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## Graphical Abstract

### Chemoselective Amination of Bromiodobenzenes with Diarylamines by Palladium/Xantphos or Ligand-free Copper Catalysts

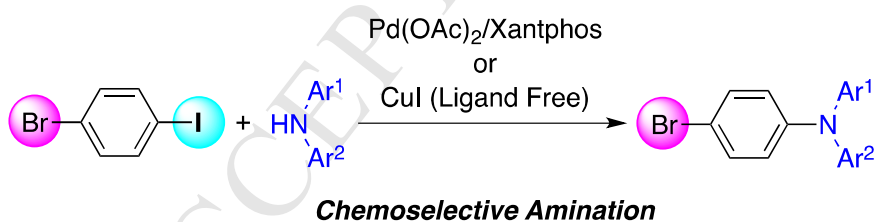
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# Chemoselective Amination of Bromiodobenzenes with Diarylamines by Palladium/Xantphos or Ligand-free Copper Catalysts

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**Abstract:** We report the chemoselective amination of bromiodobenzenes with diarylamines by palladium/Xantphos or a ligand-free copper catalyst. The reactions by these two types of catalysts proceeded with a high chemoselectivity and afforded monobrominated triarylamines in good yields. These products are useful intermediates for the synthesis of unsymmetrical bistriarylamines.

## **Keywords:**

Palladium

Copper

Amination

Chemoselectivity

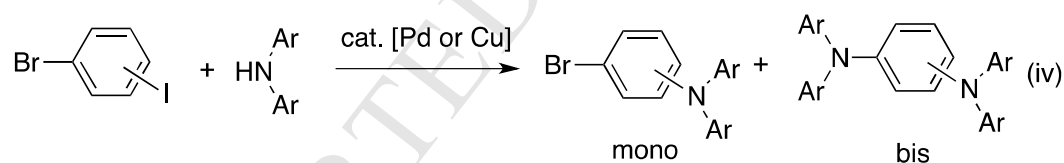
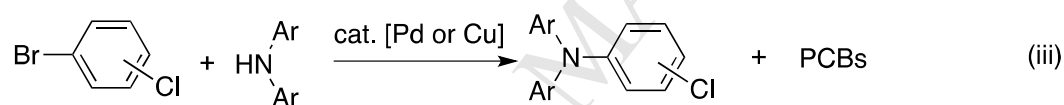
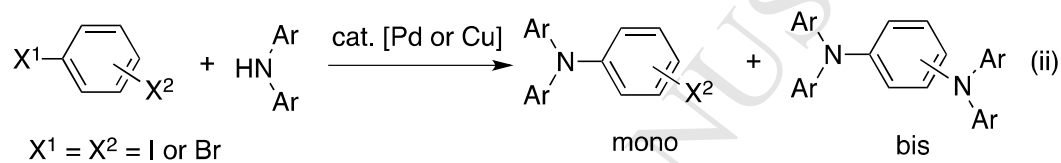
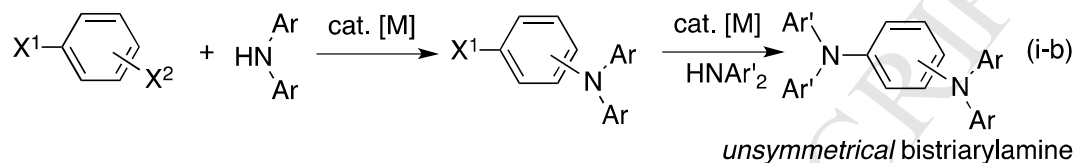
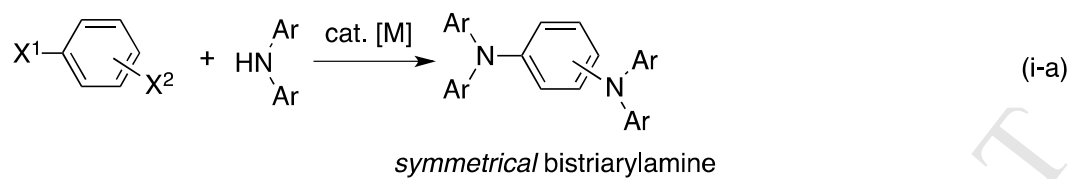
Triarylamine

## **1. Introduction**

The transition-metal-catalyzed amination of arylhalides is one of the most powerful carbon-nitrogen bond forming reactions,<sup>1</sup> and this reaction is widely used for preparing arylamines in the field of material and pharmaceutical research. For example, triarylamine is an important unit of organic electroactive materials<sup>2</sup> and the preparation of such compounds was

attained by the Buchwald-Hartwig amination reaction (palladium catalysts)<sup>3</sup> or the Ullmann type C-N coupling reaction (copper catalysts)<sup>4,6</sup> of arylhalides with diarylamines, and bistrilylamines were also prepared by the reaction of dihalogenated arenes with diarylamines. As shown in scheme 1, symmetrical bistrilylamines were easily obtained by the reaction of dihalogenated arenes with diarylamines, and this reaction is useful for preparing the symmetrical bistrilylamines (Scheme 1, i-a). The synthesis of unsymmetrical bistrilylamines requires the chemoselective monoamination reaction of dihalogenated arenes with diarylamines at first step and subsequent second amination reaction (Scheme 1, i-b). Therefore, to obtain the unsymmetrical bistrilylamine, the chemoselective monoamination reaction is essential, but the selective formation of the monoaminated triarylamine from dihalogenated arenes, which possess the same two halogen atoms on the aromatic group, is a difficult process because the reaction of dibromo- or diiodoarenes usually provides a mixture of monoaminated and bisaminated products with a low selectivity (Scheme 1, ii).<sup>7</sup> On the other hand, the bromoiodoarene or bromochloroarene, which have two different halogen atoms on the aromatic rings, can potentially provide the monoaminated product by undergoing the chemoselective reactions. Actually, the realization of the chemoselective amination of bromochloroarenes is an easy process because there is a significant difference in the reactivity between the bromoarenes and chloroarenes (Scheme 1, iii).<sup>8</sup> However, the reaction using chlorinated arenes is not suitable for industrial purposes because these reactions potentially produce PCBs (polychlorinated biphenyls) and related compounds, which are highly toxic and prohibited to produce any amount as a byproduct. Based on these reasons, for the industrial purpose, bromoiodoarene is the only usable commercially available dihalogenated arenes to realize the formation of a monoaminated product by a chemoselective process, but the reactivities of the bromoarene and iodoarene are not so different compare to the reactivities of bromoarene and chloroarene, and difficult to obtain the monoaminated product with a high chemoselectivity (Scheme 1, iv).<sup>9</sup> To the best of our knowledge, there are some examples of the chemoselective Buchwald-Hartwig reactions of bromoiodoarenes, but those reports are limited to the reaction with aliphatic amines,<sup>10</sup> while there are no reports about the reaction of bromoiodoarene with diarylamines. On the other hand, there are also some reports about the chemoselective amination of bromoiodoarenes with diarylamines using a copper catalyst, but these reactions required a relatively high temperature (>100 °C) and appropriate ligand.<sup>5a,11</sup> Based on this background, we now report the selective formation of monobrominated triarylaminines by the palladium-catalyzed chemoselective amination of bromiodobenzene with

diarylamines, and the ligand-free copper catalyzed reaction under mild reaction conditions.



Pd: low chemoselectivity  
Cu: need high temperature

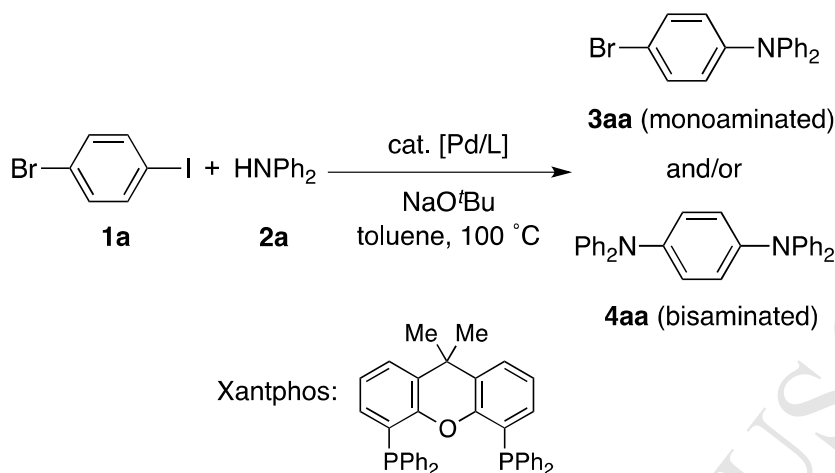
**Scheme 1.** Amination of dihalogenated arenes with diarylamines.

## 2. Results and discussion

### 2.1. Palladium Catalysts

To realize the chemoselective amination of dihalogenated arenes with diarylamines by a palladium catalyst, we first examined the reaction of 1-bromo-4-iodobenzene (**1a**) with diphenylamine (**2a**) using several palladium catalysts. As shown in Table 1, the reactions by Pd(OAc)<sub>2</sub> with monophosphine ligands, such as PPh<sub>3</sub> or P<sup>t</sup>Bu<sub>3</sub>, exhibited a low chemoselectivity and gave a mixture of mono- and bisaminated products (**3aa** and **4aa**) (Table 1, entries 1 and 2). On the other hand, we observed that the bisphosphine ligands, such as DPPE or DPPF, selectively provided the monoaminated product **3aa**, but the yields of these reactions were not satisfactory (entries 3 and 4). Based on these observations, we confirmed that bisphosphine ligands play an important role to realize the chemoselective amination reaction. Therefore, we further screened other bisphosphine ligands, such as BINAP or Xantphos, and succeeded in obtaining **3aa** in an acceptable yield with a high chemoselectivity using Xantphos as the ligand (Table 1, entries 6 and 7). We also demonstrated the reaction in dioxane, and confirmed that the reaction by 1 mol% of catalyst provided better results (89% yield, >99% chemoselectivity) than the reaction by 5 mol% (71% yield, 96% chemoselectivity) (Table 1, entries 8 and 9). We further examined the reaction of **1a** with **2a** using other palladium precatalysts, but lower yields were observed in all cases (Table 1, entries 10-13). Based on these results, we concluded that the optimized reaction conditions, which realize the intended chemoselective amination reaction of **1a**, is using the Pd(OAc)<sub>2</sub>/Xantphos catalyst in dioxane at 100 °C.<sup>11</sup>

With the optimized reaction conditions in hand, we investigated the chemoselective monoamination of bromiodobenzenes **1a-c** with some commercially available diarylamines **2a-h**. As shown in Table 2, all reactions proceeded with a high chemoselectivity and afforded the monoaminated products in good yields. For example, the reactions of 1-bromo-4-iodobenzene (**1a**) with diarylamines **2b**, **2c** and **2g** provided the desired monobrominated triarylamines **3ab**, **3ac**, and **3ag** in 87%, 95%, and 93% isolated yields, respectively (Table 2, entries 1-3). The Pd(OAc)<sub>2</sub>/Xantphos catalyzed chemoselective reactions of 1-bromo-3-iodobenzene (**1b**) with diarylamines also smoothly proceeded and gave the intended aminated products in the range of 71-97% yields (entries 4-11). Although the reaction of 1-bromo-2-iodobenzene (**1c**) with **2a** resulted in a slightly lower yield (58%), an acceptable yield (75%) was obtained by increasing the catalyst amount from 1 mol% to 5 mol% (entries 12 and 13).

**Table 1.** Palladium Catalysts for the Chemoselective Amination of 1-Bromo-4-iodobenzene (**1a**) with Diphenylamine (**2a**)<sup>a</sup>

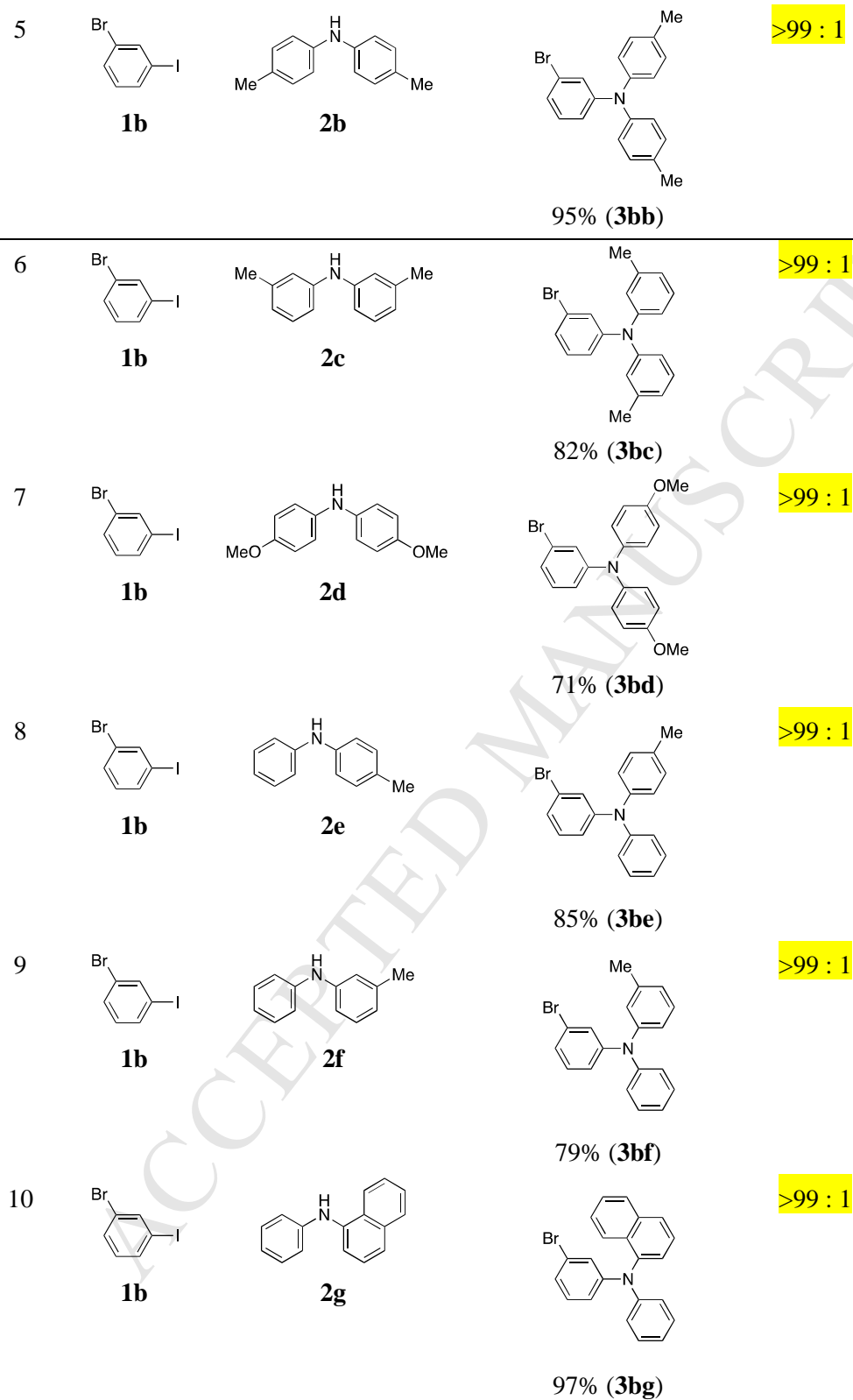
entry	[Pd] (mol%)	L (mol%)	yield <sup>b,c</sup>	<b>3aa</b> : <b>4aa</b> <sup>d</sup>
1	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	51%	71 : 29
2	Pd(OAc) <sub>2</sub> (5)	P <sup>t</sup> Bu <sub>3</sub> (5)	79%	59 : 41
3	Pd(OAc) <sub>2</sub> (5)	DPPE (5)	33%	>99 : 1
4	Pd(OAc) <sub>2</sub> (5)	DPPF (5)	74%	>99 : 1
5	Pd(OAc) <sub>2</sub> (5)	BNAP (5)	74%	84 : 16
6	Pd(OAc) <sub>2</sub> (5)	Xantphos (5)	86%	97 : 3
7	Pd(OAc) <sub>2</sub> (1)	Xantphos (1)	86%	92 : 8
8 <sup>e</sup>	Pd(OAc) <sub>2</sub> (5)	Xantphos (5)	71%	96 : 4
9 <sup>e</sup>	Pd(OAc) <sub>2</sub> (1)	Xantphos (1)	89%	>99 : 1
10 <sup>e</sup>	Pd <sub>2</sub> (dba) <sub>3</sub> (2.5)	Xantphos (5)	60%	93 : 7
11 <sup>e</sup>	[PdCl(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> (2.5)	Xantphos (5)	66%	94 : 6
12 <sup>e</sup>	[Pd(C <sub>3</sub> H <sub>5</sub> )(cod)]BF <sub>4</sub> (5)	Xantphos (5)	62%	92 : 8
13 <sup>e</sup>	PdCl <sub>2</sub> (PhCN) <sub>2</sub> (5)	Xantphos (5)	60%	93 : 7

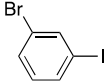
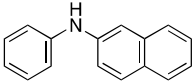
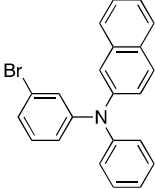

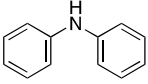
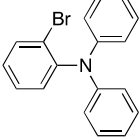
<sup>a</sup> Reaction conditions: **1a** (0.36 mmol), **2a** (0.43 mmol), NaO'Bu (0.53 mmol), palladium, and ligand in toluene (0.5 mL) for 12 h at 100 °C under nitrogen. <sup>b</sup> The yields were determined by HPLC analysis of the crude materials. <sup>c</sup> Yields of **3aa** and **4aa**. <sup>d</sup> The ratios were determined by HPLC analysis of the crude materials. <sup>e</sup> Dioxane was used as the solvent.

**Table 2.** Palladium-catalyzed Chemoselective Amination of **1a-c** with **2a-h**<sup>a</sup>

entry	<b>1</b>	<b>2</b>	yield <sup>b</sup>	<b>3 : 4</b> <sup>c</sup>
1			 87% ( <b>3ab</b> )	>99 : 1
2			 95% ( <b>3ac</b> )	>99 : 1
3			 93% ( <b>3ag</b> )	>99 : 1
4			 93% ( <b>3ba</b> )	>99 : 1





11				>99 : 1
	<b>1b</b>	<b>2h</b>		
			85% ( <b>3bh</b> )	
12				>99 : 1
	<b>1c</b>	<b>2a</b>		
			58% ( <b>3ca</b> )	
13 <sup>d</sup>	<b>1c</b>	<b>2a</b>	75% ( <b>3ca</b> )	>99 : 1

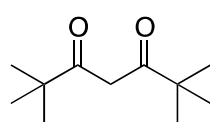
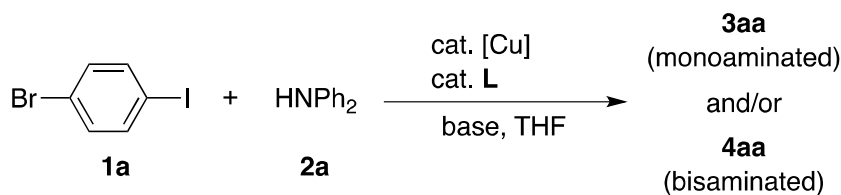
<sup>a</sup> Reaction conditions: **1** (0.36 mmol), **2** (0.43 mmol), NaO<sup>t</sup>Bu (0.53 mmol), Pd(OAc)<sub>2</sub> (0.0036 mmol), and Xantphos (0.0036 mmol) in toluene (0.5 mL) for 12 h at 100 °C under nitrogen. <sup>b</sup> Isolated yields. <sup>c</sup> The ratios were determined by HPLC analysis of the crude materials. <sup>d</sup> Conditions: 5 mol% Pd(OAc)<sub>2</sub> and Xantphos were used.

## 2.2. Copper Catalysts

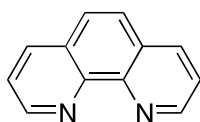
To develop an alternative chemoselective amination of bromiodobenzenes with diarylamines, we further investigated the copper-catalyzed reaction. There are some reports about the chemoselective amination of bromiodobenzenes with diarylamines by a copper catalyst,<sup>5a,12</sup> but those reactions generally required a relatively high reaction temperature (>100 °C) and an appropriate ligand. Based on such information, we initiated a study to realize the intended chemoselective amination reaction by a copper catalyst system under milder conditions.

For our objective of discovering an effective copper catalyst, we again selected the reaction of 1-bromo-4-iodobenzene (**1a**) with diphenylamine (**2a**) as the standard reaction system. As we expected, the reaction by 2 mol% of CuCl/1,10-phen in the presence of KOH (powder) at 125 °C, which is a reported reaction condition,<sup>12a,b</sup> provided the intended monoaminated product **3aa** in 87% yield with a high chemoselectivity (Table 3, entry 1). We further confirmed that CuBr and CuI also exhibited the same reactivity and chemoselectivity under the same reaction conditions (entries 2 and 3). Based on these initial results, we further tried to find the milder conditions by copper catalyst. When the reaction was conducted under

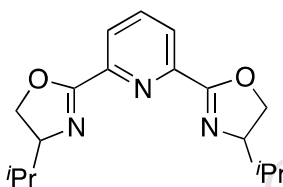
lower temperature (80 °C), the copper catalysts did not exhibit any catalytic activities, resulting in no reaction (entries 4 and 5). To our delight, changing the base from KOH to NaO<sup>t</sup>Bu<sup>12c,13</sup> was an effective way to allow the amination reaction, and the CuI/1,10-phen catalyst gave an acceptable result (75% yield, 97% chemoselectivity) at 80 °C (entry 7). To attain the perfect chemoselectivity under milder reaction conditions, we further examined the reaction at 60 °C. On the other hand, the reactions catalyzed by CuI with several ligands, such as 1,10-phen, pybox or TMHD, resulted in a low yield (entries 8-10). To our delight, we revealed that the reaction catalyzed by CuI<sup>14</sup> without a ligand exhibited higher yields (entry 11), and the increased amount of catalyst from 2 mol% to 10 mol% realized a high yield with a high chemoselectivity (entries 12 and 13). The best yield was obtained by the less use of base (2.5 equiv.) (entry 14).

**Table 3.** Copper Catalysts for the Chemoselective Amination of **1a** with **2a**<sup>a</sup>

TMHD

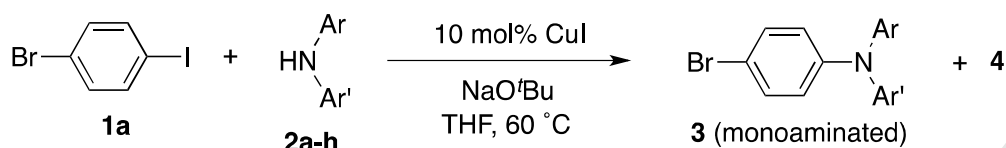


1,10-phen

*ip*-pybox

entry	[Cu] (mol%)	L (mol%)	base (equiv.)	temp (°C)	yield <sup>b</sup>	3 : 4 <sup>c</sup>
1 <sup>d</sup>	CuCl (2)	1,10-phen	KOH (5)	125	87%	>99 : 1
2 <sup>d</sup>	CuBr (2)	1,10-phen	KOH (5)	125	81%	>99 : 1
3 <sup>d</sup>	CuI (2)	1,10-phen	KOH (5)	125	87%	>99 : 1
4 <sup>d</sup>	CuCl (2)	1,10-phen	KOH (5)	80	<2%	nd
5 <sup>d</sup>	CuI (2)	1,10-phen	KOH (5)	80	<2%	nd
6	CuCl (2)	1,10-phen	NaO <sup>t</sup> Bu (5)	80	28%	90 : 10
7	CuI (2)	1,10-phen	NaO <sup>t</sup> Bu (5)	80	75%	97 : 3
8	CuI (2)	1,10-phen	NaO <sup>t</sup> Bu (5)	60	25%	96 : 4
9	CuI (2)	pybox	NaO <sup>t</sup> Bu (5)	60	26%	>99 : 1
10	CuI (2)	TMHD	NaO <sup>t</sup> Bu (5)	60	49%	96 : 4
11	CuI (2)	—	NaO <sup>t</sup> Bu (5)	60	56%	>99 : 1
12	CuI (4)	—	NaO <sup>t</sup> Bu (5)	60	75%	>99 : 1
13	CuI (10)	—	NaO <sup>t</sup> Bu (5)	60	94%	>99 : 1
14	CuI (10)	—	NaO <sup>t</sup> Bu (2.5)	60	98%	>99 : 1

<sup>a</sup>Reaction conditions: **1a** (0.36 mmol), **2a** (0.43 mmol), base, copper, and ligand in THF (0.5 mL) for 12 h under nitrogen. <sup>b</sup>The yields were determined by HPLC analysis of the crude materials. <sup>c</sup>The ratios were determined by HPLC analysis of the crude materials. <sup>d</sup>Dioxane was used as the solvent.

**Table 4.** Copper-catalyzed Chemoselective Amination of **1a** with **2**<sup>a</sup>

**2b:** Ar, Ar' = 4-MeC<sub>6</sub>H<sub>4</sub>  
**2c:** Ar, Ar' = 3-MeC<sub>6</sub>H<sub>4</sub>  
**2g:** Ar = Ph, Ar' = 1-naphthyl  
**2h:** Ar = Ph, Ar' = 2-naphthyl

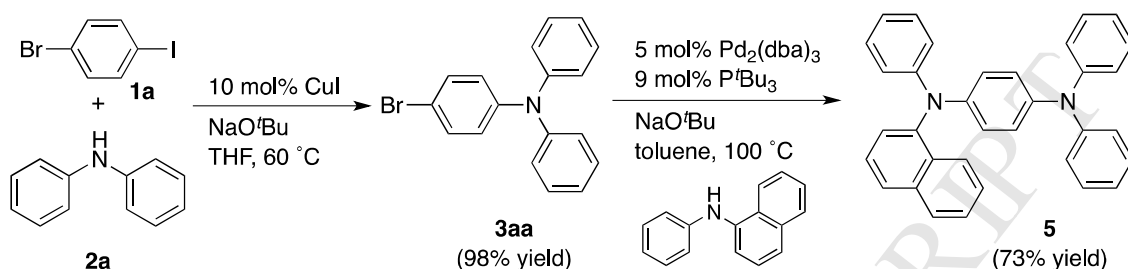
entry	<b>2</b>	yield <sup>b,c</sup>	<b>3</b> : <b>4</b> <sup>d</sup>
1	<b>2b</b>	84%	97 : 3
2	<b>2c</b>	92%	>99 : 1
3	<b>2g</b>	46%	97 : 3
4 <sup>e</sup>	<b>2g</b>	92%	94 : 6
5	<b>2h</b>	95%	94 : 6

<sup>a</sup>Reaction conditions: **1a** (0.36 mmol), **2** (0.43 mmol), NaO<sup>t</sup>Bu (0.90 mmol), CuI (0.036 mmol), and THF (0.5 mL) for 12 h at 60 °C under nitrogen. <sup>b</sup>The yields were determined by HPLC analysis of the crude materials. <sup>c</sup>Yields of **3** and **4**. <sup>d</sup>The ratios were determined by HPLC analysis of the crude materials. <sup>e</sup>The reaction was conducted at 100 °C.

The optimized copper catalyst condition also effectively worked for the reaction of **1a** with other diarylamines. For example, the reactions with **2b** or **2c** provided the intended products **4ab** and **4ac** in good yields with high chemoselectivities (Table 4, entries 1 and 2). The reaction of **1a** with **2g** resulted in a low yield (46%), but elevated reaction temperature realized a high yield (92%) with a good chemoselectivity (94%) (entries 3 and 4). The reaction of **1a** with **2h** also smoothly proceeded at 60 °C and provided the desired product **4ah** in 95% yield with a 94% chemoselectivity (entry 5).

We further demonstrated the synthesis of the unsymmetrical bistrilamine through the monobrominated triarylamine, which was obtained by the chemoselective amination reaction (eq 1). As listed in Table 3, the monobrominated triarylamine **3aa**, which was prepared by the reaction of ligand-free copper catalyzed chemoselective amination of **1a** with

**2a**, and **3aa**, was easily converted to the unsymmetrical bistriarylamine **5** under the standard conditions of the Buchwald-Hartwig reaction.



**Scheme 2.** Synthesis of **5** by copper and palladium-catalysts.

### 3. Conclusions

In conclusion, we developed the chemoselective amination of bromiodobenzenes with diarylamines using the palladium/Xantphos or ligand-free copper catalyst. The reaction proceeded with a high chemoselectivity and afforded the monobrominated triarylamines in good yields. We further demonstrated the transformation of the monobrominated triarylamines to unsymmetrical bistriarylamines by the Buchwald-Hartwig reaction.

## 4. Experimental section

### 4.1. General

All manipulations were carried out under a nitrogen atmosphere. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for  $^1\text{H}$  with  $\text{C}_6\text{D}_6$ , and 67 MHz for  $^{13}\text{C}$  with  $\text{C}_6\text{D}_6$ ), JEOL JNM LA-400 spectrometer (400 MHz for  $^1\text{H}$  with  $\text{CDCl}_3$ ,  $\text{C}_6\text{D}_6$  or acetone- $d_6$ , and 100 MHz for  $^{13}\text{C}$  with  $\text{CDCl}_3$ ,  $\text{C}_6\text{D}_6$  or acetone- $d_6$ ), or JEOL JNM ECP-500 spectrometer (500 MHz for  $^1\text{H}$  with  $\text{C}_6\text{D}_6$  or acetone- $d_6$ , and 125 MHz for  $^{13}\text{C}$  with  $\text{C}_6\text{D}_6$  or acetone- $d_6$ ). Chemical shifts are reported in  $\delta$  ppm referenced to an internal  $\text{SiMe}_4$  standard, residual acetone ( $\delta$  2.09) or residual benzene ( $\delta$  7.15) for  $^1\text{H}$  NMR, and residual chloroform ( $\delta$  77.4), residual acetone ( $\delta$  30.6) or residual benzene ( $\delta$  128.6) were used as internal reference for  $^{13}\text{C}$  NMR.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 25  $^\circ\text{C}$ . The chemoselectivity was determined by  $^1\text{H}$  NMR spectra and/or HPLC analysis using Inertsil ODS-3V ( $\text{CH}_3\text{CN}$ , flow: 1.0 mL/min, 254 nm). All chemical including palladium salts, copper salts, phosphine ligands, dihalogenated arenes and amines were purchased from commercial sources and used without further purification.

#### 4.2. General procedure for the palladium-catalyzed reaction

A solution of Pd(OAc)<sub>2</sub> (0.8 mg, 0.0036 mmol), Xantphos (2.1 mg, 0.0036 mmol), NaO<sup>t</sup>Bu (51 mg, 0.53 mmol), 1-bromo-4-iodobenzene (**1a**) (100 mg, 0.35 mmol), and *N,N*-diphenylamine (**2a**) (72 mg, 0.43 mmol) in toluene (0.5 mL) was stirred at 100 °C for 12 h. The reaction was quenched with H<sub>2</sub>O, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 3 mL). The chemoselectivity (**3aa/4aa** = 92/8) was measured by HPLC analysis using Inertsil ODS-3V. The pure monoaminated product **3aa** (99 mg, 86%) was obtained by flash chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 97/3) as a white solid.

#### 4.3. General procedure for the copper-catalyzed reaction

A solution of CuI (6.7 mg, 0.035 mmol), NaO<sup>t</sup>Bu (85 mg, 0.88 mmol), 1-bromo-4-iodobenzene (**1a**) (100 mg, 0.35 mmol), and *N,N*-diphenylamine (**2a**) (90 mg, 0.53 mmol) in THF (0.5 mL) was stirred at 60 °C for 12 h. The reaction was quenched with H<sub>2</sub>O, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 4 mL). The chemoselectivity (**3aa/4aa** = >98/2) was measured by HPLC analysis using Inertsil ODS-3V. The pure monoaminated product **3aa** (113 mg, 98%) was obtained by flash chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 97/3) as a white solid. The minor product (bisaminated product) **4aa** was also obtained by following flash chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>3</sub>N = 90/5/5) as a white solid with containing unknown impurities and triethylamine.

#### 4.4. Characterization data of products

4.4.1. *4-Bromo-N,N*-diphenylaniline (**3aa**).<sup>7a,15</sup> White solid (99 mg, 86%). Mp 106–111 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 6.92–6.94 (m, 2H), 7.02–7.07 (m, 6H), 7.28–7.32 (m, 4H), 7.38–7.41 (m, 2H). <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 114.08, 123.48, 124.48, 124.80, 129.29, 129.50, 132.12, 147.33. HPLC analysis: *t*<sub>R</sub> = 5.78 min.

4.4.2. *4-Bromo-N,N*-di-*p*-tolylaniline (**3ab**).<sup>7b</sup> White solid (108 mg, 87%). Mp 100–104 °C. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>) δ 2.30 (s, 6H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 2H). <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 20.21, 113.14, 123.70, 125.01, 130.29, 132.11, 133.29, 145.10, 147.92. HPLC analysis: *t*<sub>R</sub> = 7.48 min.

4.4.3. *N*-(4-Bromophenyl)-3-methyl-*N*-(*m*-tolyl)aniline (**3ac**). White solid (118 mg, 95%).

Mp 93–95 °C.  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  2.25 (s, 6H), 6.85 (d,  $J = 9.3$  Hz, 2H), 6.88–6.93 (m, 6H), 7.19 (t,  $J = 8.28$  Hz, 2H), 7.37–7.40 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  23.10, 116.27, 124.40, 126.92, 127.15, 127.80, 131.90, 134.61, 141.82, 149.99, 150.13. IR (KBr) 593, 765, 829, 1185, 1474, 2934  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 352.0701, found 352.0715. HPLC analysis:  $t_{\text{R}} = 7.15$  min.

4.4.4. *N*-(4-Bromophenyl)-*N*-phenylnaphthalen-1-amine (**3ag**).<sup>7a</sup> White solid (123 mg, 93%). Mp 95–97 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  6.35 (d,  $J = 8.6$  Hz, 2H), 6.48 (t,  $J = 6.8$  Hz, 1H), 6.62–6.67 (m, 4H), 6.69–6.88 (m, 6H), 7.21 (t,  $J = 7.8$  Hz, 1H), 7.33 (d,  $J = 8.2$  Hz, 1H), 7.70 (d,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  114.18, 122.62, 123.45, 124.48, 125.83, 126.52, 126.60, 126.82, 127.32, 128.30, 128.77, 129.55, 131.43, 132.37, 135.78, 143.64, 147.93, 148.40. HPLC analysis:  $t_{\text{R}} = 6.15$  min.

4.4.5. 3-Bromo-*N,N*-diphenylaniline (**3ba**).<sup>7c</sup> White solid (107 mg, 93%). Mp 91–96 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95–7.09 (m, 8H), 7.19–7.29 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  121.5, 122.7, 123.5, 124.7, 124.9, 125.7, 129.4, 130.3, 147.1, 149.3. IR (KBr) 2956  $\text{cm}^{-1}$ . HPLC analysis:  $t_{\text{R}} = 5.48$  min.

4.4.6. 3-Bromo-*N,N*-di-*p*-tolylaniline (**3bb**). White solid (118 mg, 95%). Mp 97–101 °C.  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  3.04 (s, 6H), 7.62–7.64 (m, 1H), 7.72–7.78 (m, 6H), 7.86–7.90 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  20.8, 120.4, 122.9, 124.0, 124.1, 125.9, 130.8, 131.2, 134.2, 145.2, 150.7. IR (KBr) 988, 1068, 1324, 1475, 2956  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 352.0701, found 352.0691. HPLC analysis:  $t_{\text{R}} = 6.88$  min.

4.4.7. 3-Bromo-*N,N*-di-*m*-tolylaniline (**3bc**). Pale yellow solid (102 mg, 82%). Mp 95–99 °C.  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  3.03 (s, 6H), 7.60–7.67 (m, 7H), 7.80–7.96 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  21.2, 79.0, 121.6, 124.9, 125.2, 125.4, 126.1, 126.3, 130.0, 131.4, 140.0, 147.8, 150.6. IR (KBr) 775, 1318, 1472, 1581, 2920  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 352.0701, found 352.0692. HPLC analysis:  $t_{\text{R}} = 6.57$  min.

4.4.8. 3-Bromo-*N,N*-bis(4-methoxyphenyl)aniline (**3bd**).<sup>6e</sup> Brown solid (97 mg, 71%). Mp 82–86 °C.  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  3.78 (s, 6H), 6.89–6.93 (m, 6H), 7.03–7.09 (m,



6H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  55.7, 115.5, 116.0, 118.2, 121.8, 122.9, 128.2, 131.3, 140.6, 151.5, 157.7. IR (KBr) 1474, 2840, 2933  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{BrNO}_2$  ( $\text{M}+\text{H}^+$ ) 384.0599, found 384.0591. HPLC analysis:  $t_{\text{R}} = 4.77$  min.

4.4.9. *3-Bromo-N-phenyl-N-(p-tolyl)aniline (3be)*. Semi-solid (102 mg, 85%).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  3.68 (s, 3H), 8.30–8.67 (m, 13H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  20.6, 121.1, 122.9, 124.2, 124.7, 124.8, 125.2, 126.2, 130.1, 130.9, 131.3, 134.5, 145.1, 147.8, 150.5. IR (KBr) 695, 1068, 1278, 1474, 1583, 2955  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{17}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 338.0544, found 338.0538. HPLC analysis:  $t_{\text{R}} = 6.14$  min.

4.4.10. *3-Bromo-N-phenyl-N-(m-tolyl)aniline (3bf)*. Black oil (94 mg, 79%).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  2.22–2.26 (m 3H), 6.73–6.74 (m, 1H), 6.74–6.91 (m, 1H), 7.10–7.15 (m, 5H), 7.21–7.30 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  21.6, 116.1, 118.6, 118.7, 118.8, 119.2, 119.3, 119.4, 122.8, 123.8, 129.8, 129.9, 139.4, 139.5, 144.3, 144.4, 144.5. IR (KBr) 690, 1299, 1493, 1584, 2915  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{17}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 338.0544, found 338.0534. HPLC analysis:  $t_{\text{R}} = 5.99$  min.

4.4.11. *N-(3-Bromophenyl)-N-phenylnaphthalen-1-amine (3bg)*.<sup>16</sup> Reddish brown oil (128 mg, 97%).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  6.87–6.89 (m, 1H), 7.01–7.17 (m, 6H), 7.28–7.32 (m, 2H), 7.40–7.52 (m, 2H), 7.92–8.03 (m, 3H), 7.53–7.61 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  122.0, 122.5, 123.2, 124.8, 125.1, 125.2, 125.8, 126.0, 126.1, 126.4, 127.3, 127.8, 128.4, 130.1, 130.4, 131.4, 131.7, 145.5, 147.9, 150.4. IR (KBr) 1473, 3060  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{17}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 374.0544, found 374.0535. HPLC analysis:  $t_{\text{R}} = 6.34$  min.

4.4.12. *N-(3-Bromophenyl)-N-phenylnaphthalen-2-amine (3bh)*. Reddish brown oil (112 mg, 85%).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  6.70–7.32 (m, 12H), 7.52–7.51 (m, 1H), 7.66–7.69 (m, 2H), 7.84 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  119.8, 123.2, 123.4, 123.8, 124.0, 124.4, 127.2, 127.3, 127.5, 128.0, 128.3, 129.4, 130.1, 130.5, 131.5, 131.9, 136.2, 143.4, 148.2, 151.0. IR (KBr) 774, 1392, 1473, 1583, 3060  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{17}\text{BrN}^+$  ( $\text{M}+\text{H}^+$ ) 374.0544, found 374.0537. HPLC analysis:  $t_{\text{R}} = 5.72$  min.

4.4.13. *2-Bromo-N,N-diphenylaniline (3ca)*. Yellow oil (86 mg, 75%).  $^1\text{H}$  NMR (400 MHz,

$C_6D_6$ )  $\delta$  6.59–6.62 (m, 1H), 6.80–6.84 (m, 4H), 6.97–7.06 (m, 4H), 7.19–7.27 (m, 1H), 7.29–7.30 (m, 1H), 7.39–7.41 (m, 2H), 8.07–8.09 (m, 1H).  $^{13}C$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  123.2, 128.0, 128.2, 129.4, 130.3, 130.4, 132.7, 135.6, 147.0, 148.4. IR (KBr) 697, 1277, 1472, 1580, 3451  $cm^{-1}$ . HRMS (ESI):  $m/z$ : calcd for  $C_{18}H_{15}BrN^+$  ( $M+H^+$ ) 324.0388, found 324.0407. HPLC analysis:  $t_R$  = 4.68 min.

4.4.14.  $N^1,N^1,N^4,N^4$ -Tetraphenylbenzene-1,4-diamine (**4aa**).<sup>17</sup> White solid. Mp 200–204 °C. The product contains inseparable impurities and triethylamine after silicagel column chromatography and/or recrystallization.  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta$  6.42 (t,  $J$  = 7.2 Hz, 4H), 6.63 (t,  $J$  = 7.2 Hz, 8H), 6.70–6.75 (m, 12H).  $^{13}C$  NMR (125 MHz,  $C_6D_6$ )  $\delta$  121.21, 122.68, 124.29, 128.00, 141.86, 146.85. HPLC analysis:  $t_R$  = 7.48 min.

4.4.15.  $N^1,N^4$ -Di(naphthalen-2-yl)- $N^1,N^4$ -diphenylbenzene-1,4-diamine (**4ab**).<sup>18</sup> White solid. Mp 196–200 °C. The product contains inseparable impurities and triethylamine after silicagel column chromatography and/or recrystallization.  $^1H$  NMR (270 MHz,  $C_6D_6$ )  $\delta$  6.89 (t,  $J$  = 6.8 Hz, 5H), 7.04–7.20 (m, 11H), 7.33 (dd,  $J$  = 8.9, 1.6 Hz, 4H), 7.48–7.57 (m, 8H).  $^{13}C$  NMR (125 MHz,  $C_6D_6$ ):  $\delta$  120.7, 123.1, 124.5, 124.7, 124.8, 126.5, 127.3, 129.4, 129.7, 130.6, 135.1, 143.5, 145.9, 148.4. HPLC analysis:  $t_R$  = 11.50 min.

4.4.16.  $N^1,N^1,N^4,N^4$ -Tetra-*p*-tolylbenzene-1,4-diamine (**4ah**).<sup>19</sup> White solid. Mp 209–214 °C. The product contains inseparable impurities and triethylamine after silicagel column chromatography and/or recrystallization.  $^1H$  NMR (270 MHz,  $C_6D_6$ )  $\delta$  2.09 (s, 12H), 6.88 (d,  $J$  = 8.4 Hz, 8H), 7.08 (d,  $J$  = 8.4 Hz, 8H), 7.13 (s, 4H).  $^{13}C$  NMR (67 MHz,  $C_6D_6$ ):  $\delta$  20.8, 123.5, 124.9, 130.2, 132.3, 146.1, 148.9. HPLC analysis:  $t_R$  = 7.88 min.

4.4.17.  $N^1,N^4$ -Di(naphthalen-1-yl)- $N^1,N^4$ -diphenylbenzene-1,4-diamine (**4ag**).<sup>18</sup> Pale yellow solid. Mp 197–205 °C. The product contains inseparable impurities and triethylamine after silicagel column chromatography and/or recrystallization.  $^1H$  NMR (500 MHz,  $C_6D_6$ )  $\delta$  6.29 (d,  $J$  = 8.70 Hz, 4H), 6.35 (t,  $J$  = 7.35 Hz, 2H), 6.49–6.57 (m, 2H), 6.62 (t,  $J$  = 7.80 Hz, 4H), 6.68–6.74 (m, 8H), 6.80 (t,  $J$  = 6.90 Hz, 2H), 6.95 (d,  $J$  = 6.85 Hz, 2H), 7.20 (d,  $J$  = 8.25 Hz, 2H), 7.32 (d,  $J$  = 8.25 Hz, 2H).  $^{13}C$  NMR (125 MHz,  $C_6D_6$ )  $\delta$  116.62, 117.65, 120.60, 121.19,

122.61, 123.35, 125.63, 125.70, 128.19, 128.29, 128.50, 128.73, 129.52, 135.26, 139.38, 145.37.

HPLC analysis:  $t_R = 9.10$  min.

4.4.18.  $N^1$ -(naphthalen-2-yl)- $N^1, N^4, N^4$ -triphenylbenzene-1,4-diamine (**5**).<sup>19</sup> Semi-solid (117 mg, 73%). <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>)  $\delta$  6.78 (t,  $J = 7.6$  Hz, 4H), 6.89–6.90 (m, 4H), 7.02–7.15 (m, 4H), 7.26 (t,  $J = 8.0$  Hz, 2H), 7.35 (t,  $J = 8.0$  Hz, 4H), 7.65 (d,  $J = 8.0$  Hz, 2H), 7.77 (d,  $J = 8.0$  Hz, 2H), 7.87 (d,  $J = 8.0$  Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  120.88, 121.01, 122.20, 123.41, 123.51, 124.30, 125.63, 126.09, 126.29, 126.33, 126.36, 127.09, 128.38, 129.00, 129.10, 129.32, 131.25, 135.28, 141.98, 143.52, 143.75, 147.90, 148.61.

### Supplementary data

Supplementary data related to this article can be found at [http:// dx.doi.org/10.1016/](http://dx.doi.org/10.1016/)

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- 11 Reaction with excess of Ph<sub>2</sub>NH (2.5 equiv.) gave the decreased chemoselectivity (94%) without losing the yield (87%).
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- 14 We used 99.999% purity of CuI purchased from Aldrich, and also confirmed that the other CuI (98% purity) provided same results.
- 15 Xiao, H.; Shen, H.; Lin, Y.; Su, J.; Tian, H. *Dye Pigments* **2007**, *73*, 224–229.
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**SUPPORTING INFORMATION****Chemoselective Amination of Bromiodobenzenes with Diarylamines by Palladium/Xantphos or Ligand-free Copper Catalysts**

Yoshinori Kanazawa,<sup>†</sup> Tomo Yokota,<sup>†</sup> Hiroshi Ogasa,<sup>†</sup> Hirotaka Watanabe,<sup>‡</sup> Taisyun Hanakawa,<sup>‡</sup> Shinichi Soga,<sup>§</sup> Motoi Kawatsura\*<sup>‡</sup>

<sup>†</sup>*Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Koyama, Tottori 680-8552, Japan*

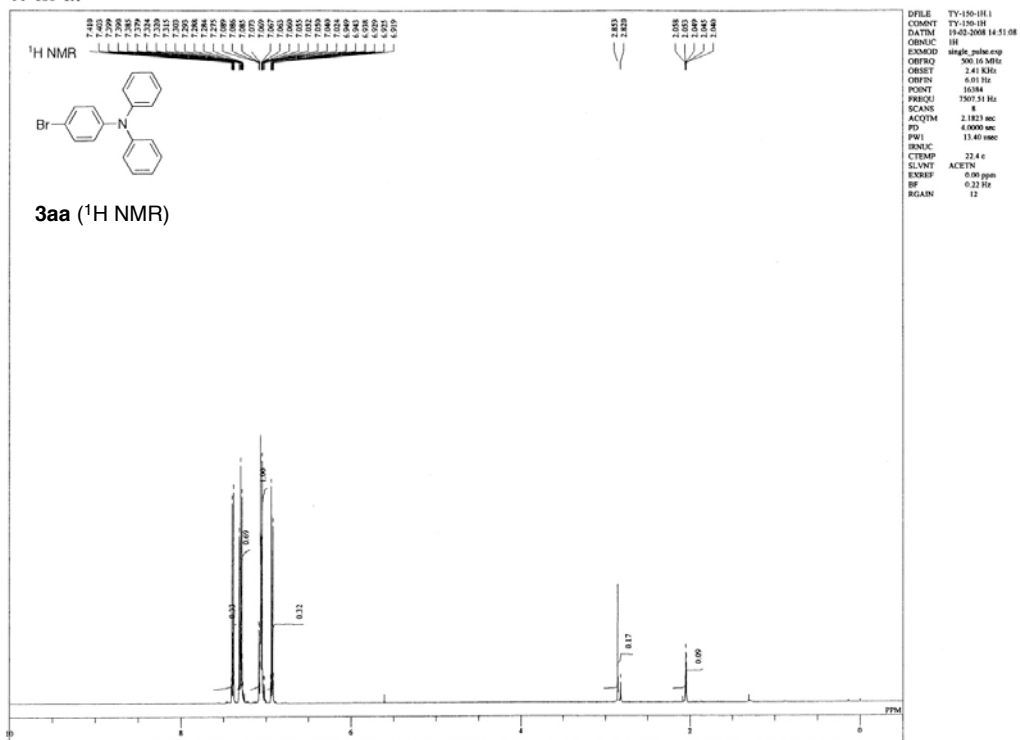
<sup>‡</sup>*Department of Chemistry, College of Humanities & Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan*

<sup>§</sup>*Tosoh Organic Chemical Co., Ltd., 4988 Kaisei-cho, Shunan, Yamaguchi 746-0006, Japan*

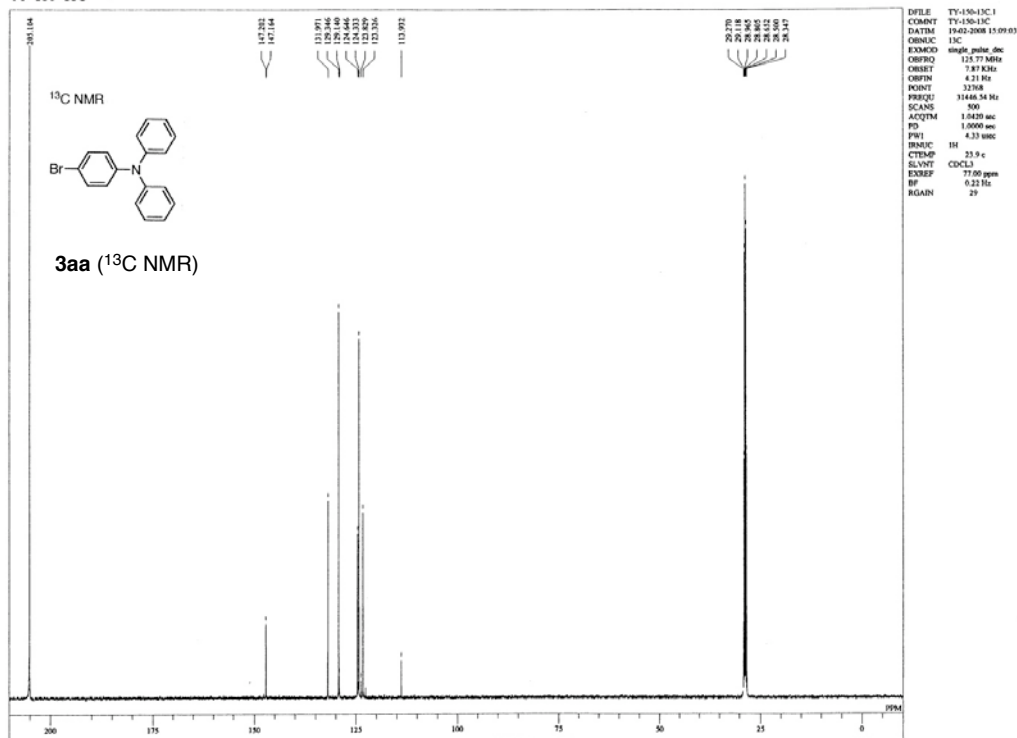
E-mail: kawatsur@chs.nihon-u.ac.jp

- **<sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds**
- **IR chart for new compounds**

TY-150-1H



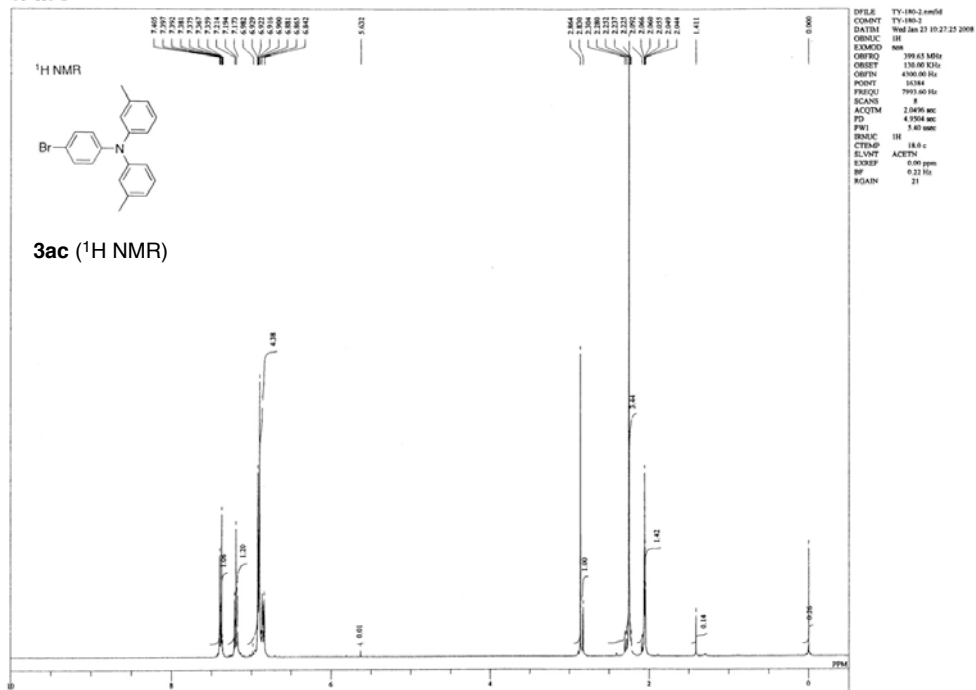
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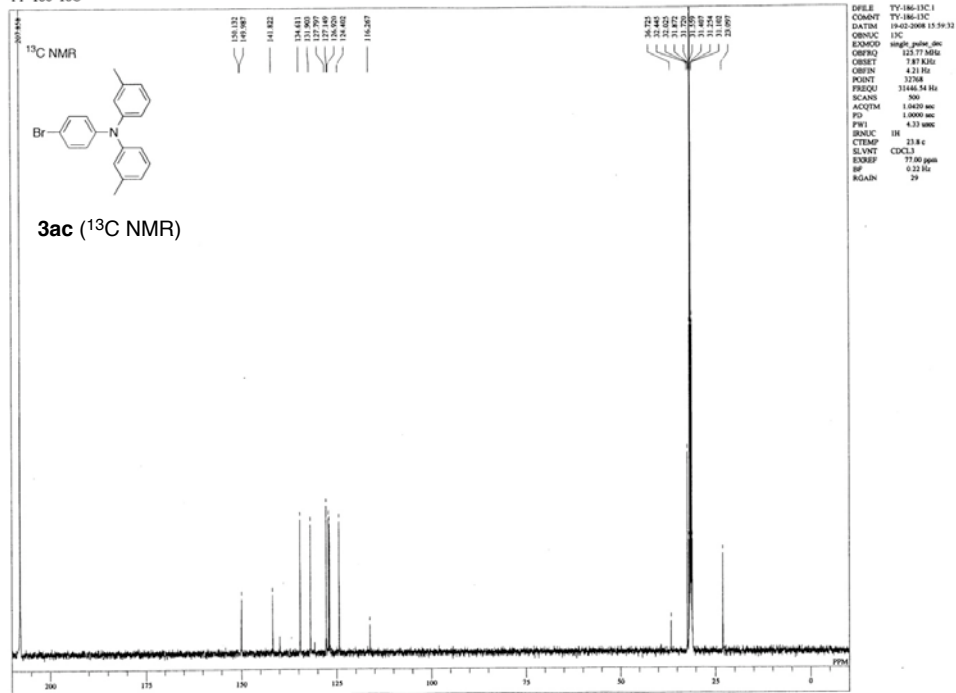


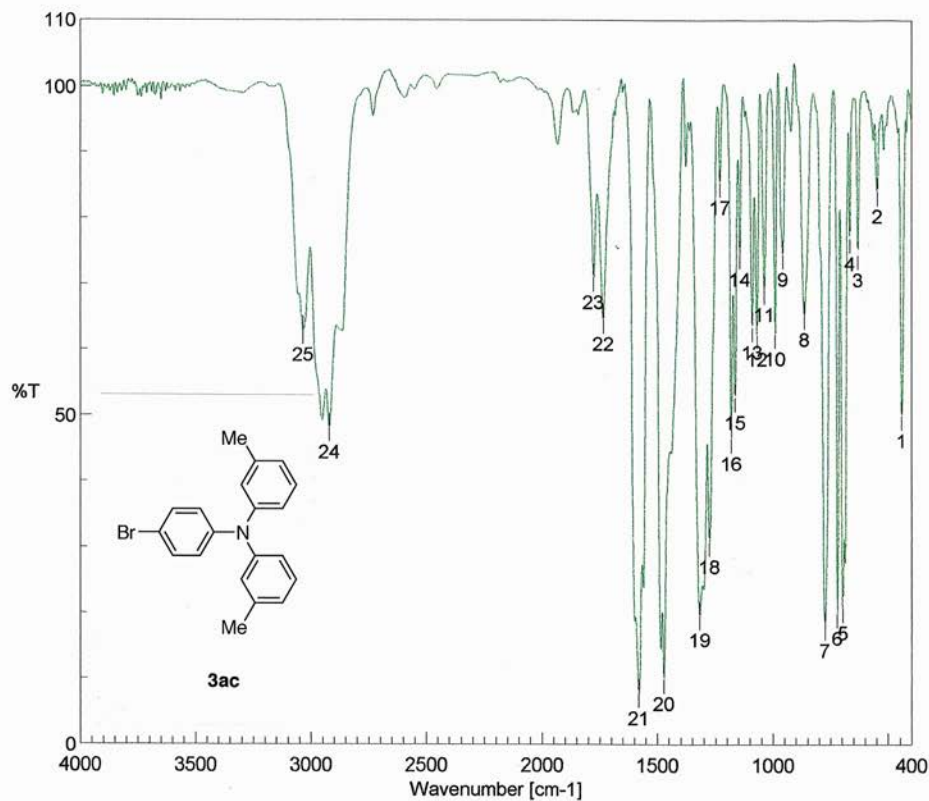


TY-180-2



TY-186-13C





## ピーク検出結果

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3	631.573	74.2824	4	666.285	76.7559
5	697.141	20.6261	6	720.282	19.8151
7	775.244	17.9597	8	864.917	65.2297
9	958.448	74.3682	10	991.232	62.3127
11	1037.52	69.0109	12	1069.33	62.2531
13	1090.55	63.2824	14	1143.58	74.4174
15	1164.79	52.6342	16	1181.19	46.417
17	1230.36	85.2209	18	1276.65	30.7152
19	1318.11	19.5972	20	1472.38	9.85865
21	1581.34	7.71614	22	1736.58	64.5358
23	1777.08	70.8686	24	2920.66	48.0413
25	3033.48	62.8463			

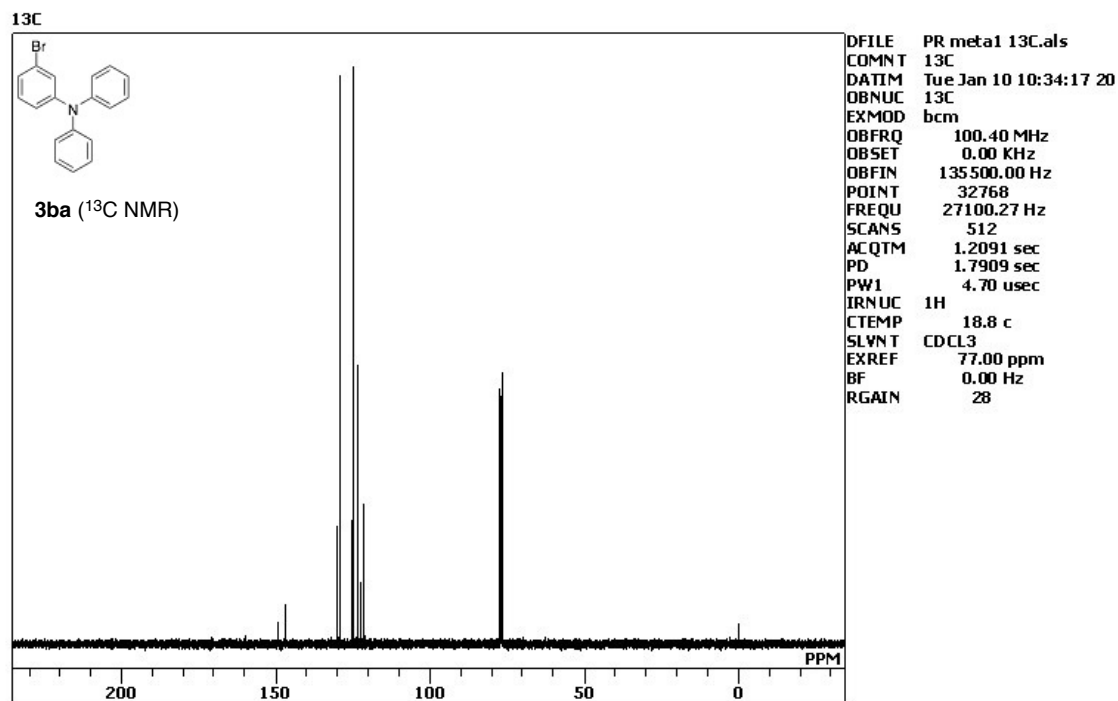
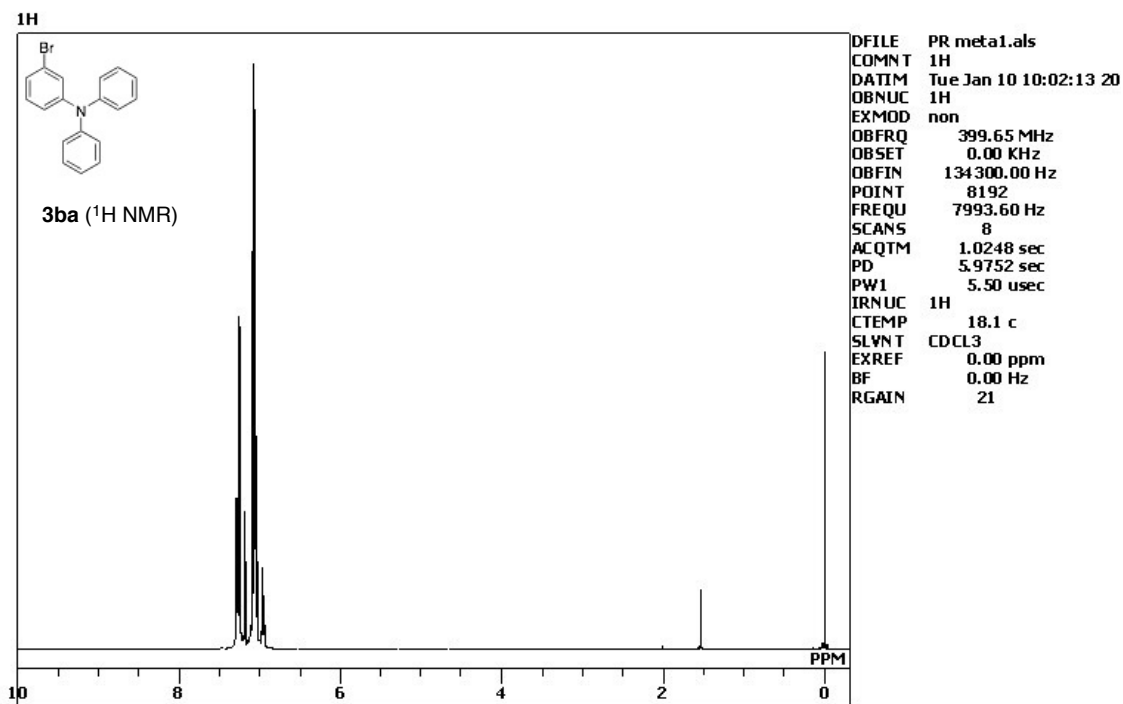
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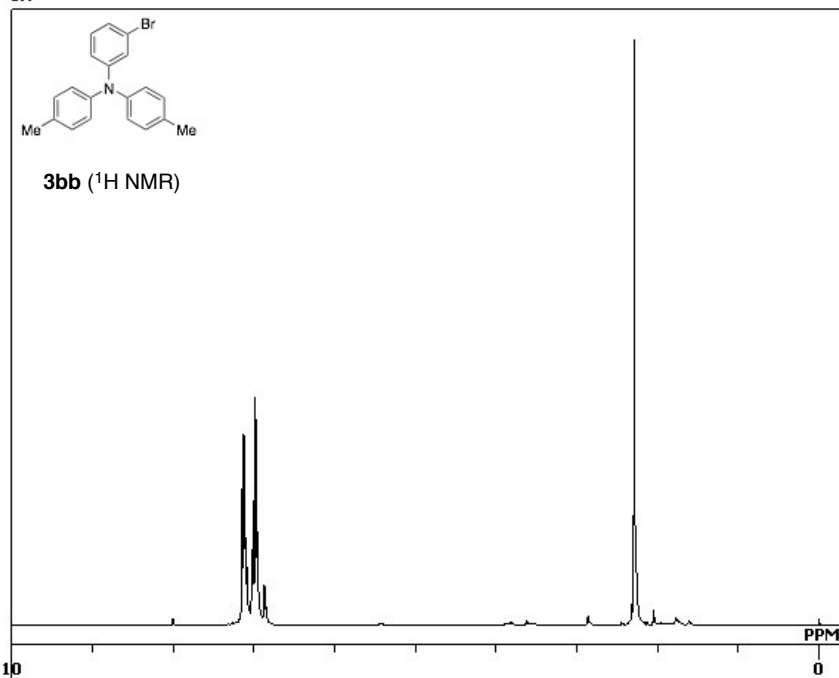
試料名 poll san^^  
 コメント poll san^^  
 測定者  
 所属  
 会社 花川漁業部次期社長代理

## [測定情報]

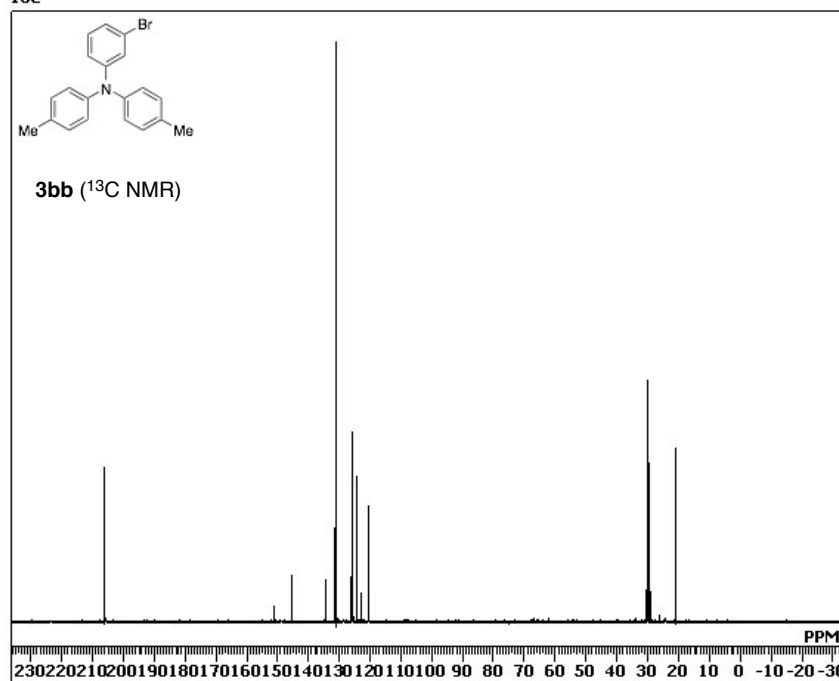
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 検出器 TGS  
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 分解 4 cm-1  
 ゼロフィリング On  
 アポダイゼーション Cosine  
 ゲイン Auto (2)  
 アパーチャー Auto (7.1 mm)  
 スキャンスピード Auto (2 mm/sec)  
 フィルタ Auto (30000 Hz)



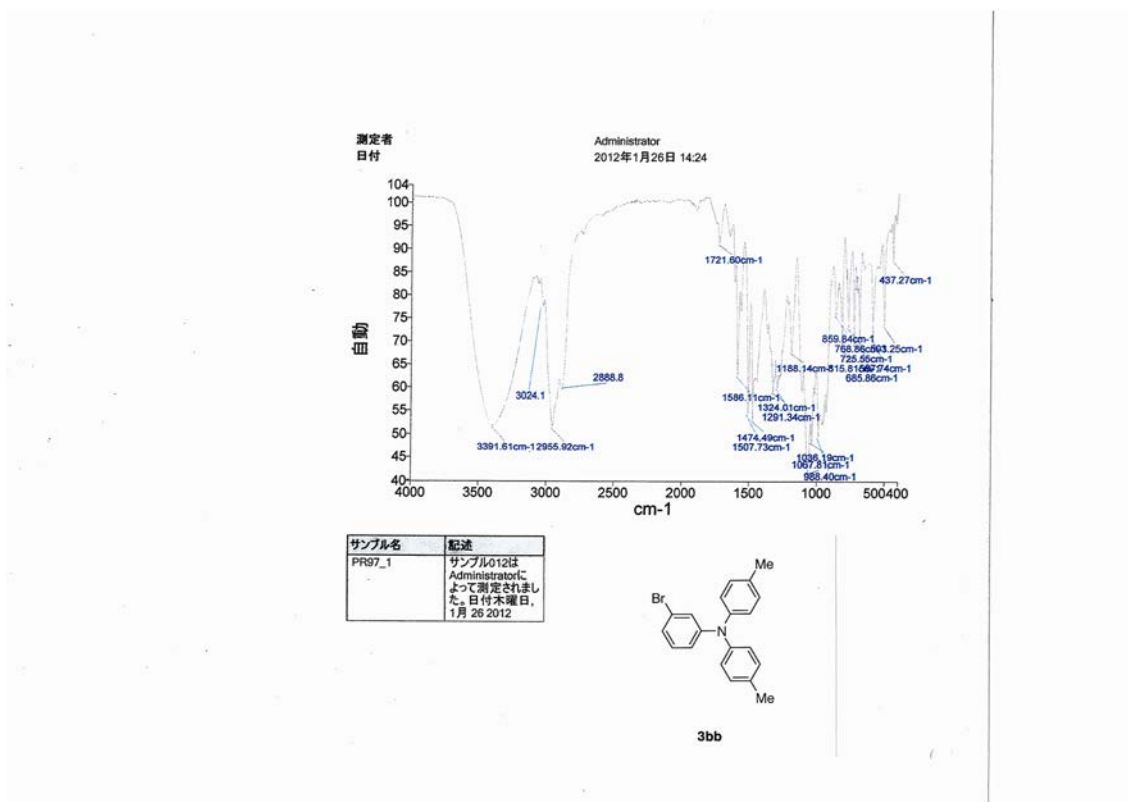


**<sup>1</sup>H**

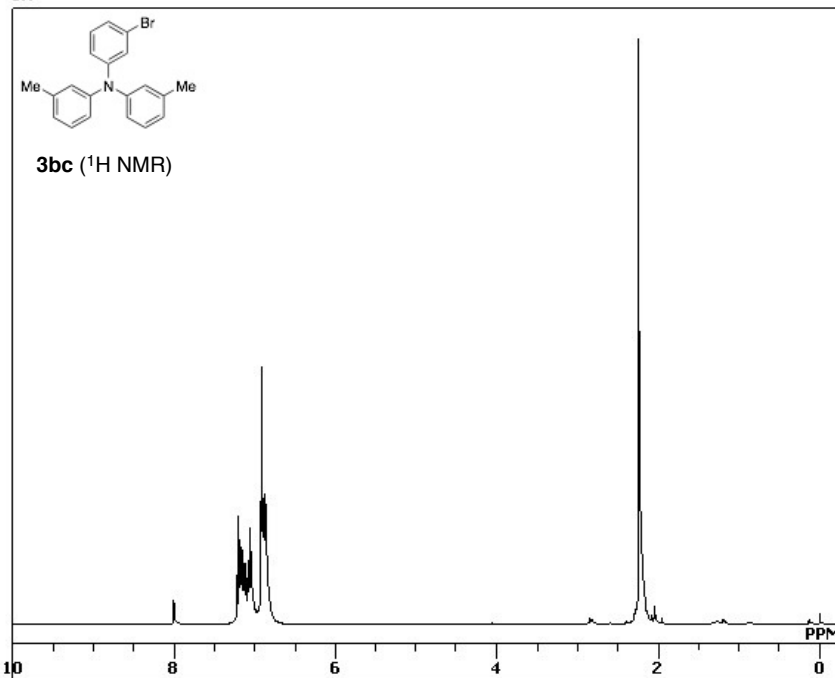
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 OBFIN 134300.00 Hz  
 POINT 8192  
 FREQU 7993.60 Hz  
 SCANS 8  
 ACQTM 1.0248 sec  
 PD 5.9752 sec  
 PW1 5.50 usec  
 IRNUC 1H  
 CTEMP 18.8 c  
 SLVNT ACETN  
 EXREF 0.00 ppm  
 BF 0.00 Hz  
 RGAIN 14

**<sup>13</sup>C**

DFILE PR-97 Fr 13C.als  
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 SLVNT ACETN  
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 RGAIN 27

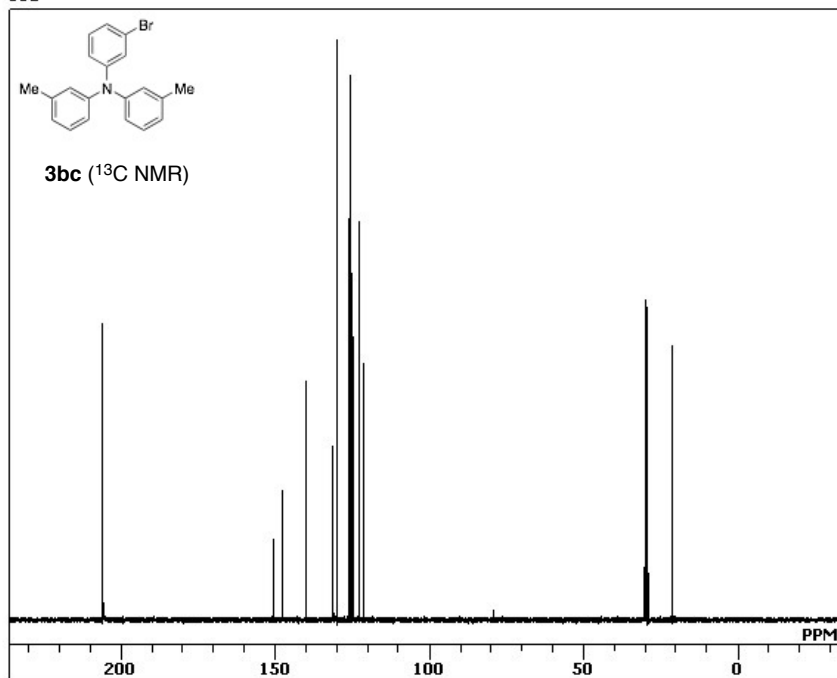


1H

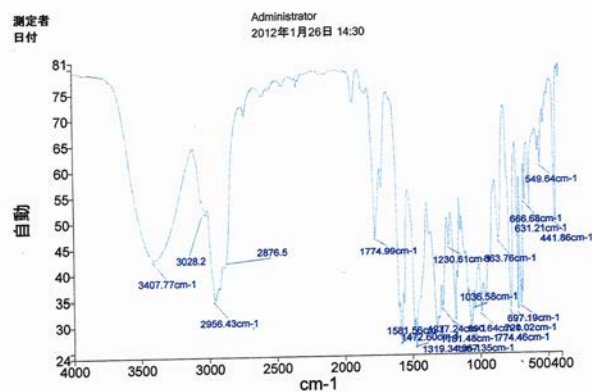


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OBSET 0.00 KHz  
OBFIN 134300.00 Hz  
POINT 8192  
FREQU 7993.60 Hz  
SCANS 8  
ACQTM 1.0248 sec  
PD 5.9752 sec  
PW1 5.50 usec  
IRNUC 1H  
CTEMP 18.7 c  
SLVNT ACETN  
EXREF 0.00 ppm  
BF 0.00 Hz  
RGAIN 13

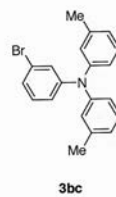
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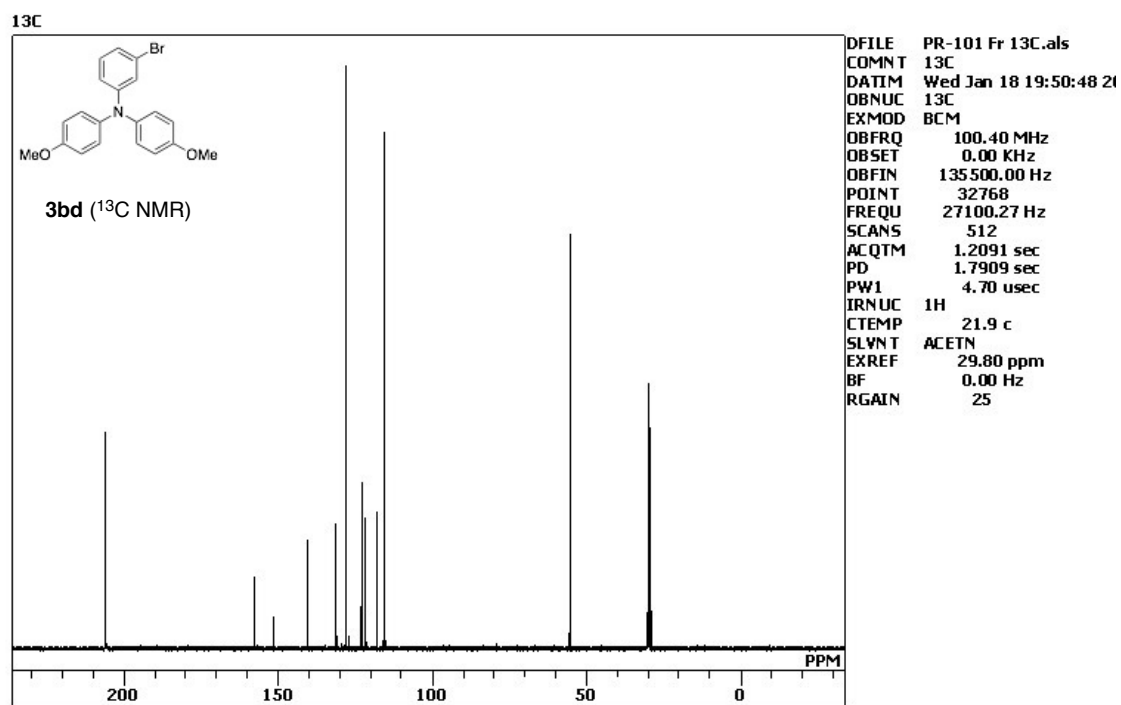
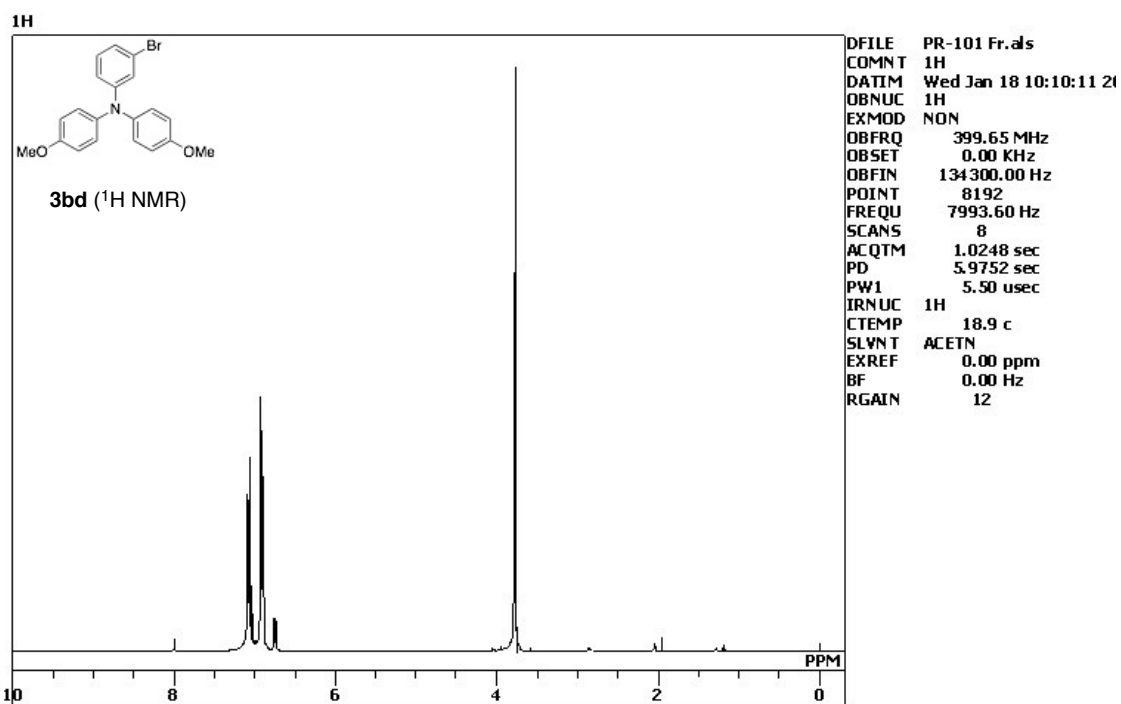


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 OBFIN 135500.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 512  
 ACQTM 1.2091 sec  
 PD 1.7909 sec  
 PW1 4.70 usec  
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 CTEMP 21.6 c  
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 RGAIN 27

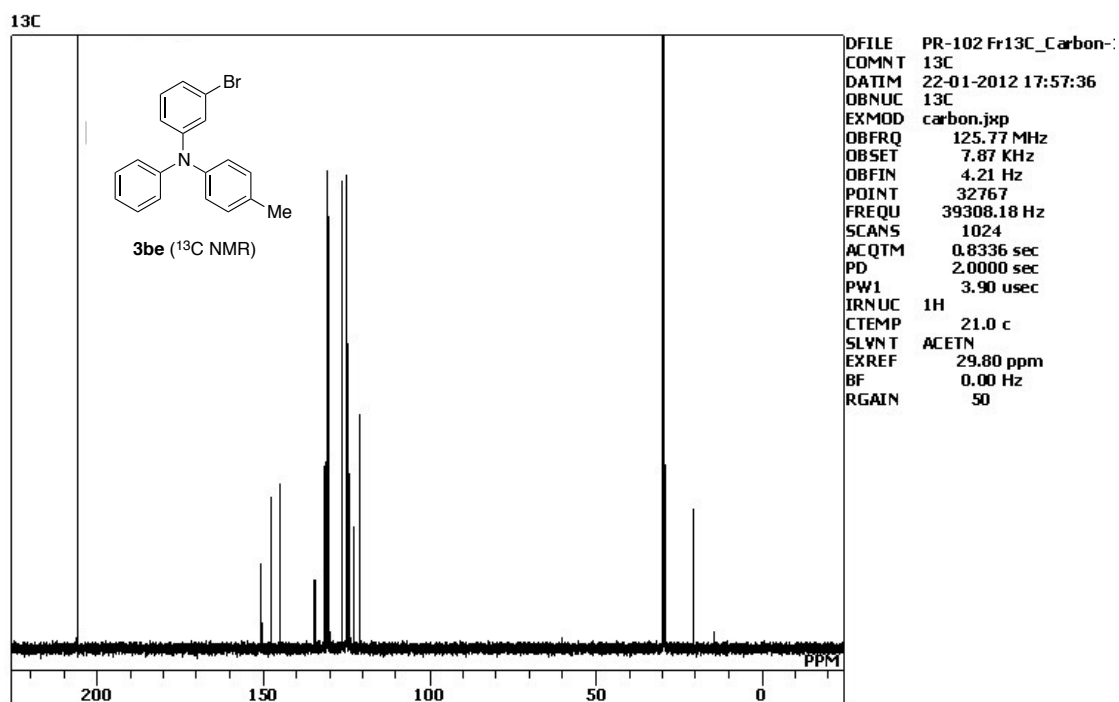
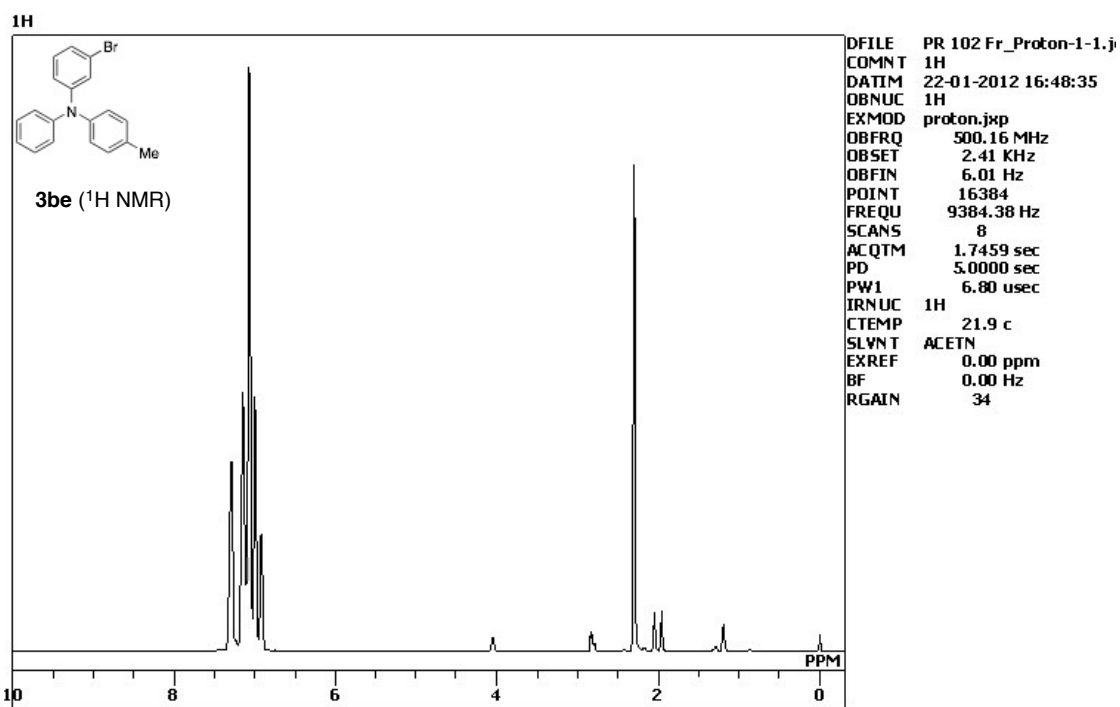


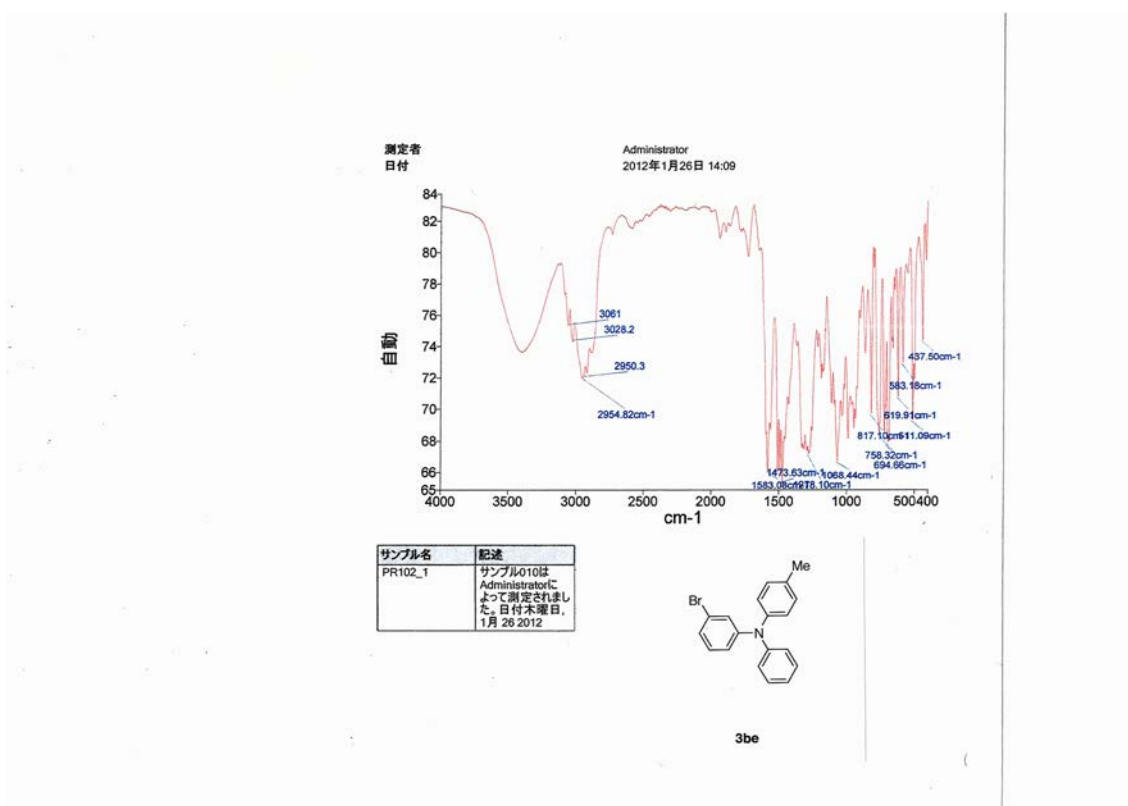
サンプル名	記述
PR98_1	サンプル013は Administratorによって測定されました。日付木曜日, 1月 26 2012



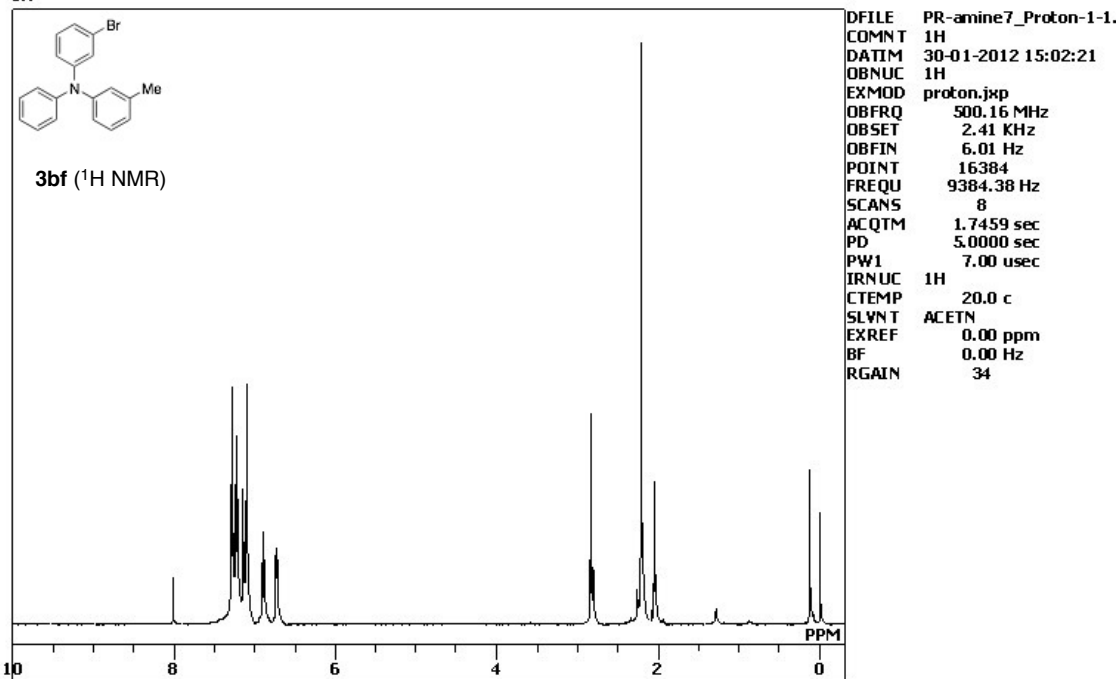




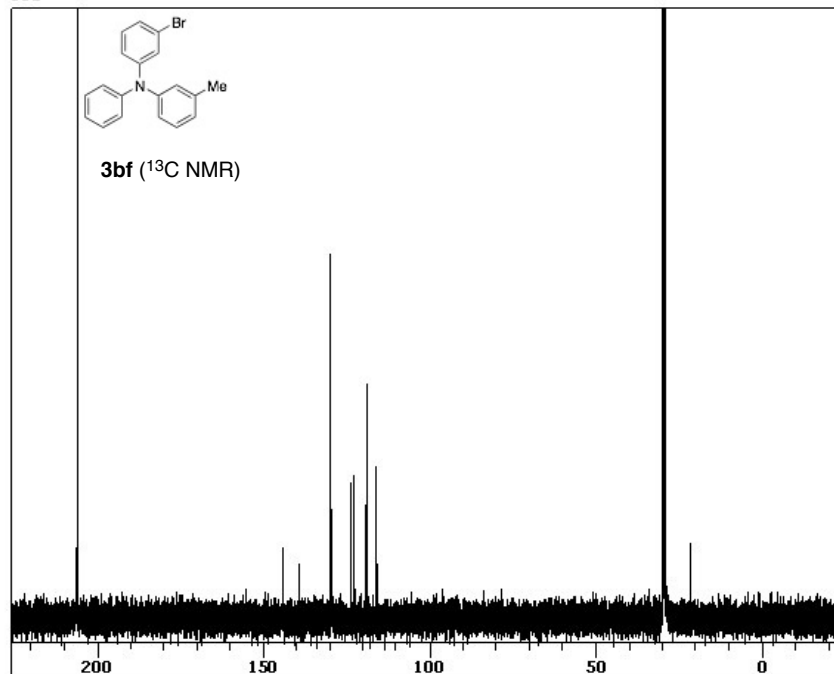




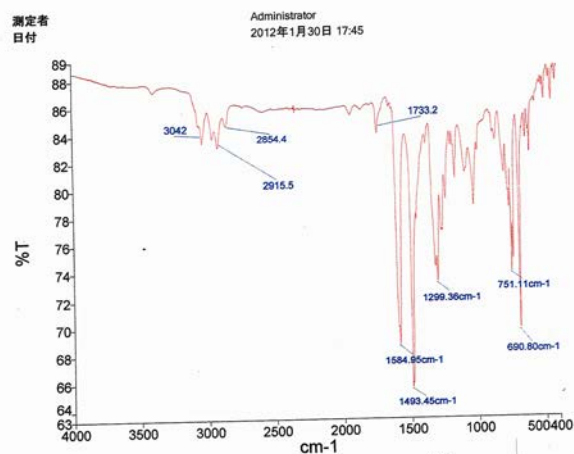
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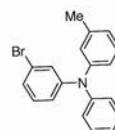
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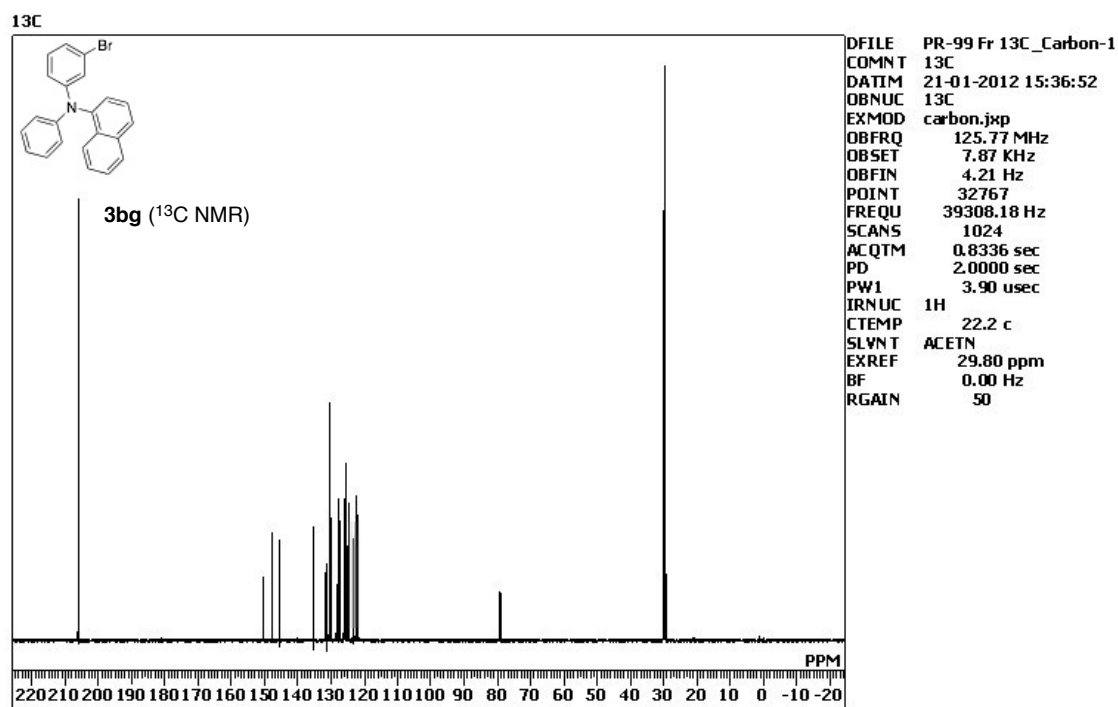
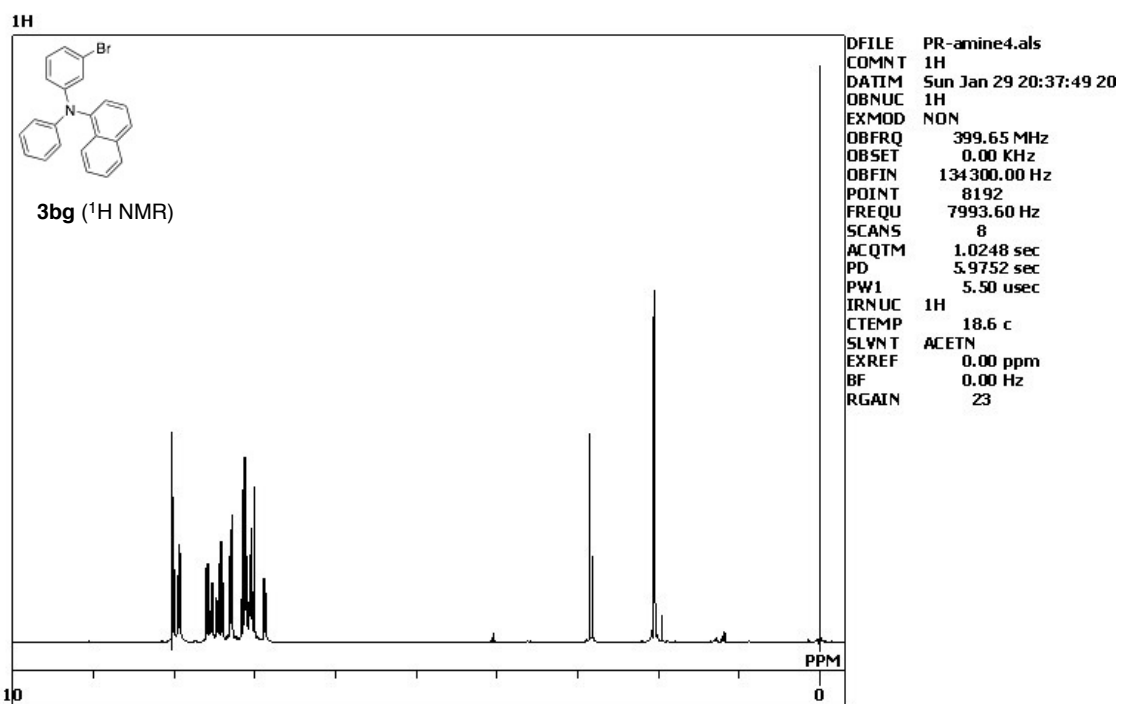
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 PD 2.0000 sec  
 PW1 3.90 usec  
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 BF 0.00 Hz  
 RGAIN 50

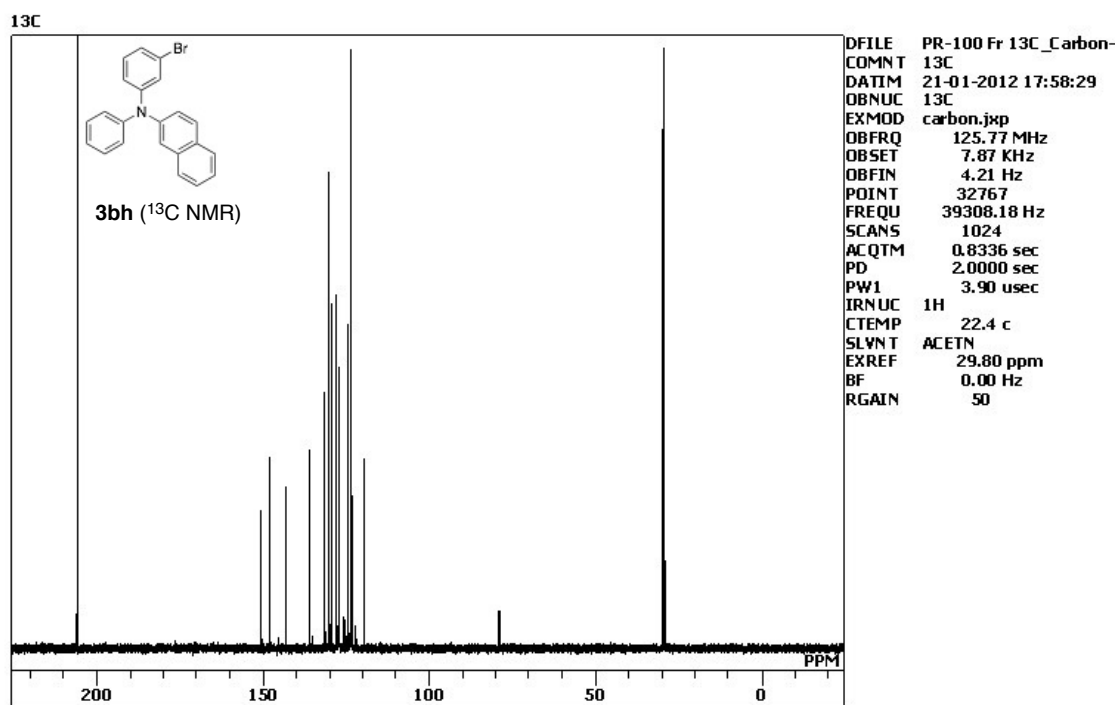
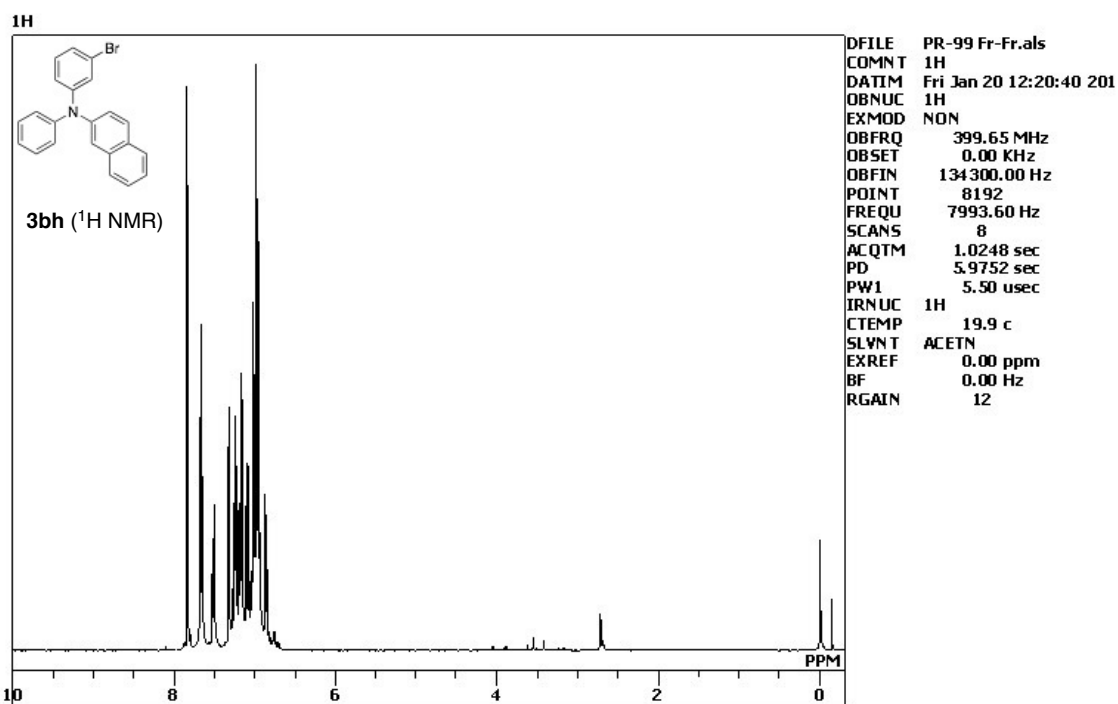


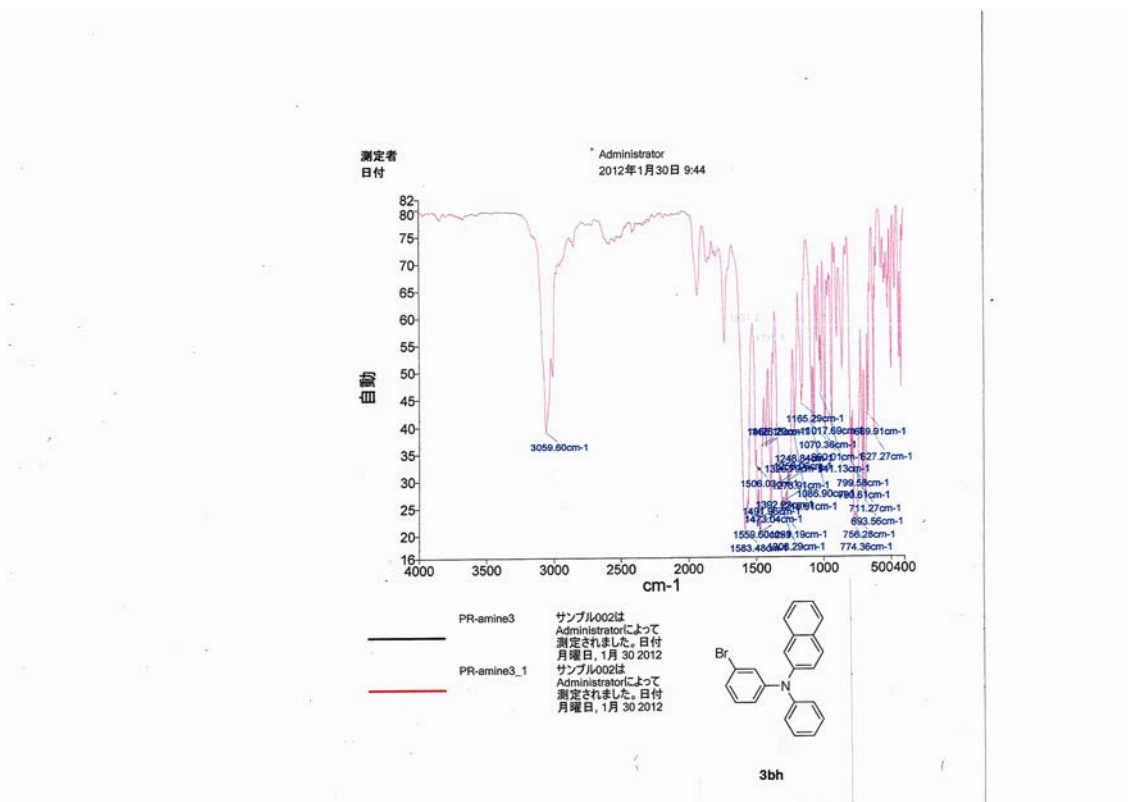
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 Administratorによって  
 測定されました。日付  
 月曜日, 1月 30 2012



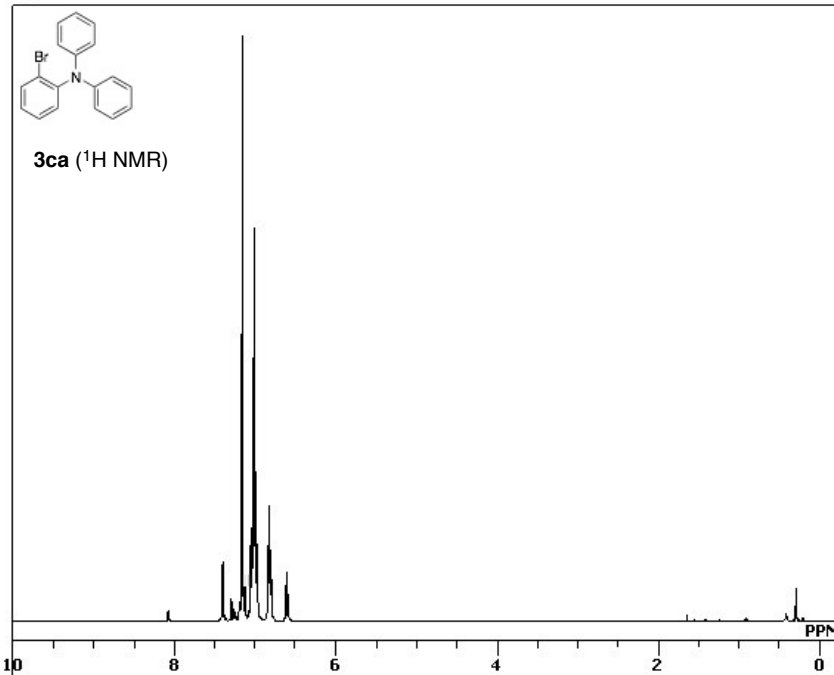
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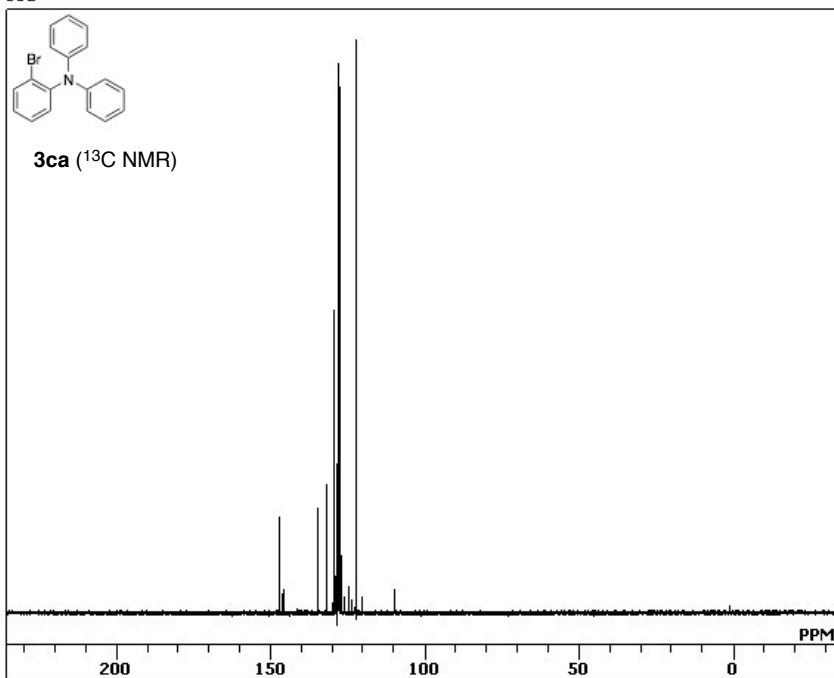


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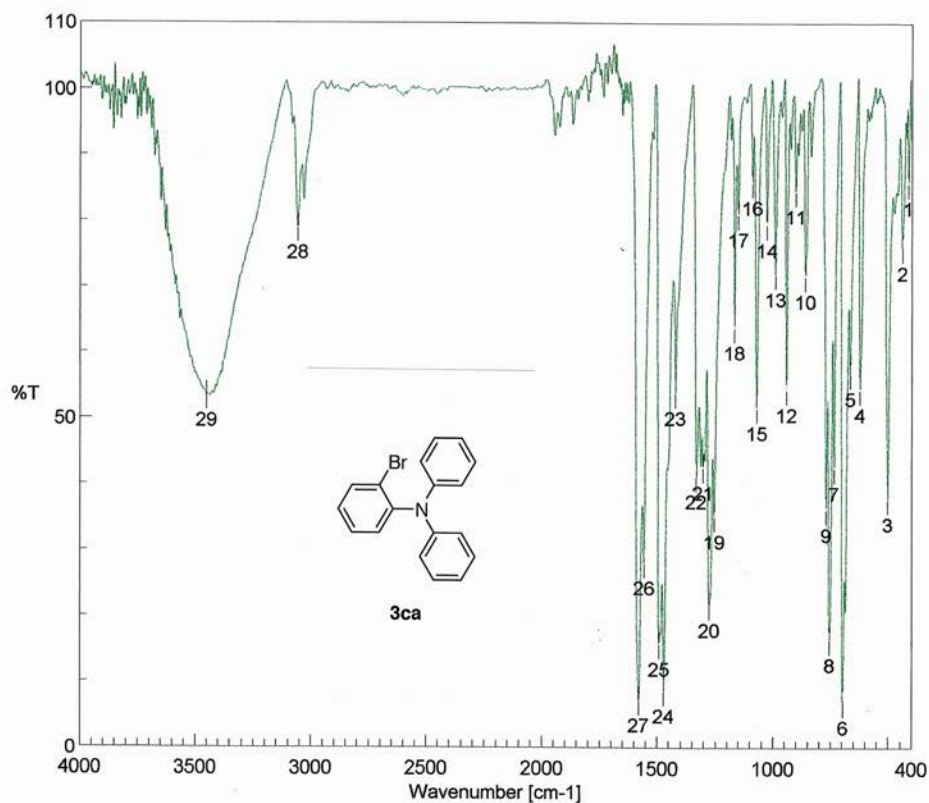
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FREQU 7993.60 Hz  
SCANS 8  
ACQTM 1.0248 sec  
PD 5.9752 sec  
PW1 5.50 usec  
IRNUC 1H  
CTEMP 18.4 c  
SLVNT C6D6  
EXREF 7.16 ppm  
BF 0.00 Hz  
RGAIN 16

13C



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OBFIN 135500.00 Hz  
POINT 32768  
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SCANS 512  
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PD 1.7909 sec  
PW1 4.70 usec  
IRNUC 1H  
CTEMP 19.6 c  
SLVNT C6D6  
EXREF 128.00 ppm  
BF 0.00 Hz  
RGAIN 23

ACCEPTED MANUSCRIPT



## ピーク検出結果

No.	位置	強度	No.	位置	強度
1	413.656	85.5832	2	439.69	75.7486
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5	665.321	56.6448	6	697.141	6.8016
7	735.71	42.2868	8	755.959	16.2814
9	769.458	35.9968	10	861.06	71.3997
11	903.487	84.3444	12	943.02	54.2151
13	990.268	71.7966	14	1027.87	79.2508
15	1071.26	51.414	16	1090.55	85.6652
17	1151.29	80.8079	18	1167.69	63.6519
19	1255.43	34.9511	20	1276.65	21.5569
21	1302.68	42.3971	22	1331.61	41.0958
23	1422.24	53.6936	24	1472.38	8.52729
25	1492.63	15.6417	26	1558.2	27.931
27	1580.38	7.09121	28	3058.55	78.8068
29	3451.96	53.2717			

## [コメント情報]

試料名 p-bromo-N,N-diphenylaniline  
 コメント p-bromo-N,N-diphenylaniline  
 測定者  
 所属  
 会社 日本大学

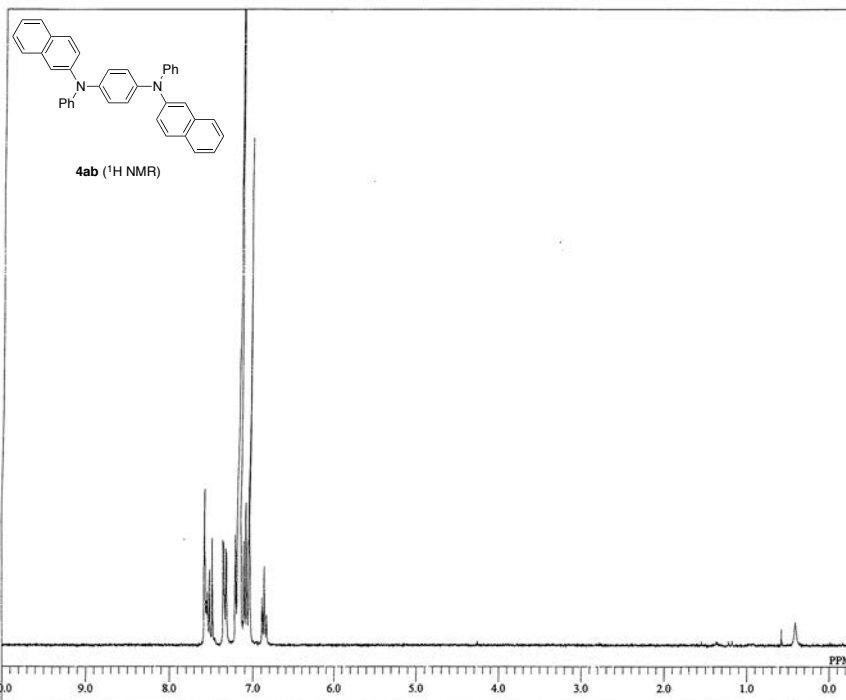
## [測定情報]

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 検出器 TGS  
 積算回数 50  
 分解 4 cm<sup>-1</sup>  
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 アポダイゼーション Cosine  
 ゲイン Auto (32)  
 アパーチャー Auto (7.1 mm)  
 スキャンスピード Auto (2 mm/sec)  
 フィルタ Auto (30000 Hz)

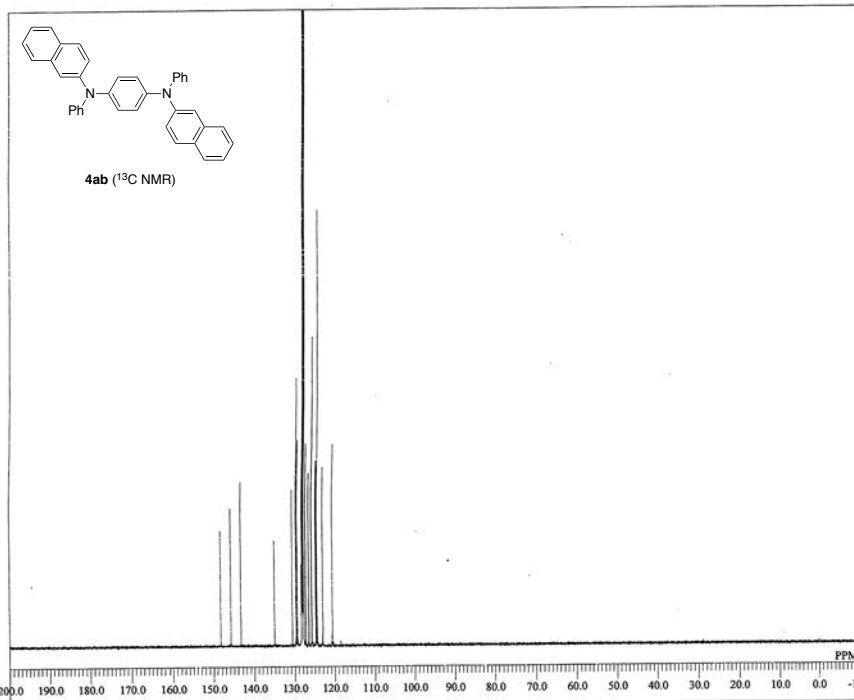




1HW-1047 F3

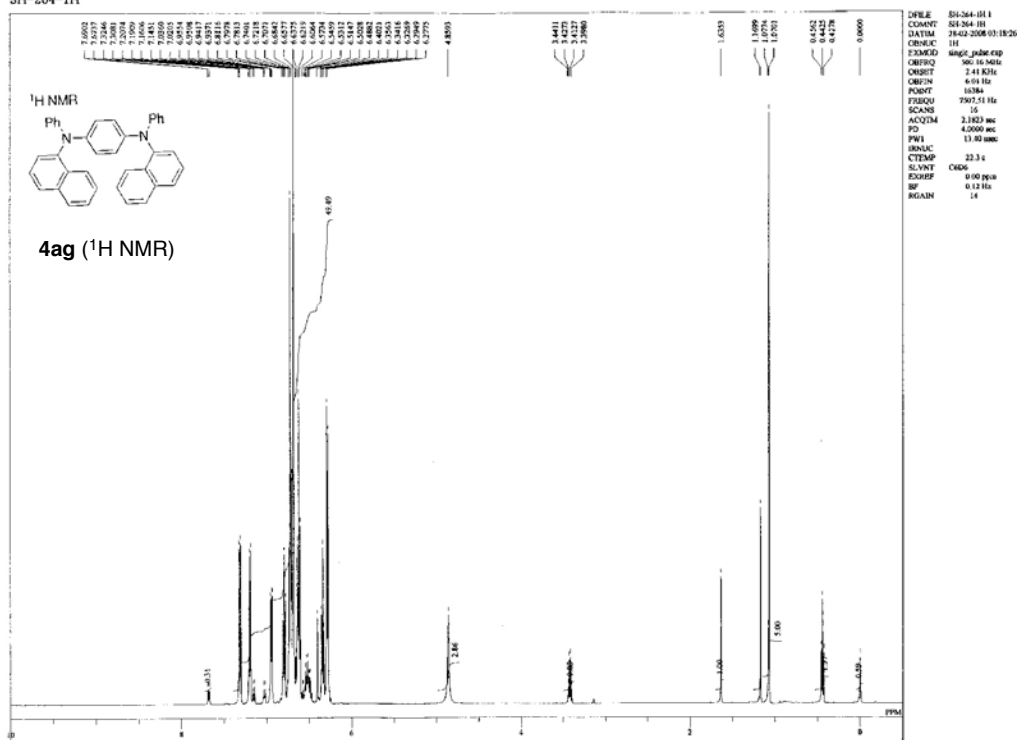


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OBSET 112.00 KHz  
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POINT 16384  
FREQU 5401.76 Hz  
SCANS 8  
ACQTM 3.0331 sec  
PD 3.9670 sec  
PW1 6.00 usec  
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CTEMP 23.2 c  
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EXREF 7.16 ppm  
BF 0.12 Hz  
RGAIN 23

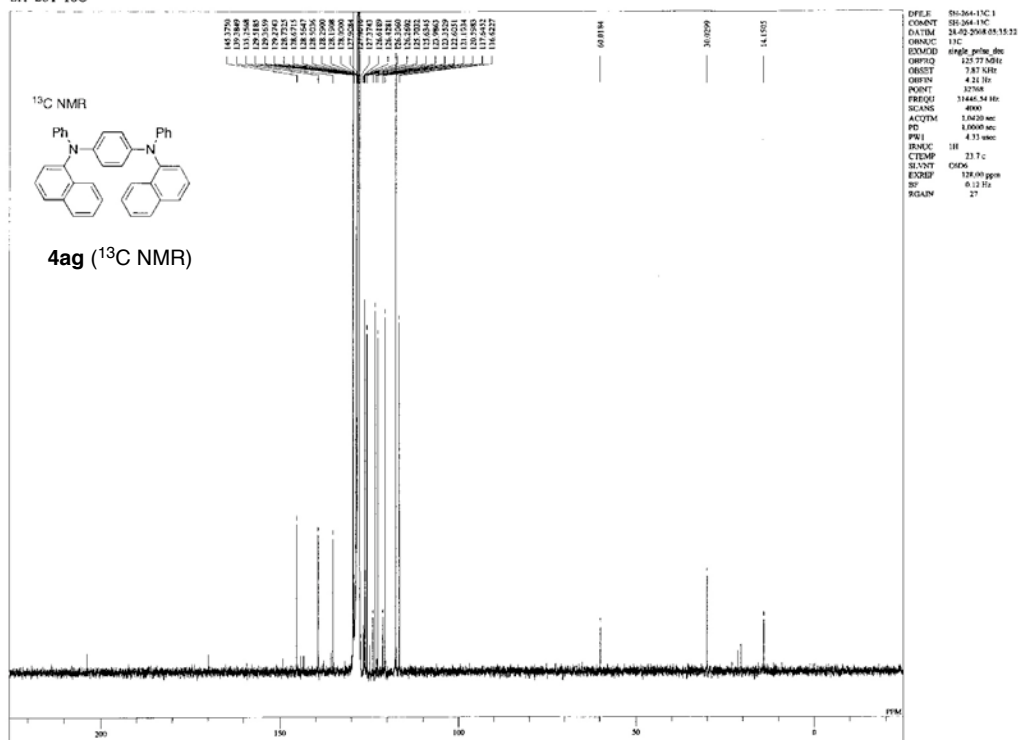


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EXMOD single\_pulse\_dco  
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OBSET 7.87 KHz  
OBFIN 4.21 Hz  
POINT 32768  
FREQU 39308.18 Hz  
SCANS 1024  
ACQTM 0.8336 sec  
PD 2.0000 sec  
PW1 3.33 usec  
IRNUC 1H  
CTEMP 21.5 c  
SLVNT C6D6  
EXREF 128.00 ppm  
BF 0.12 Hz  
RGAIN 52

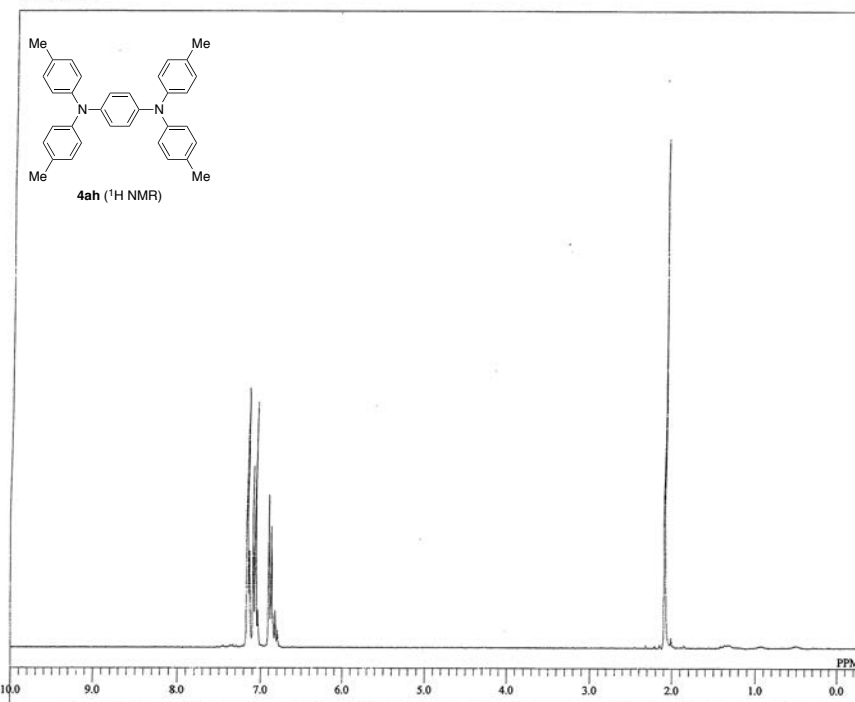
SH-264-1H



SH-264-13C

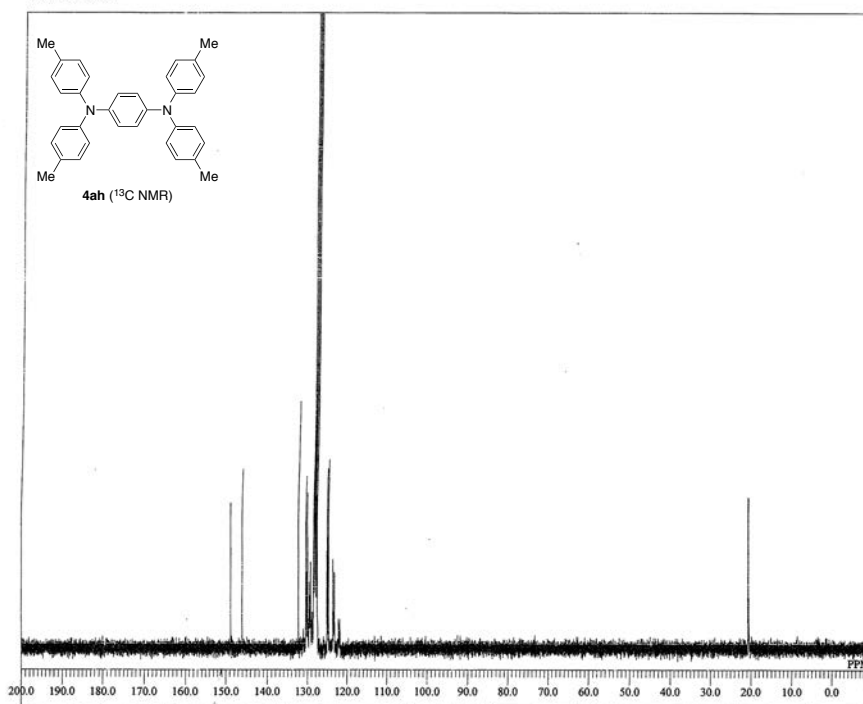


1HW-1057 F2 1H



DFILE 1HW-1057 F2 1H.als  
 COMNT 1HW-1057 F2 1H  
 DATIM Sun Nov 30 20:47:12 2014  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFIN 5800.00 Hz  
 POINT 16384  
 FREQU 5401.76 Hz  
 SCANS 8  
 ACQTM 3.0331 sec  
 PD 3.9670 sec  
 PWI 6.00 usec  
 IRNUC 1H  
 CTEMP 22.4 c  
 SLVNT C6D6  
 EXREF 7.16 ppm  
 BF 0.12 Hz  
 RGAIN 21

1HW-1057 F2 13C



DFILE 1HW-1057 F2 13C.als  
 COMNT 1HW-1057 F2 13C  
 DATIM Mon Dec 01 06:53:01 2014  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5200.00 Hz  
 POINT 32768  
 FREQU 18306.64 Hz  
 SCANS 12000  
 ACQTM 1.7900 sec  
 PD 1.2100 sec  
 PWI 4.50 usec  
 IRNUC 1H  
 CTEMP 22.5 c  
 SLVNT C6D6  
 EXREF 128.00 ppm  
 BF 0.12 Hz  
 RGAIN 25

