

一. 課程摘要:

課程名稱：光譜分析實驗 (101學年度下CHEM329001、CHEM329002)

英文名稱：Spectroscopy and Analytical Chemistry Laboratory

任課教師：陳建添 教授

實驗講師：週二班 詹京琳、林容靖；週五班 陳韋禎、廖格港

上課時間：T5 T6 T7 T8、F1 F2 F3 F4 (有機實驗室)

教室：有機實驗室

分機號碼：35651

二. 課程說明:

教導修課同學操作簡單的有機金屬合成實驗，並利用mass (MS)、infrared (IR)、nuclear magnetic resonance (NMR)、ultraviolet and photoluminescence (UV-PL) spectra來分析鑑定所合成的化合物。

三. 成績考核:

1.實驗報告: 預報 15 % (藥品性質、實驗步驟、注意事項)

結報50% (實驗紀錄、觀察、實驗產率、光譜分析)。

2.期末考: 20%

3.實驗態度: 15%。

六. 注意事項:

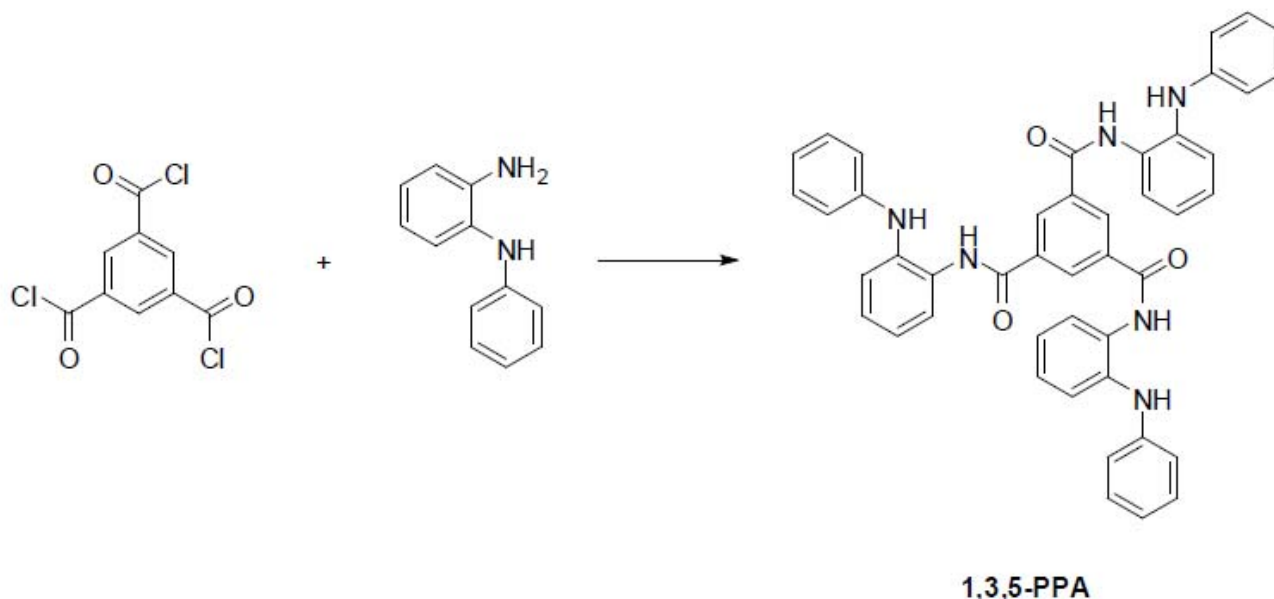
1.請每位同學準備一本A4筆記本，於實驗進行時詳細記錄實驗過程。

2.實驗安全最重要，請遵守實驗室規則。實驗時請穿實驗衣及配戴安全眼鏡。

3.若有其他規定於實驗時再告知。

Part I: Electron Transporting Materials Synthesis of TPBI

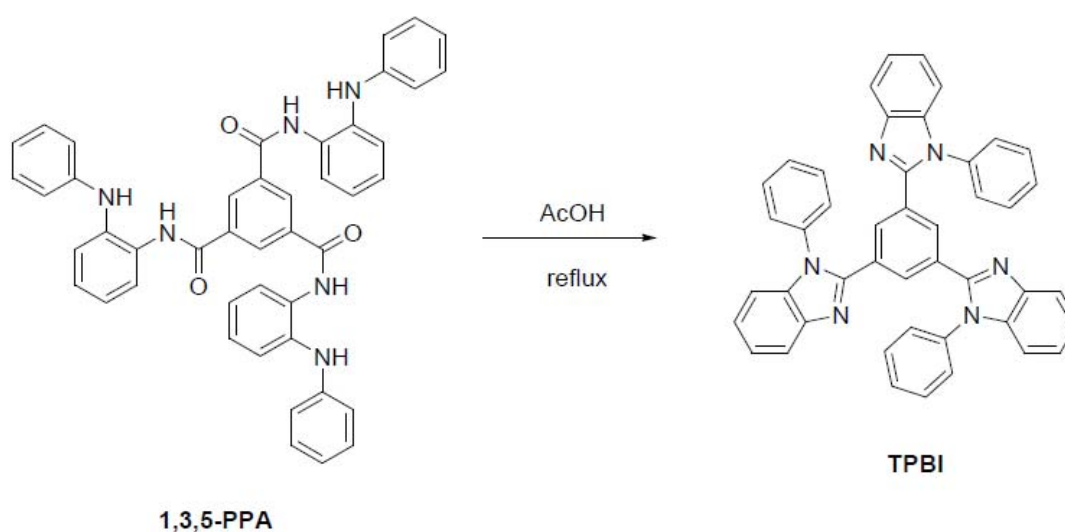
Expt. 1-1: Synthesis of 1,3,5-PPA5



Procedures

The mixture of benzene-1,3,5-tricarbonyl trichloride (0.53 g, 2 mmol), *N*-phenylbenzene-1,2-diamine (1.21 g, 6 mmol), triethylamine (4 mL), and dried THF (80 mL) was stirred for 24 h at room temperature. The solution was poured into water (100 mL) and extracted with dichloromethane. After the solvent was removed, the crude product was recrystallized from methanol and THF to afford a gray solid.

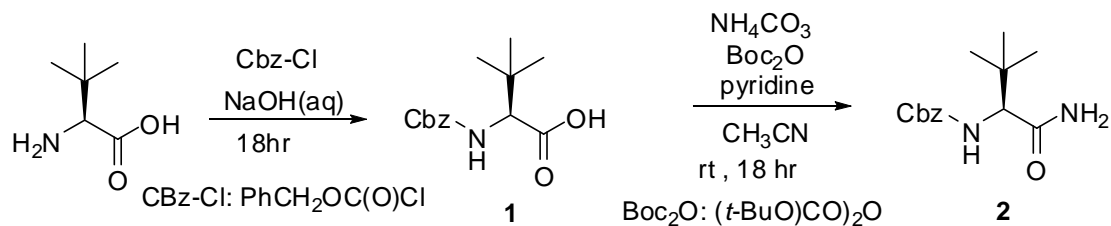
Expt. 1-1: Synthesis of TPBI



Procedures

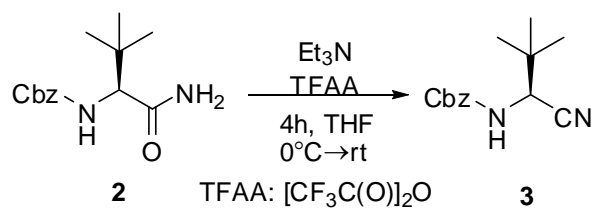
1,3,5-PPA (3.672 g, 10.0 mmol) was refluxed in acetic acid (35 mL) for 12 h before the solvent was removed to give a gray solid.

Part II.
Chiral α -Amino Tetrazole



取一 100 毫升單頸瓶，內置攪拌子，秤第三丁基白胺酸 (1975 毫克，15 毫莫耳，1 當量) 溶於氫氧化鈉水溶液 (24 毫升) 中，攪拌 10 分鐘後，取氯甲酸苄酯 (2.7 毫升，18 毫莫耳，1.2 當量) 注入單頸瓶中，室溫下反應時間 18 小時，用乙醚 (15 毫升 \times 3) 萃取，取水層，加入鹽酸水溶液中中和至 pH 值為 2，接著再用乙酸乙酯 (15 毫升 \times 3) 萃取，取有機層，加入無水硫酸鎂乾燥後過濾，接著利用迴旋濃縮儀和真空幫浦將溶劑移除得到化合物 **1**。

將 **1** (3776 毫克，14.2 毫莫耳，1 當量) 溶於乙腈 (24 毫升，0.6 M) 中，加入吡啶 (3.4 毫升，42.7 毫莫耳，3 當量) 和二碳酸二叔丁酯 (4.3 毫升，18.5 毫莫耳，1.3 當量)，攪拌約 10 分鐘後加入碳酸銨 $(\text{NH}_4)\text{HCO}_3$ (1418 毫克，17.9 毫莫耳，1.26 當量)，會有二氧化碳氣泡產生，通氮氣，攪拌 18 小時後，利用迴旋濃縮儀和真空幫浦將溶劑移除，接著用水洗 (30 毫升 \times 3)，取固體，乾燥過後用丙酮溶解其固體，再用迴旋濃縮和真空幫浦將溶劑移除，即可得到白色固體化合物 **2**。



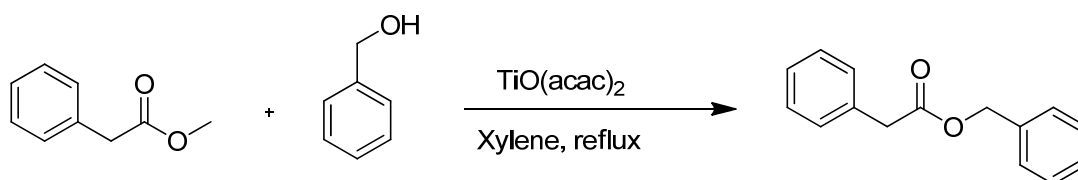
將 **2** (3224 毫克，12.2 毫莫耳，1 當量) 完全溶解於無水四氫呋喃 (15 毫升)，加入無水三乙胺 (10 毫升，73.2 毫莫耳，6 當量) 在冰浴下用針頭滴入無水三氟醋酸酐 (5.1 毫升，36.6 毫莫耳，3 當量)，加入後即可將冰浴移除，溶液呈現黃橘色，在氮氣下攪拌約莫 4 小時，加入水 (10 毫升) 淬息反應，接著用乙醚 (15 毫升 × 3) 萃取，取有機層，加入無水硫酸鎂乾燥後過濾，以迴旋濃縮儀抽乾得粗產物，以管柱層析法純化 (乙酸乙酯/正己烷，1/1) 得黃色油狀物化合物 **3**。收集氫譜、碳譜、IR 和質譜。

Part III.

α -Diazo ester Synthesis

Expt. 2-1:

Benzyl Phenylacetate



Molecular Weight: 226.27

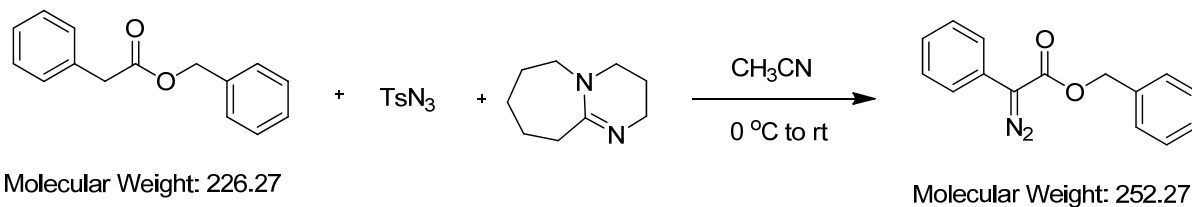
S.No.	Substrate	mw	mmol	Quantity	Equiv.
1.	Ester	150.18	13.3	1.89 mL	1
2.	Benzyl alcohol	108.14	19.97	2.07 mL	1.5
3.	$\text{TiO}(\text{acac})_2$	262.1	0.6	170 mg	0.05

Experimental Procedure:

In a 50-mL, Dean-Stark trap and condenser, then flamed dry flask. To a mixture of methyl ester (13.3 mmol, 1.89 mL), Benzyl alcohol (19.97 mmol, 2.07 mL) and $\text{TiO}(\text{acac})_2$ (0.6 mmol, 170 mg) in 30 mL xylene was refluxed at 145 °C for 10 h (5 hours two times). The resulting mixture was then neutralized by sat. aqueous NaHCO_3 (20 mL) and the mixture was extracted with Ethyl acetate (30 mL \times 3). The organic layer was separated, washed with brine (50 mL), dried over MgSO_4 and evaporated.

Expt. 2-2:

Benzyl α -Diazo-phenylacetate



Experimental Procedure:

S.No.	Substrate	mw	mmol	Quantity	Equiv.
1.	Benzyl ester	226	6.63	1.5 g	1
2.	TsN ₃	197.2	7.96	1.56 g	1.2
3.	1,8-Diaza bicycloundec-7-ene	152.2	9.28	1.39 mL	1.4

In a 50-mL two-necked round-bottomed flask crude benzyl ester (6.63 mmol, 1.5 g) and TsN₃ (7.96 mmol, 1.56 g) was dissolved in 20 mL of CH₃CN. Then 1,8-Diaza bicycloundec-7-ene (9.28 mmol, 1.39 mL) was added dropwise of at 0 °C. The reaction mixture was allowed to stirred at room temperature for 15 h, then neutralized by sat. aqueous NH₄Cl (20 mL) and the mixture was extracted with Ethyl acetate (30 mL \times 3). The organic layer was separated, washed with brine (50 mL), dried over MgSO₄ and evaporated. The crude residue was purified by column chromatography on silica gel (EtOAc/hexanes, 1/5) to give benzyl ester.