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Supporting Information

Selective Switchable Iron-Catalyzed Hydrosilylation of Carboxylic Acids

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I. General information.

All reagents were obtained from commercial sources and used as received. All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dried argon. Toluene and THF were dried over Braun MB-SPS-800 solvent purification system. Technical grade petroleum ether (40-60 °C bp.) and ethyl acetate were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60μm, 60A).

^{1}H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE 300 and 400 spectrometers at 300.1, and 400.1 MHz respectively, using the solvent as internal standard ($CDCl_3$ 7.26 ppm). ^{13}C NMR spectra were obtained at 75 or 100 MHz and referenced to the internal solvent signals ($CDCl_3$, central peak is 77.0 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad).

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M×0.25 mm×0.25 mm film thickness), which was used with N_2/air as vector gas. The following GC conditions were used: Initial temperature 80 °C, for 2 minutes, then rate 10 °C/min. until 220 °C and 220°C for 15 minutes.

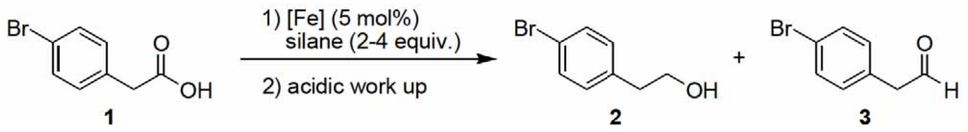
GCMS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness), which was used with helium as vector gas. The following GC-MS conditions were used: Initial temperature 100 °C, for 2 minutes, then rate 10 °C/min. until 250 °C and 250°C for 10 minutes.

HR–MS spectra were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesure Physiques de l'Ouest), University of Rennes 1.

$Fe(COD)(CO)_3$ (Cat. **A**) [1] and $Fe(PBO)(CO)_3$ (Cat. **B**) [2] were synthesized according to published procedures and stored under argon in the darkness into the freezer.

II. Optimisation: influence of the silane and of the iron catalyst.

Table S1. Optimization of the conditions for the reduction of carboxylic acids [a]



Entry	[Fe]	Silane (equiv.)	Solvent	Conditions	GC-yield[b]	
					2 /	**3**
Influence of the iron source						
1	$Fe(CO)_5$	$PhSiH_3$ (4)	toluene	UV (350 nm), 16 h	65	8
2	$Fe(CO)_5$	$PhSiH_3$ (4)	toluene	UV (350 nm) for 1h then 15h at 50°C	25	9
3	$Fe_2(CO)_9$	$PhSiH_3$ (4)	toluene	UV (350 nm), 16 h	41	8
4	$Fe_2(CO)_9$	$PhSiH_3$ (4)	toluene	80°C, 16h	30	8
5	$Fe_3(CO)_{12}$	$PhSiH_3$ (4)	Toluene	80°C, 16h	41	9
6	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	toluene	UV (350 nm), 24h	87	13
7	(tPBO)$Fe(CO)_3$	$PhSiH_3$ (4)	toluene	UV (350 nm), 16 h	38	5
Influence of the solvent						
8	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	toluene	UV (350 nm), 24h	87	13
9	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	THF	UV (350 nm), 24 h	**99**	**1**
10	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	THF	UV (350 nm), 16 h	92	8
11	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	THF	UV (350 nm), 8 h	66	11
12	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	Toluene	UV (350 nm), 8 h	44	7
13	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	Pentane	UV (350 nm), 8 h	42	7
14	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	Et_2O	UV (350 nm), 8 h	38	11
15	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	Bu_2O	UV (350 nm), 8 h	32	8
16	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	CH_2Cl_2	UV (350 nm), 8 h	29	9
17	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	Neat	UV (350 nm), 8 h	52	8
Influence of the hydrosilane source						
18	(COD)$Fe(CO)_3$	$PhSiH_3$ (4)	toluene	UV (350 nm), 24h	**87**	**13**
19	(tPBO)$Fe(CO)_3$	$PhSiH_3$ (4)	toluene	UV (350 nm), 16 h	38	5
20	(COD)$Fe(CO)_3$	Ph_2SiH_2 (4)	toluene	UV (350 nm), 16 h	41	17
21	(tPBO)$Fe(CO)_3$	Ph_2SiH_2 (4)	toluene	UV (350 nm), 16 h	29	11
22	(COD)$Fe(CO)_3$	Et_3SiH (4)	toluene	UV (350 nm), 16 h	0	0
23	(tPBO)$Fe(CO)_3$	Et_3SiH (4)	toluene	UV (350 nm), 16 h	0	0
24	(COD)$Fe(CO)_3$	$(EtO)_2MeSiH$ (4)	toluene	UV (350 nm), 16 h	6	0
25	(COD)$Fe(CO)_3$	TMDS (2)	toluene	UV (350 nm), 16 h	**11**	**89**
26	(tPBO)$Fe(CO)_3$	TMDS (2)	toluene	UV (350 nm), 16 h	4	73
27	(COD)$Fe(CO)_3$	PMHS (4)	toluene	UV (350 nm), 16 h	5	58
28	(tBPO)$Fe(CO)_3$	PMHS (4)	toluene	UV (350 nm), 16 h	7	52
29	(COD)$Fe(CO)_3$	PMHS (4)	toluene	UV (350 nm), 30 h	6	72
30	(COD)$Fe(CO)_3$	PHMS (6)	toluene	UV (350 nm), 30 h	6	79

[a] Typical procedure: carboxylic acid (0.5 mmol), silane (2-4 equiv.), iron precursor (5 mol%), solvent (2 mL). [b] Conversion determined by GC. [c] 1 mL of toluene.

Entry	[Fe]	Silane (equiv.)	Solvent	Conditions	GC-yield[b] **2**	/ **3**
31	$Fe(CO)_5$	TMDS (2)	Toluene	UV (350 nm), 16 h	10	90
32	$Fe(CO)_5$	TMDS (2)	Toluene	80°C, 16 h	0	0
33	$Fe_2(CO)_9$	TMDS (2)	Toluene	UV (350 nm), 16 h	8	92
34	$Fe_2(CO)_9$	TMDS (2)	Toluene	80°C, 16 h	6	94
35	$Fe_2(CO)_9$	TMDS (2)	Toluene	50°C, 16 h	6	69
36	$Fe_2(CO)_9$	TMDS (2)	Toluene	50°C, 24 h	11	89
37	$Fe_2(CO)_9$	TMDS (2)	Toluene	30°C, 24 h	16	70
38	$Fe_3(CO)_{12}$	TMDS (2)	Toluene	UV (350 nm), 16 h	9	79
39	$Fe_3(CO)_{12}$	TMDS (2)	Toluene	80°C, 16 h	68	12
40	$(COD)Fe(CO)_3$	TMDS (2)	Toluene	UV (350 nm), 16 h	**11**	**89**
41	$(tPBO)Fe(CO)_3$	TMDS (2)	Toluene	UV (350 nm), 16 h	4	73
42[c]	$(tPBO)Fe(CO)_3$	TMDS (2)	Toluene	30°C, 24 h	7	76
43[c]	$(tPBO)Fe(CO)_3$	TMDS (2)	Toluene	50°C, 24 h	2	98

[a] Typical procedure: carboxylic acid (0.5 mmol), silane (2-4 equiv.), iron precursor (5 mol%), solvent (2 mL). [b] Conversion determined by GC. [c] 1 mL of toluene.

III. General procedures for the iron-catalyzed hydrosilylation reactions

a) General procedure A for the iron-catalyzed hydrosilylation of carboxylic acids to alcohols.

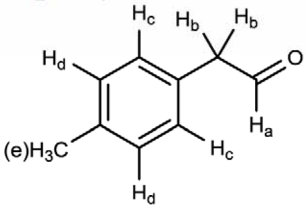
A 20 mL oven dried Schlenk tube containing a stirring bar was charged the iron complex **A** (6.0 mg, 0.025 mmol, 5 mol%), and THF (2 mL) was then added. A second Schlenk tube was loaded with the respective carboxylic acid (0.5 mmol), purged with argon/vacuum system and the $PhSiH_3$ (250 μL, 2 mmol, 4 equiv.) was added. The solution in the first Schlenk tube was transferred into the latter one and the reaction mixture was irradiated using UV-light (350 nm) for 24 h. The reaction was then quenched by adding 1 mL HCl 1N, stirred overnight at room temperature and then extracted with 3x10mL of Et_2O. The combined fractions were dried and concentrated under reduced pressure. The alcohol was then purified by using a silica gel chromatography column and a mixture of pentane/ethyl acetate as the eluent.

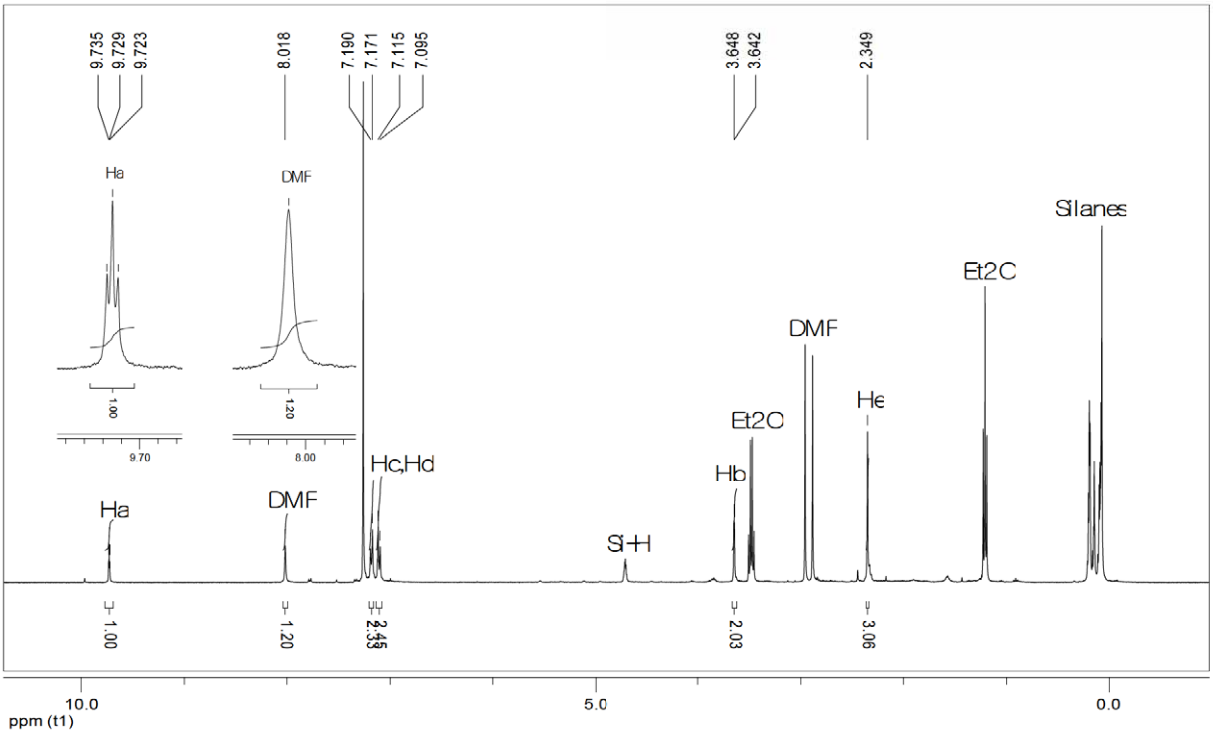
b) General procedure B for the iron-catalyzed hydrosilylation of carboxylic acids to aldehydes.

A 20 mL oven dried Schlenk tube containing a stirring bar was charged the iron complex **B** (14.0 mg, 0.05 mmol, 5 mol%), and toluene (2 mL) was then added. A second Schlenk tube was loaded with the respective carboxylic acid (1 mmol), purged with argon/vacuum system and the TMDS (180 μL, 2 mmol, 2 equiv.) was added. The solution in the first Schlenk tube was transferred into the latter one and the reaction mixture was stirred for 24 h at 50 °C. The reaction was then quenched by adding 3 mL THF and 3 mL HCl 1N, stirred overnight at room temperature and then extracted with 3x10mL of Et_2O. The combined fractions were dried and concentrated under reduced pressure. Conversion was determined by ^{1}H-NMR spectroscopy of the crude mixture after adding DMF (80 µL, 1mmol) as the internal standard. The aldehyde was further purified by using a silica gel chromatography column and a mixture of pentane/ethyl acetate as the eluent.

IV. Typical example for the determination of the yield by ^{1}H NMR for the reduction of carboxylic acids to aldehydes using DMF as internal standard.

2-(p-tolyl)ethanol

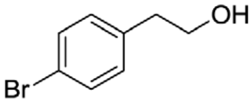




V. Characterization of the hydrosilylation products

a) Alcohol Products

2-(*p*-Bromophenyl)ethanol[7] (Table 2, Entry 1)



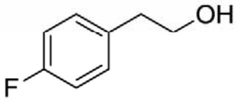
The compound was prepared as described in the general procedure (83 % isolated yield, m = 83 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 2H, *J* = 8.3), 7.11 (d, 2H, *J* = 8.3), 3.84 (m, 2H), 2.83 (t, 2H, *J* = 6.6), 1.36 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 137.5, 131.5, 130.7, 120.2, 63.3, 38.4.

GC-MS: m/z (%) 202 (M$^+$, 28), 200 (M$^+$, 28), 171 (74), 169 (75), 91 (100), 74 (56), 63 (25), 51 (20).

2-(*p*-Fluorophenyl)ethanol[4] (Table 2, Entry 2)



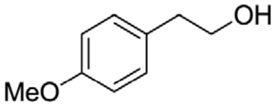
The compound was prepared as described in the general procedure (90 % isolated yield, m = 63 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, 2H, *J* = 5.6, *J* = 8.3), 7.00 (t, 2H, *J* = 8.6), 3.84 (t, 2H, *J* = 6.5), 2.84 (t, 2H, *J* = 6.5), 1.42 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.5 (d, J_{C-F} = 243.6), 134.1 (d, J_{C-F} = 3.2), 130.4 (d, J_{C-F} = 7.8), 115.3 (d, J_{C-F} = 20.9), 63.6 (d, J_{C-F} = 1.3), 38.3.

GC-MS: m/z (%) 140 (M$^+$, 18), 109 (100), 83 (20).

2-(*p*-Methoxyphenyl)ethanol[4,5] (Table 2, Entry 3)



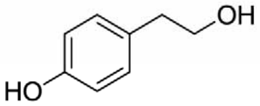
The compound was prepared as described in the general procedure (95 % isolated yield, m = 72 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, 2H, *J* = 8.5), 6.86 (d, 2H, *J* = 8.5), 3.82 (q, 2H, *J* = 6.1), 3.80 (s, 3H), 2.81 (t, 2H, *J* = 6.5), 1.36 (br s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.3, 130.4, 129.9, 114.0, 63.8, 55.3, 38.3.

GC-MS: m/z (%) 152 (M$^+$, 15), 121 (100), 91 (11), 77 (18).

2-(*p*-Hydroxyphenyl)ethanol[6] (Table 2, Entry 4)



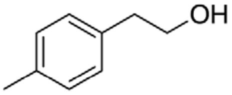
The compound was prepared as described in the general procedure (74 % isolated yield, m = 51 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 2H, *J* = 8.5), 6.78 (d, 2H, *J* = 8.5), 5.01 (br s, 1H), 3.83 (m, 2H), 2.81 (t, 2H, *J* = 6.5), 1.47 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 155.4, 129.6, 129.4, 114.8, 62.5, 38.2.

GC-MS: m/z (%) 138 (M$^+$, 20), 107 (100), 77 (22).

2-(*p*-Tolyl)ethanol[4] (Table 2, Entry 5)



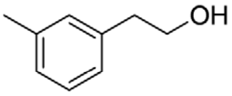
The compound was prepared as described in the general procedure (82 % isolated yield, m = 56 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (m, 4H), 3.84 (q, 2H, *J* = 6.5), 2.84 (t, 2H, *J* = 6.5), 2.33 (s, 3H), 1.39 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 135.9, 135.3, 129.2, 128.8, 63.6, 38.6, 20.9.

GC-MS: m/z (%) 136 (M$^+$, 26), 105 (100), 91 (15), 77 (17).

2-(*m*-Tolyl)ethanol[4] (Table 2, Entry 6)



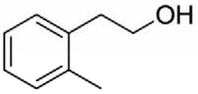
The compound was prepared as described in the general procedure (88 % isolated yield, m = 60 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, 1H, *J* = 7.8), 7.06-7.03 (m, 3H), 3.86 (t, 2H, *J* = 6.6), 2.84 (t, 2H, *J* = 6.5), 2.35 (s, 3H), 1.42 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.3, 138.1, 129.8, 128.4, 127.1, 125.9, 63.6, 39.0, 21.3.

GC-MS: m/z (%)(M$^+$, 42), 105 (100), 91 (44), 77 (25).

2-(*o*-Tolyl)ethanol[3,4] (Table 2, Entry 7)



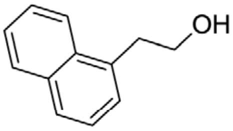
The compound was prepared as described in the general procedure (79 % isolated yield, m = 54 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17-7.16 (m, 4H), 3.84 (m, 2H), 2.91 (t, 2H, *J* = 6.8), 2.34 (s, 3H), 1.43 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.44, 136.41, 130.3, 129.6, 126.5, 126.0, 62.5, 36.3, 19.4.

GC-MS: m/z (%) 136 (M$^+$, 30), 117 (13), 105 (100), 91 (30), 79 (24).

2-(1-naphthyl)ethanol[4,8] (Table 2, Entry 8)



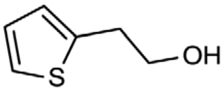
The compound was prepared as described in the general procedure (94 % isolated yield, m = 81 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 1H), 7.89-7.85 (m, 1H), 7.78-7.74 (m, 1H), 7.52-7.39 (m, 4H), 3.99 (m, 2H), 3.36 (m, 2H), 1.43 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 134.3, 133.8, 131.9, 128.7, 127.2, 127.0, 125.9, 125.5, 125.4, 123.6, 62.8, 36.1.

GC-MS: m/z (%) 172 (M$^+$, 20), 141 (100), 115 (35).

2-(2-thiophene)ethanol[8] (Table 2, Entry 9)



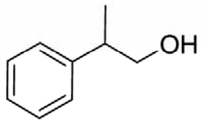
The compound was prepared as described in the general procedure (95 % isolated yield, m = 61 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, 2H, J_1 = 0.9, J_2 = 5.0), 6.96 (dd, 2H, J_1 = 3.4, J_2 = 5.0), 6.88 (dd, 2H, J_1 = 0.9, J_2 = 3.4), 3.85 (t, 2H, *J* = 6.2), 3.08 (t, 2H, *J* = 6.2), 1.75 (br s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.7, 127.0, 125.5, 124.0, 63.4, 33.3.

GC-MS: m/z (%) 128 (M$^+$, 33), 97 (100), 53 (14).

2-Phenyl-1-propanol[4] (Table 2, Entry 10)



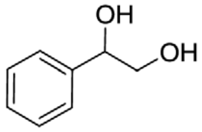
The compound was prepared as described in the general procedure (91 % isolated yield, m = 62 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.26-7.24 (m, 3H), 3.68 (d, 2H, J = 7.0), 2.95 (m, 1H, J = 6.9), 1.66 (br s, 1H), 1.29 (d, 3H, J = 6.9).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.7, 128.5, 127.4, 126.6, 68.6, 42.3, 17.5.

GC-MS: m/z (%) 136 (M$^+$, 15), 105 (100), 91 (15), 79 (24), 77 (22).

1-Phenyl-1,2-ethanediol[6] (Table 2, Entry 11)

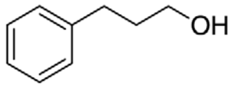


The compound was prepared as described in the general procedure (55 % isolated yield, m = 38 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 4.81 (dd, 1H, J_1 = 3.4, J_2 = 8.1), 3.75 (dd, 1H, J_1 = 3.4, J_2 = 11.3), 3.66 (dd, 1H, J_1 = 8.1, J_2 = 11.3), 2.57 (br s, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.5, 128.5, 128.0, 126.0, 74.7, 68.1.

3-Phenyl-1-propanol[8] (Table 2, Entry 12)



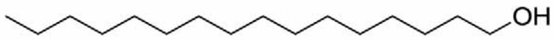
The compound was prepared as described in the general procedure (95 % isolated yield, m = 129 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.20 (m, 5H), 3.68 (t, 2H, J = 6.4), 2.72 (t, 2H, J = 7.7), 1.91 (m, 2H), 1.42 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.8, 128.40, 128.38, 125.8, 62.3, 34.2, 32.1.

GC-MS: m/z (%) 136 (M$^+$, 22), 117 (100), 105 (13), 91 (96), 77 (22), 65 (22), 51 (15).

1-Hexadecanol[6] (Table 2, Entry 13)



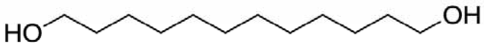
The compound was prepared as described in the general procedure (82 % isolated yield, m = 100 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (q, 2H, *J* = 6.2), 1.55 (m, 2H), 1.25 (m, 27H), 0.86 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 63.0, 32.8, 31.9, 29.68, 29.67, 29.65, 29.61, 29.60, 29.43, 29.35, 25.7, 22.7, 14.1.

GC-MS: m/z (%) 125 (15), 111 (35), 97 (67), 83 (88), 69 (83), 57 (85), 55 (100).

1,12-Dodecanediol[6] (Table 2, Entry 14)



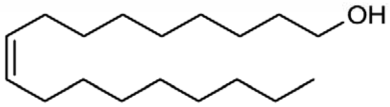
The compound was prepared as described in the general procedure (97 % isolated yield, m = 98 mg).

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.34 (br s, 2H), 4.31 (t, 2H, *J* = 5.1), 3.37 (q, 4H, *J* = 6.4), 1.39 (m, 4H), 1.24 (m, 14H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 60.6, 32.4, 29.0, 28.9, 28.8, 25.4.

GC-MS: m/z (%) 109 (13), 96 (31), 82 (70), 67 (60), 55 (100).

Oleyl alcohol[8] (Table 2, Entry 15)



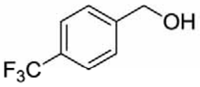
The compound was prepared as described in the general procedure (72 % isolated yield, m = 96 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (m, 2H), 3.64 (m, 2H), 2.01 (m, 3H), 1.56 (m, 2H), 1.27 (m, 24H), 0.89 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 129.9, 129.8, 63.0, 32.8, 31.9, 29.8, 29.74, 29.68, 29.65, 29.51, 29.49, 29.4, 29.3, 29.2, 27.2, 25.7, 22.7, 14.1.

GC-MS: m/z (%) 268 **(**M^+), 250 (10), 138 (10), 124 (15), 109 (28), 96 (72), 82 (100), 67 (74), 55 (98).

4-Trifluoromethybenzyl alcohol (Table 2, Entry 17)



The compound was prepared as described in the general procedure (68 % isolated yield, m = 60 mg).

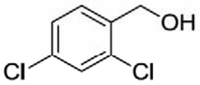
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, 2H, *J* = 8.1), 7.47 (d, 2H, *J* = 8.1), 4.76 (s, 2H), 1.96 (br s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.7, 129.8 (q, $J_{C\text{-}F}$ = 32.0), 126.9, 125.5 (q, $J_{C\text{-}F}$ = 3.9), 124.2 (q, $J_{C\text{-}F}$ = 270), 64.5.

^{19}F NMR (376.5 MHz, $CDCl_3$): -62.5.

GC-MS: m/z (%) 176 **(**M$^+$, 44), 157 (12), 145 (15), 127 (89), 107 (100), 95 (10), 79 (82), 63 (10), 51 (19).

2,4-dichlorobenzyl alcohol (Table 2, Entry 18)



The compound was prepared as described in the general procedure (67 % isolated yield, m = 59 mg).

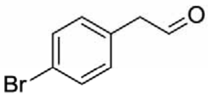
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.37 (m, 2H), 7.28-7.24 (m, 1H), 4.73 (s, 2H), 2.12 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.7, 133.8, 133.2, 129.4, 129.1, 127.2, 62.1.

GC-MS: m/z (%) 178 **(**M$^+$, 20), 176 **(**M$^+$, 25), 141 (55), 113 (60), 111 (55), 77 (100), 51 (22).

b) Aldehyde Products

2-(*p*-Bromophenyl)acetaldehyde (Table 3, Entry 5)



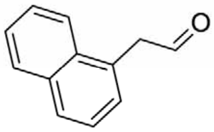
The compound was prepared as described in the general procedure.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (t, 1H, *J* = 2.0), 7.49 (d, 2H, *J* = 8.2), 7.09 (d, 2H, *J* = 8.2), 3.66 (d, 2H, *J* = 2.0).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.5, 132.0, 131.3, 130.7, 121.5, 49.8.

GC-MS: m/z (%) 200 (M$^+$, 26), 198 **(**M$^+$, 26), 171 (96), 169 (100), 90 (94), 63 (45), 50 (16).

2-(1-Naphthyl)acetaldehyde (Table 3, Entry 7)



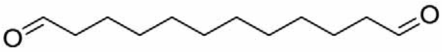
The compound was prepared as described in the general procedure (45 % isolated yield, m = 76 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (t, 2H, *J* = 2.4), 7.92-7.84 (m, 3H), 7.58-7.41 (m, 4H), 4.11 (d, 2H, *J* = 2.4).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.6, 133.9, 132.3, 128.9, 128.5, 128.4, 128.3, 126.7, 126.0, 125.6, 123.5, 48.3.

GC-MS: m/z (%) 170 (M$^+$, 23), 141 (100), 115 (45).

Dodecanedial (Table 3, Entry 11)



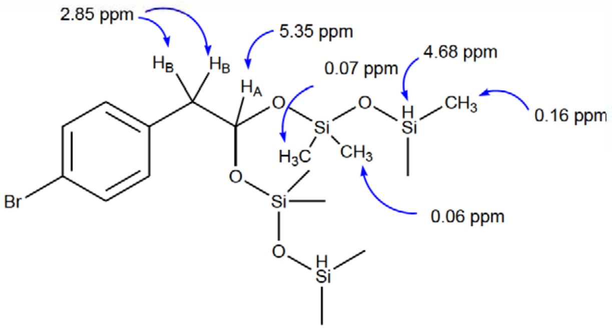
The compound was prepared as described in the general procedure (72 % isolated yield, m = 143 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, 2H, *J* = 1.6), 2.41 (dt, 4H, J_1 = 1.6, J_2 = 7.3, J_3 = 7.4), 1.62 (q, 4H, *J* = 7.0), 1.28 (m, 12H).

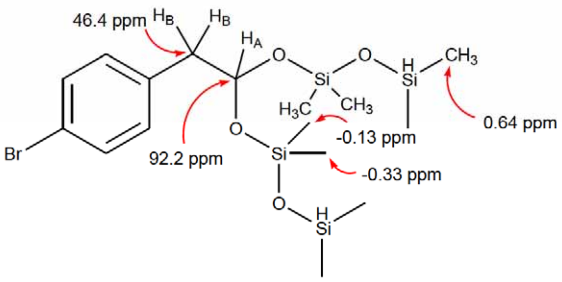
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 202.9, 43.9, 29.3, 29.3, 29.1, 22.0.

GC-MS: m/z (%) 198 (M$^+$), 136 (10), 121 (12), 98 (29), 95 (80), 81 (90), 67 (80), 55 (100).

VI. Characterization of the di-silyl acetal 4b

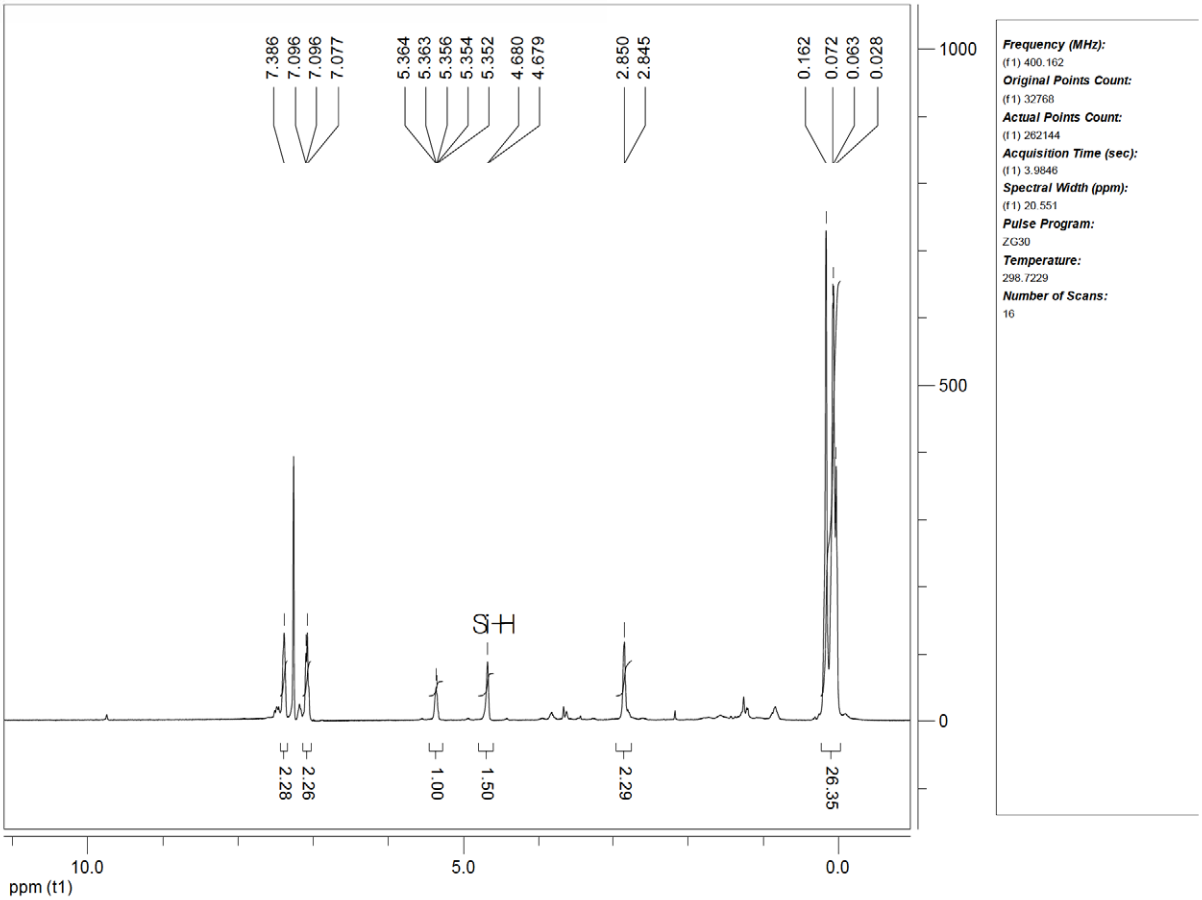


^{1}H NMR Chemical Shift



^{13}C NMR Chemical Shift

^{1}H NMR Spectrum



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Temperature:
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Number of Scans:
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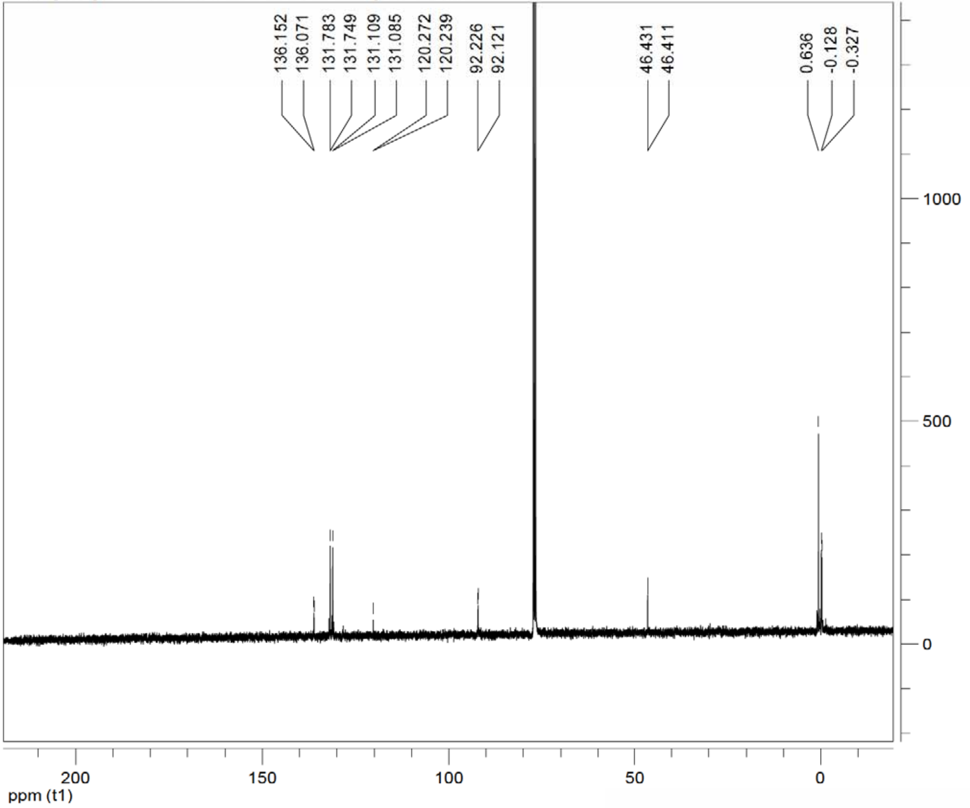
^{13}C{^{1}H} NMR and DEPT Spectra



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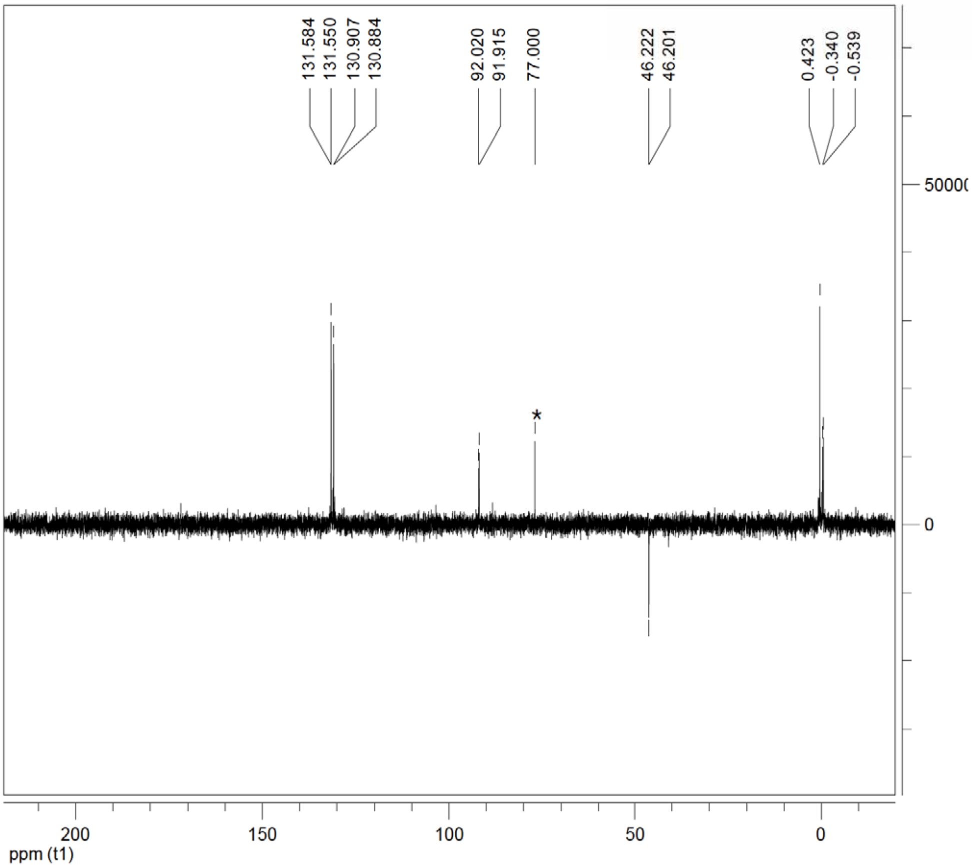

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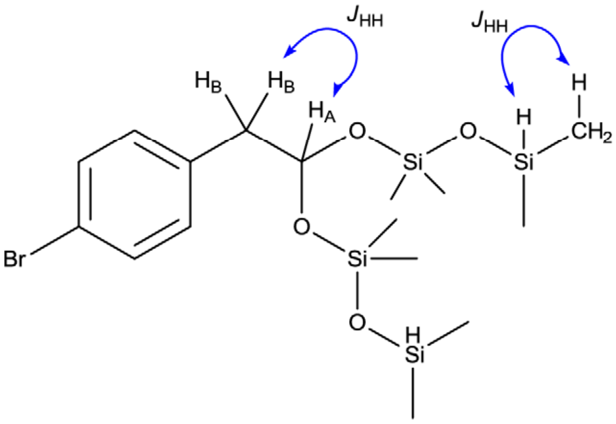
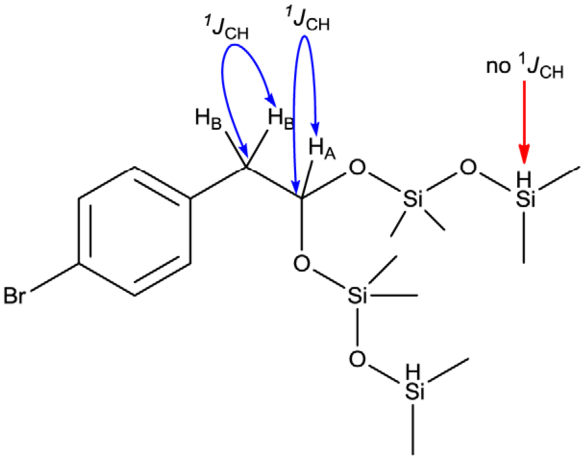
2D NMR Correlation

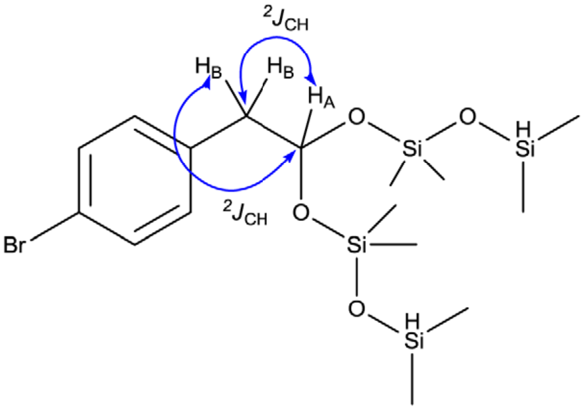
COSY



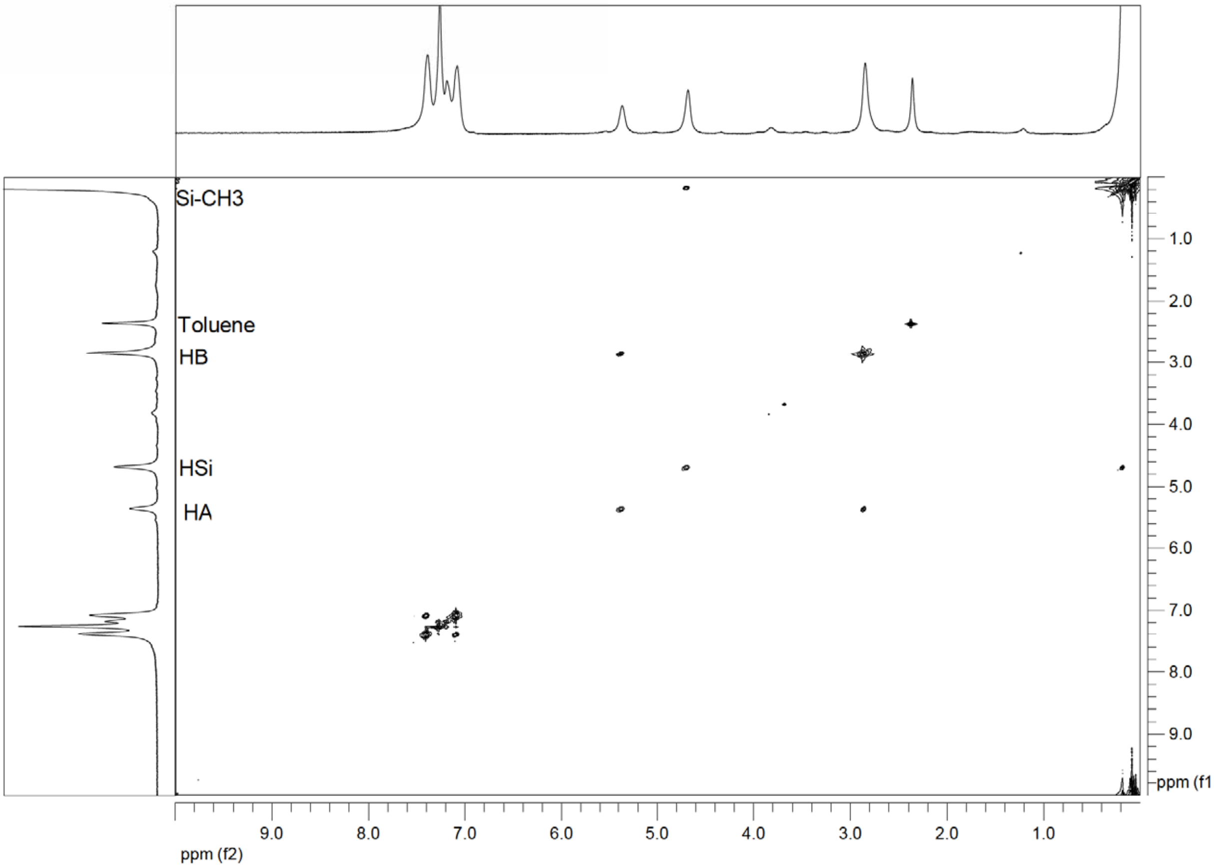
HMQC



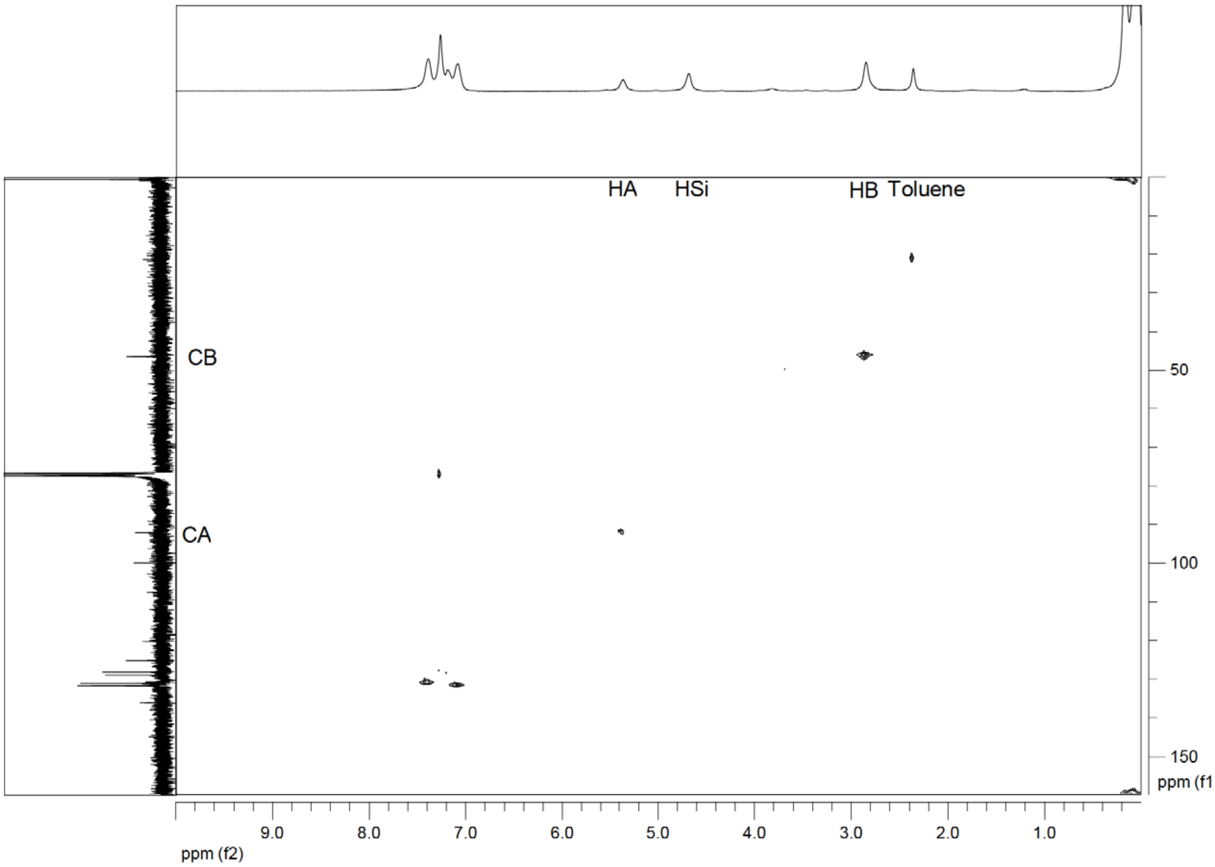
HMBC



COSY NMR



HMQC 2D NMR



VII. References

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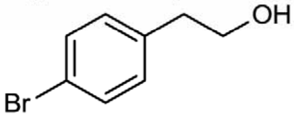
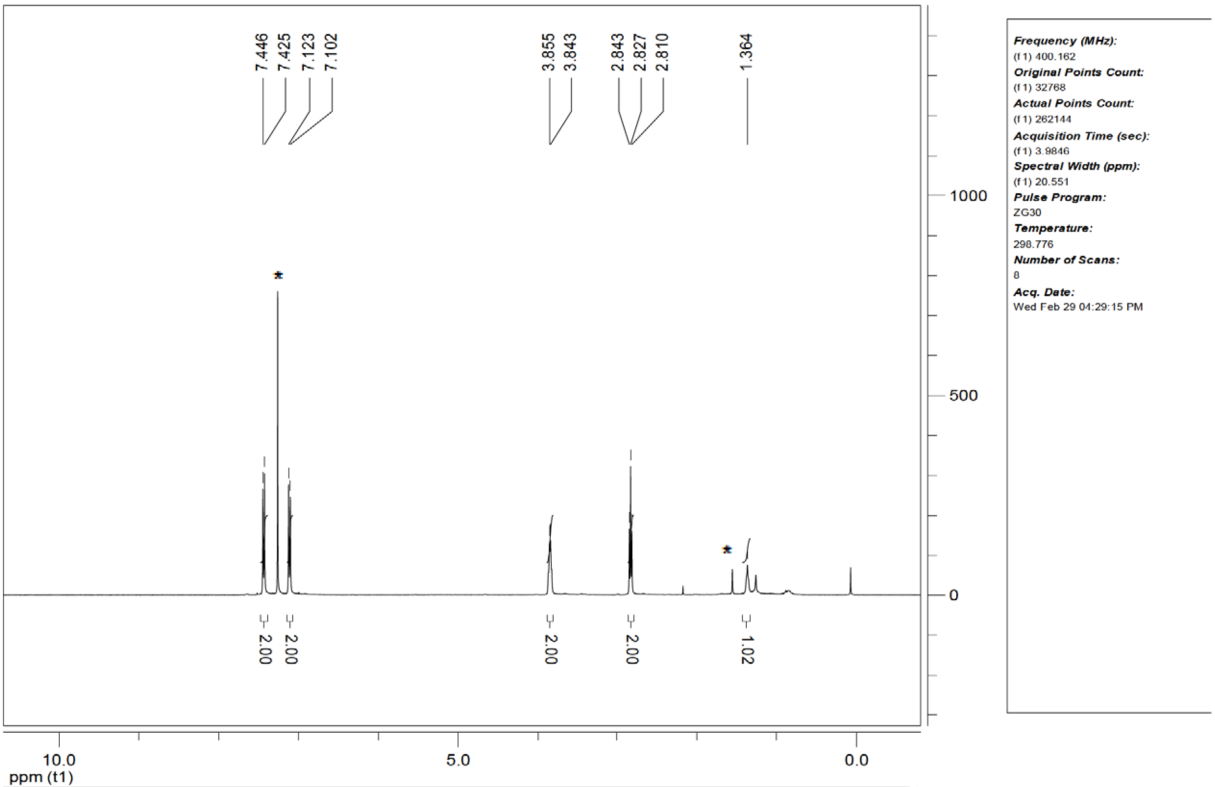
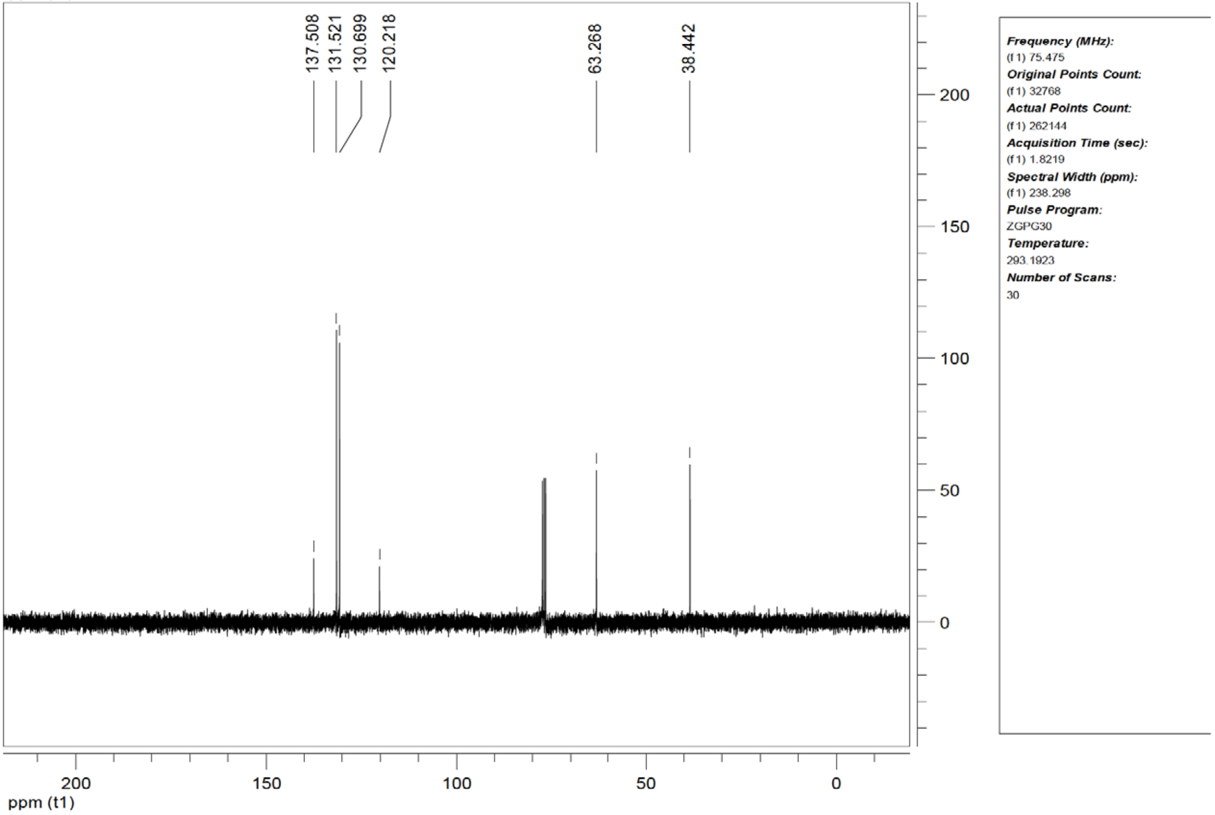
VIII. ^{1}H NMR and ^{13}C NMR spectra of the hydrosilylation products

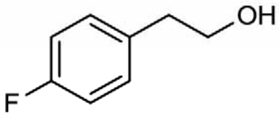
2-(*p*-Bromophenyl)ethanol (Table 2, Entry 1)

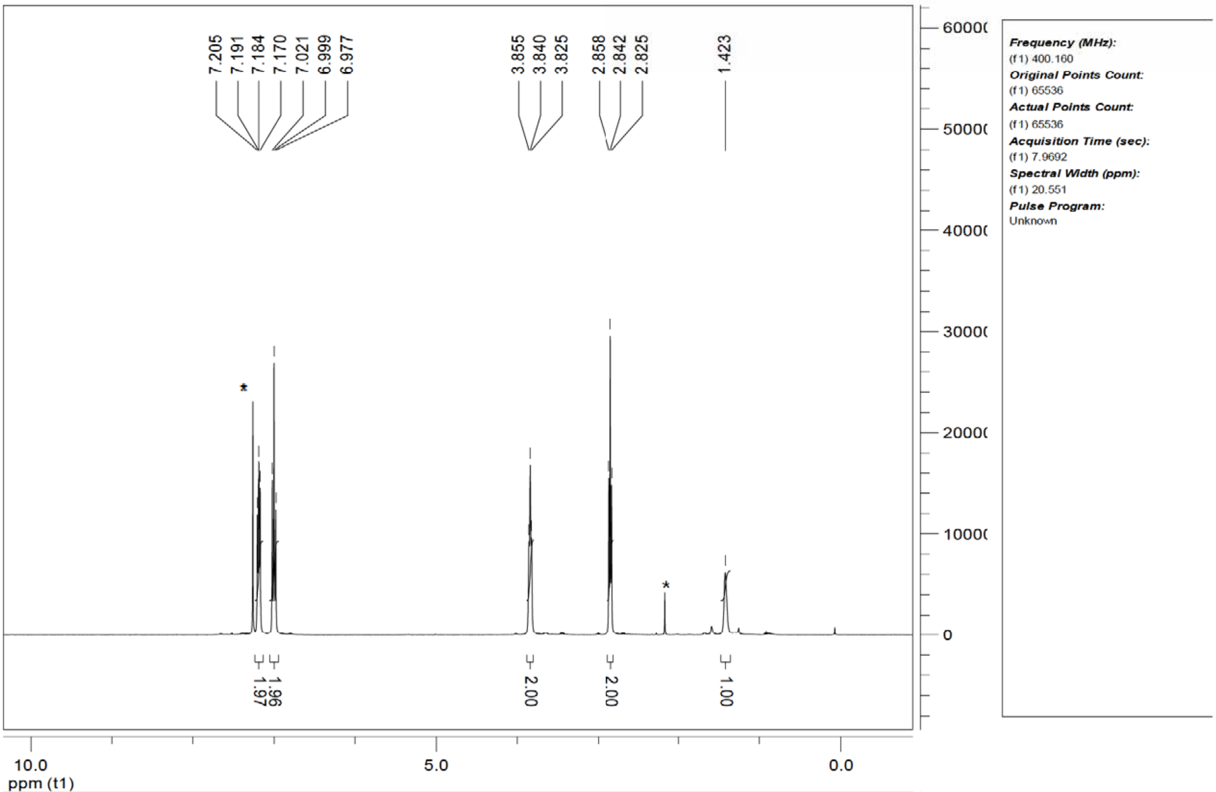


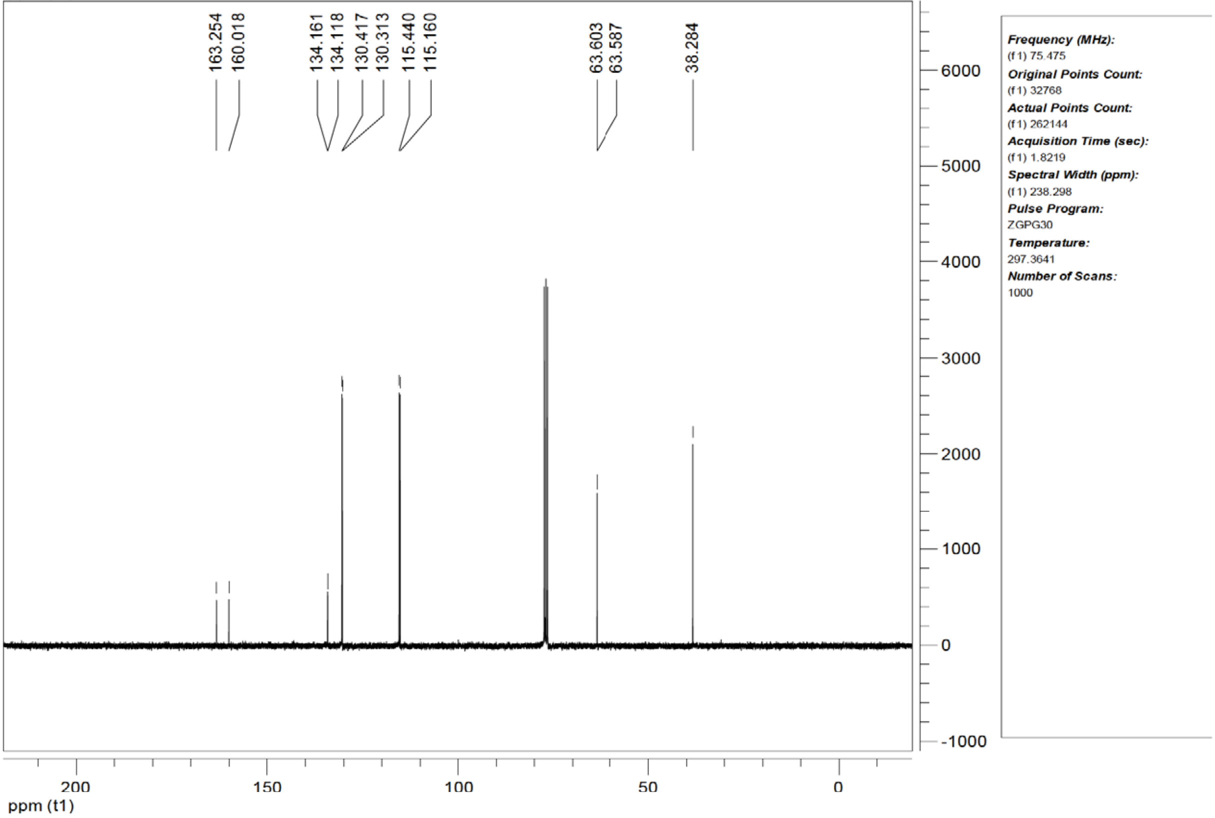




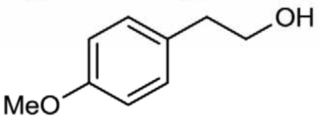
2-(*p*-Fluorophenyl)ethanol (Table 2, Entry 2)

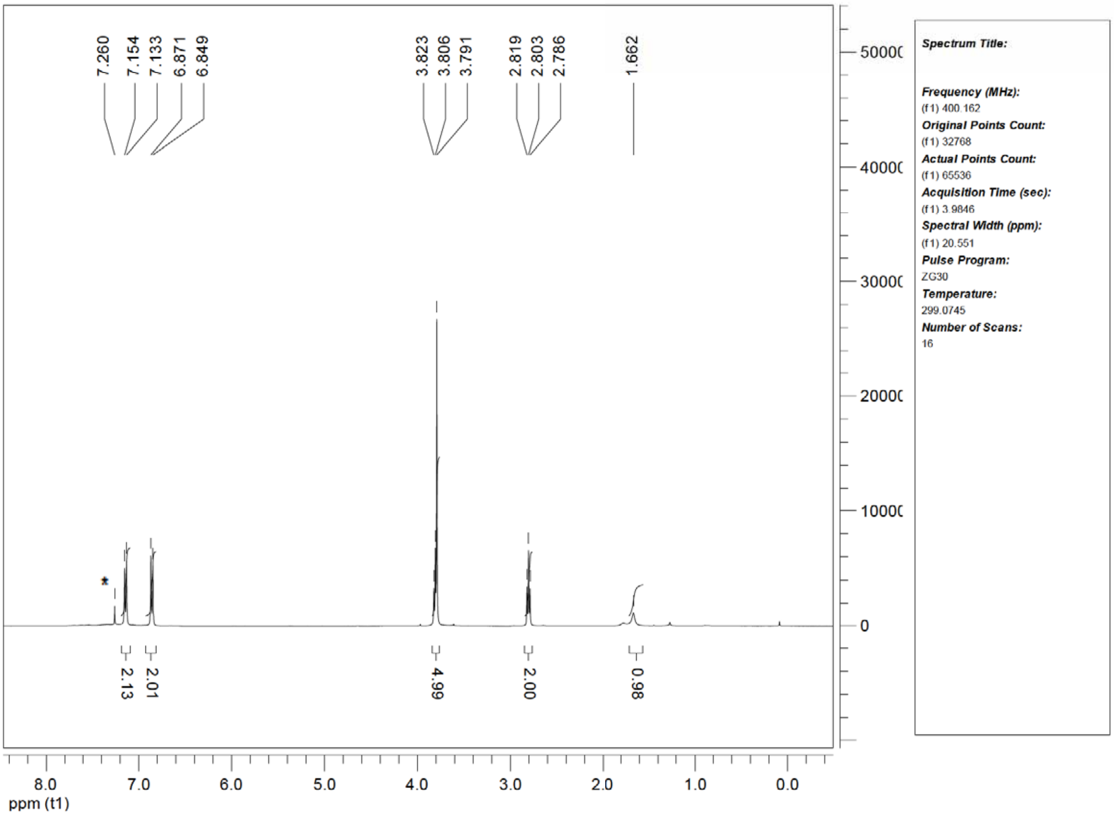


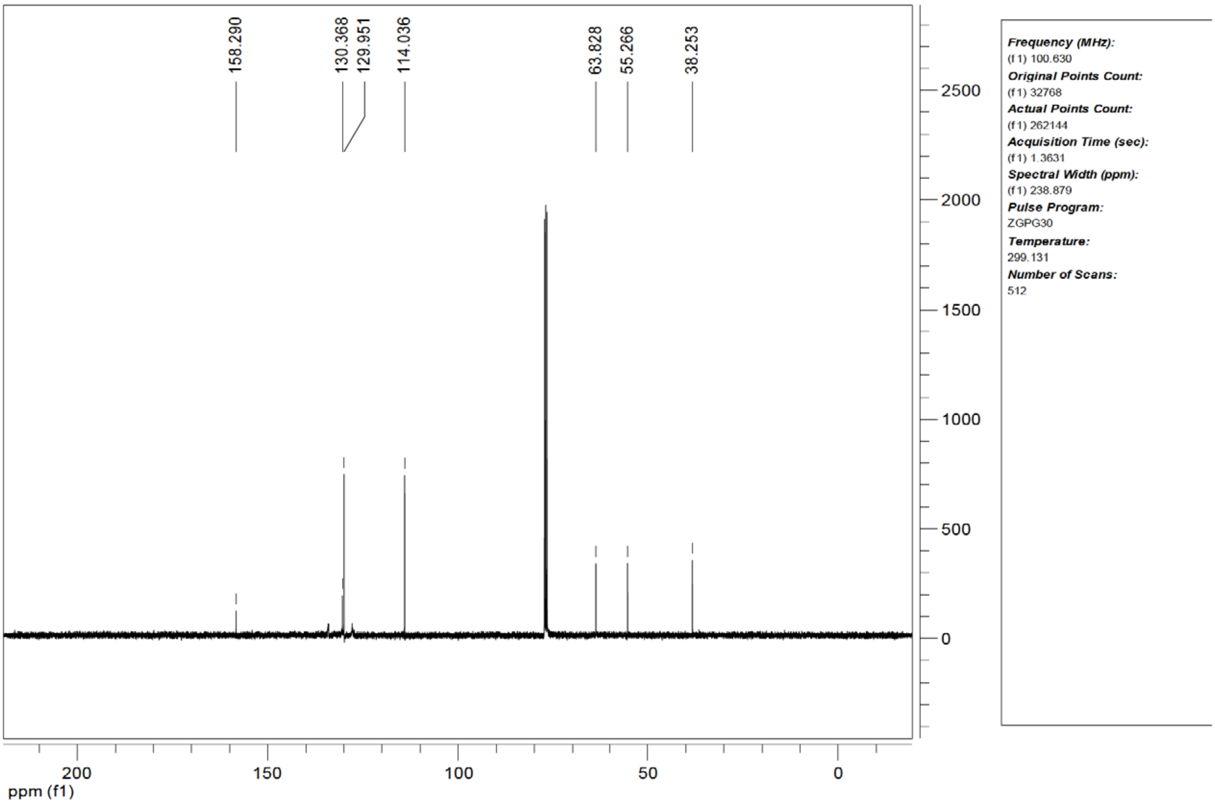




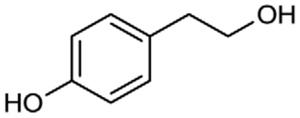
2-(*p*-Methoxyphenyl)ethanol (Table 2, Entry 3)

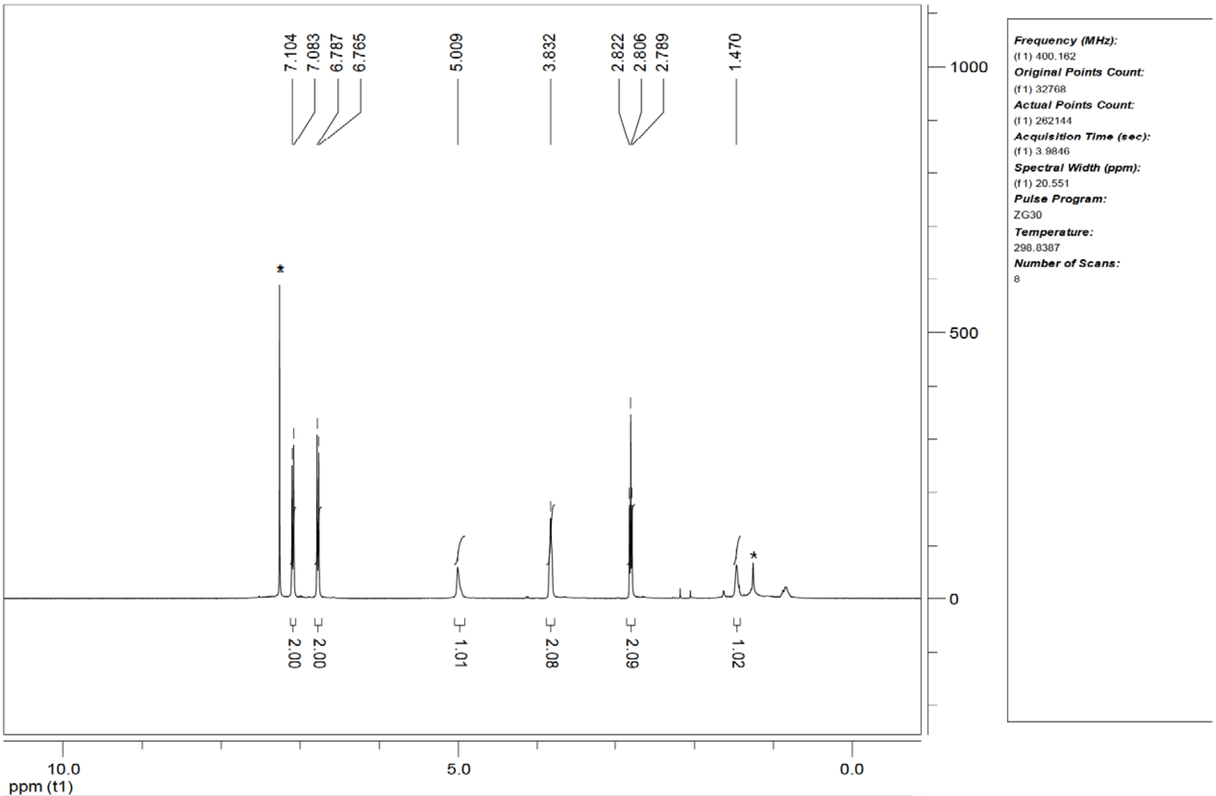






2-(*p*-Hydroxyphenyl)ethanol (Table 2, Entry 4)





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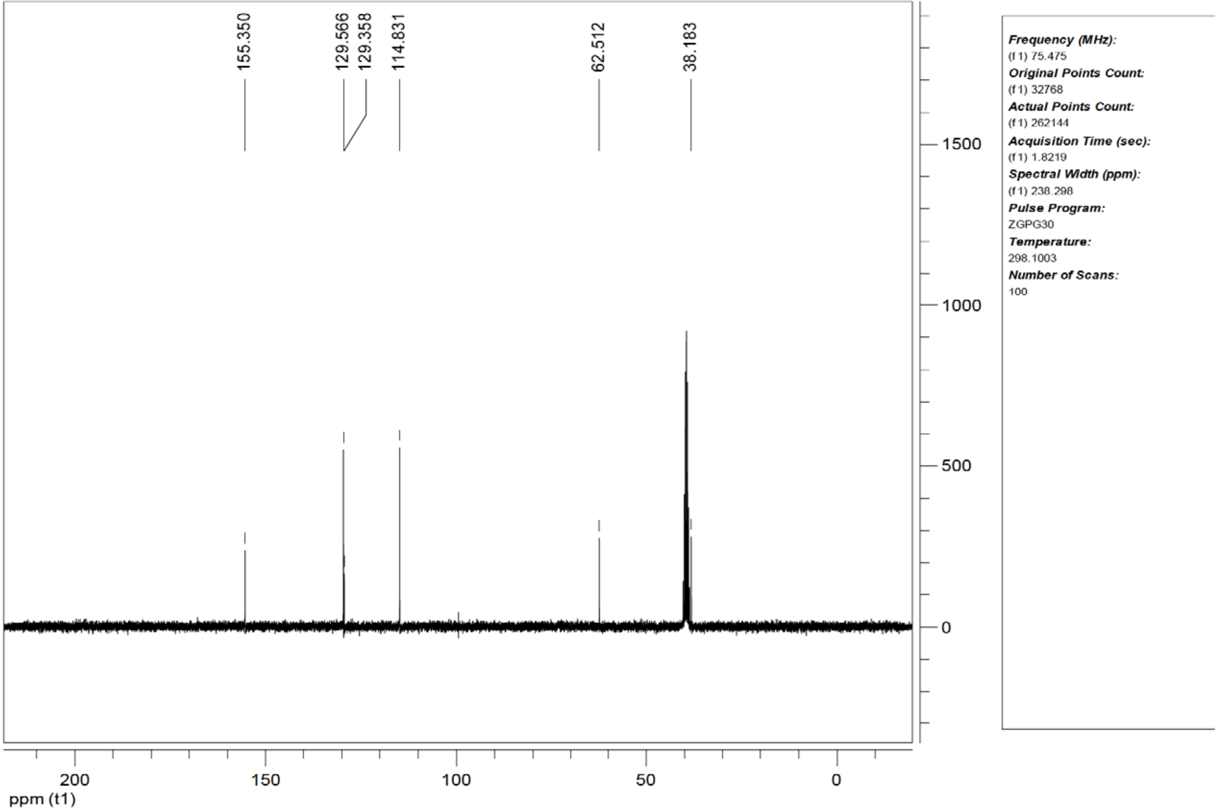

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Spectral Width (ppm):
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Temperature:
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Number of Scans:
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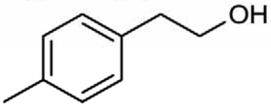
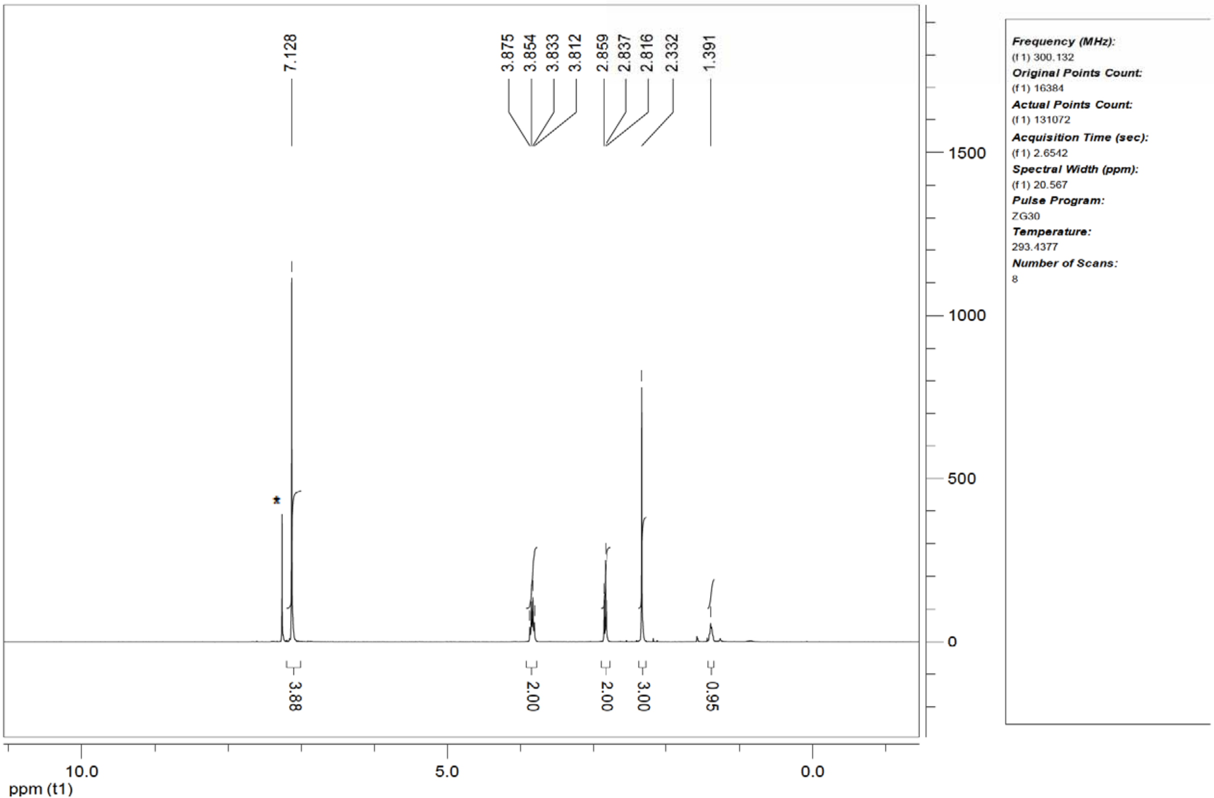
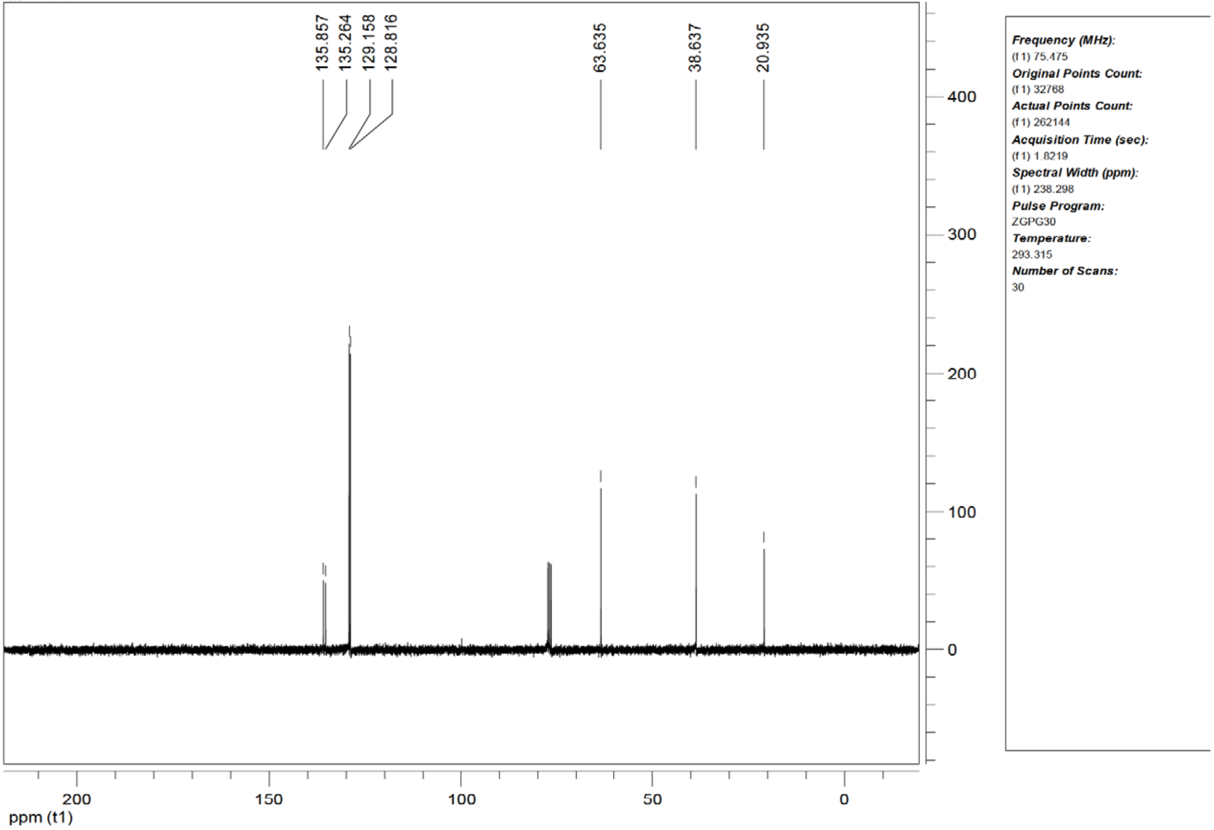
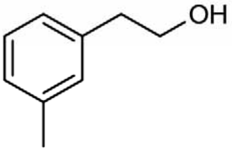
2-(*p*-Tolyl)ethanol (Table 2, Entry 5)

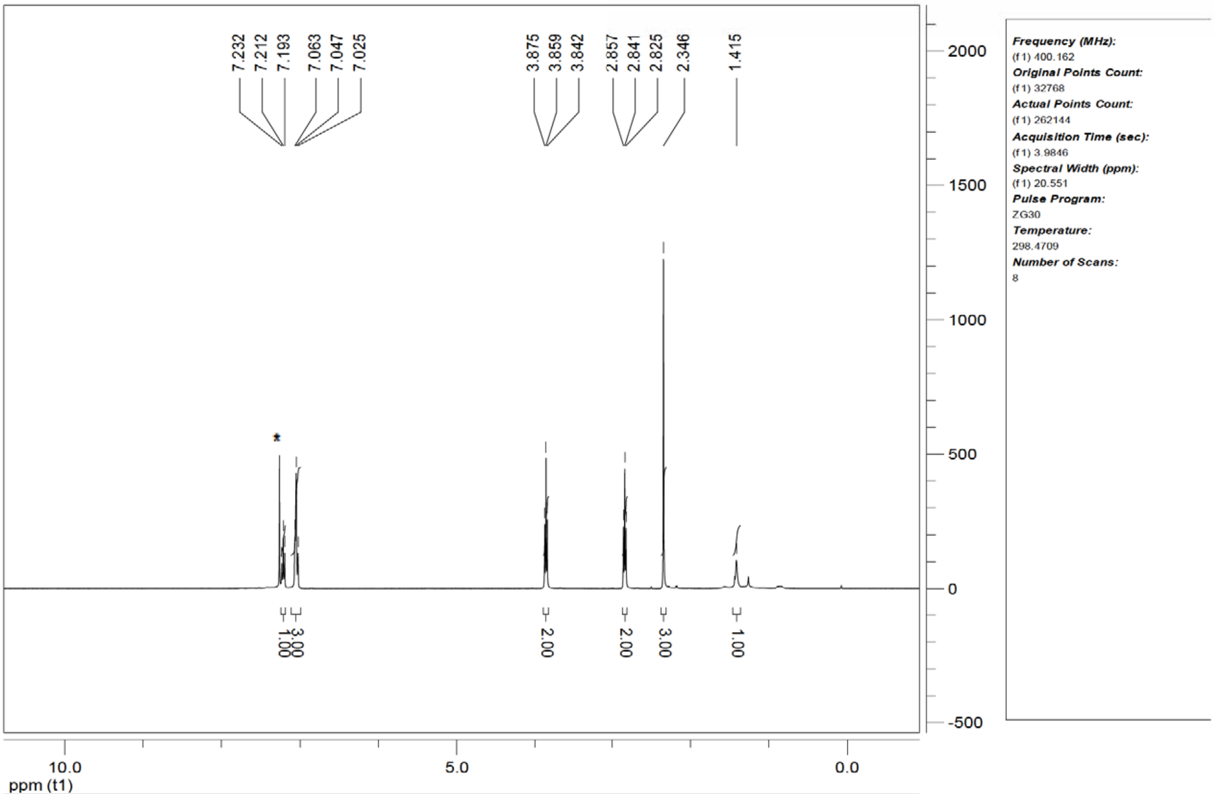


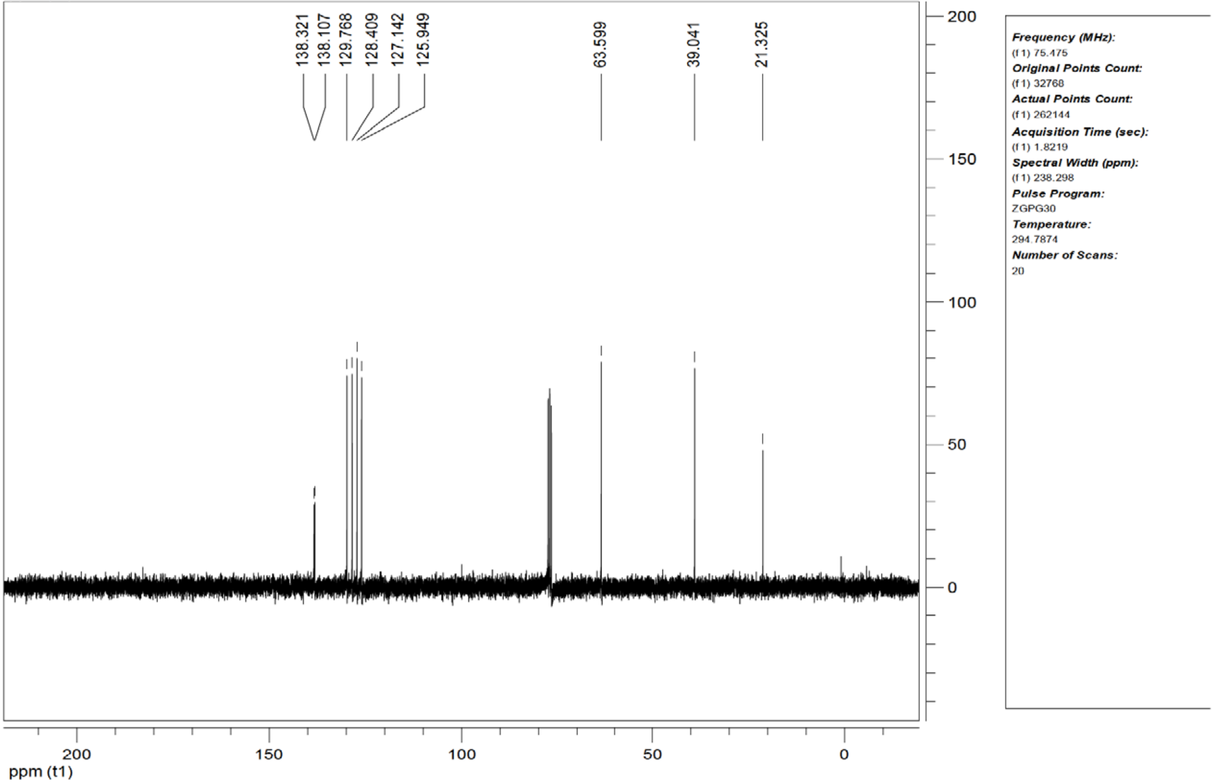




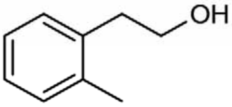
2-(*m*-Tolyl)ethanol (Table 2, Entry 6)

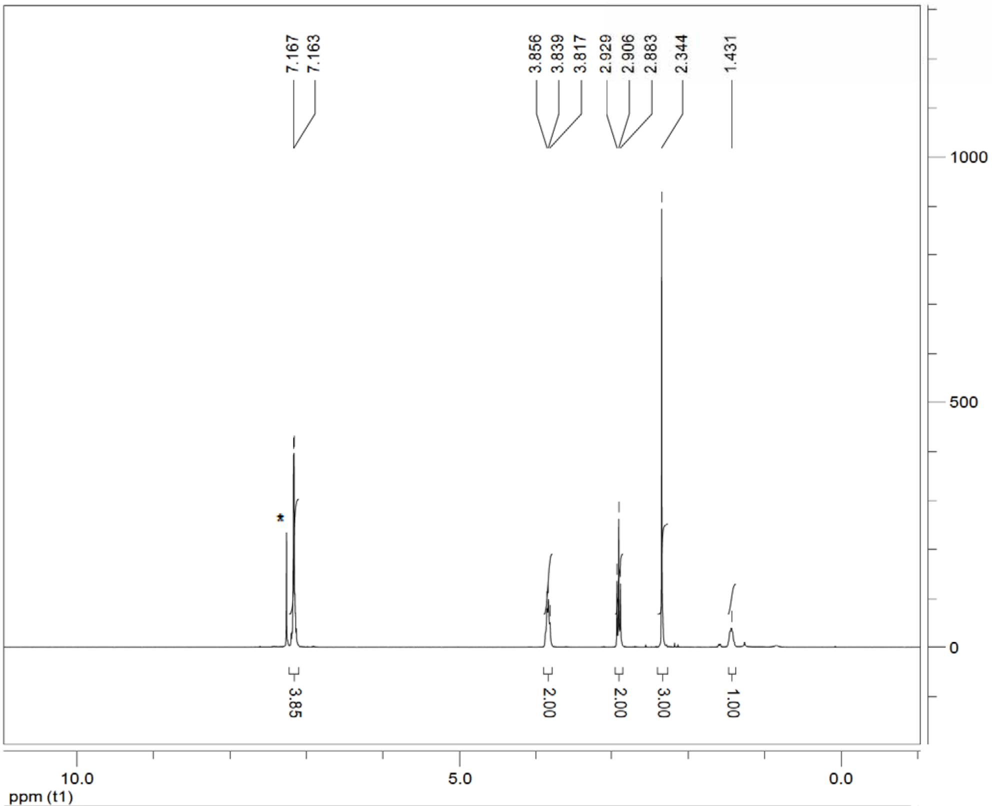






2-(*o*-Tolyl)ethanol (Table 2, Entry 7)





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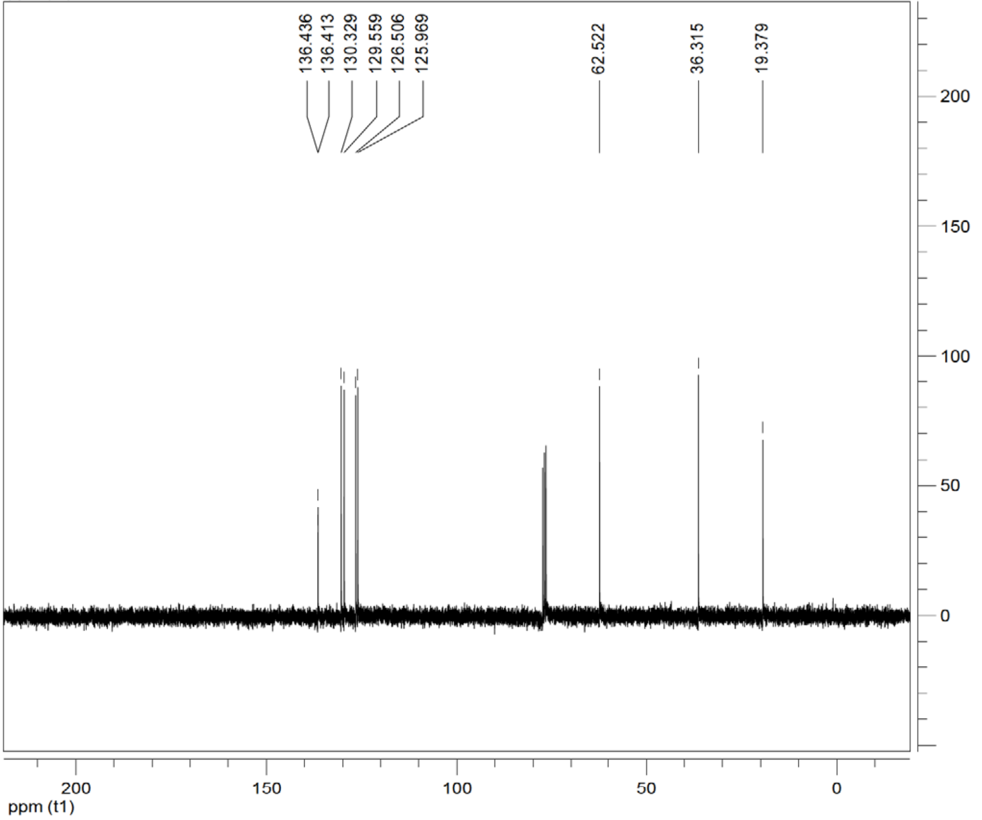

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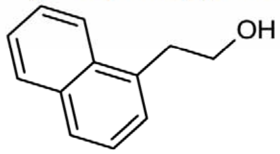
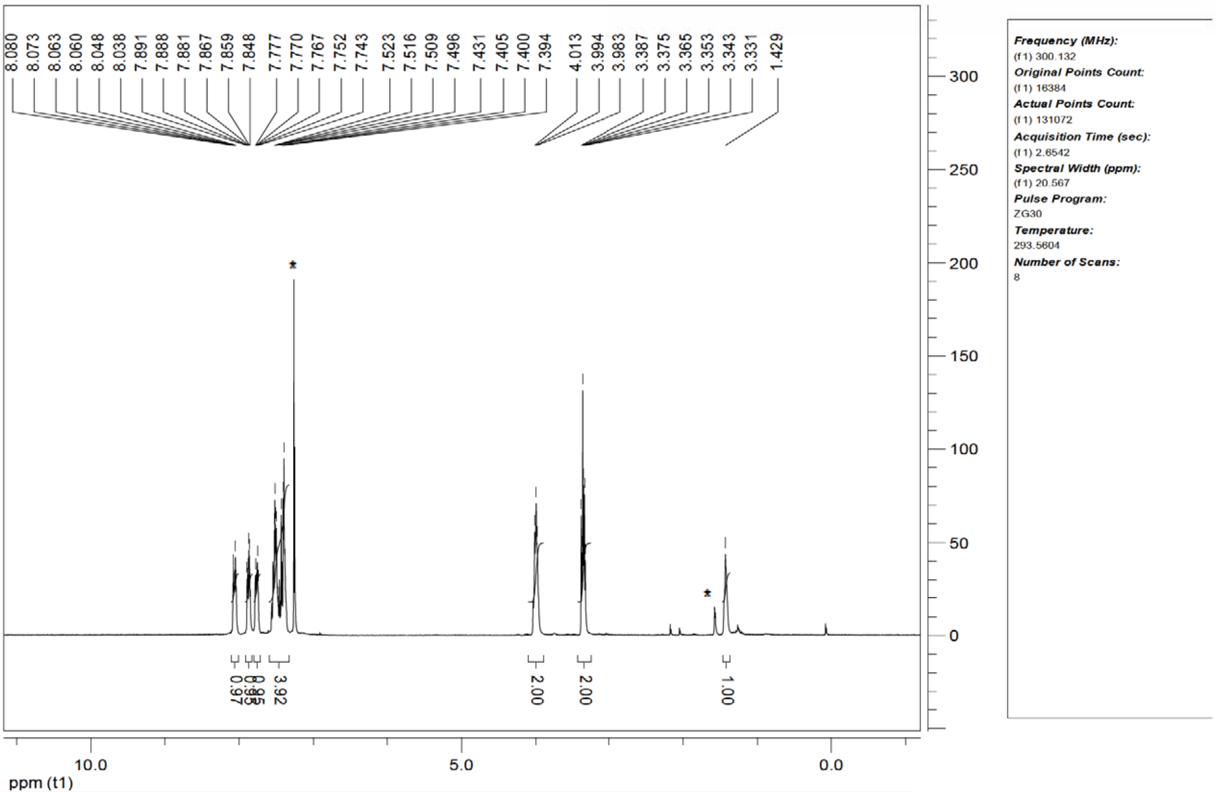
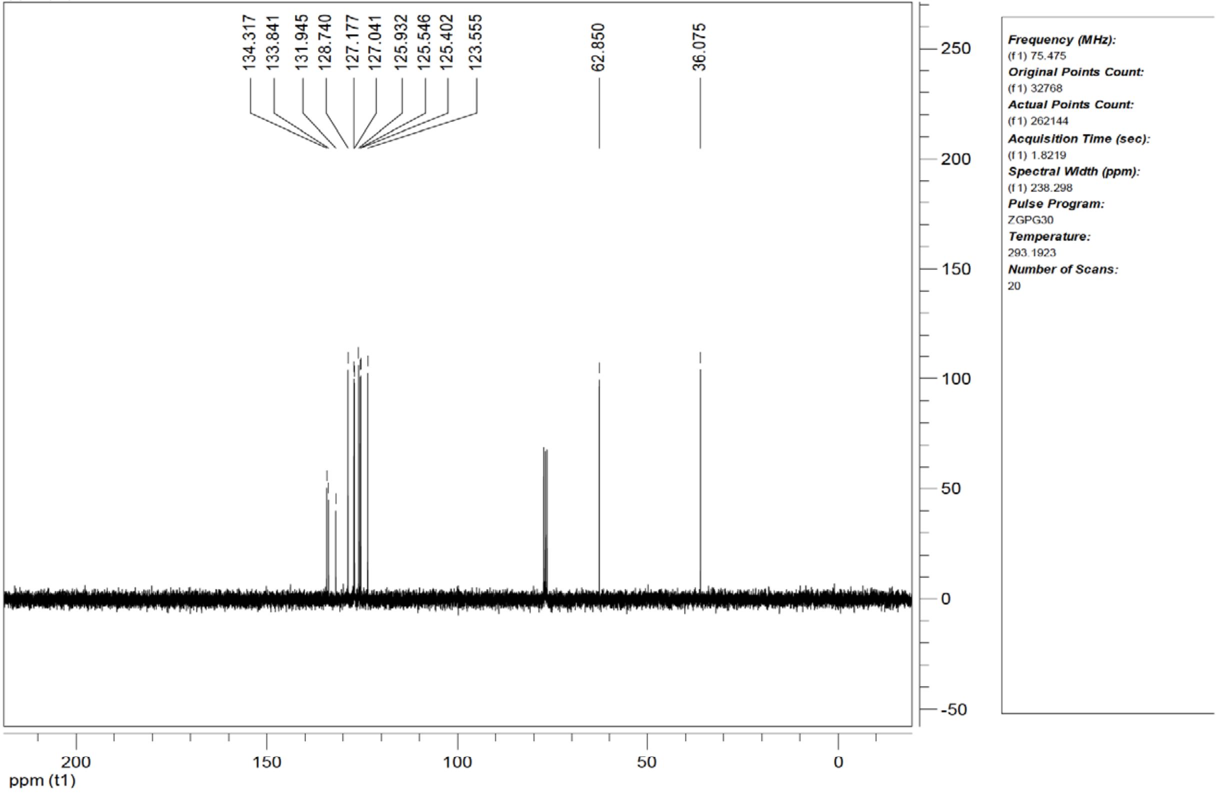
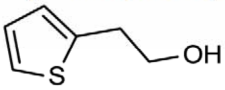
2-(1-naphthyl)ethanol (Table 2, Entry 8)

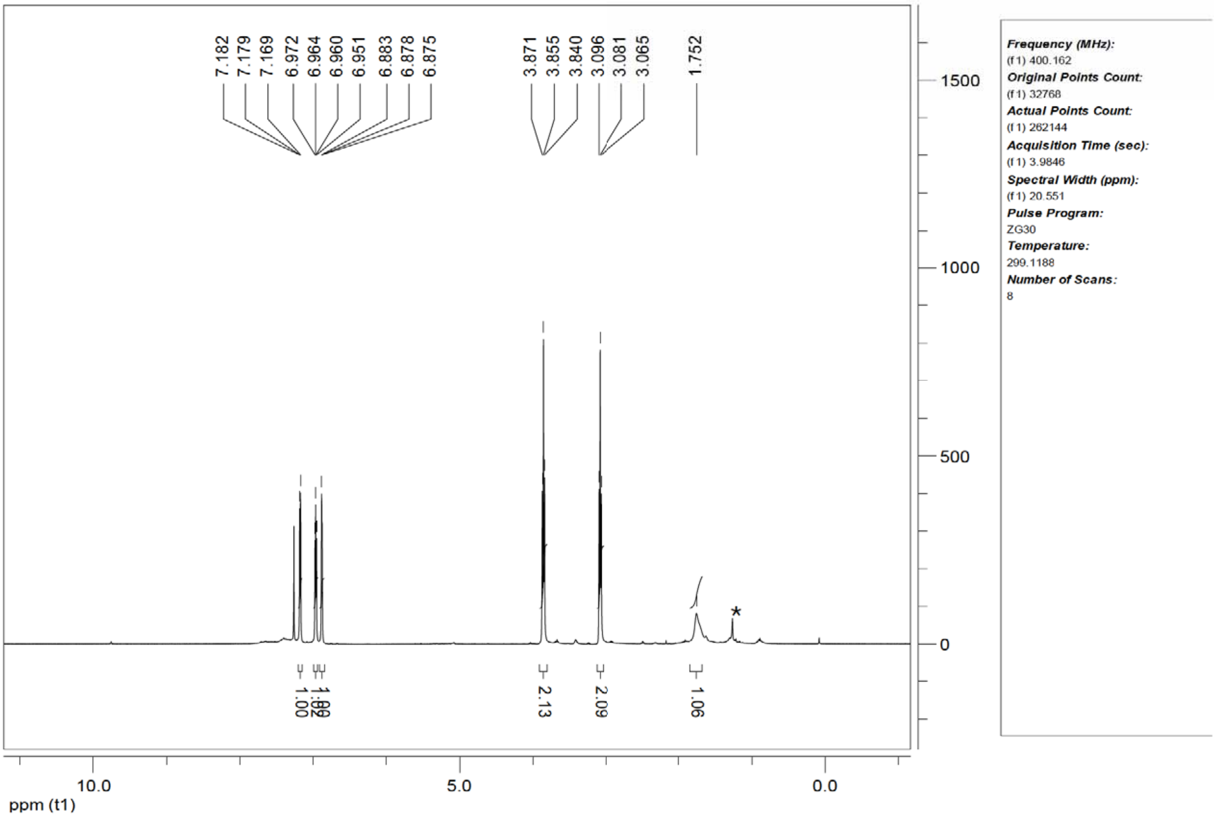


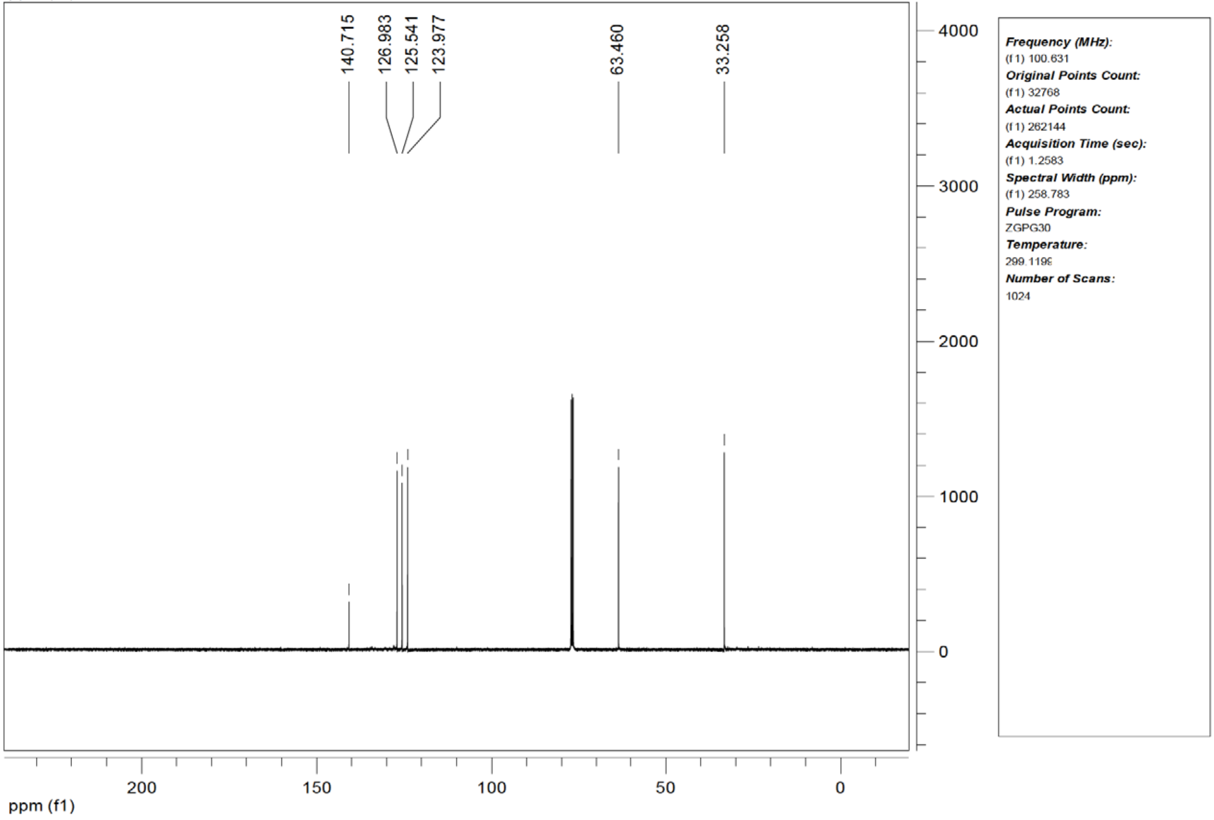




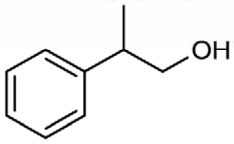
2-(2-thiophenyl)ethanol (Table 2, Entry 9)

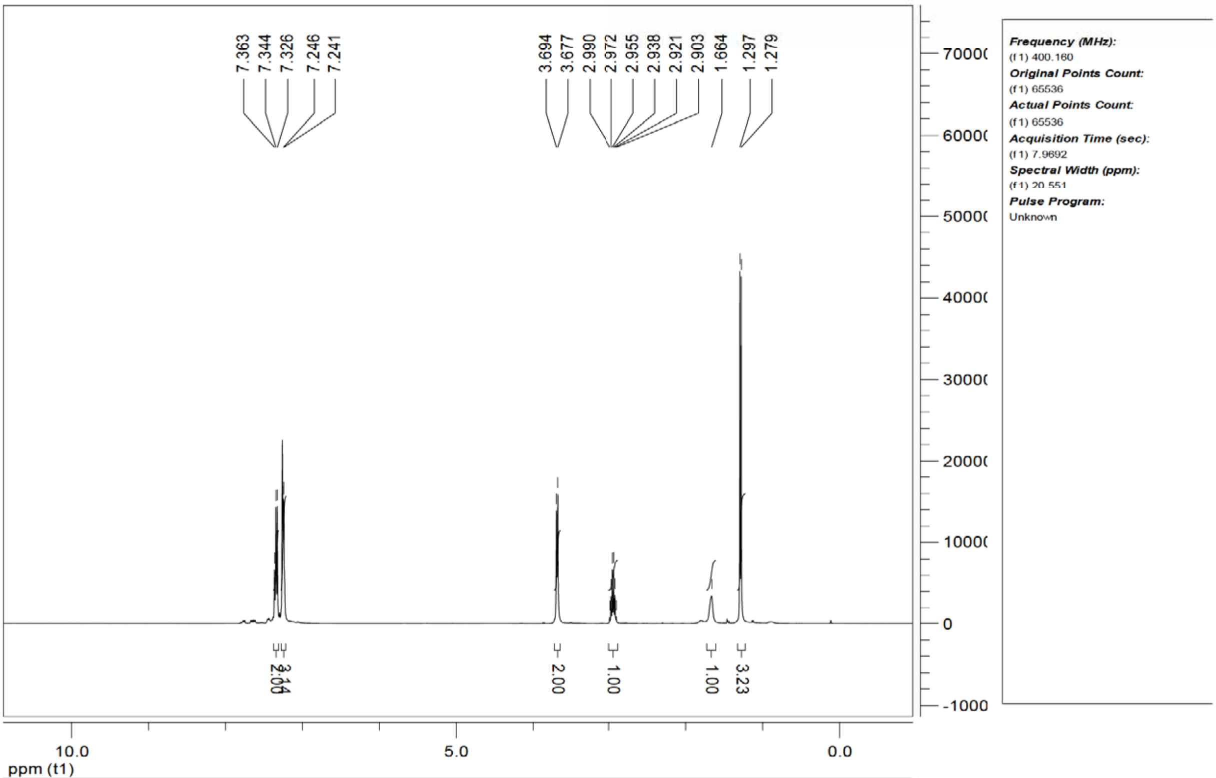


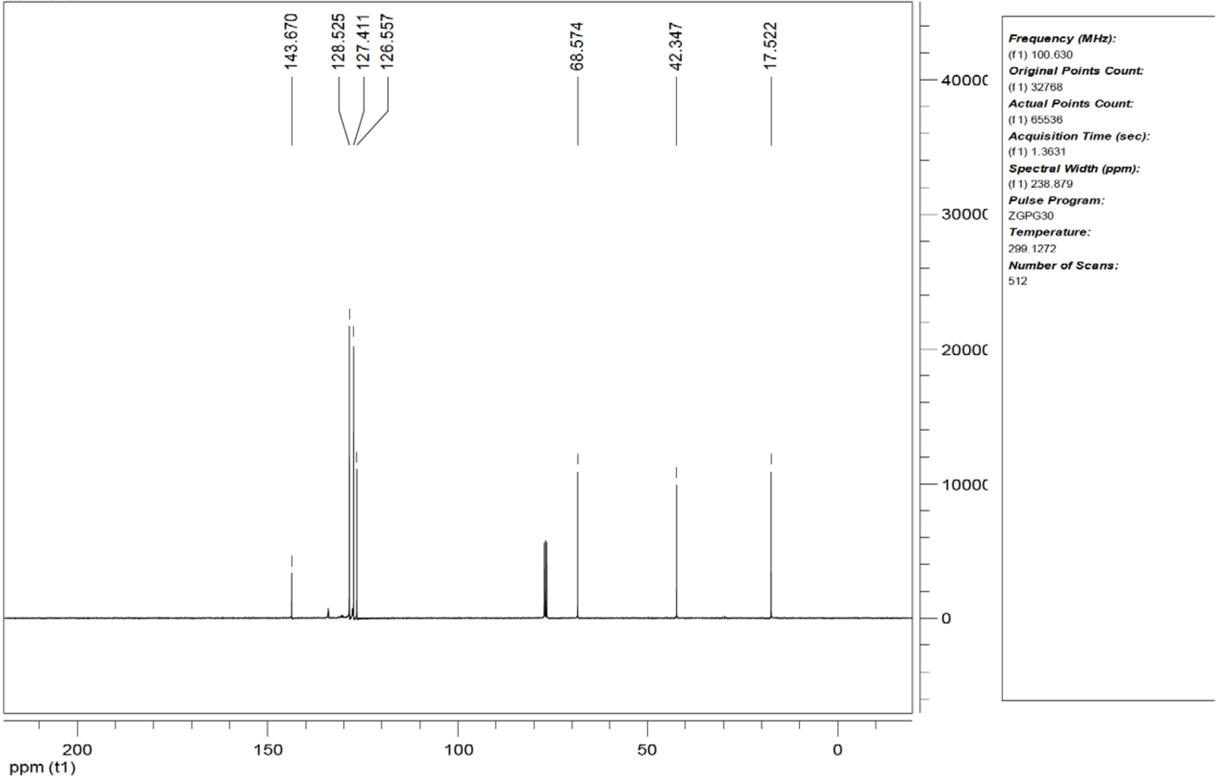




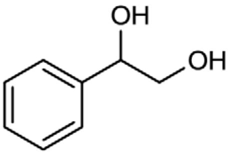
2-Phenylpropan-1-ol (Table 2, Entry 10)

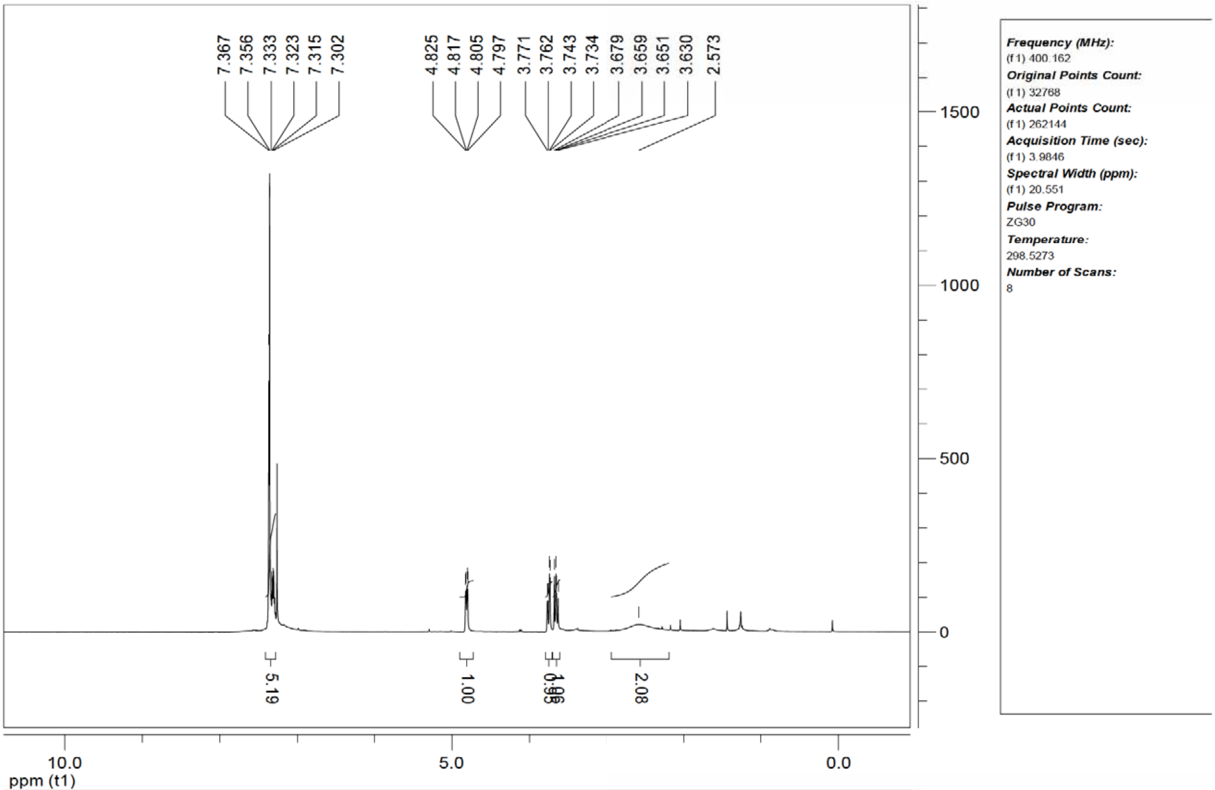


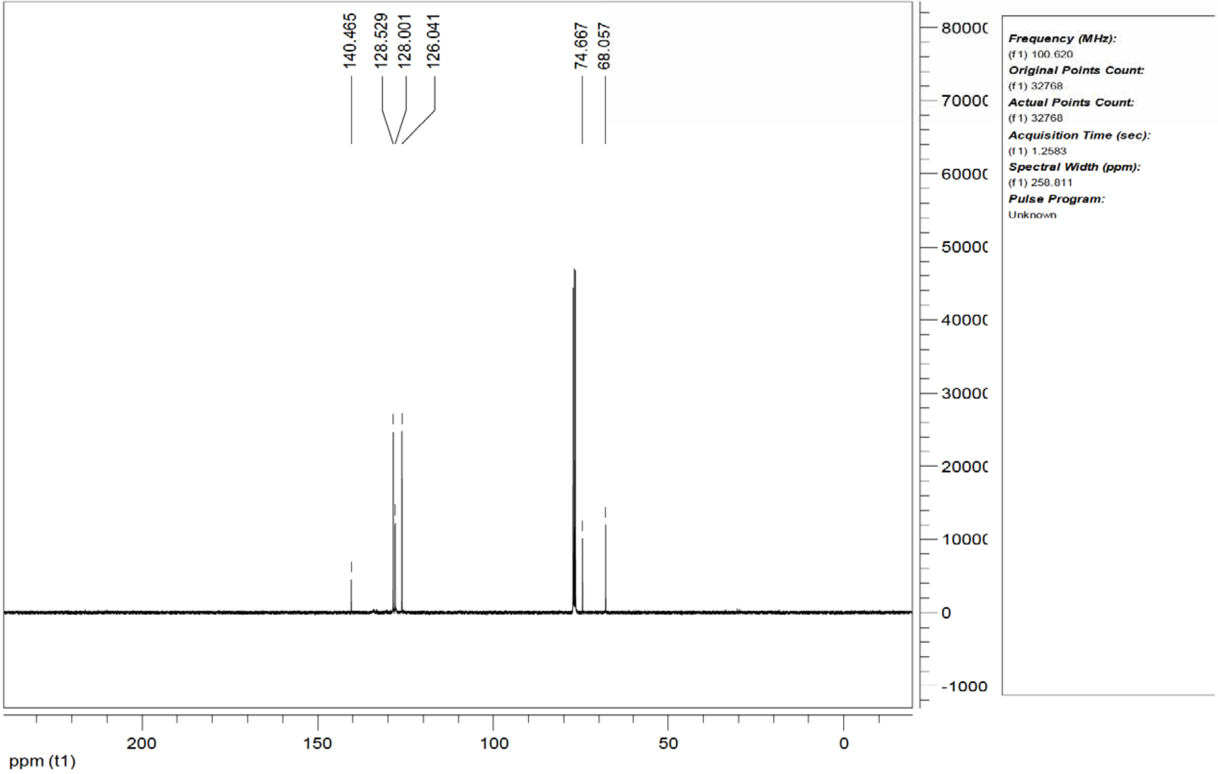




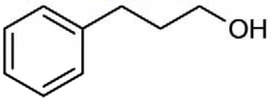
1-Phenylethane-1,2-diol (Table 2, Entry 11)

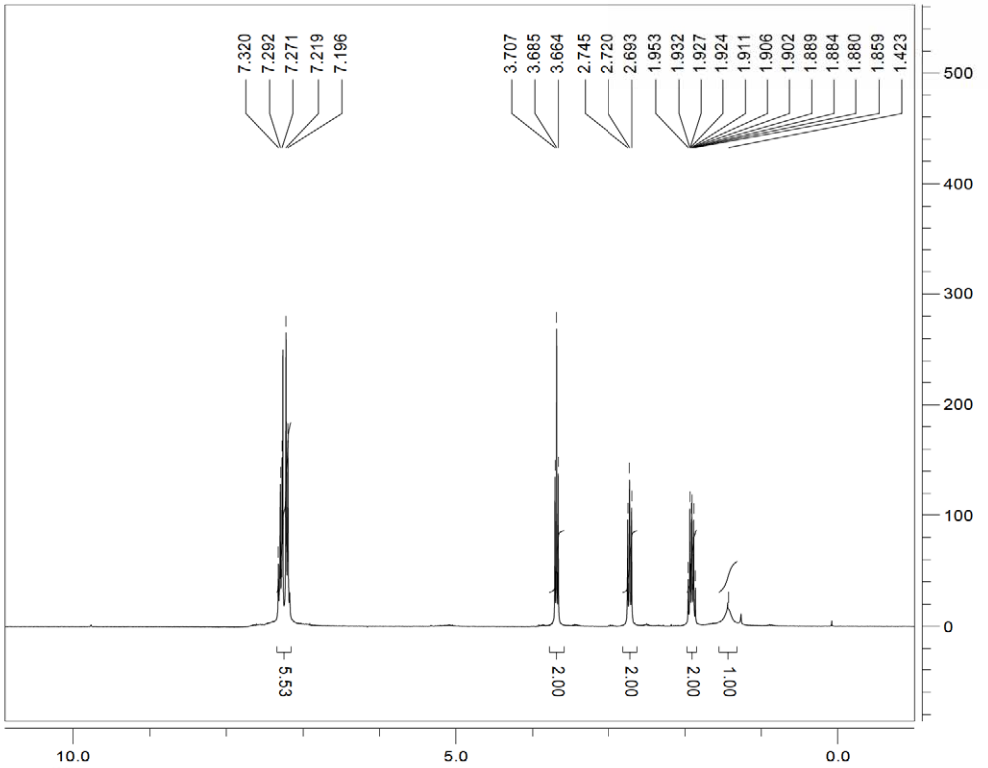






3-phenylpropan-1-ol (Table 2, Entry 12)





Frequency (MHz):
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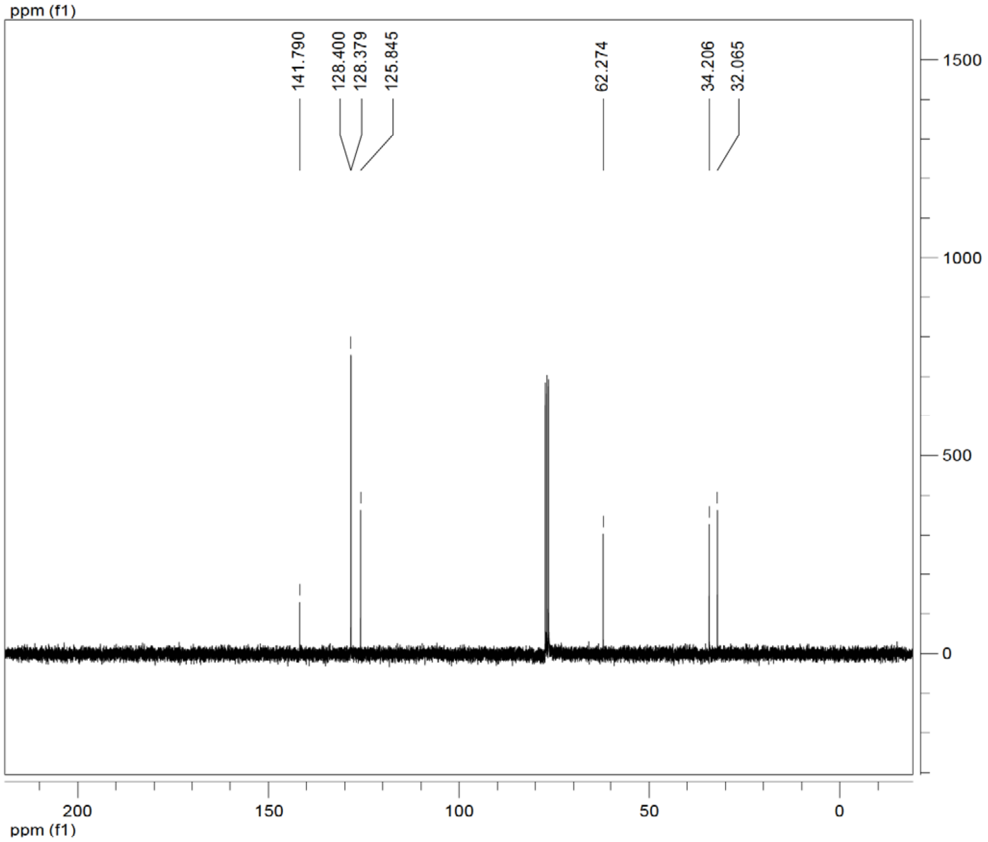
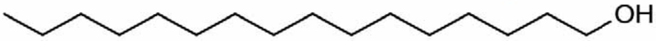
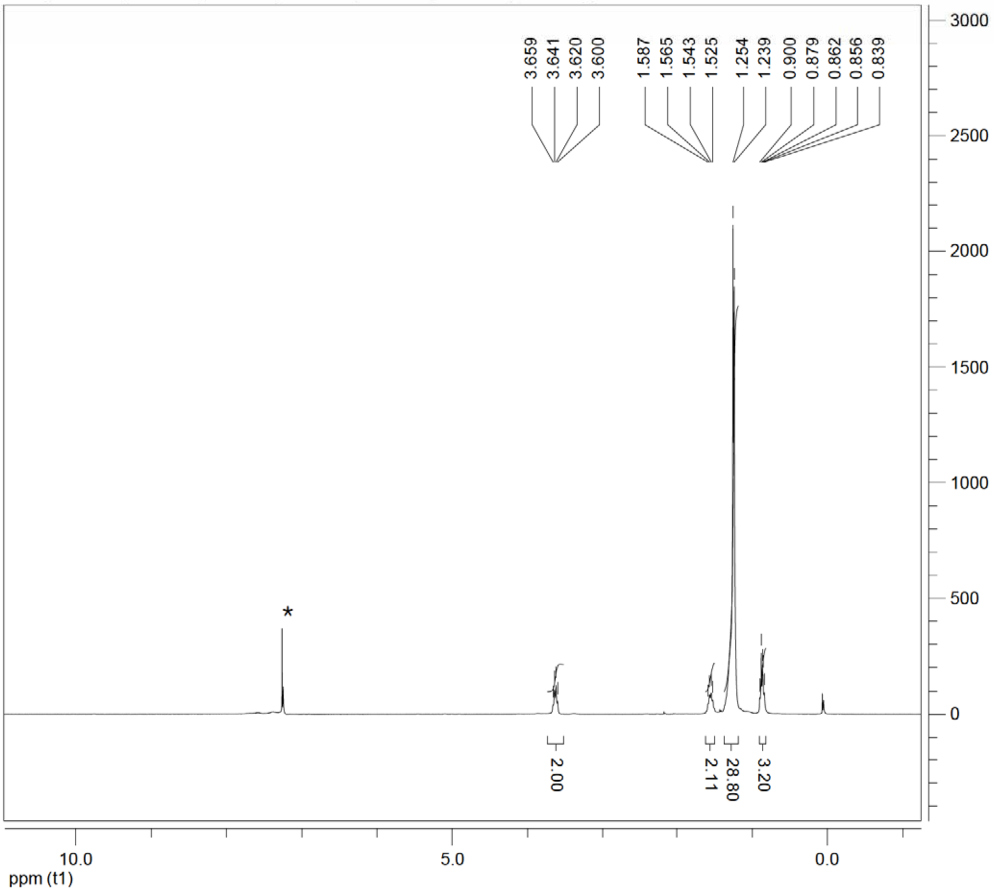
Actual Points Count:
(f1) 131072
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
298.3457
Number of Scans:
8



Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
301.2905
Number of Scans:
150

Hexadecan-1-ol (Table 2, Entry 13)





Frequency (MHz):
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Original Points Count:
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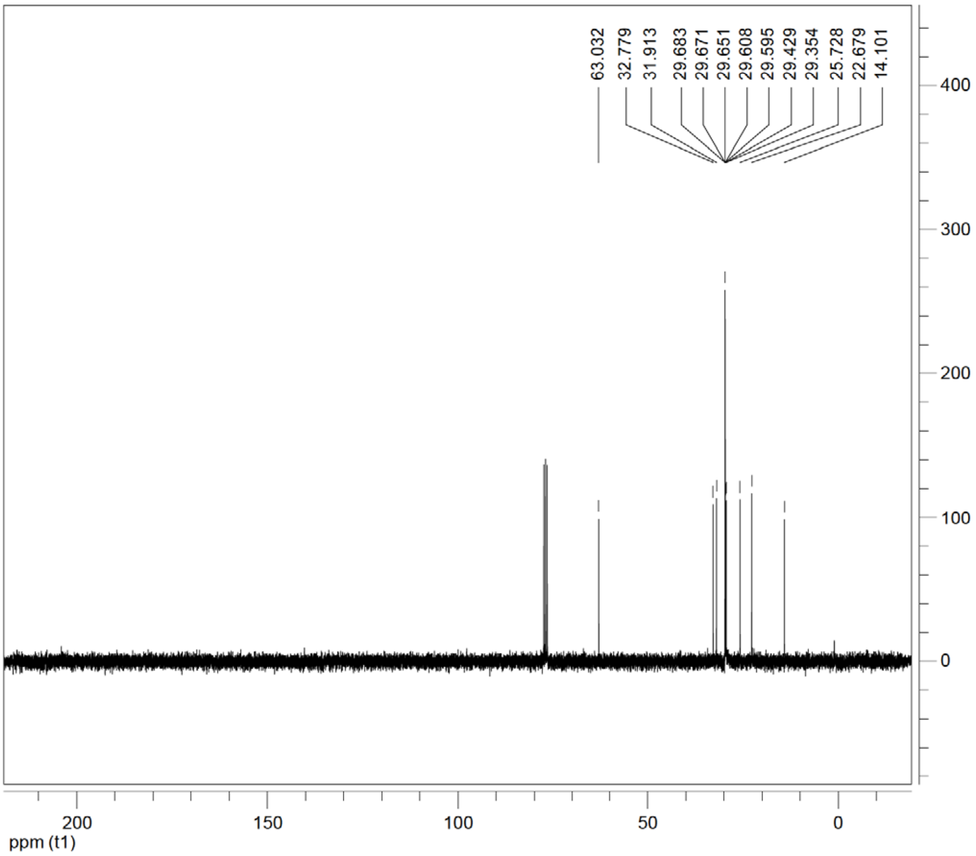
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
293.5604
Number of Scans:
8
Acq. Date:
Fri Mar 02 10:21:31 AM



Frequency (MHz):
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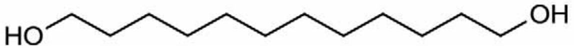
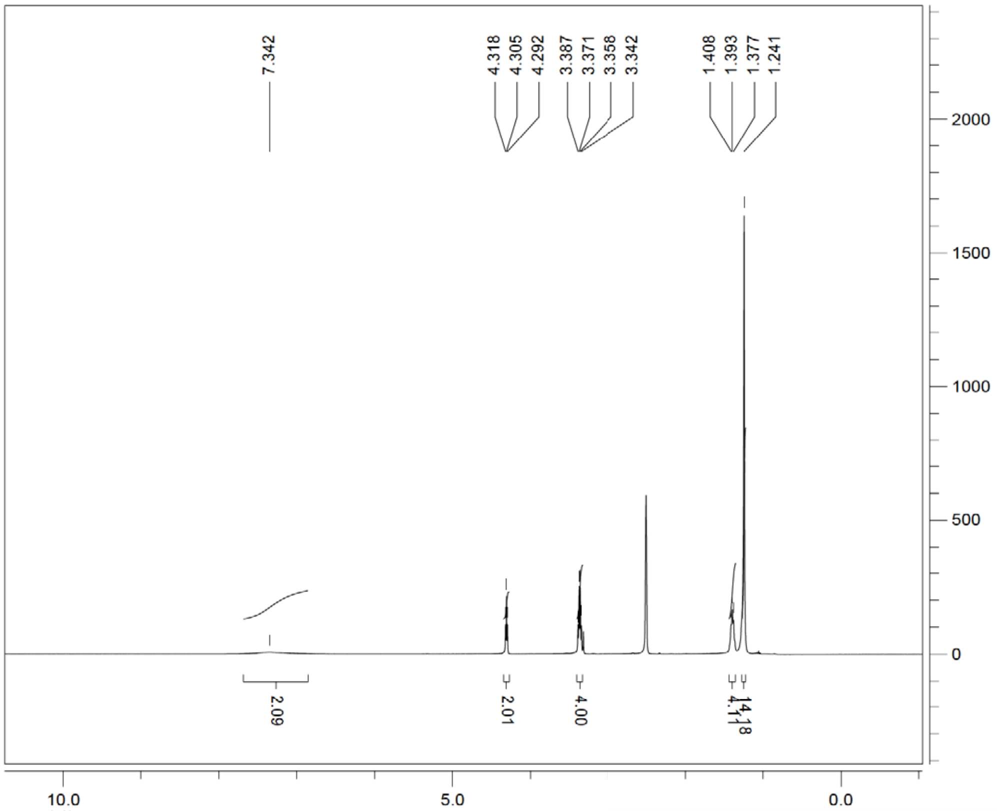
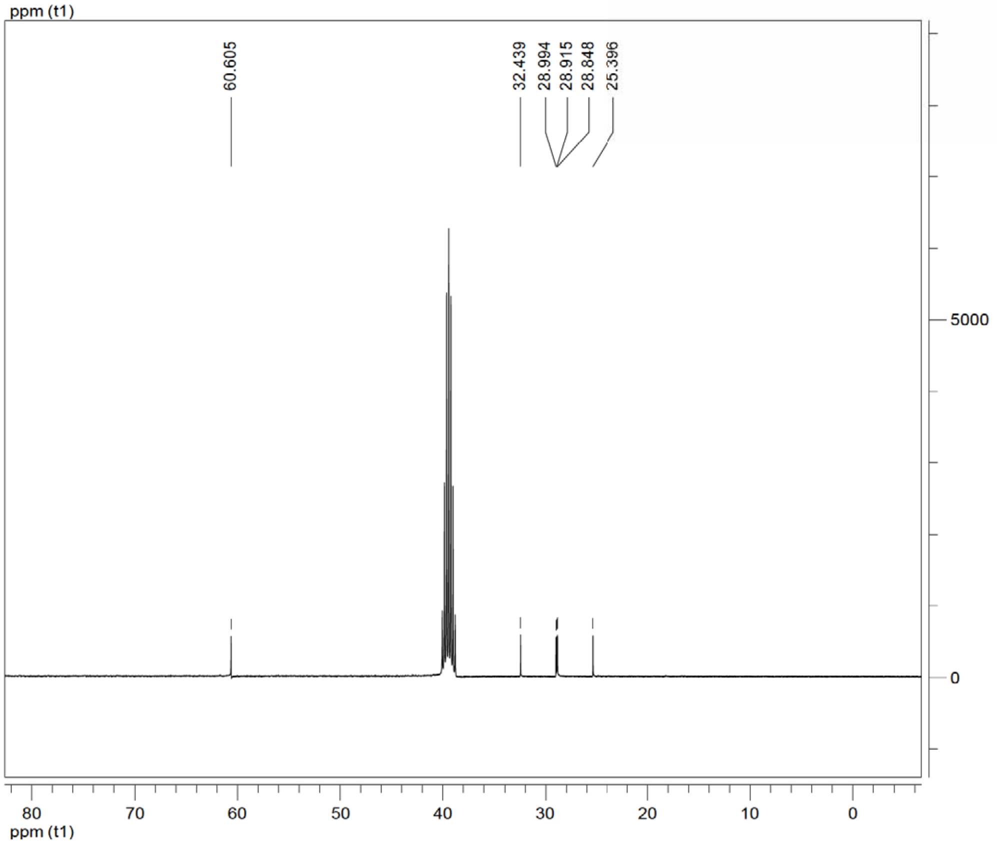
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
293.315
Number of Scans:
40

Dodecane-1,12-diol (Table 2, Entry 14)



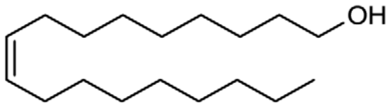


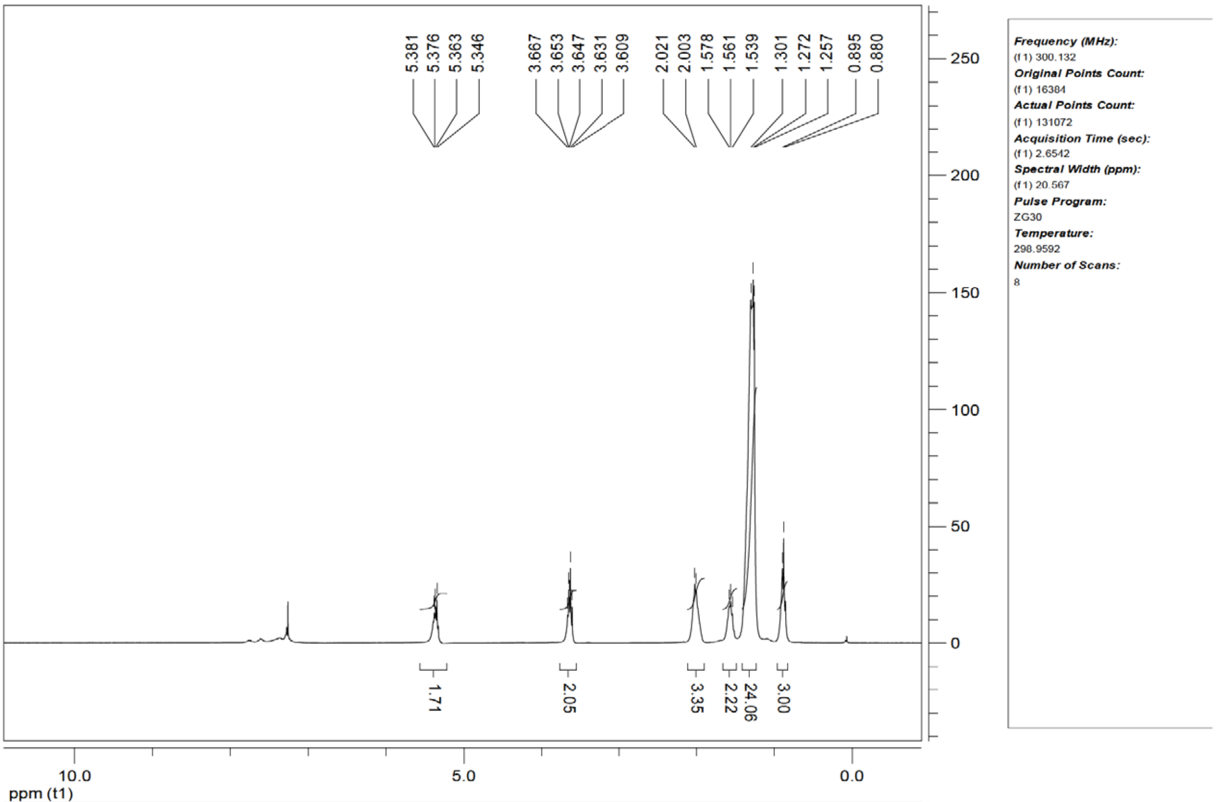
Frequency (MHz):
(f1) 400.162
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.551
Pulse Program:
ZG30
Temperature:
298.5702
Number of Scans:
8

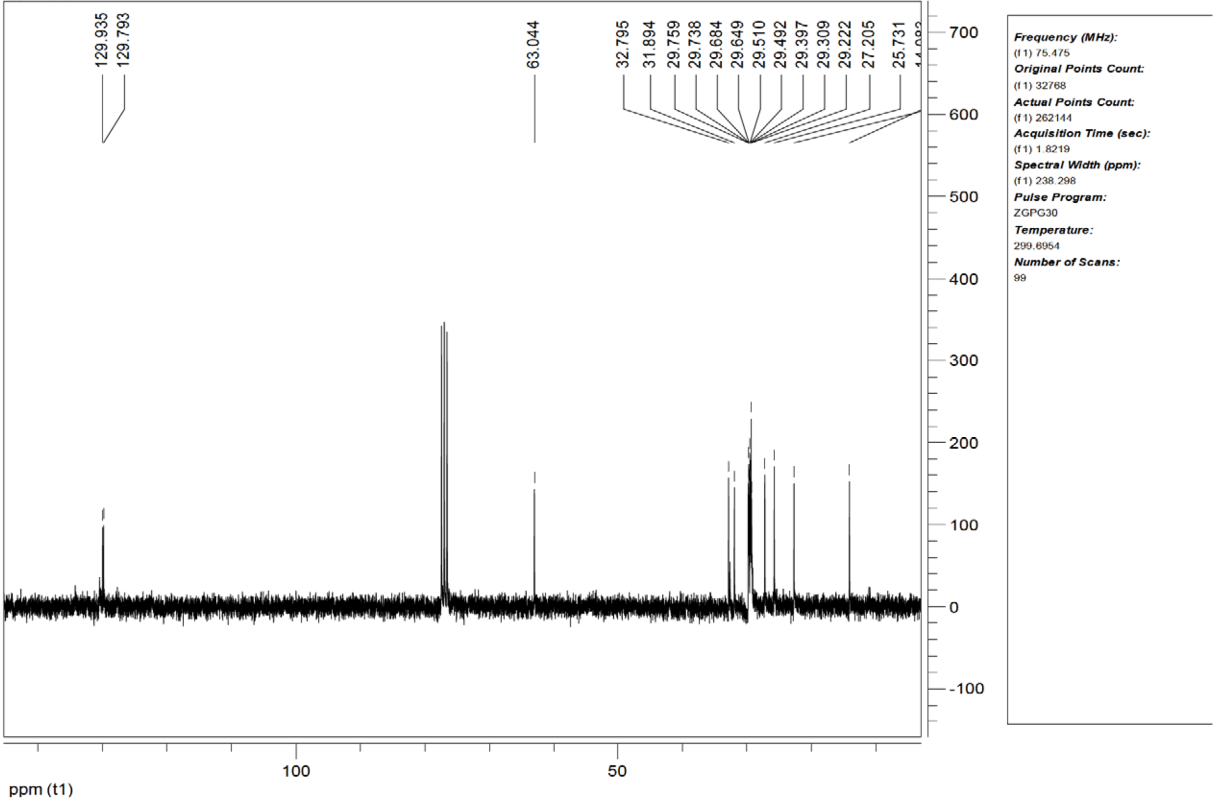


Frequency (MHz):
(f1) 100.631
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 1.2583
Spectral Width (ppm):
(f1) 258.783
Pulse Program:
ZGPG30
Temperature:
299.1164
Number of Scans:
1024

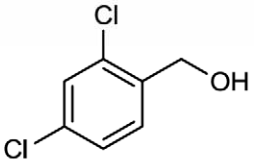
Oleyl alcohol (Table 2, Entry 15)

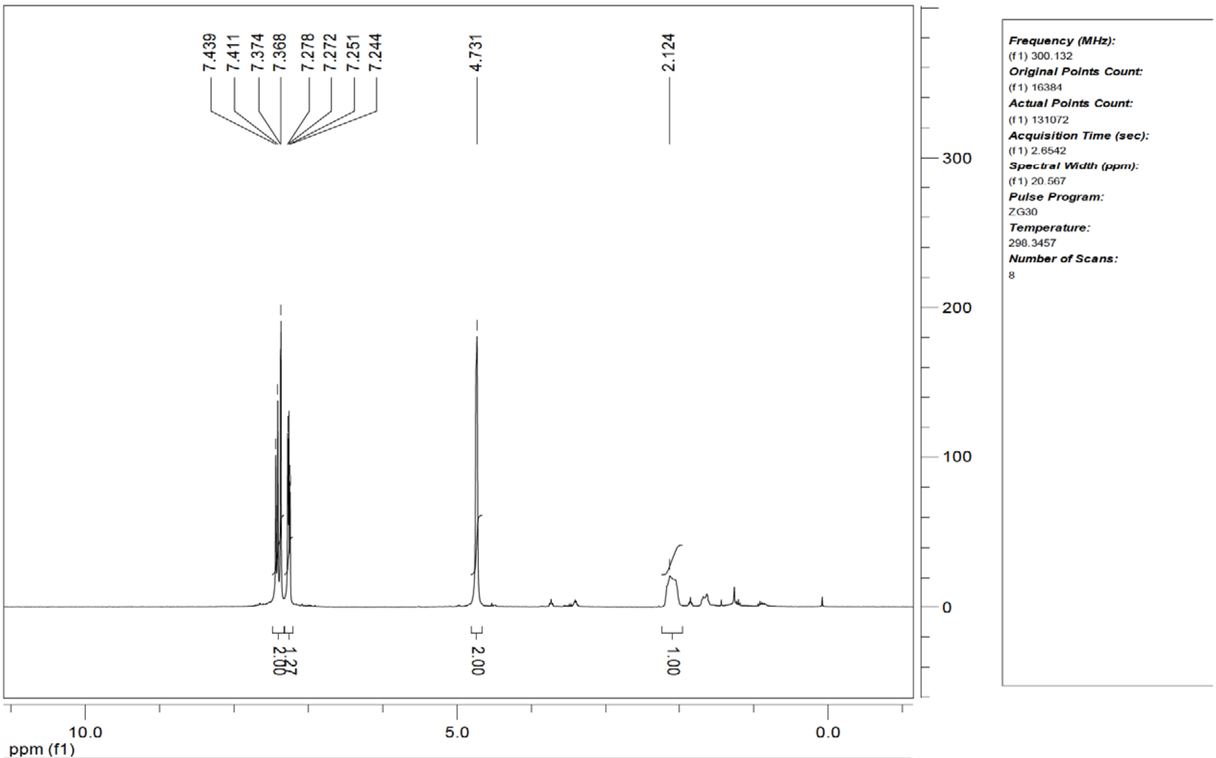






2,4-Dichlorobenzyl alcohol (Table 2, Entry 18)





Frequency (MHz):
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Original Points Count:
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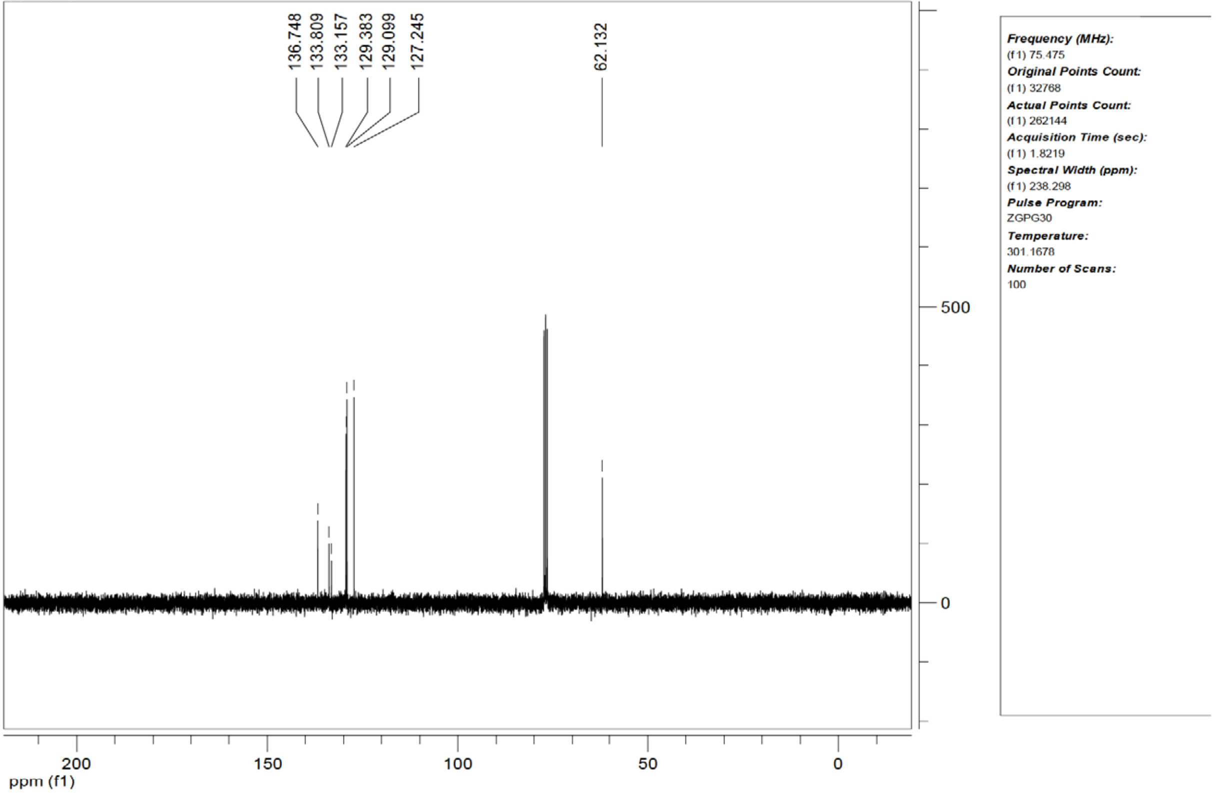
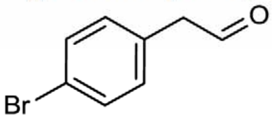
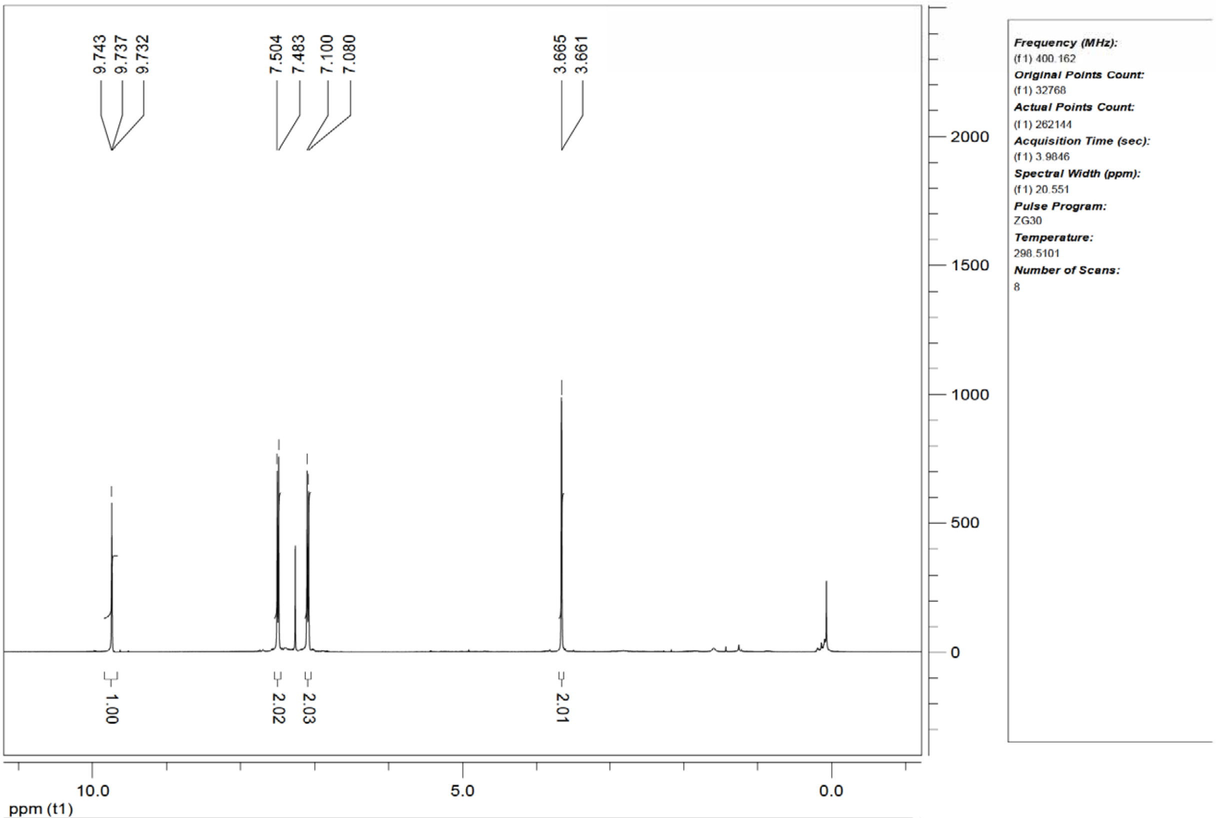
Actual Points Count:
(f1) 131072
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
298.3457
Number of Scans:
8

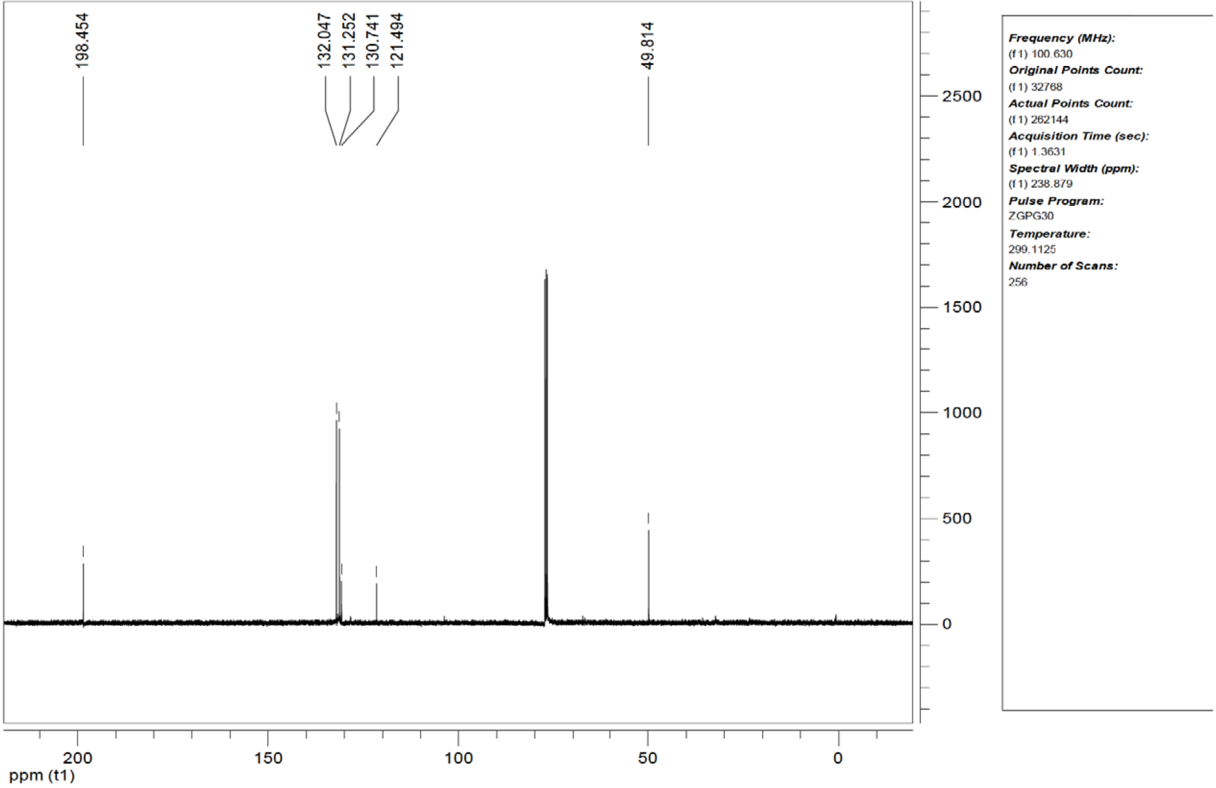


Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
301.1678
Number of Scans:
100

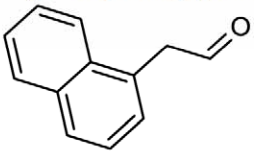
2-(*p*-bromophenyl)acetaldehyde (Table 3, Entry 5)

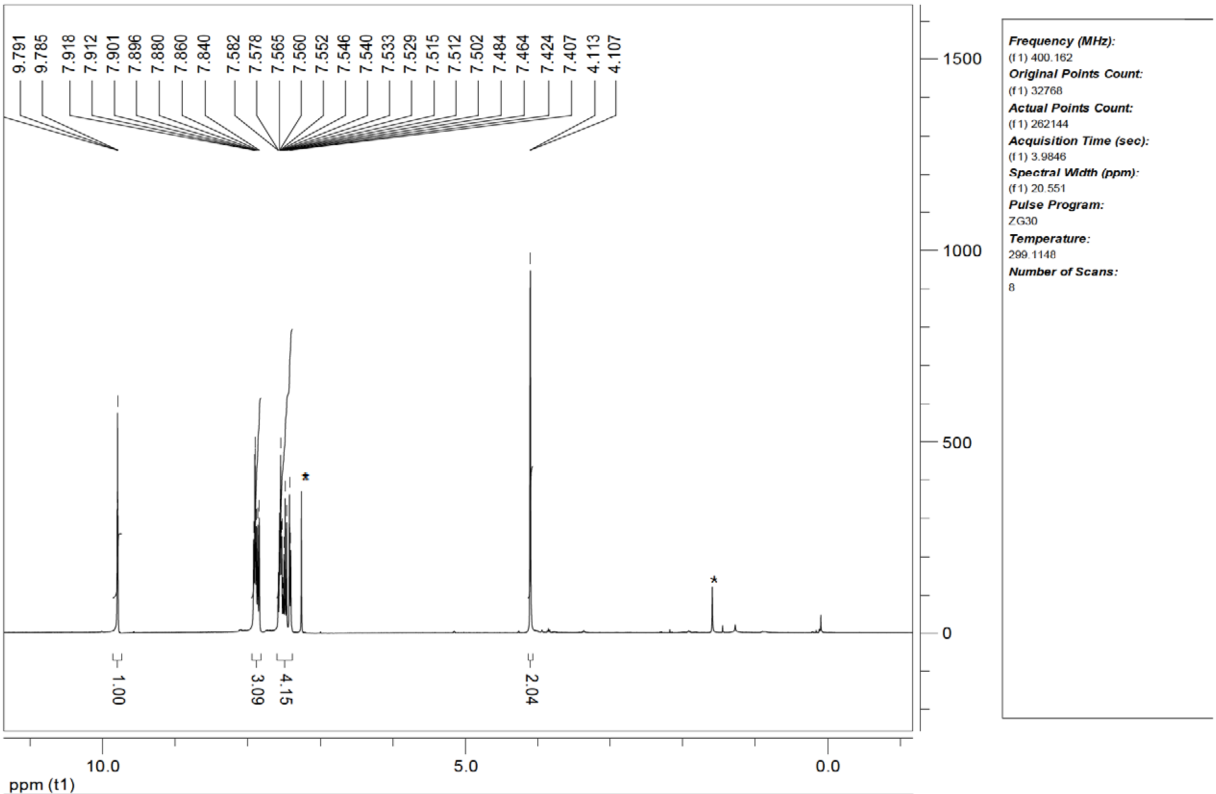






2-(1-naphthyl)acetaldehyde (Table 3, Entry 7)





Frequency (MHz):
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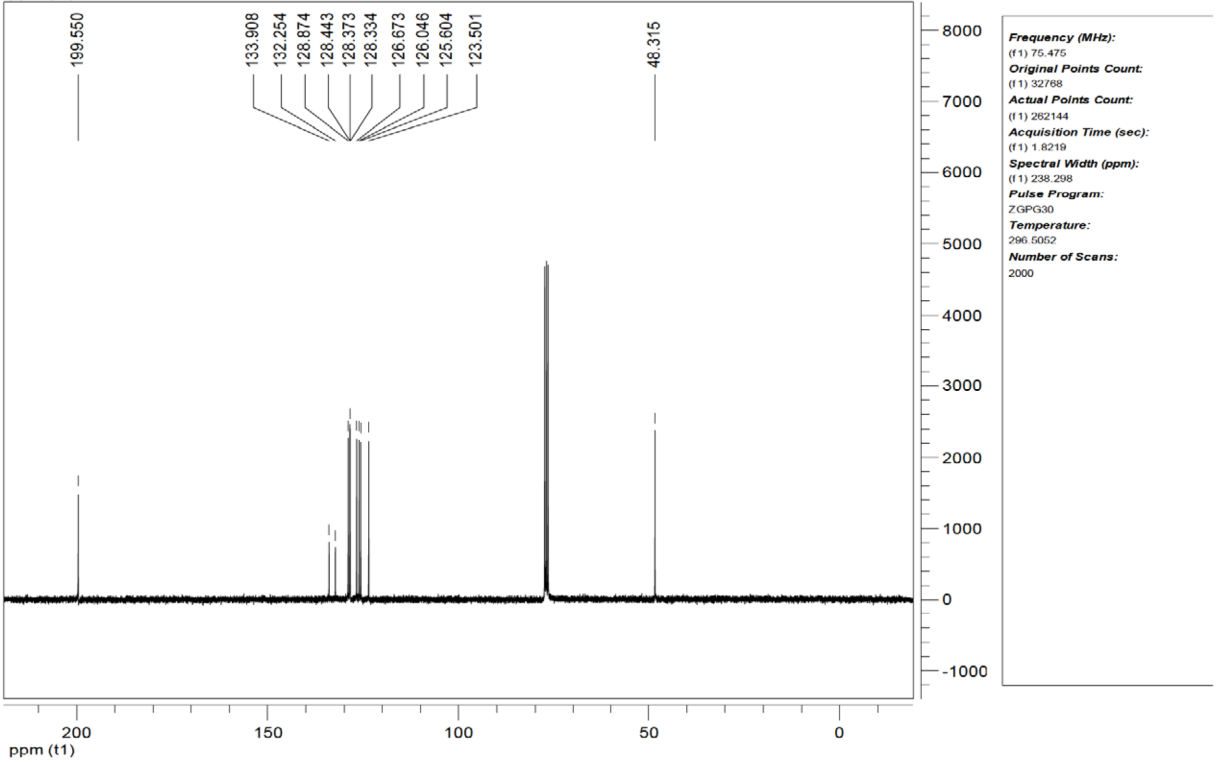
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.551
Pulse Program:
ZG30
Temperature:
299.1148
Number of Scans:
8



Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 262144
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
296.5052
Number of Scans:
2000

Dodecanedial (Table 3, Entry 11)