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Supplementary Information

Studies on the Chemical Behavior of 3-(Nitroacetyl)-1-ethyl-4-hydroxyquinolin-2(1*H*)-one towards some Electrophilic and Nucleophilic Reagents

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6-Ethyl-4-hydroxy-3-nitropyrano[3,2-c]quinoline-2,5(6H) dione (**3**)

mp 242-243 °C (lit. 240-242 °C).[12] IR (KBr) ν_{max}/cm^{-1}: 3437 (OH), 3092 ($CH_{arom.}$), 2981, 2939, 2872 ($CH_{aliphatic}$), 1765 (OC=O), 1677 (C=O), 1624 (C=C), 1577, 1340 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.28 (t, 3H, *J* 7.0 Hz, CH_2CH_3), 4.37 (q, 2H, *J* 7.0 Hz, CH_2CH_3), 7.52 (t, 1H, *J* 7.2 Hz, H-9), 7.85-7.89 (m, 2H, H-7 and H-8), 8.13 (d, 1H, *J* 7.4 Hz, H-10), 13.55 (br, 1H, OH exchangeable with D_2O). *m/z* (relative intensity): 302 (17), 278 (98), 256 (18), 232 (100), 215 (30), 204 (23), 187 (50), 177 (97), 143 (21), 119 (37), 104 (46), 91 (55), 77 (46). Anal. Calc. for $C_{14}H_{10}N_2O_6$ (302.25): C, 55.64; H, 3.33; N, 9.27%. Found: C, 55.70; H, 3.21; N, 9.31%.

1-Ethyl-4-hydroxy-3-(nitroacetyl)quinolin-2(1H)-one (**4**)

mp 212-213 °C. IR (KBr) ν_{max}/cm^{-1}: 3435 (OH), 3094 ($CH_{arom.}$), 2978, 2933 ($CH_{aliphatic}$), 1631 (2C=O), 1610 (C=C), 1523, 1335 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.18 (t, 3H, *J* 6.9 Hz, CH_2CH_3), 4.23 (q, 2H, *J* 6.9 Hz, CH_2CH_3), 6.14 (s, 2H, CH_2NO_2), 7.35 (t, 1H, *J* 6.6 Hz, H-6), 7.62 (d, 1H, *J* 8.8 Hz, H-8), 7.84 (t, 1H, *J* 8.4 Hz, H-7), 8.12 (d, 1H, *J* 8.4 Hz, H-5), 14.71 (bs, 1H, OH exchangeable with D_2O). Anal. Calc. for $C_{13}H_{12}N_2O_5$ (276.24): C, 56.52; H, 4.38; N, 10.14. Found C, 56.21; H, 4.36; N, 9.91%.

5-Ethyl-2-(hydroxyimino)-2,3,4,5-tetrahydrofuro[3,2-c] quinoline-3,4-dione (**5**)

mp 270-271 °C. IR (KBr) ν_{max}/cm^{-1}: 3416 (OH), 3068 ($CH_{arom.}$), 2922, 2871 ($CH_{aliphatic}$), 1664 (C= O), 1604 (C=N). ^{1}H NMR (DMSO-d_6, δ): 1.19 (t, 3H, CH_2CH_3), 4.36 (q, 2H, CH_2CH_3), 7.33 (m, 1H, H-6), 7.50-7.85 (m, 2H, H-7 and H-8), 8.02 (d, 1H, *J* 7.6 Hz, H-9). Anal. Calc. for $C_{13}H_{10}N_2O_4$ (258.23): C, 60.47; H, 3.90; N, 10.85%. Found: C, 60.36; H, 3.92; N, 10.64%.

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3-[Dibromo(nitro)acetyl]-1-ethyl-4-hydroxyquinolin-2(1H)-one (**6**)

mp 177-178 °C. IR (KBr) ν_{max}/cm^{-1}: 3423 (OH), 3072 ($CH_{arom.}$), 2954, 2830 ($CH_{aliphatic}$), 1660 (2C=O), 1603 (C=C), 1571, 1331 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.18 (t, 3H, CH_2CH_3), 4.24 (q, 2H, CH_2CH_3), 7.38 (t, 1H, H-6), 7.64-7.74 (m, 1H, H-8), 8.01-8.09 (m, 1H, H-7), 8.14 (d, 1H, H-5). Anal. Calc. for $C_{13}H_{10}Br_2N_2O_5$ (434.04): C, 35.97; H, 2.32; N, 6.45; Br, 36.82. Found: C, 36.40; H, 2.30; N, 6.40; Br, 36.55.

3-[Dichloro(nitro)acetyl]-1-ethyl-4-hydroxyquinolin-2(1H)-one (**8**)

mp 205-206 °C. IR (KBr) ν_{max}/cm^{-1}: 3375 (OH), 3065 ($CH_{arom.}$), 2932, 2908 ($CH_{aliphatic}$), 1650 (2C=O), 1601 (C=C). ^{1}H NMR (DMSO-d_6, δ): 1.27 (t, 3H, *J* 7.5 Hz, CH_2CH_3), 4.40 (q, 2H, *J* 7.5 Hz, CH_2CH_3), 7.55 (t, 1H, *J* 7.2 Hz, H-6), 7.88-7.97 (m, 2H, H-7 and H-8), 8.19 (d, 1H, *J* 7.5 Hz, H-5). Anal. Calc. for $C_{13}H_{10}Cl_2N_2O_5$ (345.14): C, 45.24; H, 2.92; N, 8.12%. Found: C, 44.93; H, 2.70; N, 8.04%.

3-(1-Ethyl-4-hydroxy-2-oxo-1,2-dihydroquinolin-3-yl)-2-nitro-3-oxopropanal (**9**)

mp 181-182 °C. IR (KBr) ν_{max}/cm^{-1}: 3438 (OH), 3123 ($CH_{arom.}$), 2978, 2929 ($CH_{aliphatic}$), 1735 (CHO), 1642 ($C=O_{quinoline}$ and $C=O_{ketone}$), 1580 (C=C), 1520, 1350 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.18 (t, 3H, *J* 6.8 Hz, CH_2CH_3), 4.29 (q, 2H, *J* 6.8 Hz, CH_2CH_3), 6.90 (s, 1H, $CHNO_2$), 7.41 (t, 1H, *J* 7.6 Hz, H-6), 7.70 (d, 1H, *J* 8.4 Hz, H-8), 7.76 (t, 1H, *J* 8.4 Hz, H-7), 8.10 (d, 1H, *J* 7.4 Hz, H-5), 10.29 (s, 1H, aldehydic proton), 13.95 (bs, 1H, OH exchangeable with D_2O). *m/z* (relative intensity): 304 (18), 286 (5), 271 (8), 133 (36), 120 (65), 105 (100), 92 (26), 77 (42), 65 (16). Anal. Calc. for $C_{14}H_{12}N_2O_6$ (304.26): C, 55.27; H, 3.98; N, 9.21. Found: C, 55.09; H, 3.78; N, 8.94%.

6-Ethyl-2-methyl-3-nitro-4H-pyrano[3,2-c]quinoline-4,5(6H)-dione (**11**)

mp 232-233 °C. IR (KBr) ν_{max}/cm^{-1}: 3040 ($CH_{arom.}$), 2979, 2933 ($CH_{aliphatic}$), 1670 ($C=O_{quinoline}$), 1635 ($C=O_{\gamma\text{-pyron}}$),

1590 (C=C), 1560, 1356 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.12 (t, 3H, *J* 6.9 Hz, CH_2CH_3), 3.30 (s, 3H, CH_3), 4.17 (q, 2H, *J* 6.9 Hz, CH_2CH_3), 7.18 (t, 1H, *J* 7.6 Hz, H-9), 7.47 (d, 1H, *J* 8.4 Hz, H-7), 7.57 (t, 1H, *J* 8.4 Hz, H-8), 7.86 (d, 1H, *J* 7.6 Hz, H-10). Anal. Calc. for $C_{15}H_{12}N_2O_5$ (300.27): C, 60.00; H, 4.03; N, 9.33. Found: C, 60.04; H, 3.86 N, 9.12%.

3-[3-(2-Amino-4-oxo-4H-[1]benzopyran-3-yl)-2-nitroprop-2-enoyl]-1-ethyl-4-hydroxyquinolin-2(1H)-one (**13**)

mp > 320 °C. IR (KBr) ν_{max}/cm^{-1}: 3400 (OH), 3298, 3152 (NH_2), 1674 ($C{=}O_{quinoline}$), 1614 ($C{=}O_{ketone}$ and $C{=}O_{\gamma\text{-pyrone}}$), 1570 (C=C), 1548, 1317 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.16 (t, 3H, *J* 6.9 Hz, CH_2CH_3), 4.22 (q, 2H, *J* 6.9 Hz, CH_2CH_3), 5.46 (s, 1H, methine proton), 7.22-7.27 (m, 1H, Ar-H), 7.40 (t, 1H, *J* 8.4 Hz, Ar-H), 7.45 (t, 1H, *J* 6.6 Hz, Ar-H), 7.52 (t, 1H, *J* 6.6 Hz, Ar-H), 7.66-7.76 (m, 2H, Ar-H), 7.99 (d, 1H, *J* 6.6 Hz, Ar-H), 8.45 (d, 1H, *J* 8.4 Hz, Ar-H), 9.57 (bs, 1H, 1NH exchangeable with D_2O), 10.04 (bs, 1H, 1NH exchangeable with D_2O). Anal. Calc. for $C_{23}H_{17}N_3O_7$ (447.41): C, 61.75; H, 3.83; N, 9.39. Found: C, 61.50; H, 3.62; N, 9.44%.

2-(1-Ethyl-4-hydroxy-2-oxo-1,2-dihydroquinolin-3-yl)-3-nitro-5H-benzopyrano[2,3-b]pyridin-5-one (**14**)

mp 260-261 °C. IR (KBr) ν_{max}/cm^{-1}: 3433 (OH), 3079 ($CH_{arom.}$) 2978, 2931 ($CH_{aliphatic}$), 1665 ($C{=}O_{quinoline}$ and $C{=}O_{\gamma\text{-pyrone}}$), 1600 (C=N and C=C), 1550, 1317 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.27 (t, 3H, *J* 6.9 Hz, CH_2CH_3), 4.37 (q, 2H, *J* 6.9 Hz, CH_2CH_3), 6.80-6.95 (m, 2H, Ar-H), 7.51 (t, 1H, Ar-H), 7.54 (t, 1H, Ar-H), 7.69 (d, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.91 (d, 1H, Ar-H), 7.95 (d, 1H, Ar-H), 8.69 (s, 1H, H-$4_{pyridine}$), 14.75 (bs, 1H, OH). *m/z* (relative intensity): 412 [M-17; 27], 411 [M-18; 100], 384 (29), 356 (24), 328 (7), 283 (5), 215 (43), 188 (7), 168 (5), 146 (25), 132 (17), 121 (29), 104 (11), 92 (17), 77 (35), 65 (14). Anal. Calc. for $C_{23}H_{15}N_3O_6$ (429.39): C, 64.34; H, 3.52; N, 9.79. Found: C, 64.36; H, 3.48 N, 9.82%.

5-Ethyl-3-(nitromethyl)-1-phenyl-1,5-dihydro-4H-pyrazolo[4,3-c]quinolin-4-one (**17**)

mp 187-188 °C. IR (KBr) ν_{max}/cm^{-1}: 3085 ($CH_{arom.}$), 2982, 2922 ($CH_{aliphatic}$), 1640 ($C{=}O_{quinoline}$), 1620 (C=N), 1559 (C=C). ^{1}H NMR (DMSO-d_6, δ): 1.24 (t, 3H, *J* 7.6 Hz, CH_2CH_3), 4.37 (q, 2H, *J* 7.6 Hz, CH_2CH_3), 5.60 (s, 2H, CH_2NO_2), 7.54-7.91 (m, 8H, Ar-H), 8.14 (d, 1H, *J* 8.4 Hz, Ar-H). Anal. Calc. for $C_{19}H_{16}N_4O_3$ (348.36): C, 65.51; H, 4.63; N, 16.08. Found: C, 65.42; H, 4.58; N, 16.02%.

1-(7-Chloroquinolin-4-yl)-5-ethyl-3-(nitromethyl)-1,5-dihydro-4H-pyrazolo[4,3-c]quinolin-4-one (**18**)

mp 230 °C. IR (KBr) ν_{max}/cm^{-1}: 3082 ($CH_{arom.}$), 2974, 2910 ($CH_{aliphatic}$), 1650 ($C{=}O_{quinoline}$), 1629 (C=N), 1567 (C=C), 1567, 1371 (NO_2), 767 (C–Cl). ^{1}H NMR (DMSO-d_6, δ) 1.14 (t, 3H, *J* 6.2 Hz, CH_2CH_3), 4.23 (q, 2H, *J* 6.6 Hz, CH_2CH_3), 5.43 (s, 1H, 1H of CH_2NO_2), 5.82 (s, 1H, 1H of CH_2NO_2), 7.39-7.87 (m, 5H, Ar-H), 8.06 (d, 1H, H-9), 8.25 (d, 1H, H-3`), 8.35 (d, 1H, H-2'), 8.45 (s, 1H, H-8`). Anal. Calc. for $C_{22}H_{16}N_5O_3Cl$ (433.86): C, 60.91; H, 3.72; N, 16.14%. Found: C, 60.87; H, 3.64; N, 16.03%.

6-Ethyl-4-(nitromethyl)-2-thioxo-1,2,5,6-tetrahydro-pyrimido[5,4-c]quinolin-5(1H)-one (**19**)

mp 184-185 °C. IR (KBr) ν_{max}/cm^{-1}: 3377 (NH), 2976, 2935 ($CH_{ailphatic}$), 1653 ($C{=}O_{quinoline}$), 1572 (C=N and C=C), 1307 (C=S). ^{1}H NMR (DMSO-d_6, δ): 1.28 (t, 3H, *J* 7.0 Hz, CH_2CH_3), 4.35 (q, 2H, *J* 7.2 Hz, CH_2CH_3), 5.57 (s, 2H, CH_2NO_2), 7.51 (t, 1H, *J* 7.0 Hz, H-9), 7.80-7.87 (m, 2H, H-7 and H-8), 8.09 (d, 1H, *J* 7.0 Hz, H-10), 13.43 (bs, 1H, NH exchangeable with D_2O). *m/z* (relative intensity): 316 (7), 284 (12), 256 (32), 230 (5), 202 (4), 160 (17), 147 (6), 143 (5), 119 (9), 115 (10), 91 (11), 77 (10), 69 (100), 64 (53). Anal. Calc. for $C_{14}H_{12}N_4O_3S$ (316.34): C, 53.16; H, 3.82; N, 17.71; S, 10.14%. Found: C, 53.24; H, 3.87; N, 17.58; S, 9.72%.

[6-Ethyl-4-(nitromethyl)-5-oxo-5,6-dihydropyrimido[5,4-c]quinolin-2(1H)-yl]cyanamide (**20**)

mp 239-240 °C. IR (KBr) ν_{max}/cm^{-1}: 3426 (NH), 2982, 2840 ($CH_{aliphatic}$), 2211 (C≡N), 1679 ($C{=}O_{quinoline}$), 1615 (C=N and C=C), 1514, 1296 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.24 (t, 3H, *J* 6.9 Hz, CH_2CH_3), 4.37 (q, 2H, *J* 6.9 Hz, CH_2CH_3), 5.60 (s, 2H, CH_2NO_2), 7.50 (t, 1H, *J* 6.9 Hz, H-9), 7.84-7.96 (m, 2H, H-7 and H-8), 8.12 (d, 1H, *J* 7.6 Hz, H-10), 13.47 (bs, 1H, NH exchangeable with D_2O). Anal. Calc. for $C_{15}H_{12}N_6O_3$ (324.30): C, 55.56; H, 3.73; N, 25.91%. Found: C, 55.28; H, 3.70; N, 25.60%.

5,13-Dihydro-5-ethyl-7-nitromethyl-6H-quinolino[4,3-b][1,5]benzodiazepin-6-one (**21**)

mp 274 °C. IR (KBr) ν_{max}/cm^{-1}: 3229 (NH), 3060 ($CH_{arom.}$), 2977, 2920 ($CH_{aliphatic}$), 1593 (C=N and C=C), 1545, 1325 (NO_2). ^{1}H NMR (DMSO-d_6, δ): 1.22 (t, 3H, CH_2CH_3), 4.28 (q, 2H, CH_2CH_3), 4.93 (s, 2H, CH_2NO_2), 7.19 (t, 1H, Ar-H), 7.25-7.32 (m, 2H, Ar-H), 7.45 (d, 1H, Ar-H), 7.60 (d, 1H, Ar-H), 7.69-7.75 (m, 2H, Ar-H), 8.19 (d, 1H, Ar-H), 13.65 (bs, 1H, NH exchangeable with D_2O). Anal. Calc. for $C_{19}H_{16}N_4O_3$ (348.36): C, 65.51; H, 4.63; N, 16.08%. Found: C, 65.18; H, 4.31; N, 15.86%.

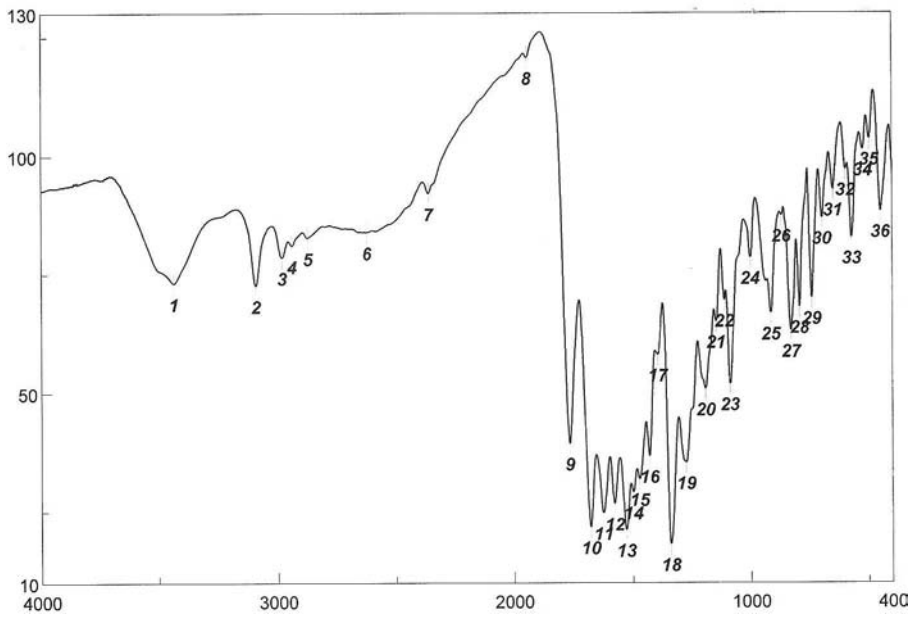

Figure S1. IR (KBr) spectrum of compound **3**.

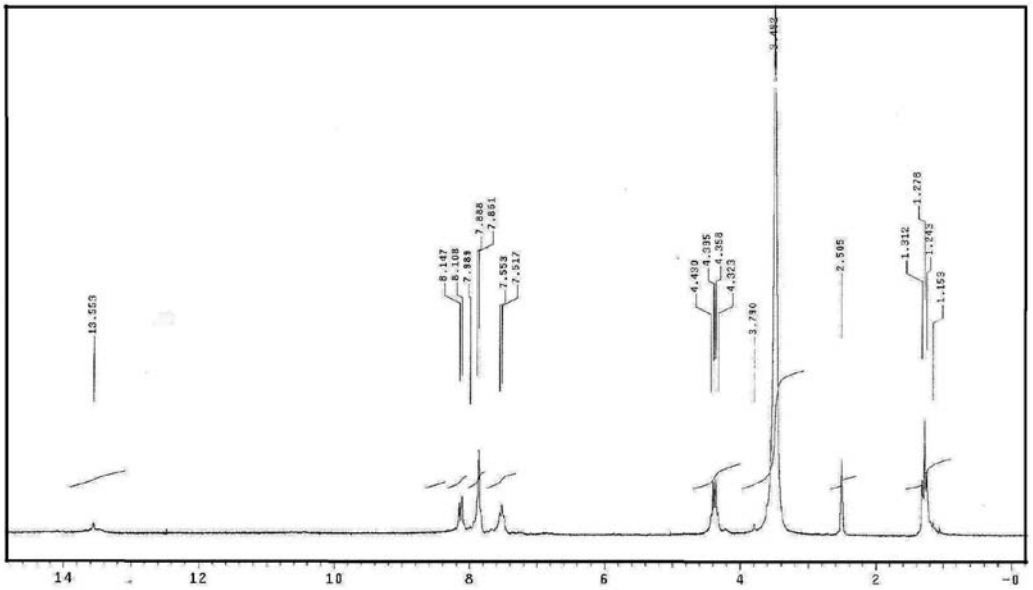

Figure S2. ^{1}H NMR spectrum of compound **3** (in DMSO-d_6, 300 MHz).

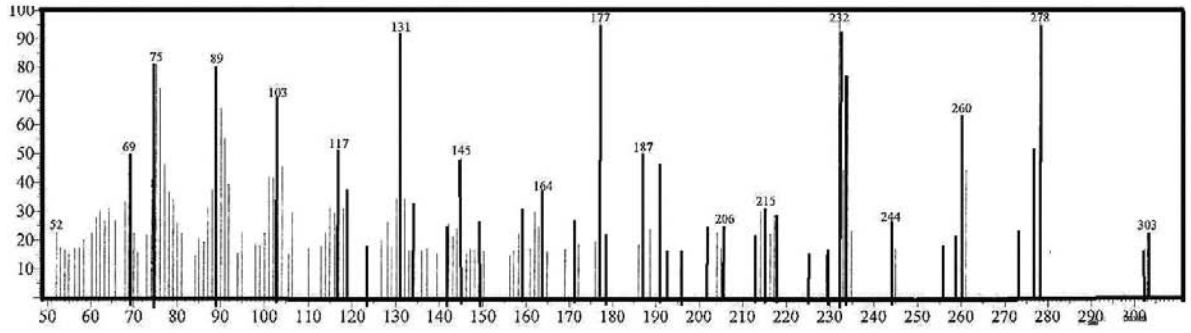

Figure S3. Mass spectrum of compound **3**.

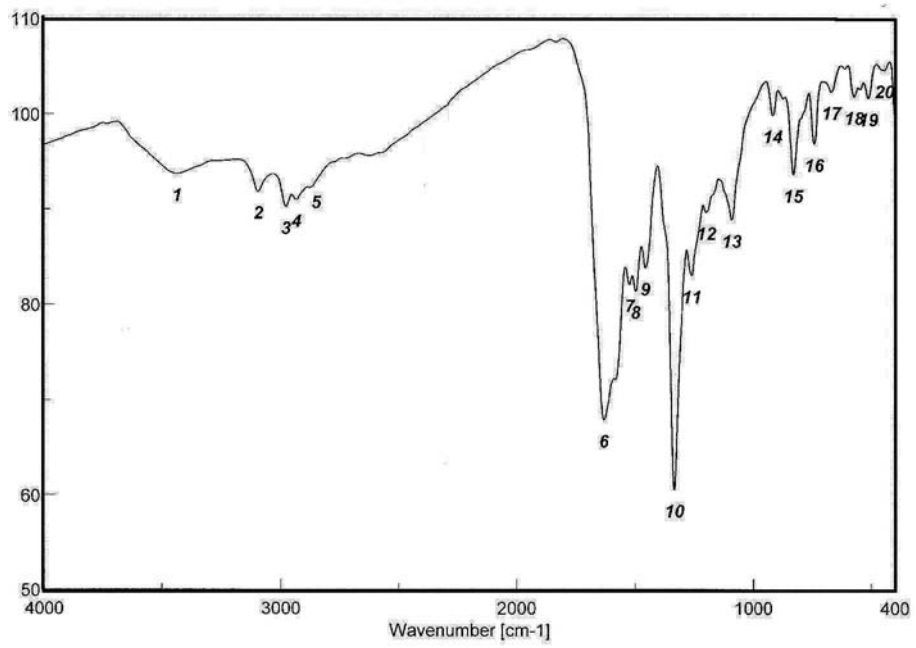

Figure S4. IR (KBr) spectrum of compound **4**.

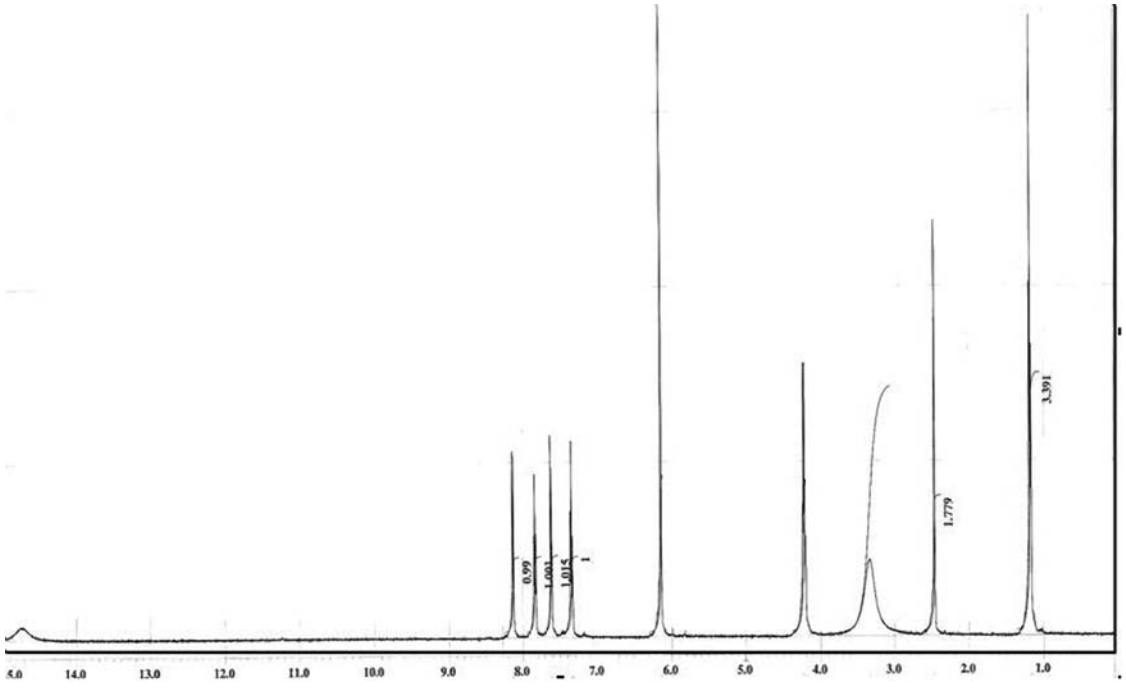

Figure S5. [1]H NMR spectrum of compound **4** (in DMSO-d_6, 500 MHz).

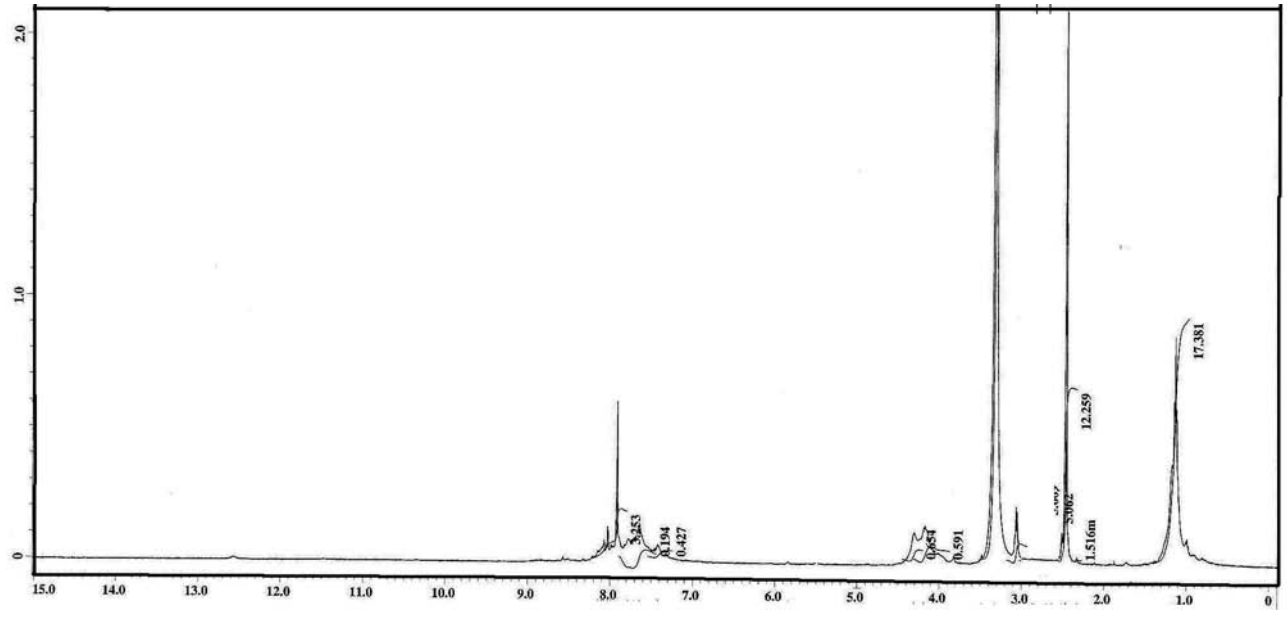

Figure S6. [1]H NMR spectrum of compound **5** (in DMSO-d_6, 500 MHz).

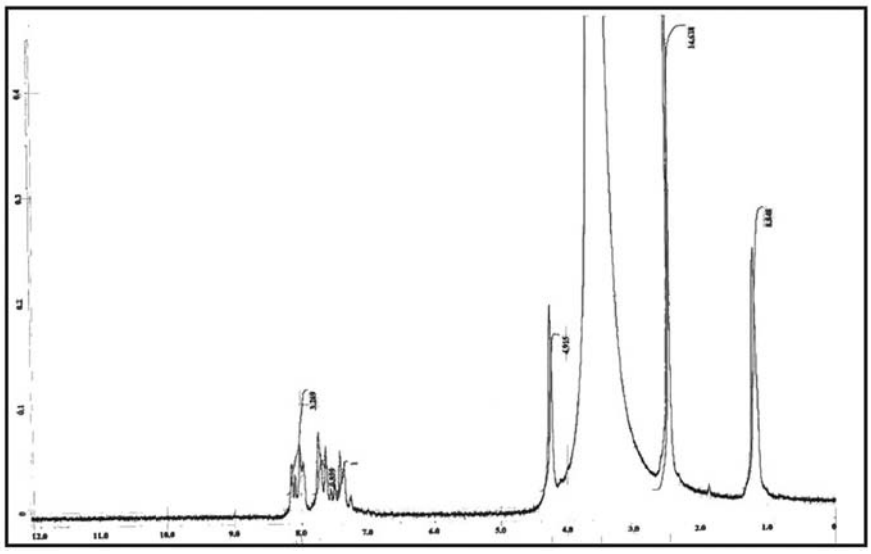

Figure S7. ^{1}H NMR spectrum of compound **6** (in DMSO-d_6, 500 MHz).

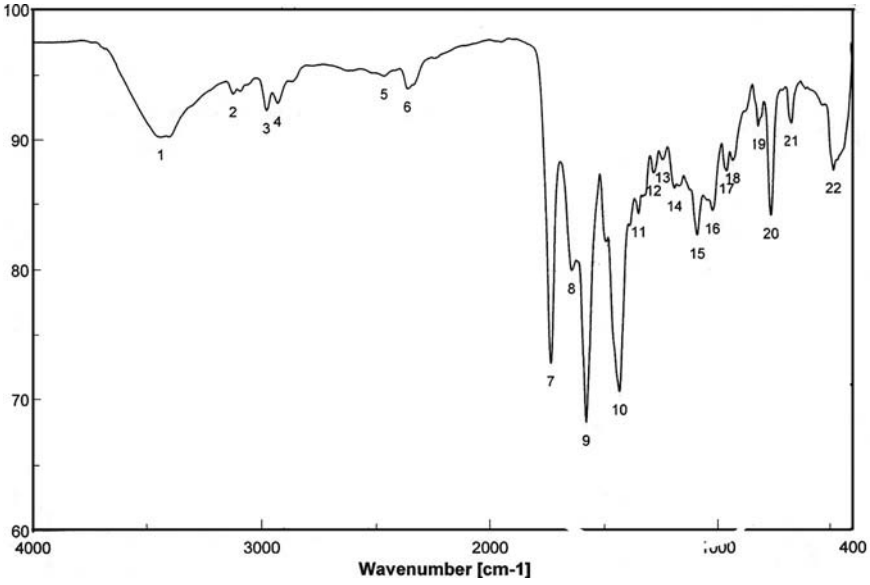

Figure S8. IR (KBr) spectrum of compound **9**.

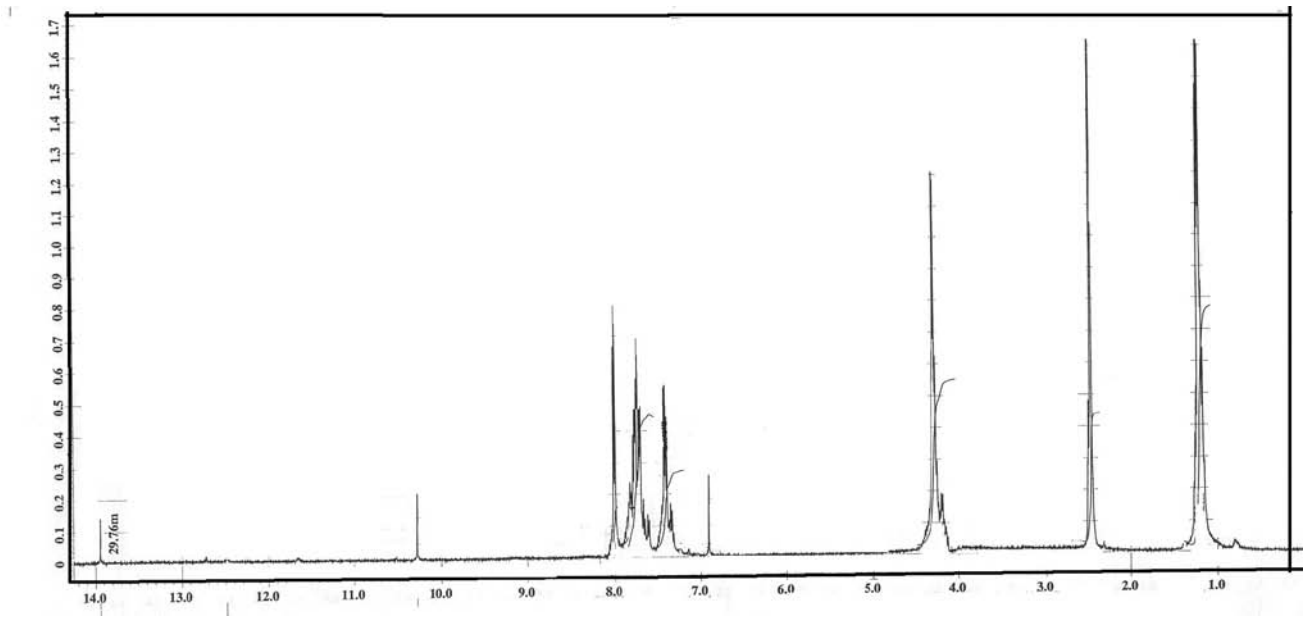

Figure S9. ^{1}H NMR spectrum of compound **9** (in DMSO-d_6, 500 MHz).

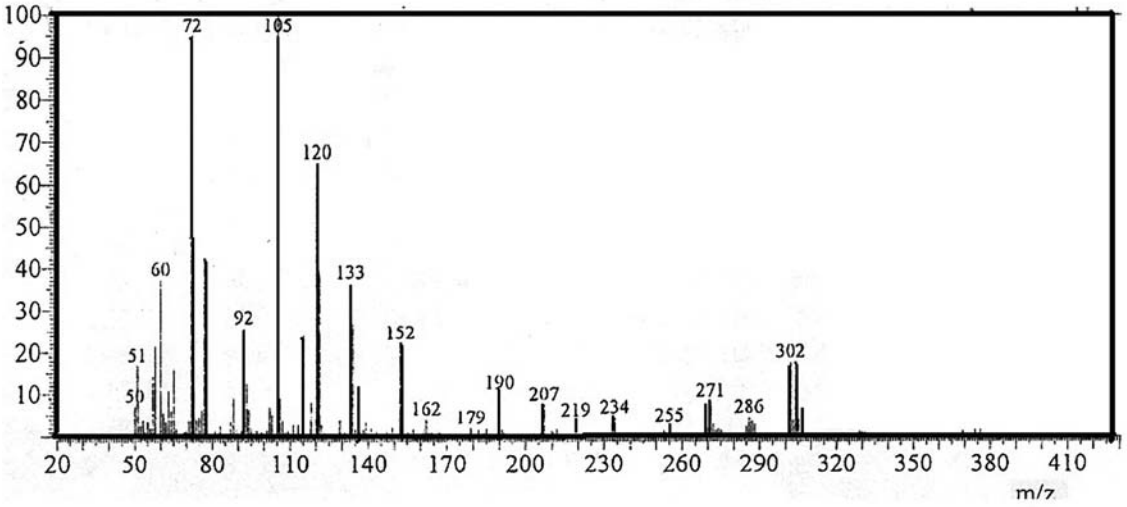

Figure S10. Mass spectrum of compound **9**.

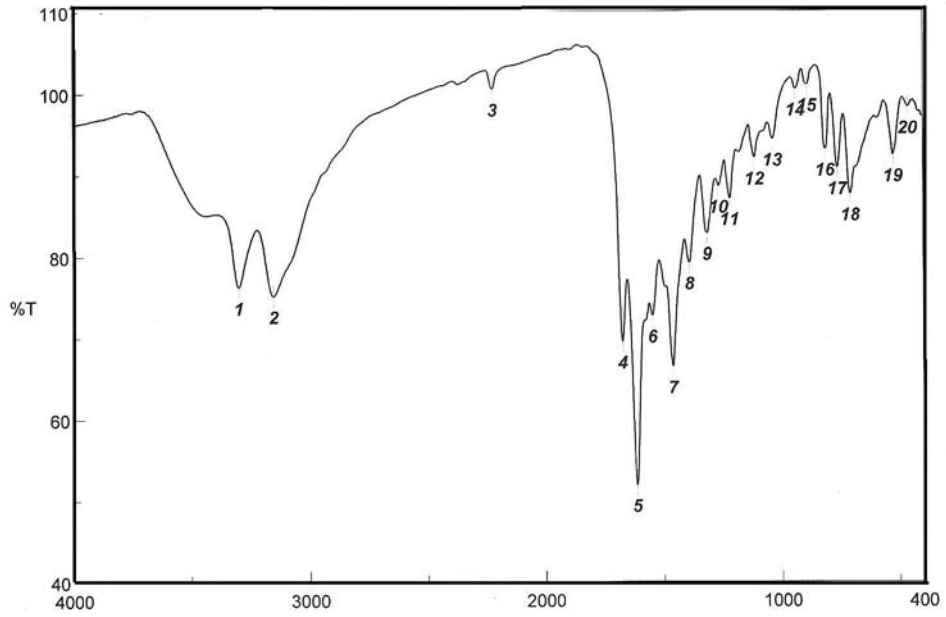

Figure S11. IR (KBr) spectrum of compound **13**.

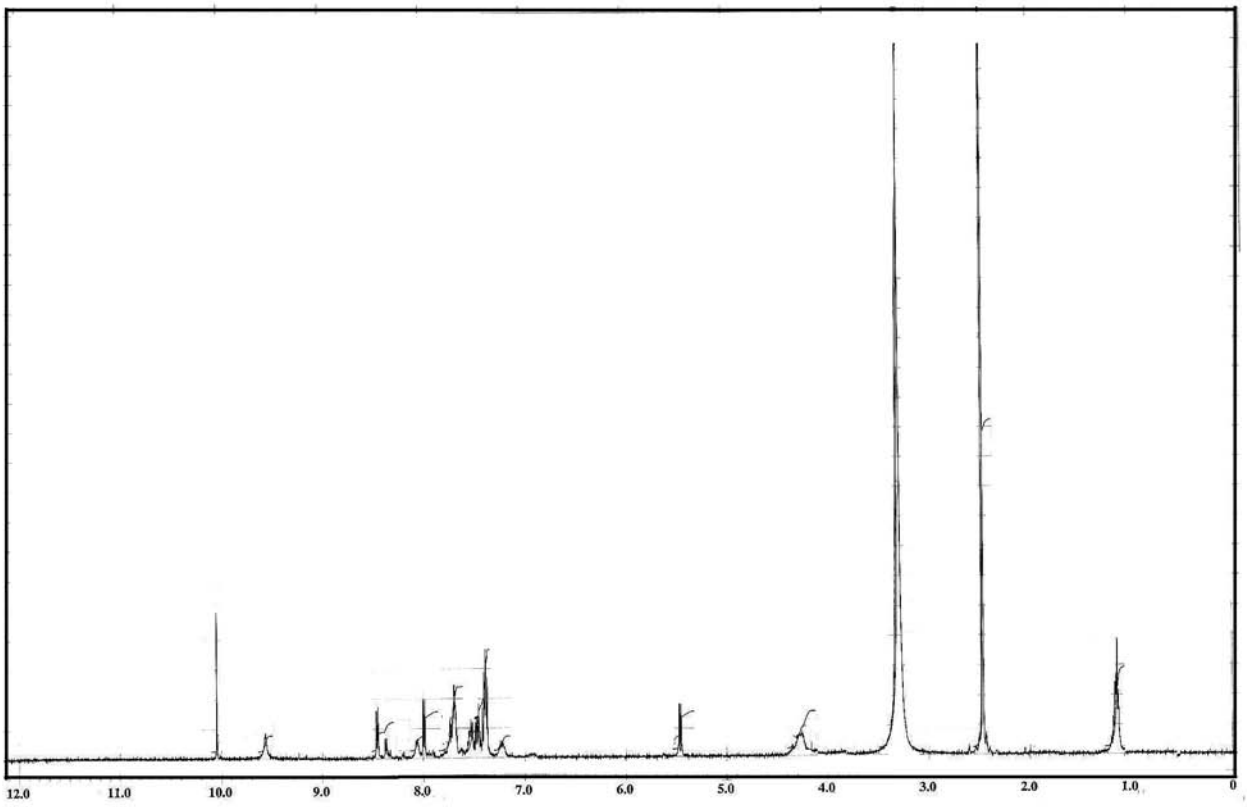

Figure S12. ^{1}H NMR spectrum of compound **13** (in DMSO-d_6, 500 MHz).

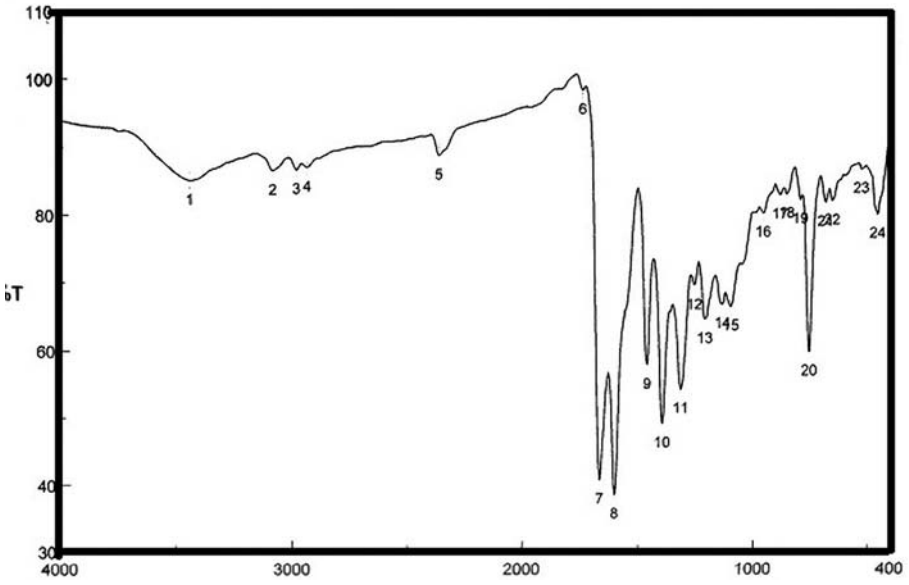

Figure S13. IR (KBr) spectrum of compound **14**.

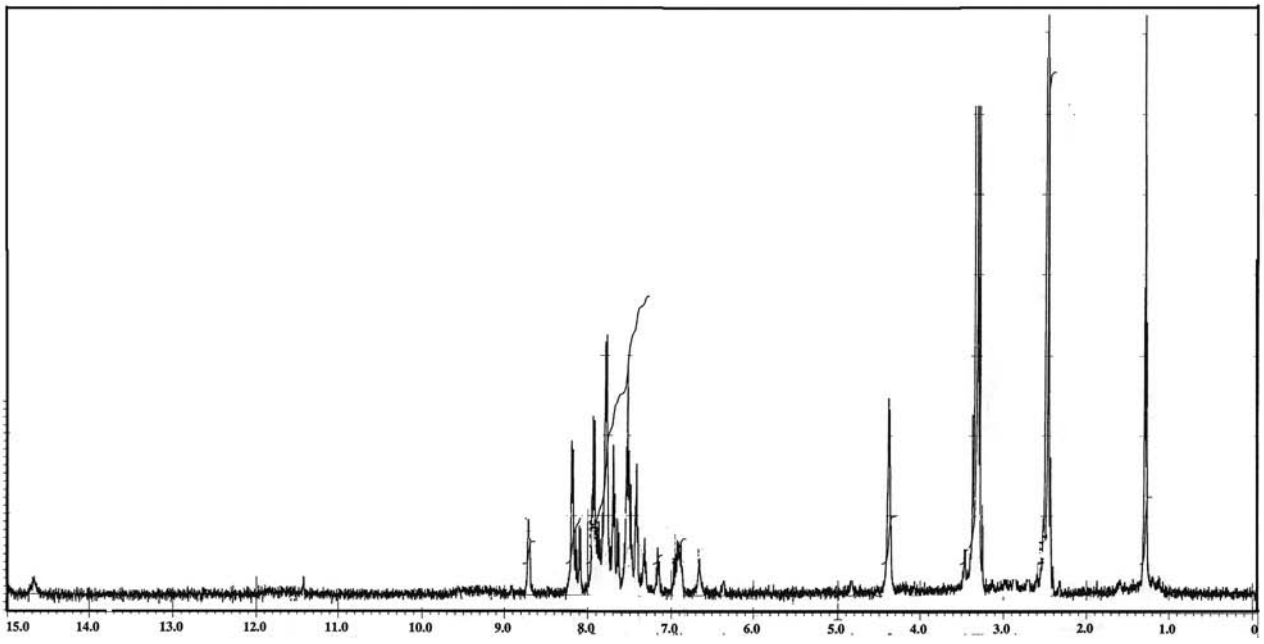

Figure S14. ^{1}H NMR spectrum of compound **14** (in DMSO-d_6, 500 MHz).

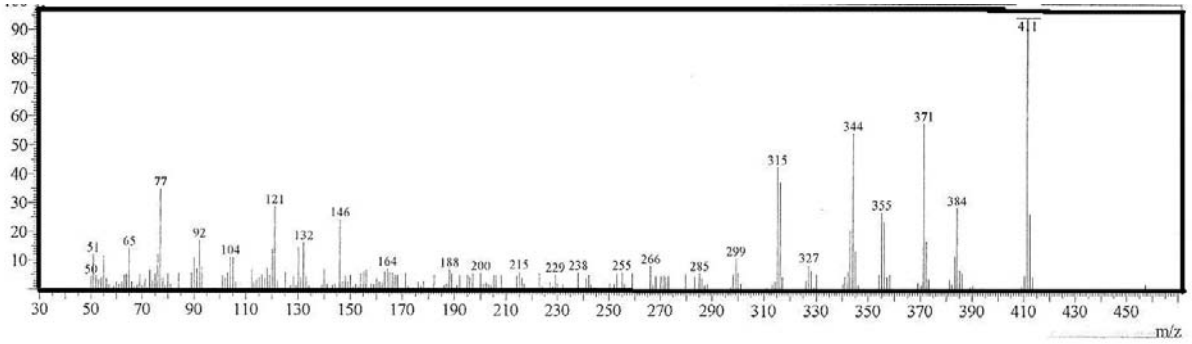

Figure S15. Mass spectrum of compound **14**.

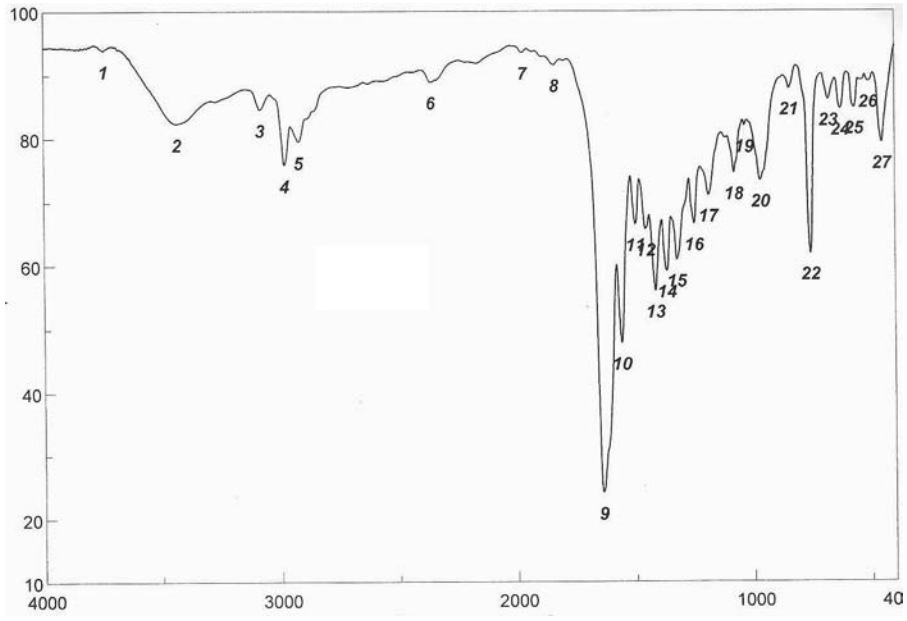

Figure S16. IR (KBr) spectrum of compound **17**.

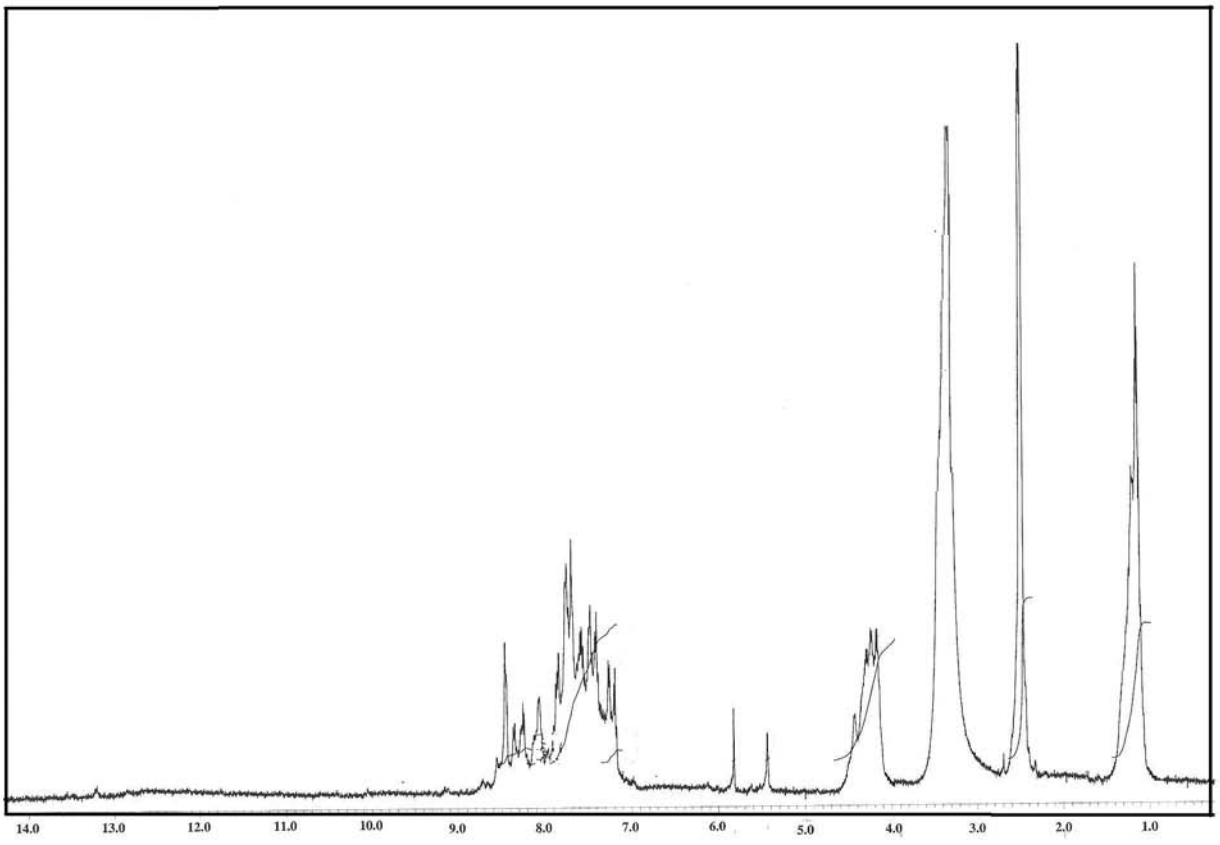

Figure S17. ^{1}H NMR spectrum of compound **18** (in DMSO-d_6, 500 MHz).

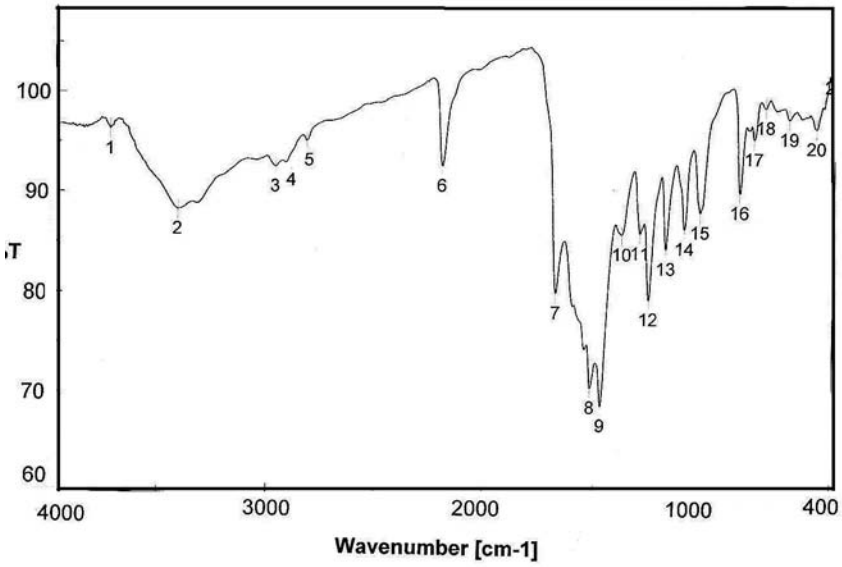

Figure S18. IR (KBr) spectrum of compound **20**.

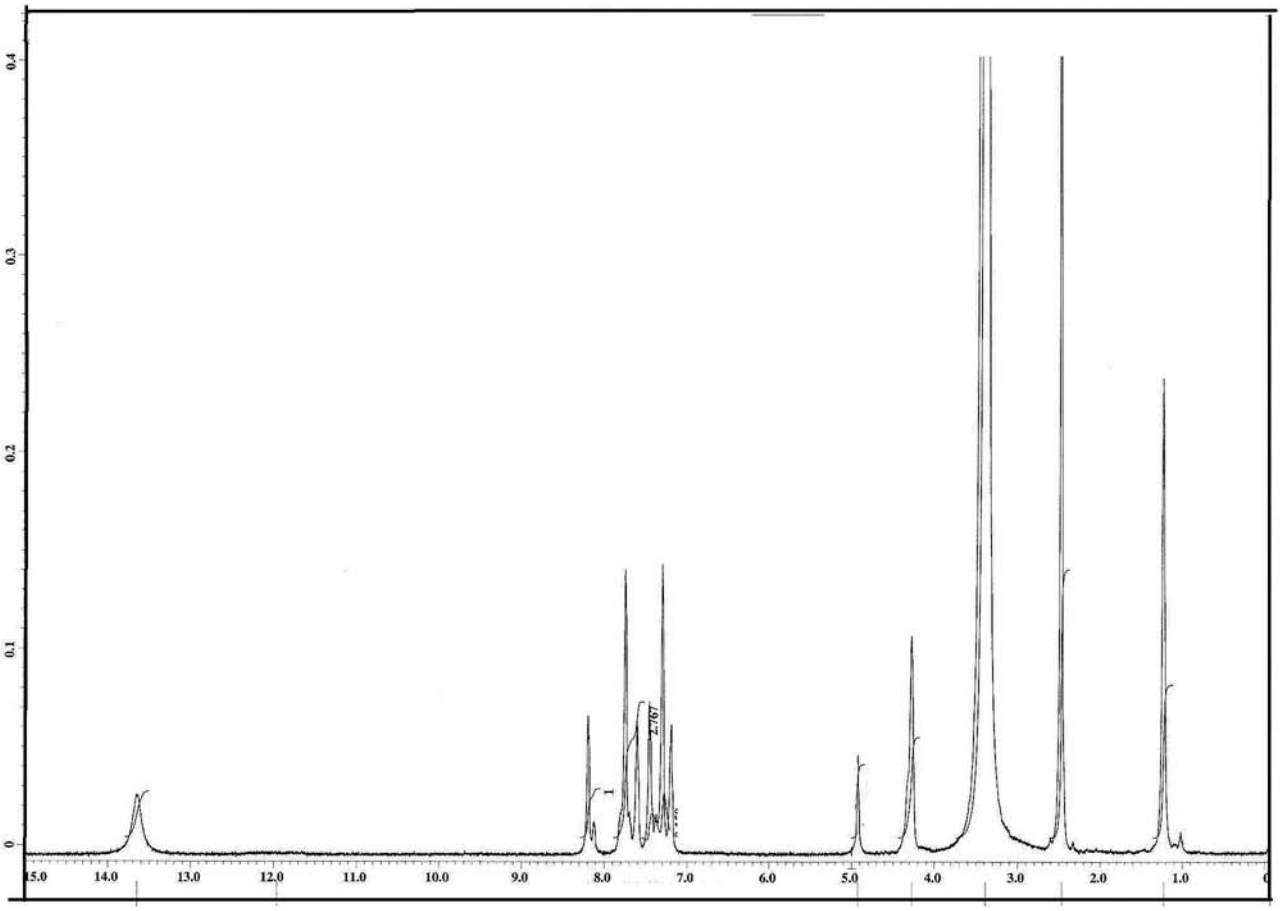

Figure S19. ^{1}H NMR spectrum of compound **21** (in DMSO-d_6, 500 MHz).