Regioselective three-component reactions of enaminones, 2-amino pyridines and enals for the synthesis of 1,2-dihydropyridines

Shuo Cao,[a] Luoting Xin[a] Yunyun Liu,[a] Jie-Ping Wan[a,*] and Chengping Wen[b,*]

[a]*Key Laboratory of Functional Small Organic Molecules, Ministry of Education, and College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P R China. E-mail: wanjieping@gmail.com*

[b]*College of Basic Medical Sciences, Zhejiang Chinese Medical University, Hangzhou, 310053, P R China. E-mail: cpwen.zcmu@yahoo.com*

Contents

General information

Enaminones were synthesized following literature procedure,[1] and all other chemicals were obtained from commercial sources. Reagents were used directly as obtained without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz apparatus. The frequencies for ^{1}H NMR and ^{13}C NMR experiments are 400 MHz and 100 MHz, respectively. The chemical shifts were recored in ppm with TMS as internal standard. An X-4A instrument was employed for measuring melting points of all solid products without temperature correction. HRMS results were obtained

under ESI model.

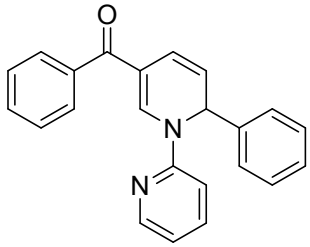
General procedure for the three-component synthesis of 1,2-DHPs

2-Aminopyridine **1** (0.3 mmol), enal **2** (0.3 mmol), enaminone **3** (0.3 mmol) , *p*-TSA (0.3mmol) and AcOH (0.3 mmol) were charged in a 25 mL round bottom flask equipped with a stirring bar. THF (2ml) were added and the mixture was stirred at reflux for 12 h (TLC). Then, the solvents were directly removed from the mixture under reduced pressure.The residue was subjected to flash silicon column chromatography to provide pure products by using mixed ethyl acetate (EA) and petroleum ether (PE) as eluent (V_{PE}/V_{EA} = 6:1).

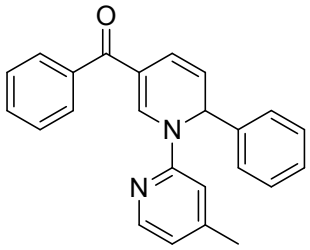
Reference

(1) F. M. A. A. El-Taweel and M. H. Elnagdi, *J. Heterocyclic Chem.,* 2001, **38**, 981.

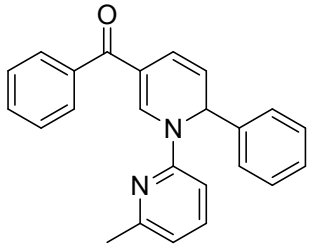
Charaterization data



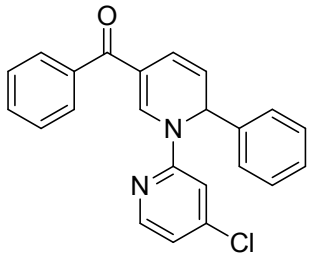
Phenyl(2-phenyl-1-(pyridin-2-yl)-1,2-dihydropyridin-5-yl)methanone (**4a**).Yellow solid; m.p. 60-63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.25 (d, *J* = 6.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.50~7.42 (m, 6H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.91 (q, *J* = 4.0 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.97 (d, *J* = 5.2 Hz, 1H), 5.75 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 153.4, 148.3, 142.2, 141.8, 139.4, 138.2, 130.8, 129.1, 128.9, 128.2, 128.0, 125.6, 120.1, 119.2, 118.8, 113.5, 110.4, 59.7; ESI-HRMS: Calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1492; Found: 339.1481.



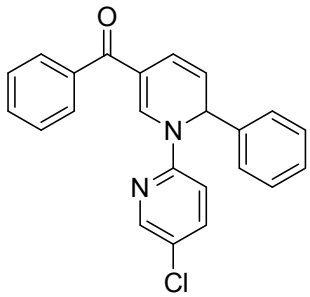
(1-(4-Methylpyridin-2-yl)-2-phenyl-1,2-dihydropyridin-5-yl)(phenyl)methanone (**4b**). Brown solid; m.p. 64-66°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.10 (d, *J* = 4.8 Hz, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.48~7.42 (m, 5H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.2Hz, 1H), 6.76 (q, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 6.00 (d, *J* = 4.8 Hz, 1H), 5.73 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 153.7, 149.7, 147.9, 142.3, 139.5, 130.9, 129.9, 129.1, 129.0, 128.2, 128.0, 125.7, 120.3, 119.9, 119.4, 113.4, 111.1, 59.6, 21.4; ESI-HRMS: Calcd for $C_{24}H_{21}N_2O$ $[M+H]^+$: 353.1648; Found: 353.1656.



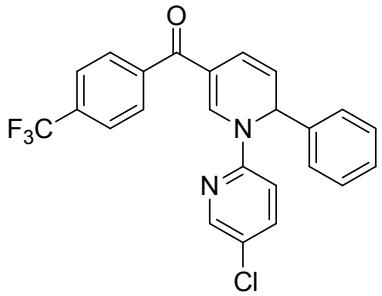
(1-(6-Methylpyridin-2-yl)-2-phenyl-1,2-dihydropyridin-5-yl)(phenyl)methanone (**4c**). Brown solid; m.p. 61-64°C; ^{1}H NMR (400 MHz, CDCl3): δ 8.61 (s, 1H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.49~7.38 (m, 5H), 7.36~7.24 (m, 4H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.99 (d, *J* = 5.2 Hz, 1H), 5.71 (dd, J_1 = 10.0 Hz, J_2 = 5.6 Hz, 1H), 2.39 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 157.5, 152.7, 142.4, 142.3, 139.5, 138.4, 130.7, 129.0, 128.9, 128.1, 127.9, 125.8, 120.0, 119.2, 118.3, 113.0, 107.2, 59.7, 24.2; ESI-HRMS: Calcd for $C_{24}H_{21}N_2O$ $[M+H]^+$: 353.1648; Found: 353.1657.



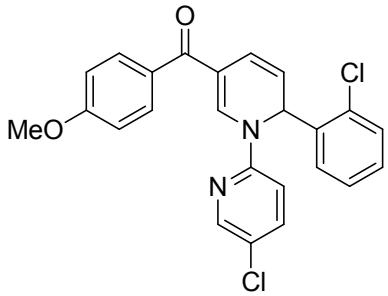
(1-(4-Chloropyridin-2-yl)-2-phenyl-1,2-dihydropyridin-5-yl)(phenyl)methanone (**4d**). Brown solid; m.p. 61-64 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.15 (d, *J* = 5.6 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.49~7.42 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 5.2 Hz, 1H), 6.78 (t, *J* = 8.40Hz, 2H), 5.93 (d, *J* = 5.2 Hz, 1H), 5.77 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 154.6, 149.0, 145.8, 141.5, 140.7, 139.1, 131.1, 129.2, 128.9, 128.3, 125.6, 120.6, 119.1, 118.9, 114.4, 110.4, 59.6; ESI-HRMS: Calcd for $C_{23}H_{18}ClN_2O$ $[M+H]^+$: 373.1102; Found: 373.1111.



(1-(5-Chloropyridin-2-yl)-2-phenyl-1,2-dihydropyridin-5-yl)(phenyl)methanone (**4e**). Brown solid; m.p. 89-92°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.48~7.44 (m, 3H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.75 (t, *J* = 9.6 Hz, 2H), 5.94 (d, *J* = 5.2 Hz, 1H), 5.76 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 151.7, 146.9, 141.7, 141.0, 139.2, 137.9, 131.0, 129.2, 128.9, 128.3, 128.2, 126.3, 125.6, 120.4, 119.1, 113.9, 110.9, 59.9; ESI-HRMS: Calcd for $C_{23}H_{18}ClN_2O$ $[M+H]^+$: 373.1102; Found: 373.1110.

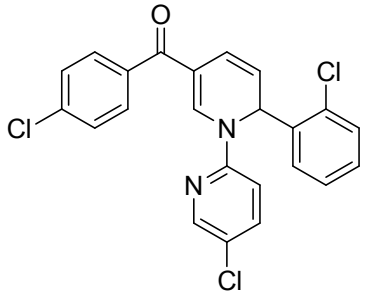


(1-(5-Chloropyridin-2-yl)-2-phenyl-1,2-dihydropyridin-5-yl)(4-(trifluoromethyl)phenyl)methanone (**4f**). Brown solid;m.p. 70-73°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.99 (d, *J* = 5.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 4.8 Hz, 1H), 6.69 (s, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 5.77 (d, *J* = 5.2 Hz, 1H), 5.64 (dd, J_1 = 10.0 Hz, J_2 = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 154.2, 149.0, 145.9, 142.5, 141.4, 141.3, 132.7, 132.3, 129.4, 129.1, 128.4, 125.5, 125.3 (q, *J* = 3.5 Hz), 121.0, 119.3, 118.5, 113.8, 110.6, 59.9; ESI-HRMS: Calcd for $C_{24}H_{17}ClF_3N_2O$ $[M+H]^+$: 441.0976; Found: 441.0981.

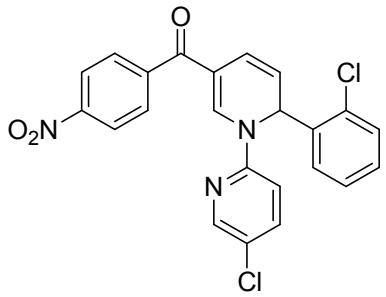


(2-(2-Chlorophenyl)-1-(5-chloropyridin-2-yl)-1,2-dihydropyridin-5-yl)(4-methoxyphenyl)methanone (**4g**). Brown solid; m.p. 63-65°C;^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.69 (s, 1H), 8.15 (d, J = 5.2 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 4.8 Hz, 1H), 7.42 (t, J = 4.4 Hz, 1H), 7.23 (dd, J_1 = 10.0 Hz, J_2 = 6.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 5.2 Hz, 1H), 6.70 (d, J = 10.4 Hz, 2H), 6.28 (d, J = 5.2 Hz, 1H), 5.86 (dd, J_1 = 10.0 Hz, J_2 = 4.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 162.2, 154.1, 149.1, 146.0, 139.8, 139.1, 131.6, 131.1, 130.0, 129.5, 129.4, 128.2, 127.0, 119.9, 118.9, 118.5, 113.7, 113.6, 109.7, 57.0, 55.4; ESI-HRMS: Calcd for $C_{24}H_{19}Cl_2N_2O_2$ $[M+H]^+$: 437.0818; Found: 437.0813.

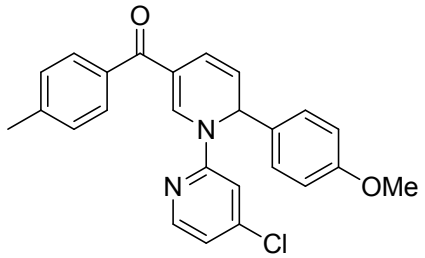


(2-(2-Chlorophenyl)-1-(5-chloropyridin-2-yl)-1,2-dihydropyridin-5-yl)(4-chlorophenyl)methanone (**4h**). Yellow solid;m.p. 98-101°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.16 (d, J = 5.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.47~7.41 (m, 4H), 7.24 (dd, J_1 = 8.8 Hz, J_2 = 4.8 Hz, 2H), 6.94 (d, J = 5.6 Hz, 1H), 6.70 (d, J = 10.0 Hz, 2H), 6.27 (d, J = 4.8 Hz, 1H), 5.86 (dd, J_1 = 10.0 Hz, J_2 = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 153.8, 149.1, 146.1, 140.8, 138.8, 137.4, 137.2, 130.3, 130.0, 129.6, 129.5, 128.6, 128.3, 127.0, 119.2, 118.8, 113.2, 109.9, 57.2; ESI-HRMS: Calcd for $C_{23}H_{16}Cl_3N_2O$ $[M+H]^+$: 441.0323; Found: 441.0310.

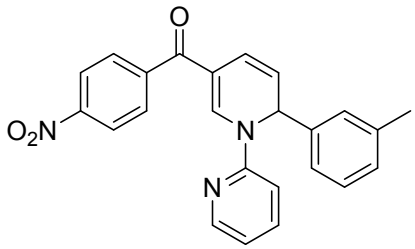


(2-(2-Chlorophenyl)-1-(5-chloropyridin-2-yl)-1,2-dihydropyridin-5-yl)(4-nitrophenyl)methanone (**4i**). Brown solid; m.p. 115-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.34 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 5.2 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.45~7.40 (m, 2H), 7.27~7.25 (m, 2H), 6.97 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz,

1H), 6.72 (d, J = 10.0 Hz, 2H), 6.29 (d, J = 4.8 Hz, 1H), 5.88 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 158.0, 153.4, 149.1, 146.3, 144.9, 141.8, 138.5, 130.1, 129.8, 129.6, 129.5, 128.4, 127.0, 123.6, 119.7, 119.2, 118.5, 112.9, 110.2,57.3; ESI-HRMS: Calcd for $C_{23}H_{16}Cl_2N_3O_3$ $[M+H]^+$: 452.0563; Found: 452.0547.

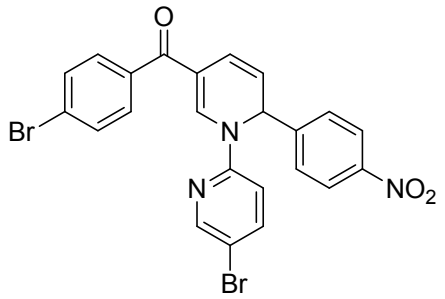


(1-(4-Chloropyridin-2-yl)-2-(4-methoxyphenyl)-1,2-dihydropyridin-5-yl)(*p*-tolyl)methanone (**4j**). Brown solid; m.p. 71-74°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.16 (d, J = 5.2 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 7.6 Hz, 1 H), 6.92~6.87 (m, 3H), 6.82 (s, 1H), 6.76 (d, J = 9.6 Hz, 1H), 5.90 (d, J = 5.2 Hz, 1H), 5.74 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 159.5, 154.7, 148.9, 145.7, 141.6, 140.1, 136.4, 133.8, 129.2, 129.0, 127.2, 120.8, 119.1, 118.8, 114.5, 110.4, 58.8, 55.3, 21.6; ESI-HRMS: Calcd for $C_{25}H_{22}ClN_2O_2$ $[M+H]^+$: 417.1364; Found: 417.1369.

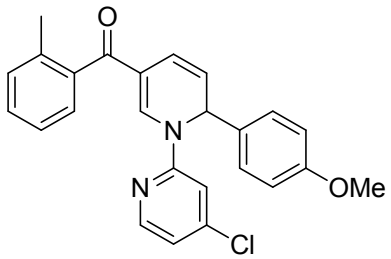


(1-(Pyridin-2-yl)-2-*m*-tolyl-1,2-dihydropyridin-5-yl)(4-nitrophenyl)methanone (**4k**). Brown solid;m.p. 81-83°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.33 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 5.6 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.54 (t, J = 8.8 Hz, 1H), 7.24 (d, J = 6.4 Hz, 1H), 7.18 (s, 2H), 7.11 (d, J = 7.2 Hz, 1H), 6.98 (q, J = 4.0 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 10.0 Hz, 1H), 5.88 (d, J = 4.8 Hz, 1H), 5.75 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 152.9, 149.0, 148.4, 145.4, 142.9, 141.8, 139.1, 138.5, 129.6, 129.2, 129.1,

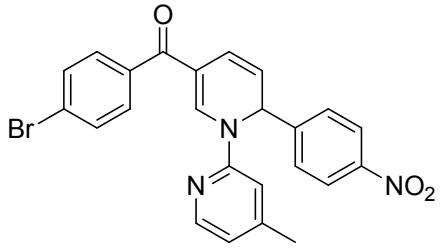
125.9, 123.5, 122.4, 120.8, 119.5 118.0, 112.7, 110.7, 60.4, 21.6; ESI-HRMS: Calcd for $C_{24}H_{20}N_3O_3$ $[M+H]^+$: 398.1499; Found: 398.1497.



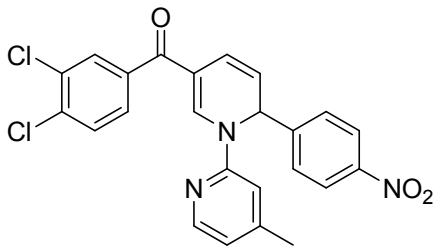
(1-(5-Bromopyridin-2-yl)-2-(4-nitrophenyl)-1,2-dihydropyridin-5-yl)(4-bromophenyl)methanone (**4l**). Brown solid;m.p. 72-75°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 2.4 Hz, 1H), 8.23 (s, 1H), 8.19 (d, J = 8.8 Hz, 2H),7.67(dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 3H), 7.55 (t, J = 7.2 Hz, 3H), 6.76 (q, J = 9.6 Hz, 2H), 6.21 (d, J = 5.2 Hz, 1H), 5.77 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 151.7, 149.3, 148.4, 147.6, 141.0, 140.3, 137.5, 131.7, 130.4, 126.8, 126.0, 124.4, 120.4, 119.3, 114.9, 114.2, 111.3, 58.7; ESI-HRMS: Calcd for $C_{23}H_{16}Br_2N_3O_3$ $[M+H]^+$: 539.9553; Found: 539.9546.



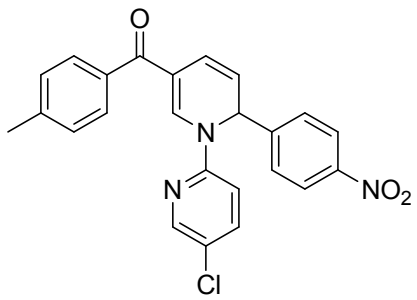
(1-(4-Chloropyridin-2-yl)-2-(4-methoxyphenyl)-1,2-dihydropyridin-5-yl)(2-methylphenyl)methanone (**4m**). Brown solid; m.p. 135-138°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.11 (d, J = 4.8 Hz, 1H), 7.31 (d, J = 8.8 Hz, 4H), 7.23 (d, J = 8.4 Hz, 2H), 6.90~6.84 (m, 3H) , 6.74 (d, J = 12.8 Hz, 2 H) , 5.87 (d, J = 4.8 Hz, 1H), 5.70 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.76 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 159.5, 154.5, 148.9, 145.7, 141.3, 139.4, 135.8, 133.7, 130.8, 129.3, 127.5, 127.2, 125.3, 120.9, 119.0, 118.0, 115.3, 114.5, 110.5, 59.1, 55.3, 19.7 ESI-HRMS: Calcd for $C_{25}H_{22}ClN_2O_2$ $[M+H]^+$: 417.1364; Found: 417.1350.



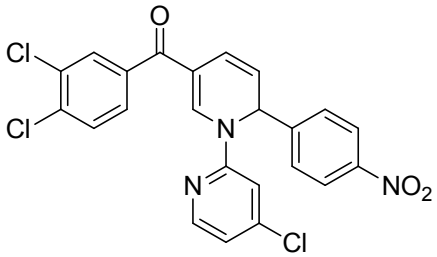
(1-(4-Methylpyridin-2-yl)-2-(4-nitrophenyl)-1,2-dihydropyridin-5-yl)(4-bromophenyl)methanone (**4n**). Brown solid; m.p. 101-104°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.20 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 4.8 Hz, 1H), 7.62~7.54 (m, 6H), 6.82 (t, J = 8.8 Hz, 2H), 6.63 (s, 1H), 6.27 (d, J = 5.2 Hz, 1H), 5.75 (dd, J_1 = 10.0 Hz, J_2 = 5.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 153.4, 150.1, 149.0, 148.1, 147.5, 141.3, 137.9, 131.6, 130.4, 126.8, 125.8, 124.3, 120.8, 118.5, 113.6, 110.9, 58.4, 21.4. ESI-HRMS: Calcd for $C_{24}H_{19}BrN_3O_3$ $[M+H]^+$: 476.0604; Found: 476.0588.



(1-(4-Methylpyridin-2-yl)-2-(4-nitrophenyl)-1,2-dihydropyridin-5-yl)(3,4-dichlorophenyl)methanone (**4o**). Brown solid; m.p. 80-83°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.20 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 4.8 Hz, 1H), 7.78 (s, 1H), 7.57 (t, J = 10.0 Hz, 3H), 7.49 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 5.2 Hz, 1H), 6.78 (d, J = 10.0 Hz, 1H), 6.64 (s, 1H), 6.27 (d, J = 5.6 Hz, 1H), 5.74 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 2.28 (s, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 153.3, 150.2, 148.8, 148.1, 141.6, 138.8, 135.4, 132.9, 130.8, 130.4, 127.9, 126.7, 124.3, 121.0, 120.6, 118.7, 113.3, 111.0, 58.6, 21.4 ESI-HRMS: Calcd for $C_{24}H_{18}Cl_2N_3O_3$ $[M+H]^+$: 466.0720; Found: 466.0721.



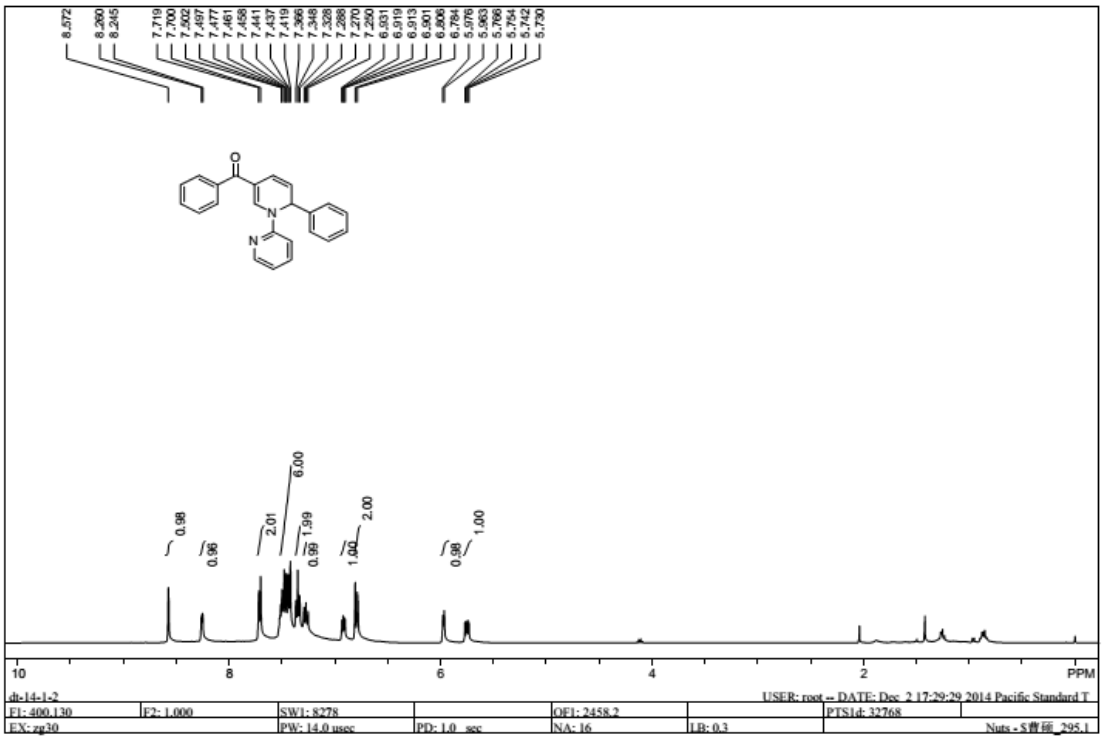
(1-(5-Chloropyridin-2-yl)-2-(4-nitrophenyl)-1,2-dihydropyridin-5-yl)(*p*-tolyl)methanone (**4p**). Brown solid;m.p. 98-101°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 9.2 Hz, 3H), 8.16 (s,1H), 7.61 (d, *J* = 3.6 Hz, 4H), 7.58 (d, *J* = 2.8 Hz, 2H), 7.27 (d, *J* = 9.6 Hz, 1H), 6.83 (d, *J* = 10.0 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.24 (d, *J* = 5.2 Hz, 1H), 5.77 (dd, J_1 = 9.2 Hz, J_2 = 5.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 151.5, 148.7, 147.5, 147.0, 141.9, 139.8, 138.1, 136.0, 129.1, 129.0, 126.9, 126.7, 124.3, 121.0, 119.0, 114.8, 110.7, 58.4, 21.6. ESI-HRMS: Calcd for $C_{24}H_{19}ClN_3O_3$ $[M+H]^+$: 432.1109; Found: 432.1118.

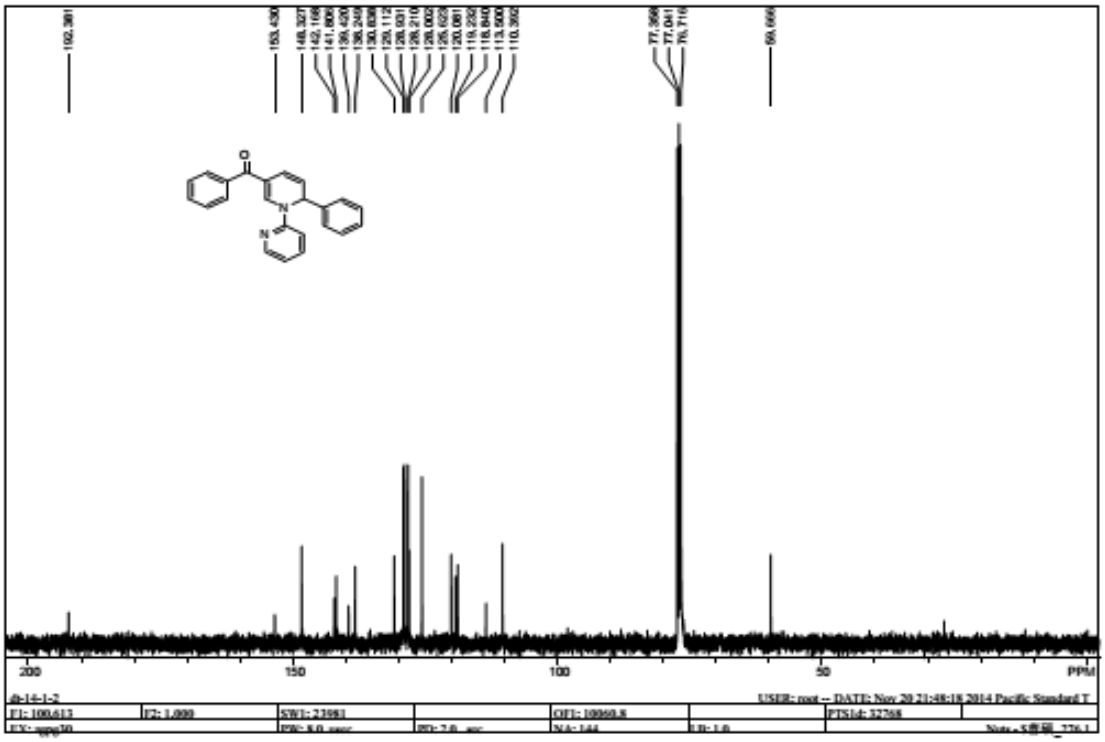


(1-(4-Chloropyridin-2-yl)-2-(4-nitrophenyl)-1,2-dihydropyridin-5-yl)(3,4-dichlorophenyl)methanone (**4q**). Brown solid;m.p. 83-86°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 3H), 7.77 (s, 1H), 7.56 (t, *J* = 8.0 Hz, 3H), 7.49 (t, *J* = 4.0 Hz, 1H), 7.01 (d, *J* = 4.8 Hz, 1H), 6.78 (t, *J* = 9.2 Hz, 2H), 6.19 (d, *J* = 4.8 Hz, 1H), 5.79 (dd, J_1 = 10.0 Hz, J_2 = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 154.0, 149.2, 148.1, 147.7, 146.3, 140.2, 138.4, 135.8, 133.1, 130.8, 130.4, 127.9, 126.7, 124.5, 120.3, 119.8, 119.5, 114.3, 110.4, 58.6, ESI-HRMS: Calcd for $C_{23}H_{15}Cl_3N_3O_3$ $[M+H]^+$: 486.0174; Found: 486.0153.

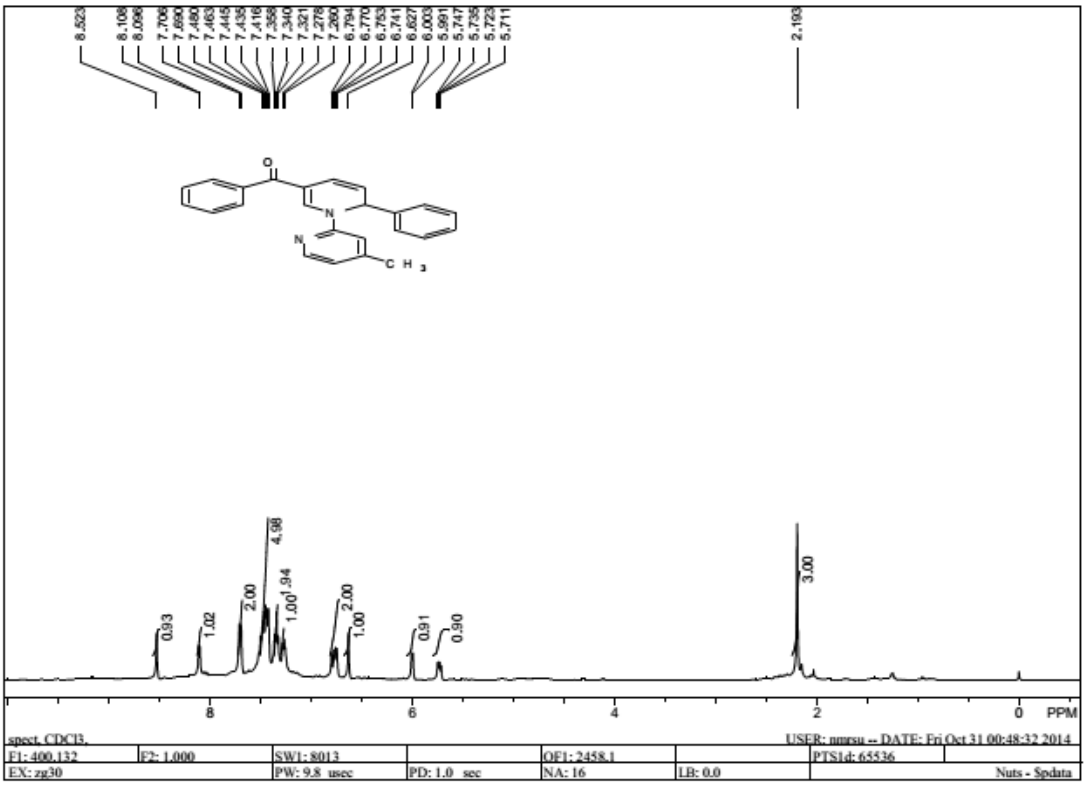
^{1}H and ^{13}C NMR of all synthesized substrates and products

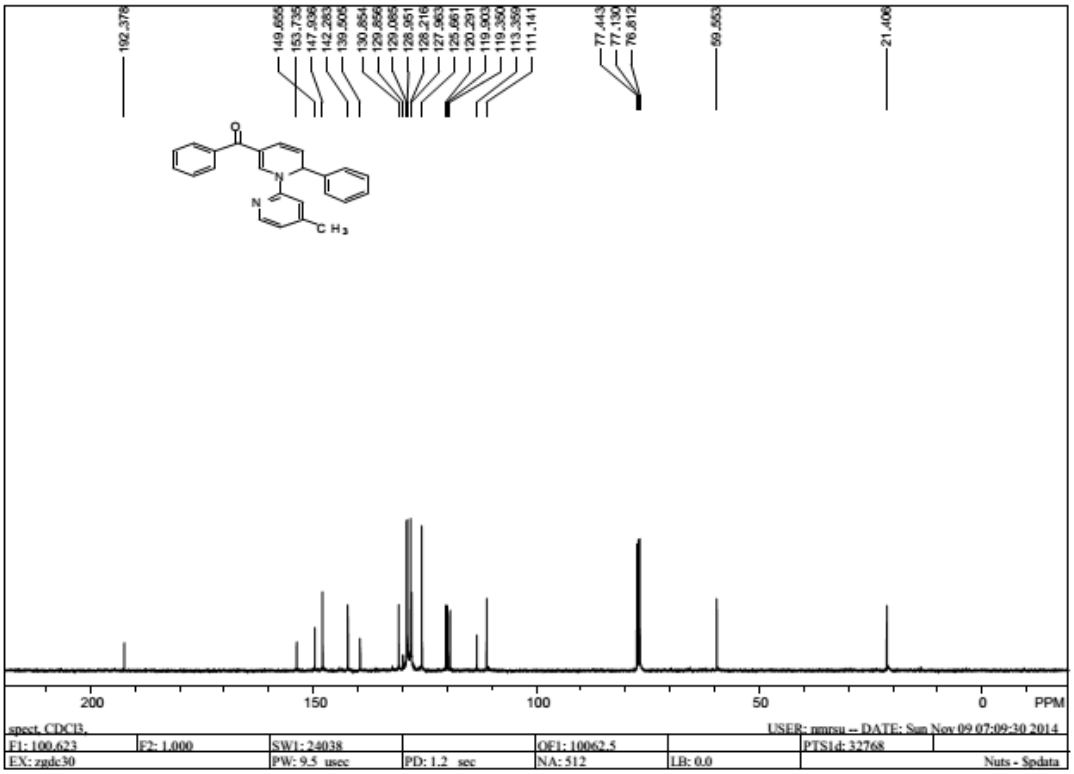
^{1}H and ^{13}C NMR of **4a**



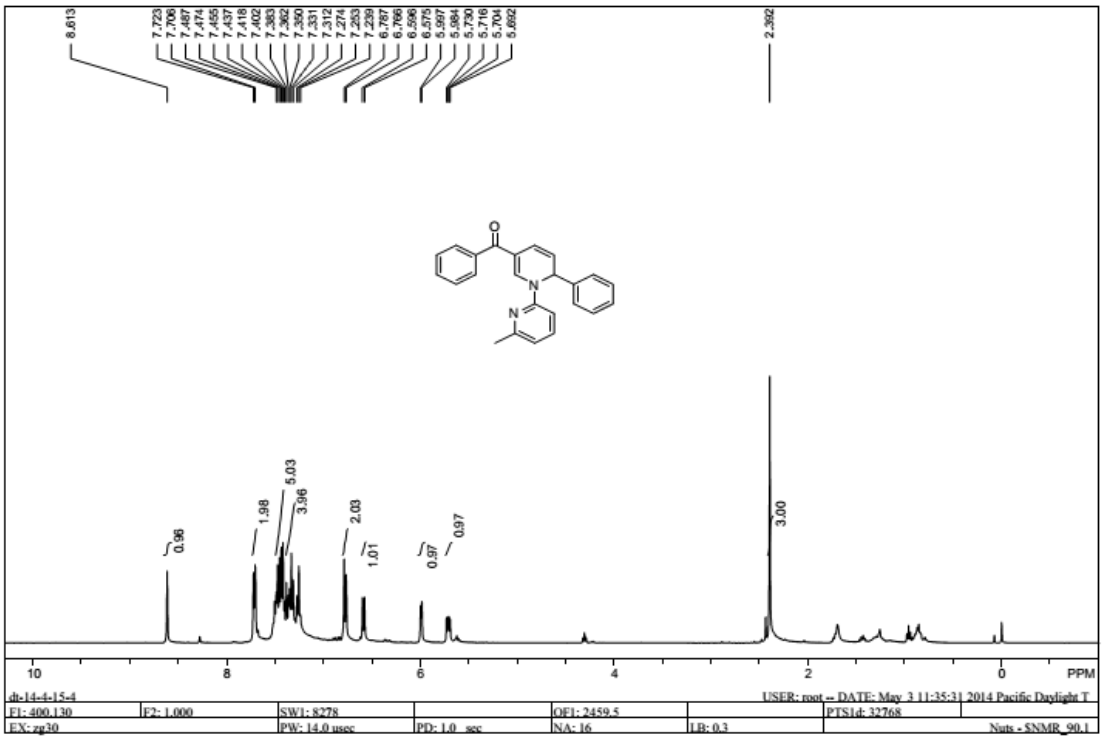


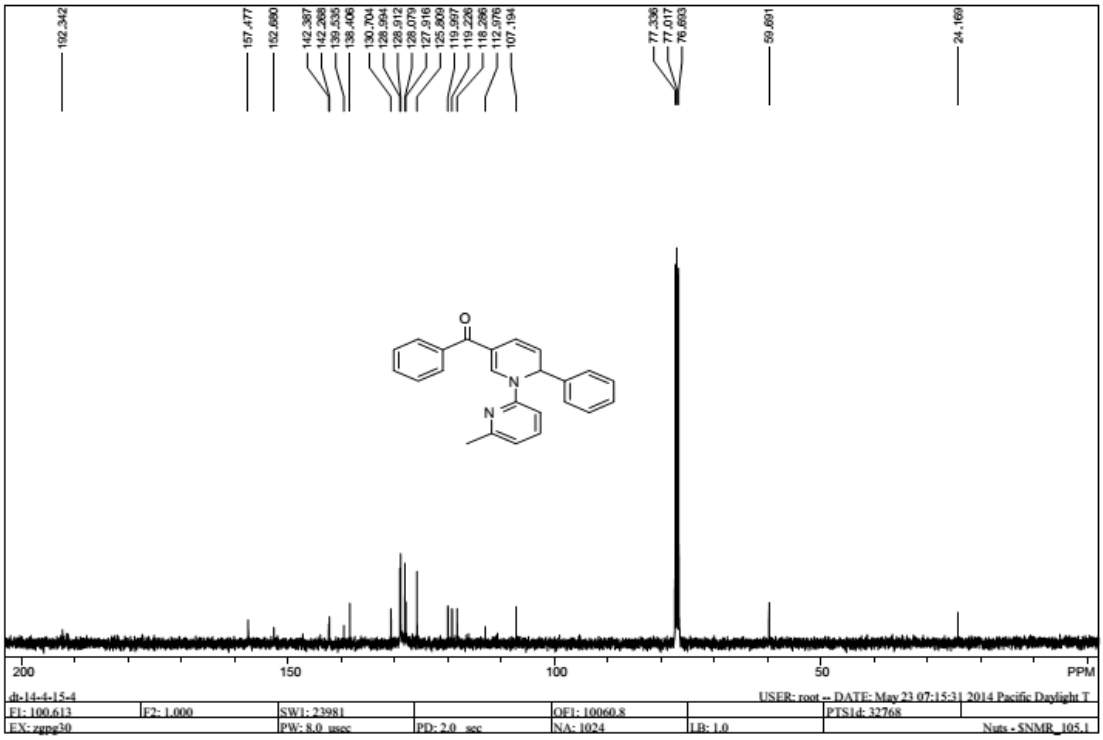
^{1}H and ^{13}C NMR of **4b**



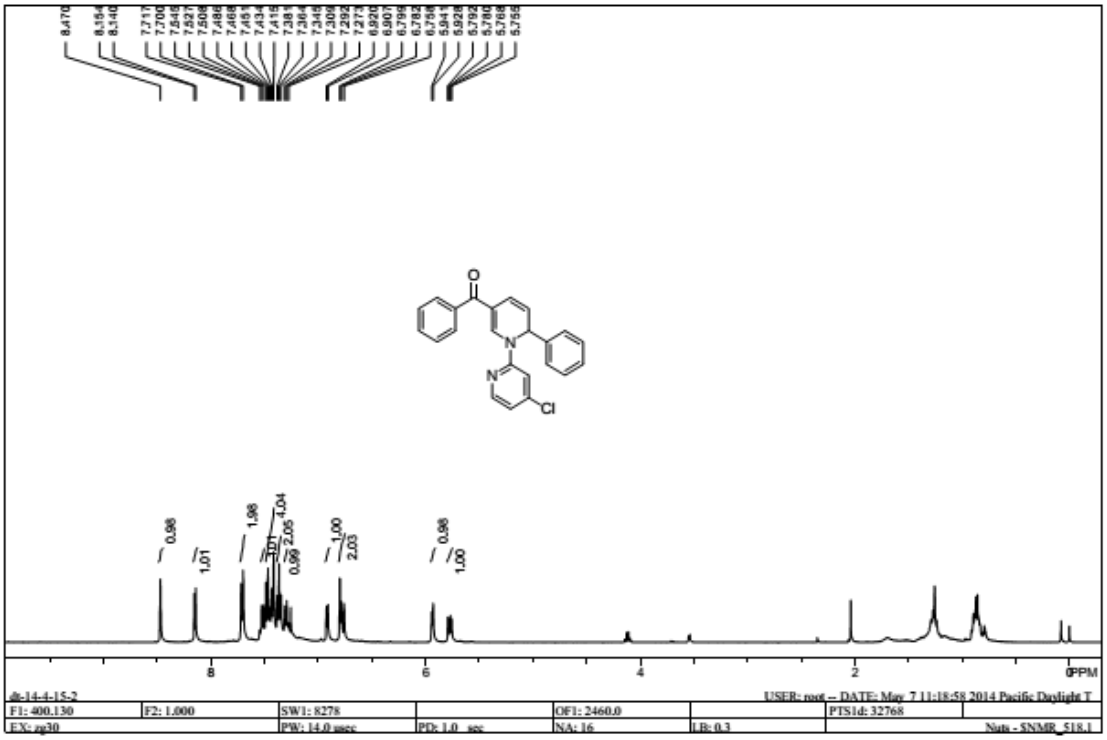


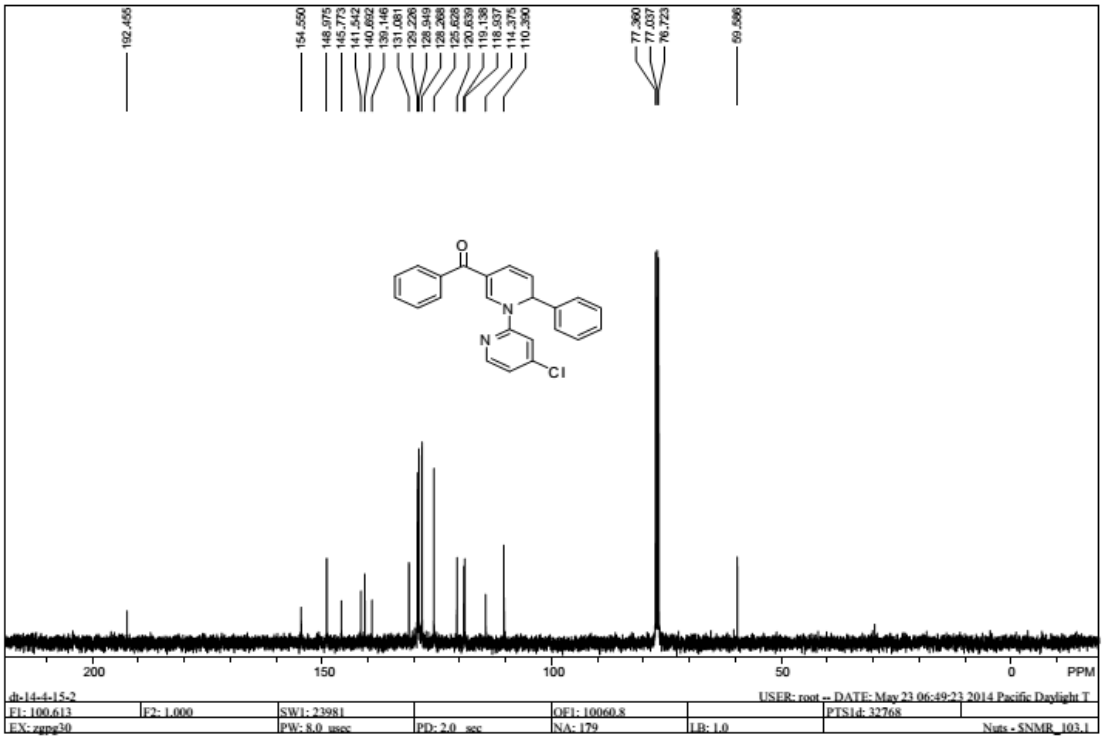
^{1}H and ^{13}C NMR of **4c**



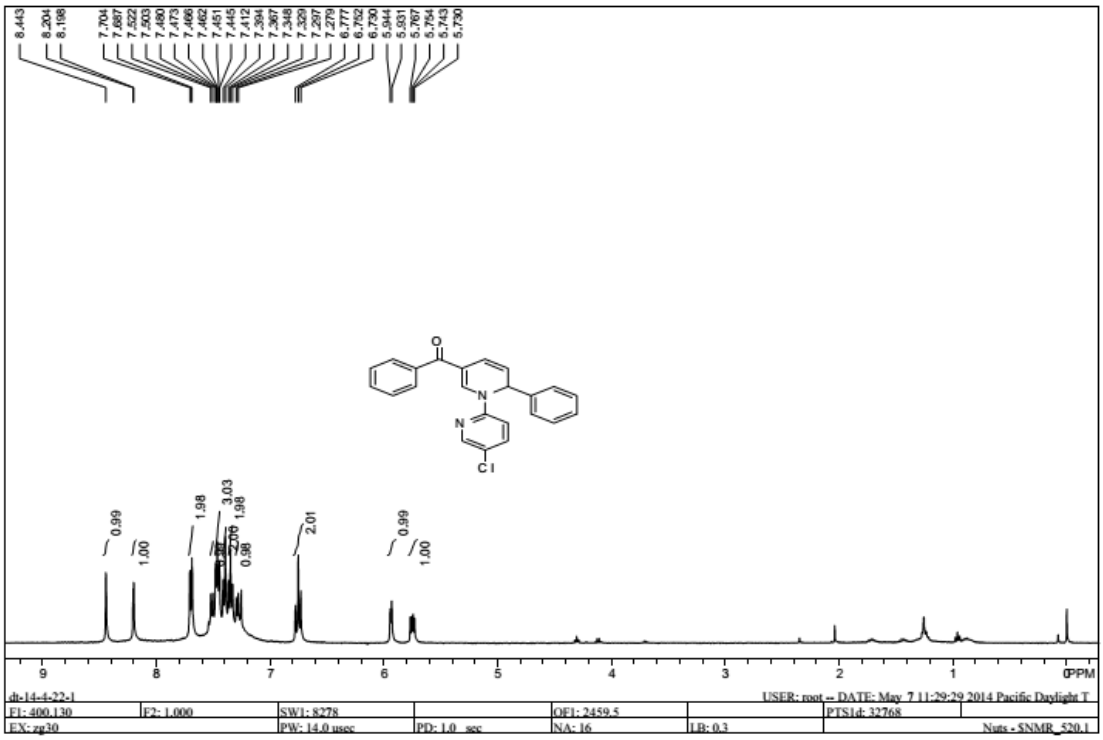


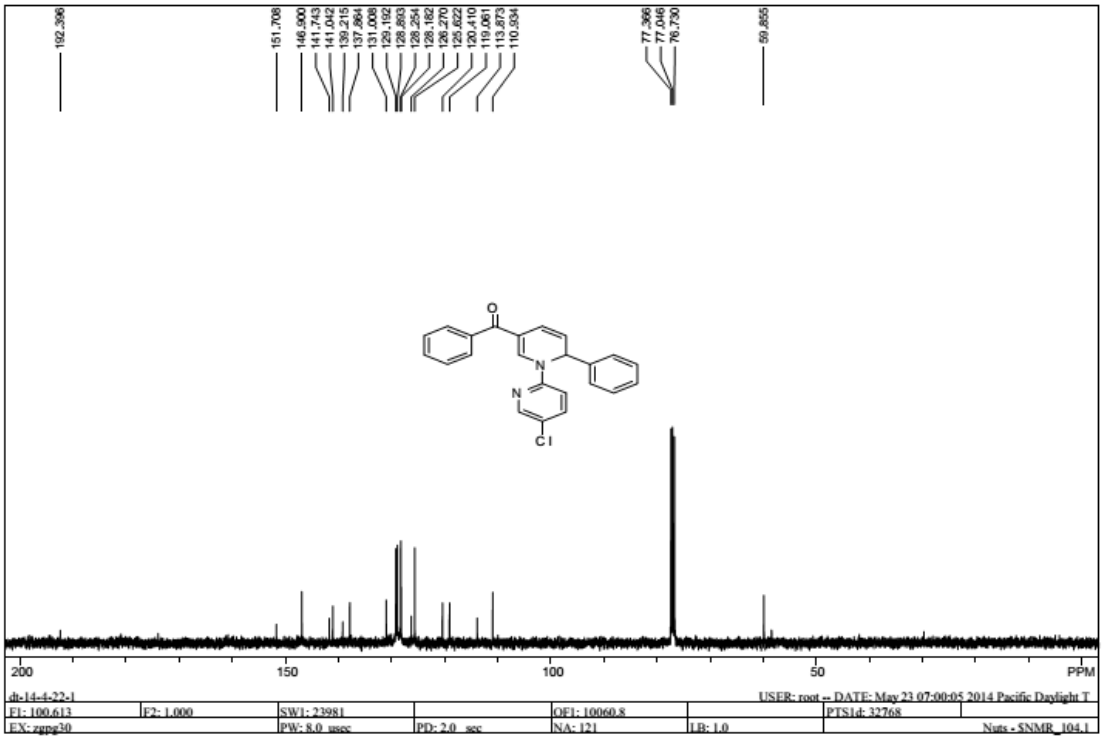
^{1}H and ^{13}C NMR of **4d**



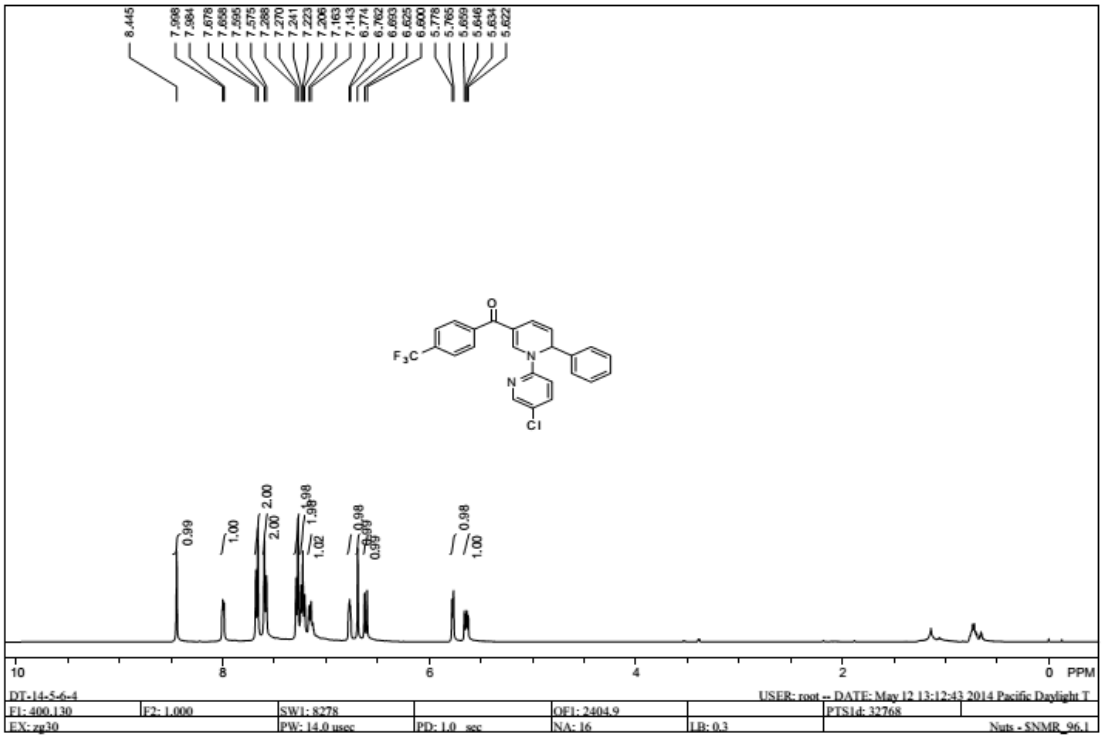


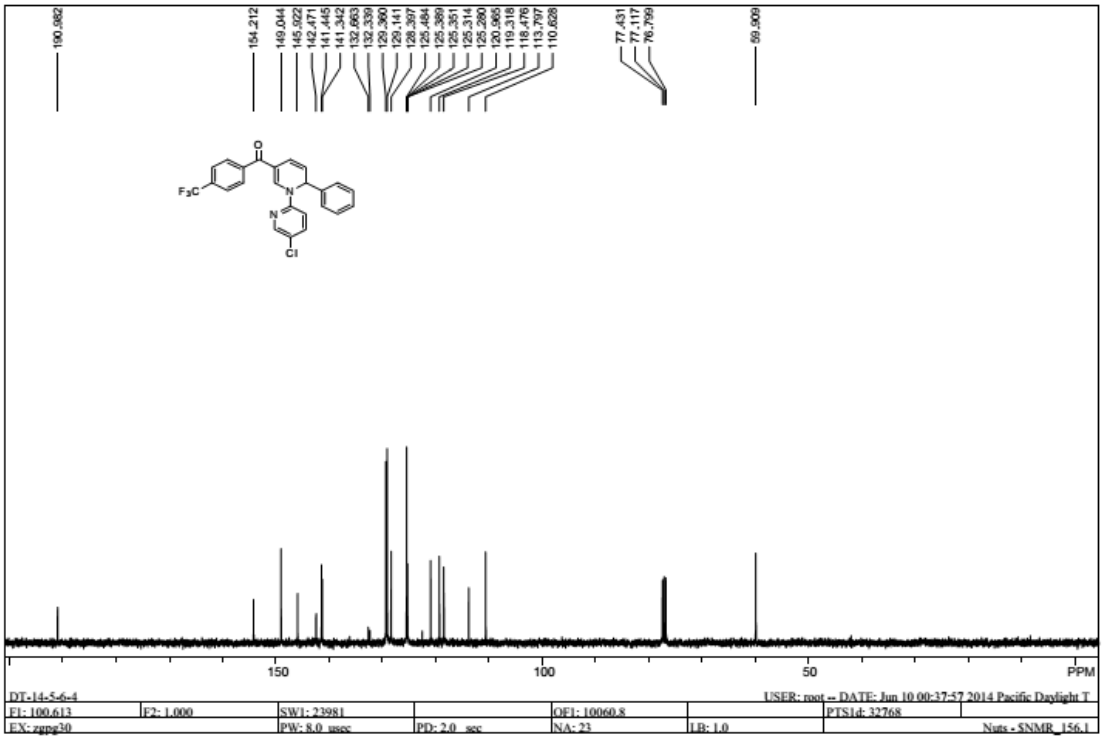
^{1}H and ^{13}C NMR of **4e**



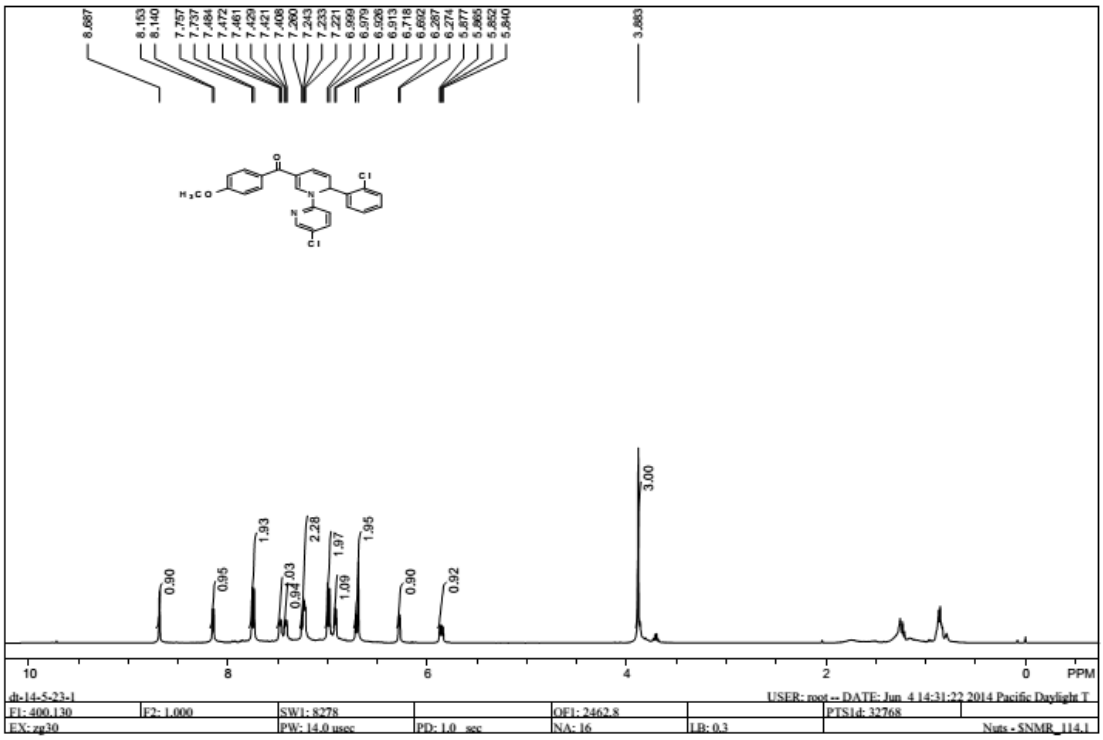


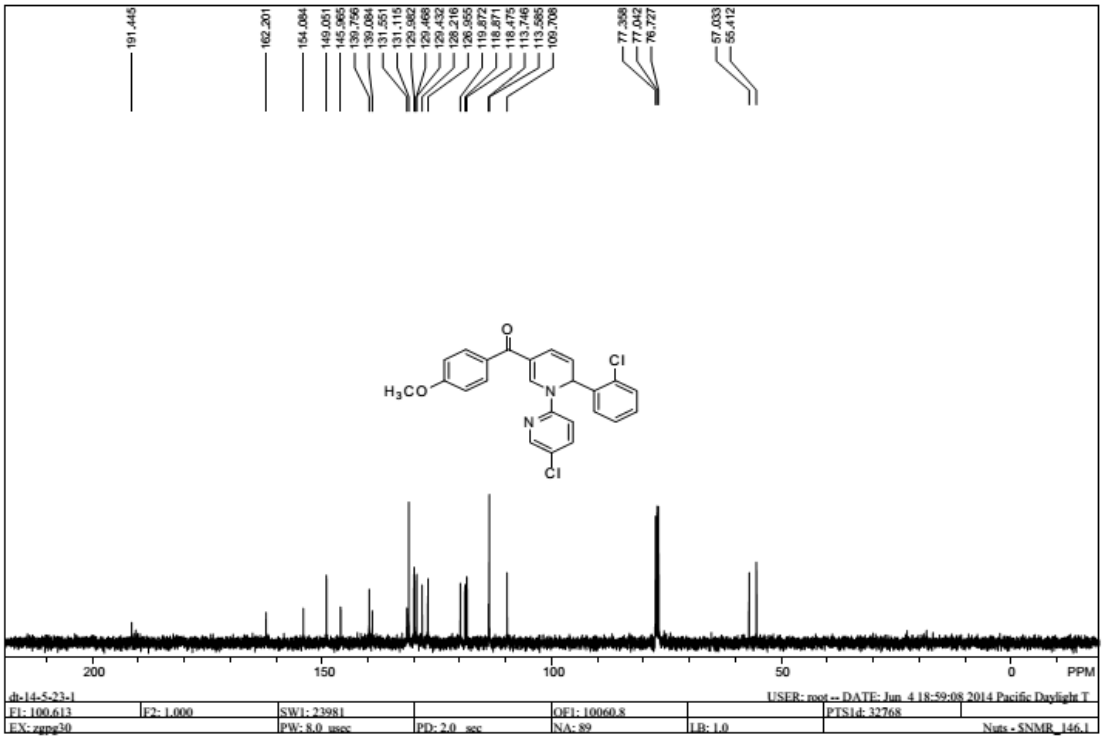
^{1}H and ^{13}C NMR of **4f**



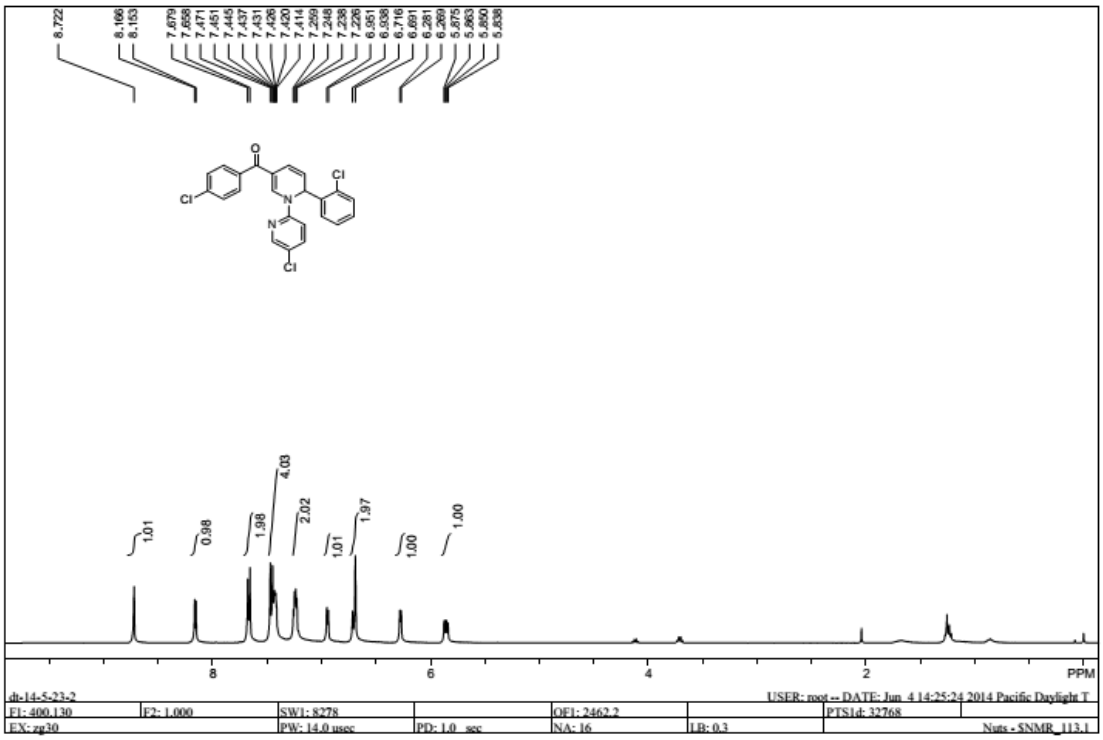


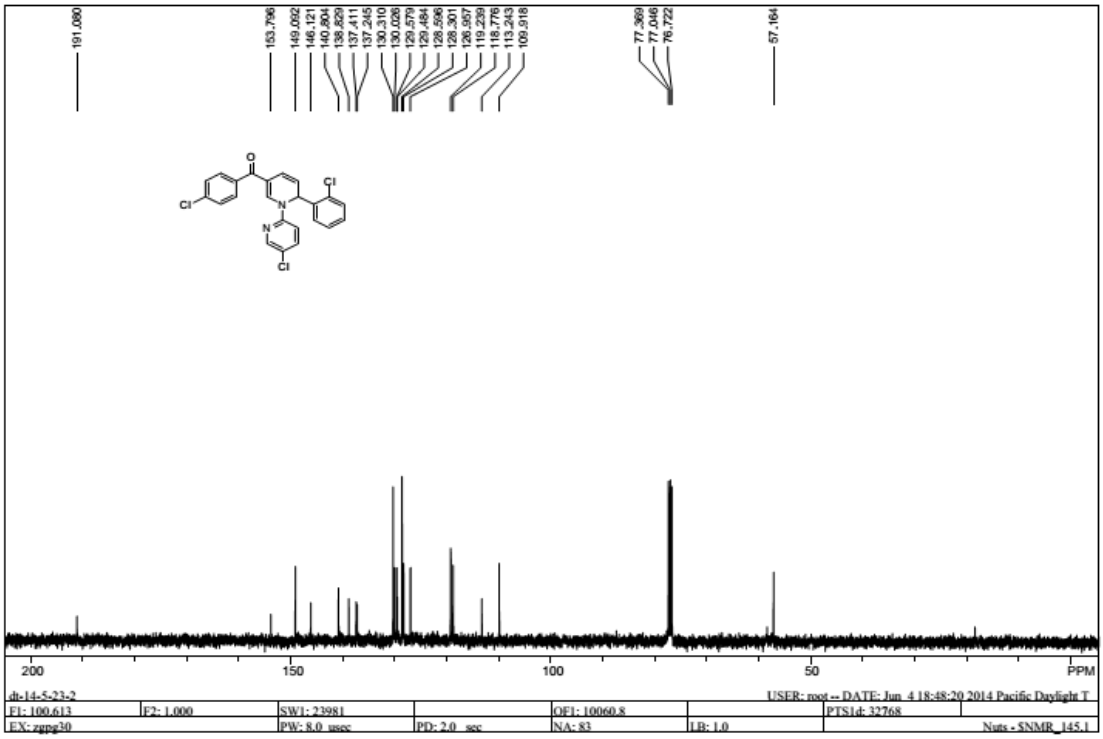
^{1}H and ^{13}C NMR of **4g**



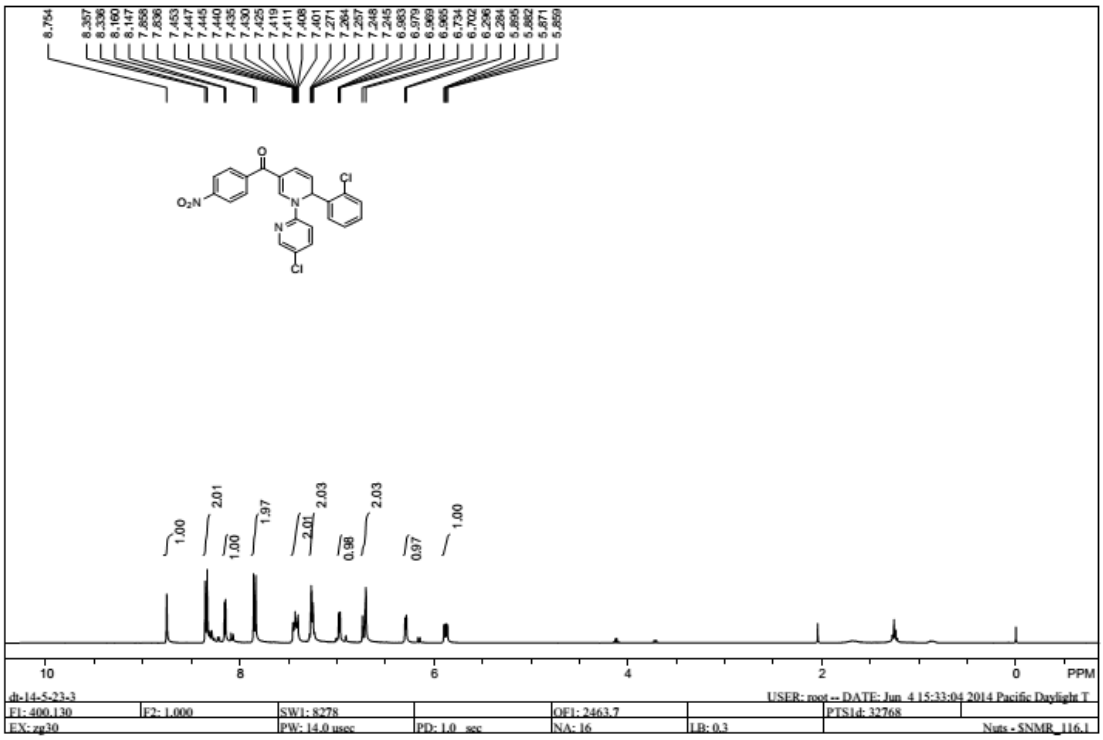


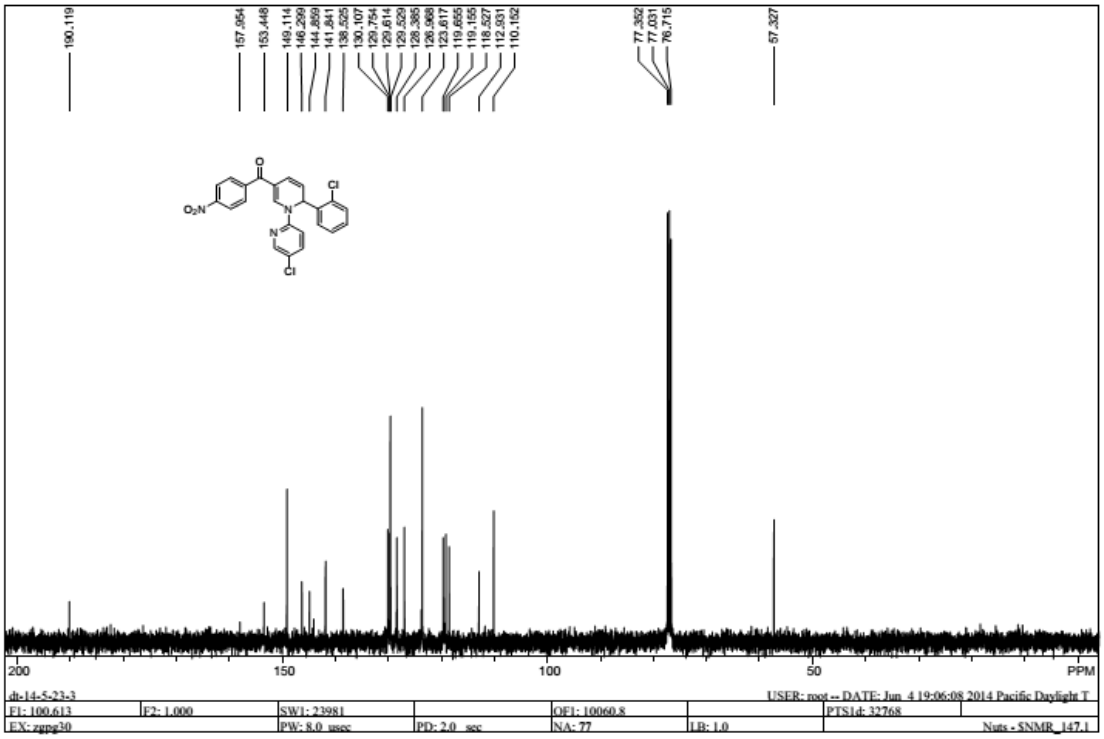
^{1}H and ^{13}C NMR of **4h**



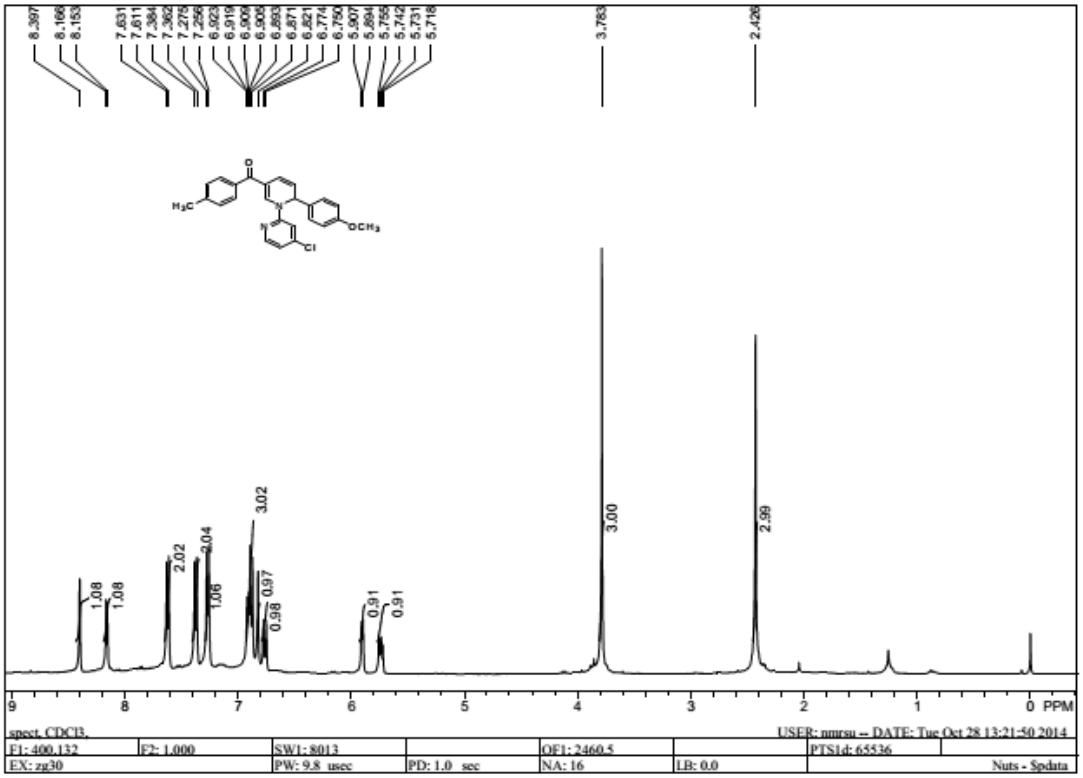


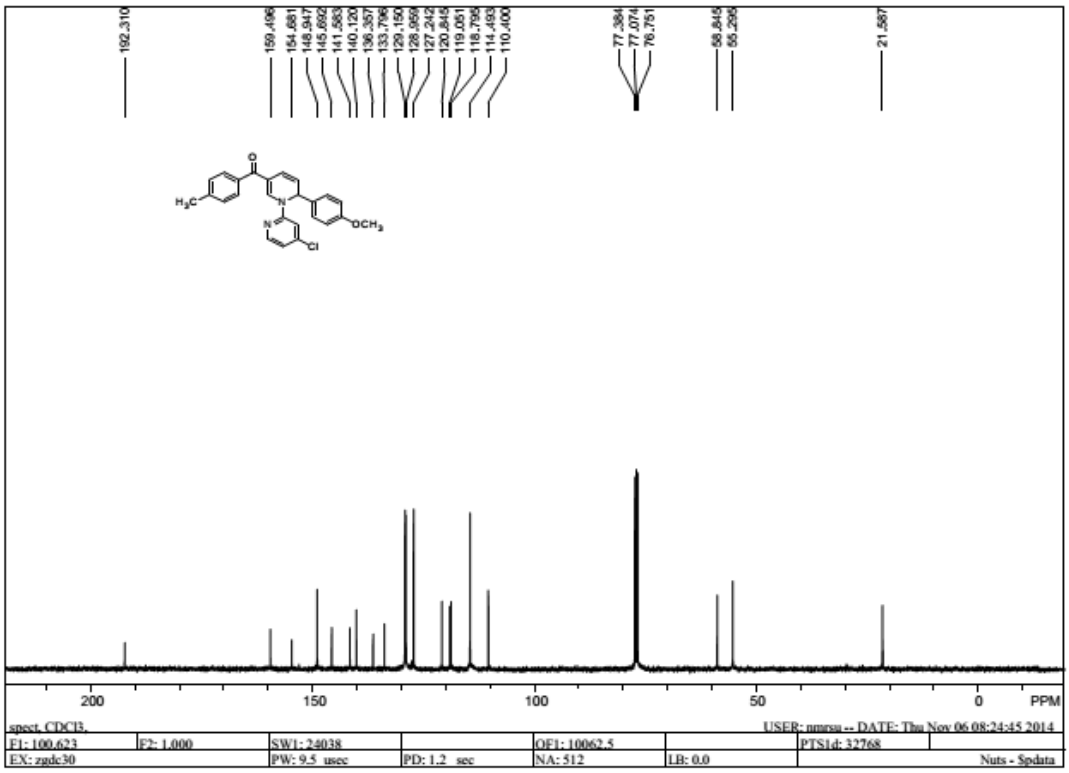
^{1}H and ^{13}C NMR of **4i**



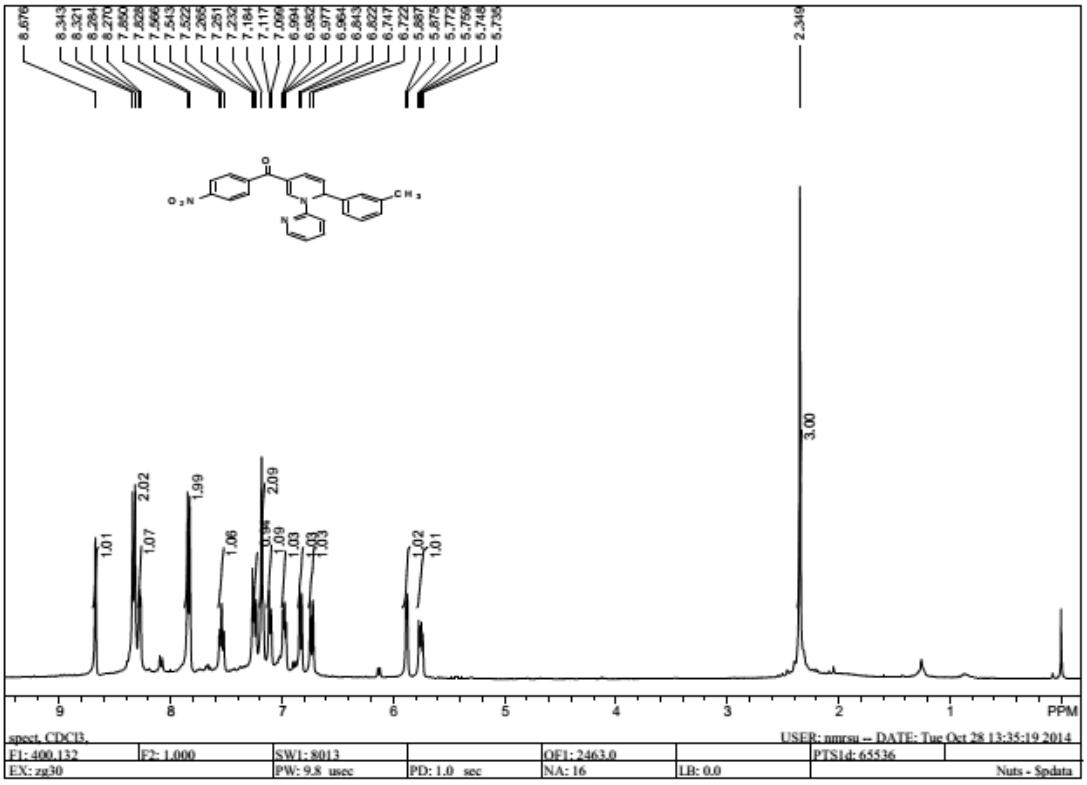


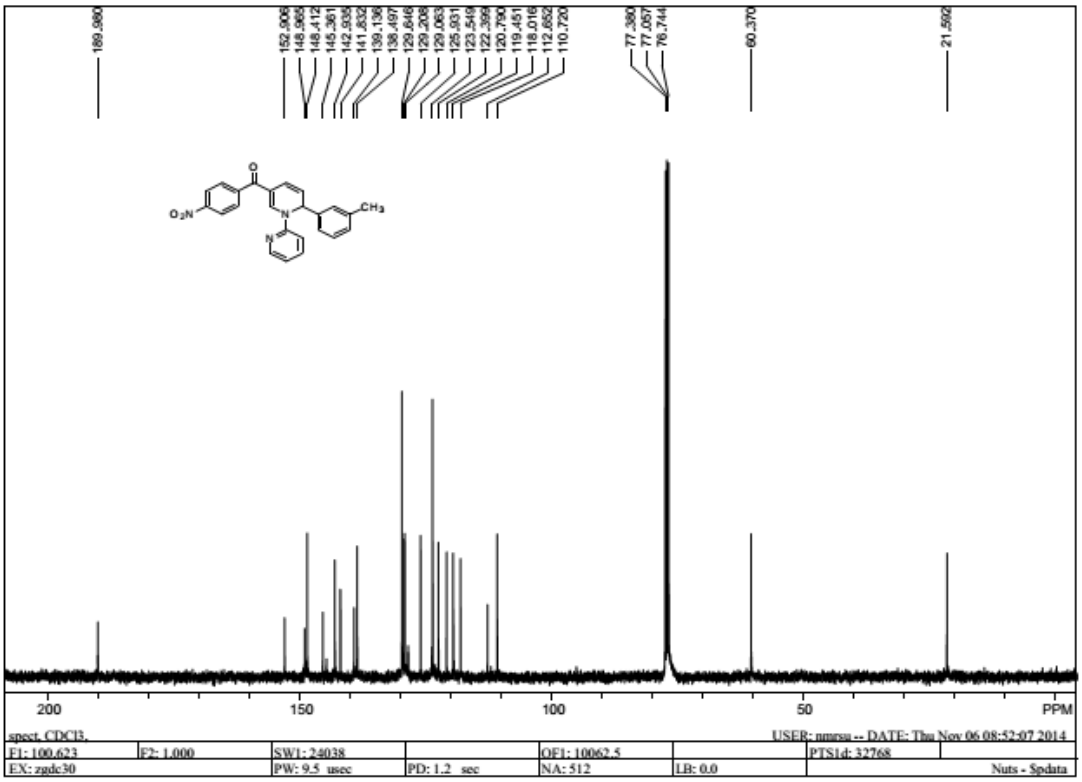
^{1}H and ^{13}C NMR of **4j**



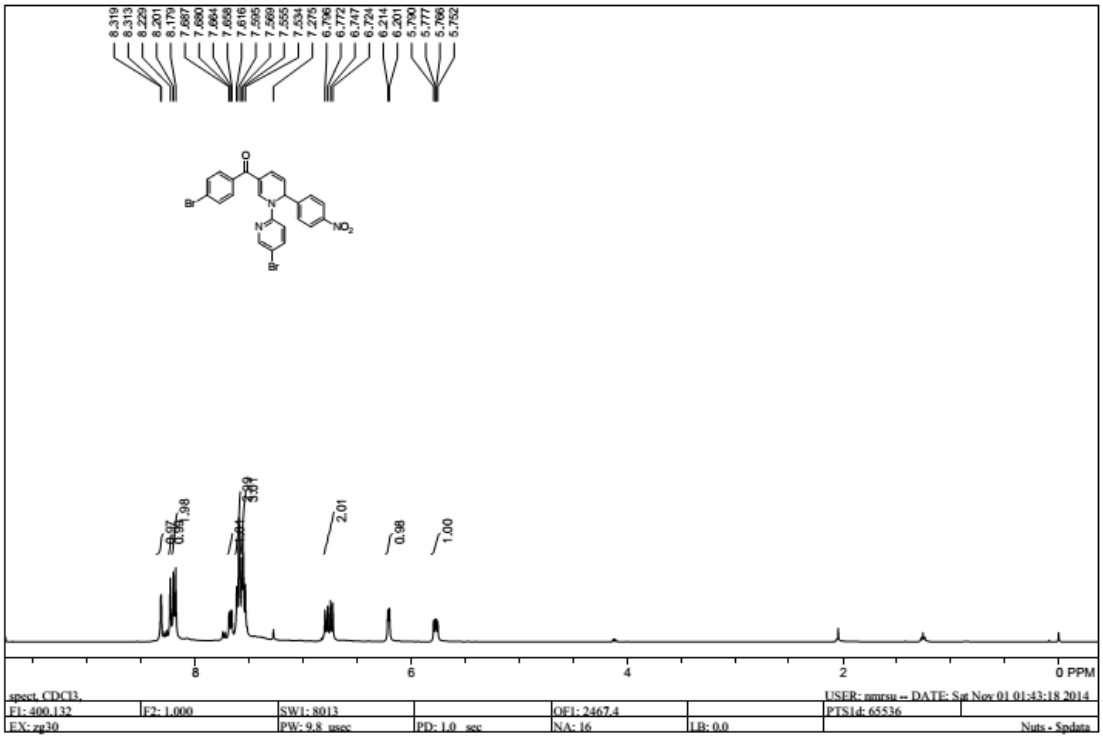


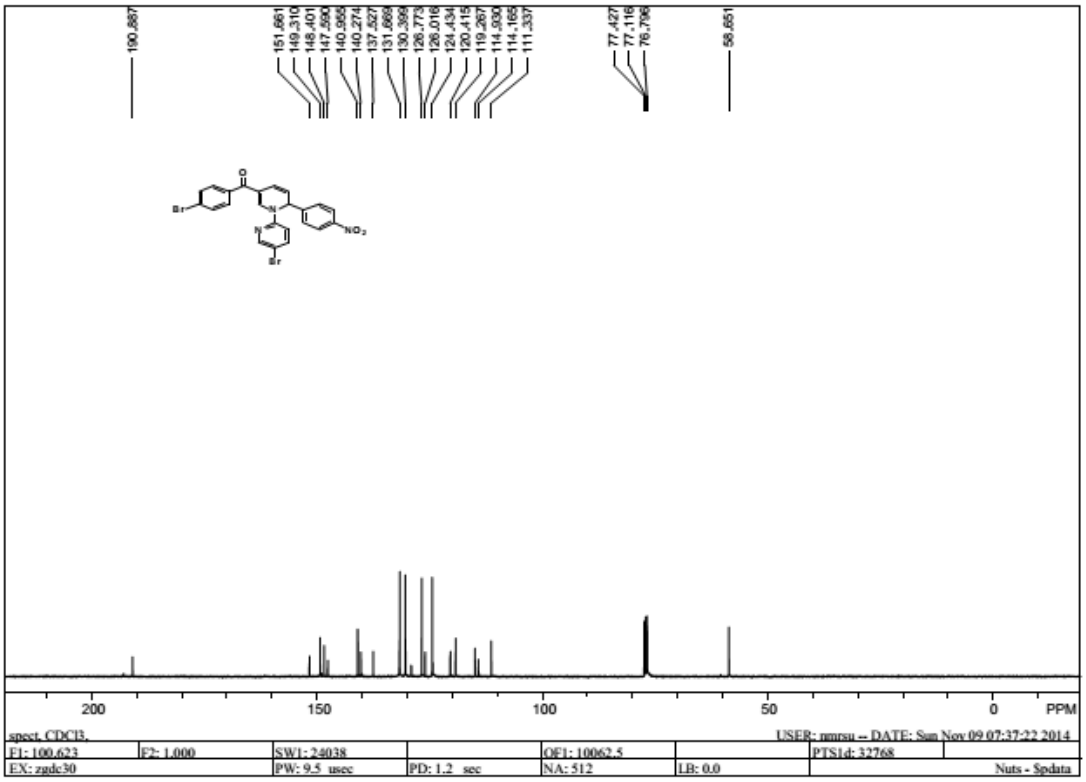
^{1}H and ^{13}C NMR of **4k**



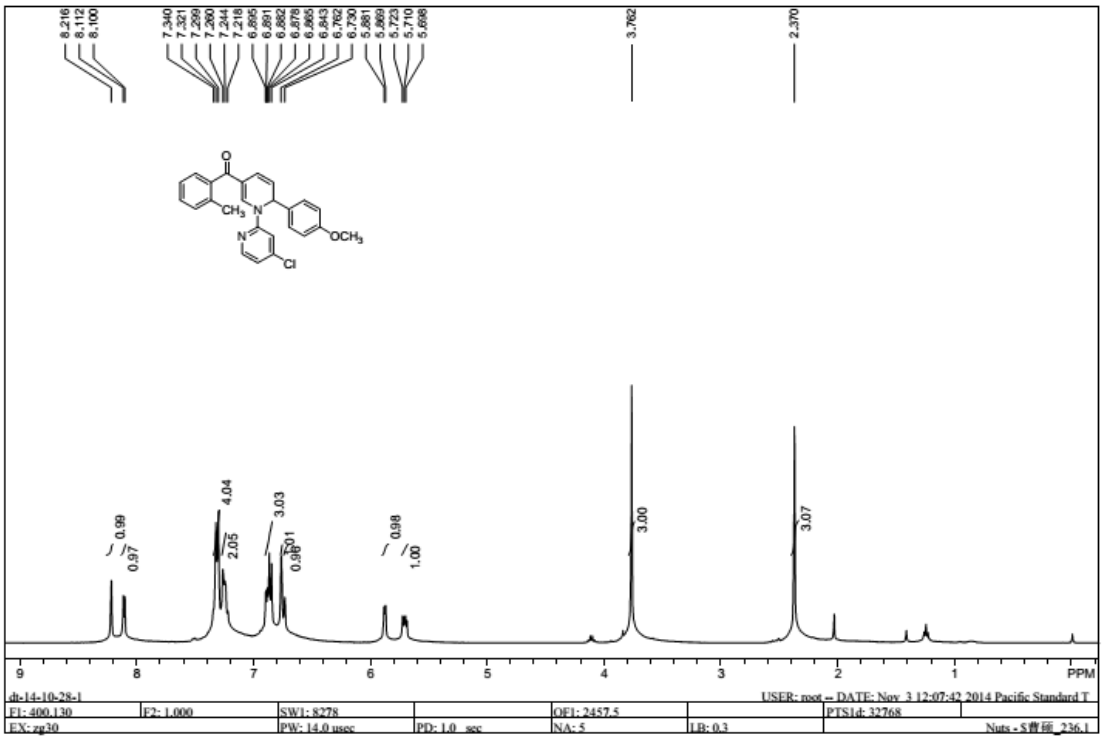


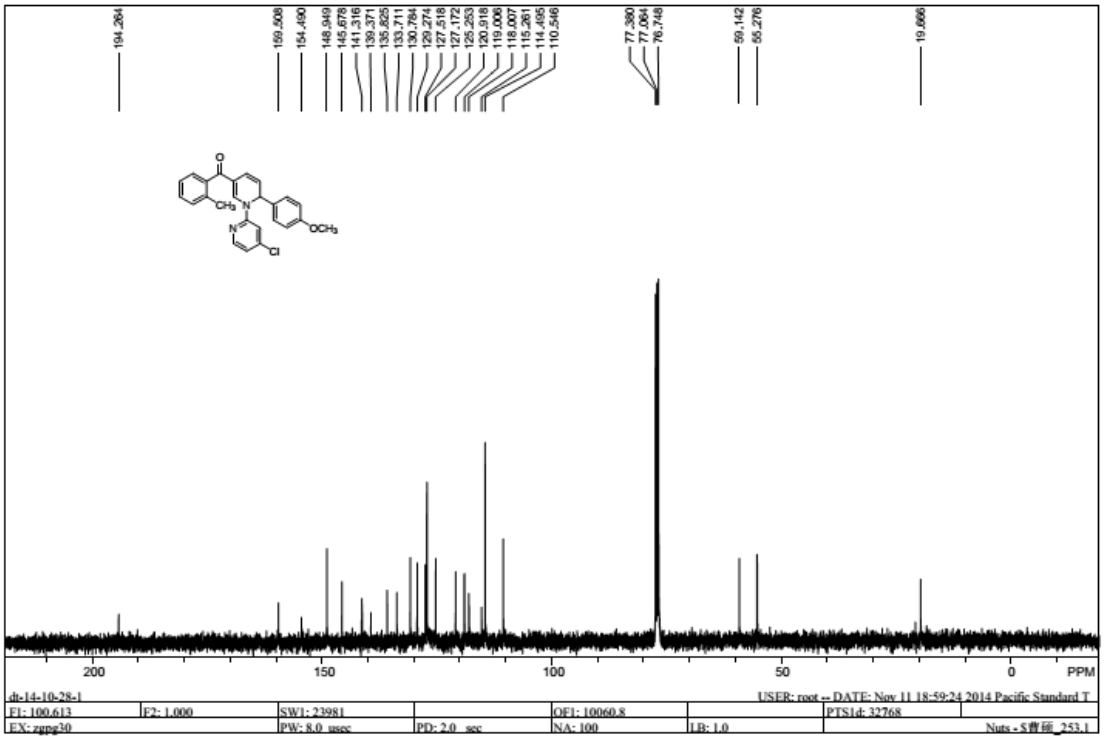
^{1}H and ^{13}C NMR of **4l**



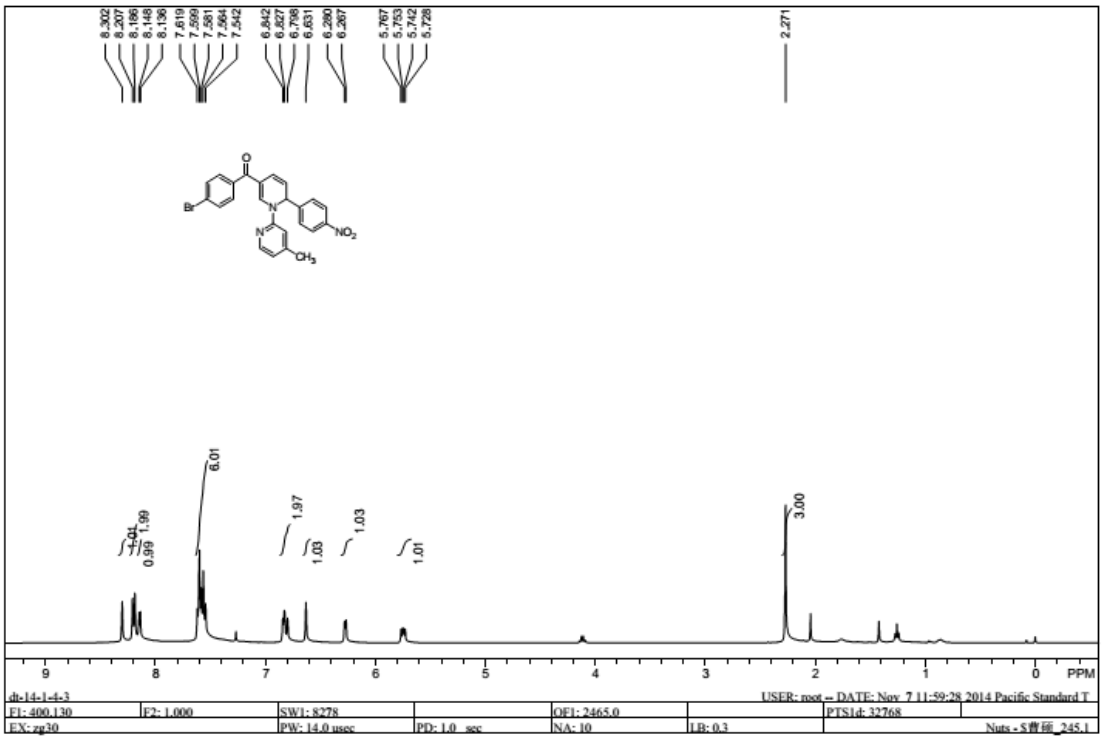


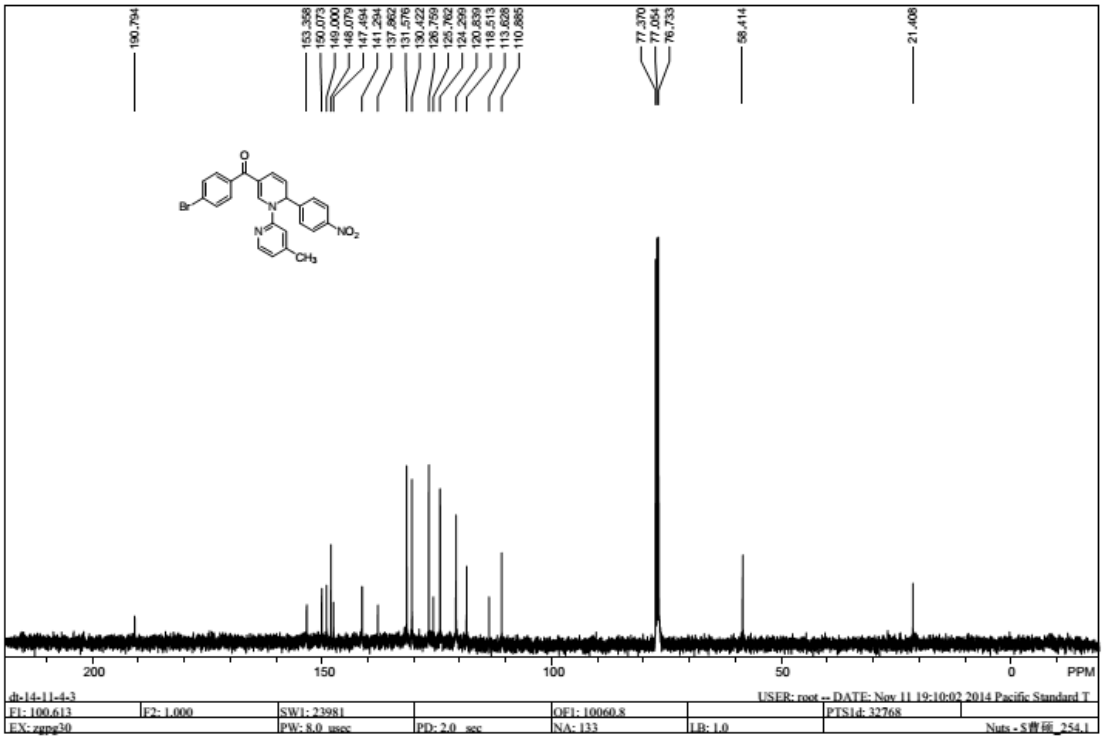
^{1}H and ^{13}C NMR of **4m**



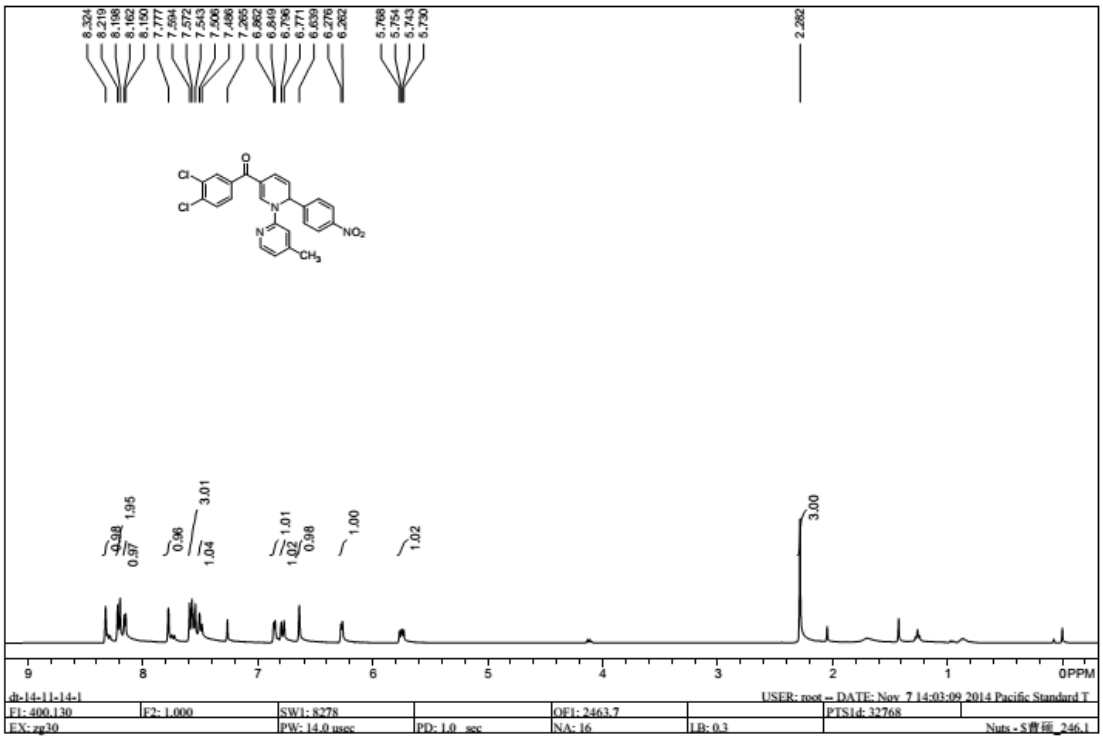


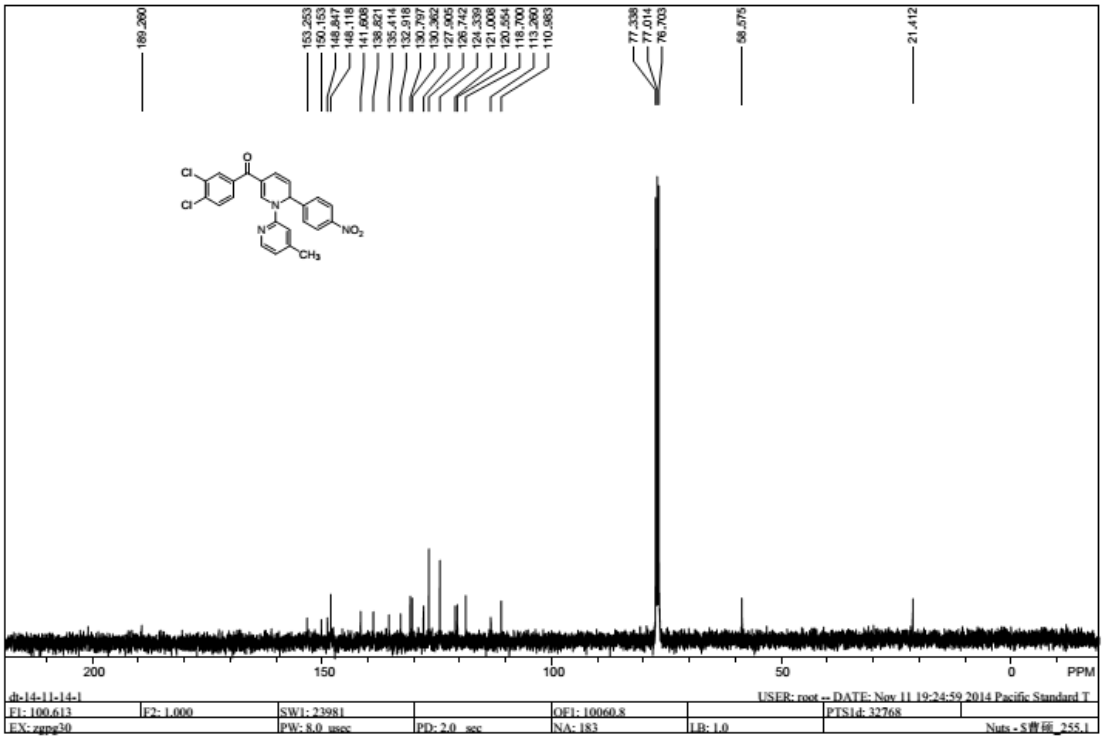
^{1}H and ^{13}C NMR of **4n**



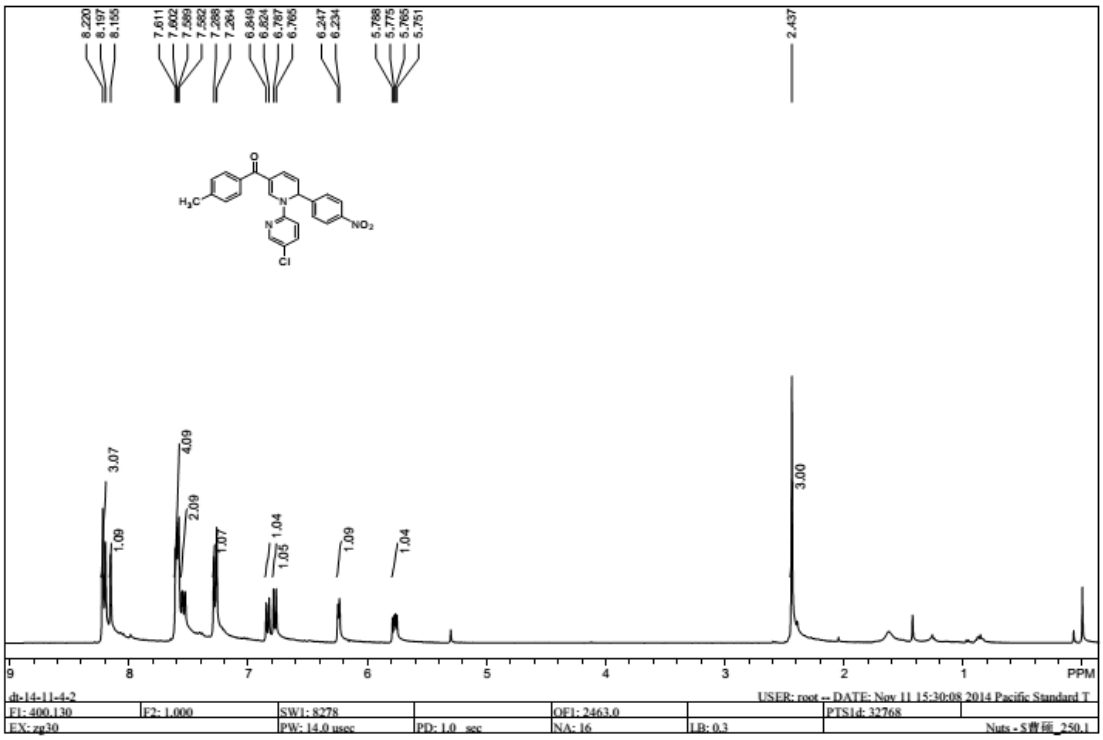


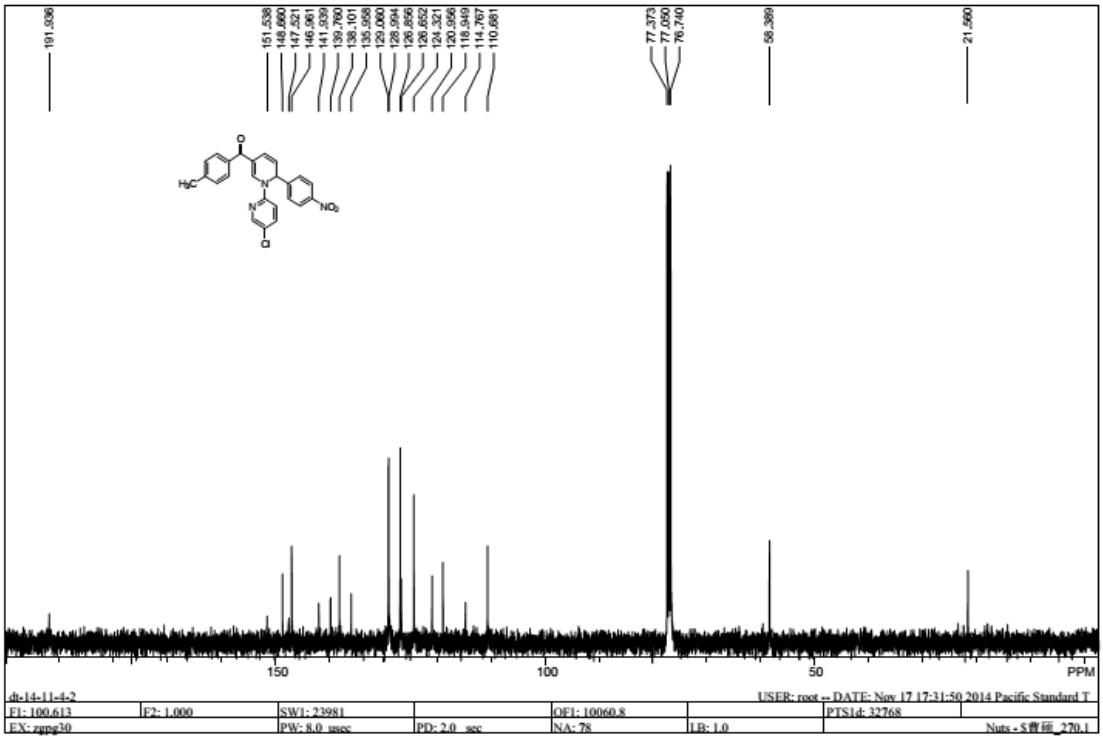
^{1}H and ^{13}C NMR of **4o**





^{1}H and ^{13}C NMR of **4p**





^{1}H and ^{13}C NMR of**4q**