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Supporting Information

69451 Weinheim, Germany

Palladium Nanoparticles Supported on Polyaniline Nanofibers as a Semi-Heterogeneous Catalyst in Water

Benjamin J. Gallon, Robert W. Kojima, Richard B. Kaner,* and Paula L. Diaconescu*

Department of Chemistry and Biochemistry, University of California, Los Angeles CA 90095

kaner@chem.ucla.edu; pld@chem.ucla.edu

Experimental

General considerations

Unless stated otherwise, all operations were performed in air with no special considerations. Solvents were purchased from EMD, reagent grade, and used as received. $CDCl_3$ was purchased from Cambridge Isotopes and was stored over 4 Å sieves. Other chemicals were used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker300 or Bruker500 spectrometers at room temperature in $CDCl_3$ unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.26 ppm (^{1}H) and 77.00 (^{13}C, $CDCl_3$).

Suzuki coupling starting from 2-bromoanisole: 2-bromoanisole (2.5 g, 0.0134 mol, 1 eq), phenylboronic acid (1.64 g, 0.0134 mol, 1 eq), and NaOH (2.15 g, 0.0537 mol, 4 eq) were added to a RB flask with DI H_20, the flask was placed in an oil bath until the temperature reached 100 °C and the solution stirred until the base was completely dissolved. 1.6 mL PANI/Pd (3.2×10^{-6} mol Pd, 0.025 mol% vs halide) was added by syringe to the stirring solution and the system capped with a glass septum and allowed to react for 4 h. The system was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. The solvent is removed by rotovap and 2-methoxybiphenyl is collected as a white solid (2.425 g, 98% yield).

4-acetylbiphenyl: 4-chloroacetophenone (5 g, 32.3 mmol, 1.0 eq), phenylboronic acid (3.94 g 32.3 mmol, 1.0 eq) and NaOH (5.1744 g, 129.36 mmol, 4 eq) were added to a round bottom flask with deionized H_20. The flask was placed in an oil bath and the mixture stirred until the temperature is 80 °C and the base is completely dissolved. An aliquot of 1.5 mL PANI/Pd (3×10^{-3} mmol, 0.01 mol%) is added by syringe to the stirring solution and the system is capped with a glass septum and allowed to react for 4 h. The system is cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts are washed with deionized H_20 (3 x 75 mL) and dried with $MgSO_4$. The solvent is removed by rotovap and the resulting product is collected. Yield = 6.28 g (99%). Yield can range between 84 and 99%.

4-phenylbenzoic acid: 4-chlorobenzoic acid (5 g, 0.031 mol, 1 eq), phenylboronic acid (5.66 g, 0.046 mol, 1.5 eq), and NaOH (4.96 g, 0.124 mol, 4 eq) were added to deionized H_20 to a RB flask, which is placed in an oil bath until the temperature is 80 °C and the solution is stirred until the base is completely dissolved. 1.0 mL of PANI/Pd (2×10^{-6} mol Pd, 0.006 mol% vs the halide) is added by syringe to the stirring solution and the system is capped with a glass septum and allowed to react for 4 h. The system is cooled to room temperature, the catalyst is removed by filtration through Celite and the aqueous layer is washed with diethyl ether (2 x 50 mL). After washing with Et_2O, aqueous layer is acidified with HCl until pH is approx 1, followed by extraction with ether (3 x 100 mL). The combined organic extracts are washed with deionized H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent is removed by rotovap and the white solid product is collected. Yield is 6.01 g (97%).

4-phenylphenol: 4-chlorophenol (2.5 g, 0.0194 mol, 1 eq), phenylboronic acid (3.55 g, 0.0290 mol, 1.5 eq), and base (3.104 g, 0.0776 mol, 4 eq) were added to a RB flask with DI H_20, the flask placed in an oil bath until the temperature reaches 100 °C, and the solution is stirred until the base is completely dissolved. 2.1 mL PANI/Pd (4.2×10^{-6} mol, 0.02 mol%) is added by syringe to the stirring solution and the system is capped with a glass septum and allowed to react for 6 h. The system is cooled to room temperature and HCl is added till the pH is 1-2. The acidified aqueous layer is extracted with diethyl ether (3 x 100 mL). The organic extracts are washed with DI H_20 (3 x 75 mL) and dried with MgSO4. Solvent is removed by rotovap and the white solid product is collected. Yield - 2.9 g (88%).

4-phenylbenzaldehyde: 4-chlorobenzaldehyde (4 g, 0.03 mol, 1 eq), phenylboronic acid (3.66 g, 0.03 mol, 1 eq), and NaOH (4.8 g, 0.12 mol, 4 eq) were added to a RB flask with DI H_20, the flask was placed in an oil bath until the temperature is 100 °C and the solution stirred until the base is completely dissolved. 2.0 mL PANI/Pd (4×10^{-6} mol Pd, 0.01 mol% vs halide) is added by syringe to the stirring solution and the system is capped with a glass septum and allowed to react for 4 h. The system is cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts are washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. The solvent is removed by rotovap and the resulting crude product is collected. Final product is recrystallized from hexanes/diethyl ether. Yield - 5.40 g (99%).

2-methoxybiphenyl: 2-chloroanisole (2 g, 0.014 mol, 1 eq), phenylboronic acid (1.71 g , 0.014 mol, 1 eq), and NaOH (2.244 g, 0.0561 mol, 4 eq) were added to a RB flask with DI H_20, the flask was placed in an oil bath until the temperature was 100 °C and the solution stirred until the base was completely dissolved. 2.0 mL PANI/Pd (4×10^{-6} mol Pd, 0.03 mol% vs halide) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 4 h. The system was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. The solvent was removed by rotovap. Final product was recrystallized from hexanes/diethyl ether. Yield - 92% (2.373 g).

4-ethoxybiphenyl: 4-chlorophenetole (1.5 g, 9.57 mmol, 1 eq), phenylboronic acid (1.749 g, 14.34 mmol, 1.5 eq), and NaOH (4 eq) were added to a RB flask with DI H_20, the flask was placed in an oil bath until the temperature was 100 °C and the solution stirred until the base was completely dissolved. 2.0 mL PANI/Pd (4×10^{-6} mol Pd, 0.04 mol% to halide) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 4 h. The system was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent is removed by rotovap and the resulting crude product is collected. Final product is recrystallized from hexanes/diethyl ether. Yield - 1.75 g (92%).

Pyridine derivatives: Chloropyridine (1.0 eq), phenylboronic acid (2.0 eq), and NaOH (4 eq) were added to deionized water, the flask immersed in an oil bath until the temperature reached 100° C and the solution was stirred until the base was completely dissolved. Pd/PANI was added by syringe to the stirring solution, the system capped with a glass septum and allowed to stir for 6 h. The reaction mixture was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with deionized water (3 x 75 mL) and dried with $MgSO_4$. The solvent was removed on the rotovap and the resulting crude product was collected and recrystallized from hexane and diethyl ether.

2,6-diphenylpyridine: 2,6-dichloropyridine (1.0 g, 6.76 mmol), phenylboronic acid (0.823 g, 6.76 mmol), 2 mL PANI/Pd (4×10^{-6} mol Pd, 0.06 mol%); yield - 96% (1.50 g).

3,5-diphenylpyridine: 3,5-dichloropyridine (1.0 g, 6.76 mmol), phenylboronic acid (0.823 g 6.757 mmol), 2 mL PANI/Pd (4×10^{-6} mol Pd, 0.06 mol%); yield - 95% (1.48 g).

4-phenylpyridine: 4-chloropyridine (1.0 g, 6.66 mmol, 1.0 eq), phenylboronic acid (0.812 g, 6.66 mmol, 1.0 eq); 2 mL PANI/Pd (4×10^{-6} mol Pd, 0.06 mol%); yield - 0.918g (89 %).

General protocol for the Suzuki coupling with different arylboronic acids. Aryl halide (1 equiv), arylboronic acid (1 equiv), and base (4 equiv) were added to a 50 mL round bottom flask. The solution was stirred in a heated oil bath at 100 °C. Pd/PANI (1 mol%) was syringed into the stirring solution, the flask was sealed with a septum, and the reaction mixture stirred for 6 h or for the time indicated. The reaction mixture was taken out of the oil bath, allowed to cool to room temperature, and transferred to a separatory funnel. The organic product was extracted with diethyl ether (3 x 75 mL). The collected organic fractions were washed with deionized water and then dried with $MgSO_4$. $MgSO_4$ was filtered away and the volatiles were removed under reduced pressure to yield the final product.

3,5-bis(trifluoromethyl)-4'-acetyl-biphenyl: 4-chloroacetophenone (0.060 g, 3.87 x 10^{-4} mol, 1 equiv), 3,5-bis(trifluoromethyl)-phenylboronic acid (0.100 g, 3.87 x 10^{-4} mol, 1 equiv), NaOH (0.061 g, 15.25 x 10^{-4} mol, 4 equiv), 1.94 mL of Pd/PANI (1 mol%); crude yield, 0.120 g (93%), final yield, 0.118 g (92%). NMR data compared to those published in Feuerstein, M.; Berthiol, F.; Doucet, H.; Santelli, M. *Synlett.* **2002**, *11*, 1807-1810.

2,4-dimethoxy-4'-acetyl-biphenyl: 4-chloroacetophenone (0.085 g, 5.55 x 10^{-4} mol, 1 equiv), 2,4-dimethoxy-phenylboronic acid (0.100 g, 5.55 x 10^{-4} mol, 1 equiv), NaOH (0.080 g, 20.00 x 10^{-4} mol, 4 equiv), 2.5 mL of Pd/PANI (1 mol%); 8 h; yield, 0.099 g (70%).

4-chloro-4'-hydroxy-biphenyl: 4-bromophenol (0.111 g, 6.4 x 10^{-4} mol, 1 equiv), 4-chloro-phenylboronic acid (0.100 g, 6.4 x 10^{-4} mol, 1 equiv), NaOH (0.102 g, 25.6 x 10^{-4} mol, 4 equiv), 3.2 mL of Pd/PANI (1 mol%); same work-up as 4-phenylphenol; yield, 0.105 g (80%).

4-chloro-4'-methoxy-biphenyl: 4-bromoanisole (0.118 g, 6.4 x 10^{-4} mol, 1 equiv), 4-chloro-phenylboronic acid (0.100 g, 6.4 x 10^{-4} mol, 1 equiv), NaOH (0.102 g, 25.6 x 10^{-4} mol, 4 equiv), 3.2 mL of Pd/PANI (1 mol%); 6.5 h; yield, 0.116 g (82%). NMR data compared to those published in Ackermann, L.; Althammer, A. *Org. Lett.* **2006**, *8*, 3457-3460.

2-(2'-anisole)-dibenzofuran: 2-chloroanisole (0.067 g, 4.7 x 10^{-4} mol, 1 equiv), dibenzofuran-2-boronic acid (0.101 g, 4.7 x 10^{-4} mol, 1 equiv), NaOH (0.055 g, 13.75 x 10^{-4} mol, 4 equiv), 2.3 mL of Pd/PANI (1 mol%); yield, 0.115 g. 1H NMR shows two compounds and relative intensities of the OMe peaks suggest that the impurity is ca. 20%. Based on this a conservative yield of 715 was calculated. NMR data for **2-(2'-anisole)-dibenzofuran** were compared to those published in Cram, D. J.; Dicker, I. B.; Lauer, M.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7150-7167.

Coupling with a fluoro aryl: A typical procedure was employed: 1,4-difluorobenzene (118 mg, 1.03 mmol), phenylboronic acid (0.250 g, 2.06 mmol), and NaOH (0.164 g, 4.12 mmol) were added to deionized water, the mixture stirred in an oil bath until temperature reached 100 °C and the base was completely dissolved. 0.5 mL PANI/Pd (1 x 10^{-6} mol, 0.1 mol%) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 24 h. The system was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with deionized water (3 x 75 mL) and dried with $MgSO_4$. The solvent was removed by rotovap and the resulting product was collected (0.143 mg, 60% yield).

Homocoupling reactions. Homocoupling of chlorobenzene: Chlorobenzene(1.0 g, 0.00892 mol) and NaOH (1.43 g, 0.036 mol) were added to a round bottom flask with deionized water, the flask placed in an oil bath until the temperature reached 80 °C, and the solution stirred until the base was completely dissolved. 2.1 mL PANI/Pd (4.2 x 10^{-6} mol, 0.05 mol%) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 2 h. The aqueous layer was extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with deionized water (3 x 75 mL) and dried with $MgSO_4$. The solvent was removed by rotovap and the white solid product was collected (1.36 g, 99% yield).

Homocoupling of fluorobenzene: Fluorobenzene(1.0 g, 0.0104 mol) and NaOH (0.832 g, 0.0208 mol) were added to a RB flask with DI H_20, the flask placed in an oil bath until temperature was 100 °C, and the solution stirred until the base was completely dissolved. 2.1 mL PANI/Pd (4.2×10^{-6} mol, 0.02 mol%) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 2 h. The aqueous layer was extracted with ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent was removed by rotovap and the white solid product was collected. Yield - 1.28 g (80%).

Synthesis of 4,4'-biphenyl-diol: 4-chlorophenol (2.5 g, 0.0194 mol, 2 eq) and NaOH (3.104 g, 0.0776 mol, 4 eq) were added to a RB flask with DI H_20, the flask placed in an oil bath until the temperature reached 100 °C, and the solution stirred until the base was completely dissolved. 2.1 mL PANI/Pd (4.2×10^{-6} mol, 0.02 mol%) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 6 h. The system was cooled to room temperature and HCl was added till the pH was 1-2. The acidified aqueous layer was extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent was removed by rotovap and the white solid product was collected. Yield - 3.25 g (90%).

Synthesis of 4,4'-^{t}Bu$_2$-biphenyl: 4-t-butylchlorobenzene(1.0 g, 0.0059 mol, 2 eq) and NaOH (0.951 g, 0.0236 mol, 4 eq) were added to a round bottom flask with DI H_20, the flask placed in an oil bath until temperature is 100 °C, and the solution stirred until the base was completely dissolved. 2.1 mL PANI/Pd (4.2×10^{-6} mol, 0.07 mol%) was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react for 2.5 h. The aqueous layer was extracted with ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent was removed by rotovap and the white solid product collected. Yield - 1.50 g (90%).

3,5-Dimethylphenol. Using the general procedure, 5-bromo-m-xylene (136 mg, 1.0 mmol), 4.0 mL PANI/Pd (8×10^{-6} mol, 0.8 mol% Pd), KOH (270 mg, 5.0 mmol) in 1,4-dioxane (0.5 mL) and deionized water (0.5 mL) were allowed to react at 100 °C for 12 h. The crude material was purified by recrystallization in hexanes to give the title compound as a white solid (114 mg, 90%).

2,6-Dimethylphenol. Using the general procedure, 2-bromo-m-xylene (136 mg, 1.0 mmol), 4.0 mL PANI/Pd (8×10^{-6} mol, 0.8 mol% Pd), KOH (270 mg, 5.0 mmol) in 1,4-dioxane (0.5 mL) and deionized water (0.5 mL) were allowed to react at 100 °C for 12 h. The crude material was purified by recrystallization in hexanes to give the title compound as a white solid (110 mg, 89%).

2-methylphenol: Using the general procedure, 2-chlorotoluene (136 mg, 1.079 mmol), 4.0 mL PANI/Pd (8×10^{-6} mol, 0.75 mol% Pd), and KOH (270 mg, 5.0 mmol) in 1,4-dioxane (0.5 mL) and deionized water (0.5 mL) were allowed to react at 100 °C for 8 h. The crude material was purified by recrystallization from hexanes to give the title compound as a white solid (105 mg, 90%).

2-Cyanophenol. Using the general procedure, 2-bromobenzonitrile (90 mg, 0.50 mmol), 3.0 mL PANI/Pd (6×10^{-6} mol, 1.2 mol% Pd), KOH (270 mg, 5.0 mmol) in 1,4-dioxane (0.5 mL) and water (0.5 mL) were allowed to react at 100 °C for 8 h. The crude material was purified by recrystallization to give the title compound as a light yellow solid (47 mg, 80%).

Recycling Procedure: The catalyst was removed from the separatory funnel and placed into a round bottom flask. The aqueous layer was collected and heated in a 50 °C oil bath to remove residual ether. After the ether was removed, the aqueous layer was loaded into a 100 mL round bottom flask and stirred for 10 min at high speed to ensure adequate mixing. Aryl halide (4-acetylphenylchloride, 4×10^{-4} mol, 1.0 eq) and phenylboronic acid (4×10^{-4} mol, 1.0 eq) were added to the catalyst solution (0.05 mol% for the first cycle) and allowed to mix for 10 min. Finally, base (NaOH, 4 eq) was added to the solution and the system capped and allowed to proceed. Yield of cycle 1 - 99%; yield of cycle 2 - 98%; yield of

cycle 3 - 97%; yield of cycle 4 - 97%; yield of cycle 5 - 96%; yield of cycle 6 - 95%; yield of cycle 7 - 95%; yield of cycle 8 - 93%; yield of cycle 9 - 93%; yield of cycle 10 - 89%.

Palladium Concentrations in filtrate

	Hot Filtered (M)	**Cold Filtered (M)**
Original Catalyst	-	7.4 E-05
Filtrate after 1st Cycle	7.9 E-06	1.1 E-05
Filtrate after 2nd Cycle	6.3 E-06	6.8 E-06

Palladium in Product

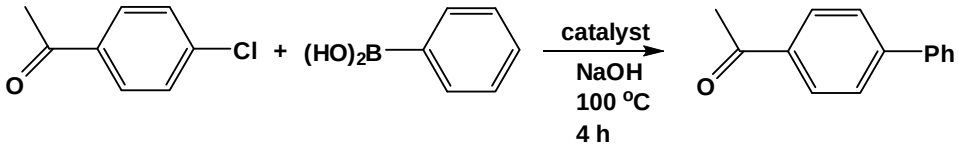
Sample	**State**	**Palladium in Product**
3,5-diphenyl-benzene	Solid	5.91 E-03 % by weight
4-phenyl-phenol	Solid	4.58 E-04 % by weight
4-phenyl-benzaldehyde	Solid	1.62 E-03 % by weight
4-Acetyl-biphenyl	Solid	4.86 E-02 % by weight
2-phenyl-benzaldehyde	Liquid	5.54 E-05 M

Catalyst loading experiments: Each experiment used the following procedure: 4-chloroacetophenone (0.500 g, 3.23 mmol, 1.0 eq), phenylboronic acid (0.394 g, 3.23 mmol, 1.0 eq), and NaOH (0.517g, 12.94 mmol, 4 eq) were added to DI H_20 and the flask stirred in an oil bath until the temperature was 80 °C and the base was completely dissolved. A stock solution of PANI/Pd was added by syringe to the stirring solution and the system was capped with a glass septum and allowed to react. Progress of the reaction was monitored at 30 min intervals by TLC analysis (0.1 mL of solution was removed by syringe, extracted with 1 mL of diethyl ether and analyzed on a TLC plate using hexanes as the eluting solvent). When all starting material was consumed, the system was cooled to room temperature and extracted with diethyl ether (3 x 100 mL). The organic extracts were washed with DI H_20 (3 x 75 mL) and dried with $MgSO_4$. Solvent was removed by rotovap and the resulting product was collected.

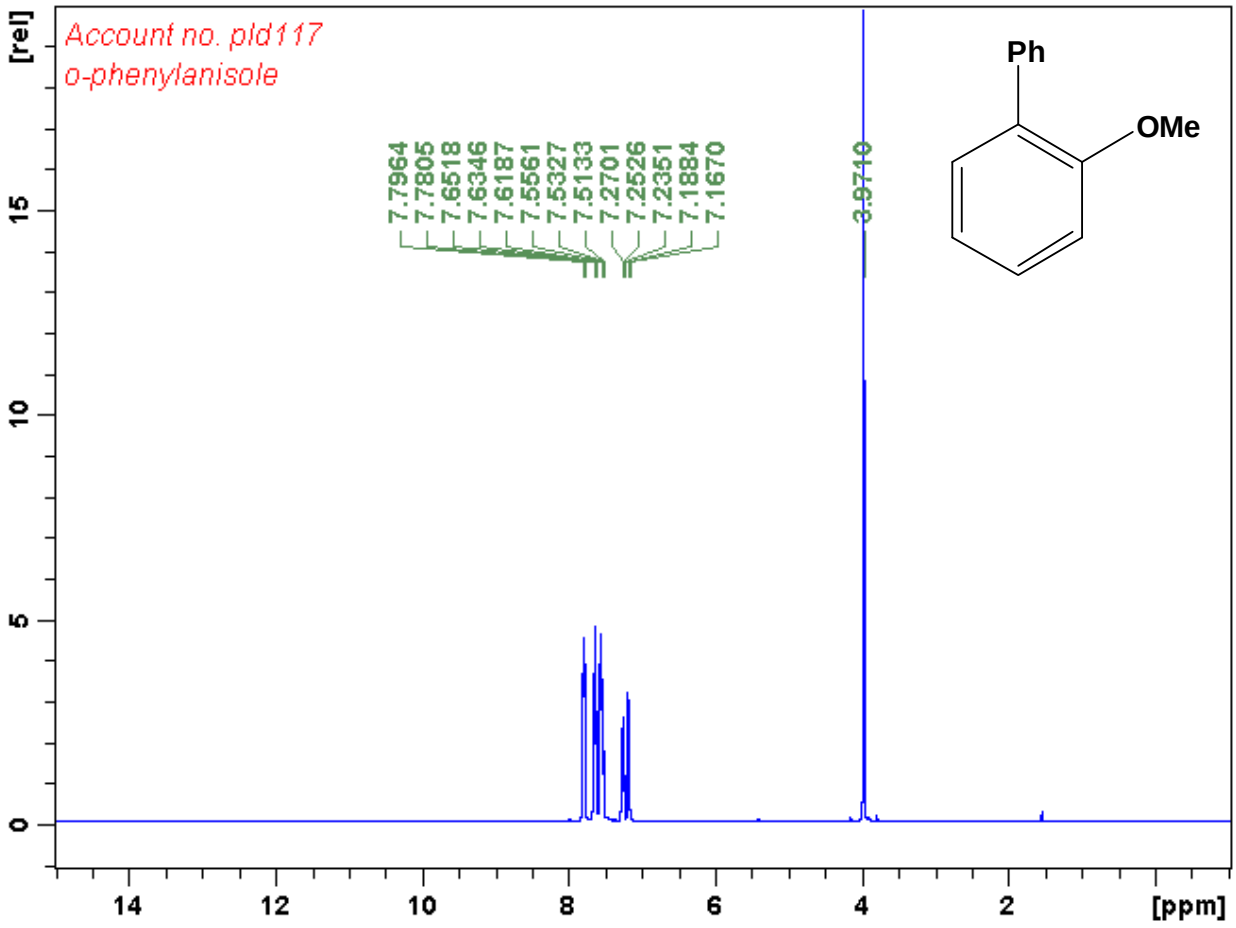
Catalyst loading (mol%)	Yield (%)	Reaction time (h)
0.1	99	4
0.05	99	4
0.01	98	4
0.001	92	12
0.0001	89	16
0.00001	88	24

Tandem reaction. Synthesis of 2-phenylphenol. 1,2-dichlorobenzene (1 g, 6.80 mmol, 1 eq), phenylboronic acid (0.83 g, 6.80 mmol, 1 eq), and NaOH (1.088 g, 27.20 mmol, 4 eq) were added to a 100 mL round bottom flask with 15 mL of deionized H_2O. The flask was then placed in a 100 °C oil bath and the solution stirred until the temperature returned to 100 °C. 1.5 mL PANI/Pd (3 x 10^{-6} mol Pd, 0.05 mol% vs halide) was syringed into the flask, the system was capped with a rubber septum and needle and allowed to react for 6 h. After 6 h, a solution of KOH (1.836 g 0.034 mol, 5 eq) in 5 mL deionized H_2O / 20 mL 1,4-dioxane was syringed into the system and the reaction was allowed to proceed for another 6 h. The system was removed from the oil bath, cooled to room temperature, and conc. HCl was added until the pH was approx 1. The aqueous layer was extracted with diethyl ether (3 x 150 mL). The organic extracts were washed with 20 mL of deionized H_2O, dried with $MgSO_4$, and the solvent removed under pressure. The crude product was recrystallized from hexanes/ether. Yield was 0.810 g (70%).

Comparison with other catalysts



catalyst	yield (%)
$Pd(OAc)_2$	0
$Pd(NO_3)_2$	0
5% Pd/C	homocoupling
$Pd(OAc)_2$ / PPh_3	homocoupling
$Pd(NO_3)_2$ / $PhNH_2$	0
$Pd(NO_3)_2$ / PANI	0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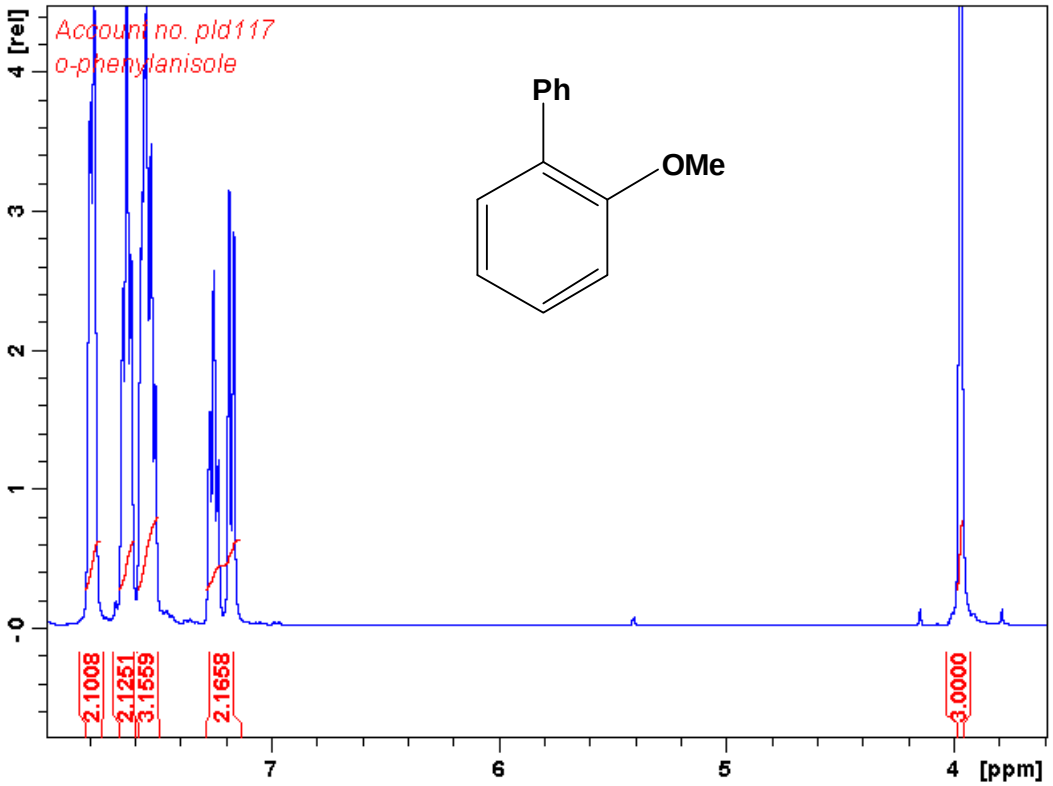
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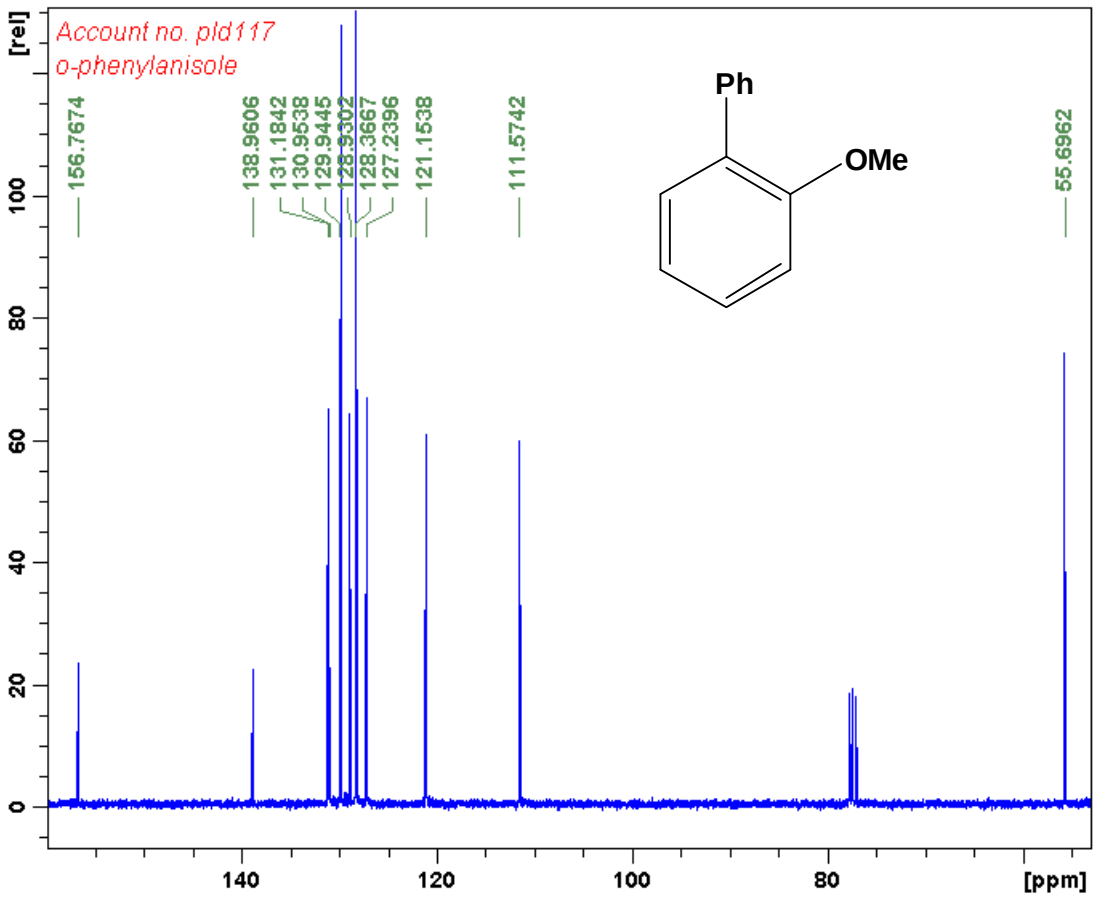


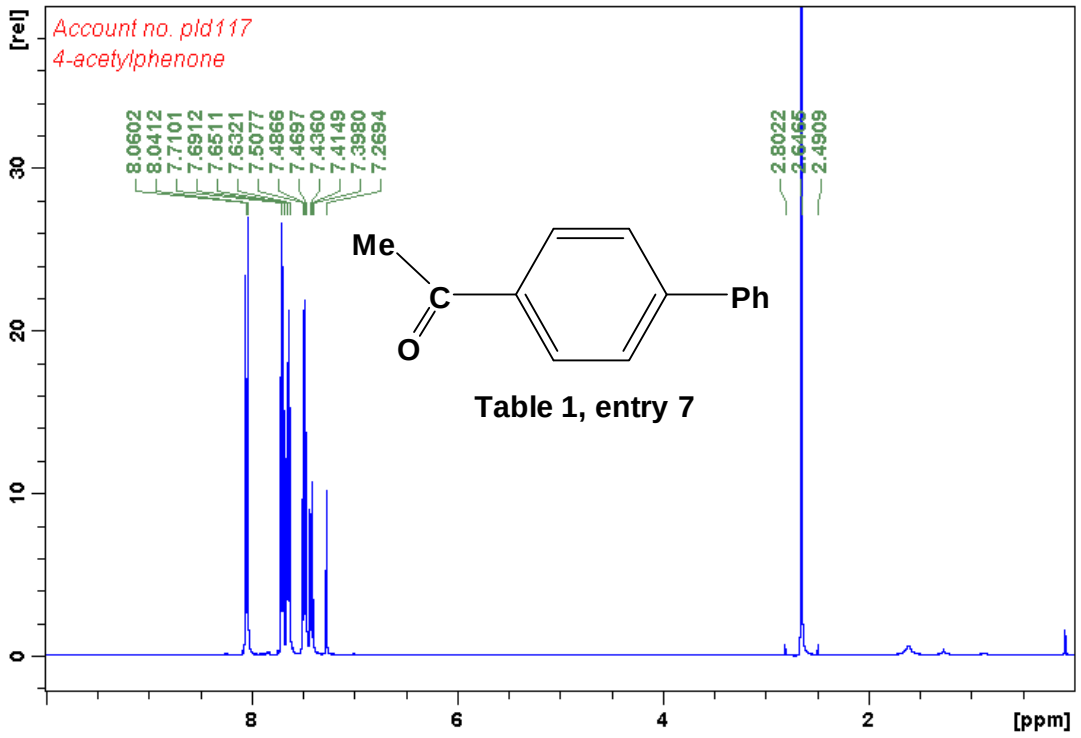
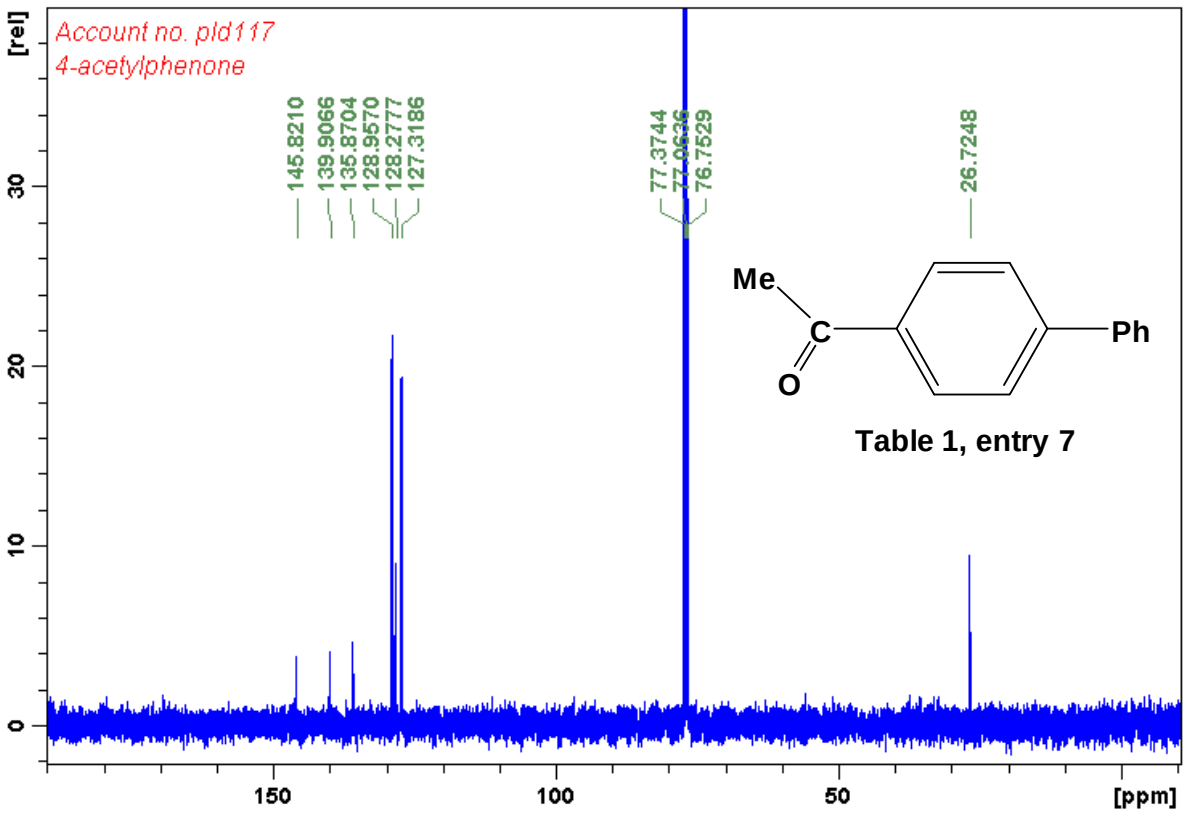


Table 1, entry 7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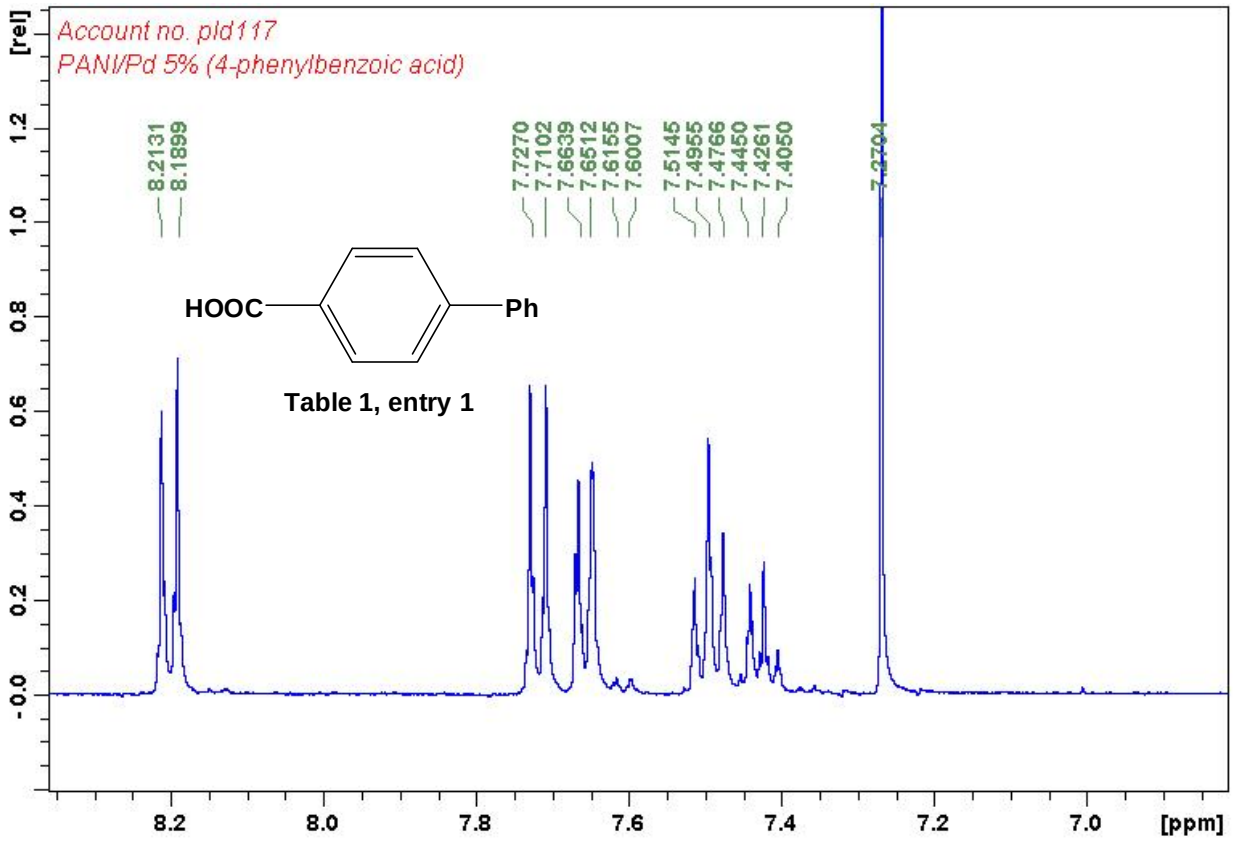
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PANI/Pd 5% (4-phenylbenzoic acid)
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Ph
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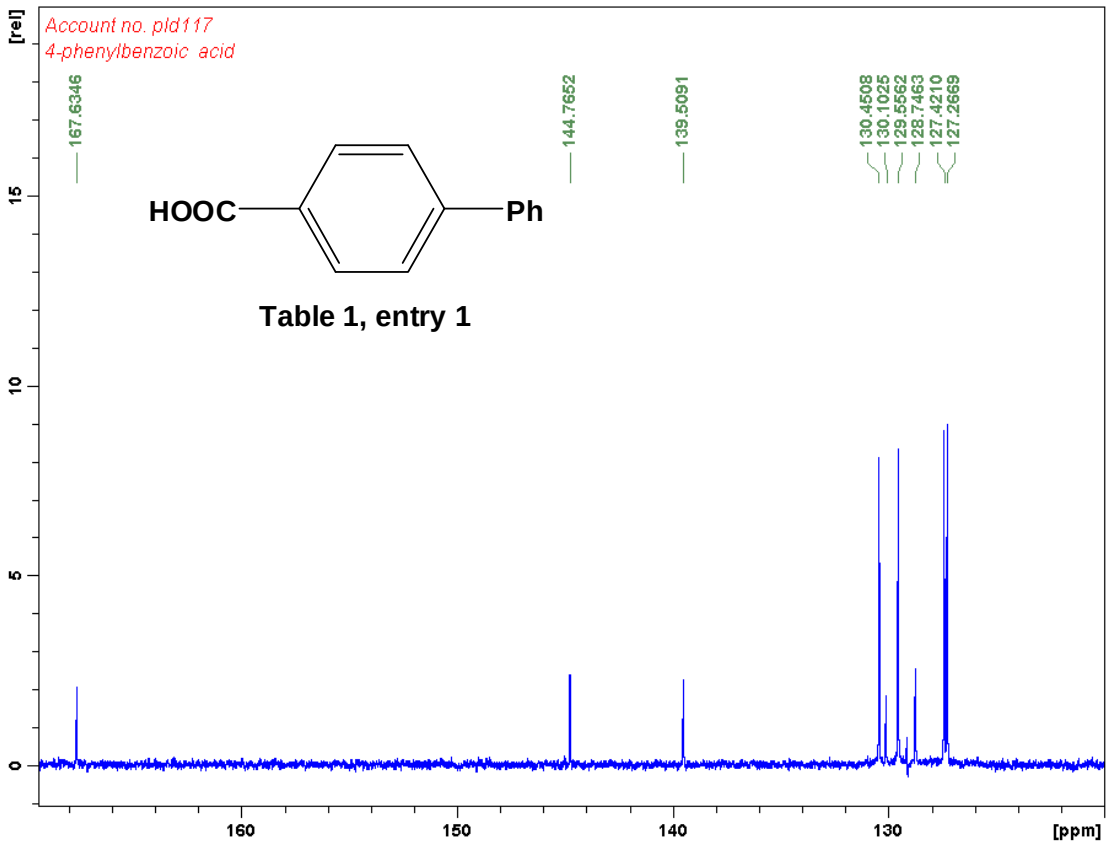
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Ph
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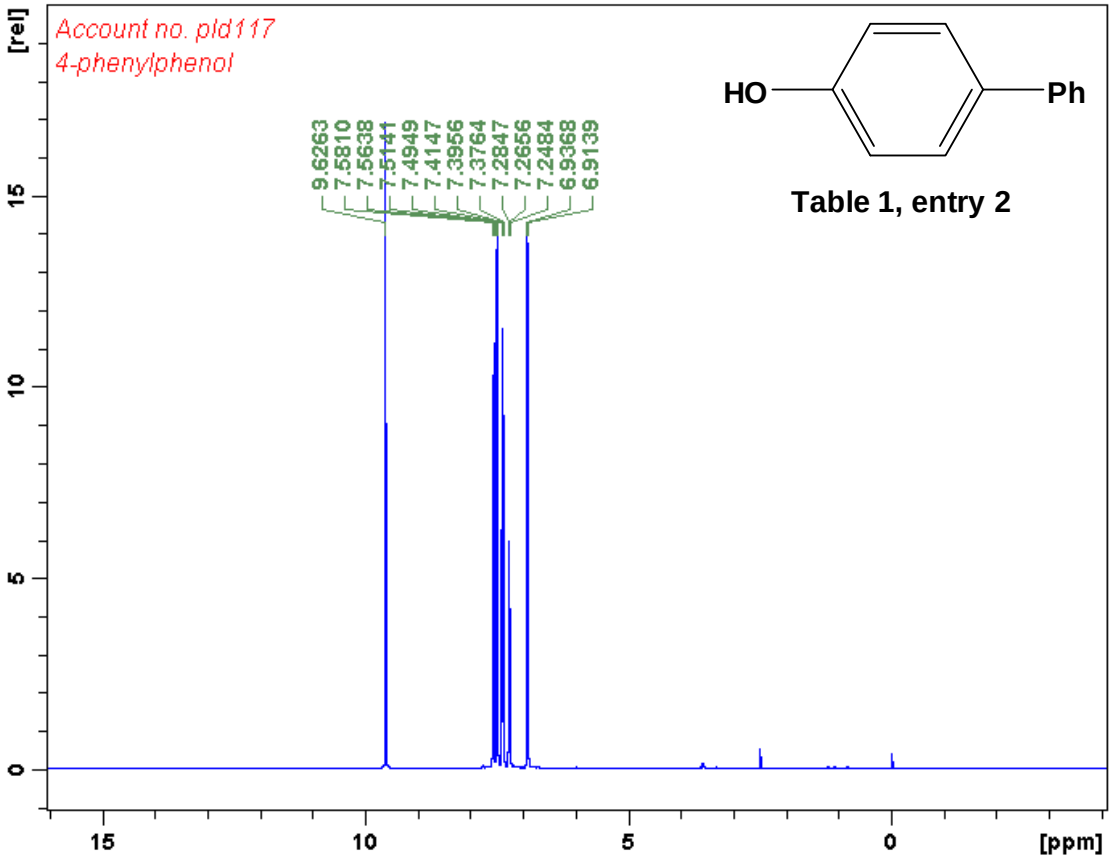
Account no. pld117
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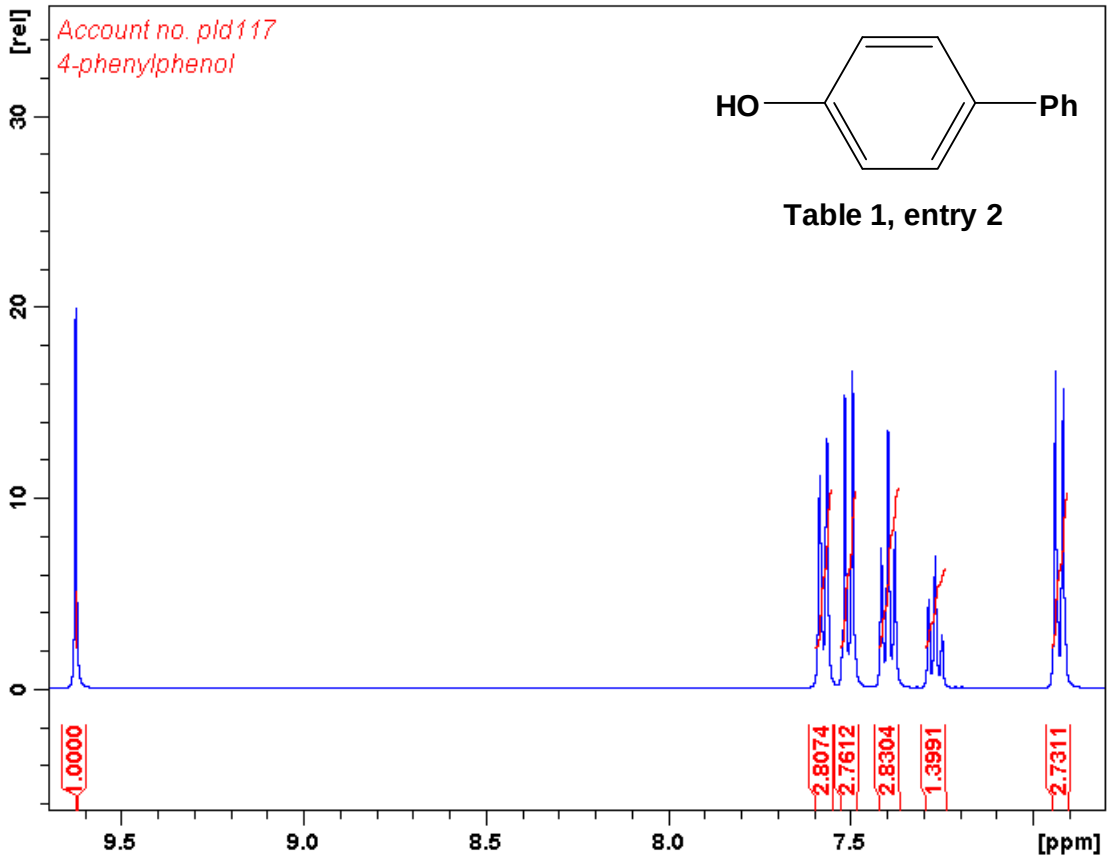
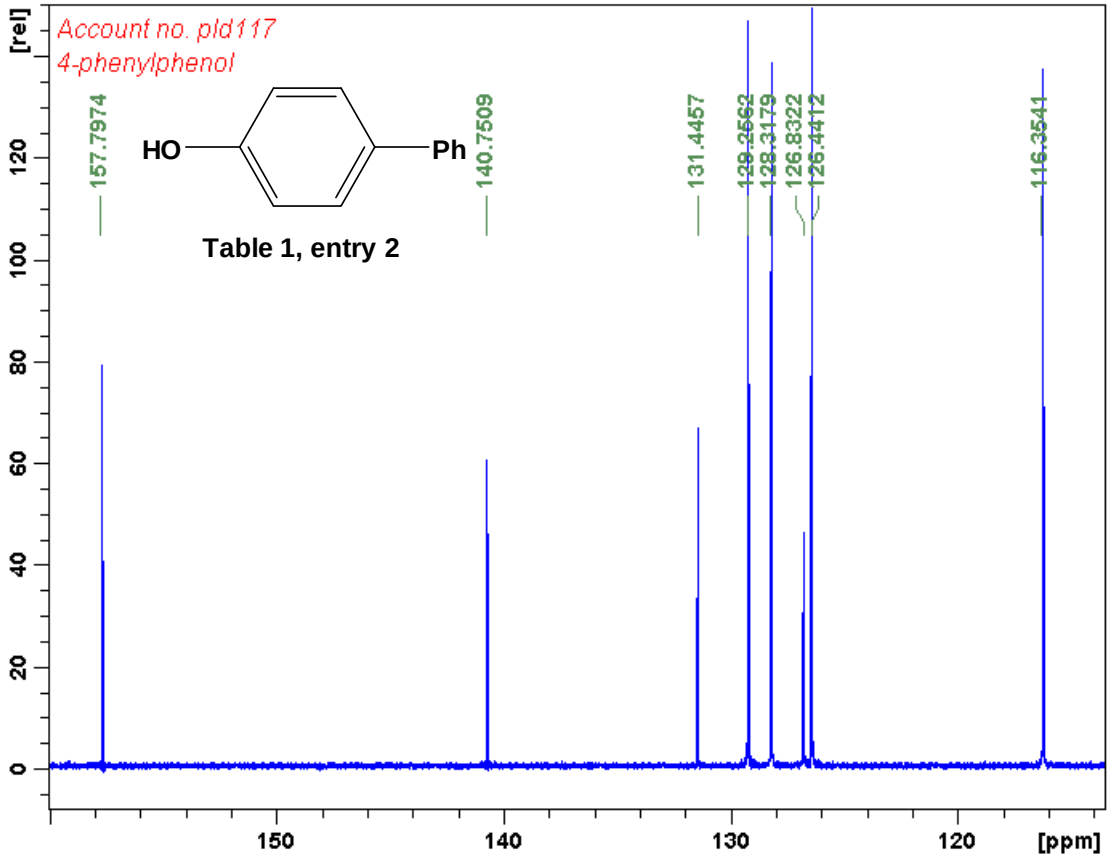
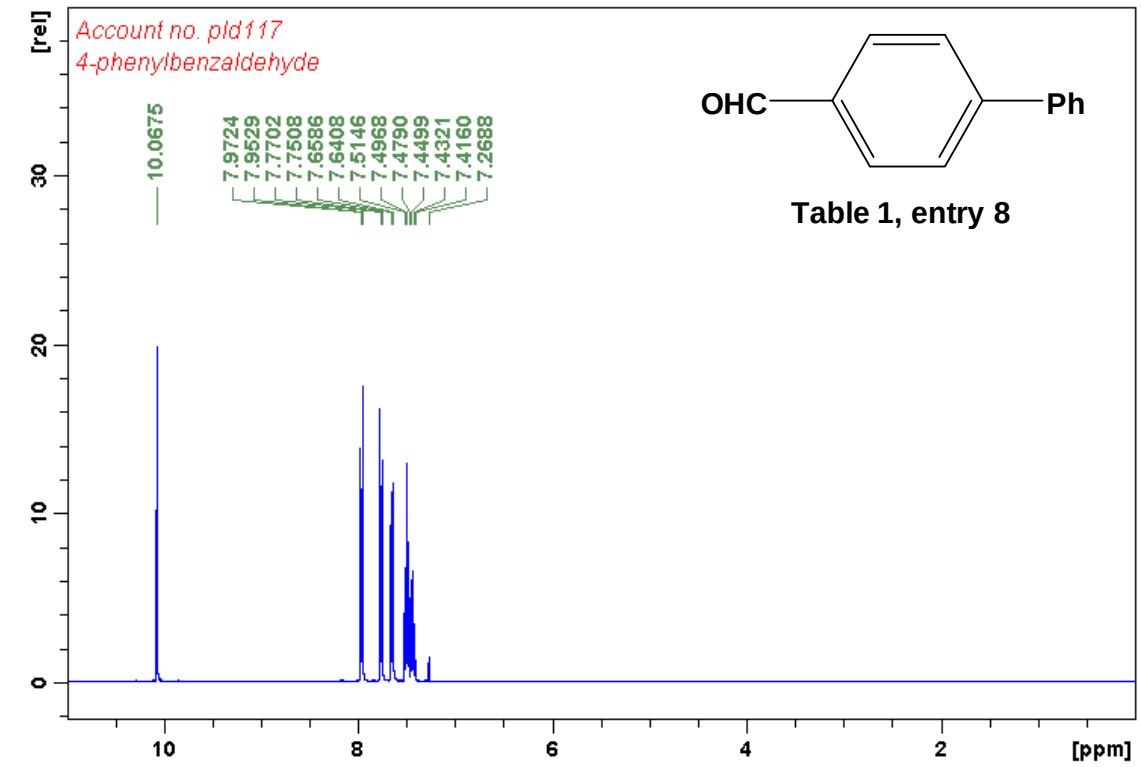
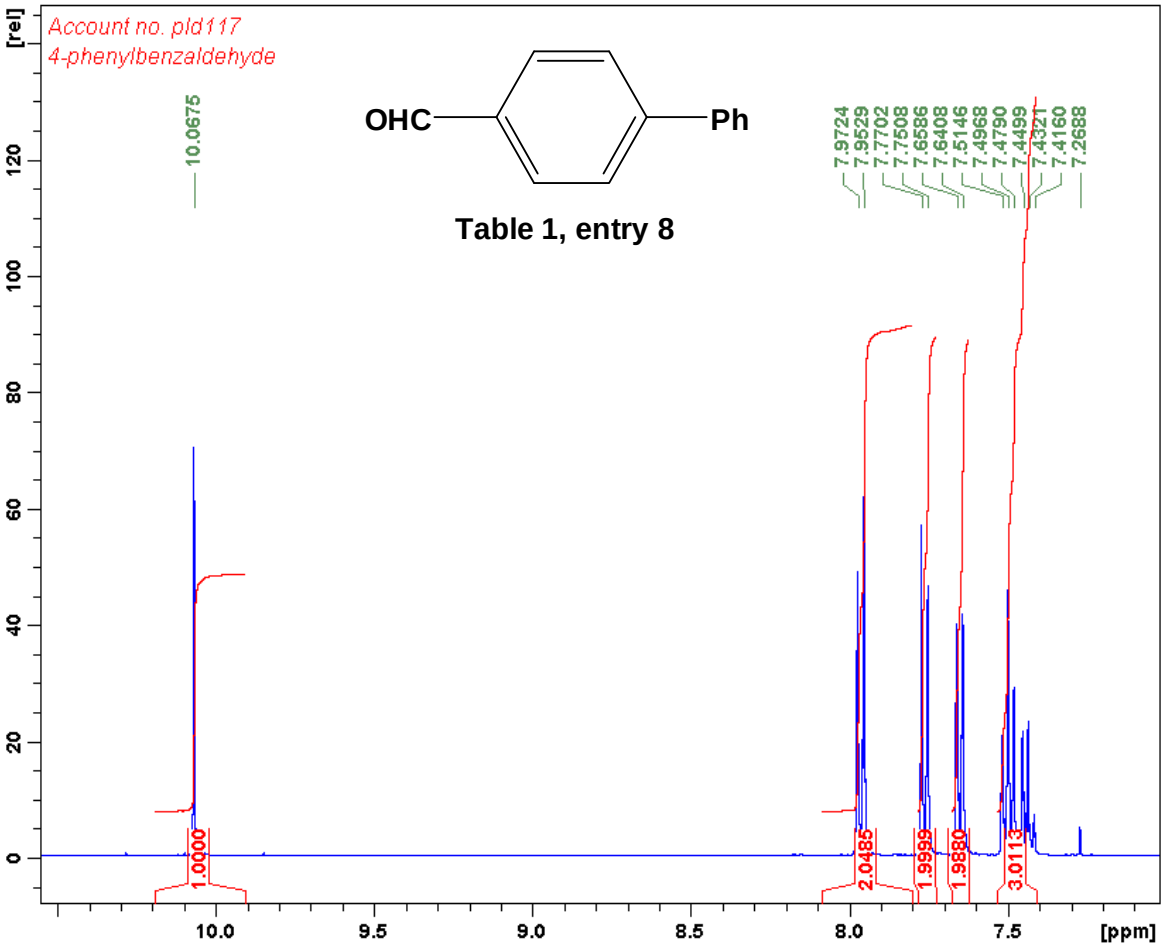
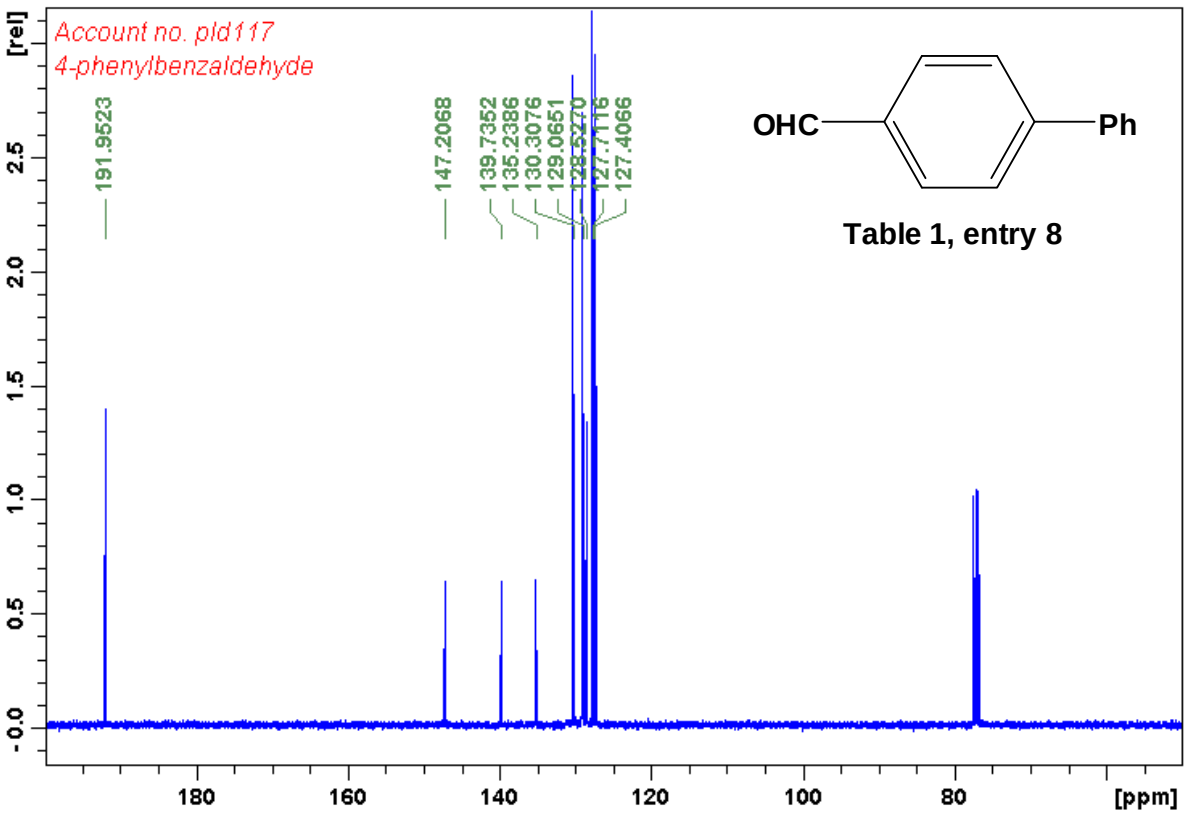
6.9139
HO
Ph
Table 1, entry 2
[rel]
[ppm]

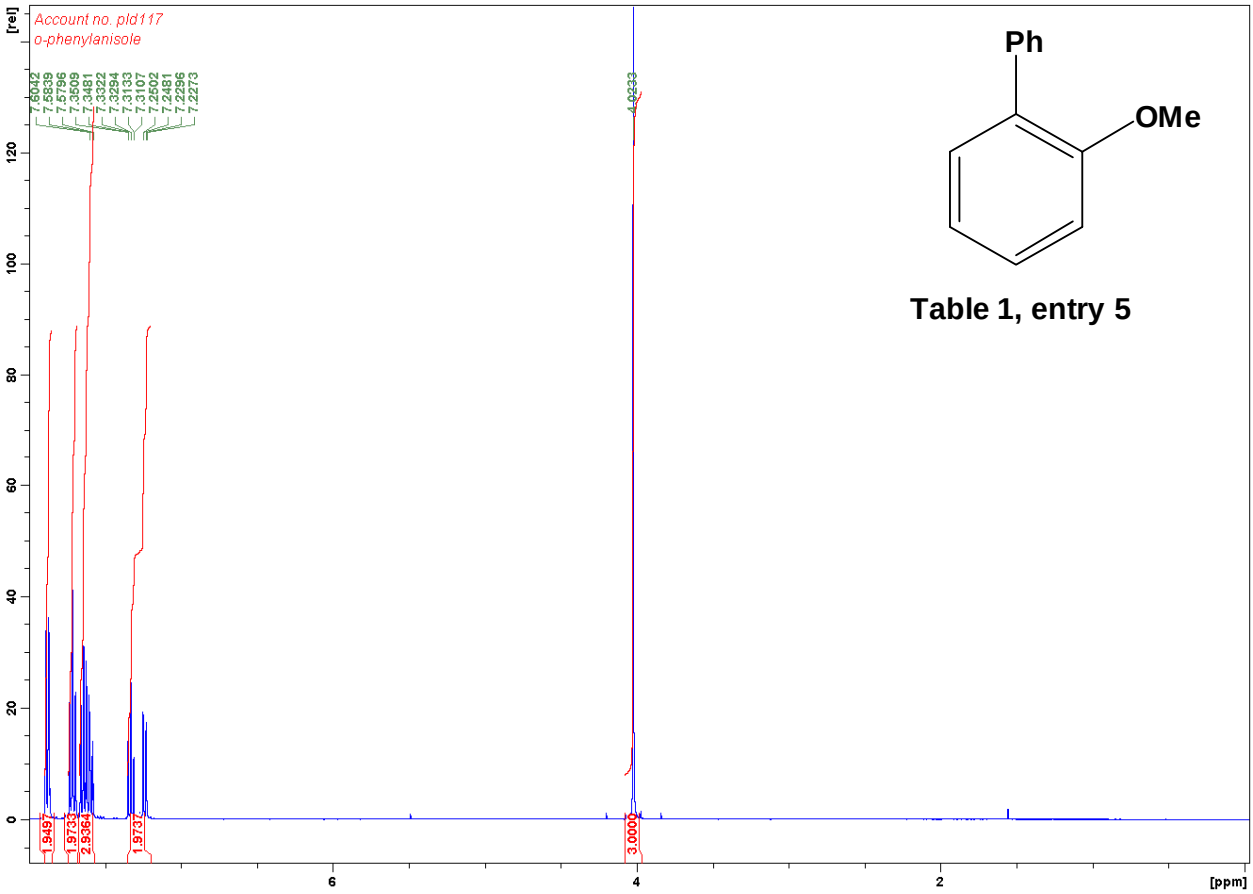

Account no. pld117
4-phenylphenol
HO
Ph
Table 1, entry 2
[rel]
30
20
10
0
1.0000
2.8074
2.7612
2.8304
1.3991
2.7311
9.5
9.0
8.5
8.0
7.5
[ppm]

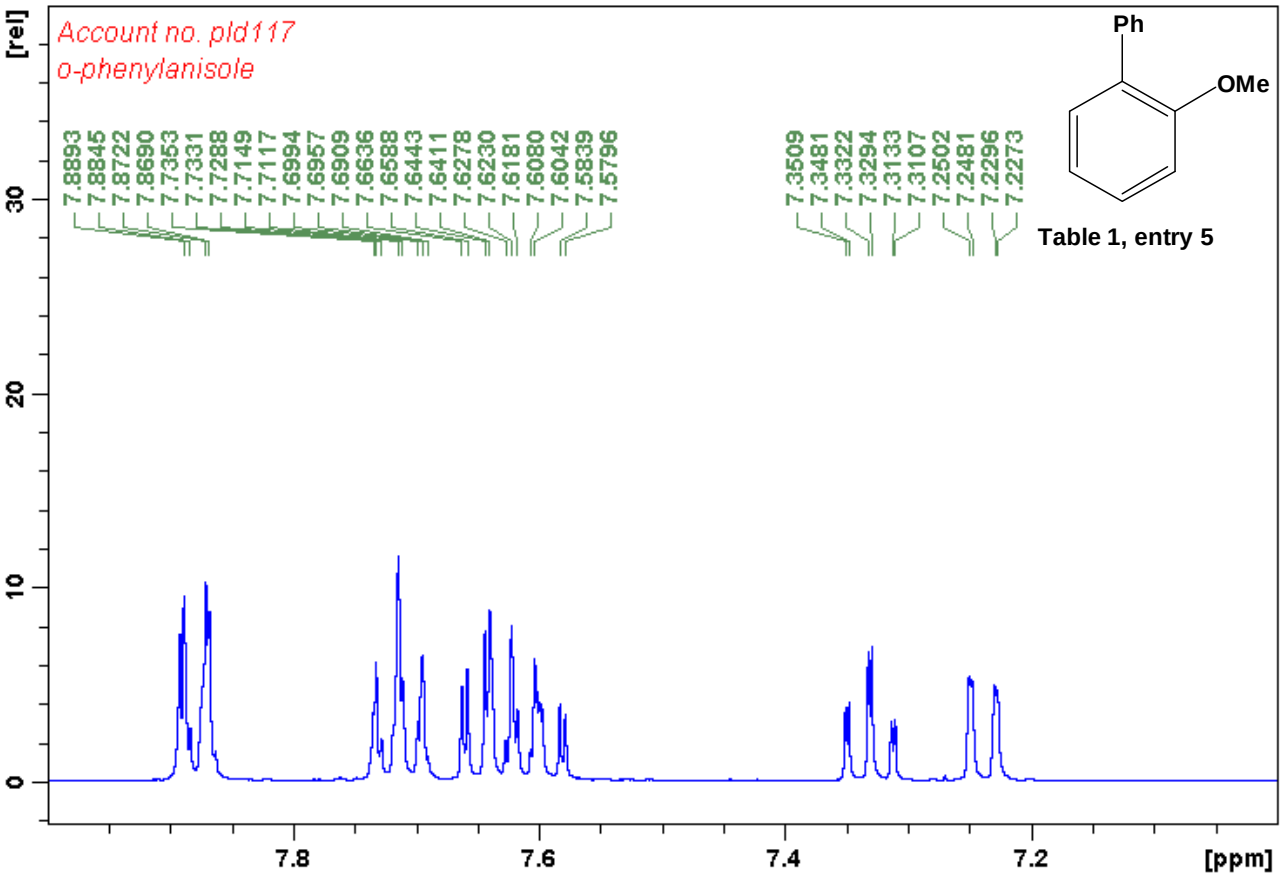

Account no. pld117
4-phenylphenol
157.7974
HO
Ph
140.7509
131.4457
129.2562
128.3179
126.8322
126.4412
116.3541
Table 1, entry 2
[rel]
120
100
80
60
40
20
0
150
140
130
120
[ppm]

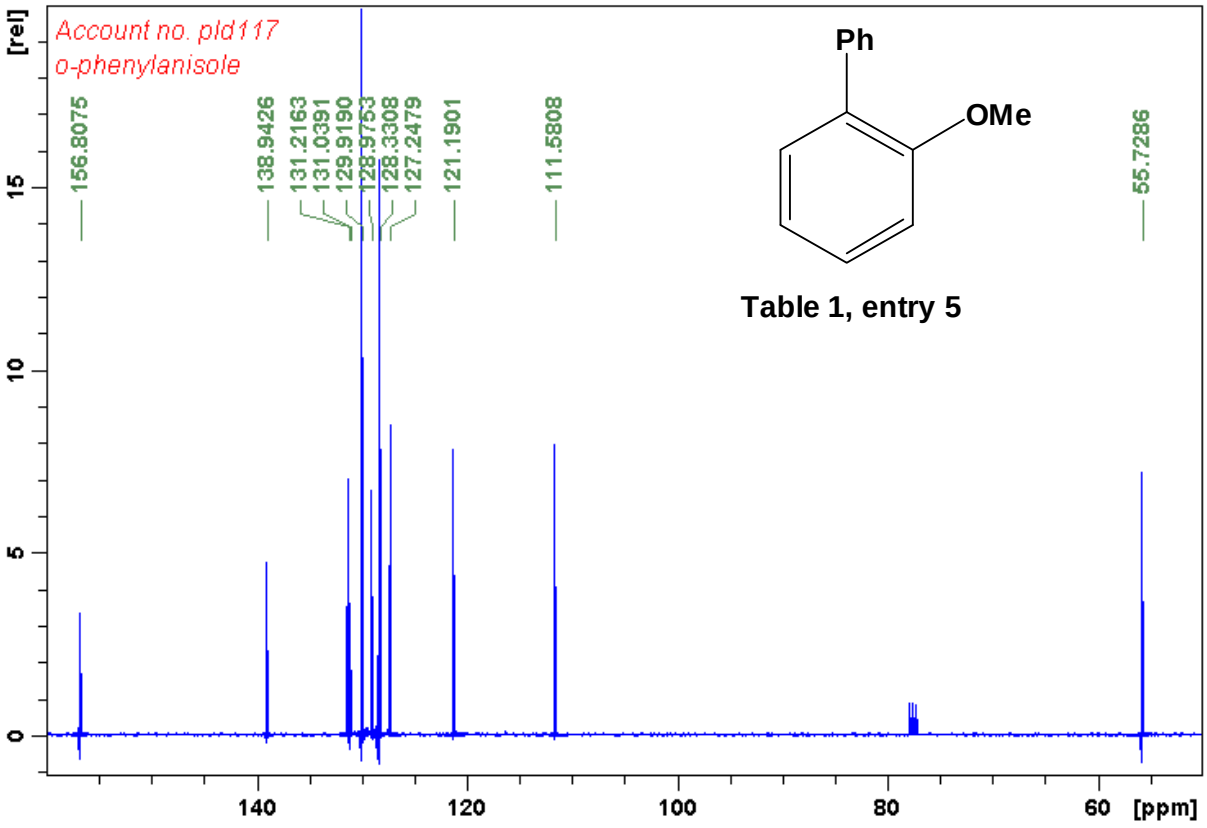

Account no. pld117
4-phenylbenzaldehyde
OHC
Ph
Table 1, entry 8
10.0675
7.9724
7.9529
7.7702
7.7508
7.6586
7.6408
7.5146
7.4968
7.4790
7.4499
7.4321
7.4160
7.2688
[rel]
[ppm]

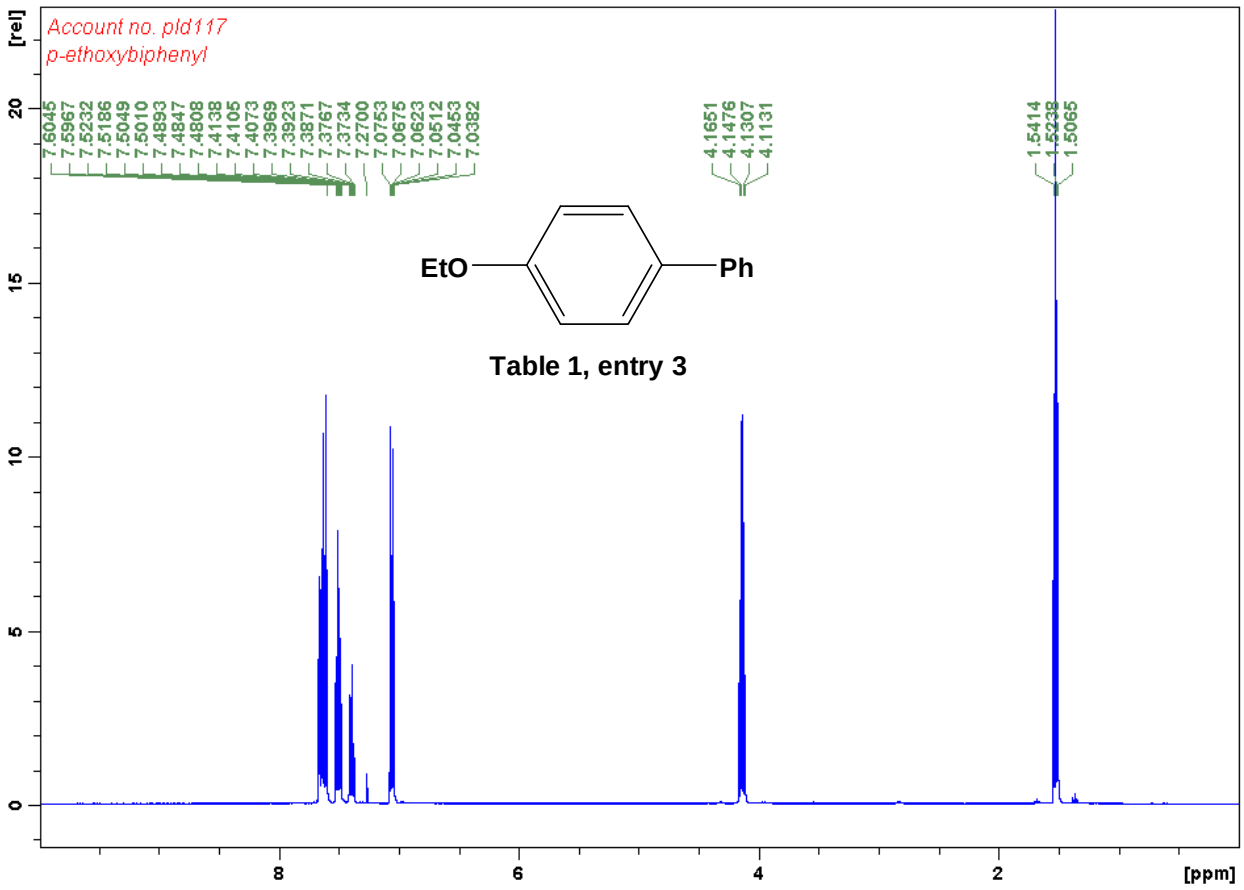

Account no. pld117
4-phenylbenzaldehyde
OHC
Ph
Table 1, entry 8
10.0675
7.9724
7.9529
7.7702
7.7508
7.6586
7.6408
7.5146
7.4968
7.4790
7.4499
7.4321
7.4160
7.2688
1.0000
2.0485
1.9999
1.9880
3.0113
[rel]
[ppm]

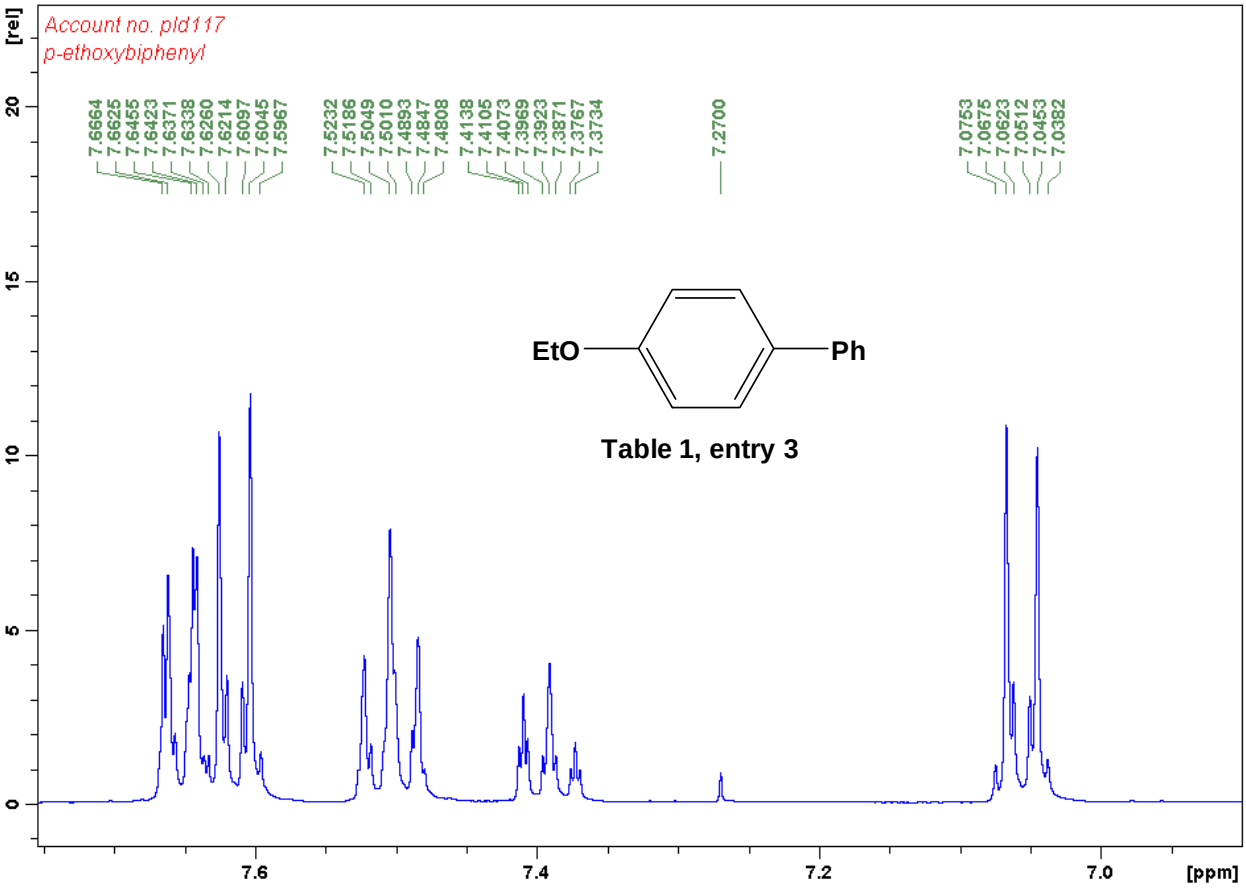

Account no. pld117
4-phenylbenzaldehyde
191.9523
147.2068
139.7352
135.2386
130.3076
129.0651
128.3270
127.7116
127.4066
OHC
Ph
Table 1, entry 8
[rel]
[ppm]


Account no. pld117
o-phenylanisole
Ph
OMe
Table 1, entry 5
[rel]
[ppm]


Account no. pld117
o-phenylanisole
[rel]
30
20
10
0
7.8893
7.8845
7.8722
7.8690
7.7353
7.7331
7.7288
7.7149
7.7117
7.6994
7.6957
7.6909
7.6636
7.6588
7.6443
7.6411
7.6278
7.6230
7.6181
7.6080
7.6042
7.5839
7.5796
7.3509
7.3481
7.3322
7.3294
7.3133
7.3107
7.2502
7.2481
7.2296
7.2273
7.8
7.6
7.4
7.2
[ppm]
Ph
OMe
Table 1, entry 5


Account no. pld117
o-phenylanisole
[rel]
15
10
5
0
156.8075
138.9426
131.2163
131.0391
129.9190
128.9753
128.3308
127.2479
121.1901
111.5808
55.7286
140
120
100
80
60
[ppm]
Ph
OMe
Table 1, entry 5


Account no. pld117
p-ethoxybiphenyl
[rel]
7.6045
7.5967
7.5232
7.5186
7.5049
7.5010
7.4893
7.4847
7.4808
7.4138
7.4105
7.4073
7.3969
7.3923
7.3871
7.3767
7.3734
7.2700
7.0753
7.0675
7.0623
7.0512
7.0453
7.0382
4.1651
4.1476
4.1307
4.1131
1.5414
1.5238
1.5065
EtO
Ph
Table 1, entry 3
[ppm]


Account no. pld117
p-ethoxybiphenyl
[rel]
7.6664
7.6625
7.6455
7.6423
7.6371
7.6338
7.6260
7.6214
7.6097
7.6045
7.5967
7.5232
7.5186
7.5049
7.5010
7.4893
7.4847
7.4808
7.4138
7.4105
7.4073
7.3969
7.3923
7.3871
7.3767
7.3734
7.2700
7.0753
7.0675
7.0623
7.0512
7.0453
7.0382
EtO
Ph
Table 1, entry 3
[ppm]

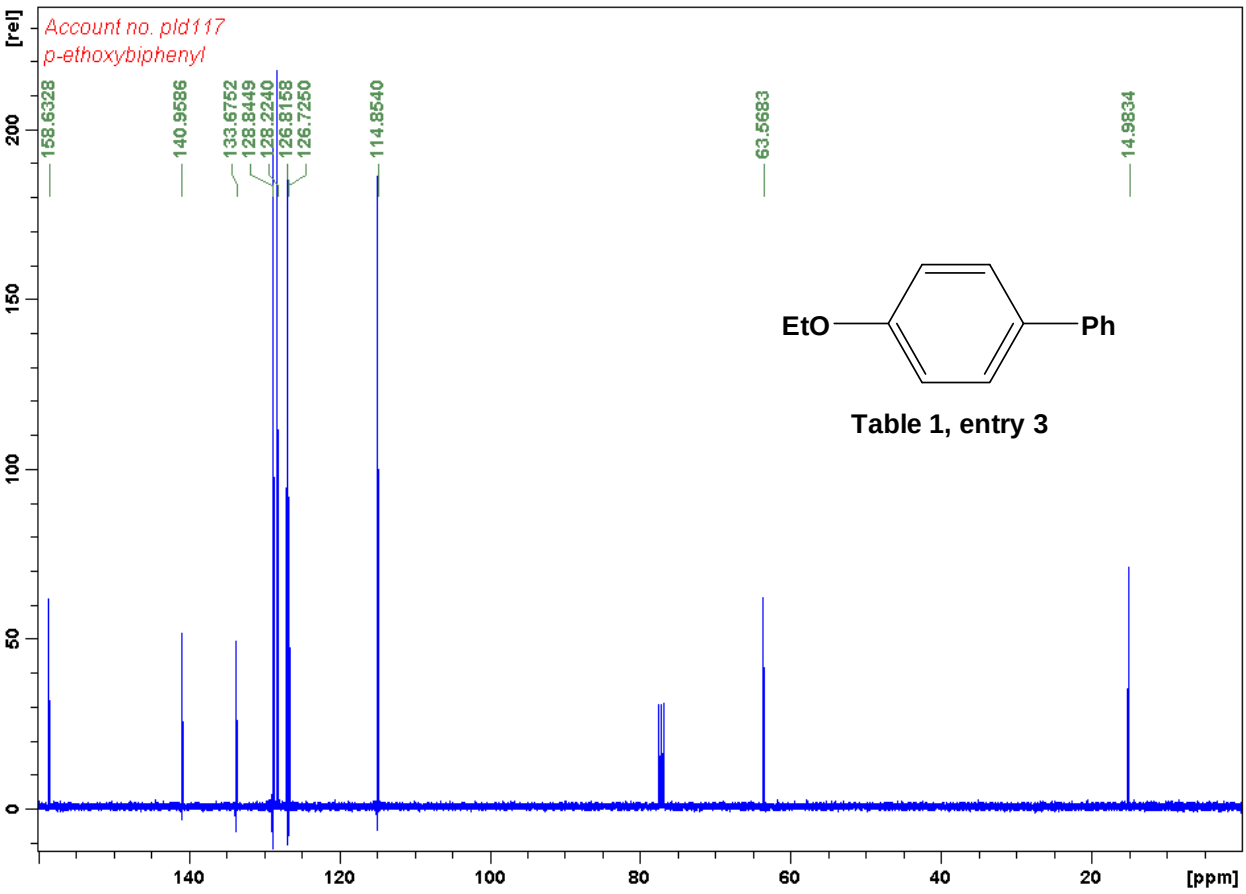


Table 1, entry 3

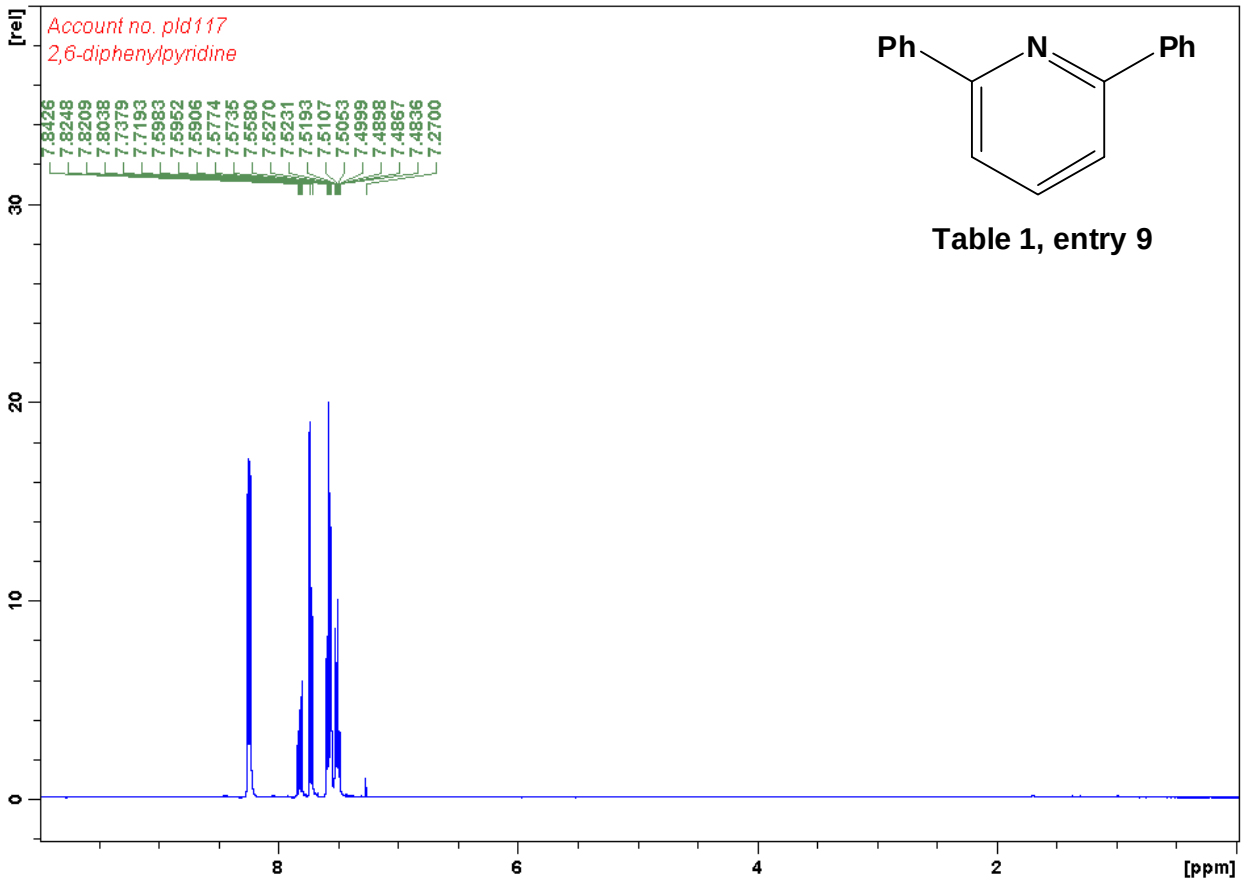
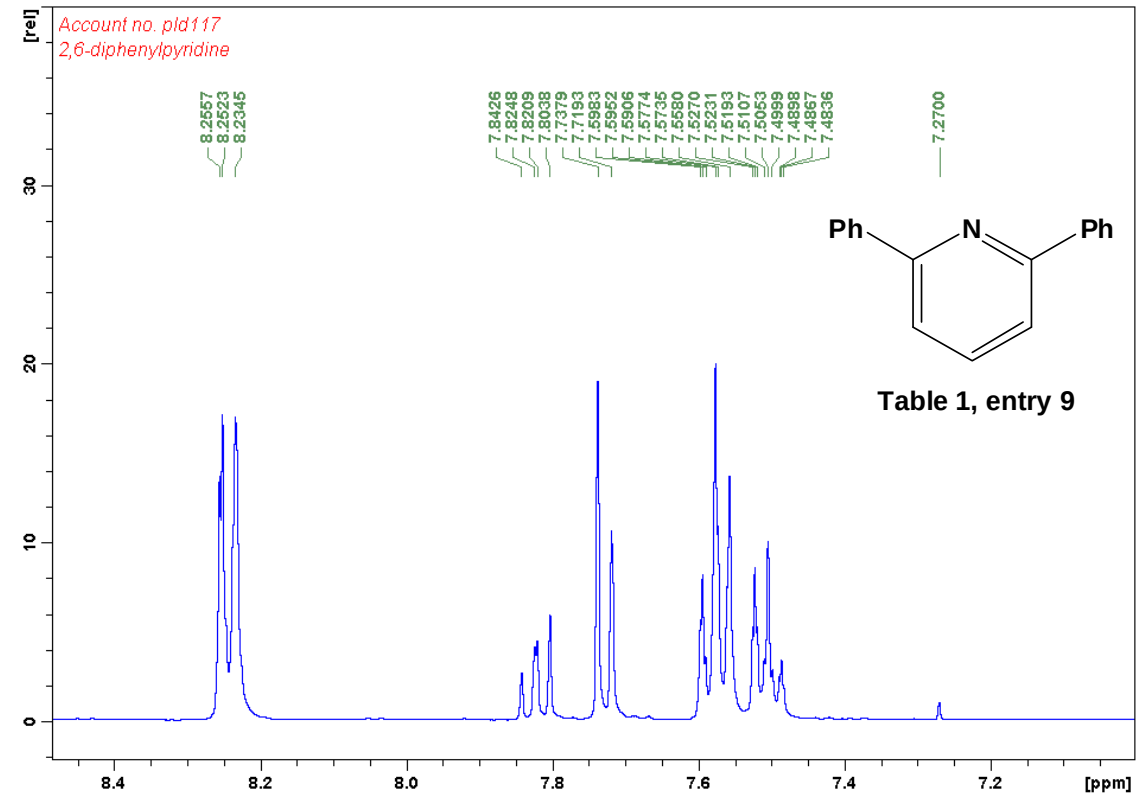
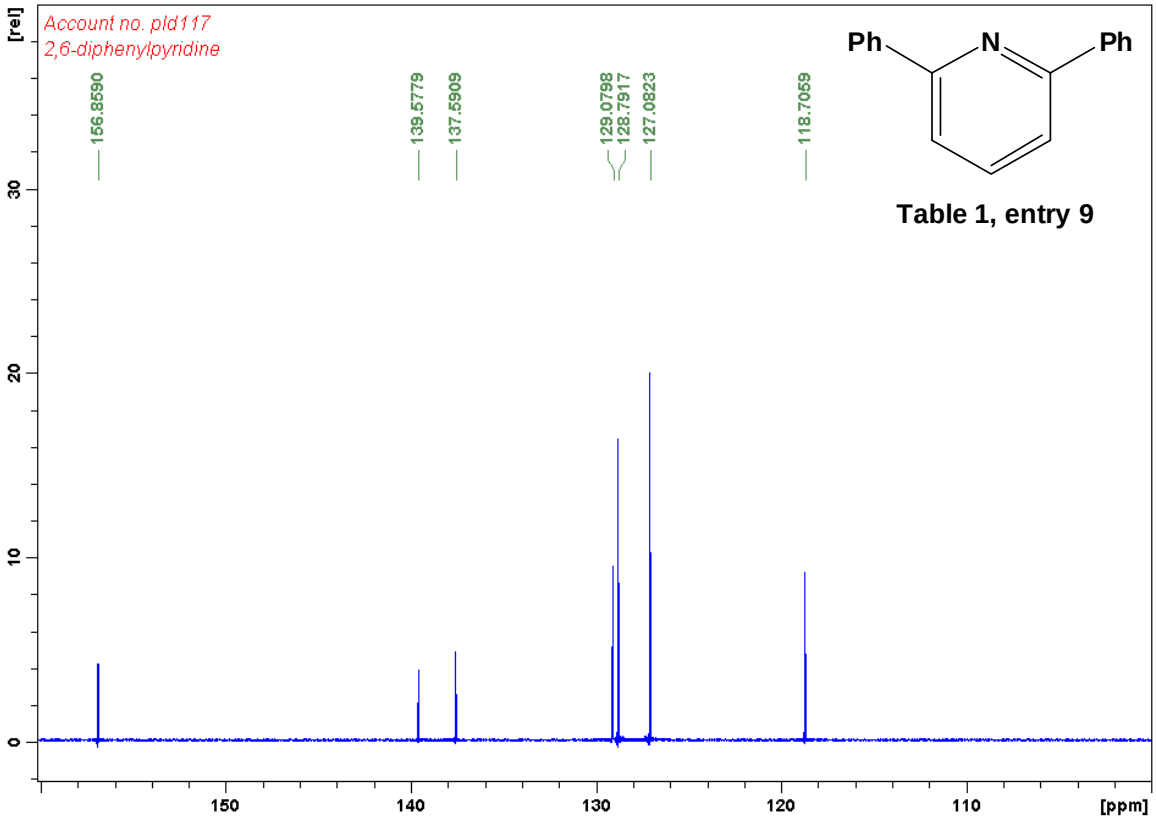
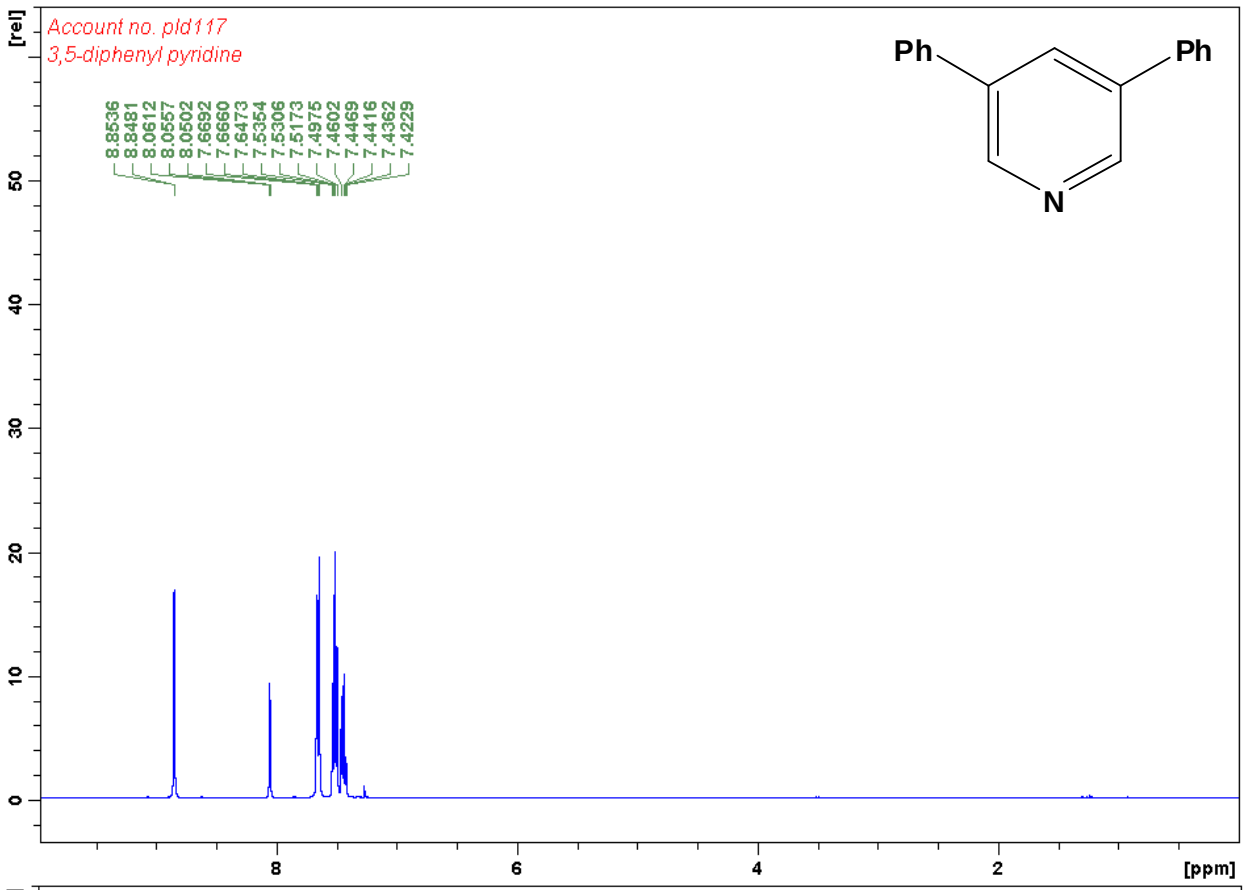
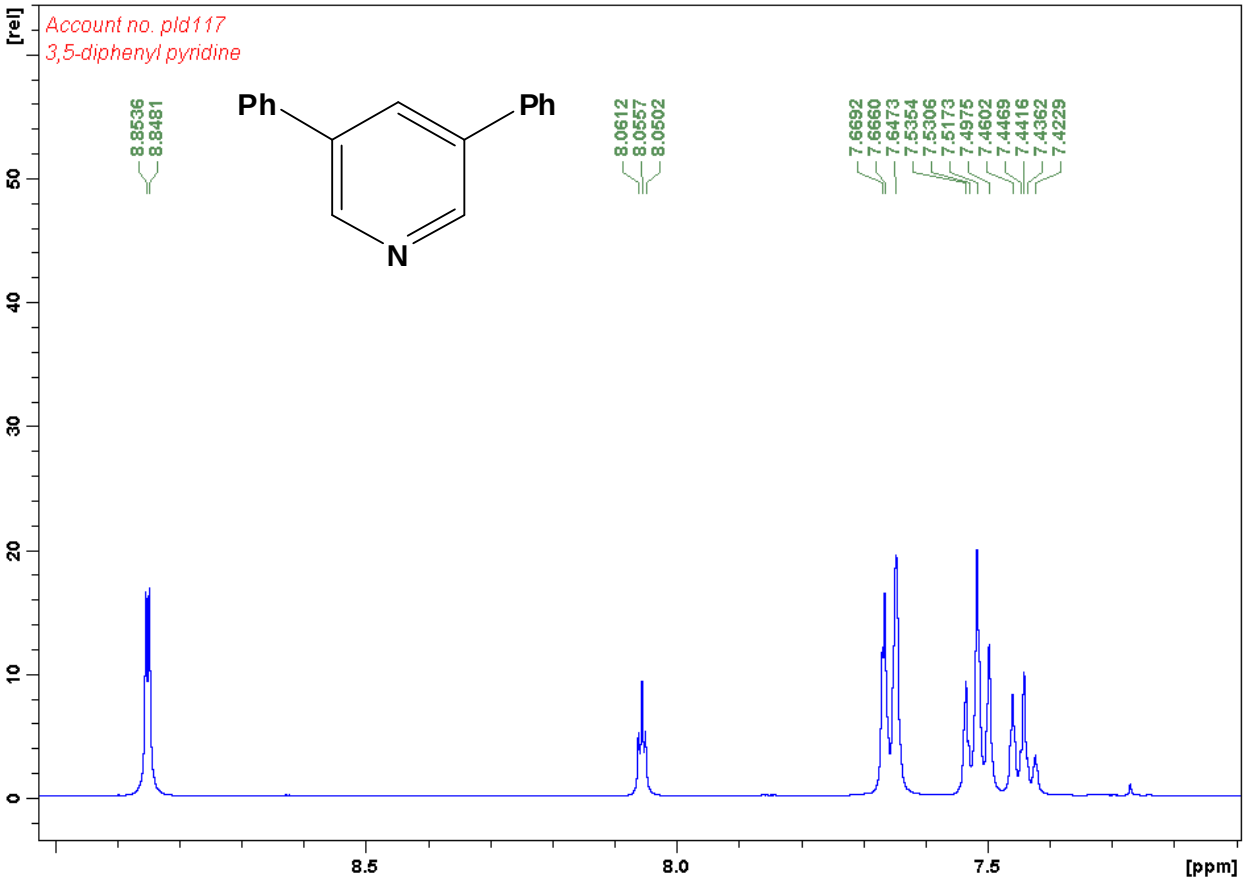


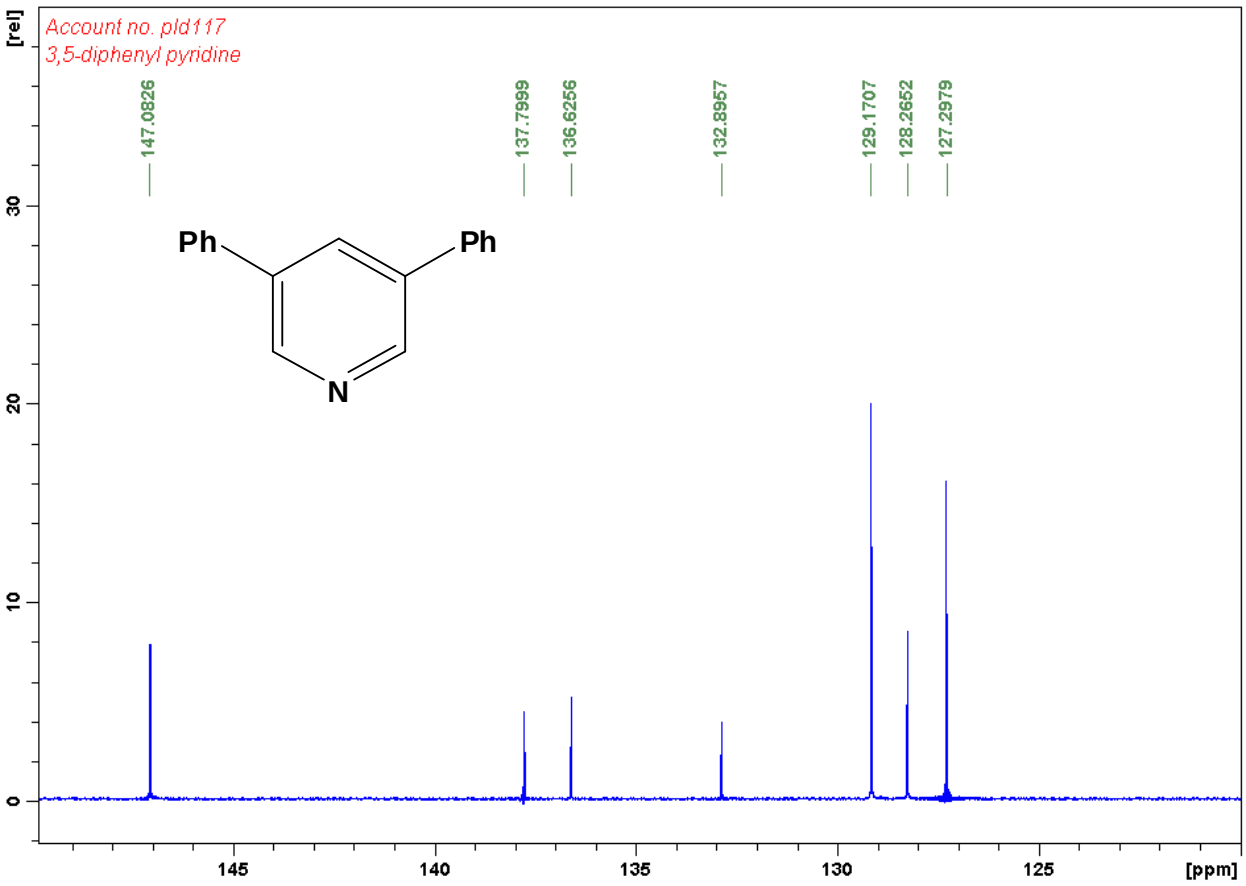
Table 1, entry 9


Account no. pld117
2,6-diphenylpyridine
8.2557
8.2523
8.2345
7.8426
7.8248
7.8209
7.8038
7.7379
7.7193
7.5983
7.5952
7.5906
7.5774
7.5735
7.5580
7.5270
7.5231
7.5193
7.5107
7.5053
7.4999
7.4898
7.4867
7.4836
7.2700
Ph
N
Ph
Table 1, entry 9
[rel]
[ppm]


Account no. pld117
2,6-diphenylpyridine
156.8590
139.5779
137.5909
129.0798
128.7917
127.0823
118.7059
Ph
N
Ph
Table 1, entry 9
[rel]
[ppm]


Account no. pld117
3,5-diphenyl pyridine
8.8536
8.8481
8.0612
8.0557
8.0502
7.6692
7.6660
7.6473
7.5354
7.5306
7.5173
7.4975
7.4602
7.4469
7.4416
7.4362
7.4229
Ph
Ph
N
[rel]
[ppm]


Account no. pld117
3,5-diphenyl pyridine
8.8536
8.8481
8.0612
8.0557
8.0502
7.6692
7.6660
7.6473
7.5354
7.5306
7.5173
7.4975
7.4602
7.4469
7.4416
7.4362
7.4229
Ph
Ph
N
[rel]
[ppm]



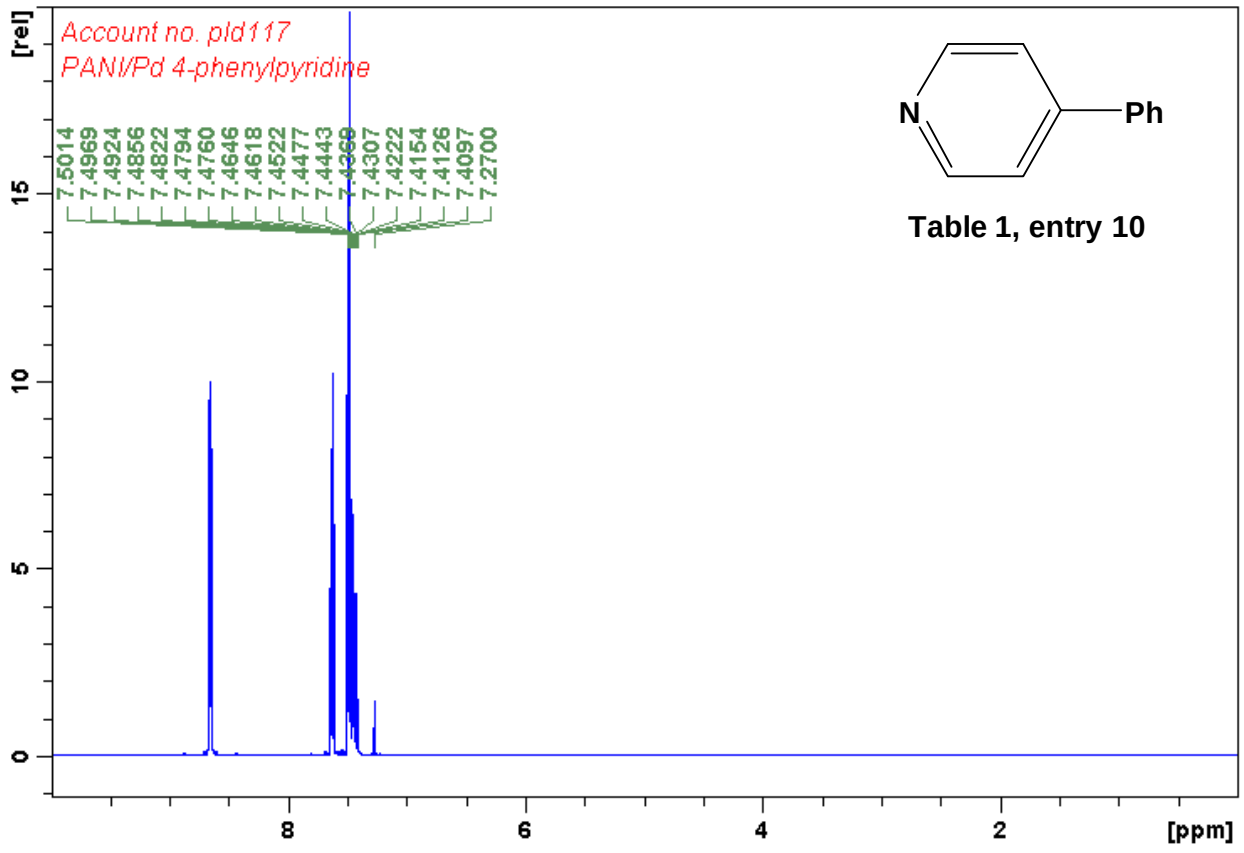
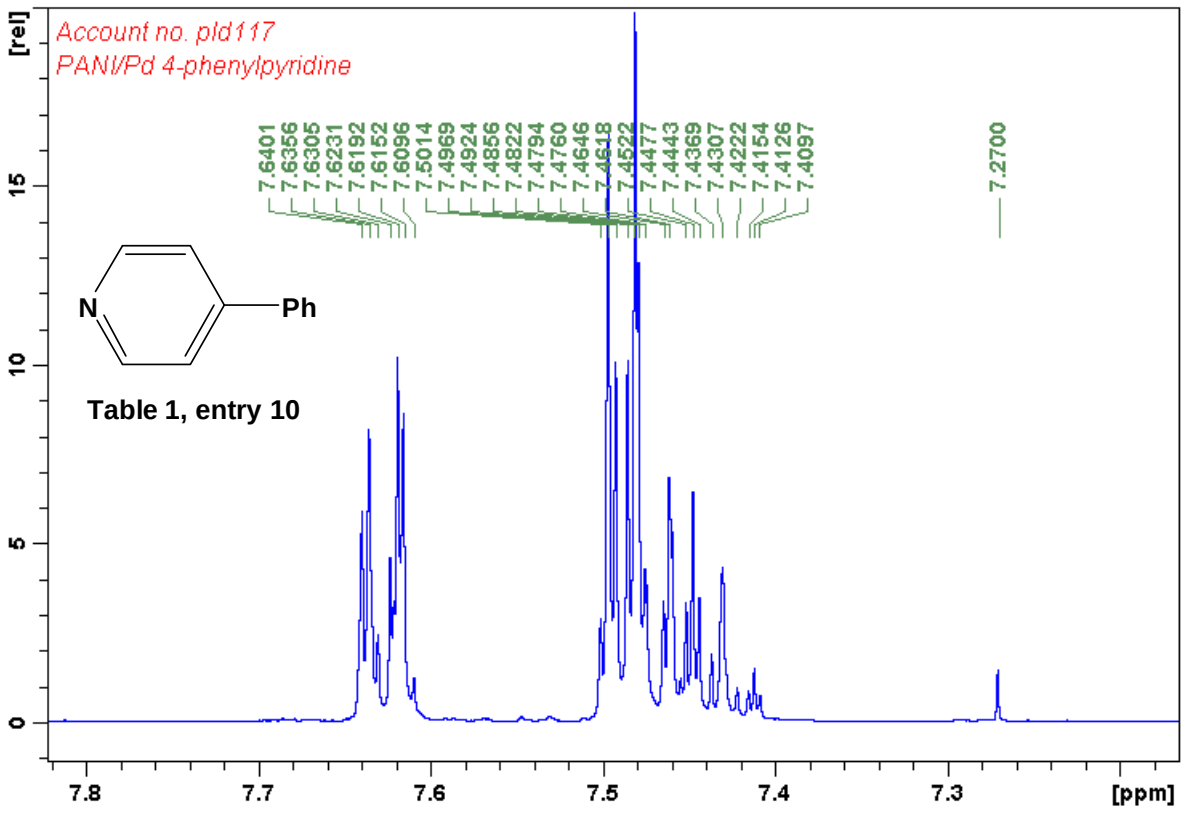
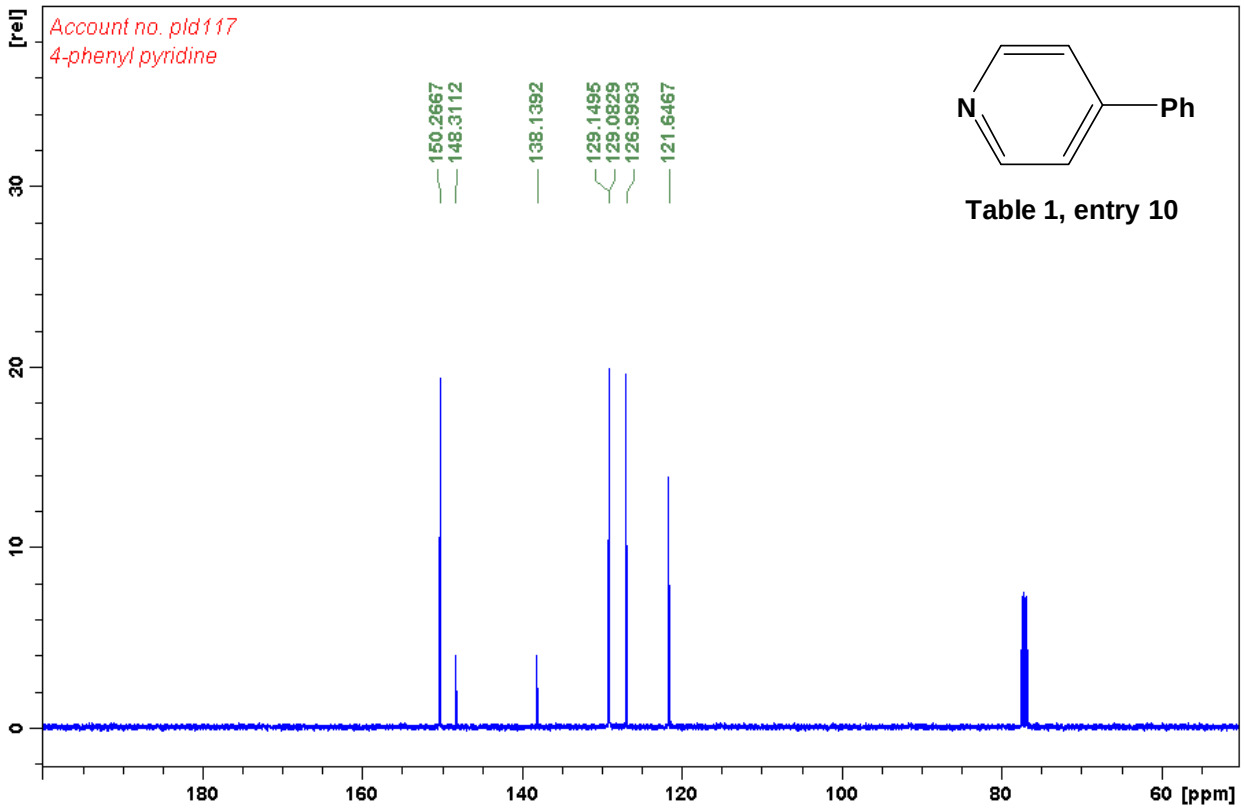
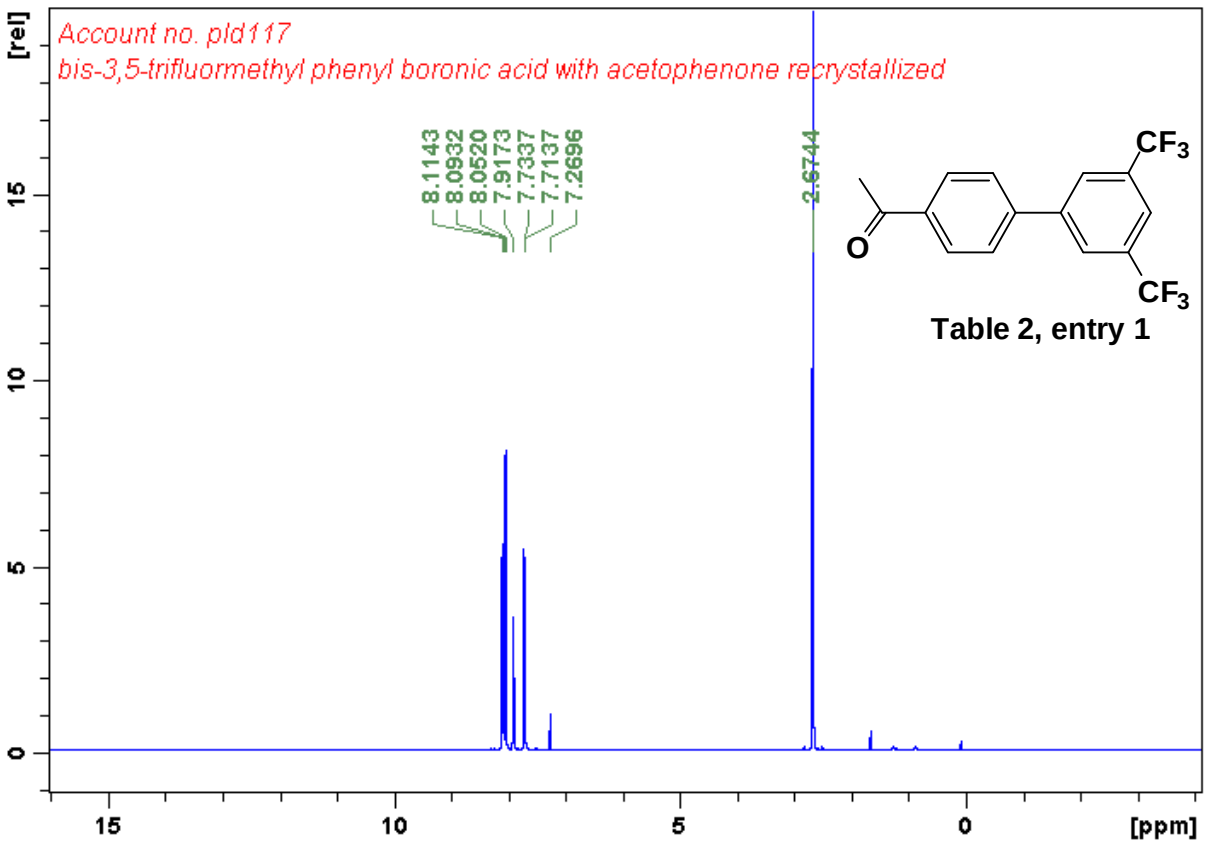
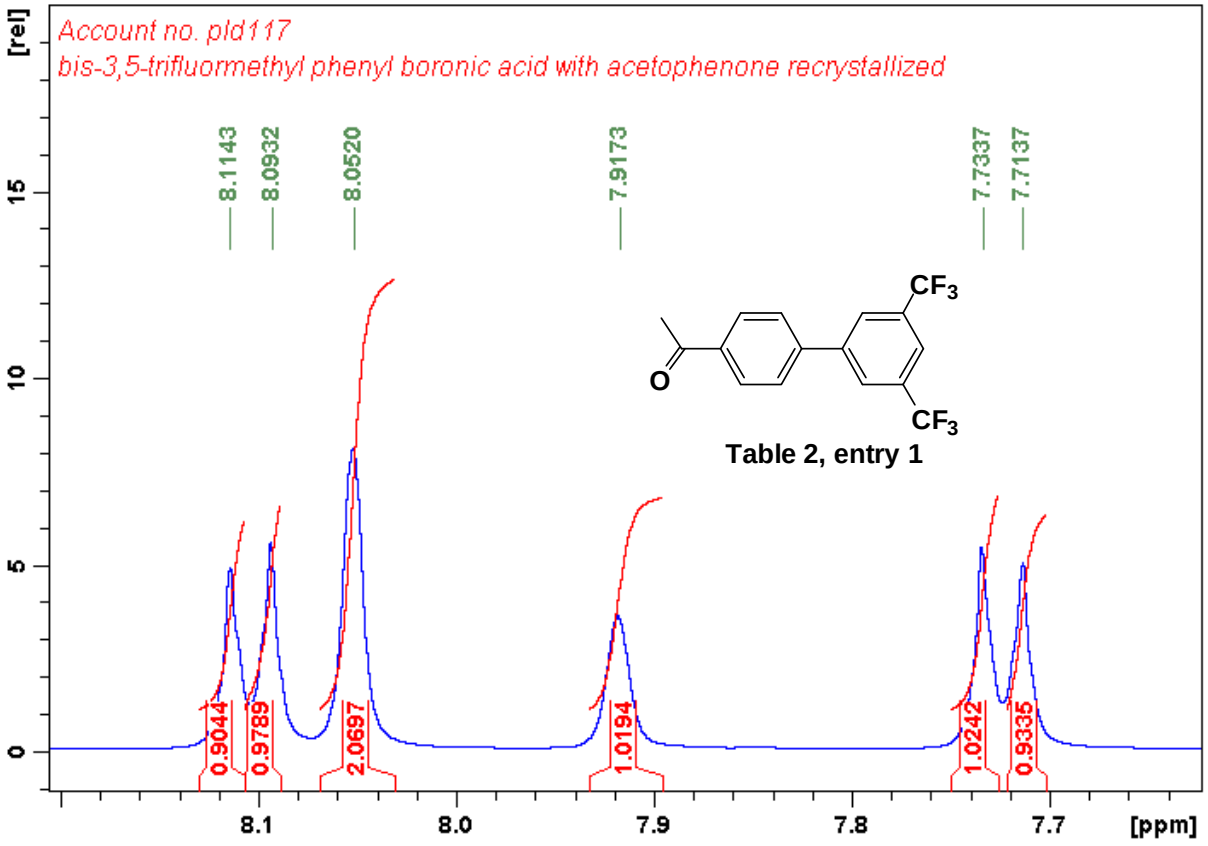


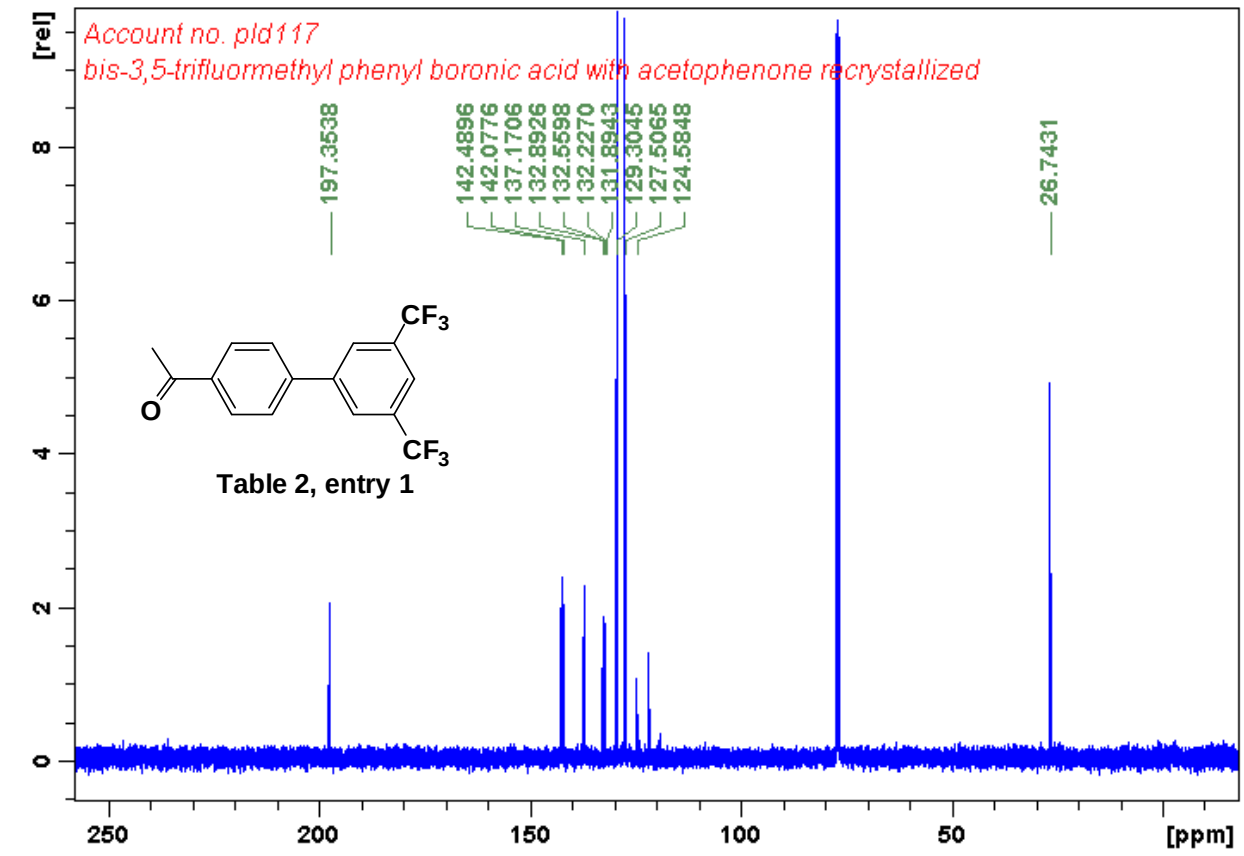
Table 1, entry 10

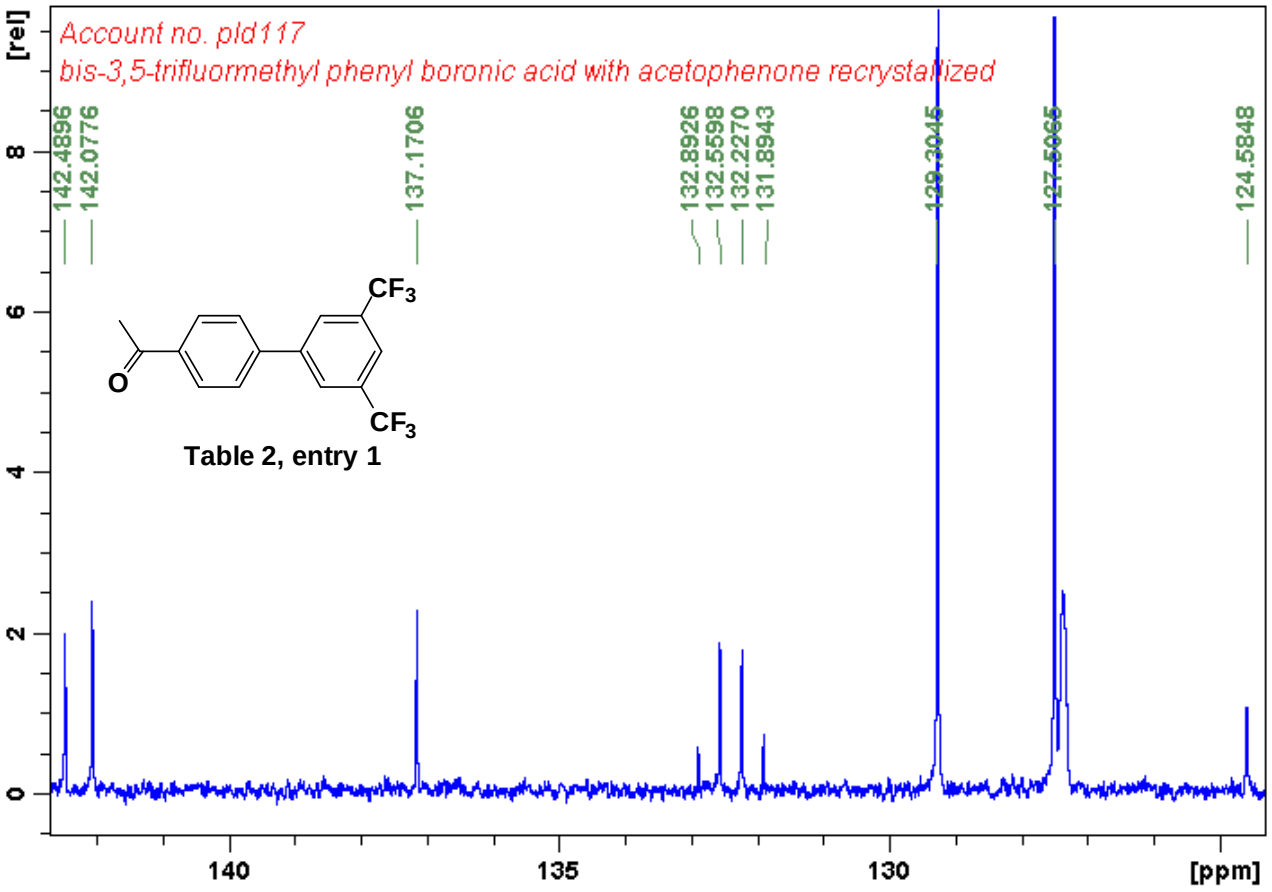

Account no. pld117
PANI/Pd 4-phenylpyridine
7.6401
7.6356
7.6305
7.6231
7.6192
7.6152
7.6096
7.5014
7.4969
7.4924
7.4856
7.4822
7.4794
7.4760
7.4646
7.4618
7.4522
7.4477
7.4443
7.4369
7.4307
7.4222
7.4154
7.4126
7.4097
7.2700
N
Ph
Table 1, entry 10
[rel]
0
5
10
15
7.8
7.7
7.6
7.5
7.4
7.3
[ppm]

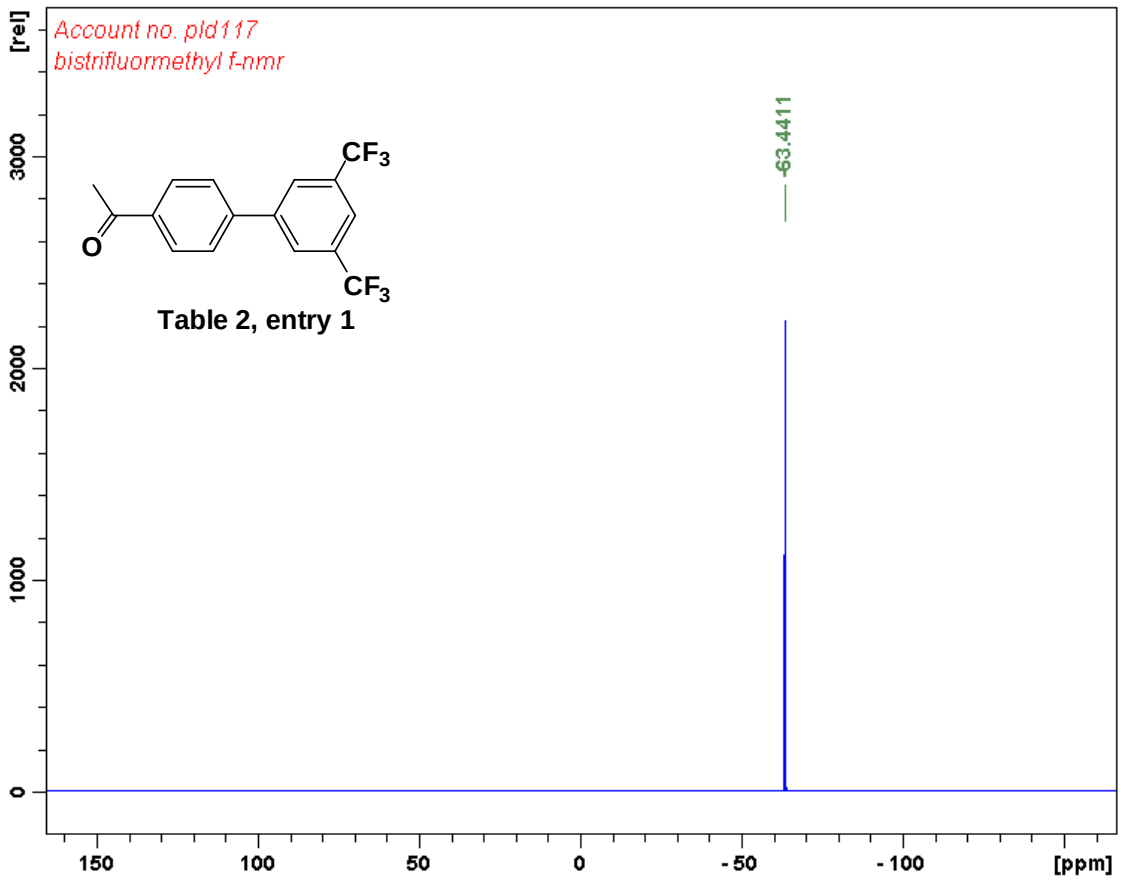

Account no. pld117
4-phenyl pyridine
150.2667
148.3112
138.1392
129.1495
129.0829
126.9993
121.6467
N
Ph
Table 1, entry 10
[rel]
0
10
20
30
180
160
140
120
100
80
60 [ppm]

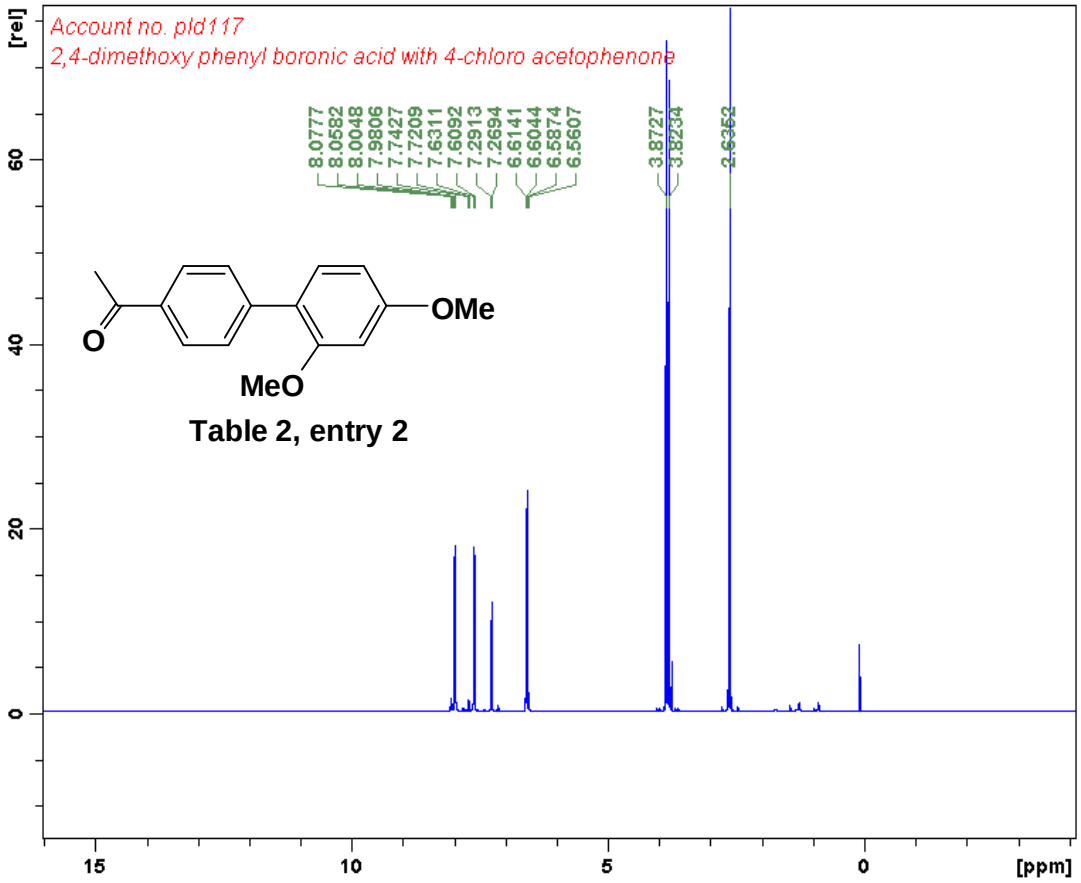

Account no. pld117
bis-3,5-trifluormethyl phenyl boronic acid with acetophenone recrystallized
8.1143
8.0932
8.0520
7.9173
7.7337
7.7137
7.2696
2.6744
CF3
CF3
O
Table 2, entry 1
[rel]
[ppm]

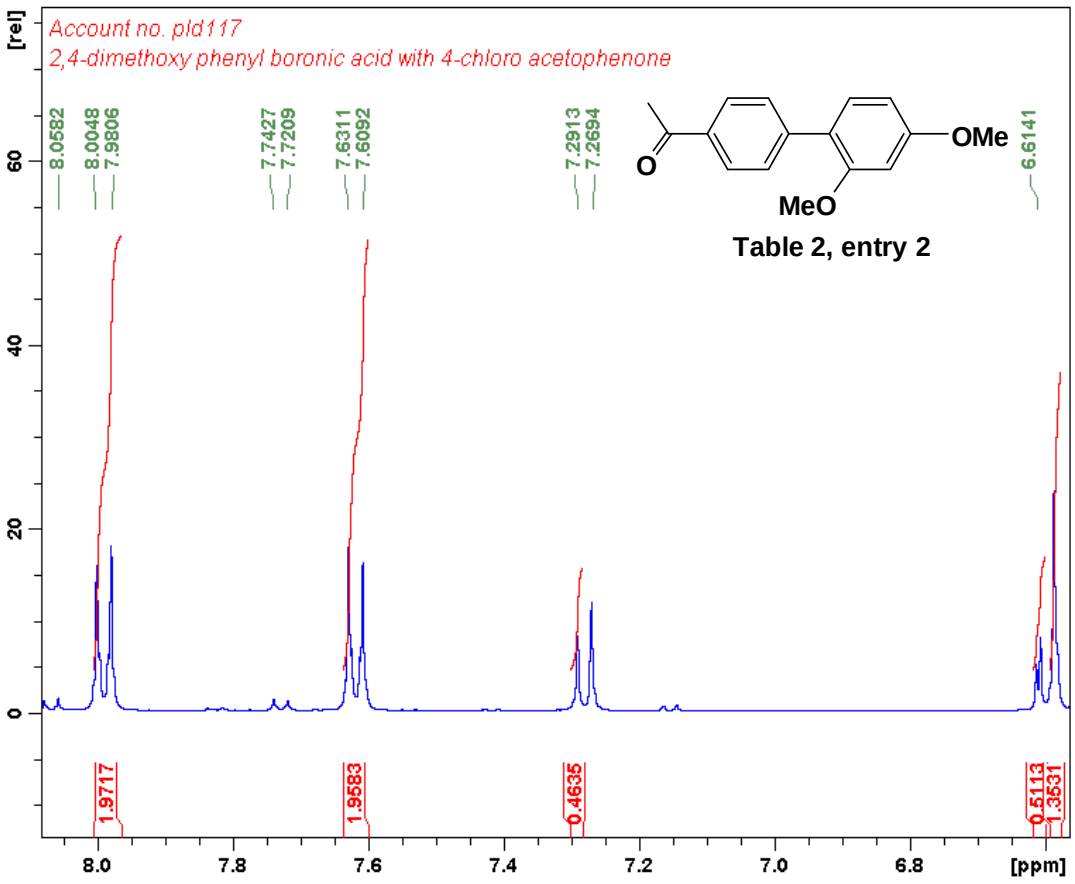

Account no. pld117
bis-3,5-trifluormethyl phenyl boronic acid with acetophenone recrystallized
8.1143
8.0932
8.0520
7.9173
7.7337
7.7137
CF3
CF3
O
Table 2, entry 1
0.9044
0.9789
2.0697
1.0194
1.0242
0.9335
[rel]
[ppm]

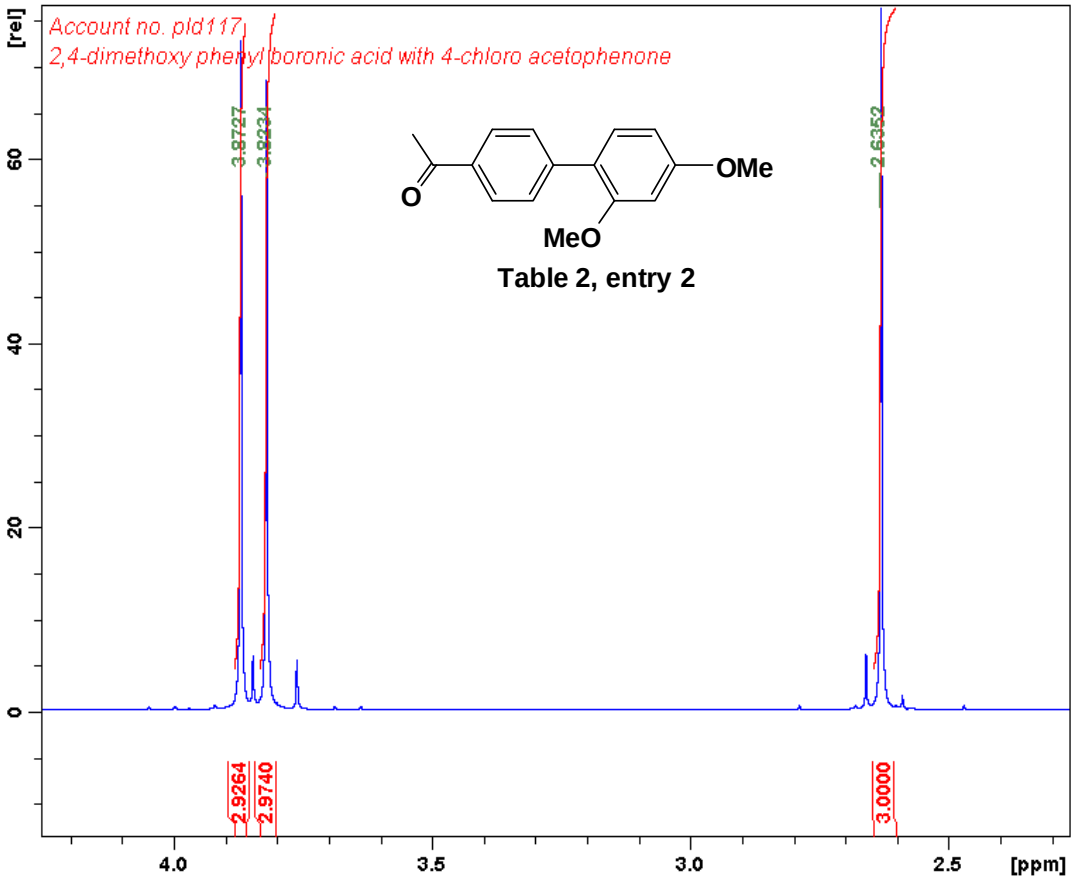

Account no. pld117
bis-3,5-trifluormethyl phenyl boronic acid with acetophenone recrystallized
[rel]
197.3538
142.4896
142.0776
137.1706
132.8926
132.5598
132.2270
131.8943
129.3045
127.5065
124.5848
26.7431
CF3
CF3
O
Table 2, entry 1
[ppm]

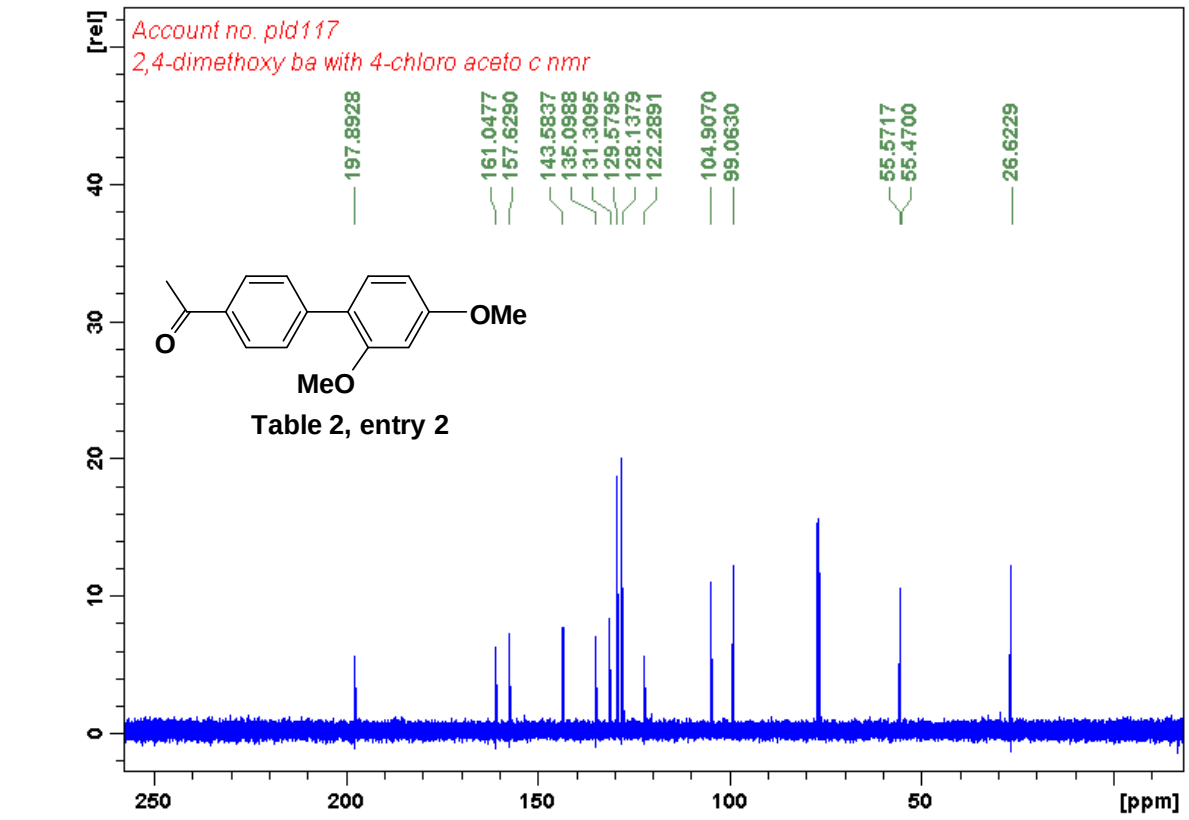

Account no. pld117
bis-3,5-trifluormethyl phenyl boronic acid with acetophenone recrystallized
[rel]
142.4896
142.0776
137.1706
132.8926
132.5598
132.2270
131.8943
129.3045
127.5065
124.5848
CF3
CF3
O
Table 2, entry 1
[ppm]

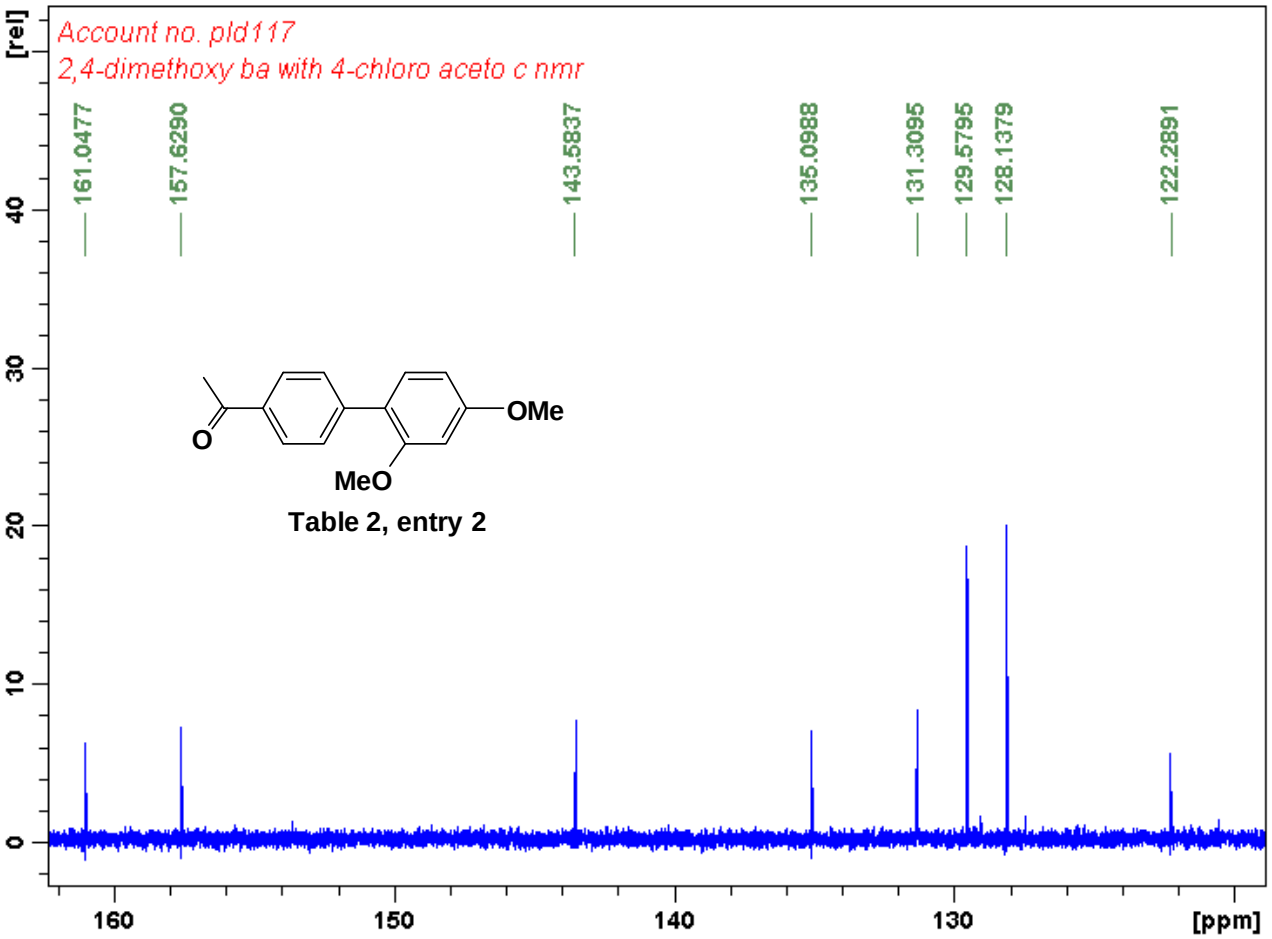

Account no. pld117
bistrifluormethyl f-nmr
CF3
O
CF3
Table 2, entry 1
-63.4411
[rel]
3000
2000
1000
0
150
100
50
0
-50
-100
[ppm]

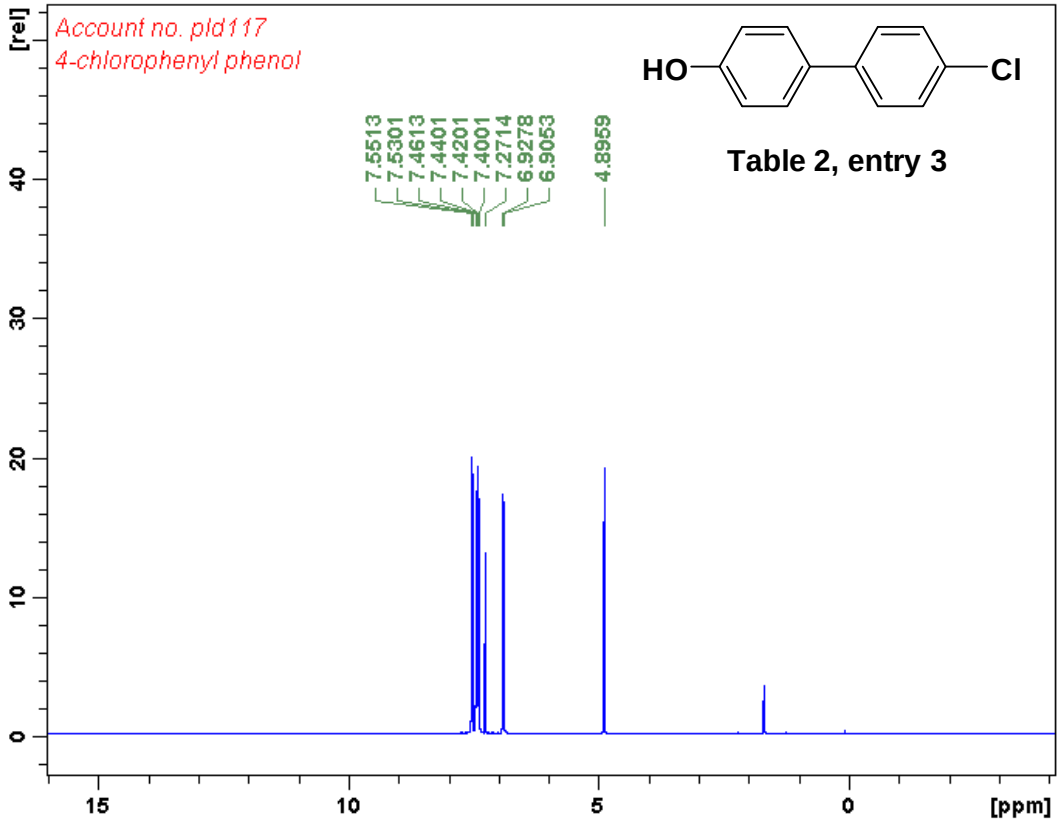

Account no. pld117
2,4-dimethoxy phenyl boronic acid with 4-chloro acetophenone
8.0777
8.0582
8.0048
7.9806
7.7427
7.7209
7.6311
7.6092
7.2913
7.2694
6.6141
6.6044
6.5874
6.5607
3.8727
3.8234
2.6352
O
OMe
MeO
Table 2, entry 2
[rel]
60
40
20
0
15
10
5
0
[ppm]

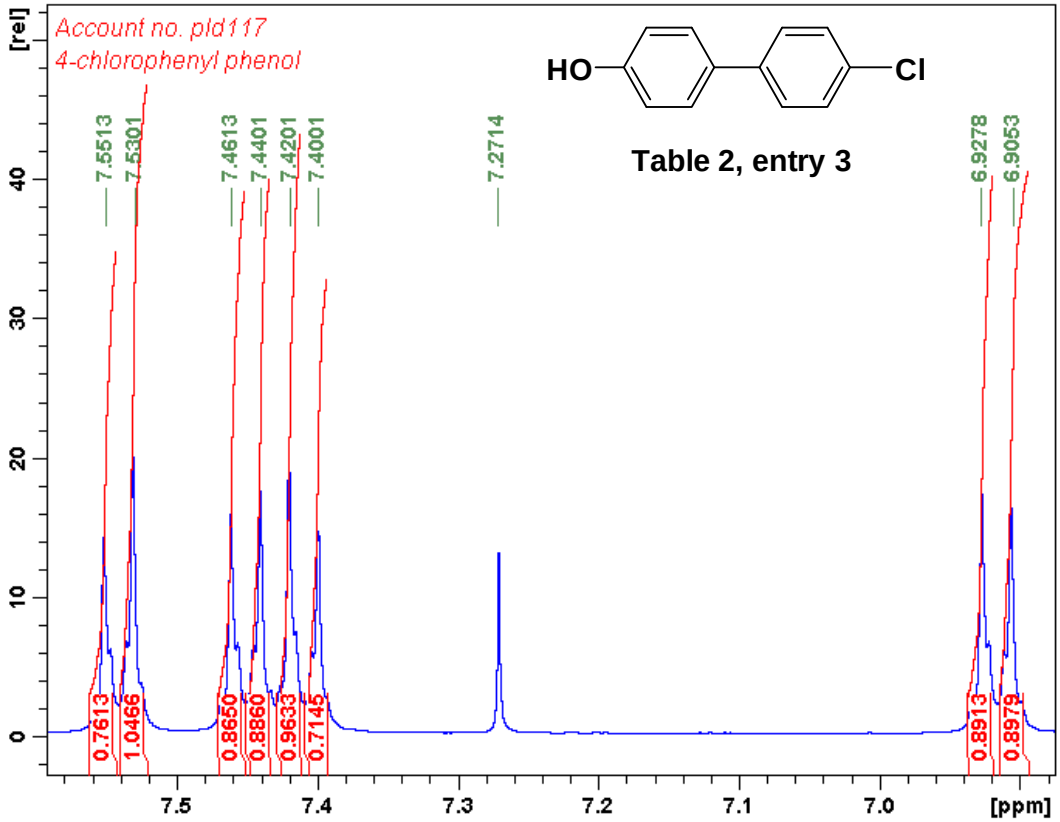

Account no. pld117
2,4-dimethoxy phenyl boronic acid with 4-chloro acetophenone
8.0582
8.0048
7.9806
7.7427
7.7209
7.6311
7.6092
7.2913
7.2694
6.6141
OMe
O
MeO
Table 2, entry 2
1.9717
1.9583
0.4635
0.5113
1.3531
[rel]
[ppm]

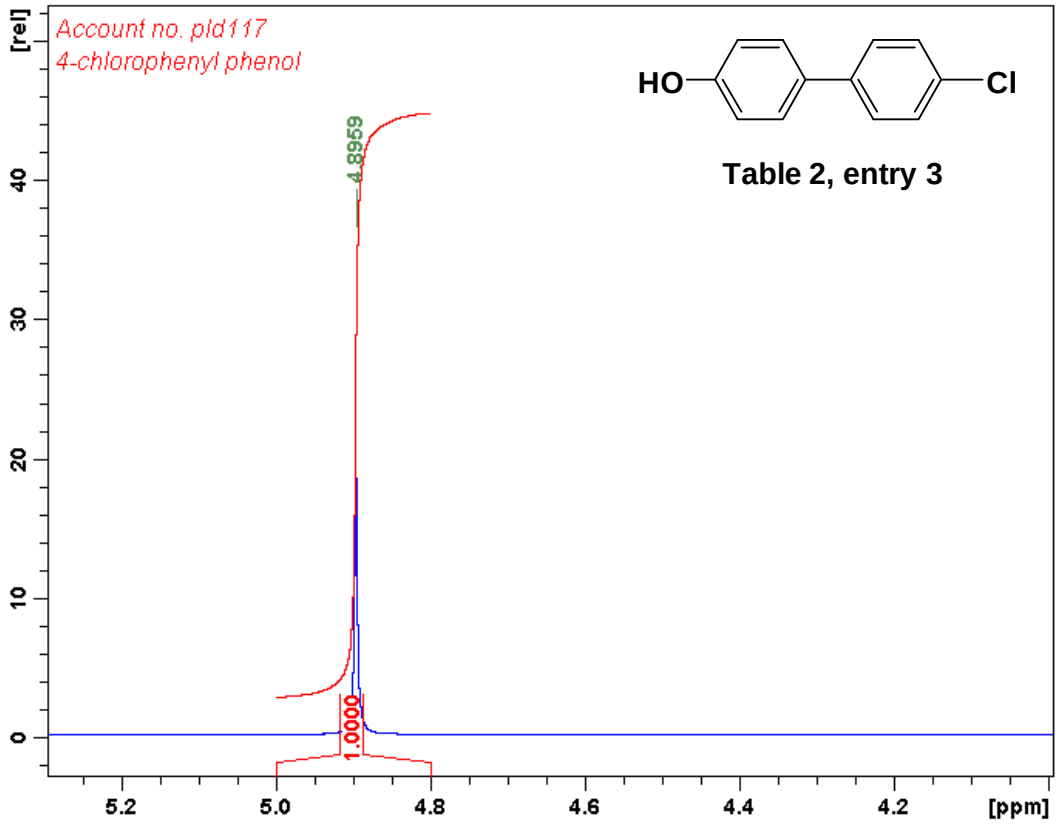

Account no. pld117
2,4-dimethoxy phenyl boronic acid with 4-chloro acetophenone
3.8727
3.8234
2.6352
OMe
O
MeO
Table 2, entry 2
2.9264
2.9740
3.0000
[rel]
[ppm]

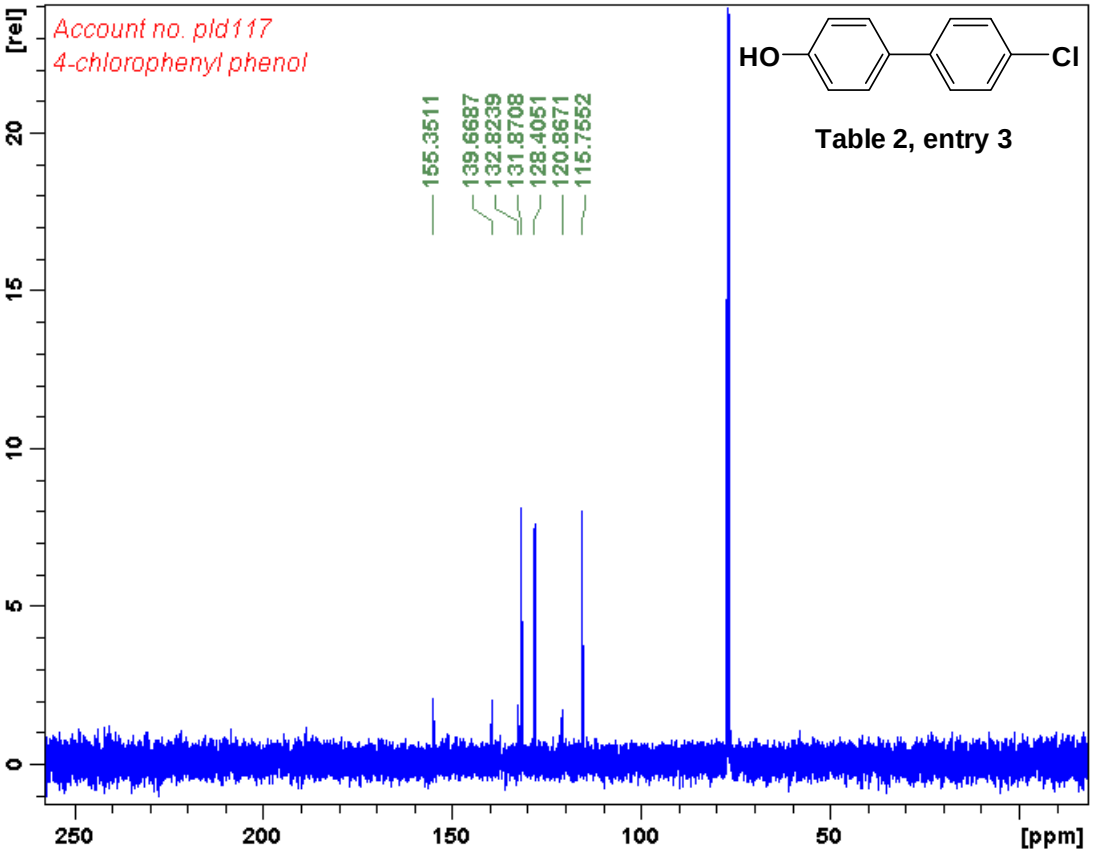

Account no. pld117
2,4-dimethoxy ba with 4-chloro aceto c nmr
197.8928
161.0477
157.6290
143.5837
135.0988
131.3095
129.5795
128.1379
122.2891
104.9070
99.0630
55.5717
55.4700
26.6229
OMe
O
MeO
Table 2, entry 2
[rel]
[ppm]

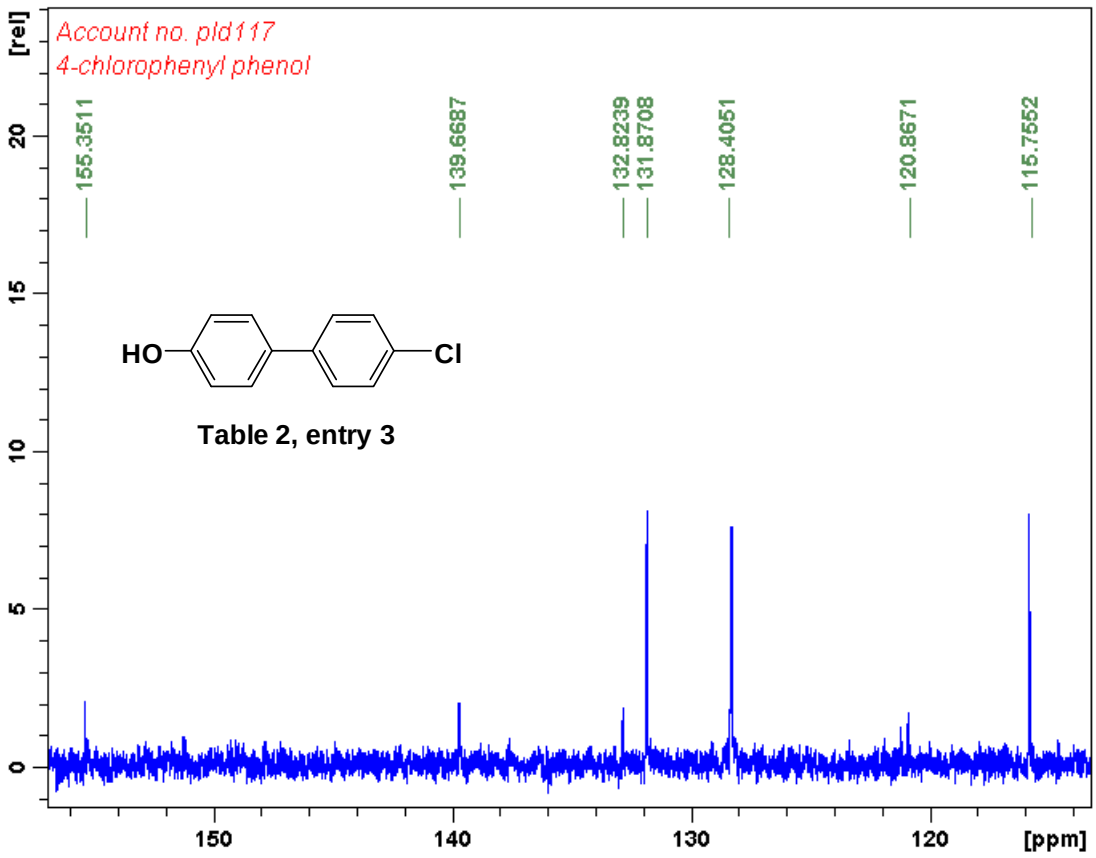

Account no. pld117
2,4-dimethoxy ba with 4-chloro aceto c nmr
161.0477
157.6290
143.5837
135.0988
131.3095
129.5795
128.1379
122.2891
OMe
O
MeO
Table 2, entry 2
[rel]
[ppm]

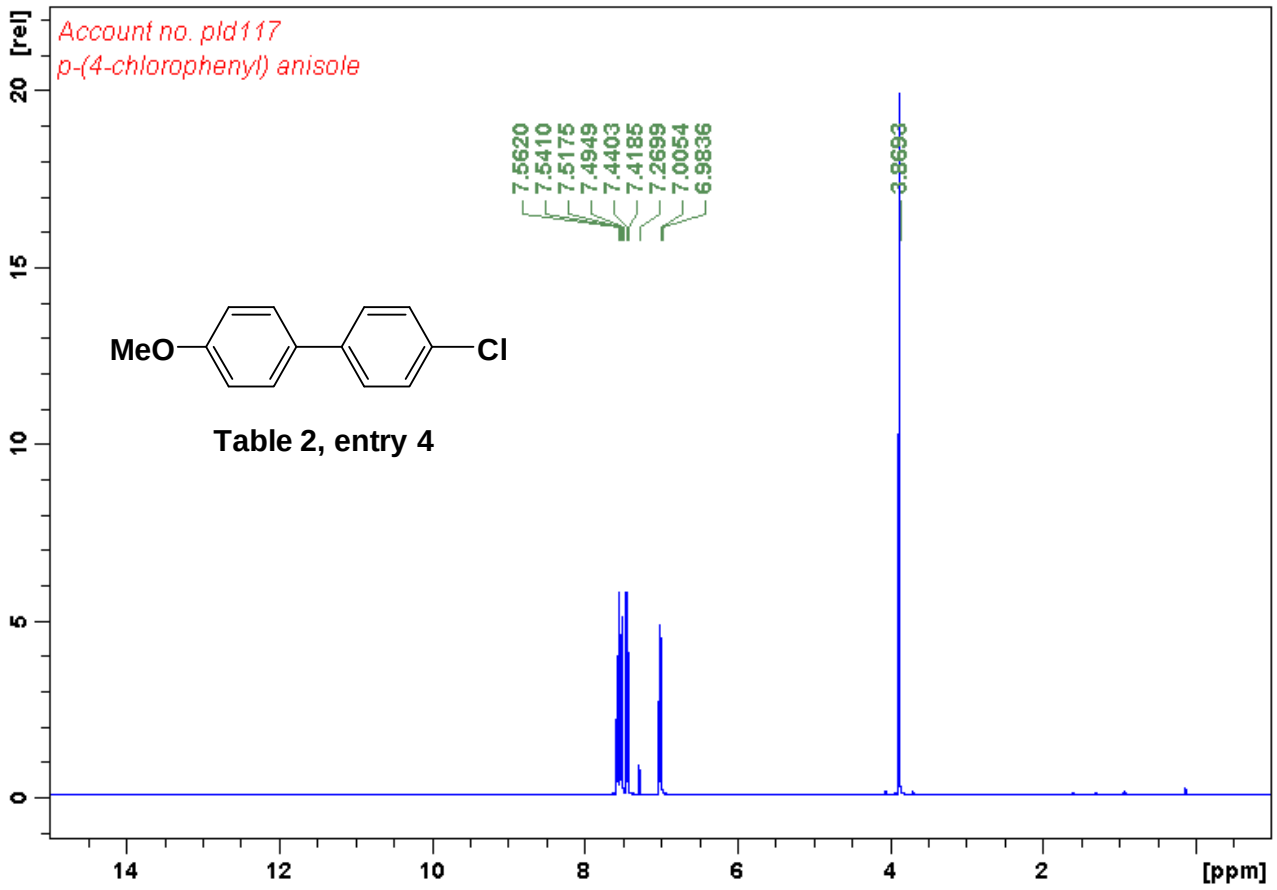

Account no. pld117
4-chlorophenyl phenol
HO
Cl
Table 2, entry 3
7.5513
7.5301
7.4613
7.4401
7.4201
7.4001
7.2714
6.9278
6.9053
4.8959
[rel]
[ppm]

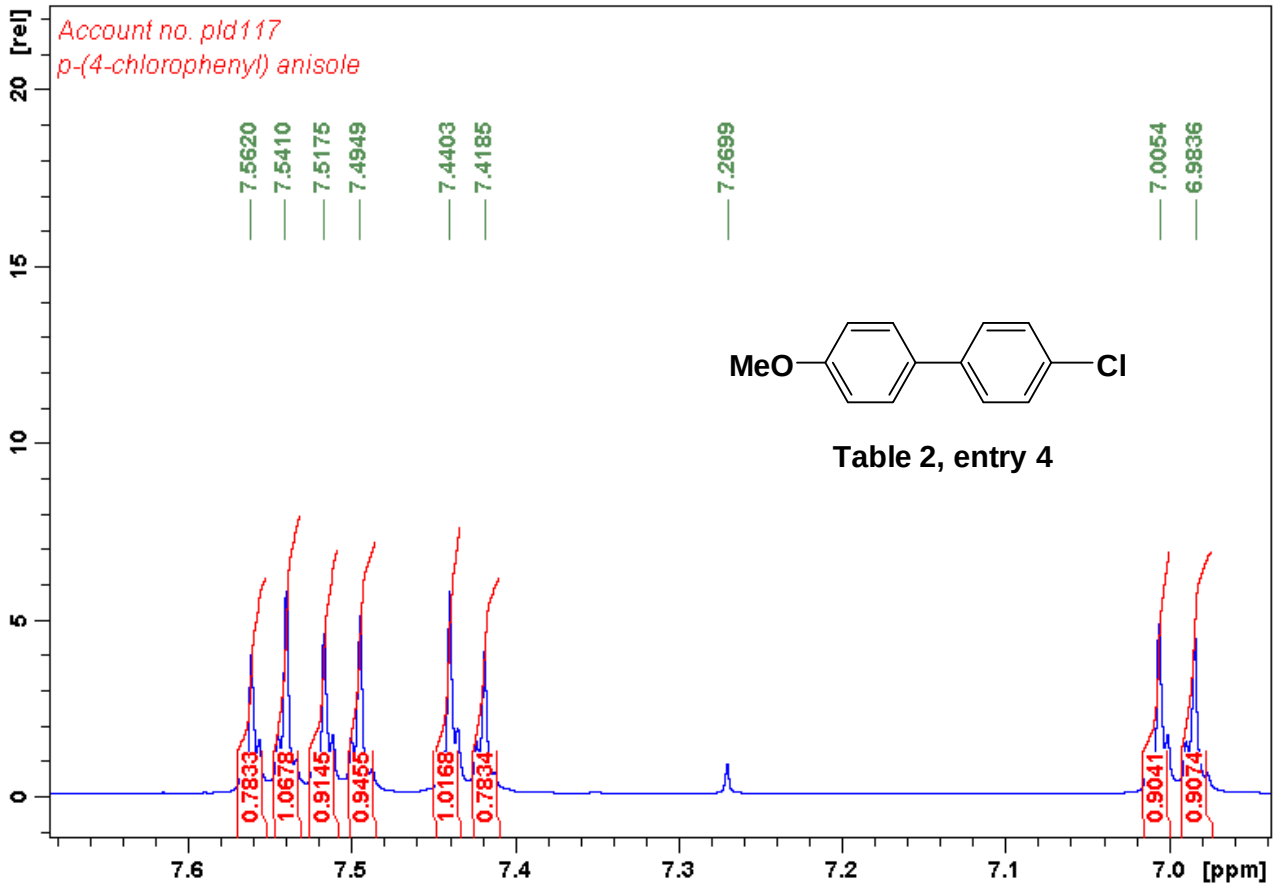

Account no. pld117
4-chlorophenyl phenol
HO
Cl
Table 2, entry 3
7.5513
7.5301
7.4613
7.4401
7.4201
7.4001
7.2714
6.9278
6.9053
0.7613
1.0466
0.8650
0.8860
0.9633
0.7145
0.8913
0.8979
[rel]
[ppm]

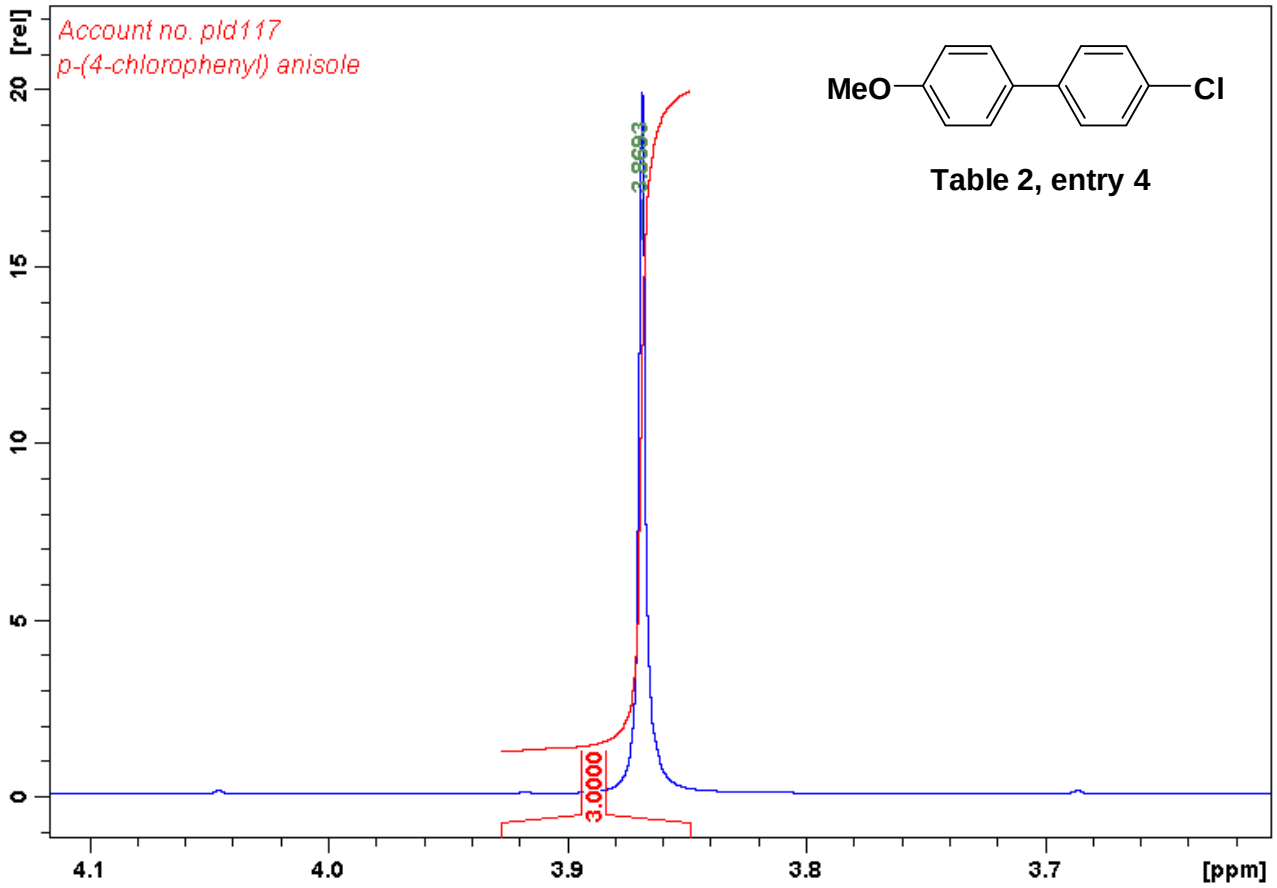

Account no. pld117
4-chlorophenyl phenol
HO
Cl
Table 2, entry 3
4.8959
1.0000
[rel]
0
10
20
30
40
5.2
5.0
4.8
4.6
4.4
4.2
[ppm]

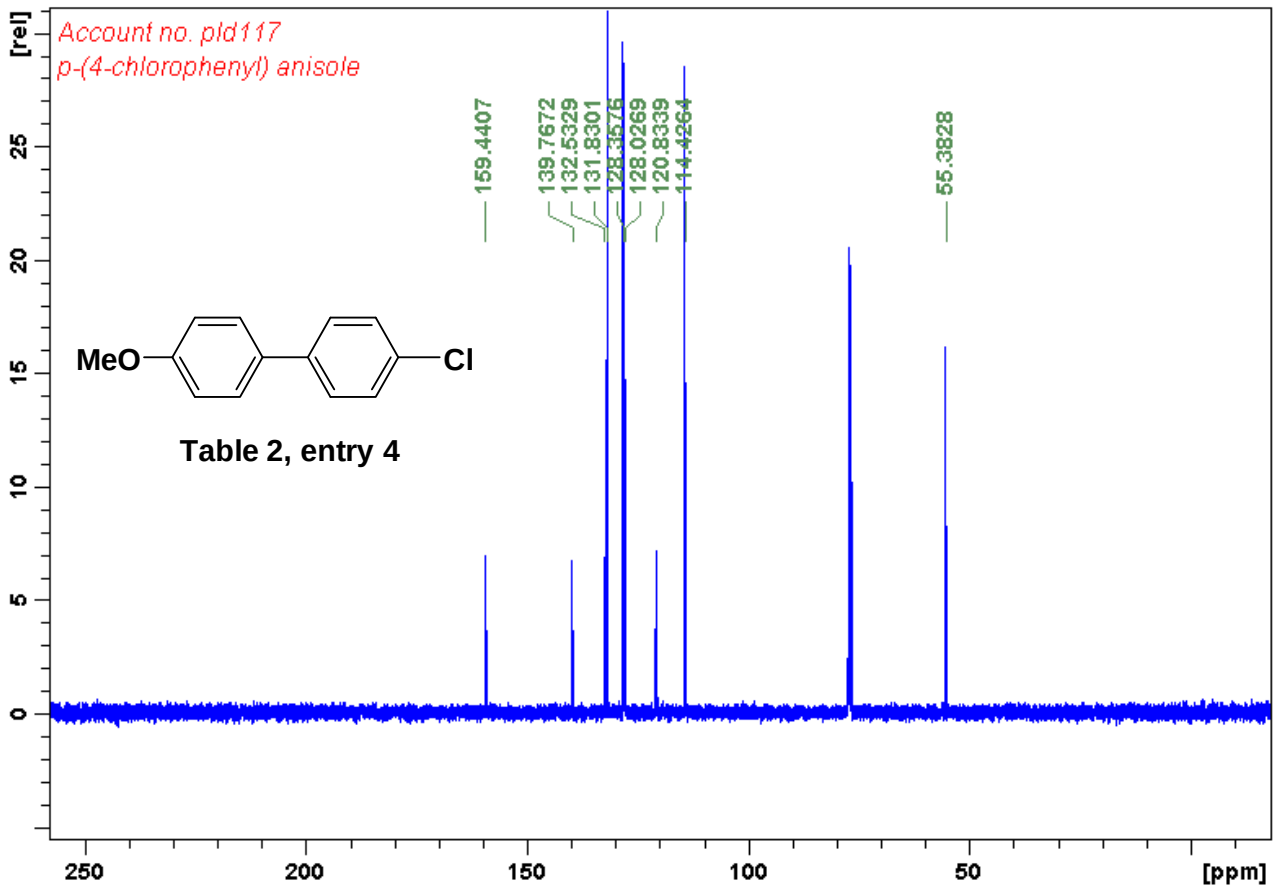

Account no. pld117
4-chlorophenyl phenol
HO
Cl
Table 2, entry 3
155.3511
139.6687
132.8239
131.8708
128.4051
120.8671
115.7552
[rel]
0
5
10
15
20
250
200
150
100
50
[ppm]

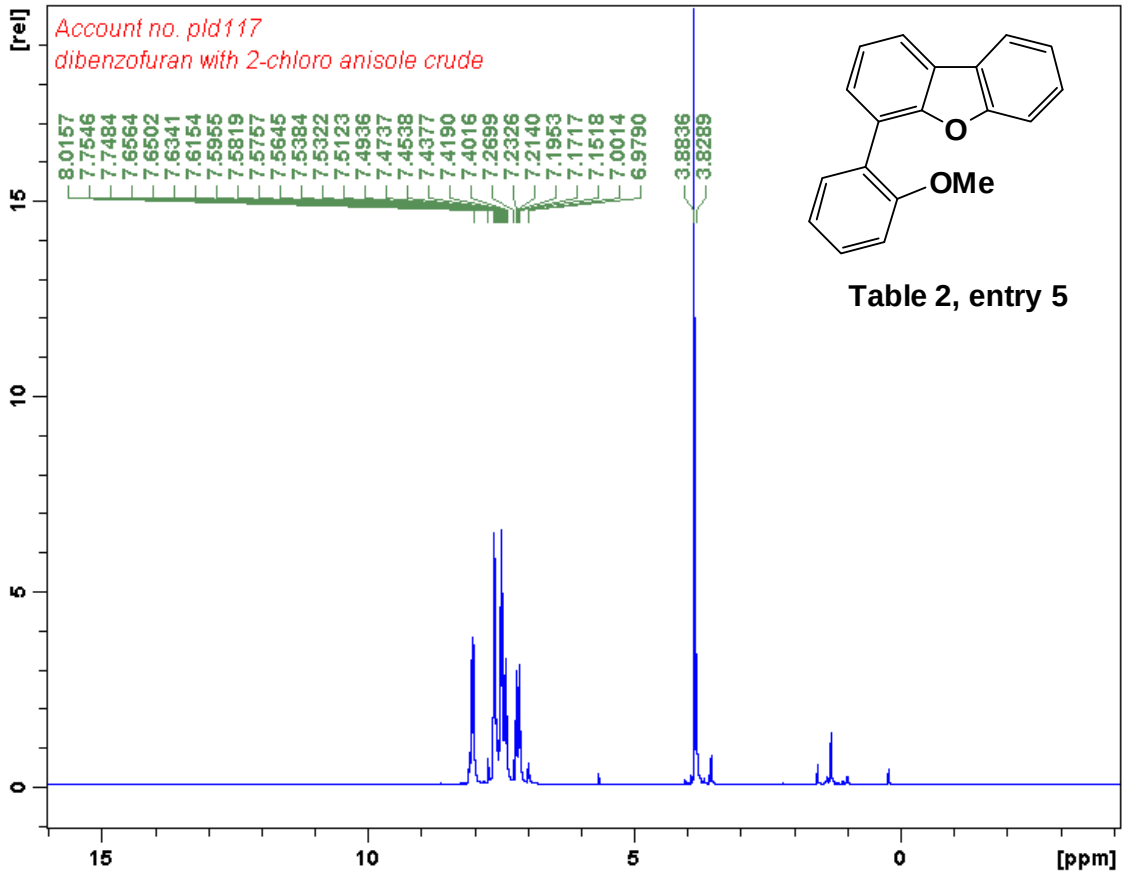

Account no. pld117
4-chlorophenyl phenol
155.3511
139.6687
132.8239
131.8708
128.4051
120.8671
115.7552
HO
Cl
Table 2, entry 3
[rel]
[ppm]

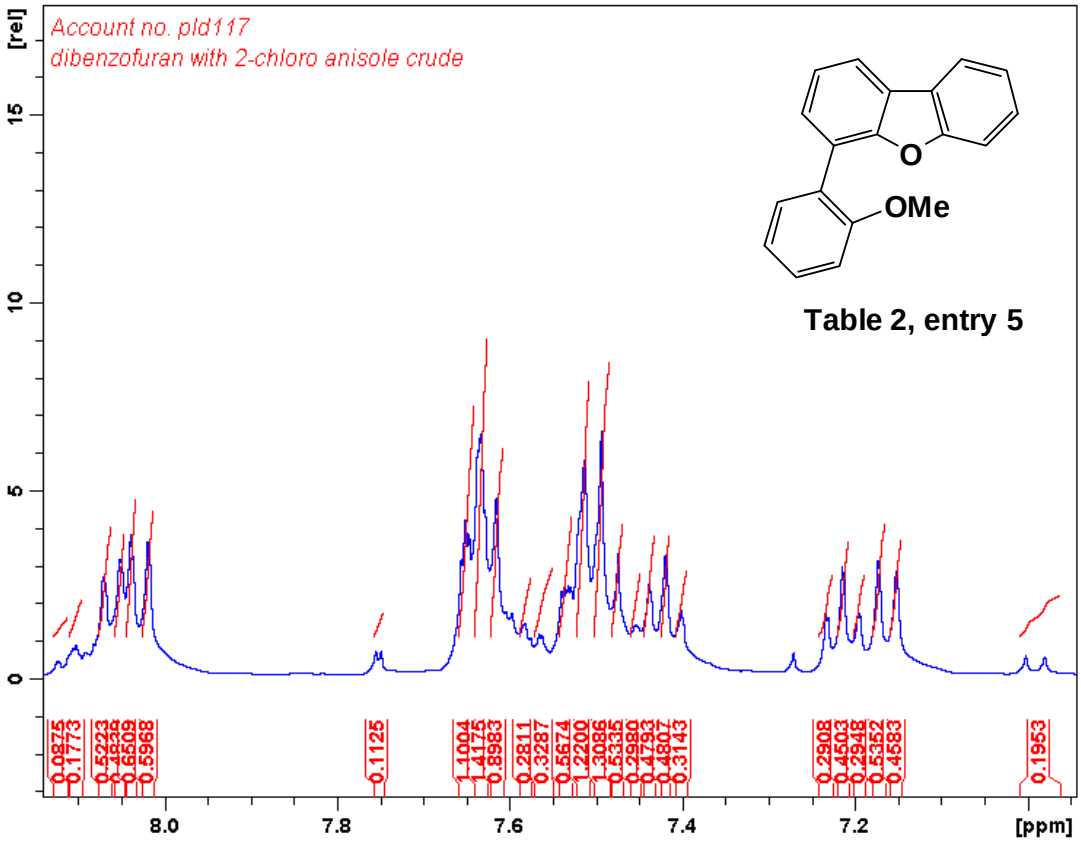

Account no. pld117
p-(4-chlorophenyl) anisole
7.5620
7.5410
7.5175
7.4949
7.4403
7.4185
7.2699
7.0054
6.9836
3.8693
MeO
Cl
Table 2, entry 4
[rel]
[ppm]

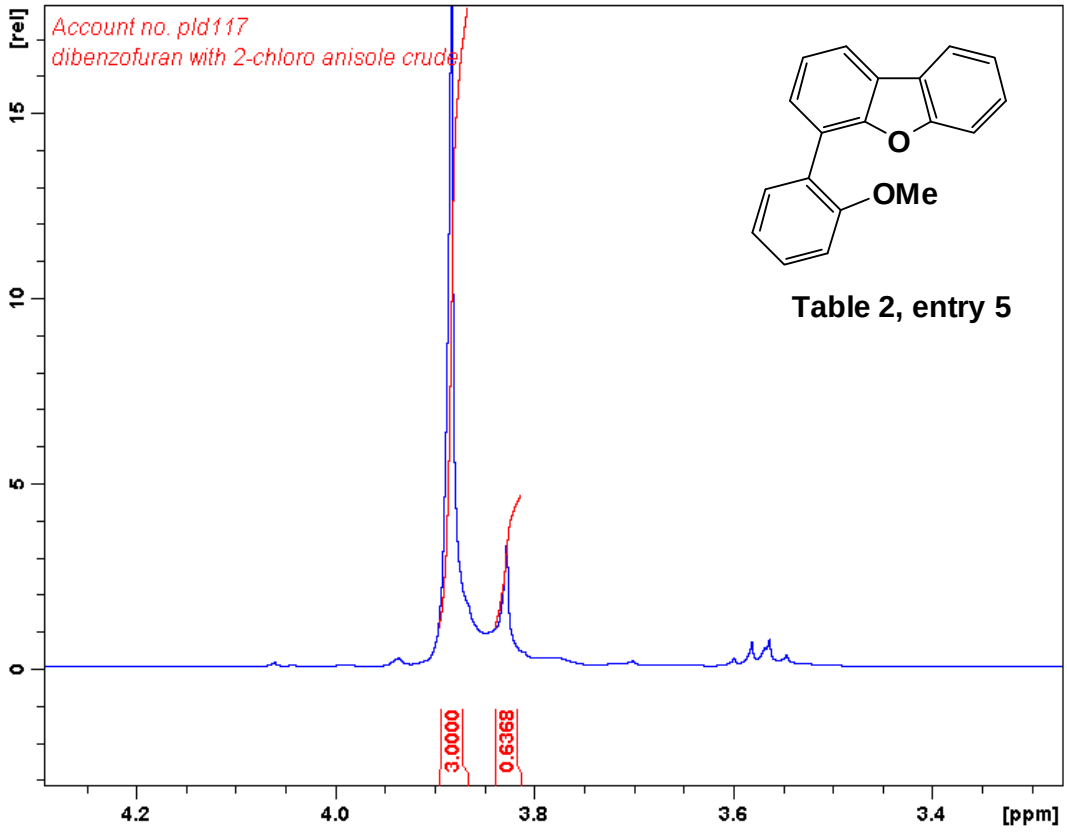

Account no. pld117
p-(4-chlorophenyl) anisole
7.5620
7.5410
7.5175
7.4949
7.4403
7.4185
7.2699
7.0054
6.9836
MeO
Cl
Table 2, entry 4
0.7833
1.0678
0.9145
0.9455
1.0168
0.7834
0.9041
0.9074
[rel]
[ppm]


Account no. pld117
p-(4-chlorophenyl) anisole
MeO
Cl
Table 2, entry 4
3.8603
3.0000
[rel]
[ppm]

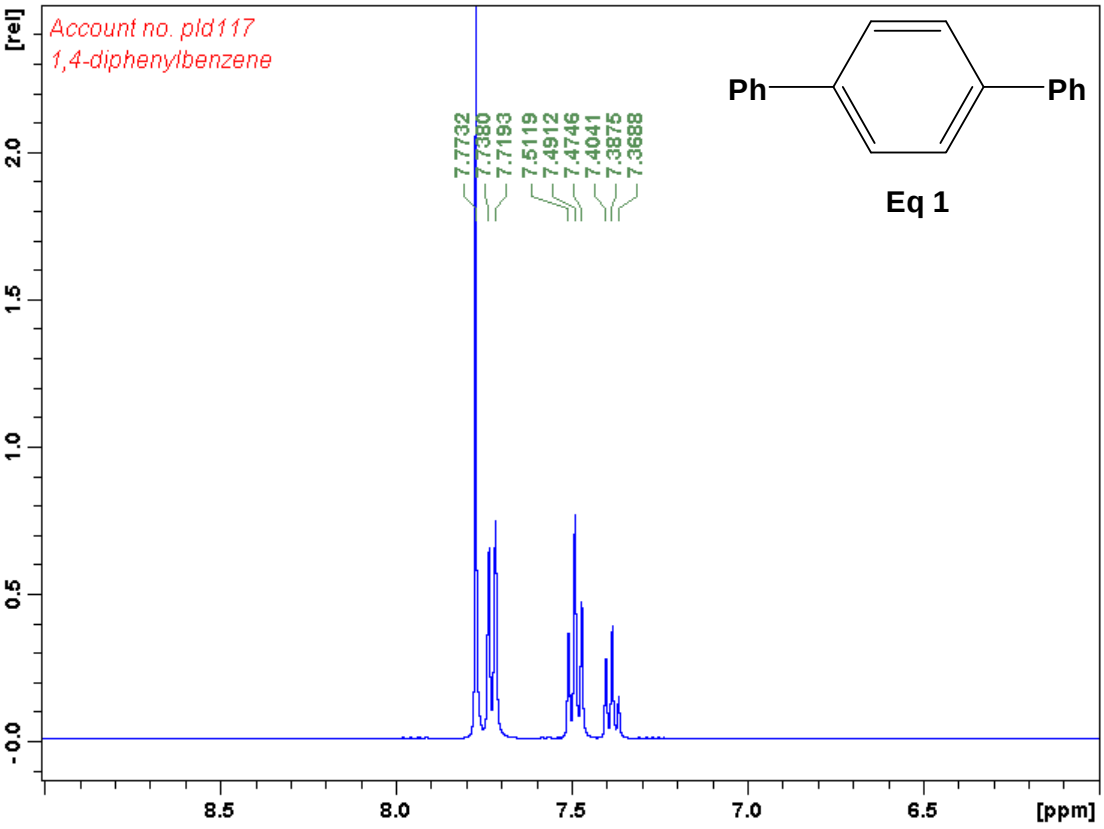

Account no. pld117
p-(4-chlorophenyl) anisole
159.4407
139.7672
132.5329
131.8301
128.3576
128.0269
120.8339
114.4264
55.3828
MeO
Cl
Table 2, entry 4
[rel]
[ppm]

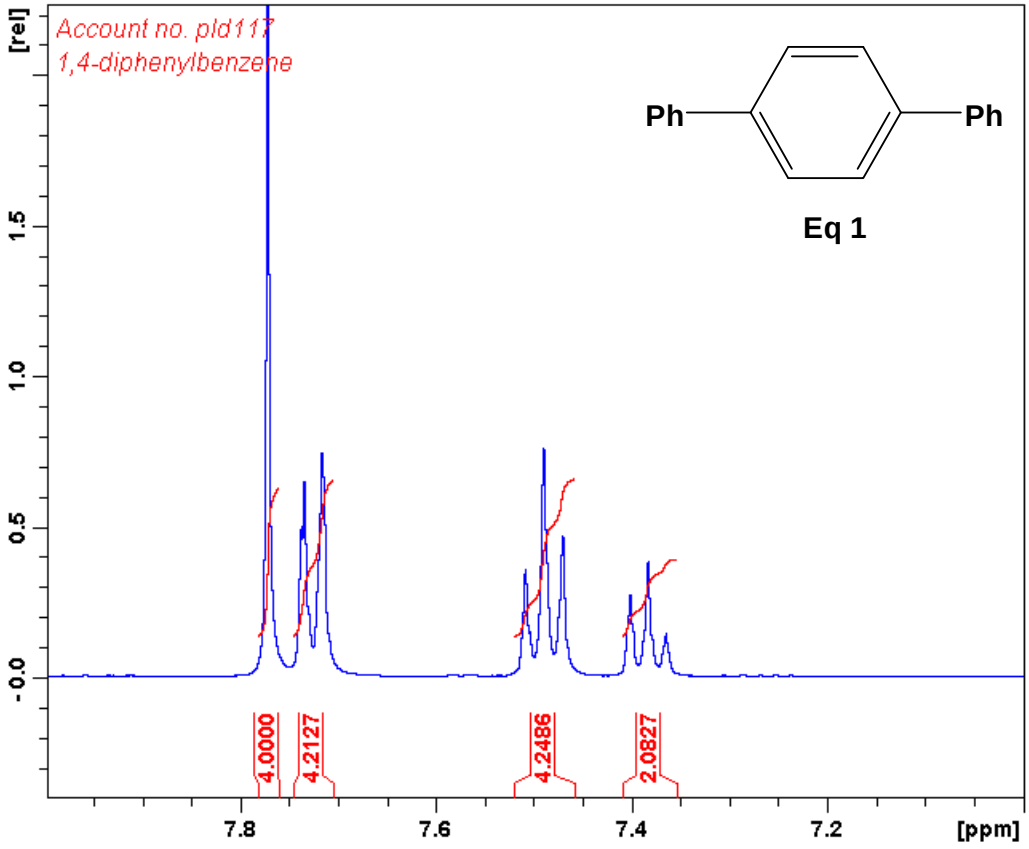

Account no. pld117
dibenzofuran with 2-chloro anisole crude
8.0157
7.7546
7.7484
7.6564
7.6502
7.6341
7.6154
7.5955
7.5819
7.5757
7.5645
7.5384
7.5322
7.5123
7.4936
7.4737
7.4538
7.4377
7.4190
7.4016
7.2699
7.2326
7.2140
7.1953
7.1717
7.1518
7.0014
6.9790
3.8836
3.8289
O
OMe
Table 2, entry 5
[rel]
[ppm]

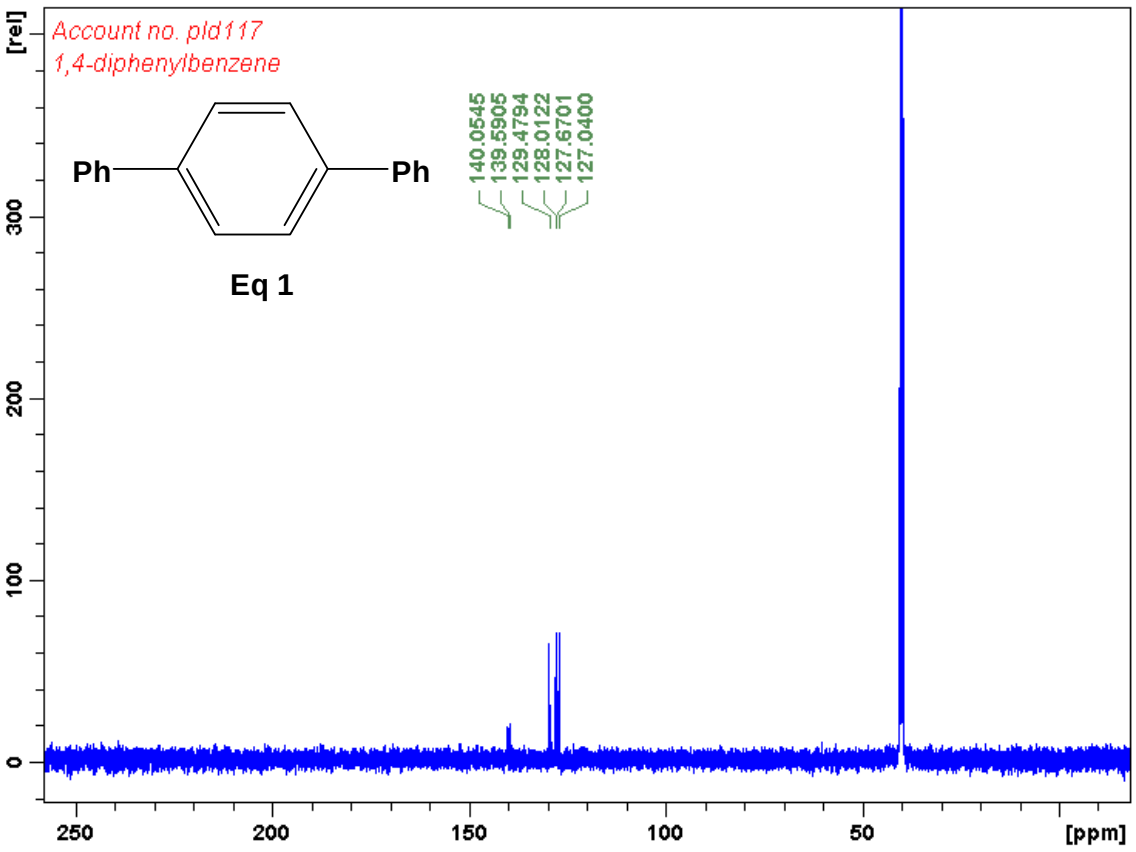


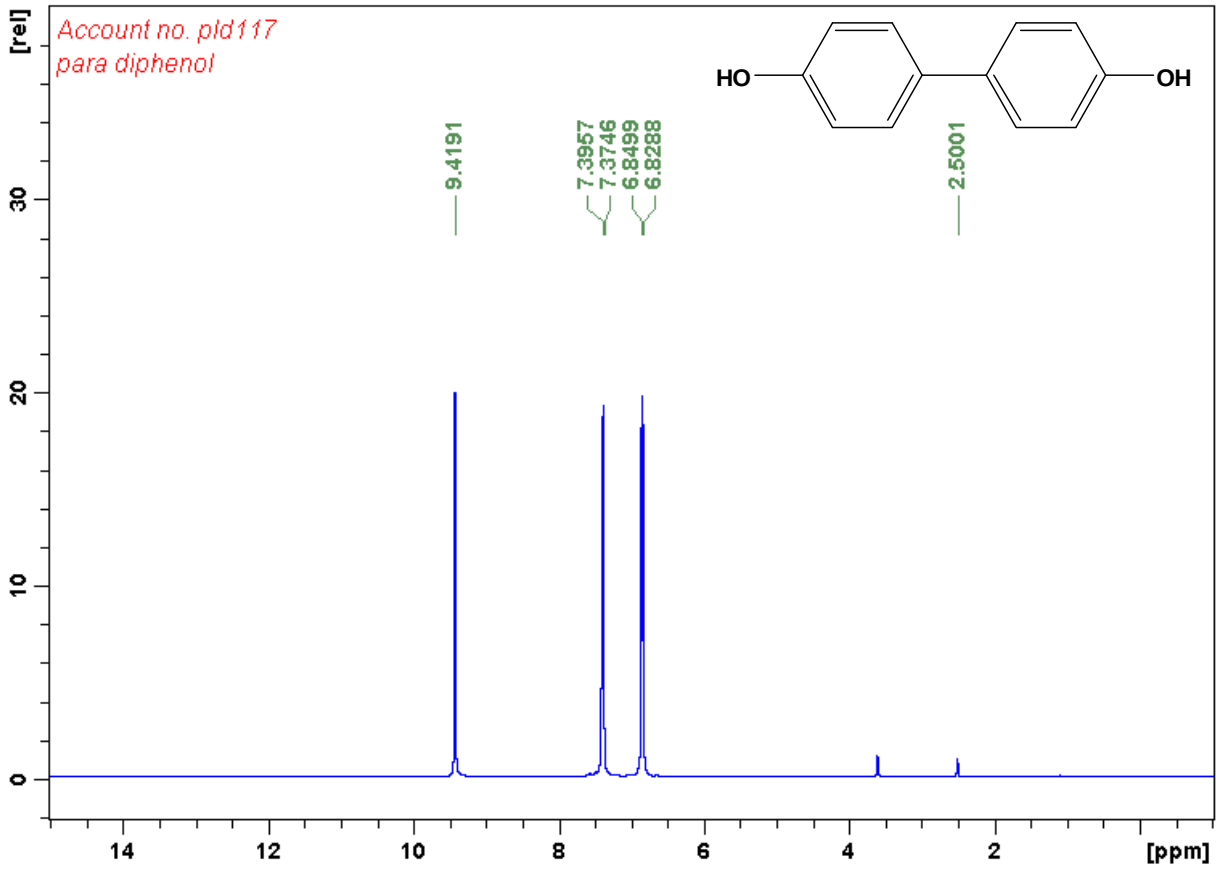


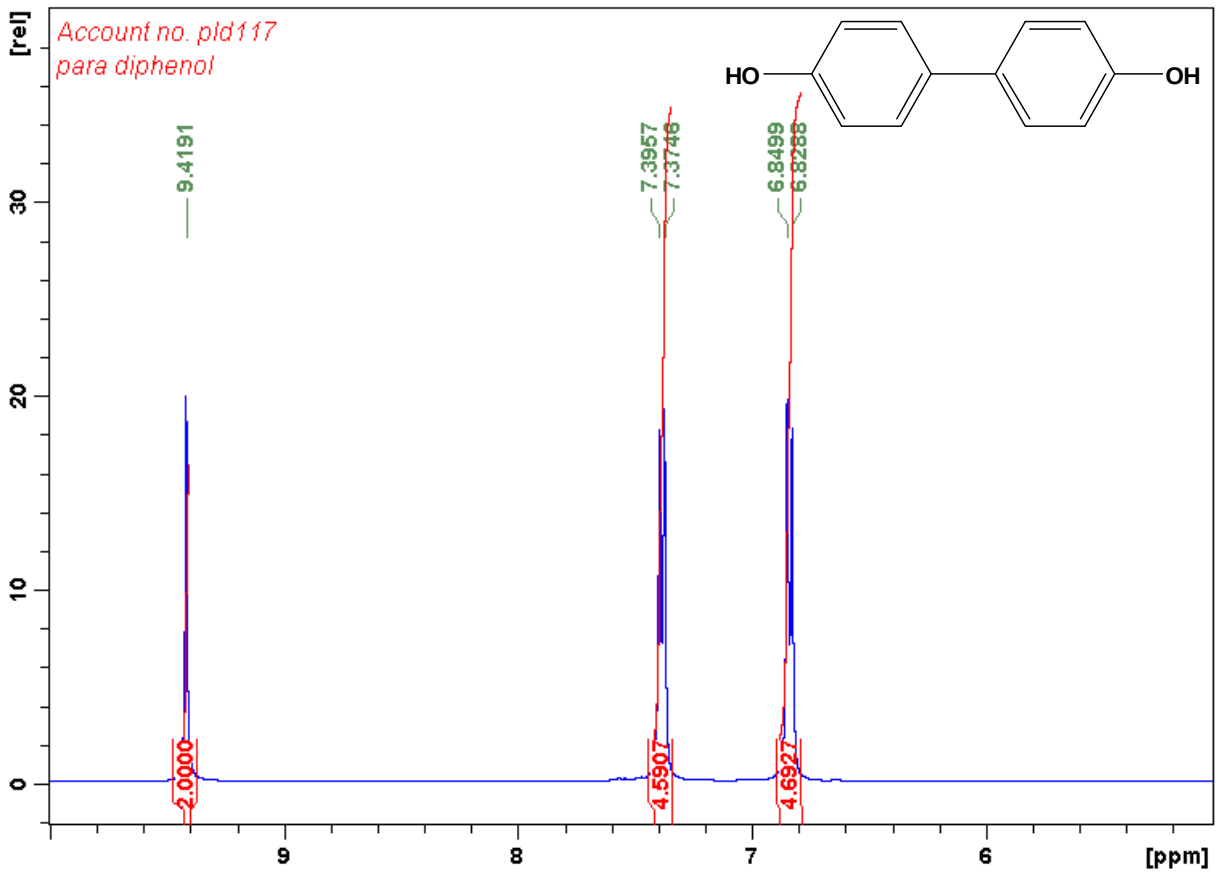
Coupling with a fluoro aryl: ^{1}H and ^{13}C NMR spectra were collected in dmso-d_6.

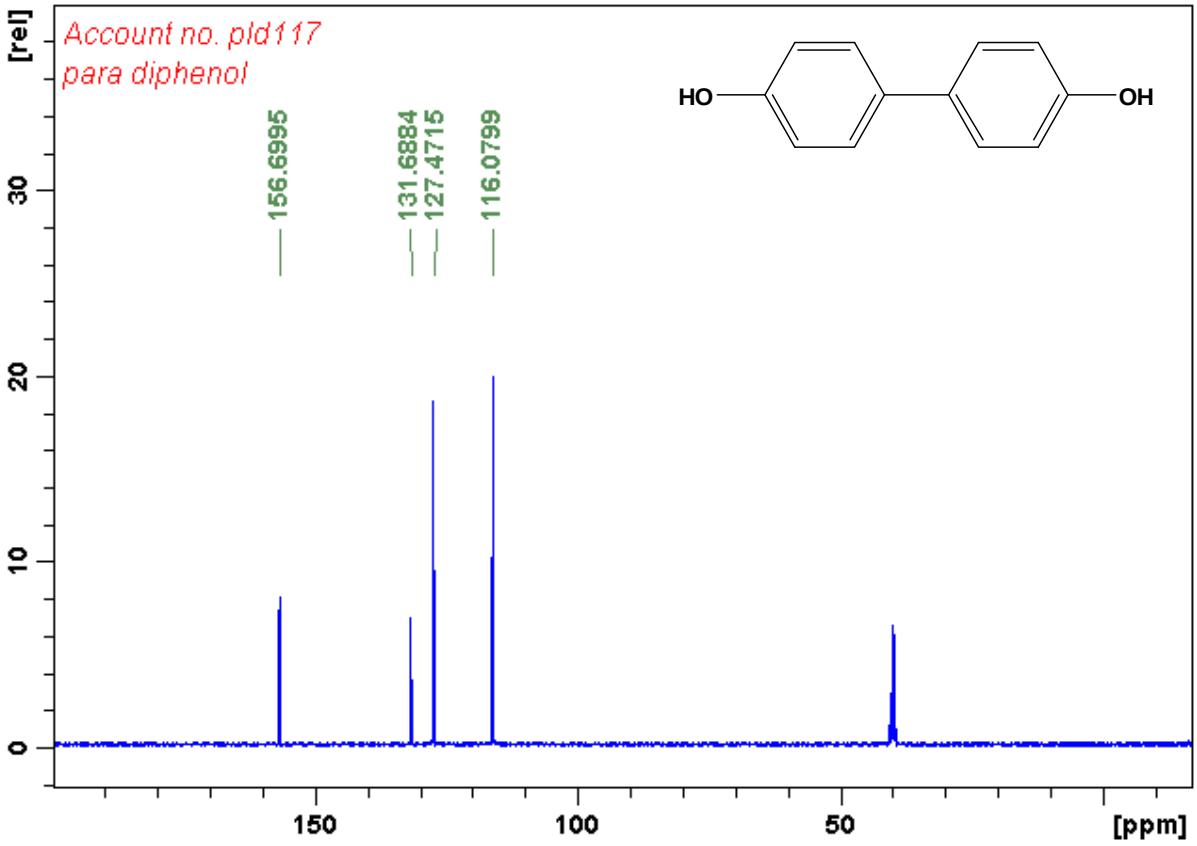

Account no. pld117
1,4-diphenylbenzene
[rel]
2.0
1.5
1.0
0.5
-0.0
7.7732
7.7380
7.7193
7.5119
7.4912
7.4746
7.4041
7.3875
7.3688
Ph
Ph
Eq 1
8.5
8.0
7.5
7.0
6.5
[ppm]

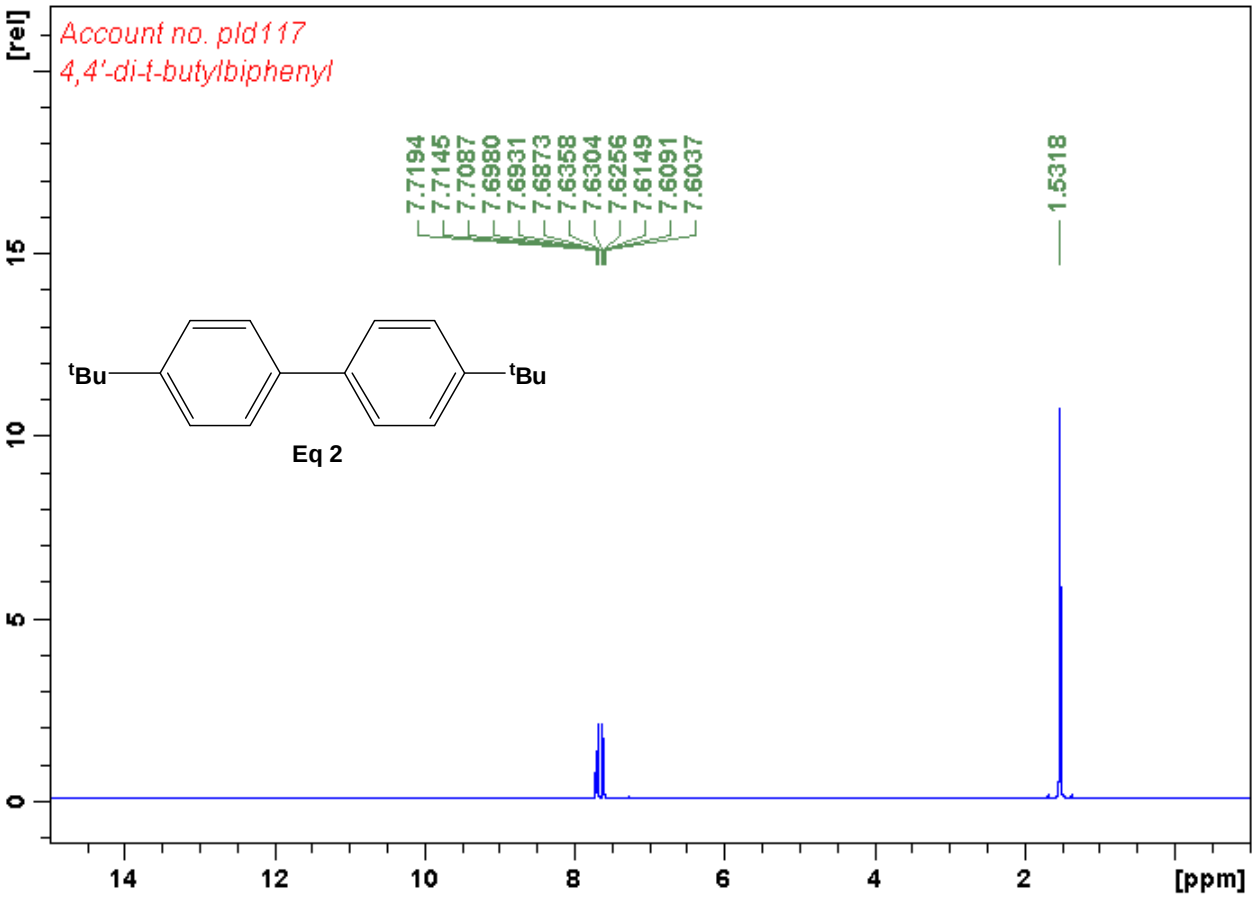

Account no. pld117
1,4-diphenylbenzene
[rel]
1.5
1.0
0.5
-0.0
Ph
Ph
Eq 1
4.0000
4.2127
4.2486
2.0827
7.8
7.6
7.4
7.2
[ppm]

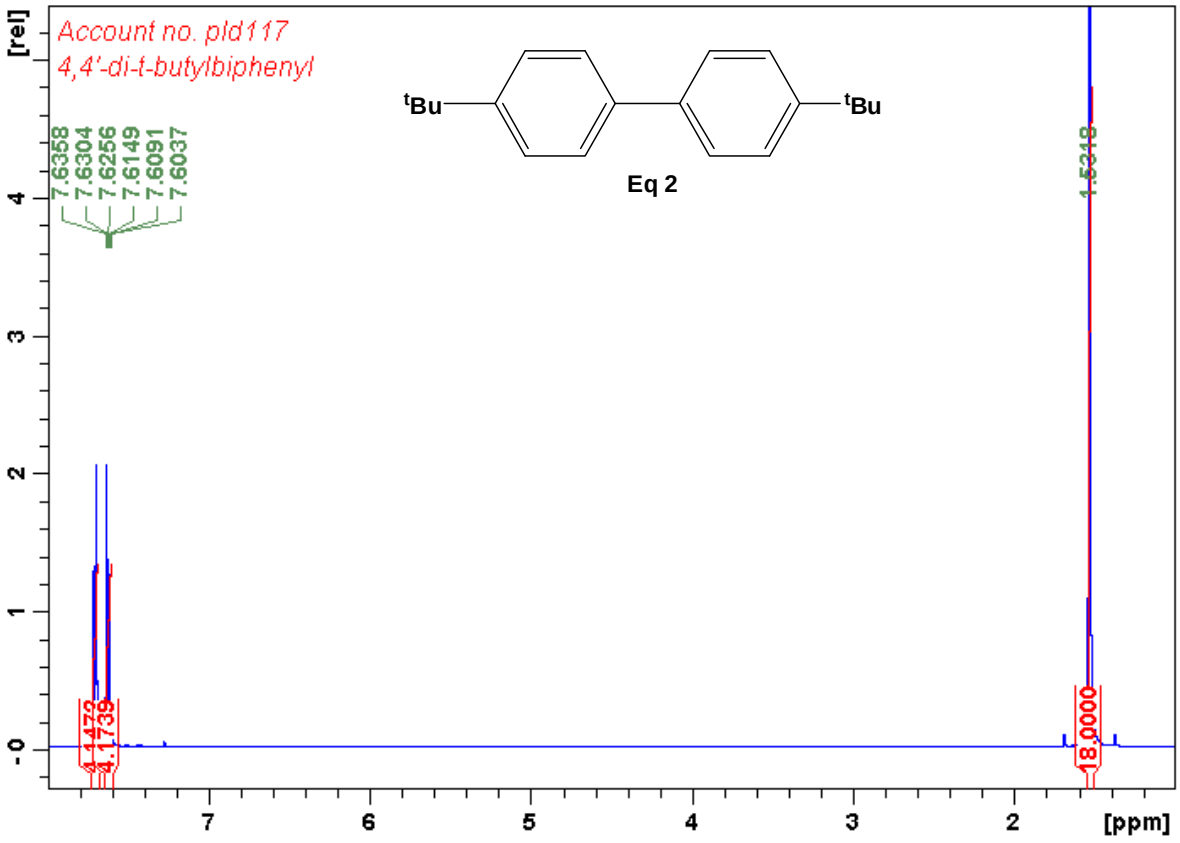

Account no. pld117
1,4-diphenylbenzene
Ph
Ph
140.0545
139.5905
129.4794
128.0122
127.6701
127.0400
Eq 1
[rel]
300
200
100
0
250
200
150
100
50
[ppm]

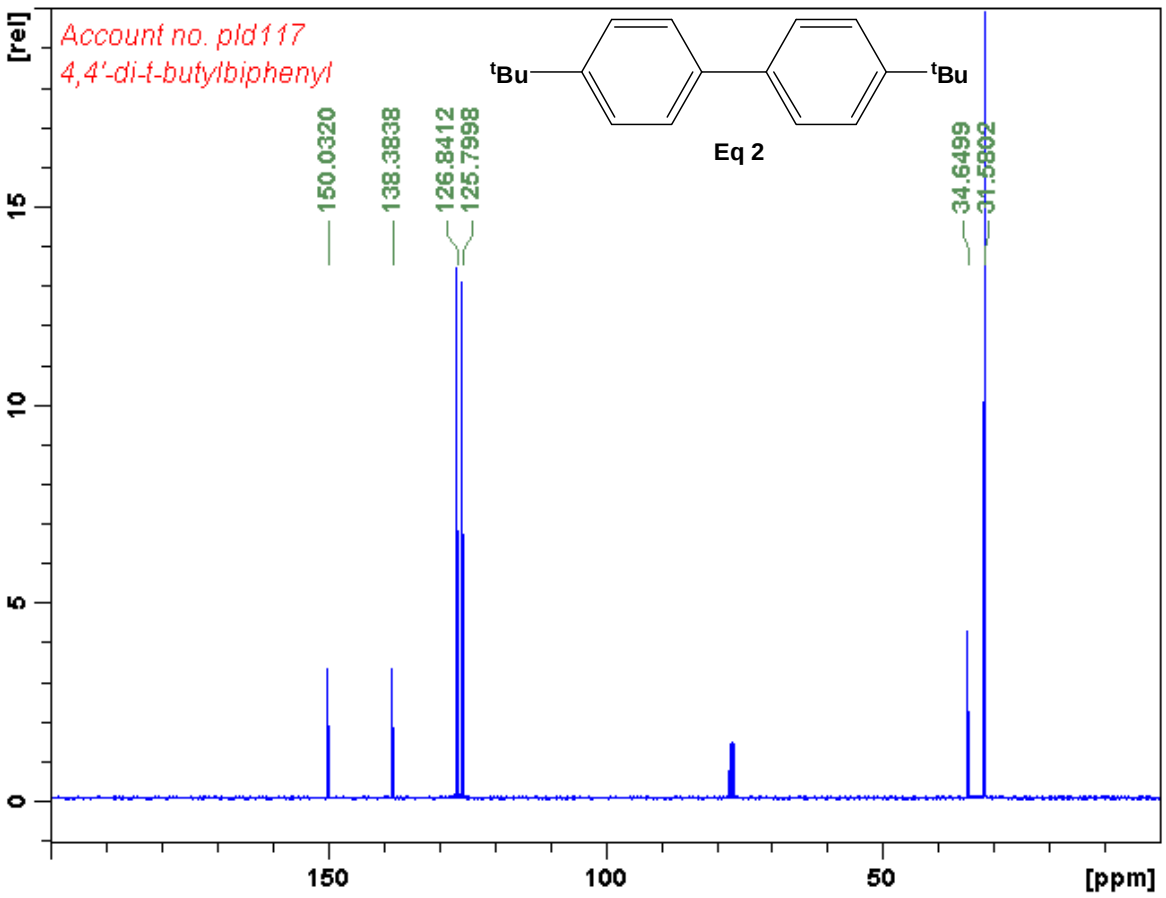

Account no. pld117
para diphenol
HO
OH
9.4191
7.3957
7.3746
6.8499
6.8288
2.5001
[rel]
30
20
10
0
14
12
10
8
6
4
2
[ppm]

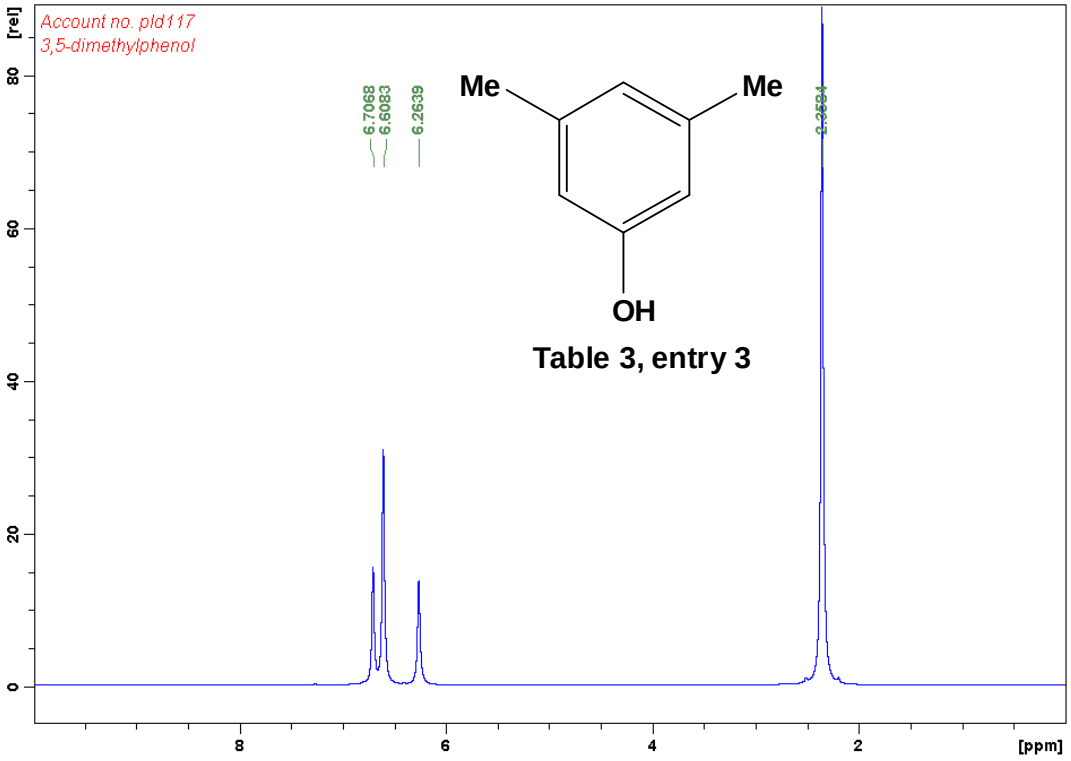

Account no. pld117
para diphenol
HO
OH
9.4191
7.3957
7.3746
6.8499
6.8288
2.0000
4.5907
4.6927
[rel]
0
10
20
30
9
8
7
6
[ppm]

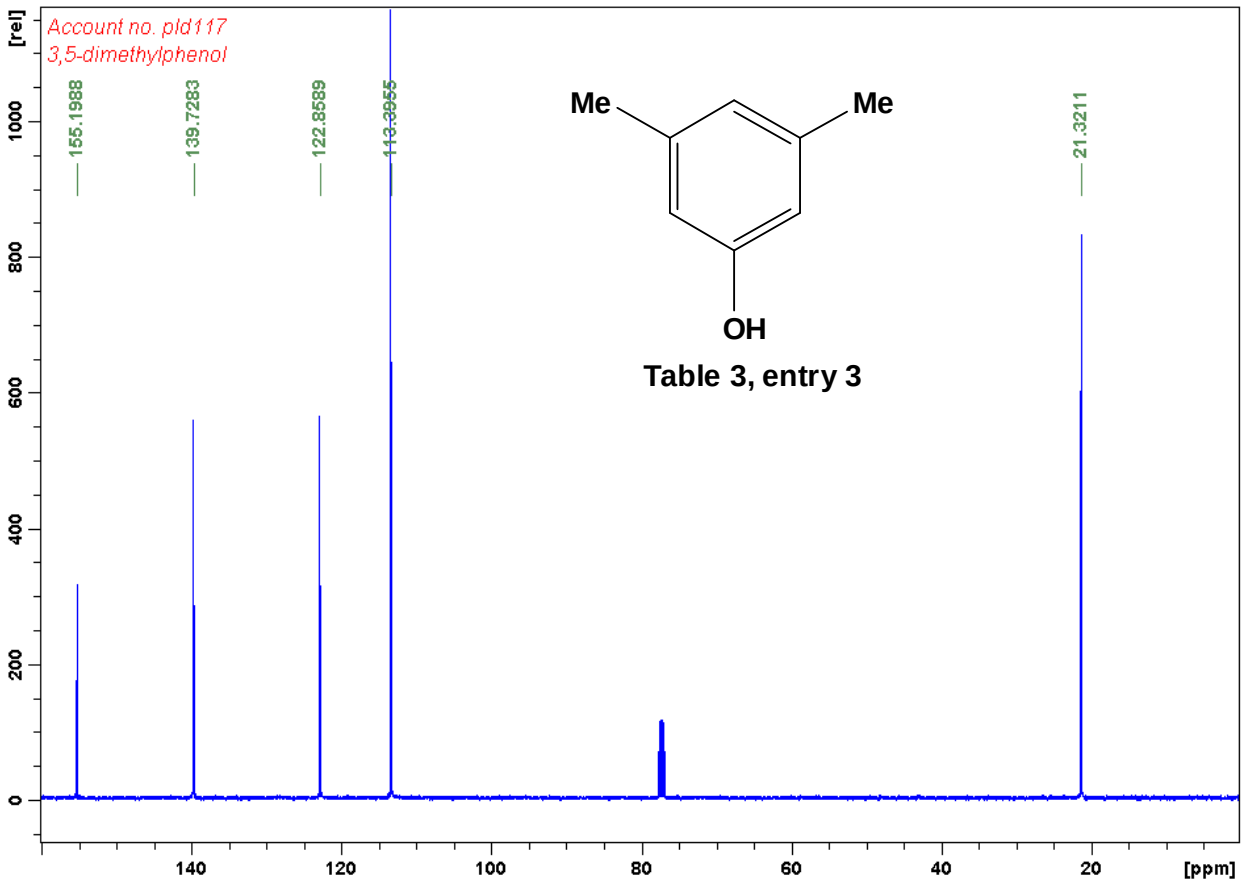

Account no. pld117
para diphenol
HO
OH
156.6995
131.6884
127.4715
116.0799
[rel]
0
10
20
30
150
100
50
[ppm]

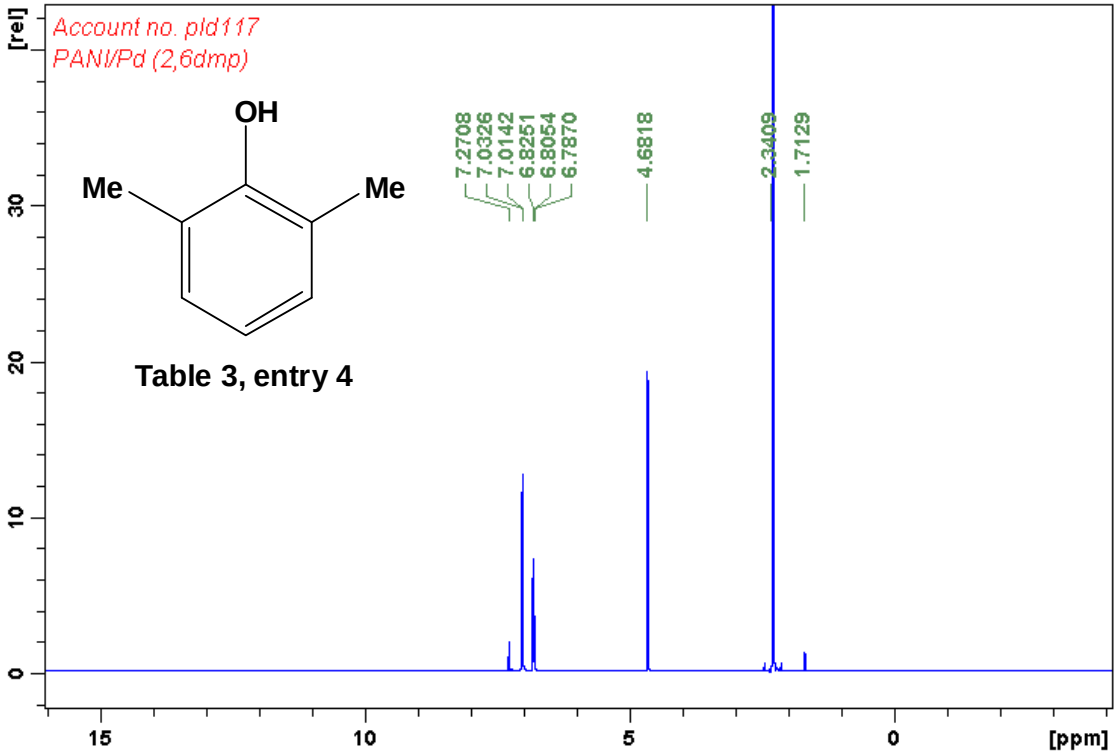

Account no. pld117
4,4'-di-t-butylbiphenyl
7.7194
7.7145
7.7087
7.6980
7.6931
7.6873
7.6358
7.6304
7.6256
7.6149
7.6091
7.6037
1.5318
tBu
tBu
Eq 2
[rel]
[ppm]

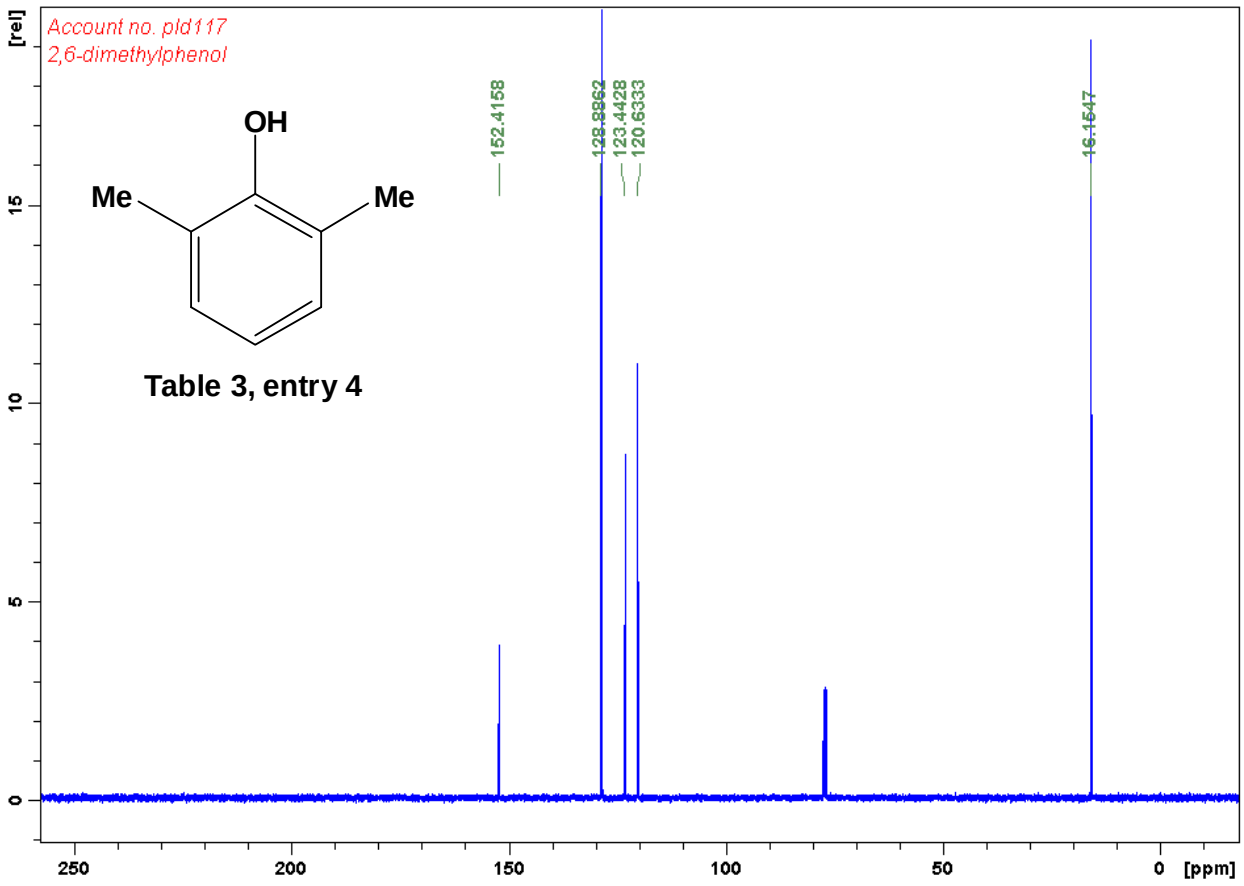

Account no. pld117
4,4'-di-t-butylbiphenyl
7.6358
7.6304
7.6256
7.6149
7.6091
7.6037
tBu
tBu
Eq 2
1.5318
4.1472
4.1738
18.0000
[rel]
[ppm]

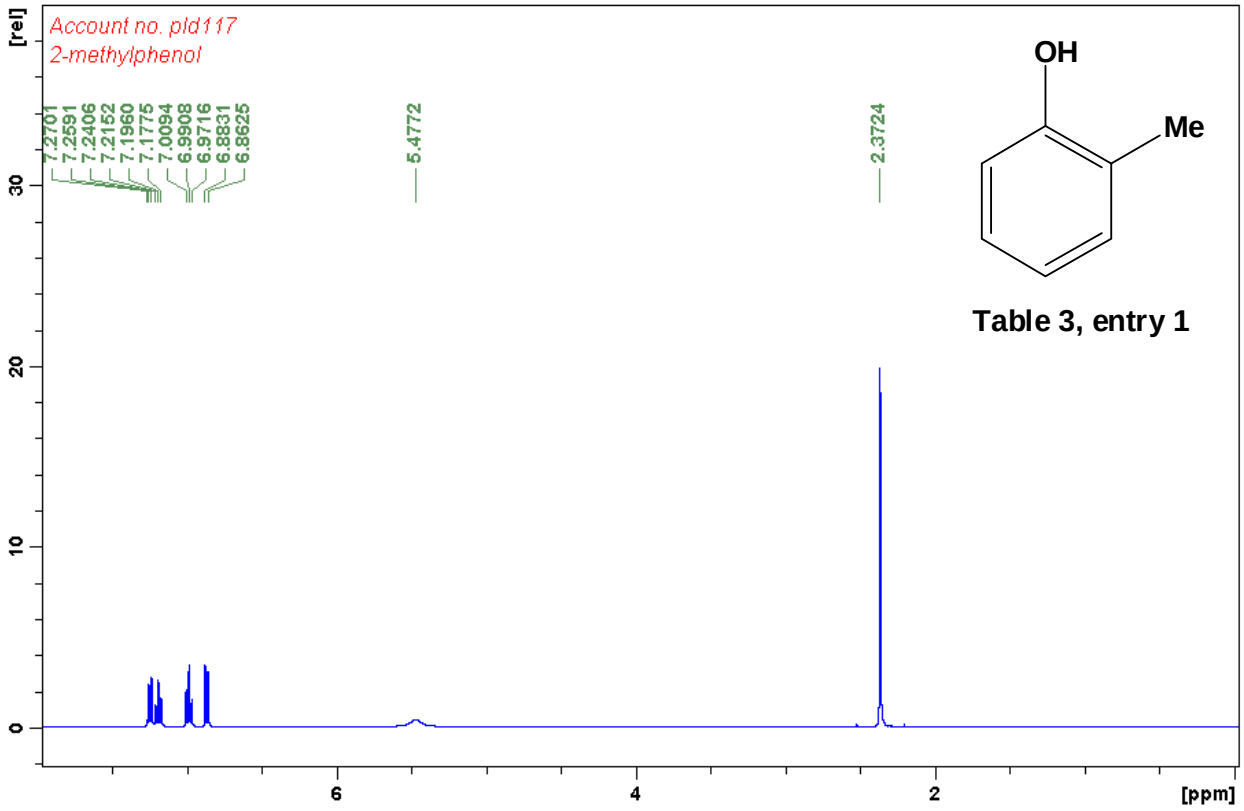

Account no. pld117
4,4'-di-t-butylbiphenyl
tBu
tBu
Eq 2
150.0320
138.3838
126.8412
125.7998
34.6499
31.5802
[rel]
15
10
5
0
150
100
50
[ppm]

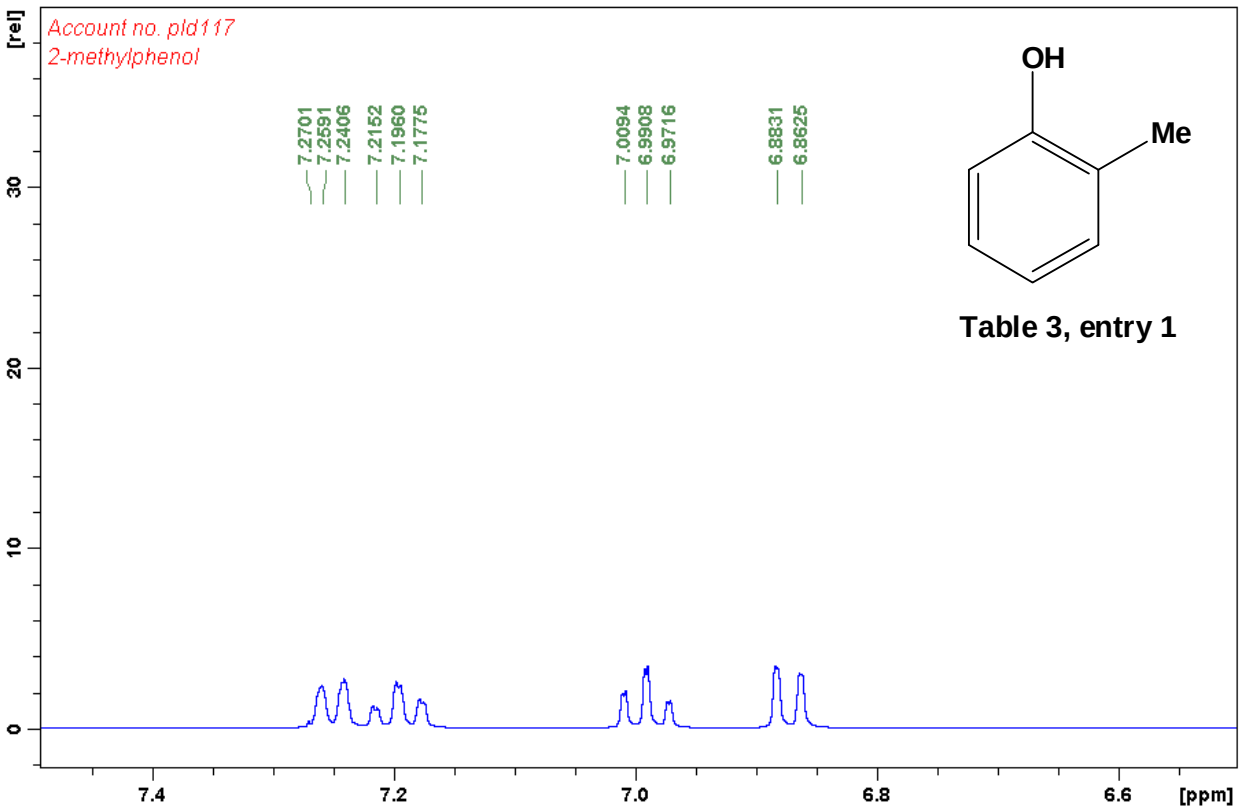

Account no. pld117
3,5-dimethylphenol
Me
Me
OH
6.7068
6.6083
6.2639
2.3584
Table 3, entry 3
[rel]
80
60
40
20
0
8
6
4
2
[ppm]

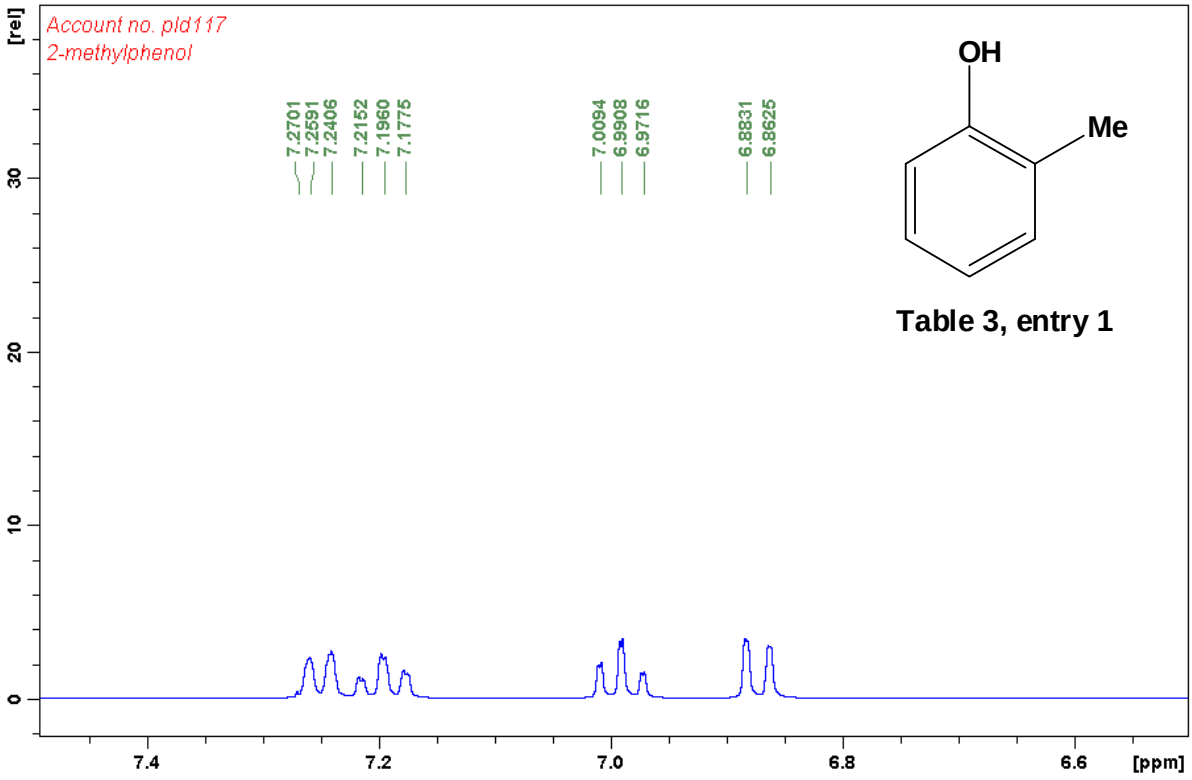

Account no. pld117
3,5-dimethylphenol
155.1988
139.7283
122.8589
113.3955
21.3211
Me
Me
OH
Table 3, entry 3
[rel]
[ppm]

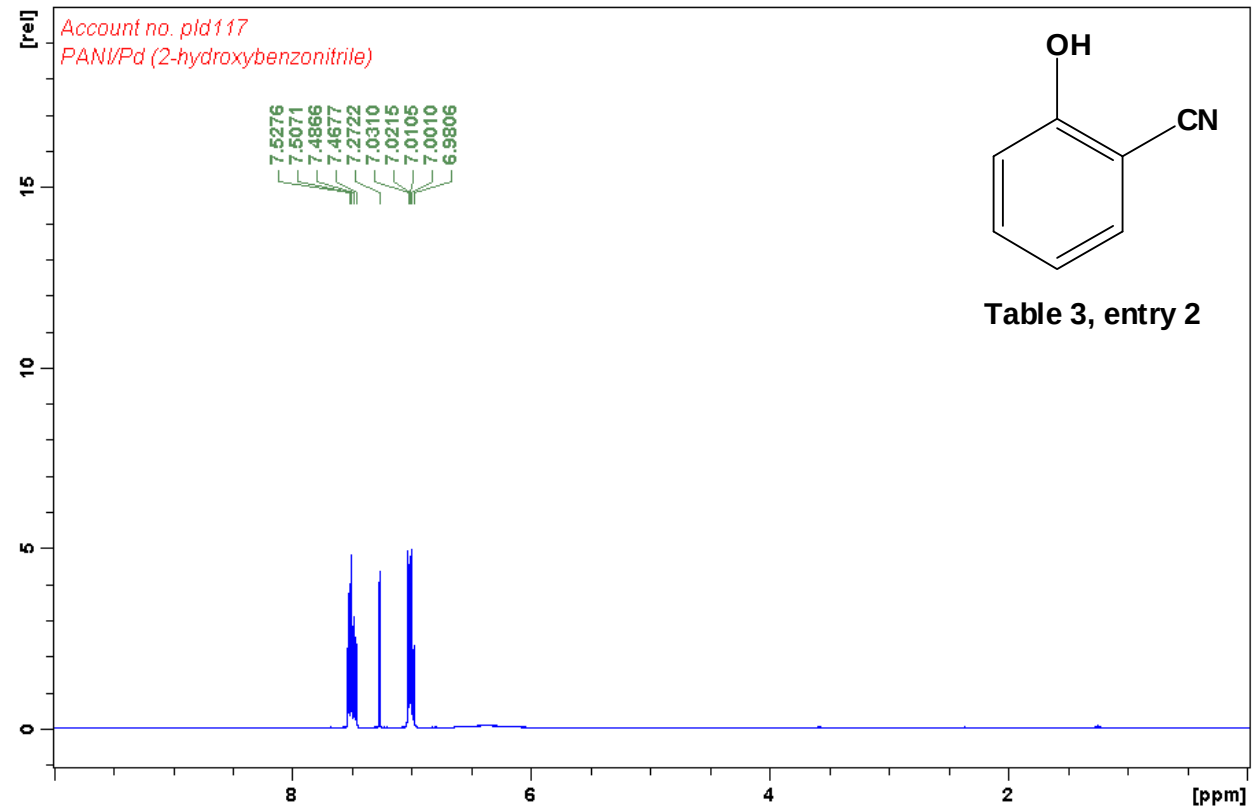

Account no. pld117
PANI/Pd (2,6dmp)
OH
Me
Me
7.2708
7.0326
7.0142
6.8251
6.8054
6.7870
4.6818
2.3409
1.7129
Table 3, entry 4
[rel]
[ppm]

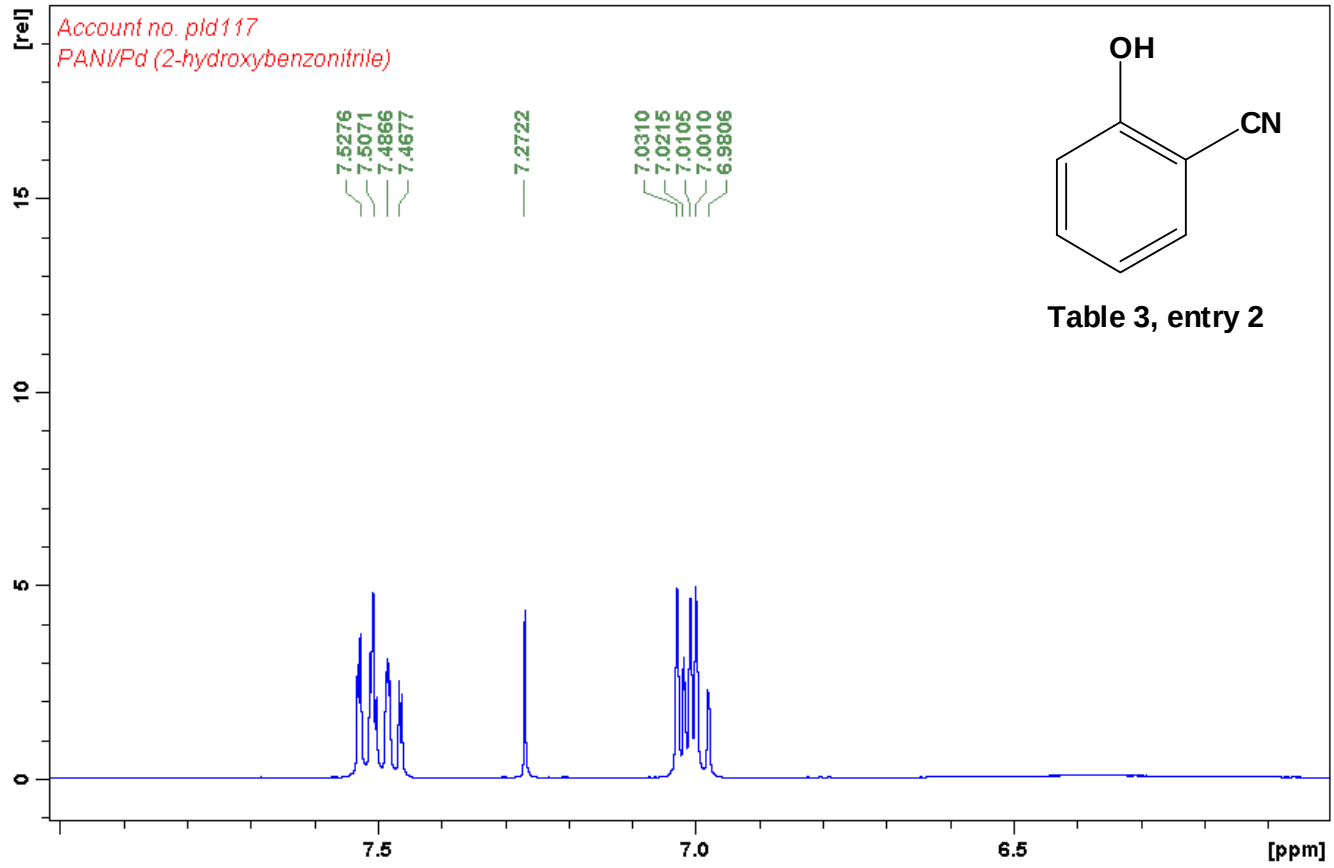

Account no. pld117
2,6-dimethylphenol
OH
Me
Me
152.4158
128.8862
123.4428
120.6333
16.1547
Table 3, entry 4
[rel]
[ppm]

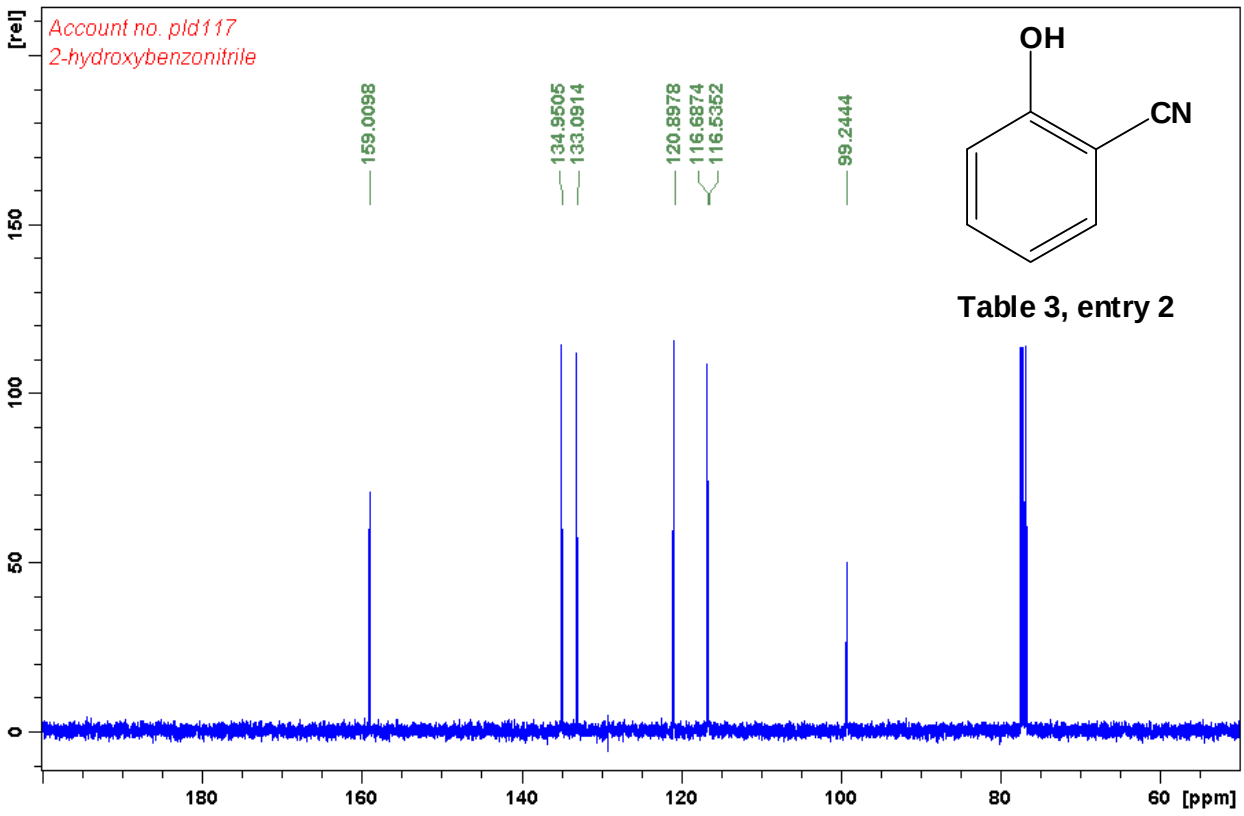

Account no. pld117
2-methylphenol
7.2701
7.2591
7.2406
7.2152
7.1960
7.1775
7.0094
6.9908
6.9716
6.8831
6.8625
5.4772
2.3724
OH
Me
Table 3, entry 1
[rel]
[ppm]

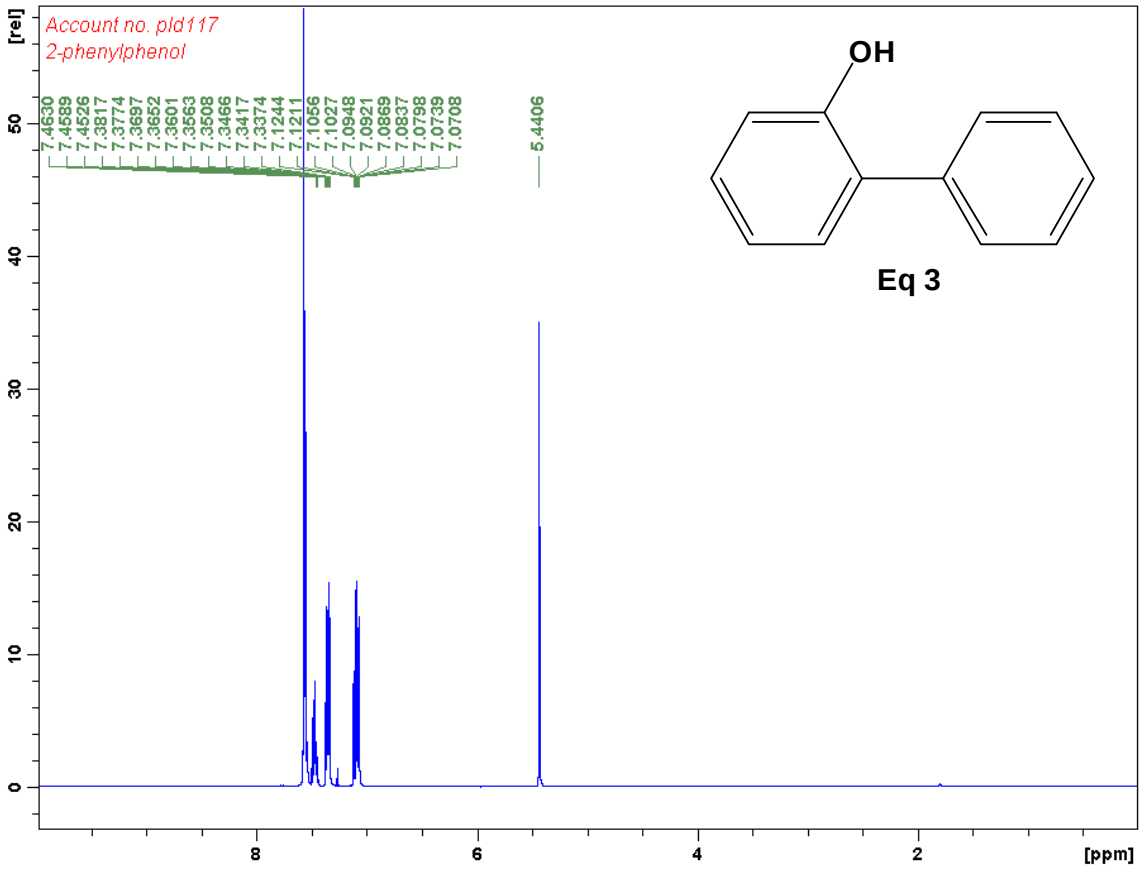

Account no. pld117
2-methylphenol
7.2701
7.2591
7.2406
7.2152
7.1960
7.1775
7.0094
6.9908
6.9716
6.8831
6.8625
OH
Me
Table 3, entry 1
[rel]
30
20
10
0
7.4
7.2
7.0
6.8
6.6
[ppm]

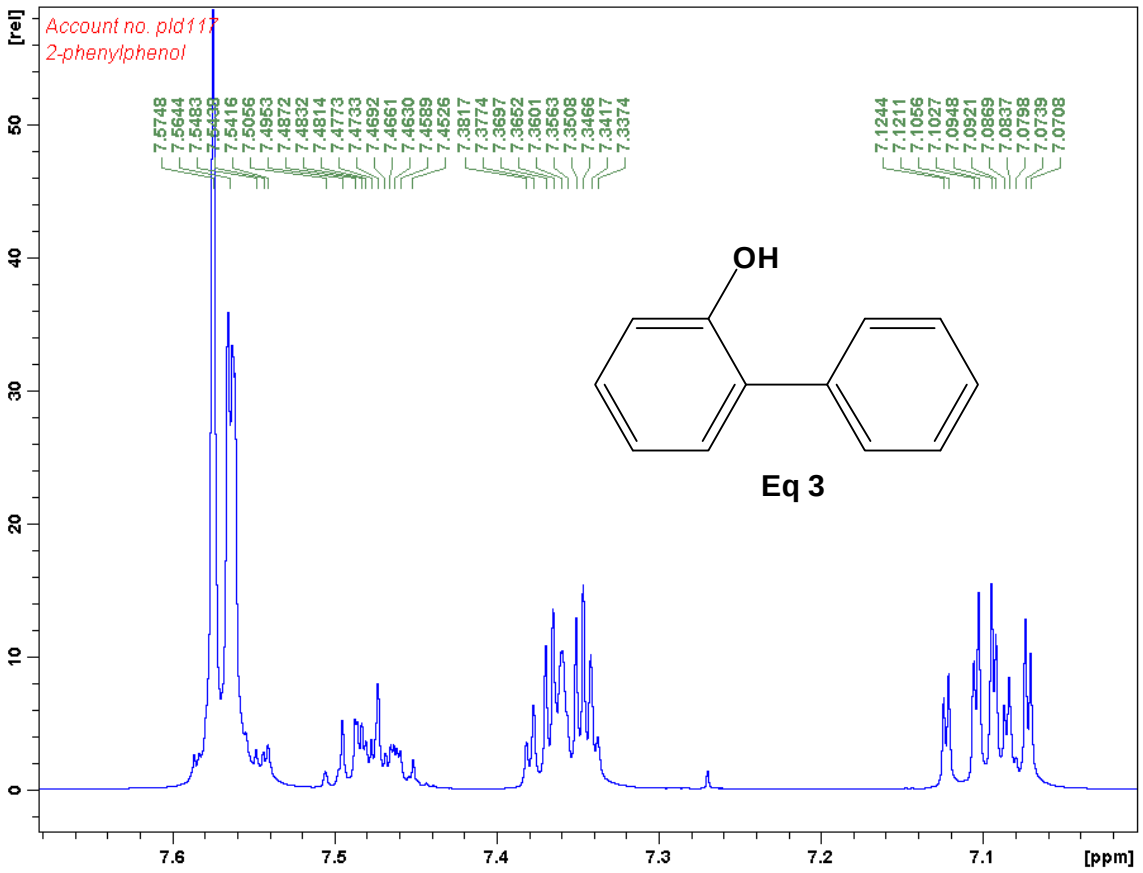

Account no. pld117
2-methylphenol
7.2701
7.2591
7.2406
7.2152
7.1960
7.1775
7.0094
6.9908
6.9716
6.8831
6.8625
OH
Me
Table 3, entry 1
[rel]
30
20
10
0
7.4
7.2
7.0
6.8
6.6
[ppm]

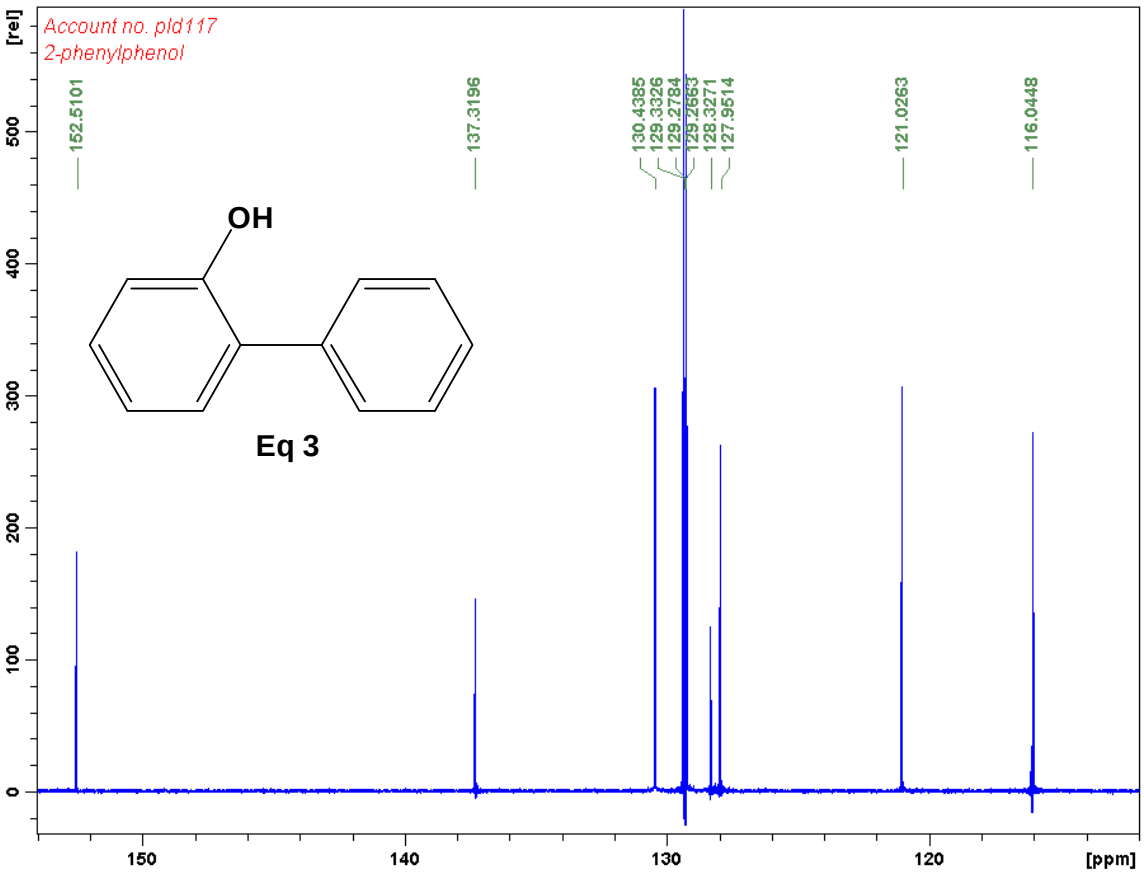

Account no. pld117
PANI/Pd (2-hydroxybenzonitrile)
7.5276
7.5071
7.4866
7.4677
7.2722
7.0310
7.0215
7.0105
7.0010
6.9806
OH
CN
Table 3, entry 2
[rel]
15
10
5
0
8
6
4
2
[ppm]


Account no. pld117
PANI/Pd (2-hydroxybenzonitrile)
7.5276
7.5071
7.4866
7.4677
7.2722
7.0310
7.0215
7.0105
7.0010
6.9806
OH
CN
Table 3, entry 2
[rel]
15
10
5
0
7.5
7.0
6.5
[ppm]

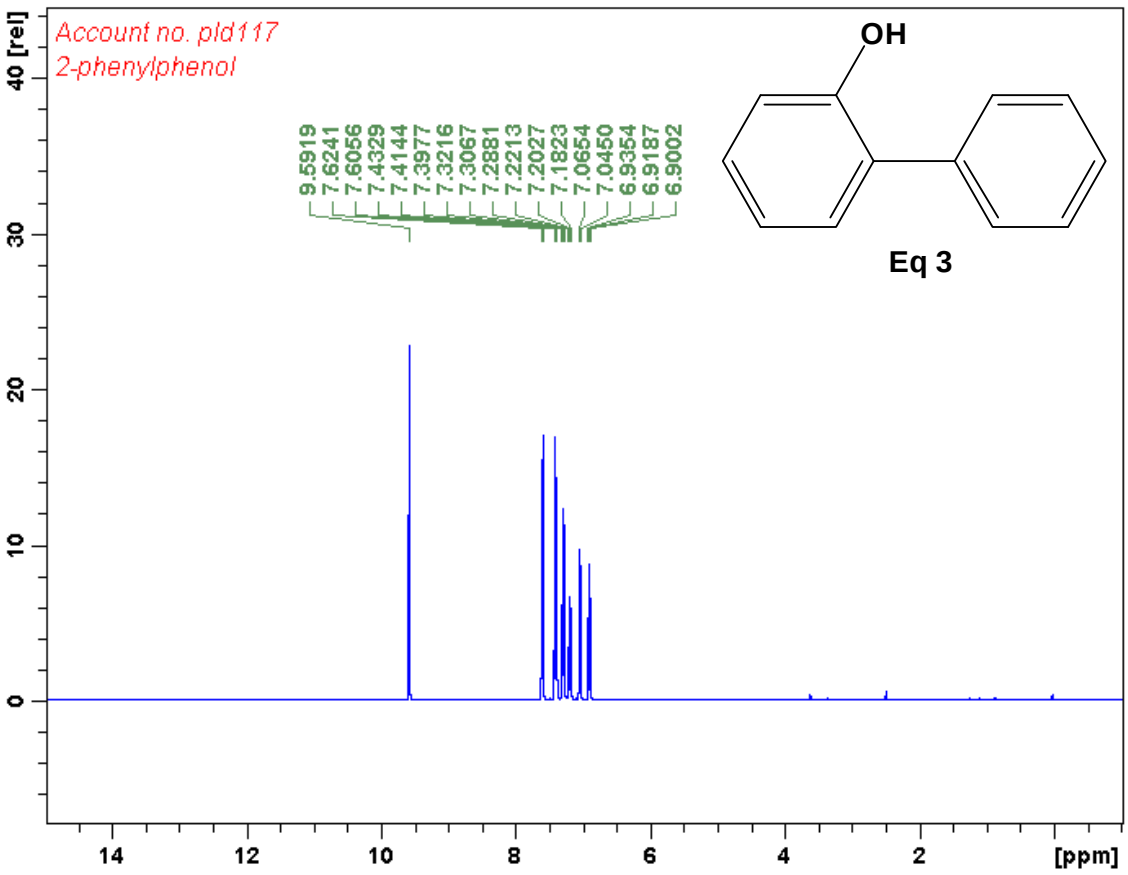

Account no. pld117
2-hydroxybenzonitrile
159.0098
134.9505
133.0914
120.8978
116.6874
116.5352
99.2444
OH
CN
Table 3, entry 2
[rel]
[ppm]

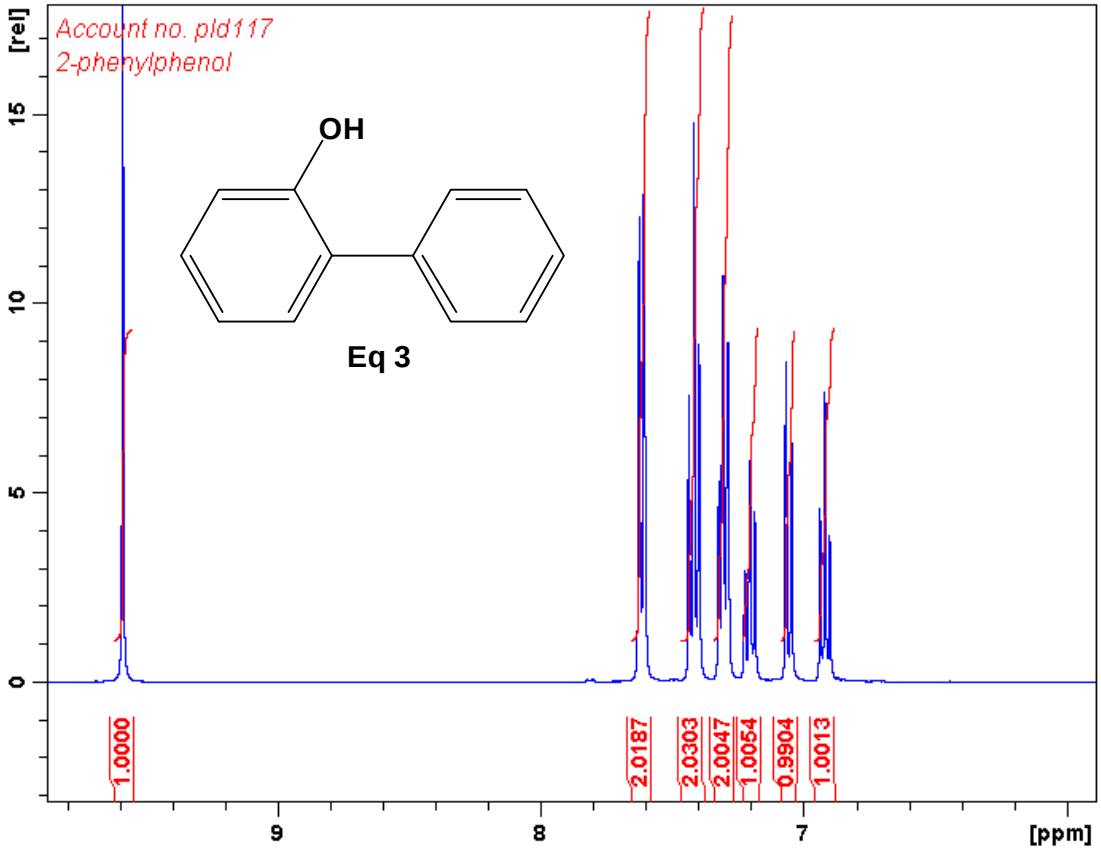

Account no. pld117
2-phenylphenol
7.4630
7.4589
7.4526
7.3817
7.3774
7.3697
7.3652
7.3601
7.3563
7.3508
7.3466
7.3417
7.3374
7.1244
7.1211
7.1056
7.1027
7.0948
7.0921
7.0869
7.0837
7.0798
7.0739
7.0708
5.4406
OH
Eq 3
[rel]
[ppm]

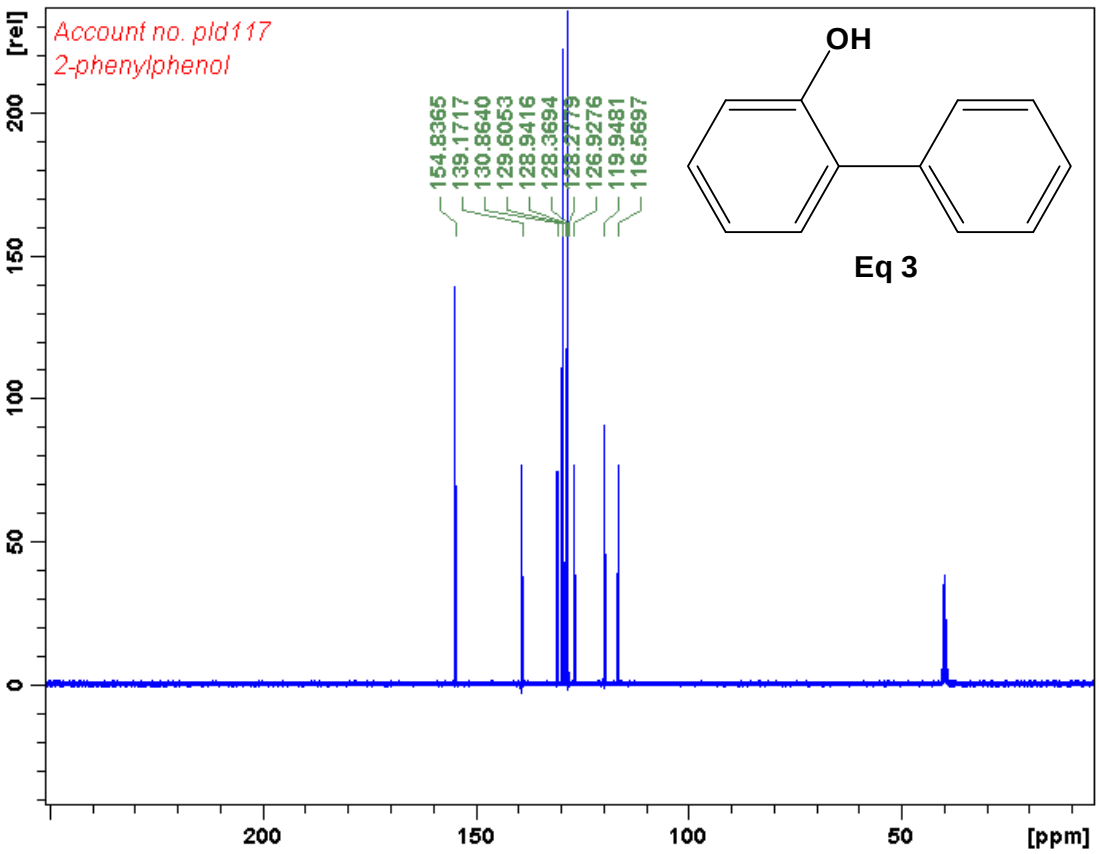


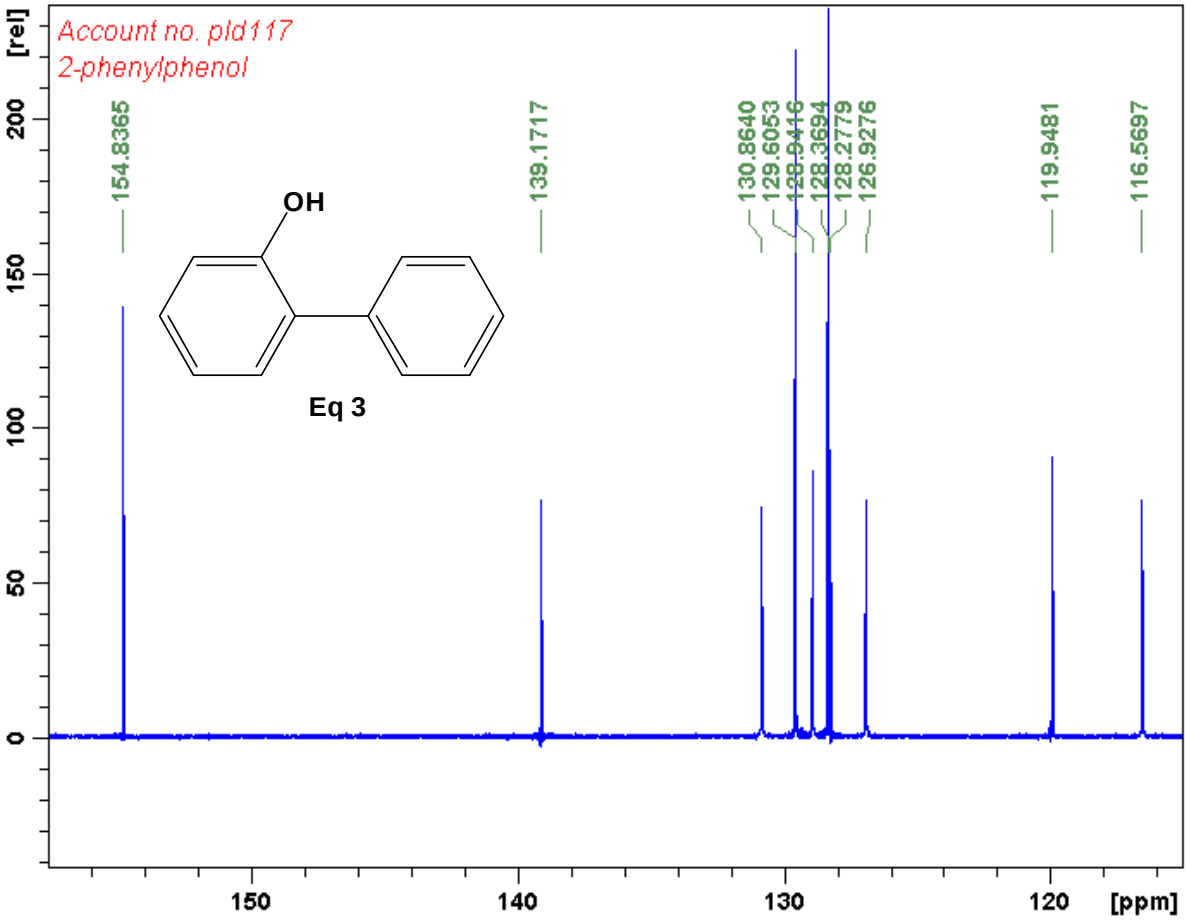


dmso-d_6 NMR spectra:


Account no. pld117
2-phenylphenol
9.5919
7.6241
7.6056
7.4329
7.4144
7.3977
7.3216
7.3067
7.2881
7.2213
7.2027
7.1823
7.0654
7.0450
6.9354
6.9187
6.9002
OH
Eq 3
40 [rel]
30
20
10
0
14
12
10
8
6
4
2
[ppm]


Account no. pld117
2-phenylphenol
OH
Eq 3
[rel]
15
10
5
0
1.0000
2.0187
2.0303
2.0047
1.0054
0.9904
1.0013
9
8
7
[ppm]


Account no. pld117
2-phenylphenol
154.8365
139.1717
130.8640
129.6053
128.9416
128.3694
128.2779
126.9276
119.9481
116.5697
OH
Eq 3
[rel]
200
150
100
50
0
200
150
100
50
[ppm]


Account no. pld117
2-phenylphenol
154.8365
139.1717
130.8640
129.6053
128.9416
128.3694
128.2779
126.9276
119.9481
116.5697
OH
Eq 3
[rel]
200
150
100
50
0
150
140
130
120
[ppm]