

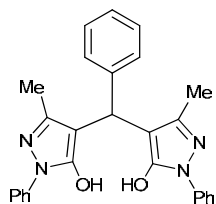
Supporting Information

Sulfonated rice husk ash (RHA-SO₃H) as a highly efficient and reusable catalyst for the synthesis of some of bis-heterocyclic compounds

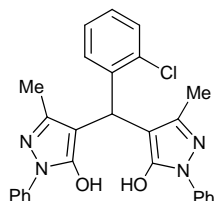
Mohadeseh Seddighi, Farhad Shirini,* and Manouchehr Mamaghani

Department of Chemistry, Faculty of Sciences, University of Guilan, Rasht, zip code: 41335,

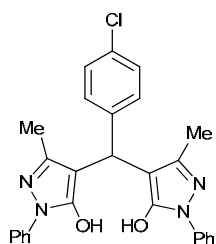
Post Box: 1914, I. R. Iran. Tel./Fax: +98 131 3233262, E-mail address: shirini@guilan.ac.ir



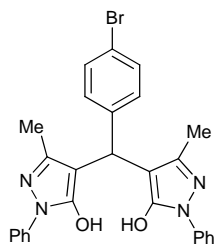
^1H NMR (DMSO- d_6 , 300 MHz): δ = 2.32 (6H, s, CH_3), 4.96 (1H, s, CH), 7.17-7.27 (7H, m), 7.44 (4H, t, J = 7.7 Hz), 7.71 (4H, d, J = 7.9), 13.96 (2H, br, OH) ppm.



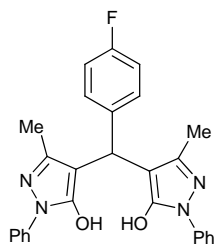
^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.29 (6H, s), 5.14 (1H, s), 7.22-7.33 (4H, m), 7.40 (1H, d, J = 7.82 Hz), 7.44 (4H, t, J = 7.57 Hz), 7.70 (4H, d, J = 7.57 Hz), 7.80 (1H, d, J = 7.06 Hz), 13.92 (2H, br, OH) ppm.



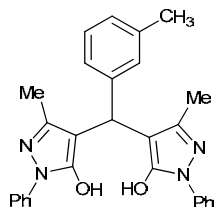
^1H NMR (DMSO- d_6 , 300 MHz): δ = 2.30 (6H, s), 4.98 (1H, s), 7.22-7.28 (4H, m), 7.35 (2H, d, J = 8.48 Hz), 7.44 (4H, t, J = 7.91 Hz), 7.71 (4H, d, J = 7.91 Hz), 13.90 (2H, br, OH) ppm.



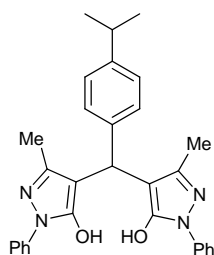
^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.32 (6H, s), 4.95 (1H, s), 7.19, 7.52 (2H, d, J = 8.0 Hz), 7.23-7.26 (2H, m), 7.42-7.48 (6H, m), 7.69 (4H, d, J = 7.6 Hz), 13.87 (2H, brs,) ppm.



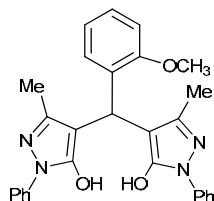
^1H NMR (DMSO- d_6 , 500 MHz): δ = 2.31 (6H, s), 4.95 (1H, s), 7.09 (2H, t, J = 8.75 Hz), 7.22-7.28 (4H, m), 7.43 (4H, t, J = 7.65 Hz), 7.70 (4H, d, J = 7.90 Hz), 12.48 (1H, br, OH), 13.91 (1H, s, OH) ppm.



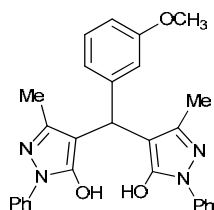
^1H NMR (DMSO- d_6 , 400 MHz): δ = 2.25 (3H, s), 2.31 (6H, s), 4.91 (1H, s), 6.98 (1H, d, J = 7.6 Hz), 7.06 (1H, s), 7.07 (1H, d, J = 6.8 Hz), 7.16 (1H, t, J = 7.2 Hz), 7.25 (2H, t, J = 7.2 Hz), 7.44 (4H, t, J = 7.6 Hz), 7.71 (4H, d, J = 7.6 Hz), 13.98 (2H, brs, OH) ppm.



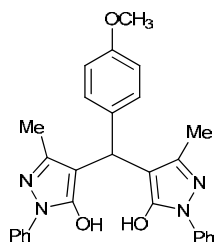
$^1\text{H NMR}$ (DMSO- d_6 , 500 MHz): δ = 1.16 (6H, d, J = 6.9 Hz), 2.31 (6H, s), 2.79–2.85 (1H, m), 4.90 (1H, s), 7.13 (2H, d, J = 8.2 Hz), 7.18 (2H, d, J = 8.1 Hz), 7.23 (2H, t, J = 7.25 Hz), 7.43 (4H, t, J = 7.3 Hz), 7.72 (4H, d, J = 7.9 Hz), 12.30 (1H, br, OH), 14.03 (1H, s, OH) ppm.



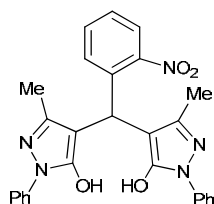
$^1\text{H NMR}$ (DMSO- d_6 , 300 MHz) δ = 2.27 (6H, s, CH_3), 3.82 (3H, s, OCH_3), 5.19 (1H, s, CH), 6.87–6.96 (2H, m), 7.17–7.27 (3H, m), 7.41–7.46 (4H, m), 7.58–7.61 (1H, m), 7.68–7.71 (4H, m), 13.95 (brs, OH) ppm.



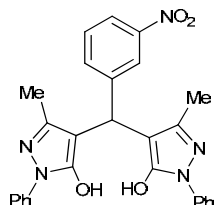
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 2.42 (6H, s, CH_3), 3.51 (3H, s, OCH_3) 4.71 (1H, s), 6.55 (1H, dd), 6.66–7.73 (13H, m), 13.25 (bs, 2H) ppm.



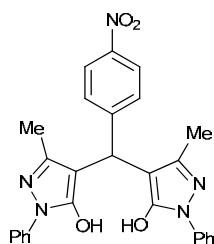
$^1\text{H NMR}$ (DMSO- d_6 , 300 MHz): δ = 2.34 (6H, s, CH_3), 3.71 (3H, s, OCH_3), 4.93 (1H, s, CH), 6.88 (2H, d), 7.18 (2H, d), 7.21–7.27 (2H, m), 7.42–7.49 (4H, m), 7.71–7.72 (4H, m), 13.94 (brs, OH) ppm.



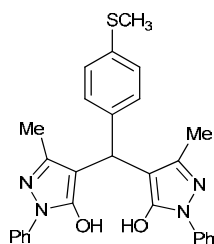
$^1\text{H NMR}$ (DMSO- d_6 , 300 MHz): δ = 2.24 (6H, s, CH_3), 5.41 (1H, s, CH), 7.21–7.27 (2H, m), 7.44–7.49 (5H, m), 7.66–7.73 (7H, m), 13.72 (brs, OH) ppm.



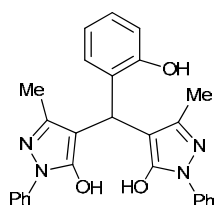
$^1\text{H NMR}$ (DMSO- d_6 , 300 MHz): δ = d 2.30 (6H, s, CH_3), 4.98 (1H, s), 7.22–7.28 (4H, m), 7.35 (2H, d, J = 8.48 Hz), 7.44 (4H, t, J = 7.91 Hz), 7.71 (4H, d, J = 7.91 Hz), 13.90 (2H, brs, OH) ppm.



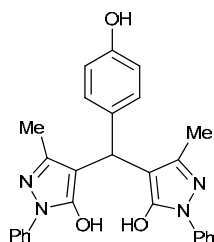
$^1\text{H NMR}$ (DMSO- d_6 , 300 MHz): δ = 2.35 (6H, s, CH_3), 5.13 (1H, s), 7.25-7.27 (2H, m), 7.43-7.46 (4H, t, J = 7.0 Hz), 7.51-7.53 (2H, d, J = 8.0 Hz), 7.70-7.72 (4H, d, J = 8.0 Hz), 8.16-8.18 (2H, d, J = 8.0 Hz), 12.64 (1H, s, OH), 13.86 (1H, s, OH) ppm.



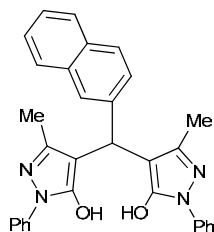
$^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ = 2.3 (6H, s, CH_3), 2.43 (3H, s, SCH_3), 4.92 (1H, s), 7.18 (4H, s), 7.25 (2H, t, J = 7.31 Hz), 7.44 (4H, t, J = 7.82 Hz), 7.70 (4H, d, J = 7.82 Hz), 13.92 (2H, brs, OH) ppm.



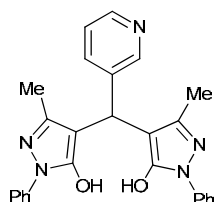
$^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ = 2.26 (6H, s, CH_3), 5.14 (1H, s, CH), 6.69-6.77 (2H, m), 7.04 (1H, t), 7.22 (2H, t), 7.44 (4H, t), 7.55 (1H, d), 7.65 (4H, d), 9.87 (1H, s, OH), 13.91 (1H, brs, OH) ppm.



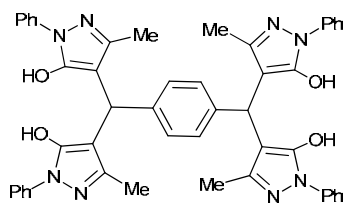
$^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ = 2.31 (6H, s, CH_3), 4.86 (1H, s), 6.67 (2H, d, J = 8.5 Hz), 7.06 (2H, d, J = 8.5 Hz), 7.24 (2H, t, J = 7.0 Hz), 7.44 (4H, t, J = 8.0 Hz), 7.72 (4H, d, J = 8.0 Hz), 9.16 (1H, s, OH), 12.40 (1H, s, OH), 13.95 (1H, s, OH) ppm.



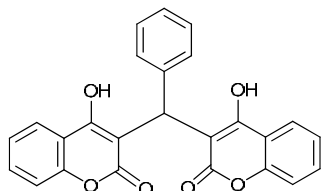
$^1\text{H NMR}$ (DMSO- d_6 , 500 MHz): δ = 2.36 (6H, s), 5.14 (1H, s), 7.24 (2H, t, J = 6.9 Hz), 7.41-7.45 (7H, m), 7.71-7.73 (5H, m), 7.81-7.85 (3H, m), 12.41 (1H, brs, OH), 13.93 (1H, s, OH) ppm.



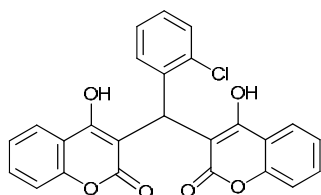
$^1\text{H NMR}$ (DMSO- d_6 , 500 MHz): δ = 2.34 (6H, s, CH_3), 5.05 (1H, s, CH_3), 7.23 (2H, t, J = 7.1 Hz), 7.34 (1H, t, J = 6.0 Hz), 7.43 (4H, t, J = 7.5 Hz), 7.71-7.73 (5H, m), 8.41 (1H, d, J = 3.6 Hz), 8.51 (1H, s), 12.10 (1H, brs, OH), 14.12 (1H, brs, OH) ppm.



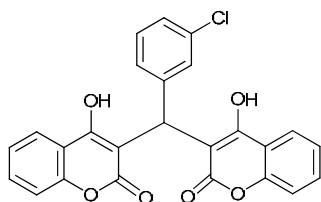
^1H NMR (DMSO- d_6 , 500 MHz): δ = 2.29 (12H, s, CH_3), 5.05 (2H, s), 7.17 (4H, s), 7.22 (4H, t, J = 7.1 Hz), 7.41 (8H, t, J = 7.8 Hz), 7.69 (8H, d, J = 7.9 Hz), 12.41 (2H, brs, OH) 14.11 (s, 2H, OH) ppm.



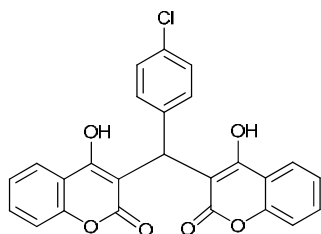
^1H NMR (CDCl_3 , 300 MHz): δ = 6.12 (1H, s, CH), 7.24–8.10 (13H, m), 11.33 (1H, s, OH), 11.56 (1H, s, OH) ppm.



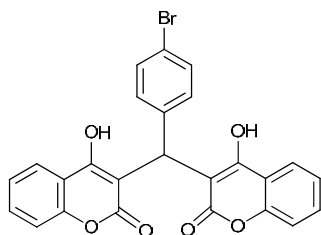
^1H NMR (CDCl_3 , 300 MHz): δ = 6.14 (1H, s, CH), 8.03–7.22 (12H, m), 10.93 (1H, s, OH), 11.63 (1H, s, OH) ppm.



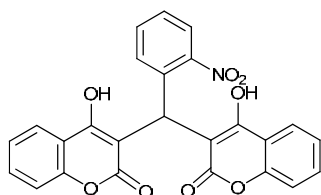
^1H NMR (DMSO- d_6 , 500 MHz): δ = 6.32 (1H, s, CH), 7.10–7.92 (12H, m), 12.37 (2H, brs, OH) ppm.



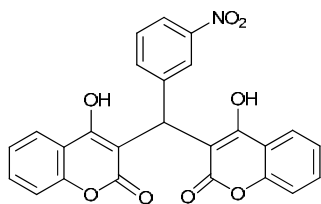
^1H NMR (CDCl_3 , 500 MHz): δ = 6.04 (1H, s, CH), 8.09–7.17 (12H, m), 11.32 (1H, s, OH), 11.54 (1H, s, OH) ppm.



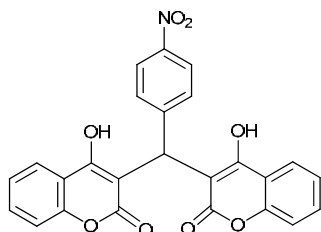
^1H NMR (CDCl_3 , 300 MHz): δ = 6.01 (s, 1H, CH), 7.10–8.06 (12H, m), 11.31 (brs, 1H, OH), 11.54 (brs, 1H, OH)



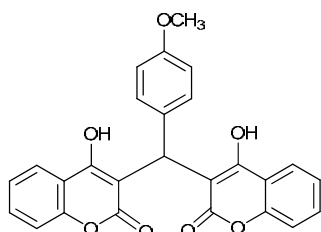
^1H NMR (CDCl_3 , 300 MHz): δ = 6.6 (1H, s), 6.72–7.94 (12H, m), 11.24 (2H, brs, OH) ppm.



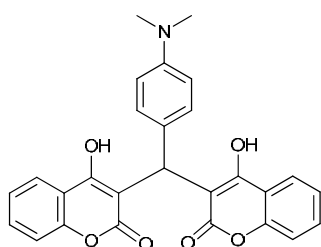
¹H NMR (DMSO-d₆, 400 MHz): δ = 6.39 (s, 1H, CH), 7.28–8.04 (m, 12H, ArH), 8.04–9.52 (m, 2H, OH) ppm.



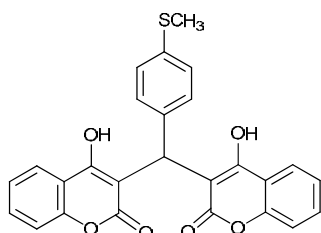
¹H NMR (CDCl₃, 300 MHz): δ = 6.14 (1H, s, CH), 7.28–8.22 (12H, m), 11.40 (1H, s, OH), 11.59 (1H, s, OH) ppm.



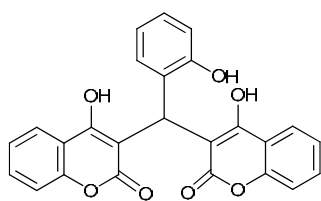
¹H NMR (CDCl₃, 300 MHz): δ = 3.80 (3H, s, OCH₃), 6.05 (1H, s), 6.85 (2H, d, *J* = 8.7 Hz), 7.13 (2H, d, *J* = 8.7 Hz), 7.30–7.42 (4H, m), 7.63 (2H, t, *J* = 8.2 Hz), 8.03 (2H, dd, *J* = 8.4 Hz), 11.29 (1H, brs, OH), 11.51 (1H, brs, OH)



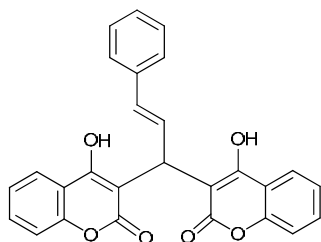
¹H NMR (DMSO-d₆, 400 MHz): δ = 3.2 (6H, s, CH₃), 6.31 (1H, s, CH), 7.23–7.84 (m, 12H) ppm.



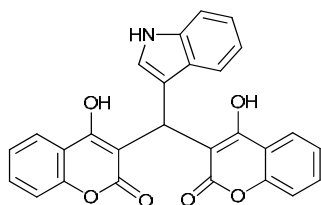
¹H NMR (CDCl₃, 400 MHz): δ = 2.50 (3H, s, CH₃), 6.08 (1H, s, CH), 7.16 (2H, d, *J* = 8 Hz), 7.23 (2H, d, *J* = 8.4 Hz), 7.39–7.45 (4H, m), 7.6 (2H, td, *J*₁ = 7.6 Hz, *J*₂ = 1.6 Hz), 8.02–8.11 (2H, m), 11.34 (1H, s, OH), 11.55 (1H, s, OH) ppm.



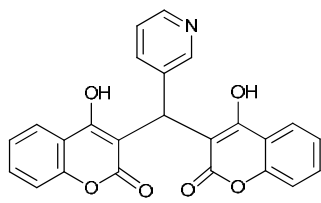
¹H NMR (CDCl₃, 500 MHz): δ = 5.41 (1H, s, CH), 7.10–7.20 (2H, m), 7.23 (1H, d, *J* = 8.0 Hz), 7.30–7.38 (3H, m), 7.40–7.50 (2H, m), 7.53 (1H, td, *J*₁ = 7.5, *J*₂ = 1.5 Hz), 7.67 (1H, td, *J*₁ = 7.8, *J*₂ = 1.5 Hz), 8.07 (1H, dd, *J*₁ = 7.9, *J*₂ = 1.5 Hz), 8.19 (1H, dd, *J*₁ = 8.0, *J*₂ = 1.5 Hz), 10.43 (1H, s, OH) ppm.



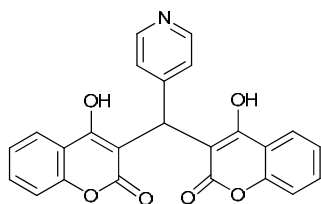
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 4.9 (d, 1H, J =3.5 Hz) 6.85 (d, 1H, J = 15.4 Hz), 7.15–7.18 (5H, m), 7.20 (td, 2H, J_1 = 8.0, J_2 = 2.5 Hz), 7.25 (dd, 1H, J_1 = 15.4, J_2 = 3.5 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.51 (td, 2H, J_1 = 8.0, J_2 = 1.7 Hz), 7.89 (d, 2H, J = 8.0 Hz) ppm.



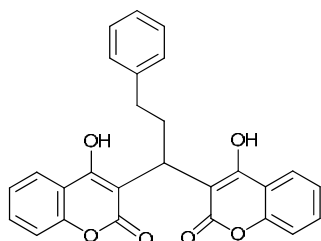
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 6.03 (s, 1H), 7.10–7.18 (m, 1H), 7.20 (td, 2H, J_1 = 7.8, J_2 = 2.0 Hz), 7.28 (d, 2H, J = 7.8 Hz), 7.59 (td, 2H, J_1 = 7.8, J_2 = 2.0 Hz), 7.79 (d, 2H, J = 7.8 Hz) ppm.



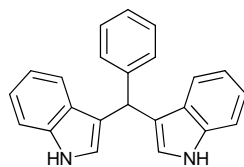
$^1\text{H NMR}$ (DMSO-d_6 , 400 MHz): δ = 6.43 (1H, s, CH), 7.26 (2H, t, J = 7.6 Hz), 7.3 (2H, d, J = 8 Hz), 7.56 (2H, td, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.82 (2H, dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 7.94 (1H, td, J_1 = 7 Hz, J_2 = 2 Hz), 8.37 (1H, d, J = 8 Hz), 8.66 (1H, s), 8.72 (1H, d, J = 5.2 Hz), 16.93 (bs, OH) ppm.



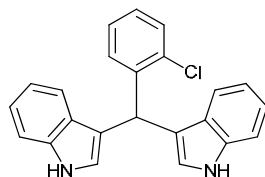
$^1\text{H NMR}$ (DMSO-d_6 , 400 MHz): δ = 6.49 (1H, s, CH), 7.23 (2H, t, J = 7.2 Hz), 7.28 (2H, d, J = 8.4 Hz), 7.5 (2H, t, J = 7.2 Hz), 7.81–7.83 (4H, m), 8.6 (2H, d, J = 6 Hz), 16.97 (bs, OH) ppm.



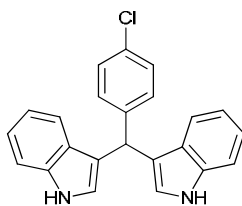
$^1\text{H NMR}$ (DMSO-d_6 , 400 MHz): δ = 1.89 (2H, m), 2.67 (2H, m), 5.8 (1H, t, J = 6.8 Hz), 6.5–6.8 (5H, m), 7.30 (2H, td, J_1 = 8.0, J_2 = 2.4 Hz), 7.33 (2H, d, J = 8.0 Hz), 7.65 (2H, td, J_1 = 8.0, J_2 = 2.2 Hz), 7.88 (2H, d, J_1 = 8.0 Hz) ppm.



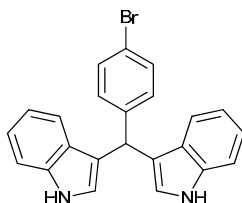
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 5.91 (1H, s, CH), 6.68 (2H, s), 7.10 (2H, t, J = 7.3 Hz), 7.22 (2H, t, J = 7.3 Hz), 7.23 (1H, t, J = 7.2 Hz), 7.30–7.40 (2H, m), 7.35–7.45 (4H, m), 7.41 (2H, d, J = 7.9 Hz), 7.90 (2H, brs, NH) ppm.



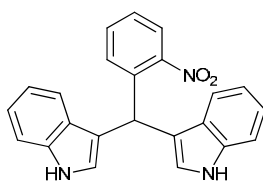
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 6.34 (1H, s, CH), 6.66 (2H, s), 7.02 (2H, t, J = 8.0 Hz), 7.11–7.23 (6H, m), 7.36–7.43 (4H, m), 7.96 (2H, brs, NH) ppm.



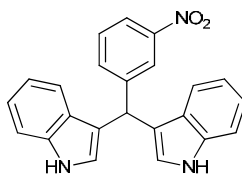
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 5.86 (1H, s, CH), 6.66 (2H, s), 7.02 (2H, t, J = 8.3 Hz), 7.23–7.38 (8H, m), 7.4 (2H, d, J = 8.1 Hz), 7.85 (2H, brs, NH) ppm.



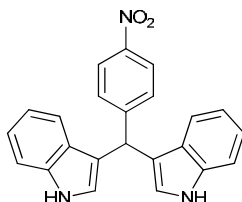
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 5.82 (1H, s, CH), 6.56 (2H, s), 7.03–6.99 (2H, m), 7.38–7.15 (10H, m), 7.82 (2H, brs, NH) ppm.



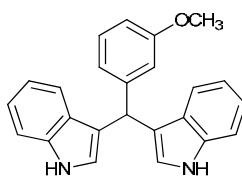
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 6.12 (1H, s), 6.91 (2H, s), 7.08–7.17 (4H, m), 7.29 (2H, d, J = 7.8 Hz), 7.47 (2H, d, J = 7.9 Hz), 7.57–7.66 (2H, m), 7.79–7.90 (2H, m), 8.21 (2H, d, J = 8.6 Hz) ppm.



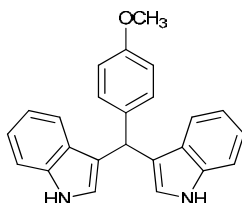
$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 6.03 (1H, s), 6.72 (2H, s), 7.05 (2H, t, J = 6.75 Hz), 7.23 (2H, t, J = 7.25 Hz), 7.38 (2H, d, J = 8 Hz), 7.41 (2H, d, J = 8 Hz), 7.47 (1H, t, J = 8 Hz), 7.72 (1H, d, J = 8 Hz), 8.04 (2H, s, NH), 8.11 (1H, d, J = 8 Hz), 8.23 (1H, s) ppm.



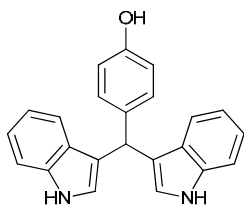
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 6.00 (1H, s), 6.70 (2H, s), 7.00–7.05 (3H, m), 7.35 (3H, d, J = 8.0 Hz), 7.40 (2H, d, J = 8.0 Hz), 7.52 (2H, d, J = 8.8 Hz), 8.04 (1H, brs, NH) ppm.



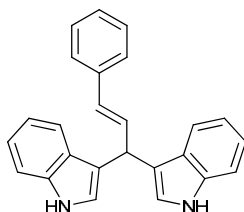
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 3.76 (3H, s), 3.85 (3H, s), 5.83 (1H, s), 6.65 (2H, d), 6.78 (2H, d), 7.0 (3H, t), 7.17 (2H, t), 7.29–7.43 (4H, m), 7.91 (2H, bs, NH) ppm.



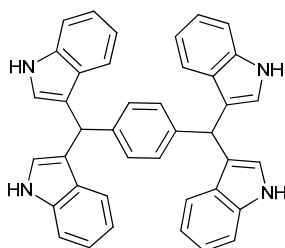
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 3.76 (3H, s), 5.85 (1H, s), 6.68 (2H, s), 6.91 (2H, d, J = 8.2 Hz), 7.02 (2H, t, J = 7.3 Hz), 7.16 (2H, t, J = 7.3 Hz), 7.20 (2H, m), 7.35–7.41 (4H, m), 7.95 (s, NH) ppm.



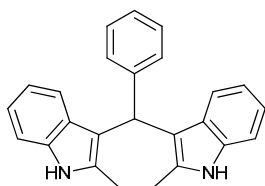
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 5.83(1H, s), 6.66(2H, s), 6.74(2H, d, J = 8.1 Hz), 7.0(2H, t, J = 8 Hz), 7.14-7.40(8H, m), 7.92(2H, brs, NH) ppm.



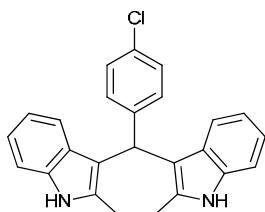
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 5.41 (1H, d, J = 7.1 Hz); 6.54 (1H, d, J = 15.7 Hz), 6.80 (1H, dd, J_1 = 15.7, J_2 = 7.1 Hz), 6.71 (2H, s), 7.04 (2H, t, J = 7.0 Hz), 7.18 (2H, t, J = 7.0 Hz); 7.24-7.28 (m, 3H); 7.35-7.38 (4H, m); 7.60 (2H, d, J = 7.4 Hz), 7.94 (2H, brs) ppm.



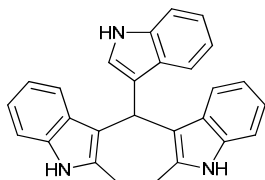
$^1\text{H NMR}$ (DMSO-d_6 , 300 MHz): δ = 5.75 (2H, s), 6.29 (4H, s), 7.05 (4H, t, J = 7.6 Hz), 7.16 (4H, t, J = 7.6 Hz), 7.24-7.40 (12H, m), 7.31 (4H, brs) ppm.



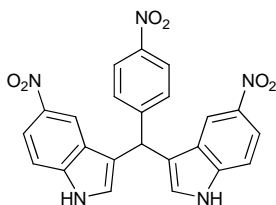
$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 2.05 (6H, s, CH₃), 5.88 (1H, s, CH), 6.78-7.01 (6H, m), 7.14-7.22 (5H, m), 7.28-7.31 (2H, m), 8.02 (s, NH) ppm.



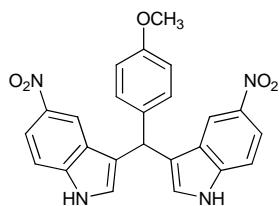
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 2.10 (6H, s, CH₃), 5.96 (1H, s, CH), 6.91 (2H, dt, J_1 = 6.4 Hz, J_2 = 0.6 Hz), 7.01 (2H, d, J = 6.4 Hz), 7.09 (2H, dt, J_1 = 6.4 Hz, J_2 = 0.6 Hz), 7.19 (2H, d, J = 6.8 Hz), 7.30 (2H, dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.40 (2H, dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz), 7.80 (s, NH) ppm.



$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ = 2.39 (6H, s), 6.19 (1H, s), 6.82 (1H, s), 7.07 (2H, t, J = 7.70 Hz), 7.19 (4H, t, J = 7.59 Hz), 7.42 (2H, d, J = 8.13 Hz), 7.5 (2H, d, J = 9.47 Hz), 7.79 (2H, d, J = 7.83 Hz), 8.01 (2H, brs, NH), 8.29 (1H, brs, NH) ppm.



$^1\text{H NMR}$ (DMSO-d_6 , 400 MHz): δ = 6.50 (1H, s, CH), 7.24 (2H, s), 7.57 (2H, d, J = 8.8 Hz), 7.68 (2H, d, J = 8.8 Hz), 8.0 (2H, dd, J_1 = 9 Hz, J_2 = 2 Hz), 8.22 (2H, d, J = 8.8 Hz), 8.40 (2H, d, J = 2.4 Hz), 11.9 (s, NH) ppm.



¹H NMR (DMSO-d₆, 400 MHz): δ = 3.73 (3H, s, OCH₃), 6.15 (1H, s, CH), 6.89 (2H, d, J = 8.4 Hz), 7.12 (2H, s), 7.30 (2H, d, J = 8.8 Hz), 7.55 (2H, d, J = 9.2 Hz), 7.98 (2H, dd, J_1 = 9 Hz, J_2 = 2 Hz), 8.32 (2H, d, J = 2.4 Hz), 11.67 (s, NH) ppm.

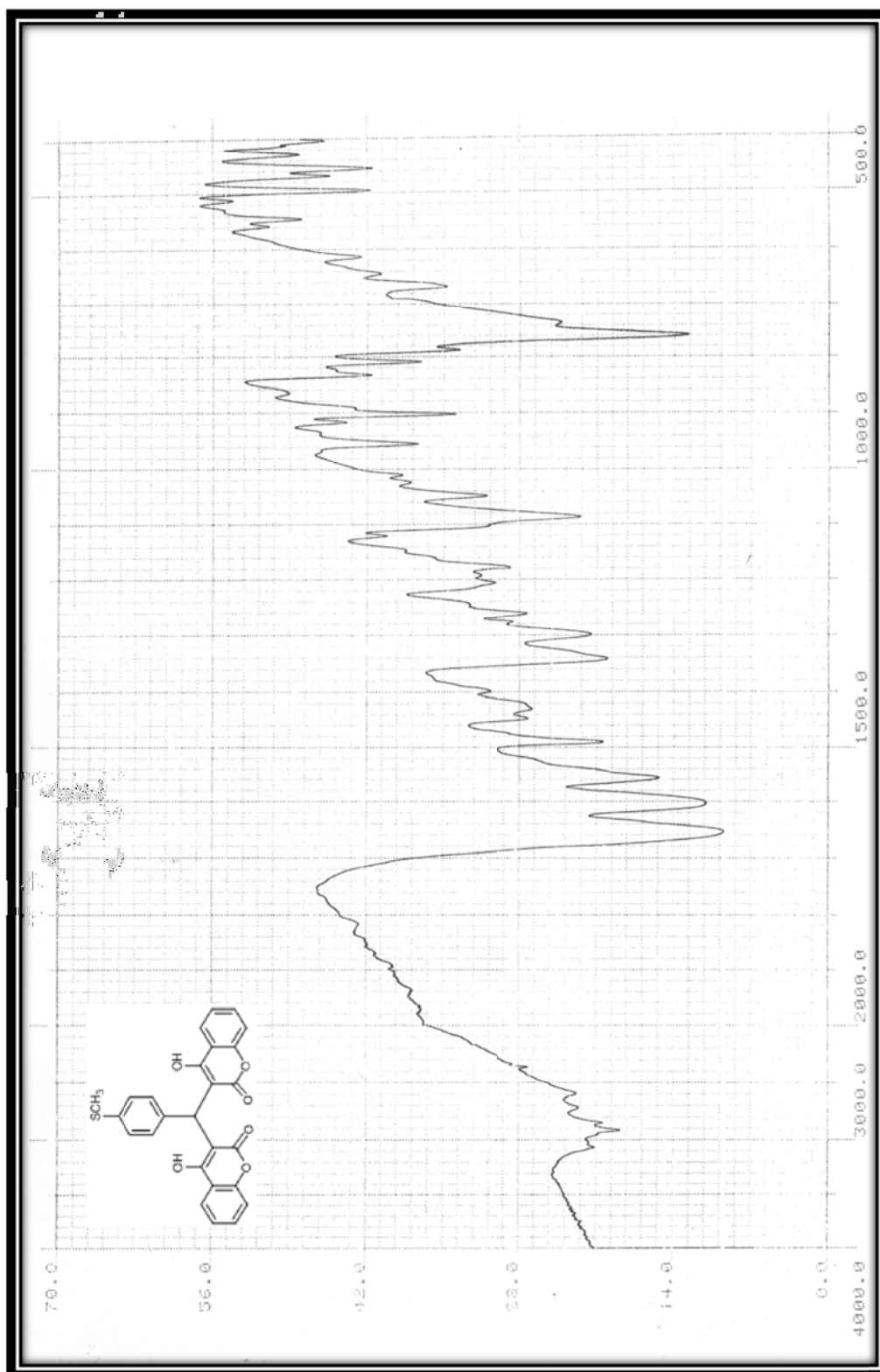


Fig 1. IR spectrum of 3,3'-(4-thiomethylbenzylidene)-bis-(4-hydroxycoumarin).

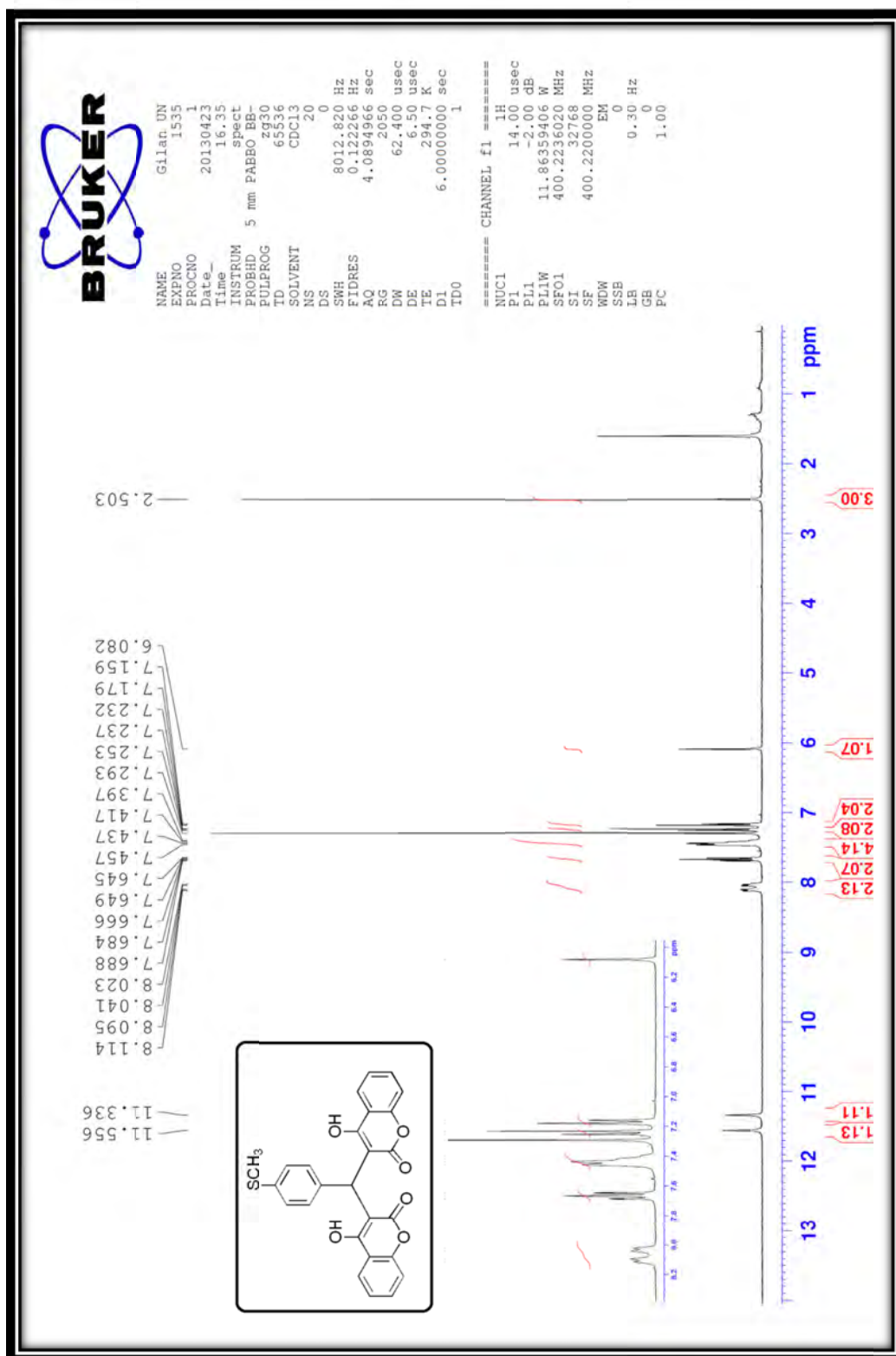


Fig 2. ¹H-NMR of 3,3'-(4-thiomethylbenzylidene)-bis-(4-hydroxycoumarin).

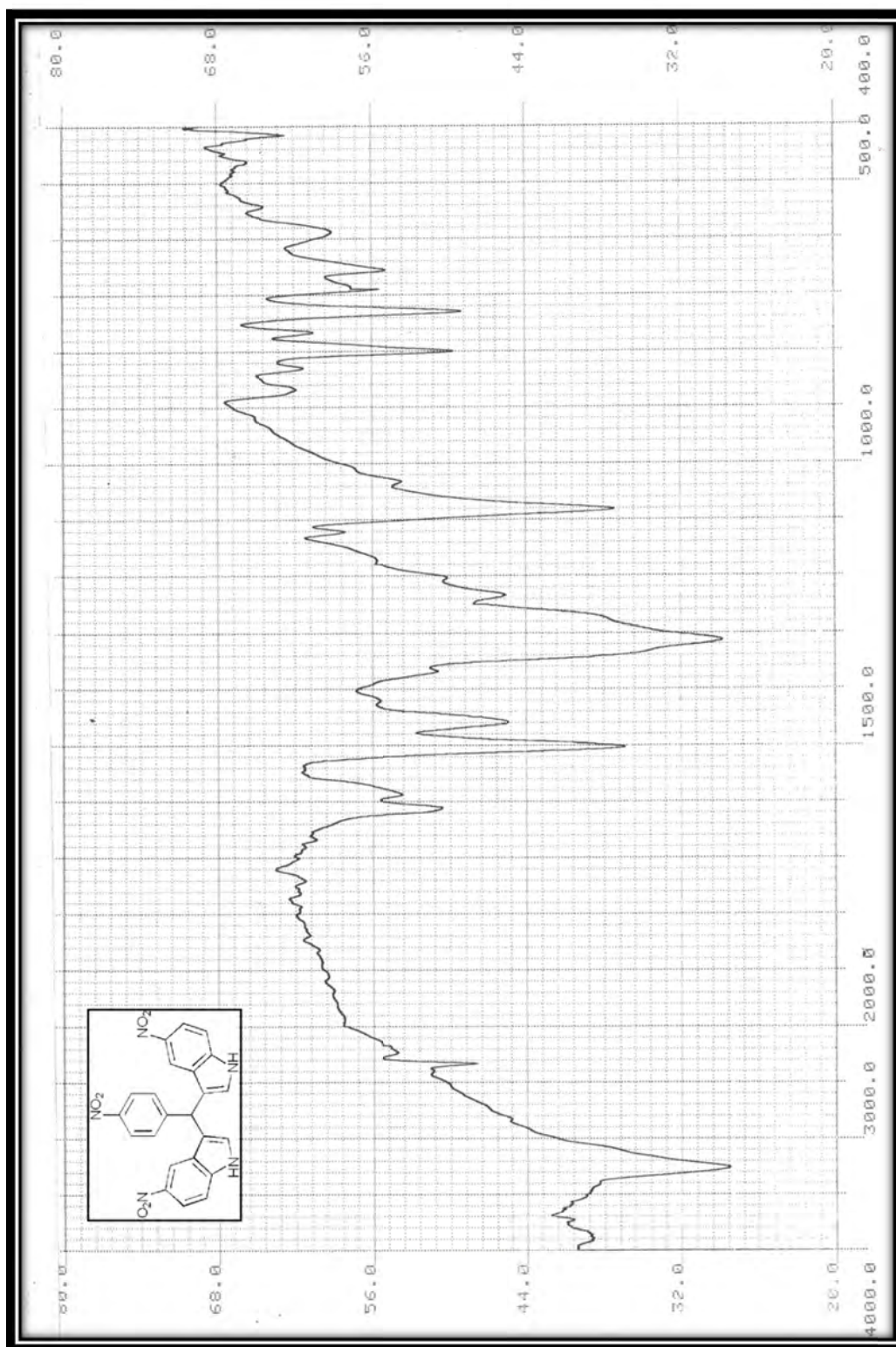


Fig 3. IR spectrum of 3,3'-(4-nitrophenylmethylene)-bis-(5-nitroindole).

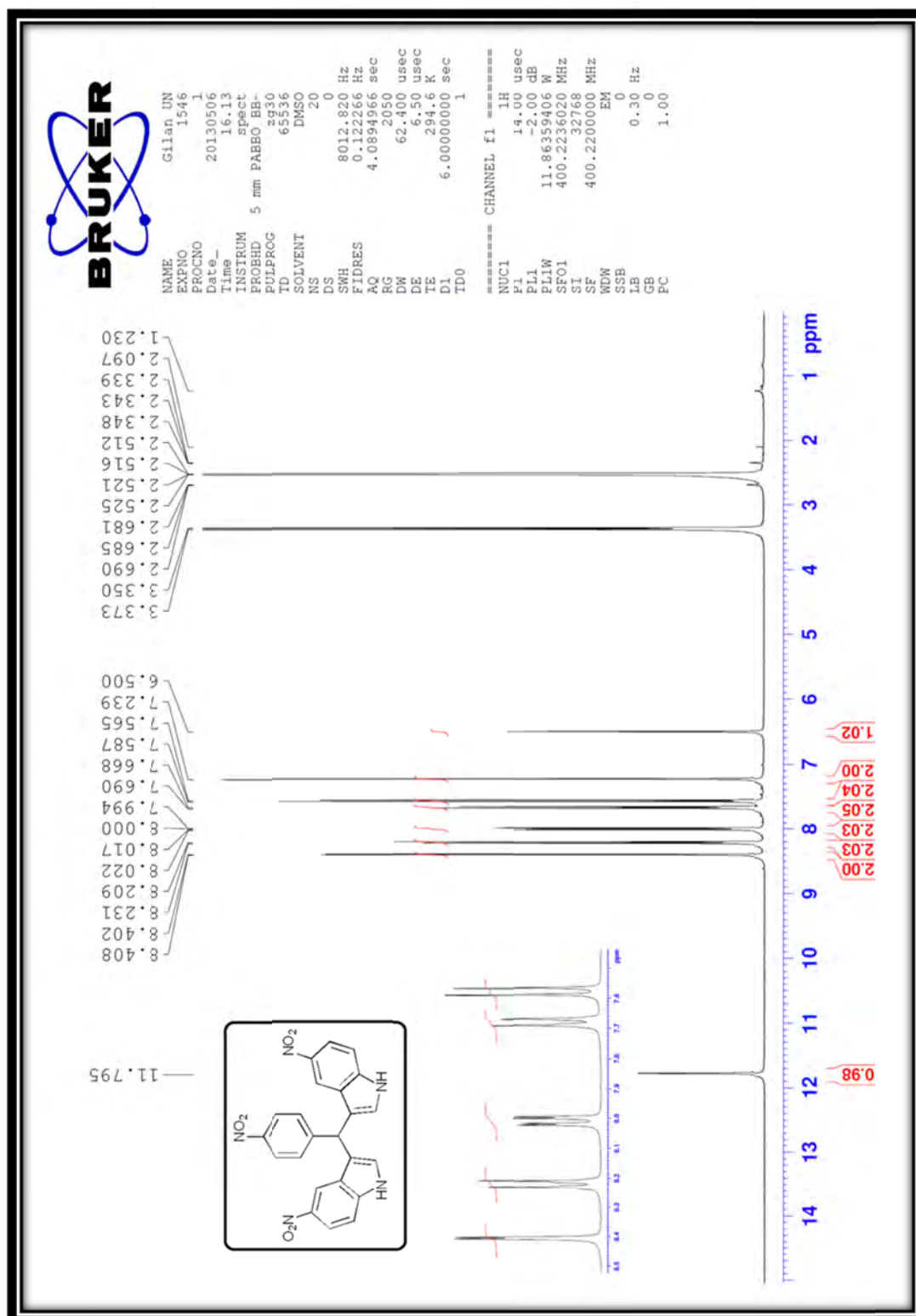


Fig 4. $^1\text{H-NMR}$ of 3,3'-(4-nitrophenylmethylene)-bis(5-nitroindole).

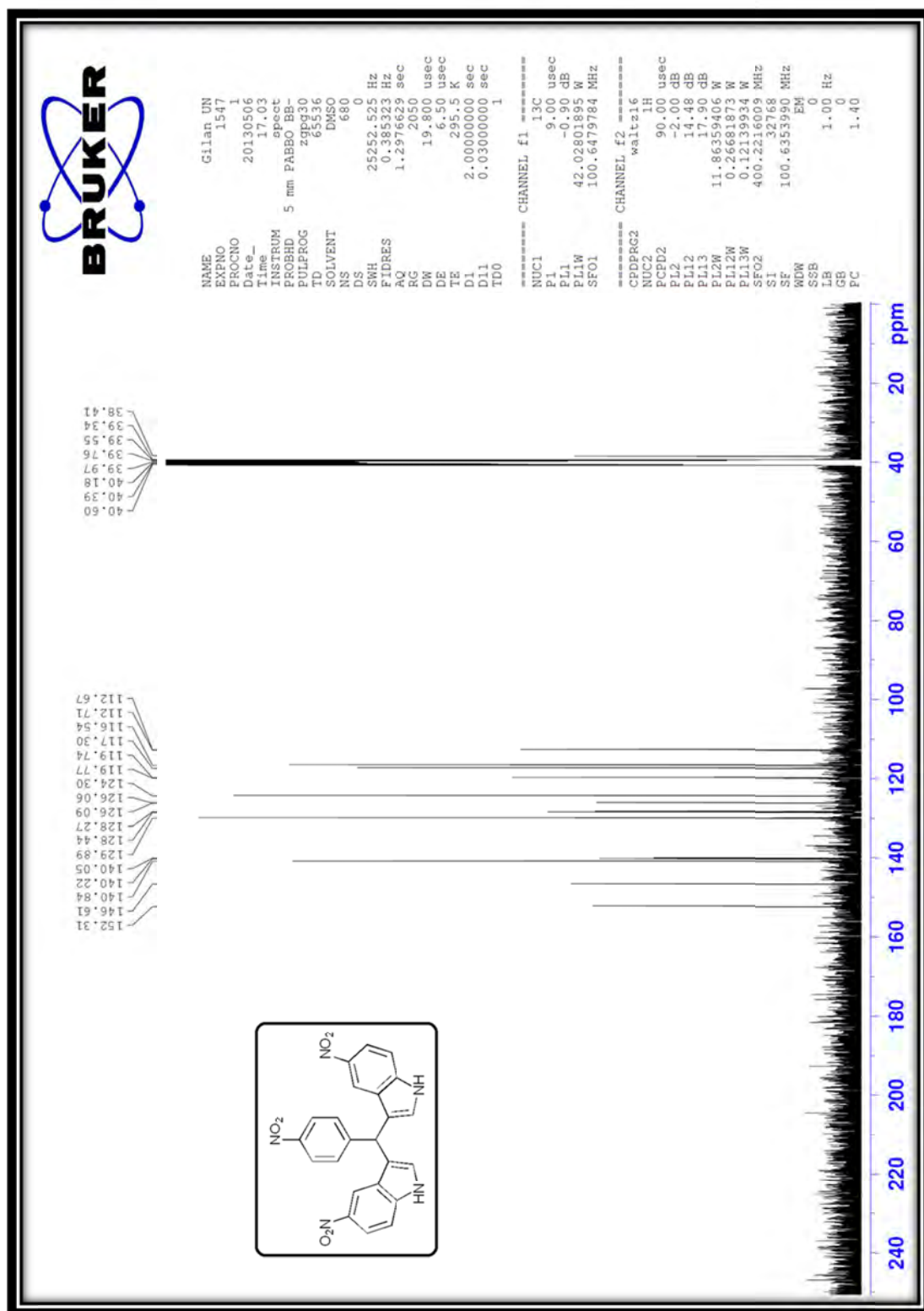


Fig 5. ^{13}C -NMR of 3,3'-(4-nitrophenylmethylene)-bis-(5-nitroindole).

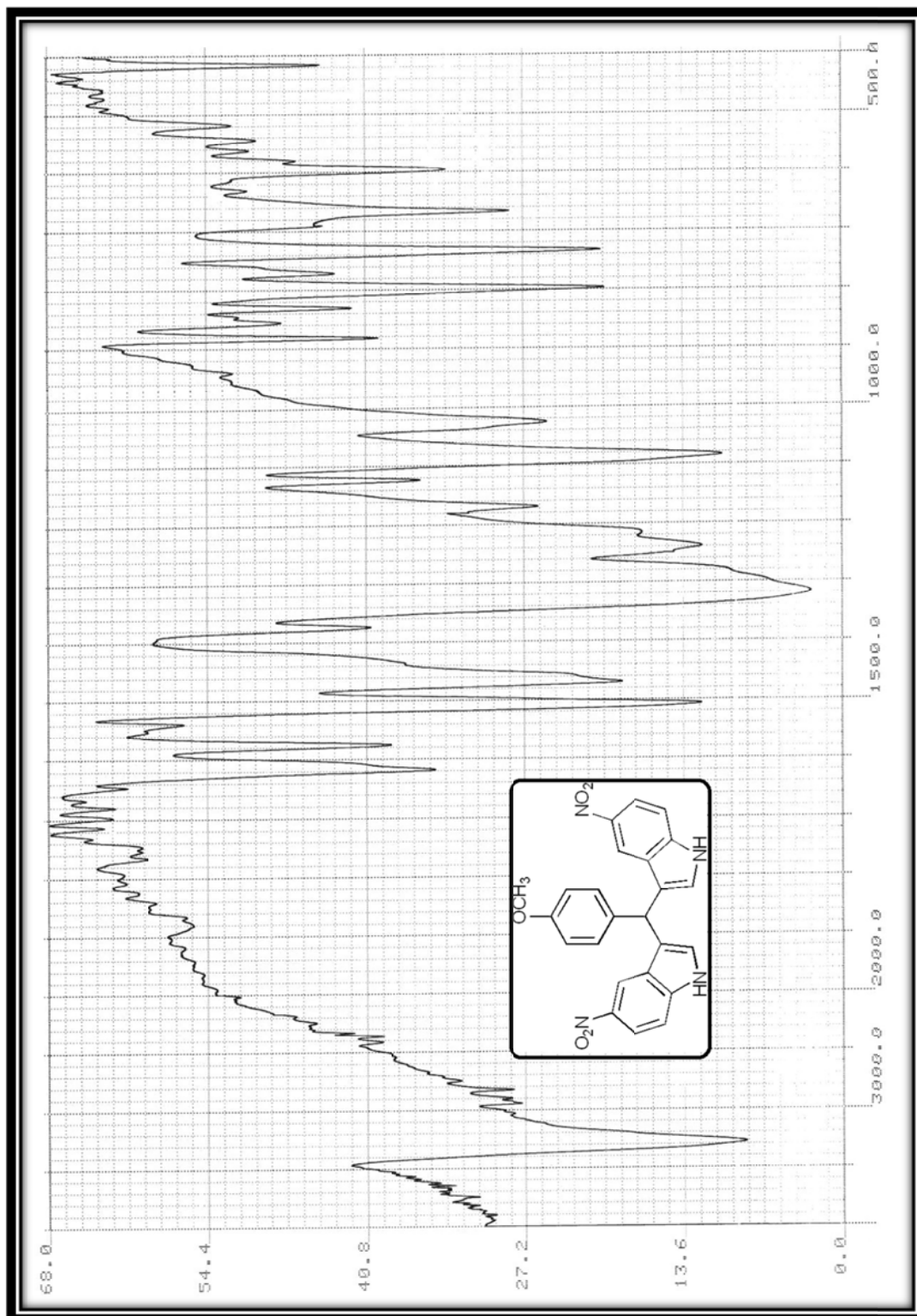


Fig 6. IR spectrum of 3,3'-(4-methoxyphenylmethylene)-bis-(5-nitroindole).

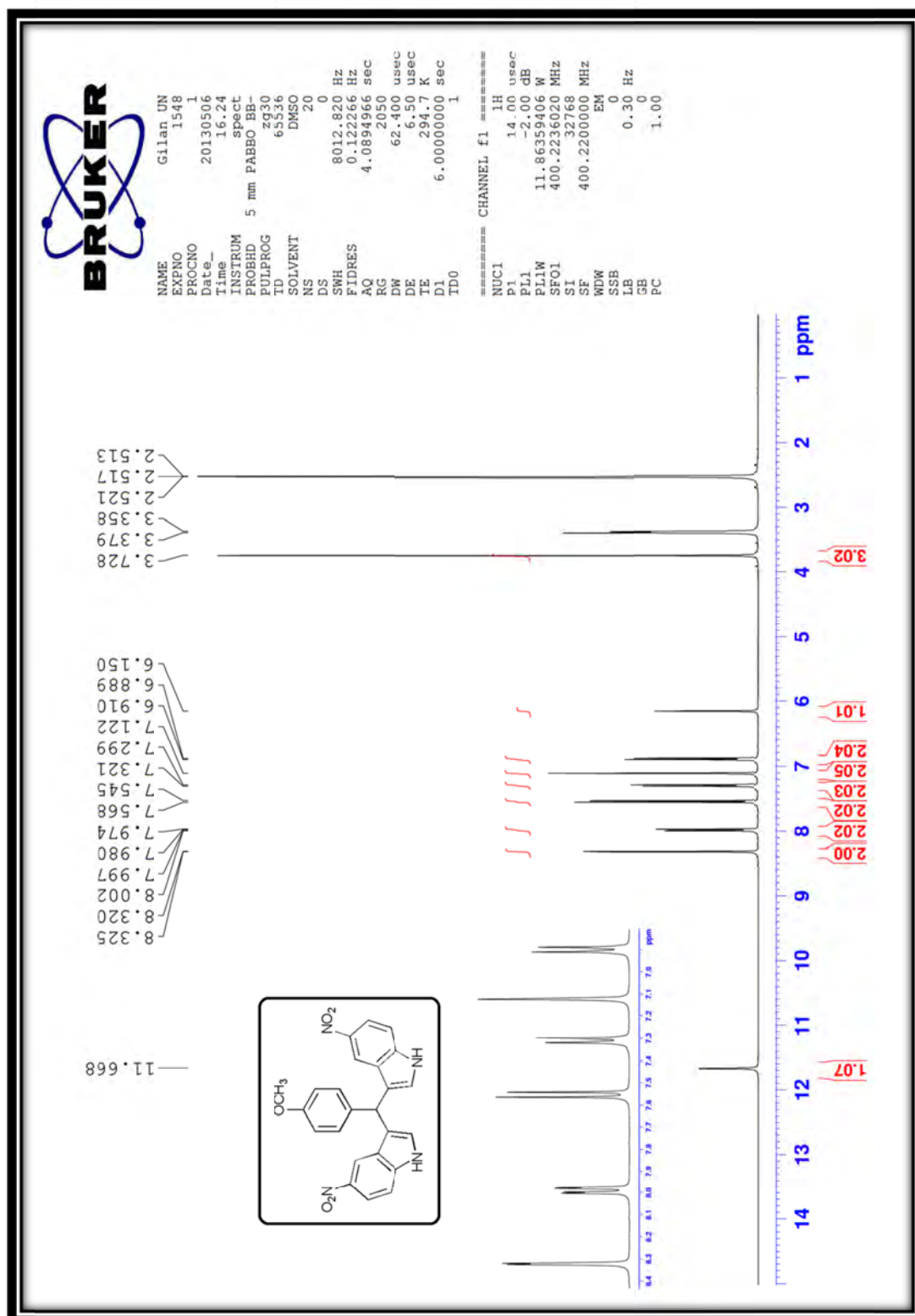


Fig 7. ¹H-NMR of 3,3'-(4-methoxyphenylmethylene)-bis-(5-nitroindole).

