**One-Pot Synthesis of Substituted Dibenzoxazepinones and Pyridobenzoxazepinones Using Octacarbonyldicobalt as an Effective CO Source**

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**1. Experimental section**

**1.1 General procedure for the synthesis of substituted dibenzoxazepinones:** A sealed tube equipped with a magnetic stir bar was charged with the corresponding 1-bromo -2-fluoro (or chloro) benzene/ 1-fluoro-2-iodobenzene (1 mmol), amino phenol (1 mmol), Pd(OAc)2 (5 mol%), xantphos (5 mol%) and DBU (2.5 mmol). The tube was purged with argon. Then DMF (10 V) was added followed by the addition of Co2(CO)8 (0.25 mmol). The tube was closed with seal plug instantly. The reaction tube was placed in a pre heated oil bath at 150 0C for 16 h. On completion, the reaction mixture was cooled to room temperature, added water and ethyl acetate (1:1). Precipitated solid was filtered through a Celite bed. The bed was washed thoroughly with ethyl acetate. Organic layer was separated. Aqueous layer extracted with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous sodium sulphate. Organic layer was concentrated under reduced pressure and purified by flash column chromatography on silica gel (230-400 mesh) with ethyl acetate and petroleum ether as eluent to afford the corresponding dibenzoxazepinones.

**1.2 General procedure for the synthesis of substituted pyridobenzoxazepinones:**

**Method A:** A sealed tube equipped with a magnetic stir bar was charged with the corresponding 3-bromo-2-fluoropyridine (1 mmol), amino phenol (1 mmol), Pd(OAc)2 (5 mol%), xantphos (5 mol%) and DMAP (2.5 mmol). The tube was purged with argon. Then DMF (10V) was added followed by the addition of Co2(CO)8 (0.25 mmol). The tube was closed with seal plug instantly. The reaction tube was placed in a preheated oil bath at 120 0C for 8 h. On completion, the reaction mixture was cooled to room temperature, added water and ethyl acetate (1:1). Precipitated solid was filtered through a Celite bed. The bed was washed thoroughly with ethyl acetate. Organic layer was separated. Aqueous layer extracted with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous sodium sulphate. Organic layer was concentrated under reduced pressure and purified by flash column chromatography on silica gel (230-400 mesh) with ethyl acetate and petroleum ether as eluent to afford the corresponding pyridobenzoxazepinone.

**Method B:** A sealed tube equipped with a magnetic stir bar was charged with the corresponding 3-bromo-2-chloropyridine (1 mmol), amino phenol (1 mmol), Pd(OAc)2 (5 mol%), xantphos (5 mol%) and DBU (2.5 mmol). The tube was purged with argon. Then DMF (10 V) was added followed by the addition of Co2(CO)8 (0.25 mmol). The tube was closed with seal plug instantly. The reaction tube was placed in a pre heated oil bath at 135 0C for 12 h. On completion, the reaction mixture was cooled to room temperature, added water and ethyl acetate (1:1). Precipitated solid was filtered through a Celite bed. The bed was washed thoroughly with ethyl acetate. Organic layer was separated. Aqueous layer extracted with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous sodium sulphate. Organic layer was concentrated under reduced pressure and purified by flash column chromatography on silica gel (230-400 mesh) with ethyl acetate and petroleum ether as eluent to afford the corresponding pyridobenzoxazepinone.

**2. Analytical data**

**dibenzo[b,f][1,4]oxazepin-11(10H)-one (3a)[1, 2, 3]**

Following the general procedure using 1-bromo-2-fluorobenzene (175 mg, 1 mmol) and 2-aminophenol (110 mg, 1 mmol) provided 188 mg (89% yield) of **3a** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.54 (s, 1H), 7.77 (dd, *J* = 1.60, 7.80 Hz, 1H), 7.64-7.59 (m, 1H), 7.36-7.30 (m, 3H), 7.19-7.11 (m, 3H); 13C-NMR (100 MHz, CDCl3): δ 167.5, 159.7, 150.9, 134.5, 132.0, 130.6, 125.9, 125.8, 125.2, 125.1, 121.7, 121.3, 120.8; LCMS (APCI-MS) calcd. for C13H9NO2: 211.06, found [M+H]+ = 212.4.

**7-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3b)[2]**

Following the general procedure using 1-bromo-2-fluorobenzene (175 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 204 mg (91% yield) of **3b** as a white solid. Following the general procedure using 1-bromo-2-chlorobenzene (190 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 178 mg (79% yield) of **3b** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.44 (s, 1H), 7.77-7.74 (m, 1H), 7.62-7.58 (m, 1H), 7.34-7.28 (m, 2H), 7.15 (s, 1H), 7.05-7.03 (m, 1H), 6.99-6.97 (m, 1H), 2.25 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): 166.2, 159.4, 150.8, 135.4, 134.7, 131.8, 128.9, 126.8, 126.3, 125.8, 121.9, 121.8, 121.1, 20.6; LCMS (APCI-MS) calcd. for C14H11NO2: 225.08, found (M+H)+ = 226.4.

**8-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one (3c)[2]**

Following the general procedure using 1-bromo-2-fluorobenzene (175 mg, 1 mmol) and 2-amino-4-chlorophenol (143 mg, 1 mmol) provided 215 mg (88% yield) of **3c** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.64 (s, 1H), 7.79 (dd, *J* = 1.72, 7.76 Hz, 1H), 7.67-7.63 (m, 1H), 7.40-7.33 (m, 3H), 7.21-7.19 (m, 2H); 13C-NMR (75 MHz, DMSO-d6): δ 165.9, 158.9, 149.5, 135.1, 133.2, 131.9, 129.9, 126.1, 125.9, 125.2, 123.4, 121.5, 121.1; LCMS (APCI-MS) calcd. for C13H8ClNO2: 245.02, found (M-H)+ = 244.4.

**2-fluorodibenzo[b,f][1,4]oxazepin-11(10H)-one (3d)[2]**

Following the general procedure using 2-bromo-1,4-difluorobenzene (192 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 165 mg (72% yield) of **3d** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.67 (s, 1H), 7.51-7.46 (m, 2H), 7.44-7.41 (m, 1H), 7.35-7.33 (m, 1H), 7.22-7.13 (m, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 165.0, 160.5, 158.1, 155.6, 150.9, 131.4, 127.7, 126.6, 125.9, 123.2, 122.2, 121.7, 117.6; LCMS (APCI-MS) calcd. for C13H8FNO2: 229.05, found (M+H)+ = 230.2.

**7-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one(3e)[4]**

Following the general procedure using 1-bromo-2-fluorobenzene (175 mg, 1 mmol) and 2-amino-5-chlorophenol (143 mg, 1 mmol) provided 208 mg (85% yield) of **3e** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.64 (s, 1H), 7.78 (dd, *J* = 1.64, 7.68 Hz, 1H), 7.64 (ddd, *J* = 1.82, 7.30, 8.20 Hz 1H), 7.52 (d, *J* = 2.40 Hz, 1H), 7.40-7.33 (m, 2H), 7.29 (dd, *J* = 2.36, 8.54 Hz, 1H), 7.18 (d, *J* = 8.56 Hz, 1H); 13C-NMR (100 MHz, DMSO-d6): δ 165.9, 158.9, 151.1, 135.1, 131.9, 130.9, 128.8, 126.5, 126.3, 125.9, 123.2, 121.9, 121.2; LCMS (APCI-MS) calcd. for C13H8ClNO2: 245.02, found (M+H)+ = 246.2.

**2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3f)[2]**

Following the general procedure using 2-bromo-1-fluoro-4-methylbenzene (188 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 206 mg (92% yield) of **3f** as a white solid. Following the general procedure using 1-fluoro-2-iodo-4-methylbenzene (236 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 202 mg (90% yield) of **3f** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.47 (s, 1H), 7.56 (d, *J* = 1.20 Hz, 1H), 7.40 (dd, *J* = 1.20, 8.20 Hz, 1H), 7.30 (d, *J* = 7.20 Hz, 1H), 7.22 (d, *J* = 8.00 Hz, 1H), 7.17-7.10 (m, 3H), 2.30 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 166.3, 157.3, 151.0, 135.2, 135.1, 131.7, 131.6, 126.3, 125.7, 125.6, 122.0, 121.6, 120.8, 20.5; LCMS (APCI-MS) calcd. for C14H11NO2: 225.08, found (M+H)+ = 226.4.

**2, 8-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one(3g)[2]**

Following the general procedure using 2-bromo-1-fluoro-4-methylbenzene (188 mg, 1 mmol) and 2-amino-4-methylphenol (123 mg, 1 mmol) provided 215 mg (90% yield) of **3g** as a white solid. Following the general procedure using 2-bromo-1-chloro-4-methylbenzene (204 mg, 1 mmol) and 2-amino-4-methylphenol (123 mg, 1 mmol) provided 176 mg (74% yield) of **3g** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.42 (s, 1H), 7.56 (s, 1H), 7.40 (d, *J* = 7.60 Hz, 1H), 7.19 (t, *J* = 8.80 Hz, 2H), 6.94-6.91 (m, 2H), 2.31 (s, 3H), 2.24 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 166.4, 157.4, 148.9, 135.5, 135.1, 134.9, 131.7, 131.3, 126.0, 125.8,122.2, 121.3, 120.7, 20.8, 20.6; LCMS (APCI-MS) calcd. for C15H13NO2: 239.09, found (M+H)+ = 240.4.

**3-methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (3h)[5]**

Following the general procedure using 1-bromo-2-fluoro-4-methoxybenzene (204 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 173 mg (72% yield) of **3h** as a white solid. Following the general procedure using 2-fluoro-1-iodo-4-methoxybenzene (252 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 180 mg (75% yield) of **3h** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.34 (s, 1H), 7.72 (d, *J* = 8.80 Hz, 1H), 7.33 (d, *J* = 7.60 Hz, 1H), 7.19-7.11 (m, 3H), 6.92 (d, *J* = 2.40 Hz, 1H), 6.89 (dd, *J* = 2.40, 8.80 Hz, 1H),, 3.85 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 165.9, 164.5, 160.7, 150.4, 133.1, 131.8, 126.4, 125.4, 121.9, 121.8, 118.2, 112.3, 105.8, 56.3; LCMS (APCI-MS) calcd. for C14H11NO3: 241.07, found (M+H)+ = 242.4.

**3-methoxy-8-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3i)**

Following the general procedure using 1-bromo-2-fluoro-4-methoxybenzene (204 mg, 1 mmol) and 2-amino-4-methylphenol (123 mg, 1 mmol) provided 194 mg (76% yield) of **3i** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.30 (s, 1H), 7.69 (d, *J* = 8.40 Hz, 1H), 7.18 (d, *J* = 8.00 Hz, 1H), 6.95-6.85 (m, 4H), 3.83 (s, 3H), 2.23 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 166.0, 164.4, 160.8, 148.3, 135.6, 133.1, 131.4, 125.8, 122.1, 121.5, 118.3, 112.1, 105.7, 56.3, 20.8; LCMS (APCI-MS) calcd. for C15H13NO3: 255.09, found (M+H)+ = 256.4; Anal calc. for C15H13NO3: C, 70.58; H, 5.13; N, 5.49%, found C, 70.56; H, 5.14; N, 5.49%.

**3-methoxy-9-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3j)**

Following the general procedure using 1-bromo-2-fluoro-4-methoxybenzene (204 mg, 1 mmol) and 2-amino-3-methylphenol (123 mg, 1 mmol) provided 204 mg (80% yield) of **3j** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 9.74 (s, 1H), 7.65 (d, *J* = 8.40 Hz, 1H), 7.19 (t, *J* = 4.80 Hz, 1H), 7.04 (d, *J* = 0.80 Hz, 2H), 6.91 (d, *J* = 2.40 Hz, 1H), 6.87 (dd, *J* = 2.40, 8.80 Hz, 1H), 3.82 (s, 3H), 2.32 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 166.1, 164.2, 161.3, 152.5, 132.8, 131.7, 130.2, 127.9, 125.6, 119.4, 118.7, 112.4, 105.6, 56.3, 18.3; LCMS (APCI-MS) calcd. for C15H13NO3: 255.09, found (M+H)+ = 256.4. Anal calc. for C15H13NO3: C, 70.58; H, 5.13; N, 5.49% found C, 70.56; H, 5.14; N, 5.49%.

**2, 9-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one(3k)[2]**

Following the general procedure using 2-bromo-1-fluoro-4-methylbenzene (187 mg, 1 mmol) and 2-amino-3-methylphenol (123 mg, 1 mmol) provided 184 mg (77% yield) of **3k** as a white solid.1H -NMR (400 MHz, DMSO-d6): δ 9.91 (s, 1H), 7.51 (d, *J* = 2.00 Hz, 1H), 7.37 (dd, *J* = 2.00, 8.40 Hz, 1H), 7.21-7.15 (m, 2H), 7.04 (d, *J* = 5.20 Hz, 2H), 02.31 (s, 3H), 2.29 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 166.6, 157.9, 153.2, 135.2, 134.9, 131.9, 131.5, 130.0, 127.8, 126.3, 125.8, 120.6, 119.6, 20.6, 18.3; LCMS (APCI-MS) calcd. for C15H13NO2: 239.09, found (M+H)+ = 240.4.

**benzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one(7a)[6]**

Following the general procedure using 3-bromo-2-fluoropyridine (175 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 161 mg (76% yield) of **7a** as a white solid. Following the general procedure using 3-bromo-2-chloropyridine (190 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 174 mg (82% yield) of **7a** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.75 (s, 1H), 8.51 (dd, *J* = 1.96, 4.74 Hz, 1H), 8.28 (dd, *J* = 1.92, 7.58 Hz, 1H), 7.47 (dd, *J* = 4.80, 7.56 Hz, 1H), 7.36-7.34 (m, 1H), 7.26-7.16 (m, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 164.4, 162.4, 152.5, 148.2, 142.5, 130.6, 126.5, 125.6, 122.6, 121.9, 121.8, 120.1; LCMS (APCI-MS) calcd. for C12H8N2O2: 212.05, found [M+H]+ = 213.2.

**8-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one(7b)[6]**

Following the general procedure using 3-bromo-2-fluoropyridine (175 mg, 1 mmol) and 2-amino-4-chlorophenol (143 mg, 1 mmol) provided 172 mg (70% yield) of **7b** as a white solid. Following the general procedure using 3-bromo-2-chloropyridine (190 mg, 1 mmol) and 2-amino-4-chlorophenol (143 mg, 1 mmol) provided 160 mg (65% yield) of **7b** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.84 (s, 1H), 8.53 (dd, *J* = 2.00, 4.76 Hz, 1H), 8.29 (dd, *J* = 2.04, 7.58 Hz, 1H), 7.49 (dd, *J* = 4.80, 7.58 Hz, 1H), 7.39-7.37 (m, 1H), 7.244 -7.21 (m, 2H); 13C-NMR (100 MHz, DMSO-d6): δ 164.7, 162.4, 153.1, 147.2, 143.0, 132.5, 130.4, 125.6, 124.0, 123.3, 121.6, 120.3; LCMS (APCI-MS) calcd. for C12H7ClN2O2: 246.02, found (M+H)+ = 247.0.

**9-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7c)[6]**

Following the general procedure using 3-bromo-2-fluoropyridine (175 mg, 1 mmol) and 2-amino-5-chlorophenol (143 mg, 1 mmol) provided 191 mg (78% yield) of **7c** as a yellow solid. Following the general procedure using 3-bromo-2-chloropyridine (190 mg, 1 mmol) and 2-amino-5-chlorophenol (143 mg, 1 mmol) provided 177 mg (72% yield) of **7c** as a yellow solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.83 (s, 1H), 8.52 (dd, *J* = 2.00, 4.80 Hz, 1H), 8.28 (dd, *J* = 2.00, 7.60 Hz, 1H), 7.50-7.45 (m, 2H), 7.33 (dd, *J* = 2.40, 8.80 Hz, 1H), 7.20 (d, *J* = 8.40 Hz, 1H); 13C-NMR (100 MHz, DMSO-d6): δ 164.6, 162.3, 153.0, 148.8, 143.0, 130.3, 129.2, 126.9, 123.4, 123.4, 122.4, 120.3; LCMS (APCI-MS) calcd. for C12H7ClN2O2: 246.02, found (M+H)+ = 247.2.

**8, 9-dichlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7d)**

Following the general procedure using 3-bromo-2-fluoropyridine (175 mg, 1 mmol) and 2-amino-4,5-dichlorophenol (177 mg, 1 mmol) provided 190 mg (68% yield) of **7d** as a white solid. Following the general procedure using 3-bromo-2-chloropyridine (190 mg, 1 mmol) and 2-amino-4,5-dichlorophenol (177 mg, 1 mmol) provided 157 mg (56% yield) of **7d** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.91 (s, 1H), 8.54 (dd, *J* = 2.00, 4.80 Hz, 1H), 8.30 (dd, *J* = 2.00, 7.60 Hz, 1H), 7.72 (s, 1H), 7.53-7.42 (m, 1H), 7.42 (s, 1H); 13C-NMR (100 MHz, DMSO-d6): δ 164.5, 161.9, 153.2, 147.4, 143.2, 131.6, 128.8, 127.1, 124.2, 123.5, 122.9, 120.2; LCMS (APCI-MS) calcd. for C12H6Cl2N2O2: 279.98, found (M-H)+ = 279.4; Anal calc. for C12H6Cl2N2O2: C, 51.27; H, 2.15; N, 9.97%, found C, 51.25; H, 2.17; N, 9.98%.

**9-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one(7e)[6]**

Following the general procedure using 3-bromo-2-fluoropyridine (175 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 198 mg (88% yield) of **7e** as a white solid. Following the general procedure using 3-bromo-2-chloropyridine (190 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 183 mg (81% yield) of **7e** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.66 (s, 1H), 8.50 (dd, *J* = 2.00, 4.80 Hz, 1H), 8.26 (dd, *J* = 2.00, 7.40 Hz, 1H), 7.46 (dd, *J* = 4.80, 7.60 Hz, 1H), 7.17 (s, 1H), 7.09-7.05 (m, 2H), 2.27 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 164.9, 162.9, 152.8, 148.5, 142.8, 135.9, 128.3, 127.3, 122.9, 122.6, 121.9, 120.7, 20.6; LCMS (APCI-MS) calcd. for C13H10N2O2: 226.07, found (M+H)+ = 227.4.

**3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7f)[6]**

Following the general procedure using 3-bromo-2-chloro-5-methylpyridine (205 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 151 mg (67% yield) of **7f** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.70 (s, 1H), 8.32 (d, *J* = 2.00 Hz, 1H), 8.08 (d, *J* = 2.00 Hz, 1H), 7.33 (d, *J* = 8.00 Hz, 1H), 7.23-7.14 (m, 3H), 2.32 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 165.1, 161.1, 152.6, 148.8, 142.7, 132.4, 131.1, 126.7, 126.0, 122.3, 122.2, 119.7, 17.3; LCMS (APCI-MS) calcd. for C13H10N2O2: 226.07, found (M+H)+ = 227.4.

**8-chloro-3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one(7g)[6]**

Following the general procedure using 3-bromo-2-chloro-5-methylpyridine (205 mg, 1 mmol) and 2-amino-4-chlorophenol (143 mg, 1 mmol) provided 190 mg (73% yield) of **7g** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.79 (s, 1H), 8.33 (s, 1H), 8.09 (s, 1H), 7.36 (d, *J* = 8.40 Hz, 1H), 7.23-7.20 (m, 2H), 2.33 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 164.8, 160.6, 152.8, 147.4, 142.8, 132.7, 132.6, 130.2, 125.5, 123.9, 121.6, 119.5, 17.3; LCMS (APCI-MS) calcd. for C13H9ClN2O2: 260.03, found (M+H)+ = 261.2.

**3,9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7h)[6]**

Following the general procedure using 3-bromo-2-chloro-5-methylpyridine (205 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 170 mg (71% yield) of **7h** as a pale yellow solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.60 (s, 1H), 8.31 (s, 1H), 8.06 (d, *J* = 2.40 Hz, 1H), 7.15 (s, 1H), 7.06-7.03 (m, 2H), 2.32 (s, 3H), 2.27 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 164.6, 160.7, 152.1, 148.3, 142.2, 135.4, 131.9, 127.9, 126.8, 122.1, 121.5, 119.4, 20.2, 16.9; LCMS (APCI-MS) calcd. for C14H12N2O2: 240.09, found (M+H)+ = 241.4.

**2-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7i)[6]**

Following the general procedure using 3-bromo-2-chloro-6-methylpyridine (205 mg, 1 mmol) and 2-aminophenol (109 mg, 1 mmol) provided 158 mg (70% yield) of **7i** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.65 (s, 1H), 8.15 (d, *J* = 7.72 Hz, 1H), 7.35-7.30 (m, 2H), 7.25-7.14 (m, 3H), 2.49 (s, 3H, overlapped by the solvent residual peak of DMSO-d6); 13C-NMR (100 MHz,CDCl3): δ 166.3, 163.4, 162.5, 148.6, 142.8, 129.9, 126.3, 126.2, 122.7, 121.4, 121.3, 116.5, 24.3; LCMS (APCI-MS) calcd. for C13H10N2O2: 226.07, found(M+H)+ = 227.4.

**2, 9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7j)[6]**

Following the general procedure using 3-bromo-2-chloro-6-methylpyridine (205 mg, 1 mmol) and 2-amino-5-methylphenol (123 mg, 1 mmol) provided 175 mg (73% yield) of **7j** as a white solid. 1H-NMR (400 MHz, DMSO-d6): δ 10.55 (s, 1H), 8.13 (d, *J* = 8.00 Hz, 1H), 7.30 (d, *J* = 7.60 Hz, 1H), 7.17 (s, 1H), 7.07-7.01 (m, 2H), 2.50 (s, 3H, overlapped by the solvent residual peak of DMSO-d6), 2.27 (s, 3H); 13C-NMR (100 MHz, DMSO-d6): δ 165.0, 162.8, 162.2, 148.4, 142.8, 135.7, 128.4, 128.3, 127.2, 122.6, 122.1, 121.9, 117.5, 24.2, 20.5; LCMS (APCI-MS) calcd. for C14H12N2O2: 240.09, found (M+H)+ = 241.4.

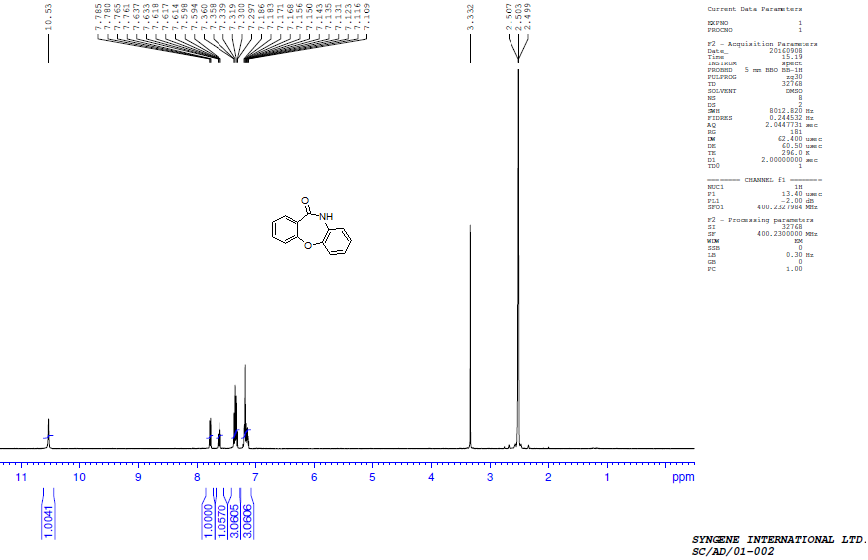
**5-(4-Methylpiperazin-1-yl)-8-chloro-pyrido[2,3-b][1,5]-benzoxazepine (JL 13)[7]**

A solution of 8-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one **7b** (100 mg, 0.41 mmol) in POCl3 (2 mL) was heated to reflux for 16 h. On completion, the reaction mixture was cooled to RT; the excess phosphorus oxychloride was removed under reduced pressure. The residue obtained was co evaporated with toluene (2x 10 mL) to afford crude iminochloride as a brown sticky residue which was used without further purification. It was dissolved in toluene (2 mL), and an excess of 1-Methylpiperazine (406 mg, 4.1 mmol) was added. The mixture was heated to reflux for 2 h. The solvent was then evaporated under reduced pressure, and the residue was dissolved in chloroform (15 mL) and washed with water (2× 10 mL), brine (1× 10 mL), dried over anhydrous sodium sulphate filtered through a cotton plug and concentrated under reduced pressure to afford crude. Crude obtained was purified by flash column chromatography on silica gel (230-400 mesh) with MeOH and dichloromethane as eluent to afford 133 mg (75% yield) of **JL 13** as beige solid. 1H-NMR (400 MHz, CDCl3): δ 8.51 (dd, *J* = 1.20, 4.60 Hz, 1H), 7.60 (dd, *J* = 1.20, 8.20 Hz, 1H), 7.43 (dd, *J* = 4.40, 8.20 Hz, 1H), 7.16 (d, *J* = 2.80 Hz, 1H), 7.06 (d, *J* = 8.40 Hz, 1H), 06.91 (dd, *J* = 2.40, 8.60 Hz, 1H), 3.74-3.73 (m, 4H), 2.60-2.50 (m, 4H), 2.38 (s, 3H); LCMS (APCI-MS) calcd. for C17H17ClN4O: 328.10, found [M+H]+ = 329.0.

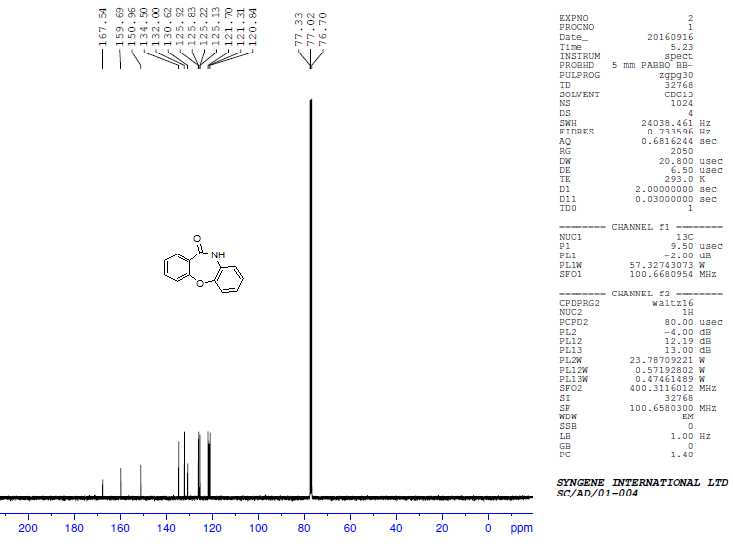
**3. References**

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2. Shen, C.; Neumann, H.; Wu, X.-F. *Green Chem.* **2015**, 17, 2994.
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4. Kathryn, R.; Holger, P. *Envivo Pharmaceuticals, Inc., USA; MethylGene Inc*. **2009**, WO 2009137462 A2.
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6. Shen, C.; Wu, X.-F. *Catal. Sci. Technol.* **2015**, 5(9), 4433.
7. Liebgeois, J. -F.; Rogistert, F. A.; Bruhwyler, J.; Damas, J.; Nguyen, T. P.; Inarejos, M. O.; Chleide, E. M. G.; Mercier, M. G. A.; Delarge, J. E. *J. Med. Chem.* **1994**, 37, 519.

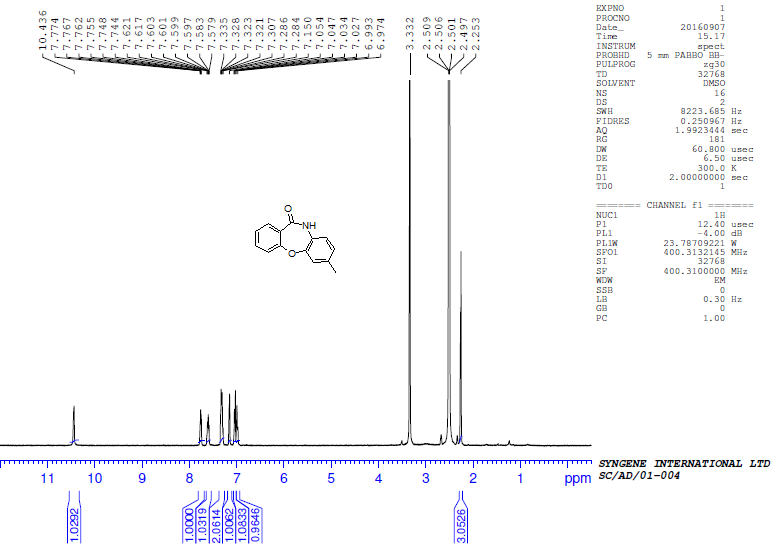
**4. 1H and 13C NMR spectra**

**IH NMR of dibenzo[b,f][1,4]oxazepin-11(10H)-one (3a)**

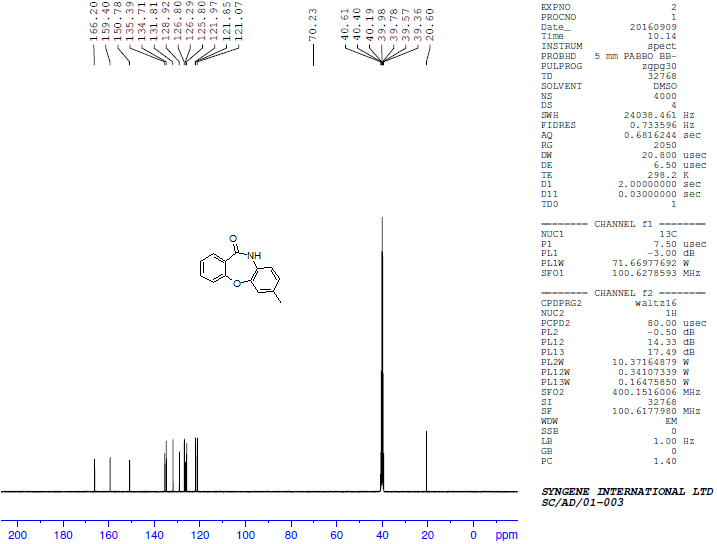
**I3C NMR of dibenzo[b,f][1,4]oxazepin-11(10H)-one (3a)**

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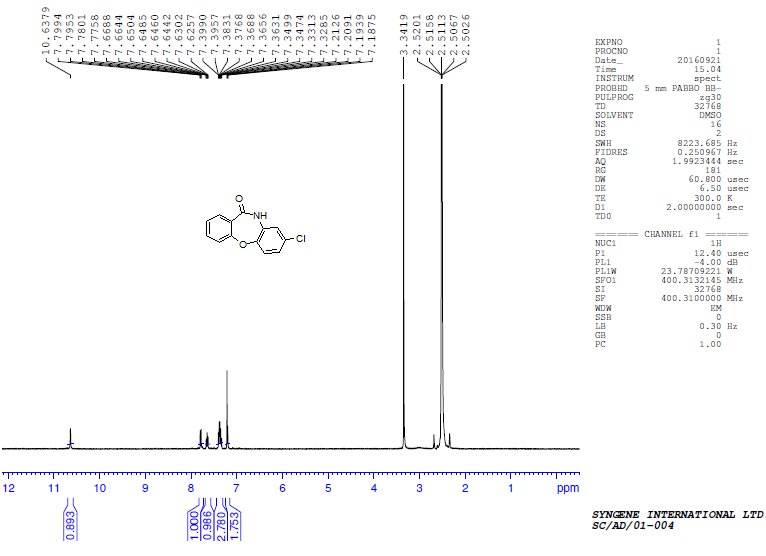
**IH NMR of 7-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3b)**



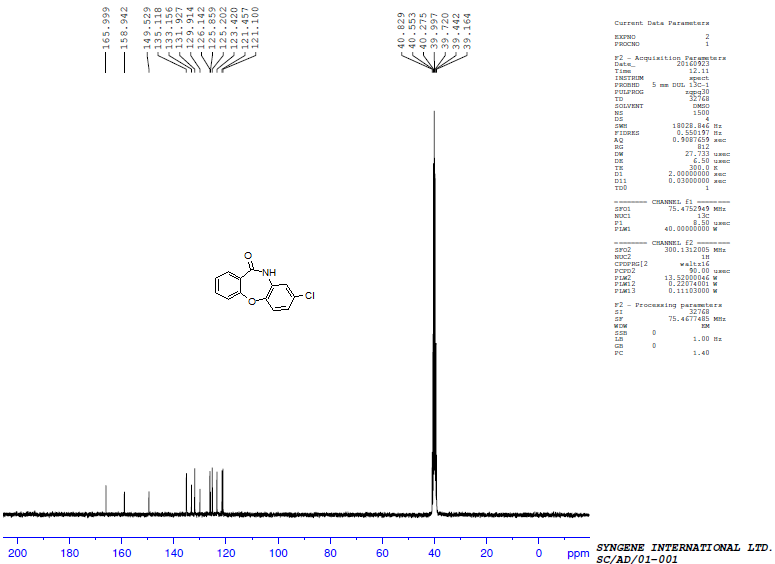
**I3C NMR of 7-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3b)**

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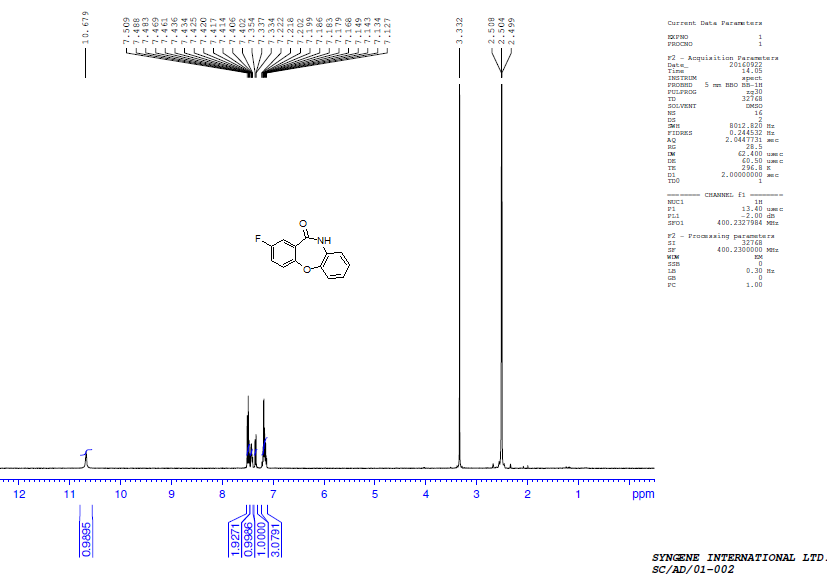
**IH NMR of 8-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one (3c)**

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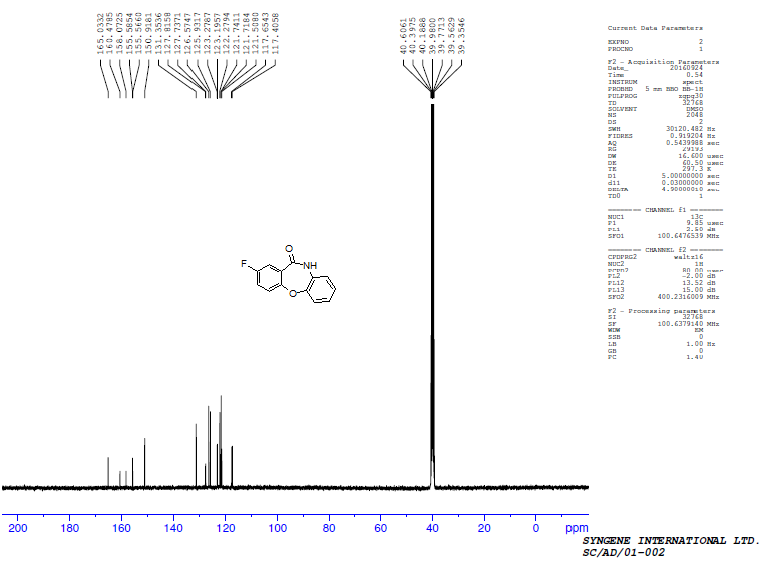
**I3C NMR of 8-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one (3c)**

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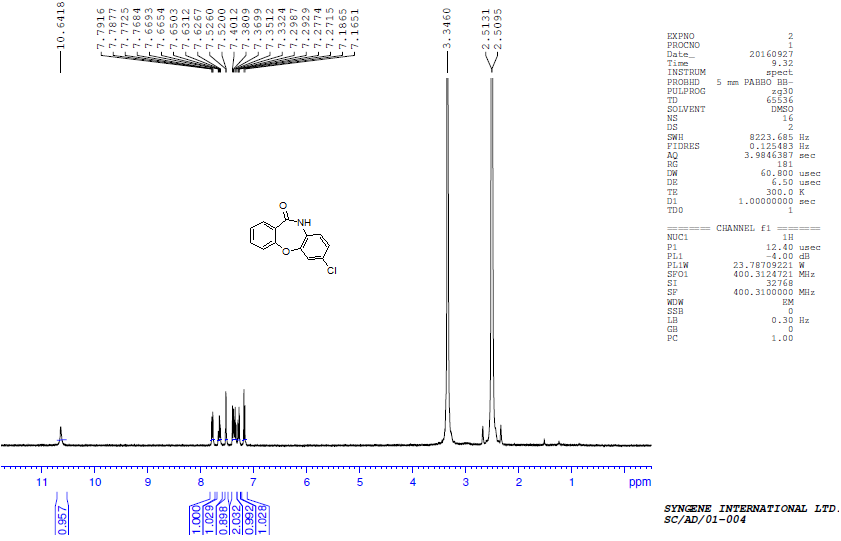
**IH NMR of 2-fluorodibenzo[b,f][1,4]oxazepin-11(10H)-one (3d)**

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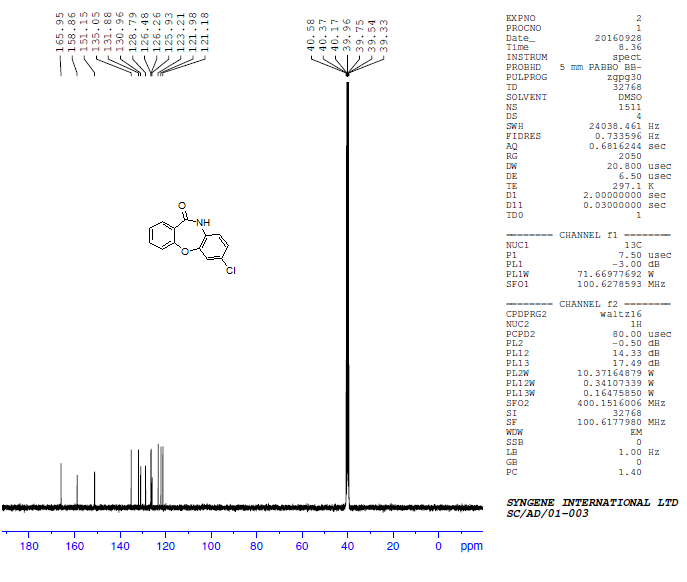
**I3C NMR of 2-fluorodibenzo[b,f][1,4]oxazepin-11(10H)-one (3d)**

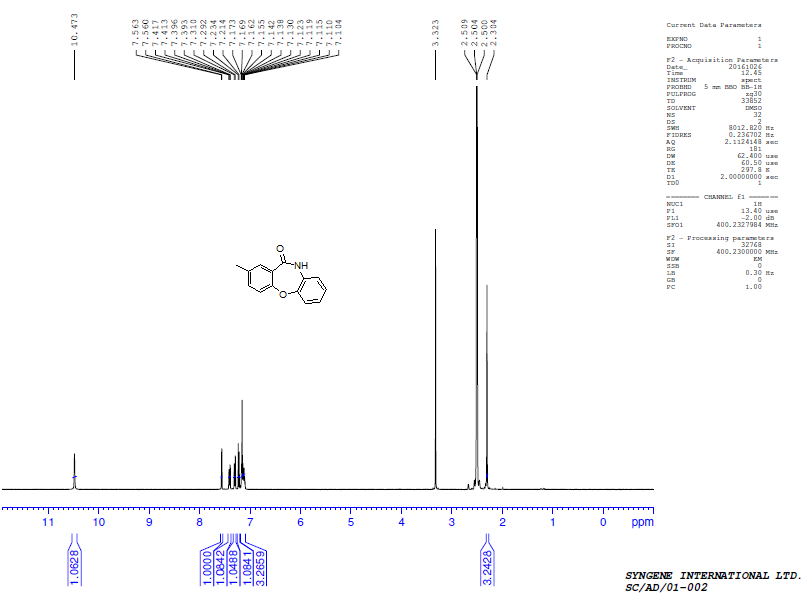
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**IH NMR of 7-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one (3e)**

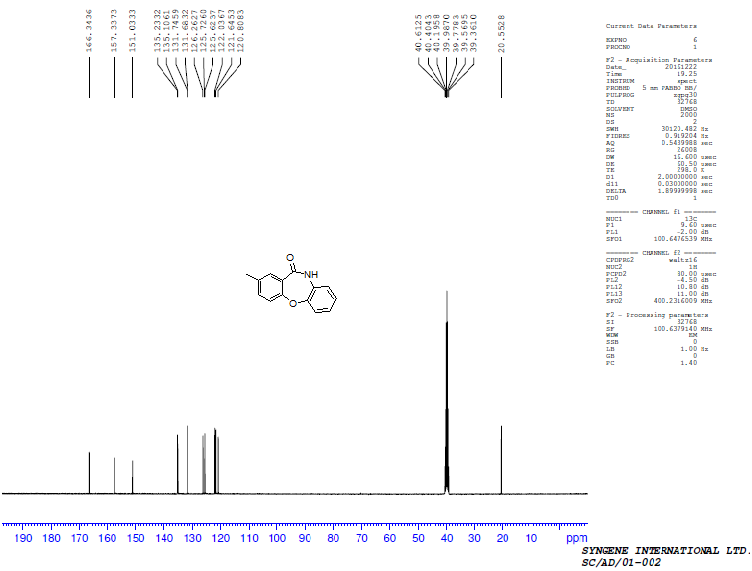
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**I3C NMR of 7-chloroldibenzo[b,f][1,4]oxazepin-11(10H)-one (3e)**

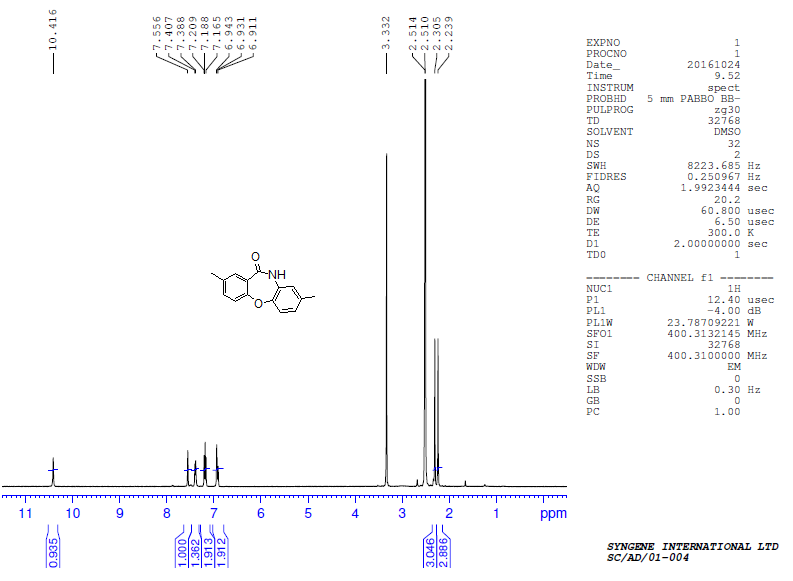
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**IH NMR of 2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3f)**

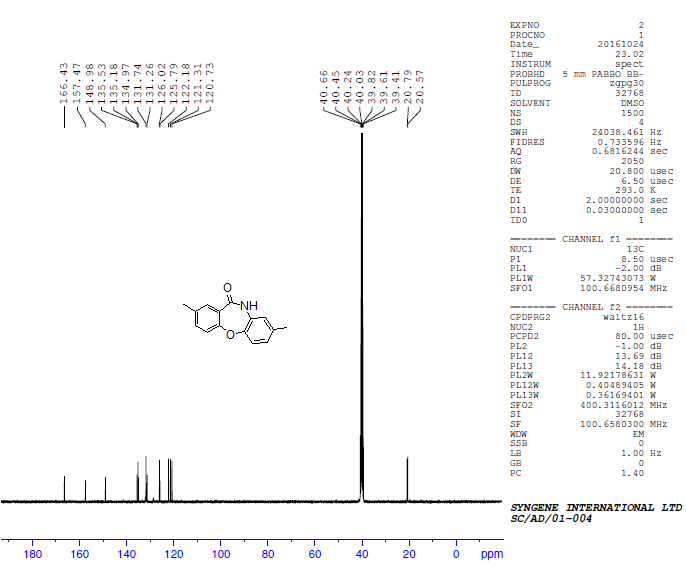
**I3C NMR of 2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3f)**

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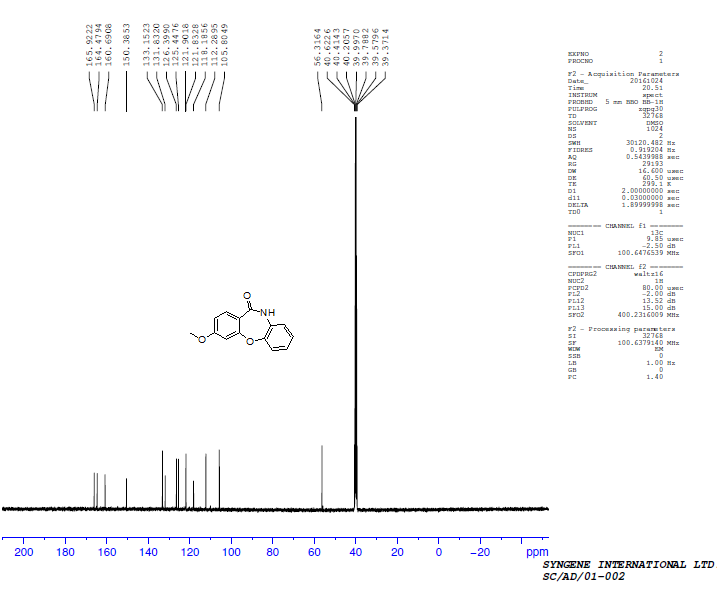
**IH NMR of 2, 8-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3g)**

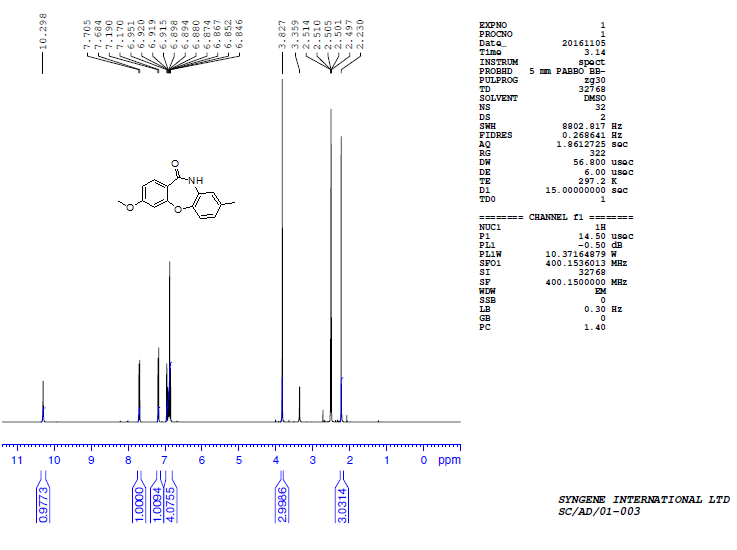
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**I3C NMR of 2, 8-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3g)**

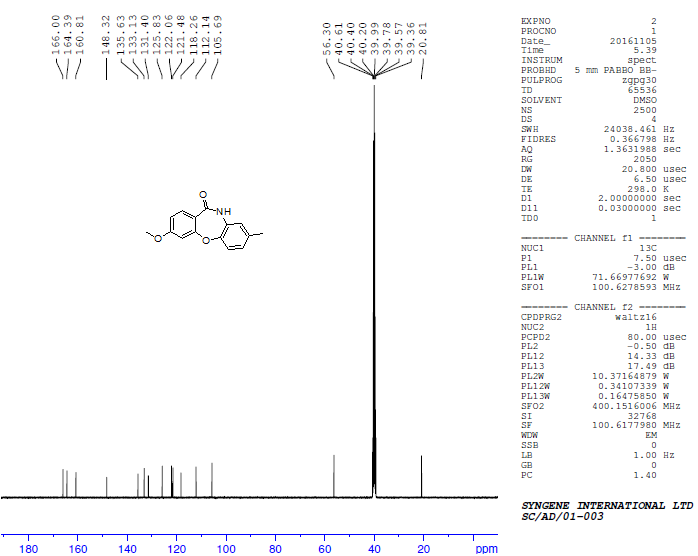
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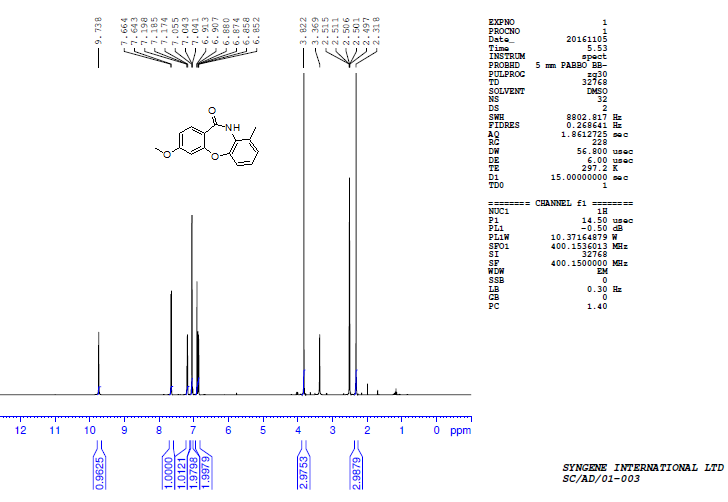
**IH NMR of 3-methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (3h)**

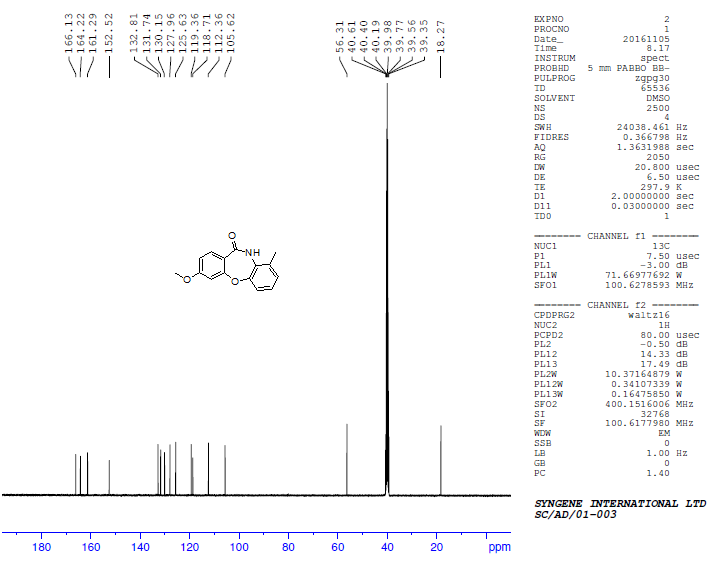
**I3C NMR of 3-methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (3h)**

**IH NMR of 3-methoxy-8-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3i)**

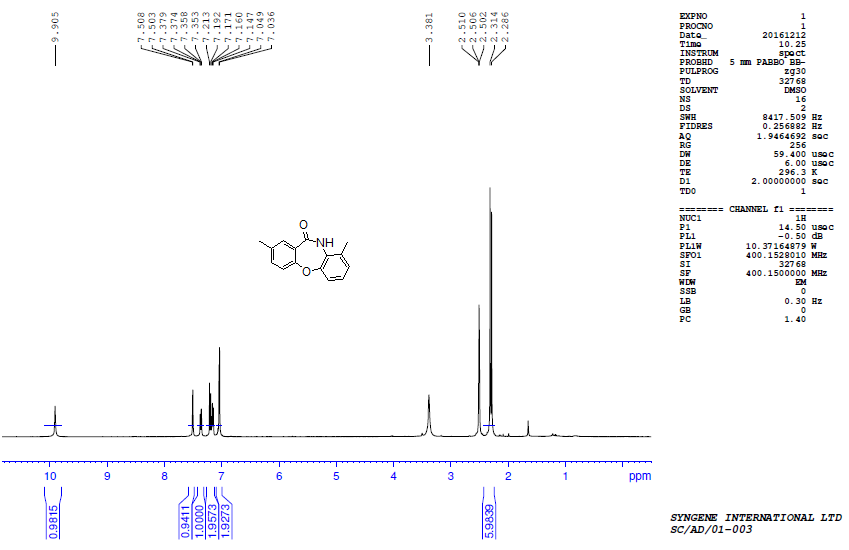
**I3C NMR of 3-methoxy-8-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3i)**

****

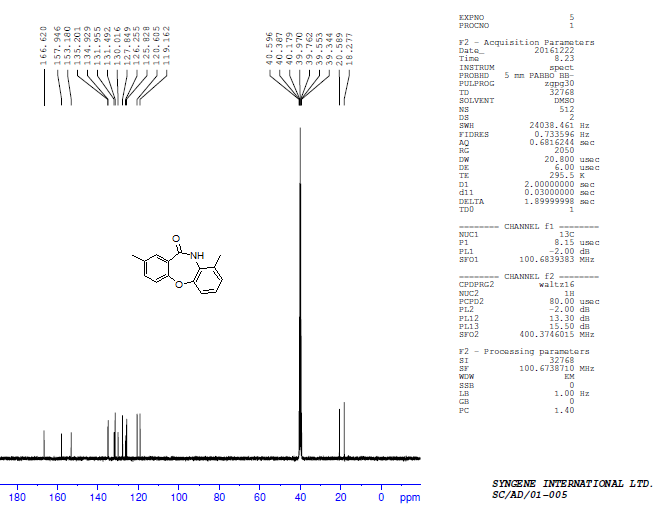
**IH NMR of 3-methoxy-9-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3j)**

**I3C NMR of 3-methoxy-9-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3j)**

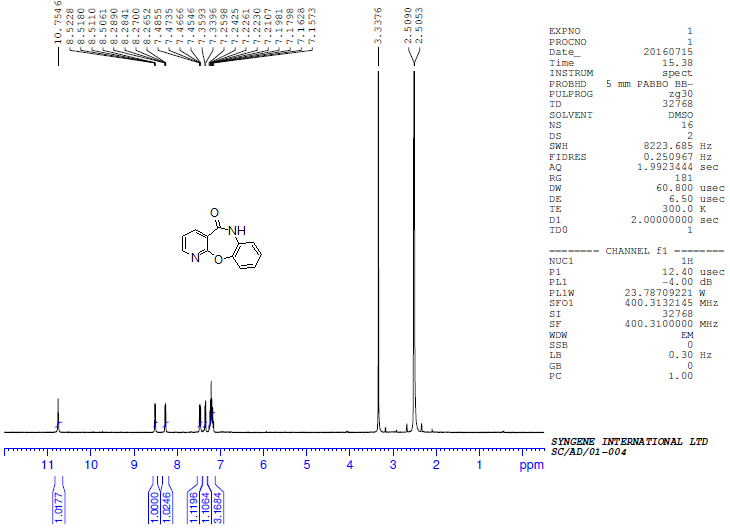
**IH NMR of 2, 9-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3k)**

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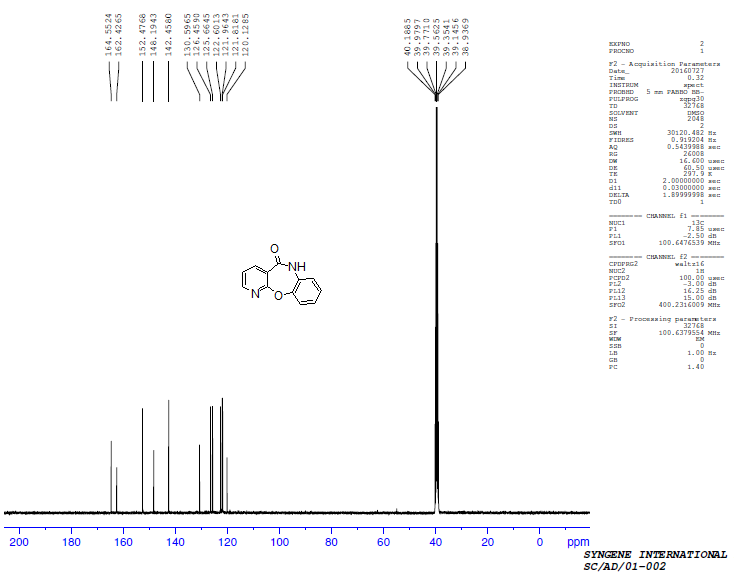
**I3C NMR of 2, 9-dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (3k)**

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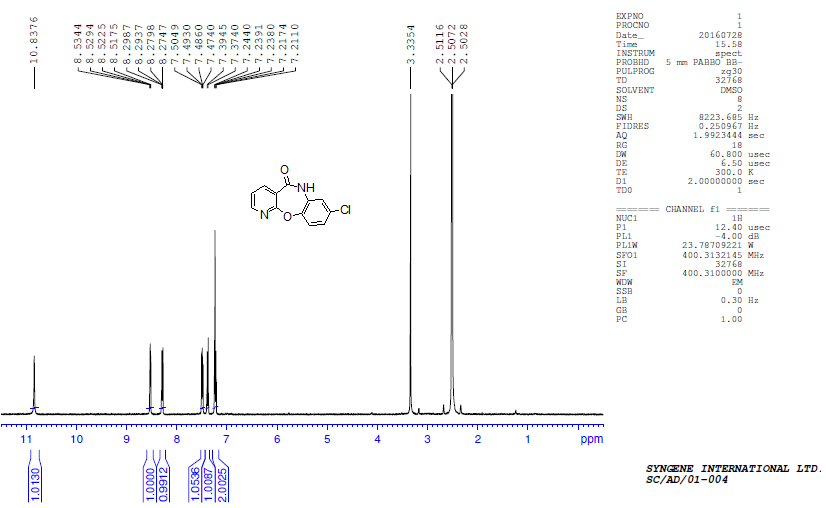
**IH NMR of benzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7a)**

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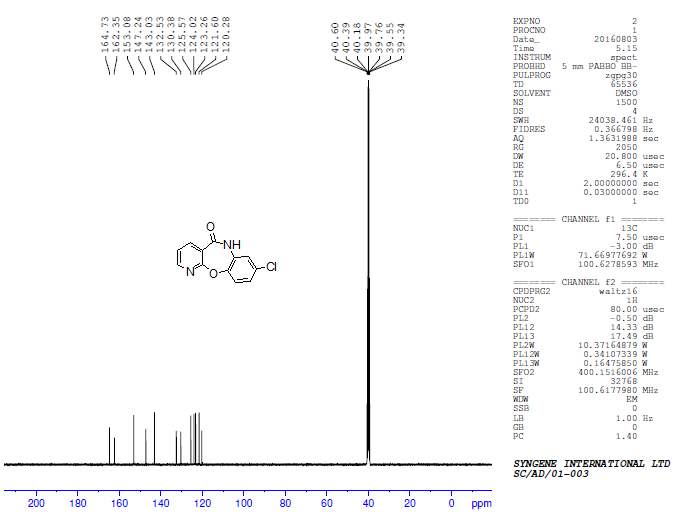
**I3C NMR of benzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7a)**

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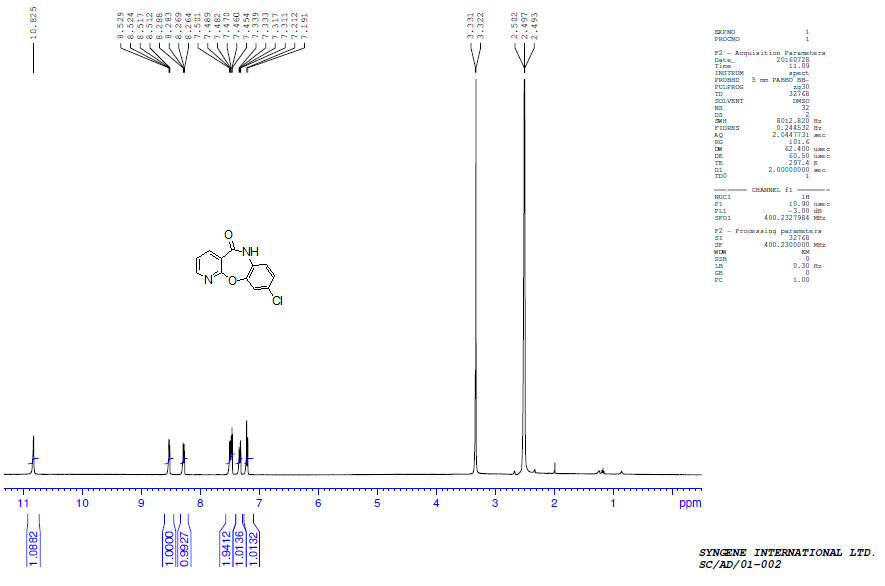
**IH NMR of 8-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7b)**

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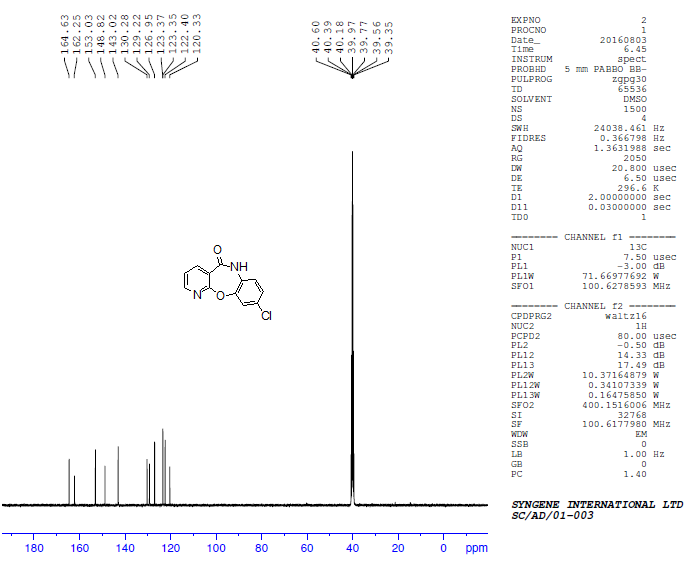
**I3C NMR of 8-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7b)**

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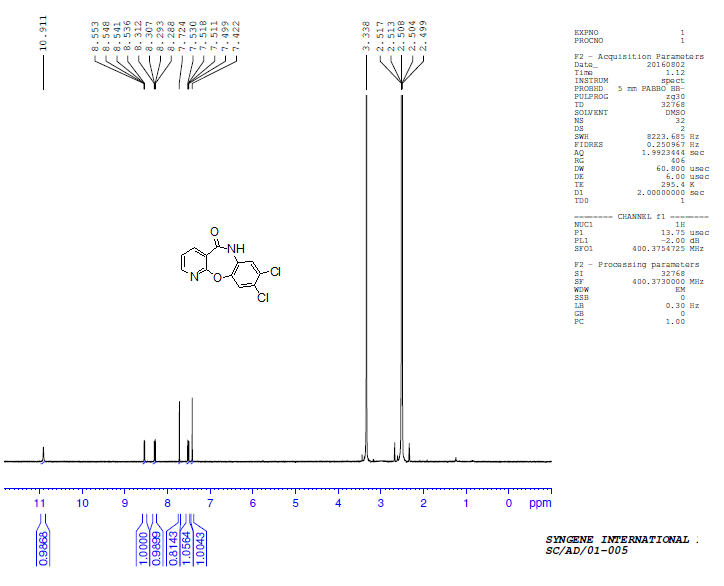
**IH NMR of 9-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7c)**

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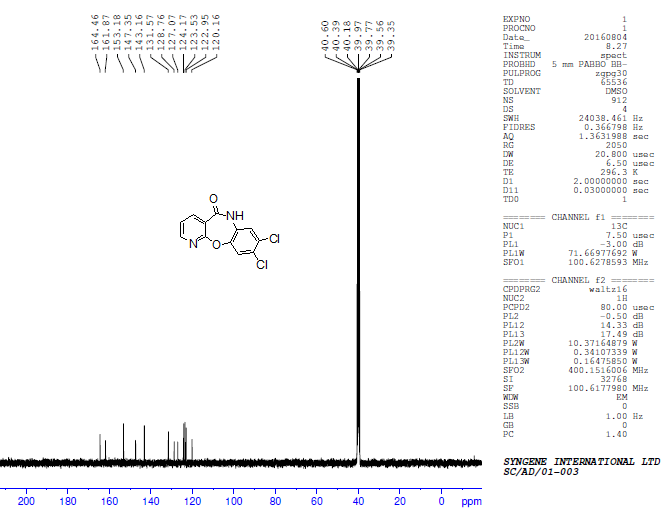
**I3C NMR of 9-chlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7c)**

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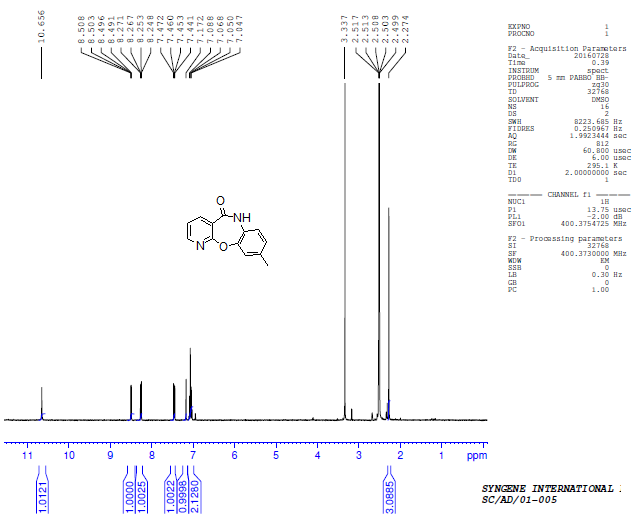
**IH NMR of 8, 9-dichlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7d)**

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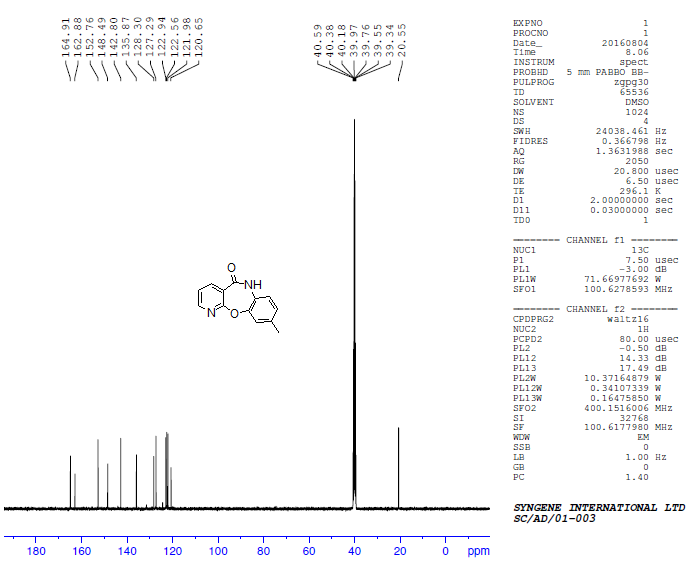
**I3C NMR of 8, 9-dichlorobenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7d)**

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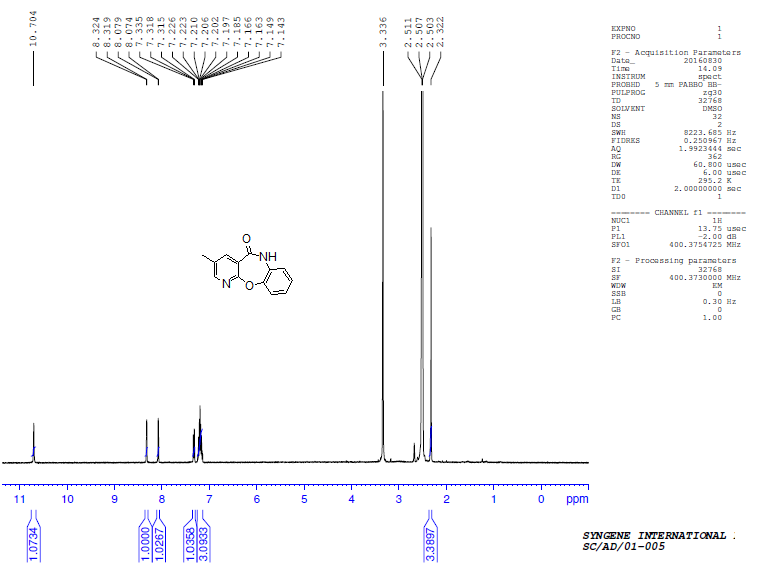
**IH NMR of 9-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7e)**

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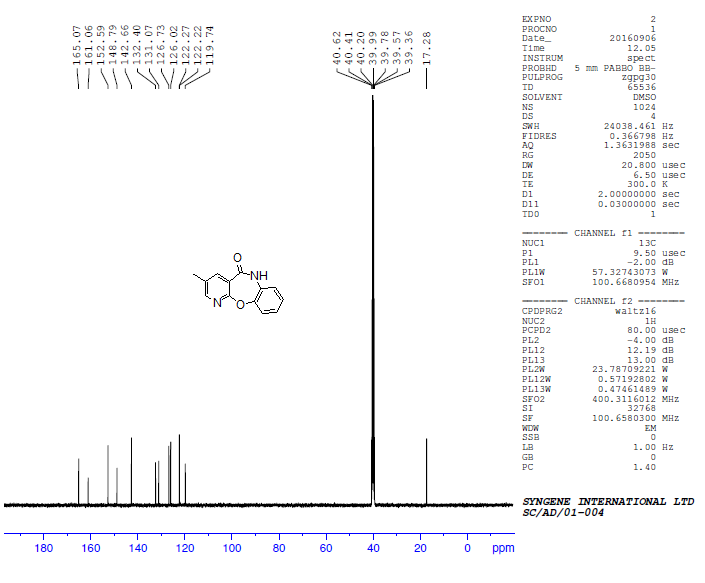
**I3C NMR of 9-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7e)**

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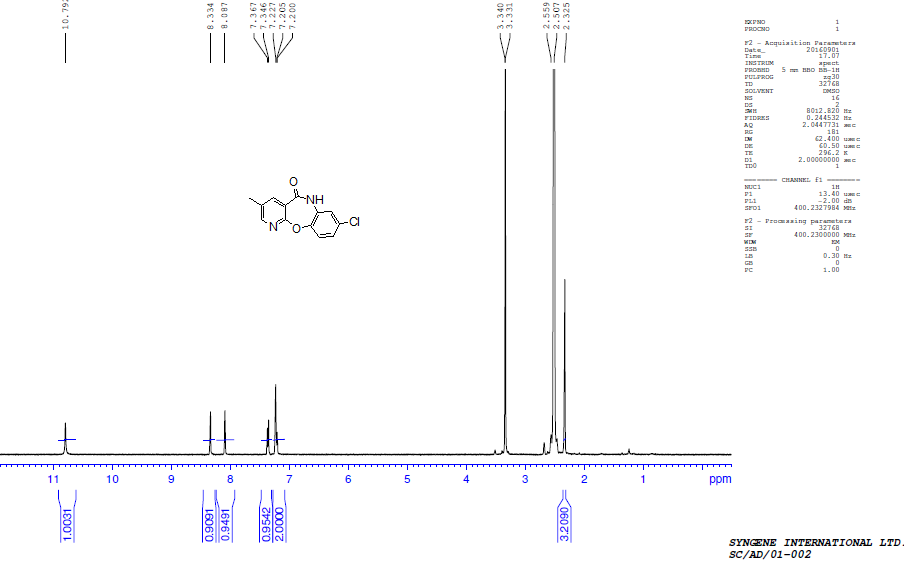
**IH NMR of 3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7f)**

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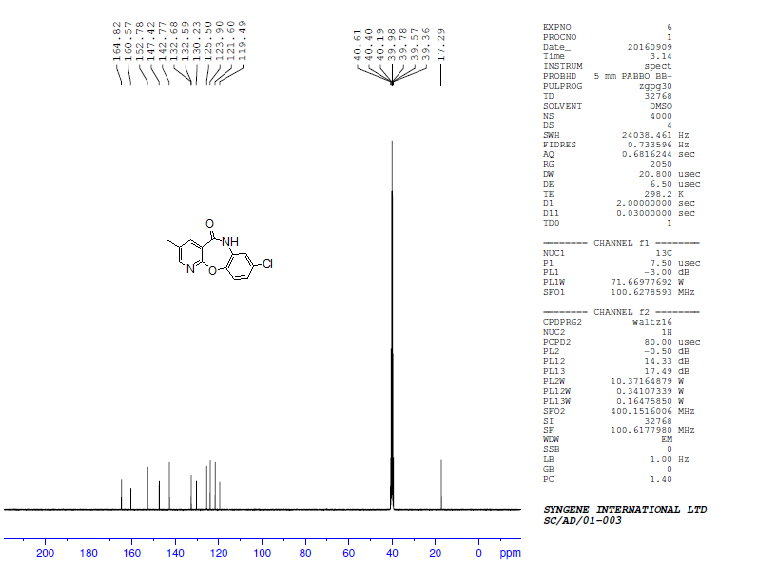
**I3C NMR of 3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7f)**

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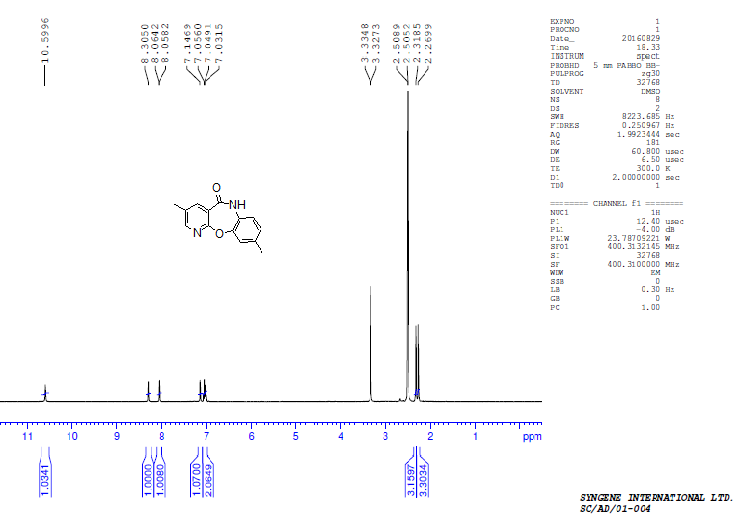
**IH NMR of 8-chloro-3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7g)**

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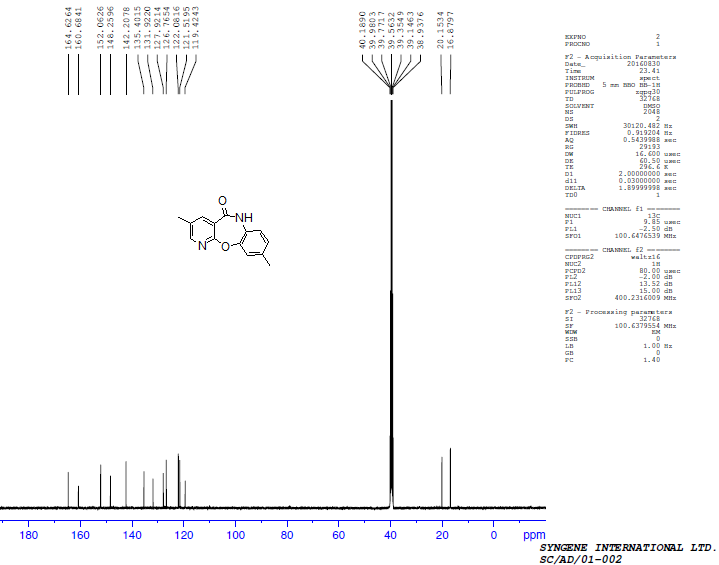
**I3C NMR of 8-chloro-3-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7g)**

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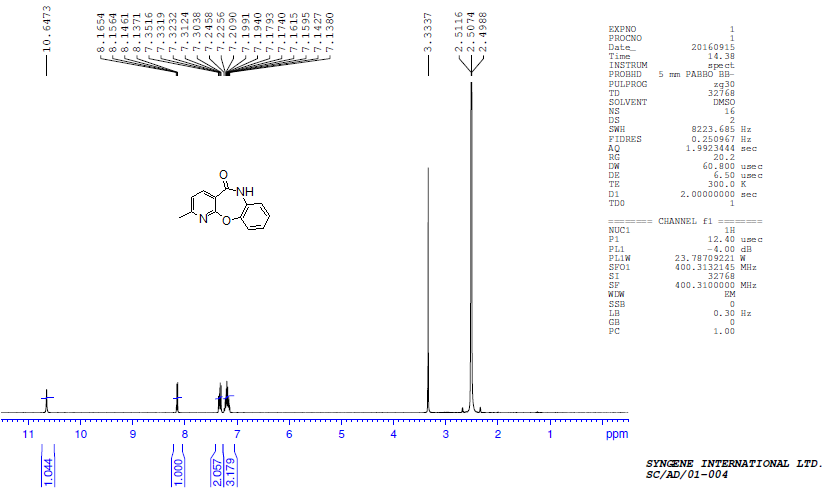
**IH NMR of 3, 9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7h)**

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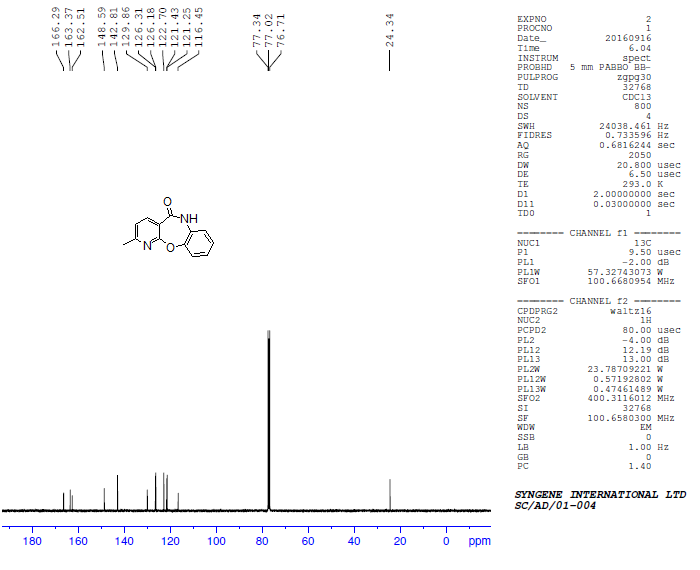
**I3C NMR of 3, 9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7h)**

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**IH NMR of 2-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7i)**

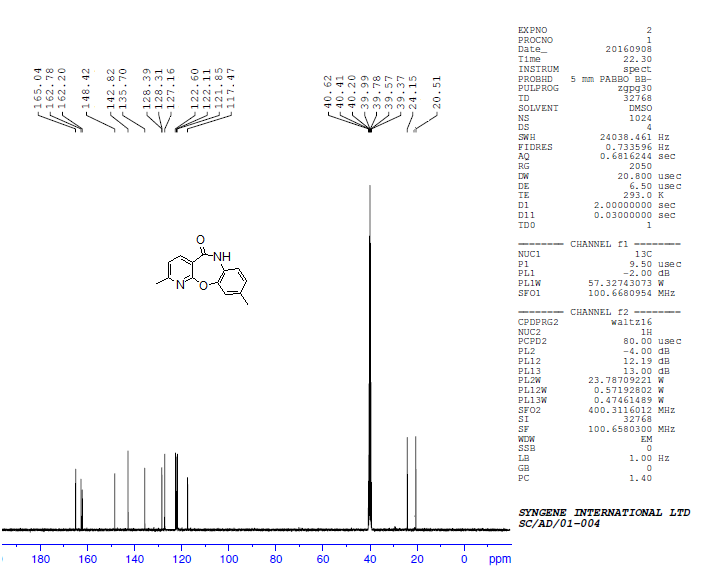
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**I3C NMR of 2-methylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7i)**

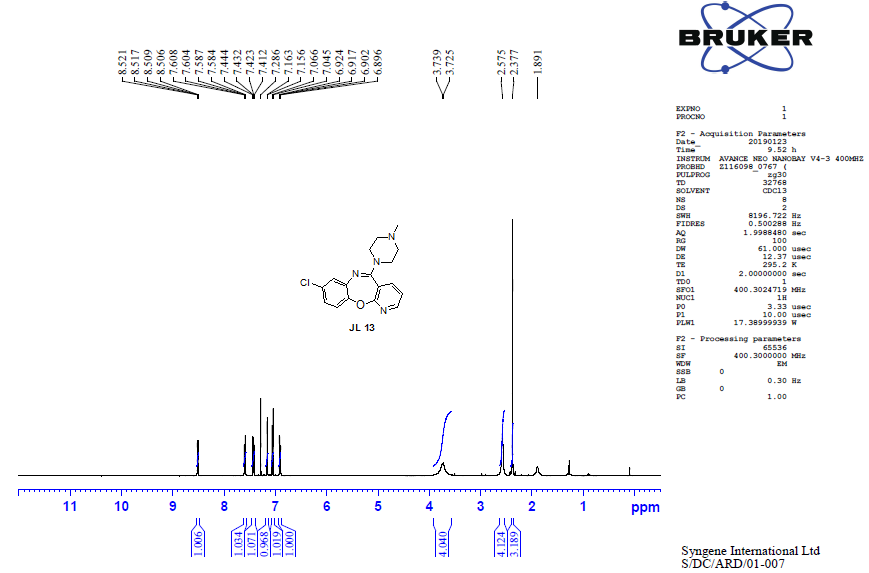
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**IH NMR of 2, 9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7j)**

****

**I3C NMR of 2, 9-dimethylbenzo[b]pyrido[3,2-f][1,4]oxazepin-5(6H)-one (7j)**

**IH NMR of 5-(4-Methylpiperazin-1-yl)-8-chloro-pyrido[2,3-b][1,5]-benzoxazepine (JL 13)**

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