# Supporting Information

## Indium-Mediated Synthesis of Heterobiaryls

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**General procedure.** All reactions were carried out in dried glassware. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. 3-Iodopyridine, 2-iodopyridine, iodobenzene, 2-iodothiophene, 4-iodopyrazole, *tert*-butyllithium, 2-thienyllithium, indium (III) choride, tetrakis(triphenylphosphine) palladium (0) and 3,4-dihydro-2*H*-pyran are commercially available, and were used as received. 5-Iodo-1-methyl-1*H*-pyrazole was prepared according to described procedures.[1]

**Preparation of organolithium compounds.** A commercial solution of *t*-BuLi in pentane (4.2 mmol, 1.7 M) was diluted with dry THF (10 mL) and cooled to -78 ºC. To the resulting solution was slowly added the corresponding aryl iodide (2.1 mmol) in dry THF (2 mL). The mixture was stirred for 2 hours.

**Preparation of organoindium compounds.** A 50 mL round-bottomed flask with a stir bar and indium (III) chloride (0.7 mmol) was dried under a positive argon pressure with a heat gun. After cooling, dry THF (10 mL) was added. The mixture was added to the previously described solution of the organolithium compound at -78 ºC and stirred for 1 hour, the cooling bath was removed, and the reaction mixture was warmed to room temperature.

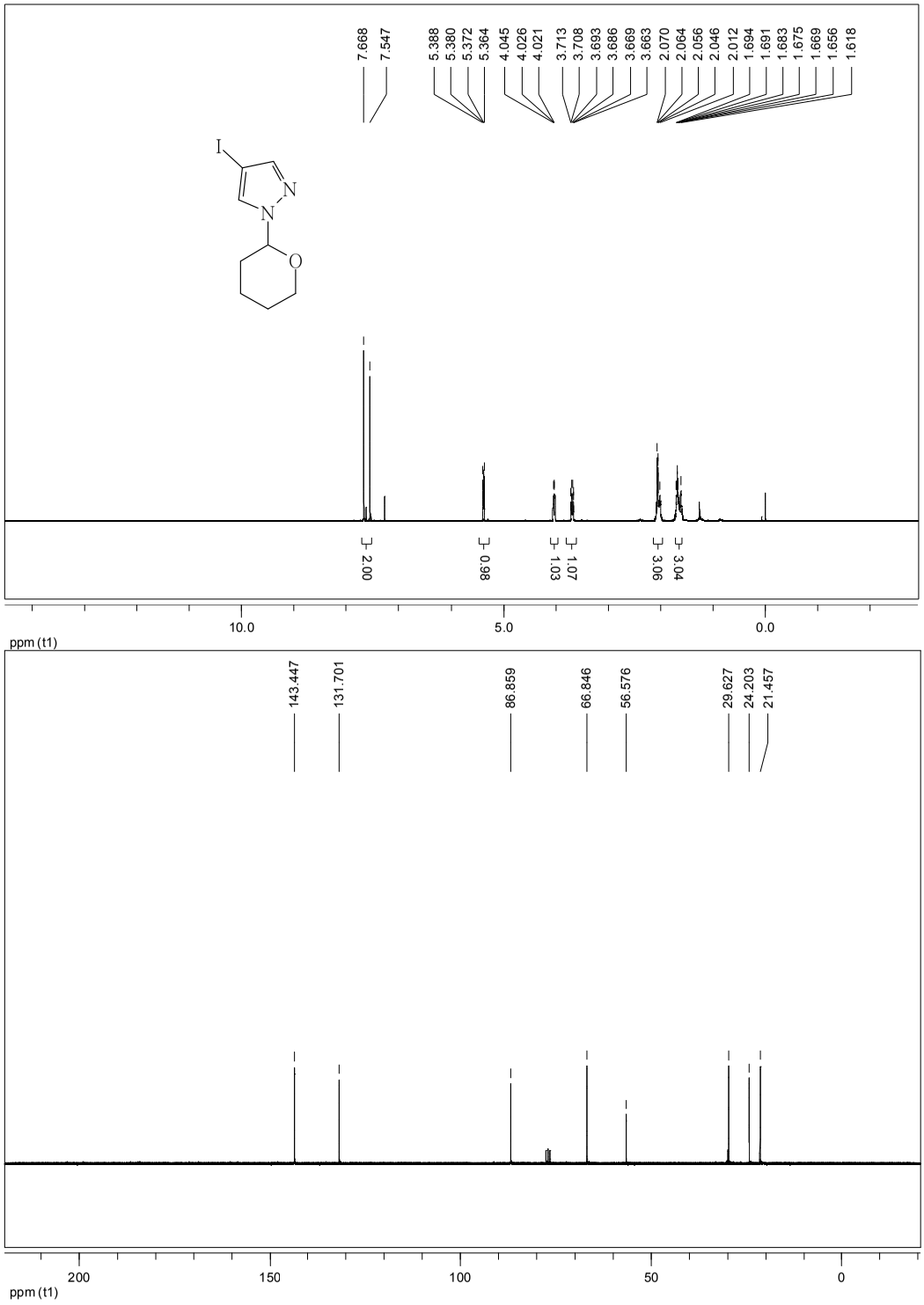
**Procedure for the cross-coupling reaction.** One third of the previous solution of $(Ar)_3In$ (0.7 mmol) in dry THF was added to a refluxing mixture of the electrophile (2.5 mmol) and $Pd(PPh_3)_4$ (0.06 mmol) in dry THF (10 mL). The resulting mixture was refluxed under argon atmosphere overnight, and the reaction quenched by addition of methanol. The mixture was concentrated, and diethyl ether (50 mL) was added. The organic phase was washed with water and dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography.

[1] Effenberger, F.; Krebs, A. *J. Org. Chem.* **1984**, *49*, 4687.

**Synthesis of 4-iodo-1-(tetrahydro-2*H*-2-pyranyl)-1*H*-pyrazole (8).** A solution of 4-iodopyrazole (3.88 g, 20 mmol) and dihydropyran (2.5 g, 20 mmol) in dichloromethane (150 mL) containing pyridinium toluene-*p*-sulphonate (0.5g, 2 mmol) was stirred for 24 hours at room temperature. Then, the solution was diluted with ethyl acetate and washed to remove the catalyst. The organic phase was dried and concentrated. The residue was purified by flash column chromatography (hexane: ethyl acetate; 2:1) to afford an oil (4.88g, 88%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.61-1.81 (m, 3 H), 1.95-2.05 (m, 3 H), 3.62-3.76 (m, 1 H), 4.01-4.04 (m, 1 H), 5.37-5.41 (m, 1 H), 7.52 (s, 1 H), 7.68 (s, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 21.9, 24.7, 30.2, 57.0, 67.5, 87.5, 132.1, 144.2; MS (EI) m/z: 278 ($M^+$, 42%), 194 (24), 84 (100). Anal. Calcd for $C_8H_{11}IN_2O$: C, 34.55; H, 3.99; N, 10.07. Found: C, 34.24; H, 3.97; N, 9.91 %.

## NMR spectra of 8

## 4-iodo-1-(tetrahydro-2*H*-2-pyranyl)-1*H*-pyrazole (8)



## Spectroscopic and analytical data of new Heterobiaryls

**1-methyl-5-(2-thienyl)-1*H*-pyrazole (4).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3 H), 6.38 (d, 1 H, *J* = 1.9 Hz), 7.09-7.11 (m, 1 H), 7.15 (dd, 1 H, *J* = 3.6, 1.1 Hz), 7.38 (dd, 1 H, *J* = 5.2, 1.1 Hz), 7.47 (d, 1 H, *J* = 1.9 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 37.7, 106.6, 126.4, 126.7, 127.5, 131.2, 136.4, 138.3; MS (EI) m/z: 164 ($M^+$, 100%), 136 (57), 121 (40), 109 (23). Anal. Calcd for $C_8H_8N_2S \cdot 1/2\ H_2O$: C, 55.47; H, 5.24; N, 16.17; S, 18.51. Found: C, 55.84; H, 4.82; N, 15.90; S, 18.26 %.

**4-phenyl-1-(tetrahydro-2*H*-2-pyranyl)-1*H*-pyrazole (9).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.61-1.71 (m, 3 H), 2.03-2.10 (m, 3 H), 3.68-3.73 (m, 1 H), 4.06-4.08 (m, 1 H), 5.37-5.41 (m, 1 H), 7.20-7.23 (m, 1 H), 7.33-7.36 (m, 2 H), 7.48 (d, 2 H, *J* = 7.5 Hz), 7.82 (s, 1 H), 7.85 (s, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 22.2, 24.7, 30.3, 67.6, 87.5, 123.2, 124.3, 125.4, 126.3, 128.6, 132.3, 136.9; MS (EI) m/z: 228 ($M^+$, 27%), 144 (100). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.66; H, 7.08; N, 11.95 %.

**3-[1-(tetrahydro-2*H*-2-pyranyl)-1*H*-4-pyrazolyl]pyridine (10).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.61-1.72 (m, 3 H), 2.04-2.11 (m, 3 H), 3.69-3.74 (m, 1 H), 4.06-4.08 (m, 1 H), 5.38-5.42 (m, 1 H), 7.17 (m, 1 H), 7.78 (s, 1 H), 7.80 (m, 1 H), 8.15 (s, 1 H), 8.24 (dd, 1 H, *J* = 5.4, 1.5 Hz), 8.69 (d, 1 H, *J* = 1.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 22.3, 24.9, 30.6, 67.9, 87.9, 123.6, 124.7, 128.5, 132.1, 132.7, 137.1, 147.0, 147.7; MS (EI) m/z: 229 ($M^+$, 77%), 145 (100), 84 (34). Anal. Calcd for $C_{13}H_{15}N_3O \cdot 1/4\ H_2O$: C, 66.79; H, 6.68; N, 17.97. Found: C, 66.62; H, 6.63; N, 17.82 %.

**1-(tetrahydro-2*H*-2-pyranyl)-4-(2-thienyl)-1*H*-pyrazole (11).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.60-1.71 (m, 3 H), 2.02-2.12 (m, 3 H), 3.68-3.73 (m, 1 H), 4.05-4.08 (m, 1 H), 5.37-5.39 (m, 1 H), 6.99-7.01 (m, 1 H), 7.06 (d, 1 H, *J* = 3.5 Hz), 7.15 (d, 1 H, *J* = 5.1 Hz), 7.72 (s, 1 H), 7.78 (s, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 22.2, 24.8, 30.4, 67.7, 87.6, 117.2, 122.6, 123.0, 124.5, 127.5, 134.7, 137.2; MS (EI) m/z: 234 ($M^+$, 13%), 150 (100). Anal. Calcd for $C_{12}H_{14}N_2OS \cdot 1/2\ H_2O$: C, 59.23; H, 6.21; N, 11.51; S, 13.18. Found: C, 59.61; H, 6.47; N, 11.22; S, 12.91 %.

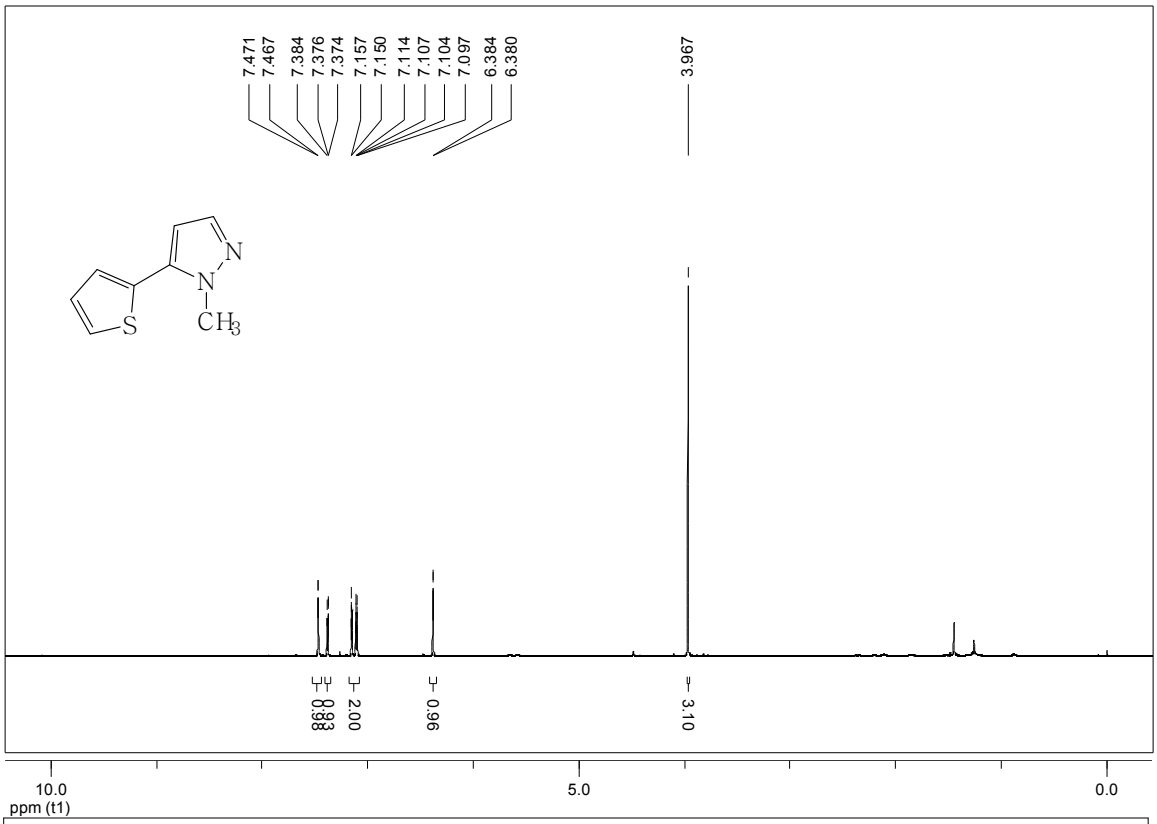
**1-methyl-5-phenyl-1*H*-pyrazole (12).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3 H), 6.29 (d, 1 H, *J* = 1.8 Hz), 7.38-7.45 (m, 5 H), 7.51 (d, 1 H, *J* = 1.8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 37.3, 105.9, 128.3, 128.5, 128.6, 130.6, 138.3, 143.4; MS (EI) m/z: 158 ($M^+$, 100%), 130 (33), 115 (26), 103 (27), 77 (20). Anal. Calcd for $C_{10}H_{10}N_2 \cdot 1/2\ H_2O$: C, 71.83; H, 6.63; N, 16.75. Found: C, 72.14; H, 6.26; N, 16.34 %.

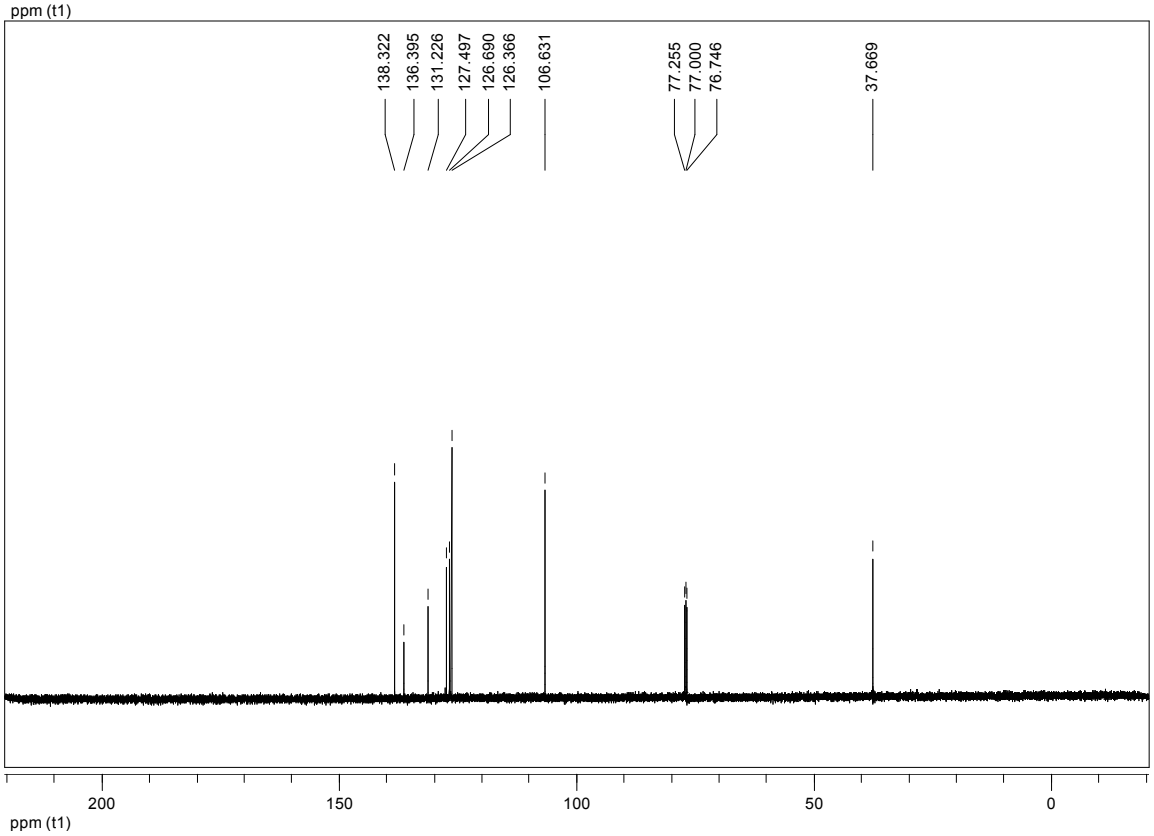
**3-(1-methyl-1*H*-5-pyrazolyl)pyridine (13).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 3 H), 6.37 (d, 1 H, *J* = 1.9 Hz), 7.39-7.41 (m, 1 H), 7.55 (d, 1 H, *J* = 1.9 Hz), 7.73-7.75 (m, 1 H), 8.65 (dd, 1 H, *J* = 4.9, 1.6 Hz), 8.70 (d, 1 H, *J* = 1.6 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 37.4, 106.7, 123.3, 126.7, 135.8, 138.7, 139.9, 149.2, 149.4; MS (EI) m/z: 159 ($M^+$, 100%), 131 (92), 104 (46), 78 (21). Anal. Calcd for $C_9H_9N_3 \cdot 1/2\ H_2O$: C, 64.27; H, 5.99; N, 24.98. Found: C, 64.52; H, 5.58; N, 24.60 %.

**2-(1-methyl-1*H*-5-pyrazolyl)pyridine (14).** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3 H), 6.25 (d, 1 H, $J$ = 1.9 Hz), 6.88-6.91 (m, 1 H), 7.18 (d, 1 H, $J$ = 1.9 Hz), 7.24 (d, 1 H, $J$ = 7.9 Hz), 7.38-7.41 (m, 1 H), 8.33 (d, 1 H, $J$ = 4.8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 39.2, 106.3, 122.1, 122.6, 136.5, 137.9, 141.1, 149.0, 149.8; MS (EI) m/z: 159 ($M^+$, 67%), 158 (100), 131 (20), 104 (54), 78 (28). Anal. Calcd for $C_9H_9N_3$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.67; H, 5.74; N, 26.81 %.

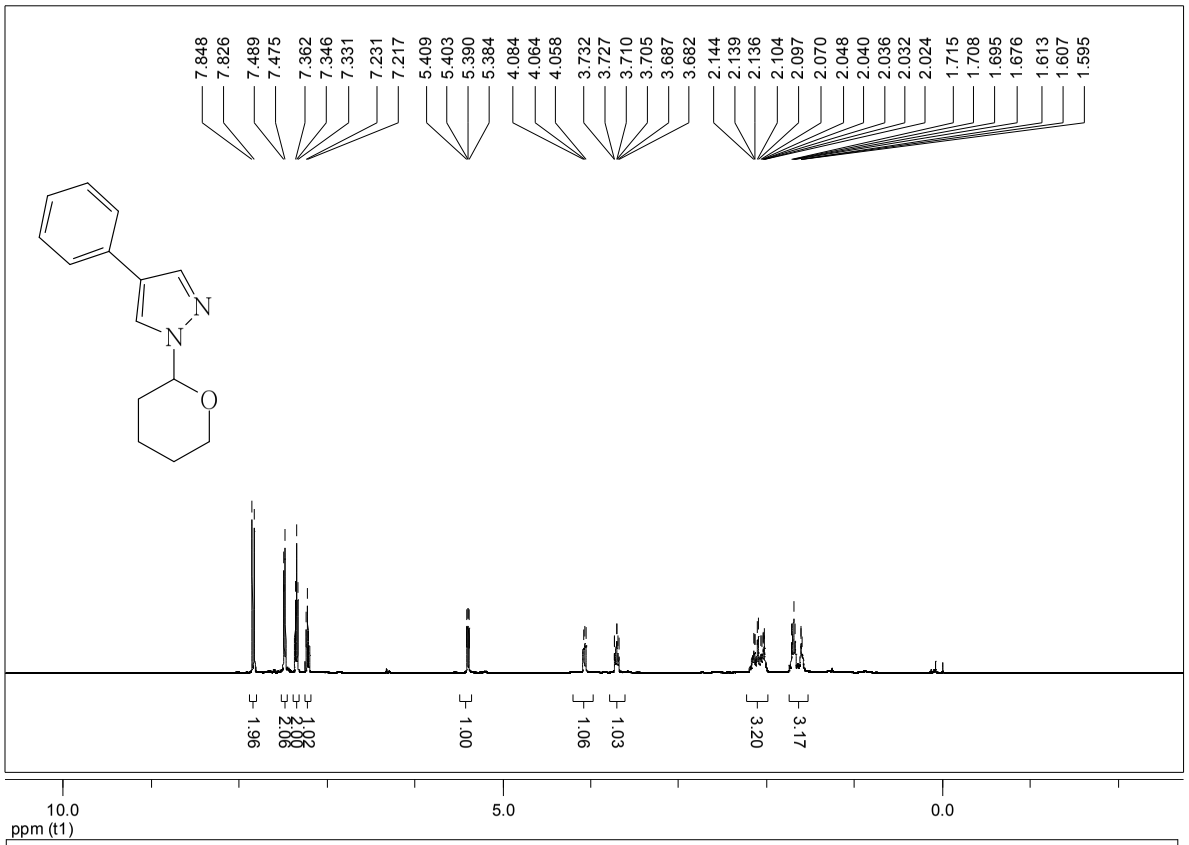
**NMR spectra of new Heterobiaryls**

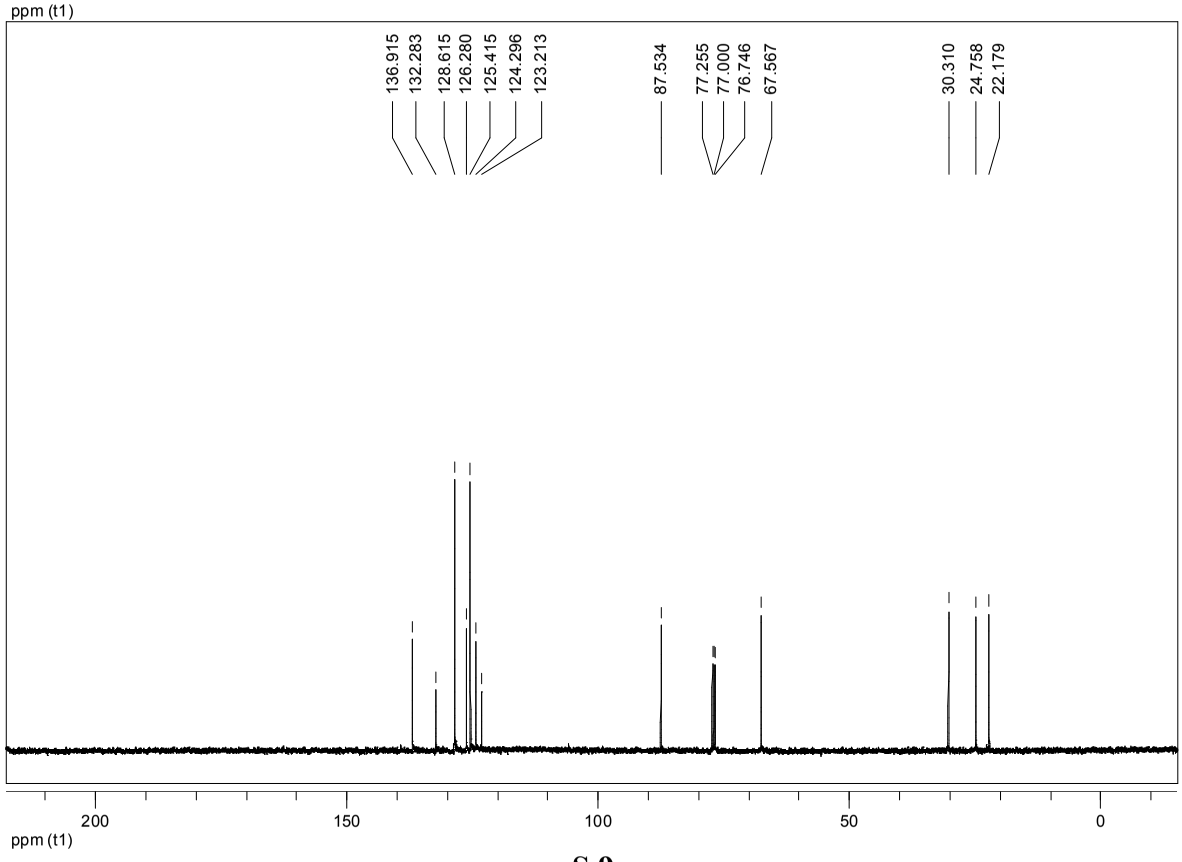
**1-methyl-5-(2-thienyl)-1*H*-pyrazole (4)**



## 4-phenyl-1-(tetrahydro-2*H*-2-pyranyl)-1*H*-pyrazole (9)



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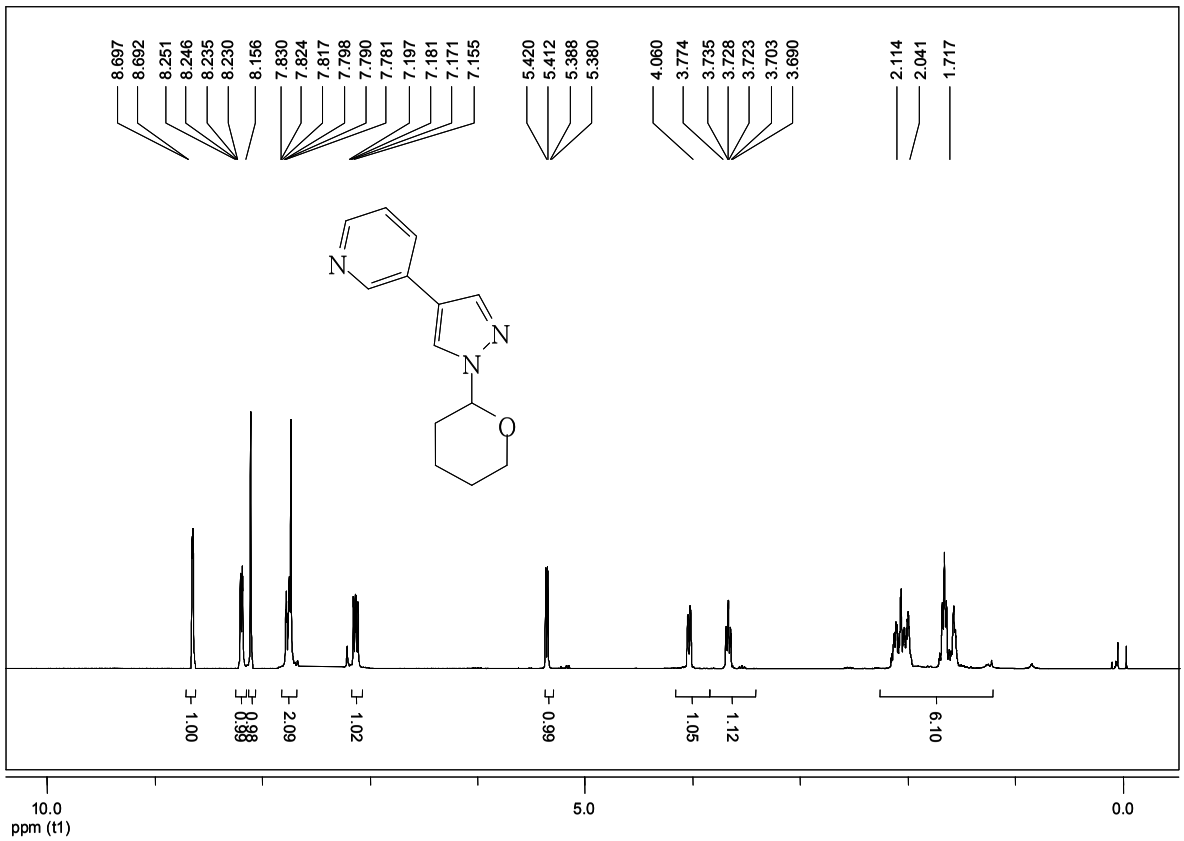
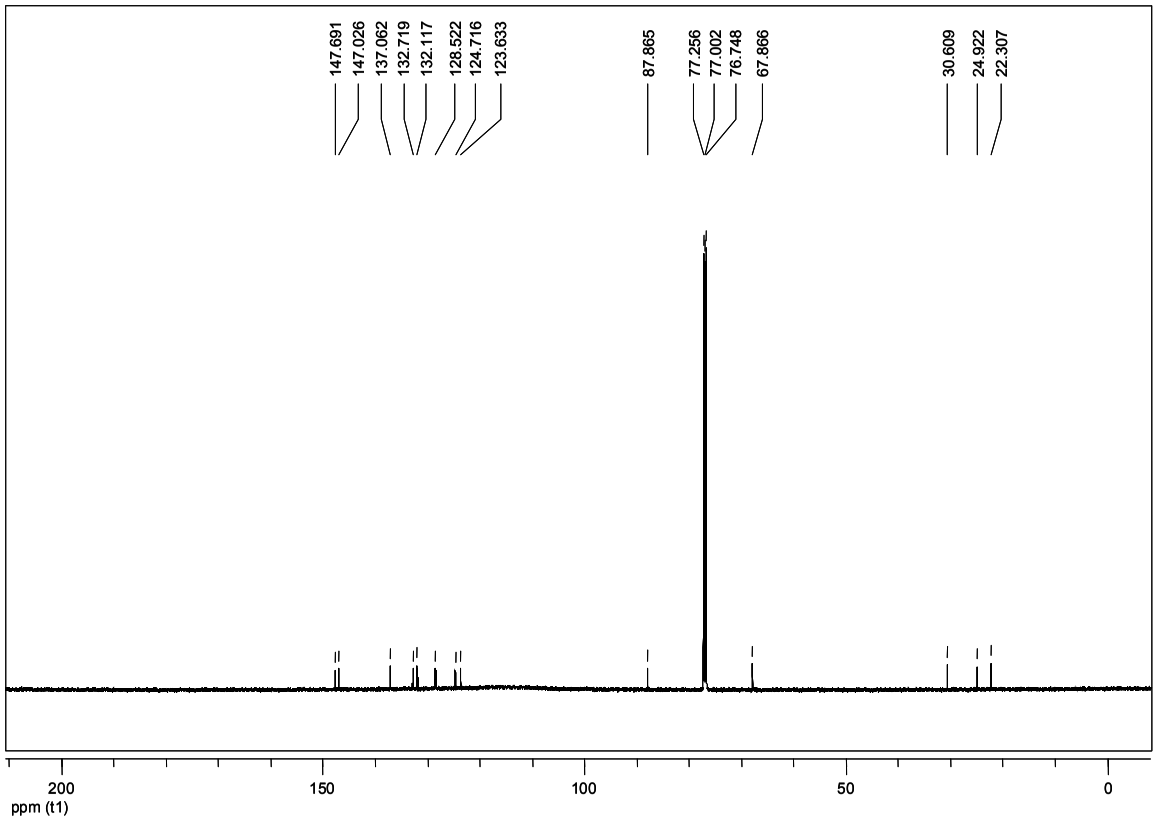
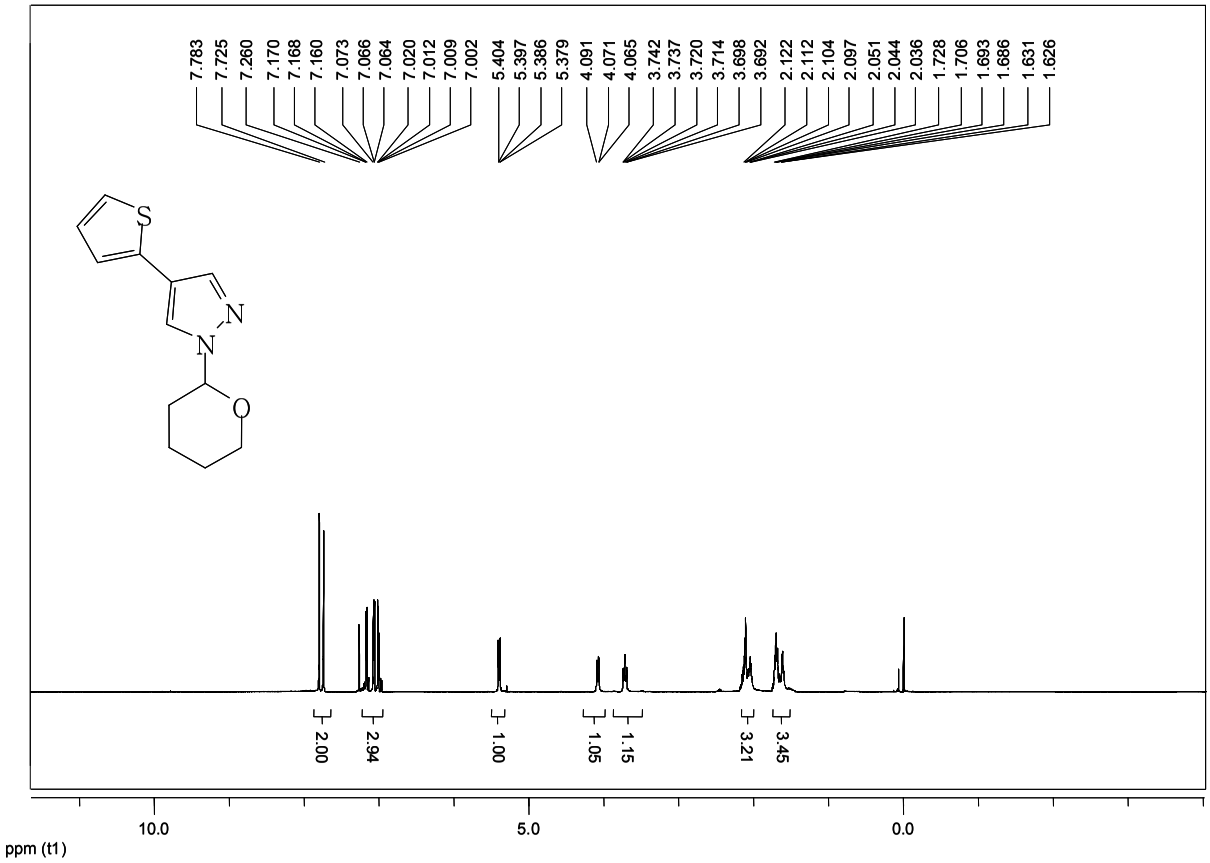
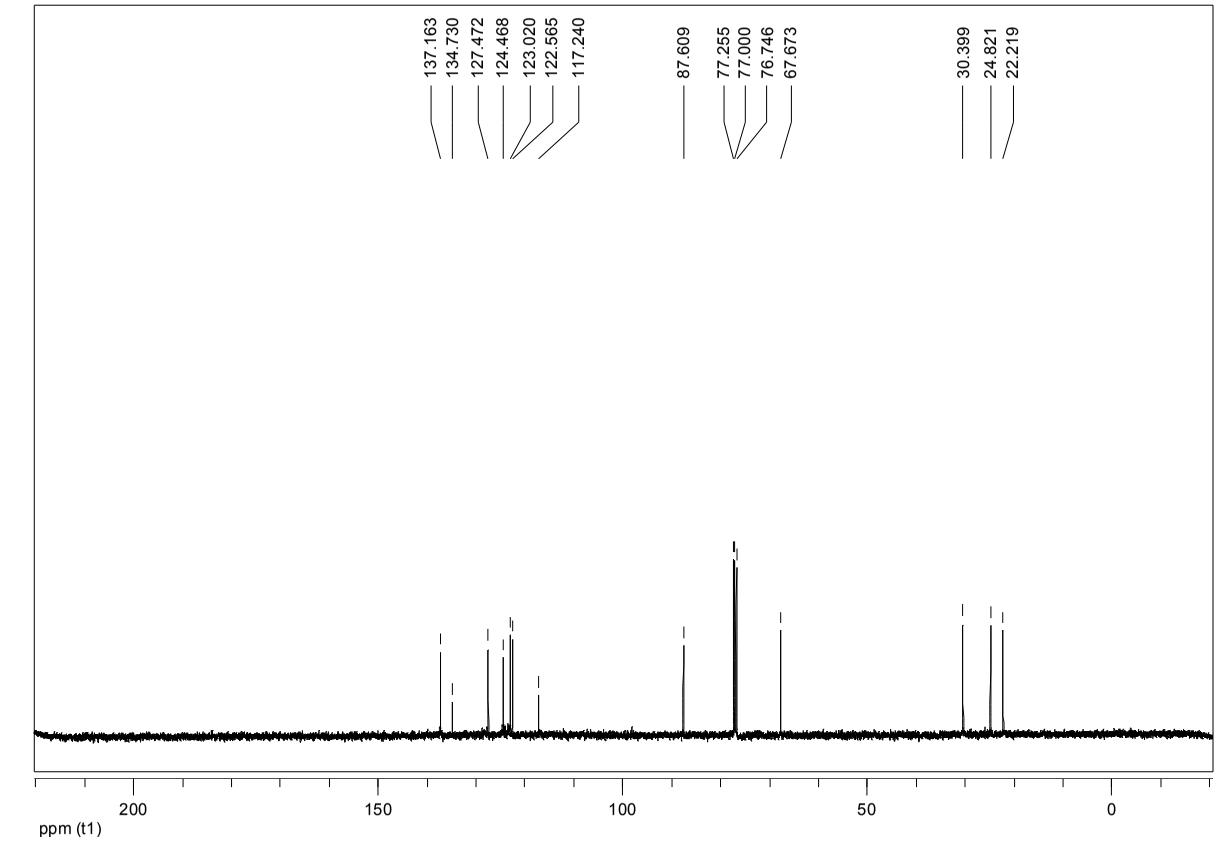


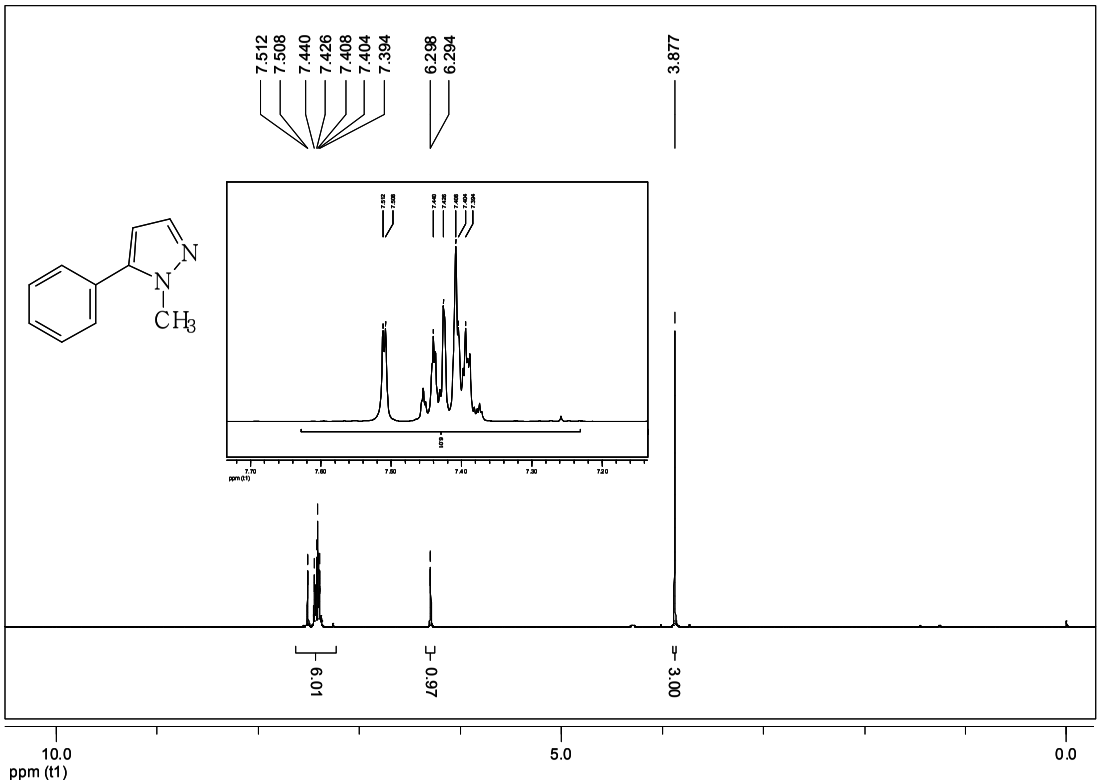



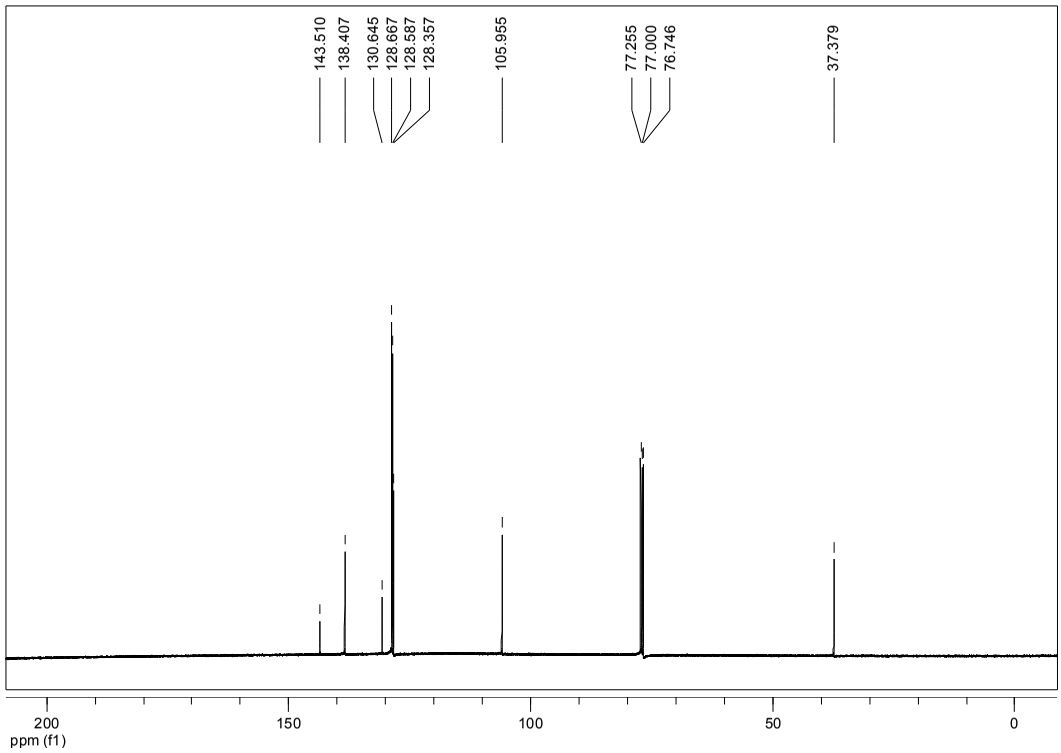
**1-(tetrahydro-2*H*-2-pyranyl)-4-(2-thienyl)-1*H*-pyrazole (11)**



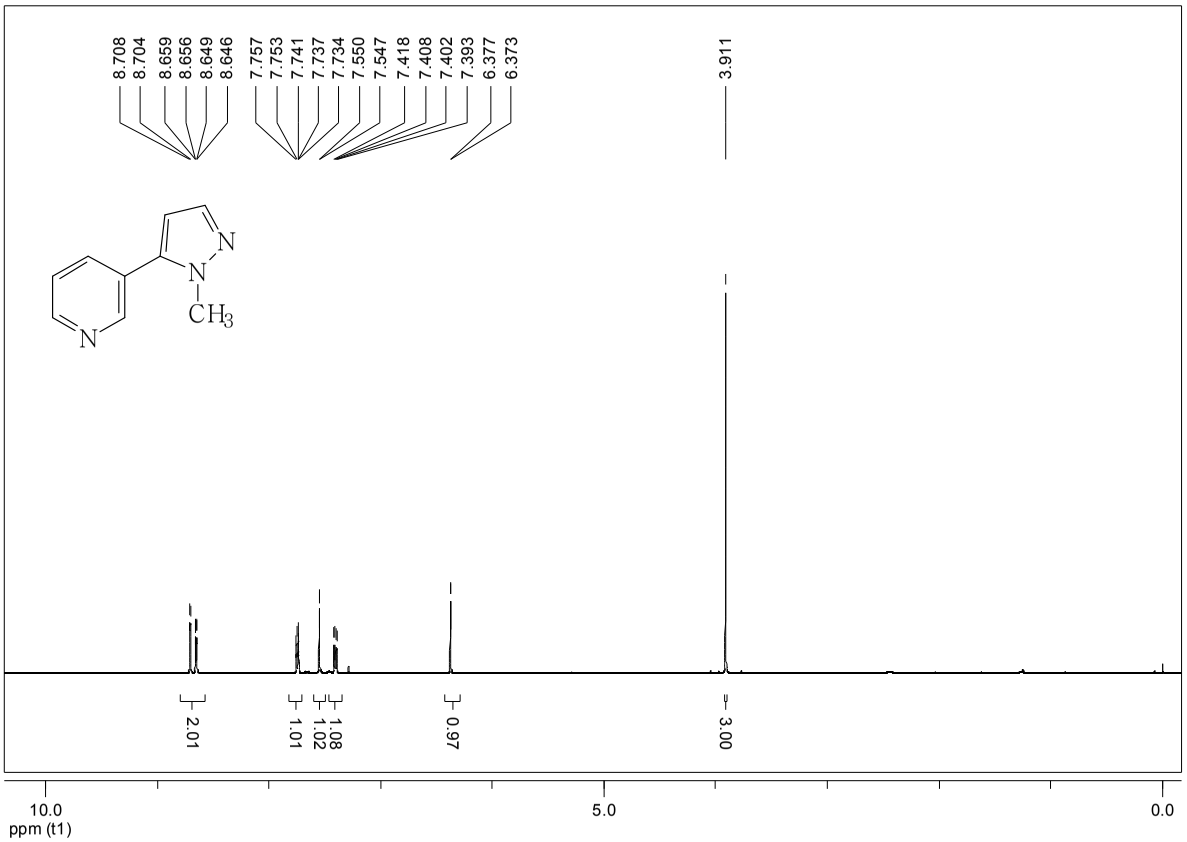



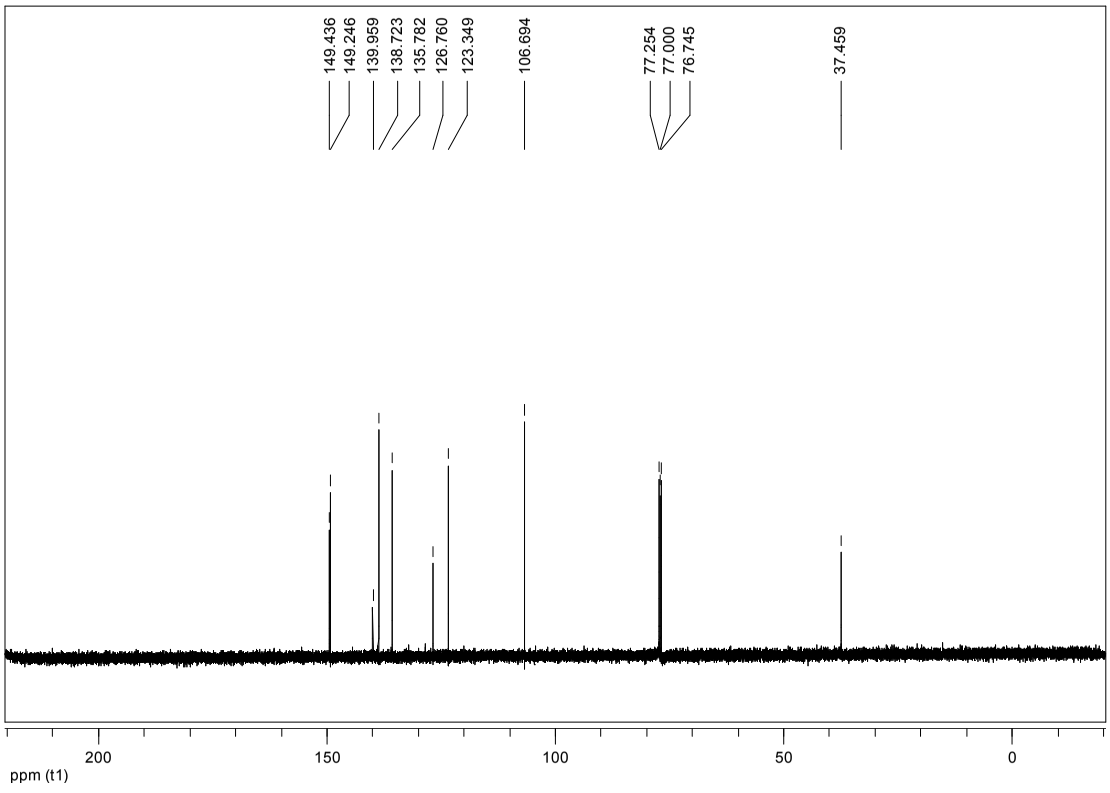
## 1-methyl-5-phenyl-1*H*-pyrazole (12)



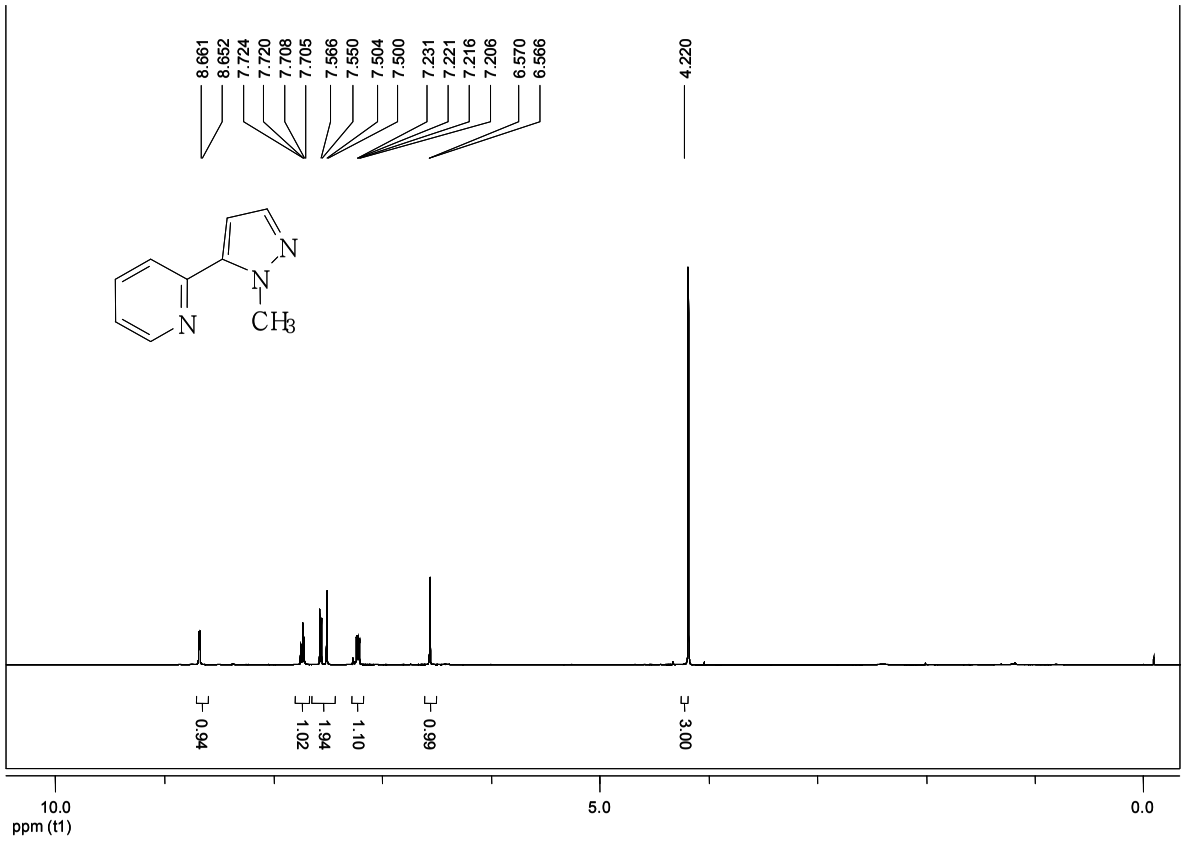



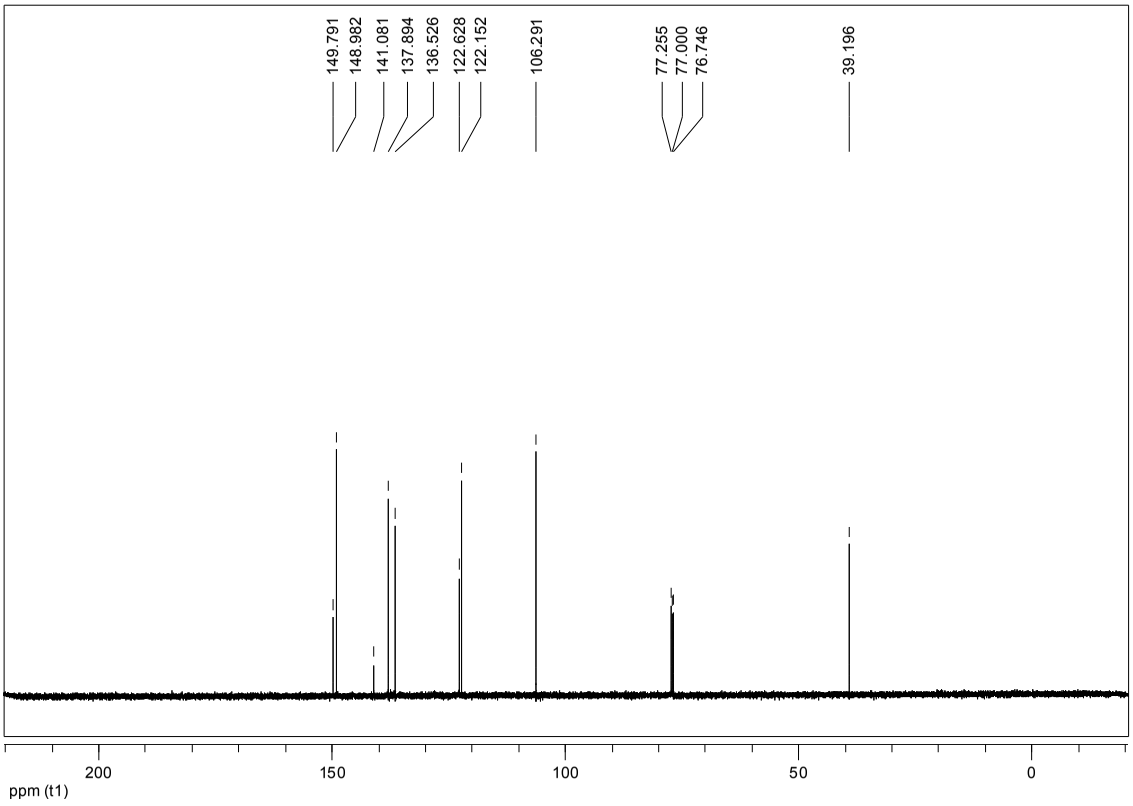
## 3-(1-methyl-1*H*-5-pyrazolyl)pyridine (13)



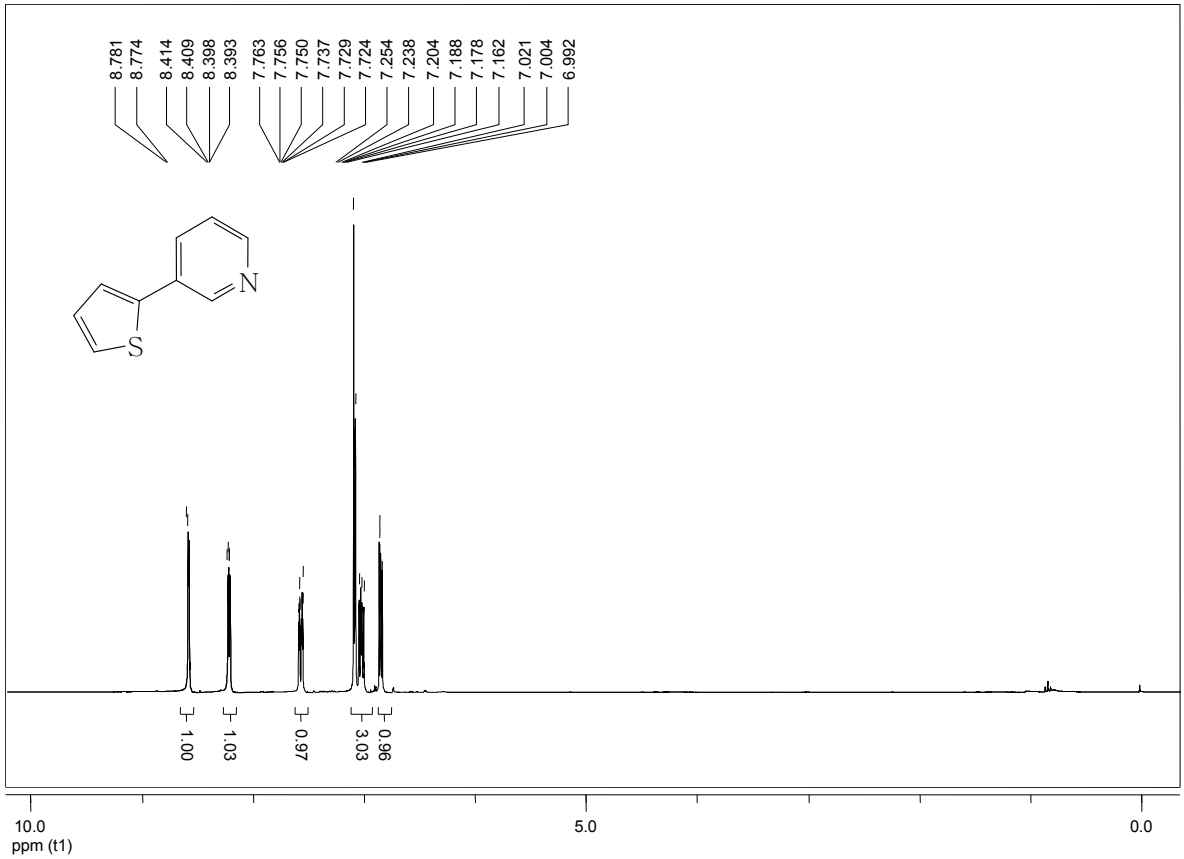
## 2-(1-methyl-1*H*-5-pyrazolyl)pyridine (14)



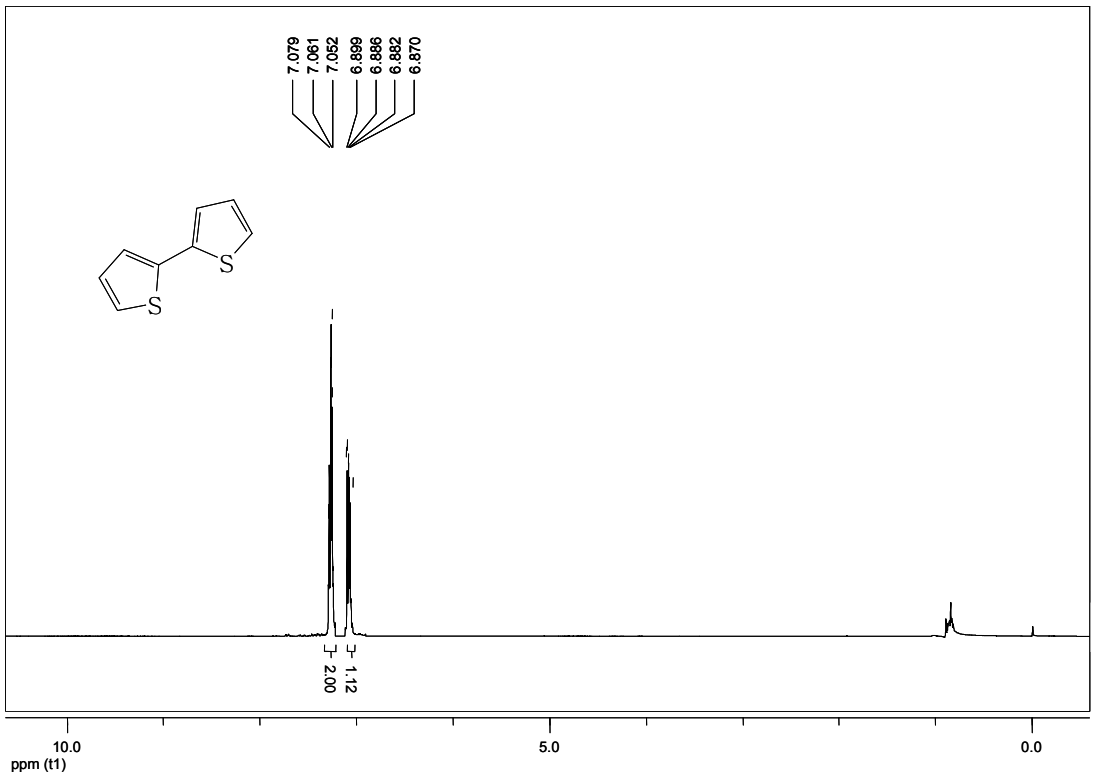



## NMR spectra of already known Heterobiaryls

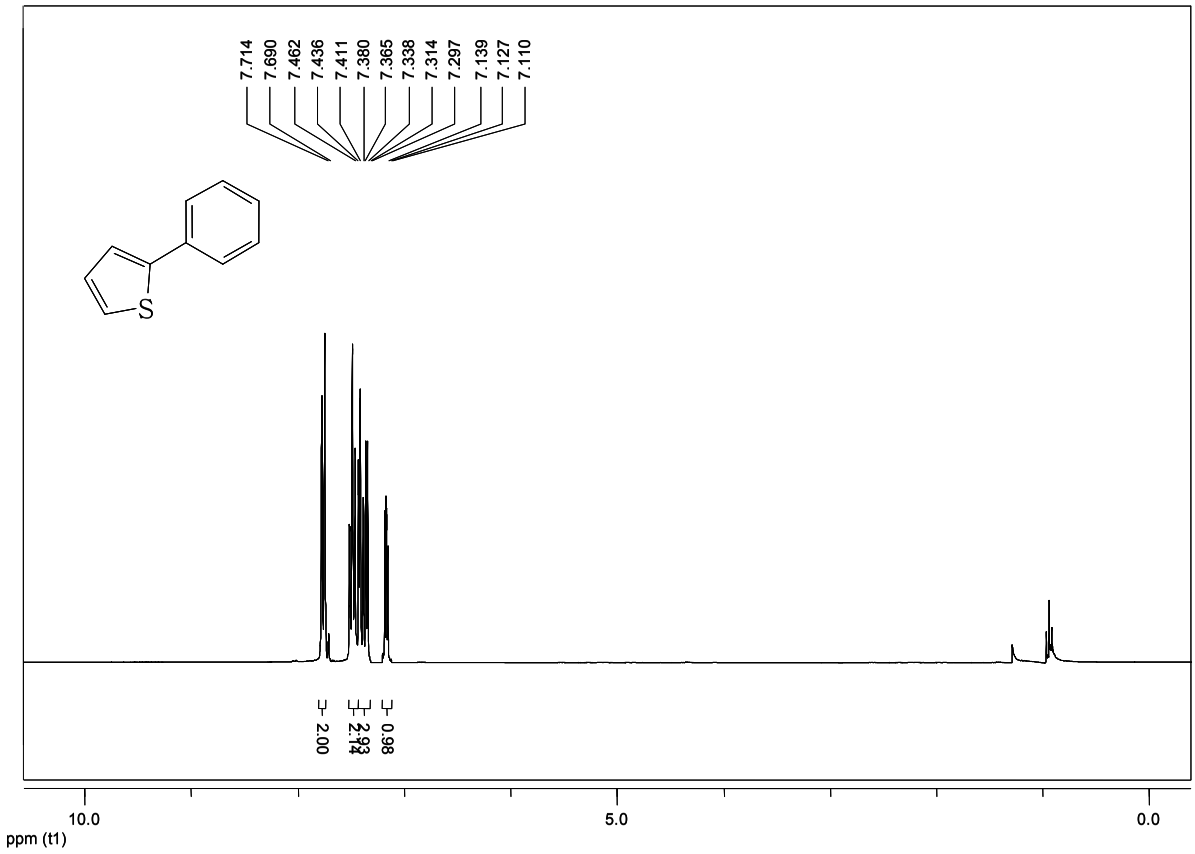
### 3-(2-thienyl)pyridine (1)



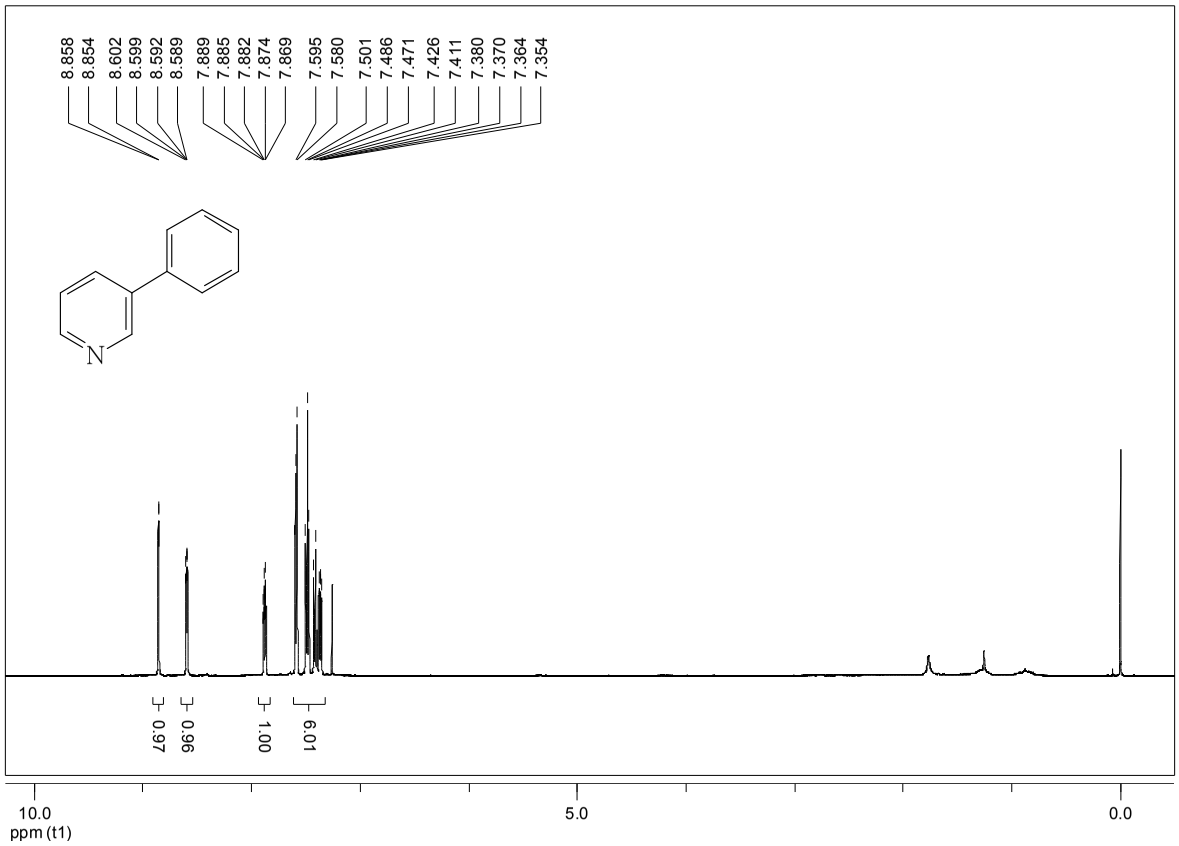
**[2,2']bithienyl (2)**



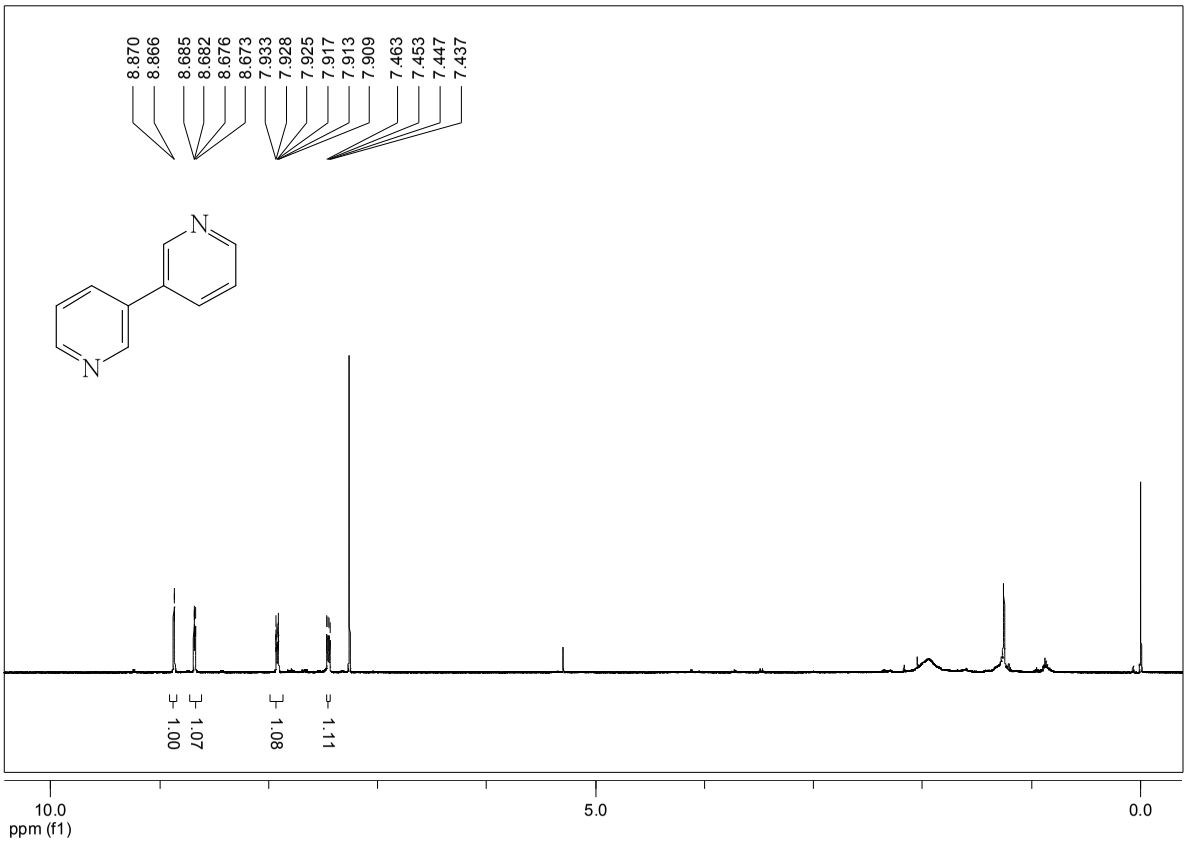
## 2-phenylthiophene (3)



## 3-phenylpyridine (5)



**[3,3']bipyridinyl (6)**



**[2,3']bipyridinyl (7)**