Supporting Information

A biomass-involved strategy for the synthesis of N-arylated dibenzo[b,e][1,4]oxazepin-11(5*H*)-ones, acridones, 7, 12-dihydro-dibenzo[b,e][1,4]oxazocin-6*H*-ones and dibenzo[b,f]azepin-10(11*H*)-ones

Ensheng Zhang,[a,c] Xuejing Zhang,[b] Wen Wei,[a] Dejian Wang,[a,c] Yuchen Cai,[b] Tianlong Xu,[a,c] Ming Yan,[b] Yong Zou*[a,b]

[a] *Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, P. R. China, E-mail: zou_jinan@163.com.*

[b] *School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, P. R. China.*

[c] *University of Chinese Academy of Sciences, Beijing, 100039, P. R. China.*

Contents

I- Instruments and Chemicals

(-)-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). Melting points

were measured on a Thiele apparatus and were uncorrected. Column chromatography was performed with silica gel (200-300 mesh) using EtOAc-PE system as the eluent. Microwave experiments were carried out with a scientific WBFY microwave reactor in a flask connected with a condenser (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 $CDCl_3$ or DMSO-d_6 as the solvent at 298K or 323K. Chemical shifts were reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference. HRMS spectras were recorded on a LC-Q-TOF (ESI) apparatus. Mass spectrometry were measured on a Shimadzu GC-MS QP5050A in electron 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 ~~white powder~~ (-)-methyl shikimate ~~16.9g (90%) as a white powder.~~ 16.9g (90%).

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 3-MDHS as a white

solid. The crude product was recrystallized from EtOAc to give 3-MDHS 6.23g (67%) in pure form as white crystals.

II-2 General procedure for the preparation of the starting materials N-arylated 2-aminophenols (1a-1p)

Based on our previous studies, an improved method for the synthesis of platform compounds N-arylated 2-aminophenols (**1a-1p)** under microwave condition has been established as follows:

To a flask (25 ml) were added 3-MDHS (1.02 g, 5.5 mmol), arylamine (5.0 mmol), *p*-TsOH (0.5 mmol) and DMF (10 ml). The mixture was stirred for 5-30 minutes at 110 °C (240 W). After completion of the reaction as indicated by TLC the mixture was poured into brine and stirred vigorously. The resulting solid was filtered and dried to furnish the desired product in pure form (80-99% yields). If necessary, these products could be further purified by recrystallization from EtOAc/PE.

II-3 General procedure for the preparation of the N-aryl dibenzo[b,e][1,4] oxazepin-11(5*H*)-ones (4a-4r)

To a flask (25 ml) were added **1** (1.0 mmol), 2-halogenated benzoic (1.0 mmol), Cu_2O (0.2 mmol), K_2CO_3 (0.42 g, 3 mmol) and DMF (5 ml). The mixture was stirred at 120 °C under microwave irradiation with the protection of N_2 for the indicated minutes (t_1). After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the solid was washed with EtOH (1ml). Then, the filtrate was poured into water (50 ml) and acidified with hydrochloric acid (1N). The resulting solid was filtered and dried to furnish the triarylamine intermediates **3** (**3a-3r**). Then, to a flask (25 ml) were added the isolated intermediate **3**, DCM (5 ml), Et_3N (4 mmol), and BTC (1 mmol BTC dissolved in 3 ml DCM and 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

(20 ml, 5 %) and extracted with ethyl acetate (3 × 20 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 or by column chromatography using EtOAc-PE as eluent.

II-4 General procedure for the preparation of the N-aryl acridones (5a-5f, 5h, 5p and 5q)

To a flask (25 ml) were added **1** (1.0 mmol), 2-halogenated benzoic (1.0 mmol), Cu_2O (0.2 mmol), K_2CO_3 (0.42 g, 3 mmol) and DMF (5 ml). The mixture was stirred at 120 °C under microwave irradiation with the protection of N_2 for the indicated minutes (t_1). After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the solid was washed with EtOH (1ml). Then, the filtrate was poured into water (50 ml) and acidified with hydrochloric acid (1N). The resulting solid was filtered and dried to furnish the triarylamine intermediates **3** (**3a-3h**, **3q and 3r**). Then, to a flask (25 ml) were added intermediate **3** and $BF_3{\cdot}Et_2O$ (5 ml), the mixture was stirred at 60 °C for the indicated hours (t_2). After completion of the reaction as indicated by TLC, the mixture was poured into brine (20 ml) and extracted with ethyl acetate (3 × 20 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-5 General procedure for the preparation of the N-aryl 7, 12-dihydro-dibenzo[b,e][1,4]oxazocin-6(*H*)-ones (6d and 6e)

To a flask (25 ml) were added **1** (1.0 mmol), 2-bromophenylacetic acid (1.0 mmol), Cu_2O (0.2 mmol), K_2CO_3 (0.42 g, 3 mmol) and DMF (5 ml). The mixture was stirred at 120 °C under microwave irradiation with the protection of N_2 for the indicated minutes (t_1). After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the solid was washed with EtOH (1ml). Then, the filtrate was poured into water (50 ml) and acidified with hydrochloric acid (1N). The resulting solid was filtered and dried to furnish the triarylamine intermediates **3**. Then, to a

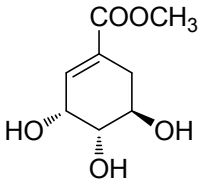
flask (25 ml) were added intermediate **3,** DCM (5 ml), Et_3N (4 mmol) and BTC (1 mmol BTC dissolved in 3 ml DCM and added dropwise). The mixture was stirred for the indicated hours (t_2) at room temperature. After completion of the reaction as indicated by TLC, the mixture was washed with sodium carbonate solution (20 ml, 5 %) and extracted with ethyl acetate (3 × 20 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 column chromatography using EtOAc-PE (1: 8) as eluent.

II-6 General procedure for the preparation of the N-aryl dibenzo [b,f]azepin-10(11*H*)-ones (7d and 7e)

To a flask (25 ml) were added **1** (1.0 mmol), 2-bromophenylacetic acid (1.0 mmol), Cu_2O (0.2 mmol), K_2CO_3 (0.42 g, 3 mmol) and DMF (5 ml). The mixture was stirred at 120 °C under microwave irradiation with the protection of N_2 for the indicated minutes (t_1). After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the solid was washed with EtOH (1ml). Then, the filtrate was poured into water (50 ml) and acidified with hydrochloric acid (1N). The resulting solid was filtered and dried to furnish the triarylamine intermediates **3**. Then, to a flask (25 ml) were added intermediates **3** and $BF_3 \cdot Et_2O$ (5 ml), the mixture was stirred at 60 °C for the indicated hours (t_2). After completion of the reaction as indicated by TLC, the mixture was poured into brine (20 ml) and extracted with ethyl acetate (3 × 20 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.

III-Characterization data for Products

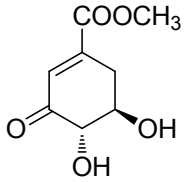
III-1 Characterization data for (-)-methyl shikimate and 3-MDHS



(-)-Methyl shikimate

White solid, 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_1 = 17.6 Hz, J_2 = 4.4 Hz, 1H, 6α-H), 2.18

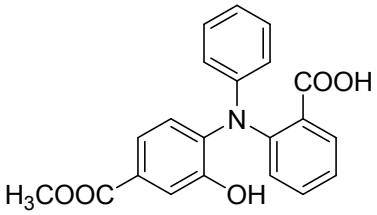
(dd, J_1 = 17.6 Hz, J_2 =6.8 Hz, 1H, 6β-H); MS (EI): m/z =188 $[M]^+$, 170 $[M-H_2O]^+$, 157 $[M-OCH_3]^+$, 129 $[M-COOCH_3]^+$.



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

White solid, 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_1 = 10.4 Hz, J_2 = 3.6 Hz, 1H, 4-H), 3.85(m, 1H, 5-H), 3.81(s, 3H, OCH_3), 3.06 (dd, J_1 = 18.4 Hz, J_2 = 5.2 Hz, 1H, 6α-H), 2.18 (ddd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, J_3 = 3.2 Hz, 1H, 6β-H); MS (EI): m/z = 186 $[M]^+$, 155 $[M-OCH_3]^+$, 127 $[M-COOCH_3]^+$.

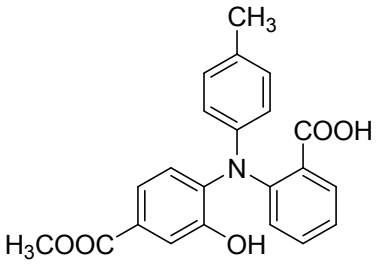
III-2 Characterization data for representative triarylamine intermediates 3a and 3b.



2-((2-hydroxy-4-(methoxycarbonyl)phenyl)(phenyl)amino)benzoic acid (3a)

White solid. m.p. ＞200–℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 13.20 (s, 1H), 10.49 (s, 1H), 7.83 (d, J = 2.00 Hz, 1H)，7.75 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.70 (dd, J_1 = 7.60 Hz, J_2 = 1.20 Hz, 1H)，7.53 (m, 1H)，7.27 (m, 1H)，7.12 (m, 3H)，

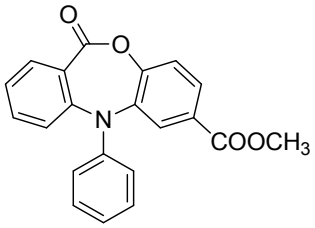
7.02 (d, J = 8.40 Hz, 1H)，6.77 (t, J = 7.20 Hz, 1H), 6.50 (d, J = 8.00 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 169.2 (C=O), 165.7 (C=O), 158.7, 148.0, 144.4, 133.1, 132.8, 131.6, 130.5, 129.2, 129.0, 128.8, 128.5, 125.0, 121.4, 119.7, 117.0, 117.0, 51.8; IR (KBr) V_{max}/cm^{-1} 3070, 2643, 2572, 2544, 2495, 1785, 1698, 1594, 1577, 1490, 1437, 1400, 1316, 1297, 1255, 1218, 1163, 1143, 1120, 1104, 1083, 1037, 772, 750, 643；MS (EI): m/z = 363 $[M]^+$, 345, 286, 77； HRMS (ESI-TOF) calcd. for $C_{21}H_{18}NO_5$ $[M+H]^+$ 364.1179, found: 364.1183.



2-((2-hydroxy-4-(methoxycarbonyl)phenyl)(p-tolyl)amino)benzoic acid（3b）

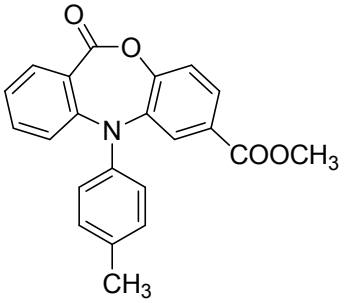
Pale yellow solid. m.p. ＞200–℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 13.04 (s, 1H), 10.39 (s, 1H), 7.76 (d, J = 2.00 Hz, 1H)，7.72 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.66 (dd, J_1 = 7.60 Hz, J_2 = 1.20 Hz, 1H)，7.49 (m, 1H)，7.22 (t, J = 7.60 Hz, 1H), 7.08 (d, J = 8.00 Hz, 1H)，6.99 (d, J = 8.80 Hz, 1H), 6.92 (d, J = 8.00 Hz, 2H), 6.43 (d, J = 8.40 Hz, 2H), 3.75 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 169.3 (C=O), 165.7 (C=O), 158.7, 145.8, 144.7, 133.2, 132.8, 131.3, 130.4, 129.4, 129.1, 128.8, 128.7, 128.1, 124.5, 121.3, 117.7, 117.0, 51.8, 20.1; IR (KBr) V_{max}/cm^{-1} 3074, 2643, 2572, 2544, 2495, 1700, 1670, 1608, 1577, 1513, 1431, 1398, 1297, 1246, 1210, 1161, 1143, 1117, 1096, 1086, 811, 788, 768; MS (EI): m/z = 377 $[M]^+$, 359, 346, 77; HRMS (ESI-TOF) calcd. for $C_{22}H_{20}NO_5$ $[M+H]^+$ 378.1336, found: 378.1339.

Ⅲ-3 Characterization Data for N-aryl dibenzo[b,e][1,4]oxazepin-11(5*H*)-ones (Table 3 and Table 4).



Methyl -5-phenyl dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4a)

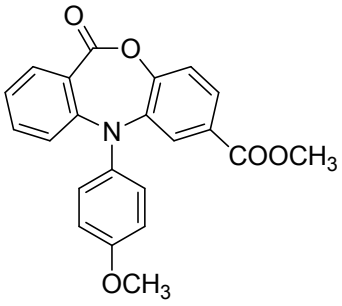
White solid; yield: 0.31g (91%); m. p.162～164℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.18 (d, J = 2.00 Hz, 1H), 7.98 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.88 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.77-7.82 (m, 1H), 7.71 (d, J = 8.00 Hz, 1H), 7.56 (d, J = 8.80 Hz, 1H), 7.52-7.56 (m, 1H), 7.16-7.20 (m, 2H), 6.85 (t, J = 7.20 Hz, 1H), 6.60 (d, J = 7.60 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.8 (C=O), 163.2 (C=O), 153.0, 145.8, 145.7, 136.5, 135.3, 133.7, 131.2, 130.1, 129.5, 128.7, 128.4, 128.2, 126.3, 122.8, 119.9, 112.6, 52.5; IR (KBr) ν_{max}/cm^{-1} 3058, 3045, 2954, 2844, 1731, 1717, 1593, 1494, 1440, 1418, 1285, 1246, 1126, 1104, 1028, 690, 749; MS (EI): m/z = 345 $[M]^+$, 314 $[M\text{-}OCH_3]^+$, 286 $[M\text{-}COOCH_3]^+$, 77; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}NNaO_4$ $[M+Na]^+$ 368.0893, found: 368.0887.



Methyl -5-(4-methylphenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4b)

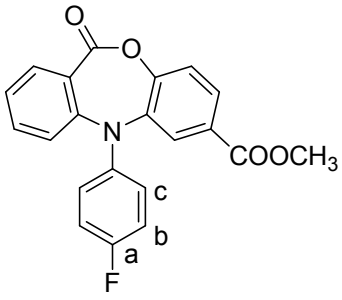
White solid; yield: 0.33g (91%); m. p.151～153℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.14 (d, J = 2.00 Hz, 1H), 7.96 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.86 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.55-7.97 (m, 1H), 7.66 (d, J = 7.60 Hz, 1H), 7.53 (t, J = 8.80 Hz, 1H), 7.50 (d, J = 7.60 Hz, 1H), 7.00 (d, J = 8.40 Hz, 2H), 6.54 (d, J = 8.40 Hz, 2H), 3.84 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.8 (C=O), 163.3 (C=O), 152.9, 146.2, 143.5, 136.9, 135.2, 133.6, 131.0, 129.8, 129.0, 128.4, 128.1, 126.1, 122.7, 113.2, 52.5, 19.9; IR (KBr) ν_{max}/cm^{-1} 3029, 2988, 2991, 2945, 2916, 2856, 1740, 1729, 1595, 1517, 1485, 1453, 1432, 1330, 1305, 1280, 1244,

1214, 1190, 1122, 1150, 1050, 810, 762, 707; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}NNaO_4$ $[M+Na]^+$ 382.1050, found: 382.1059.



Methyl-5-(4-methoxylphenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4c)

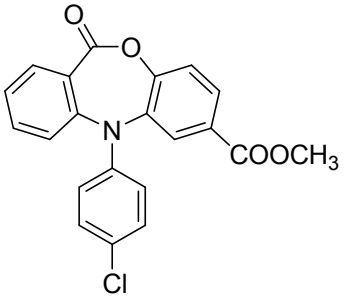
White solid; yield: 0.35g (93%); m. p.108～110 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.10 (d, J = 2.00 Hz, 1H), 7.94 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.89 (dd, J_1 = 7.60 Hz, J_2 = 1.60 Hz, 1H), 7.72-7.77 (m, 1H), 7.58 (dd, J_1 = 8.00 Hz, J_2 = 0.80 Hz, 1H), 7.54 (d, J = 8.80 Hz, 1H), 7.44-7.49 (m, 1H), 6.85-6.87 (m, 2H), 6.74-6.77 (m, 2H), 3.86 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.9 (C=O), 163.6 (C=O), 154.2, 152.4, 147.2, 138.9, 137.7, 135.2, 133.8, 130.1, 129.3, 128.0, 127.3, 127.1, 125.1, 122.7, 116.9, 114.9, 55.3, 52.5; IR (KBr) ν_{max}/cm^{-1} 3052, 2993, 2948, 2906, 2833, 1744, 1729, 1595, 1510, 1457, 1434, 1408, 1331, 1285, 1248, 1211, 1187, 1117, 1107, 1057, 1026, 818, 768, 706; HRMS (ESI-TOF) calcd. for $C_{22}H_{18}NO_5$ $[M+H]^+$ 376.1179, found: 376.1183.



Methyl-5-(4-fluorophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4d)

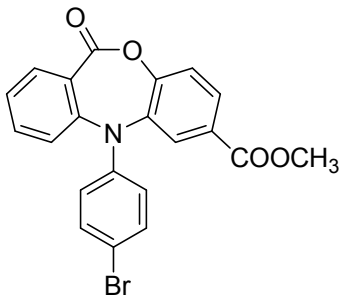
White solid; yield: 0.30g (83 %); m. p. 174～176 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.17 (d, J = 2.40 Hz, 1H), 7.98 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.88 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.77-7.81 (m, 1H), 7.70 (d, J = 8.00 Hz, 1H), 7.52-7.57 (m, 2H), 7.02-7.06 (m, 2H), 7.61-7.65 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100

MHz, DMSO-d_6) δ: ppm 164.7 (C=O), 163.1 (C=O), 156.0 (d, $^1J_{CF}$ = 235.2 Hz, C-a), 152.9, 145.9, 142.4, 136.7, 135.3, 133.7, 130.9, 130.0, 128.4 (d, $^3J_{CF}$ = 7.9 Hz, C-c), 128.2, 126.1, 122.8, 116.0 (d, $^2J_{CF}$ = 22.5 Hz, C-b), 114.4, 114.3, 52.4; IR (KBr) ν_{max}/cm^{-1} 3112, 3057, 2998, 2948, 2838, 1741, 1712, 1593, 1511, 1482, 1454, 1427, 1407, 1119, 1103, 1056, 1022, 862, 763, 702; HRMS (ESI-TOF) calcd. for $C_{21}H_{14}FNNaO_4$ $[M+Na]^+$ 386.0799, found: 386.0791.



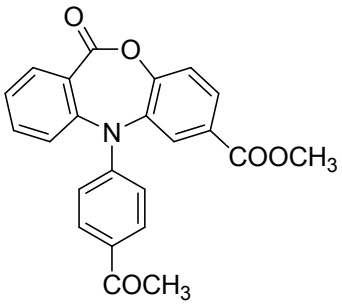
Methyl-_5-(4-chlorophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4e)

White solid; yield: 0.32g (85%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.19 (d, J = 2.00 Hz, 1H), 7.99 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.88 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.78-7.83 (m, 1H), 7.73 (d, J = 7.60 Hz, 1H), 7.54-7.59 (m, 2H), 7.23 (d, J = 8.80 Hz, 2H), 6.62 (d, J = 8.80 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.8 (C=O), 163.0 (C=O), 152.9, 145.3, 144.8, 136.2, 135.4, 133.7, 131.0, 130.3, 129.2, 128.7, 128.5, 128.3, 126.2, 123.6, 122.9, 114.1, 52.5; IR (KBr) ν_{max}/cm^{-1} 3094, 2999, 2947, 2836, 1742, 1727, 1591, 1493, 1455, 1431, 1405, 1125, 1103, 1053, 1023, 820, 762, 712, 701; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}Cl^{35}NO_4$ $[M+H]^+$ 380.0684, found: 380.0692.



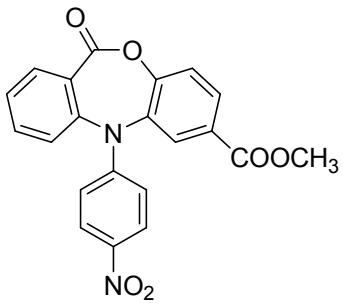
Methyl-_5-(4-bromophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4f)

White solid; yield: 0.36g (85%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.19 (d, J = 2.00 Hz, 1H), 7.99 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.88 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.79-7.83 (m, 1H), 7.73 (d, J = 7.60 Hz, 1H), 7.54-7.59 (m, 2H), 7.34 (d, J = 8.80 Hz, 2H), 6.55 (d, J = 8.80 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.8 (C=O), 163.1 (C=O), 152.9, 145.2, 145.2, 136.1, 135.5, 133.8, 132.1, 131.0, 130.4, 128.7, 128.5, 128.3, 126.2, 122.9, 114.6, 111.3, 52.5; IR (KBr) ν_{max}/cm^{-1} 3087, 3050, 3033, 2998, 2946, 2829, 1741, 1730, 1584, 1507, 1492, 1456, 1430, 1106, 1053, 1019, 818, 764, 754, 711; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}Br^{79}NO_4$ $[M+H]^+$ 424.0179, found: 424.0183.



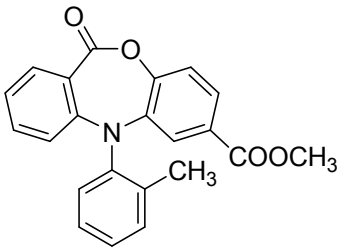
Methyl-5-(4-acetylphenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4g)

White solid; yield: 0.30g (78%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.27 (d, J = 2.00 Hz, 1H), 8.05 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.92 (dd, J_1 = 7.60 Hz, J_2 = 1.20 Hz, 1H), 7.80-7.89 (m, 4H), 7.60-7.64 (m, 2H), 6.69 (d, J = 8.80 Hz, 2H), 3.88 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 195.8 (C=O), 164.7 (C=O), 162.9 (C=O), 152.6, 149.4, 144.5, 135.6, 135.5, 133.7, 130.8, 130.6, 130.5, 129.0, 128.8, 128.4, 128.4, 126.0, 122.9, 111.7, 52.5, 26.2; IR (KBr) ν_{max}/cm^{-1} 3083, 3068, 3047, 2997, 2944, 1740, 1725, 1659, 1590, 1515, 1502, 1484, 1457, 1426, 1358, 1107, 1058, 1025, 841, 765, 722, 705; HRMS (ESI-TOF) calcd. for $C_{23}H_{18}NO_5$ $[M+H]^+$ 388.1178, found: 388.1183.



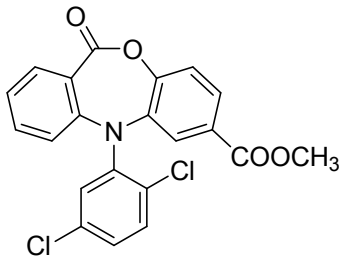
Methyl-5-(4-nitrophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4h)

Yellow solid; yield: 0.31g (80%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.31 (d, J = 1.60 Hz, 1H), 8.09 (d, J = 9.20 Hz, 2H), 8.05 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.92 (d, J = 7.60 Hz, 1H), 7.85-7.87 (m, 2H), 7.63 (d, J = 8.40 Hz, 2H), 6.77 (d, J = 9.60 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.7 (C=O), 162.7 (C=O), 152.3, 151.0, 143.8, 139.7, 135.7, 135.1, 133.8, 130.9, 130.6, 129.4, 128.6, 128.2, 126.1, 125.8, 123.1, 112.2, 52.6; IR (KBr) ν_{max}/cm^{-1} 3109, 3085, 3073, 2999, 2948, 1742, 1721, 1592, 1588, 1459, 1432, 1103, 1057, 1022, 846, 764, 712; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}N_2O_6$ [M+H]$^+$ 391.0925, found: 391.0925.



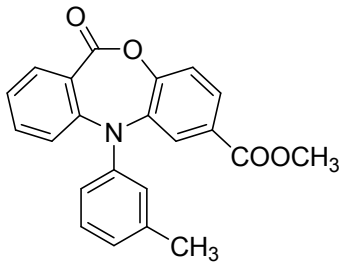
Methyl-5-(2-methylphenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4i)

White solid; yield: 0.31g (87%); m. p. 99～101℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 7.96-8.01 (m, 2H), 7.77 (dd, J_1 = 8.40 Hz, J_2 = 1.60 Hz, 1H), 7.72 (d, J = 2.00 Hz, 1H), 7.54-7.59 (m, 1H), 7.45-7.52 (m, 4H), 7.10 (t, J = 7.60 Hz, 1H), 6.93 (d, J = 2.00 Hz, 1H), 3.78 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 165.0 (C=O), 164.6 (C=O), 149.0, 148.7, 139.9, 138.9, 137.3, 135.1, 134.8, 132.6, 132.4, 129.1, 127.4, 127.2, 126.7, 124.8, 123.1, 121.8, 120.1, 117.9, 52.5, 17.3; IR (KBr) ν_{max}/cm^{-1} 3075, 2996, 2946, 2835, 1725, 1595, 1565, 1502, 1476, 1449, 1432, 1118, 1105, 1067, 1039, 1000, 762, 742, 730, 701; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}NNaO_4$ [M+Na]$^+$ 382.1050, found: 382.1055.



Methyl-5-(2,5-dichlorophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4j)

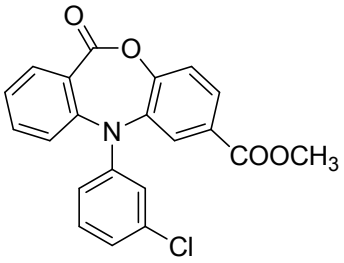
Pink solid; yield: 0.27g (65%); m. p.186～188℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.56 (d, J = 2.40 Hz, 1H), 7.93 (dd, J_1 = 8.00 Hz, J_2 = 1.60 Hz, 1H), 7.91 (d, J = 1.60 Hz, 1H), 7.82 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.72 (d, J = 8.80 Hz, 1H), 7.62 (dd, J_1 = 8.40 Hz, J_2 = 2.40 Hz, 1H), 7.57-7.59 (m, 1H), 7.48 (d, J = 8.40 Hz, 1H), 7.24 (t, J = 7.60 Hz, 1H), 7.15 (d, J = 8.40 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.9 (C=O), 164.2 (C=O), 149.8, 147.8, 140.3, 138.0, 135.0, 134.1, 132.8, 132.4, 132.4, 131.5, 129.8, 127.7, 127.4, 125.9, 124.0, 122.7, 122.1, 121.1, 52.5; IR (KBr) ν_{max}/cm^{-1} 3118, 3087, 3065, 2989, 2945, 1739, 1700, 1597, 1573, 1498, 1487, 1452, 1414, 1394, 1123, 1092, 1071, 1041, 821, 764, 728, 698; HRMS (ESI-TOF) calcd. for $C_{21}H_{14}Cl_2{}^{35}NO_4$ $[M+H]^+$ 414.0294, found: 414.0289.



Methyl-5-(3-methylphenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4k)

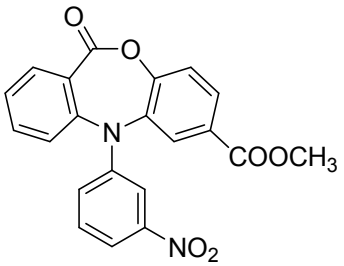
White solid; yield: 0.32g (90%); m. p.141～143℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.17 (d, J = 2.00 Hz, 1H), 7.98 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.88 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.78-7.82 (m, 1H), 7.69 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 7.57 (d, J = 8.40 Hz, 1H), 7.53-7.57 (m, 1H), 7.07 (t, J = 8.00 Hz, 1H), 6.67 (d, J = 7.20 Hz, 1H), 6.42 (s, 1H), 6.38 (dd, J_1 = 8.00 Hz, J_2 = 2.00 Hz, 1H), 3.85(s, 3H), 2.15(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 165.5 (C=O), 164.0 (C=O), 153.5, 146.4, 146.3, 139.4, 137.1, 135.9, 134.1, 131.7, 130.7, 129.8, 129.2, 129.0,

128.7, 126.7, 123.2, 121.4, 113.5, 110.4, 53.0, 21.7; IR (KBr) ν_{max}/cm^{-1} 3078, 3054 ,3026, 2996, 2948, 2920, 2840, 1734, 1603, 1580, 1490, 1436, 1414, 1116, 1104, 1055, 1023, 853, 769, 738, 707, 693; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}NNaO_4$ $[M+Na]^+$ 382.1050, found: 382.1059.



Methyl 5-(3-chlorophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4l)

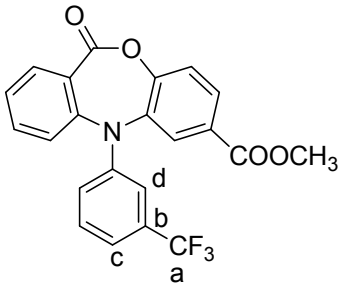
White solid; yield: 0.31g (83%); m. p.140～142℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.21 (d, J = 2.00 Hz, 1H), 8.01 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.90 (dd, J_1 = 7.60 Hz, J_2 = 1.20 Hz, 1H), 7.80-7.85 (m, 1H), 7.76 (d, J = 8.40 Hz, 1H), 7.56-7.60 (m, 2H), 7.21 (t, J = 8.00 Hz, 1H), 6.91 (d, J = 8.80 Hz, 1H), 6.53-6.55 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.7 (C=O), 163.0 (C=O), 152.8, 147.3, 144.8, 135.8, 135.5, 134.1, 133.8, 131.2, 131.0, 130.5, 128.9, 128.6, 128.4, 126.2, 122.9, 119.6, 111.8, 111.2, 52.5; IR (KBr) ν_{max}/cm^{-1} 3088, 3053, 2986, 2940, 2841, 1740, 1726, 1591, 1564, 1504, 1486, 1457, 1453, 1342, 1123, 1126, 1057, 1026, 837, 763, 713, 682, 627; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}Cl^{35}NO_4$ $[M+H]^+$ 380.0684, found: 380.0692.



Methyl 5-(3-nitrophenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4m)

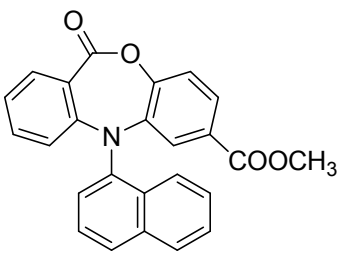
Yellow solid; yield: 0.32g (82%); m. p.164～166℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.32 (d, J = 2.00 Hz, 1H), 8.06 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.96 (d, J = 7.60 Hz, 1H), 7.86-7.92 (m, 2H), 7.72 (dd, J_1 = 8.40 Hz, J_2 = 1.60 Hz, 1H), 7.63-7.67 (m, 2H), 7.50 (t, J = 8.00 Hz, 1H), 7.35 (t, J = 2.00 Hz, 1H), 7.10 (dd, J_1 = 8.00

Hz, J_2 = 2.00 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.7 (C=O), 162.8 (C=O), 152.7, 148.7, 146.7, 144.4, 135.7, 135.5, 134.0, 131.0, 130.8, 130.8, 129.2, 128.6, 128.3, 126.1, 123.1, 118.6, 114.4, 106.0, 52.6; IR (KBr) ν_{max}/cm^{-1} 3054,,3039, 2988, 2947, 2839, 1741, 1718, 1594, 1573, 1528, 1500, 1433, 1124, 1108, 1058, 1026, 889, 870, 840, 826, 800, 765, 737, 707, 671; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}N_2O_6$ $[M+H]^+$ 391.0925, found: 391.0925.



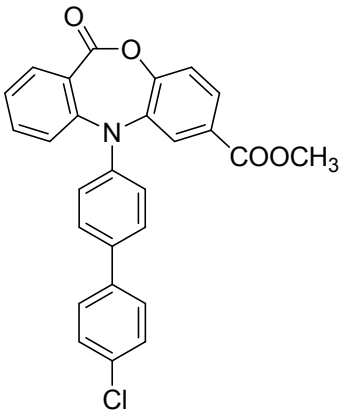
Methyl 5-(3-(trifluoromethyl)phenyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4n)

White solid; yield: 0.31g (75%); m. p.141～143℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.28 (d, J = 2.00 Hz, 1H), 8.04 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.93 (d, J = 8.80 Hz, 1H), 7.82-7.89 (m, 2H), 7.59-7.63 (m, 2H)， 7.45 (t, J = 8.00 Hz, 1H), 7.21 (d, J = 7.60 Hz, 1H), 6.92 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 6.79 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.7 (C=O), 162.9 (C=O), 152.7, 146.3, 144.6, 135.7, 135.5, 133.8, 130.9, 130.8, 130.5, 129.9 (q, $^2J_{CF}$ = 31.2 Hz, C-b), 129.0, 128.4, 126.1, 125.2 (q, $^1J_{CF}$ = 270.9 Hz, C-a), 122.9, 122.5, 119.8, 116.2, 107.8, 52.5; IR (KBr) ν_{max}/cm^{-1} 3092, 3073, 3035, 3997, 2949, 2839, 1741, 1724, 1596, 1497, 1463, 1443, 1174, 1132, 1109, 1074, 1057, 886, 870, 843, 789, 766, 709; HRMS (ESI-TOF) calcd. for $C_{22}H_{15}F_3NO_4$ $[M+H]^+$ 414.0948, found: 414.0947.



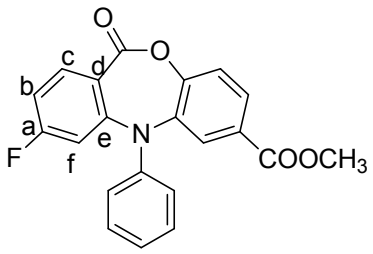
Methyl 5-(1-naphthyl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4o)

Pink crystals; yield: 0.27g (68%); m.p.119～121℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.32 (d, J = 6.80 Hz, 1H), 8.19 (d, J = 8.40 Hz, 1H), 8.06-8.15 (m, 3H), 7.89 (d, J = 7.60 Hz, 1H), 7.86 (d, J = 1.20 Hz, 1H), 7.77 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.58-7.64 (m, 2H), 7.54 (d, J = 8.40 Hz, 1H), 7.44-7.49 (m, 1H), 7.12 (t, J = 7.20 Hz, 1H), 7.06 (d, J = 8.40 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.9 (C=O), 164.5 (C=O), 149.5, 148.9, 139.5, 137.0, 135.1, 134.9, 134.9, 131.3, 131.0, 129.4, 128.8, 127.9, 127.4, 127.0, 127.0, 125.7, 124.7, 123.1, 122.1, 121.8, 120.0, 117.8, 52.4; IR (KBr) ν_{max}/cm^{-1} 3097, 3056, 3011, 2994, 2950, 2836, 1721, 1594, 1563, 1503, 1475, 1445, 1190, 1105, 1038, 889, 842, 813, 782, 759, 735, 709, 633; HRMS (ESI-TOF) calcd. for $C_{25}H_{18}NO_4$ $[M+H]^+$ 396.1230, found: 396.1232.



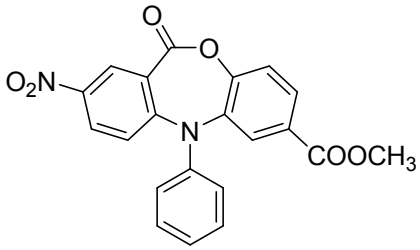
Methyl-5-(4-chlorobiphenyl-4-yl)-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4p)

White solid; yield: 0.39g (85%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.23 (d, J = 2.00 Hz, 1H), 8.01 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.90 (d, J = 8.80 Hz, 1H), 7.81-7.85 (m, 1H), 7.77 (d, J = 7.60 Hz, 1H), 7.56-7.60 (m, 4H), 7.52 (d, J = 8.80 Hz, 2H), 7.44 (d, J = 8.40 Hz, 2H), 6.70 (d, J = 8.80 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.8 (C=O), 163.2 (C=O), 153.0, 145.5, 145.4, 138.4, 136.3, 135.4, 133.7, 131.4, 131.1, 130.4, 130.2, 128.8, 128.6, 128.6, 128.3, 127.7, 127.6, 126.3, 122.9, 113.0, 52.5; IR (KBr) ν_{max}/cm^{-1} 3076, 3048, 3028, 2993, 2945, 2832, 1741, 1725, 1595, 1517, 1484, 1456, 1428, 1108, 1058, 1028, 815, 765, 707; HRMS (ESI-TOF) calcd. for $C_{27}H_{19}Cl^{35}NO_4$ $[M+H]^+$ 456.0997, found: 456.0995.



Methyl-3-fluoro-5-phenyl-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4q)

White solid; yield: 0.32g (87%); m. p.167～169℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.22 (d, J = 2.00 Hz, 1H), 8.01 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.95-7.99 (m, 1H), 7.71 (dd, J_1 = 8.40 Hz, J_2 = 2.40 Hz, 1H), 7.59 (d, J = 8.40 Hz, 1H), 7.41-7.46 (m, 1H), 7.23 (t, J = 7.20 Hz, 2H), 6.91 (t, J = 7.20 Hz, 1H), 6.71 (d, J = 8.00 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 166.7 (C=O), 164.2 (C=O), 163.0 (d, $^{1}J_{CF}$ = 235.2 Hz, C-a), 152.8, 147.8 (d, $^{3}J_{CF}$ = 11.5 Hz, C-e), 145.2, 136.4 (d, $^{3}J_{CF}$ = 10.7 Hz, C-c), 136.1, 131.1, 130.1, 129.5, 128.2, 122.8, 122.7 (d, $^{4}J_{CF}$ = 3.0 Hz, C-d), 120.4, 116.0 (d, $^{2}J_{CF}$ = 22.3 Hz, C-f), 115.7 (d, $^{2}J_{CF}$ = 22.7 Hz, C-b), 113.1, 52.5; IR (KBr) ν_{max}/cm^{-1} 3114, 3090, 3054, 2951, 2844, 1746, 1726, 1595, 1496, 1425, 1412, 1330, 1151, 1099, 1042, 765, 750, 710, 692; HRMS (ESI-TOF) calcd. for $C_{21}H_{14}FNNaO_4$ $[M+Na]^+$ 386.0799, found: 386.0791.

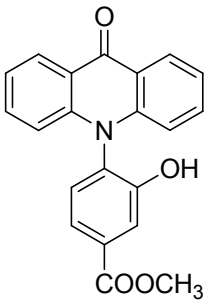


Methyl-5-Phenyl-2-3-Nitro-dibenzo[b,e][1,4]oxazepin-11(5*H*)-one-7-carboxylate (4r)

Yellow solid; yield: 0.30g (79%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 8.63 (d, J = 2.8 Hz, 1H), 8.48 (dd, J_1 = 9.20 Hz, J_2 = 2.80 Hz, 1H), 8.18 (d, J = 1.60 Hz, 1H), 8.00 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.82 (d, J = 8.80 Hz, 1H), 7.61 (d, J = 8.40 Hz, 1H), 7.35 (t, J = 7.60 Hz, 2H), 7.09 (t, J = 7.60 Hz, 1H), 7.02 (d, J = 8.00 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 164.6 (C=O), 162.0 (C=O), 151.3, 144.5, 143.5, 135.9, 129.8, 129.7, 129.7, 129.6, 129.5, 129.2,

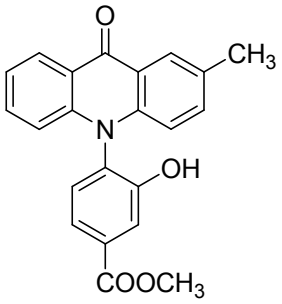
128.1, 127.6, 124.8, 123.1, 122.7, 116.8, 52.4; IR (KBr) ν_{max}/cm^{-1} 3080, 3046, 2999, 2954, 2833, 1754, 1717, 1608, 1574, 1524, 1496, 1476, 1238, 1190, 1128, 1106, 1067; 773, 747, 707, 689; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}N_2O_6$ $[M+H]^+$ 391.0925, found: 391.0925.

III-3 Characterization data for N-arylated acridones (Table 5 and Scheme 2).



10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5a)

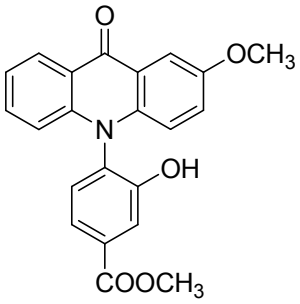
Yellow crystal; yield: 0.30g (87%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.08 (s, 1H), 8.38 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 2H), 8.14 (dd, J_1 = 8.40 Hz, J_2 = 2.40 Hz, 1H), 7.96 (d, J = 2.40 Hz, 1H), 7.63-7.68 (m, 2H), 7.32-7.36 (m, 3H), 6.81(d, J = 8.40 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.8 (C=O), 165.2 (C=O), 159.1, 142.4, 134.0, 132.8, 132.7, 126.4, 124.5, 122.3, 121.6, 121.4, 118.0, 116.4, 52.0; IR (KBr) ν_{max}/cm^{-1} 3414, 3130, 3070, 2945, 2836, 1713, 1631, 1609, 1594, 1569, 1484, 1276, 1204, 1161, 1087, 848, 751, 667; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}NNaO_4$ $[M+Na]^+$ 368.0893, found: 368.0887.



2-methyl-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5b)

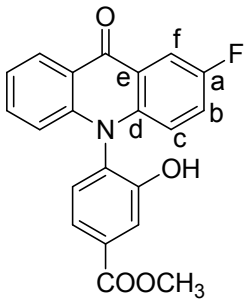
Yellow crystal; yield: 0.31g (87%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.02 (s, 1H), 8.35 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 8.15 (s, 1H), 8.11 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.90 (d, J = 2.00 Hz, 1H), 7.59 (t, J = 2.00 Hz, 1H),

7.45 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.27-7.33 (m, 2H), 6.77 (d, J = 8.80 Hz, 1H), 6.70 (d, J = 8.40 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.7 (C=O), 165.2 (C=O), 159.1, 159.1, 142.3, 140.6, 135.2, 133.7, 132.7, 132.6, 130.9, 126.4, 125.6, 124.6, 122.3, 121.4, 121.2, 117.9, 116.5, 116.3, 52.0, 20.3; IR (KBr) ν_{max}/cm^{-1} 3417, 3066, 3024, 2951, 2839, 1717, 1636, 1614, 1591, 1566, 1499, 1479, 1464, 1435, 1206, 1159, 1109, 1087, 850, 805, 770, 756; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}NNaO_4$ $[M+Na]^+$ 382.1050, found: 382.1059.



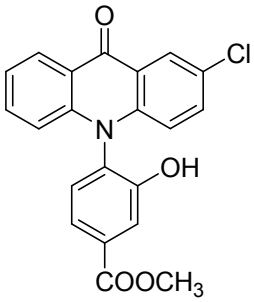
2-methoxyl-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5c)

Yellow crystal; yield: 0.33g (89%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.06 (s, 1H), 8.37 (dd, J_1 = 8.40 Hz, J_2 = 1.60 Hz, 1H), 8.13 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.93 (d, J = 2.40 Hz, 1H), 7.78 (d, J = 3.20 Hz, 1H), 7.60-7.65 (m, 1H), 7.29-7.33 (m, 3H), 6.77-6.81 (m, 2H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.3 (C=O), 165.2 (C=O), 159.1, 154.3, 141.9, 137.2, 133.6, 132.8, 132.6, 126.4, 124.6, 124.0, 122.3 121.9, 121.3, 120.6, 118.3, 117.9, 116.3, 105.8, 55.5, 52.0; IR (KBr) ν_{max}/cm^{-1} 3403, 3052, 2996, 2942, 2905, 2834, 1711, 1612, 1590, 1543, 1500, 1463, 1428, 1164, 1121, 1030, 862, 822, 754, 694; HRMS (ESI-TOF) calcd. for $C_{22}H_{18}NO_5$ $[M+H]^+$ 376.1179, found: 376.1184.



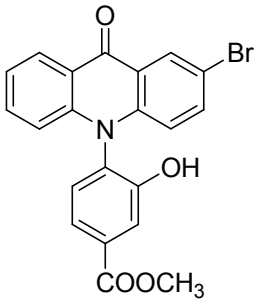
2-fluoro-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5d)

Yellow crystal; yield: 0.26g (72%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.12 (s, 1H), 8.37 (dd, J_1 = 8.00 Hz, J_2 = 1.60 Hz, 1H), 8.15 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 8.03 (dd, J_1 = 8.80 Hz, J_2 = 2.80 Hz, 1H), 8.00 (d, J = 2.00 Hz, 1H), 7.65-7.70 (m, 1H), 7.54-7.60 (m, 1H), 7.34-7.37 (m, 2H), 6.88 (dd, J_1 = 9.20 Hz, J_2 = 4.40 Hz, 1H), 6.83 (d, J = 8.80 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.2 (C=O), 165.2, 159.0, 157.2 (d, $^{1}J_{CF}$ = 239.6 Hz, C-a), 142.3, 139.2, 134.2, 132.8, 132.7, 126.3, 124.4, 122.5 (d, $^{2}J_{CF}$ = 24.7 Hz, C-b), 122.4, 122.1 (d, $^{3}J_{CF}$ = 6.4 Hz, C-e), 121.8, 120.6, 119.3 (d, $^{3}J_{CF}$ = 7.4Hz, C-c), 118.0, 116.5, 110.3 (d, $^{2}J_{CF}$ = 22.2 Hz, C-f), 52.0; IR (KBr) ν_{max}/cm^{-1} 3473, 3015, 2951, 2833, 1720, 1618, 1601, 1576, 1495, 1480, 1459, 1433, 1276, 1195, 1159, 1149, 1085, 1036, 832, 813, 751, 692; HRMS (ESI-TOF) calcd. for $C_{21}H_{14}FNNaO_4$ $[M+Na]^+$ 386.0799, found: 386.0791.



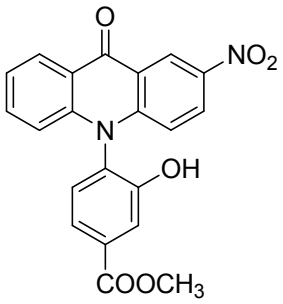
2-chloro-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5e)

Yellow crystal; yield: 0.30g (78%); m. p.＞200℃;^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.12 (s, 1H), 8.37 (d, J = 8.00 Hz, 1H), 8.28 (d, J = 2.40 Hz, 1H), 8.14 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 8.00 (d, J = 2.00 Hz, 1H), 7.65-7.70 (m, 2H), 7.37 (d, J = 7.60 Hz, 1H), 7.34 (d, J = 8.40 Hz, 1H), 6.85 (d, J = 9.20 Hz, 1H), 6.82 (d, J = 8.80 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 175.9 (C=O), 165.2 (C=O), 158.9, 142.3, 141.1, 134.4, 133.8, 132.9, 132.7, 126.4, 126.2, 125.1, 124.2, 122.4, 122.2, 122.1, 121.2, 119.0, 118.0, 116.6, 52.0; IR (KBr) ν_{max}/cm^{-1} 3508, 3171, 2952, 2839, 1714, 1625, 1597, 1574, 1508, 1487, 1457, 1437, 1195, 1166, 1125, 1085, 896, 855, 810, 771, 754, 692; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}Cl^{35}NO_4$ $[M+H]^+$ 380.0684, found: 380.0692.



2-bromo-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5f)

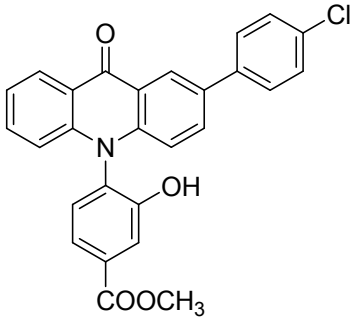
Yellow crystal; yield: 0.35g (82%); m. p.＞200℃;^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.10 (s, 1H), 8.40 (d, J = 2.40 Hz, 1H), 8.35 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 8.12 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.96-7.98 (m, 1H), 7.76 (dd, J_1 = 9.12 Hz, J_2 = 2.48 Hz, 1H), 7.64-7.68 (m, 1H), 7.30-7.36 (m, 2H), 6.76-6.81 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 175.8 (C=O), 165.2 (C=O), 158.9, 142.4, 141.4, 136.4, 134.4, 132.9, 132.7, 128.2, 126.5, 124.2, 122.7, 122.4, 122.1, 121.3, 119.2, 118.0, 116.6, 114.0, 52.0; IR (KBr) ν_{max}/cm^{-1} 3178, 2951, 1744, 1711, 1626, 1595, 1574, 1491, 1455, 1437, 1320, 1279, 1088, 1057, 1024, 898, 853, 815, 768, 752; HRMS (ESI-TOF) calcd. for $C_{21}H_{15}BrNO_4$ $[M+H]^+$ 424.0179, found: 424.0183.



2-nitro-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5h)

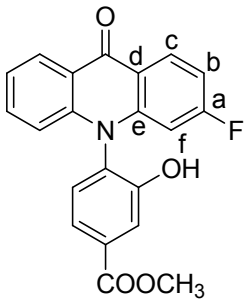
Yellow crystal; yield: 0.29g (75%);m. p.＞200℃;^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.26 (s, 1H), 9.09 (d, J = 2.80 Hz, 1H), 8.38-8.42 (m, 2H), 8.16 (dd, J_1 = 8.40 Hz, J_2 = 1.20 Hz, 1H), 8.09 (d, J = 1.20 Hz, 1H), 7.72 (t, J = 7.60 Hz, 1H), 7.45 (t, J = 7.60 Hz, 1H), 7.36 (d, J = 8.40 Hz, 1H), 7.00 (d, J = 9.20 Hz, 1H), 6.87 (d, J = 8.40 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.5 (C=O), 165.2 (C=O), 158.7, 145.9, 142.4, 141.3, 135.1, 133.2, 132.5, 127.9, 126.6, 123.9, 123.4, 122.9, 122.5, 121.7, 120.4, 118.3, 118.1, 117.2, 52.1; HRMS (ESI-TOF) calcd. for

$C_{21}H_{15}N_2O_6$ $[M+H]^+$ 391.0925, found: 391.0925.



2-(4-chlorophenyl)-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5p)

Yellow crystal; yield: 0.39g (85%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.11(s, 1H), 8.58 (d, J = 2.40 Hz, 1H), 8.38 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 8.15 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.99 (d, J = 2.00 Hz, 1H), 7.97 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.75 (d, J = 8.80 Hz, 2H), 7.63-7.67 (m, 1H), 7.54 (d, J = 8.40 Hz, 2H), 7.33-7.36 (m, 2H), 6.88 (d, J = 8.80 Hz, 1H), 6.81 (d, J = 8.80 Hz, 1H), 3.80(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 176.8 (C=O), 165.2 (C=O), 159.0, 142.3, 141.9, 137.8, 134.1, 132.7, 132.3, 132.1, 129.1, 128.8, 128.2, 127.7, 126.5, 124.4, 123.7, 122.3, 121.9, 121.5, 118.0, 117.4, 116.5, 113.0, 52.0; IR (KBr) ν_{max}/cm^{-1} 3459, 3189, 3055, 2993, 2947, 1742, 1715, 1594, 1573, 1508, 1482, 1461, 1321, 1283, 1207, 1162, 1095, 814, 767, 711, 691; HRMS (ESI-TOF) calcd. for $C_{27}H_{19}ClNO_4$ $[M+H]^+$ 456.0997, found: 456.0995.

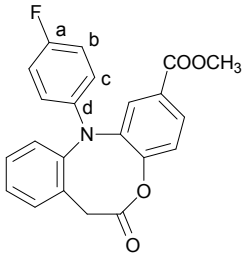


3-fluoro-10-((2-hydroxyl-4-methoxycarbonyl)phenyl)-acridin-9(10*H*)-one (5q)

Yellow crystal; yield: 0.30g (83%); m. p.＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.14 (s, 1H), 8.42-8.46 (m, 1H), 8.36 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 8.14 (dd, J_1 = 8.00 Hz, J_2 = 2.00 Hz, 1H), 8.00 (d, J = 2.00 Hz, 1H), 7.64-7.68 (m, 1H), 7.33-7.38 (m, 2H), 7.17-7.22 (m, 1H), 6.79 (d, J = 8.80 Hz, 1H), 6.45 (d, J = 1.20 Hz,

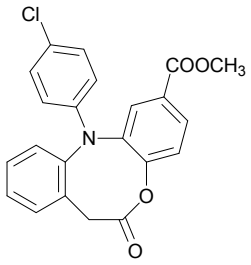
1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 175.9 (C=O), 165.2 (d, $^{1}J_{CF}$ = 248.3 Hz, C-a), 165.1 (C=O), 158.7, 144.1 (d, $^{3}J_{CF}$ = 11.9 Hz, C-e), 142.5, 134.0, 132.8, 132.5, 130.0 (d, $^{3}J_{CF}$ = 11.1 Hz, C-c), 129.9, 126.3, 124.0, 122.3, 122.0, 121.3, 118.3, 117.9, 116.3, 110.3 (d, $^{2}J_{CF}$ = 23.3 Hz, C-f), 101.8 (d, $^{2}J_{CF}$ = 26.8 Hz, C-b), 51.8; IR (KBr) ν_{max}/cm^{-1} 3142, 3083, 2954, 2833, 1714, 1636, 1611, 1597, 1571, 1504, 1462, 1434, 1325, 1283, 1210, 1157, 1084, 840, 756, 666; HRMS (ESI-TOF) calcd. for $C_{21}H_{14}FNNaO_4$ $[M+Na]^+$ 386.0799, found: 386.0793.

III-4 Characterization Data for N-aryl 7, 12-dihydrodibenzo[b,e][1,4]oxa zocin-6(*H*)-ones and dibenzo[b,f]azepin-10(11*H*)-ones



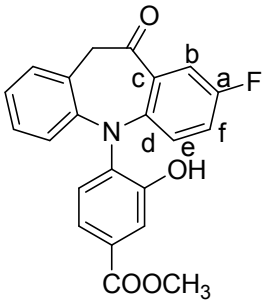
Methyl -12-(4-fluorophenyl)-6-oxo-7,12-dihydro-6*H*-dibenzo[b,e][1,4]oxazocine-2- carboxylate (6d)

White crystal; yield: 0.32g (85%); m. p. 78-80 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) (T = 323 K) δ: ppm 8.08 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.96 (d, J = 2.00 Hz, 1H), 7.56 (d, J = 8.40 Hz, 1H), 7.51-7.55 (m, 1H), 7.40 (t, d, J = 8.40 Hz, 2H), 7.21-7.25 (m, 1H), 6.94-6.98 (m, 2H), 6.33-6.37 (m, 2H), 3.82 (s, 3H), 3.56 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 169.4 (C=O), 165.3 (C=O), 157.0 (d, $^{1}J_{CF}$ = 235.4 Hz, C-a), 156.0, 143.0, 142.2, 134.9, 133.5, 131.5, 131.4, 131.2, 129.6, 129.3,127.4, 126.7, 121.2, 116.6 (d, $^{3}J_{CF}$ = 7.8 Hz, C-c), 116.0 (d, $^{2}J_{CF}$ = 22.5 Hz, C-b), 52.8, 37.8; IR (KBr) ν_{max}/cm^{-1} 3053, 2951, 2867, 2842, 1776, 1720, 1605, 1580, 1501, 1437, 1246, 1215, 1117, 1075, 802, 764, 744, 711; HRMS (ESI-TOF) calcd. for $C_{21}H_{17}FNO_4$ $[M+H]^+$ 378.1136, found: 378.1143.



Methyl -12-(4-chlorophenyl)-6-oxo-7,12-dihydro-6*H*-dibenzo[b,e][1,4]oxazocine-2-carboxylate (6e)

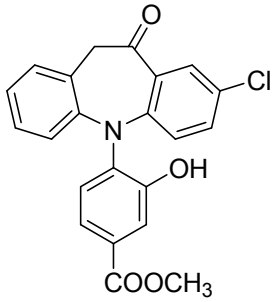
White crystal; yield: 0.35g (89%); m. p. 86-88 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) (T = 323 K) δ: ppm 8.12 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.98 (d, J = 2.00 Hz, 1H), 7.59 (d, J = 8.40 Hz, 1H), 7.57-7.58 (m, 1H), 7.43-7.46 (m, 2H), 7.27-7.31 (m, 1H), 7.17-7.19 (m, 2H), 6.34-6.37 (m, 2H), 3.84 (s, 3H), 3.60 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 169.3 (C=O), 165.3 (C=O), 155.8, 145.5, 141.5, 135.0, 133.3, 131.8, 131.5, 130.9, 129.7, 129.5, 129.3, 127.7, 127.1, 124.3, 121.4, 116.4, 52.9, 37.9; IR (KBr) ν_{max}/cm^{-1} 3080, 3031, 2977, 2954, 2925, 2853, 1776, 1720, 1594, 1491, 1437, 1318, 1248, 1221, 1193, 1174, 1110, 884, 867, 855, 818, 764, 741, 721; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}Cl^{35}NO_4$ $[M+H]^+$ 394.0841, found: 394.0847.



Methyl-8-fluoro-5-((2-hydroxyl-4-methoxycarbonyl)phenyl)-5*H*-dibenzo[b,f]azepin-10(11*H*)-one (7d)

Yellow crystal; yield: 0.29g (78%); m. p. 184-186 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.24 (s, 1H), 8.08 (d, J = 2.00 Hz, 1H), 7.97 (dd, J_1 = 8.40 Hz, J_2 = 2.00 Hz, 1H), 7.57 (dd, J_1 = 9.20 Hz, J_2 = 3.20 Hz, 1H), 7.30-7.39 (m, 2H), 7.19-7.23 (m, 4H), 6.82-6.85 (m, 1H), 4.08 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 188.2 (C=O), 165.4 (C=O), 159.2, 155.0 (d, $^{1}J_{CF}$ = 236.4 Hz, C-a), 144.0, 143.7, 133.4, 131.4, 128.9, 128.9, 127.4, 126.3, 124.6 (d, $^{3}J_{CF}$ = 4.7 Hz, C-c), 123.5, 123.5,

121.6, 121.1 (d, $^{3}J_{CF}$ = 6.9 Hz, C-e),120.9 (d, $^{2}J_{CF}$ = 23.0 Hz, C-f), 117.3, 114.4 (d, $^{2}J_{CF}$ = 22.6 Hz, C-b), 51.9, 48.2; IR (KBr) ν_{max}/cm^{-1} 3082, 2951, 1720, 1647, 1604, 1477, 1418, 1302, 1254, 1202, 1152, 1120, 1104, 1085, 941, 884, 836, 809, 768, 755, 711, 651; HRMS (ESI-TOF) calcd. for $C_{21}H_{17}FNO_4$ $[M+H]^+$ 378.1136, found: 378.1143.



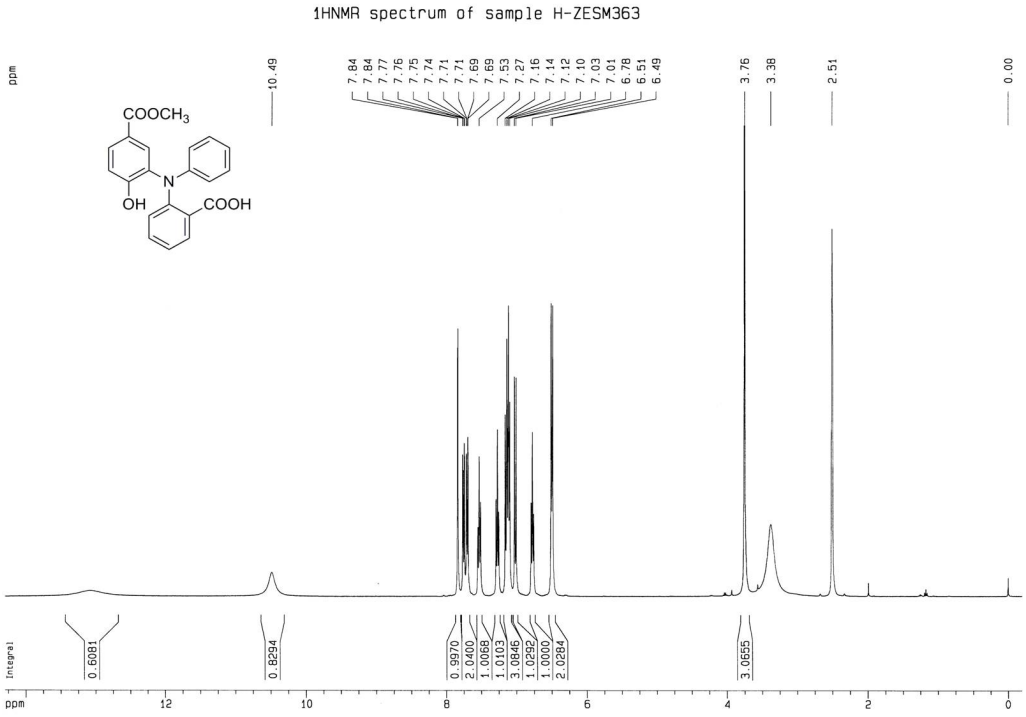
Methyl-8-chloro-5-((2-hydroxyl-4-methoxycarbonyl)phenyl)-5*H*-dibenzo[b,f]azepin-10(11*H*)-one (7e)

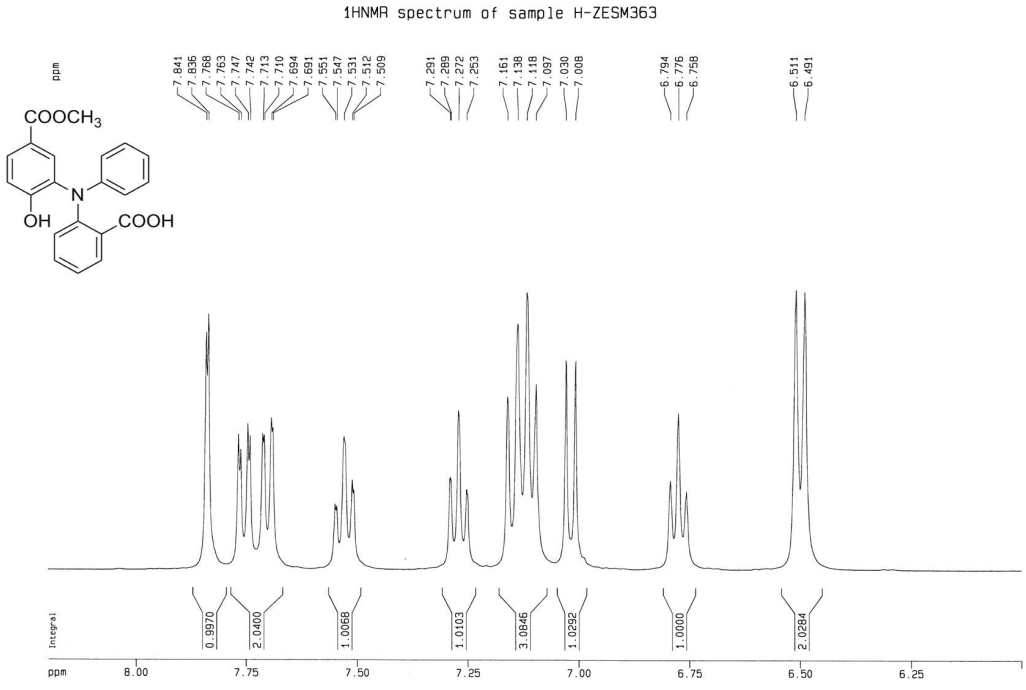
Yellow crystal; yield: 0.31g (80%); m. p. ＞200℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: ppm 11.26 (s, 1H), 8.06 (d, J = 1.60 Hz, 1H), 7.97 (dd, J_1 = 8.80 Hz, J_2 = 2.00 Hz, 1H), 7.80 (d, J = 2.80 Hz, 1H), 7.44 (dd, J_1 = 9.20 Hz, J_2 = 2.80 Hz, 1H), 7.38 (d, J = 6.80 Hz, 1H), 7.16-7.26 (m, 4H), 6.80 (d, J = 9.20 Hz, 1H), 4.06 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: ppm 187.8 (C=O), 165.3 (C=O), 159.0, 145.8, 143.2, 133.2, 132.6, 131.5, 131.0, 128.9, 128.6, 128.5, 127.4, 126.4, 124.9, 123.4, 122.8, 121.6, 120.9, 117.3, 51.9, 48.2; IR (KBr) ν_{max}/cm^{-1} 3082, 3023, 2947, 1721, 1645, 1592, 1467, 1433, 1405, 1296, 1249, 1190, 1157, 1122, 988, 953, 900, 839, 812, 770, 752; HRMS (ESI-TOF) calcd. for $C_{22}H_{17}ClNO_4$ $[M+H]^+$ 394.0841, found: 394.0847.

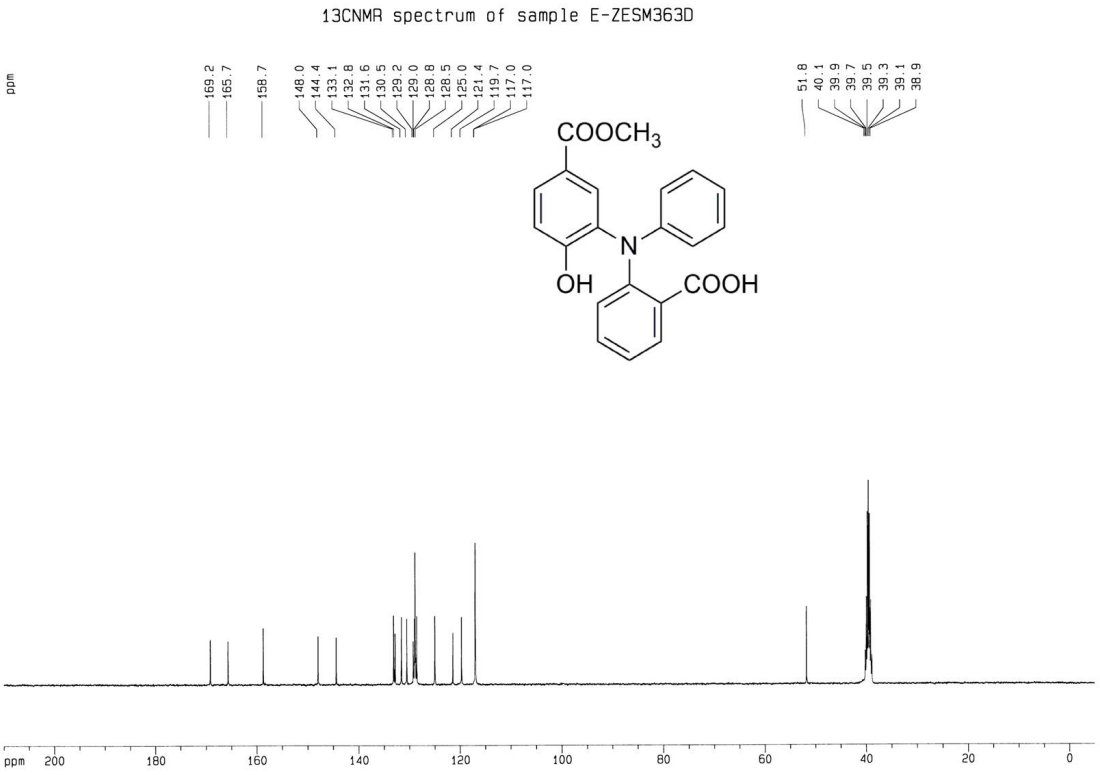
Ⅳ ^{1}H NMR and ^{13}C NMR spectra of compounds

Ⅳ-1 ^{1}H NMR and ^{13}C NMR spectra of intermediate 3a and 3b

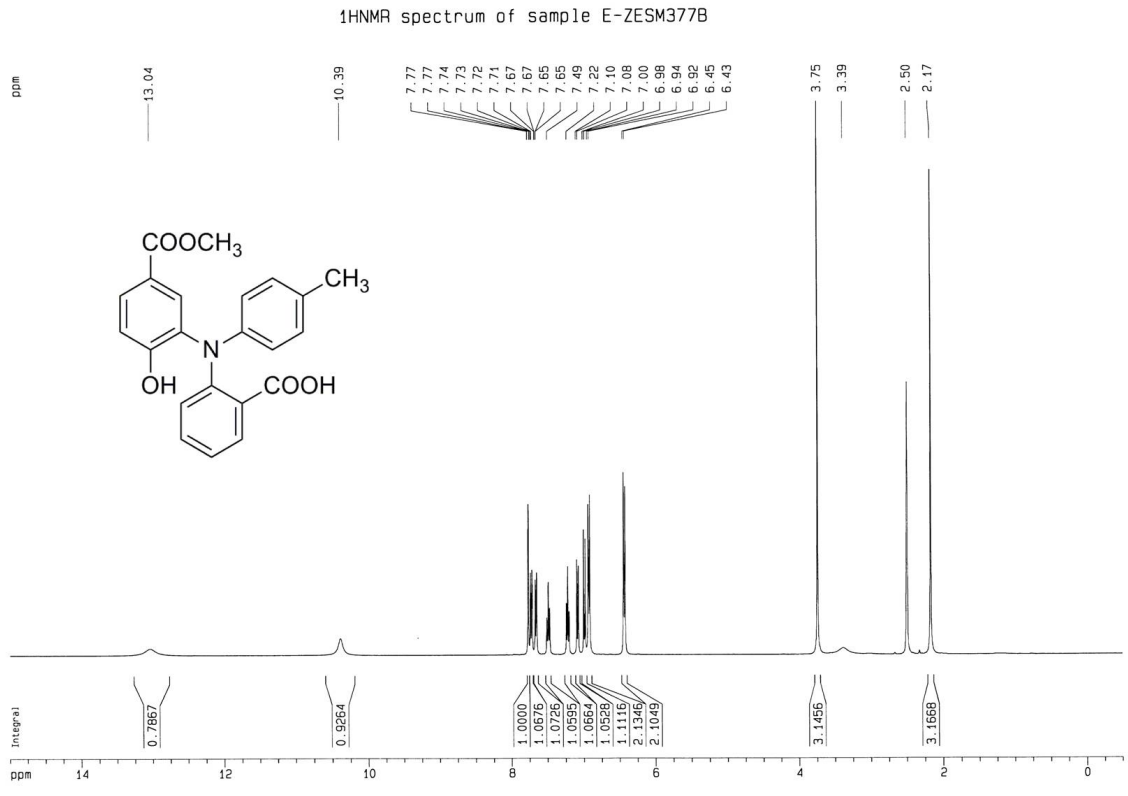
[^{1}H NMR and ^{13}C NMR spectrum of 3a in DMSO-d_6]



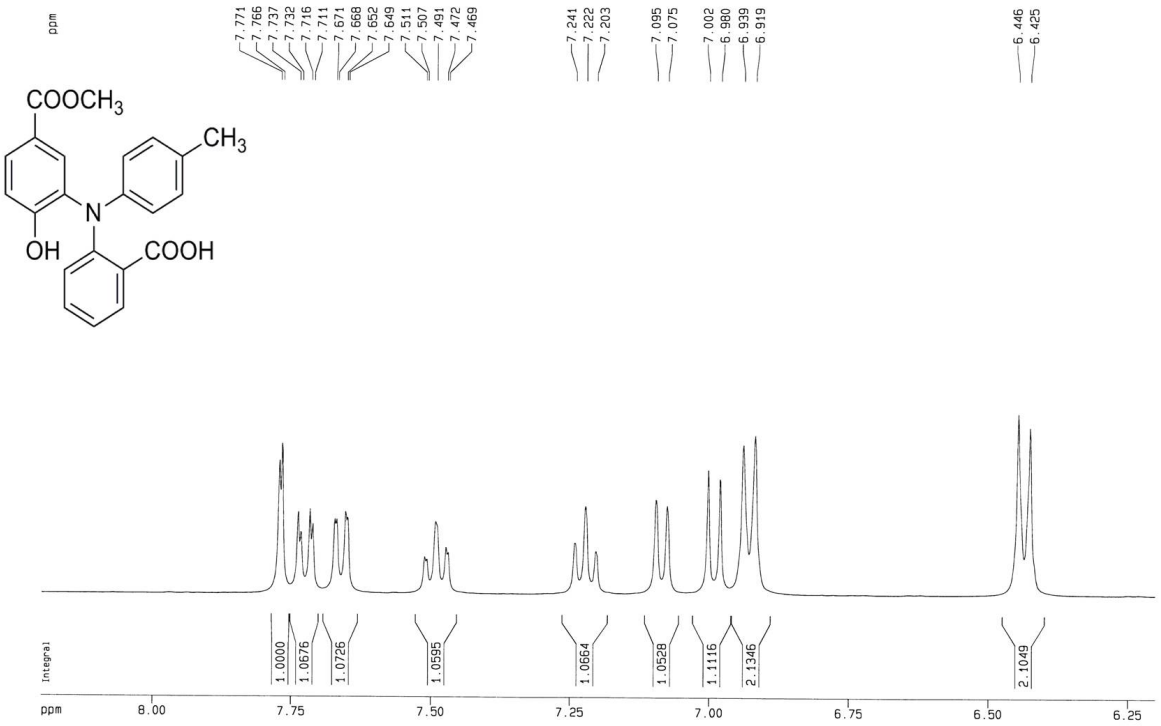




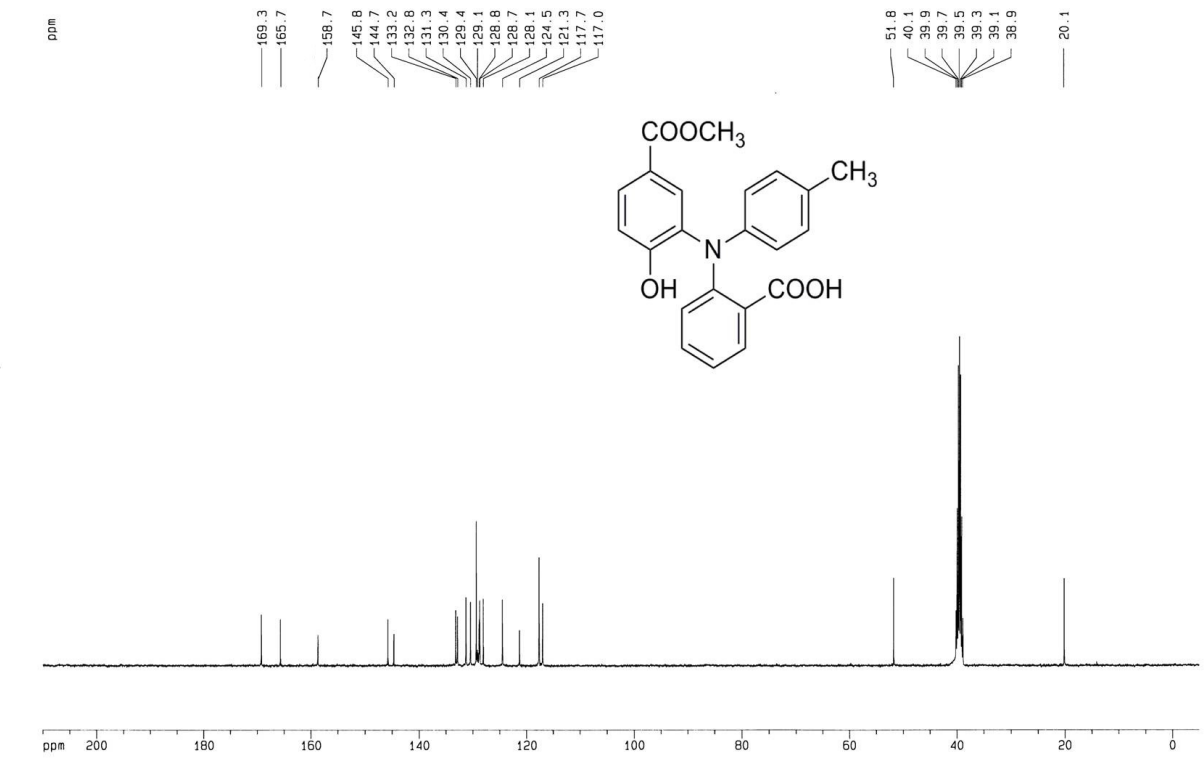
[^{1}H NMR and ^{13}C NMR spectrum of 3b in DMSO-d_6]



1HNMR spectrum of sample E-ZESM377B

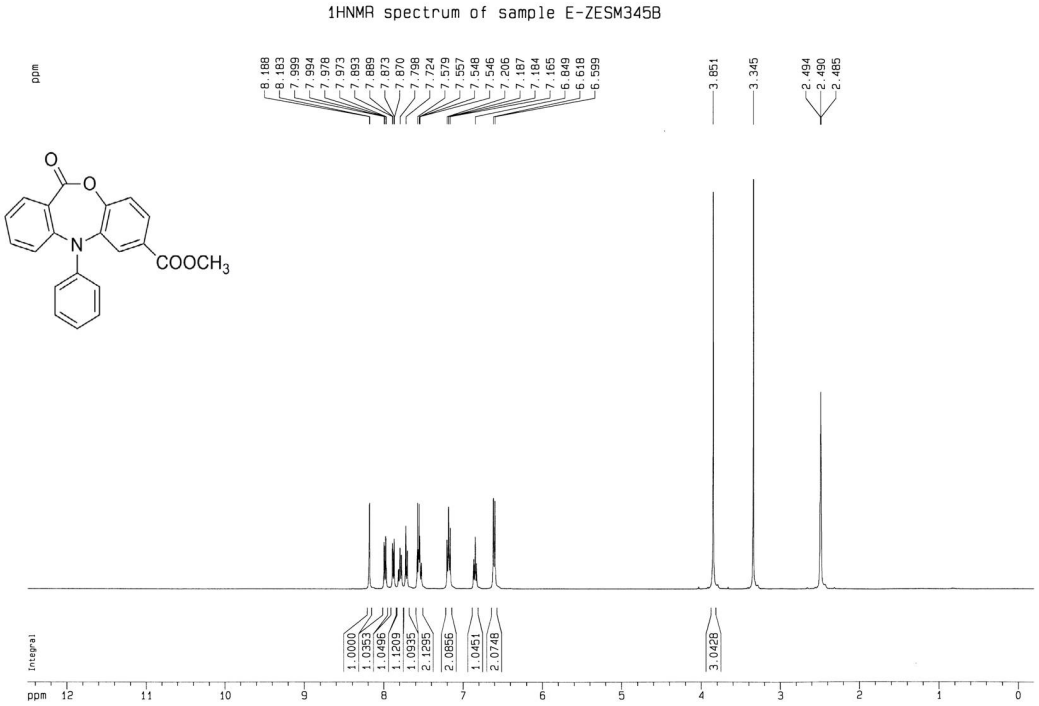


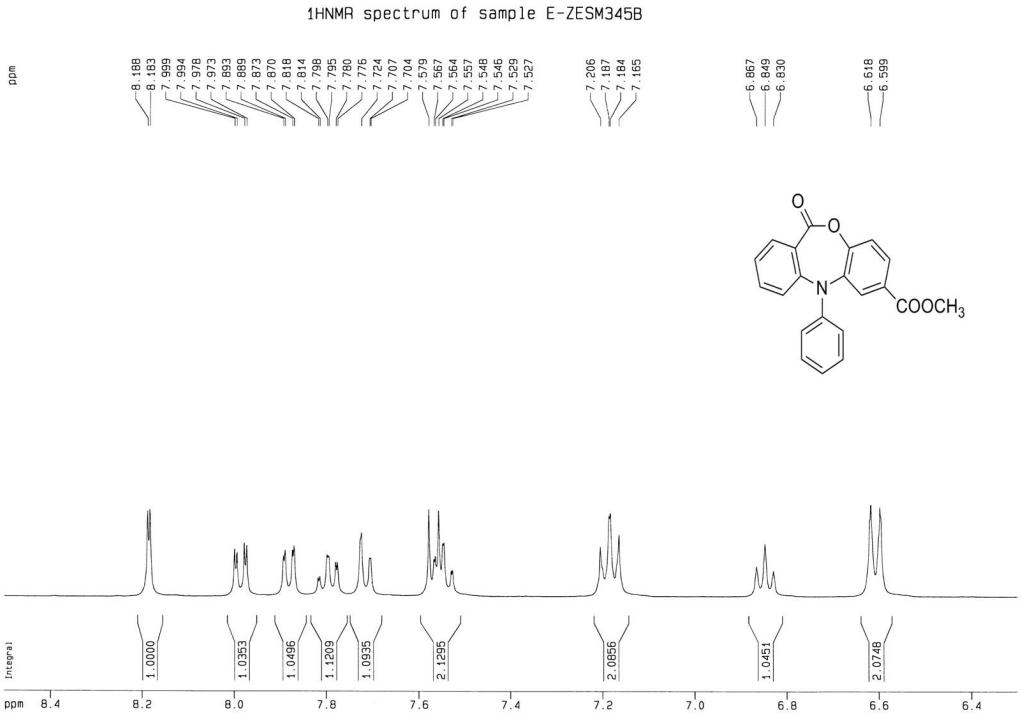
13CNMR spectrum of sample E-ZESM377D

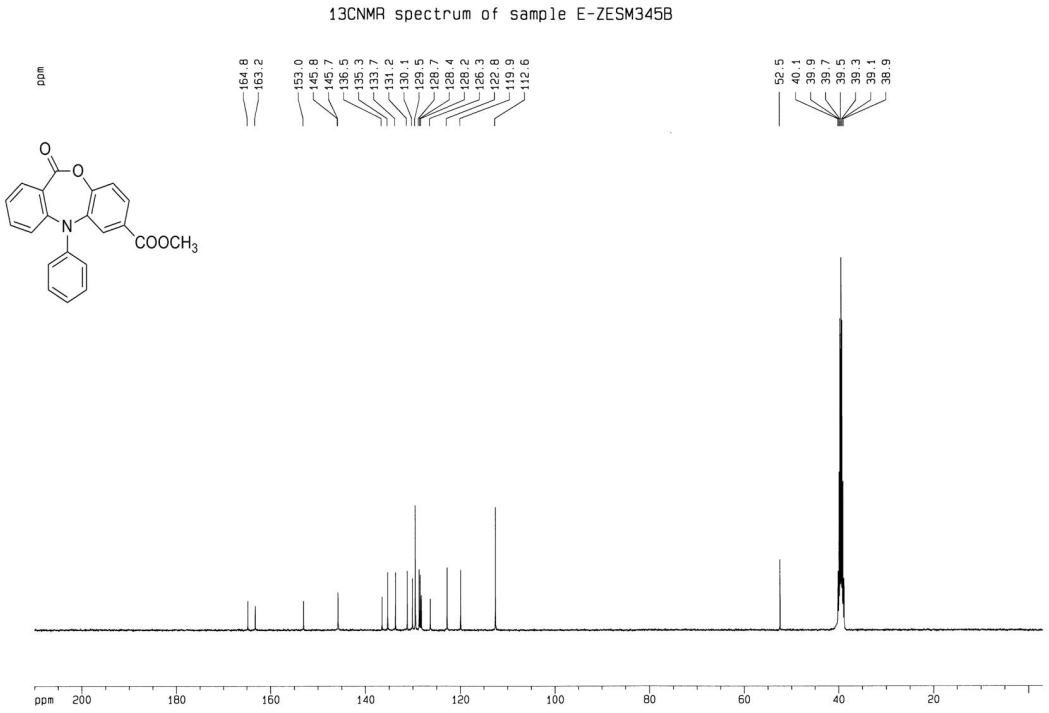


Ⅳ-2 ^{1}H NMR and ^{13}C NMR spectra of products

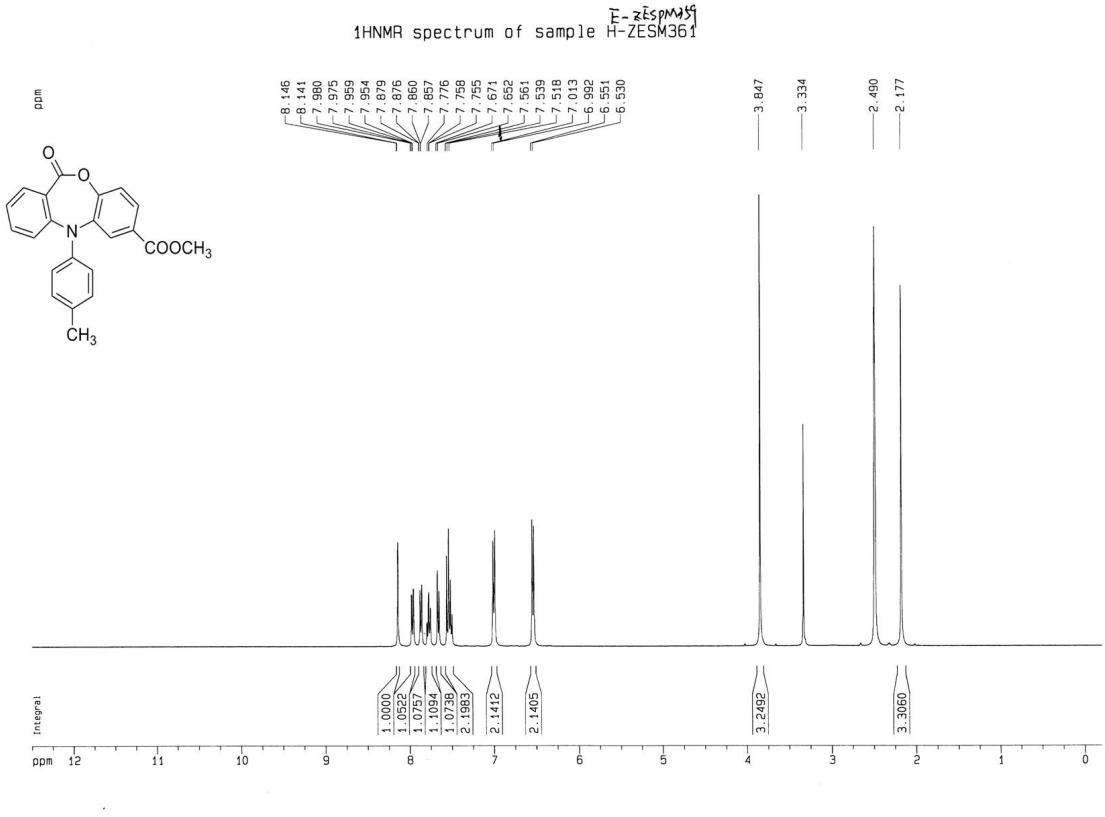
[^{1}H NMR and ^{13}C NMR spectrum of 4a in DMSO-d_6]



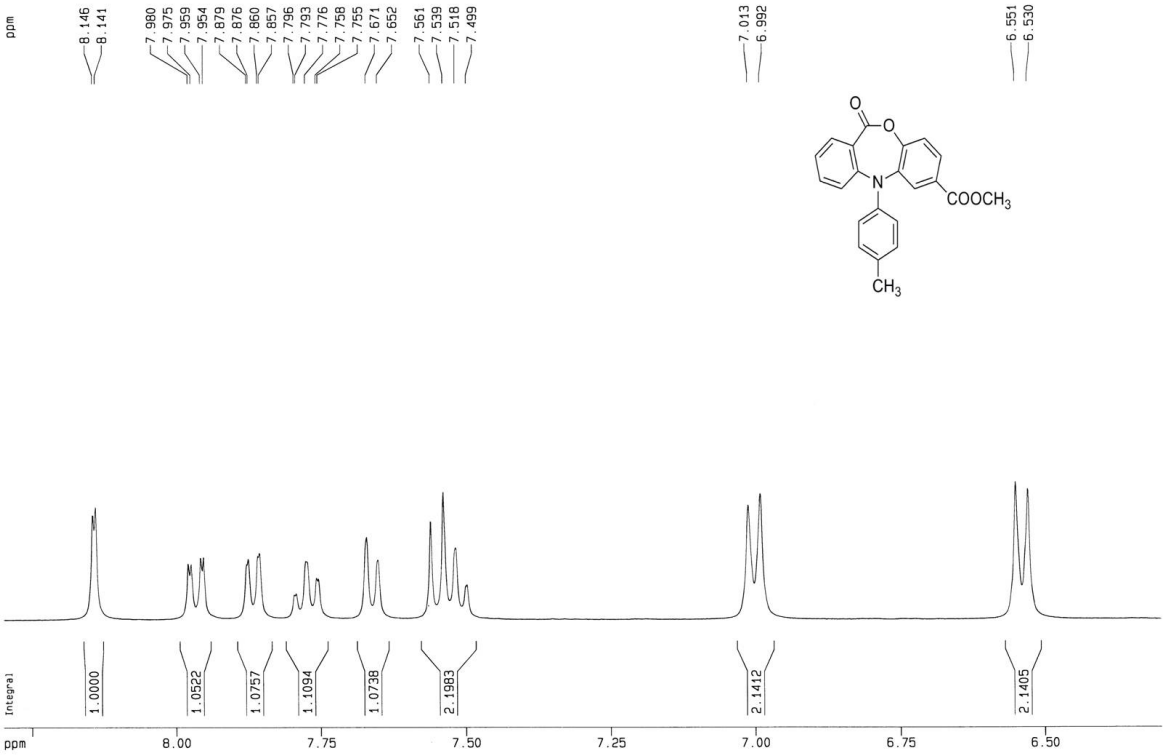




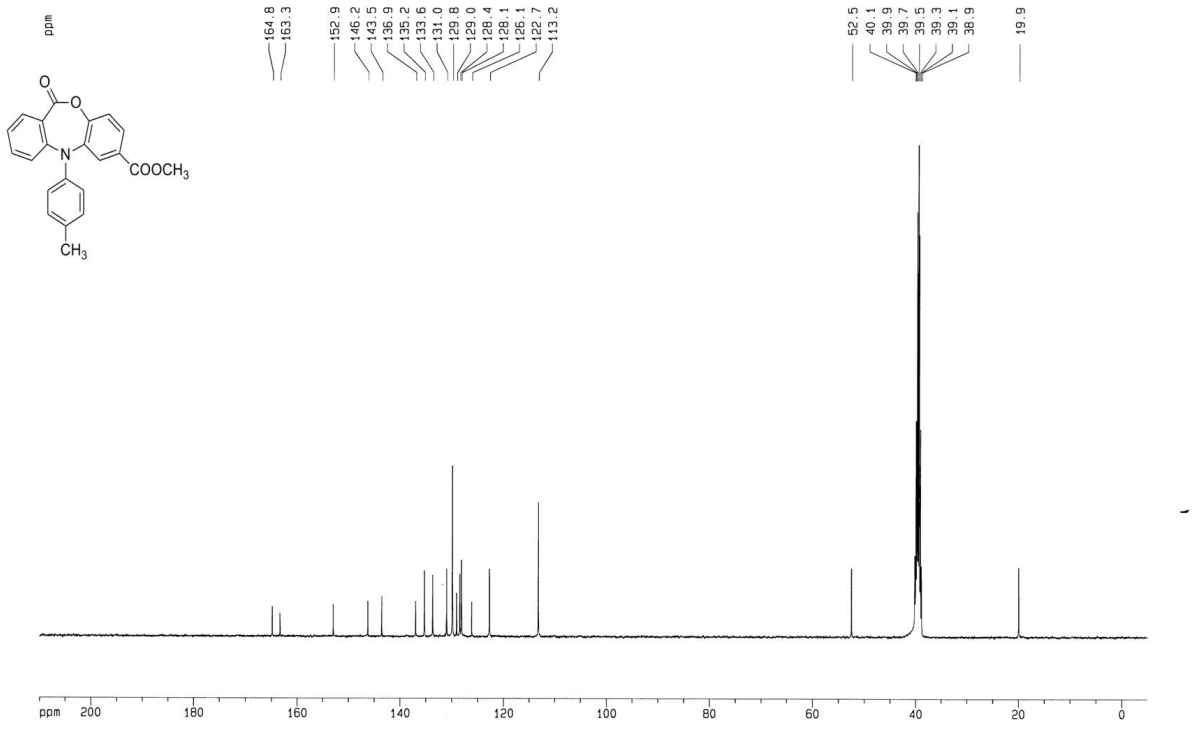
[^{1}H NMR and ^{13}C NMR spectrum of 4b in DMSO-d_6]



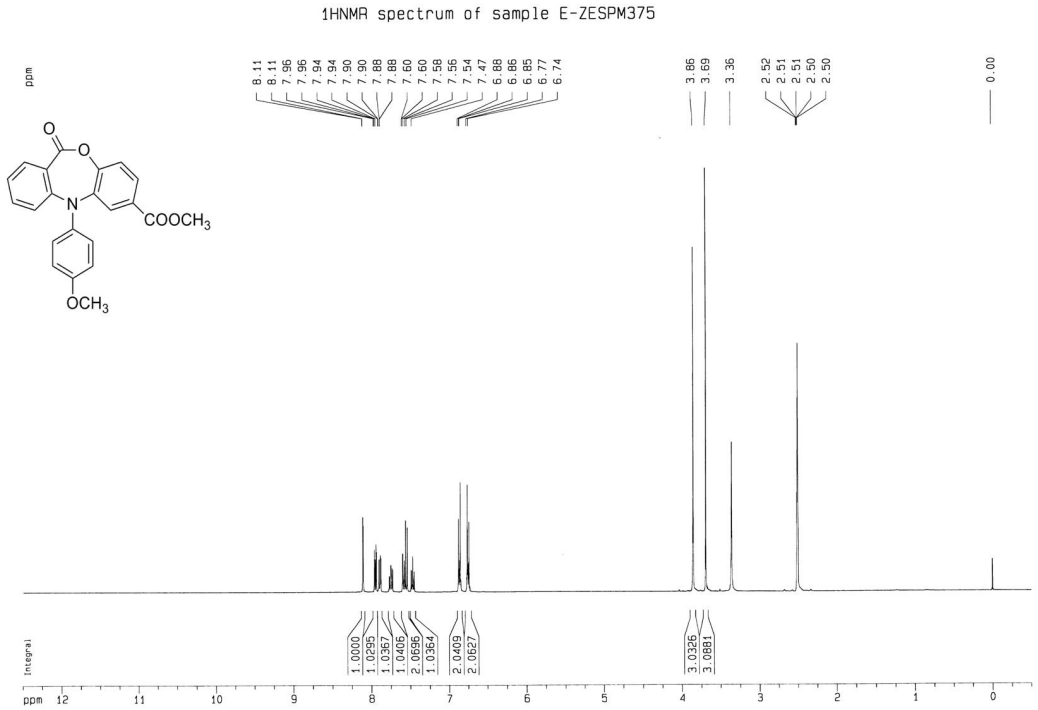
1HNMR spectrum of sample H-ZESM361

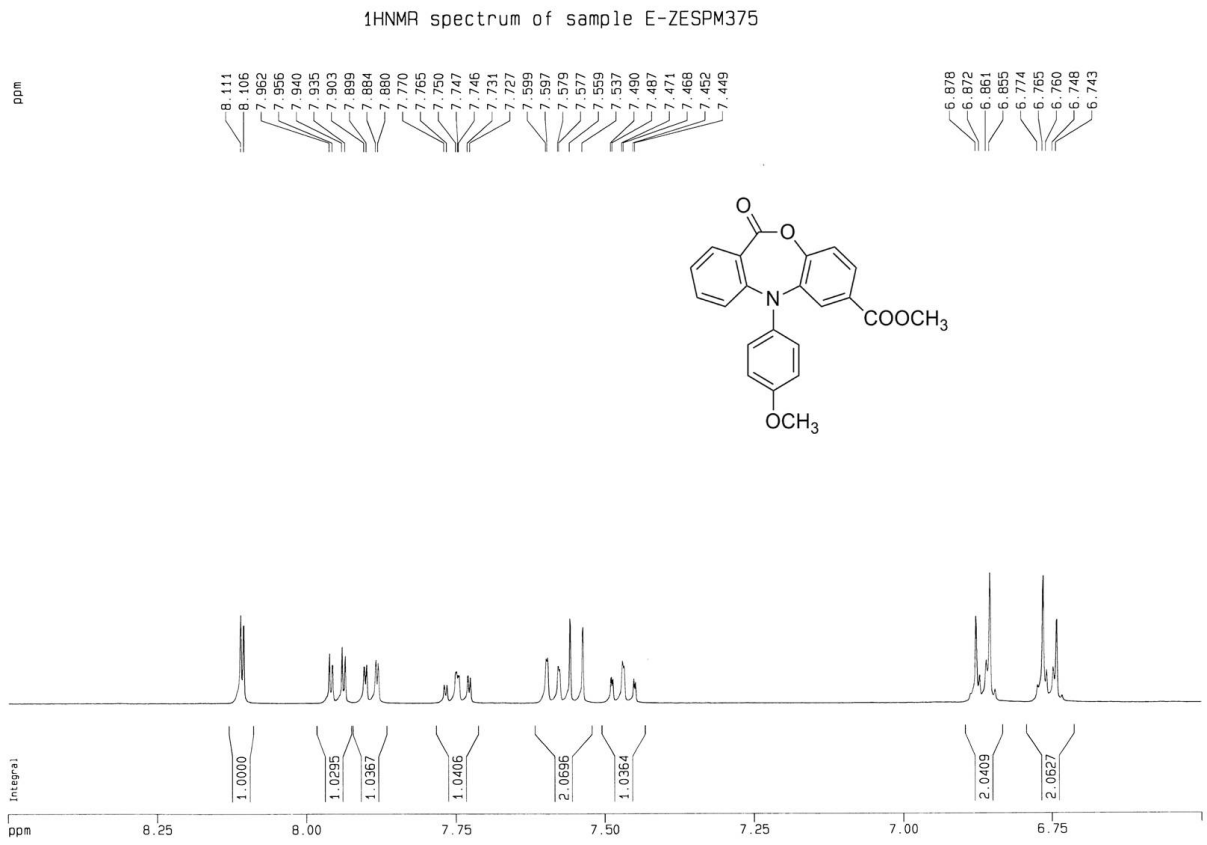


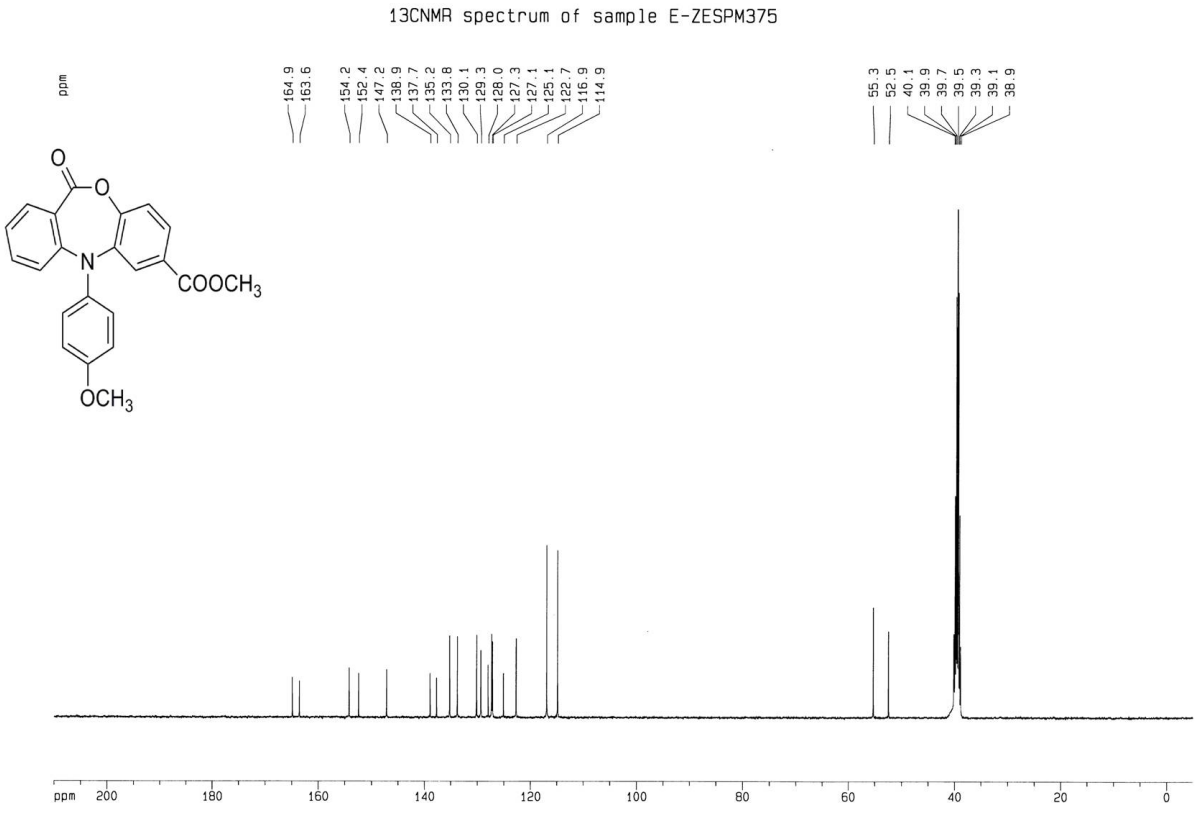
13CNMR spectrum of sample H-ZESM361



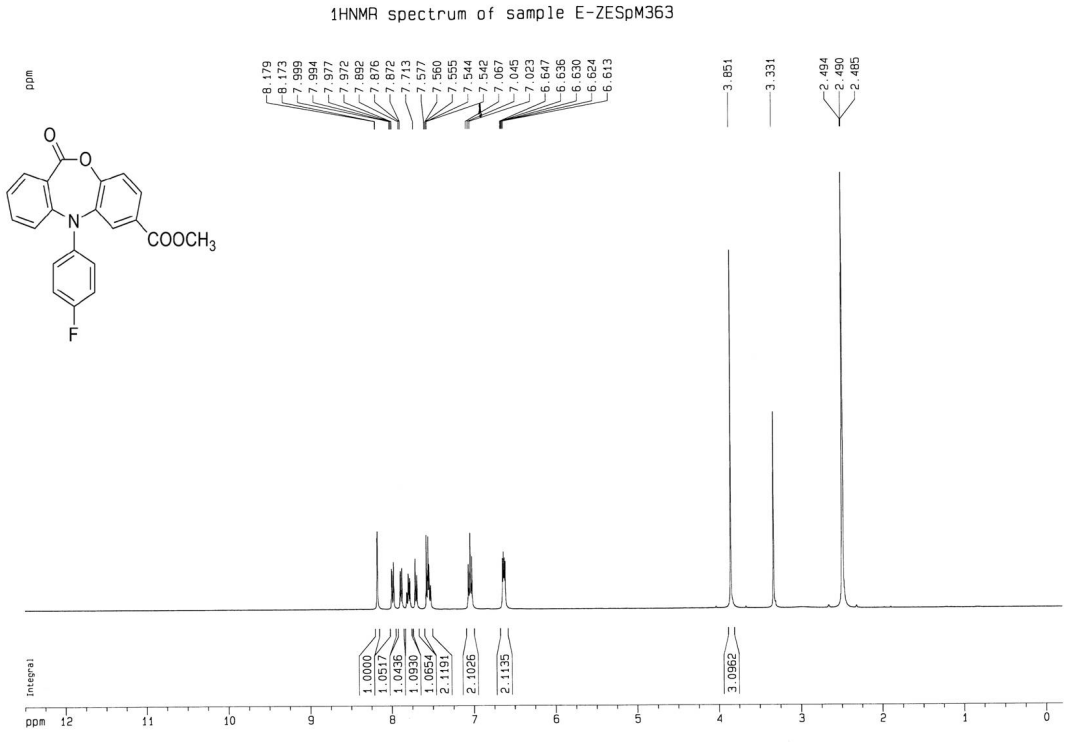
[^{1}H NMR and ^{13}C NMR spectrum of 4c in DMSO-d_6]



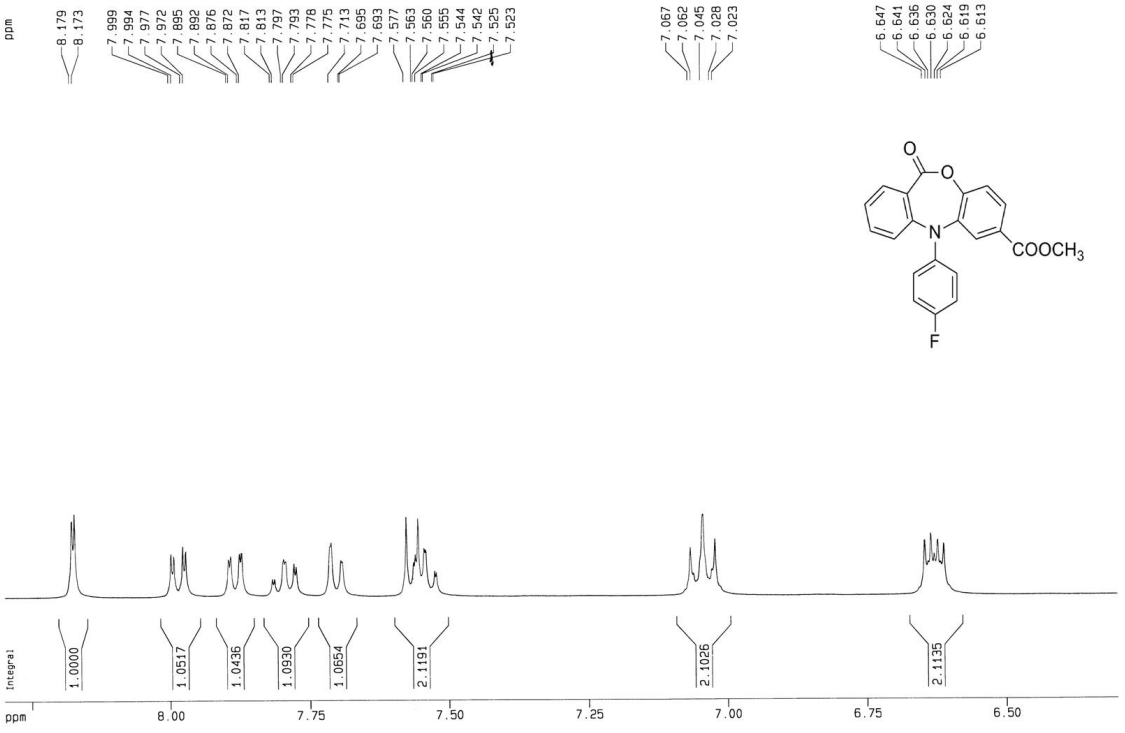




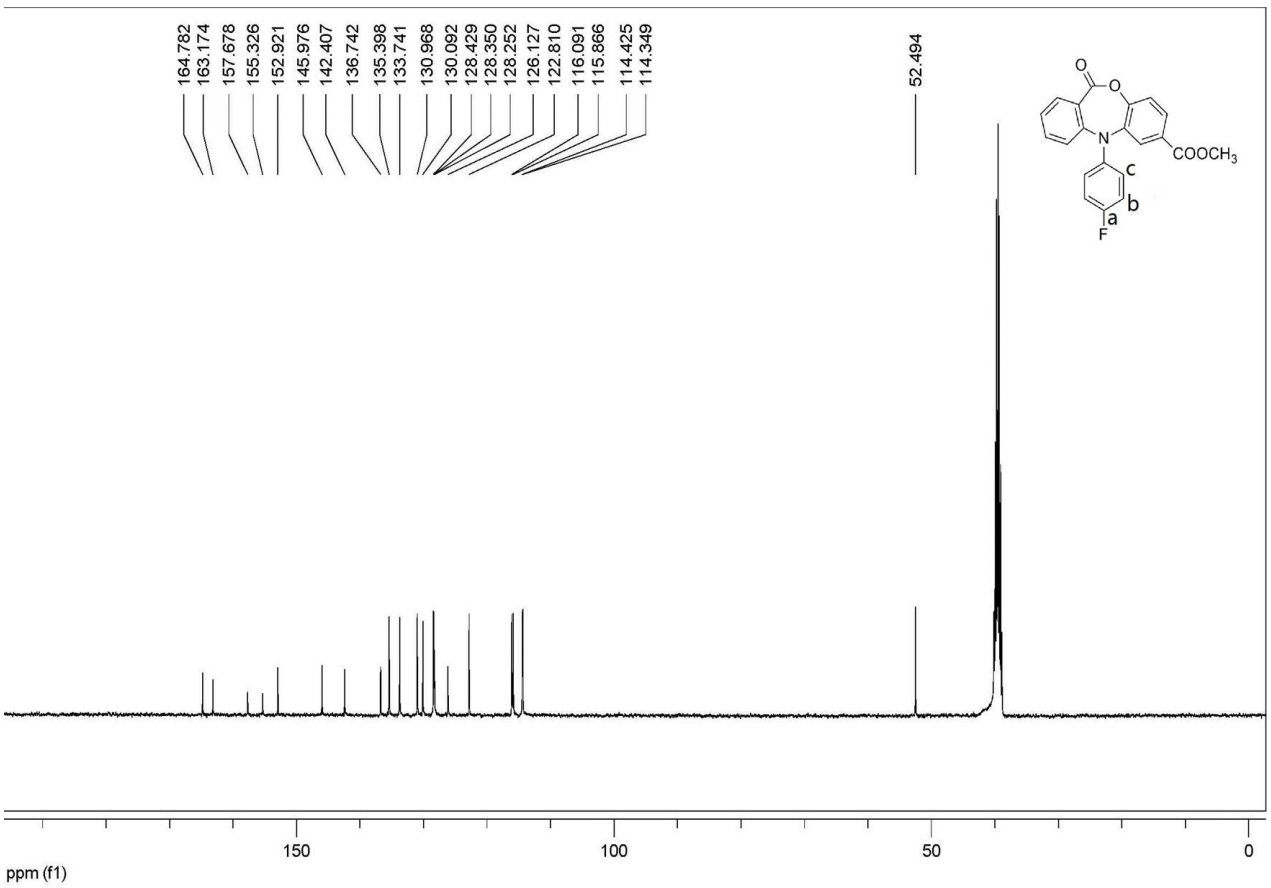
[^{1}H NMR and ^{13}C NMR spectrum of 4d in DMSO-d_6]

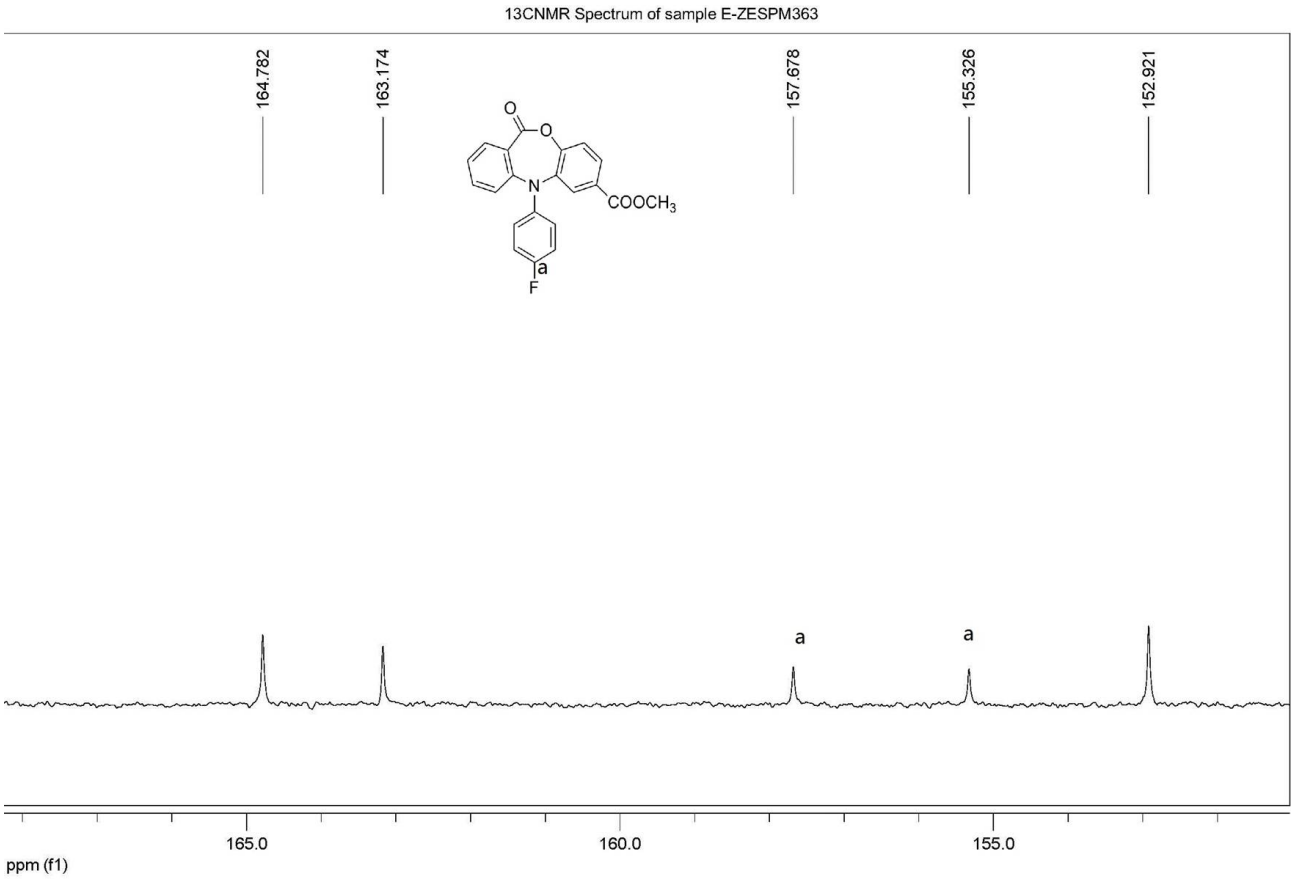


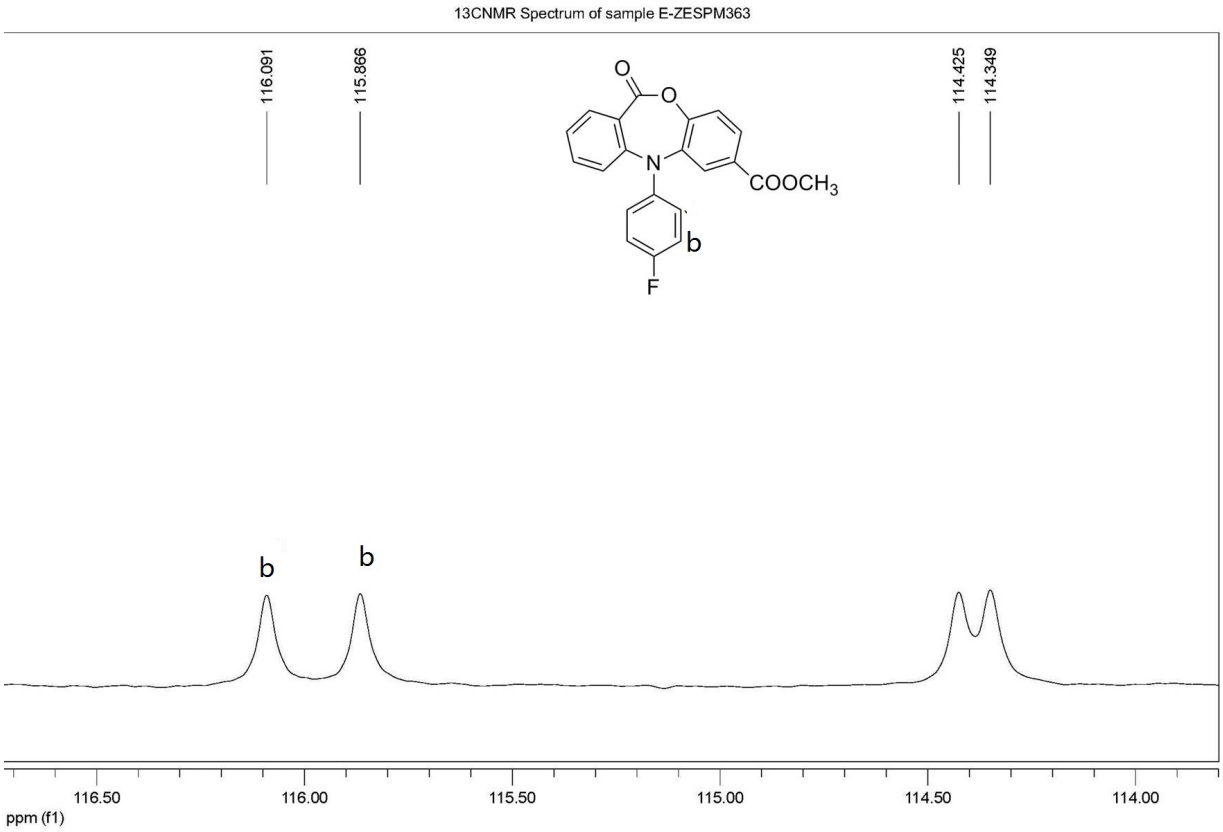
1HNMR spectrum of sample E-ZESpM363

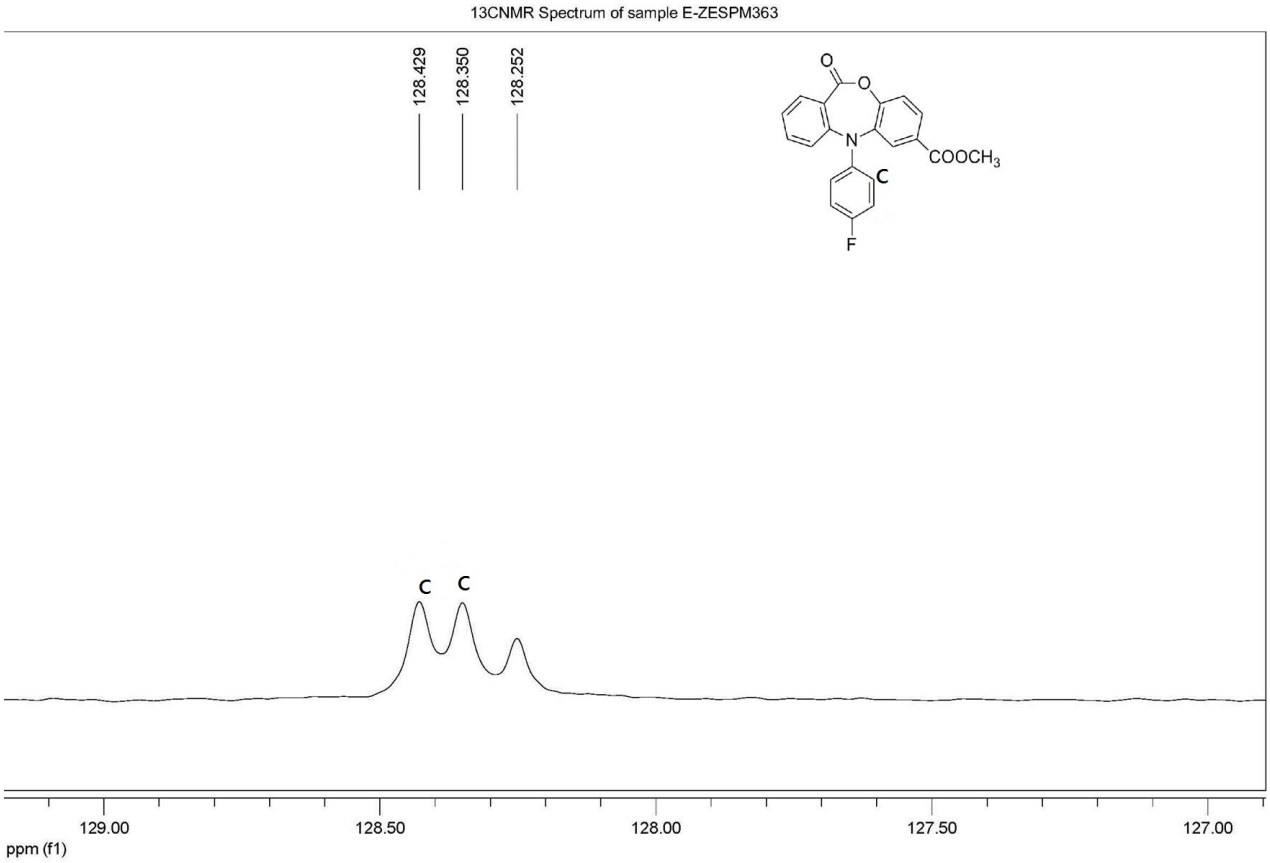


13CNMR Spectrum of sample E-ZESPM363

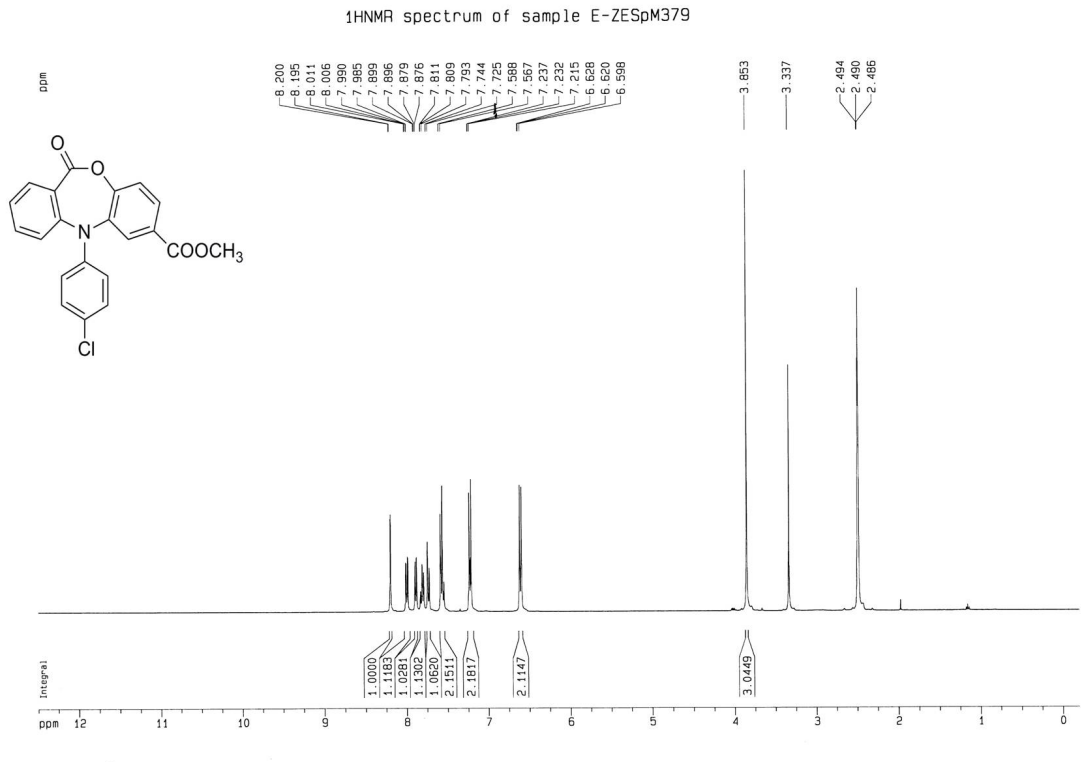



13CNMR Spectrum of sample E-ZESPM363
164.782
163.174
157.678
155.326
152.921
O
O
N
COOCH3
a
F
a
a
165.0
160.0
155.0
ppm (f1)

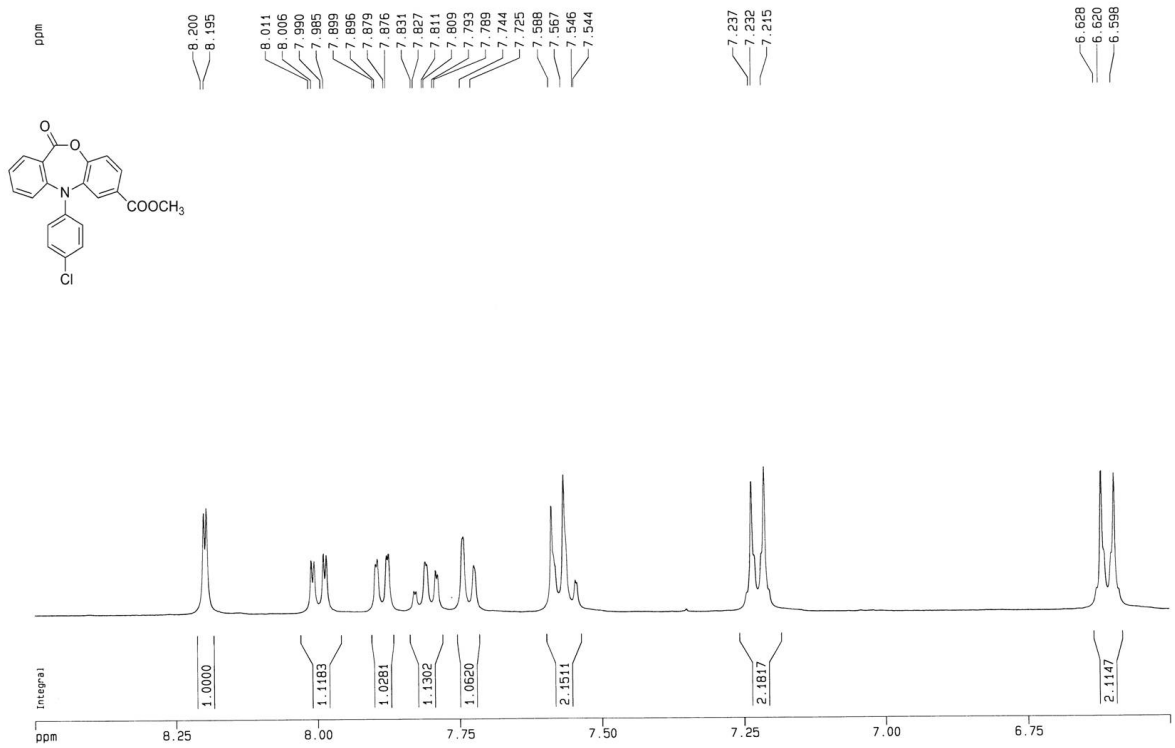

13CNMR Spectrum of sample E-ZESPM363
116.091
115.866
114.425
114.349
O
O
N
COOCH3
b
F
b
b
116.50
116.00
115.50
115.00
114.50
114.00
ppm (f1)



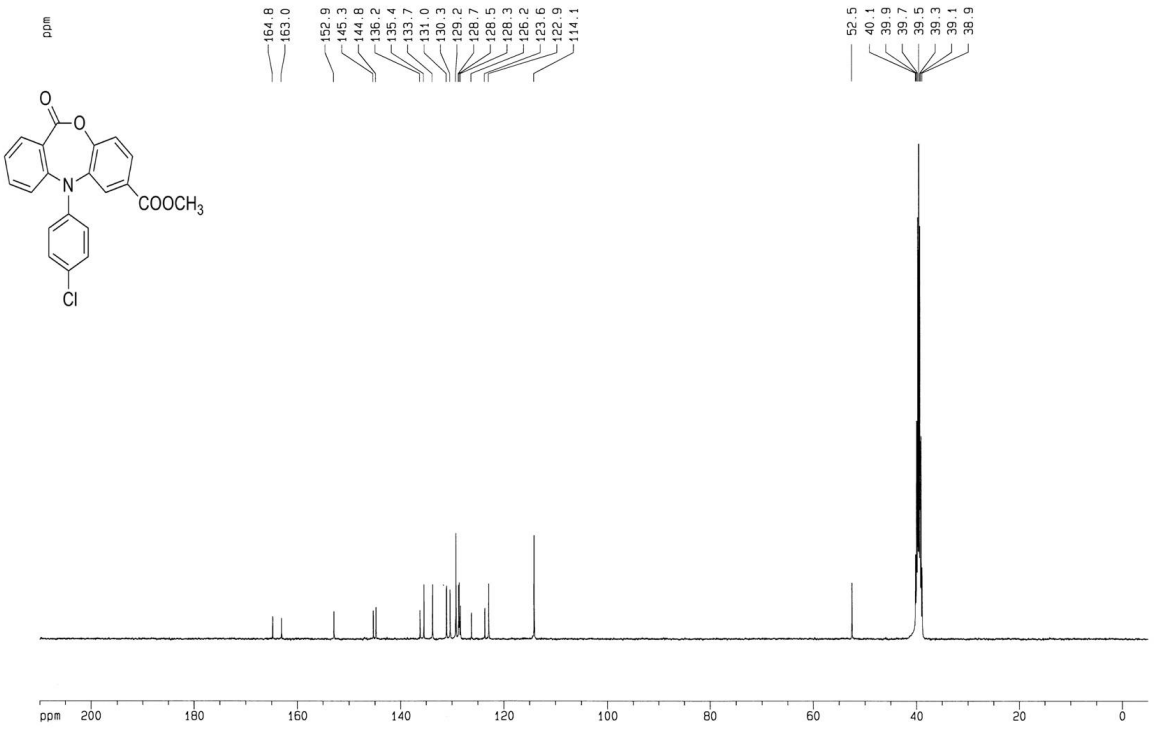
[^{1}H NMR and ^{13}C NMR spectrum of 4e in DMSO-d_6]



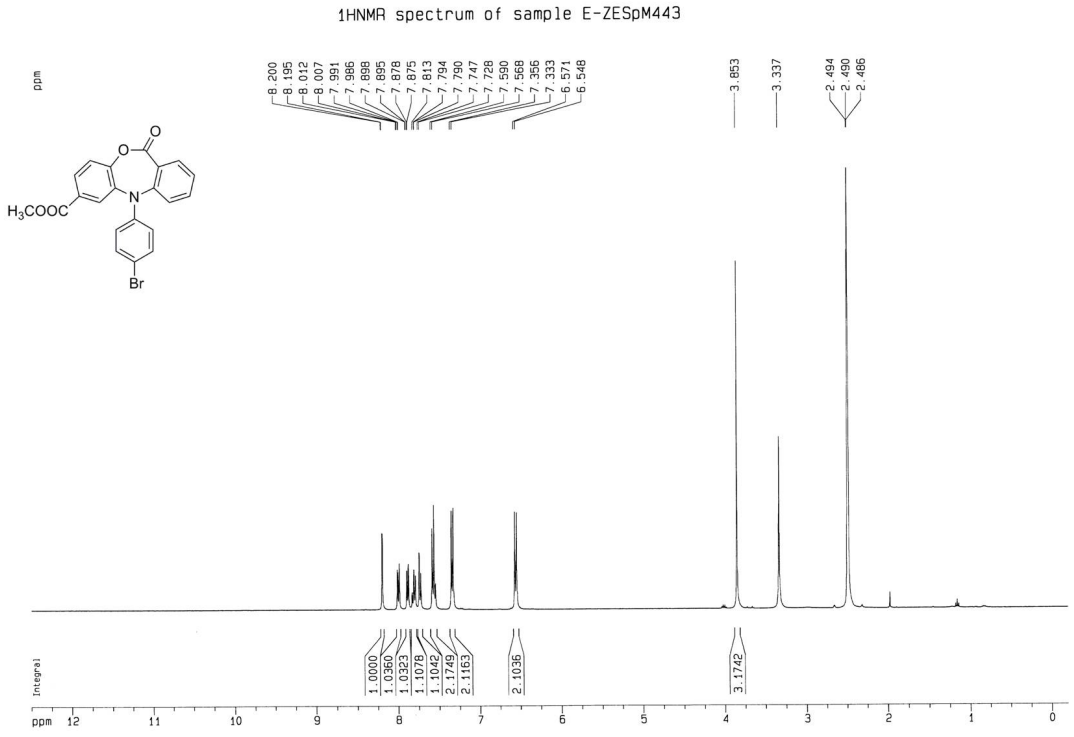
1HNMR spectrum of sample E-ZESpM379

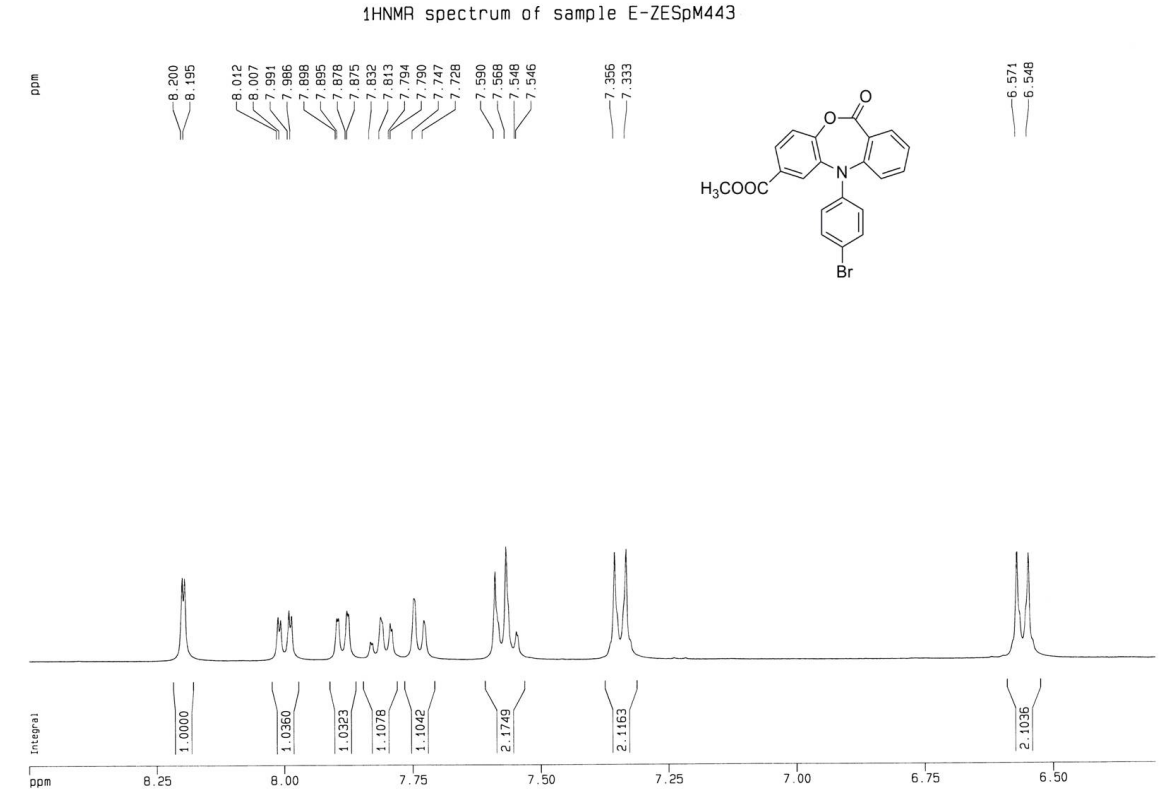


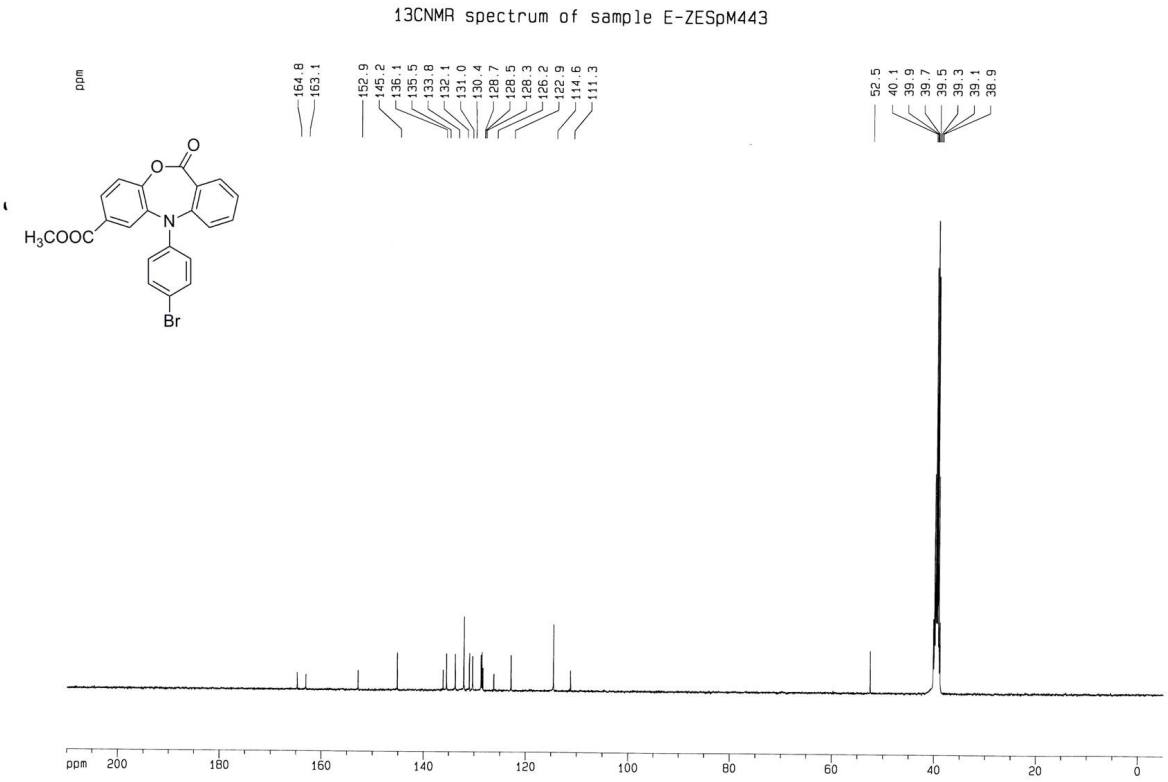
13CNMR spectrum of sample E-ZESpM379



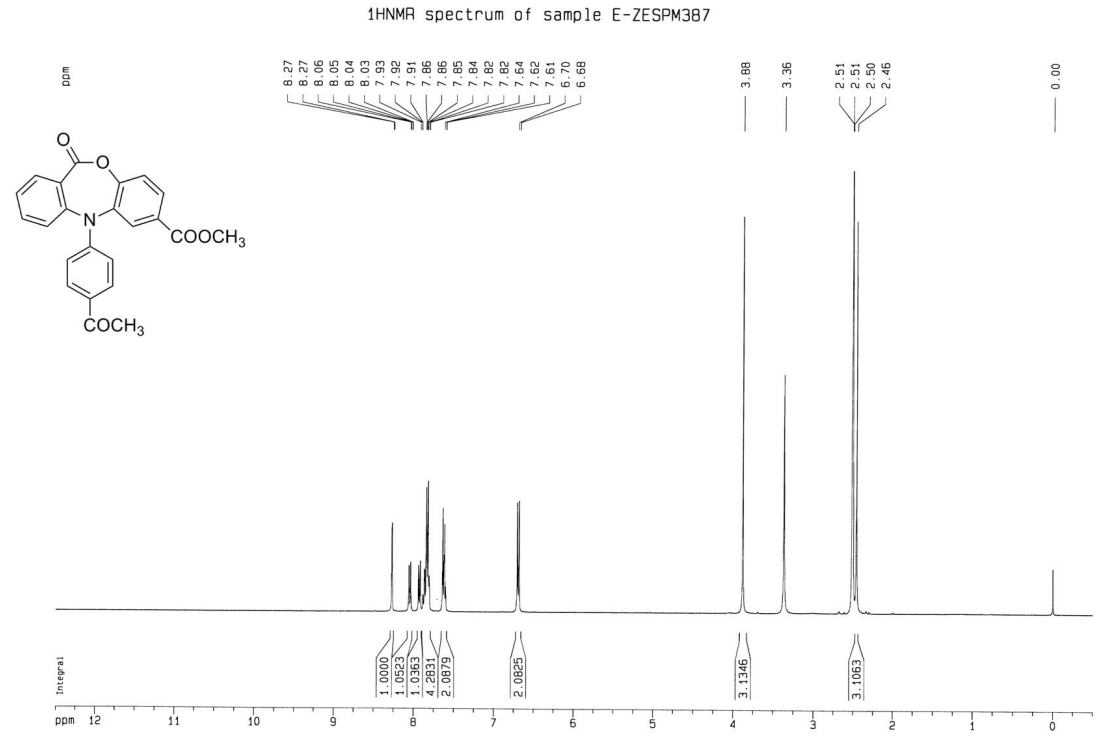
[^{1}H NMR and ^{13}C NMR spectrum of 4f in DMSO-d_6]



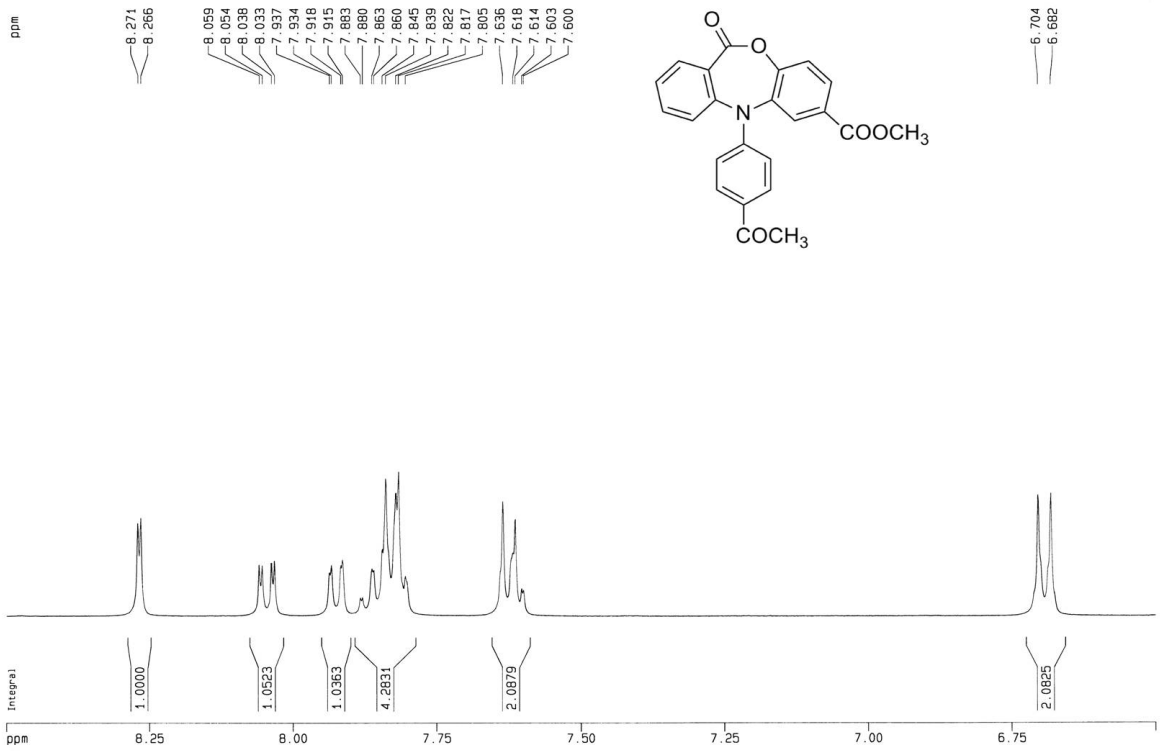




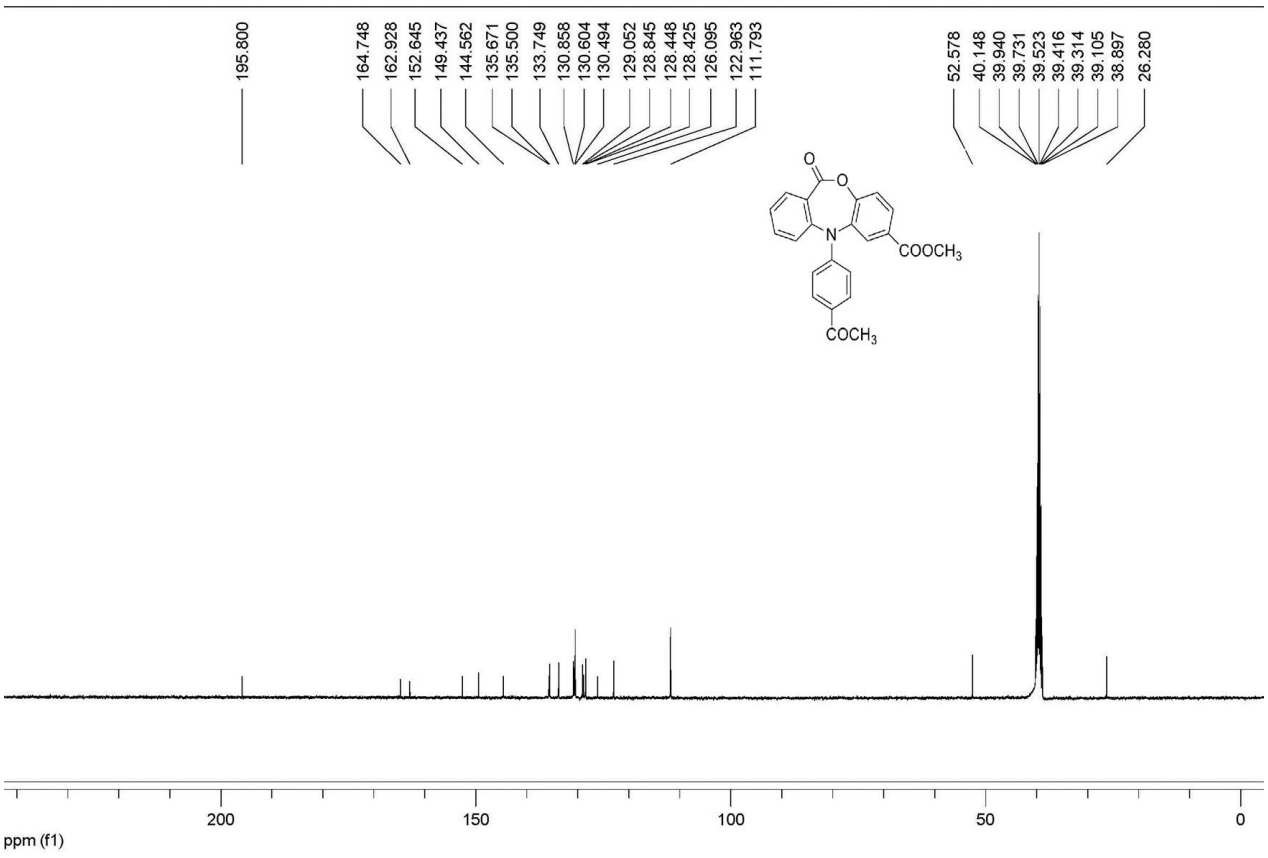
[^{1}H NMR and ^{13}C NMR spectrum of 4g in DMSO-d_6]



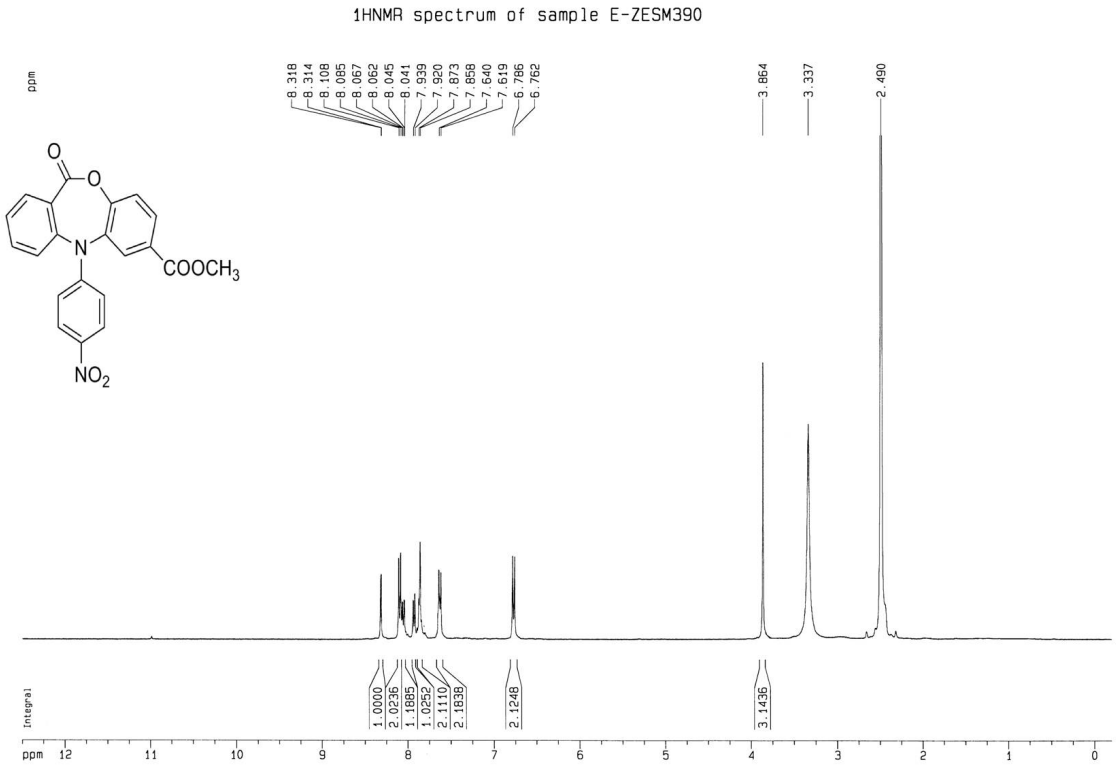
1HNMR spectrum of sample E-ZESPM387

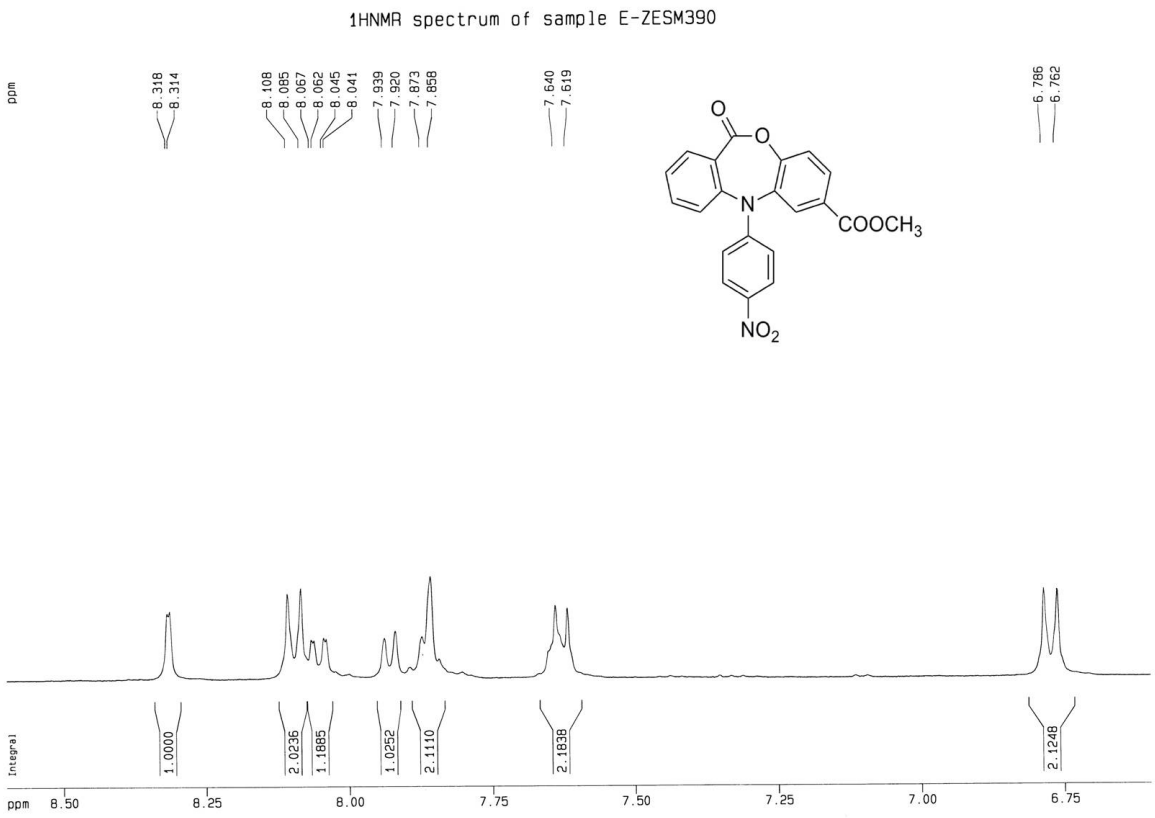


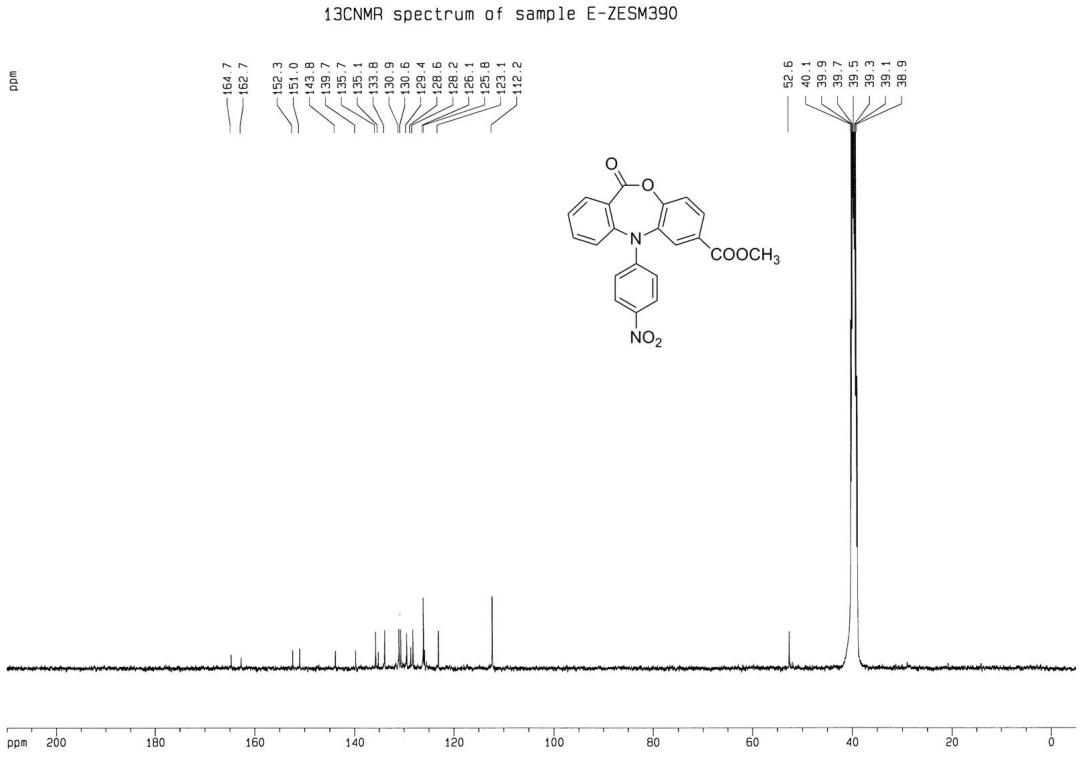
13C Spectrum of sample E-ZESPM387



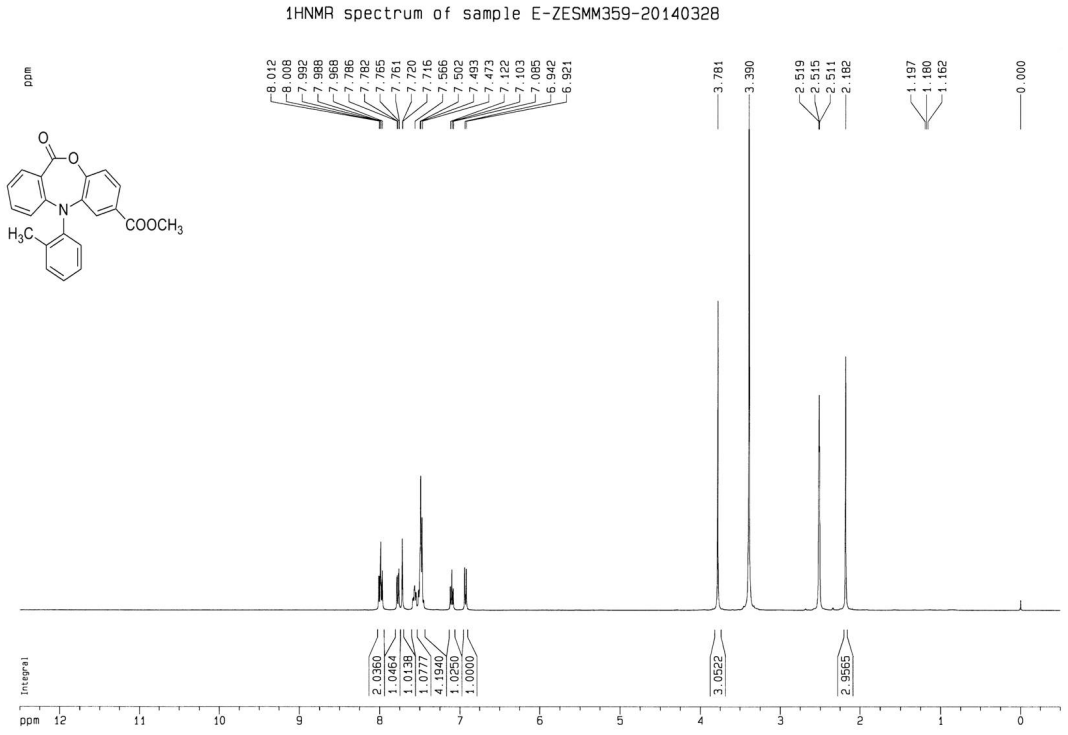
[^{1}H NMR and ^{13}C NMR spectrum of 4h in DMSO-d_6]



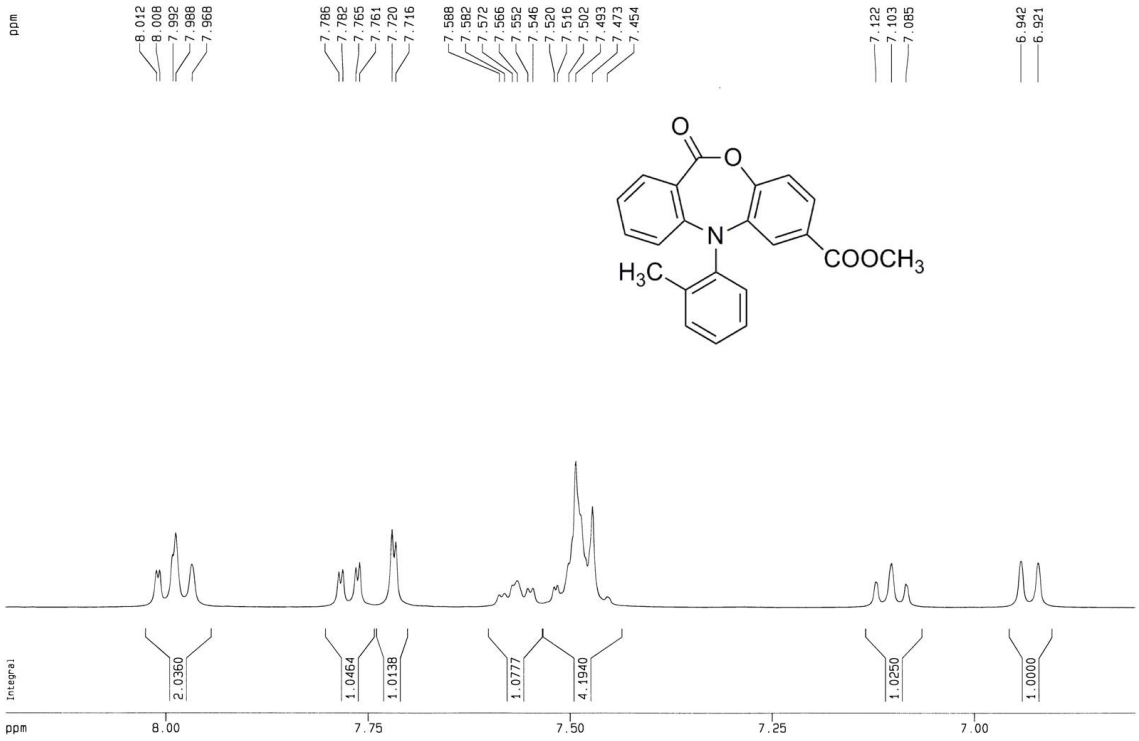




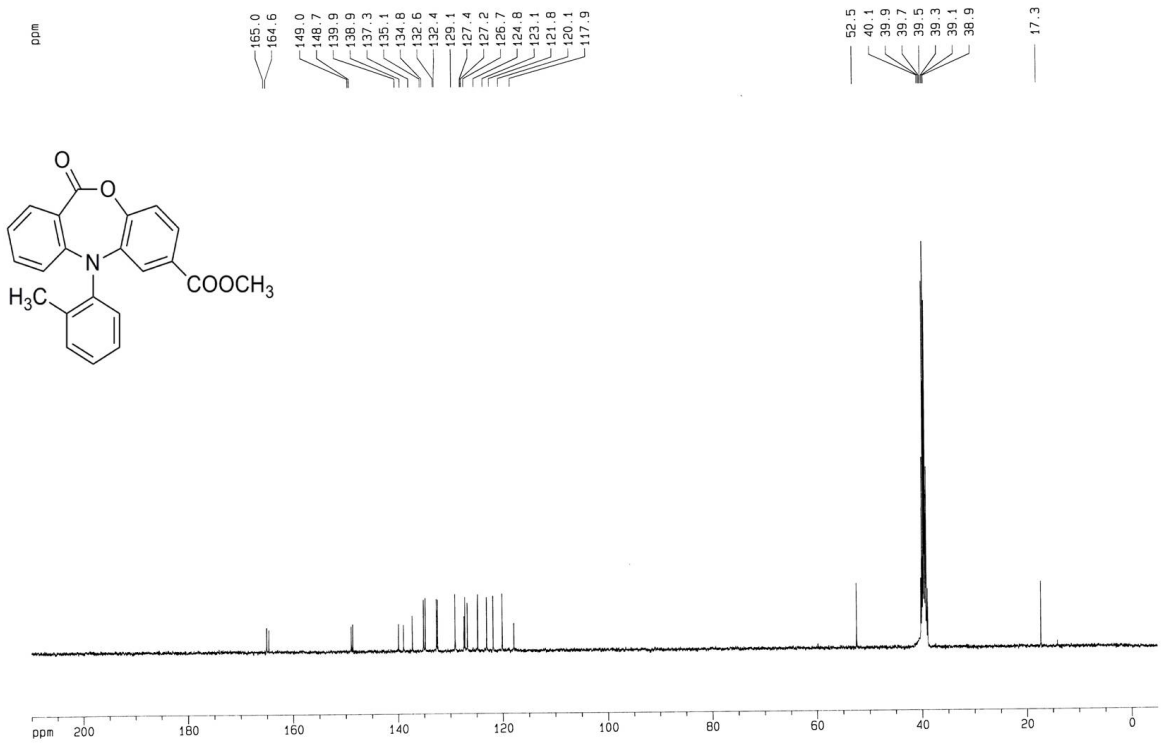
[^{1}H NMR and ^{13}C NMR spectrum of 4i in DMSO-d_6]



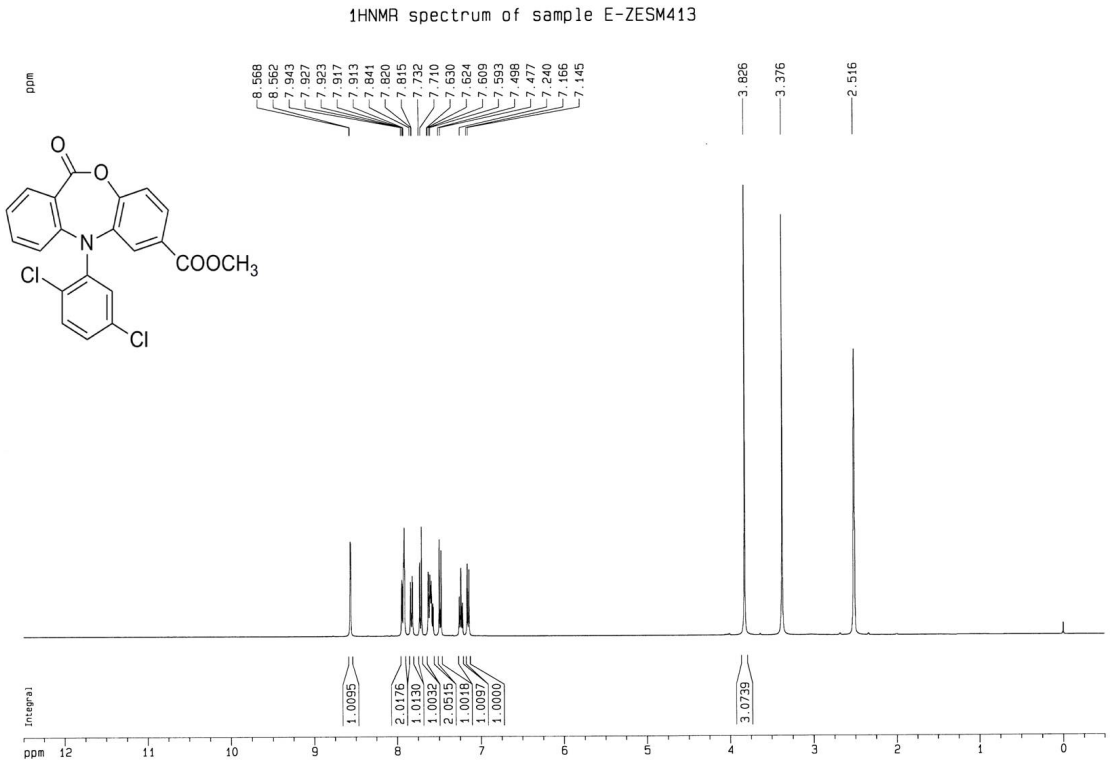
1HNMR spectrum of sample E-ZESMM359-20140328

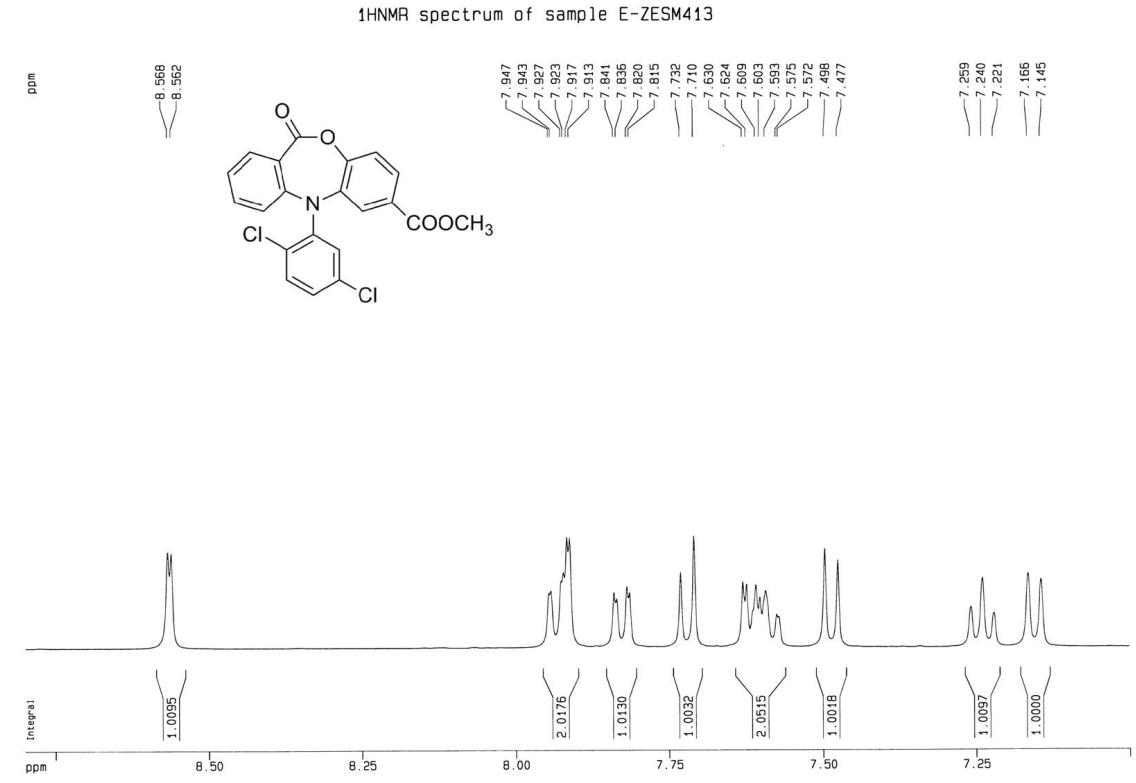


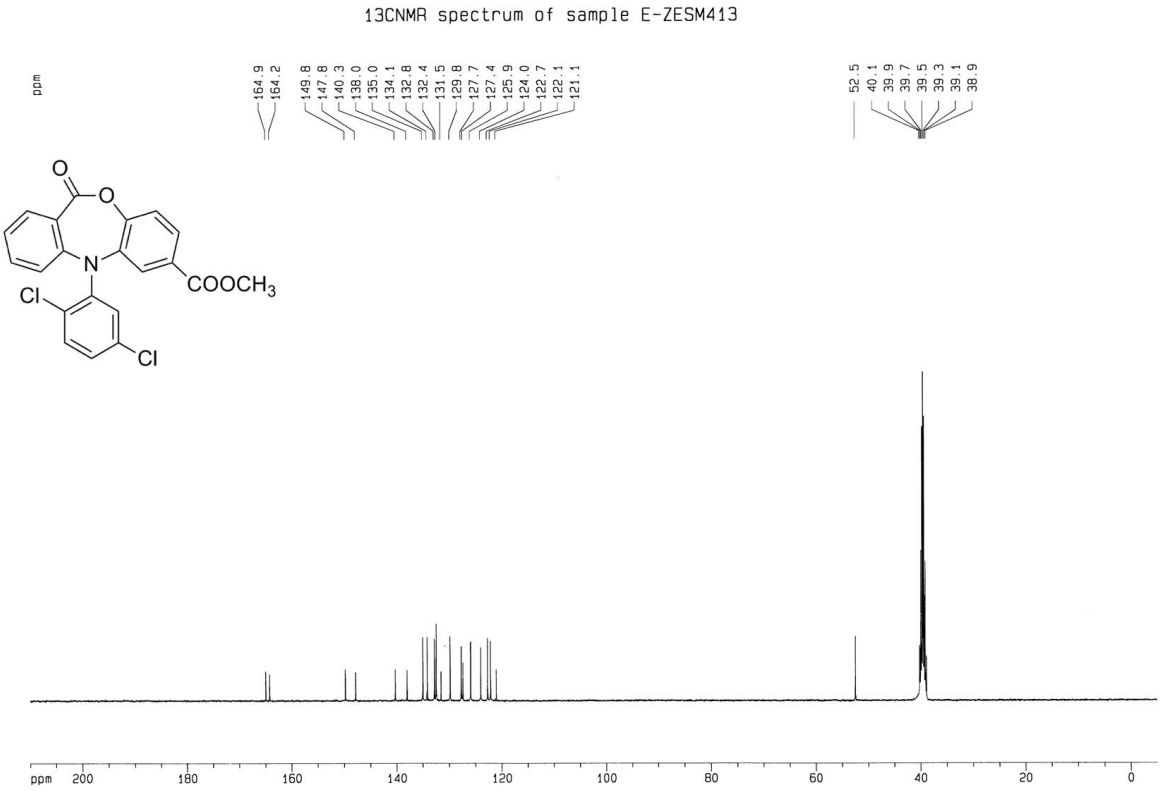
13CNMR spectrum of sample E-ZESOM359



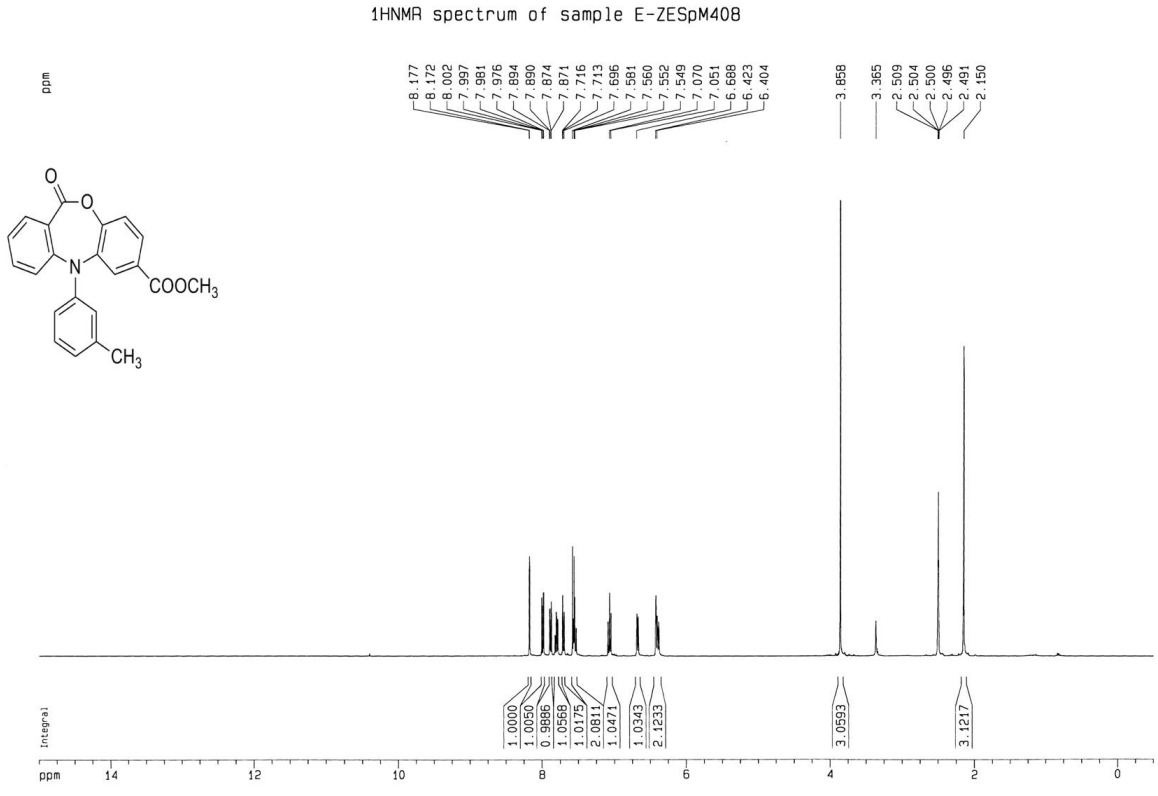
[^{1}H NMR and ^{13}C NMR spectrum of 4j in DMSO-d_6]



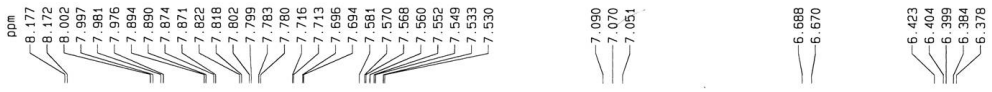


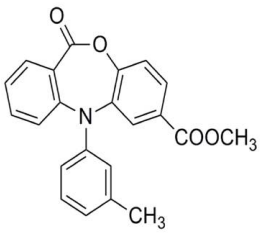


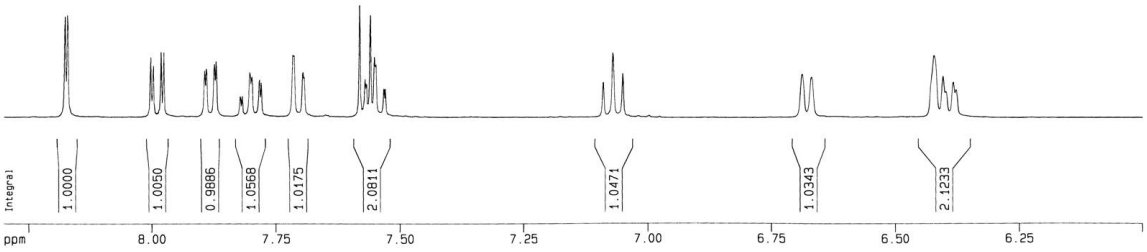
[^{1}H NMR and ^{13}C NMR spectrum of 4k in DMSO-d_6]



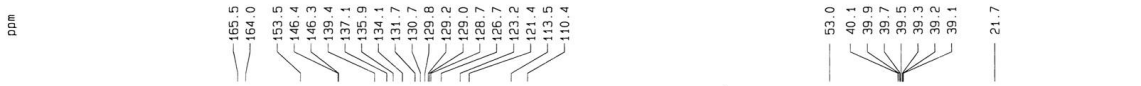
1HNMR spectrum of sample E-ZESpM408

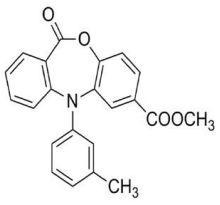


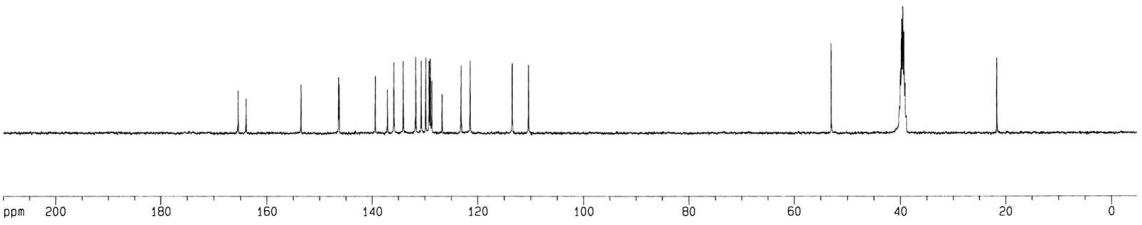




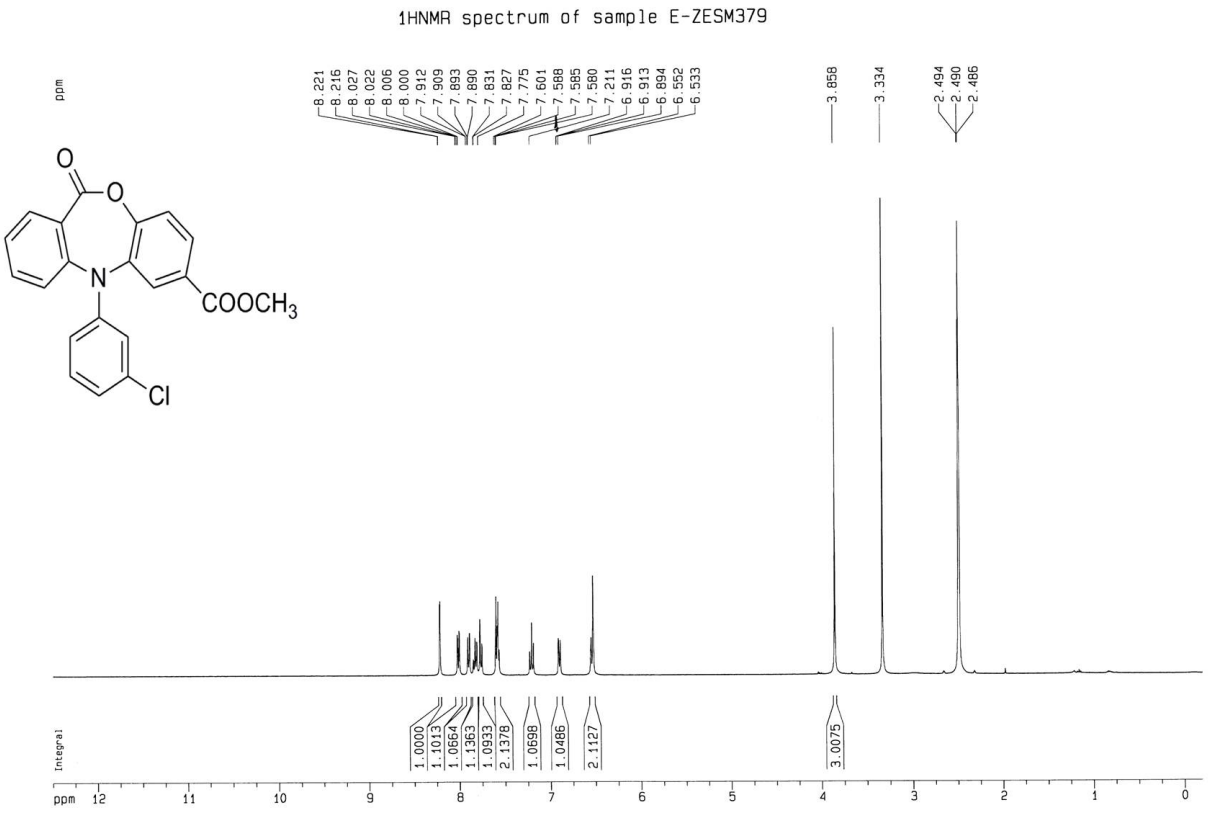
13CNMR spectrum of sample E-ZESMM359

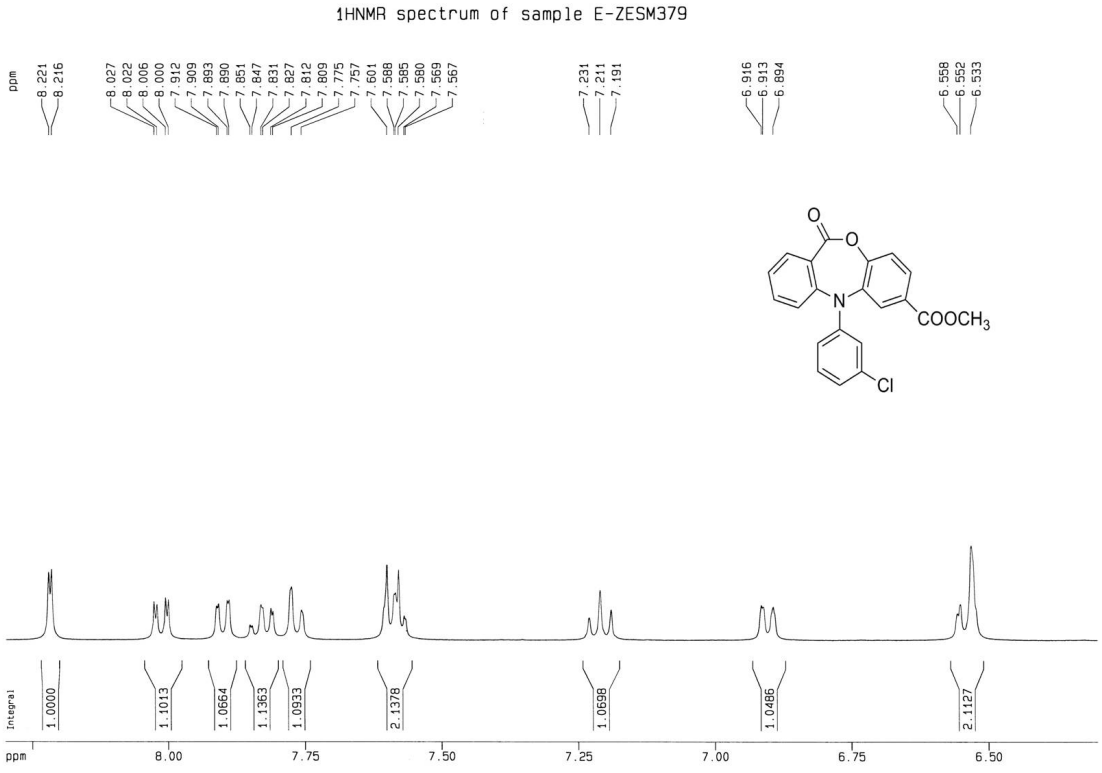


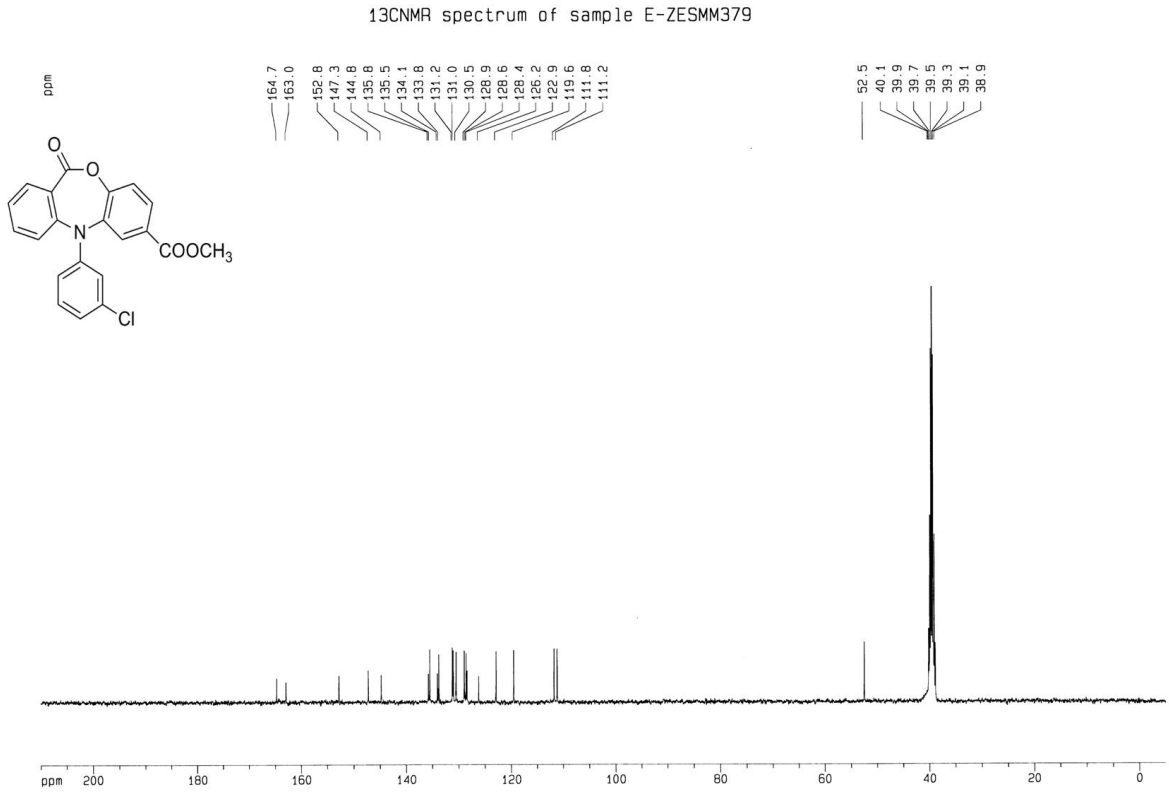




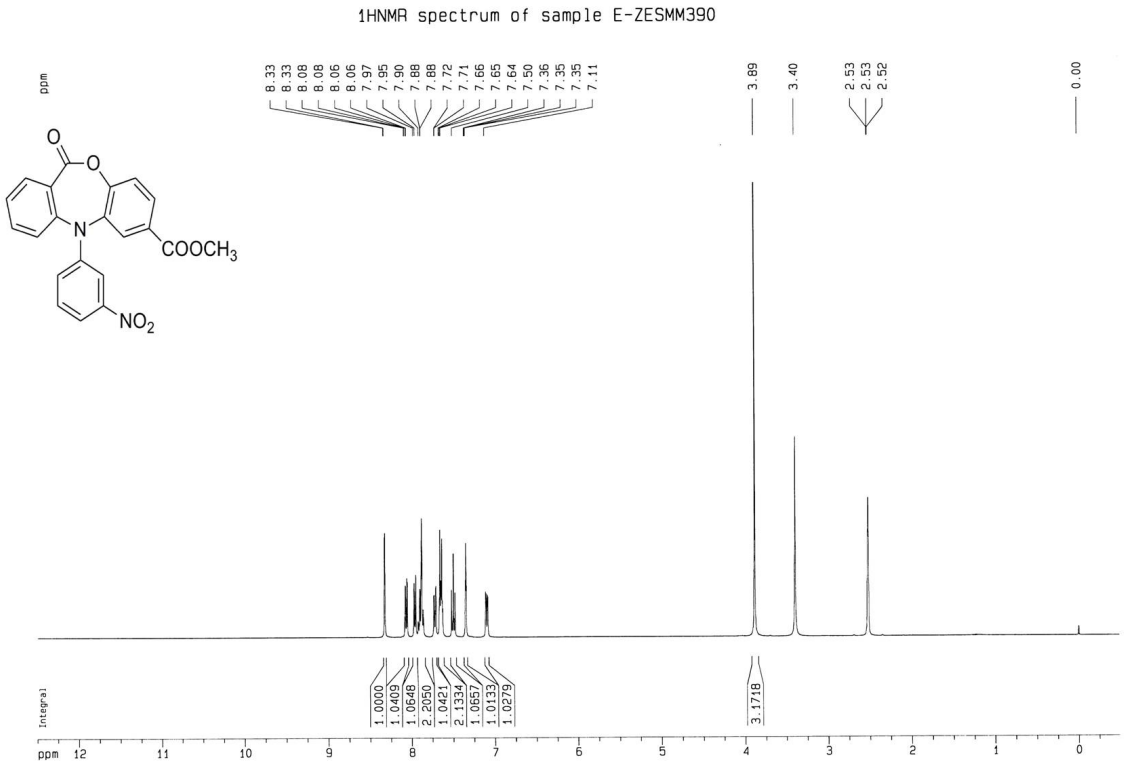
[^{1}H NMR and ^{13}C NMR spectrum of 4l in DMSO-d_6]



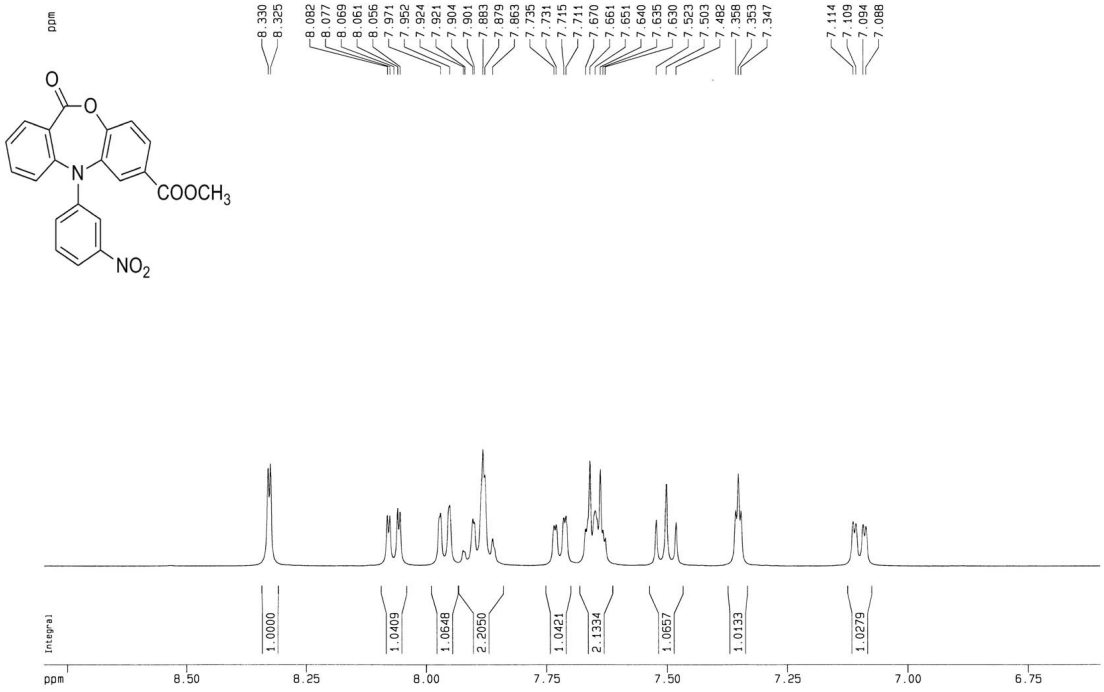




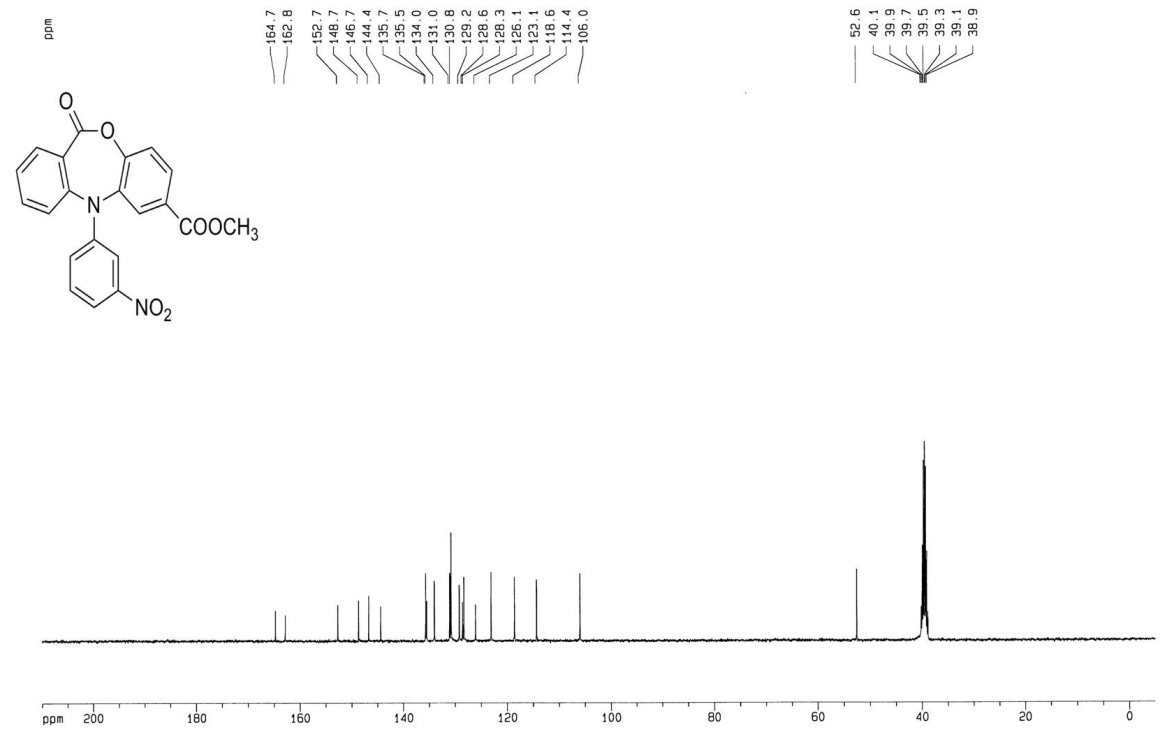
[^{1}H NMR and ^{13}C NMR spectrum of 4m in DMSO-d_6]



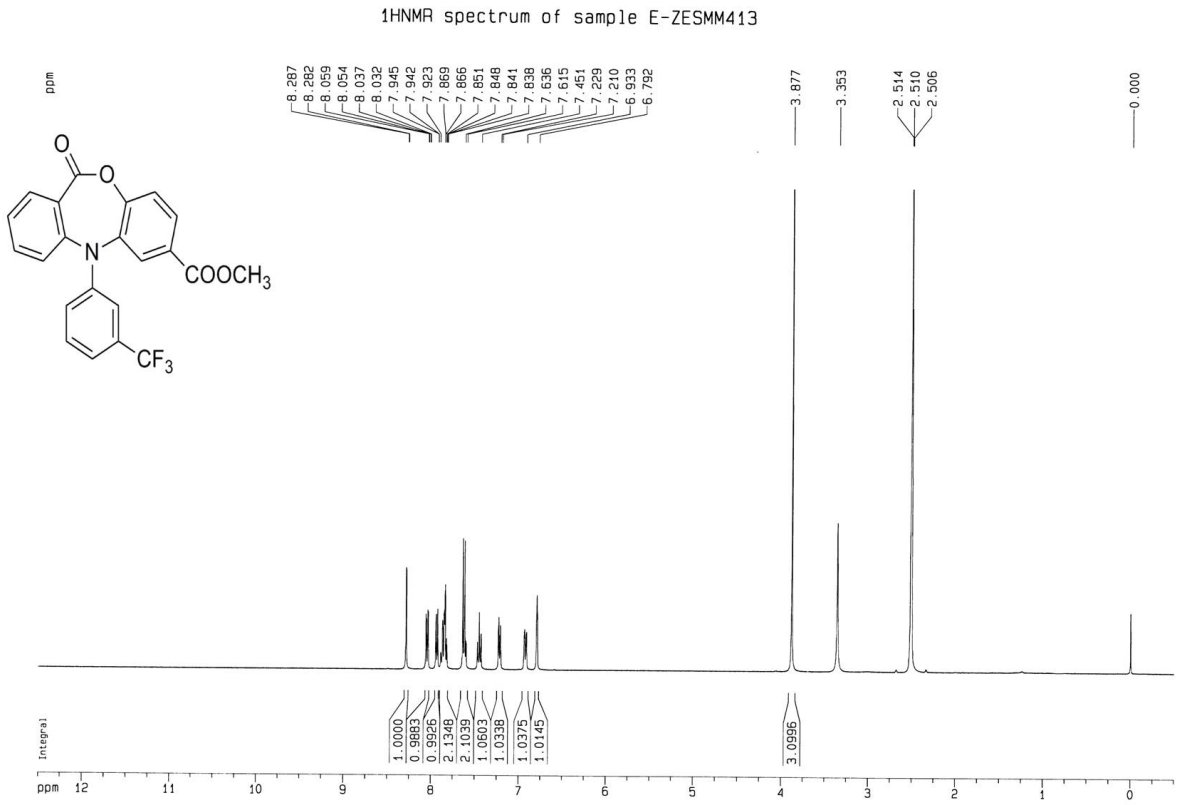
1HNMR spectrum of sample E-ZESMM390

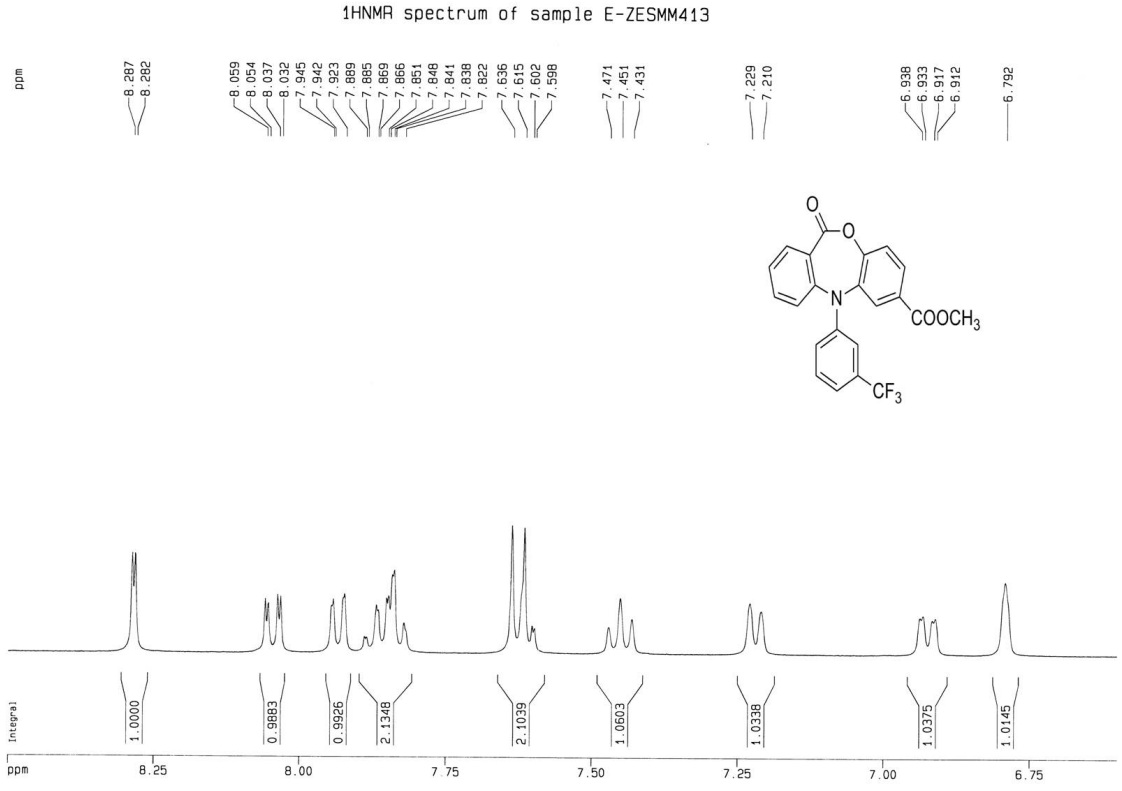


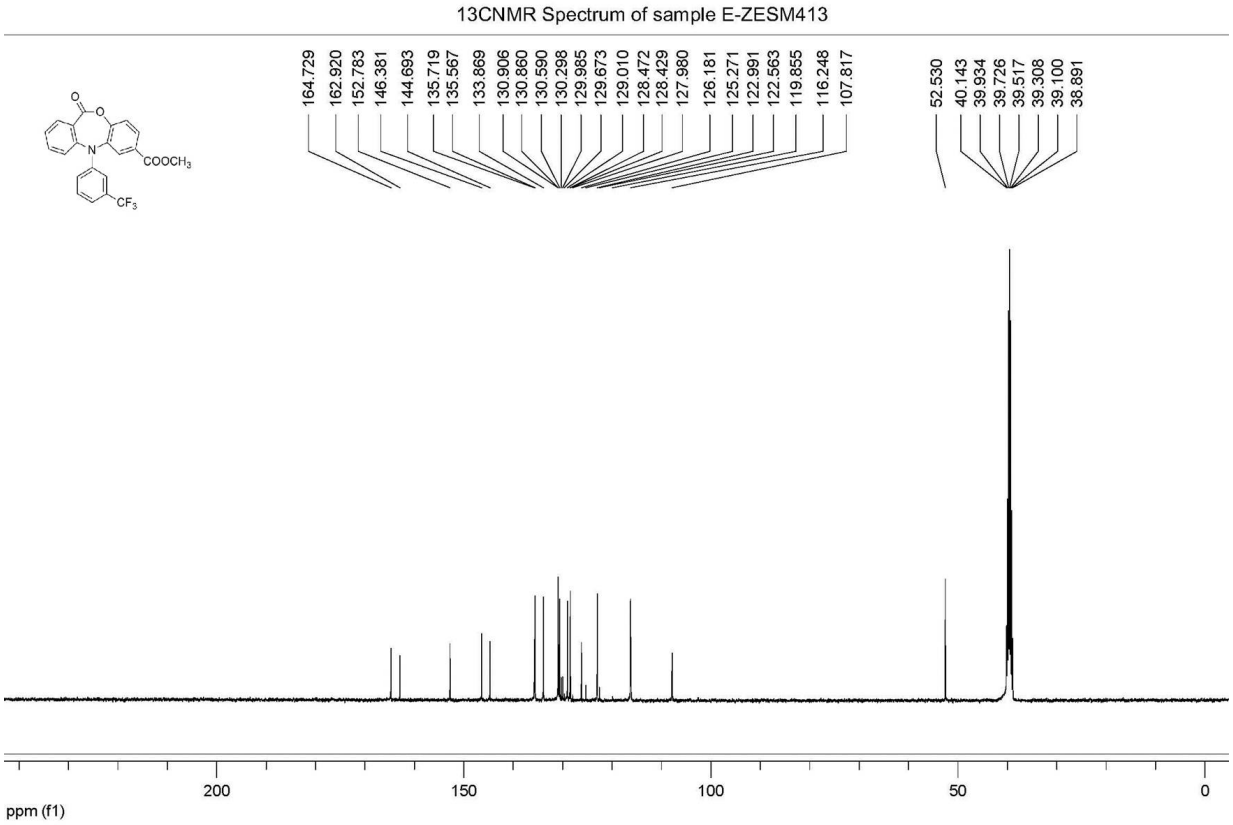
13CNMR spectrum of sample E-ZESMM390

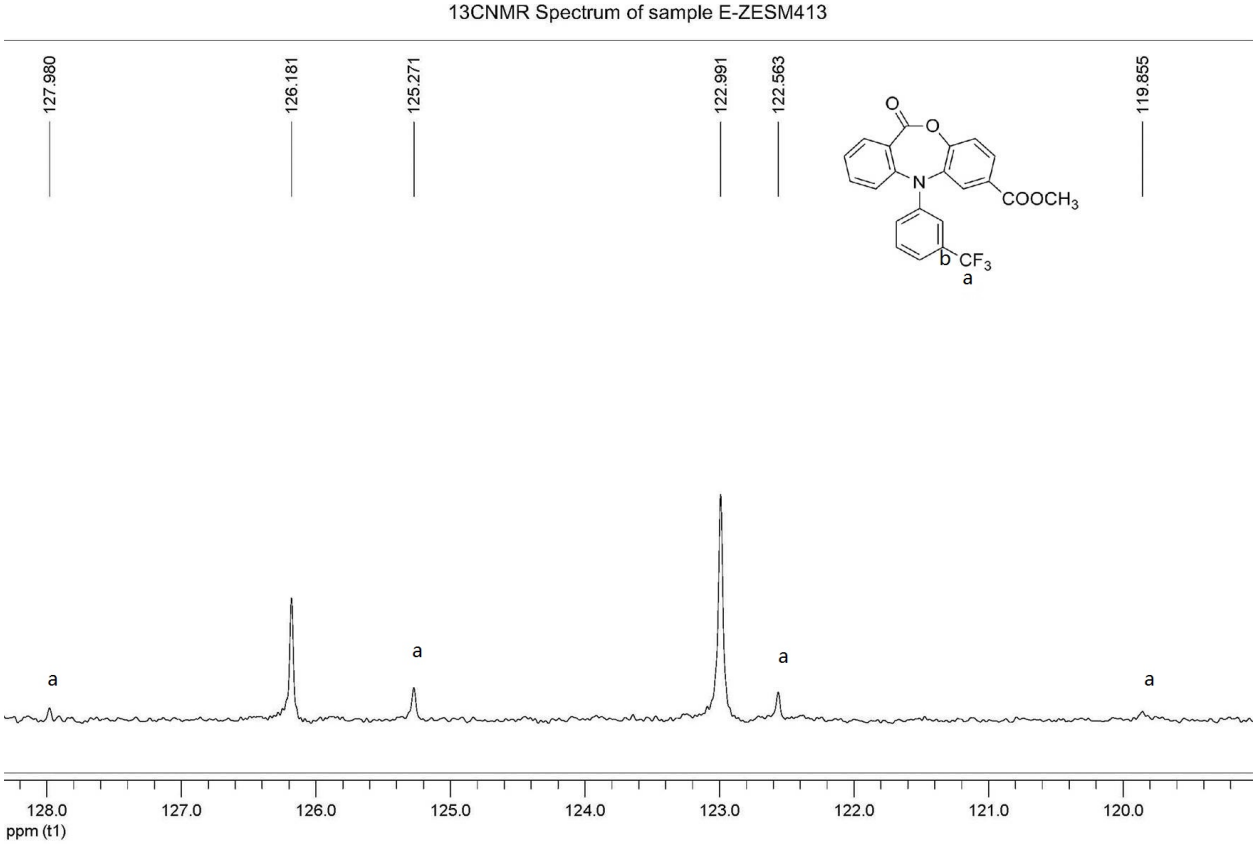


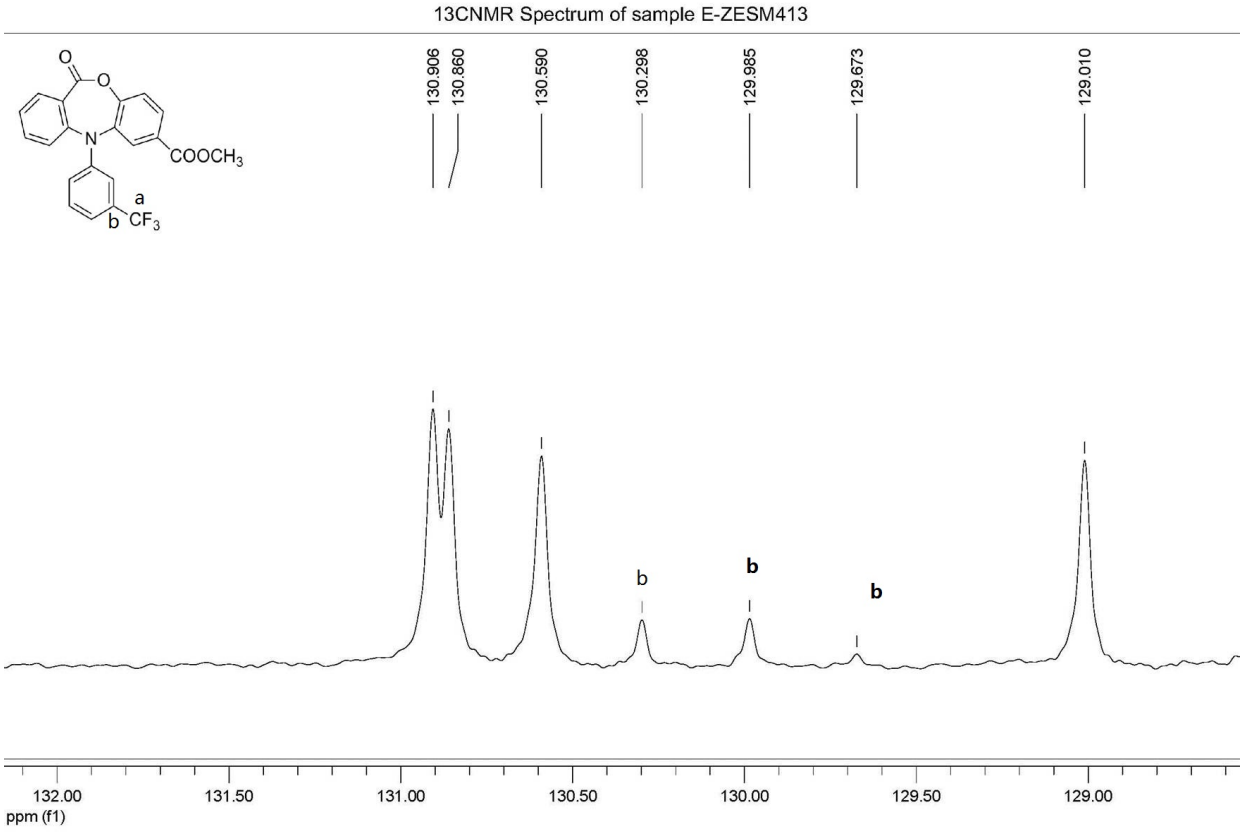
[^{1}H NMR and ^{13}C NMR spectrum of 4n in DMSO-d_6]



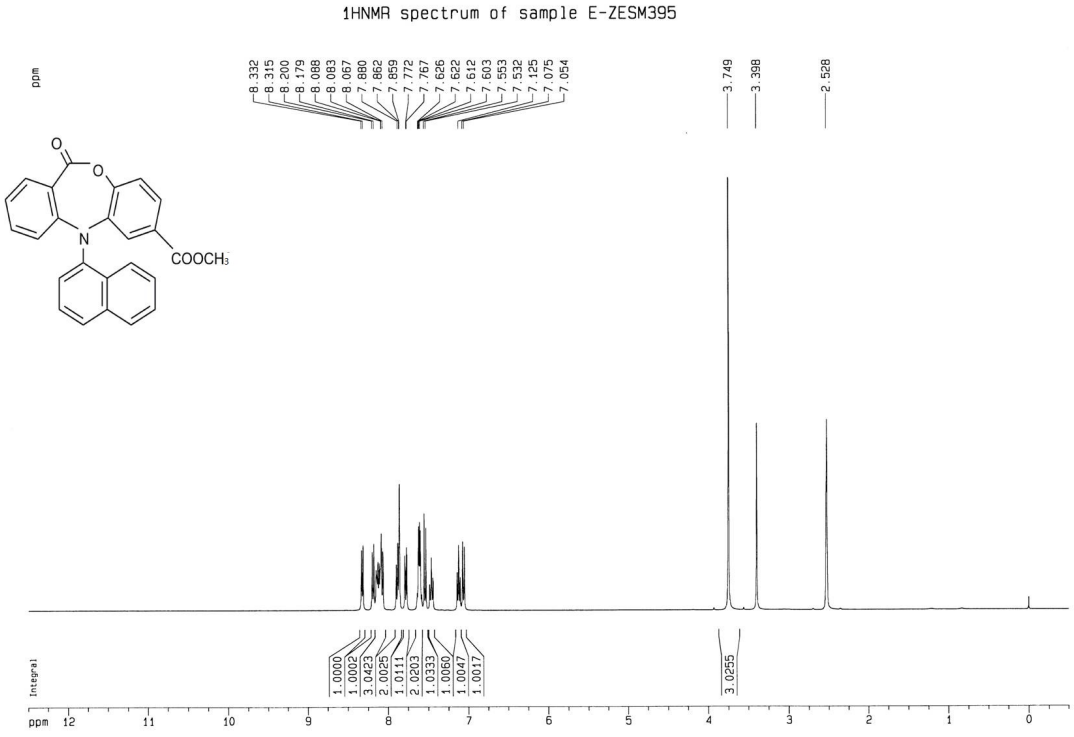



13CNMR Spectrum of sample E-ZESM413
164.729
162.920
152.783
146.381
144.693
135.719
135.567
133.869
130.906
130.860
130.590
130.298
129.985
129.673
129.010
128.472
128.429
127.980
126.181
125.271
122.991
122.563
119.855
116.248
107.817
52.530
40.143
39.934
39.726
39.517
39.308
39.100
38.891
COOCH3
CF3
200
150
100
50
0
ppm (f1)

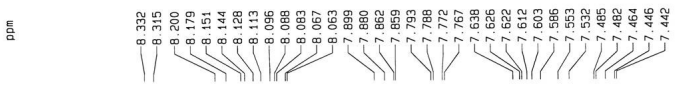

13CNMR Spectrum of sample E-ZESM413
127.980
126.181
125.271
122.991
122.563
119.855
COOCH3
b
CF3
a
a
a
a
a
128.0
127.0
126.0
125.0
124.0
123.0
122.0
121.0
120.0
ppm (t1)

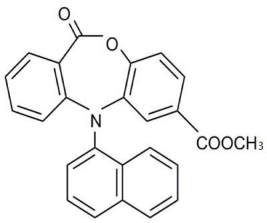


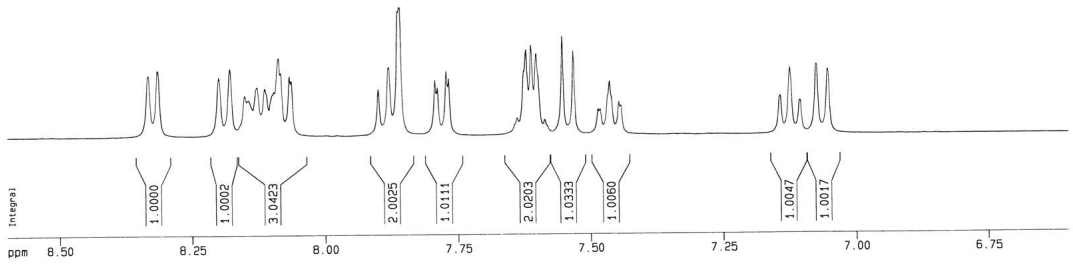
[^{1}H NMR and ^{13}C NMR spectrum of 4o in DMSO-d_6]



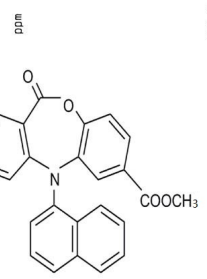
1HNMR spectrum of sample E-ZESM395

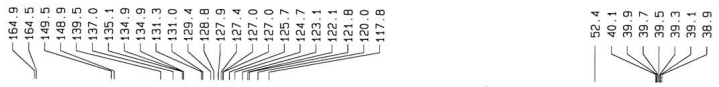


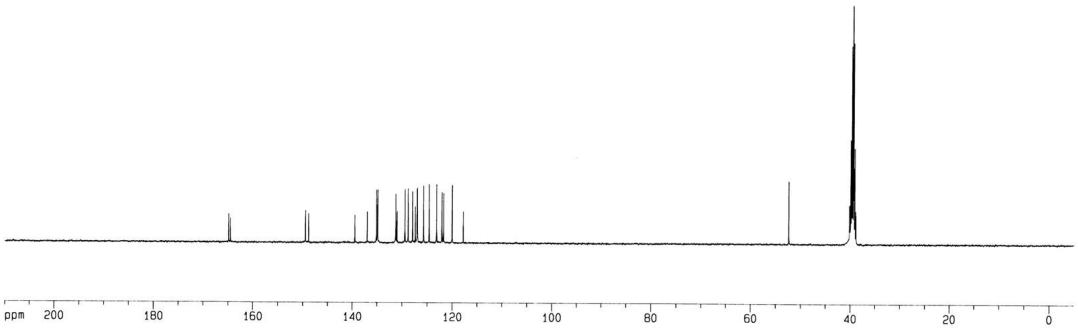




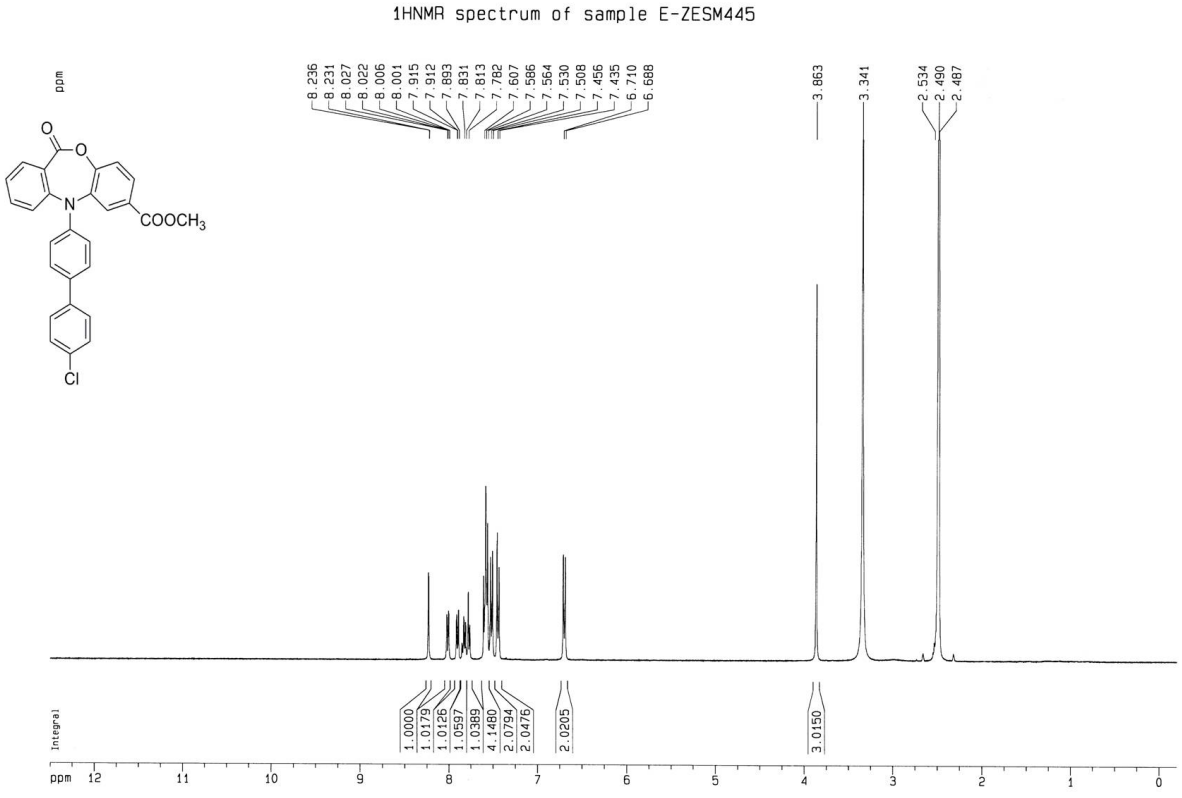
13CNMR spectrum of sample E-ZESM395

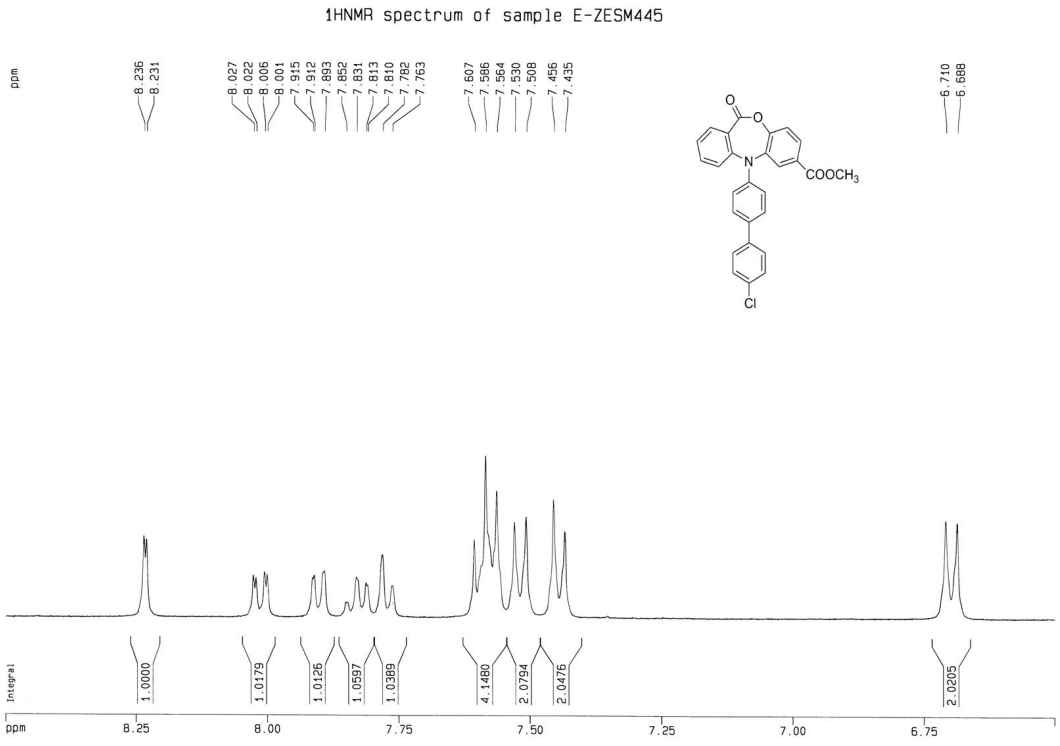


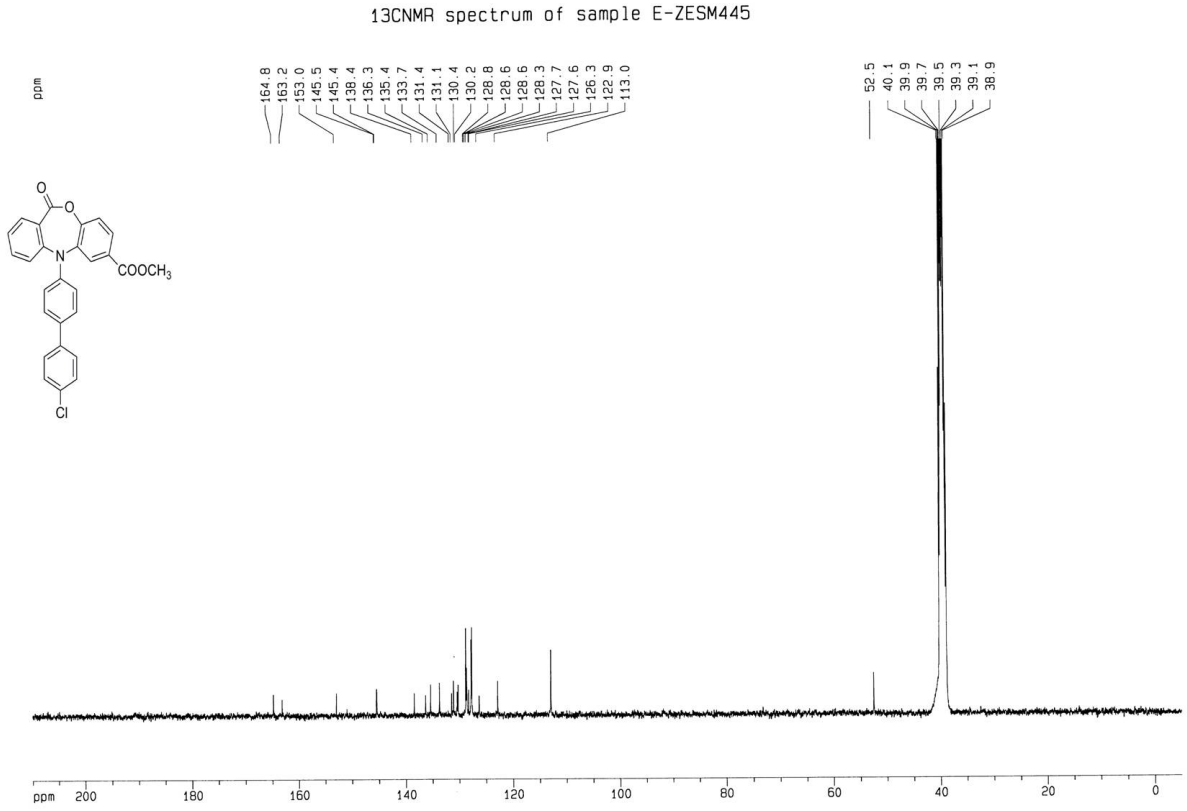




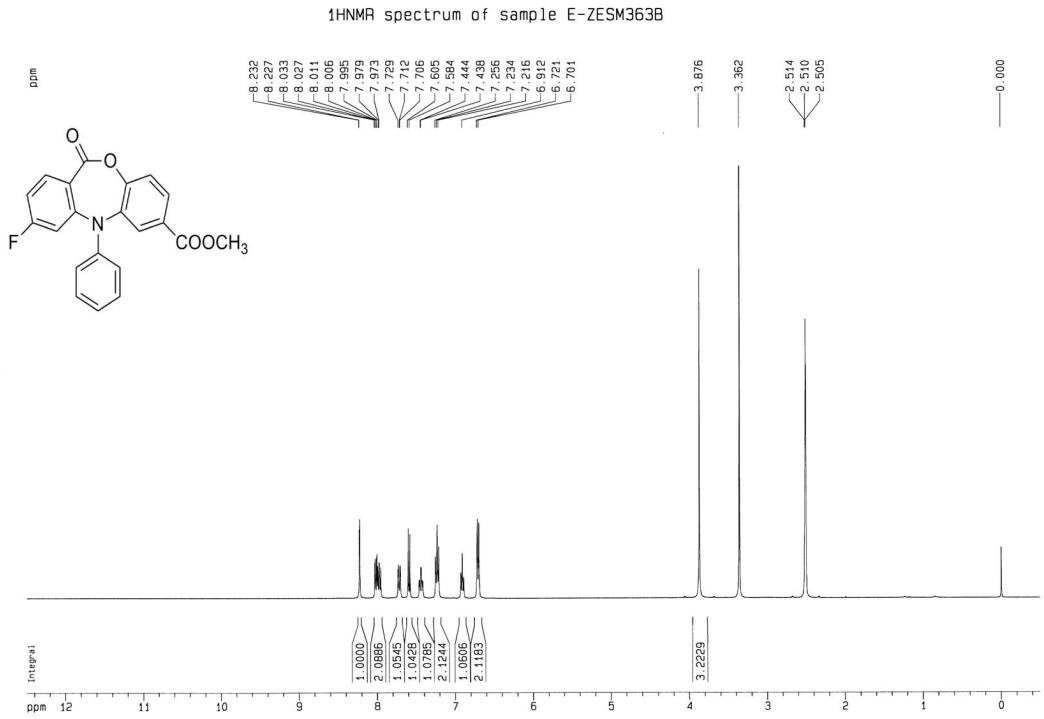
[^{1}H NMR and ^{13}C NMR spectrum of 4p in DMSO-d_6]



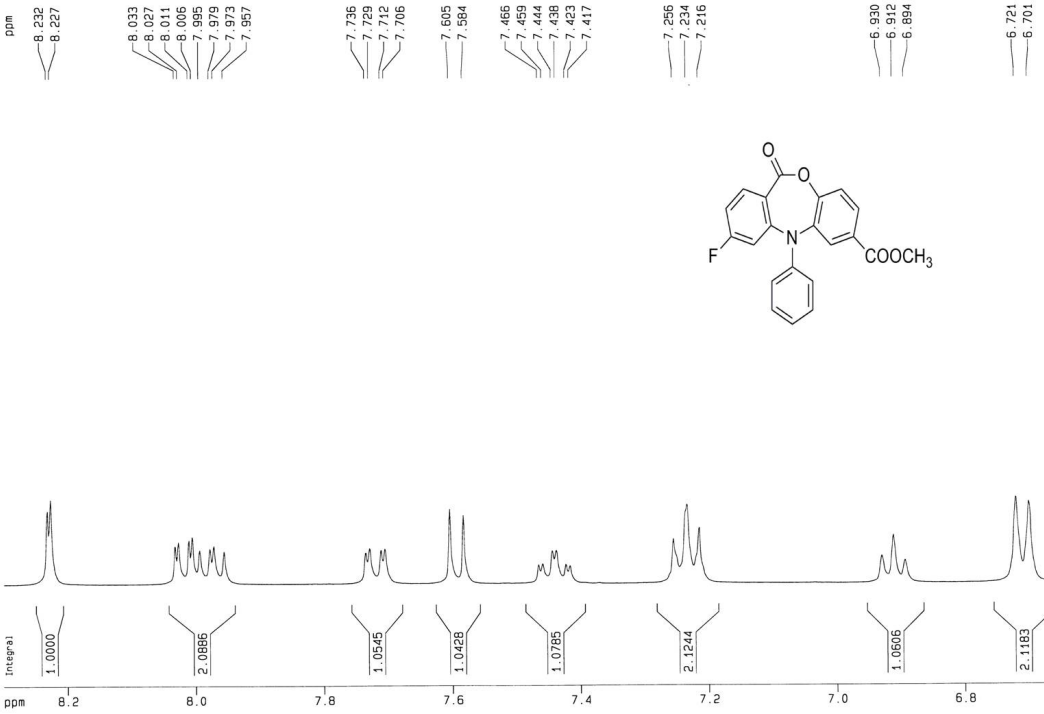




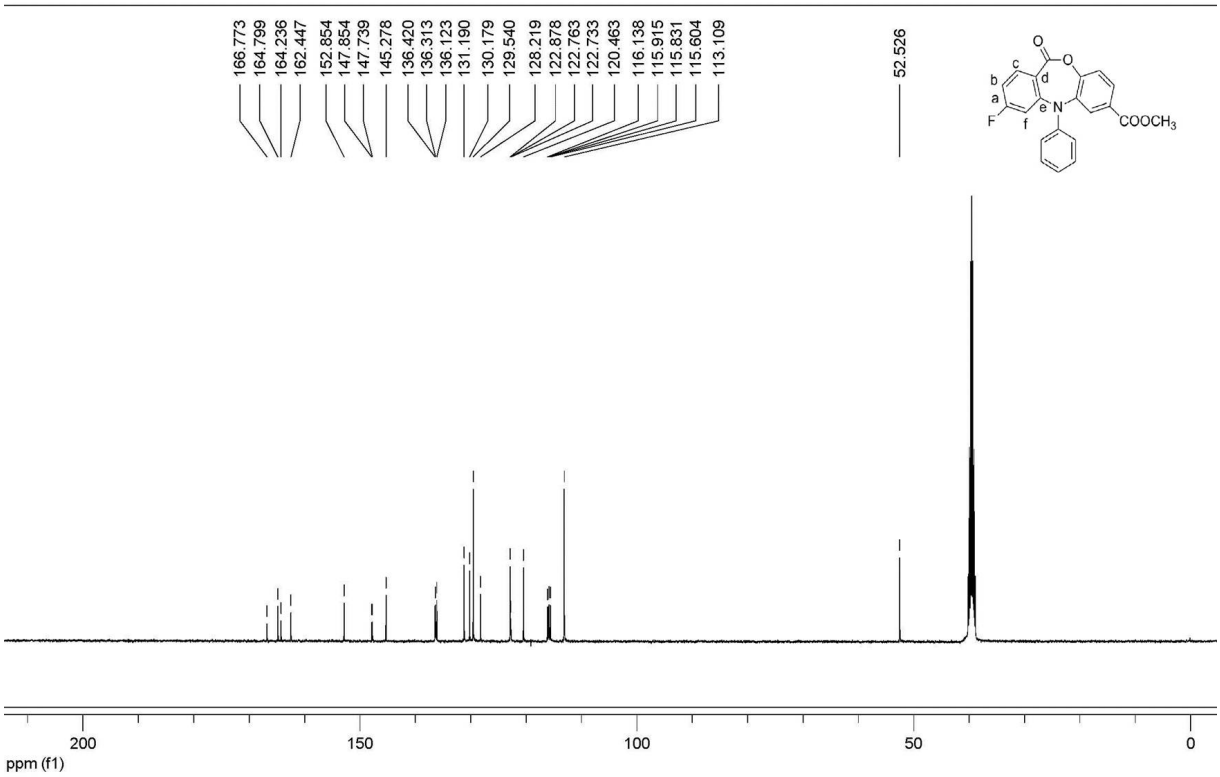
[^{1}H NMR and ^{13}C NMR spectrum of 4q in DMSO-d_6]



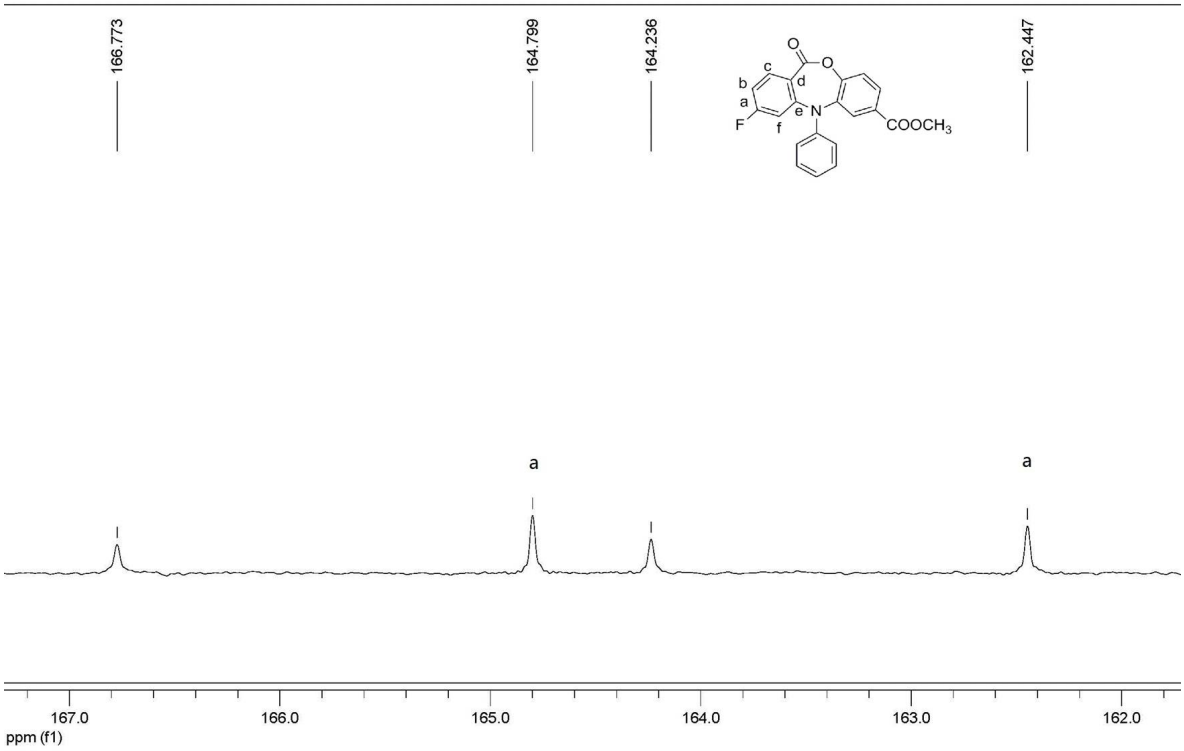
1HNMR spectrum of sample E-ZESM363B



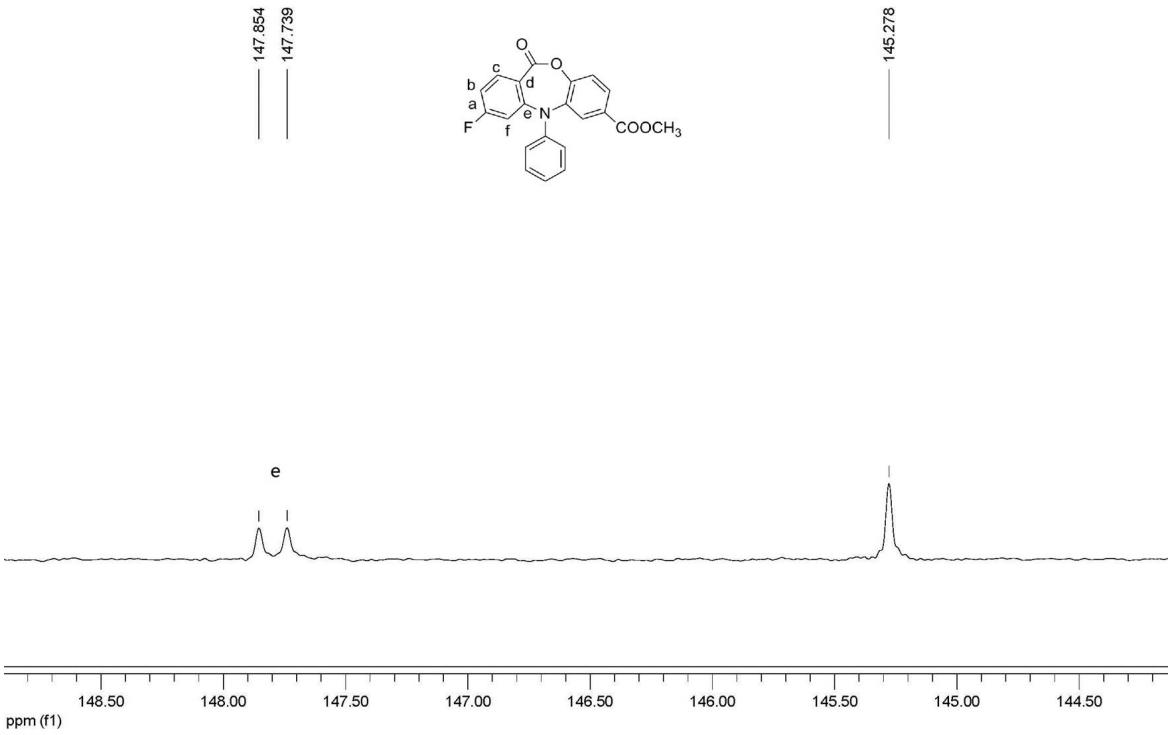
13CNMR Spectrum of sample E-ZESM363B



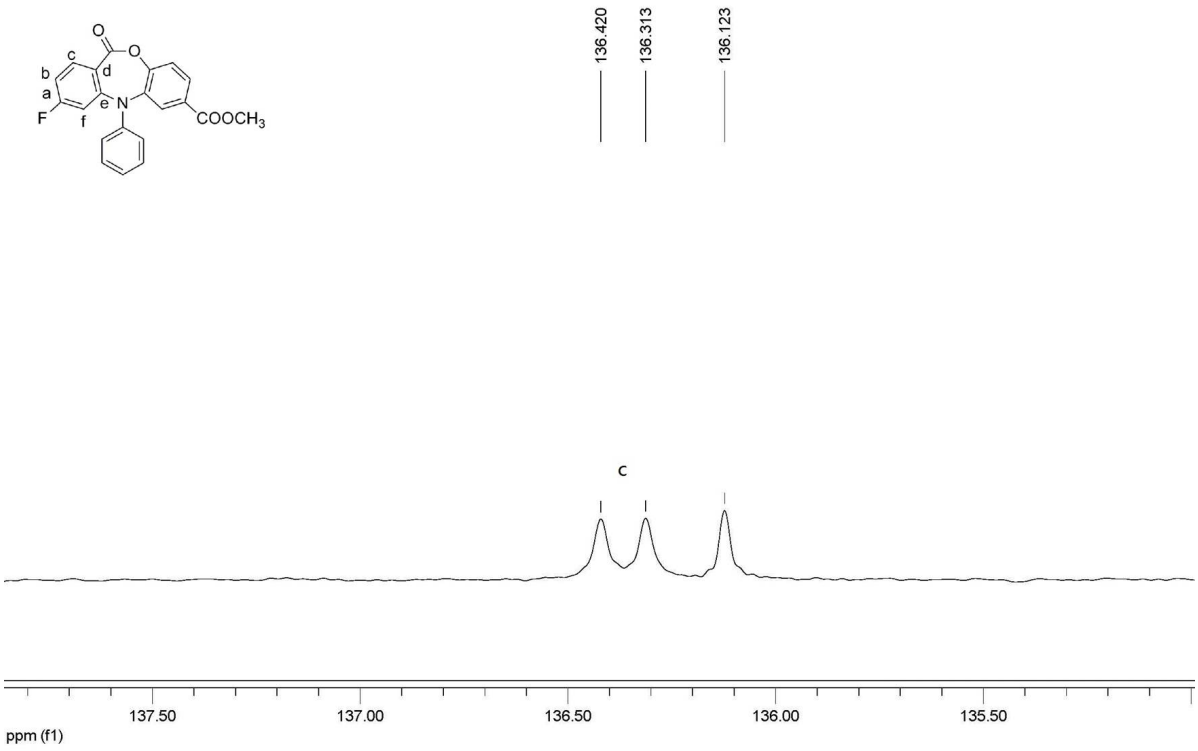
13CNMR Spectrum of sample E-ZESM363B



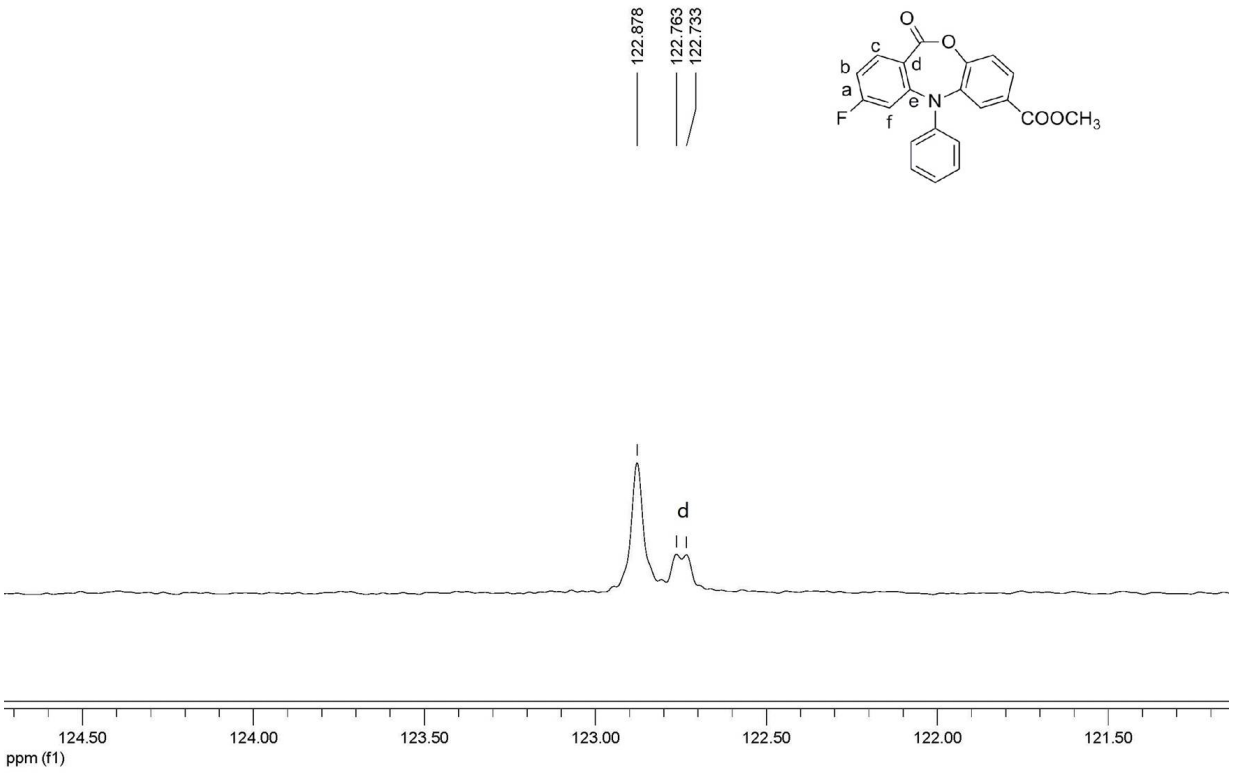
13CNMR Spectrum of sample E-ZESM363B

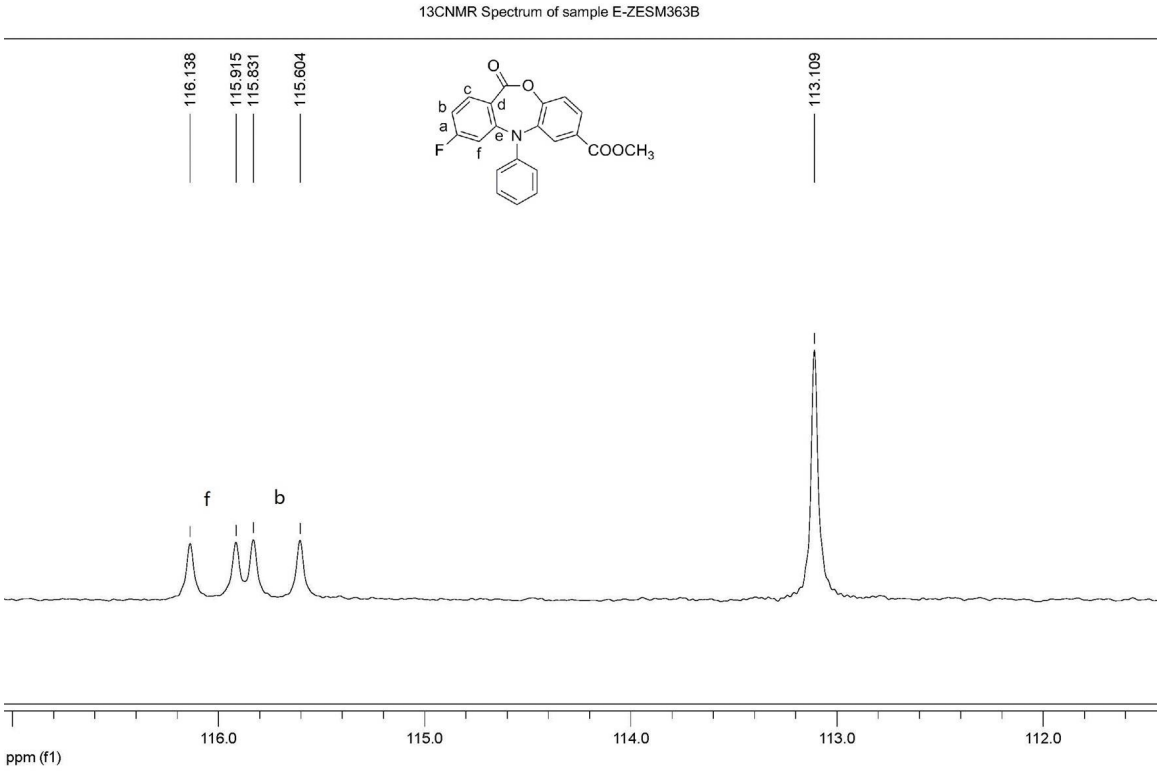


13CNMR Spectrum of sample E-ZESM363B

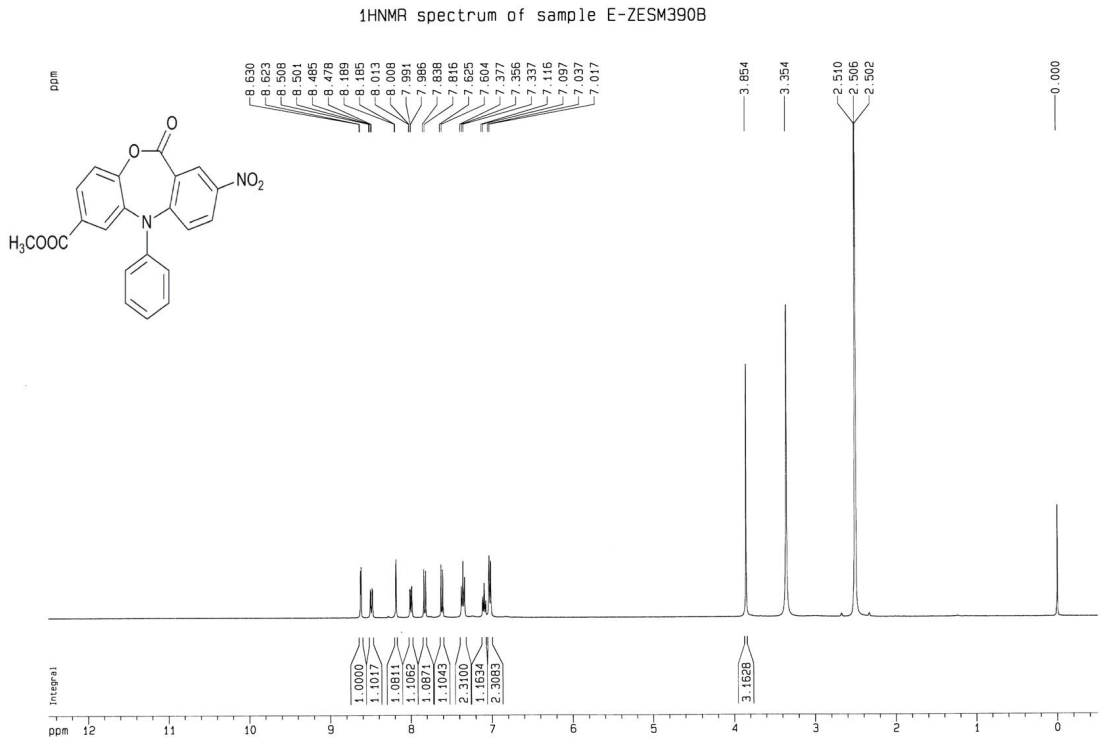


13CNMR Spectrum of sample E-ZESM363B

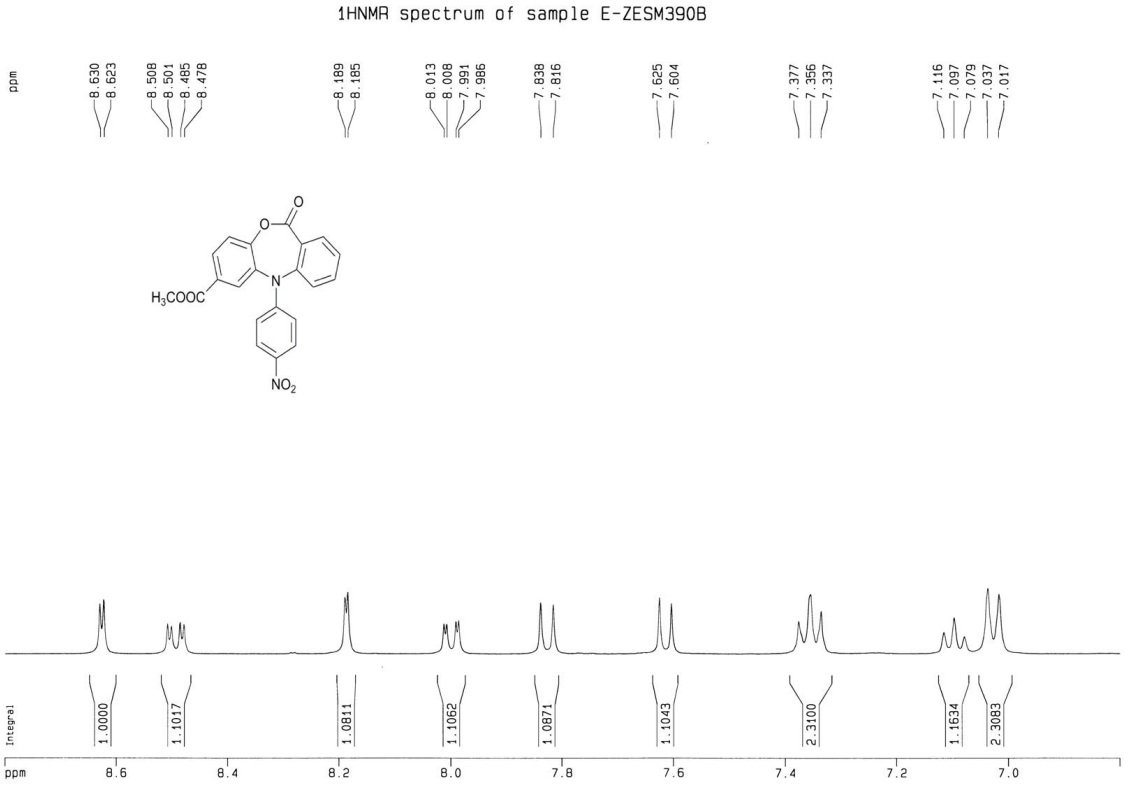




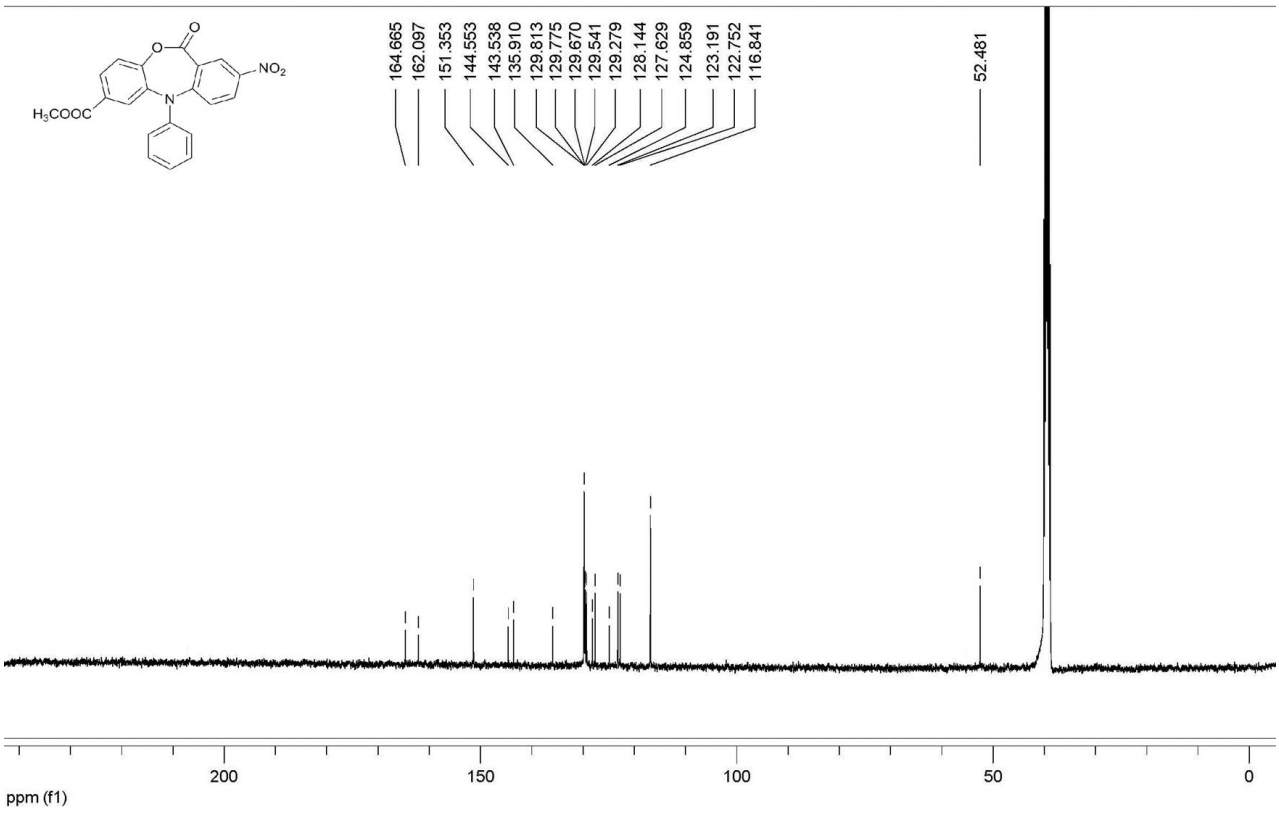
[^{1}H NMR and ^{13}C NMR spectrum of 4r in DMSO-d_6]



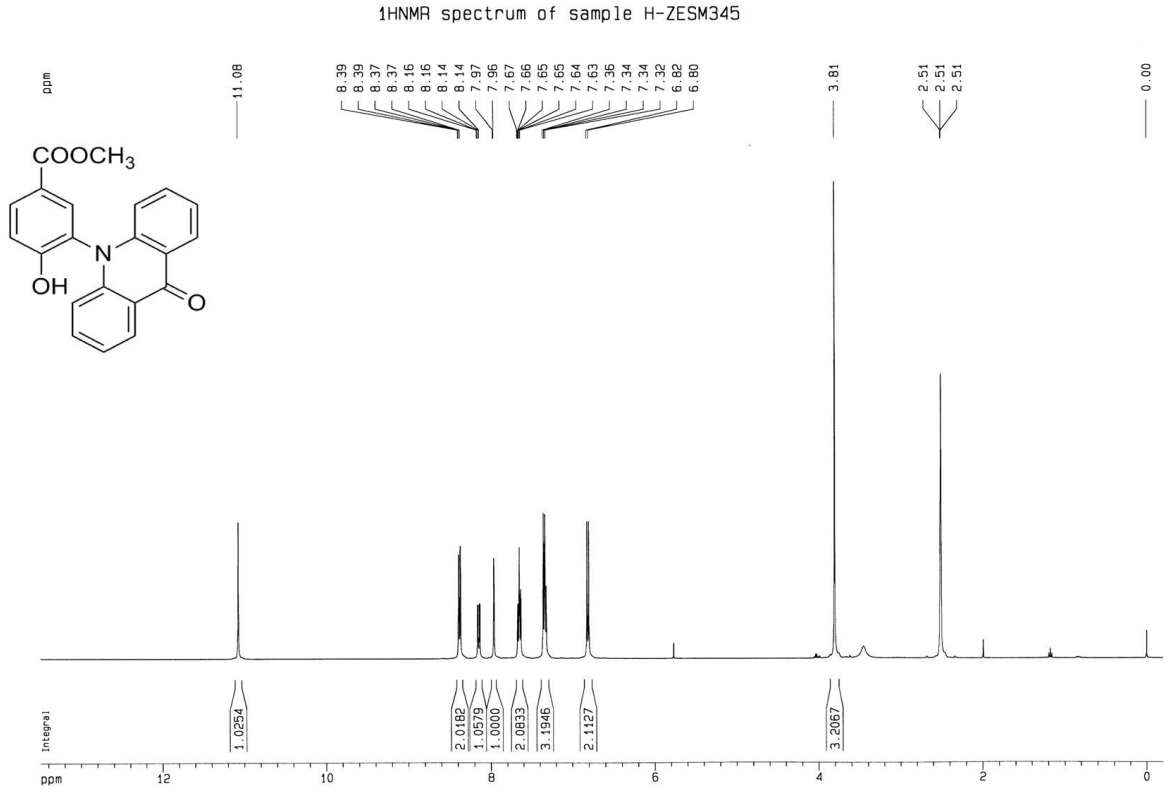
1HNMR spectrum of sample E-ZESM390B

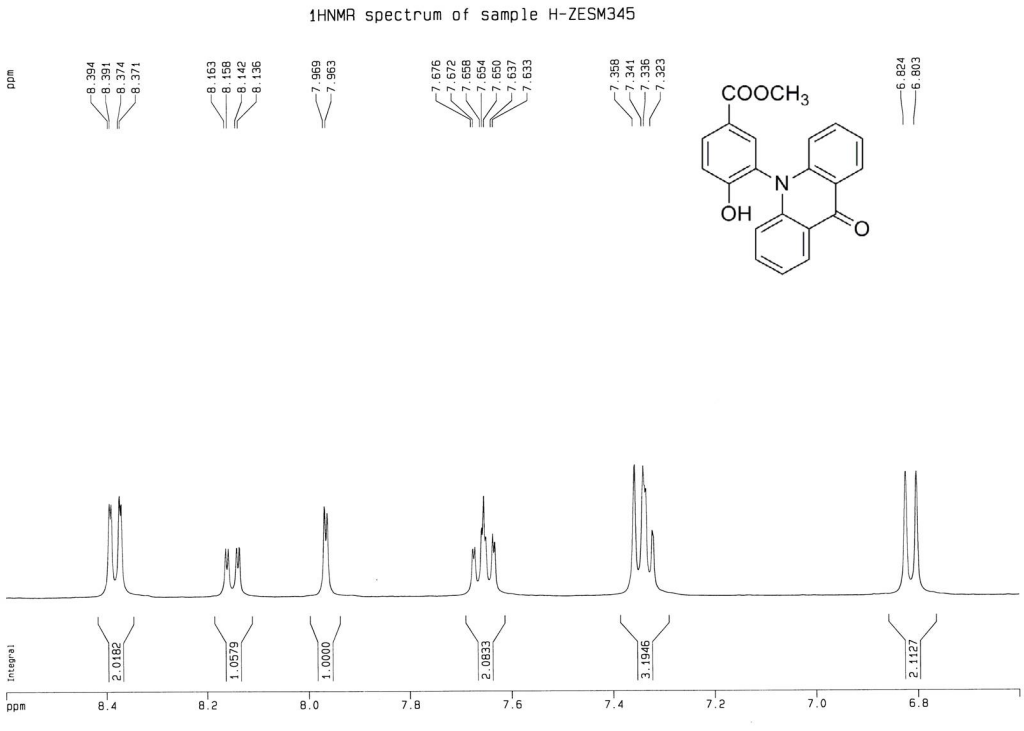


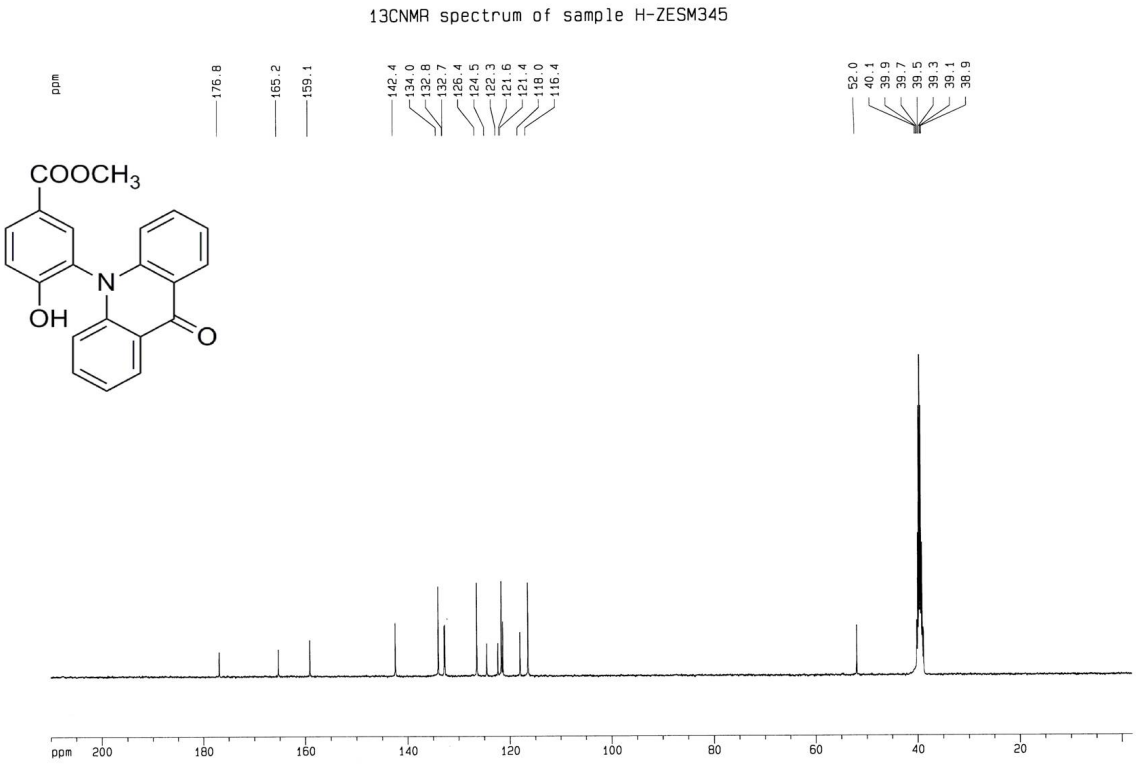
13CNMR Spectrum of sample E-ZESM390B



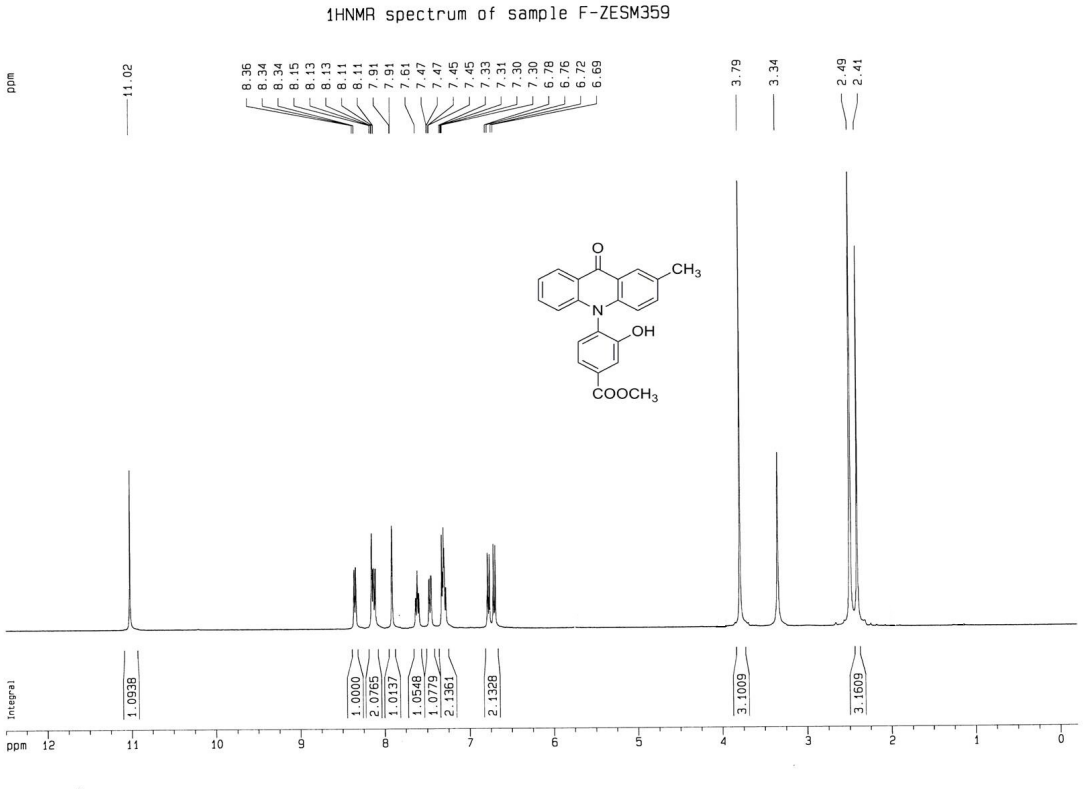
[^{1}H NMR and ^{13}C NMR spectrum of 5a in DMSO-d_6]



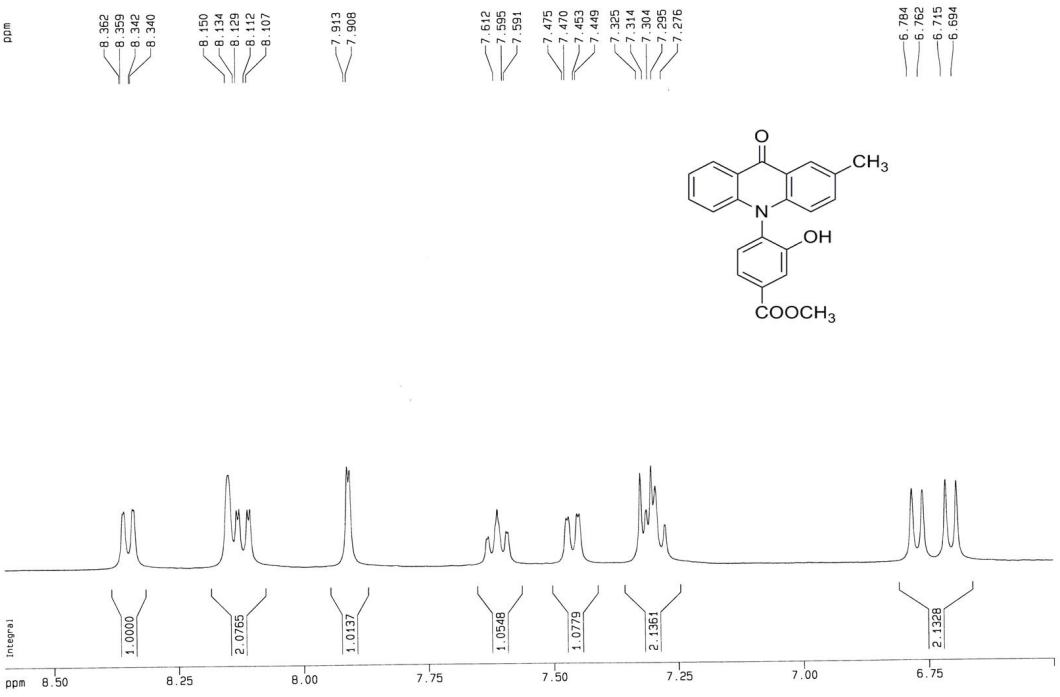




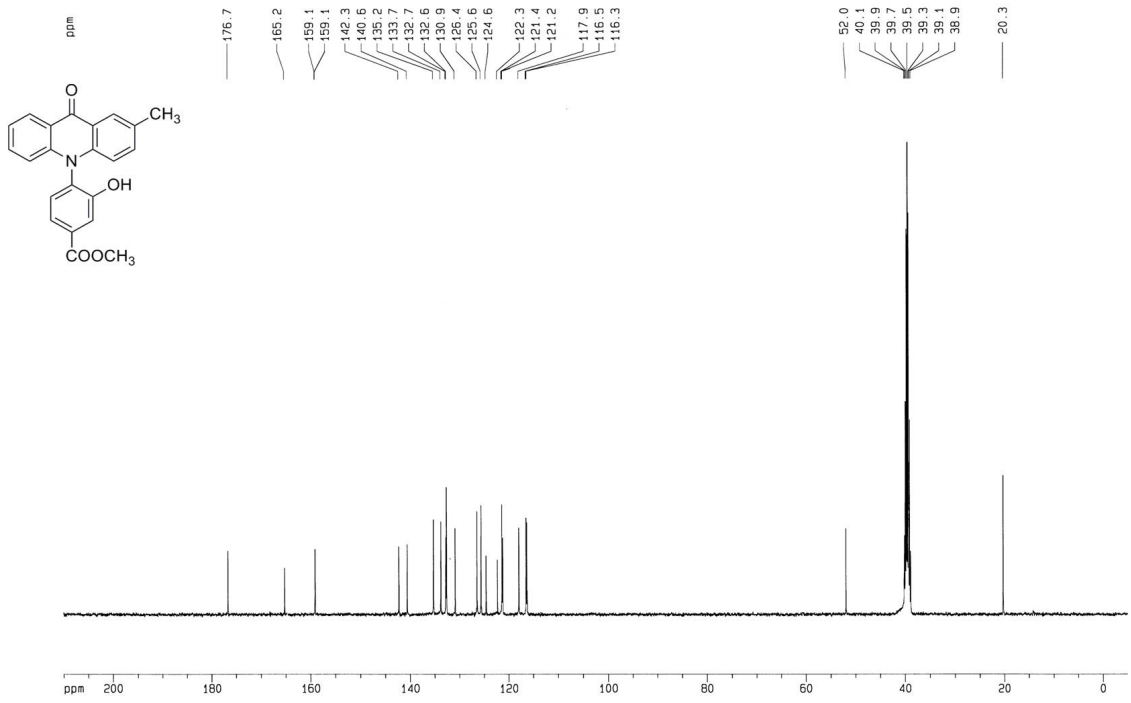
[^{1}H NMR and ^{13}C NMR spectrum of 5b in DMSO-d_6]



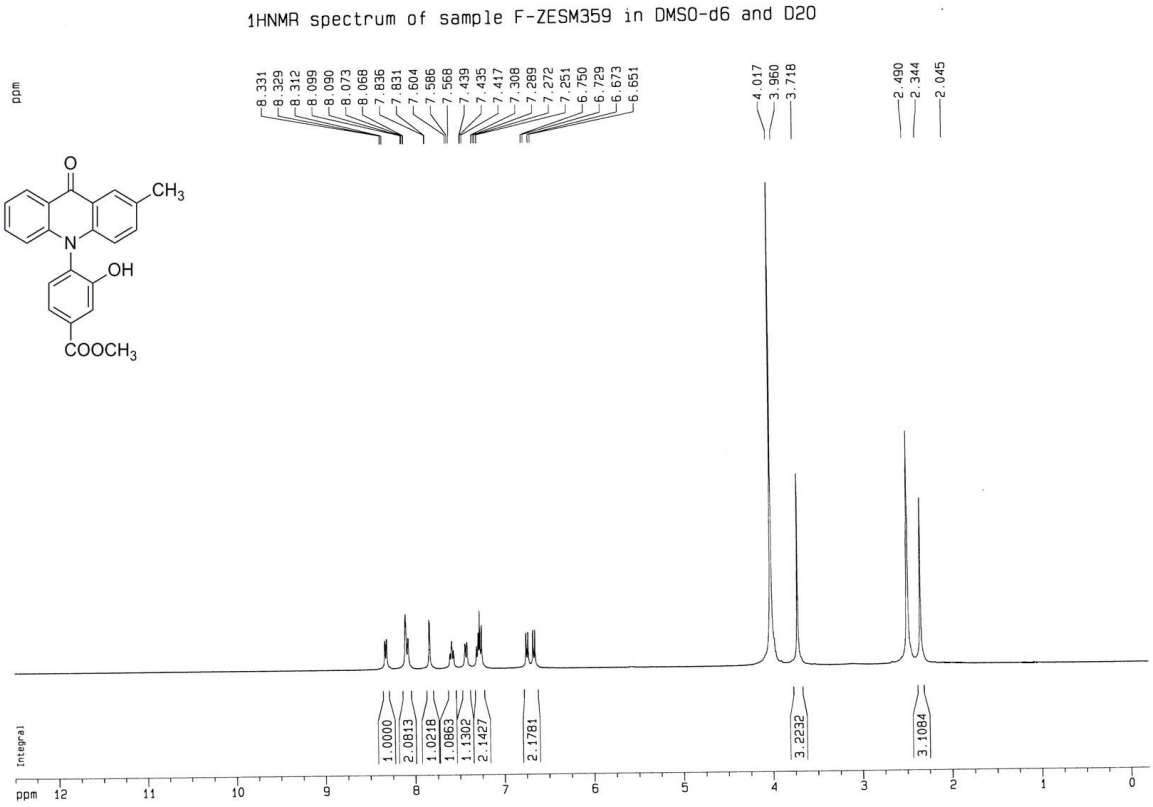
1HNMR spectrum of sample F-ZESM359

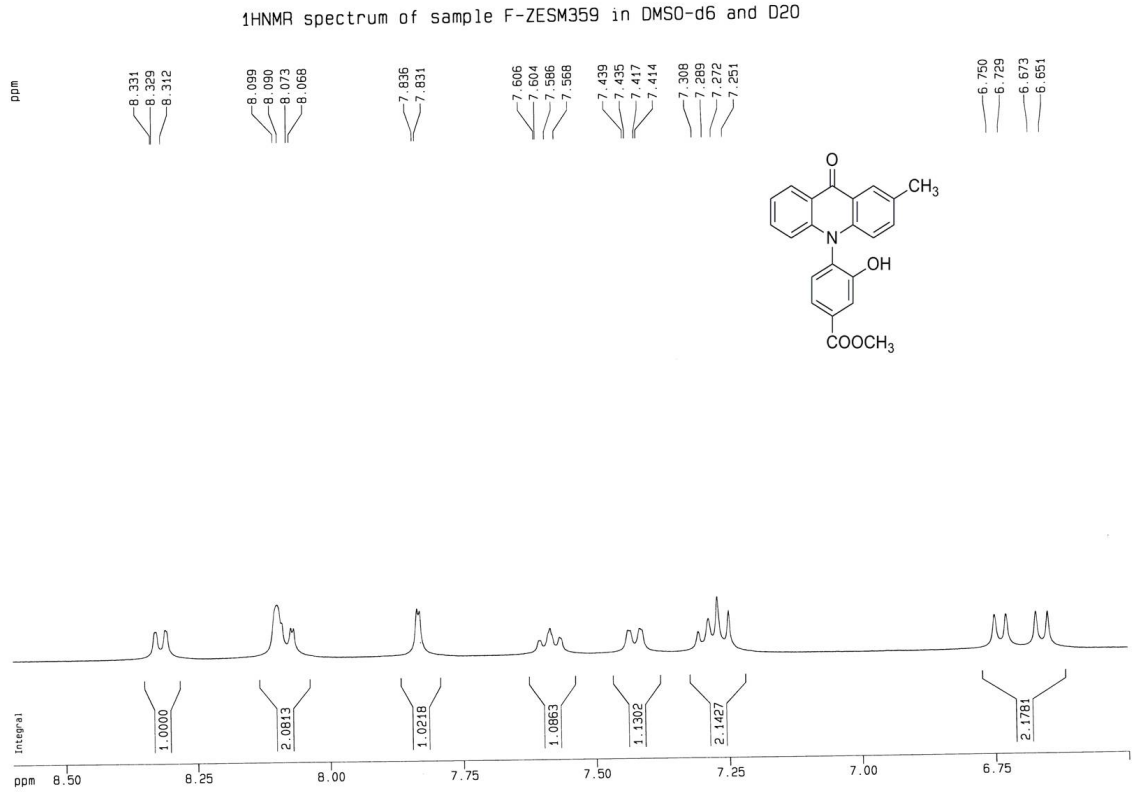


13CNMR spectrum of sample H-ZESPM359

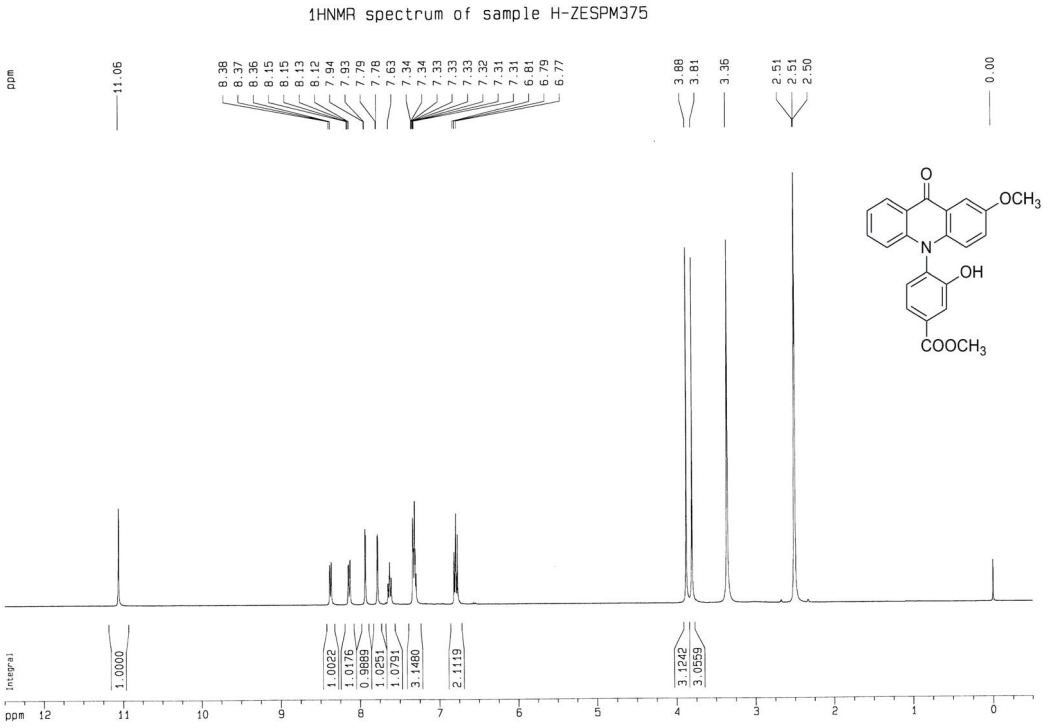


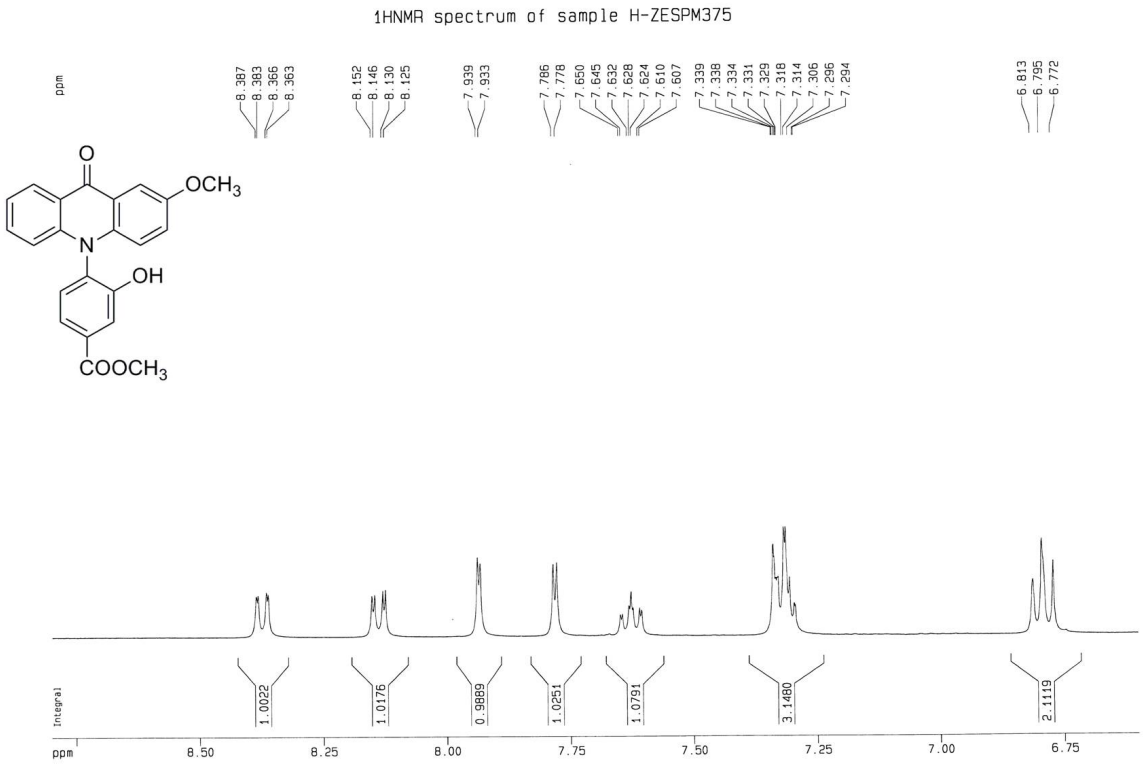
[^{1}H NMR and ^{13}C NMR spectrum of 5b in DMSO-d_6 and D_2O]

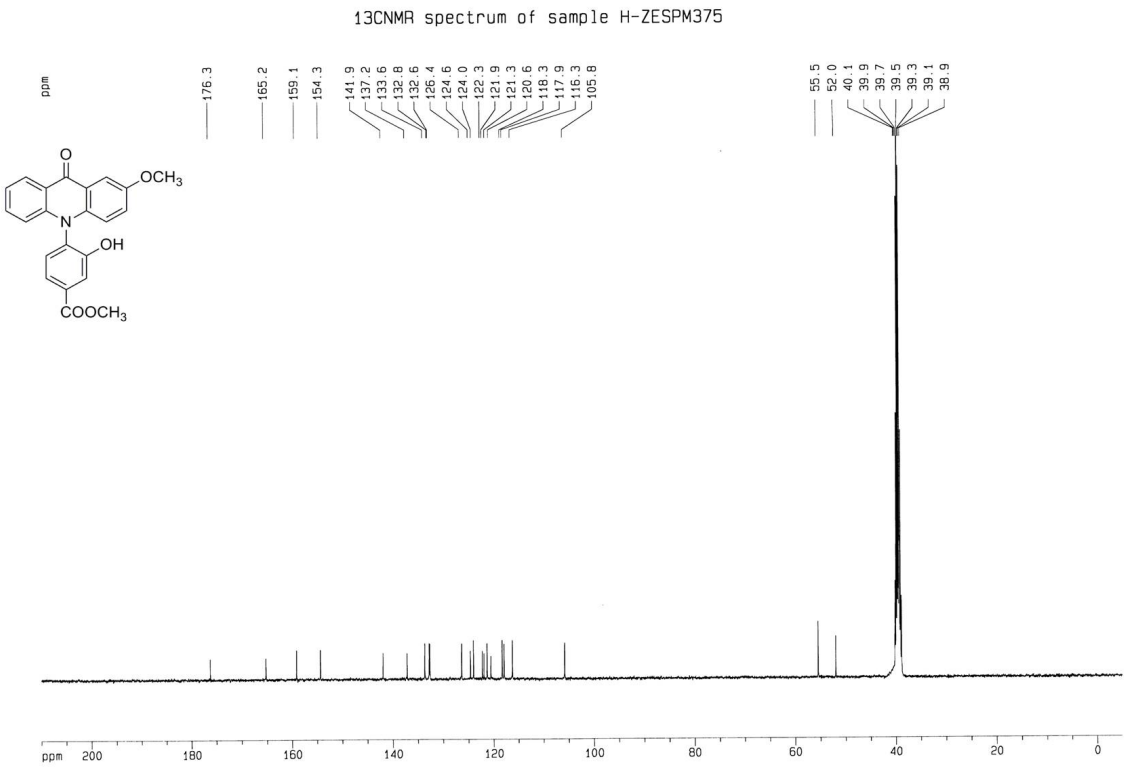




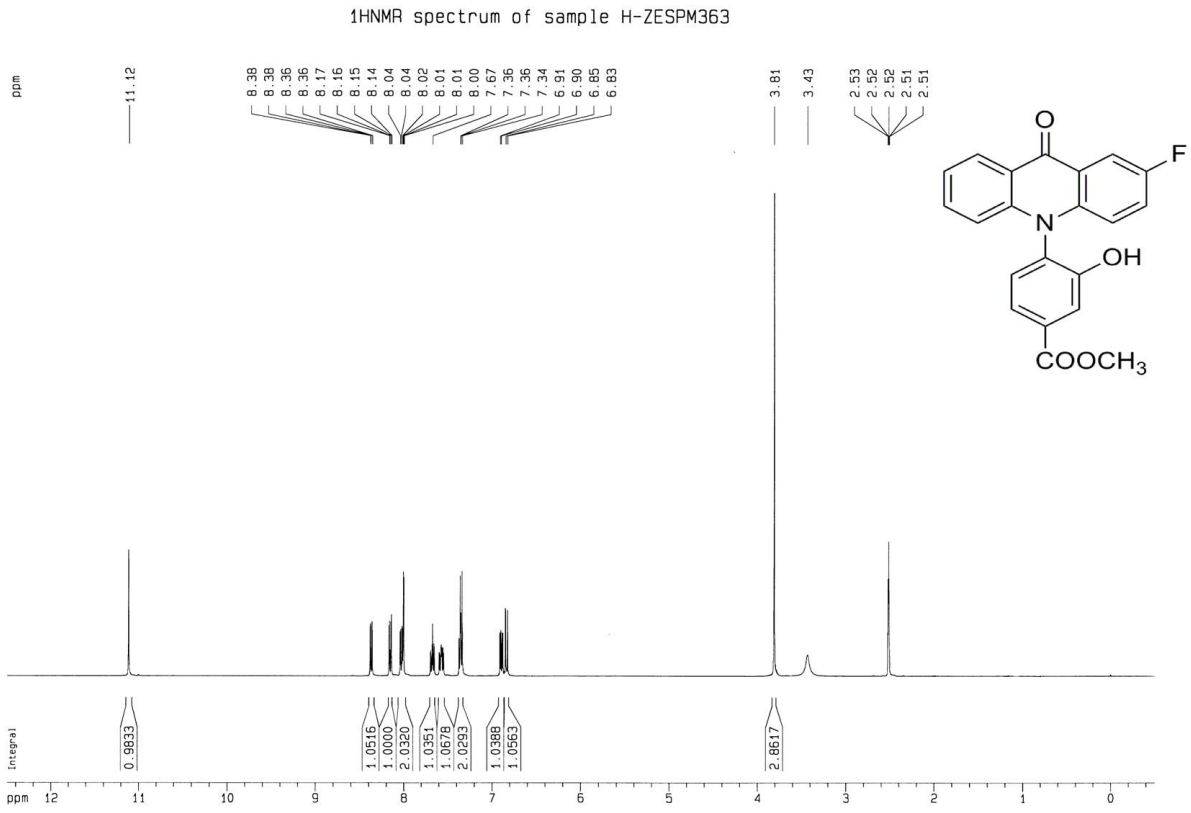
[^{1}H NMR and ^{13}C NMR spectrum of 5c in DMSO-d_6]



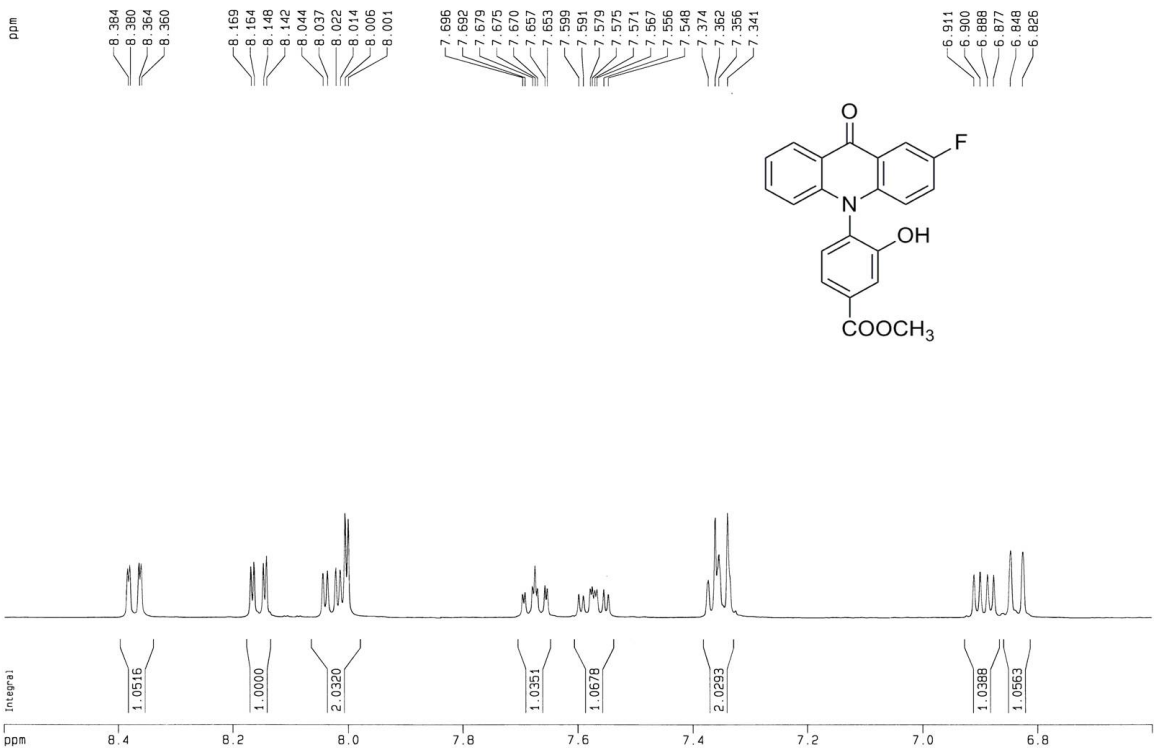




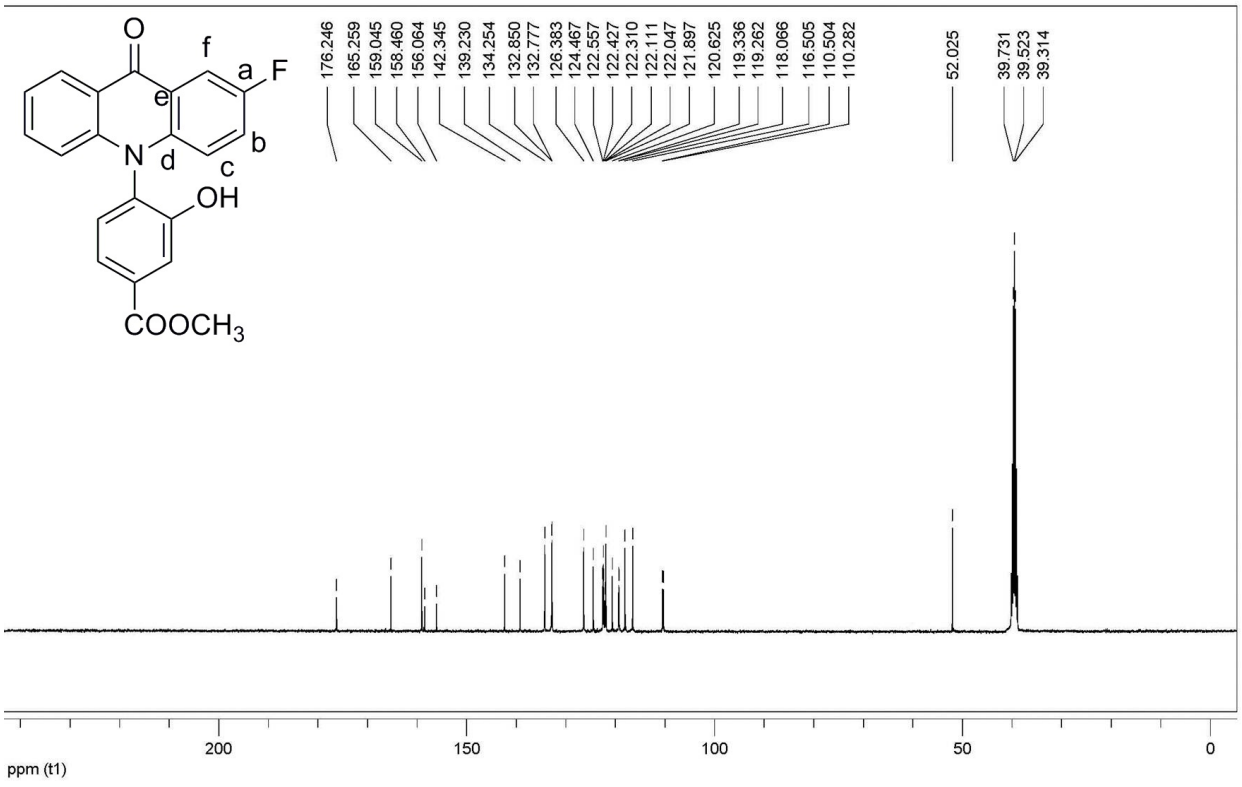
[^{1}H NMR and ^{13}C NMR spectrum of 5d in DMSO-d_6]



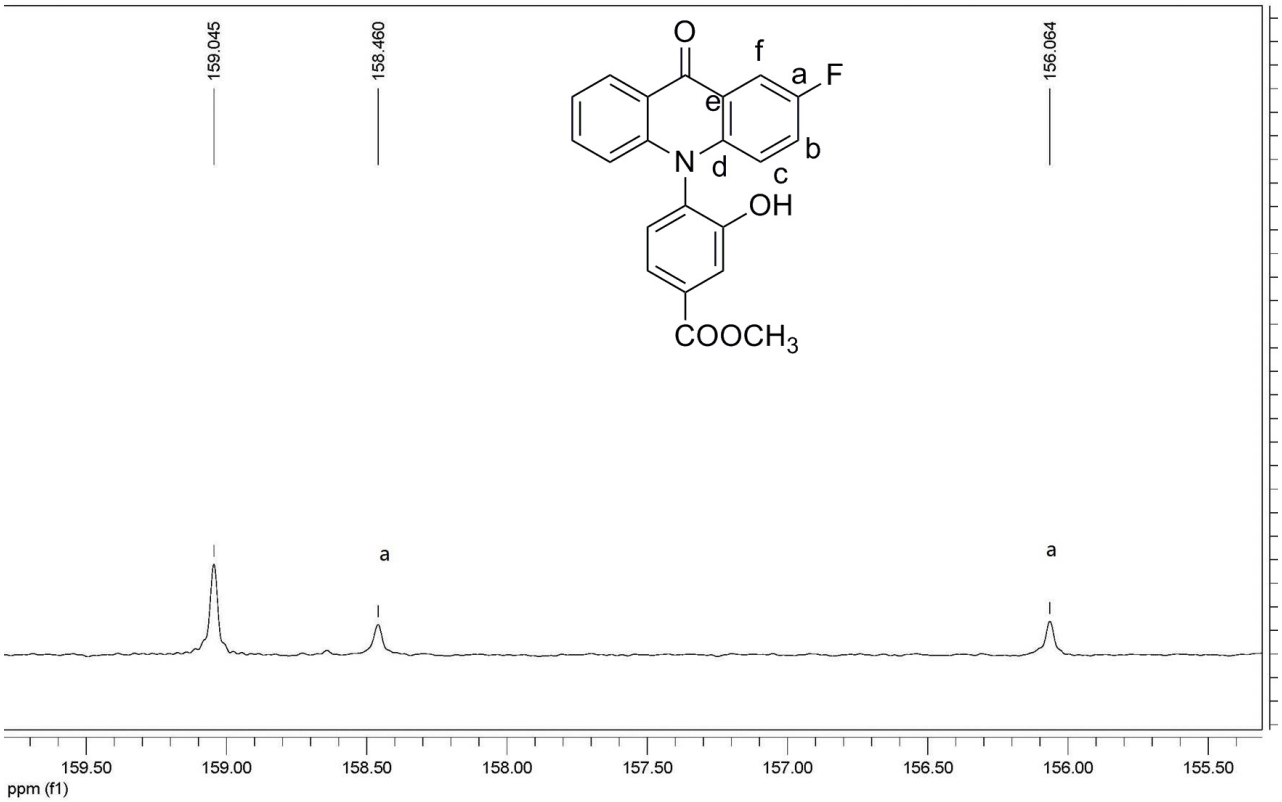
1HNMR spectrum of sample H-ZESPM363



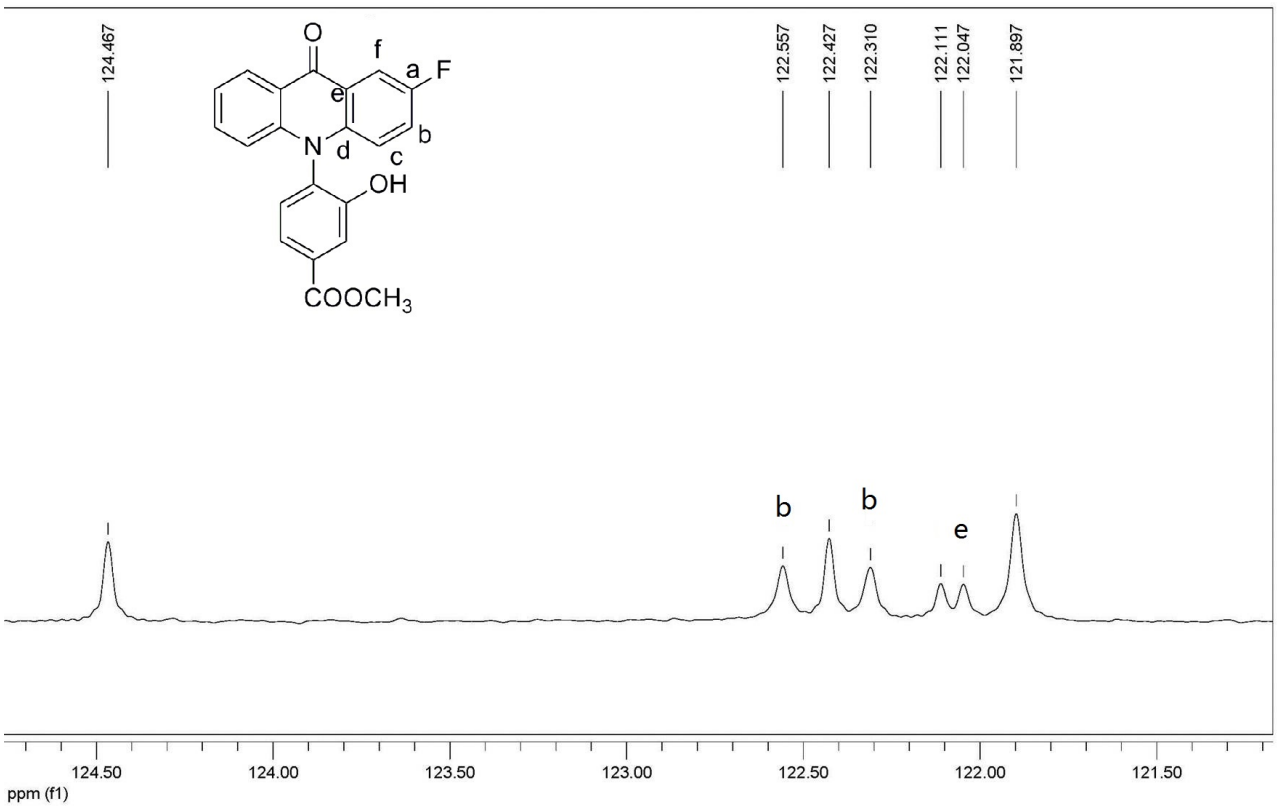
13CNMR spectrum of sample H-ZESPM363



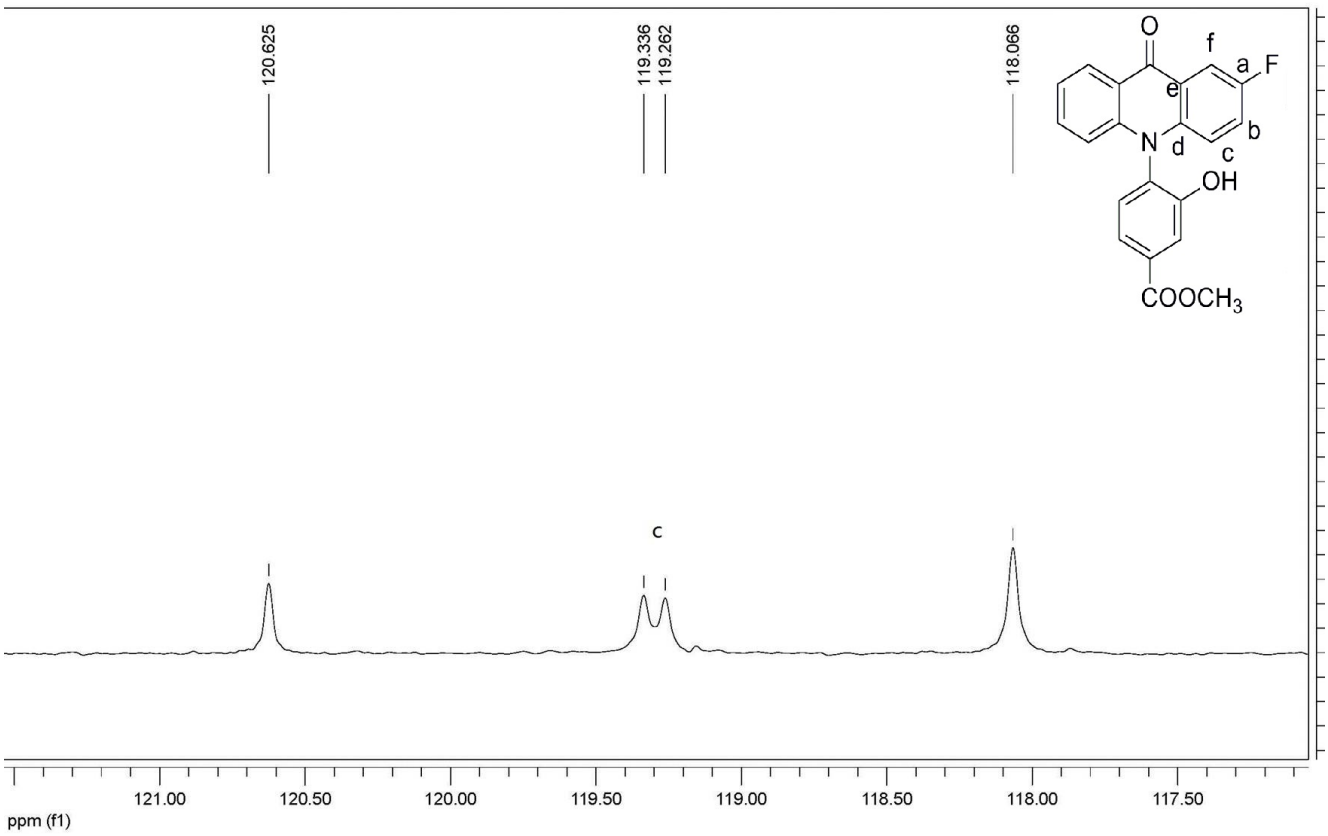
13CNMR spectrum of sample H-ZESPM363



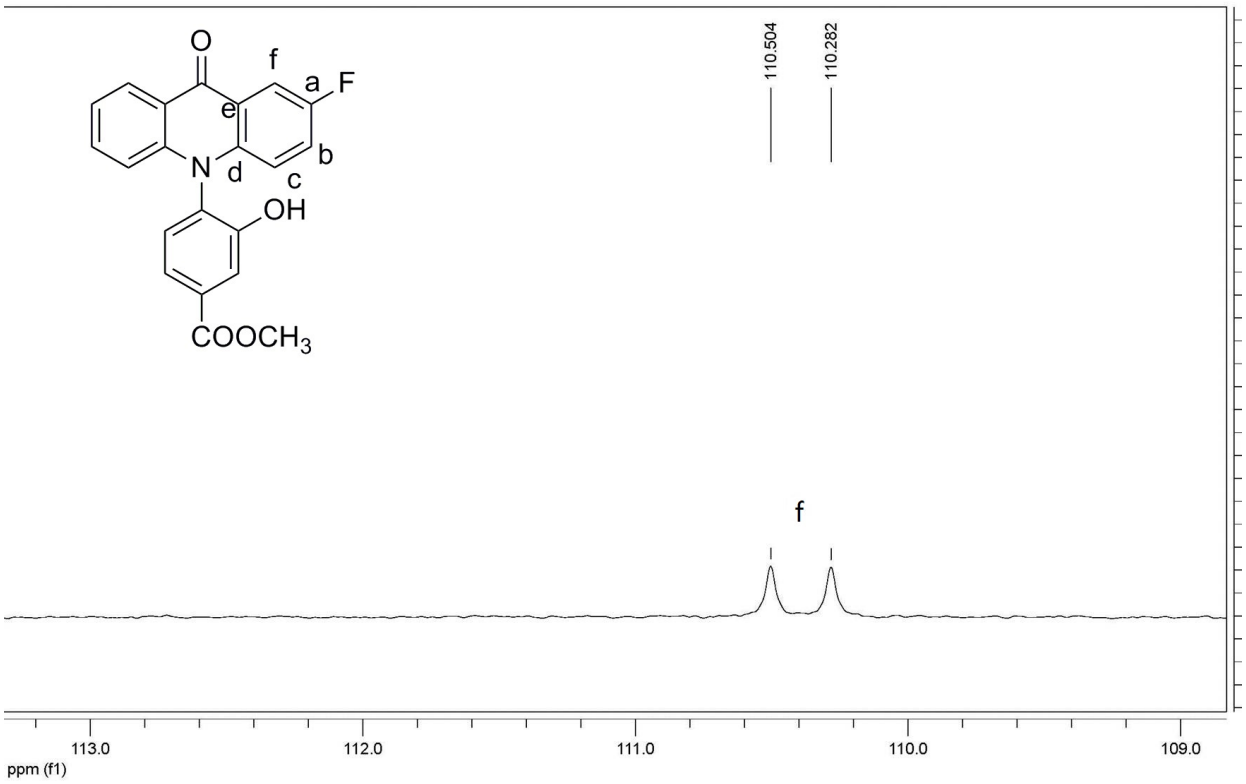
13CNMR spectrum of sample H-ZESPM363



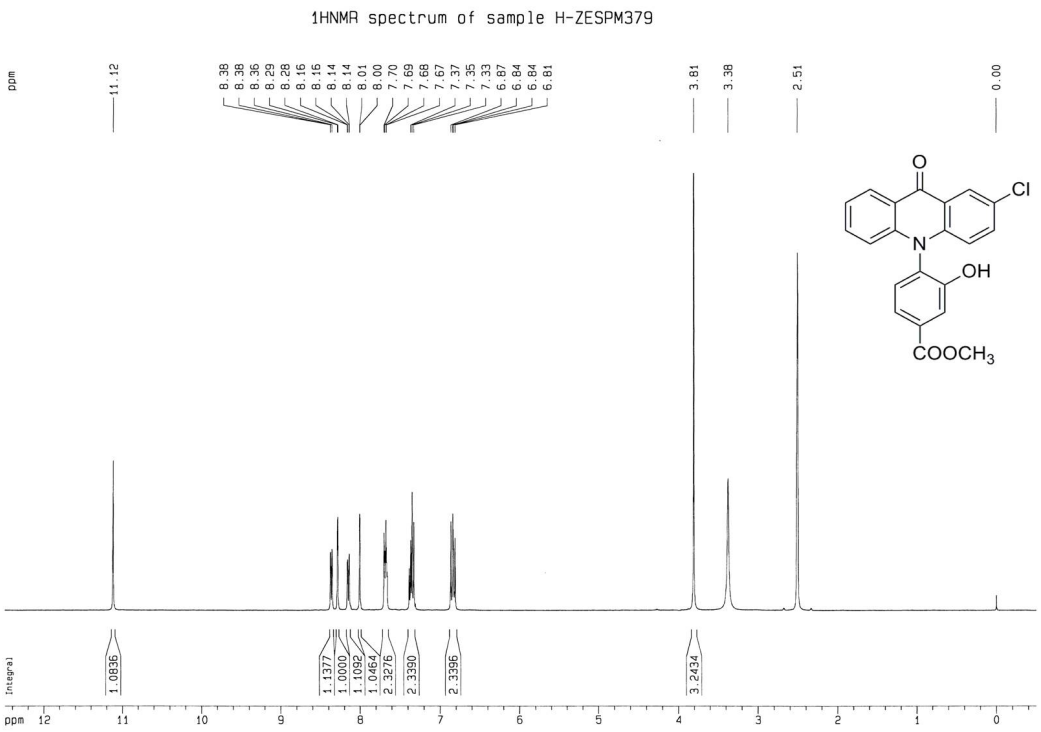
13CNMR spectrum of sample H-ZESPM363

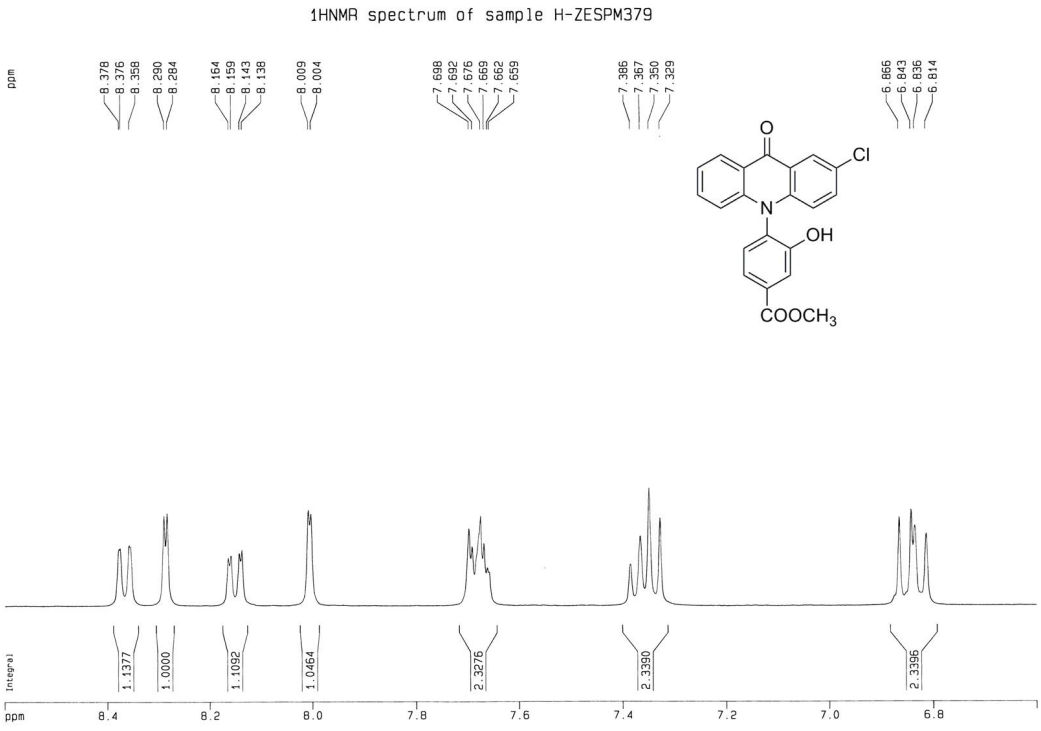


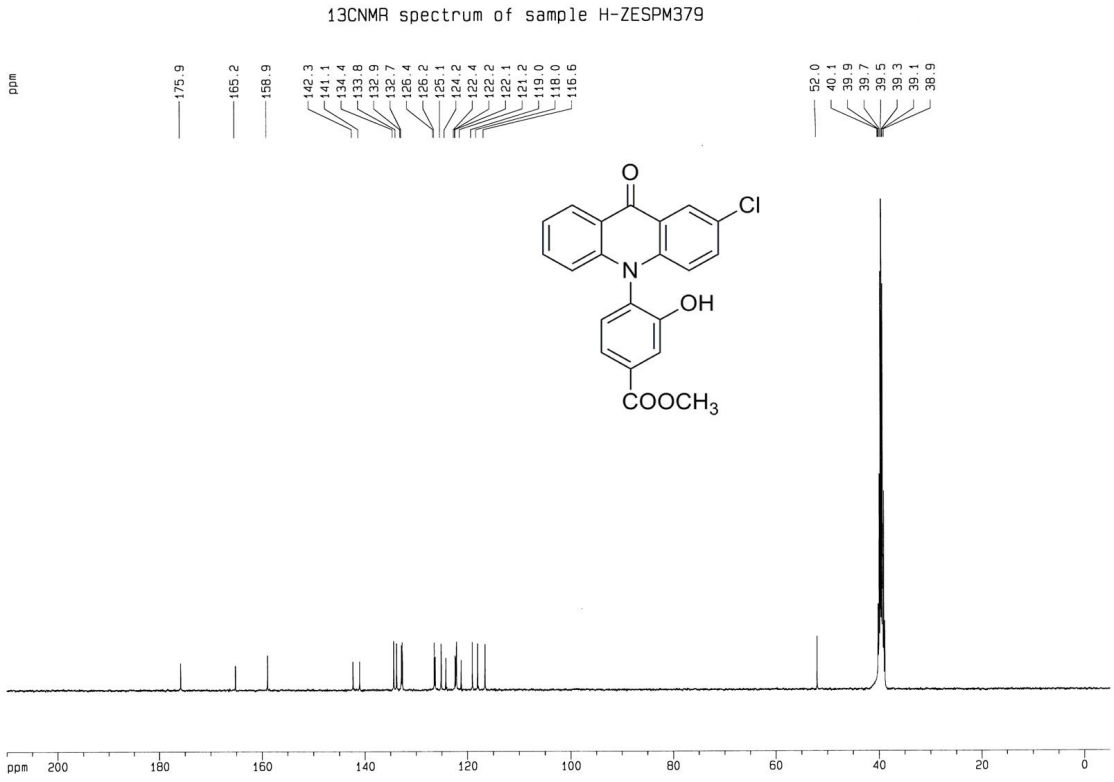
13CNMR spectrum of sample H-ZESPM363



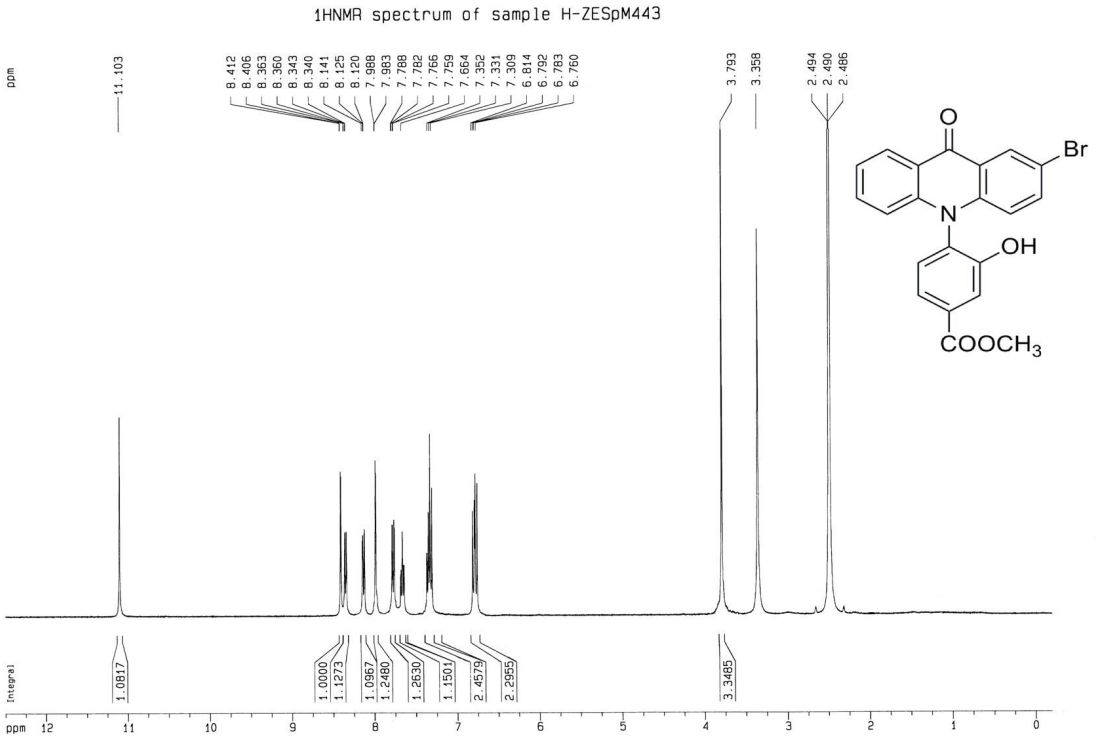
[^{1}H NMR and ^{13}C NMR spectrum of 5e in DMSO-d_6]



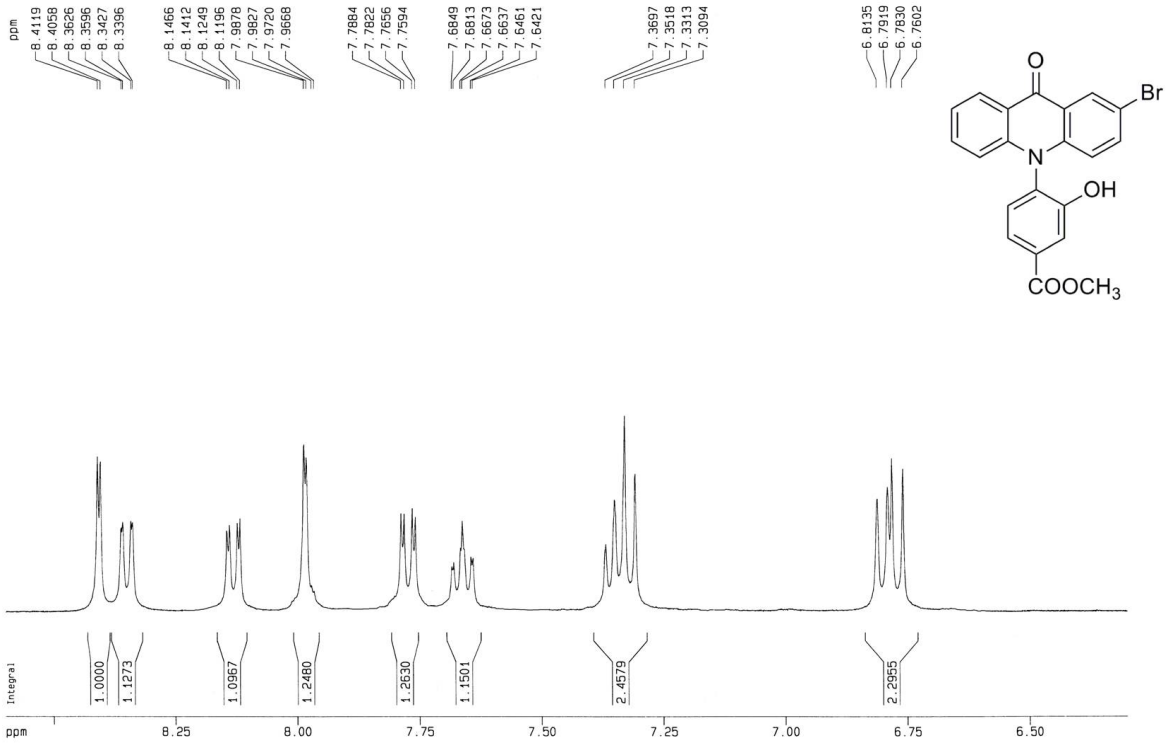




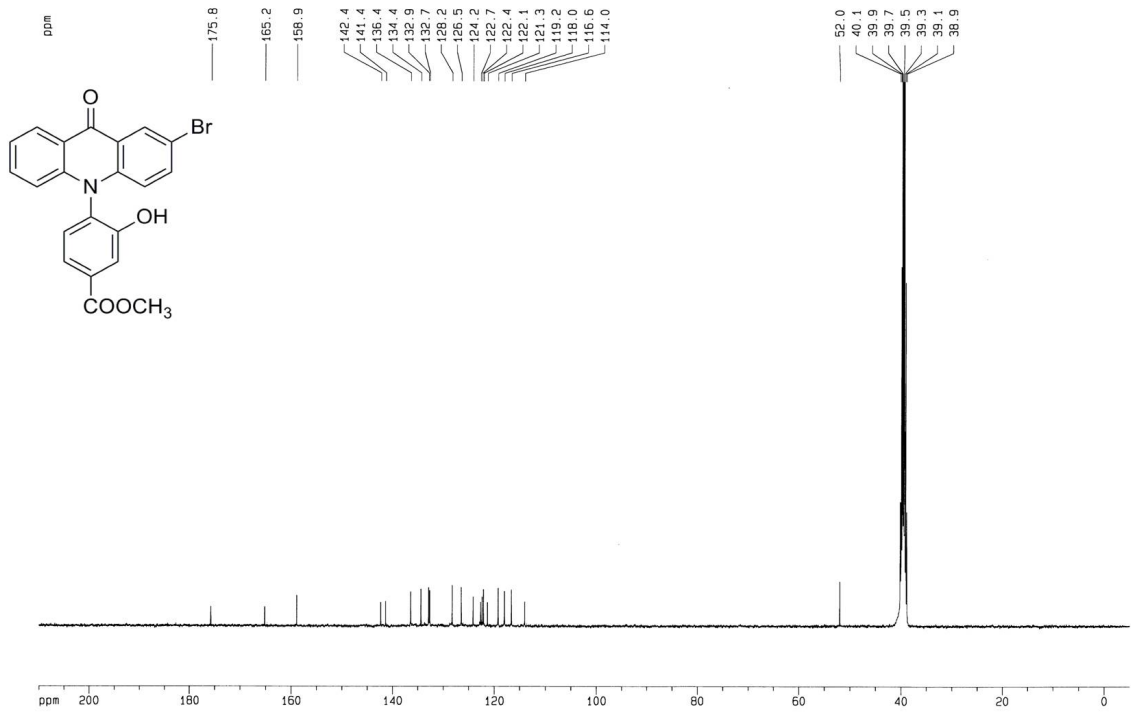
[^{1}H NMR and ^{13}C NMR spectrum of 5f in DMSO-d_6]



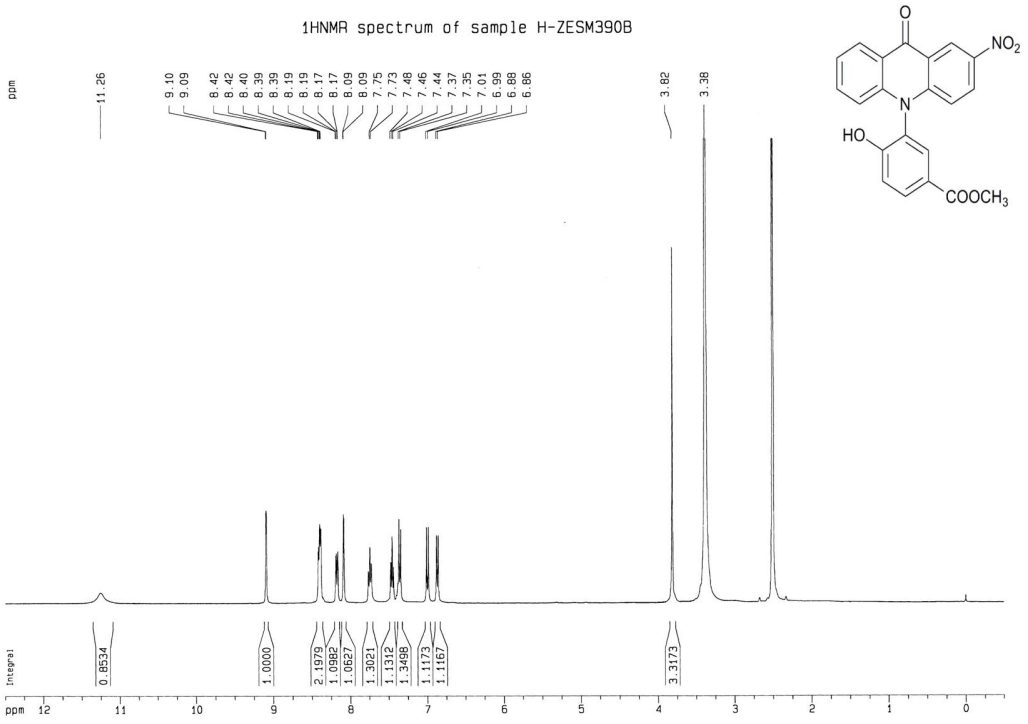
1HNMR spectrum of sample H-ZESpM443

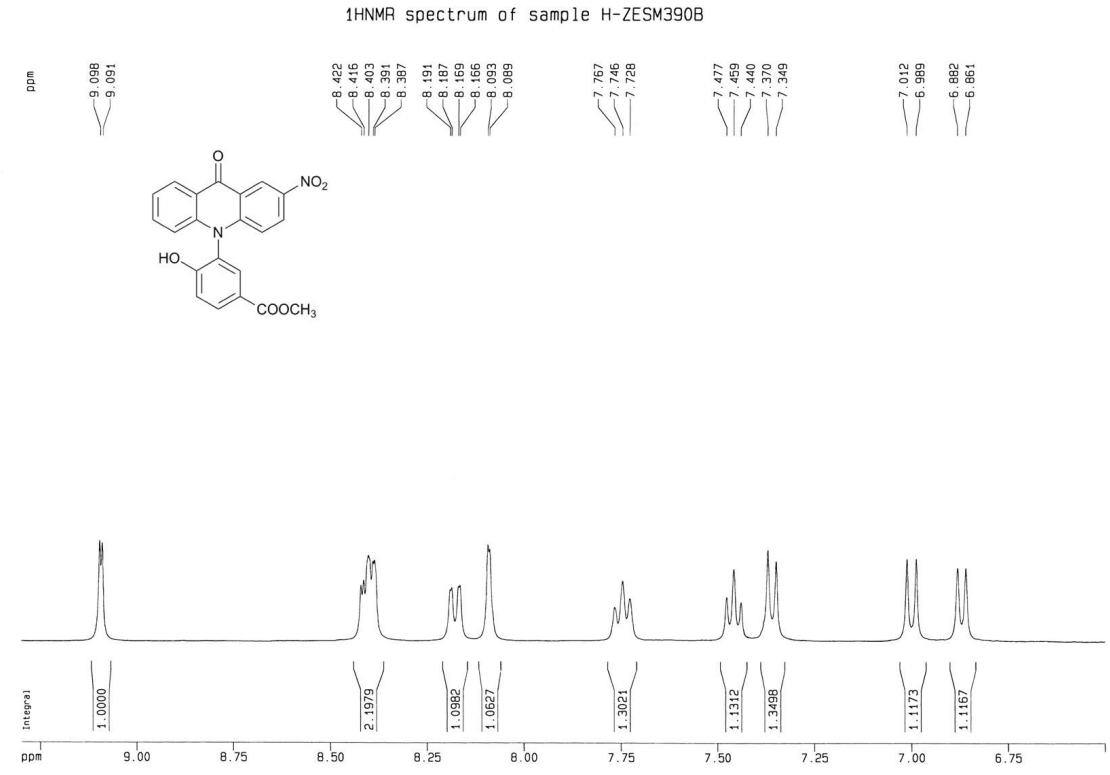


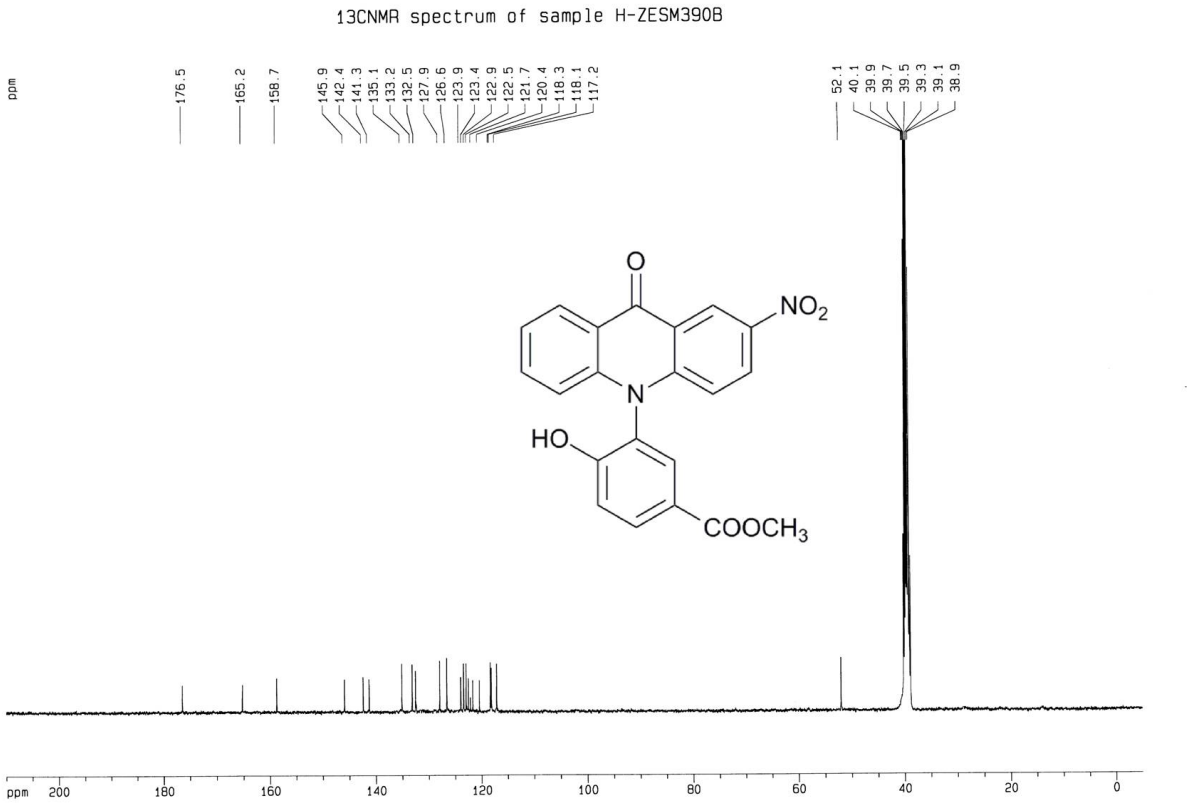
13CNMR spectrum of sample H-ZESPM423



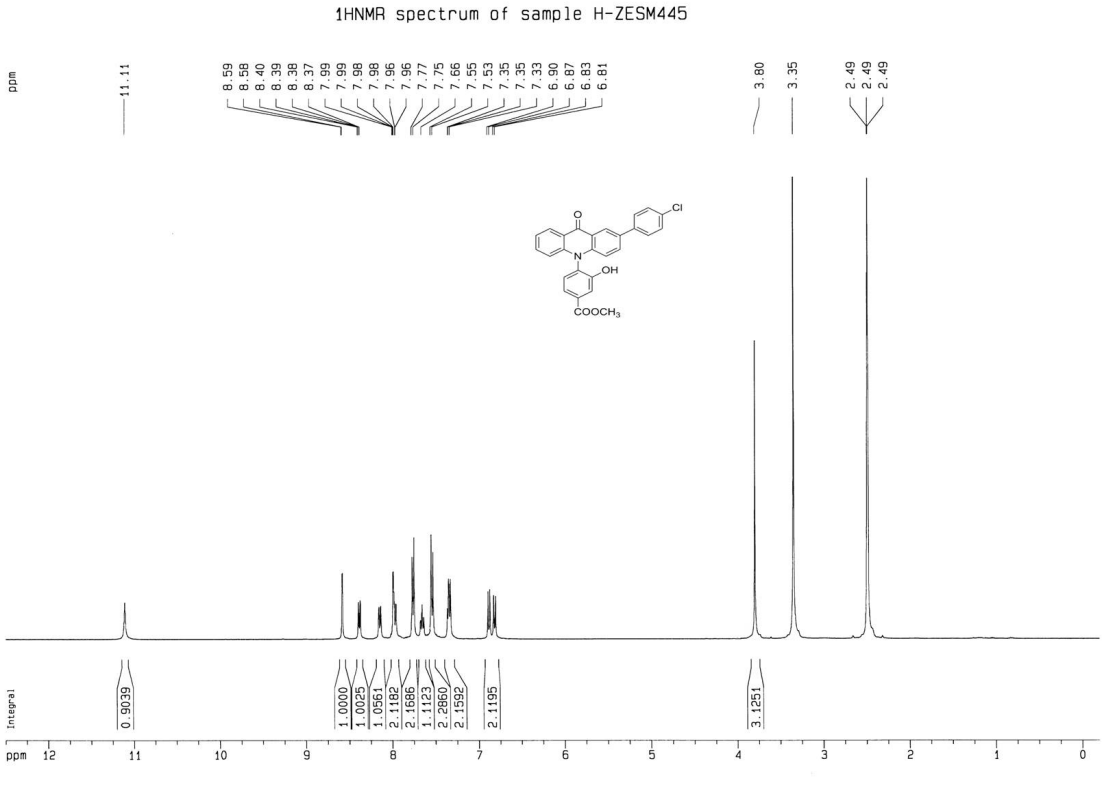
[^{1}H NMR and ^{13}C NMR spectrum of 5h in DMSO-d_6]



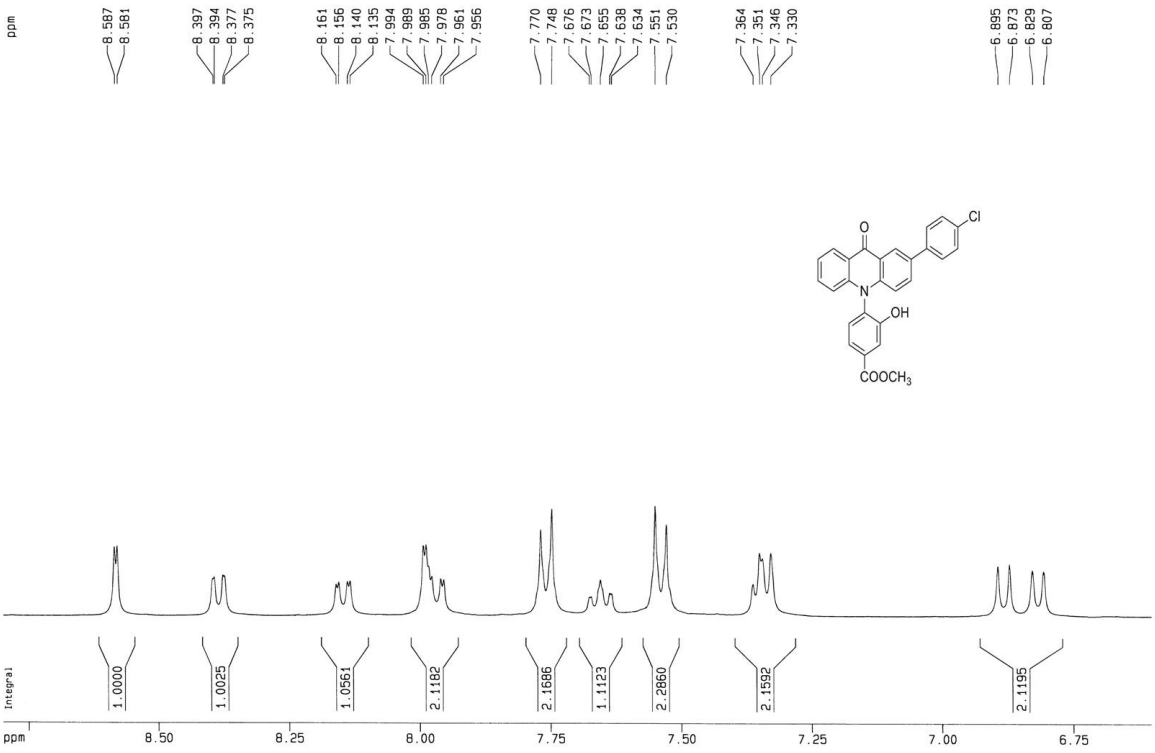




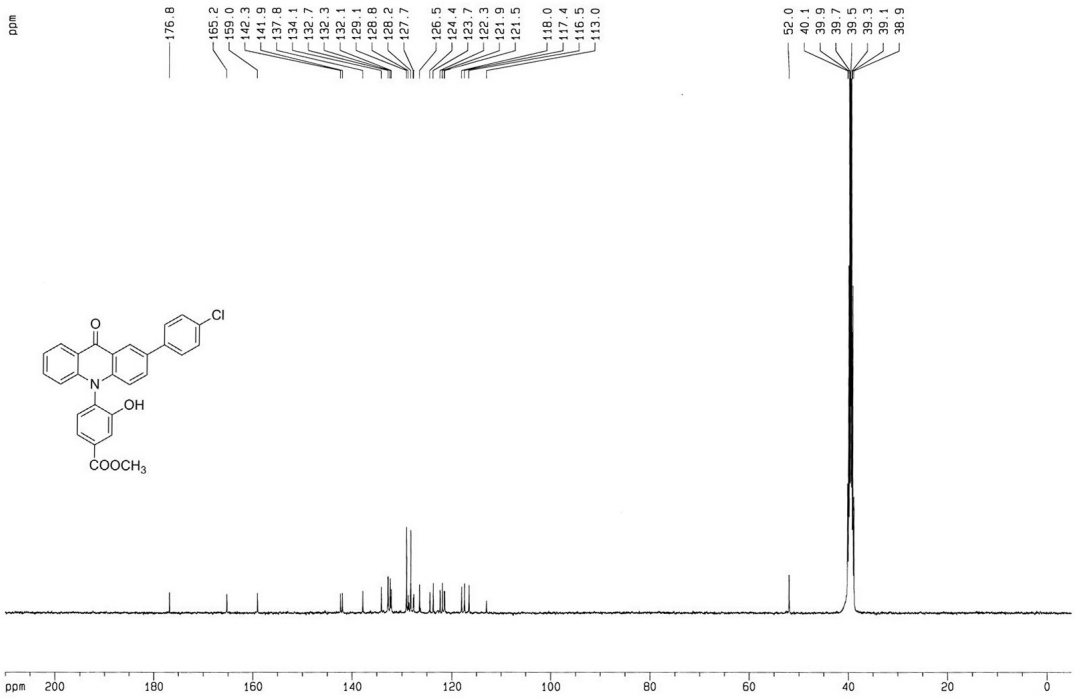
[^{1}H NMR and ^{13}C NMR spectrum of 5p in DMSO-d_6]



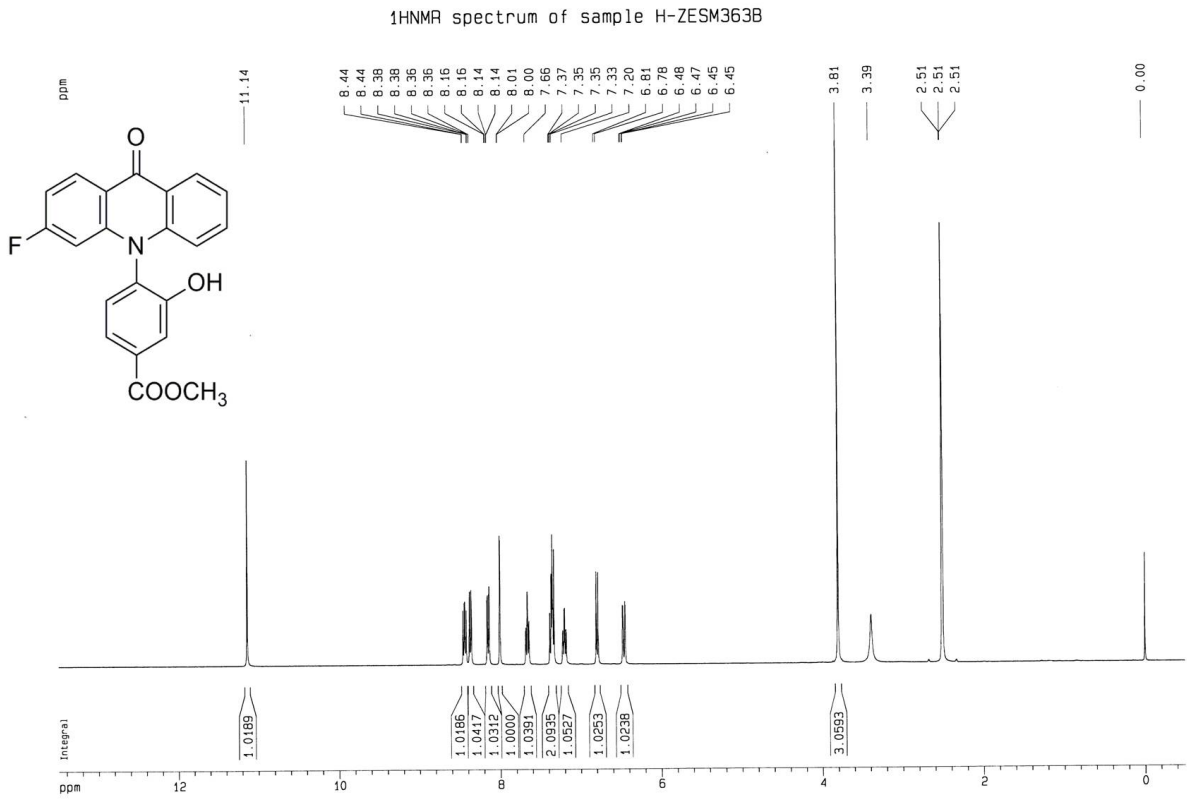
1HNMR spectrum of sample H-ZESM445

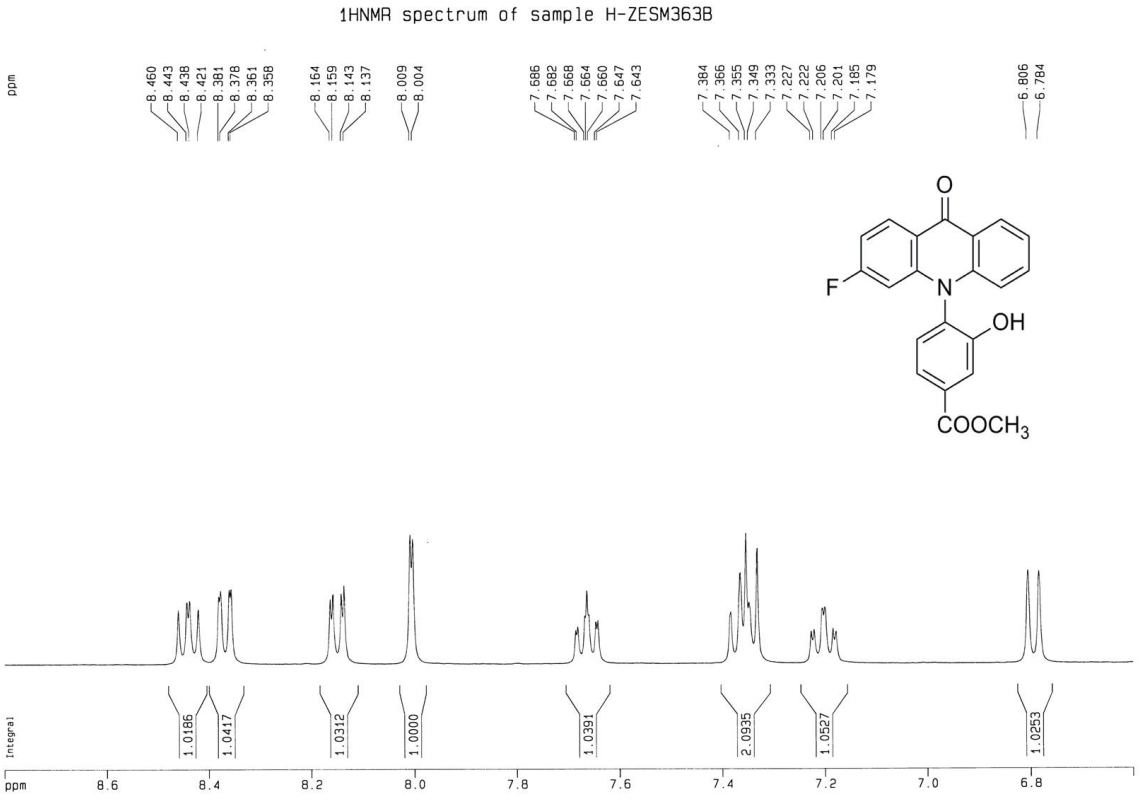


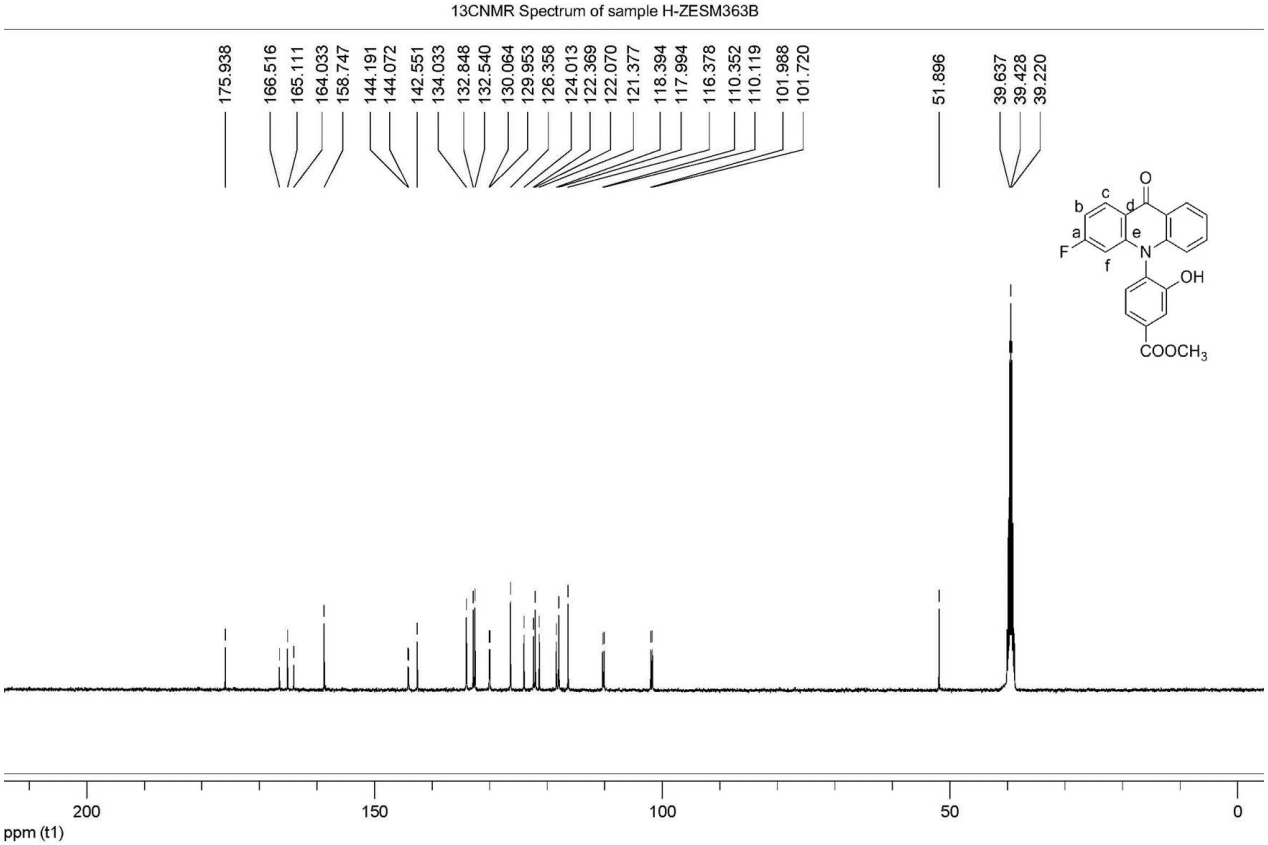
13CNMR spectrum of sample H-ZESM445

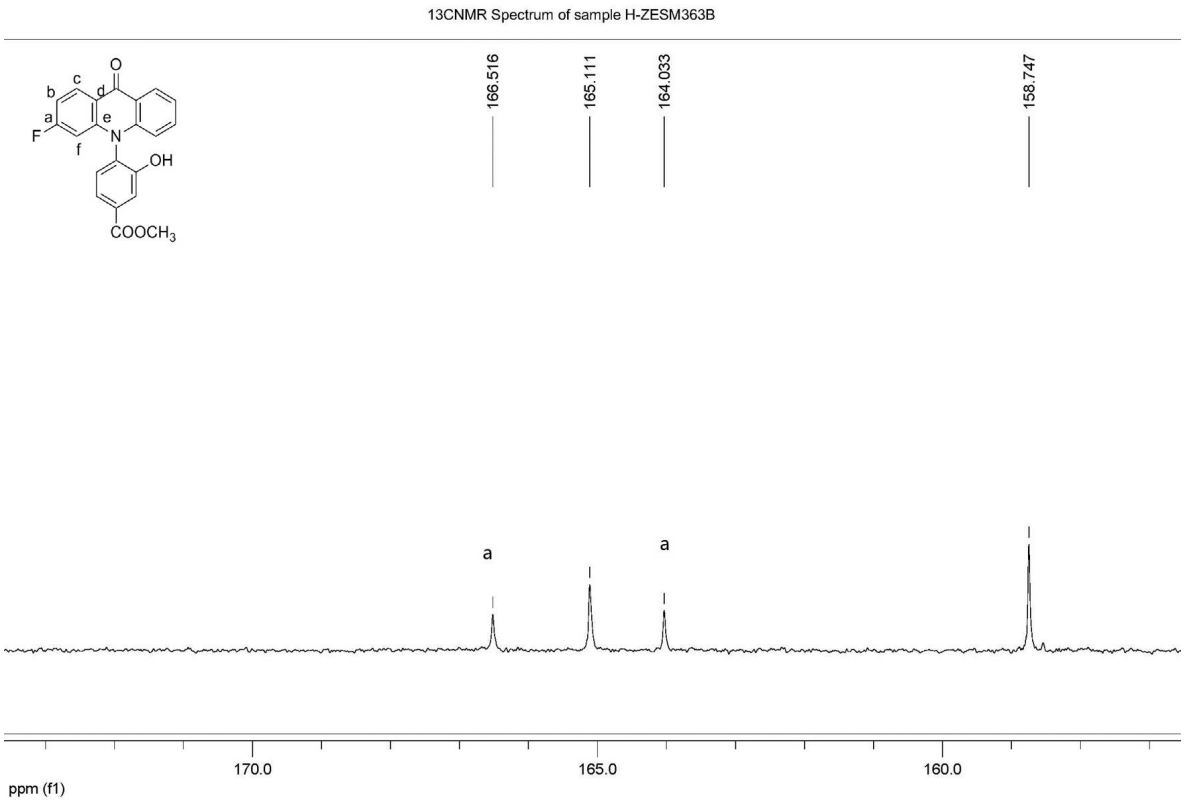


[^{1}H NMR and ^{13}C NMR spectrum of 5q in DMSO-d_6]

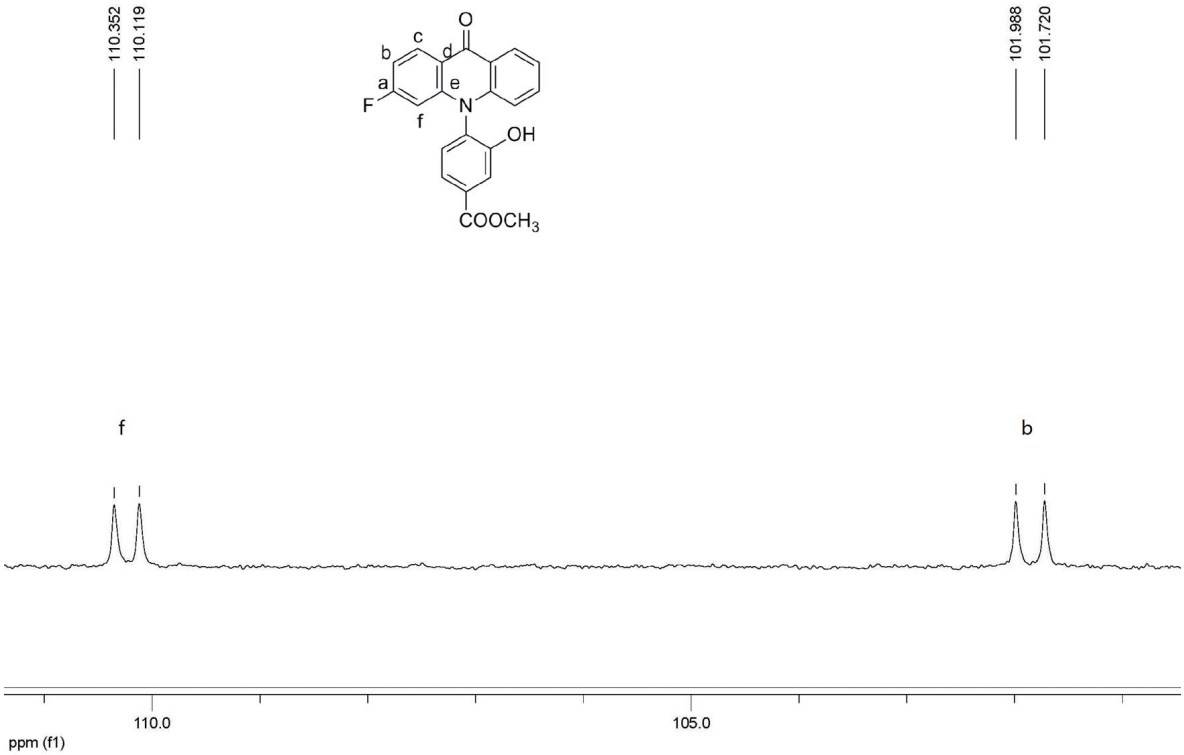




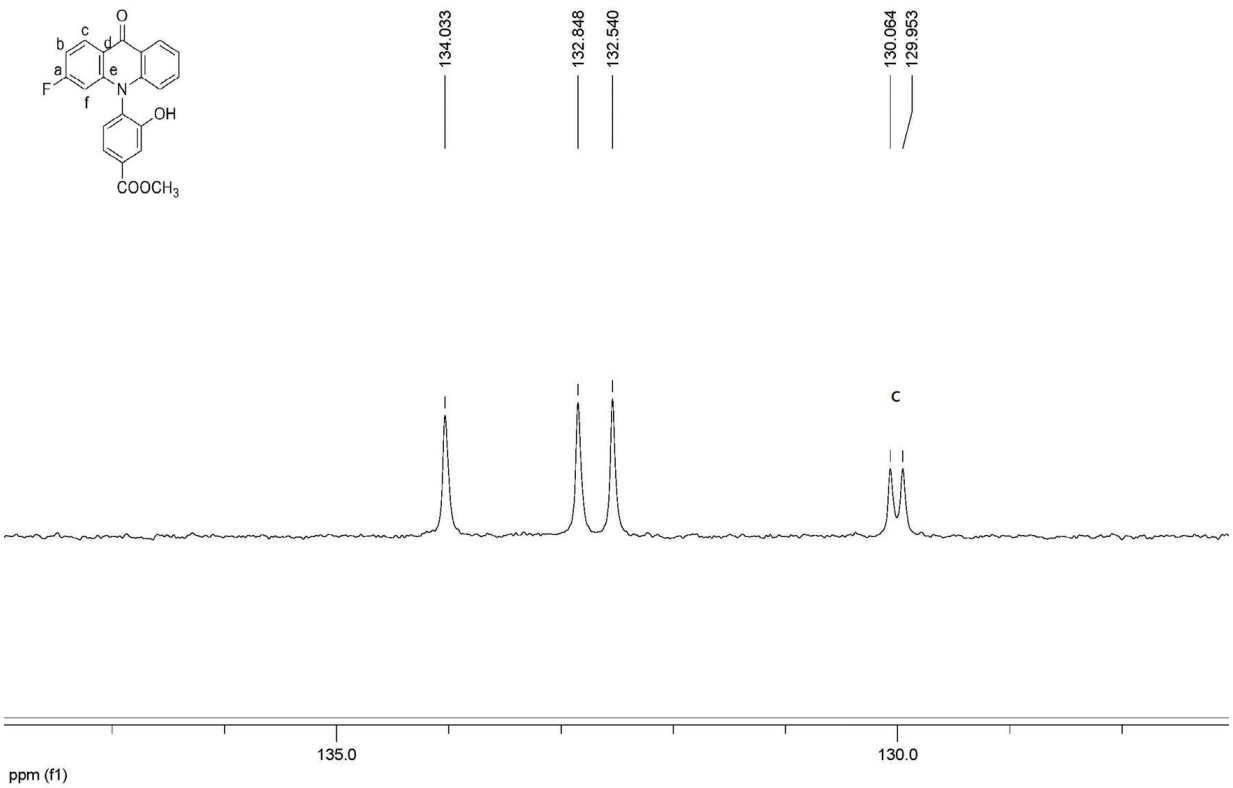

13CNMR Spectrum of sample H-ZESM363B
175.938
166.516
165.111
164.033
158.747
144.191
144.072
142.551
134.033
132.848
132.540
130.064
129.953
126.358
124.013
122.369
122.070
121.377
118.394
117.994
116.378
110.352
110.119
101.988
101.720
51.896
39.637
39.428
39.220
200
150
100
50
0
ppm (t1)

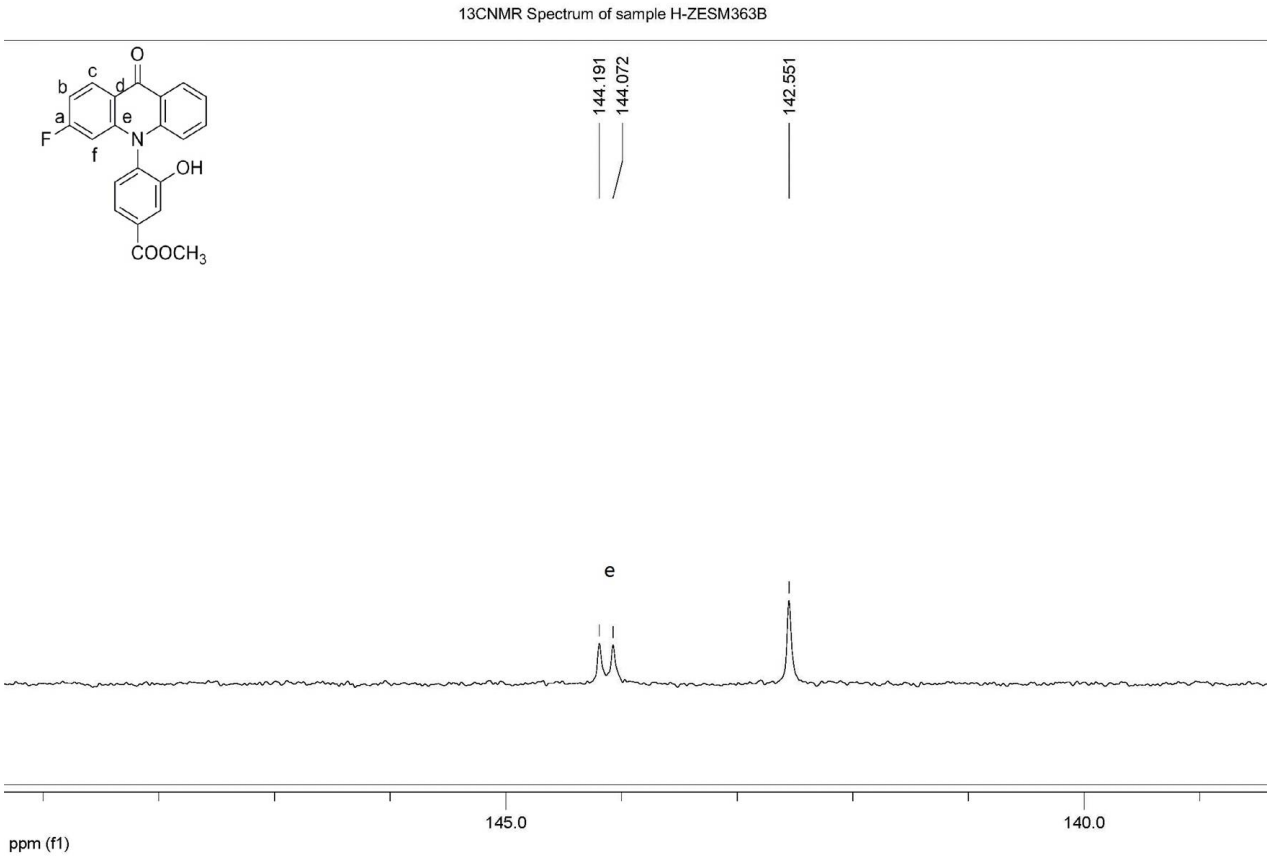

13CNMR Spectrum of sample H-ZESM363B
166.516
165.111
164.033
158.747
a
a
170.0
165.0
160.0
ppm (f1)

13CNMR Spectrum of sample H-ZESM363B

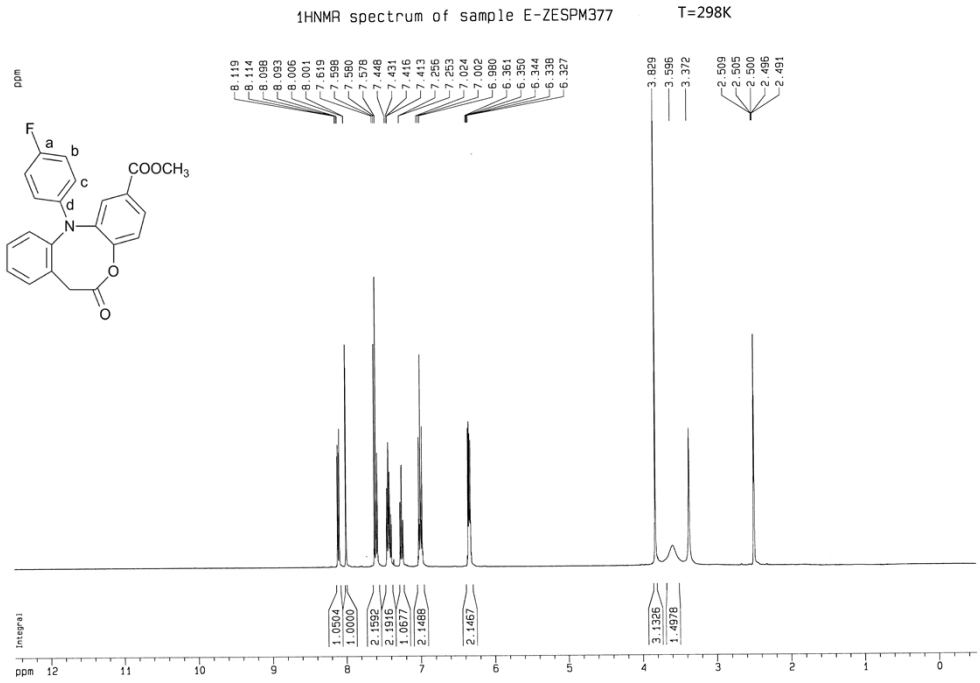


13CNMR Spectrum of sample H-ZESM363B

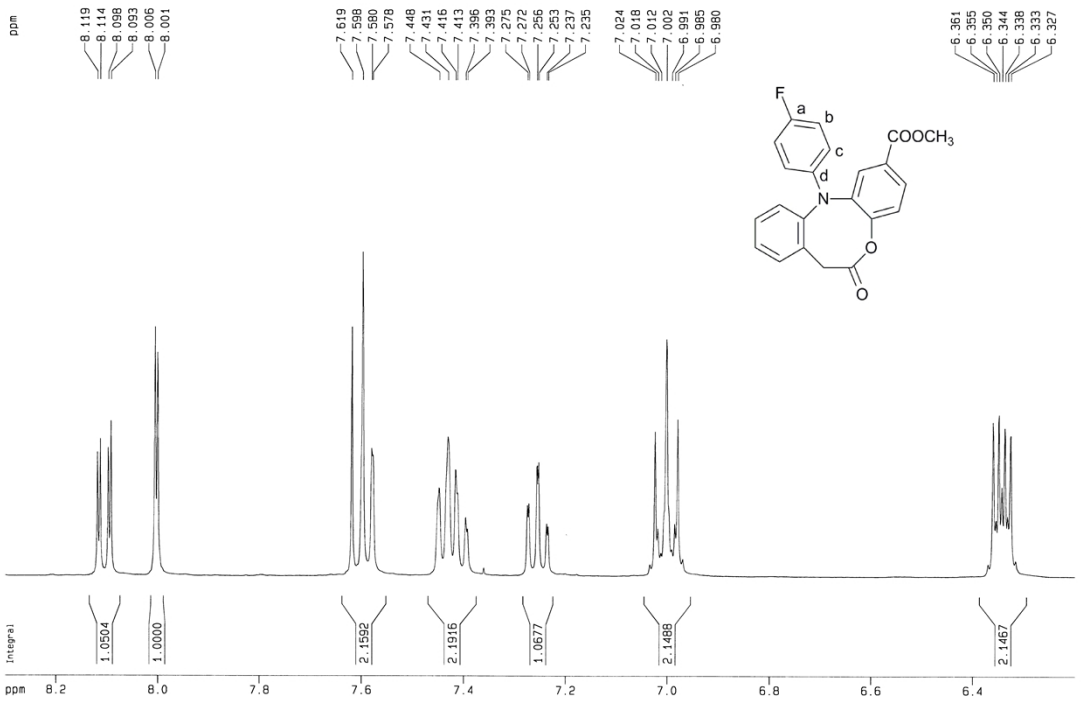




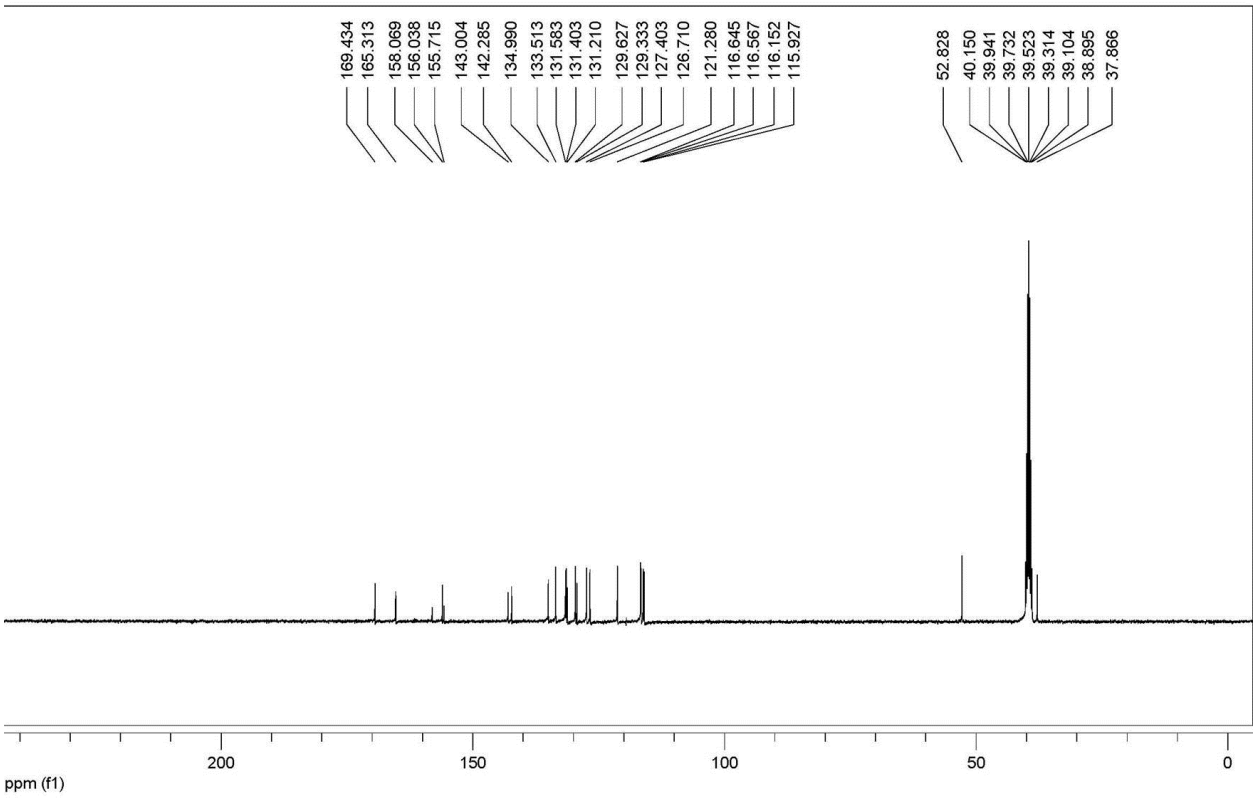
^{1}H NMR and ^{13}C NMR spectrum of 6d in DMSO-d_6, T = 298 K]



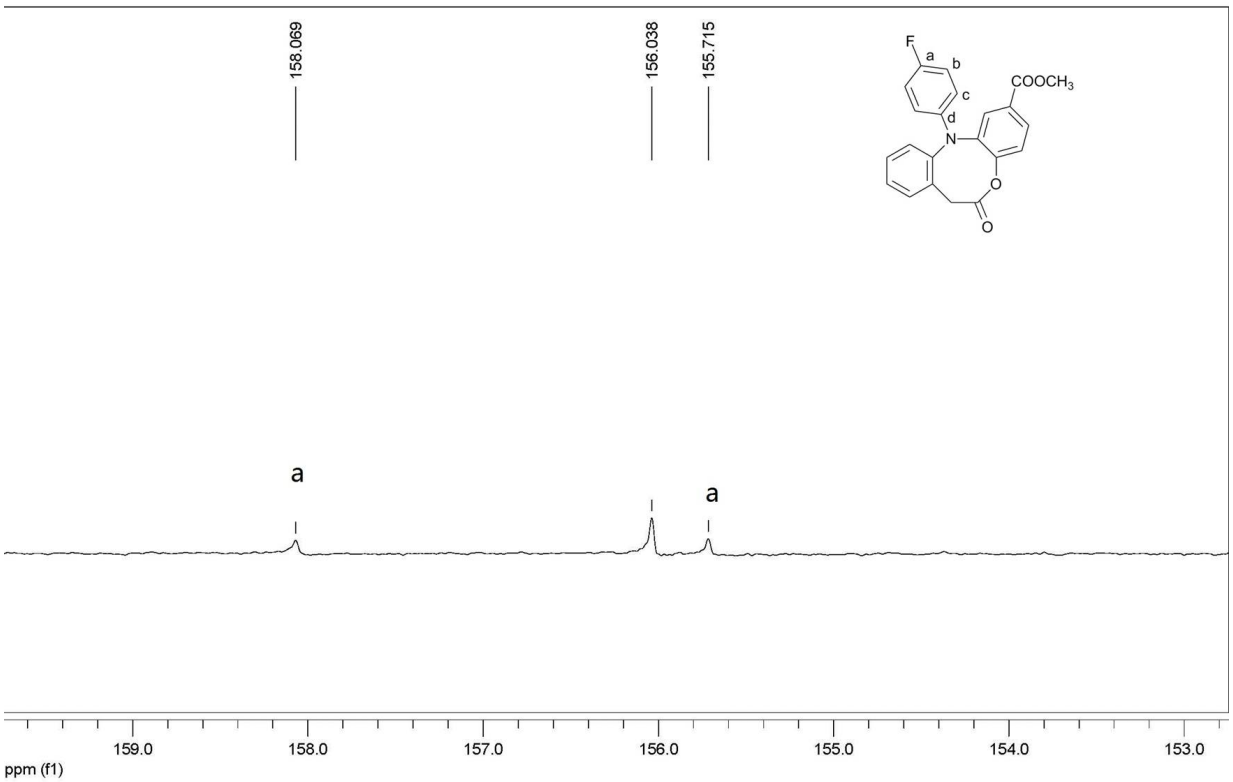
1HNMR spectrum of sample E-ZESPM377 T= 298K



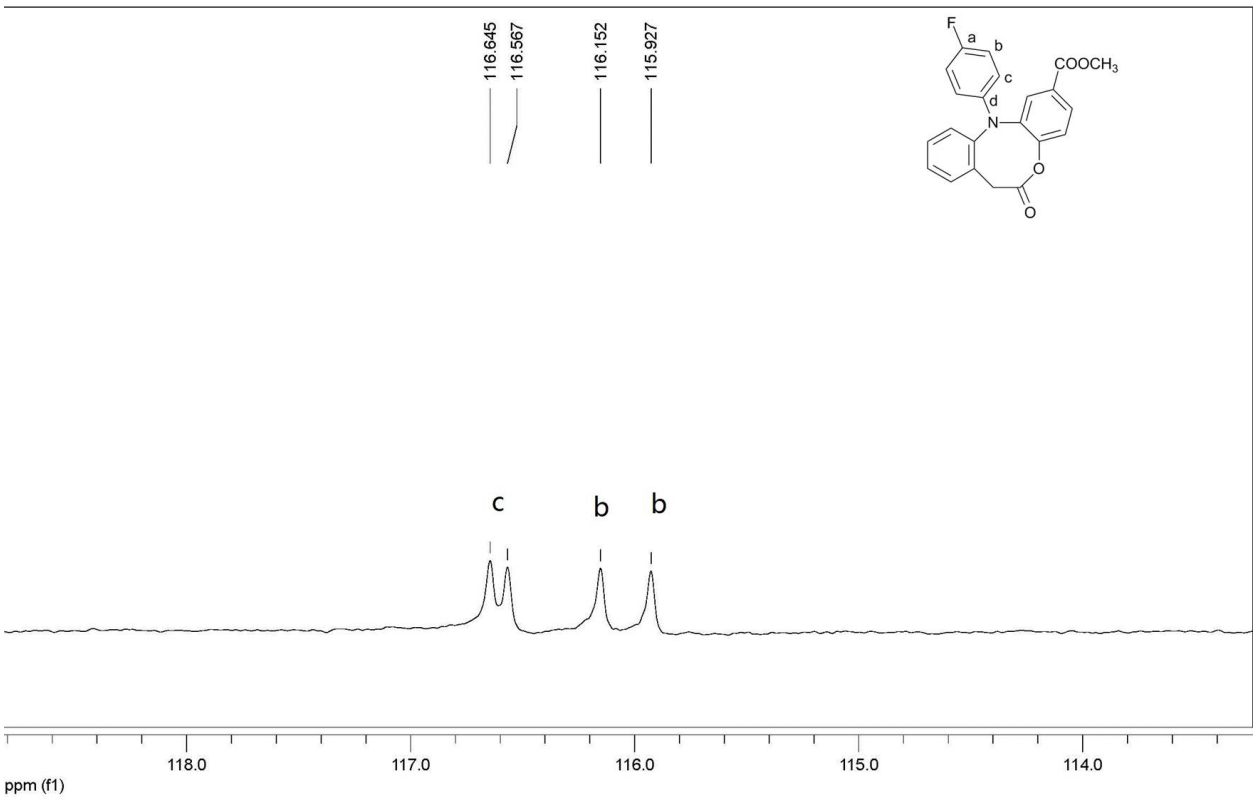
13CNMR Spectrum of sample E-ZESPM377

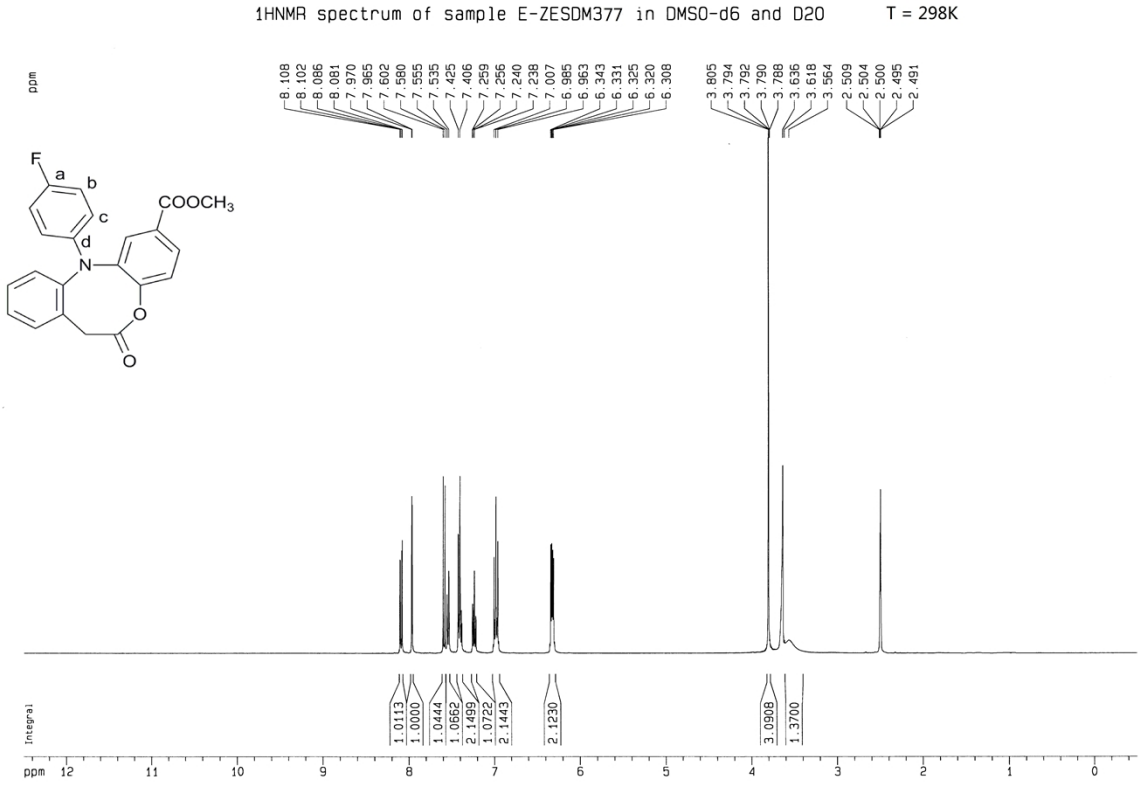


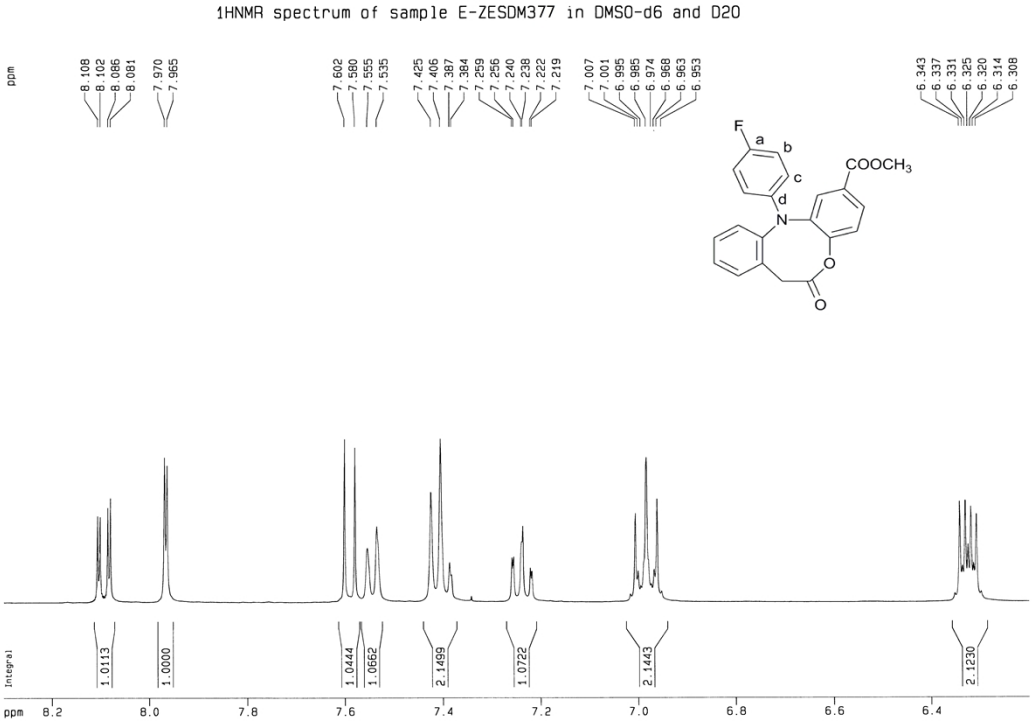
13CNMR Spectrum of sample E-ZESPM377



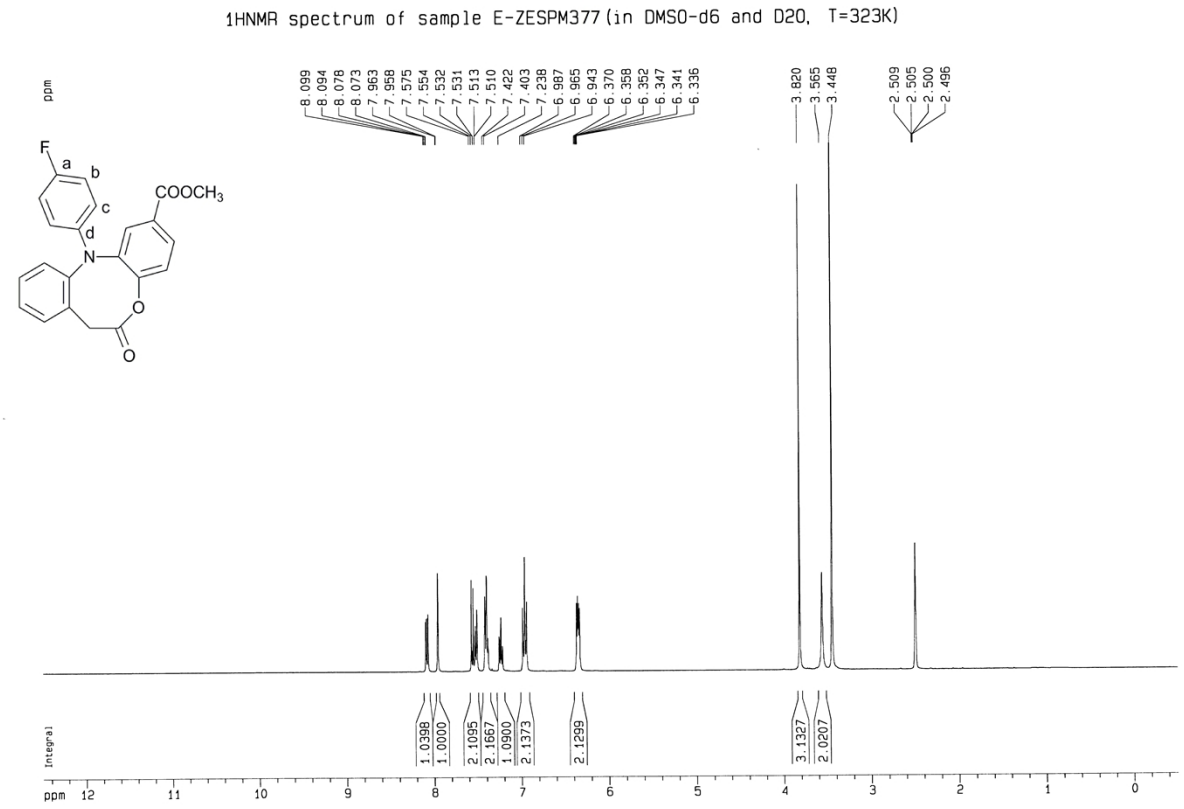
13CNMR Spectrum of sample E-ZESPM377

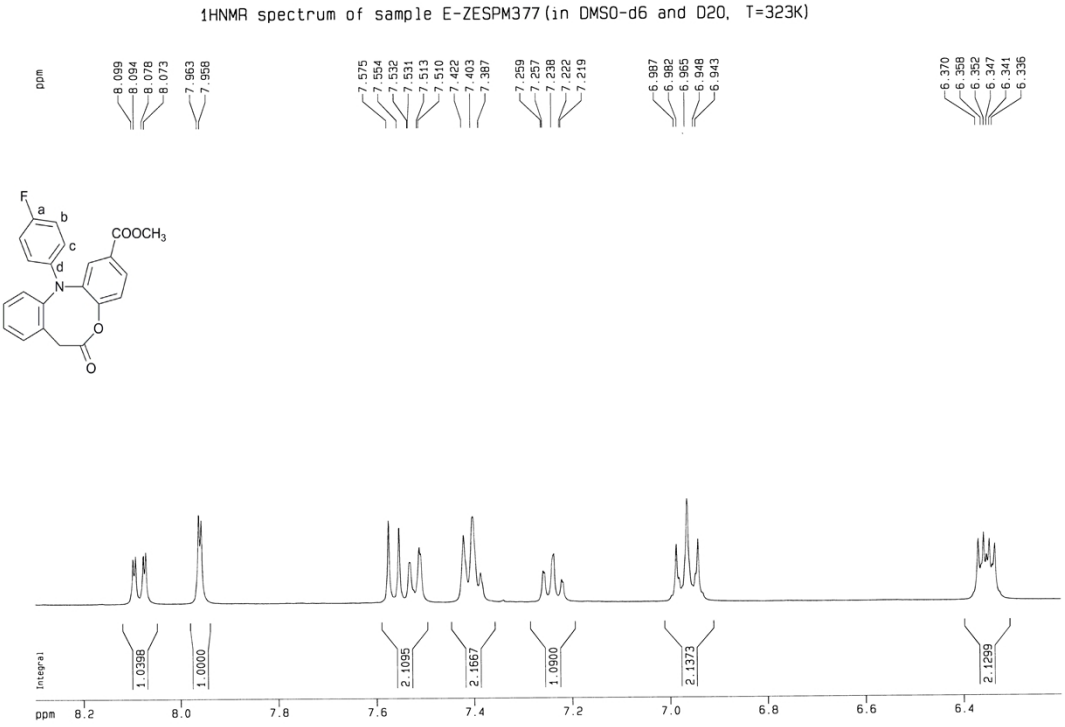



1HNMR spectrum of sample E-ZESDM377 in DMSO-d6 and D20 T = 298K
ppm
8.108
8.102
8.086
8.081
7.970
7.965
7.602
7.580
7.555
7.535
7.425
7.406
7.259
7.256
7.240
7.238
7.007
6.985
6.963
6.343
6.331
6.325
6.320
6.308
3.805
3.794
3.792
3.790
3.788
3.636
3.618
3.564
2.509
2.504
2.500
2.495
2.491
F
a
b
c
d
N
O
O
COOCH3
Integral
1.0113
1.0000
1.0444
1.0662
2.1499
1.0722
2.1443
2.1230
3.0908
1.3700
ppm 12 11 10 9 8 7 6 5 4 3 2 1 0

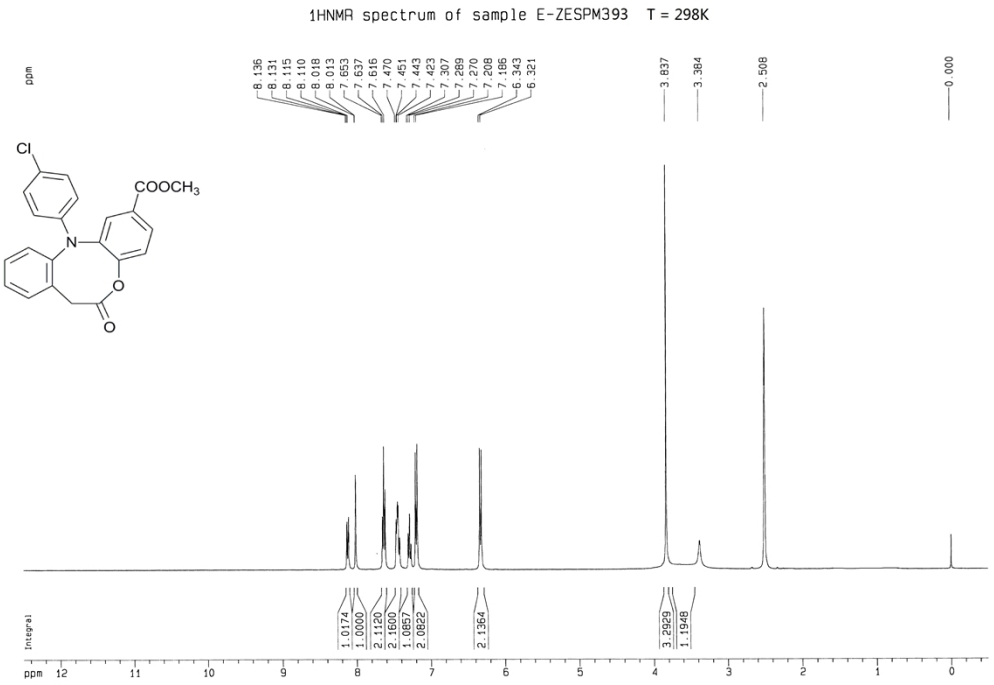

1HNMR spectrum of sample E-ZESDM377 in DMSO-d6 and D20
ppm
8.108
8.102
8.086
8.081
7.970
7.965
7.602
7.580
7.555
7.535
7.425
7.406
7.387
7.384
7.259
7.256
7.240
7.238
7.222
7.219
7.007
7.001
6.995
6.985
6.974
6.968
6.963
6.953
6.343
6.337
6.331
6.325
6.320
6.314
6.308
F
a
b
c
d
N
O
O
COOCH3
Integral
1.0113
1.0000
1.0444
1.0662
2.1499
1.0722
2.1443
2.1230
ppm 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4

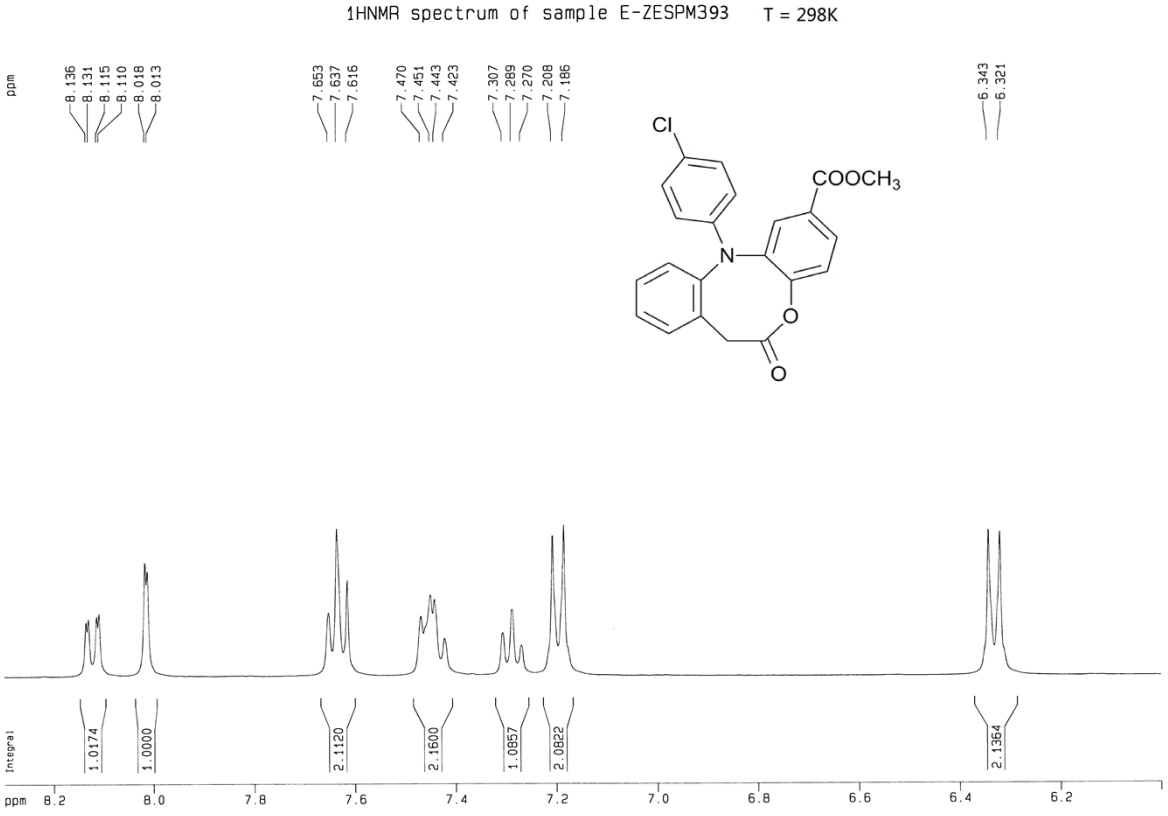
[^{1}H NMR spectrum of 6d in DMSO-d_6 and in D_2O, T = 323K]

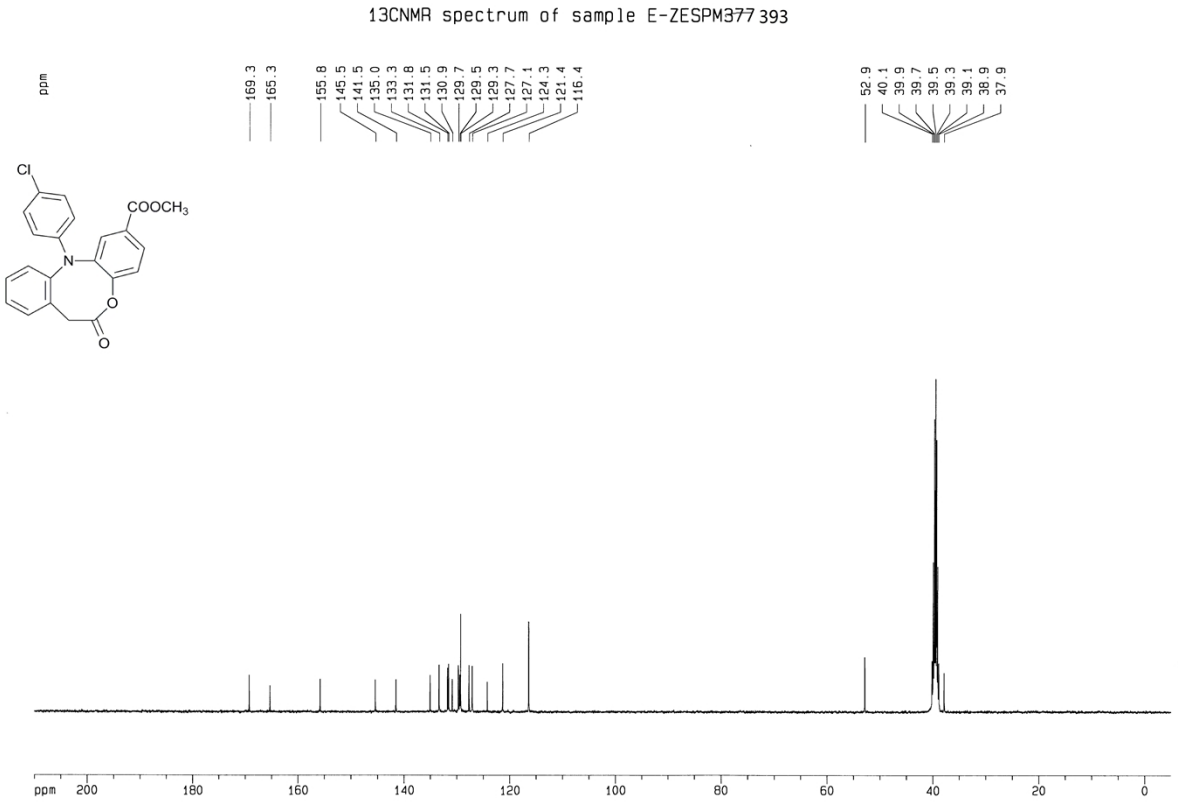




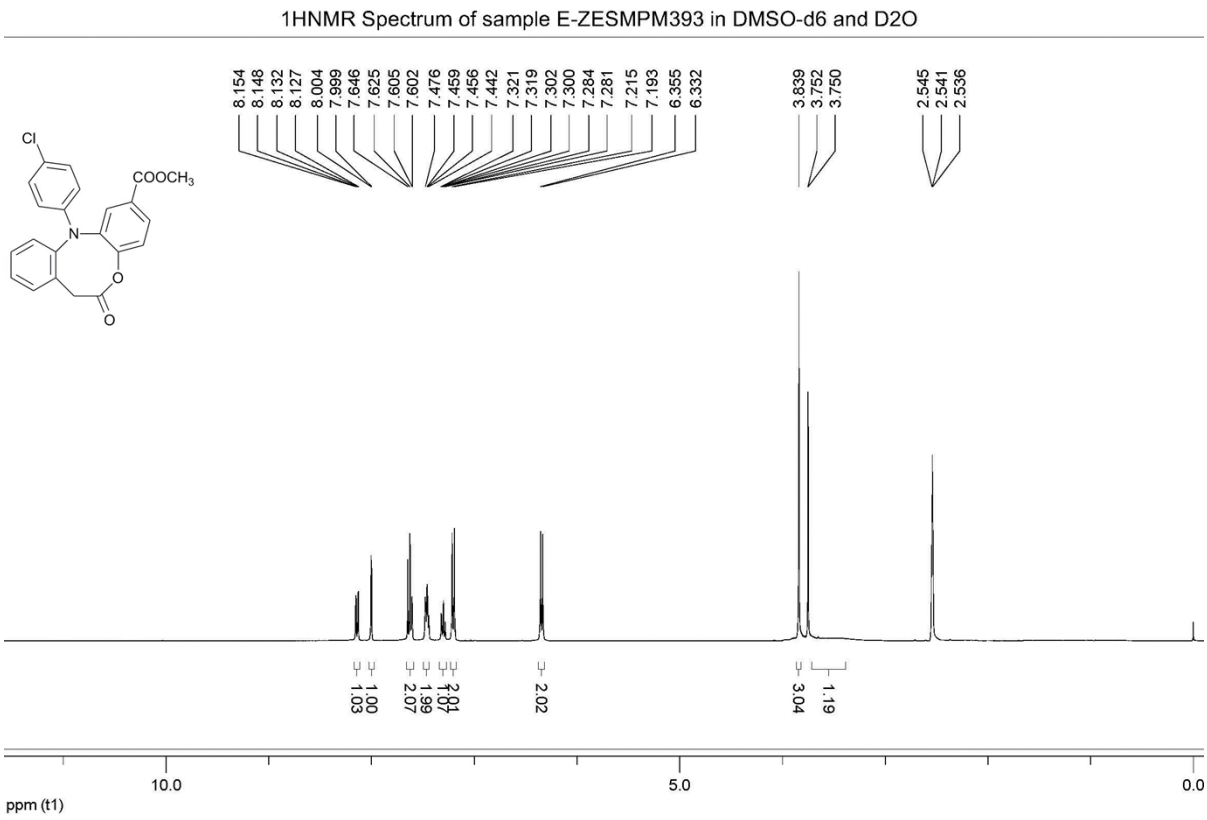
[^{1}H NMR spectrum of 6e in DMSO-d_6, T = 298K]



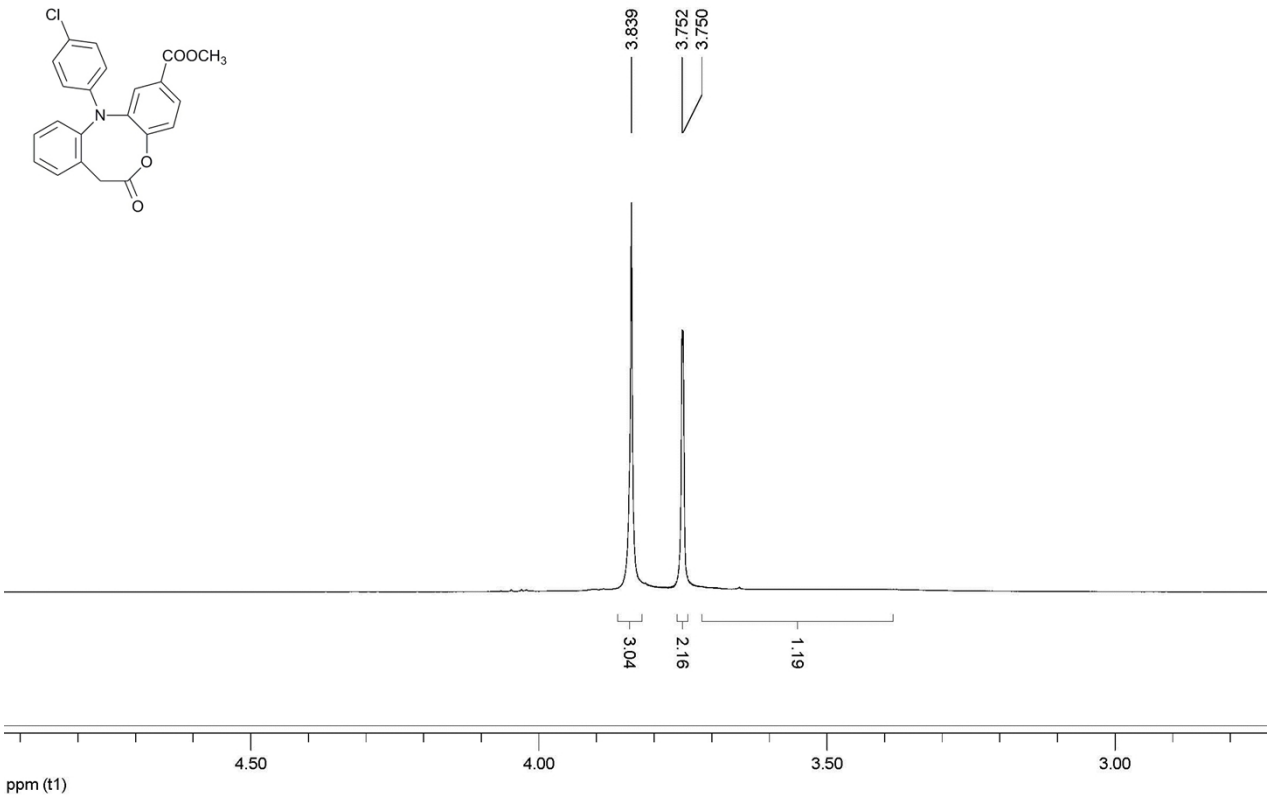




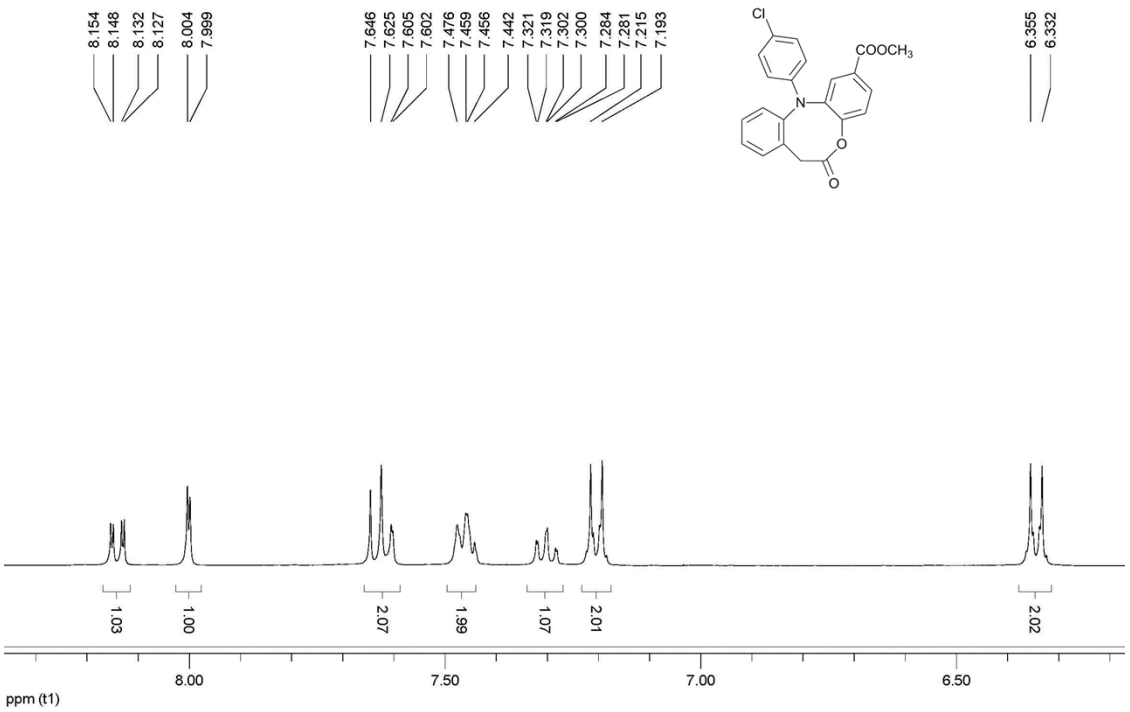
[^{1}H NMR spectrum of 6e in DMSO-d_6 and D_2O, T = 298K]



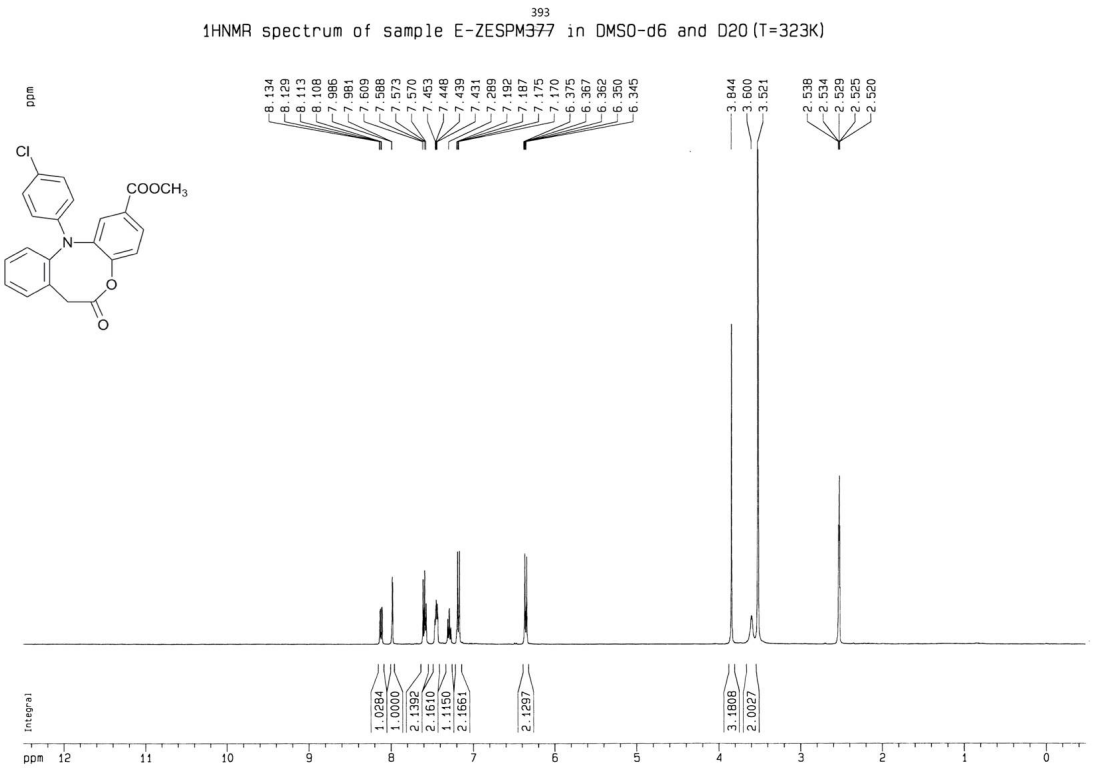
1HNMR Spectrum of sample E-ZESMPM393 in DMSO-d6 and D2O

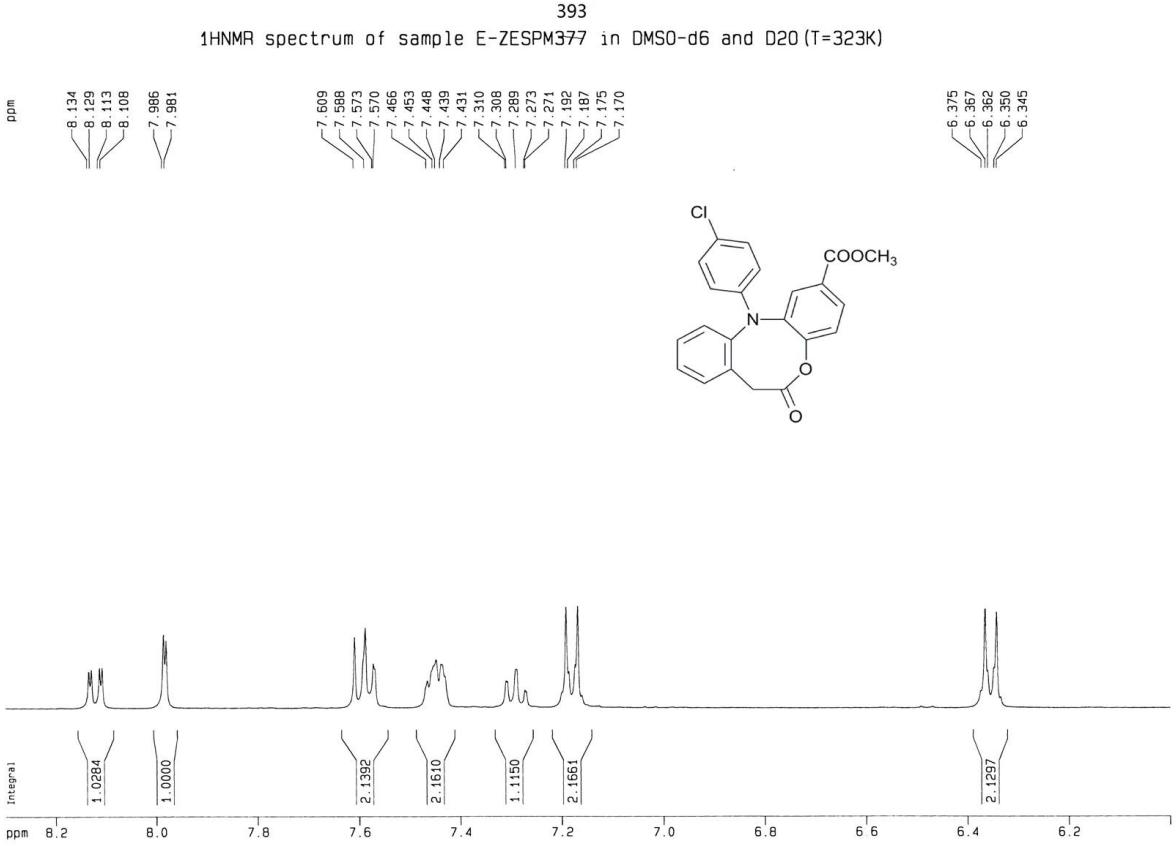


1HNMR Spectrum of sample E-ZESMPM393 in DMSO-d6 and D2O

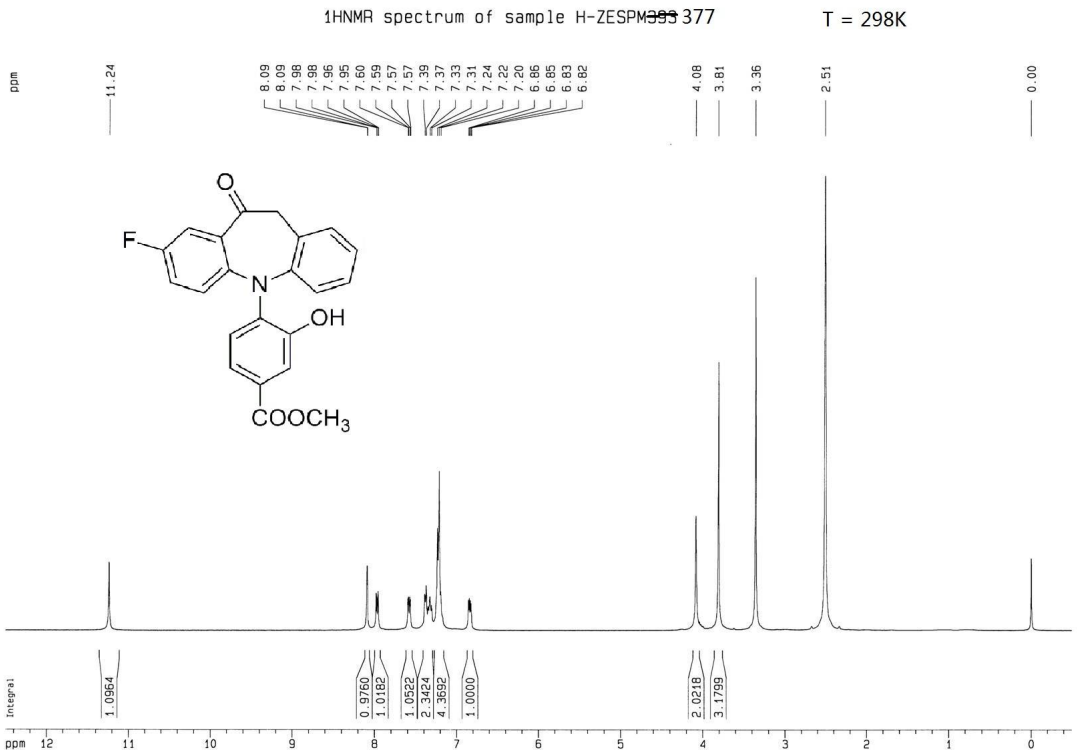


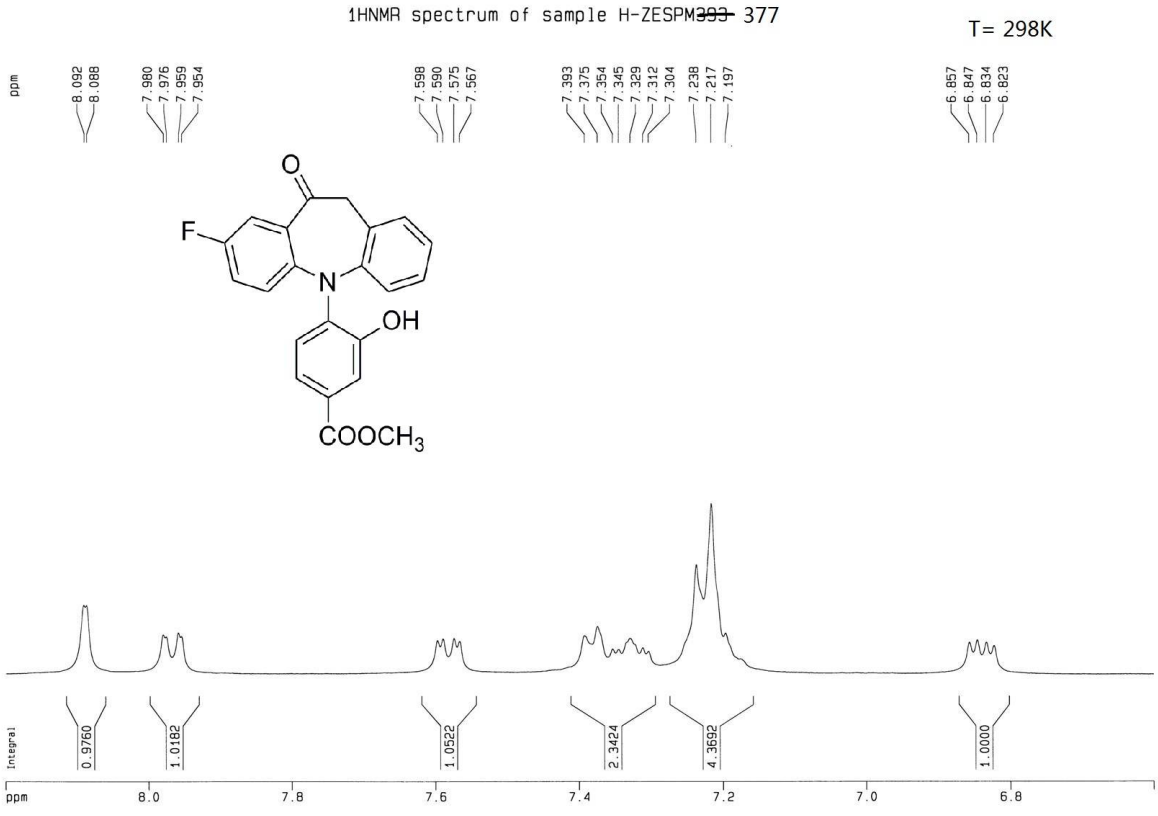
[^{1}H NMR spectrum of 6e in DMSO-d_6 and D_2O, T = 323K]

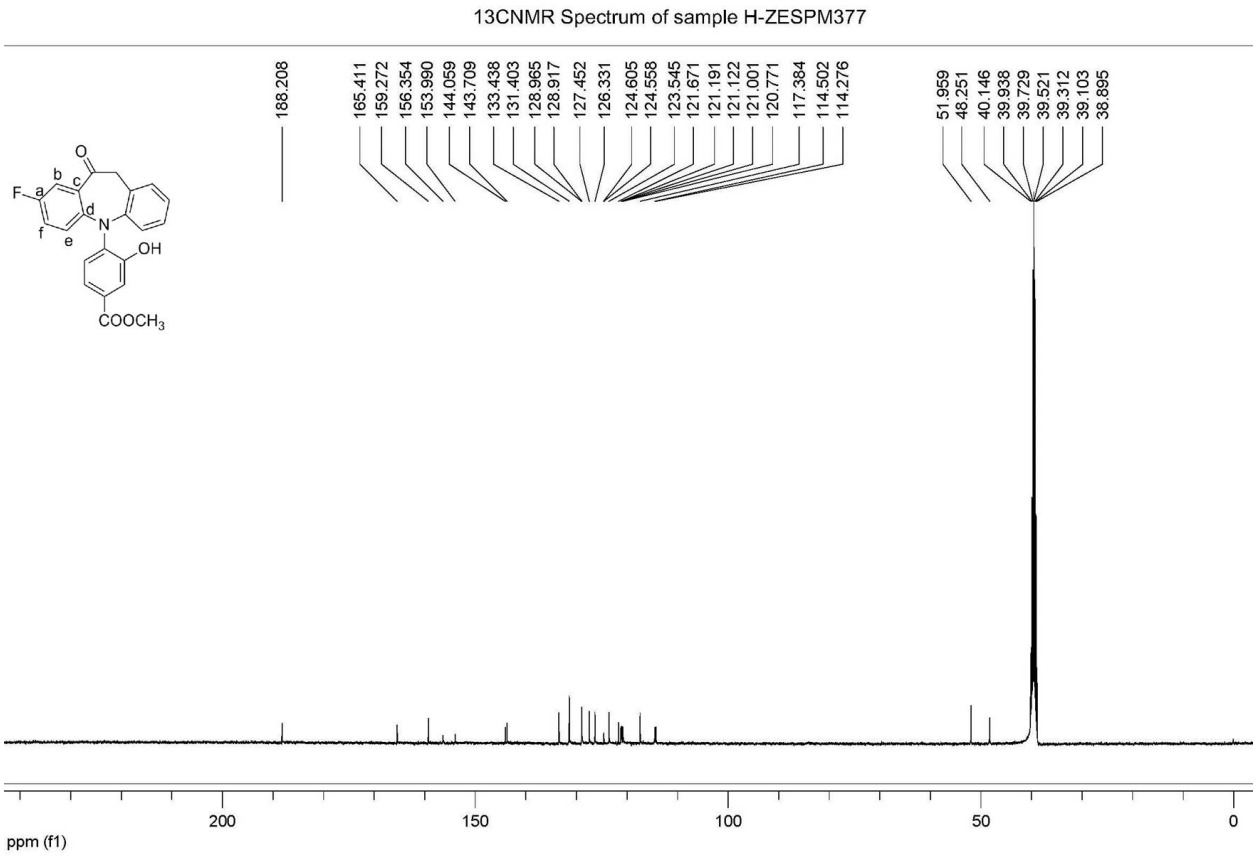


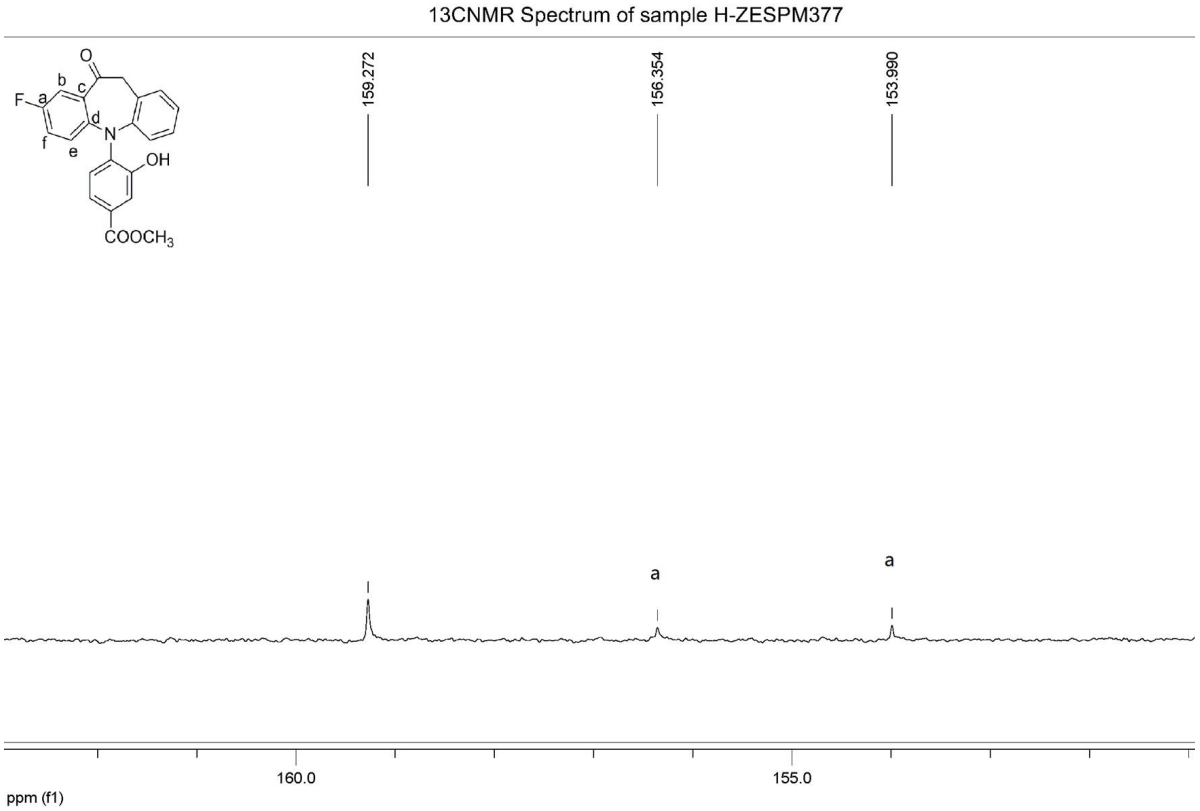


[^{1}H NMR and ^{13}C NMR spectrum of 7d in DMSO-d_6]

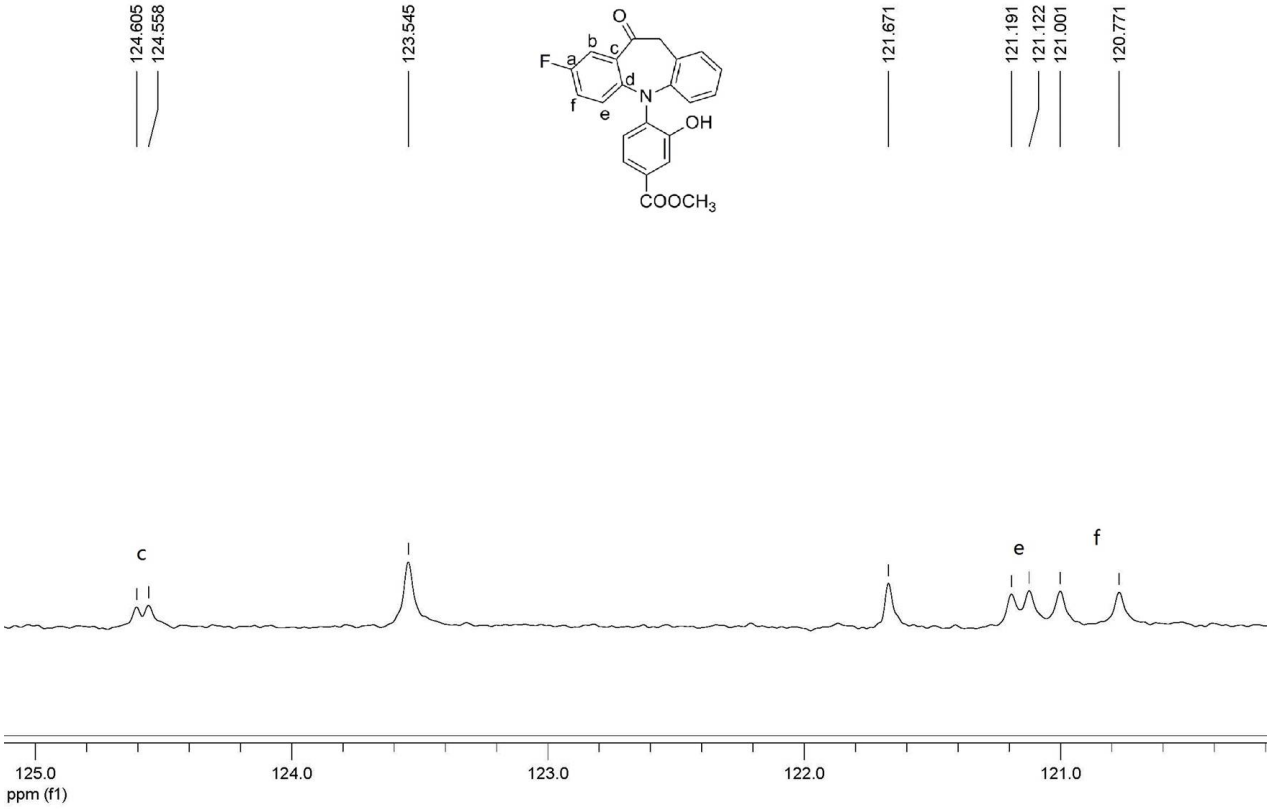




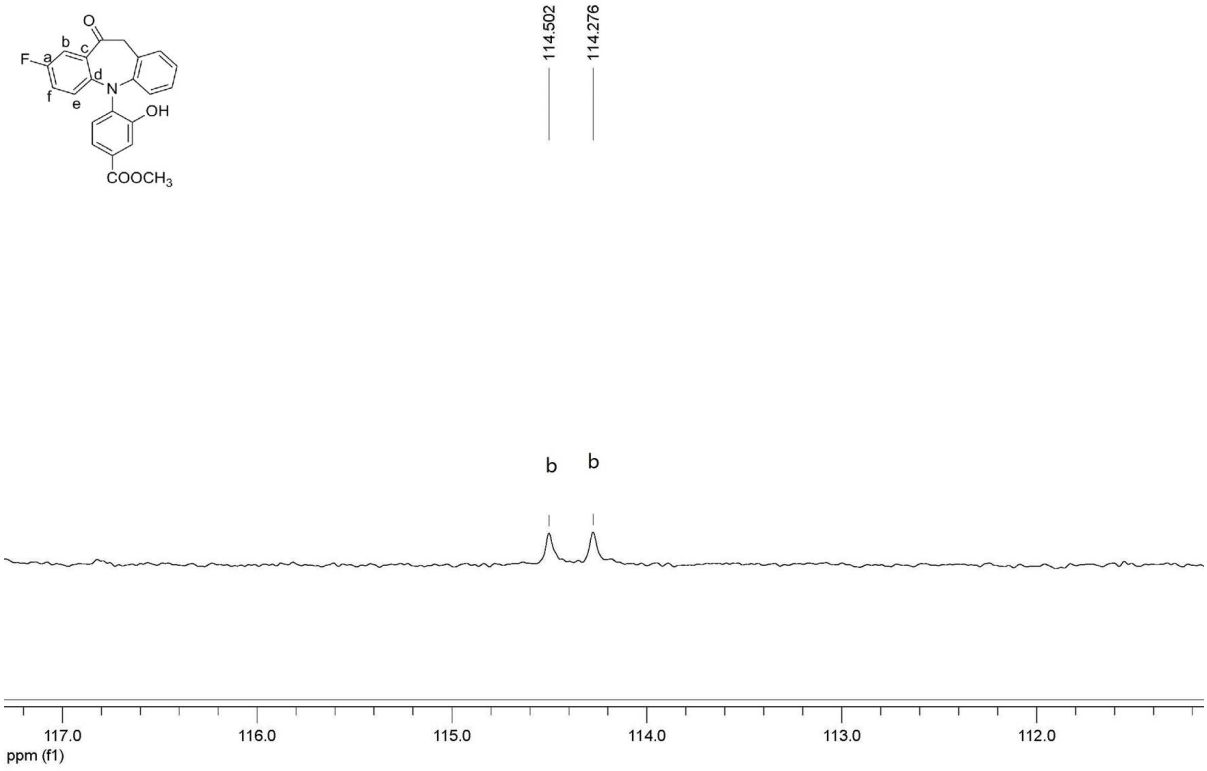

13CNMR Spectrum of sample H-ZESPM377
188.208
165.411
159.272
156.354
153.990
144.059
143.709
133.438
131.403
128.965
128.917
127.452
126.331
124.605
124.558
123.545
121.671
121.191
121.122
121.001
120.771
117.384
114.502
114.276
51.959
48.251
40.146
39.938
39.729
39.521
39.312
39.103
38.895
O
F
a
b
c
d
N
e
f
OH
COOCH3
200
150
100
50
0
ppm (f1)


13CNMR Spectrum of sample H-ZESPM377
159.272
156.354
153.990
O
F
a
b
c
d
N
e
f
OH
COOCH3
a
a
160.0
155.0
ppm (f1)

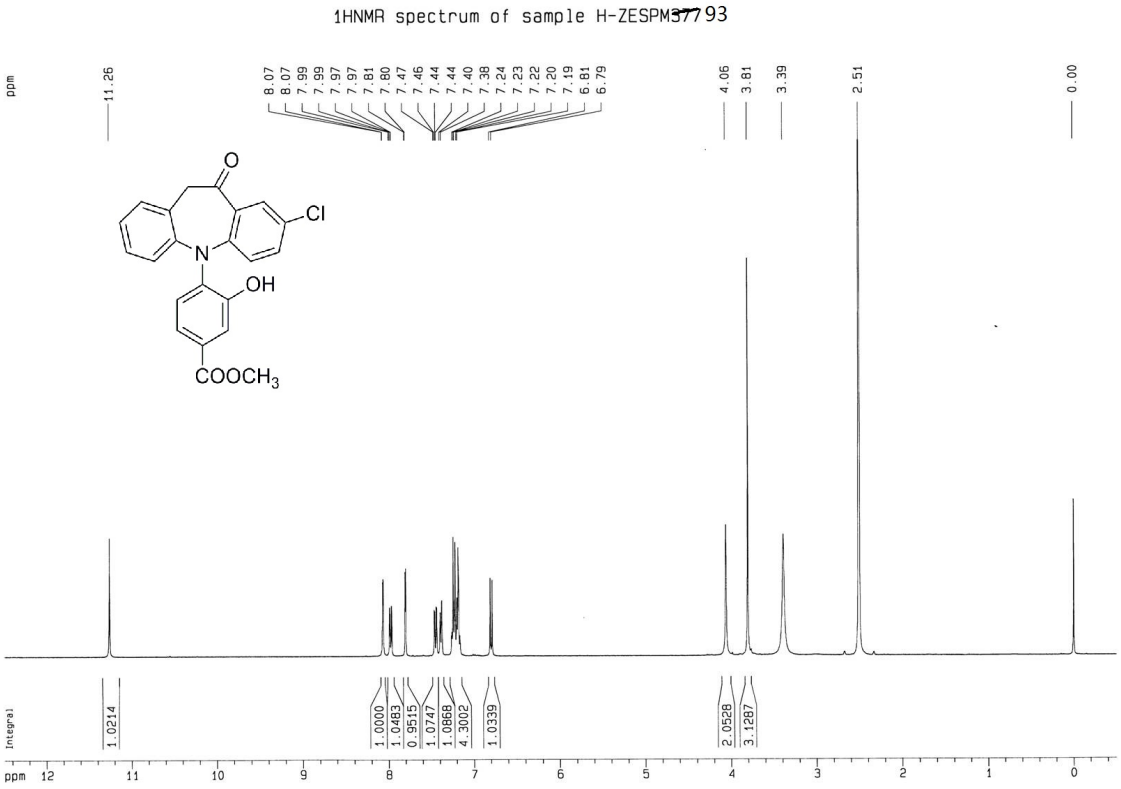
13CNMR Spectrum of sample H-ZESPM377

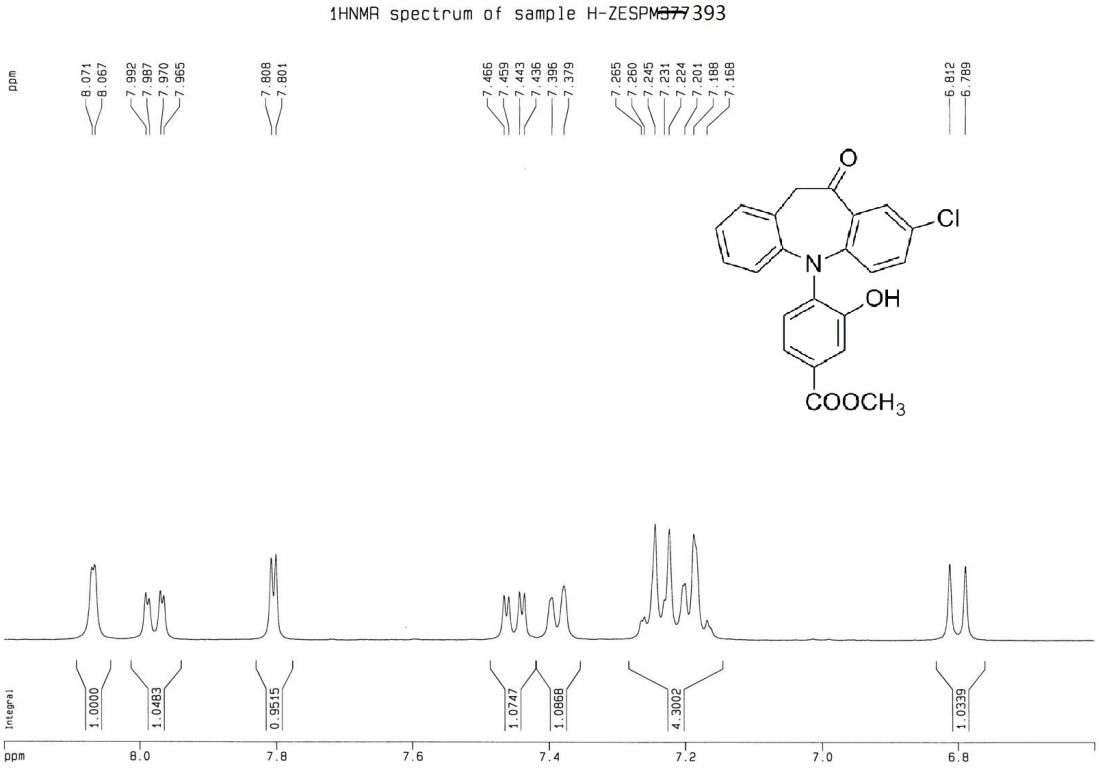


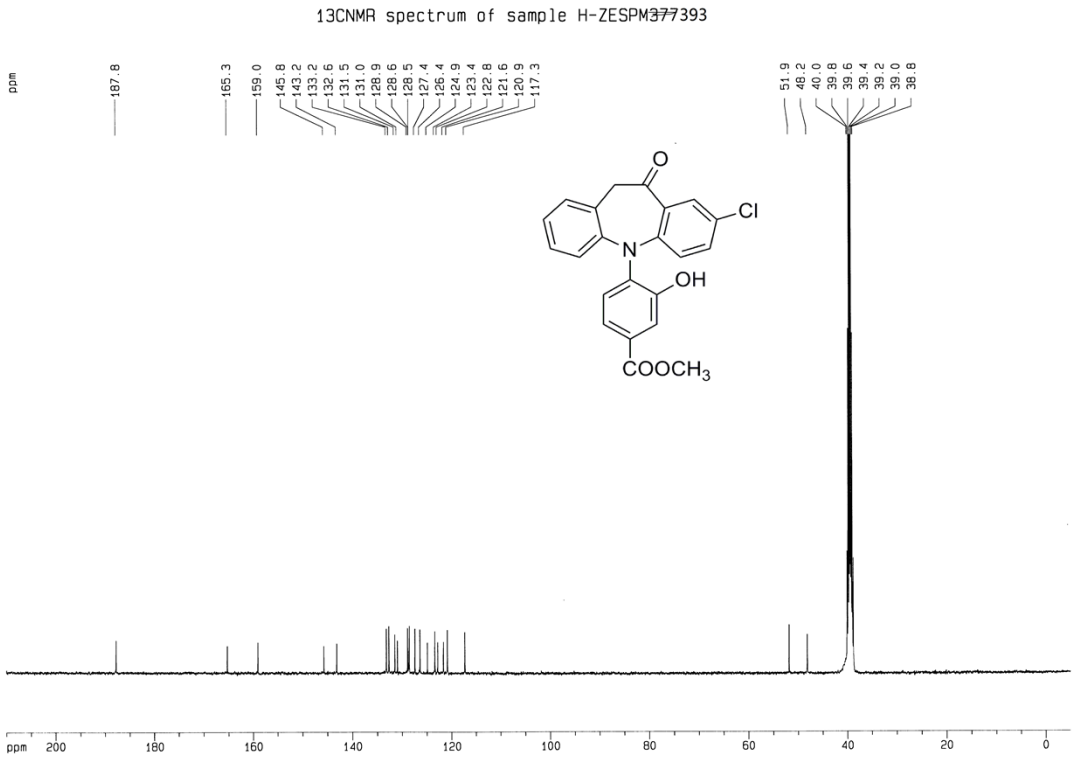
13CNMR Spectrum of sample H-ZESPM377



[^{1}H NMR and ^{13}C NMR spectrum of 7e in DMSO-d_6]






13CNMR spectrum of sample H-ZESPM377393
ppm
187.8
165.3
159.0
145.8
143.2
133.2
132.6
131.5
131.0
128.9
128.6
128.5
127.4
126.4
124.9
123.4
122.8
121.6
120.9
117.3
51.9
48.2
40.0
39.8
39.6
39.4
39.2
39.0
38.8
O
Cl
N
OH
COOCH3
ppm 200 180 160 140 120 100 80 60 40 20 0