國立臺灣大學理學院化學系

碩士論文

Department of Chemistry
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Master Thesis

多牙氮配位基及雙金屬鈀錯合物的合成與其催化應用

Synthesis and Catalytic Application of Dipalladium Complexes with Multidentate Ligands

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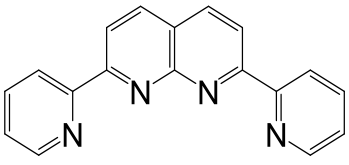
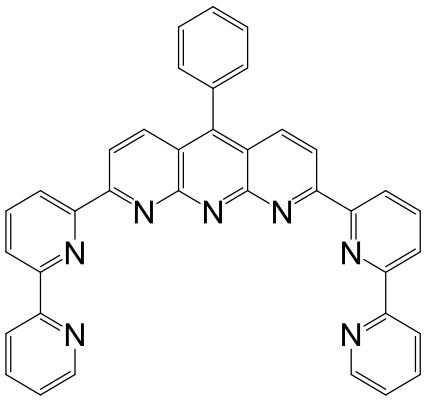
摘要

本篇論文分別合成 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) 和 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**) 作為多牙配位基，利用這些配體與鈀金屬進行錯合反應，探討所生成錯合物的結構和催化應用。多牙氮配位基 **bpnp** 與乙酸鈀在甲醇和三氟醋酸下反應生成 Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**)，**pbbpa** 與 $Pd(MeCN)_2Cl_2$ 反應，合成出雙金屬錯合物。由於其溶解度不佳，使用六氟磷酸鉀置換陰離子，生成 [Pd_2(**pbbpa**)Cl_2]$(PF_6)_2$ (**11**)，以核磁共振光譜和質譜分析分別鑑定結構。

論文中比較 **9** 和 **11** 對於硝基還原反應之催化活性之差異。在先前的研究工作中發現 [Pd_2(**pbbpa**)Cl_2]$(PF_6)_2$ (**11**) 經過少量的 $NaBH_3CN$ 活化後，能夠在氫氣下還原硝基苯衍生物，而 Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**) 則是可以作為催化劑直接在氫氣下進行該還原反應。另外，對此催化系統的應用範圍做了廣泛性測試，並藉由動力學和可能的反應中間體的實驗，解析此催化的反應機構。發現 **9** 的催化過程是遵循縮合路徑，由 *N*-苯基羥胺和亞硝基苯縮合成氧化偶氮苯後，藉由雙金屬的協助進行後續的還原得到苯胺；而 **11** 的催化過程則和單金屬錯合物 $Pd(bpy)(TFA)_2$ 相同，是直接將 *N*-苯基羥胺還原成產物。



bpnp



pbbpa

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Abstract

The use of bimetallic complexes as catalysts for the catalytic reactions has received much attraction due to the possible synergistic effect between the metal ions. In this study, a naphthyridine-based multidentate ligand 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) and an anthyridine-based ligand 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**) were synthesized. Coordination of **bpnp** with $Pd(OAc)_2$ in a mixture of MeOH and trifluoroacetic acid yielded the dipalladium complex Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**). Treatment of **pbbpa** with $Pd(MeCN)_2Cl_2$ followed by anion exchange resulted in the formation of $[Pd_2$(**pbbpa**$)Cl_2](PF_6)_2$ (**11**). The structures of both complexes were confirmed by ^{1}H-, ^{13}C-NMR and ESI-HRMS.

In a previous work, the resulting complex obtained from treatment of **11** with $NaBH_3CN$ was catalytically active toward the reduction of nitroarenes in the presence of H_2. In this work, complex **9** showed a similar activity without any pre-treatment. Comparison of the catalytic activity between these complexes was revealed. This catalytic system is applicable for various nitroarenes. The possible reaction mechanism of this catalytic system is established by the kinetic studies and the reactivity of possible intermediates under the catalytic conditions. **9** catalyzed through the condensation pathway, in which *N*-phenylhydroxylamine and nitrosobenzene formed azoxybenzene, and gave aniline by following reduction with the assistance of dimetal complex. On the other hand, **11** and $Pd(bpy)(TFA)_2$ catalyzed through direct pathway, in which aniline was obtained by reduction of *N*-phenylhydroxylamine.

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第一章 緒論

1.1 萘啶類多牙基 (naphthyridine-based multidentate ligand) 與其雙金屬錯合物

在過去的數十年間，在有機合成中使用雙金屬錯合物作為匀相催化劑受到化學家們高度關注。在雙金屬錯合物中，由於金屬離子間距離短，在催化反應中會展現協同效應 (synergistic effect)[1]，和相對應的單金屬錯合物比較往往具有較好的催化活性或選擇性。因此，設計出能夠鉗合雙金屬離子的配基，使雙金屬接近就顯得格外重要。近年來，1,8-萘啶被大量使用作為雙金屬系統中有效的橋接配基，2、7號位置可修飾出其他具有配位能力的多牙氮配位基，增加與金屬的螯合能力，部分整理如 **Figure 1-1** [2-7]。

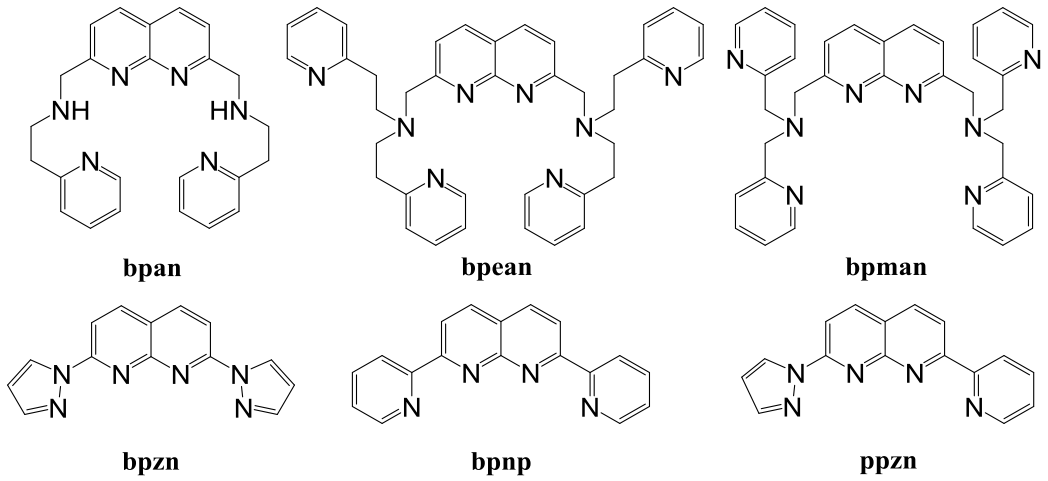

Figure 1-1 Naphthyridine-based multidentate ligands

其中，1979 年 Caluwe 以有機方法合成出一具有多氮原子的雜環平面分子，以1,8-萘啶主體結構，在2、7號位置上用吡啶修飾，稱為 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) [8]。此分子可作為金屬錯合物之配位基，利用吡啶和萘啶上的氮原子和金屬鍵結，形成之金屬錯合物可應用於催化合成反應。多牙配位基與金屬形成穩定的錯合物，其金屬距離多在 2－3Å 間，使雙金屬間產生特別的性質和協

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同效應。其中 **bpnp** 之雙金屬錯合物發展彙整於 **Scheme 1-1**：1980 年代 Kaska 利用 **bpnp** 與 $Ru_2(OAc)_4Cl$ 反應，得到 $[Ru_2(\mathbf{bpnp})(\mu\text{-}CH_3CO_2)_3]PF_6$ (**Scheme 1-1**, structure **A**) [9]，以 X 光繞射光譜鑑定其結構；與二價雙銠金屬 $Rh_2(OAc)_4$ 反應，得到類似結構的 $[Rh_2(\mathbf{bpnp})(\mu\text{-}CH_3CO_2)_3]PF_6$ (**Scheme 1-1**, structure **B**) [10,11]；另外，取 **bpnp** 與二價氯化銅反應得到雙銅配位錯合物 $[Cu_2(\mathbf{bpnp})(Cl)_2(\mu\text{-}Cl)(\mu\text{-}OH)]$ (**Scheme 1-1**, structure **C**) [12]，X 光繞射光譜鑑定結果顯示其以氯和氫氧根為架橋連接。這一系列錯合物開啟了 **bpnp** 雙金屬錯合物的濫觴，但其文獻中並未針對催化活性作探討。

近年來，本實驗室對於 **bpnp** 和不同金屬反應形成之錯合物亦有一系列研究。2012 年利用 $[Cu_2(CF_3CO_2)_4]$ 與 **bpnp** 反應，合成出雙銅金屬錯合物 $[Cu_2(\mathbf{bpnp})(CF_3CO_2)_2(\mu\text{-}CF_3CO_2)(\mu\text{-}OH)]$ (**Scheme 1-1**, structure **D**) [13]，雙銅皆為二價，以氫氧根和三氟醋酸根為架橋基團，其結構類似於 Kaska 於 1984 年所報導之雙銅錯合物 $[Cu_2(\mathbf{bpnp})(Cl)_2(\mu\text{-}Cl)(\mu\text{-}OH)]$。該錯合物可催化 2,6-雙取代酚類的氧化耦合，在反應過程中可觀察到雙銅金屬中心連接兩分子酚類之中間體，利於發生分子內耦合，展現了雙金屬協同效應。以 Cu_2O 在甲酸中和 **bpnp** 作用，得到另一結構類似的雙銅錯合物 $[Cu_2(\mathbf{bpnp})(HCO_2)_2(\mu\text{-}HCO_2)(\mu\text{-}OH)]$ (**Scheme 1-1**, structure **E**) [14]，可在氧氣下催化醇類及胺類的氧化耦合。使用 $[Cu(MeCN)_4](PF_6)$ 和 **bpnp** 錯合形成 $[Cu_2(\mathbf{bpnp})(MeCN)_4](PF_6)_2$，再經過陰離子置換得一價雙銅錯合物 $[Cu_2(\mathbf{bpnp})(MeCN)_4](BAr^F{}_4)_2$ (**Scheme 1-1**, structure **F**) 和 $[Cu_2(\mathbf{bpnp})(\mu\text{-}Cl)_2]$ (**Scheme 1-1**, structure **G**) [15]，後者經由 X 光繞射光譜鑑定其為一蝴蝶形結構，銅金屬中心和 **bpnp** 與氯呈正四面體配位，三者皆能催化 2-溴苯甲酸和脒 (amidines) 合成喹唑啉酮 (quinazolinone) 的環化反應。

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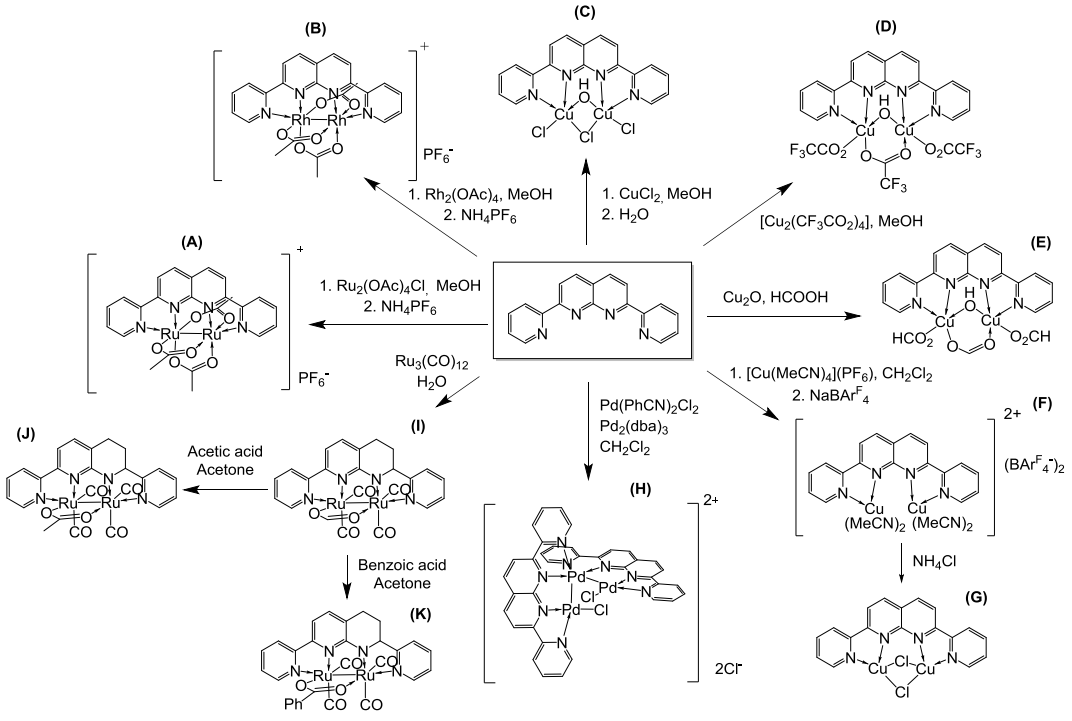
另外，利用 **bpnp** 與 $Pd(PhCN)_2Cl_2$ 和 $Pd_2(dba)_3$ 錯合，可得一具特殊金屬中心的水溶性三鈀金屬錯合物 $[Pd_3(\mathbf{bpnp})_2Cl_2]Cl_2$ (**Scheme 1-1**, structure **H**) [16]。由 X 光繞射分析此錯合物結構，三鈀金屬間夾角為 79.10°，形成一近 L 型結構，兩 **bpnp** 以正交形式與金屬配位。電子密度分析儀可推測三核金屬的中心鈀為零價，並以六配位型態存在。若分別加入 NaOH、KBr 和 NaN_3，皆可置換金屬上的氯配位基，再以 $NaPF_6$ 置換陰離子即可得到 $[Pd_3(\mathbf{bpnp})_2(OH)_2](PF_6)_2$、$[Pd_3(\mathbf{bpnp})_2Br_2](PF_6)_2$ 和 $[Pd_3(\mathbf{bpnp})_2(N_3)_2](PF_6)_2$。此文獻為目前發表 **bpnp** 多鈀金屬錯合物的唯一案例，但尚未發表任何催化應用。

另外若以 $Ru_3(CO)_{12}$ 和 **bpnp** 反應，形成一甲酸根架橋之雙釘錯合物 $[Ru_2(\mathbf{bpnp}\text{-}H_3)(\mu\text{-}HCO_2)(CO)_4]$ (**Scheme 1-1**, structure **I**)，其 **bpnp** 的萘啶被部分還原。分別以醋酸和苯甲酸置換配位基，可得到 $[Ru_2(\mathbf{bpnp}\text{-}H_3)(\mu\text{-}CH_3CO_2)(CO)_4]$ (**Scheme 1-1**, structure **J**) 和 $[Ru_2(\mathbf{bpnp}\text{-}H_3)(\mu\text{-}PhCO_2)(CO)_4]$ (**Scheme 1-1**, structure **K**) [17]。



Scheme 1-1 Bimetallic complexes $[(\mathbf{bpnp})M_2L_n]$

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1.2 蒽啶類多牙基 (anthyridine-based multidentate ligand) 與其雙金屬錯合物

文獻中已被合成的蒽啶類多牙基整理如下 (**Figure 1-2**) [18-23]，其側基團間距離較長，使其雙金屬錯合物可以具有較長的金屬－金屬距離 (*ca.* 5 Å)。

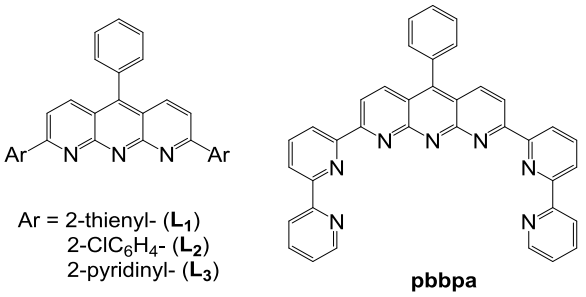
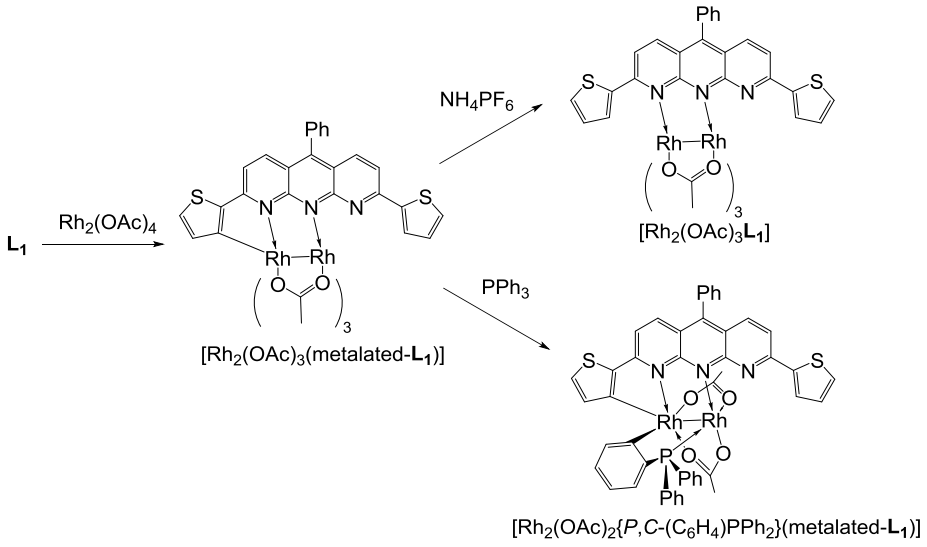


Figure 1-2 Anthyridine-based multidentate ligands

L1 和 **L2** 與 $Rh_2(OAc)_4$ 反應，側基團行環金屬化 (cyclometalation) 生成 Rh－C 鍵得雙銠金屬錯合物 [$Rh_2(OAc)_3$(metalated-**L1**)] 和 [$Rh_2(OAc)_3$(metalated-**L2**)]，因配位到銠金屬上的是蒽啶上鄰近的氮，其金屬鍵長僅 2.44 Å (**Scheme 1-2**) [20]。在酸性環境下 Rh－C 鍵斷裂，形成 [$Rh_2(OAc)_3$**L1**] 和 [$Rh_2(OAc)_3$**L2**]；加入三苯基膦 (triphenylphosphine, PPh_3) 時苯環上 C－H 鍵被活化，得膦－環金屬化產物 [$Rh_2(OAc)_2${*P*,*C*-(C_6H_4)PPh_2}(metalated-**L1**)] 和 [$Rh_2(OAc)_2${*P*,*C*-(C_6H_4)PPh_2}(metalated-**L2**)]。



Scheme 1-2 Cyclometalation of **L1** with dirhodium acetate

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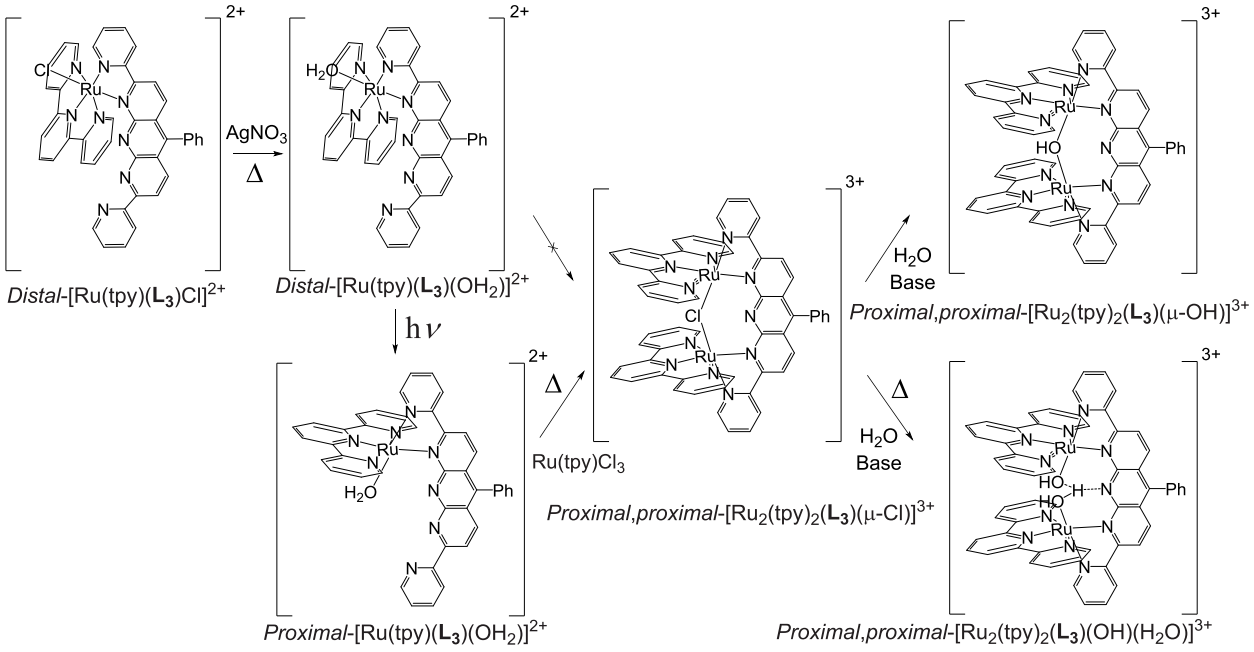
L3 和 $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ 作用可得雙釘金屬錯合物 $[Ru_2(\mathbf{L_3})(p\text{-cymene})_2Cl_2]$，能催化三級芳香胺類的氧化氰化[23]。**L3** 和 $Ru(tpy)Cl_3$ (tpy = 2,2';6',2''-terpyridine) 反應形成 *Distal*-$[Ru(tpy)(\mathbf{L_3})Cl]^{2+}$，加入硝酸銀和氯離子沉澱得到 *Distal*-$[Ru(tpy)(\mathbf{L_3})(OH_2)]^{2+}$，經光異構化 (photoisomerization) 得 *Proximal*-$[Ru(tpy)(\mathbf{L_3})(OH_2)]^{2+}$，可再和一分子 $Ru(tpy)Cl_3$ 錯合形成 *Proximal,proximal*-$[Ru_2(tpy)_2(\mathbf{L_3})(\mu\text{-}Cl)]^{3+}$，雙金屬距離為 4.193 Å。在鹼性水溶液中進行配基取代 (ligand substitution) 得 *Proximal,proximal*-$[Ru_2(tpy)_2(\mathbf{L_3})(\mu\text{-}OH)]^{3+}$ 和 *Proximal,proximal*-$[Ru_2(tpy)_2(\mathbf{L_3})(OH)(H_2O)]^{3+}$，後者 **L3** 上蒽啶中心的氮和 H_2O 上的氫能夠形成氫鍵，增加額外的穩定度 (**Scheme 1-3**)[18]。



Scheme 1-3 Diruthenium(II) complexes synthesized using photoisomerization

另外，於 **L3** 吡啶下方增加了額外的吡啶，即為 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**)。此三聯吡啶 (terpyridine, tpy) 的平面結構為一鉗合配基 (pincer ligand)，可能增強配位基的螯合效應 (chelate effect)。以 $Cu(ClO_4)_2$ 之六水合物分別和 **L3** 和 **pbbpa** 錯合得到 $[Cu_2(\mathbf{L_3})(H_2O)_4(MeCN)_2](ClO_4)_4$ 和

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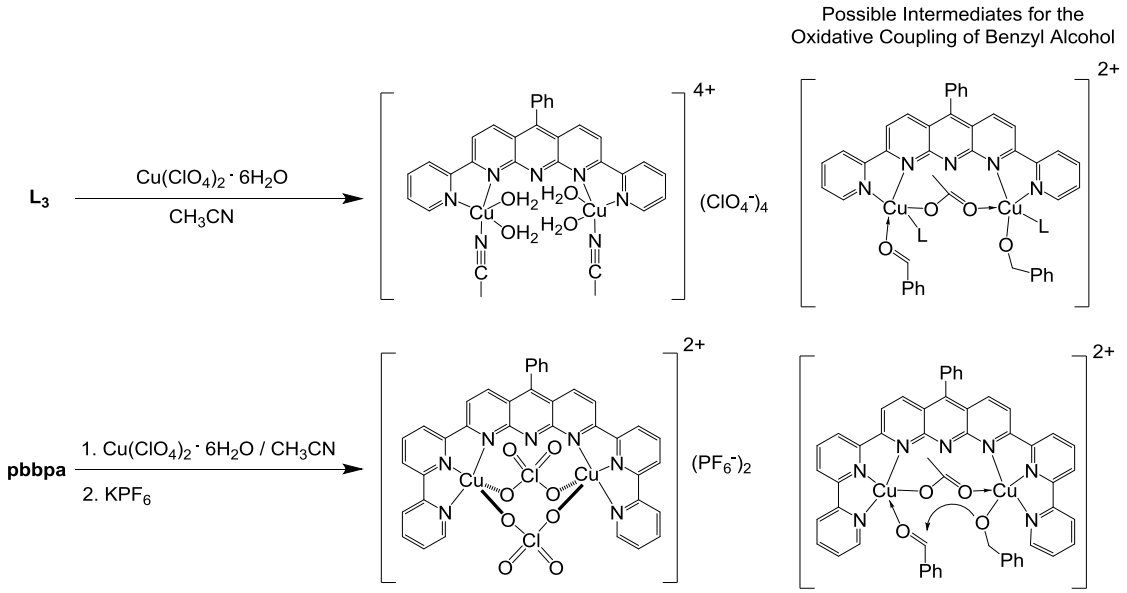
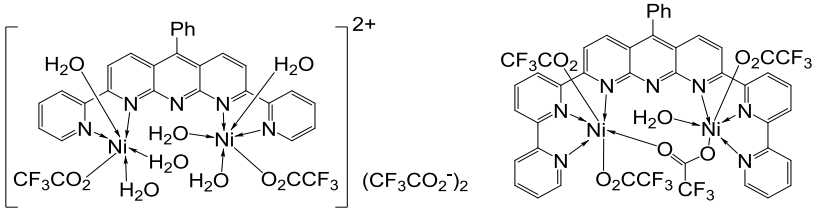
$[Cu_2(\mathbf{pbbpa})(\mu\text{-}ClO_4)_2](PF_6)_2$ 雙銅錯合物 [21]，兩者皆可催化苯甲醇的氧化。另外，$[Cu_2(\mathbf{pbbpa})(\mu\text{-}ClO_4)_2](PF_6)_2$ 在雙氧水中能有效地催化一級醇的氧化耦合反應得到酯類化合物，以質譜觀察到反應中間體為雙銅金屬中心分別連接一分子苯甲醇和一分子苯甲醛，有利於分子內攻擊 (intramolecular attack)，即展現了雙金屬協同效應。反觀 $[Cu_2(\mathbf{L_3})(H_2O)_4(MeCN)_2](ClO_4)_4$ 由於金屬上空配位較多，容易行其他競爭反應而非分子內反應 (**Scheme 1-4**)。



Scheme 1-4 Dicopper complexes with anthyridine-based ligands

使用 $Ni(OAc)_2$ 分別和 $\mathbf{L_3}$ 和 **pbbpa** 反應形成雙鎳錯合物 $[Ni_2(\mathbf{L_3})(H_2O)_6(CF_3CO_2)_2](CF_3CO_2)_2$ 和 $[Ni_2(\mathbf{pbbpa})(CF_3CO_2)_4(H_2O)]$ [22]，雙金屬距離為 5.409 和 5.014 Å。比較兩者對於羧酸還原反應的催化活性，發現後者具有良好的效果，可能是由於三聯吡啶的螯合效應和較短的金屬距離 (**Scheme 1-5**)。



Scheme 1-5 Dinickel complexes with anthyridine-based ligands

doi:10.6342/NTU201700680

1.3 硝基苯還原反應

苯胺類化合物是工業上重要的化合物，其合成方式亦成為有機合成上重要的目標之一。其中最常見的合成路徑是藉由催化加氫反應 (catalytic hydrogenation) 還原相對應之硝基苯，非勻相催化劑如金屬銅 [24]、鈷、鈀 [25] 和鎳 [26] 都常被使用，後兩者由於活性較高，可能需要加入抑制劑以防止芳香環被氫化 [27]。大多以氫氣或合成氣 (syngas) 作為還原劑，但也有甲烷 [28] 和甲酸 [29,30] 的例子。非勻相催化劑可運用在工業上，以連續攪拌槽反應器 (continuous stirred tank reactors, CSTR) 大量生產苯胺類。勻相催化劑亦常使用 VIII B 的過渡金屬錯合物如鐵、鈷、鎳、釕、銠和鈀催化硝基苯還原，雖無法取代非勻相催化劑的工業用途，但因可能具有較佳的還原選擇性 [31,32] 且反應條件溫和，適合用在多官能基的起始物。

$Rh(py)_3Cl_3$ (py = pyridine) 在二甲基甲醯胺 (dimethylformamide, DMF) 下和等當量 $NaBH_4$ 作用形成活性物種 $Rh(Py)_2Cl_2(DMF)(BH_4)$ ，在氫氣下可催化還原反應，若不加入 $NaBH_4$ 則無法催化，加入過量 $NaBH_4$ 亦會抑制反應 [33]。雙釕錯合物 $[Ru\mathbf{L}(CO)_2Cl]_2$ （**L**H = 2-phenylpyridine, benzo[h]quinoline, 1-phenylpyrazole 和 azobenzene 等含氮配基）可選擇性催化硝基苯還原，苯環上的氯取代基不會被氫解。反應時雙金屬分解成單金屬和溶劑加成，形成催化活性物種 $[Ru\mathbf{L}(CO)Cl\cdot S]$ (S = DMF, DMSO)，在高壓氫氣和高溫下氫置換氯開啟循環。但此催化系統活性較相對應之鈀錯合物高，會還原氰基和芳香酮類 [34]。

若結合水煤氣轉化反應 (water-gas shift reaction) 和硝基苯還原，即可以一氧化碳還原硝基苯，通常使用羰基錯合物作為催化劑 (**Scheme 1-6**)。1980 年代 Alper 提出三個勻相催化硝基苯還原的系統：$Ru_3(CO)_{12}$ 在室溫、一大氣壓一氧化碳下還原硝基苯，此系統具有良好的選擇性，苯環上的氯和醛均不會被還原 [35]；[Rh(1,5-hexadiene)Cl]$_2$ 和 $Co_2(CO)_8$ 組成的雙金屬系統也有類似的效果 [36]；$RuCl_2(PPh_3)_3$

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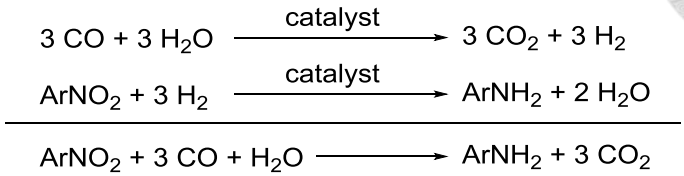
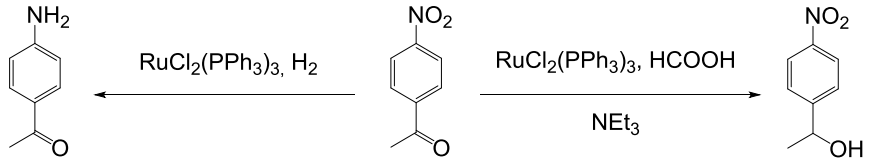
在室溫、一大氣壓合成氣下亦可還原立體障礙小的硝基苯，不會還原烯類、羰基和鹵素，在純氫氣或一氧化碳下產率則較差 [37]。



Scheme 1-6 Combined water-gas shift reaction and nitroarene hydrogenation

除了以氣體作為還原劑以外，使用低碳數脂肪醇和甲酸以催化轉移氫化 (catalytic transfer hydrogenation) 還原硝基苯提供了合成苯胺的另一選擇，且可能得到不同的選擇性，如 $RuCl_2(PPh_3)_3$ 亦可以甲酸還原 4'-硝基苯乙酮 (4'-nitroacetophenone) [38]，但選擇性不同於氫氣還原 (**Scheme 1-7**)。



Scheme 1-7 Chemoselectivity in hydrogenation with $RuCl_2(PPh_3)_3$

2010 年起 Beller 發表了三個催化轉移氫化系統：以 $FeBr_2－PPh_3$ 催化，$PhSiH_3$ 作為還原劑 [39]、$Fe(BF_4)_2・6H_2O－P(CH_2CH_2PPh_2)_3$ 催化，甲酸為還原劑 [40] 和 $RuCl_2(tpy)$ 催化，異丙醇為還原劑 [41]，三者皆具有很好的選擇性，能夠保留反應物上的鹵基、烯、羰基。一系列的釕、銥錯合物被合成並應用在轉移氫化硝基苯還原反應上，探討金屬和配基效應對產物選擇性的影響 [42]。

以鈀催化的硝基苯還原反應早期大多是以 Pd/C 催化，近幾年有在反應中以聚甲基氫矽氧烷 (polymethylhydrosiloxane, PMHS)[43,44]、三乙基矽烷 (triethylsilane)[43] 或一氧化碳 [45] 等，將 $Pd(OAc)_2$ 或其他 Pd(II) 還原成 Pd(0) 催化的例子，以氫氣還原 Pd(II) 的例子目前為止則並未有詳細的報導。

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1.4 研究目的

目前為止許多含氮多牙基已被製備並應用於合成雙金屬錯合物，其中 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) 和 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**) 引起我們的關注。在文獻中，金屬－金屬距離在約莫 3 Å 的 [M_2(**bpnp**)L_n] 和金屬－金屬距離在 5 Å 左右的 [M_2(**pbbpa**)L_n] 多在催化反應中展現了協同效應。因此，藉由比較兩配位基 **bpnp** 和 **pbbpa** 之雙鈀金屬錯合物，我們期望能夠探討金屬－金屬距離對硝基還原反應催化活性的影響。

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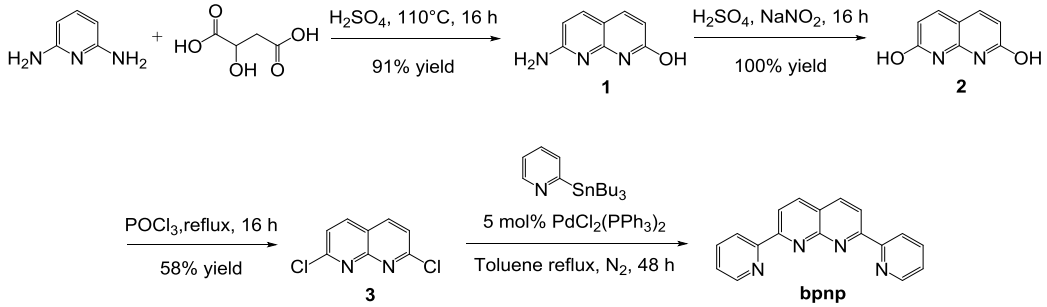
第二章 雙鈀金屬錯合物之合成與鑑定

2.1 配位基之合成

在 1979 年，Caluwe 首次利用 4-aminopyrimidine-5-carboxaldehyde 經過兩次 Friedländer 縮合反應合成出 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) [8] ，然而在此論文中我們採用另一方法，經由 Stille 耦合反應連結萘啶中心骨架 2,7-dichloro-1,8-naphthyridine (**3**) 和側基團 2-tributylstannylpyridine [46]。

首先，取 2,6-diaminopyridine 在酸性環境下和 malic acid 縮合得到 2-amino-7-hydroxy-l,8-naphthyridine (**1**)，經重氮化並水解取得 2,7-dihydroxy-1,8-naphthyridine (**2**)。接著以三氯氧化磷進行氯化得到化合物 **3** [47]，總產率 53%。**3** 和 2-tributylstannylpyridine 在 $PdCl_2(PPh_3)_2$ 催化下進行雙 Stille 耦合即可得 **bpnp** (**Scheme 2-1**)。此配位基為已知物，以核磁共振光譜 (NMR spectroscopy) 鑑定其結構，其氫譜共 6 組訊號在芳香環區，積分值為 12 個氫，化學位移和耦合常數均與文獻相符。



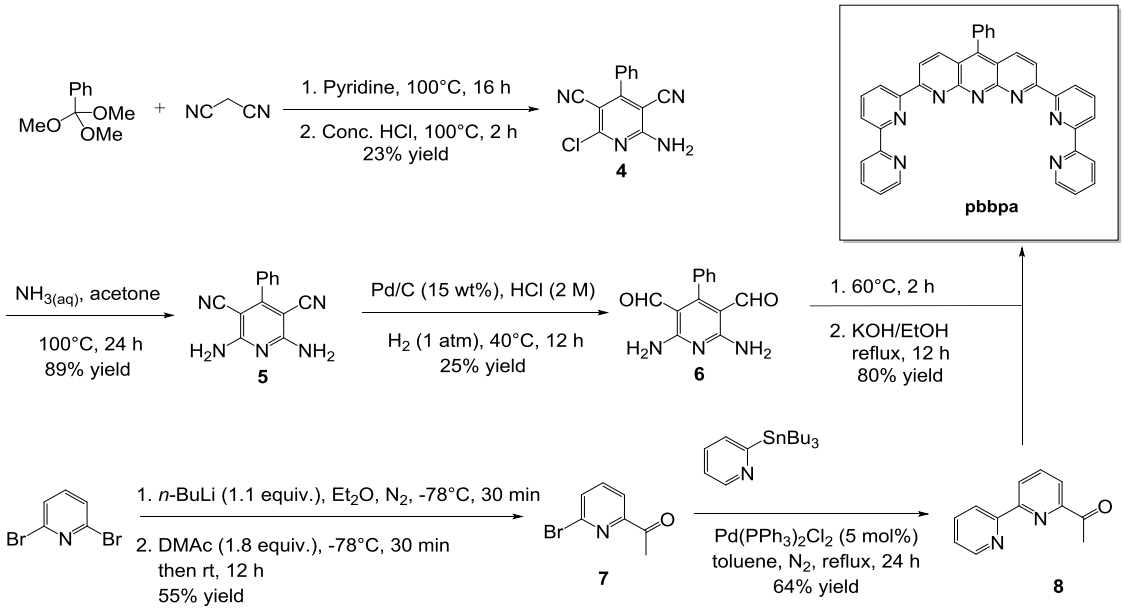
Scheme 2-1 Synthesis of **bpnp**[46,47]

Caluwe 在 1977 年以 2,6-diaminopyridine-3,5-dicarboxaldehyde 和兩當量甲基酮經兩次 Friedländer 縮合反應合成出 2,8-雙取代之蒽啶 [48]。然而我們使用 Zimmerman 的改良方法製備 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-

doi:10.6342/NTU201700680

anthyridine (**pbbpa**) [49]。合成路徑如 **Scheme 2-2** 所示。trimethyl benzoate 在吡啶 (pyridine) 中和 malononitrile 反應，加入濃鹽酸得到 2-amino-6-chloro-4-phenylpyridine-3,5-dicarbonitrile (**4**)。接著在濃氨水中進行親核芳香取代 (nucleophilic aromatic substitution) 得到 2,6-diamino-4-phenylpyridine-3,5-dicarbonitrile (**5**)。最後在氫氣下以 Pd/C 催化氫化得到 2,6-diamino-4-phenylpyridine-3,5-dicarbaldehyde (**6**)，總產率 5%。

2,6-二溴吡啶加入正丁基鋰和二甲基乙醯胺 (dimethylacetamide, DMAc) 進行乙醯化得到 1-(6-bromopyridin-2-yl)ethanone (**7**)，和 2-tributylstannylpyridine 經過 Stille 耦合反應得到 1-(2,2′-bipyridin-6-yl)ethanone (**8**)，總產率 32%。**6** 和 **8** 在鹼性環境下進行兩次 Friedländer 縮合反應得到目標產物 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**)。此配位基為已知物，以核磁共振光譜鑑定其結構，其氫譜有 11 組訊號在芳香環區，共 23 個氫，化學位移、積分值和耦合常數均與文獻相符。



Scheme 2-2 Synthesis of **pbbpa** [49]

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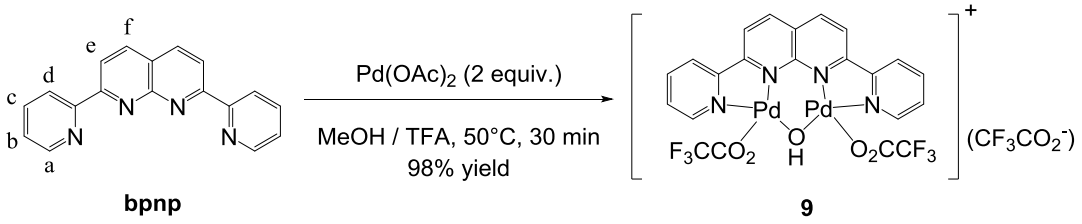
2.2 雙鈀金屬錯合物之合成與鑑定

bpnp 和兩當量之醋酸鈀在甲醇和三氟醋酸下錯合得到可溶於乙腈之黃色固體 Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**)，產率 98% (**Scheme 2-3**)。氫譜中苯環區共有六個訊號 (**Figure 2-1**)，顯示產物具有對稱結構。和配位基的氫譜比較，最接近金屬的 H_a 往高場移動，而其餘所有訊號皆往低場移動，位移量以 H_f 最多。氟譜中僅有一組寬訊號，顯示外圍離子和配位的三氟醋酸根在溶液中可以進行交換。而在電灑式高解析質譜 (electrospray ionization-high-resolution mass spectrometry, ESI-HRMS) 中，$[Pd_2$(**bpnp**)$(TFA)_2(OH)]^+$ 理論計算的荷質比 (*m/z*) 為 740.8869，得到的結果是 740.8892，且同位素模擬結果亦一致 (**Figure 2-2**)；質譜中最高峰之 *m/z* 為 644.9099，同位素模擬和 $[Pd_2$(**bpnp**)$(TFA)(OH)_2]^+$ 相符（附錄一），可能為 $[Pd_2$(**bpnp**)$(TFA)_2(OH)]^+$ 在游離過程中被水氣進行配基置換產生。



Scheme 2-3 Synthesis of Pd_2(**bpnp**)$(OH)(TFA)_3$ (**9**)

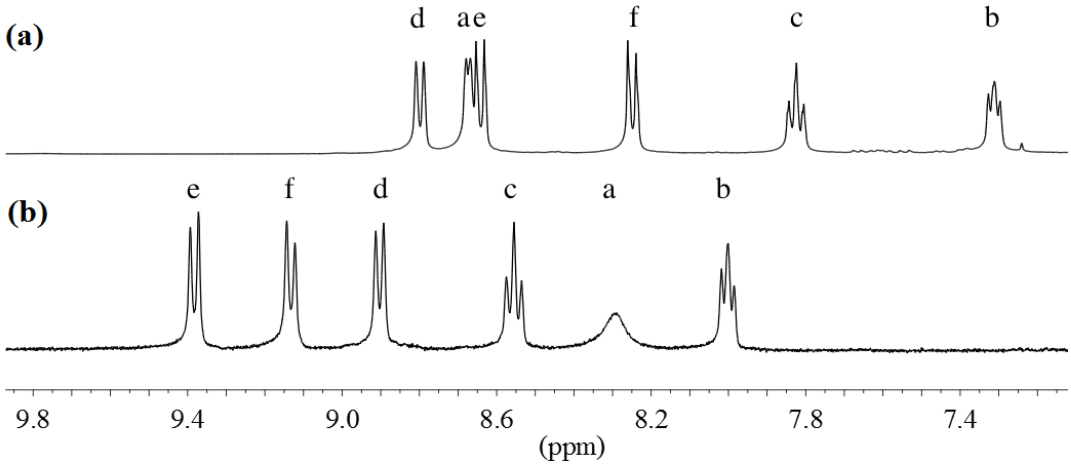


Figure 2-1 Partial ^{1}H NMR spectrum of (a) **bpnp** in $CDCl_3$ and (b) **9** in DMSO-d_6

doi:10.6342/NTU201700680

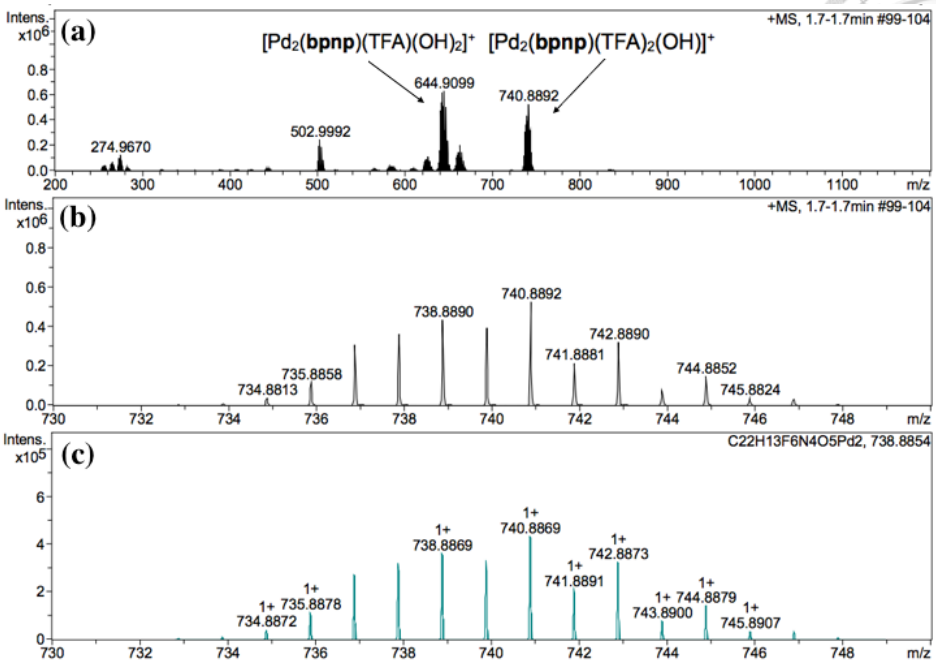


Figure 2-2 ESI-HRMS spectrum of **9**: (a) full, (b) partial and (c) simulation

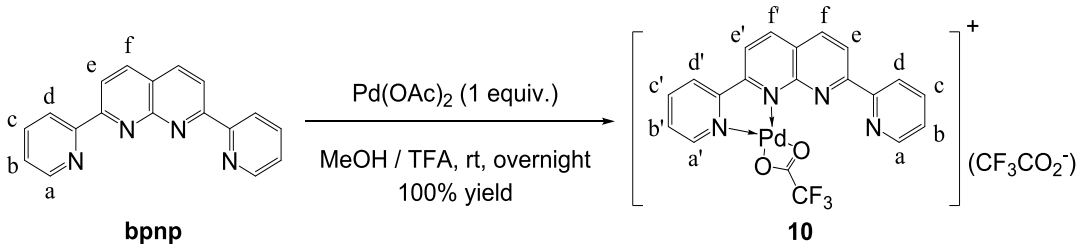
藉由測量莫耳導電度來判斷錯合物 **9** 於溶液態中解離的狀況是否與推測結構吻合。將 **9** 溶於二甲基亞碸 (dimethyl sulfoxide, DMSO) 中，於 0.40 mM 濃度下測得莫耳導電度為 54 (ohm^{-1} cm^2 mol^{-1})，溶於硝基甲烷 (nitromethane, $MeNO_2$) 中，於 0.40 mM 濃度下測得莫耳導電度為 81 (ohm^{-1} cm^2 mol^{-1})。根據文獻報導 (**Table 2-1**) [50]，當錯合物在溶液中解離成一個陽離子和一個陰離子時，在 DMSO 中莫耳導電度會在 50–90 ohm^{-1} cm^2 mol^{-1}，在 $MeNO_2$ 中莫耳導電度則在 75–95 ohm^{-1} cm^2 mol^{-1}，此二實驗數據符合推測結構，主配位基 **bpnp**、兩個三氟醋酸根和一個氫氧根與雙鈀金屬為陽離子，其外圍有一個三氟醋酸根為陰離子。

Table 2-1 The ranges of molar conductivity of complexes with different ratios

Molar conductivity (ohm^{-1} cm^2 mol^{-1}) ranges				
Solvent	Non-electrolyte	1:1 Electrolyte	2:1 Electrolyte	3:1 Electrolyte
DMSO	< 50	50–90	110–195	200–240
$MeNO_2$	< 75	75–95	150–180	220–260

doi:10.6342/NTU201700680

為了測試是否具有雙金屬協同效應，合成 **bpnp** 單核鈀金屬錯合物比較催化活性。將 **bpnp** 和一當量之醋酸鈀在甲醇和三氟醋酸下錯合得到可溶於乙腈之淺黃色固體 [Pd (**bpnp**)(TFA)$_2$] (**10**)，產率 100% (**Scheme 2-4**)。



Scheme 2-4 Synthesis of [Pd(**bpnp**)(TFA)$_2$] (**10**)

氫譜中苯環區共有十二個訊號 (**Figure 2-3**)，顯示產物具有不對稱結構。和配位基的氫譜比較， $H_{a'}$、 H_c、 H_d、$H_{d'}$和 $H_{e'}$往高場移動，其餘訊號則往低場移動，位移量以 $H_{f'}$最多，$H_a - H_f$ 和 $H_{a'} - H_{f'}$ 相較之下位移量均較小，位移變化最多的是離金屬最近的 H_a 和 H_b。而在電灑式高解析質譜中，[Pd(**bpnp**)(TFA)]$^+$ 理論計算的荷質比 (*m/z*) 為 502.9950，得到的結果是 503.0006，且同位素模擬結果亦一致 (**Figure 2-4**)。質譜中次高峰之 *m/z* 為 444.9949，同位素模擬和 [Pd(**bpnp**)(H$_2$O)$_2$(OH)]$^+$ 相符（附錄一），可能為 [Pd(**bpnp**)(TFA)]$^+$ 在游離過程中被水氣進行配基置換產生。

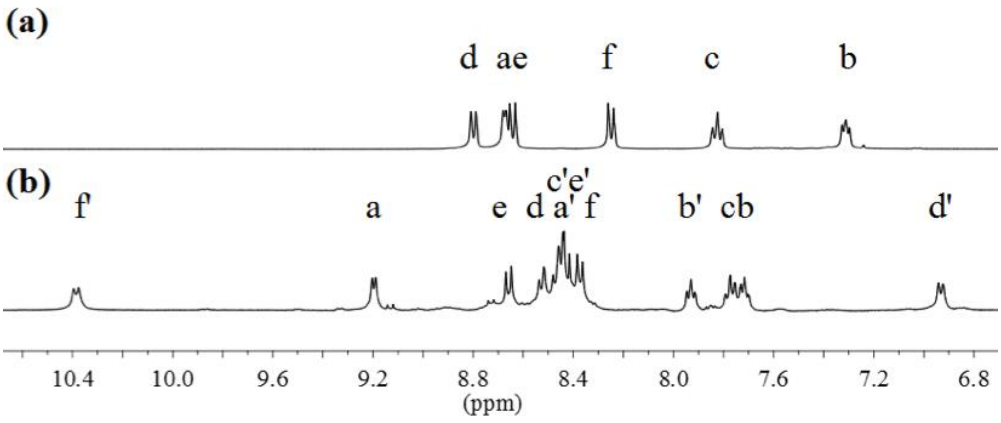


Figure 2-3 Partial ^{1}H NMR spectrum of (a) **bpnp** and (b) **10** in CD_3CN

doi:10.6342/NTU201700680

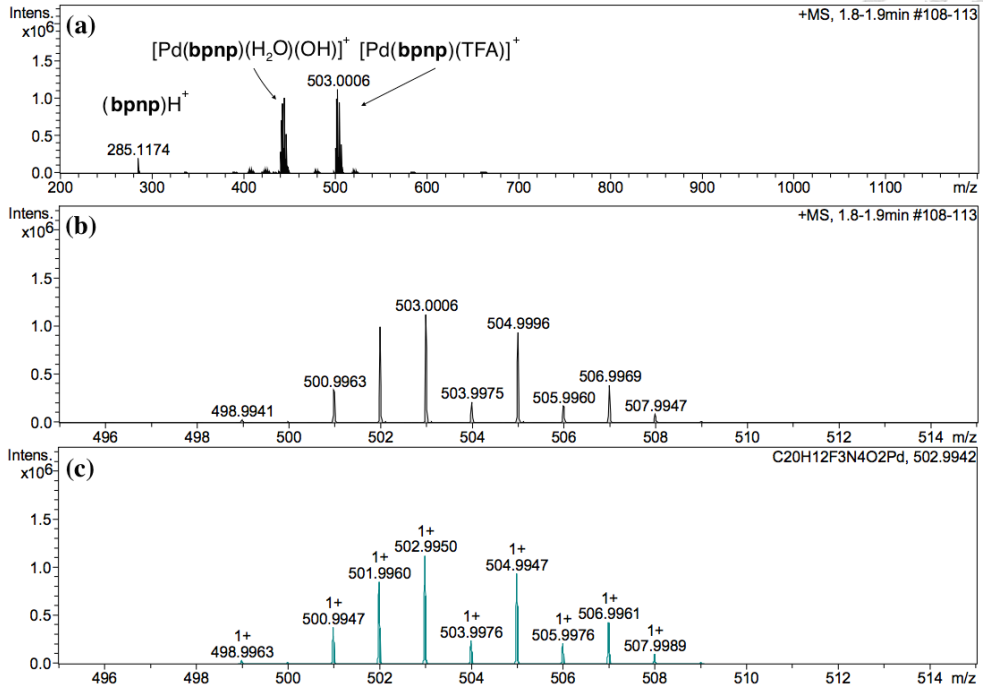
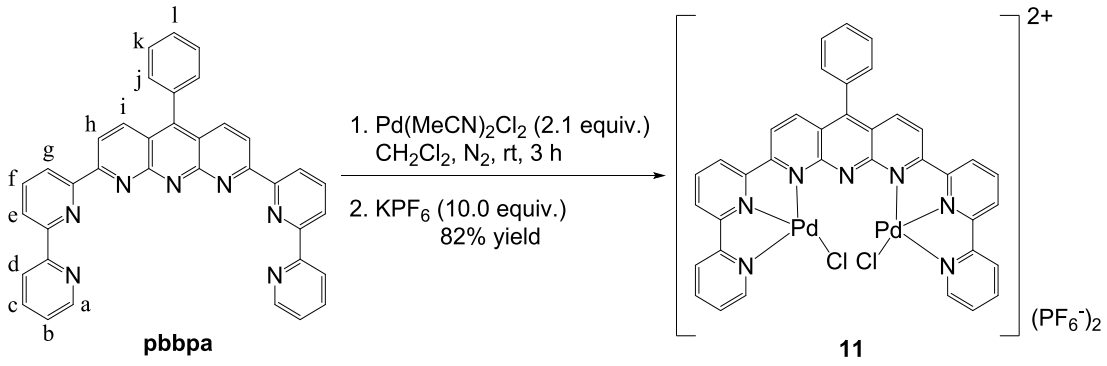


Figure 2-4 ESI-HRMS spectrum of **10**: (a) full, (b) partial and (c) simulation

將 **10** 溶於 DMSO 中，於 0.40 mM 濃度下測得莫耳導電度為 68 (ohm^{-1} cm^2 mol^{-1})；而溶於 $MeNO_2$ 中，於 0.40 mM 濃度下則測得莫耳導電度為 96 (ohm^{-1} cm^2 mol^{-1})，此二數據皆符合文獻中陰陽離子比例為 1:1 的電解質，與推測結構相符，主配位基 **bpnp**、一個三氟醋酸根與雙鈀金屬形成陽離子，其外圍有一個三氟醋酸根為陰離子。

$Pd(MeCN)_2Cl_2$ 和 **pbbpa** 錯合後以 KPF_6 置換陰離子得到錯合物 $[Pd_2(pbbpa)Cl_2](PF_6)_2$ (**11**)，產率 82% (**Scheme 2-5**)。



Scheme 2-5 Synthesis of $[Pd_2(\mathbf{pbbpa})Cl_2](PF_6)_2$ (**11**)

doi:10.6342/NTU201700680

以核磁共振光譜 (**Figure 2-5** b) 和電灑式游離高解析質譜 (**Figure 2-6**) 鑑定錯合物 **11**，氫譜顯示錯合物為一對稱結構，和配位基 **pbbpa** 相比，兩者之氫譜訊號變化並無明顯的趨勢，H_b、H_c 和 H_f 向高場移動，其餘質子向低場移動，其中以 H_h 位移最多。在電灑式游離高解析質譜中，$[Pd_2(\mathbf{pbbpa})Cl_2]^{2+}$ 理論計算的荷質比 (*m/z*) 為 424.4729，實驗結果為 424.4712，同位素模擬亦相符 (**Figure 2-6** c)。質譜中強度最高峰之 *m/z* 為 415.4925，同位素模擬和 $[Pd_2(\mathbf{pbbpa})Cl(OH)]^{2+}$ 相符（附錄一），可能為 $[Pd_2(\mathbf{pbbpa})Cl_2]^{2+}$ 在游離過程中被水氣進行配基置換產生。

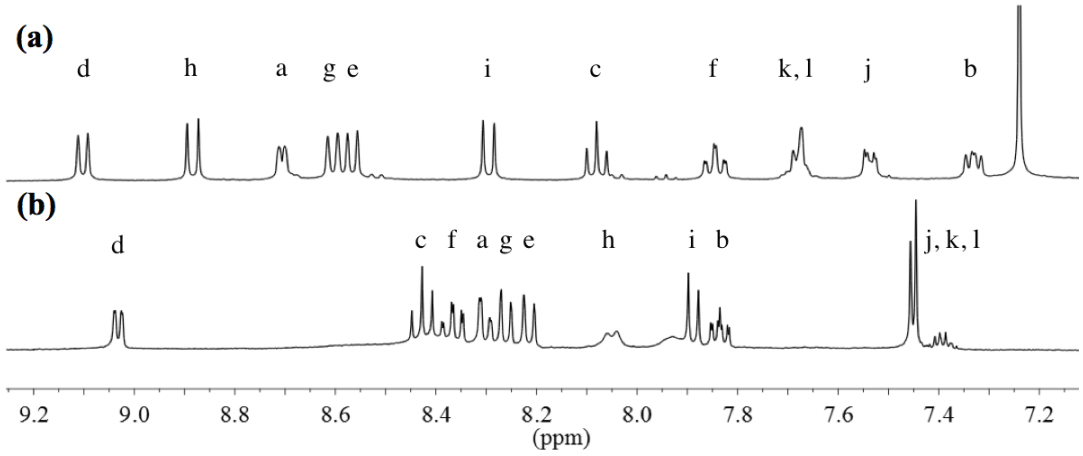


Figure 2-5 Partial ^{1}H NMR spectrum of (a) **pbbpa** in $CDCl_3$ and (b) **11** in CD_3CN

將 **11** 溶於 DMSO 中，於 0.40 mM 濃度下測得莫耳導電度為 160 (ohm^{-1} cm^2 mol^{-1})， 溶於 $MeNO_2$ 中，於 1.0 mM 濃度下測得莫耳導電度為 180 (ohm^{-1} cm^2 mol^{-1})，文獻中陰陽離子比例為 1:2 的電解質在 DMSO 中莫耳導電度範圍會在 110–195 ohm^{-1} cm^2 mol^{-1}，在 $MeNO_2$ 中則在 150– 180 ohm^{-1} cm^2 mol^{-1} (**Table 2-1**)[50]，故此數據符合推測結構，主配位基 **pbbpa**、兩個氯與雙鈀金屬形成陽離子，其外圍有兩個六氟磷酸根。

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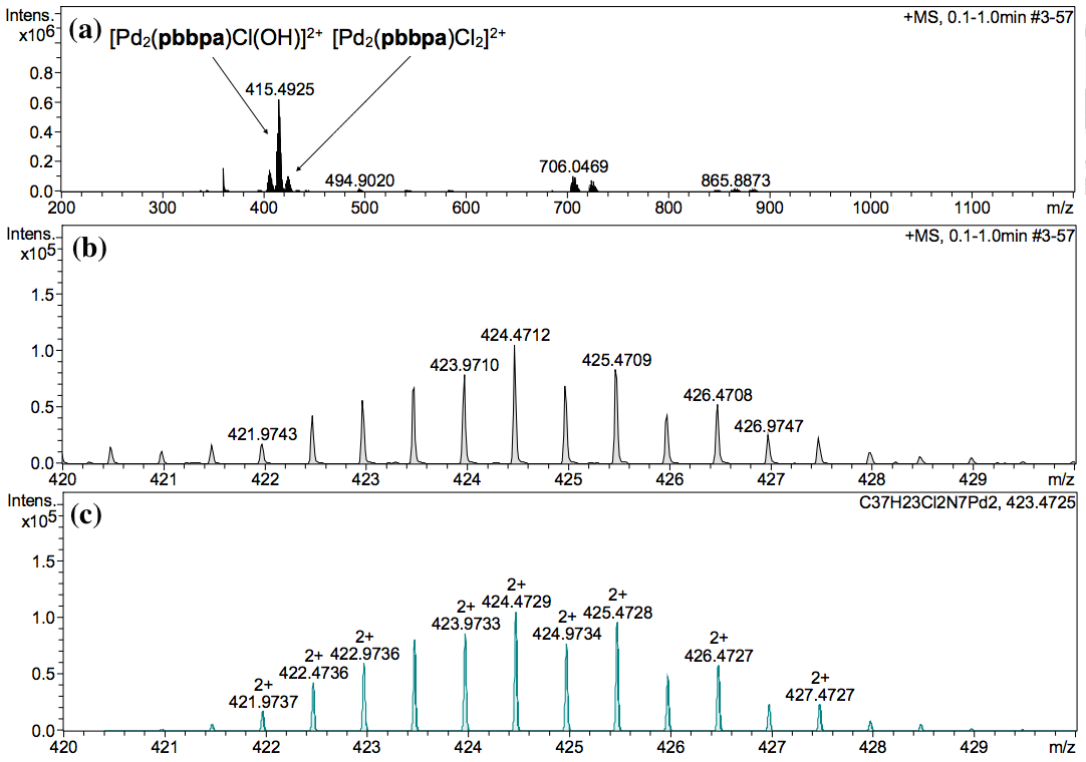

Figure 2-6 ESI-HRMS spectrum of **11**: (a) full, (b) partial and (c) simulation

2.3 雙鈀金屬錯合物 9 之配位基置換

嘗試將 **9** 上的三氟醋酸根換成其他配位基。在室溫氮氣下將 **9** 溶於甲醇中，加入 3 當量的 PPh_3，氫譜訊號變寬，顯示配基正在進行可逆交換，但無法得到單一產物；在室溫下加入 3 當量的醋酸鈉，溶液顏色和氫譜皆沒有改變，在甲醇下迴流半小時則溶液顏色由黃色轉棕色，氫譜訊號變寬，但位置仍和原本相同；若改以大量醋酸置換，則氫譜為 **9** 和自由配基之疊加，顯示醋酸將 **bpnp** 置換下來。將 **9** 溶於 DMSO 以質譜鑑定，顯示 DMSO 並未配位；溶於 DMF，質譜同樣沒有變化。

在室溫 CO/N_2 下將 **9** 溶於甲醇中，溶液由黃轉黑，可知 **9** 被 CO 還原為 Pd(0)，氫譜訊號變寬。在室溫氮氣環境下將 **9** 和過量 KI 溶於甲醇中，溶液初呈黃色，攪拌後呈暗紅色且出現黑色固體，氫譜上苯環區僅看到自由配基的訊號，顯示碘將

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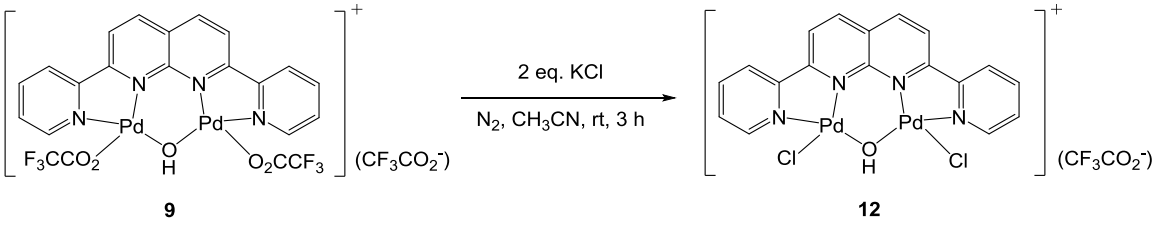
bpnp 置換下來了。接著選用 Na_2S 進行配基置換，為了避免過量的硫置換 **bpnp**，僅使用一當量的 Na_2S 和 **9** 在氮氣下溶於無水乙腈，溶液迅速由黃轉黑棕色，但氫譜十分雜亂。

以兩當量 KCl 置換配基，在氮氣下和 **9** 溶於無水乙腈，在室溫下攪拌三小時後由全溶轉為混濁，離心並以乙醚清洗後得到黃色固體 $[Pd_2(\mathbf{bpnp})Cl_2(OH)](TFA)$ (**12**)，其溶解度較 **9** 差，僅微溶於乙腈和甲醇，全溶於 DMSO (**Scheme 2-6**)。



Scheme 2-6 Synthesis of $[Pd_2(\mathbf{bpnp})Cl_2(OH)](TFA)$ (**12**)

氫譜顯示其具有對稱結構，因此猜測 **9** 之三氟醋酸根被氯取代。氫譜中大部份訊號皆稍微往高場移動，唯獨吡啶 6 號位上的氫向低場移動 (**Figure 2-7**)。在電灑式游離高解析質譜中，$[Pd_2(\mathbf{bpnp})Cl_2(OH)]^+$ 理論計算的荷質比 (*m/z*) 為 584.8532，實驗結果為 584.8597，同位素模擬亦相符 (**Figure 2-8** c)。

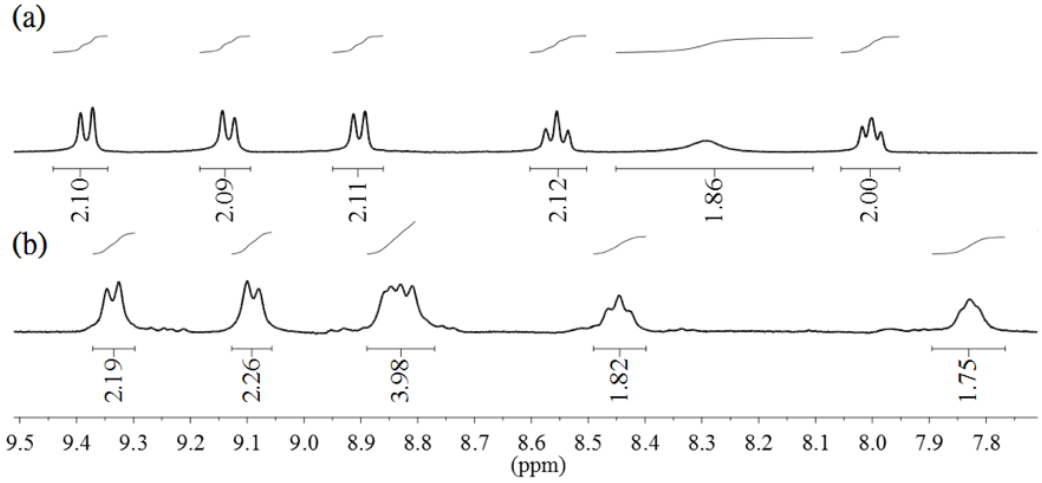


Figure 2-7 Partial ^1H NMR spectrum of (a) **9** and (b) **12** in DMSO

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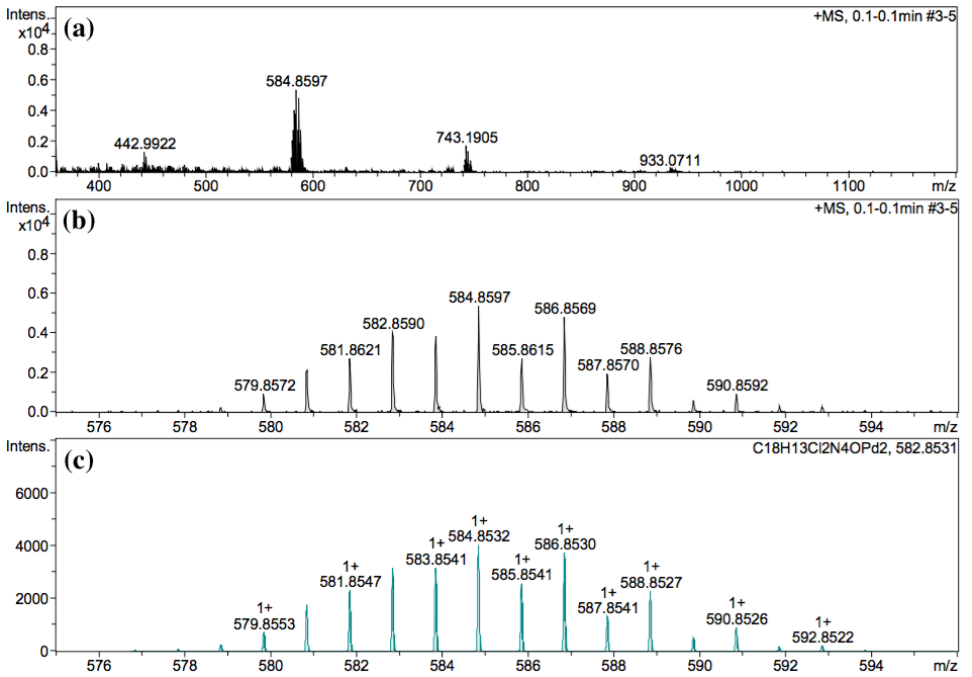

Figure 2-8 ESI-HRMS of **12**: (a) full, (b) partial and (c) simulation

將 **12** 溶於 DMSO 中，於 0.40 mM 濃度下測得莫耳導電度為 54 ($ohm^{-1}\ cm^2\ mol^{-1}$)，同濃度下 $MeNO_2$ 中莫耳導電度為 100 ($ohm^{-1}\ cm^2\ mol^{-1}$)，符合文獻中陰陽離子比例為 1:1 的電解質。推測結構為主配位基 **bpnp**、一個氫氧根和兩個氯與雙鈀金屬形成陽離子，其外圍有一個三氟醋酸根為陰離子。

欲以氯同時置換氫氧根和三氟醋酸根，取四當量 KCl 在氮氣下和 **9** 溶於無水乙腈，在室溫下攪拌三小時後溶液同樣由全溶轉為混濁，離心以 DMSO 測譜，但其氫譜變寬，顯示氯離子會和配基進行可逆交換。

以兩當量 KBr 置換配基，在氮氣下和 **9** 溶於無水乙腈，在室溫下攪三小時後溶液由全溶轉混濁，離心並以少量乙醚清洗得黃色固體 [Pd_2(**bpnp**)Br_2(OH)](TFA) (**13**)，其溶解度較 **9** 差，微溶於乙腈和甲醇，全溶於 DMSO (**Scheme 2-7**)。

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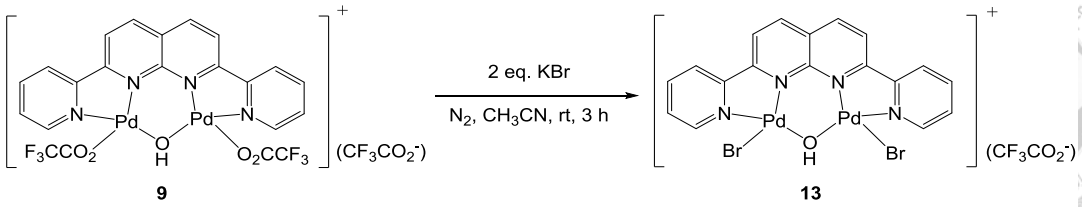

9 13

Scheme 2-7 Synthesis of [Pd_2(**bpnp**)Br_2(OH)](TFA) (**13**)

氫譜顯示其具有對稱結構，因此猜測其結構應為 **9** 上的三氟醋酸根被溴取代。氫譜中吡啶 6 號位上的氫向低場移動，離溴較遠的萘啶上的氫位移幾乎不變，其餘氫則稍微向高場移動 (**Figure 2-9**)。在電灑式游離高解析質譜中，[Pd_2(**bpnp**)Br_2(OH)]$^+$ 理論計算的荷質比 (*m/z*) 為 674.7513，實驗結果為 674.7503，同位素模擬亦相符 (**Figure 2-10** c)。質譜中強度次高峰之 *m/z* 為 630.8002，同位素模擬和 [Pd_2(**bpnp**)Br(H_2O)($OH)_2$]$^+$ 相符（附錄一），可能為 [Pd_2(**bpnp**)Br_2(OH)]$^+$ 在游離過程中被水氣進行配基置換產生。

將 **13** 溶於 DMSO 中，於 0.40 mM 濃度下測得莫耳導電度為 56 (ohm^{-1} cm^2 mol^{-1})，同樣濃度在 $MeNO_2$ 中莫耳導電度為 86 (ohm^{-1} cm^2 mol^{-1})，此數據符合文獻中陰陽離子比例為 1:1 的電解質，與推測結構相符，主配位基 **bpnp**、一個氫氧根和兩個溴與雙鈀金屬形成陽離子，其外圍有一個三氟醋酸根為陰離子。

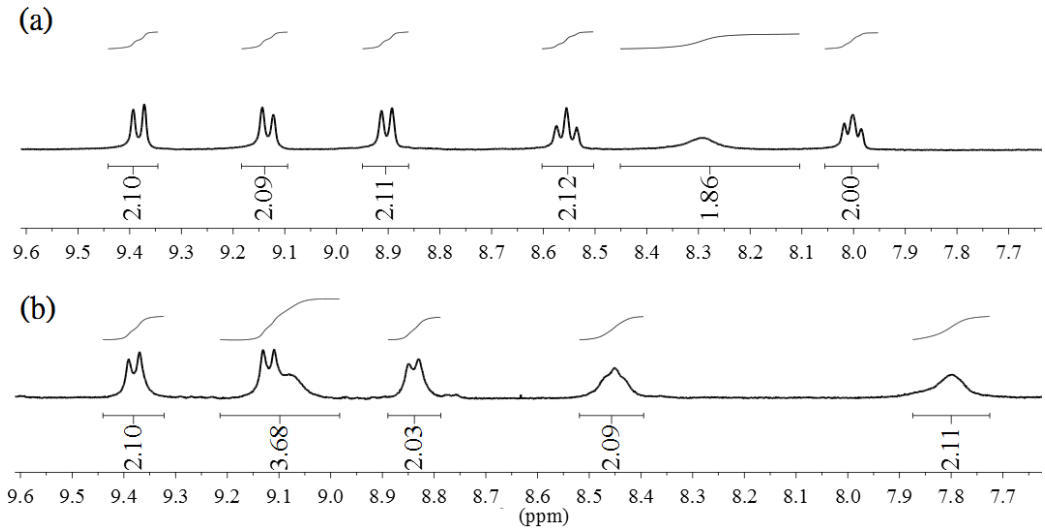

Figure 2-9 Partial ^{1}H NMR of (a) **9** and (b) **13** in DMSO

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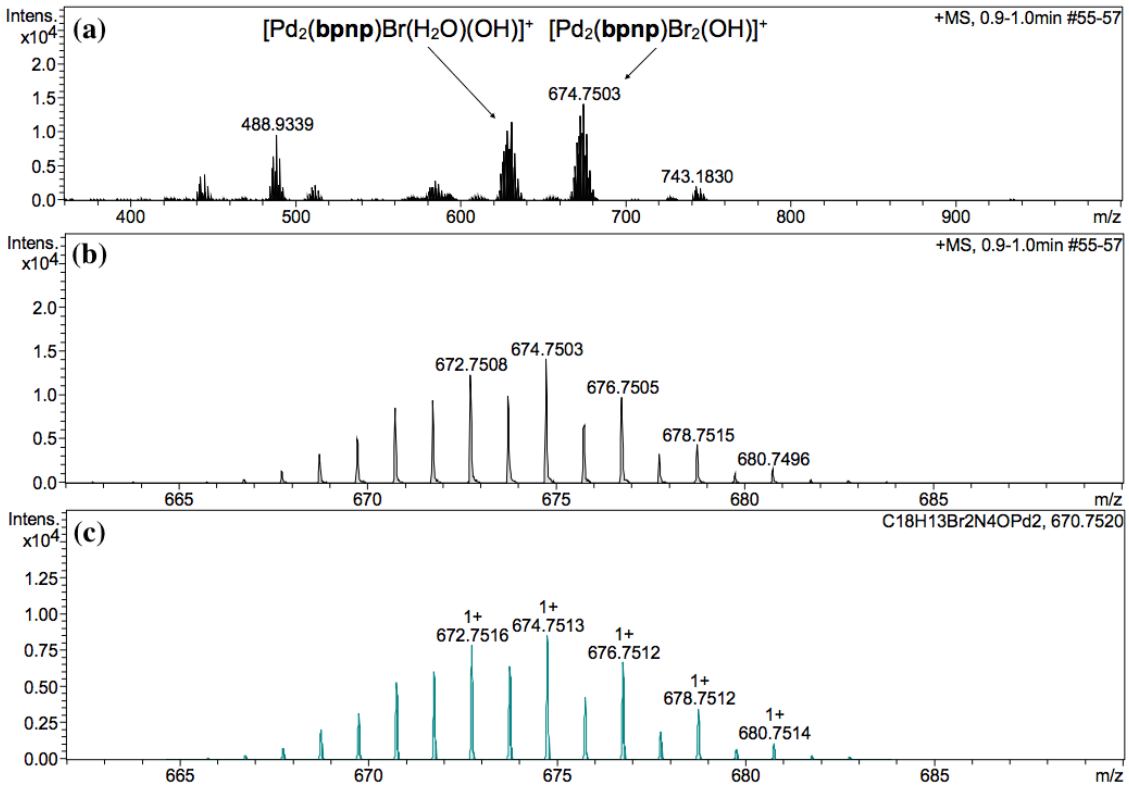

Figure 2-10 ESI-HRMS of **13**: (a) full, (b) partial and (c) simulation

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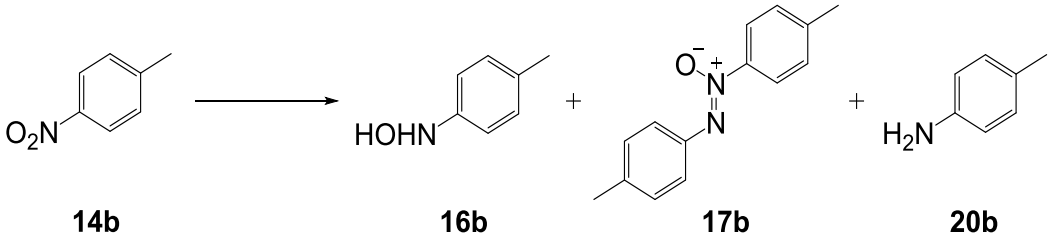
第三章 雙鈀金屬錯合物之催化應用

許多鈀催化反應已被報導，如耦合反應、氧化反應、還原反應、異構化反應等[51-53]。因此，在此節我們探討雙鈀金屬錯合物 Pd_2(**bpnp**)(OH)$(TFA)_3$ (**9**) 對於硝基苯還原之催化活性。

3.1 反應條件最佳化

選擇 4-硝基甲苯 (4-nitrotoluene) 作為起始物進行硝基苯還原反應最佳化測試 (**Scheme 3-1**)，結果如 **Table 3-1**。



Scheme 3-1 Reduction of *p*-nitrotoluene

由於文獻中鈀催化硝基苯還原中的活性物種皆為 Pd(0) [29,30,43-45,54,55]，若使用 Pd(II) 則需搭配還原劑如聚甲基氫矽氧烷 (polymethylhydrosiloxane, PMHS) [43,44]、三乙基矽烷 (triethylsilane) [43] 或一氧化碳 [45] 等，將 Pd(II) 還原成 Pd(0) 後才能開啟催化循環。在本實驗室先前的研究工作中探討 $[Pd_2$(**pbbpa**)$Cl_2](PF_6)_2$ (**11**) 對硝基苯還原的催化效果，測試了多種氫陰離子 (hydride) 來源（$NaBH_3CN$、Et_4NBH_4、$NaBH_4$、NaH、HCO_2Na 和 HCO_2NH_4），發現 $NaBH_3CN$ 活化 **11** 的效果最好，因此一開始選用 $NaBH_3CN$ 作為活化劑。

加入 2.5 mol% 之 $NaBH_3CN$ 還原鈀金屬，但得到的產率並不佳 (entry 1)；反應加熱至迴流溫度，則產率稍微上升 (entry 2)；增加 $NaBH_3CN$ 量至 10 mol% ，則產率大幅上升 (entry 3)；但使用 50 mol% 之 $NaBH_3CN$ 得到的產率不佳 (entry 4)，推測是由於金屬錯合物分解成為鈀黑 (palladium black)。為了減少鈀黑的生成，

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參考文獻加入了 DMSO 或對苯醌 (*p*-benzoquinone)[56]，但效果並不顯著（entries 5 和 6）。然而另外嘗試不加入額外的活化劑，發現產率亦相當高，表示預催化劑 (precatalyst) Pd_2(**bpnp**)(OH)$(TFA)_3$ (**9**) 能夠直接被氫氣活化 (entry 7)，於是接下來即不加入額外的活化劑進行反應最佳化。

Table 3-1 Preliminary optimization for the reduction of 4-nitrotoluene [a]

Entry	Additives	Conv. (%)[b]	Yield (%)[b]		
			16b	**17b**	**20b**
1	$NaBH_3CN$ 2.5 mol%	< 5	< 5	0	< 5
2[c]	$NaBH_3CN$ 2.5 mol%	35	< 5	0	32
3	$NaBH_3CN$ 10 mol%	76	< 5	0	69
4	$NaBH_3CN$ 50 mol%	6	< 5	0	< 5
5	$NaBH_3CN$ 50 mol%, DMSO 10 mol%	6	< 5	0	< 5
6	$NaBH_3CN$ 50 mol%, benzoquinone 10 mol%	< 5	0	0	0
7	**None**	**100**	**0**	**0**	**100**

[a] Standard conditions: a mixture of 4-nitrotoluene (0.50 mmol), additives and **9** (0.0025 mmol) was stirred in MeOH (0.5 mL) at 50℃ under H_2 for 6 h. [b] Conversion and yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] under refluxing temperature.

進一步的實驗參數最佳化結果整理在 **Table 3-2**。低溫時反應的轉化率並不理想，但隨溫度上升而有所提升 (entries 2–4)，在 50℃ 時能夠達到 100% (entry 1)，但在 60℃ 時轉化率和產率反而下降，可能是 **9** 在高溫下分解 (entry 5)。另外室溫反應的氫譜中可以觀察到 17% 的 *N*-hydroxy-*p*-toluidine (**16b**) 的生成，可能為反應中間體 (entry 3)。至於不同溶劑的影響，在極性溶劑如甲醇、乙腈和丙酮等中都能夠得到很好的產率（entries 1, 7 和 8），但在水中由於反應物溶解度差轉化率並不佳 (entry 6)。另一方面，催化反應在低極性溶劑 (less polar solvent) 如二氯甲烷、四氫呋喃和甲苯中則不易進行 (entries 9–11)。因此，以甲醇作為此鈀催化劑對

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硝基苯還原的最佳溶劑。在不同的預催化劑 **9** 使用量，發現需要 0.5 mol% 的催化劑才能得到最佳效益 (entries 12–14)。值得注意的是，在 0.1 mol%催化劑量的實驗中，觀察到微量的 4,4'-azoxytoluene (**17b**) 伴隨生成，猜測 **17b** 可能為催化中間體，將於 3.4 節作進一步的探討。

Table 3-2 Reaction optimization for the reduction of 4-nitrotoluene [a]

Entry	Temp.	Solvent	Cat. Loading	Conv. (%)[b]	Yield (%)[b]		
					16b	**17b**	**20b**
1	**50℃**	**MeOH**	**0.5 mol%**	**100**	**0**	**0**	**100**
2	5℃	MeOH	0.5 mol%	< 5	0	0	0
3	25℃	MeOH	0.5 mol%	25	17	0	8
4	40℃	MeOH	0.5 mol%	76	0	0	68
5	64℃	MeOH	0.5 mol%	87	0	0	87
6[c]	50℃	H_2O	0.5 mol%	45	< 5	< 5	32
7	50℃	MeCN	0.5 mol%	100	< 5	< 5	87
8	50℃	Acetone	0.5 mol%	75	< 5	7	41
9[d]	40℃	CH_2Cl_2	0.5 mol%	32	< 5	< 5	23
10	50℃	THF	0.5 mol%	41	10	< 5	0
11	50℃	Toluene	0.5 mol%	17	< 5	< 5	8
12	50℃	MeOH	0.1 mol%	59	0	< 5	37
13	50℃	MeOH	0.2 mol%	95	0	0	89
14	50℃	MeOH	1.0 mol%	100	0	0	100

[a] Standard conditions: a mixture of 4-nitrotoluene (0.50 mmol) and **9** (0.0025 mmol) in MeOH (0.5 mL) was stirred at 50℃ under H_2 (1 atm) for 6 h. [b] Conversion and yields were determined by ^{1}H NMR integration using CH_2Br_2 as the internal standard. [c] Using CH_3NO_2 as the internal standard for determination. [d] under refluxing temperature.

為了展現催化劑 **9** 的獨特之處，比較了一系列鈀錯合物在上述最佳化條件下對 4-nitrotoluene 還原反應的催化活性，結果如 **Table 3-3**。與 **9** 相似的雙金屬鈀

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錯合物 **11** 在相同條件下產率不佳，但加入 $NaBH_3CN$ 活化金屬中心後產率大幅提升（entries 2 和 3）。若直接以 $NaBH_3CN$ 而非氫氣作為還原劑，則 **11** 的催化反應僅能得到微量的 **20b**，顯示 $NaBH_3CN$ 在反應中的角色是作為催化劑活化劑，而非還原劑 (entry 4)。錯合物 **13** 的催化效果不佳，僅能得到 16% 的 **20b** (entry 5)。[Pd(tpy)Cl](PF_6) [57] 和含膦配基鈀錯合物 $PdCl_2(PPh_3)_2$ 在此條件下皆無法催化此還原反應（entries 6 和 11），而其他含氮配基鈀單金屬催化劑 Pd(bpy)$(TFA)_2$ [58]、Pd(bpy)Cl_2 [59]、Pd(**bpnp**)$(TFA)_2$ (**10**) 和 [Pd(dien)Cl]Cl [60] (**Figure 3-1**)亦具有良好的催化效果 (entries 7–10)。$Pd(MeCN)_2Cl_2$ 和 $Pd(OAc)_2$ 雖然也展現出不錯的催化活性，但其產率和選擇性均不如 **9** (entries 12–13)。

Table 3-3 Comparison of various Pd complexes on reduction of 4-nitrotoluene [a]

Entry	Pd catalyst (mol%)	Conv. (%)[b]	Yield (%)[b]		
			16b	**17b**	**20b**
1	**9** (0.5)	100	0	0	100
2	**11** (0.5)	20	0	0	19
3[c]	**11** (0.5)	100	0	0	100
4[d]	**11** (0.5)	< 5	0	0	< 5
5	**13** (0.5)	27	< 5	6	16
6	[Pd(tpy)Cl](PF_6) (1.0)	0	0	0	0
7	Pd(bpy)$(TFA)_2$ (1.0)	100	0	0	100
8	Pd(bpy)Cl_2 (1.0)	92	0	0	92
9	**10** (1.0)	100	0	0	100
10	[Pd(dien)Cl]Cl (1.0)	100	< 5	0	100
11	$PdCl_2(PPh_3)_2$ (1.0)	0	0	0	0
12	$Pd(MeCN)_2Cl_2$ (1.0)	57	0	< 5	50
13	$Pd(OAc)_2$ (1.0)	89	< 5	< 5	65

[a] Reaction conditions: a mixture of 4-nitrotoluene (0.50 mmol) and Pd catalyst was stirred in MeOH (0.5 mL) under H_2 for 6 h. [b] Conversion and yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] $NaBH_3CN$ (2.5 mol%) was added. [d] 2.0 eq. of $NaBH_3CN$ was used under N_2.

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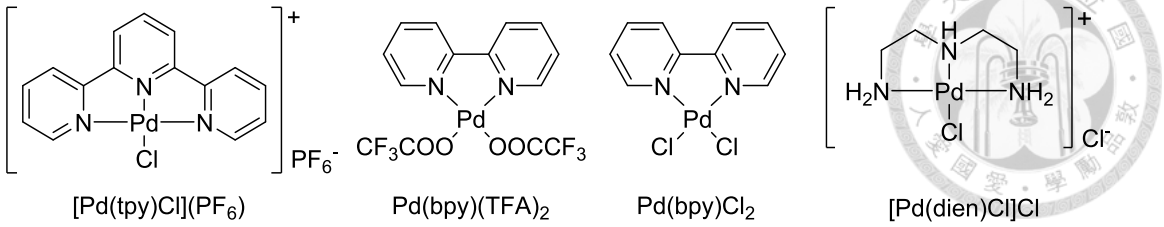

Figure 3-1 Mono-palladium(II) complexes with N-donating ligands

3.2 反應應用範圍

得到反應最佳化條件後，進一步測試該催化系統的應用範圍。**Table 3-4** 中列出各種取代硝基苯類的反應結果，該反應容許許多官能基如烷基 (alkyl groups, **20b**)、羥基 (hydroxy groups, **20c**)、胺基 (amino groups, **20d**)、芳基氟化物 (aryl fluoride, **20e**)、氰基 (cyano group, **20h**)、酮基 (keto group, **20i**) 和羧基 (carboxyl group, **20j**)，皆能夠在催化系統中保留，此外具有立體障礙的反應物如 1,3-二甲基-2-硝基苯 (1,3-dimethyl-2-nitrobenzene, **14k**) 和 1-硝基萘 (1-nitronaphthalene, **14l**) 也能夠成功轉換成相對應的苯胺類。具有多個取代基的硝基苯，如 2,3-二甲基-6-硝基苯胺 (2,3-dimethyl-6-nitroaniline, **14m**)，和多硝基苯如間二硝基苯 (*o*-dinitrobenzene, **14n**) 均有很好的產率。然而，含氯或溴之苯化物如 1-氯-4-硝基苯 (1-chloro-4-nitrobenzene, **14f**) 和 1-溴-4-硝基苯 (1-bromo-4-nitrobenzene) 反應性較差，或甚至不反應；含有芳香雜環噻吩 (thiophene) 和吡啶 (pyridine) 的 2-硝基噻吩 (2-nitrothiophene) 和 3-羥基-2-硝基吡啶 (3-hydroxy-2-nitropyridine) 毫無反應；脂肪類 (aliphatic) 反應物如 2,3-二甲基-2,3-二硝基丁烷 (2,3-dimethyl-2,3-dinitrobutane) 亦無法還原得到對應的產物。

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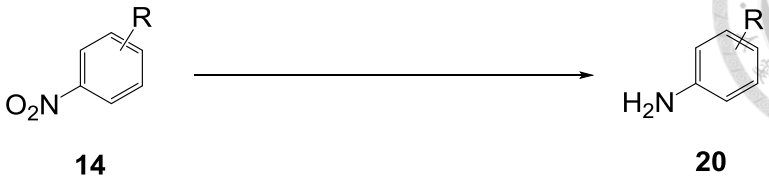
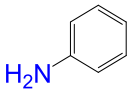
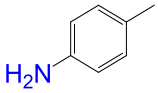
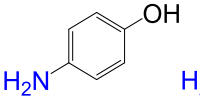
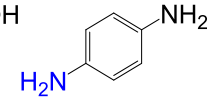
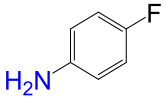
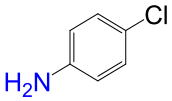
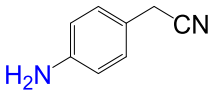
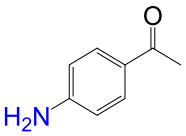
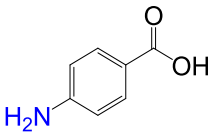
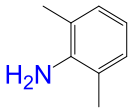
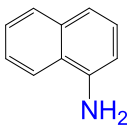
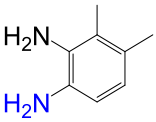
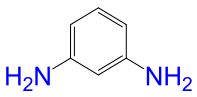
Table 3-4 Scope of catalysis with various nitroarenes [a]



14 **20**

Product (Yield, %)[b]				
				
20a (95%)	**20b** (96%)	**20c** (99%)	**20d** (95%[c,e])	**20e** (89%)
				
20f (28%[d])	**20h** (100%)	**20i** (88%[c])	**20j** (86%)	
				
20k (100%)	**20l** (100%)	**20m** (99%)	**20n** (92%)	

[a] Reaction conditions: a mixture of nitroarene (0.5 mmol) and **9** (0.0025 mmol) was stirred in MeOH (0.5 mL) at 50℃ under H_2 for 12 h. [b] Isolated yield. [c] 1 mol% of **9** was used. [d] 28% of **20f** and 30% of aniline was observed. [e] *p*-nitroaniline was used.

3.3 芳基鹵化物之還原反應探討

儘管多數反應物能夠順利進行催化還原得到高產率預期產物，但 1-chloro-4-nitrobenzene (**14f**) 和 1-bromo-4-nitrobenzene (**14g**) 卻不然。為了探究溴基對催化反應的影響，在一已知可行的硝基苯還原反應中加入了溴化鉀和 1,3,5-三溴苯，可以發現溴離子對反應沒有影響，而芳溴化物則會減低催化活性，但拉長反應時間仍然能夠反應完全 (**Table 3-5**)。

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Table 3-5 Influence of bromide in reduction of nitroarenes [a]

Entry	Additive	Time (h)	Yield of **20a** (%) [b]
1	None	6	100
2	KBr	6	100
3	1,3,5-tribromobenzene	6	39
4	1,3,5-tribromobenzene	16	100

[a] Reaction conditions: a mixture of bromide source (10 mol%) and **9** (0.5 mol%) was stirred in 0.5 mL MeOH at 50℃ under H_2 for 2 h, and then nitrobenzene (0.50 mmol) was added and stirred for specific time. [b] Conversion and yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

另外，添加鹼或銀鹽以進一步觀察反應，結果如 **Table 3-6**。選用無機鹼 Cs_2CO_3 時能夠觀察到鈀黑出現，且反應毫無變化，可能是因為銫能夠和配位基配位[61-63]，大量的銫將鈀置換掉成為鈀黑而失去反應活性；無機鹼 K_2CO_3 能夠還原去鹵化 (reductive dehalogenation) 後再進一步還原部分硝基苯，由產物分佈可知還原去鹵化發生在硝基還原之前[64]。若在反應中加入非親核鹼如 2,2,6,6-四甲基哌啶 (2,2,6,6-tetramethyl-piperidine, TMP)、三乙基胺 (triethylamine, NEt_3) 和 1,4-二氮雜二環[2.2.2]辛烷 (1,4-diazabicyclo[2.2.2]octane, DABCO)，能夠大幅提升轉化率 (entries 4–6)，然而由於還原去鹵化較容易發生，主產物為還原去溴—硝基還原的產物苯胺 **20a**。雖然 NEt_3 和 DABCO 都具有很好的效果，但考量毒性以及操作的方便性，在後續的實驗中選用 DABCO 進行測試。接著進一步降低 DABCO 的用量，發現使用 0.25 當量亦可達到同樣的效果 (entries 6–9)。在原反應系統中芳基鹵化物能夠氧化加成到金屬上，金屬催化劑被佔據而無法催化硝基苯還原，當其和鈀上的氫陰離子還原脫去時生成一分子芳香族和一分子溴化氫，由於鹼能夠中和反應中產生的溴化氫，加入鹼有利於還原脫去，反應因而能夠順利完成[65,66]。加入銀鹽的目的為使溴沉澱，效果不佳可能是因為銀離子為強氧化劑，會氧化催化劑 Pd(0) 使反應無法進行（entries 10 和 11）。我們將改良後的反應條件運用到 1-

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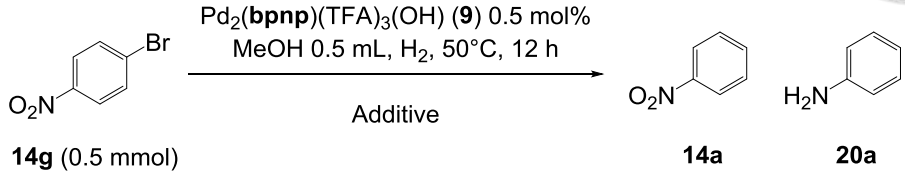
chloro-4-nitrobenzene (**14f**)，亦可得到預期的產物苯胺 (**Scheme 3-2**)。

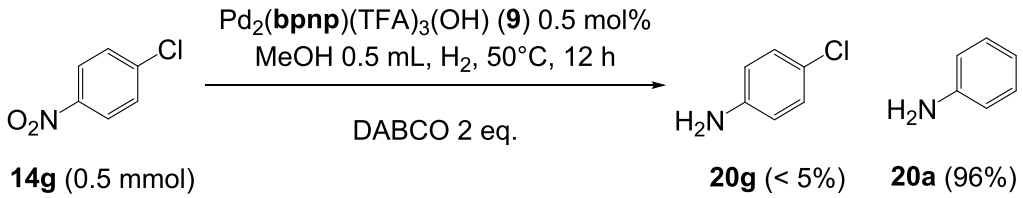
Table 3-6 Reduction of 1-bromo-4-nitrobenzene (**14g**) [a]



14g (0.5 mmol) **14a** **20a**

Entry	Additive	Conv. (%)[b]	Yield (%)[b]	
			Nitrobenzene	Aniline
1	None	0	0	0
2	Cs_2CO_3 1 eq.	0	0	0
3	K_2CO_3 1 eq.	100	62	19
4	TMP 2 eq.	100	33	57
5	NEt_3 2 eq.	100	0	90
6	DABCO 2 eq.	100	0	83
7	DABCO 1 eq.	100	0	87
8	DABCO 0.5 eq.	100	0	85
9	DABCO 0.25 eq.	100	0	83
10	$AgNO_3$ 1 eq.	0	0	0
11	$AgBF_4$ 1 eq.	0	0	0

[a] Reaction conditions: a mixture of 1-bromo-4-nitrotoluene (0.50 mmol), additive and **9** (0.0025 mmol) was stirred in 0.5 mL MeOH at 50℃ under H_2 for 12 h. [b] Conversion and yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.



14g (0.5 mmol) **20g** (< 5%) **20a** (96%)

Scheme 3-2 Reduction of 1-chloro-4-nitrobenzene

doi:10.6342/NTU201700680

將此條件應用到芳鹵化物，如溴苯、氯苯上，我們發現芳鹵化物會進行還原去鹵化並得到苯 (**Table 3-7**, entries 1–2)；苯環上有其他取代基的芳鹵化物，如 4-bromo-*N*,*N*-dimethylaniline 亦可順利去鹵化 (entry 3)；選用 2,4′-dibromoacetophenone 進行測試，發現苯環上和 α 位的溴均會被氫取代，且乙醯基更進一步還原為醇類 (entry 4)；多溴取代的芳香化合物如 1,3,5-三溴苯 (1,3,5-tribromobenzene) 能夠完全被還原成苯。此外，比較在氮氣下和氫氣下的反應結果可以確認氫氣在此作為還原劑（entries 1 和 6）。

Table 3-7 Reductive dehalogenation of aryl halides [a]

Entry	Aryl halide	Atmosphere	Product (yield)[b]
1	Bromobenzene	H_2	Benzene (95)
2	Chlorobenzene	H_2	Benzene (97)
3	4-Bromo-*N*,*N*-dimethylaniline	H_2	*N*,*N*-dimethylaniline (96)
4	2,4′-Dibromoacetophenone	H_2	Acetophenone (16) 1-Phenylethanol (79)
5[c]	1,3,5-Tribromobenzene	H_2	Benzene (97)
6	Bromobenzene	N_2	Benzene (0)

[a] Reaction conditions: a mixture of aryl halide (0.50 mmol), DABCO (1.0 mmol) and **9** (0.0025 mmol) was stirred in 0.5 mL MeOH at 50℃ under certain atmosphere for 12 h. [b] Yields were determined by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard. [c] 1.5 mmol of DABCO was used.

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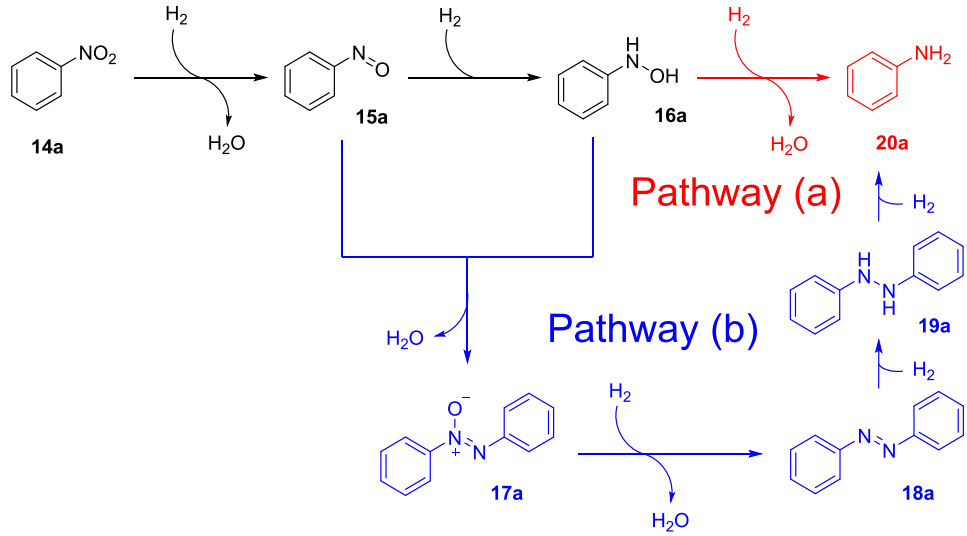
3.4 反應機構探討和與其他鈀催化劑之比較

文獻報導的硝基苯還原成苯胺路徑有二[42]：硝基苯還原成亞硝基苯 (nitrosobenzene) 後，進一步加氫還原成 *N*-苯基羥胺 (*N*-phenylhydroxylamine)，接著 *N*-苯基羥胺可直接加氫脫水得到苯胺 (**Scheme 3-3** a)，或亦可和亞硝基縮合 (condensation) 形成氧化偶氮苯 (azoxybenzene)再加氫脫水得偶氮苯 (azobenzene)，氫化得到二苯肼 (hydrazobenzene)，最後加氫分解得苯胺 (**Scheme 3-3** b)。



Scheme 3-3 Proposed mechanism of the reduction of nitroarenes

為了決定主要的反應路徑，以較溫和的反應條件用 **9** 為催化劑，分別以 *N*-苯基羥胺 **16a** 和偶氮苯 **18a** 為起始物測試其反應性[42,67]，結果整理於 **Table 3-8**。在 40℃ 下，**14a** 的轉化率有 80%，且觀察到中間體 **18a** 與 **19a** (entry 1)。遂以相同條件探討 **16a** 和 **18a** 的性質。僅以 **16a** 為起始物時，雖然反應的轉化率高達 97%，卻只得到 38% 的目標產物 **20a**，遠低於在相同條件下以 **14a** 為起始物的 73%，另外還產生較多量的 **18a** 與 **19a**。這顯示在 **9** 催化下 **16a** 不容易直接還原成 **20a**，而需先氧化成 **15a** 後，縮合得到 **17a**，接著才會還原成 **18a**、**19a** 和 **20a**。而以 **18a**

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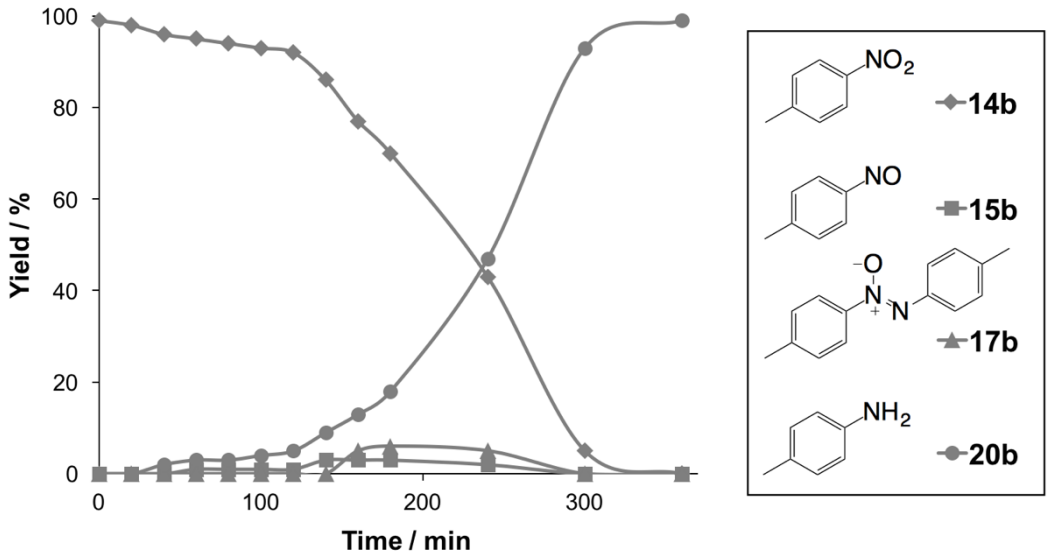
為起始物時，則能夠得到 81% 的目標產物，因此合理推測反應較可能遵循路徑 (b)。為確認此推論，更進一步做了反應的產物與時間的動力探討。

Table 3-8 Reduction of **14a**, **16a** and **18a** catalyzed by **9**

Entry	Starting material	Conv. (%)[b]	**17a** (%)[b]	**18a** (%)[b]	**19a** (%)[b]	**20a** (%)[b]
1[a]	**14a** (0.50 mmol)	80	0	< 5	< 5	73
2[a]	**16a** (0.50 mmol)	97	< 5	30	25	38
3[a]	**18a** (0.25 mmol)	99	0	--	18	81

[a] Reaction conditions: a mixture of starting material and **9** (0.0025 mmol) was stirred in 0.5 mL MeOH at 40℃ under H_2 for 6 h. [b] Yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

追蹤以 **9** 催化硝基苯還原的反應，其反應動力學曲線圖如 **Figure 3-2**。在反應前 120 分鐘中苯胺 **20b** 的產率和起始物 **14b** 的轉化率僅不到 10%，亞硝基苯 **15b** 開始緩慢地生成，這段誘導期 (induction period) 主要是 Pd(II)被還原成 Pd(0) 的步驟。之後，**15b** 開始和已被還原的 *N*-苯基羥胺 **16a** 縮合產生氧化偶氮苯 **17b**。在開始反應 180 分鐘後 **17b** 的量遂達到穩定態 (steady state)，即濃度保持固定，此結果表示其是此催化反應中的一個中間體，和前述的反應路徑推論符合。這區間伴隨產物 **20b** 逐漸生成，在 300 分鐘時反應幾乎已完成。



[a] Reaction conditions: a mixture of **14b** (0.5 mmol) and **9** (0.0025 mmol, 0.5 mol%) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-2 Kinetic time course of **9**-catalyzed reduction of **14b** [a, b]

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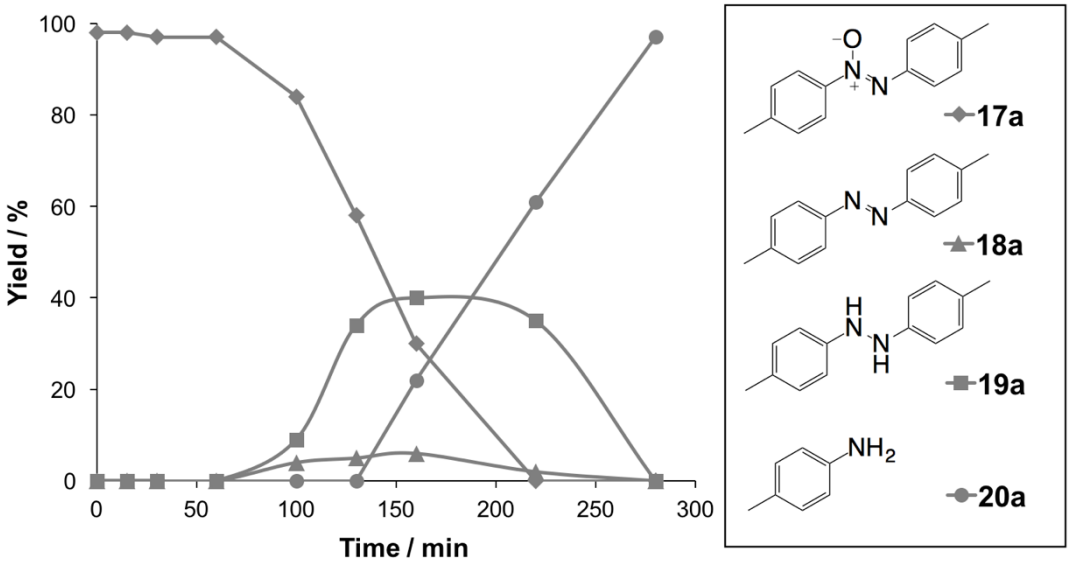
為了進一步確認反應路徑，將 **15a** 和 **16a** 混合在反應中生成 **17a**，觀察各成分的變化 (**Figure 3-3**)。由圖中可發現誘導期仍然存在，隨後 **17a** 始開始反應生成 **18a** 和 **19a**，且 **19a** 持續累積。**20a** 在氧化偶氮苯 **17a** 幾乎消耗後才開始生成，表示氫化偶氮苯 **18a** 的速率要比氫解二苯肼 **19a** 快很多，這可說明由 **17a** 還原至 **20a** 的速率決定步驟應為 N－N 鍵的氫解。



[a] Reaction conditions: a mixture of **15a** (0.25 mmol), **16a** (0.25 mmol) and **9** (0.0025 mmol) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^1H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-3 Kinetic time course of **9**-catalyzed reduction of **17a** [a, b]

以同樣的方式來決定 **11** 催化硝基苯還原的反應路徑，結果如表 **Table 3-9**。在相同條件下 (40℃)，以 **16a** 為起始物時，得到 53% 的苯胺 **20a**，而 **14a** 與 **18a** 為起始物，則分別得到 36% 與 27% 的苯胺 **20a**，這與催化劑 **9** 的性質截然不同。由於反應過程中僅有極少量 **18a** 與 **19a** 伴隨生成，同時對於 **18a** 的活性相對較低，所以推論以 **11** 為催化劑的催化系統是遵循路徑 (a)。

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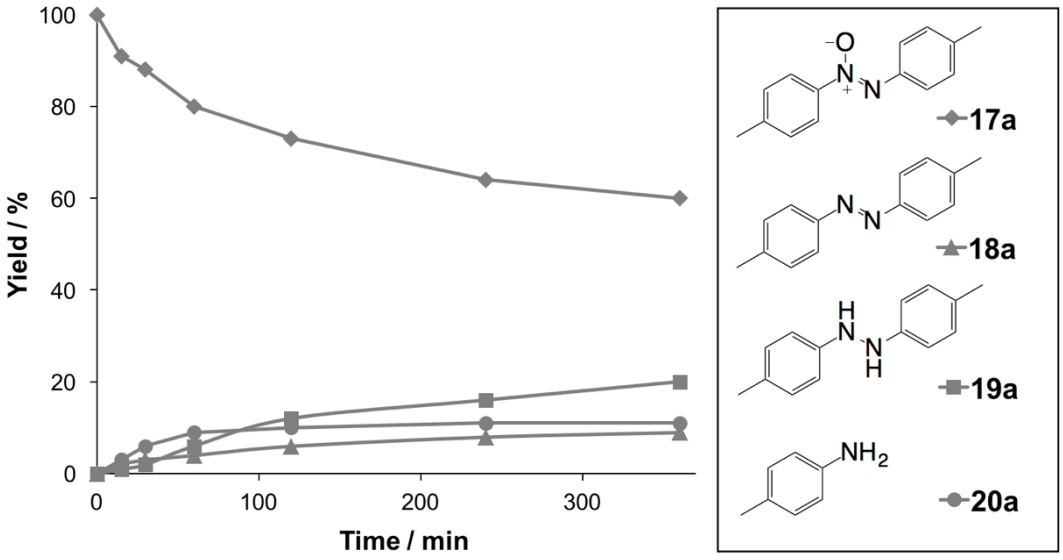
Table 3-9 Reduction of **14a**, **16a** and **18a** catalyzed by **11**

Entry	Starting material	Conv. (%)[b]	**17a** (%)[b]	**18a** (%)[b]	**19a** (%)[b]	**20a** (%)[b]
1[a]	**14a** (0.50 mmol)	40	0	< 5	0	36
2[a]	**16a** (0.50 mmol)	80	17	0	0	53
3[a]	**18a** (0.25 mmol)	27	< 5	--	< 5	27
4[c]	**14a** (0.50 mmol)	100	0	0	0	94

[a] Reaction conditions: a mixture of starting material, $NaBH_3CN$ (0.0125 mmol) and **11** (0.0025 mmol) was stirred in 0.5 mL MeOH at 40℃ under H_2 for 6 h. [b] Yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] Reaction conducted at 50℃.

追蹤 **17a** 在 **11** 催化下的表現，於 50℃ 的條件，360 分鐘內僅反應了 40%，相較於直接以 **14a** 反應的 100% 轉換率 (**Table 3-9**, entry 4) 少了許多，說明該反應主要路徑非以 **17a** 為中間體，和前述推論相吻合 (**Figure 3-4**)。



[a] Reaction conditions: a mixture of **15a** (0.25 mmol), **16a** (0.25 mmol), $NaBH_3CN$ (0.0125 mmol) and **11** (0.0025 mmol) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^1H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-4 Kinetic time course of **11**-catalyzed reduction of **17a** [a, b]

在 **11** 催化的對硝基甲苯 **14b** 還原反應中，60 分鐘內產物 **20b** 即大量累積超過 50%，反應過程可觀察到中間體亞硝基苯 **15b**，但是沒有中間體 **17b**。100 分鐘後反應趨緩，並在 360 分鐘時反應完全 (**Figure 3-5**)。

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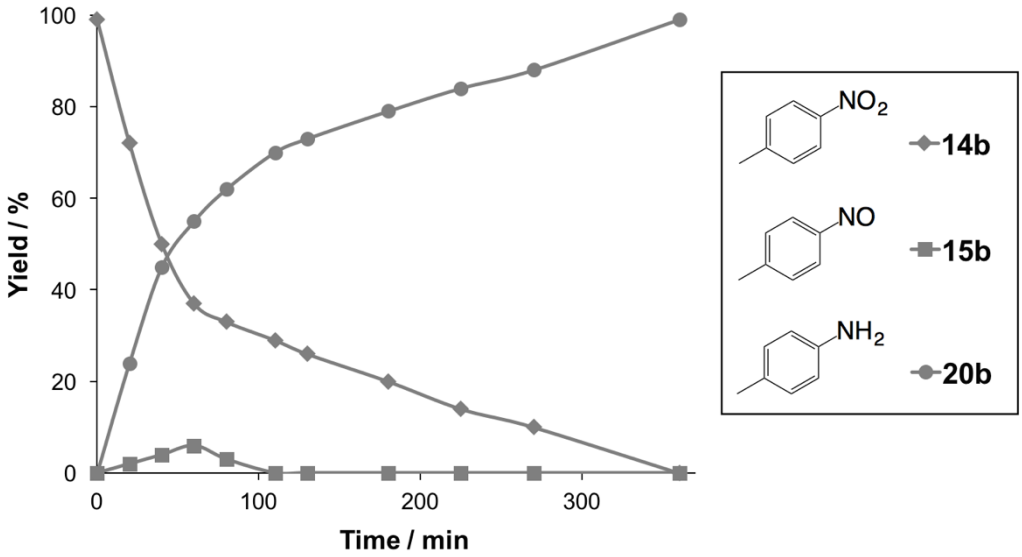

[a] Reaction conditions: a mixture of **14b** (0.5 mmol), **11** (0.0025 mmol, 0.5 mol%) and $NaBH_3CN$ (0.00625 mmol, 2.5 mol%) was stirred in MeOH (0.5 mL) at 50 ℃ under H_2. [b] Conversion and yields were determined by ^1H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-5 Kinetic time course of **11**-catalyzed reduction of **14b** [a, b]

比較 **9** 和 **11** 動力學實驗曲線（**Figure 3-2** 和 **Figure 3-5**），可發現 **9** 的催化反應需要經過誘導期，而 **11** 則否。因為 **11** 需加入 $NaBH_3CN$ 後才能進行催化反應，**9** 則不需額外加入還原劑活化，可知 **9** 能夠直接被氫氣還原得到具有活性的催化劑，開啟催化反應。由於 **9** 使用氫氣活化需要較長的時間，因此看到誘導期；而預催化劑 **11** 無法直接被氫氣還原，加入 $NaBH_3CN$ 後催化反應即進行。

若在 **9** 的催化反應中也加入 $NaBH_3CN$ 作為活化劑，則反應速率保持一定，誘導期消失，但整體反應性變差，且反應過程中有鈀黑生成，約需 500 分鐘才能反應完全 (**Figure 3-6**)。這可能是因為 $NaBH_3CN$ 還原力過強，而快速將鈀金屬還原，並且聚集 (aggregate) 生成鈀黑沉澱 [33]。

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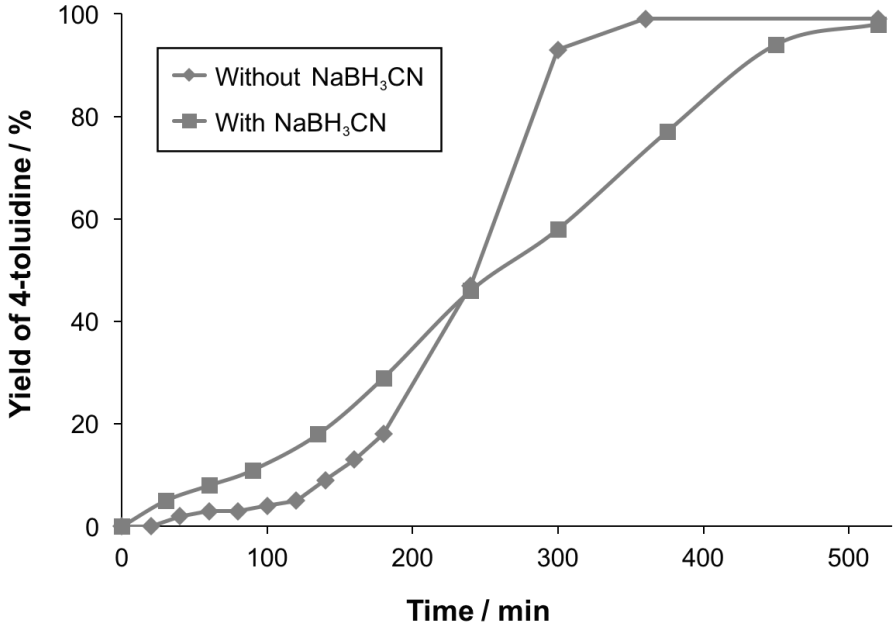

[a] Reaction condition: a mixture of **14b** (0.5 mmol), **9** (0.0025 mmol, 0.5 mol%) and $NaBH_3CN$ (0.05 mmol, 10 mol%) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^1H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-6 9-catalyzed reduction of **14b** w/ or w/o $NaBH_3CN$ [a, b]

氫陰離子能夠還原 Pd(II) 使生成鈀奈米粒子文獻中已多有報導 [43,44]，但目前為止以氫氣還原 Pd(II) 的例子未有較詳細報導。為了證明反應中生成了 Pd(0) 粒子，在反應中加入汞測試反應是否會被毒化，發現在加入汞之後反應即終止。由於汞能夠和 Pd(0) 形成汞齊 (amalgam) 而使反應中止，實驗結果說明催化活性物種含有為零價的鈀，但 **bpnp** 配位體仍具有穩定 Pd(0) 的功能，而動力學曲線中觀察到的反應誘導期，亦符合此催化系統的特徵 [68]。

此外，為了比較單核和雙核的催化劑，同樣以 **16a** 和 **18a** 為起始物測試催化劑 $Pd(bpy)(TFA)_2$ 之反應路徑，其結果如 **Table 3-10**。以 **18a** 為起始物時幾乎毫無反應，而以 **16a** 為起始物時則能夠得到 94% 的苯胺 **20a** (entries 2–3)，因此推測反應應是遵循路徑 (a)。以 $Pd(bpy)(TFA)_2$ 催化 **17a** 的還原，**17a** 在 50℃ 下加熱 360 分鐘後並沒有變化，此結果更可確認反應經由路徑 (a) (entry 4)。

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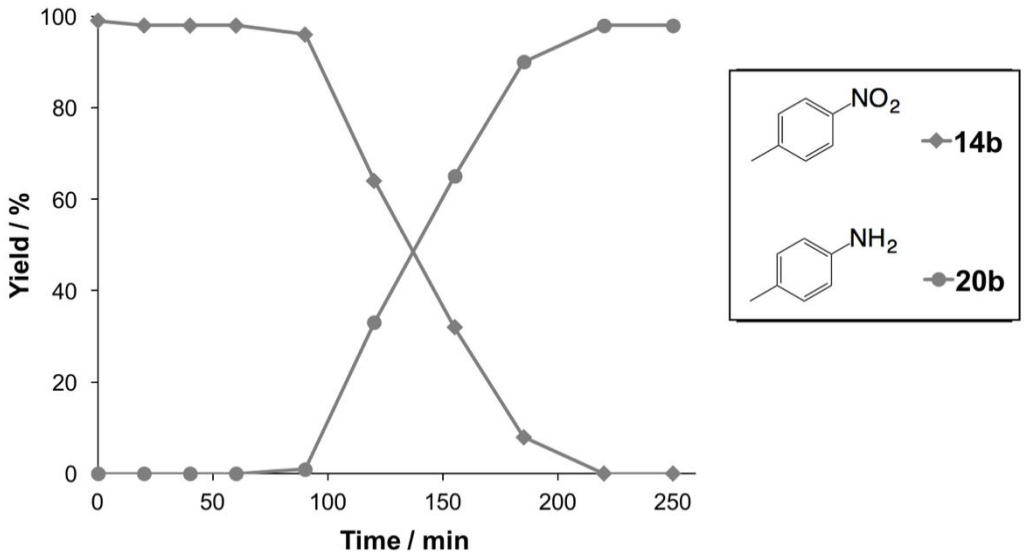
Table 3-10 Reduction of **14a**, **16a**, **17a** and **18a** catalyzed by Pd(bpy)(TFA)$_2$

Entry	Starting material	Conv. (%)[b]	**17a** (%)[b]	**18a** (%)[b]	**19a** (%)[b]	**20a** (%)[b]
1[a]	**14a** (0.50 mmol)	93	< 5	< 5	< 5	92
2[a]	**16a** (0.50 mmol)	100	6	0	0	94
3[a]	**18a** (0.25 mmol)	< 5	< 5	--	< 5	< 5
4[c]	**17a** (0.25 mmol)	0	--	0	0	0

[a] Reaction conditions: a mixture of starting material and Pd(bpy)(TFA)$_2$ (0.005 mmol) was stirred in 0.5 mL MeOH at 40℃ under H_2 for 6 h. [b] Yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] Reaction conditions: a mixture of **15a** (0.25 mmol), **16a** (0.25 mmol) and Pd(bpy)(TFA)$_2$ (0.005 mmol) was stirred in 0.5 mL MeOH at 50℃ under H_2 for 6 h.

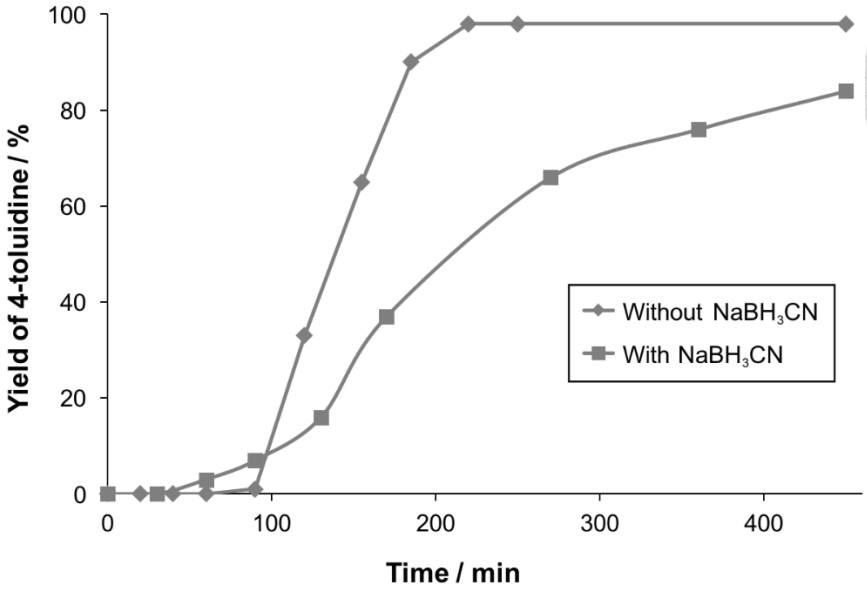
觀察 Pd(bpy)(TFA)$_2$ 催化的動力學曲線，可以發現在前 90 分鐘都沒有反應，在接下來到 210 分鐘之間硝基苯 **14b** 快速還原生成苯胺 **20b**，並未觀察到中間體，由於反應是經由不同的路徑，反應曲線明顯和 **9** 不同 (**Figure 3-7**)。值得注意的是 Pd(bpy)(TFA)$_2$ 和 **9** 同樣不需加入額外的還原劑活化，因此也需經過誘導期。加入 $NaBH_3CN$ 後誘導期消失但反應中生成鈀黑，催化活性下降 (**Figure 3-8**)。



[a] Reaction conditions: a mixture of **14b** (0.5 mmol) and Pd(bpy)(TFA)$_2$ (0.0050 mmol, 1.0 mol%) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-7 Kinetic time course of Pd(bpy)(TFA)$_2$-catalyzed reduction of **14b** [a, b]

doi:10.6342/NTU201700680



[a] Reaction conditions: a mixture of **14b** (0.5 mmol), Pd(bpy)(TFA)$_2$ (0.0050 mmol, 1.0 mol%) and $NaBH_3CN$ (0.05 mmol, 10 mol%) was stirred in MeOH (0.5 mL) at 50℃ under H_2. [b] Conversion and yields were determined by ^1H NMR spectroscopy using dimethyl sulfone as the internal standard.

Figure 3-8 Pd(bpy)(TFA)$_2$-catalyzed reduction of **14b** w/ or w/o $NaBH_3CN$ [a, b]

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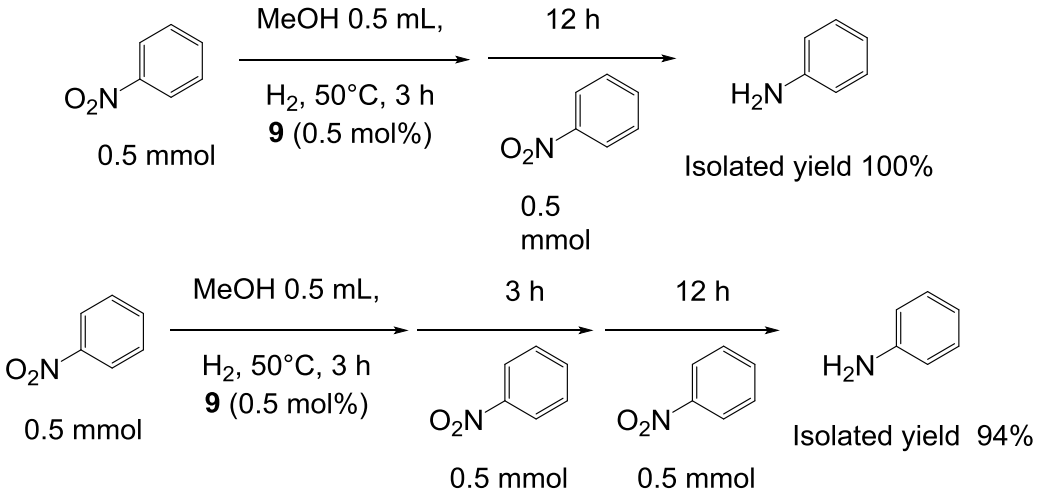
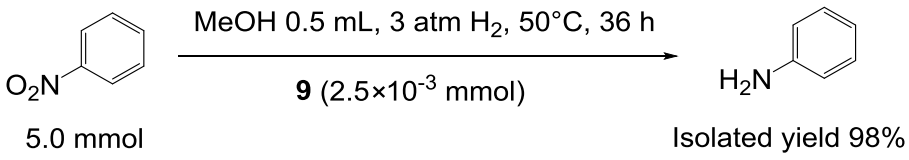
3.5 催化劑重複反應測試

為了測試催化劑的穩定性，於反應三小時後再加入一批硝基苯，反應後分離產率 (isolated yield) 達 100%。但若在加入第二批反應物後三小時時，再加入一批起始物反應 12 小時，則會觀察到少量未反應完的起始物，其分離產率可達到 94% (**Scheme 3-4**)。



Scheme 3-4 Multiple rounds of **9**-catalyzed reduction of nitroarenes

另外，若使用三大氣壓的氫氣作為還原劑，在高壓釜內反應，則最多可將轉換數 (turnover number, *TON*) 提升至 2000 仍可以保有 98% 的分離產率 (**Scheme 3-5**)。

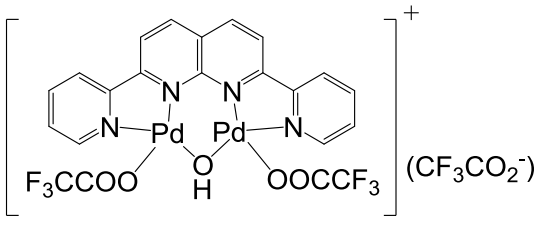


Scheme 3-5 High-pressure reaction

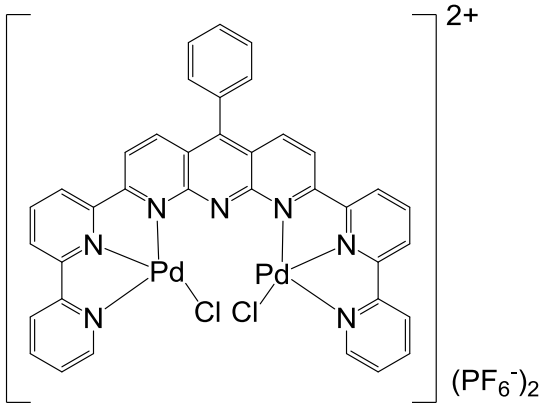
doi:10.6342/NTU201700680

第四章 結論

於本論文中，依照文獻方式成功合成出配位基 2,7-bis(2-pyridyl)-1,8-naphthyridine (**bpnp**) 和 5-phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (**pbbpa**)，並分別於甲醇和二氯甲烷下合成出鈀金屬錯合物 **9** 和 **11**，透過核磁共振光譜鑑定確定其結構，兩者皆是雙金屬錯合物。



9



11

鈀金屬錯合物 **9** 可作為硝基苯還原反應的催化試劑，此催化系統不需額外添加其他還原劑來活化，即可在一大氣壓氫氣下還原硝基苯，得到單一產物苯胺，其反應相當乾淨，和文獻相比幾乎不會得到副產物氧化偶氮苯。這個催化反應容忍具有官能基如烷基、羥基、胺基、氟基、氰基與酮基的分子；對於具立體障礙的反應物如 1,3-二甲基-2-硝基苯和 1-硝基萘也能夠轉換成相對應的苯胺。然而，芳香雜環如噻吩、吡啶和脂肪類之硝基物在本催化系統中無法被還原；含氯或溴之苯化物亦會減低反應性，此乃由於鹵素基團會被活化。有趣的是氯或溴之硝基苯化物在鹼性條件下，兩官能基皆會被還原。鈀金屬錯合物 **11** 在經 $NaBH_3CN$ 處理後，則能夠在氫氣下還原硝基苯。

以各種中間體如 *N*-苯基羥胺、氧化偶氮苯和偶氮苯等在催化系統中的變化來解析其反應機制。錯合物 **9** 的催化過程，是先將硝基苯還原成亞硝基苯與 *N*-苯基

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羥胺，縮合成氧化偶氮苯後，藉由雙金屬的協助進行後續的還原得到苯胺 (**Scheme 3-3**, pathway b)；而錯合物 **11** 與 $Pd(bpy)(TFA)_2$ 則是直接將 *N*-苯基羥胺還原成產物 (**Scheme 3-3**, pathway a)。雖然錯合物 **11** 是雙金屬化合物，但是兩金屬的距離約在 5 Å，比錯合物 **9** 中的距離長約 2 Å，不利於氧化偶氮苯的還原，因此錯合物 **11** 的活性與單金屬較為相似，這些結果說明了雙鈀金屬錯合物 **9** 的協同作用，使其金屬活性有不同的效應。

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第五章 實驗部分

5.1 General part

All reagents were reagent grade and used without further purification unless otherwise specified. MeOH was dried by refluxing over CaH_2 and distilled under N_2 before use. CH_2Cl_2 was dried by refluxing over P_2O_5 or CaH_2 and distilled under N_2 before use. THF was dried by refluxing over sodium benzophenone ketyl and distilled under N_2 before use. Acetonitrile was dried by refluxing over CaH_2 and distilled under N_2 before use. Toluene was dried by passing through the molecular sieves packed drying column under N_2. Other reagents and solvents were obtained from the commercial sources (Sigma-Aldrich Co., Acros Organics Co., Alfa Aesar Co. and Merck Co.) and used without further purification. All non-aqueous reactions were carried out in oven-dried glassware unless otherwise noted. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) on E. Merck silica gel 60 F_{254} aluminium sheets. Compounds were visualized by UV, or using potassium permanganate as visualizing agents. E. Merck silica gel 60 (60–200 μm particle sizes) were used for column chromatography.

Infrared (IR) spectra were recorded on Varian 640-IR FT-IR spectrometer. Nuclear

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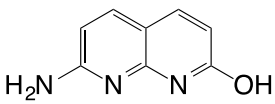
magnetic resonance (NMR) spectra were obtained on Varian Advance-400 (400 MHz NMR) spectrometers. Chemical shifts (δ) are given in parts per million (ppm) relative to δ_H 7.26/ δ_C 77.0 (central line of t) for $CHCl_3/CDCl_3$, δ_H 3.31/ δ_C 49.0 for CH_3OH/CD_3OD, δ_H 1.94/ δ_C 1.32 (central line of septet) for CH_3CN/CD_3CN, δ_H 4.80 for H_2O/D_2O, δ_H 4.33 for CH_3NO_2/CD_3NO_2 and δ_H 2.50 (m)/ δ_C 39.5 (m) for $(CH_3)_2SO/(CD_3)_2SO$. The splitting patterns are reported as s (singlet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), m (multiplet), quin (quintet), septet and br (broad). Coupling constants (*J*) are given in Hz. High resolution mass spectrometry (HRMS) diagrams under electrospray ionization were obtained on a Micromass® LCT Premier™ XE instrument or a Bruker micrOTOF-Q II instrument and were reported in mass-to-charge ratio (*m/z*).

5.2 Synthetic procedures and characterization of compounds

5.2.1 Synthesis of ligands and palladium(II) complexes

2-Amino-7-hydroxy-1,8-naphthyridine (1) [47]



2,6-diaminopyridine (0.20 mol, 22.10 g) and malic acid (0.22 mol, 30.10 g) were

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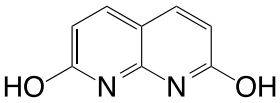
cooled in an ice bath, and then concentrated H_2SO_4 (100 mL) was added dropwise. The solution was warmed up to room temperature for 30 min, and then heated to 110℃ overnight. After completion of the reaction, the mixture was poured over ice and basified to pH = 8 with NaOH. The mixture was filtered and washed with H_2O. The desired product yielded as yellow to brown solid (29.33 g, 91%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.61 (s, br, 1H), 7.62 (d, *J* = 9 Hz, 2H), 6.81 (s, br, 2H), 6.32 (d, *J* = 9 Hz, 1H), 6.09 (d, *J* = 9 Hz, 1H).

2,7-Dihydroxy-1,8-naphthyridine (2) [47]



Compound **1** (63 mmol, 10.16 g) and $NaNO_2$ (78 mmol, 5.41 g) were cooled in an ice bath, and concentrated H_2SO_4 (100 mL) was added dropwise. The mixture was stirred in an ice bath until NO_2 evolution stopped, and warmed up to room temperature overnight. After completion of the reaction, the mixture was poured into ice water and neutralized to pH = 7 with NaOH. The mixture was filtered and washed with H_2O. The desired product was obtained in *ca.* 100% yield as brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, *J* = 8 Hz, 2H), 6.13 (d, *J* = 8 Hz, 2H).

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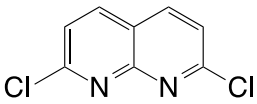
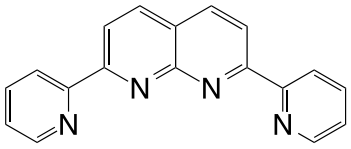
2,7-Dichloroxy-1,8-naphthyridine (3) [47]



The mixture of **2** (11.79 g) and phosphoryl chloride (60 mL) was refluxed overnight. The solution was poured into ice water and neutralized to pH = 7 with NaOH. After filtration, the resulting dark brown solid was purified by Soxhlet extraction with CH_2Cl_2. The solvent was removed and the desired product yielded as pale yellow solid (7.27 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H).

2,7-Bis(2-pyridyl)-1,8-naphthyridine (bpnp) [46]



Compound **3** (2.5 mmol, 502 mg), 2-tributylstannylpyridine (4 mL) and $PdCl_2(PPh_3)_2$ (0.12 mmol, 85 mg) were degassed and filled with N_2, and then dried toluene (40 mL) was added. The reaction mixture was refluxed for 48 h. After removal of the solvent, the residue was filtered and washed with hexane. The filtrate was concentrated and purified by column chromatography on silica gel using CH_2Cl_2: acetone (3:1) as eluent to provide the desired product as golden solid (498 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 7 Hz, 2H), 8.67 (d, *J* = 5 Hz, 2H), 8.64 (d, *J* = 8 Hz,

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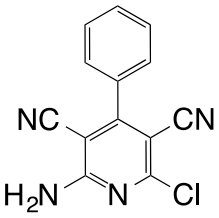
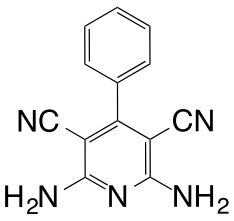
2H), 8.25 (d, *J* = 8 Hz, 2H), 7.82 (t, *J* = 7 Hz, 2H), 7.31 (dd, J = 7, 5 Hz, 2H).

2-Amino-6-chloro-4-phenylpyridine-3,5-dicarbonitrile (4) [49]



To a solution of trimethyl orthobenzoate (27.4 mmol, 5.00 g) and malononitrile (57.5 mmol, 3.80 g) was added pyridine (55.6 mmol, 4.40 g). The resulting mixture was heated to 100℃ overnight. After the reaction mixture returned to room temperature, concentrated HCl (15 mL) was added dropwise under ice bath. The solution was heated at 100℃ for 2 h. After filtration and drying, the desired product was obtained as brown solid (1.60 g, 23%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, br, 1H), 8.18 (s, br, 1H), 7.60 – 7.53 (m, 5H).

2,6-Diamino-4-phenylpyridine-3,5-dicarbonitrile (5) [49]



A mixture of NH_4OH (80 mL) and acetone (20 mL) was slowly added to **4** (6.3

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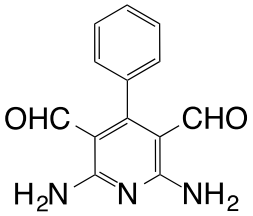
mmol, 1.61 g) in a 120 mL autoclave. The autoclave was sealed tightly and heated to 100℃ for 24 h. After removal of acetone, the residue was filtered to obtain desired product as beige solid (1.32 g, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 – 7.50 (m, 3H), 7.47 – 7.44 (m, 2H), 7.24 (s, br, 4H).

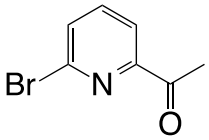
2,6-Diamino-4-phenylpyridine-3,5-dicarbaldehyde (6) [49]



Compound **5** (2.1 mmol, 500 mg), Pd/C (75 mg, 15 wt%) and 2 M HCl (60 mL) were stirred for 15 min and purged with N_2 for 2 h. The resulting mixture was degassed by water pump and filled with H_2 for 30 min. It was stirred vigorously and heated at 40℃ for 12 h. After filtration, NH_4OH (20 mL) was added to the filtrate. The desired product precipitated as white solid (128 mg, 25%) in the basified solution. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 2H), 8.69 (s, br, 2H), 7.92 (s, br, 2H), 7.53 – 7.51 (m, 3H), 7.44 – 7.41 (m, 2H).

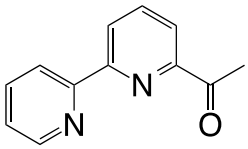
doi:10.6342/NTU201700680

1-(6-Bromopyridin-2-yl)ethanone (7) [21]



To a solution of 2,6-dibromopypridine (12.7 mmol, 3.00 g) in dried Et_2O (30 mL) was added *n*-BuLi (14.0 mmol, 8.7 mL, 1.6 M in hexane) dropwise at -78℃. The resulting mixture was stirred for 30 min at -78℃. Dimethylacetamide (22.9 mmol, 2.1 mL) was slowly added to the solution. The solution was kept at -78℃ for 15 min, and then stirred under room temperature for 12 h. The mixture was quenched by saturated NH_4Cl aqueous solution (40 mL) and stirred for 1 h. After extraction with Et_2O (30 mL × 3) and removal of solvent, the residue was purified by column chromatography on silica gel using Hexane: EA (19:1) as eluent. The desired product yielded as pale yellow solid (1.39 g, 55%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (m, 1H), 7.71 – 7.63 (m, 2H), 2.69 (m, 3H).

1-(2,2′-Bipyridin-6-yl)ethanone (8) [21]



A mixture of **7** (5.0 mmol, 1.00 g), 2-tributylstannylpyridine (10 mmol, 3.66 g), and $PdCl_2(PPh_3)_2$ (0.25 mmol, 175 mg, 5 mol %) in dried toluene (10 mL) was heated under

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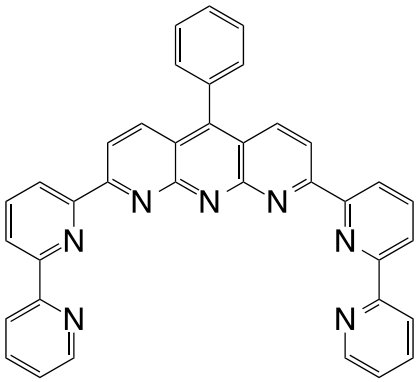
reflux for 24 h. After removal of solvent, the mixture was extracted with CH_2Cl_2 (15 mL × 3). Further purification by column chromatography on silica gel with elution of hexane/ethyl acetate (3:2) provide the desired compound as white solids (0.63 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 1H), 8.60 (dd, *J* = 8, 1 Hz, 1H), 8.52 (d, *J* = 8 Hz, 1H), 8.04 (dd, *J* = 7.7, 1 Hz, 1H), 7.94 (t, *J* = 8 Hz, 1H), 7.85 (td, *J* = 7.7, 1 Hz, 1H), 7.34 (ddd, *J* = 7.7, 4.8, 1 Hz, 1H), 2.82 (s, 3H).

5-Phenyl-2,8-bis(2,2'-bipyridin-6-yl)-1,9,10-anthyridine (pbbpa) [21]



A mixture of **7** (0.42 mmol, 100 mg) and **9** (0.91 mmol, 180 mg) in ethanol (4 mL) was heated at 60℃ for 2 h. Then 10% KOH in ethanol (0.1 mL) was added to the above solution. The resulting mixture was heated to reflux for 12 h. The reaction mixture was washed with ethanol (5 mL × 3). After drying under vacuum, the desired compound was obtained as yellow solids (189 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 7

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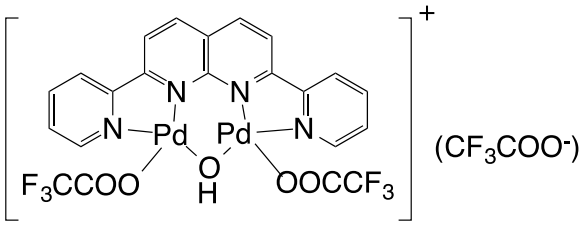
Hz, 2H), 8.88 (d, *J* = 9.0 Hz, 2H), 8.71 (d, *J* = 4.8 Hz, 2H), 8.61 (d, *J* = 7.8 Hz, 2H), 8.57 (d, *J* = 7.8 Hz, 2H), 8.30 (d, *J* = 9.0 Hz, 2H), 8.08 (t, *J* = 7 Hz, 2H), 7.84 (t, *J* = 7.8 Hz, 2H), 7.68 (m, 3H), 7.56 – 7.51 (m, 2H), 7.33 (dd, *J* = 7, 4.8 Hz, 2H).

Pd_2(bpnp)$(TFA)_3$(OH) (9)



To a stirred solution of **bpnp** (0.044 mmol, 12.5 mg) and $Pd(OAc)_2$ (0.090 mmol, 20.2 mg) in MeOH (1 mL) was added CF_3COOH (0.25 mL). The reaction was then heated to 50℃ for 30 min. After removal of MeOH, the residue was washed with Et_2O (1 mL × 3) to get desired product as yellow solid (32.0 mg, 98%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.38 (d, *J* = 8.4 Hz, 2H), 9.13 (d, *J* = 8.4 Hz, 2H), 8.90 (d, *J* = 8 Hz, 2H), 8.56 (t, *J* = 8 Hz, 2H), 8.29 (s, br, 2H), 8.20 – 7.85 (m, 2H), 4.68 (s, br, 1H); ^{19}F NMR (375 MHz, DMSO-*d*$_6$) δ -73.43 (s, br); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 163.73, 156.45, 151.40, 150.26 (q, *J* = 23 Hz), 149.24, 146.46, 142.81, 129.61, 128.69, 126.45, 124.06, 40.48 (q, *J* = 2000 Hz). HRMS (ESI) *m*/*z* [M – CF_3COO]$^+$ calculated for $C_{22}H_{13}F_6N_4O_5Pd_2$:

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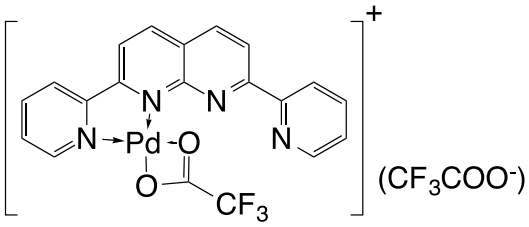
740.8869, found: 740.8892. Elemental analysis calculated for [**9** + 2H_2O]: C, 32.42; H, 1.93; N, 6.30, found: C, 32.30; H, 1.57; N, 6.01.

Pd(bpnp)(TFA)$_2$ (10)



To a stirred solution of **bpnp** (0.044 mmol, 12.5 mg) and $Pd(OAc)_2$ (0.045 mmol, 10.1 mg) in MeOH (1 mL) was added CF_3COOH (0.25 mL). The reaction was then stirred at room temperature overnight. After removal of MeOH, the residue was washed with Et_2O (1 mL × 3) to get desired product as pale yellow solid (25.7 mg, 100%). ^{1}H NMR (400 MHz, CD_3CN) δ 10.39 (d, *J* = 7.9 Hz, 1H), 9.20 (d, *J* = 5.7 Hz, 1H), 8.66 (d, *J* = 8.6 Hz, 1H), 8.53 (d, *J* = 7.6 Hz, 1H), 8.49 – 8.41 (m, 3H), 8.37 (d, *J* = 8.6 Hz, 1H), 7.93 (t, *J* = 6.0 Hz, 1H), 7.77 (t, *J* = 7.6, 1H), 7.72 (t, *J* = 5.7 Hz, 1H), 6.93 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 163.20, 162.98, 160.78 (q, *J* = 68 Hz), 159.46, 157.89, 153.23, 151.80, 150.69, 148.25 (q, *J* = 470 Hz), 146.08, 144.29, 142.22, 141.53, 130.51, 127.96, 127.64, 126.69, 125.71, 125.26, 122.58, 62.74(q, *J* = 915 Hz). *m*/*z* [M – $CF_3COO]^+$ calculated for $C_{20}H_{12}F_3N_4O_2Pd$: 502.9950, found: 503.0006.

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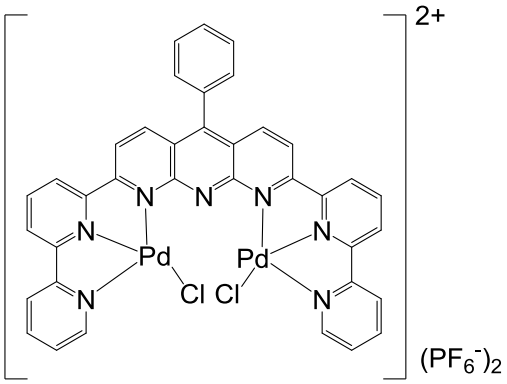
$[Pd_2(pbbpa)Cl_2](PF_6)_2$ (11)



A mixture of **pbbpa** (0.11 mmol, 60 mg) and $Pd(MeCN)_2Cl_2$ (0.23 mmol, 60 mg) in dried CH_2Cl_2 (15 mL) was stirred at room temperature under N_2 for 3 h. KPF_6 (1.1 mmol, 210 mg) was then added to the reaction mixture and the mixture was stirred overnight. The solvent was evaporated and CH_3CN (*ca.* 20 mL) was added. The suspension was passed through a pad of Celite® and concentrated to *ca.* 5 mL. The solution was added to Et_2O to provide the yellow solid. The solid was washed with MeOH (5 mL × 3) and dried *in vacuo* to obtain the desired product as brown solid (99 mg, 82%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.02 (d, *J* = 4.8 Hz, 2H), 8.42 (t, *J* = 8.0 Hz, 2H), 8.37 (t, *J* = 8 Hz, 2H), 8.33 – 8.28 (m, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 8.09 – 8.02 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.86 – 7.80 (m, 2H), 7.48 – 7.42 (m, 5H); ^{13}C NMR (125 MHz, CD_3CN) δ 159.5, 156.8, 156.4, 156.2, 153.1, 146.7, 143.9, 143.9, 143.7, 130.0, 129.9, 129.9, 129.8, 129.6, 129.3, 127.3, 126.2, 125.8, 125.5, 120.2; HRMS (ESI) m/z [M –

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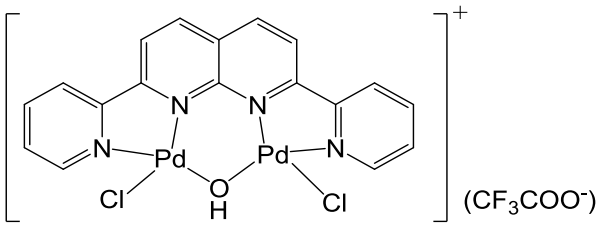
$2PF_6]^{2+}$ calculated for $C_{37}H_{23}Cl_2N_7Pd_2$: 424.4729, found: 424.4712; *m/z* [M – $2PF_6$ – Cl + OH]$^{2+}$ calculated for $C_{37}H_{24}ClN_7OPd_2$: 415.4901, found: 415.4940. Elemental analysis calculated for [**11** + $6H_2O$]: C, 35.63; H, 2.83; N, 7.86, found: C, 35.42; H, 2.78; N, 7.37.

[Pd_2(bpnp)Cl_2(OH)](TFA) (12)



A mixture of **9** (0.03 mmol, 25.4 mg) and KCl (0.06 mmol, 5.0 mg) in dried CH_3CN (2 mL) was stirred at room temperature under N_2 for 3 h. The solution was centrifuged, washed with Et_2O and dried under vacuum to provide the yellow solid (18.8 mg, 90%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (d, *J* = 8 Hz, 2H), 9.09 (d, *J* = 8 Hz, 2H), 8.93 – 8.74 (m, 4H), 8.45 (t, *J* = 8 Hz, 2H), 7.83 (t, *J* = 7 Hz, 2H); ^{19}F NMR (375 MHz, DMSO-d_6) δ -73.84 (s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.7, 156.5, 151.9, 149.9, 145.6, 141.8, 128.8, 128.2, 126.2, 123.6; HRMS (ESI) m/z [M – TFA]$^+$ calculated for $C_{18}H_{13}Cl_2N_4OPd_2$: 584.8532, found: 584.8597.

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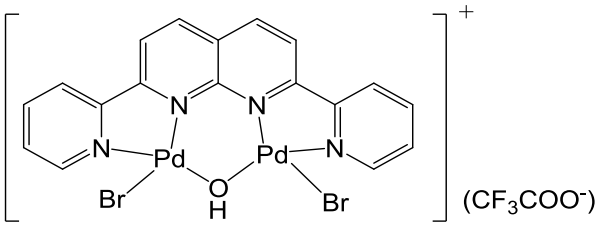
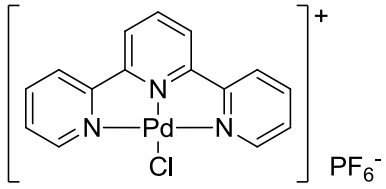
[Pd_2(bpnp)Br_2(OH)](TFA) (13)



A mixture of **9** (0.03 mmol, 25.4 mg) and KBr (0.06 mmol, 7.0 mg) in dried CH_3CN (2 mL) was stirred at room temperature under N_2 for 3 h. The solution was centrifuged, washed with CH_3CN and dried under vacuum to provide the yellow solid (17.0 mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.38 (d, J = 8 Hz, 2H), 9.12 (d, J = 8 Hz, 2H), 9.07 (s, br, 2H), 8.84 (d, J = 8 Hz, 2H), 8.43 – 8.48 (m, 2H), 7.80 (s, br, 2H); ^{19}F NMR (375 MHz, DMSO-d_6) δ -73.84 (s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.0, 159.9, 157.1, 154.8, 145.9, 142.1, 141.7 (q, J = 70 Hz), 129.6, 128.8, 126.5, 124.1, 53.1 (q, J = 2700); HRMS (ESI) m/z [M – TFA]$^+$ calculated for $C_{18}H_{13}Br_2N_4OPd_2$: 674.7513, found: 674.7503.

[Pd(tpy)Cl](PF$_6$) [57]



A mixture of 2,2':6',2''-terpyridine (0.20 mmol, 47 mg,) and $Pd(MeCN)_2Cl_2$ (0.23 mmol, 59 mg) in dried MeCN (8 mL) was stirred at room temperature under N_2 for 30

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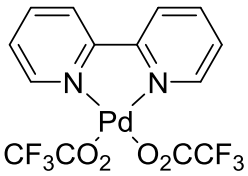
min. KPF_6 (0.57 mmol, 104 mg) was then added to the reaction mixture and the mixture was heated to 50℃ for 3 h. After cooled to room temperature, the solvent was evaporated and CH_3NO_2 (*ca.* 10 mL) was added. The suspension was passed through a pad of Celite® and concentrated to *ca.* 3 mL. The solution was added to Et_2O to provide the pink precipitate. The solid was filtered and washed with MeOH and Et_2O, and dried *in vacuo* to provide the desired product as white solid (94 mg, 90%). ^{1}H NMR (400 MHz, CD_3NO_2) δ 8.90 – 8.79 (m, 2H), 8.53 (dd, *J* = 8.6, 7.8 Hz, 1H), 8.42 – 8.32 (m, 6H), 7.88 – 7.77 (m, 2H).

Pd(bpy)(TFA)$_2$ [58]

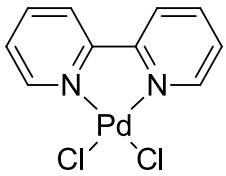


$Pd(OAc)_2$ (0.044 mmol, 9.9 mg) and 2,2'-bipyridine (0.053 mmol, 8.3 mg) were dissolved in MeOH at room temperature under N_2 for 30 min, and an excess of CF_3COOH (100 μL) was added. Precipitate was filtered off, washed with cold MeOH and dried *in vacuo* to get the desired product as pale yellow solid (15 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (d, *J* = 8 Hz, 2H), 8.44 (t, *J* = 8 Hz, 2H), 8.09 (s, br, 2H), 7.85 (t, *J* = 8

doi:10.6342/NTU201700680

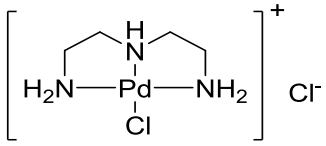
Hz, 2H).

Pd(bpy)Cl$_2$ [59]



A mixture of 2,2'-bipyridine (0.34 mmol, 53 mg) and $PdCl_2$ (0.28 mmol, 50 mg) in dried MeOH (2 mL) was stirred at room temperature under N_2 for 18 h. The resulting solid was filtered and washed with MeOH, $CHCl_3$ and Et_2O. The solid was dried *in vacuo* to provide the desired product as pale yellow solid (70 mg, 74%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (d, J = 6.9 Hz, 2H), 8.58 (d, J = 6.9 Hz, 2H), 8.36 (t, J = 6.9 Hz, 2H), 7.81 (t, J = 6.9 Hz, 2H).

[Pd(dien)Cl]Cl [60]



A mixture of diethylenetriamine (0.64 mmol, 66 mg) and $PdCl_2$ (0.29 mmol, 51 mg) in H_2O (2 mL) was stirred at 70°C until a yellow solution resulted (*ca.* 1 h). The solution was acidified with conc. HCl, and half of the solvent was evaporated. To the residue was

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added EtOH (10 mL). The resulting solid was filtered and washed with cold EtOH and Et_2O. The solid was dried *in vacuo* to provide the desired product as tan solid (51 mg, 71%). ^1H NMR (400 MHz, D_2O) δ 3.22 – 3.08 (m, 2H), 3.08 – 2.93 (m, 4H), 2.80 – 2.69 (m, 2H).

5.2.2 Reduction of Nitroarenes

General procedure for reduction of nitroarenes

A mixture of nitroarene (0.5 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2 for 12 h. After completion of the reaction, the reaction mixture was diluted with MeOH or CH_2Cl_2 and passed through a pad of Celite®. The residue was concentrated and purified by column chromatography on silica gel to provide the desired product if needed.

General procedure for reduction of aryl halides

A mixture of aryl halide (0.5 mmol), **9** (0.0025 mmol, 2.1 mg) and DABCO (1.0 mmol, 112 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added

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dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2 for 12 h. After completion of the reaction, the mixture was cooled to room temperature and small amount of dimethyl sulfone was added as the internal standard to determined conversion and yields by ^1H NMR spectroscopy.

Procedure of multiple rounds of 9-catalyzed reduction of nitroarenes

9 (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. Nitrobenzene (0.50 mmol) and dried MeOH (0.5 mL) were added and the mixture was stirred at 50℃ under H_2 for 3 h. Another 0.50 mmol of nitrobenzene was added. After 3 h, the third portion of nitrobenzene (0.50 mmol) was added and the mixture was stirred overnight. After completion of the reaction, the reaction mixture was diluted with MeOH or CH_2Cl_2 and passed through a pad of Celite®. The residue was concentrated to get desired product.

High-pressure reaction

9 (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a short test tube capped with a silicone stopper. Nitrobenzene (5.0 mmol) and dried MeOH (0.5 mL) were

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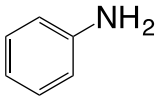
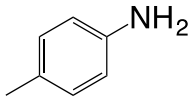
added and then the test tube was placed in an autoclave reactor with silicone oil inside. A needle was pierced through the silicone stopper to enable gas exchange and the autoclave reactor was quickly closed. After that the reactor was repeated degraded and refilled with H_2 for 3 times. After stirred at 50℃ for 36 h, the reaction mixture was diluted with MeOH or CH_2Cl_2 and passed through a pad of Celite®. The residue was concentrated to get desired product.

Aniline (20a)



Yield: 95%. Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 2H), 6.84 – 6.75 (m, 1H), 6.75 – 6.66 (m, 2H), 3.52 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 129.2, 118.5, 115.0.

4-Toluidine (20b)



Yield: 96%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.3 Hz, 2H), 6.65 (d *J* = 8.3 Hz, 2H), 3.50 (s, br, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7,

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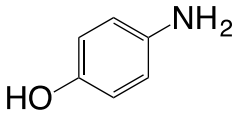
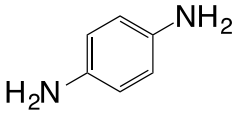
129.6, 127.6, 115.2, 20.3.

4-Aminophenol (20c)



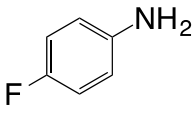
Yield: 99%. Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (s, br, 1H), 6.48 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 8.2 Hz, 2H), 4.37 (s, br, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.2, 141.6, 116.5, 116.2.

4-Phenylenediamine (20d)



Yield: 95%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 4H), 3.29 (s, br, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 117.0

4-Fluoroaniline (20e)



Yield: 89%. Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.84 (m, 2H), 6.67 –

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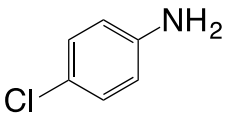
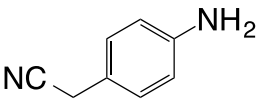
6.57 (m, 2H), 3.45 (s, br, 2H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -127.27 (tt, J = 6.7, 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4 (d, J = 235.7 Hz), 142.3, 116.1 (d, J = 7.5 Hz), 115.6 (d, J = 22.5 Hz).

4-Chloroaniline (20f)



Yield: 28%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.8 Hz, 2H), 3.65 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 129.3, 123.4, 116.5.

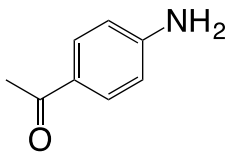
4-Aminophenylacetonitrile (20h)



Yield: 100%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 3.73 (s, br, 2H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 128.7, 119.0, 118.5, 115.3, 22.6. IR (KBr): 3453, 3370, 3223, 3035, 3007, 2909, 2248, 1629, 1518, 1438, 1415, 1284, 1201, 1182, 1129, 1087, 1015, 824, 775 cm^{-1}.

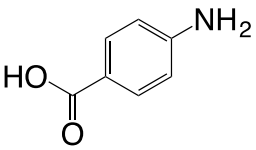
doi:10.6342/NTU201700680

4'-Aminoacetophenone (20i)



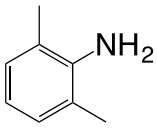
Yield: 88%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.13 (s, br, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 151.5, 130.9, 127.7, 113.8, 26.2. IR (KBr): 3395, 3323, 3218, 1652, 1603, 1566, 1513, 1438, 1361, 1305, 1281, 1231, 1178, 961, 838, 820 cm^{-1}.

4-Aminobenzoic acid (20j)



Yield: 86%. White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.2 Hz, 2H), 5.85 (s, br, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 153.1, 131.3, 117.3, 112.7.

2,6-Xylidine (20k)



Yield: 100%. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.5 Hz, 2H), 6.66

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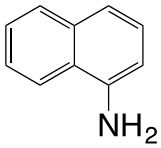
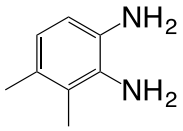
(t, J = 7.5 Hz, 1H), 3.58 (s br, 2H), 2.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.2, 121.6, 117.9, 17.6.

1-Naphthylamine (20l)



Yield: 100%. Red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.51 – 7.44 (m, 2H), 7.34 – 7.33 (m, 2H), 6.79 – 6.77 (m,1H), 4.05 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 134.4, 128.7, 126.4, 126.0, 125.1, 124.0, 120.9, 119.4, 110.2.

3,4-Dimethylbenzene-1,2-diamine (20m)



Yield: 99%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 7.8 Hz, 1H), 3.48 (s, br, 4H), 2.31 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 131.4, 128.19, 120.1, 114.3, 19.9, 12.8.

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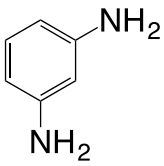
1,3-Diaminobenzene (20n)



Yield: 92%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (t, *J* = 7.9 Hz, 1H), 6.10 (d, *J* = 7.9, 2H), 5.99 (s, 1H), 3.46 (s, br, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 130.0, 105.8, 101.9.

5.2.3 Investigation of Reaction Intermediates and Mechanism

Reaction of nitrobenzene (14a)

9 (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added nitrobenzene (0.5 mmol) and dried MeOH (0.5 mL) and the mixture was stirred at 40℃ under H_2 for 6 h. Conversion and yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. The reaction catalyzed by **11** was conducted similarly with 0.0025 mmol of **11** and 0.0125 mmol of $NaBH_3CN$. 0.0050 mmol of $Pd(bpy)(TFA)_2$ was used in the reaction catalyzed by $Pd(bpy)(TFA)_2$.

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Reaction of *N*-phenylhydroxylamine (16a)

A mixture of *N*-phenylhydroxylamine (0.5 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 40℃ under H_2 for 6 h. Conversion and yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. The reaction catalyzed by **11** was conducted similarly with 0.0025 mmol of **11** and 0.0125 mmol of $NaBH_3CN$. 0.0050 mmol of $Pd(bpy)(TFA)_2$ was used in the reaction catalyzed by $Pd(bpy)(TFA)_2$.

Reaction of azobenzene (18a)

A mixture of azobenzene (0.25 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 40℃ under H_2 for 6 h. Conversion and yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. The reaction catalyzed by **11** was conducted similarly with 0.0025 mmol of **11** and 0.0125 mmol of $NaBH_3CN$. 0.0050 mmol of $Pd(bpy)(TFA)_2$ was used in the reaction catalyzed by $Pd(bpy)(TFA)_2$.

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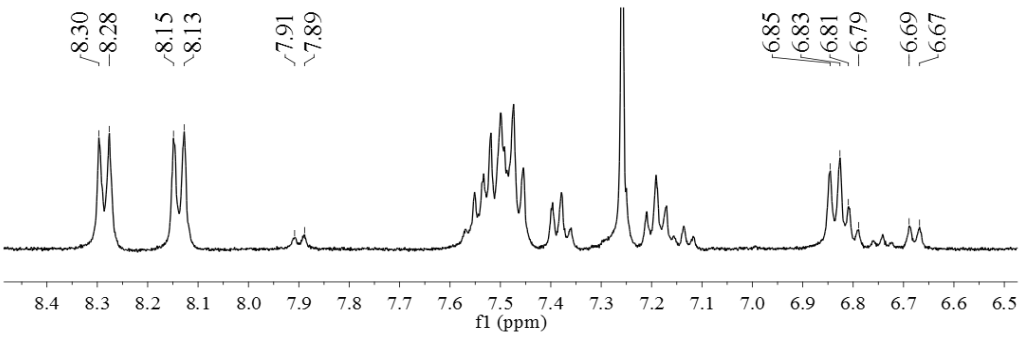
Kinetic study of reduction of azoxybenzene (17a)

A mixture of *N*-phenylhydroxylamine (0.25 mmol), nitrosobenzene (0.25 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2. The reaction was followed by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard. Condensation of *N*-phenylhydroxylamine and nitrosobenzene occurred immediately after mixing and generated azoxybenzene. Azoxybenzene was quantified by ^{1}H NMR integration of doublets at δ 8.29 (2H) and δ 8.14 (2H); azobenzene was quantified by ^{1}H NMR integration of doublet at δ 7.90 (4H); hydrazobenzene was quantified by ^{1}H NMR integration of multiplet at δ 6.79 – 6.85 (3H); aniline was quantified by ^{1}H NMR integration of doublet at δ 6.68 (2H). The procedure for **11**-catalyzed reaction was same as **9**, except that 0.0125 $NaBH_3CN$ was added to the reaction mixture. The reaction catalyzed by $Pd(bpy)(TFA)_2$ was conducted similarly with 0.0050 mmol of $Pd(bpy)(TFA)_2$.



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Kinetic study of reduction of *p*-nitrotoluene (14b)

A mixture of **14b** (0.50 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2. The reaction was followed by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard. The reaction catalyzed by Pd(bpy)$(TFA)_2$ was conducted similarly with 0.0050 mmol of Pd(bpy)$(TFA)_2$.

Kinetic study of reduction of 14b activated by $NaBH_3CN$

A mixture of **14b** (0.50 mmol), $NaBH_3CN$ (0.050 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2. The reaction was followed by ^{1}H NMR spectroscopy using dimethyl sulfone as the internal standard. In the kinetic study of the reaction catalyzed by Pd(bpy)$(TFA)_2$, 0.0050 mmol of Pd(bpy)$(TFA)_2$ was used. The reaction catalyzed by **11** was conducted similarly with 0.0025 mmol of **11** and 0.0125 mmol of $NaBH_3CN$.

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Mercury poisoning experiment

A mixture of **14b** (0.50 mmol) and **9** (0.0025 mmol, 2.1 mg) was degassed and refilled with H_2 in a test tube. To the mixture was added dried MeOH (0.5 mL) and the mixture was stirred at 50℃ under H_2 for 4 h. Afterward a drop of mercury was added to the reaction mixture. The reaction was followed by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

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附錄一

化合物之光譜資料

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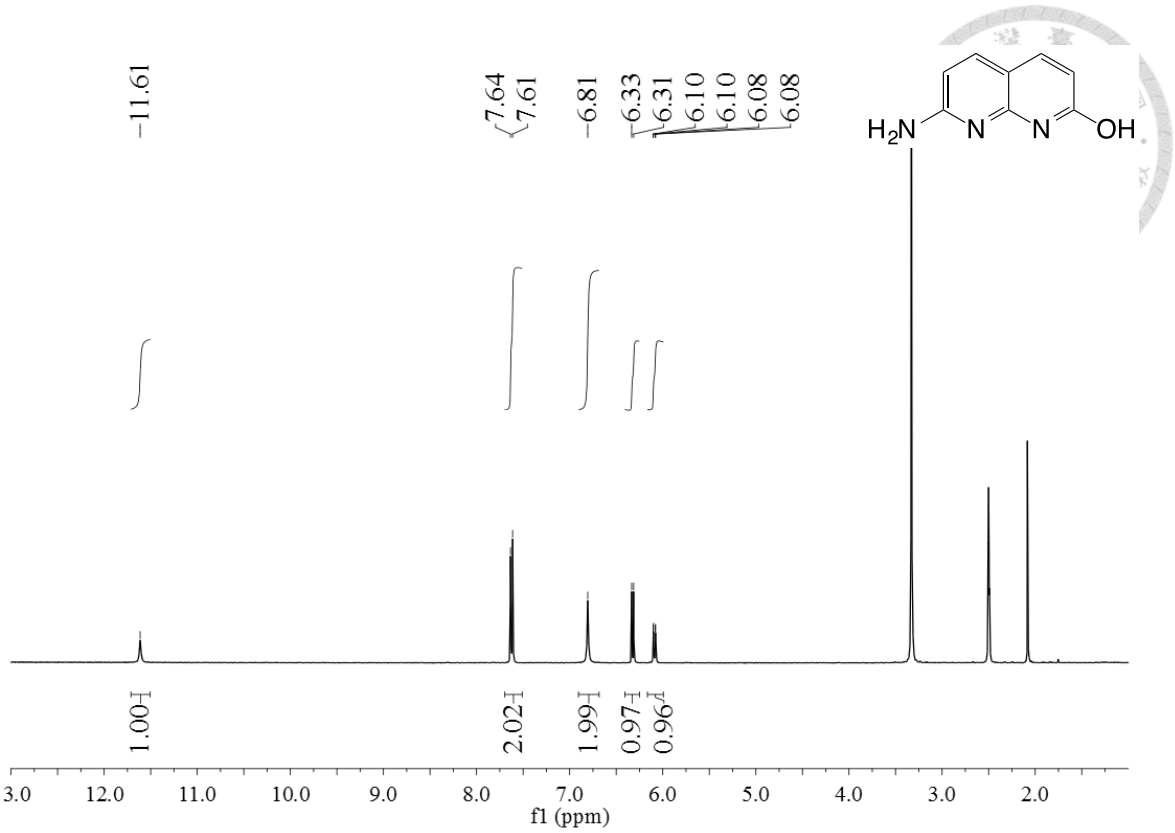
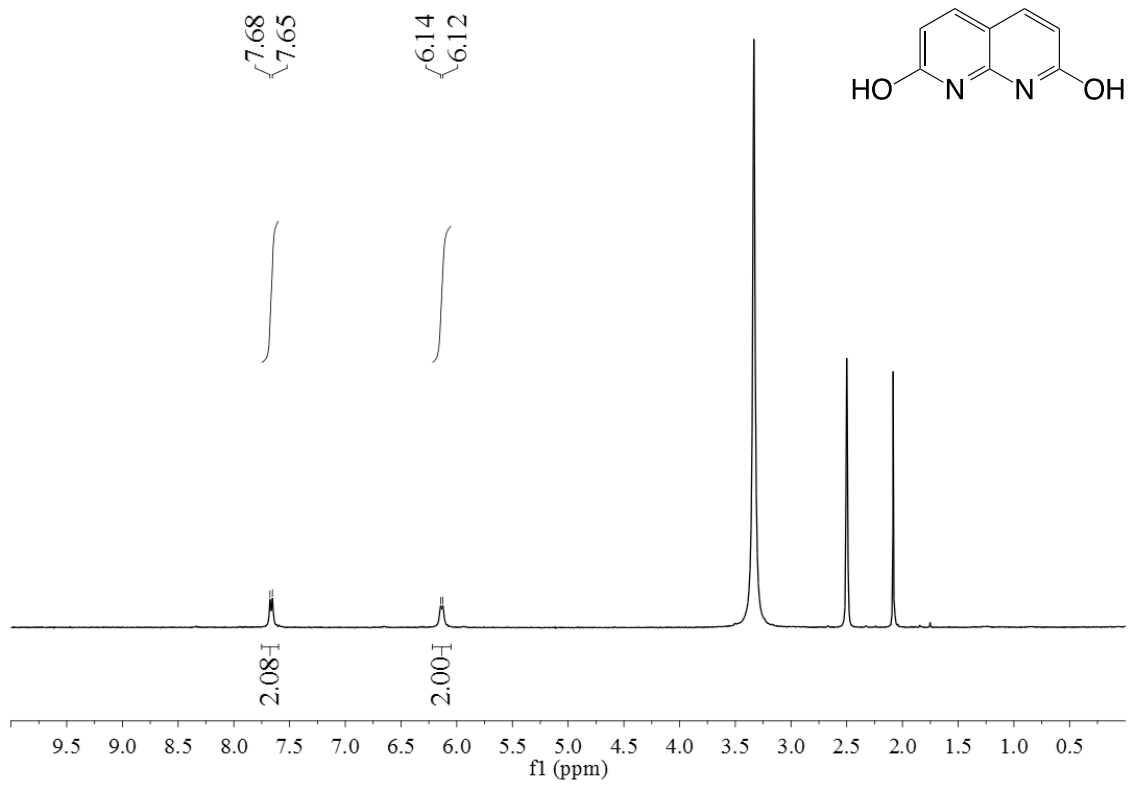


^{1}H NMR spectrum of compound **1** (400 MHz, DMSO-d_6)



^{1}H NMR spectrum of compound **2** (400 MHz, DMSO-d_6)

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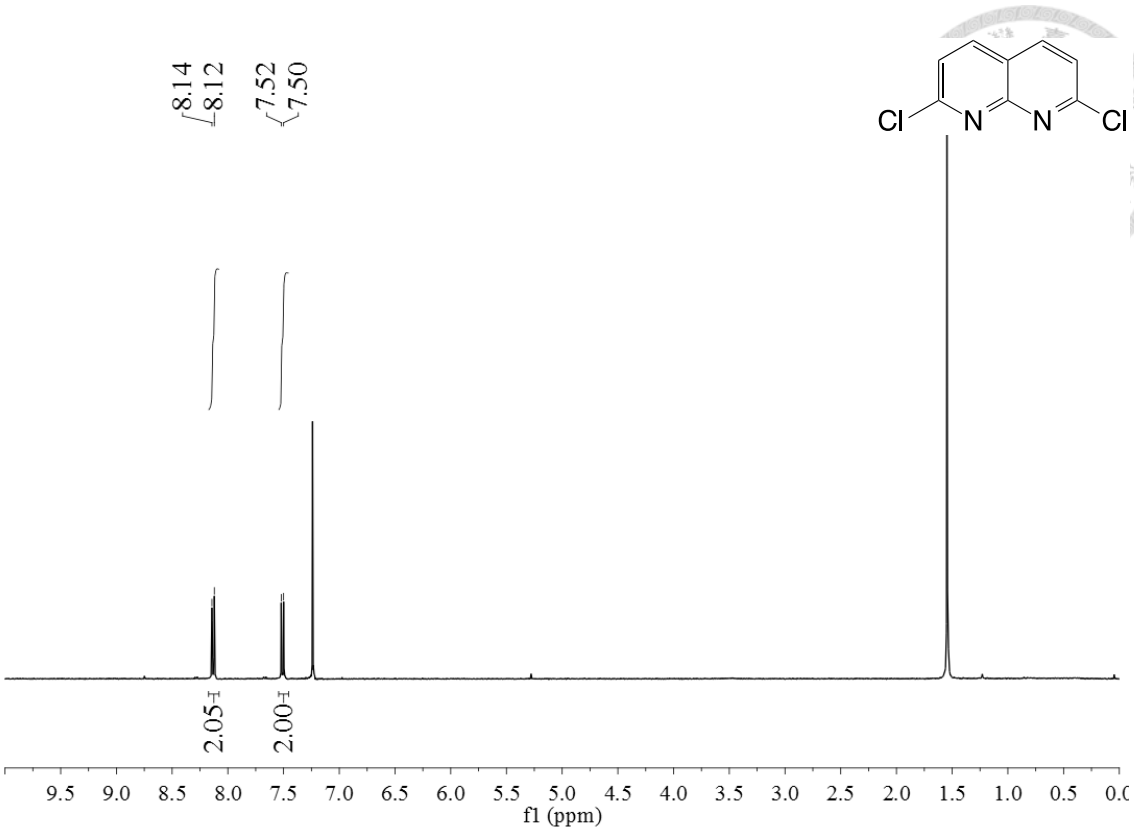
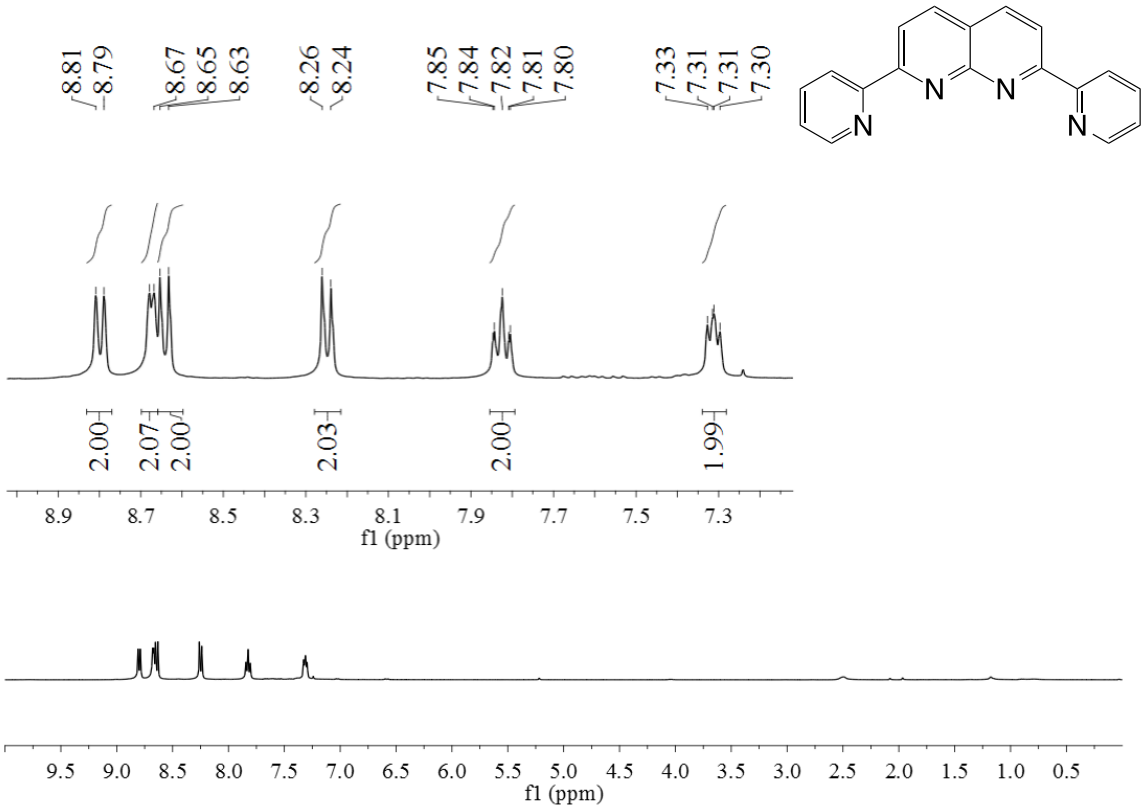
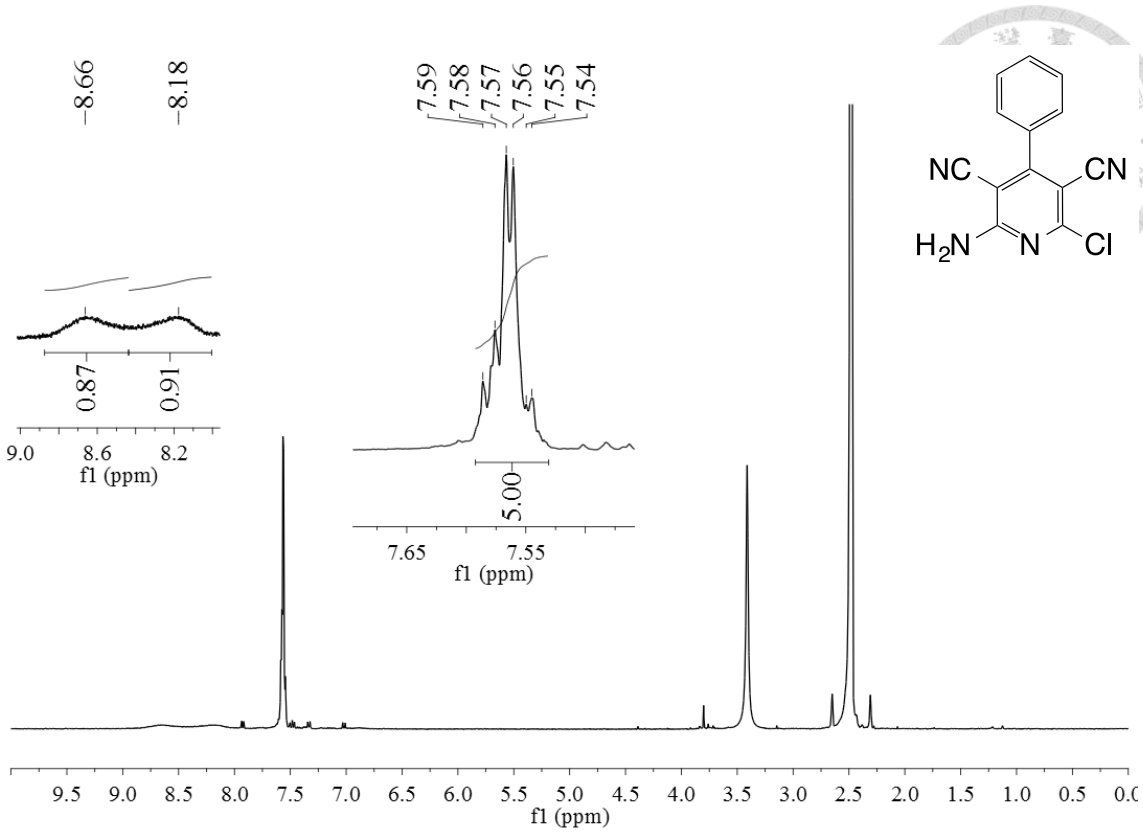


^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$)

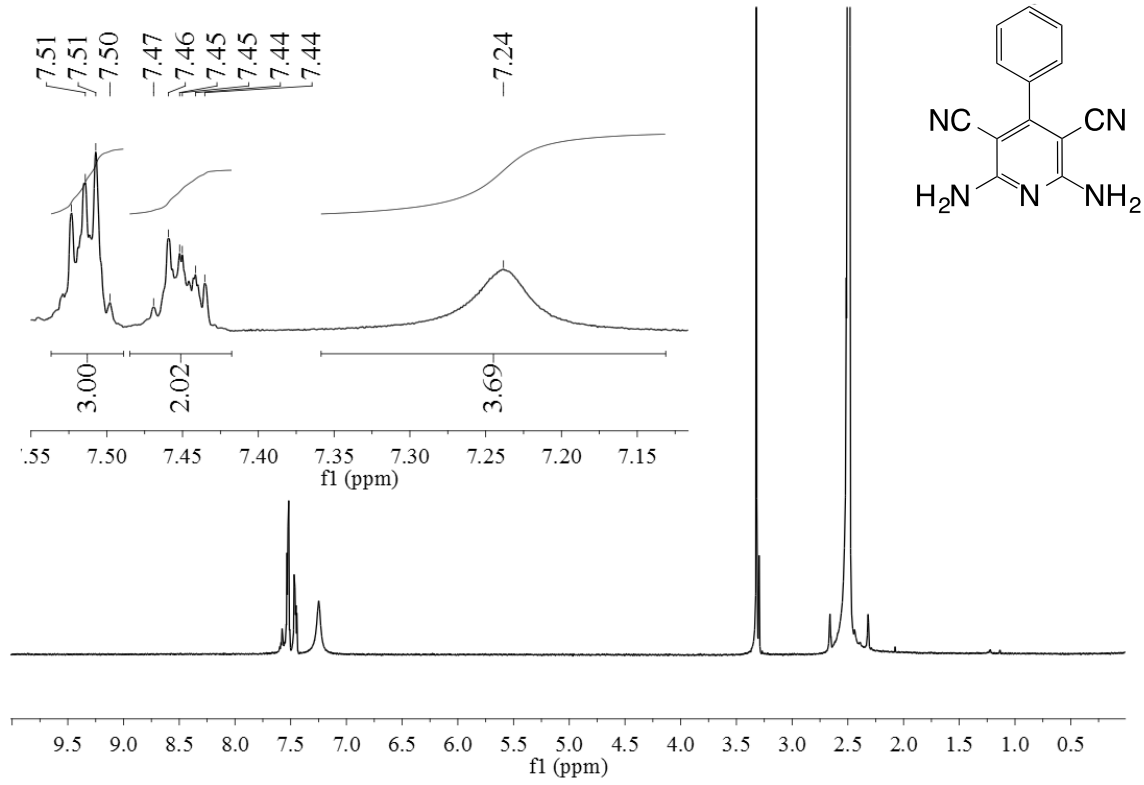


^{1}H NMR spectrum of **bpnp** (400 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

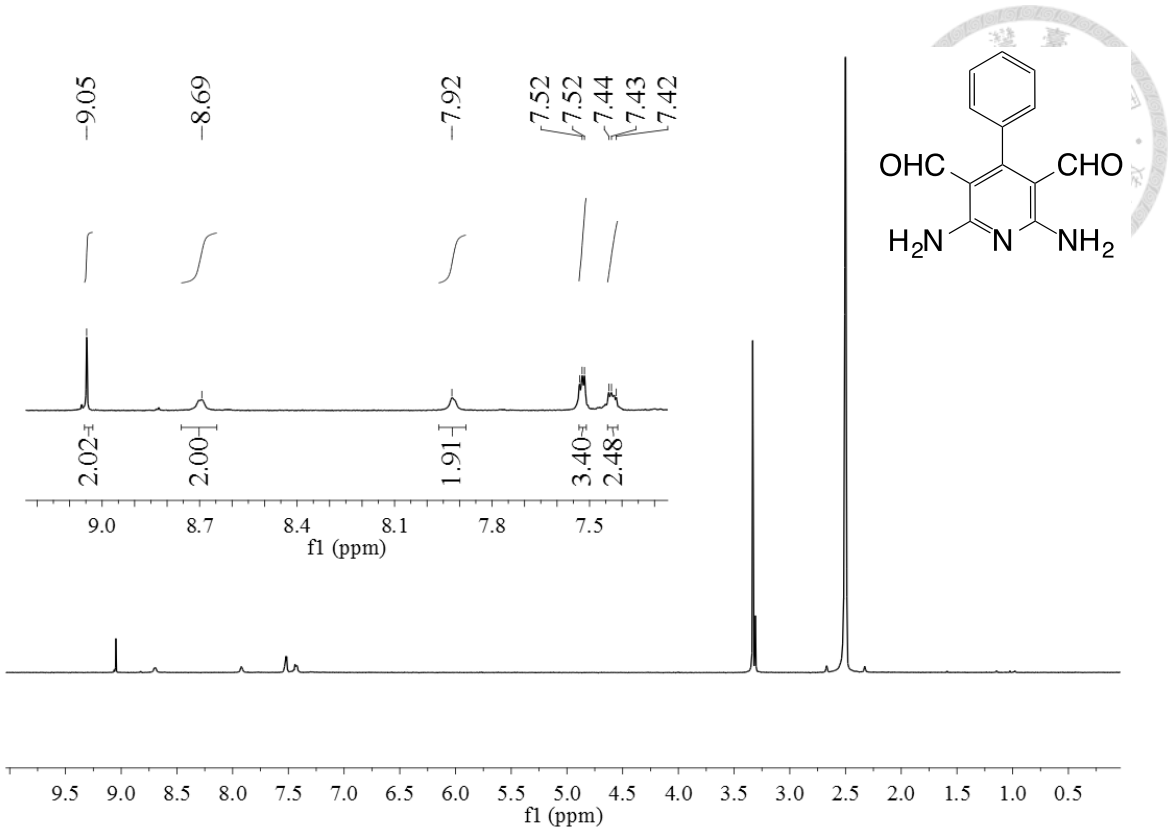


^{1}H NMR spectrum of compound **4** (400 MHz, DMSO-d_6)

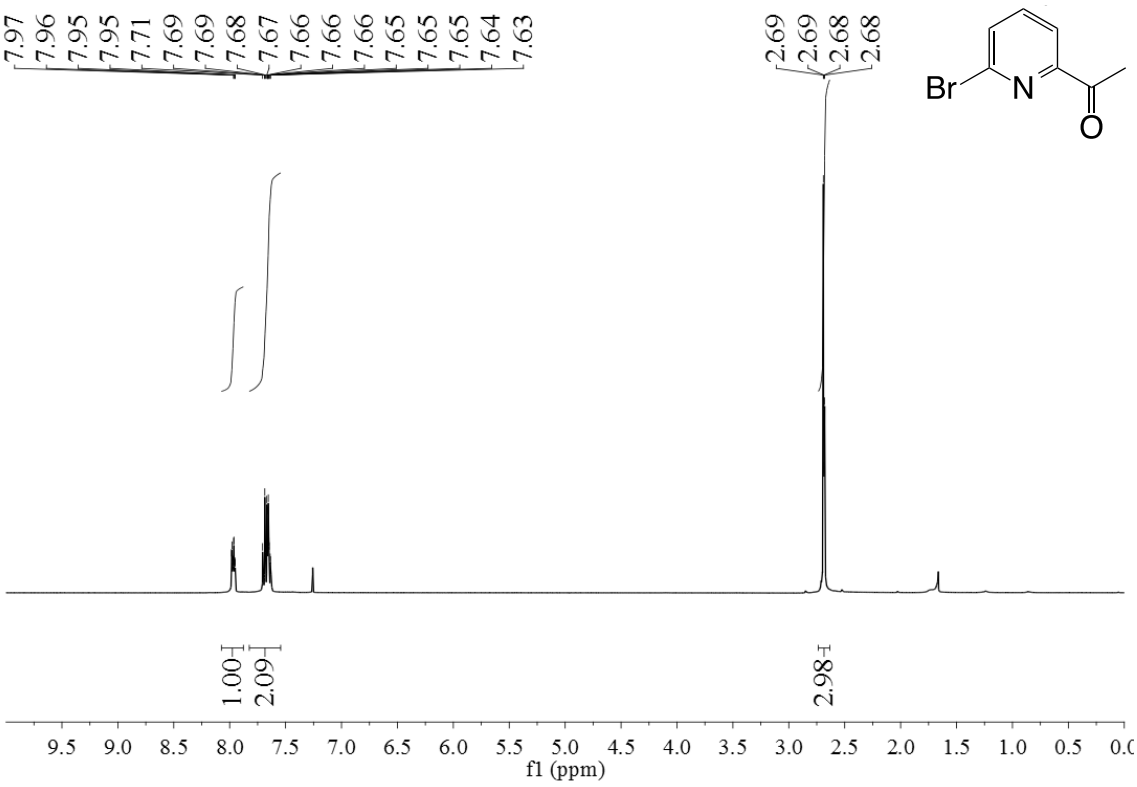


^{1}H NMR spectrum of compound **5** (400 MHz, DMSO-d_6)

doi:10.6342/NTU201700680

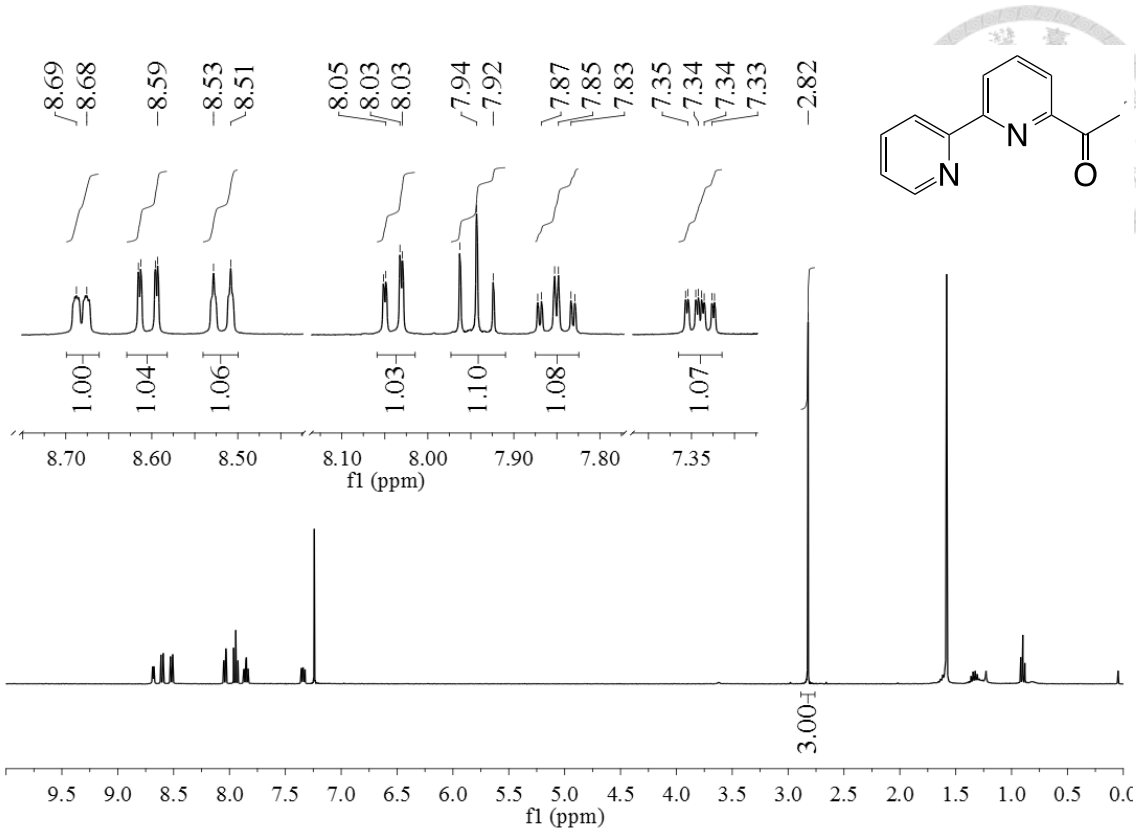


^{1}H NMR spectrum of compound **6** (400 MHz, DMSO-d_6)

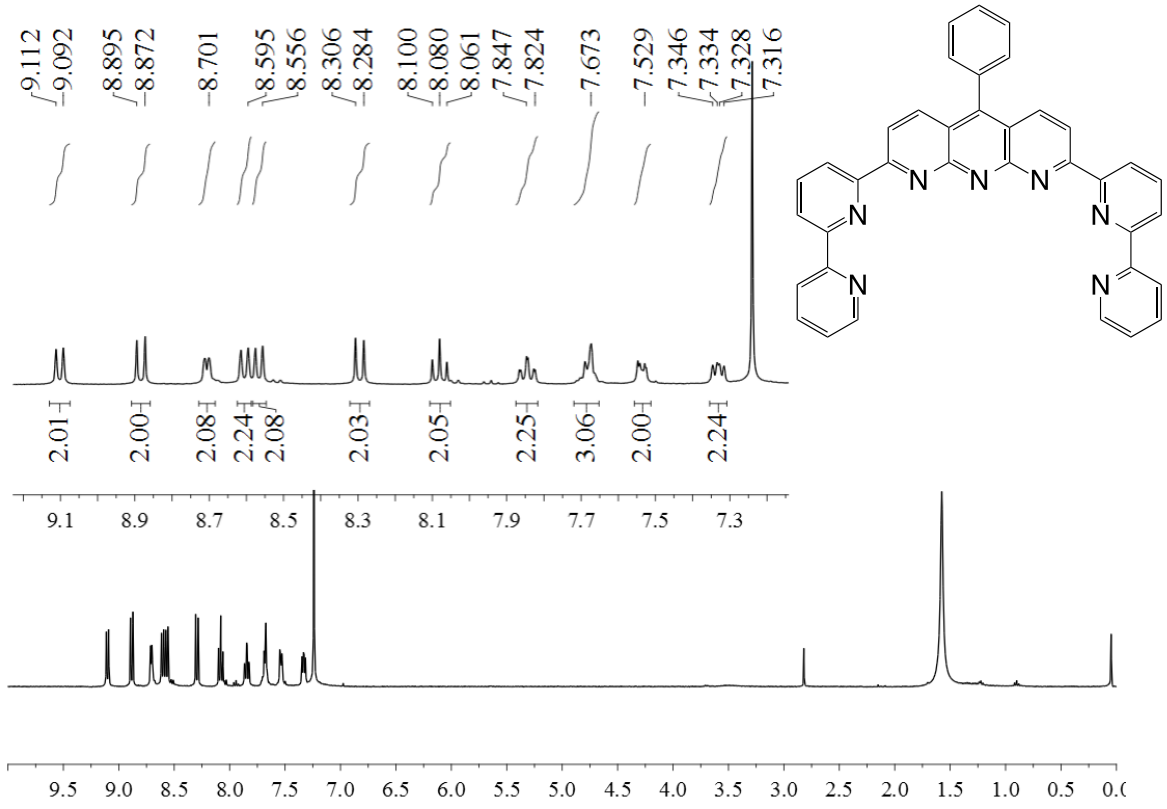


^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

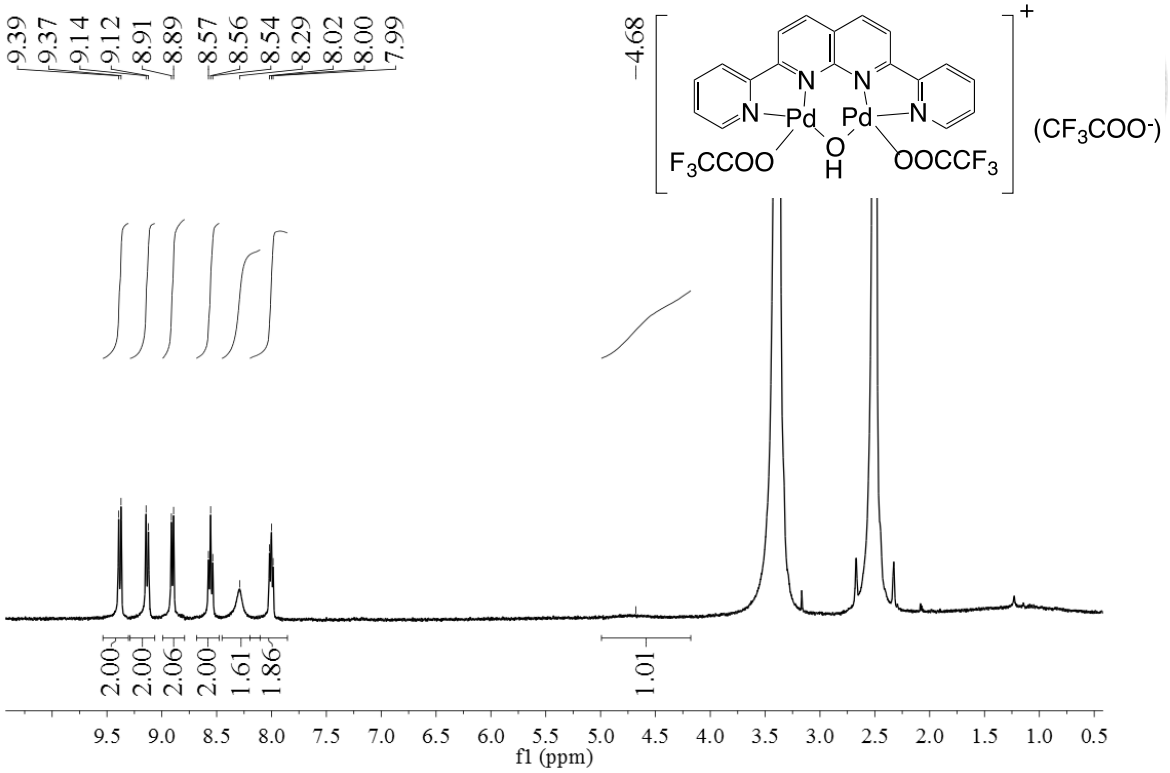


^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$)

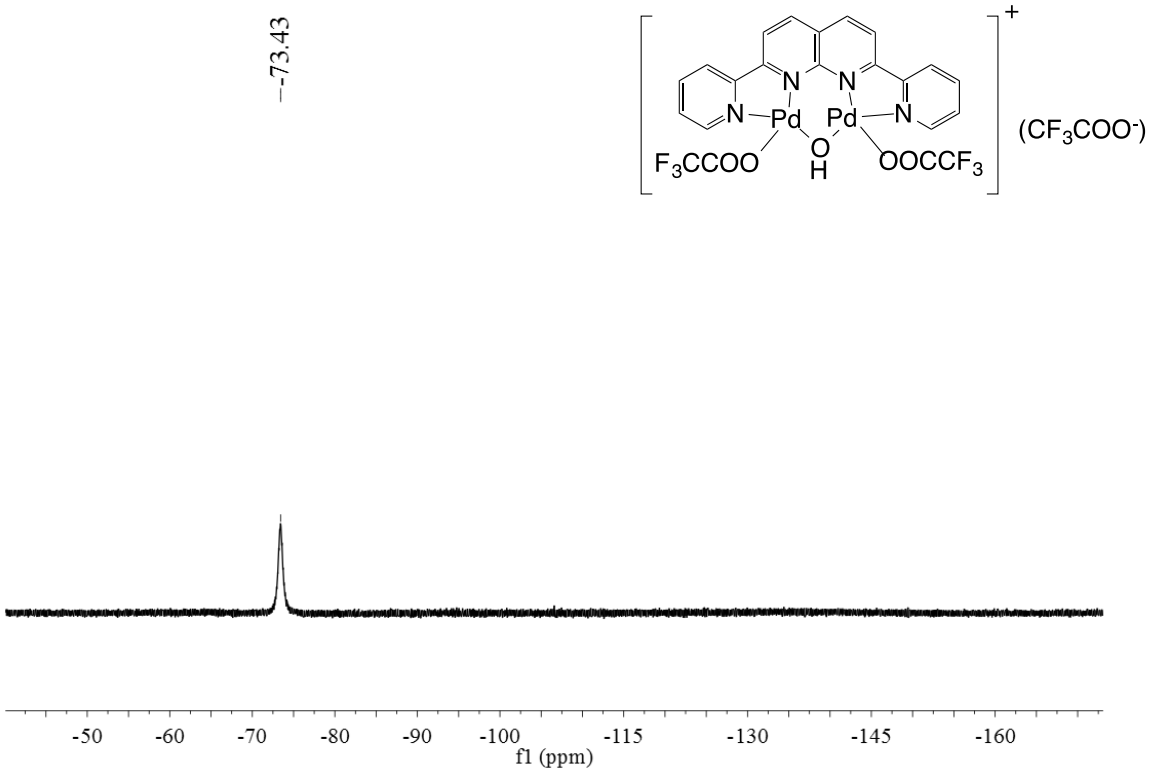


^{1}H NMR spectrum of compound **pbbpa** (400 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

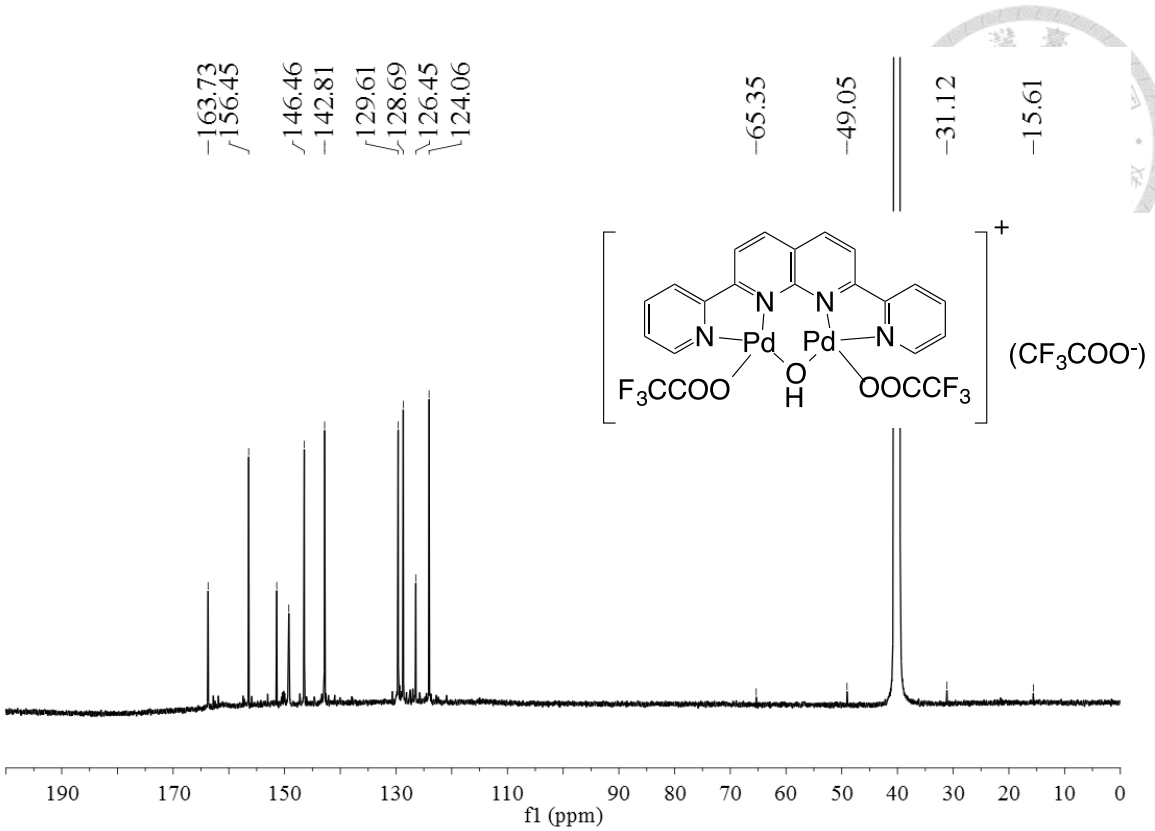


^{1}H NMR spectrum of compound Pd_2(**bpnp**)$(TFA)_3$(OH) (**9**) (400 MHz, DMSO-d_6)



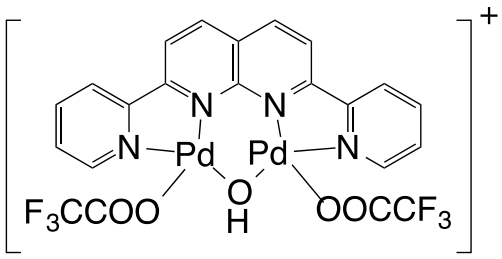
^{19}F NMR spectrum of compound Pd_2(**bpnp**)$(TFA)_3$(OH) (**9**) (375 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



^{13}C NMR spectrum of compound Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**) (125 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

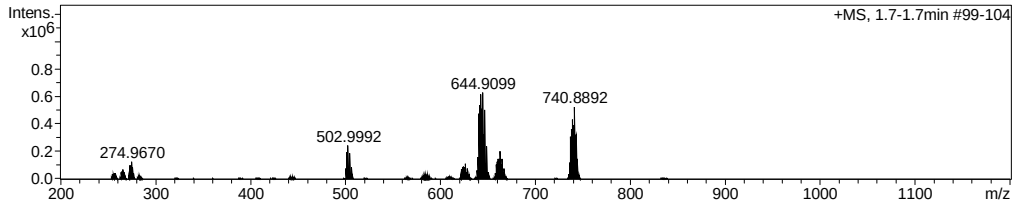
Analysis Info

Analysis Name	D:\Data\Fish\Data\170106\MS170106_Pd2_pw.d	Acquisition Date	1/6/2017 4:12:55 PM
Method	1501110_70acn_pw_3min_direction injection.m	Operator	Bruker microTOF-Q II
Sample Name	MS170106_acn_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

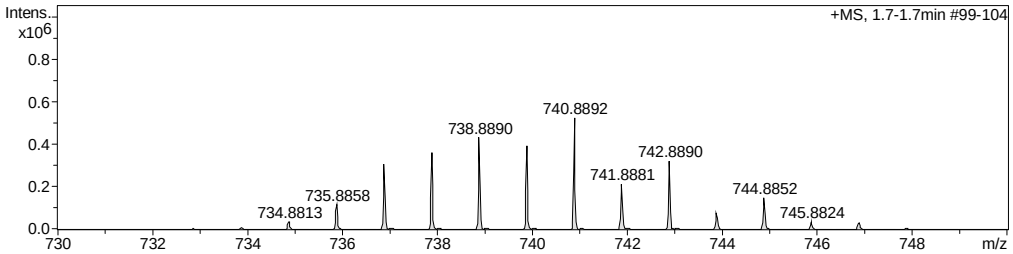
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

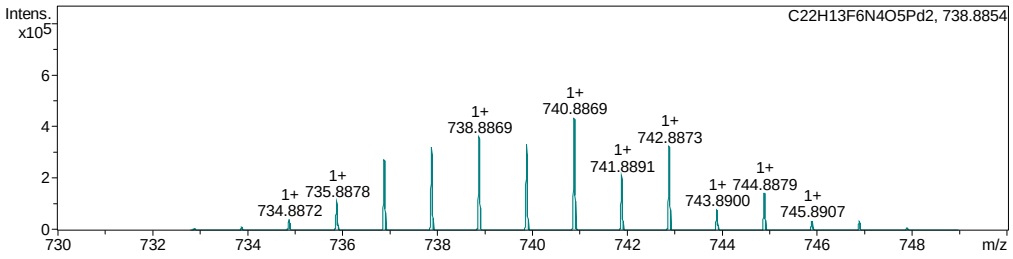
+MS, 1.7-1.7min #99-104



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
738.8890	1	100.00	C22H13F6N4O5Pd2	738.8869	-3.6	-4.9	46.9	15.5	even	ok

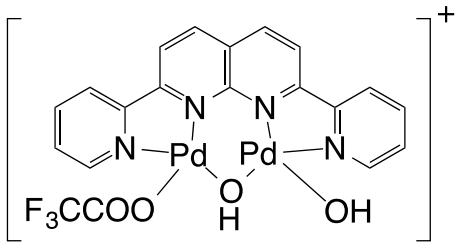
+MS, 1.7-1.7min #99-104





ESI-HRMS of $[Pd_2(\mathbf{bpnp})(TFA)_2(OH)]^+$ and isotope simulation

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

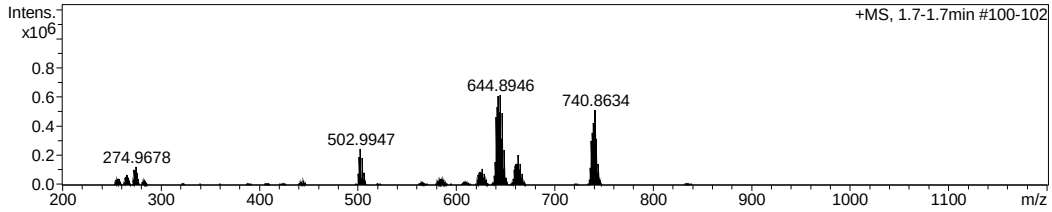
Analysis Info

Analysis Name	D:\Data\Fish\Data\170106\MS170106_Pd2_pw.d	Acquisition Date	1/6/2017 4:12:55 PM
Method	1501110_70acn_pw_3min_direction injection.m	Operator	Bruker microTOF-Q II
Sample Name	MS170106_acn_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

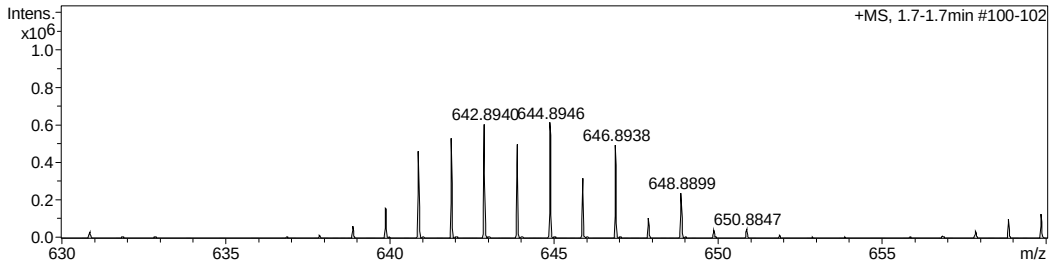
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

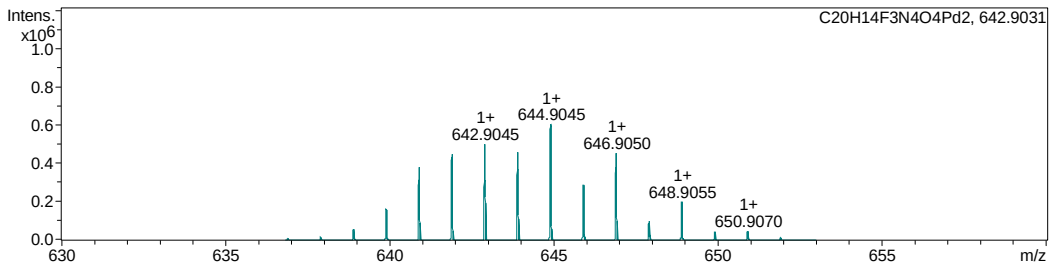
+MS, 1.7-1.7min #100-102



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
642.8940	1	100.00	C20H14F3N4O4Pd2	642.9045	9.1	14.2	64.5	14.5	even	ok

+MS, 1.7-1.7min #100-102





ESI-HRMS of $[Pd_2(\mathbf{bpnp})(TFA)(OH)_2]^+$ and isotope simulation

doi:10.6342/NTU201700680

國立台灣大學理學院貴重儀器使用中心 元素分析儀報告書

Precision Instrumentation Center--Elemental Analysis Report
College of Science, National Taiwan University

說明： **1.**本文件為學檢測成果，不作認證、法律訴訟及商業廣告使用。
This result is for academic use only, not to be used for any judicial or commercial advertising purpose.

2. Instrument： 德國 **elementar Vario EL cube** 型 **(for NCSH, German)**

Accuracy: ±0.1%
Precision: ±0.2%

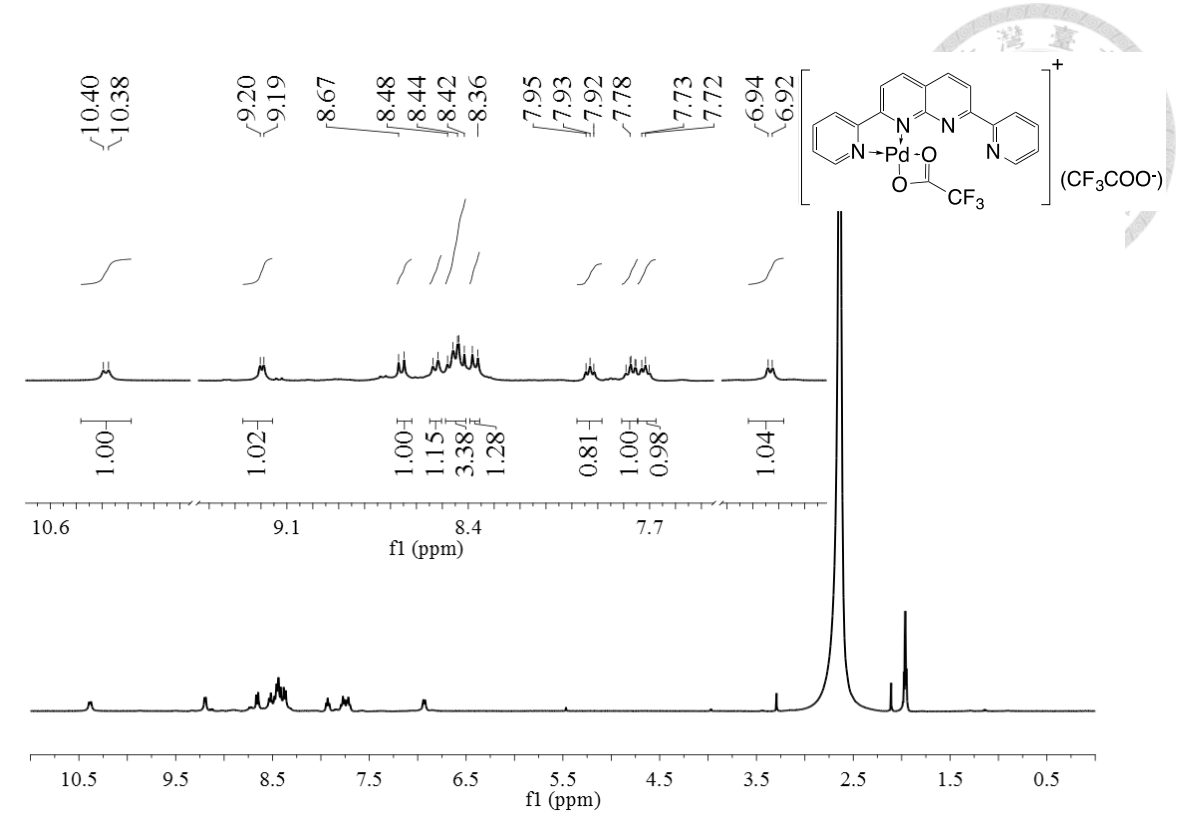
3.儀器負責人：汪根欉教授 技術員：陸靖蔚
Instrument Director: Prof. Wong, Ken-Tsung Operator: Ching-Wei Lu

Web. NO. 52017020148
User name 楊舒庭
Supervisor 劉緒宗
Department 台大 化學系
Acceptance date 2017/2/22
Analysis date 2017/2/23

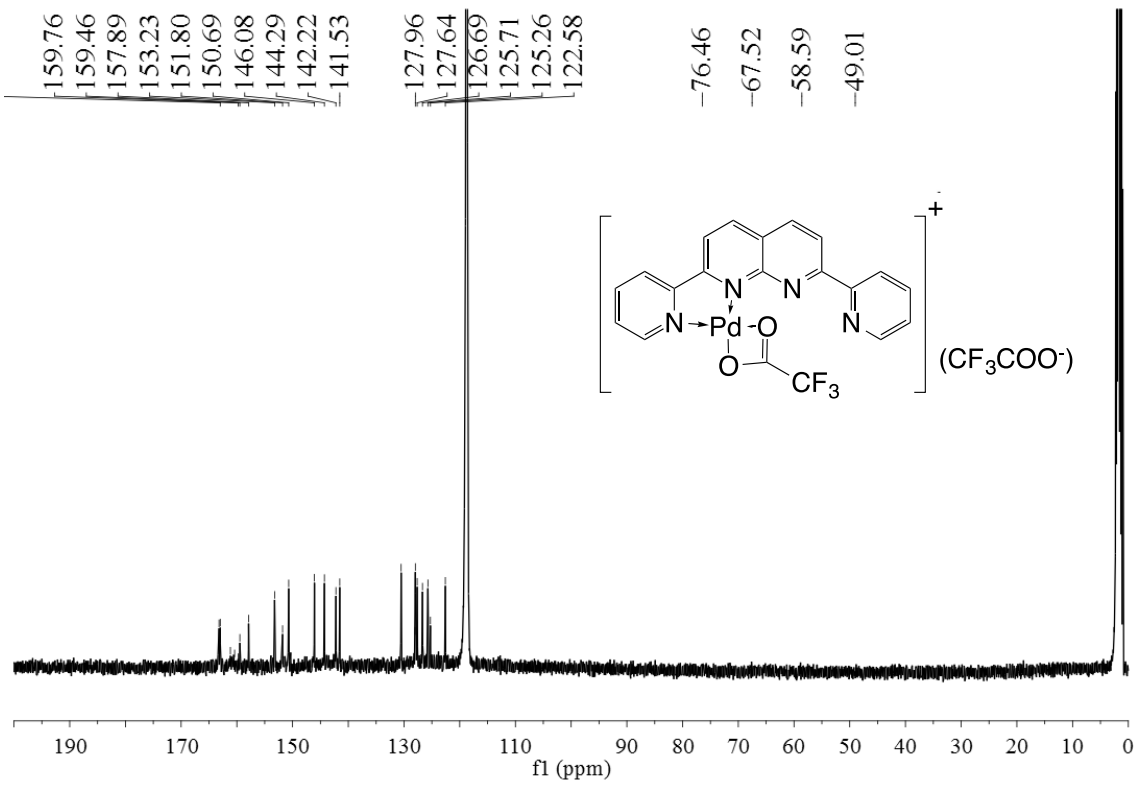
Sample code	Date Time	Weight(mg)	Grp	N%	C%	S%	H%	Repeat	Charge
acetanilide	23.02.2017	3.325	Standard	10.360	71.090	0.000	6.710		
standard 測出值	23.02.2017	2.876		10.354	71.205	0.000	6.697		
11	23.02.2017	4.750		2.733	11.806		1.008	1	
11	23.02.2017	4.427		2.757	11.836		0.999	1	$ 1,500
9	23.02.2017	3.040		6.006	32.324		1.595	1	
9	23.02.2017	3.028		6.018	32.267		1.546	1	$ 1,500
								4	$ 3,000

Elemental analysis report of compound Pd_2(**bpnp**)$(TFA)_3(OH)$ (**9**)

doi:10.6342/NTU201700680

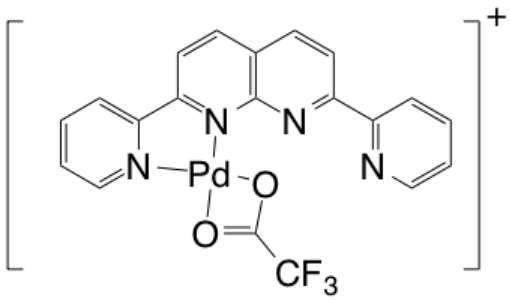


^{1}H NMR spectrum of complex [Pd(**bpnp**)TFA$_2$] (**10**) (400 MHz, CD_3CN)



^{13}C NMR spectrum of compound [Pd(**bpnp**)TFA$_2$] (**10**) (400 MHz, CD_3CN)

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

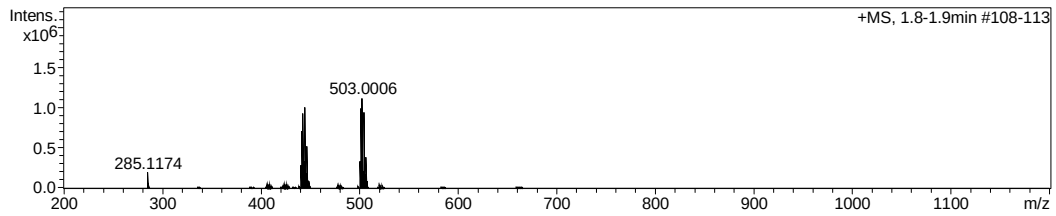
Analysis Info

Analysis Name	D:\Data\Fish\Data\170109\MS170109_Pd 1_pw.d	Acquisition Date	1/9/2017 3:18:12 PM
Method	170109_100acn_pw_3min_direction injection.m	Operator	Bruker microTOF-Q II
Sample Name	MS170109_acn_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

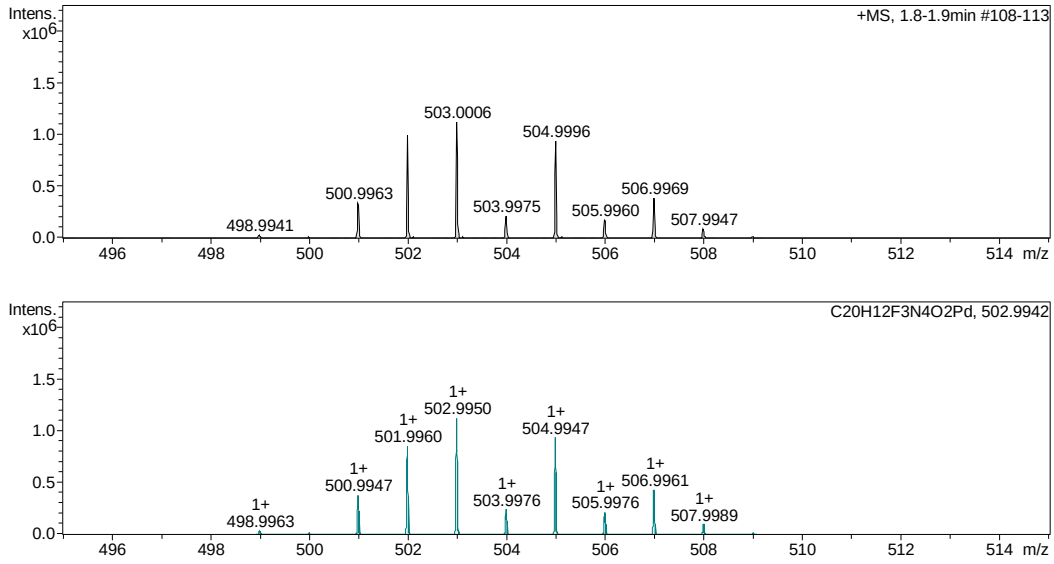
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

+MS, 1.8-1.9min #108-113



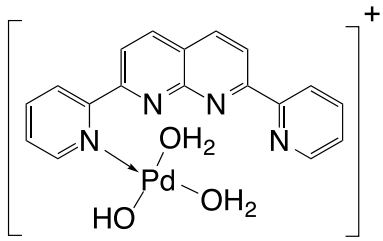
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
503.0006	1	C20H12F3N4O2Pd	502.9950	-11.1	43.6	1	100.00	15.5	even	ok

+MS, 1.8-1.9min #108-113



ESI-HRMS of [Pd(**bpnp**)(TFA)]$^+$ and isotope simulation

doi:10.6342/NTU201700680



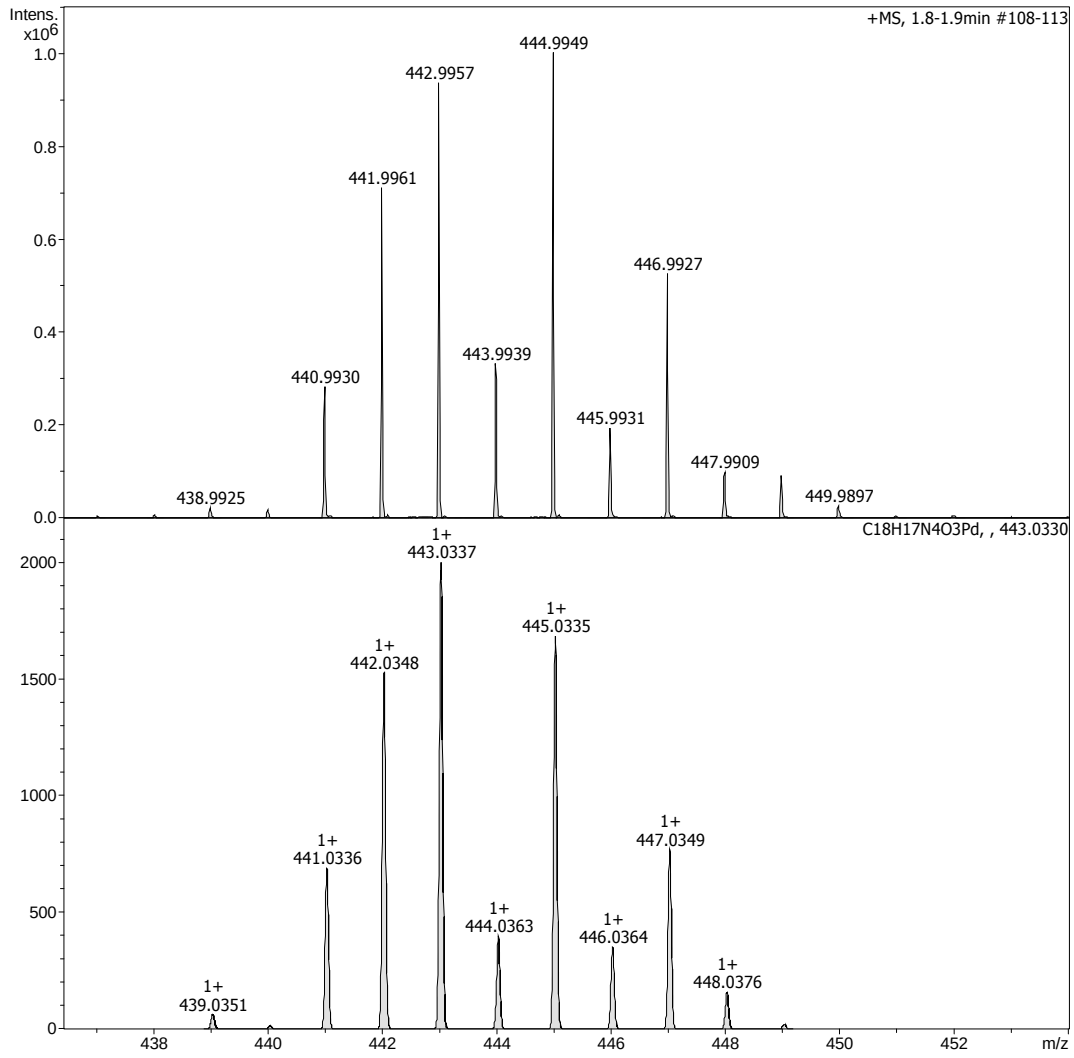
Display Report

Analysis Info

Analysis Name	D:\Data\Fish\Data\170109\MS170109_Pd 1_pw.d	Acquisition Date	1/9/2017 3:18:12 PM
Method	170109_100acn_pw_3min_direction injection.m	Operator	Bruker microTOF-Q II
Sample Name	MS170109_acn_pw	Instrument	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

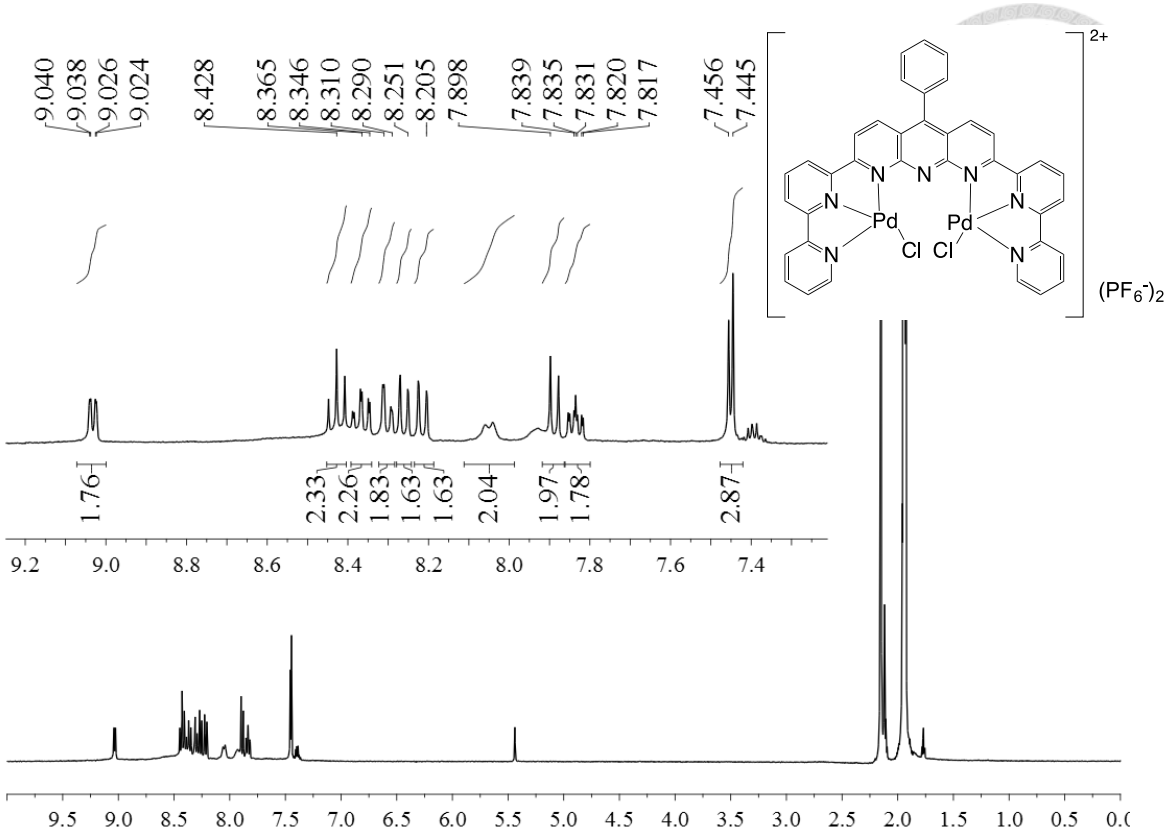
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source



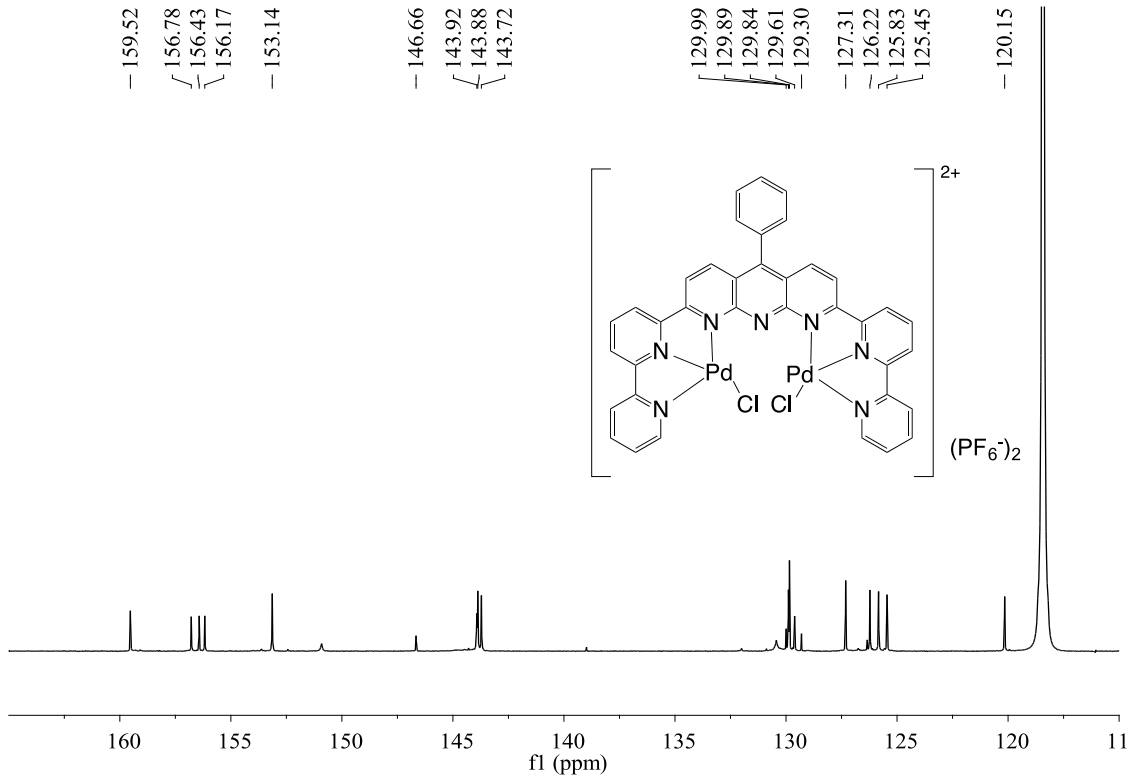
Bruker Compass DataAnalysis 4.1 printed: 2/7/2017 3:51:08 PM Page 1 of 1

ESI-HRMS of $[Pd(\mathbf{bpnp})(H_2O)_2(OH)]^+$ and isotope simulation

doi:10.6342/NTU201700680

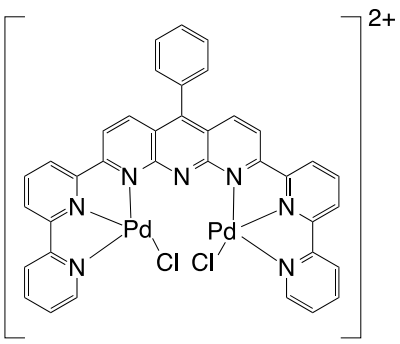


^{1}H NMR spectrum of compound $[Pd_2(\mathbf{pbbpa})Cl_2][PF_6]_2$ (**11**) (400 MHz, CD_3CN)



^{13}C NMR spectrum of compound $[Pd_2(\mathbf{pbbpa})Cl_2][PF_6]_2$ (**11**) (125 MHz, CD_3CN)

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

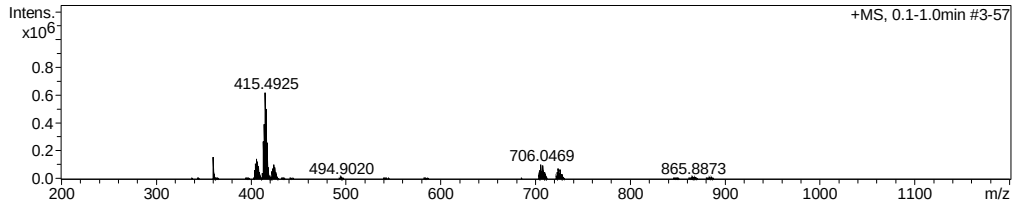
Analysis Info

Analysis Name	D:\Data\Fish\Data\170110\MS170110_Cl2_pw.d	Acquisition Date	1/10/2017 2:04:48 PM
Method	170109_100acn_pw_3min_direction injection.m	Operator	Bruker microTOF-Q II
Sample Name	MS170110_1014.27_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

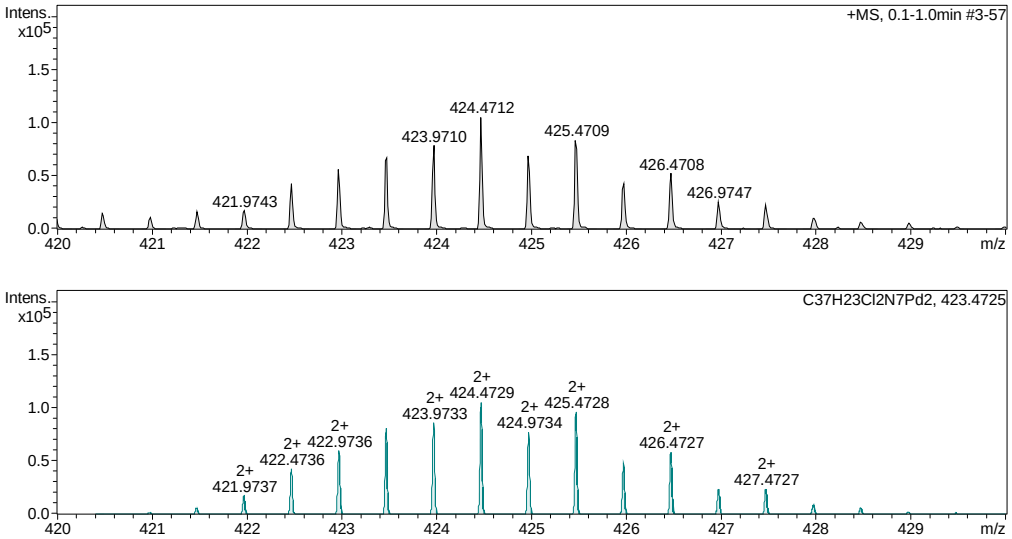
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

+MS, 0.1-1.0min #3-57



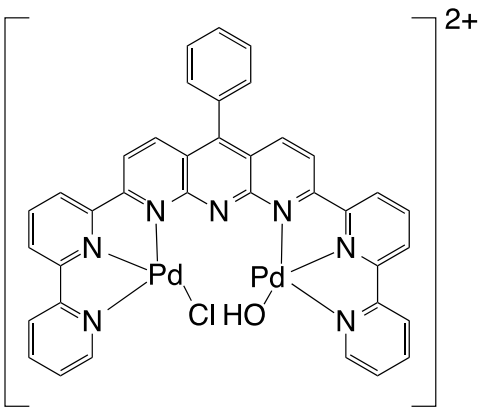
Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
423.4711	1	100.00	C37H23Cl2N7Pd2	423.4731	-2.0	-4.7	67.3	29.0	even	ok

+MS, 0.1-1.0min #3-57



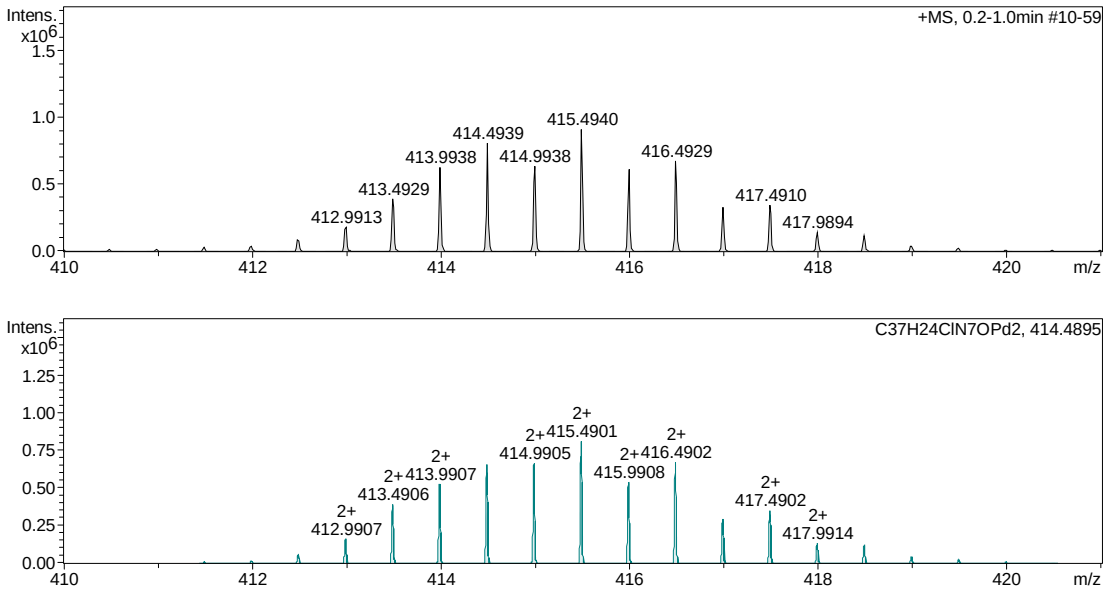
ESI-HRMS of $[Pd_2(\mathbf{pbbpa})Cl_2]^{2+}$ and isotope simulation

doi:10.6342/NTU201700680



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
414.4939	1	100.00	C37H24ClN7OPd2	414.4902	3.7	8.9	46.5	29.0	even	ok

+MS, 0.2-1.0min #10-59



ESI-HRMS of $[Pd_2(\mathbf{pbbpa})Cl(OH)]^{2+}$ and isotope simulation

doi:10.6342/NTU201700680

國立台灣大學理學院貴重儀器使用中心 元素分析儀報告書

Precision Instrumentation Center--Elemental Analysis Report
College of Science, National Taiwan University

說明： **1.**本文件為學檢測成果，不作認證、法律訴訟及商業廣告使用。
This result is for academic use only, not to be used for any judicial or commercial advertising purpose.

2. Instrument： 德國 **elementar Vario EL cube** 型 **(for NCSH, German)**

Accuracy: ± 0.1%
Precision: ± 0.2%

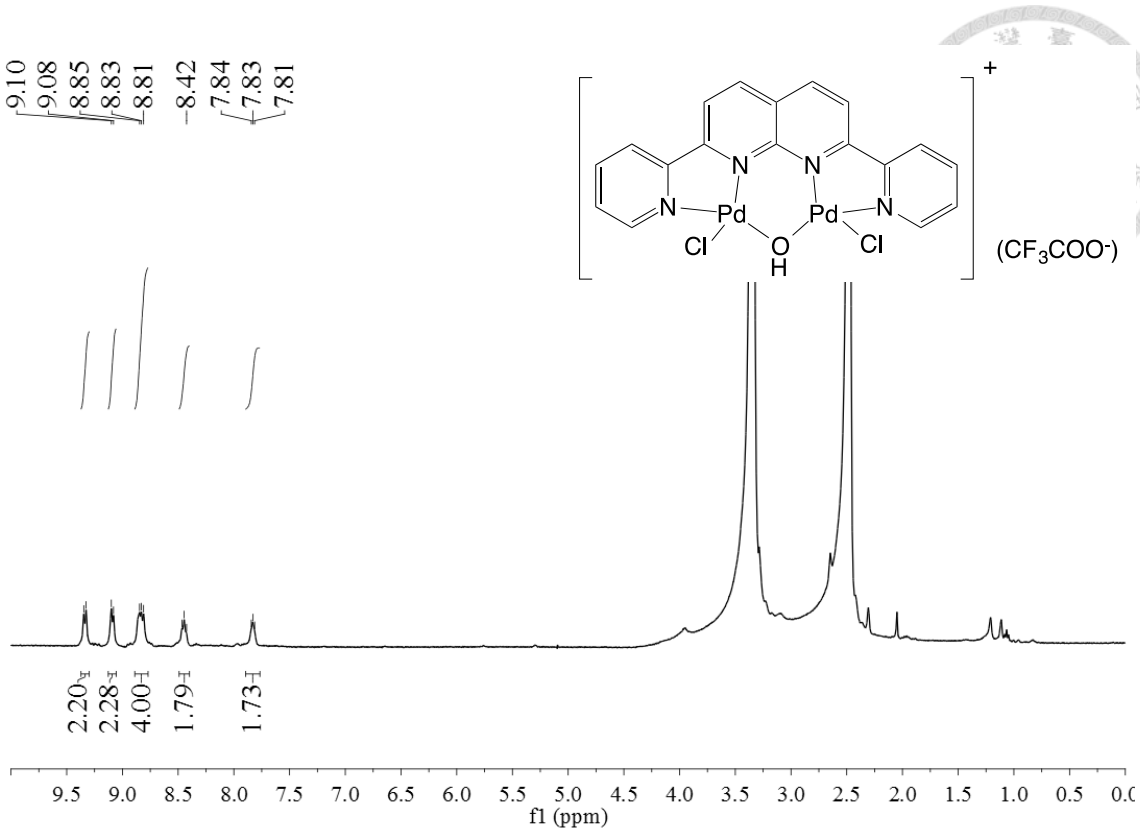
3.儀器負責人：汪根欉教授 技術員：陸靖蔚
Instrument Director: Prof. Wong, Ken-Tsung **Operator: Ching-Wei Lu**

Web. NO.	52017030108
User name	楊舒庭
Supervisor	劉緒宗
Department	台大 化學系
Acceptance date	2017/3/3
Analysis date	2017/3/6

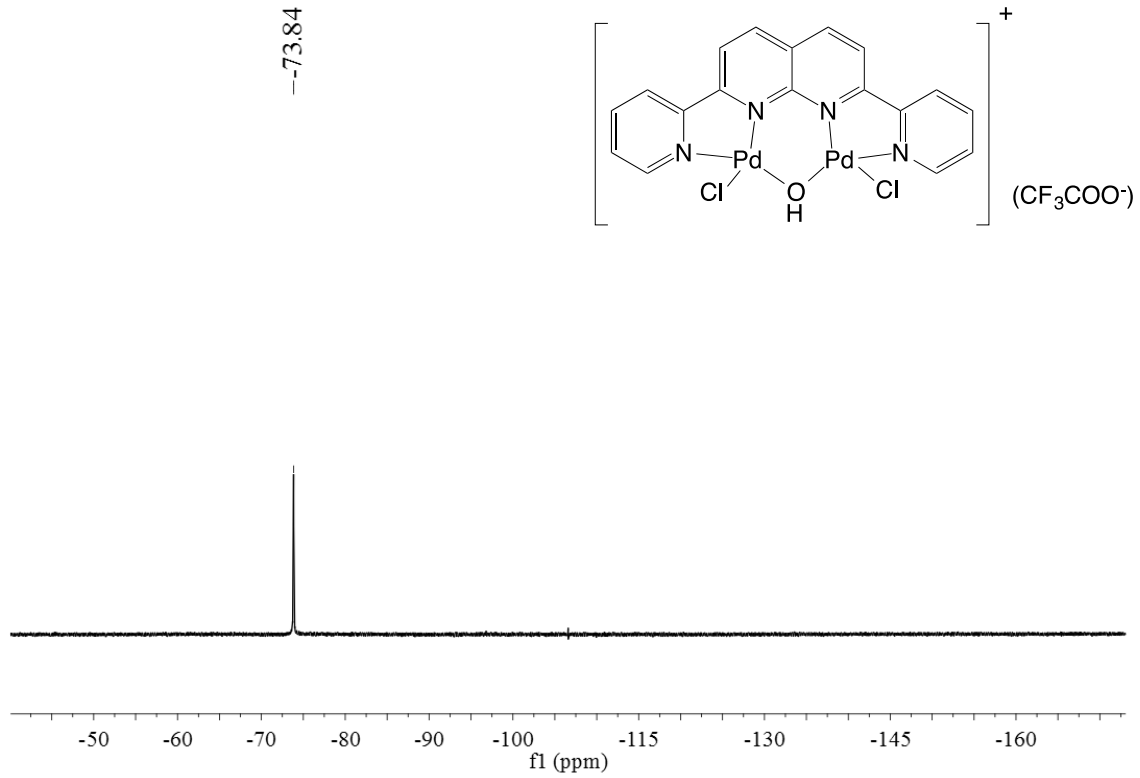
Sample code	Date Time	Weight(mg)	Grp	N%	C%	S%	H%	Repeat	Charge
sulfanilic acid	06.03.2017	3.003	Standard	8.090	41.610	18.500	4.070		
standard 測出值	06.03.2017	3.037		8.078	41.698	18.485	4.092		
11	06.03.2017	3.393		7.408	35.502		2.710	1	
11	06.03.2017	3.029		7.334	35.339		2.845	1	$ 1,500
								2	$ 1,500

Elemental analysis report of compound $[Pd_2(\mathbf{pbbpa})Cl_2][PF_6]_2$ (**11**)

doi:10.6342/NTU201700680

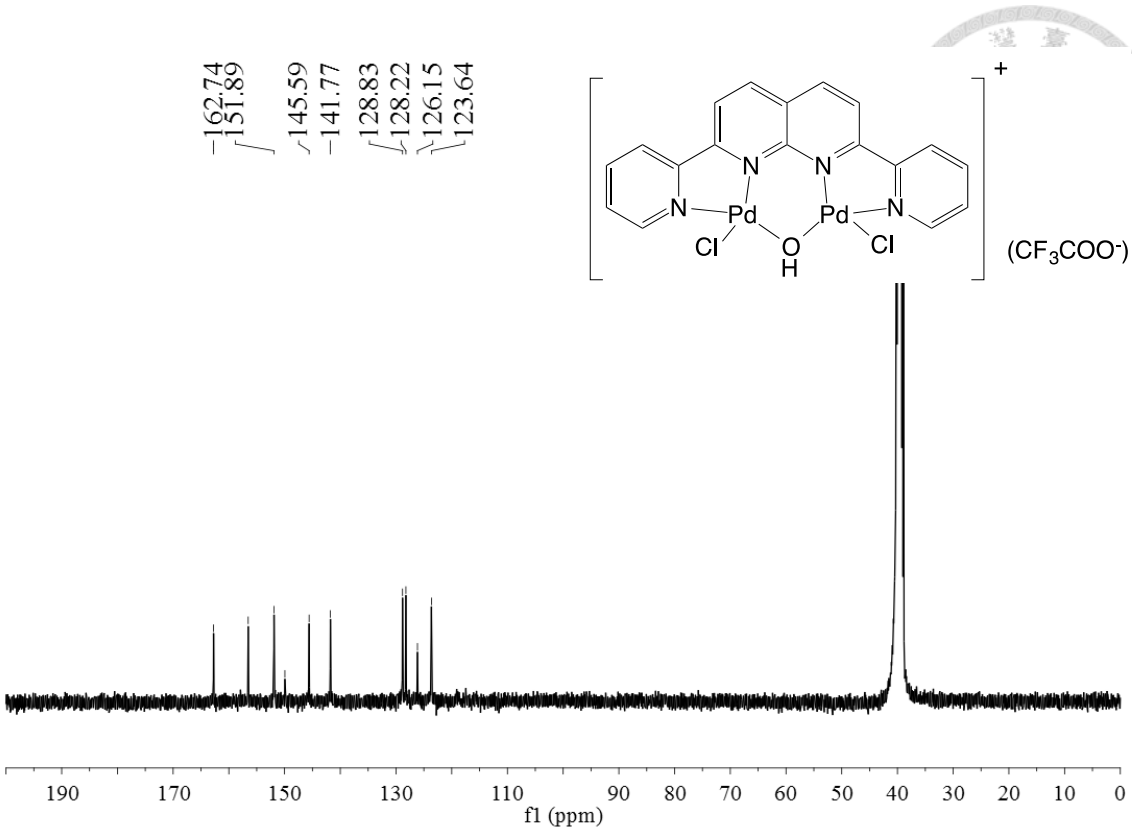


^{1}H NMR spectrum of compound **[**Pd_2(**bpnp**)Cl_2(OH)](TFA) (**12**) (400 MHz, DMSO-d_6)



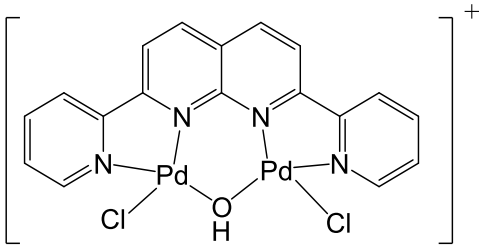
^{19}F NMR spectrum of compound **12** (375 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



^{13}C NMR spectrum of compound **12** (100 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

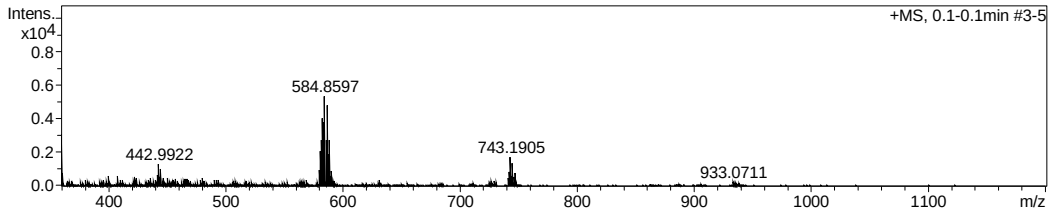
Analysis Info

Analysis Name	D:\Data\Fish\Data\170208\MS170208_10+KCl_pw000001.d	Acquisition Date	2/8/2017 3:58:29 PM
Method	tune_wide_pos_direction injection_20160719.m	Operator	Bruker microTOF-Q II
Sample Name	MS170208_trp reaction	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

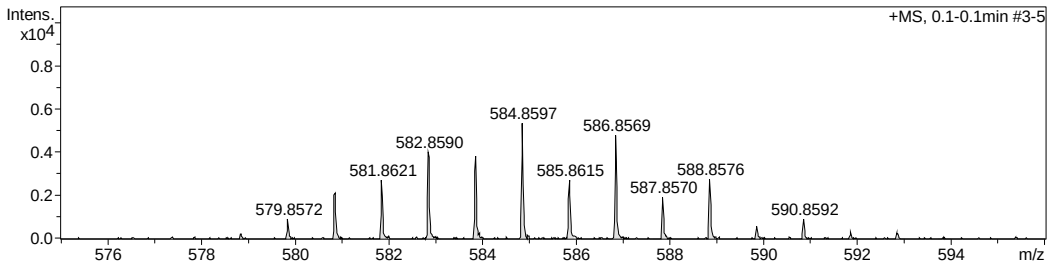
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

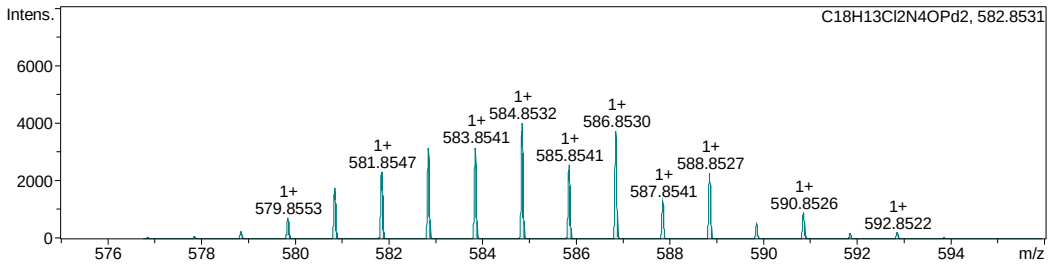
+MS, 0.1-0.1min #3-5



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
582.8590	1	100.00	C18H13Cl2N4OPd2	582.8536	5.5	9.4	44.5	13.5	even	ok

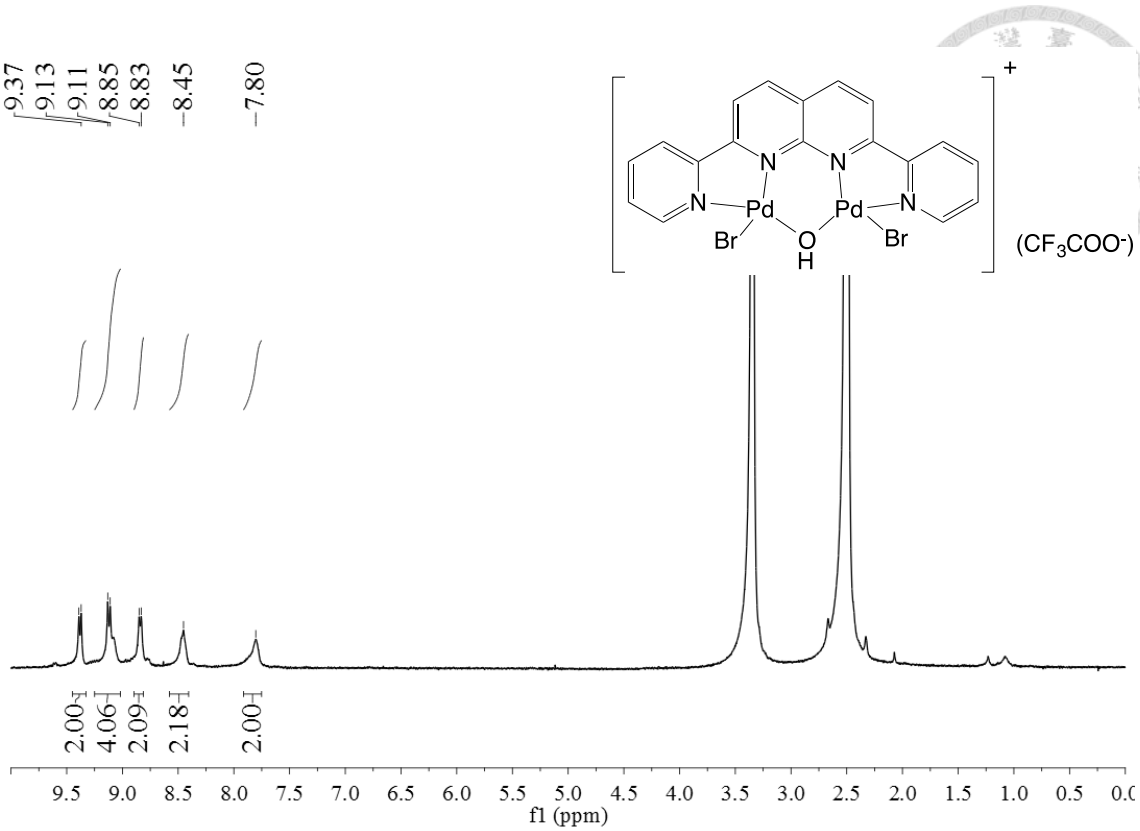
+MS, 0.1-0.1min #3-5



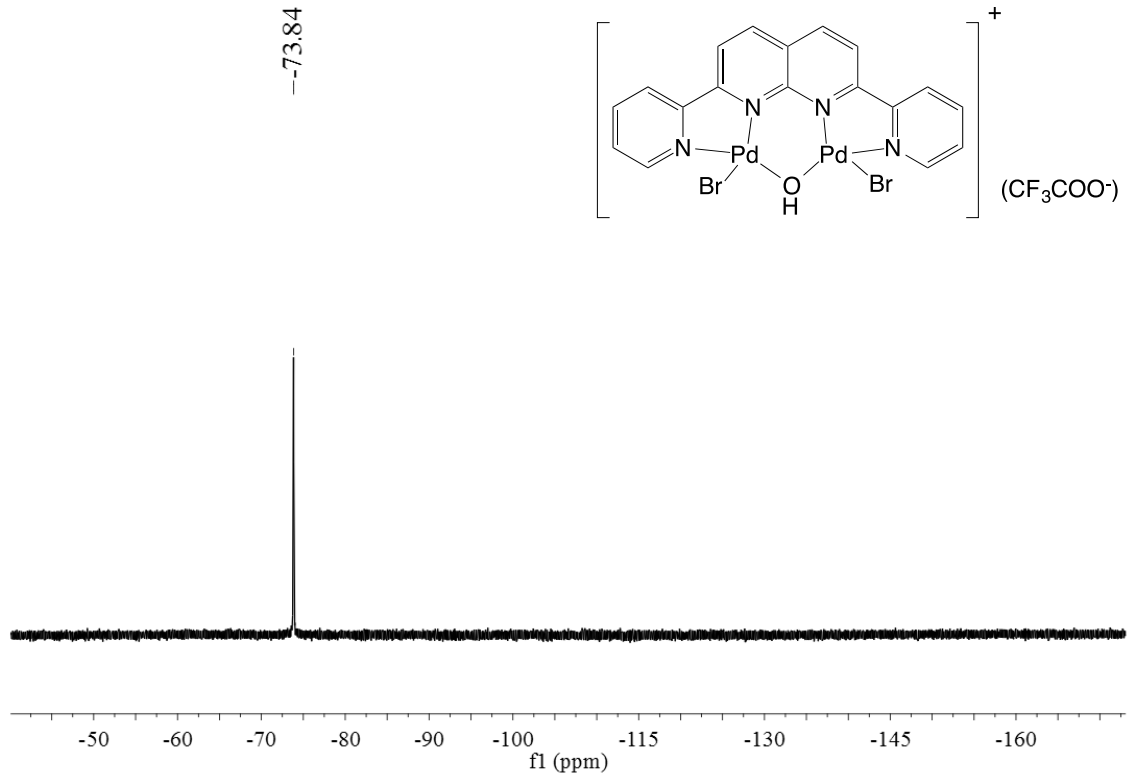


ESI-HRMS of **[**Pd_2(**bpnp**)Cl_2(OH)]$^+$ and isotope simulation

doi:10.6342/NTU201700680

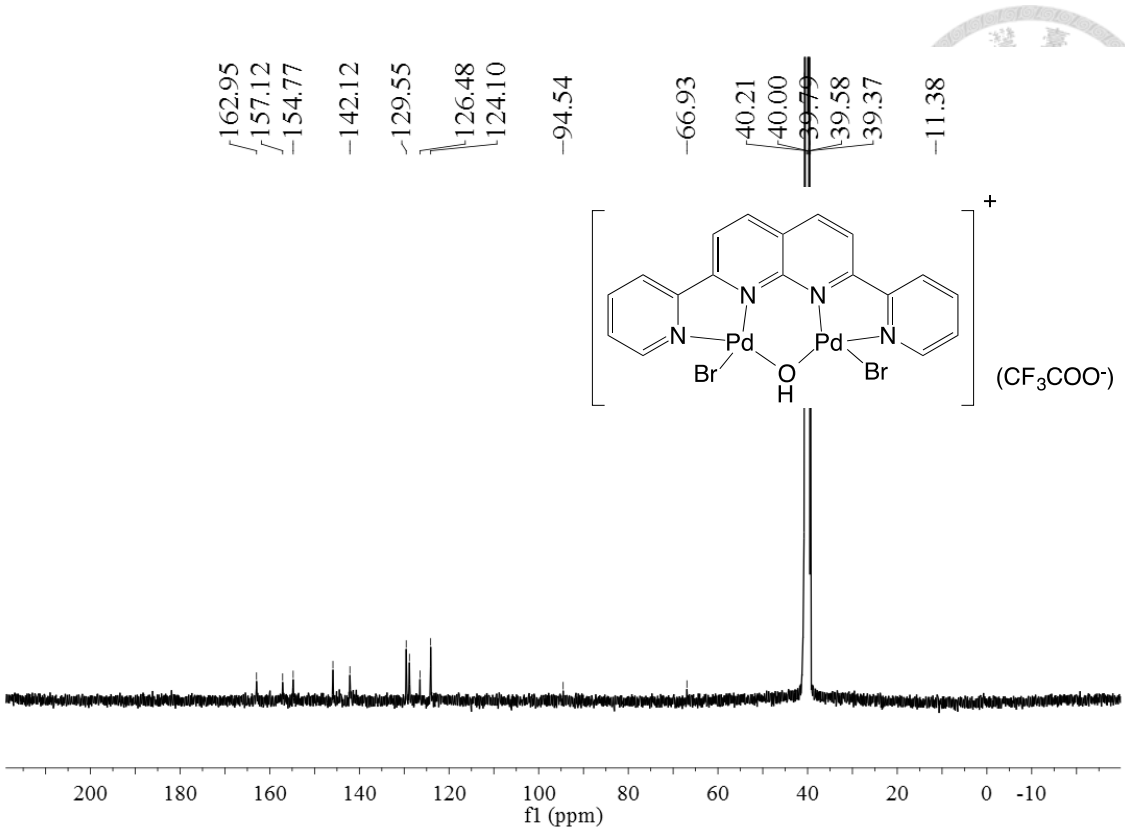


^{1}H NMR spectrum of compound **13** (400 MHz, DMSO-d_6)



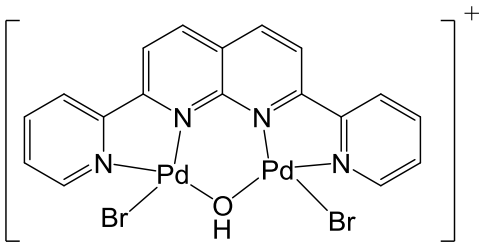
^{19}F NMR spectrum of compound **13** (375 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



^{13}C NMR spectrum of compound **13** (100 MHz, DMSO-d_6)

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

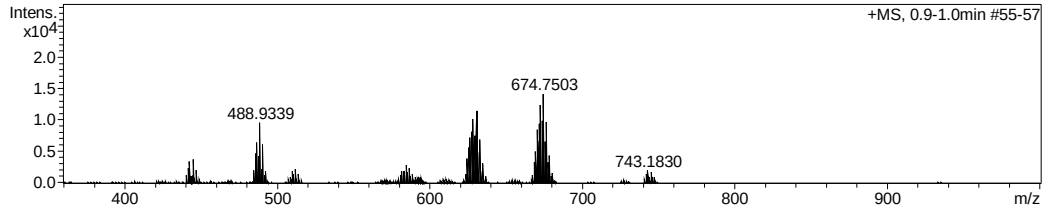
Analysis Info

Analysis Name	D:\Data\Fish\Data\170208\MS170208_10+KBr_pw000004.d	Acquisition Date	2/8/2017 4:46:18 PM
Method	tune_wide_pos_direction injection_20160719.m	Operator	Bruker microTOF-Q II
Sample Name	MS170208_trp reaction	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

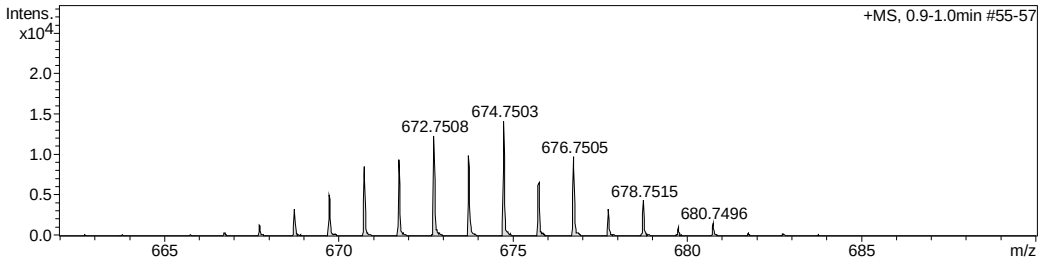
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

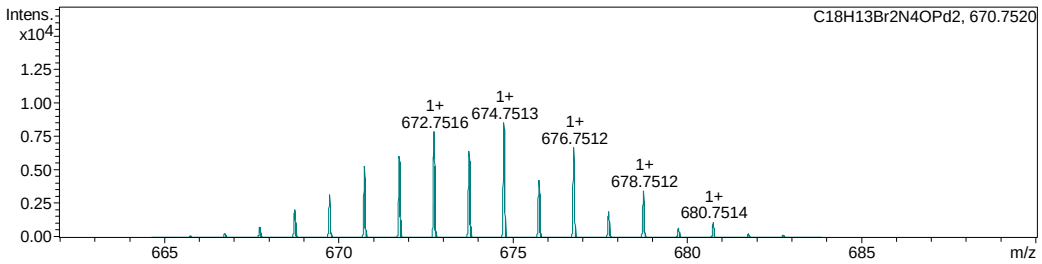
+MS, 0.9-1.0min #55-57



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
670.7517	1	100.00	C18H13Br2N4OPd2	670.7524	0.7	1.0	38.1	13.5	even	ok

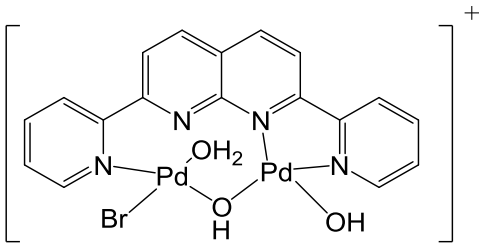
+MS, 0.9-1.0min #55-57





ESI-HRMS of **[**Pd_2(**bpnp**)Br_2(OH)]$^+$ and isotope simulation

doi:10.6342/NTU201700680



Mass Spectrum SmartFormula Report

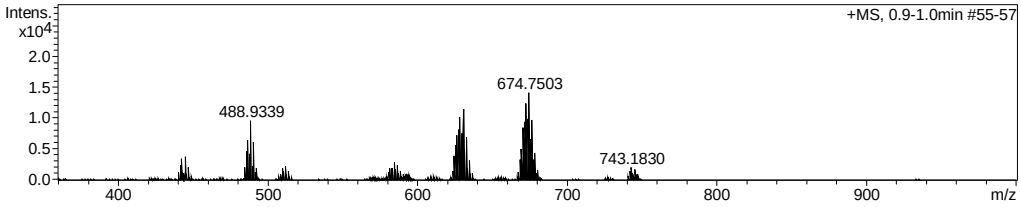
Analysis Info

Analysis Name	D:\Data\Fish\Data\170208\MS170208_10+KBr_pw000004.d	Acquisition Date	2/8/2017 4:46:18 PM
Method	tune_wide_pos_direction injection_20160719.m	Operator	Bruker microTOF-Q II
Sample Name	MS170208_trp reaction	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

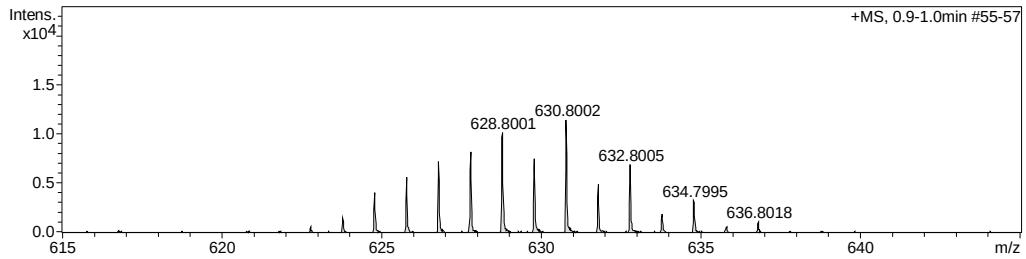
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

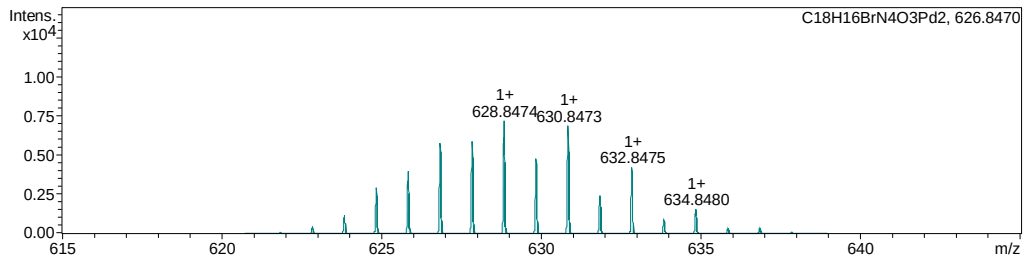
+MS, 0.9-1.0min #55-57



Meas. m/z	#	Score	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
626.8015	1	100.00	C18H16BrN4O3Pd2	626.8477	-46.3	-73.8	66.9	12.5	even	ok
670.7517	1	100.00	C18H13Br2N4OPd2	670.7524	0.7	1.0	38.1	13.5	even	ok

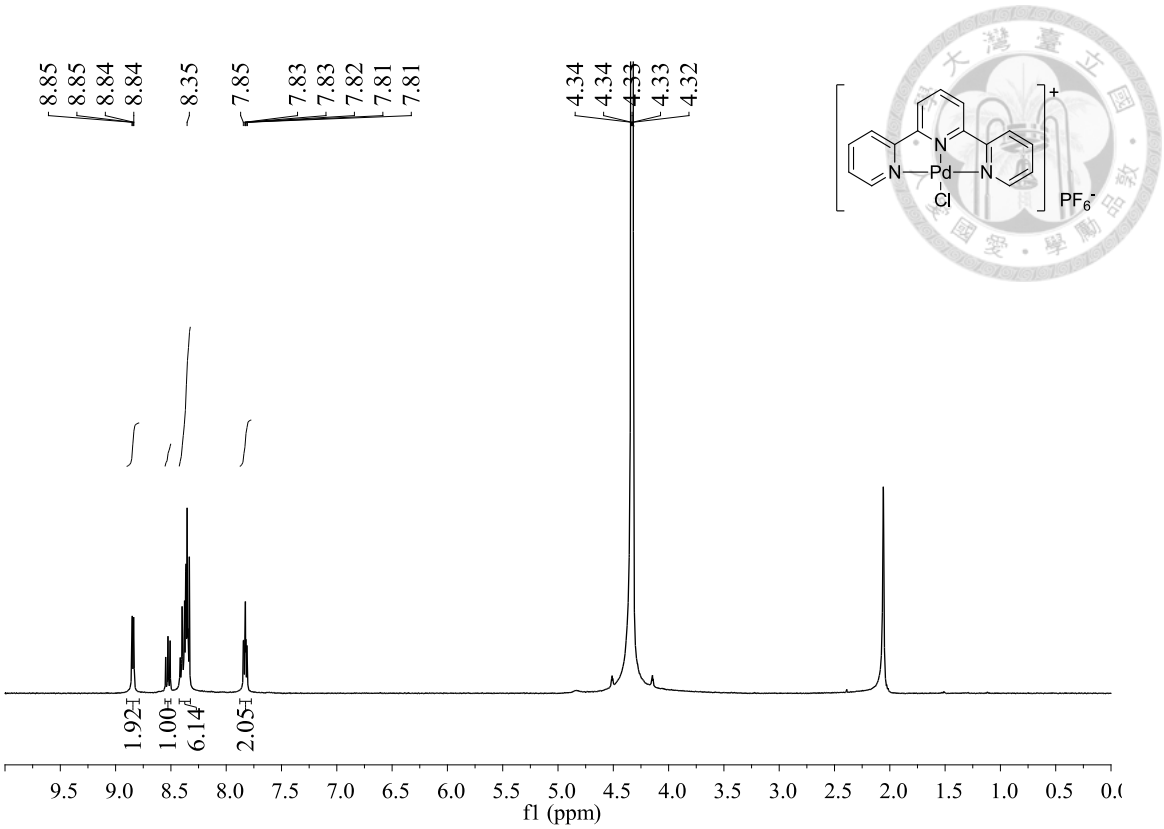
+MS, 0.9-1.0min #55-57



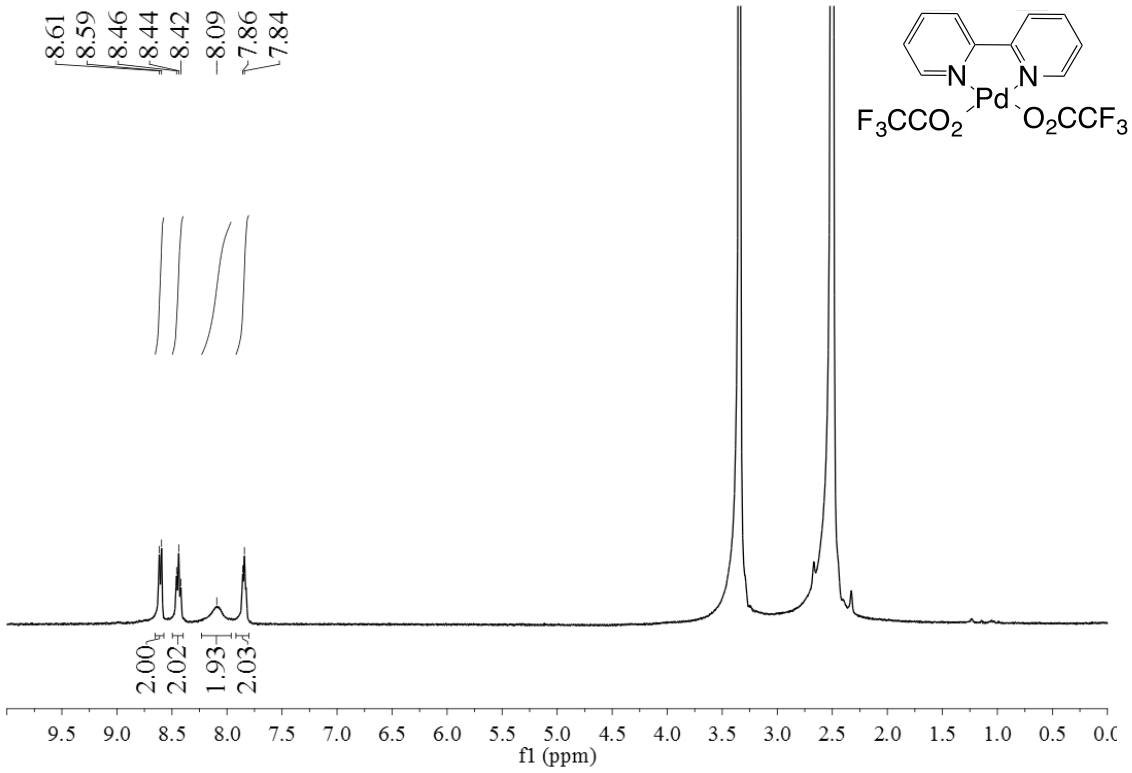


ESI-HRMS of **[**Pd_2(**bpnp**)$Br(H_2O)(OH)_2]^+$ and isotope simulation

doi:10.6342/NTU201700680

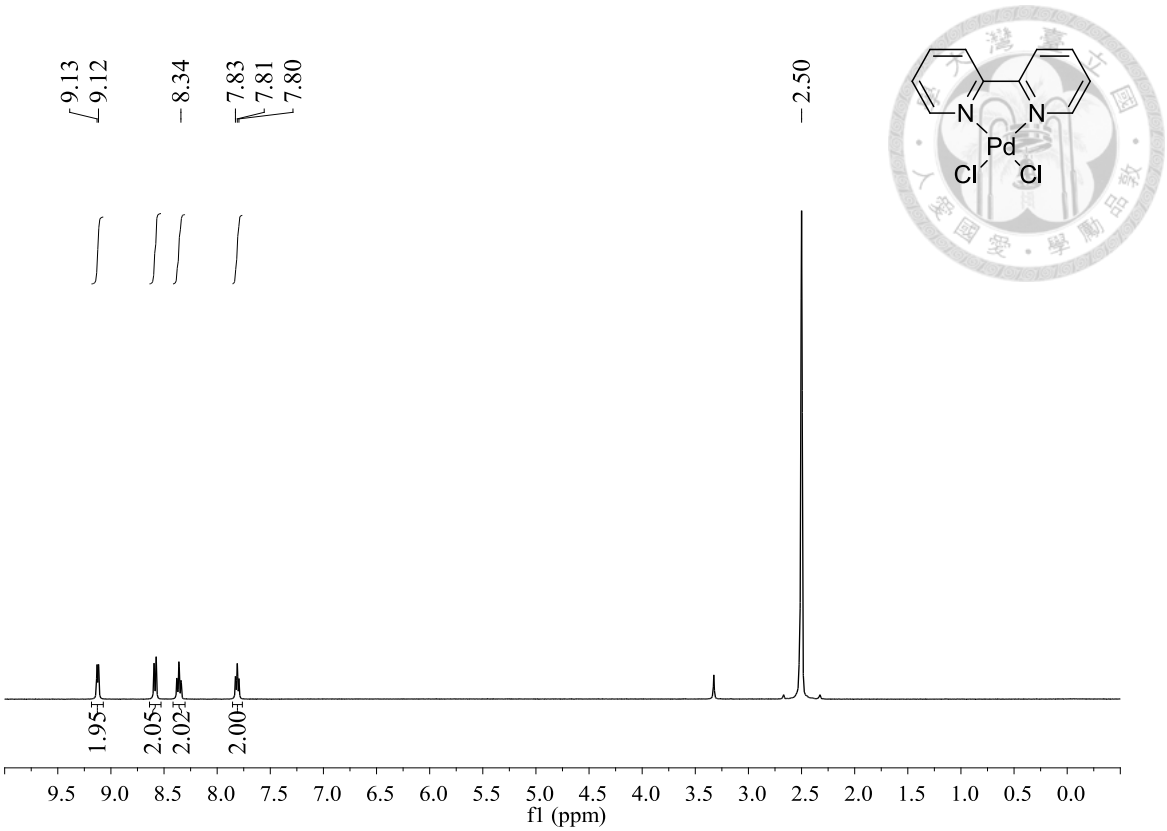


^{1}H NMR spectrum of compound [Pd(tpy)Cl](PF$_6$) (400 MHz, CD_3NO_2)

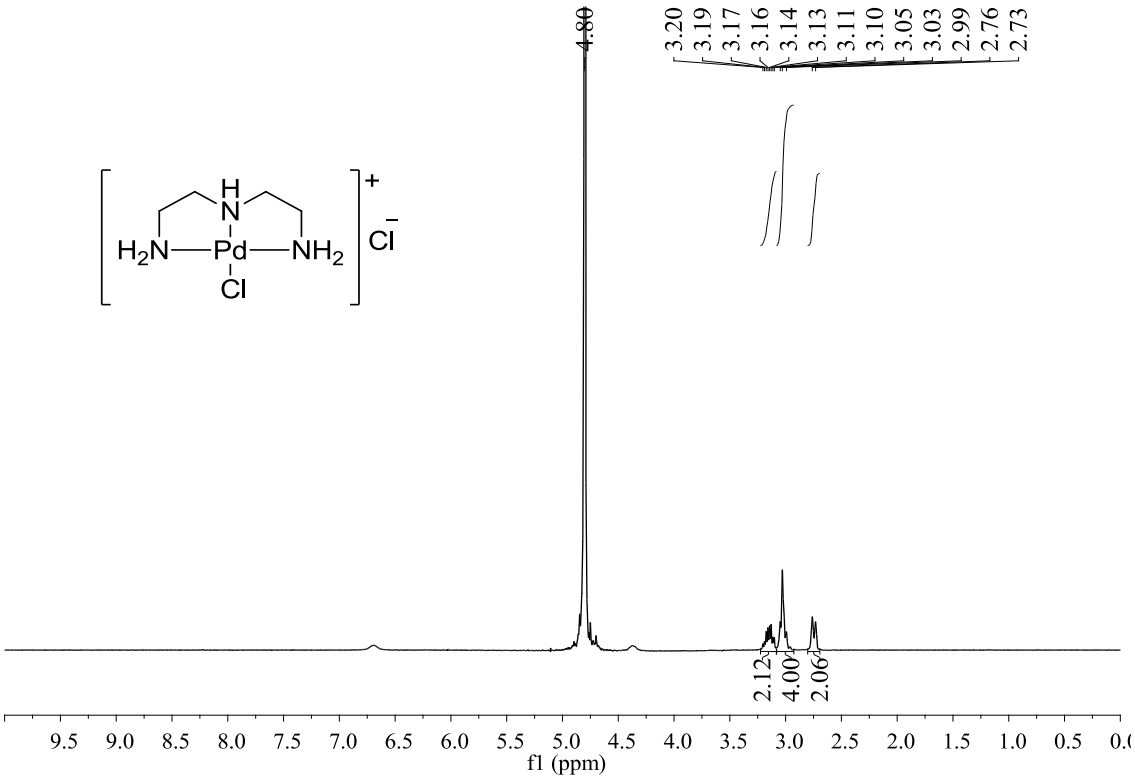


^{1}H NMR spectrum of compound Pd(bpy)(TFA)$_2$ (400 MHz, DMSO-d_6)

doi:10.6342/NTU201700680

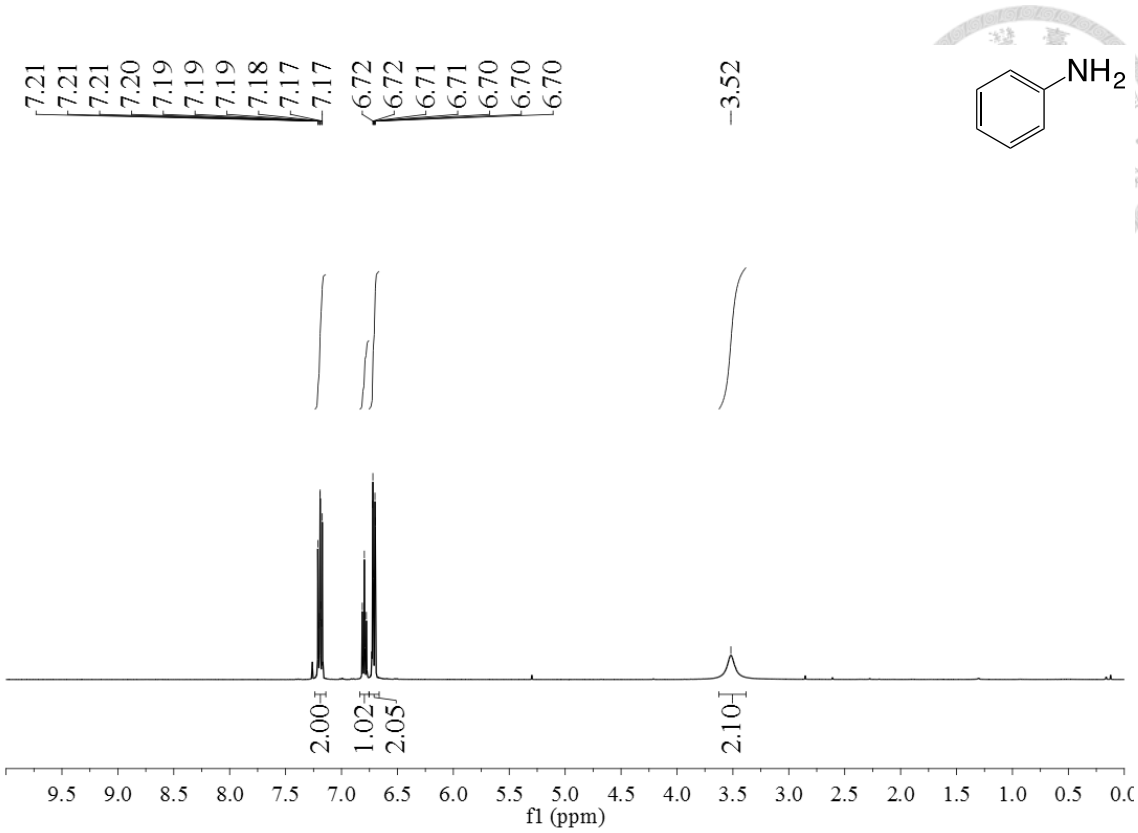


^{1}H NMR spectrum of compound Pd(bpy)Cl_2 (400 MHz, DMSO-d_6)

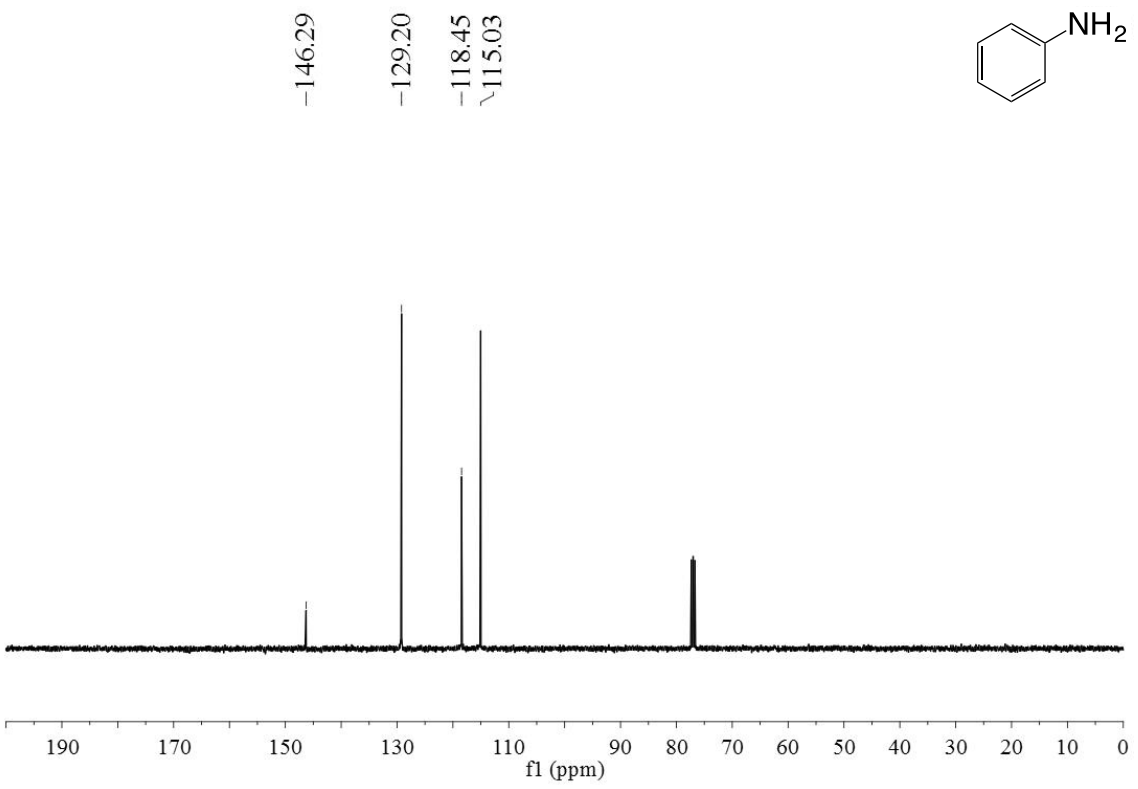


^{1}H NMR spectrum of compound [Pd(dien)Cl]Cl (400 MHz, D_2O)

doi:10.6342/NTU201700680

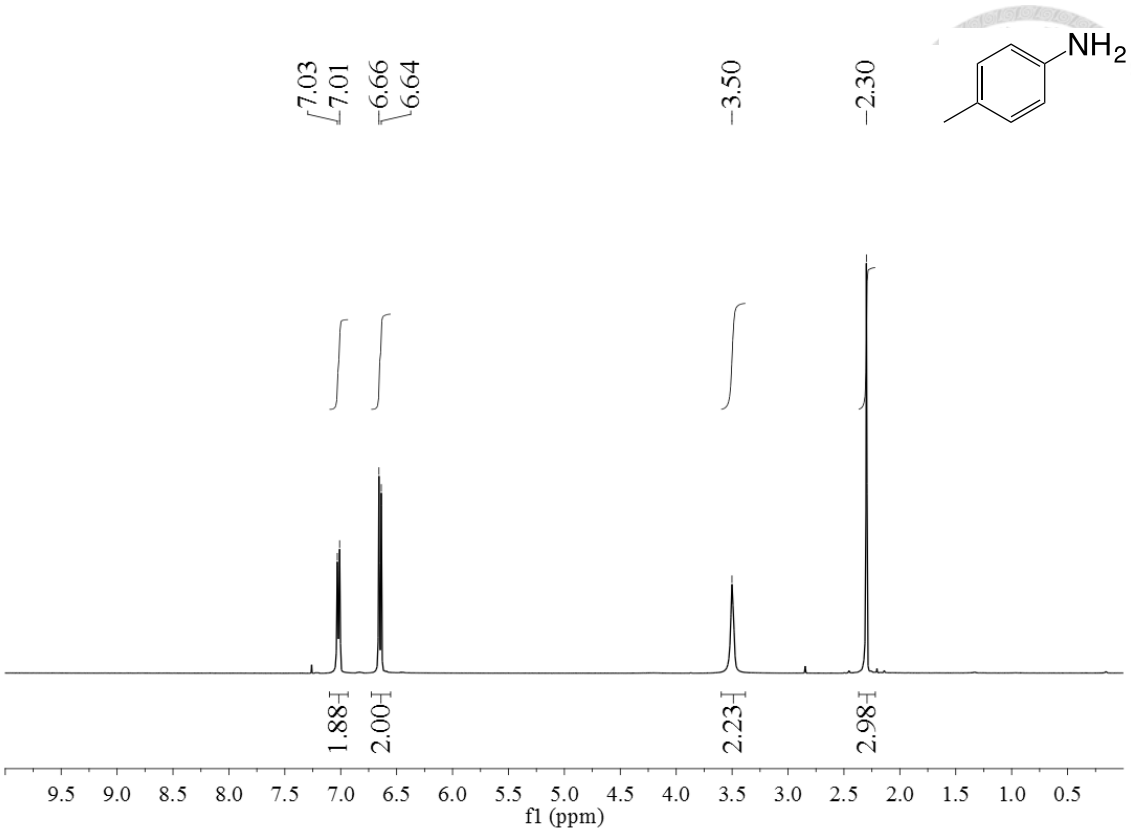


^{1}H NMR spectrum of compound **20a** (400 MHz, $CDCl_3$)

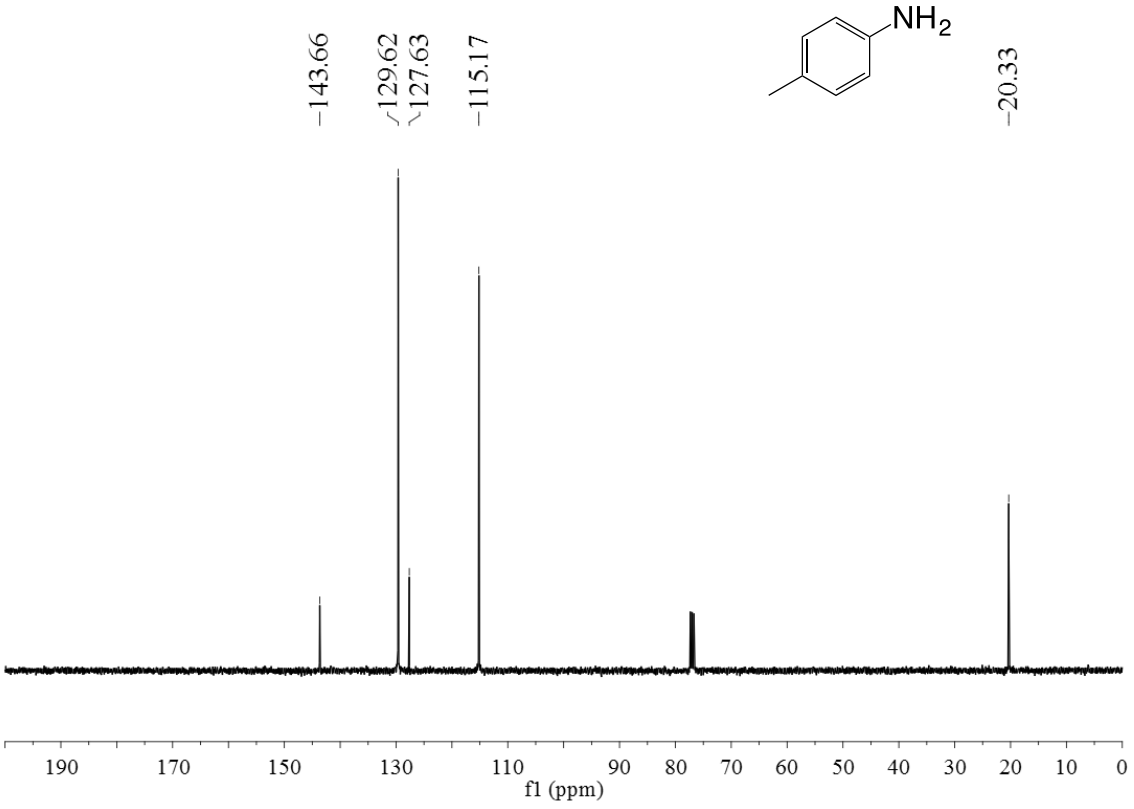


^{13}C NMR spectrum of compound **20a** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

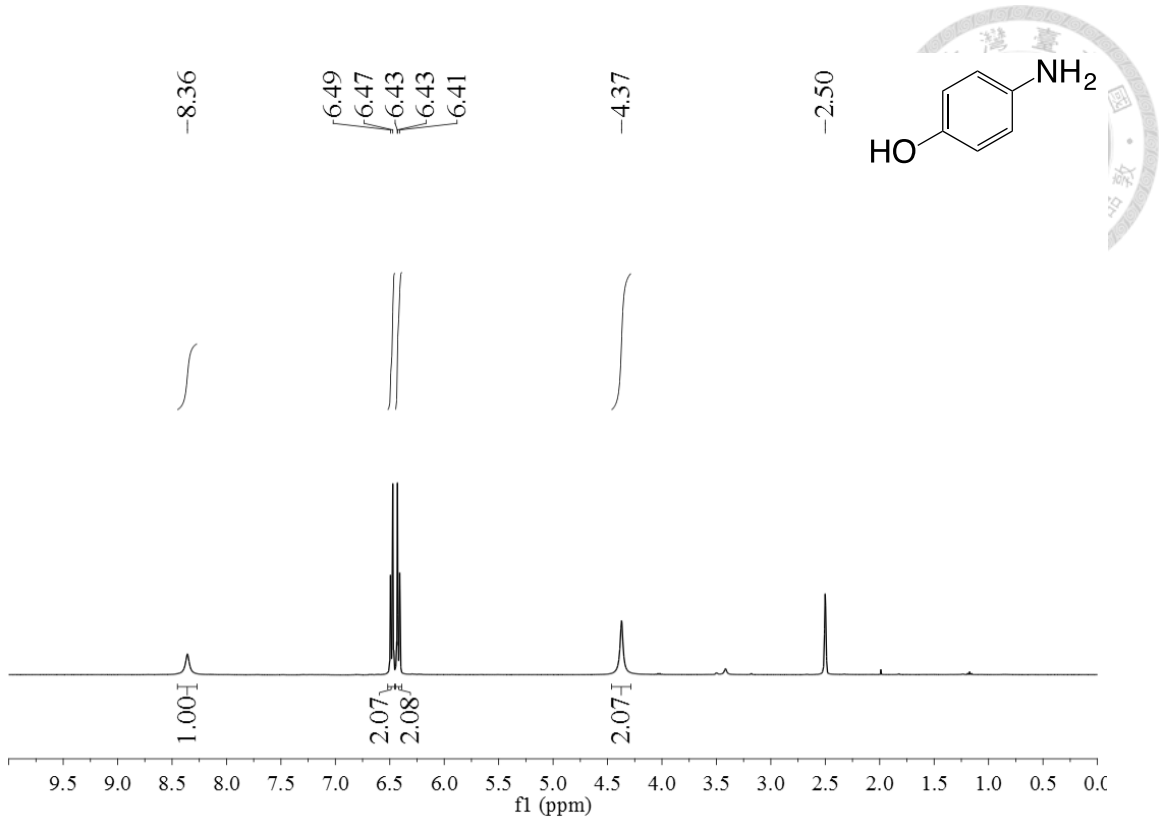


^{1}H NMR spectrum of compound **20b** (400 MHz, $CDCl_3$)

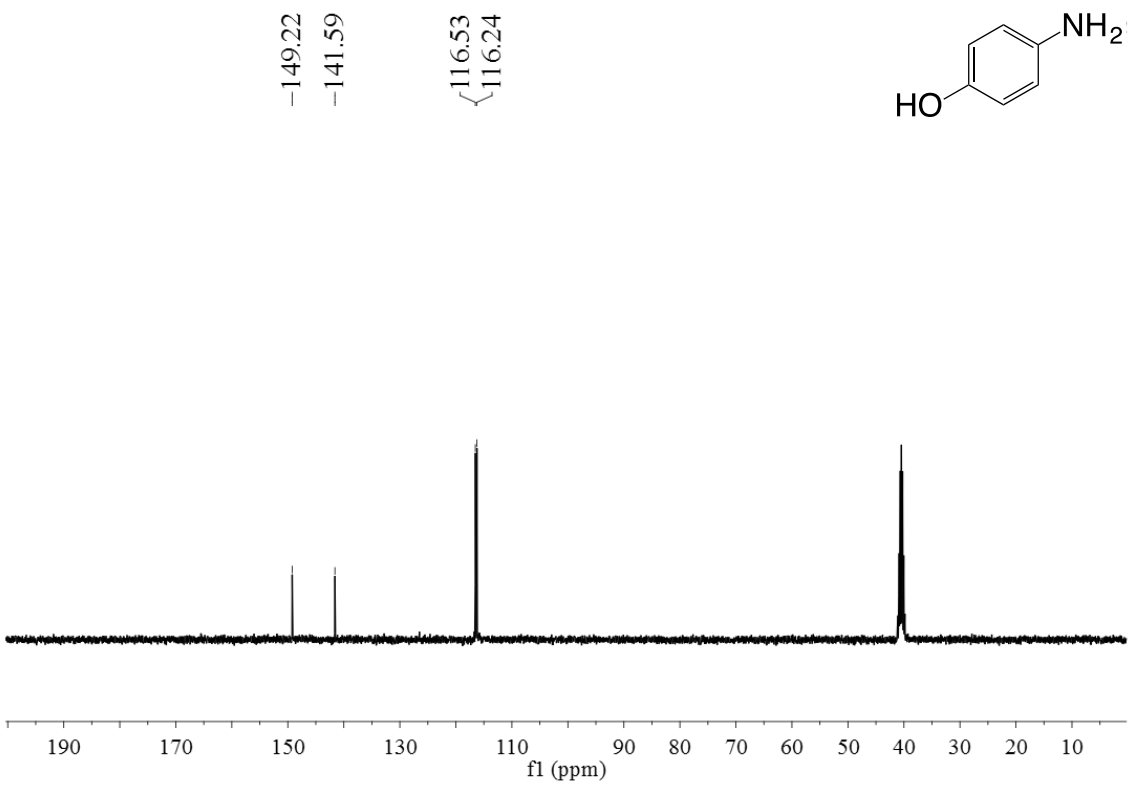


^{13}C NMR spectrum of compound **20b** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

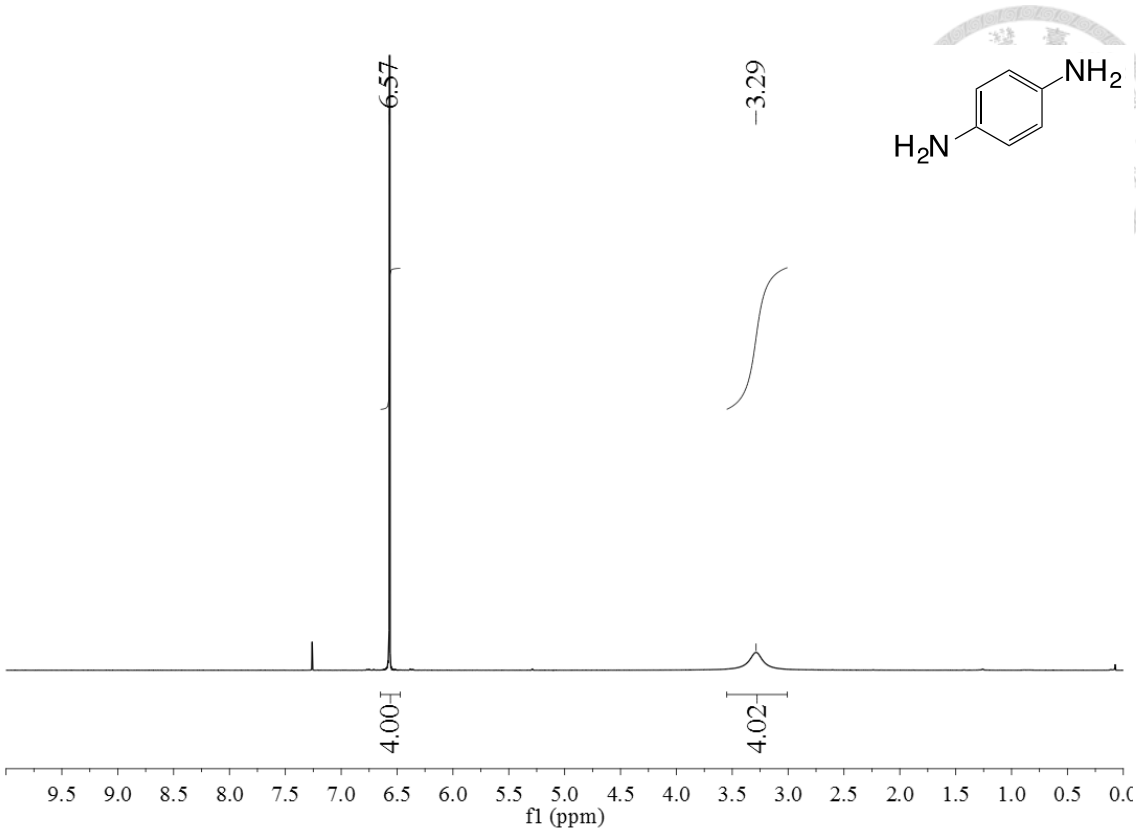


^{1}H NMR spectrum of compound **20c** (400 MHz, DMSO-d_6)

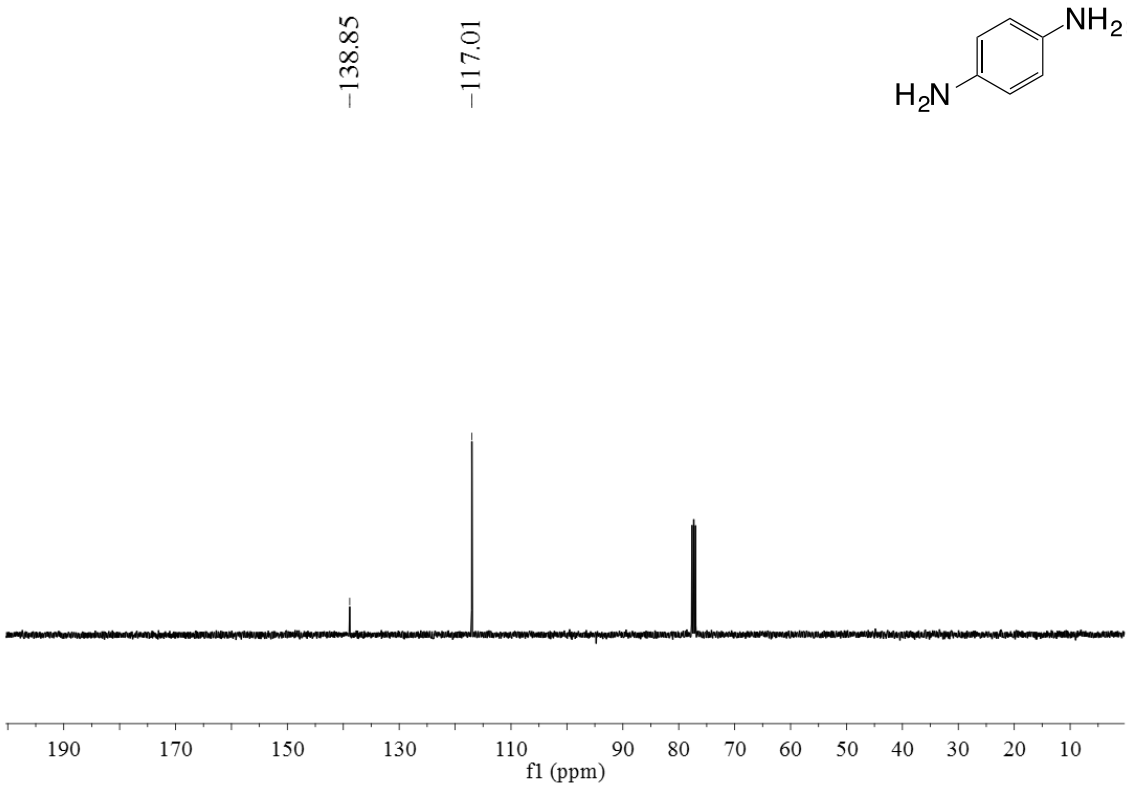


^{1}H NMR spectrum of compound **20c** (100 MHz, DMSO-d_6)

doi:10.6342/NTU201700680

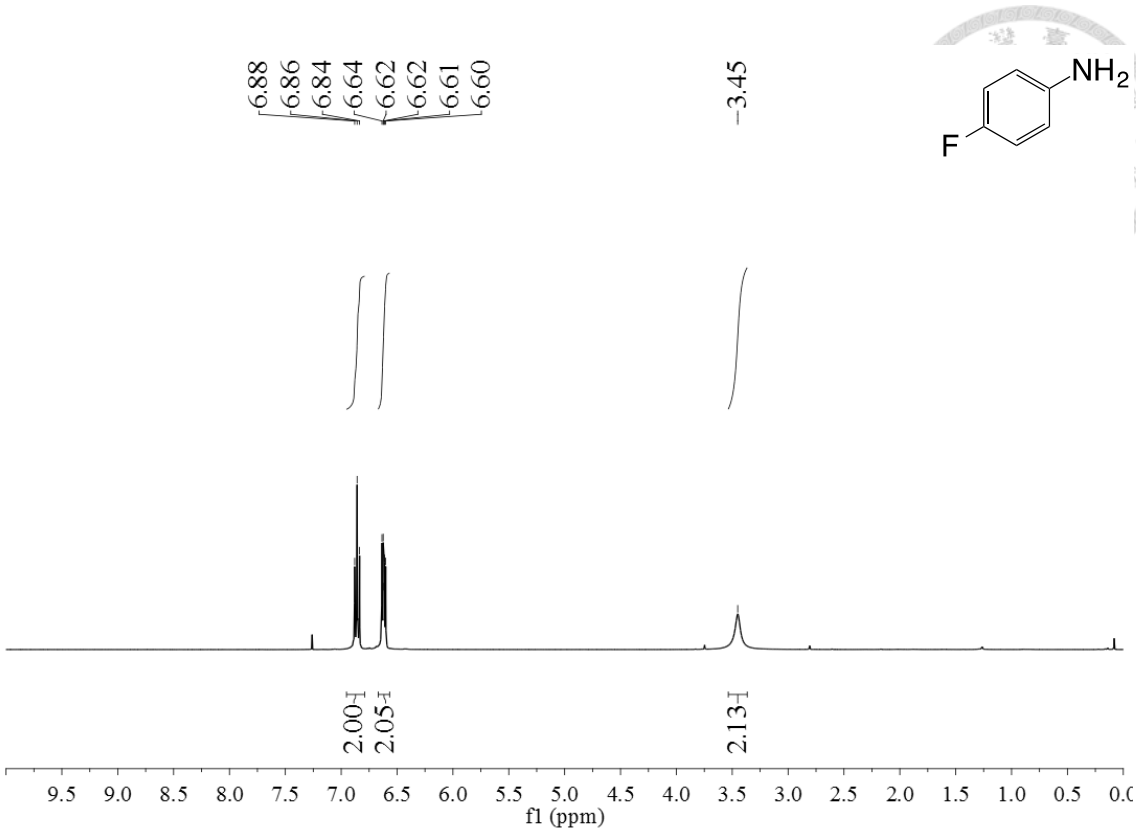


^{1}H NMR spectrum of compound **20d** (400 MHz, $CDCl_3$)

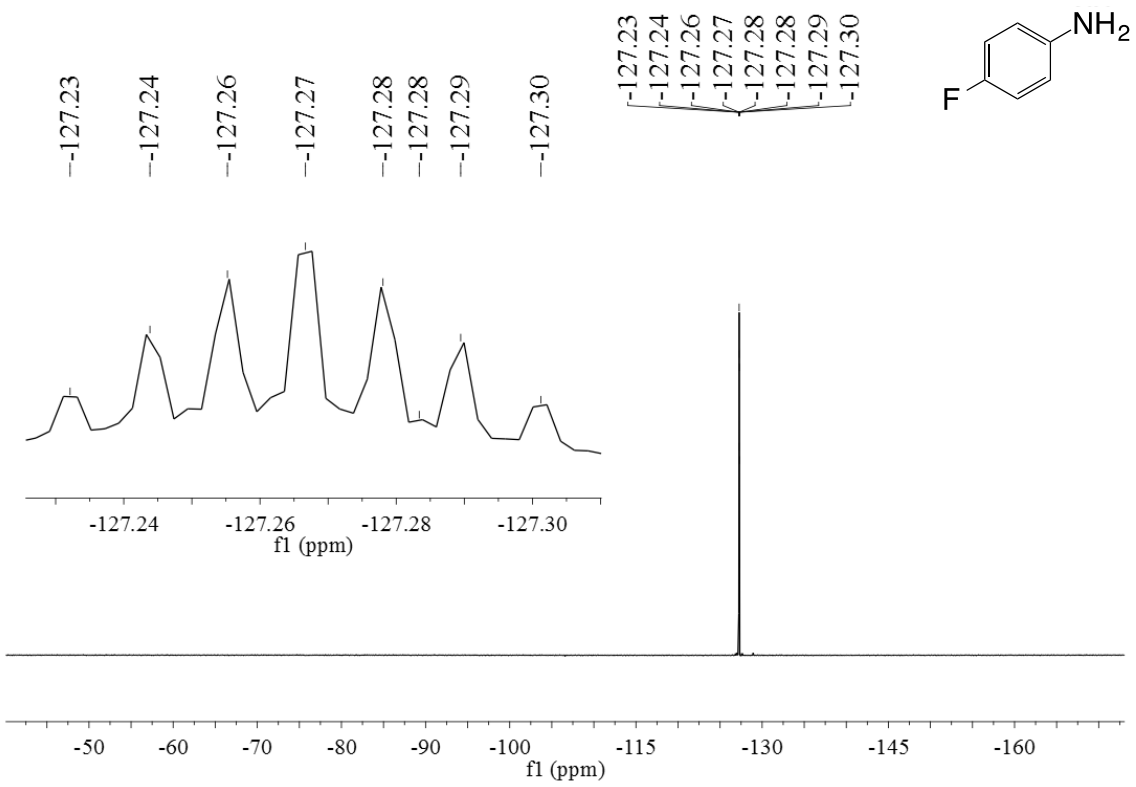


^{13}C NMR spectrum of compound **20d** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

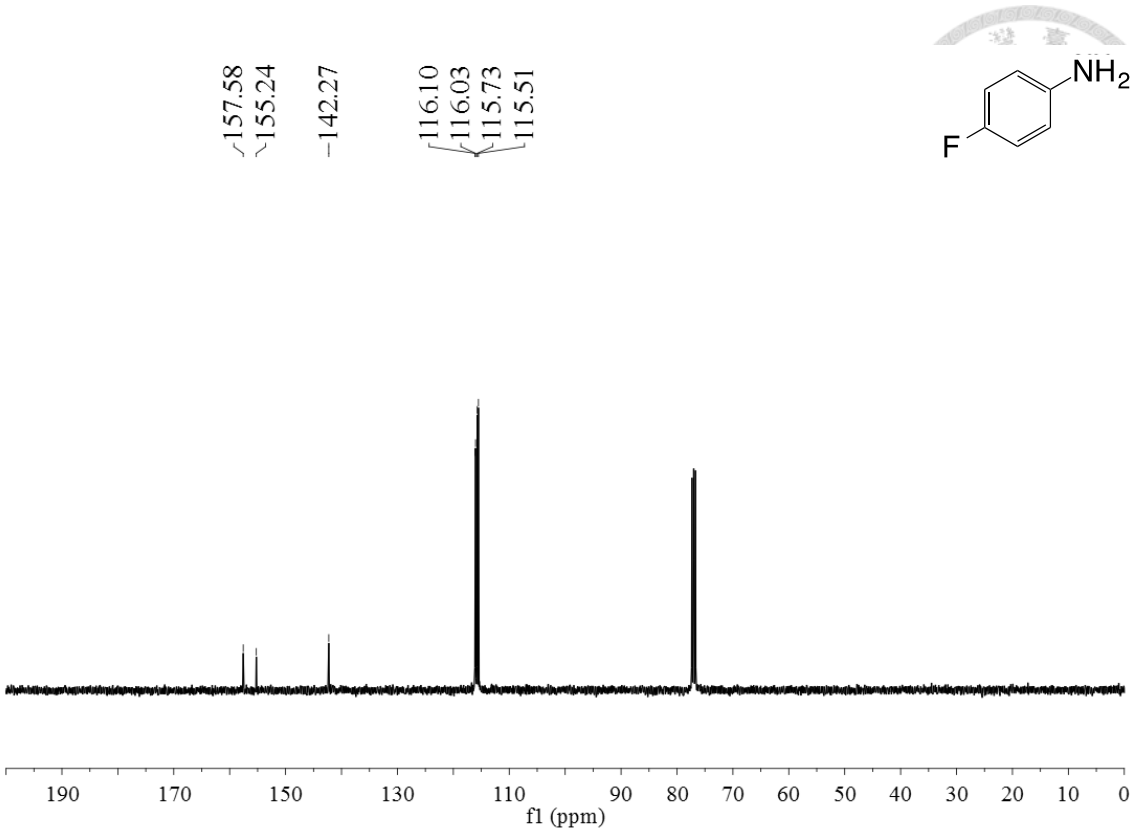


^{1}H NMR spectrum of compound **20e** (400 MHz, $CDCl_3$)

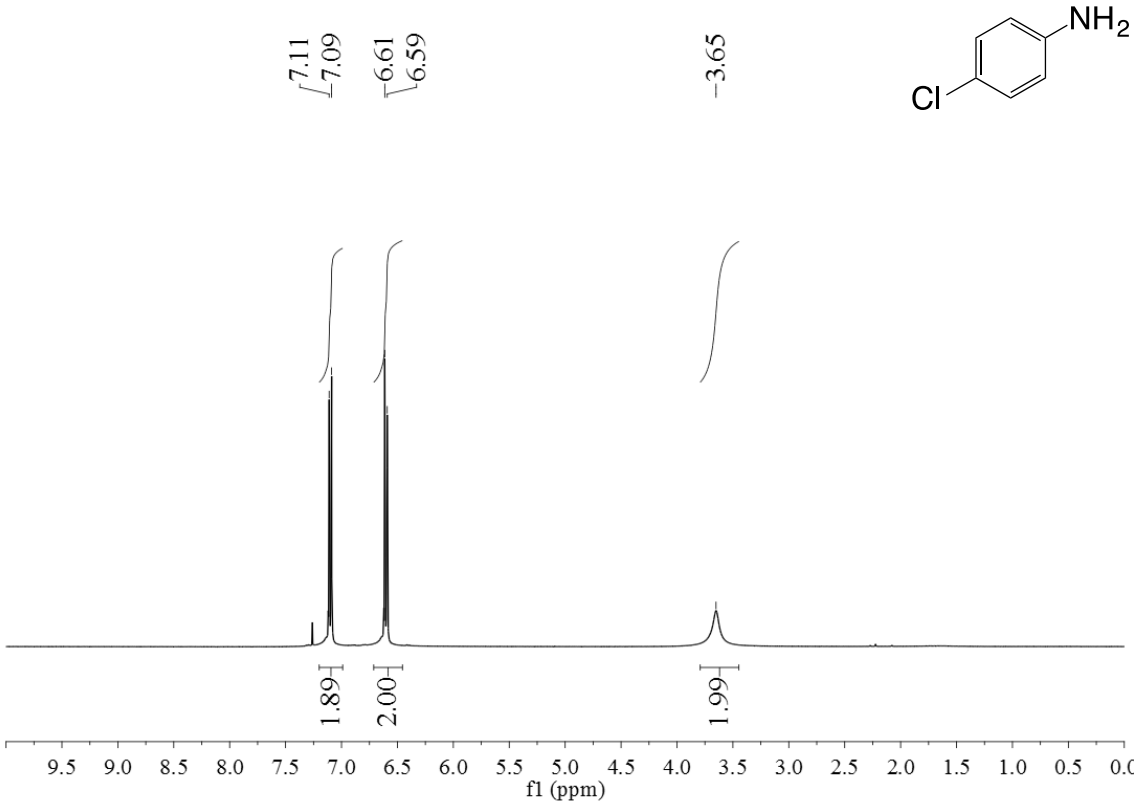


^{19}F NMR spectrum of compound **20e** (375 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

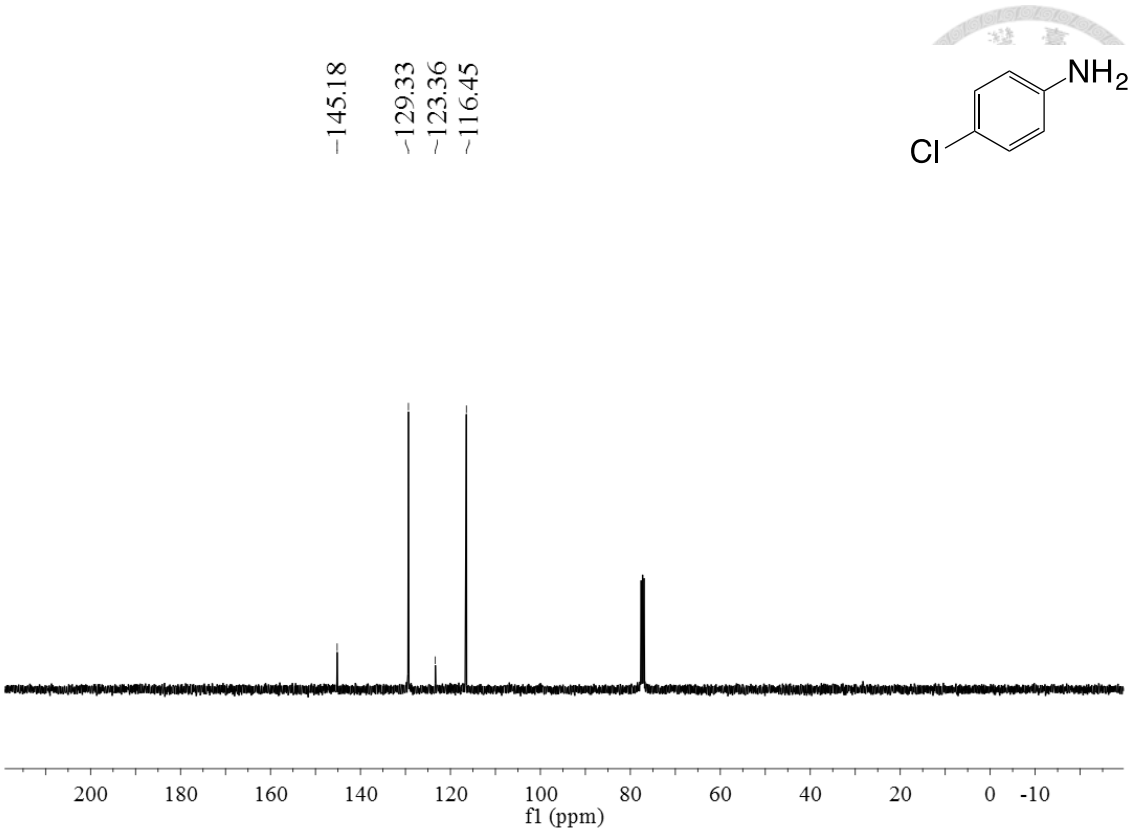


^{13}C NMR spectrum of compound **20e** (100 MHz, $CDCl_3$)

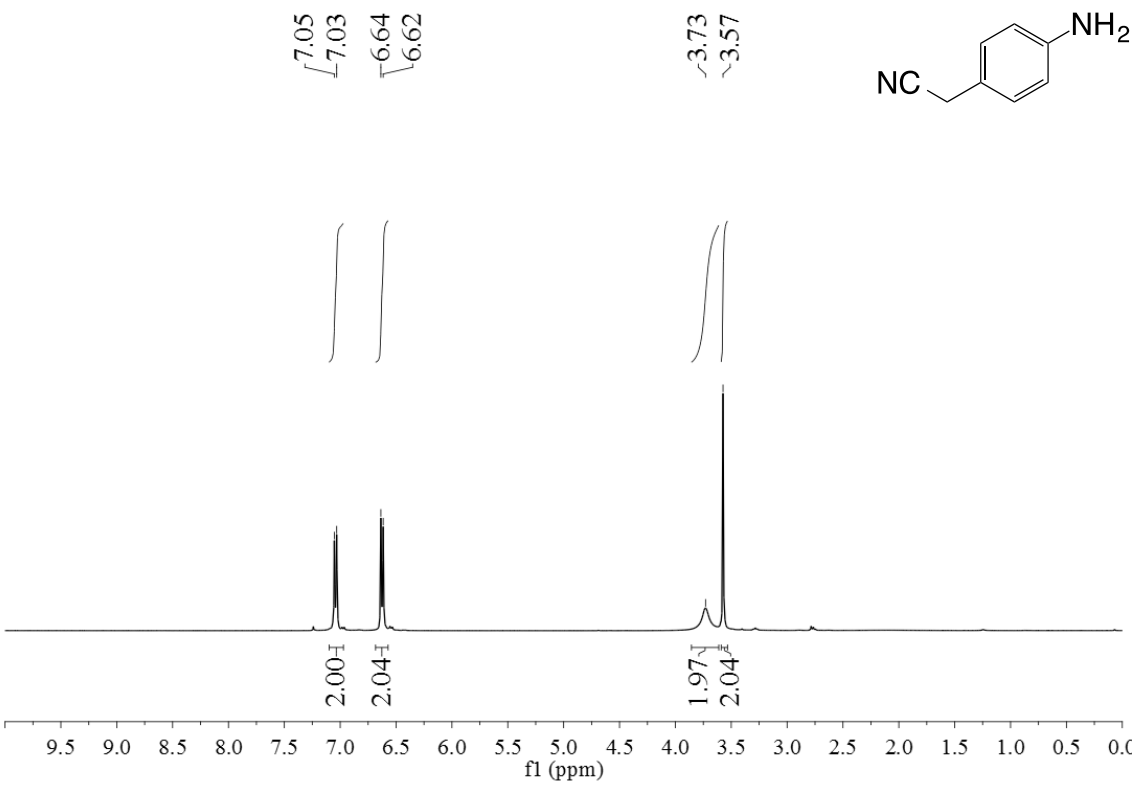


^{1}H NMR spectrum of compound **20f** (400 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

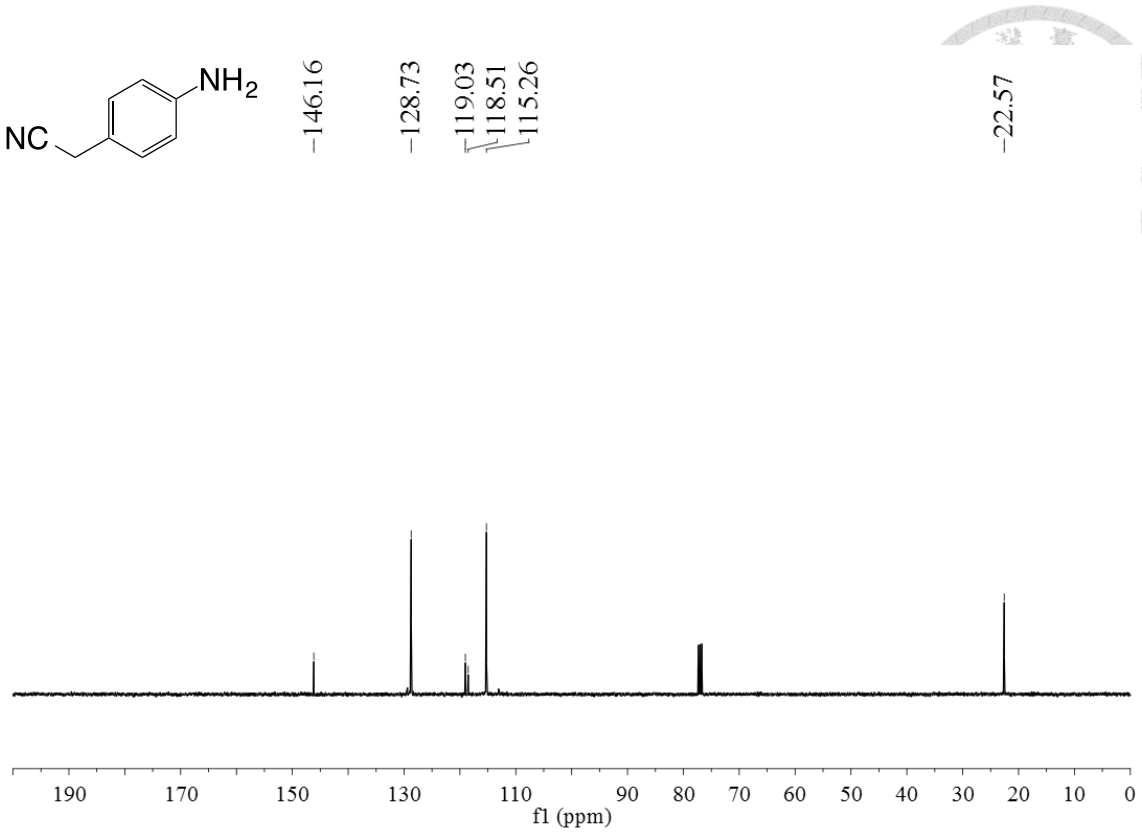


^{13}C NMR spectrum of compound **20f** (100 MHz, $CDCl_3$)

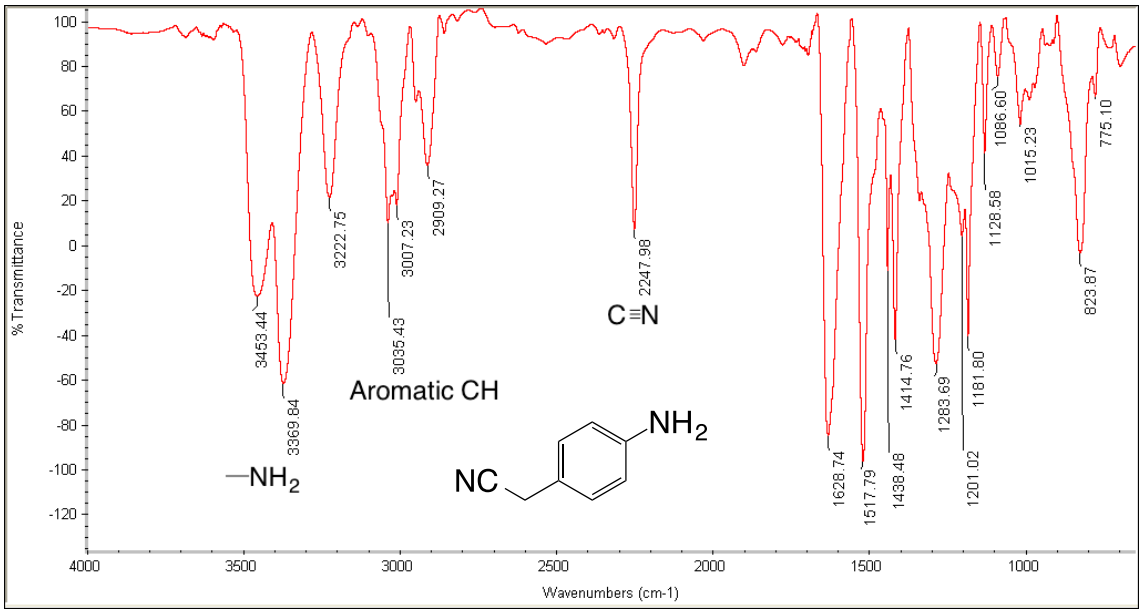


^{1}H NMR spectrum of compound **20h** (400 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

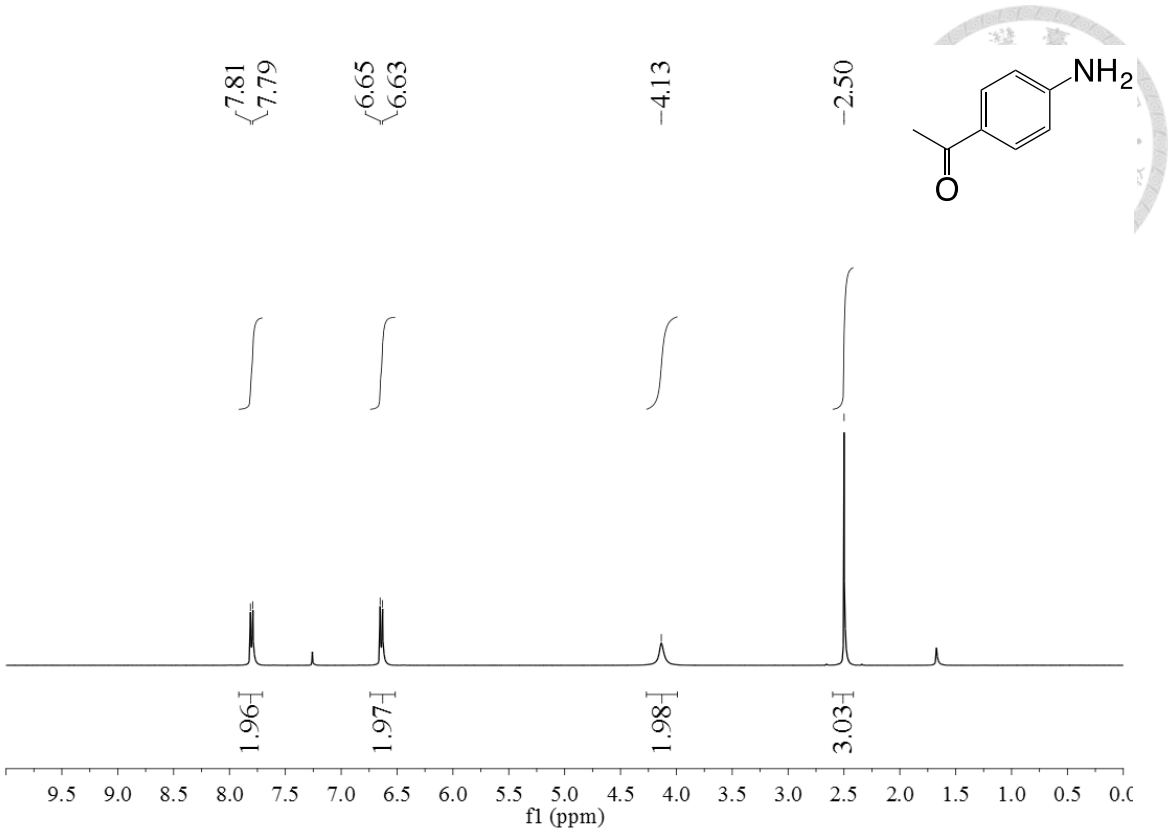


^{13}C NMR spectrum of compound **20h** (100 MHz, $CDCl_3$)

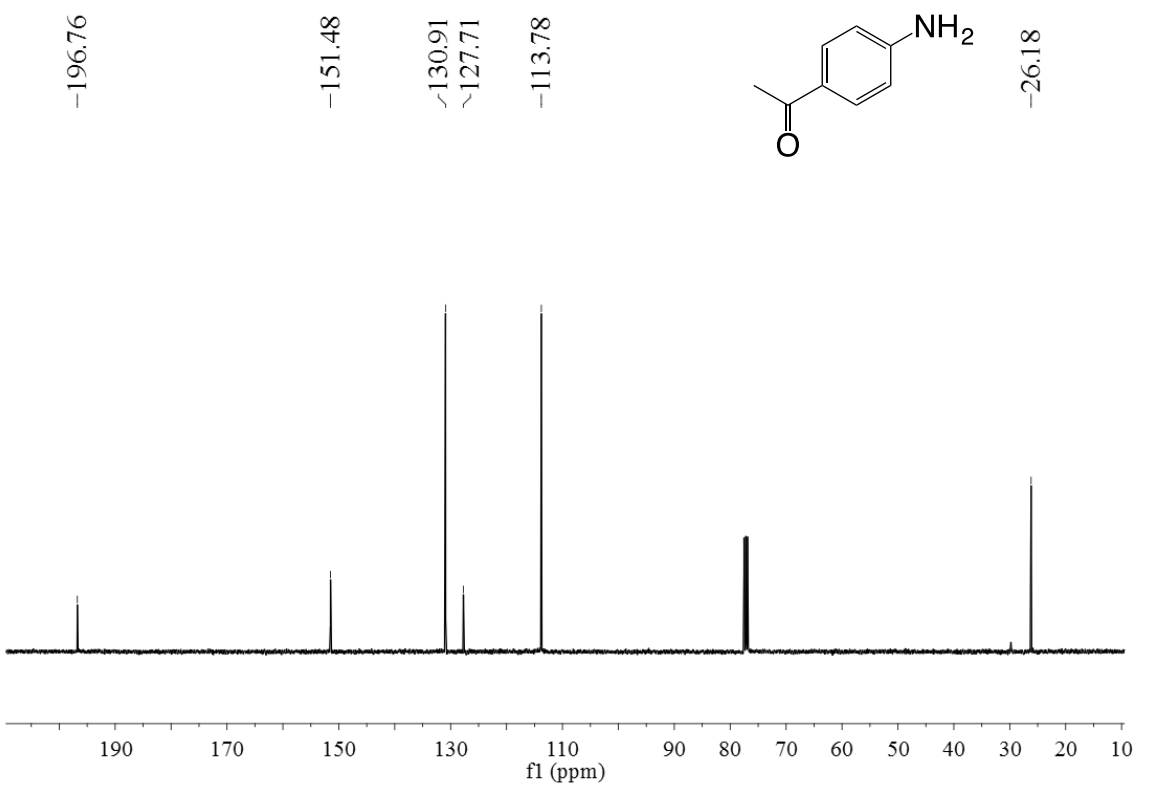


IR(KBr) spectrum of compound **20h**

doi:10.6342/NTU201700680

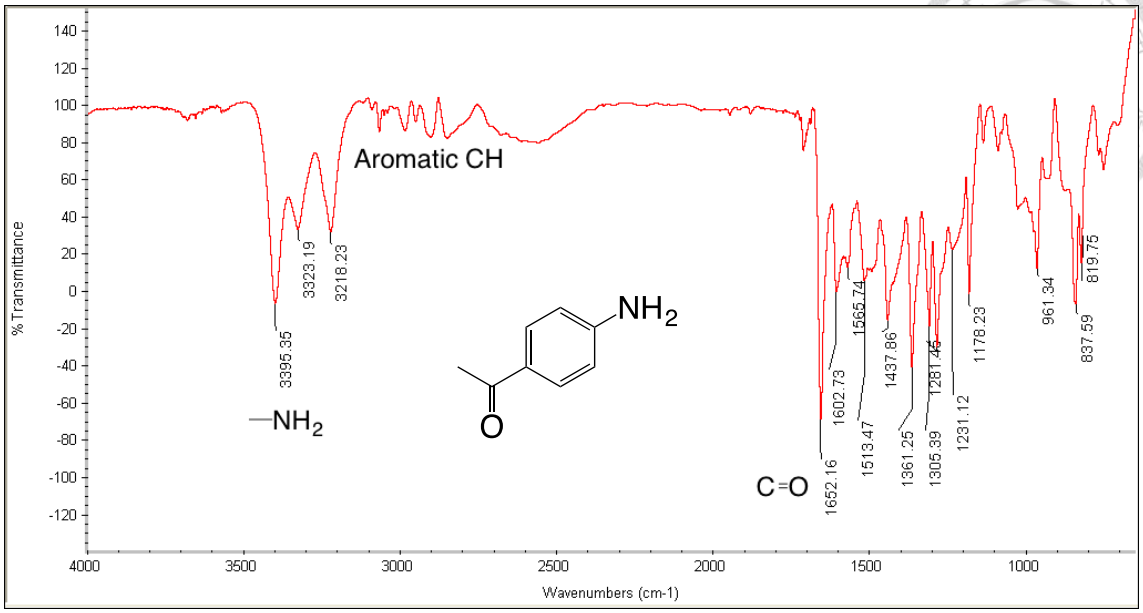


^{1}H NMR spectrum of compound **20i** (400 MHz, $CDCl_3$)



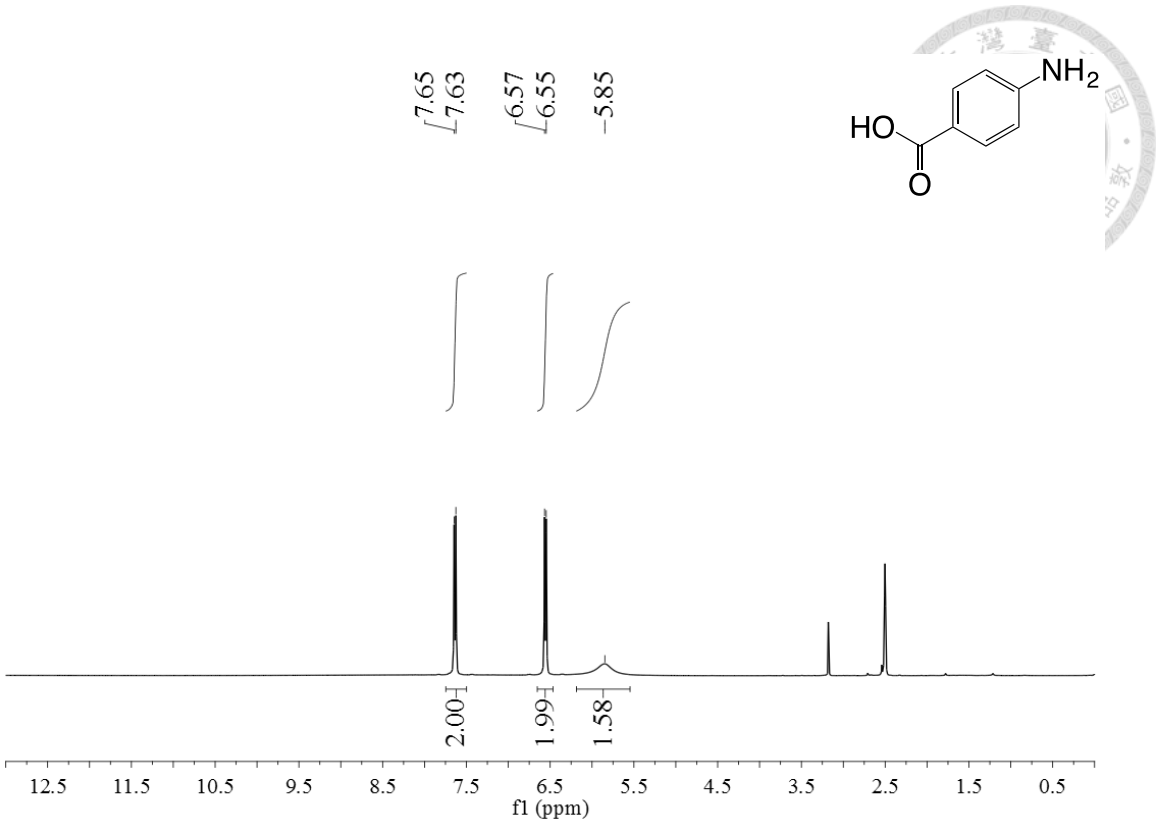
^{13}C NMR spectrum of compound **20i** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

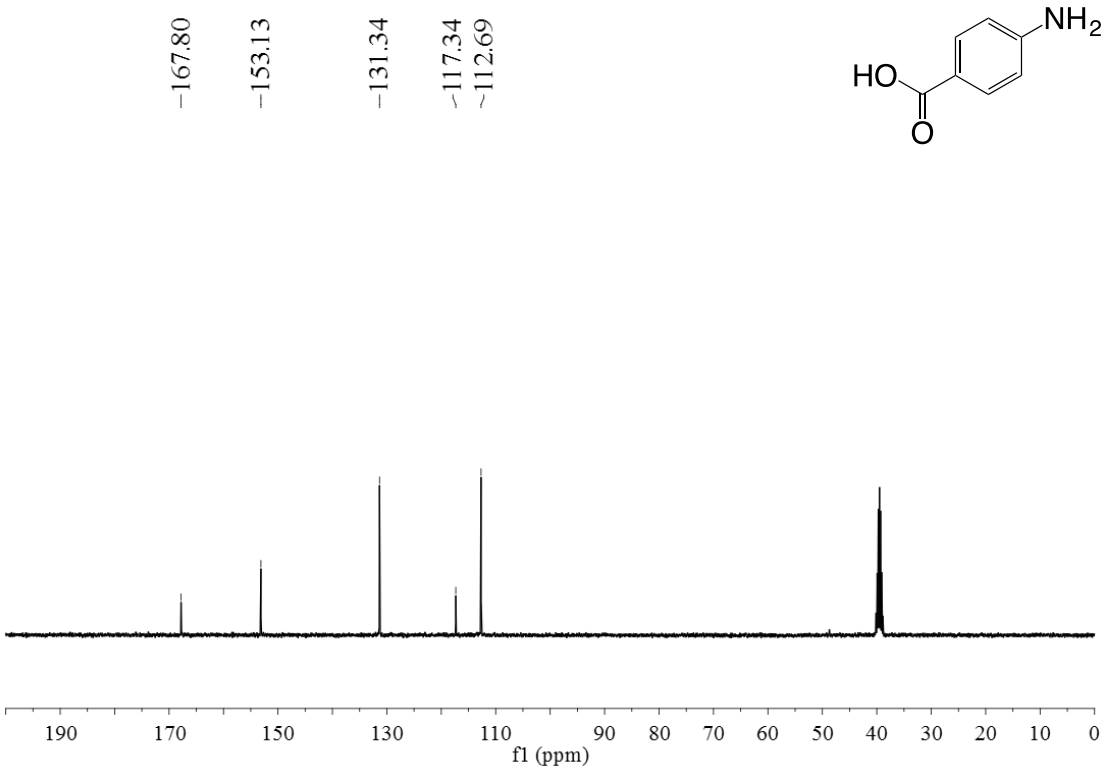


IR(KBr) spectrum of compound **20i**

doi:10.6342/NTU201700680

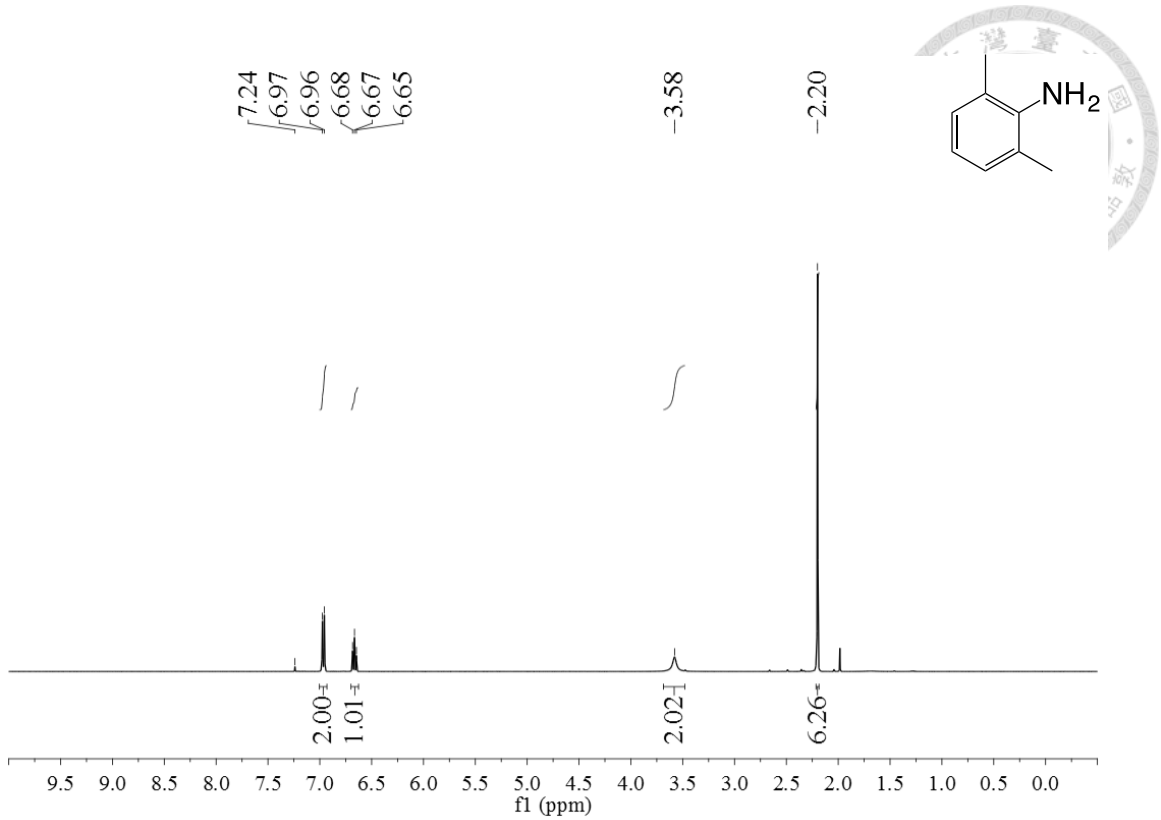


^{1}H NMR spectrum of compound **20j** (400 MHz, DMSO-d_6)

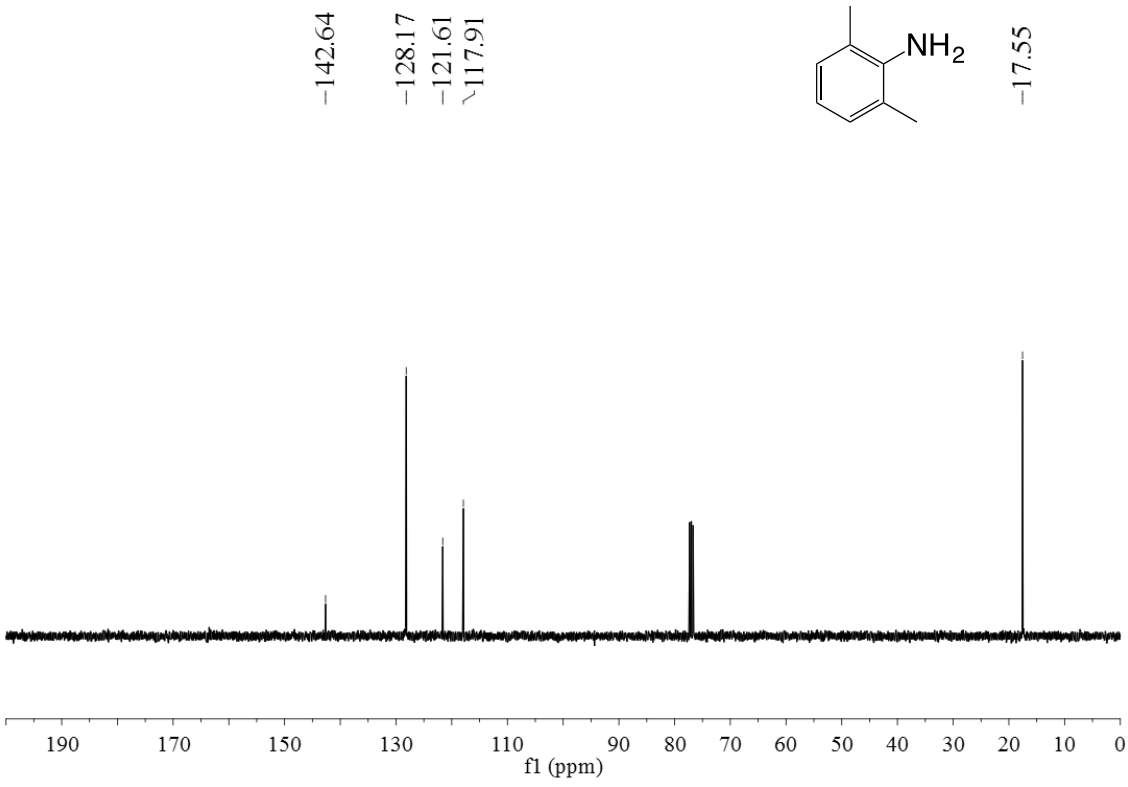


^{13}C NMR spectrum of compound **20j** (100 MHz, DMSO-d_6)

doi:10.6342/NTU201700680

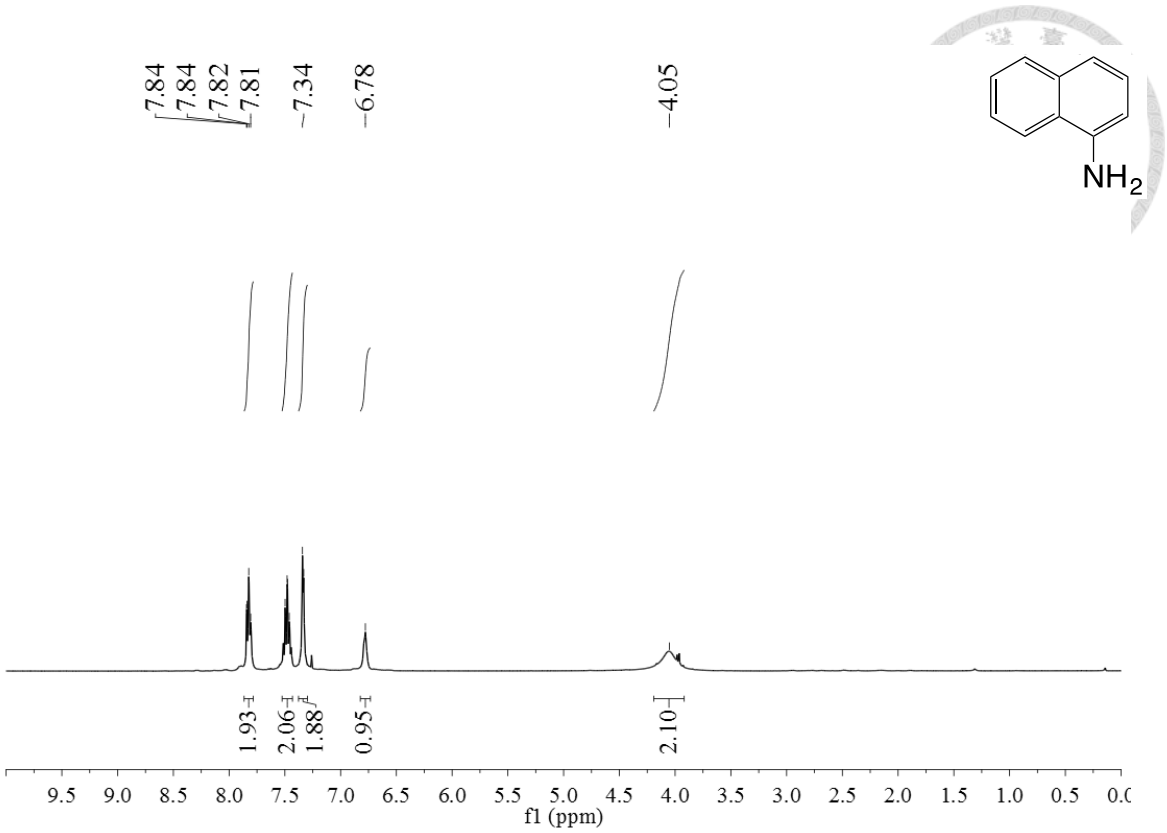


^{1}H NMR spectrum of compound **20k** (400 MHz, $CDCl_3$)

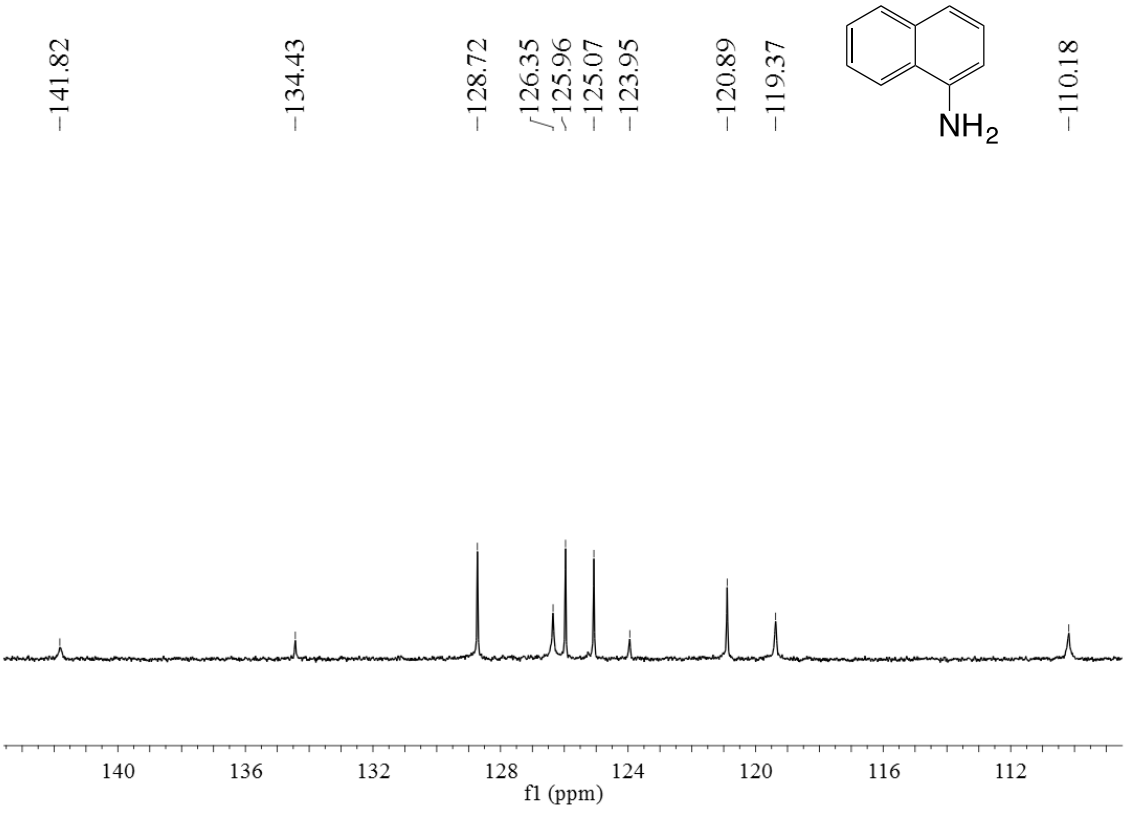


^{13}C NMR spectrum of compound **20k** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

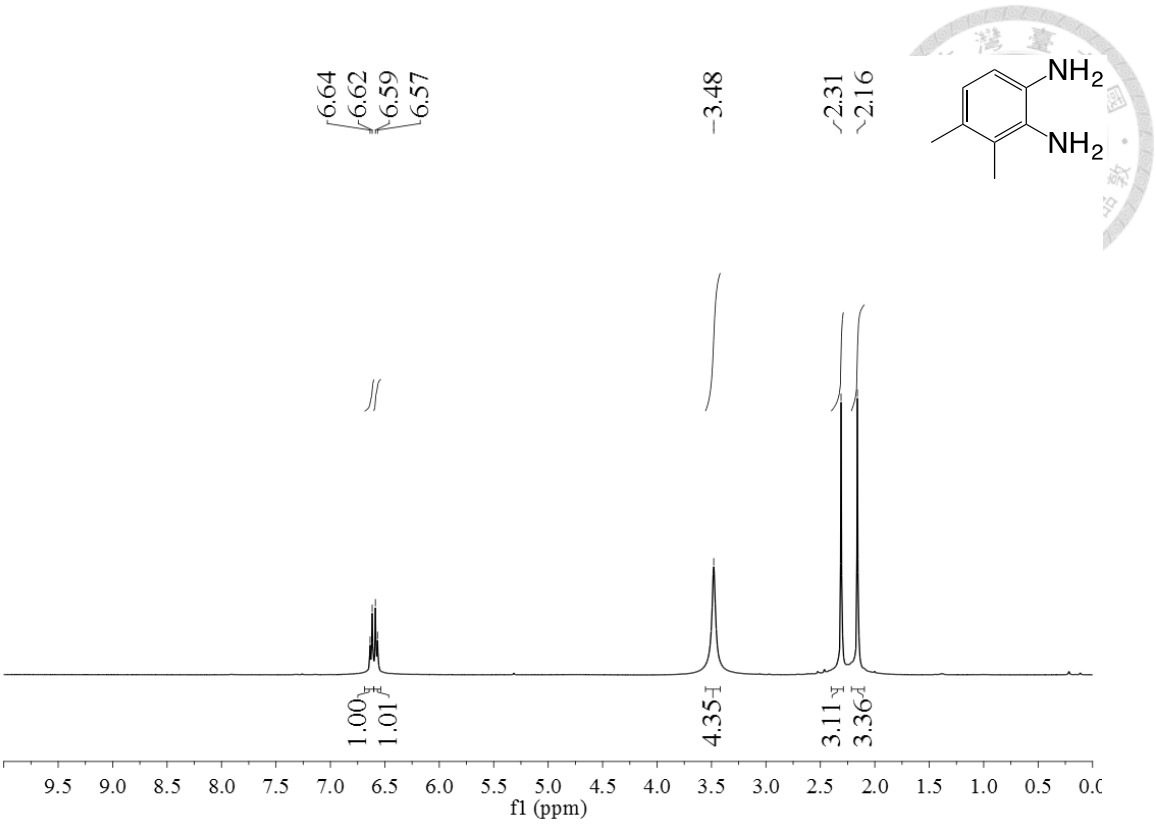


^{1}H NMR spectrum of compound **20l** (400 MHz, $CDCl_3$)

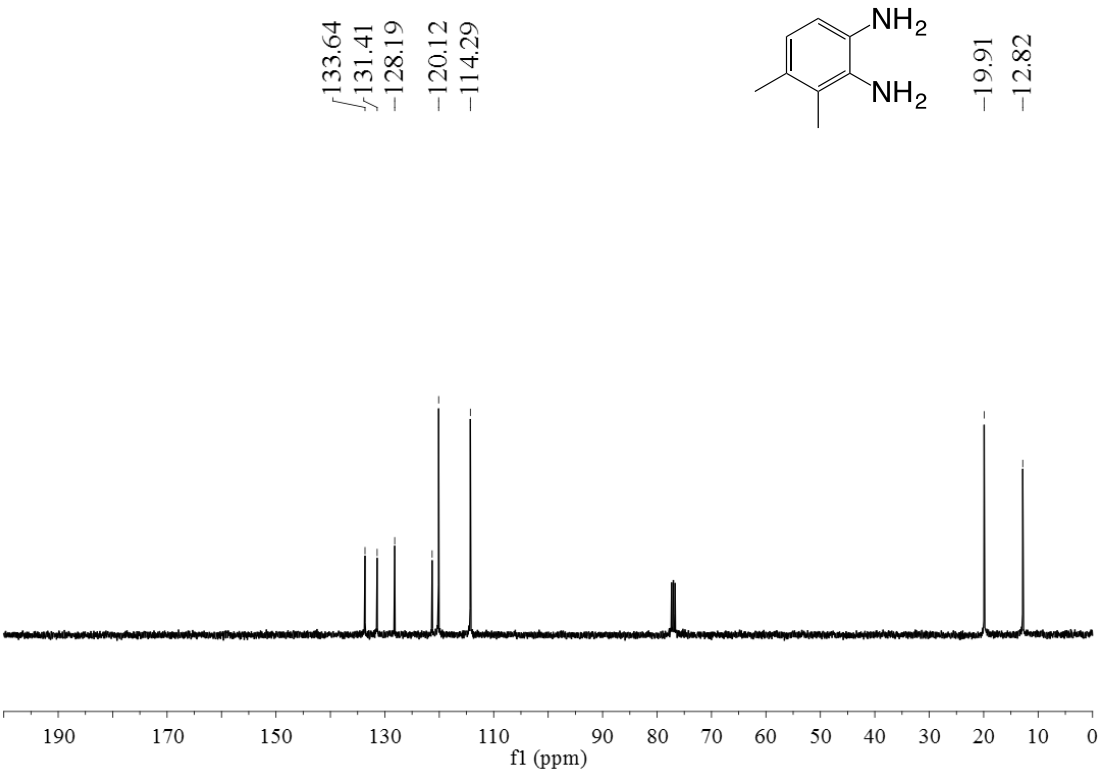


^{13}C NMR spectrum of compound **20l** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680

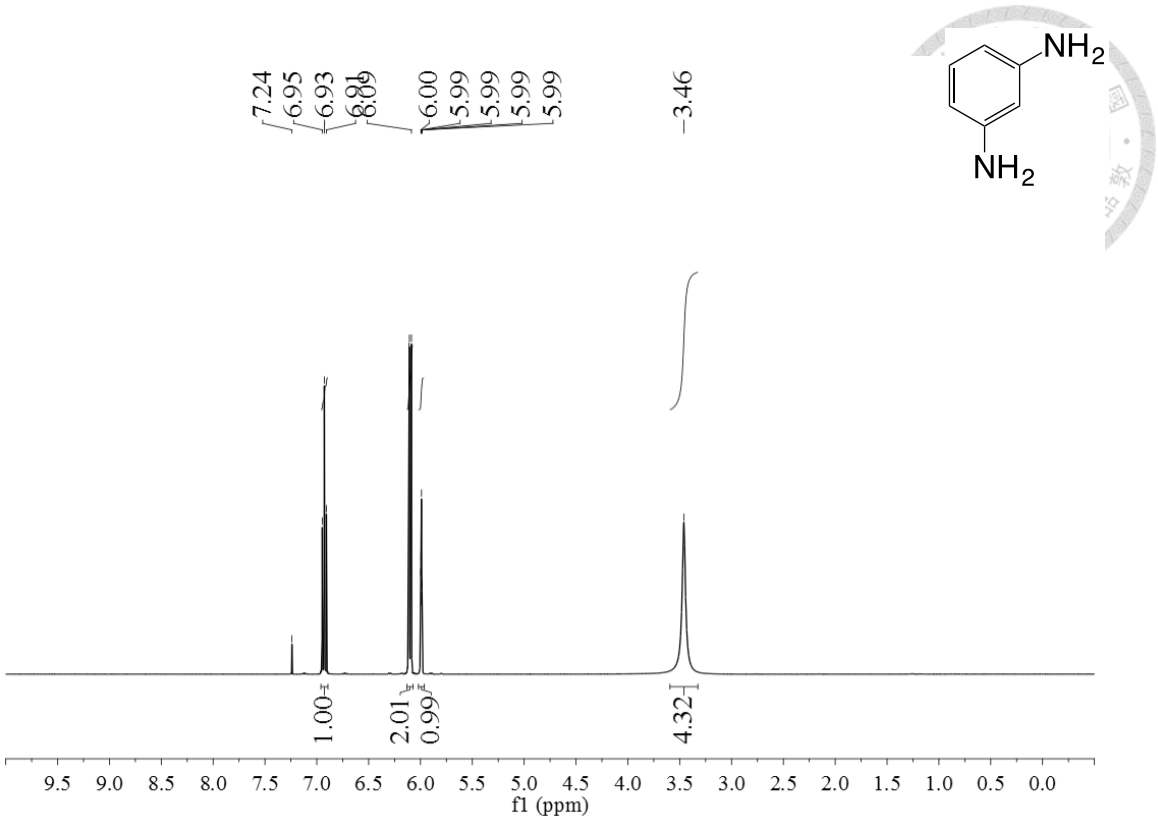


^{1}H NMR spectrum of compound **20m** (400 MHz, $CDCl_3$)

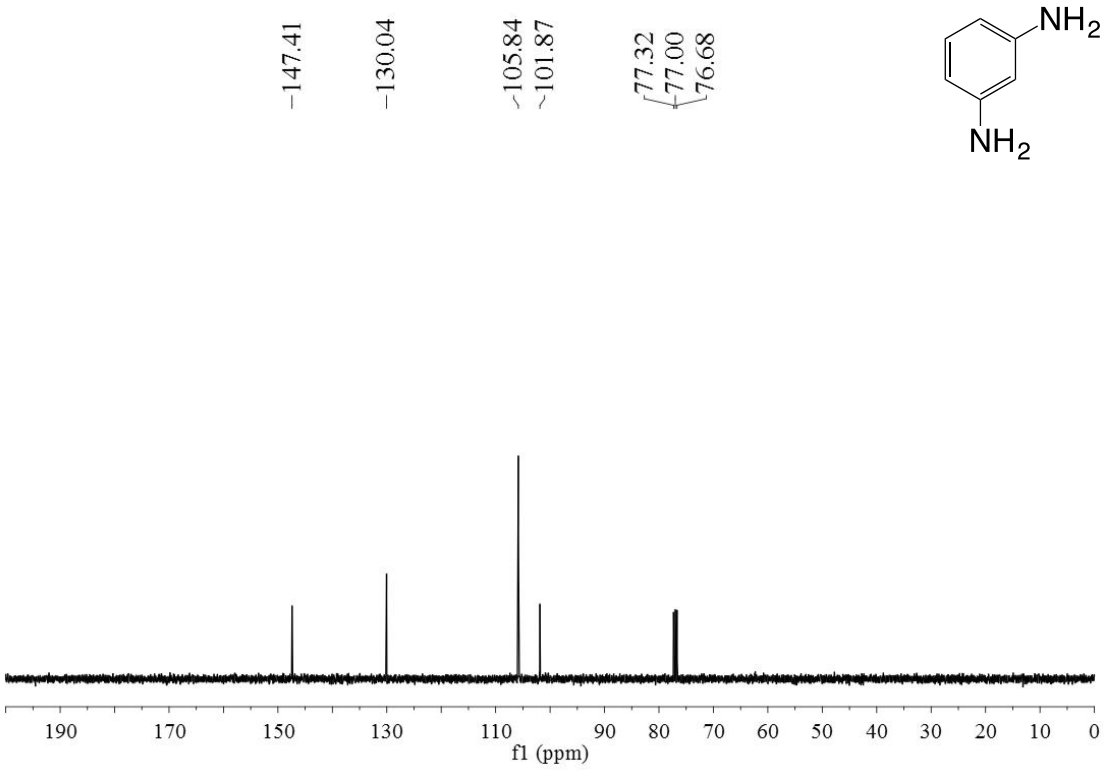


^{13}C NMR spectrum of compound **20m** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680



^{1}H NMR spectrum of compound **20n** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **20n** (100 MHz, $CDCl_3$)

doi:10.6342/NTU201700680