-Supporting information-

Flexible Graphene Paper for Large-Scale Electroorganic Synthesis: C-H Amination of Benzoxazole Derivatives

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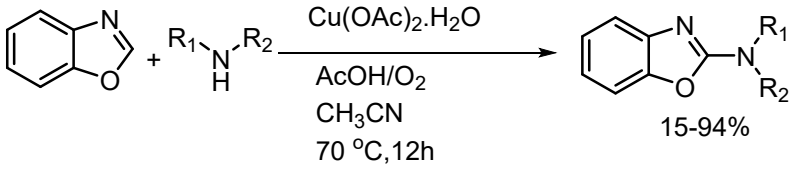
Contents

Scheme S1. Details of previous and current reports regarding the C-H amination reactions of benzoxazole.



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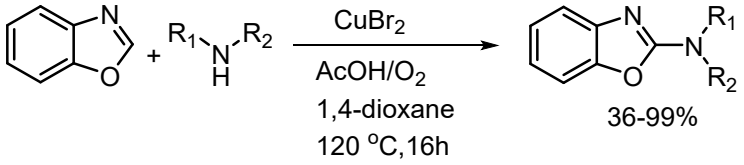

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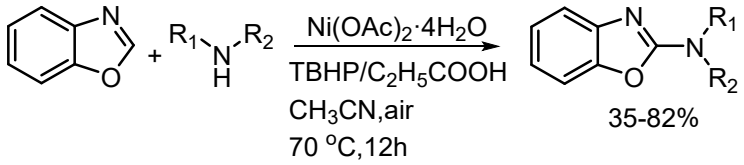

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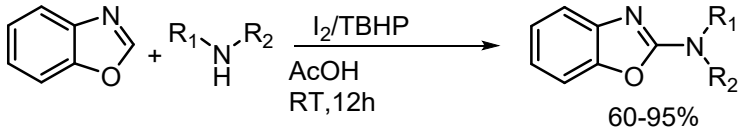

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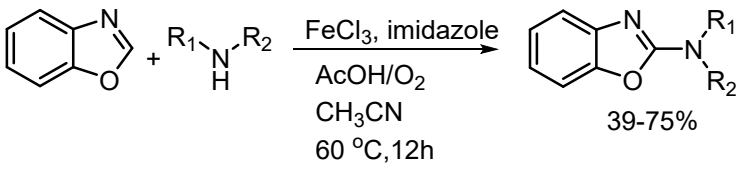

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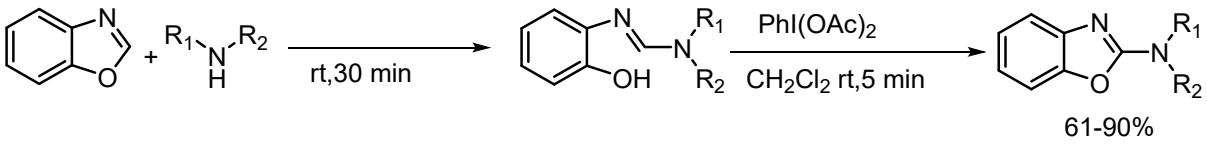

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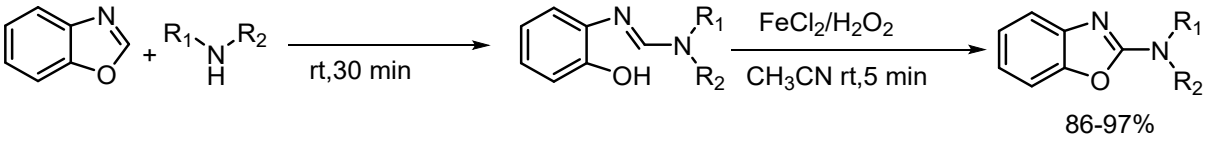

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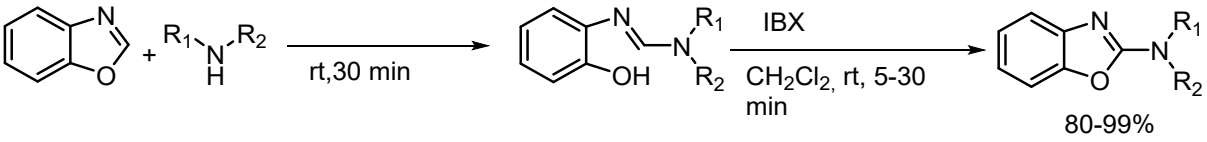

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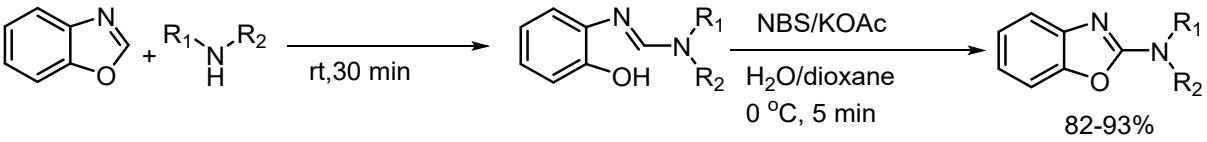

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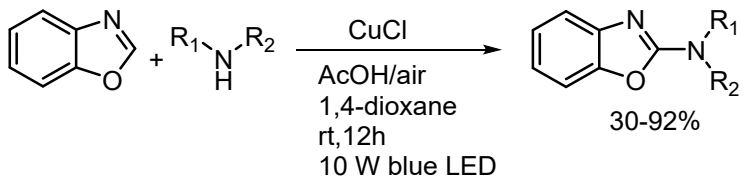

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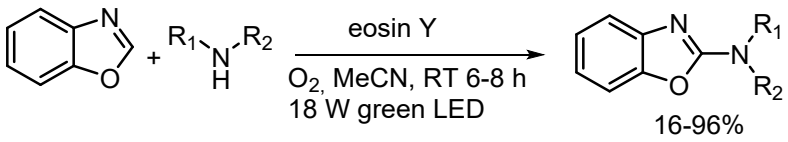

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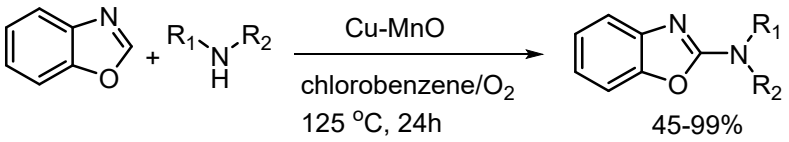

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1. Synthesis of GO flakes

First, 3.0 g of graphite powder was added to a solution containing 12.5 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$, and 2.5 g of P_2O_5 at 80 °C and mixed for the pre-oxidation of graphite to graphite oxide. After the resulting bubbly product had settled, the mixture was left at 80 °C for 5 h. The dark colored mixture was cooled to room temperature and diluted by adding 500 mL of pure water. The resulting product was left to stand overnight, then filtered and washed several times with pure water to remove residual chemicals. The pre-oxidation process was completed by keeping the resulting product at room temperature overnight.

The product obtained after the pre-oxidation process was added to 120 mL of concentrated H_2SO_4 solution cooled to 0 °C and stirred. 15 g of $KMnO_4$ was slowly added to this mixture, and the temperature of the mixture was kept at 10 °C. After this process, the mixture was stirred at 35 °C for two hours. At the end of this period, 250 mL of pure water was added so that the temperature of the mixture did not exceed 50 °C, and it was stirred at room temperature for another two hours. Then, 250 mL of distilled water and 20 mL of 30% H_2O_2 solution were added to this mixture, and the product, which turned mustard yellow, was left overnight. The clear upper part was decanted, and the milky brown lower part was filtered. The filtrate was washed several times with 150 mL of 1:10 HCl and finally with pure water. A 2% dispersion of the resulting brown product (graphite oxide) in water was prepared and subjected to dialysis for 3 weeks to obliterate metal ions. The resulting graphite oxide has a stable structure that can be used for many years. Graphite oxide was turned into GO dispersion by ultrasonication in a suitable solvent. In this work, pure water was used as the solvent. A stable dispersion of GO in pure water with a concentration of 7.0 mg mL^{-1} was prepared. To prepare this stable dispersion, GO, weighed at the desired concentration, was subjected to ultrasonication in pure water for approximately five hours to ensure that the GO layers were well dispersed. Then, the prepared dispersion was left overnight to settle the unstable structures and to obtain a stable dispersion.

2. Supplementary figures

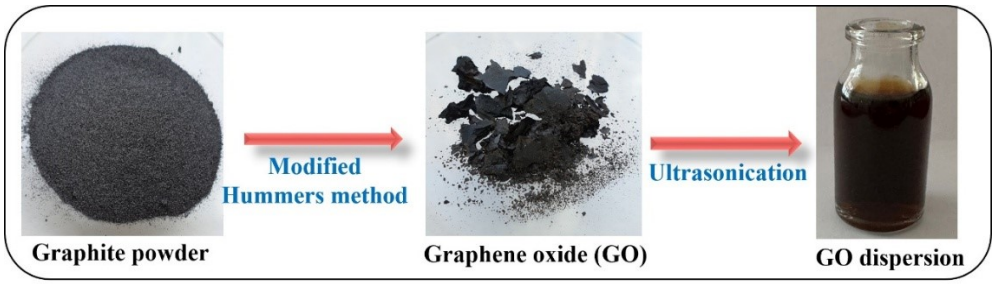


Figure S1. A schematic presentation of synthesis procedure GO dispersion.

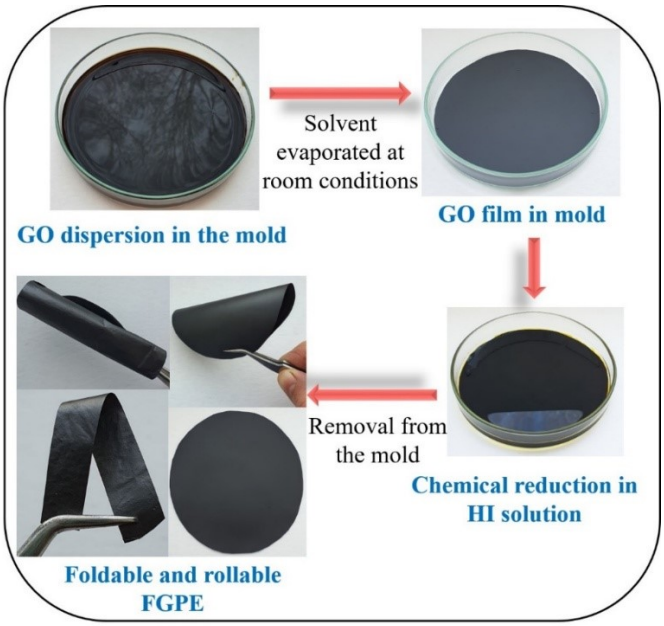


Figure S2. Preparation route of FGPEs.

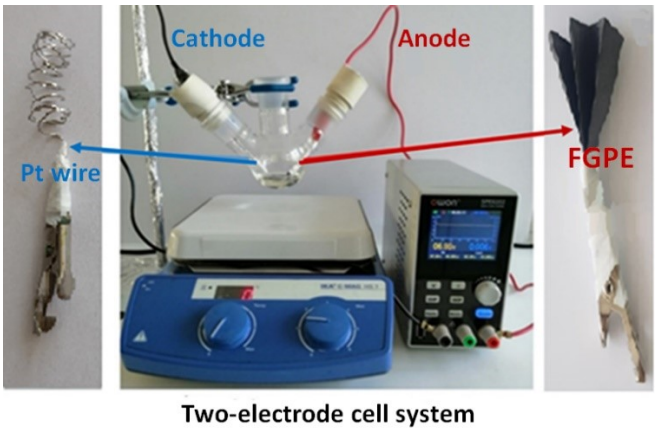


Figure S3. Two-electrode cell system designed for electroorganic synthesis.

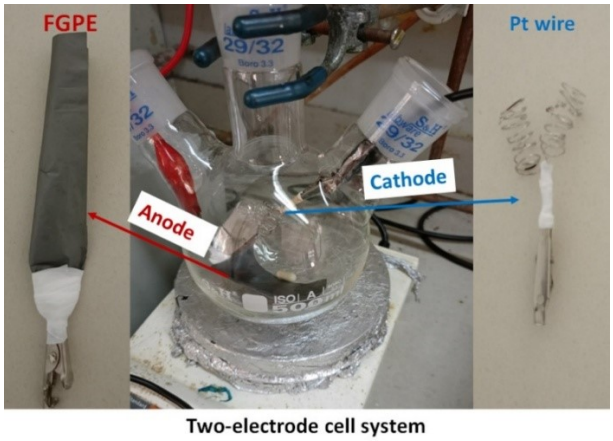


Figure S4. Two-electrode cell system for gram-scale synthesis.

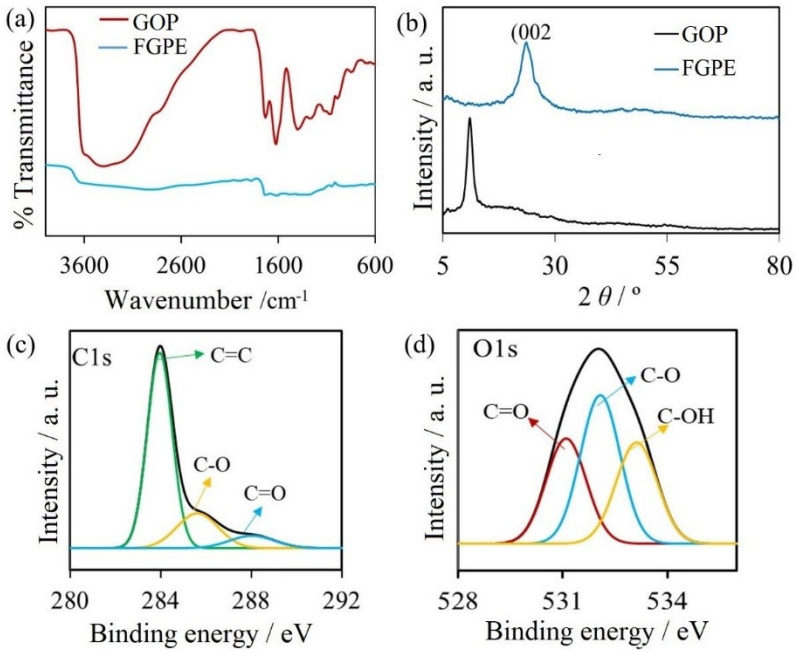


Figure S5. (a) FTIR, (b) powder XRD spectra of GOP and FGPE. Detailed XPS spectra of (c) C1s and (d) O1s region of FGPE.

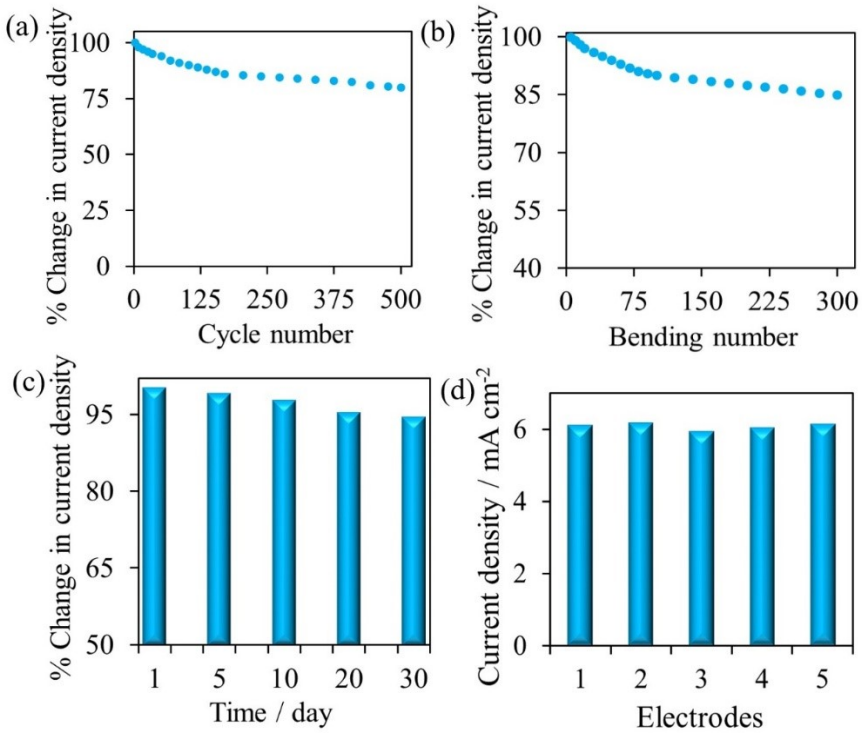
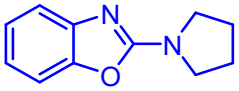


Figure S6. Graphs of the test results of FGPE for (a) successive reusability; (b) flexibility; (c) stability over time, and (d) reproducibility. (Electrochemical performances were obtained in the solution containing 0.10 M KNO_3 and 10 mM $Fe(CN)_6^{3-/4-}$).

3. Characterization of the synthesized molecules

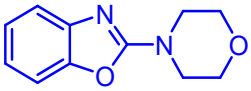
3.1. 2-(Pyrrolidin-1-yl)benzo[d]oxazole (3a)



Brown solid 90 mg 95% yield Mp: 58-60 °C .

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 3.66 – 3.61 (m, 4H), 2.06 – 1.97 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0 149.0, 143.5, 123.9, 120.2, 116.0, 108.8, 47.5, 25.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{11}H_{13}N_2O$: 189.1028, found: 189.1020.

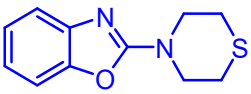
3.2. 2-Morpholinebenzo[d]oxazole (3b)



Brown solid 94 mg 94% yield Mp**:** 90-92 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 3,82 – 3.80 (m, 4H), 3.69-3.67 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 148.8, 142.9, 124.2, 121.0, 116.6, 108.9, 66.3, 45.8. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{11}H_{13}N_2O_2$: 205.0978, found: 205.0973

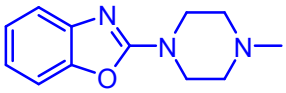
3.3. 2-Thiomorpholinobenzo[d]oxazole (3c)



Brown solid 103mg 93% yield Mp: 95-97 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 3,99 – 3.93 (m, 4H), 2.73– 2.69 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 148.7, 143.0, 124.2, 120.9, 116.4, 108.9, 48.2, 26.8. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{11}H_{13}N_2OS$: 221.0749, found: 221.0744

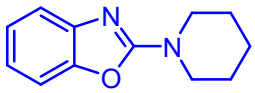
3.4. 2-(4-Methylpiperazin-1-yl)benzo[d]oxazole (3d)



Brown solid 99 mg 90% yield Mp**:** 36-38 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H),3.73 (t, *J* = 5.2 Hz, 4H), 2.53 (t, *J* = 5.2 Hz 4H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 148.8, 143.2, 124.1, 120.8, 116.4, 108.8, 54.3, 46.4, 45.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{16}N_3O$: 218.1293, found: 218.1288

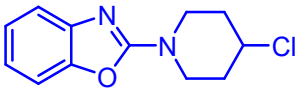
3.5. 2-(Piperidin-1-yl)benzo[d]oxazole (3e)



Brown solid 97 mg 95% yield Mp: 54-56 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 3.66 (s, 4H), 1.68 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 148.8, 143.5, 123.9, 120.4, 116.1, 108.7, 46.7, 25.3, 24.2. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_2O$: 203.1184, found: 203.1178

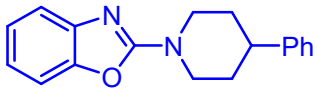
3.6. 2-(4-Chloropiperidin-1-yl)benzo[d]oxazole (3f)



Brown solid 109 mg 91% yield Mp: 113-115 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 4.28-4.20 (m 1H), 3.93-3,86 (m, 2H), 3.65-3.58 (m 2H), 2.16-2.08 (m, 2H), 1.97-1.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 148.7, 143.0, 124.0, 120.7, 116.3, 108.8, 56.1, 42.9, 34.1. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{14}ClN_2O$: 237.0795, found: 237.0793

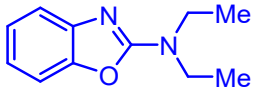
3.7. 2-(4-Fenilpiperidin-1-il)benzo[d]oksazol (3g)



Brown solid 126 mg 90% yield Mp: 91-93 °C

^{1}H NMR (**400 MHz**, $CDCl_3$): δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.26-7.22 (m, 2H), 7.20-7,08 (m, 5H), 6.95 (t, *J* = 7.7 Hz, 1H), 4,39-4.35 (m, 2H), 3.11-3.04 (m, 2H) 2.70-2.62 (m, 1H), 1.89-1.85 (m, 2H), 1.78-1.67 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 148.7, 145.1, 143.2, 128.5, 126.7, 126.5, 123.9, 120.5, 116.1, 108.6, 46.3, 42.2, 32.5. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{18}H_{19}N_2O$: 279.1497, found: 279.1494

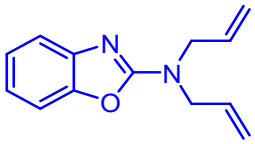
3.8. N,N-diethylbenzo[d]oxazole-2-amine (3h)



Brown liquid 86 mg 90% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 3.58 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 148.9, 143.5, 124.0, 120.1, 115.8, 108.7, 43.1, 13.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{11}H_{15}N_2O$: 191.1184, found: 191.1179

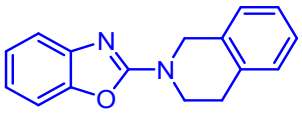
3.9. N,N-diallylbenzo[d]oxazole-2-amine (3i)



Brown liquid 95 mg 88% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 5.91-5.81 (m, 2H), 5.22 (t, *J* = 9.2 Hz, 4H), 4.15 (d, *J* = 5.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 148.9, 143.4, 132.5, 123.9, 120.4, 117.9, 116.1, 108.7, 49.9. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{13}H_{15}N_2O$: 215.1184, found: 215.1180

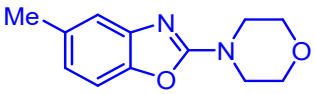
3.10. 2-(3,4-dihydroisoquinolin-2(1H)-yl)benzo[d]oxazole(3j)



Light yellow solid 107 mg % 85 yield Mp: 82-84 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.38 (m, 1H), 7.30 – 7.27 (m, 1H), 7.24 – 7.15 (m, 5H), 7.06 – 7.01 (m, 1H), 4.86 (s, 2H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.01 (t, *J* = 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 148.8, 143.0, 134.1, 132.4, 128.9, 127.0, 126.7, 126.5, 124.2, 120.8, 116.3, 108.9, 47.3, 43.2, 28.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{16}H_{15}N_2O$: 251.1184, found: 251.1178

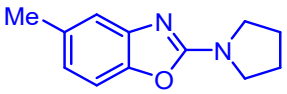
3.11. 5-methyl-2-morpholinobenzo[d]oxazole(6a)



Brown solid 101 mg %92 yield Mp: 120-122 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (s, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.81-3.79 (m, 4H), 3.67-3.65 (m, 4H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 146.9, 142.9, 133.7, 121.6, 116.8, 108.2, 66.1, 45.7, 21.5. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_2O_2$: 219.1134, found: 219.1129

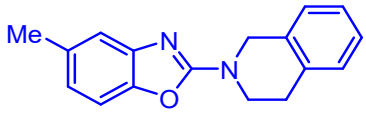
3.12. 5-methyl-2-(pyrrolidin-1-yl)benzo[d]oxazole(6b)



Brown solid 95 mg %93 yield Mp: 94-96 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 3.62-3.58 (m, 4H), 2.36 (s, 3H), 2.0-1.96 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 147.2, 143.8 , 133.4, 120.7, 116.4 , 107.9 , 47.4 , 25.6, 21.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_2O$: 203.1184, found: 203.1180

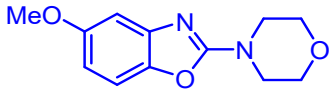
3.13. 2-(3,4-dihydroisoquinolin-2(1H)-yl)-5-methylbenzo[d]oxazole(6c)



Brown solid 110.4 mg % 83 yield Mp: 95-97 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 6H), 6.85 – 6.80 (m, 1H), 4.84 (s, 2H), 3.94 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 5.9 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 147.1, 143.4, 134.2, 133.7, 132.5, 128.9, 126.9, 126.6, 126.5, 121.3, 116.7, 108.2, 47.2, 43.1, 28.6, 21.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{17}N_2O$: 265.1341, found: 265.1337

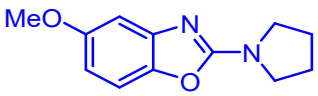
3.14. 5-methoxy-2-morpholinobenzo[d]oxazole(6d)



Brown solid 106 mg %90 yield Mp: 89-91 °C

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 2.5 Hz, 1H), 6.56 (dd, J = 8.7, 2.5 Hz, 1H), 3.78 – 3.75 (m, 7H), 3.63 – 3.61 (m, 4H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 162.8 , 157.1, 143.8, 143.3, 108.7, 107.4,101.5 ,66.2, 55.8 , 45.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_2O_3$: 235.1083, found: 235.1079

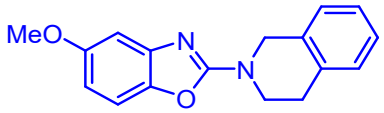
3.15. 5-methoxy-2-(pyrrolidin-1-yl)benzo[d]oxazole(6e)



Brown solid 106mg %90 yield Mp: 72-74 °C

^{1}HNMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.53(dd, *J* = 8.6, 2.5 Hz, 1H), 3.79 (s, 3H), 3.64-3.61 (m, 4H), 2.04-2.00 (m, 4H). **^{13}CNMR** (100 MHz, $CDCl_3$) δ 161.9, 157.0, 144.7, 143.7, 108.5, 106.4, 101.3, 56.0, 47.7, 25.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{12}H_{15}N_2O_2$: 219.1134, found: 219.1133

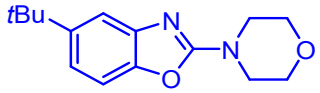
3.16. 2-(3,4-dihydroisoquinolin-2(1H)-yl)-5-methoxybenzo[d]oxazole(6f)



Brown solid 115.6 mg %82 yield Mp: 72-74 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 5H), 6.97 – 6.94 (m, 1H), 6.61 – 6.56 (m, 1H), 4.84 (s, 2H), 3.94 (t, *J* = 5.9 Hz, 2H), 3.81 (s, 3H), 3.00 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 157.2, 144.3, 143.5, 134.2, 132.5, 128.9, 127.0, 126.7, 126.5, 108.7, 107.1, 101.5, 56.0, 47.2, 43.2, 28.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2$: 281.1290, found: 281.1287

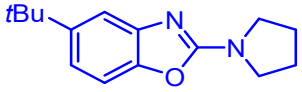
3.17. 5-(tert-butyl)-2-morpholinobenzo[d]oxazole(6g)



Brown solid 119 mg %91 yield Mp: 86-88 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.17 (d, *J* = 8.4,Hz, 1H), 7.08 (d, *J* = 8.4,Hz, 1H), 3.82-3.79 (m, 4H), 3.68-3.66 (m, 4H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 147.6, 146.7 142.6, 118.2, 113.7, 108.0, 66.3, 45.8, 34.9, 31.8. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{15}H_{21}N_2O_2$: 261.1603, found: 261.1599

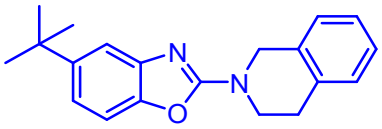
3.18. 5-(tert-butyl)-2-(pyrrolidine-1-il)benzo[d]oxazole (6h)



Brown solid 113 mg %92 yield Mp: 58-60 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.65-3.58 (m, 4H), 2.04-1.98 (m, 4H), 1.33 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 147.3, 147.1, 143.5, 117.2, 113.3, 107.7, 47.5, 34.9, 31.9, 25.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{15}H_{21}N_2O$: 245.1654, found: 245.1652

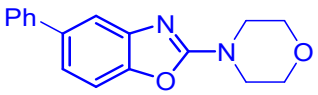
3.19. 5-(tert-butyl)-2-(3,4-dihydroisoquinolin-2(1H)-yl)benzo[d]oxazole(6i)



Light yellow solid 123 mg % 80 yield Mp: 43-45 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 1.9, 0.5 Hz, 1H), 7.24 – 7.15 (m, 5H), 7.08 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.84 (s, 2H), 3.94 (t, *J* = 5.9 Hz, 2H), 2.99 (t, *J* = 5.9 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 147.6, 146.9, 143.0, 134.2, 132.6, 128.9, 126.9, 126.6, 126.5, 117.9, 113.5, 107.9, 47.34, 43.3, 31.9, 28.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{20}H_{23}N_2O$: 307.1810, found: 307.1809

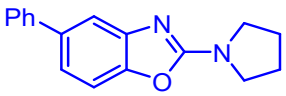
3.20. 2-morpholino-5-phenylbenzo[d]oxazole(6j)



Brown solid 127 mg %90 yield Mp: 102-104 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.26-7.17 (m, 3H), 3.75-3,73 (m, 4H), 3.63-3,61 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 148.4, 143.5, 141.6, 138.0, 128.9, 127.4, 127.1, 120.5, 115.3, 108.9, 66.3, 45.8. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2$: 281.1290, found: 281.1286

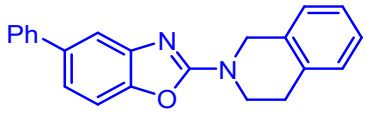
3.21. 5-phenyl-2-(pyrrolidin-1-yl)benzo[d]oxazole(6k)



Brown solid 119 mg %90 yield Mp: 116-118 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.26-7.13 (m, 3H), 3.60-3.57 (m, 4H), 1.97-1.94 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 148.8, 144.3, 141.8, 137.6, 128.8, 127.4, 126.9, 119.5, 114.7, 108.6, 47.5, 25.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{17}H_{17}N_2O$: 265.1341, found: 265.1338

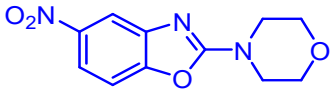
3.22. 2-(3,4-dihydroisoquinolin-2(1H)-yl)-5-phenylbenzo[d]oxazole(6l)



Light yellow solid 132.7 mg %81 yield Mp:126-128 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.60 (t, *J* = 1.1 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.28 – 7.19 (m, 5H), 4.89 (s, 2H), 3.98 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 148.6, 143.9, 141.8, 137.9, 134.1, 132.4, 128.9, 128.8, 127.4, 127.0, 127.0, 126.7, 126.5, 120.1, 115.0, 108.8, 47.3, 43.2, 28.6. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{22}H_{19}N_2O$: 327.1497, found: 327.1499

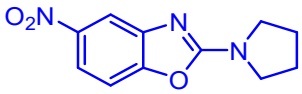
3.23. 2-morpholino-5-nitrobenzo[d]oxazole(6m)



Brown solid 106mg %85 yield Mp: 138 -140 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.3 Hz, 1H), 7.98 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 3.84 – 3.80 (m, 4H), 3.74 – 3.70 (m, 4H). **^{13}C-NMR (**100 MHz, $CDCl_3$) δ 163.5, 152.7, 145.3, 143.9, 117.5,112.0, 108.6, 66.2, 45.7. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{11}H_{12}N_3O_4$: 250.0828, found: 250.0822

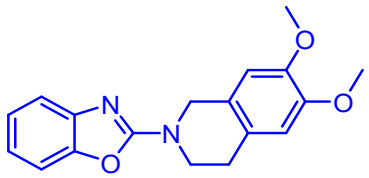
3.24. 5-nitro-2-(pyrrolidin-1-yl)benzo[d]oxazole(6n)



Brown solid 101 mg %87 yield Mp: 66-68 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.3 Hz, 1H), 7.93 (dd, J = 8.6, 2.4 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 3.67-3.63 (m, 4H), 2.07-2.03 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 153.0, 145.1, 144.7, 116.6, 111.4, 108.1, 47.6, 25.5. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{13}H_{15}N_2O$: 234.0879, found: 234.0873

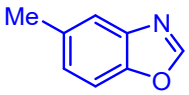
3.25. 2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)benzo[d]oxazole(6o)



Brown solid 125.8 mg %80 yield Mp:101-103 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.27 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.08 – 6.97 (m, 1H), 6.64 (d, *J* = 2.6 Hz, 2H), 4.77 (s, 2H), 3.93 (t, *J* = 5.9 Hz, 2H), 3.88 – 3.81 (m, 6H), 2.91 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1, 148.8, 148.0, 147.9, 142.9, 125.9, 124.2, 124.1, 120.8, 116.2, 111.6, 109.1, 108.9, 56.1, 56.0, 47.0, 43.3, 27.9. **HRMS** (Q-TOF): m/z $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_3$: 311.1396, found: 311.1398

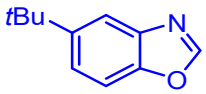
3.26. 5-Methylbenzo[d]oxazole) (7)



beige solid 586 mg 87% yield Mp: 48-50 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.57 (s, 1H), 7.45 (d, *J* 8.3 Hz, 1H), 7.2 (d, *J* = 8.3 Hz, 1H), 2.47 (s, 3H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 148.4, 140.4, 134.6, 126.8, 120.5, 110.4, 21.5.

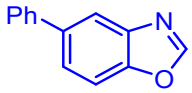
3.27. 5-(Tert-butyl)benzo[d]oxazole (8)



yellow liquid 745 mg 85% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.81 (s, 1H), 7.49 (m, 2H), 1.39 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 148.3, 148.1, 140.1, 123.5, 117.1, 110.2, 35.1, 31.9

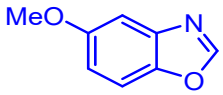
3.28. 5-Phenylbenzo[d]oxazole (9)



beige solid 811 mg 83% yield Mp: 63-65 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.99 (s, 1H), 7.64-7.61 (m, 4H), 7.49-7.45 (m, 2H), 7.40-7.36 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 149.7, 141.0, 140.8, 138.8, 129.0, 127.6, 127.5, 125.4, 119.2, 111.1.

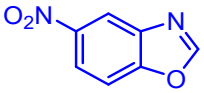
3.29. 5-Methoxybenzo[d]oxazole (10)



beige solid 642 mg 86% yield **Mp:** 50-52 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 2,6 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 1H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 153.3, 144.6, 140.9, 114.6, 111.2, 103.1, 56.0.

3.30. 5-Nitro benzo[d]oxazole (11)

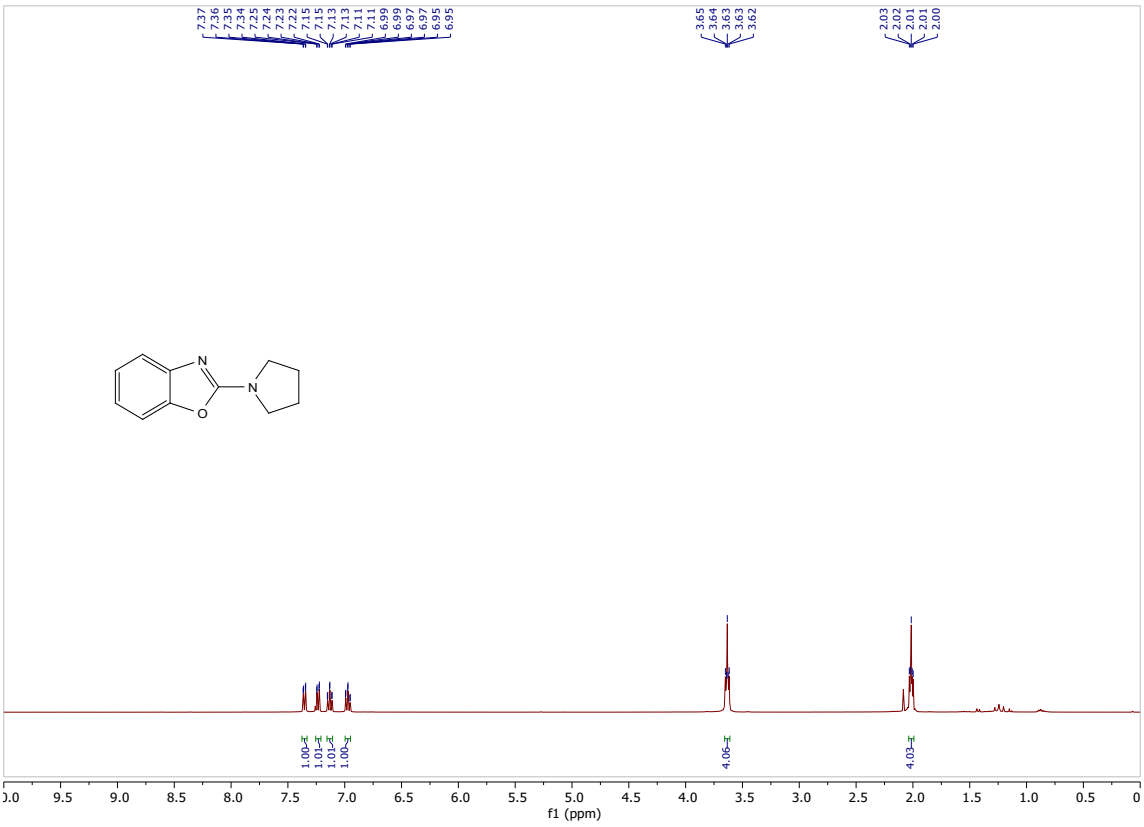


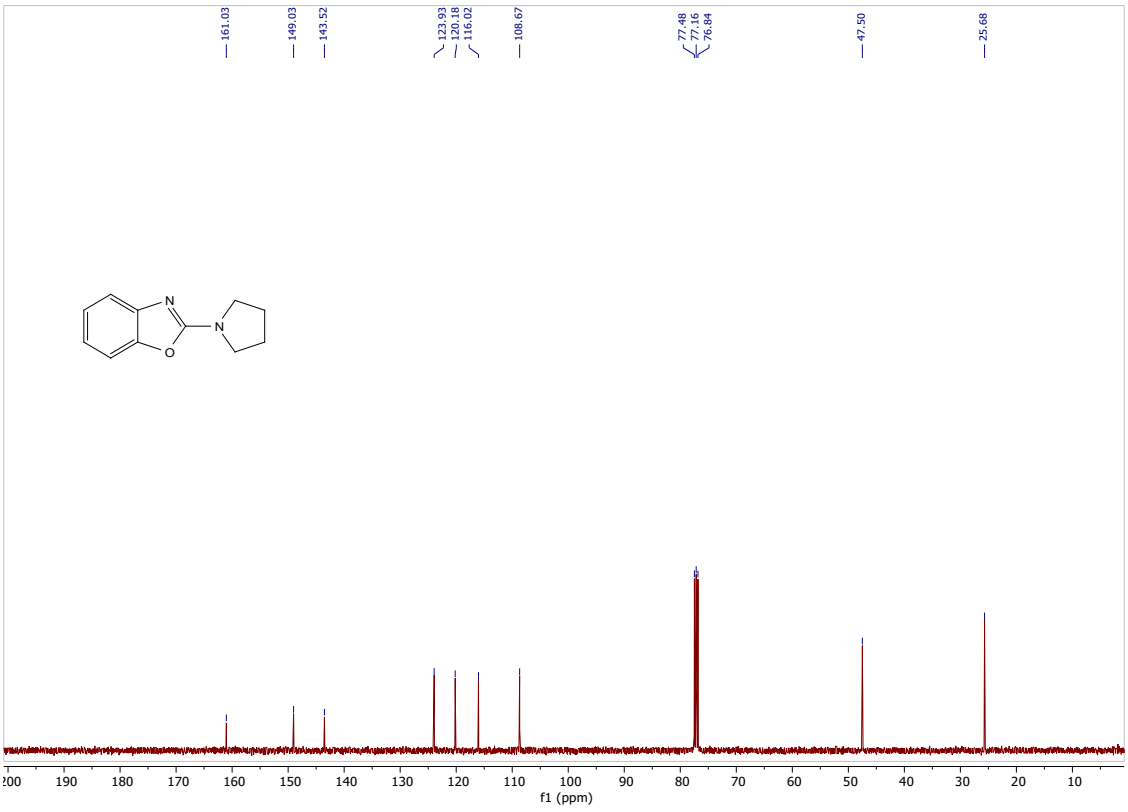
Orange solid 590 mg 72% yield Mp: 112–114 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.39 (d, *J* =9 Hz, 1H), 8.27 (s, 1H), 7.71(d, *J* =9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 153.6, 145.7, 140.7, 121.9, 117.4, 111.5.

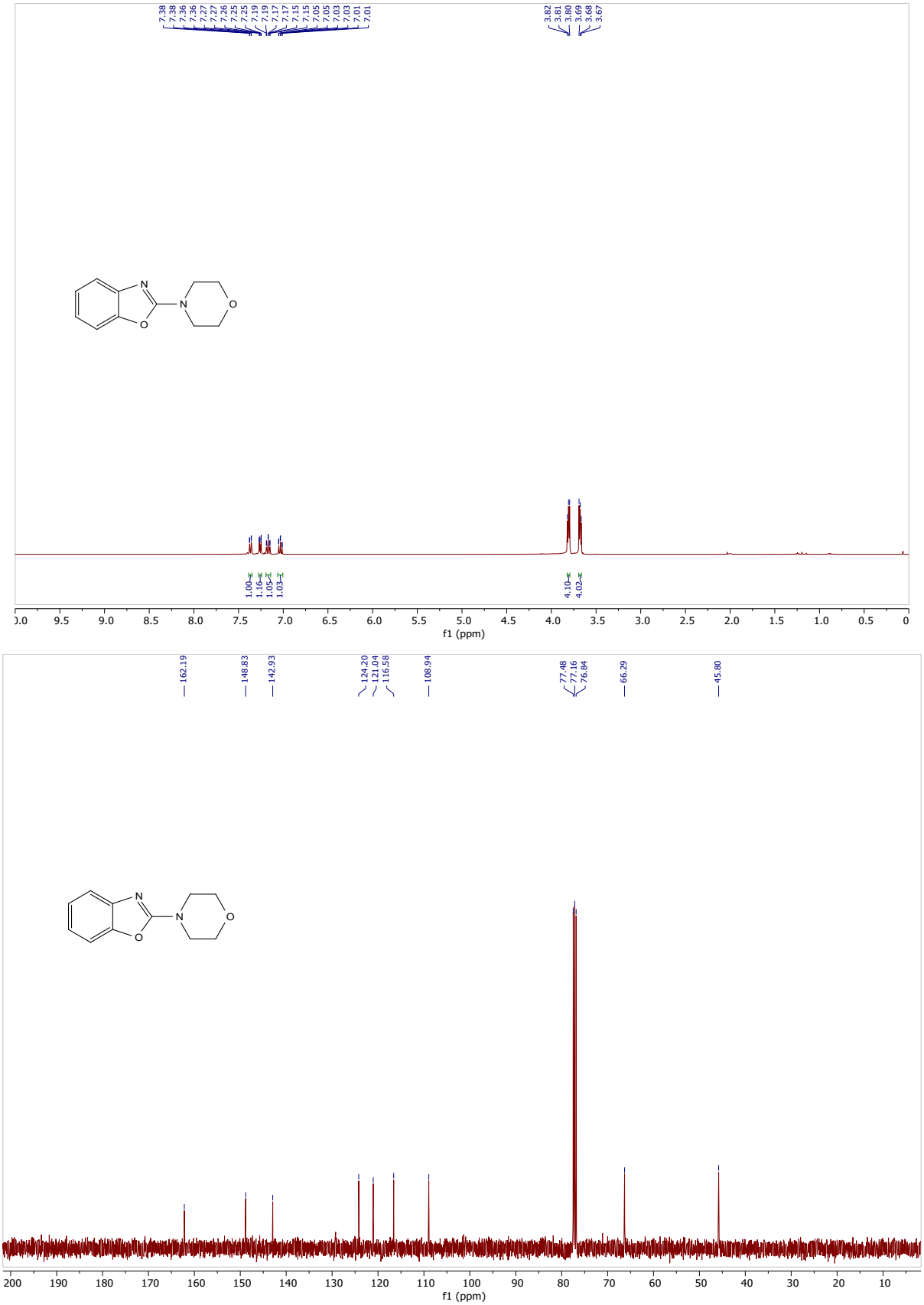
4. ^{1}H-NMR and ^{13}C-NMR spectra

4.1. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3a)

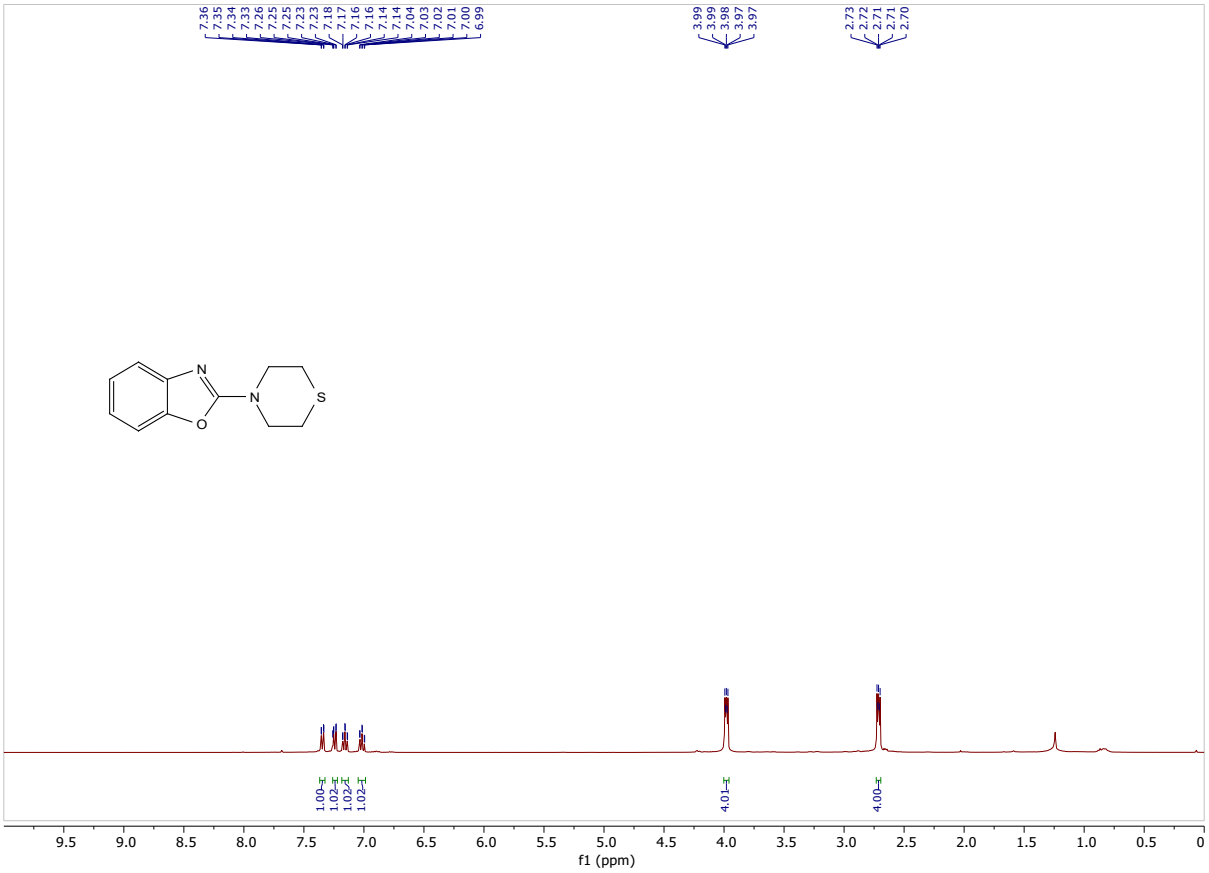


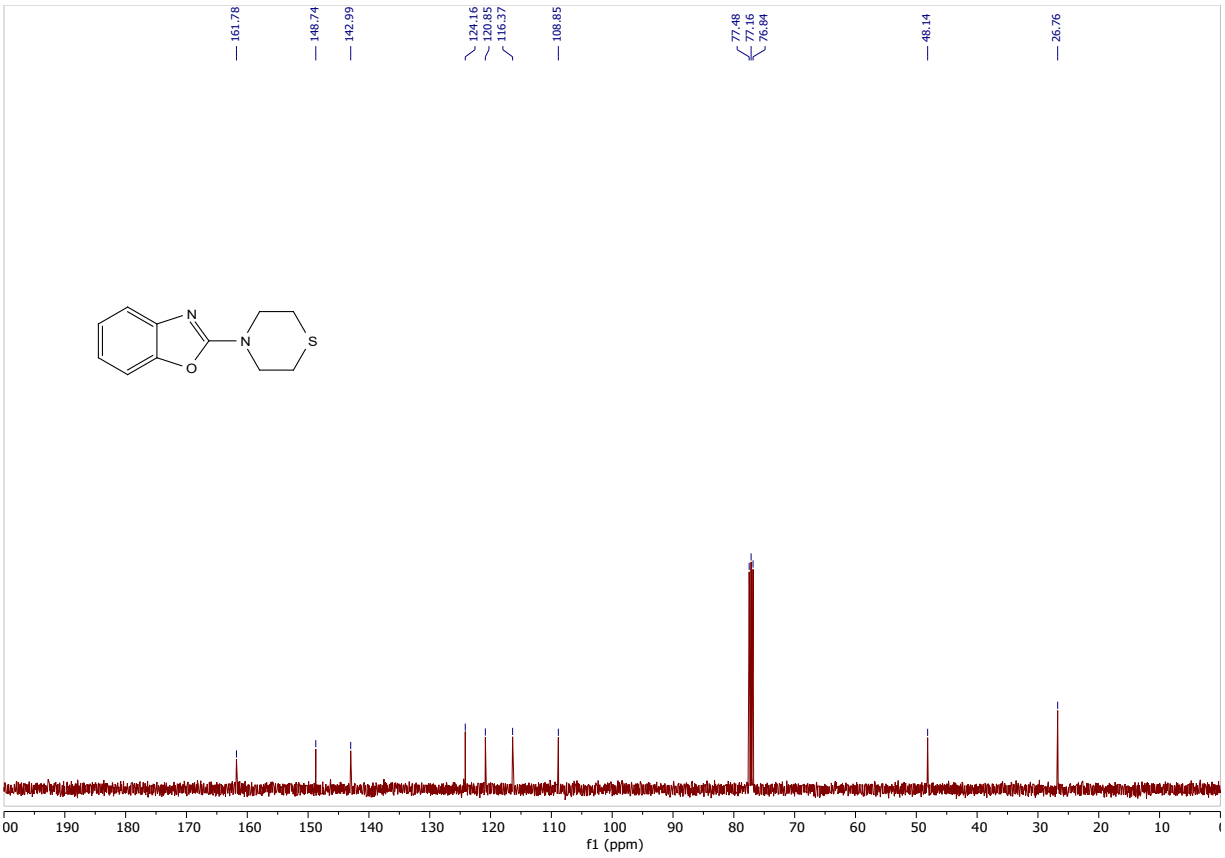


4.2. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3b)

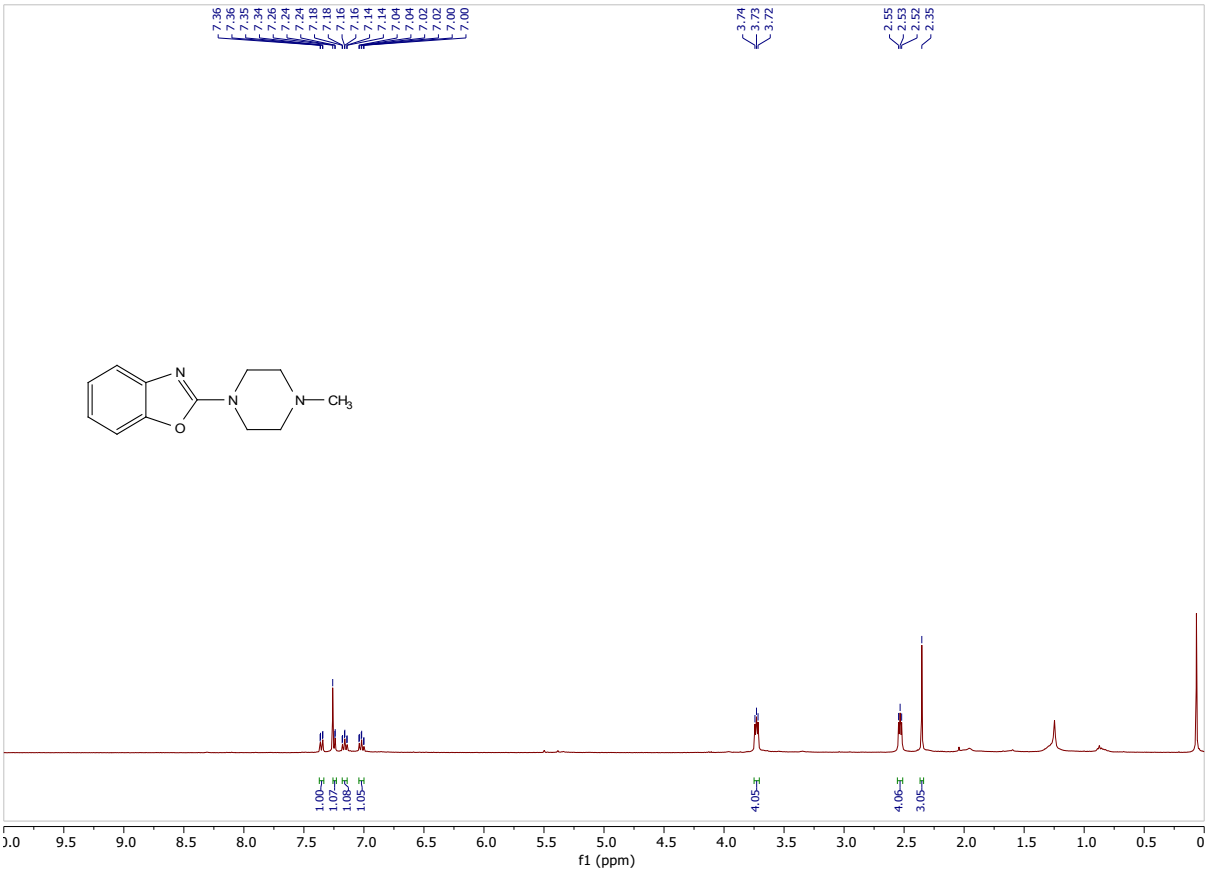


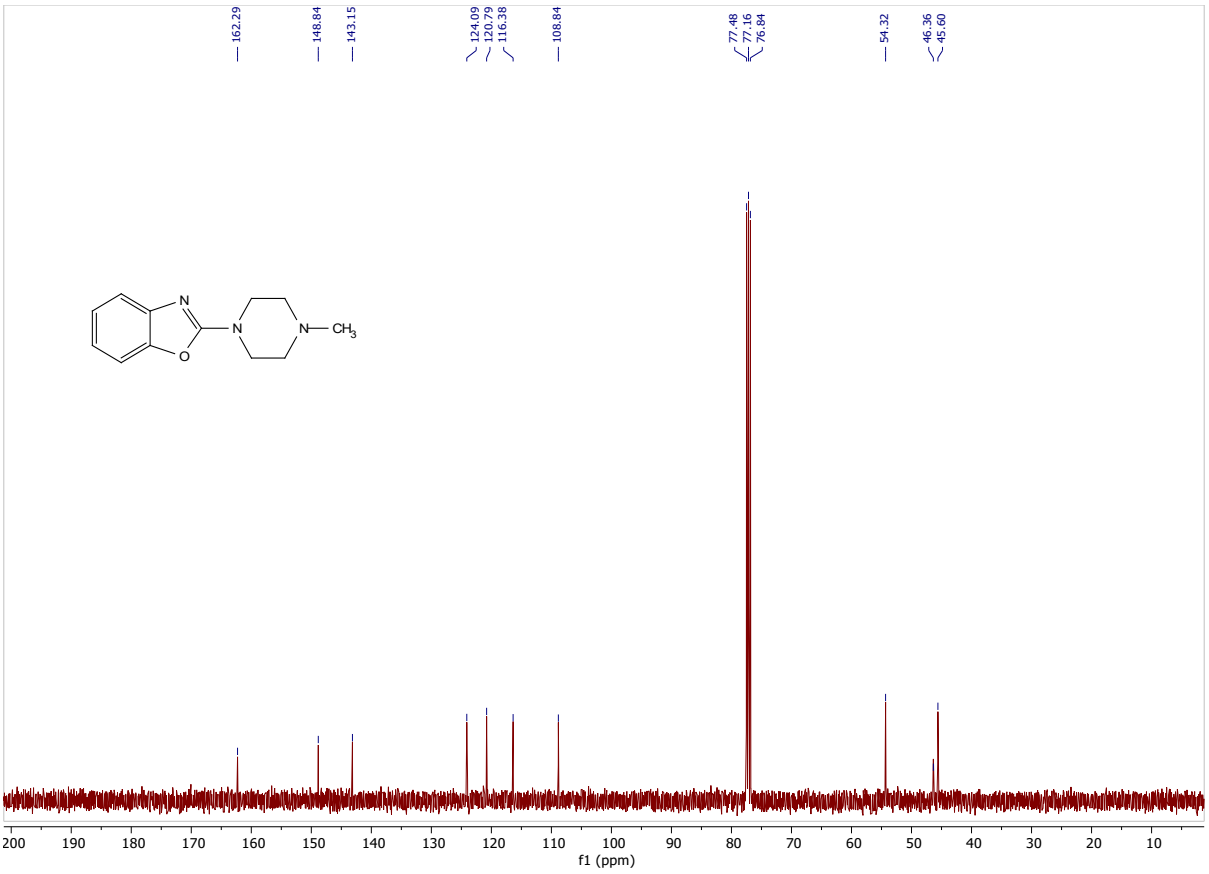
4.3. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3c)



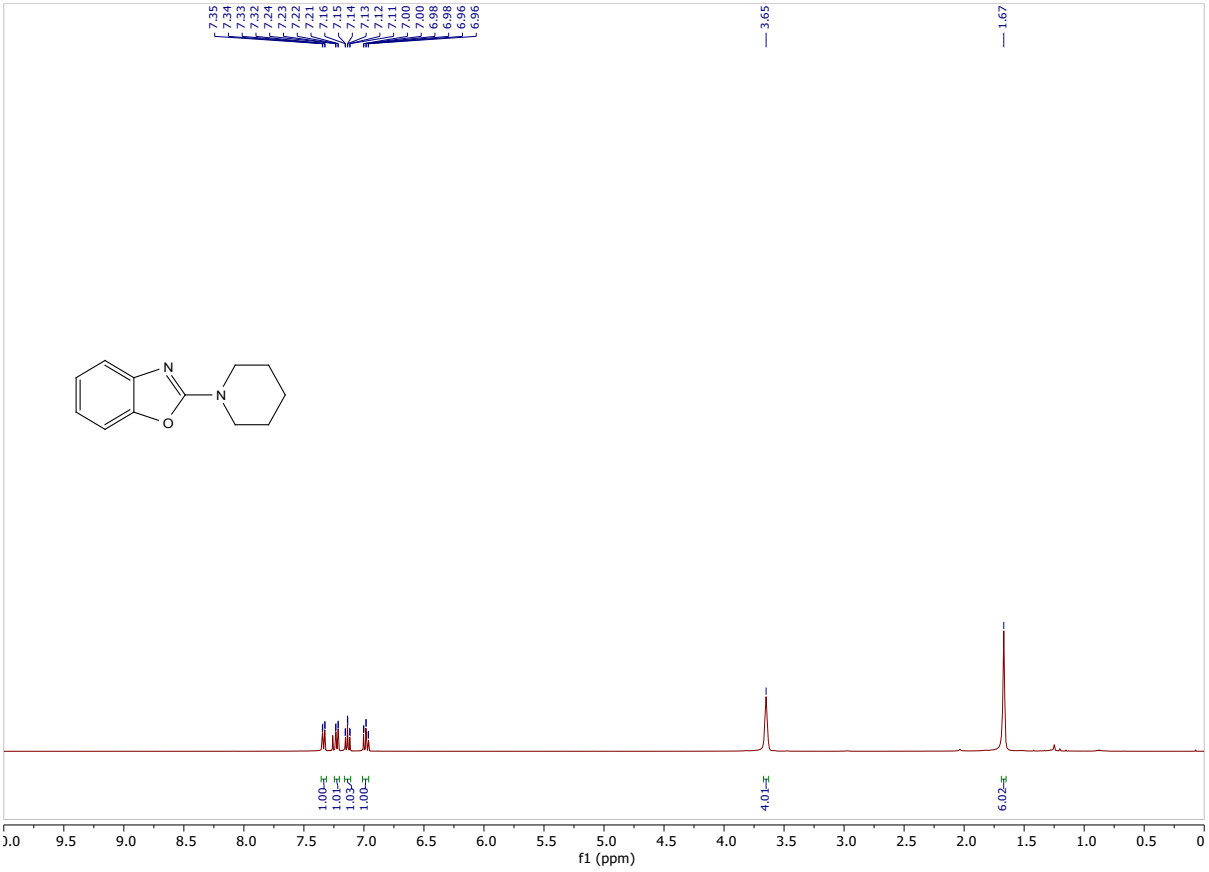


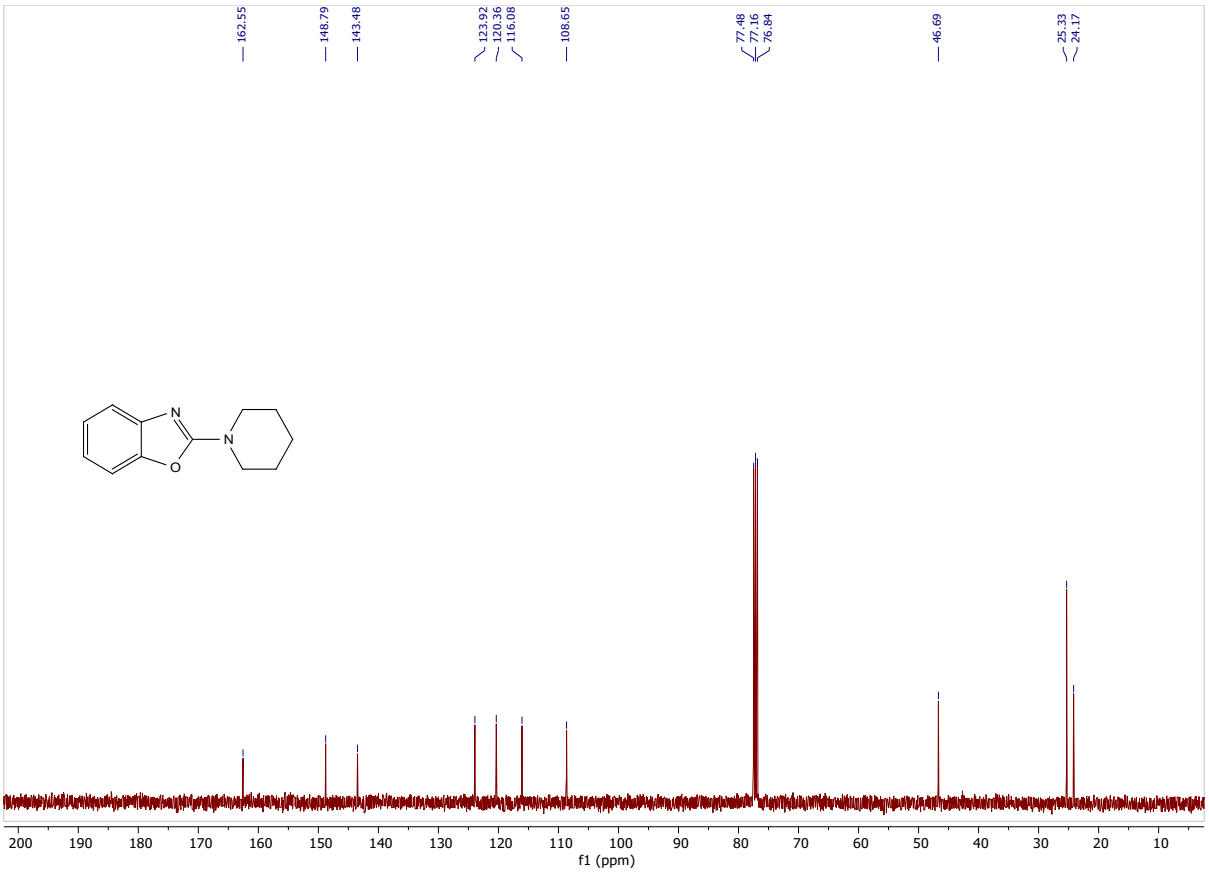
4.4. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3d)



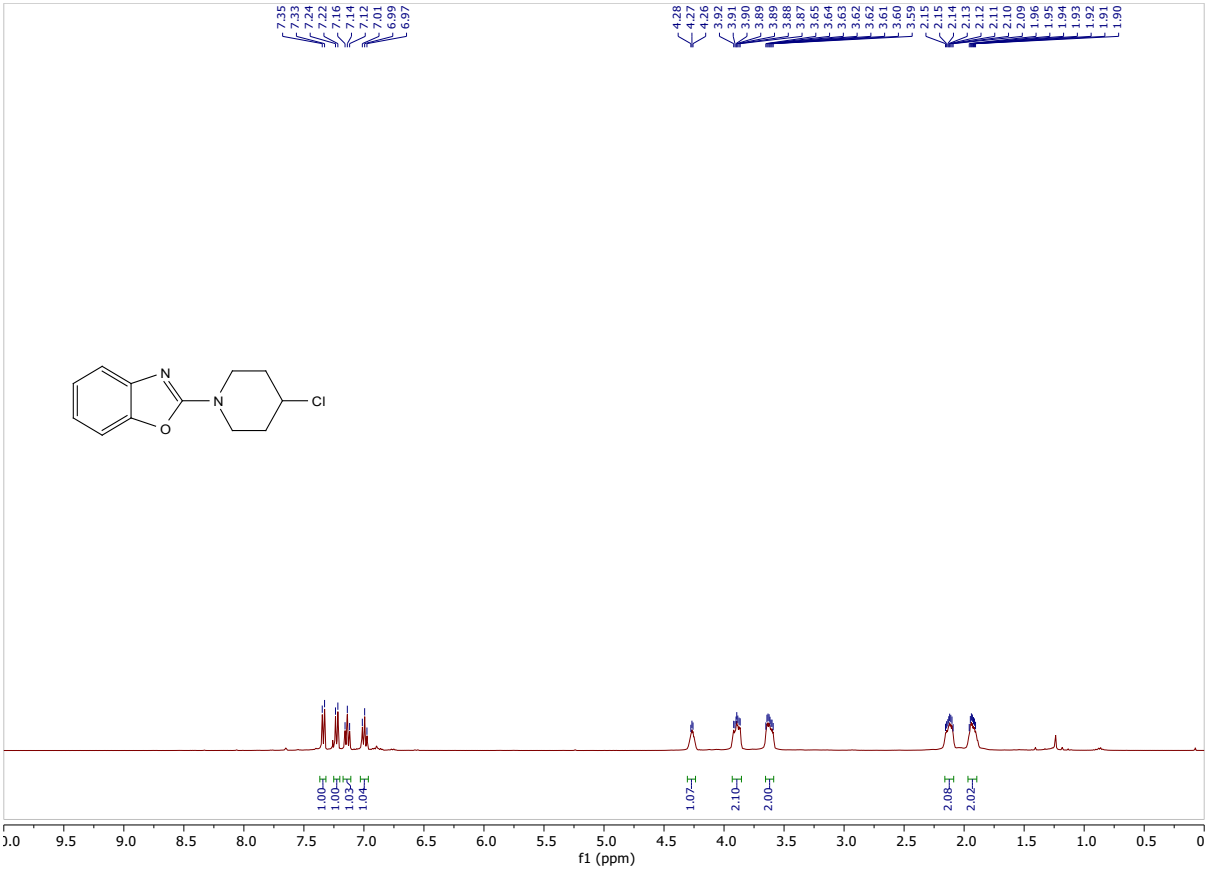


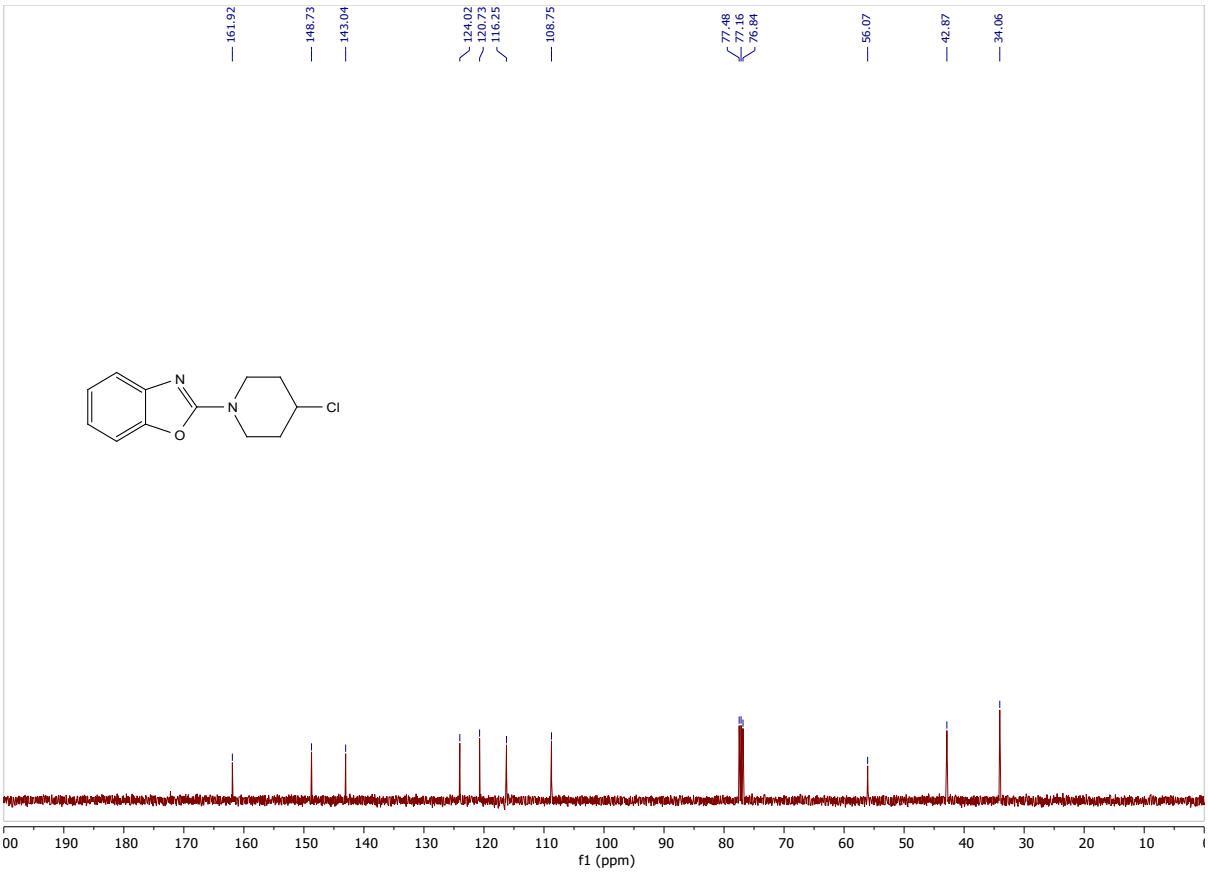
4.5. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3e)



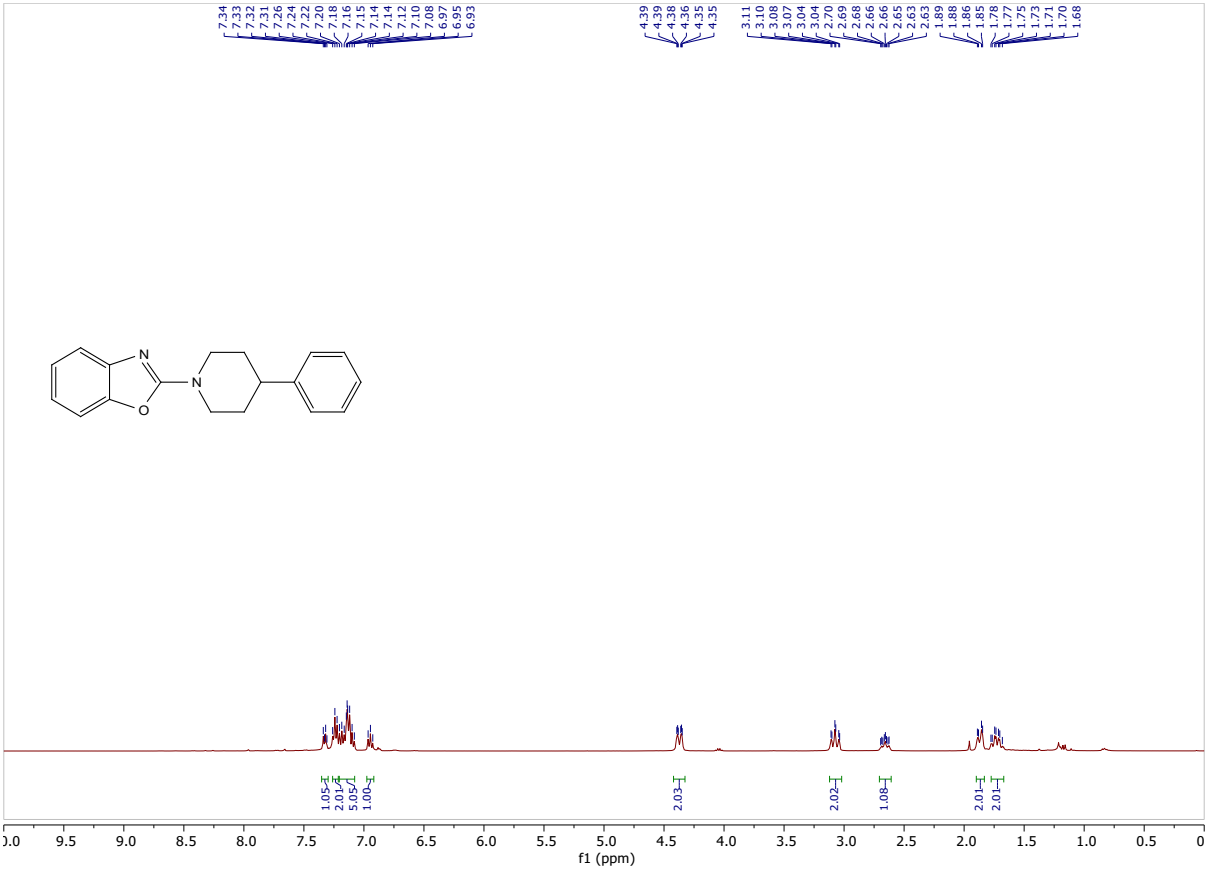


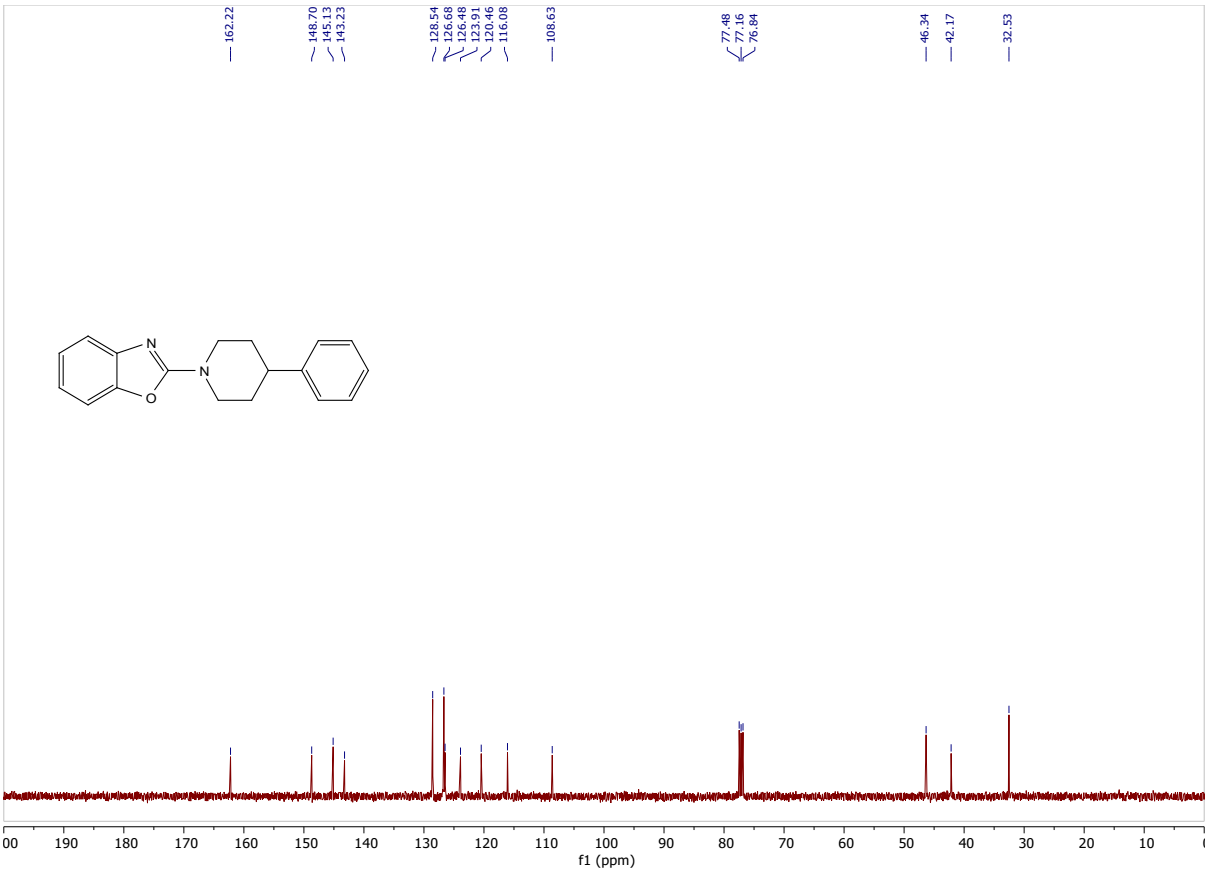
4.6. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3f)



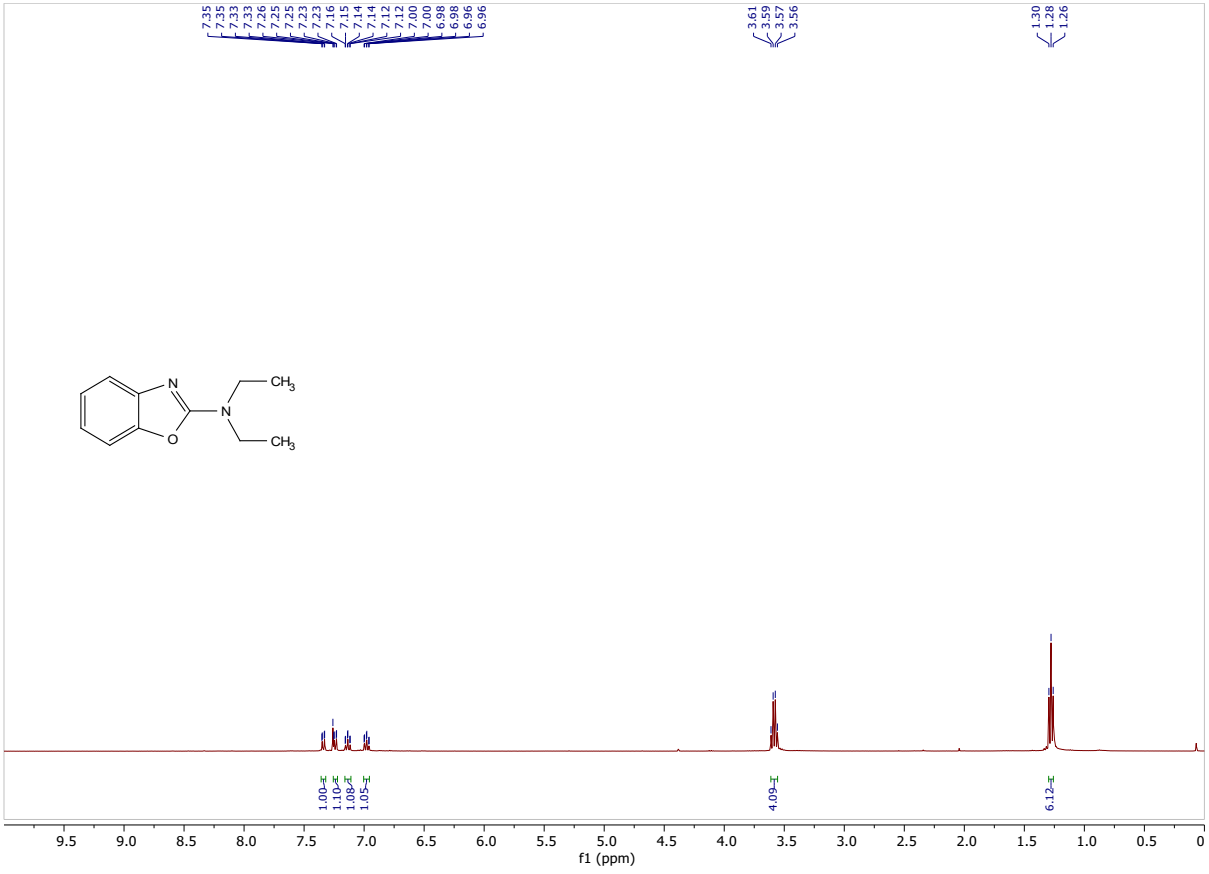


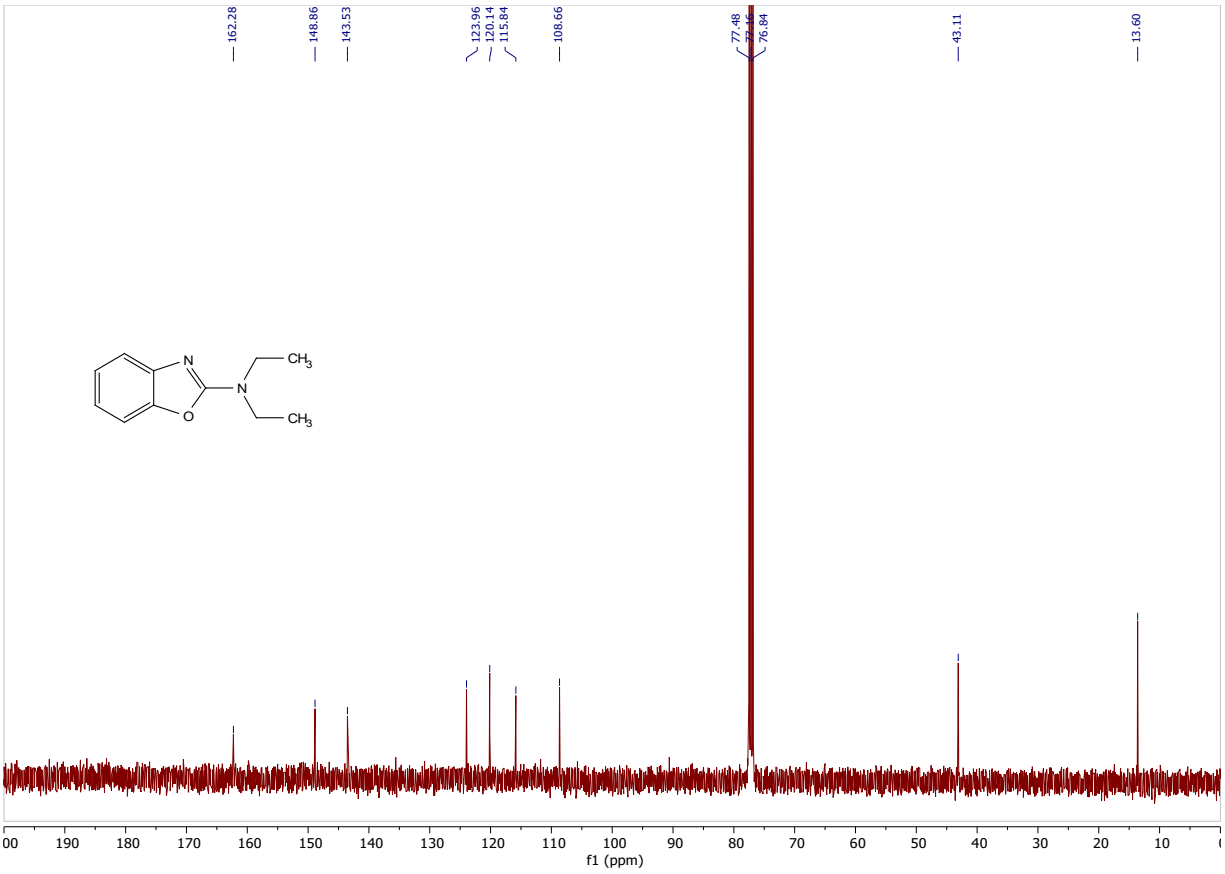
4.7. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3g)



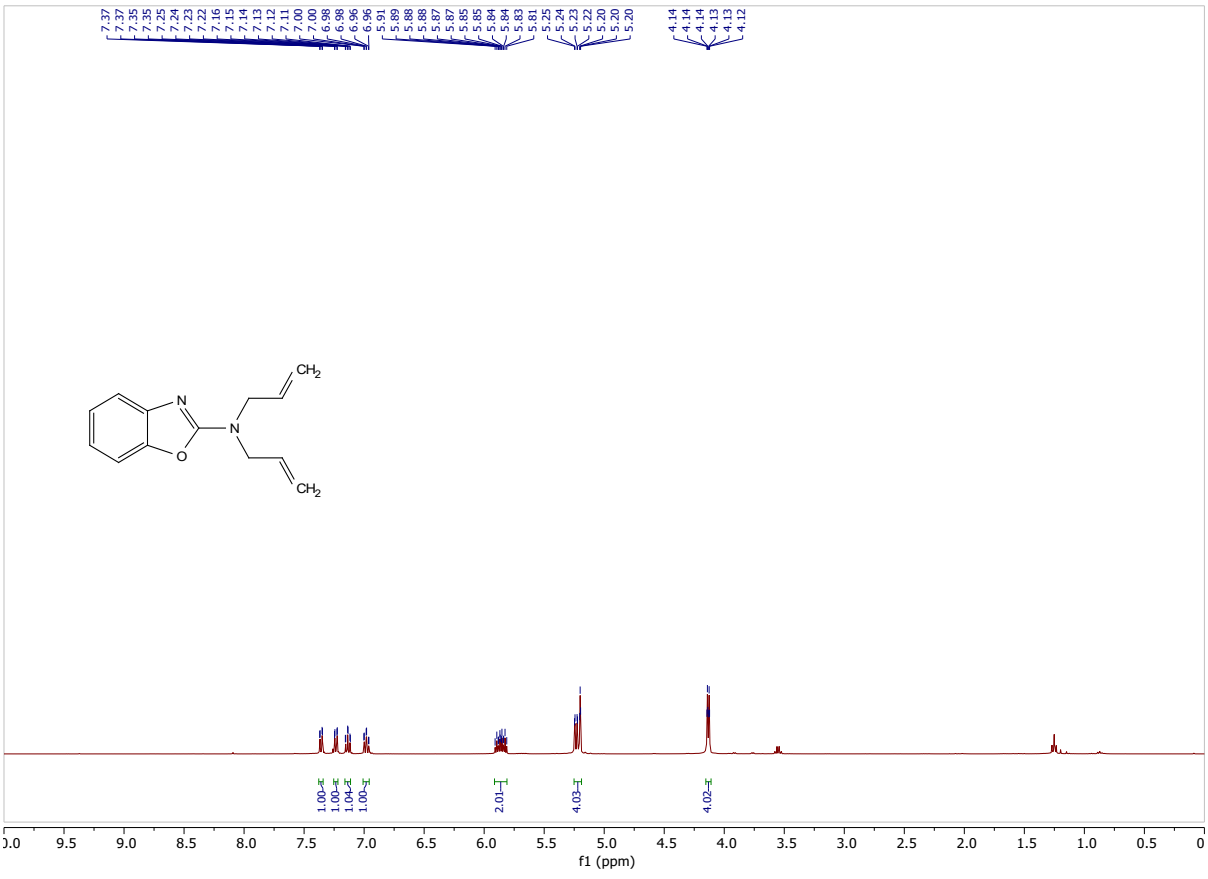


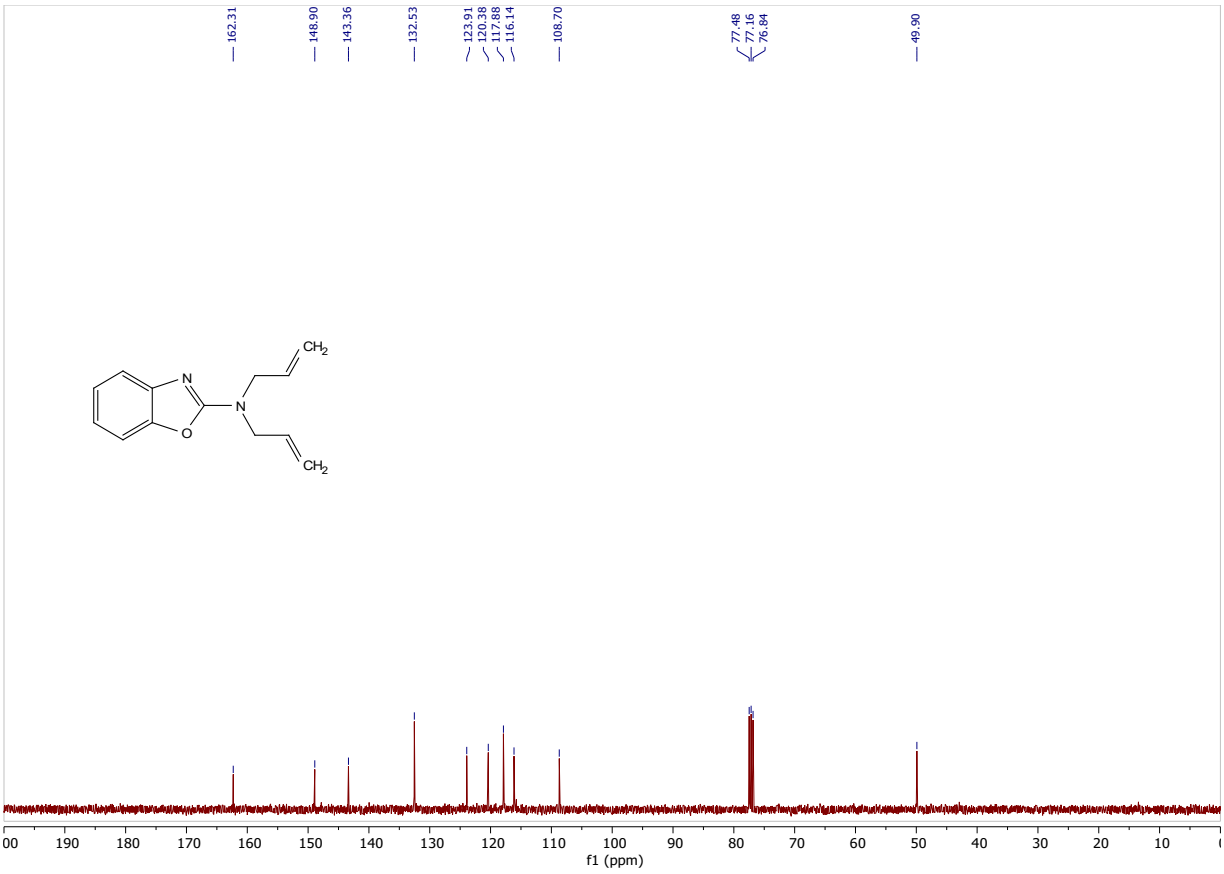
4.8. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3h)



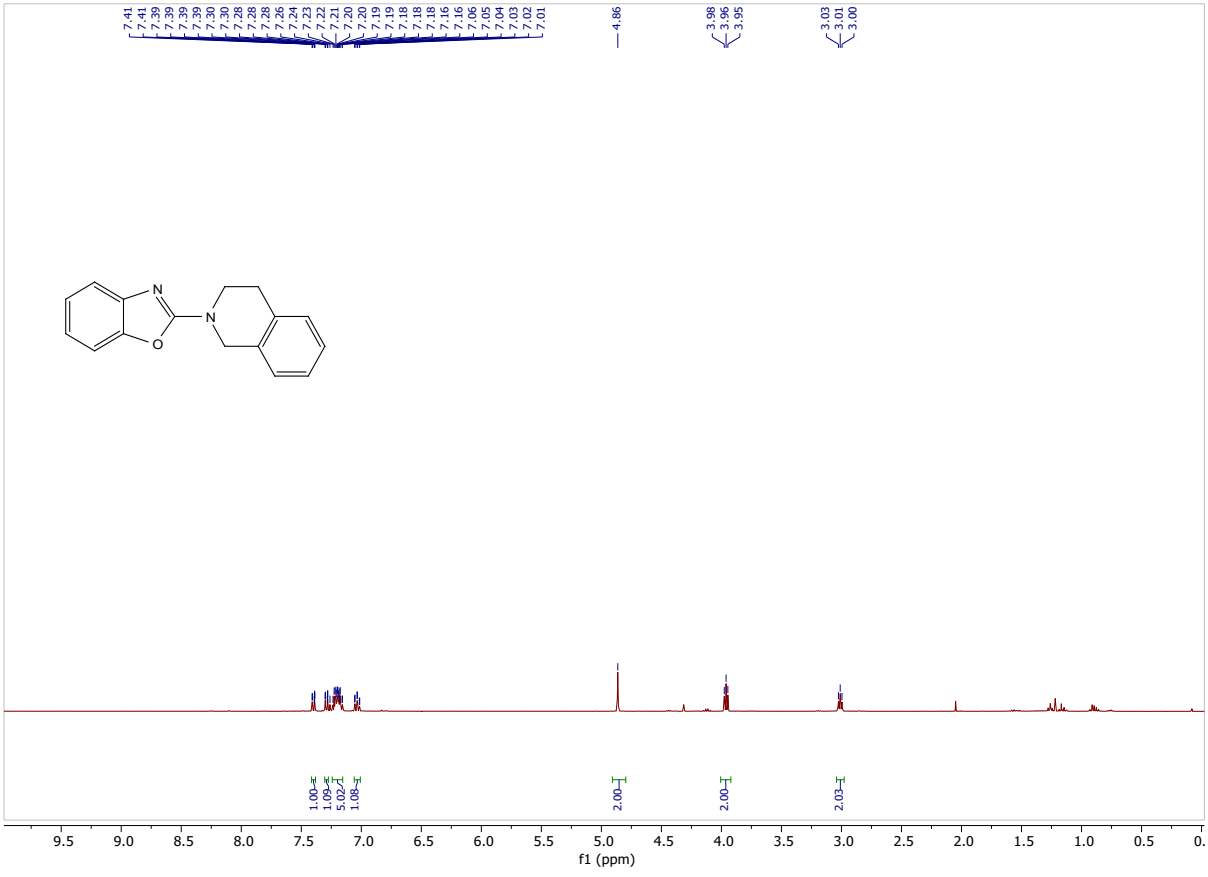


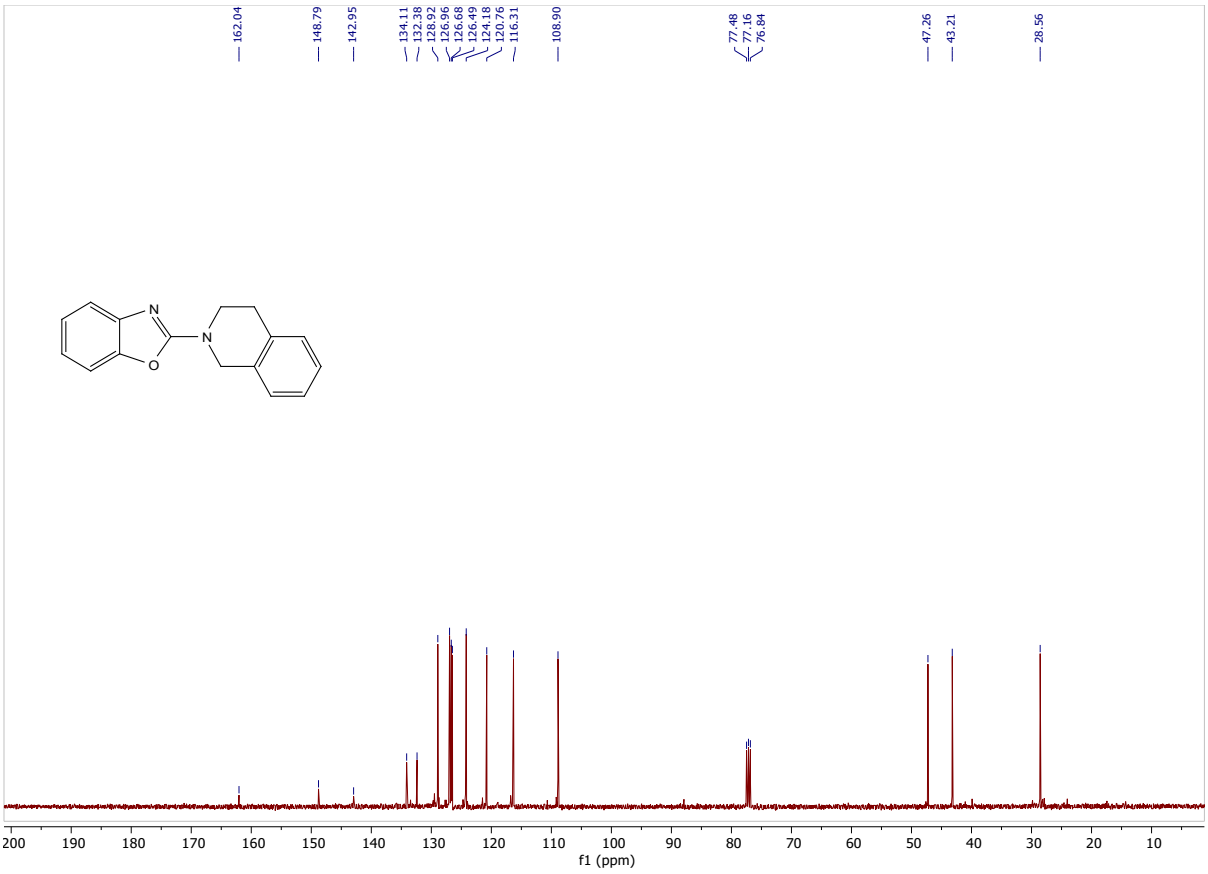
4.9. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3i)



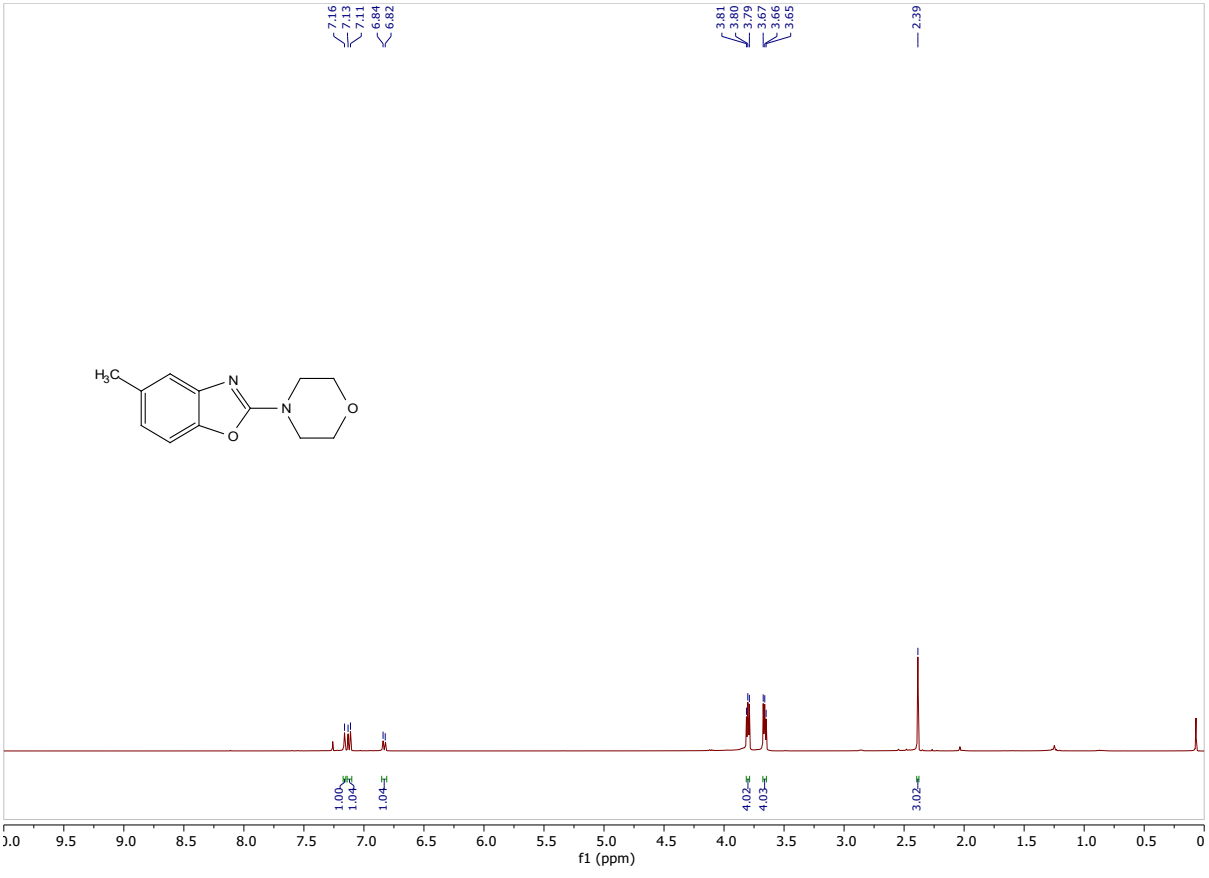


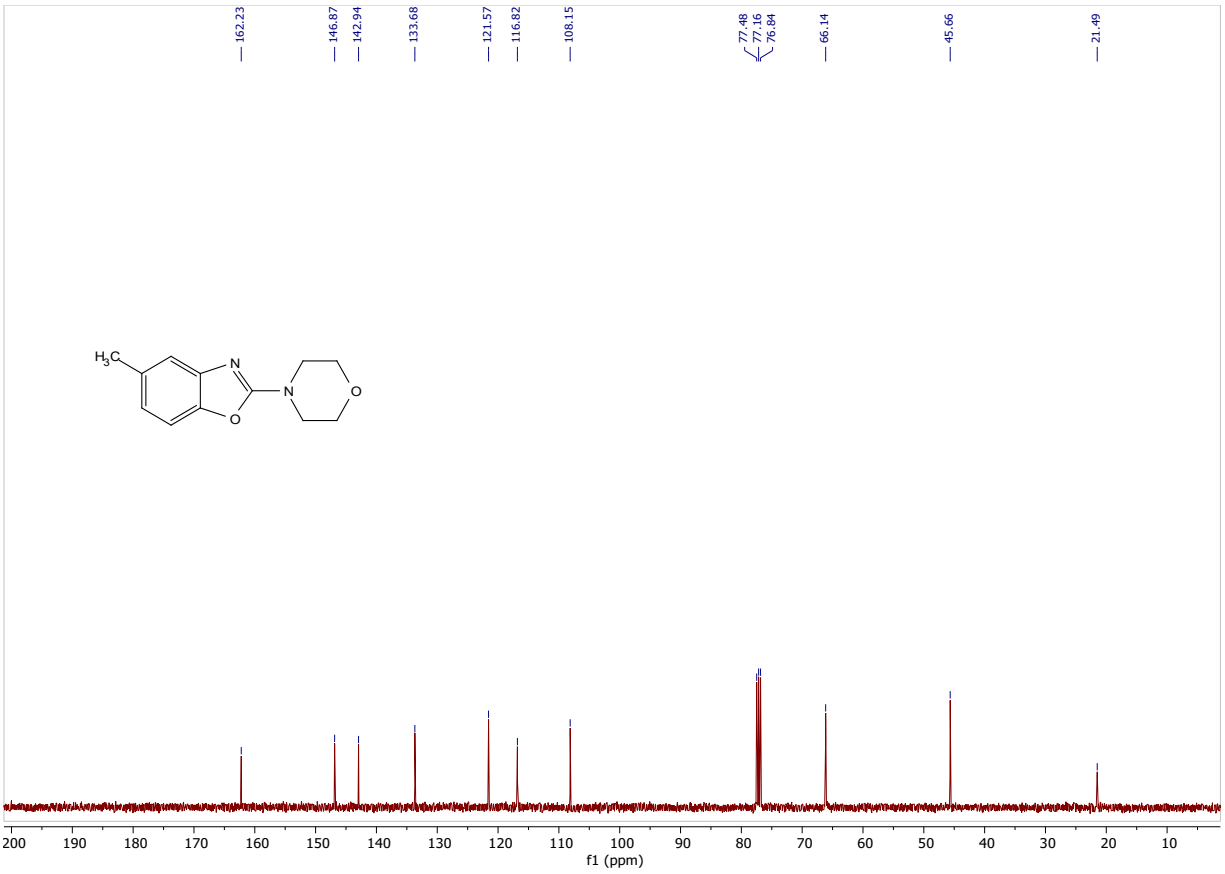
4.10. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (3j)



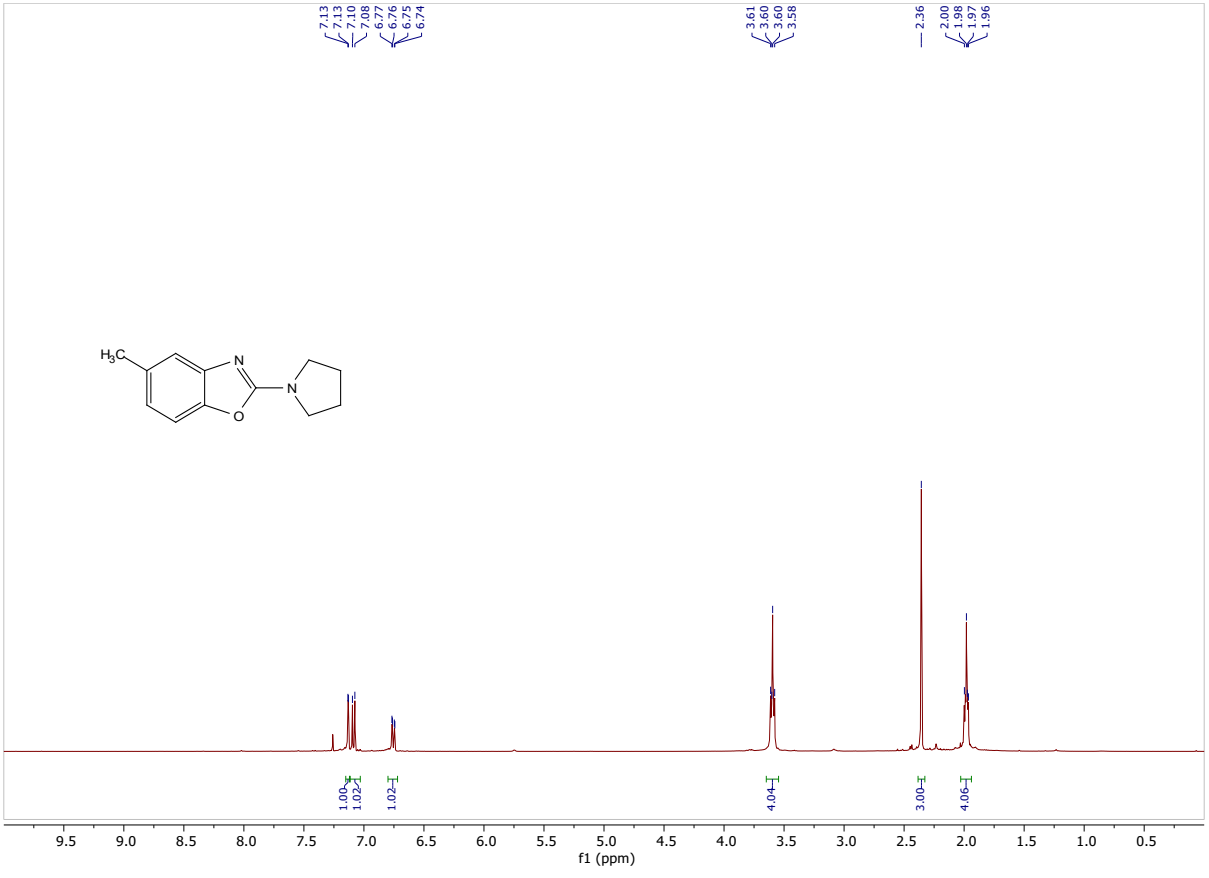


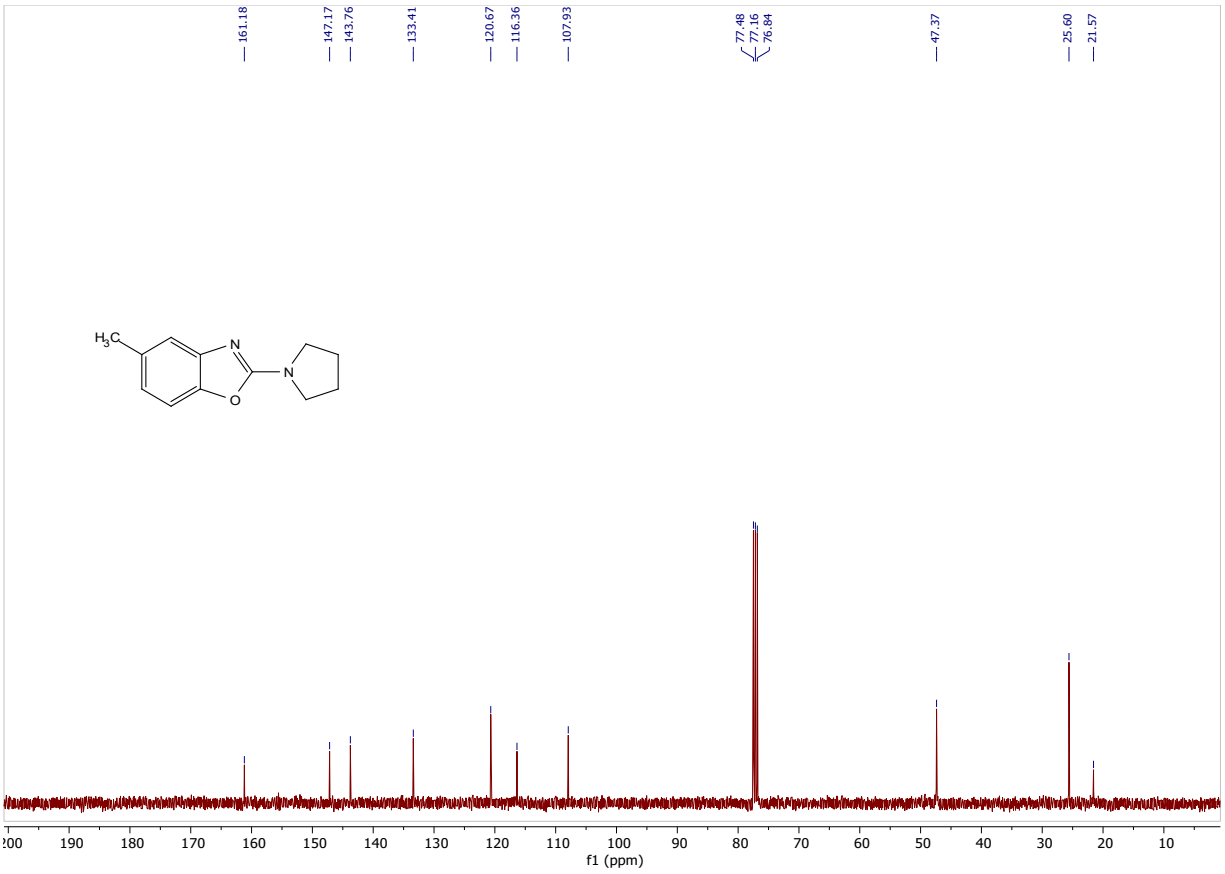
4.11. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6a)



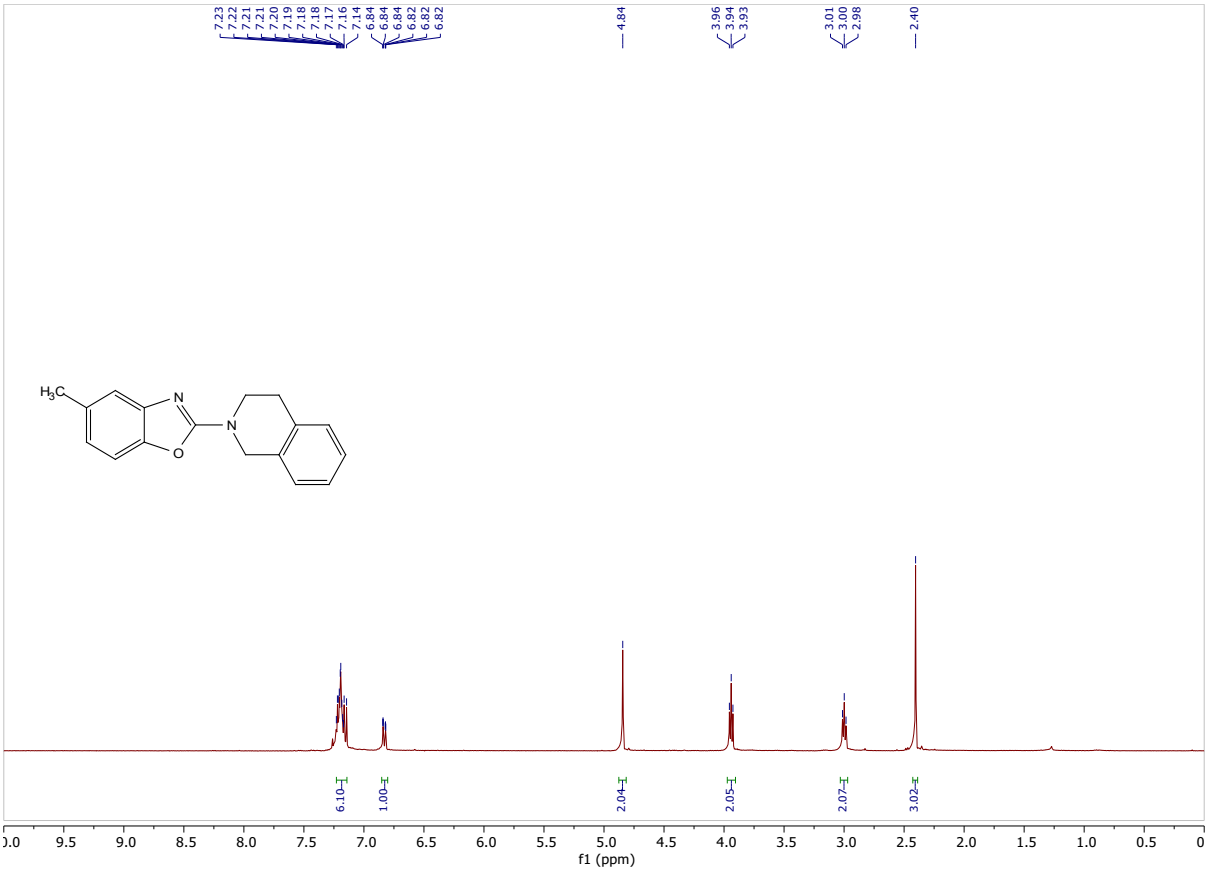


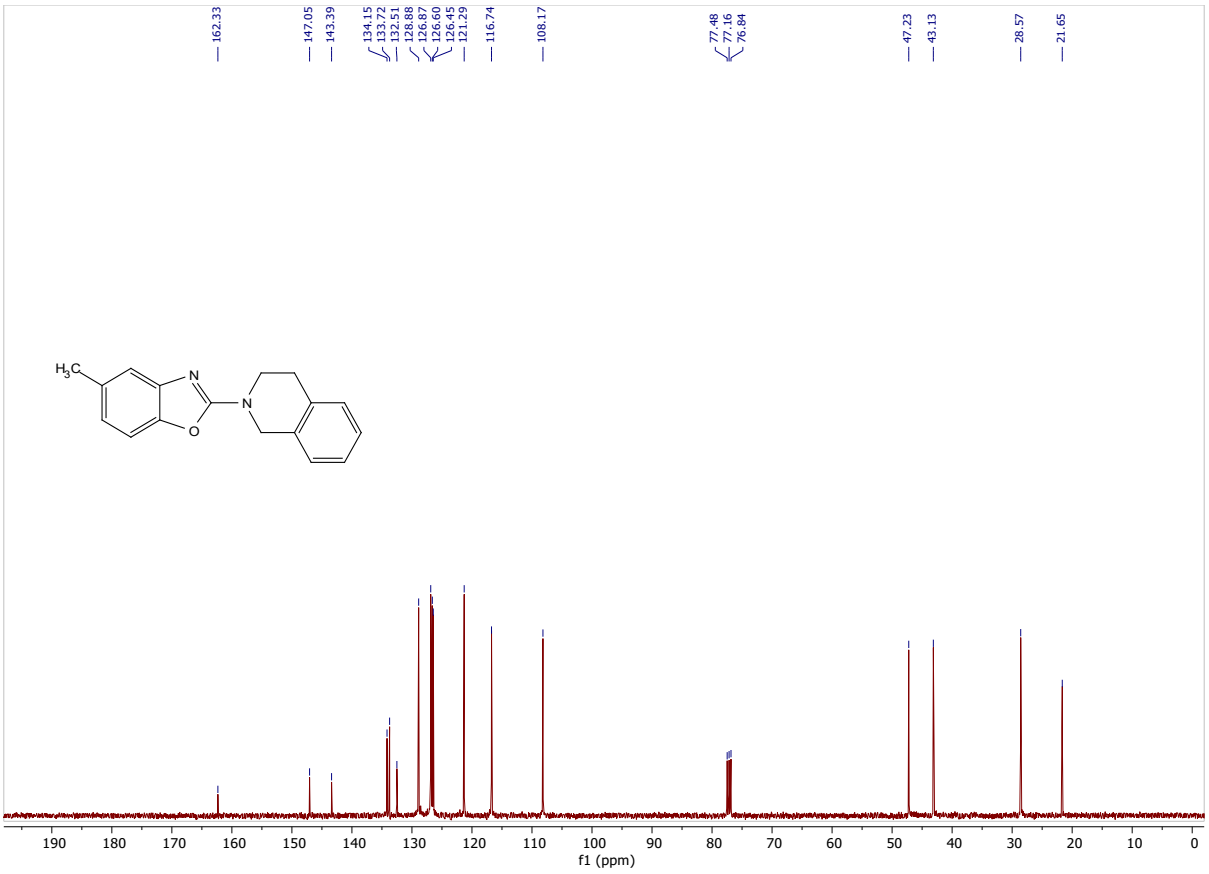
4.12. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (6b)



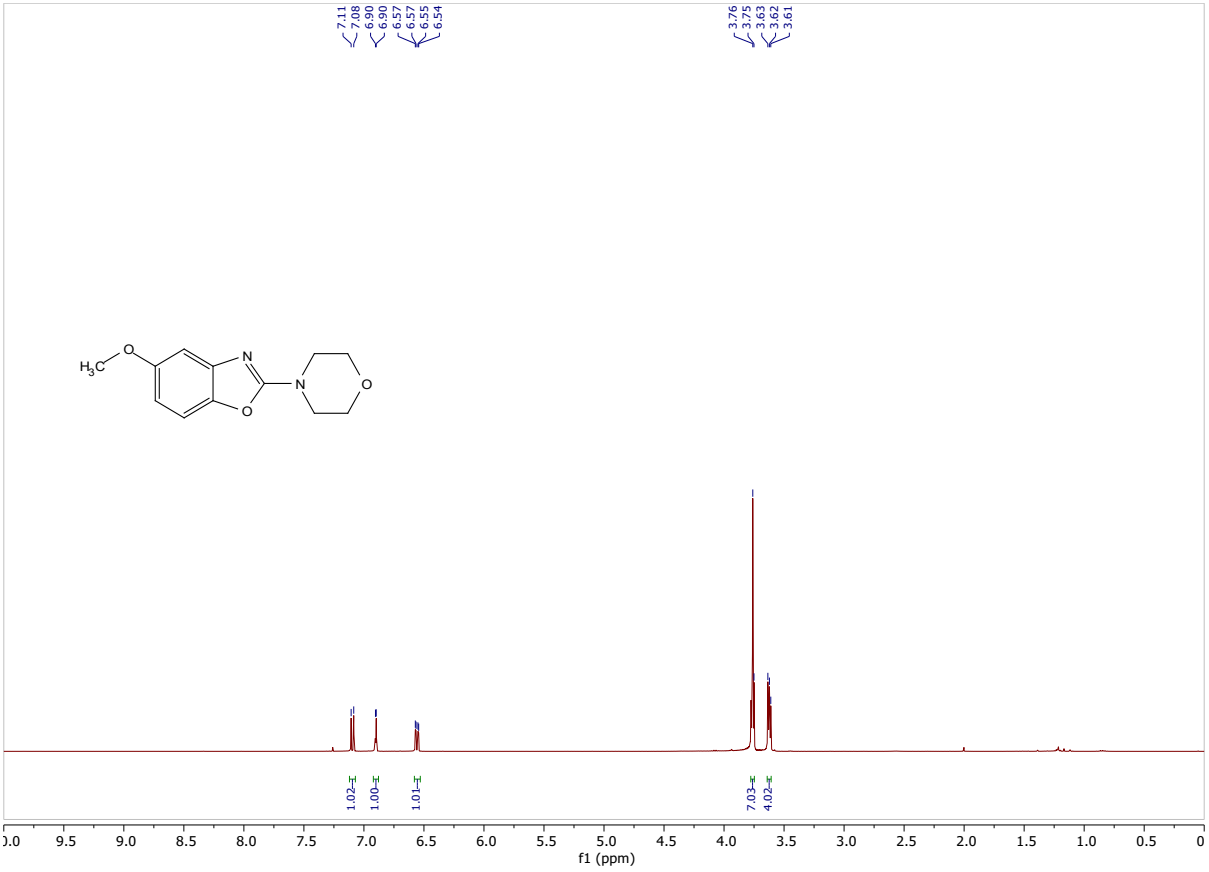


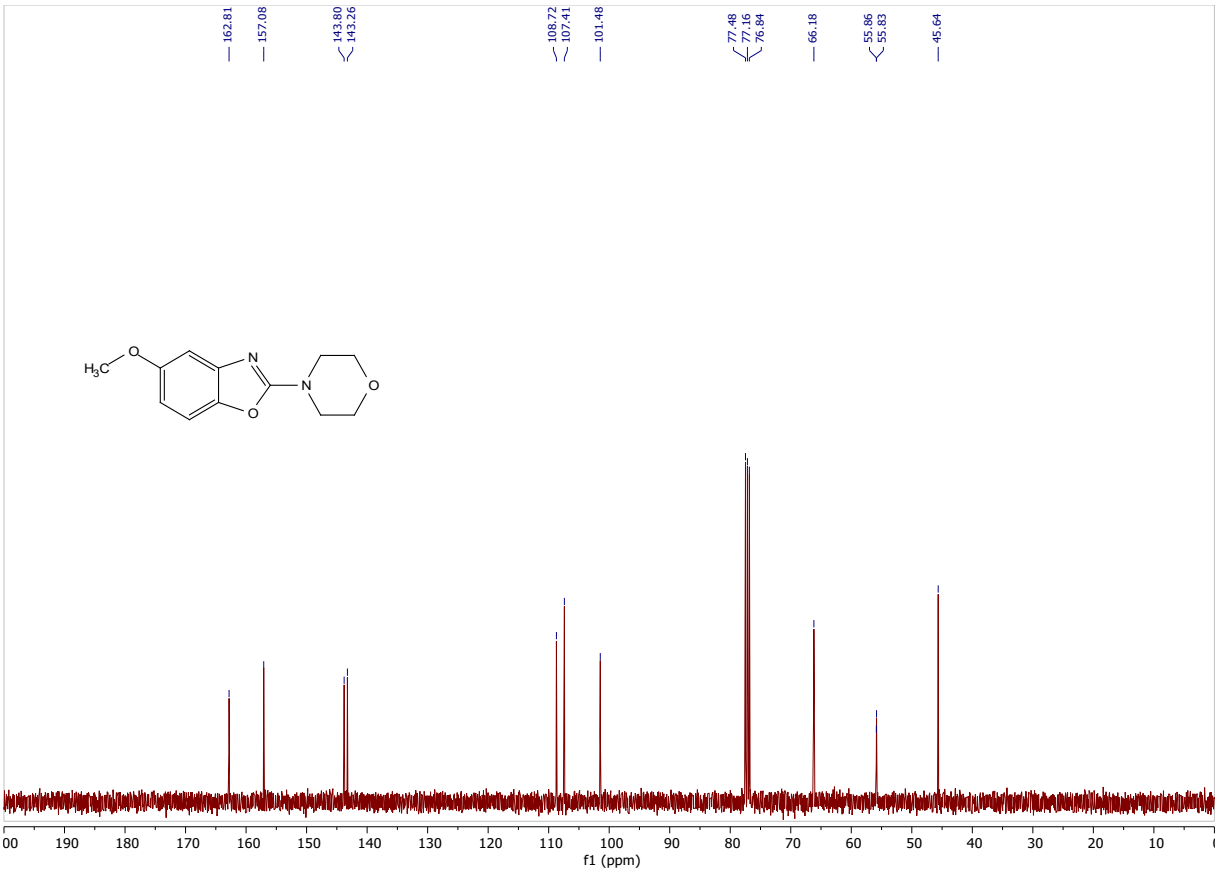
4.13. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6c)



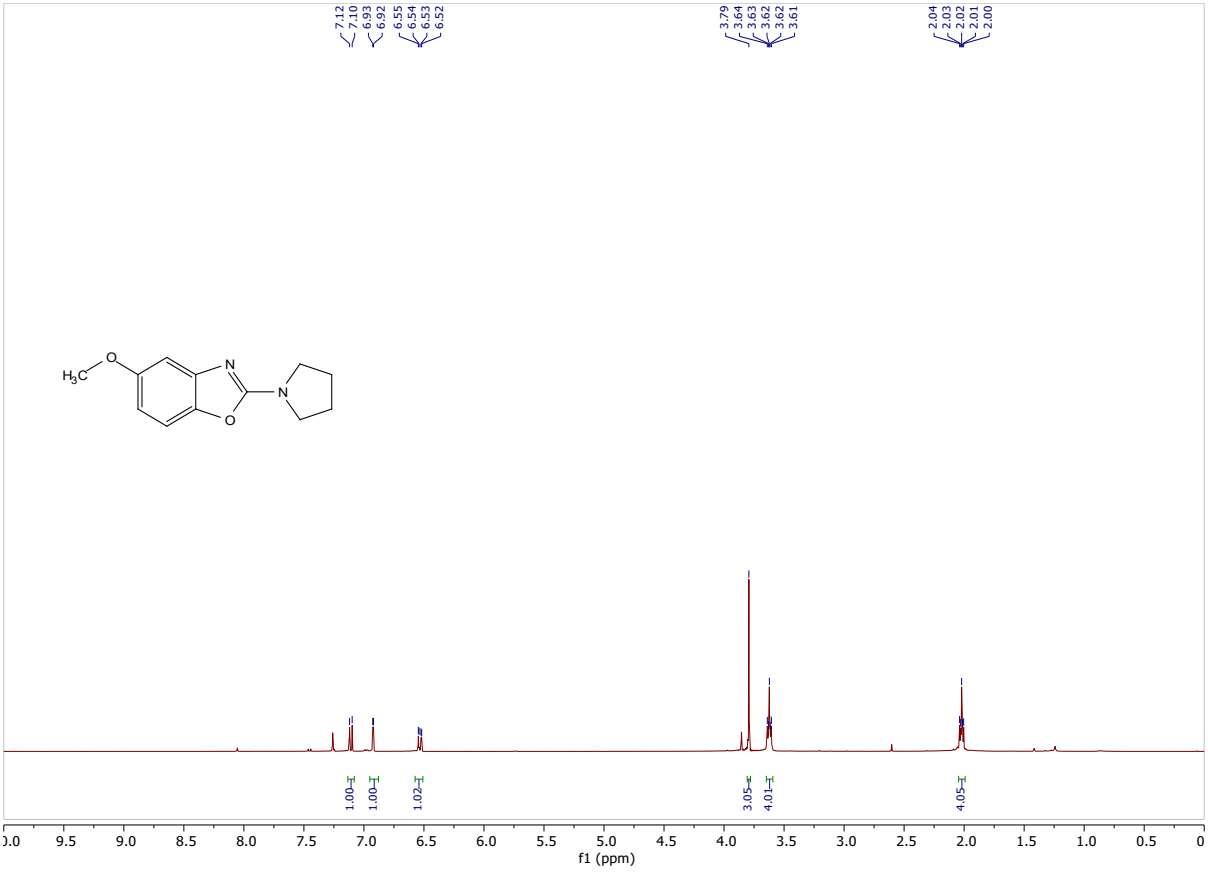


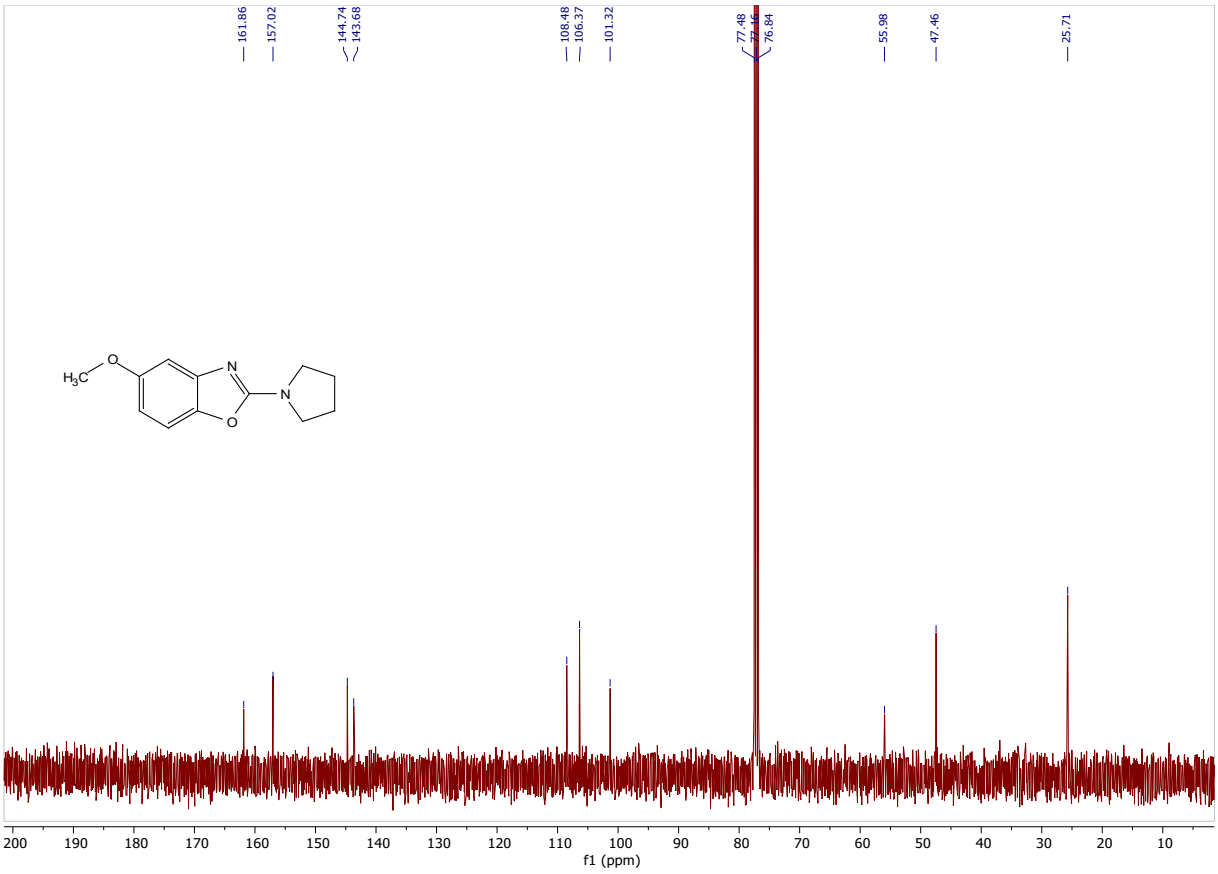
4.14. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (6d)



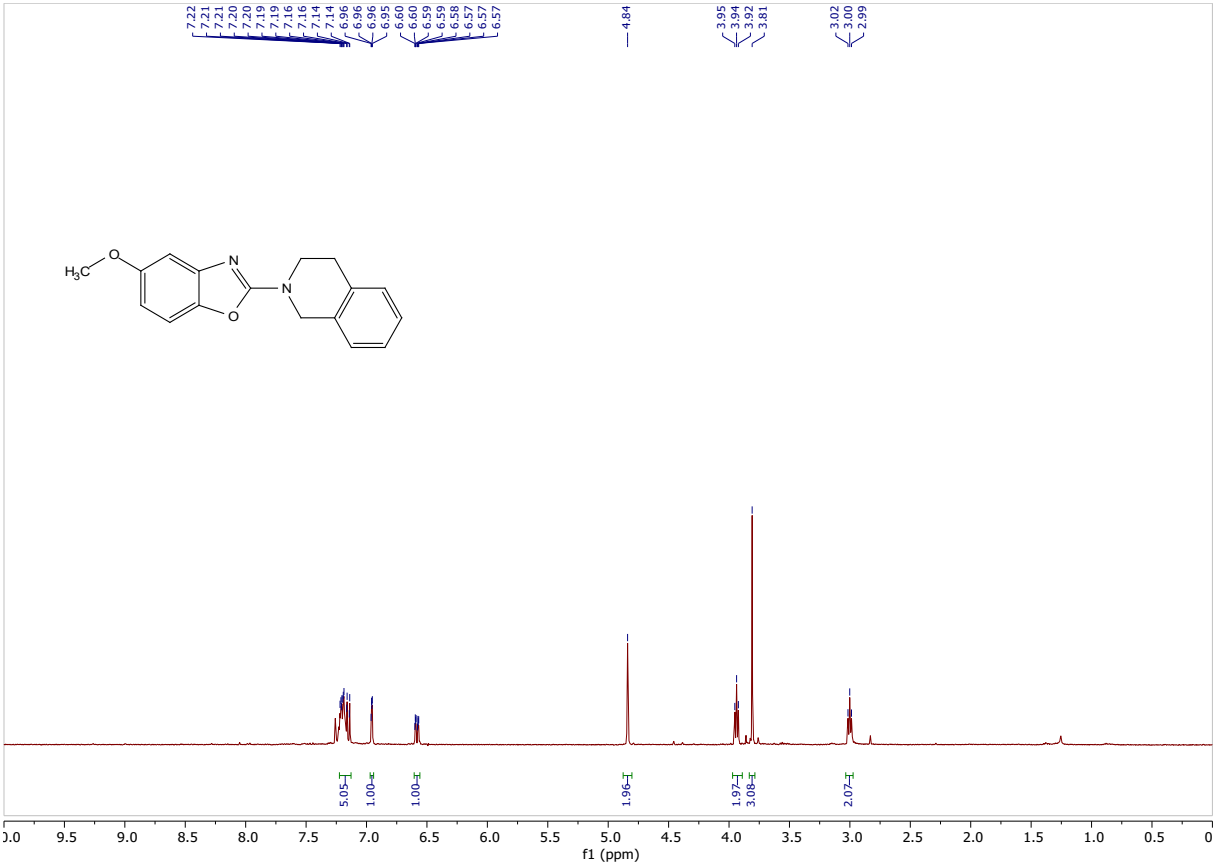


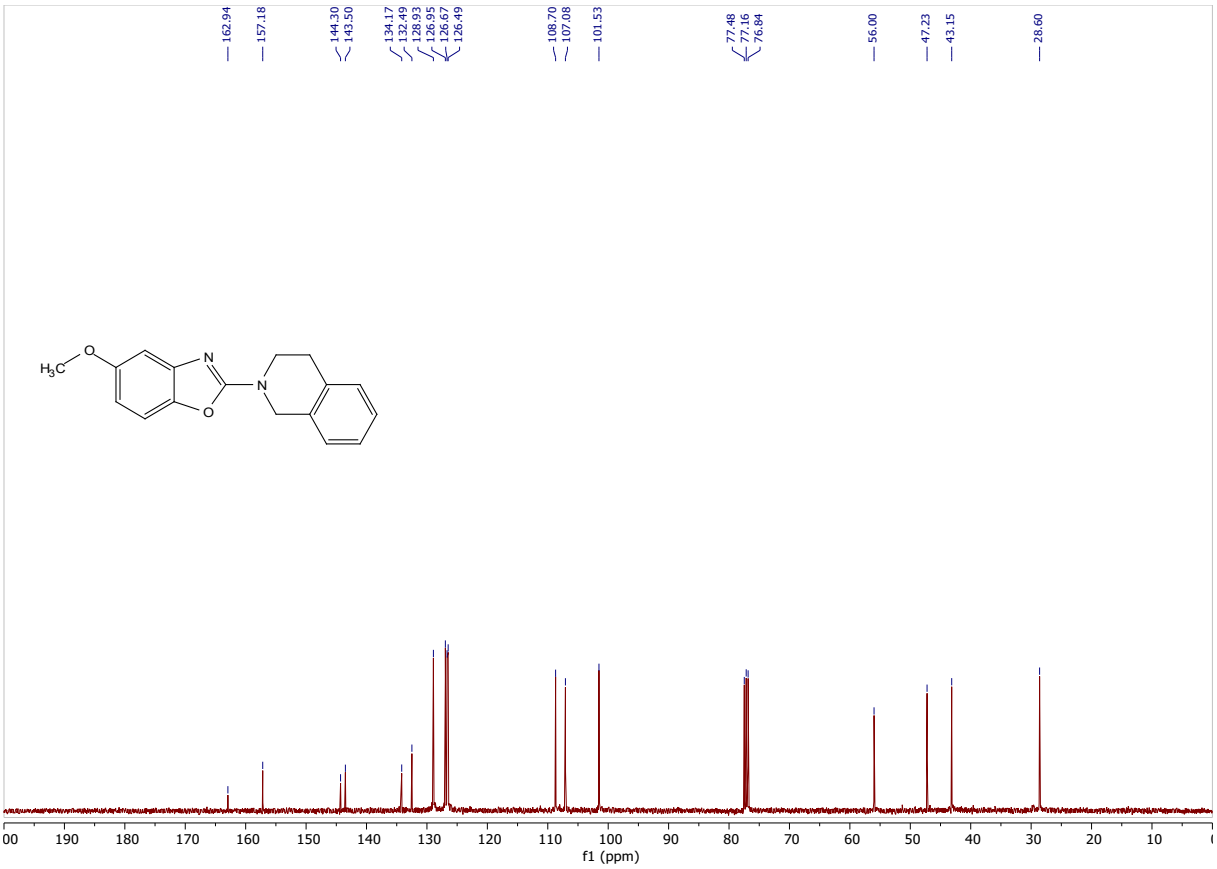
4.15. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6e)



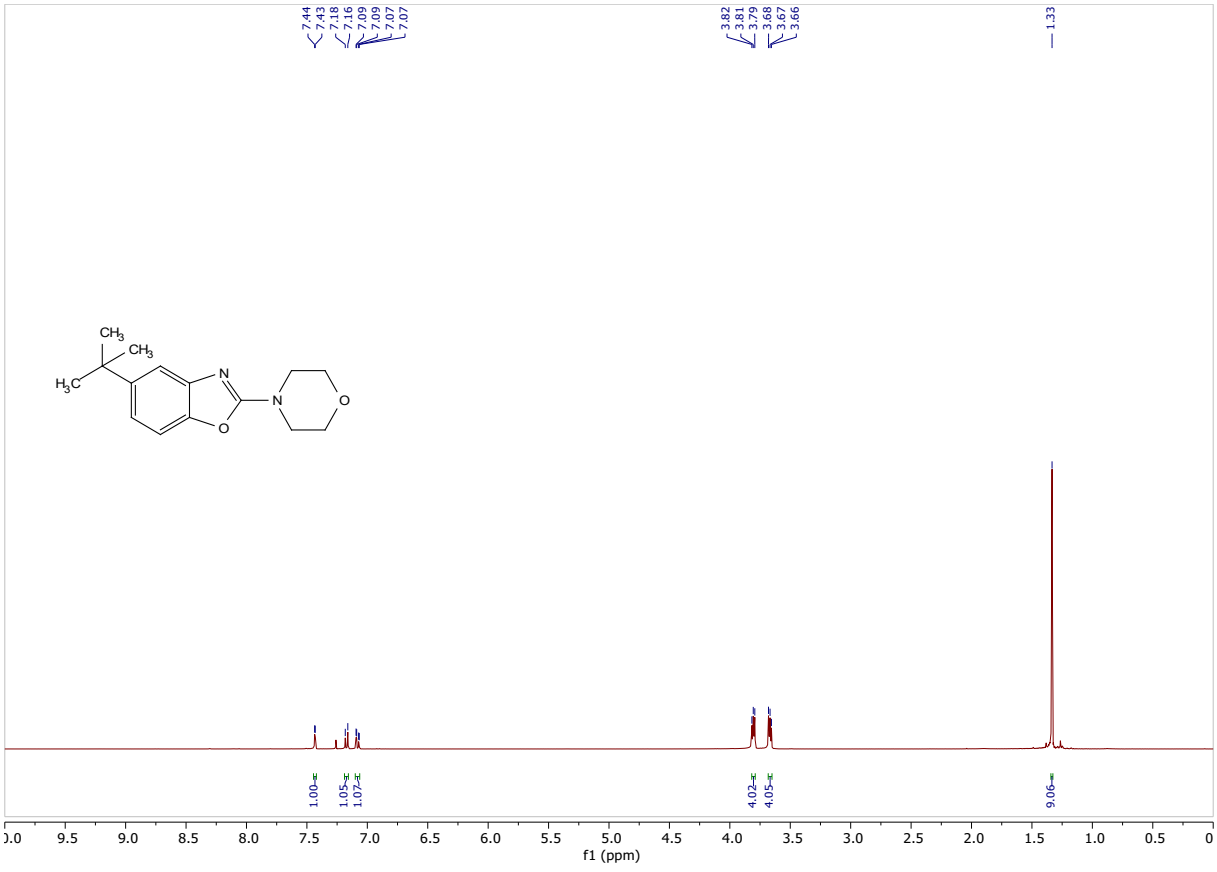


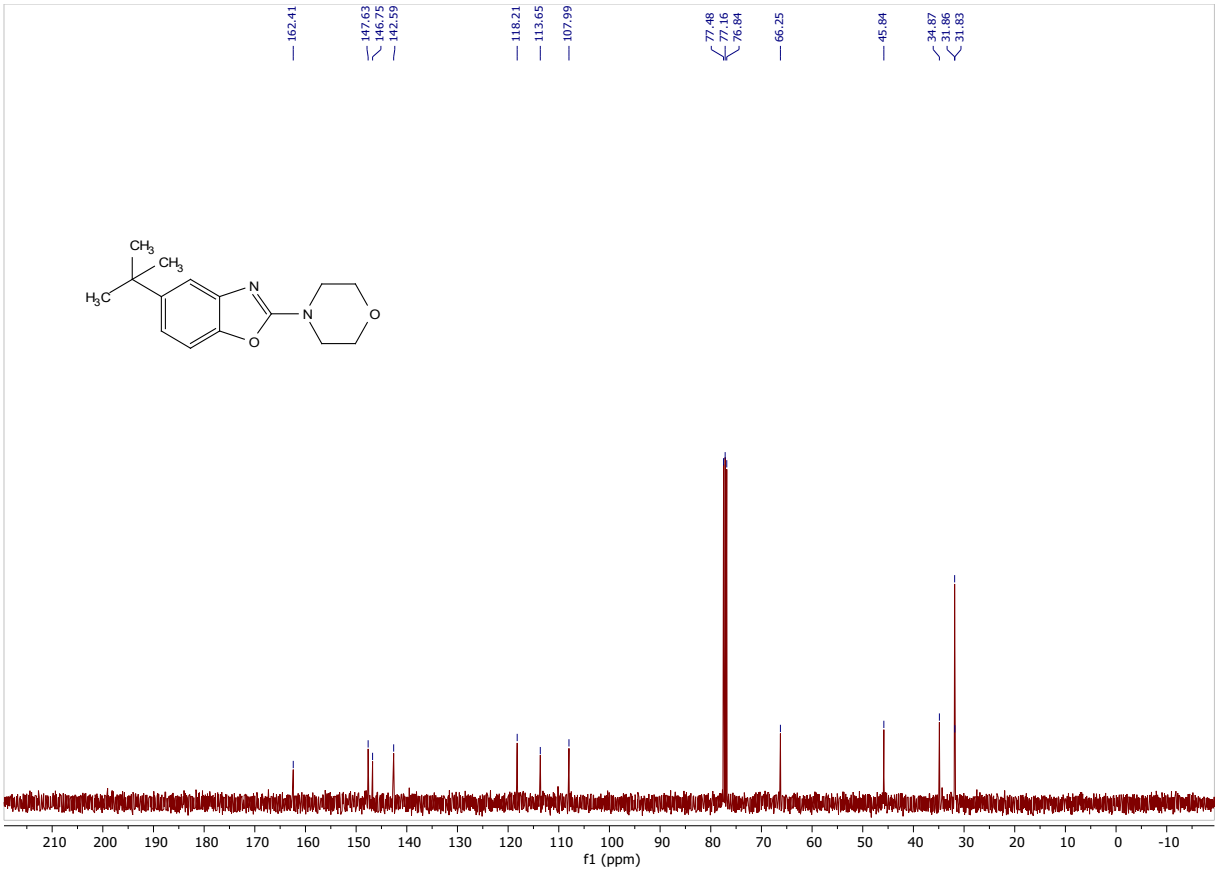
4.16. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6f)



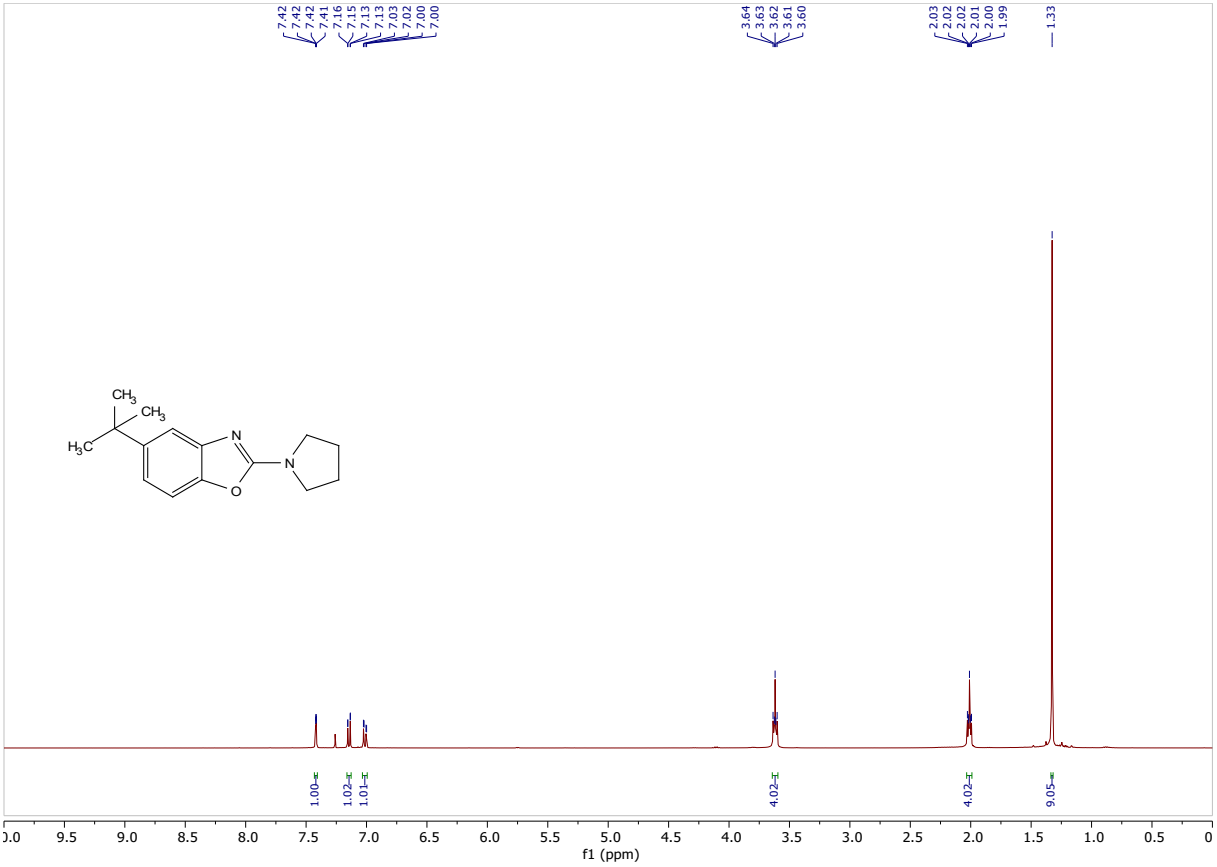


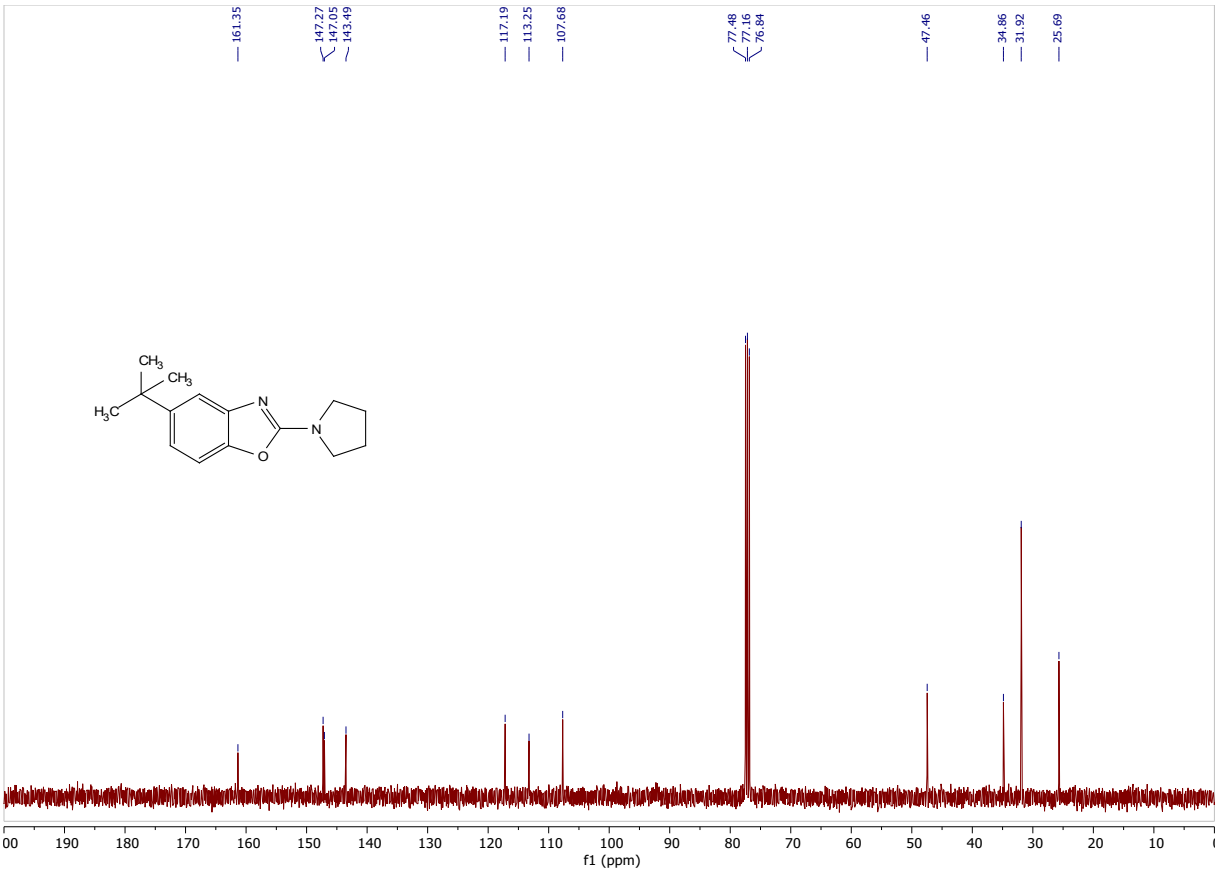
4.17. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6g)



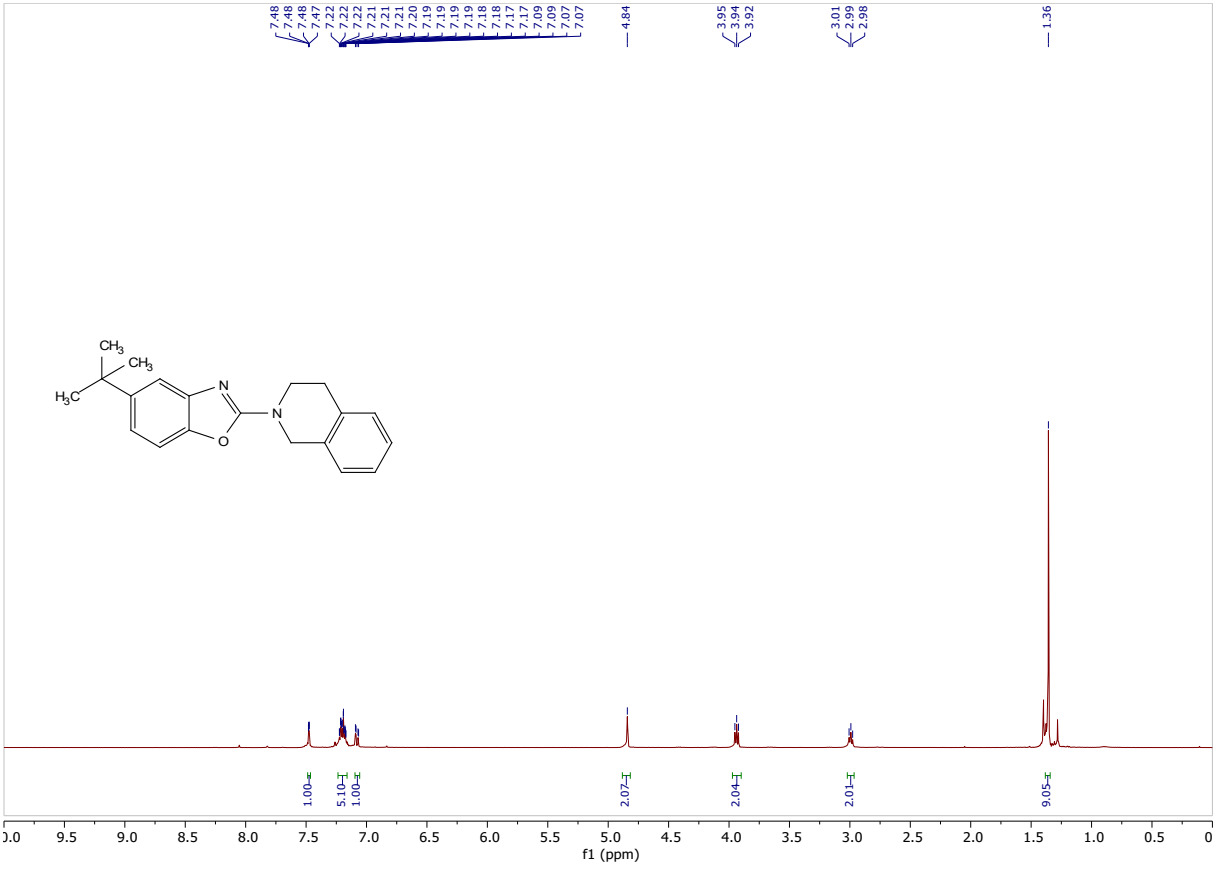


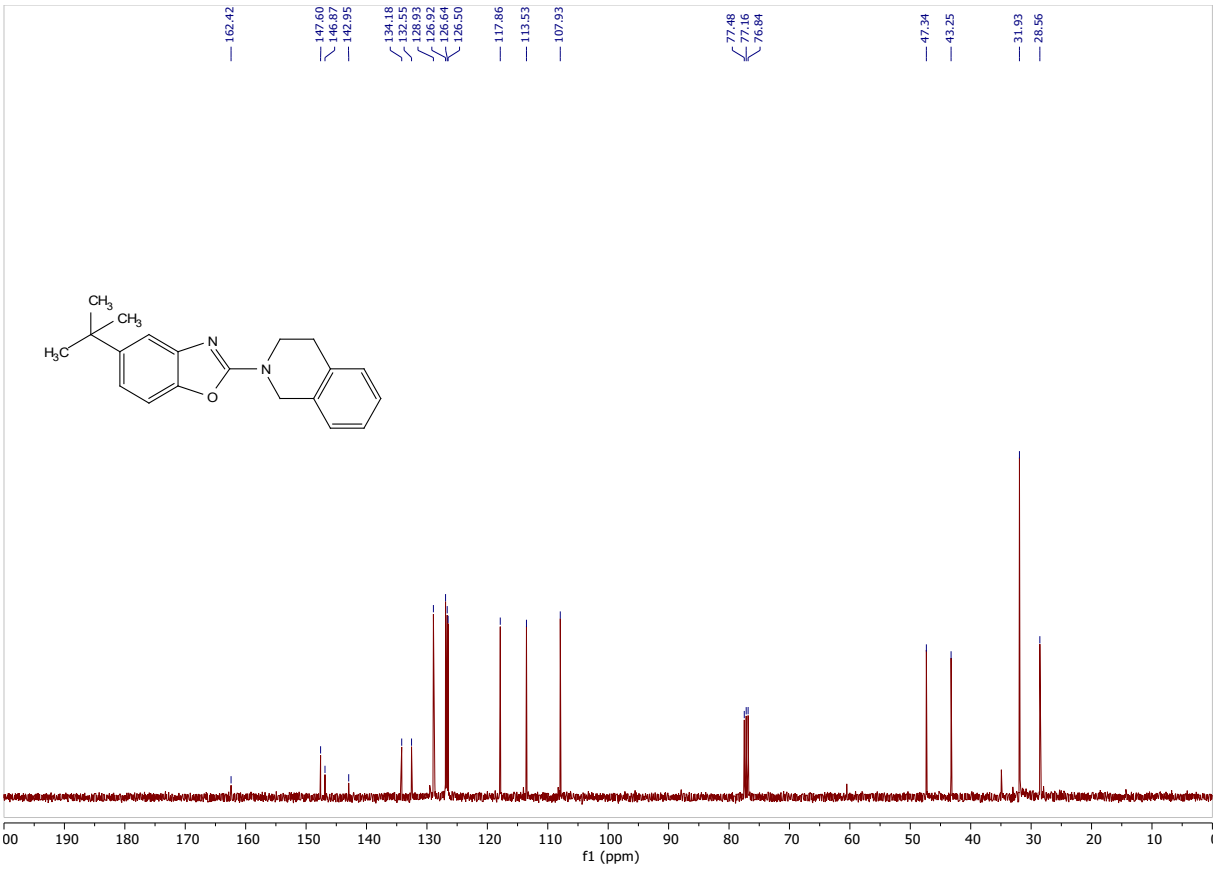
4.18. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6h)



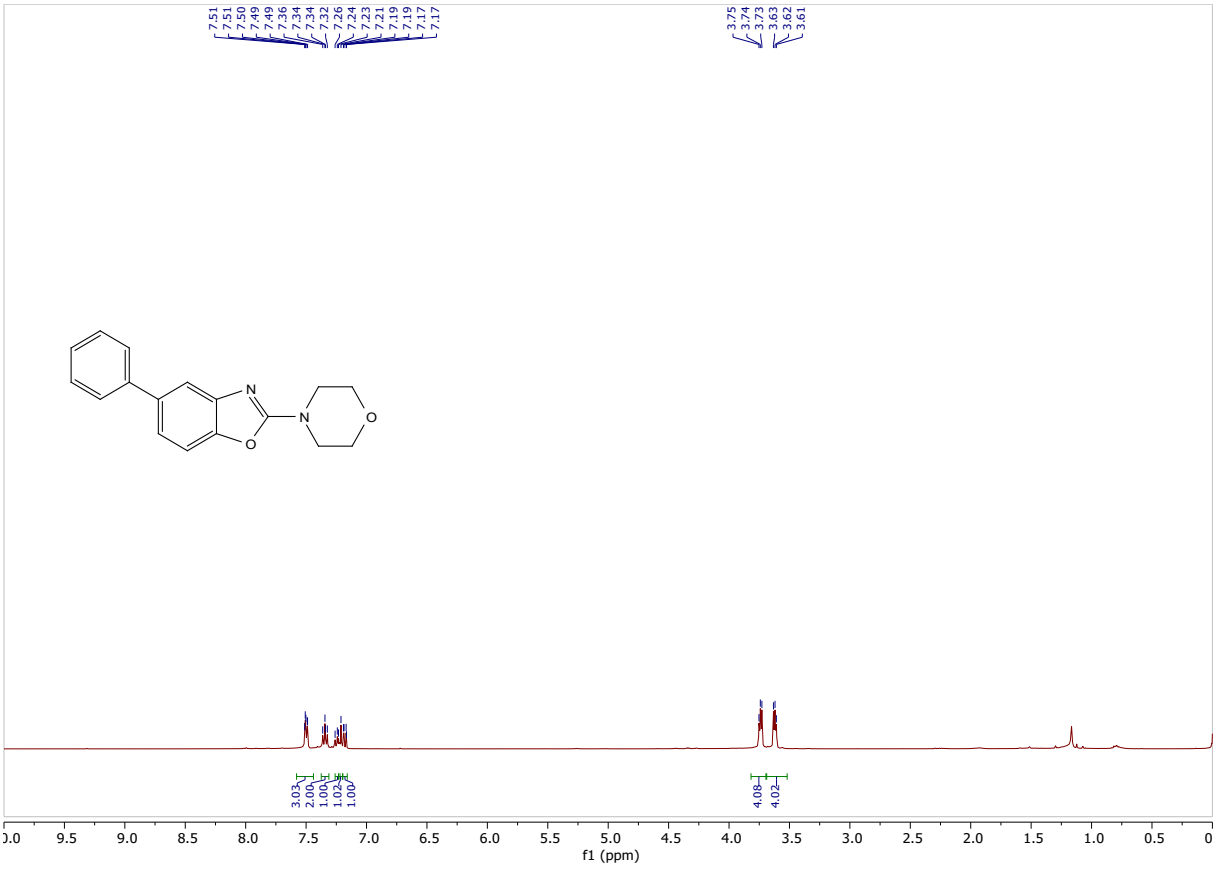


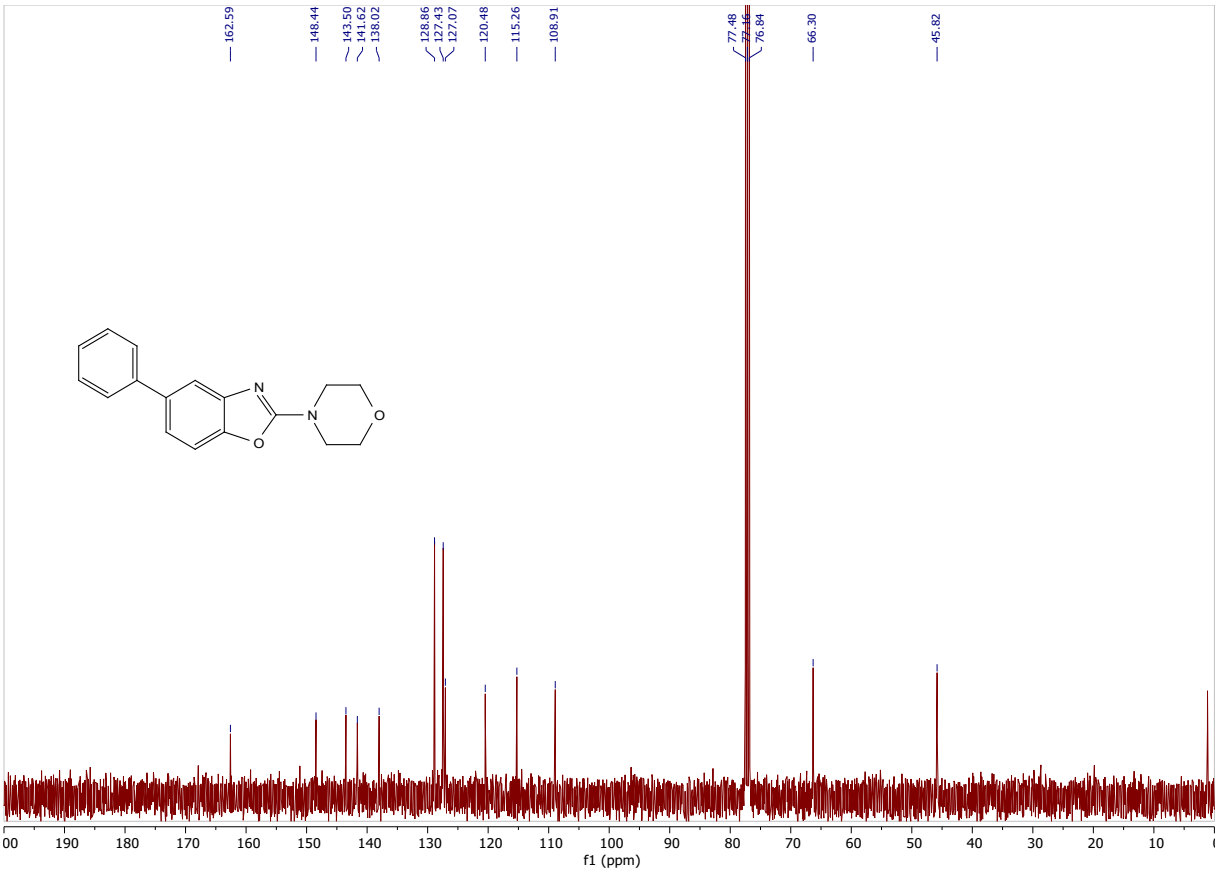
4.19. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6i)



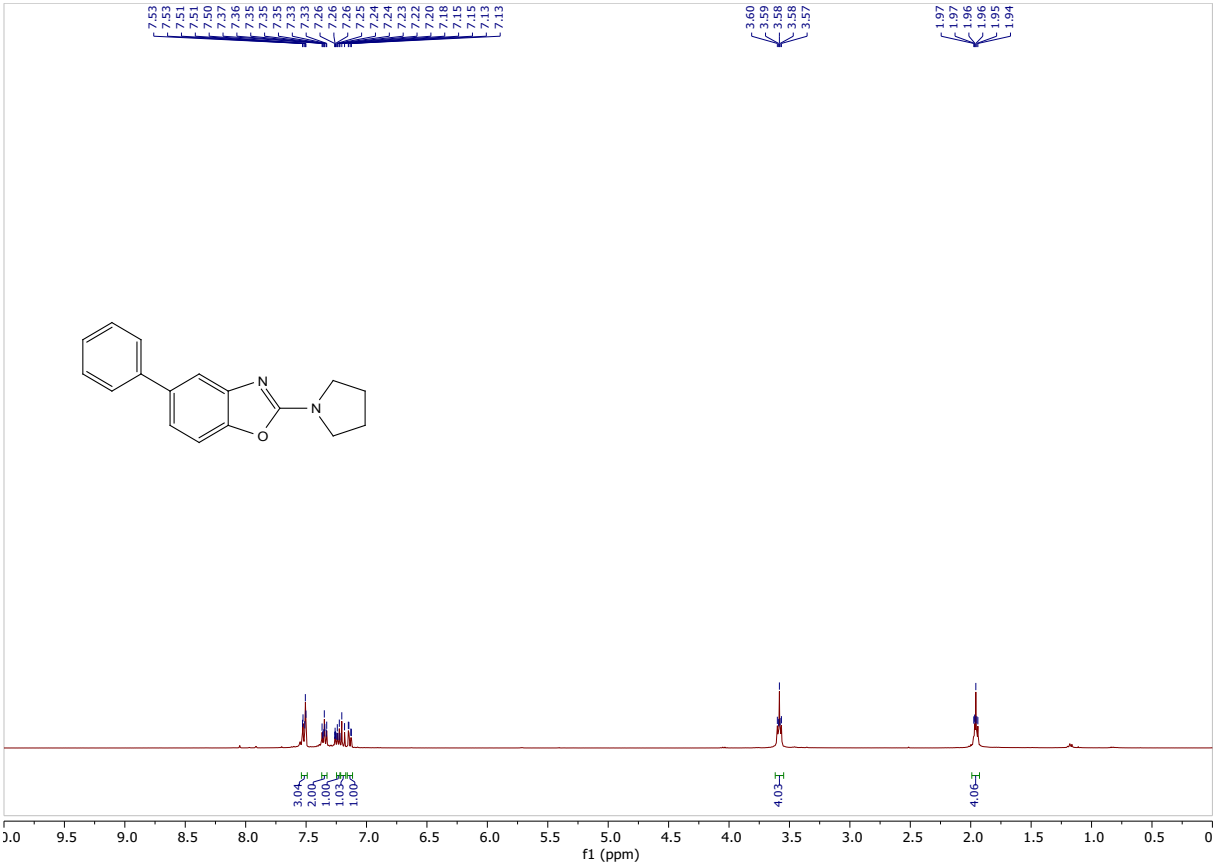


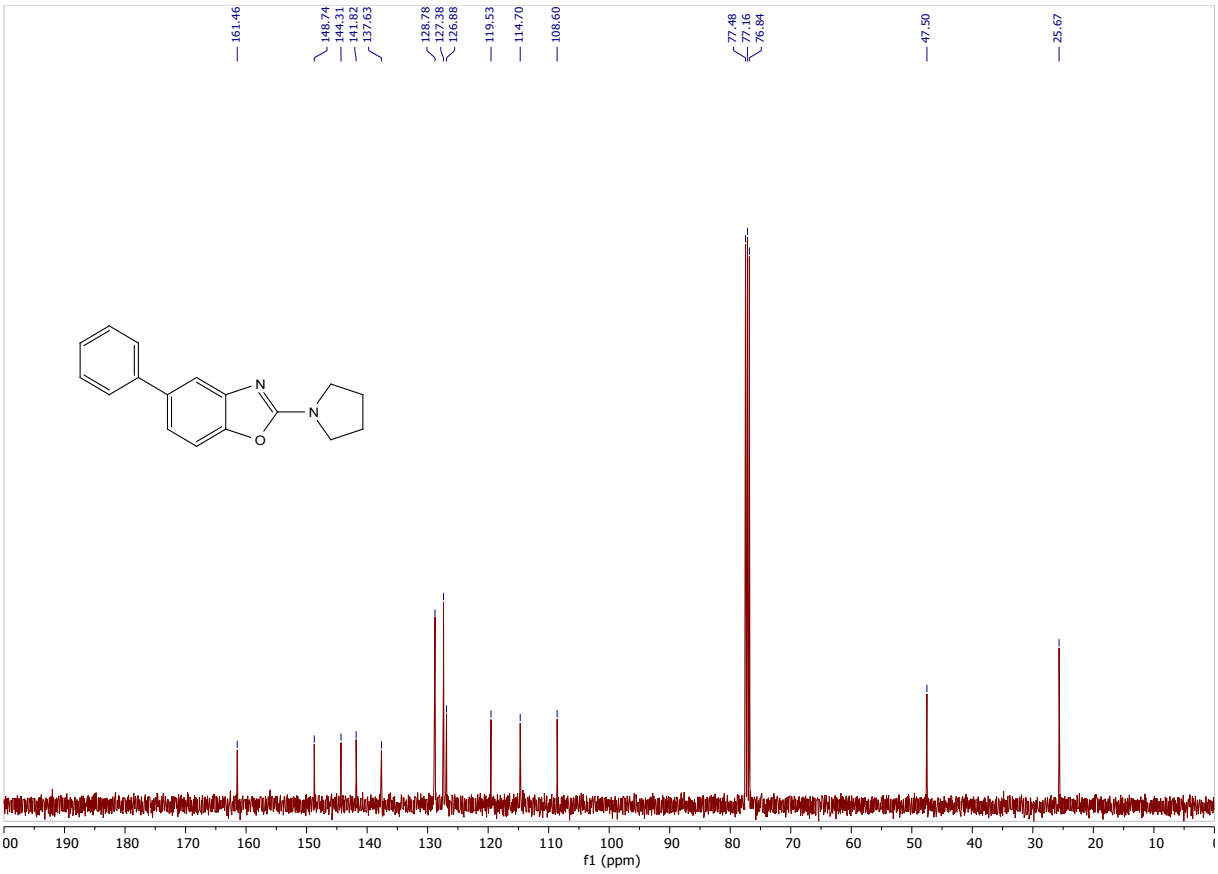
4.20. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (6j)



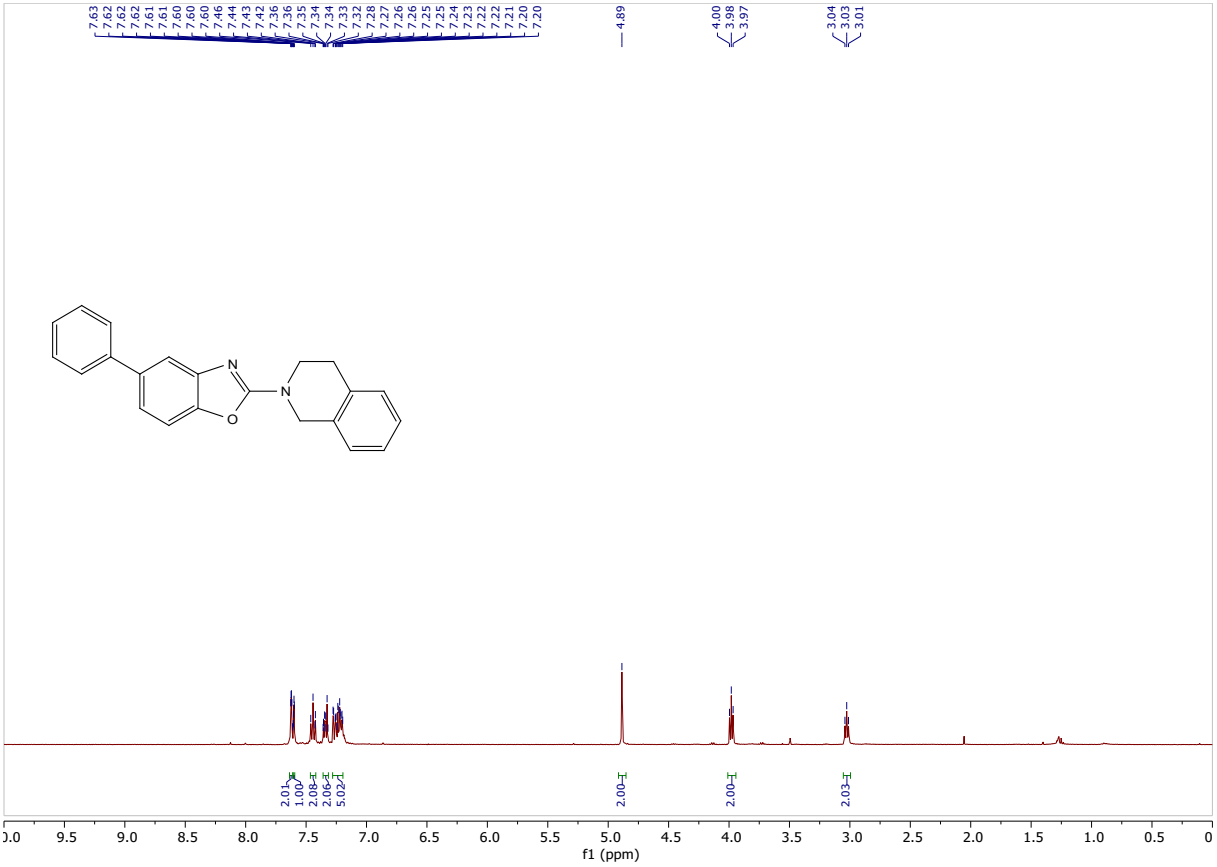


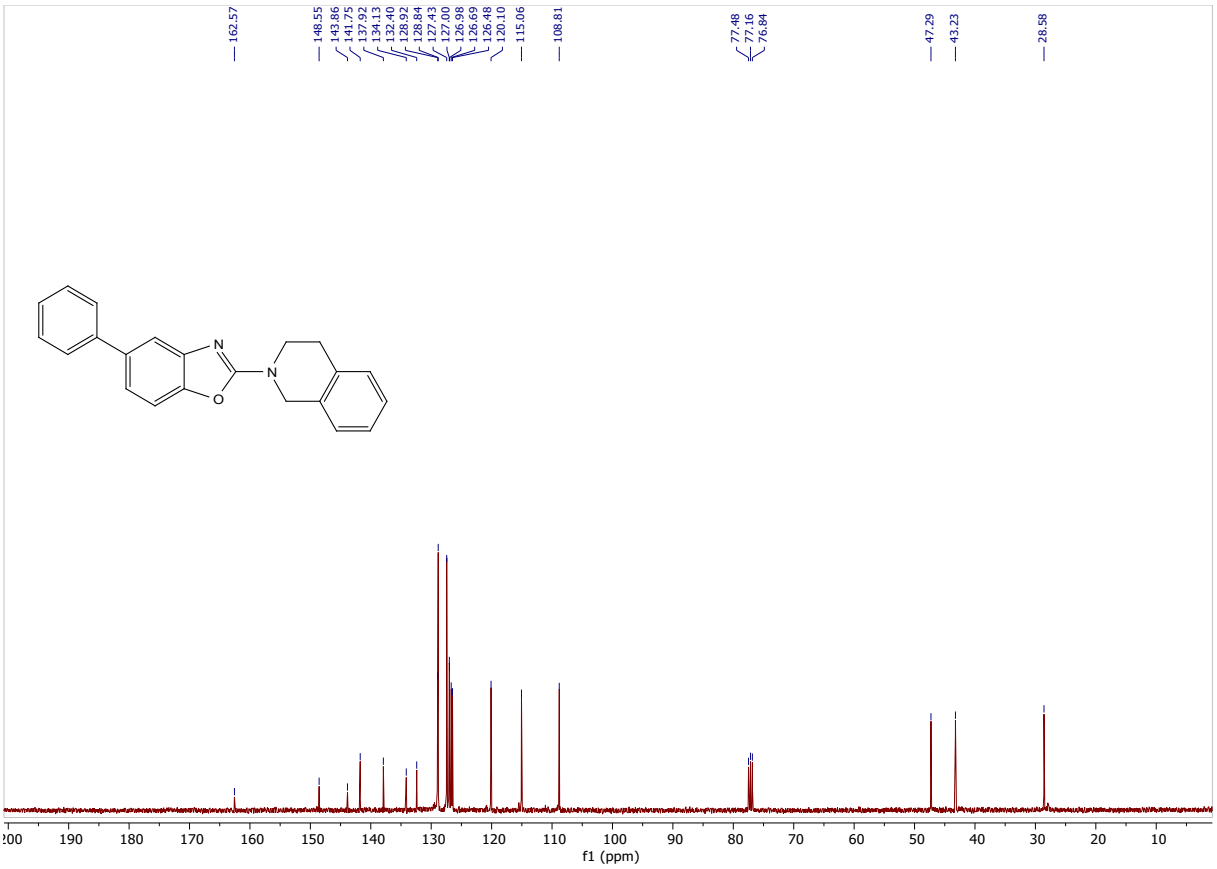
4.21. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6k)



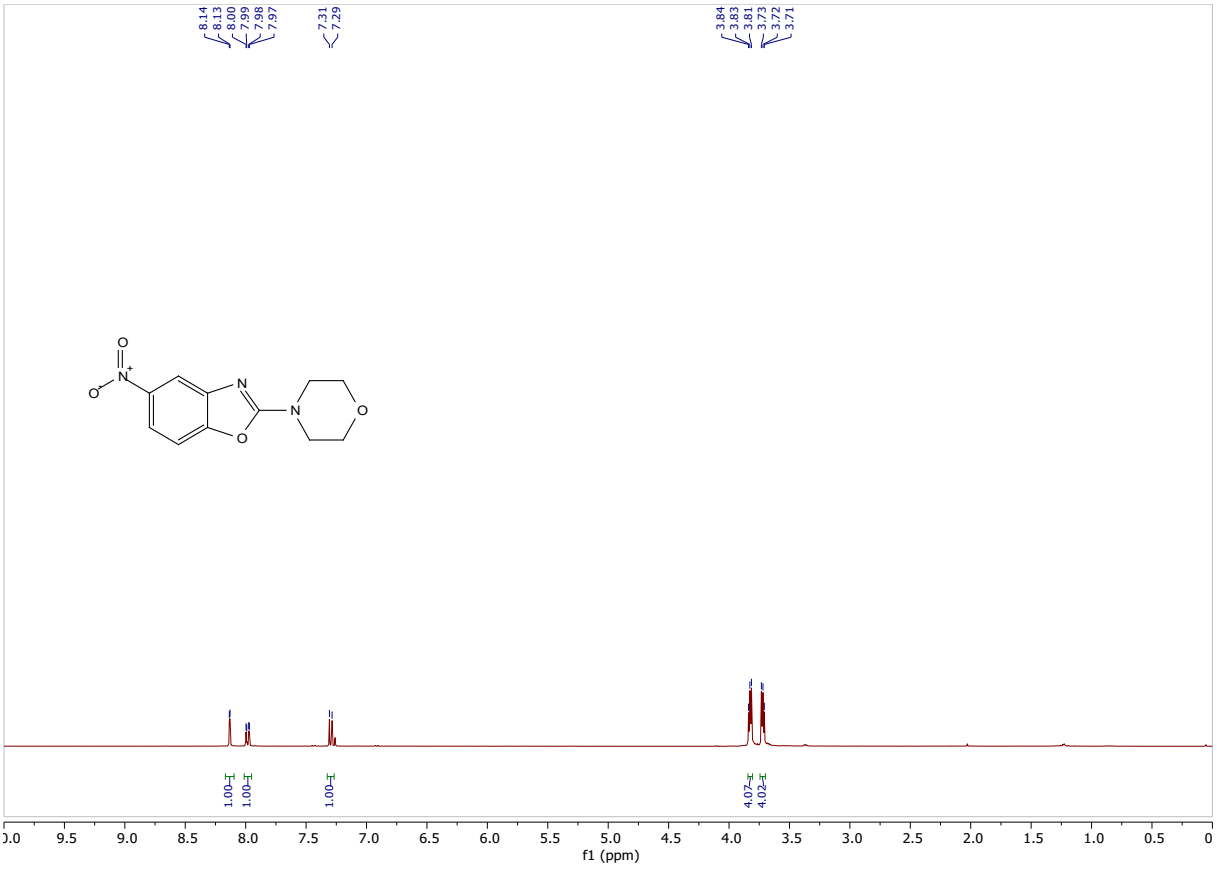


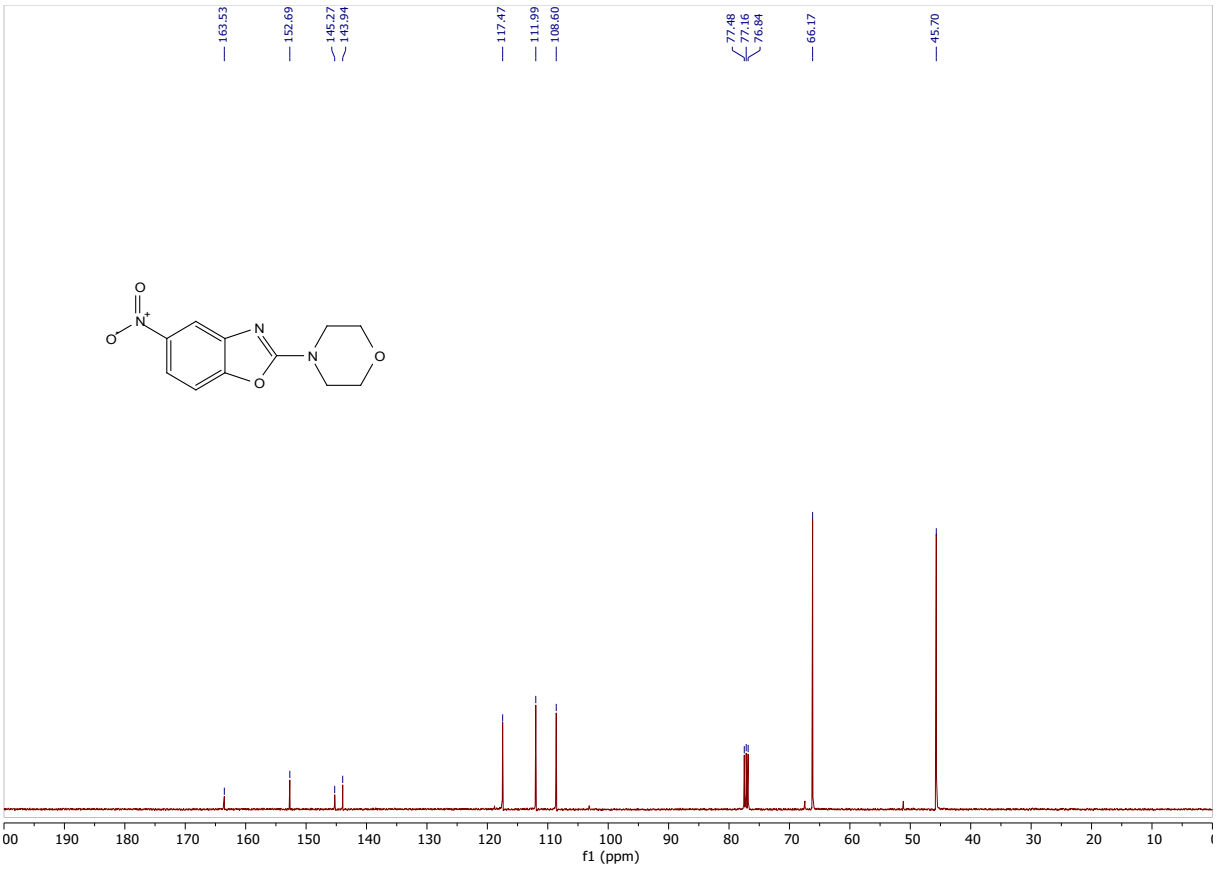
4.22. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6l)



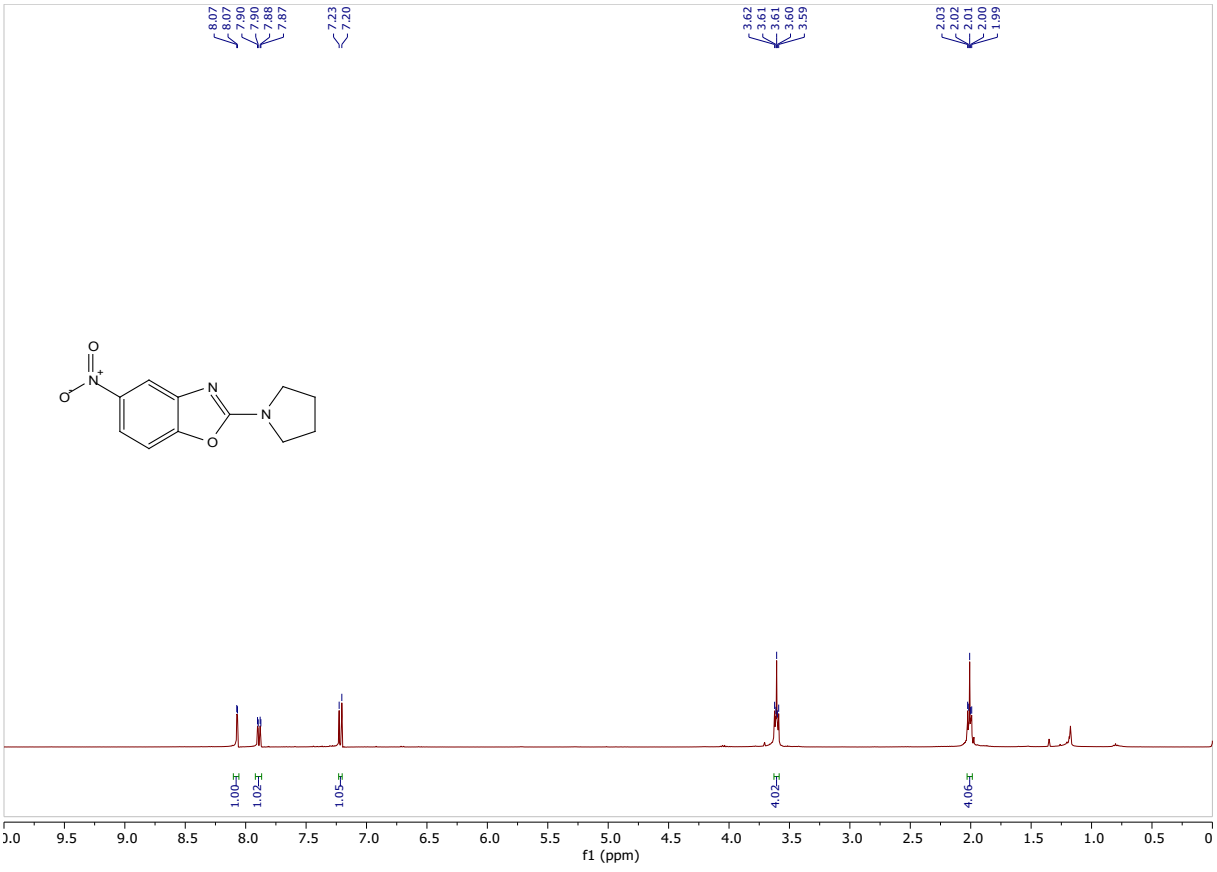


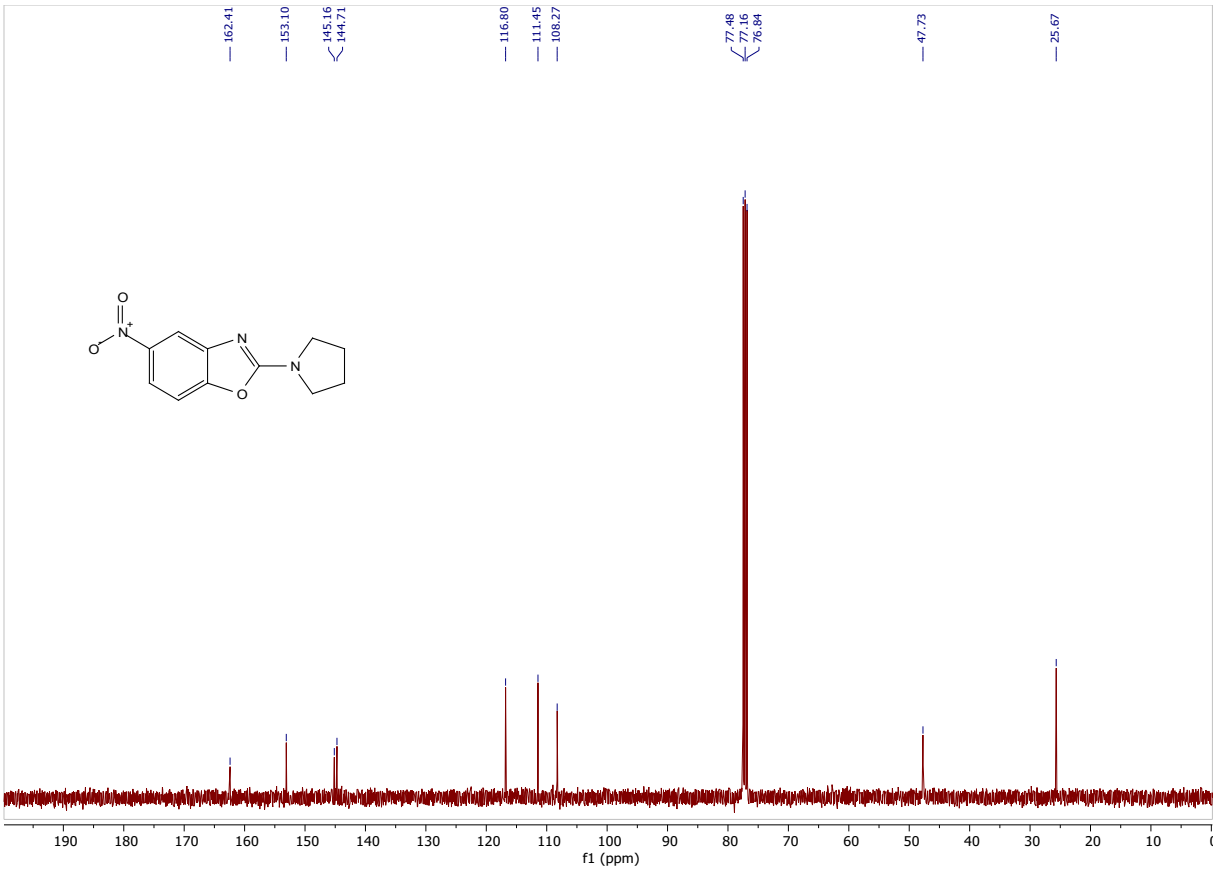
4.23. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (6m)



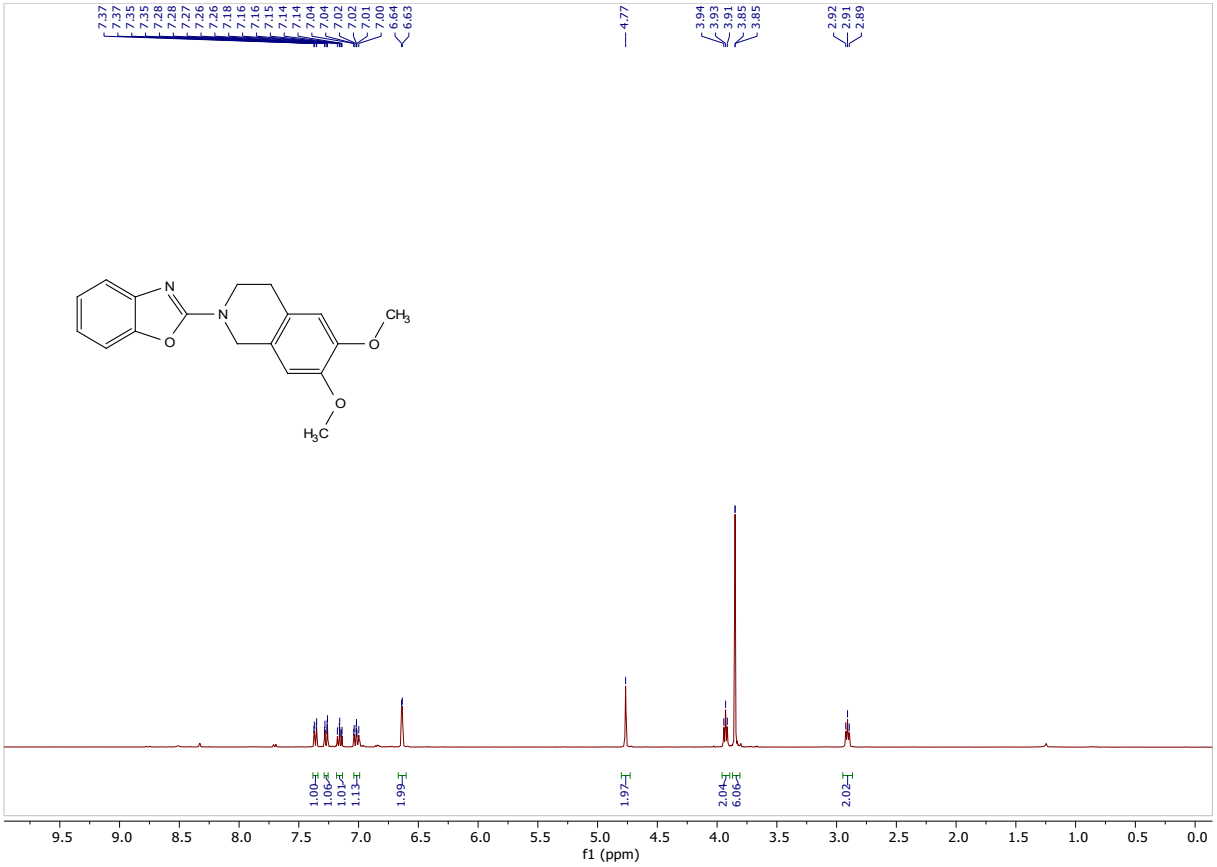


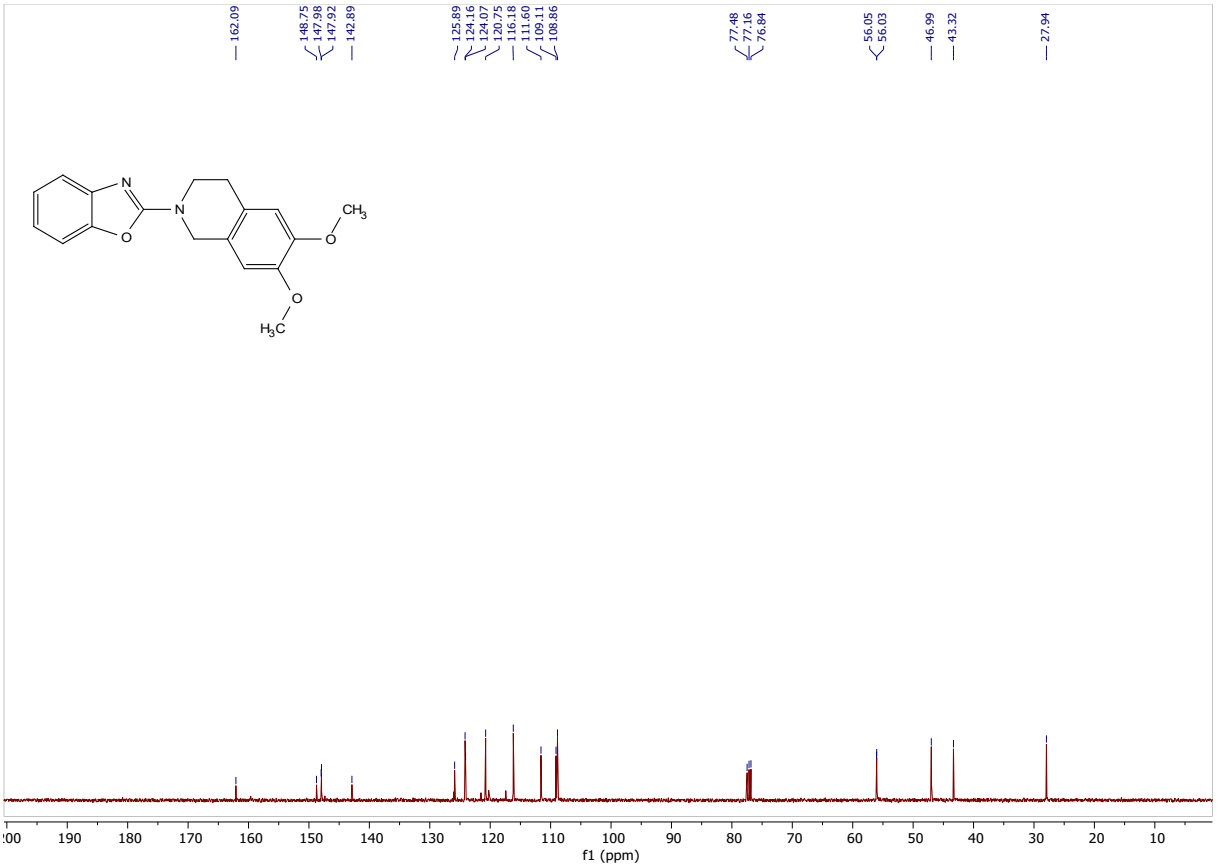
4.24. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6n)



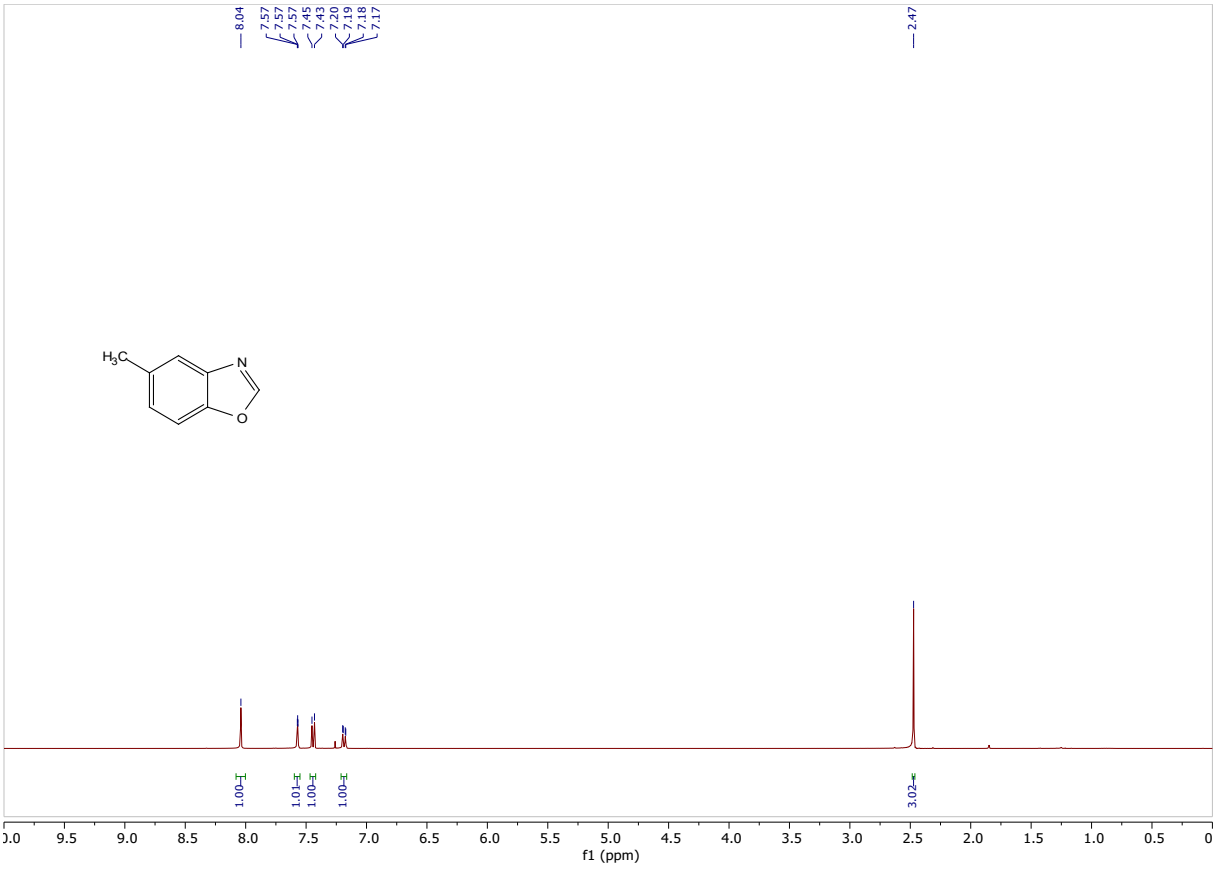


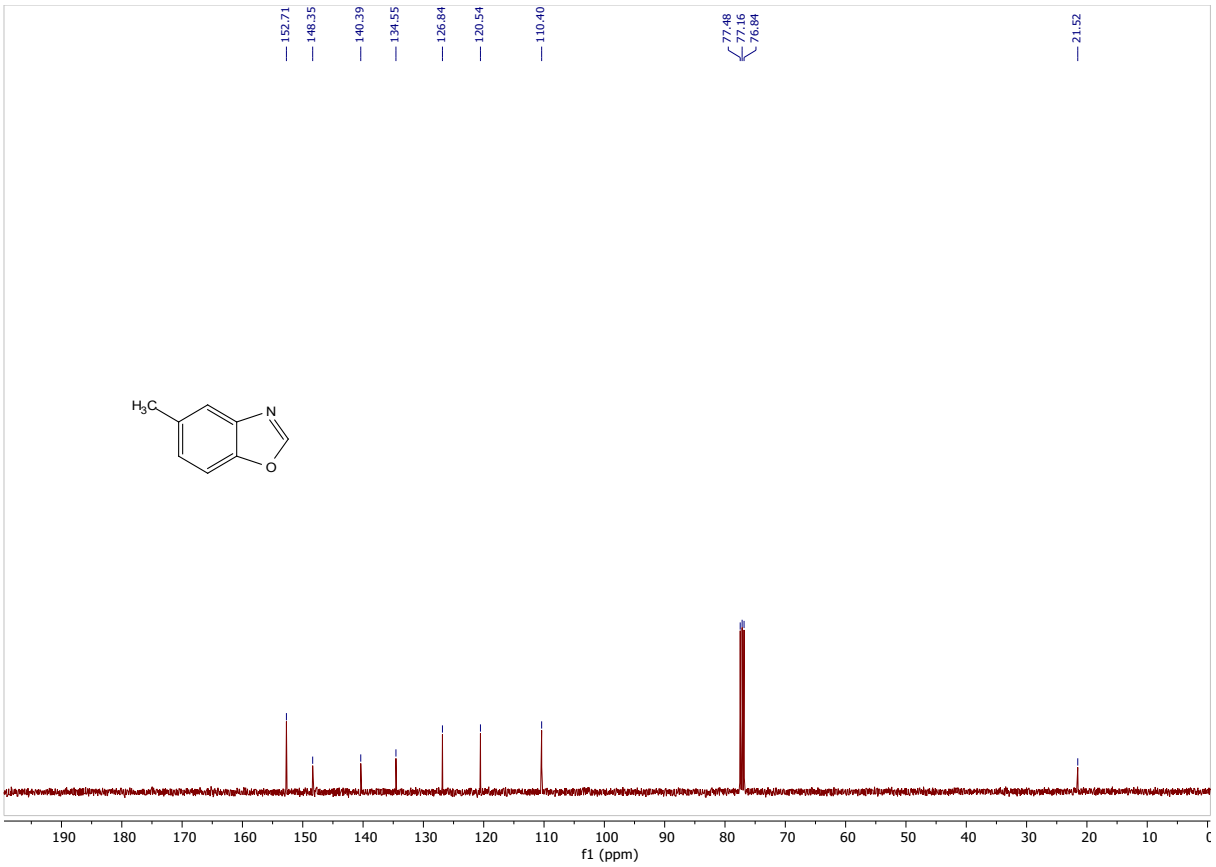
4.25. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (6o)



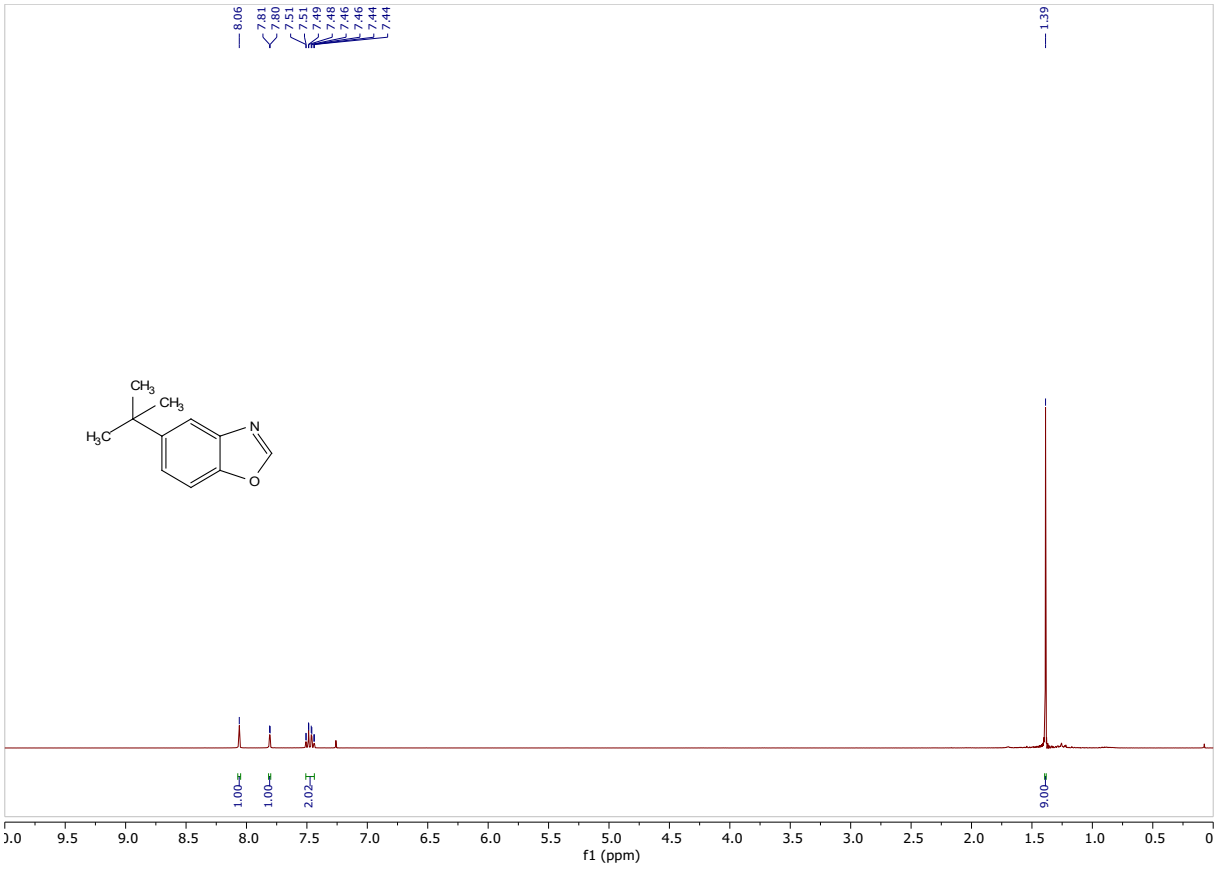


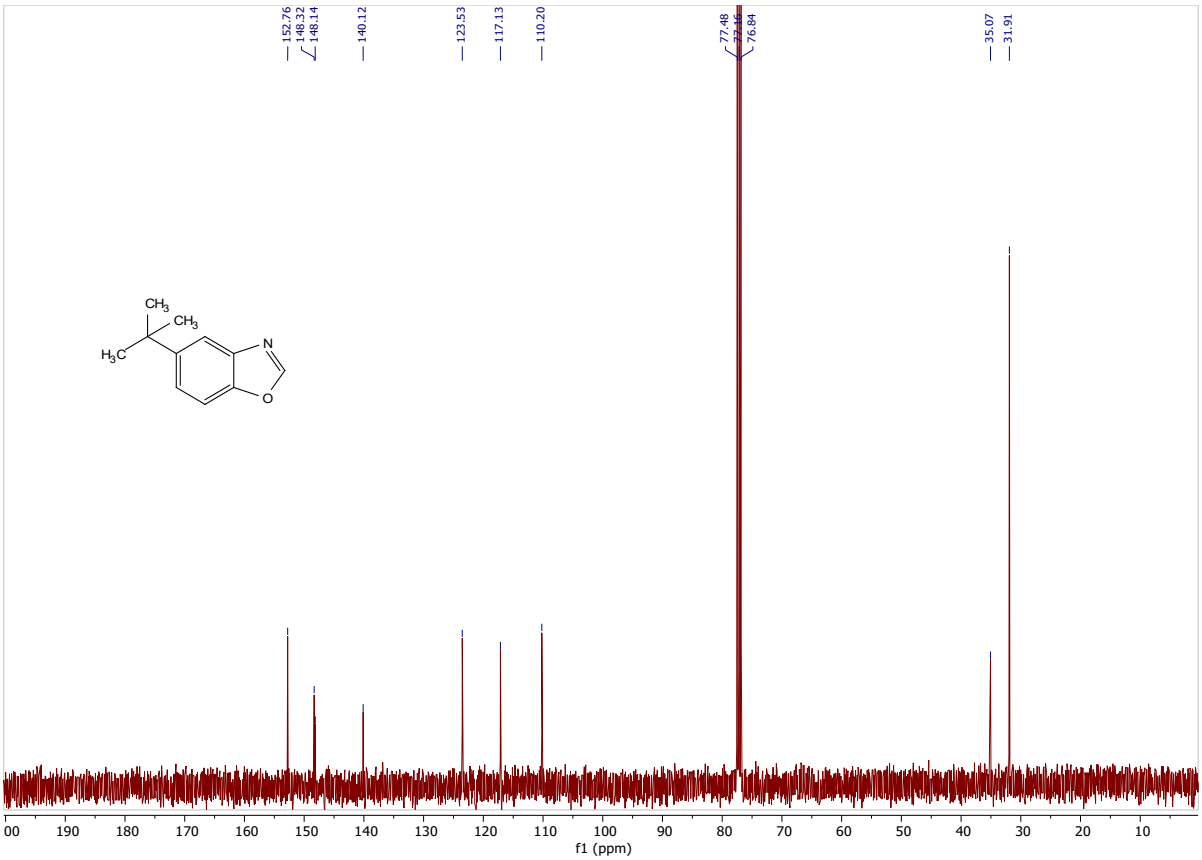
4.26. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (7)



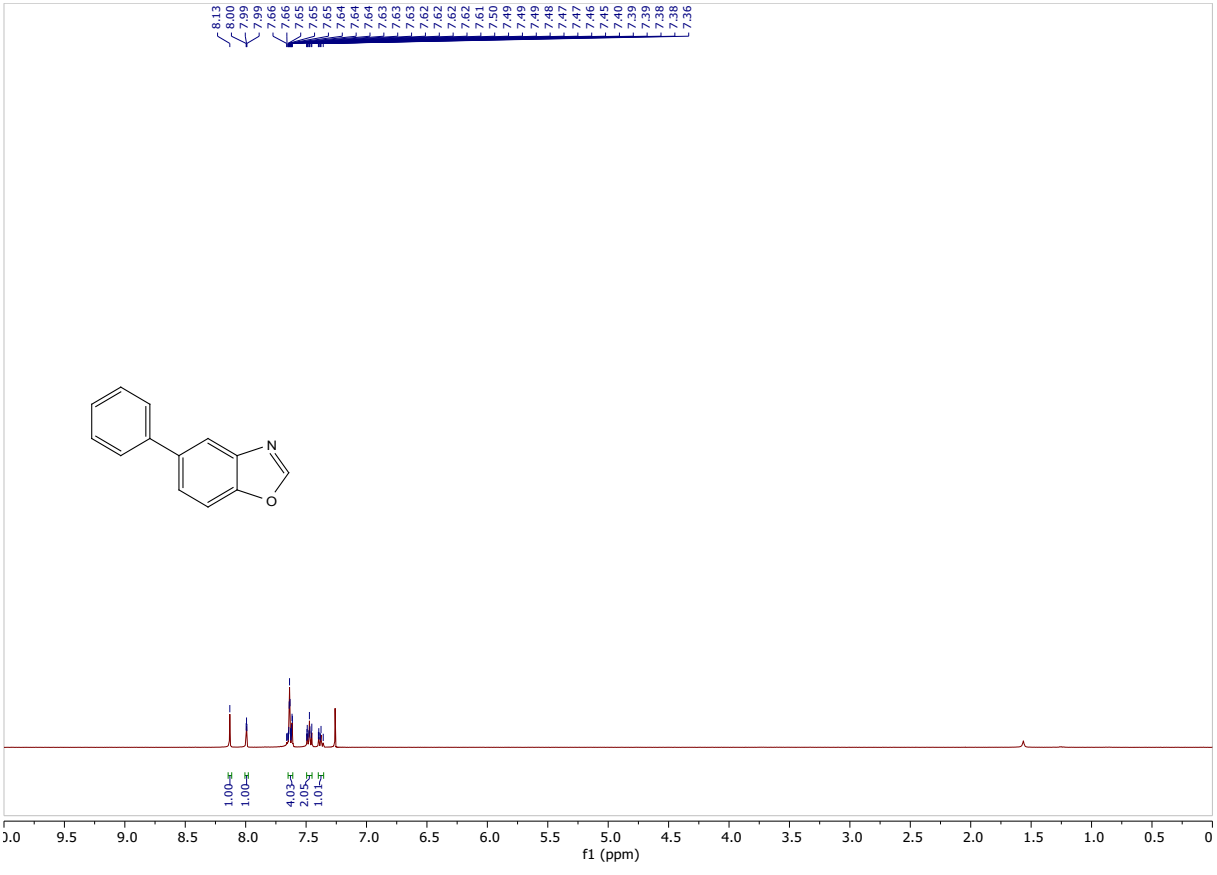


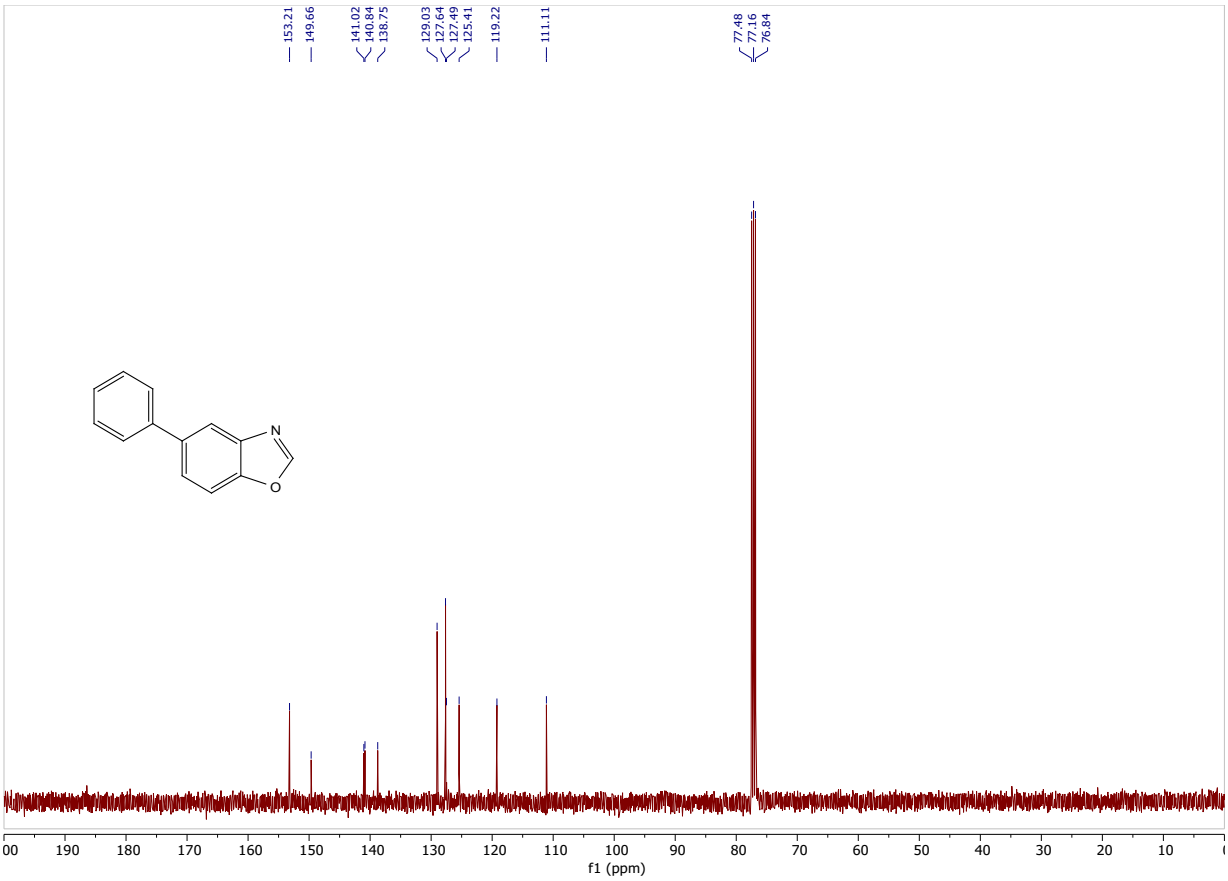
4.27. 400 MHz [1]H-NMR spectrum and 100 MHz [13]C-NMR spectrum ($CDCl_3$) of (8)



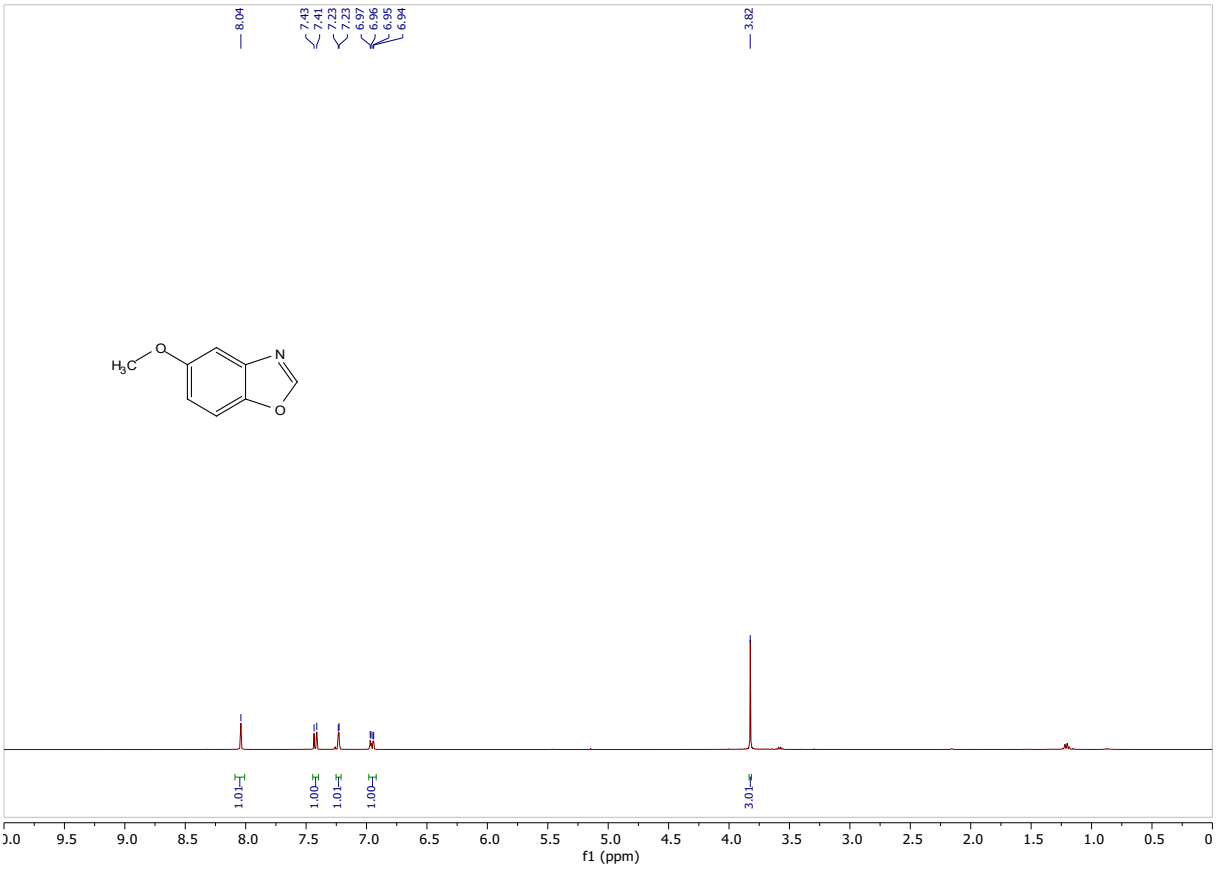


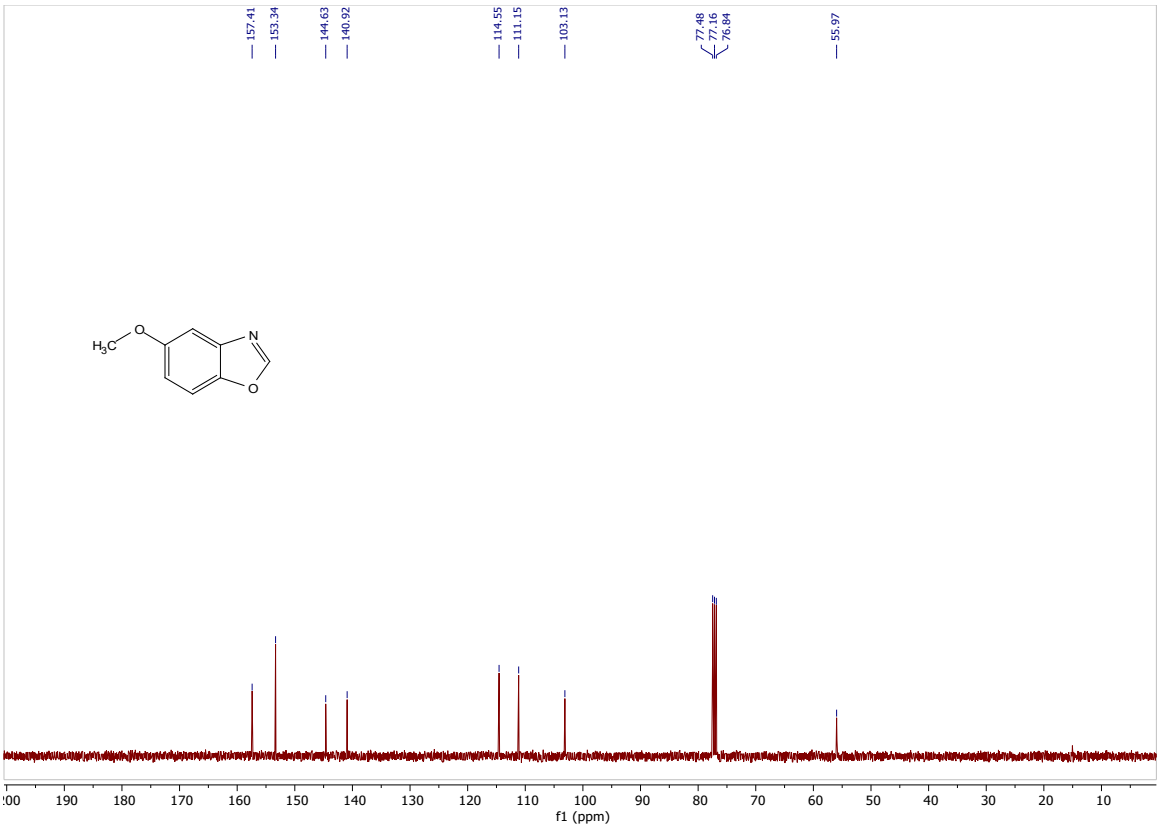
4.28. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (9)



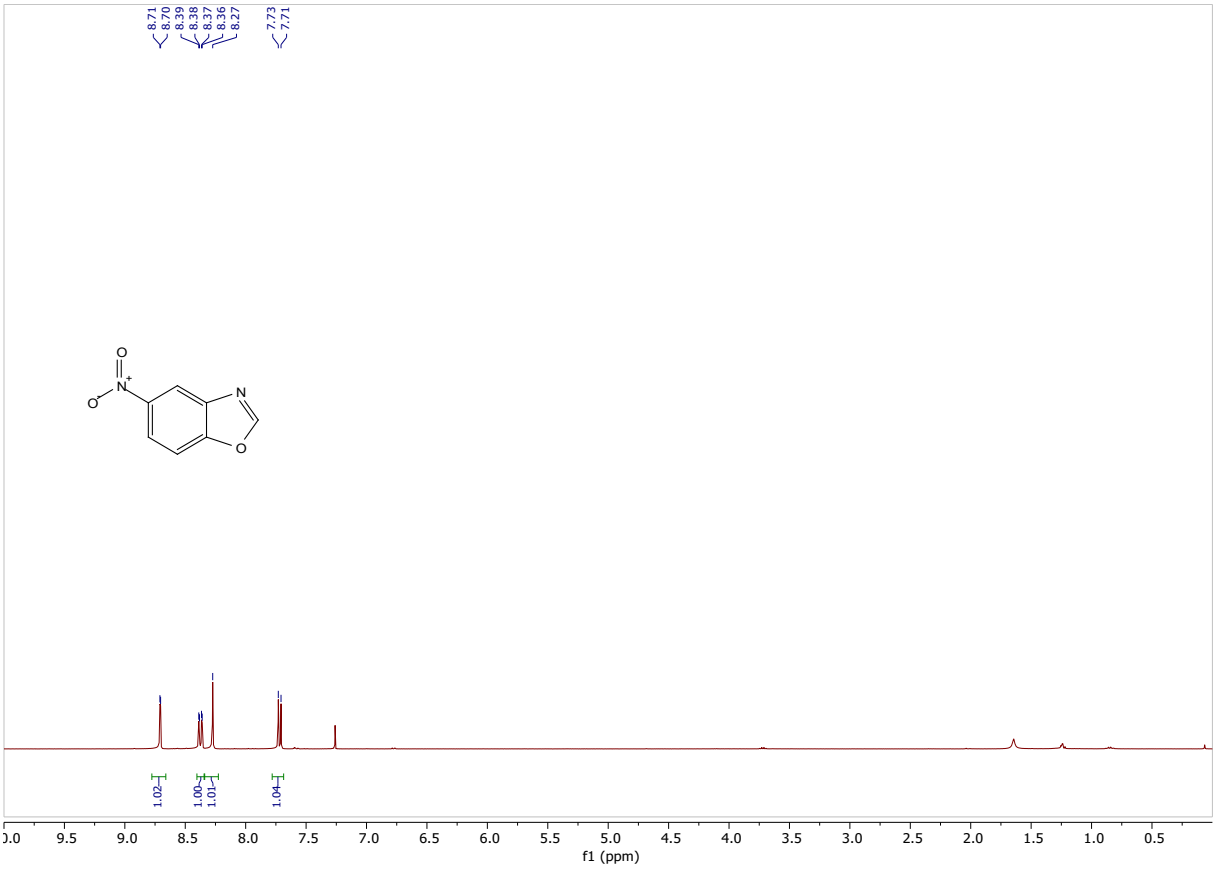


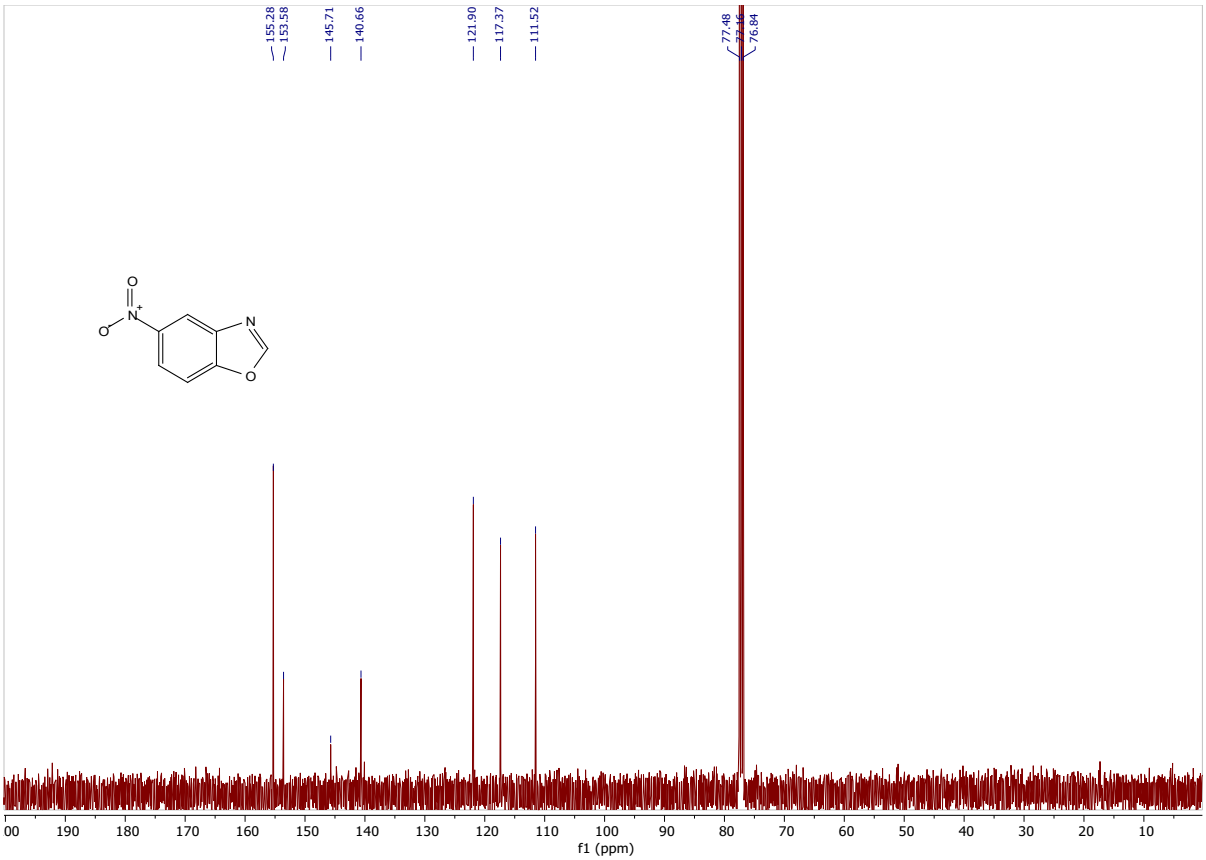
4.29. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (10)





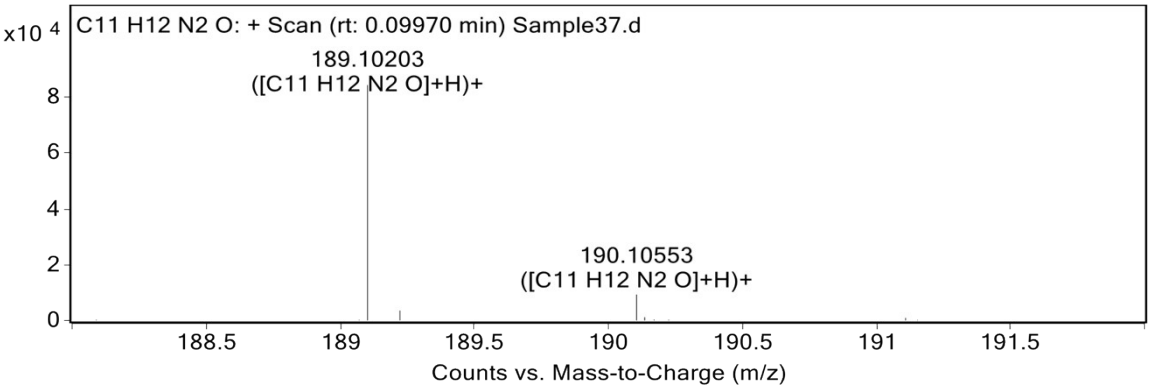
4.30. 400 MHz ^{1}H-NMR spectrum and 100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of (11)



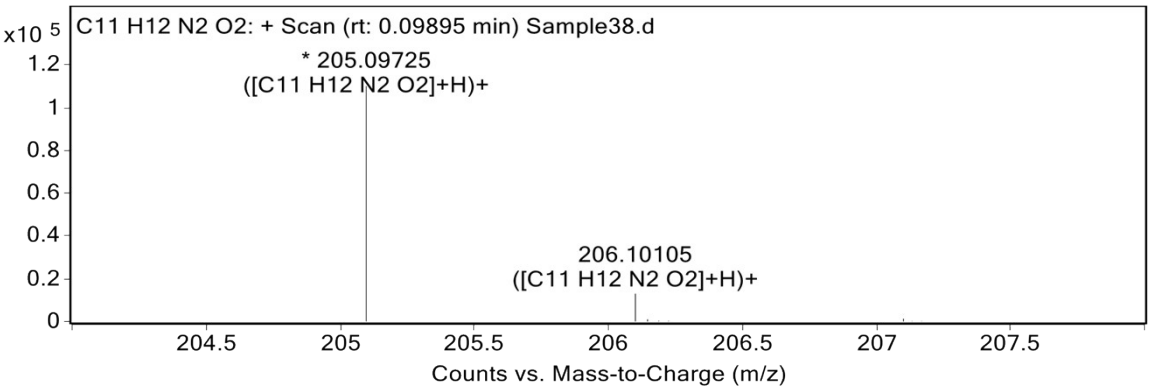


5. HRMS spectra

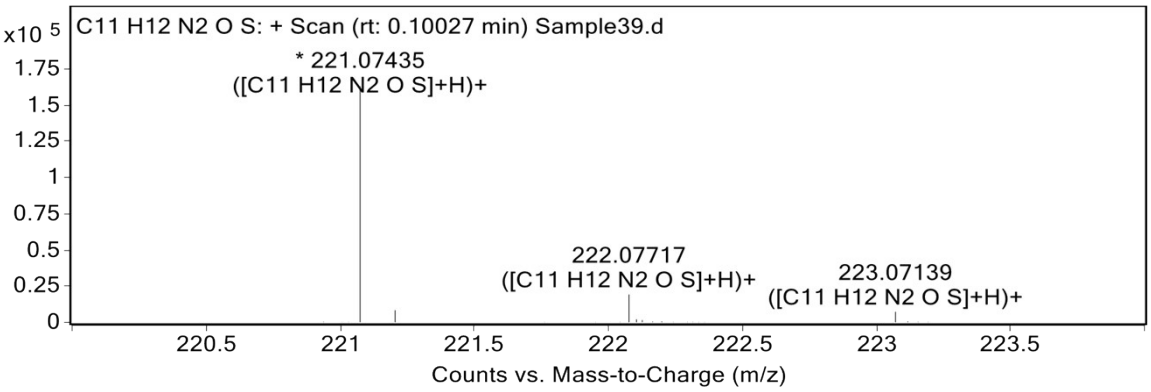
5.1. HRMS spectrum of 3a



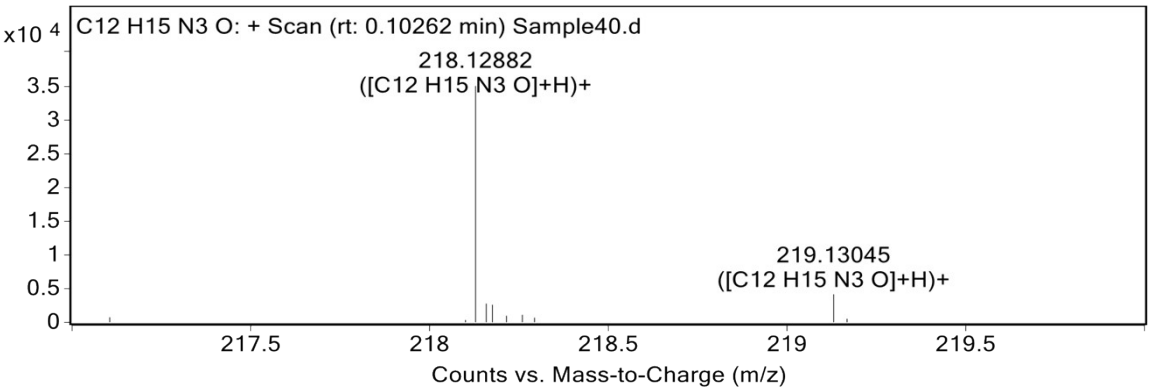
5.2. HRMS spectrum of 3b



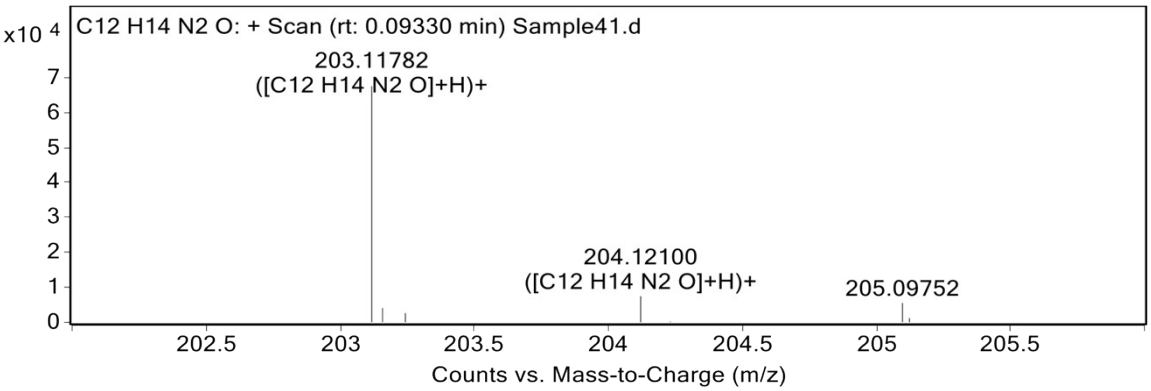
5.3. HRMS spectrum of 3c



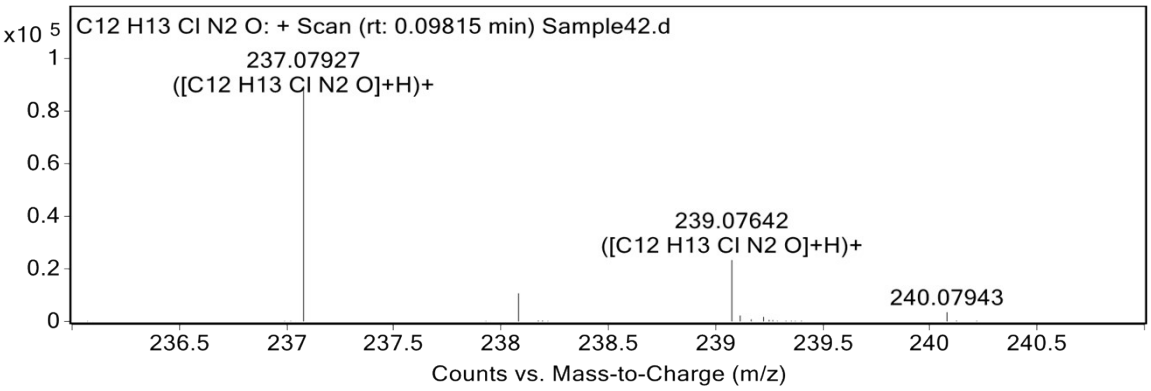
5.4. HRMS spectrum of 3d



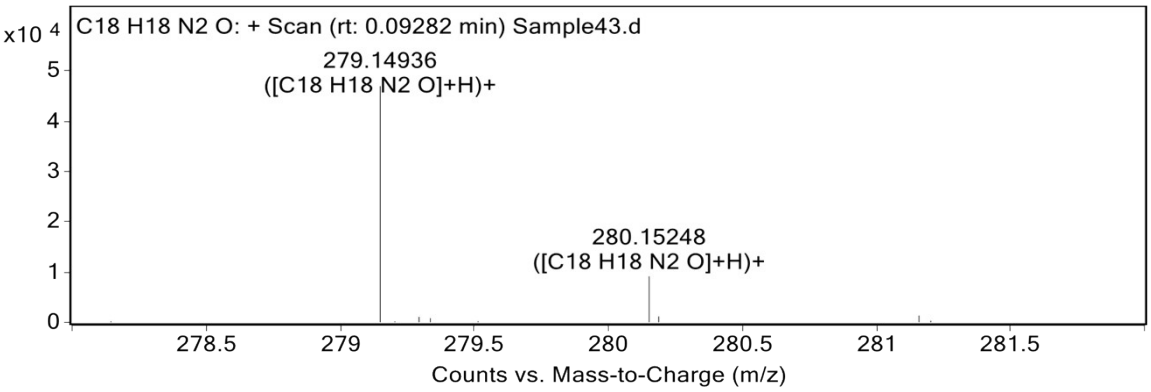
5.5. HRMS spectrum of 3e



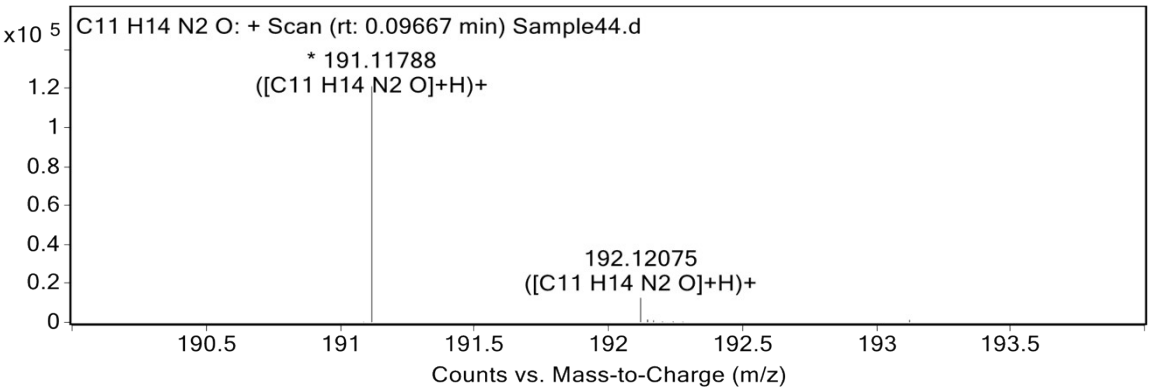
5.6. HRMS spectrum of 3f



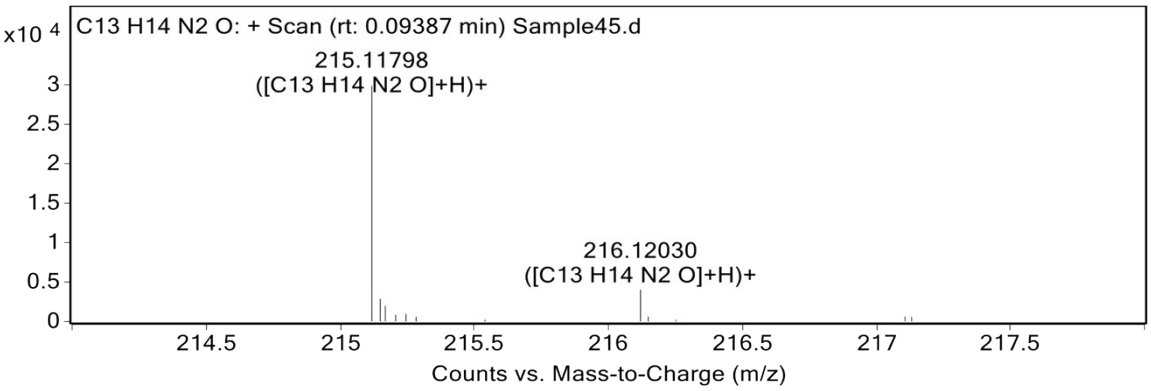
5.7. HRMS spectrum of 3g



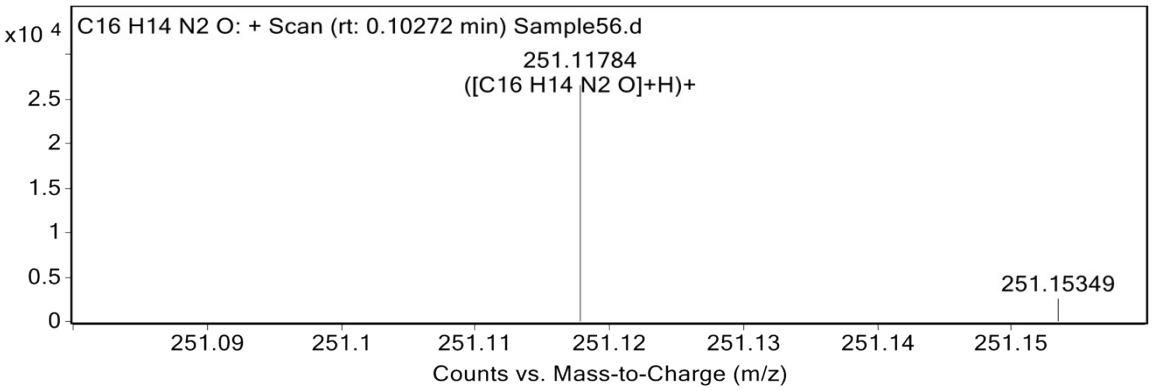
5.8. HRMS spectrum of 3h



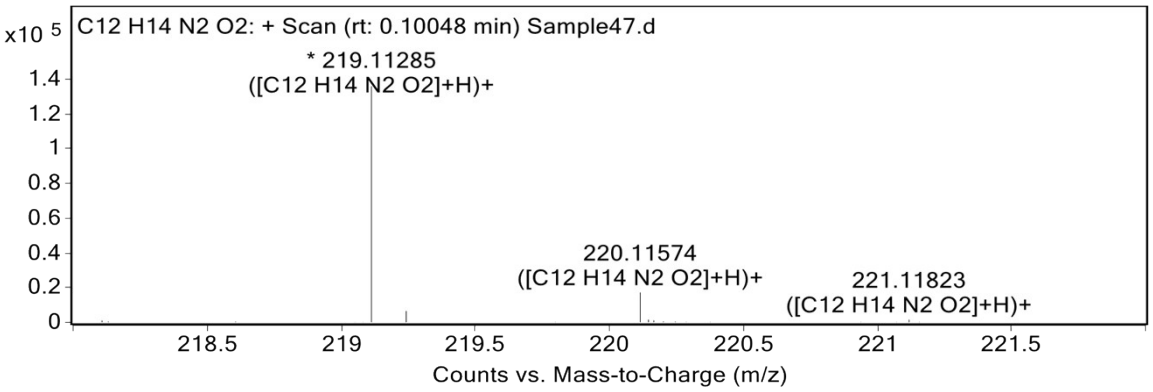
5.9. HRMS spectrum of 3i



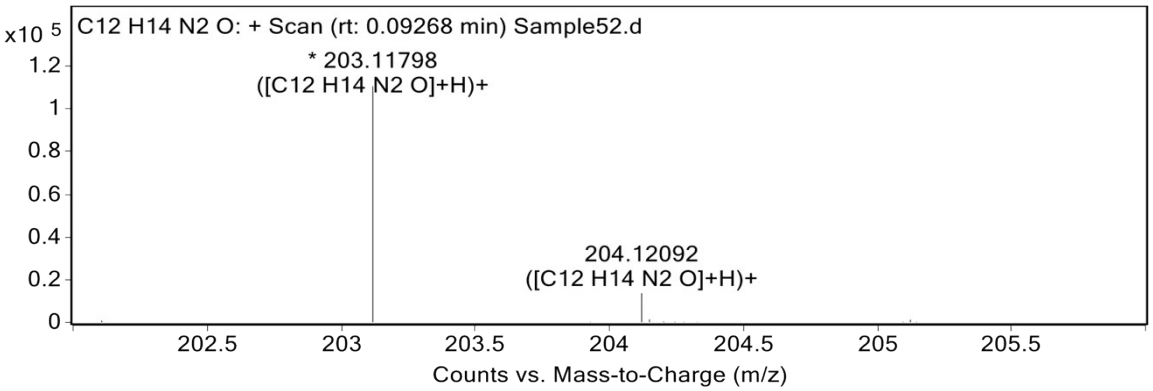
5.10. HRMS spectrum of 3j



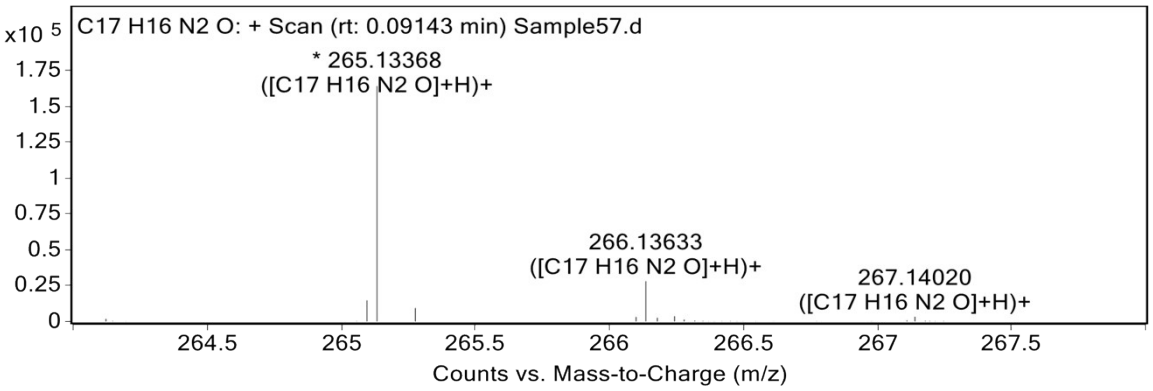
5.11. HRMS spectrum of 6a



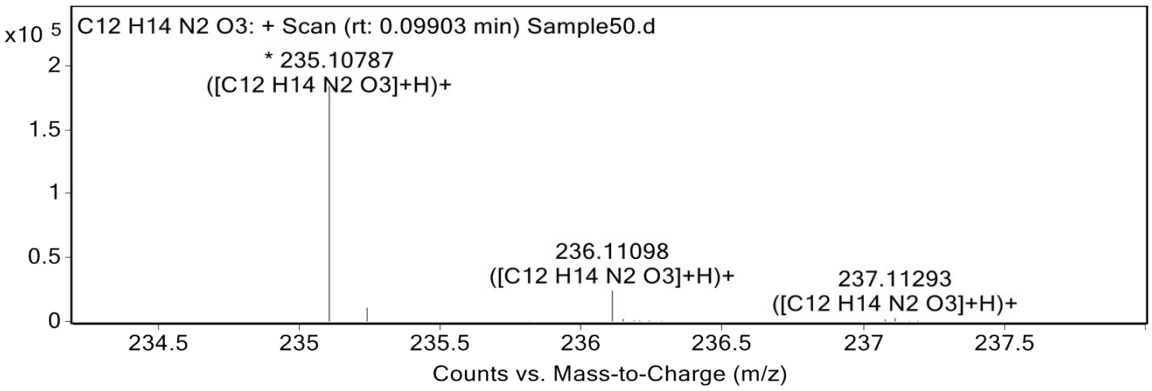
5.12. HRMS spectrum of 6b



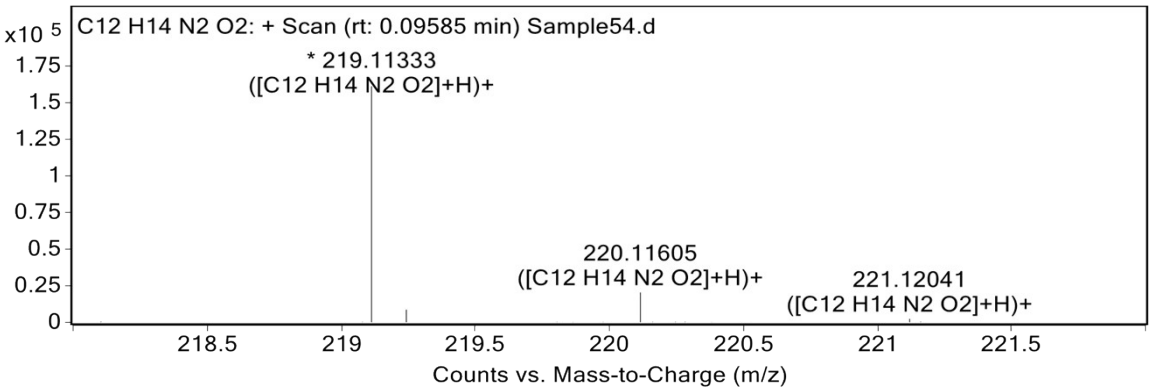
5.13. HRMS spectrum of 6c



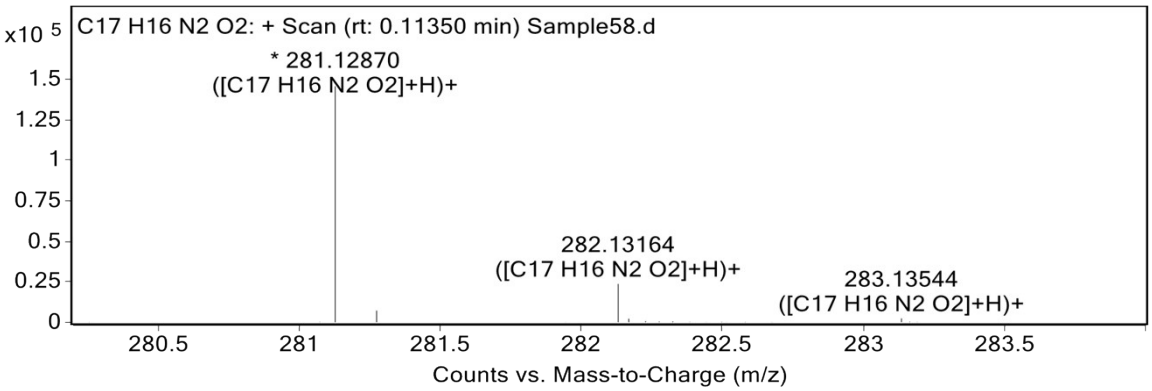
5.14. HRMS spectrum of 6d



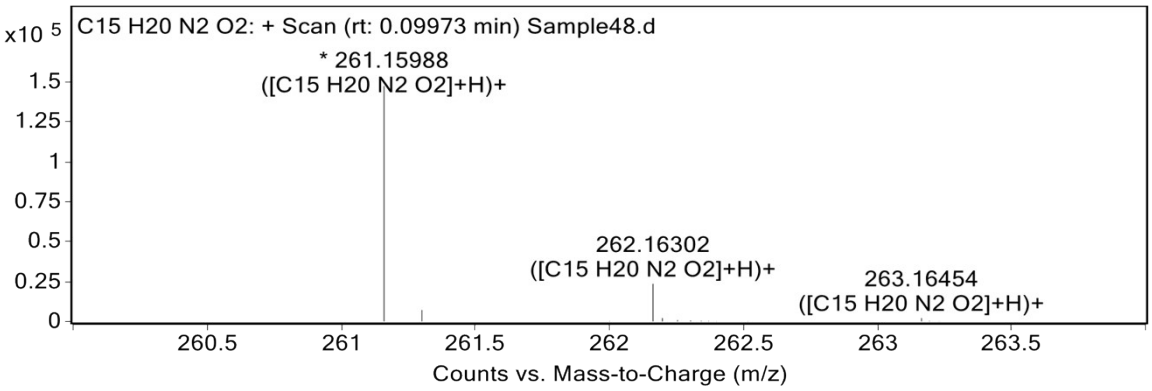
5.15. HRMS spectrum of 6e



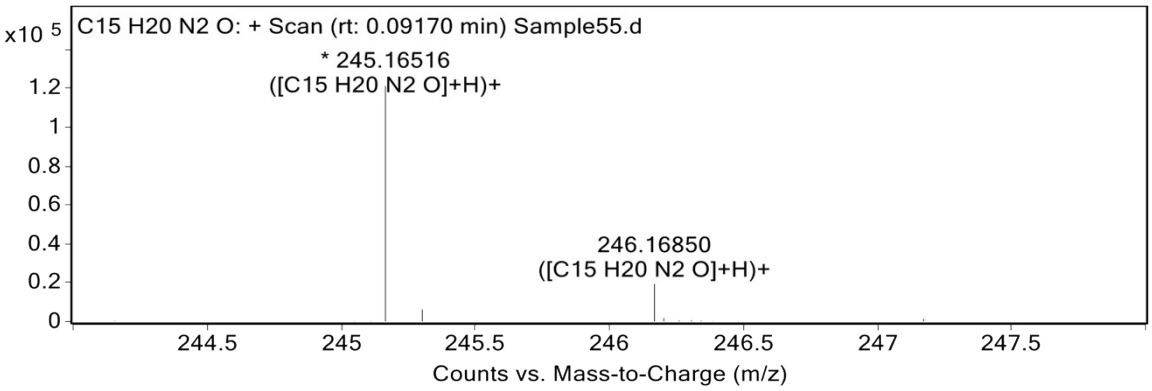
5.16. HRMS spectrum of 6f



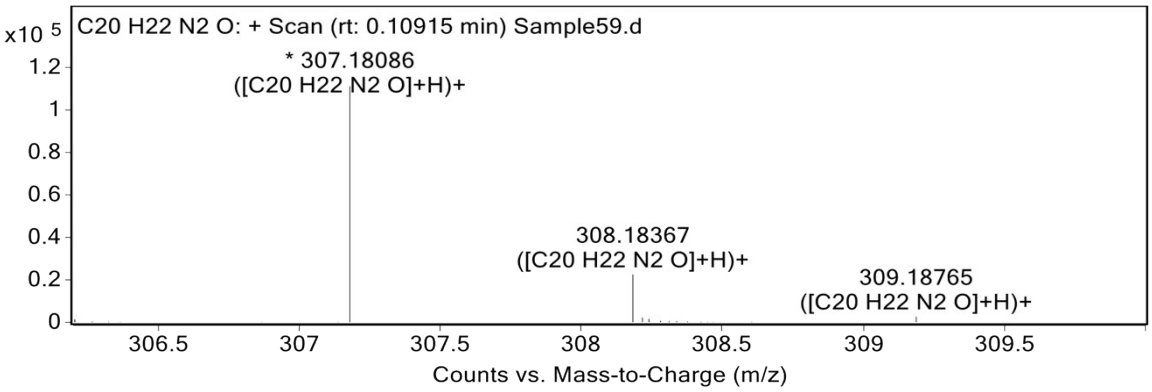
5.17. HRMS spectrum of 6g



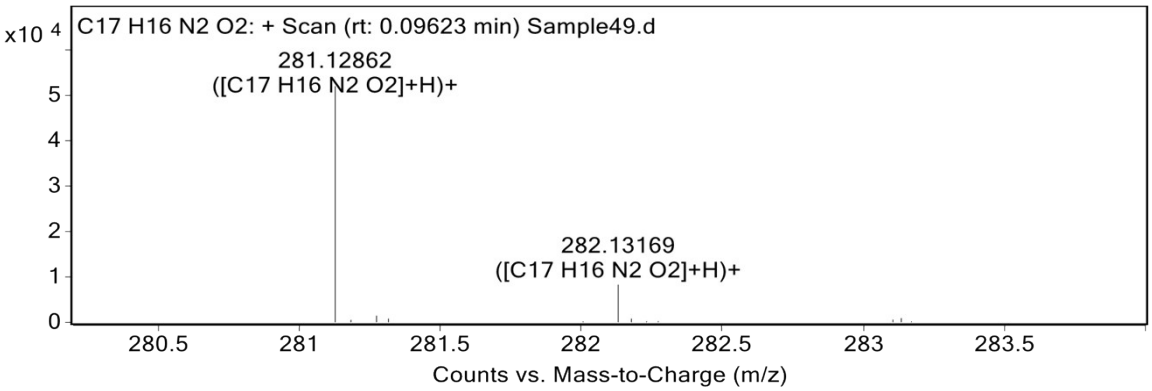
5.18. HRMS spectrum of 6h



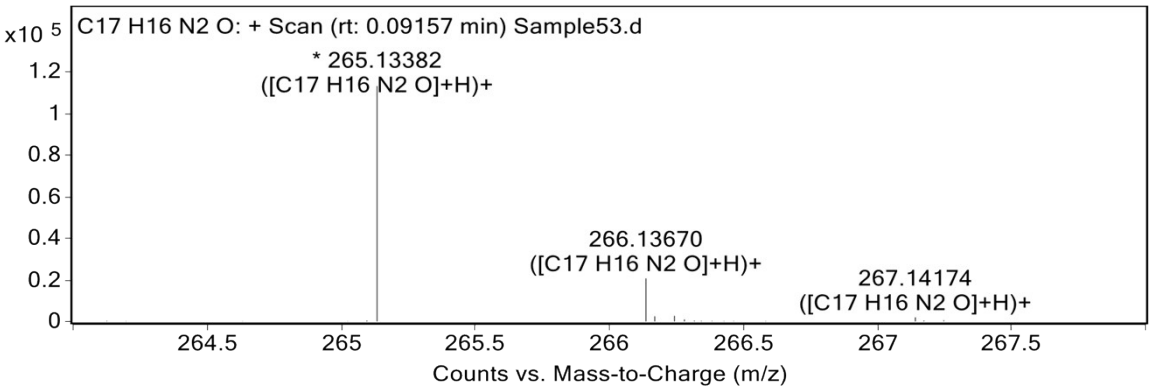
5.19. HRMS spectrum of 6i



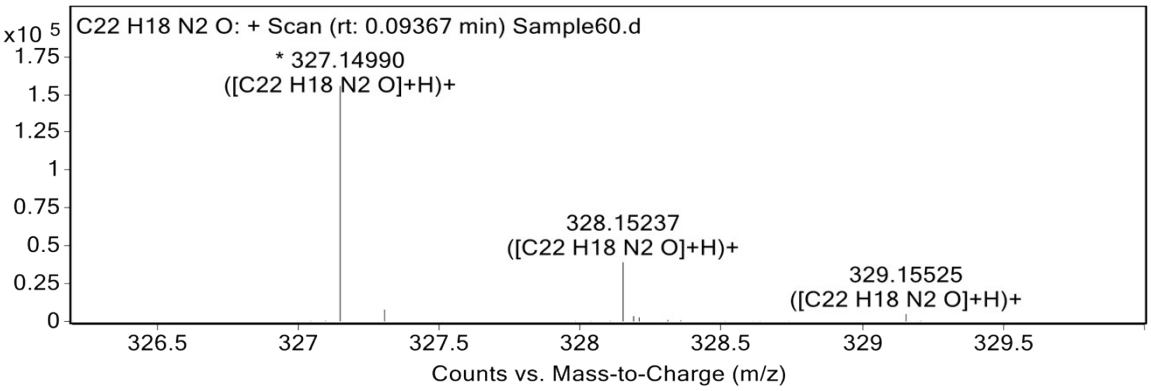
5.20. HRMS spectrum of 6j



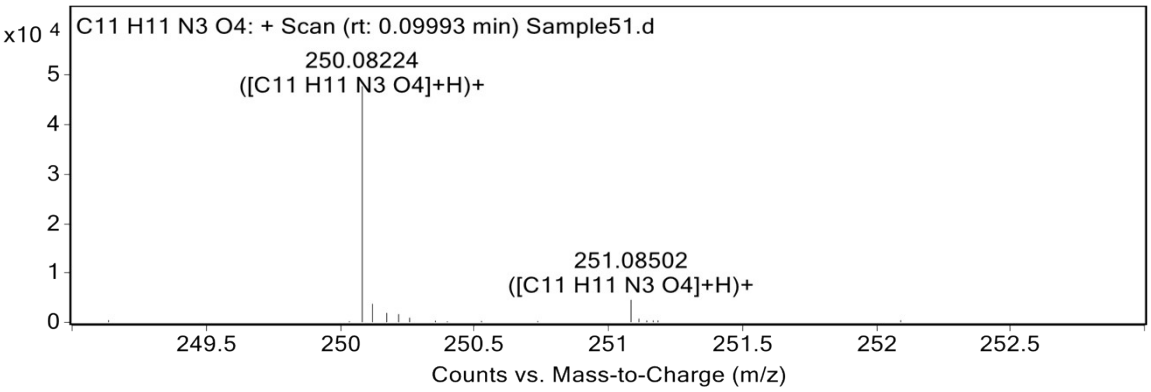
5.21. HRMS spectrum of 6k



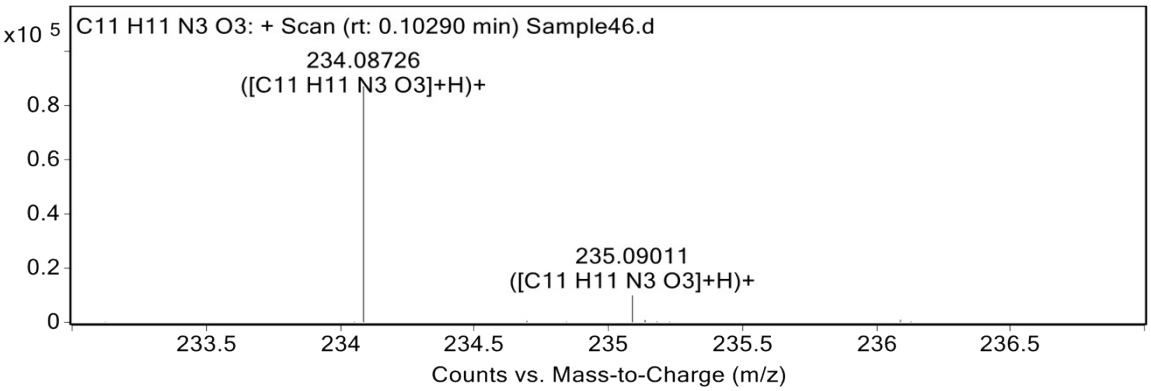
5.22. HRMS spectrum of 6l



5.23. HRMS spectrum of 6m



5.24. HRMS spectrum of 6n



5.25. HRMS spectrum of 6o