Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Transition-metal-free, visible-light-mediated cyclization of *o*-azidoarylalkynes with aryl diazonium salts

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Supporting Information

List of Contents

(A) Materials and equipment

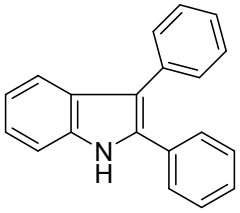
Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. *o*-azidoarylalkynes **2** were prepared according the literature methods.[1] All title products were characterized by Infrared (IR), MS, ^{1}H NMR, ^{13}C NMR and High Resolution mass spectrometer (HRMS). IR spectra were reported in frequency of the absorption (cm^{-1}). ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (*J*) were measured in Hz. Mass spectra were obtained with ionization voltages of 70 eV. HRMS spectra were obtained by ESI on a TOF mass. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure

Typical Experimental Procedure for the Synthesis of compounds 3:

To a Schlenk tube were added *o*-azidoarylalkynes **1** (0.3 mmol), aryldiazonium tetrafluoroborates **2** (0.35 mmol), Eosin Y (3 mol%), DMSO (2.0 mL), 1,4-CHD (0.45 mmol), K_2HPO_4 (0.3 mmol). Then the tube was charged with argon, and was stirred at room temperature with the irradiation of a 5 W blue LED (λ_{max} = 455 nm) for about 14 h. After the reaction was finished, the reaction mixture was diluted in 35 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated $NaHCO_3$ (10 mL), a saturated solution of brine (8 mL), dried (Na_2SO_4) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

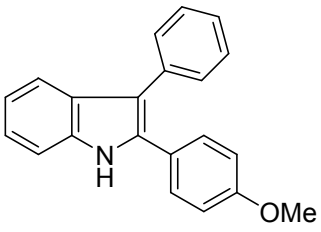
(C) Analytical data



3aa

2,3-Diphenyl-1H-indole (3aa):

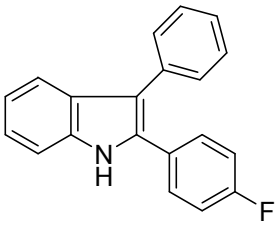
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (brs, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.54-7.27 (m, 12H), 7.16 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.0 135.1, 134.2, 132.8, 132.6, 130.2, 128.8, 128.7, 128.5, 128.2, 127.7, 126.4, 122.8, 120.5, 119.7, 110.6; LRMS (EI 70 ev) *m/z* (%): 269 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1279.



3ab

2-(4-Methoxyphenyl)-3-phenyl-1H-indole (3ab):

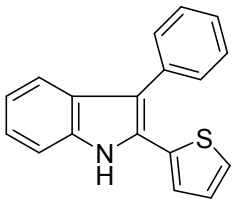
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (brs, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.54-7.36 (m, 7H), 7.29 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 5.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 137.2, 136.7, 135.1, 130.8, 130.2, 129.5, 129.2, 126.7, 126.0, 122.7, 120.6, 119.5, 114.7, 112.0, 111.8, 55.4; LRMS (EI 70 ev) *m/z* (%): 299 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 300.1383, found 300.1389.



3ac

2-(4-Fluorophenyl)-3-phenyl-1H-indole (3ac):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (brs, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.47-7.37 (m, 5H), 7.32-7.29 (m, 1H), 7.27-7.21 (m, 2H), 7.16 (dd, J = 10.4 Hz, J = 2.0 Hz, 2H), 7.10-7.06 (m, 1H), 6.99-6.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 161.7, 136.0, 134.8, 134.7, 134.6, 132.7, 130.4, 130.3, 128.9, 128.8, 126.7, 123.94, 123.90, 123.2, 120.7, 120.0, 116.0, 115.1, 114.8, 114.7, 114.5, 111.0; LRMS (EI 70 ev) *m/z* (%): 287 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{15}FN$ $(M+H)^+$ 288.1189, found 288.1197.

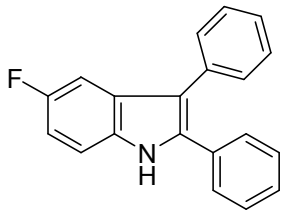


3ad

3-Phenyl-2-(thiophen-2-yl)-1H-indole (3ad):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (brs, 1H), 7.56-7.52 (m, 3H), 7.49 (dd, J = 10.0 Hz, J = 2.4 Hz, 2H), 7.42-7.37 (m, 3H), 7.23 (dd, J = 1.2 Hz, J = 8.4 Hz, 1H), 7.14-7.10 (m, 1H), 6.38 (dd, J = 3.2 Hz, J = 2.8 Hz, 1H), 6.35 (d, J = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 141.5, 135.4,

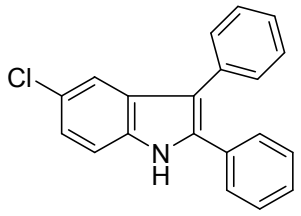
134.7, 130.3, 128.9, 128.5, 127.1, 125.4, 123.0, 120.4, 119.5, 114.7, 112.0, 1108, 106.9; HRMS m/z (ESI) calcd for $C_{18}H_{14}NS$ $(M+H)^+$ 276.0841, found 276.0844.



3af

5-Fluoro-2,3-diphenyl-1H-indole (3af):

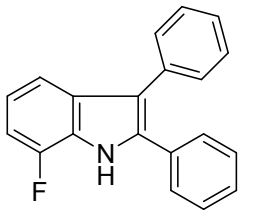
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (brs, 1H), 7.54-7.41 (m, 6H), 7.40-7.28 (m, 6H), 7.03-6.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 157.1, 135.7, 134.4, 132.4, 130.0, 129.29, 129.20, 128.8, 128.7, 128.0, 127.8, 126.5, 115.2, 111.6, 111.5, 111.2, 110.9, 104.7, 104.4; LRMS (EI 70 ev) *m/z* (%): 287 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{15}FN$ $(M+H)^+$ 288.1189, found 288.1196.



3ag

5-Chloro-2,3-diphenyl-1H-indole (3ag):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (brs, 1H), 7.67 (d, J = 2.8 Hz, 1H), 7.51-7.43 (m, 5H), 7.41-7.29 (m, 6H), 7.22 (dd, J = 6.8 Hz, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.3, 134.2, 134.1, 132.0, 130.1, 129.8, 128.7, 128.6, 128.1, 128.0, 126.6, 126.2, 122.9, 119.1, 114.8, 111.7; LRMS (EI 70 ev) *m/z* (%): 303 (M^+, 66); HRMS m/z (ESI) calcd for $C_{20}H_{15}ClN$ $(M+H)^+$ 304.0894, found 304.0890.

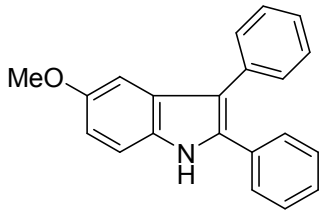


3ah

7-Fluoro-2,3-diphenyl-1H-indole (3ah):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (brs, 1H), 7.55-7.29 (m, 11H), 7.10-7.04 (m, 1H), 7.03 (ddd, J = 6.0 Hz, J = 2.4 Hz, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 147.6, 135.1, 134.7, 132.53, 132.51, 132.3, 130.1, 128.9, 128.3, 128.1, 126.5, 124.4, 124.1, 120.7, 115.7, 115.6, 115.3, 107.5, 107.4; LRMS (EI 70 ev) *m/z* (%): 287 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{15}FN$ $(M+H)^+$

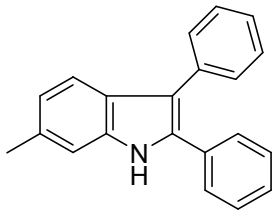
288.1189, found 288.1191.



3ai

5-Methoxy-2,3-diphenyl-1H-indole (3ai):

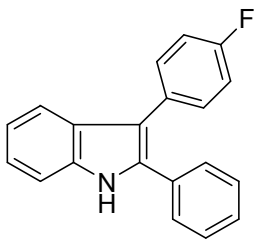
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (brs, 1H), 7.47-7.34 (m, 6H), 7.32-7.28 (m, 5H), 7.15 (d, J = 2.4 Hz, 1H), 6.94 (dd, J = 10.0 Hz, J = 2.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 135.3, 134.8, 132.6, 131.1, 130.0, 129.2, 128.6, 128.5, 128.1, 127.6, 126.2, 114.8, 112.9, 111.7, 101.2, 55.8; LRMS (EI 70 ev) *m/z* (%): 299 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 300.1383, found 300.1380.



3aj

6-Methyl-2,3-diphenyl-1H-indole (3aj):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (brs, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51-7.29 (m, 10H), 7.23 (s, 1H), 7.05 (dd, J = 8.4 Hz, J = 0.8 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3, 135.2, 133.4, 132.7, 132.5, 130.0, 128.7, 128.3, 127.9, 127.4, 126.5, 126.0, 122.1, 119.5, 114.9, 110.6, 21.4; LRMS (EI 70 ev) *m/z* (%): 283 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 284.1435, found 284.1437.

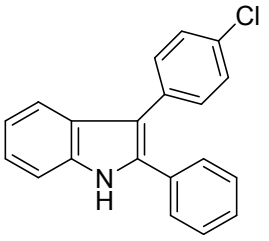


3ba

3-(4-Fluorophenyl)-2-phenyl-1H-indole (3ba):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.40-7.34 (m, 5H), 7.31-7.28 (m, 3H), 7.23-7.20 (m, 1H), 7.16-7.13 (m, 1H), 7.09-7.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.7, 160.3, 136.0, 134.3, 132.7, 131.88, 131.82, 131.1, 131.0, 129.09, 129.05, 128.4, 128.0, 122.9,

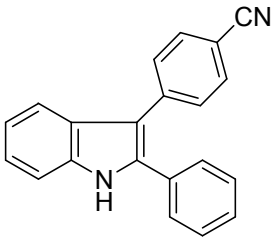
120.7, 119.5, 115.4, 115.2, 114.2, 111.1; LRMS (EI 70 ev) *m/z* (%): 287 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{15}FN$ $(M+H)^+$ 288.1189, found 288.1193.



3ca

3-(4-Chlorophenyl)-2-phenyl-1H-indole (3ca):

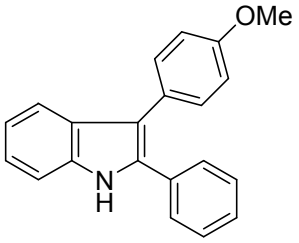
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (brs, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.46-7.30 (m, 10H), 7.25 (t, J = 6.2 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.1, 134.5, 133.7, 132.4, 132.0, 131.4, 129.1, 128.8, 128.5, 128.3, 128.1, 123.0, 120.8, 119.5, 113.9, 111.0; LRMS (EI 70 ev) *m/z* (%): 303 (M^+, 72); HRMS m/z (ESI) calcd for $C_{20}H_{15}ClN$ $(M+H)^+$ 304.0894, found 304.0898.



3da

4-(3-Phenyl-1H-indol-2-yl)benzonitrile (3da):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (brs, 1H), 7.76 (d, J = 6.8 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.51-7.45 (m, 4H), 7.39-7.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: LRMS (EI 70 ev) *m/z* (%): 294 (M^+, 91); HRMS m/z (ESI) calcd for $C_{21}H_{15}NO_2$ $(M+H)^+$ 295.1230, found 295.1237.

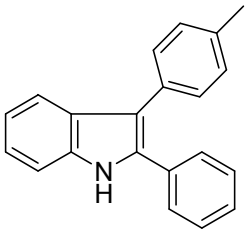


3ea

3-(4-Methoxyphenyl)-2-phenyl-1H-indole (3ea):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (brs, 1H), 7.55-7.51 (m, 3H), 7.48-7.46 (m, 1H), 7.35-7.30 (m, 4H), 7.27-7.25 (m, 1H), 7.16 (t, J = 6.8 Hz, 1H), 7.06 (t, J = 6.8 Hz, 1H), 6.98 (t, J = 7.6 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 136.4, 133.8, 133.2, 130.9, 128.8, 128.4, 128.3, 128.1, 127.6, 127.1, 122.1, 119.6, 118.7, 114.1, 111.3, 54.5; LRMS (EI 70 ev) *m/z* (%): 299 (M^+, 100); HRMS

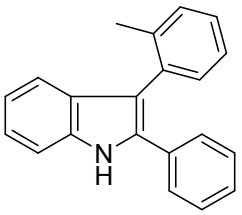
m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 300.1383, found 300.1390.



3fa

2-Phenyl-3-*p*-tolyl-1H-indole (3fa):

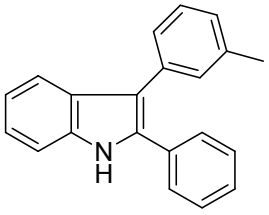
^1H NMR (400 MHz, $CDCl_3$) δ: 8.20 (brs, 1H), 7.74 (d, J = 80 Hz, 1H), 7.50-7.20 (m, 12H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.0, 135.9, 134.1, 132.8, 132.1, 130.0, 129.3, 129.0, 128.7, 128.2, 127.7, 122.7, 120.5, 119.8, 115.1, 111.1, 21.5; LRMS (EI 70 ev) *m/z* (%): 283 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 284.1435, found 284.1441.



3ga

2-Phenyl-3-*o*-tolyl-1H-indole (3ga):

^1H NMR (400 MHz, $CDCl_3$) δ: 8.25 (brs, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.37-7.29 (m, 7H), 7.25-7.19 (m, 4H), 7.12 (dd, J = 10.8 Hz, J = 1.6 Hz,1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 136.1, 134.6, 133.8, 133.1, 131.7, 130.3, 129.8, 128.8, 127.7, 127.2, 126.8, 125.9, 122.8, 120.3, 120.2, 114.9, 110.8, 20.4; LRMS (EI 70 ev) *m/z* (%): 283 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 284.1435, found 284.1444.



3ha

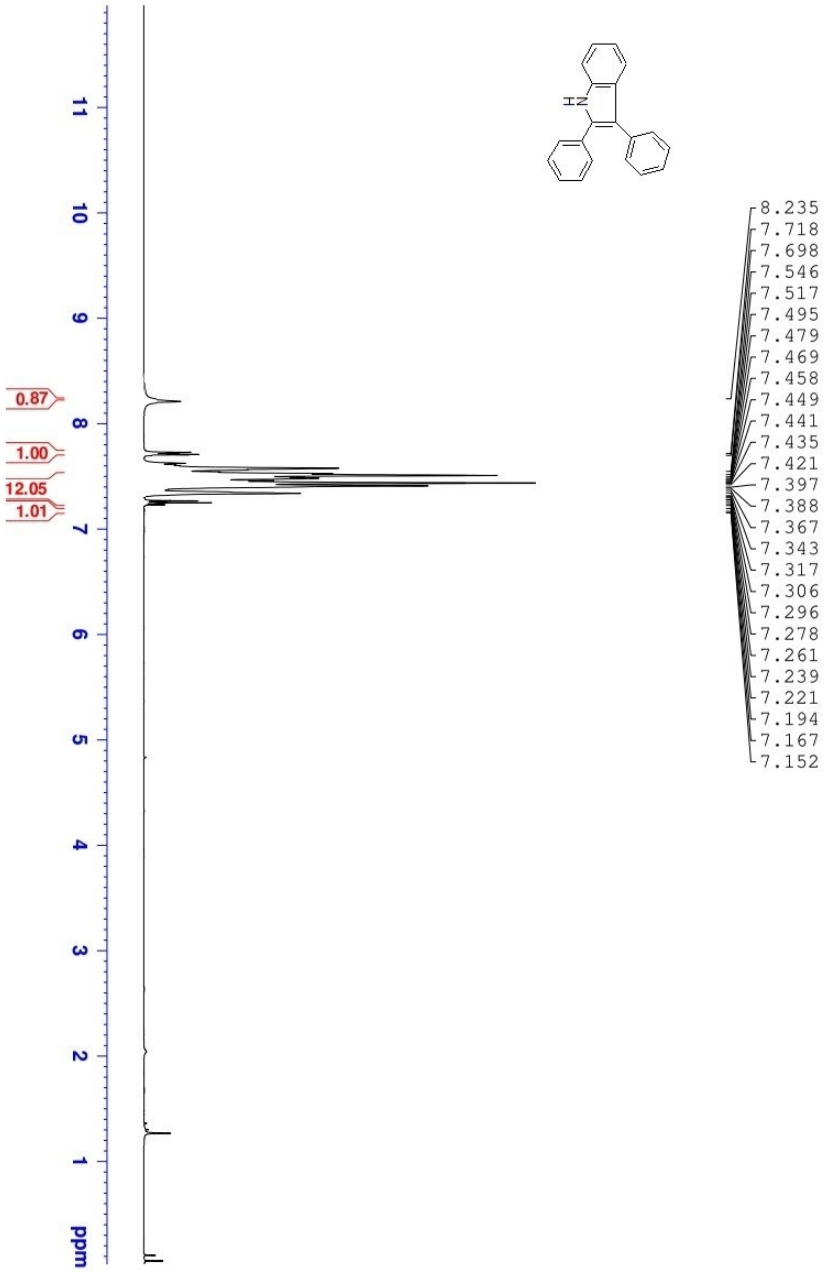
2-Phenyl-3-*m*-tolyl-1H-indole (3ha):

^1H NMR (400 MHz, $CDCl_3$) δ: 8.24 (brs, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.50-7.46 (m, 3H), 7.41-7.35 (m, 4H), 7.34-7.19 (m, 5H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ: 138.8, 136.4, 136.1, 135..5, 134.1, 133.0, 129.3, 129.0, 128.8, 128.3, 127.4, 126.0, 125.3, 124.3, 122.1, 120.1, 118.7, 111.4, 25.1; LRMS (EI 70 ev) *m/z* (%): 283 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}NO$ $(M+H)^+$ 284.1435, found 284.1439.

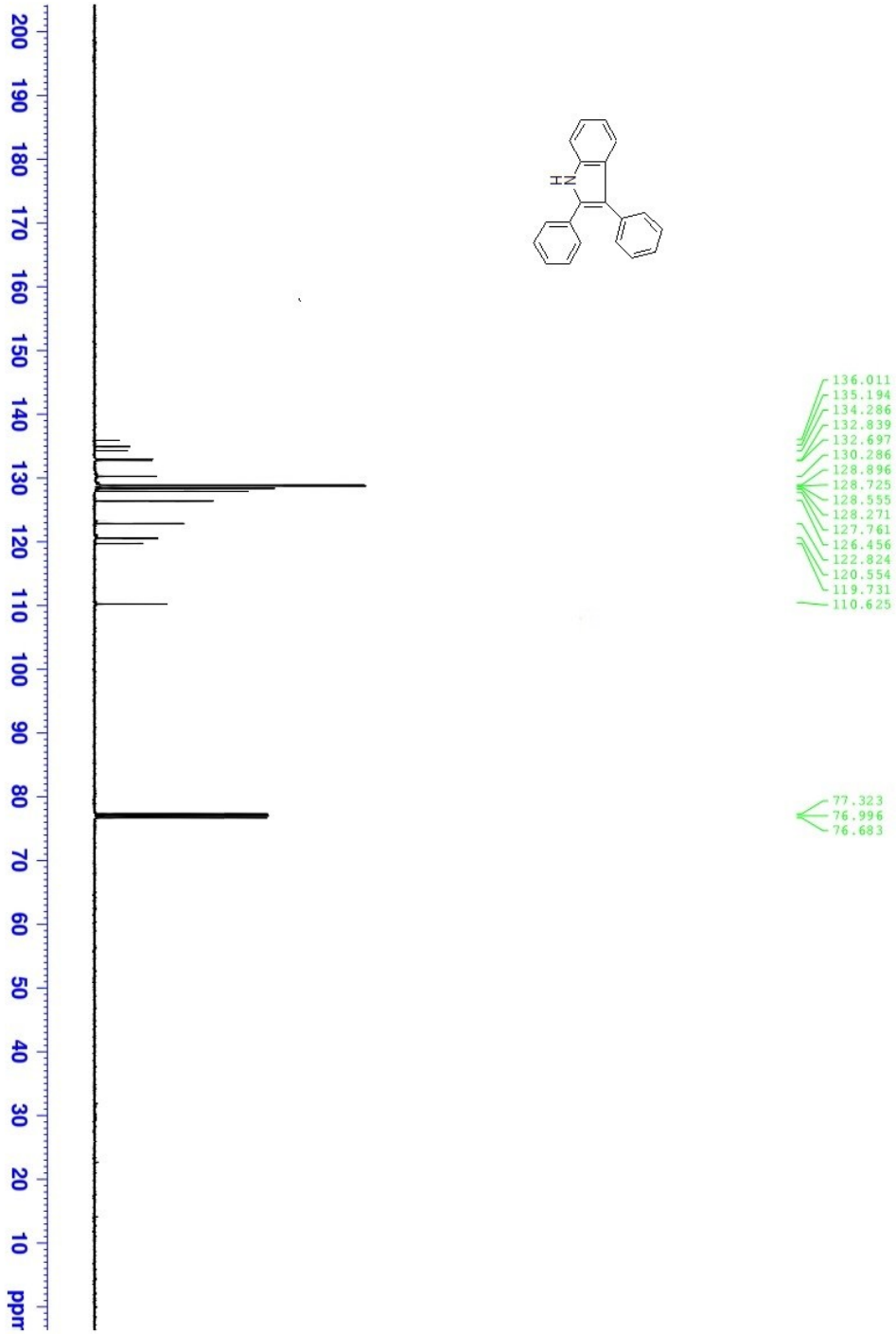
References

1. Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 8358.

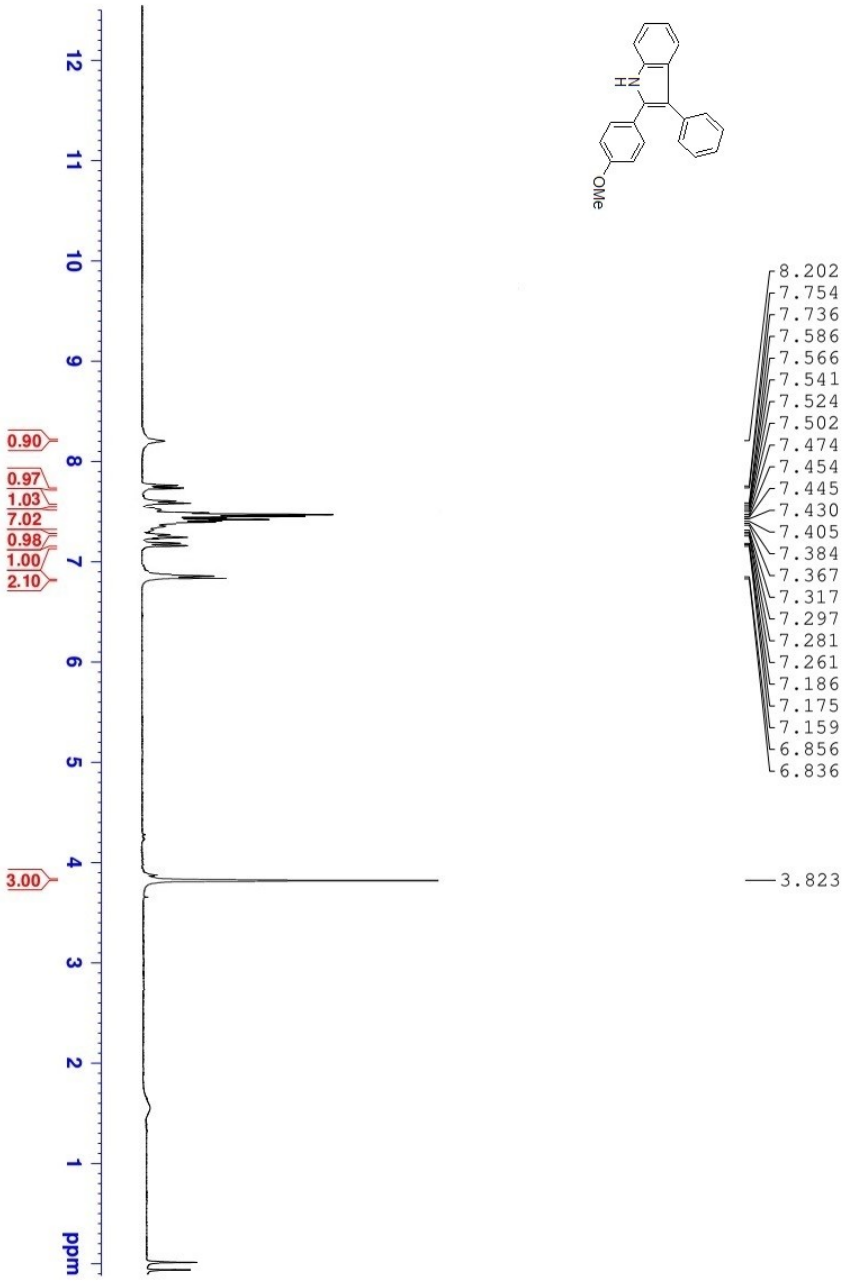
(E) **Spectra**



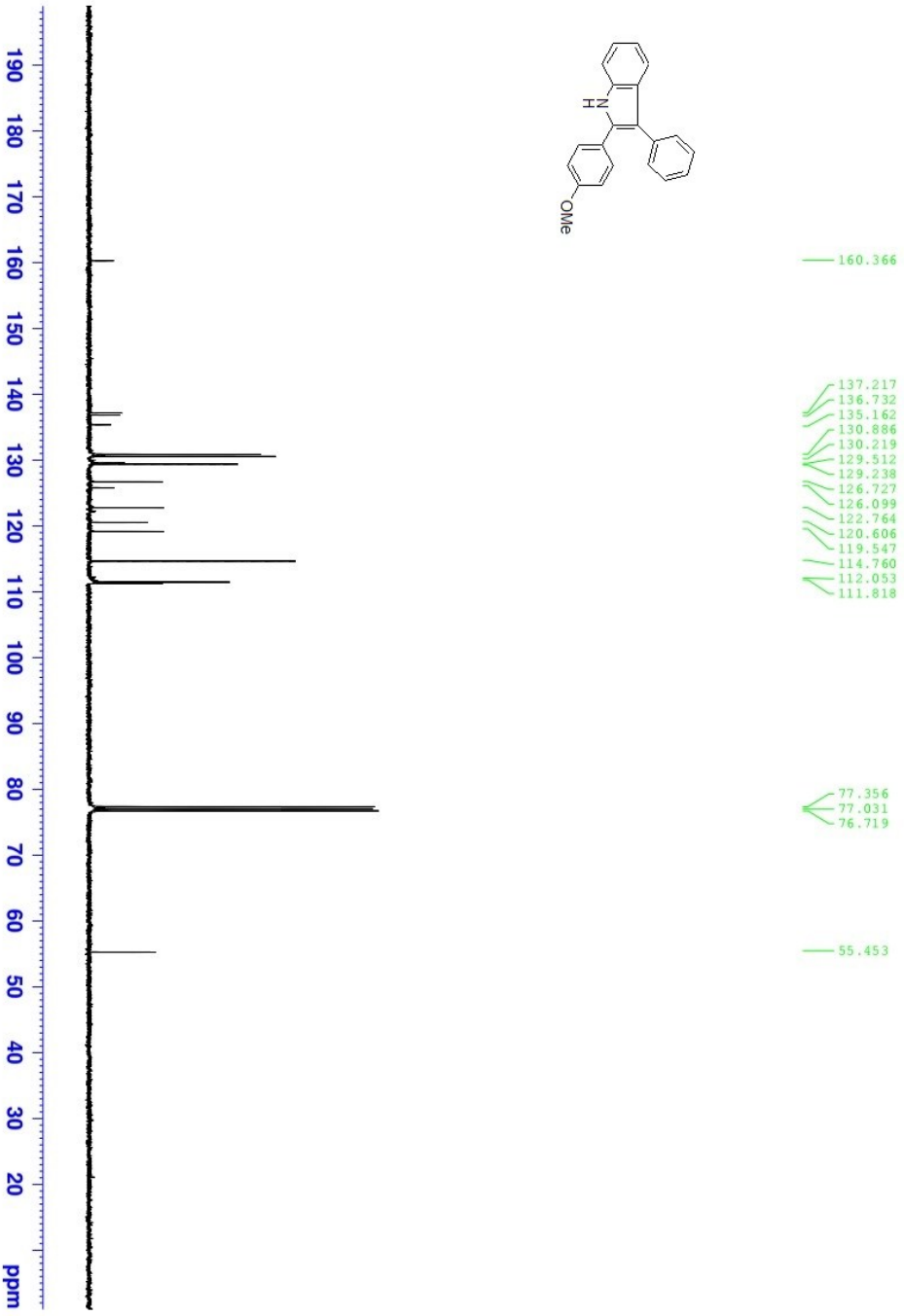
^{1}H NMR of Compound 3aa



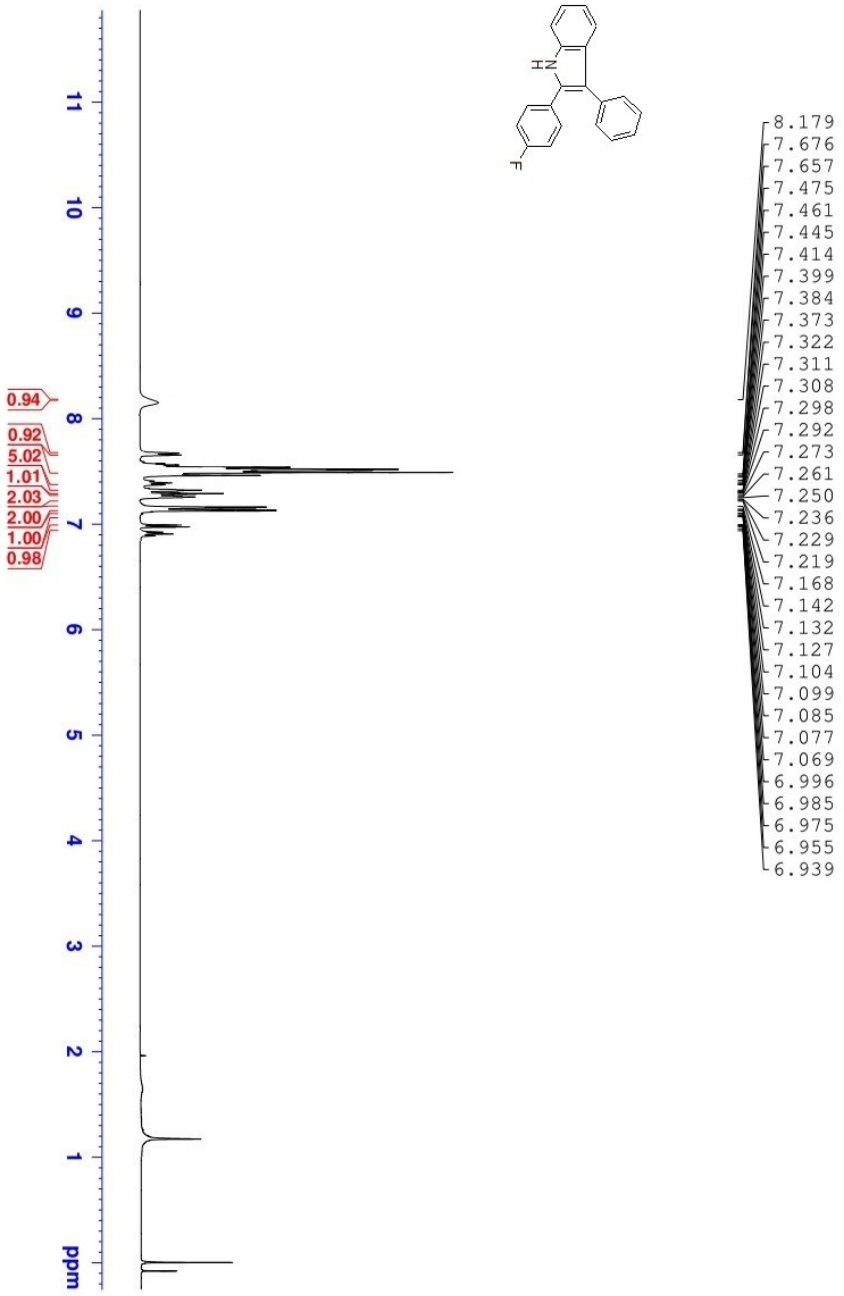
^{13}C NMR of Compound 3aa



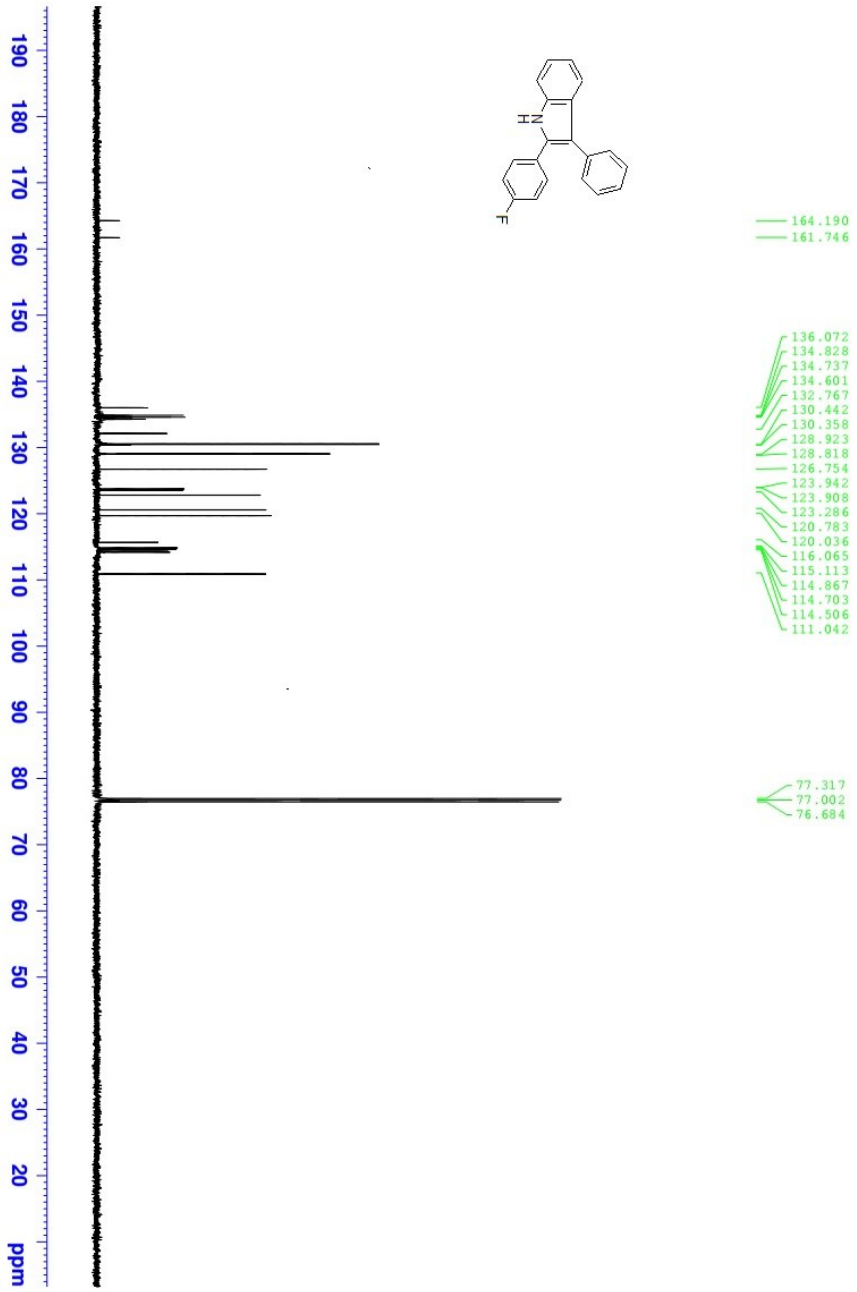
^{1}H NMR of Compound 3ab



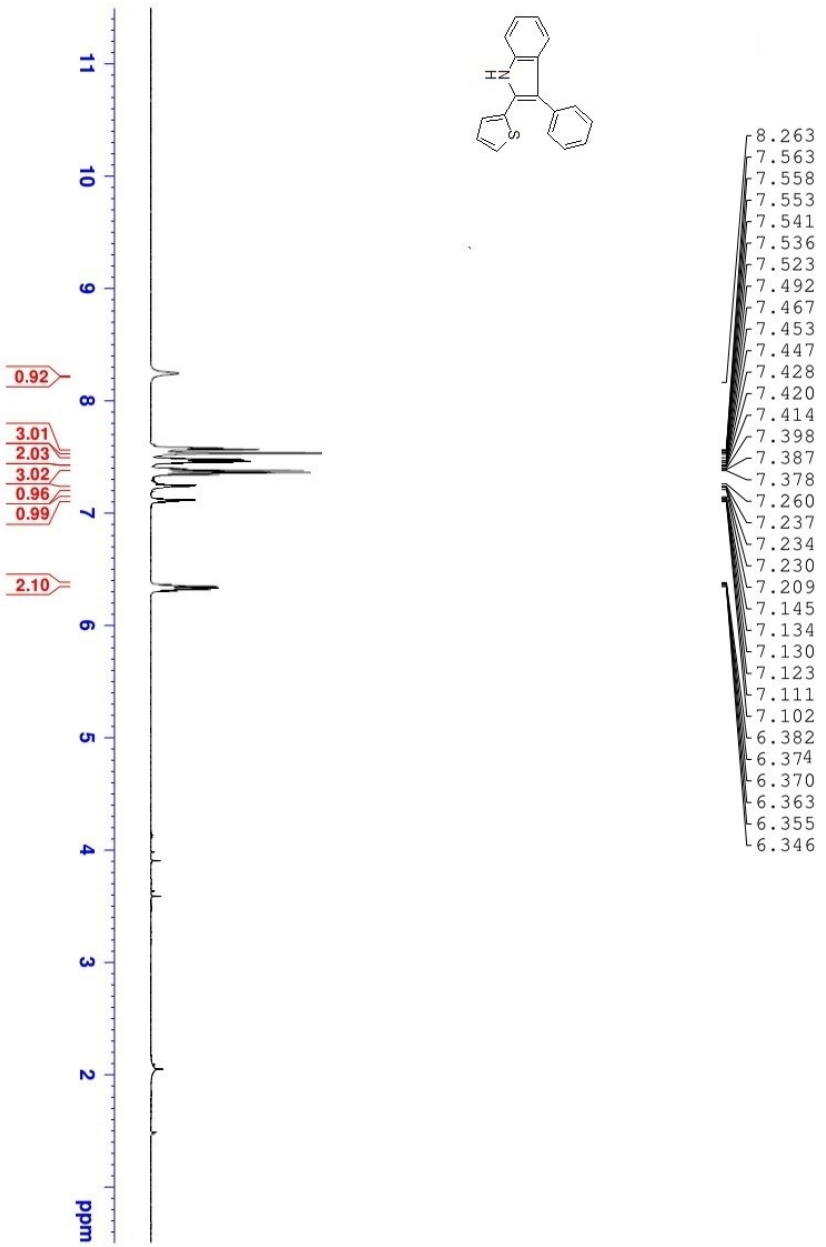
^{13}C NMR of Compound 3ab



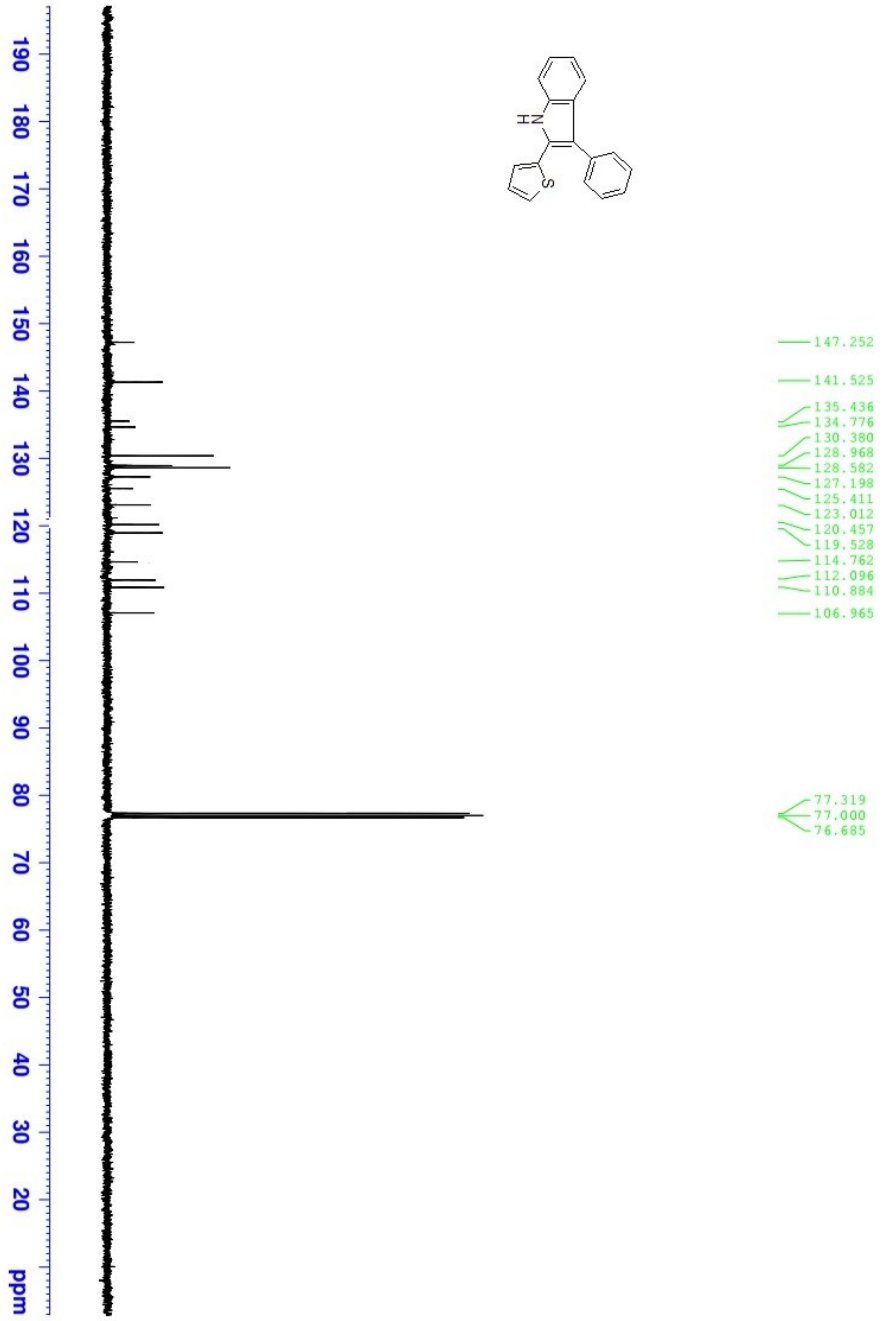
^{1}H NMR of Compound 3ac



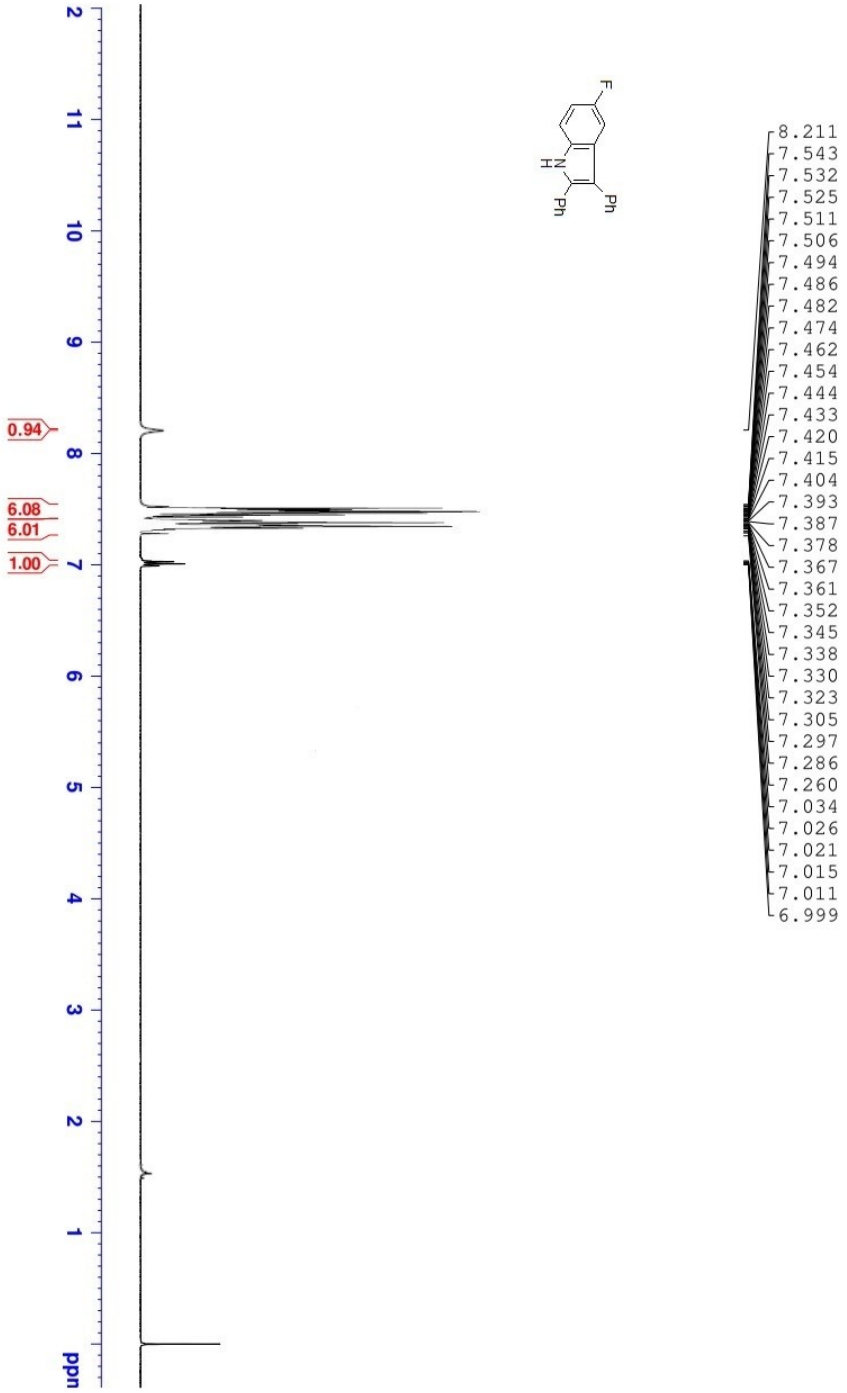
^{13}C NMR of Compound 3ac



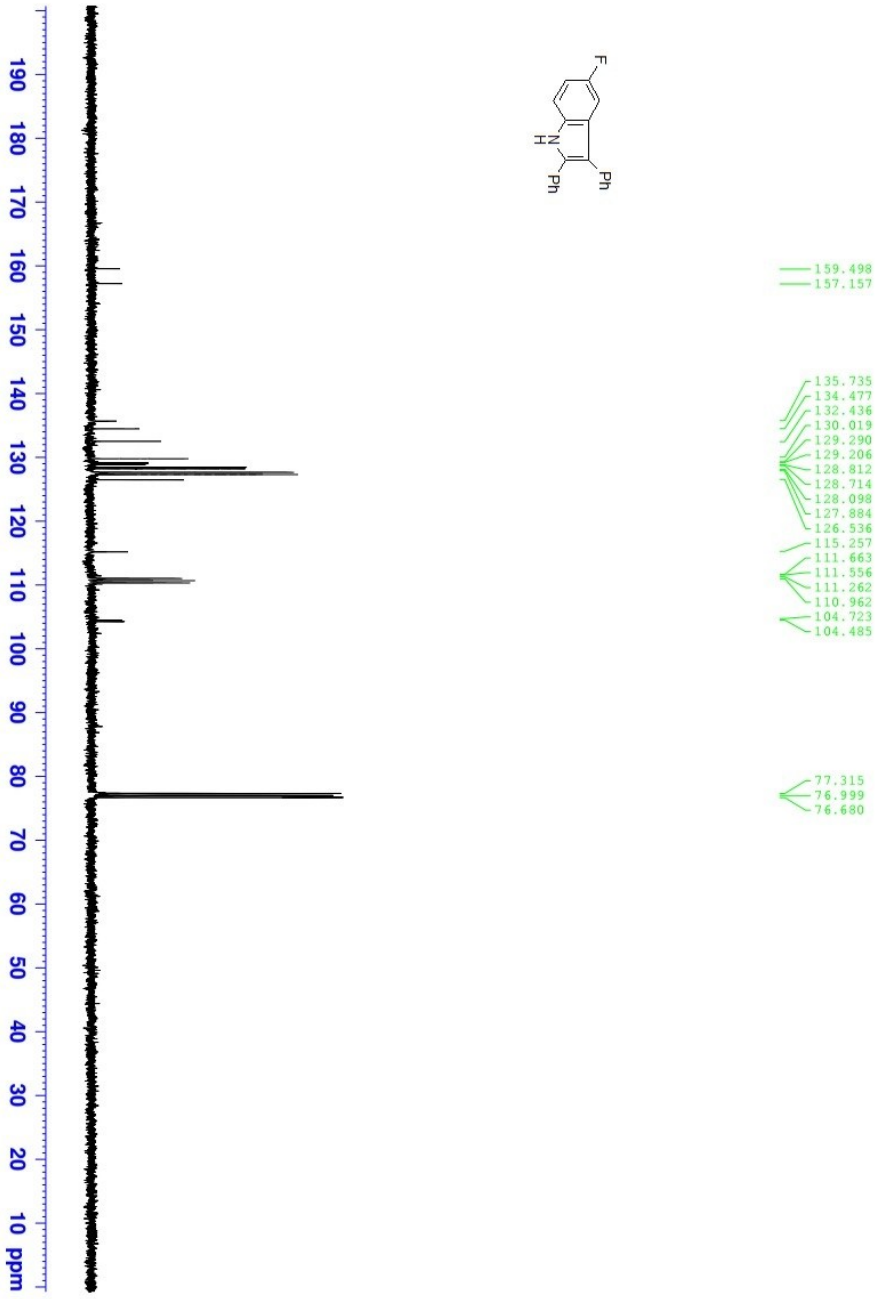
^{1}H NMR of Compound 3ad



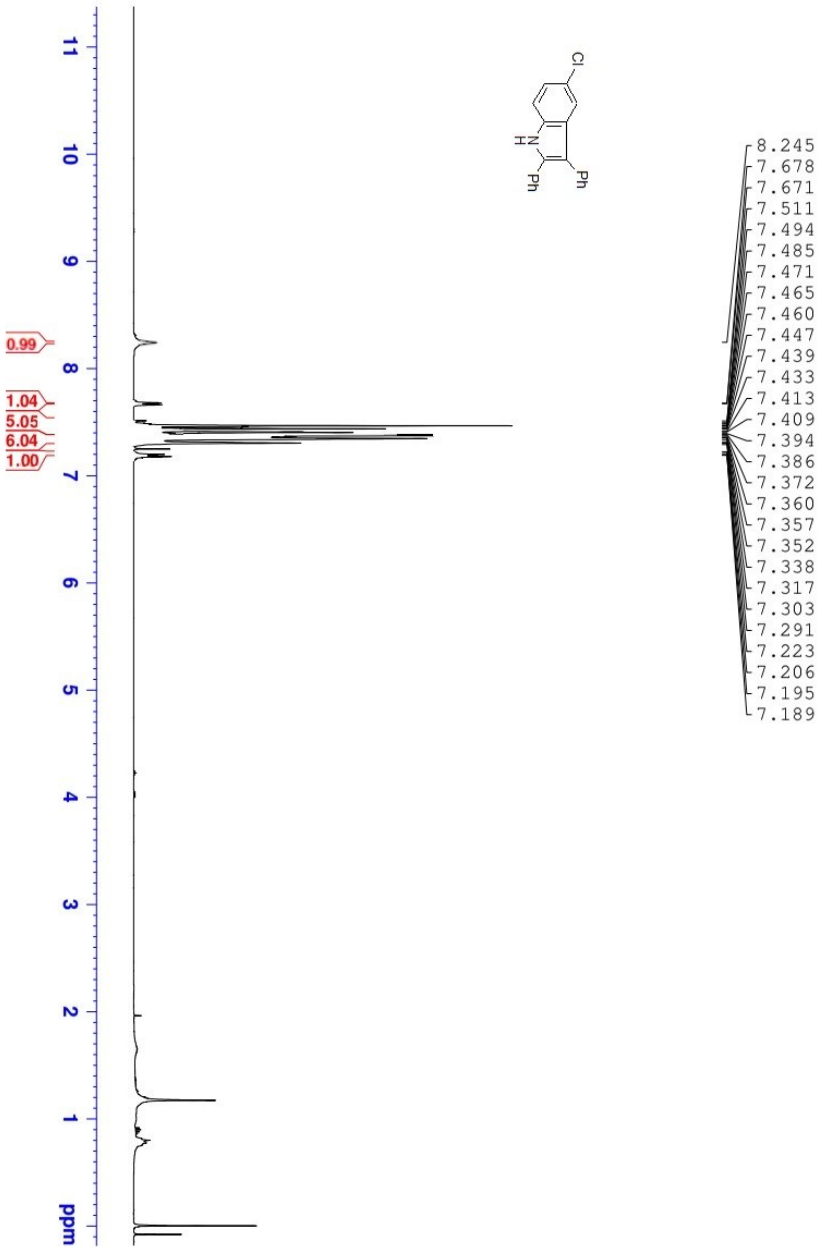
^{13}C NMR of Compound 3ad



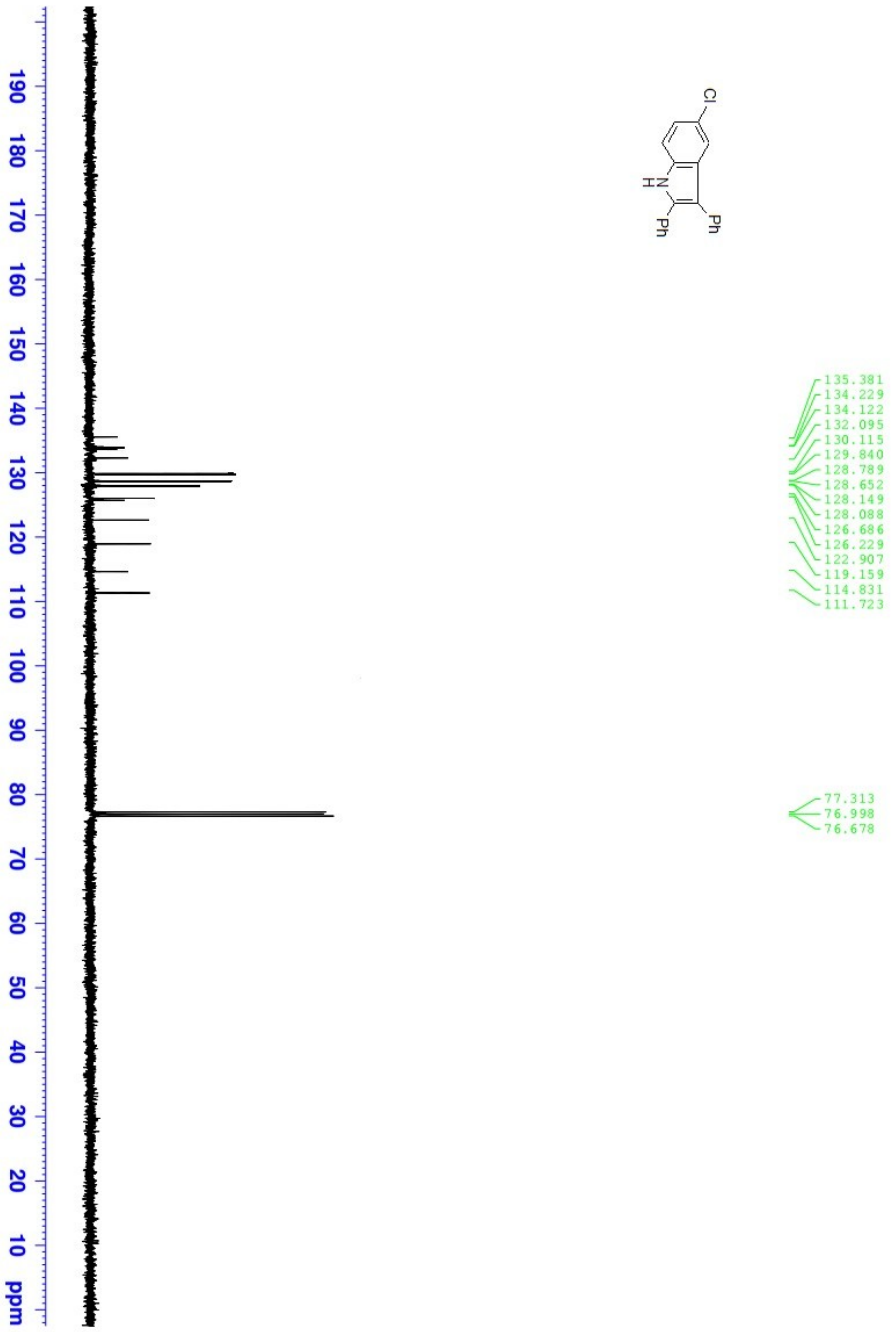
^{1}H NMR of Compound 3af



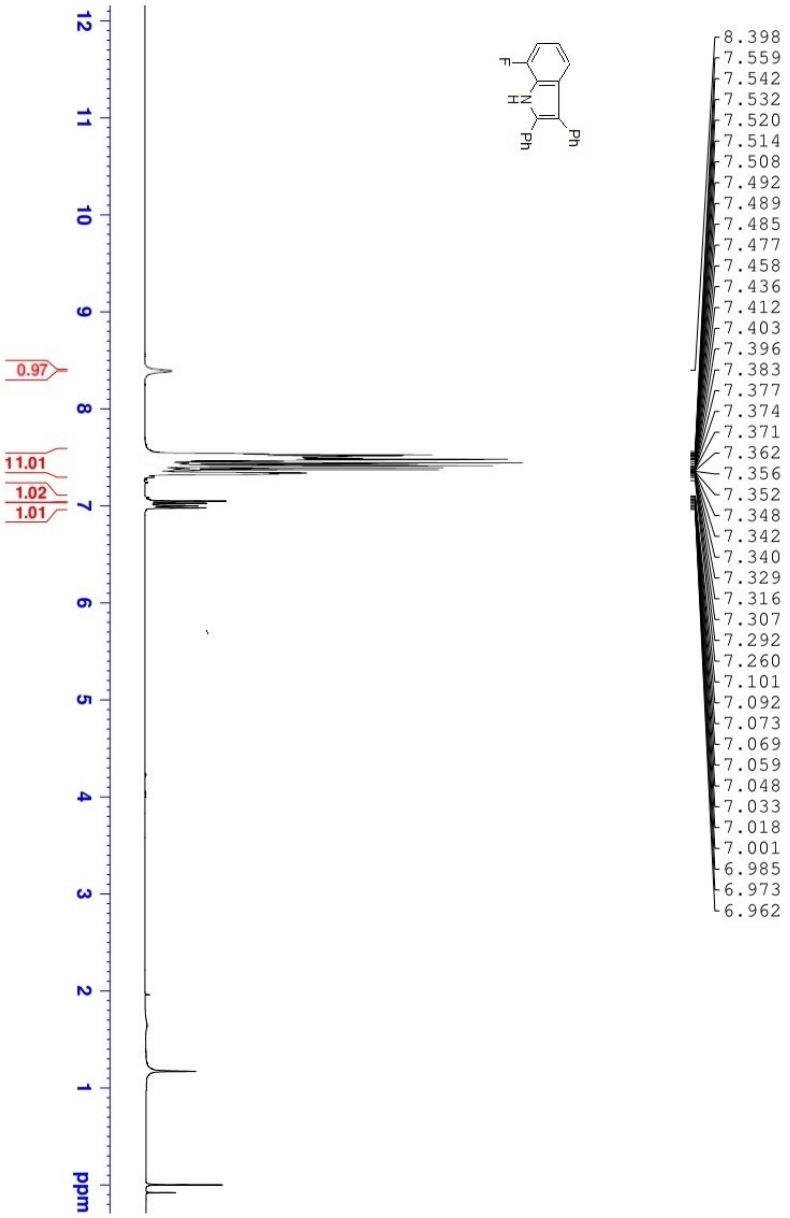
^{13}C NMR of Compound 3af



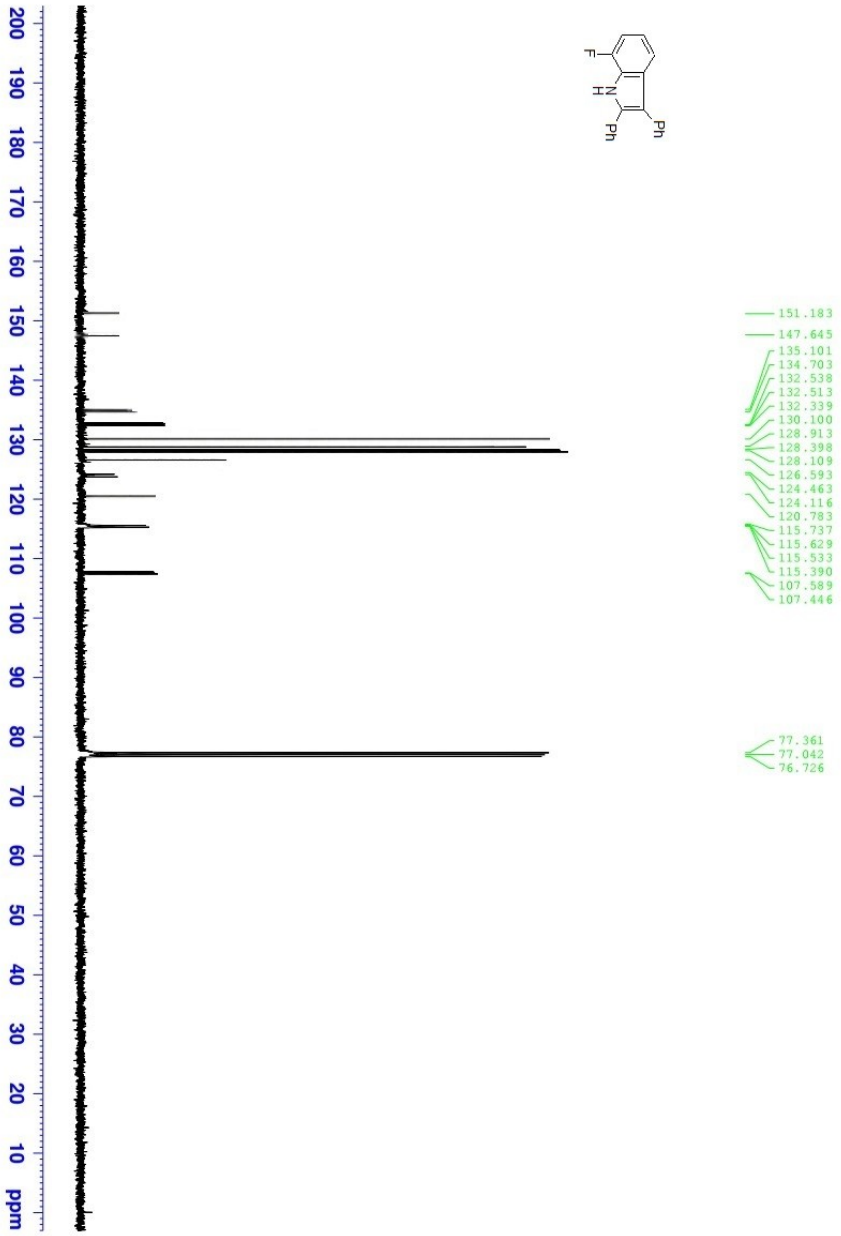
^{1}H NMR of Compound 3ag



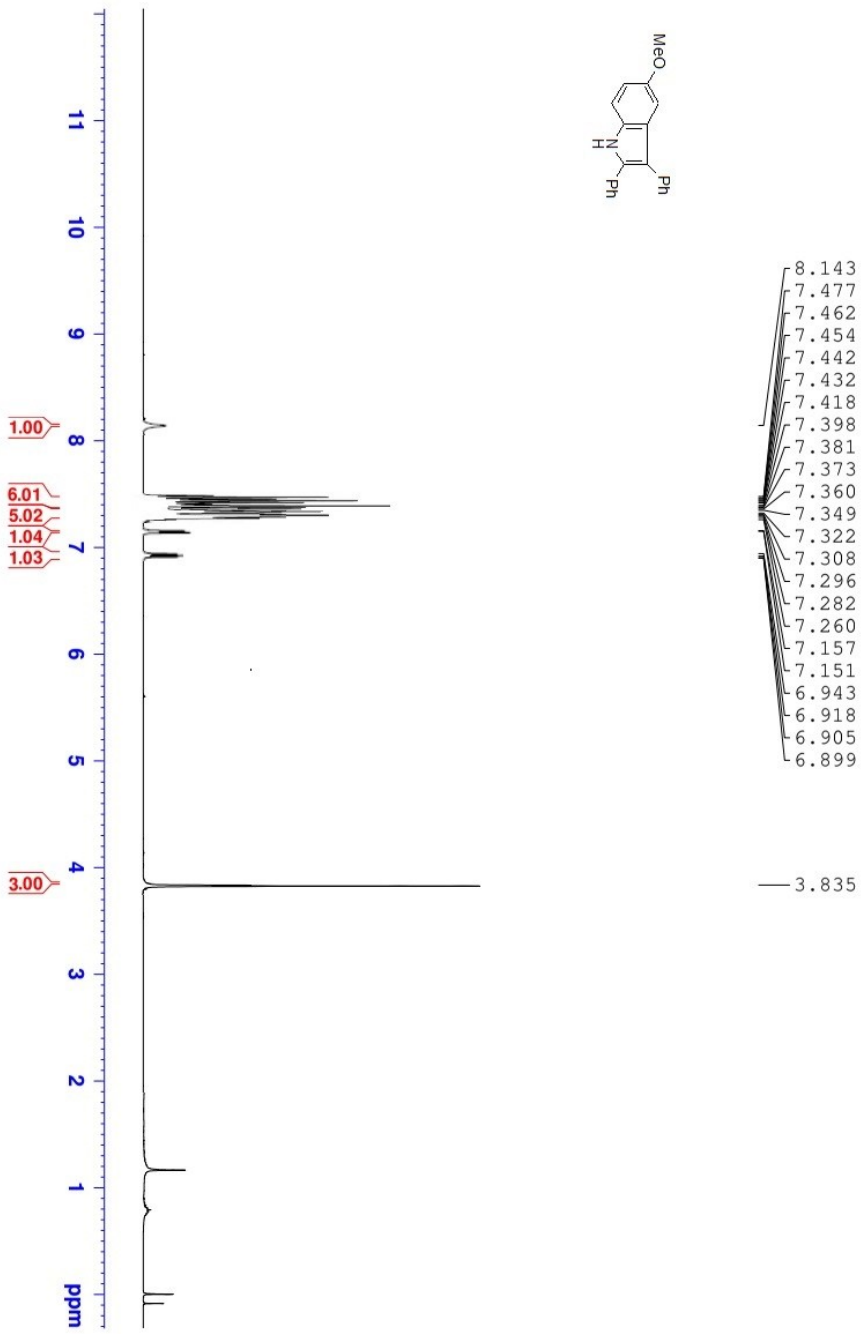
^{13}C NMR of Compound 3ag



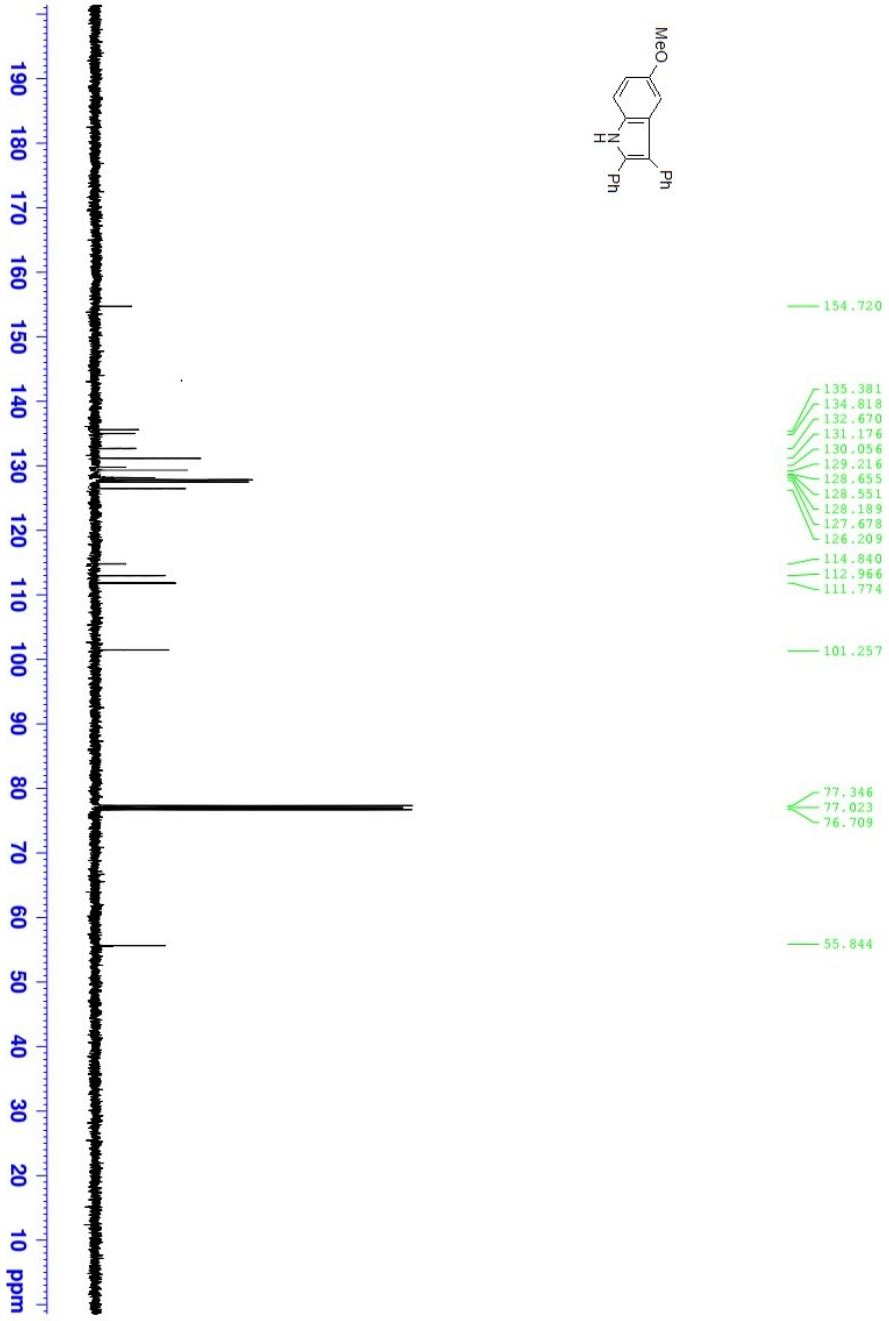
^{1}H NMR of Compound 3ah



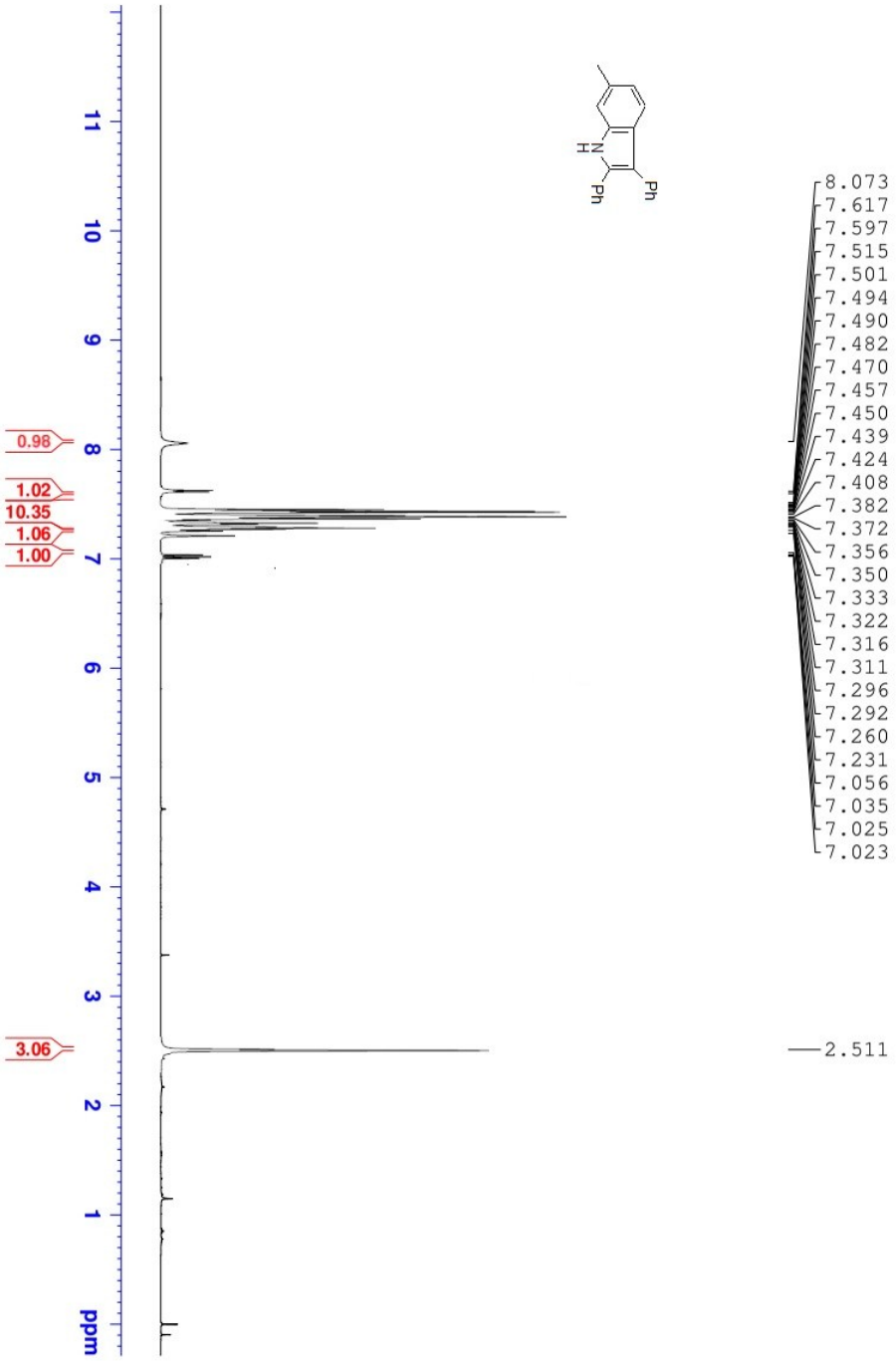
^{13}C NMR of Compound 3ah



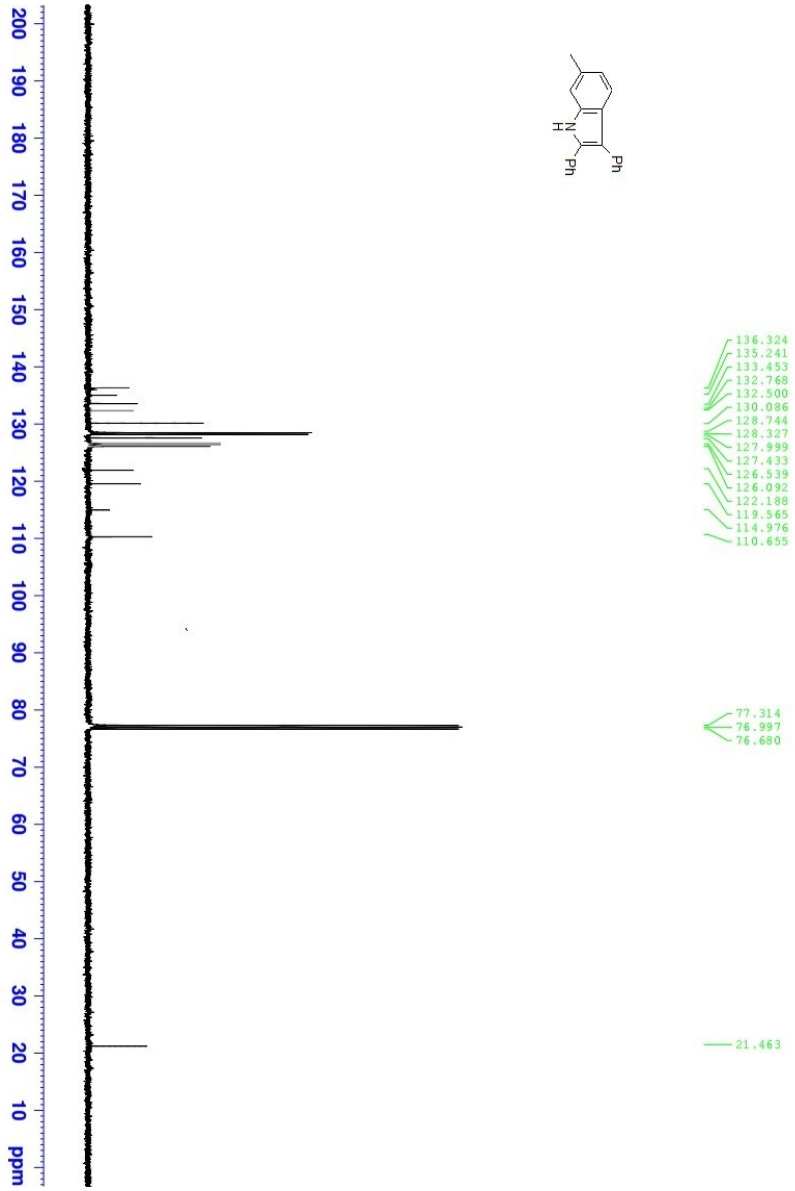
^{1}H NMR of Compound 3ai



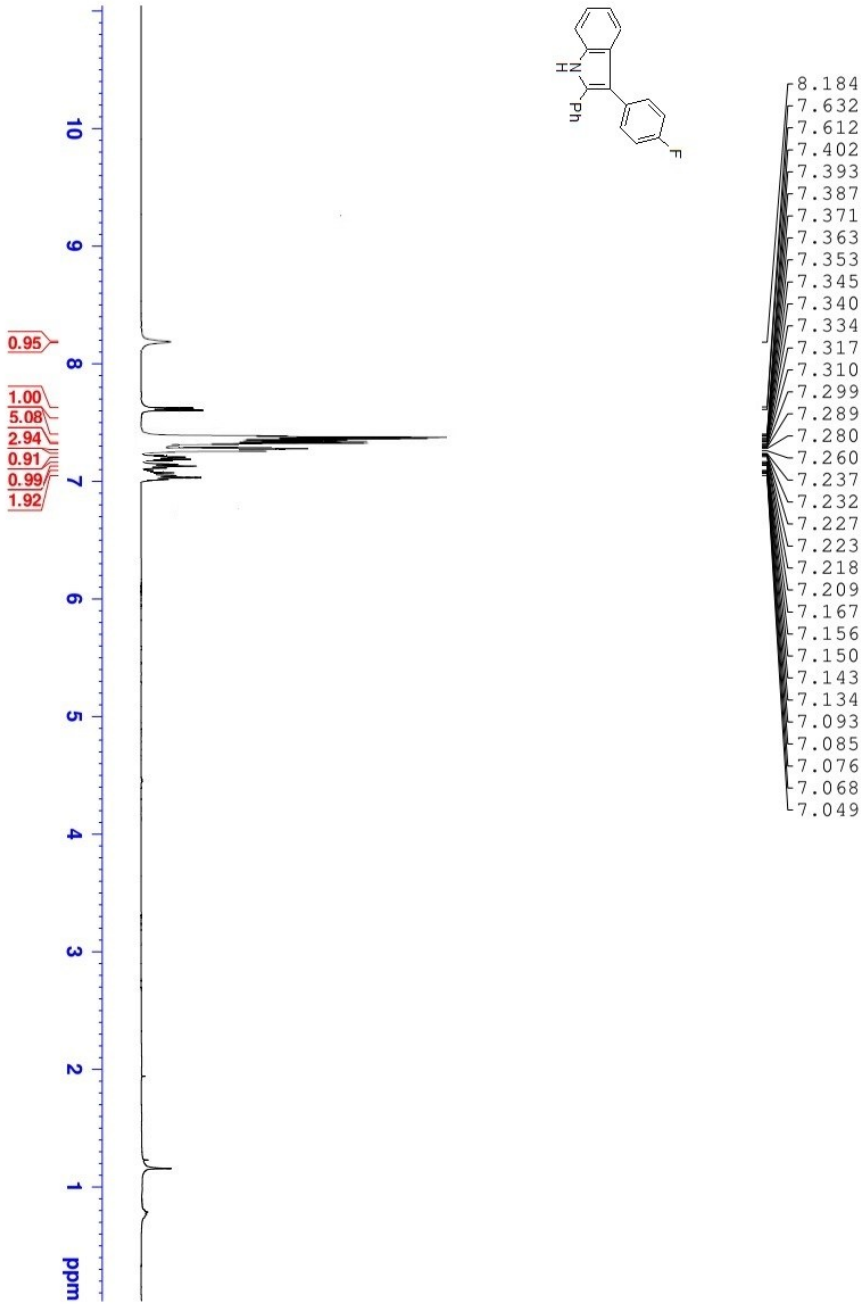
^{13}C NMR of Compound 3ai



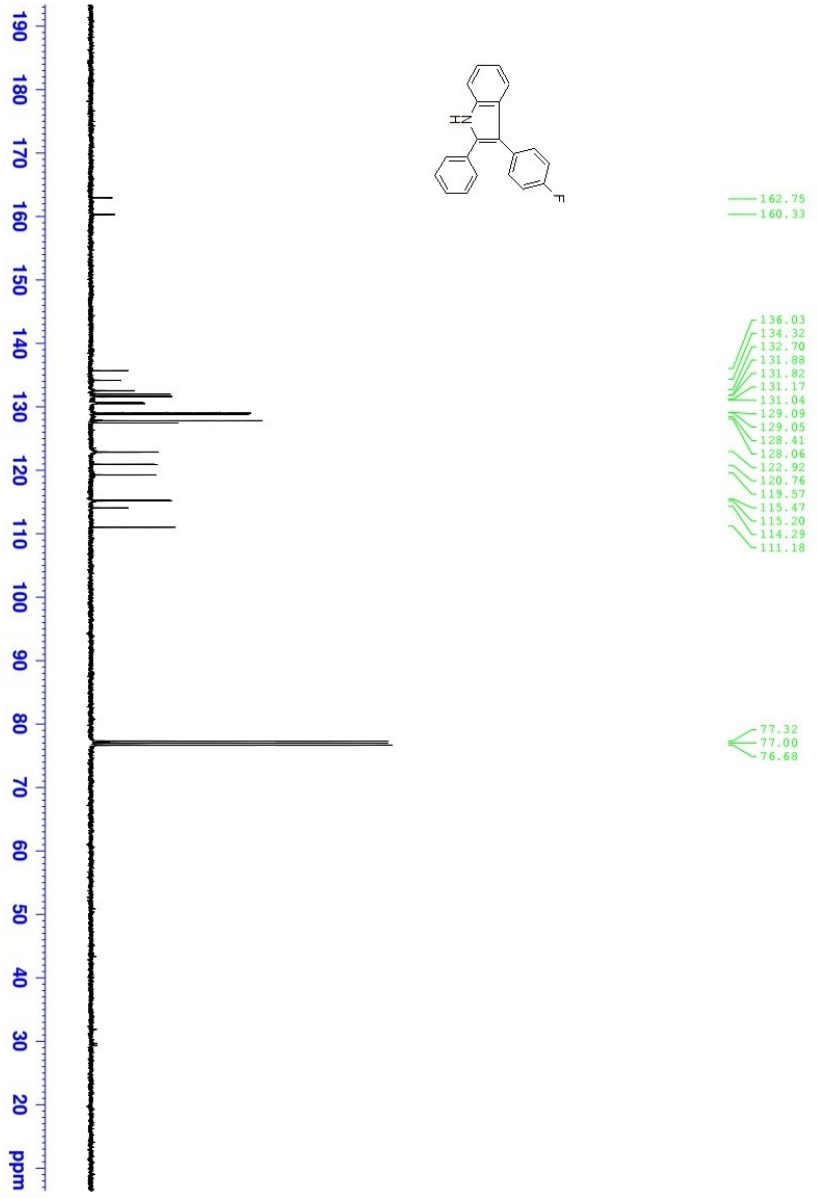
^{1}H NMR of Compound 3aj



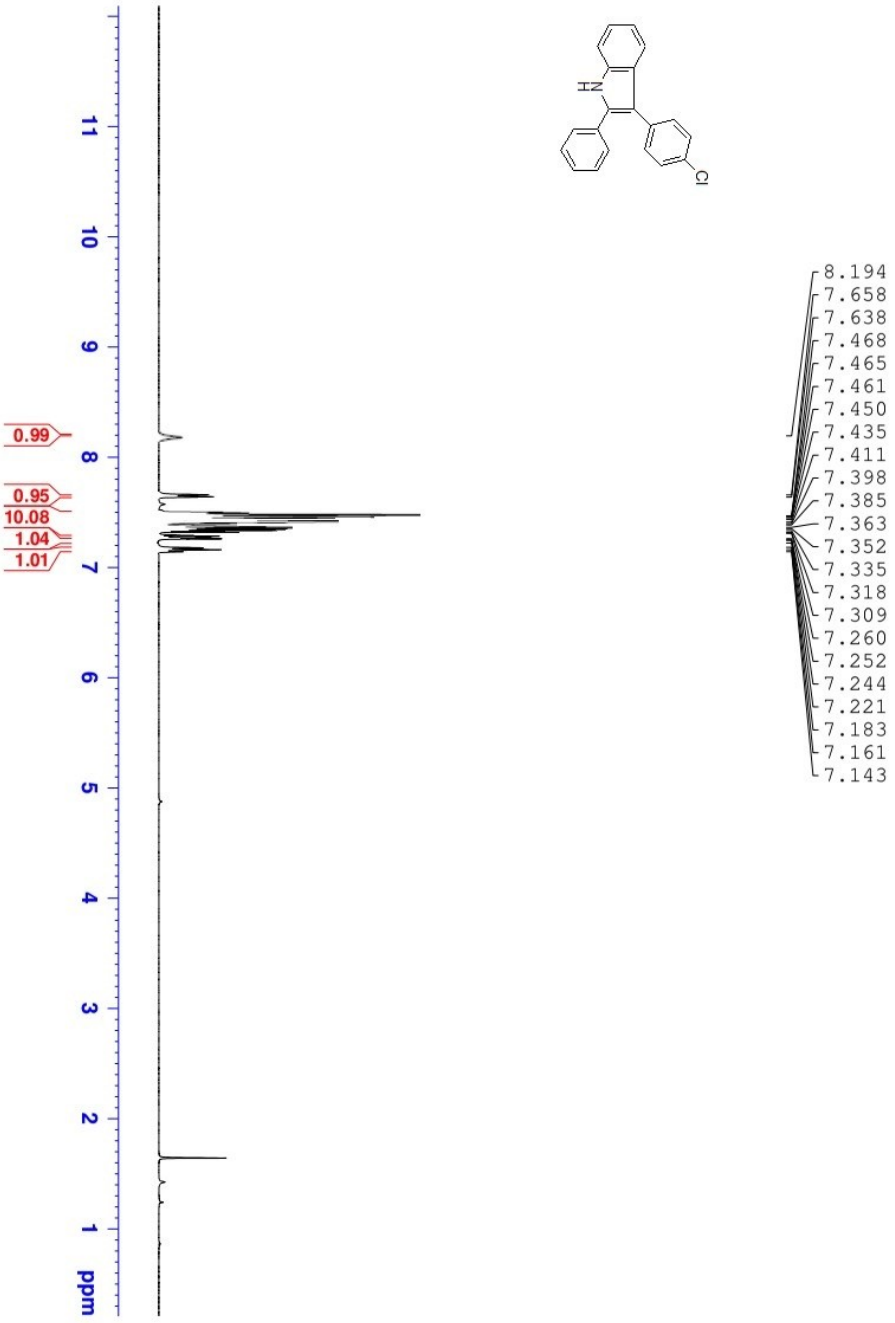
^{13}C NMR of Compound 3aj



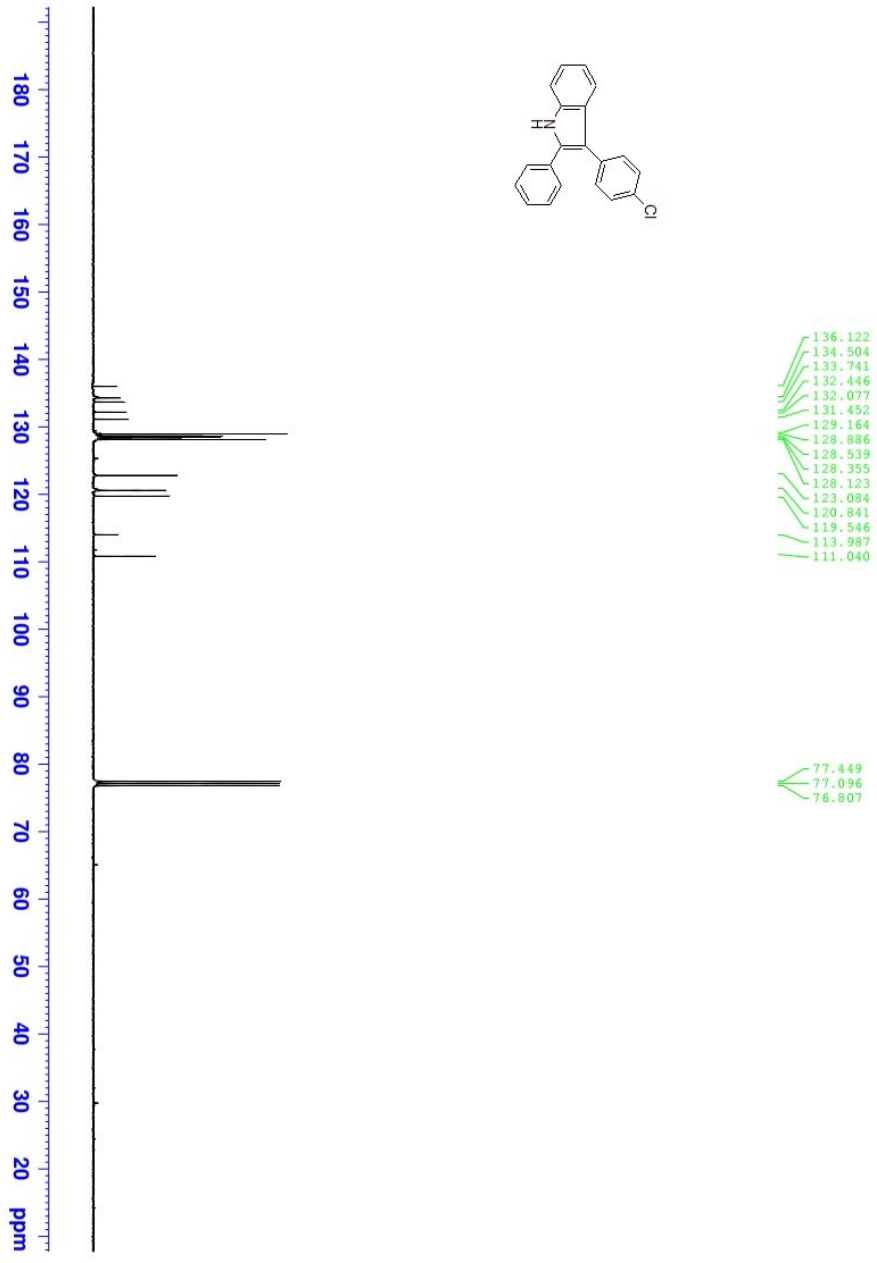
^{1}H NMR of Compound 3ba



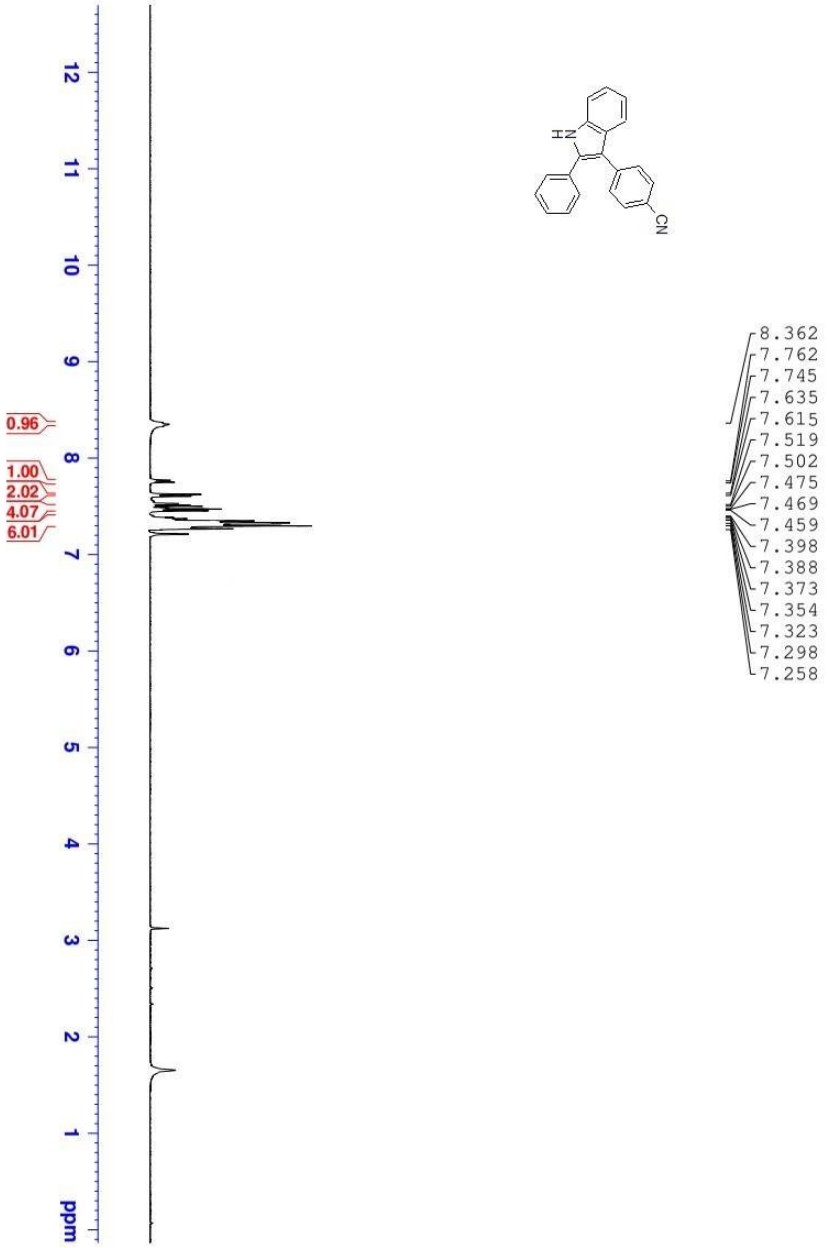
^{13}C NMR of Compound 3ba



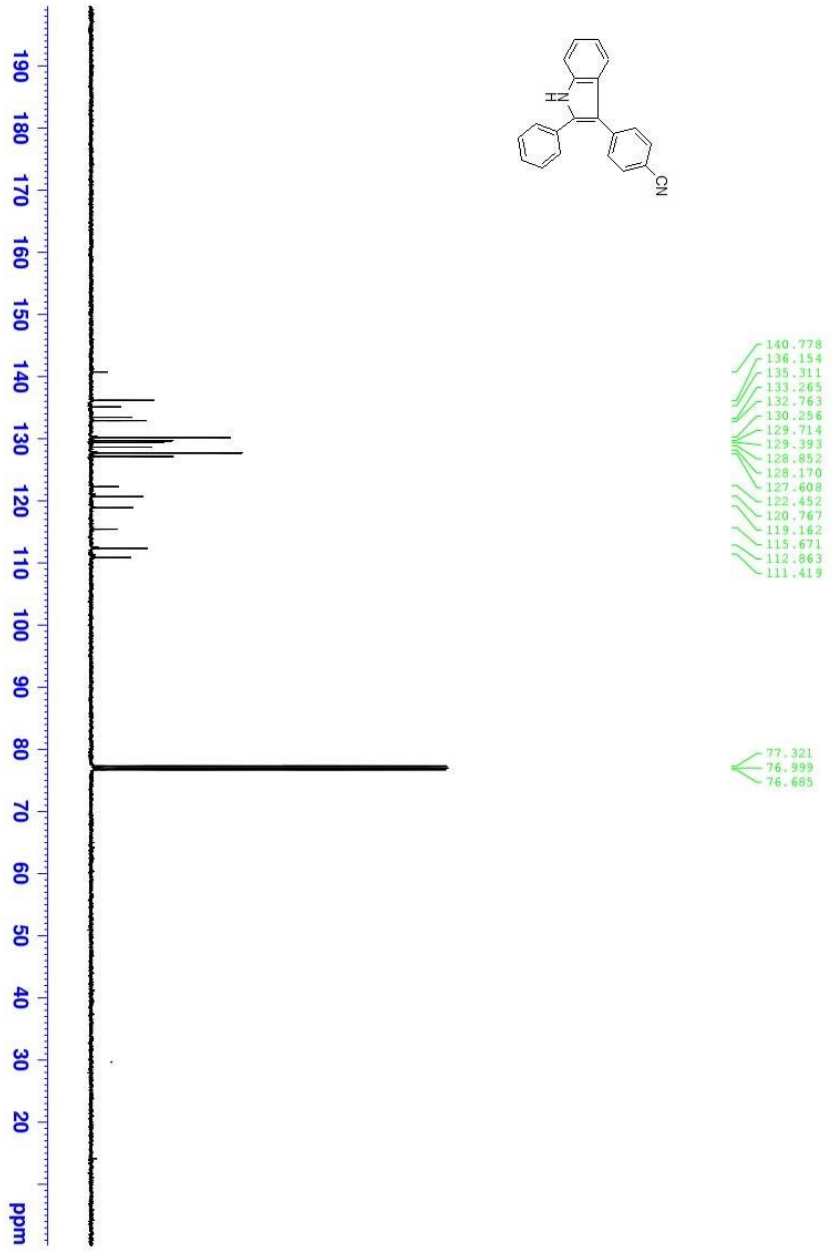
^{1}H NMR of Compound 3ca



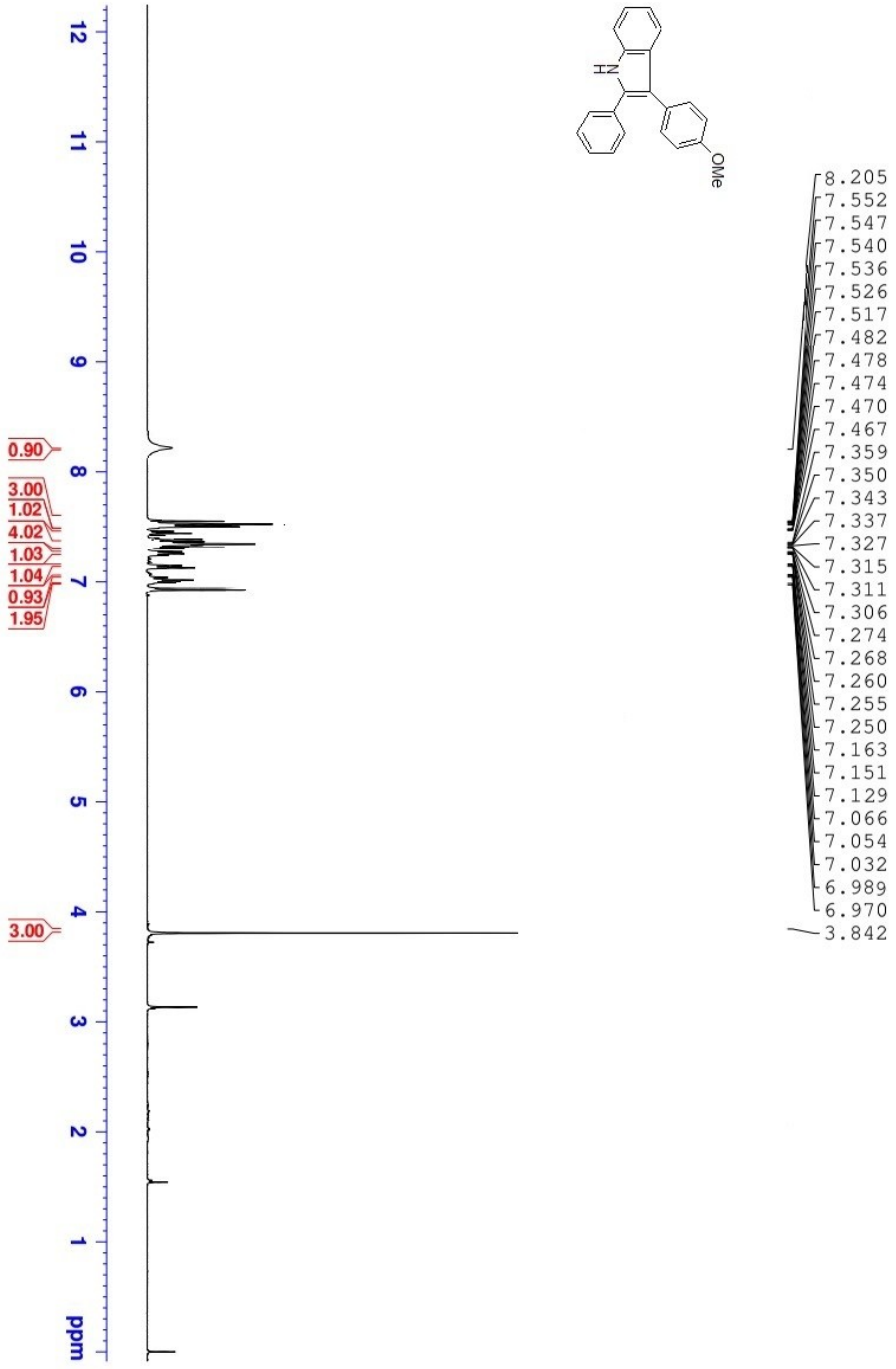
^{13}C NMR of Compound 3ca



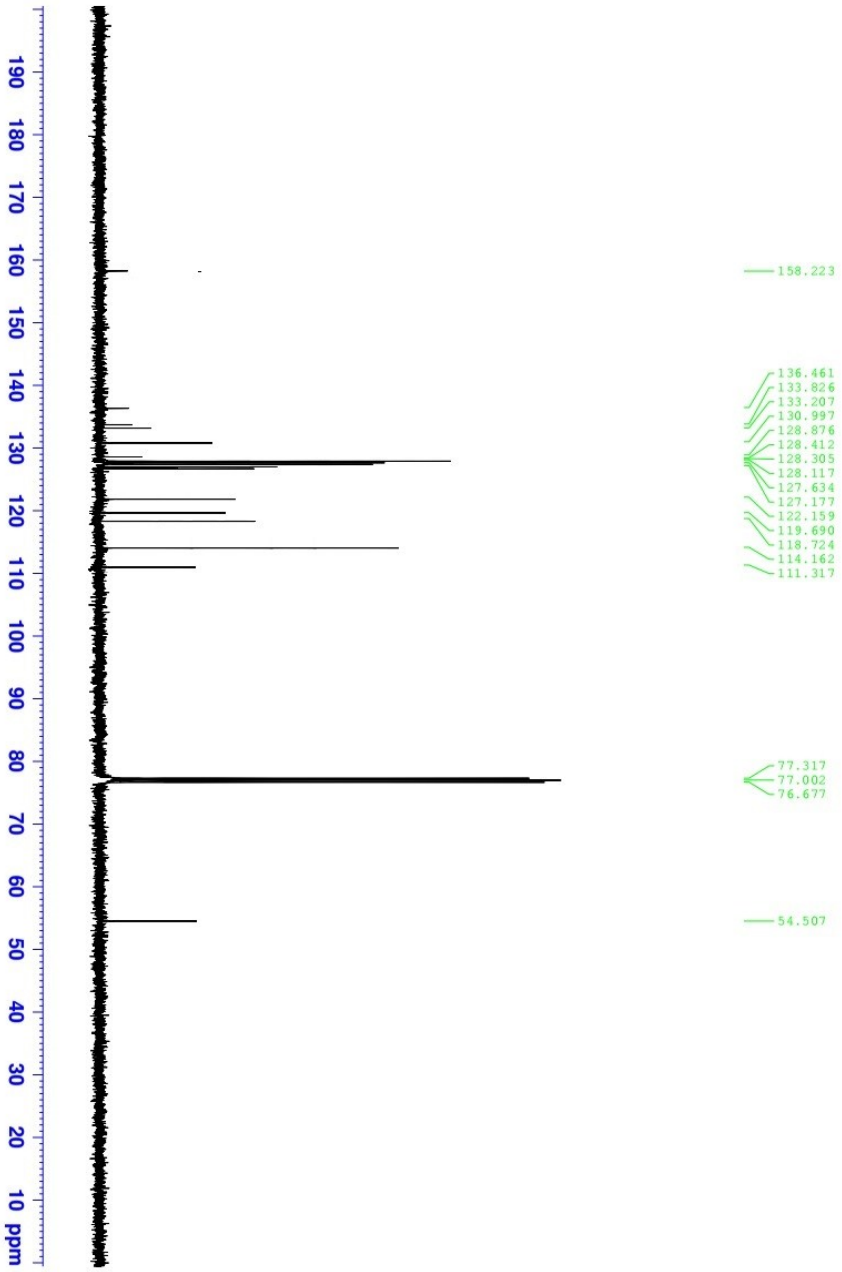
^{1}H NMR of Compound 3da



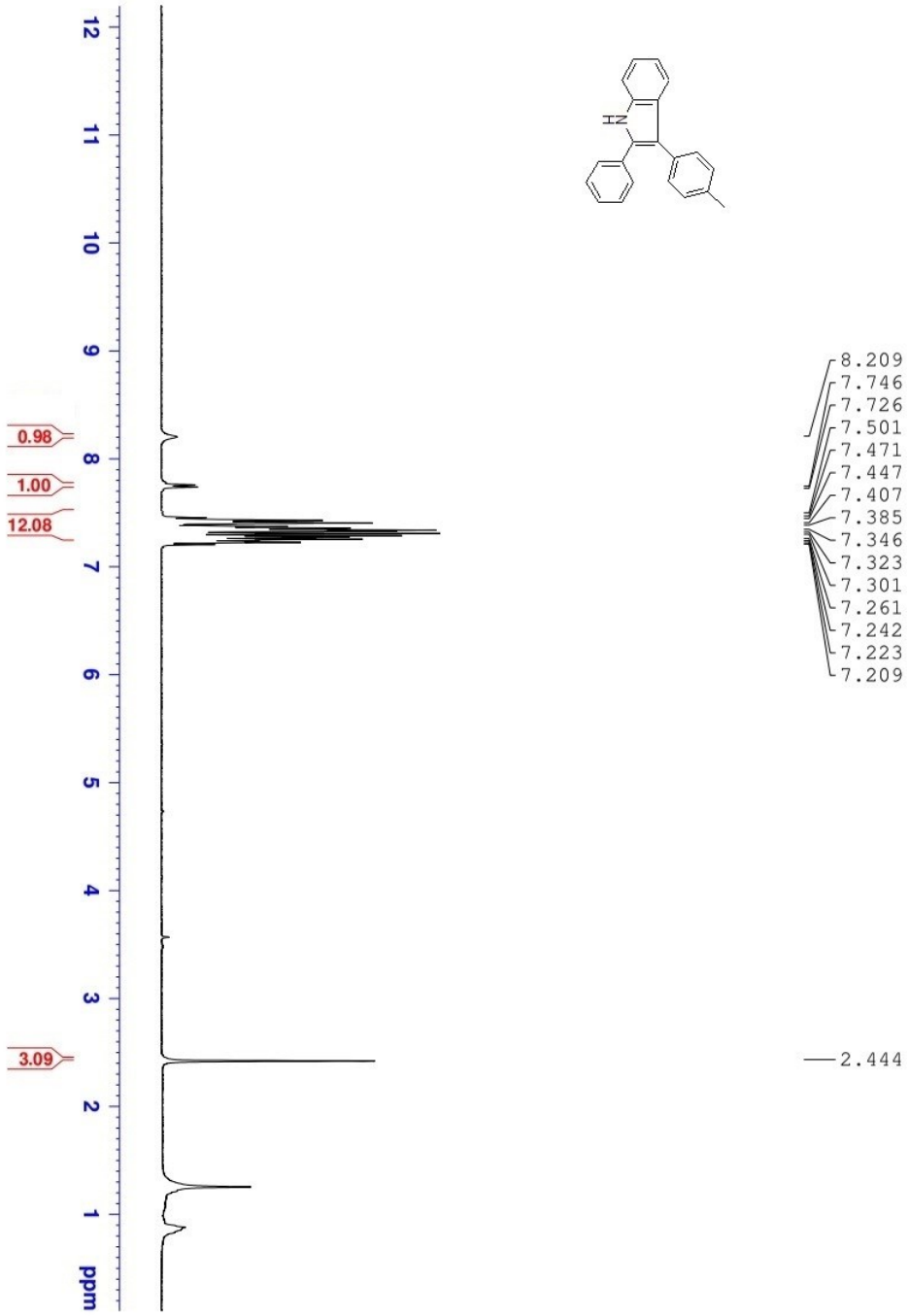
^{13}C NMR of Compound 3da



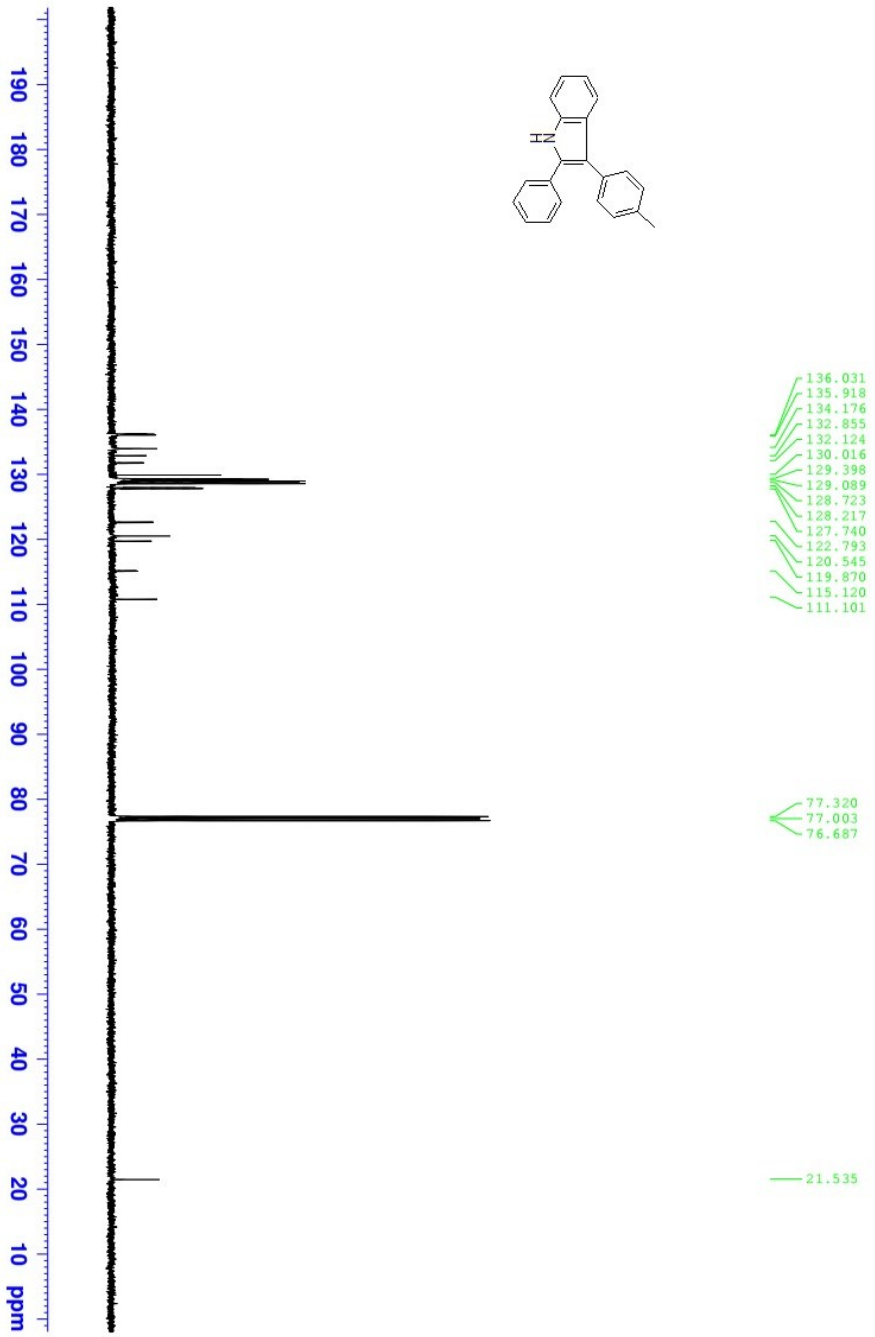
^{1}H NMR of Compound 3ea



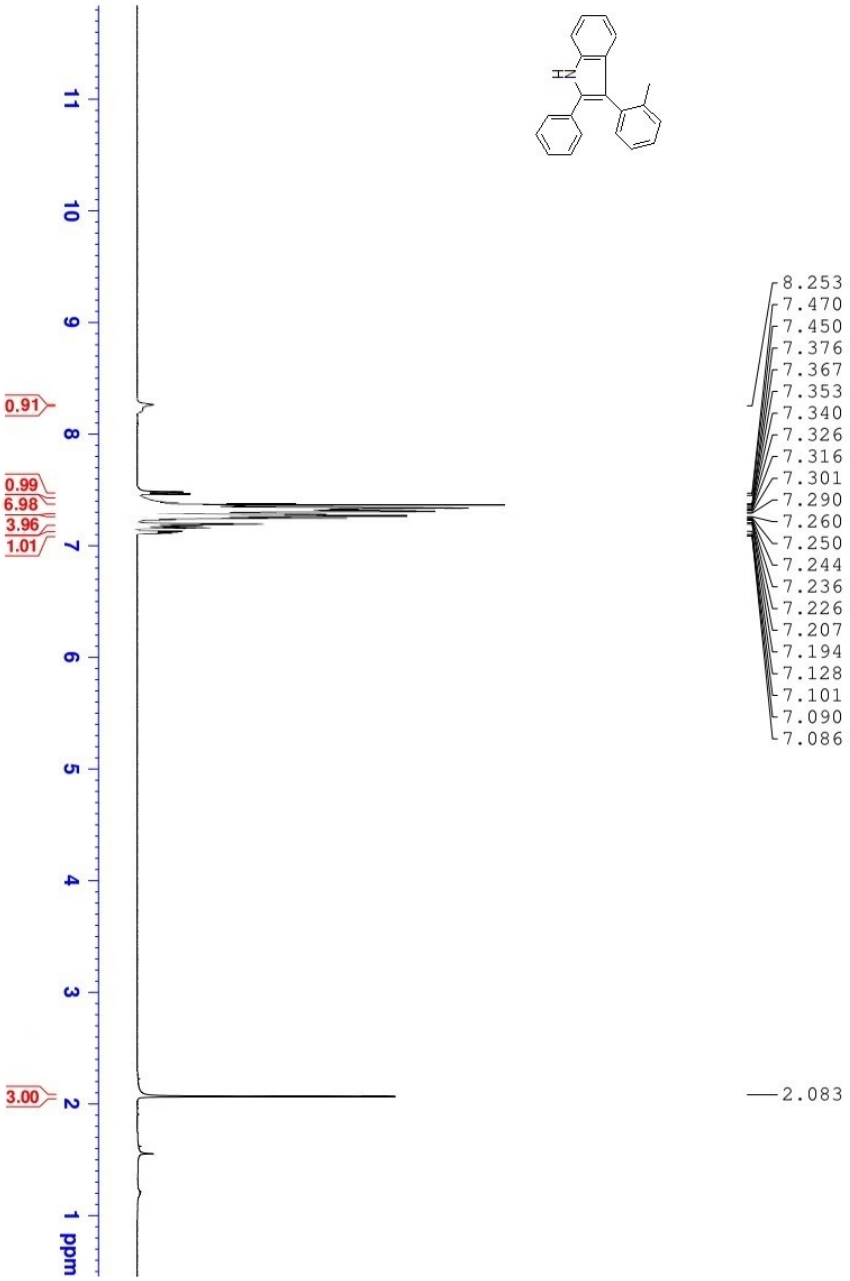
^{13}C NMR of Compound 3ea



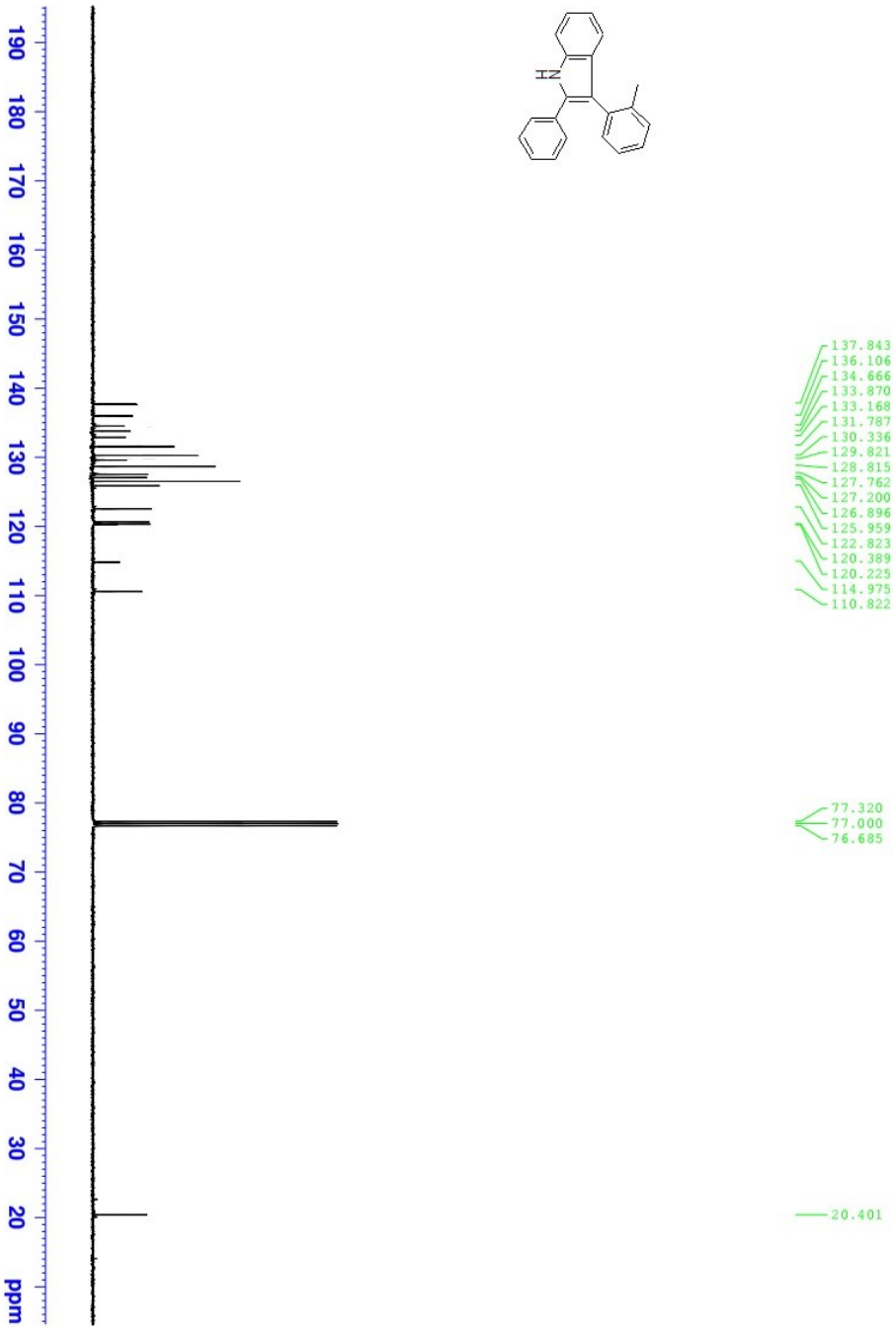
^{1}H NMR of Compound 3fa



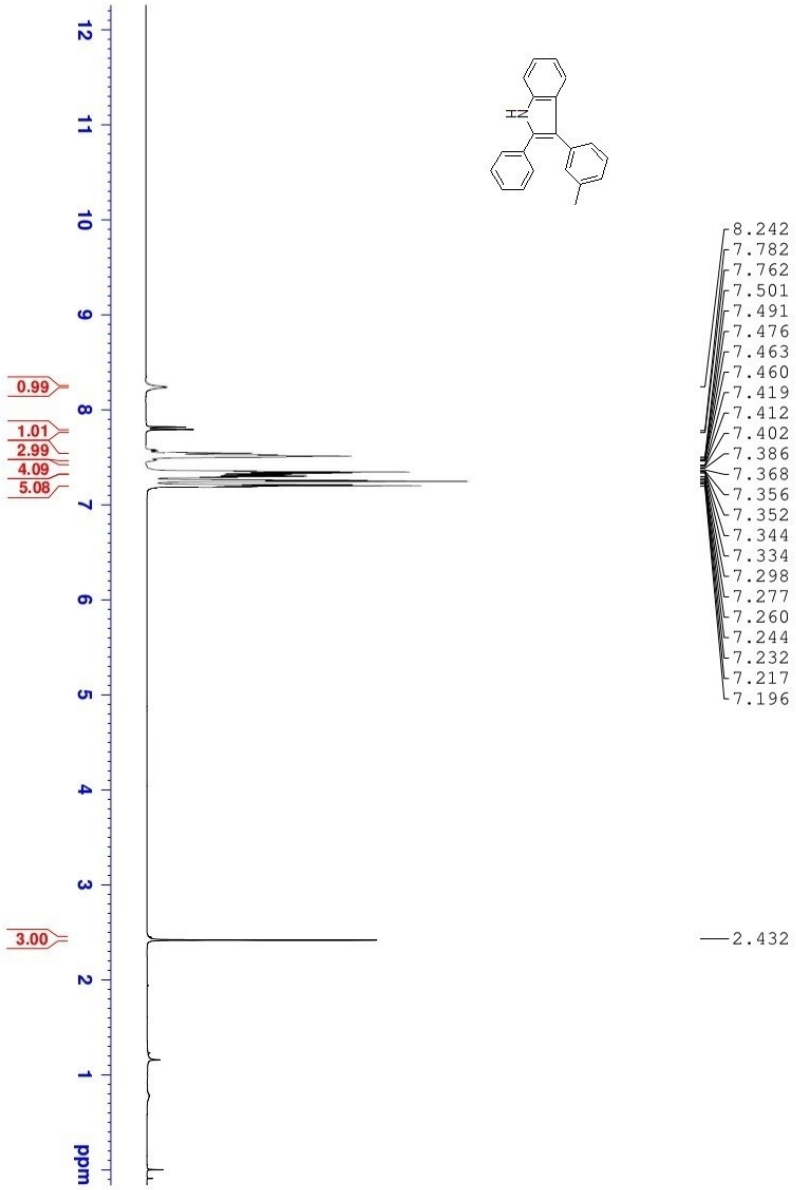
^{13}C NMR of Compound 3fa



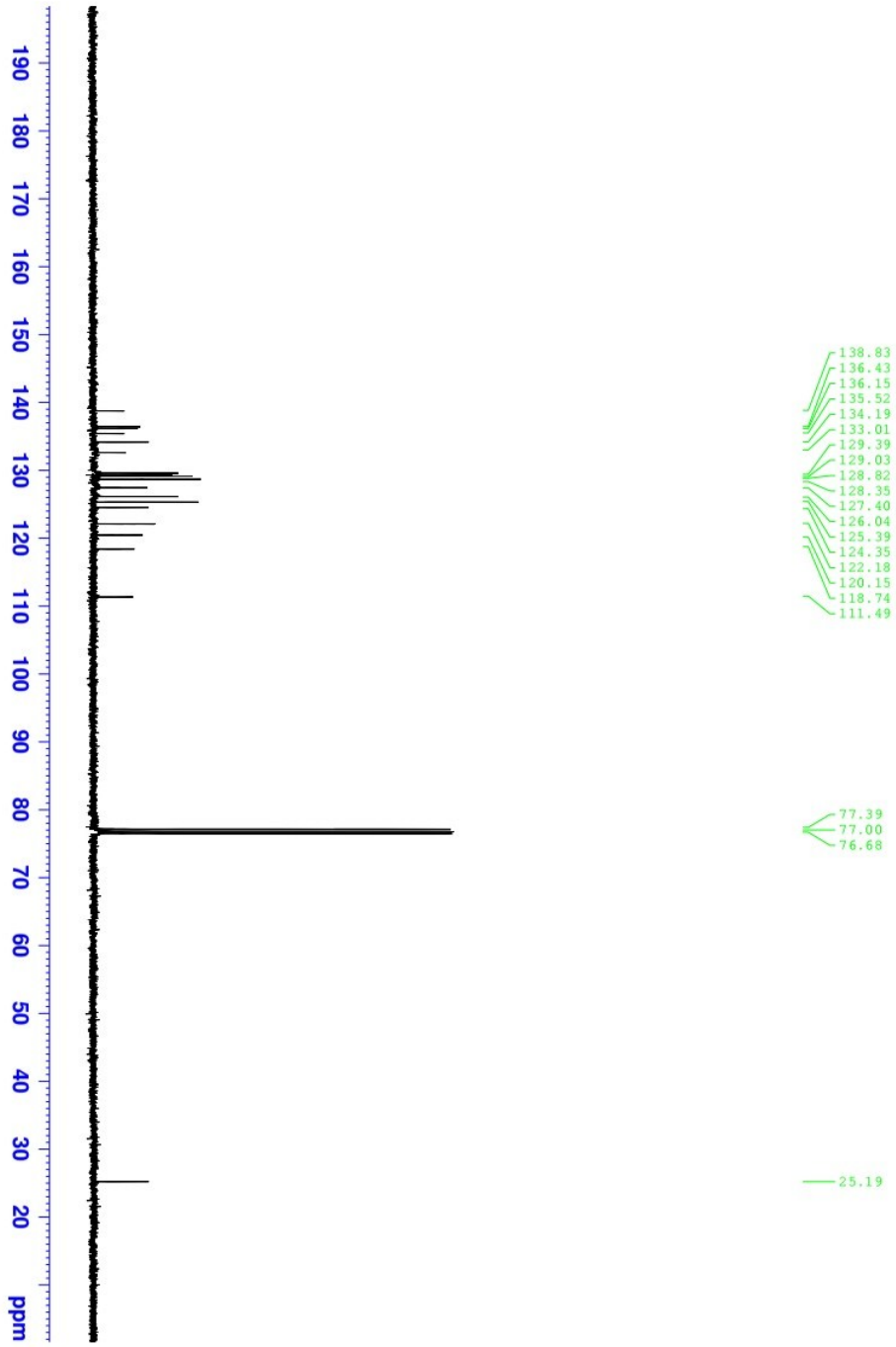
^{1}H NMR of Compound 3ga



^{13}C NMR of Compound 3ga



^{1}H NMR of Compound 3ha



^{13}C NMR of Compound 3ha