Synthesis of new ferrocene bis thiocarbazones under solvent-free conditions using microwave

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A simple efficient method for the synthesis of new ferrocene bis thiocarbazones via microwave irradiation under solvent-free conditions has been developed. Compared to the conventional method, its major advantages are short reaction times, good conversions and actually accorded the green synthesis technology. The structures of target compounds were confirmed by ^{1}H NMR, IR, ESI-MS spectra data and elemental analysis. Preliminary bioassay results showed that some of these compounds possess inhibitory effects against *S. aureus*, *S. pyogenes* and *E. coli* bacteria.

Keywords: ferrocene, bis thiocarbazones, microwave irradiation, solvent-free conditions

Ferrocene derivatives are important compounds that have attracted attention owing to their remarkable biological, medical and microbiological properties.[1] Incorporation of a ferrocene fragment into the molecule of an organic compound often leads to unexpected biological activity, which is due to their different structure.[2–4] For example, ferrocenic pyrrolo [1, 2-a]quinoxaline derivatives possess antimalarial activity,[5] ferrocenyl chalcone derivatives have antitumor activity[6] and other ferrocenyl derivatives are antimycobacterial agents.[7]

Thiocarbazones are considered to be one of the most important scaffolds and are embedded in many biologically active compounds.[8] Ferrocenyl modifications of thiocarbazones could lead to significant change in biological activity.[9]

Environmental concerns have led to the use of environmentally benign solvents such as water and solvent-free reactions in green chemical procedures with both the economic and synthetic advanyages. Microwave-assisted solvent-free synthesis is an environmentally friendly synthetic method which is widely used in organic synthesis. It can reduce reaction times affording cleaner reactions, enhanced conversions and simplified work-up.[10–12] It clearly constitutes an eco-friendly green approach.[13,14]

We have already synthesised a series of compounds under solvent-free conditions using microwave methods.[15–17] Our previous work focused on the synthesis of steroidal thiocarbazones[18] and we have now turned our attention toward ferrocenyl thiocarbazones. We report here the synthsis of novel ferrocenyl bis thiocarbazones under microwave assisted solvent-free conditions. The synthetic route is depicted in Scheme **1**.

Results and discussion

The structures of the compounds **4a–j** were confirmed by IR, mass, ^{1}H NMR and elementary analysis. Their mass spectra showed the expected molecular ions in high intensity. The IR spectra of these compounds exhibited a characteristic strong absorption at 3260–3526 cm^{-1} due to N–H stretching vibration; The strong bands in the region 2928–3096 cm^{-1} indicated the absorption of ferrocenyl C–H; The strong absorption bands falling within the range of 1520–1615 cm^{-1} and the range of 1215–1317 cm^{-1} were assigned to the C=N and C=S respectively. In the ^{1}H NMR spectra, the singlet peaks between δ 11.59 and 12.56 ppm were assigned to the protons in the NH, and a singlet peaks due to the other NH proton was observed at 10.71–10.97 ppm. In addition, the singlet peaks at 4.17–4.38 ppm, 4.44–4.74 ppm and 4.82–4.99 ppm were characteristic of ferrocene structures. The singlet peaks between δ 2.28 and 2.43 ppm were assigned to the protons of the CH_3 group.

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As shown in Table 1, it is obvious that microwave irradiation greatly decreased the reaction time from 360–600 min to 3–5 min. The yields also increased from 55–72% to 86–94%. Consequently, the use of microwave technology in conjunction with the use of solvent-free conditions allowed an expeditious and efficient procedures for their synthesis.

In vitro *antibacterial activity*

Compounds **4a**, **4b**, **4e** and **4j** were evaluated for their *in vitro* antibacterial activity against *Staphylococcus aureus*, *Staphylococcus pyogenes* and *Escherichia coli* using an agar dilution method. The preliminary results seemed promising and these thiocarbazones showed good inhibitory effect. More research work is underway.

In conclusion, we have used an inexpensive, nonpoisonous, and highly effective method for the preparation of ferrocene bis thiocarbazones. Its major advantages are short reaction times, good conversions and follow a green synthetic technology. In addition, these compounds may have good antibacterial activity which needs further research. The importance of such work lies in the possibility that the new compounds might be useful in designing more potent antibacterial agents with therapeutic uses.

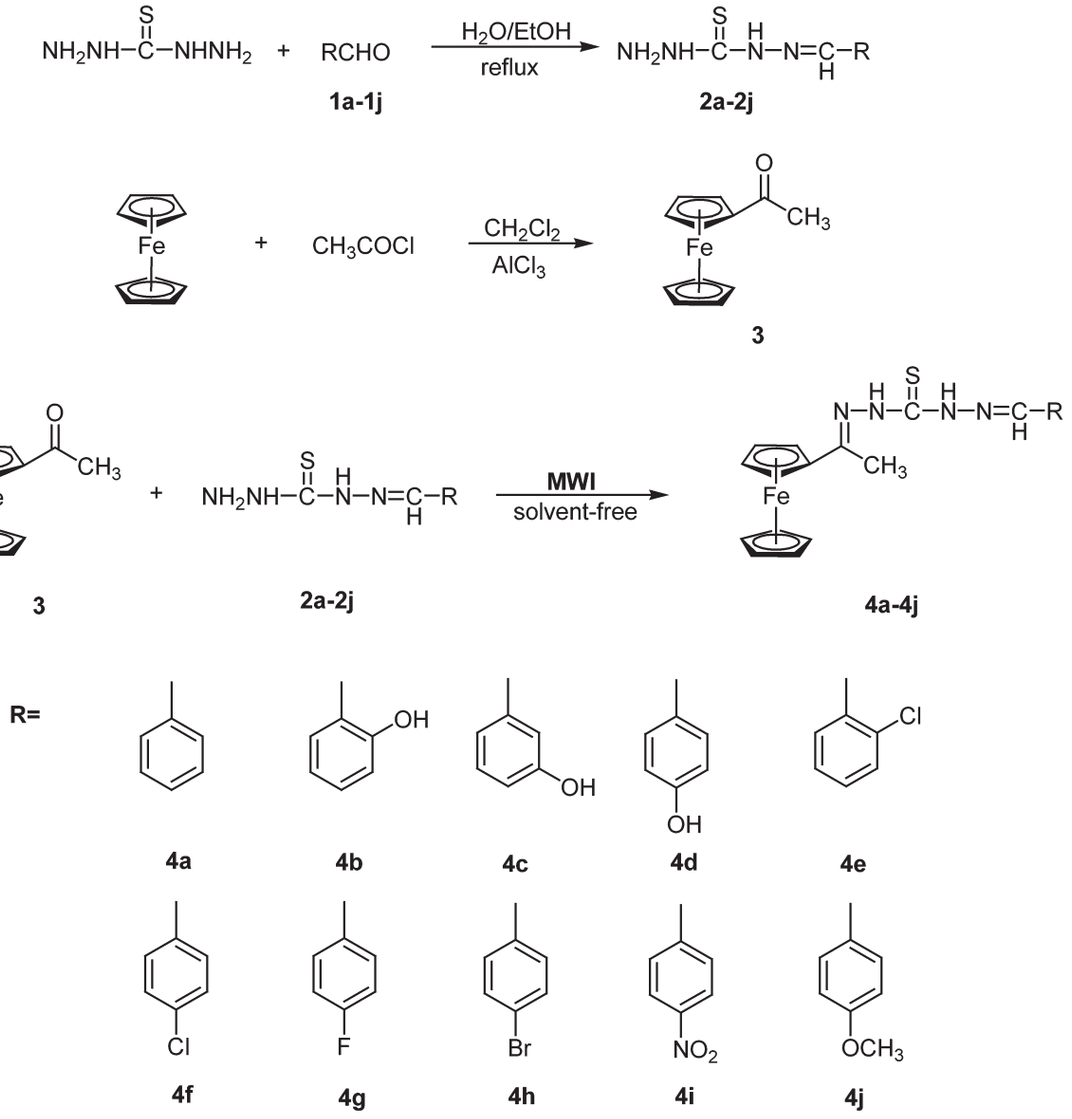
Experimental

Melting points were determined on a micro-melting point apparatus and the thermometer was uncorrected. IR spectra were obtained on 1700 PerkinElmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using DMSO-d_6 and $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were determined on FinniganLCQ^{DECA} instrument. Elemental analysis was performed on a Carlo-Erba-1106 auto analyzer. All reactions were performed in a commercial scientific microwave oven (XH-100A, 100-1000W, Beijing XiangHu Science and Technology Development Co. Ltd, Beijing, P.R. China). All the chemicals and solvents were dried and purified by standard methods.

Synthesis of substituted benzaldehyde thiocarbohydrazones **2a–j**[19]

A solution of thiocarbohydrazide (15 mmol) in H_2O (50 mL) and acetic acid (1 mL), was treated with aromatic aldehyde (10 mmol) in ethanol (40 mL) dropwise over 1 h under reflux. After the addition, the mixture was refluxed for a further 3 h. Then the precipitate was collected by filtration and washed with water (3×10 mL). The resulting solid was recrystallised from ethanol to give the pure product. The analytical data for **2c**, **2f**, **2g** and **2h** are given below. The melting point of benzaldehyde thiocarbohydrazones **2a–j** was shown in Table 2.

2c: Yellow solid, yield 72%, m.p. 200–201 °C, IR (KBr)(cm^{-1}): 3241, 3174, 2983, 1609, 1580, 1515, 1279, 1158, 1011; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.34 (s, 1H, NH), 9.72 (s, 1H, NH), 9.48 (s, 1H, OH), 7.92 (s, 1H, =CH), 7.24–7.16 (m, 3H, ArH), 6.79 (d, 1H, J = 7.6 Hz, ArH), 4.85 (s, 2H, NH_2); ESI-MS *m/z* (%): 421 ([2M+1]$^+$, 100). Ana1. Calcd for $C_8H_{10}N_4OS$: C, 45.70; H, 4.79; N, 26.65. Found: C, 45.57; H, 4.82; N, 26.69%.



Scheme 1 The synthetic route of the bis thiocarbazones **4a–j**.

Table 1 Synthetic comparison of compounds **4a–j** between solvent-free conditions under microwave irradiation and conventional heating

Compd	Conventional method		Microwave method		t_C/t_{MW}[a]
	t/min	Yield/%	t/min	Yield/%	
4a	360	70	3	92	120
4b	420	63	4	89	105
4c	420	57	5	91	84
4d	420	67	4	86	100
4e	480	70	4	93	120
4f	540	72	4	87	135
4g	360	70	3	90	120
4h	420	68	5	94	84
4i	600	55	5	88	120
4j	600	66	5	90	120

t_C, Conventional method time; t_{MW}, microwave method time.

2f: Yellow solid, yield 78%, m.p. 210–211 °C, IR (KBr)(cm^{-1}): 3311, 3273, 3153, 2968, 1597, 1543, 1505, 1249, 1079; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.50 (s, 1H, NH), 9.93 (s, 1H, NH), 7.98 (s, 1H, =CH), 7.89 (d, 2H, *J* = 8.4 Hz, ArH), 7.45 (d, 2H, *J* = 8.4 Hz, ArH), 4.88 (s, 2H, NH_2); ESI-MS *m/z* (%): 269 ([M+39]$^+$, 100). Ana1. Calcd for $C_8H_9ClN_4S$: C, 42.01; H, 3.97; N, 24.50. Found: C, 41.94; H, 3.92; N, 24.40%.

2g: White solid, yield 74%, m.p. 208–209 °C, IR (KBr)(cm^{-1}): 3300, 3151, 2976, 1598, 1504, 1268, 1205, 1074; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.46 (s, 1H, NH), 9.90 (s, 1H, NH), 7.99 (s, 1H, =CH), 7.94–7.91 (m, 2H, ArH), 7.24 (t, 2H, *J* = 8.8 Hz, ArH), 4.88 (s, 2H, NH_2); ESI-MS *m/z* (%): 235 ([M+23]$^+$, 100). Ana1. Calcd for $C_8H_9FN_4S$: C, 45.27; H, 4.27; N, 26.40. Found: C, 45.17; H, 4.23; N, 26.42%.

2h: Yellow solid, yield 80%, m.p. 211–212 °C, IR (KBr)(cm^{-1}): 3253, 3168, 2997, 1619, 1589, 1530, 1484, 1244, 1067; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.46 (s, 1H, NH), 9.90 (s, 1H, NH), 7.97 (s, 1H, =CH), 7.81 (d, 2H, *J* = 8.4 Hz, ArH), 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 4.87 (s, 2H, NH_2); ESI-MS *m/z* (%): 545 ([2M+1]$^+$, 100). Ana1. Calcd for $C_8H_9BrN_4S$: C, 35.18; H, 3.32; N, 20.51. Found: C, 35.09; H, 3.36; N, 20.47%.

Preparation of acetylferrocene (**3**)[22]

To a solution of ferrocene (2.23 g, 12 mmol) in dried CH_2Cl_2 (15 mL) at 0 °C, a solution of acetylchloride (0.75 mL, 10 mmol) and aluminium chloride (1.60 g, 10 mmol) in dried CH_2Cl_2 (15 mL) was

Table 2 The melting points of substituted benzaldehyde thiocarbohydrazones **2a–j**

Entry	Compd	Formula	M.p./°C	Lit M.p./°C
1	**2a**	$C_8H_{10}N_4S$	196–197	198[19]
2	**2b**	$C_8H_{10}N_4OS$	217–218	218[19]
3	**2c**	$C_8H_{10}N_4OS$	200–201	—
4	**2d**	$C_8H_{10}N_4OS$	210–211	210[19]
5	**2e**	$C_8H_9ClN_4S$	209–210	210[19]
6	**2f**	$C_8H_9ClN_4S$	210–211	—
7	**2g**	$C_8H_9FN_4S$	208–209	—
8	**2h**	$C_8H_9BrN_4S$	211–212	—
9	**2i**	$C_8H_9N_5O_2S$	206–207	204–206[20]
10	**2j**	$C_9H_{12}N_4OS$	199–200	198–200[21]

added dropwise. After being stirred at room temperature for 8 h, water was added. The organic layer was separated and washed by water and brine. The resulting solution was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum. The crude product was purified by chromatography on silica gel using V($CH_3COOC_2H_5$): V(Petroleum ether) =1: 10 to give an orange solid, yield 89%, m.p. 85–86 °C (lit.[23] m.p. 87 °C); IR (KBr)(cm^{-1}): 3436, 3090, 2924, 1657, 1454, 1107, 824, 496; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.78 (t, 2H, J = 1.8 Hz, H-2 H-5, Fc), 4.52 (t, 2H, J = 1.8 Hz, H-3 H-4, Fc), 4.21 (s, 5H, Fc-unsubst. ring), 2.40 (s, 3H, CH_3); ESI-MS *m/z* (%): 229 ([M+1]$^+$, 100).

Preparation of bis thiocarbazones **4a–j**

Conventional method: Acetylferrocene (**3**) (0.114 g, 0.5 mmol) and the substituted benzaldehyde thiocarbohydrazones (**2a–j**) (0.45 mmol) were dissolved in ethanol (10 mL). After completely dissolving, two drops of hydrochloric acid were added. The mixture was stirred for 6–10 h at room temperature. The crude products were filtered and recrystallised from DMSO and H_2O to afford the pure products in 55–72% yields.

Microwave irradiation method: Acetylferrocene (**3**) (0.114 g, 0.5 mmol), substituted benzaldehyde thiocarbohydrazones (**2a–j**) (0.45 mmol) and neutral aluminium oxide (0.3 g) were put in a porcelain mortar, then concentrated hydrochloric acid (two drops) was added. After grinding, the mixture was put in a round-bottom flask (25 mL) and then placed in the microwave oven. Then it was irradiated for 3–5 min at 250–500W. The reaction mixture was cooled to room temperature and dissolved in DMSO and filtered. Water was added to the filtrate and the product was precipitated. The product was recrystallised from DMSO and H_2O in 86–94% yields. The physical and spectroscopic data of the compounds **4a–j** are as follows.

4a: Pink solid, yield 92%, m.p. 174–175 °C; IR (KBr)(cm^{-1}): 3440, 3081, 2973, 1609, 1440, 1261, 1107, 1068, 823, 491; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.06 (s, 1H, NH), 10.81 (s, 1H, NH), 8.88 (s, 1H, =CH), 7.81 (s, 2H, ArH), 7.48 (d, 3H, J = 6.4 Hz, ArH), 4.90 (s, 2H, H-2 H-5, Fc), 4.62 (s, 2H, H-3 H-4, Fc), 4.32 (s, 5H, Fc-unsubst. ring), 2.43 (s, 3H, CH_3); ESI-MS *m/z* (%): 405 ([M+1]$^+$, 100). Ana1. Calcd for $C_{20}H_{20}FeN_4S$: C, 59.41; H, 4.99; N, 13.86. Found: C, 59.37; H, 4.98; N, 13.83%.

4b: Yellow solid, yield 89%, m.p. 204–205 °C; IR (KBr)(cm^{-1}): 3445, 3260, 2928, 1615, 1520, 1269, 1154, 1040, 838, 486; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.68 (s, 1H, OH), 11.59 (s, 1H, NH); 10.75 (s, 1H, NH), 8.76 (s, 1H, =CH), 7.39 (s, 1H, ArH), 7.33 (t, 1H, J = 7.8 Hz, ArH), 6.94 (t, 2H, J = 4.2 Hz, ArH), 4.91 (s, 2H, H-2 H-5, Fc), 4.44 (s, 2H, H-3 H-4, Fc), 4.23 (s, 5H, Fc-unsubst. ring), 2.28 (s, 3H, CH_3); ESI-MS *m/z* (%): 421 ([M+1]$^+$, 100). Ana1. Calcd for $C_{20}H_{20}FeN_4OS$: C, 57.15; H, 4.80; N, 13.33. Found: C, 57.17; H, 4.81; N, 13.30%.

4c: Purple solid, yield 91%, m.p. 178–179 °C; IR (KBr)(cm^{-1}): 3428, 3095, 2925, 1588, 1475, 1215, 1109, 1047, 833, 490; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.02 (s, 1H, NH); 10.77 (s, 1H, NH), 9.66 (s, 1H, OH), 8.48 (s, 1H, =CH), 7.28–7.20 (m, 3H, ArH), 6.86 (s, 1H, ArH), 4.83 (s, 2H, H-2 H-5, Fc), 4.64 (s, 2H, H-3 H-4, Fc), 4.33 (s, 5H, Fc-unsubst. ring), 2.35 (s, 3H, CH_3); ESI-MS *m/z* (%): 863 ([2M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{20}FeN_4OS$: C, 57.15; H, 4.80; N, 13.33. Found: C, 57.13; H, 4.79; N, 13.35%.

4d: Purple solid, yield 86%, m.p. 160–161 °C; IR (KBr)(cm^{-1}): 3526, 3096, 2970, 1610, 1448, 1270, 1105, 1070, 830, 491; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.01 (s, 1H, NH); 10.85 (s, 1H, NH), 10.32 (s, 1H, OH), 8.09 (s, 1H, =CH), 7.66 (s, 2H, ArH), 6.87 (d, 2H, J = 7.6 Hz, ArH), 4.99 (s, 2H, H-2 H-5, Fc), 4.74 (s, 2H, H-3 H-4, Fc), 4.39 (s, 5H, Fc-unsubst. ring), 2.41 (s, 3H, CH_3); ESI-MS *m/z* (%): 863 ([2M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{20}FeN_4OS$: C, 57.15; H, 4.80; N, 13.33. Found: C, 57.16; H, 4.81; N, 13.31%.

4e: Pinky solid, yield 93%, m.p. 175–176 °C; IR (KBr)(cm^{-1}): 3424, 3085, 2965, 1603, 1438, 1223, 1108, 1066, 834, 484; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.20 (s, 1H, NH); 10.75 (s, 1H, NH), 8.57 (s, 1H, =CH), 8.25–8.05 (m, 1H, ArH), 7.55 (t, 1H, J = 4.0 Hz, ArH), 7.47 (t, 2H, J = 3.6 Hz, ArH), 4.90 (s, 2H, H-2 H-5, Fc), 4.62 (s, 2H, H-3 H-4, Fc), 4.33 (s, 5H, Fc-unsubst. ring), 2.34 (s, 3H, CH_3); ESI-MS *m/z* (%): 461 ([M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{19}ClFeN_4S$: C, 54.75; H, 4.36; N, 12.77. Found: C, 54.73; H, 4.35; N, 12.79%.

4f: Pinky solid, yield 87%, m.p. 173–174 °C; IR (KBr)(cm^{-1}): 3446, 3084, 2968, 1601, 1488, 1317, 1176, 1087, 825, 513; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.10 (s, 1H, NH); 10.87 (s, 1H, NH), 8.16 (s, 1H, =CH), 7.84 (s, 2H, ArH), 7.59–7.53 (m, 2H, ArH), 4.90 (s, 2H, H-2 H-5, Fc), 4.64 (s, 2H, H-3 H-4, Fc), 4.33 (s, 5H, Fc-unsubst. ring), 2.35 (s, 3H, CH_3); ESI-MS *m/z* (%): 461 ([M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{19}ClFeN_4S$: C, 54.75; H, 4.36; N, 12.77. Found: C, 54.78; H, 4.37; N, 12.70%.

4g: Purple solid, yield 90%, m.p. 153–154 °C; IR (KBr)(cm^{-1}): 3449, 3082, 2966, 1603, 1442, 1234, 1108, 1079, 834, 483; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.11 (s, 1H, NH); 10.89 (s, 1H, NH), 8.17 (s, 1H, =CH), 7.89 (s, 2H, ArH), 7.34 (t, 2H, J = 8.8 Hz, ArH), 4.91 (s, 2H, H-2 H-5, Fc), 4.67 (s, 2H, H-3 H-4, Fc), 4.35 (s, 5H, Fc-unsubst. ring), 2.36 (s, 3H, CH_3); ESI-MS *m/z* (%): 867 ([2M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{19}FFeN_4S$: C, 56.88; H, 4.53; N, 13.27. Found: C, 56.80; H, 4.54; N, 13.29%.

4h: Purple solid, yield 94%, m.p. 151–152 °C; IR (KBr)(cm^{-1}): 3440, 3081, 2973, 1609, 1440, 1261, 1107, 1068, 823, 491; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.15 (s, 1H, NH); 10.94 (s, 1H, NH), 8.13 (s, 1H, =CH), 7.84–7.78 (m, 2H, ArH), 7.69 (d, 2H, J = 6.4 Hz, ArH), 4.93 (s, 2H, H-2 H-5, Fc), 4.68 (s, 2H, H-3 H-4, Fc), 4.36 (s, 5H, Fc-unsubst. ring), 2.37 (s, 3H, CH_3); ESI-MS *m/z* (%): 989 ([2M+23]$^+$, 100). Ana1. Calcd for $C_{20}H_{19}BrFeN_4S$: C, 49.71; H, 3.96; N, 11.59. Found: C, 49.75; H, 3.95; N, 11.57%.

4i: Brown solid, yield 88%, m.p. 154–155 °C; IR (KBr)(cm^{-1}): 3441, 3082, 2963, 1610, 1439, 1243, 1088, 1005, 846, 500; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.56 (s, 1H, NH); 10.71 (s, 1H, NH), 8.69 (s, 1H, =CH), 8.30–8.22 (m, 2H, ArH), 8.08–8.01 (m, 2H, ArH), 4.82 (s, 2H, H-2 H-5, Fc), 4.47 (s, 2H, H-3 H-4, Fc), 4.20 (s, 5H, Fc-unsubst. ring), 2.32 (s, 3H, CH_3); ESI-MS *m/z* (%): 450 ([M+1]$^+$, 100). Ana1. Calcd for $C_{20}H_{19}FeN_5O_2S$: C, 53.46; H, 4.26; N, 15.59. Found: C, 53.41; H, 4.25; N, 15.60%.

4j: Pinky solid, yield 90%, m.p. 154–155 °C; IR (KBr)(cm^{-1}): 3441, 3090, 2961, 1606, 1441, 1253, 1109, 1031, 831, 483; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.92 (s, 1H, NH); 10.71 (s, 1H, NH), 8.49 (s, 1H, =CH), 8.12 (s, 2H, ArH), 7.05 (d, 2H, J = 8.4 Hz, ArH), 4.87 (s, 2H, H-2 H-5, Fc), 4.59 (s, 2H, H-3 H-4, Fc), 4.31 (s, 5H, Fc-unsubst. ring), 3.82 (s, 3H, -OCH_3), 2.33 (s, 3H, CH_3); ESI-MS *m/z* (%): 891 ([2M+23]$^+$, 100). Ana1. Calcd for $C_{21}H_{22}FeN_4OS$: C, 58.07; H, 5.11; N, 12.90. Found: C, 58.11; H, 5.10; N, 12.92%.

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