Supplementary information

TOWARDS PRACTICAL EARTH ABUNDANT REDUCTION CATALYSIS: DESIGN OF IMPROVED CATALYSTS FOR MANGANESE CATALYZED HYDROGENATION

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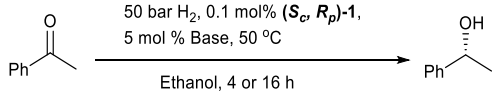
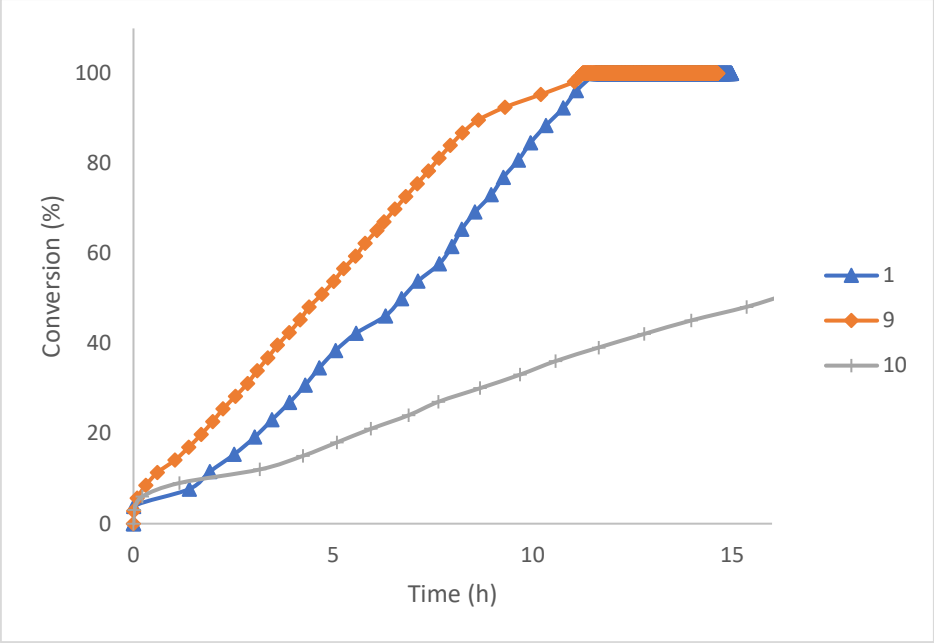
1. Tables and graphs

TABLE S1. Expanded base investigation[a]



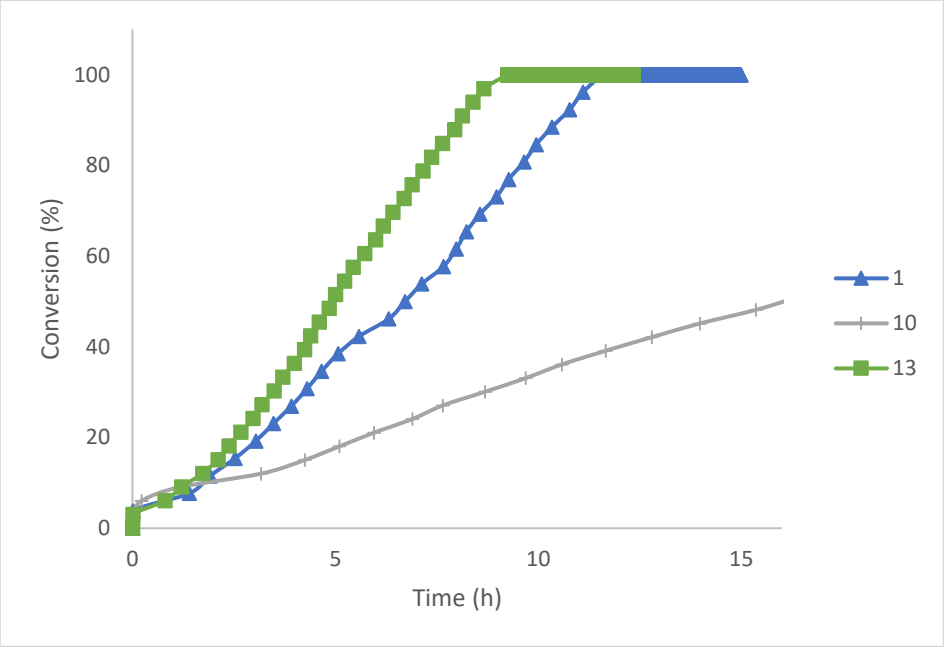
Entry	Base	Reaction time (h)	Conversion (%)[b]	er[c]
1	KO^{t}Bu	4	39	81:19 (*R*)
2	KO^{t}Bu	16	>99	75:25 (*R*)
3[d]	KO^{t}Bu	16	>99	60:40 (*R*)
4[e]	KO^{t}Bu	16	>99	54:46 (*R*)
5	K_2CO_3	16	>99	85:15 (*R*)
6	K_2CO_3	4	37	81:19(*R*)
7[f]	K_2CO_3 / 18-C-6	4	42	81:19(*R*)
8	NaO^{t}Bu	4	43.	84:16 (*R*)
9[g]	NaO^{t}Bu	4	51	81:19(*R*)
10[h]	NaO^{t}Bu / KBr	4	42	86:14 (*R*)
11	Na_2CO_3	4	16	84:16(*R*)
12[i]	Na_2CO_3 / KBr	4	3	ND
13[j]	Na_2CO_3 / TBAB	4	7	ND
14	Li_2CO_3	4	1.6	ND
15	LiOH	4	26	82:18 (*R*)
16	LiO^{t}Bu	4	35	81:19 (*R*)
17	Ag_2CO_3	4	0	ND
18	DBU	4	12	89:11 (*R*)
19[k]	DBU	16	>99	80:10 (*R*)

a. typical conditions: 2.1 mmol substrate, 0.002 mmol catalyst, 0.10 mmol base and internal standard (0.21 mmol) in 3.0 mL ethanol (0.6 M) under 50 bar of H_2 at 50 °C for 4 h; b. Conversion determined by ^{1}H-NMR using 1-methylnaphthalene as internal standard; c. determined by chiral HPLC, configuration in brackets, ND = not determined; d. 10 mol% base, 1 mol% catalysts; e. 1 mol% catalyst; f. 10 mol% crown-ether 18-C-6 used; g. 2 mol% base used; h. 2 mol% base and 3 mol% KBr used; i. 10 mol% tetra-^{n}butylammonium bromide used; j. 0.2 mol% (*S_c, R_p*)-3.003, 16 h .



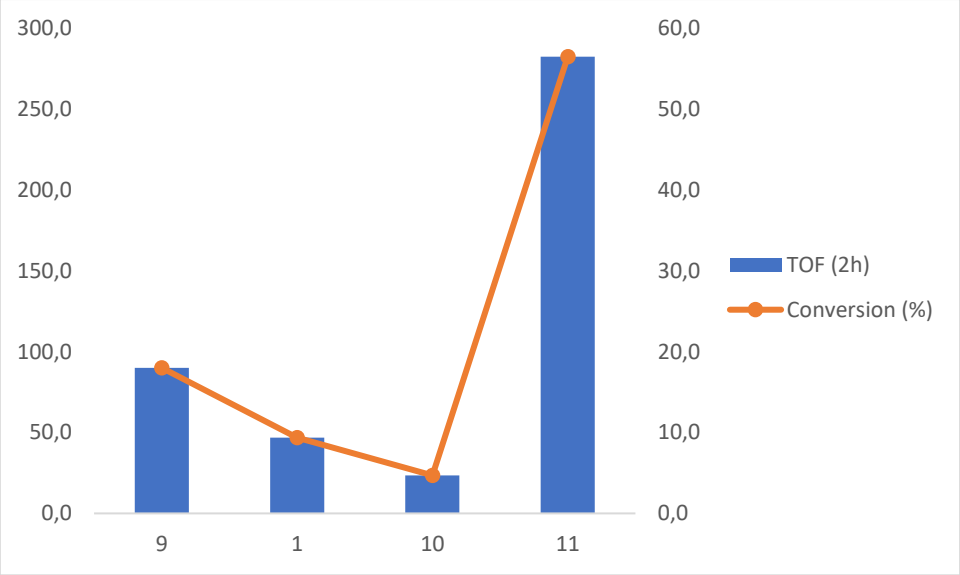
Experimental conditions: 20.81 mmol acetophenone, 0.021 mmol catalyst, 1.04 mmol K_2CO_3, 20 bar H_2, 50 °C, 16 h, ethanol (0.62 M),

Figure S1. Conversion over time for the hydrogenation of acetophenone using Mn complexes 1, 9 and 10.



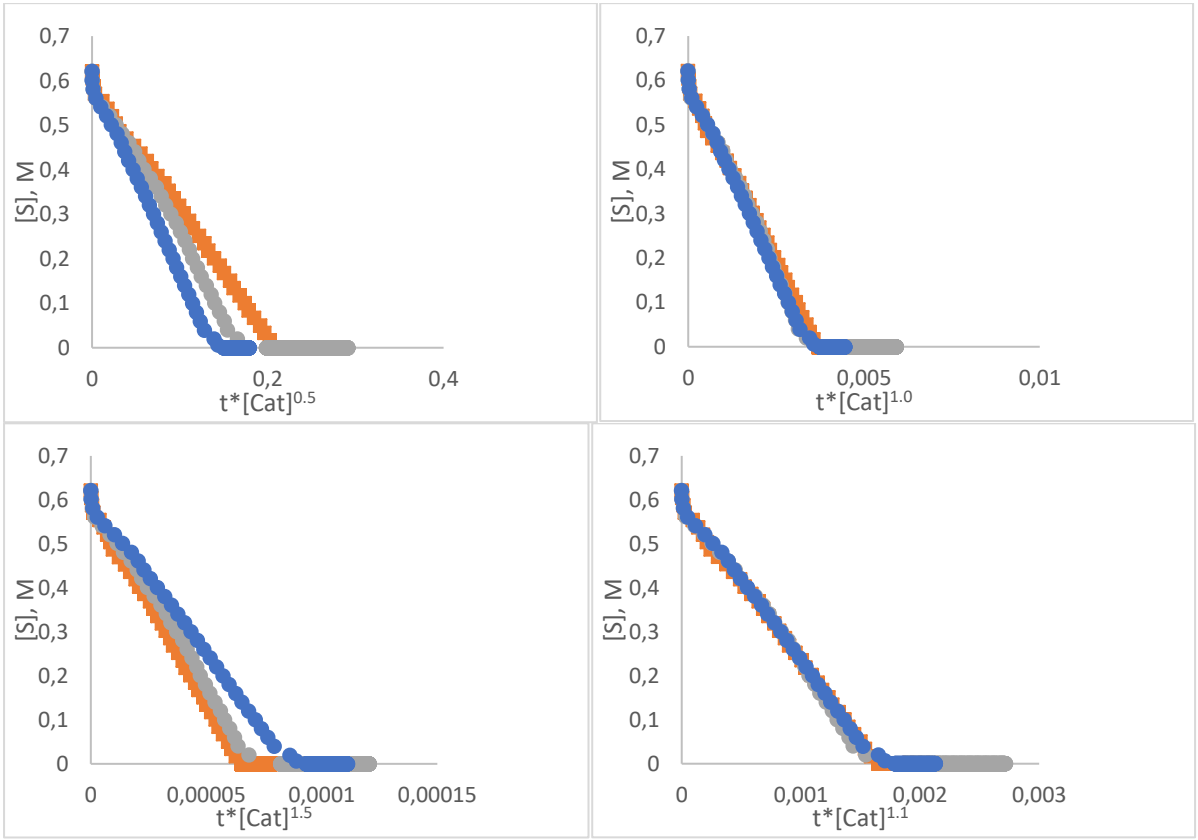
Experimental conditions: 20.81 mmol acetophenone, 0.021 mmol catalyst, 1.04 mmol K_2CO_3, 20 bar H_2, 50 °C, 16 h, ethanol (0.62 M)

Figure S2. Conversion over time comparing the electron-poor phosphine catalysts **10** and **13** with the original catalyst **1**.



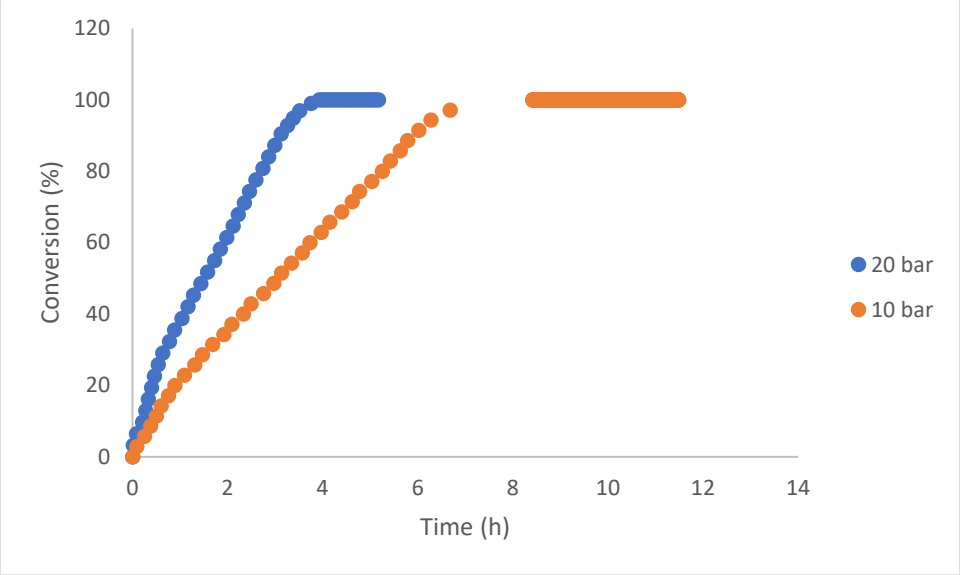
Experimental conditions: 3.1 mmol acetophenone, 0.0031 mmol catalyst, 0.31 mmol K_2CO_3, 50 bar H_2, 50 °C, 2 h, ethanol (0.62 M)

Figure S3. Single-point experiments for the hydrogenation of acetophenone after 2 h reaction time.



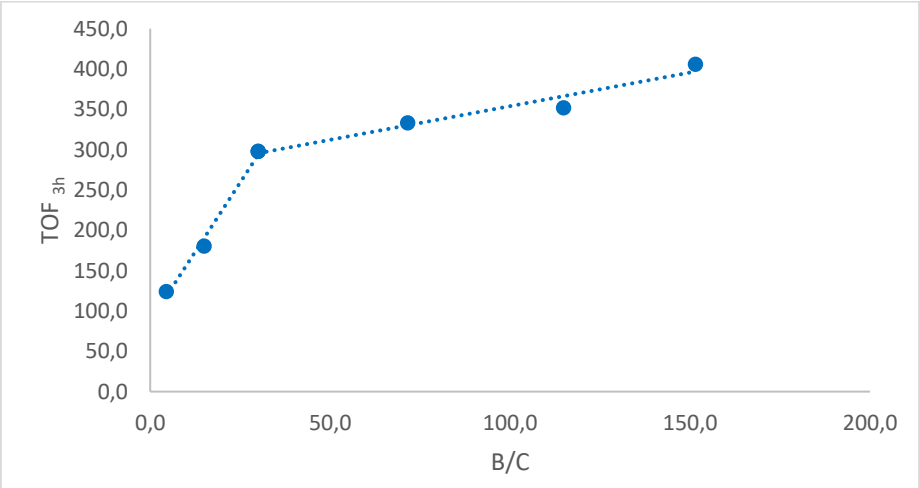
Experimental conditions: 20.81 mmol acetophenone, 0.021-0.011 mmol **11**, 1.04 mmol K_2CO_3, 20 bar H_2, 50 °C, 16 h, ethanol (0.62 M)

Figure S4. Reaction order in catalyst according to Burés method[1] using complex **11.** A catalyst order of around 1 gives a good fit.



Experimental conditions: 20.81 mmol acetophenone, 0.021 mmol **11**, 1.04 mmol K_2CO_3, 10 or 20 bar H_2, 50 °C, 16 h, ethanol (0.62 M)

Figure S5. Influence of pressure on conversion over time using **11**



B/C = base to catalyst ratio

Experimental conditions: 3.1 mmol acetophenone, 0.0031 mmol catalyst, 0.31 mmol K_2CO_3, 50 bar H_2, 50 °C, 2 h, ethanol (0.62 M)

Figure S6. Impact of potassium carbonate on the hydrogenation of acetophenone after 3 h using complex 11

Further discussion of kinetic experiments.

The family of catalysts were tested in batch experiments with magnetic stirring at 50 bar hydrogen pressure to generate the data in Table 4 entries 7-11 in the paper. This clearly shows the pronounced electronic effect with catalyst 11 giving several times higher TOF.

Experiments were then backed up by measuring gas uptake in the reactions at a constant pressure of 20 bar of hydrogen gas. This is not the optimised pressure for these reactions, but was chosen due to technical limitations of the experimental set-up. Most of the catalysts were too insoluble to be added as a solution, so had to be added as solids at the start of the reaction and the reactions started at low pressure of hydrogen (2 bar) while the vessel reached the reaction temperature, before charging with further hydrogen to 20 bar pressure. This itself caused a temperature fluctuation. This protocol leads to initial rates being slightly too high for the less soluble and less active catalysts, 1,9, 10, 12, and 13. These less active catalysts may be subject to a small error that slightly inflates their activity, although the rates observed mean only a small amount of conversion is taking place during this temperature stabilisation period. This error is therefore deemed insignificant, and if it was not it would lead to us underestimating the magnitude of the improvement the new catalyst 11 delivers.

Studying the most active catalyst 11 under these exact conditions is NOT reported in the paper, since significant amount of conversion occurred during the temperature stabilisation period, since the catalyst is much faster, and leads to a meaningful

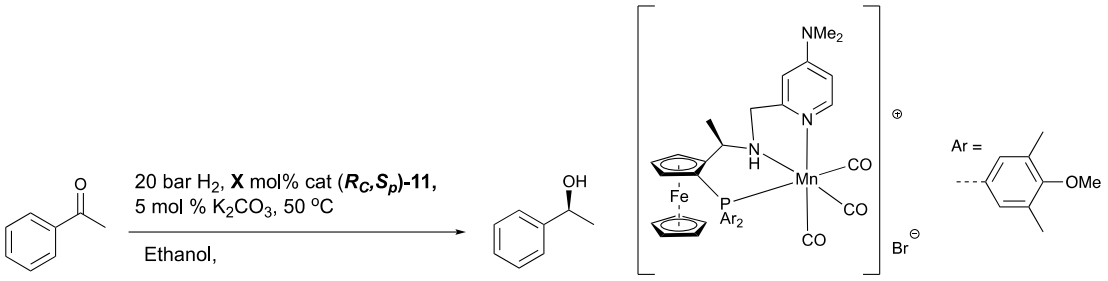
error in the initial TOF value (inflated to around 4-500). Making use of the enhanced solubility, an alternative protocol in which the catalyst is added as a solution after the vessel is at the desired temperature was therefore followed allowing greater control of temperature in the initial stages.

The results from the gas-uptake measurements were in agreement with the results found using batch experiments. The striking results using catalyst 11 were then carried out three times and the average value used for table 4, entry 4 in the paper. The variation in the numbers of around 10%, presumably from typical errors such as the combined effects of error in the amount of catalyst charged, differences in the amount of base in solution, temperature fluctuation as the heater stabilises at the reaction temperature. These errors are therefore completely insignificant relative to the conclusion of rates being around 3-fold (e.g. 260-330%) relative to the original catalyst.

The substrate order is clear-cut as fitting a mechanistic cycle with zero order dependence in acetophenone concentration (straight line not the curves observed in Fig. 4 of the paper, first order in ester, determined using the same equipment).

In addition to this, to determine catalyst order, further experiments were carried out at lower catalyst loading (Table S2, entry 5 and 6). These give a good agreement for first order in catalyst as shown in Figure S4.

Table S2 Measurement of TOF from gas uptake experiments using catalyst 11.

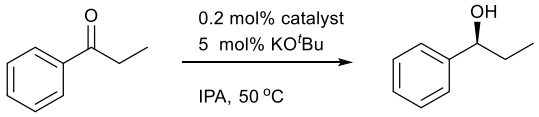


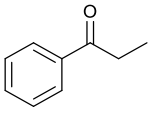
(***R*C,*S*p*)-11**

Entry	Catalyst loading, X	TOF (h^{-1})[b]	$t_{1/2}$ (h)[c]	Conv. (2 h) (%)[d]	Conversion after 16h (%)[e]
1	**0.1**	235	2.3	43	>99
2	**0.1**	173	3.0	34	>99
3	**0.1**	195	3.1	37	>99
4 (average (1-3)	**0.1**	200	2.8	38.7	>99
5	**0.0667**	177	4.4	22	>99
6	**0.005**	190	4.4	26	>99

a. experimental conditions: *entries 1-6:* 20.81 mmol acetophenone, 0.021 mmol catalyst, 1.04 mmol K_2CO_3, 20 bar H_2, 50 °C, ethanol (0.62 M), 16h; b. calculated at 25 % conversion; c. time at which 50 % conversion was achieved. d. based on gas uptake; e. conversion to product after 16h measured by NMR spectroscopy.

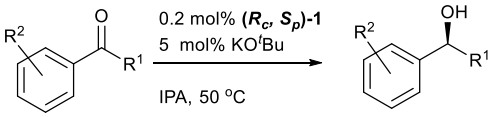
Table S3. Initial investigation into transfer hydrogenation of ketones[a]

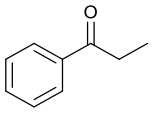
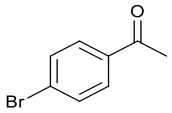
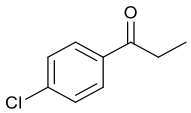
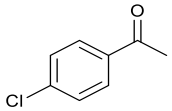
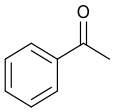
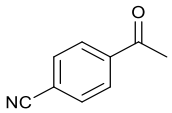
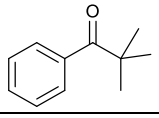


Entry	Catalyst	Substrate	Conversion (%)	*er* (%)[b]
1	(R_c, S_p)-1		93	87:13 (*S*)
2	(R_c, S_p)-9	-"-	93	82:18 (*S*)
3	(R_c, S_p)-10	-"-	91	89:11 (*S*)

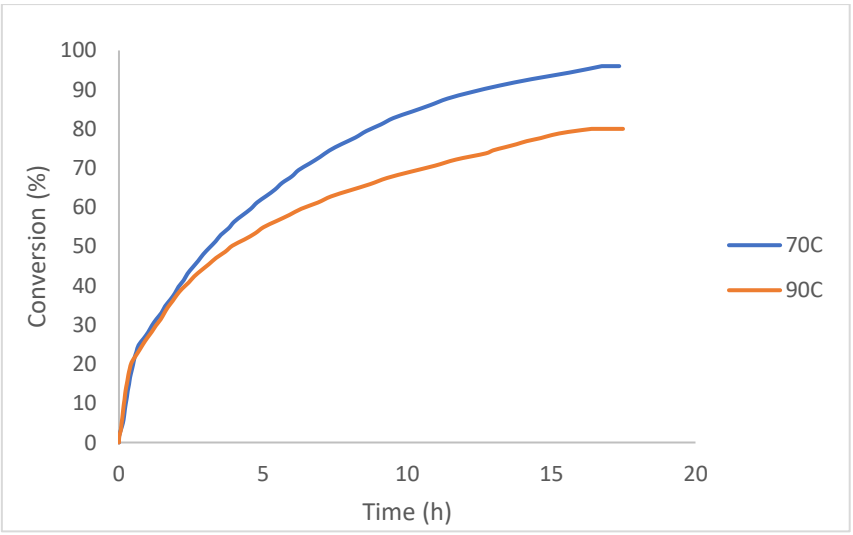
a. conditions: 2.0 mmol substrate, 0.004 mmol catalyst, 0.10 mmol potassium *tert*-butoxide, IPA (0.4 M), 50 °C, 1 h; b. determined by chiral HPLC, known configuration in brackets.

Table S4. Transfer hydrogenation of ketones using catalyst 1[a]



Entry	Substrate	Reaction time (h)	Conversion (%)[b]	*er*[c]
1		1	93 (ND)	87:13 (*S*)
2		1	>95 (74)	66:34 (*S*)
3		1	>95 (76)	85:15 (*S*)
4		1	>95 (91)	80:20 (*S*)
5		1	>95 (72)	66:34 (*S*)
6		1	>97 (79)	73:27 (*S*)
7		4	50 (ND)	ND

a. conditions: 1.5 mmol substrate, 0.003 mmol catalyst, 0.08 mmol potassium *tert*-butoxide, IPA (0.4 M), 50 °C, 1 h; b. determined by ^{1}H-NMR, isolated yields in brackets, ND = not determined; c. determined by chiral HPLC, known configuration in brackets, ND= not determined.



Experimental conditions: 20.81 mmol 0.021 mmol **11**, 1.04 mmol K_2CO_3, 20 bar H_2, 70 and 90 °C, 16 h, ethanol (0.62 M)
Figure S7. Hydrogenation of ethyl p-fluorobenzoate at 70 and 90 °C using **11**.

2. Experimental

The preparation of solutions for the use in catalytic reactions were carried out under either argon or nitrogen atmospheres. All glassware was used oven dried or flame dried and cooled under vacuum before use. Solvents were degassed either by bubbling argon or nitrogen through the solvent for at least 1 h prior to use or freeze-pumped-thawed before use. Unless otherwise noted all precursor, chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Strem or TCI and used as received (excepts when further degassed as stated above or distilled as mentioned in the text). Solvents used in hydrogenation reactions were bought extra dry and sealed under argon and fitted with a sure-seal septa. Ligand precursors were generously donated by Solvias AG. Room temperature or ambient temperature refers to the temperature range 15-25 ^{o}C. Heating the reaction mixtures were affected by either an oil bath or a Drysyn heating block. Reported temperature is the oil bath or heating block temperature and not internal temperature unless stated and was measured using a contact thermometer (PT-1000). In vacuo refers to either the use of a Heidolph Laborota 4001 rotary evaporator or the use of a high-vacuum line. Analytical thin layer chromatography (TLC) was carried out on pre-coated plastic plates (Kieselgel 60 F254 silica). TLC visualization was carried out using a UV lamp (254nm) or using a 1% potassium permanganate aqueous solution. Flash silica chromatography was performed using Kieselgel 60 silica. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR was carried out using either a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 121 MHz for ^{31}P and 282 MHz for ^{19}F), a Bruker Avance II 400 (400 MHz ^{1}H, 100 MHz ^{13}C, 161 MHz ^{31}P and 376 MHz for ^{19}F) or a Bruker Ultrashield 500 (500 MHz ^{1}H, 125 MHz ^{13}C, 201 MHz ^{31}P and 470 MHz for ^{19}F). NMR analyses were carried out at room temperature in the deuterated. The chemical shifts are quoted as parts per million (ppm). Coupling constants, J, are quoted in Hz. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The abbreviation “br” is used to denote broad peak shape and app is used to denote apparent. Infrared spectra were recorded on a Shimadzu IRAffinity-1 using Pike attenuated total reflectance (ATR) accessory. Peaks are reported as weak (w), medium (m) or strong (s). The abbreviation “br” denote a broad peak shape and “sh” denote a sharp peak shape. All units are reported in cm^{-1}. Mass spectrometric (m/z) data were acquired by electrospray ionisation (ESI) or electron impact (EI) either at the University of St Andrews Mass Spectrometry facility (using Micromass LCT spectrometer or Micromass GCT spectrometer) or at the EPRSC National Mass Spectrometry Service Centre, Swansea (using Orbitrap nano-ESI, Finnigan MAT 900 XLT or Finnigan MAT 95 XP). Values are reported as a ratio of mass to charge in Daltons. Optical rotations were measured on a Perkin Elmer 341 polarimeter using a 1 ml cell with a 1 dm path length at room temperature using the sodium D-line, and a suitable solvent that is reported along with the concentration (c = g/100ml). HPLC analysis has been determined using a Varian Prostar operated by Galaxie workstation PC software.
Catalyst **1** was prepared as per previous published procedure.[2] Compound **18**e was prepared as previously published. [3]

General procedure for reduction of ketones using PNN-catalyst and potassium carbonate
The ketone (1.0 equivalents) and 1-methylnaphthalene (50 μL) was added to a Schlenk flask under argon atmosphere. Ethanol (2.7 mL) was added via syringe and the mixture shaken to ensure homogeneity. The solution was degassed by bubbling argon or nitrogen through the solution >30 min.
Catalyst (0.001-0.0001 equivalents) and potassium carbonate (0.05 equivalents) was charged to a microwave vial. The vial was capped and evacuated and refilled with argon gas (three times). The content of the Schlenk flask was transferred via a syringe to the vial. The lid was pierced with two needles and placed in a stainless-steel autoclave under argon atmosphere. The vessel was pressurized with hydrogen gas (50 bar) and vented to the atmosphere. This was repeated twice, then the pressure was set to 50 bar with hydrogen gas and the vessel sealed and placed in a pre-heated oil bath (50-65^{o}C) for 16-24 h. After cooling to ambient temperature, the vessel was vented and opened. The solvent was removed, and the product purified by column chromatography.

Gas-uptake experiments of ketones - method 1 (Table 4 entries 1-6)
Acetophenone (2.5 g, 20.81 mmol, 1.0 equiv.) was dissolved in ethanol (30 mL) and degassed by bubbling argon gas through the solution for 1 h. Catalyst (0.011 - 0.021 mmol, 0.0005-0.001 equiv.) and potassium carbonate (144 mg, 1.04 mmol, 0.05 equiv.) was charged to an autoclave. The vessel was sealed and pressurized with hydrogen gas (5 bar) and vented. This was repeated twice. The degassed ethanol solution was added via an injection port and the vessel sealed and pressurized with hydrogen gas (20 bar) and vented. This was repeated twice. The pressure was set to 2 bar and the mixture heated to 50 ^{o}C at which time the pressure was increased to 10 or 20 bar and the experiment started. Gas uptake was monitored by reduction of the pressure in the burette. The reaction was considered complete after no gas uptake was observed for >2 h. The vessel was cooled to room temperature, vented and the content concentrated to dryness and analyzed by ^{1}H-NMR to confirm full conversion. The uptake curve was converted to conversion by dividing the gas uptake at a time-point by total uptake and multiplied by 100 to get percentage conversion. From the data substrate and product concentrations could be calculated and from those TON and TOF. The TOF was reported at 25 % conversion to minimize temperature influence of the vessel setup.

The internal temperature usually over-shoot to around 60-65 °C during the start of the experiment and cooled down to the target temperature within 30-40 min. When catalyst **11** was used with this method the $TOF_{25\%}$ was generally found to be >500 h^{-1}. Since we were concerned that the temperature fluctuations at the beginning of the reaction would influence the TOF data we decided to use method 2 detailed below, which gave lower TOF, but had better temperature control. The low solubility of the other catalysts in the media precluded this method from being used with other catalysts than **11**.

Gas-uptake experiments of ketones – method 2 (for catalyst **11**)
Acetophenone (2.5 – 5.0 g, 20.81 – 41.62 mmol, 1.0 equiv.) was dissolved in ethanol (25 mL) and degassed by bubbling argon gas through the solution for 1 h. Potassium carbonate (144 mg, 1.04 mmol, 0.05-0.025 equiv.) was charged to an autoclave fitted with an overhead stirred, internal thermometer and a gas burette. The vessel was sealed and pressurized with hydrogen gas (5 bar) and vented. This was repeated twice. The degassed ethanol / substrate solution was added via an injection port and the vessel sealed and pressurized with hydrogen gas (20 bar) and vented. This was repeated twice. The pressure was set to 2 bar and the mixture heated to 50 °C. The vessel was vented and the catalyst (0.011 - 0.021 mmol, 0.0005-0.001 equiv.) in degassed ethanol (5 mL) added via the injection port. The vessel was sealed and pressurized with hydrogen gas to 20 bar and vented. This was repeated twice. The hydrogen pressure was set to 20 bar and the experiment started. The reaction was considered complete after no gas uptake was observed for >2 h. The vessel was cooled to room temperature, vented and the content concentrated to dryness and analyzed by ^{1}H-NMR to confirm full conversion. The uptake curve was converted to conversion by dividing the gas uptake at a time-point by total uptake and multiplied by 100 to get percentage conversion. From the data substrate and product concentrations could be calculated and from those TON and TOF. The TOF was reported at 25 % conversion.

Batch experiment for catalyst reaction order study (Table 4 entries 7-11)
The ketone (1.0 equivalents) and 1-methylnaphthalene (50 μL) was added to a Schlenk flask under argon atmosphere. Ethanol (2.7 mL) was added via syringe and the mixture shaken to ensure homogeneity. The solution was degassed by bubbling argon or nitrogen through the solution >30 min. Catalyst (0.001-0.0003 equivalents) and potassium carbonate (0.05 equivalents) was charged to a microwave vial. The vial was capped and evacuated and refilled with argon gas (three times). The content of the Schlenk flask was transferred via a syringe to the vial. The lid was pierced with two needles and placed in a stainless-steel autoclave under argon atmosphere. The vessel was pressurized with hydrogen gas (50 bar) and vented to the atmosphere. This was repeated twice, then the pressure was set to 50 bar with hydrogen gas and the vessel sealed and placed in a pre-heated oil bath (50 °C) for 2 h. After cooling to room temperature, the vessel was vented, opened and the content analyzed by 1H-NMR. Conversion was calculated on the ratio of substrate to product.

Transfer hydrogenation using PNN catalyst (Figure 3 and Table S3)
To a Schlenk flask was added substrate (1.0 equivalents), internal standard (1-methylnaphthalene, 50 μL) and isopropanol (5-10 mL) and degassed by bubbling using either nitrogen or argon for 30-45 min. Catalyst (0.01-0.002 equivalents) were added followed by potassium *tert*-butoxide (0.05 equivalents as a 1 M solution in *tert*-butanol). The flask was inserted in an oil-bath pre-heated to 50 °C for 1-5 h. Once the reaction was finished the mixture was quenched with 0.1 mL concentrated hydrochloric acid and concentrated to dryness and analyzed by ^{1}H-NMR and chiral HPLC. The product was purified by column chromatography.

Transfer hydrogenation using PNN catalyst – kinetic analysis (Figure 3)
To a Schlenk flask was added substrate (1.0 equivalents), internal standard (1-methylnaphthalene, 50 μL) and isopropanol (5-10 mL) and degassed by bubbling using either nitrogen or argon for 30-45 min. Catalyst (0.01-0.002 equivalents) were added followed by potassium *tert*-butoxide (0.05 equivalents as a 1 M solution in *tert*-butanol). The flask was inserted in an oil-bath pre-heated to 50 °C. Aliquots were taken at regular intervals, quenched with 1 drop concentrated hydrochloric acid and analyzed by ^{1}H-NMR. Once the reaction was finished the mixture was quenched with 0.1 mL concentrated hydrochloric acid and concentrated to dryness and analyzed by ^{1}H-NMR.

General procedure for ester hydrogenation using PNN catalyst and potassium carbonate (Scheme 4)
Substrate (1.0 equivalent) was added to a Schlenk flask together with 1-methylnaphthalene (0.25 equiv.) and ethanol (3.2 mL) and degassed by bubbling argon gas through the solution for at least 30 min. To a microwave vial containing a magnetic bead was added catalyst (0.001-0.01 depending on substrate) and base (0.10 equiv.). The vial was capped and put under an inert atmosphere using vacuum / argon cycles (3). The degassed substrate solution was added to the vial under argon. The vial was pierced by two 18G needles and placed in a stainless-steel autoclave under argon atmosphere. The vessel was sealed and pressurized with hydrogen gas to 50 bar. The pressure was released, and the procedure repeated twice. Finally, the vessel was pressurized with hydrogen gas (50 bar), sealed and placed in a pre-heated oil-bath at the designated reaction temperature (90 °C) for 16 h. The vessel was cooled to ambient temperature and the pressure slowly released. The vial was uncapped, and an aliquot was taken, diluted with deuterated chloroform and analyzed by ^{1}H-NMR to assess the conversion

using 1-methylnaphthalene as internal standard. The crude products were purified by column chromatography (as detailed below).

General procedure for chiral ester hydrogenation using PNN catalyst and potassium carbonate (Scheme 4)
Substrate (1.00 mmol, 1.0 equiv.) was added to a Schlenk flask together with 1-methylnaphthalene (50 μL, 0.35 mmol, 0.35 equiv.) and isopropanol (2.8 mL) and degassed by bubbling argon gas through the solution for at least 30 min. To a microwave vial, containing a magnetic bead, was added catalyst (7.3 mg, 0.01 mmol, 0.01 equiv.) and potassium carbonate (14 mg, 0.10 mmol, 0.10 equiv.). The vial was capped and put under an inert atmosphere using vacuum / argon cycles (3). The degassed substrate solution was added to the vial under argon. The vial was pierced by two 18G needles and placed in a stainless-steel autoclave under argon atmosphere. The vessel was sealed and pressurized with hydrogen gas to 50 bar. The pressure was released, and the procedure repeated twice. Finally, the vessel was pressurized with hydrogen gas (50 bar), sealed and placed in a pre-heated oil-bath at the designated reaction temperature (50 °C to 110 °C) for 16 h. The vessel was cooled to ambient temperature and the pressure slowly released. The vial was uncapped, and an aliquot was taken, diluted with deuterated chloroform and analyzed by ^{1}H-NMR to assess the conversion using 1-methylnaphthalene as internal standard. The crude products were purified by column chromatography and analyzed by chiral HPLC and NMR as detailed below.

Gas uptake experiments – esters (Figure 4 and 5, Table 5)
Ethyl *p*-fluorobenzoate (3.5 g, 20.81 mmol, 1.0 equiv.) was dissolved in ethanol (30 mL) and degassed for 1 h using argon gas bubbling. The catalyst (0.021 mmol, 0.001 equiv.) and potassium carbonate (288 mg, 2.08 mmol, 0.10 equiv.) was charged to an autoclave fitted with an overhead stirred, internal thermometer and a gas burette. The vessel was sealed and pressurized with hydrogen gas (5 bar) and vented. This was repeated twice. The degassed ethanol solution was added via an injection port and stirring started (1300 rpm). The vessel was pressurized to 20 bar using hydrogen gas and then vented. This was repeated twice. The vessel was pressurized to 2 bar of hydrogen gas and heated to an internal temperature of either 70 or 90 °C at which time the pressure was increased to 20 bar and the reaction started. Gas uptake was monitored by reduction of the pressure in the burette. The reaction was assumed complete when no uptake of gas was observed for >2 h. The vessel was cooled to room temperature, vented and the content concentrated to dryness and analyzed by ^{1}H-NMR to confirm full conversion. The uptake curve was converted to conversion by dividing the gas uptake at a time-point by total uptake and multiplied by 100 to get percentage conversion. From the data, substrate and product concentrations could be calculated and from those TON and TOF.

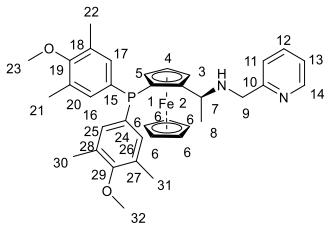
Batch experiments in vials – esters (Table 6)
Ethyl *p*-fluorobenzoate (300 mg, 1.78 mmol, 1.0 equiv.) and 1-methylnaphthalene (25 □L, 0.18 mmol, 0.1 equiv.) was dissolved in ethanol (3 mL) and degassed for 1 h using argon gas bubbling. The catalyst (0.002 mmol, 0.001 equiv.) and potassium carbonate (24.7 mg, 0.18 mmol, 0.10 equiv.) was charged to a microwave vial containing a stir-bead. The vial was capped and evacuated and refilled with argon. This was repeated twice. The vial cap was pierced with two 18G needles and placed in a stainless-steel autoclave under an argon atmosphere. The vessel was sealed and pressurized with hydrogen gas (50 bar) and vented. This was repeated twice. The vessel was pressurized again to 50 bar using hydrogen gas, sealed and placed in a pre-heated oil bath at the desired temperature for the desired time. The vessel was cooled to room temperature and vented. The vial was uncapped, and the content analyzed by ^{1}H-NMR. The conversion was determined using 1-methylnaphthalene as the internal standard.

Large scale hydrogenation of Sclareolide (reproduced from reference 3)
Degassed (by argon sparging) ethanol (40 mL) was added to an open stainless-steel autoclave fitted with a glass insert and a cross-shaped stir bar, followed by manganese catalyst (14 mg, 0.02 mmol, 0.001 equiv.), potassium carbonate (276 mg, 2.00 mmol, 0.10 equiv.) and finally (R)-Sclareolide (5.0 g, 20.0 mmol, 1.0 equiv.). The material was washed in with degassed ethanol (10 mL). The vessel was sealed and pressurized with hydrogen gas (50 bar) and vented to the atmosphere. This was repeated 4 times. The vessel as pressurized to 50 bar with hydrogen gas and placed in an oil-bath pre-heated to 90 °C for 16 h, then cooled to ambient temperature and the pressure carefully vented to the atmosphere. The yellow solution was transferred to a round-bottom flask and concentrated to about 20 mL volume *in vacuo* and left to cool to ambient temperature under gentle stirring and filtered to remove residual inorganic material and washed with ethanol (5 mL). Water (75 mL) was added which resulted in the formation of a white slurry which was aged for 1 h, then filtered and washed with water (30 mL) and hexanes (50 mL) to give sclareodiol as a white solid (3.8 g, 14.9 mmol, 75 % isolated yield).

3. Synthesis and characterization data

Synthesis of ligands and their manganese complexes

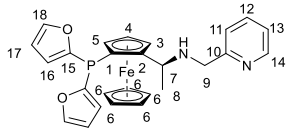
(*R*$_c$, *S*$_p$)-*N*-2-picolinyl-1-(2-bis[4-methoxy-3, 5-dimethylphenyl]phosphine)-ferrocenylethylamine, **(*R*$_c$, *S*$_p$)-4**



(*R*$_c$, *S*$_p$)-*N, N*-dimethyl-1-(2-bis(4-methoxy-3, 5-dimethylphenyl)phosphine)ferrocenylethylamine (1.0 g, 1.79 mmol, 1.0 equiv.) was dissolved in degassed acetic anhydride (10 mL) at room temperature and stirred for 16 h. Volatiles were removed in vacuo and the crude residue dissolved in toluene and evaporated to dryness. This was repeated twice. The crude acetate was dissolved in degassed methanol (10 mL) and reacted with 2-aminomethylpyridine (0.37 mL, 3.59 mmol, 2.0 equiv.) at reflux for 2 h. The crude material was added degassed dichloromethane (10 mL) and degassed saturated aqueous sodium bicarbonate (10 mL). The organic layer was cannulated to a Schlenk flask containing magnesium sulfate. The aqueous layer was extracted with dichloromethane (10 mL) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. The crude product was purified by column chromatography using dichloromethane / methanol (9/1) the target compound as a yellow foam (0.84 g, 1.35 mmol, 76 %).

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.38 (1H, br d, J = 4.8 Hz, $C_{Ar}H^{14}$), 7.40 (1H, t, J = 7.8 Hz, $C_{Ar}H^{12}$), 7.22 (1H, s, $C_{Ar}H^{17}$), 7.21 (1H, s, $C_{Ar}H^{25}$), 7.02 (1H, t, J = 6.7 Hz, $C_{Ar}H^{13}$), 6.92 (1H, s, $C_{Ar}H^{20}$), 6.90 (1H, s, $C_{Ar}H^{26}$), 6.59 (1H, d, J = 7.8 Hz, $C_{Ar}H^{11}$), 4.54 (1H, m, Fc-H^5), 4.32 (1H, m, Fc-H^3), 4.23 (1H, m, -CH^7-), 4.06 (5H, s, Fc-H^6), 3.83 (1H, s, Fc-H^4), 3.77 (3H, m, -$OCH^{23}{}_3$), 3.62 (2H, br s, Py$CH^9{}_2$N-), 3.57 (3H, s, -$OCH^{32}{}_3$), 2.31 (6H, s, -$CH^{22,30}{}_3$), 2.09 (6H, s, -$CH^{21,31}{}_3$), 1.58 (3H, br s, $CHCH^8{}_3$, overlapped with water peak); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ: 160.09 ($C^{19}{}_{Ar}$), 157.83 ($C^{29}{}_{Ar}$), 157.39 ($C^{10}{}_{Ar}$), 148.69 ($C^{14}{}_{Ar}$), 135.96 ($C^{18}{}_{Ar}$),135.40 ($C^{28}{}_{Ar}$), 135.19 ($C^{11}{}_{Ar}$), 134.34 (d, J_{PC} = 8.7 Hz, $C^{15}{}_{Ar}$), 133.34 ($C^{26}{}_{Ar}$), 133.14 ($C^{20}{}_{Ar}$), 131.66 (d, J_{PC} = 8.7 Hz, $C^{24}{}_{Ar}$), 130.81 (d, J_{PC} = 7.2 Hz, $C^{17}{}_{Ar}$), 130.48 (d, J_{PC} = 8.9 Hz, $C^{25}{}_{Ar}$), 121.31 ($C^{12}{}_{Ar}$), 121.08 ($C^{13}{}_{Ar}$), 97.11 (d, J_{PC} = 24.3 Hz, $C^1{}_{Fc}$), 76.13 (d, J_{PC} = 6.9 Hz, $C^2{}_{Fc}$), 71.27 (d, J_{PC} = 4.6 Hz, $C^5{}_{Fc}$), 69.62 ($C^6{}_{Fc}$), 69.38 (d, J_{PC} = 4.6 Hz, $C^3{}_{Fc}$), 68.75 ($C^4{}_{Fc}$), 59.74 (-O$\underline{C}^{23}H_3$), 59.52 (-O$\underline{C}^{32}H_3$), 51.84 (Py$\underline{C}^9H_2$-), 51.10 (d, J_{PC} = 10.7 Hz, Fc-$\underline{C}^7$H(CH_3)-N), 19.30 (Fc-CH($\underline{C}^8H_3$)-N), 16.23 (-$\underline{C}^{22,30}H_3$), 16.08 (-$\underline{C}^{21,31}H_3$); ^{31}P{^{1}H}-NMR (201 MHz, $CDCl_3$) δ: -27.3 ppm; IR (ATR): 2931.8 (w), 1587.4 (w), 1471.7 (m), 1273.0 (m), 1215.2 (s), 1109.1 (s), 1010.7 (m), 754.2 (m), 607.6 (m) cm^{-1}; HRMS: (ES+) calculated for $[C_{36}H_{42}FeN_2O_2P]^+$ 621.2328; found 621.2316; M.P.: 48-50 °C; $[\alpha]_D^{20}$: - 224.8 (c 1.0, chloroform); Elemental analysis: expected for $C_{36}H_{41}FeN_2O_2P$: C, 69.68 %; H, 6.66 %; N, 4.51 %, found C, 69.86 %, H, 6.84 %; N, 4.46 %;

(*R*$_c$, *S*$_p$)-*N*-2-picolinyl-1-(2-di[furan-2-yl]phosphino)ferrocenylethylamine, **(*R*$_c$, *S*$_p$)-5**

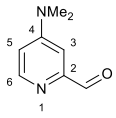


(*R*$_c$, *S*$_p$)-*N, N*-dimethyl-1-(2-di(furan-2-yl)phosphino)ferrocenylethylamine (0.8 g, 1.90 mmol, 1.0 equiv.) was dissolved in degassed acetic anhydride (10 mL) at room temperature and stirred for 16 h. Volatiles were removed in vacuo and the crude residue dissolved in toluene and evaporated to dryness. This was repeated twice. The crude acetate was dissolved in degassed methanol (10 mL) and reacted with 2-aminomethylpyridine (0.55 mL, 5.32 mmol, 2.8 equiv.) at reflux for 2 h. The crude material was added degassed dichloromethane (10 mL) and degassed saturated aqueous sodium bicarbonate (10 mL). The organic layer was cannulated to a Schlenk flask containing magnesium sulfate. The aqueous layer was extracted with dichloromethane (10 mL) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. The crude product was purified by column chromatography using degassed DCM / MeOH gradient (1/0 – 95/5) the title compound as an orange solid (560 mg, 1.16 mmol, 61 %).

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.09 (1H, d, J = 6.6 Hz, $C_{Ar}H^{14}$), 7.74 (1H, br s, $C_{Ar}H^{19}$), 7.46 (1H, s, $C_{Ar}H^{19}$), 6.88 (1H, t, J = 2.8 Hz, $C_{Ar}H^{18}$), 6.52 (1H, d, J = 3.4 Hz, $C_{Ar}H^{18}$), 6.49 (1H, m, $C_{Ar}H^{17}$), 6.34 (2H, m, $C_{Ar}H^{11,13}$), 6.21 (1H, m, $C_{Ar}H^{17}$), 4.47 (2H, m, Fc-$H^{3,5}$), 4.34 (1H, t, J = 2.8 Hz, Fc-H^4), 4.17 (1H, m,-$C\underline{H}^7$-), 4.01 (5H, s, Fc-H^6), 3.60 (2H, br s, Py$C\underline{H}_2{}^9$N-), 2.97 (6H, br s, N($C\underline{H}_3{}^{15}$)$_2$), 1.57 (3H, d, J = 6.6 Hz, $CHC\underline{H}_3{}^8$); ^{13}C{^{1}H}-NMR (125 MHz,$CDCl_3$) δ: 159.40 ($C^{12}{}_{Ar}$), 154.94 ($C^{10}{}_{Ar}$), 152.99 (d, J_{PC} = 4.1 Hz, $C^{16}{}_{Ar}$), 151.67 (d, J_{PC} = 10.7 Hz, $C^{16}{}_{Ar}$), 148.40 ($C^{14}{}_{Ar}$), 146.76, ($C^{19}{}_{Ar}$), 146.40 ($C^{19}{}_{Ar}$), 121.06 (d, J_{PC} = 25.0 Hz, $C^{18}{}_{Ar}$), 118.85 (d, J_{PC} = 18.8 Hz, $C^{18}{}_{Ar}$), 110.73 (d, J_{PC} = 7.5 Hz, $C^{18}{}_{Ar}$), 110.45 (d, J_{PC} = 5.0 Hz, $C^{17}{}_{Ar}$), 104.90 ($C^{11}{}_{Ar}$), 104.56 ($C^{13}{}_{Ar}$), 98.03 (d, J_{PC} = 28.6 Hz, $C^1{}_{Fc}$), 72.58 (d, J_{PC} = 3.5 Hz, $C^2{}_{Fc}$), 71.60 (d, J_{PC} = 3.5 Hz, $C^3{}_{Fc}$), 69.62 ($C^6{}_{Fc}$), 68.88 (d, J_{PC} = 5.4 Hz, $C^{4,5}{}_{Fc}$), 52.19 (Py-$\underline{C}^9H_2$-N), 51.00 (d, J_{PC} = 8.31 Hz, Fc-$\underline{C}^7$H(CH_3)-N), 39.23 (N($\underline{C}^{15}H_3$)$_2$) 19.85 (Fc-CH($\underline{C}^8H_3$)-N); ^{31}P-{^{1}H}-NMR (201 MHz, $CDCl_3$) δ: -70.6 (s) ppm; IR (ATR): 2968.5 (w), 2927.9 (w), 2900.9 (w), 2358.9 (w), 2181.5 (w), 1597.0 (s), 1541.1 (m), 1506.4 (m), 1448.5 (m), 1437.0 (m),

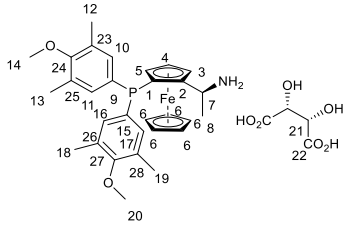
1367.5 (m), 1105.2 (m), 1001.1 (s), 900.8 (m), 808.2 (s), 727.2 (s) cm^{-1}; HRMS: (ES+) calculated for $[C_{28}H_{31}FeN_3O_2P]^+$ 528.1498; found 528.1492; $[\alpha]_D^{20}$: -348.3 (c 0.9, chloroform);

4-(dimethylamino)pyridine-2-carboxaldehyde



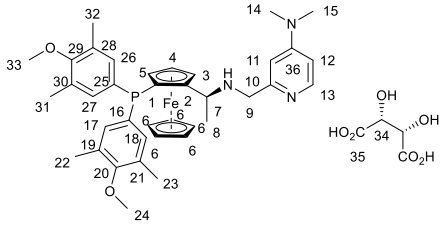
2-dimethylaminoethanol (1.7 mL, 17.0 mmol, 2.1 equiv.) was dissolved in ^{n}hexane(20 mL) and cooled to -10 oC under an inert atmosphere. ^{n}Butyl lithium (1.6 M, 20 mL, 32 mmol, 3.9 equiv.) was slowly added to the cold solution. The formed clear colorless solution was stirred at -10 oC for 30 min then 4-dimethylaminopyridine (1.0 g, 8.2 mmol, 1.0 equiv.) was added as a solid. The yellow slurry was stirred at -10 ^{o}C for 2 h then cooled to -78 ^{o}C and dimethylformamide (1 mL, 12.9 mmol, 1.6 equiv.) in THF (15 mL) was added. 1N aqueous hydrochloric acid (50 mL) was added after 1 h and the mixture allowed to warm to room temperature and the layers separated. The aqueous layer was found to have a pH of 1 and was extracted with diethyl ether (3 x 50 mL). The organic extractions were discarded. The pH was adjusted to 7 using solid sodium bicarbonate and the mixture again extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated to dryness to give the title compound as a pale brown oil (0.65 g, 4.3 mmol, 53 %).
^{1}H-NMR (500 MHz, $CDCl_3$) δ: 10.01 (1H, s, -C<u>H</u>O), 8.40 (1H, d, J = 6.0 Hz, $C_{Ar}H^5$), 7.20 (1H, d, J = 2.8 Hz, $C_{Ar}H^3$), 6.68 (1H, dd, J = 6.0 / 2.8 Hz, $C_{Ar}H^6$), 3.09 (6H, s, -N(C<u>H</u>$_3$)$_2$; ^{13}C-{^{1}H}-NMR (125 MHz, $CDCl_3$) δ: 194.59 (-<u>C</u>HO), 154.70 (C^2_{Ar}), 152.95 (C^4_{Ar}), 150.05 (C^3_{Ar}), 109.87 (C^5_{Ar}), 104.37 (C^6_{Ar}), 39.24 (-N(<u>C</u>H$_3$)$_2$); HMRS: (ES+) calc. $[C_8H_{11}N_2O]^+$: 151.0866; found: 151.0865; IR (ATR): 2814 (w), 1705.1 (s), 1597.1 (s), 1535.3 (m), 1508.3 (s), 1379.1 (m), 1222.9 (m), 1001.1 (m), 976.0 (m), 893.0 (m), 731.0 (s) cm^{-1};

(*R$_c$, S$_p$*)-1-(2-bis[4-methoxy-3, 5-dimethylphenyl]phosphino)ferrocenylethylamine L-tartrate salt



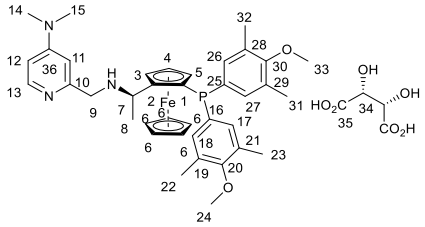
(*R$_c$, S$_p$*)-*N, N*-dimethyl-1-(2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine (6.3 g, 11.3 mmol) was dissolved in degassed acetic anhydride (60 mL) at room temperature and stirred for 16 h. Volatiles were removed *in vacuo* and the crude residue dissolved in toluene and evaporated to dryness. This was repeated twice. The crude acetate was dissolved in degassed methanol (60 mL) and THF (60 mL) and 30 wt% aqueous ammonium hydroxide (60 mL) added. The mixture was stirred at 60 ^{o}C for 2-4 h then cooled to room temperature and volatiles removed *in vacuo*. The crude material was added degassed dichloromethane (50 mL) and degassed saturated 20 wt% aqueous potassium carbonate (50 mL). The organic layer was cannulated to a Schlenk flask containing magnesium sulfate. The aqueous layer was extracted with dichloromethane (50 mL/g) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. After isolation of the crude material was dissolved in degassed ethanol (60 mL) and *L*-tartaric acid (1.44g, 9.6 mmol, 0.85 equiv.) added. The mixture was heated to reflux under an argon atmosphere and distilled to half-volume, cooled to room temperature and the product salt precipitated by the addition of diethyl ether (200 mL). Isolation by filtration and washing with diethyl ether gave the title compound as a yellow solid (6.0 g, 8.8 mmol, 78% yield).
^{1}H-NMR (500 MHz, MeOD) δ: 7.29 (1H, s, $C_{Ar}H^{10}$), 7.27 (1H, s, $C_{Ar}H^{16}$), 6.87 (1H, s, $C_{Ar}H^{11}$), 6.86 (1H, s, $C_{Ar}H^{17}$), 4.97 (7H, br s, H_2O, -OH, -NH_2, CO_2H), 4.69 (1H, s, Fc-H^5), 4.56 (2H, br s, -C<u>H</u>^{7}- and Fc-H^4), 4.43 (2H, m, $HO_2C(C\underline{H}^{21}OH)_2CO_2H$), 4.12 (1H, m, Fc-H^3), 4.05 (5H, s, Fc-H^6), 3.77 (3H, s, -OCH_3^{14}), 3.71 (3H, s, -OCH_3^{20}), 3.64 (ethanol) 2.32 (6H, s, -C<u>H</u>$_3^{12,18}$), 2.20 (6H, s, -C<u>H</u>$_3^{13,19}$), 1.79 (3H, br d, J = 8.1 Hz, CHC<u>H</u>$_3^8$), 1.24 (ethanol); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ: 158.33 (s, C^{24}_{Ar}), 157.40 (s, C^{27}_{Ar}), 135.41 (s, C^{25}_{Ar}), 135.23 (s, C^{28}_{Ar}), 134.06 (d, J_{PC} = 5.9 Hz, C^9_{Ar}), 132.68 (s, C^{23}_{Ar}), 132.53 (s, C^{26}_{Ar}), 131.46 (d, J_{PC} = 5.8 Hz, C^{15}_{Ar}), 131.02 (d, J_{PC} = 7.3 Hz, C^{11}_{Ar}), 130.07 (d, J_{PC} = 9.7 Hz, C^{17}_{Ar}), 91.02 (d, J_{PC} = 26.8 Hz, Fc-C^1-P), 76.3 (d, J_{PC} = 11.3 Hz, C^2_{Fc}), 72.80 (C^5_{Fc}), 72.37 ($HO_2C(\underline{C}^{21}HOH)_2CO2H$), 70.05 ($C^4_{Fc}$), 69.77 ($C^3_{Fc}$), 69.19 ($C^6_{Fc}$), 58.83 (-$OC^{14}H_3$), 58.72 (-$OC^{20}H_3$), 56.80 (ethanol), 46.30 (d, J_{PC} = 9.7 Hz, Fc-<u>C</u>^{7}H(CH_3)-N), 19.15 (Fc-CH(<u>C</u>^{9}H$_3$)-N), 17.06 (ethanol), 14.88 (Ar-<u>C</u>^{12,13,18,19}H$_3$); ^{31}P{^{1}H}-NMR (201 MHz, $CDCl_3$) δ: -28.7 (s) ppm; IR (ATR): 2927.9 (m), 2358.9 (w), 2160.3 (m), 2019.5 (w), 1473.6 (m), 1273.0 (m), 1217.1 (s), 1109.1 (s), 1072.4 (s), 1010.7 (s), 817.8 (m), 678.9 (m), 607.6 (m) cm^{-1}; HRMS: (ES+) calculated for $[C_{30}H_{37}FeNO_2P]^+$ 530.1906; found 530.1890; M.P.: 185-186 ^{o}C (decomposition); $[\alpha]_D^{20}$: -246.5 (c 0.6, methanol);

(*R*$_c$, *S*$_p$) – *N* - [4-(dimethylamino)pyridine-2-methyl]-1-(2-bis[4-methoxy- 3, 5-dimethylphenyl]phosphino)ferrocenylethylamine L-tartrate salt, **(*R*$_c$, *S*$_p$)-6**



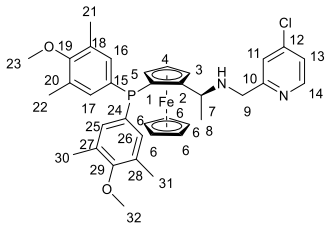
(*R*$_c$, *S*$_p$)-1-(2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine (2.1 g, 4.0 mmol, 1.0 equiv.) was treated with 4-(dimethylamino)pyridine-2-carboxaldehyde (0.60 g, 4.0 mmol, 1.0 equiv.) and sodium borohydride (303 mg, 8.0 mmol, 2.0 equiv.) in methanol (20 mL) to give the title compound as a free base as an orange foam (2.6 g, 3.92 mmol, 98 %) as described above. The material was found to be pure enough for downstream chemistry. 200 mg (0.30 mmol, 1.0 equiv.) was treated with 45 mg (0.30 mmol, 1.0 equiv) of *L*-tartaric acid in isopropanol (5 mL) as per the previous prescription to give the title compound as a yellow solid (147 mg, 0.18 mmol, 60 %).
^{1}H-NMR (500 MHz, MeOD) δ: 7.81 (1H, br s, Py-H^{13}), 7.25 (1H, s, C$_{Ar}$H^{17}), 7.23 (1H, s, C$_{Ar}$H^{26}), 6.91 (1H, s, C$_{Ar}$H^{18}), 6.90 (1H, s, C$_{Ar}$H^{27}), 6.77 (1H, br s, Py-H^{11}), 6.36 (1H, br s, Py-H^{12}), 4.94 (12H, br s, H$_2$O, -OH, -NH$_2$, CO$_2$H), 4.64 (1H, s, Fc-H^5), 4.48 (3H, br s, HO$_2$C(C<u>H</u>^{34}OH)$_2$CO$_2$H and Fc-H^3), 4.43 (1H, br s,-C<u>H</u>^{7}(CH$_3$)-), 4.04 (5H, s, Fc-H^6), 4.02 (1H, s, Fc-H^4), 3.76 (3H, -OCH$^{33}_3$), 3.61 (3H, s, -OCH$^{24}_3$), 3.53 (2H, m, -CH$^9_2$Py), 3.13 (6H, s, -N(C<u>H</u>$^{14,15}_3$)$_2$), 2.30 (6H, s, -CH$^{23,32}_3$), 2.09 (6H, s, -CH$^{23,31}_3$), 1.79 (3H, br d, J = 7.5 Hz, CHC<u>H</u>$^8_3$); ^{13}C{^{1}H}-NMR (125 MHz, MeOD) δ: 158.09 (s, C^{30}$_{Ar}$), 157.24 (s, C^{20}$_{Ar}$), 151.59 (s, C^{36}$_{Ar}$), 139.09 (s, C^{13}$_{Ar}$), 135.25 (s, C^{26}$_{Ar}$), 135.08 (s, C^{18}$_{Ar}$), 134.75 (d, J$_{PC}$ = 8.6 Hz, C^{25}$_{Ar}$), 133.0 (s, C^{28}$_{Ar}$), 132.84 (s, C^{21}$_{Ar}$), 131.30 (d, J$_{PC}$ = 6.6 Hz, C^{27}$_{Ar}$), 130.81 (d, J$_{PC}$ = 6.6 Hz, C^{17}$_{Ar}$), 130.49 (d, J$_{PC}$ = 8.6 Hz, C^{16}$_{Ar}$), 105.83 (C^{12}$_{Ar}$), 103.75 (s, C^{11}$_{Ar}$), 94.64 (d, J$_{PC}$ = 26.4 Hz, C^1$_{Fc}$), 76.06 (d, J$_{PC}$ = 8.2 Hz, C^2$_{Fc}$), 72.72 (HO$_2$C(<u>C</u>^{34}HOH)$_2$CO$_2$H), 71.57 (C^5$_{Fc}$), 69.53 (C^3$_{Fc}$), 69.24 (C^6$_{Fc}$), 69.19 (C^4$_{Fc}$), 58.83 (-OC^{33}H$_3$), 57.83 (-OC^{24}H$_3$), 51.74 (d, J$_{PC}$ = 10.4 Hz, Fc-<u>C</u>^{7}H(CH$_3$)-N), 45.79 (s, -<u>C</u>^{9}H$_2$Py), 38.67 (s, -N(<u>C</u>^{14,15}H$_3$)$_2$), 17.70 (Fc-CH(<u>C</u>^{8}H$_3$)-N), 14.78 (Ar-<u>C</u>^{22,23,31,32}H$_3$); ^{31}P-{^{1}H}-NMR (201 MHz, MeOD) δ: -28.4 (s) ppm; IR (ATR): 2933.7 (w), 2158.4 (w), 2034.9 (w), 1722.4 (w), 1641.4 (s), 1556.6 (m), 1217.1 (s), 1111.0 (s), 1070.5 (m), 1004.9 (m), 817.8 (m), 607.6 (m) cm^{-1}; HRMS: (ES+) calculated for [C$_{38}$H$_{47}$FeN$_3$O$_2$P]$^+$ 664.2750; found 664.2733; M.P.: 98-100 ^{o}C; [α]$_D^{20}$: - 160.6 (c 1.0, methanol);

(*S*$_c$, *R*$_p$) – *N* -[4-(dimethylamino)pyridine-2-methyl]-1-(2-bis[4-methoxy- 3, 5-dimethylphenyl]phosphino)ferrocenylethylamine L-tartrate salt, **(*S*$_c$, *R*$_p$)-6**



Prepared the same way as above. The NMR data was found to be identical.
[α]$_D^{20}$: + 190.6 (c 1.0, methanol);

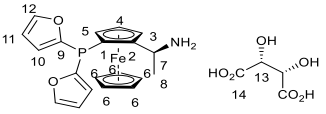
(*R*$_c$, *S*$_p$) -*N*- [4-chloropyridine-2-methyl)-1-(2-bis[4-methoxy- 3, 5- dimethylphenyl)phosphino]-ferrocenylethylamine, **(*R*$_c$, *S*$_p$)-7**



(*R*$_c$, *S*$_p$)-1-(2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine (230 mg, 0.43 mmol, 1.0 equiv.) was reacted with 4-chloropyridine-2-carboxaldehyde (70 mg, 0.50 mmol, 1.15 equiv.) at room temperature for 16 h after which sodium borohydride (33 mg, 0.86 mmol, 2.0 equiv.) was added. The mixture was stirred at room temperature for 4 h then concentrated to dryness. The crude material was added degassed dichloromethane (10 mL) and degassed saturated aqueous

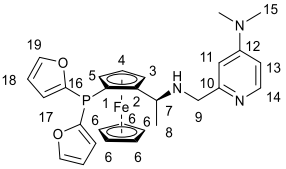
sodium bicarbonate (10 mL). The organic layer was cannulated to a Schlenk flask containing magnesium sulfate. The aqueous layer was extracted with dichloromethane (10 mL) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. The title product was purified by column chromatography (triethylamine treated silica, hexane / ethyl acetate 4/1 to 1/1) and isolated as an orange foam (120 mg, 0.185 mmol, 43 %).
^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.28 (1H, d, J = 5.6 Hz, $C_{Ar}H^{14}$), 7.20 (1H, s, $C_{Ar}H^{16}$), 7.18 (1H, s, $C_{Ar}H^{25}$), 7.05 (1H, dd, J = 7.5 / 1.9 Hz, $C_{Ar}H^{13}$), 6.91 (1H, s, $C_{Ar}H^{17}$), 6.90 (1H, s, $C_{Ar}H^{26}$), 6.86 (1H, d, J = 1.9 Hz, $C_{Ar}H^{11}$), 4.51 (1H, s, Fc-H^5), 4.32 (1H, s, Fc-H^3), 4.23 (1H, m,-C<u>H</u>^{7}(CH_3)-), 4.06 (5H, s, Fc-H^6), 3.82 (1H, s, Fc-H^4), 3.76 (3H, -OCH_3^{23}), 3.59-3.51 (5H, m, -CH_2^9Py and -OCH_3^{32}), 2.31 (6H, s, -$CH_3^{21,30}$), 2.09 (6H, s, -$CH_3^{22,31}$), 1.53 (3H, d, J = 6.2 Hz, CHC<u>H</u>$_3^8$), 1.31 (alkane), 0.72 (alkane);
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ: 162.3 (s, C^{12}_{Ar}), 157.82 (s, C^{19}_{Ar}), 157.48 (s, C^{29}_{Ar}), 149.50 (s, C^{14}_{Ar}), 144.20 (s, C^{10}_{Ar}), 135.30 (s, C^{18}_{Ar}), 135.13(s, C^{27}_{Ar}), 134.07 (d, J_{PC} = 8.2 Hz, C^{15}_{Ar}), 133.27 (s, C^{20}_{Ar}), 133.11 (s, C^{28}_{Ar}), 131.57 (d, J_{PC} = 8.2 Hz, C^{24}_{Ar}), 130.86 (d, J_{PC} = 8.2 Hz, $C^{16,25}_{Ar}$), 130.52 (d, J_{PC} = 8.2 Hz, $C^{17,26}_{Ar}$), 121.75 (C^{13}_{Ar}), 120.16 (C^{11}_{Ar}), 96.72 (d, J_{PC} = 24.0 Hz, C^{1}_{Fc}), 76.33 (d, J_{PC} = 7.7 Hz, C^{2}_{Fc}), 71.33 (d, J_{PC} = 4.3 Hz, C^{5}_{Fc}), 69.65 (s, C^{6}_{Fc}), 69.31 (d, J_{PC} = 3.8 Hz, C^{3}_{Fc}), 68.76 (C^{4}_{Fc}), 59.75 (s, -O<u>C</u>^{23}H_3), 59.44 (s, -O<u>C</u>^{32}H_3), 50.97(s, -<u>C</u>^{9}H_2Py), 50.88 (d, J_{PC} =10.1 Hz, Fc-<u>C</u>^{7}H(CH_3)-N), 19.13 (Fc-CH(<u>C</u>^{8}H_3)-N), 16.25 (Ar-<u>C</u>^{21,30}H_3), 16.10 (Ar-<u>C</u>^{22,31}H_3); ^{31}P-{^{1}H}-NMR (201 MHz, $CDCl_3$) δ: -27.4 (s) ppm; IR (ATR): 2935.6 (w), 2922.2 (w), 2362.8 (w), 1573.9 (m), 1473.6 (m), 1273.0 (m), 1215.2 (s), 1109.1 (s), 1010.7 (s), 817.8 (s), 700.2 (s) cm^{-1}; HRMS: (ES+) calculated for $[C_{36}H_{40}FeN_2NaO_2P]^+$ 677.1758; found 677.1753; M.P.: 70-71 °C; $[\alpha]_D^{20}$: - 140.5 (c 0.7, chloroform);

(*R_c, S_p*)-1-(2-di[2-furanyl]phosphino)ferrocenylethylamine L-tartrate



(*R_c, S_p*)-*N*, *N*-dimethyl-1-(2-di(furan-2yl)phosphino)ferrocenylethylamine (1.0 g, 2.37 mmol, 1.0 equiv.) was dissolved in degassed acetic anhydride (10 mL) at room temperature and stirred for 16 h. Volatiles were removed *in vacuo* and the crude residue dissolved in toluene and evaporated to dryness. This was repeated twice. The crude acetate was dissolved in degassed methanol (10 mL) and THF (10 mL) and 30 wt% aqueous ammonium hydroxide (10 mL) added. The mixture was stirred at 60 °C for 2-4 h then cooled to room temperature and volatiles removed *in vacuo*. The crude material was added degassed dichloromethane (20 mL) and degassed saturated 20 wt% aqueous potassium carbonate (10 mL). The organic layer was cannulated to a Schlenk flask containing magnesium sulfate. The aqueous layer was extracted with dichloromethane (10 mL/g) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. The crude material was dissolved in 15 mL ethanol and treated with *L*-tartaric acid (290 mg, 1.93 mmol, 0.84 equiv.) at reflux. After cooling to room temperature, the mixture was diluted with diethyl ether (40 mL) and filtered. The solid was washed with diethyl ether (2x25 mL) and ^{n}hexane (2x10 mL) to give the title compound as a yellow solid (0.9 g, 1.66 mmol, 70 % yield).
^{1}H-NMR (500 MHz, MeOD) δ: 7.91 (1H, br s, $C_{Ar}H^{12}$), 7.73 (1H, s, $C_{Ar}H^{12}$), 7.01 (1H, s, $C_{Ar}H^{10}$), 6.64 (1H, s, $C_{Ar}H^{10}$), 6.59 (1H, s, $C_{Ar}H^{11}$), 6.44 (1H, s, $C_{Ar}H^{11}$), 4.70 (1H, m, Fc-H^5), 4.67 (1H, s, Fc-H^3), 4.63 (1H, s, C<u>H</u>^{7}(CH_3)), 4.56 (1H, s, Fc-H^4), 4.09 (5H, s, Fc-H^6), 1.80 (3H, br s, -CH(C<u>H</u>$_3^8$)); ^{13}C{^{1}H}-NMR (125 MHz, MeOD) δ: 151.73 (s, <u>C</u>O_2H), 150.38 (d, J_{PC} = 9.8 Hz, C^9_{Ar}), 147.38 (s, C^{12}_{Ar}), 146.91 (s, C^{12}_{Ar}), 121.64 (C^{10}_{Ar}), 118.79 (C^{10}_{Ar}), 110.58 (d, J_{PC} = 8.8 Hz, C^{11}_{Ar}), 110.47 (d, J_{PC} = 4.7 Hz, C^{11}_{Ar}), 90.66 (d, J_{PC} = 26.13 Hz, C^{1}_{Fc}), 74.50 (d, J_{PC} = 3.7 Hz, C^{2}_{Fc}), 72.94 (HO_2C(<u>C</u>^{13}H(OH))$_2$$CO_2$H), 72.51 ($C^{3}_{Fc}$), 70.76 ($C^{4}_{Fc}$), 69.96 ($C^{6}_{Fc}$), 68.67 (d, J_{PC} = 4.3 Hz, C^{5}_{Fc}), 45.74 (d, J_{PC} = 9.9 Hz, Fc-<u>C</u>^{7}H(CH_3)-N), 19.01 (Fc-CH(<u>C</u>^{8}H_3)-N);
^{31}P-{^{1}H}-NMR (201 MHz, MeOD) δ: -71.96 (s) ppm; IR (ATR): 3080.3 (w), 2987.4 (w), 2357.1 (w), 1668.4 (m), 1070.5 (m), 1004.9 (m), 825.5 (m), 750.3 (s) cm^{-1}; HRMS: (ES+) calculated for $[C_{20}H_{21}FeNO_2P]^+$ 394.0654; found 377.0384 (fits $[C_{20}H_{18}FeO_2P]^+$:377.0388); M.P.: 182-185 °C (decomposition); $[\alpha]_D^{20}$: +37.4 (c 0.9, methanol);

(*R_c, S_p*)-*N*-[4-(dimethylamino)pyridine-2-methyl)-1-(2-di[2-furanyl]phosphino)ferrocenylethylamine, **(*R_c, S_p*)-8**



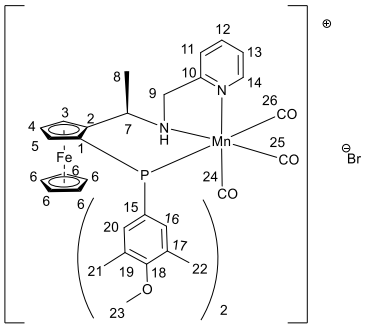
(*R_c, S_p*)-1-(2-di(2-furanyl)phosphino)ferrocenylethylamine (0.56g, 1.42 mmol, 1.0 equiv.) was reacted with 4-dimethylaminopyridine-2-carboxaldehyde (210 mg, 1.42 mmol, 1.0 equiv.) in methanol (10 mL) at room temperature for 16 h after which sodium borohydride (110 mg, 2.84 mmol, 2.0 equiv) was added. The mixture was stirred at room temperature for 4 h then concentrated to dryness. The crude material was added degassed dichloromethane (10 mL) and degassed saturated aqueous sodium bicarbonate (10 mL). The organic layer was cannulated to a Schlenk flask containing magnesium

sulfate. The aqueous layer was extracted with dichloromethane (10 mL) two times, each layer cannulated to the same Schlenk flask above. The combined dried organic layer was filtered using a cannula fitted with a filter paper to a round bottom flask and evaporated to dryness. The title product was purified by column chromatography (triethylamine treated silica, hexane / ethyl acetate 1/2) as a yellow oil (560 mg, 1.07 mmol, 75 %).

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.09 (1H, d, J = 6.6 Hz, $C_{Ar}H^{14}$), 7.74 (1H, br s, $C_{Ar}H^{19}$), 7.46 (1H, s, $C_{Ar}H^{19}$), 6.88 (1H, t, J = 2.8 Hz, $C_{Ar}H^{18}$), 6.52 (1H, d, J = 3.4 Hz, $C_{Ar}H^{18}$), 6.49 (1H, m, $C_{Ar}H^{17}$), 6.34 (2H, m, $C_{Ar}H^{11,13}$), 6.21 (1H, m, $C_{Ar}H^{17}$), 4.47 (2H, m, Fc-$H^{3,5}$), 4.34 (1H, t, J = 2.8 Hz, Fc-H^{4}), 4.17 (1H, m,-C$\underline{H}^{7}$-), 4.01 (5H, s, Fc-H^{6}), 3.60 (2H, br s, PyC$\underline{H}_2{}^{9}$N-), 2.97 (6H, br s, N($C\underline{H}_3{}^{15}$)$_2$), 1.57 (3H, d, J = 6.6 Hz, CHC$\underline{H}_3{}^{8}$); ^{13}C{^{1}H}-NMR (125 MHz,$CDCl_3$) δ: 159.40 ($C^{12}{}_{Ar}$), 154.94 ($C^{10}{}_{Ar}$), 152.99 (d, J_{PC} = 4.1 Hz, $C^{16}{}_{Ar}$), 151.67 (d, J_{PC} = 10.7 Hz, $C^{16}{}_{Ar}$), 148.40 ($C^{14}{}_{Ar}$), 146.76, ($C^{19}{}_{Ar}$), 146.40 ($C^{19}{}_{Ar}$), 121.06 (d, J_{PC} = 25.0 Hz, $C^{18}{}_{Ar}$), 118.85 (d, J_{PC} = 18.8 Hz, $C^{18}{}_{Ar}$), 110.73 (d, J_{PC} = 7.5 Hz, $C^{18}{}_{Ar}$), 110.45 (d, J_{PC} = 5.0 Hz, $C^{17}{}_{Ar}$), 104.90 ($C^{11}{}_{Ar}$), 104.56 ($C^{13}{}_{Ar}$), 98.03 (d, J_{PC} = 28.6 Hz, $C^{1}{}_{Fc}$), 72.58 (d, J_{PC} = 3.5 Hz, $C^{2}{}_{Fc}$), 71.60 (d, J_{PC} = 3.5 Hz, $C^{3}{}_{Fc}$), 69.62 ($C^{6}{}_{Fc}$), 68.88 (d, J_{PC} = 5.4 Hz, $C^{4,5}{}_{Fc}$), 52.19 (Py-$\underline{C}^{9}H_2$-N), 51.00 (d, J_{PC} = 8.31 Hz, Fc-$\underline{C}^{7}$H(CH_3)-N), 39.23 (N($\underline{C}^{15}H_3$)$_2$) 19.85 (Fc-CH($\underline{C}^{8}H_3$)-N); ^{31}P-{^{1}H}-NMR (201 MHz, $CDCl_3$) δ: -70.6 (s) ppm; IR (ATR): 2968.5 (w), 2927.9 (w), 2900.9 (w), 2358.9 (w), 2181.5 (w), 1597.0 (s), 1541.1 (m), 1506.4 (m), 1448.5 (m), 1437.0 (m), 1367.5 (m), 1105.2 (m), 1001.1 (s), 900.8 (m), 808.2 (s), 727.2 (s) cm^{-1}; HRMS: (ES+) calculated for $[C_{28}H_{31}FeN_3O_2P]^+$ 528.1498; found 528.1492;

$[\alpha]_D{}^{20}$: -348.3 (c 0.9, chloroform);

[(*R_c, S_p*)-*N*-2-picolynyl-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, ***(R_c, S_p)*-9**



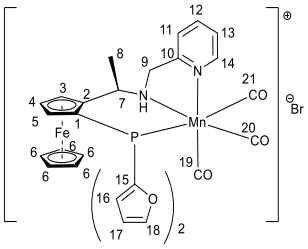
(*R_c, S_p*)-*N*-2-picolinyl-1-(2-bis(4-methoxy-3, 5-dimethylphenyl)phosphine)ferrocenylethylamine (205 mg, 0.33 mmol, 1.02 equiv.) and bromopentacarbonylmanganese (I) (89 mg, 0.32 mmol, 1.0 equiv.) were stirred in degassed cyclohexane (10 mL) at room temperature under an argon atmosphere. The mixture was refluxed for 16 h under which time an orange slurry formed. The mixture was cooled to room temperature, diluted with *n*-pentane (20 mL) and filtered, washed with *n*-pentane (2x 20 mL) and dried to give the title compound as a yellow solid (200 mg, 0.26 mmol, 82 %). Analysis showed the presence of cyclohexane. Assignment of protons and carbons have been done when possible using ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC.

^{1}H-NMR (500 MHz, CD_2Cl_2) δ: 8.60 (1H, br d, J = 4.8 Hz, $C_{Ar}H^{14}$), 7.65 (1H, s, $C_{Ar}H^{20}$), 7.62 (1H, s, $C_{Ar}H^{20}$), 7.33 (1H, t, J = 6.9 Hz, $C_{Ar}H^{11}$), 6.79 (2H, m, $C_{Ar}H^{12,13}$), 6.29 (1H, s, $C_{Ar}H^{16}$), 6.28 (1H, s, $C_{Ar}H^{16}$), 5.58 (1H, m, -C$\underline{H}^{7}$-), 4.87 (1H, s, NH), 4.62 (1H, s, Fc-H^{5}), 4.48 (1H, s, Fc-H^{3}), 4.35 (1H, s, Fc-H^{4}), 4.11 (1H, m, PyC$\underline{H}_2{}^{9}$NH-), 3.85 (5H, s, Fc-H^{6}), 3.81 (3H, s, -OC$\underline{H}_3{}^{23}$), 3.68 (1H, m, PyC$\underline{H}_2{}^{9}$NH), 3.54 (3H, s, -$OCH_3{}^{23}$), 2.40 (6H, s, -$CH_3{}^{21}$), 1.96 (6H, s, -$CH_3{}^{22}$), 1.70 (3H, br d, J = 7.0 Hz, CHC$\underline{H}_3{}^{8}$), 1.44 (cyclohexane); ^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2) δ: 232.6 (d, J_{PC} = 22.0 Hz, $C^{26,27}$O), 229.7 (d, J_{PC} = 25.2 Hz, C^{25}O), 159.71 ($C^{18}{}_{Ar}$), 158.96 ($C^{18}{}_{Ar}$), 156.65 ($C^{10}{}_{Ar}$), 152.87 ($C^{14}{}_{Ar}$), 135.80 ($C^{17,19}{}_{Ar}$), 135.02 ($C^{11}{}_{Ar}$), 134.91 (d, J_{PC} = 11.3 Hz, $C^{15}{}_{Ar}$), 134.20 ($C^{17}{}_{Ar}$), 133.82 ($C^{19}{}_{Ar}$), 131.26 (C_{Ar}), 130.93 (d, J_{PC} = 10.2 Hz, $C^{16}{}_{Ar}$), 130.33 (d, J_{PC} = 11.3 Hz, $C^{20}{}_{Ar}$), 129.93 (d, J_{PC} = 10.1 Hz, C_{Ar}), 122.31 ($C^{12}{}_{Ar}$), 119.16 ($C^{13}{}_{Ar}$), 91.40 (d, J_{PC} = 19.3 Hz, $C^{1}{}_{Fc}$), 73.27 (d, J_{PC} = 28.9 Hz, $C^{2}{}_{Fc}$), 72.84 ($C^{5}{}_{Fc}$), 70.58 ($C^{6}{}_{Fc}$), 69.84 ($C^{3}{}_{Fc}$), 59.70 (O$\underline{C}^{23}H_3$), 59.32 (O$\underline{C}^{23}H_3$), 56.48 (Fc-$\underline{C}^{7}$H(CH_3)-N), 59.27 ($C^{4}{}_{Fc}$), 48.66 (Py$\underline{C}^{9}H_2$), 20.43 (Fc-CH($\underline{C}^{8}H_3$)-N), 16.14 (Ar-$\underline{C}^{22}H_3$), 15.54 (Ar-$\underline{C}^{21}H_3$); ^{31}P-{^{1}H}-NMR (201 MHz, CD_2Cl_2) δ: +86.8 (s) ppm; IR (ATR): 2927.9 (w), 1924.9 (s), 1845.9 (s), 1473.6 (m), 1217.1 (w), 1111.0 (m), 1008.8 (m), 771.5 (w), 615.3 (m) cm^{-1};

HRMS: (ESI positive): expected $[C_{39}H_{41}FeMnN_2O_3P]^+$: 759.1478, found: 759.1462; M.P.: 190-194 °C (decomposition)

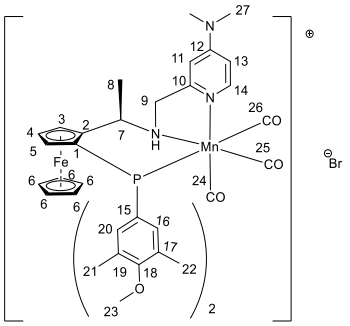
$[\alpha]_D{}^{20}$: + 100.6 (c 1.1, dichloromethane);

[(R_c, S_p)-*N*-2-picolynyl-1-(-2-di(furan-2-yl)phosphinoferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_c, S_p)-10**



(R_c, S_p)-*N*-2-picolynyl-1-(2-di(furan-2yl)phosphino)ferrocenylethylamine (360 mg, 0.74 mmol, 1.0 equiv.) and bromopentacarbonylmanganese (I) (204 mg, 0.74 mmol, 1.0 equiv.) was stirred in degassed cyclohexane (10 mL) at reflux under an argon atmosphere for 19 h to form a yellow-orange slurry. After cooling to room temperature the mixture was diluted with ^{n}hexane (10 mL), filtered and washed with ^{n}hexane (2 x 10 mL) to give the crude product as a yellow solid. Analysis indicated that the product was a 1:1 cyclohexane adduct. The product was further purified by dissolving the crude in DCM (15 mL), clear filtered and then precipitated by the addition of ^{n}hexane (80 mL). The product was filtered off and washed with ^{n}hexane (20 mL) to give the title product as an orange solid (265 mg, 0.38 mmol, 51 %). Assignment of protons and carbons have been done when possible using ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC.
^{1}H-NMR (500 MHz, CD_2Cl_2) δ: 8.90 (1H, s, $C_{Ar}H^{14}$), 7.82 (1H, s, $C_{Ar}H^{16}$), 7.50 (1H, s, $C_{Ar}H^{13}$), 7.44 (1H, s, $C_{Ar}H^{17}$), 7.10 (1H, s, $C_{Ar}H^{16}$), 6.98 (2H, s, $C_{Ar}H^{12,18}$), 6.68 (1H, s, $C_{Ar}H^{11}$), 5.99 (1H, s, $C_{Ar}H^{17}$), 5.93 (1H, s, $C_{Ar}H^{18}$), 5.55 (1H, s, NH), 4.86 (1H, s, -C$\underline{H}^7$-), 4.70 (1H, m, Fc-H^5), 4.60 (1H, s, Fc-H^3), 4.51 (1H, s, Fc-H^4), 4.12 (1H, s, PyC$\underline{H}_2{}^9$N-), 4.00 (5H, s, Fc-H^6), 3.73 (1H, br s, PyC$\underline{H}_2{}^9$N-), 1.71 (3H, br d, J = 6.3 Hz, CHC$\underline{H}_3{}^8$); ^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2) δ: 228.29 ($C^{23,24,25}$O), 160.5 ($C^{10}{}_{Ar}$), 152.97 ($C^{14}{}_{Ar}$), 151.16 ($C^{15}{}_{Ar}$), 150.70 ($C^{15}{}_{Ar}$), 150.07 (C_{Ar}), 149.51 ($C^{17}{}_{Ar}$), 146.83 (d, J_{PC} = 25.5 Hz, $C^{16}{}_{Ar}$), 136.56 ($C^{13}{}_{Ar}$), 122.96 (d, J_{PC} = 24.7 Hz, $C^{17}{}_{Ar}$), 119.86 ($C^{12}{}_{Ar}$), 116.48 (d, J_{PC} = 7.8 Hz, $C^{18}{}_{Ar}$), 111.28 (d, J_{PC} = 8.4 Hz, $C^{11}{}_{Ar}$), 109.94 ($C^{18}{}_{Ar}$), 90.94 (d, J_{PC} = 22.8 Hz, $C^1{}_{Fc}$), 74.02 ($C^2{}_{Fc}$), 70.71 ($C^6{}_{Fc}$), 70.32 ($C^5{}_{Fc}$), 70.05 ($C^3{}_{Fc}$), 69.81 ($C^4{}_{Fc}$), 56.79 (Fc-$\underline{C}^7$H(CH$_3$)-N), 48.52 (Py$\underline{C}^9$H$_2$), 20.34 (Fc-CH($\underline{C}^8$H$_3$)-N); ^{31}P-{^{1}H}-NMR (201 MHz, CD_2Cl_2) δ: +64.1 ppm (s) IR (ATR): 2976.2 (w), 2900.9 (w), 2358.9 (w), 2322.3 (w), 1923.0 (s), 1842.0 (s), 1234.4 (w), 1091.7 (m), 1047.4 (w), 1006.8 (w), 756.1 (m) cm^{-1}
HRMS: (ESI positive): expected $[C_{29}H_{25}FeMnN_2O_5P]^+$: 623.0226, found: 623.0212; M.P.: 194-196 ^{o}C (decomposition)
$[\alpha]_D{}^{20}$: + 166.8 (c 1.0, dichloromethane);

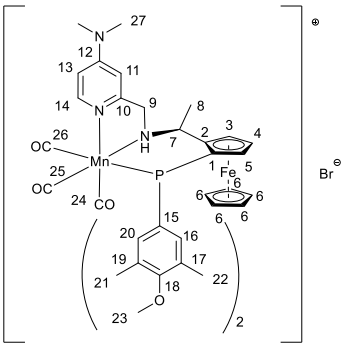
[(R_c, S_p)-*N*-(4-(dimethylamino)pyridine-2-methyl)-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_c, S_p)-11**



(R_c, S_p)-*N*-(4-dimethylaminopyridine-2-methyl)-1-(2-bis(4-methoxy- 3, 5 -dimethylphenyl) phosphino)ferrocenylethylamine (2.4 g, 3.62 mmol, 1.02 equiv.) and bromopentacarbonylmanganese (I) (975 mg, 3.55 mmol, 1.0 equiv.) were stirred in degassed cyclohexane (50 mL) at room temperature under an argon atmosphere. The mixture was refluxed for 16 h under which time an orange slurry formed. The mixture was cooled to room temperature, diluted with ^{n}hexane (40 mL) and filtered, washed with ^{n}hexane (20 mL). The crude material was dissolved in dichloromethane (10 mL) and filtered. ^{n}hexane (30 mL) was added and the formed mixture slowly evaporated until product precipitated. The product was filtered and washed with ^{n}hexane and dried to give the title compound as a yellow solid (2.87 g, 3.27 mmol, 92 %). Analysis showed two species that could not be separated. The minor species was believed to be the *facial*-coordinated species. Assignment of protons and carbons have been done when possible using ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC.
^{1}H-NMR (500 MHz, CD_2Cl_2) δ(major): 8.04 (1H, br d, J = 7.5 Hz, $C_{Ar}H^{14}$), 7.65 (1H, s, $C_{Ar}H^{16}$), 7.63 (1H, s, $C_{Ar}H^{16}$), 6.33 (2H, m, $C_{Ar}H^{20}$ overlap with minor), 6.01 (1H, s, $C_{Ar}H^{11,13}$, overlap with minor), 5.58 (1H, d, J = 6.9 Hz, -C$\underline{H}^7$-, overlaps with minor), 4.84 (1H, s, NH), 4.60 (1H, s, Fc-H^5), 4.45 (1H, s, Fc-H^3), 4.33 (1H, s, Fc-H^4), 3.95 (1H, m, PyC$\underline{H}_2{}^9$NH-, overlap with minor), 3.84 (5H, s, Fc-H^6, overlap with minor), 3.80 (3H, s, -OC$\underline{H}_3{}^{23}$, overlap with minor), 3.58 (1H, m, PyC$\underline{H}_2{}^9$NH, overlap with minor), 3.52 (3H, s, -OC$\underline{H}_3{}^{23}$), 2.86 (6H, s, -N(C$\underline{H}_3{}^{27}$)$_2$, overlap with minor) 2.39 (6H, s, -C$\underline{H}_3{}^{21}$), 1.98 (6H, s, -C$\underline{H}_3{}^{22}$, overlap with minor), 1.68 (3H, br d, J = 6.9 Hz, CHC$\underline{H}_3{}^8$, overlap with minor); δ(minor): 7.69 (1H, s, $C_{Ar}H^{16}$), 7.67 (1H, s, $C_{Ar}H^{16}$), 7.37 (1H, br d, J = 6.2 Hz, $C_{Ar}H^{14}$) 6.33 (2H, $C_{Ar}H^{20}$ overlap with major), 6.01 (1H, s, $C_{Ar}H^{11}$, overlap with major), 5.95 (1H, s, $C_{Ar}H^{13}$), 5.58 (1H, d, J = 6.9 Hz, -C$\underline{H}^7$-, overlap with major), 4.93 (1H, s, NH), 4.69 (1H, s, Fc-H^5), 4.57 (1H, s, Fc-H^3), 3.95 (1H, m, PyC$\underline{H}^9{}_2$NH-, overlap with

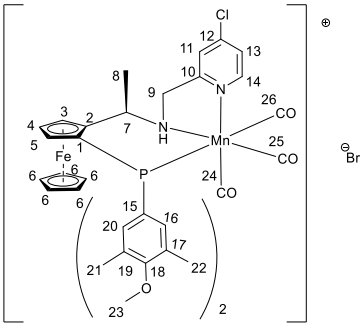
major), 3.84 (5H, s, Fc-H^6, overlap with major), 3.80 (3H, s, -OC$\underline{H}^{23}{}_3$, overlap with major), 3.58 (4H, m, PyC$\underline{H}^9{}_2$NH and -OC$\underline{H}^{23}{}_3$, overlap with major), 2.86 (6H, s, -N(C$\underline{H}^{27}{}_3$)$_2$, Overlap with major) 2.43 (6H, s, -C$\underline{H}^{21}{}_3$), 1.98 (6H, s, -C$\underline{H}^{22}{}_3$, overlap with major), 1.68 (3H, br d, J = 6.9 Hz, CHC$\underline{H}^8{}_3$, overlap with major); ^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2) δ(major): 231.10 (d, J_{PC} = 24.8 Hz, C^{24}O), 230.27 (d, J_{PC} = 22.1 Hz, C^{25}O), 158.81 ($C^{18}{}_{Ar}$), 156.68 ($C^{18}{}_{Ar}$), 153.74 ($C^{12}{}_{Ar}$), 151.55 ($C^{14}{}_{Ar}$), 135.01 (d, J_{PC} = 13.0 Hz, $C^{16}{}_{Ar}$), 131.09 (d, J_{PC} = 9.9 Hz, $C^{20}{}_{Ar}$), 130.61 (d, J_{PC} = 8.6 Hz, $C^{17}{}_{Ar}$), 130.17 (d, J_{PC} = 12.2 Hz, $C^{19}{}_{Ar}$), 129.71 (d, J_{PC} = 9.2 Hz, $C^{15}{}_{Ar}$), 106.27 ($C^{13}{}_{Ar}$), 101.25 ($C^{11}{}_{Ar}$), 91.72 (d, J_{PC} = 22.7 Hz, $C^1{}_{Fc}$), 72.74 ($C^2{}_{Fc}$), 70.52 ($C^6{}_{Fc}$), 59.72 (-O$\underline{C}^{23}H_3$), 59.09 (-O$\underline{C}^{23}H_3$), 56.57 (Py-$\underline{C}^9H_2$-N), 48.60 (Fc-$\underline{C}^7$H(CH$_3$)-N), 39.01 (-N($\underline{C}^{27}H_3$)$_2$), 20.50 (Fc-CH($\underline{C}^8H_3$)-N), 16.17 (-$\underline{C}^{21}H_3$), 15.65 (-$\underline{C}^{22}H_3$); δ (minor): 160.30 ($C^{18}{}_{Ar}$), 159.71 ($C^{18}{}_{Ar}$), 157.67 ($C^{12}{}_{Ar}$), 154.13 ($C^{10}{}_{Ar}$), 150.39 ($C^{14}{}_{Ar}$), 135.19 (d, J_{PC} = 12.2 Hz, $C^{15}{}_{Ar}$), 134.67 ($C^{20}{}_{Ar}$), 131.60 (d, J_{PC} = 12.9 Hz, $C^{17}{}_{Ar}$), 130.17 (d, J_{PC} = 9.9 Hz, $C^{19}{}_{Ar}$), 129.34 ($C^{20}{}_{Ar}$), 128.93 ($C^{16}{}_{Ar}$), 107.12 ($C^{13}{}_{Ar}$), 102.16 ($C^{11}{}_{Ar}$), 92.39 (d, J_{PC} = 24.1 Hz, $C^1{}_{Fc}$), 73.52 ($C^5{}_{Fc}$), 73.29 ($C^3{}_{Fc}$), 70.77 ($C^6{}_{Fc}$), 69.73 ($C^4{}_{Fc}$), 59.87 (-O$\underline{C}^{18}H_3$), 59.28 (-O$\underline{C}^{18}H_3$), 56.57 (Py-$\underline{C}^9H_2$-N, overlap with major), 48.60 (Fc-$\underline{C}^7$H(CH$_3$)-N, overlap with major), 39.12 (-N($\underline{C}^{27}H_3$)$_2$), 20.50 (Fc-CH($\underline{C}^8H_3$)-N, overlap with major), 16.25 (-$\underline{C}^{21}H_3$), 15.73 (-$\underline{C}^{22}H_3$); ^{31}P-{^{1}H}-NMR (201 MHz, CD_2Cl_2) δ: +89.1 (s, major), 43.6 (br s, minor) ppm;
IR (ATR): 2953.0 (w), 2918.3 (w), 2895.2 (w), 2025.3 (s), 1942.3 (m), 1909.5 (s), 1830.5 (s), 1616.4 (s), 1473.6 (m), 1276.9 (m), 1219.0 (m), 1111.0 (s), 1008.8 (s), 839.0 (s), 617.2 (s) cm^{-1}; HRMS: (ESI positive): expected [$C_{41}H_{46}FeMnN_3O_5P$]$^+$: 802.1900, found: 802.1889; M.P.: 188-190 ^{o}C (decomposition); Elemental analysis: calculated for [$C_{41}H_{46}BrFeMnN_3O_5P$]: C, 55.78 %, H, 5.26 %, N, 4.76 %; Found C, 55.55 %, H, 5.37 %, N, 4.72 %
[$\alpha_D{}^{20}$]: + 157.3 (c 1.0, dichloromethane);

[(*S$_c$,R$_p$*)-*N*-(4-(dimethylamino)pyridine-2-methyl)-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(*S$_c$, R$_p$*)-11**



(S$_c$, *R$_p$*)-*N*-(4-dimethylaminopyridine-2-methyl)-1-(2-bis(4-methoxy- 3, 5 -dimethylphenyl) phosphine)ferrocenylethylamine (221 mg, 0.333 mmol, 1.05 equiv.) and bromopentacarbonylmanganese (I) (87 mg, 0.317 mmol, 1.0 equiv.) were stirred in degassed cyclohexane (15 mL) at room temperature under an argon atmosphere. The mixture was refluxed for 16 h under which time an orange slurry formed. The mixture was cooled to room temperature, diluted with ^{n}hexane (25 mL) and filtered, washed with ^{n}hexane (25 mL). The crude material was dissolved in dichloromethane (5 mL) and filtered. ^{n}hexane (30 mL) was added and the formed mixture slowly evaporated until product precipitated. The product was filtered and washed with ^{n}hexane and dried to give the title compound as a yellow solid (230 mg, 0.260 mmol, 82 %). Analysis showed the compound to be identical to **(*R$_c$, S$_p$*)-5.015 Br** above.
[α]$_D{}^{20}$: + 532.9 (c 0.80, dichloromethane);

[(*R$_c$,S$_p$*)-*N*-(4-chloropyridine-2-methyl)-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(*R$_c$, S$_p$*)-12**

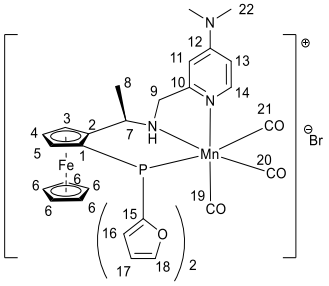


(*R$_c$,S$_p$*)-*N*-(4-chloropyridine-2-methyl)-1-(2-bis(4-methoxy- 3, 5 -dimethylphenyl)phosphino)ferrocenylethylamine (110 mg, 0.168 mmol, 1.02 equiv.) and bromopentacarbonylmanganese (I) (45 mg, 0.165 mmol, 1.0 equiv.) were stirred in degassed cyclohexane (10 mL) at room temperature under an argon atmosphere. The mixture was refluxed for 16 h under which time

an orange slurry formed. The mixture was cooled to room temperature, diluted with ^{n}hexane (20 mL) and filtered, washed with ^{n}hexane (2x 10 mL) and dried. The crude material was dissolved in dichloromethane, filtered over celite and concentrated to give the title compound as an orange solid (80 mg, 0.091 mmol, 55 %). Assignment of protons and carbons have been done when possible using ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC.

^{1}H-NMR (DCM-d_2) δ: 8.45 (1H, br s, $C_{Ar}H^{14}$), 7.65 (1H, s, $C_{Ar}H^{16}$), 7.62 (1H, s, $C_{Ar}H^{16}$), 6.87 (1H, s, $C_{Ar}H^{13}$), 6.74 (1H, s, $C_{Ar}H^{11}$), 6.27 (2H, s, $C_{Ar}H^{20}$), 5.56 (1H, m, -C<u>H</u>^{7}-), 4.89 (1H, s, NH), 4.62 (1H, s, Fc-H^{5}), 4.48 (1H, s, Fc-H^{3}), 4.35 (1H, s, Fc-H^{4}), 4.10 (1H, m, PyC<u>H</u>$^{9}{}_2$NH-), 3.84 (5H, s, Fc-H^{6}), 3.81 (3H, s, -OC<u>H</u>$^{23}{}_3$), 3.74 (1H, m, PyC<u>H</u>$^{9}{}_2$NH), 3.54 (3H, s, -OC<u>H</u>$^{23}{}_3$), 2.40 (6H, s, -C<u>H</u>$^{21}{}_3$), 2.00 (6H, s, -C<u>H</u>$^{22}{}_3$), 1.70 (3H, br s, CHC<u>H</u>$^{8}{}_3$); ^{13}C{^{1}H}-NMR (DCM-d_2) δ: 232.59 (d, J_{PC} = 27.0 Hz, C^{25}O), 229.49 (d, J_{PC} = 19.1 Hz, C^{24}O), 161.28 ($C^{12}{}_{Ar}$), 159.02 ($C^{18}{}_{Ar}$), 156.9 ($C^{18}{}_{Ar}$), 153.26 ($C^{10}{}_{Ar}$), 143.91 ($C^{15}{}_{Ar}$), 134.95 (d, J_{PC} = 11.4 Hz, $C^{15}{}_{Ar}$), 134.57 ($C^{16}{}_{Ar}$), 134.27 ($C^{16}{}_{Ar}$), 130.97 ($C^{20}{}_{Ar}$), 130.74 (d, J_{PC} = 7.3 Hz, $C^{20}{}_{Ar}$), 130.74 (d, J_{PC} = 11.4 Hz, $C^{20}{}_{Ar}$), 122.91 ($C^{11}{}_{Ar}$), 119.40 ($C^{13}{}_{Ar}$), 91.16 (d, J_{PC} = 21.6 Hz, $C^{1}{}_{Fc}$), 72.90 ($C^{2}{}_{Fc}$), 70.72 ($C^{5}{}_{Fc}$), 70.60 ($C^{3,4}{}_{Fc}$), 70.02 ($C^{6}{}_{Fc}$), 59.73 (-O<u>C</u>$^{23}H_3$), 59.40 (-O<u>C</u>$^{23}H_3$), 56.77 (Fc-<u>C</u>^{7}H(CH_3)-N), 48.39 (Py<u>C</u>$^{9}H_2$), 20.39 (Fc-CH(<u>C</u>$^{8}H_3$)-N), 16.17 (Ar-<u>C</u>$^{21}H_3$), 15.67 (Ar-<u>C</u>$^{22}H_3$); ^{31}P-{^{1}H}-NMR (DCM-d_2) δ: +86.3 (s) ppm; IR (ATR): 2918.3 (w), 2351.2 (w), 2322.3 (w), 2025.6 (w), 1921.1 (s), 1842.0 (s), 1593.2 (w), 1473.6 (m), 1417.7 (w), 1361.7 (w), 1274.9 (w), 1219.0 (m), 1109.1 (s), 1095.6 (w), 1001.1 (w), 823.6 (w), 617.2 (m) cm^{-1}; HRMS: (ESI positive): expected $[C_{39}H_{40}ClFeMnN_2O_5P]^+$: 793.1088 / 794.1121, found: 793.1073 / 794.1103; M.P.: 186-188 °C (decomposition); $[\alpha]_D^{20}$: + 94.2(c 1.0, dichloromethane);

[(*R*$_c$,*S*$_p$)-*N*-(4-(dimethylamino)pyridine-2-methyl)-1-(-2-di(furan-2-yl)phosphineferrocenylethylamine]-κN^{1}-κN^{2}-κP-tricarbonyl manganese (I) bromide, **(*R*$_c$, *S*$_p$)-13**

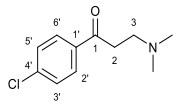


(*R*$_c$, *S*$_p$)-*N*-(4-dimethylaminopyridine-2-methyl)-1-(2-di(furan-2yl)phosphine)ferrocenylethylamine (278 mg, 0.527 mmol, 1.05 equiv.) and bromopentacarbonylmanganese (I) (138 mg, 0.502 mmol, 1.0 equiv.) was stirred in degassed cyclohexane (10 mL) at reflux under an argon atmosphere for 19 h to form a yellow-orange slurry. After cooling to room temperature the mixture was diluted with pentanes (20 mL), filtered and washed with pentanes (2 x 10 mL) to give the crude product as a yellow solid. The product was recrystallized from dichloromethane (25 mL) and ^{n}hexane (35 mL) to give the title compound as a yellow solid (240 mg, 0.32 mmol, 64 %). Assignment of protons and carbons have been done when possible using ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC.

^{1}H-NMR (CD_2Cl_2) δ: 8.34 (1H, br s, $C_{Ar}H^{14}$), 7.80 (1H, br s, $C_{Ar}H^{16}$), 7.42 (1H, br s, $C_{Ar}H^{13}$), 7.20 (1H, br s, $C_{Ar}H^{17}$), 6.66 (1H, br s, $C_{Ar}H^{16}$), 6.21 (1H, br s, $C_{Ar}H^{18}$), 6.14 (1H, br s, $C_{Ar}H^{11}$), 6.04 (1H, br s, $C_{Ar}H^{17}$), 5.96 (1H, br s, $C_{Ar}H^{18}$), 5.54 (1H, br s, -C<u>H</u>^{7}-), 4.80 (1H, s, -NH), 4.70 (1H, s, Fc-H^{5}), 4.57 (1H, s, Fc-H^{3}), 4.49 (1H, s, Fc-H^{4}), 3.99 (5H, s, Fc-H^{6}), 3.94 (1H, br s, PyC<u>H</u>$^{9}{}_2$N-), 3.62 (1H, br s, PyC<u>H</u>$^{9}{}_2$N-), 2.92 (6H, s, N(C<u>H</u>$^{22}{}_3$)$_2$), 1.69 (3H, br s, CHC<u>H</u>$^{8}{}_3$); ^{13}C{^{1}H}-NMR ($CDCl_3$) δ: 193.77 ($C^{19,20}$O), 185.43 (C^{21}O), 159.04 ($C^{10}{}_{Ar}$), 154.23 ($C^{12}{}_{Ar}$), 151.77 ($C^{14}{}_{Ar}$), 146.89 ($C^{15}{}_{Ar}$), 146.46 ($C^{15}{}_{Ar}$), 122.49 (d, J_{PC} = 25.0 Hz, $C^{16}{}_{Ar}$), 116.44 (d, J_{PC} = 11.2 Hz, $C^{16}{}_{Ar}$), 111.19 (d, J_{PC} = 15.1 Hz, $C^{18}{}_{Ar}$), 109.80 ($C^{11}{}_{Ar}$), 106.42 ($C^{17}{}_{Ar}$), 101.83 ($C^{18}{}_{Ar}$), 90.19 (d, J_{PC} = 22.3 Hz, $C^{1}{}_{Fc}$), 73.95 ($C^{2}{}_{Fc}$), 70.65 ($C^{6}{}_{Fc}$), 69.76 ($C^{3,4}{}_{Fc}$), 56.71 (Fc-<u>C</u>^{7}H(CH_3)-N), 48.49 (Py<u>C</u>$^{9}H_2$), 39.01 (-N(<u>C</u>$^{22}H_3$)$_2$), 20.26 (Fc-CH(<u>C</u>$^{8}H_3$)-N); ^{31}P-{^{1}H}-NMR (DCM-d_2) δ: +65.7 ppm (s); IR (ATR): 2972.3 (w), 2900.9 (w), 2322.3 (w), 2029.1 (w), 1923.0 (s), 1845.9 (s), 1624.0 (m), 1541.1 (w), 1521.8 (w), 1384.9 (w), 1008.8 (m), 759.9 (m), 738.7 (m) cm^{-1}; HRMS: (ESI positive): expected $[C_{31}H_{30}FeMnN_3O_5P]^+$: 666.0648, found: 666.0631; M.P.: 168-170 °C (decomposition); $[\alpha]_D^{20}$: + 174.4 (c 1.0, dichloromethane)

Substrate synthesis

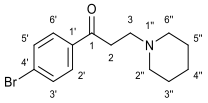
N, N-dimethyl-3-amino-1-(4'-chlorophenyl)-1-propanone, **20p**



4'-Chloroacetophenone (2.0 g, 12.9 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) in a 50 mL round-bottom flask fitted with a condenser and argon inlet at room temperature under an inert atmosphere. Paraformaldehyde (0.6 g, 19.4 mmol, 1.5 equiv.) and aqueous dimethylamine (40 wt%, 2.5 mL, 19.4 mmol, 1.5 equiv.) added. Concentrated hydrochloric acid (2.7 mL, 32.3 mmol, 2,5 equiv.) was added and the formed slurry was heated to reflux for 16 h. After cooling the yellow solution to room temperature volatiles were removed *in vacuo* and the formed mixture diluted with water (10 mL) and extracted with

diethyl ether (2 x 10 mL). The organic layers were discarded. The pH of the aqueous layer was adjusted to >10 using solid K_2CO_3 and the mixture extracted with dichloromethane (3 x 10 mL). The combined organic layers was dried over anhydrous magnesium sulfate, filtered and concentrated to give the title compound as a pale yellow solid (400 mg, 1.89 mmol, 15 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.93 (2H, d, J = 9.2 Hz, $C_{Ar}H^{2',6'}$), 7.46 (2H, d, J = 9.2 Hz, $C_{Ar}H^{3',5'}$), 3.16 (2H, t, J = 7.6 Hz, -C$\underline{H}_2^2$-), 2.77 (2H, d, J = 7.6 Hz, -C$\underline{H}_2^3$-), 2.31 (6H, s, -N(C$\underline{H}_3$)$_2$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 197.92 (-$\underline{C}^1$O-), 139.44 ($C^{1'}_{Ar}$-COR), 135.20 ($\underline{C}^{4'}_{Ar}$Cl), 129.49 ($\underline{C}^{2',6'}_{Ar}$), 128.46 ($\underline{C}^{3',5'}_{Ar}$), 54.37 ($\underline{C}^2H_2$COR), 45.48 (-N($\underline{C}H_3$)$_2$), 36.96 (-$\underline{C}^3H_2$-); HRMS (ES+): calculated for $[C_{11}H_{15}ClNO]^+$: 212.0837 found: 212.0832

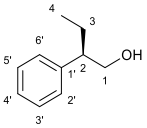
1-(4-bromophenyl)-3-(piperidin-1-yl)propan-1-one, **20q**



Propiophenone (5.0 g, 25.1 mmol, 1.0 equiv.) was dissolved in ethanol (25 mL) in a 100 mL round bottom flask fitted with a condenser and a gas inlet. Paraformaldehyde (1.13 g, 37.7 mmol, 1.5 equiv.) and piperidine (3.7 mL, 37.7 mmol, 1.5 equiv.) added. Concentrated hydrochloric acid (5.2 mL) was added to the white slurry and the mixture heated to reflux for 16 h. Over time a yellow solution formed. The solution was cooled to room temperature and volatiles removed *in vacuo*. The crude mixture was added water (20 mL) and filtered. The formed aqueous solution was extracted with diethyl ether (2 x 25 mL). The organic layers were discarded. The aqueous phase pH was adjusted to >12 using KOH (s) and extracted with dichloromethane (4 x 25 mL). The combined organic layers were dried over $MgSO_4$ (s), filtered and concentrated to dryness. The formed yellow solid was dissolved in isopropanol (10 mL) and 3 mL concentrated hydrochloric acid. The water was azeotroped out by continuously distilling off solvent *in vacuo* and repeating that until a white solid was obtained. The crude hydrochloride salt was stirred in diethyl ether and filtered. The salt was free based using dichloromethane and aqueous potassium carbonate to give the title compound as a yellow solid (1.4 g, 4.7 mmol, 19 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.85 (2H, d, J = 6.9 Hz, $C_{Ar}H^{2',6'}$), 7.63 (2H, d, J = 6.9 Hz, $C_{Ar}H^{3',5'}$), 3.18 (2H, t, J = 7.1 Hz, -C$\underline{H}_2^2$-), 2.80 (2H, d, J = 7.1 Hz, -C$\underline{H}_2^3$-), 2.41 (4H, m, -(C$\underline{H}_2^{2'',6''}$)$_5$), 1.60 (4H, m, -(C$\underline{H}_2^{3'',5''}$)$_5$), 1.46 (2H, m, -(C$\underline{H}_2^{6''}$)$_5$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 198.42 (-$\underline{C}^1$O-), 135.65 ($C^{1'}_{Ar}$-COR), 131.93 ($\underline{C}^{2',6'}_{Ar}$), 129.60 ($\underline{C}^{3',5'}_{Ar}$), 128.24 ($\underline{C}^{4'}_{Ar}$Br), 54.66 ($\underline{C}^2H_2$COR), 53.80 (-N($\underline{C}^{2''}H_2$)-), 53.09 (-N($\underline{C}^{6''}H_2$)-), 36.43 (-$\underline{C}^{4''}H_2$-), 25.98 (-$\underline{C}^{3''}H_2$-), 25.90 (-$\underline{C}^{3''}H_2$-), 24.86 (-$\underline{C}^{5''}H_2$-), 24.26 (-$\underline{C}^{5''}H_2$-); HRMS (ES+): calculated for $[C_{14}H_{19}BrNO]^+$: 296.0645 / 298.0624 found: 296.0637 / 298.0616;

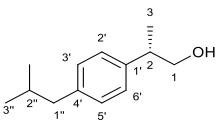
Product data

(*R*)-2-phenyl-1-butanol (Reproduced from reference 3)



The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography using 100% hexane followed by hexane / ethyl acetate (1/1) to give the (*S*)-2-phenylbutan-1-ol as a colourless oil. (*R*)-Ethyl 2-phenylbutyrate (200 mg, 1.04 mmol, 1 equiv., 99.0 % ee) gave 140 mg product (0.93 mmol, 90 %).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36 (2H, m, $C_{Ar}H^{2',6'}$), 7.24 (3H, m, $C_{Ar}H^{3',4',5'}$), 3.78 (2H, m, C$\underline{H}_2^1$OH), 2.72 (1H, m, PhC$\underline{H}^2$(C_2H_5)CH_2OH), 1.78 (1H, m, C$\underline{H}_2^3CH_3$), 1.61 (1H, m, C$\underline{H}_2^3CH_3$), 0.86 (3H, t, J = 7.5 Hz, -C$\underline{H}_3^4$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 142.25 ($\underline{C}^{1'}_{Ar}$-CH), 128.64 ($\underline{C}^{2',6'}_{Ar}$), 128.12 ($\underline{C}^{3',5'}_{Ar}$), 126.73 ($\underline{C}^{4'}_{Ar}$), 67.36 (-$\underline{C}^1H_2$OH), 50.52 (Ph$\underline{C}^2$H($C_2H_5$)-), 25.01 ($\underline{C}^3H_2CH_3$), 12.00 (-$\underline{C}^4H_3$); HRMS (EI+): calculated for $[C_{10}H_{14}O]$: 150.1045 found: 150.1044; $[\alpha]_D^{20}$: -22.3 (c. 1.4, $CHCl_3$) Lit.[4]: -15.1 (c. 0.95, $CHCl_3$); Chiral analysis was performed using a Chiralpak AD-H column using ^{n}hexane / isopropanol (98/2) mobile phase, flow 1.0 mL/min; t_R (R-enantiomer, major): 14.9 min; t_R (S-enantiomer, minor): 16.3 min, ee 98 %. Fits with previously published data.[4]

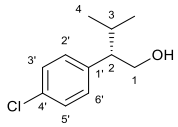
(*S*)-2-(4-isobutylphenyl)propan-1-ol (Reproduced from reference 3)



The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography using 100% hexane followed by dichloromethane / methanol (95/5) to give the (*S*)-2-(4-isobutylphenyl)propan-1-ol as a colourless oil. (*S*)-Ethyl ibuprofen (235 mg, 1.00 mmol, 1 equiv., 99.0 % ee) gave 185 mg product (0.96 mmol, 96 %).

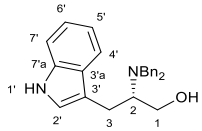
^{1}H-NMR ($CDCl_3$) δ: 7.17 (2H, d, J = 8.4 Hz, $C_{Ar}H^{2',6'}$), 7.13 (2H, d, J = 8.4 Hz, $C_{Ar}H^{3',5'}$), 3.71 (2H, d, J = 7.6 Hz, -CH_2^1OH), 2.95 (1H, m, ArCH^2-), 2.48 (2H, d, J = 7.8 Hz,-C$H_2^{1''}$Ar), 1.88 (1H, m, -C$H^{2''}$-), 1.29 (3H, d, J = 6.9 Hz, -CH_3^3), 0.93 (6H, d, J = 6.3 Hz, -(C$H_3^{3''}$)$_2$); ^{13}C -{^{1}H}-NMR ($CDCl_3$) δ: 140.68 ($C^{1'}_{Ar}$-CH), 140.09 ($C^{4'}_{Ar}$-CH_2), 129.48 ($C^{2',6'}_{Ar}$), 127.17 ($C^{3',5'}_{Ar}$), 68.81 (-C^1H_2OH), 45.04 (-C^2H-), 42.04 (Ar$C^{1''}H_2$-), 30.24 (-$C^{2''}$H-), 22.43 (-C^3H_3), 17.63 (-$C^{3''}H_3$); HRMS (EI+): calculated for [$C_{13}H_{20}O$]: 192.1514 found: 192.1517; $[\alpha]_D^{20}$: -36 (c. 1.00, $CHCl_3$); Chiral analysis was performed using a Chiralpak AD-H column using ^{n}hexane / isopropanol (90/10) mobile phase, flow 1.0 mL/min; t_R (R-enantiomer, minor): 19.2 min; t_R (S-enantiomer, major): 20.2 min, ee 98.8 %.

(*S*)-2-(4-chlorophenyl)-3-methylbutanol (Reproduced from reference 3)



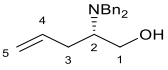
The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography using 100% hexane followed by dichloromethane / methanol (95/5) to give the (*S*)-2-(4-chlorophenyl)-2-methylbutan-1-ol as a colourless oil. (*S*)-Ethyl 3-methyl-(4-chlorophenyl)-butyrate (241 mg, 1.00 mmol, 1 equiv., 96 % ee) gave 181 mg product (0.91 mmol, 91 %).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.32 (2H, d, J = 8.6 Hz, $C_{Ar}H^{2',6'}$), 7.26 (2H, d, J = 8.6 Hz, $C_{Ar}H^{3',5'}$), 3.95 (1H, dd, J = 10.8 /4.8 Hz, -CH_2^1OH), 3.83 (1H, dd, J = 10.8/4.8 Hz, -CH_2^1OH), 2.52 (1H, m, ArCH^2-), 1.93 (1H, m,-CH^3-), 1.02 (3H, d, J = 6.6 Hz, -(CH_3^4)$_2$), 0.75 (3H, d, J = 6.6 Hz, -(CH_3^4)$_2$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 140.33 ($C^{1'}_{Ar}$-CH), 132.37 ($C^{4'}_{Ar}$-Cl), 130.06 ($C^{2',6'}_{Ar}$), 128.70 ($C^{3',5'}_{Ar}$), 65.06 (-C^1H_2OH), 55.16 (-C^2H-), 29.99 (-C^3H-), 20.86 (-C^4H_3); HRMS (EI+): calculated for [$C_{11}H_{15}ClO$]: 198.0811/200.0872 found: 198.0809 / 200.0810; $[\alpha]_D^{20}$: +6.7 (c. 1.00, $CHCl_3$); Chiral analysis was performed using a Chiralpak AD-H column using ^{n}hexane / isopropanol (99/1) mobile phase, flow 1.0 mL/min; t_R (R-enantiomer, minor): 27.1 min; t_R (S-enantiomer, major): 34.1 min, ee 96 %.

(*2S*)-2-[Bis(phenylmethyl)amino]-1H-indole-3-propan-1-ol (Reproduced from reference 3)



The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography using 100% hexane followed by ethyl acetate to give the (*S*)-*N,N*-dibenzyltryptphanol as a white solid. (*S*)-Ethyl *N*, *N*-dibenzyltryptophan (1000 mg, 2.42 mmol, 1 equiv., 99.8 % ee) gave 830 mg product (2.24 mmol, 93 %)
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.09 (1H, s, N$H^{1'}$), 7.85-7.25 (12H, m, $C_{Ar}H^{benzylic+4',7'}$), 7.22 (1H, t, J = 8.2 Hz, $C_{Ar}H^{6'}$), 7.13 (1H, t, J = 8.1 Hz, $C_{Ar}H^{5'}$), 6.93 (1H, s, $C_{Ar}H^{2'}$), 4.02 (2H, d, J = 12.9 Hz, PhCH_2N), 3.63 (2H, d, J = 12.9 Hz, PhCH_2N), 3.57 (1H, d, J = 10.2 Hz, CH_2^1OH), 3.47 (1H, dd, J = 10.5 Hz / 4.3 Hz, CH_2^1OH), 3.30 (2H, m, -CH_2^3-), 2.70 (1H, m, -CH^2-); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 139.31 ($C_{Ar}CH_2$N), 136.29 ($C^{7'a}_{Ar}$), 129.05 ($C^{3'a}_{Ar}$), 128.54 ($C^{benzylic}_{Ar}$), 127.30 ($C_{Ar}^{benzylic}$), 122.13 ($C^{2'}_{Ar}$), 121.96 ($C^{6'}_{Ar}$), 119.31 ($C^{5'}_{Ar}$), 118.70 ($C^{4'}_{Ar}$), 112.93 ($C^{3'}_{Ar}$), 111.21 ($C^{7'}_{Ar}$), 61.00 (-C^1H_2OH), 59.47 (PhCH$_2$N), 53.28 (-C^2H-), 20.79 (-C^3H_2-); HRMS (ES+): calculated for [$C_{25}H_{27}ON_2^+$]: 371.2118 found: 371.2110; $[\alpha]_D^{20}$: +44.5 (c. 1.00, $CHCl_3$); Chiral analysis was performed using a Chiralpak AD-H column using ^{n}hexane / isopropanol (90/10) mobile phase, flow 1.0 mL/min; t_R (R-enantiomer, minor): 26.8 min; t_R (S-enantiomer, major): 30.6 min, ee >99 %.

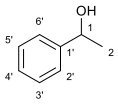
(*S*)-2-(dibenzylamino)pent-4-en-1-ol (Reproduced from reference 3)



The crude product was purified by column chromatography using 100% hexane followed by hexane / diethyl ether (90/10) to give the (*S*)-N, N-dibenzylallyl glycinol as a colourless oil. (*S*)-Benzyl *N*, *N*-dibenzylallylglycine (400 mg, 1.04 mmol, 1 equiv., 98 % ee) gave 212 mg product (0.75 mmol, 72 %).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36-7.26 (10H, m, C_{Ar}H), 5.77 (1H, m, -CH^4=CH_2), 5.14-5.06 (2H, m, -CH=CH_2^5), 3.88 (2H, d, J = 13.9 Hz, PhCH_2N), 3.47 (4H, m, PhCH_2N and -CH_2^1OH), 3.07 (1H, s, -OH), 2.92 (1H, m, -CH^2(NBn_2)-), 2.56 (1H, m, -CH_2^3-), 2.00 (1H, m, -CH_2^3-); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 139.12 ($C_{Ar}CH_2$N), 135.38 (C_{Ar}), 129.05 (C_{Ar}), 128.53 (C_{Ar}), 127.29 (C_{Ar}), 117.05 (C_{Ar}), 60.69 (-C^1H_2OH), 55.68 (-CH=C^5H_2), 53.22 (-C^4H=CH_2), 29.66 (-C^3H_2-); HRMS (ES+): calculated for [$C_{19}H_{24}NO^+$]: 282.1852 found: 282.1844; $[\alpha]_D^{20}$: +63.1° (c. 1.20, $CHCl_3$); Lit. $[\alpha]_D^{20}$: +60.1° (c. 0.5, $CHCl_3$)[5]; Chiral analysis was performed

using a Chiralcel OD-H column using ^{n}hexane / isopropanol (90/10) mobile phase, flow 0.5 mL/min; t_R (R-enantiomer, minor): 11.8 min; t_R (S-enantiomer, major): 16.1 min, ee >99 %. Fits with previously published data.[5]

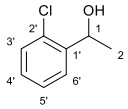
1-phenyl-1-ethanol, **15**



The product was purified by column chromatography using first hexanes and then hexanes / ethyl acetate (1/1) as the eluent to give the product as a colourless oil. Using 400 mg (3.33 mmol) of acetophenone, 398 mg (3.26 mmol) of the title compound was isolated (98 % yield);

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.39 (4H, m, $C_{Ar}H^{2',3',5',6'}$), 7.31 (1H, m, $C_{Ar}H^{4'}$), 4.93 (1H, q, J = 6.2 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 1.53 (3H, d, J = 6.2 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 145.80 ($C^{1'}{}_{Ar}$-CH(OH)-), 128.52 ($C^{2',6'}{}_{Ar}$), 127.50 ($C^{4'}{}_{Ar}$), 125.39 ($C^{3',5'}{}_{Ar}$), 70.46 (-$\underline{C}^{1}$H(OH)-), 25.20 (-$\underline{C}^{2}H_3$); HRMS (EI+): calculated for [$C_8H_{10}O$]: 122.0732; found: 122.0734; $[\alpha]_D^{20}$: -29.0 (c. 1.0, $CHCl_3$) (using **(R_c, S_p)-11**, S/C 5000), -32.6 (c. 1.0, $CHCl_3$) (using **(R_c, S_p)-11**, S/C 10000), Lit.[6]: - 50 (c. 1.00, dichloromethane, >99 % ee S); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 0.5 mL/min. t_R (R): 19 min; t_R (S): 24 min; *er*: 84:16 (S) – 80:20 (S) (S/C 10000). Fits with previously published data.[6]

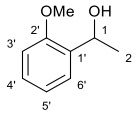
1-(2-chlorophenyl)-1-ethanol, **21a**



The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as an oil. Using 143 mg (0.92 mmol) of 2'-chloroacetophenone, 120 mg (0.76 mmol) of product was isolated (83 % yield);

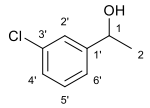
^{1}H-NMR ($CDCl_3$) δ: 7.61 (1H, d, J = 7.5 Hz, $C_{Ar}H$), 7.33 (2H, m, $C_{Ar}H$), 7.22 (1H, t, J = 8.6 Hz, $C_{Ar}H$), 5.31 (1H, q, J = 6.6 Hz, Ar-C$\underline{H}$(OH)-CH_3), 1.51 (3H, d, J = 6.4 Hz, Ar-CH(OH)-C$\underline{H}_3$); ^{13}C -{^{1}H}-NMR (DEPT, $CDCl_3$) δ: 143.05 (Cl-C_{Ar}), 131.63 ((CH(OH)-C_{Ar}), 129.04 (C_{Ar}), 128.41 (C_{Ar}), 127.22 (C_{Ar}), 126.41 (C_{Ar}), 66.97 (-$\underline{C}$H(OH)-), 23.52 (-$\underline{C}H_3$); HRMS (EI+): calculated for [C_8H_9ClO]: 156.0342 (100%) / 158.0312 (32%); found: 156.0345 (100%) / 158.0313 (32%); $[\alpha]_D^{20}$: -33.5 (c. 1.0, $CHCl_3$) (using ***(R_c, S_p)*-11**), Lit.[7]: + 62.5 (c. 0.75, $CHCl_3$, *erI 98:2 R*) and Lit.[8]: -56.5 (c. 0.0463, $CHCl_3$, *er* 95:5 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 0.5 mL/min. t_R (R): 14.6 min; t_R (S): 15.6 min; *er* 78:22 (*S*)
Fits with previously published data.[7]

1-(2-methoxyphenyl)-1-ethanol, **21b**



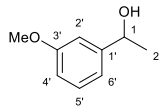
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as an oil. Using 289 mg (1.92 mmol) of 2'-methoxyacetophenone, 266 mg (1.75 mmol) of product was isolated (91 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.37 (1H, d, J = 6.8 Hz, $C_{Ar}H^{3'}$), 7.28 (1H, m, $C_{Ar}H^{4'}$), 6.99 (1H, t, J = 8.1 Hz, $C_{Ar}H^{5'}$), 6.91 (1H, d, J = 7.9 Hz, $C_{Ar}H^{6'}$), 5.12 (1H, q, J = 6.5 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 3.89 (3H, s, -OC$\underline{H}_3$), 1.54 (3H, d, J = 6.5 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 156.57 (MeO-$C^{2'}{}_{Ar}$), 133.37 ((CH(OH)-$C^{1'}{}_{Ar}$), 128.32 ($C^{3'}{}_{Ar}$), 126.12 ($C^{6'}{}_{Ar}$), 120.80 ($C^{4'}{}_{Ar}$), 110.42 ($C^{5'}{}_{Ar}$), 66.62 (-O$\underline{C}H_3$) 55.27 (-$\underline{C}^{1}$H(OH)-), 22.83 (-$\underline{C}^{2}H_3$); HRMS (EI+): calculated for [$C_9H_{12}O_2$]: 152.0837 (100%); found: 152.0836 (100%); $[\alpha]_D^{20}$: -15.8 (c. 1.0, $CHCl_3$), Lit.[9]: -24.1 (c. 1.0, $CHCl_3$, 99 % ee S); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase at a flowrate of 1.0 mL/min. t_R (S): 21.5 min; t_R (R): 22.8 min, *er* 82:18 (S)
Fits with published data.[10]

1-(3-chlorophenyl)-1-ethanol, **21c**



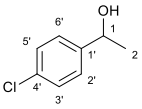
The product was purified by column chromatography using first hexane followed by hexane / ethyl acetate (1/1) as the mobile phase to give the product as an oil. Using 185 mg (1.20 mmol) of 3'-chloroacetophenone, 185 mg (1.18 mmol) of product was isolated (98 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.41 (1H, m, $C_{Ar}\underline{H}^{5'}$), 7.32-7.25 (3H, m, $C_{Ar}\underline{H}^{2',4',6'}$), 4.90 (1H, m, Ar-C$\underline{H}^{1}$(OH)-$CH_3$), 1.93 (1H, d, J = 3.6 Hz, Ar-CH(O$\underline{H}$)-CH_3), 1.51 (3H, d, J = 6.9 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 147.85 (Cl-$C^{3'}{}_{Ar}$), 134.38 ((CH(OH)-$C^{1'}{}_{Ar}$), 129.81 ($C^{5'}{}_{Ar}$), 127.55 ($C^{6'}{}_{Ar}$), 125.64 ($C^{2'}{}_{Ar}$), 123.54 ($C^{4'}{}_{Ar}$), 69.84 (-$\underline{C}^{1}$H(OH)-), 25.28(-$\underline{C}^{2}H_3$); HRMS (EI+): calculated for [C_8H_9ClO]: 156.0342 / 158.0312 (32%); found: 156.0337 (100%) / 158.0306 (32%);
$[\alpha]_D^{20}$:+28.1 (c. 1.0, $CHCl_3$) Lit.[11]: -32.9 (c. 1.0, $CHCl_3$, 86:14 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (99/1) mobile phase at a flowrate of 1.0 mL/min. t_R (R): 30.3 min; t_R (S): 31.5 min,
er 85:15 (*R*)
Fits with previously published data.[11]

1-(3-methoxyphenyl)-1-ethanol, **21d**



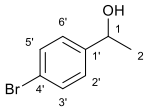
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate as the mobile phase to give the product as an oil. Using 289 mg (1.92 mmol) of 3'-methoxacetophenone 290 mg (1.90 mmol) of product was isolated (99 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.28 (1H, app t, J = 8.2 Hz, $C_{Ar}\underline{H}^{5'}$), 6.97 (2H, m, $C_{Ar}\underline{H}^{2',4'}$), 6.83 (1H, d, J = 6.7 Hz, $C_{Ar}\underline{H}^{6'}$), 4.89 (1H, m, Ar-C$\underline{H}^{1}$(OH)-CH_3), 3.84 (3H, s, -O$C\underline{H}_3$), 1.99 (1H, d, J = 3.7 Hz, -OH), 1.54 (3H, d, J = 6.7 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 159.77 (MeO-$C^{3'}{}_{Ar}$), 147.60 ((CH(OH)-$C^{1'}{}_{Ar}$), 129.55 ($C^{5'}{}_{Ar}$), 117.69 ($C^{4'}{}_{Ar}$), 112.90 ($C^{2'}{}_{Ar}$), 110.89 ($C^{6'}{}_{Ar}$), 70.36 (-O$\underline{C}H_3$), 55.24 (-$\underline{C}$H^{1}(OH)-), 25.16 (-$\underline{C}^{2}H_3$); HRMS (ES+): calculated for $[C_9H_{12}NaO_2]^+$: 175.0730, found: 175.0728; $[\alpha]_D^{20}$: -30.1 (c. 1.0, $CHCl_3$) Lit.[9]: -42.1 (c. 1.0, $CHCl_3$, *er* 99.5:0.5 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (90/10) mobile phase at a flowrate of 0.5 mL/min. t_R (R): 17.4 min; t_R (S): 21.5 min; *er* 85:15 (*S*)
Fits with previous published data.[9]

1-(4-chlorophenyl)-1-ethanol, **21e**



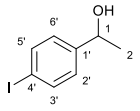
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the eluent to give the product as a pale yellow oil. Using 210 mg (1.36 mmol) of 4'-chloroacetophenone, 210 mg (1.35 mmol) of product was isolated (99 % yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.37-7.32 (4H, m, $C_{Ar}H^{2',3',5',6'}$), 4.91 (1H, q, J = 6.9 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 1.50 (3H, d, J = 6.4 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{1}H-NMR (400 MHz, C_6D_6) δ: 7.11 (2H, d, J = 8.7 Hz, $C_{Ar}H^{2',6'}$), 6.89 (2H, d, J = 8.7 Hz, $C_{Ar}H^{3',5'}$), 4.32 (1H, q, J = 6.0 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 1.50 (3H, d, J = 6.0 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 144.24 ($C^{4'}{}_{Ar}$-Cl), 133.08 ((CH(OH)-$C^{1'}{}_{Ar}$), 128.61 ($C^{3',5'}{}_{Ar}$), 126.79 ($C^{2',6'}{}_{Ar}$), 69.77 (-$\underline{C}^{1}$H(OH)-), 25.30 (-$\underline{C}^{2}H_3$); HRMS (EI+): calculated for [C_8H_9ClO]: 156.0342 (100%) / 158.0312 (32%); found: 156.0345 (100%) / 158.0318 (32%); $[\alpha]_D^{20}$: -26.9 (c. 1.0, $CHCl_3$), Lit.[7]: + 45.2 (c. 1.3, diethyl ether, *er* 98:2 *R*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 0.5 mL/min. t_R (S): 16.6 min; t_R (R): 17.9 min, *er* 90:10 (*S*)
Fits with previously published data.[7]

1-(4-bromophenyl)-1-ethanol, **21f**



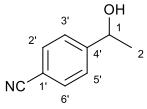
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the eluent to give the product as a pale yellow oil. Using 324 mg (1.63 mmol) of 4'-bromoacetophenone, 290 mg (1.44 mmol) of product was isolated (89 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.48 (2H, d, J = 8.5 Hz, $C_{Ar}H^{3',5'}$), 7.26 (2H, d, J = 8.5 Hz, $C_{Ar}H^{2',6'}$), 4.87 (1H, q, J = 6.5 Hz, Ar-C<u>H</u>^{1}(OH)-CH_3), 1.48 (3H, d, J = 6.5 Hz, Ar-CH(OH)-C<u>H</u>$_3^2$); ^{13}C {^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 144.76 ((CH(OH)-$C^{1'}_{Ar}$), 131.56 ($C^{2',6'}_{Ar}$), 127.17 ($C^{3',5'}_{Ar}$), 121.26 ($C^{4'}_{Ar}$-Br), 69.90 (-<u>C</u>^{1}H(OH)-), 25.28 (-<u>C</u>$^2H_3$); HRMS (EI+): calculated for [C_8H_9BrO]: 199.9837 (100 %) / 210.9816 (100 %); found: 199.9836 (100%) / 201.9828 (100%); $[\alpha]_D^{20}$: -27.8 (c. 1.0, $CHCl_3$), Lit.[12]: -46.2 (c. 1.0, $CHCl_3$, *er* 98:2 *S*);
Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 1.0 mL/min. t_R (S): 9.1 min; t_R (R): 9.9 min; *er* 89:11 (*S*).
Fits with previously published data.[12]

1-(4-Iodophenyl)-1-ethanol, **21g**



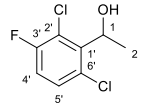
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the eluent to give the product as a yellow solid. Using 400 mg (1.63 mmol) of 4'-iodoacetophenone, 330 mg (1.34 mmol) of product was isolated (82 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.70 (2H, d, J = 8.8 Hz, $C_{Ar}H^{3',5'}$), 7.14 (2H, d, J = 8.8 Hz, $C_{Ar}H^{2',6'}$), 4.86 (1H, q, J = 5.8 Hz, Ar-C<u>H</u>^{1}(OH)-CH_3), 1.47 (3H, d, J = 5.8 Hz, Ar-CH(OH)-C<u>H</u>$_3^2$); ^{13}C {^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 145.45 ((CH(OH)-$C^{1'}_{Ar}$), 137.53 ($C^{2',6'}_{Ar}$), 127.43 ($C^{3',5'}_{Ar}$), 92.75 ($C^{4'}_{Ar}$-I), 69.96 (-<u>C</u>^{1}H(OH)-), 25.27 (-<u>C</u>$^2H_3$); HRMS (EI+): calculated for [C_8H_9IO]: 247.9698; found: 247.9701; $[\alpha]_D^{20}$:-24.1 (c. 1.0 $CHCl_3$) Lit.[13]: +25.3 (c. 0.63, $CHCl_3$, *er* 95:5 *R*);
Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase at a flowrate of 1.0 mL/min. t_R (S): 22.6 min; t_R (R): 23.7 min, *er* 90:10 (*S*)
Fits with previously published data.[13]

1-(4-cyanophenyl)-1-ethanol, **21h**



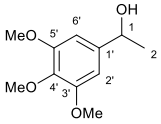
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (4/1 to 1/1) as the eluent to give the product as a colorless oil. Using 240 mg (1.65 mmol) of 4'-iodoacetophenone, 220 mg (1.49 mmol) of product was isolated (90 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.64 (2H, d, J = 8.3 Hz, $C_{Ar}H^{2',6'}$), 7.49 (2H, d, J = 8.3 Hz, $C_{Ar}H^{3',5'}$), 4.98 (1H, q, J = 5.8 Hz, Ar-C<u>H</u>^{1}(OH)-CH_3), 2.19 (1H, br s, -O<u>H</u>), 1.51 (3H, d, J = 5.8 Hz, Ar-CH(OH)-C<u>H</u>$_3^2$); ^{13}C {^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 151.13 ((CH(OH)-$C^{4'}_{Ar}$), 132.36 ($C^{2',6'}_{Ar}$), 126.07 ($C^{3',5'}_{Ar}$), 118.90 (-CN), 111.01 ($C^{1'}_{Ar}$-CN), 69.66 (-<u>C</u>^{1}H(OH)-), 25.43 (-<u>C</u>$^2H_3$);
HRMS (EI+): calculated for [C_9H_9NO]: 147.0684; found: 147.0688; $[\alpha]_D^{20}$: -36.0 (c. 1.0, $CHCl_3$) Lit.[14]: +36.3 (c. 1.3, MeOH, *er* 97:3 *R*); Lit.[15]: -40.1 (2.23, $CHCl_3$, 75:15 (*S*)); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase at a flowrate of 1.0 mL/min. t_R (S): 17.4 min; t_R (R): 18.7 min; *er* 85:15 (*S*)
Fits with previously published data.[16]

1-(2,6-dichloro-3-fluorophenyl)-1-ethanol, **21i**



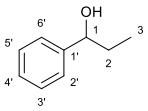
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as highly viscous oil. Using 345 mg (1.66 mmol) of 2',6'-dichloro-3'-fluoroacetophenone, 312 mg (1.49 mmol) of product was isolated (90 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29 (1H, dd, J = 7.9 / 4.4 Hz $C_{Ar}H^{4'}$), 7.05 (1H, dd, J = 9.5 / 7.9 Hz, $C_{Ar}H^{5'}$), 5.60 (1H, q, J = 6.4 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 1.67 (3H, d, J = 6.4 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$);
^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 157.28 (d, J_{FC} = 217.6 Hz, $C^{3'}{}_{Ar}$), 140.52 ($C^{6'}{}_{Ar}$-Cl), 129.64 (d, J_{FC} = 7.6 Hz, $C^{2'}{}_{Ar}$-Cl), 128.25 (CH(OH)-$C^{1'}{}_{Ar}$), 121.39 (d, J_{FC} = 19.6 Hz, $C^{5'}{}_{Ar}$), 115.69 (d, J_{FC} = 24.8Hz, $C^{4'}{}_{Ar}$), 68.44 (-$\underline{C}^{1}$H(OH)-), 21.38 (-$\underline{C}^{2}H_3$);
^{19}F-{^{1}H}-NMR (282 MHz, $CDCl_3$): -113.32 ppm; HRMS (EI+): calculated for [$C_8H_7Cl_2FO$]: 207.9858 (100%) / 209.9828; found: 207.9868 / 209.9845; $[\alpha]_D^{20}$: +24.1 (c 0.7, $CHCl_3$); Lit.[17]: + 6.9 (c. 0.87, MeOH, *er* 99:1 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase at a flowrate of 0.5 mL/min. t_R (S): 18.7 min; t_R (R): 19.7 min; *er* 90:10 (*S*)
Fits with previous published data.[17]

1-(3,4,5-trimethoxyphenyl)-1-ethanol, **21j**



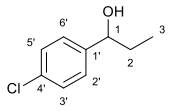
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as a colorless oil. Using 300 mg (1.43 mmol) of 3', 4', 5' - trimethoxyacetophenone, 260 mg (1.22 mmol) of product was isolated (86 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.62 (2H, s, $C_{Ar}H^{2',6'}$), 4.86 (1H, q, J = 6.2 Hz, Ar-C$\underline{H}^{1}$(OH)-CH_3), 3.89 (6H, s, Ar-OC$\underline{H}_3$), 3.85 (3H, s, Ar-OC$\underline{H}_3$), 1.51 (3H, d, J = 6.2 Hz, Ar-CH(OH)-C$\underline{H}_3^{2}$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 153.27 ($C^{5'6'}{}_{Ar}$-OMe), 141.71 ((CH(OH)-$C^{1'}{}_{Ar}$), 137.06 ($C^{4'}{}_{Ar}$-OMe), 102.19 ($C^{2',6'}{}_{Ar}$), 70.61 (-$\underline{C}^{1}$H(OH)-), 60.85 (C_{Ar}-O$\underline{C}H_3$), 56.09 (C_{Ar}-O$\underline{C}H_3$), 25.25 (-$\underline{C}H_3^{2}$); HRMS (EI+): calculated for [$C_{11}H_{16}O_4$]: 212.1049; found: 212.1051; $[\alpha]_D^{20}$: -25.3 (c. 1.0, $CHCl_3$) Lit.[18]: -27.8 (c. 2.8, $CHCl_3$ *er* 99.5:0.5 *S*); Chiral analysis was performed using a Chiralpak AS-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 1.0 mL/min. t_R (major): 22.6 min; t_R (minor): 26.1 min; *er* 90:10 (*S*)
Fits with previously published data.[18]

1-phenyl-1-propanol, **21k**



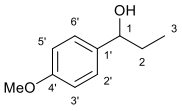
The product was purified by column chromatography using first hexanes and hexanes / ethyl acetate (1/1) to give the product as a pale-yellow oil. Using 281 mg (2.095 mmol) of propiophenone 250 mg (1.84 mmol) of title compound was isolated (88 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.40-7.28 (5H, m, $C_{Ar}H^{2',3',4',5',6'}$), 4.62 (1H, t, J = 6.7 Hz, Ph-C$\underline{H}^{1}$(OH)-), 1.81 (2H, m, -C$\underline{H}_2^{2}CH_3$), 0.95 (3H, t, J = 6.1 Hz, -C$\underline{H}_3^{3}$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 144.59 (($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 128.42 ($C^{2',6'}{}_{Ar}$), 127.52 ($C^{4'}{}_{Ar}$), 125.99 ($C^{3',5'}{}_{Ar}$), 76.05 (-$\underline{C}^{1}$H(OH)-), 31.91 (-$\underline{C}^{2}H_2$), 10.18 (-$\underline{C}^{3}H_3$); HRMS (EI+): calculated for [$C_{10}H_{12}O$]: 136.0888 found: 136.0881; $[\alpha]_D^{20}$: -34.5 (c. 1.0, $CHCl_3$); Lit.[19]: -47.4 (c. 1.48, $CHCl_3$, *er* 99:1 (*S*)); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase, flow 1.0 mL/min, t_R (R): 8.5 min; t_R (S): 10.0 min; *er* 86:14 (*S*);
Fits with previously published data.[19]

1-(4-chlorophenyl)-1-propanol, **21l**



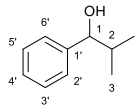
The product was purified by column chromatography using first hexane and then methylene chloride / methanol (95 /5) as the mobile phase to give the product as an oil. Using 229 mg (1.36 mmol) of 4'-chloropropiophene, 200 mg (1.17 mmol) of product was isolated (86 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.34 (2H, d, J = 8.9 Hz, $C_{Ar}H^{2',6'}$), 7.28 (2H, d, J = 8.9 Hz, $C_{Ar}H^{3',5'}$) 4.61 (1H, t, J = 6.9 Hz, Ar-C$\underline{H}^1$(OH)CH_2CH_3), 1.78 (2H, m, Ar-CH(OH)C$\underline{H}_2{}^2CH_3$), 0.98 (3H, t, J = 7.8 Hz, -C$\underline{H}_3{}^3$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 143.00 ($C^{4'}{}_{Ar}$-Cl), 133.09 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)-), 128.52 ($C^{3',5'}{}_{Ar}$), 127.36 ($C^{2',6'}{}_{Ar}$), 75.10 (-$\underline{C}^1$H(OH)-), 31.97 (-$\underline{C}^2H_2$-), 10.00 (-$\underline{C}^3H_3$); HRMS (EI+): calculated for [$C_9H_{11}ClO$]: 170.0498 (100%) / 172.0469 (32%); found: 170.0498 (100%) / 172.0488 (32%); $[\alpha]_D{}^{20}$:-33.1 (c. 1.0, $CHCl_3$), Lit.[20]: -38.4 (c. 1.09, $CHCl_3$, *er* 98:2 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase at a flowrate of 0.5 mL/min. t_R (*S*): 14.2 min; t_R (*R*): 15.2 min; *er* 93:7 (*S*);
Fits with previously published data.[20]

1-(4-methoxyphenyl)-1-propanol, **21m**



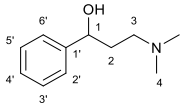
The product was purified by column chromatography using first hexane and then methylene chloride / methanol (95 /5) as the mobile phase to give the product as an oil. Using 268 mg (1.63 mmol) of 4'-methoxypropiophenone, 240 mg (1.44 mmol) of product was isolated (88 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29 (2H, d, J = 8.6 Hz, $C_{Ar}H^{3',5'}$), 6.91 (2H, d, J = 8.6 Hz, $C_{Ar}H^{2',6'}$), 4.57 (1H, t, J = 6.7 Hz, Ar-C$\underline{H}^1$(OH)-CH_3), 3.83 (3H, s, -OC$\underline{H}_3$), 1.95-1.39 (2H, m, -C$\underline{H}_2{}^2$-), 0.92 (3H, t, J = 7.4 Hz, Ar-CH(OH)CH_2C$\underline{H}_3{}^3$); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 159.00 (MeO-$C^{4'}{}_{Ar}$), 136.75 ((CH(OH)-$\underline{C}^{1'}{}_{Ar}$), 127.22 ($C^{3',5'}{}_{Ar}$), 113.78 ($C^{2',6'}{}_{Ar}$), 75.69 (-O$\underline{C}H_3$) 55.30 (-$\underline{C}^1$H(OH)-), 31.79 (-$\underline{C}^2H_2$-), 10.25 (-$\underline{C}^3H_3$); HRMS (EI+): calculated for [$C_{10}H_{14}O_2$]: 166.0990 (100%); found: 166.0994 (100%); $[\alpha]_D{}^{20}$: -32.7 (c. 1.0, $CHCl_3$), Lit.[21]: -23.4 (c. 0.30, $CHCl_3$, 83:17 *S*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (96/4) mobile phase at a flowrate of 1.0 mL/min. t_R (R): 15.3 min; t_R (S): 16.2 min; *er* 91:9 (*S*);
Fits with previously published data.[21]

2-methyl-1-phenyl-1-propanol, **21n**



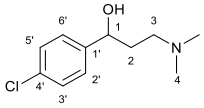
The product was purified by column chromatography using first hexanes and then hexane / ethyl acetate (1/1) to give the product as a pale-yellow oil. Using 247 mg (1.66 mmol) of isobutyrophenone, 239 mg (1.59 mmol) of title compound was isolated (96 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38-7.28 (5H, m, $C_{Ar}H^{2',3',4',5',6'}$), 4.38 (1H, d, J = 7.6 Hz, Ph-C$\underline{H}^1$(OH)-), 2.24 (2H, m, -C$\underline{H}^2$-$(CH_3)_2$ and -O$\underline{H}$), 1.03 (3H, d, J = 6.7 Hz, -CH-(C$\underline{H}_3{}^3)_2$), 0.82 (3H, d, J = 6.7 Hz, -CH-(C$\underline{H}_3{}^3)_2$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 143.65 (($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 128.19 ($C^{2',6'}{}_{Ar}$), 127.42 ($C^{4'}{}_{Ar}$), 126.59 ($C^{3',5'}{}_{Ar}$), 80.05 (-$\underline{C}^1$H(OH)-), 35.27 (-$\underline{C}^2H(CH_3)_2$), 19.02 (-CH($\underline{C}^3H_3)_2$), 18.29 (-CH($\underline{C}^3H_3)_2$); HRMS (EI+): calculated for [$C_{10}H_{14}O$]: 150.105 found: 150.104; $[\alpha]_D{}^{20}$: -25.3 (c. 1.0, $CHCl_3$); Lit.[22]: +12.3 (c. 1.2, $CHCl_3$, *er* 69:31*R*); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase, flow 0.5 mL/min, t_R (*S*): 21.8 min; t_R (*R*): 23.3 min; *er* 91:9 (S)
Fits with previous published data.[22]

3-dimethylamino-1-phenylpropan-1-ol, **21o**



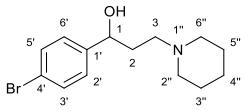
The product was purified by column chromatography using first hexane and then methylene chloride / methanol (95 /5) as the mobile phase to give the product as a colorless oil. Using 289 mg (1.63 mmol) of starting material, 260 mg (1.45 mmol) of product was isolated (89 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38 (4H, m, $C_{Ar}H^{2',3',5',6'}$), 7.27 (1H, m, $C_{Ar}H^{4'}$), 4.96 (1H, m, Ph-C$\underline{H}^{1}$(OH)), 2.69 (1H, m, -C$\underline{H}_2{}^{2}$-), 2.51 (1H, m, -C$\underline{H}_2{}^{2}$-), 2.33 (6H, s, -N(C$\underline{H}_3{}^{4}$)$_2$), 1.85 (2H, m, -C$\underline{H}_2{}^{3}$-); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 145.09 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 128.20 ($\underline{C}^{2',6'}{}_{Ar}$), 126.88 ($\underline{C}^{3',5'}{}_{Ar}$), 125.58 ($\underline{C}^{4'}{}_{Ar}$), 75.76 (-$\underline{C}^{1}$H(OH)-), 58.43 (-$\underline{C}^{3}H_2$-N(CH$_3$)$_2$), 45.32 (-$\underline{C}^{4}H_3$), 34.52 (-$\underline{C}^{2}H_2$-); HRMS (EI+): calculated for $[C_{11}H_{18}O]^+$: 180.1383 found: 180.1380; $[\alpha]_D{}^{20}$: - 19.2 (c. 1.0, $CHCl_3$), Lit.[23]: -32.3 (c. 0.60, methanol, *er* 99:1 (*S*)); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (95/5) mobile phase, flow 0.5 mL/min, t_R (R): 17.4 min; t_R (S): 23.1 min, *er* 86:14 (*S*)
Fits with previously published data.[23]

3-dimethylamino-1-(4-chlorophenyl)propan-1-ol, **21p**



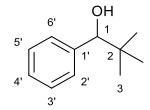
The product was isolated by dissolving the crude in 1N HCl (aq) and extracting with ether. The pH of the aqueous layer was adjusted to >12 and extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered and concentrated to dryness to give the title compound as a yellow oil. Using 300 mg (1.43 mmol) of starting material, 250 mg (1.17 mmol) of product was isolated (82 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.33 (4H, m, $C_{Ar}H^{2',3',5',6'}$), 4.93 (1H, dd, J = 8.2 / 3.6 Hz, Ar-C$\underline{H}^{1}$(OH)), 2.69 (1H, m, -C$\underline{H}_2{}^{2}$-), 2.49 (1H, m, -C$\underline{H}_2{}^{2}$-), 2.32 (6H, s, -N(C$\underline{H}_3{}^{4}$)$_2$), 1.81 (2H, m, -C$\underline{H}_2{}^{3}$-); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 143.67 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 132.41 ($\underline{C}^{4'}{}_{Ar}$-Cl), 128.30 ($\underline{C}^{2',6'}{}_{Ar}$), 126.97 ($\underline{C}^{3',5'}{}_{Ar}$), 75.27 (-$\underline{C}^{1}$H(OH)-), 58.42 (-$\underline{C}^{3}H_2$-N(CH$_3$)$_2$), 45.31 (-$\underline{C}^{4}H_3$), 34.40 (-$\underline{C}^{2}H_2$-); HRMS (ES+): calculated for $[C_{11}H_{17}ClNO]^+$: 214.0993 found: 214.0987; $[\alpha]_D{}^{20}$: -15.7 (c. 1.0, $CHCl_3$);
Chiral analysis was performed using a Chiralpak AD column using ^{n}hexane / isopropanol (98/2) mobile phase, flow 1.0 mL/min, t_R (Enantiomer 1): 16.3 min; t_R (Enantiomer 2): 20.0 min; *er* 89:11

1-(4-bromophenyl)-3-(piperidin-1-yl)propan-1-ol, **21q**



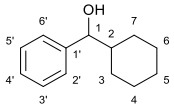
The product was isolated by dissolving the crude in 1N HCl (aq) and extracting with ether. The pH of the aqueous layer was adjusted to >12 and extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered and concentrated to dryness to give the title compound as a yellow oil. Using 423mg (1.43 mmol) of starting material, 360 mg (1.20 mmol) of product was isolated (84 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.48 (2H, d, J = 7.4 Hz, $C_{Ar}H^{2',6'}$), 7.28 (2H, d, J = 7.4 Hz, $C_{Ar}H^{3',5'}$), 4.93 (1H, dd, J = 7.8 / 3.6 Hz, Ar-C$\underline{H}^{1}$(OH)), 2.65 – 2.23 (6H, m, -C$\underline{H}_2{}^{2,2'',6''}$-), 1.81 (2H, m, -C$\underline{H}^{4''}$-), 1.64-1.49 (6H, m, -C$\underline{H}_2{}^{3,3'',5''}$-); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 144.27 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 131.21 ($\underline{C}^{2',6'}{}_{Ar}$), 127.4 ($\underline{C}^{3',5'}{}_{Ar}$), 120.45 ($\underline{C}^{4'}{}_{Ar}$-Br), 75.13 (-$\underline{C}^{1}$H(OH)-), 57.70 (-$\underline{C}^{2'',6''}H_2$-), 54.61 (-$\underline{C}^{3}H_2$-), 53.05 (-$\underline{C}^{2}H_2$-), 33.54 (-$\underline{C}^{4''}H_2$-), 26.05 (-$\underline{C}^{3''}H_2$-), 24.20 (-$\underline{C}^{5''}H_2$-); HRMS (ES+): calculated for $[C_{14}H_{21}BrNO]^+$: 298.0801 / 300.0781 found: 298.0795 / 300.0774; $[\alpha]_D{}^{20}$: -19.5 (c. 1.0, MeOH as HCl salt); Chiral analysis was performed using a Chiralpak AS-H column using ^{n}hexane / isopropanol (95/5) mobile phase, flow 0.5 mL/min, t_R (enantiomer 1): 20.4 min; t_R (enantiomer 2): 23.8 min; *er* 90:10 (*S*)

2,2-dimethyl-1-phenyl-1-propanol, **21r**



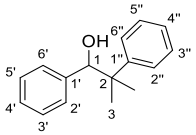
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as a white solid. Using 275 mg (1.70 mmol) of 2,2,2-trimethylacetophenone, 270 mg (1.65 mmol) of product was isolated (97 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36-7.25 (5H, m, $C_{Ar}H^{2',3',4',5',6'}$), 4.43 (1H, s, Ph-C$\underline{H}^{1}$(OH)-C$(CH_3)_3$), 1.88 (1H, s, -O$\underline{H}$), 0.95 (9H, s, C$(C\underline{H}_3{}^3)_3$); ^{13}C -{^{1}H}-NMR (DEPT, $CDCl_3$) δ: 142.17 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 127.61 ($C^{2',6'}{}_{Ar}$), 127.57 ($C^{4'}{}_{Ar}$), 127.29 ($C^{3',5'}{}_{Ar}$), 82.41 (-$\underline{C}^{1}$H(OH)-), 35.64 (-$\underline{C}^{2}(CH_3)_3$), 25.94 (-$\underline{C}^{3}H_3$); M.P.: 62-64 °C; HRMS (EI+): calculated for [$C_{11}H_{16}O$]: 164.120 found: 164.119; $[\alpha]_D{}^{20}$: -27.5 (c. 1.0, $CHCl_3$), Lit.[24]: -30.3 (c. 3.64, Acetone, *er* 87:13 (*S*));
Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase, flow 0.5 mL/min, t_R (S): 21.9 min; t_R (R): 30.5 min; *er* 90:10 (*S*)
Fits with previously published data.[24]

Cyclohexylphenylmethanol, **21s**



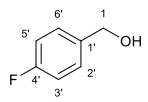
The product was purified by column chromatography using first hexane and then hexane / ethyl acetate (1/1) as the mobile phase to give the product as a white solid. Using 255 mg (1.36 mmol) of cyclohexylphenyl ketone, 230 mg (1.21 mmol) of product was isolated (89 % yield);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.33 (5H, m, $C_{Ar}H^{2',3',4',5',6'}$), 4.39 (1H, dd, J = 7.2 / 2.9 Hz, Ph-C$\underline{H}^{1}$(OH)-C_6H_{11}), 2.02 (1H, m, -C$\underline{H}_2{}^{3,7}$-), 1.87 (1H, m, -C$\underline{H}^{2}$-), 1.80 (1H, m, -C$\underline{H}_2{}^{3,7}$-), 1.66 (3H, m, -C$\underline{H}_2{}^{3,4}$-), 1.40 (1H, m, -C$\underline{H}_2{}^{7}$-), 1.32-0.91 (5H, m, -C$\underline{H}_2{}^{4,5,6}$-); ^{13}C -{^{1}H}-NMR (100 MHz, DEPT, $CDCl_3$) δ: 143.62 ($\underline{C}^{1'}{}_{Ar}$-CH(OH)), 128.20 ($\underline{C}^{2',6'}{}_{Ar}$), 127.43 ($\underline{C}^{3',5'}{}_{Ar}$), 126.65 ($\underline{C}^{4'}{}_{Ar}$), 79.42 (-$\underline{C}^{1}$H(OH)-), 44.97 (-$\underline{C}^{2}H(CH_2)_5$), 29.32 (-$\underline{C}^{3}H_2$-), 28.85 (-$\underline{C}^{7}H_2$-), 26.44 (-$\underline{C}^{4}H_2$-), 26.11 (-$\underline{C}^{6}H_2$-), 26.03 (-$\underline{C}^{5}H_2$-); HRMS (ES+): calculated for [$C_{13}H_{18}NaO$]: 213.1250, found: 213.1249; $[\alpha]_D{}^{20}$: -28.6 (c. 1.00, $CHCl_3$), Lit.[25]: -18.4 (c. 1.0, $CHCl_3$ *er* 95:5 (*S*)); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (98/2) mobile phase, flow 0.5 mL/min, t_R (S): 27.6 min; t_R (R): 28.9 min; *er* 91:9 (*S*)
Fits with previously reported data.[25]

2-methyl-1,2-diphenylpropan-1-ol, **21t**



Purified by column chromatography using a petroleum ether / ethyl acetate gradient (100/0 to 1/1) as the mobile phase to give the product as a colorless oil. Using 350 mg (1.56 mmol) of **20t**, 300 mg (1.33 mmol) of **21t** was isolated (85 % yield).
^{1}H-NMR($CDCl_3$) δ: 7.44-7.39 (2H, m, $C_{Ar}H^{2',6'}$), 7.38-7.33 (2H, m, $C_{Ar}H^{2'',6''}$), 7.30-7.24 (4H, m, $C_{Ar}H^{3',4',5',5''}$), 7.19-7.13 (2H, m, $C_{Ar}H^{3'',4''}$), 4.78 (1H, br d, *J*= 2.2 Hz, C$\underline{H}^{1}$OH), 1.81 (1H, br d, J = 2.5 Hz, CHO$\underline{H}$), 1.35 (3H, s, C$(C\underline{H}_3{}^3)_2$) and 1.31 (3H, s, C$(CH_3{}^3)_2$); ^{13}C-{^{1}H}-NMR ($CDCl_3$) δ: 146.3 ($\underline{C}^{1'}{}_{Ar}$), 140.8 ($\underline{C}_{Ar}{}^{1''}$), 128.3 ($\underline{C}^{2'}{}_{Ar}$), 127.9 ($\underline{C}^{6'}{}_{Ar}$), 127.5 ($\underline{C}^{2'',6''}{}_{Ar}$), 127.1 ($\underline{C}^{3',4',5',5''}{}_{Ar}$), 126.5 ($\underline{C}^{3'',4''}{}_{Ar}$), 82.2 ($\underline{C}^{1}$HOH), 43.3 ($\underline{C}^{2}(CH_3)_2$), 25.9 (C($\underline{C}^{3}H_3)_2$), 22.5 (C($\underline{C}^{3}H_3)_2$); $[\alpha]_D{}^{20}$: -5.0 (c. 1.20, $CHCl_3$), HRMS (EI^+): calculated for [$C_{16}H_{18}O$]: 226.1358; found: 226.1340; Enantioselectivity determined by chiral HPLC. Chiralcel ODH, 95/5, *n*-hexane / isopropanol, flow 1mL/min. Retention times: 13.8 min (minor enantiomer) and 16.7 min (major enantiomer). *er*: 92:8

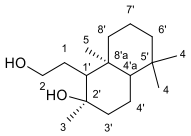
4-fluorobenzyl alcohol, **17**



The product was purified by column chromatography using 100 % hexane followed by dichloromethane / methanol (95/5) to give the title compound as a colorless oil. 250 mg (1.49 mmol) ethyl *p*-fluorobenzoate gave 170 mg (1.35 mmol) *p*-fluorobenzyl alcohol (90 %);

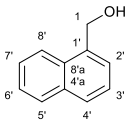
^{1}H-NMR (400 MHZ, $CDCl_3$) δ: 7.39 (2H, m, $C_{Ar}H^{2',6'}$), 7.10 (2H, m, $C_{Ar}H^{3',5'}$), 4.70 (2H, s, Ar-C$\underline{H}^{1}_2$OH); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 162.29 (d, J_{FC} = 245.5 Hz, $\underline{C}^{4'}_{Ar}$-F), 136.59 ($\underline{C}^{1'}_{Ar}$-CH_2OH), 128.81 (d, J_{FC} = 4.3 Hz, $\underline{C}^{2',6'}_{Ar}$), 115.50 (d, J_{FC} = 26.6 Hz, $\underline{C}^{3',5'}_{Ar}$), 64.72 (Ar-$\underline{C}^{1}H_2$OH); ^{19}F-{^{1}H}-NMR (282 MHz, $CDCl_3$): δ: -114.89; HRMS (EI+): calculated for [C_7H_7FO]: 126.0481, found: 126.0477.
Fits with previously published data.[26]

(*R*)-Sclareodiol, **19a**



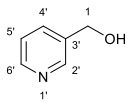
The crude reaction solution was concentrated to 1/3 volume and filtered to remove inorganic material. The mother liquor was diluted with water (75 mL) to precipitate the product as a white solid which was isolated by filtration, washed with water (30 mL) and hexanes (50 mL) and air dried. (*R*)-Sclareolide (350 mg, 1.40 mmol) gave 274 mg sclareodiol (1.08 mmol, 77 % isolated yield).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.81 (1H, m, -C$\underline{H}_2{}^{2}$OH), 3.49 (1H, m, -C$\underline{H}_2{}^{2}$OH), 1.90 (1H, d, J = 12.9 Hz, -CH-), 1.66 (8H, m, -CH_2-)), 1.45 (5H, m, -CH_2-), 1.22 (3H, s, -C$\underline{H}_3{}^{3}$), 1.16 (1H, m, -$CH^{1'}$-), 0.98 (1H, m, -CH-), 0.95 (1H, m, -$CH^{4'a}$-), 0.91 (3H, s,-C$\underline{H}_3{}^{5}$), 0.81 (6H, s,-C$\underline{H}_3{}^{4}$); ^{13}C -{^{1}H}-DEPT-NMR (100 MHZ, $CDCl_3$) δ: 73.16 (-$C^{2'}(CH_3)$OH), 64.22 (-$C^{2}H_2$OH), 59.07(-$C^{1'}$H-), 56.01 (-$C^{4'a}$H-), 44.32 (-$C^{3'}H_2$)-, 41.88 (-$C^{6'}H_2$-), 39.32 (-$C^{8'a}H_2$-), 33.42 (-$C^{8'a}$), 33.29 (-$C^{5'}$-), 27.88 (-$C^{1}H_2$-), 24.70 (-$C^{3}H_3$), 21.49 (-$C^{4}H_3$), 20.49 (-$C^{4'}H_2$-), 18.41 (-$C^{7'}H_2$-), 15.32 (-$C^{5}H_3$); M.P.: 120-122 °C; HRMS (EI+): calculated for [$C_{16}H_{30}O_2$-H_2O]: 236.2140 found: 236.2179; $[\alpha]_D{}^{20}$: -17.2 (c. 1.00, $CHCl_3$) Lit.: -16.9 (c. 0.99, $CHCl_3$)[23]
Fits with previously published data.[24]

1-hydroxymethylnaphthalene, **19b**



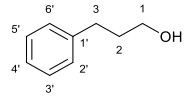
The product was purified by column chromatography using 100 % hexane followed by dichloromethane / methanol (95/5) to give the title compound as a white solid. 320 mg (1.60 mmol) ethyl 1-naphthanoate gave 240 mg (1.52 mmol) 1-hydroxymethylnaphthalene (95 %);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.15 (1H, d, J = 7.5 Hz, $C_{Ar}H^{8'}$), 7.91 (1H, d, J = 7.9 Hz, $C_{Ar}H^{5'}$), 7.85 (1H, d, J = 8.4 Hz, $C_{Ar}H^{4'}$), 7.56 (3H, m, $C_{Ar}H^{3',6',7'}$), 7.48 (1H, m, $C_{Ar}H^{2'}$), 5.17 (2H, d, J = 3.9 Hz, Ar-C$\underline{H}_2{}^{1}$OH), 1.91 (1H, m, Ar-CH_2O$\underline{H}$); ^{13}C -{^{1}H}-DEPT NMR (100 MHz, $CDCl_3$) δ: 136.26 ($\underline{C}^{1'}_{Ar}$-CH_2OH), 133.80 ($\underline{C}^{8'a}_{Ar}$), 131.23 ($\underline{C}^{4'a}_{Ar}$), 128.69 ($\underline{C}^{5'}_{Ar}$), 128.61 ($\underline{C}^{4'}_{Ar}$) 126.37 ($\underline{C}^{7'}_{Ar}$), 125.91 ($\underline{C}^{6'}_{Ar}$), 125.91 ($\underline{C}^{3'}_{Ar}$), 125.36 ($\underline{C}^{8'}_{Ar}$), 123.66 ($\underline{C}^{2'}_{Ar}$), 63.72 (-$\underline{C}^{1}H_2$OH); HRMS (EI+): calculated for [$C_{11}H_{10}O$]: 158.0732 found 158.0729.
Fits with previously published data.[27]

3-hydroxymethylpyridine, **19c**



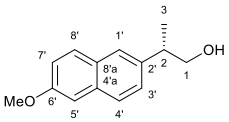
The product was purified by column chromatography using 100 % hexane followed by dichloromethane / methanol (9/1) to give the title compound as a white solid. 225 mg (1.64 mmol) methyl nicotinate gave 140 mg (1.31 mmol) 3-hydroxymethylpyridine (80 %); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, s, $C_{Ar}H^{2'}$), 8.50 (1H, d, J = 3.3 Hz, $C_{Ar}H^{6'}$), 7.75 (1H, d, J = 8.4 Hz, $C_{Ar}H^{4'}$), 7.30 (1H, m, $C_{Ar}H^{5'}$), 4.74 (2H, s, -C$\underline{H}_2{}^{1}$OH), 3.30 (1H, s, -OH); ^{13}C -{^{1}H}-DEPT NMR (100 MHz, $CDCl_3$) δ: 148.69 ($\underline{C}^{2'}_{Ar}$), 148.34 ($\underline{C}^{6'}_{Ar}$), 136.54 ($\underline{C}^{3'}_{Ar}$-CH_2OH), 135.00 ($\underline{C}^{4'}_{Ar}$), 123.58 ($\underline{C}^{5'}_{Ar}$), 62.51 (-$\underline{C}^{1}H_2$OH); HRMS (ES+): calculated for [$C_6H_8NO^+$]: 110.0600 found 110.0599.
Fits with previously published data.[28]

3-phenylpropan-1-ol, **19d**



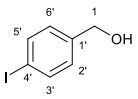
The product was purified by column chromatography using hexanes / diethyl ether (3/2) to give the title compound as a colorless oil. 220 mg (1.23 mmol) ethyl 3-phenylpropionate gave 142 mg (1.05 mmol) 3-phenylpropan-1-ol (85 %);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.32 (2H, m, $C_{Ar}H^{2',6'}$), 7.22 (3H, m, $C_{Ar}H^{3',4',5'}$), 3.71 (2H, t, J = 6.4 Hz, -C$\underline{H}_2{}^1$OH), 2.74 (2H, t, J = 7.4 Hz, Ph-C$\underline{H}_2{}^3$-), 1.93 (2H, m, -C$\underline{H}_2{}^2CH_2$OH); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 141.82 ($\underline{C}^{1'}{}_{Ar}$-$CH_2$-), 128.44 ($\underline{C}^{2',6'}{}_{Ar}$), 128.41 ($\underline{C}^{4'}{}_{Ar}$), 125.88 ($\underline{C}^{3',5'}{}_{Ar}$) 62.33 (-$\underline{C}^1H_2$OH), 34.24 (Ph$\underline{C}^3H_2$-), 32.09 (-$\underline{C}^2H_2$-); HRMS (EI+): calculated for [$C_9H_{12}O$]: 136.0888 found 136.0884.
Fits with previously published data.[1]

(*S*)-Naproxol, **19e**



The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography using 100% hexane followed by hexane / ethyl acetate (1/1) to give the (*S*)-2-(6-methoxynaphthalene-2-yl)propan-1-ol as a white solid. (*S*)-Ethyl naproxen (500 mg, 1.94 mmol, 1 equiv., 99.8 % ee) gave 450 mg product (2.08 mmol, 90 %).
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.74 (2H, t, J = 8.9 Hz, $C_{Ar}H^{4',8'}$), 7.64 (1H, s, $C_{Ar}H^{1'}$), 7.37 (1H, d, J = 7.7 Hz, $C_{Ar}H^{3'}$), 7.16 (2H, m, $C_{Ar}H^{7'}$), 3.94 (3H, s, -OCH_3), 3.80 (2H, d, J = 7.1 Hz, -C$\underline{H}_2{}^1$OH), 3.12 (1H, m, C$\underline{H}^2$(CH_3)-), 1.38 (3H, d, J = 7.2 Hz, -C$\underline{H}_3{}^3$);
^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 157.23 ($\underline{C}^{6'}{}_{Ar}$-$OCH_3$), 138.63 ($\underline{C}^{2'}{}_{Ar}$-CH), 133.55 ($\underline{C}^{4'a}{}_{Ar}$), 129.11($\underline{C}^{8'a}{}_{Ar}$), 129.03 ($\underline{C}^{8'}{}_{Ar}$), 127.24 ($\underline{C}^{3'}{}_{Ar}$), 126.27 ($\underline{C}^{4'}{}_{Ar}$), 125.93 ($\underline{C}^{1'}{}_{Ar}$), 118.93 ($\underline{C}^{5',7'}{}_{Ar}$), 105.58 ($\underline{C}^{5'}{}_{Ar}$), 68.66 (-O$\underline{C}H_3$), 55.33 (-$\underline{C}^1H_2$OH), 42.39 (Ar$\underline{C}^2$H($CH_3$)), 17.66 (-$\underline{C}^3H_3$); HRMS (ES+): calculated for [$C_{41}H_{16}NaO_2{}^+$]: 239.1043 found: 239.1038;
$[\alpha]_D{}^{20}$: -19.1 (c. 1.00, $CHCl_3$) Lit.[29]: -17.9 (c.0.8, $CHCl_3$, 99.05:0.5 (*S*)); Chiral analysis was performed using a Chiralcel OD-H column using ^{n}hexane / isopropanol (96/4) mobile phase, flow 1.0 mL/min; t_R (S-enantiomer, major): 18.1 min; t_R (R-enantiomer, minor): 19.2 min, *er* 97:3 (*S*).
Fits with previously published data[29]

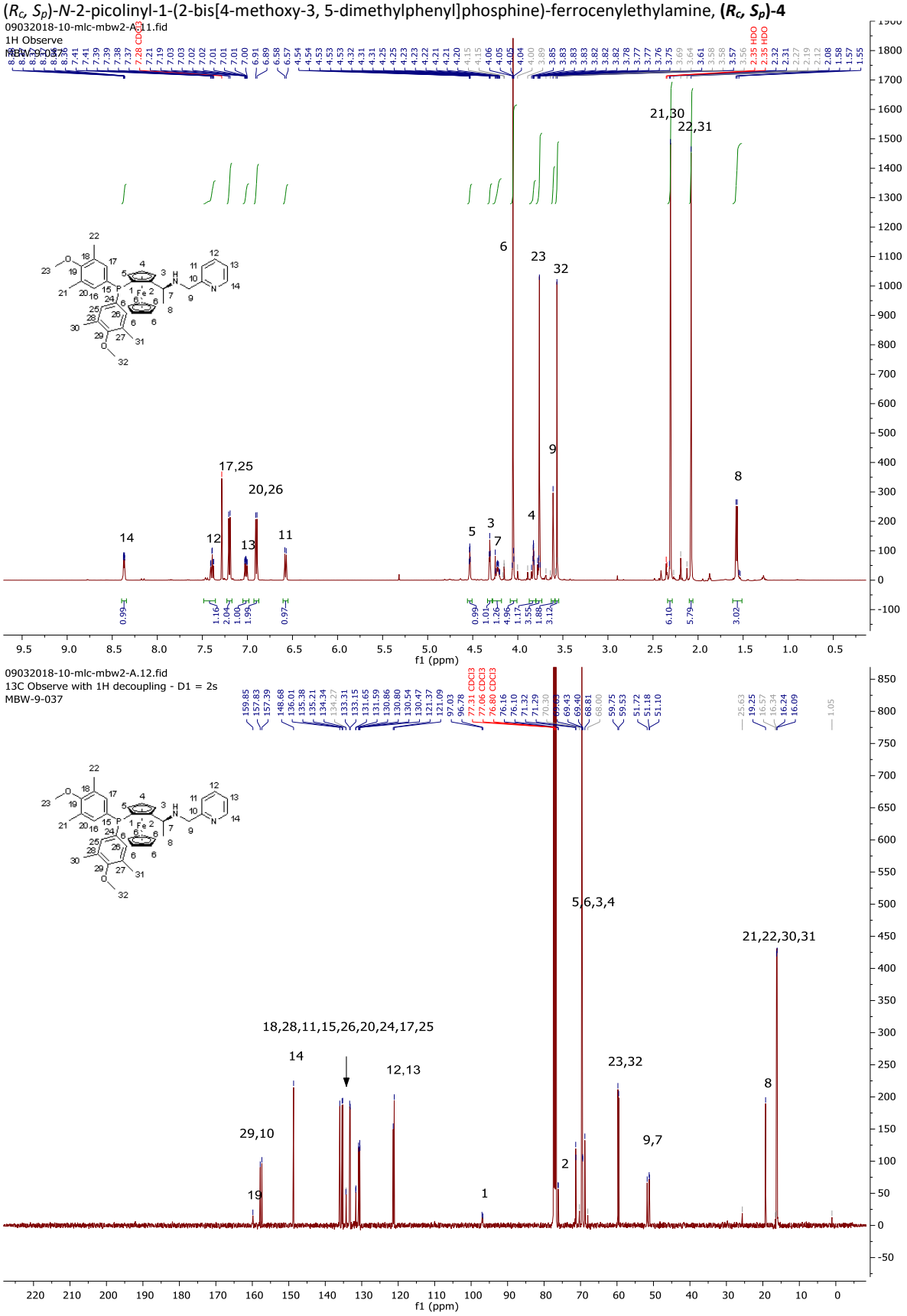
4-iodobenzyl alcohol, **19f**

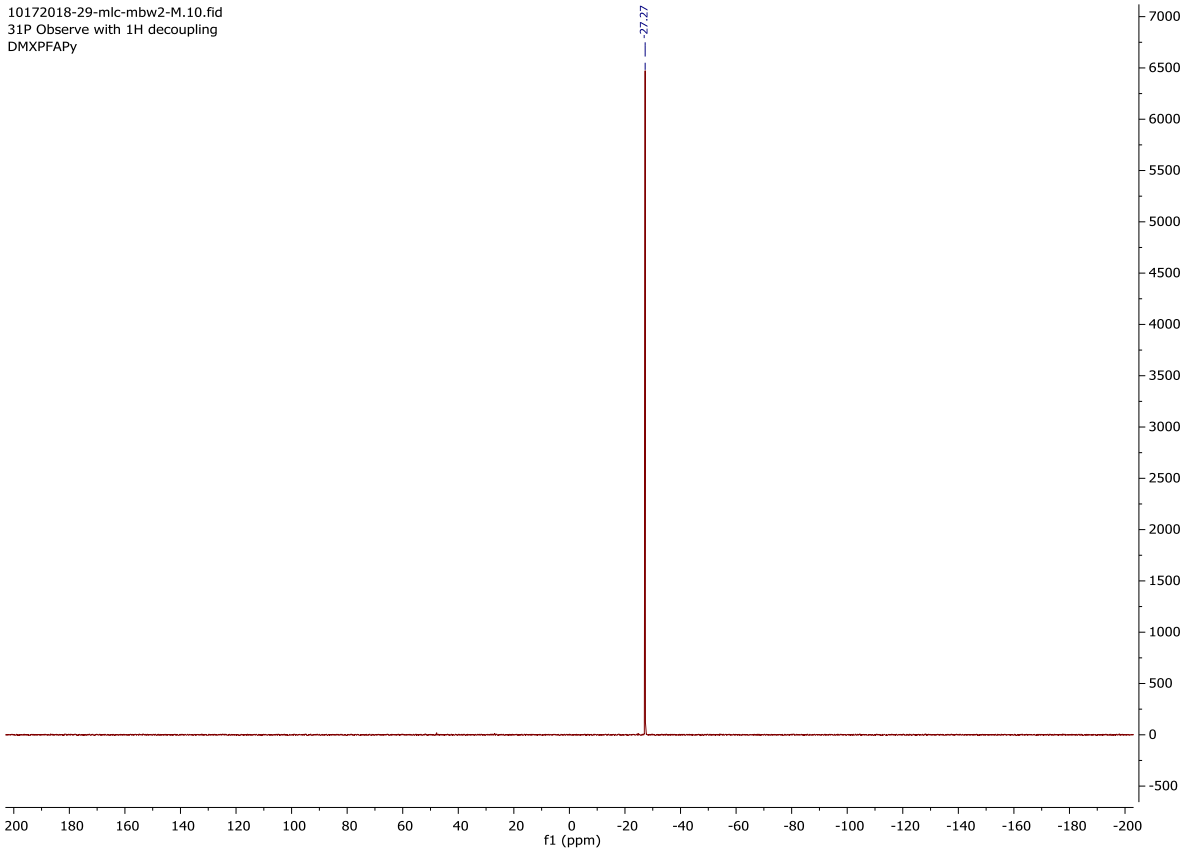


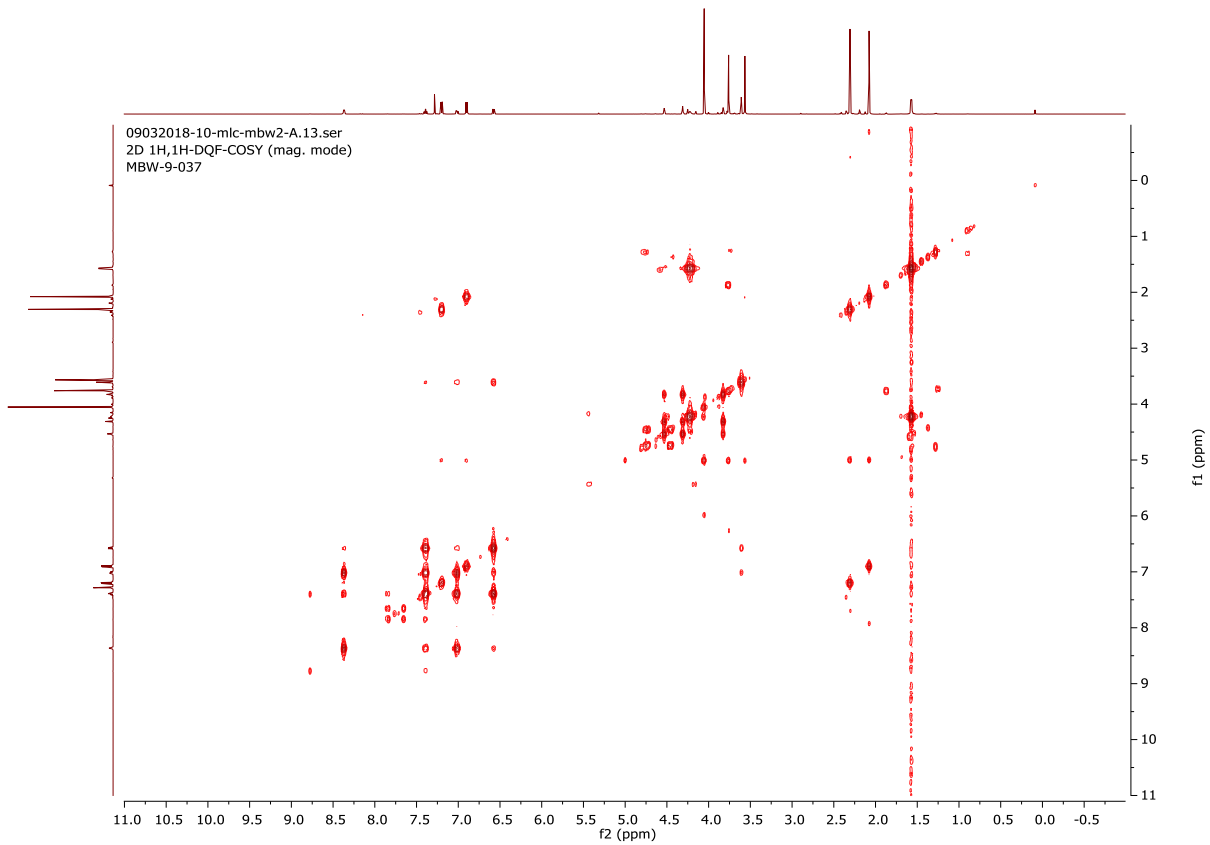
The product was purified by column chromatography using 100 % hexane followed by hexane / ethyl acetate (1/1) to give the title compound as a white solid. 400 mg (1.45 mmol) ethyl p-iodobenzoate gave 305 mg (1.31 mmol) p-iodobenzyl alcohol (90 %);
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.71 (2H, d, J = 8.5 Hz, $C_{Ar}H^{2',6'}$), 7.13 (2H, d, J = 8.5 Hz, $C_{Ar}H^{3',5'}$), 4.62 (2H, s, Ar-C$\underline{H}_2{}^1$OH); 1.90 (1H, s, -O$\underline{H}$); ^{13}C -{^{1}H}-NMR (100 MHz, $CDCl_3$) δ: 140.42 ($\underline{C}^{1'}{}_{Ar}$-$CH_2$OH), 137.60 ($\underline{C}^{2',6'}{}_{Ar}$), 128.62 ($\underline{C}^{3',5'}{}_{Ar}$), 93.02 (I-$\underline{C}^{4'}{}_{Ar}$), 64.67 (Ar-$\underline{C}^1H_2$OH); HRMS (EI+): calculated for [C_7H_7IO]: 233.9542, found: 233.9541.
Fits with previously reported data.[30]

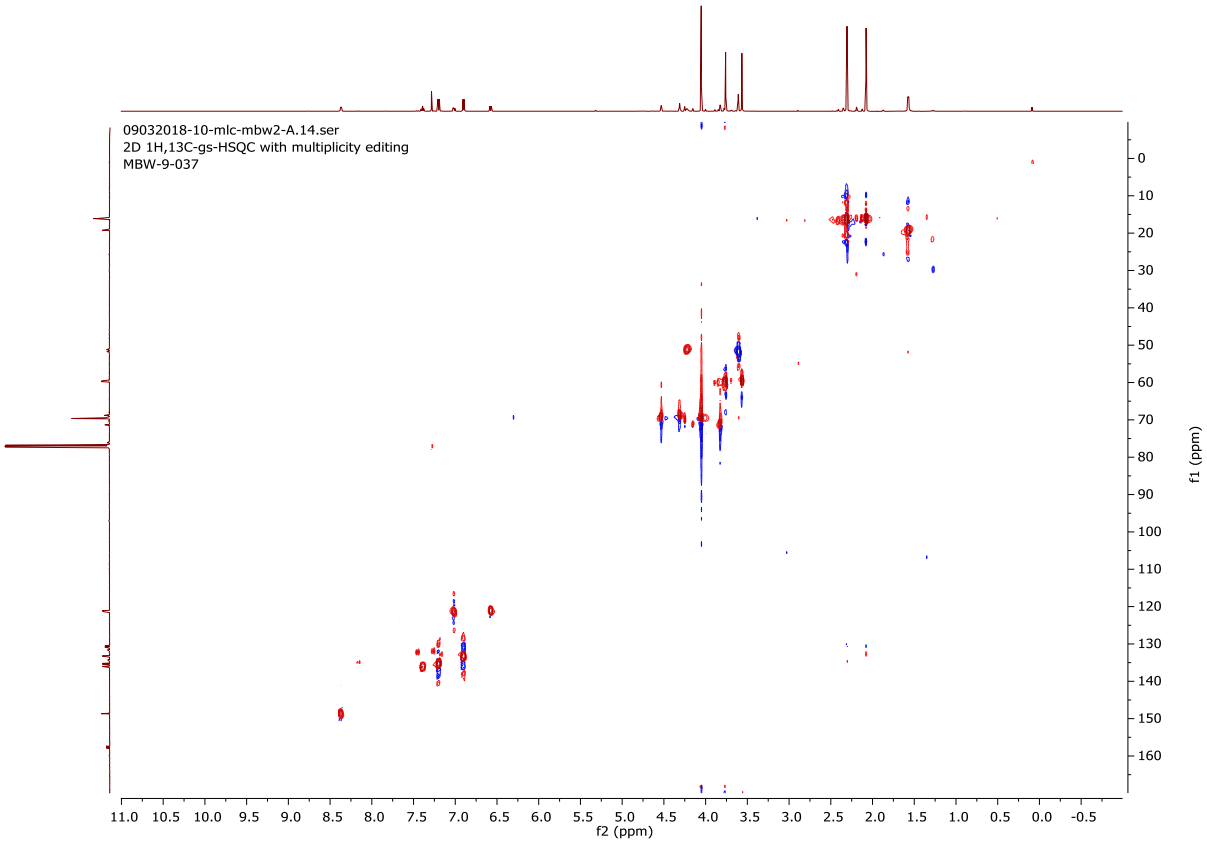
4. Spectra

(R_c, S_p)-*N*-2-picolinyl-1-(2-bis[4-methoxy-3, 5-dimethylphenyl]phosphine)-ferrocenylethylamine, **(R_c, S_p)-4**

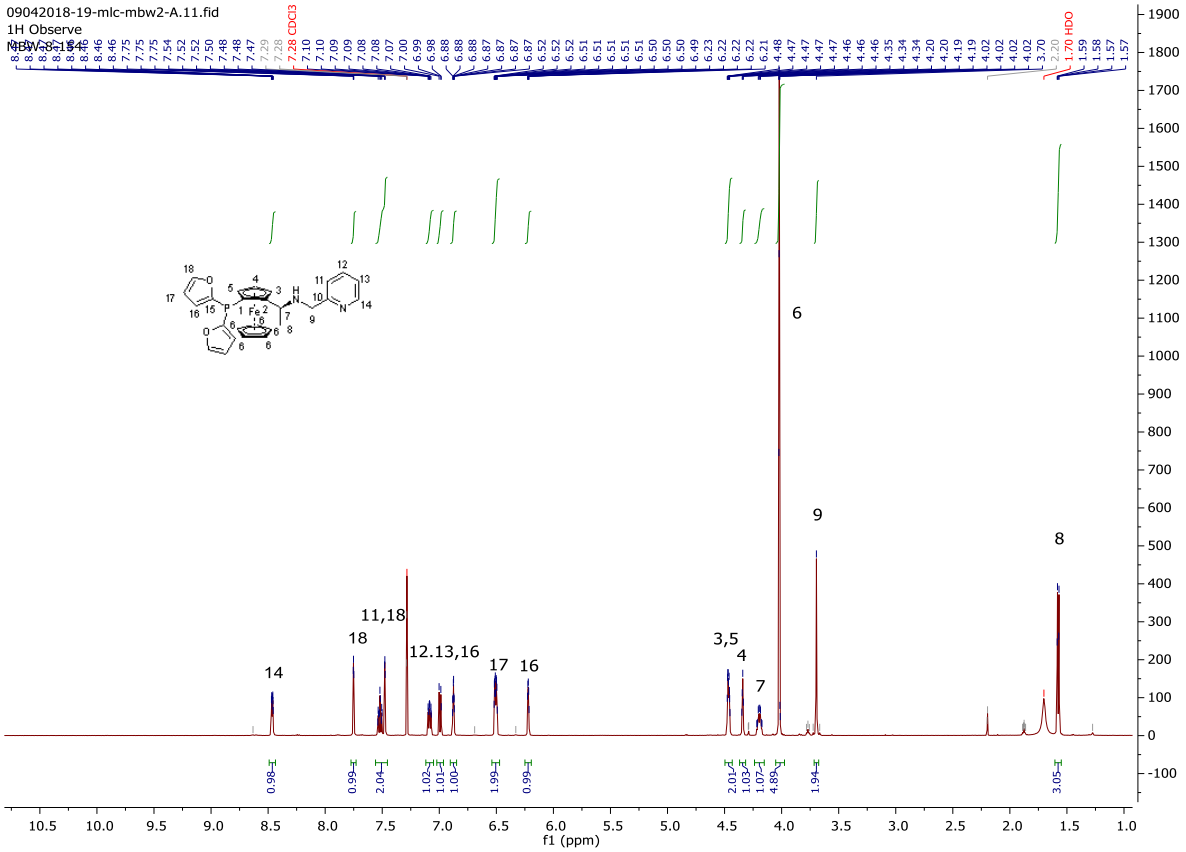


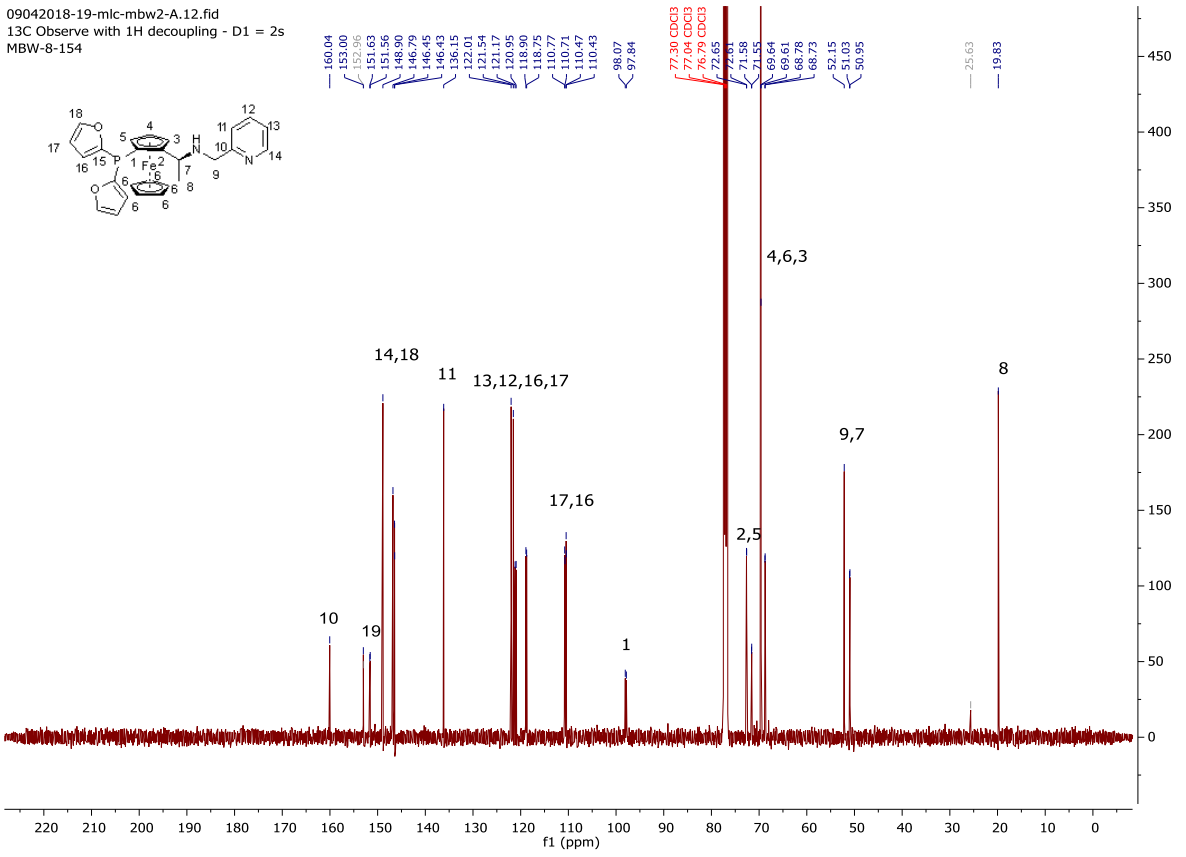

10172018-29-mlc-mbw2-M.10.fid
31P Observe with 1H decoupling
DMXPFAPy
-27.27
f1 (ppm)

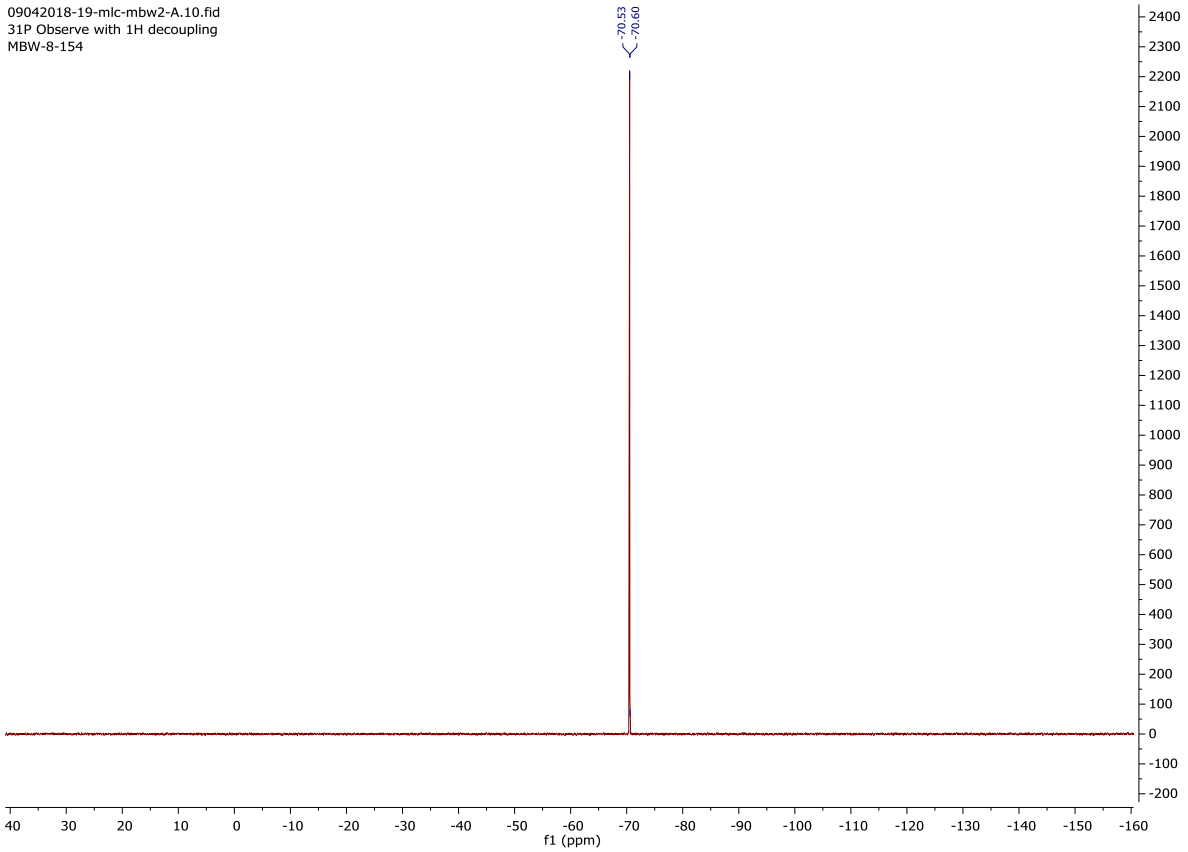

09032018-10-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-9-037
f2 (ppm)
f1 (ppm)

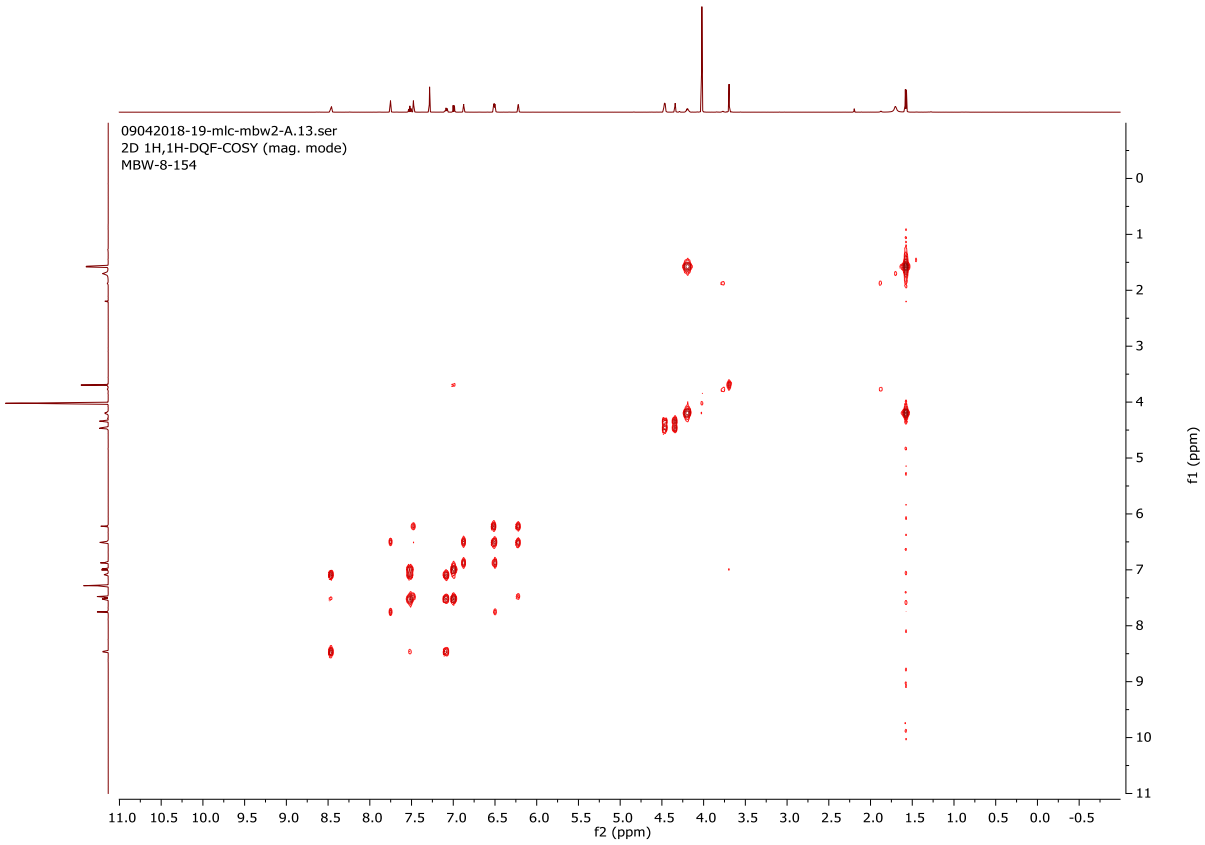

09032018-10-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-9-037
f1 (ppm)
f2 (ppm)

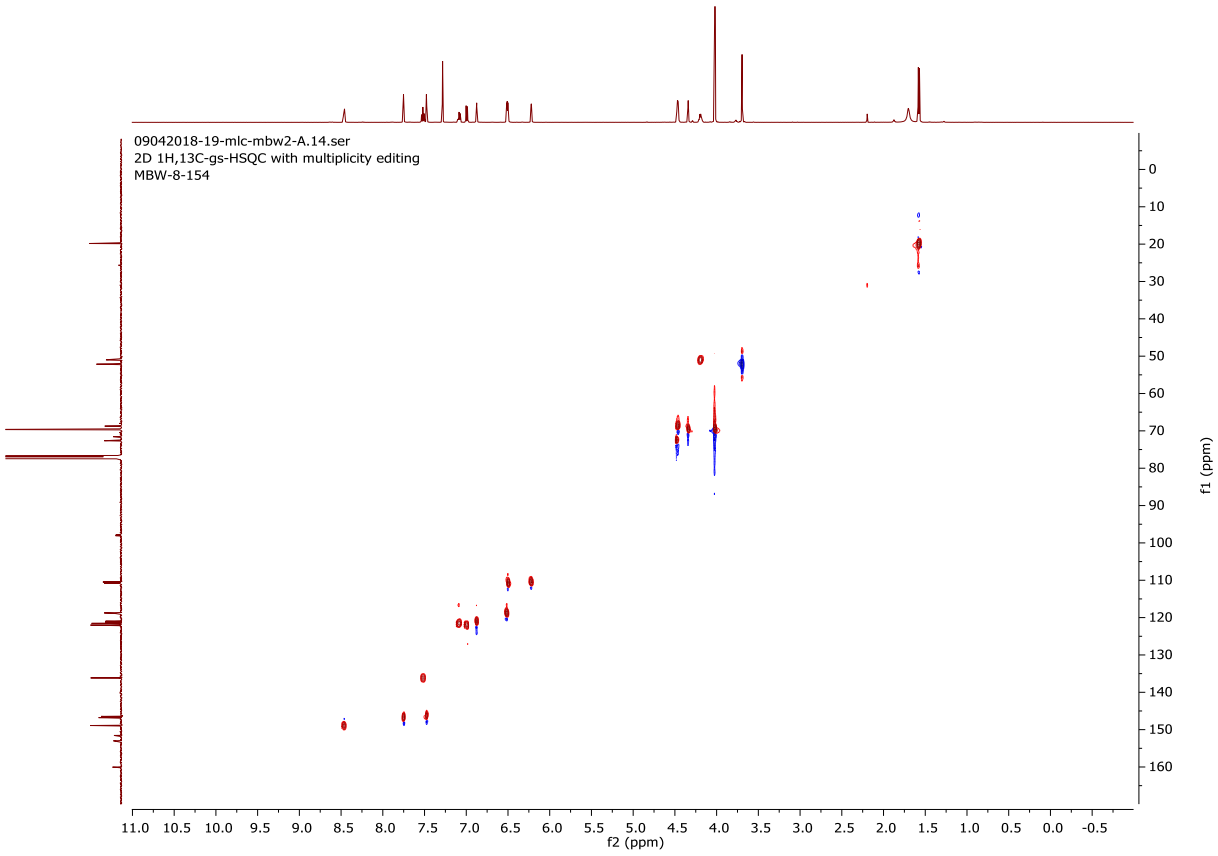
(R_c, S_p)-*N*-2-picolinyl-1-(2-di[furan-2-yl]phosphine)ferrocenylethylamine, **(R_c, S_p)-5**



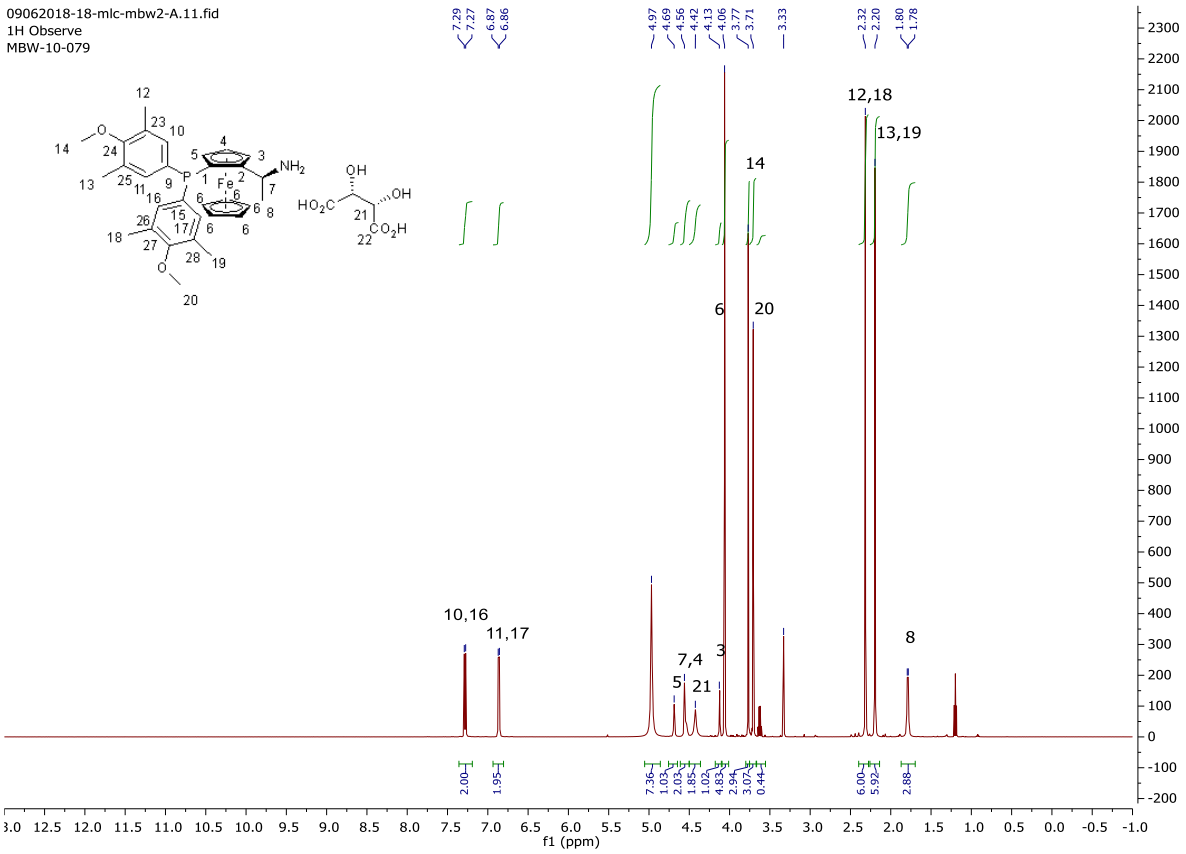


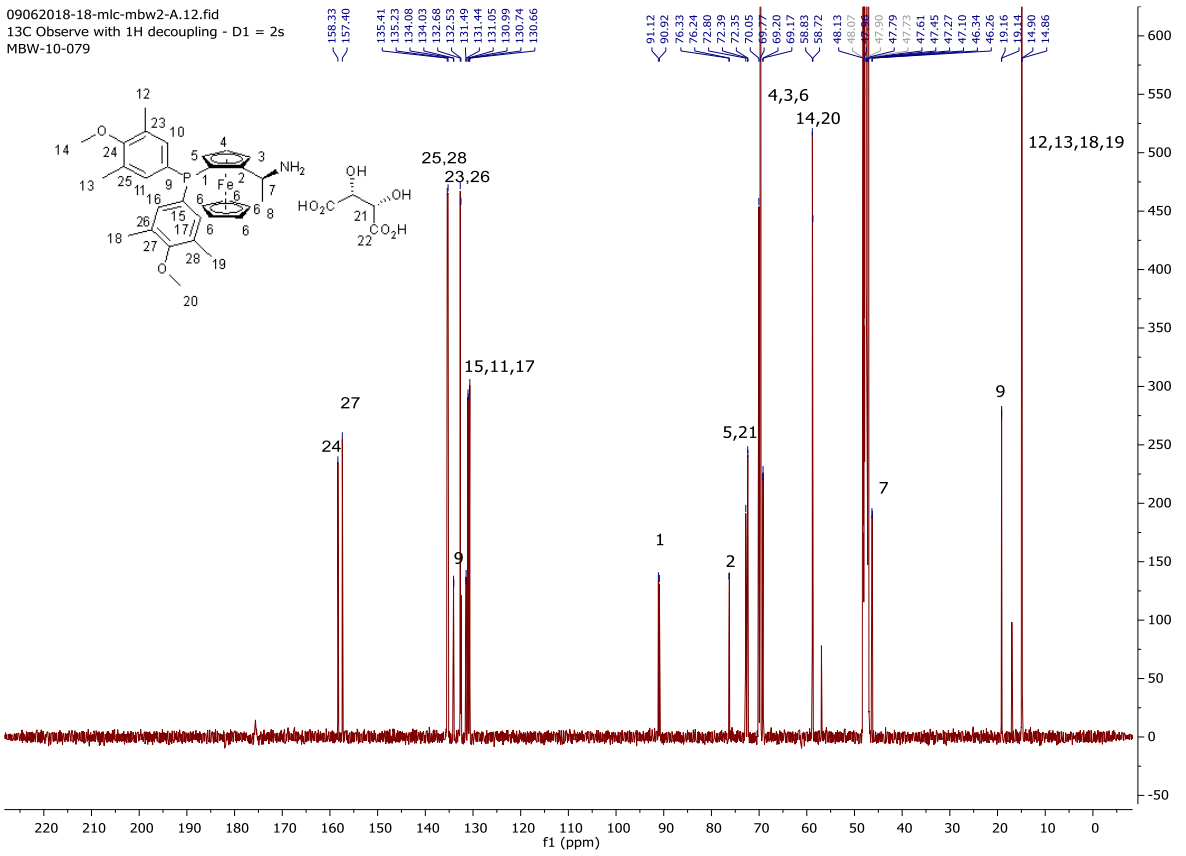

09042018-19-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-8-154
-70.53
-70.60
f1 (ppm)

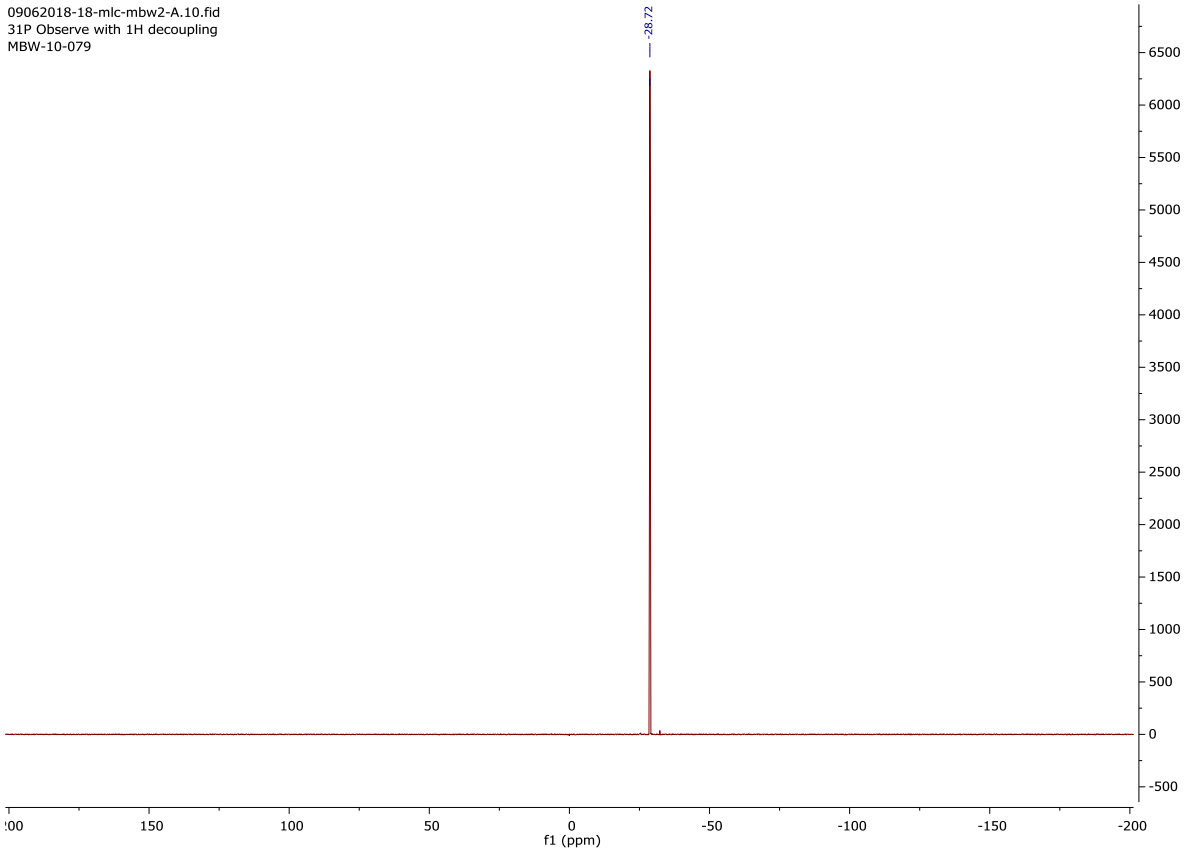

09042018-19-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-8-154
f2 (ppm)
f1 (ppm)

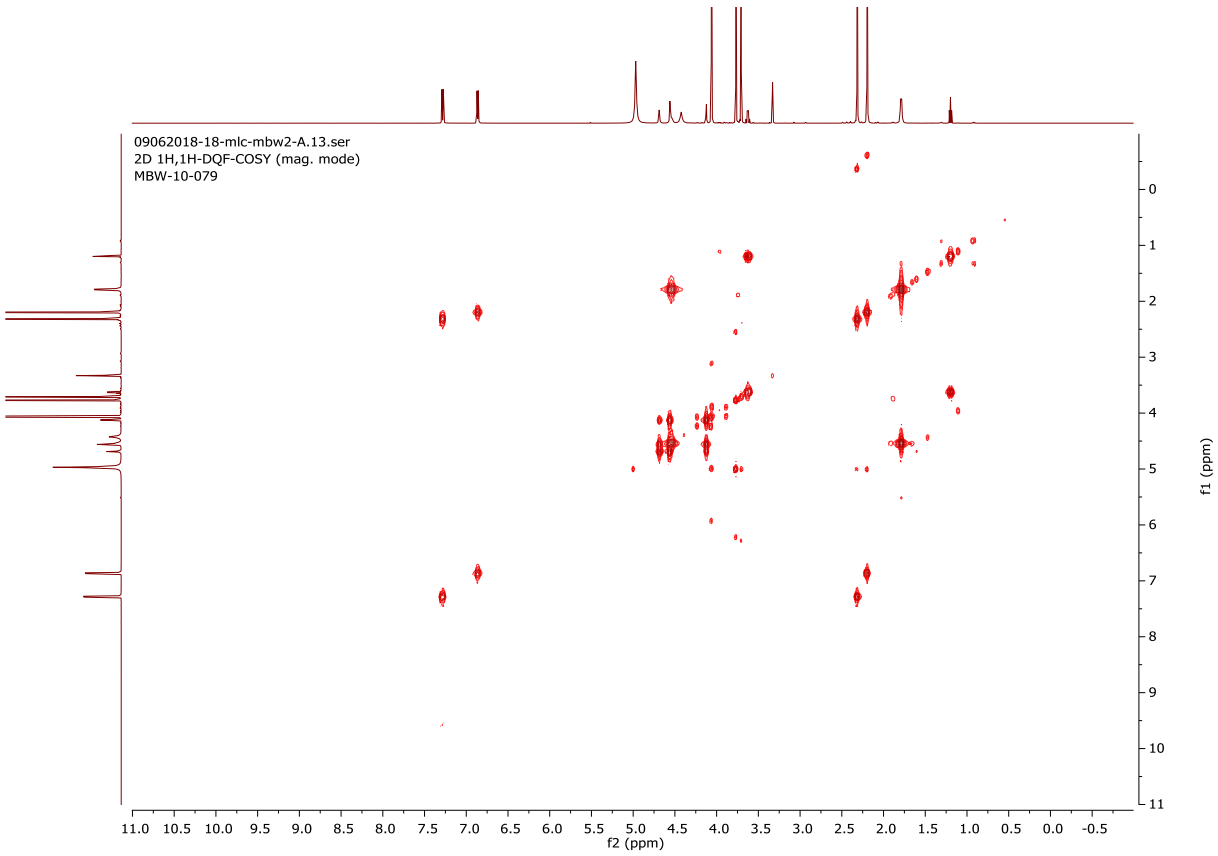

09042018-19-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-8-154
f1 (ppm)
f2 (ppm)

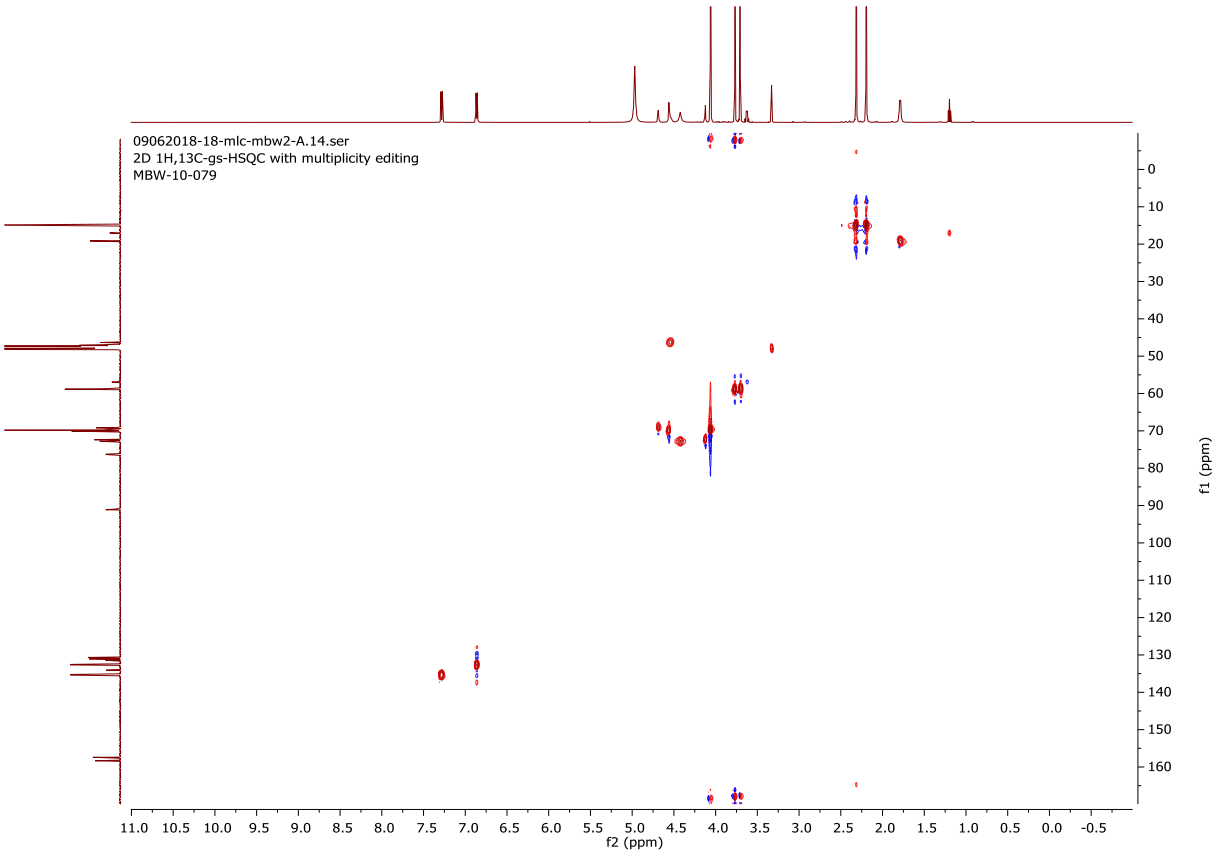
(R_c, S_p)-1-(2-bis[4-methoxy-3, 5-dimethylphenyl]phosphine)ferrocenylethylamine L-tartrate salt



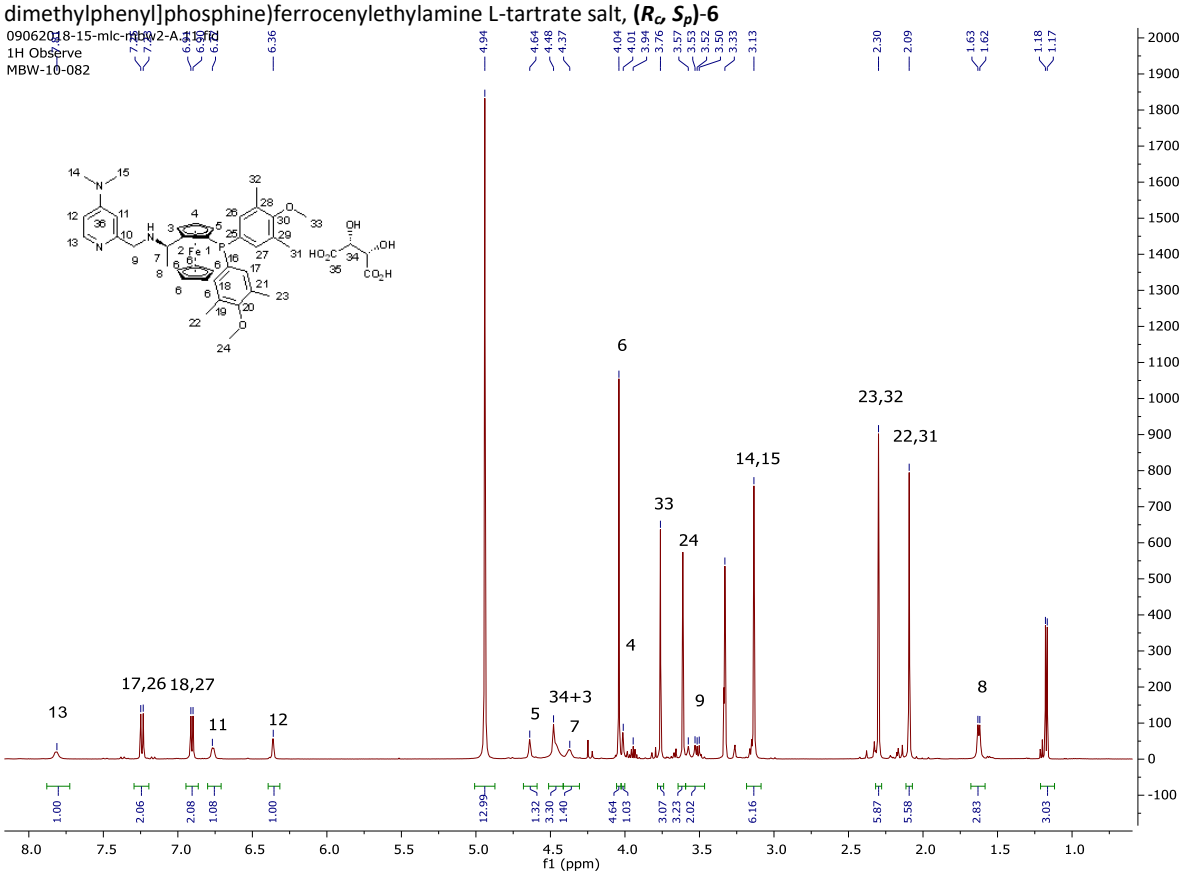


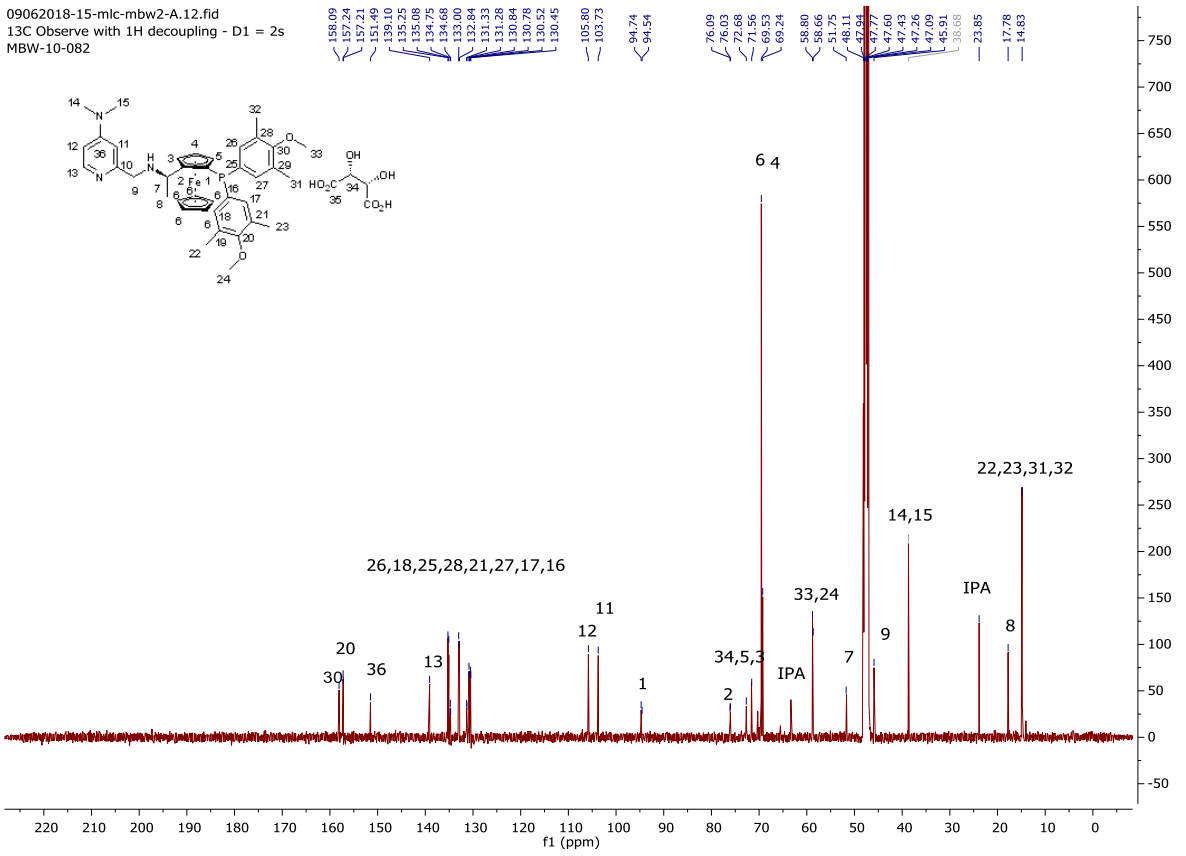

09062018-18-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-10-079
-28.72
f1 (ppm)

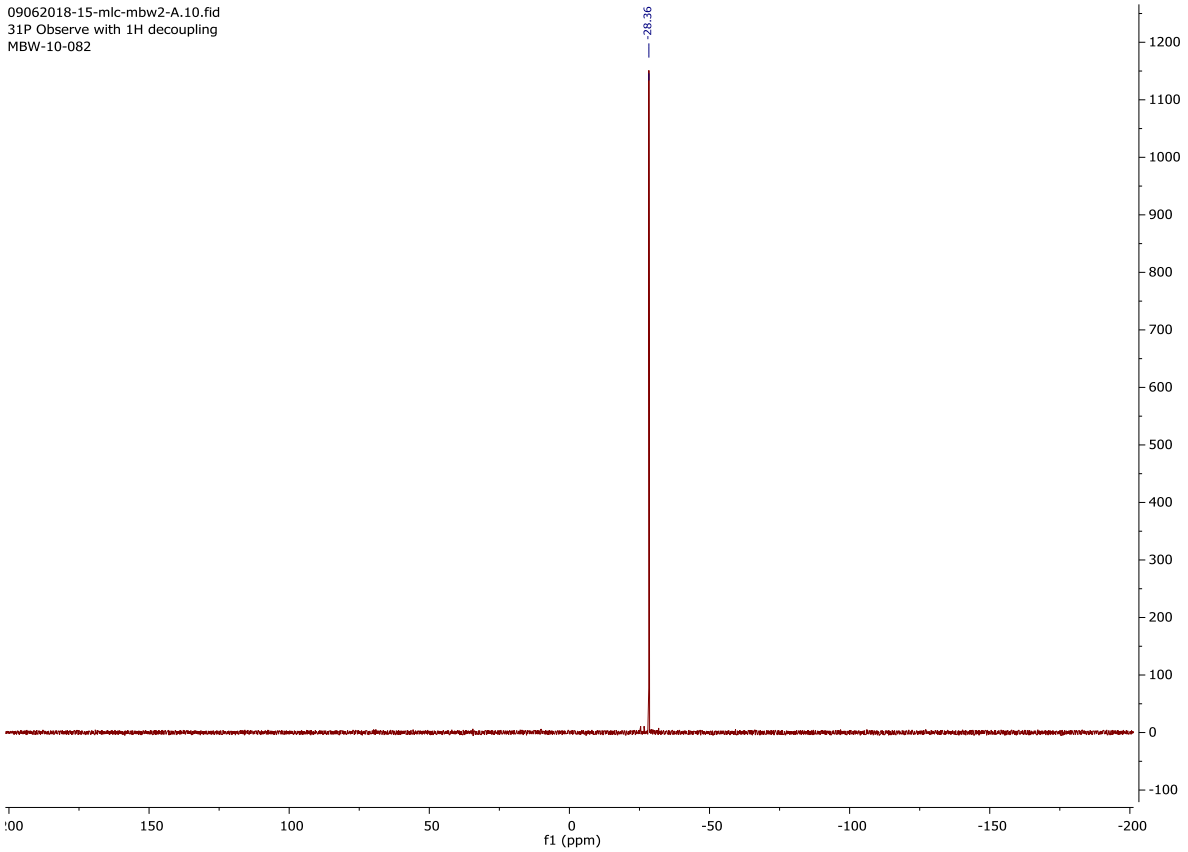

09062018-18-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-10-079
f2 (ppm)
f1 (ppm)

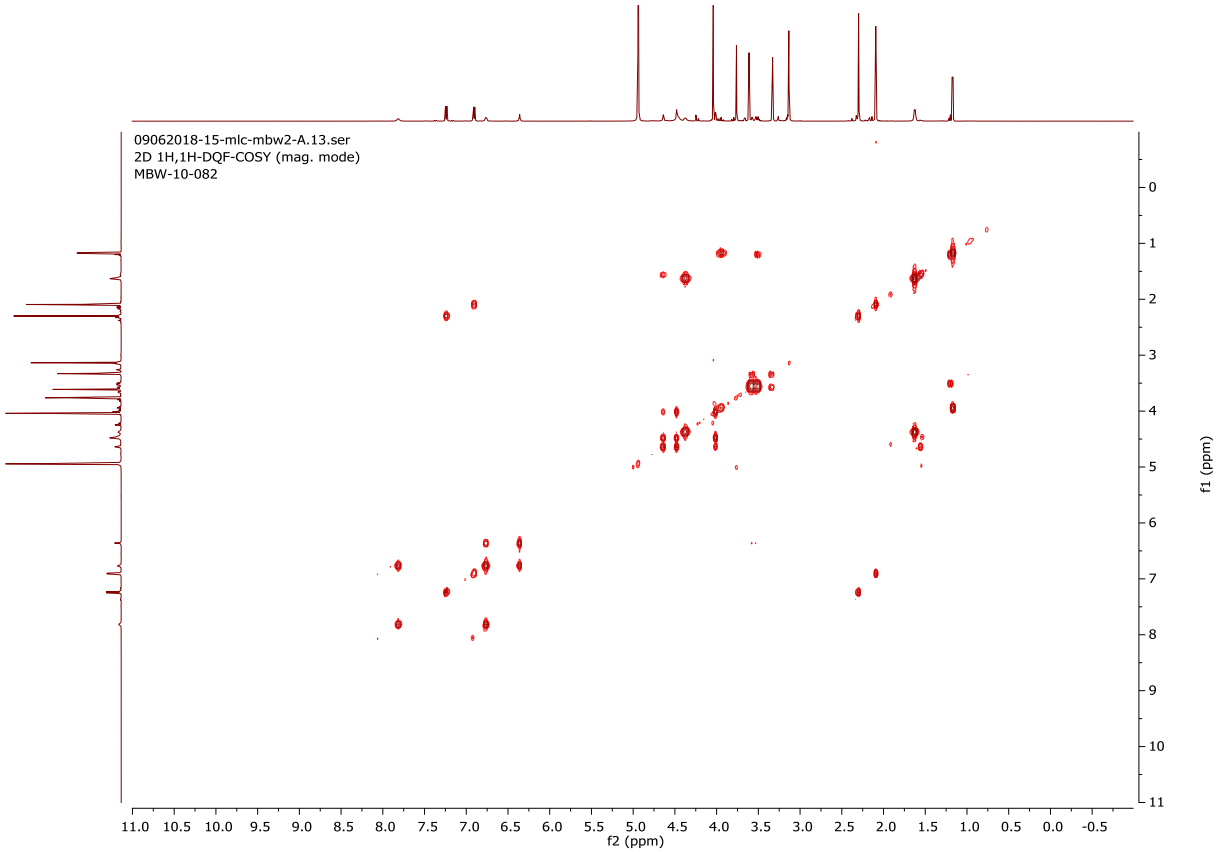

09062018-18-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-10-079
f2 (ppm)
f1 (ppm)

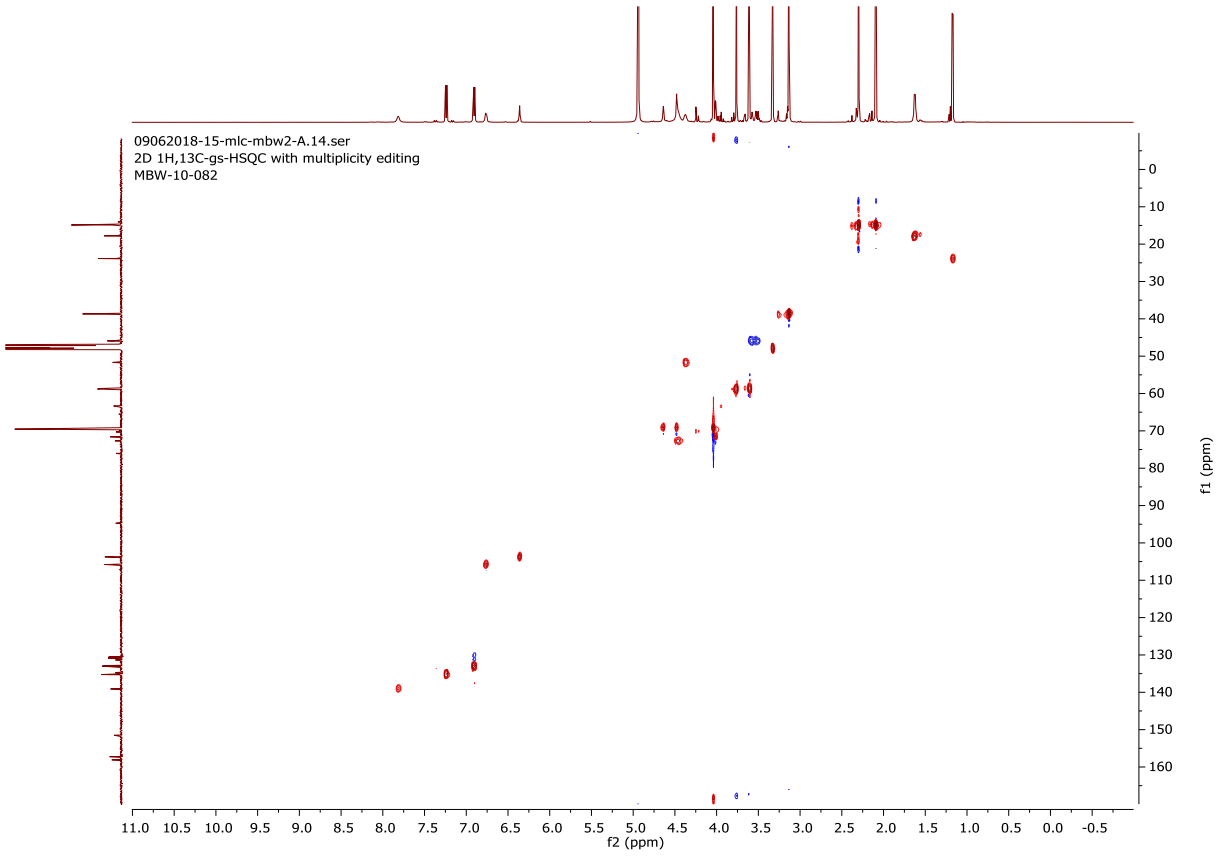
(R_c, S_p) – *N* - [4-(dimethylamino)pyridine-2-methyl]-1-(2-bis[4-methoxy- 3, 5-dimethylphenyl]phosphine)ferrocenylethylamine L-tartrate salt, **(R_c, S_p)-6**



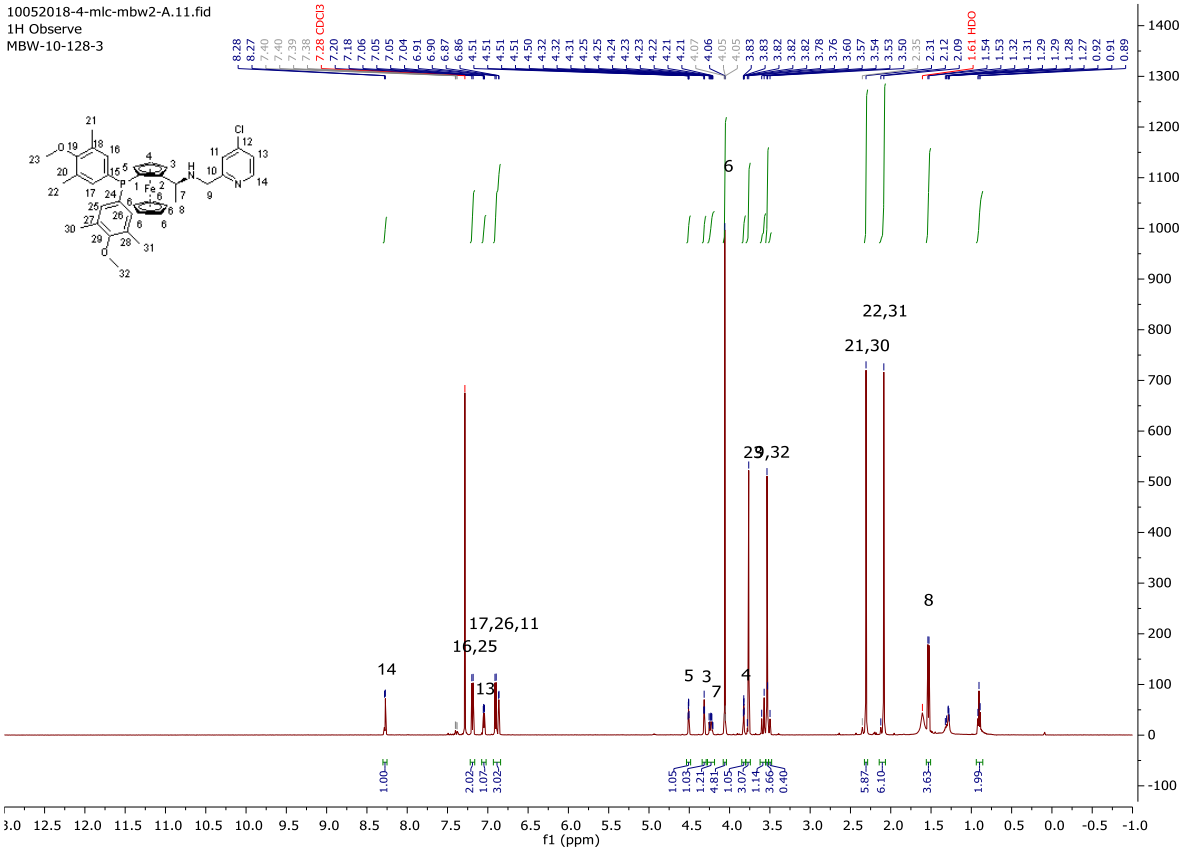


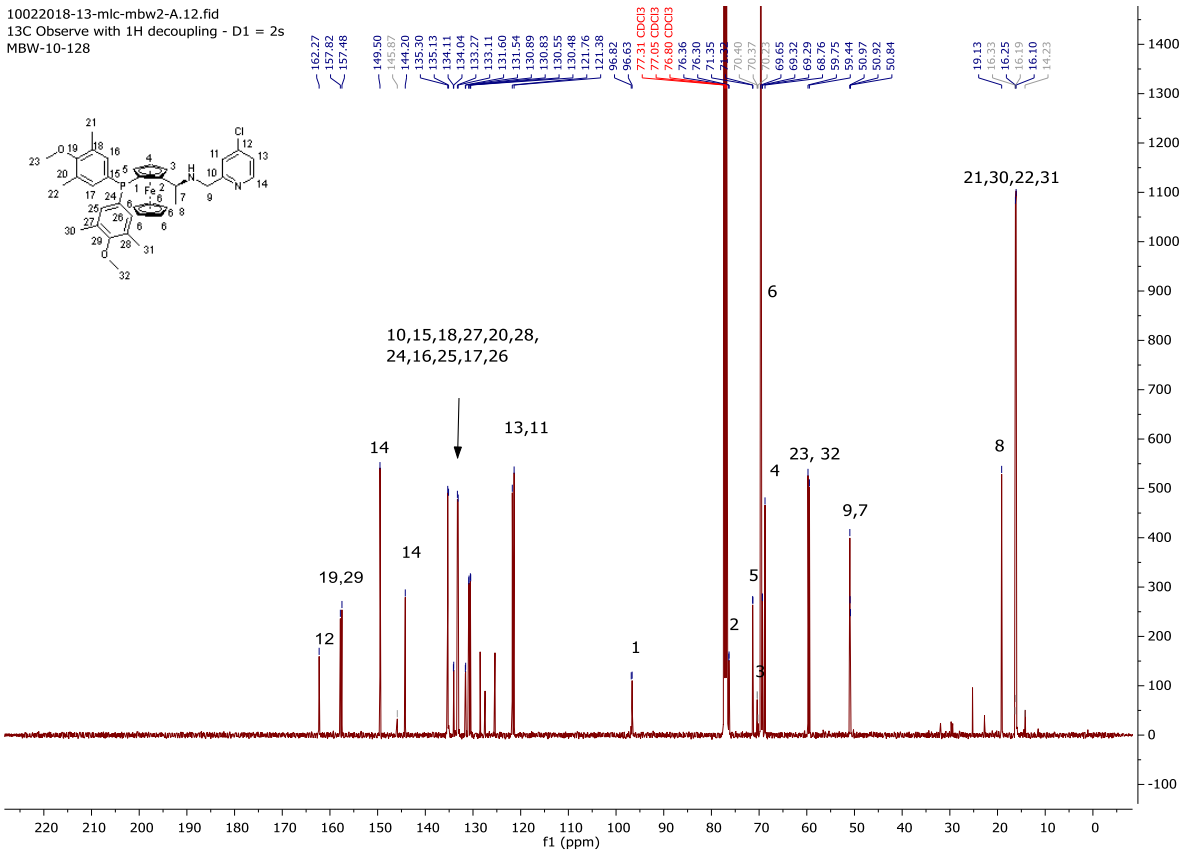

09062018-15-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-10-082
-28.36
f1 (ppm)

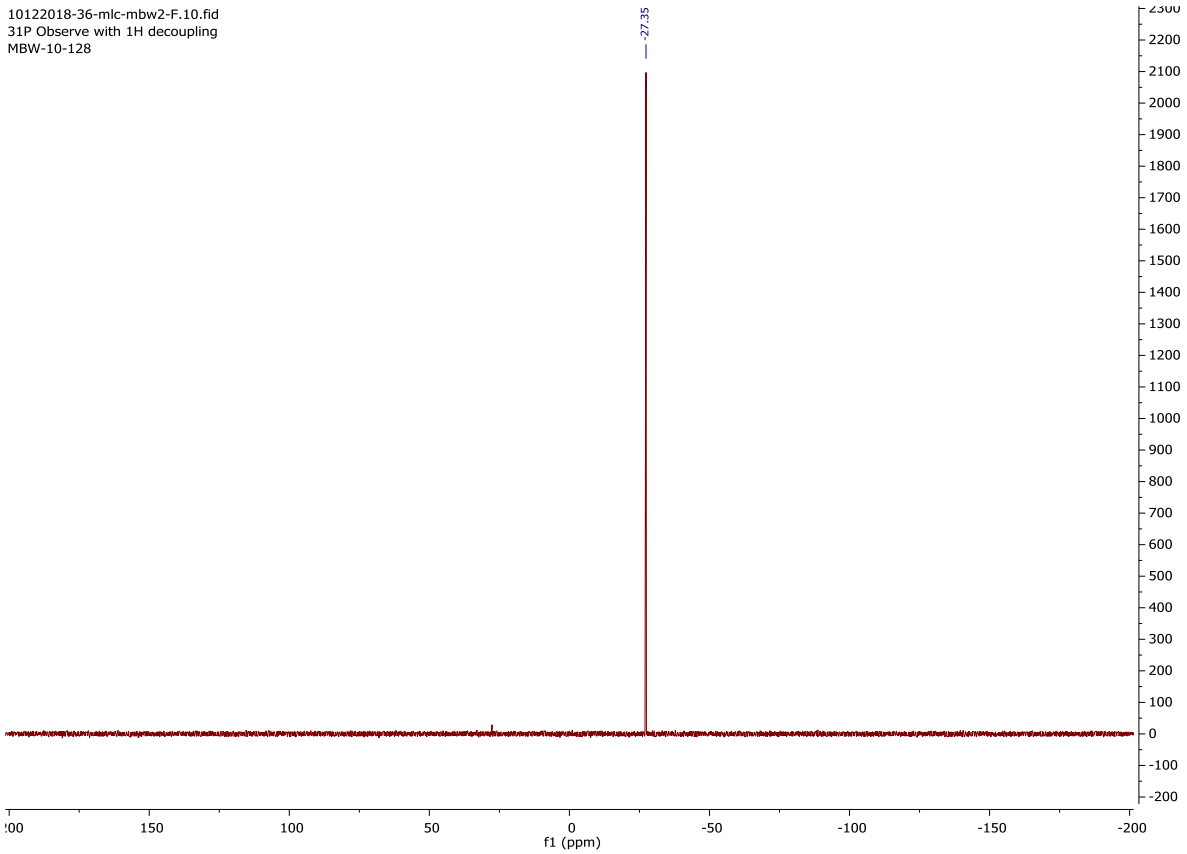

09062018-15-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-10-082
f2 (ppm)
f1 (ppm)

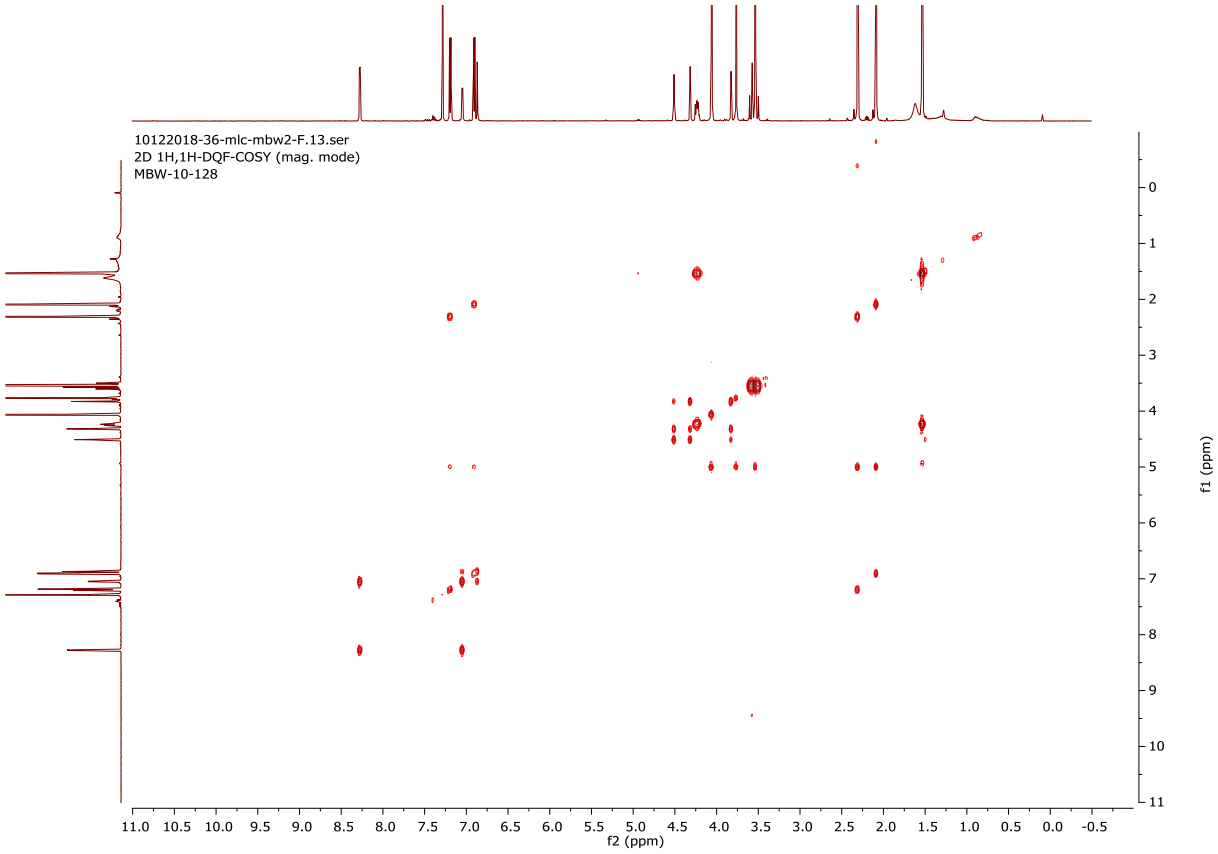

09062018-15-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-10-082
f2 (ppm)
f1 (ppm)

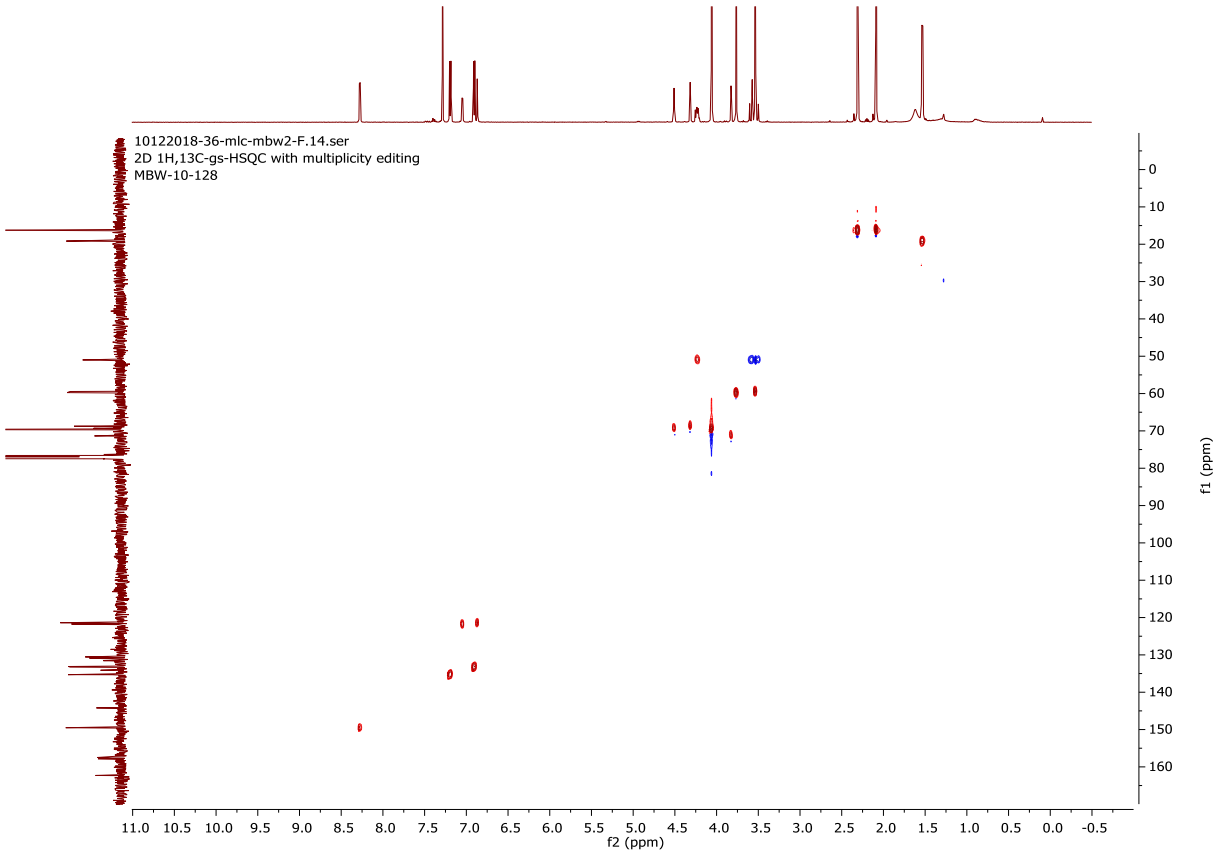
(R_c, S_p) -*N*- [4-chloropyridine-2-methyl)-1-(2-bis[4-methoxy- 3, 5- dimethylphenyl)phosphine]-ferrocenylethylamine, **(R_c, S_p)-7**



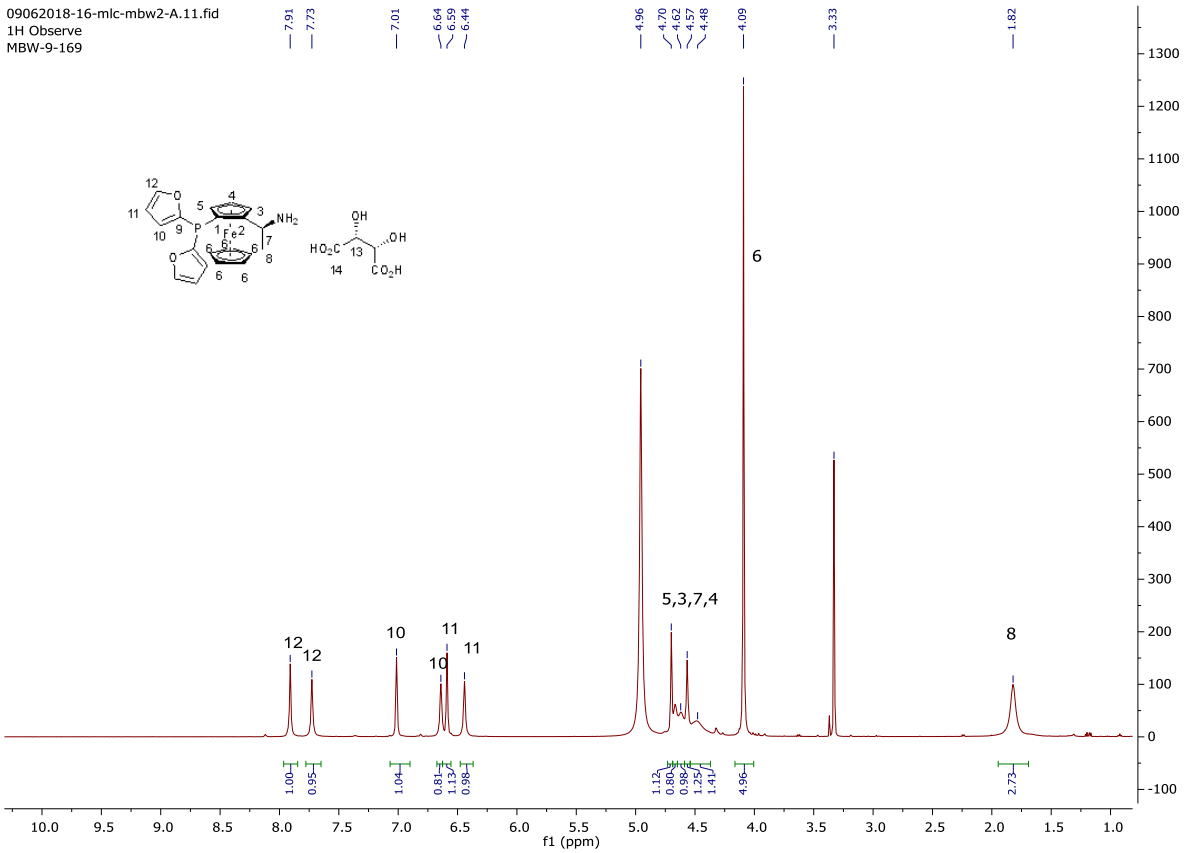


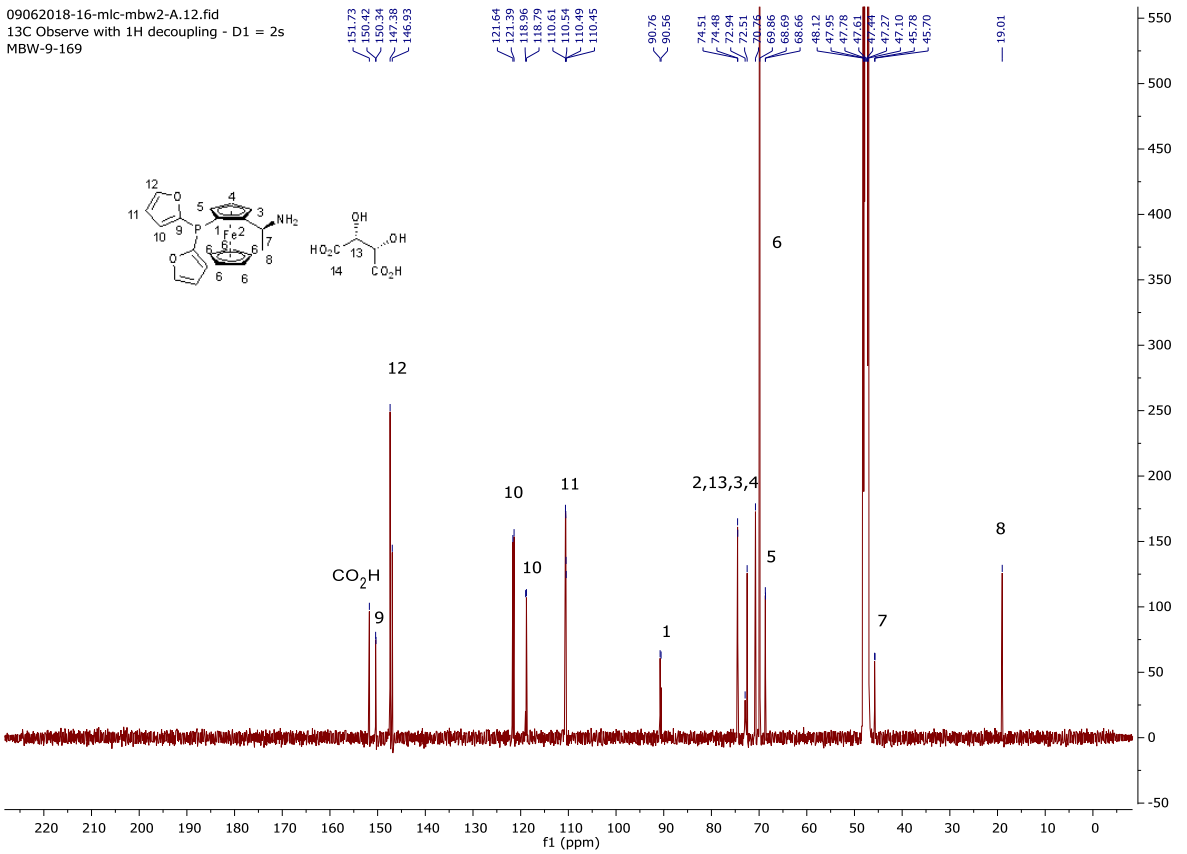

10122018-36-mlc-mbw2-F.10.fid
31P Observe with 1H decoupling
MBW-10-128
-27.35
f1 (ppm)

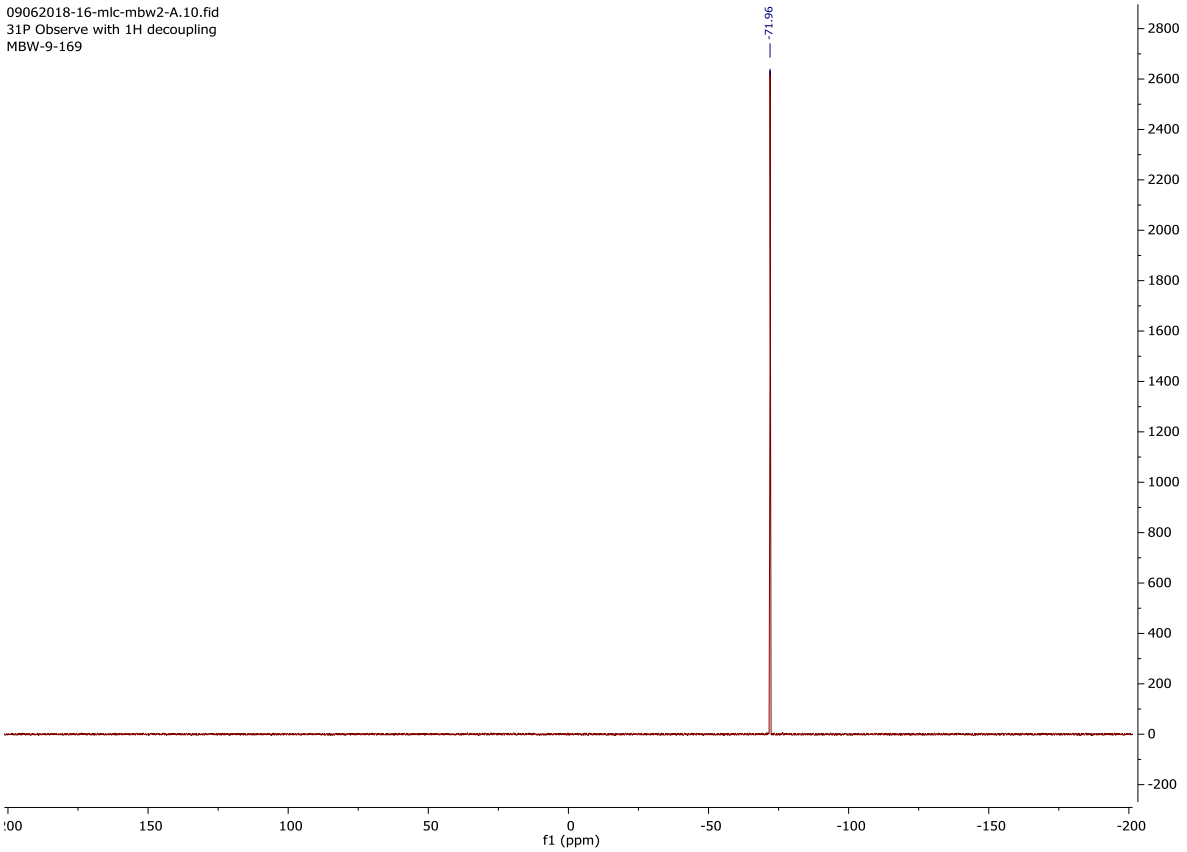

10122018-36-mlc-mbw2-F.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-10-128
f2 (ppm)
f1 (ppm)

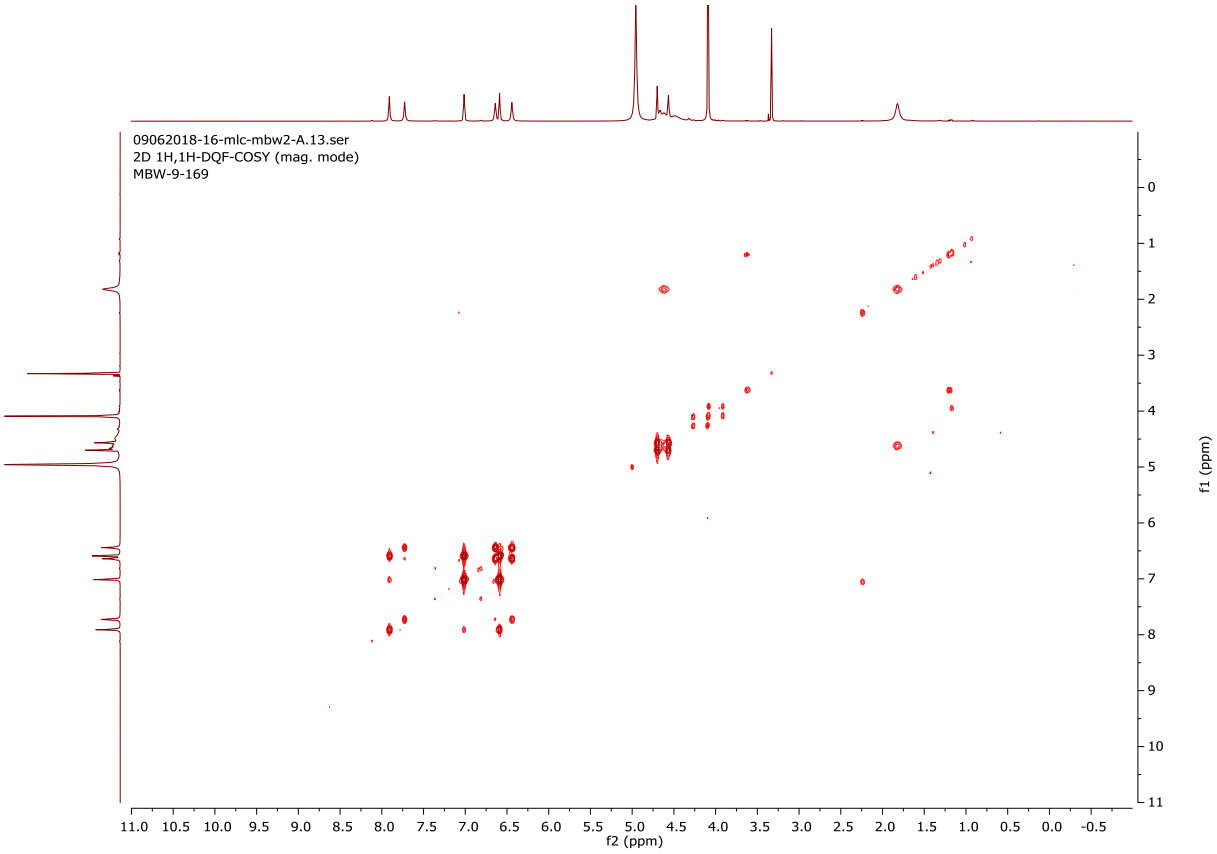

10122018-36-mlc-mbw2-F.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-10-128
f2 (ppm)
f1 (ppm)

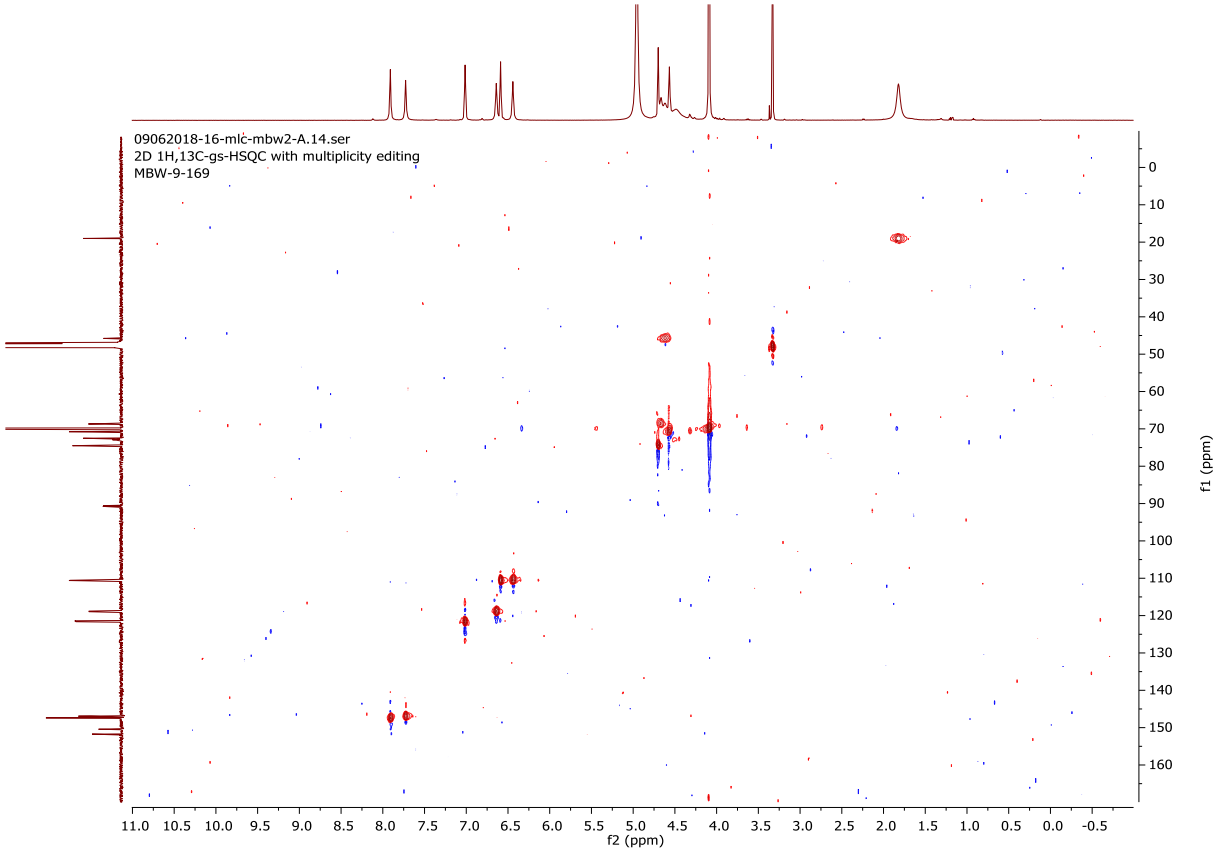
(R_c, S_p)-1-(2-di[2-furanyl]phosphine)ferrocenylethylamine L-tartrate



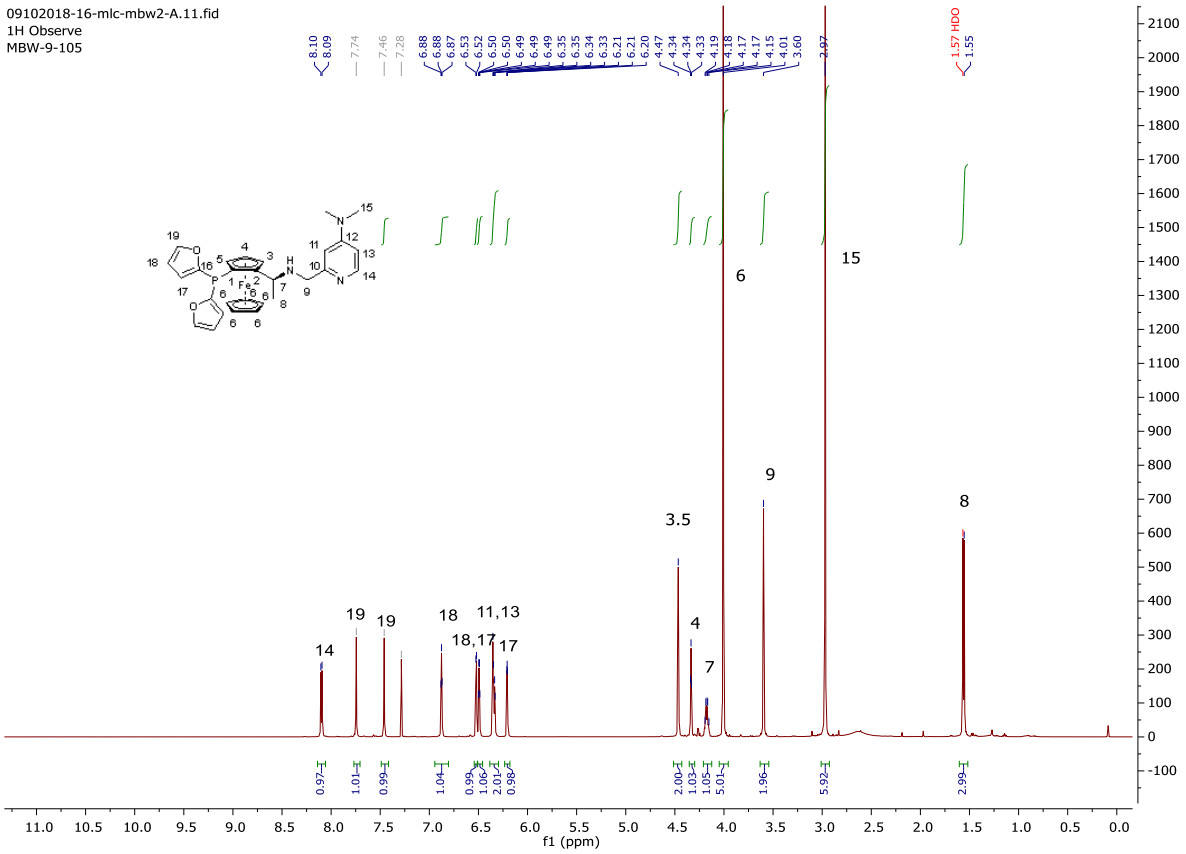


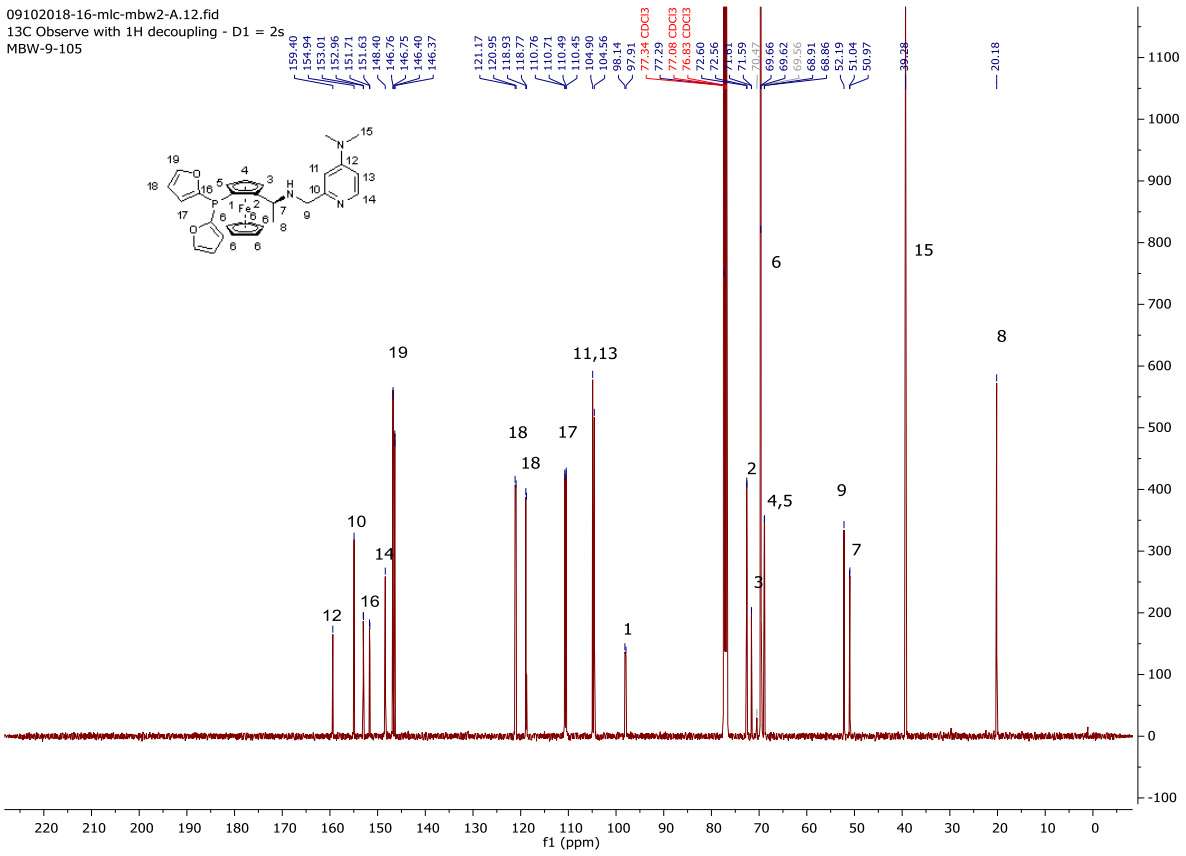

09062018-16-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-9-169
-71.96
f1 (ppm)

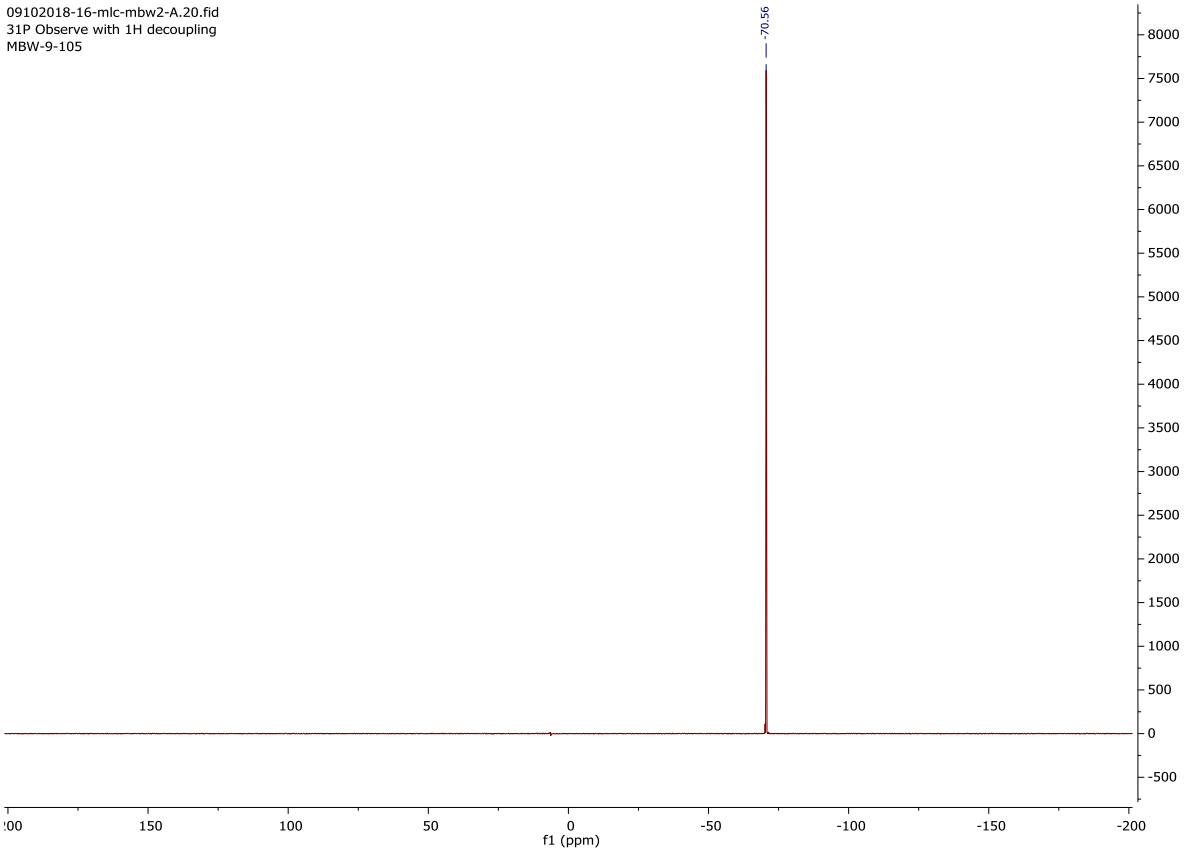

09062018-16-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-9-169
f2 (ppm)
f1 (ppm)

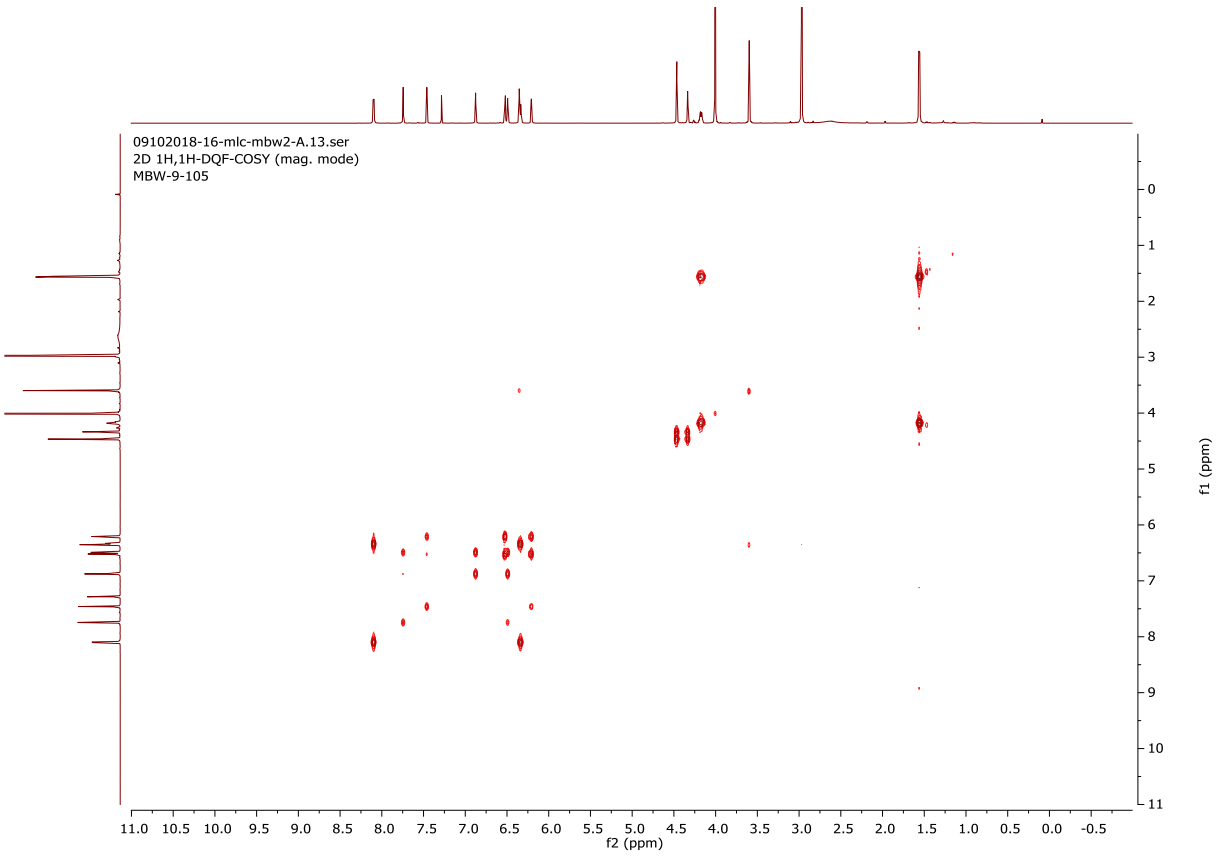

09062018-16-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-9-169
f2 (ppm)
f1 (ppm)

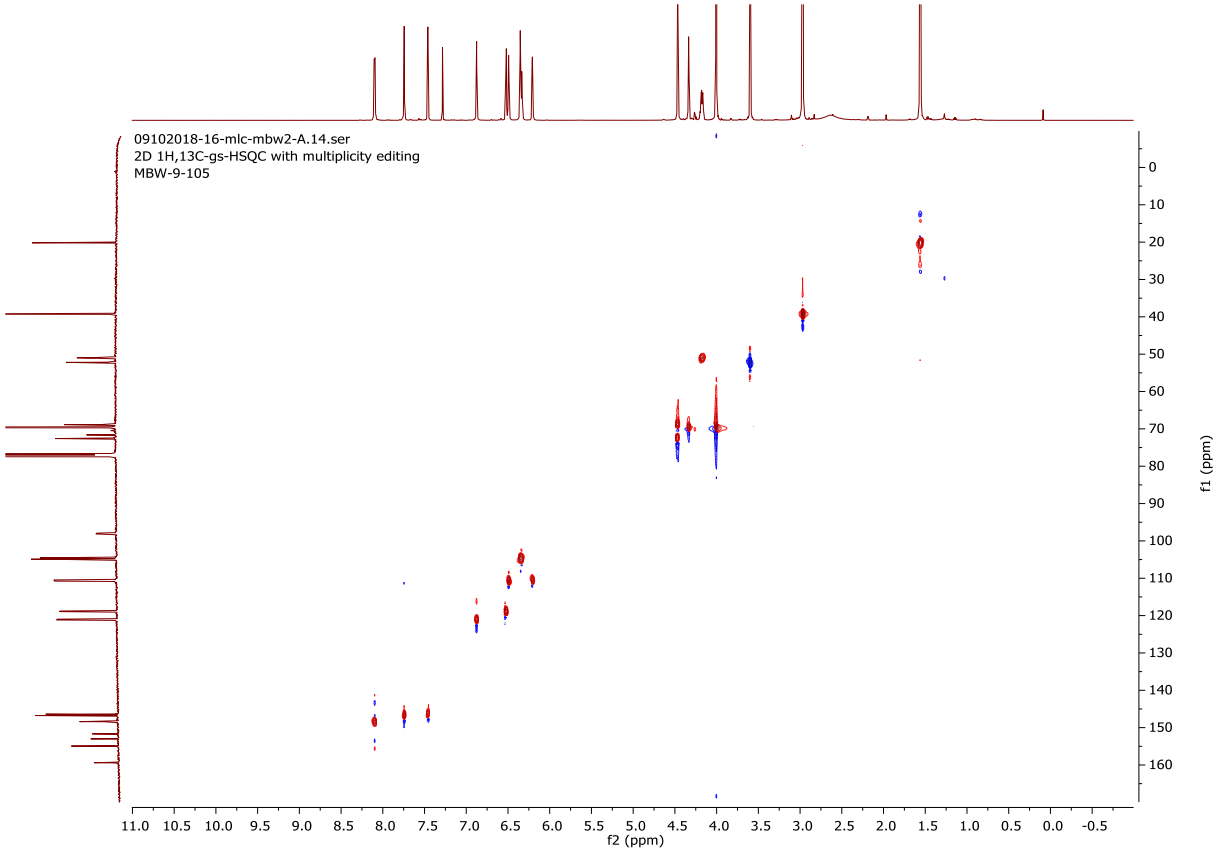
(R_c, S_p)-*N*-[4-(dimethylamino)pyridine-2-methyl)-1-(2-di[2-furanyl]phosphine)ferrocenylethylamine, **(R_c, S_p)-8**



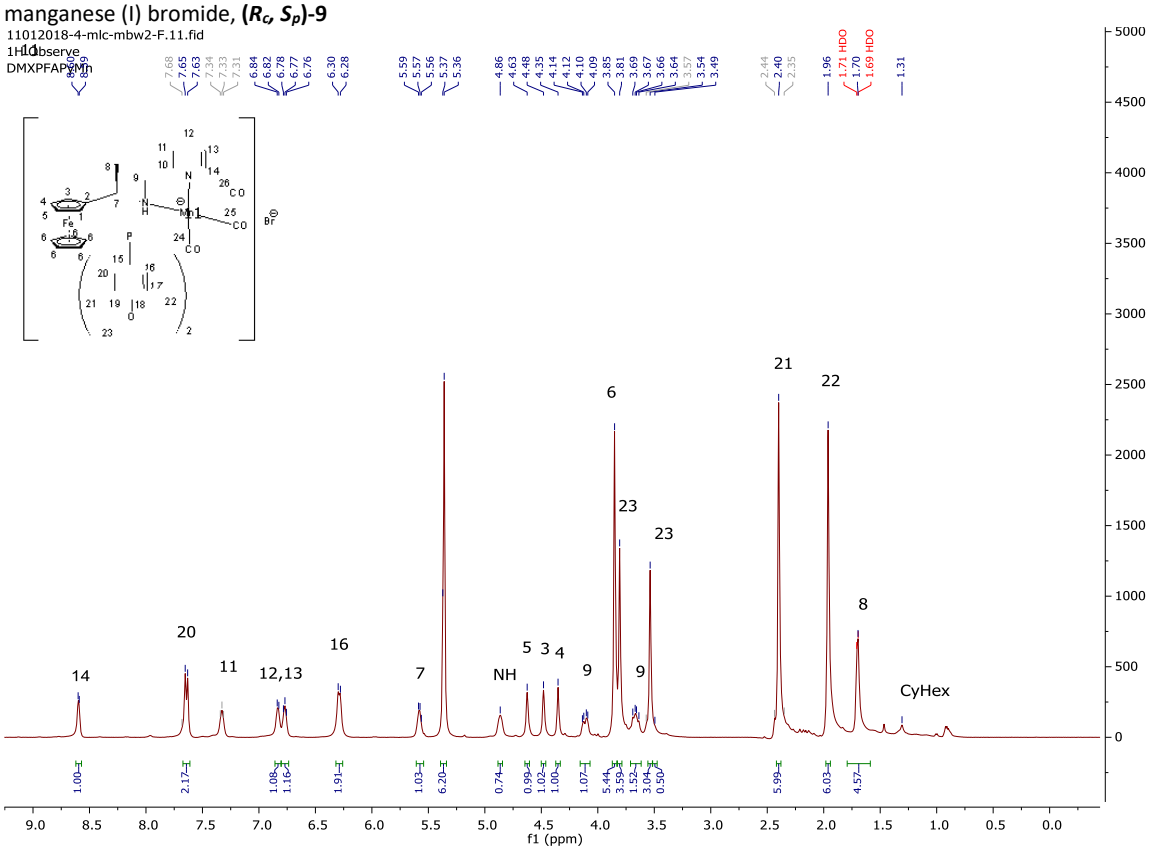


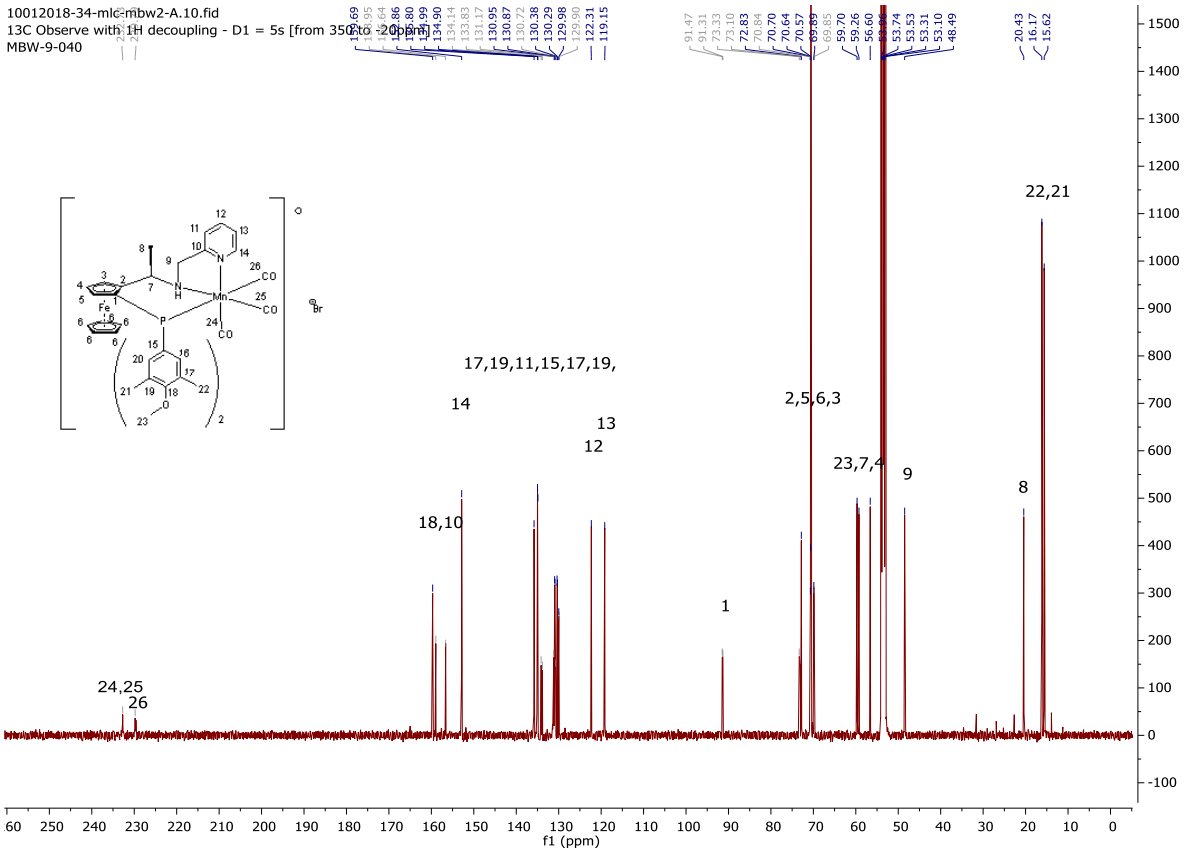

09102018-16-mlc-mbw2-A.20.fid
31P Observe with 1H decoupling
MBW-9-105
-70.56
f1 (ppm)

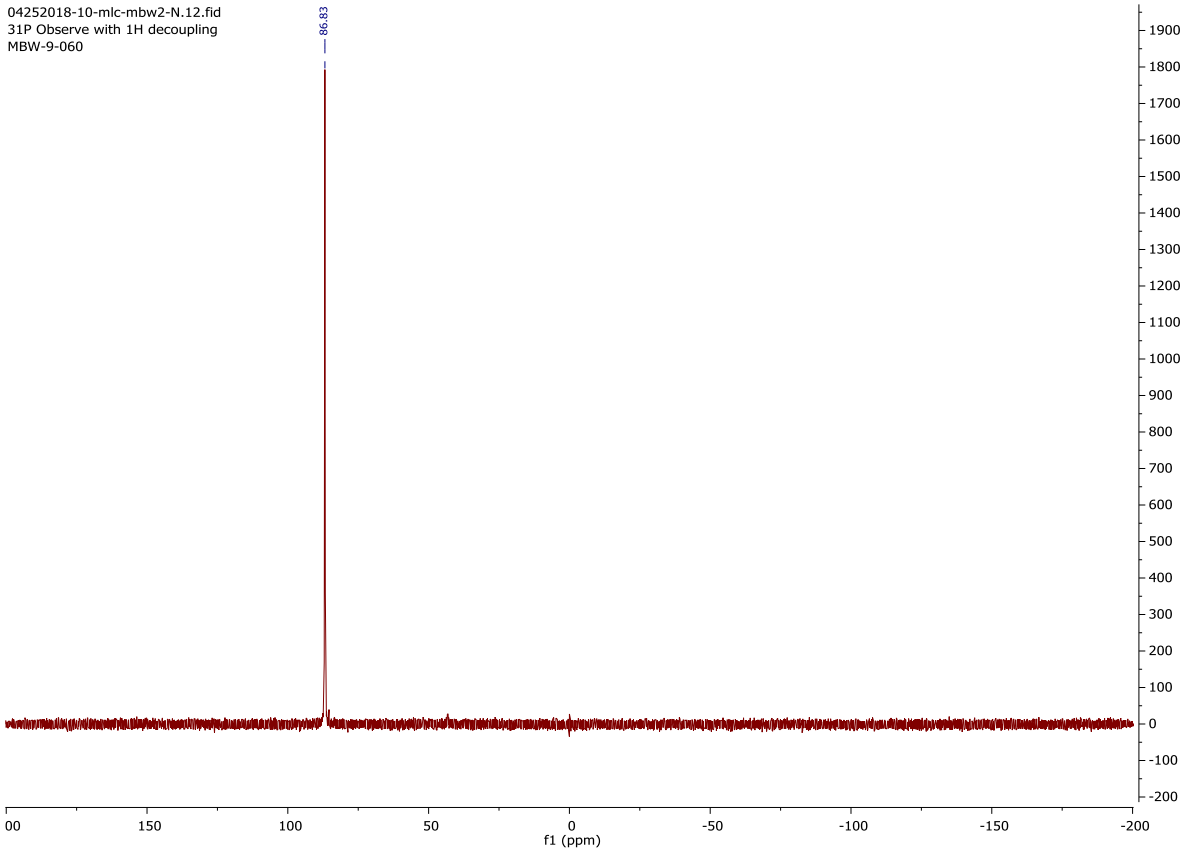

09102018-16-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-9-105
f2 (ppm)
f1 (ppm)

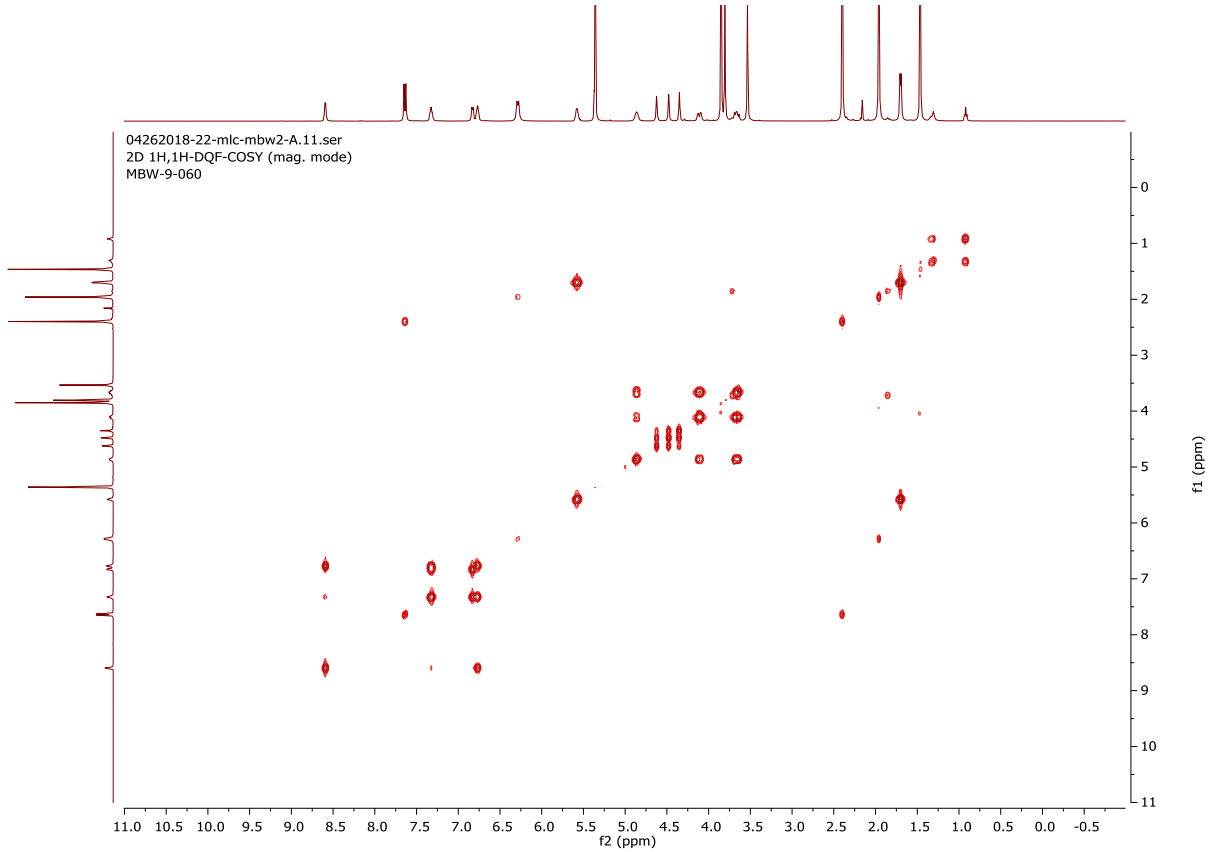

09102018-16-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-9-105
f2 (ppm)
f1 (ppm)

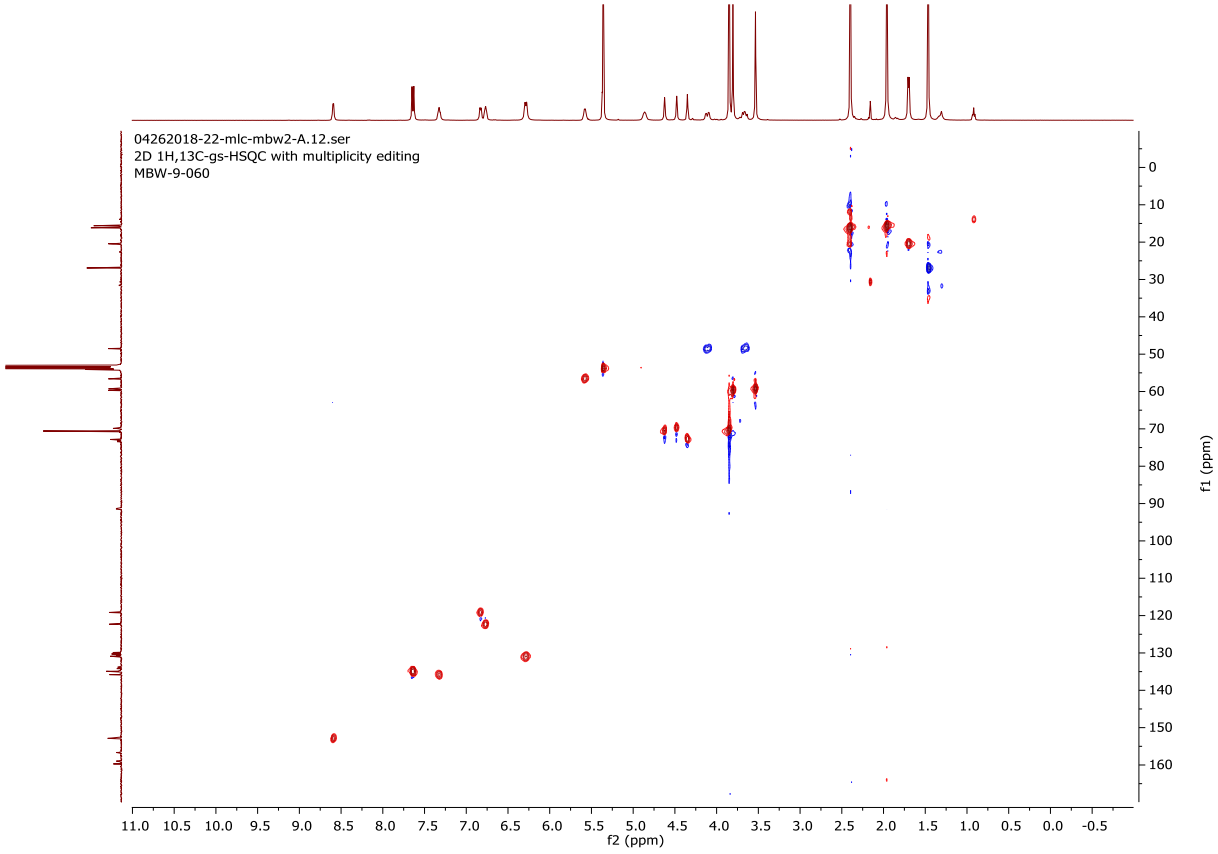
[(R_C, S_p)-*N*-2-picolynyl-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, (***R_C, S_p*)-9**



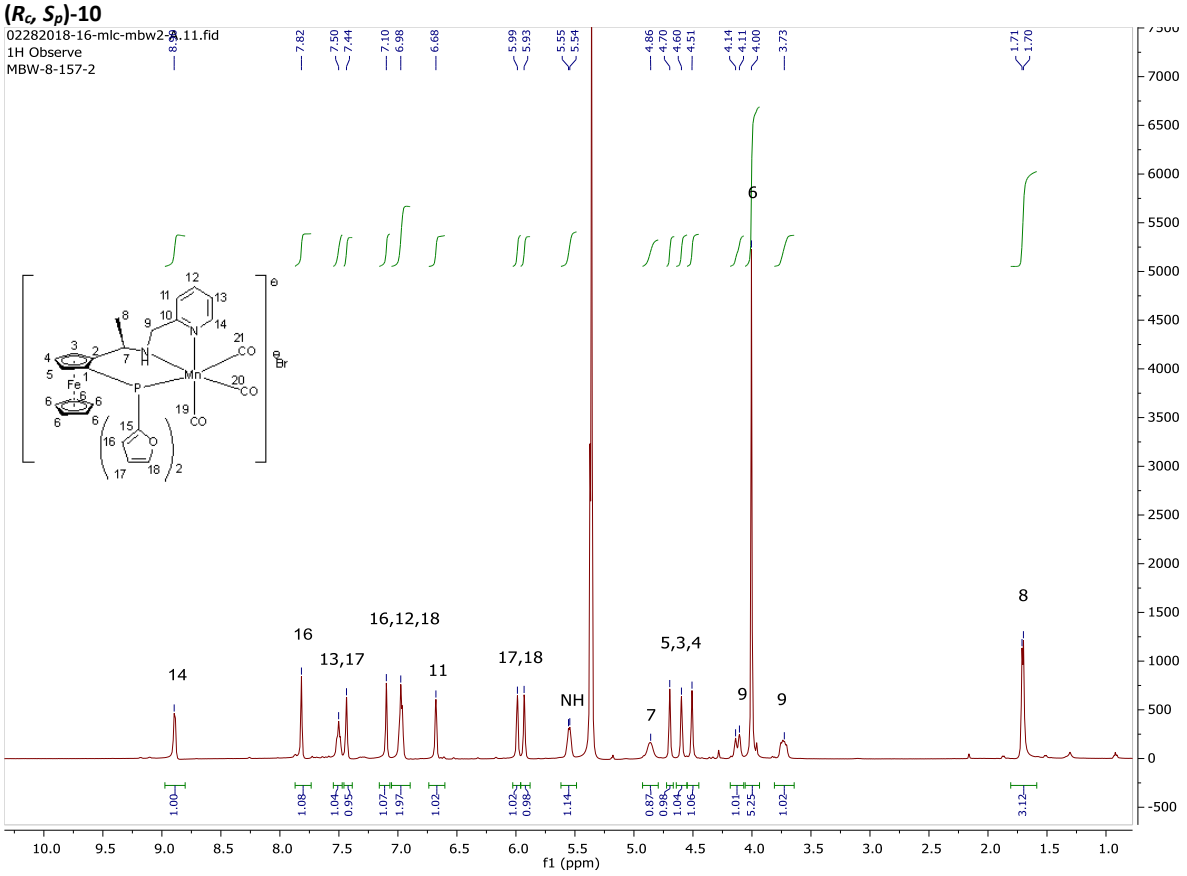


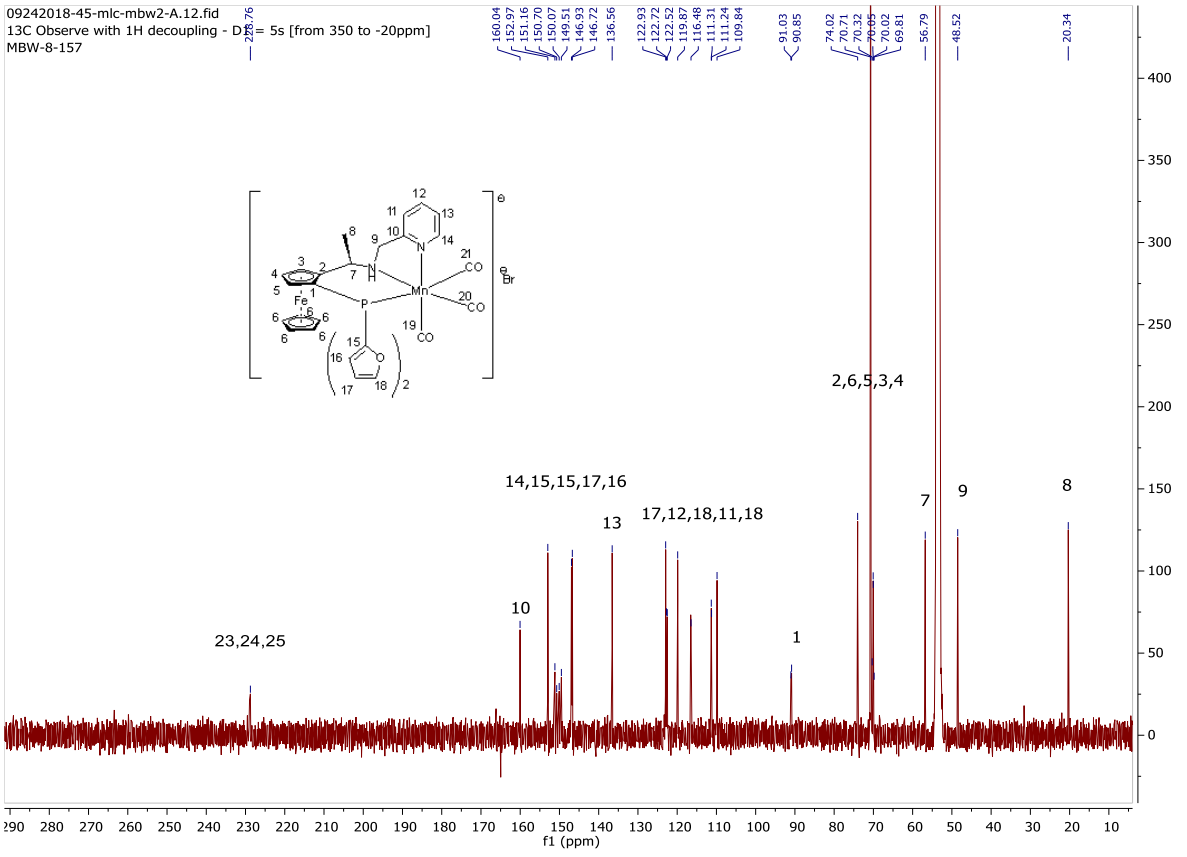

04252018-10-mlc-mbw2-N.12.fid
31P Observe with 1H decoupling
MBW-9-060
86.83
f1 (ppm)

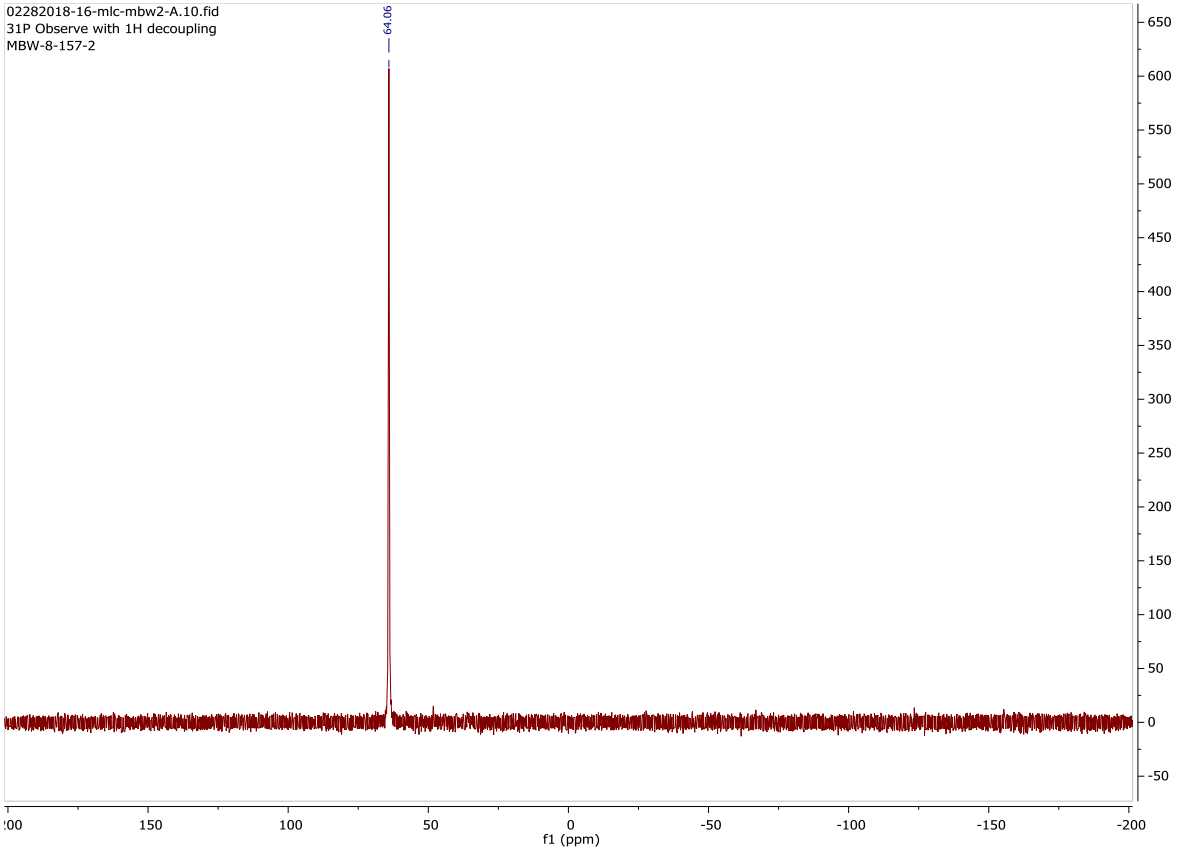

04262018-22-mlc-mbw2-A.11.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-9-060
f2 (ppm)
f1 (ppm)

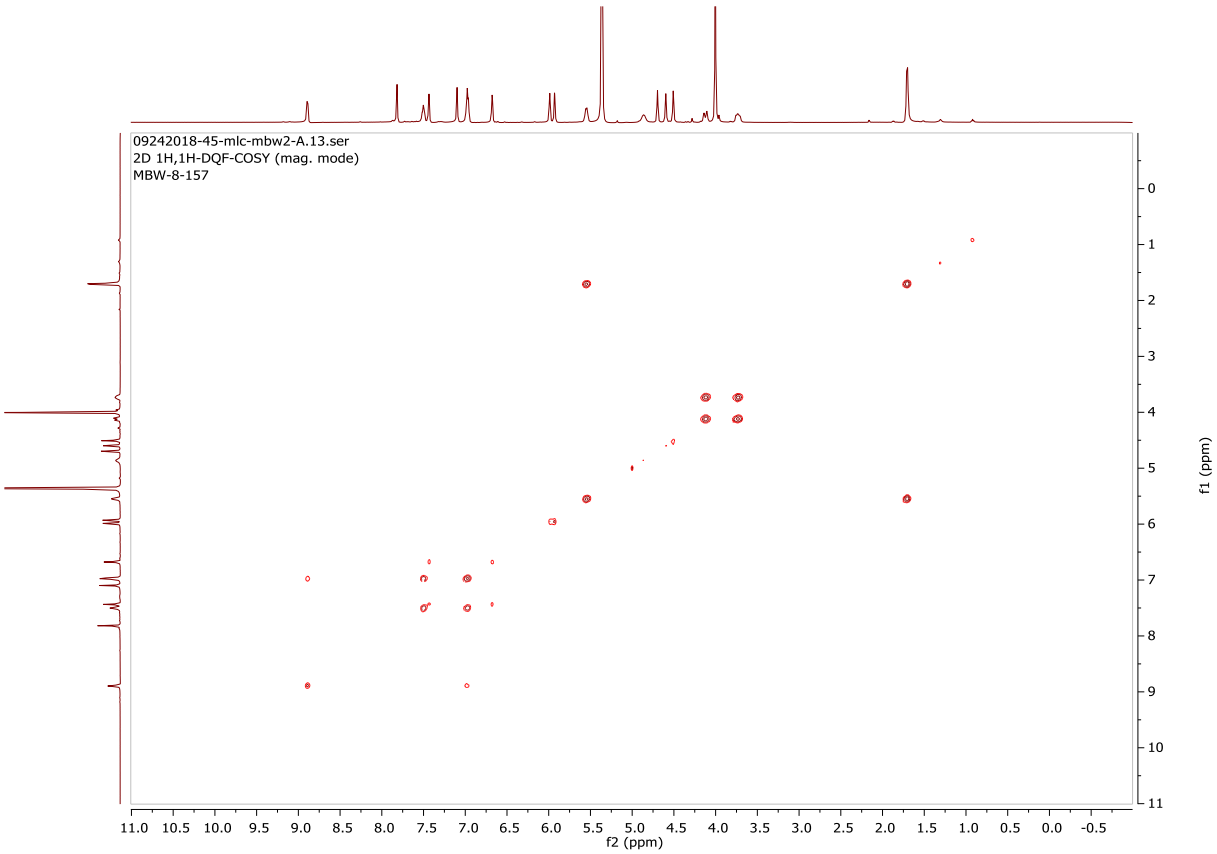

04262018-22-mlc-mbw2-A.12.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-9-060
f1 (ppm)
f2 (ppm)

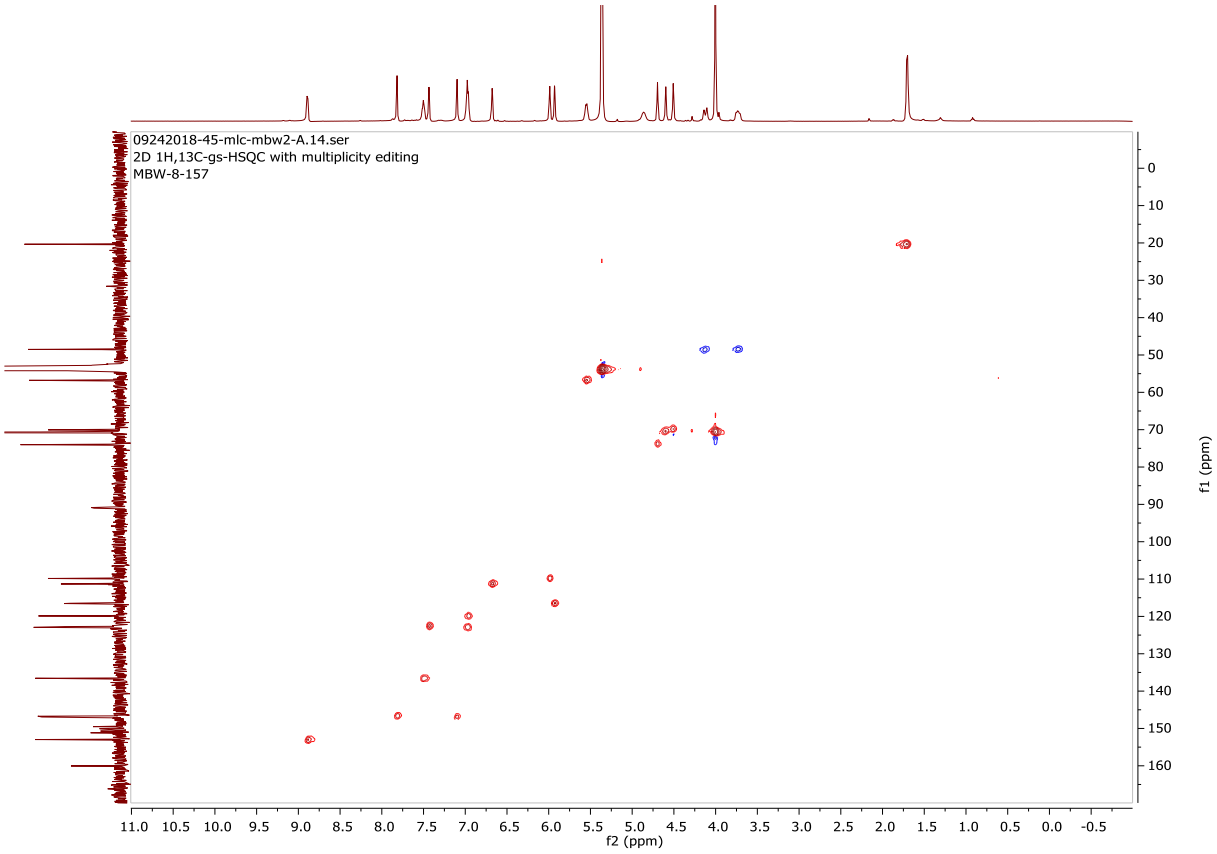
[(R_C, S_p)-*N*-2-picolynyl-1-(-2-di(furan-2-yl)phosphineferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_C, S_p)-10**



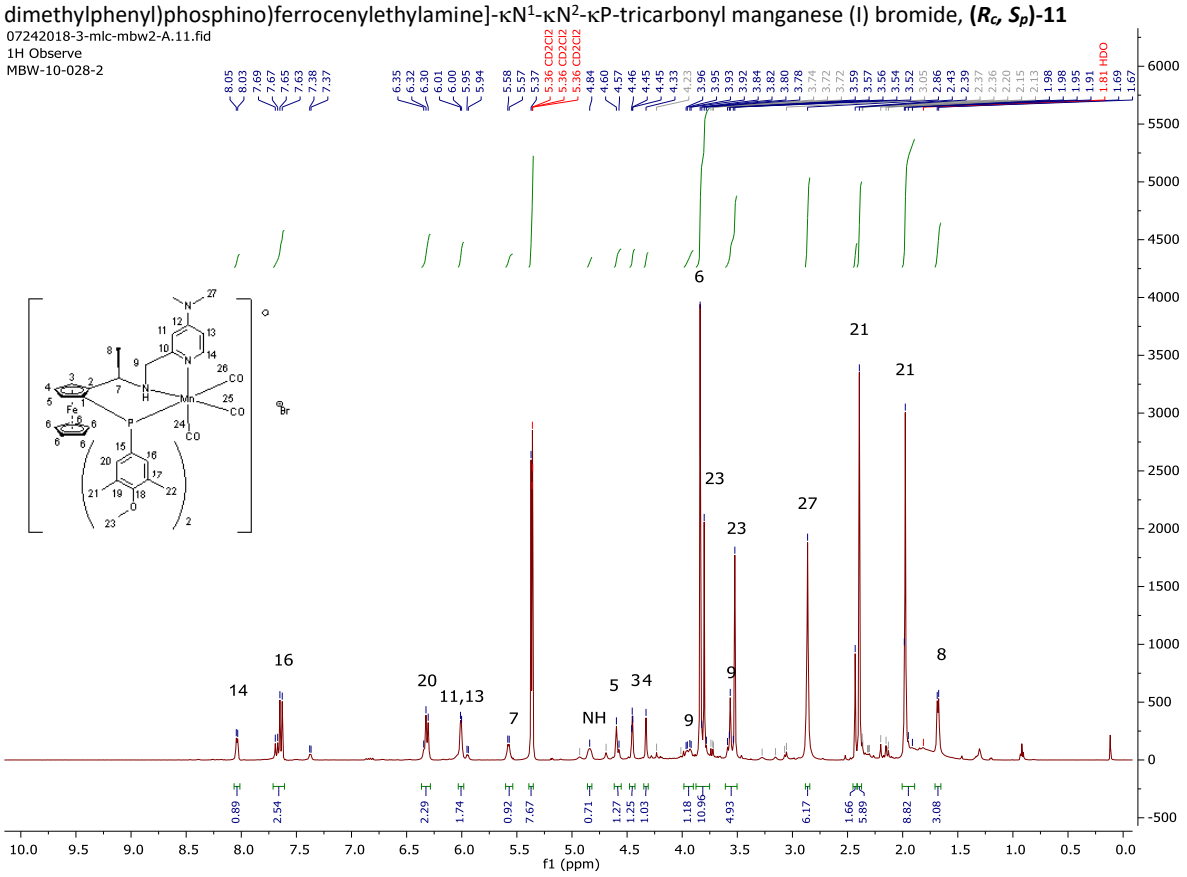


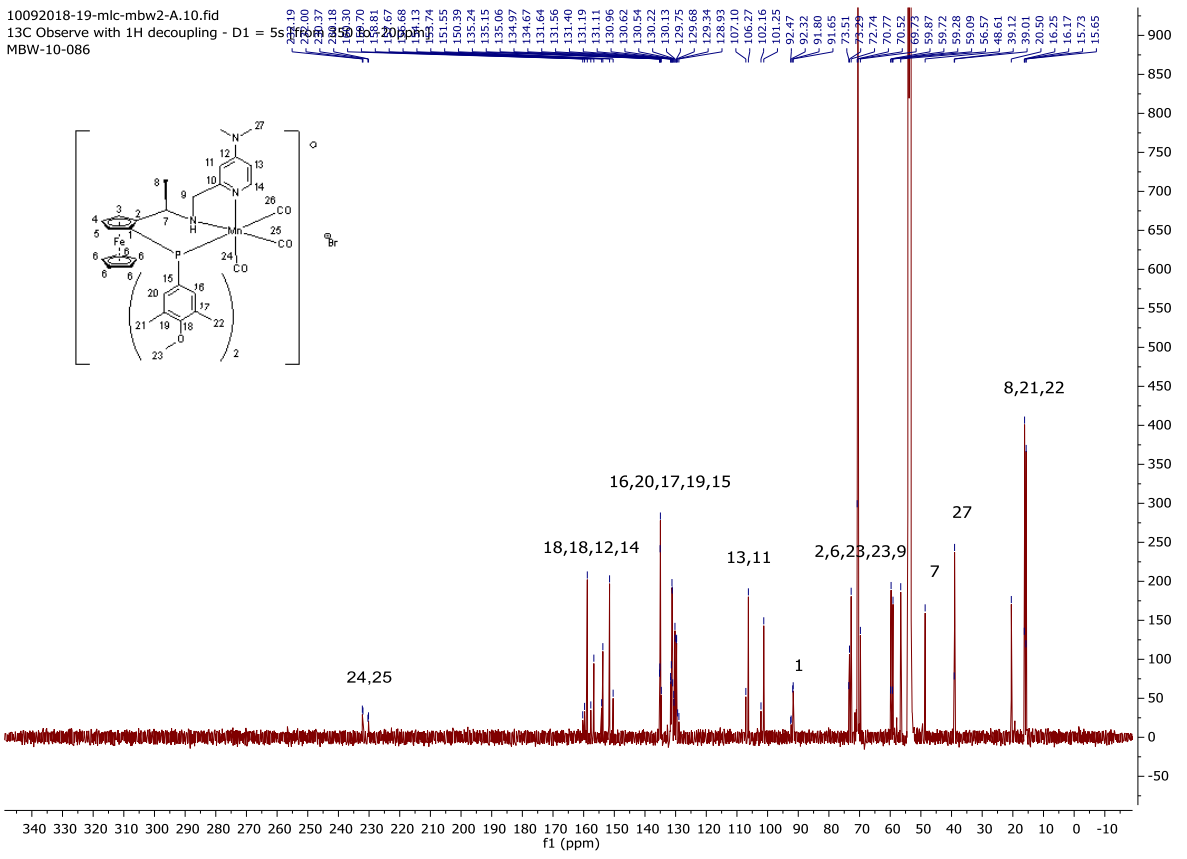

02282018-16-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-8-157-2
64.06
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
150
100
50
0
-50
-100
-150
-200
f1 (ppm)


09242018-45-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-8-157
f2 (ppm)
f1 (ppm)

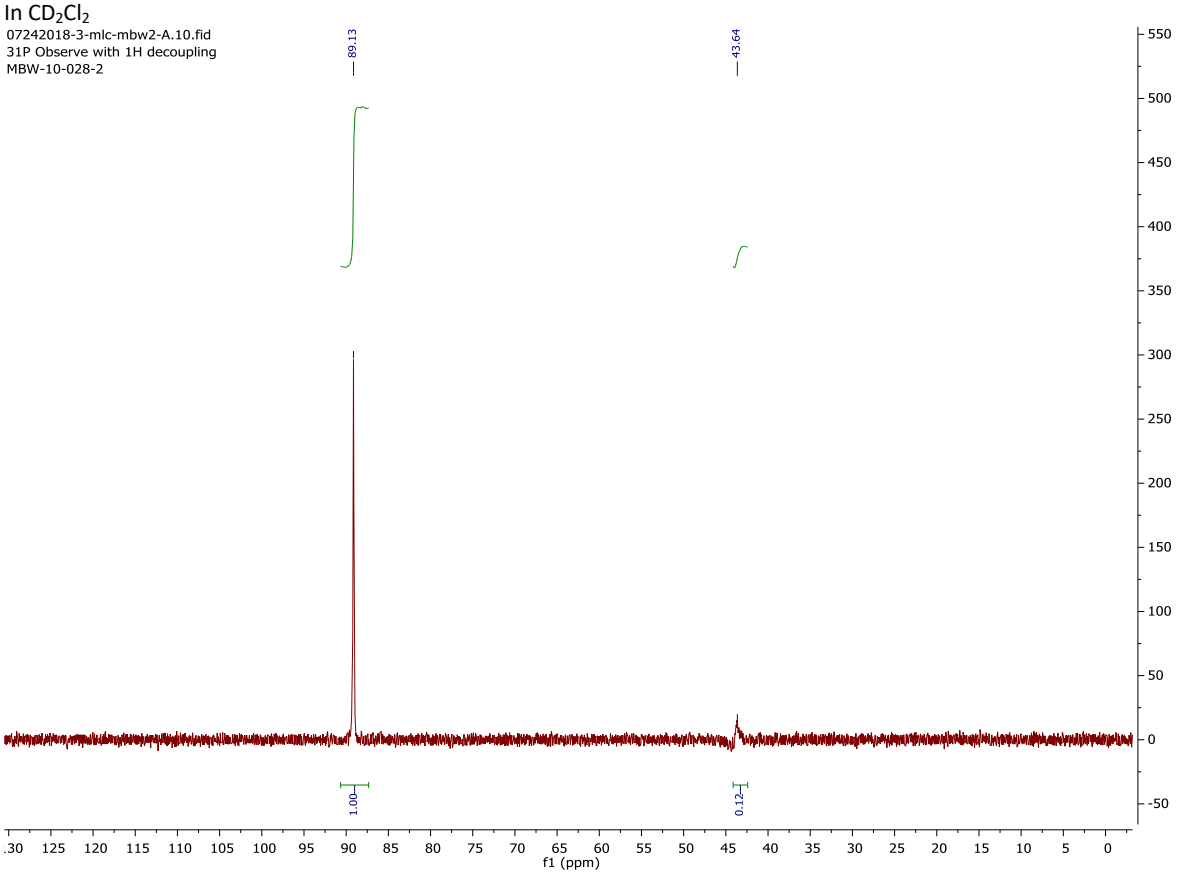

09242018-45-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-8-157
f2 (ppm)
f1 (ppm)

[(R_c, S_p)-*N*-(4-(dimethylamino)pyridine-2-methyl)-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_c, S_p)-11**

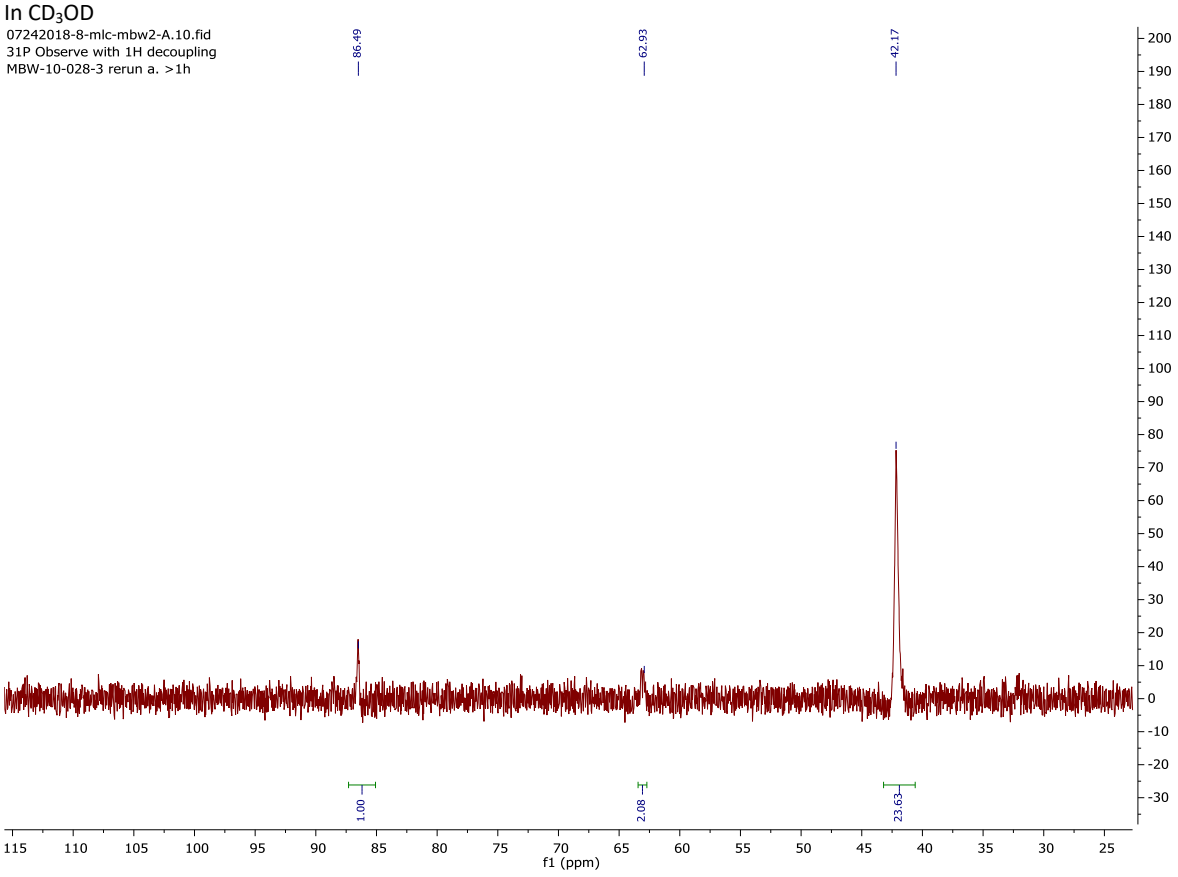




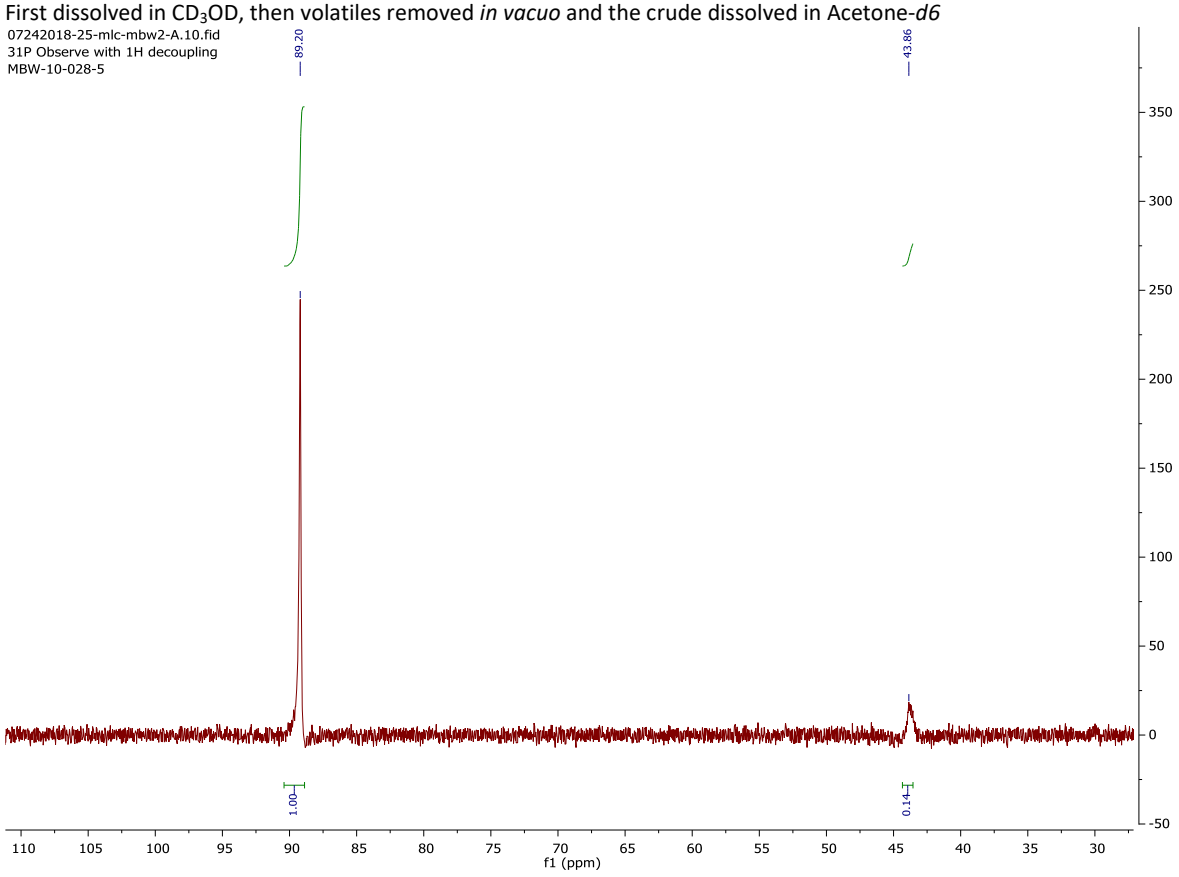
In CD_2Cl_2



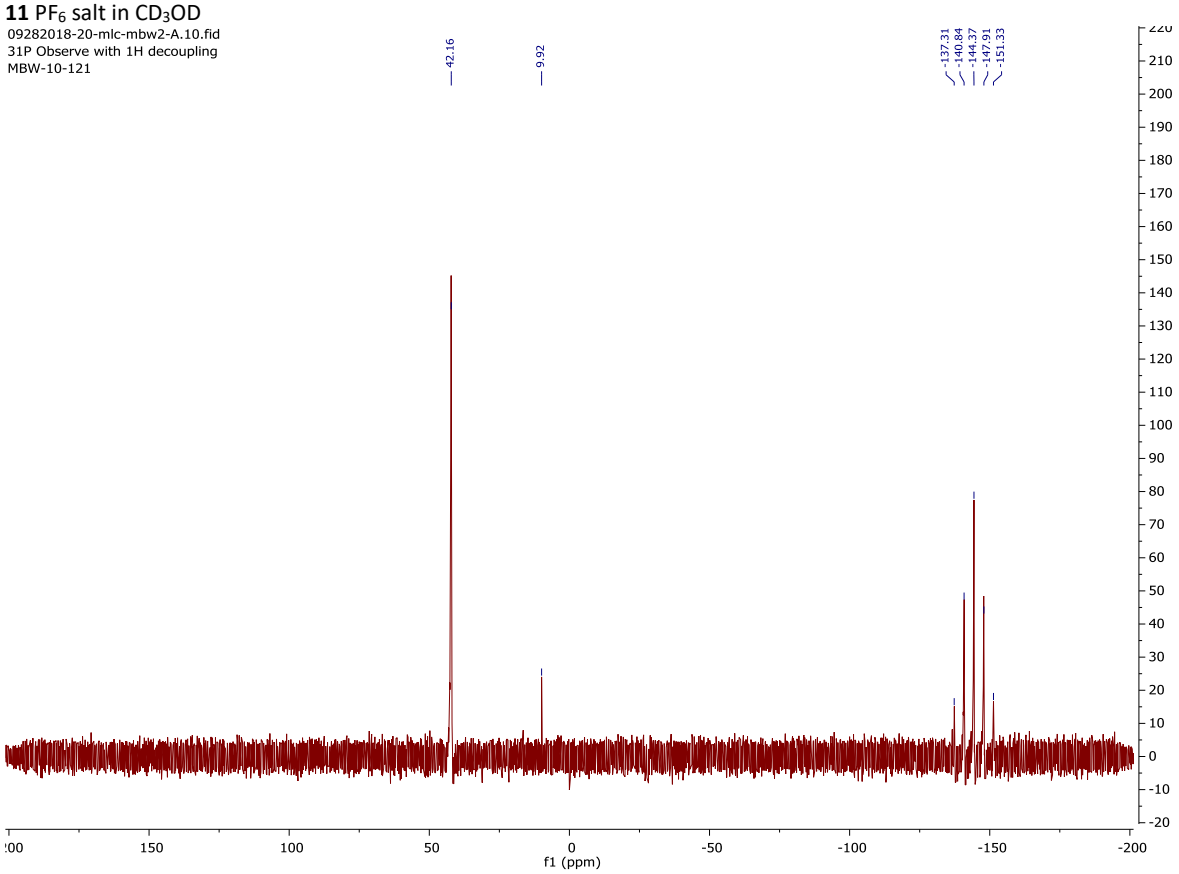
In CD_3OD



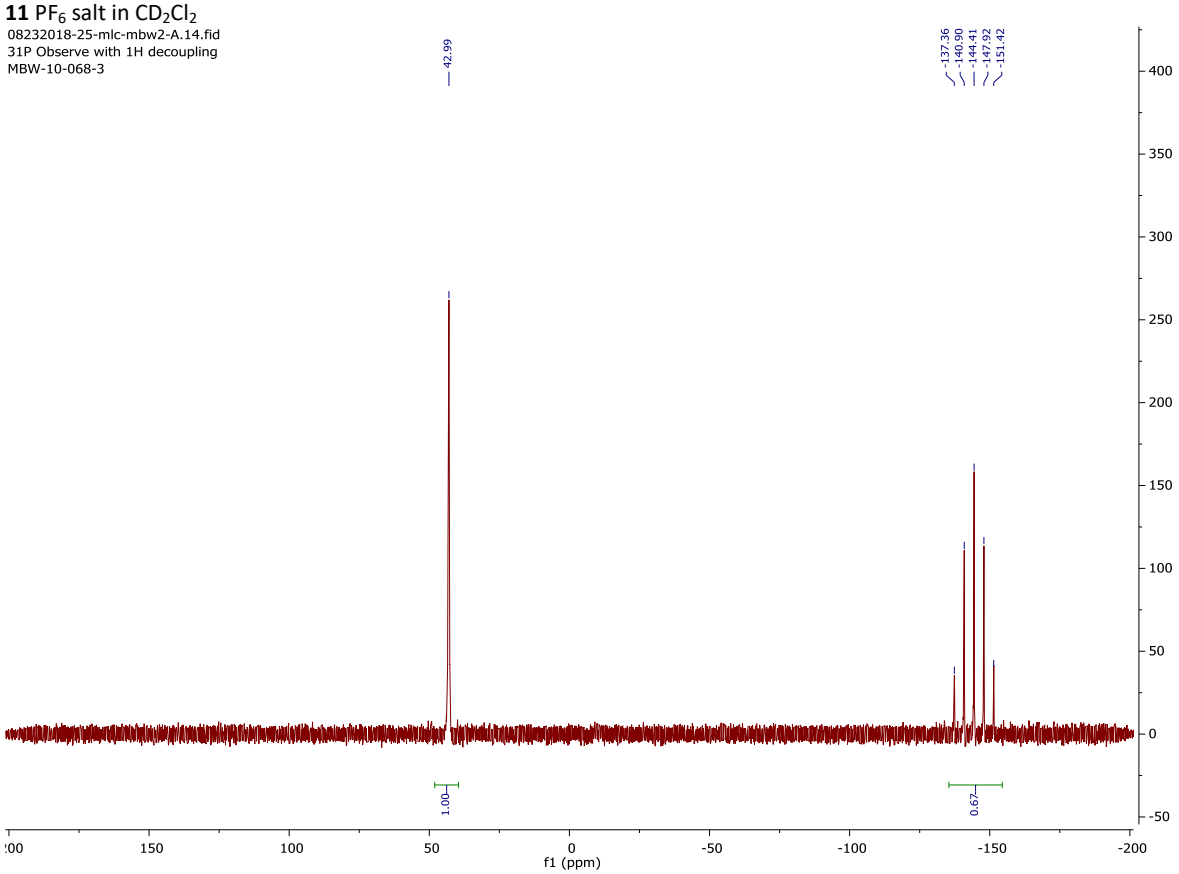
First dissolved in CD_3OD, then volatiles removed *in vacuo* and the crude dissolved in Acetone-*d6*

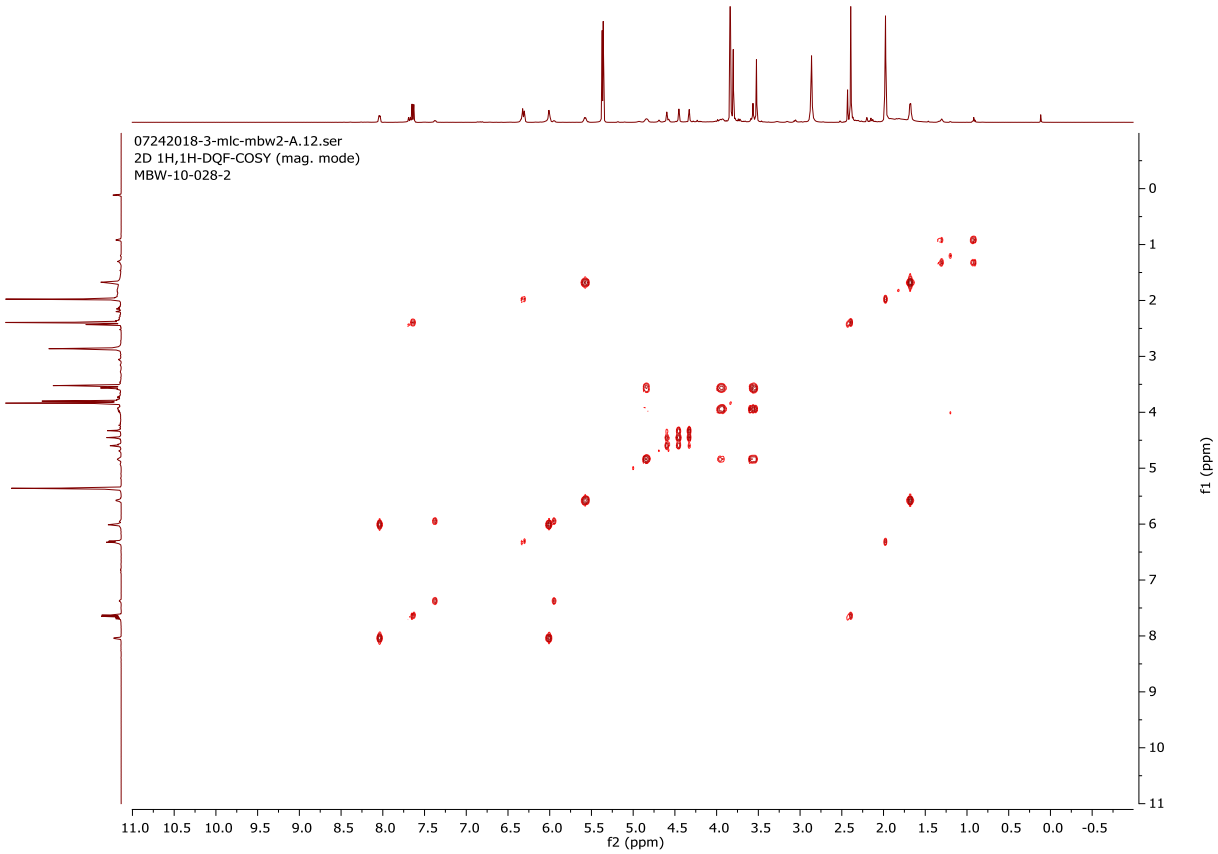


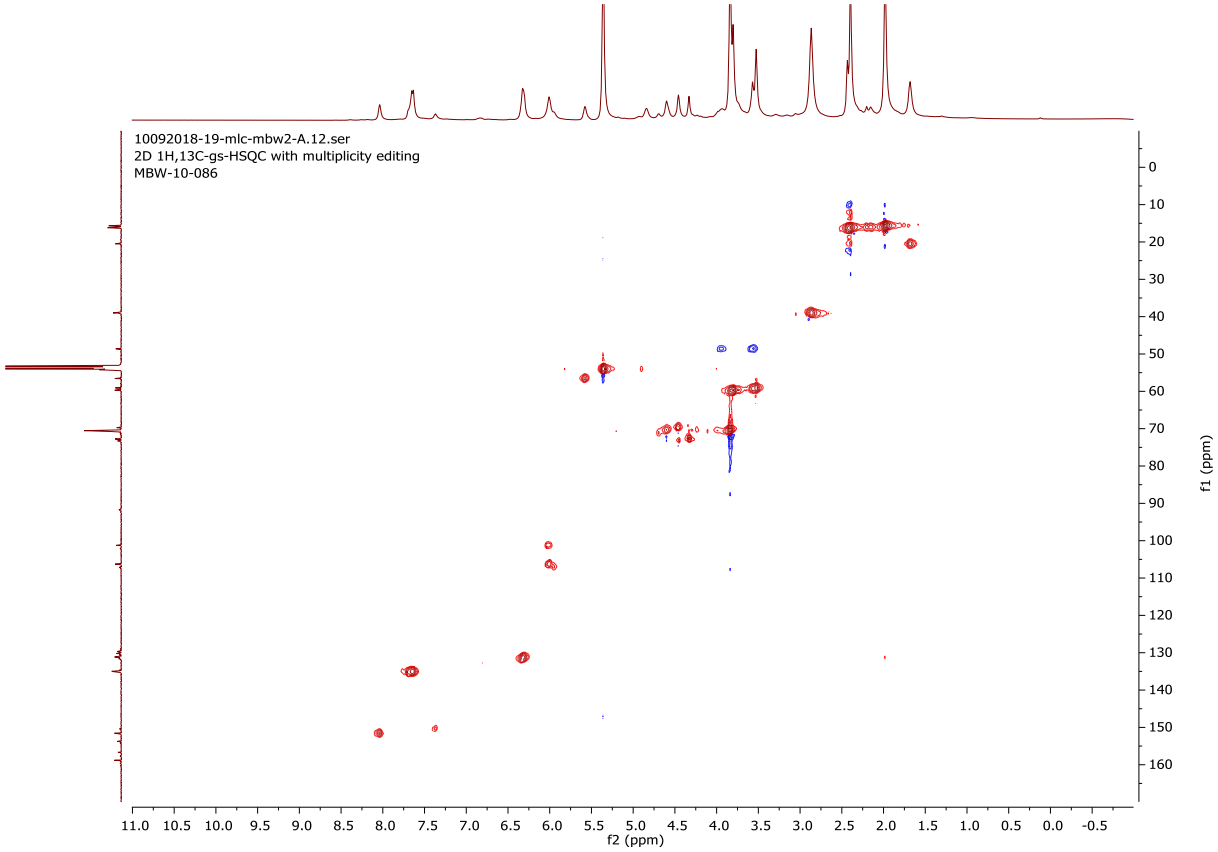
11 PF_6 salt in CD_3OD



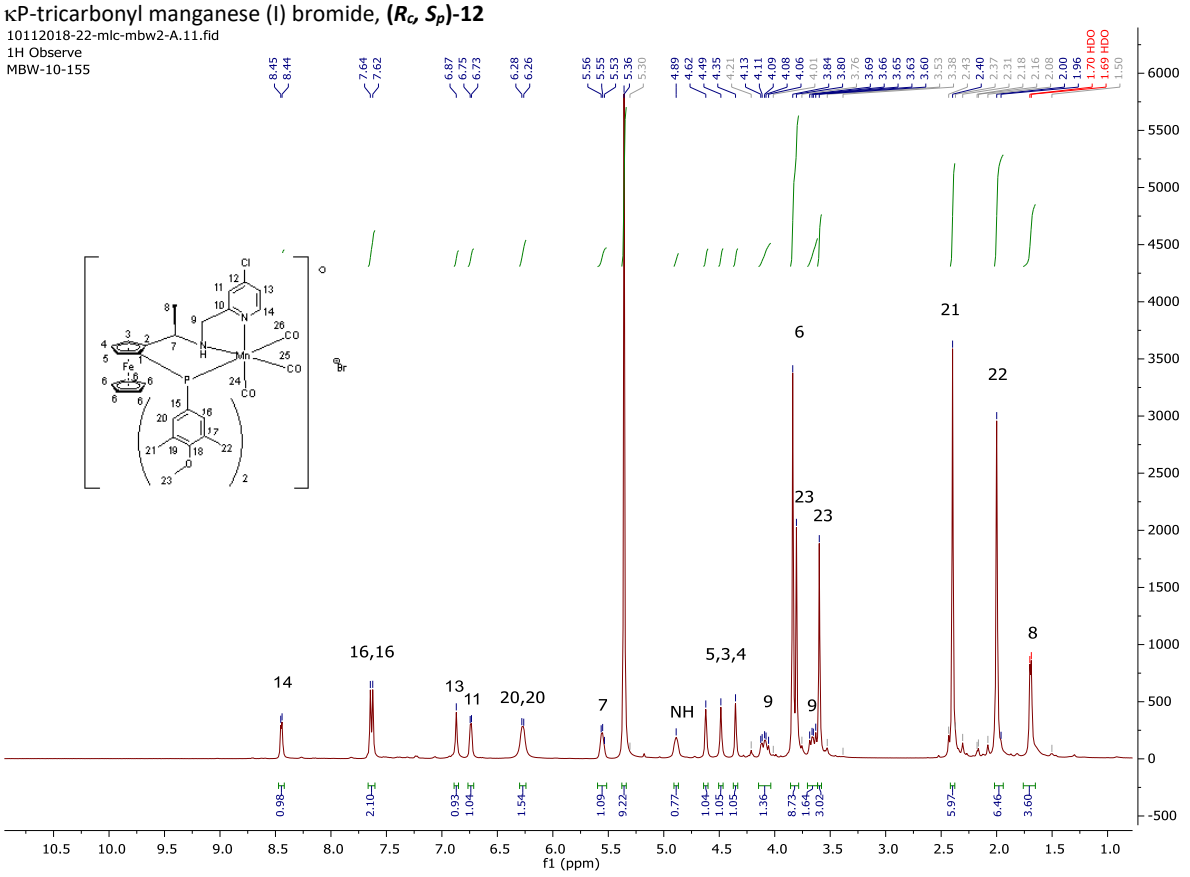
11 PF_6 salt in CD_2Cl_2

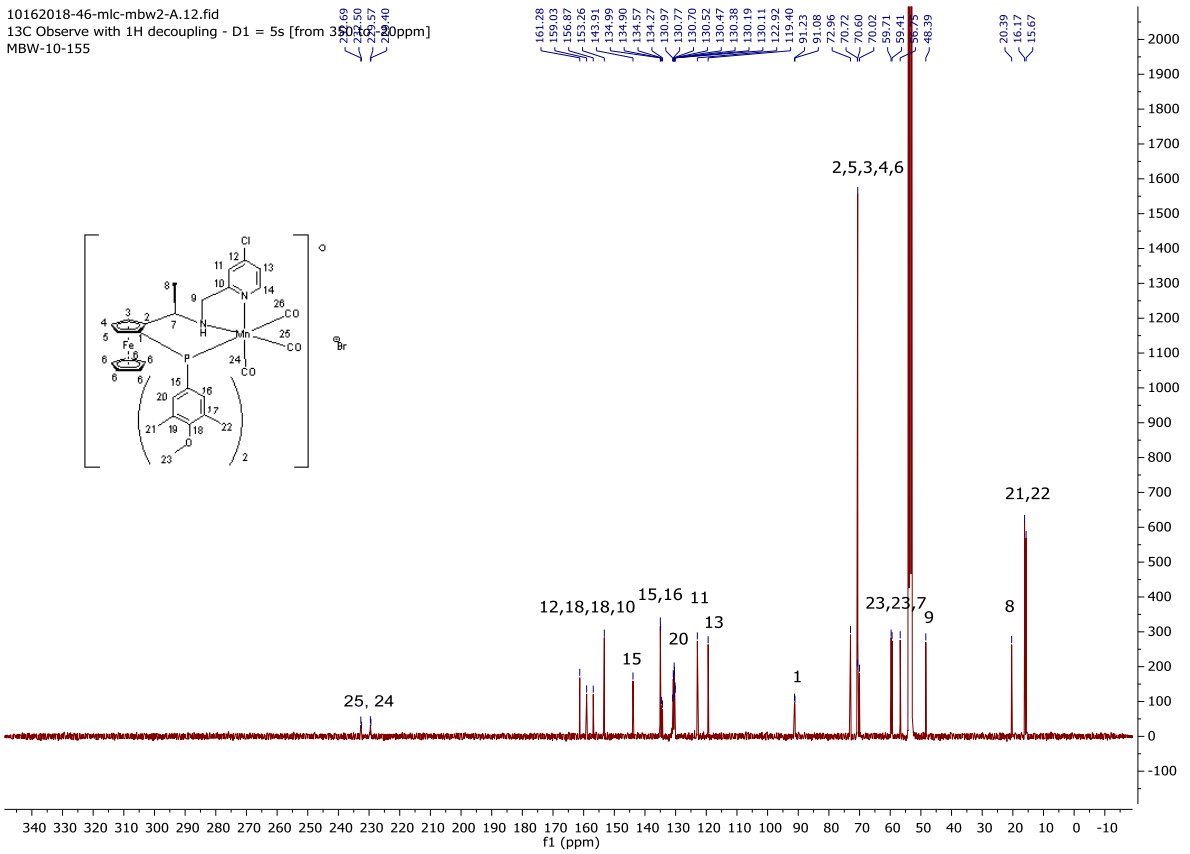


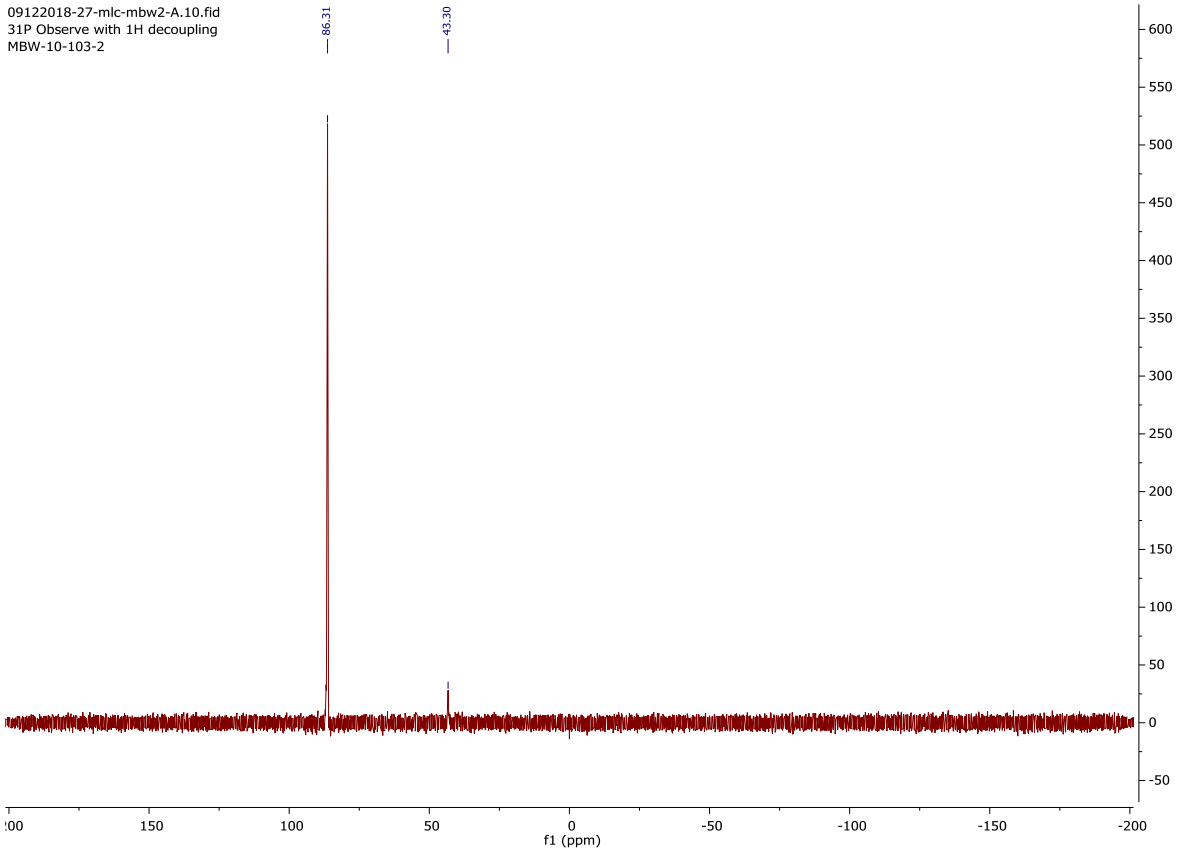

07242018-3-mlc-mbw2-A.12.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-10-028-2
f1 (ppm)
f2 (ppm)

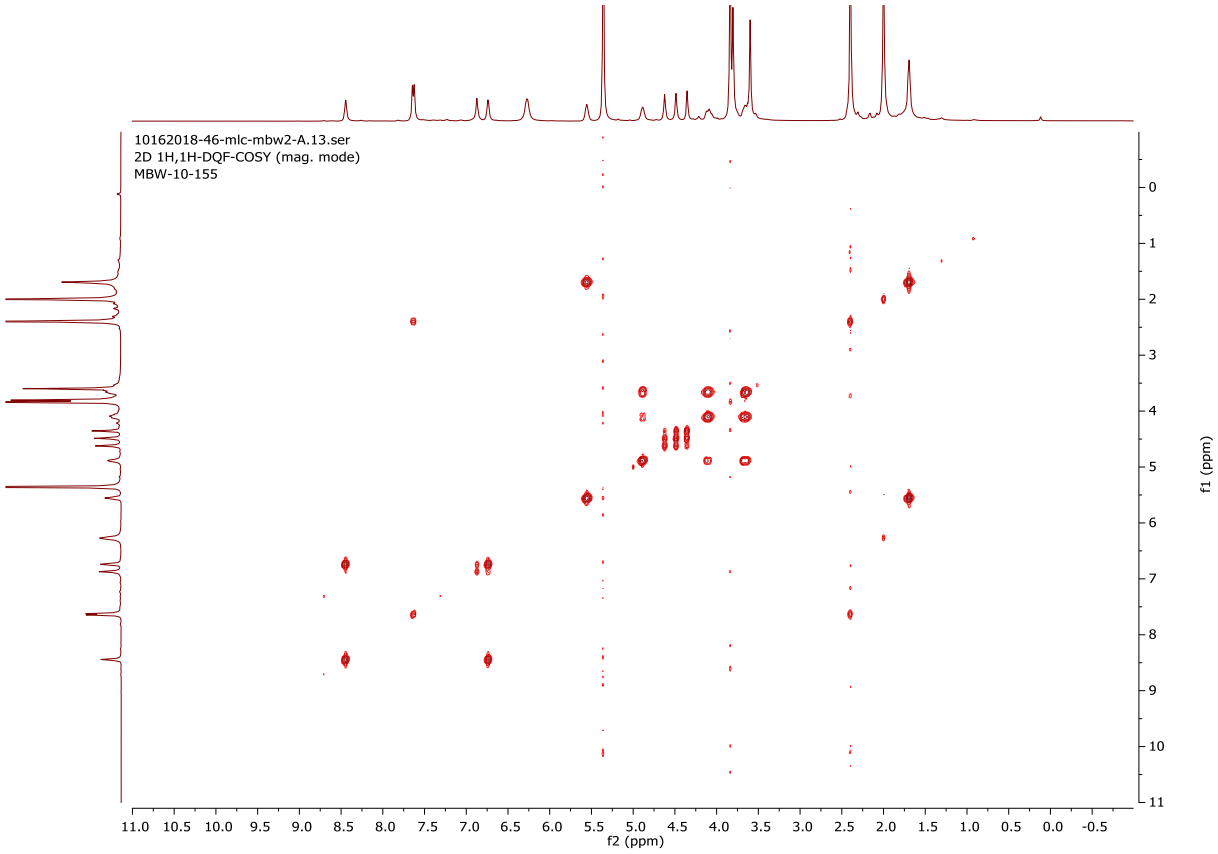

10092018-19-mlc-mbw2-A.12.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-10-086
f1 (ppm)
f2 (ppm)

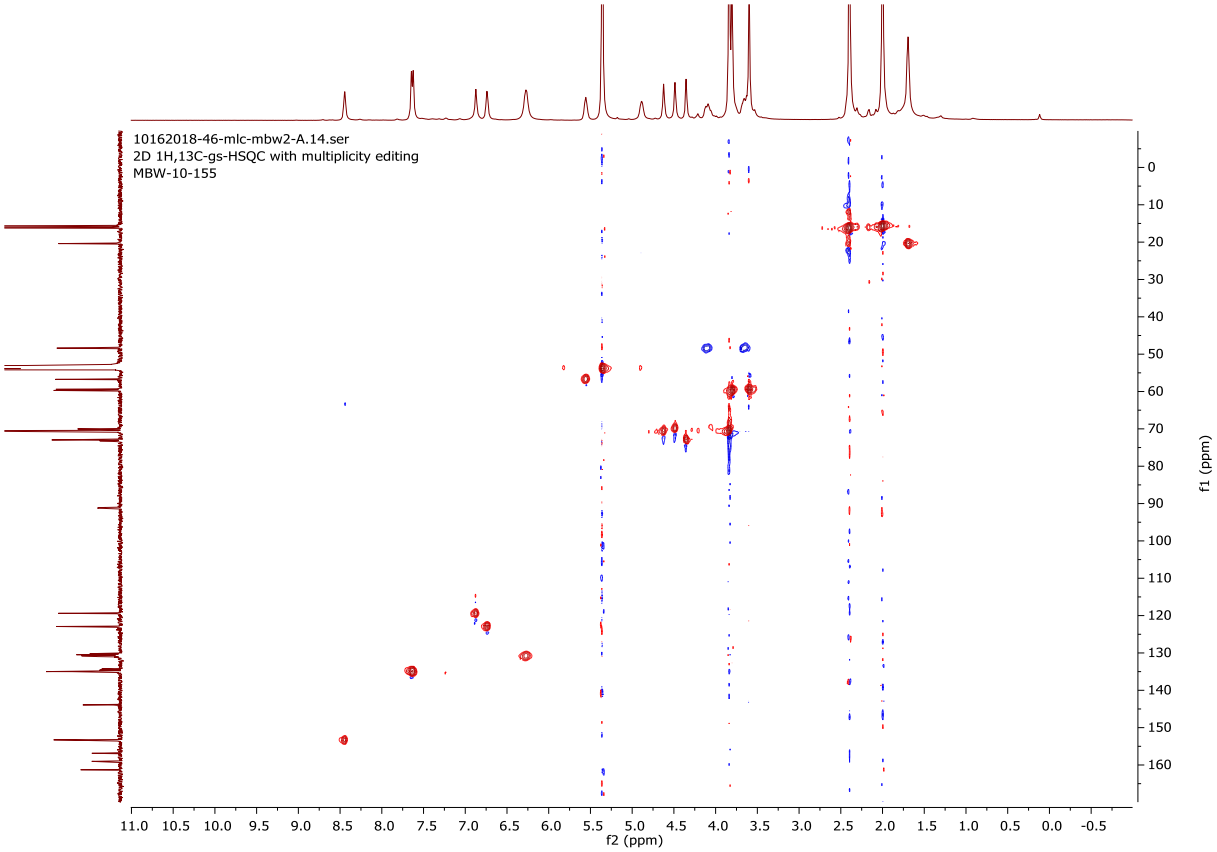
[(R_c,S_p)-*N*-(4-chloropyridine-2-methyl)-1-(-2-bis(4-methoxy-3,5-dimethylphenyl)phosphino)ferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_c, S_p)-12**



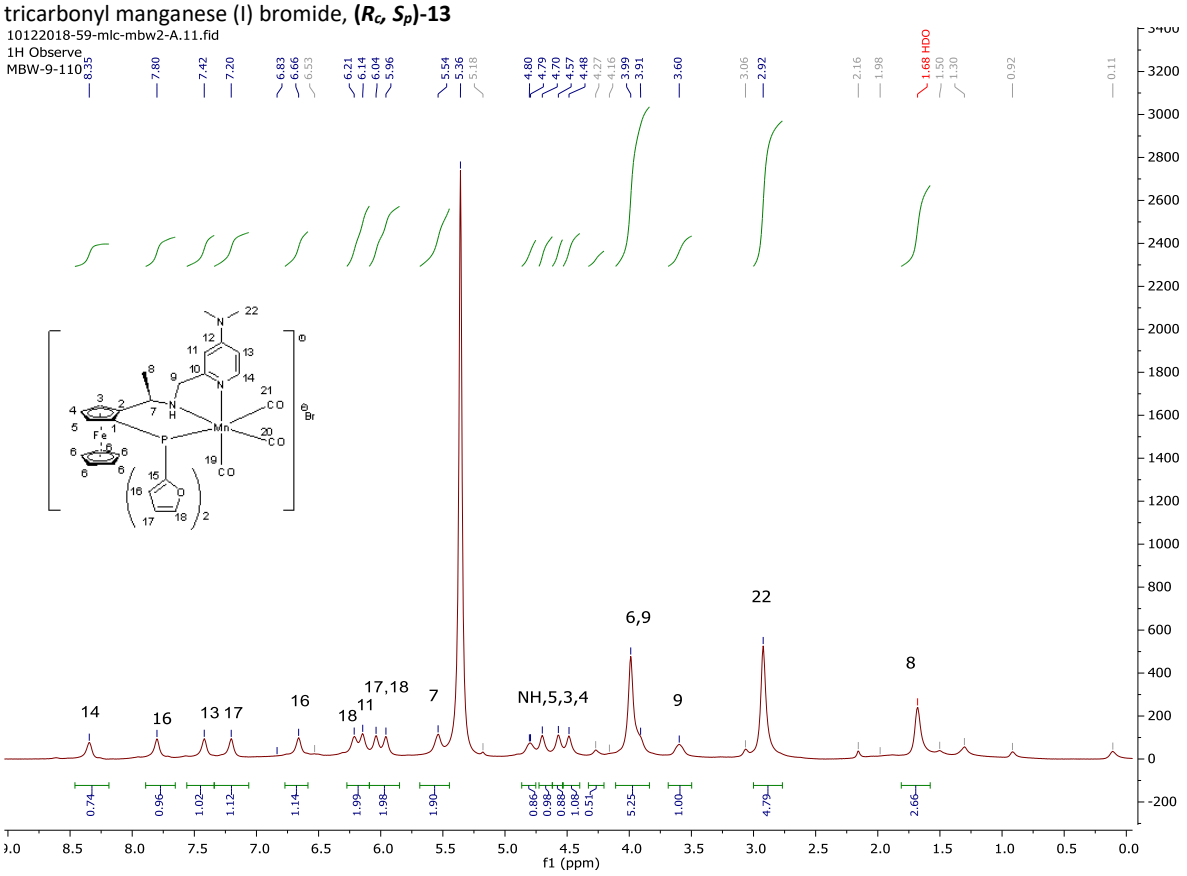


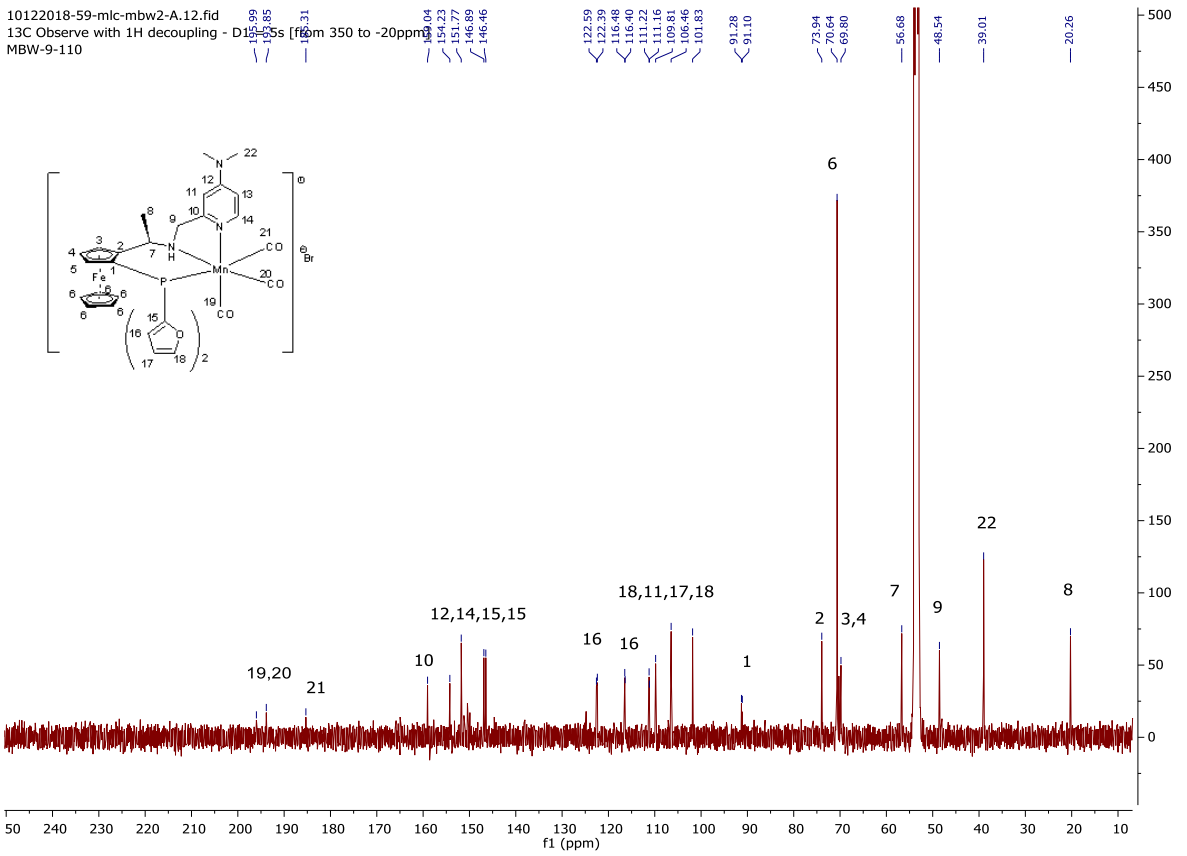

09122018-27-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-10-103-2
86.31
43.30
f1 (ppm)

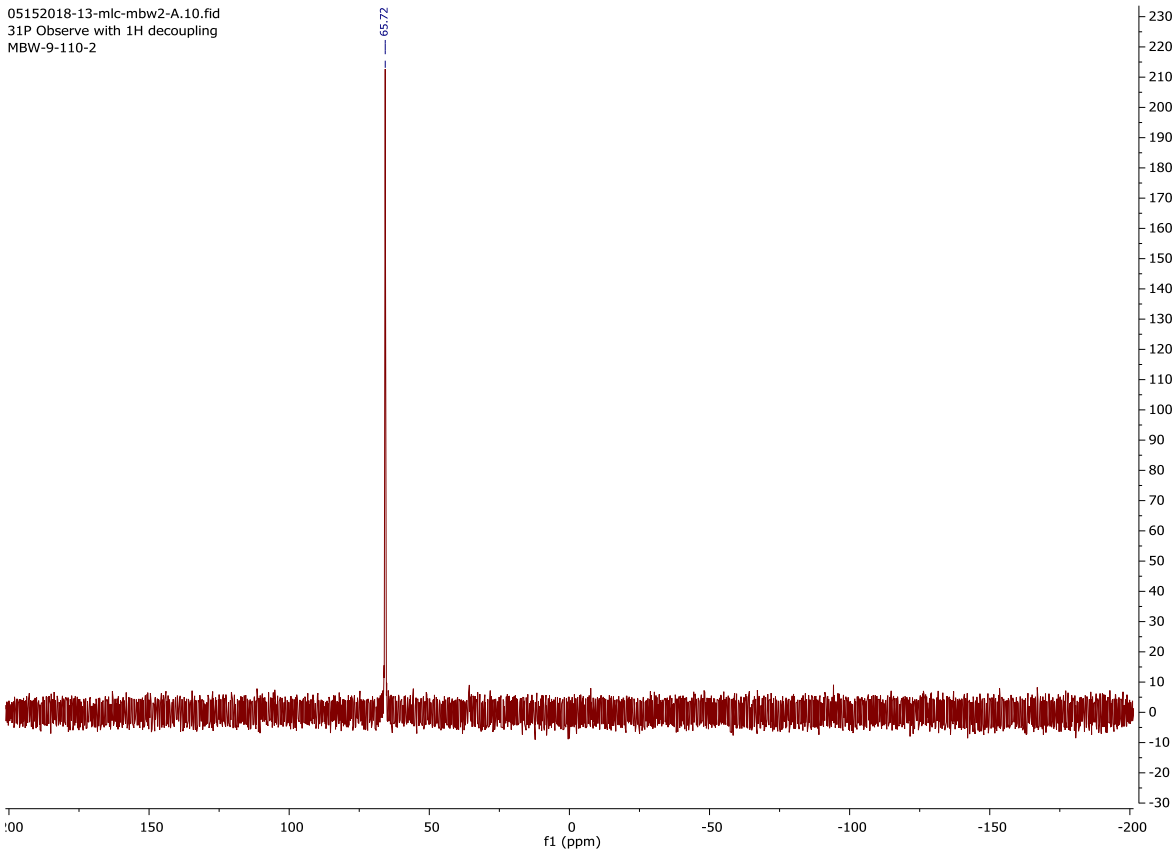

10162018-46-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-10-155
f2 (ppm)
f1 (ppm)

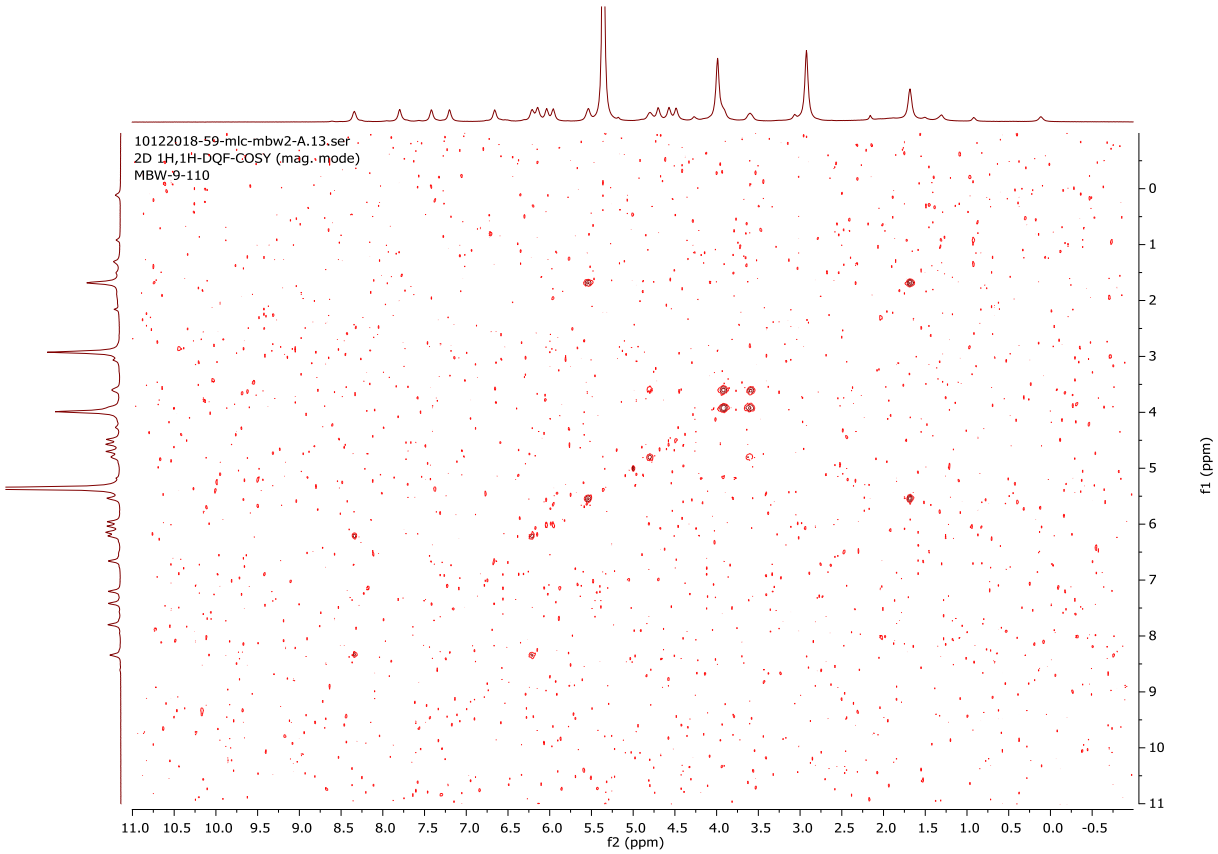

10162018-46-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-10-155
f2 (ppm)
f1 (ppm)

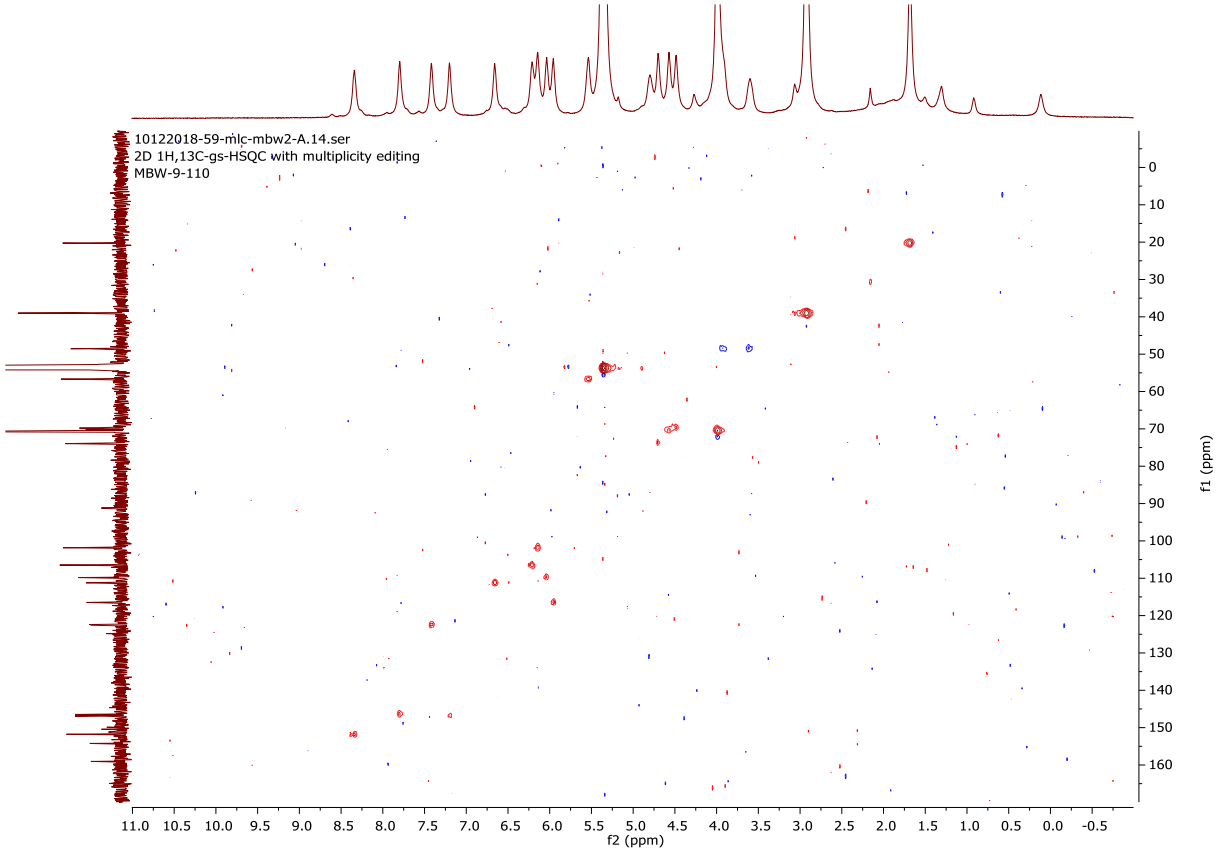
[(R_c,S_p)-*N*-(4-(dimethylamino)pyridine-2-methyl)-1-(-2-di(furan-2-yl)phosphineferrocenylethylamine]-κN^1-κN^2-κP-tricarbonyl manganese (I) bromide, **(R_c, S_p)-13**



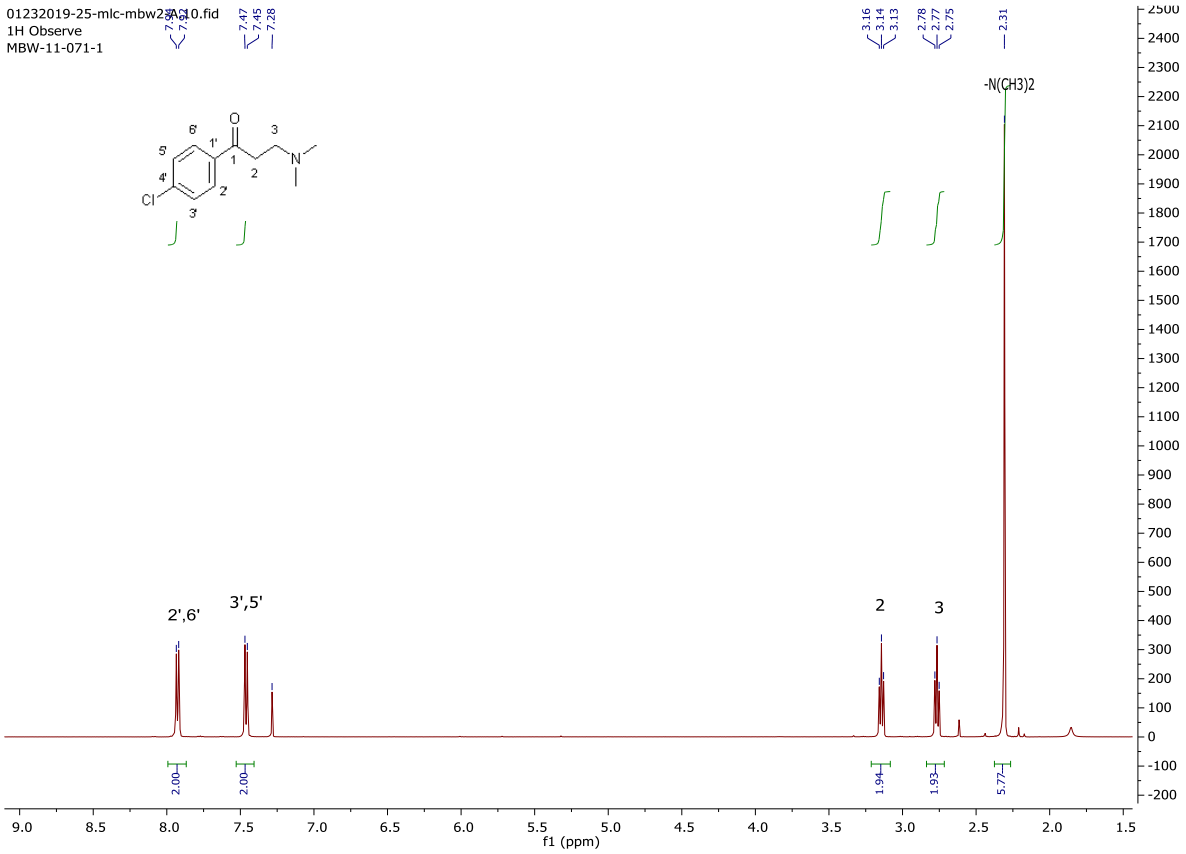


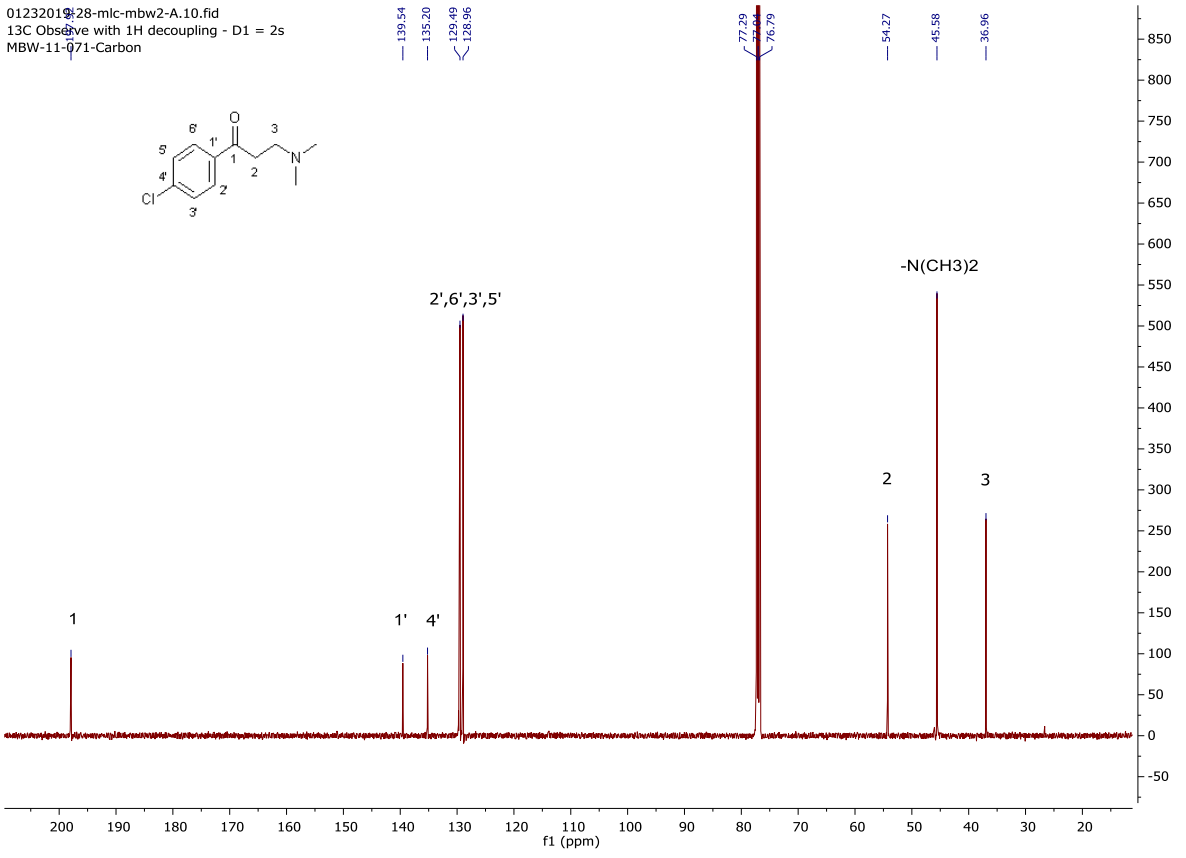

05152018-13-mlc-mbw2-A.10.fid
31P Observe with 1H decoupling
MBW-9-110-2
65.72
f1 (ppm)


10122018-59-mlc-mbw2-A.13.ser
2D 1H,1H-DQF-COSY (mag. mode)
MBW-9-110
f2 (ppm)
f1 (ppm)

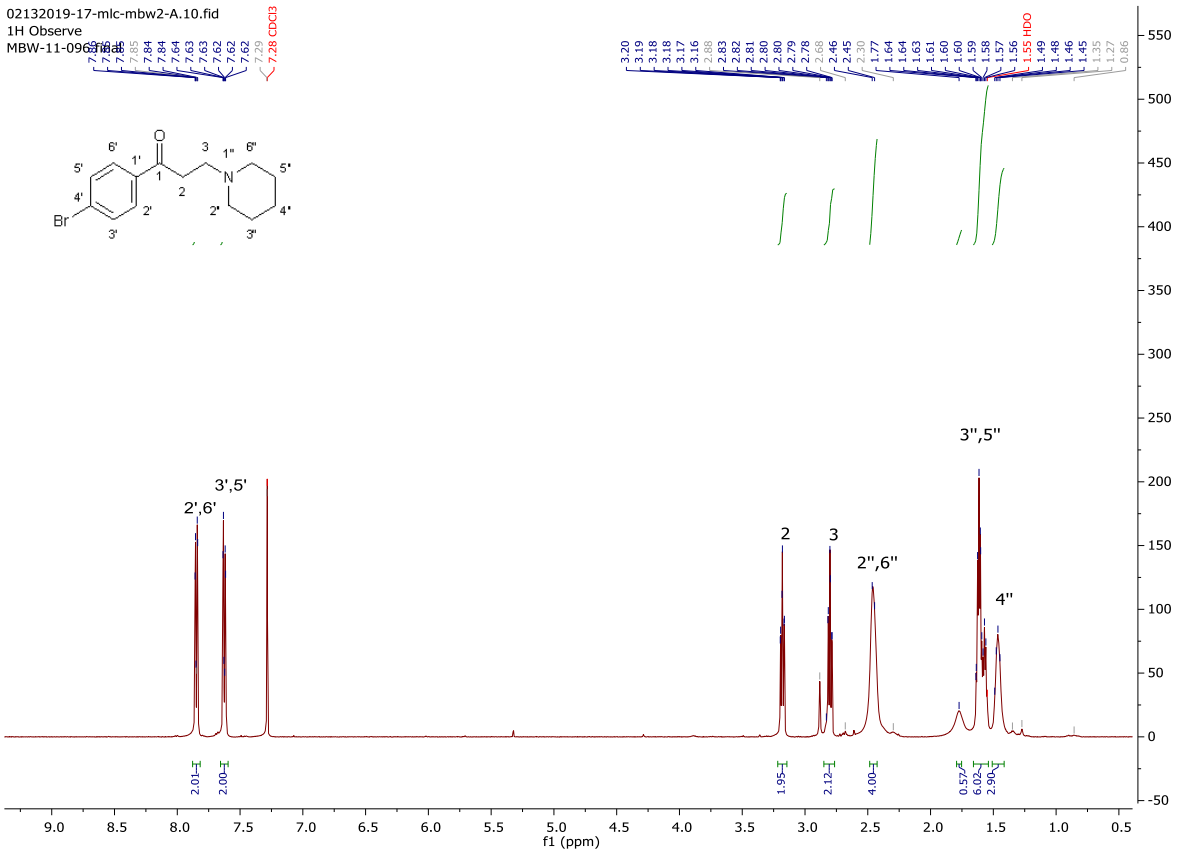

10122018-59-mlc-mbw2-A.14.ser
2D 1H,13C-gs-HSQC with multiplicity editing
MBW-9-110
f2 (ppm)
f1 (ppm)

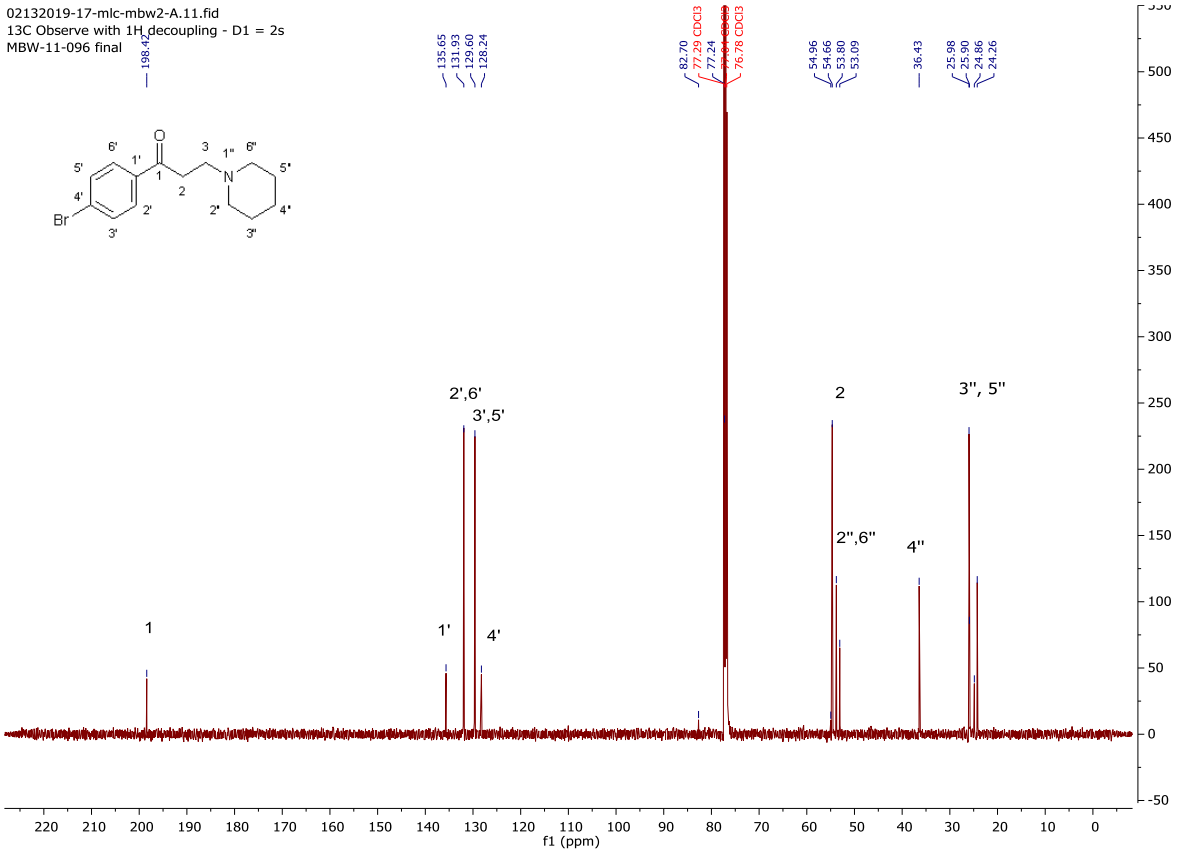
3-dimethylamino-1-(4-chlorophenyl)-1-propanone, **20p**



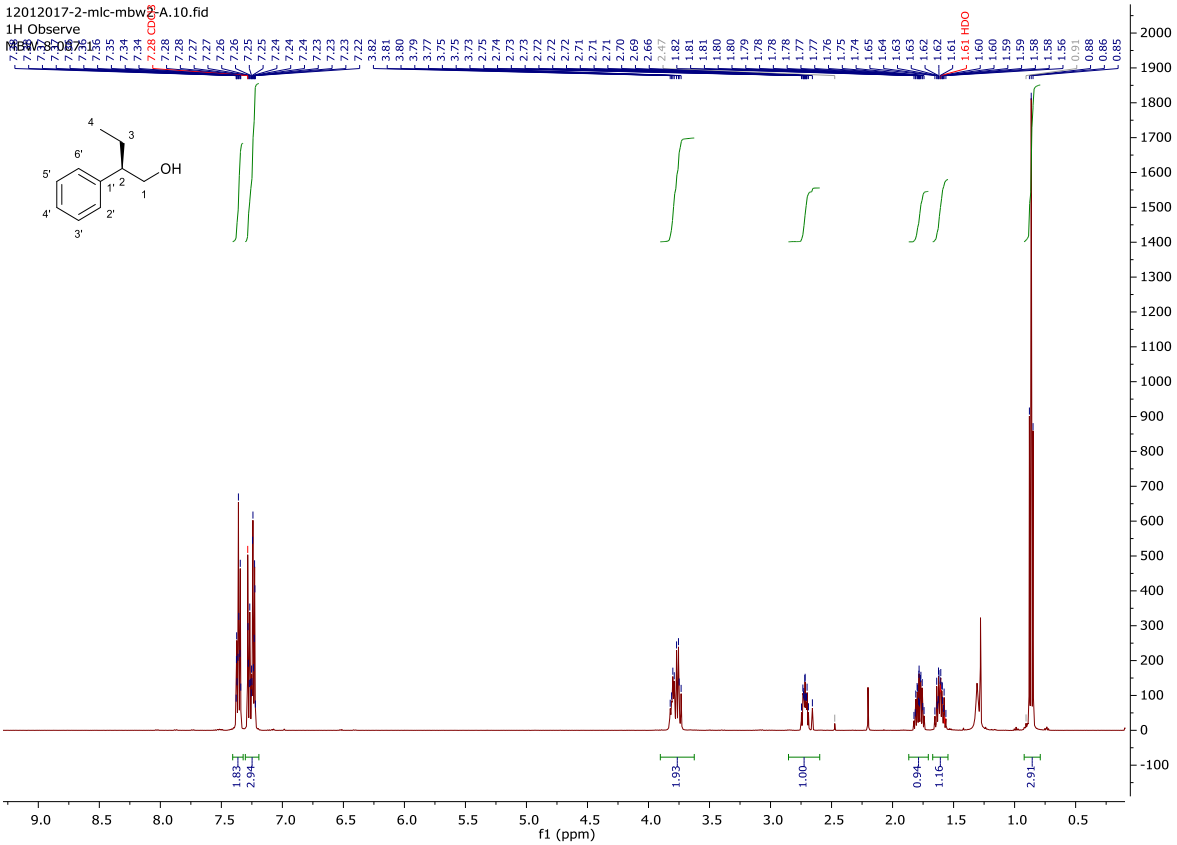


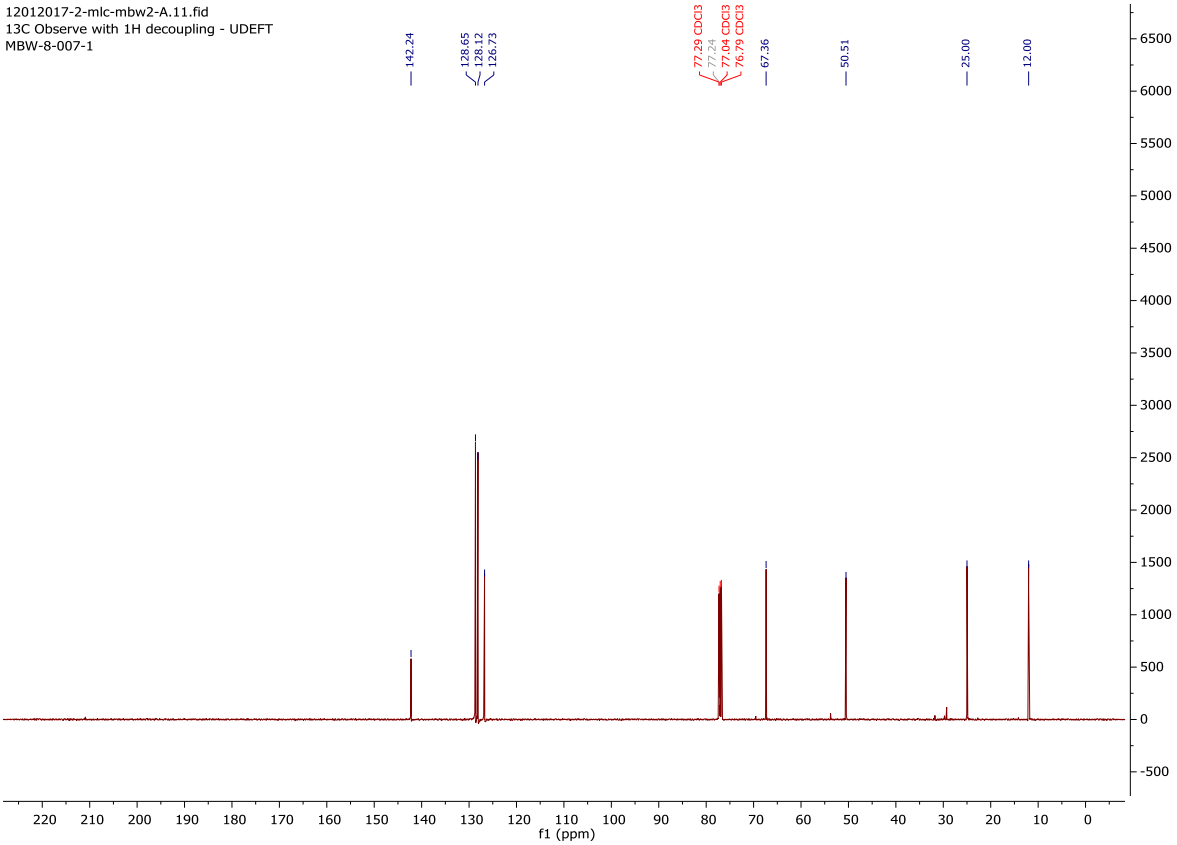
1-(4-bromophenyl)-3-(piperidin-1-yl)-1-propanone, **20q**



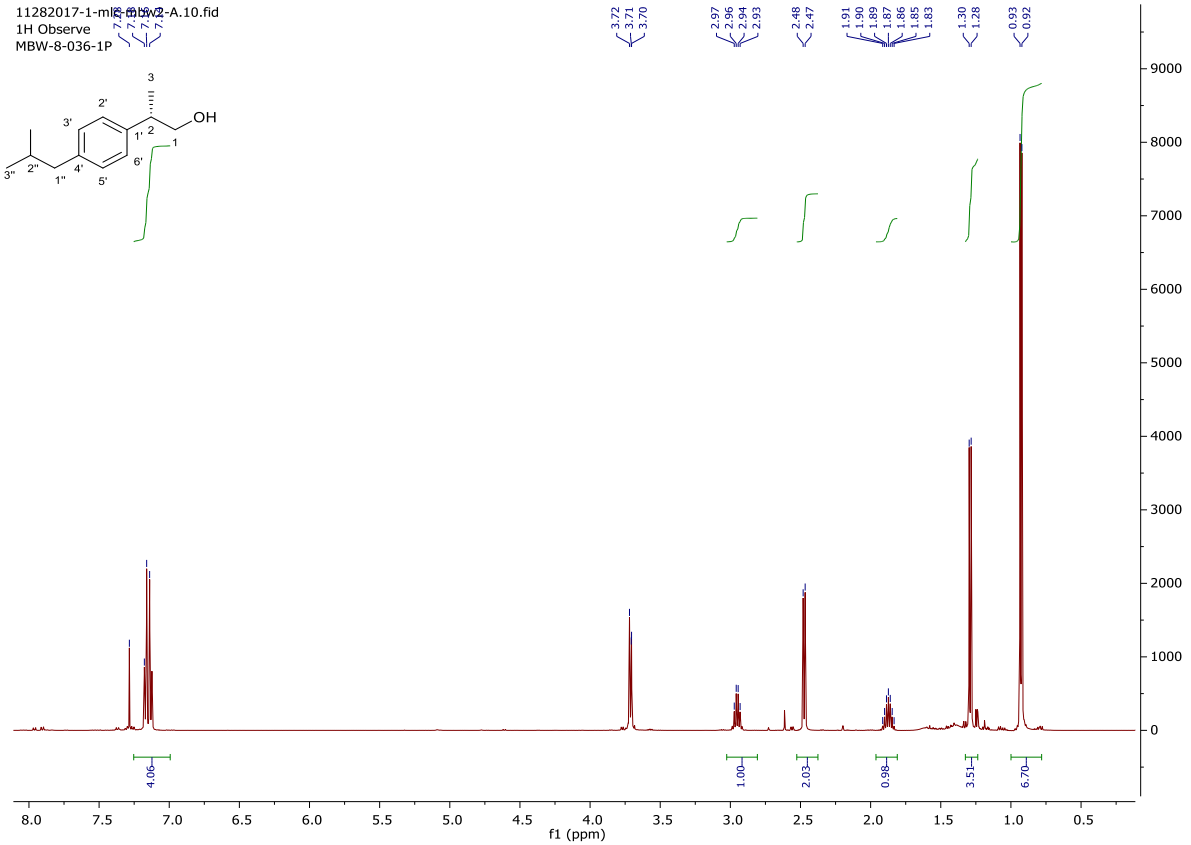


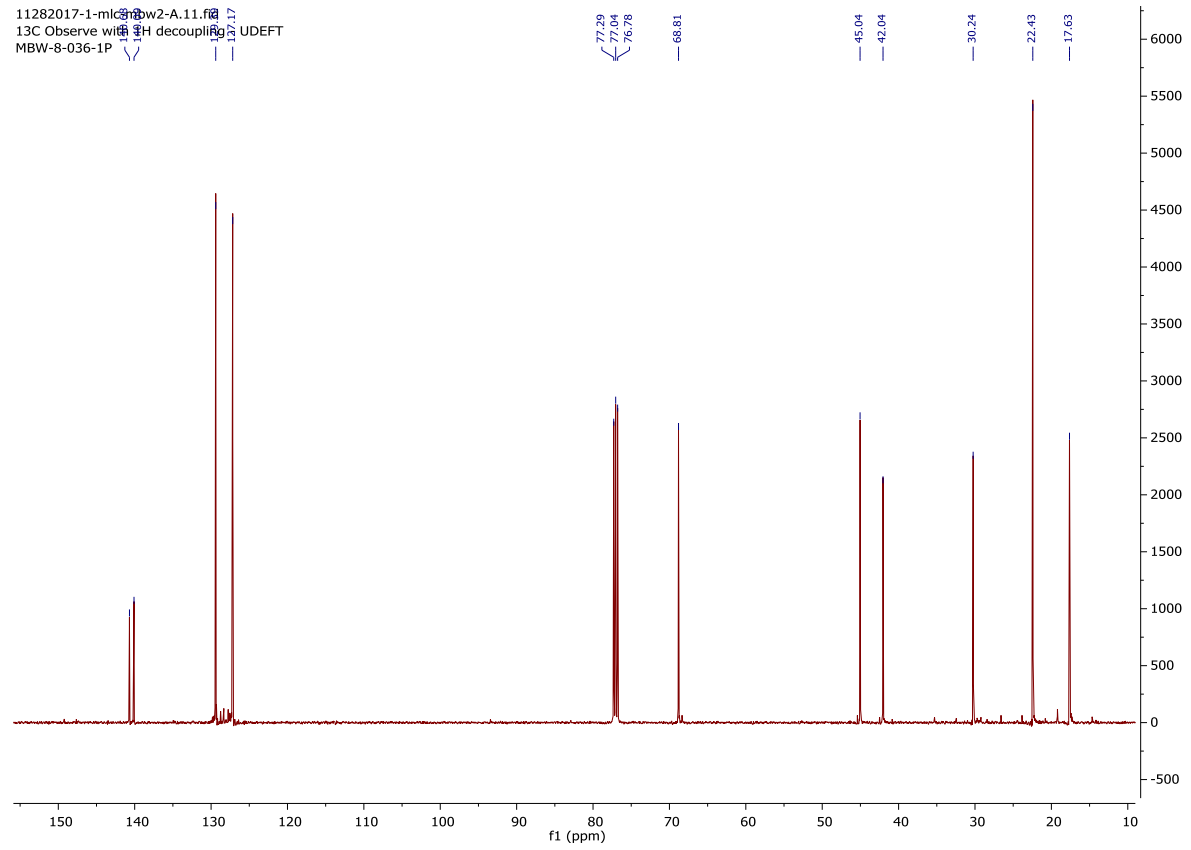
(*R*)-2-phenylbutan-1-ol (Reproduced from reference 3)



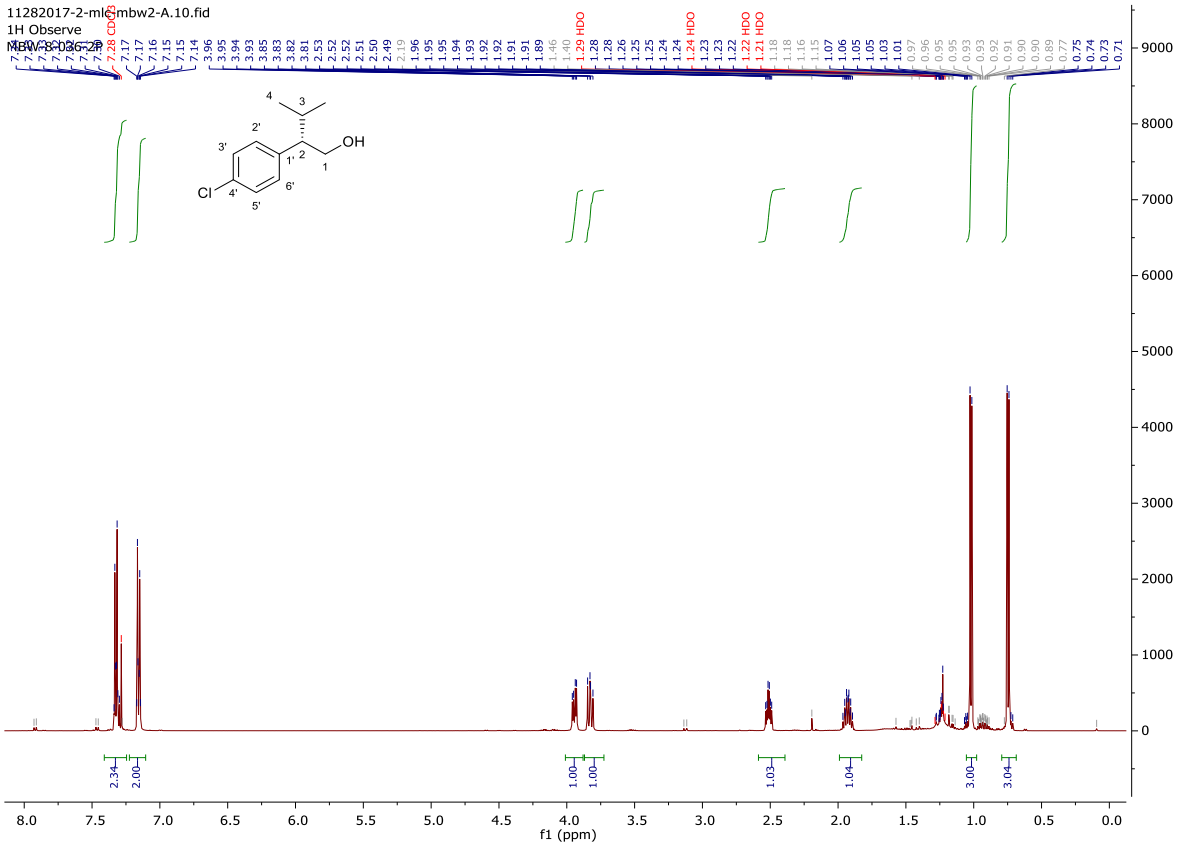


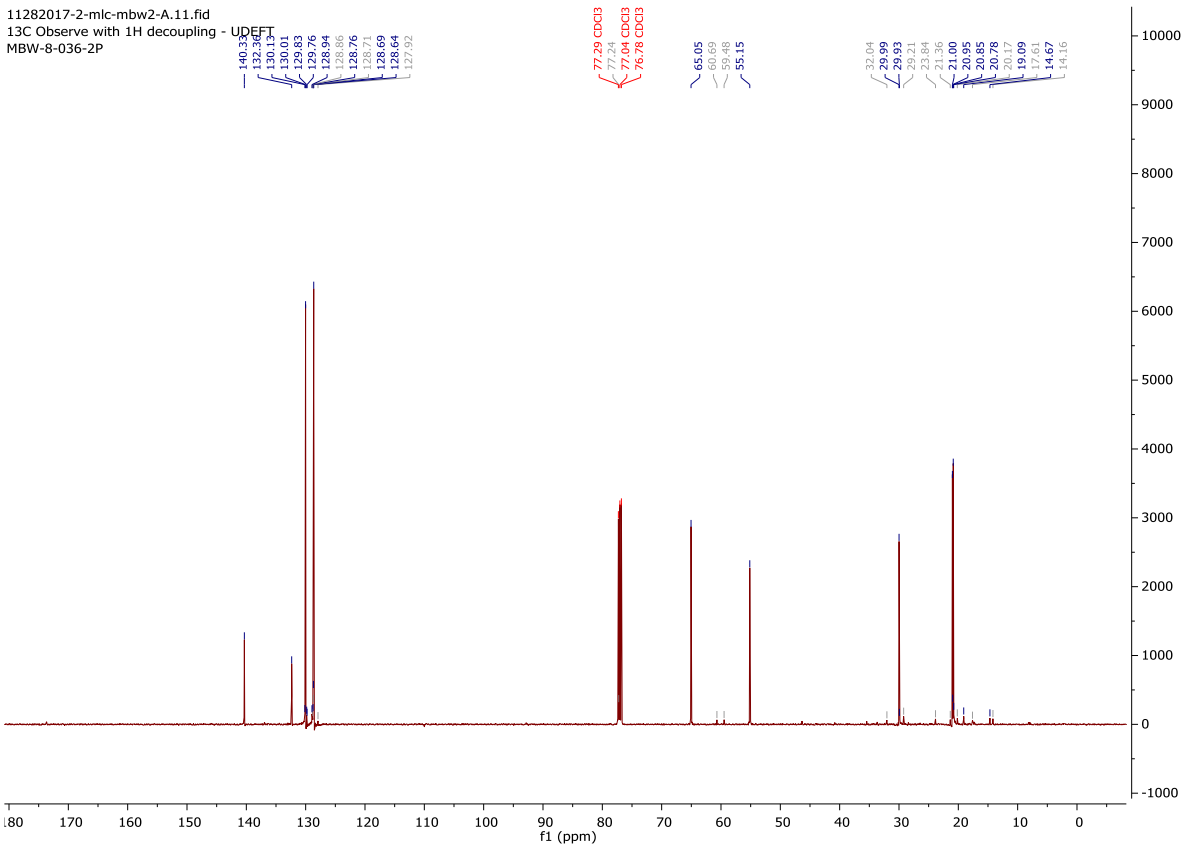
(S)-2-(4-isobutylphenyl)propan-1-ol (Reproduced from reference 3)



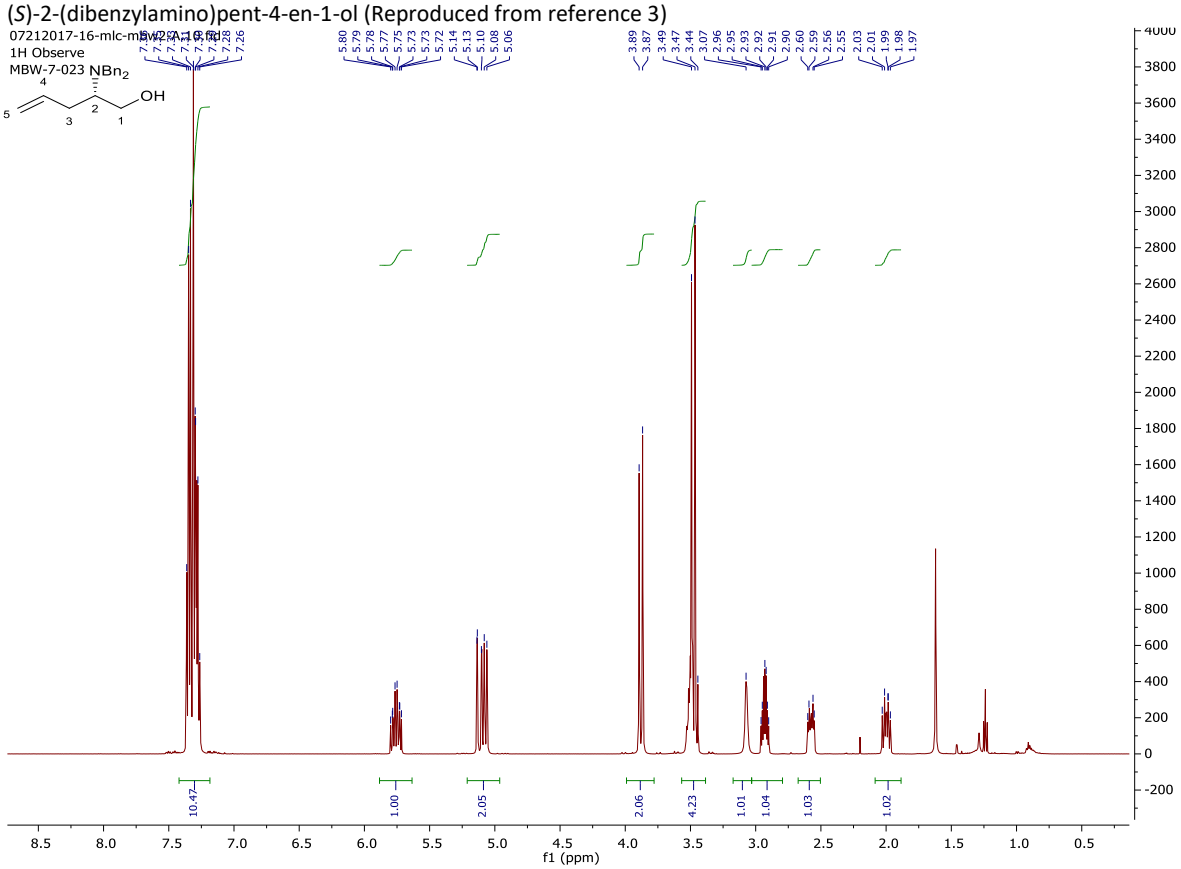


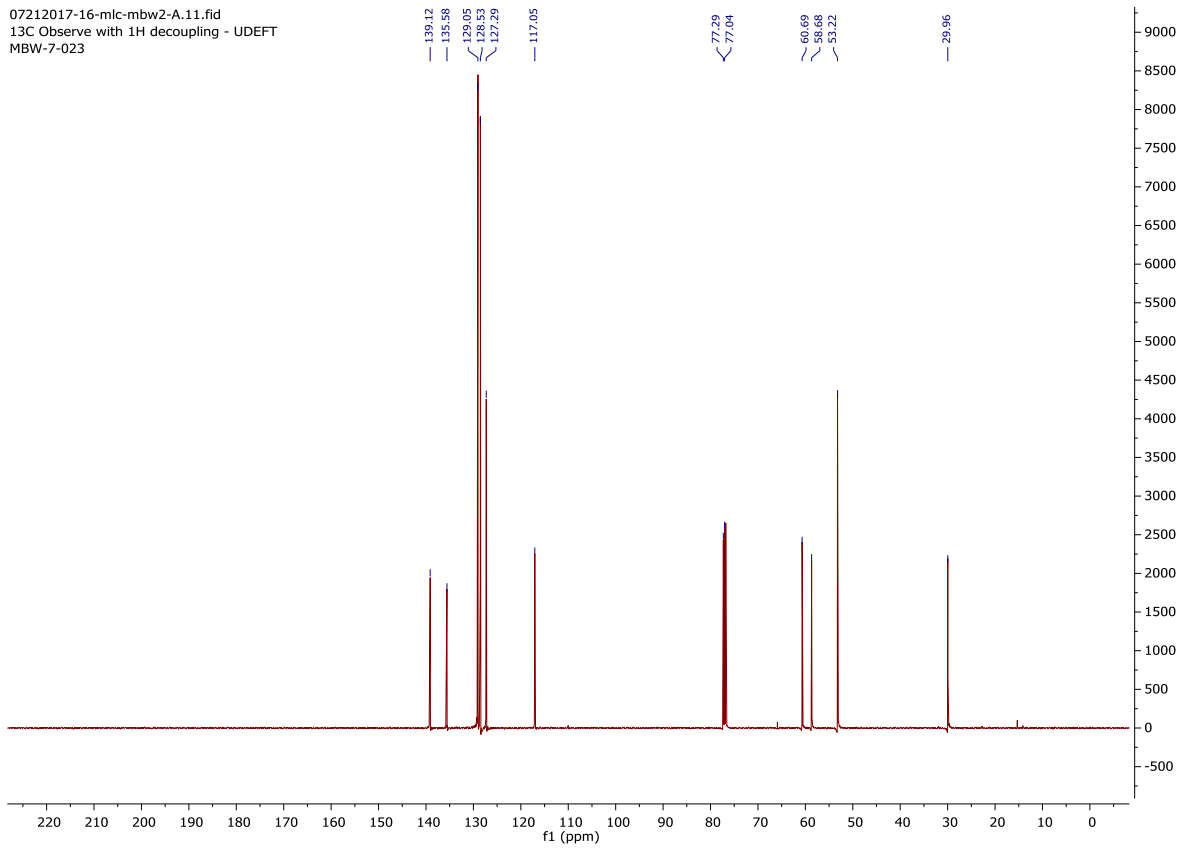
(*S*)-2-(4-chlorophenyl)-3-methylbutanol (Reproduced from reference 3)


11282017-2-mlc-mbw2-A.10.fid
1H Observe
MBW-8-036-2P
f1 (ppm)

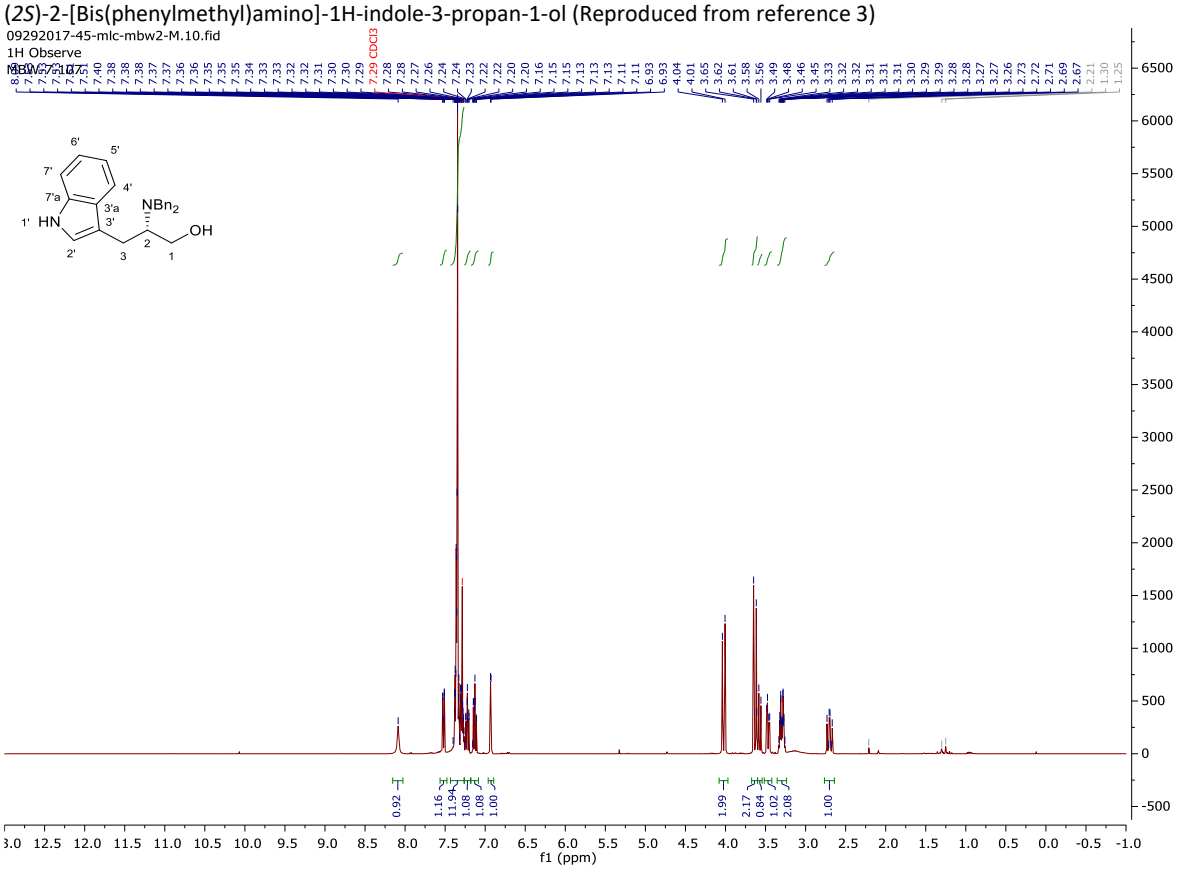

11282017-2-mlc-mbw2-A.11.fid
13C Observe with 1H decoupling - UDEFT
MBW-8-036-2P
f1 (ppm)

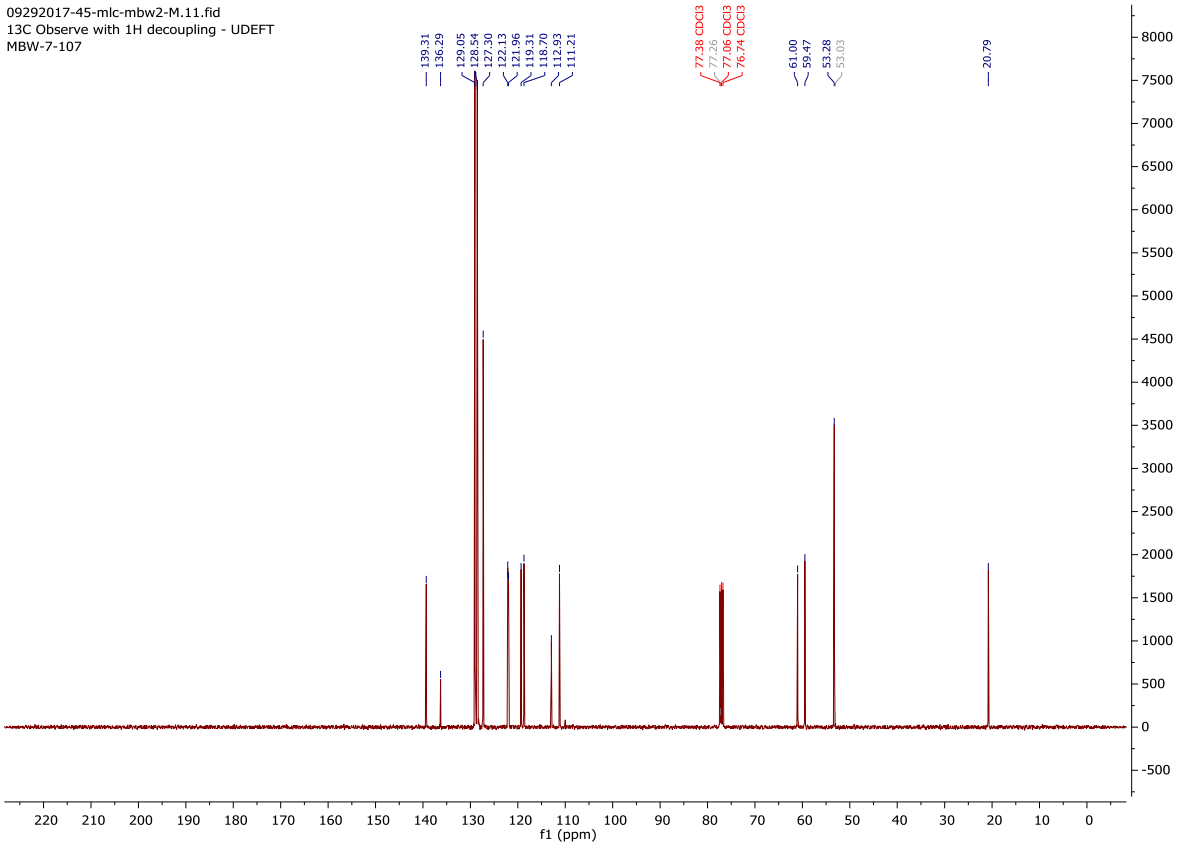
(*S*)-2-(dibenzylamino)pent-4-en-1-ol (Reproduced from reference 3)



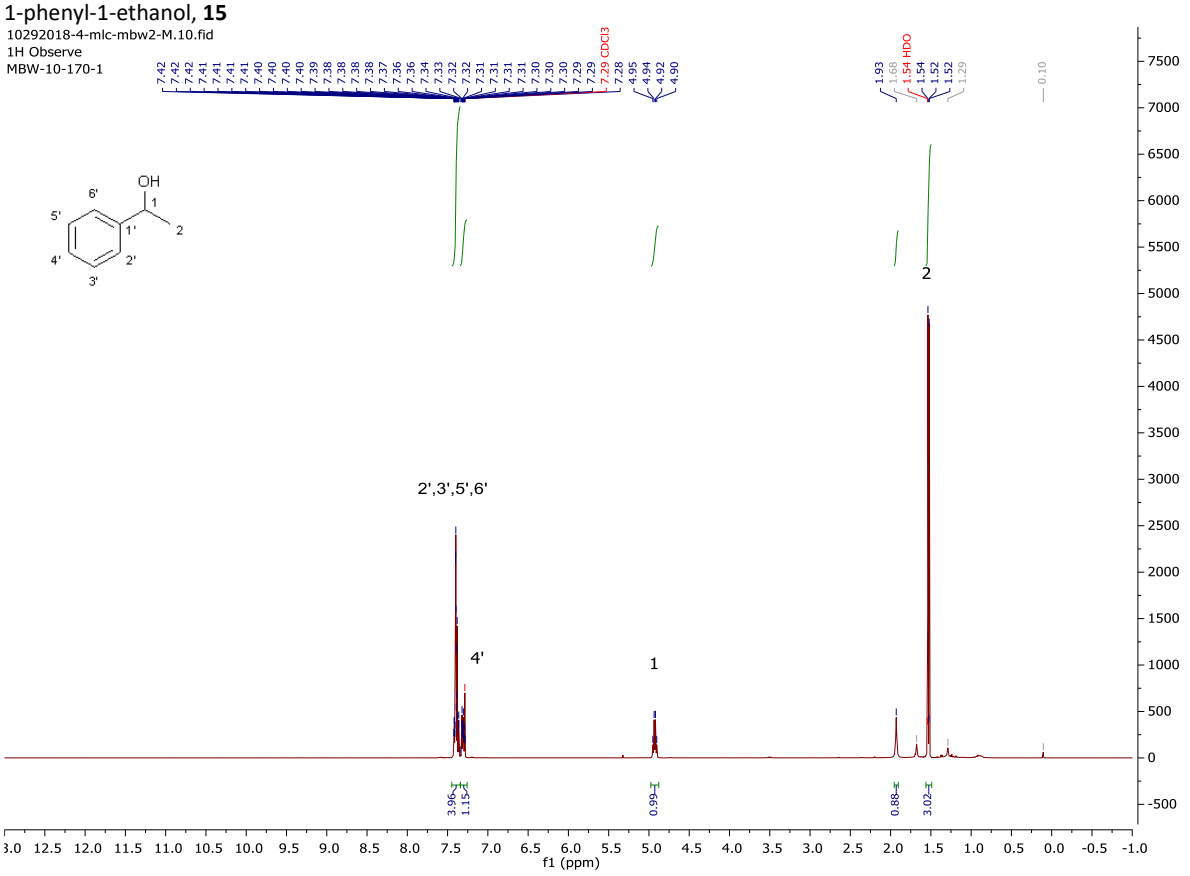


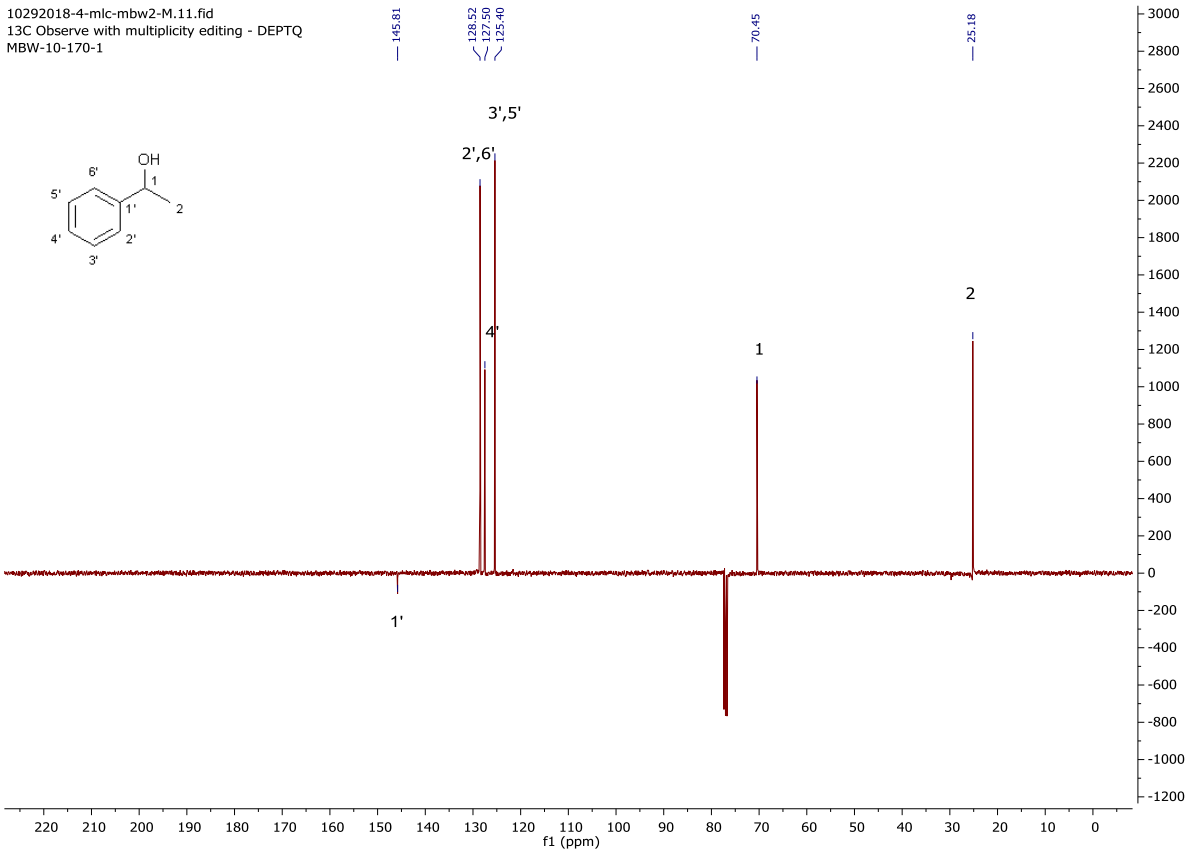
(*2S*)-2-[Bis(phenylmethyl)amino]-1H-indole-3-propan-1-ol (Reproduced from reference 3)



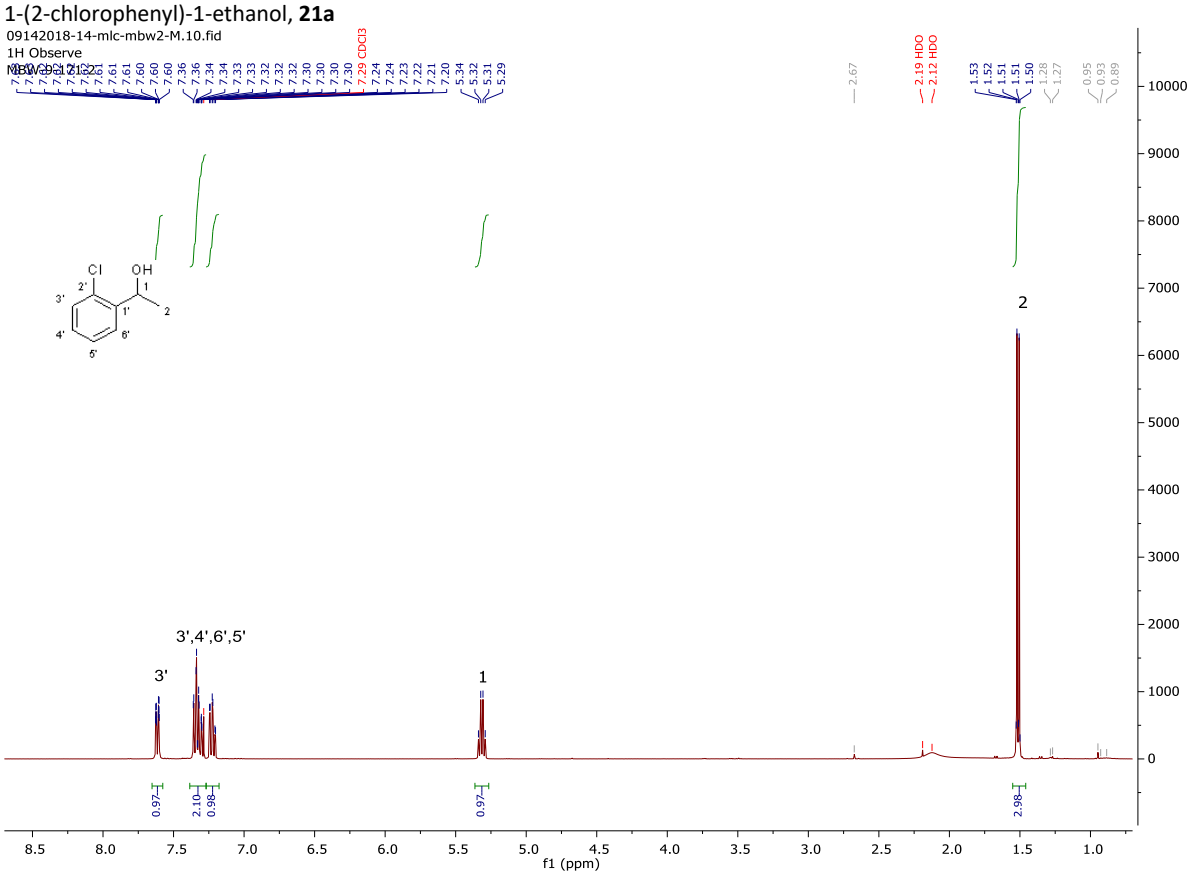


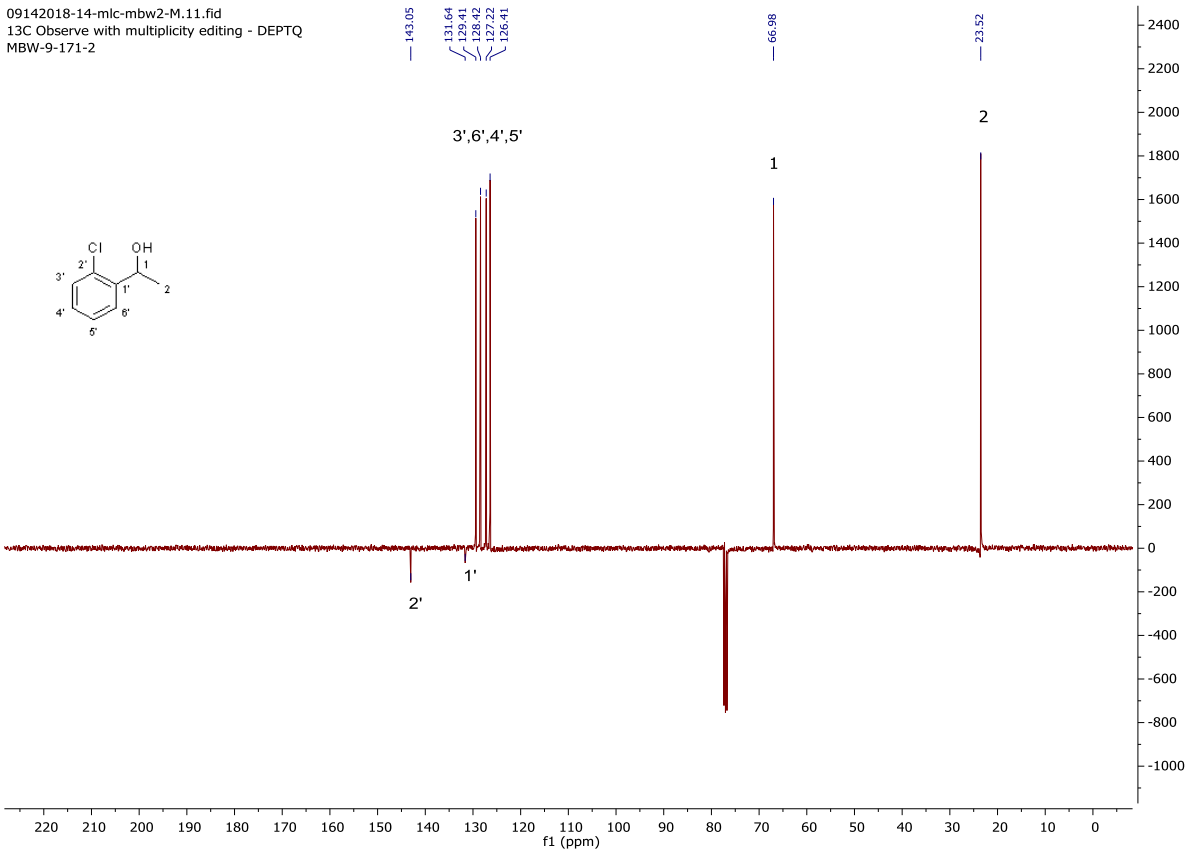
1-phenyl-1-ethanol, **15**



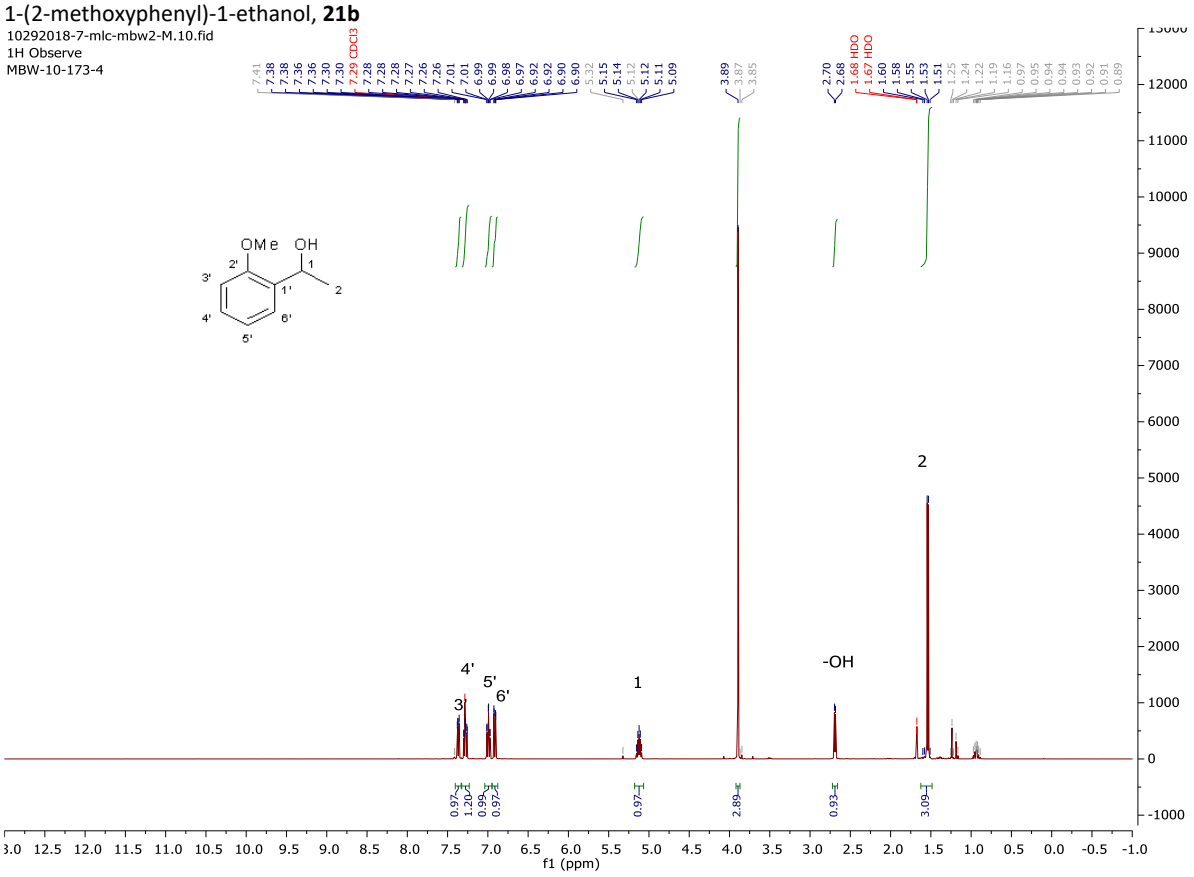


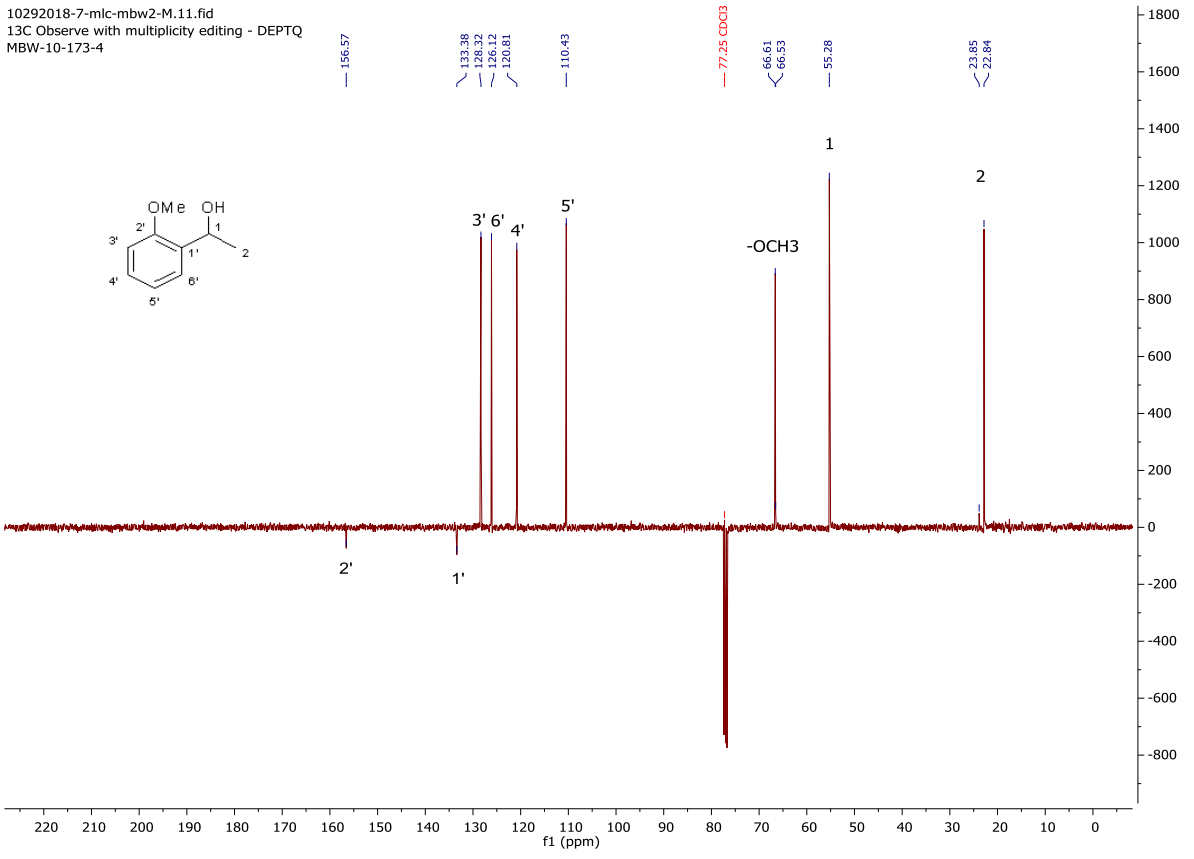
1-(2-chlorophenyl)-1-ethanol, **21a**



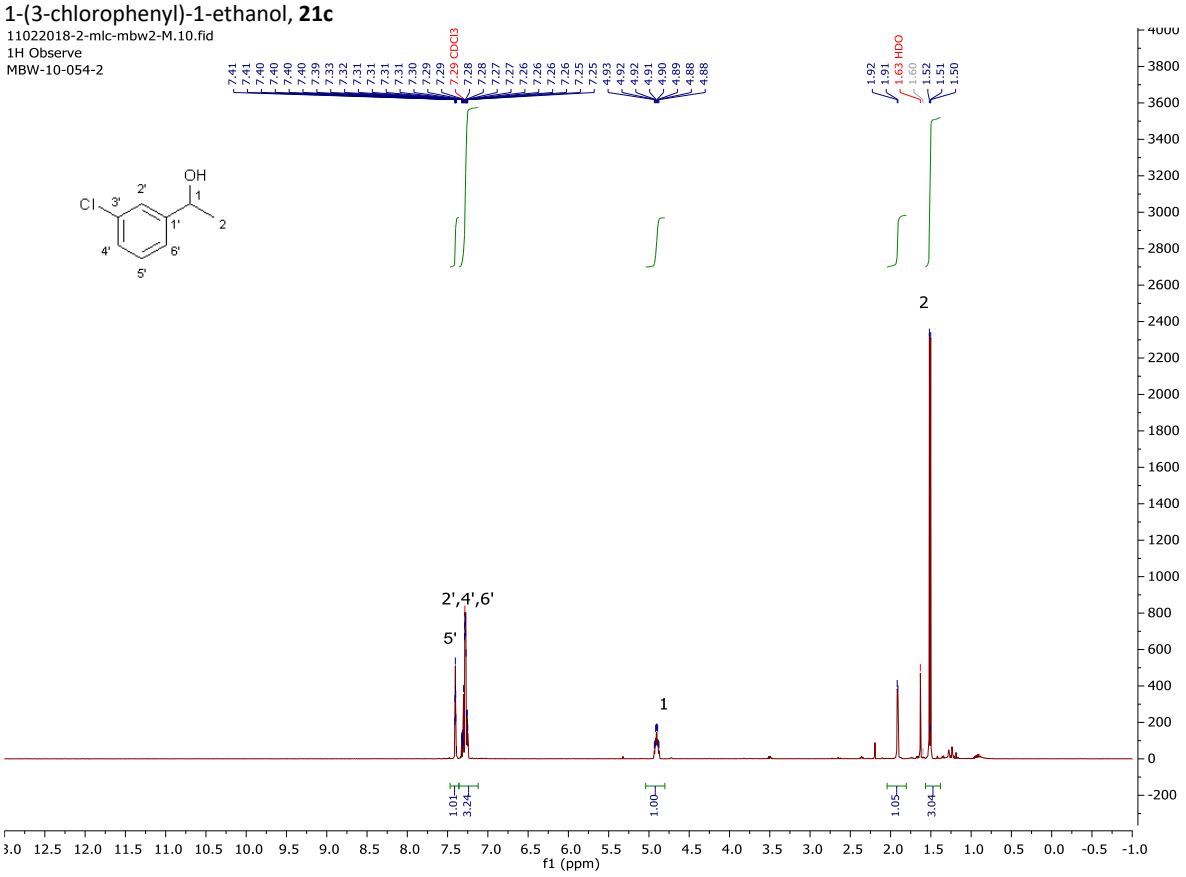


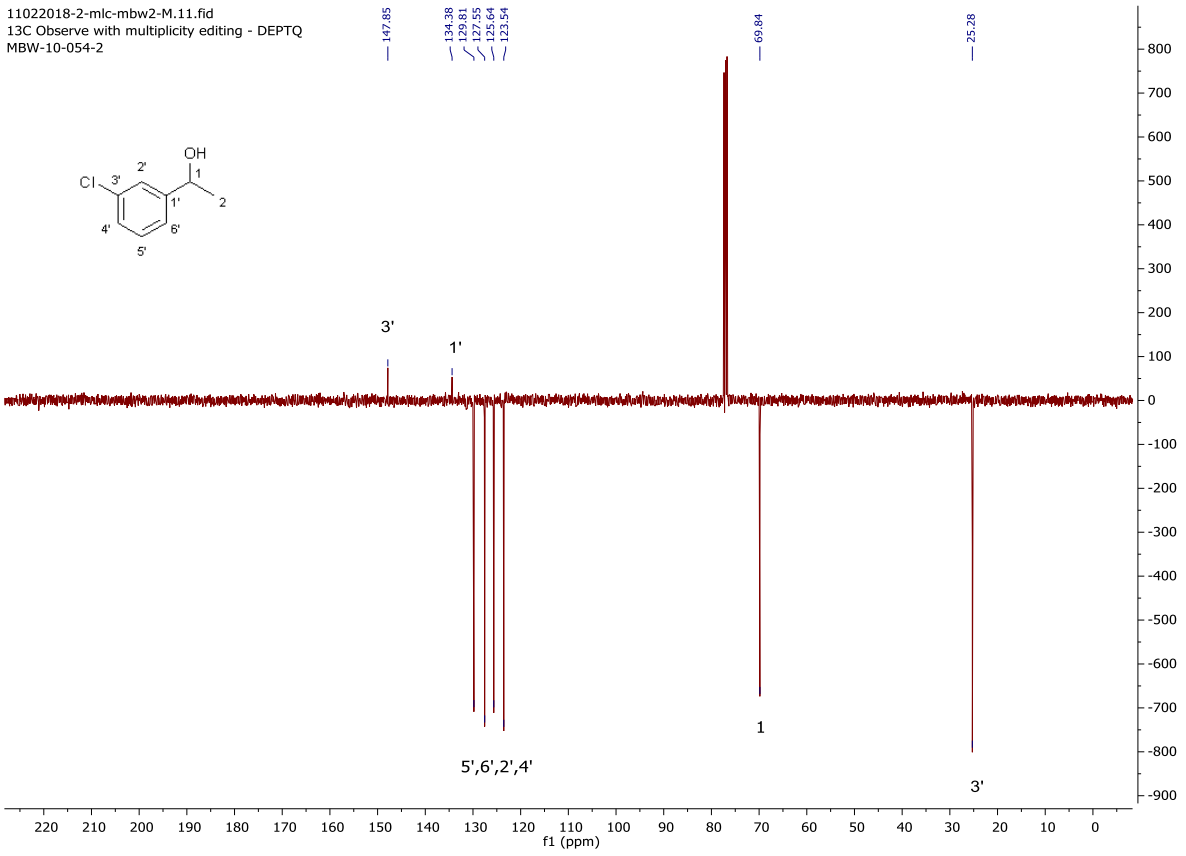
1-(2-methoxyphenyl)-1-ethanol, **21b**



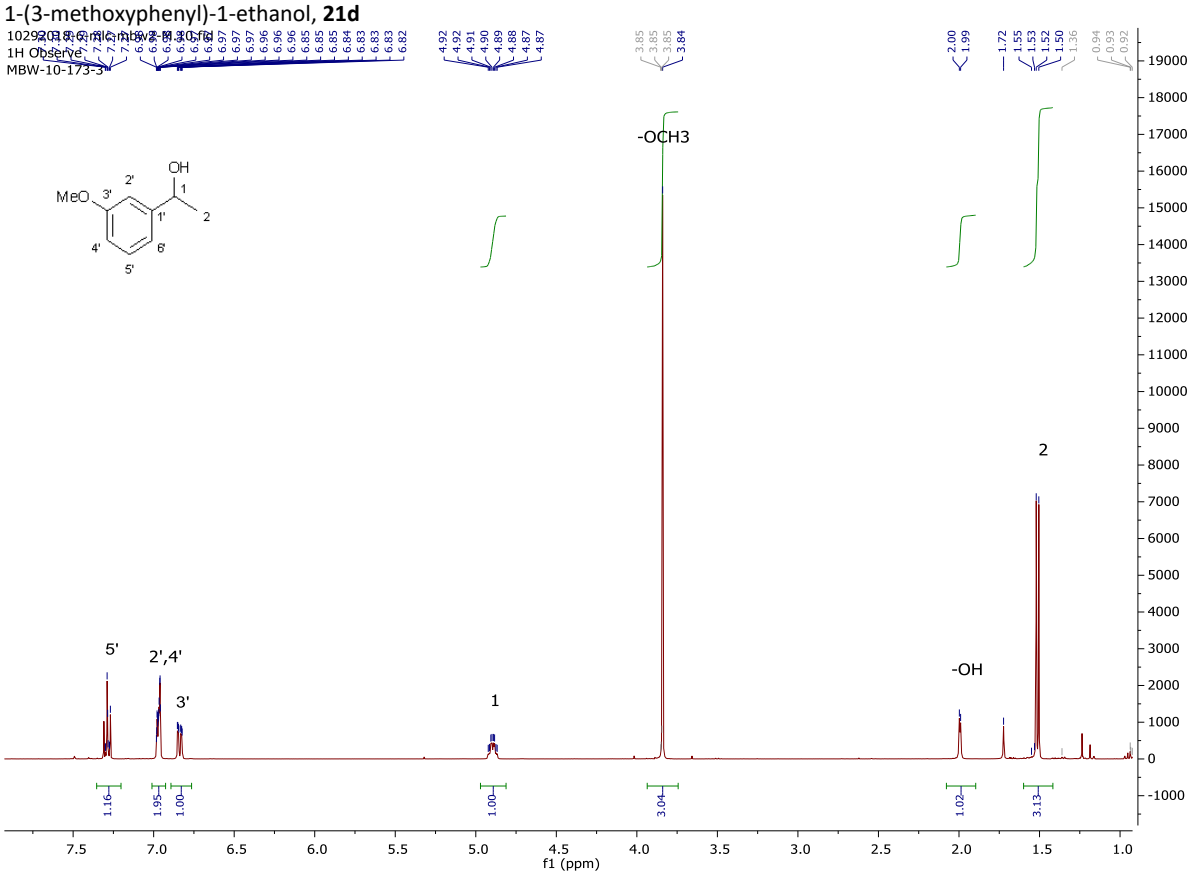


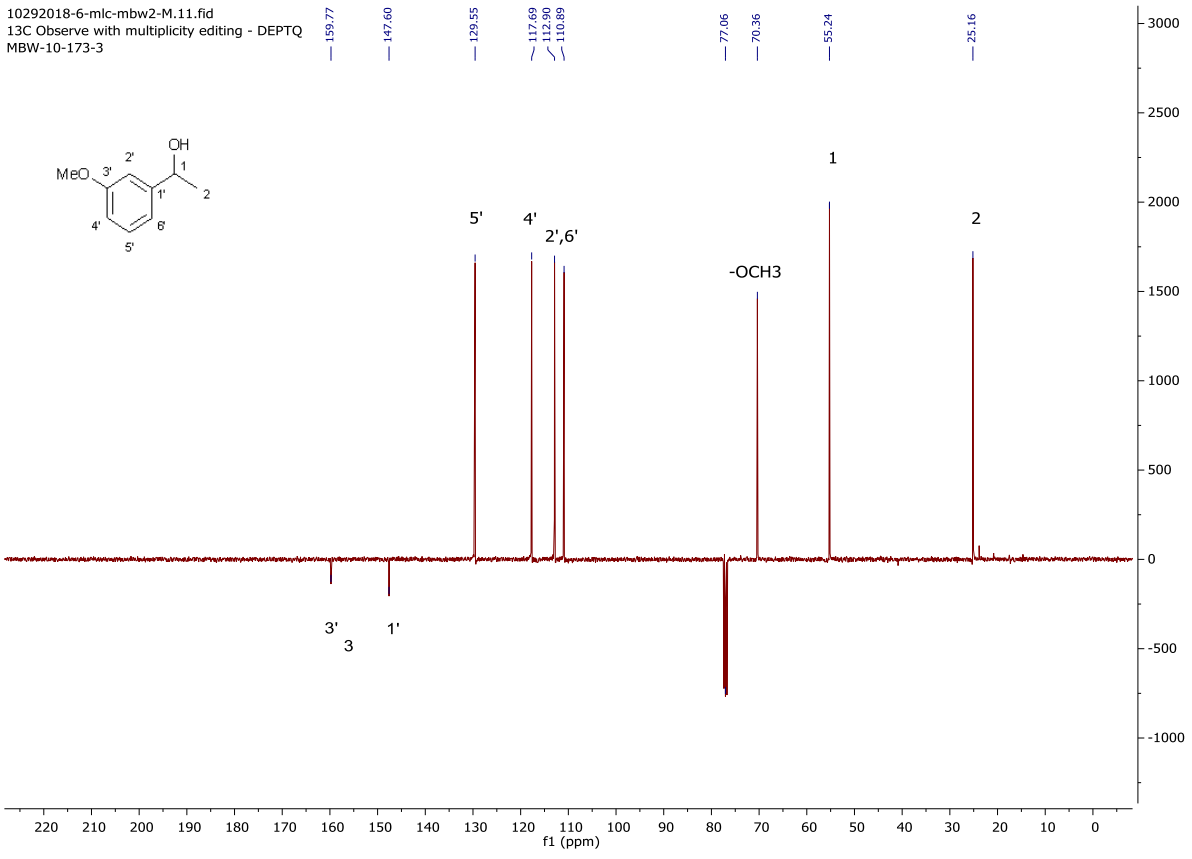
1-(3-chlorophenyl)-1-ethanol, **21c**



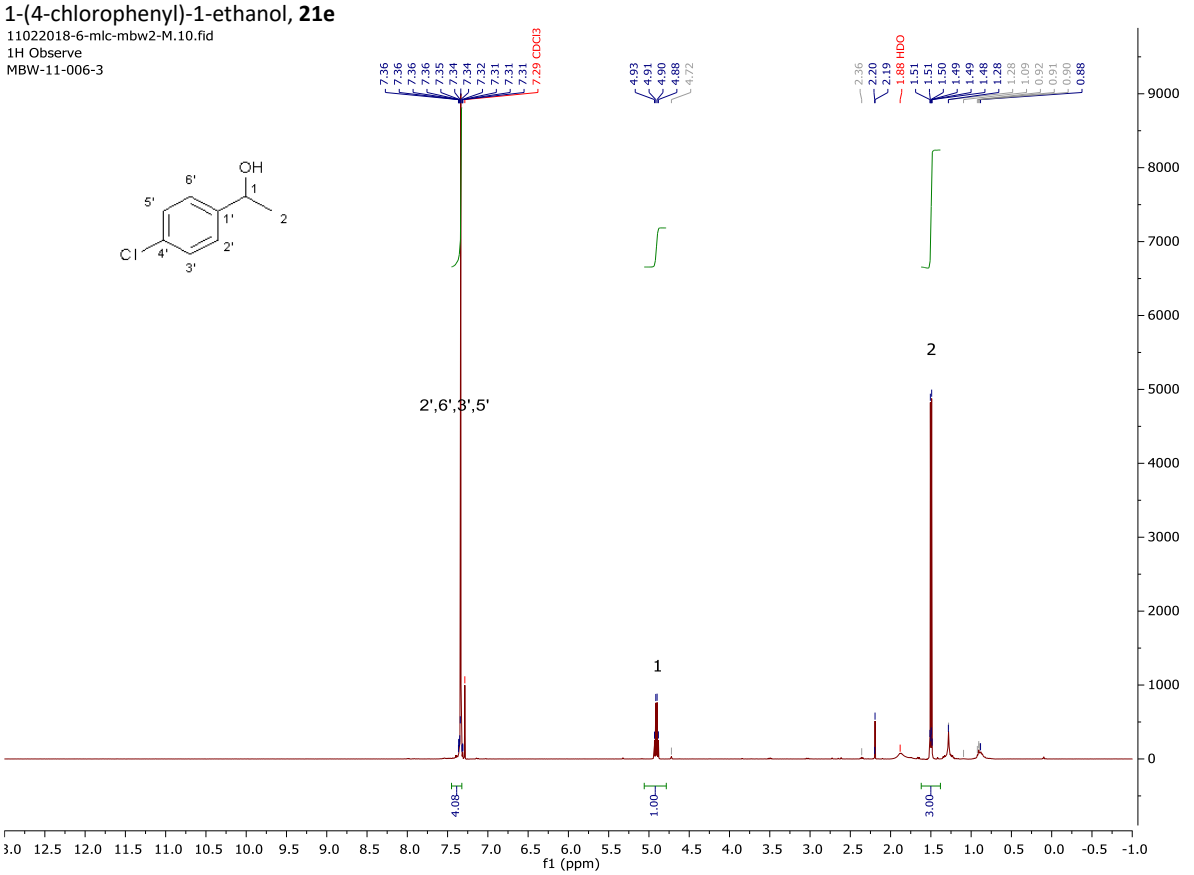


1-(3-methoxyphenyl)-1-ethanol, **21d**

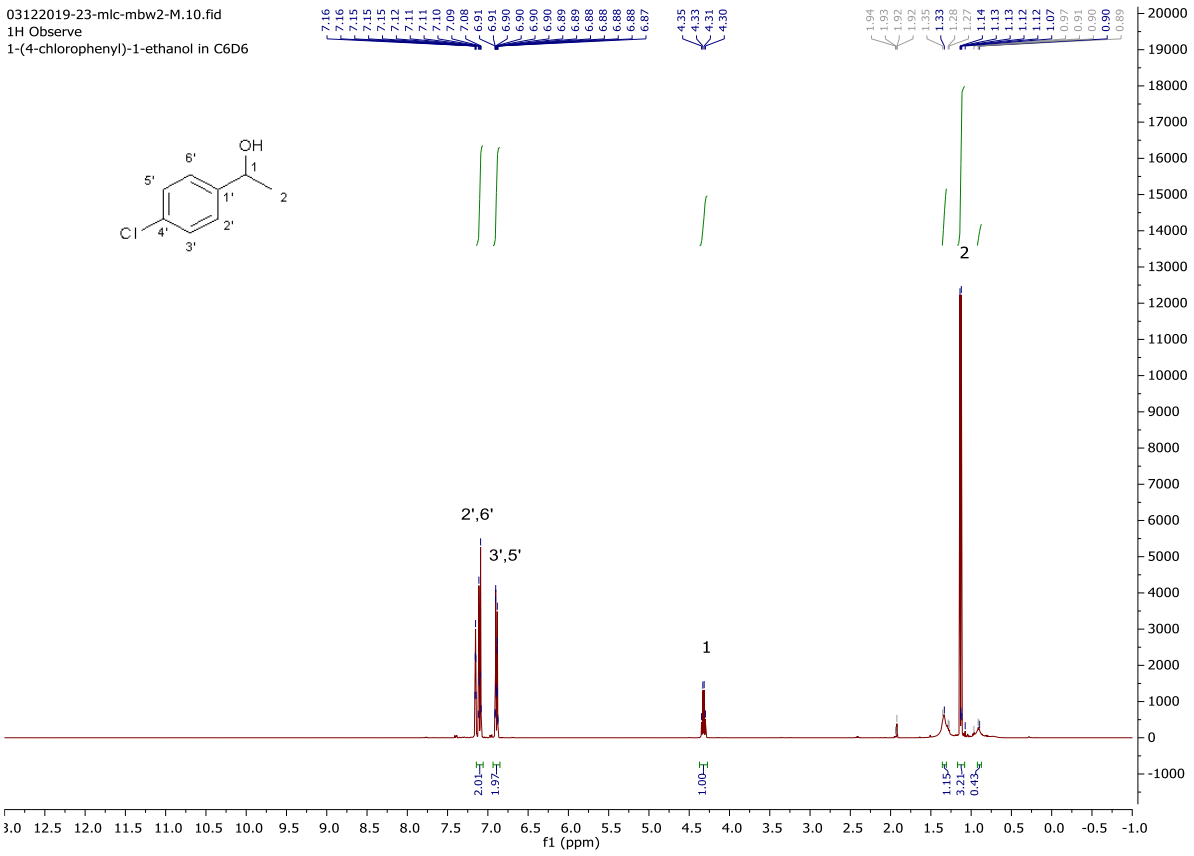


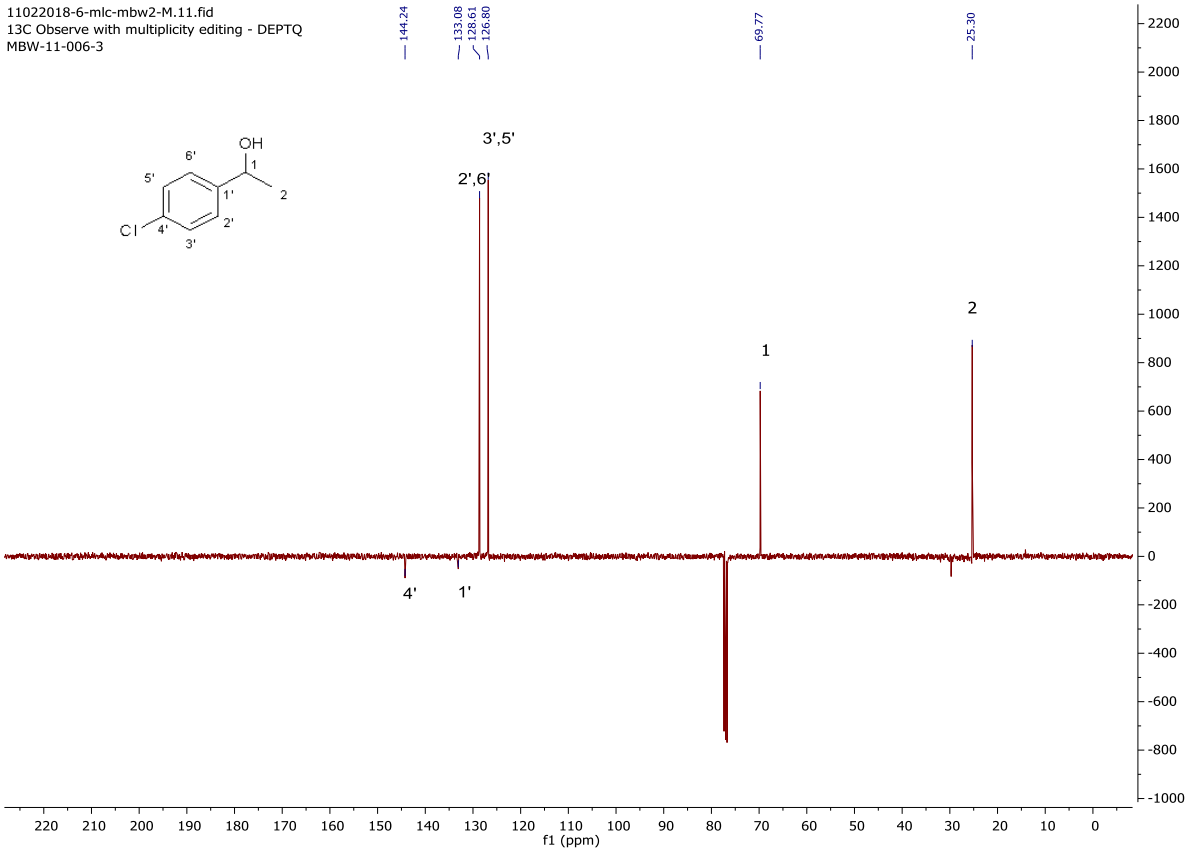


1-(4-chlorophenyl)-1-ethanol, **21e**

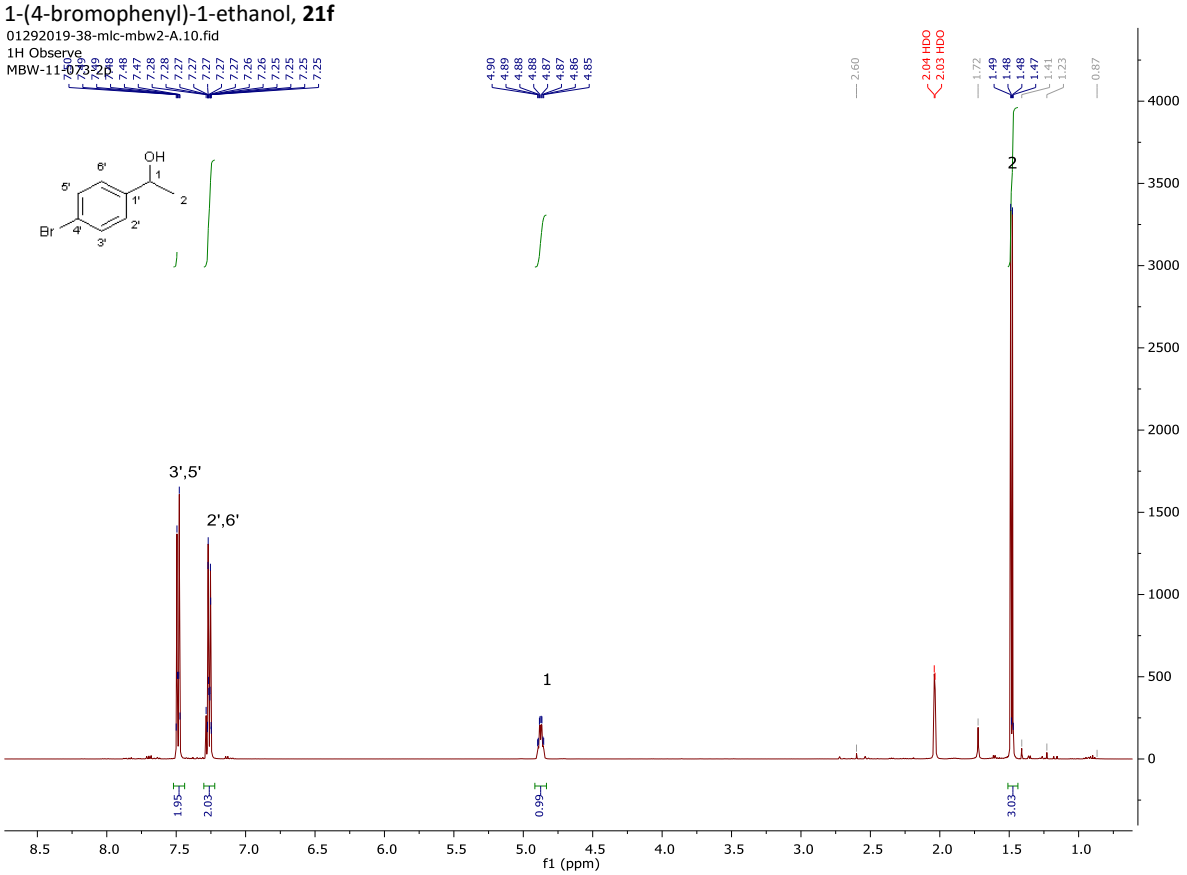


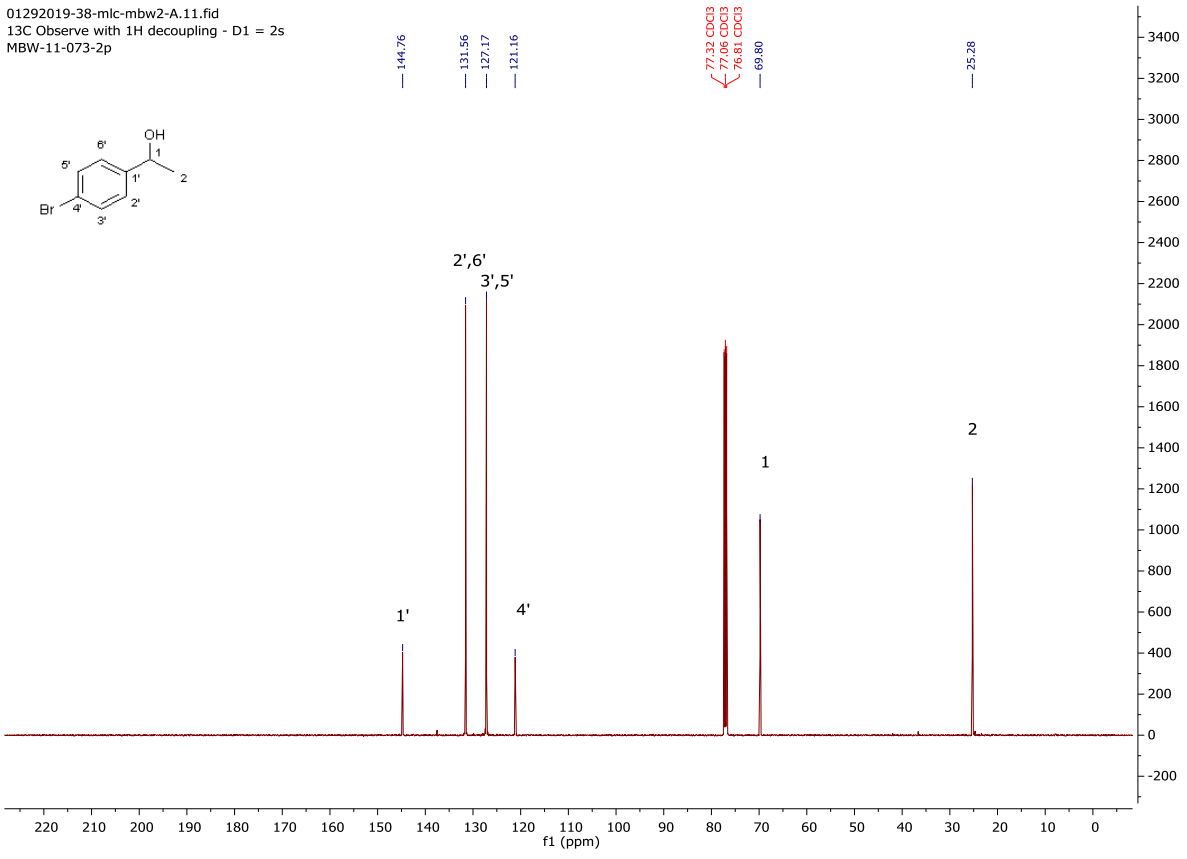
In C_6D_6



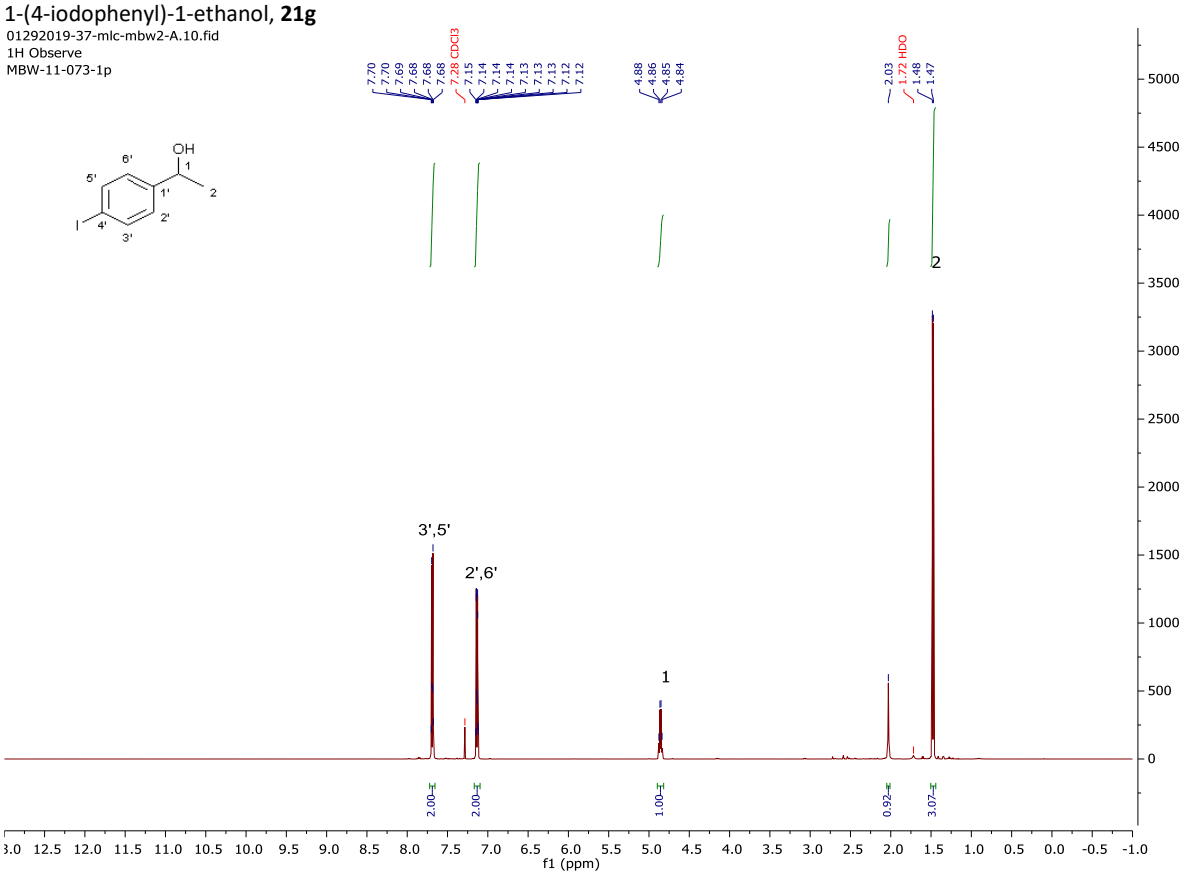

11022018-6-mlc-mbw2-M.11.fid
13C Observe with multiplicity editing - DEPTQ
MBW-11-006-3
144.24
133.08
128.61
126.80
69.77
25.30
OH
6'
1
5'
1'
2
2'
Cl
4'
3'
3',5'
2',6'
1
2
4'
1'
f1 (ppm)

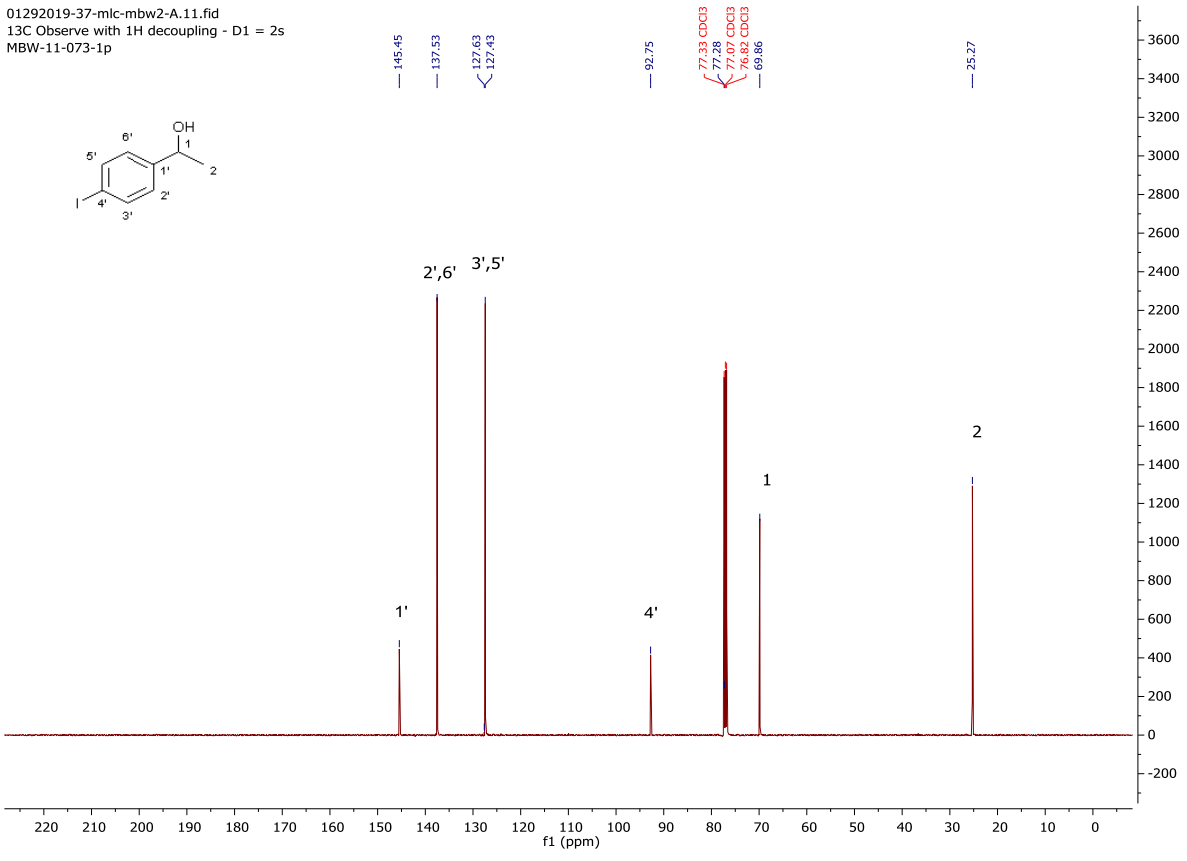
1-(4-bromophenyl)-1-ethanol, **21f**



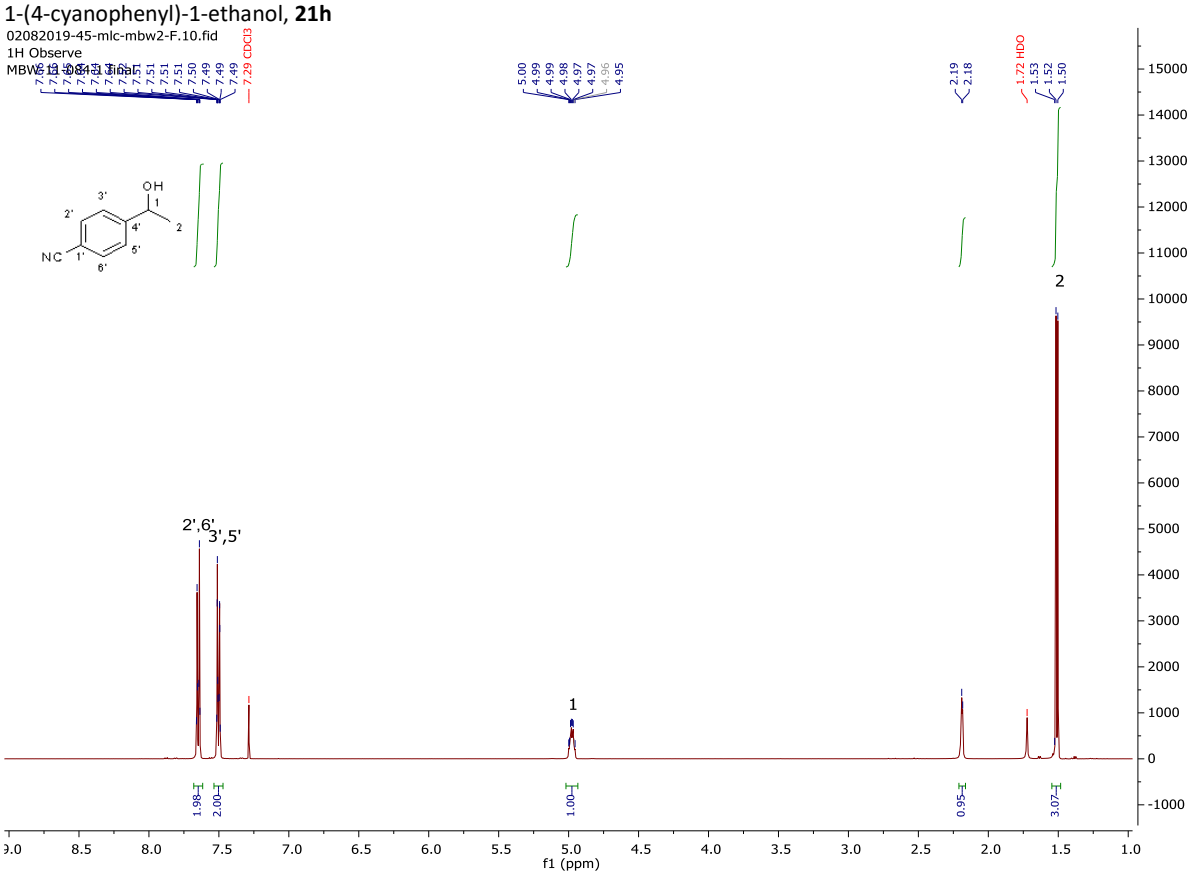


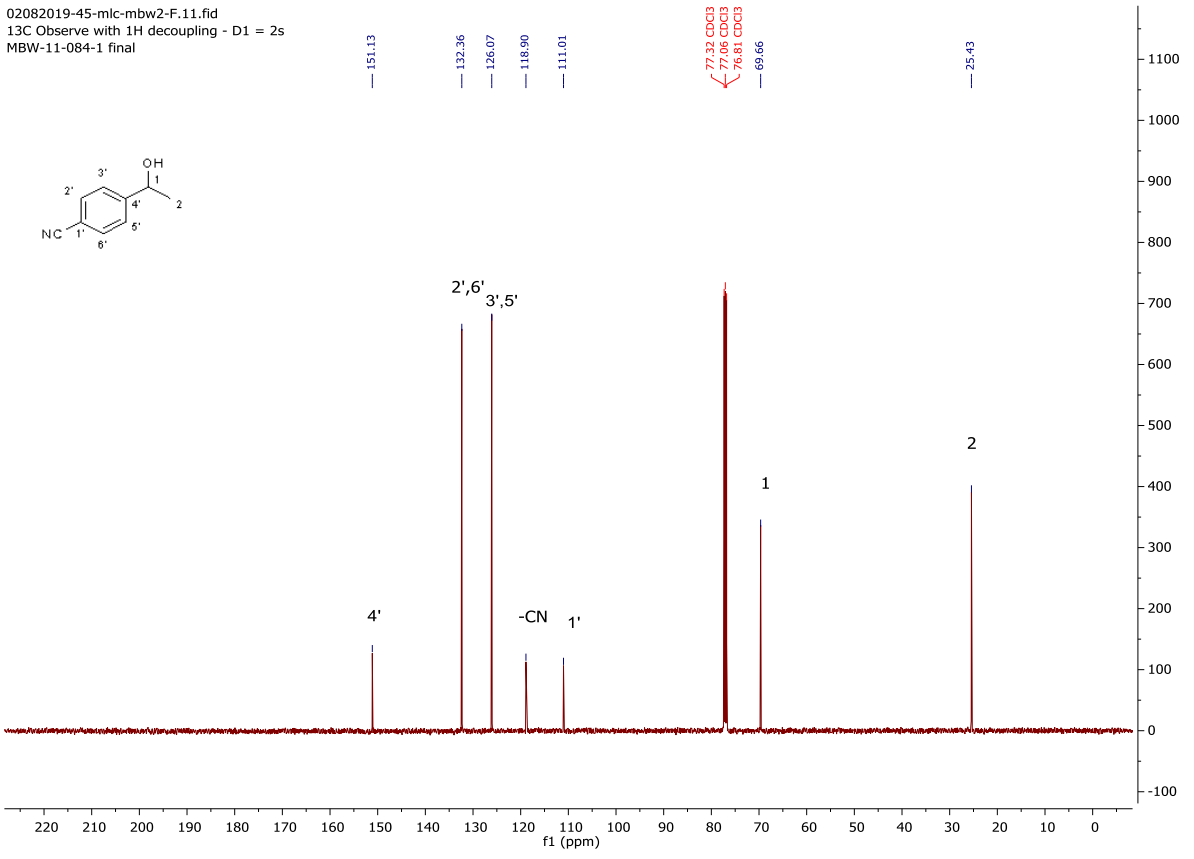
1-(4-iodophenyl)-1-ethanol, **21g**



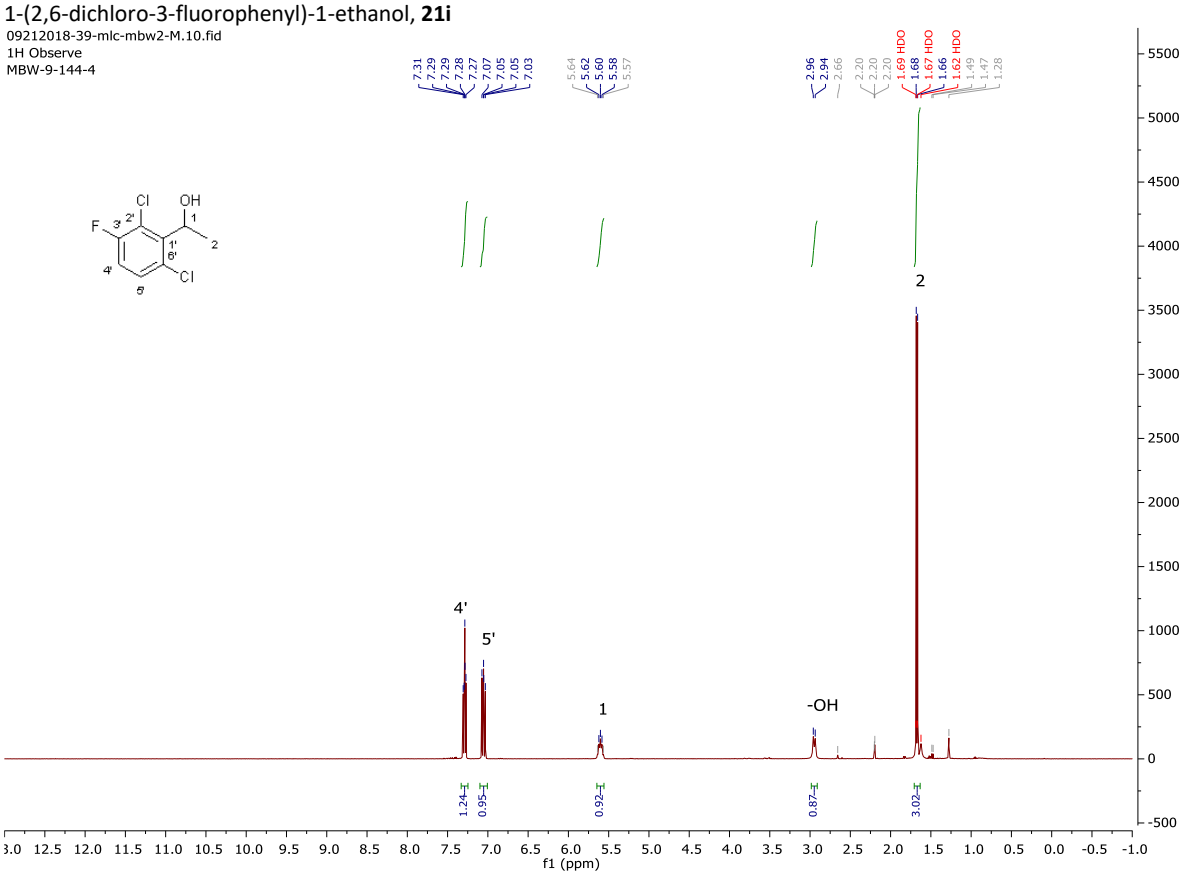


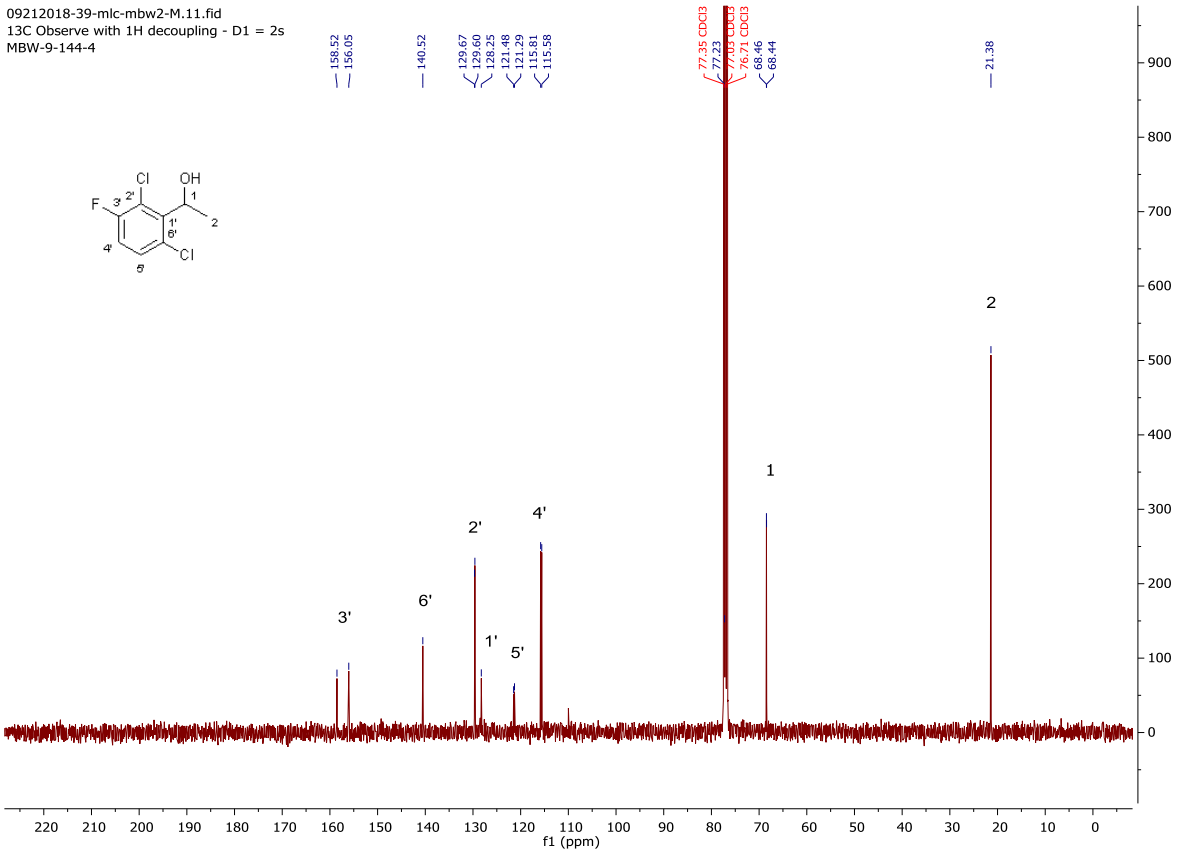
1-(4-cyanophenyl)-1-ethanol, **21h**

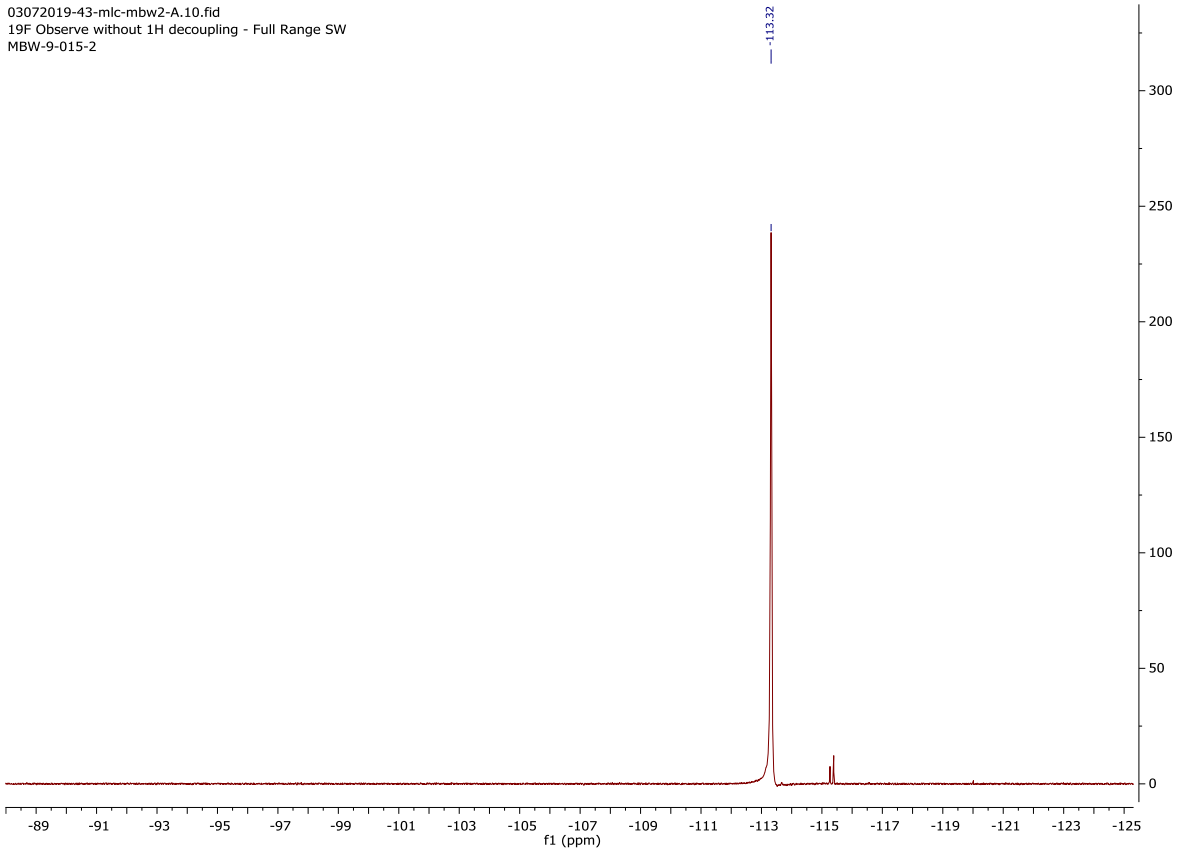




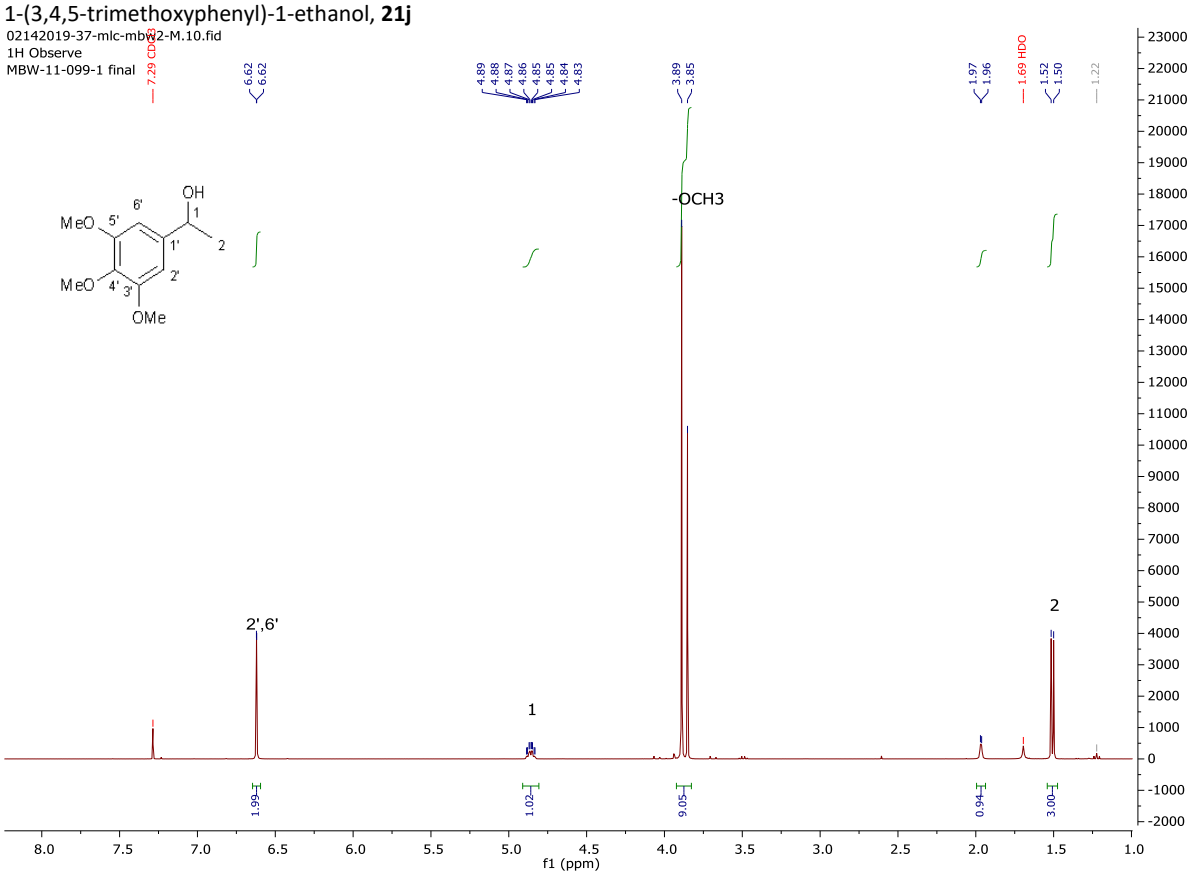
1-(2,6-dichloro-3-fluorophenyl)-1-ethanol, **21i**

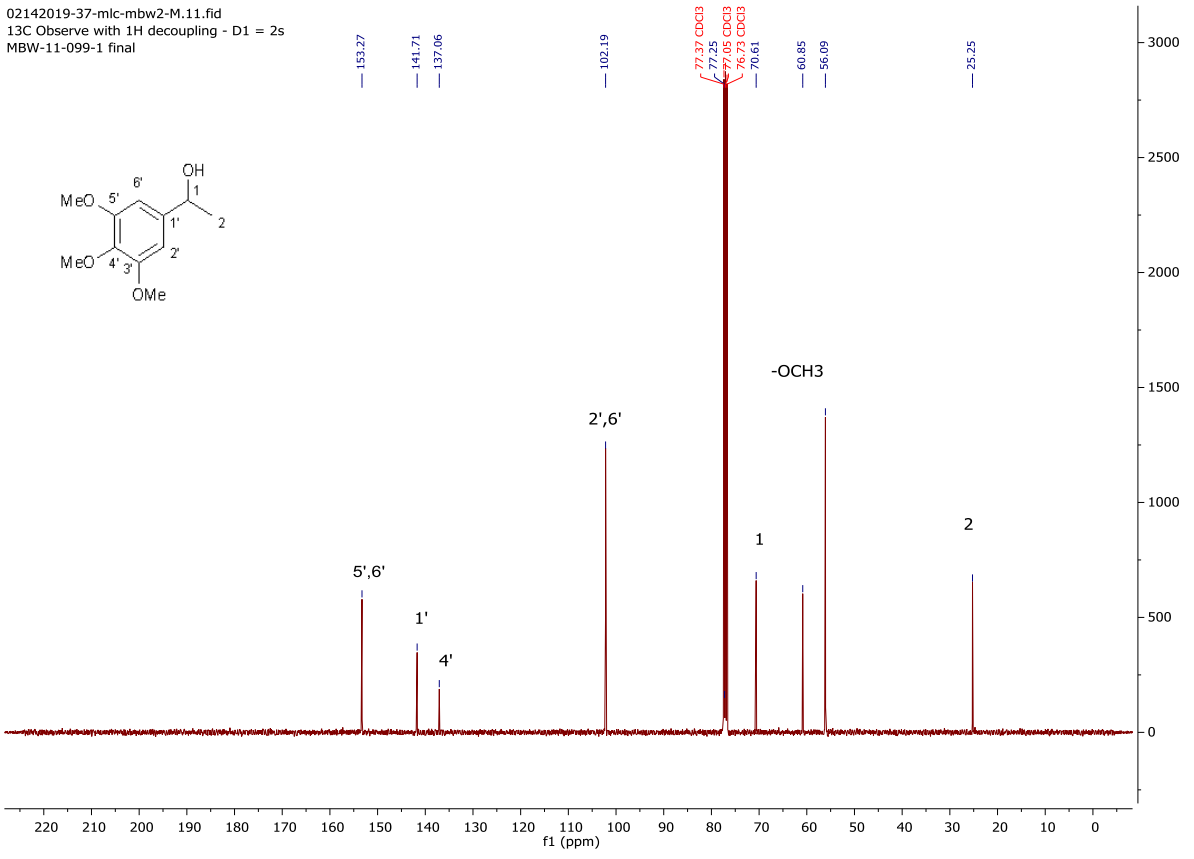




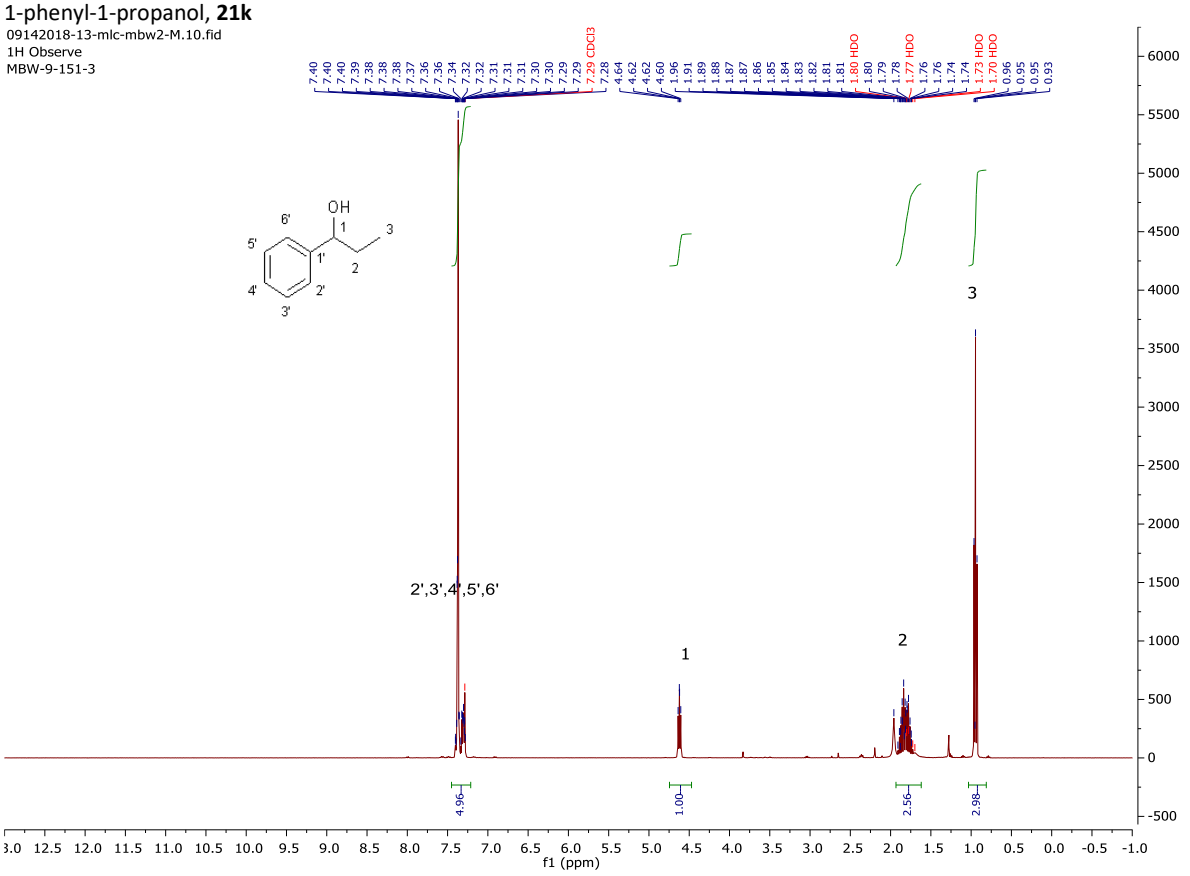

03072019-43-mlc-mbw2-A.10.fid
19F Observe without 1H decoupling - Full Range SW
MBW-9-015-2
-113.32
300
250
200
150
100
50
0
-89
-91
-93
-95
-97
-99
-101
-103
-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
f1 (ppm)

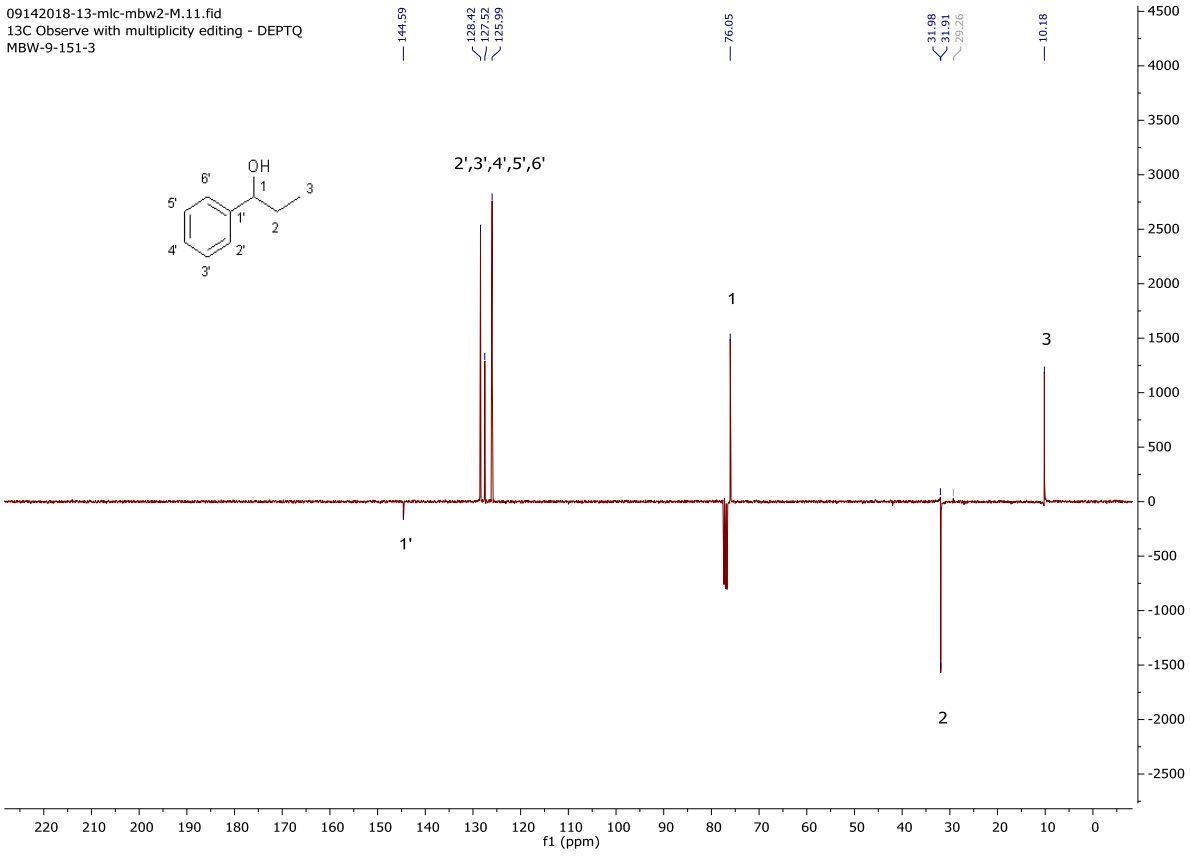
1-(3,4,5-trimethoxyphenyl)-1-ethanol, **21j**



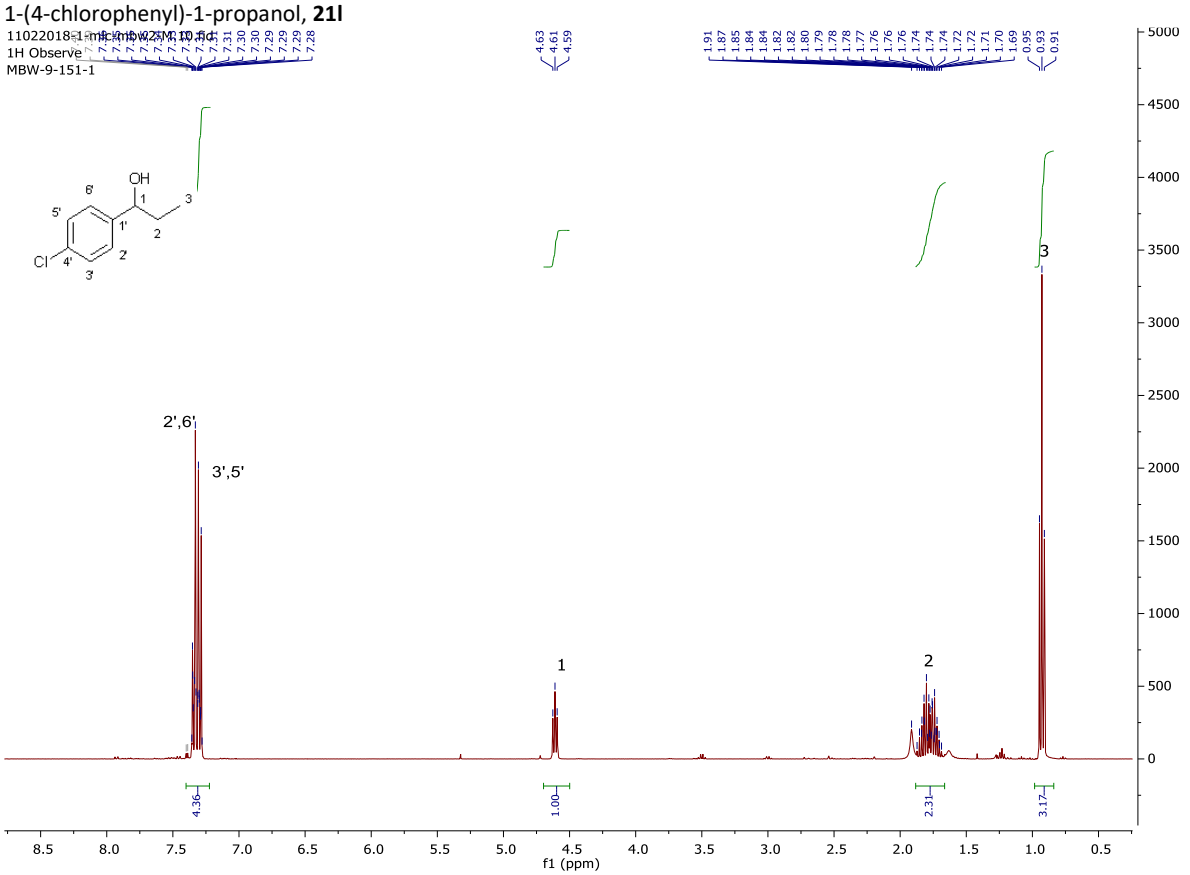


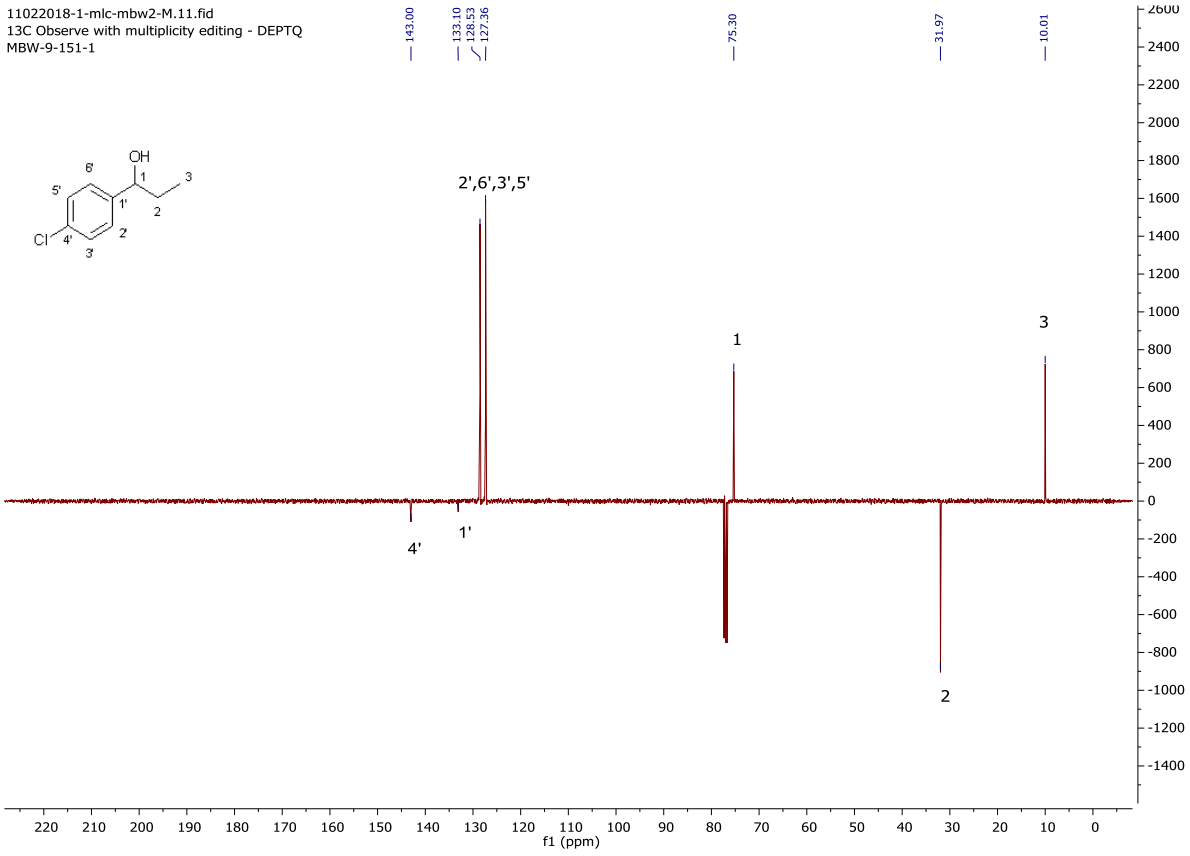
1-phenyl-1-propanol, **21k**



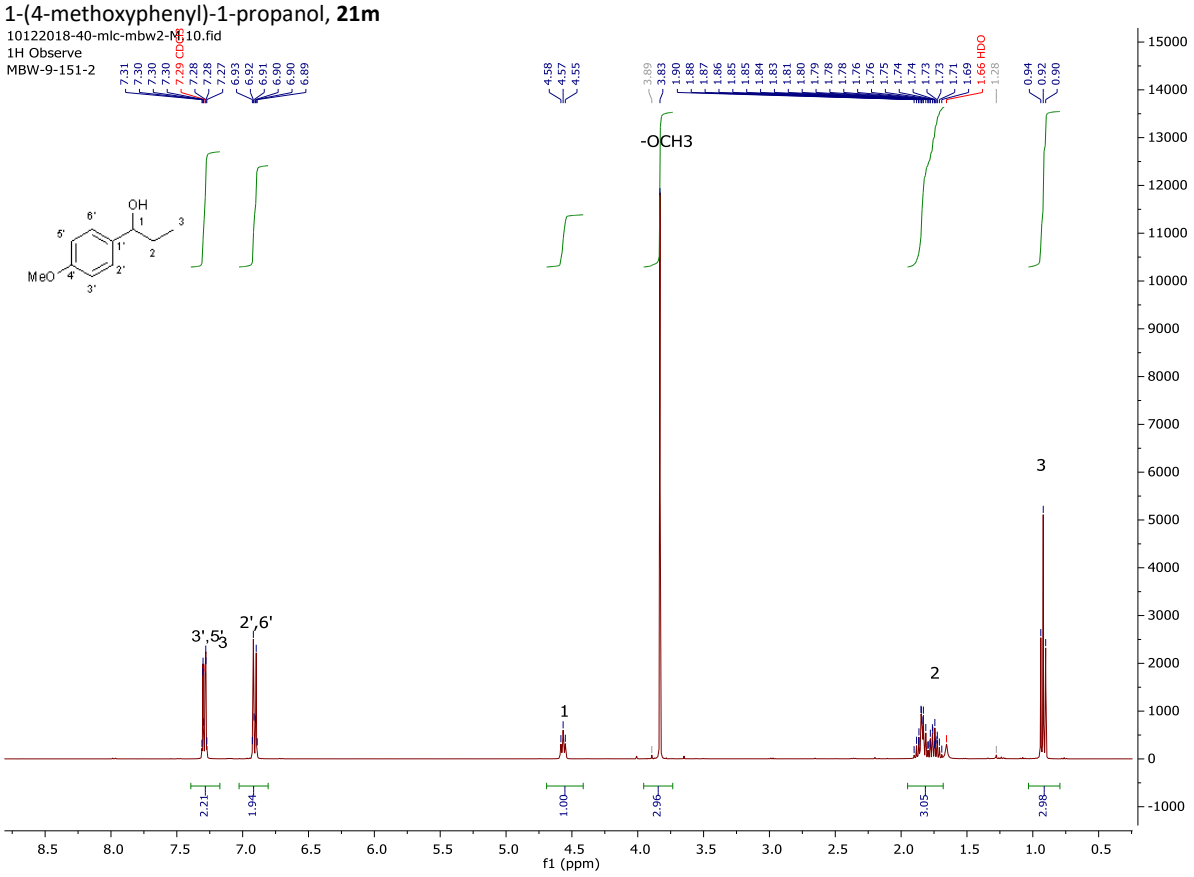


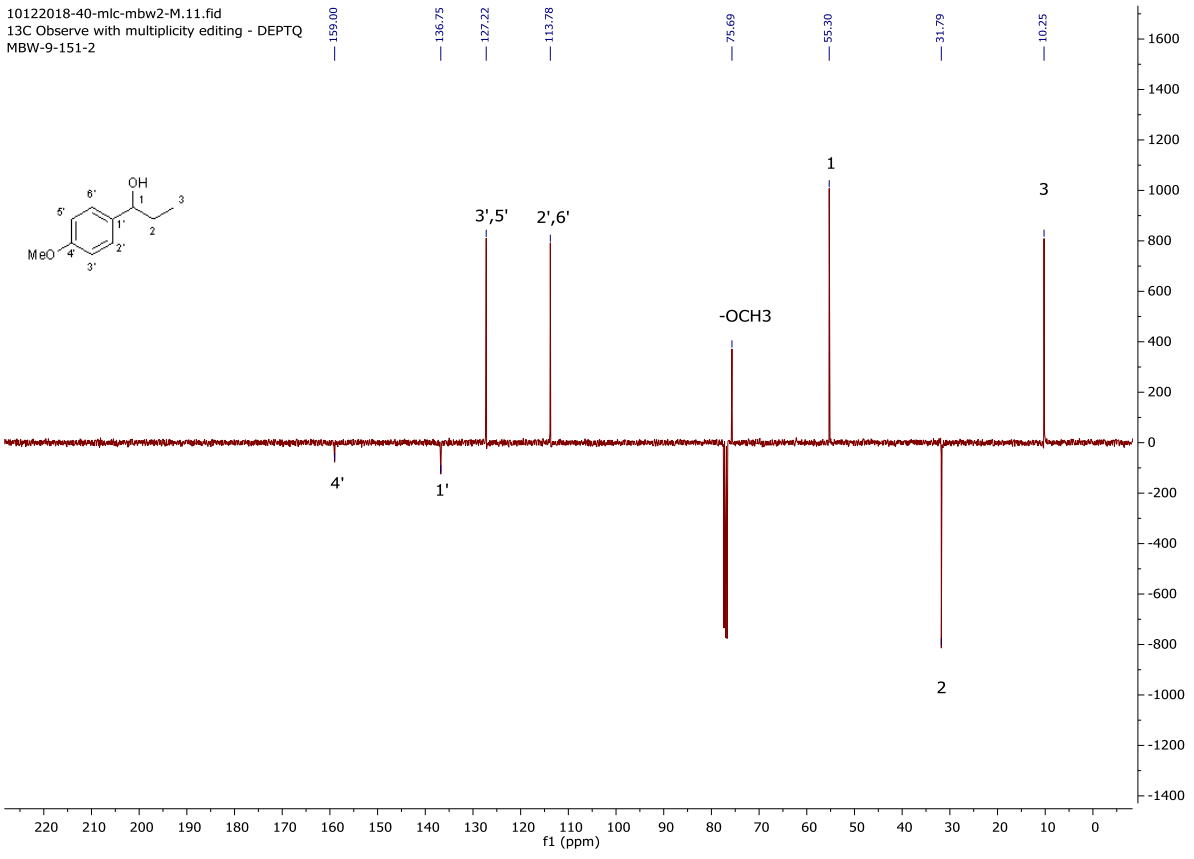
1-(4-chlorophenyl)-1-propanol, **21l**



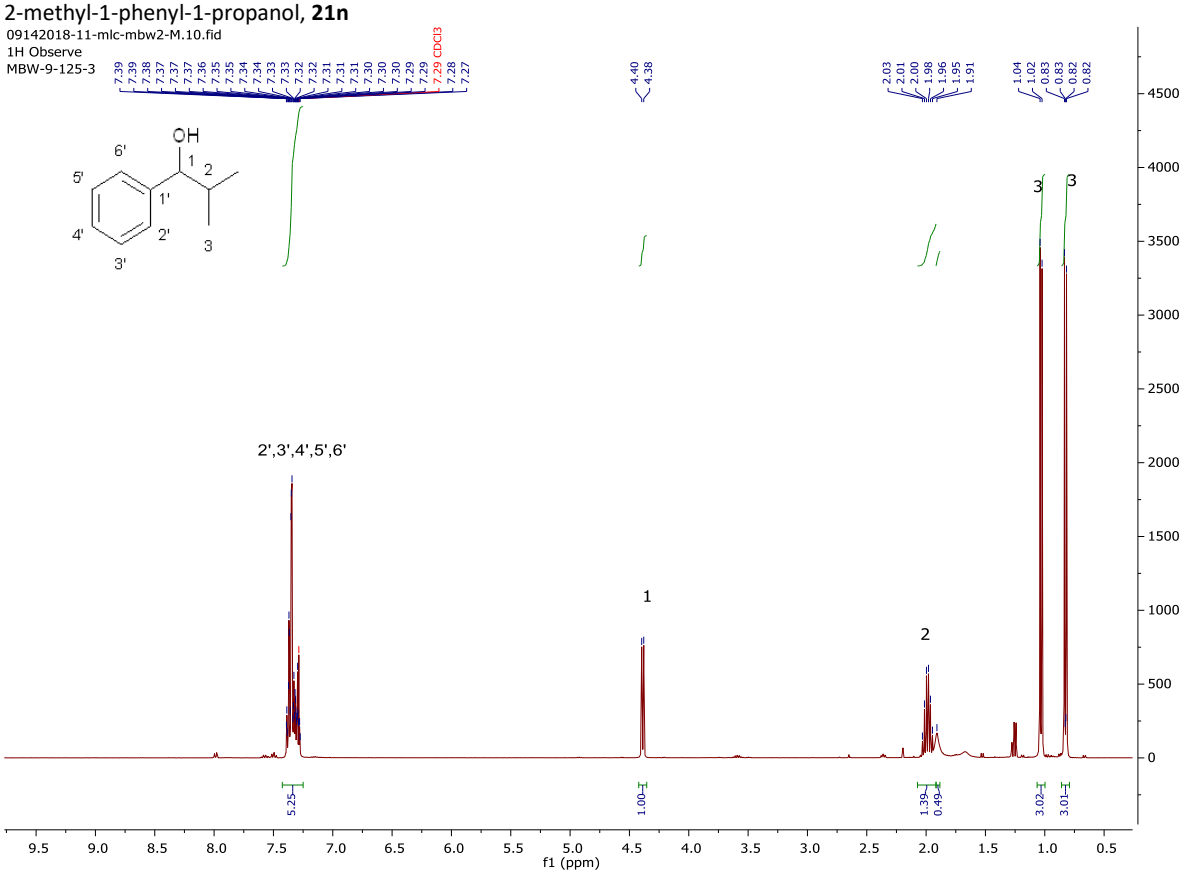


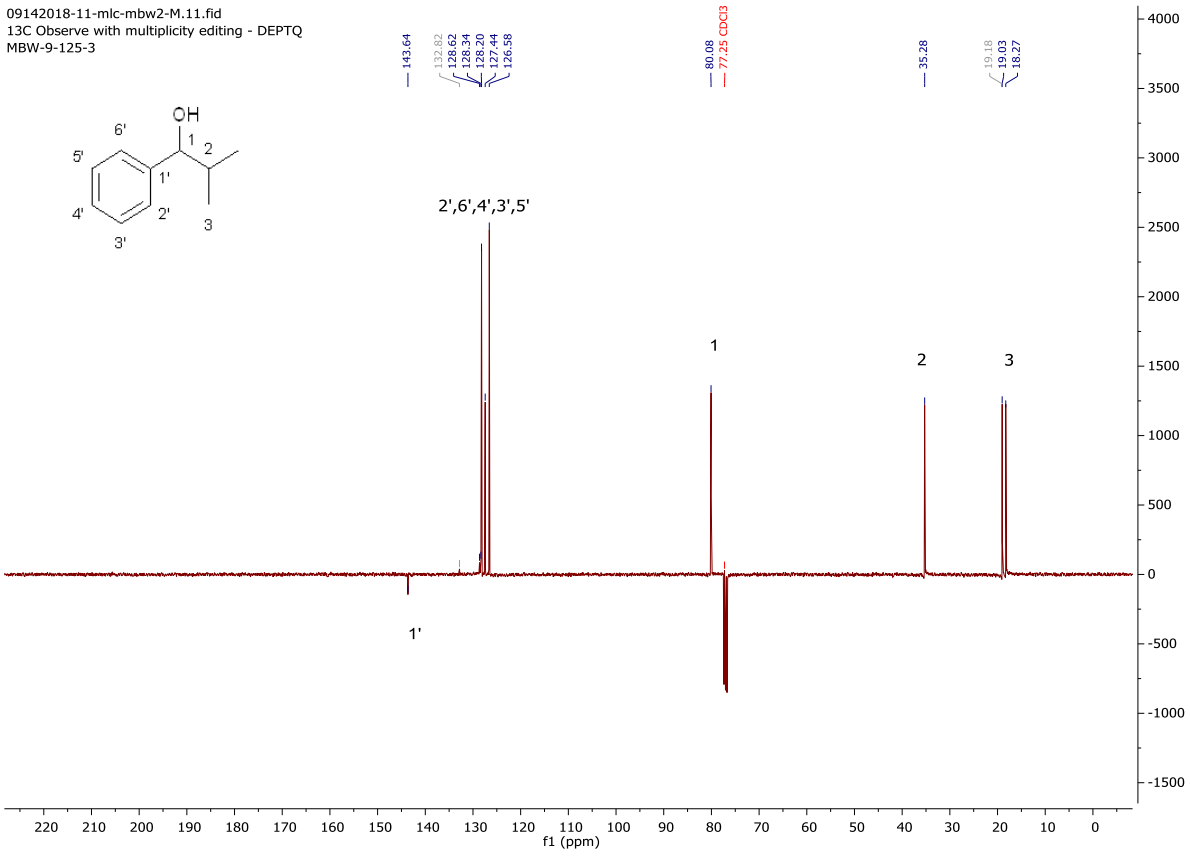
1-(4-methoxyphenyl)-1-propanol, **21m**



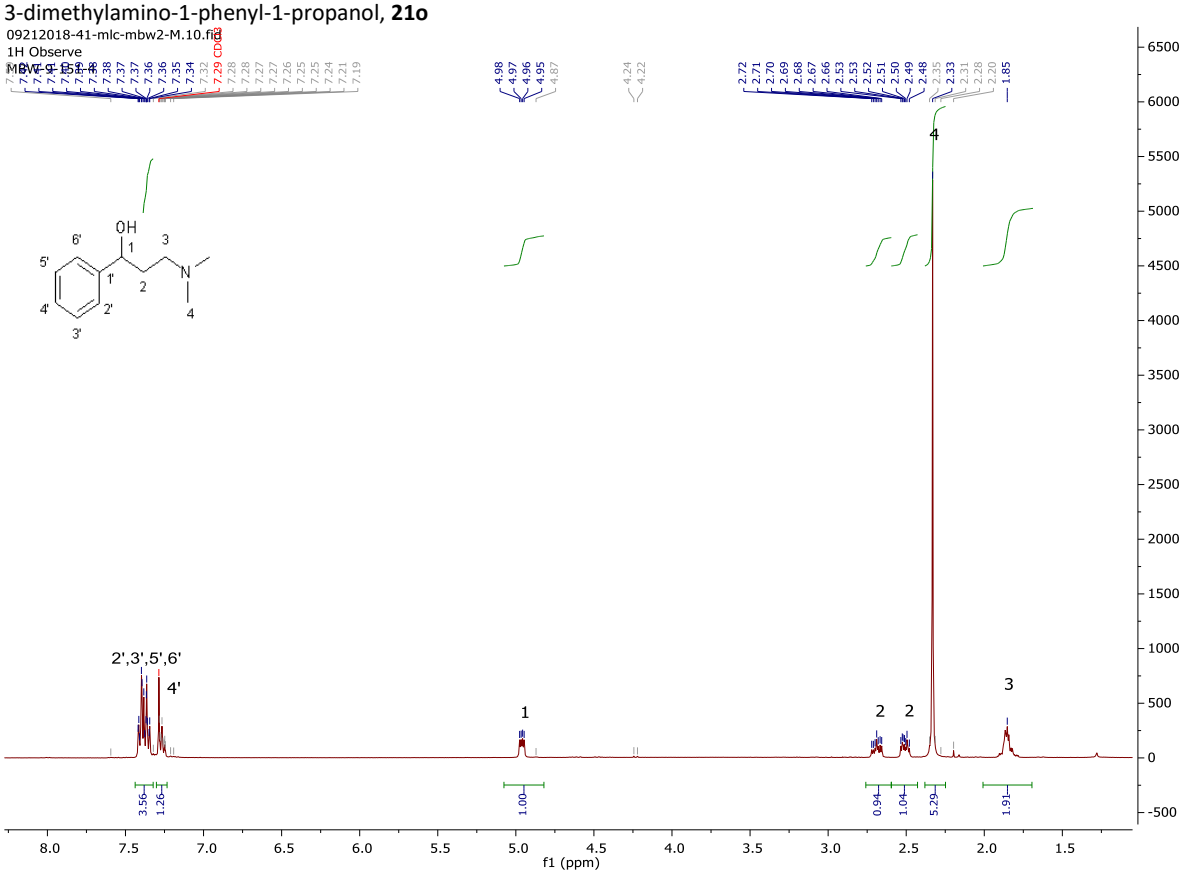


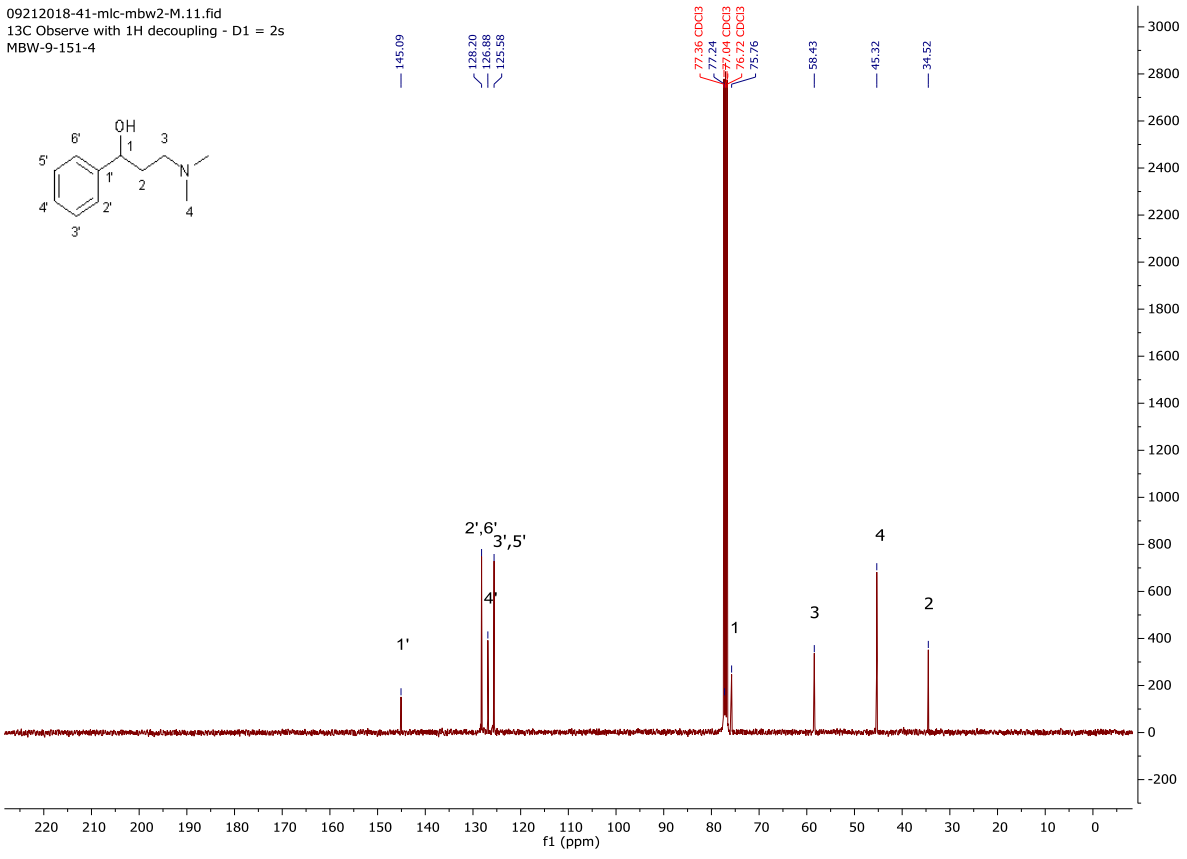
2-methyl-1-phenyl-1-propanol, **21n**



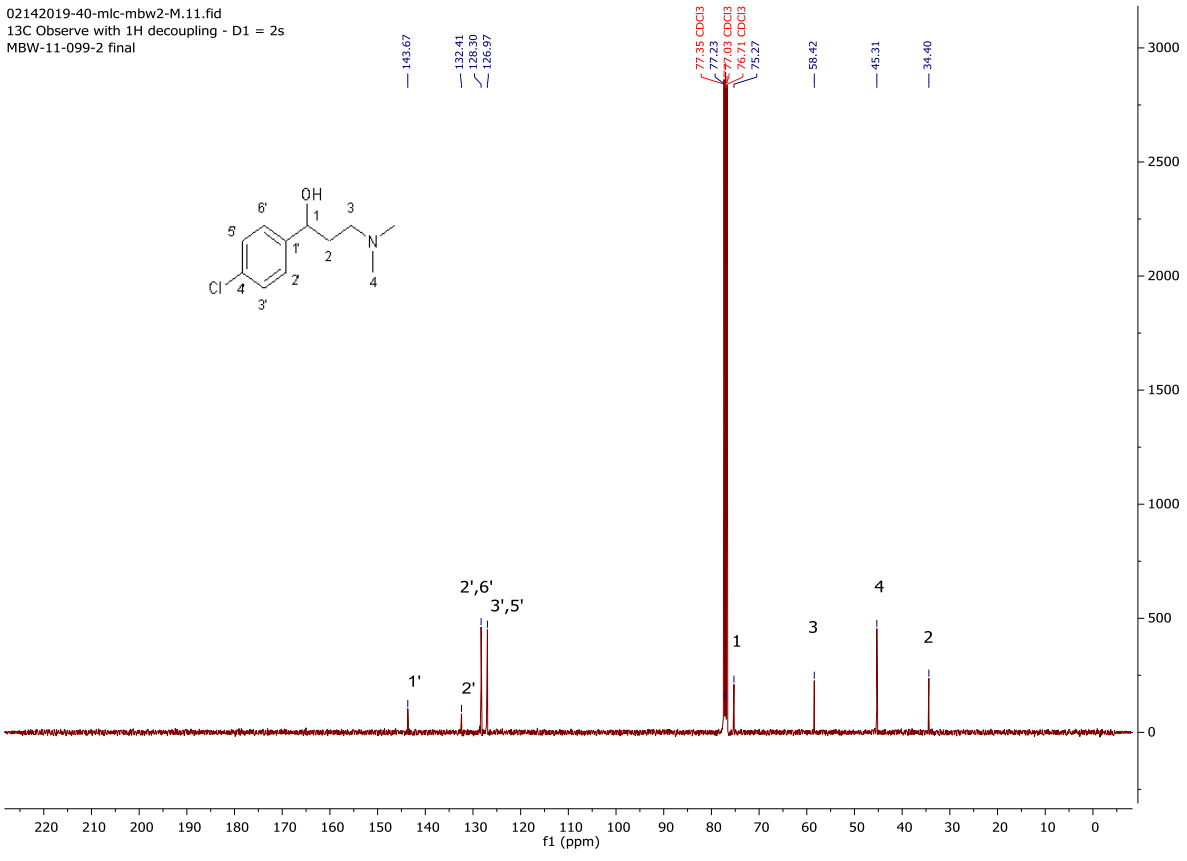


3-dimethylamino-1-phenyl-1-propanol, **21o**

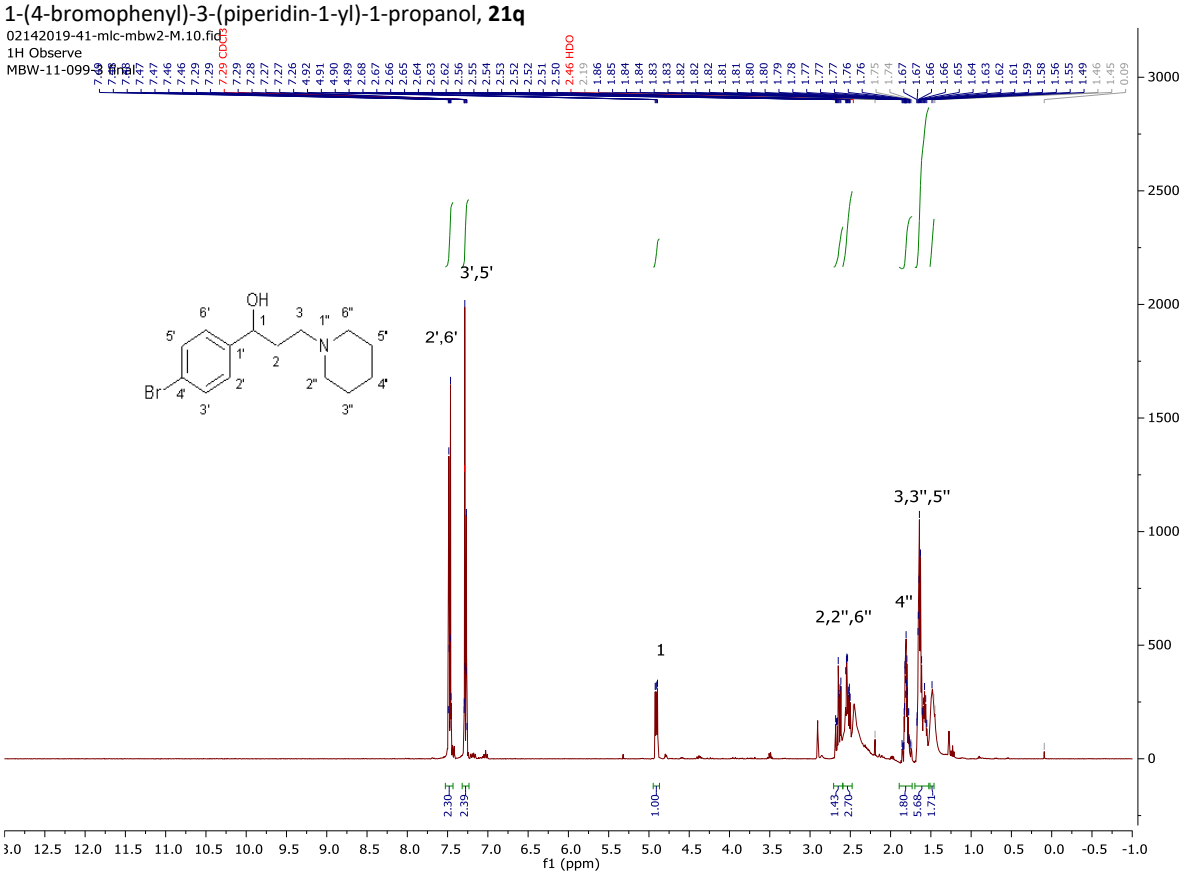


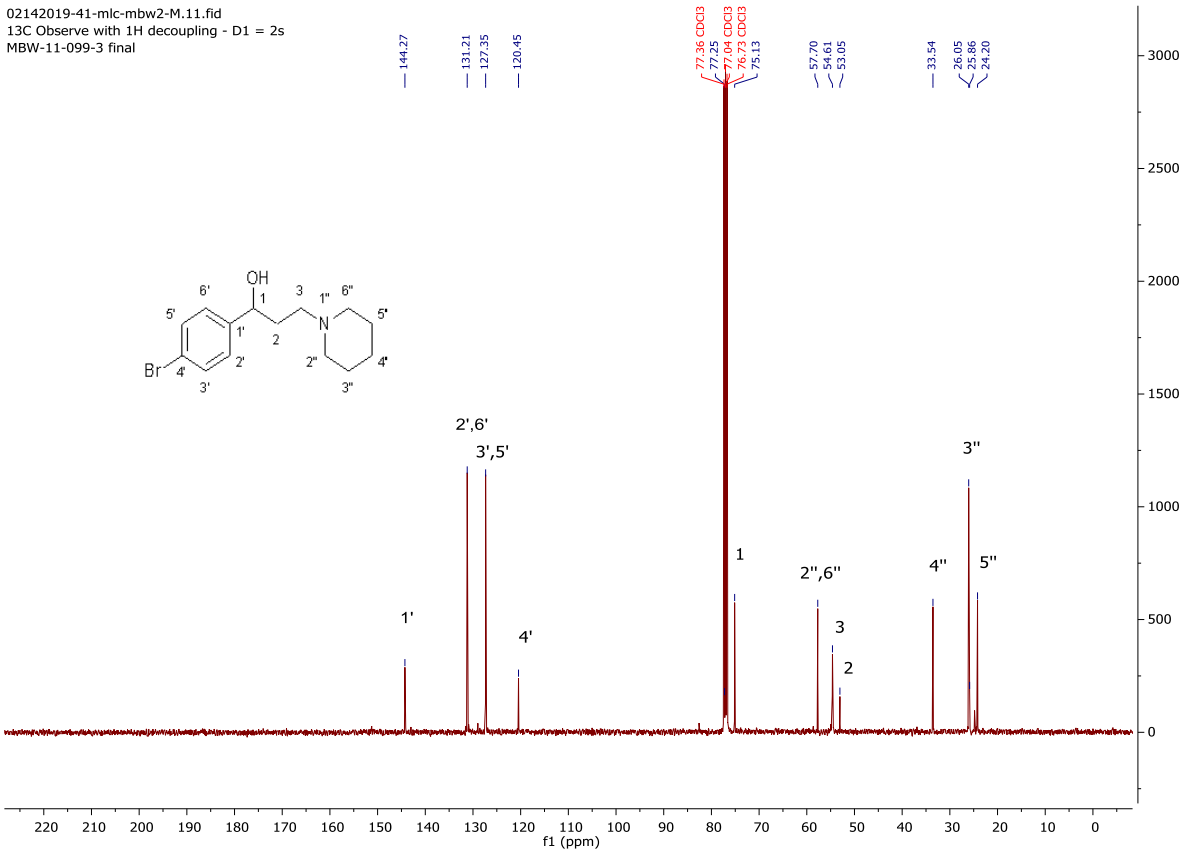


3-dimethylamino-1-(4-chlorophenyl)-1-propanol, **21p**

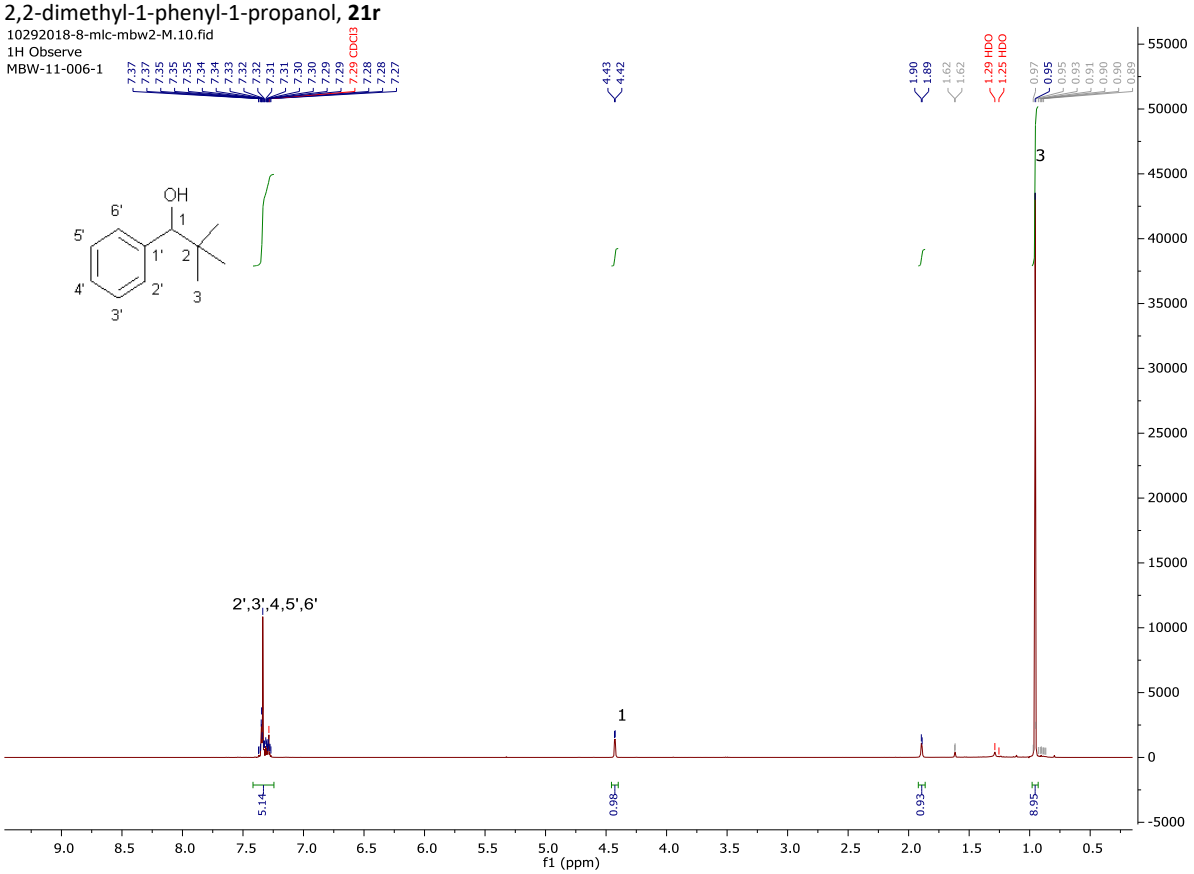


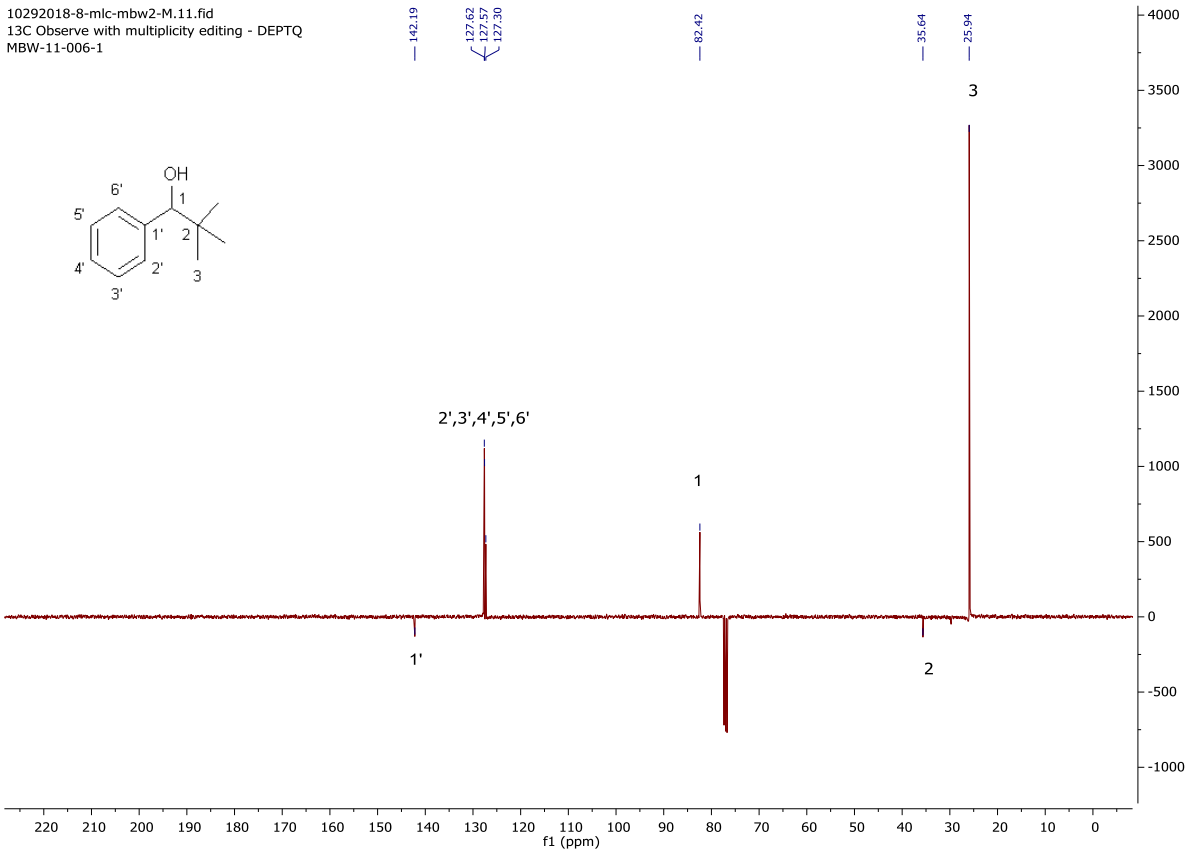
1-(4-bromophenyl)-3-(piperidin-1-yl)-1-propanol, **21q**



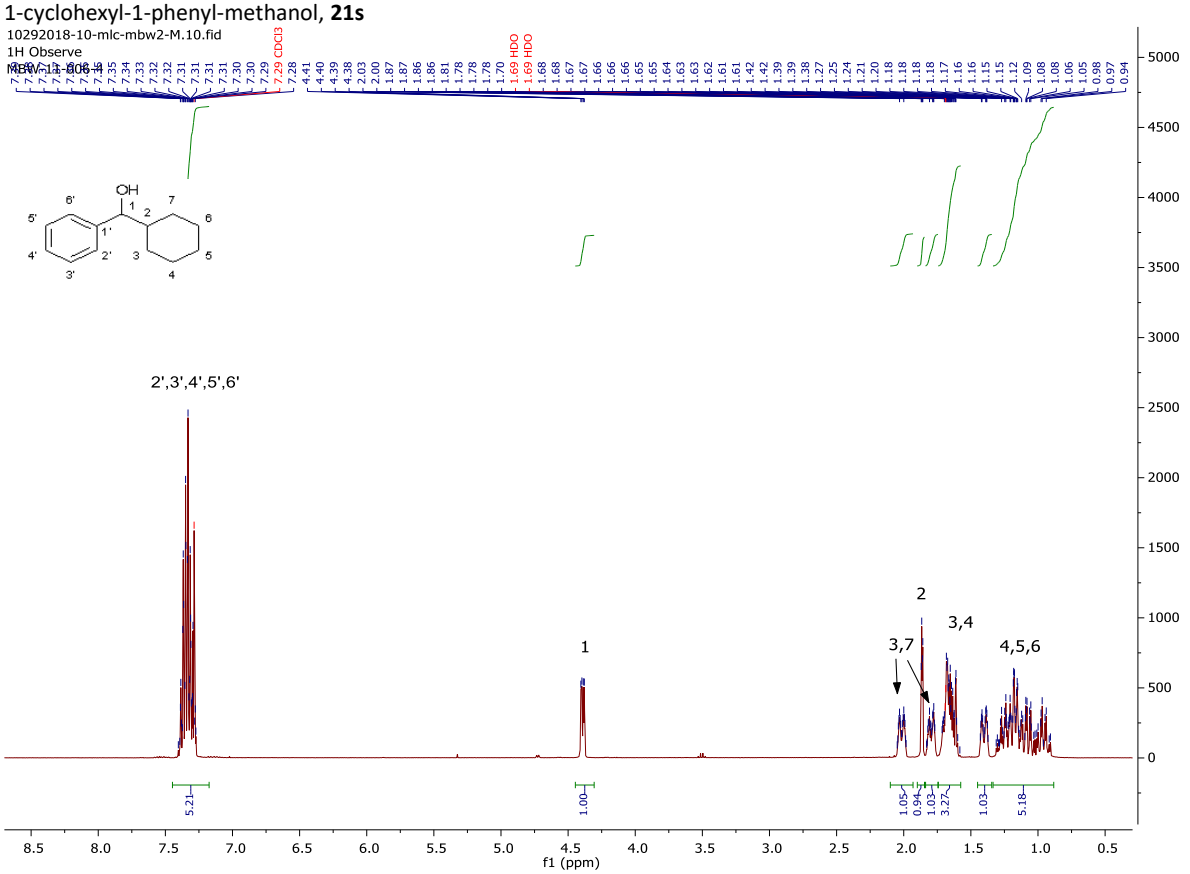


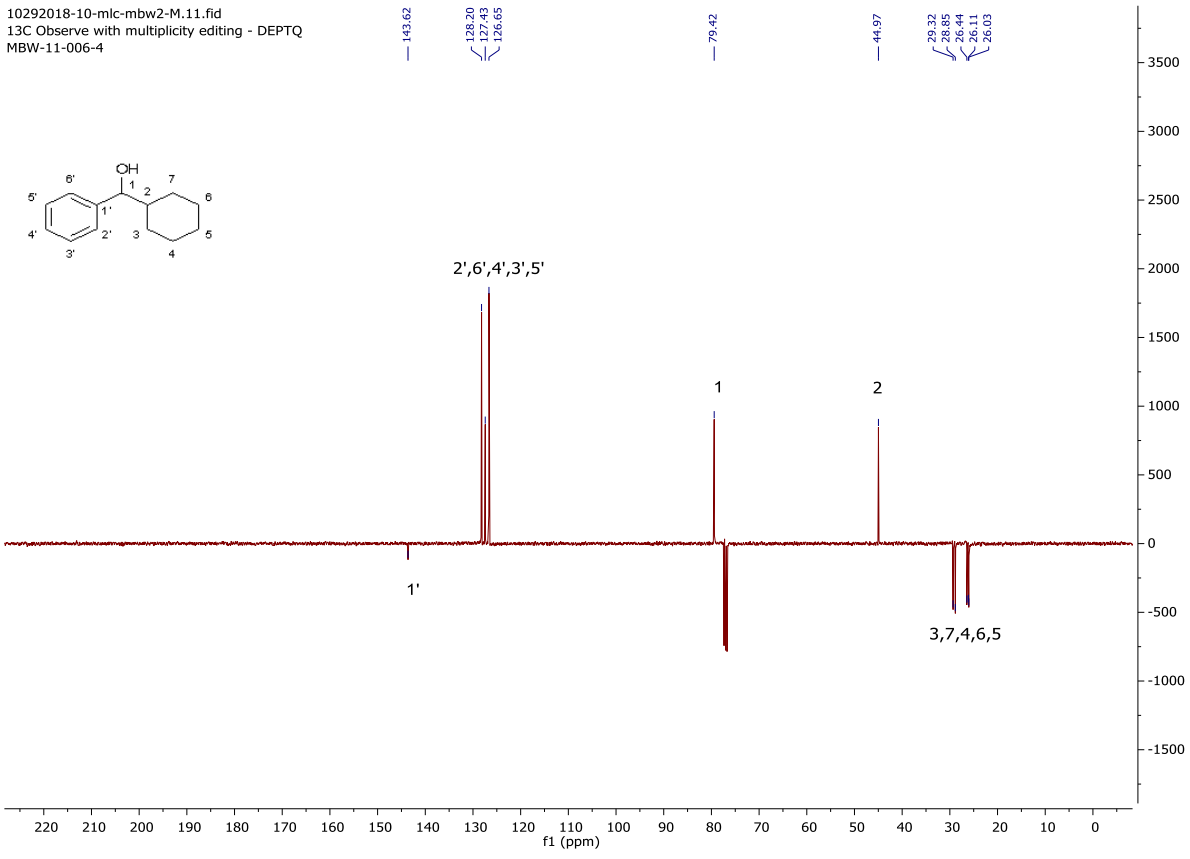
2,2-dimethyl-1-phenyl-1-propanol, **21r**



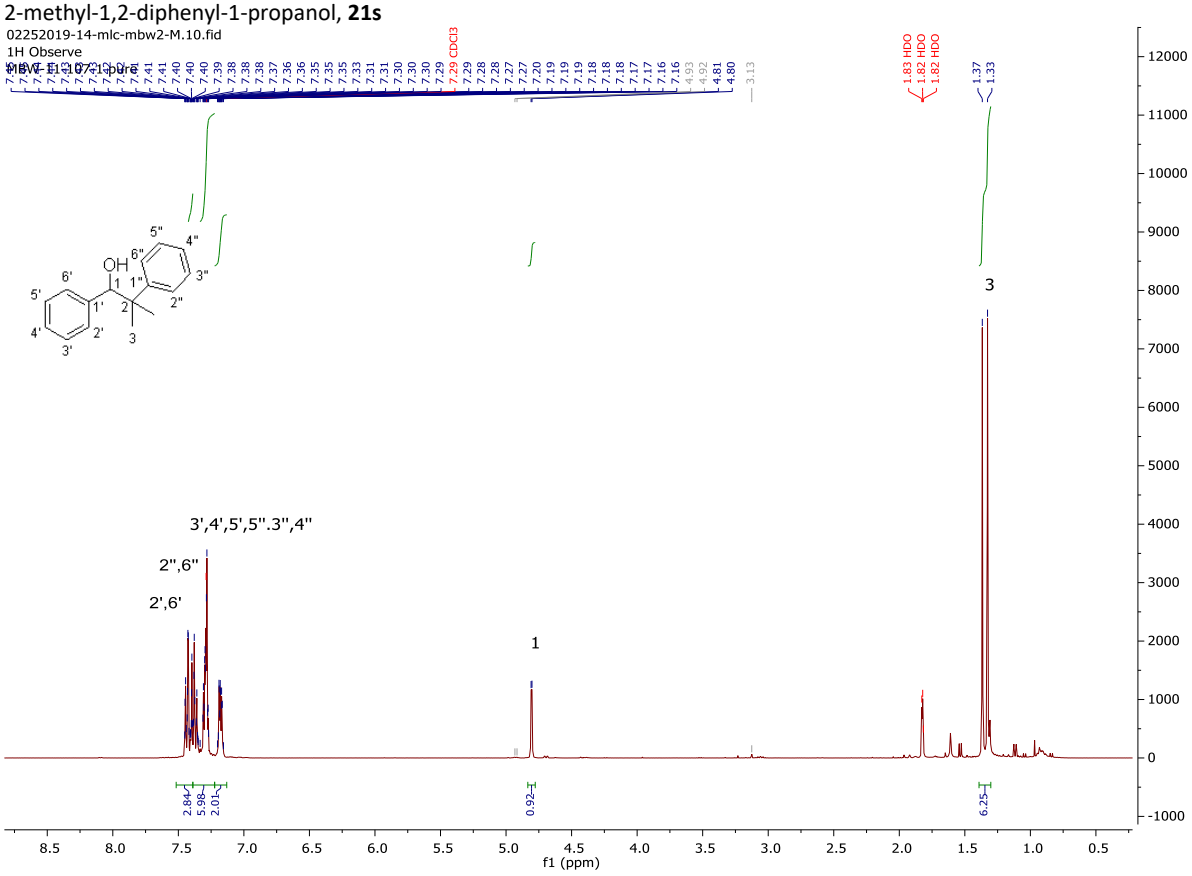


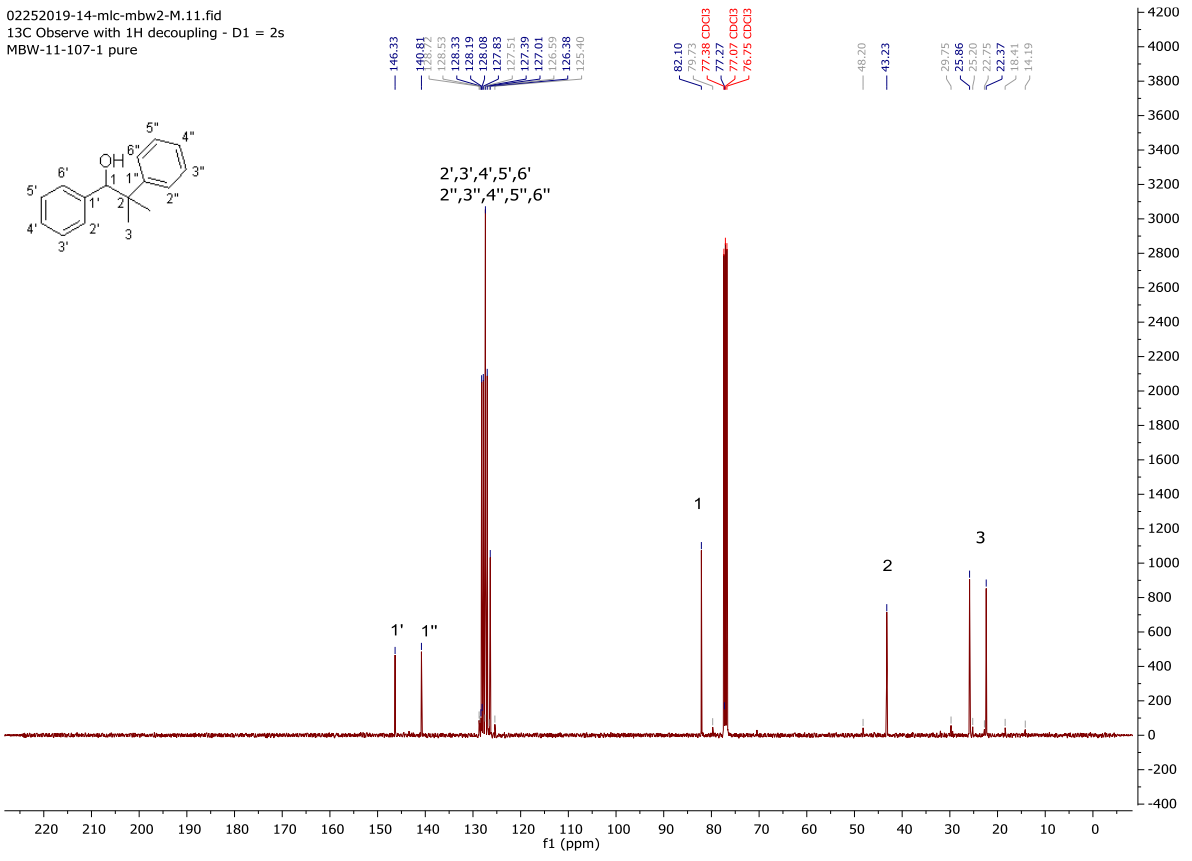
1-cyclohexyl-1-phenyl-methanol, **21s**



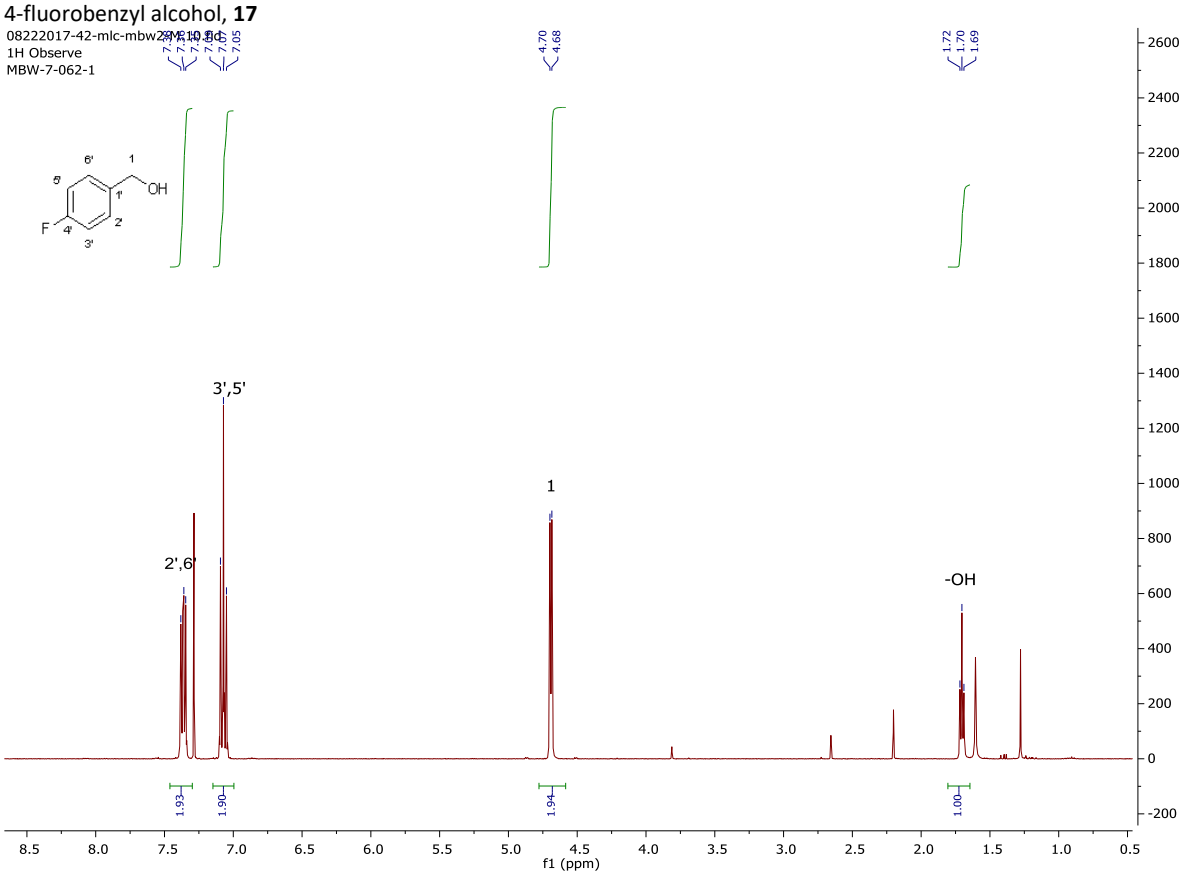


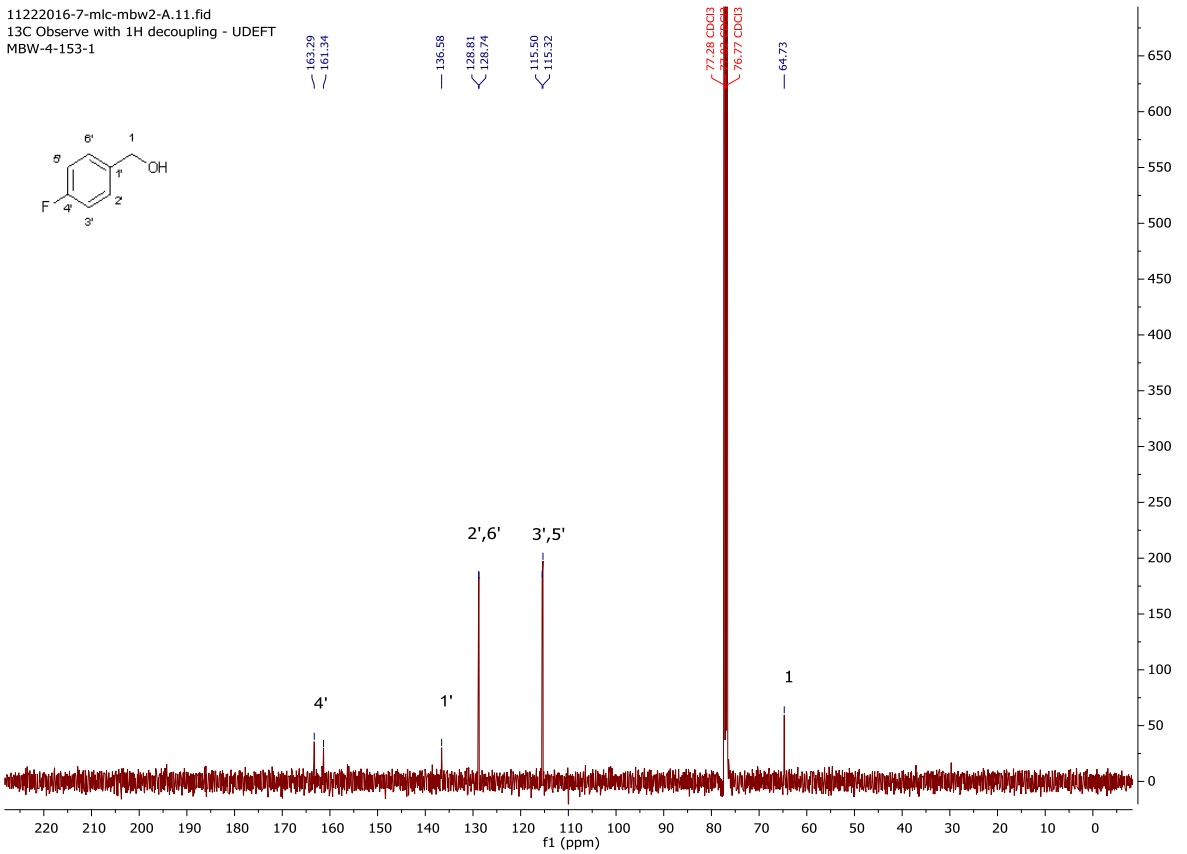
2-methyl-1,2-diphenyl-1-propanol, **21s**

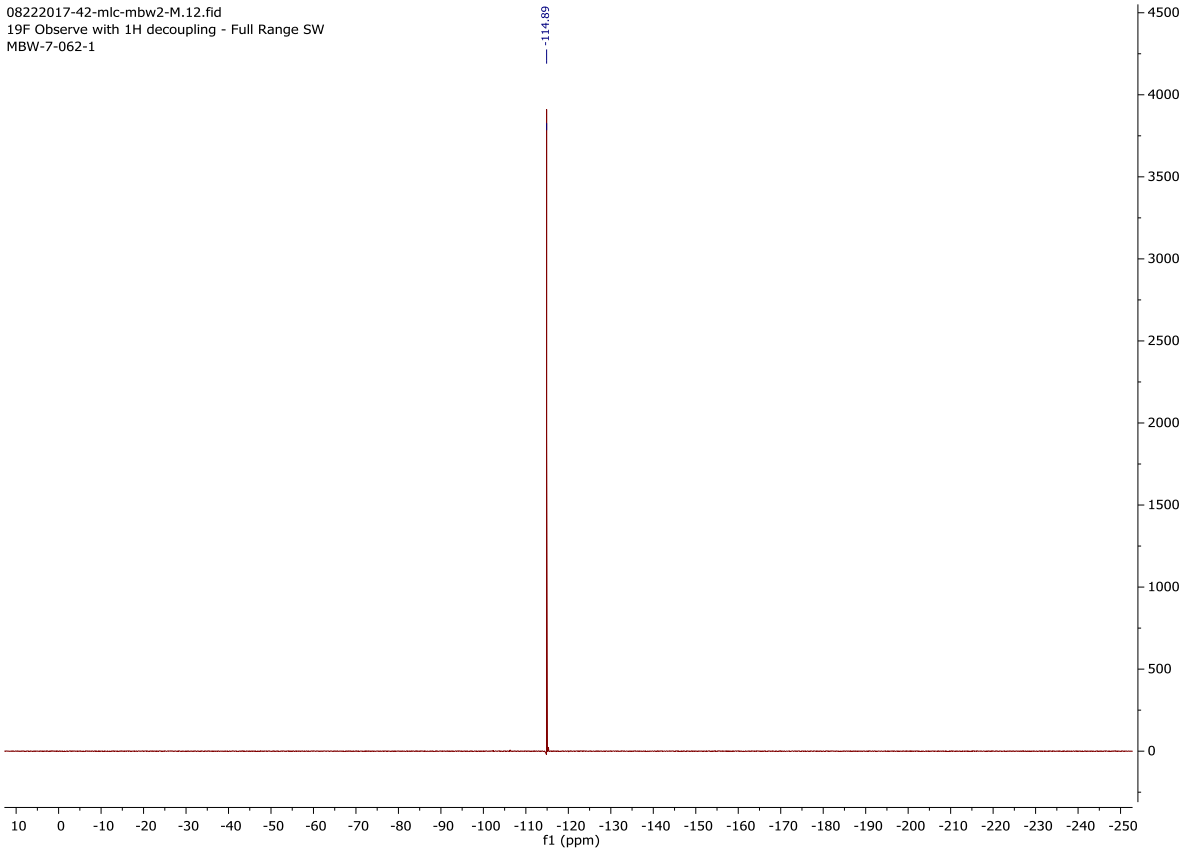




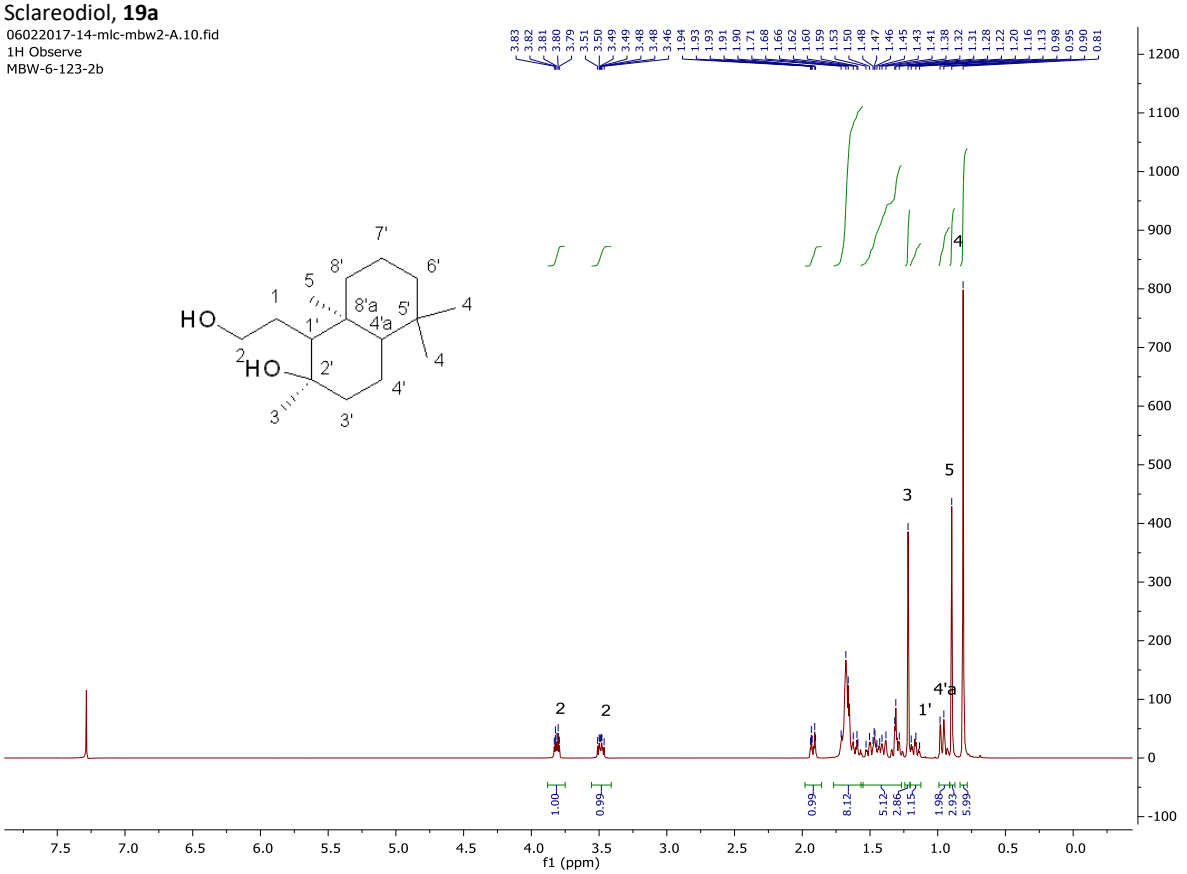
4-fluorobenzyl alcohol, **17**

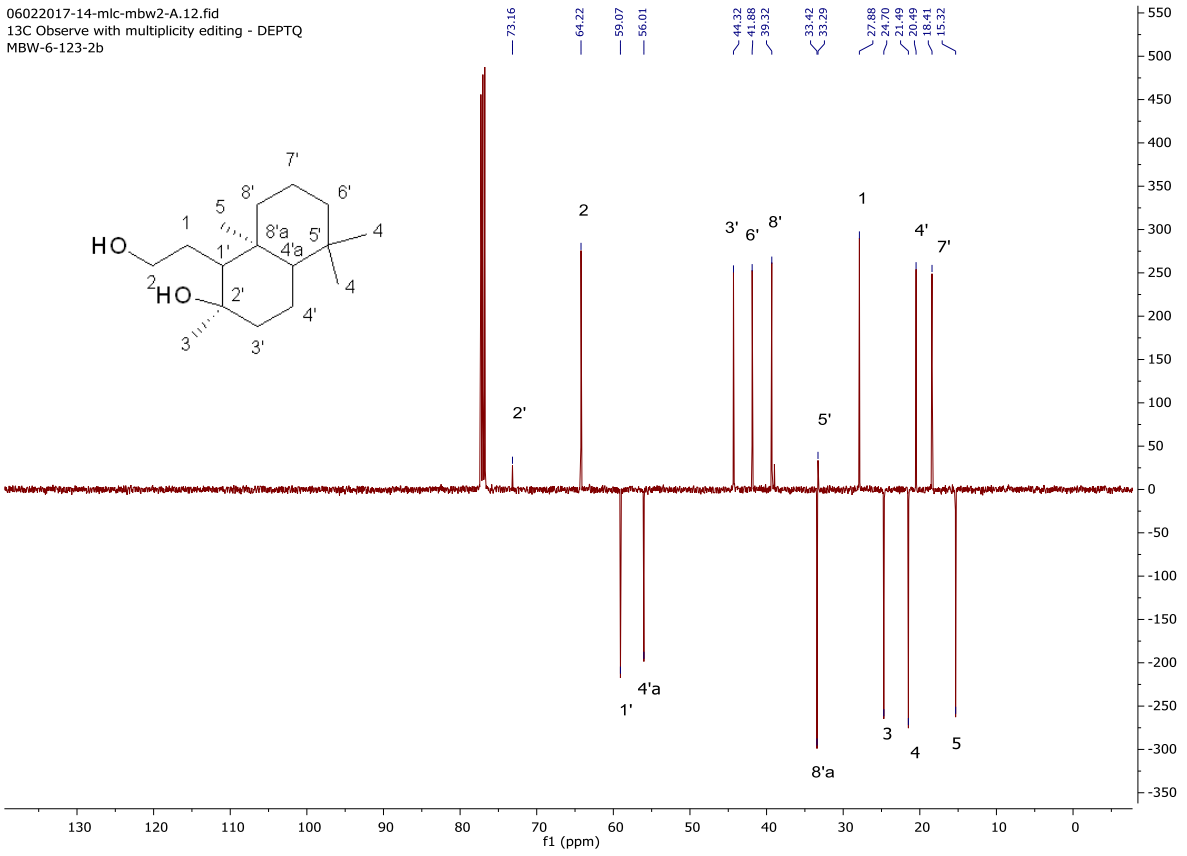




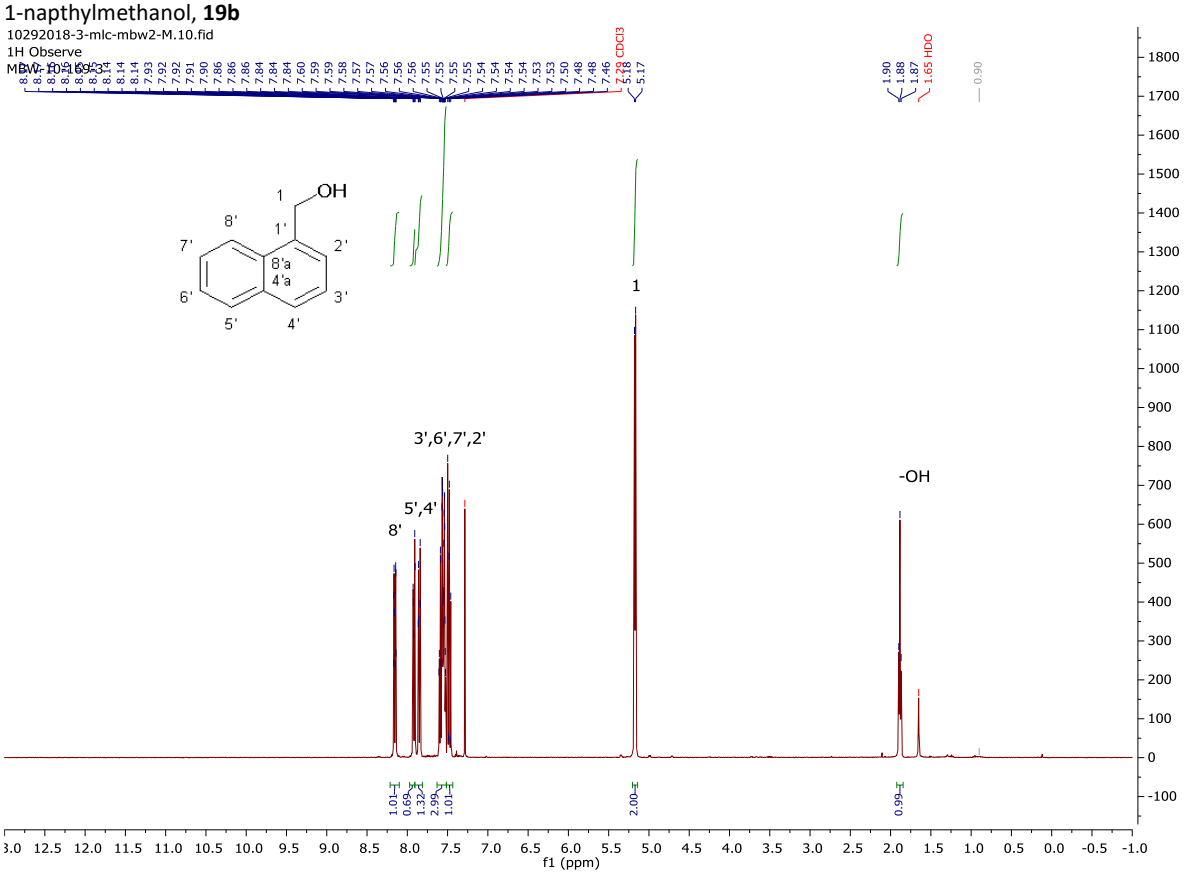

08222017-42-mlc-mbw2-M.12.fid
19F Observe with 1H decoupling - Full Range SW
MBW-7-062-1
-114.89
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

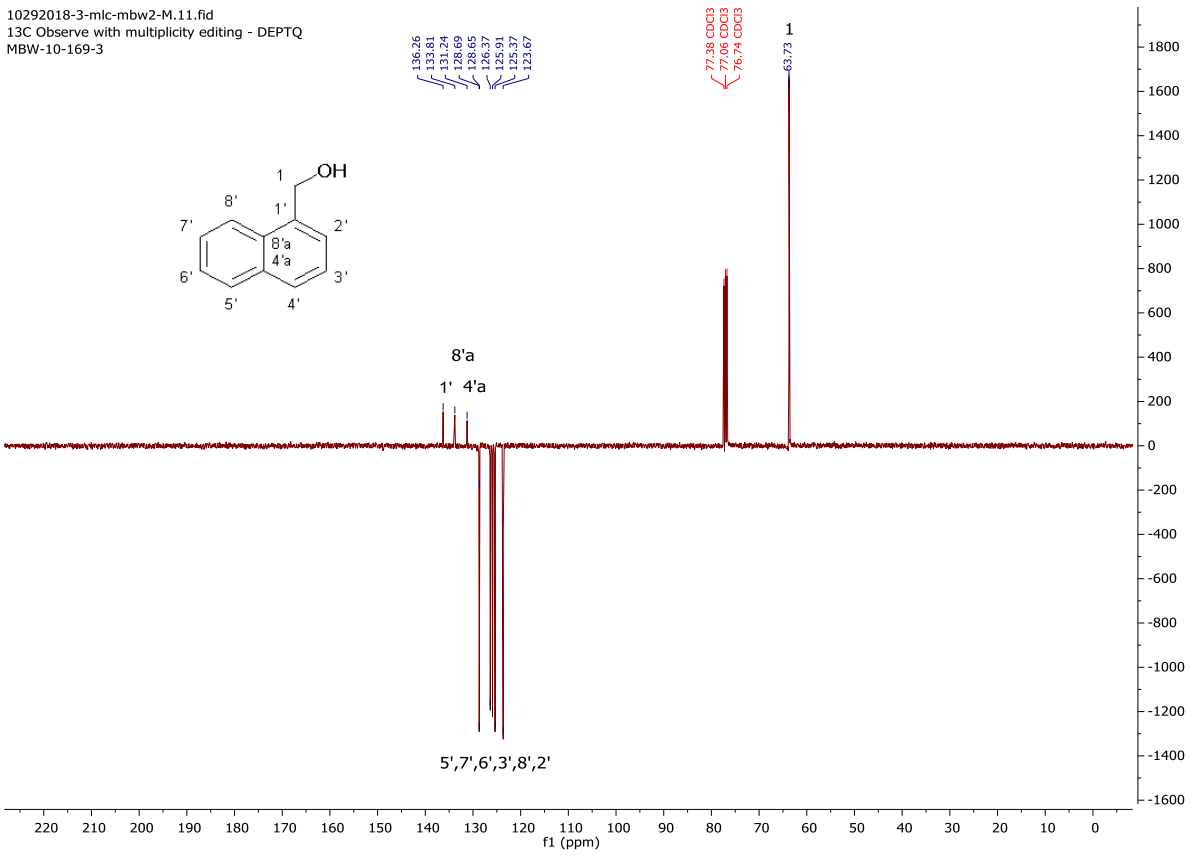
Sclareodiol, **19a**



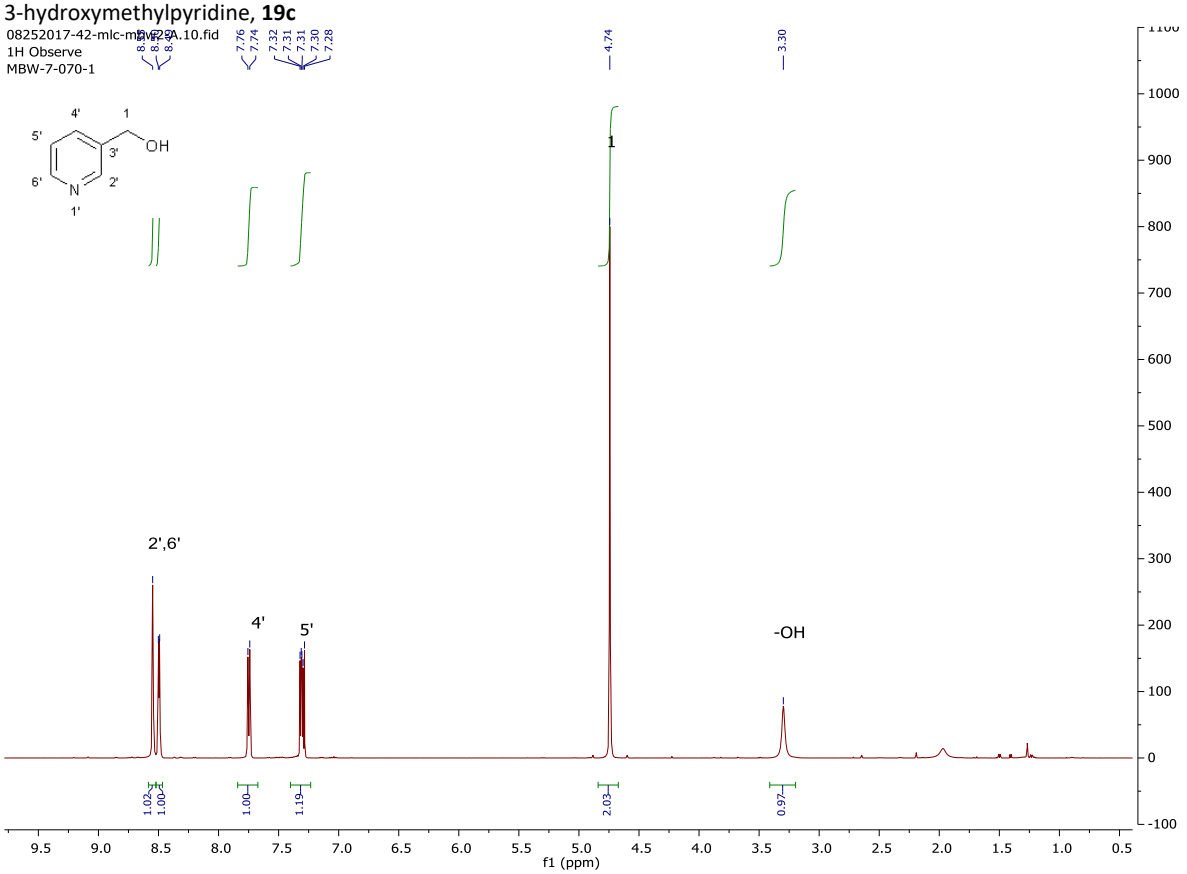


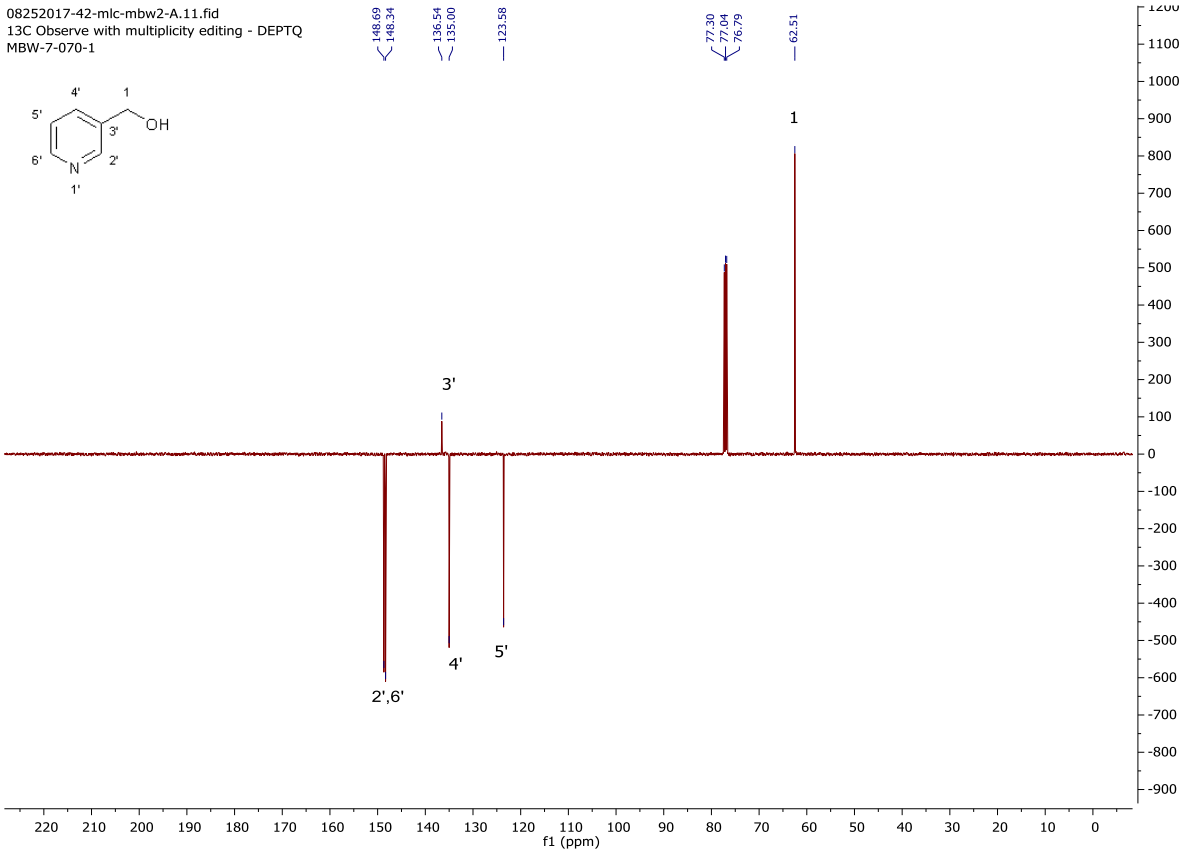
1-napthylmethanol, **19b**



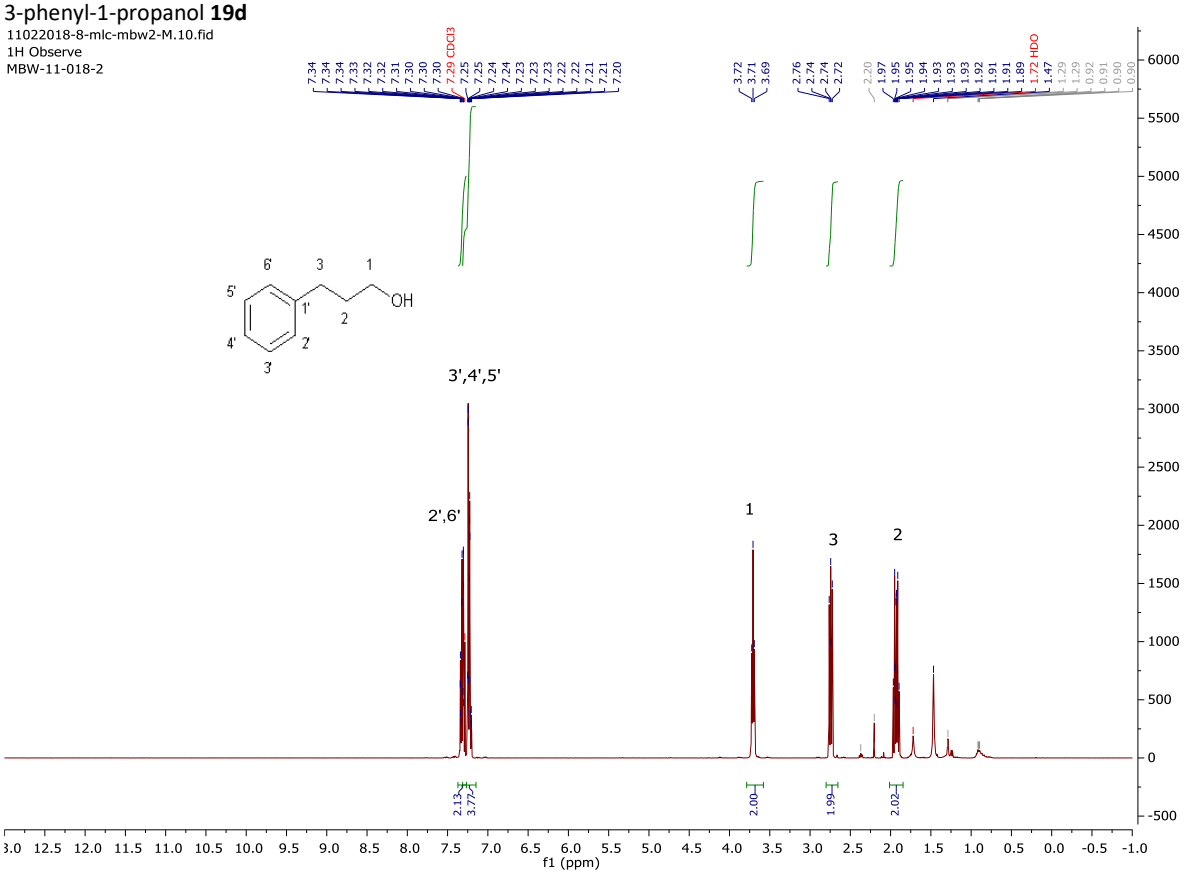


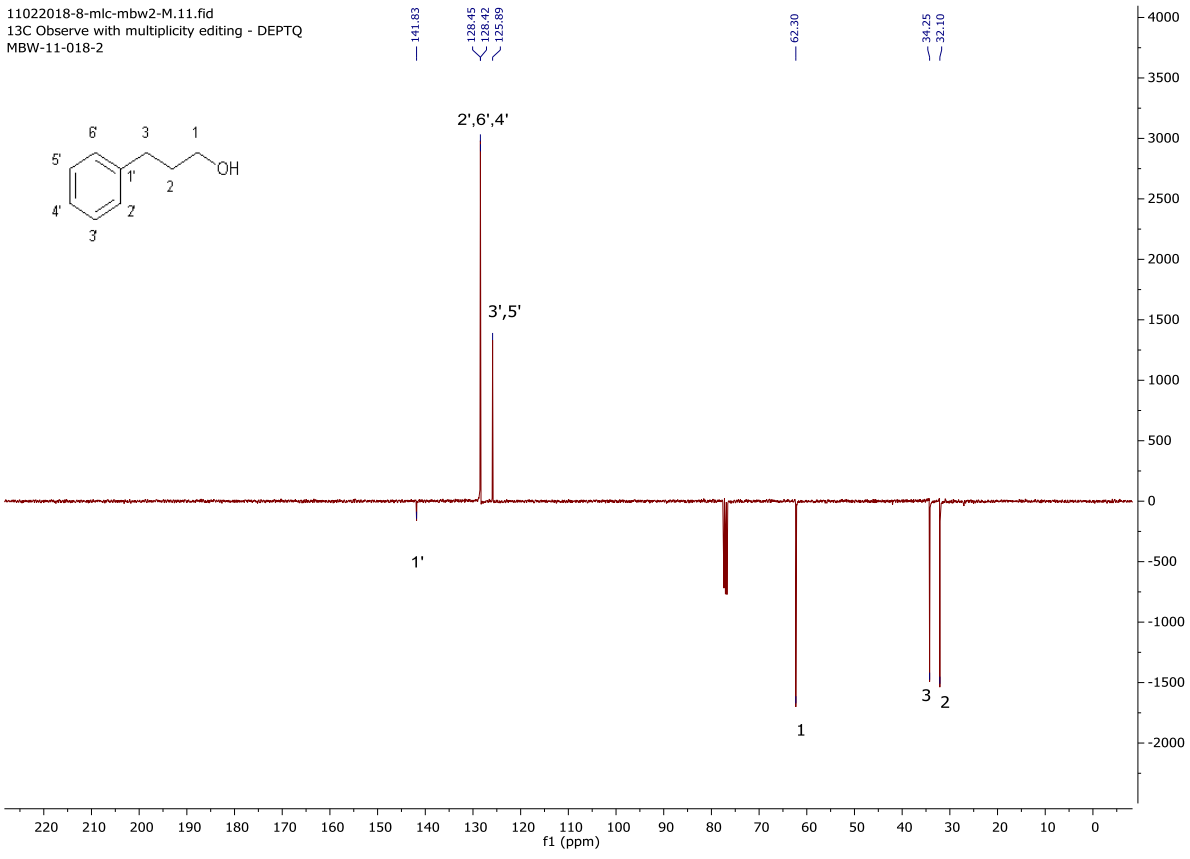
3-hydroxymethylpyridine, **19c**





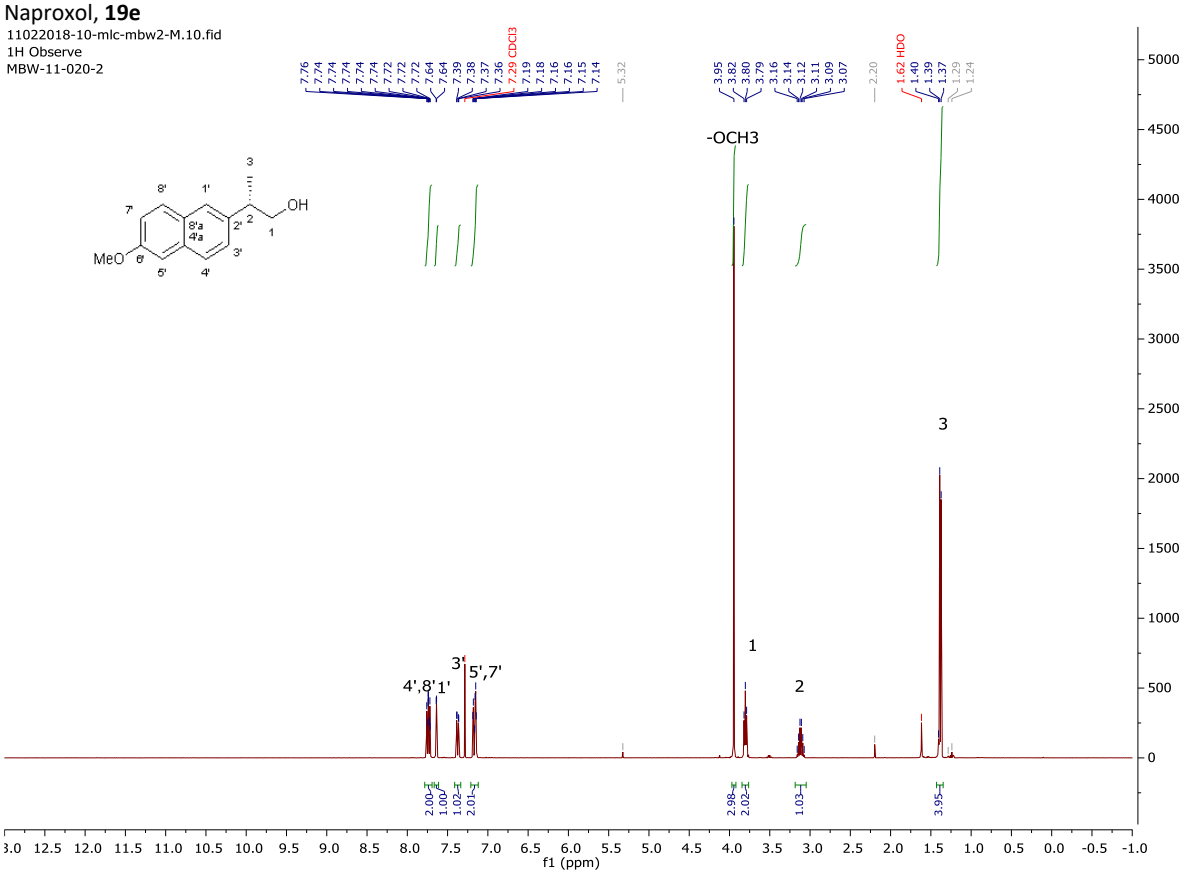
3-phenyl-1-propanol **19d**



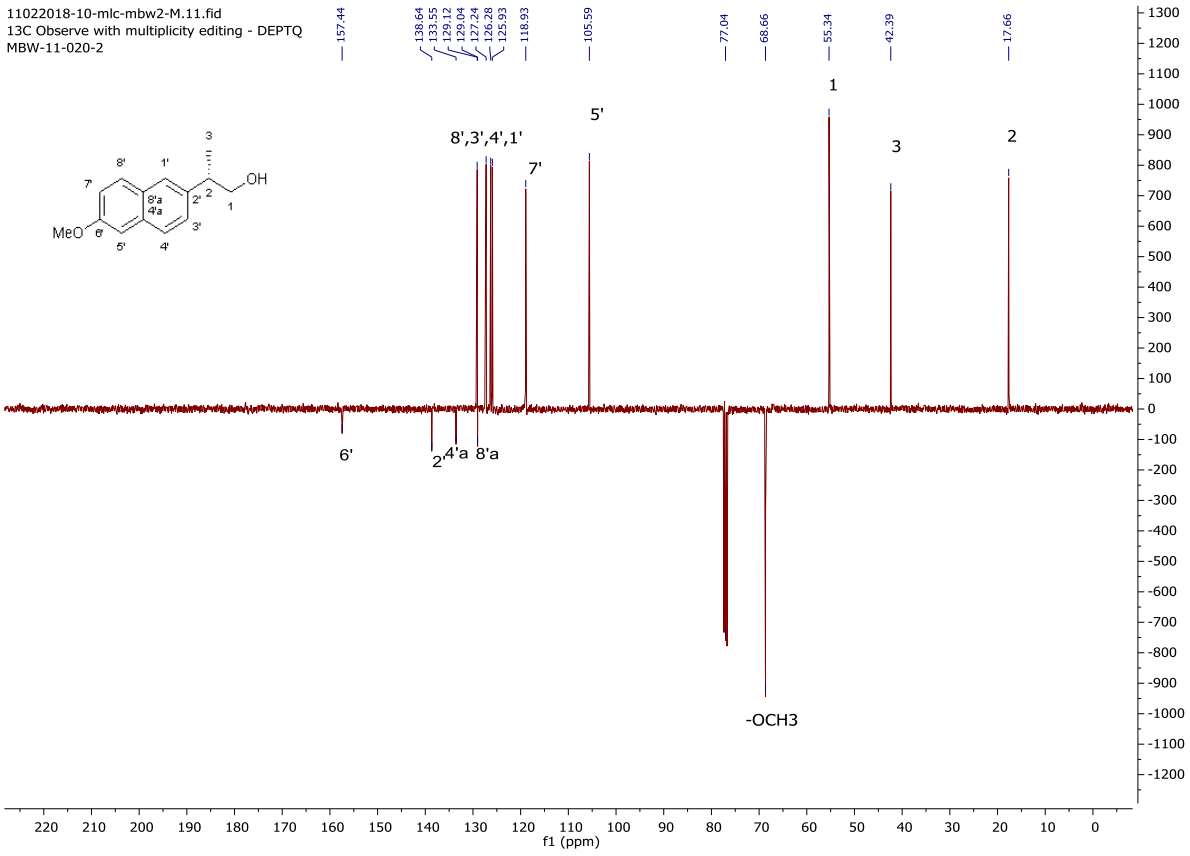


Naproxol, **19e**

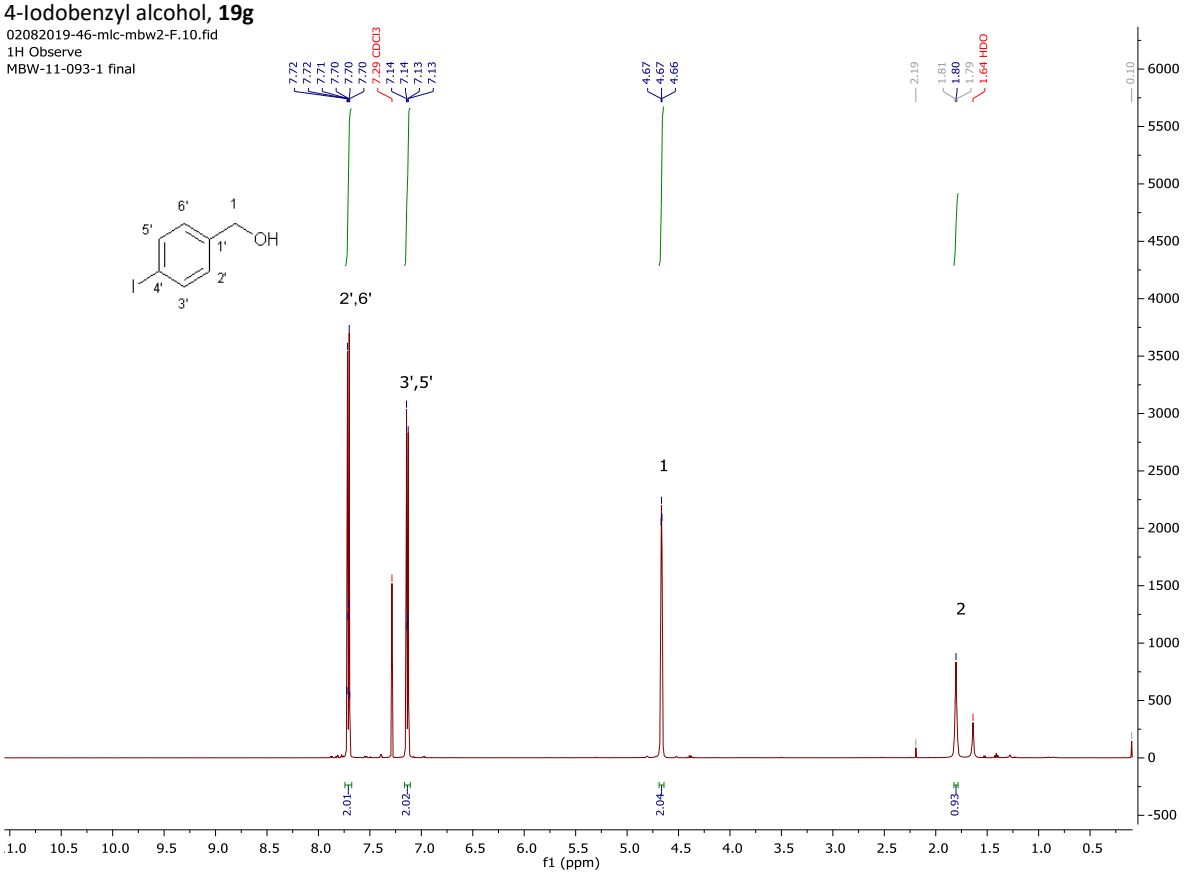
11022018-10-mlc-mbw2-M.10.fid
1H Observe
MBW-11-020-2

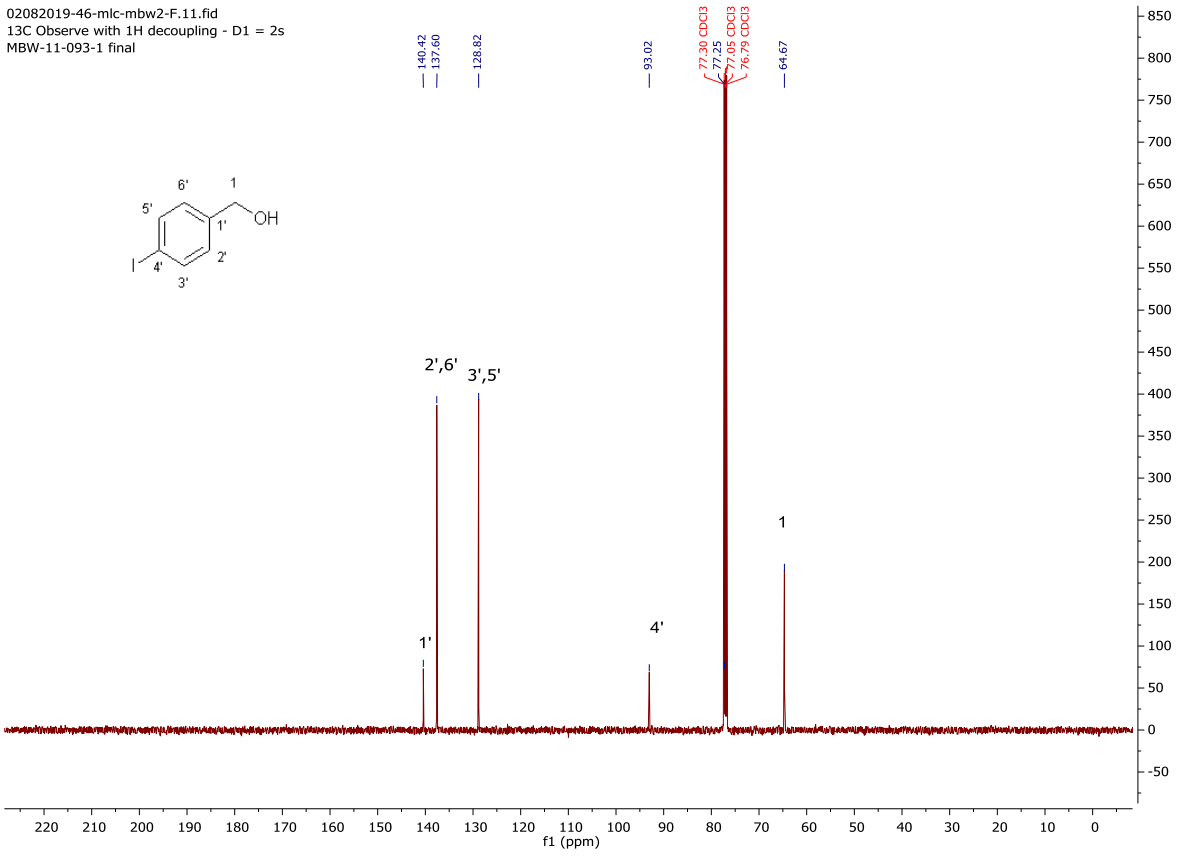


11022018-10-mlc-mbw2-M.11.fid
13C Observe with multiplicity editing - DEPTQ
MBW-11-020-2



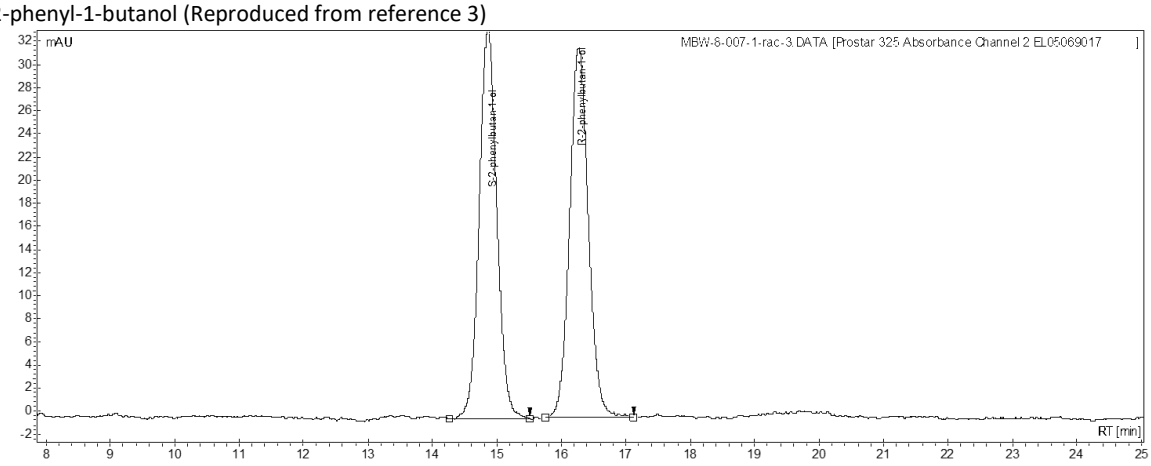
4-Iodobenzyl alcohol, **19g**





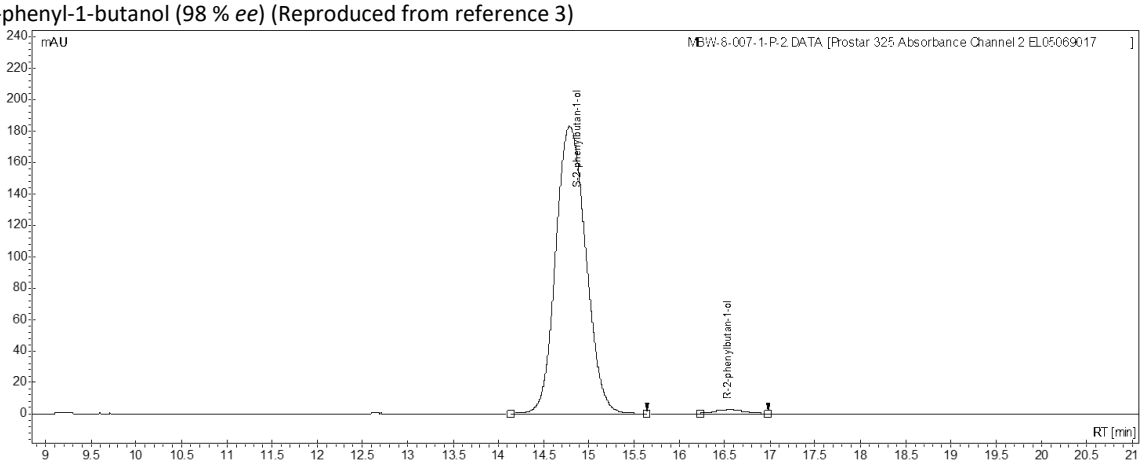
5. HPLC traces

rac-2-phenyl-1-butanol (Reproduced from reference 3)



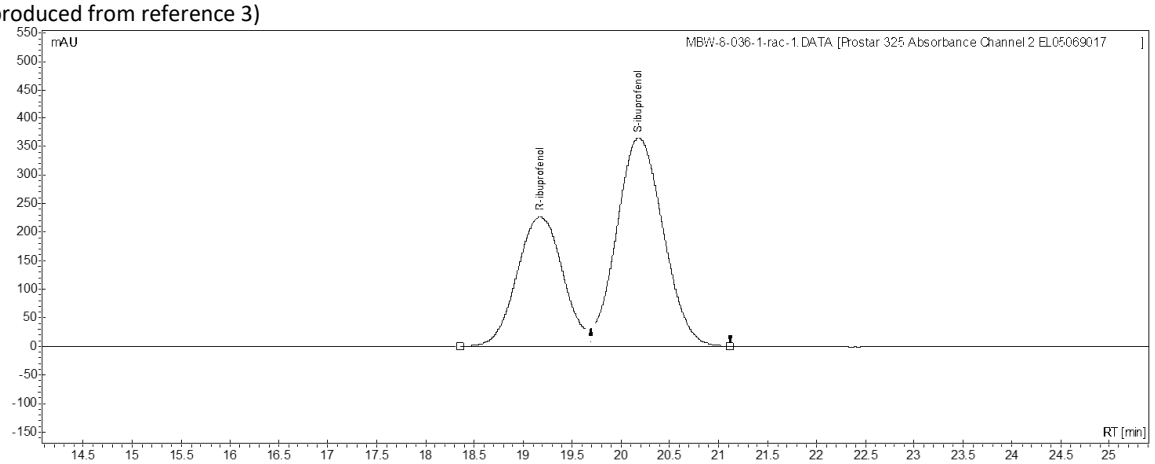
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	S-2-phenylbutan-1-ol	14.86	33.7	10.7	49.831
2	R-2-phenylbutan-1-ol	16.27	32.0	10.8	50.169
Total			65.7	21.5	100.000

(*R*)-2-phenyl-1-butanol (98 % *ee*) (Reproduced from reference 3)



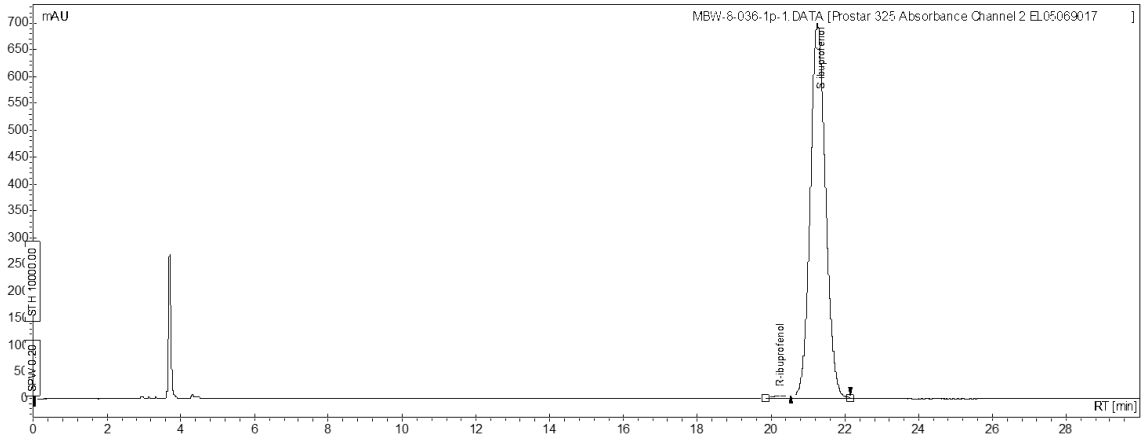
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	S-2-phenylbutan-1-ol	14.79	183.2	70.3	98.840
2	R-2-phenylbutan-1-ol	16.54	2.4	0.8	1.160
Total			185.5	71.1	100.000

rac-2-(4-isobutylphenyl)propan-1-ol, (scalemic sample made from reduction of *(S)*-Ethyl ibuprofen using KO^{t}Bu, 24 % *ee*) (Reproduced from reference 3)



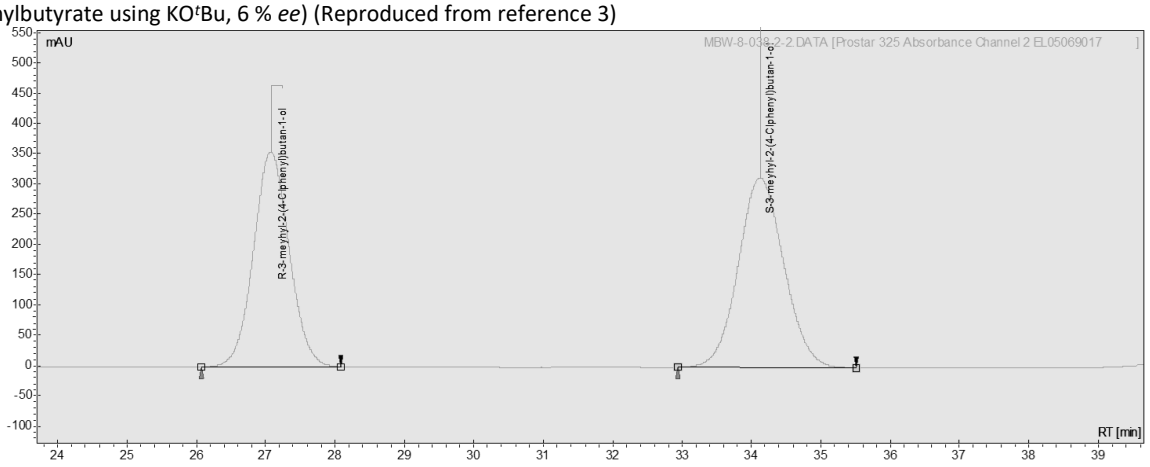
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	R-enantiomer	19.17	226.5	123.9	38.073
2	S-enantiomer	20.18	365.4	201.5	61.927
Total			591.9	325.4	100.000

(S)-2-(4-isobutylphenyl)propan-1-ol (99 % *ee*) (Reproduced from reference 3)



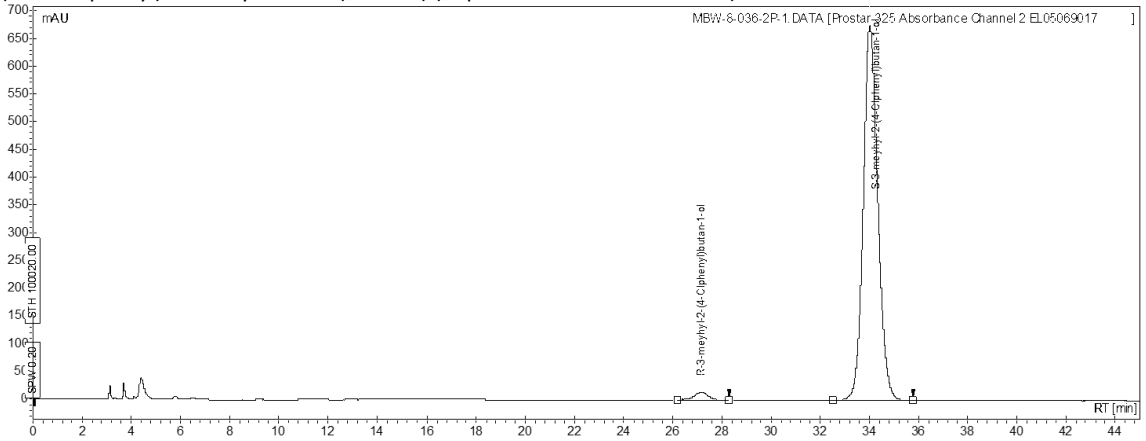
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	R-enantiomer	20.26	4.6	2.0	0.595
2	S-enantiomer	21.26	696.7	335.2	99.405
Total			701.3	337.2	100.000

2-(4-chlorophenyl)-3-methylbutanol (scalemic sample made from reduction of *(S)*-Ethyl 2-(4-chlorophenyl)-3-methylbutyrate using KO^{t}Bu, 6 % *ee*) (Reproduced from reference 3)



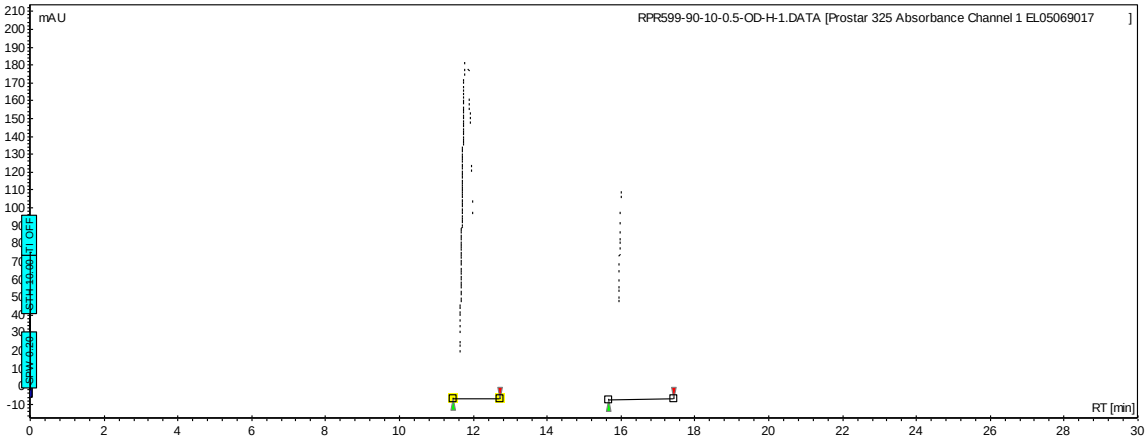
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	R-enantiomer	27.07	355.4	211.6	46.972
2	S-enantiomer	34.12	313.9	238.9	53.028
Total			669.2	450.5	100.000

(*S*)-2-(4-chlorophenyl)-3-methylbutanol (96 % *ee*) (Reproduced from reference 3)



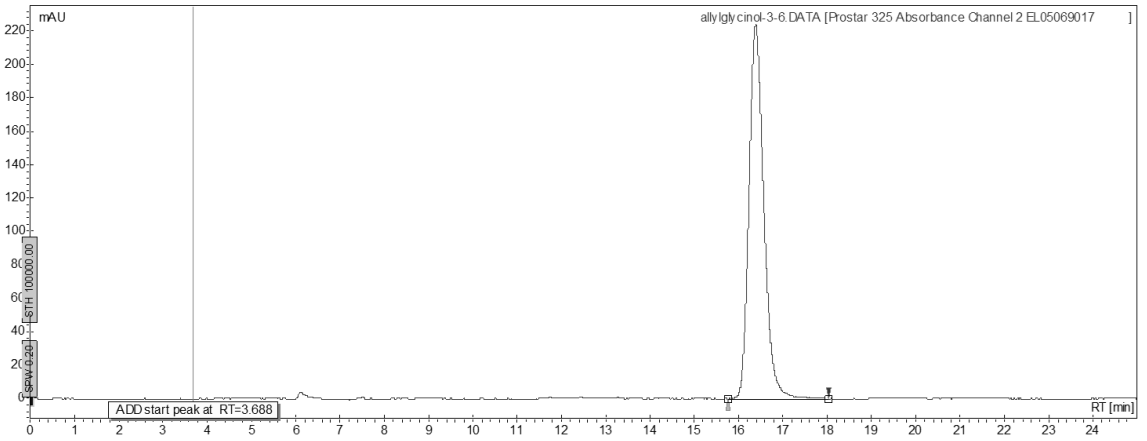
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	R-enantiomer	27.16	13.8	8.7	1.851
2	S-enantiomer	34.02	675.2	461.2	98.149
Total			689.0	469.9	100.000

rac-2-(dibenzylamino)pent-4-en-1-ol (Reproduced from reference 3)



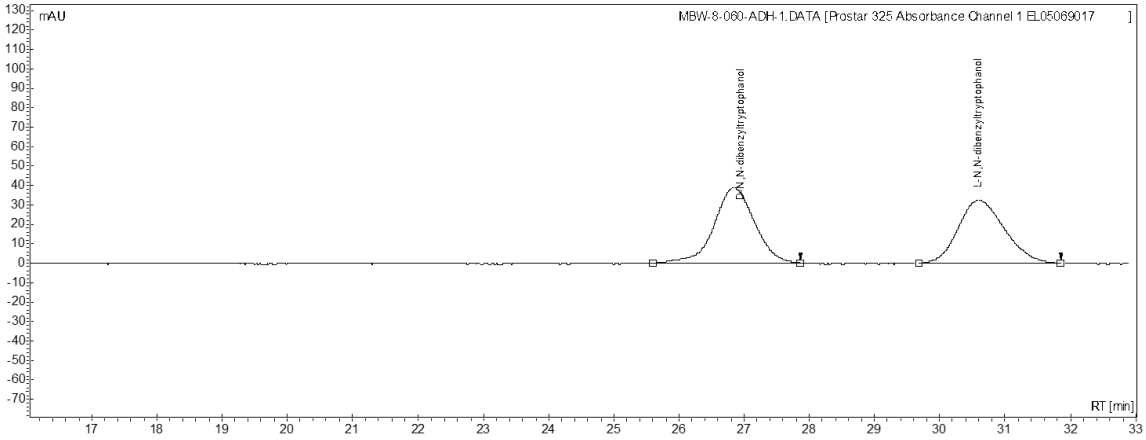
(*S*)-2-(dibenzylamino)pent-4-en-1-ol (>99 % *ee*) (Reproduced from reference 3)

#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.81	209.8	65.9	49.561
2	UNKNOWN	16.10	153.1	67.0	50.439
Total				132.9	100.000



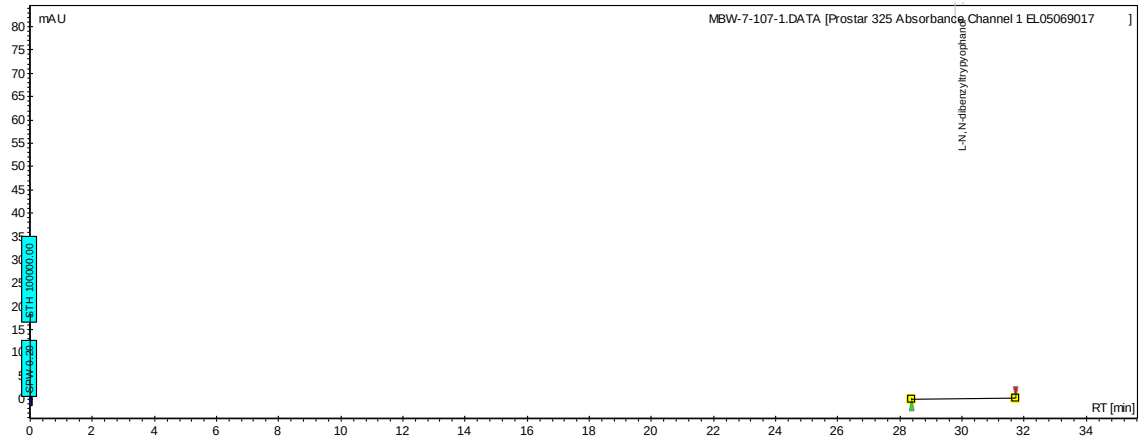
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.38	223.9	87.1	100.000
Total			100.000		

rac-2-[Bis(phenylmethyl)amino]-1*H*-indole-3-propan-1-ol (Reproduced from reference 3)



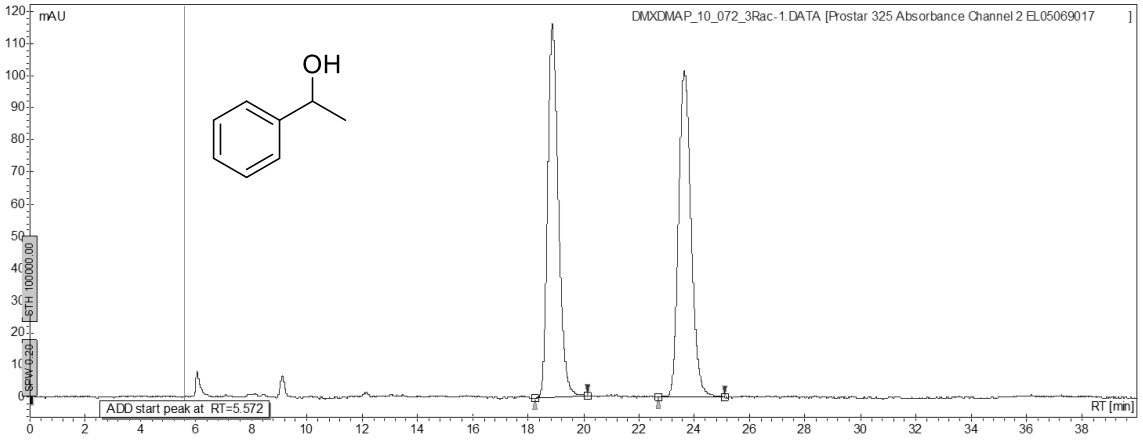
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	D-enantiomer	26.84	38.7	27.6	51.106
2	L-enantiomer	30.59	32.3	26.5	48.894
Total			71.1	54.1	100.000

(*2S*)-2-[Bis(phenylmethyl)amino]-1*H*-indole-3-propan-1-ol (>99 % *ee*) (Reproduced from reference 3)



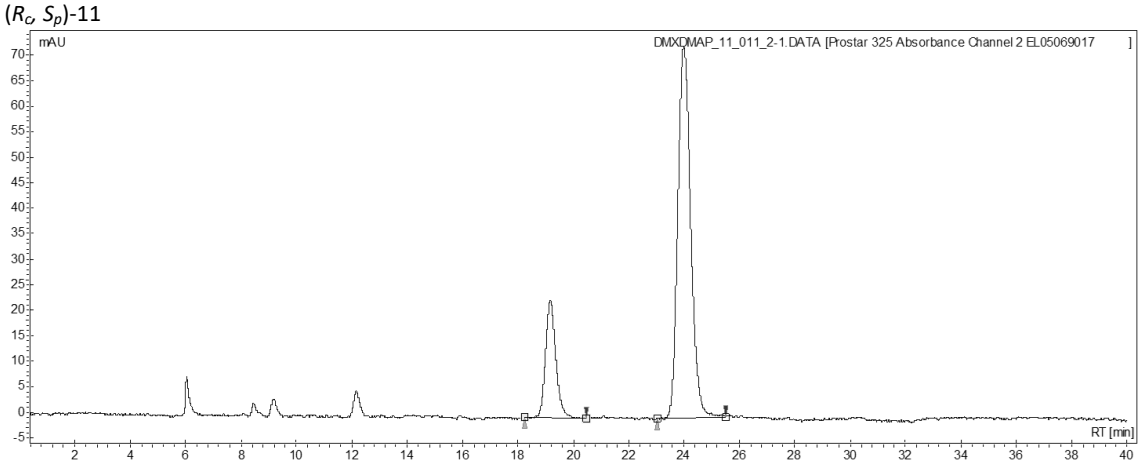
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	L-enantiomer	29.78	80.3	69.7	100.000
Total			80.3	69.7	100.000

Racemic 1-phenyl-1-ethanol, **15**



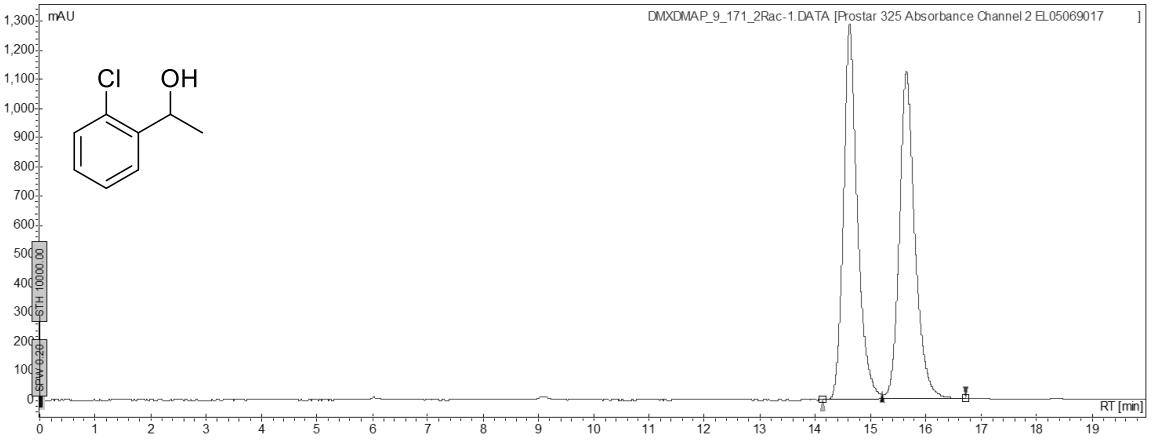
#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area %
1	R-enantiomer	18.87	116.5	52.3	49.625
2	S-enantiomer	23.64	101.7	53.1	50.375
Total			218.2	105.4	100.000

Using (R_o, S_p)-11



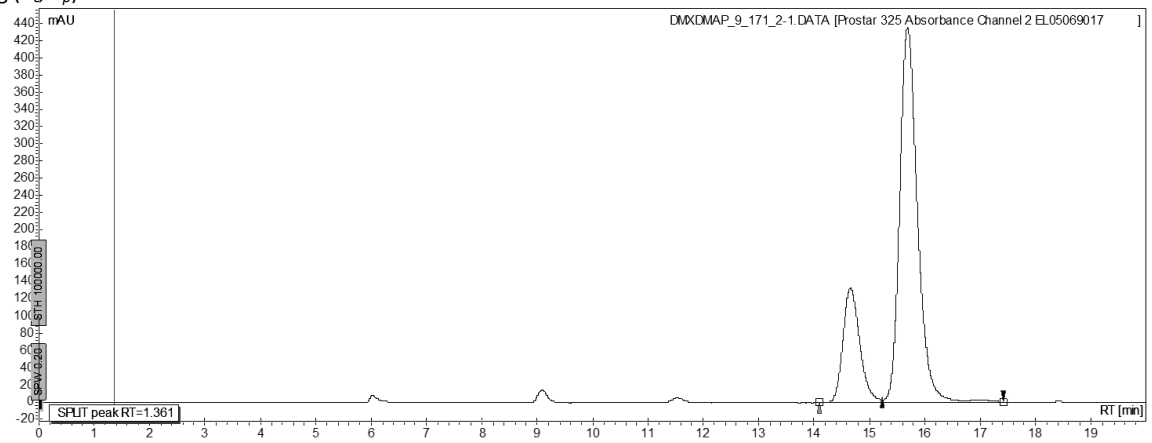
#	Name	Time [Min]	[% Area]	Height [mAU]	Area [mAU.Min]
1	R-enantiomer	19.16	20.20	23.0	9.9
2	S-enantiomer	23.99	79.80	72.7	39.1
Total			100.00	95.7	49.0

Racemic 1-(2-chlorophenyl)-1-ethanol, **21a**



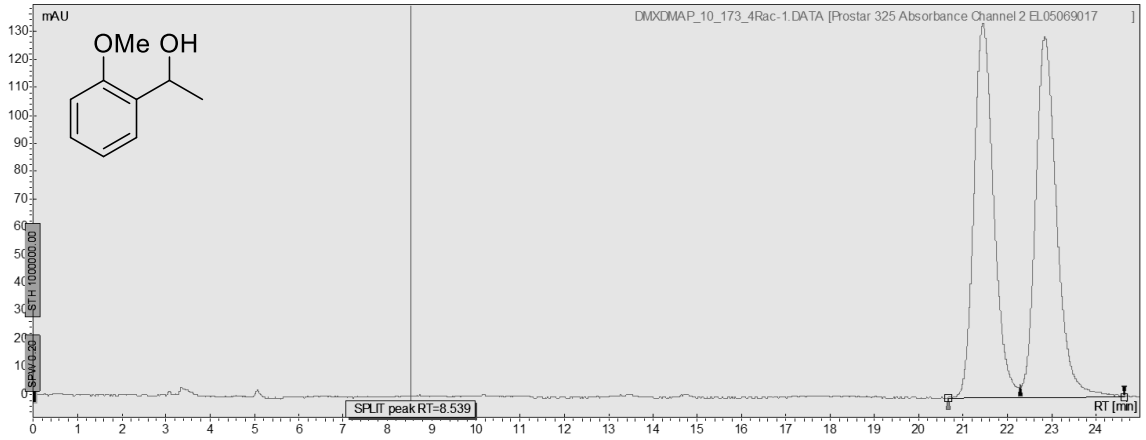
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	R-enantiomer	14.62	50.54	1287.0	374.0
2	S-enantiomer	15.65	49.46	1124.5	366.0
Total			100.00	2411.5	740.0

Using (R_c, S_p)-11



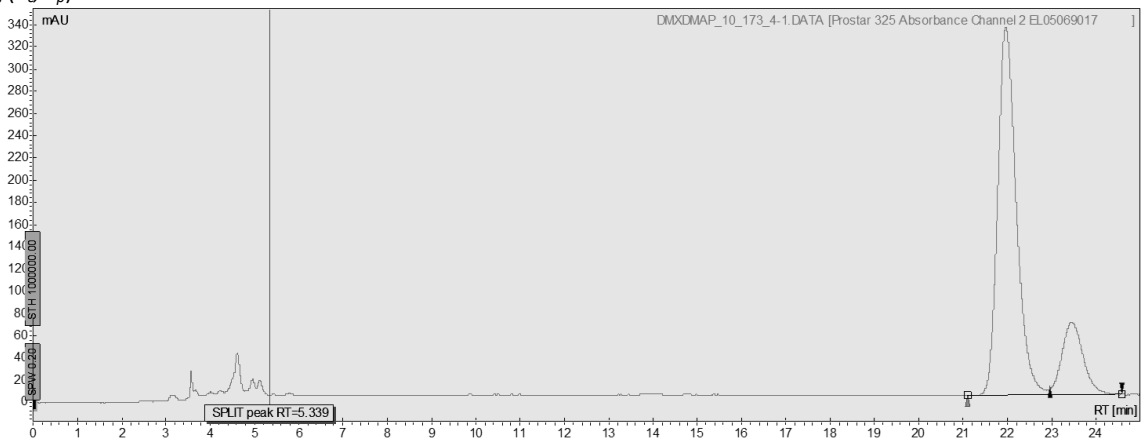
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	14.66	22.35	132.7	46.6
2	UNKNOWN	15.69	77.65	435.2	162.1
Total			100.00	567.9	208.7

Racemic 1-(2'-methoxyphenyl)-1-ethanol, **21b**



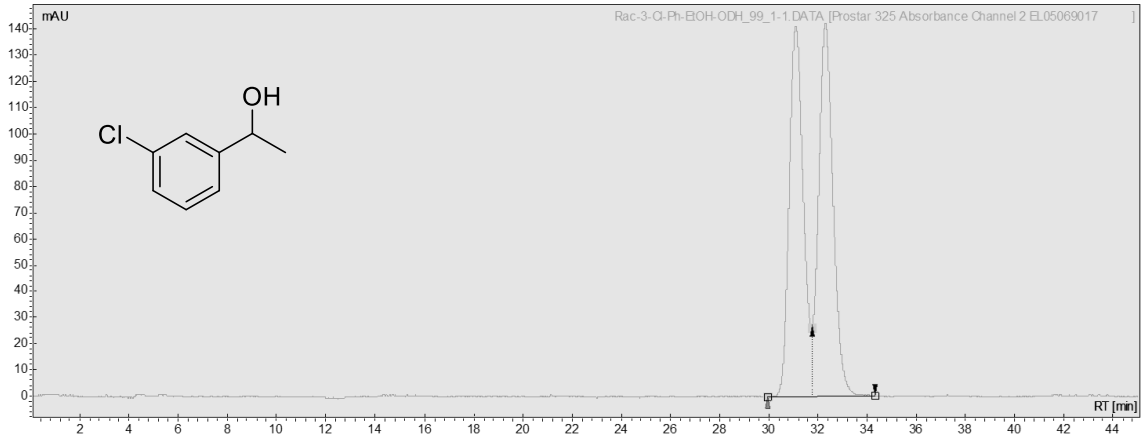
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	21.45	49.23	133.9	69.0
2	R-enantiomer	22.85	50.77	129.1	71.1
Total			100.00	263.0	140.1

Using (R_c, S_p)-11



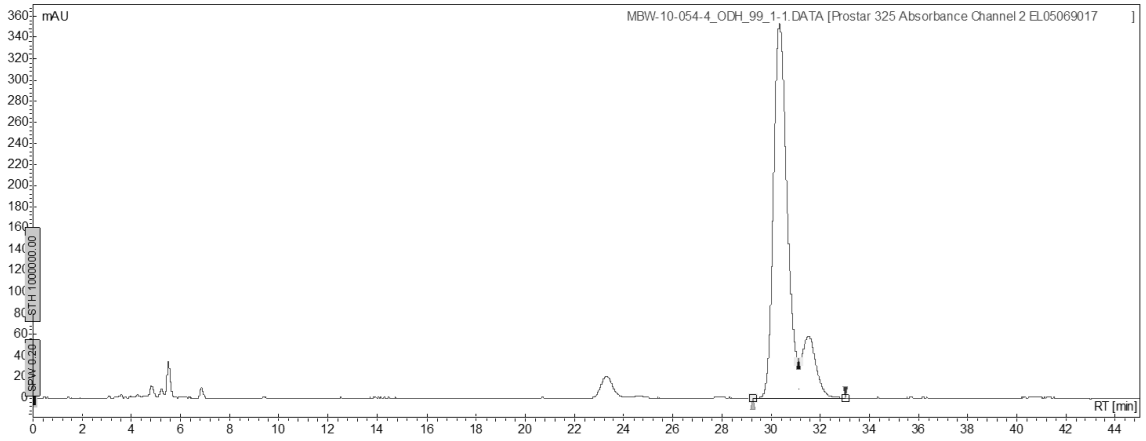
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	21.96	81.65	330.7	161.9
2	R-enantiomer	23.45	18.35	65.7	36.4
Total			100.00	396.4	198.3

Racemic 1-(3-chlorophenyl)-1-ethanol, **21c**



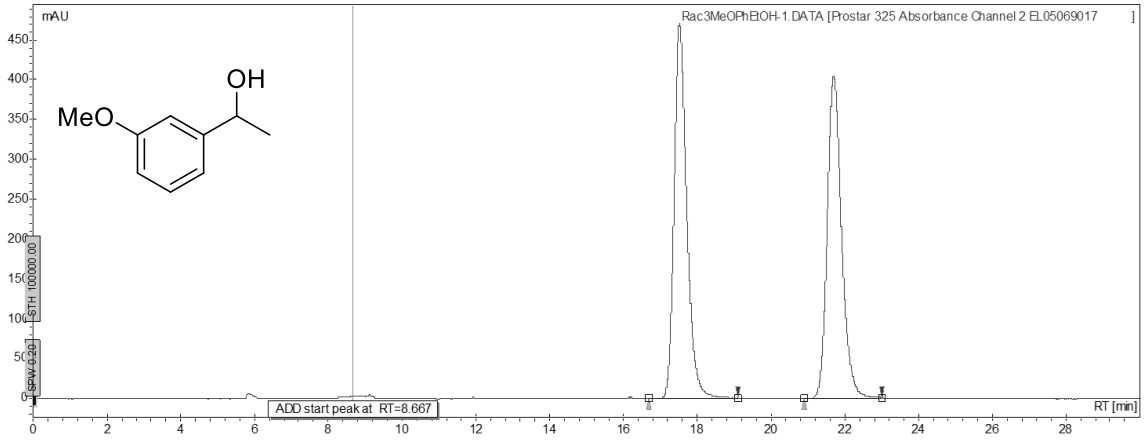
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	31.09	49.21	141.4	94.0
2	UNKNOWN	32.30	50.79	142.3	97.0
Total			100.00	283.7	191.0

Using (S_c, R_p)-11



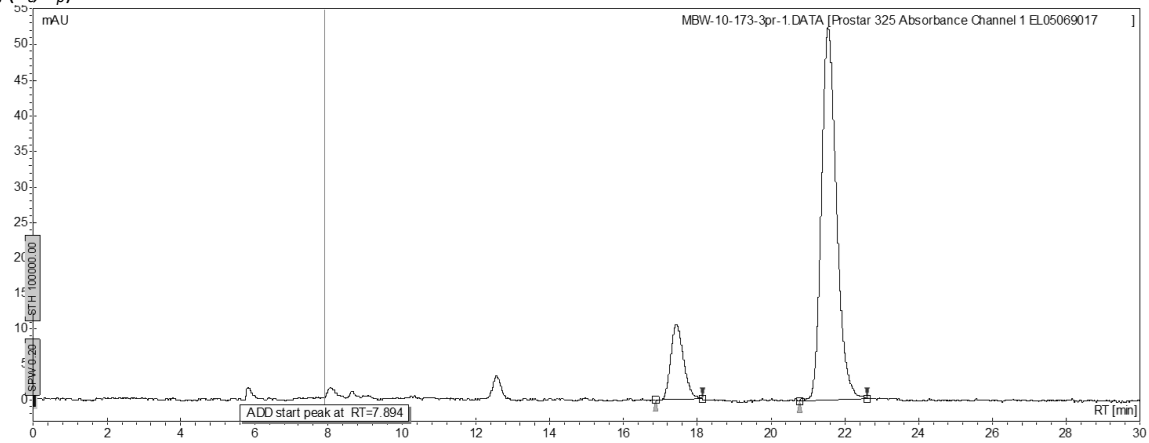
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	30.34	84.95	353.2	226.2
2	UNKNOWN	31.50	15.05	58.5	40.1
Total			100.00	411.8	266.2

Racemic 1-(3-methoxyphenyl)-1-ethanol, **21d**



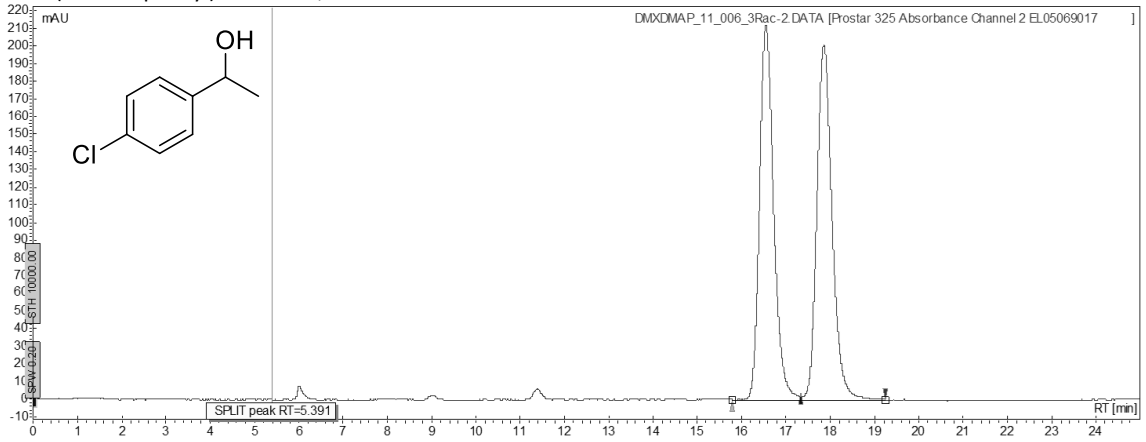
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	17.52	50.46	469.7	185.3
2	UNKNOWN	21.69	49.54	404.0	181.9
Total		100.00 873.7	367.2	100.000	

Using (R_c, S_p)-11



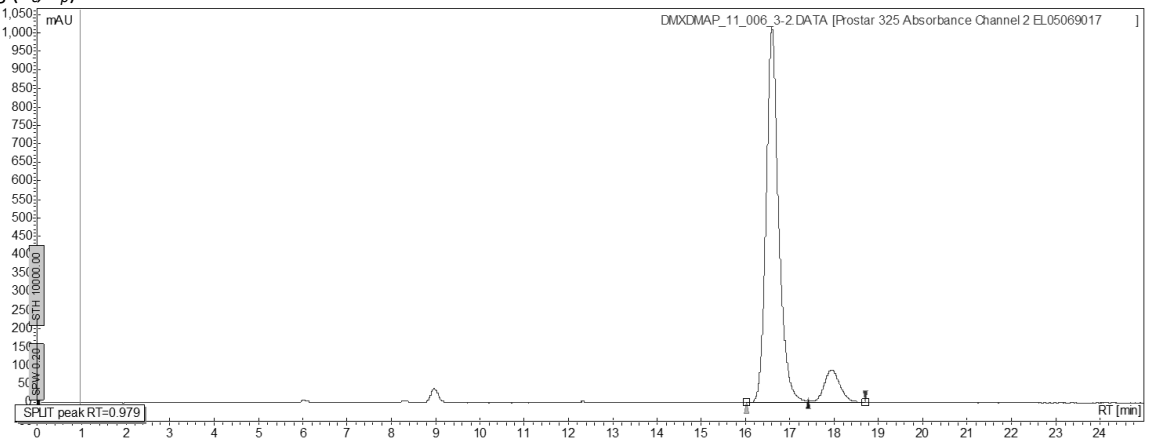
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	R-enantiomer	17.44	14.79	10.6	4.3
2	S-enantiomer	21.54	85.21	52.4	24.7
Total			100.00	63.1	29.0

Racemic 1-(4-chlorophenyl)-1-ethanol, **21e**



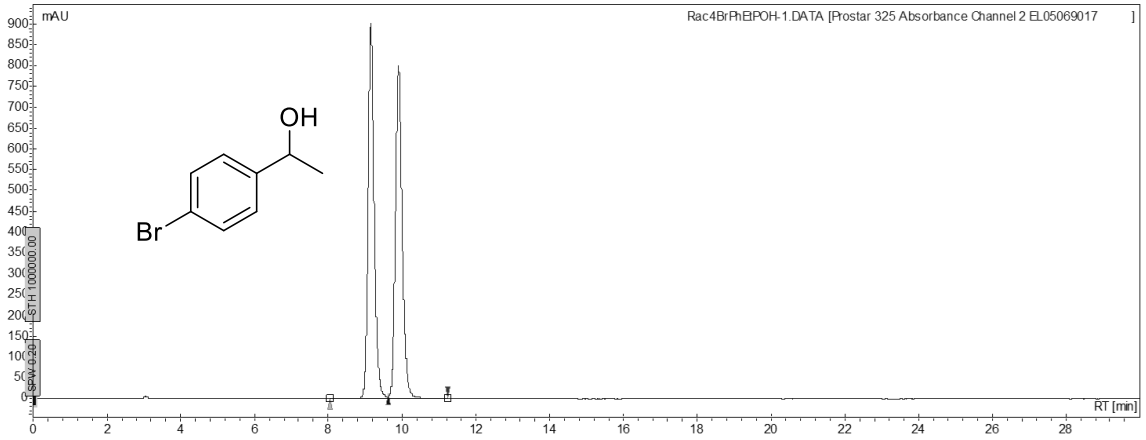
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	S-enantiomer	16.55	49.48	211.9	78.2	
2	R-enantiomer	17.85	50.52	201.1	79.8	
Total			100.00	413.0	158.0	

Using (R_c, S_p)-11



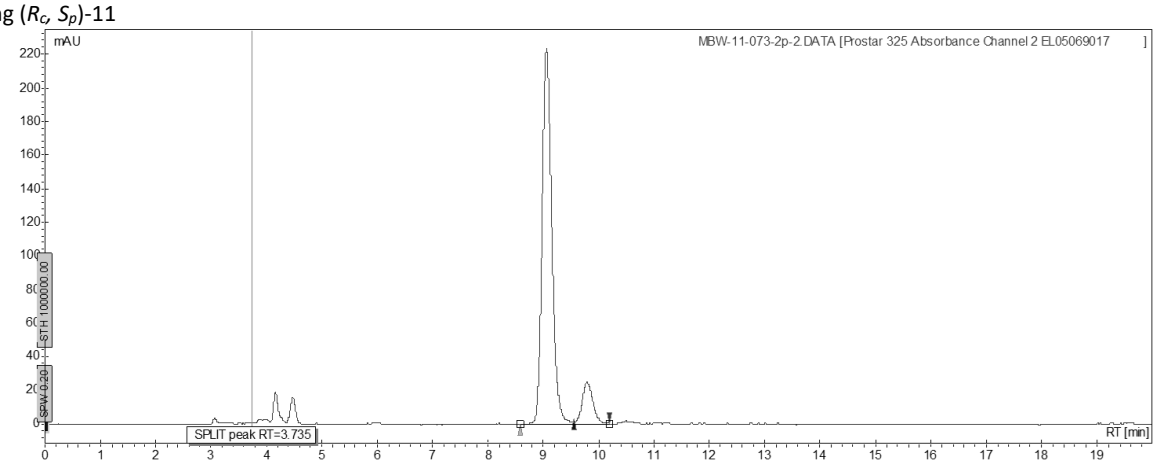
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	S-enantiomer	16.59	90.07	1014.1	333.3	
2	R-enantiomer	17.94	9.93	88.1	36.8	
Total			100.00	1102.2	370.1	

Racemic 1-(4-bromophenyl)-1-ethanol, **21f**



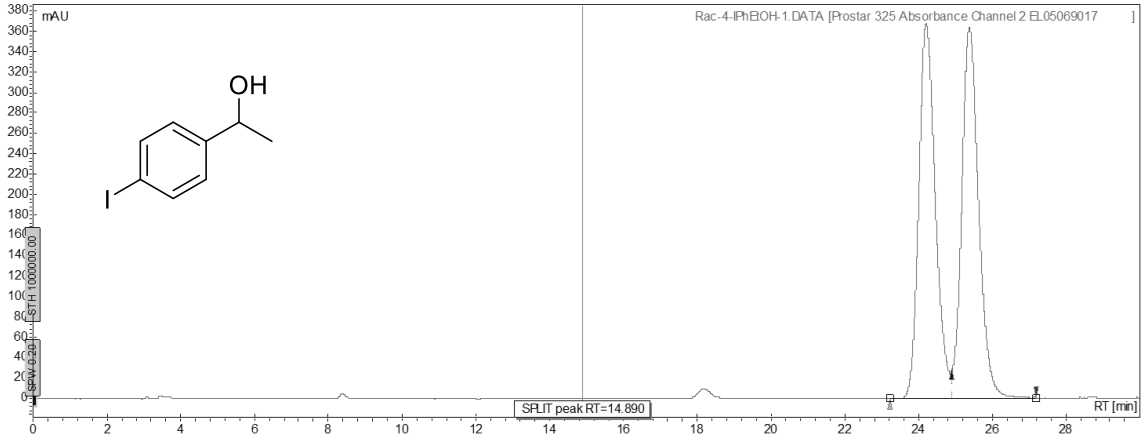
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	9.16	50.50	900.5	169.9
2	UNKNOWN	9.91	49.50	800.1	166.5
Total			100.00	1700.6	336.5

Using (R_c, S_p)-11



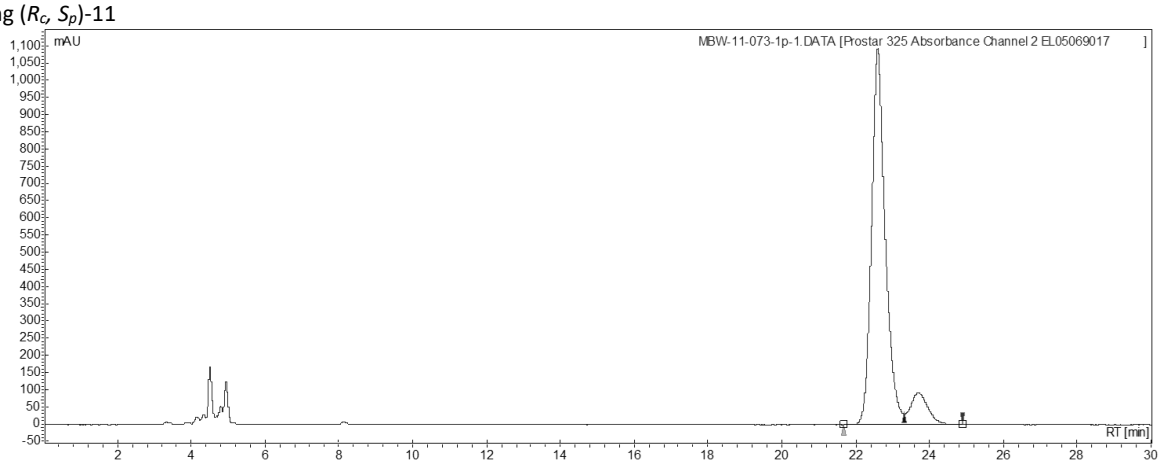
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	9.06	89.16	223.4	45.1
2	UNKNOWN	9.79	10.84	24.7	5.5
Total			100.00	248.1	50.5

Racemic 1-(4-iodophenyl)-1-ethanol, **21g**



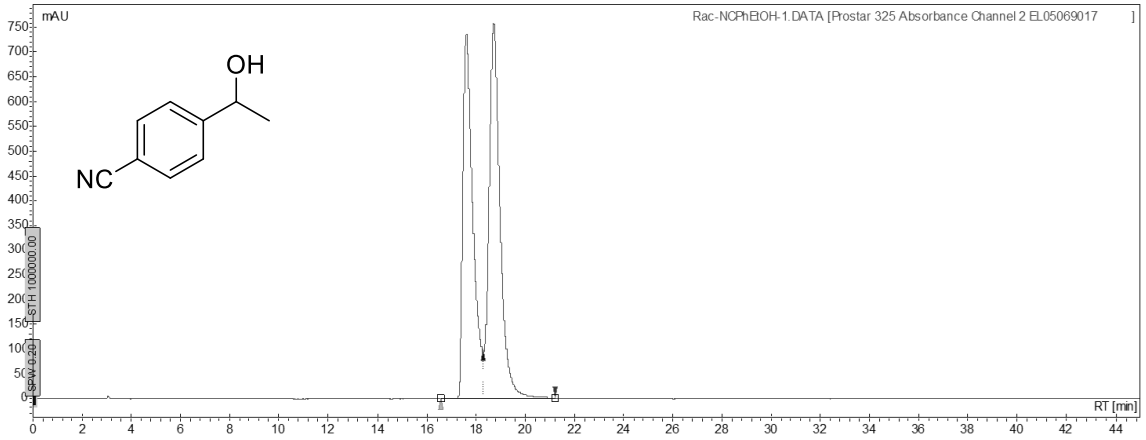
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	24.20	49.89	367.5	191.4
2	UNKNOWN	25.37	50.11	363.5	192.2
Total			100.00	731.1	383.5

Using (R_c, S_p)-11



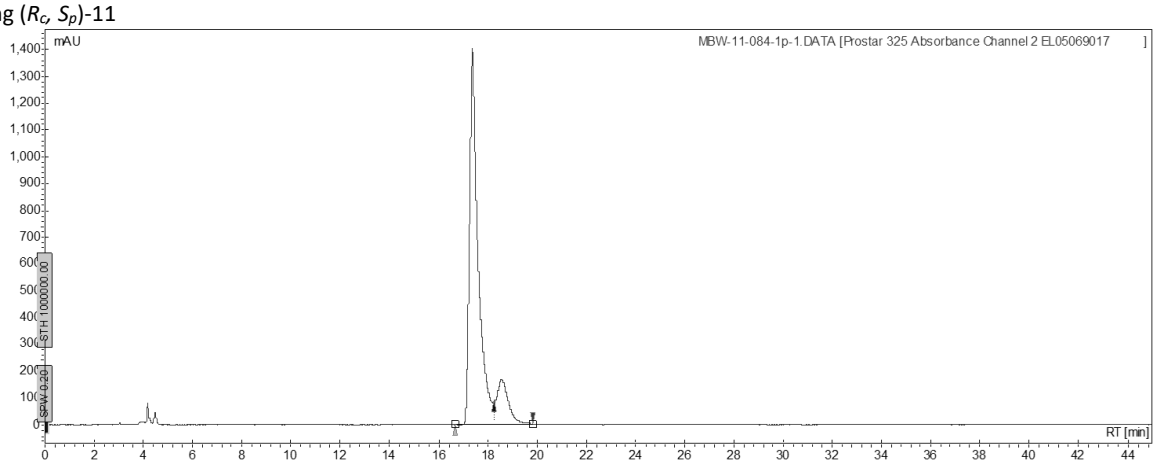
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	22.59	90.32	1092.6	469.1
2	UNKNOWN	23.70	9.68	92.1	50.2
Total			100.00	1184.7	519.3

Racemic 1-(4-iodophenyl)-1-ethanol, **21h**



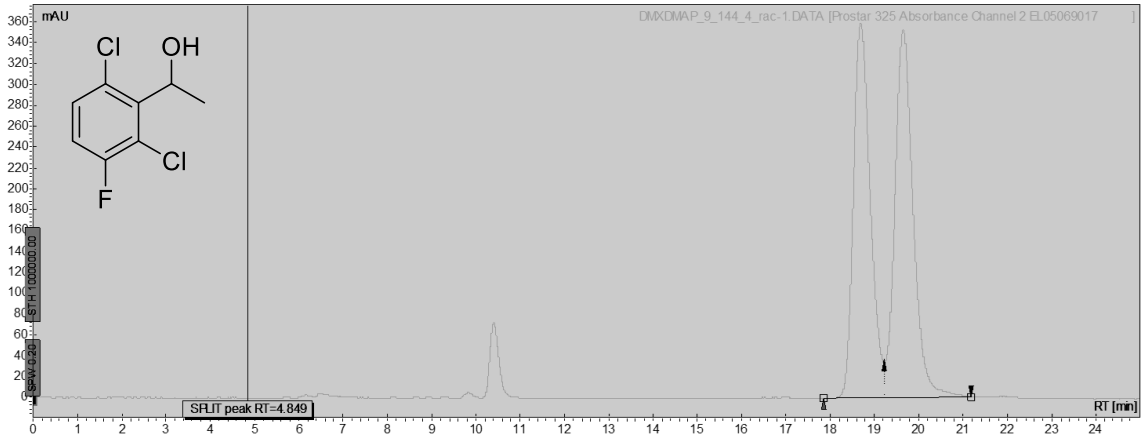
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	17.61	46.59	735.7	341.8
2	UNKNOWN	18.73	53.41	757.1	391.8
Total			100.00	1492.9	733.6

Using (R_c, S_p)-11



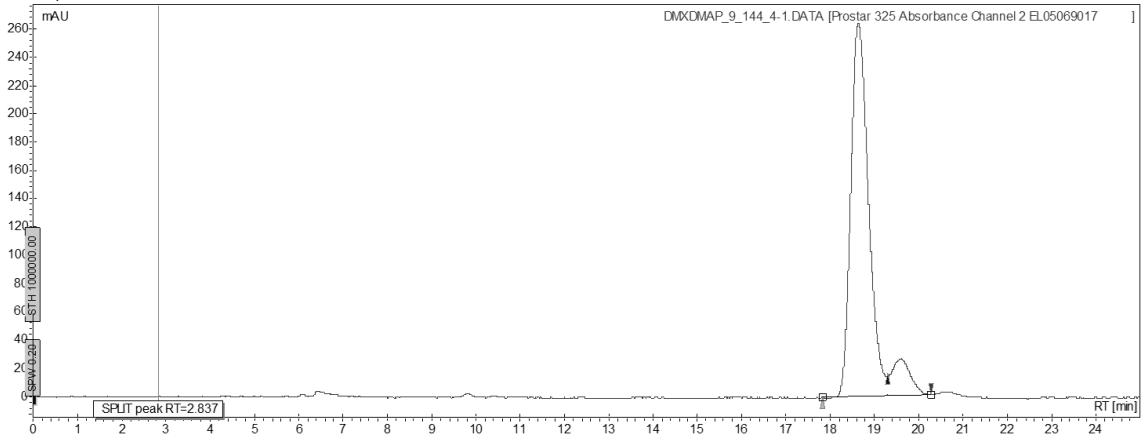
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	17.37	86.24	1402.8	567.3
2	UNKNOWN	18.57	13.76	165.4	90.5
Total			100.00	1568.2	657.8

Racemic 1-(2,6-dichloro-3-fluorophenyl)-1-ethanol, **21i**



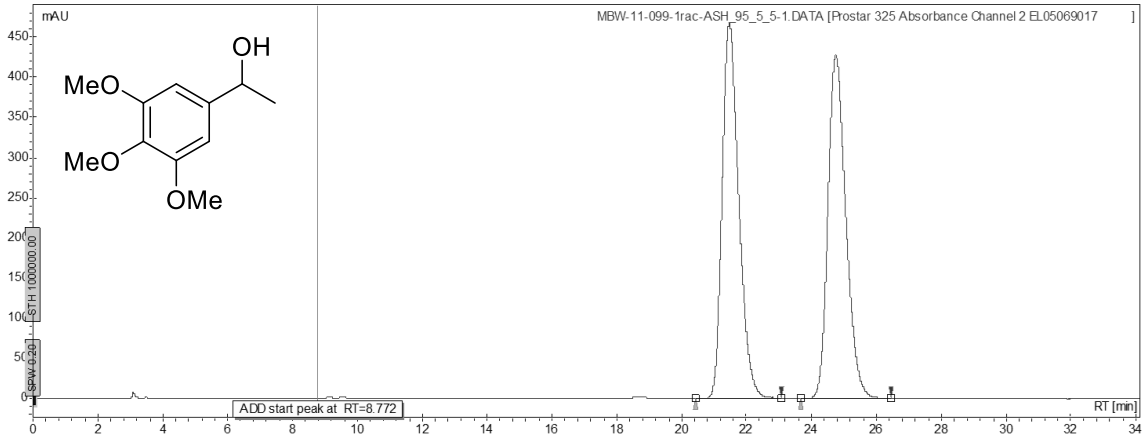
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	UNKNOWN	18.69	48.38	358.3	157.5	
2	UNKNOWN	19.65	51.62	352.2	168.0	
Total			100.00	710.5	325.5	

Using (R_c, S_p)-11



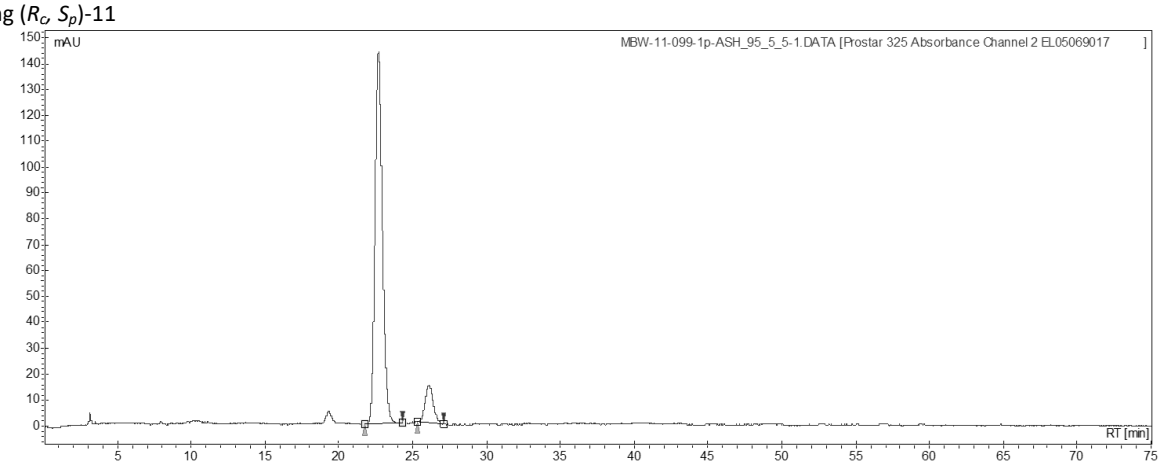
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	S-enantiomer	18.64	90.55	263.8	122.0	
2	R-enantiomer	19.61	9.45	26.1	12.7	
Total			100.00	289.9	134.7	

Racemic 1-(3,4,5-trimethoxyphenyl)-1-ethanol, **21j**



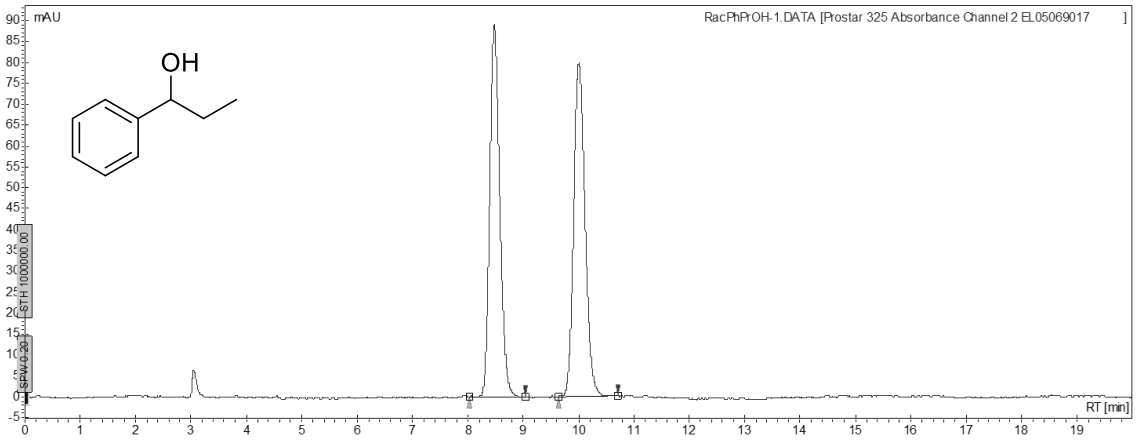
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	21.47	50.25	467.2	275.8
2	UNKNOWN	24.75	49.75	428.3	273.1
Total			100.00	895.4	548.9

Using (R_a, S_p)-11



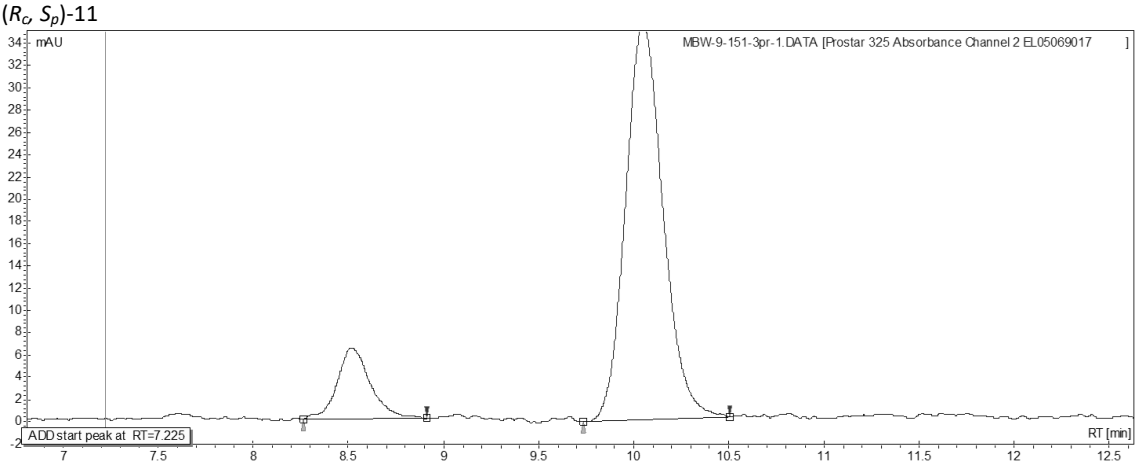
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	22.66	90.10	143.7	84.6
2	UNKNOWN	26.08	9.90	14.4	9.3
Total			100.00	158.2	93.9

Racemic 1-phenyl-1-propanol, **21k**



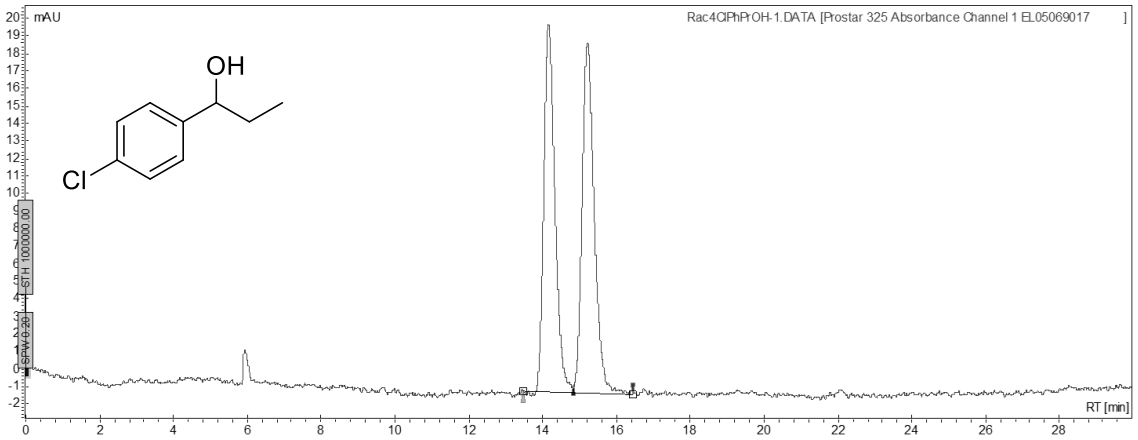
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	R-enantiomer	8.48	49.83	89.2	18.8	
2	S-enantiomer	10.01	50.17	79.8	18.9	
Total			100.00	169.0	37.7	

Using (R_c, S_p)-11



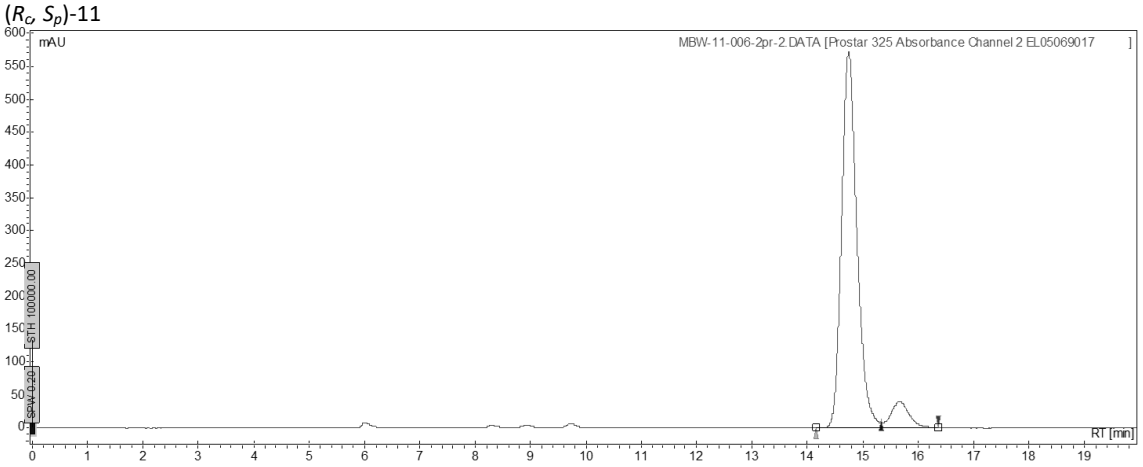
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	R-enantiomer	8.52	13.77	6.4		1.3
2	S-enantiomer	10.05	86.23	35.7		8.1
Total			100.00	42.1		9.4

Racemic 1-(4-chlorophenyl)-1-propanol, **21l**



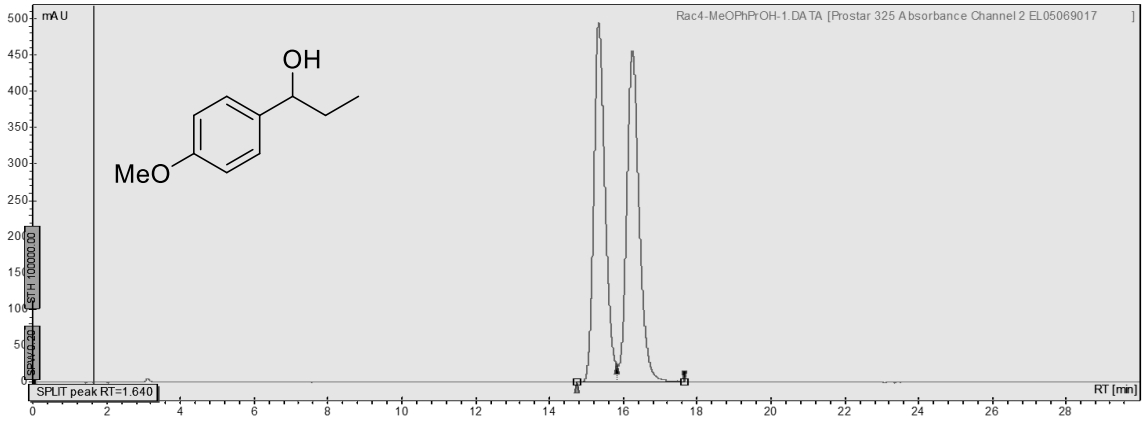
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	14.16	48.76	20.9	7.3
2	R-enantiomer	15.21	51.24	19.9	7.6
Total			100.00	40.9	14.9

Using (R_a, S_p)-11



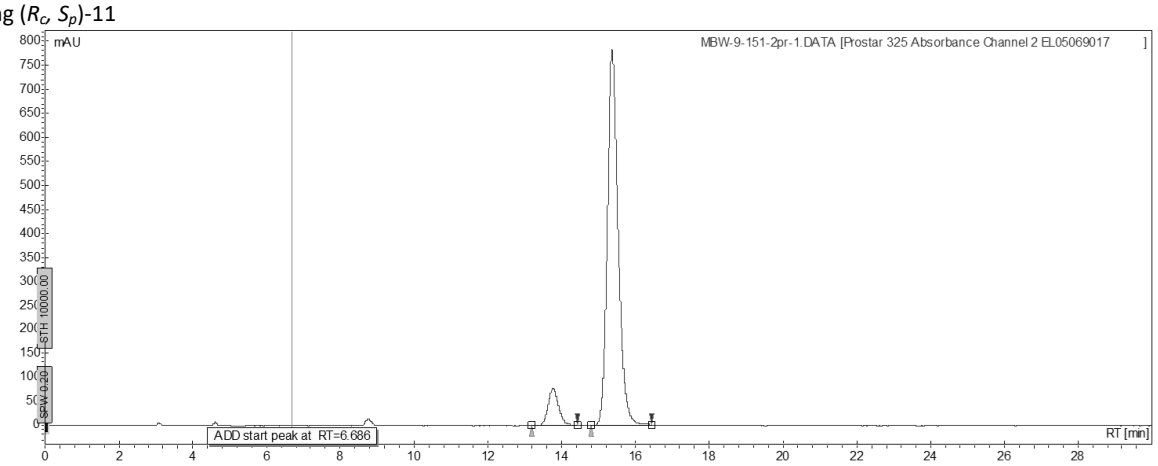
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	14.75	92.47	571.8	183.5
2	R-enantiomer	15.66	7.53	39.3	14.9
Total			100.00	611.1	198.4

Racemic 1-(4-methoxyphenyl)-1-propanol, **21m**



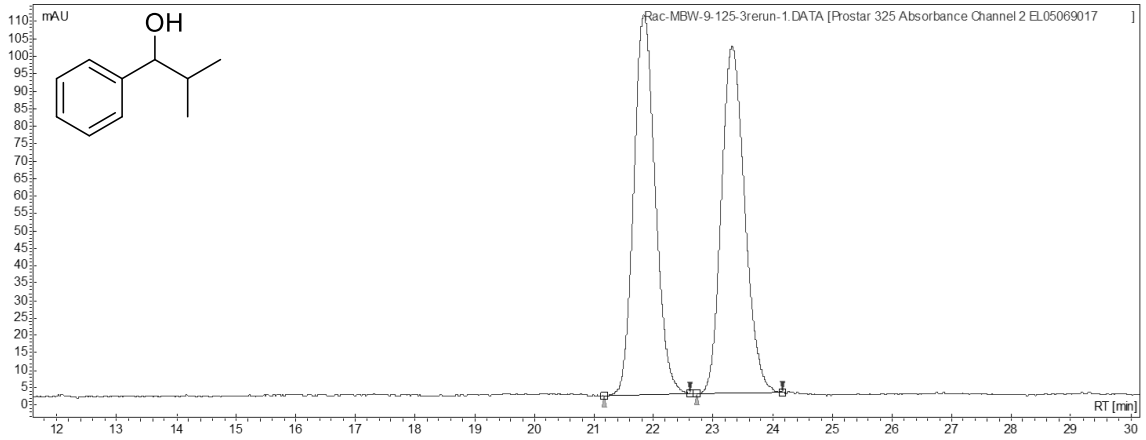
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	R-enantiomer	15.33	49.35	494.4	173.8
2	S-enantiomer	16.24	50.65	455.4	178.4
Total			100.00	949.8	352.2

Using (R_o, S_p)-11



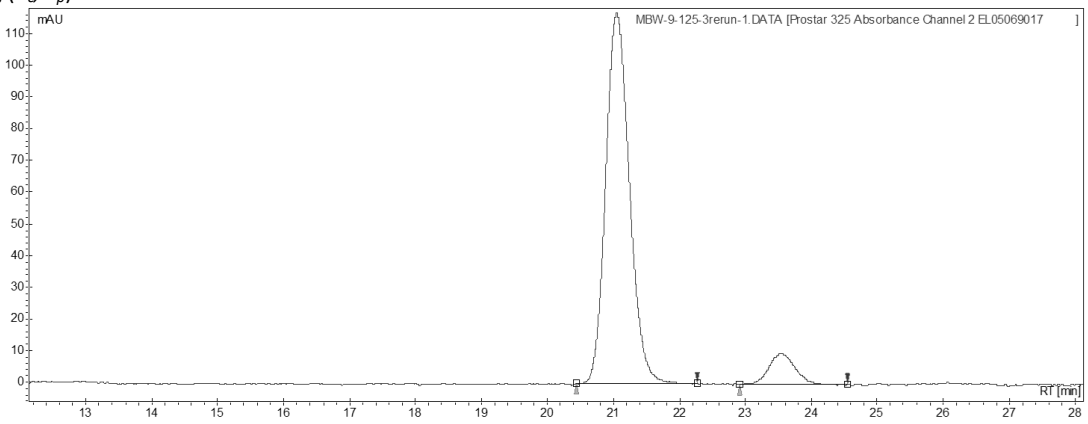
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	R-enantiomer	13.76	8.71	76.8	25.3
2	S-enantiomer	15.37	91.29	781.5	265.0
Total			100.00	858.3	290.3

Racemic 2-methyl-1-phenyl-1-propanol, **21n**



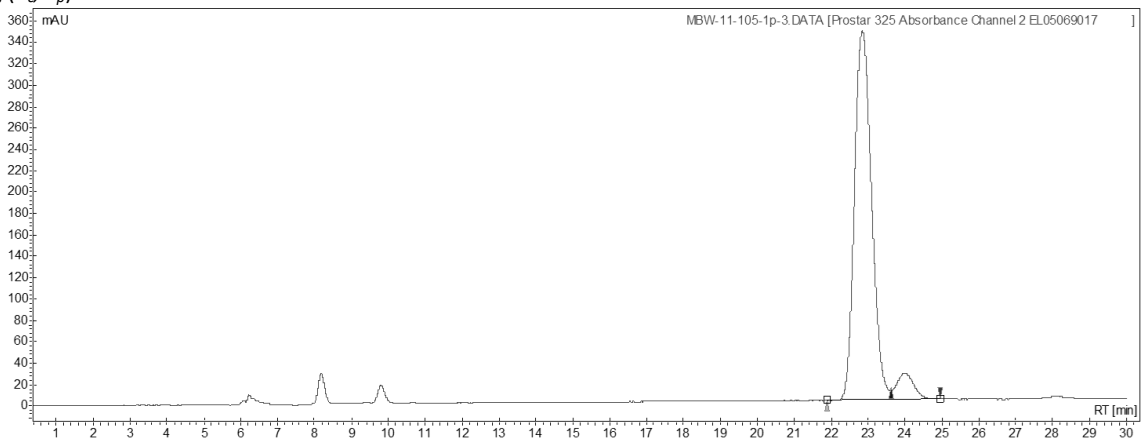
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	21.84	50.16	108.8	45.3
2	UNKNOWN	23.32	49.84	99.5	45.0
Total		100.00	208.3	90.3	100.000

Using (R_c, S_p)-11



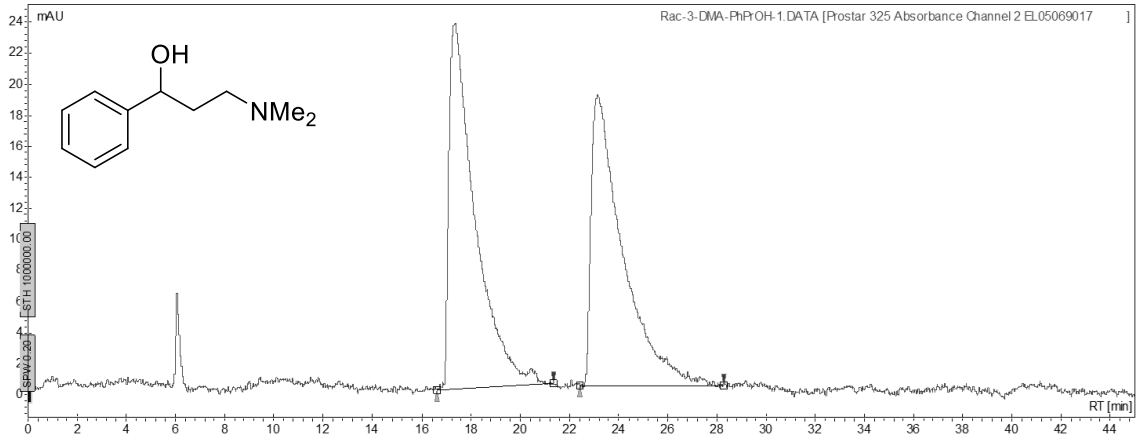
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	21.05	91.64	117.1	48.5
2	UNKNOWN	23.54	8.36	9.7	4.4
Total			100.00	126.8	53.0

Using (R_a, S_p)-9



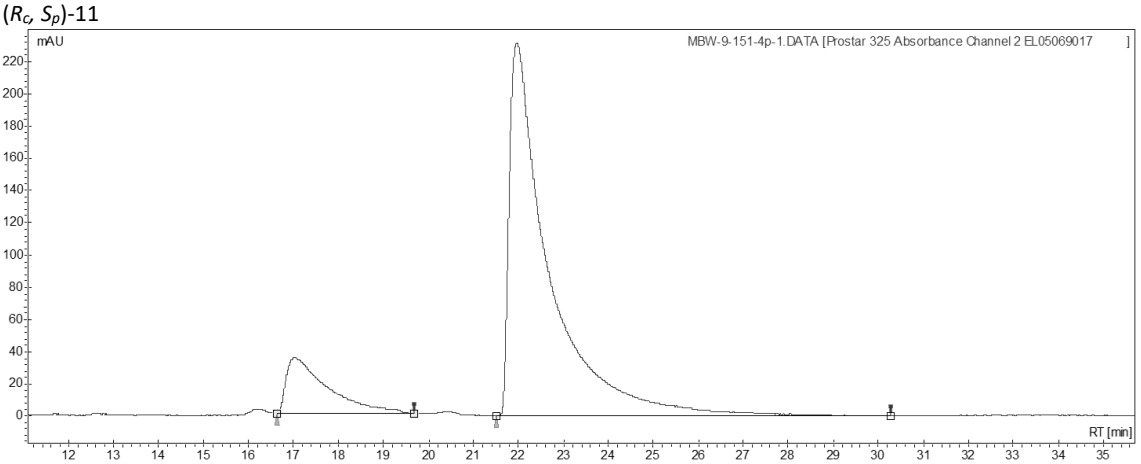
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	22.84	93.44	345.1	185.8
2	UNKNOWN	24.01	6.56	24.4	13.0
Total			100.00	369.4	198.8

Racemic 3-dimethylamino-1-phenyl-1-propanol, **21o**



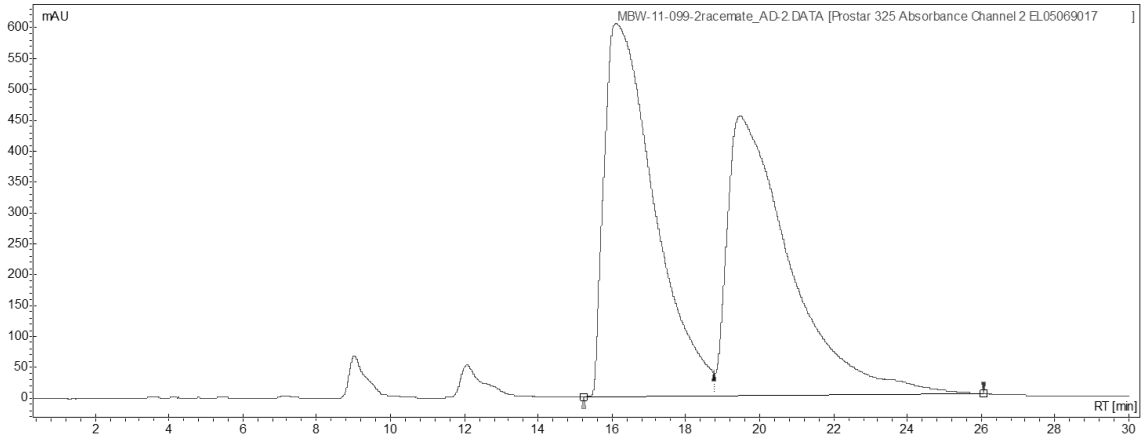
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	UNKNOWN	17.36	51.08	23.5	29.0	
2	UNKNOWN	23.13	48.92	18.7	27.7	
Total			100.00	42.2	56.7	

Using (R_c, S_p)-11

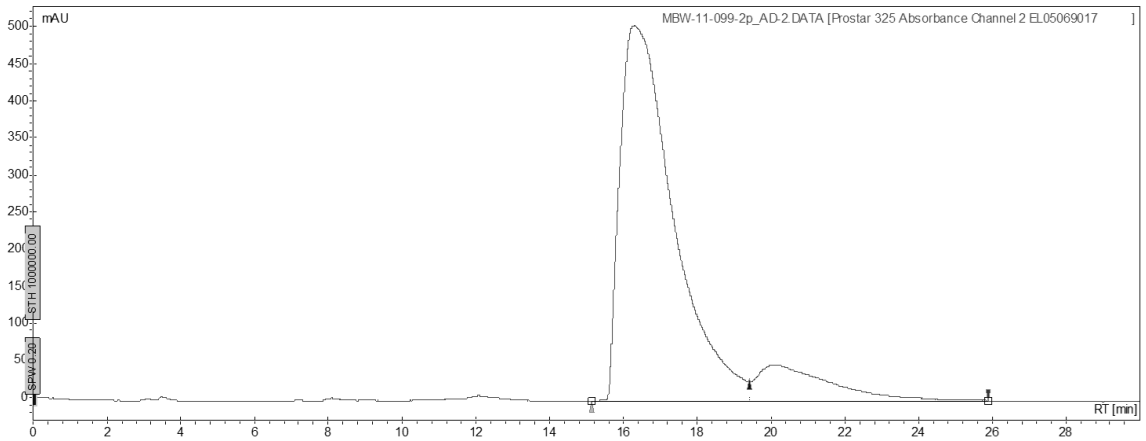


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area	[mAU.Min]
1	UNKNOWN	17.02	13.70	34.6	37.4	
2	UNKNOWN	21.97	86.30	231.7	235.6	
Total			100.00	266.3	272.9	

Racemic 3-dimethylamino-1-(4-chlorophenyl)-1-propanol, **21p**

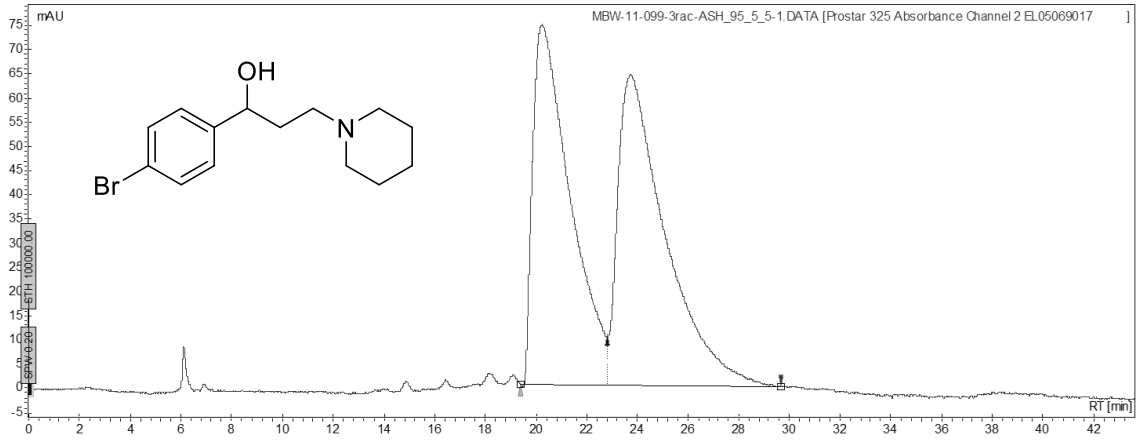


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	16.12	51.46	603.4	946.9
2	UNKNOWN	19.47	48.54	452.3	893.2
Total			100.00	1055.7	1840.2



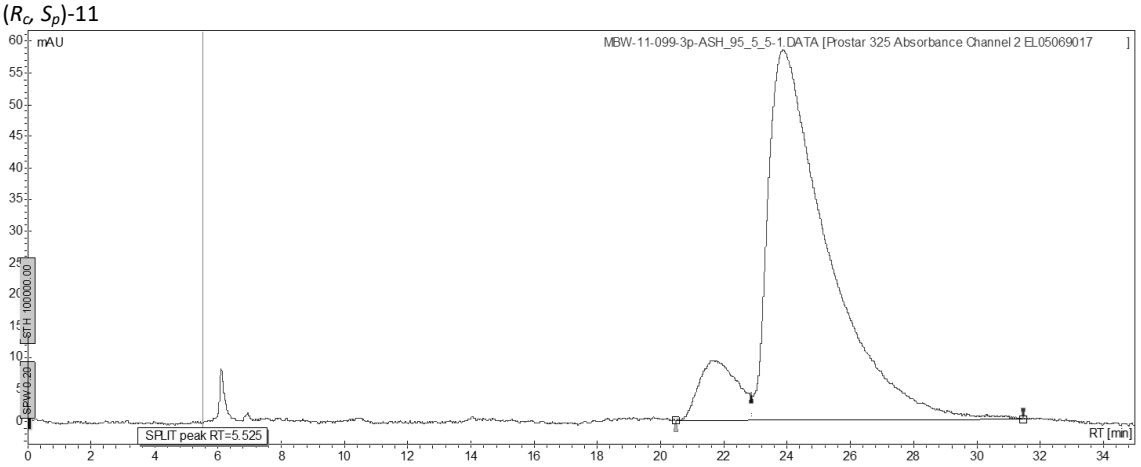
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	16.29	88.44	507.0	848.6
2	UNKNOWN	20.02	11.56	48.2	111.0
Total			100.00	555.2	959.6

Racemic 1-(4-bromophenyl)-3-(piperidin-1-yl)-1-propanol, **21q**



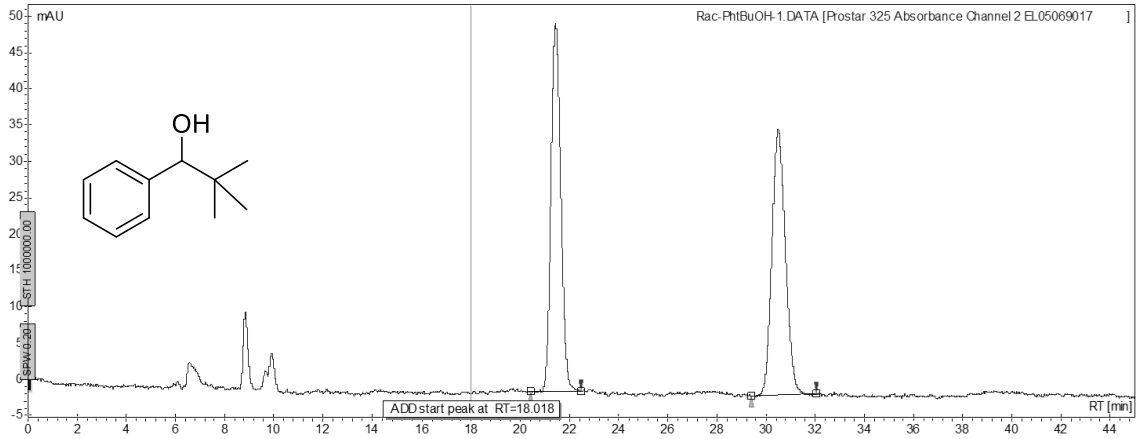
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	20.25	47.66	74.3	127.0
2	UNKNOWN	23.75	52.34	64.1	139.5
Total			100.00	138.4	266.4

Using (R_C, S_P)-11



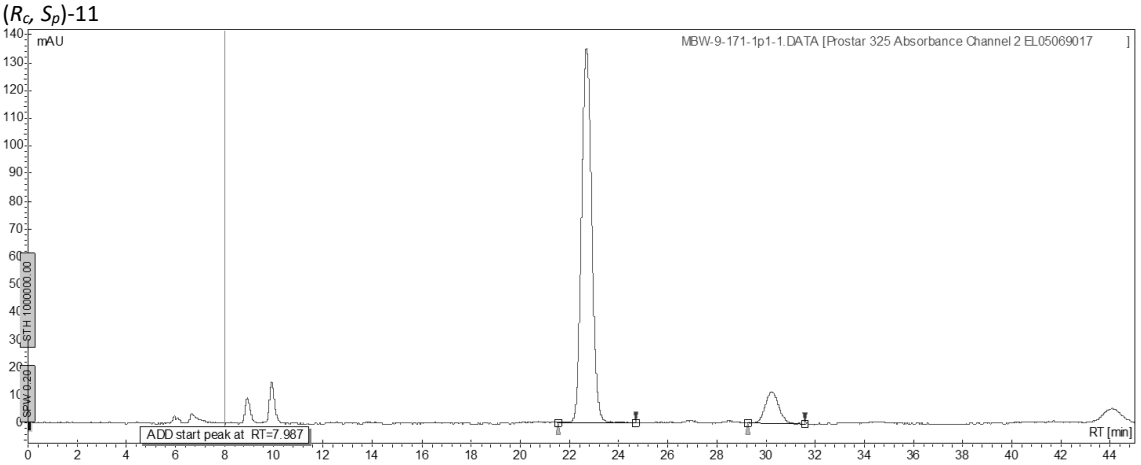
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	21.65	9.49	9.5	13.4
2	UNKNOWN	23.88	90.51	58.6	127.5
Total			100.00	68.1	140.9

Racemic 2,2-dimethyl-1-phenyl-1-propanol, **21r**



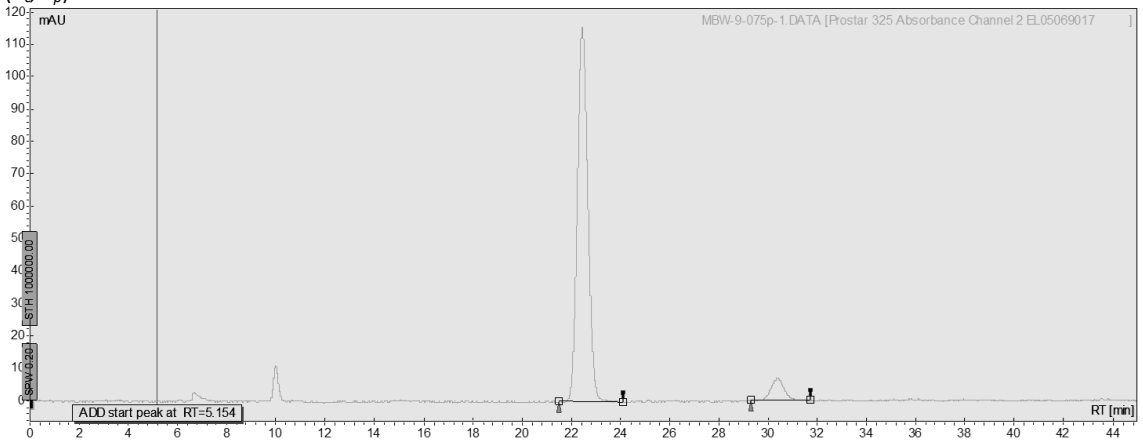
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	21.45	50.05	50.6	23.1
2	UNKNOWN	30.49	49.95	36.5	23.1
Total			100.00	87.1	46.2

Using (R_c, S_p)-11



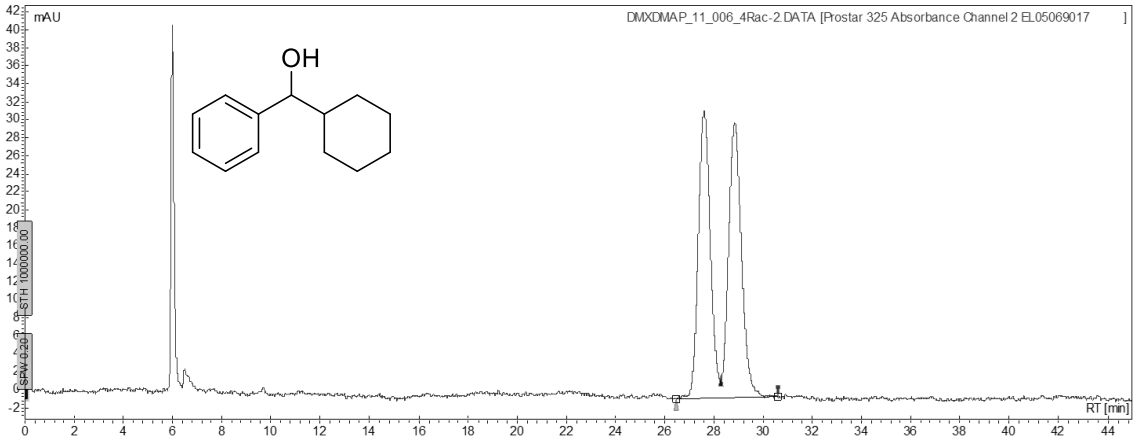
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	22.70	90.20	134.8	64.2
2	UNKNOWN	30.22	9.80	11.3	7.0
Total			100.00	146.1	71.1

Using (R_c, S_p)-9



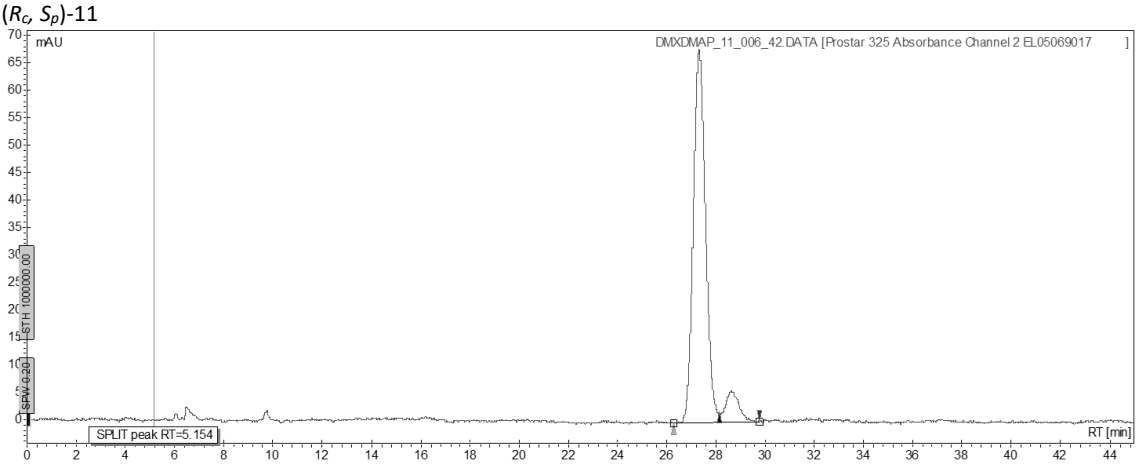
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	22.45	93.29	115.4	56.9
2	UNKNOWN	30.37	6.71	6.8	4.1
Total			100.00	122.3	61.0

Racemic 1-cyclohexyl-1-phenylmethanol, **21s**



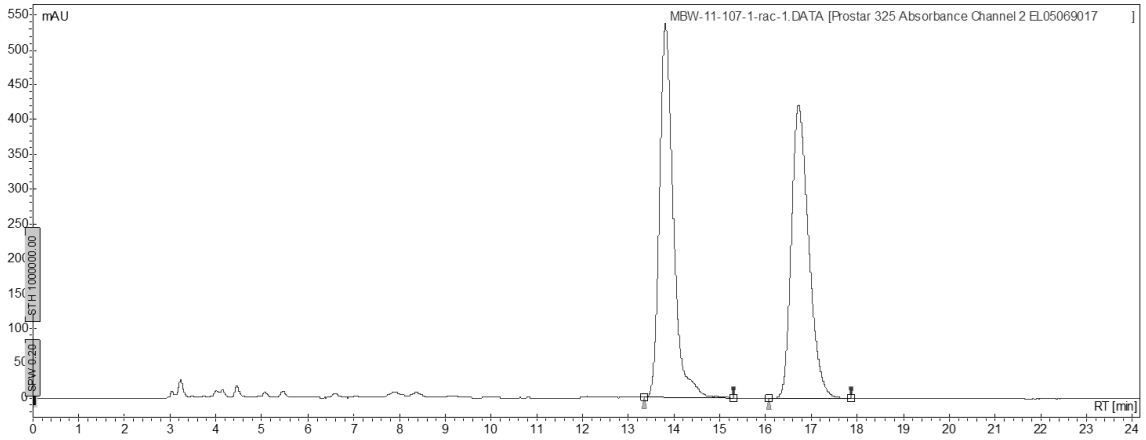
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	27.60	49.27	32.0	18.2
2	R-enantiomer	28.85	50.73	30.5	18.7
Total			100.00	62.5	36.9

Using (R_c, S_p)-11

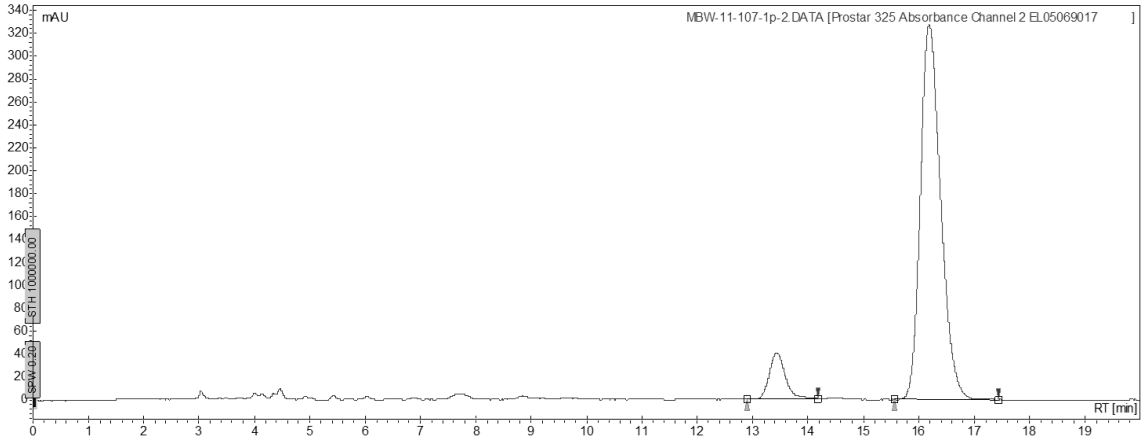


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-enantiomer	27.32	91.29	68.0	39.3
2	R-enantiomer	28.61	8.71	5.8	3.7
Total			100.00	73.9	43.0

Racemic 2-methyl-1,2-diphenyl-1-propanol, **21t**

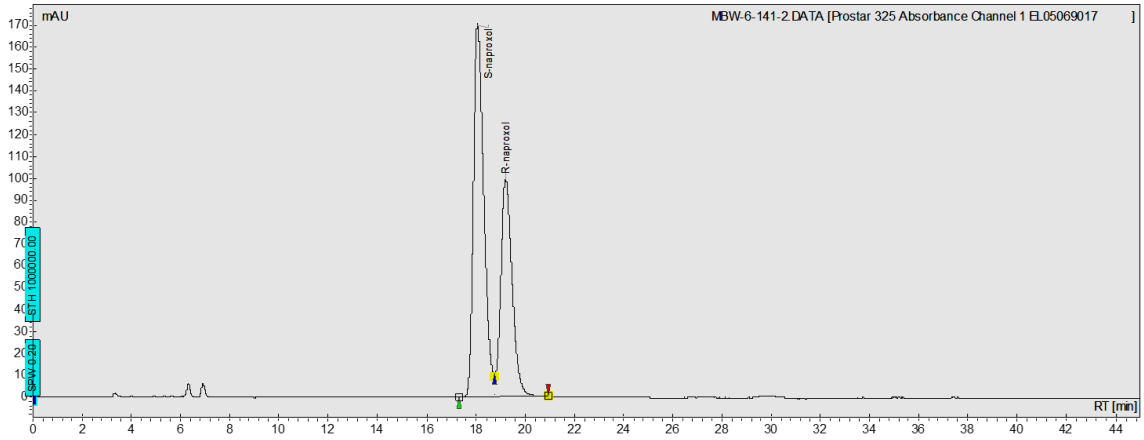


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	13.81	50.49	537.3	187.5
2	UNKNOWN	16.72	49.51	422.6	183.8
Total			100.00	959.9	371.3



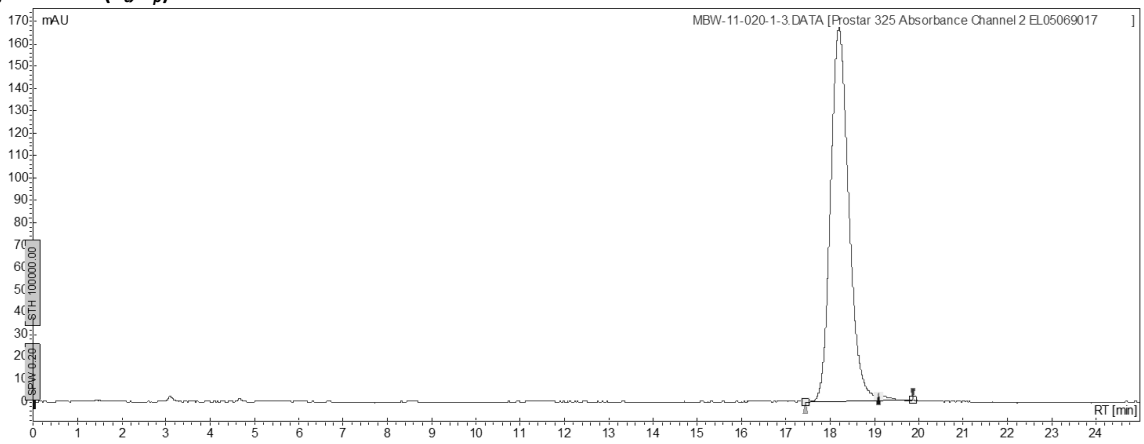
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	13.43	8.75	40.1	13.3
2	UNKNOWN	16.18	91.25	326.7	138.7
Total			100.00	366.8	152.0

Scalemic naproxol, **19e**



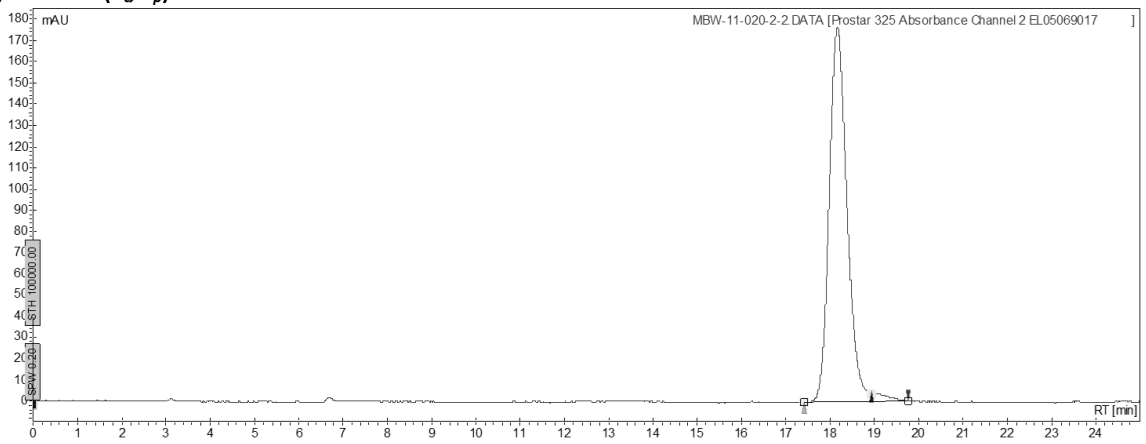
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	S-naproxol	18.07	60.93	170.7	83.4
2	R-naproxol	19.21	39.07	99.4	53.5
Total			100.00	270.2	136.9

Using 1.0 mol% ***(R_c, S_p)*-9**



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	18.20	99.22	167.1	79.5
2	UNKNOWN	19.11	0.78	2.2	0.6
Total			100.00	169.3	80.2

Using 0.5 mol% (***R_c, S_p*)-9**



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]
1	UNKNOWN	18.16	98.10	176.6	81.9
2	UNKNOWN	18.94	1.90	3.8	1.6
Total		100.00 180.3	83.5		

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