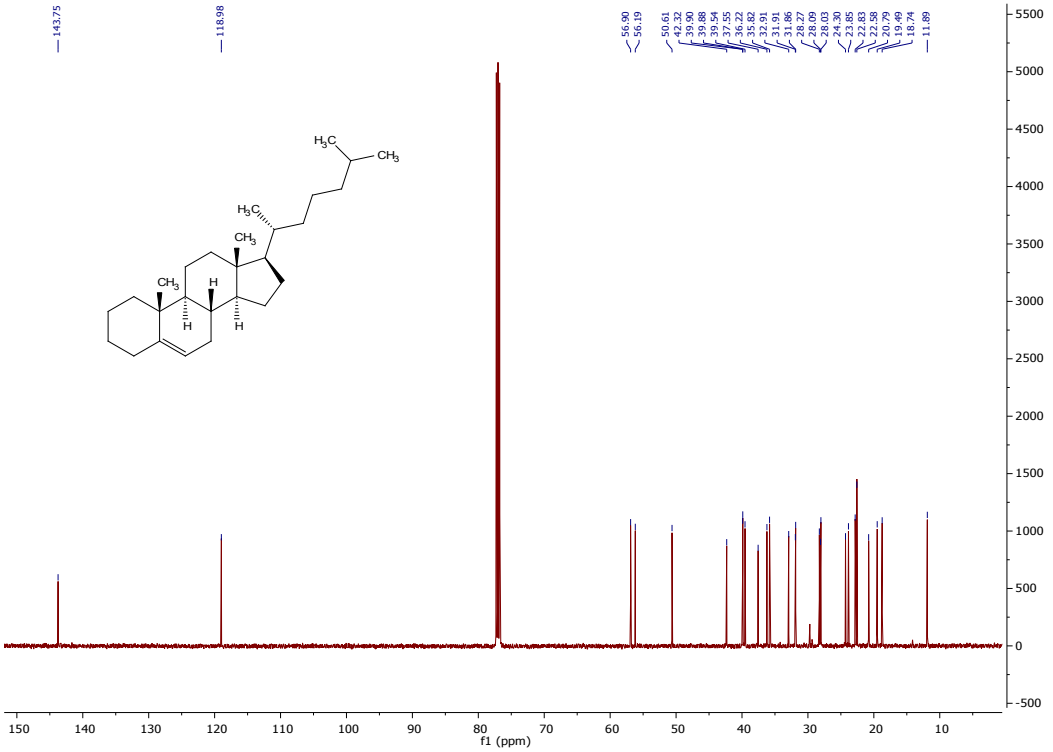
Triphenylmethane (1l)



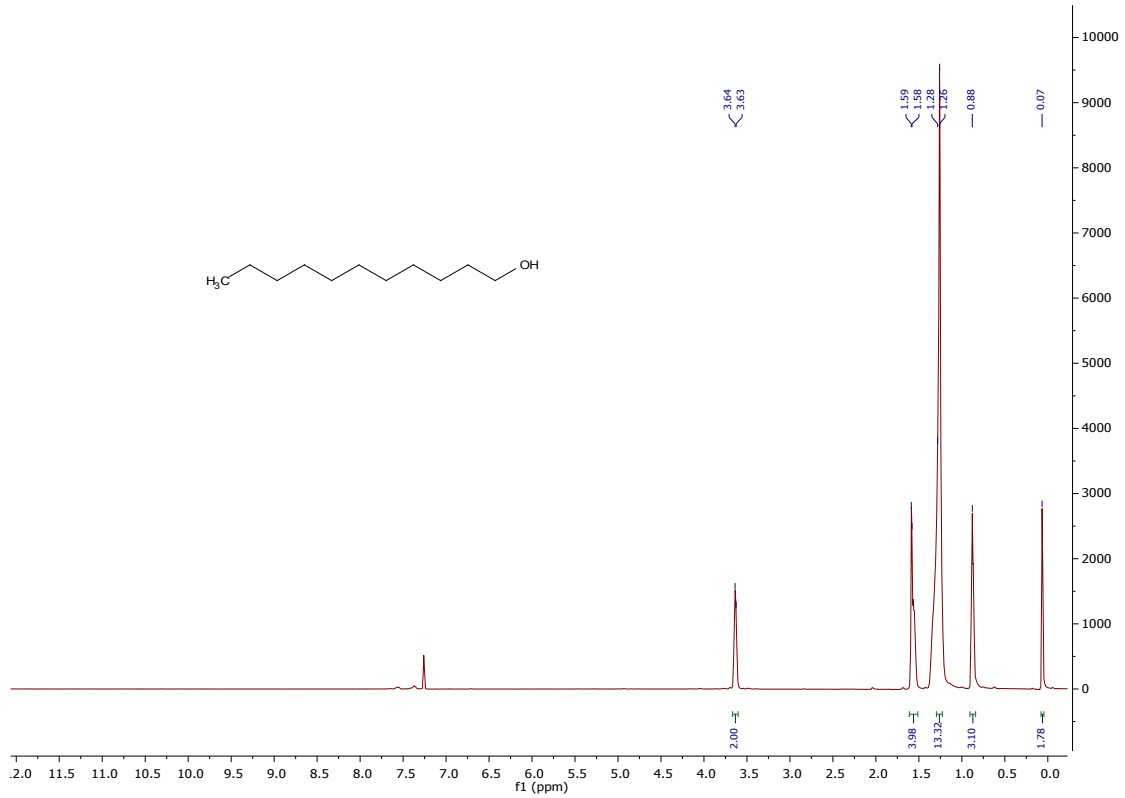


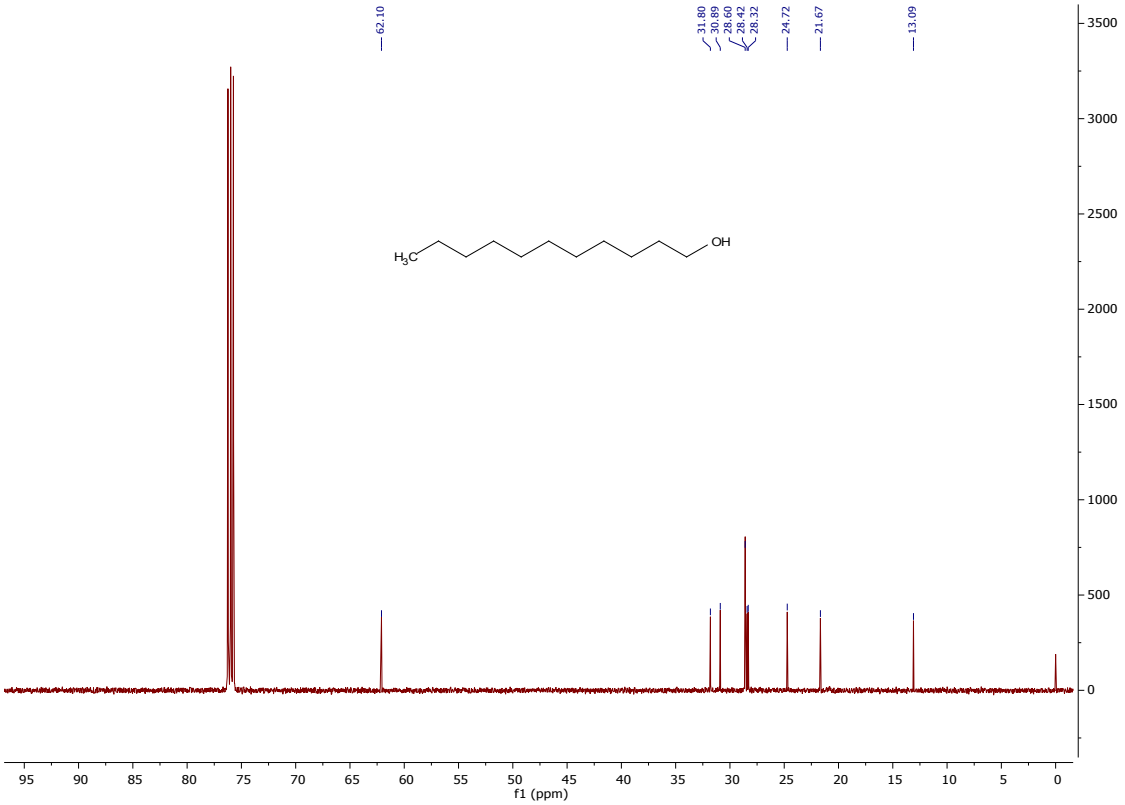
Cholest-5-ene (1m)



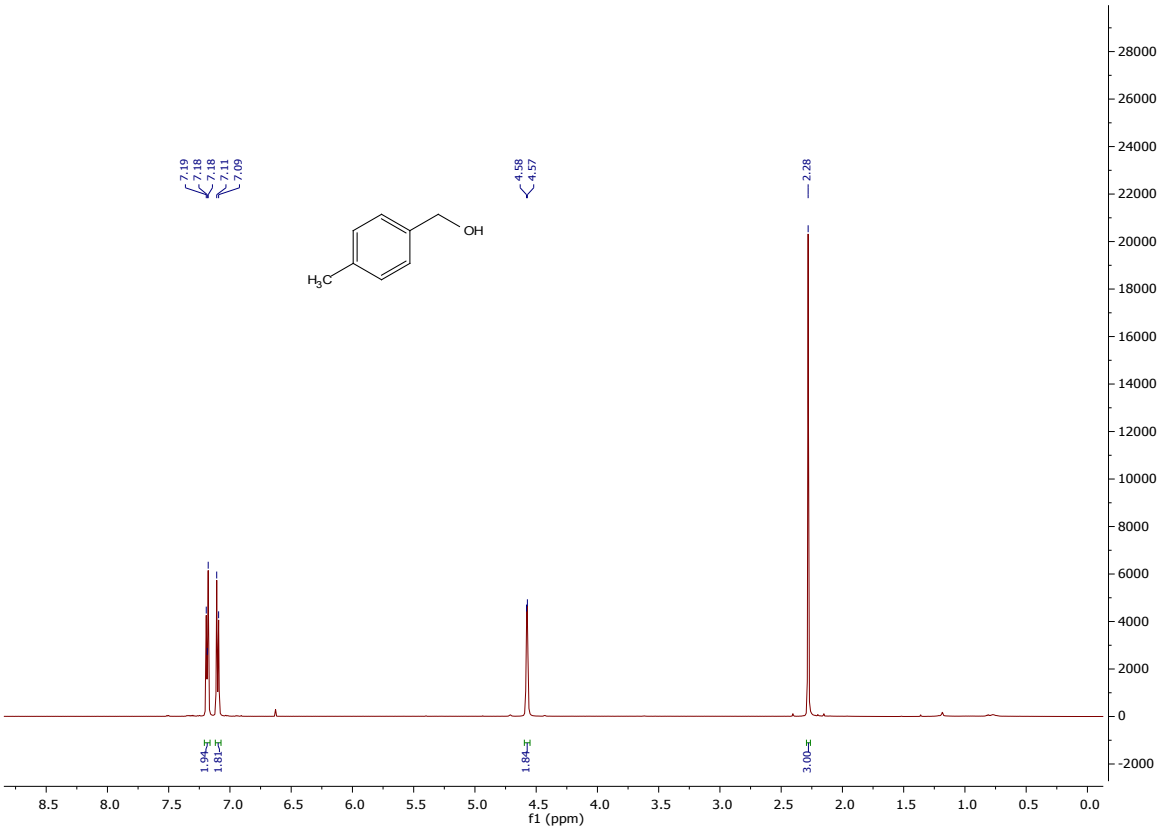


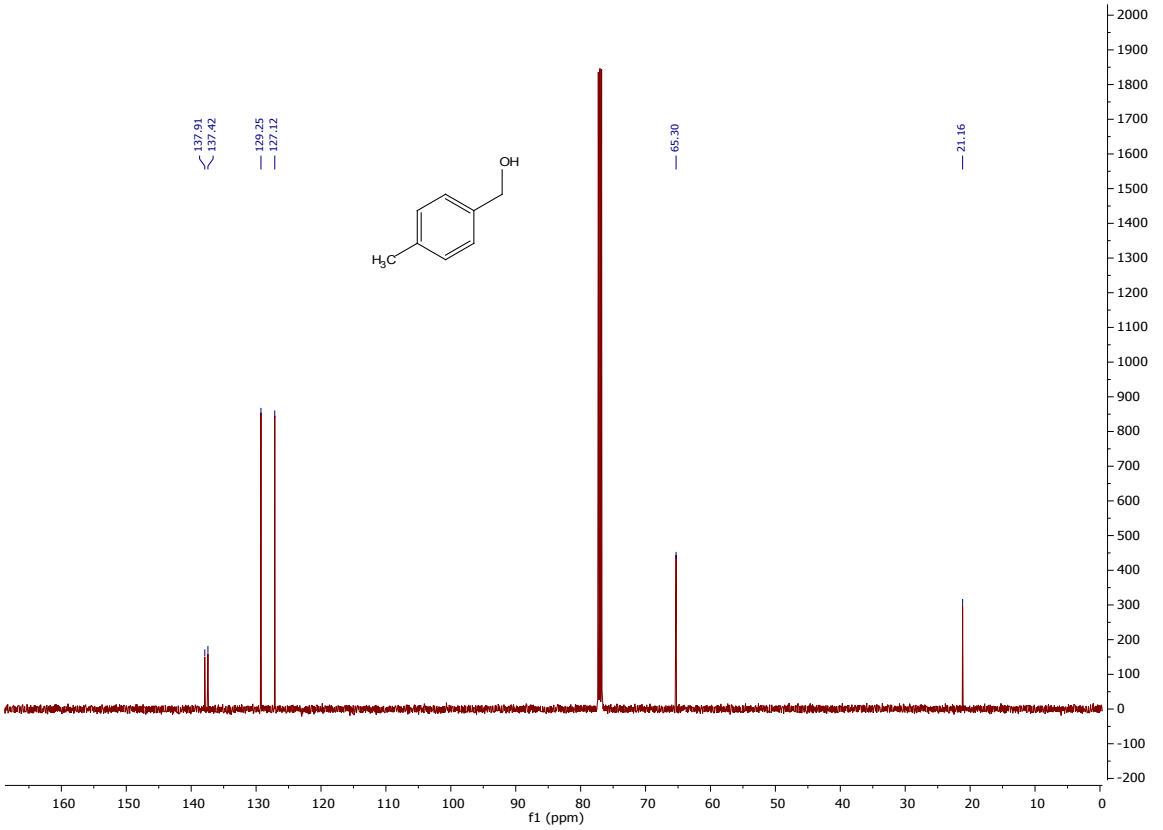
1-undecanol (1o)



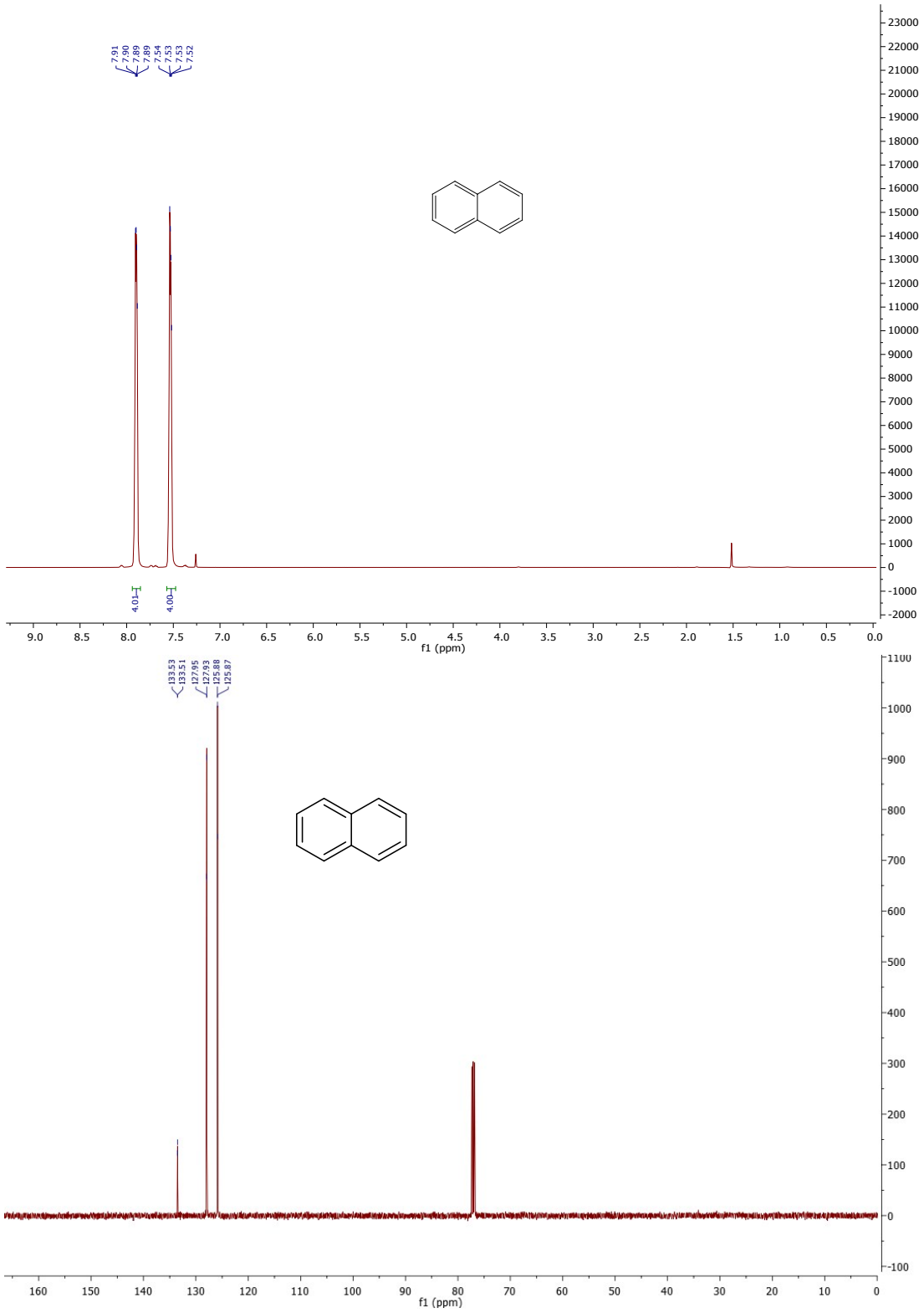


4-methylbenzylalcohol (1p)

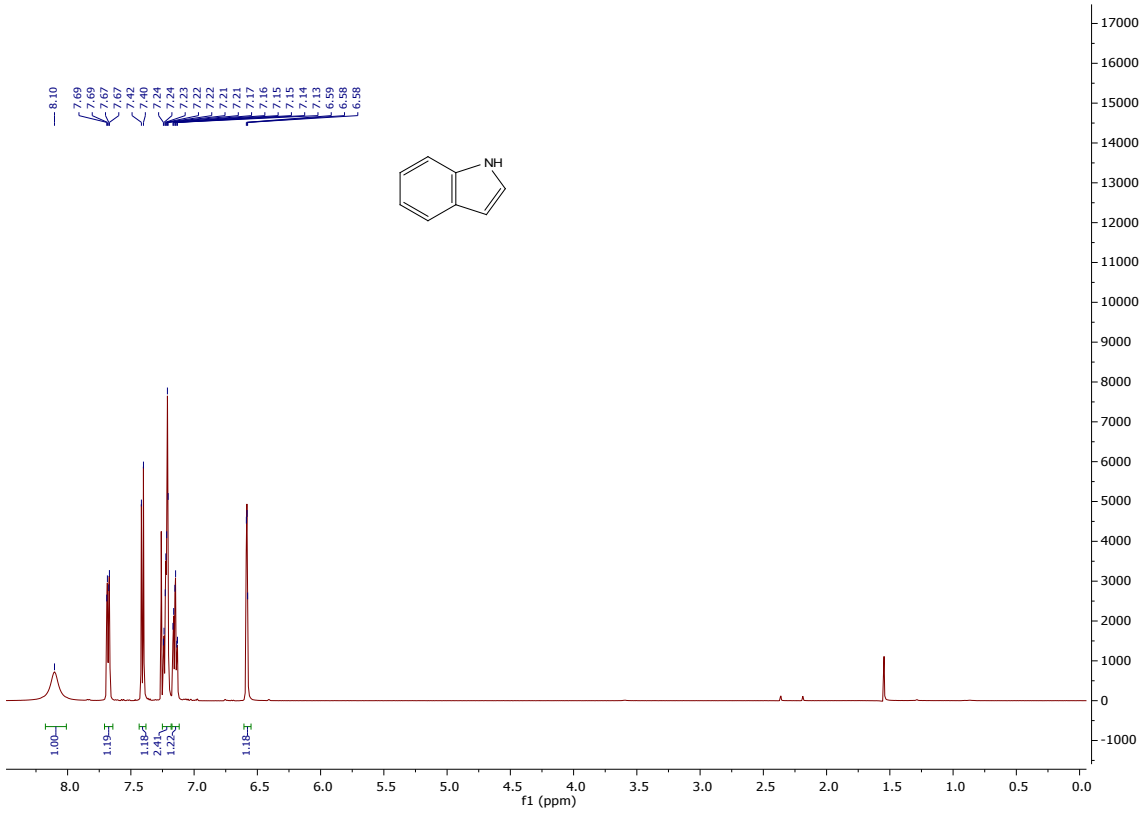


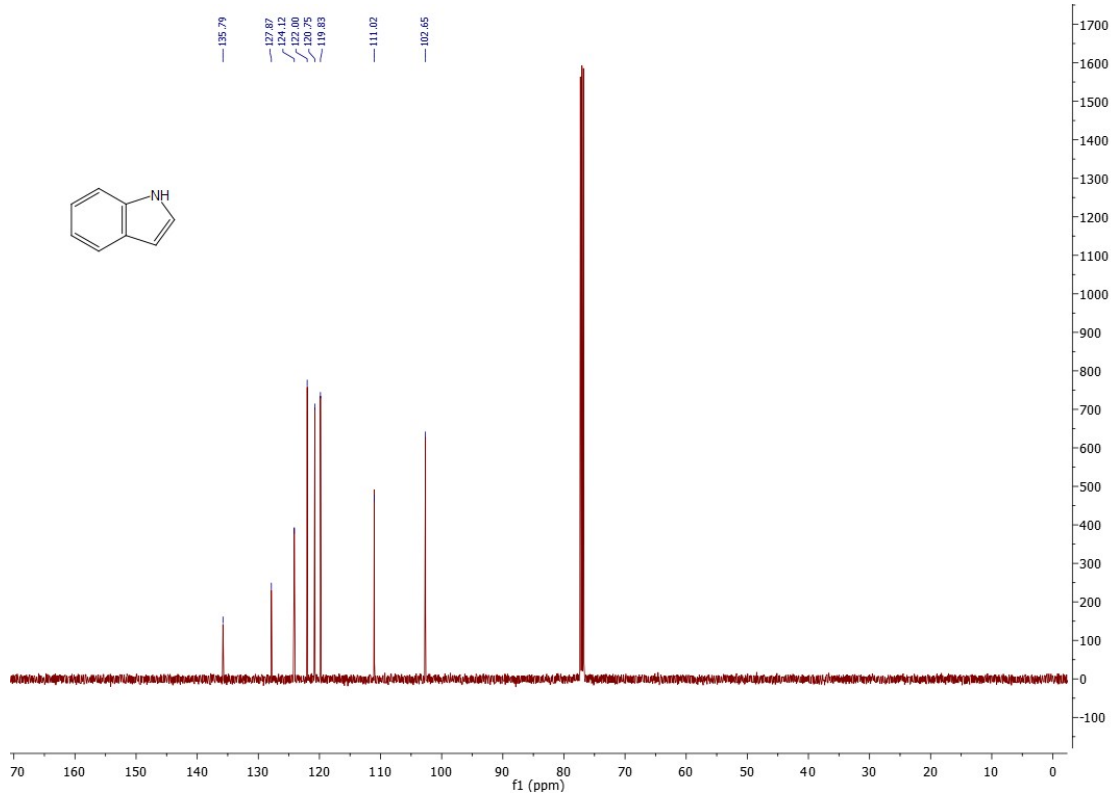


Naphthalene (4a-4b)

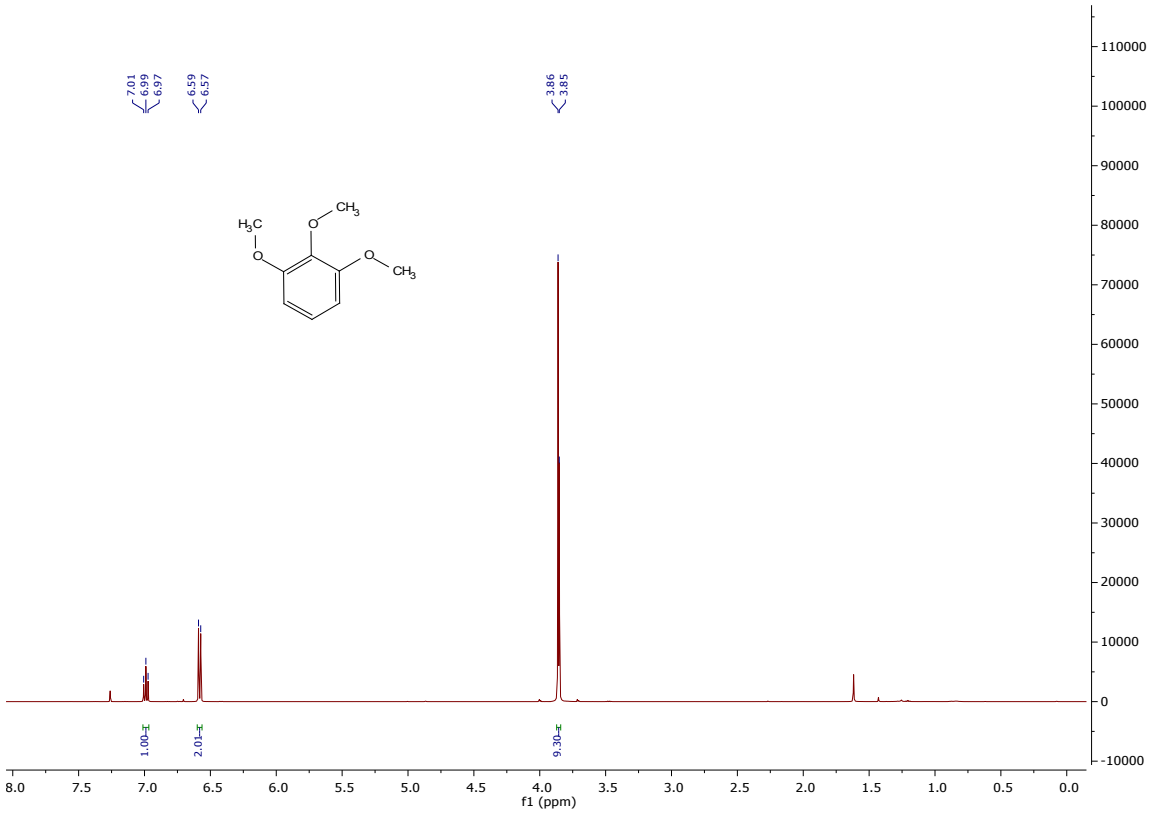


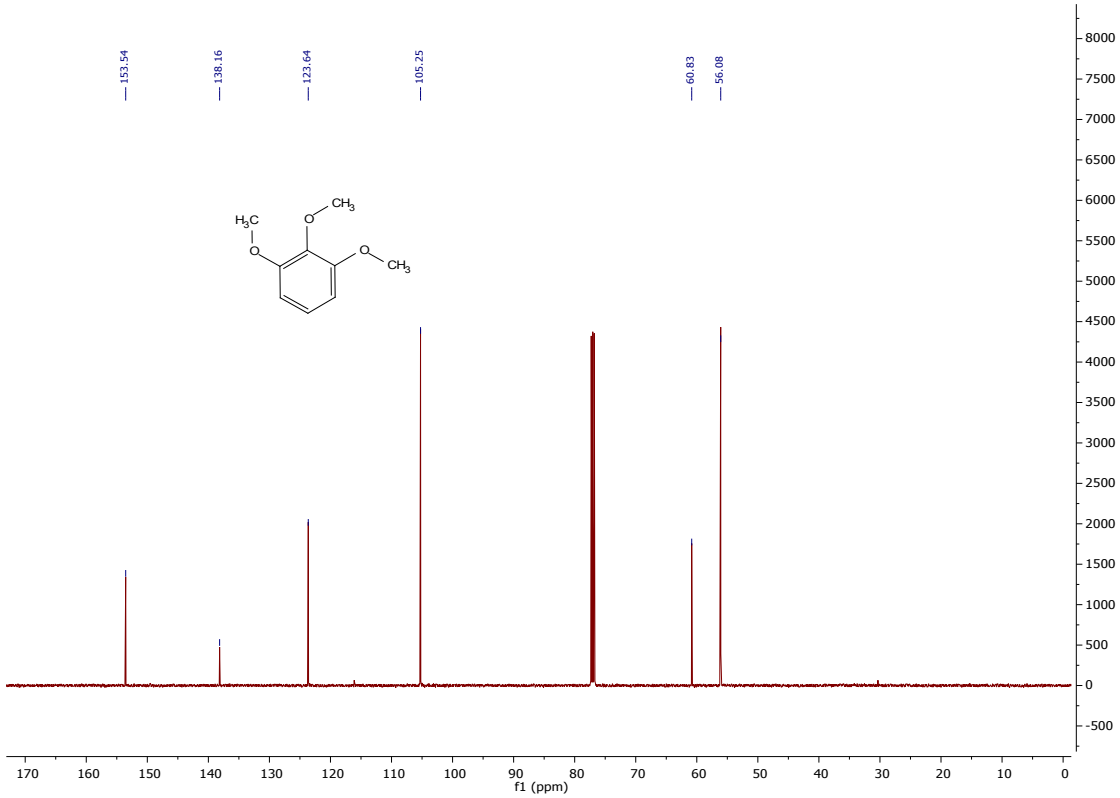
Indole (4d)


8.10
7.69
7.69
7.67
7.67
7.42
7.40
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.17
7.16
7.15
7.15
7.14
7.13
6.59
6.58
6.58
NH
1.00
1.19
1.18
2.41
1.22
1.18
f1 (ppm)

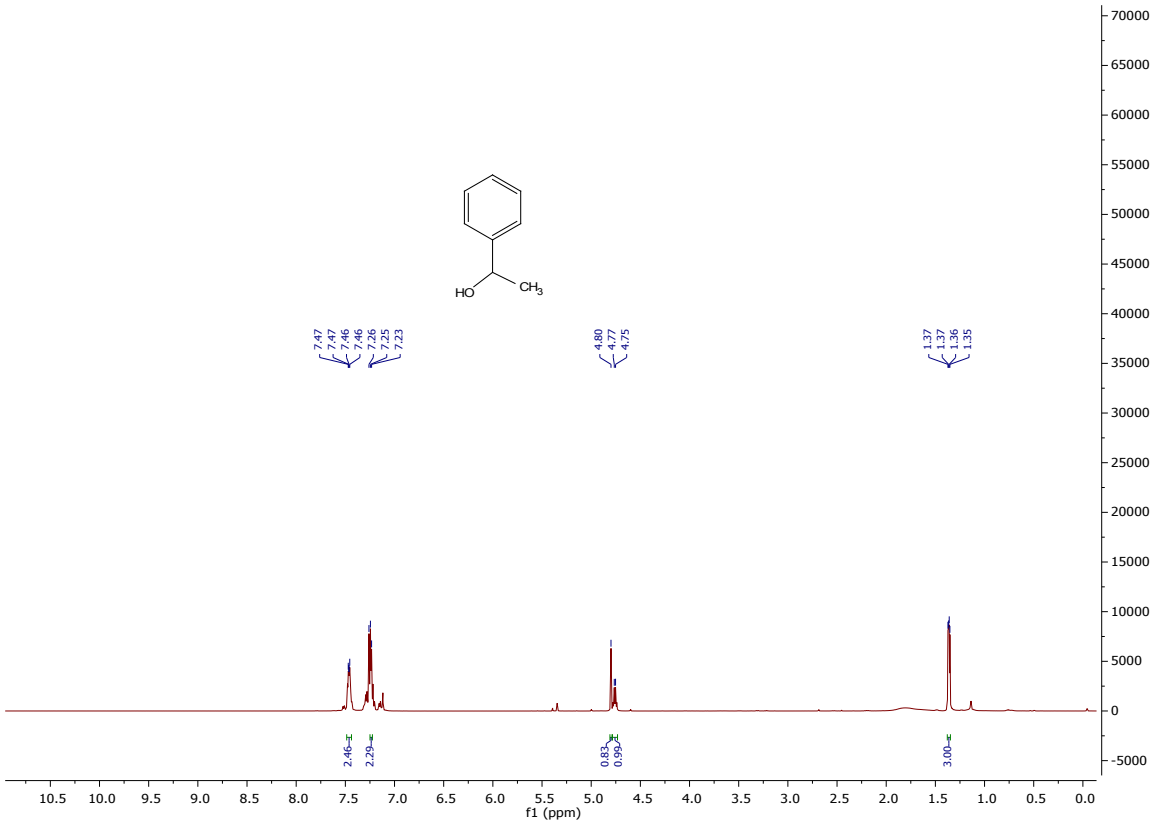

135.79
127.87
124.12
122.00
120.75
119.83
111.02
102.65
NH
f1 (ppm)

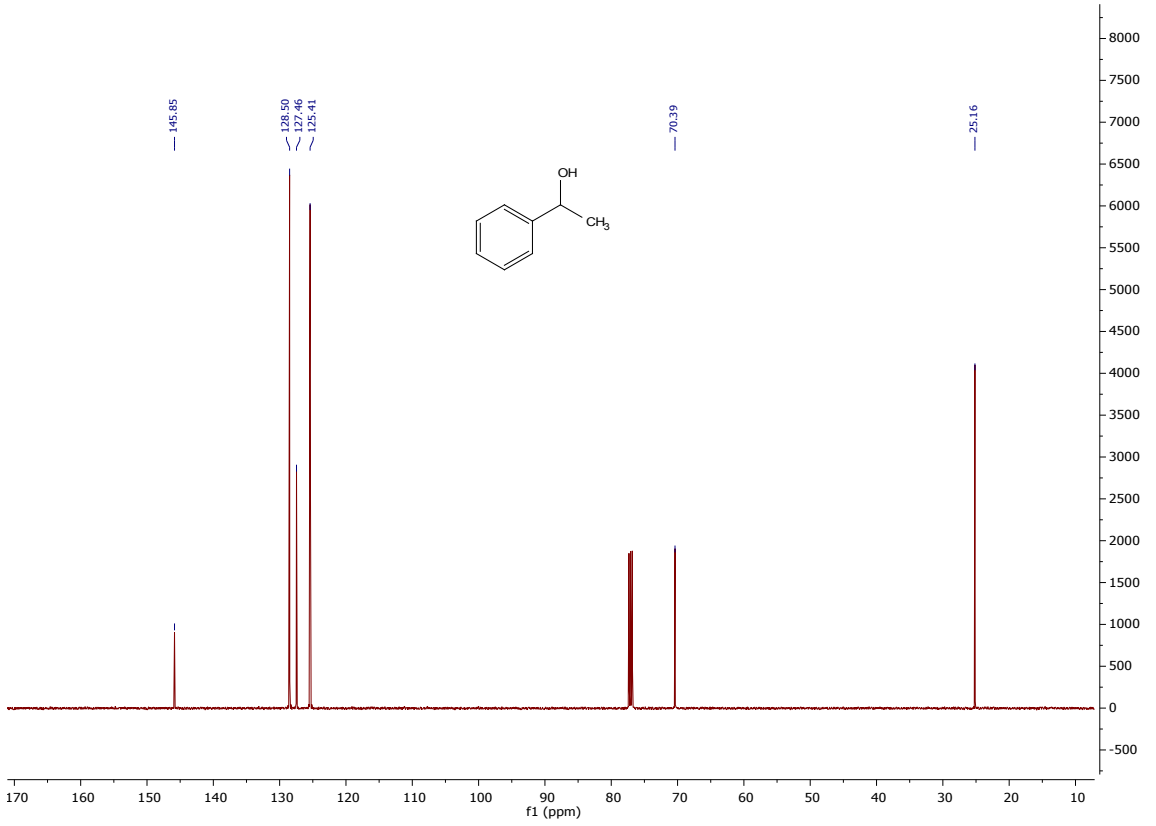
1,2,3-trimethoxybenzene (4f)



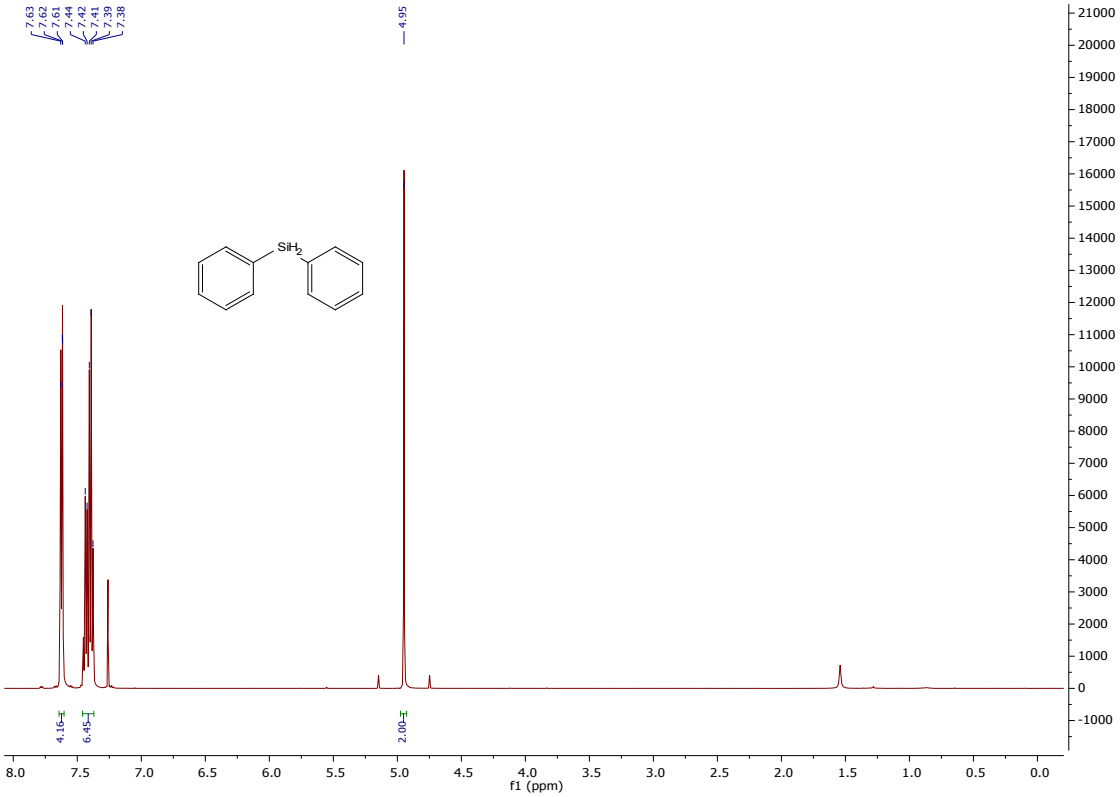


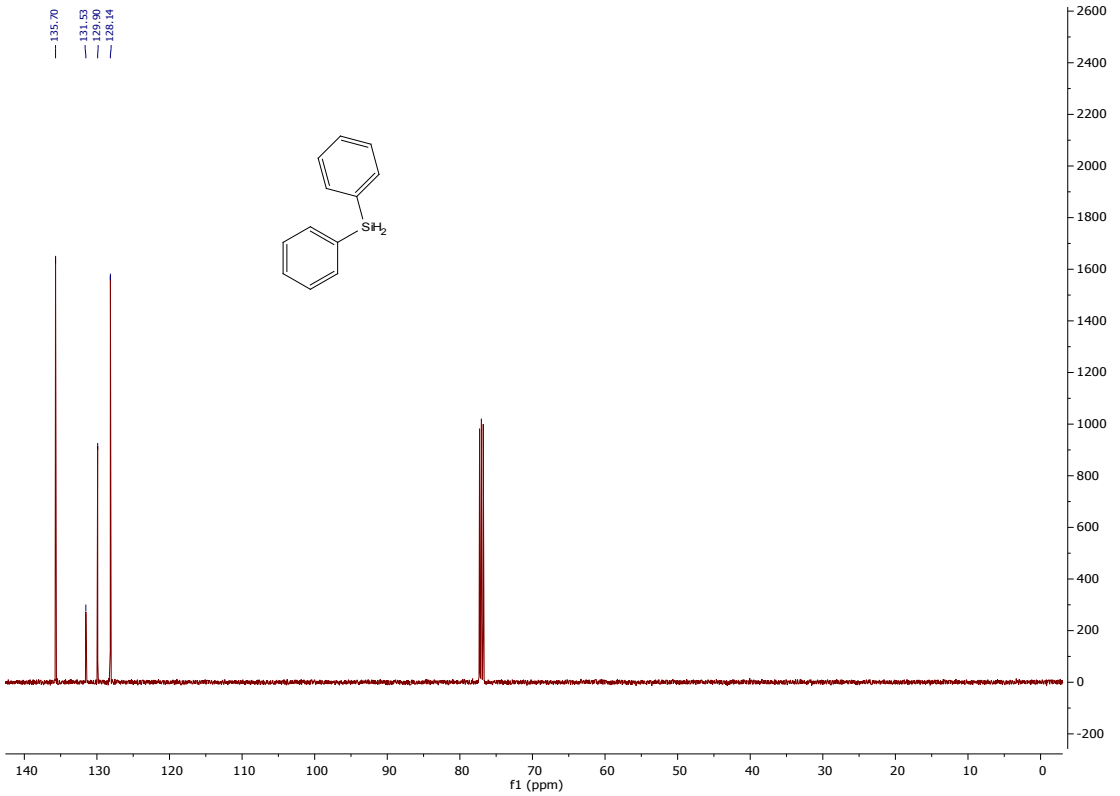
1-Phenylethanol (4j)



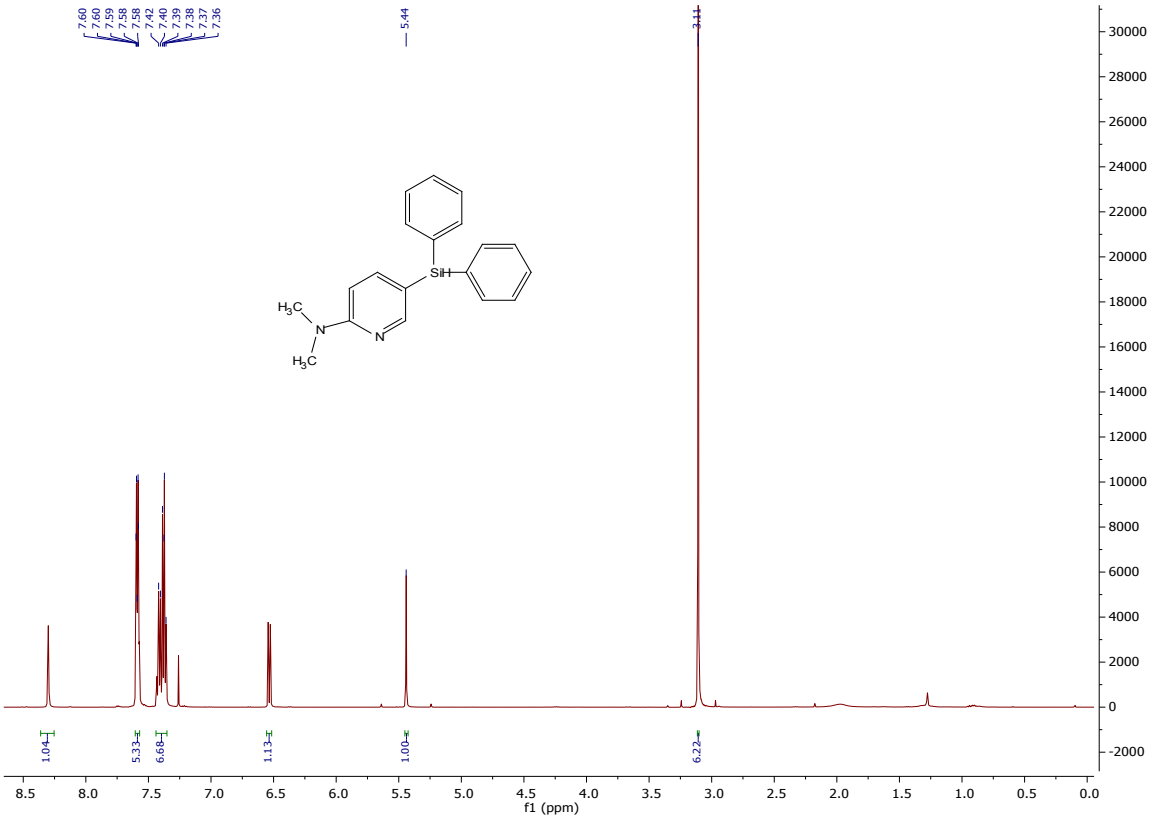


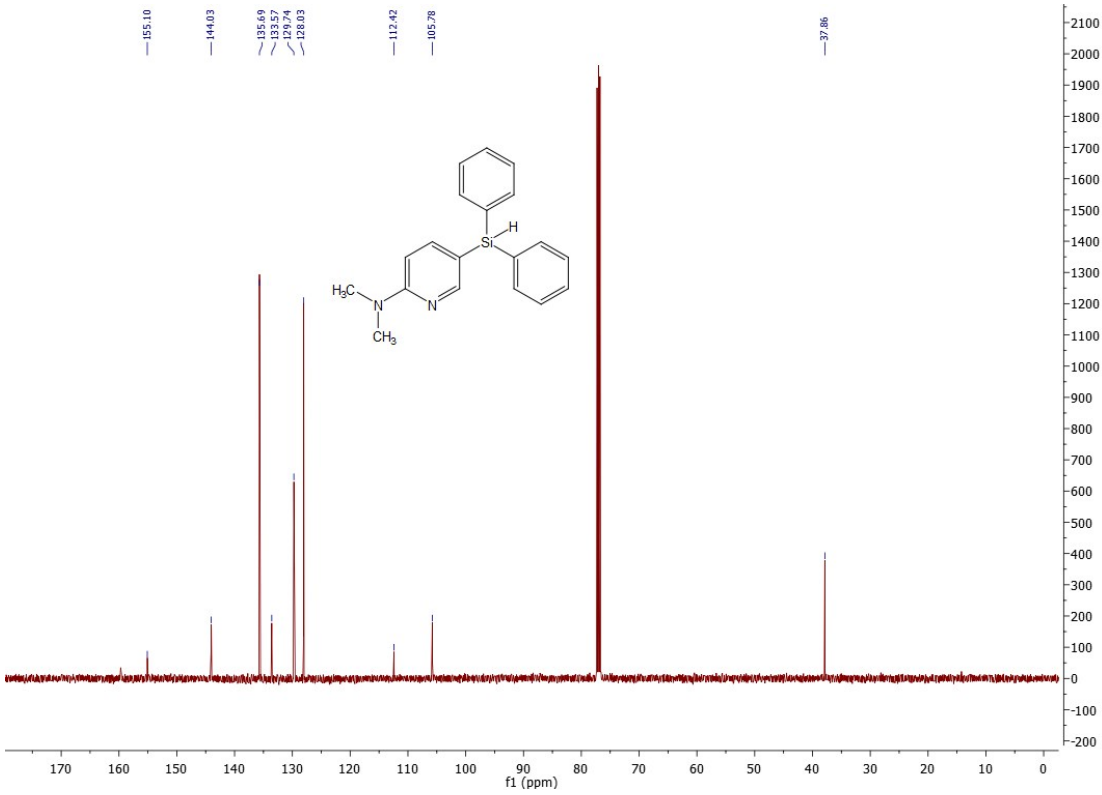
Diphenylsilane



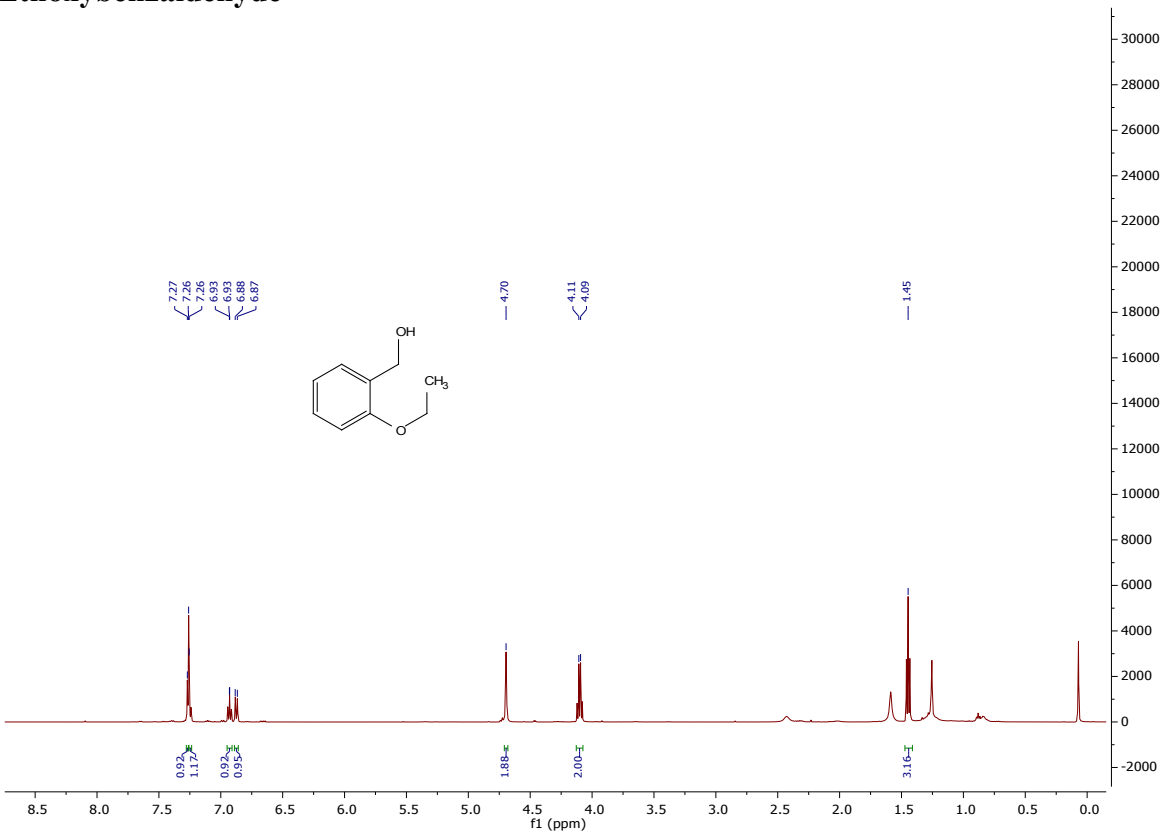


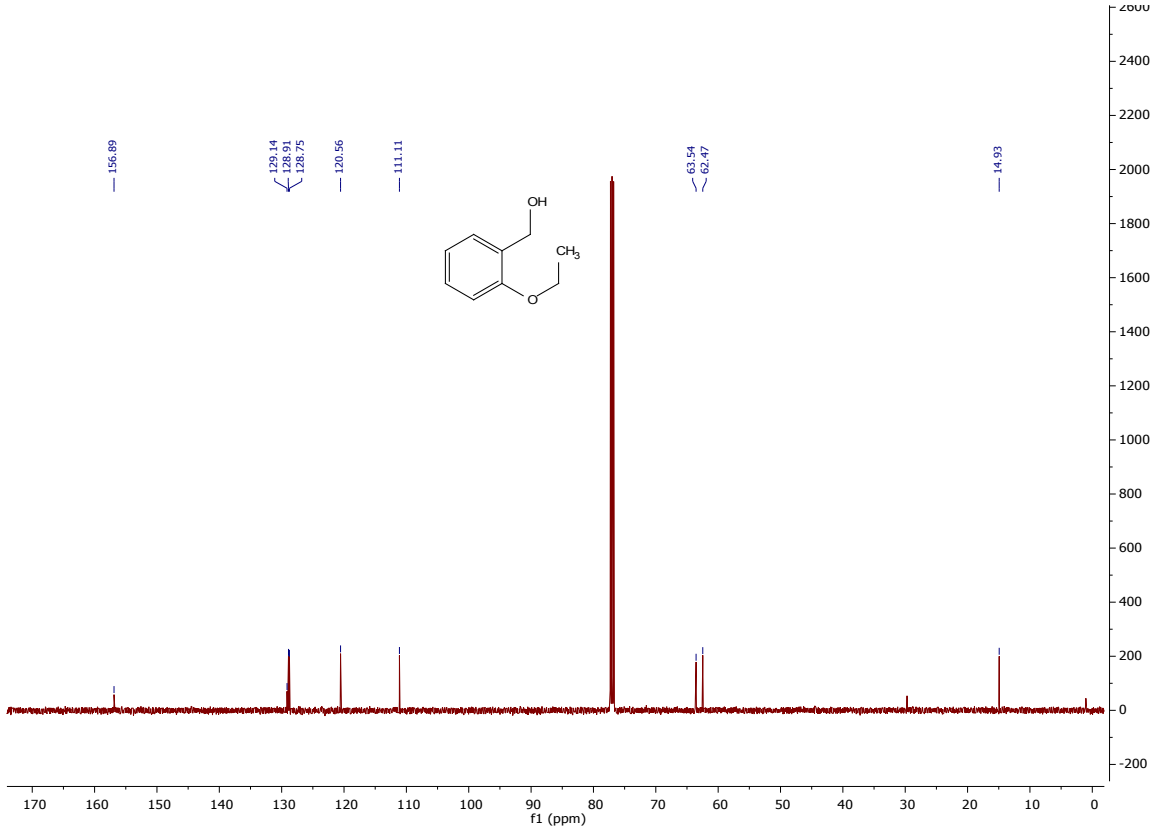
5-(diphenylsilyl)-N, N-dimethylpyridin-2-amine



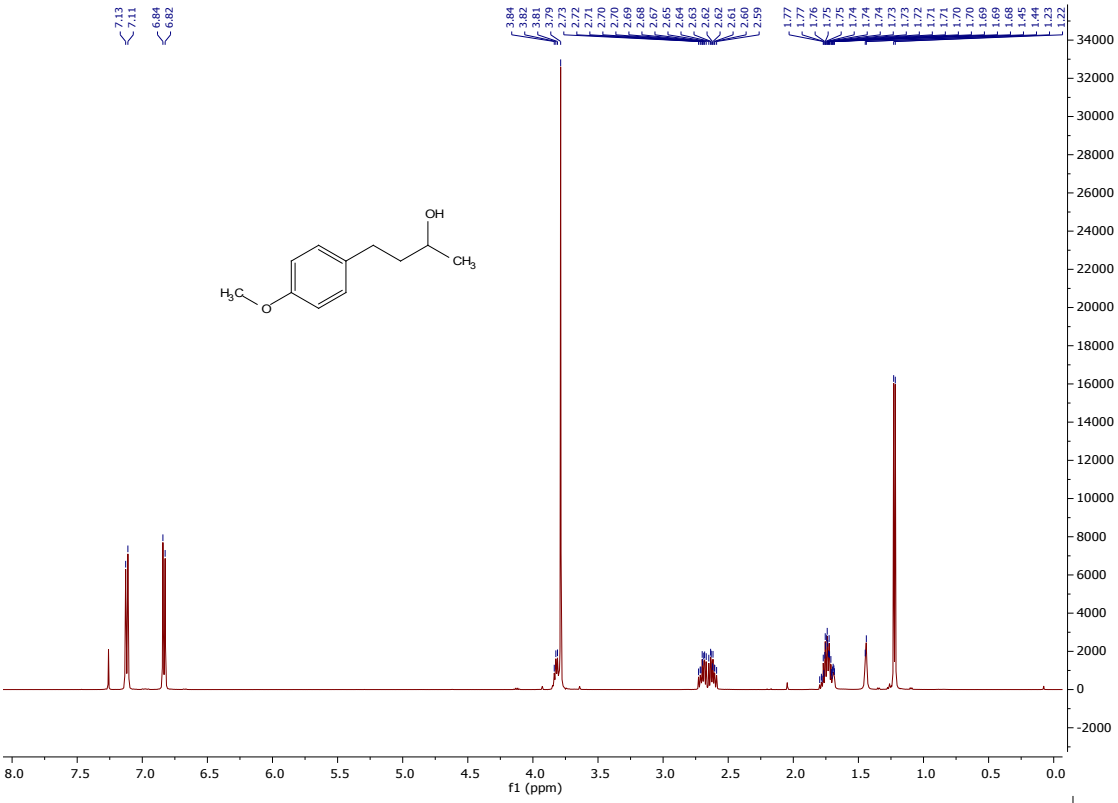


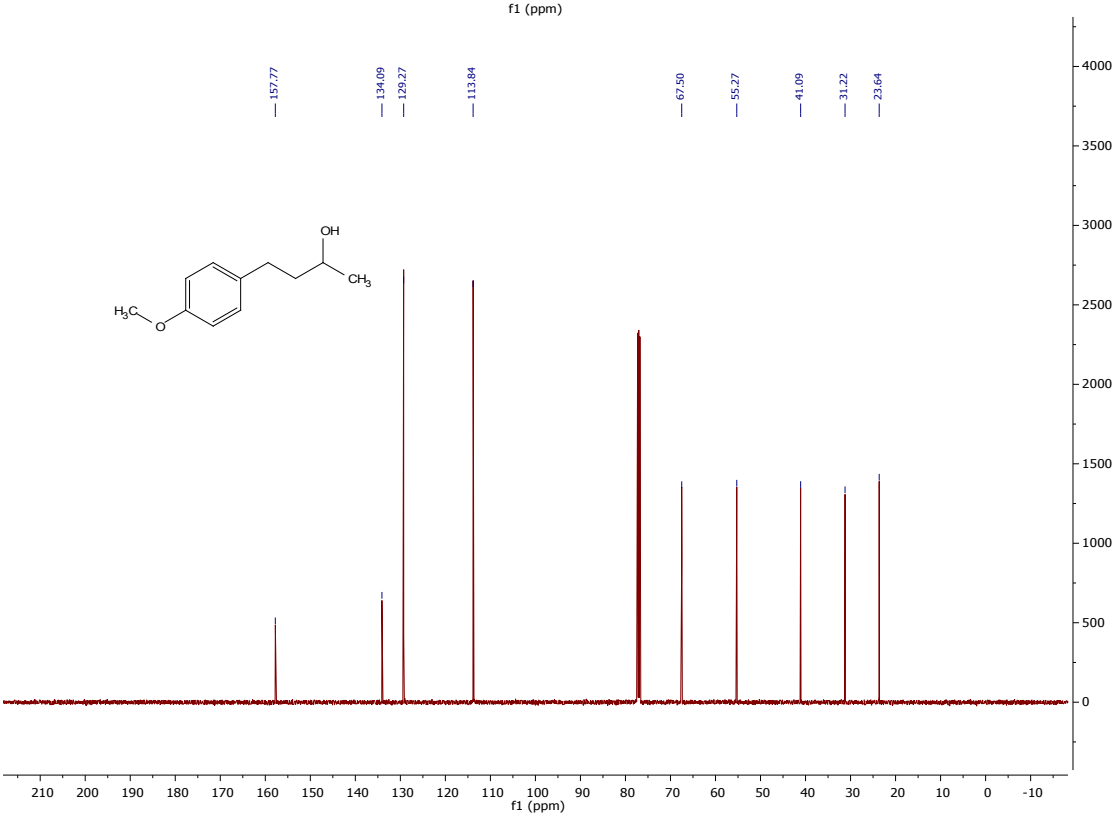
2-Ethoxybenzaldehyde



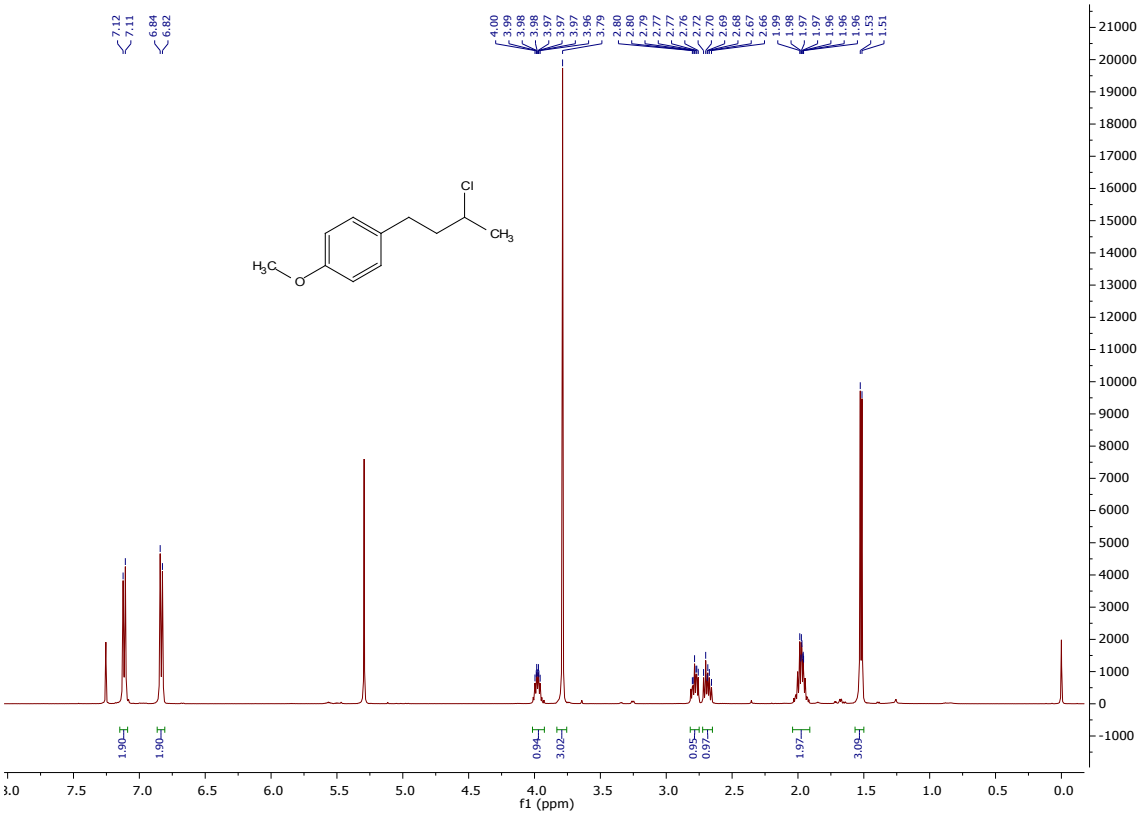


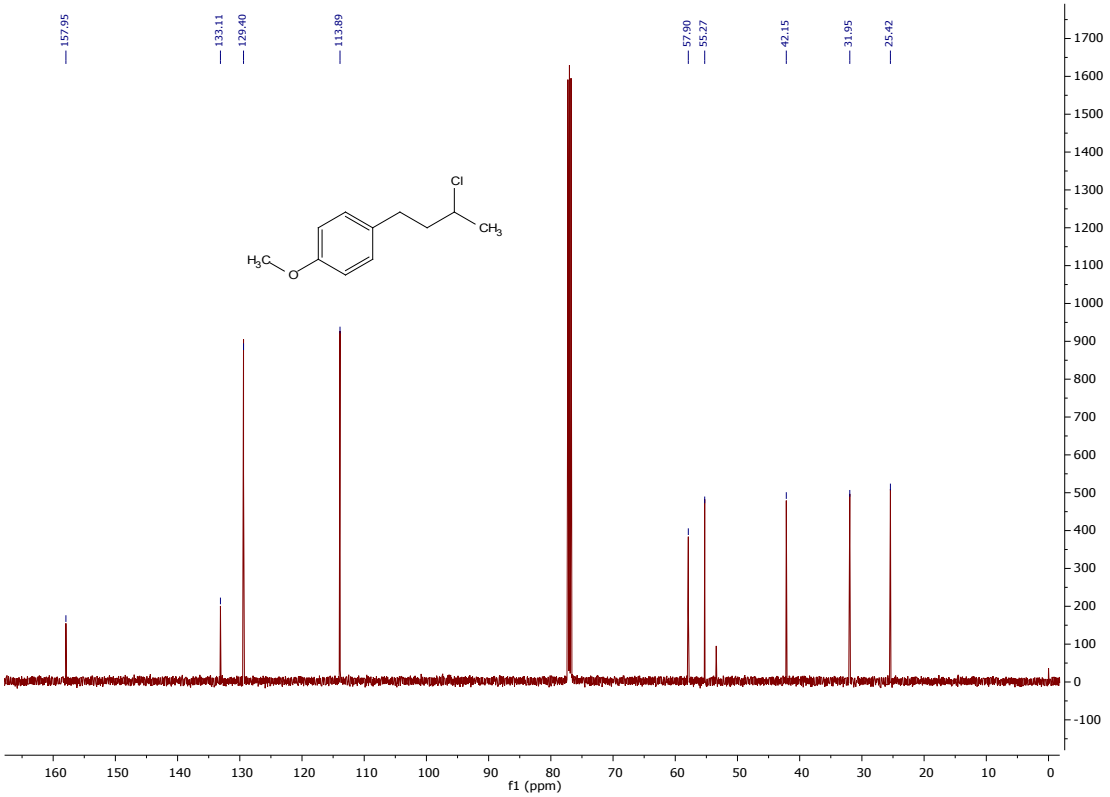
4-(4-methoxyphenyl)butan-2-ol



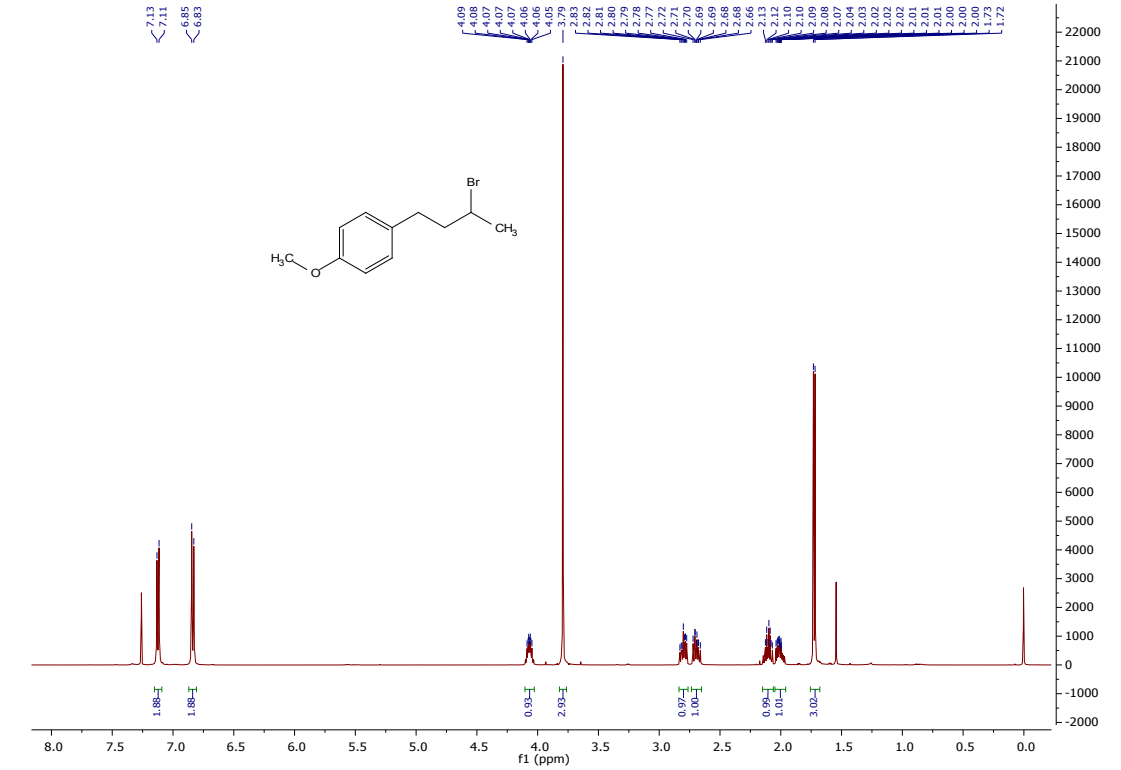


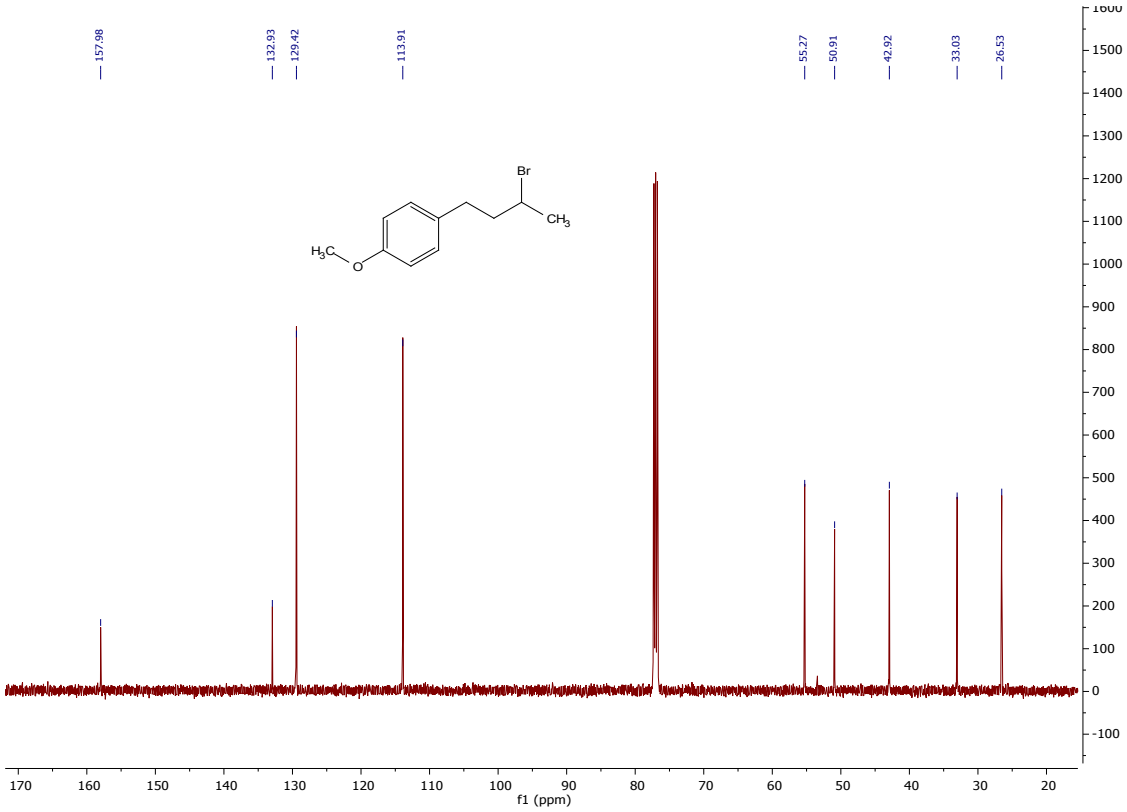
4-(P-methoxy)phenyl-2-chlorobutane



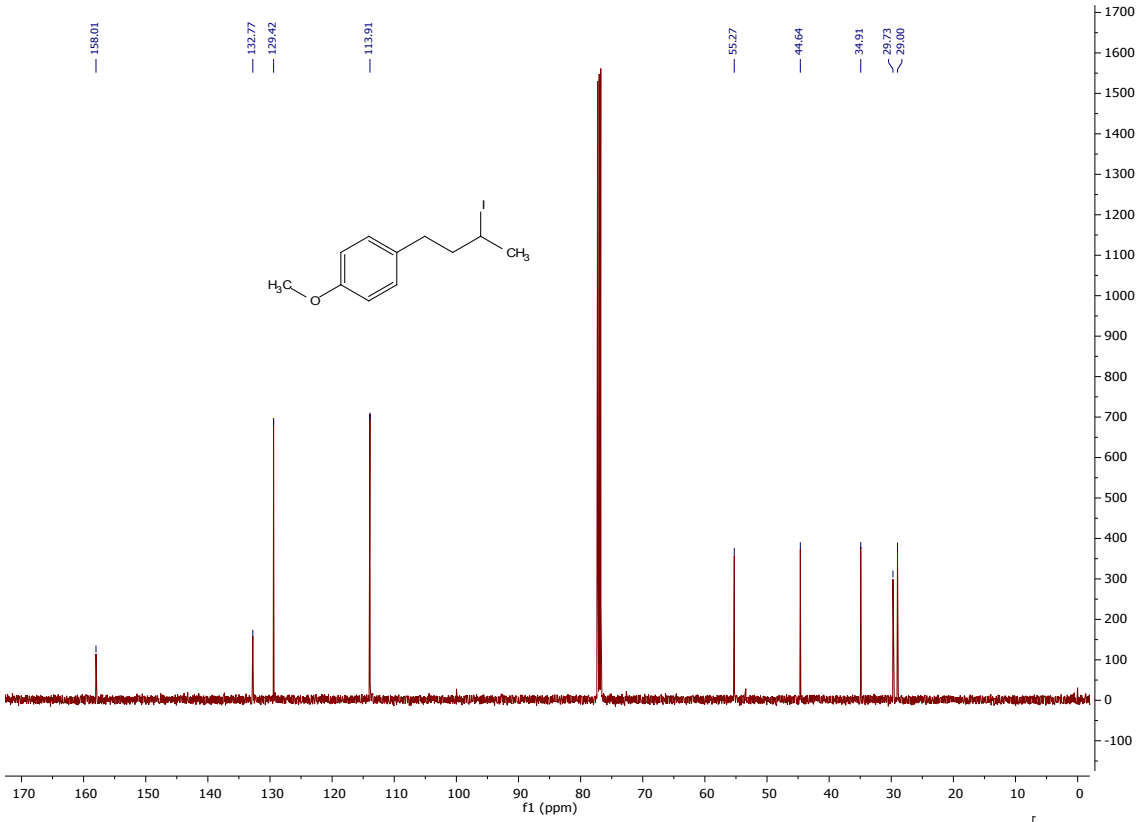


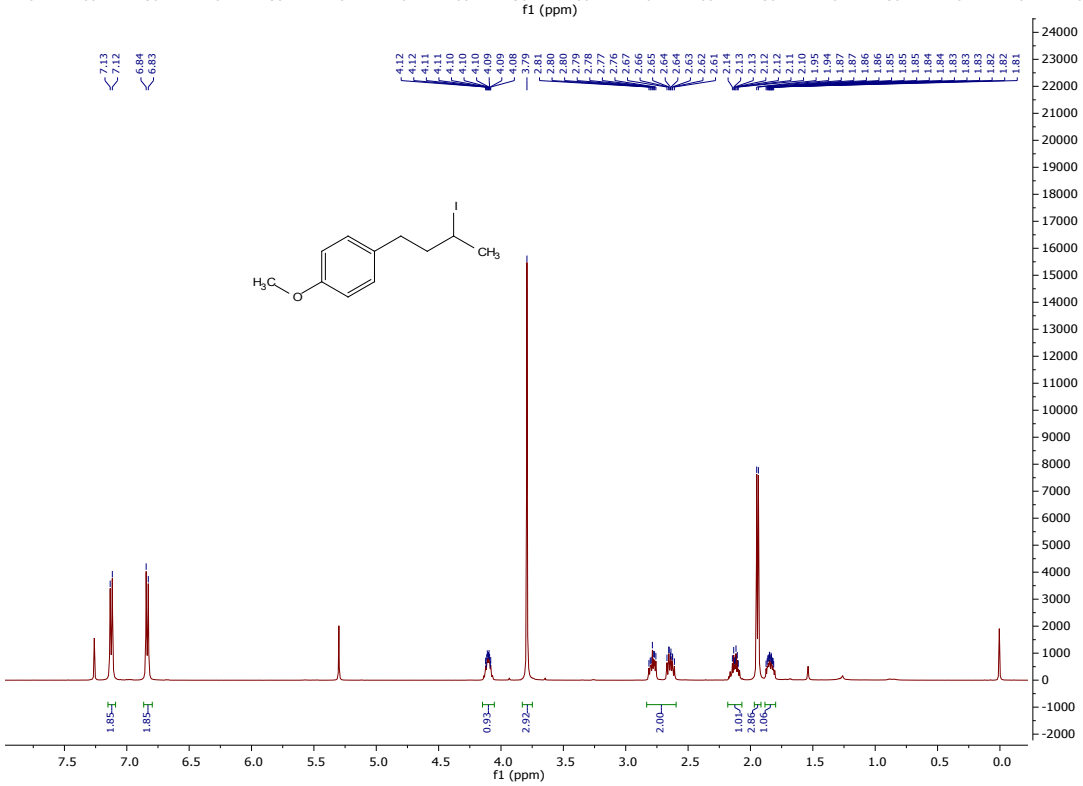
4-(P-methoxy)phenyl-2-bromobutane



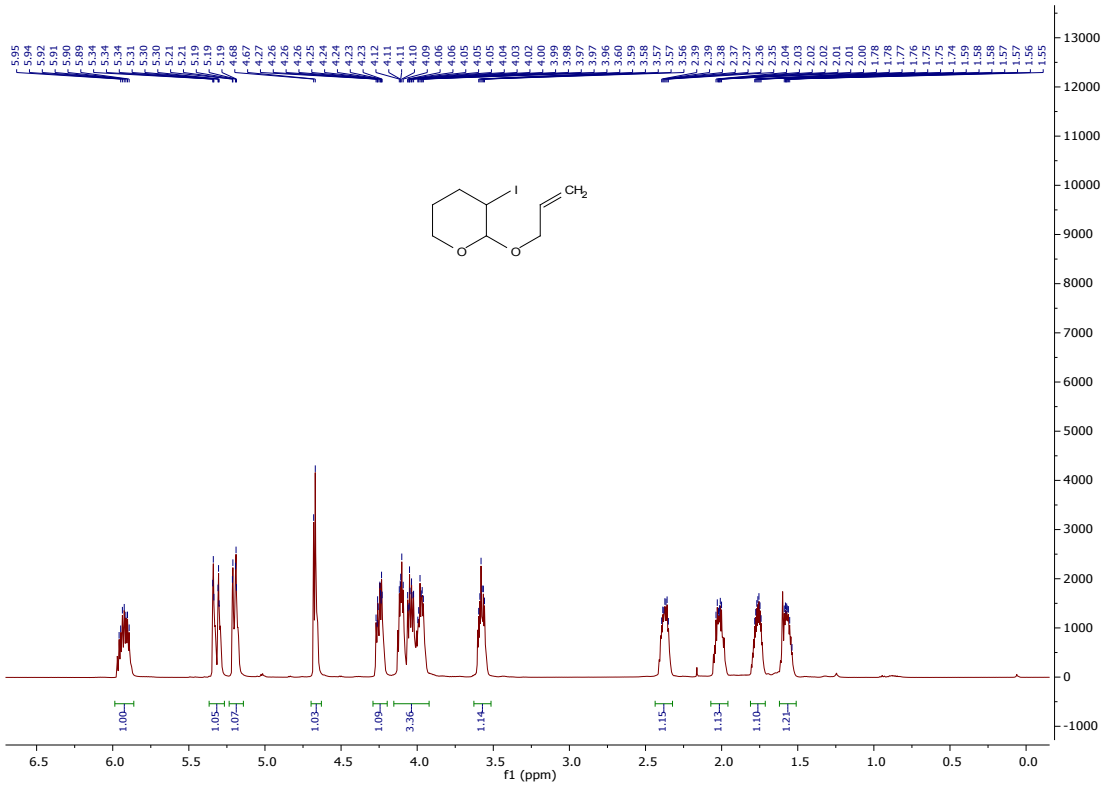


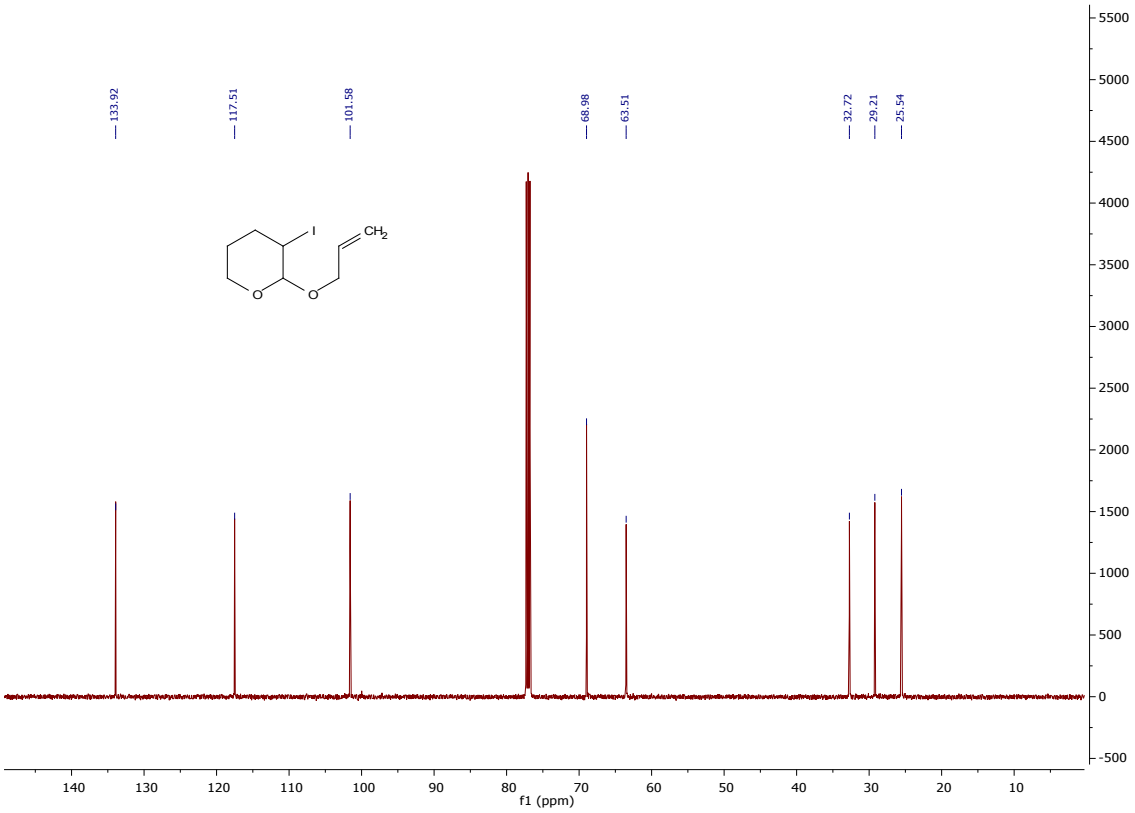
4-(P-methoxy)phenyl-2-iodobutane



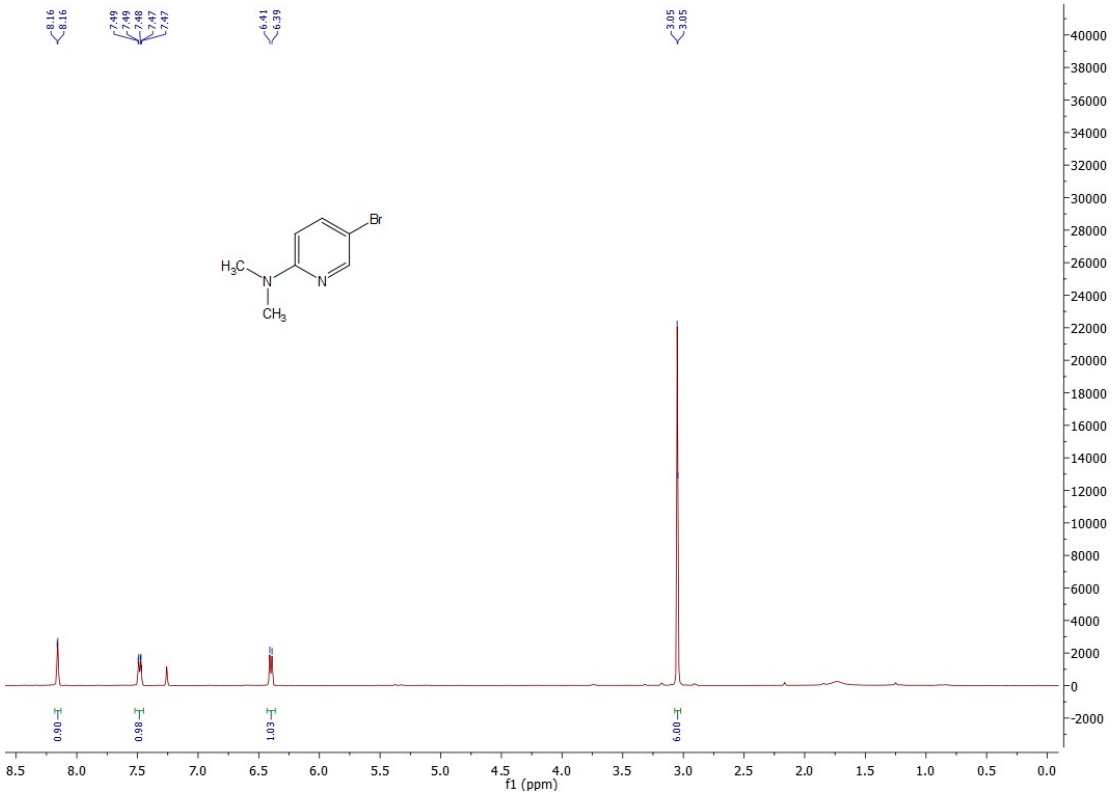


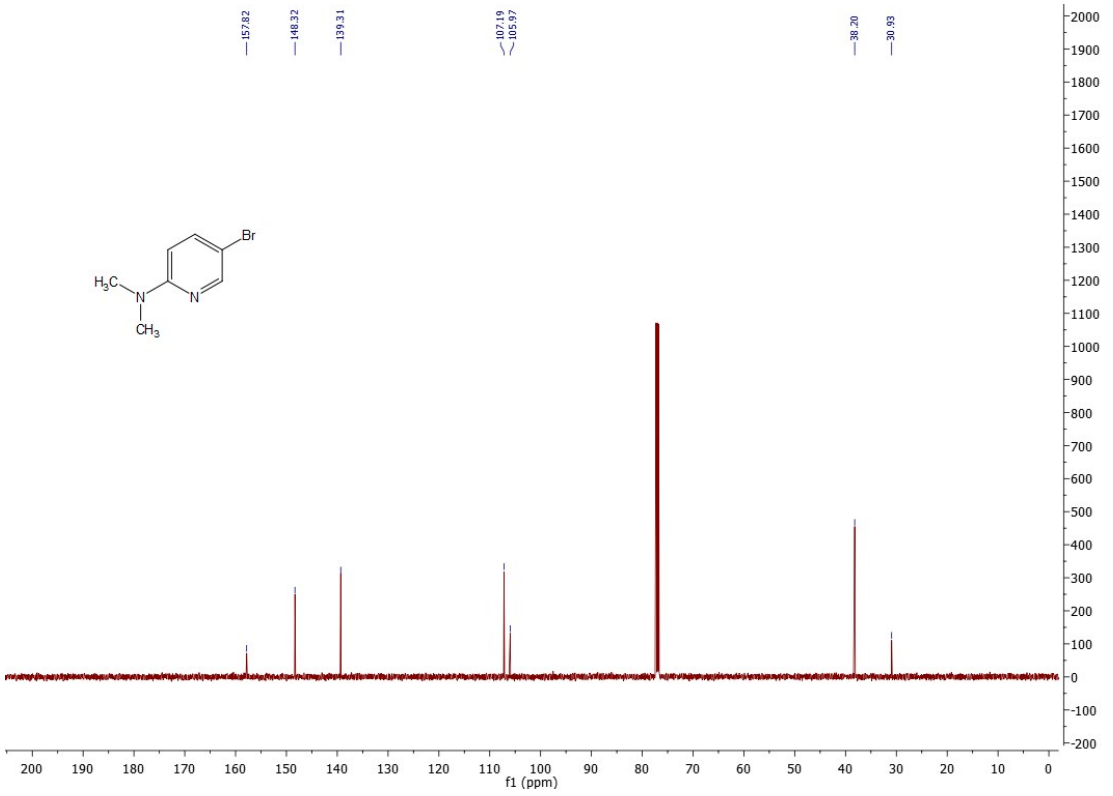
2-(allyloxy)-3-iodotetrahydro-2H-pyran



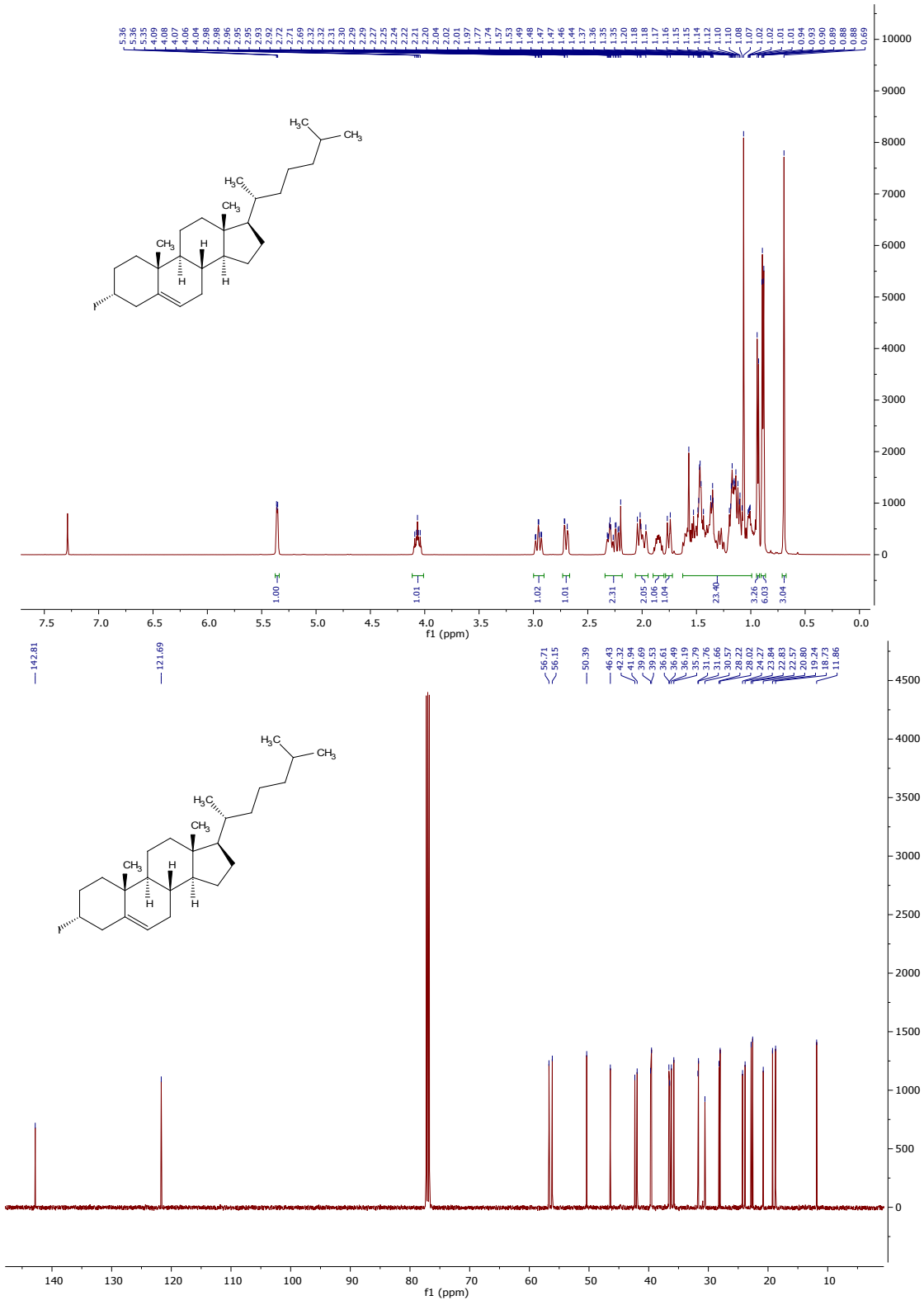


5-Bromo-N,N-dimethylpyridin-2-amine





Cholesteryl Iodide



2-(2-bromoethoxy)benzaldehyde