Supporting Information

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(A) Materials and equipment

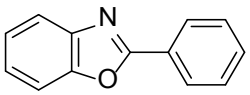
Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. [1] IR spectra were recorded on an EQUINOX-55 spectrometer on a KBr matrix. ^{1}H NMR spectra were recorded on a Bruker-400 NMR spectrometer using TMS as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (J) were measured in Hz. GC-MS analyses were performed on a SHIMADZU QP2010. Elemental analyses were performed on a Vario EL III CHNS analyzer. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure

Typical Experimental Procedure for the Synthesis of substituted benzoxazoles (3):

To a Schlenk tube were added methylarene **1** (1.0 mL), 2-aminophenol **2** (0.3 mmol), $FeBr_2$ (10% mol), DTBP (4 equiv). Then the tube was charged with argon, and was stirred at 110 ˚C for about 18-22 h. After the reaction was finished, the reaction mixture was diluted in 30 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated $NaHCO_3$ (8 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 substituted benzoxazoles **3**.

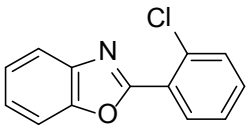
(C) Analytical data



3aa

2-Phenylbenzoxazole (3aa): [1]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, J = 3.2 Hz, 2H), 7.82-7.80 (m, 1H), 7.63-7.57 (m, 4H), 7.38 (dd, J = 2.0 Hz, J = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4, 149.7, 141.1, 131.1, 128.4, 126.8, 125.7, 124.3, 123.2, 119.4, 111.1; LRMS (EI 70 ev) m/z (%):195 (M^+, 100); Anal. Calcd for $C_{13}H_9NO$: C 79.98, H 4.65, N 7.17; found: C 79.88, H 4.63, N 7.21.

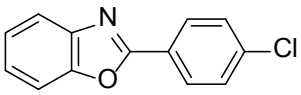


3ba

2-(2-Chlorophenyl)benzoxazole (3ba): [2]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J = 7.6 Hz, 1H), 7.88-7.87 (m, 1H), 7.61-7.54 (m, 1H), 7.43-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 150.4, 141.4, 133.8, 132.0, 131.3, 130.5, 126.7, 126.2, 125.4, 124.3, 120.2, 110.4; LRMS (EI 70 ev) m/z (%):229 (M^+, 100);

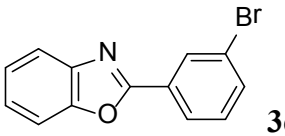
Anal. Calcd for $C_{13}H_9ClNO$: C 67.99, H 3.51, N 6.10; found: C 68.03, H 3.48, N 6.19.



3ca

2-(2-Chlorophenyl)benzoxazole (3ca): [1]

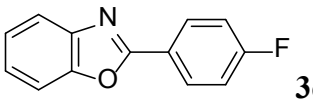
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, J = 8.8 Hz, 2H), 7.82-7.76 (m, 1H), 7.63-7.61 (m, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.40-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 151.1, 141.8, 137.7, 129.1, 128.6, 125.7, 124.9, 124.4, 119.8, 111.3; LRMS (EI 70 ev) m/z (%):229 (M^+, 100); Anal. Calcd for $C_{13}H_9ClNO$: C 67.99, H 3.51, N 6.10; found: C 67.91, H 3.60, N 6.04.



3da

2-(3-Bromophenyl)benzoxazole (3da): [3]

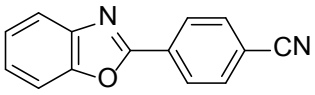
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (t, J = 1.4 Hz, 1H), 8.11-8.05 (m, 1H), 7.90-7.84 (m, 3H), 7.48-7.43 (m, 1H), 7.40-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 150.4, 140.9, 134.5, 131.5, 129.3, 128.1, 126.6, 126.0, 125.1, 122.4, 120.1, 112.2; LRMS (EI 70 ev) m/z (%):274 (M^+, 58), 273 (86), 272 (54); Anal. calcd for $C_{13}H_8BrNO$: C 56.96, H 2.94, N 5.11; found: C 56.92, H 2.86, N 5.07.



3ea

2-(4-Fluorophenylbenzoxazole (3ea): [2]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (dd, J = 9.2 Hz, J = 5.6 Hz, 2H), 7.98-7.96 (m, 1H), 7.58-7.54 (m, 1H), 7.38-7.34 (m, 1H), 7.20 (t, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.8 (d, J =254.2 Hz), 161.4, 150.4, 142.1, 128.9 (d, J =14.5 Hz), 125.4, 124.3, 123.1, 120.1, 116.2 (d, J =21.9 Hz), 110.2; LRMS (EI 70 ev) m/z (%):213 (M^+, 100); Anal. calcd for $C_{13}H_8FNO$: C 73.23, H 3.78, N 6.57; found: C 73.17, H 3.70, N 6.51.

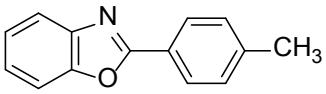


3fa

2-(4-Benzoxazole)benzonitrile (3fa): [1]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.41-7.33 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3, 150.1, 141.1, 132.7, 131.8, 128.8, 126.4, 124.2, 120.7, 118.5, 114.6, 111.4; LRMS (EI 70 ev) m/z

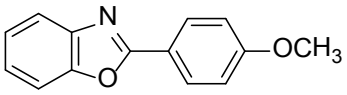
(%):220 (M^+, 100); Anal. calcd for $C_{14}H_8N_2O$: C 76.35, H 3.66, N 12.72; found C 76.41, H 3.61, N 12.66.



3ga

2-(*p*-Tolyl)benzoxazole (3ga): [1]

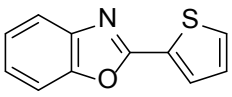
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J = 8.4 Hz, 2H), 7.75-7.73 (m, 1H), 7.56-7.52 (m, 1H), 7.40-7.34 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 151.4, 141.1, 131.8, 129.1, 127.7, 125.2, 123.6, 120.7, 119.5, 110.9, 21.3; LRMS (EI 70 ev) *m/z* (%):209 (M^+, 100); Anal. calcd for $C_{14}H_{11}NO$: C 80.36, H 5.30, N 6.69; found C 80.29, H 5.33, N 6.75.



3ha

2-(4-Methoxyphenyl)benzoxazole (3ha): [1]

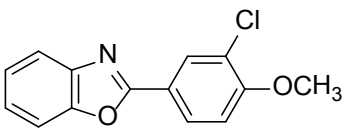
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, J = 9.2 Hz, 2H), 7.78-7.73 (m, 1H), 7.57-7.53 (m, 1H), 7.37-7.30 (m, 2H), 7.11 (d, J = 9.2 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.4, 151.2, 141.7, 128.6, 127.4, 124.5, 123.4, 119.6, 118.9, 114.2, 110.0, 55.2; LRMS (EI 70 ev) *m/z* (%):225 (M^+, 100); Anal. calcd for $C_{14}H_{11}NO_2$: C 74.65, H 4.92, N 6.22; found C 74.59, H 4.97, N 6.30.



3ia

2-(Thiophen-2-yl)benzoxazole (3ia): [4]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (dd, J = 3.6 Hz, J = 0.8 Hz, 1H), 7.73-7.69 (m, 1H), 7.55-7.47 (m, 2H), 7.35-7.31 (m, 2H), 7.19 (dd, J = 4.8 Hz, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 151.2, 142.2, 130.7, 129.9, 129.0, 128.8, 125.3, 124.1, 119.8, 110.2; LRMS (EI 70 ev) *m/z* (%):201 (M^+, 100); Anal. calcd for $C_{11}H_7NOS$: C 65.65, H 3.51, N 6.96, S 15.93; found C 65.58, H 3.54, N 6.90, S 15.91.

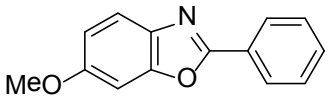


3ja

2-(3-Chloro-4-methoxyphenyl)benzoxazole (3ja): [5]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, J = 1.6 Hz, 1H), 8.14 (dd, J = 2.0 Hz, J = 6.8

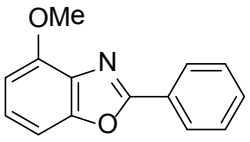
Hz, 1H), 7.70-7.67 (m, 1H), 7.44-7.39 (m, 1H), 7.33-7.29 (m, 2H), 6.99 (d, J = 9.2 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 157.7, 150.6, 142.3, 128.8, 127.8, 125.0, 123.9, 123.1, 120.1, 119.4, 112.2, 110.7, 55.3; LRMS (EI 70 ev) *m/z* (%):259 (M^+, 100); Anal. calcd for $C_{14}H_{10}ClNO_2$: C 64.75, H 3.88, N 5.39; found C 64.81, H 3.80, N 5.33.



3ab

6-Methoxy-2-phenylbenzoxazole (3ab): [6]

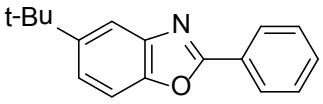
Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19-8.16 (m, 2H), 7.70 (d, J = 8.8 Hz, 1H), 7.44-7.39 (m, 3H), 7.12 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.2, 158.6, 151.5, 136.3, 131.5, 128.8, 128.5, 127.6, 120.1, 112.9, 95.5, 55.6; LRMS (EI 70 ev) *m/z* (%):225 (M^+, 100); Anal. calcd for $C_{14}H_{11}NO_2$: C 74.65, H 4.92, N 6.22; found C 74.58, H 4.96, N 6.16.



3ac

4-Methoxy-2-phenylbenzoxazole (3ac): [7]

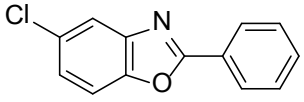
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.21 (m, 2H), 7.45-7.40 (m, 3H), 7.24-7.14 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.2, 152.2, 151.3, 132.0, 131.4, 129.1, 128.1, 127.4, 126.3, 106.1, 103.5, 56.1; LRMS (EI 70 ev) *m/z* (%):225 (M^+, 100); Anal. calcd for $C_{14}H_{11}NO_2$: C 74.65, H 4.92, N 6.22; found C 74.71, H 4.88, N 6.30.



3ad

5-(*tert*-Butyl)-2-phenylbenzoxazole (3ad): [8]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27-8.25 (m, 2H), 7.84 (d, J = 6.4 Hz, 1H), 7.55-7.46 (m, 4H), 7.42-7.40 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.9, 149.1, 148.1, 142.2, 130.8, 128.4, 127.5, 126.6, 122.5, 116.6, 109.6, 35.2, 32.1; LRMS (EI 70 ev) *m/z* (%):251 (M^+, 100); Anal. calcd for $C_{17}H_{17}NO$: C 81.24, H 6.82, N 5.57; found C 81.30, H 6.87, N 5.50.

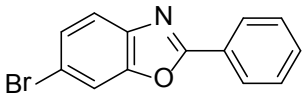


3ae

5-Chloro-2-phenylbenzoxazole (3ae): [2]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17-8.13 (m, 2H), 7.75 (d, J = 2.0 Hz, 1H),

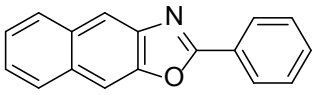
7.55-7.40 (m, 4H), 7.31 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 149.4, 143.2, 130.7, 129.9, 128.4, 127.6, 126.6, 125.3, 120.1, 111.4; LRMS (EI 70 ev) *m/z* (%):229 (M^+, 100); Anal. calcd for $C_{13}H_8ClNO$: C 67.99, H 3.51, N 6.10; found C 67.89, H 3.58, N 6.03.



3af

6-Bromo-2-phenylbenzoxazole (3ea): [7]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.19 (m, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.56-7.47 (m, 4H), 7.76 (dd, J = 1.2 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.2, 151.2, 141.1, 131.9, 129.6, 128.6, 127.7, 126.6, 121.3, 118.2, 114.2; LRMS (EI 70 ev) *m/z* (%):274 (M^+, 51), 273 (72), 272 (59); Anal. calcd for $C_{13}H_8BrNO$: C 56.96, H 2.94, N 5.11; found: C 57.02, H 2.99, N 5.03.



3ag

2-Phenylnaphtho[2,3-d]oxazole (3ag): [7]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (m, 2H), 8.18 (s, 1H), 8.00-7.95 (m, 3H), 7.60-7.52 (m, 3H), 7.47-7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 149.8, 142.1, 132.4, 131.9, 131.2, 129.7, 128.3, 128.0, 127.3, 126.6, 125.4, 124.7, 117.4, 106.6; LRMS (EI 70 ev) *m/z* (%):245 (M^+, 100); Anal. calcd for $C_{17}H_{11}NO$: C 83.25, H 4.52, N 5.71; found C 83.33, H 4.54, N 5.64.

(D) References

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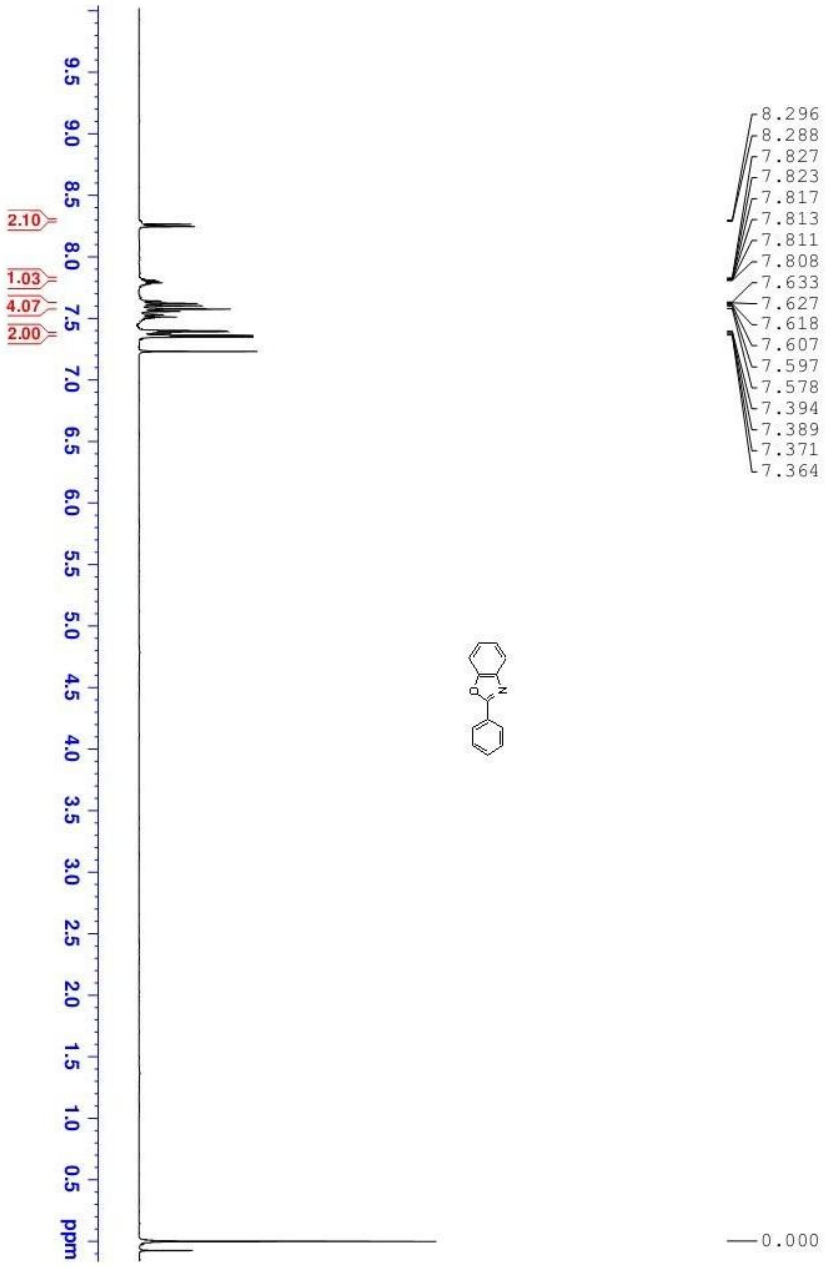
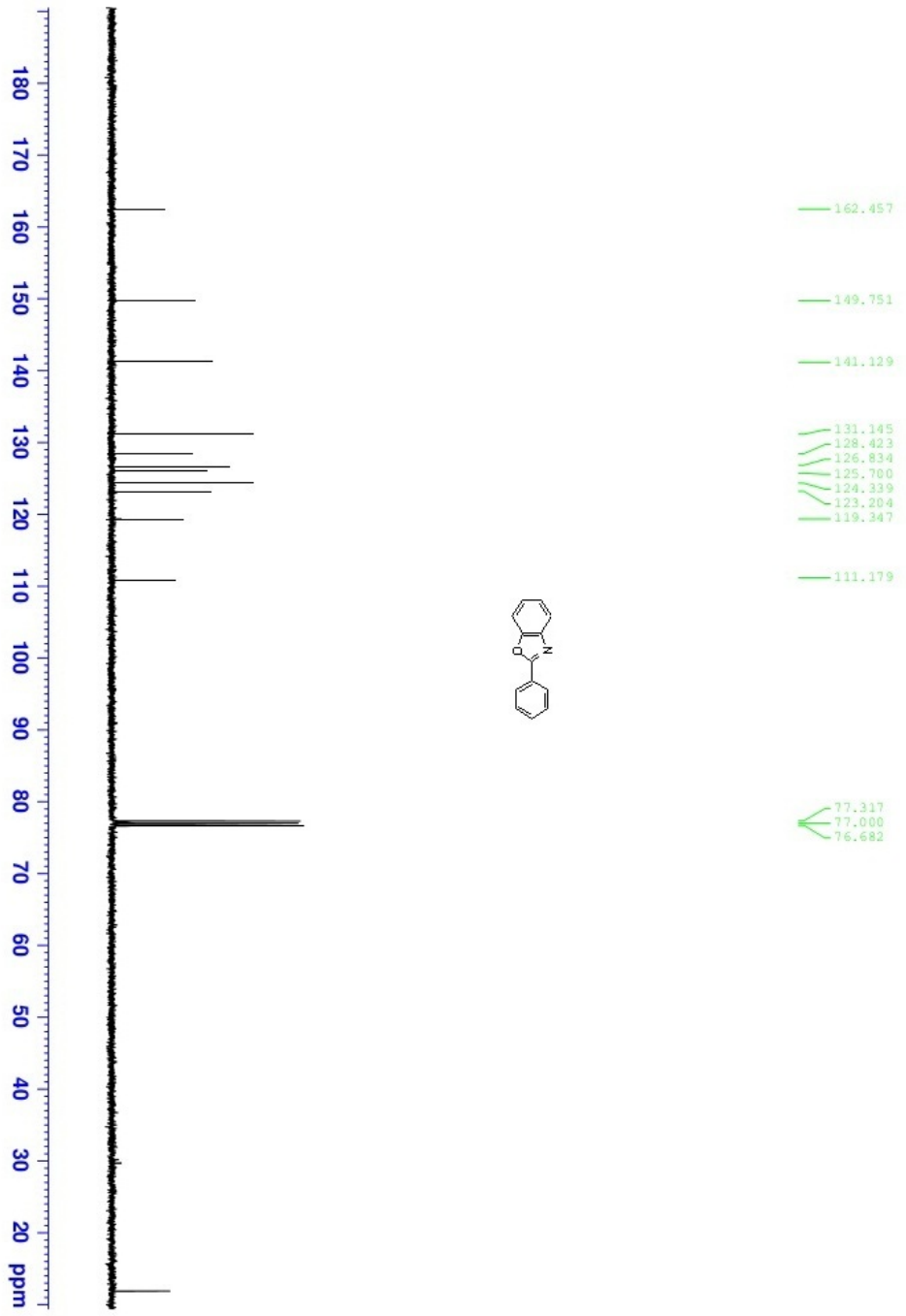
(E) Spectra

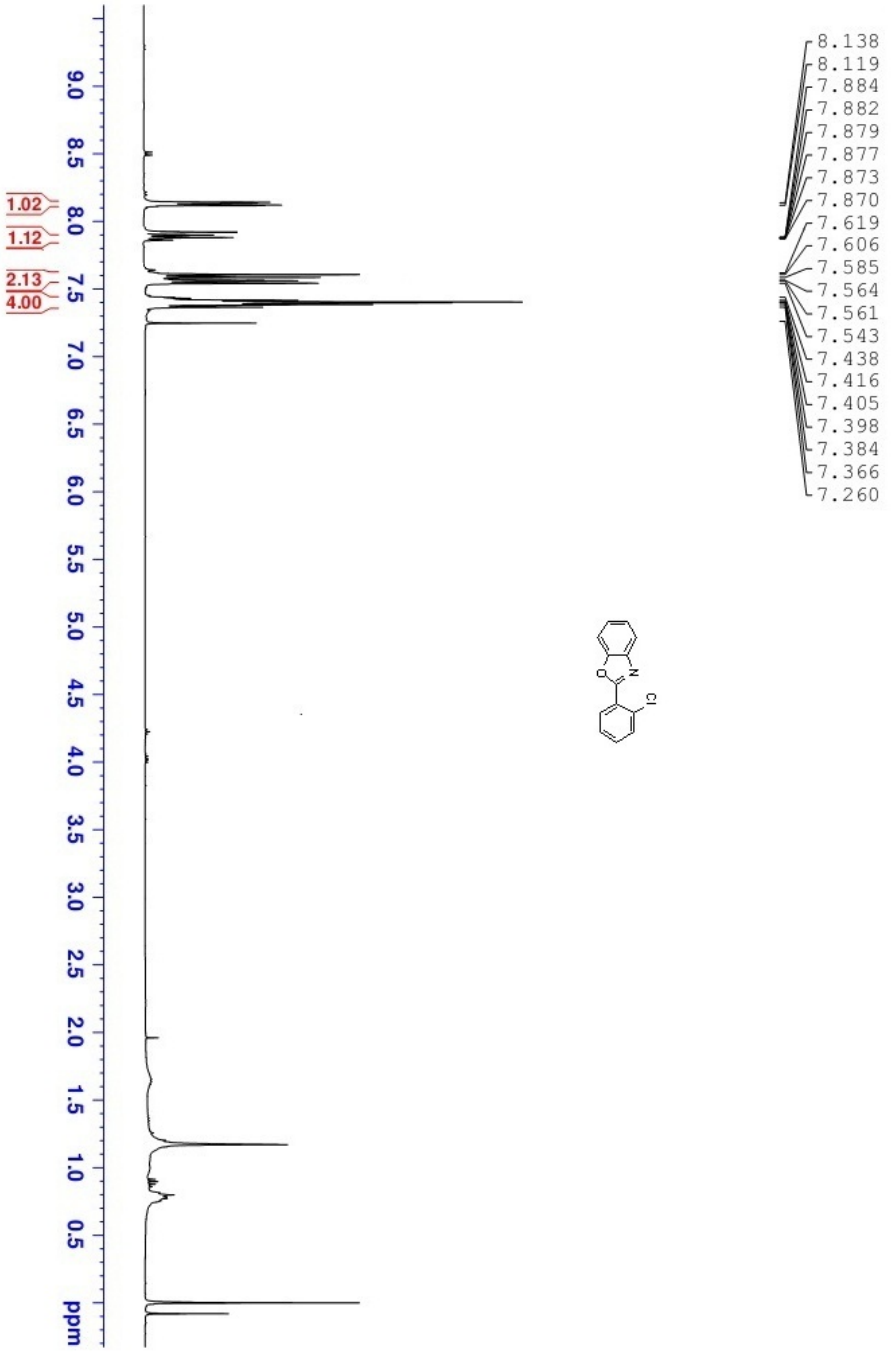
^{1}H NMR of Compound 3aa



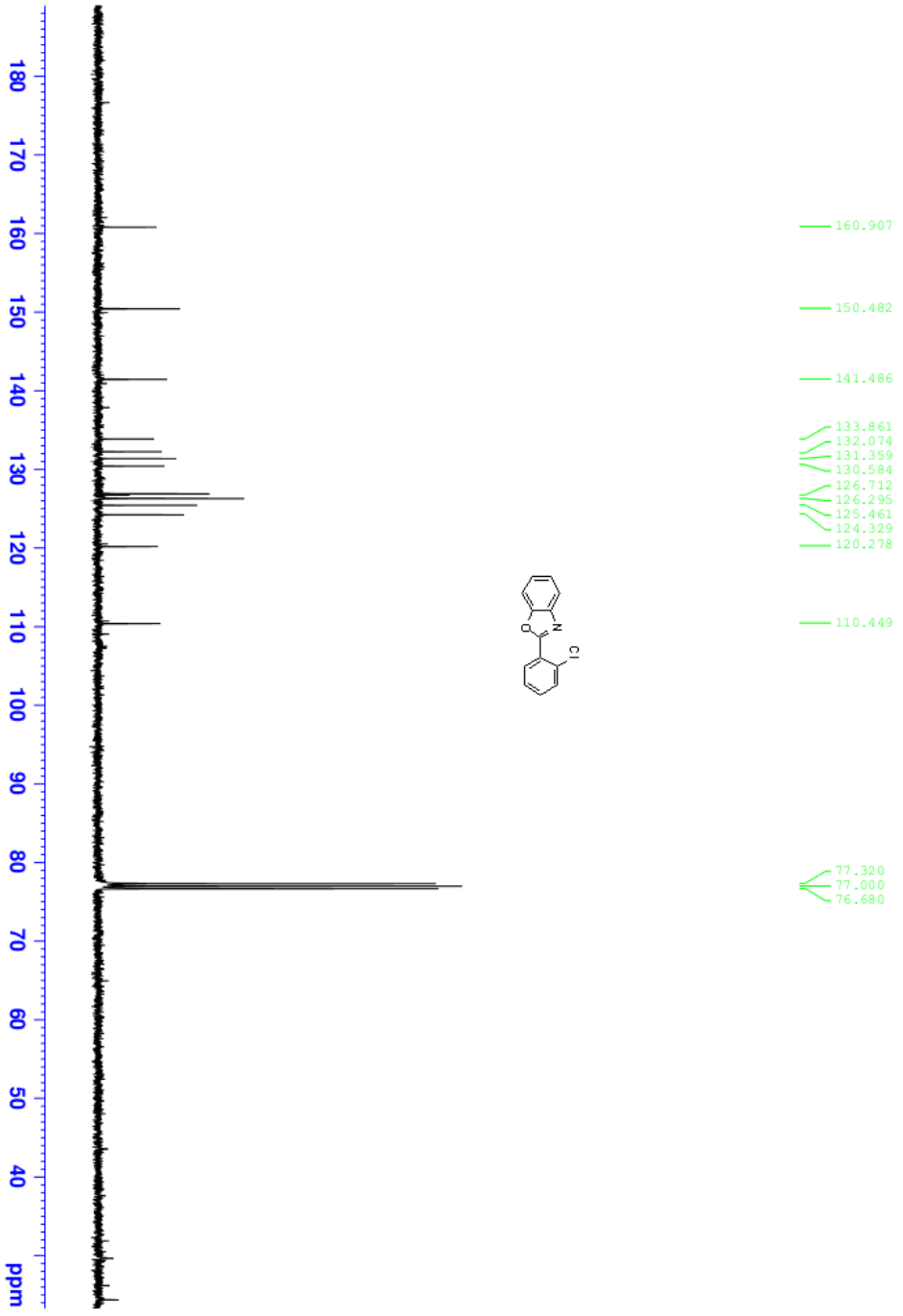
^{13}C NMR of Compound 3aa



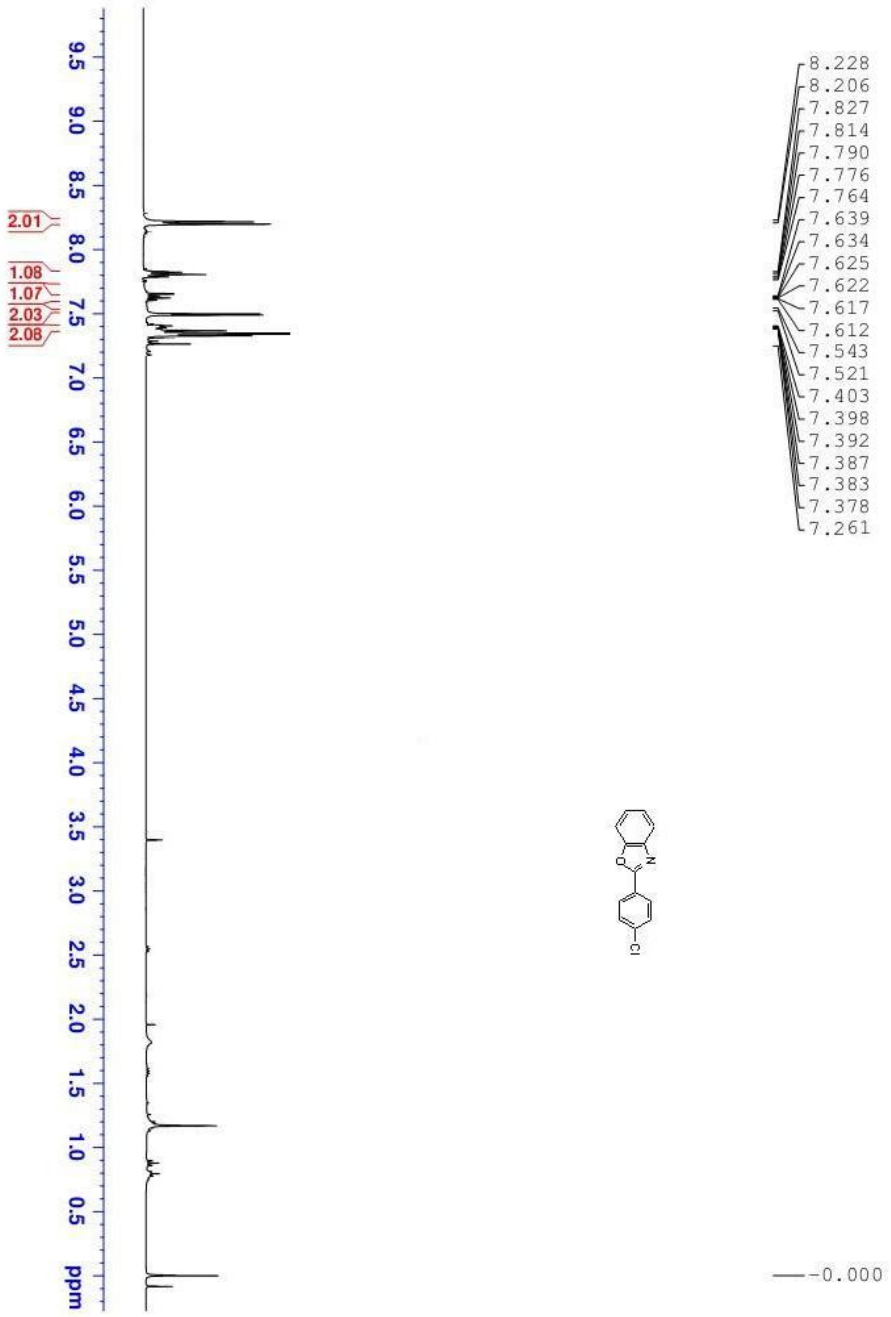
^{1}H NMR of Compound 3ba



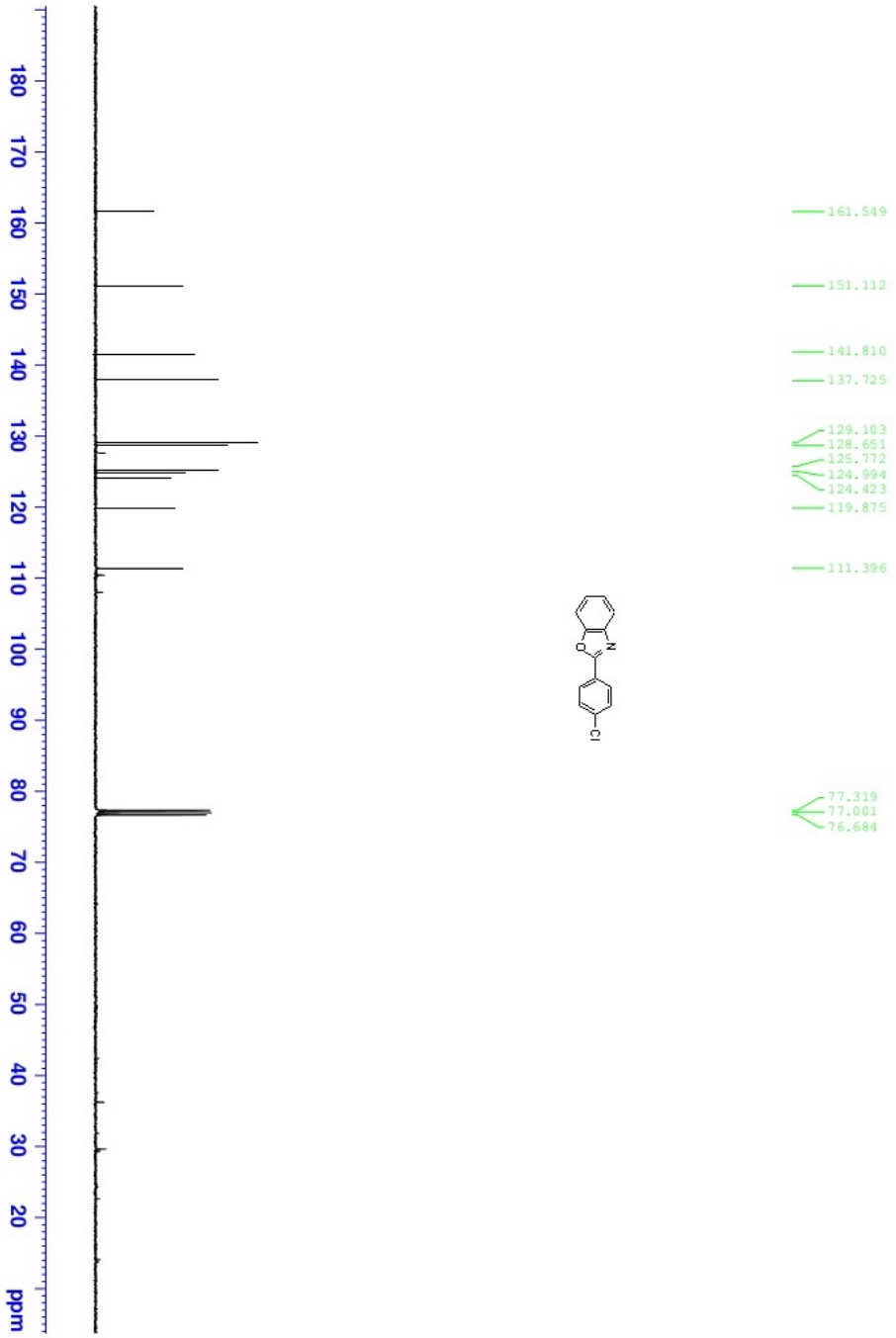
^{13}C NMR of Compound 3ba



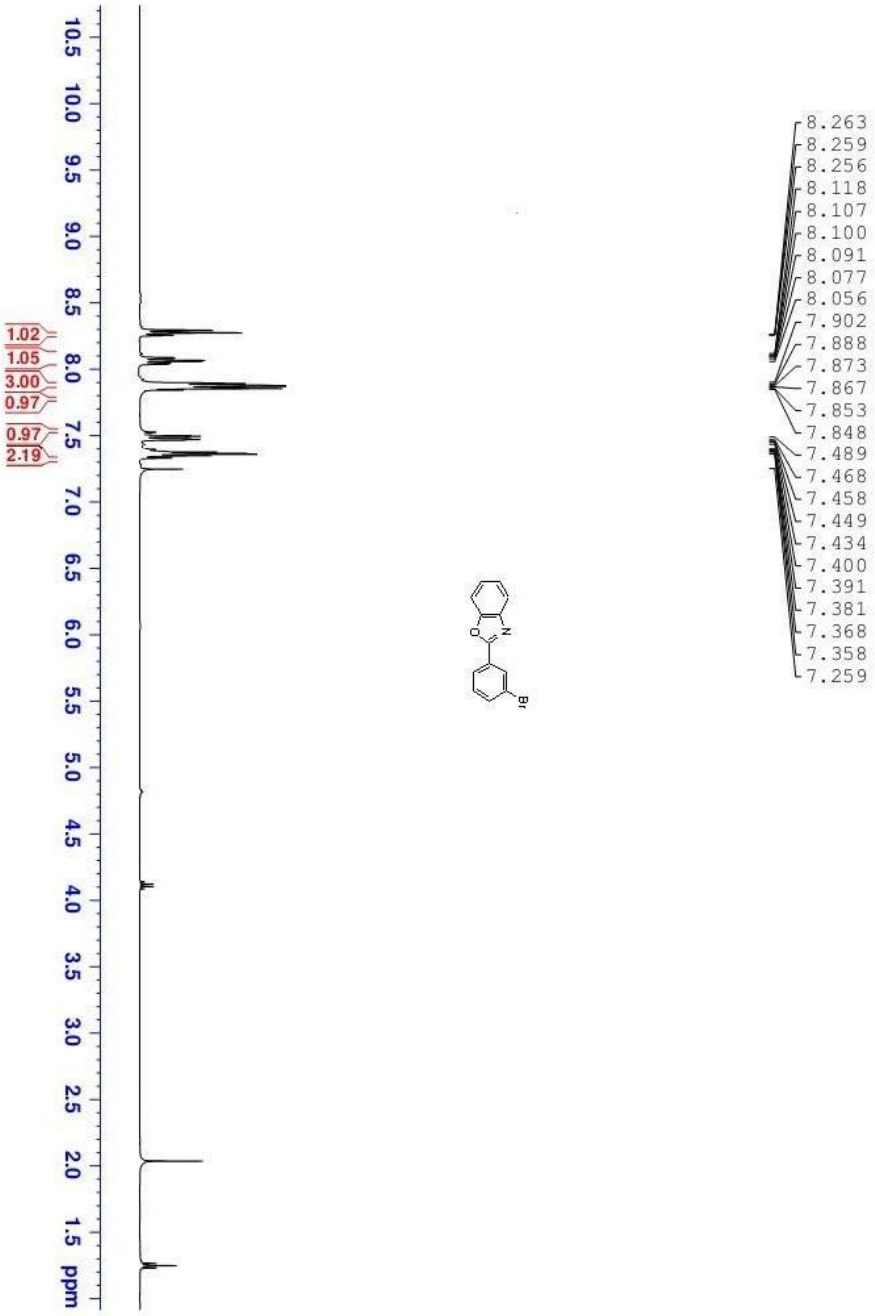
^{1}H NMR of Compound 3ca



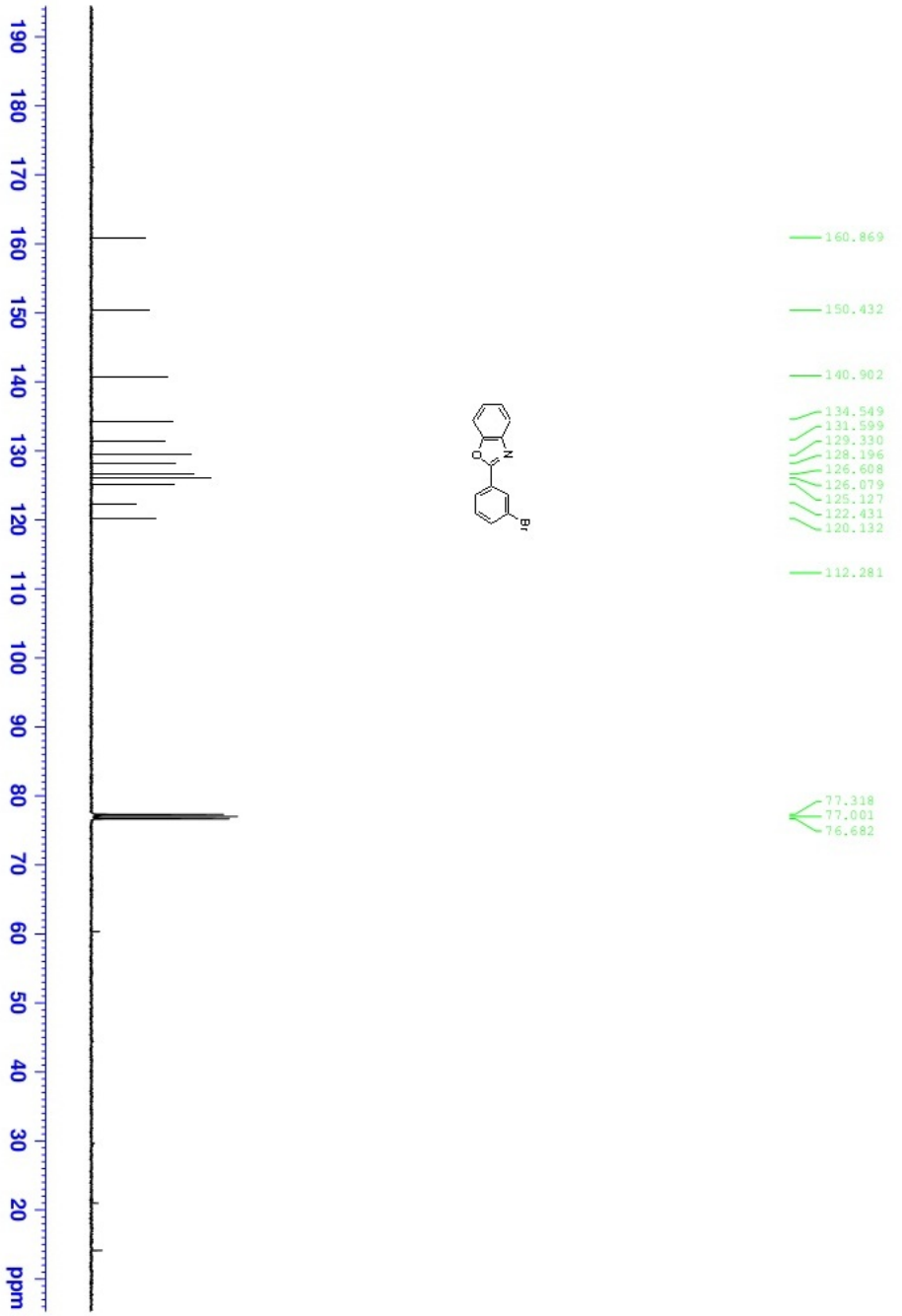
^{13}C NMR of Compound 3ca



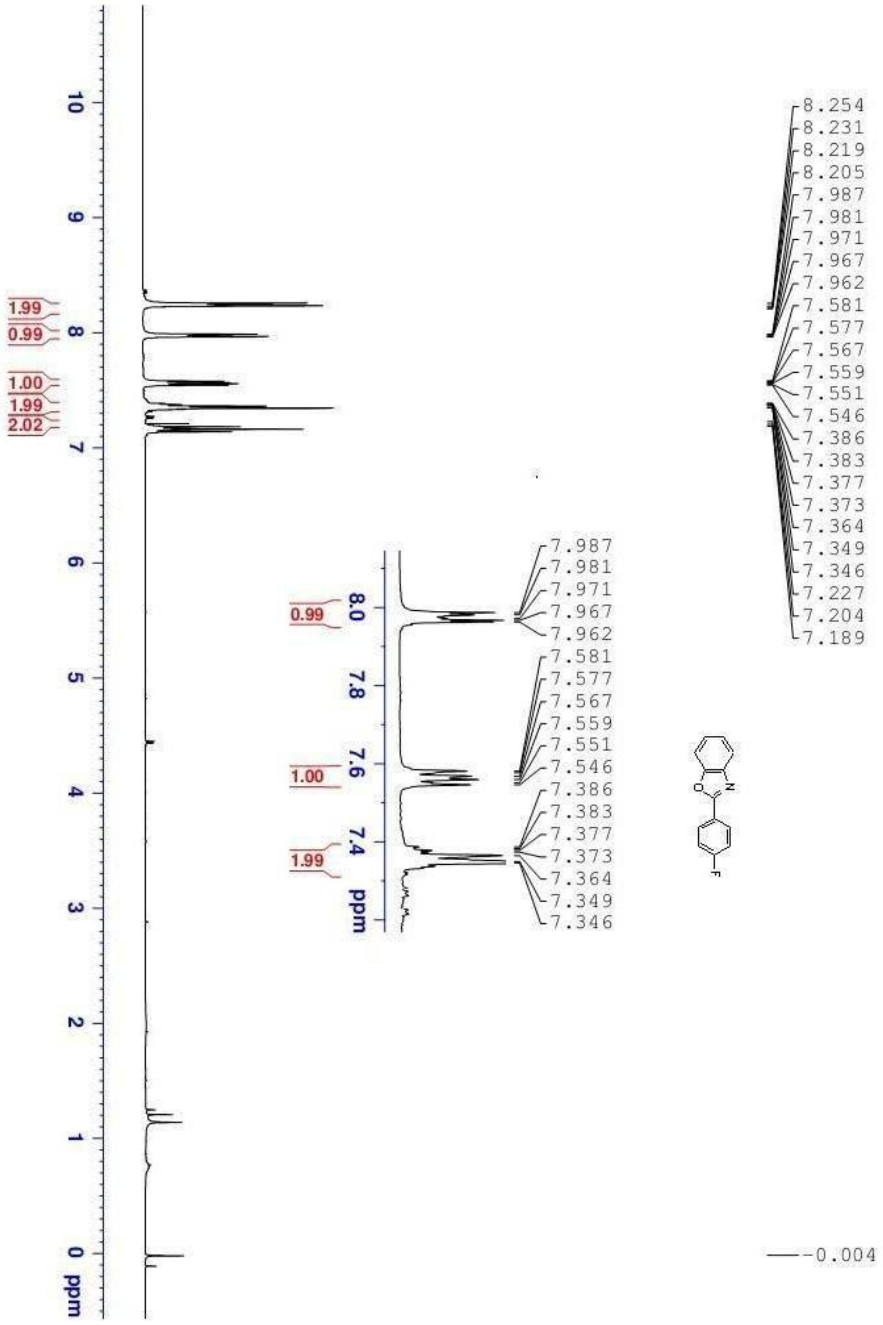
^{1}H NMR of Compound 3da



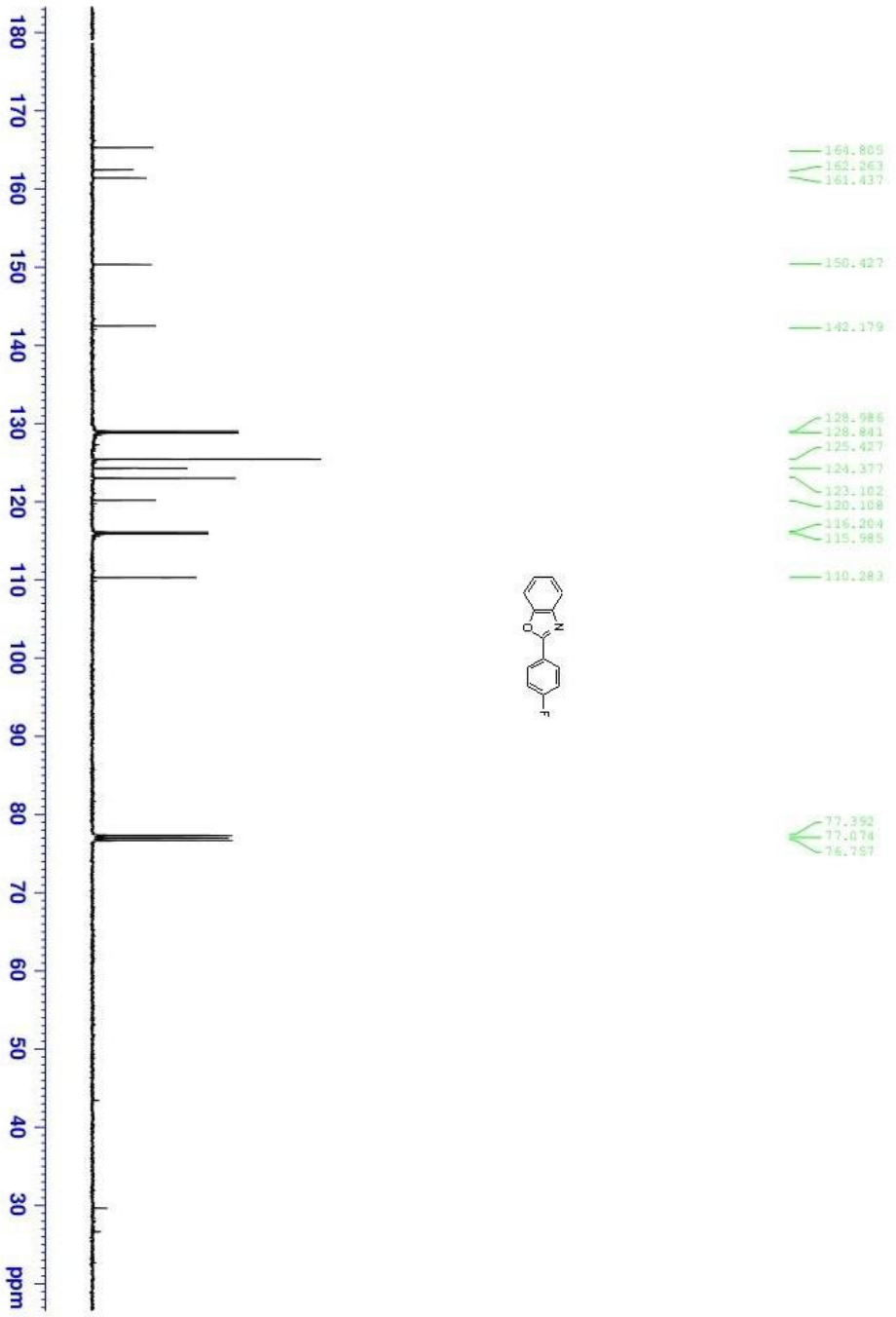
^{13}C NMR of Compound 3da



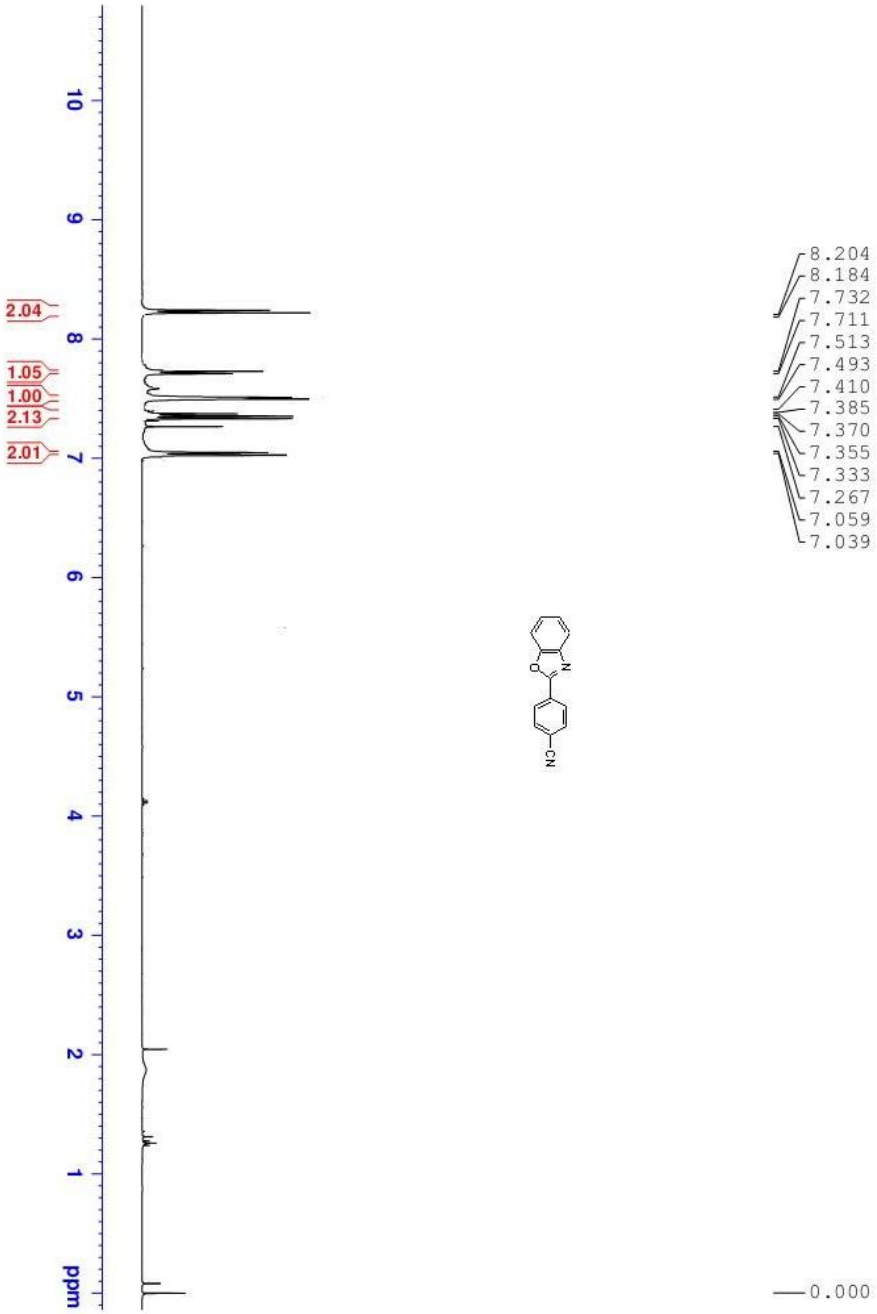
^{1}H NMR of Compound 3ea



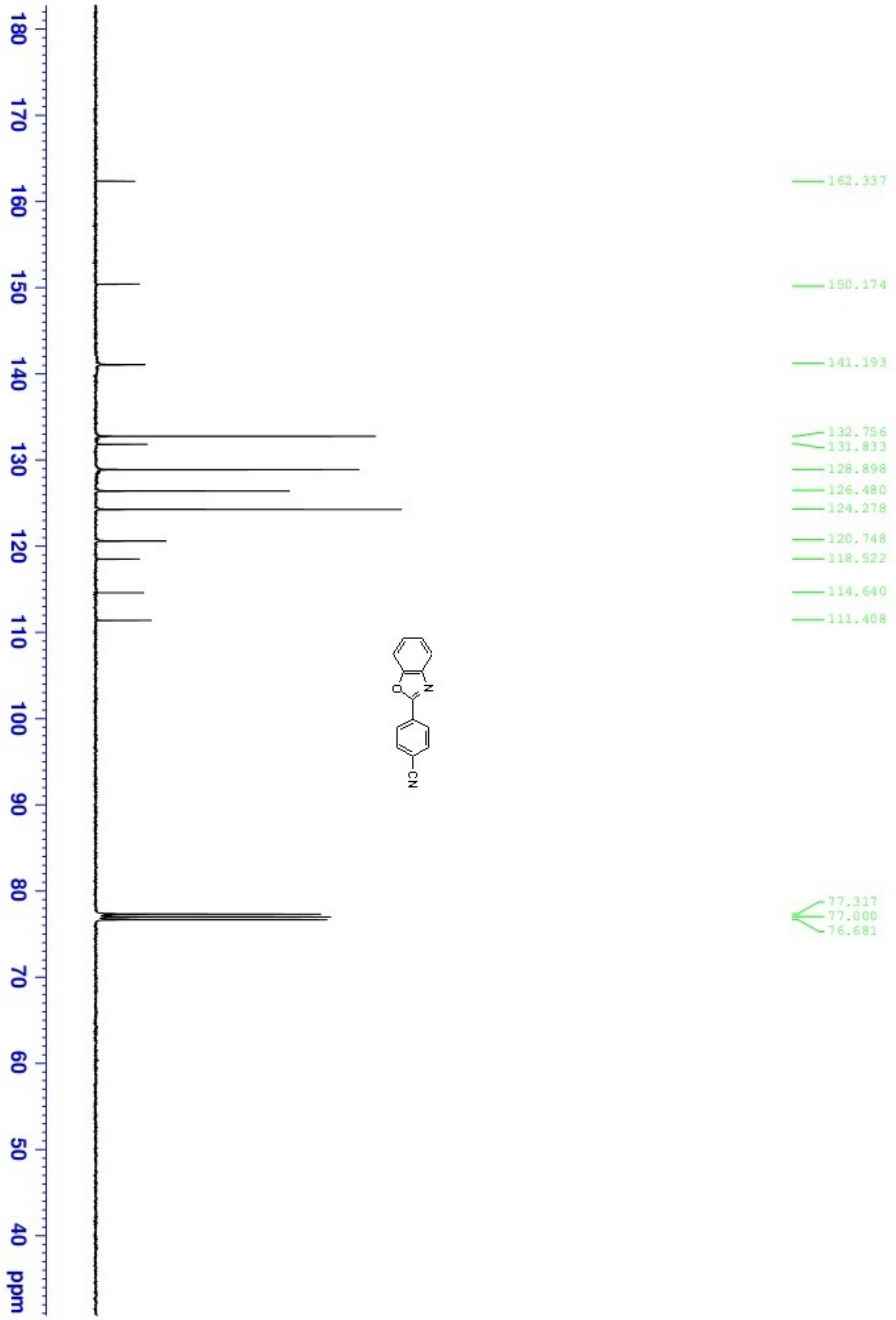
^{13}C NMR of Compound 3ea



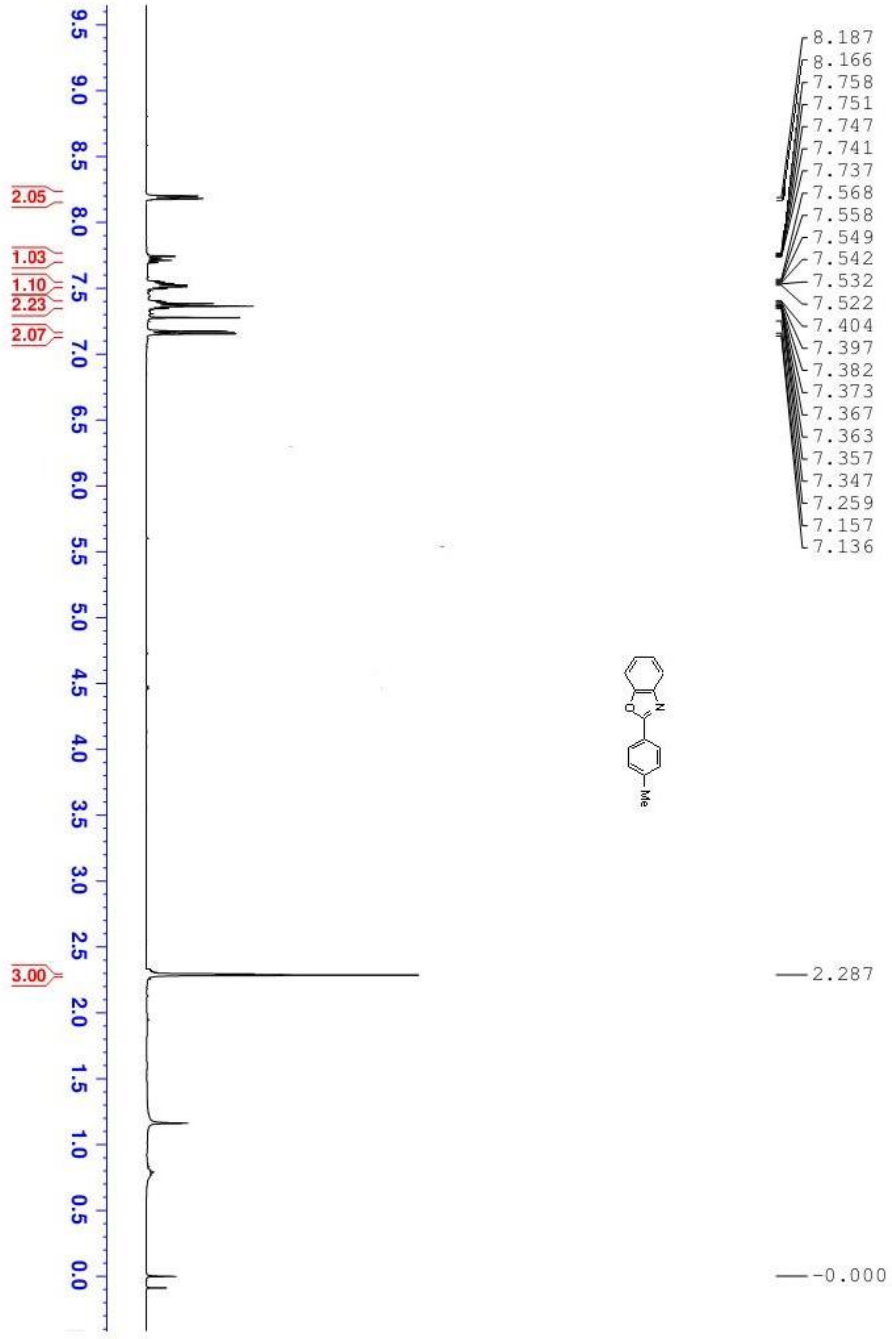
^{1}H NMR of Compound 3fa



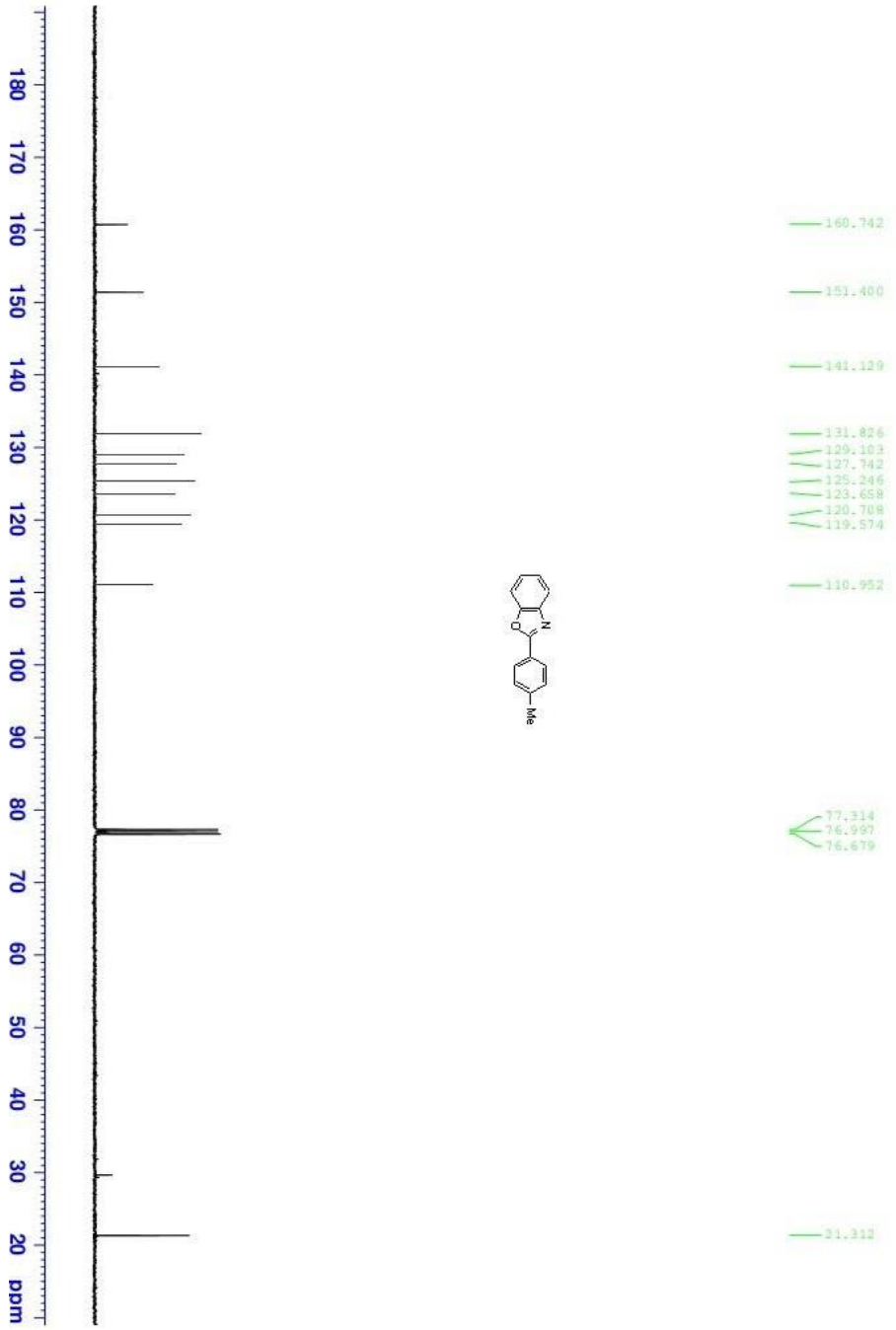
^{13}C NMR of Compound 3fa



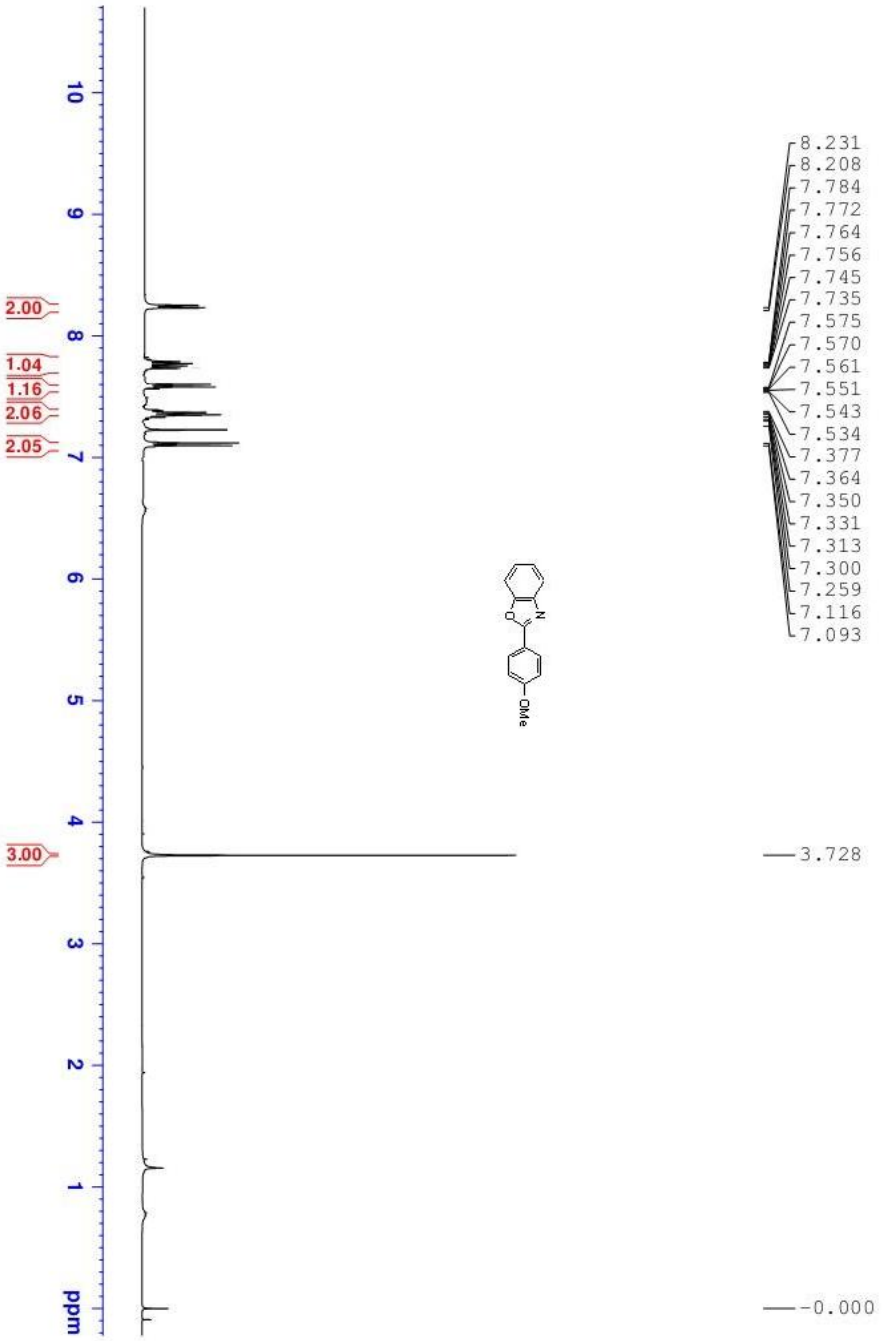
^{1}H NMR of Compound 3ga



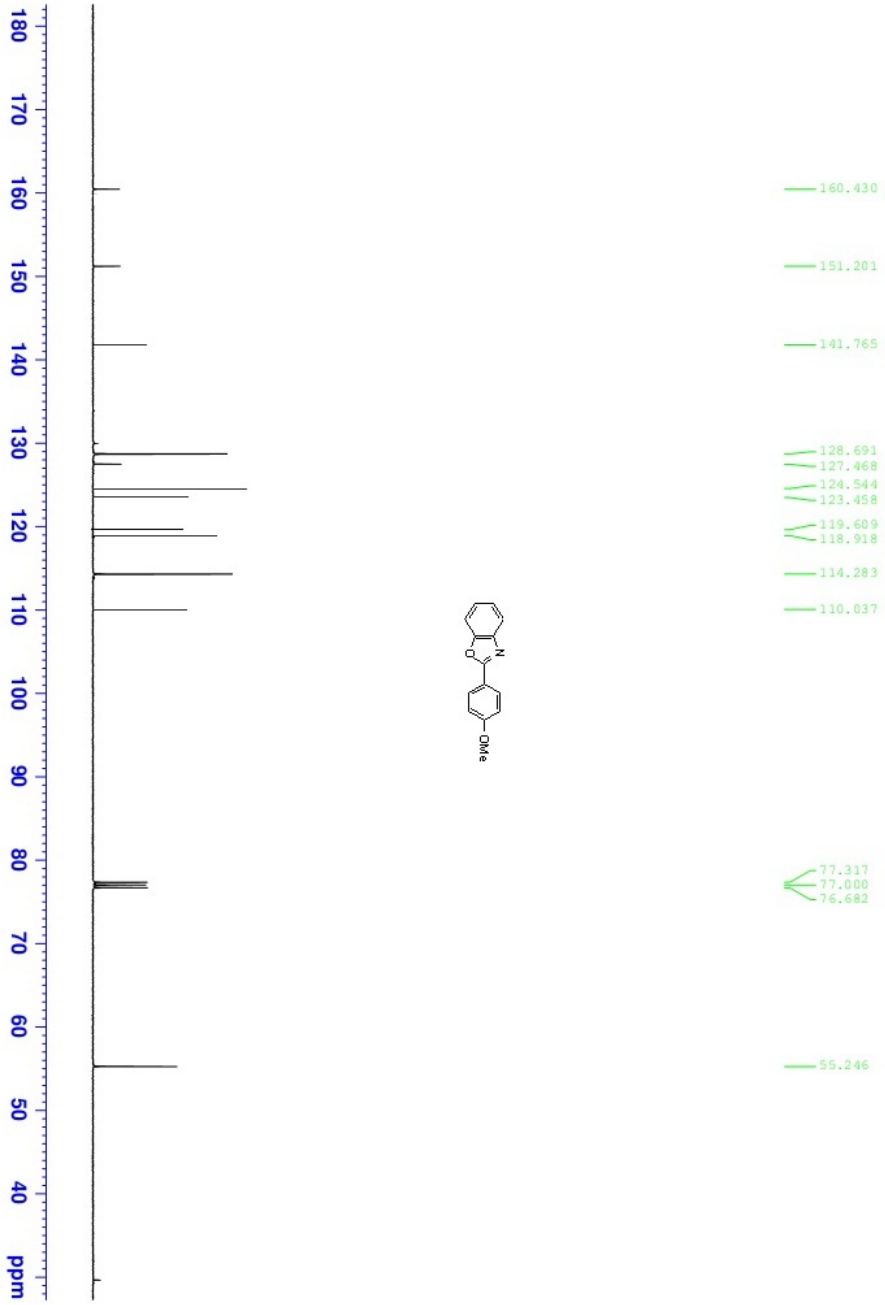
^{13}C NMR of Compound 3ga



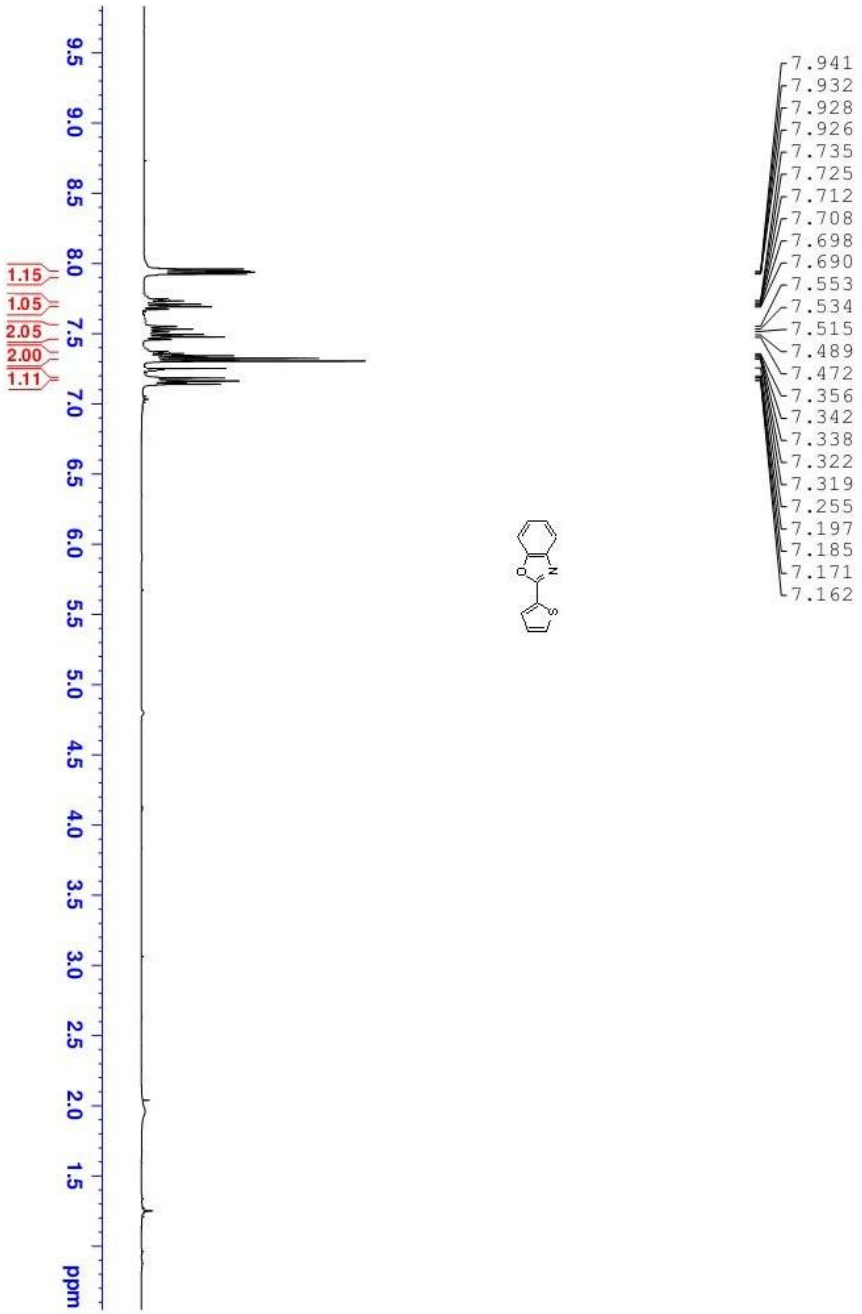
^{1}H NMR of Compound 3ha



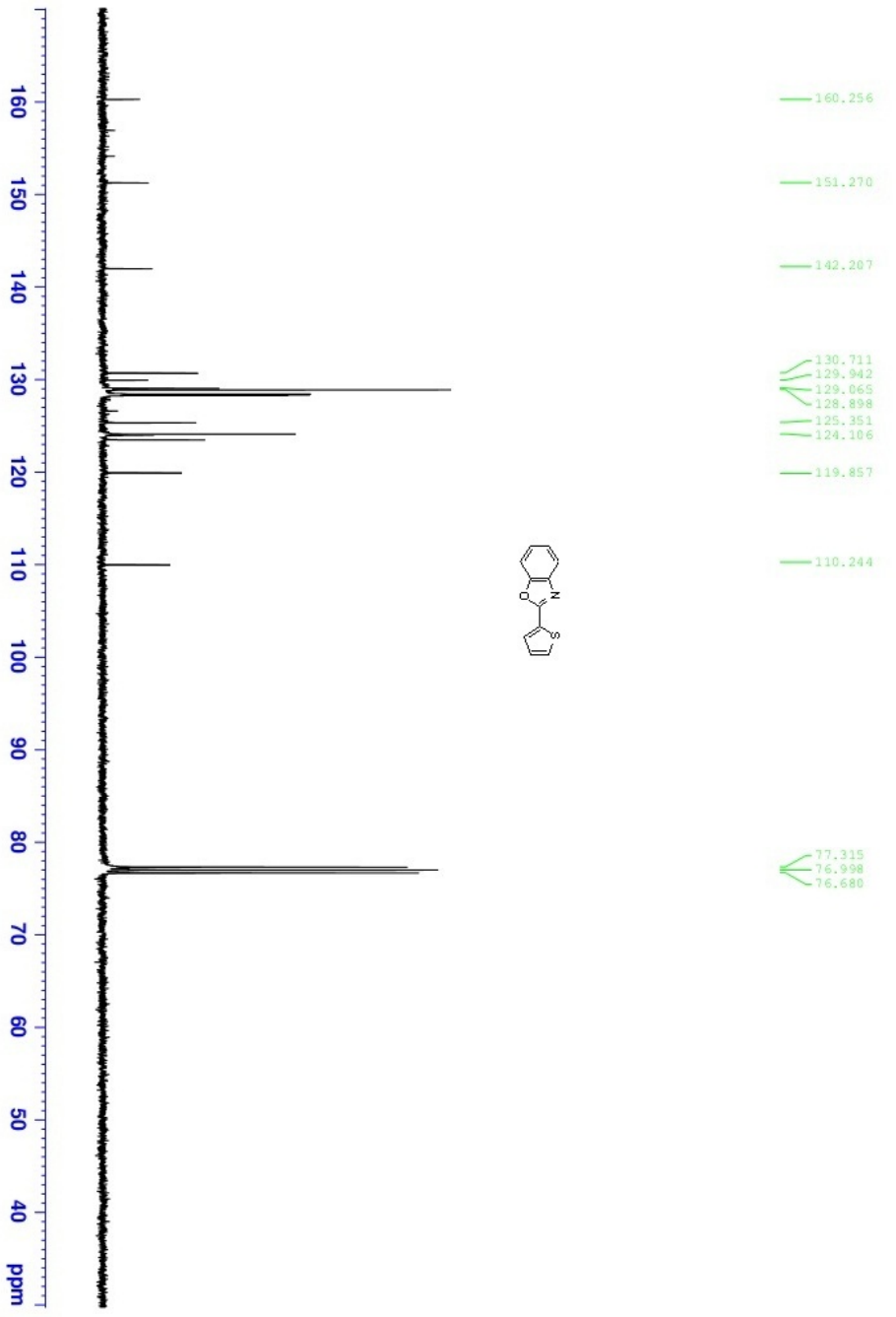
^{13}C NMR of Compound 3ha



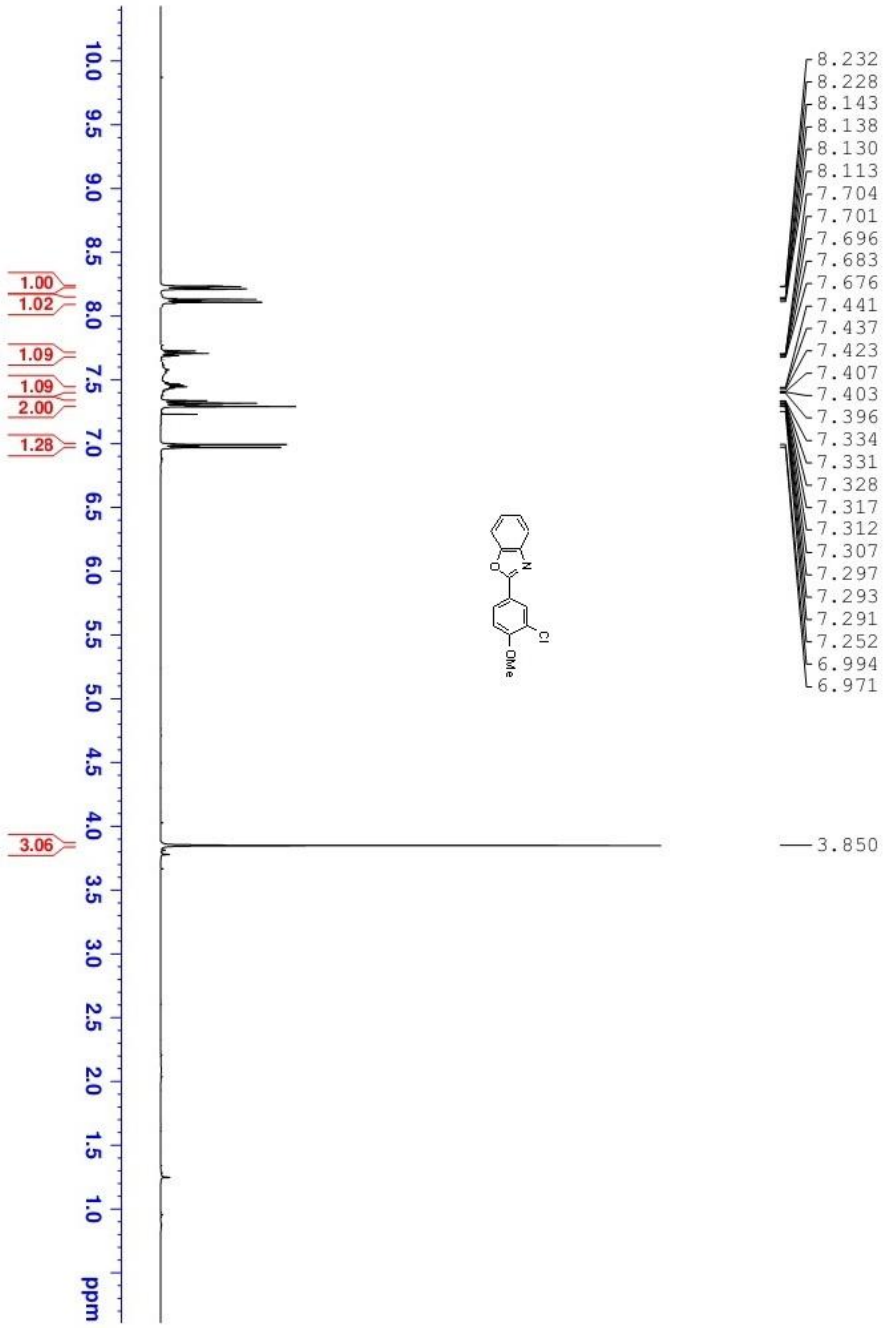
^{1}H NMR of Compound 3ia



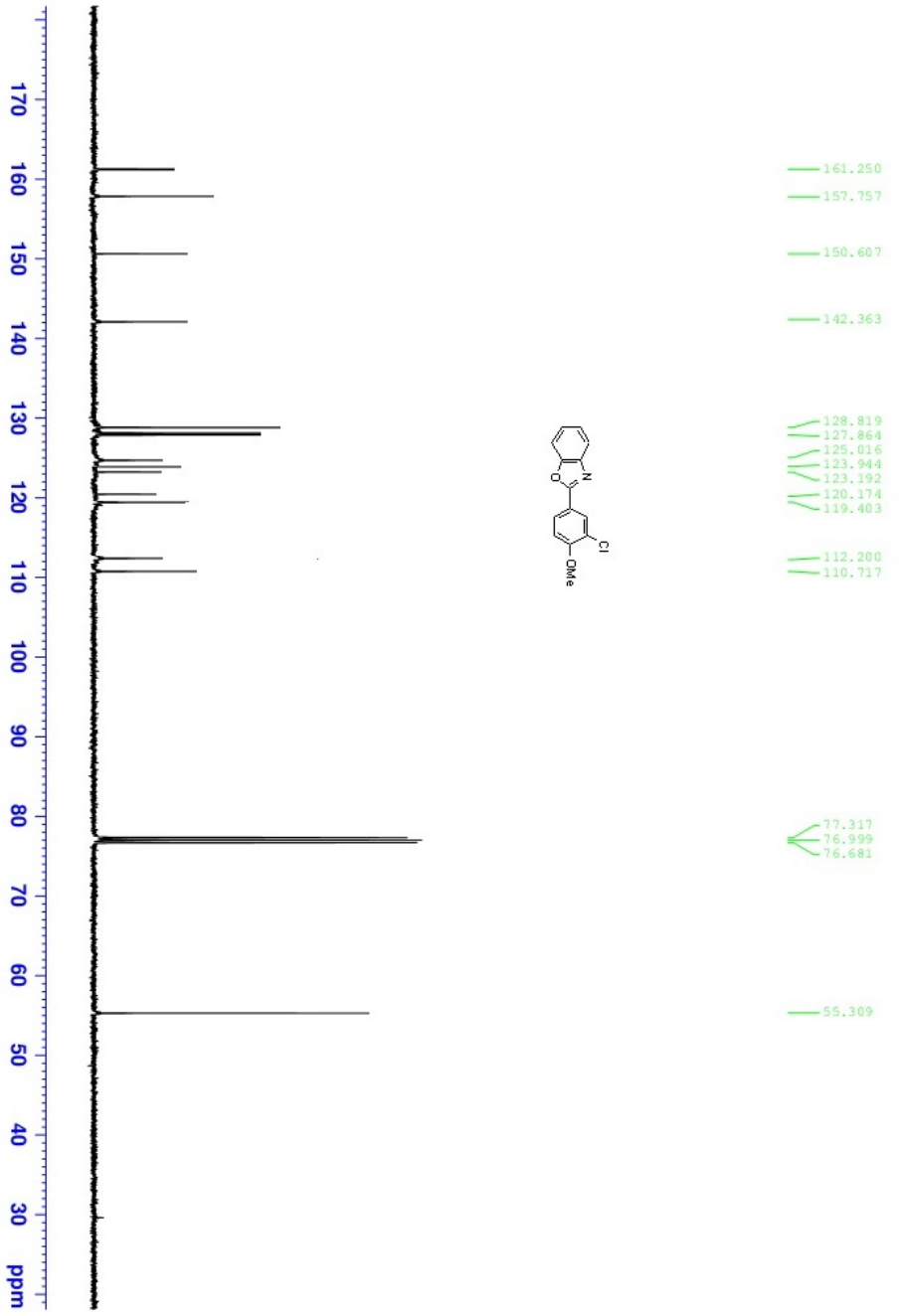
^{13}C NMR of Compound 3ia



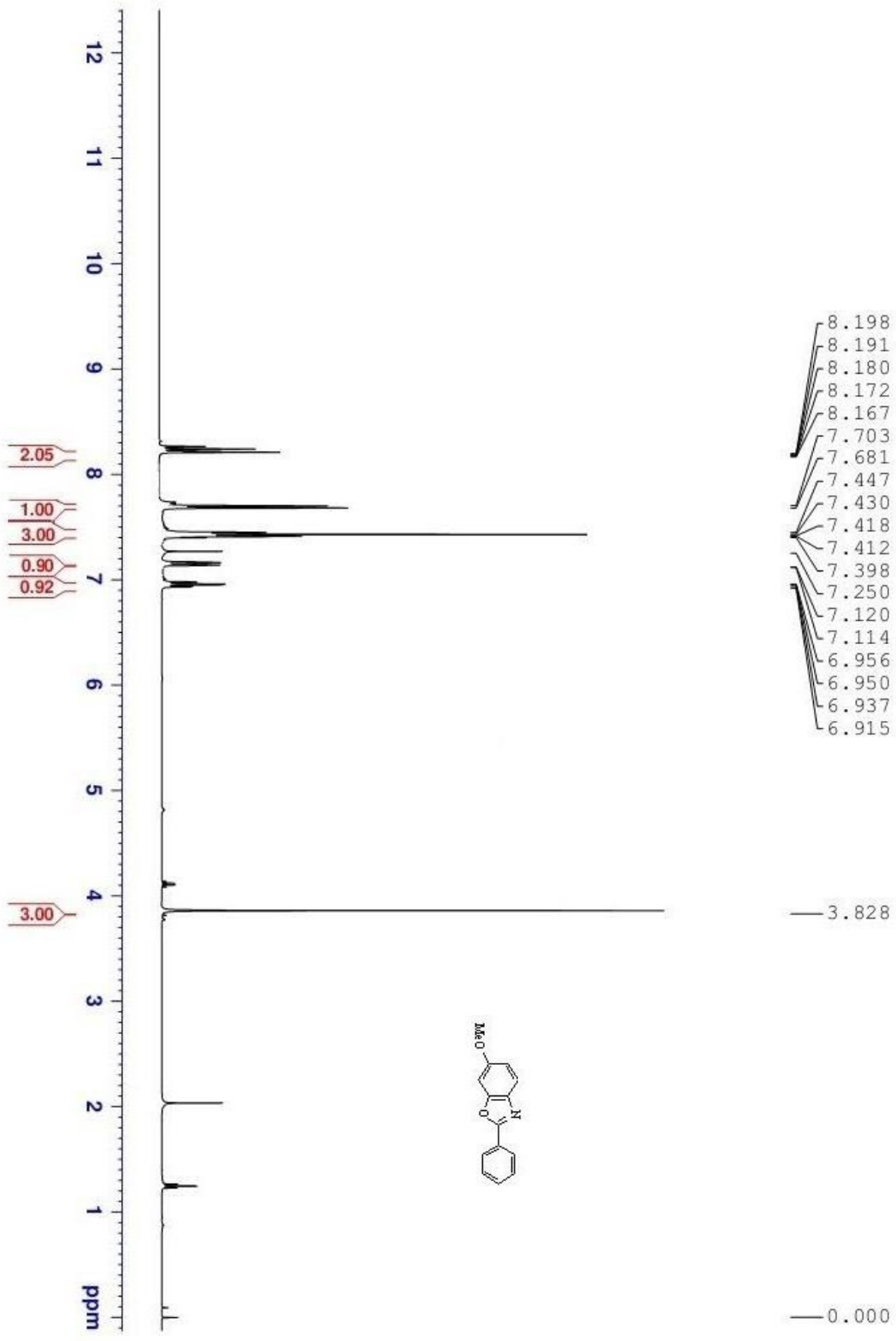
^{1}H NMR of Compound 3ja



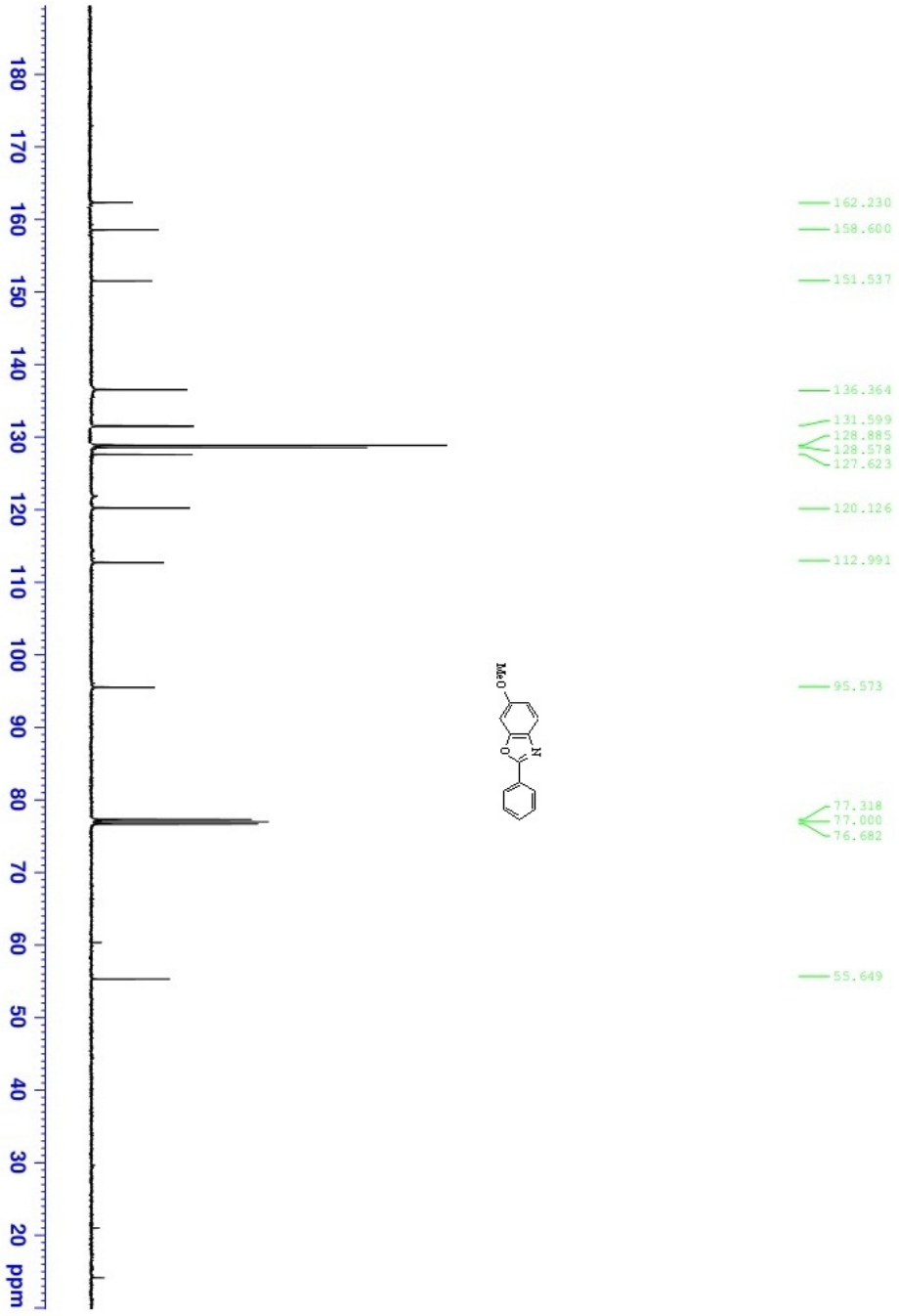
^{13}C NMR of Compound 3ja



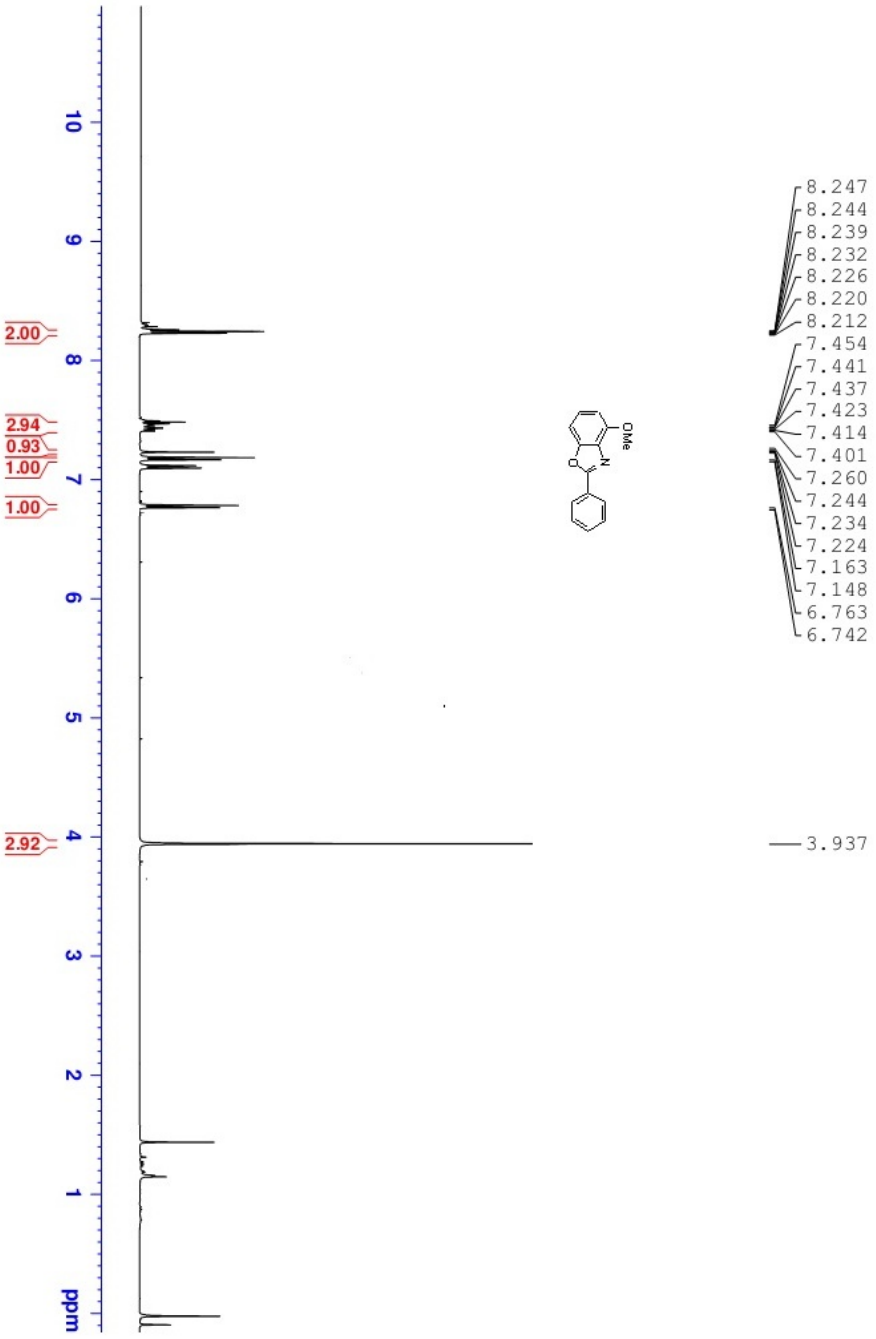
^{1}H NMR of Compound 3ab



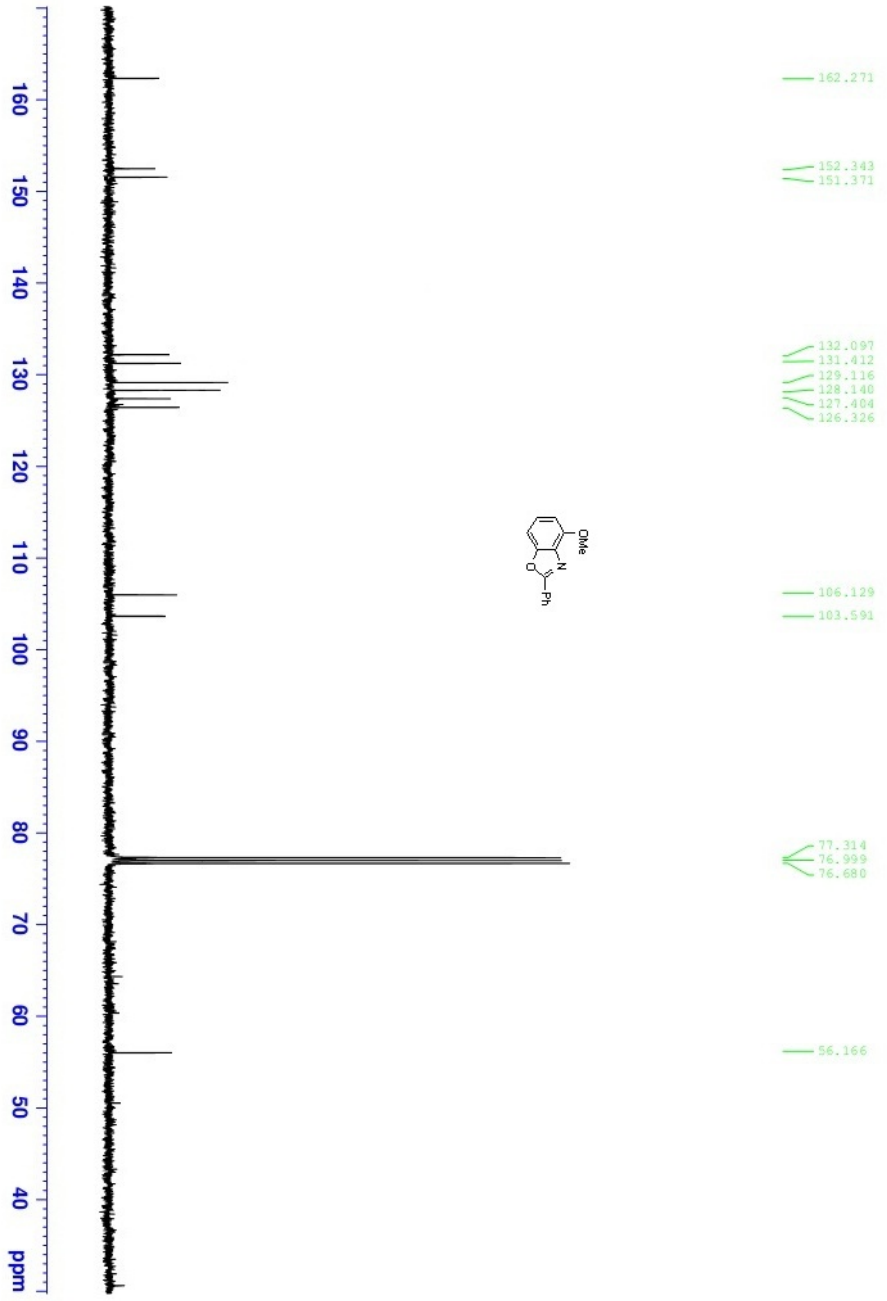
^{13}C NMR of Compound 3ab



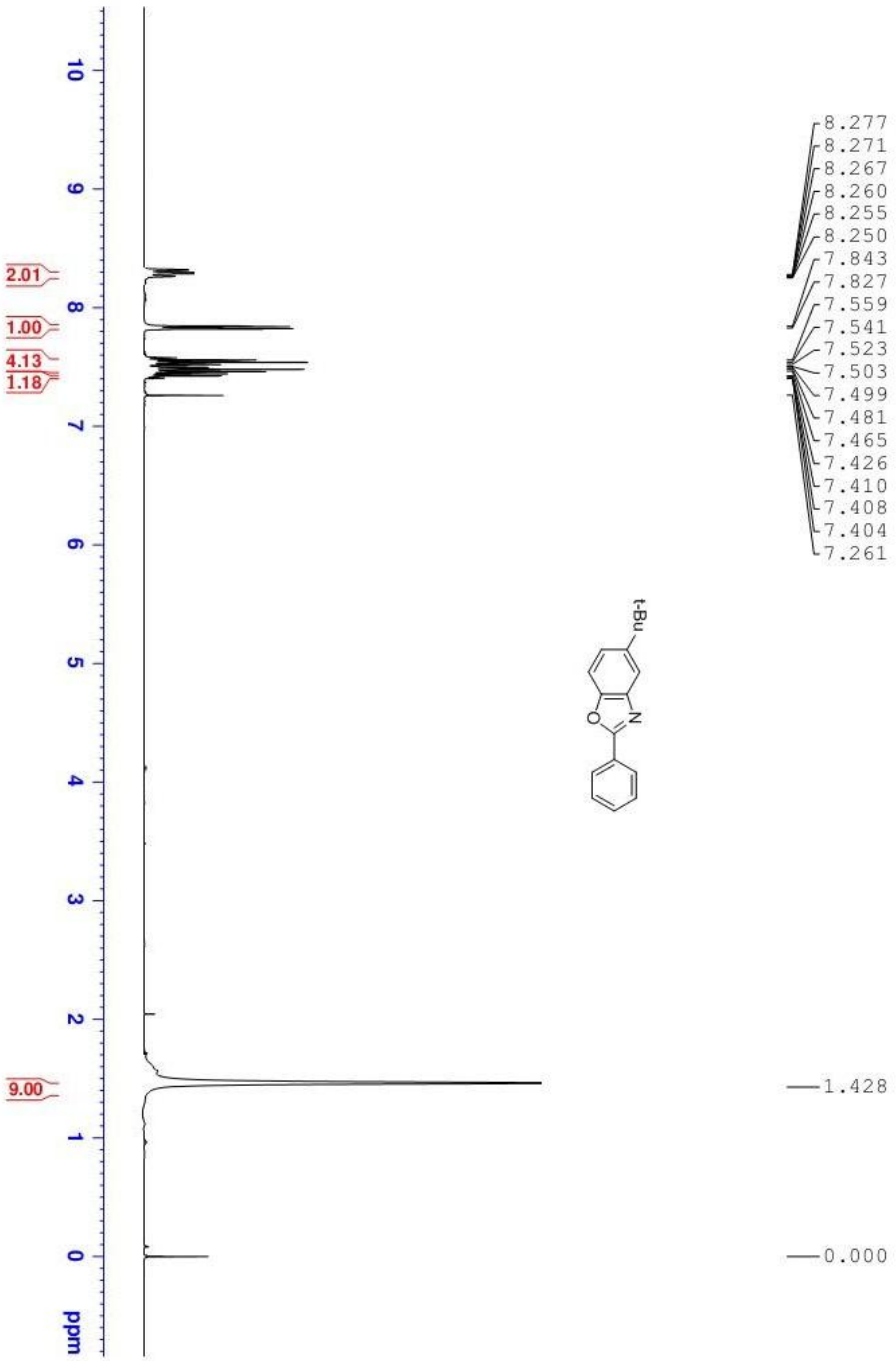
^{1}H NMR of Compound 3ac



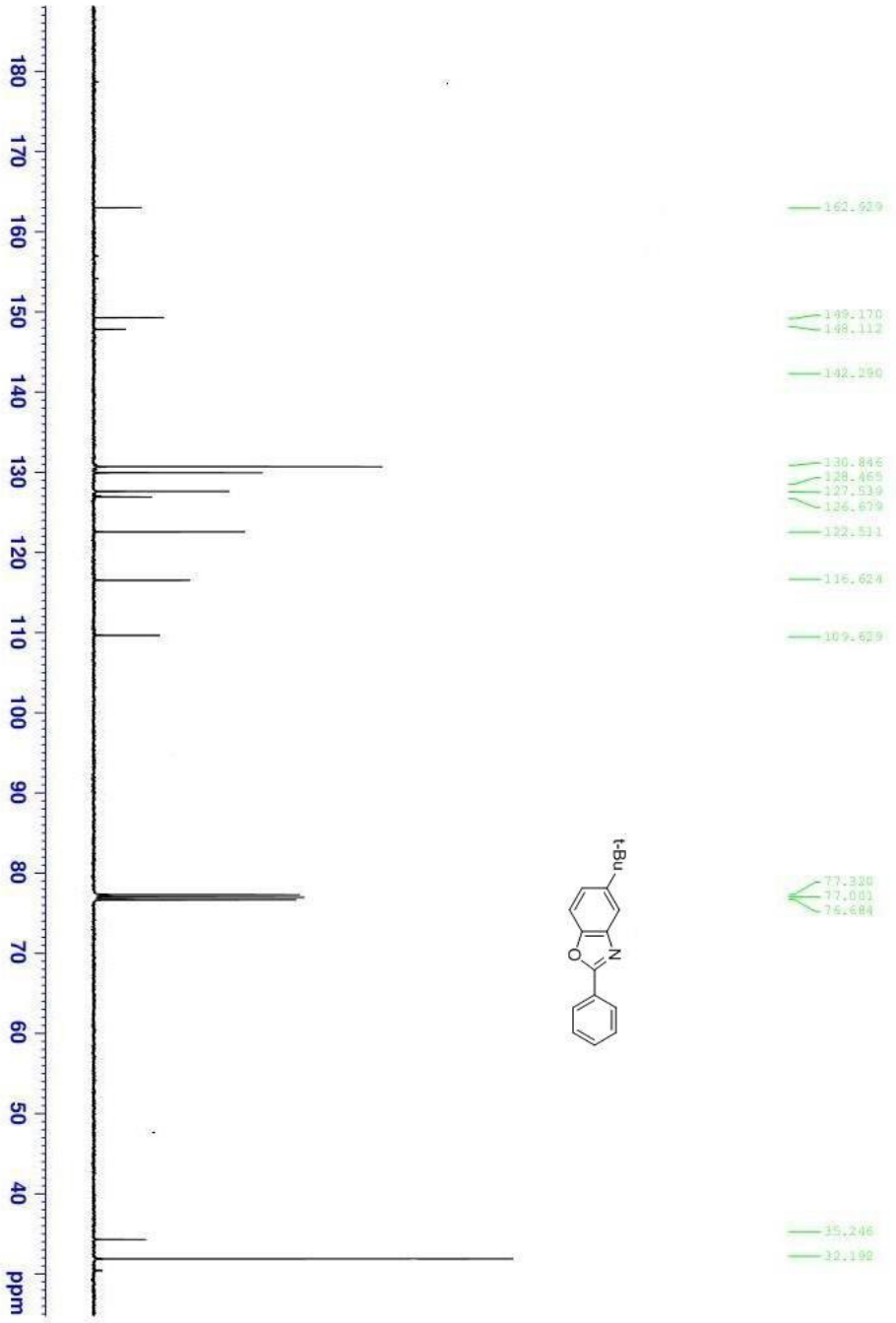
^{13}C NMR of Compound 3ac



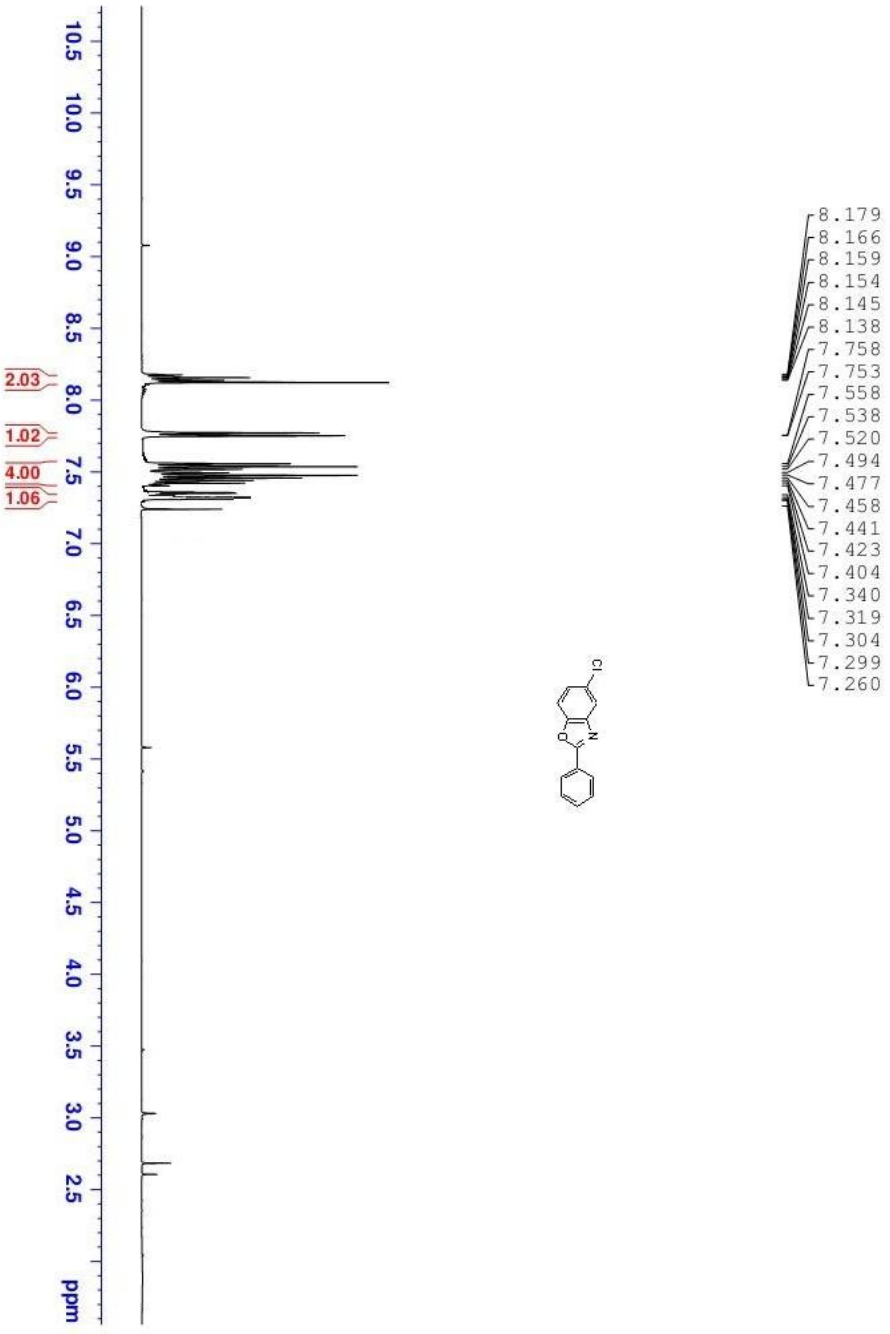
^{1}H NMR of Compound 3ad



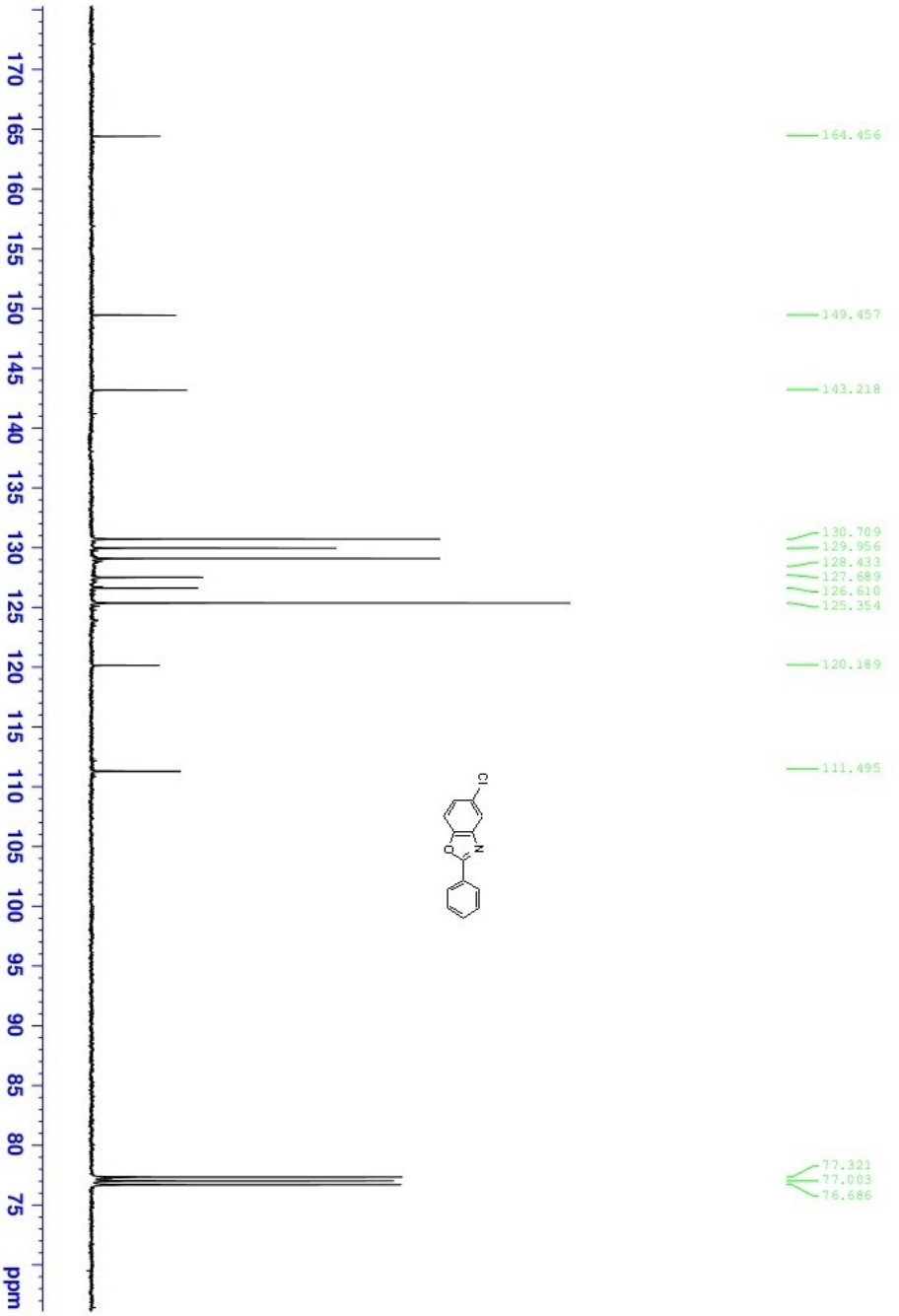
^{13}C NMR of Compound 3ad



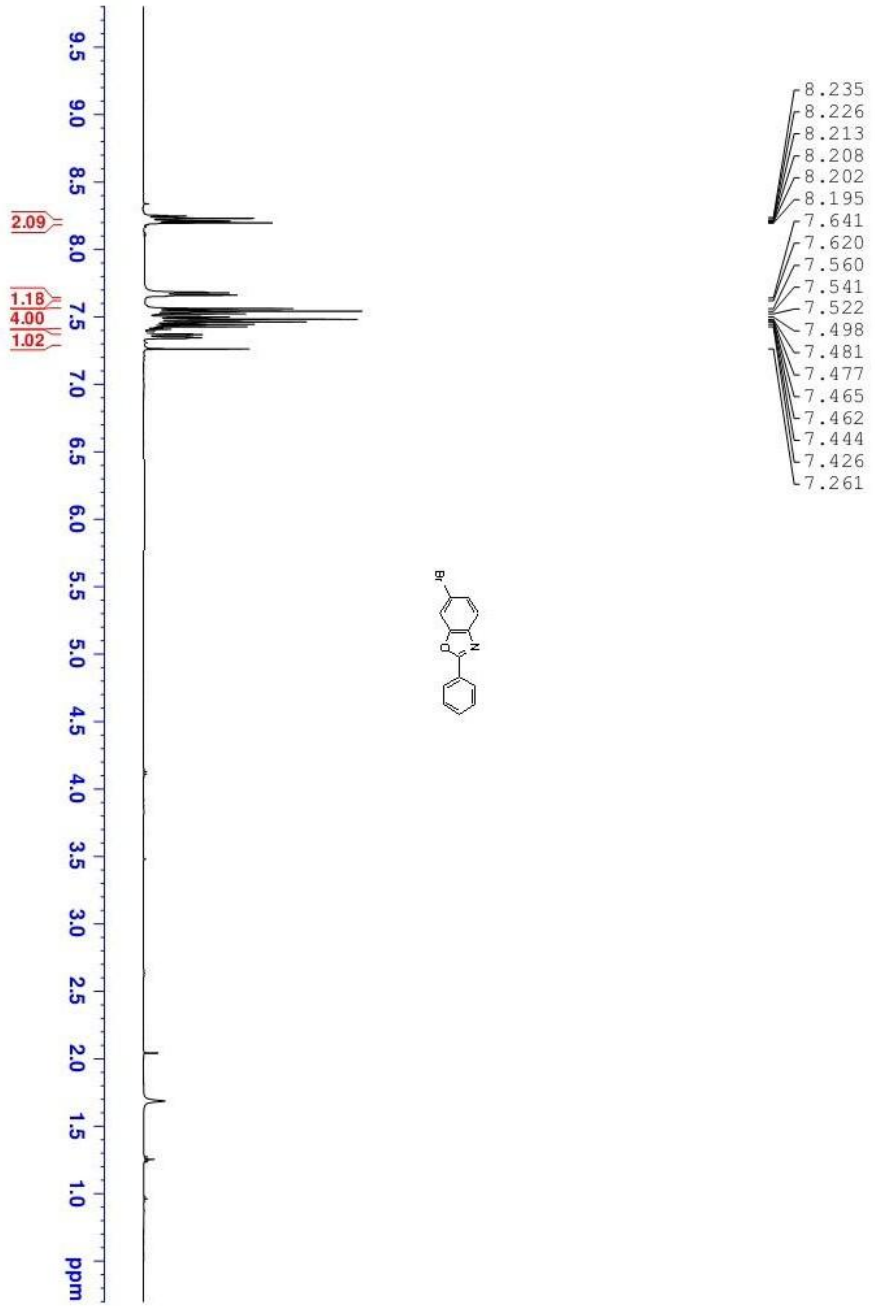
^{1}H NMR of Compound 3ae



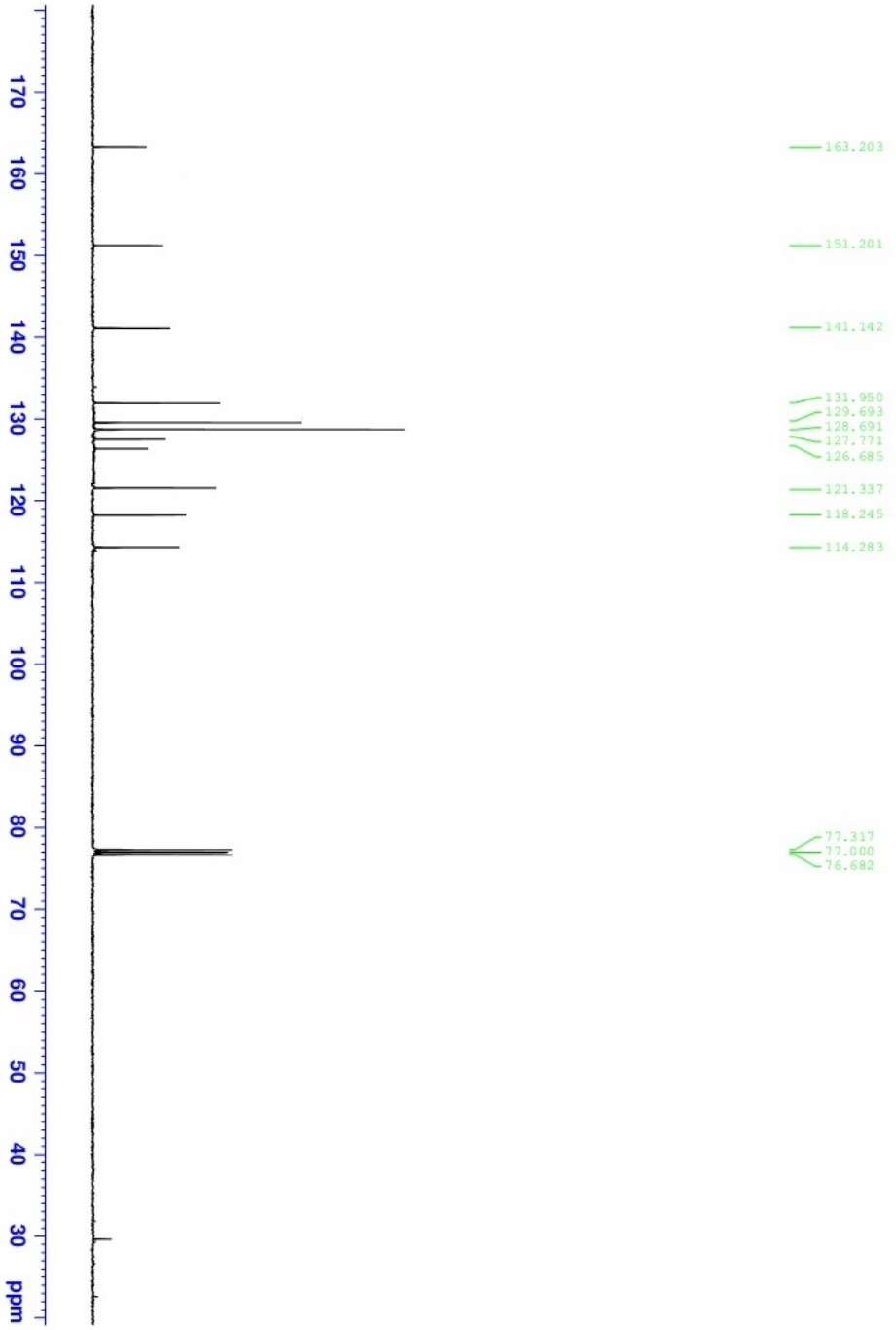
^{13}C NMR of Compound 3ae



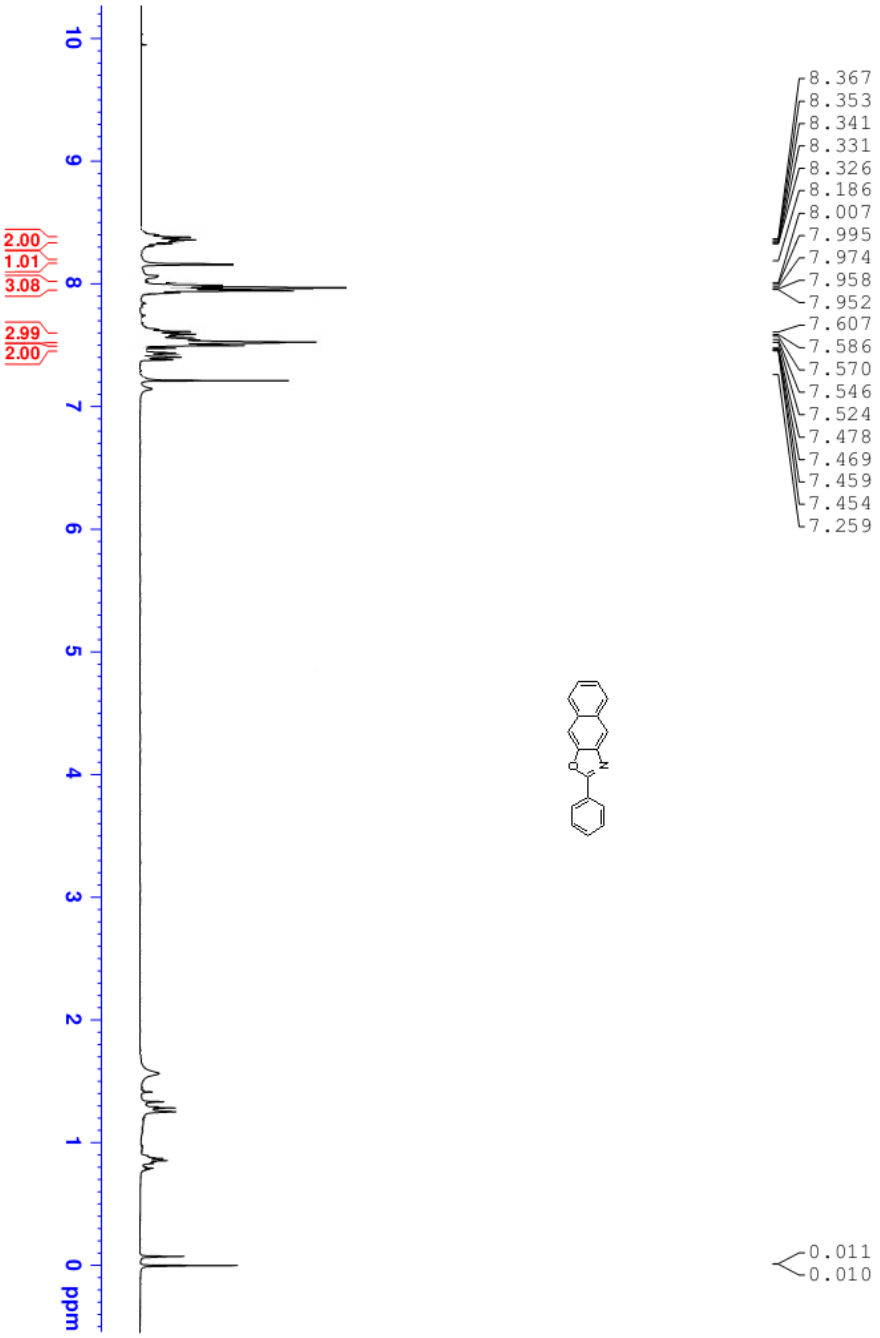
^{1}H NMR of Compound 3af



^{13}C NMR of Compound 3af



^{1}H NMR of Compound 3ag



^{13}C NMR of Compound 3ag