Synthetic Utilization of Polynitroaromatic Compounds. 3. Preparation of Substituted Dibenz[*b,f*][1,4]oxazepine-11(10H)-ones Starting from 2,4,6-Trinitrobenzoic Acid via Nucleophilic Displacement of Nitro Groups.

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Characterization data for compounds 3b,c,f,g,i-o, 4b,d,f-h, 9c-f

3-Ethoxy-1-nitrodibenz[*b,f*][1,4]oxazepin-11(10H)-one (3b): m.p. 219-221°C . ^{1}H NMR (DMSO-d_6, δ): 1.35 (t, *J* = 7.5 Hz, 3H), 4.18 (q, *J* = 7.5 Hz, 2H), 7.15-7.23 (m, 4H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 10.71 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 300 [M^+, 100], 255 [40]. Anal. Calcd. for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 59.79; H, 4.10; N, 9.23.

1-Nitro-3-propoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (3c): m.p. 228-229°C (разл.). ^{1}H NMR (DMSO-d_6, δ): 0.98 (t, *J* = 7.4 Hz, 3H), 1.74 (m, 2H), 4.11 (t, *J* = 7.5 Hz, 2H), 7.17-7.26 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 10.71 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 314 [M^+, 100], 269 [38]. Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91. Found: C, 60.64; H, 4.57; N, 9.01.

3- (2-Hydroxyethoxy)-1-nitrodibenz[*b,f*][1,4]oxazepin-11(10H)-one (3f): m.p. 207-210°C . ^{1}H NMR (DMSO-d_6, δ): 3.72 (m, 2H), 4.13 (m, 2H), 4.85 (br.s, 1H), 7.15-7.23 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 10.72 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 316 [M^+, 98], 271 [43], 45 [100]. Anal. Calcd. for $C_{15}H_{12}N_2O_6$: C, 56.97; H, 3.82; N, 8.86. Found: C, 56.80; H, 3.89; N, 8.76.

3-Benzyloxy-1-nitrodibenz[*b,f*][1,4]oxazepin-11(10H)-one (3g): m.p. 200-201°C (разл.). ^{1}H NMR (DMSO-d_6, δ): 5.23 (s, 2H), 7.15-7.22 (m, 3H), 7.30-7.45 (m, 8H), 10.70 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 362 [M^+, 8], 91 [100]. Calcd. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73. Found: C, 66.18 ; H, 3.93; N, 7.67.

3-(3-Methylphenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3i): m.p. 197-199°C . ^{1}H NMR (DMSO-d_6, δ): 2.36 (s, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 7.10-7.17 (m, 3H),

7.19-7.26 (m, 3H), 7.31 (d, 1H, *J* = 7.9 Hz), 7.36 (t, *J* = 8.0 Hz, 1H), 10.77 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 362 [M^+, 100], 317 [45]. Anal. Calcd. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73. Found: C, 66.18; H, 3.95; N, 7.66.

3-(4-Methylphenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3j): m.p. 213-215°C (decomp.). ^{1}H NMR (DMSO-d_6, δ): 2.36 (s, 3H), 7.03-7.12 (m, 3H), 7.13-7.26 (m, 4H), 7.27-7.37 (m, 3H), 10.76 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 362 [M^+, 100], 317 [50], 91 [45]. Anal. Calcd. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73. Found: C, 66.21; H, 3.96; N, 7.65 .

3-(2-Methoxyphenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3k): m.p. 237-239°C (decomp.). ^{1}H NMR (DMSO-d_6, δ): 3.77 (s, 3H), 6.97 (s, 1H), 7.03-7.08 (m, 1H), 7.09 (s, 1H), 7.10-7.25 (m, 5H), 7.27-7.37 (m, 2H), 10.72 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 378 [M^+, 100], 333 [27], 77 [40]. Anal. Calcd. for $C_{20}H_{14}N_2O_6$: C, 63.50; H, 3.73; N, 7.40. Found: C, 63.40; H, 3.84; N, 7.31.

3-(4-Methoxyphenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3l): m.p. 211-213°C . ^{1}H NMR (DMSO-d_6, δ): 3.83 (s, 3H), 7.02-7.06 (m, 3H), 7.13-7.27 (m, 6H), 7.32 (d, *J* = 8.2 Hz, 1H), 10.72 (br.s, NH). Anal. Calcd. for $C_{20}H_{14}N_2O_6$: C, 63.50; H, 3.73; N, 7.40. Found: C, 63.41; H, 3.80; N, 7.33.

3-(2-Bromophenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3m): m.p. 224-226°C . ^{1}H NMR (DMSO-d_6, δ): 7.07 (s, 1H), 7.12-7.17 (m, 1H), 7.20-7.40 (m, 6H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 10.78 (br.s, NH). Anal. Calcd. for $C_{19}H_{11}BrN_2O_5$: C, 53.42; H, 2.60; N, 6.56; Br, 18.70. Found: C, 53.33; H, 2.57; N, 6.46; Br, 18.59.

3-(4-Bromophenoxy)-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3n): m.p. 218-219°C . ^{1}H NMR (DMSO-d_6, δ): 7.16-7.23 (m, 6H), 7.28-7.36 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 10.76 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 426 [M^+, 100], 428 [M^+, 95]. Anal. Calcd. for

$C_{19}H_{11}BrN_2O_5$: C, 53.42; H, 2.60; N, 6.56; Br, 18.70. Found: C, 53.32; H, 2.61; N, 6.47; Br, 18.61

3-Benzylsulfanyl-1-nitrodibenz[*b,f*][1,4]oxazepine-11(10H)-one (3o): m.p. 208-210°C . ^{1}H NMR (DMSO-d_6, δ): 4.38 (s, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.22-7.28 (m, 3H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.38-7.42 (m, 3H), 7.47 (s, 1H), 10.68 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 378 [M^+, 10], 348 [14], 91 [100]. Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73; N, 7.40; S, 8.47. Found: C, 63.40 ; H, 3.80; N, 7.35; S, 8.39.

1,3-Bis(3-methylphenoxy)dibenz[*b,f*][1,4]oxazepin-11(10H)-one (4b): m.p. 168-171°C. ^{1}H NMR (DMSO-d_6, δ): 2.23 (s, 3H), 2.28 (s, 3H), 6.27 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.10 (m, 5H), 7.20 (m, 2H), 7.32 (m, 3H), 7.40 (t, *J* = 8.1 Hz, 2H), 10.25 (br.s, 1H). Anal. Calcd. for $C_{27}H_{21}NO_4$: C, 76.58; H, 5.00; N, 3.31. Found: C, 76.84; H, 5.09; N, 3.08.

1-Butylsulfanyl-3-methoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (4d): m.p. 102-104°C. ^{1}H NMR (DMSO-d_6, δ): 0.87 (t, *J* = 7.2 Hz, 3H), 1.39 (m, 2H), 1.54 (m, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 6.71 (s, 2H), 7.1-7.2 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 1H), 10.28 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 329 [M^+, 86], 300 [75], 287 [68], 272 [100]. Anal. Calcd. for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25; S, 9.73. Found: C, 65.86; H, 5.75; N, 4.49; S, 9.51.

1-((4-Methylphenyl)sulfanyl)-3-phenoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (4f): m.p. 233-235°C. ^{1}H NMR (DMSO-d_6, δ): 2.34 (s, 3H), 5.98 (s, 1H), 6.69 (s,1H), 6.95 (d, *J* = 8.3 Hz, 2H), 7.11-7.24 (m, 6H), 7.28-7.36 (m, 5H), 10.52 (br.s, NH). EI-MS (70 eV) (*m/z*, *I*, %): 425 [M^+, 100], 333 [25], 303 [30] . Anal. Calcd. for $C_{26}H_{19}NO_3S$: C, 73.39; H, 4.50; N, 3.29; S, 7.54. Found: C, 73.24; H, 4.54; N, 3.34; S, 7.47.

1,3-Bis((4-methylphenyl)sulfanyl)dibenz[*b,f*][1,4]oxazepin-11(10H)-one (4g): m.p. 245-246°C. ^{1}H NMR (DMSO-d_6, δ): 2.36 (s, 3H), 2.38 (s, 3H), 6.12 (s, 1H), 6.97 (s, 1H), 7.08-7.25 (m, 11H), 7.33 (d, *J* = 8.0 Hz, 1H), 10.57 (br.s, NH). Anal. Calcd. for $C_{27}H_{21}NO_2S_2$: C, 71.18; H, 4.65; N, 3.07; S, 14.08. Found: C, 71.09; H, 4.74; N, 3.18; S, 14.00.

1,3-Di(butylsulfanyl)dibenz[*b,f*][1,4]oxazepin-11(10H)-one (4h): m.p. 115-117°C. ^{1}H NMR (DMSO-d_6, δ): 0.87 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.40 (m, 4H), 1.51 (m, 2H), 1.59 (m, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 7.01 (s, 1H), 7.03 (s, 1H), 7.1-7.2 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 1H), 10.43 (br.s, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 387 [M^+, 93], 331 [100], 330 [92] . Anal. Calcd. for $C_{21}H_{25}NO_2S_2$: C, 65.08; H, 6.50; N, 3.61; S, 16.55. Found: C, 65.23; H, 6.54; N, 3.23; S, 16.73.

10-Methyl-1-nitro-3-phenoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (9c): MeI is used as alkylating agent. M.p. 132-133°C . ^{1}H NMR (DMSO-d_6, δ): 3.54 (s, 3H), 7.02 (br.s, 1H), 7.14 (m, 3H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.30 (m, 3H), 7.48 (t, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 362 [M^+, 61], 334 [63], 77 [100]. Anal. Calcd. for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73. Found: C, 66.64; H, 3.72; N, 7.90 .

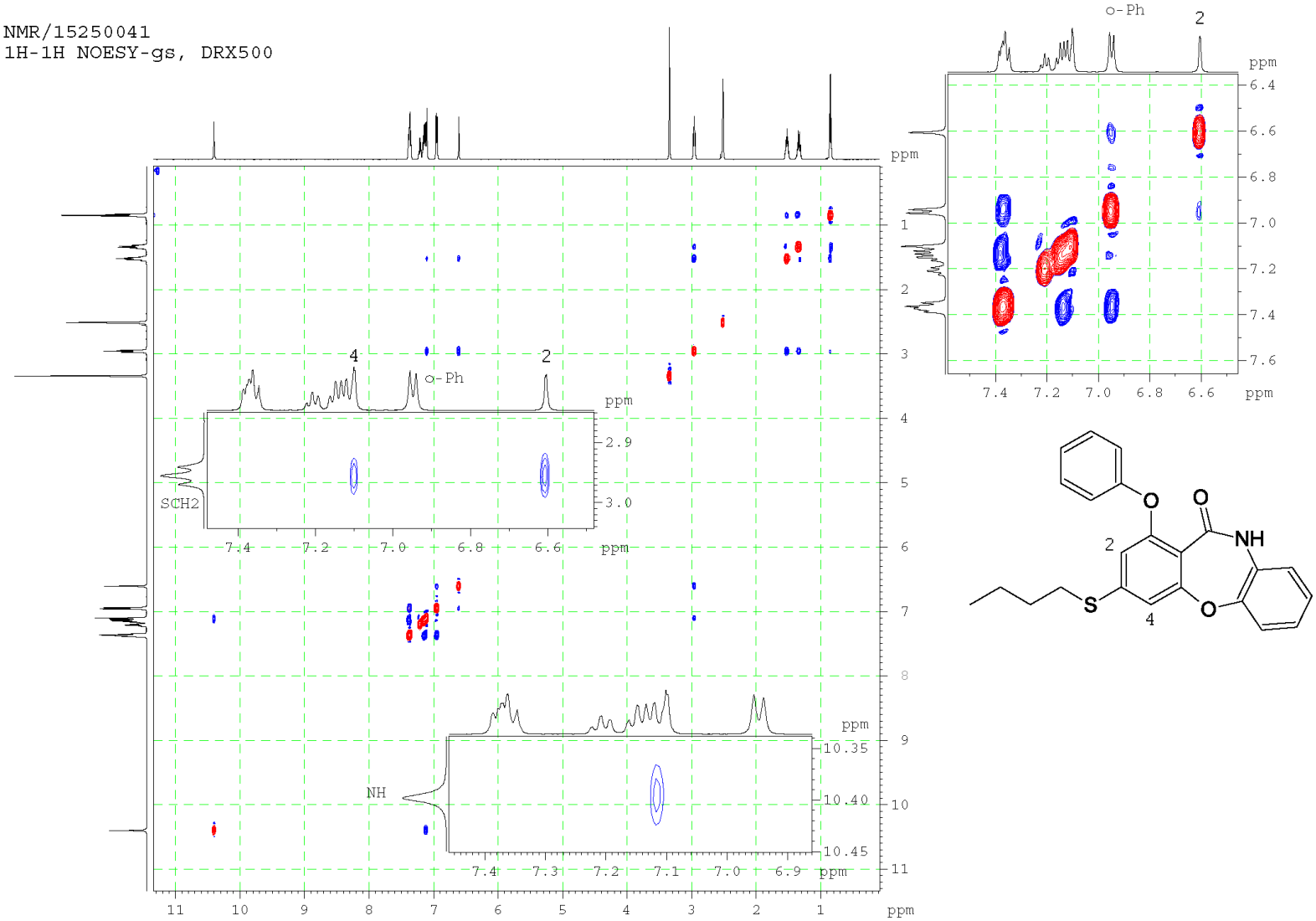
10-Allyl-1-nitro-3-phenoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (9d): allyl bromide is used as alkylating agent. M.p. 133-137°C (decomp.). ^{1}H NMR (DMSO-d_6, δ): 4.6 (br.s, 2H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.94 (m, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.29 (m, 3H), 7.48 (t, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H). EI-MS (70 eV) (*m/z*, *I*, %): 388 [M^+, 67], 77 [91], 43 [100]. Anal. Calcd. for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.15; N, 7.21. Found: C, 67.78; H, 4.02; N, 7.49.

10-(4-Nitrobenzyl)-1-nitro-3-phenoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (9e): 4-nitrobenzyl bromide is used as alkylating agent. Decomp.>230°C. ^{1}H NMR spectrum (DMSO-d_6,

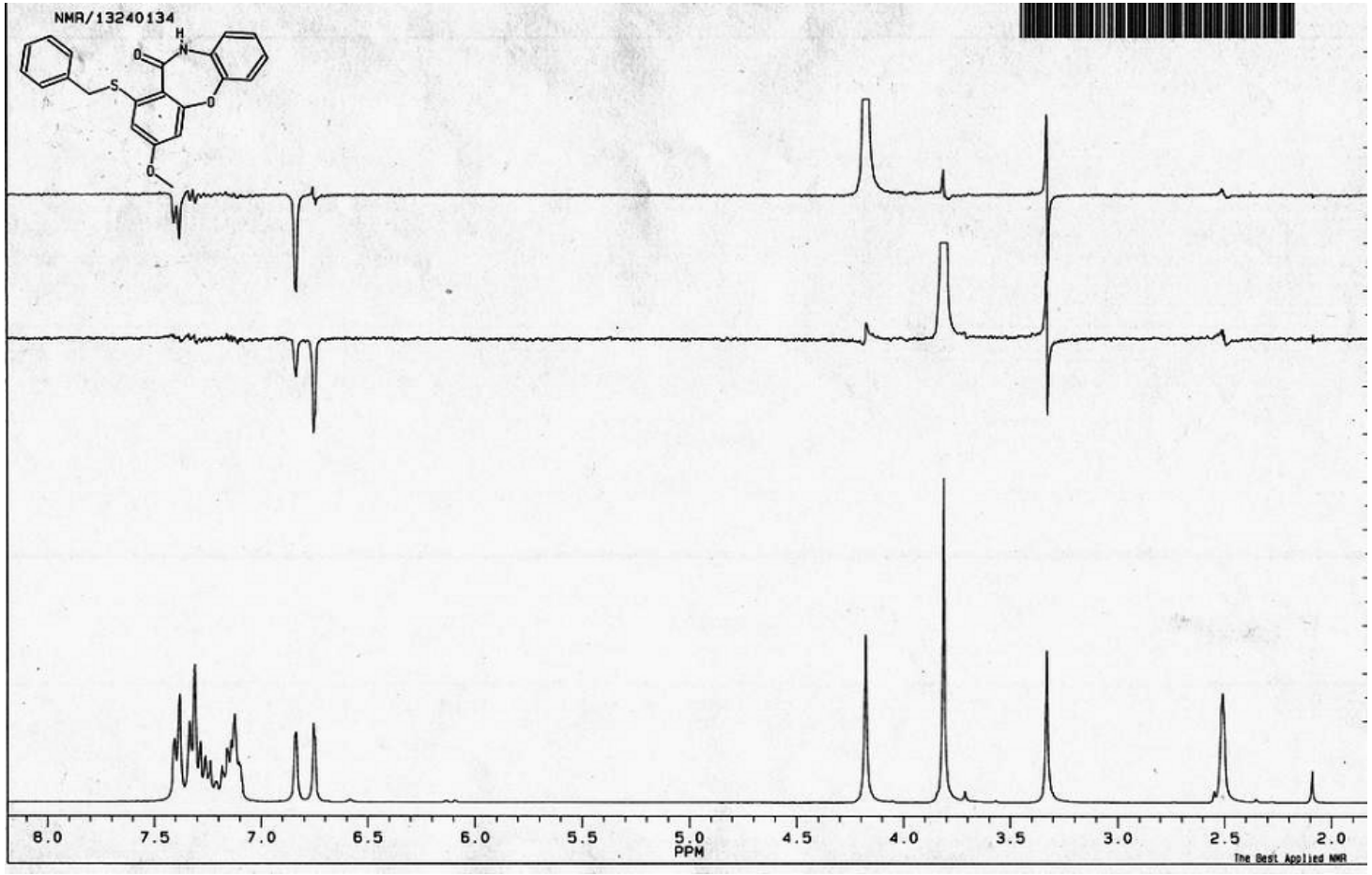
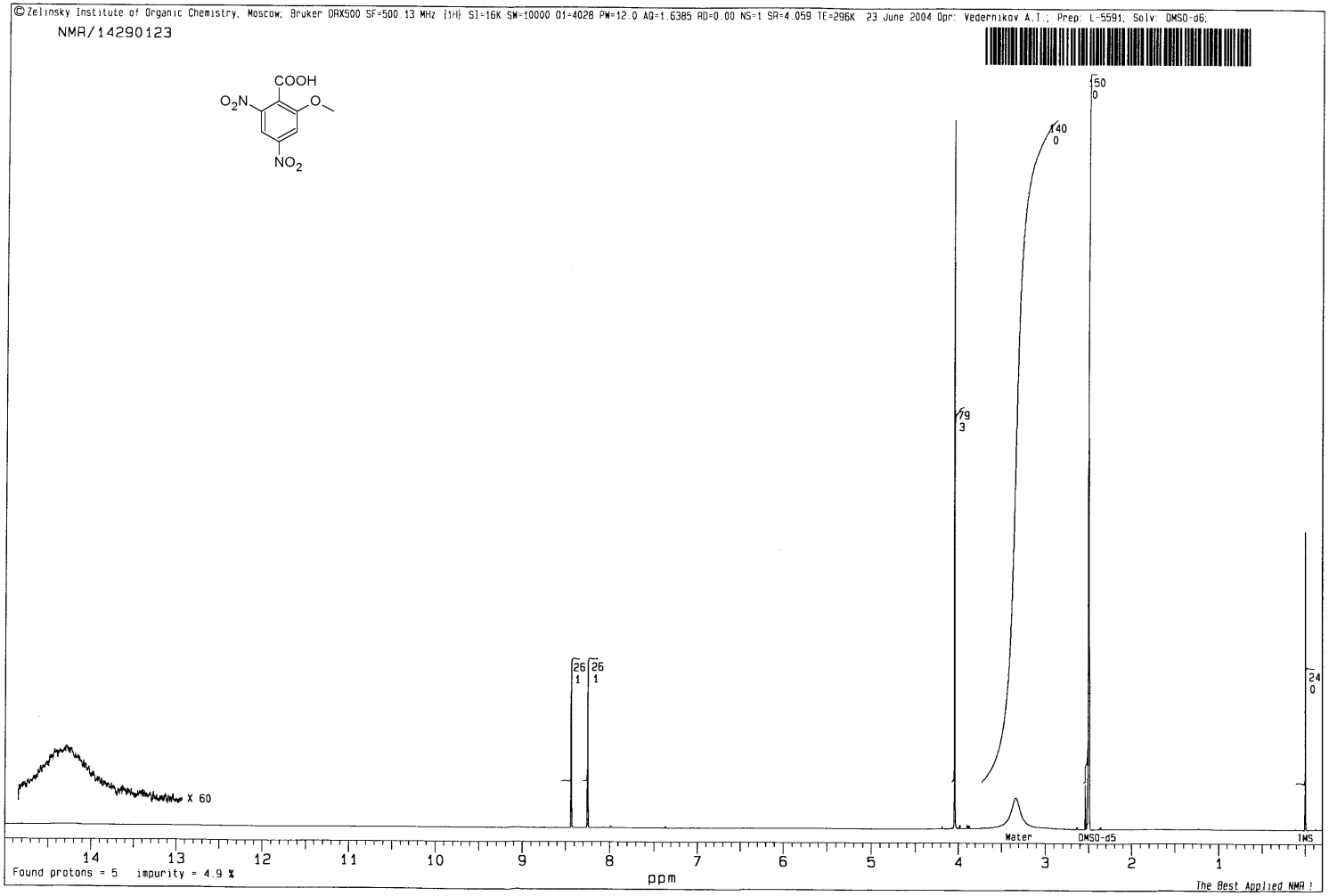
δ, ppm): 5.4 (br.s, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.22 (m, 3H), 7.31 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 2H). EI-MS (70 eV) (*m/z*, *I*, %): 483 [M^+, 13], 136 [54], 43 [100]. Anal. Calcd. for $C_{26}H_{17}N_3O_7$: C, 64.60; H, 3.54; N, 8.69. Found: C, 64.29; H, 3.65; N, 9.04.

1-Nitro-10-phenacyl-3-phenoxydibenz[*b,f*][1,4]oxazepin-11(10H)-one (9f): phenacyl bromide is used as alkylating agent. M.p.184-185°C. ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 5.5 (br.s, 2H), 7.07 (br.s, 1H), 7.15-7.35 (m, 6H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H). EI-MS (70 eV) (*m/z*, *I*, %): 466 [M^+, 5], 361 [17], 105 [100]. Anal. Calcd. for $C_{27}H_{18}N_2O_6$: C, 69.52; H, 3.89; N, 6.00. Found: C, 69.91; H, 4.12; N, 5.95.

2D NOESY spectrum of 4c



NOE difference spectrum of 4e



^{1}H NMR spectrum of 7b