Supporting Information for:

Microwave-assisted solvent- and ligand-free copper-catalysed cross-couplings between halo pyridines and nitrogen nucleophiles

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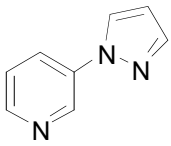
General information: All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under argon. Flash chromatography was carried out with Merck silica gel 60 (63-200 mesh). Analytical TLC was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz. HRMS were recorded on a Finnigan MAT 95 system.

General Procedure for *N*-Heteroarylation of Nitrogen Nucleophiles: An oven-dried tube was cooled to room temperature under argon and charged with the halo pyridine (if solid, 1.0 equiv), the *N*-nucleophile (if solid, 1.3 equiv), Cu_2O (0.10 equiv) and $K_3PO_4 \cdot H_2O$ (2.0 equiv). The tube was then evacuated and backfilled with argon (3 cycles). (Liquid substrates were added by syringe at room temperature, and in those cases, 1.0 equiv of the halo pyridine and 1.3 equiv of the *N*-nucleophile were used.) The tube was sealed under argon and placed into a CEM Discover microwave apparatus. Initially, an irradiation power of 50 W was applied. When the temperature reached 100 °C, the instrument automatically adjusted the power to maintain a

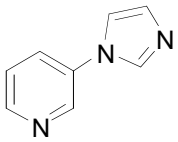
constant temperature. After a total heating time of 1 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL; use of less solvent can reduce the yield.) The resulting solution was filtered through a pad of silica gel and concentrated to give the crude product. Purification by silica gel chromatography (1:1 pentane/ethyl acetate) gave the *N*-heteroarylated product. The identity and purity of the product was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

3-(1*H*-Pyrazol-1-yl)pyridine (3a)[1]



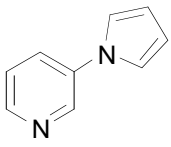
Yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, J = 2.8 Hz, 1H), 8.51 (dd, J = 1.4, 4.7 Hz, 1H), 8.02 (ddd, J = 1.4, 2.8, 8.3 Hz, 1H), 7.95 (d, J = 2.7 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.37 (ddd, J = 0.7, 4.7, 8.3 Hz, 1H), 6.49 (dd, J = 1.6, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 141.9, 140.5, 136.5, 126.7, 126.5, 123.9, 108.4; EI-MS (*m/z*, %): 145.1 (M^+, 100), 146.2 (M^++1, 30.21), 118.2 (48.33), 78.3 (26.12).
All spectral data correspond to those given in the literature.[1]

3-(1*H*-Imidazol-1-yl)pyridine (3b)[2]



Yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 2.8 Hz, 1H), 8.56 (dd, J = 1.4, 5.0 Hz, 1H), 7.81 (s, 1H), 7.67 (ddd, J = 1.4, 2.8, 8.3 Hz, 1H), 7.38 (dd, J = 5.0, 8.3 Hz, 1H), 7.24 (s, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 142.8, 135.4, 133.8, 131.0, 128.7, 124.2, 118.0; EI-MS (*m/z*, %): 145.1 (M^+, 100), 146.2 (M^++1, 23.28), 118.2 (42.02), 78.3 (19.75).
All spectral data correspond to those given in the literature.[2]

3-(1*H*-Pyrrol-1-yl)pyridine (3c)[3]

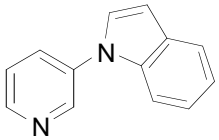


Yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 2.7 Hz, 1H), 8.42 (dd, J = 1.4,

4.7 Hz, 1H), 7.61 (ddd, J = 1.4, 2.7, 8.3 Hz, 1H), 7.28 (ddd, J = 0.7, 4.7, 8.3 Hz, 1H), 7.01 (t, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 142.0, 137.0, 127.4, 124.0, 119.1, 111.4; EI-MS (*m/z*, %): 144.1 (M^+, 100), 145.1 (M^++1, 16.70), 117.1 (25.14). HRMS calcd. for $C_9H_9N_2$ [M^++1]: 145.0760; Found: 145.0754

All spectral data correspond to those given in the literature.[3]

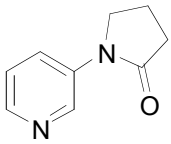
1-(3-Pyridyl)-1*H*-indole (3d)[3,4]



Yield 64%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 2.2 Hz, 1H), 8.54 (dd, J = 1.4, 4.7 Hz, 1H), 7,76 (ddd, J = 1.4, 2.2, 8.0 Hz, 1H), 7.61-7.64 (m, 1H), 7.44-7.46 (m, 1H), 7.37-7.41 (m, 1H), 7.25 (d, J = 3.3 Hz, 1H), 7.11-7.20 (m, 2H), 6.67 (dd, J = 0.9, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 145.6, 136.4, 135.7, 131.3, 129.4, 127.4, 124.1, 122.9, 121.4, 120.9, 110.0, 104.8; EI-MS (*m/z*, %): 194.1 (M^+, 100), 195.2 (M^++1, 41.18), 116.1 (5.98).

All spectral data correspond to those given in the literature.[3,4]

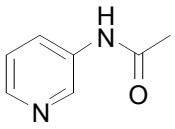
1-(3-Pyridyl)pyrrolidin-2-one (3e)[5]



Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.30 (s, 1H), 8.11-8.15 (m, 1H), 7.20-7.25 (m, 1H), 3.78-3.83 (m, 2H), 2.51-2.56 (m, 2H), 2.09-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 145.1, 140.4, 136.0, 126.8, 123.3, 48.0, 32.4, 18.1; EI-MS (*m/z*, %): 162.2 (M^+, 50.23), 163.2 (M^++1, 11.37), 107.2 (100), 78.2 (18.20).

All spectral data correspond to those given in the literature.[5]

***N*-(3-pyridyl)acetamide (3f)[6]**

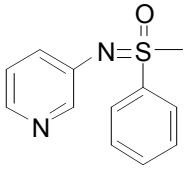


Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.60 (d, J = 2.2 Hz, 1H),

8.27 (dd, J = 1.2, 4.7 Hz, 1H), 8.13 (ddd, J = 1.2, 2.2, 8.2 Hz, 1H), 7.24 (dd, J = 4.7, 8.2 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 144.6, 141.0, 135.6, 127.5, 123.9, 24.2; EI-MS (*m/z*, %): 136.2 (M^+, 60.86), 137.2 (M^++1, 9.39), 94.3 (100).

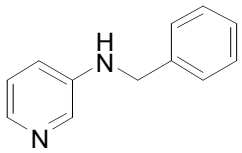
All spectral data correspond to those given in the literature.[6]

_N_-(3-pyridyl)-_S_-methyl-_S_-phenylsulfoximine (3g)



Yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 2.4 Hz, 1H), 8.03 (dd, J = 1.4, 4.7 Hz, 1H), 7.87-7.90 (m, 2H), 7.45-7.56 (m, 3H), 7.21 (ddd, J = 1.4, 2.4, 8.3 Hz, 1H), 6.94 (dd, J = 4.7, 8.3 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 142.6, 141.7, 138.6, 133.5, 129.7, 129.4, 128.5, 123.4, 46.3; EI-MS (*m/z*, %): 232.1 (M^+, 77.47), 233.1 (M^++1, 12.78), 169.1 (100), 124.1 (40.30); HRMS calcd. for $C_{12}H_{12}N_2OS$ [M^+]: 232.0665; Found: 232.0666.

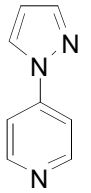
_N_-Benzylpyridin-3-amine (3h)[1c,2a,7]



Yield 12%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 2.2 Hz, 1H), 7.88 (d, J = 4.4 Hz, 1H), 7.18-7.27 (m, 5H), 6.97 (dd, J = 4.4, 8.3 Hz, 1H), 6.78 (ddd, J = 1.3, 2.2, 8.3 Hz, 1H), 4.25 (d, J = 5.2 Hz, 2H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.96, 138.85, 138.48, 136.15, 128.72, 127.44, 127.37, 123.66, 118.48, 47.92; EI-MS (*m/z*, %): 184.2 (M^+, 100), 185.3 (M^++1, 19.01), 91.2 (95.41).

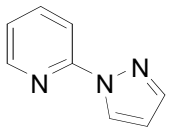
All spectral data correspond to those given in the literature.[1c,2a,7]

4-(1_H_-pyrazol-1-yl)pyridine (4)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.61 (m, 2H), 7.95-7.96 (m, 1H), 7.66-7.72 (m, 1H), 7.54-7.56 (m, 2H), 6.43-6.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 145.8, 142.4, 126.5, 112.4, 109.0; EI-MS (*m/z*, %): 145.2 (M^+, 34.14), 146.2 (M^++1, 2.60), 118.1 (32.26), 78.2 (26.12), 51.2 (100); HRMS calcd. for $C_8H_7N_3$ [M^+]: 145.06345; Found: 145.06351.

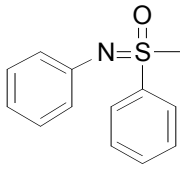
2-(1*H*-Pyrazol-1-yl)pyridine (5)[1a,1c]



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 2.5 Hz, 1H), 8.32 (dd, J = 0.8, 4.7 Hz, 1H), 7.90 (dd, J = 0.8, 8.3 Hz, 1H), 7.69-7.74 (m, 1H), 7.66 (s, 1H), 7.07-7.10 (m, 1H), 6.37-6.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 147.9, 141.9, 138.6, 126.9, 121.3, 112.4, 107.7.

All spectral data correspond to those given in the literature.[1a,1c]

***N*-Phenyl-*S*-methyl-*S*-phenylsulfoximine (6)[8]**



Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.97 (m, 2H), 7.48-7.58 (m, 3H), 7.07-7.12 (m, 2H), 6.98-7.01 (m, 2H), 6.83-6.87 (m, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): _ 144.9, 139.3, 133.2, 129.5, 128.9, 128.6, 123.2, 121.6, 46.1.

All spectral data correspond to those given in the literature.[8]

References

1. (a) Lee, H. W.; Chan, A. S. C.; Kwong, F. Y. *Tetrahedron Lett.* **2009**, *50*, 5868-5871. (b) Cristau, H.-J.; Cellier, P. P.; Spindler, J.-F.; Taillefer, M. *Eur. J. Org. Chem.* **2004**, 695-709. (c) Zhu, D,; Wang, R.; Mao, J.; Xu, L.; Wu, F.; Wan, B. *J. Mol. Catal. A: Chem.* **2006**, *256*, 256-260. (d) Khan, M. A.; Pinto, A. A. A. *J. Heterocycl. Chem.* **1981**, *18*, 9-14.
2. (a) Zhang, Z.; Mao, J.; Zhu, D.; Wu, F.; Chen, H.; Wan, B. *Tetrahedron* **2006**, *62*,

4435-4443. (b) Cheng, D.; Gan, F.; Qian, W.; Bao, W. *Green Chem.* **2008**, *10*, 171-173. (c) Denton, T. T.; Zhang, X.; Cashman, J. R. *J. Med. Chem.* **2005**, *48*, 224-239.

3. (a) Romero, M.; Harrak, Y.; Basset, J.; Ginet, L.; Constans, P.; Pujol, M. D. *Tetrahedron* **2006**, *62*, 9010-9016.
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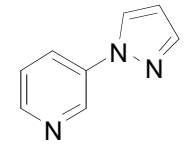
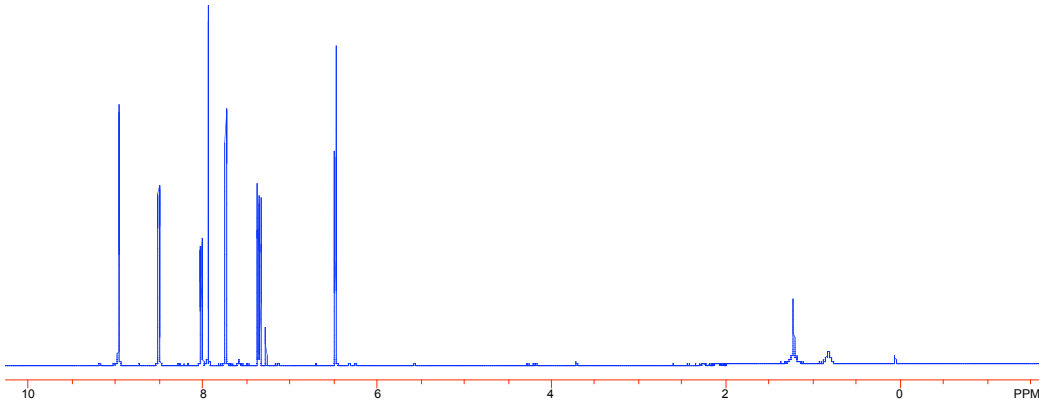
8. (a) Cho, G. Y.; Rémy, P.; Jansson, J.; Moessner, C.; Bolm, C. *Org. Lett.* **2004**, *6*, 3293-3296. (b) Correa, A.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 2673-2676.

Copies of NMR Spectra

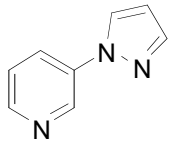
^{1}H NMR ($CDCl_3$)



(3a)



^{13}C NMR ($CDCl_3$)



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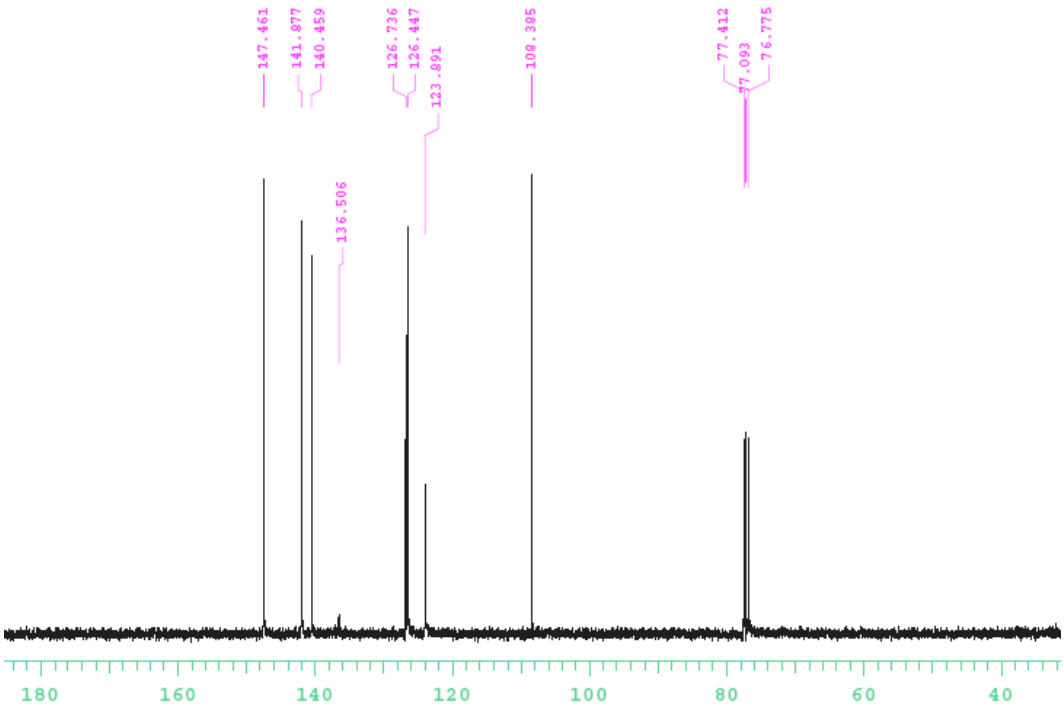
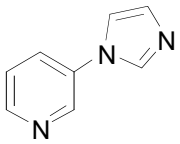
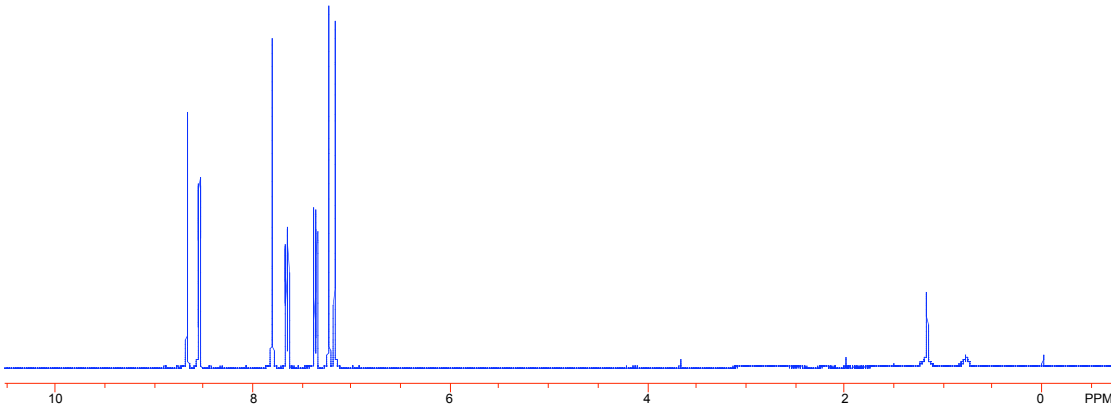


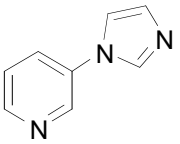
^{1}H NMR ($CDCl_3$)



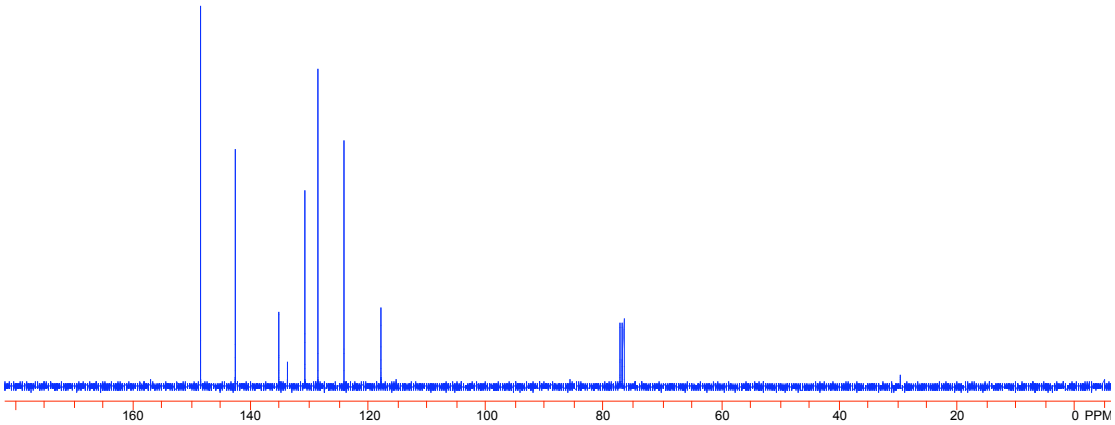
(**3b**)



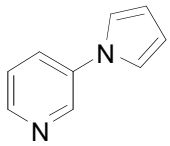
^{13}C NMR ($CDCl_3$)



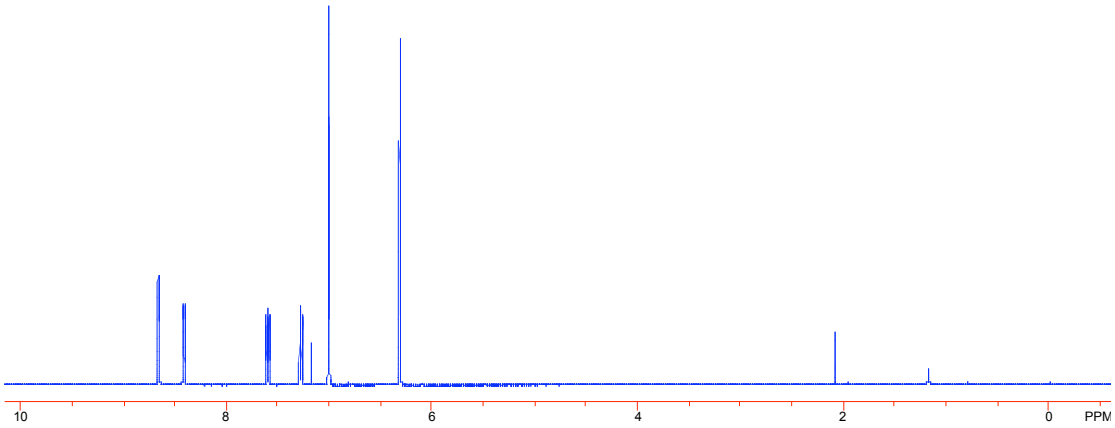
(**3b**)



^{1}H NMR ($CDCl_3$)



(**3c**)



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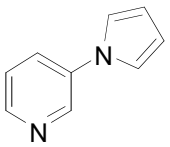
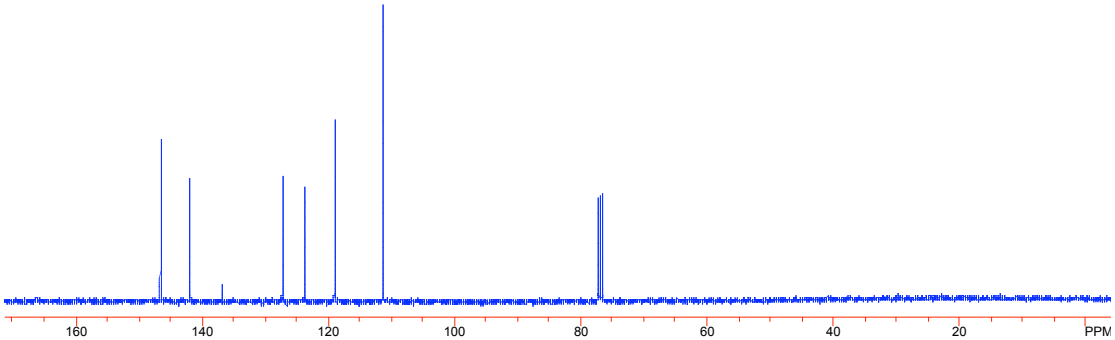
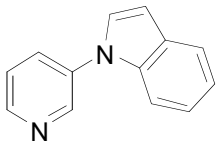


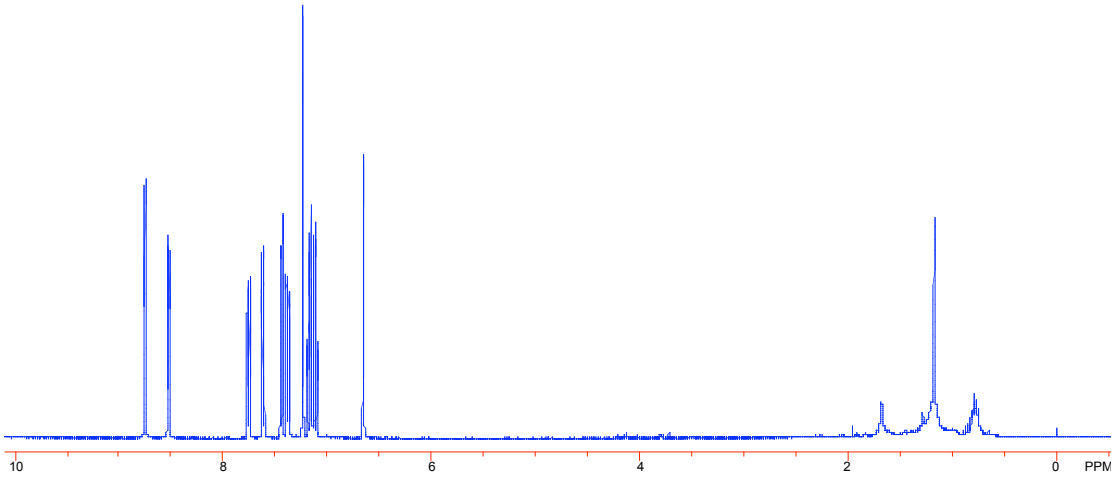
(**3c**)



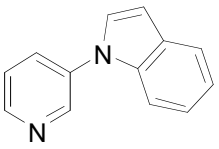
^{1}H NMR ($CDCl_3$)



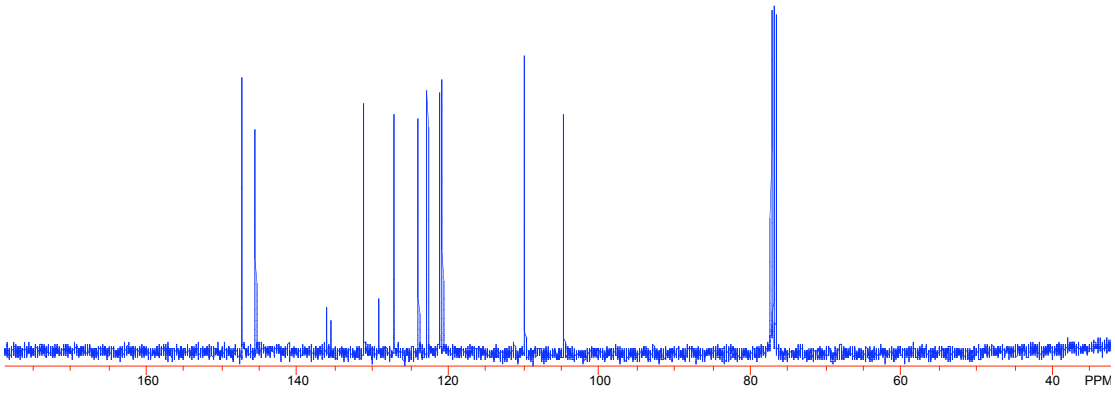
(**3d**)



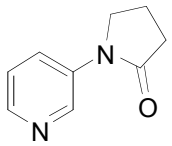
^{13}C NMR ($CDCl_3$)



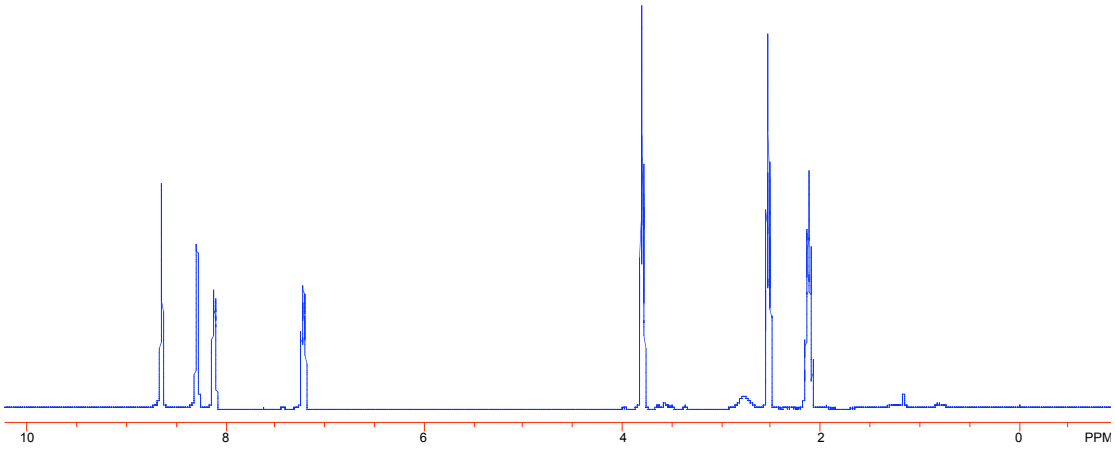
(**3d**)



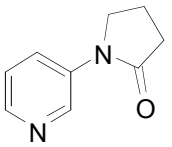
^{1}H NMR ($CDCl_3$)



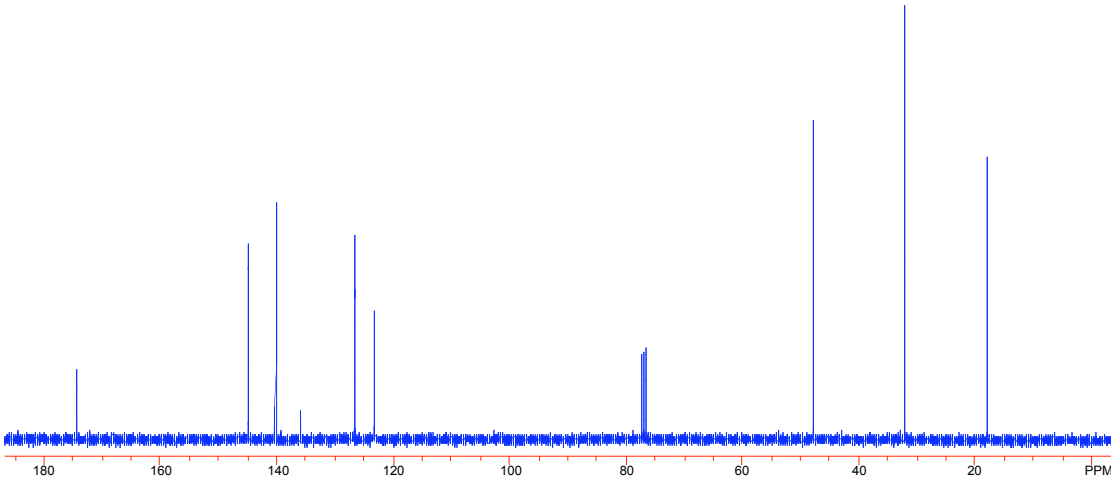
(**3e**)



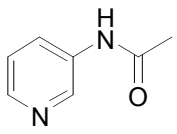
^{13}C NMR ($CDCl_3$)



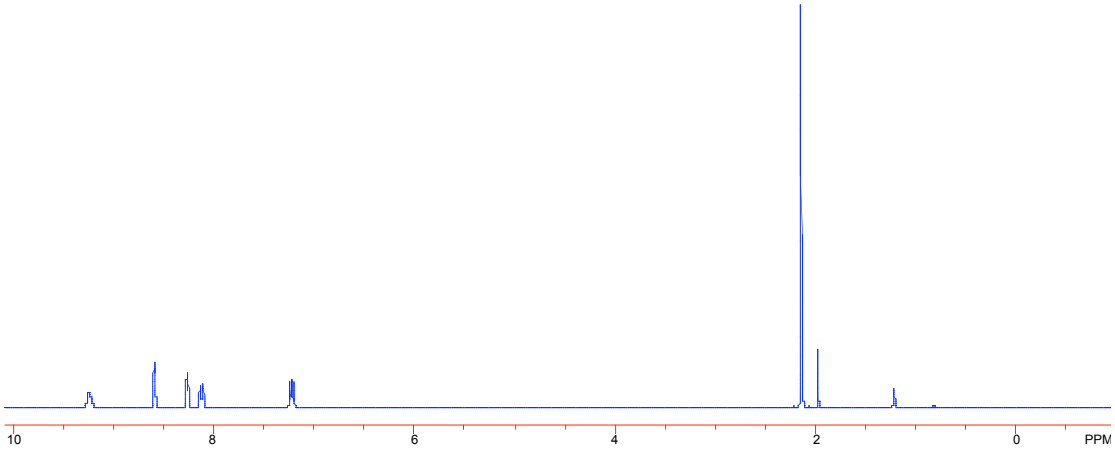
(**3e**)



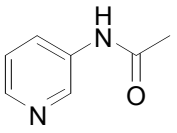
^{1}H NMR ($CDCl_3$)



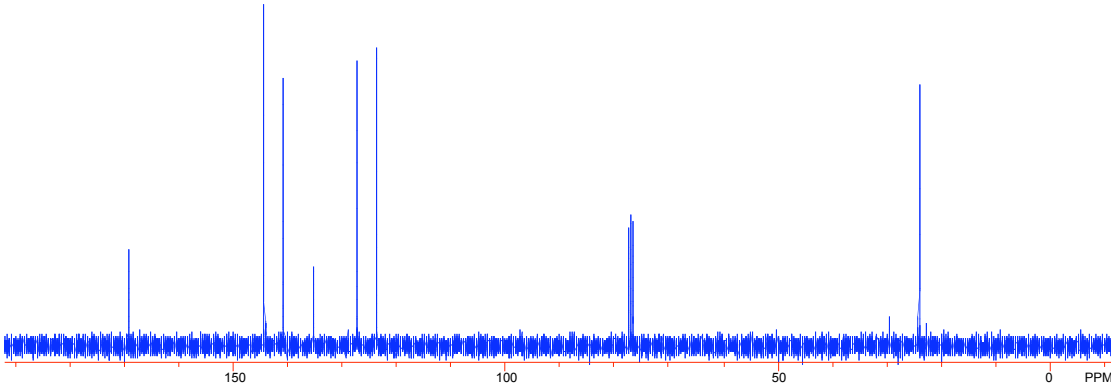
(**3f**)



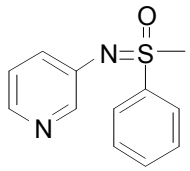
^{13}C NMR ($CDCl_3$)



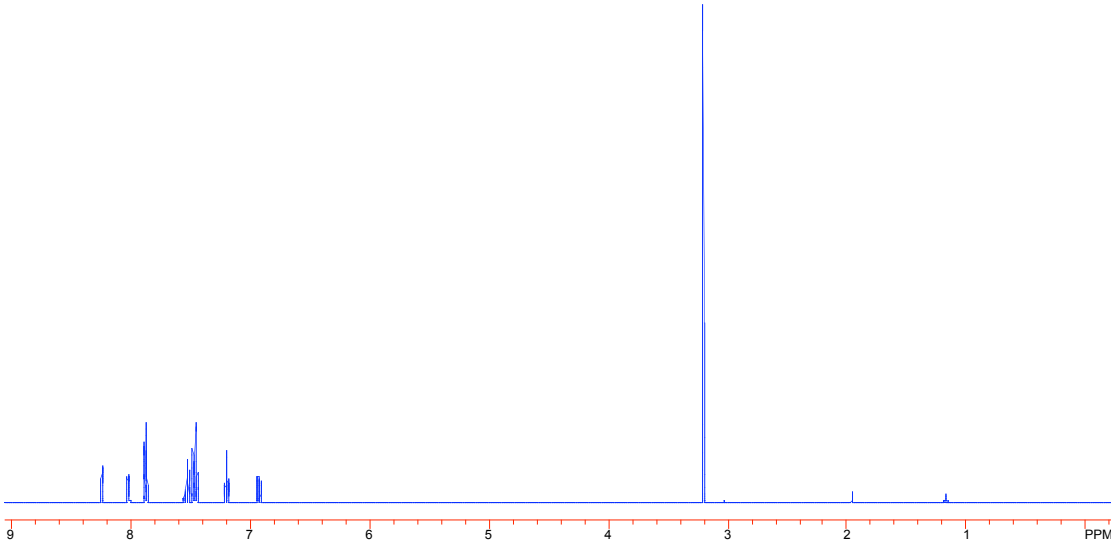
(**3f**)



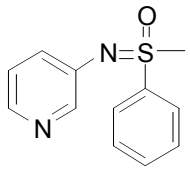
^{1}H NMR ($CDCl_3$)



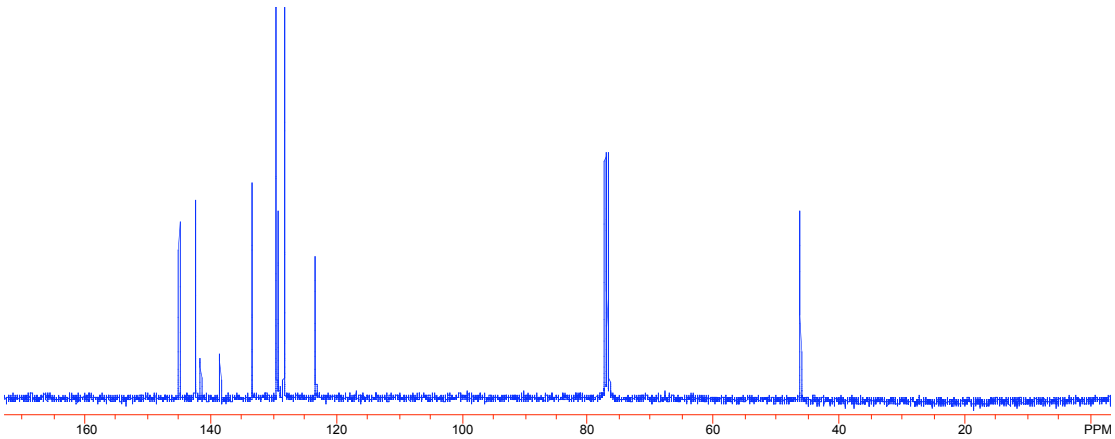
(**3g**)



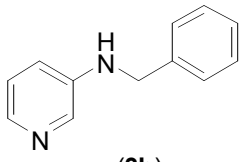
^{13}C NMR ($CDCl_3$)



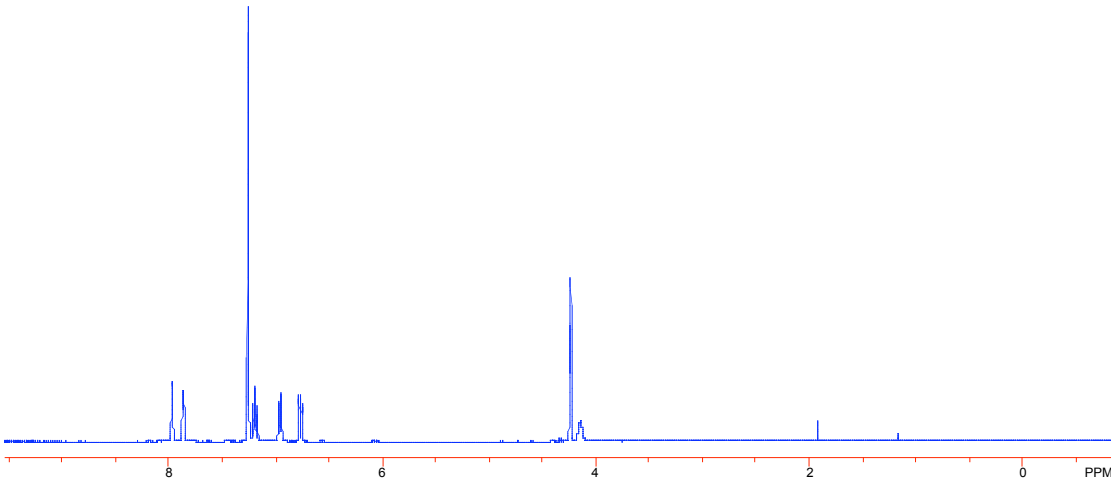
(**3g**)



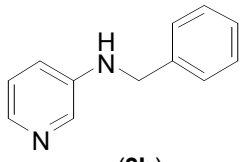
^{1}H NMR ($CDCl_3$)



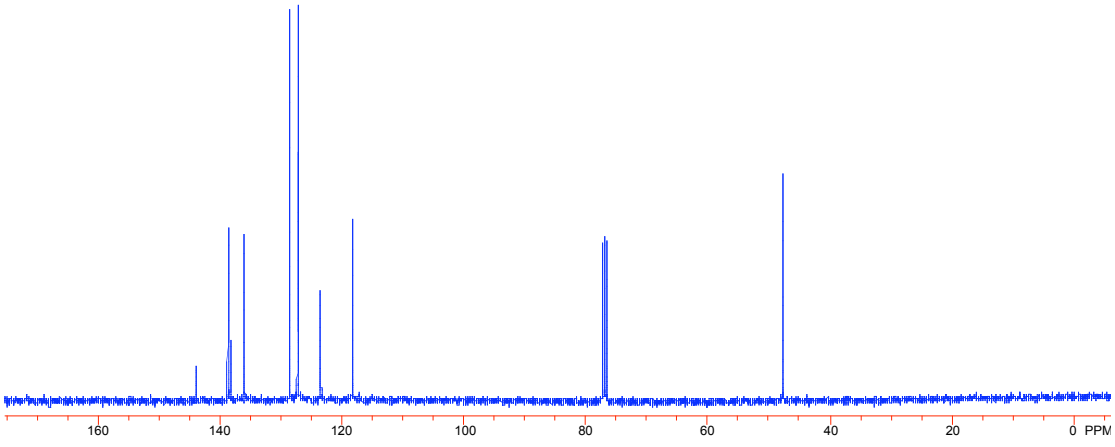
(**3h**)



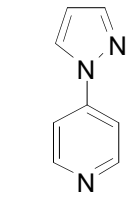
^{13}C NMR ($CDCl_3$)



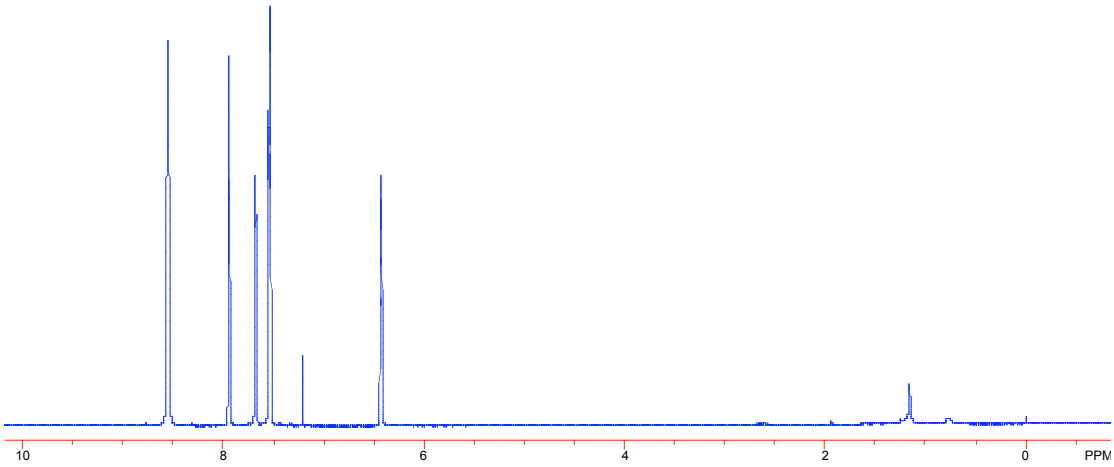
(**3h**)



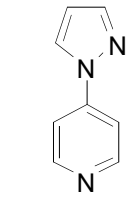
^{1}H NMR ($CDCl_3$)



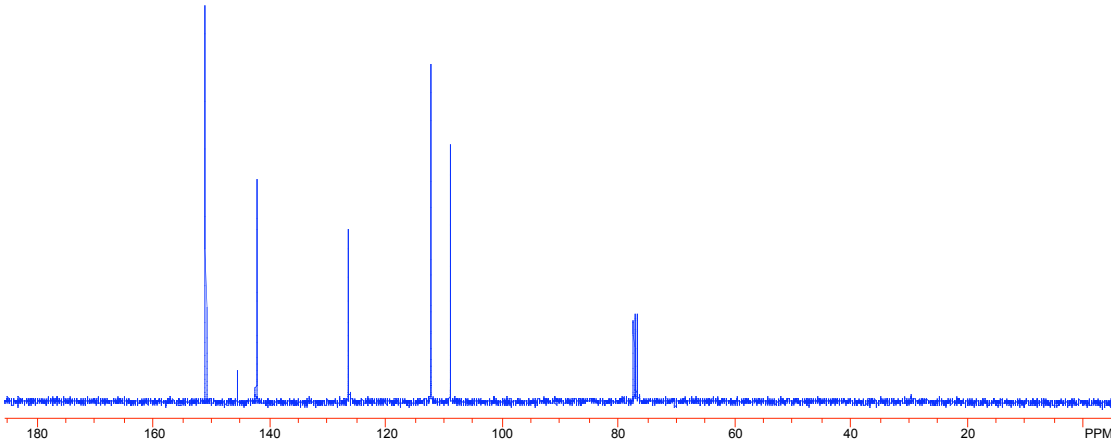
(**4**)



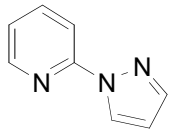
^{13}C NMR ($CDCl_3$)



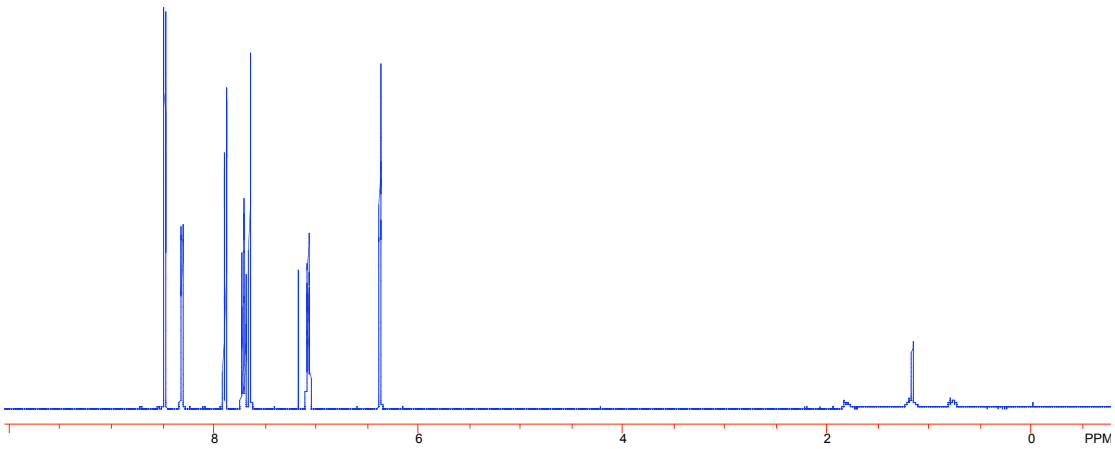
(**4**)



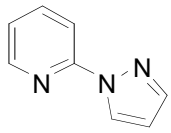
^{1}H NMR ($CDCl_3$)



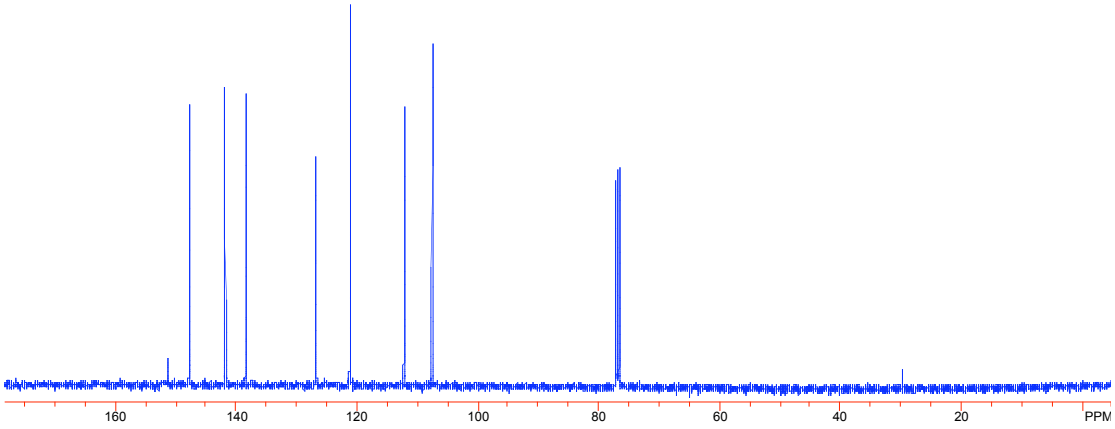
(**5**)



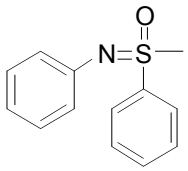
^{13}C NMR ($CDCl_3$)



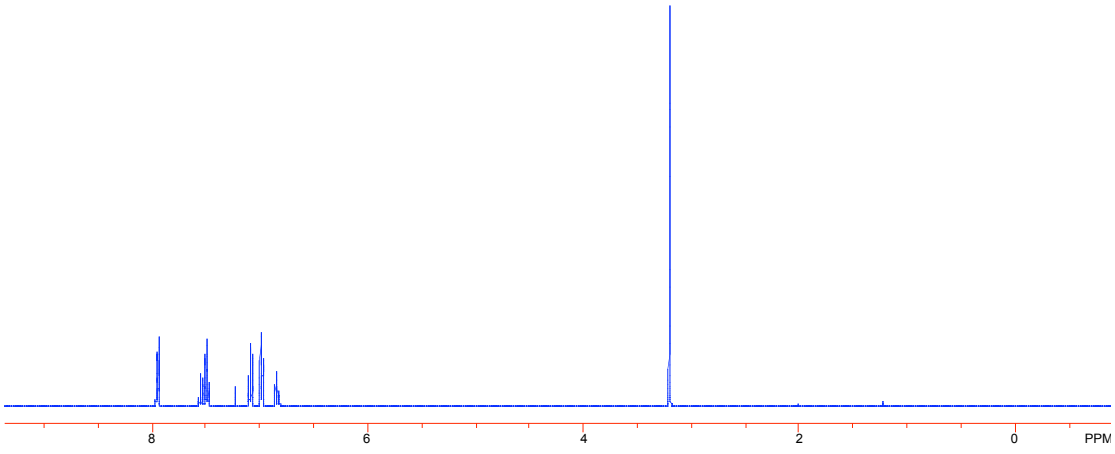
(**5**)



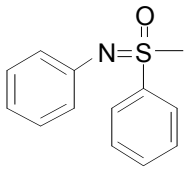
^{1}H NMR ($CDCl_3$)



(**6**)



^{13}C NMR ($CDCl_3$)



(**6**)