Electronic Supplementary Information

Biomass-involved, facile and one-pot synthesis of N-aryl-2(3*H*)-benzoxazolones from methyl 3-dehydroshikimiate

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Contents

I- General Details

(-)-Shikimic acid was kindly provided as a natural product by Guangxi Wan Shan Spice Co. Ltd. with chromatography grade. (-)-Methyl 3-dehydroshikimate was readily prepared from (-)-shikimic acid through an improved strategy of our previous report. Petroleum ether (PE) used in the experiments refers to the boiling fraction of 60-90 °C. Other reagents and solvents were purchased from commercial sources and

used without further purification unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC). Column chromatography was performed on silica gel (200-300 mesh) using EtOAc-PE system as eluent. Melting points were measured on a Thiele apparatus and were uncorrected. Microwave experiments were carried out with a scientific WBFY microwave reactor in a flask connected with a condenser under atmosphere pressure. (This microwave reactor was a monomode device with a tunable power controller from 80 W to 800 W). Reaction temperature was detected using an infrared thermometer and the ramp time is included as part of the reaction time. ^{1}H NMR and ^{13}C NMR spectra were measured on a 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) using CD_3COCD_3 or DMSO-d_6 as the solvent at room temperature. Chemical shifts were reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference. HRMS spectra were recorded on a LC-Q-TOF (ESI) apparatus. Mass spectrometry were measured on a Shimadzu GC-MS QP5050A in electron ionization mode and a Thermo Finnigan LCQ DECA XP ion trap mass spectrometer in electrospray ionization mode.

II- Experimental Procedure

II-1 Synthesis of (-)-methyl 3-dehydroshikimate (3-MDHS)

Based on our previous studies, an improved method for the synthesis of (-)-methyl 3-dehydroshikimate has been established as follows:

Step 1:

To a solution of (-)-shikimic acid (17.4 g, 100 mmol) in MeOH (150 ml) was added *p*-TsOH (1.90 g, 10 mmol). The resulting mixture was heated to reflux until completion of the reaction (monitored by TLC). The mixture was filtered and the filtrate was evaporated under reduced pressure to afford a pale yellow oil, which was purified by recrystallization from EtOAc to give (-)-methyl shikimate as a white powder**.**

Step 2:

To a mixture of (-)-methyl shikimate (9.40 g, 0.05 mol) in THF (220 ml) was added IBX (16.8 g, 0.06 mol). The resulting mixture was stirred at 10-20 °C for the completion of the reaction (monitored by TLC). The iodosylbenzoic acid (IBA) byproduct was filtered off and recycled via oxidation into IBX with oxone. The filtrate was concentrated under reduced pressure to afford crude (-)-methyl 3-dehydroshikimate as a white solid. The crude product was recrystallized from EtOAc to give methyl 3-dehydroshikimiate (3-MDHS) in pure form as white crystals.

II-2 General procedure for the preparation of compound 4a (Table 1, entries 1-9)

To a solution of methyl 3-MDHS (0.19 g, 1 mmol), arylamine (1.0 mmol) in solvent (5 ml) was added *p*-TsOH (0.10 mmol). The flask was then placed into the microwave reactor and the mixture was irradiated with stirring for indicated minutes (t_1) at T_1 ºC. Then, Et_3N (6 mmol) was added to the mixture, and BTC (1.5 mmol) in CH_3CN (3 ml) was added dropwise. The mixture was stirred for the indicated hours (t_2) at room temperature. After completion of the reaction as indicated by TLC, the mixture was washed with sodium carbonate solution (50 ml, 5 %) and extracted with ethyl acetate (3 × 50 ml). The combined organic layers was dried over anhydrous $MgSO_4$ and concentrated under vacuum to furnish the crude product, which could be further purified by recrystallization from EtOAc-PE.

II-3 General procedure for the preparation of compound 4a-4m and 4q-4x (Table 2, entry 1-13, 17-21 and Scheme 2)

To a solution of 3-MDHS (0.19 g, 1.0 mmol), arylamine (1.0 mmol) in CH_3CN (5 ml) was added *p*-TsOH (0.05 mmol). The flask was then placed into the microwave reactor and the mixture was refluxed (240 W) with stirring for indicated minutes (t_1). Then, BTC (1.5 mmol) was added and the resulting mixture was refluxed (240 W) for the indicated minutes (t_2). After completion of the reaction as indicated by TLC, the reaction mixture was poured into sodium carbonate solution (50 ml, 5 %) and stirred vigorously. The resulting solid was filtered and dried to furnish the desired product in pure form. The isolated products could be further purified by recrystallization from EtOAc-PE or by column chromatography using EtOAc-PE as eluent if necessary.

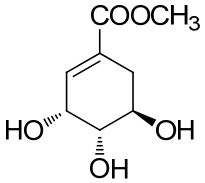
II-4 Procedure for the preparation of compounds 4n and 4o (Table 2, entry 14-15)

To a solution of 3-MDHS (0.19 g, 1 mmol), arylamines (1.0 mmol) in CH_3CN (5 ml) was added *p*-TsOH (0.10 mmol). The flask was then placed into the microwave reactor and the mixture was refluxed (240 W) with stirring for indicated minutes (t_1). Then, BTC (1.5 mmol) was added and the resulting mixture was refluxed (240 W) with stirring for the indicated minutes (t_2). After completion of the reaction as indicated by TLC, the reaction mixture was washed with sodium carbonate solution (50 ml, 5 %) and extracted with ethyl acetate (3 × 50 ml). The combined organic layers was dried over anhydrous $MgSO_4$ and concentrated under vacuum to furnish the crude product, which was purified by column chromatography on silica gel (200-300 mesh) using EtOAc-PE (1: 6) as eluent to afford 4n and 4o in pure form.

II-5 General procedure for the preparation of compound Ⅰ (Scheme 3)

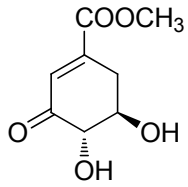
To a solution of 3-MDHS (0.19 g, 1.0 mmol), 2-amino-4-chlorobenzoic acid (0.17 g, 1.0 mmol) in CH_3CN (5 ml) was added *p*-TsOH (0.05 mmol). The flask was then placed into the microwave reactor and the mixture was refluxed (240 W) with stirring for 10 minutes. Then, Et_3N (6 mmol) was added to the mixture, and BTC (1.5 mmol) in CH_3CN (3 ml) was added dropwise. The mixture was stirred for 3 hours at room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was poured into sodium carbonate solution (50 ml, 5 %) and stirred vigorously. The resulting solid was filtered and dried to furnish the desired product in pure form. The isolated products could be further purified by recrystallization from EtOAc-PE.

Ⅲ-1 Characterization Data for (-)-methyl shikimate and 3-MDHS



(-)-Methyl shikimate

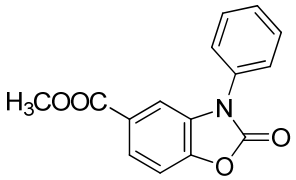
White solid, (yield: 16 g, 85 %). m.p.112~113 ℃; $[\alpha]_D^{20}$ = -142°(c = 0.2, MeOH)； ^{1}H NMR (CD_3COCD_3, 400 MHz) δ: 6.73 (m, 1H, 2-H)，4.38 (m, 1H, 3-H), 4.02 (s, 1H, 4-OH D_2O exchangeable), 4.00 (brs, 2H, 3,5-OH D_2O exchangeable), 3.69 (s, 3H, OCH_3), 3.85 (m, 1H, 5-H), 3.68 (m, 1H, 4-H), 2.64 (dd, *J* = 17.6, 4.4 Hz, 1H, 6α-H), 2.18 (dd, *J* = 17.6, 6.8 Hz, 1H, 6β-H); MS (EI): m/z = 188 $[M]^+$, 170 $[M - H_2O]^+$, 157 $[M - OCH_3]^+$, 129 $[M - COOCH_3]^+$.



(-)-Methyl-3-dehydroshikimate (3-MDHS)

White solid, (yield: 6.70 g, 72 %). m.p.122~123 °C; $[\alpha]_D^{20}$ = -55° (c = 0.2, MeOH) ^{1}H NMR (CD_3COCD_3, 400 MHz) δ: 6.45 (d, *J* = 2.8 Hz, 1H, 2-H)，4.57 (d, *J* = 3.6 Hz, 1H, 4-OH D_2O exchangeable), 4.47 (d, *J* = 3.6 Hz, 1H, 5-OH D_2O exchangeable), 4.57 (dd, *J* = 10.4, 3.6 Hz, 1H, 4-H), 3.85 (m, 1H, 5-H), 3.81 (s, 3H, OCH_3), 3.06 (dd, *J* = 18.4, 5.2 Hz, 1H, 6α-H), 2.18 (ddd, *J* = 18.4, 8.8, 3.2 Hz, 1H, 6β-H); MS (EI): m/z = 186 $[M]^+$, 155 $[M - OCH_3]^+$, 127 $[M - COOCH_3]^+$

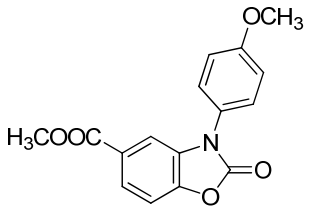
Ⅲ-2 Characterization Data for products



5-methoxycarbonyl-3-phenyl-2(3*H*)-benzoxazolone (**4a**).

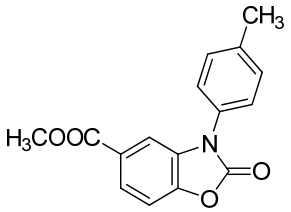
White flake crystal; yield: 0.25 g (92 %); mp 138-140 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.85 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.63 (d, *J* = 4.0 Hz, 4H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.53 (m, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.3 (C=O), 145.6, 132.8, 131.7, 129.9, 128.8, 125.8,

125.5, 124.9, 110.2, 109.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3050, 2988, 2950, 1777, 1709, 1620, 1596, 1505, 1467, 1380, 1284, 1246, 761, 691; MS (EI): m/z (%) = 269 ([M]$^+$, 100), 238 ([M - OCH_3]$^+$, 94), 210 ([M - $COOCH_3$]$^+$, 15), 194 (18), 166 (16); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_4$: 270.0761; found: 270.0763.



5-methoxycarbonyl-3-(4-methoxyphenyl)-2(3*H*)-benzoxazolone (**4b**).

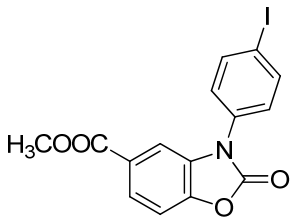
White crystal; yield: 0.28 g (95 %); mp.124-126 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.54-7.57 (m, 3H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.16 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.5 (C=O), 159.4 (C=O), 152.6, 145.5, 132.3, 127.6, 125.5, 125.1, 124.7, 115.1, 110.1, 109.1, 55.5, 52.3; MS (EI): m/z (%) = 299 ([M]$^+$, 100), 284 ([M - CH_3]$^+$, 7), 268 ([M - OCH_3]$^+$, 18), 240 ([M - $COOCH_3$]$^+$, 14), 196 (7); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_5$: 300.0866; found: 300.0874.



5-methoxycarbonyl-3-(4-methylphenyl)-2(3*H*)-benzoxazolone (**4c**).

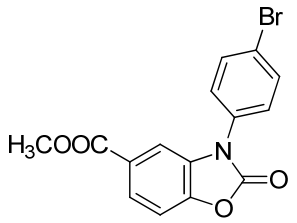
White acicular crystal; yield: 0.26 g (93 %); mp 147-149 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.4 (C=O), 145.5, 138.6, 131.9, 130.3, 130.1, 125.7, 125.5, 124.8, 110.1, 109.2, 52.3, 20.7; IR (KBr) ν_{max}/cm^{-1} 3120, 3095, 3002, 2954, 2924, 1780, 1733, 1609, 1521, 1490, 1452, 1388, 1289, 1248,

835; MS (EI): m/z (%) = 283 ($[M]^+$, 100), 252 ($[M - OCH_3]^+$, 48), 224 ($[M - COOCH_3]^+$, 6), 180 (18), 152 (4); HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0921.



3-(4-iodophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4d**).

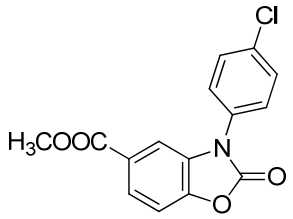
Grey solid; yield: 0.34 g (87 %); mp 169-171 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.1 (C=O), 145.6, 138.7, 132.6, 131.3, 127.8, 125.5, 125.0, 110.2, 109.3, 94.7, 52.3; IR (KBr) ν_{max}/cm^{-1} 3112, 3083, 3059, 2964, 1776, 1713, 1618, 1497, 1458, 1422, 1382, 1290, 1250, 1199, 1004, 824; MS (EI): m/z (%) = 395 ($[M]^+$, 100), 364 ($[M - OCH_3]^+$, 38), 182 (16), 153 (13); HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}INO_4$: 395.9727; found: 395.9730.



3-(4-bromophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4e**).

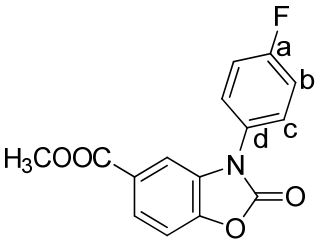
White solid; yield: 0.30 g (87 %); mp 168-170 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.83-7.88 (m, 3H), 7.62 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.1 (C=O), 145.5, 132.9, 132.1, 131.4, 127.9, 125.6, 125.0, 121.6, 110.2, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3102, 3069, 2992, 2838, 1776, 1727, 1619, 1498, 1459, 1401,

1382, 1281, 1237, 1149, 1005, 829; MS (EI): m/z (%) = 349 ($[M + 2]^+$, 94), 347 ($[M]^+$, 100), 318 (53), 316 ($[M - OCH_3]^+$, 55); HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}Br^{79}NO_4$: 347.9866; found: 347.9862.



3-(4-chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4f**).

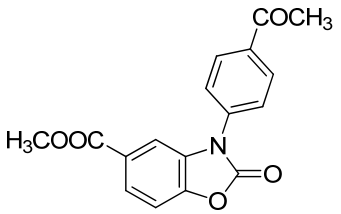
White acicular crystal; yield: 0.26 g (85 %); mp 144-146 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.66-7.72 (m, 4H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.1 (C=O), 145.5, 133.2, 131.7, 131.4, 129.9, 127.6, 125.5, 125.0, 110.2, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3096, 3057, 2994, 2946, 2888, 2839, 1781, 1710, 1623, 1502, 1460, 1434, 1409, 1385, 1284, 1242, 1107, 1006, 837; MS(EI): m/z (%) = 305 ($[M + 2]^+$, 33), 303 ($[M]^+$, 100), 272 ($[M - OCH_3]^+$, 62), 244 ($[M - COOCH_3]^+$, 11); HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0364.



3-(4-fluorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4g**).

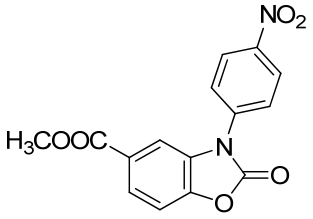
White solid; yield: 0.23 g (79 %); mp > 200 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69-7.73 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46-7.50 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 162.8 (d, $^1J_{CF}$ = 244.7 Hz, C-a), 152.4, 145.5, 131.8, 129.0 (d, $^4J_{CF}$ = 2.6

Hz, C-d), 128.5 (d, $^{3}J_{CF}$ = 9.0 Hz, C-c), 125.5, 124.9, 116.9 (d, $^{2}J_{CF}$= 23.0 Hz, C-b), 110.1, 109.1, 52.3; IR (KBr) ν_{max}/cm^{-1} 3064, 2997, 2953, 2845, 1782, 1707, 1624, 1514, 1459, 1420, 1384, 1285, 1249, 1103, 1008, 844, 765; MS (EI): m/z (%) = 287 ([M]$^{+}$, 100), 256 ([M - OCH_3]$^{+}$, 73), 228 ([M - $COOCH_3$]$^{+}$, 11), 212 (17); HRMS (ESI-TOF): *m/z* [M + H]$^{+}$ calcd for $C_{15}H_{11}FNO_4$: 288.0667; found: 288.0660.



3-(4-acetylphenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4h**).

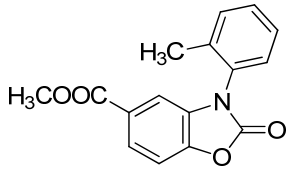
Gray solid; yield: 0.26 g (83 %); mp > 200 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.19 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.1 (C=O), 165.4 (C=O), 152.0 (C=O), 145.6, 136.8, 136.4, 131.1, 129.8, 125.6, 125.4, 125.2, 110.3, 109.5, 52.4, 26.8; IR (KBr) ν_{max}/cm^{-1} 3012, 2961, 2857, 1778, 1711, 1678, 1600, 1514, 1490, 1451, 1380, 1294, 1264, 1091, 1006, 844, 766; MS (EI): m/z (%) = 311 ([M]$^{+}$, 54), 296 ([M - CH_3]$^{+}$, 100), 280 ([M - OCH_3]$^{+}$, 12); HRMS (ESI-TOF): *m/z* [M + H]$^{+}$ calcd for $C_{17}H_{14}NO_5$: 312.0866; found: 312.0864.



5-methoxycarbonyl-3-(4-nitrophenyl)-2(3*H*)-benzoxazolone (**4i**).

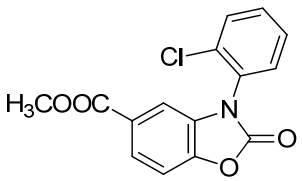
Yellow solid; yield: 0.25 g (80 %); mp > 200 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.48 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.96 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.90 (dd, *J* = 8.4, 1.6 Hz,

1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 151.8 (C=O), 146.5, 145.7, 138.6, 130.7, 126.2, 125.7, 125.5, 125.2, 110.4, 109.7, 52.4; IR (KBr) ν_{max}/cm^{-1} 3122, 3084, 3062, 3003, 2950, 2840, 1788, 1727, 1596, 1523, 1503, 1455, 1380, 1314, 1288, 1263, 1148, 1006, 830, 761; MS (EI): m/z (%) = 314 ([M]$^+$, 100), 283 ([M - OCH_3]$^+$, 94), 255 ([M - $COOCH_3$]$^+$, 6); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{15}H_{10}N_2NaO_6$: 337.0431; found: 337.0432.



5-methoxycarbonyl-3-(2-methylphenyl)-2(3*H*)-benzoxazolone (**4j**).

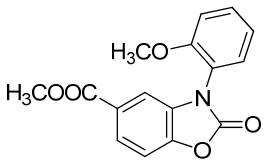
White solid; yield: 0.25 g (89 %); mp 138-140 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50-7.55 (m, 3H), 7.42-7.46 (m, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 3.79 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.1 (C=O), 145.8, 136.0, 132.1, 131.6, 131.0, 130.1, 128.1, 127.6, 125.7, 124.9, 110.3, 109.1, 52.3, 17.0; IR (KBr) ν_{max}/cm^{-1} 3116, 3084, 3056, 3001, 2955, 1777, 1720, 1620, 1499, 1450, 1378, 1354, 1288, 1247, 1145, 1089, 998, 761; MS (EI): m/z (%) = 283 ([M]$^+$, 100), 252 ([M - OCH_3]$^+$, 32), 224 ([M - $COOCH_3$]$^+$, 5); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0920.



3-(2-chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4k**).

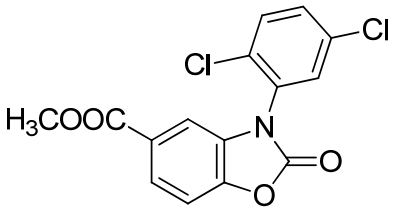
White solid; yield: 0.23 g (76 %); mp 152-154 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.88 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.80-7.85 (m, 2H), 7.60-7.69 (m, 3H), 7.19 (d, *J* =

1.2 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C=O), 151.8 (C=O), 145.6, 132.0, 131.6, 131.5, 130.8, 130.6, 129.6, 129.1, 125.8, 125.2, 110.5, 109.3, 52.3; IR (KBr) ν_{max}/cm^{-1} 3070, 2954, 1782, 1715, 1620, 1587, 1499, 1458, 1382, 1283, 1248, 1091, 1001, 956, 761; MS (EI): m/z (%) = 305 ([M + 2]$^+$, 33), 303 ([M]$^+$, 100), 272 ([M - OCH_3]$^+$, 80), 244 ([M - $COOCH_3$]$^+$, 12); HRMS: (ESI-TOF) *m/z* [M + H]$^+$ calcd. for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0364.



5-methoxycarbonyl-3-(2-methoxyphenyl)-2(3*H*)-benzoxazolone (**4l**).

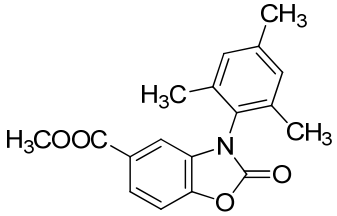
White acicular crystal; yield: 0.27 g (90 %); mp 164-166 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 7.84 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56-7.60 (m, 3H) , 7.33 (d, *J* = 8.4 Hz, 1H), 7.14-7.19 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.7 (C=O), 155.1 (C=O), 152.6, 145.8, 132.3, 131.8, 129.5, 125.9, 125.1, 121.4, 120.4, 113.3, 110.4, 109.7, 56.2, 52.6; IR (KBr) ν_{max}/cm^{-1} 3139, 3081, 3023, 2979, 2956, 2834, 1781, 1731, 1618, 1599, 1510, 1490, 1380, 1289, 1250, 1095, 1019, 759, 743; MS (EI): m/z (%) = 299 ([M]$^+$, 100), 268 ([M - OCH_3]$^+$, 22), 240 ([M - $COOCH_3$]$^+$, 8); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_5$: 300.0866; found: 300.0872.



5-methoxycarbonyl-3-(2,5-dichlorophenyl)-2(3*H*)-benzoxazolone (**4m**).

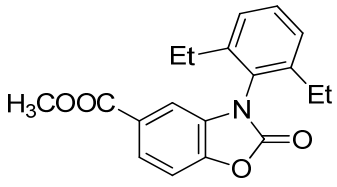
White solid; yield: 0.23 g (69 %); mp 182-184 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.04 (d, *J* = 2.4 Hz, 1H) 7.88 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H) , 7.76 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 3.80

(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C=O), 151.7 (C=O), 145.5, 132.8, 132.1, 132.0, 131.2, 130.9, 130.7, 130.6, 125.9, 125.4, 110.5, 109.7, 52.4; IR (KBr) ν_{max}/cm^{-1} 3121, 3095, 3036, 2997, 2953, 2846, 1770, 1722, 1617, 1568, 1492, 1453, 1409, 1362, 1287, 1253, 1196, 1150, 1100, 1006, 765, 717; MS (EI): m/z (%) = 341 ([M + 4]$^+$, 12), 339 ([M + 2]$^+$, 69), 337 ([M]$^+$, 100), 306 ([M - OCH_3]$^+$, 82), 278 ([M - $COOCH_3$]$^+$, 4); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{15}H_{10}Cl_2{}^{35}NO_4$: 337.9981; found: 337.9976.



5-methoxycarbonyl-3-(2,4,6-trimethylphenyl)-2(3*H*)-benzoxazolone (**4n**).

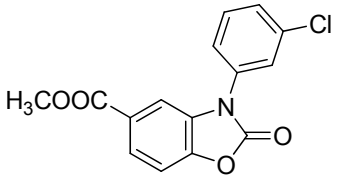
White solid; yield: 0.21 g (67 %); mp 164-166 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.47 (d, *J* = 8.2 Hz, 1H) 7.25 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.98 (s, 2H), 6.60 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 3H), 2.26 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.9 (C=O), 151.2 (C=O), 140.5, 139.5, 136.5, 135.7, 133.8, 129.6, 129.1, 122.9, 117.2, 112.1, 52.1, 20.6, 17.6; IR (KBr) ν_{max}/cm^{-1} 3012, 2951, 2918, 2856, 1781, 1728, 1697, 1612, 1520, 1483, 1444, 1377, 1299, 1207, 1160, 1001, 762; MS (EI): m/z (%) = 311 ([M]$^+$, 33), 285 (100); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_4$: 334.1050; found: 334.1048.



3-(2,6-diethylphenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4o**).

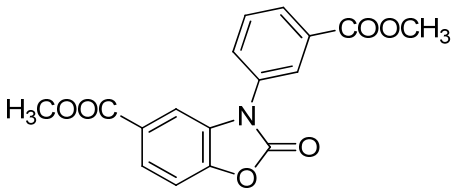
White solid; yield: 0.19 g (60 %); mp 173-175 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.49 (d, *J* = 8.4 Hz, 2H), 7.21-7.28 (m, 3H), 6.63 (d, *J* = 1.6 Hz, 1H), 3.71 (s, 3H),

2.46-2.52 (m, 4H), 1.01 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.8 (C=O), 151.2 (C=O), 142.7, 140.3, 140.1, 135.3, 128.5, 127.4, 126.7, 122.9, 117.1, 112.4, 52.1, 23.9, 14.5; IR (KBr) ν_{max}/cm^{-1} 3067, 3030, 2963, 2875, 1781, 1731, 1693, 1611, 1520, 1444, 1373, 1209, 1160, 1115, 1000, 798, 762, 716; MS (EI): m/z (%) = 325 ([M]$^+$, 20), 299 (100), 294 ([M - OCH_3]$^+$, 8), 266 ([M - $COOCH_3$]$^+$, 10); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{19}H_{19}NNaO_4$: 348.1206; found: 348.1207.



3-(3-chlorophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4q**).

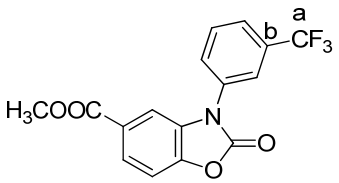
White solid; yield: 0.25 g (84 %); mp 145-147 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.86 (dd, J = 8.4, 1.6 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.58-7.70 (m, 4H), 7.47 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.2 (C=O), 145.5, 134.1, 133.9, 131.5, 131.4, 128.9, 126.0, 125.6, 125.1, 124.6, 110.3, 109.3, 52.4; IR (KBr) ν_{max}/cm^{-1} 3125, 3093, 3063, 2959, 1798, 1725, 1623, 1594, 1496, 1459, 1437, 1383, 1293, 1265, 1149, 1094, 1008, 868, 783, 709; MS (EI): m/z (%) = 305 ([M + 2]$^+$, 33), 303 ([M]$^+$, 100), 272 ([M - OCH_3]$^+$, 84), 244 ([M - $COOCH_3$]$^+$, 11); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. for $C_{15}H_{11}Cl^{35}NO_4$: 304.0371; found: 304.0367.



5-methoxycarbonyl-3-(3-(methoxycarbonyl)phenyl)-2(3*H*)-benzoxazolone (**4r**).

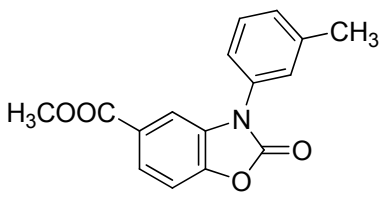
White solid; yield: 0.25 g (76 %); mp > 200 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.21 (s, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 0.8 Hz, 1H), 7.87(dd, J = 8.4, 1.6

Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 1.2 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 165.3 (C=O), 152.3 (C=O), 145.6, 133.3, 131.6, 131.3, 130.5, 130.5, 129.3, 126.6, 125.5, 125.0, 110.2, 109.1, 52.5, 52.3; IR (KBr) ν_{max}/cm^{-1} 3095, 3077, 3060, 3005, 2958, 2845, 1779, 1713, 1623, 1587, 1492, 1349, 1281, 1243, 1110, 1016, 890, 755, 697; MS (EI): m/z (%) = 327 ([M]$^+$, 100), 296 ([M - OCH_3]$^+$, 82), 268 ([M - $COOCH_3$]$^+$, 4); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{13}NaO_6$: 350.0635; found: 350.0640.



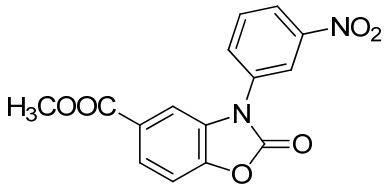
3-(3-(trifluoromethyl)phenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4s**).

White solid; yield: 0.25 g (75 %); mp 128-130 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.86-7.93 (m, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.2 (C=O), 145.5, 133.7, 131.4, 131.2, 130.6 (q, $^2J_{CF}$ = 32.1 Hz, C-b), 130.0, 125.6, 125.5 (q, $^3J_{CF}$ = 3.4 Hz), 125.1, 123.0 (q, $^3J_{CF}$ = 3.4 Hz), 122.2 (q, $^1J_{CF}$ = 271.2 Hz, C-a), 110.2, 109.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3086, 3056, 3018, 2964, 1787, 1720, 1625, 1503, 1460, 1435, 1387, 1329, 1294, 1260, 1182, 1116, 882, 765, 700; MS (EI): m/z (%) = 337 ([M]$^+$, 90), 306 ([M - OCH_3]$^+$, 100), 278 ([M - $COOCH_3$]$^+$, 15); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{10}F_3NNaO_4$: 360.0454; found: 360.0460.



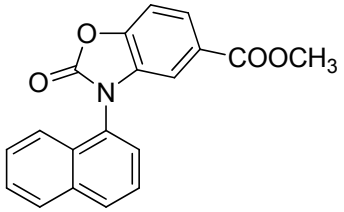
5-methoxycarbonyl-3-(3-methylphenyl)-2(3*H*)-benzoxazoone (**4t**).

White solid; 0.26 g (93 %); mp 114-116 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 8.0 Hz 1H), 7.40-7.44 (m, 3H), 7.35 (d, J = 7.6 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.4 (C=O), 152.3 (C=O), 145.5, 139.6, 132.6, 131.7, 129.7, 129.5, 126.2, 125.5, 124.9, 122.8, 110.1, 109.2, 52.3, 20.8; IR (KBr) ν_{max}/cm^{-1} 3073, 3002, 2955, 2924, 2848, 1776, 1712, 1623, 1606, 1590, 1499, 1457, 1384, 1283, 1247, 1087, 999, 887, 763, 702; MS (EI): m/z (%) = 283 ([M]$^+$, 100), 252 ([M - OCH_3]$^+$, 54), 224 ([M - $COOCH_3$]$^+$, 7); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{16}H_{14}NO_4$: 284.0917; found: 284.0920.



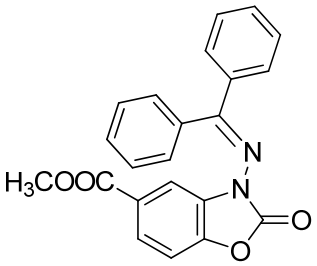
3-(3-nitrophenyl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4u**).

Yellow solid; 0.26 g (82 %); mp > 200 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.53 (t, J = 2.0 Hz, 1H), 8.35-8.39 (m, 1H), 8.12-8.15 (m, 1H), 7.93 (t, J = 8.0 Hz, 1H), 7.88 (dd, J = 8.4, 1.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.7 (C=O), 152.4 (C=O), 148.7, 145.8, 134.1, 132.5, 131.6, 131.4, 125.8, 125.5, 123.7, 121.2, 110.5, 109.6, 52.6; IR (KBr) ν_{max}/cm^{-1} 3132, 3102, 2999, 2952, 1780, 1710, 1621, 1536, 1494, 1439, 1373, 1297, 1258, 1151, 1094, 885, 767, 701; MS (EI): m/z (%) = 314 ([M]$^+$, 100), 283 ([M - OCH_3]$^+$, 90), 255 ([M - $COOCH_3$]$^+$, 6); HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{15}H_{10}N_2NaO_6$: 337.0431; found: 337.0431.

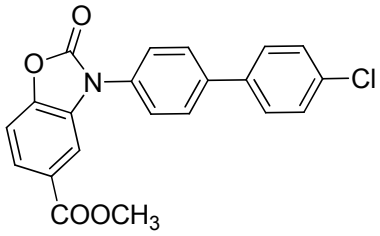


5-methoxycarbonyl-3-(naphthalen-1-yl)-2(3*H*)-benzoxazolone (**4v**).

Yellow solid; 0.26 g (80 %); mp 120-122 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.23 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.87-7.91 (m, 2H), 7.73-7.80 (m, 2H), 7.65-7.69 (m, 2H), 7.57-7.61 (m, 1H), 7.02 (d, J = 1.2 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C=O), 152.8 (C=O), 146.0, 134.1, 132.9, 130.4, 129.0, 128.7, 128.5, 127.7, 127.1, 126.8, 126.1, 125.6, 124.9, 122.2, 110.3, 109.1, 52.2; IR (KBr) ν_{max}/cm^{-1} 3058, 3000, 2953, 2846, 1790, 1723, 1621, 1599, 1511, 1492, 1455, 1373, 1291, 1247, 1148, 1047, 800, 773; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{19}H_{14}NO_4$: 320.0917; found: 320.0922.

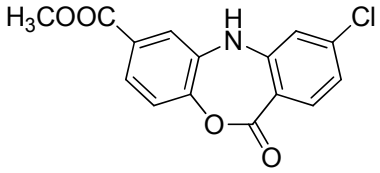


3-((diphenylmethylene)amino))-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4w**). White solid; 0.29 g (78 %); mp 119-121 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.82 (dd, J = 8.4, 1.6 Hz, 1H), 7.66-7.74 (m, 4H), 7.53-7.57 (m, 2H), 7.40-7.57 (m, 4H), 7.29-7.31 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 178.6 (C=O), 165.4 (C=O), 147.7, 144.1, 135.3, 133.6, 132.6, 130.5, 130.2, 129.5, 128.7, 128.5, 127.7, 125.9, 124.9, 110.2, 109.7, 52.3; IR (KBr) ν_{max}/cm^{-1} 3056, 3032, 3007, 2957, 2848, 1787, 1717, 1620, 1560, 1490, 1460, 1366, 1288, 1244, 1093, 1003, 763, 695; MS (EI): m/z (%) = 372 ([M]$^+$, 28), 341 ([M - OCH_3]$^+$, 4), 180 (100); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{22}H_{17}N_2O_4$: 373.1183; found: 373.1185.



3-(4'-chloro-[1,1'-biphenyl]-4-yl)-5-methoxycarbonyl-2(3*H*)-benzoxazolone (**4x**). White solid; 0.34 g (90 %); mp 187-189 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.94

(d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.75(d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: ppm 165.5 (C=O), 152.4 (C=O), 145.6, 139.1, 137.8, 132.9, 132.4, 131.6, 129.0, 128.7, 128.1, 126.3, 125.6, 125.0, 110.3, 109.3, 52.4; IR (KBr) ν_{max}/cm^{-1} 3042, 2960, 1786, 1719, 1620, 1522, 1490, 1459, 1383, 1286, 1241, 1092, 1007, 810, 762; HRMS: (ESI-TOF) *m/z* [M + H]$^+$ calcd. for $C_{21}H_{15}ClNO_4$: 380.0684; found: 380.0681.

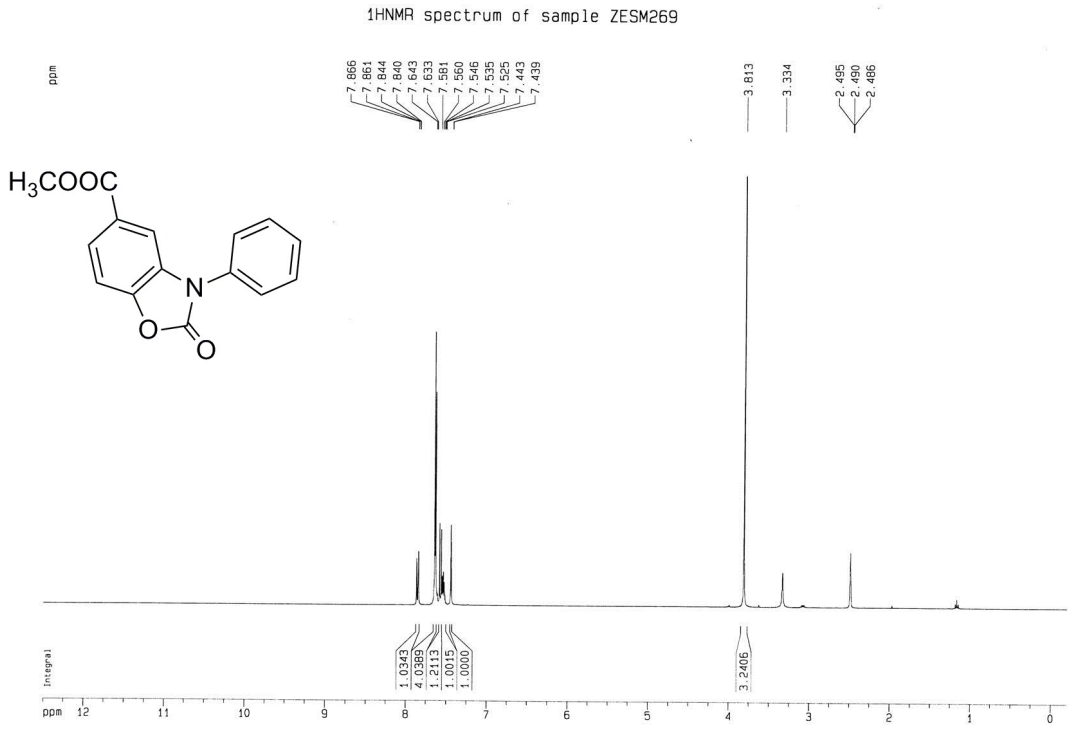


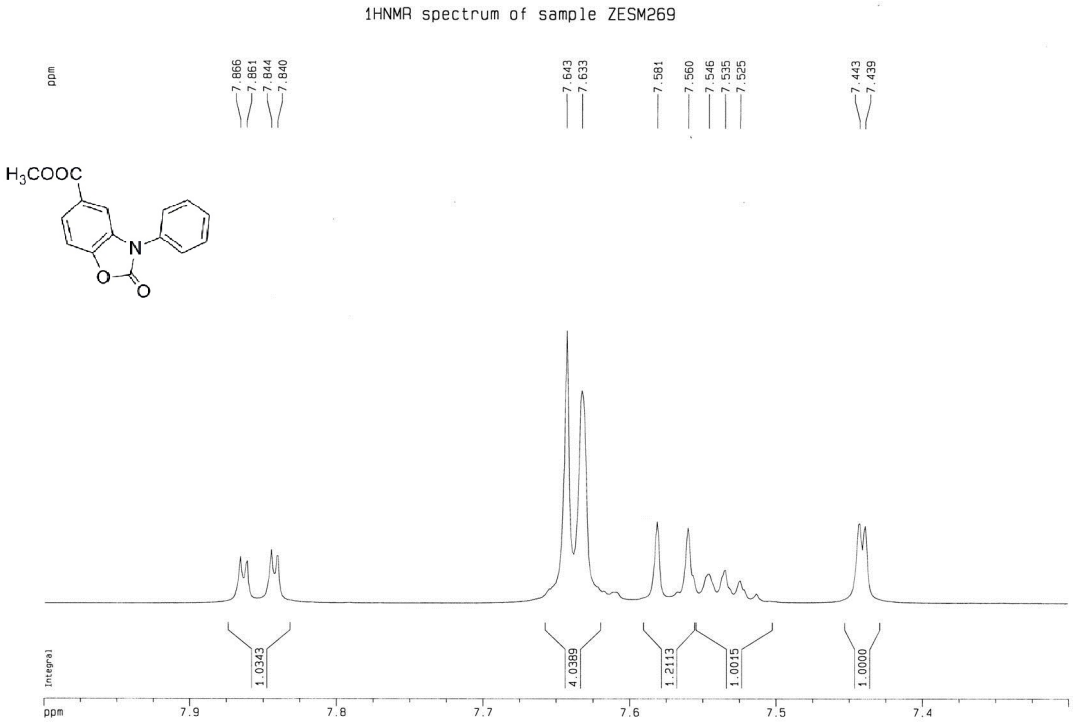
Methyl-3-chloro-11-oxo-5,11-dihydrodibenzo[b,e][1,4]oxazepine-7-carboxylate(Ⅰ).

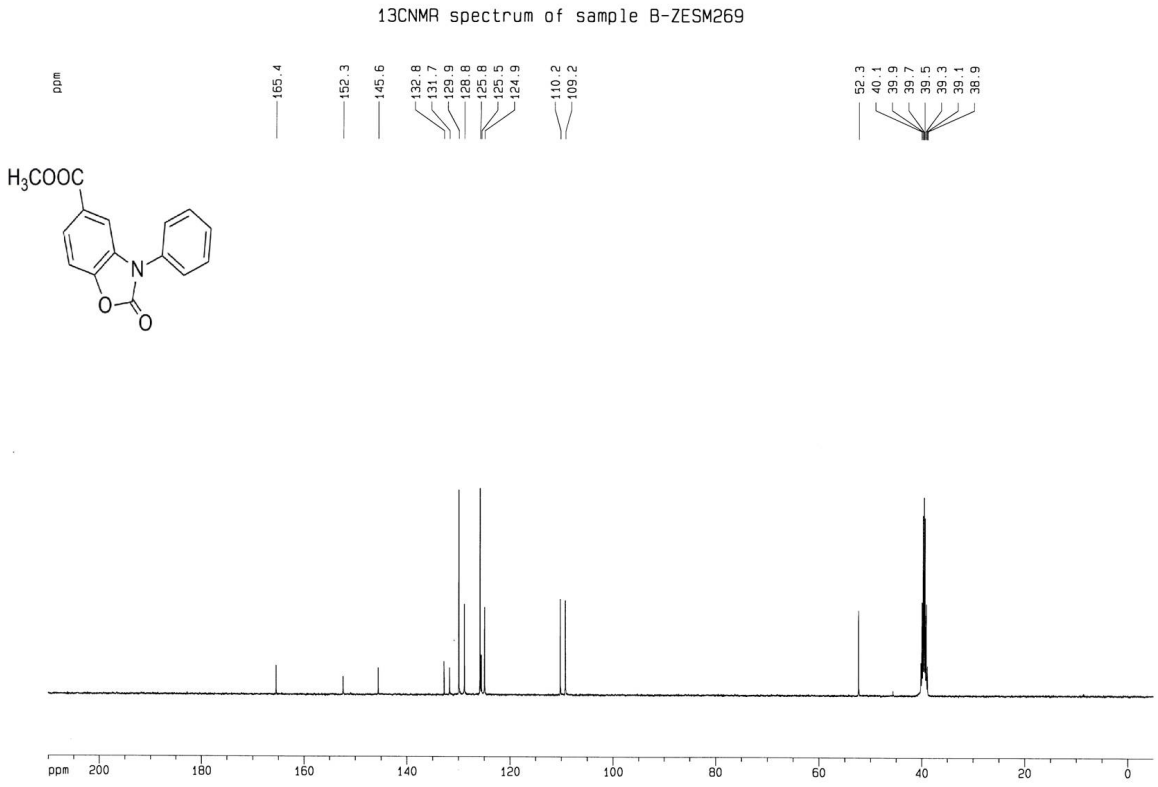
Yellow solid; 0.25 g (82 %); mp ＞200 ℃; ^{1}HNMR (400 MHz, DMSO-*d*$_6$) : δ = 9.33 (s, 1H), 7.87 (d, *J* = 8.8 Hz , 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz ,1H), 7.24 (d, *J* = 2.0 Hz ,1H), 6.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.84 (s, 3H) ; ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: ppm 165.1 (C=O), 163.3 (C=O), 149.6, 145.1, 139.8, 136.7, 136.3, 127.5, 125.1, 122.5, 121.2, 120.5, 118.4, 114.2, 52.3; IR (KBr) ν_{max}/cm^{-1} 3313, 3079, 3038, 3010, 2963, 2921, 1725, 1698, 1617, 1600, 1536, 1509, 1477, 1436, 1409, 1281, 1211, 1025, 1021, 766; MS (EI): m/z (%) = 303 ([M]$^+$, 16), 272 ([M - OCH_3]$^+$, 36), 244 ([M - $COOCH_3$]$^+$, 22); HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{15}H_{11}ClNO_4$: 304.0371; found: 304.0366.

Ⅳ ^{1}H-NMR and ^{13}C-NMR spectra of compounds 4a -4x and Ⅰ

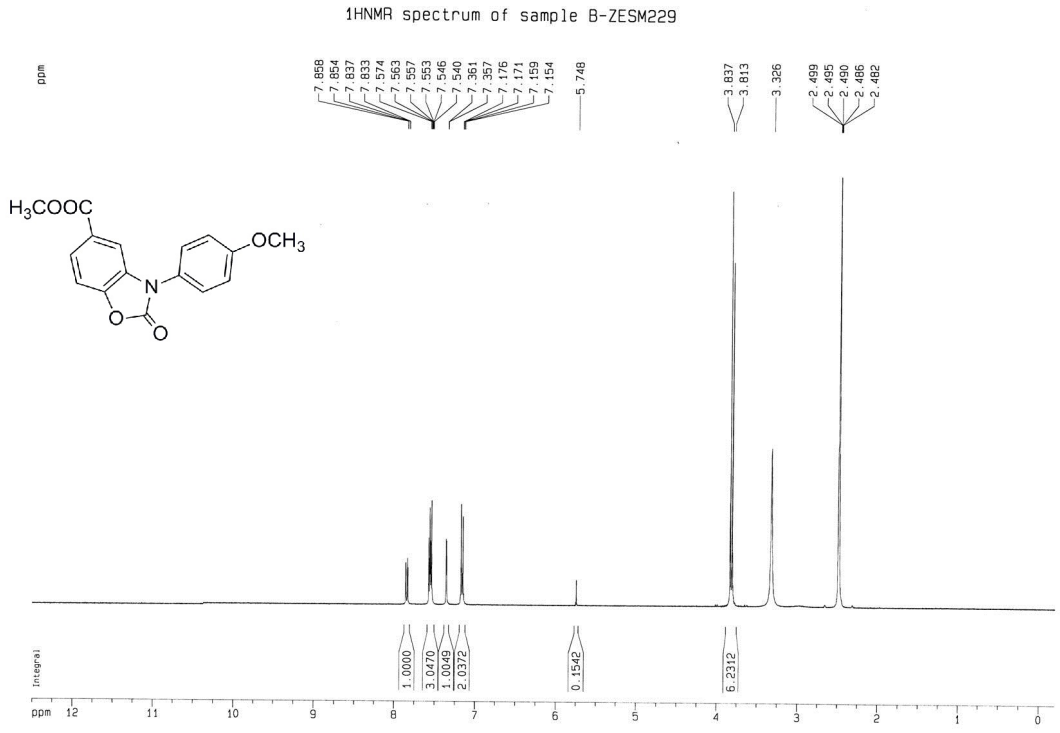
[^{1}H NMR and ^{13}C NMR spectrum of 4a in DMSO-d_6]



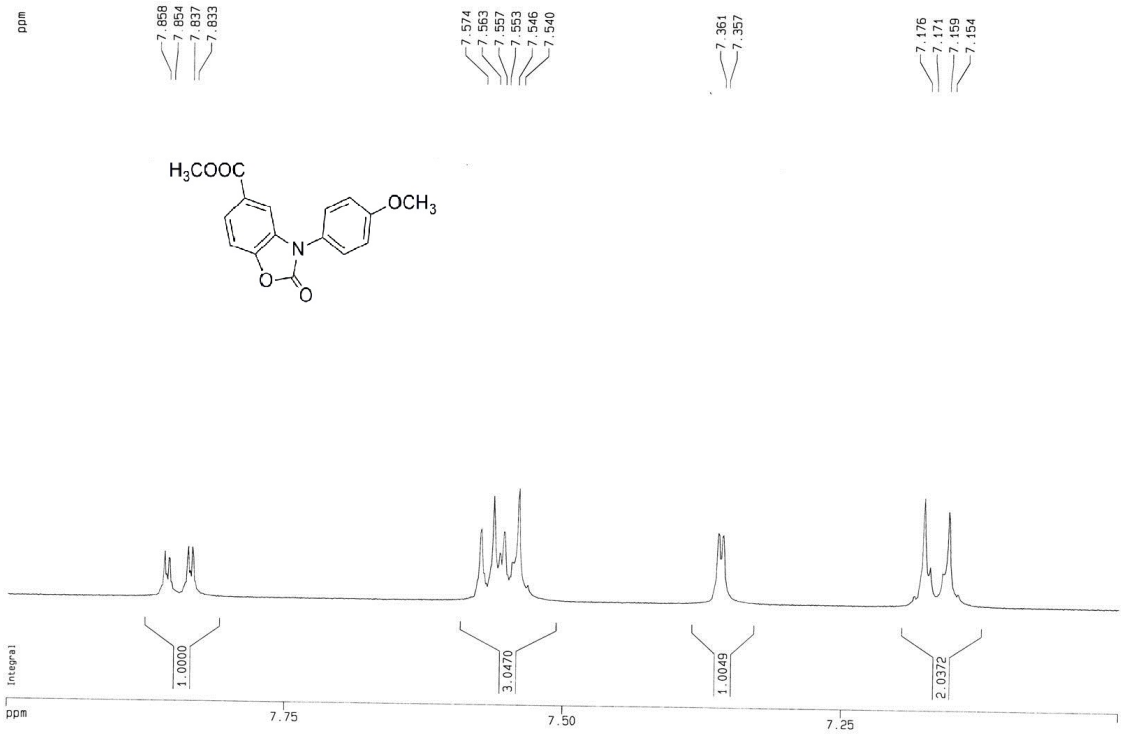




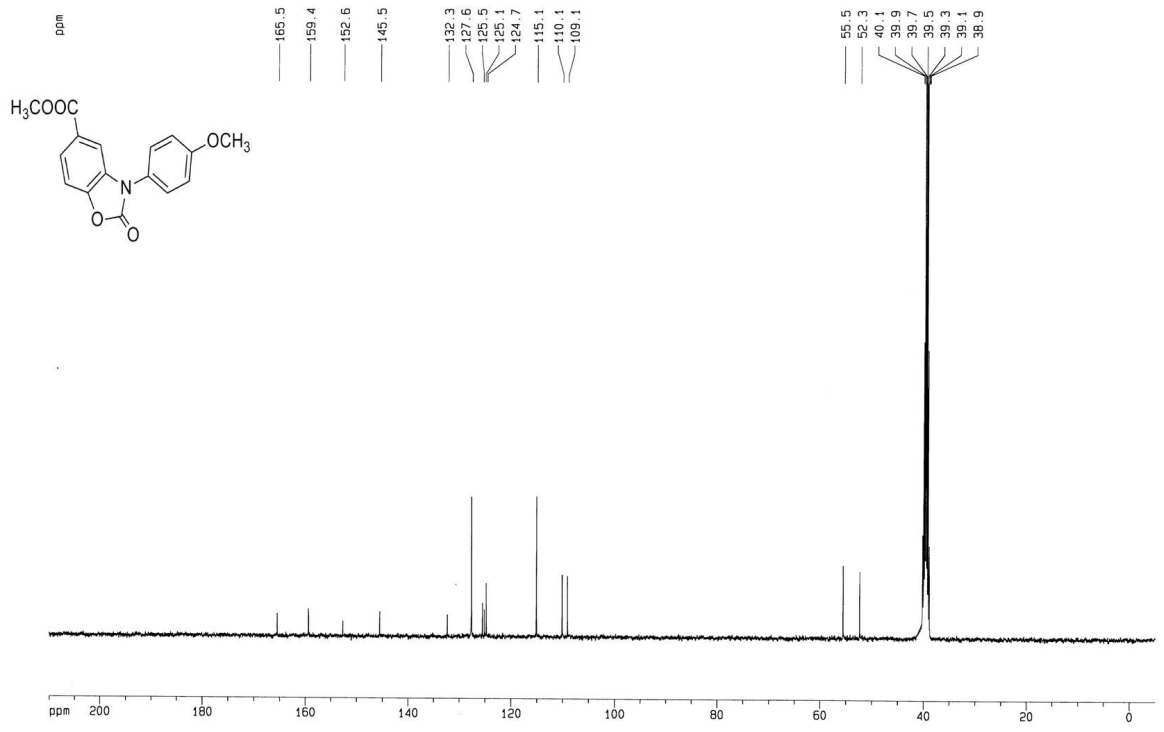
[^{1}H NMR and ^{13}C NMR spectrum of 4b in DMSO-d_6]



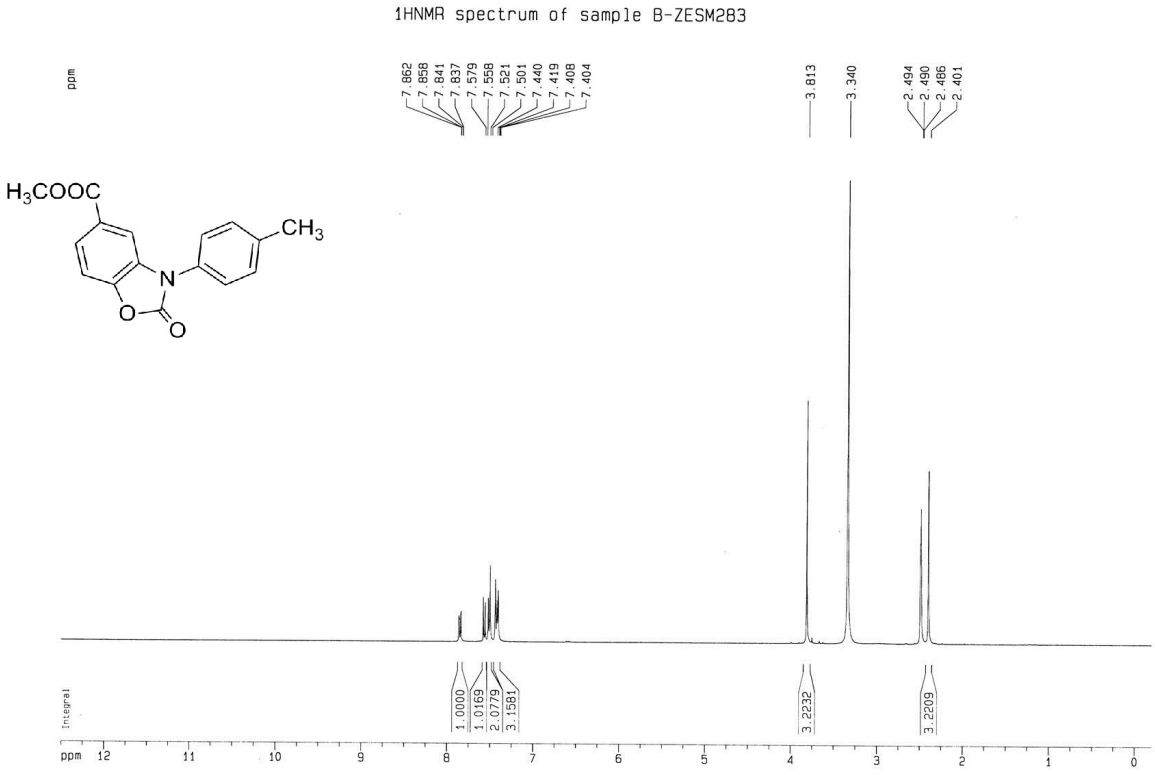
1HNMR spectrum of sample B-ZESM229

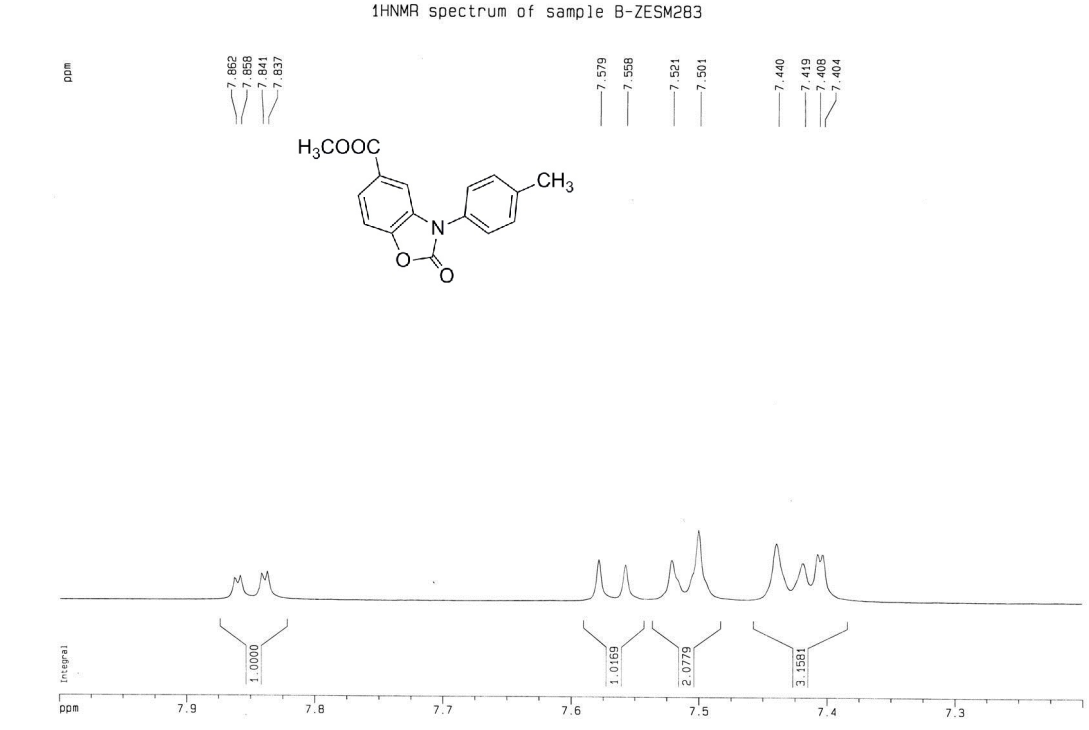


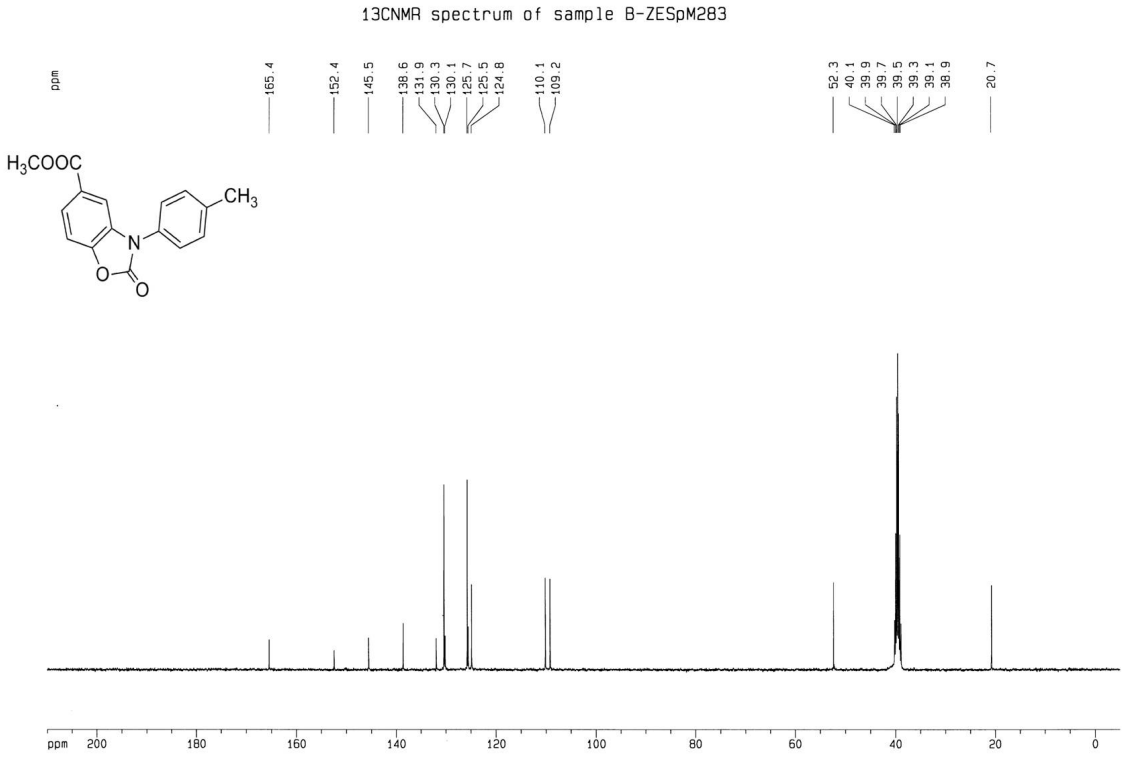
13CNMR spectrum of sample B-ZESpM299



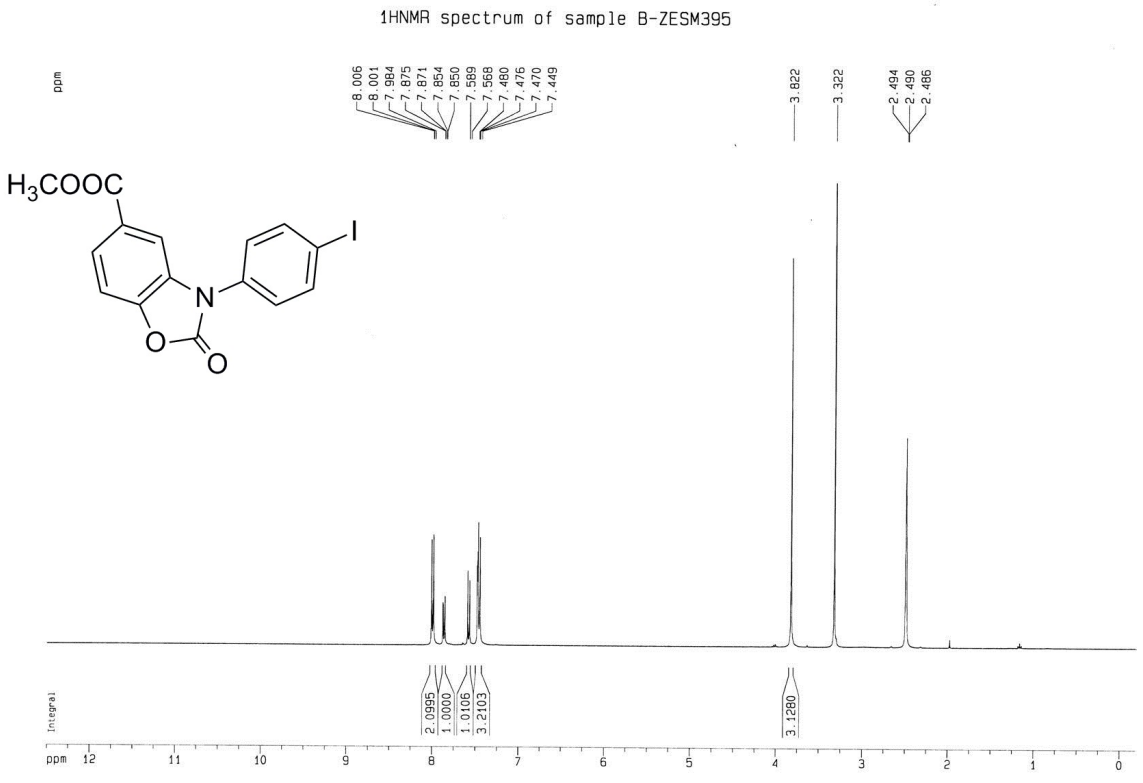
[^{1}H NMR and ^{13}C NMR spectrum of 4c in DMSO-d_6]



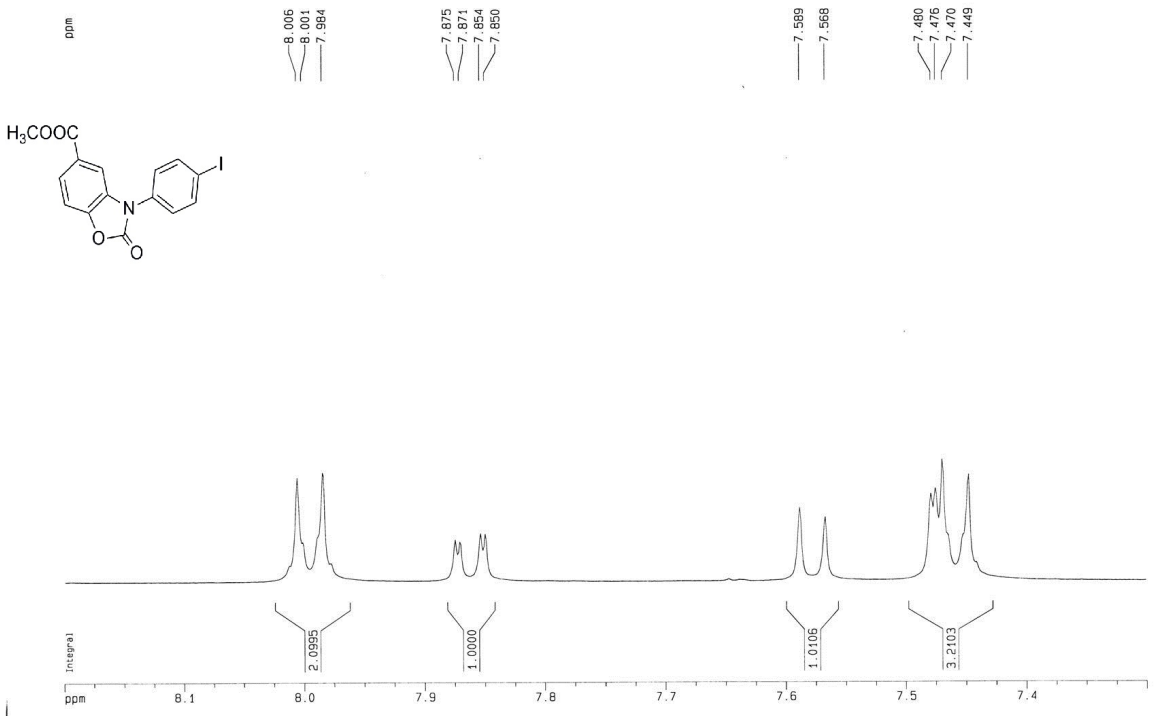




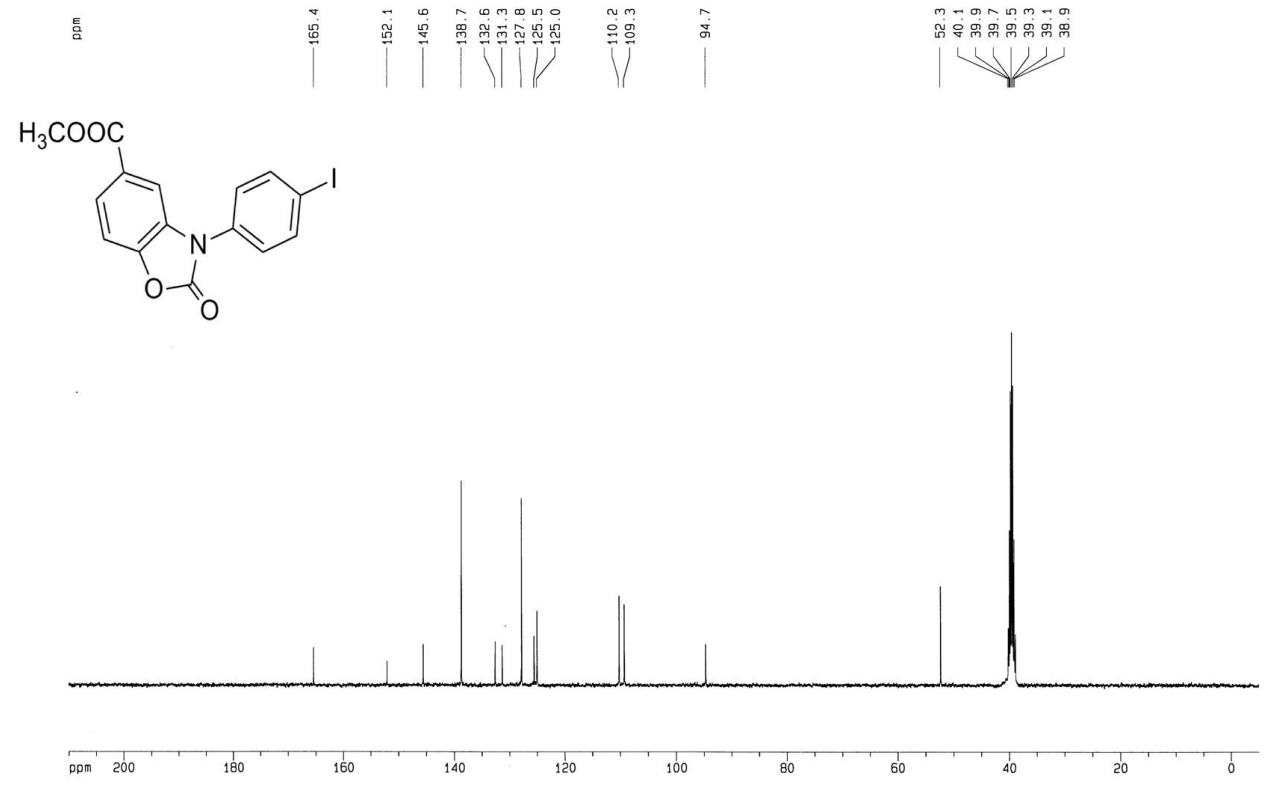
[^{1}H NMR and ^{13}C NMR spectrum of 4d in DMSO-d_6]



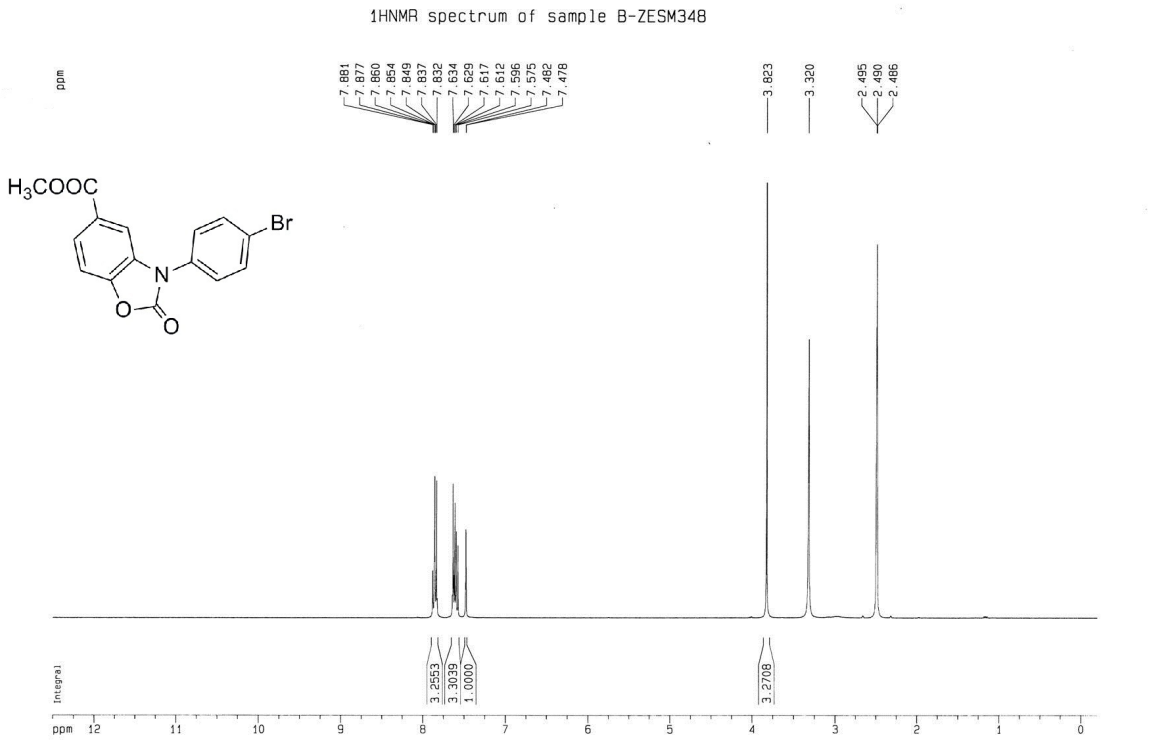
1HNMR spectrum of sample B-ZESM395

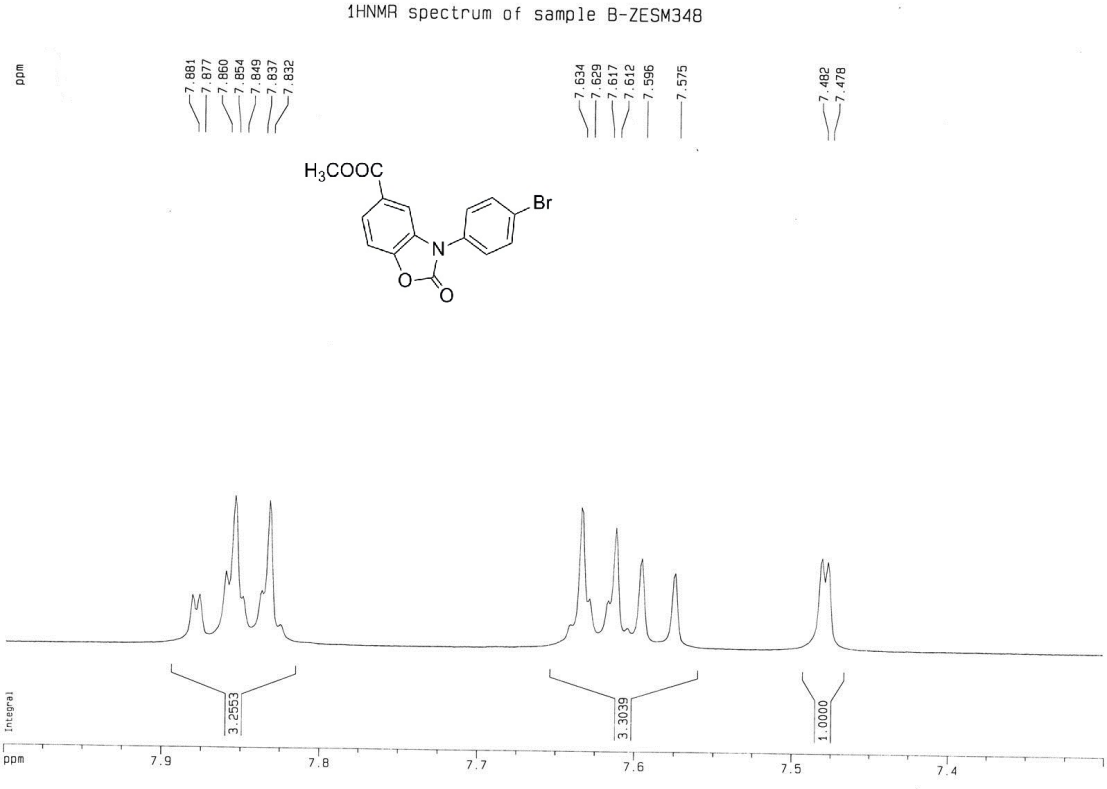


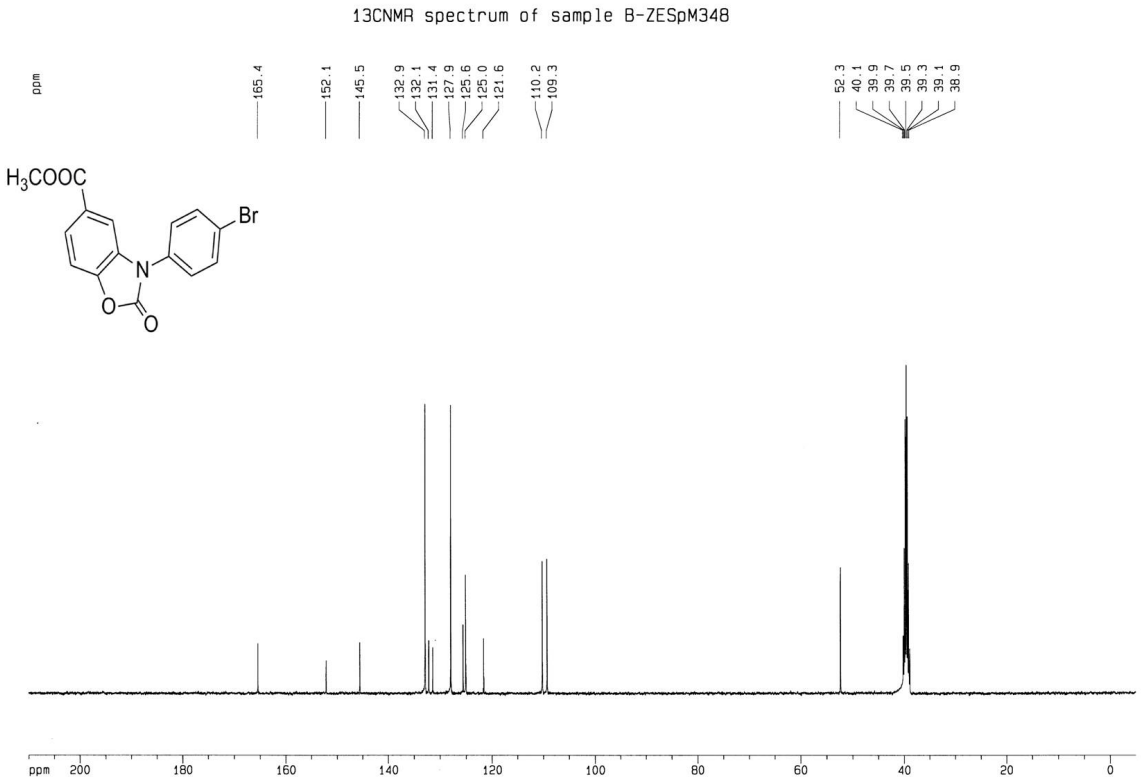
13CNMR spectrum of sample B-ZESpM395



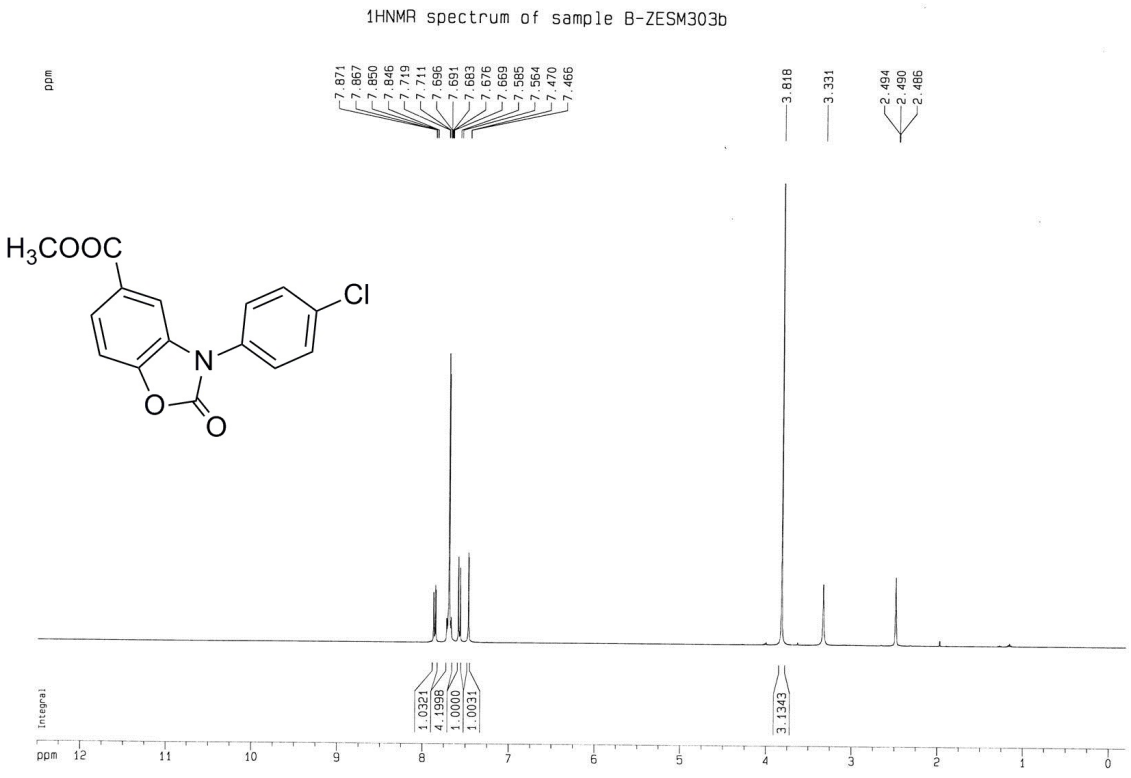
[^{1}H NMR and ^{13}C NMR spectrum of 4e in DMSO-d_6]



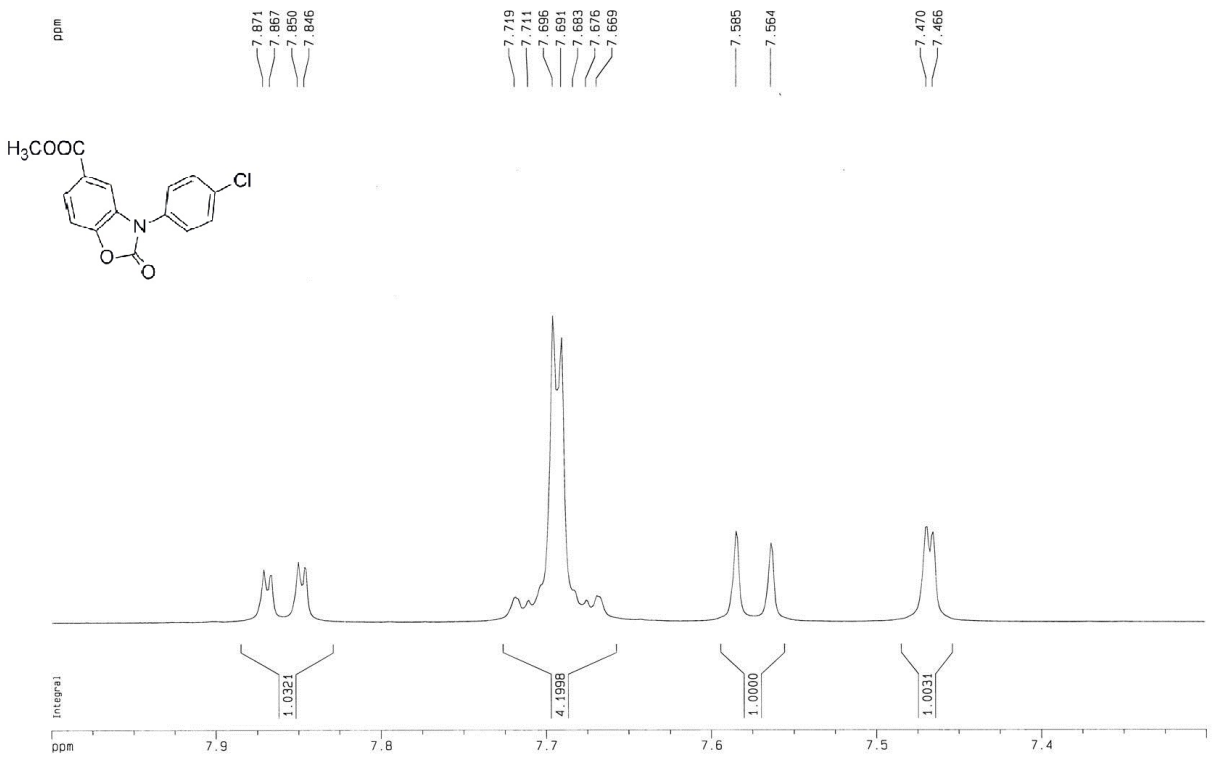




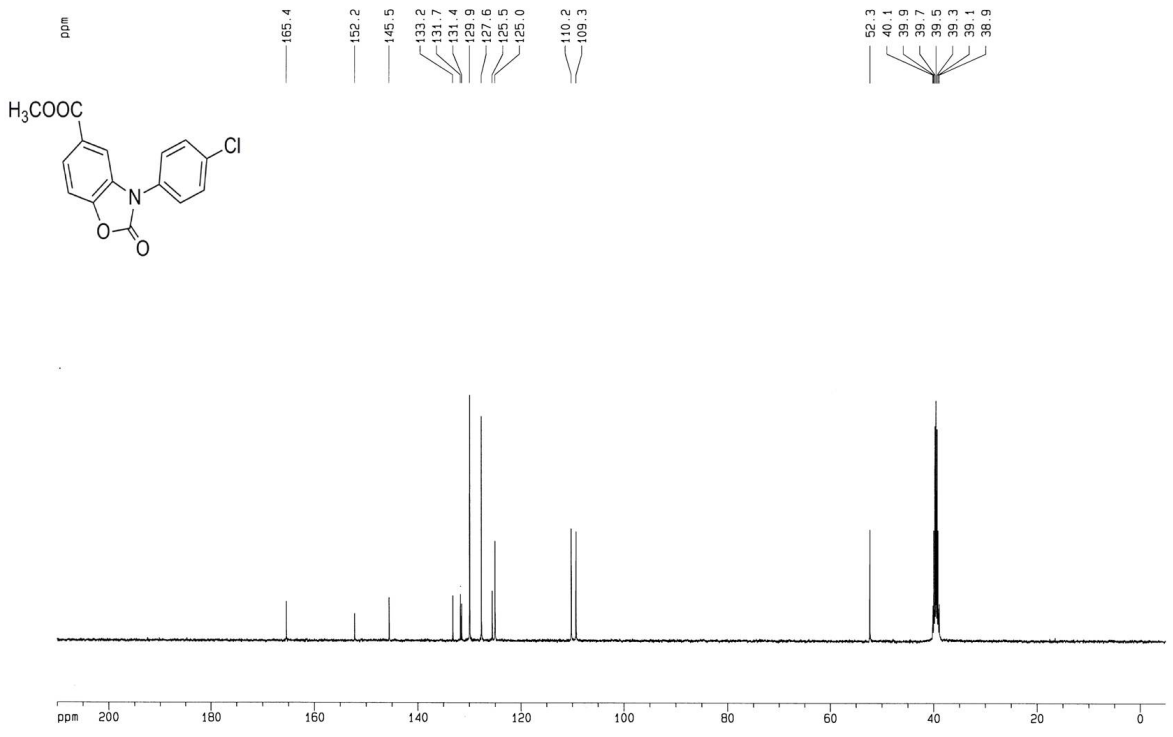
[^{1}H NMR and ^{13}C NMR spectrum of 4f in DMSO-d_6]



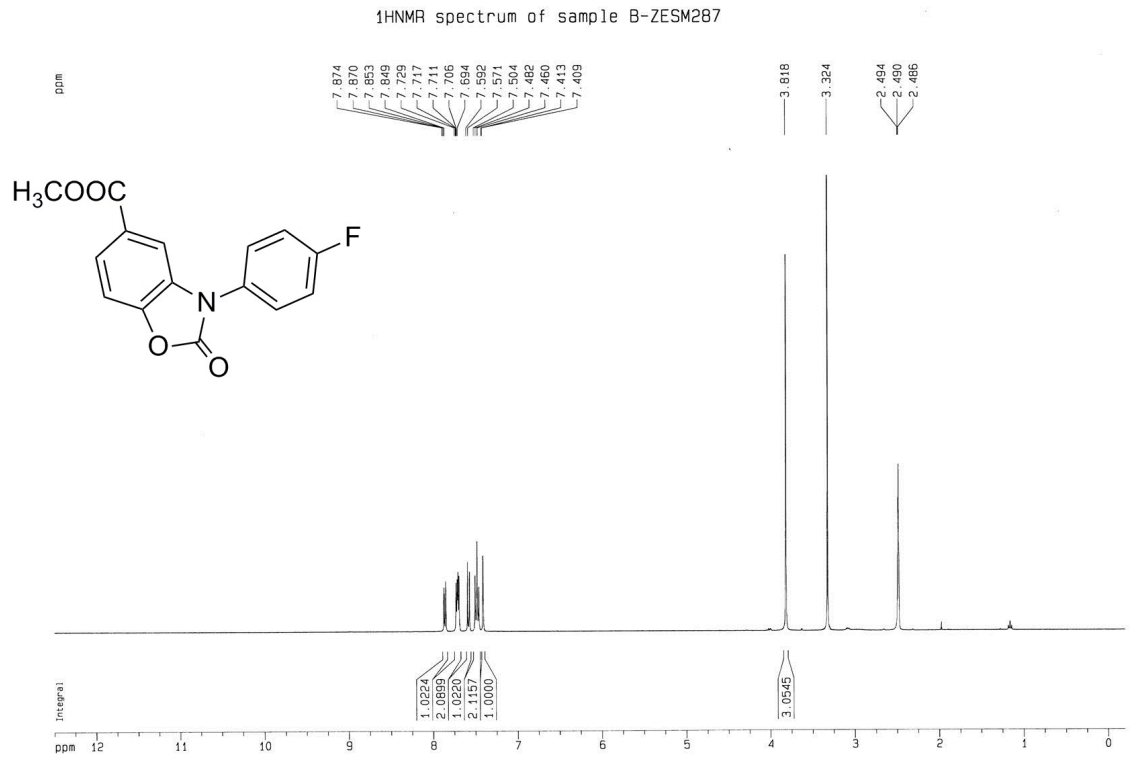
1HNMR spectrum of sample B-ZESM303b

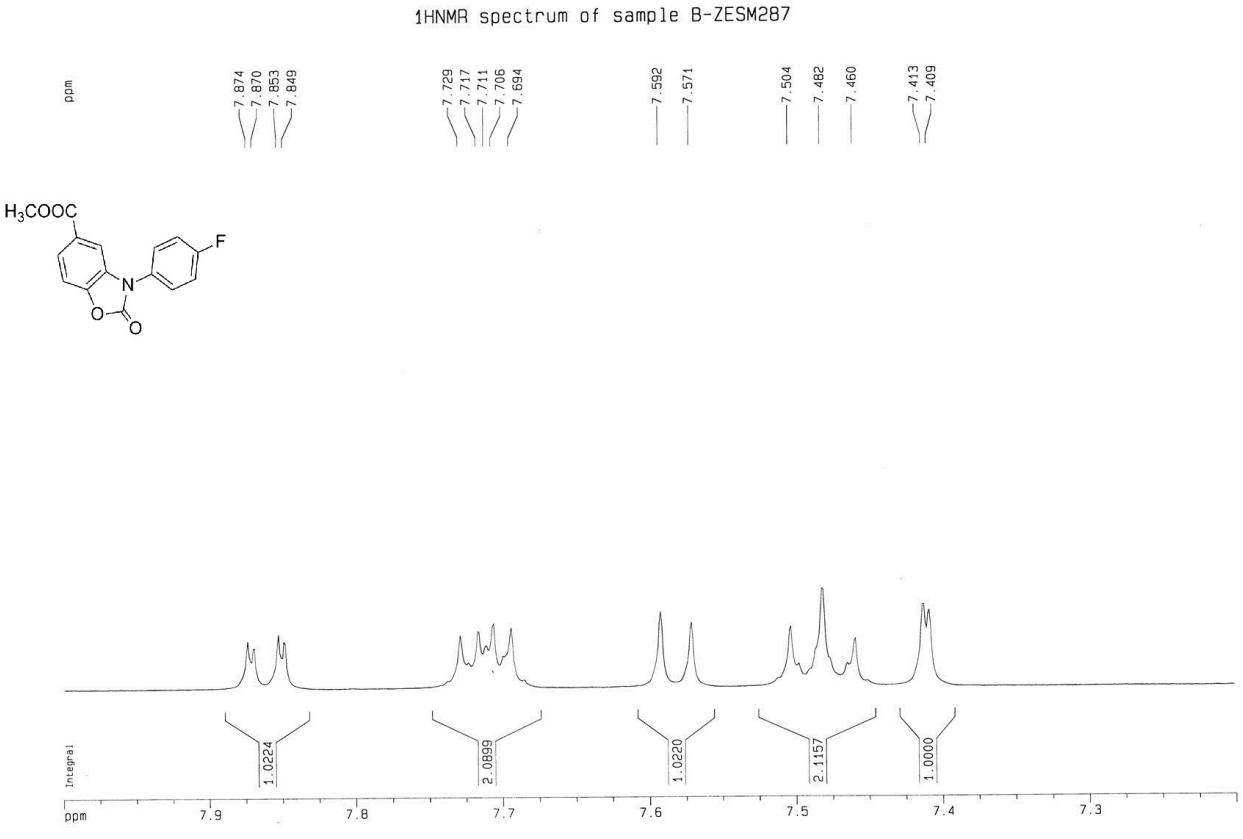


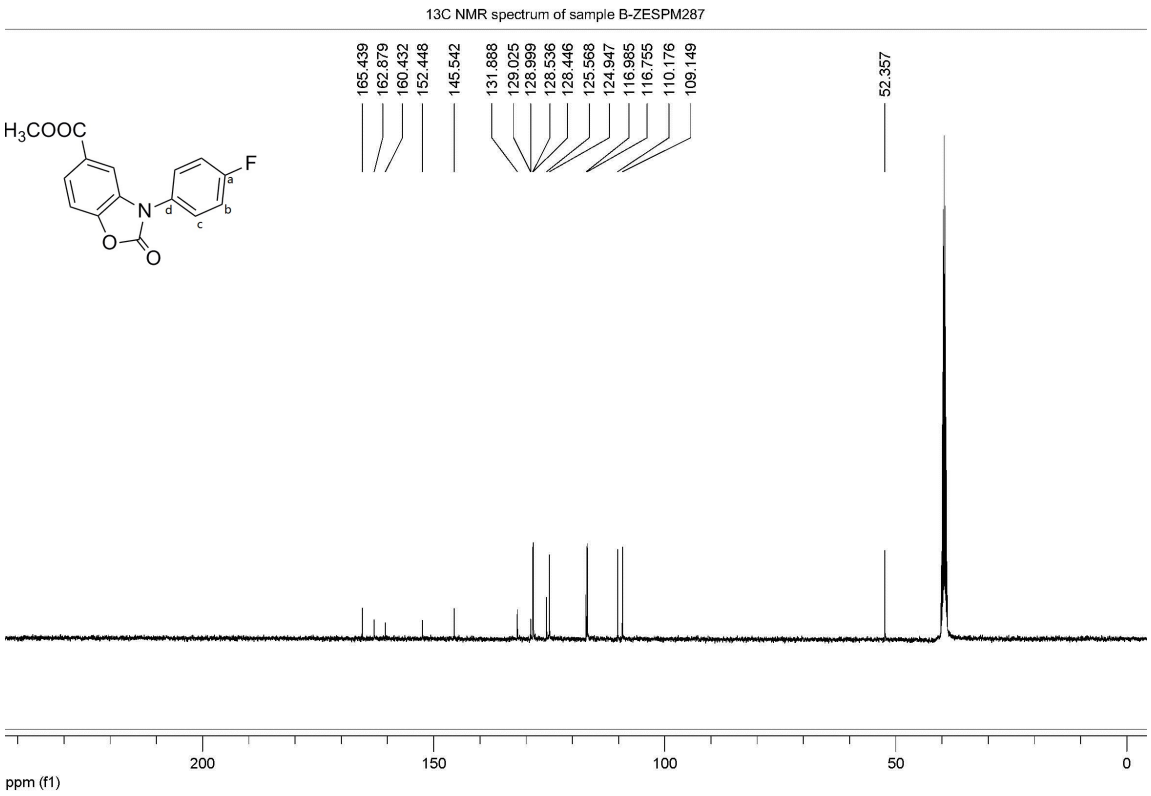
13CNMR spectrum of sample B-ZESpM303

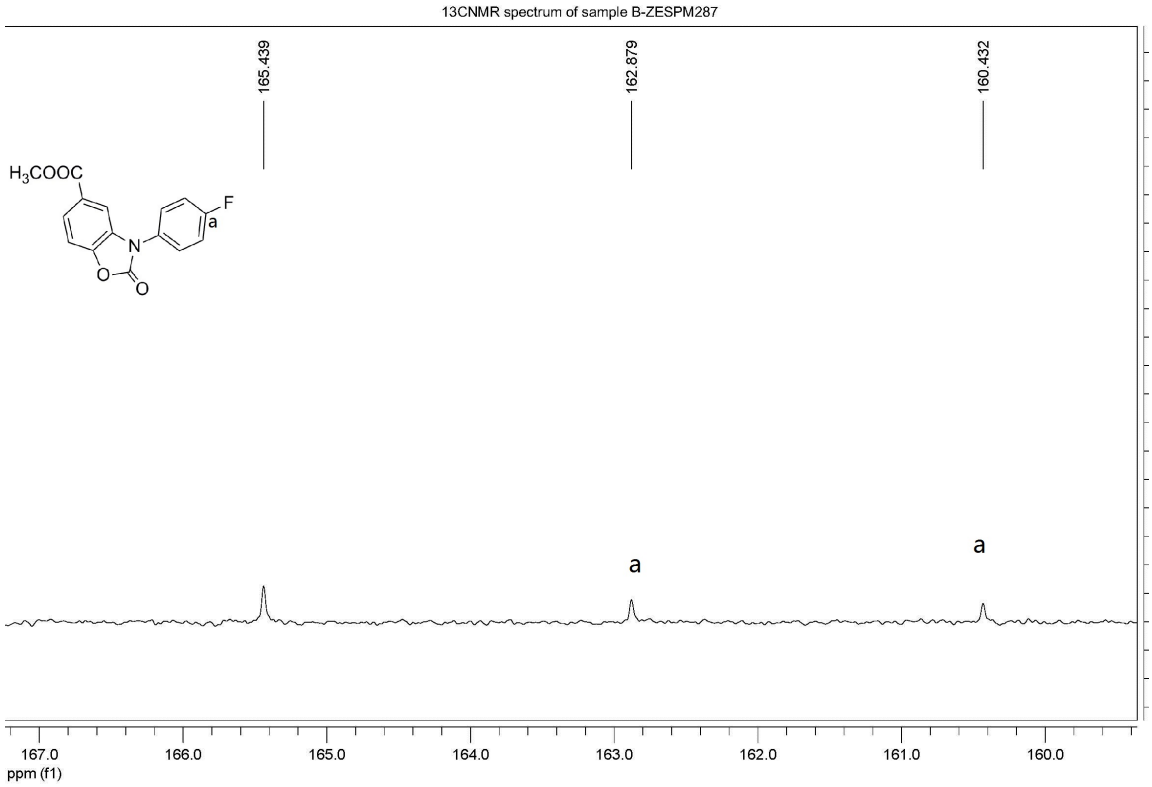


[^{1}H NMR and ^{13}C NMR spectrum of 4g in DMSO-d_6]

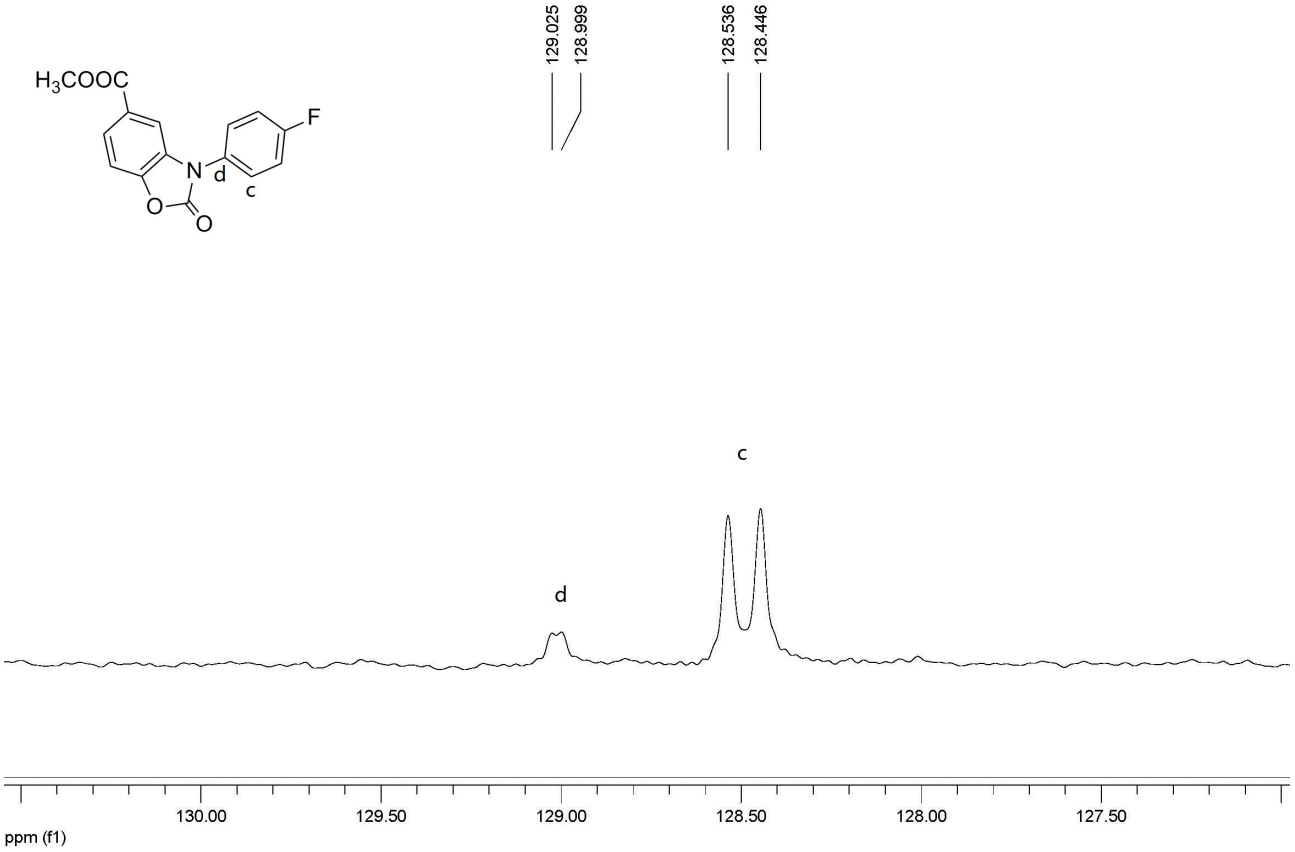




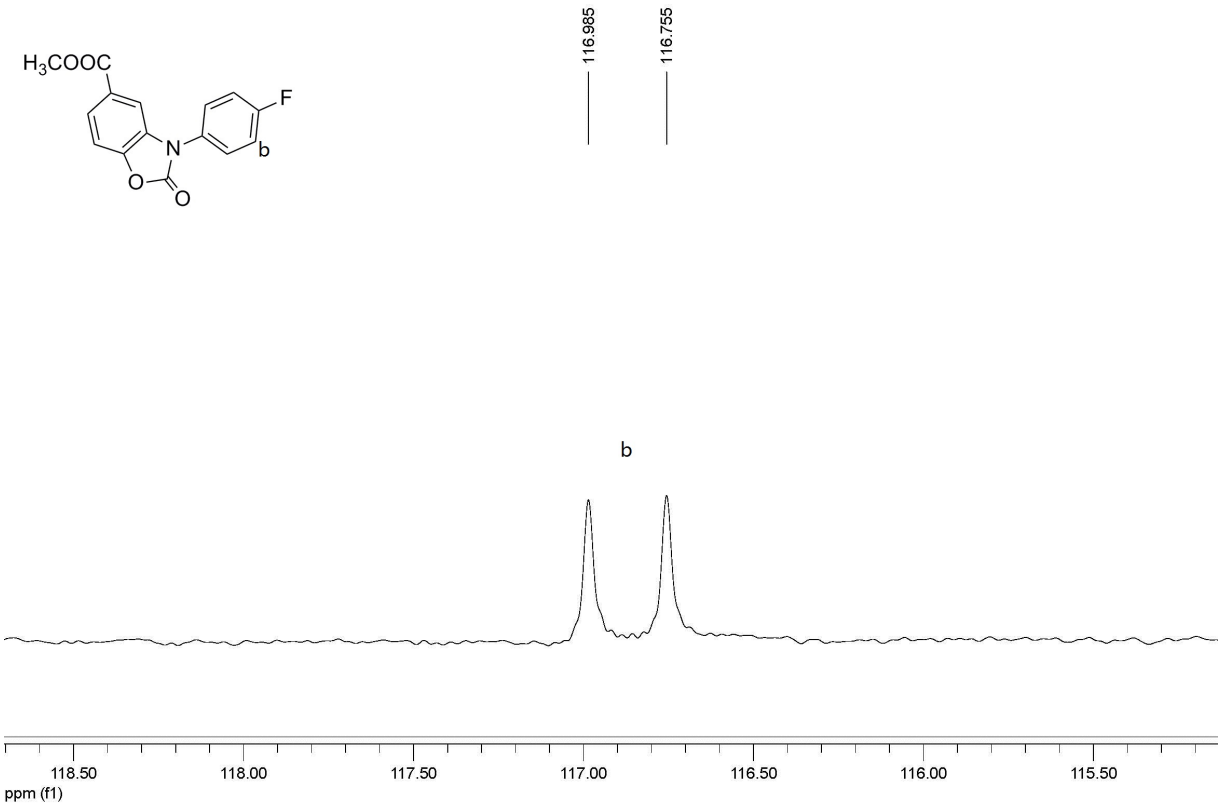

13C NMR spectrum of sample B-ZESPM287
165.439
162.879
160.432
152.448
145.542
131.888
129.025
128.999
128.536
128.446
125.568
124.947
116.985
116.755
110.176
109.149
52.357
H3COOC
F
a
b
c
d
N
O
O
200
150
100
50
0
ppm (f1)


13CNMR spectrum of sample B-ZESPM287
165.439
162.879
160.432
H3COOC
F
a
N
O
O
a
a
167.0
166.0
165.0
164.0
163.0
162.0
161.0
160.0
ppm (f1)

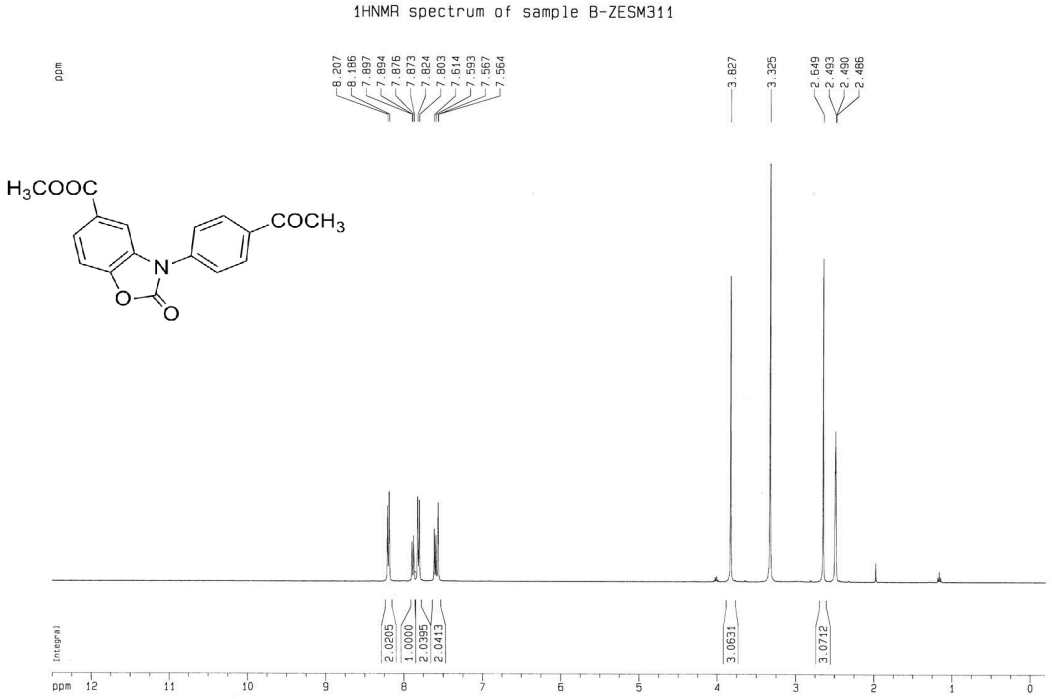
13C NMR spectrum of sample B-ZESPM287

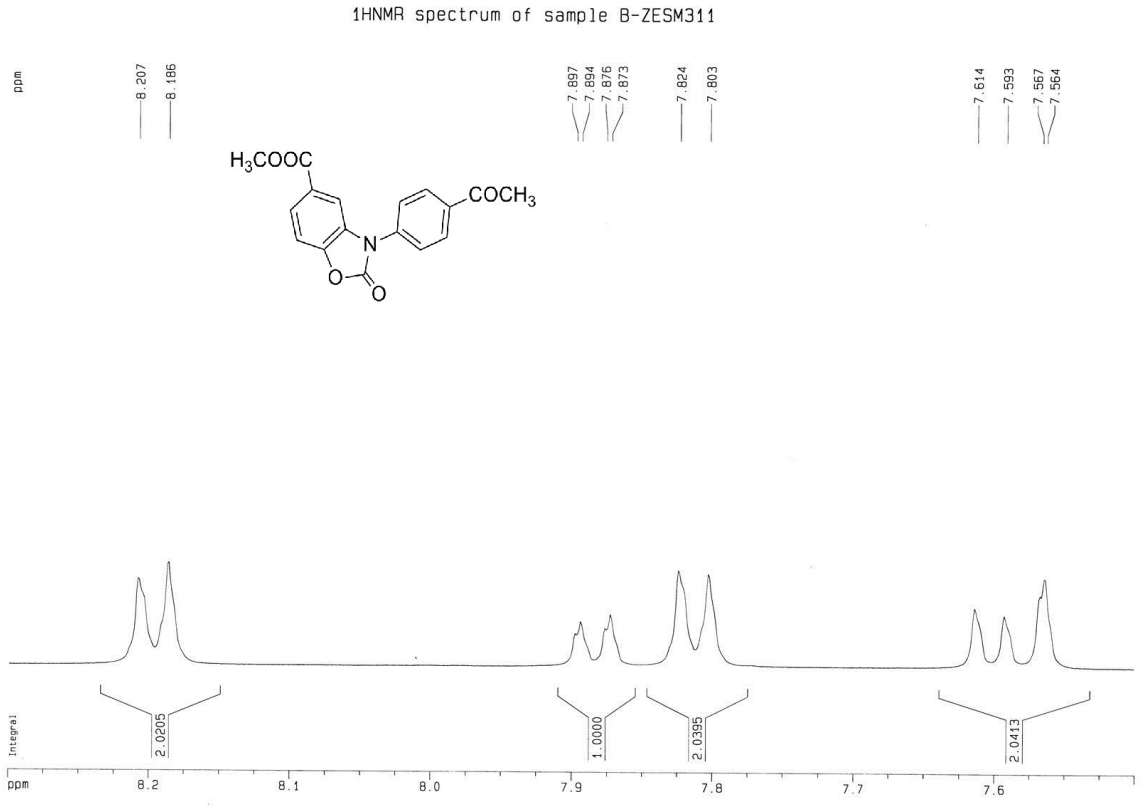


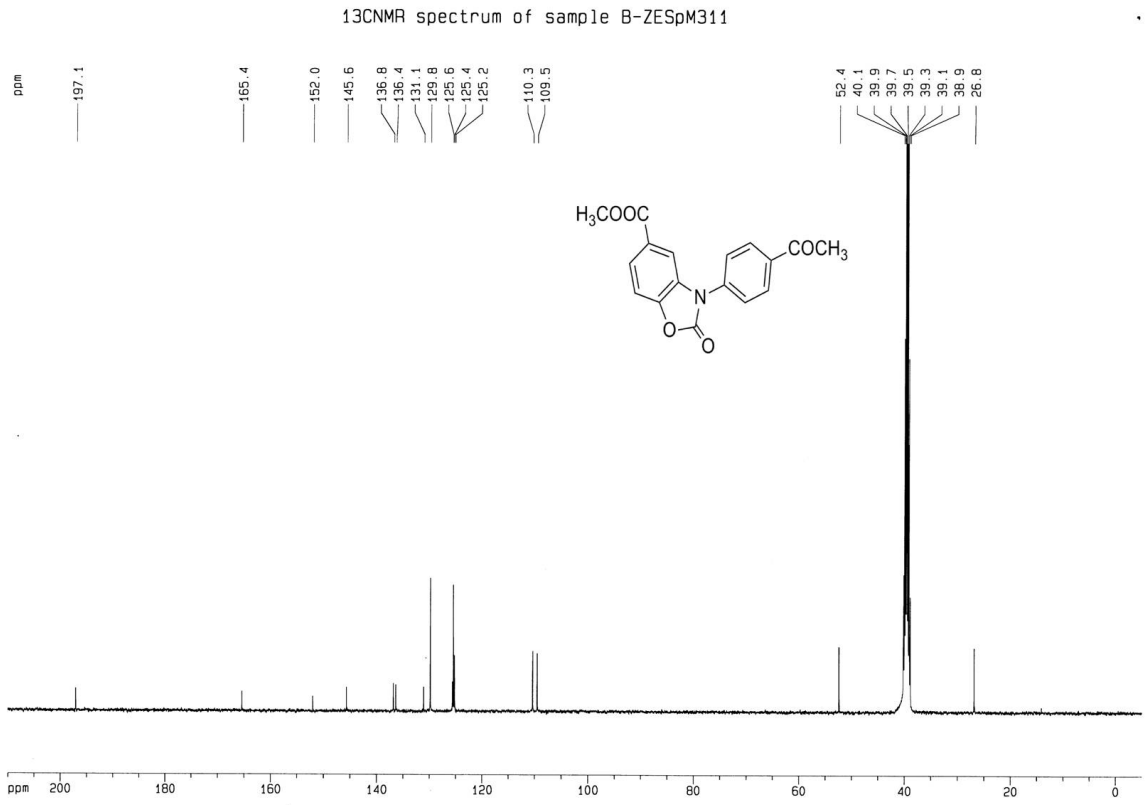
13C NMR spectrum of sample B-ZESPM287



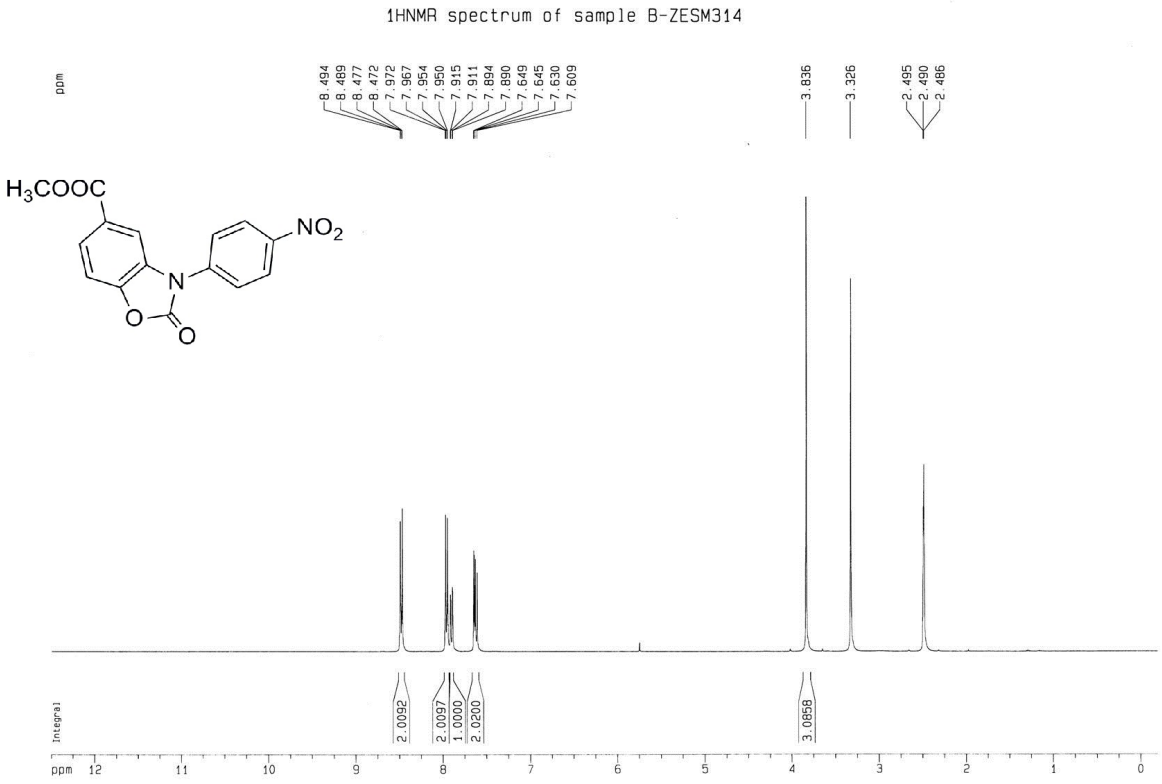
[^{1}H NMR and ^{13}C NMR spectrum of 4h in DMSO-d_6]



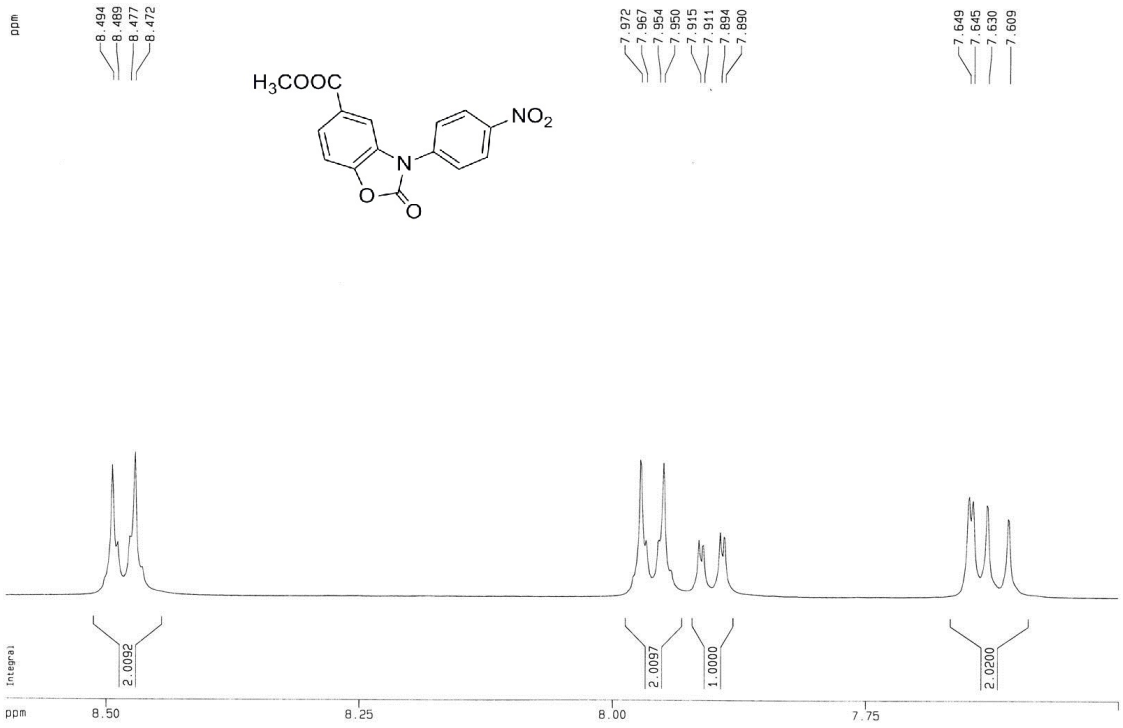




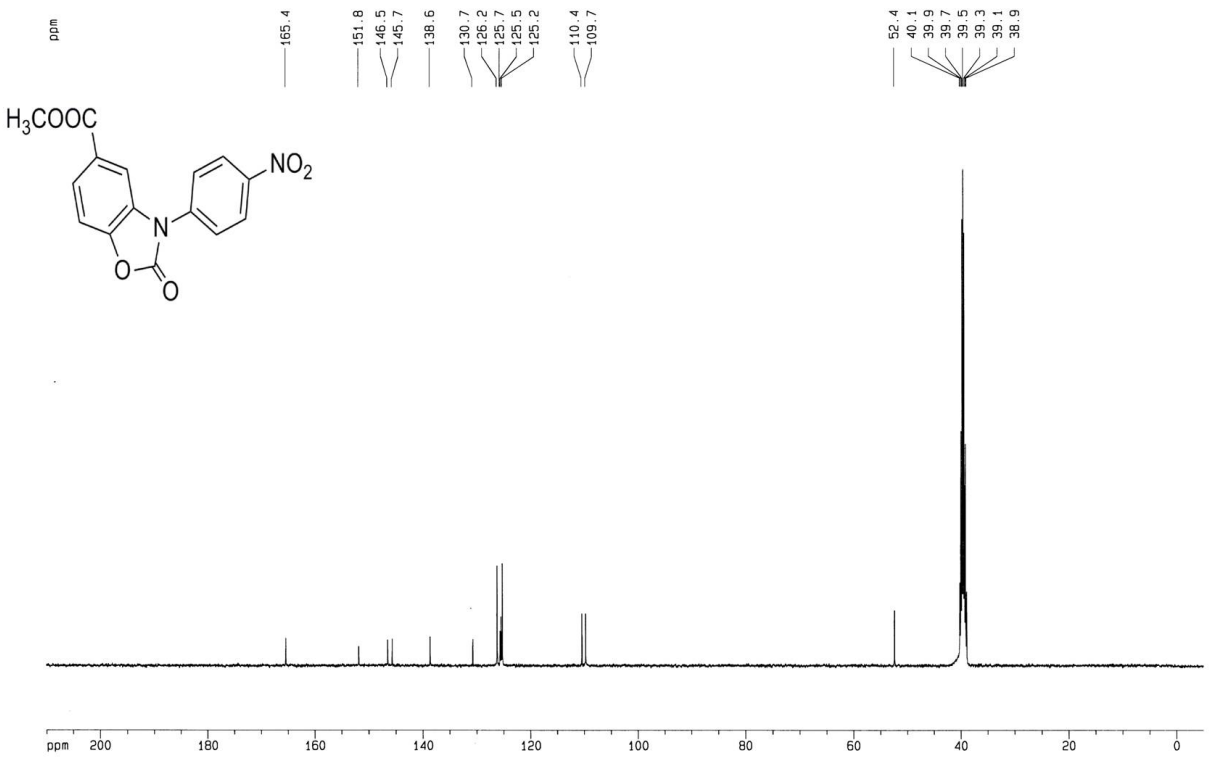
[^{1}H NMR and ^{13}C NMR spectrum of 4i in DMSO-d$_6$]



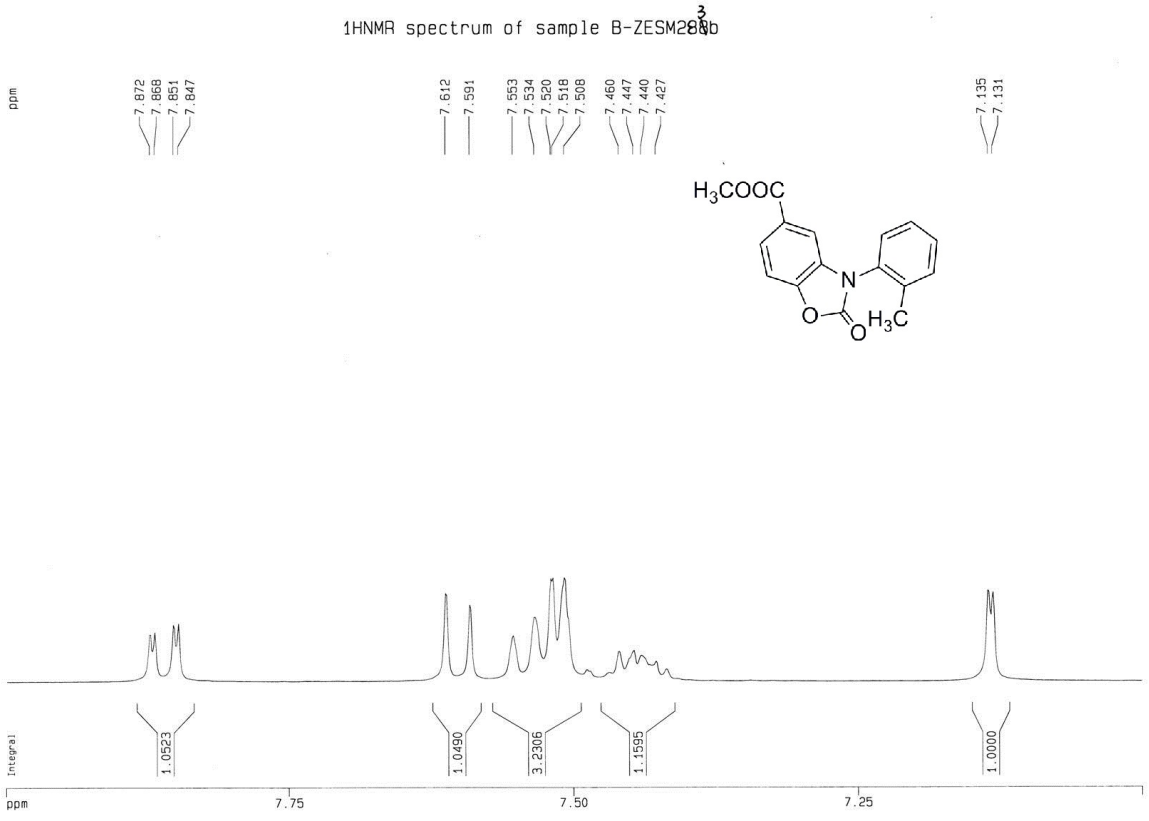
1HNMR spectrum of sample B-ZESM314

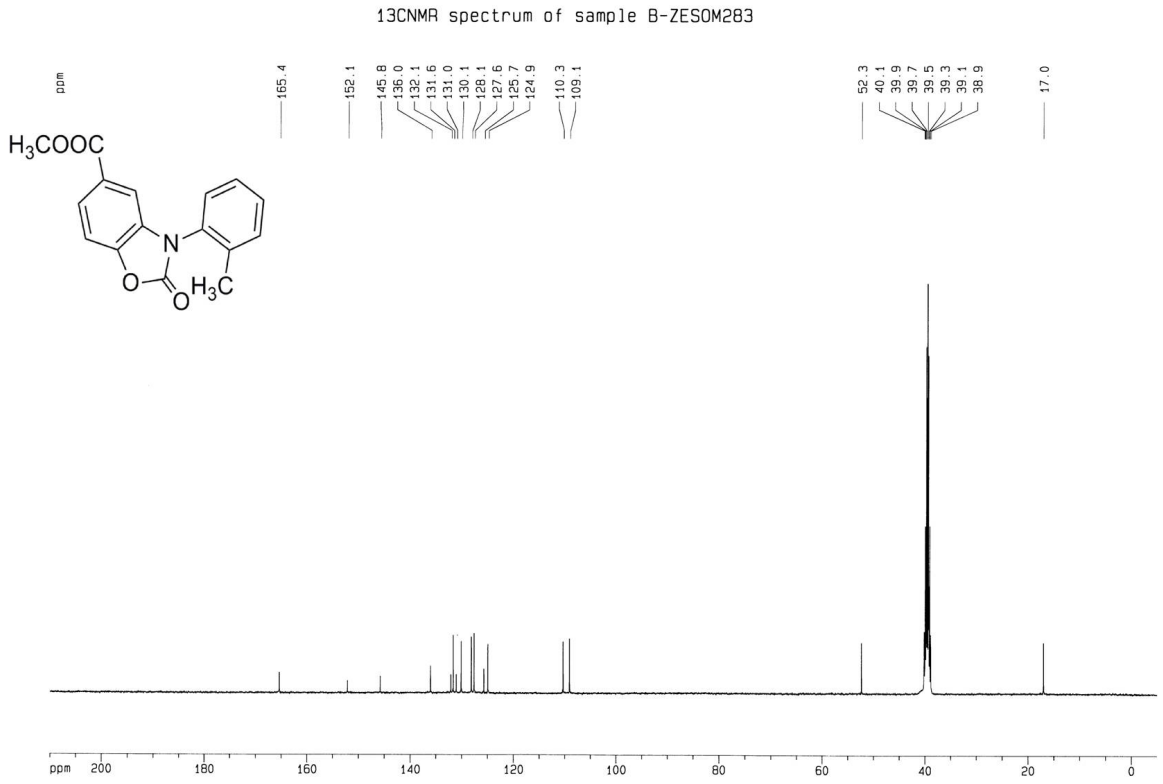


13CNMR spectrum of sample B-ZESpM314

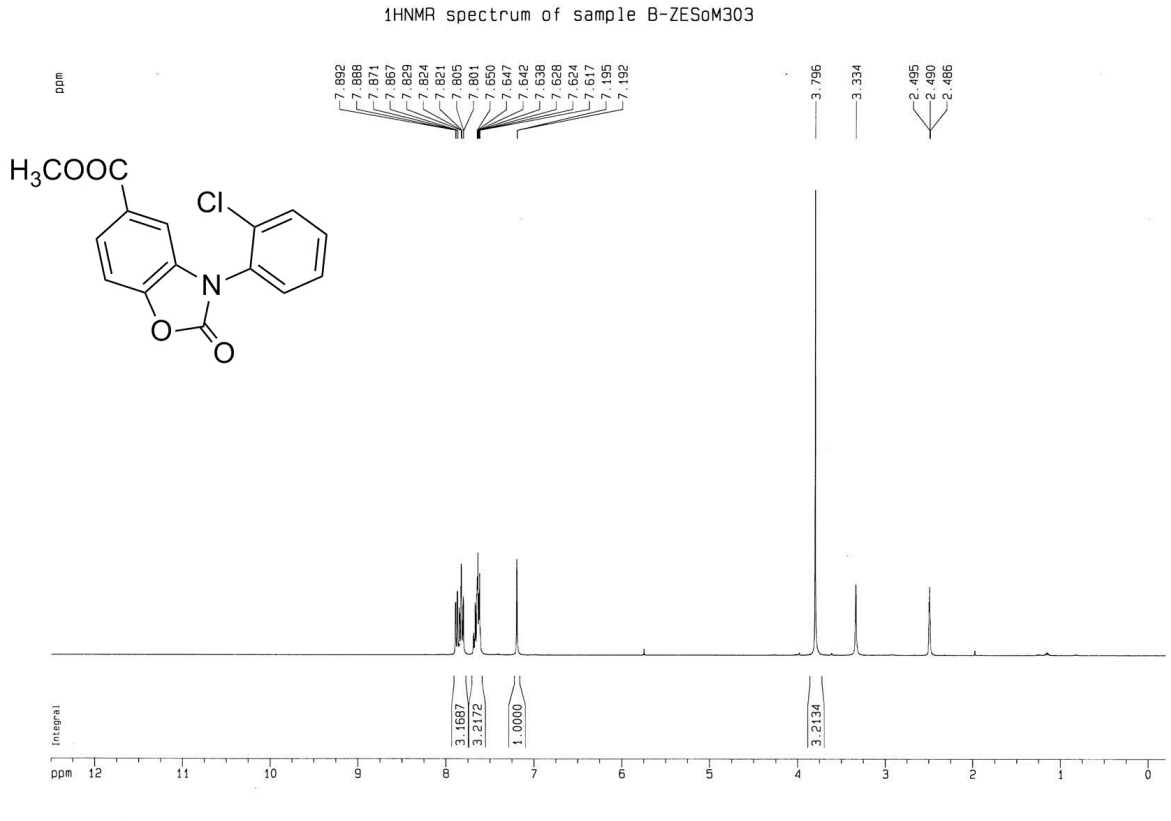


[^{1}H NMR and ^{13}C NMR spectrum of 4j in DMSO-d_6]

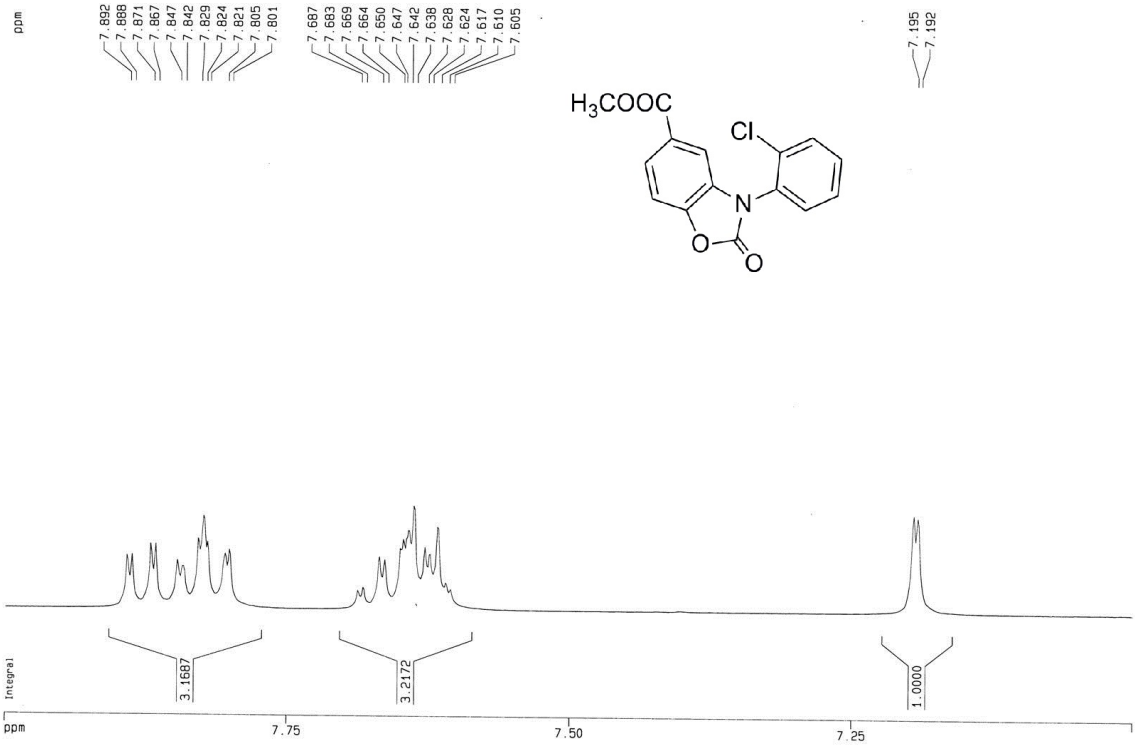




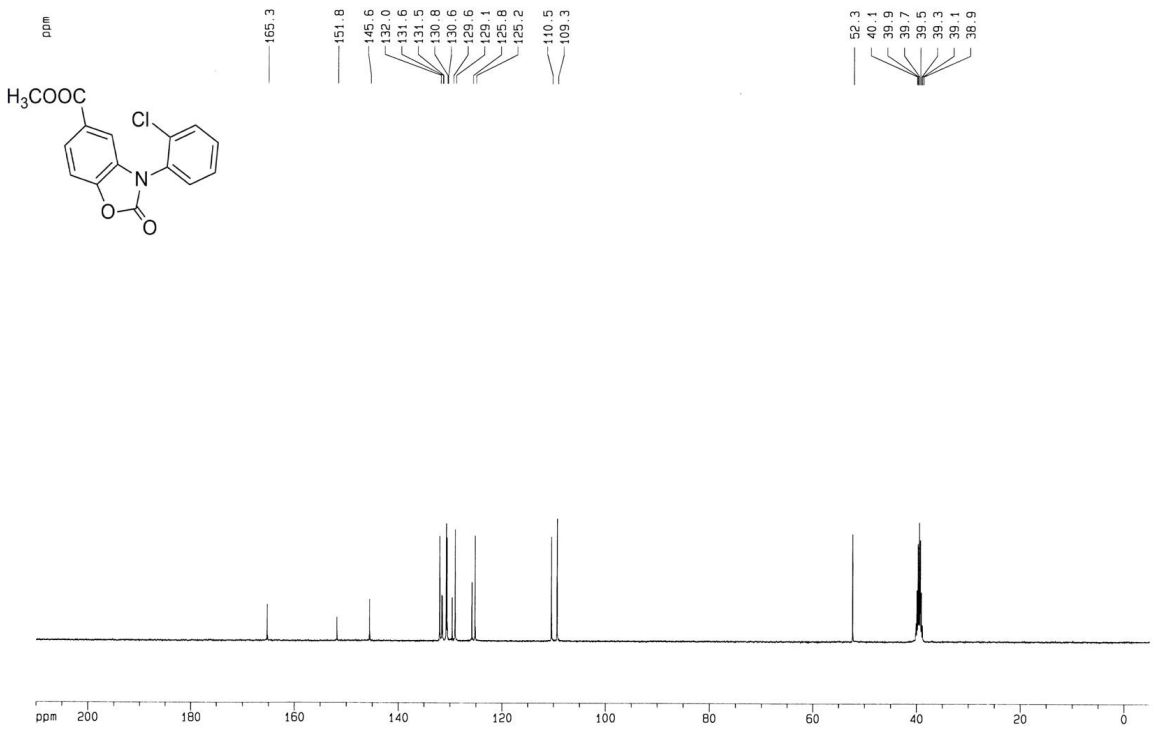
[^{1}H NMR and ^{13}C NMR spectrum of 4k in DMSO-d_6]



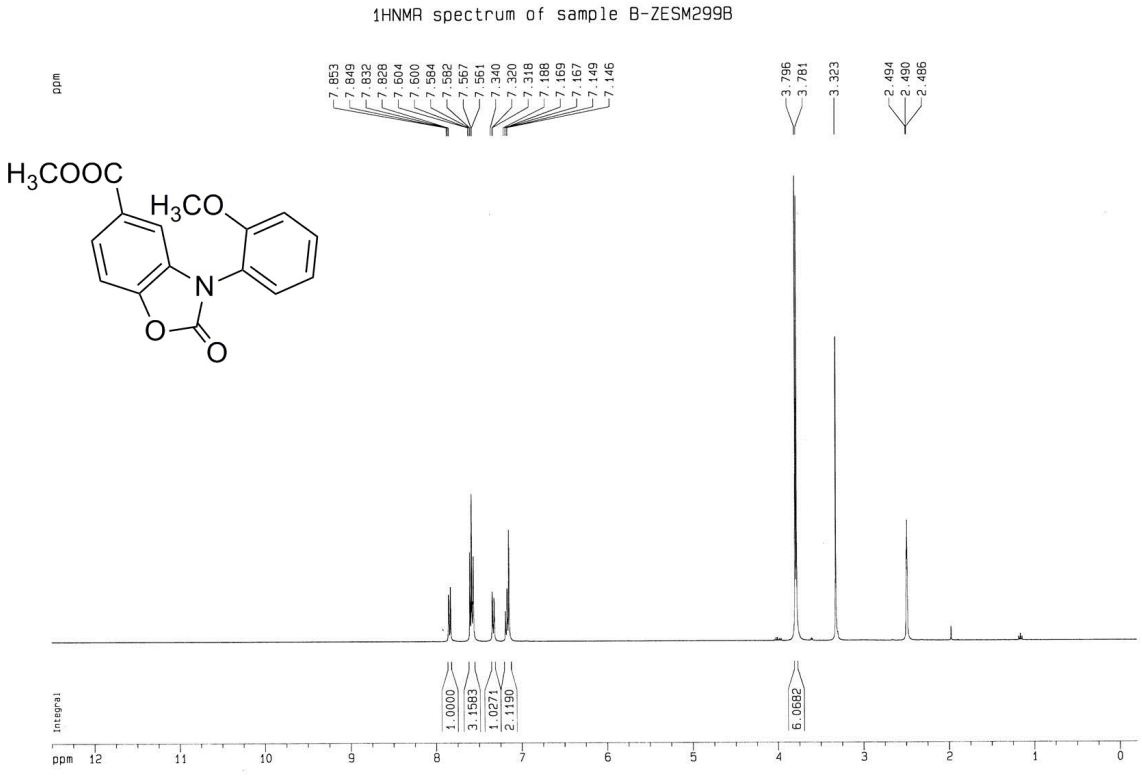
1HNMR spectrum of sample B-ZESoM303

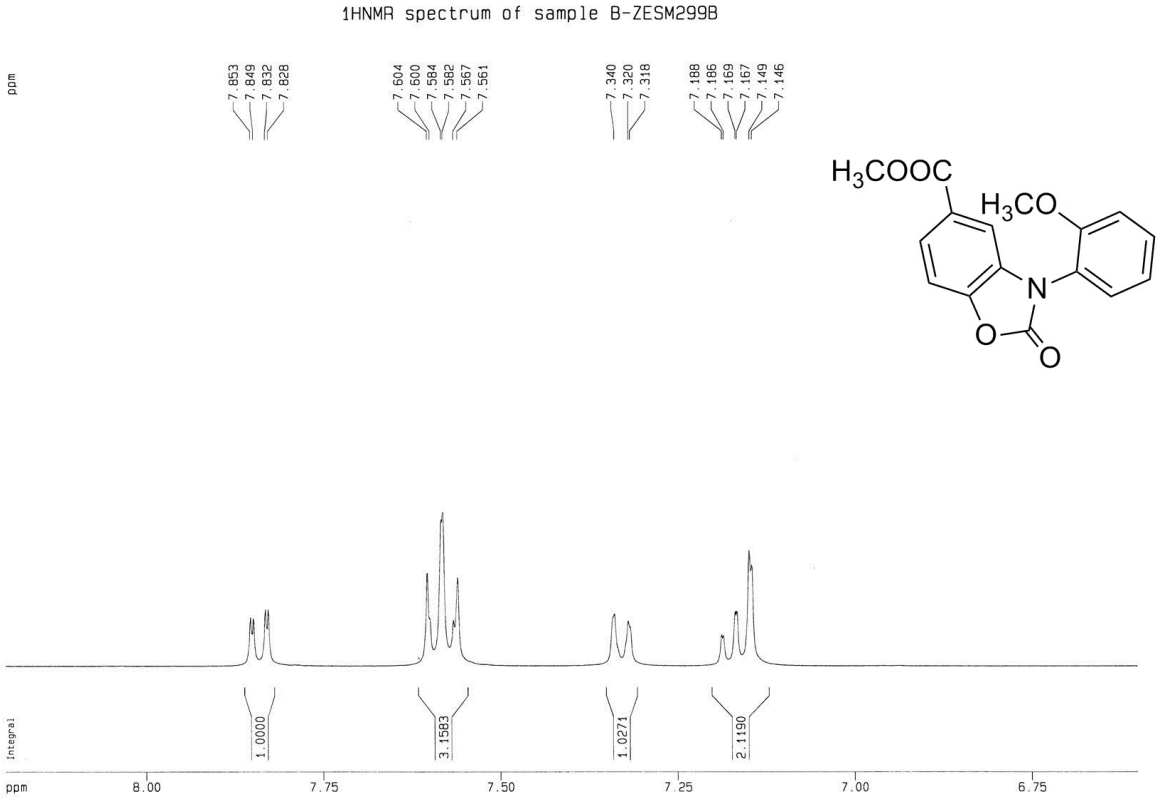


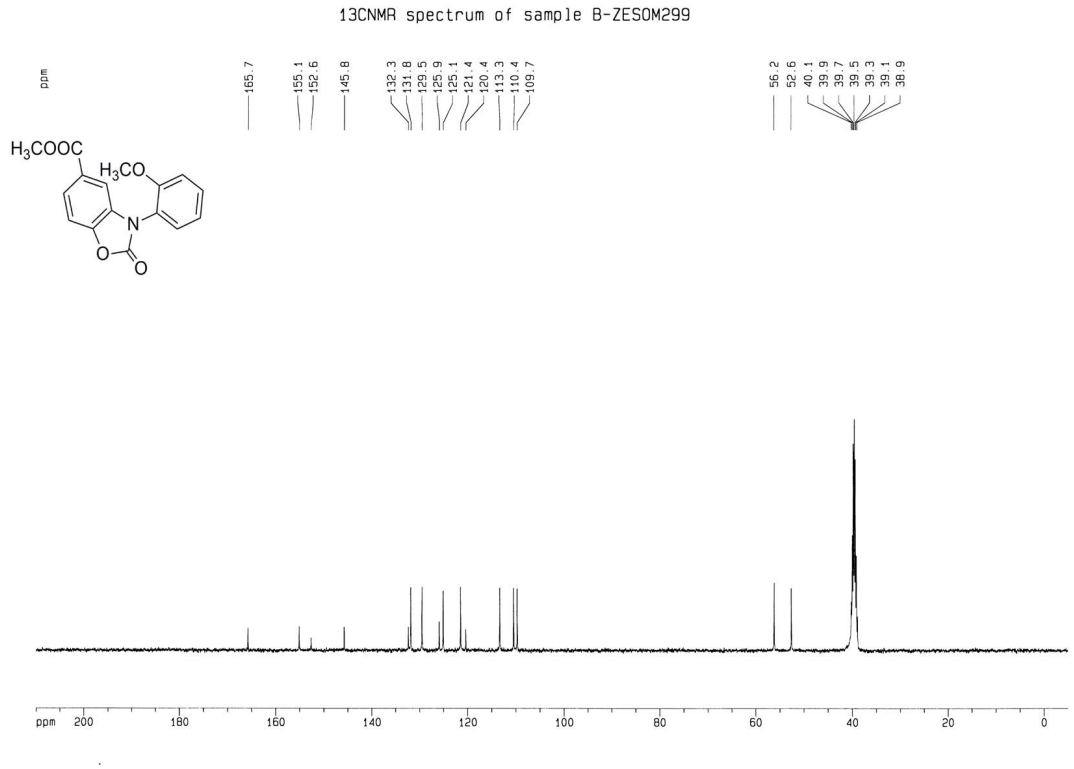
1HNMR spectrum of sample B-ZESOM303



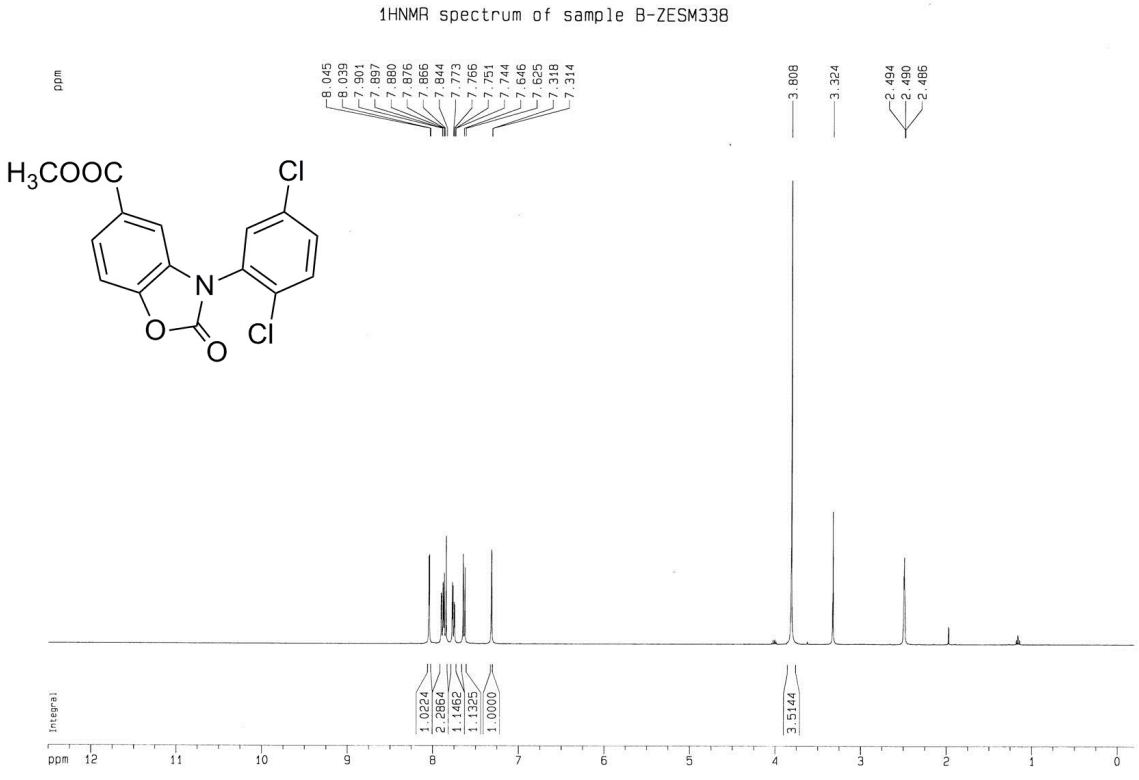
[^{1}H NMR and ^{13}C NMR spectrum of 4l in DMSO-d_6]



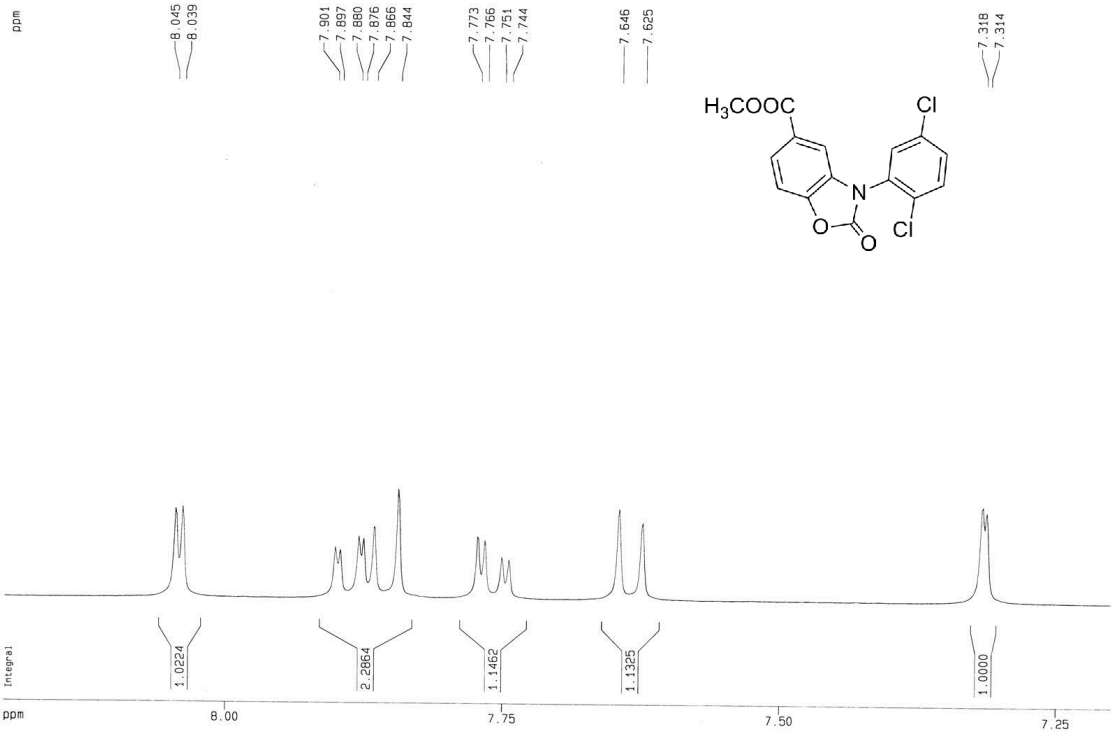




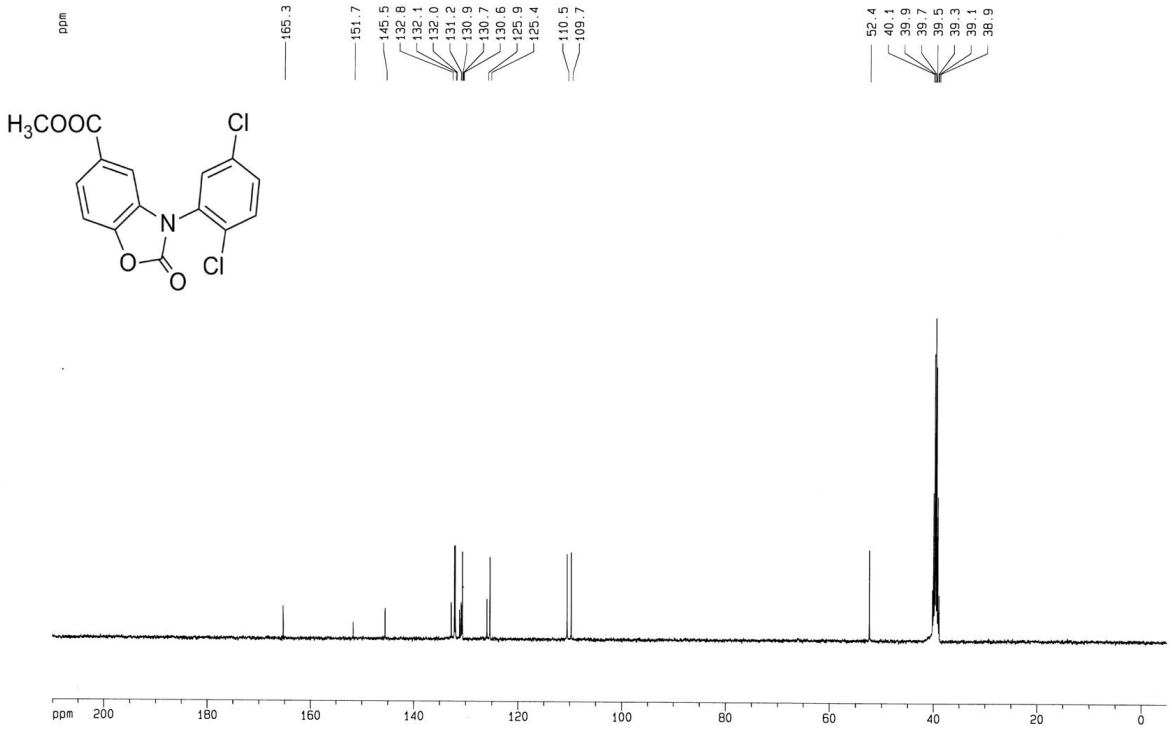
[^{1}H NMR and ^{13}C NMR spectrum of 4m in DMSO-d_6]



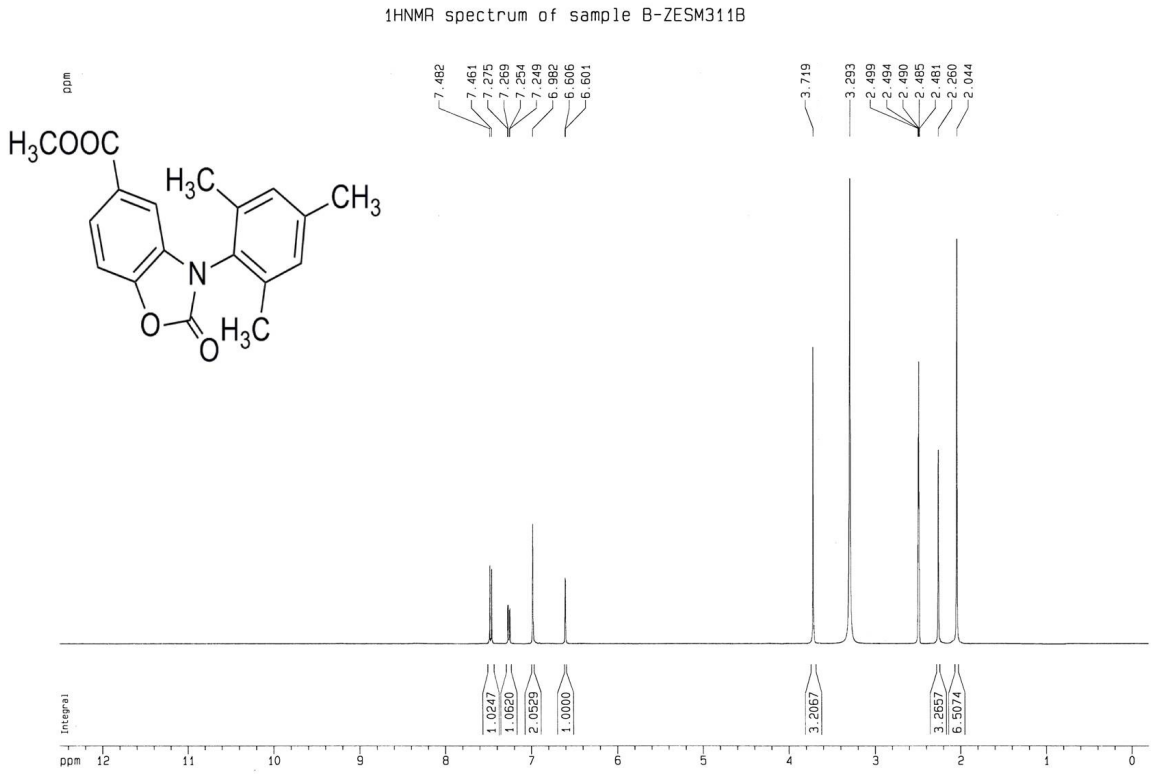
1HNMR spectrum of sample B-ZESM338

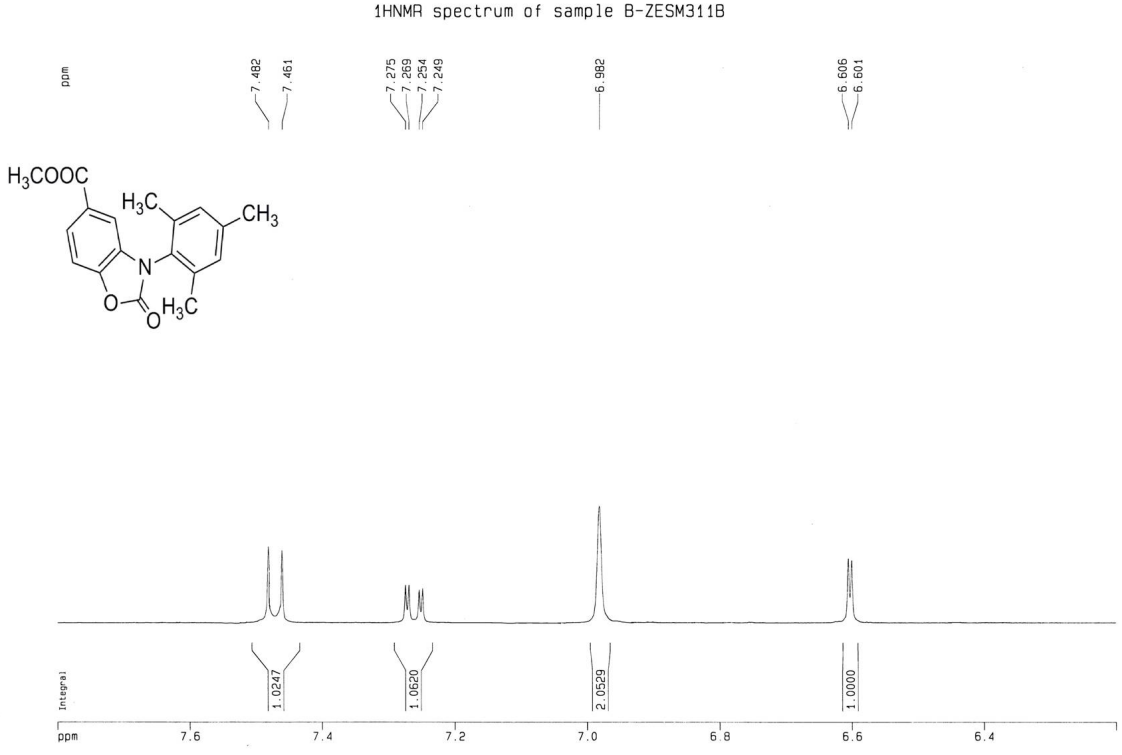


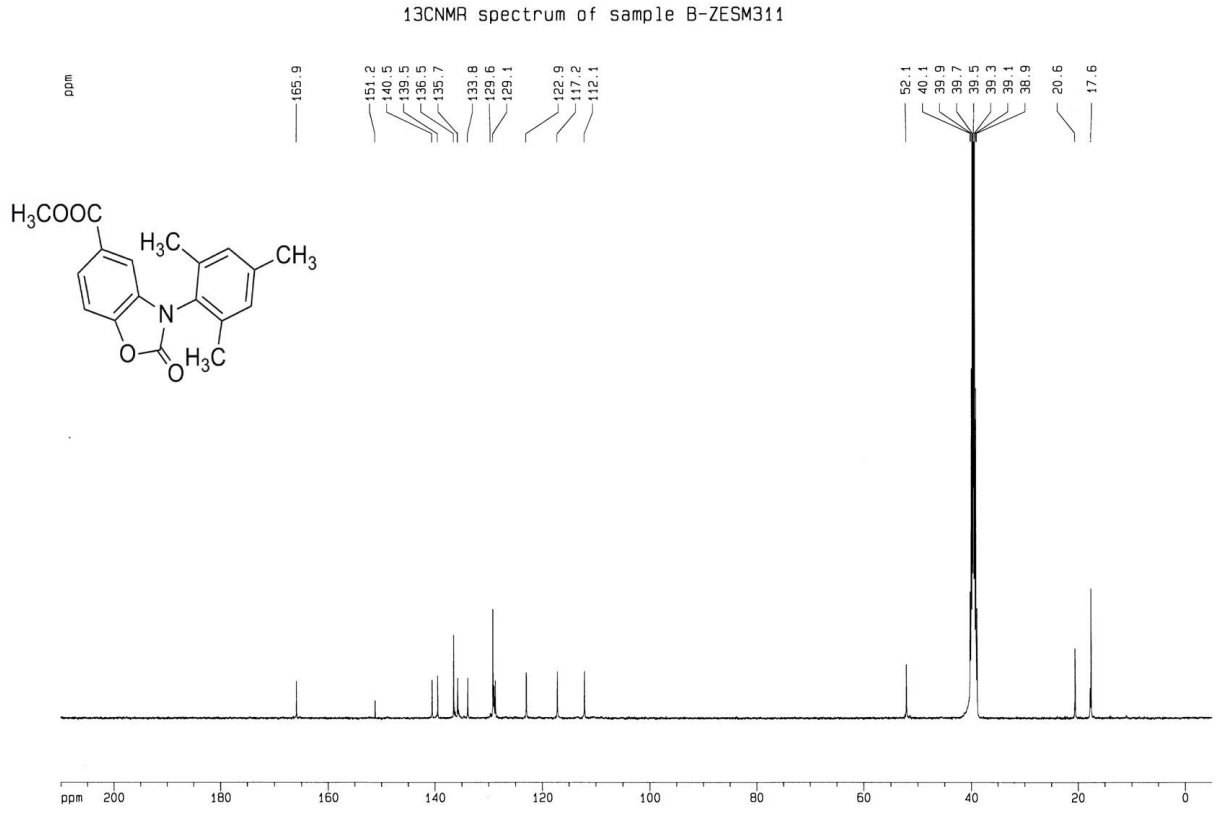
13CNMR spectrum of sample B-ZESM338



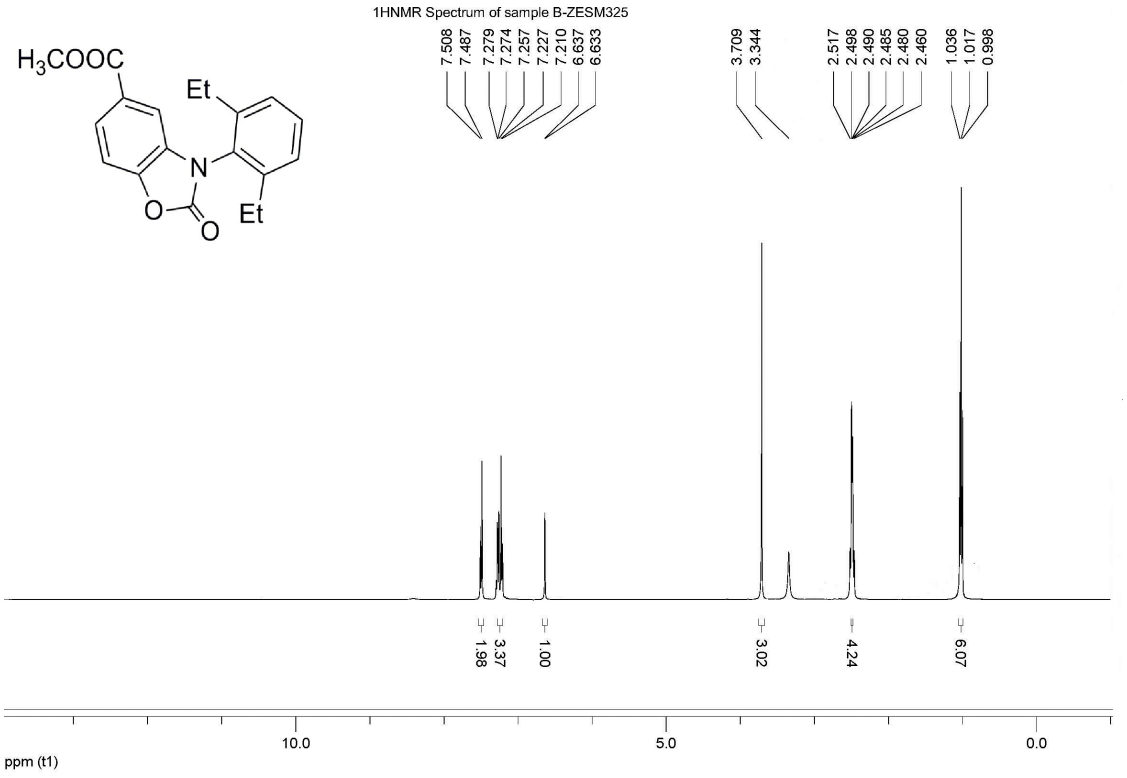
[^{1}H NMR and ^{13}C NMR spectrum of 4n in DMSO-d_6]



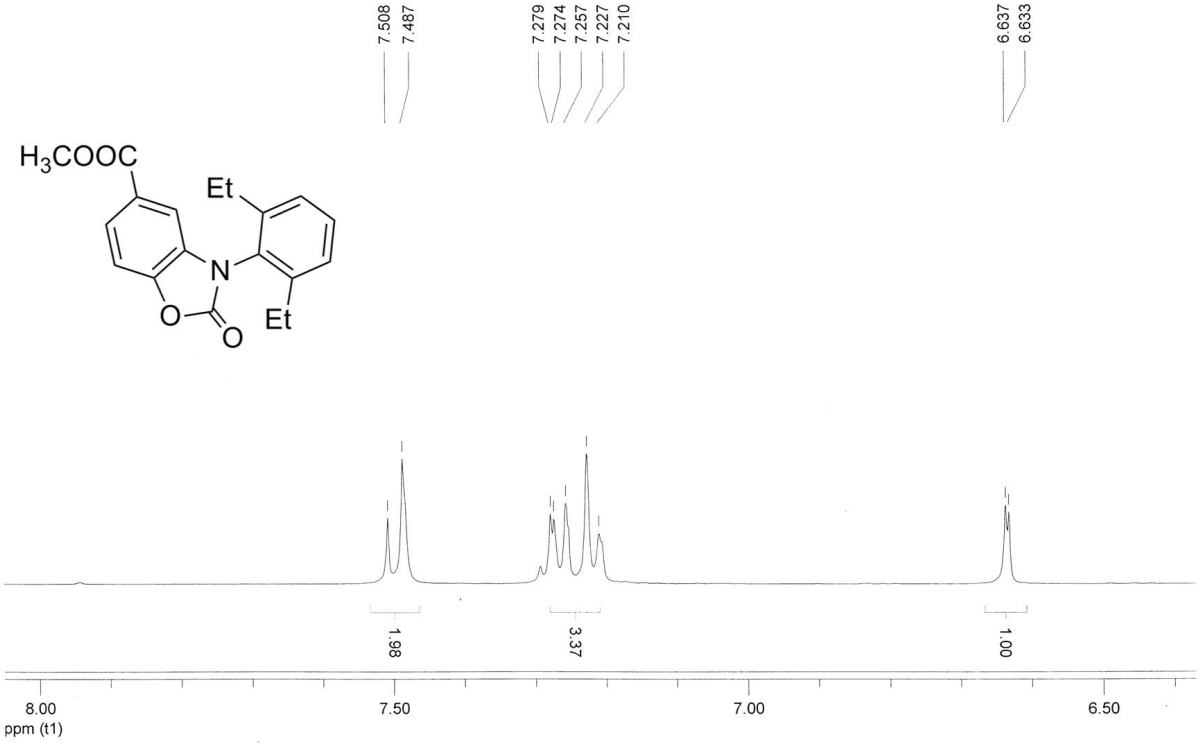




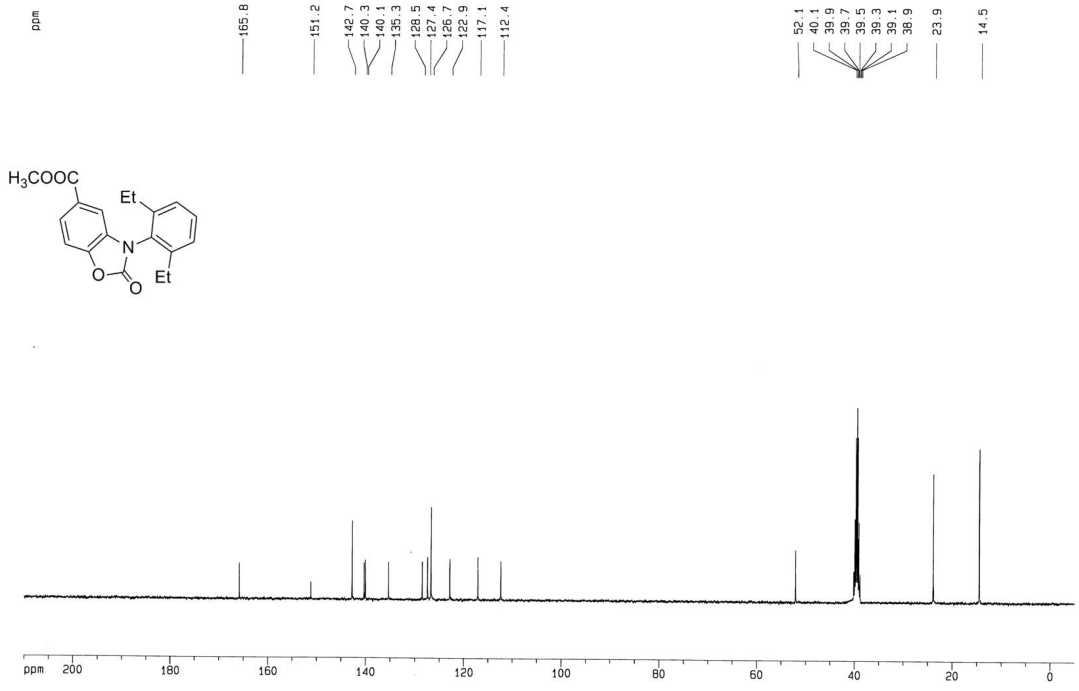
[^{1}H NMR and ^{13}C NMR spectrum of 4o in DMSO-d_6]



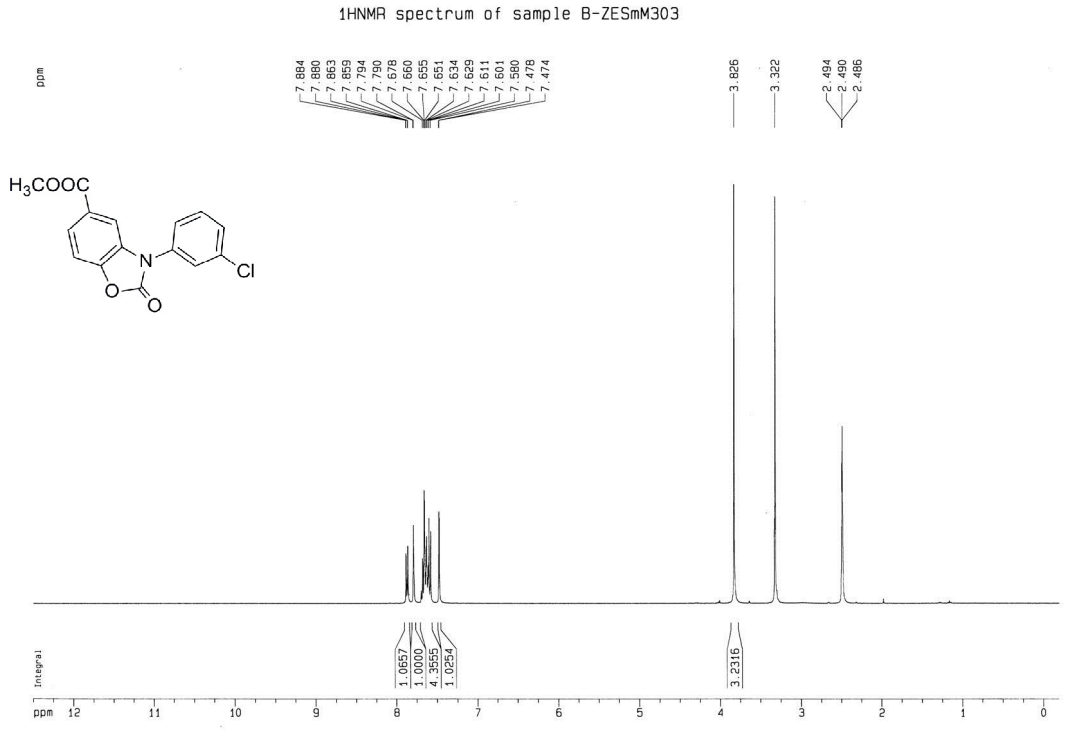
1H NMR Spectrum of sample B-ZESM325 in DMSO-d6

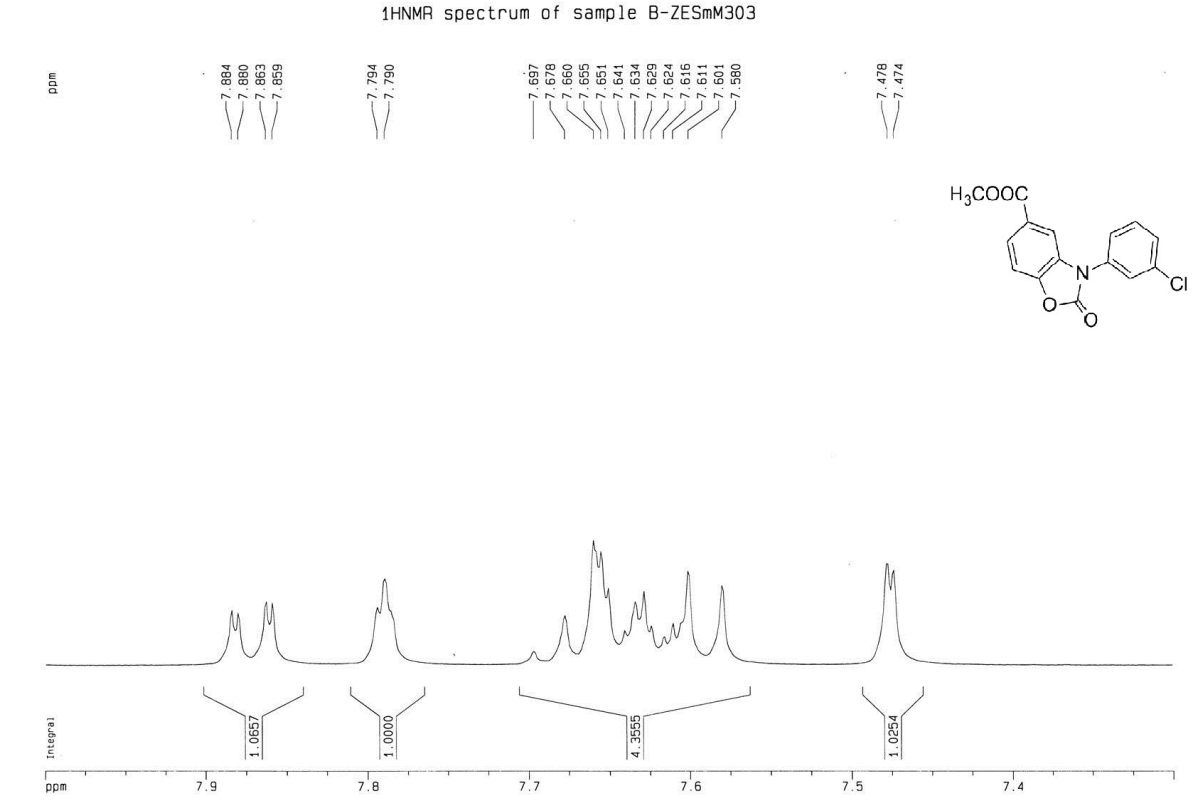


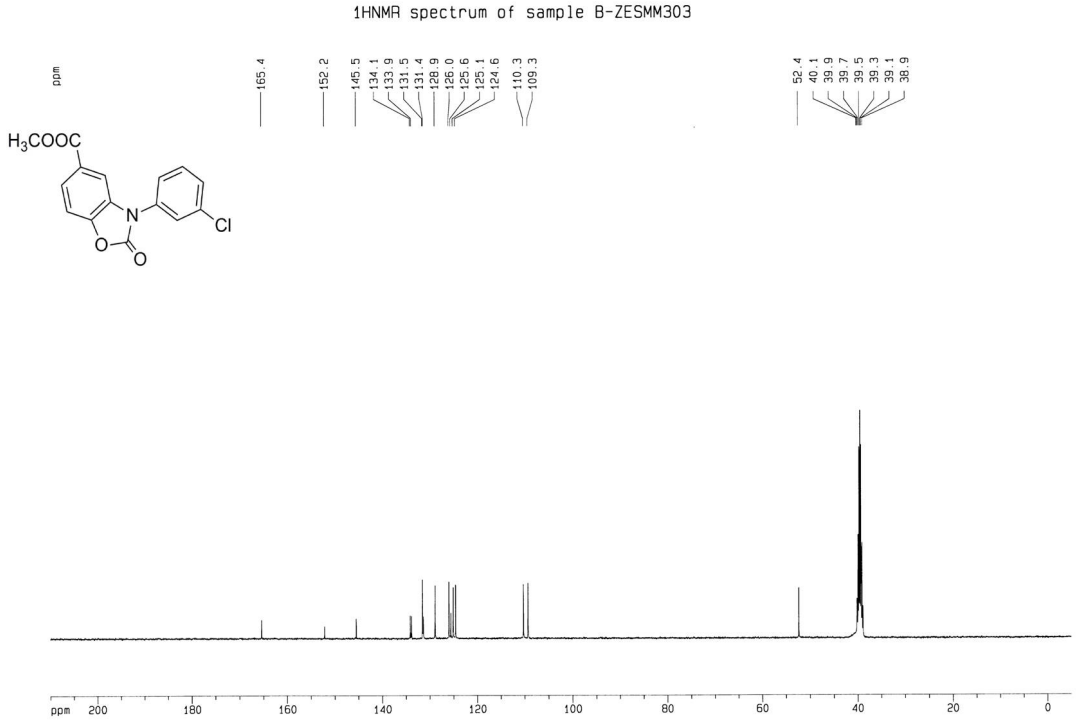
13CNMR spectrum of sample B-ZESM325



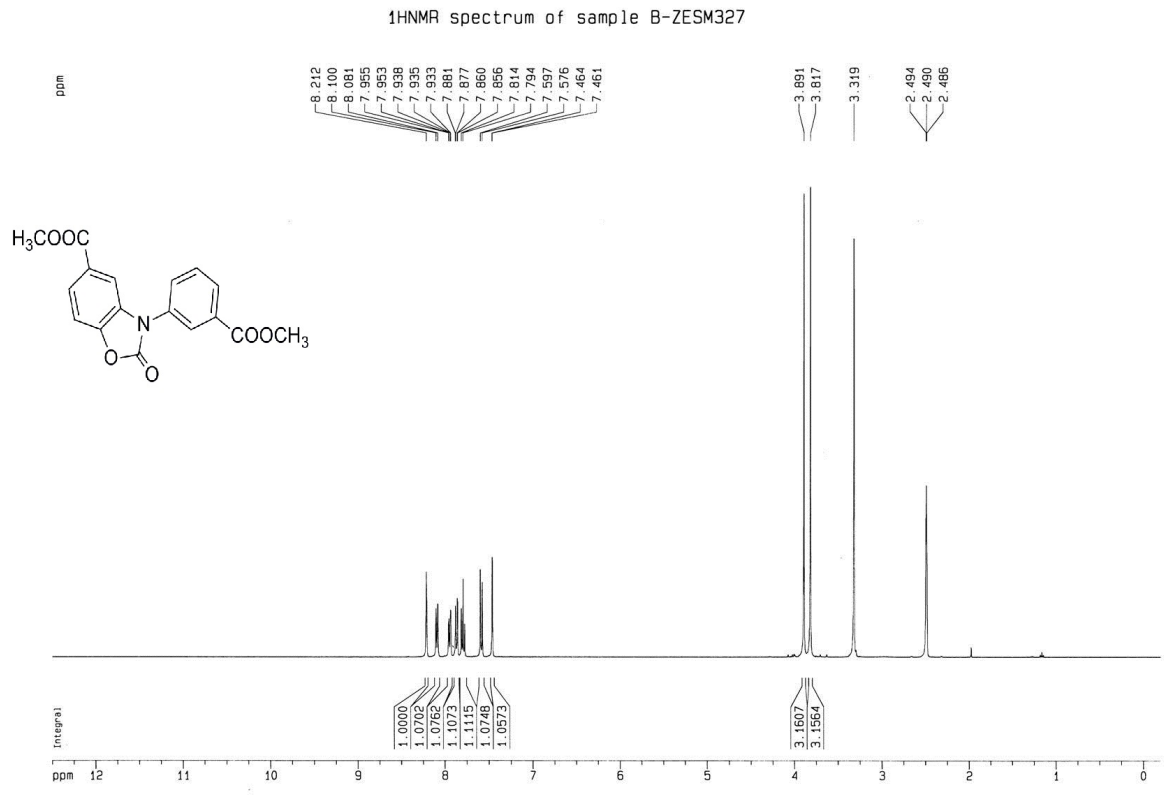
[^{1}H NMR and ^{13}C NMR spectrum of 4q in DMSO-d_6]



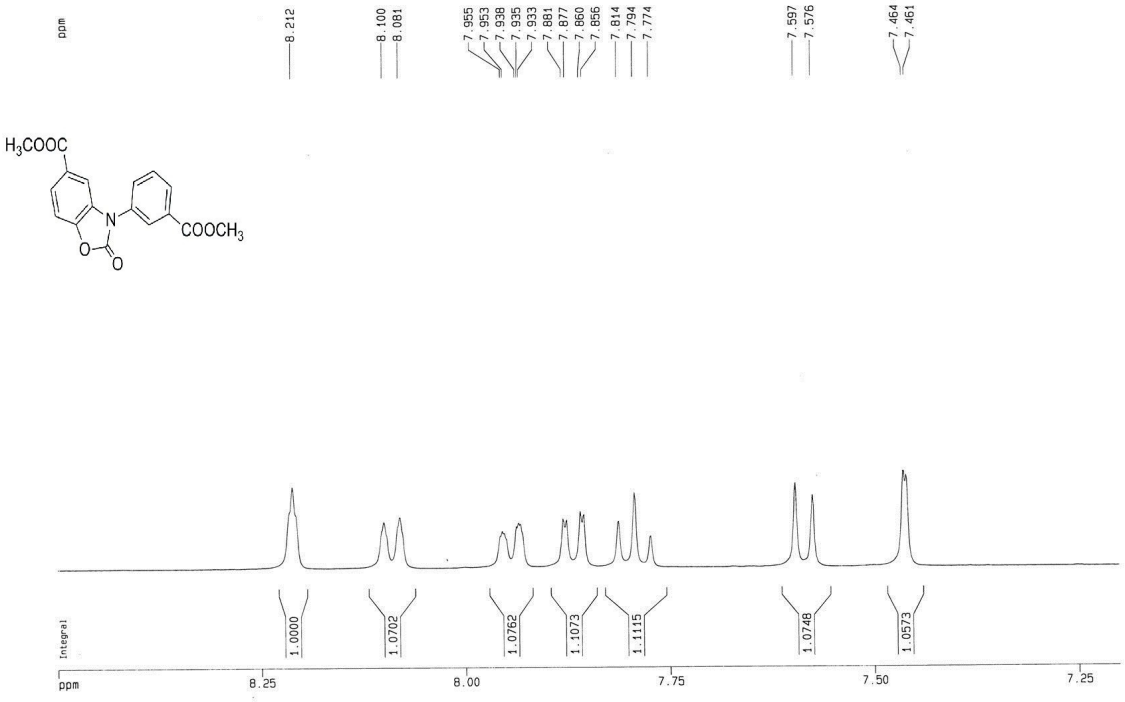




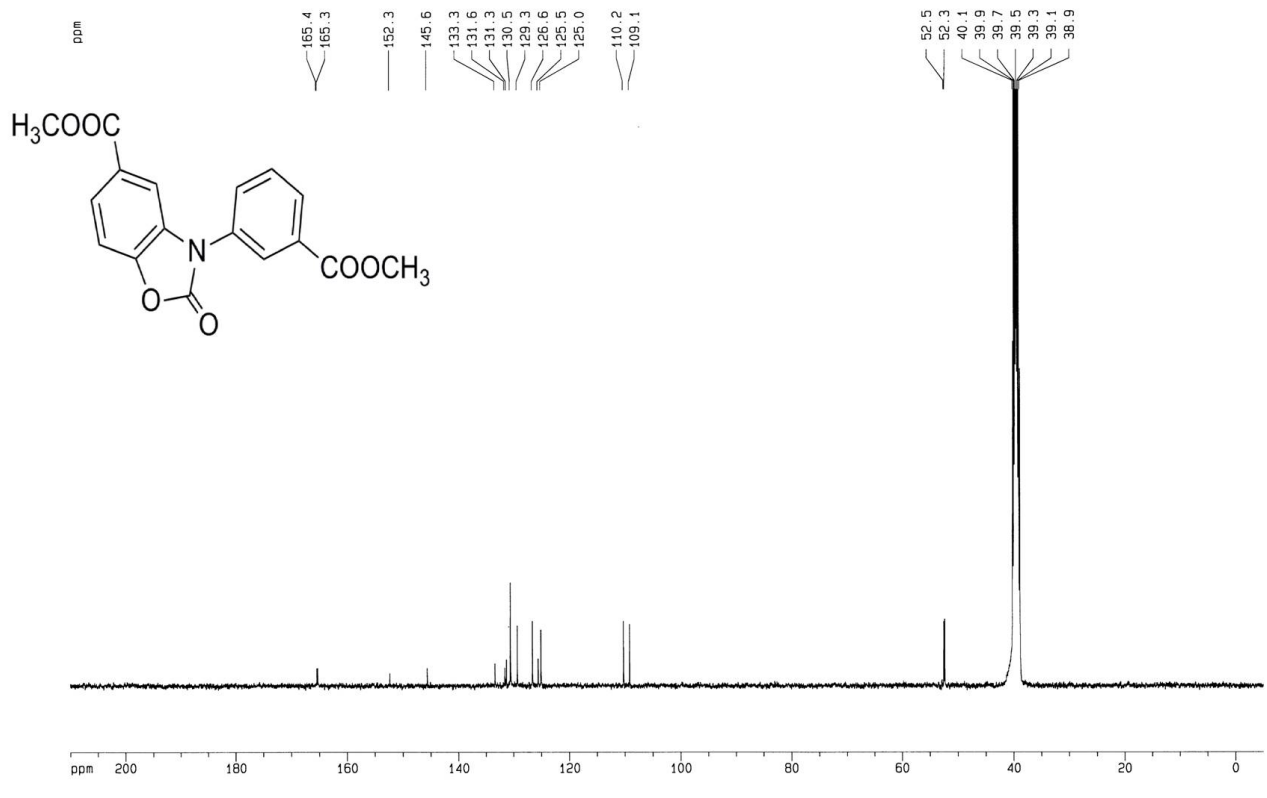
[^{1}H NMR and ^{13}C NMR spectrum of 4r in DMSO-d_6]



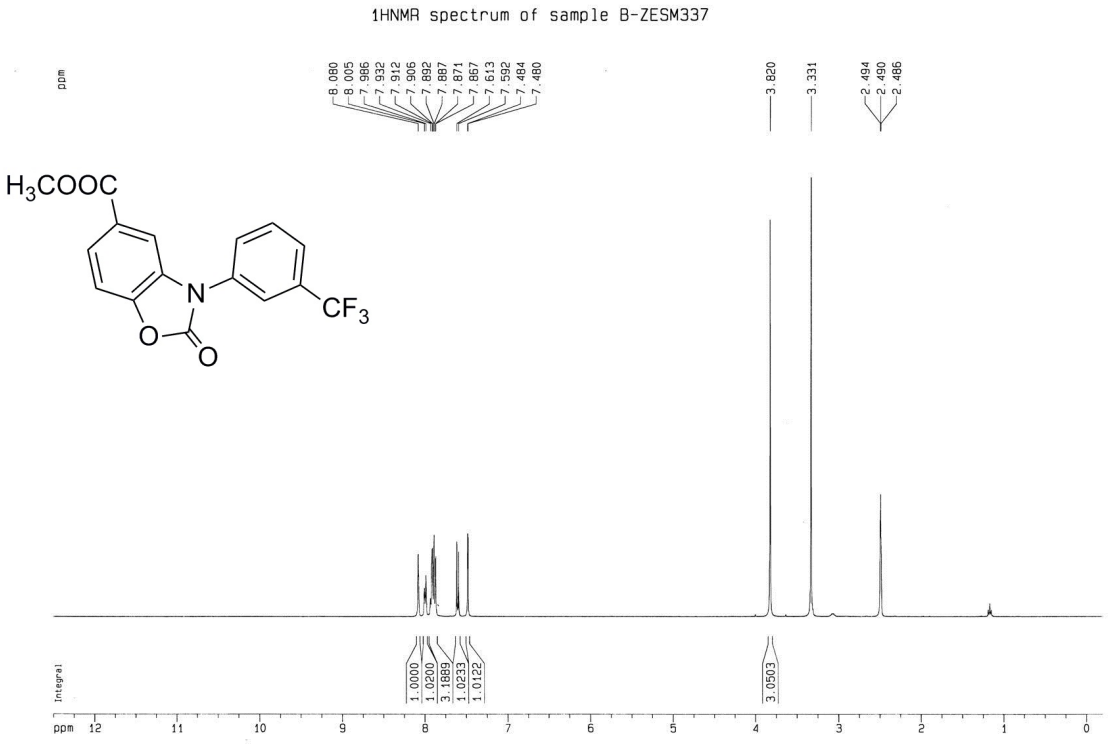
1HNMR spectrum of sample B-ZESM327

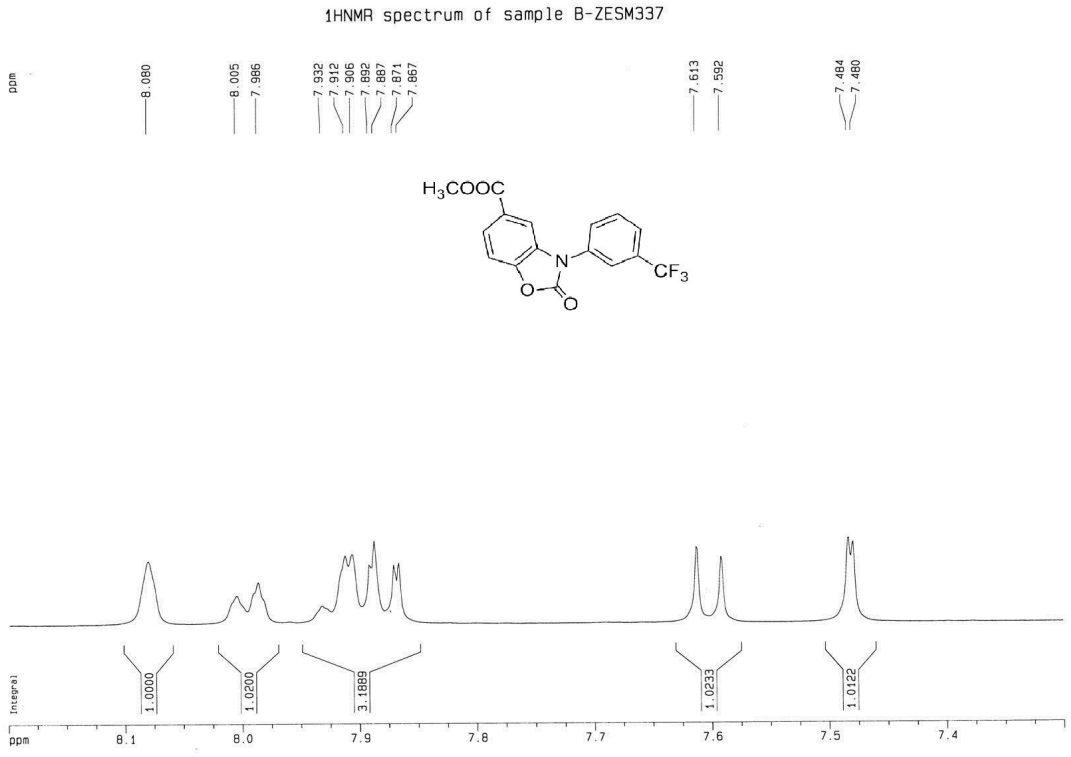


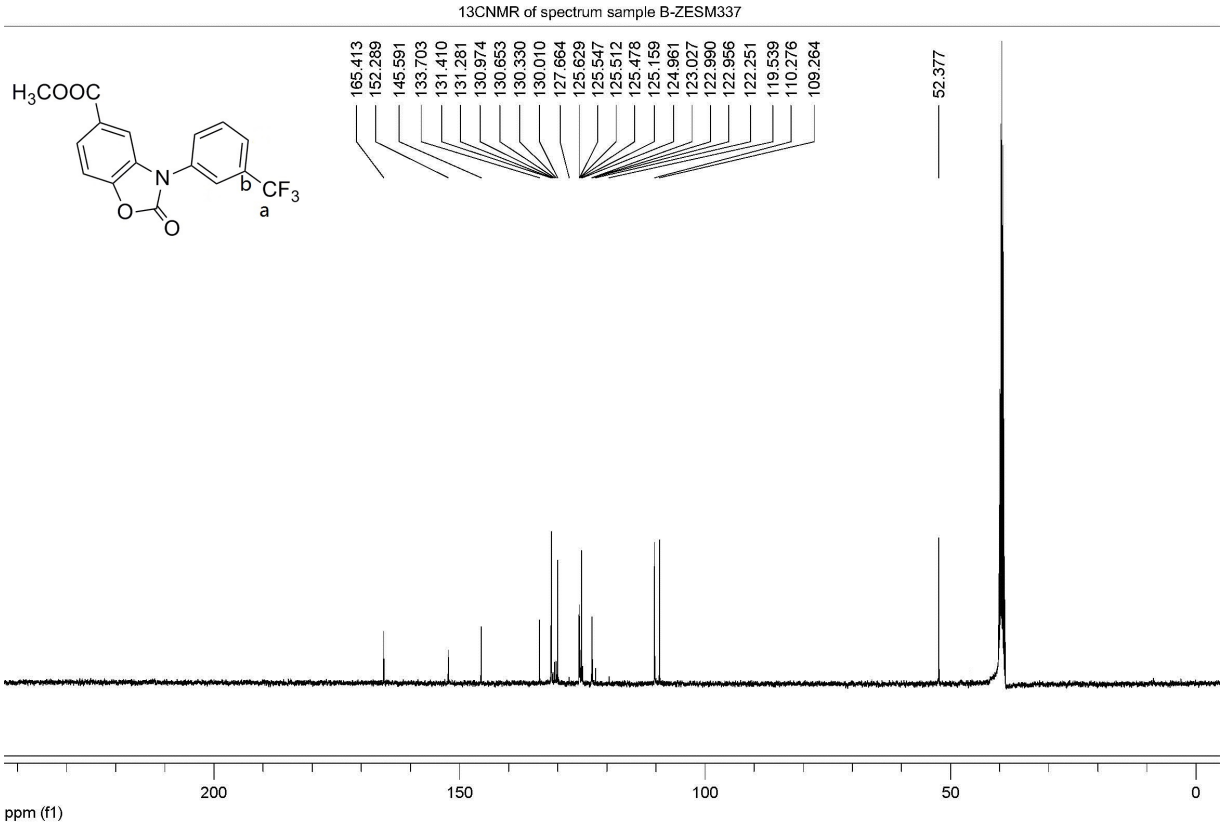
13CNMR spectrum of sample B-ZESM327

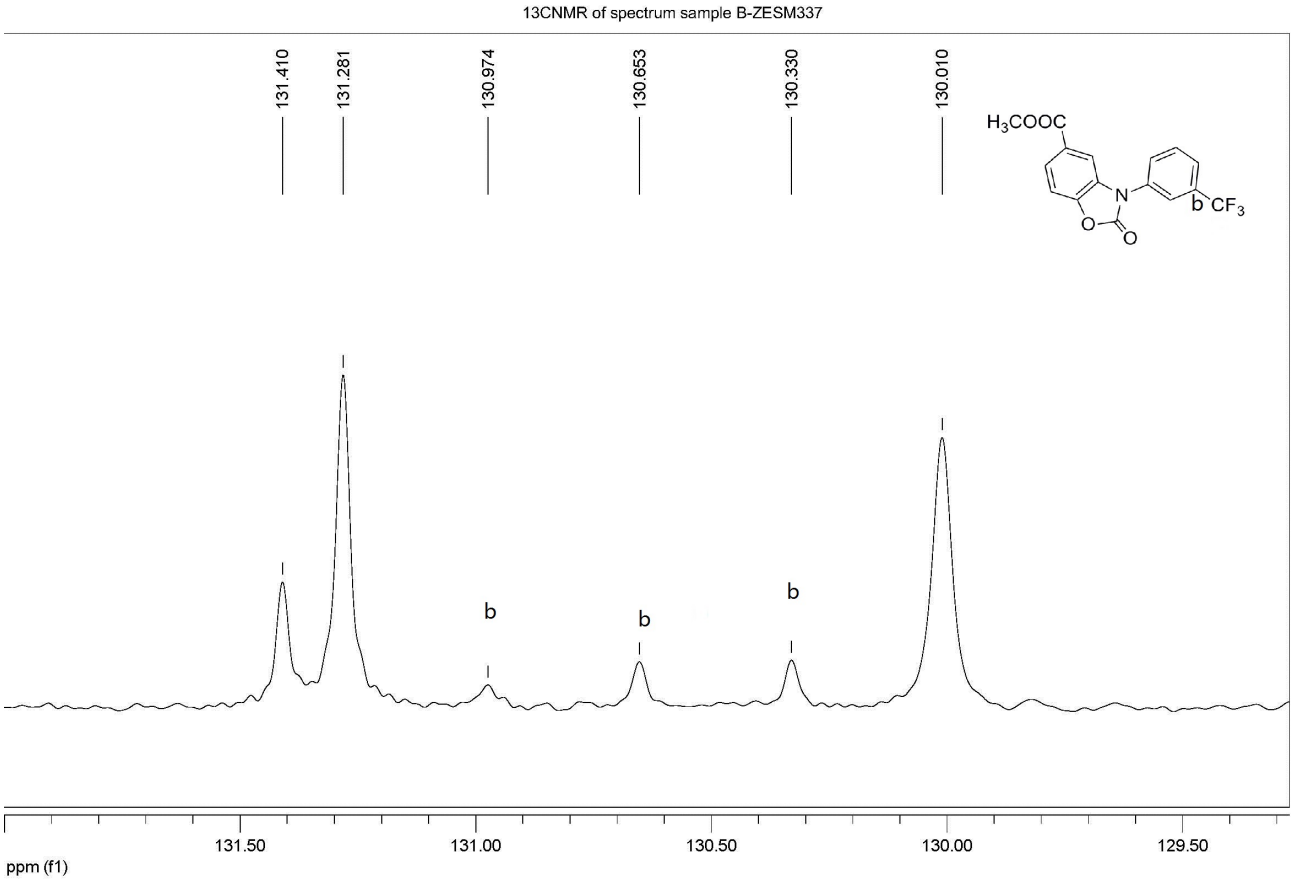


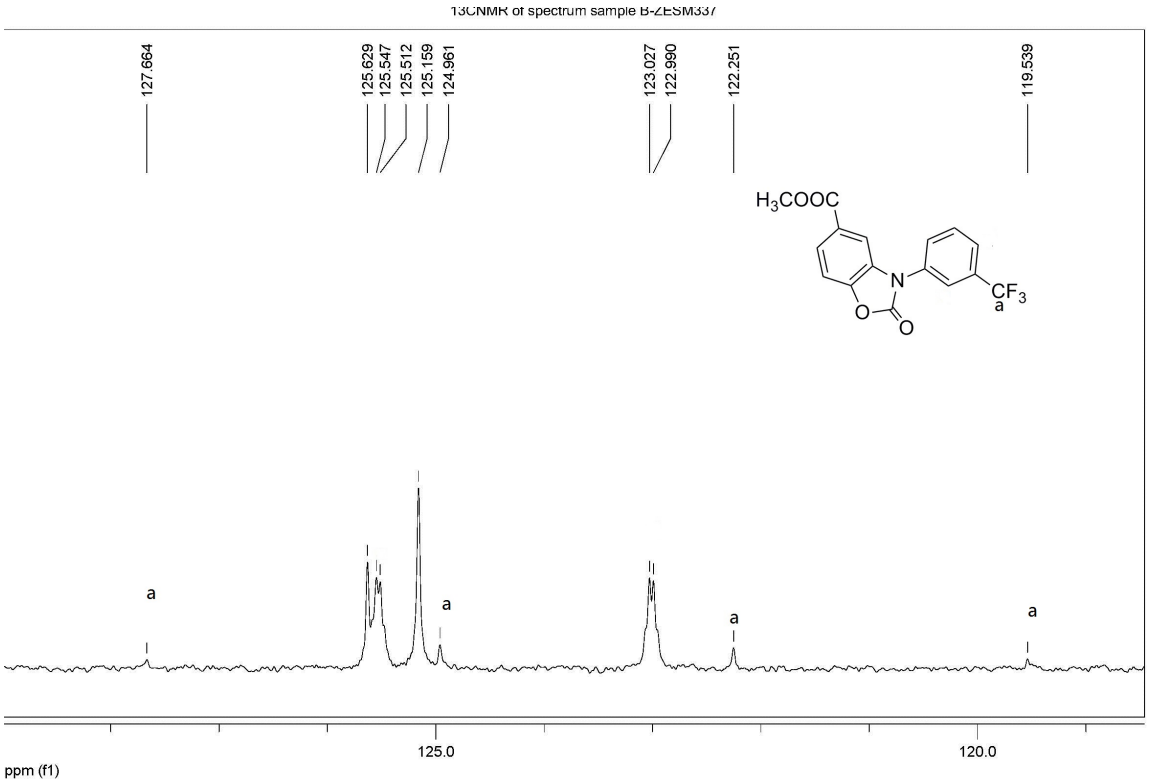
[^{1}H NMR and ^{13}C NMR spectrum of 4s in DMSO-d_6]

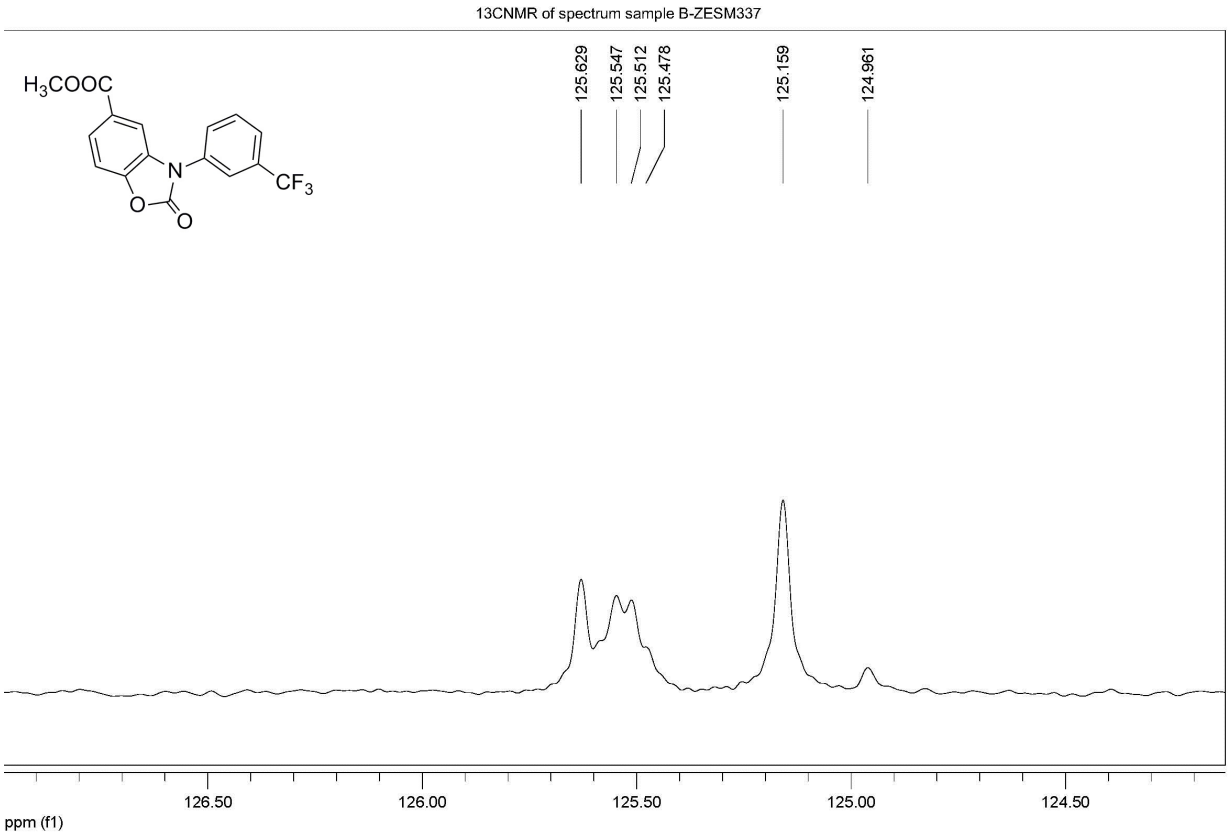


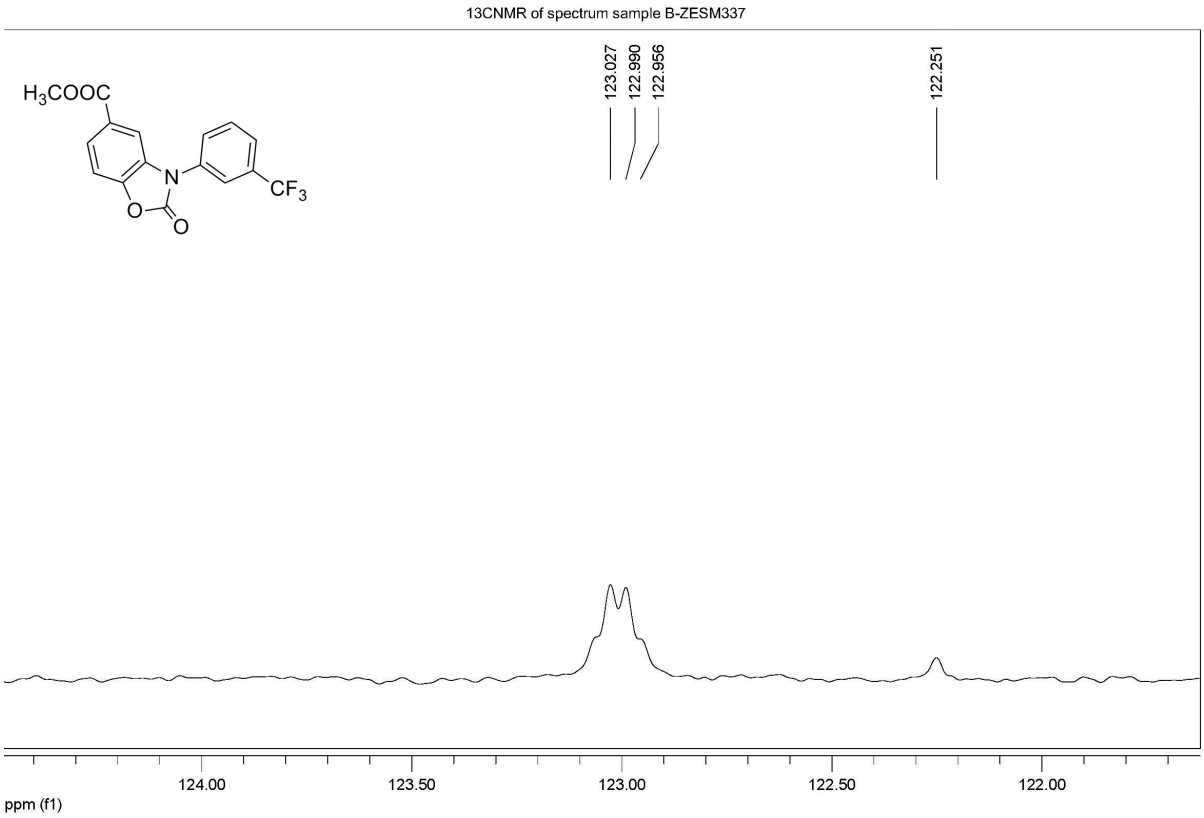



13CNMR of spectrum sample B-ZESM337
H3COOC
N
O
O
b
CF3
a
165.413
152.289
145.591
133.703
131.410
131.281
130.974
130.653
130.330
130.010
127.664
125.629
125.547
125.512
125.478
125.159
124.961
123.027
122.990
122.956
122.251
119.539
110.276
109.264
52.377
200
150
100
50
0
ppm (f1)

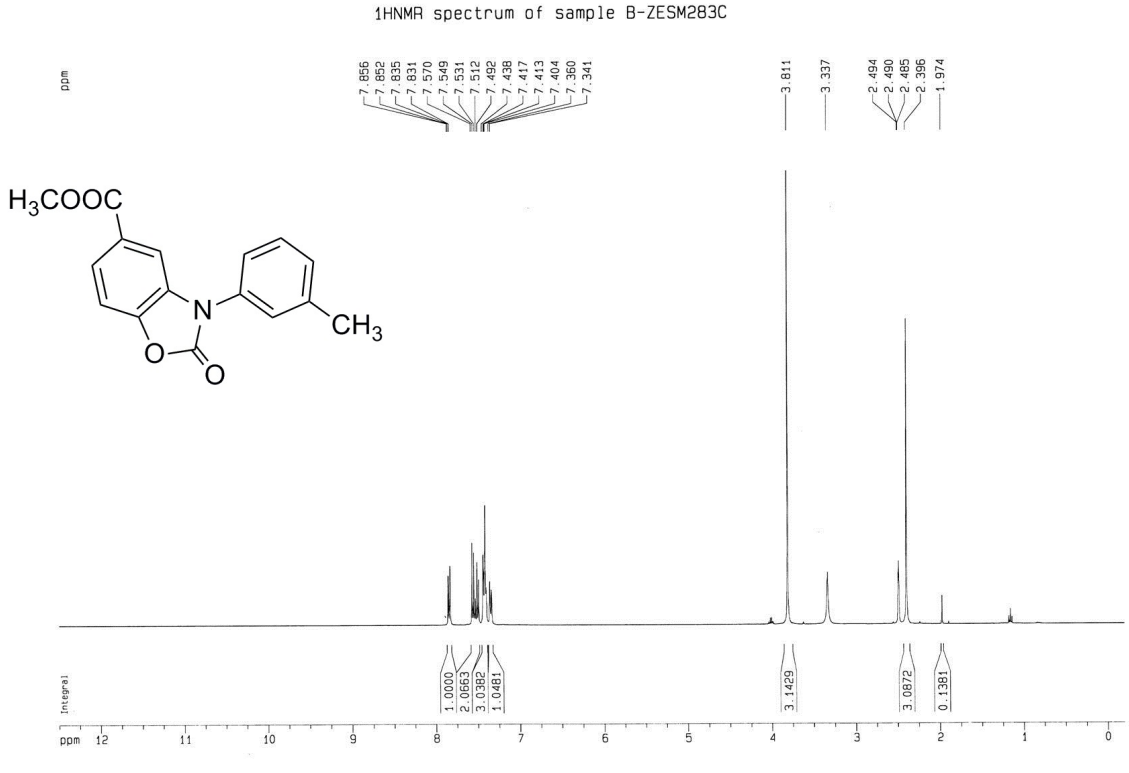

13CNMR of spectrum sample B-ZESM337
131.410
131.281
130.974
130.653
130.330
130.010
H3COOC
N
O
O
b
CF3
b
b
b
131.50
131.00
130.50
130.00
129.50
ppm (f1)


13CNMR of spectrum sample B-ZESM337
127.664
125.629
125.547
125.512
125.159
124.961
123.027
122.990
122.251
119.539
H3COOC
N
O
O
CF3
a
a
a
a
a
125.0
120.0
ppm (f1)

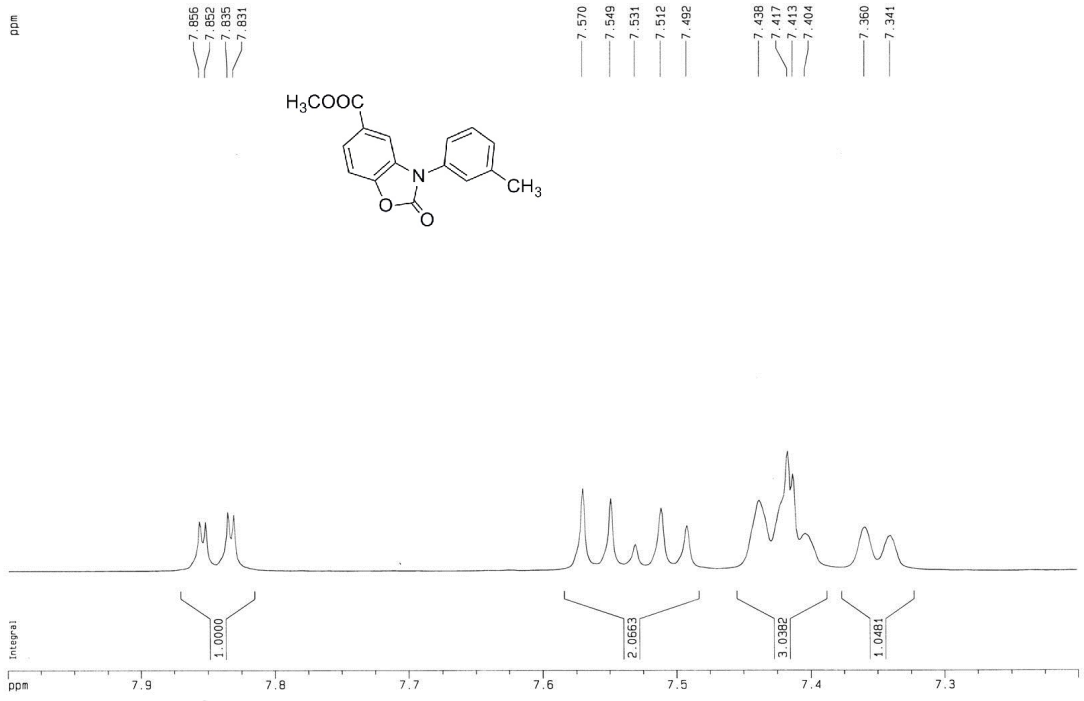

13CNMR of spectrum sample B-ZESM337
H3COOC
N
O
O
CF3
125.629
125.547
125.512
125.478
125.159
124.961
126.50
126.00
125.50
125.00
124.50
ppm (f1)



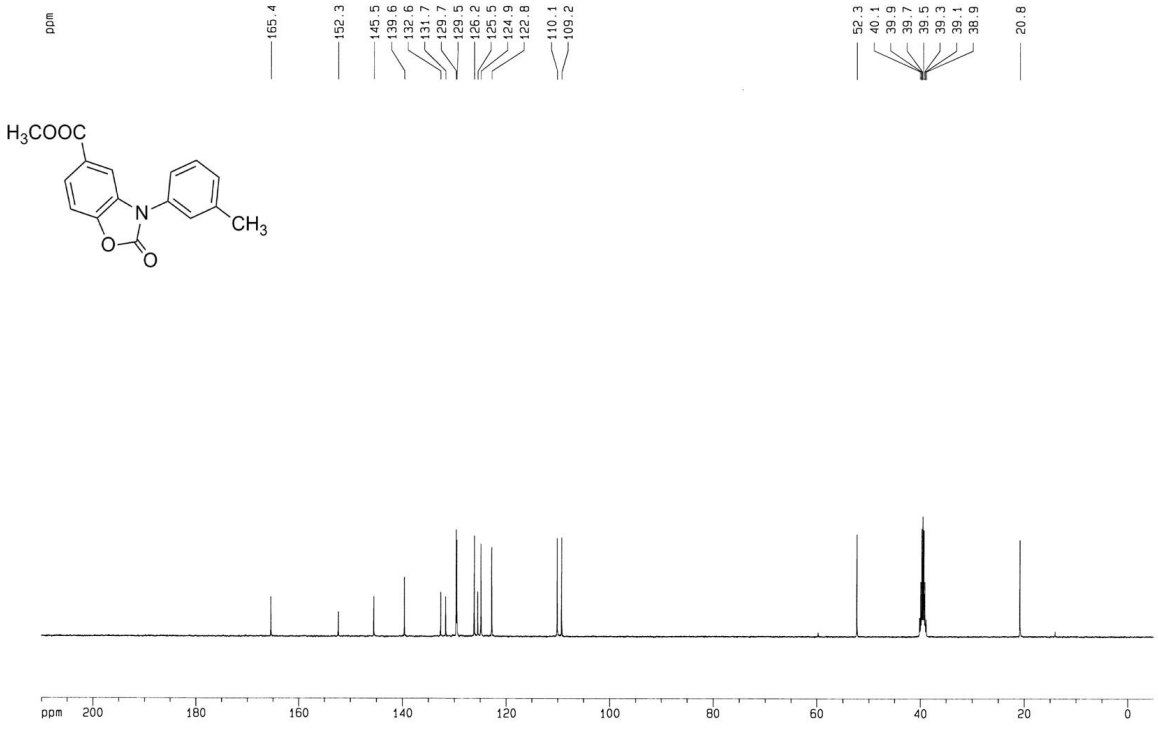
[^{1}H NMR and ^{13}C NMR spectrum of 4t in DMSO-d_6]



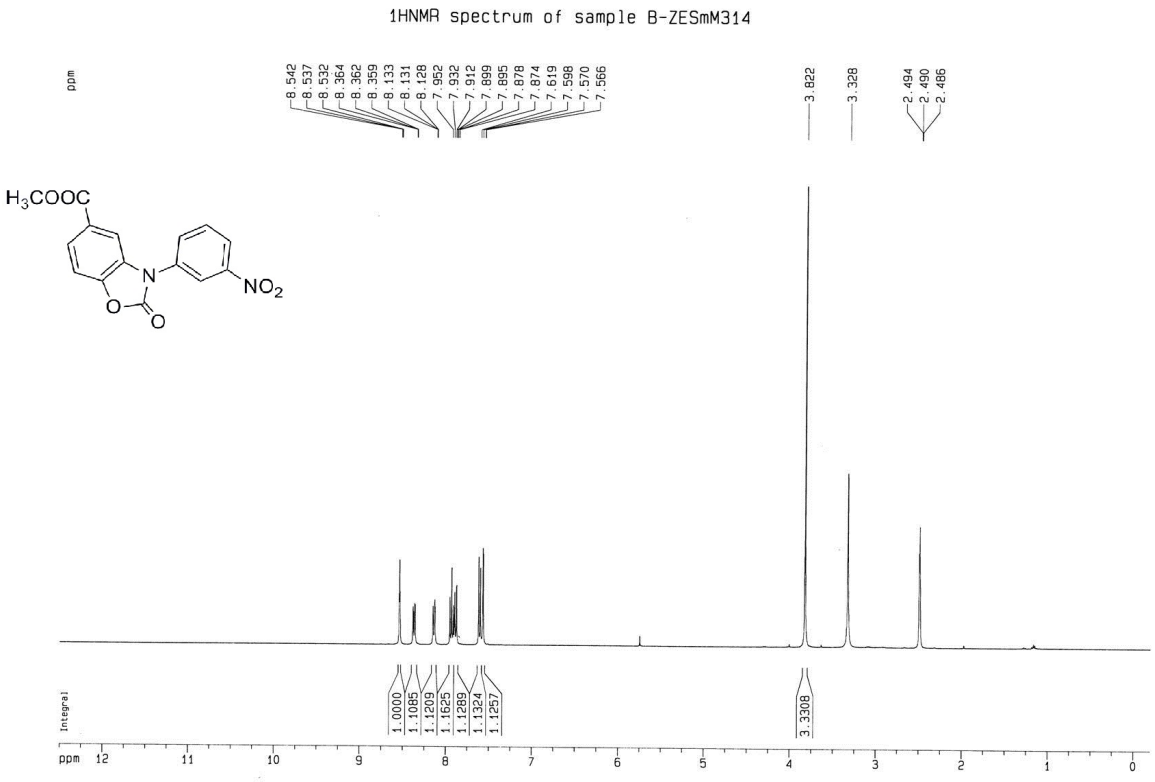
1HNMR spectrum of sample B-ZESM283C

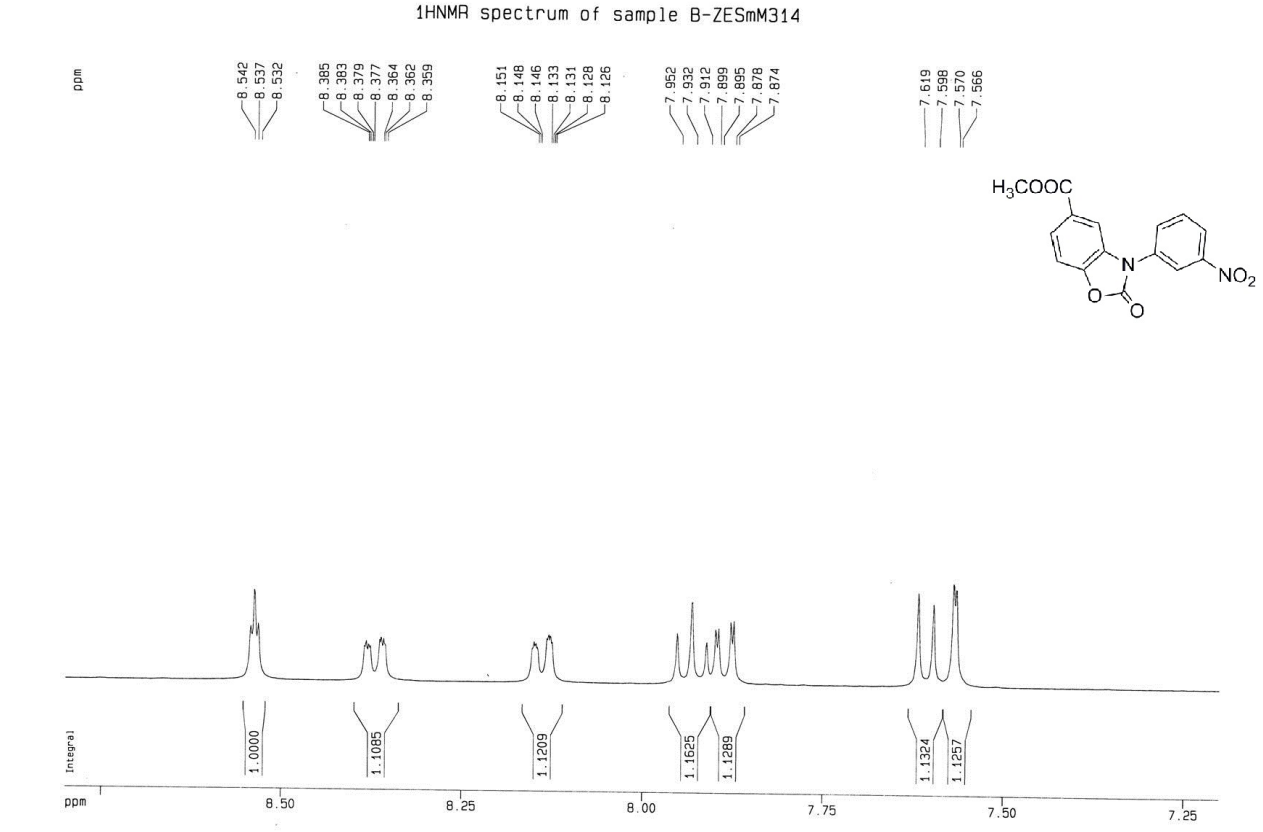


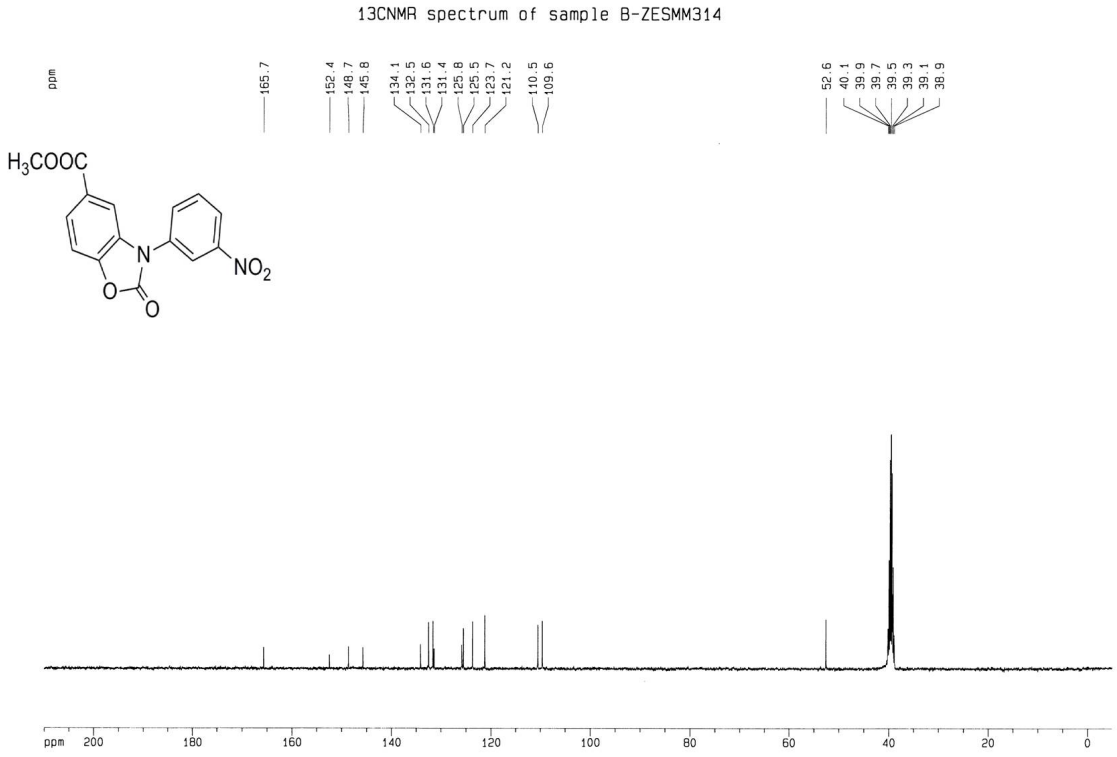
13CNMR spectrum of sample B-ZESMM283



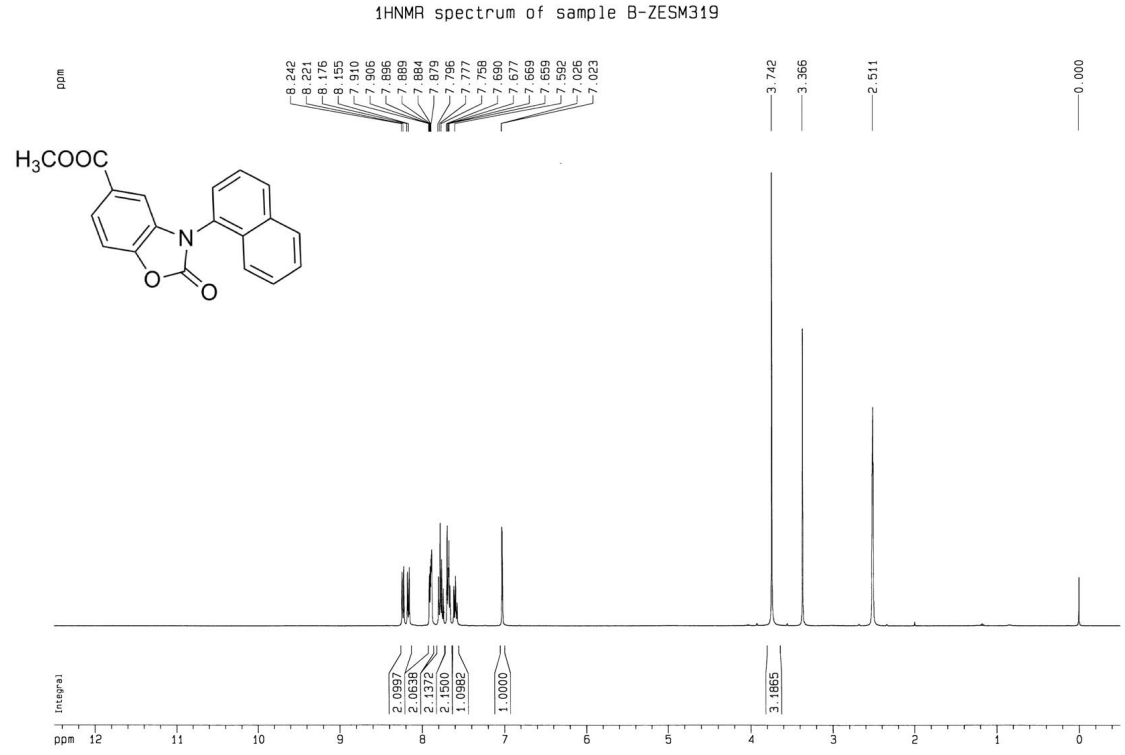
[^{1}H NMR and ^{13}C NMR spectrum of 4u in DMSO-d_6]



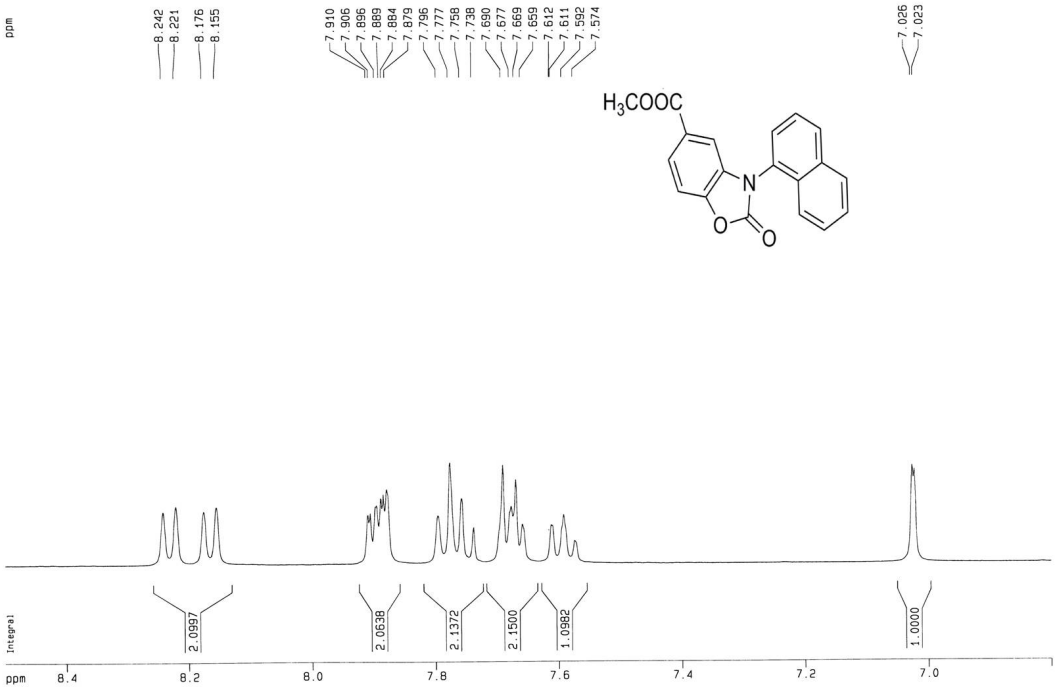




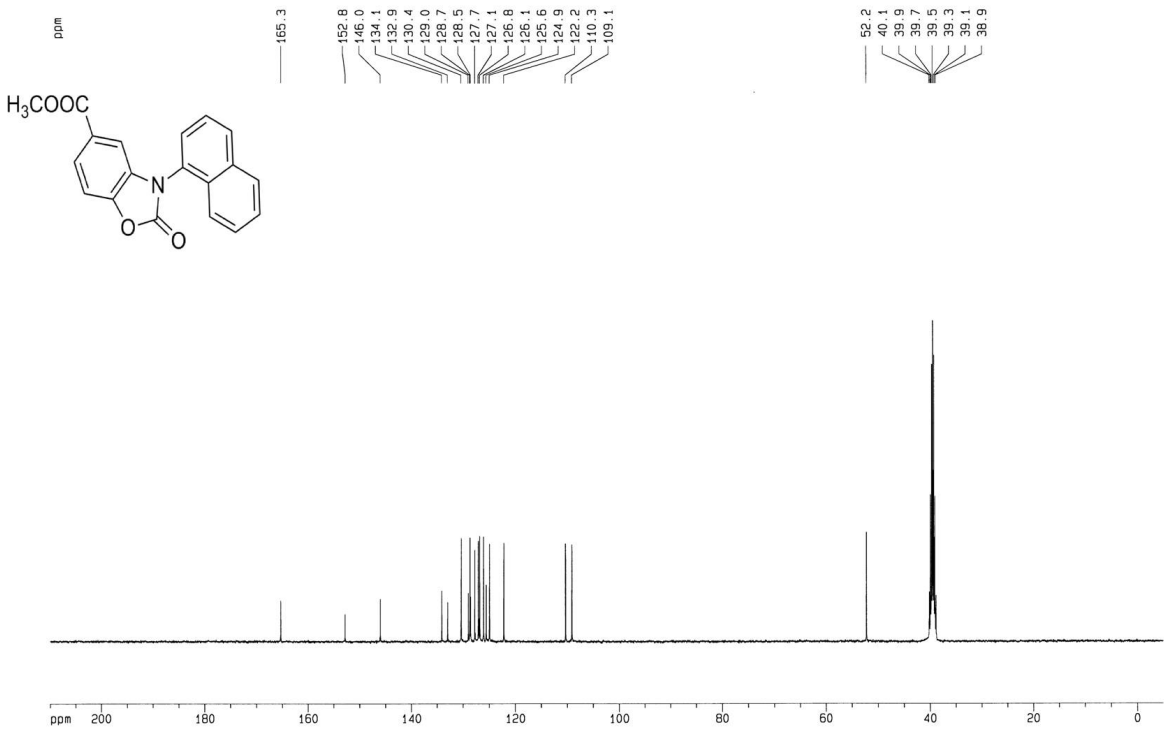
[^{1}H NMR and ^{13}C NMR spectrum of 4v in DMSO-d_6]



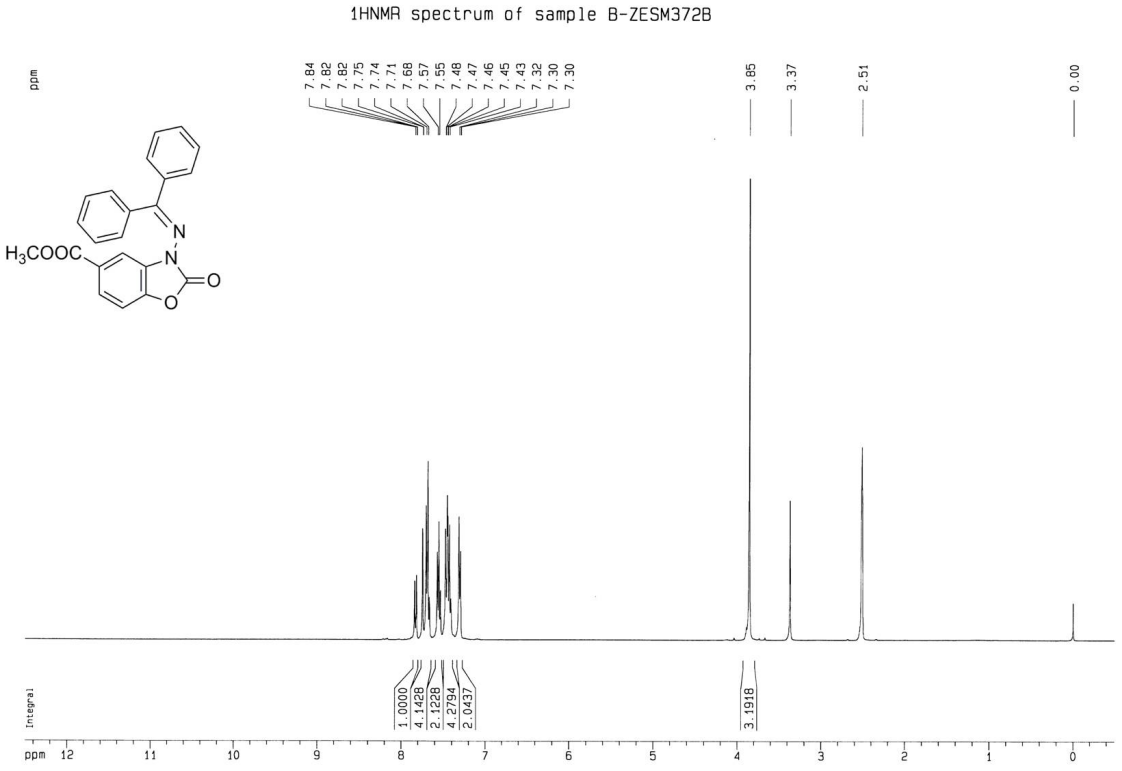
1HNMR spectrum of sample B-ZESM319

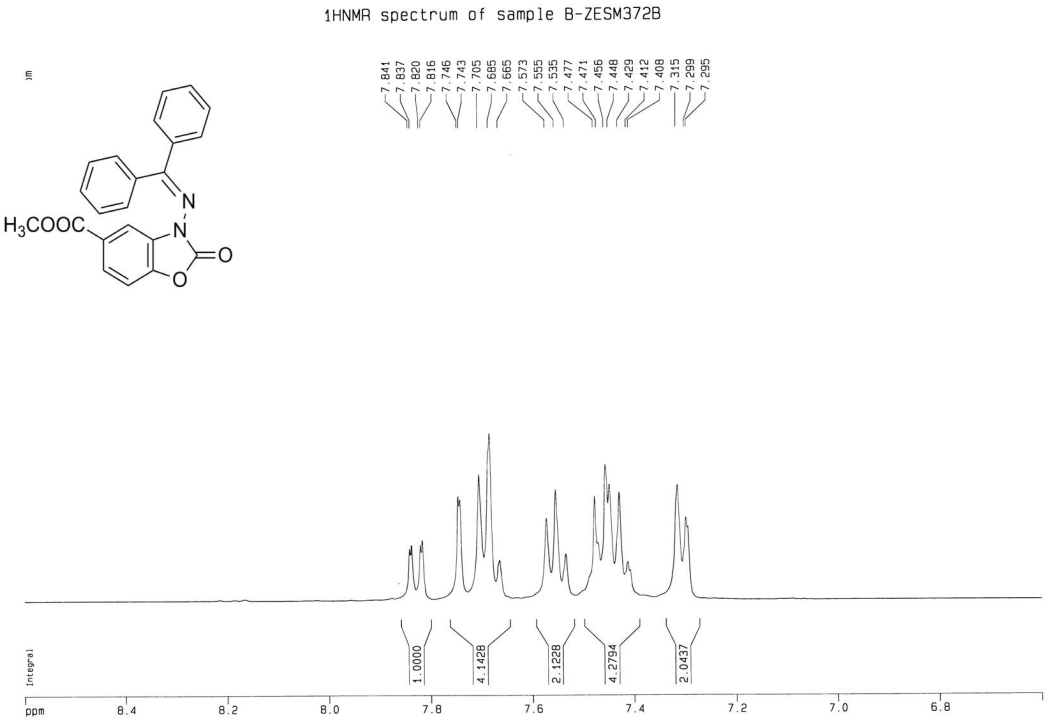


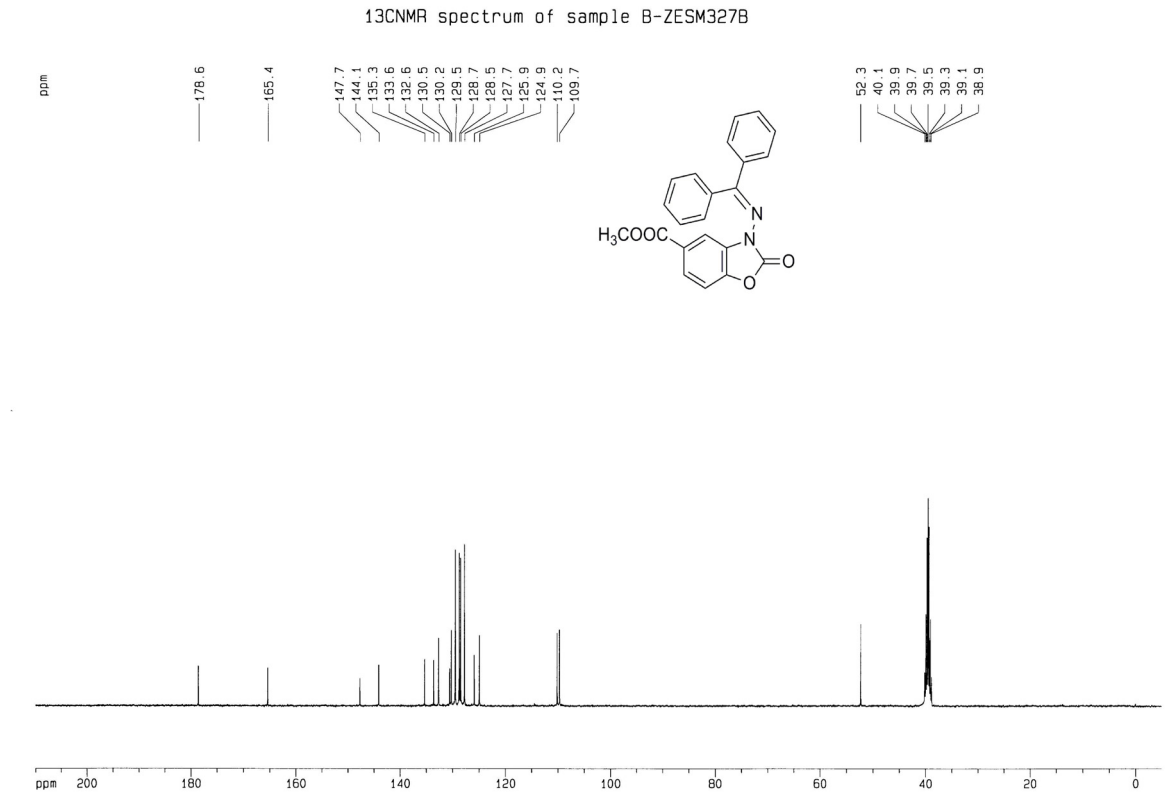
13CNMR spectrum of sample B-ZESM319



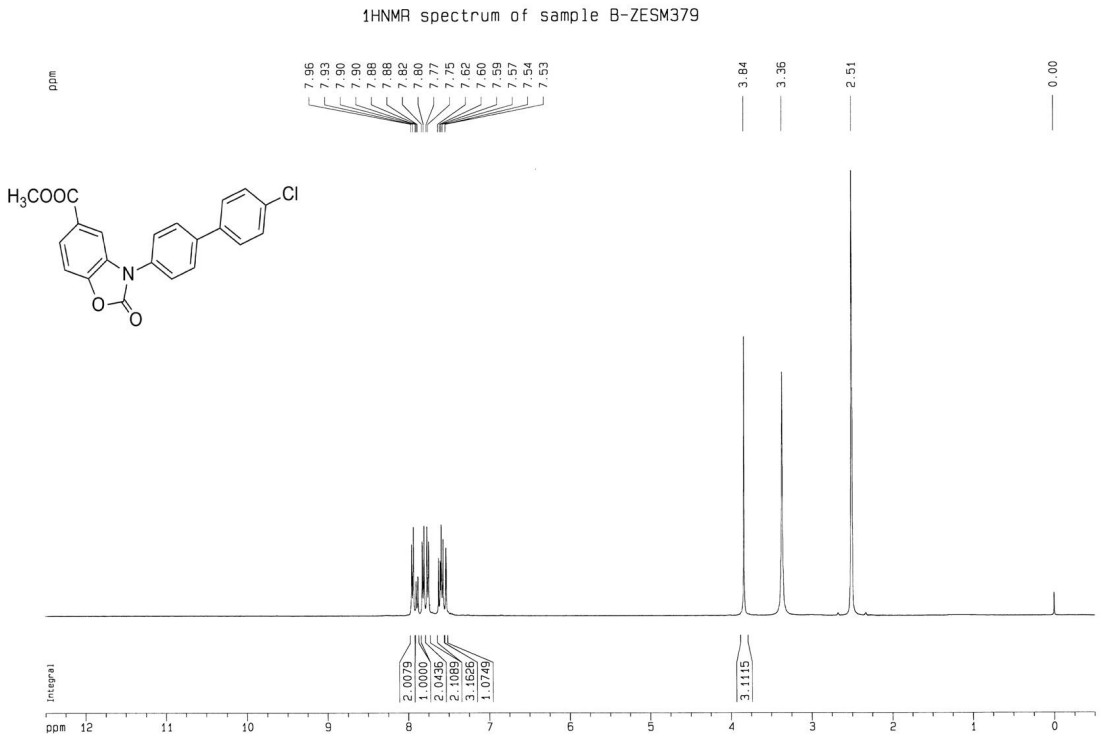
[^{1}H NMR and ^{13}C NMR spectrum of 4w in DMSO-d_6]



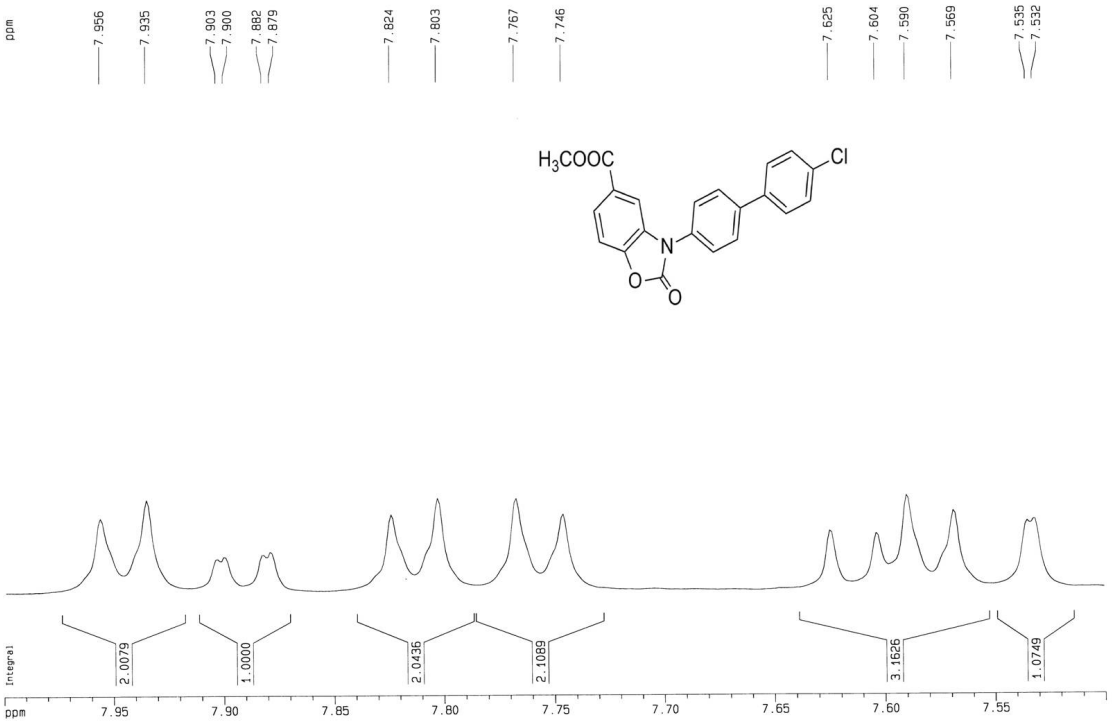




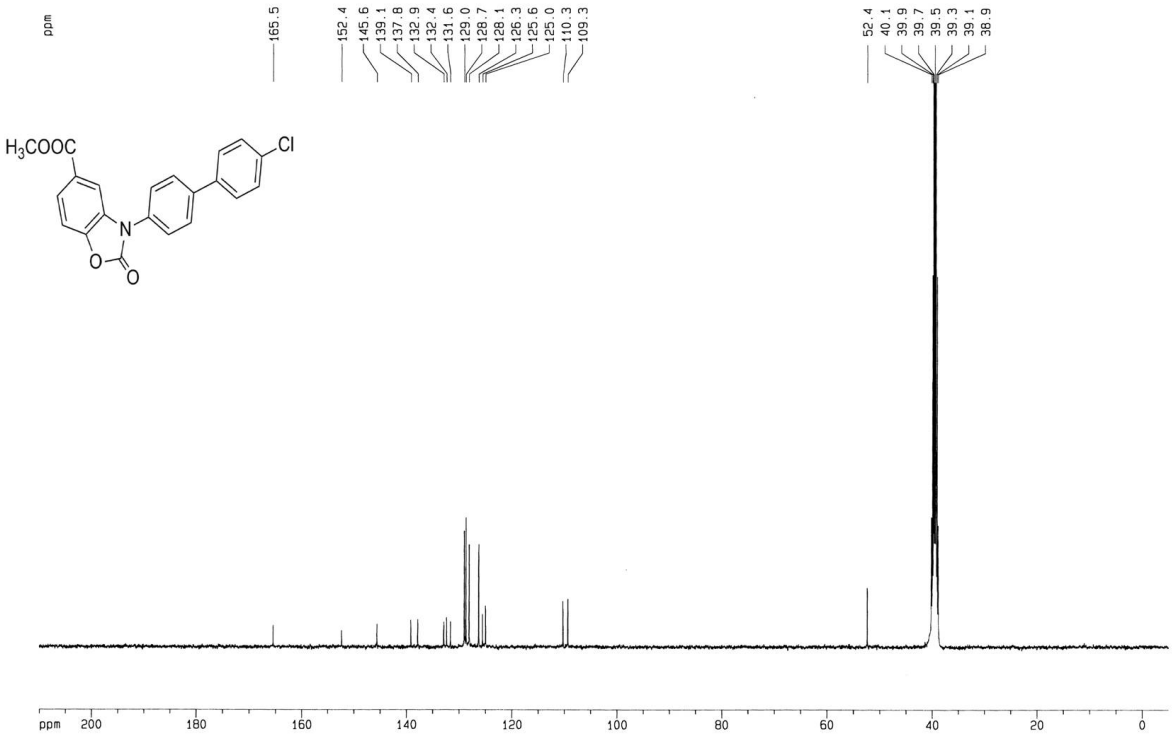
[^{1}H NMR and ^{13}C NMR spectrum of 4x in DMSO-d_6]



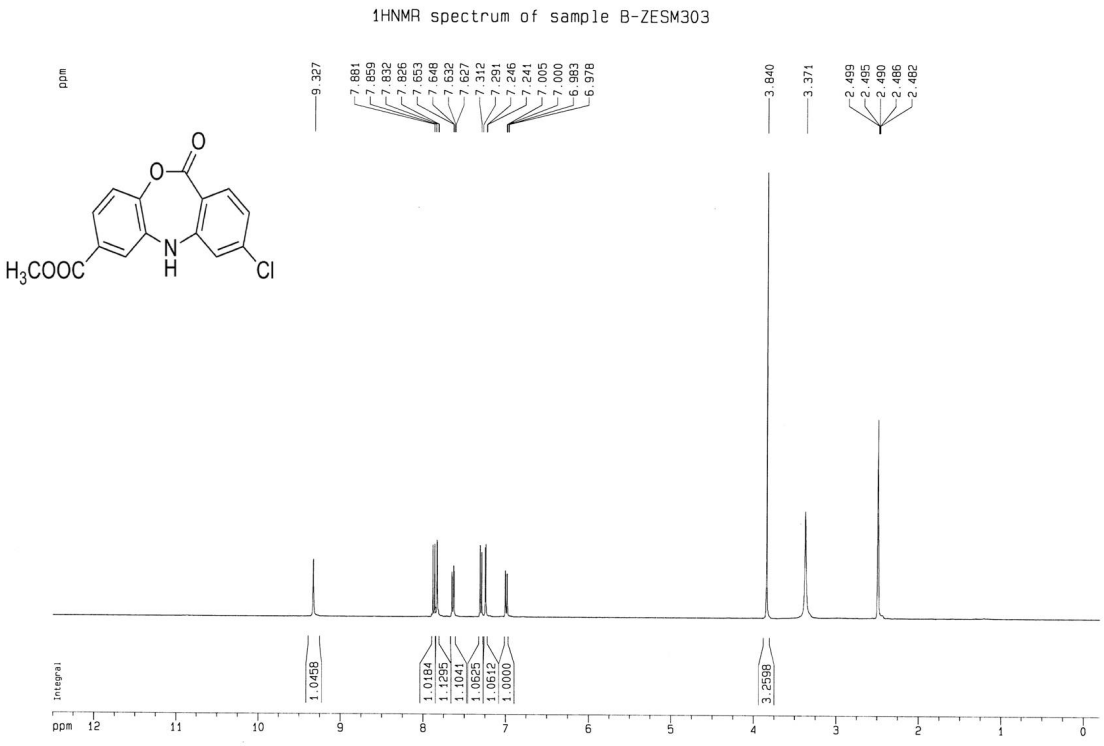
1HNMR spectrum of sample B-ZESM379

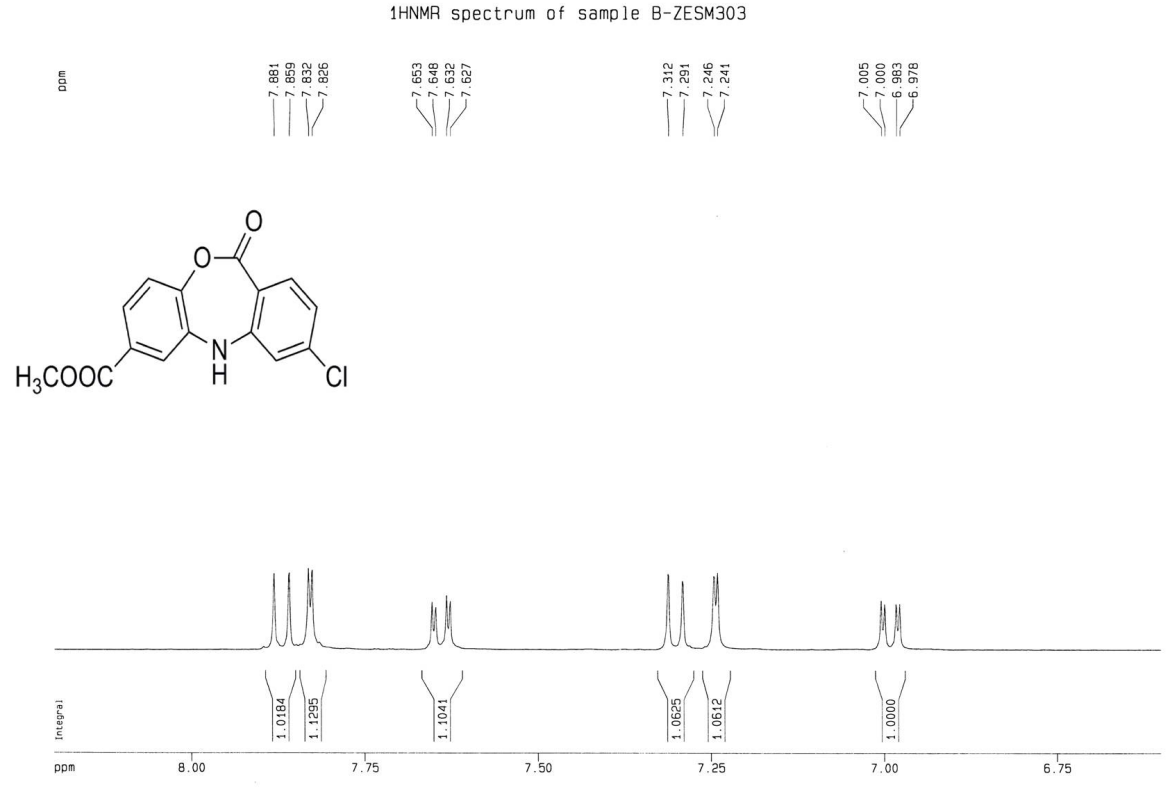


13CNMR spectrum of sample B-ZESM379



[^{1}H NMR and ^{13}C NMR spectrum of Ⅰ in DMSO-d_6]





13CNMR spectrum of sample B-ZESM303