Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Magnetically Separable Gold Catalyst for Chemoselective Reduction of Nitro Compounds

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1. Reagents and Materials

Commercial chemicals were used without further purification unless noted. *N*,*N*-dimethyl-4-nitrobenzamide,[1] 4-benzyloxynitrobenzene[2] and benzyl 4-nitrophenylcarbamate[3] were prepared following literature procedures. 1-Fluoro-4-nitrobenzene and 4-nitrobenzyl alcohol were purified by column chromatography before use. Deionized water was used after degassing by Ar-bubbling. Flash column chromatography was carried out on silica-gel (Merck; 230-400 mesh) as the stationary phase. ^{1}H NMR and ^{13}C NMR spectra were recorded with 300 MHz instrument using TMS as internal standard and $CDCl_3$ as the solvent, unless otherwise noted.

2. Preparation of Au/Fe Oxide (**1**)

$FeSO_4 \cdot 7H_2O$ (800 mg, 2.9 mmol) aqueous solution (**A**) (15 mL, 0.19 M) was prepared in a 50 mL round bottom flask at r.t. The solution (**B**) of $HAuCl_4 \cdot xH_2O$ (30 mg, 49% Au) in water (5.0 mL) was basified by adding NaOH solution (2.0 mL, 5.0 M) (pH >11). The solution (**B**) was quickly added to the solution (**A**) while vigorously stirring (600 rpm) to obtain black suspension. The mixture was stirred under air for 4 hours with mild stirring (200 rpm). After magnetic decantation, the resulting black solid was washed with water (2 x 20 mL) and ethanol (2 x 20 mL) successively and dried under vacuum at 80℃ overnight to give **1** as magnetic black solid catalyst (260 mg; 5.7 wt% of Au).

3. General Procedure for Nitroarene Reductions

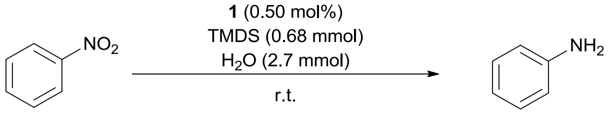
The catalyst **1** (1.0 mol%) was dispersed in ethanol (3.0 mL) with sonication and vigorous stirring (1100 rpm). A nitro compound (0.30 mmol), a hydrosilane and *p*-cymene (30 μL, 0.19 mmol) as an internal standard were added under argon. The reaction progress was monitored by GC. The catalyst was separated by magnetic decantation, and the volatiles were removed by rotary evaporator. The resulting residue was purified by column chromatography (silica gel; *n*-hexane/ethyl acetate).

4. Preparation of Au/Fe Oxide (**2**) from Commercial Iron Oxide

The catalyst was prepared by deposition-precipitation method following the procedure in the reference.[4] Fe(II, III) oxide nanopowder (<50 nm, Aldrich, 100 mg) was dispersed in H_2O (3.5 mg/mL) by mechanical stirring. $HAuCl_4 \cdot xH_2O$ aqueous solution (0.29 mL, 0.1 M) was added dropwise to the suspension while vigorously stirring, followed by addition of NaOH solution (0.2 M) to adjust pH value to 9. The mixture was stirred overnight, washed with water and dried under vacuum at 100℃ to give black solid catalyst. (102 mg; 4.8 wt% of Au)

5. Solvent Screening

Table S1 Solvent screening for nitrobenzene hydrogenation[a]



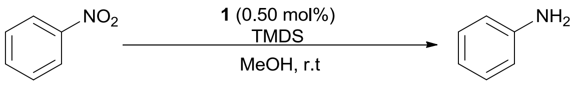
Entry	Solvent	Time (min)	Conv. (%)[b]	Yield (%)[b]
1	Toluene	720	14	6.3
2	THF	60	64	63
3	MeCN	60	31	31
4	Acetone	60	64	61
5	EtOAc	60	75	75
6[c]	Methanol	15	>99	92
7[c]	Ethanol	30	97	96
8[c]	1-Propanol	30	93	90
9[c]	2-Propanol	30	72	45

[a] General conditions : nitrobenzene (0.30 mmol), **1** (0.50 mol%), solvent (3.0 mL), *p*-cymene (0.19 mmol), water (2.7 mmol), TMDS (0.68 mmol) at r.t. under Ar balloon. [b] Determined by GC using *p*-cymene as an internal standard. [c] The reaction was carried out without adding water.

6. Recycling Test

General recycling procedure: after designated time of the reaction, catalyst was isolated by magnetic decantation using an external magnet. As washed with the solvent (3 x 3.0 mL), the catalyst was used for the next run.

Table S2 Recycling test for **1** in the reduction of nitrobenzene using MeOH as solvent.[a]

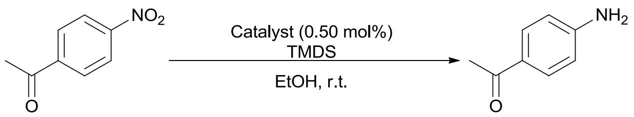


Run	1	2	3[c]	4[c]
Time (min)	15	15	45	45
Yield (%)[b]	>99	61	>99	46

[a] General conditions : nitrobenzene (0.30 mmol), **1** (0.50 mol%), MeOH (3.0 mL) and TMDS (0.83 mmol) at r.t. under Ar. [b] Determined by GC using *p*-cymene as an internal standard. [c] 0.98 mmol of TMDS was used.

7. Catalytic Activity Comparison

Table S2 Activity Comparison of the Catalysts[a]



Entry	Catalyst	Time (min)	Conv. (%)[b]	Yield (%)[b]
1	**1**	30	>99[b]	99[b]
2[c,d]	**2**	30	88	35

[a] General conditions : 1-(4-nitrophenyl)ethanone (0.30 mmol), Au catalyst (0.50 mol%), EtOH (3.0 mL) and TMDS (0.68 mmol) at r.t. 30 min under Ar. [b] Determined by GC using *p*-cymene as an internal standard. [c] Catalyst was prepared from commercial Fe_3O_4 support. [d] Corresponding hydroxylamine and azoxy compound were formed as side products (determined by ^1H NMR).

8. TEM Images of Our Catalyst after Recycling Test

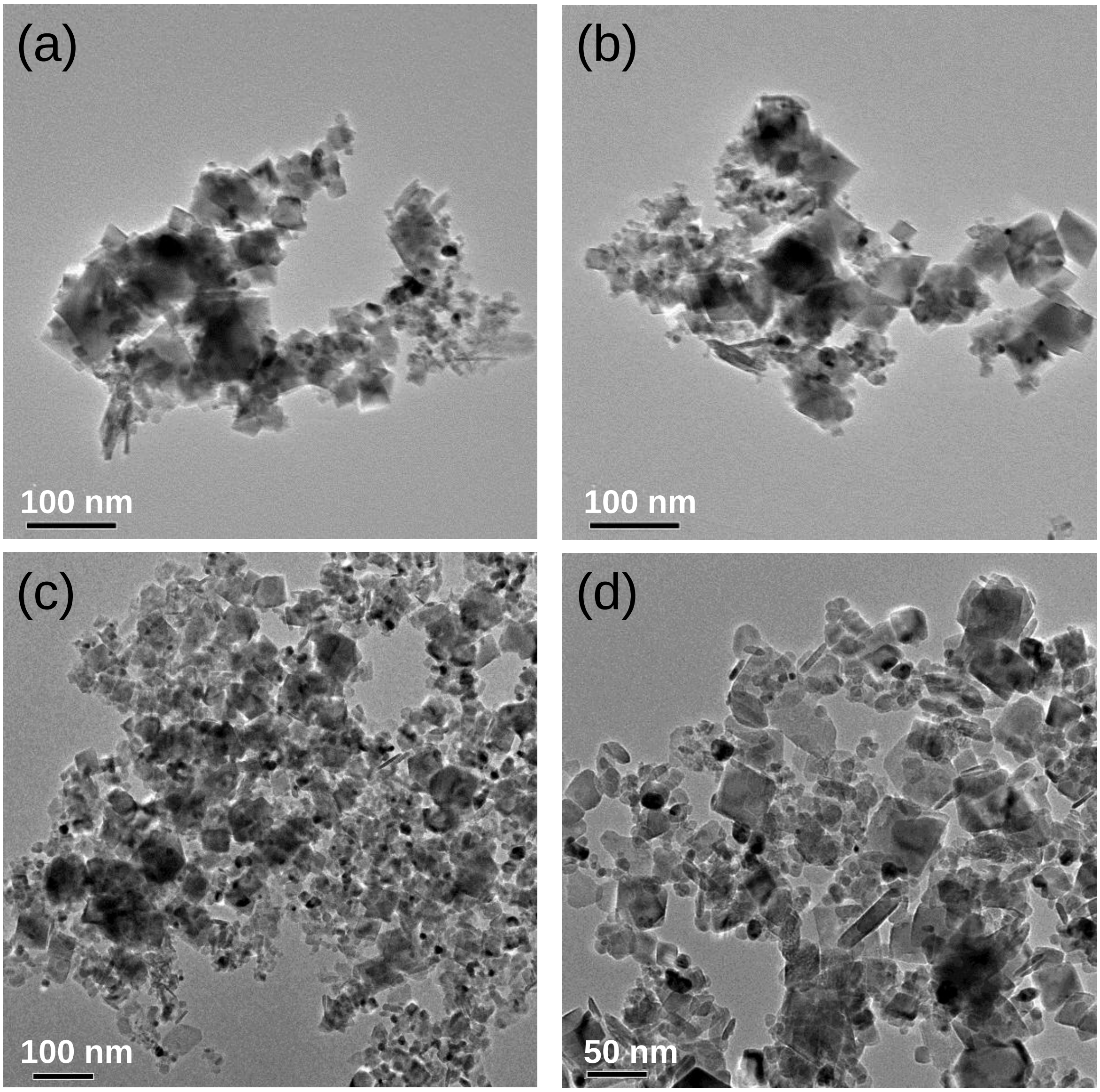


Fig. S1 TEM images of **1**: (a) and (b) before recycling test; (c) and (d) after recycling test.

9. Large Scale Reaction

1 (110 mg, 5.5 wt%) was dispersed in ethanol (30 mL) uniformly by magnetic stirring and sonication in a round bottom flask. 1-(4-nitrophenyl)ethanone (1.7 g, 10 mmol) and *p*-cymene (500 μL, 3.2 mmol) were added to the flask. While vigorously stirring the solution under Ar, TMDS (3.3 mL, 18 mmol) was added portionwise (300 μL added every 10 min). The reaction progress was monitored by GC.

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10. Catalyst Systems for the Reduction of Nitroarenes

Ref.	Catalyst	Substrate	Reductant	Solvent	Substrate/ reductant (mmol/mmol)	Cat. (mol%)	Pressure	Temp. (°C)	Time (min)	Yield (%)	Remarks
This work	**1**	Nitrobenzene	TMDS	EtOH	0.3/ 0.68	1	ambient	r.t.	10	99	
[5]	Au-NAP-Mg	Nitrobenzene	$NaBH_4$	H_2O	1.078/ 50	1	ambient	r.t.	60	91	
[6]	Au-Fe_3O_4	4-nitrophenol	$NaBH_4$	H_2O	0.0004/ 0.016	4.85	ambient	r.t.	600	>99	
[7]	Au/TiO_2	Nitrobenzene	$HCOONH_4$	EtOH	1/ 5	1	ambient	25	180	>99	
[8]	Au-Fe3O4-(core-shell)	4-nitrophenol	$NaBH_4$	H_2O	□□□□8 / 1.2	10 mg	ambient	25	30	>99	
[9]	Au/$Fe(OH)_x$	4'-Nitro acetophenone	CO/H_2O	2-ethoxyethanol	15/5~15atm	5	5~15 atm (CO)	100	150	>99	
[10]	Au/TiO_2- VS	Nitrobenzene	CO/H_2O	EtOH/H_2O (2/1)	1/1~5atm	1	1~5 atm (CO)	25	60~180	>99	
[11]	Au/Fe(OH)x	4'-Nitro acetophenone	H_2	THF	1.2/ 10 atm	0.42	10 atm	95	45	99	
[12]	Au/TiO2	3-nitrostyrene	H_2	Toluene	1/9 bar	0.23	9 bar	120	360	96	
[13]	AgNP-CeO_2	3-nitrostyrene	H_2	dodecane	0.5/ 6 atm	19	6 atm	110	360	98	
[14]	Cu or Co/phthalocyanine	Nitrobenzene	N_2H_4 H_2O	ethylene glycol	0.67/ 1.34	0.5	ambient	70	120	93	
[15]	$Fe(acac)_3$	Nitrobenzene	N_2H_4 H_2O	MeOH	2/3.6	0.25	ambient	150	2	99	microwave
[16]	$Fe(acac)_3$	Nitrobenzene	TMDS	THF	2/3	10	ambient	60	1440	>99	
[17]	Fe_3O_4	Nitrobenzene	N_2H_4 H_2O	EtOH	1/4	20	ambient	80	60	99	Low selectivity for the alkene functionality.
[18]	FePc/$FeSO_4 \cdot 7H_2O$	4-nitrobenzonitrile	N_2H_4 H_2O	EtOH/H_2O (1/1)	0.67/ 1.34	0.5	ambient	120	420	99	
[19]	Fe-phenanthrolin/C	Nitrobenzene	N_2H_4 H_2O	THF	0.5/ 2	1	ambient	100	600	99	

[20]	$FeBr_2$	Nitrobenzene	$PhSiH_3$	Toluene	1/7.5	10	ambient	110	960	85	Phosphine ligand required, 3-nitro styrene is not available.
[21]	$Fe(acac)_3$	Nitrobenzene	TMDS	THF	2/8	10	ambient	60	1440	>99	
[22]	Fe oxide hydroxide	Nitrobenzene	N_2H_4 H_2O-polymer supported	*i*-PrOH	1/ 12	200 mg	ambient	reflux (82^{o}C)	44	98	
[23]	$FeCl_3$-alumina	Nitrobenzene	N_2H_4 H_2O	neat	10/ 30	5	ambient	108	7	89	Microwave
[24]	$FeCl_3$ $6H_2O$	Nitrobenzene	H_2N-NMe_2	MeOH	3/ 31.6	1.3	ambient	85	1080	89	
[25]	InI_3	Nitrobenzene	TMDS	$CHCl_3$	0.6/1.2	5	ambient	r.t.	900	99	
[26]	$[Mo_3S_4H_3(dmpe)_3]$ BPh_4	4-methylnitrobenzene	HCOOH/Et_3N (5:2)	THF	0.1/0.35	3	ambient	70	600	99	
[27]	Ni-Fe_3O_4	Nitrobenzene	glycerol	glycerol	1/ 41	8.85	ambient	80	180	94	KOH (2 equiv.) required.
[28]	Ni-Fe mixed oxide	Nitrobenzene	N_2H_4 H_2O	*i*-PrOH	4.1/ 21	150 mg	ambient	reflux (82^{o}C)	89	93	
[29]	Pd(0) silica*Cat*	Nitrobenzene	H_2	MeOH	2/ 1 atm	0.5	1 atm	r.t.	60	100	Dechlorination occurs.
[30]	Pd(0) silica-Ionic liquid	Nitrobenzene	H_2	H_2O	17.5/ 1 atm	0.028	1 atm	30	480	100	Dechlorination occurs.
[31]	$PdCl_2$	Nitrobenzene	Et_3SiH	EtOH	1.62/ 6.48	10	ambient	r.t.	10	100	No selectivity for carbonyl, hydroxyl functionalities.
[32]	Pd/AlO(OH)	2-nitroaniline	H_2	neat	0.2/ 1 atm	2	1 atm	r.t.	5	99	No selectivity for the alkene functionality.
[33]	Pd-Fe_3O_4	Nitrobenzene	H_2	EtOH	2/ 1 atm	0.203	1 atm	r.t.	60	99	No selectivity for alkene, alkyne functionalities.
[34]	Pd-NAP-Mg	Nitrobenzene	H_2	THF	1/1 atm	1.48	1 atm	r.t.	120	98	Alkene substance is not shown.
[35]	$Pd(OAc)_2$	2-nitrotoluene	PMHS	THF	1/4	5	ambient	r.t.	30	>99	Alkene substance is not shown. Aromatic bromide, chloride is not available.
[36]	Pt/Fe_3O_4	2-chloronitrobenzene	H_2	neat	62/ 20 atm	0.099	20 atm	50	112	99	
[37]	Pt-polymer	Nitrobenzene	H_2	THF	1/1 atm	0.5	1 atm	r.t.	60	99	No selectivity for 3-nitro styrene.

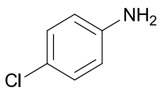
[38]	Pt/CNF-H	4-chloronitrobenzene	H_2	EA	1 / 10 atm	0.077	10 atm	r.t.	360	98	
[39]	Pt/Carbon nanofiber	4-chloronitrobenzene	H_2	EA	1/ 10 atm	0.082	10 atm	r.t.	120	99	No selectivity for the alkene functionality.
[40]	$ReIO_2(PPh_3)_2$	Nitrobenzene	$PhMe_2SiH$	Toluene	1/3.6	5	ambient	110	1440	95	Low selectivity for the alkene functionality.
[41]	Rh-polymer	Nitrobenzene	N_2H_4 H_2O	EtOH	1/ 2	0.1	ambient	60	60	99	
[42]	Rh-Fe_3O_4	Nitrobenzene	hydrazine	EtOH	1/2	1	ambient	80	60	99	No selectivity for the alkene functionality.
[43]	[{$RuCl_2$(p-cymene)}$_2$]	Nitrobenzene	iPrOH	iPrOH	0.5/solvent	2.5	ambient	100	900	98	Ligand and base are required. Low selectivity for the alkene functionality.
[44]	$Ru_3(CO)_{12}$ $N(Et)_3$	Nitrobenzene	CO/H_2O	diglyme/H_2O (15/5)	5/ 20 atm	0.2	20 atm	150	120	99	
[45]	Zn-phthalocyanine	Nitrobenzene	N_2H_4 H_2O	PEG-400	1.34/ 2.68	1	ambient	100	480	96	
[46]	reduced graphene oxide	Nitrobenzene	N_2H_4 H_2O	N_2H_4 H_2O /H_2O	0.81/ 41	10 wt%	ambient	30	2880	97	

11. Catalyst Systems for the Reduction of Nitroarenes with Hydrosilanes

Ref.	Catalyst	Substrate	Reductant	Solvent	Substrate/ Reductant (mmol/mmol)	Cat. (mol%)	Pressure	Temp (℃)	Time (h)	Yield (%)	**TON**	**TOF (h^{-1})**
This work	**1**	1-(4-nitrophenyl)ethanone	TMDS	EtOH	10/ 18	0.3	ambient	r.t.	2.5	>99	**333**	**130**
This work	**1**	Nitrobenzene	"	"	"	0.3	ambient	"	3.5	>99	**333**	**95**
[16]	$Fe(acac)_3$	"	TMDS	THF	2/ 3	10	ambient	60	24	>99	**10**	**0.42**
[20]	$FeBr_2$	"	$PhSiH_3$	Toluene	1/ 2.5	10	ambient	110	16	85	**8.5**	**0.53**
[25]	InI_3	"	TMDS	$CHCl_3$	0.6/ 1.2	5	ambient	r.t.	15	99	**20**	**1.3**
[35]	$Pd(OAc)_2$	2-Nitrotoluene	PMHS	THF	1/ 4	5	ambient	r.t.	0.5	>99	**20**	**40**
[40]	$ReIO_2(PPh_3)_2$	Nitrobenzene	$PhMe_2SiH$	Toluene	1/ 3.6	5	ambient	110	24	95	**19**	**0.79**

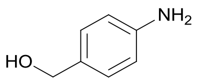
12. Spectral Data of Aniline Derivatives

4-Chloroaniline (Table 2, entry 3):[39]



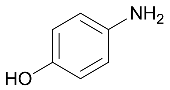
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.09 (d, J=8.7 Hz, 2H), 6.60 (d, J=8.7 Hz, 2H), 3.65 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=144.9, 129.1, 123.1, 116.2

4-Aminobenzylalcohol (Table 2, entry 5):[47]



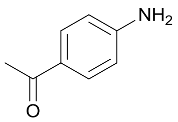
^{1}H NMR (300 MHz, $CDCl_3$)0: δ=7.14 (d, J=8.1 Hz, 2H), 6.65 (d, J=8.3 Hz, 2H), 4.53 (s, 2H), 3.42 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 146.0, 131.0, 128.7, 115.1, 65.2

4-Aminophenol (Table 2, entry 6): [39]



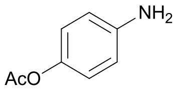
^{1}H NMR (300 MHz, DMSO-d_6): δ=8.32 (s, 1H), 6.47 (d, J=8.7 Hz, 2H), 6.41 (d, J=8.7 Hz, 2H), 4.36 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ= 148.2, 140.7, 115.5, 115.2

4-Aminoacetophenone (Table 2, entry 7): [39]



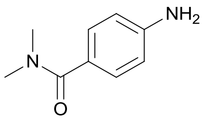
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.81 (d, J=8.7 Hz, 2H), 6.64 (d, J=8.7 Hz, 2H), 4.18 (bs, 2H), 2.50 (s, 3H)
^{13}C NMR (75 MHz, $CDCl_3$): δ= 196.5, 151.1, 130.8, 127.8, 113.7, 26.0

4-Acetoxyaniline (Table 2, entry 8):[35(b)]



^{1}H NMR (300 MHz, $CDCl_3$) : δ= 6.85 (d, J=8.7 Hz, 2H), 6.63 (d, J=7.8 Hz, 2H), 3.63 (bs, 2H), 2.24 (s, 3H)
^{13}C NMR (75 MHz, $CDCl_3$) : δ= 170.2, 144.2, 142.7, 122.0, 115.5, 21.0

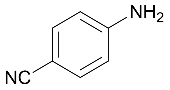
N,*N*-dimethyl-*p*-aminobenzamide (Table 2, entry 9):[1]



^{1}H NMR (300 MHz, $CDCl_3$) : δ= 7.27 (d, J=8.4, 2H), 6.63 (d, J=8.4, 2H), 3.92 (bs, 2H), 3.05 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$) : δ= 171.9, 148.0, 129.2, 125.5, 114.0, 39.8, 35.7

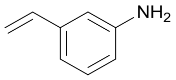
4-Cyanoaniline (Table 2, entry 10): [39]



^{1}H NMR (300 MHz, $CDCl_3$) : δ=7.42 (d, J=8.7, 2H), 6.65 (d, J=8.7, 2H), 4.15 (bs, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) : δ= 150.4, 133.7, 120.1, 114.4, 100.0

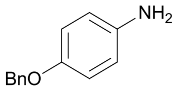
3-Vinylaniline (Table 2, entry 11): [39]



^{1}H NMR (300 MHz, $CDCl_3$) : δ= 7.11 (t, J=7.8, 1H), 6.82 (d, J=7.8, 1H), 6.72~6.56 (m, 3H), 5.68 (d, J=17.4, 1H), 5.20 (d, J=10.8, 1H), 3.63 (bs, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) : δ=146.4, 138.6, 136.9, 129.4, 116.8, 114.7, 113.6, 112.7

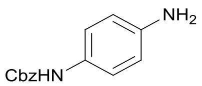
4-Benzyloxyaniline (Table 2, entry 12): [39]



^{1}H NMR (300 MHz, $CDCl_3$) : δ= 7.42~7.21 (m, 5H), 6.80 (d, J=6.6, 2H), 6.6 (d, J=6.6, 2H), 4.96 (s, 2H), 3.38 (bs, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) : δ= 151.8, 140.2, 137.4, 128.4, 127.7, 127.4, 116.2, 115.9, 70.6

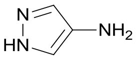
Benzyl-4-aminophenylcarbamate (Table 2, entry 13): [48]



^{1}H NMR (300 MHz, $CDCl_3$) : δ= 7.39 (m, 5H), 7.13 (d, J=7.2, 2H), 6.60 (m, 3H), 5.16 (s, 2H), 3.55 (bs, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) : δ=153.8, 142.7, 136.2, 129.0, 128.5, 128.3, 128.1, 121.0, 115.5, 66.7

1*H*-pyrazol-4-amine (Table 2, entry 14): [49]



^{1}H NMR (300 MHz, DMSO-d$_6$) : δ= 11.77 (bs, 1H), 6.99 (s, 2H), 3.42 (bs, 2H)

^{13}C NMR (75 MHz, DMSO-d$_6$) : δ= 130.1, 122.7

13. References

[1] Y. Sunada, H. Kawakami, T. Imaoka, Y. Motoyama and H. Nagashima, *Angew. Chem. Int. Ed.*, 2009, **48**, 9511-9514.

[2] A. K. Chakraborti and S. V. Chankeshwara, *J. Org. Chem.*, 2008, **74**, 1367-1370.

[3] J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller and J. S. Fowler, *Angew. Chem. Int. Ed.*, 2009, **48**, 3482-3485.

[4] Z.-M. Cui, Z. Chen, L.-Y. Jiang, W.-G. Song and L. Jiang, *Mater. Lett.*, 2011, **65**, 82-84.

[5] K. Layek, M. Lakshmi Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki and M. H, *Green Chem.*, 2012, **14**, 3164-3174.

[6] F.-h. Lin and R.-a. Doong, *J. Phys. Chem. C*, 2011, **115**, 6591-6598.

[7] X.-B. Lou, L. He, Y. Qian, Y.-M. Liu, Y. Cao and K.-N. Fan, *Adv. Synth. Catal.*, 2011, **353**, 281-286.

[8] Y. Wu, T. Zhang, Z. Zheng, X. Ding and Y. Peng, *Mater. Res. Bull.*, 2010, **45**, 513-517.

[9] L. Liu, B. Qiao, Z. Chen, J. Zhang and Y. Deng, *Chem. Commun.*, 2009, 653-655.

[10] L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He and K.-N. Fan, *Angew. Chem., Int. Ed.*, 2009, **48**, 9538-9541.

[11] L. Liu, B. Qiao, Y. Ma, J. Zhang and Y. Deng, *Dalton Trans.*, 2008, 2542-2548.

[12] A. Corma and P. Serna, *Science*, 2006, **313**, 332-334.

[13] T. Mitsudome, Y. Mikami, M. Matoba, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2012, **51**, 136-139.

[14] U. Sharma, P. Kumar, N. Kumar, V. Kumar and B. Singh, *Adv. Synth. Catal.*, 2010, **352**, 1834-1840.

[15] D. Cantillo, M. Baghbanzadeh and C. O. Kappe, *Angew. Chem., Int. Ed.*, 2012, **51**, 10190-10193.

[16] L. Pehlivan, E. Métay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani and M. Lemaire, *Tetrahedron*, 2011, **67**, 1971-1976.

[17] S. Kim, E. Kim and B. M. Kim, *Chem. Asian J.*, 2011, **6**, 1921-1925.

[18] U. Sharma, P. K. Verma, N. Kumar, V. Kumar, M. Bala and B. Singh, *Chem. Eur. J.*, 2011, **17**, 5903-5907.

[19] R. V. Jagadeesh, G. Wienhofer, F. A. Westerhaus, A.-E. Surkus, M.-M. Pohl, H. Junge, K. Junge and M. Beller, *Chem. Commun.*, 2011, **47**, 10972-10974.

[20] K. Junge, B. Wendt, N. Shaikh and M. Beller, *Chem. Commun.*, 2010, **46**, 1769-1771.

[21] L. Pehlivan, E. Metay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani and M. Lemaire, *Tetrahedron Lett.*, 2010, **51**, 1939-1941.

[22] Q. Shi, R. Lu, K. Jin, Z. Zhang and D. Zhao, *Green Chem.*, 2006, **8**, 868-870.

[23] A. Vass, J. Dudás, J. Tóth and R. S. Varma, *Tetrahedron Lett.*, 2001, **42**, 5347-5349.

[24] S. R. Boothroyd and M. A. Kerr, *Tetrahedron Lett.*, 1995, **36**, 2411-2414.

[25] N. Sakai, K. Fujii, S. Nabeshima, R. Ikeda and T. Konakahara, *Chem. Commun.*, 2010, **46**, 3173-3175.

[26] I. Sorribes, G. Wienhöfer, C. Vicent, K. Junge, R. Llusar and M. Beller, *Angew. Chem., Int. Ed.*, 2012, **51**, 7794-7798.

[27] M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski and O. M. N. D. Teodoro, *Chem. Eur. J.*, 2012, **18**, 12628-12632.

[28] Q. Shi, R. Lu, L. Lu, X. Fu and D. Zhao, *Adv. Synth. Catal.*, 2007, **349**, 1877-1881.

[29] V. Pandarus, R. Ciriminna, F. Beland and M. Pagliaro, *Catal. Sci. Technol.*, 2011, **1**, 1616-1623.

[30] J. Li, X.-Y. Shi, Y.-Y. Bi, J.-F. Wei and Z.-G. Chen, *ACS Catalysis*, 2011, **1**, 657-664.

[31] M. Mirza-Aghayan, R. Boukherroub, M. Rahimifard and M. Bolourtchian, *Appl. Organomet. Chem.*, 2010, **24**, 477-480.

[32] F. Chang, H. Kim, B. Lee, S. Park and J. Park, *Tetrahedron Lett.*, 2010, **51**, 4250-4252.

[33] A. J. Amali and R. K. Rana, *Green Chem.*, 2009, **11**, 1781-1786.

[34] M. L. Kantam, R. Chakravarti, U. Pal, B. Sreedhar and S. Bhargava, *Adv. Synth. Catal.*, 2008, **350**, 822-827.

[35] (a) R. J. Rahaim Jr and R. E. Maleczka Jr, *Synthesis*, 2006, 3316-3340.; (b) R. J. Rahaim and R. E. Maleczka, *Org. Lett.*, 2005, **7**, 5087-5090.

[36] C. Lian, H. Liu, C. Xiao, W. Yang, K. Zhang, Y. Liu and Y. Wang, *Chem. Commun.*, 2012, **48**, 3124-3126.

[37] K. Xu, Y. Zhang, X. Chen, L. Huang, R. Zhang and J. Huang, *Adv. Synth. Catal.*, 2011, **353**, 1260-1264.

[38] Y. Motoyama, Y. Lee, K. Tsuji, S.-H. Yoon, I. Mochida and H. Nagashima, *ChemCatChem*, 2011, **3**, 1578-1581.

[39] M. Takasaki, Y. Motoyama, K. Higashi, S.-H. Yoon, I. Mochida and H. Nagashima, *Org. Lett.*, 2008, **10**, 1601-1604.

[40] R. G. de Noronha, C. C. Romão and A. C. Fernandes, *J. Org. Chem.*, 2009, **74**, 6960-6964.

[41] P. Luo, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing and J. Huang, *Catal. Sci. Technol.*, 2012, **2**, 301-304.

[42] Y. Jang, S. Kim, S. W. Jun, B. H. Kim, S. Hwang, I. K. Song, B. M. Kim and T. Hyeon, *Chem. Commun.*, 2011, **47**, 3601-3603.

[43] R. V. Jagadeesh, G. Wienhöfer, F. A. Westerhaus, A.-E. Surkus, H. Junge, K. Junge and M. Beller, *Chem. Eur. J.*, 2011, **17**, 14375-14379.

[44] N. Kotohiro, *J. Mol. Catal. A: Chem.*, 1995, **95**, 203-210.

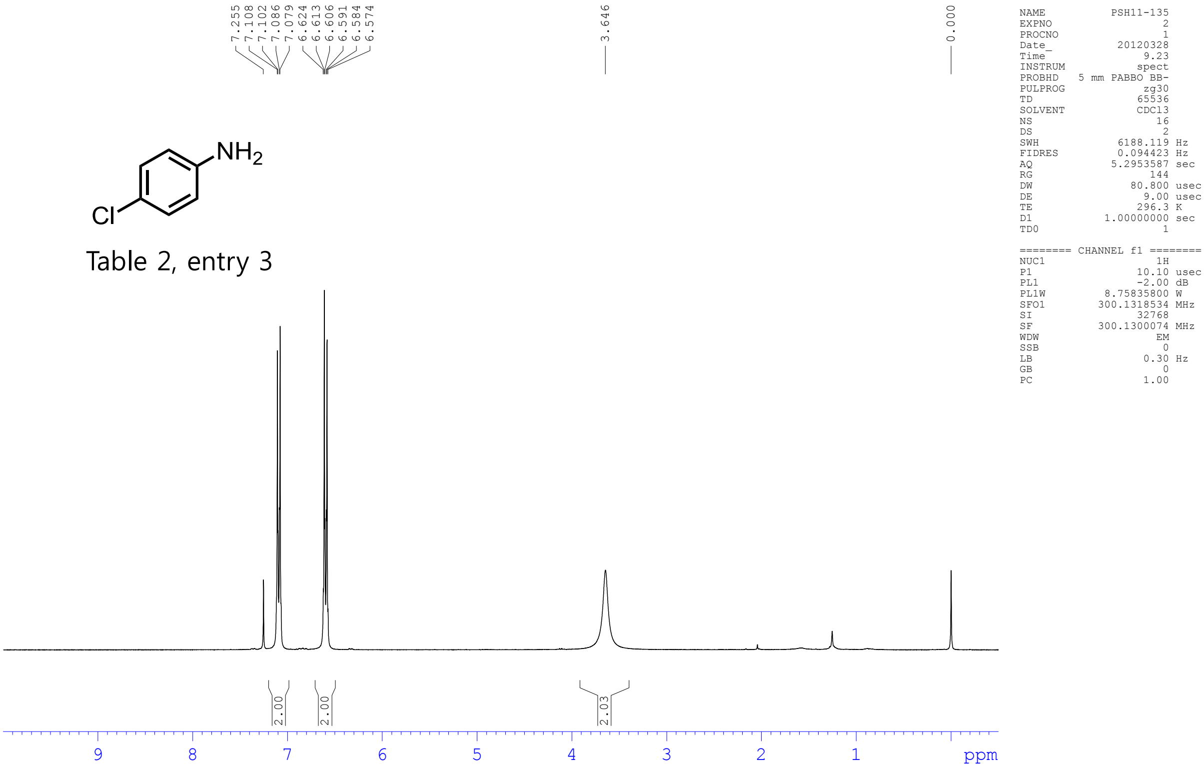
[45] U. Sharma, N. Kumar, P. K. Verma, V. Kumar and B. Singh, *Green Chem.*, 2012, **14**, 2289-2293.

[46] Y. Gao, D. Ma, C. Wang, J. Guan and X. Bao, *Chem. Commun.*, 2011, **47**, 2432-2434.

[47] J. Kim and S. Chang, *Chem. Commun.*, 2008, 3052-3054.

[48] *Eu. Pat.*, 2 070 899, 2008.

[49] *WO Pat.*, 075542, 2010.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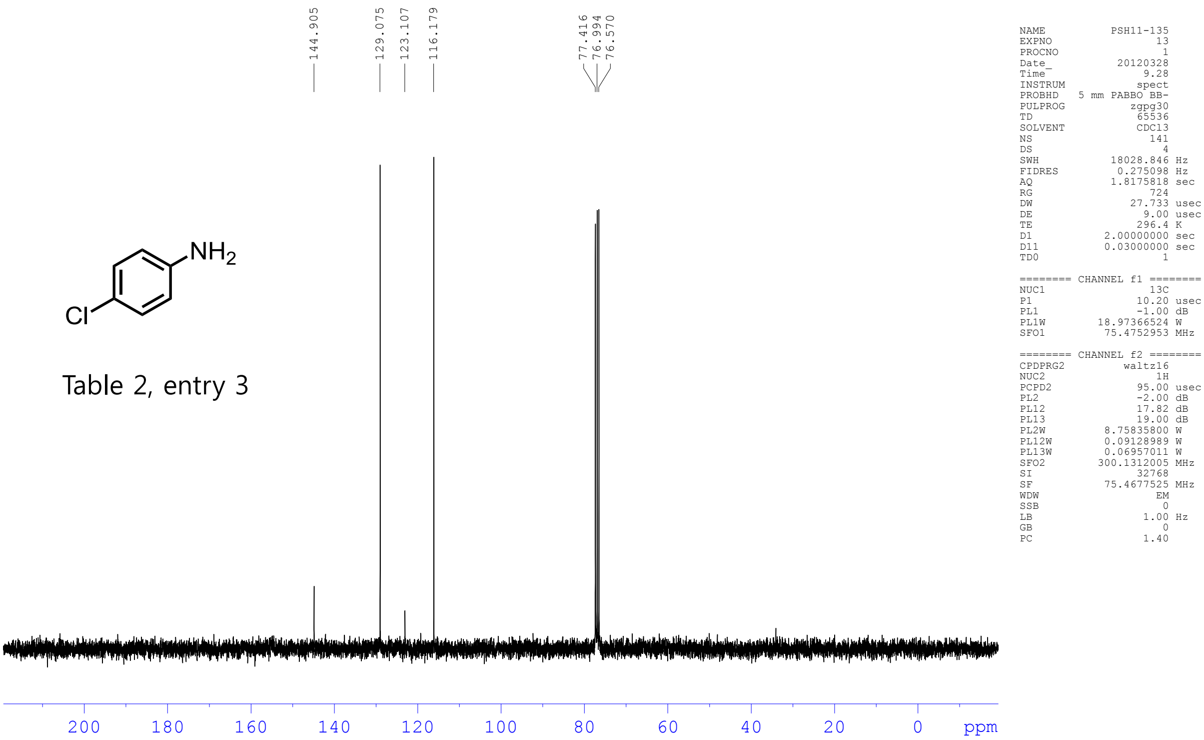
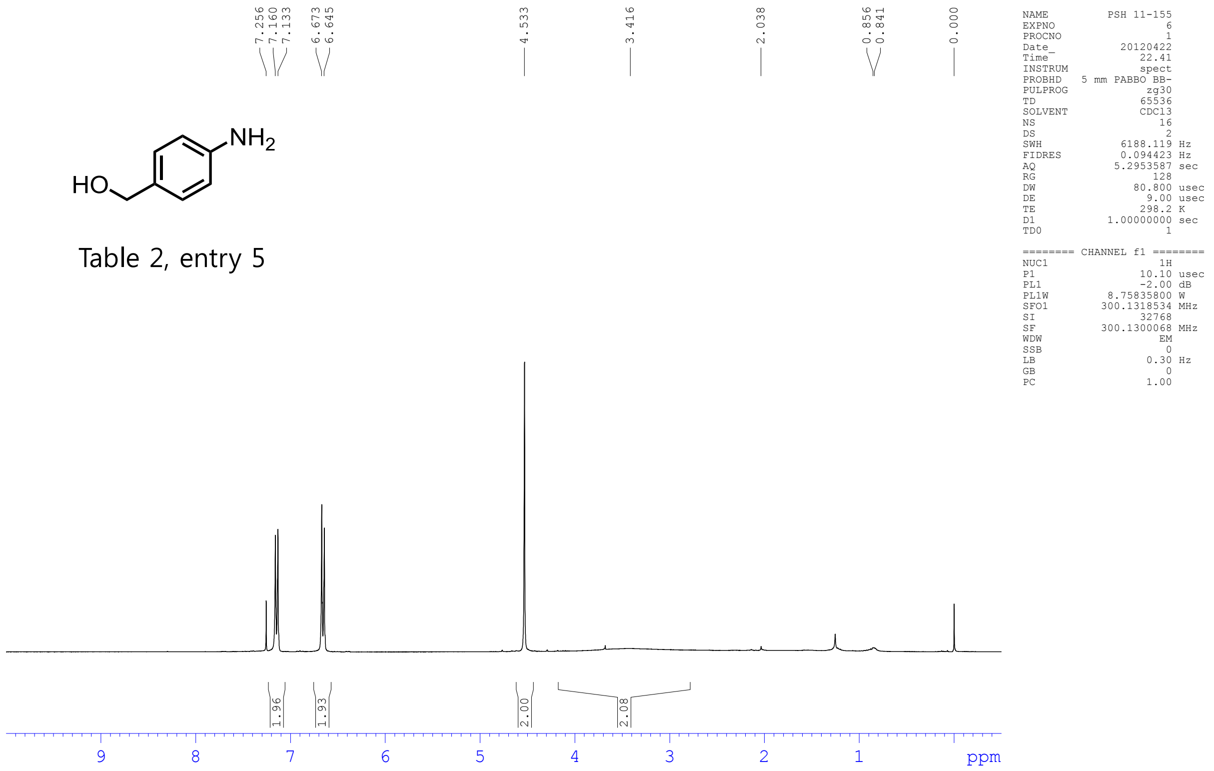
7.102
7.086
7.079
6.624
6.613
6.606
6.591
6.584
6.574
3.646
0.000
NH2
Cl
Table 2, entry 3
NAME PSH11-135
EXPNO 2
PROCNO 1
Date_ 20120328
Time 9.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 144
DW 80.800 usec
DE 9.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.00
2.00
2.03
9
8
7
6
5
4
3
2
1
ppm


144.905
129.075
123.107
116.179
77.416
76.994
76.570
NH2
Cl
Table 2, entry 3
NAME PSH11-135
EXPNO 13
PROCNO 1
Date_ 20120328
Time 9.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 141
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 724
DW 27.733 usec
DE 9.00 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm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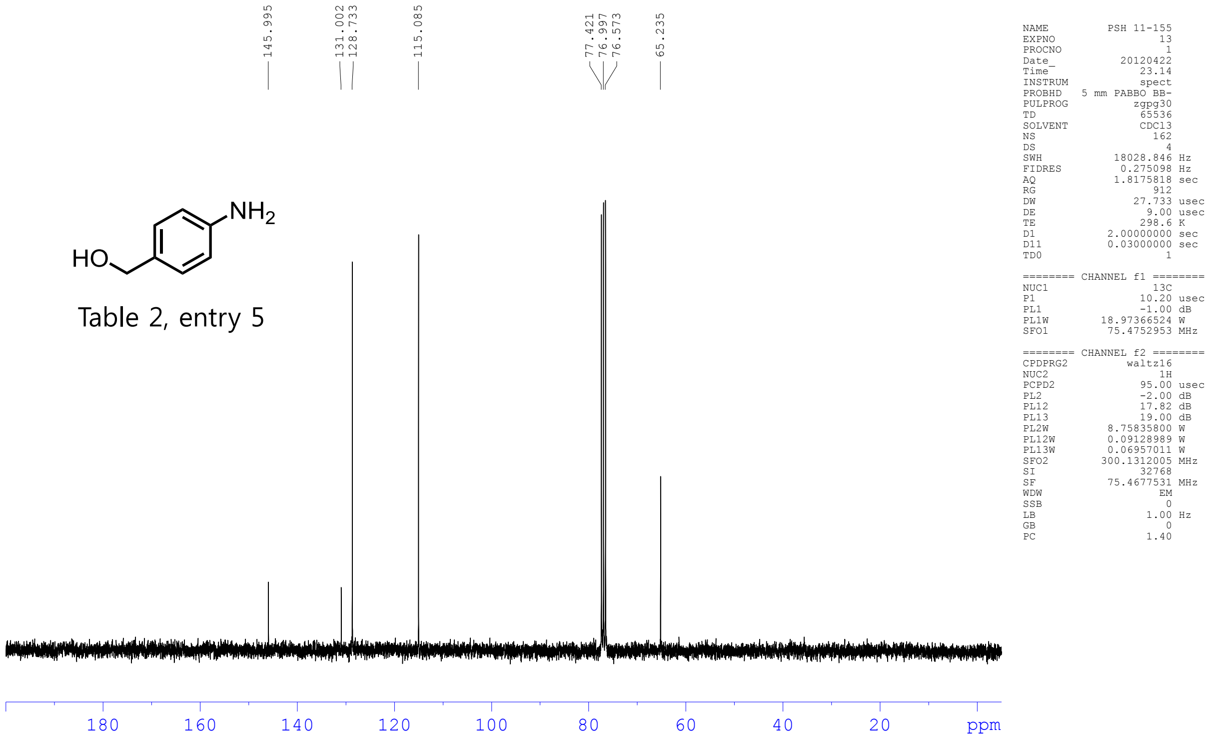
7.160
7.133
6.673
6.645
4.533
3.416
2.038
0.856
0.841
0.000
NH2
HO
Table 2, entry 5
1.96
1.93
2.00
2.08
9
8
7
6
5
4
3
2
1
ppm
NAME PSH 11-155
EXPNO 6
PROCNO 1
Date_ 20120422
Time 22.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 128
DW 80.800 usec
DE 9.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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131.002
128.733
115.085
77.421
76.997
76.573
65.235
NH2
HO
Table 2, entry 5
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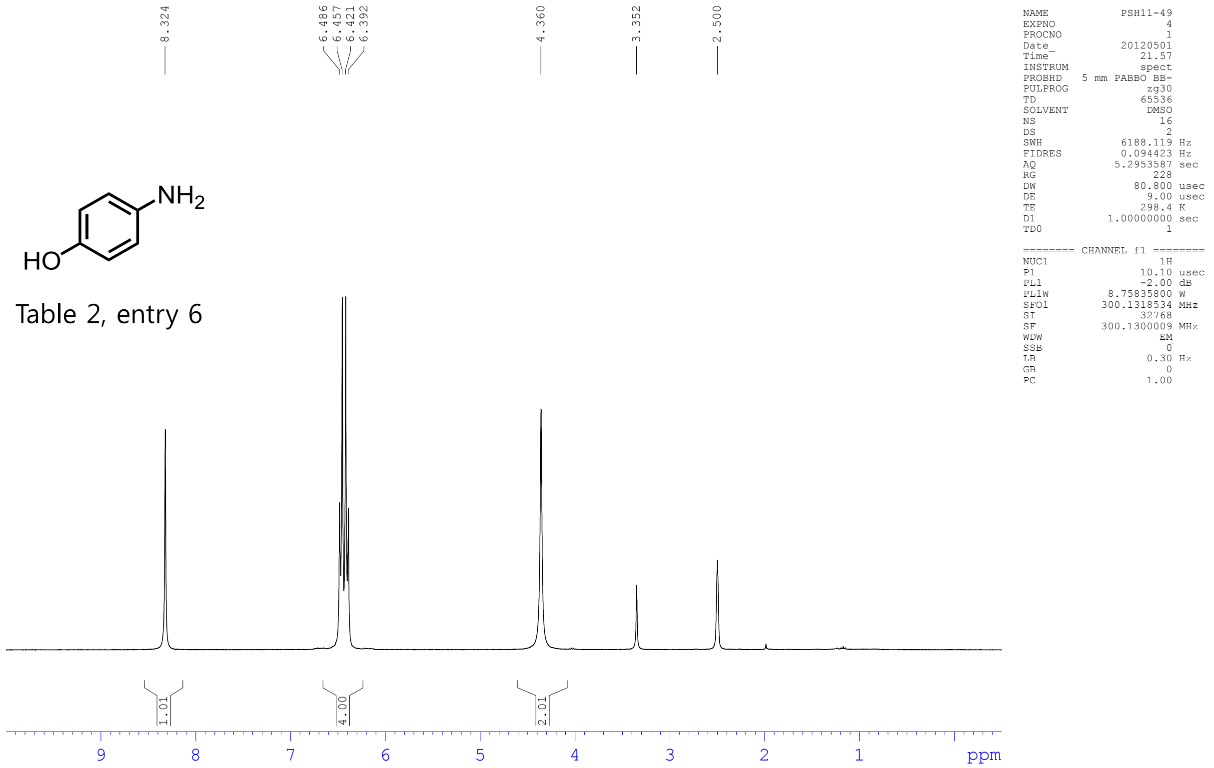
160
140
120
100
80
60
40
20
ppm
NAME PSH 11-155
EXPNO 13
PROCNO 1
Date_ 20120422
Time 23.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 162
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 912
DW 27.733 usec
DE 9.00 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677531 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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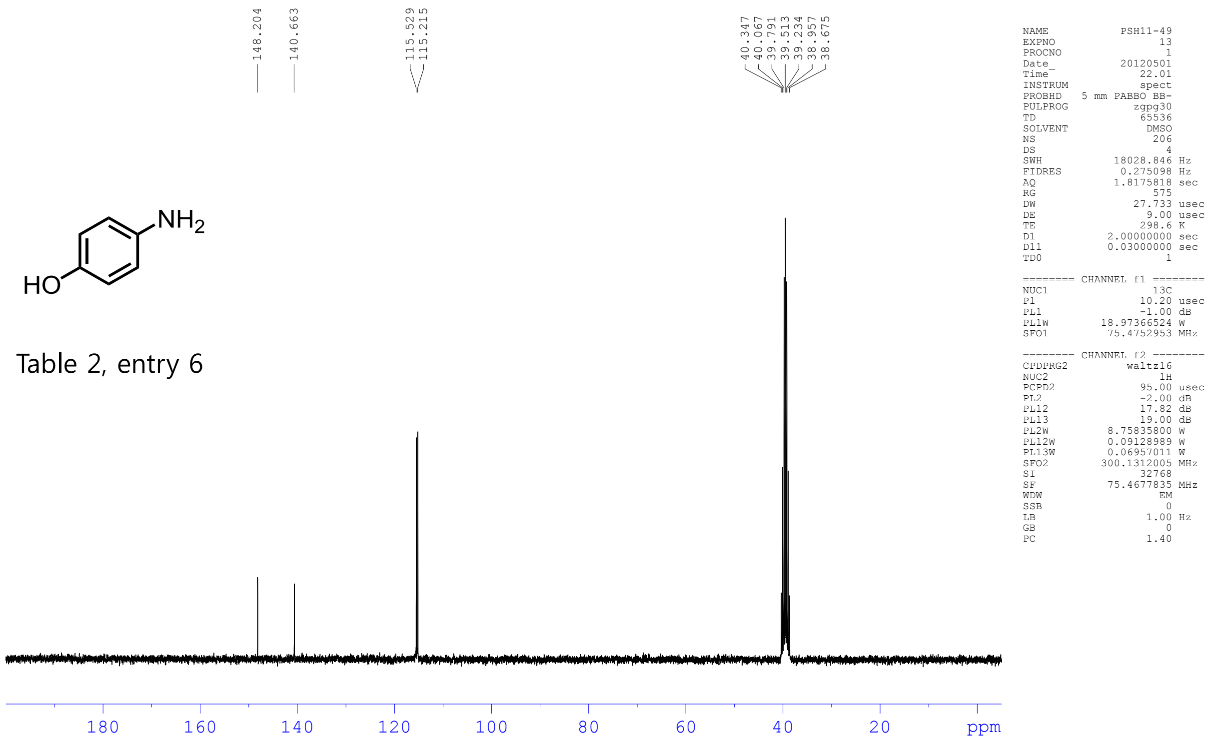
6.486
6.457
6.421
6.392
4.360
3.352
2.500
NH2
HO
Table 2, entry 6
1.01
4.00
2.01
9
8
7
6
5
4
3
2
1
ppm
NAME PSH11-49
EXPNO 4
PROCNO 1
Date_ 20120501
Time 21.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 228
DW 80.800 usec
DE 9.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300009 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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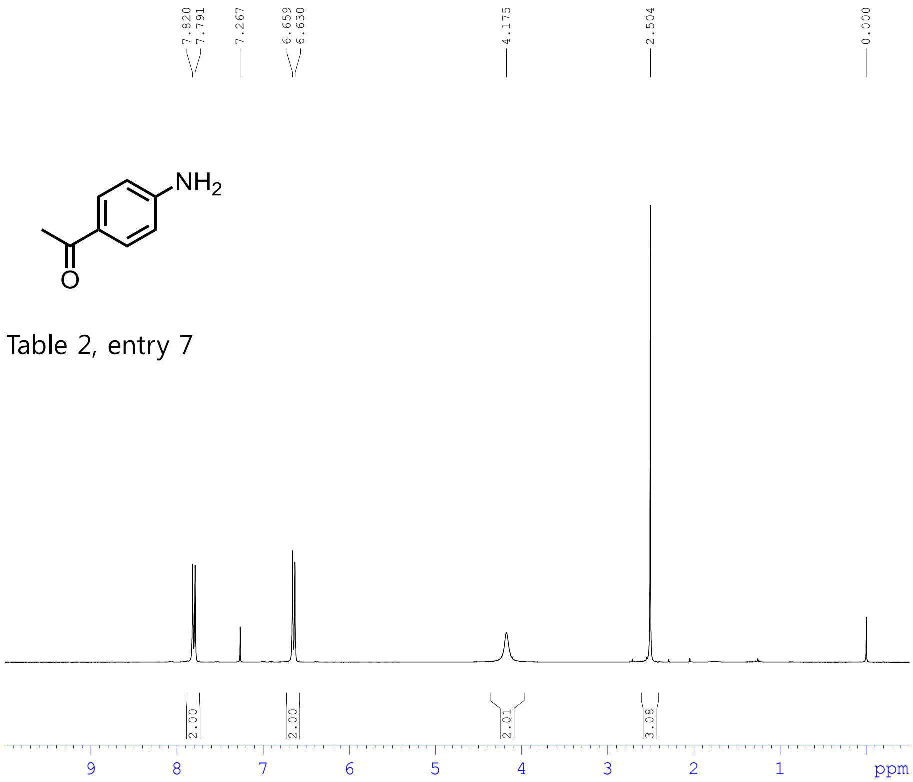
140.663
115.529
115.215
40.347
40.067
39.791
39.513
39.234
38.957
38.675
NH2
HO
Table 2, entry 6
180
160
140
120
100
80
60
40
20
ppm
NAME PSH11-49
EXPNO 13
PROCNO 1
Date_ 20120501
Time 22.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 206
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 575
DW 27.733 usec
DE 9.00 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677835 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
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EXPNO                 1
PROCNO                1
Date_          20120313
Time              23.29
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PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ            5.2953587 sec
RG                  128
DW               80.800 usec
DE                 9.00 usec
TE                296.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.10 usec
PL1               -2.00 dB
PL1W         8.75835800 W
SFO1        300.1318534 MHz
SI                32768
SF          300.1300040 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

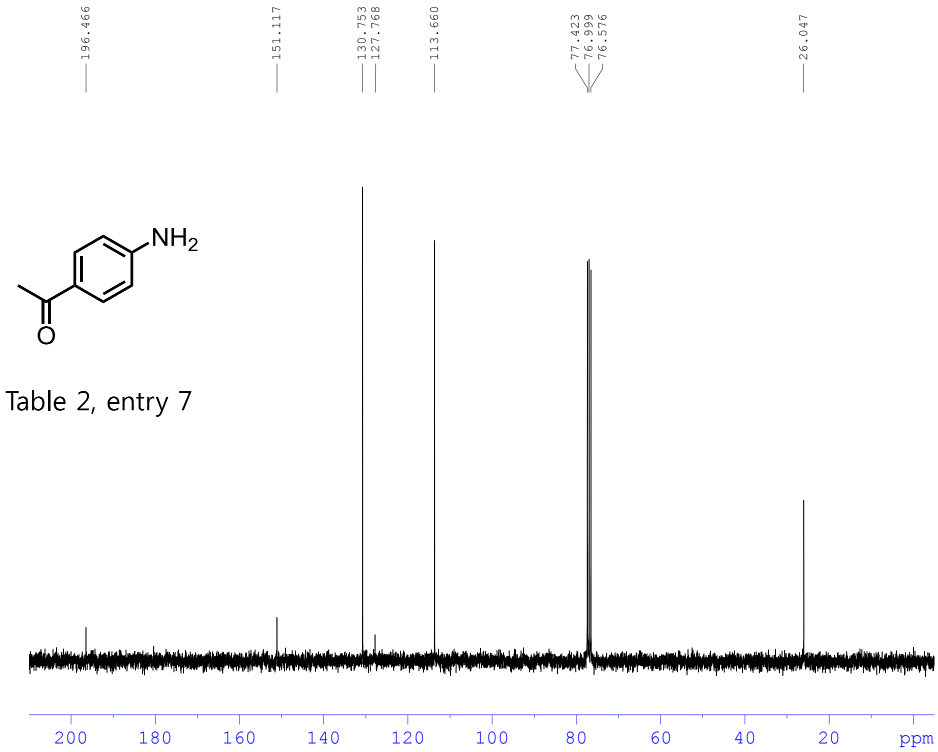


```
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EXPNO                13
PROCNO                1
Date_          20120313
Time              23.34
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  135
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175818 sec
RG                  456
DW               27.733 usec
DE                 9.00 usec
TE                296.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.20 usec
PL1               -1.00 dB
PL1W        18.97366524 W
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             95.00 usec
PL2               -2.00 dB
PL12              17.82 dB
PL13              19.00 dB
PL2W         8.75835800 W
PL12W        0.09128989 W
PL13W        0.06957011 W
SFO2        300.1312005 MHz
SI                32768
SF           75.4677531 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

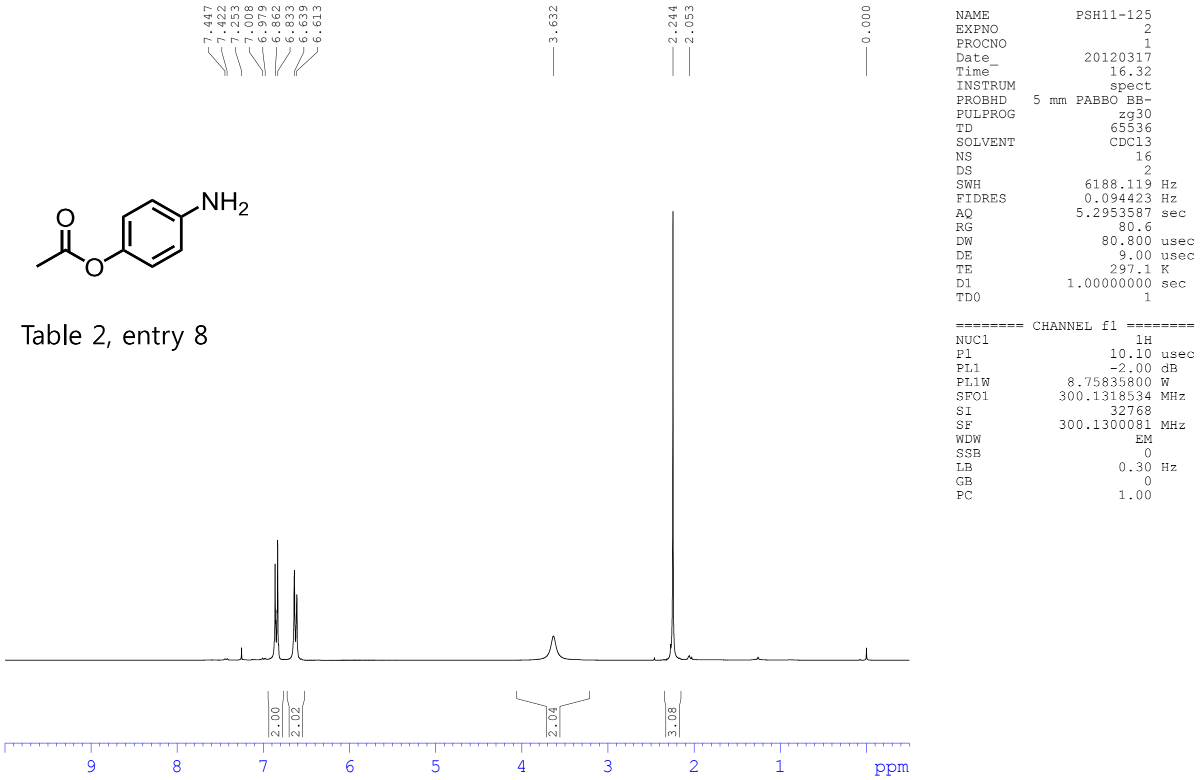
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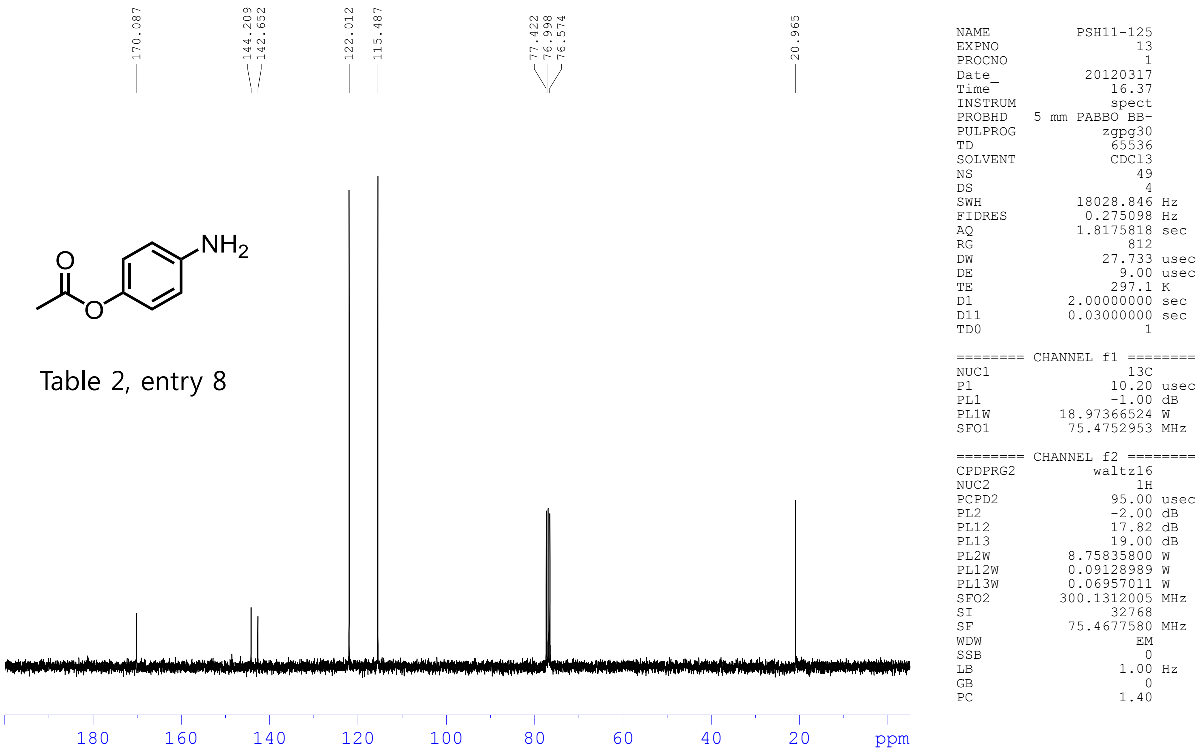
7.008
6.979
6.862
6.833
6.639
6.613
3.632
2.244
2.053
0.000
NH2
O
O
Table 2, entry 8
2.00
2.02
2.04
3.08
9
8
7
6
5
4
3
2
1
ppm
NAME PSH11-125
EXPNO 2
PROCNO 1
Date_ 20120317
Time 16.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 80.6
DW 80.800 usec
DE 9.00 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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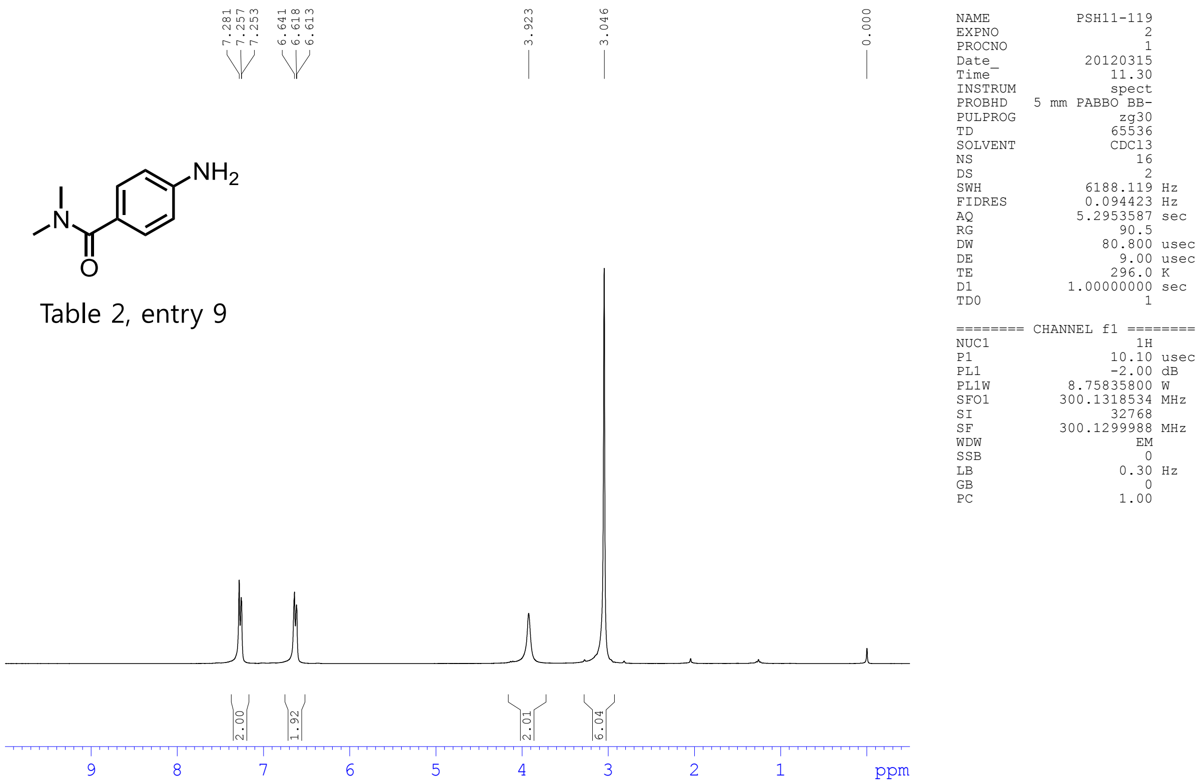
142.652
122.012
115.487
77.422
76.998
76.574
20.965
NH2
O
O
Table 2, entry 8
180
160
140
120
100
80
60
40
20
ppm
NAME PSH11-125
EXPNO 13
PROCNO 1
Date_ 20120317
Time 16.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 49
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 812
DW 27.733 usec
DE 9.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677580 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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6.641
6.618
6.613
3.923
3.046
0.000
NH2
N
O
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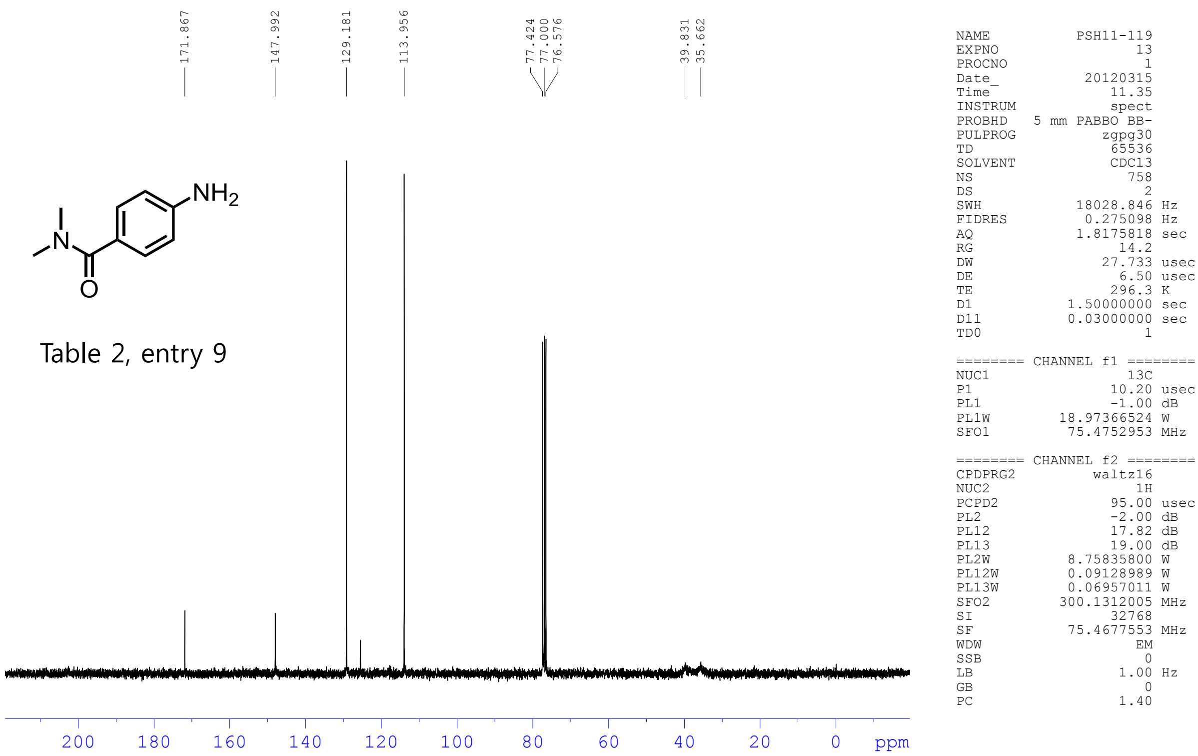
2.00
1.92
2.01
6.04
9 8 7 6 5 4 3 2 1 ppm
NAME PSH11-119
EXPNO 2
PROCNO 1
Date_ 20120315
Time 11.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 90.5
DW 80.800 usec
DE 9.00 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1299988 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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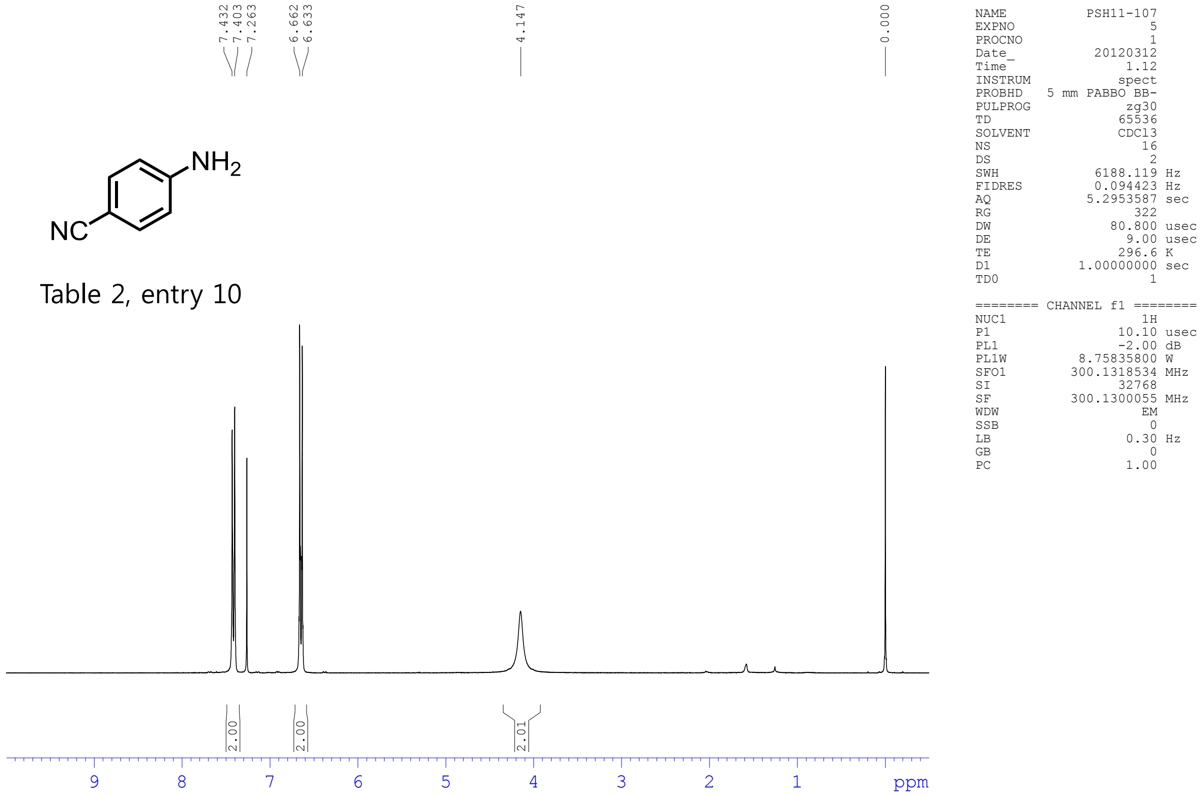
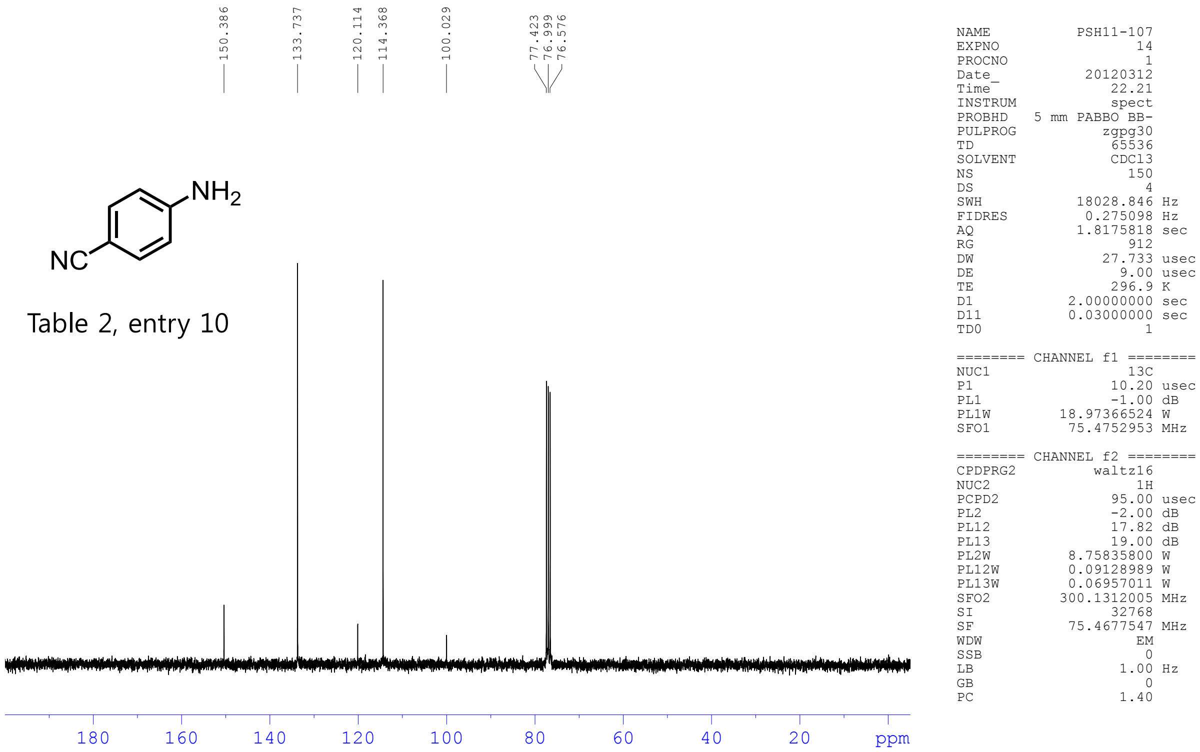
147.992
129.181
113.956
77.424
77.000
76.576
39.831
35.662
NH2
N
O
Table 2, entry 9
200 180 160 140 120 100 80 60 40 20 0 ppm
NAME PSH11-119
EXPNO 13
PROCNO 1
Date_ 20120315
Time 11.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 758
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 14.2
DW 27.733 usec
DE 6.50 usec
TE 296.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677553 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.432
7.403
7.263
6.662
6.633
4.147
0.000
NH2
NC
Table 2, entry 10
2.00
2.00
2.01
9
8
7
6
5
4
3
2
1
ppm
NAME PSH11-107
EXPNO 5
PROCNO 1
Date_ 20120312
Time 1.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 322
DW 80.800 usec
DE 9.00 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


150.386
133.737
120.114
114.368
100.029
77.423
76.999
76.576
NH2
NC
Table 2, entry 10
180
160
140
120
100
80
60
40
20
ppm
NAME PSH11-107
EXPNO 14
PROCNO 1
Date_ 20120312
Time 22.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 150
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 912
DW 27.733 usec
DE 9.00 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

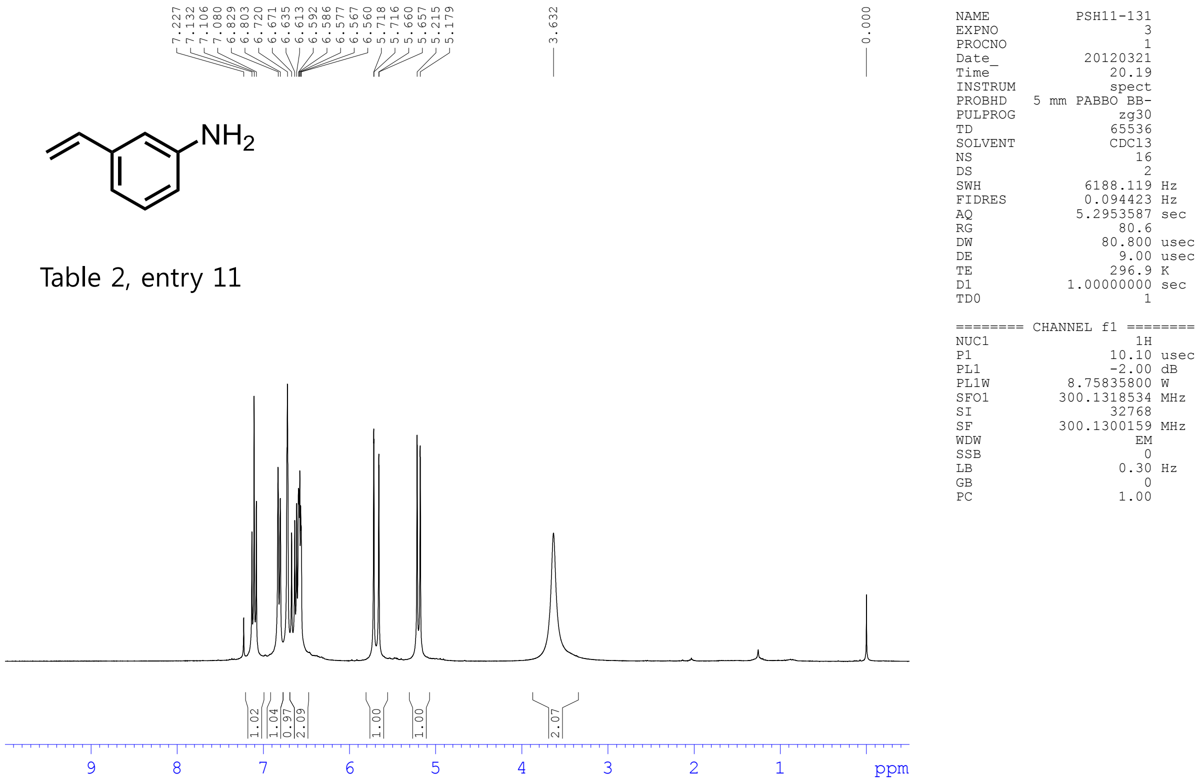


Table 2, entry 11

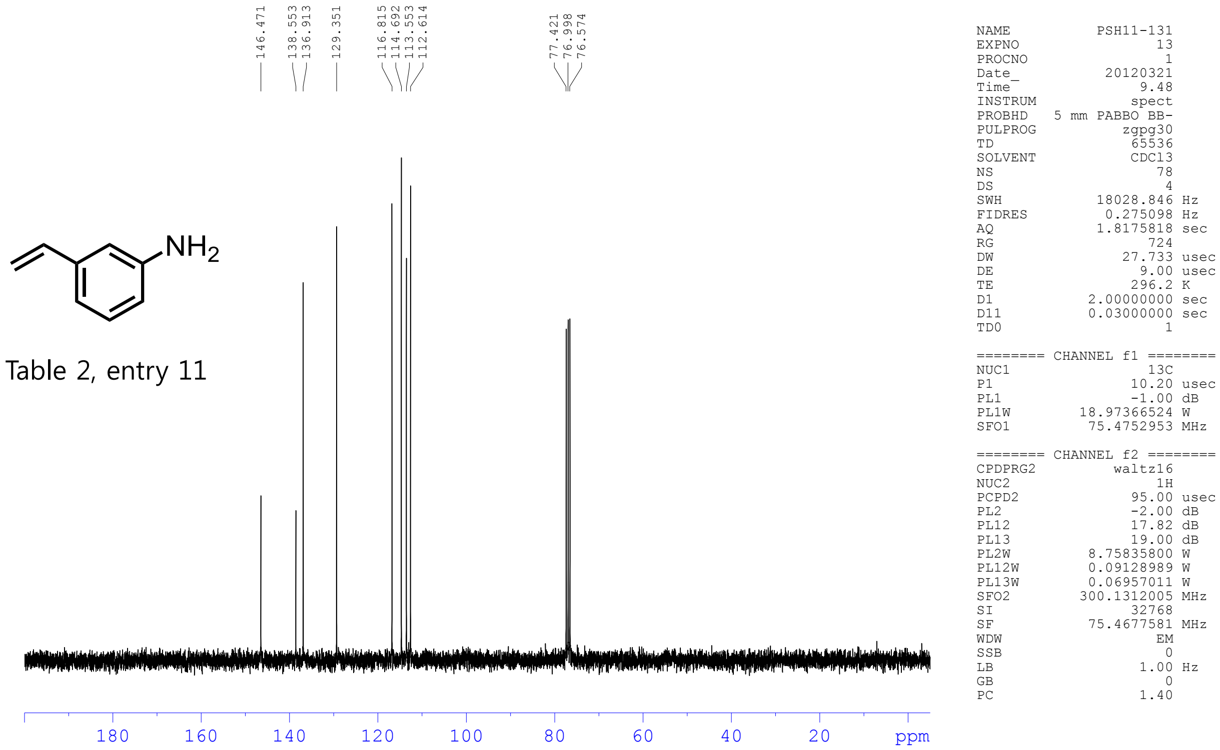
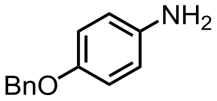


Table 2, entry 11



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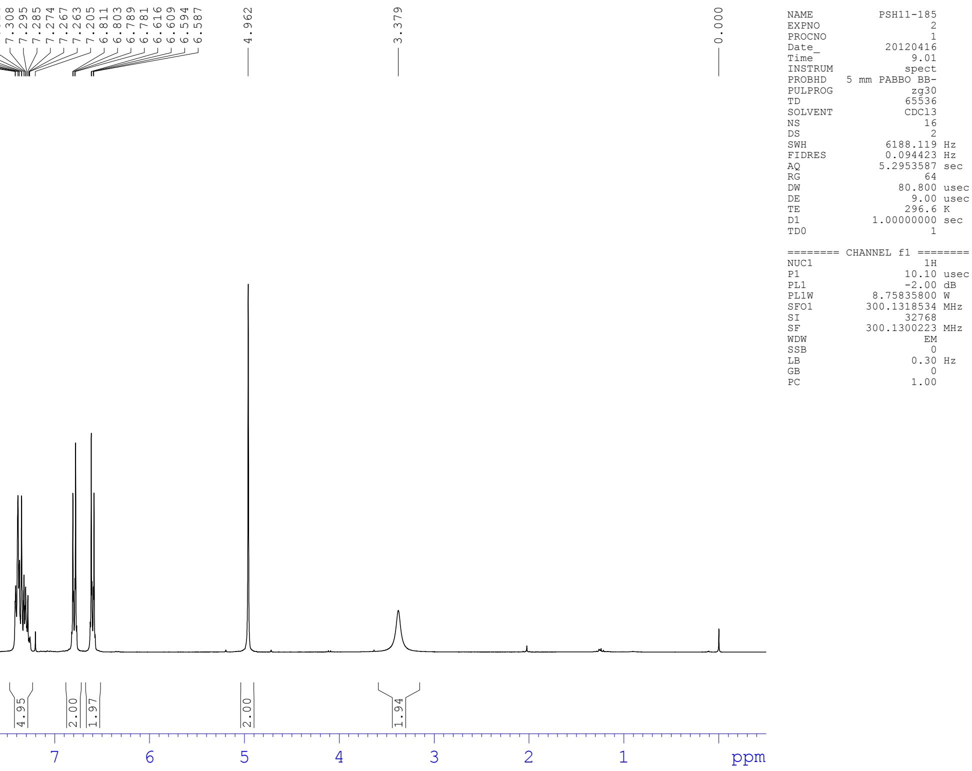


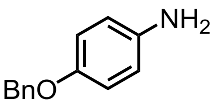
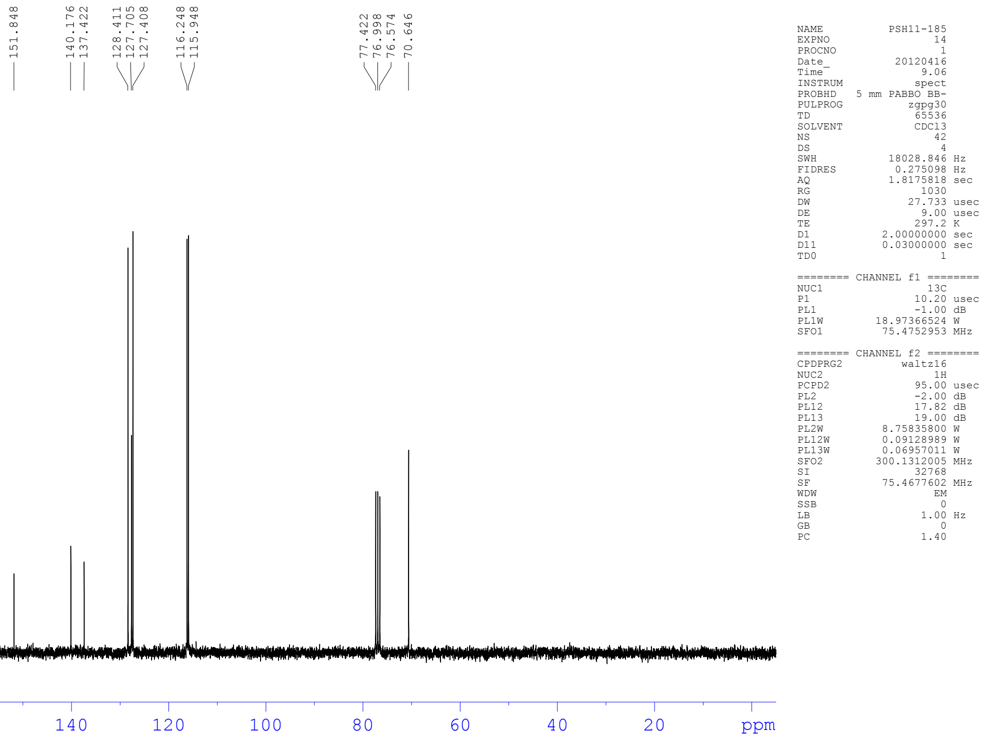
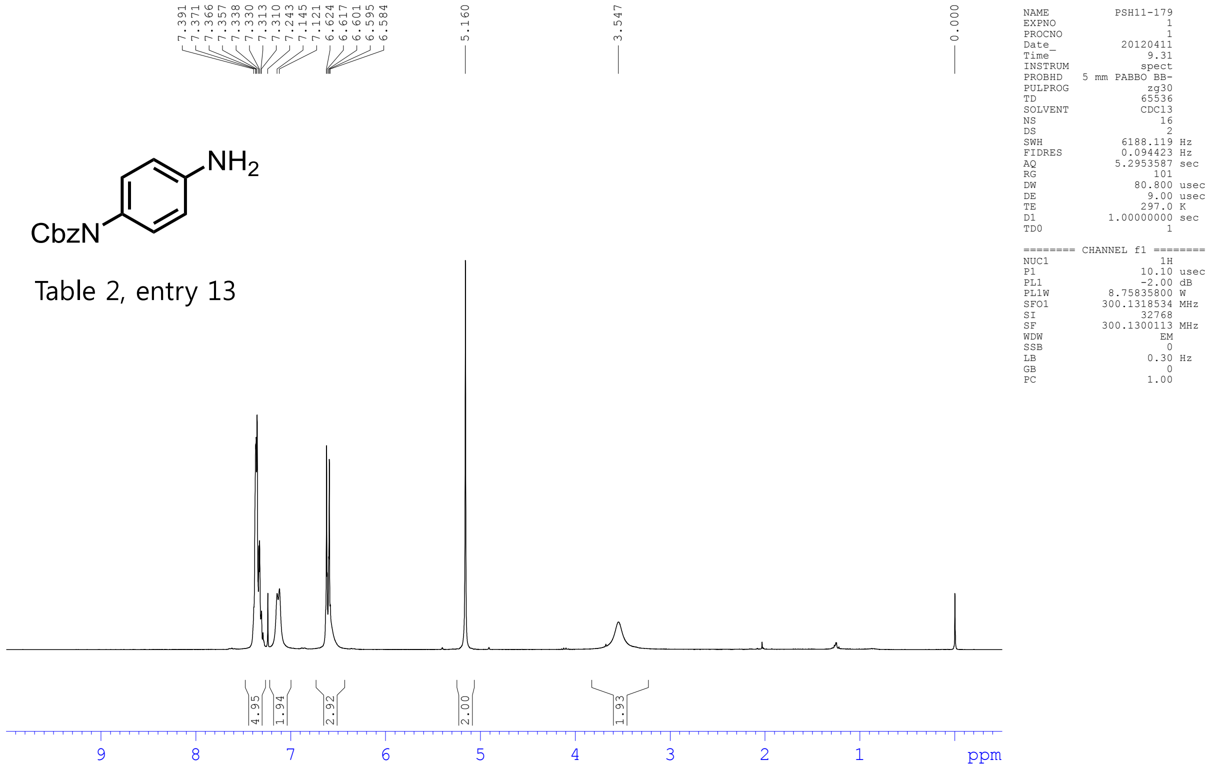


Table 2, entry 12





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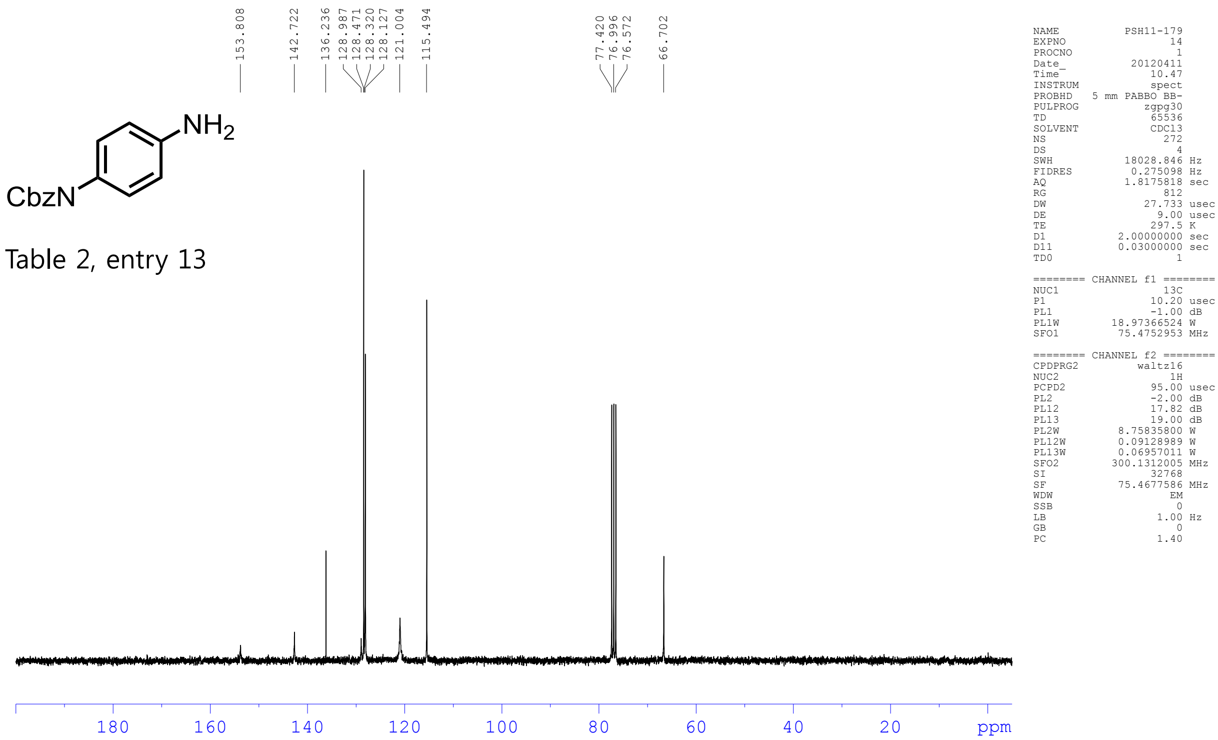
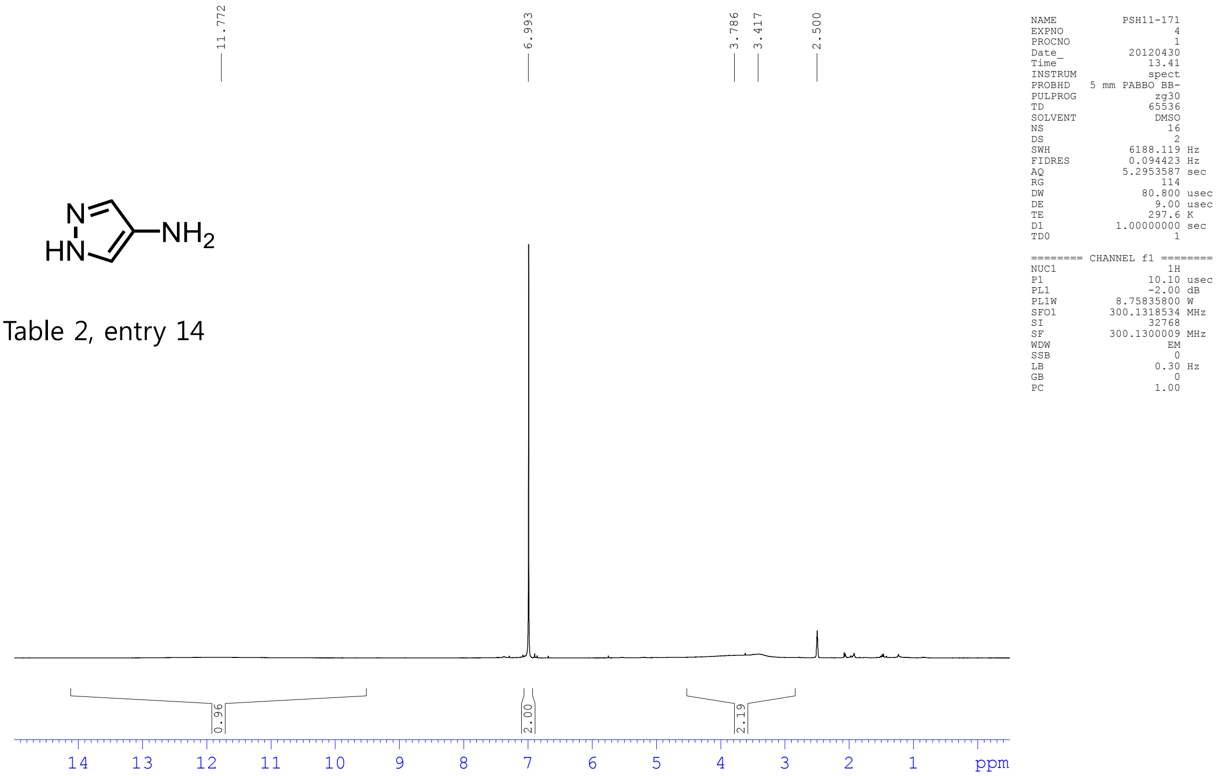


Table 2, entry 13



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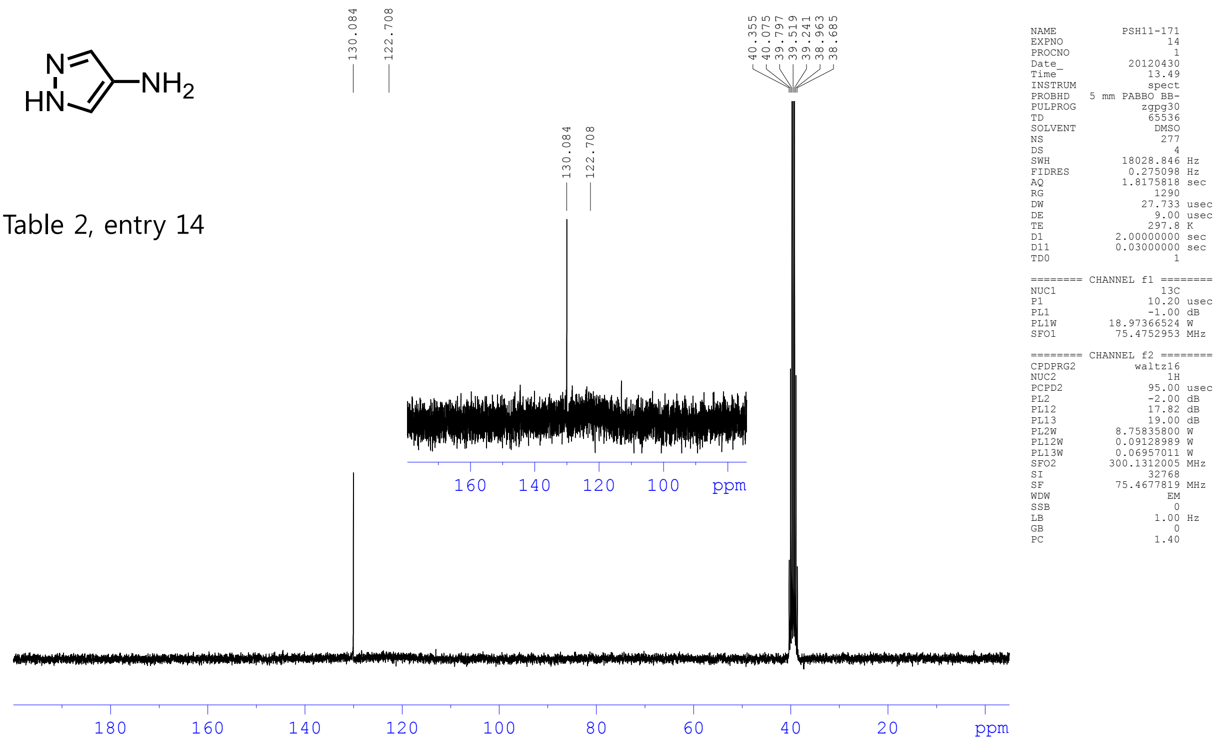

Table 2, entry 14