Supporting Information

New synthesis of *meso*-free-[14]triphyrin(2.1.1) by McMurry coupling and its derivatization to Mn(I) complex

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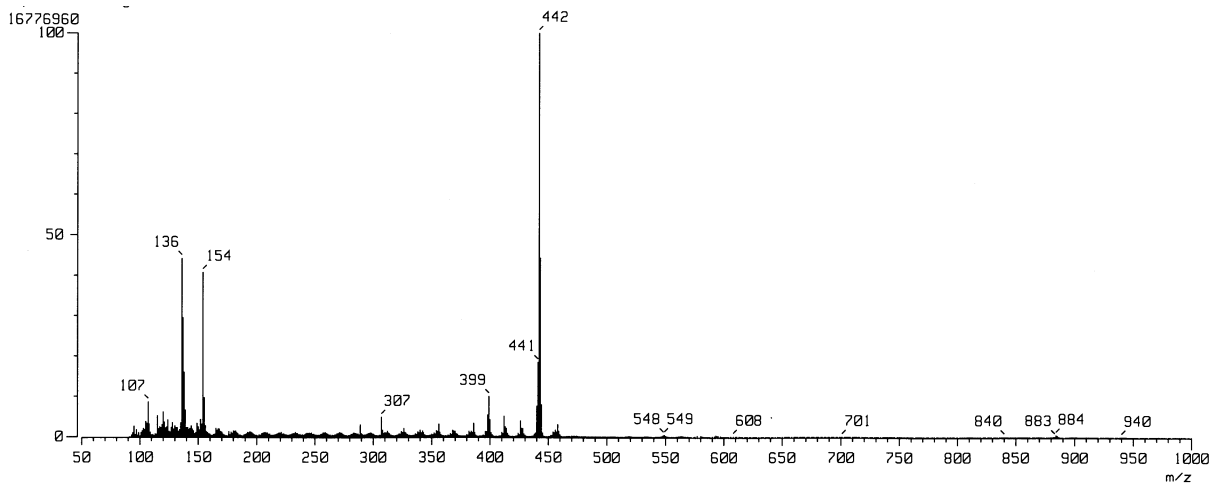

Figure S1. FAB mass specrum of **1**.

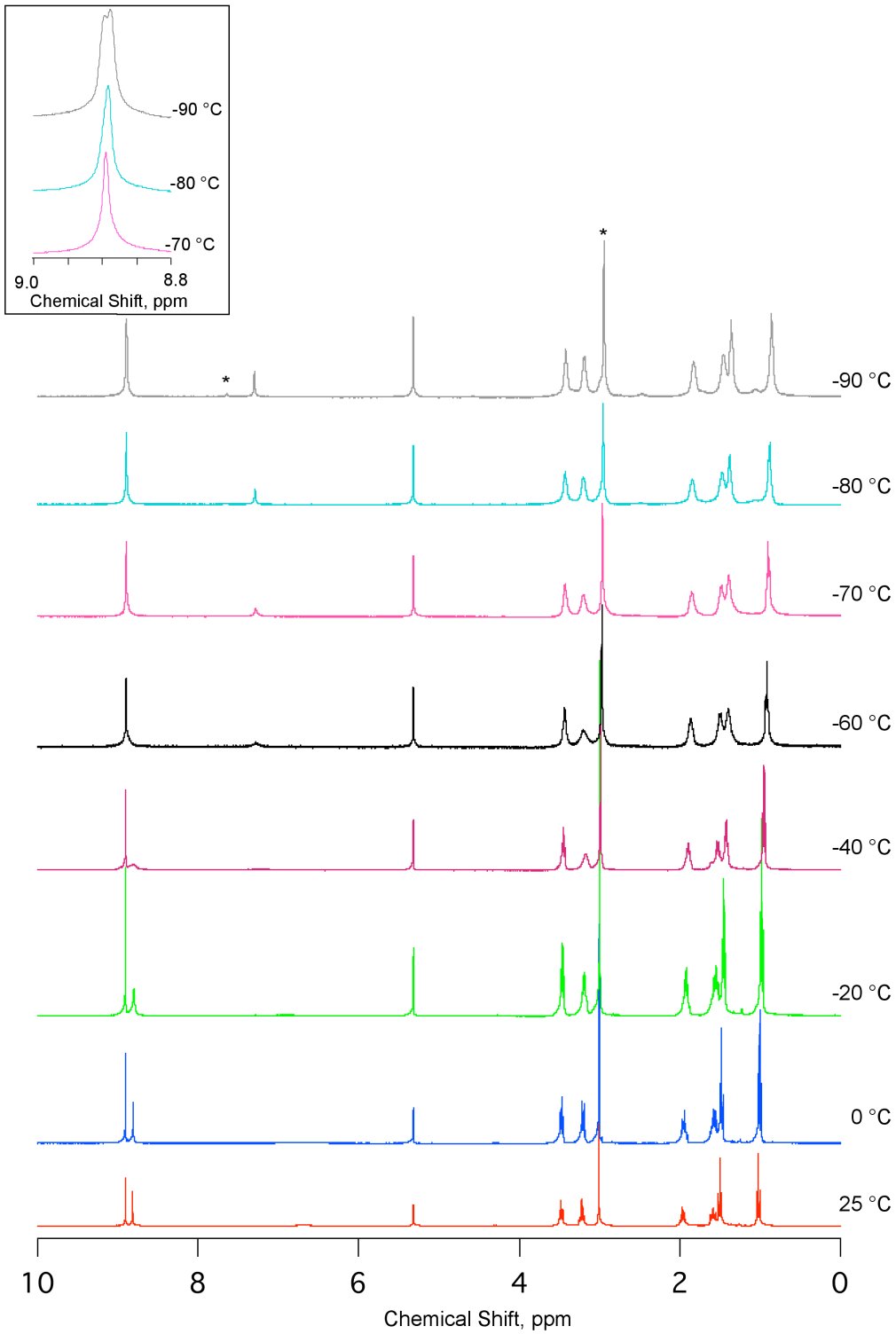

Figure S2. ^{1}H-NMR spectra of **1** at lower temperature in CD_2Cl_2. Insertions are the expanded spectra at 8.8-9.0 ppm. * represents the peaks of solvent and impurity from solvent.

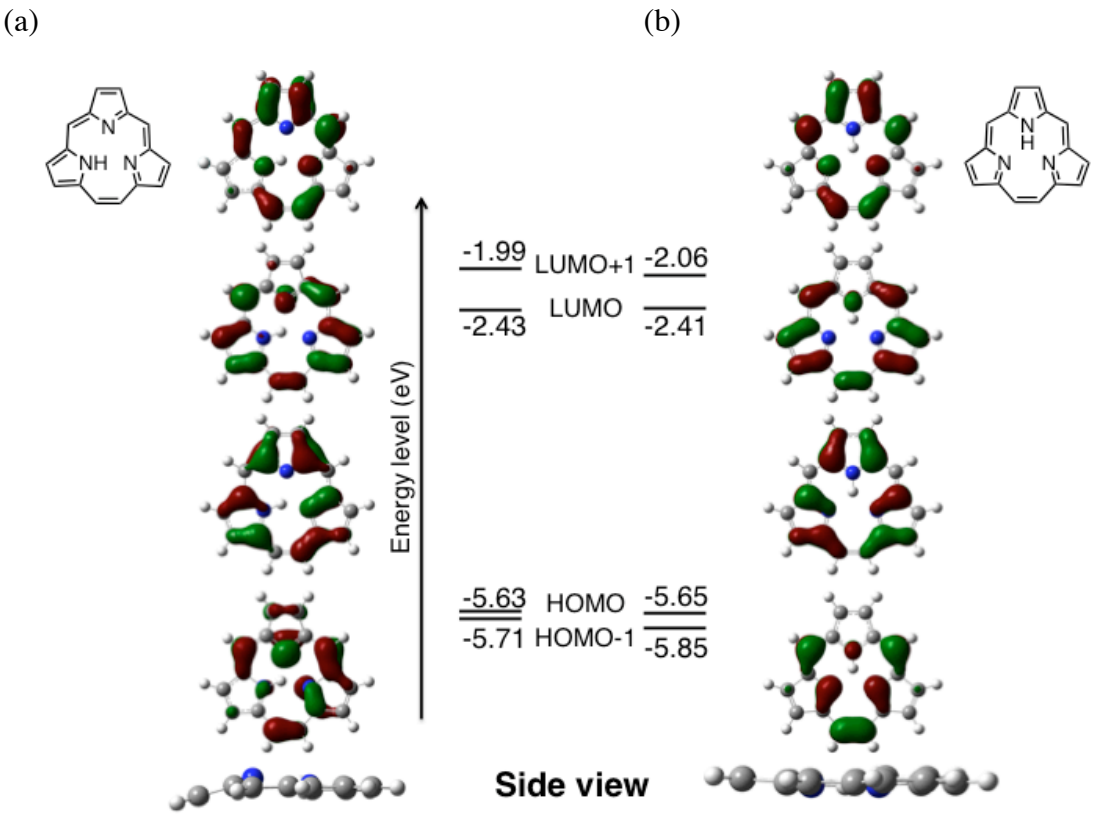

Figure S3. Optimized structures and electron distributions of (a) N1-H and (b) N2-H tautomers of **1** calculated at the B3LYP/6-31G(*) level.

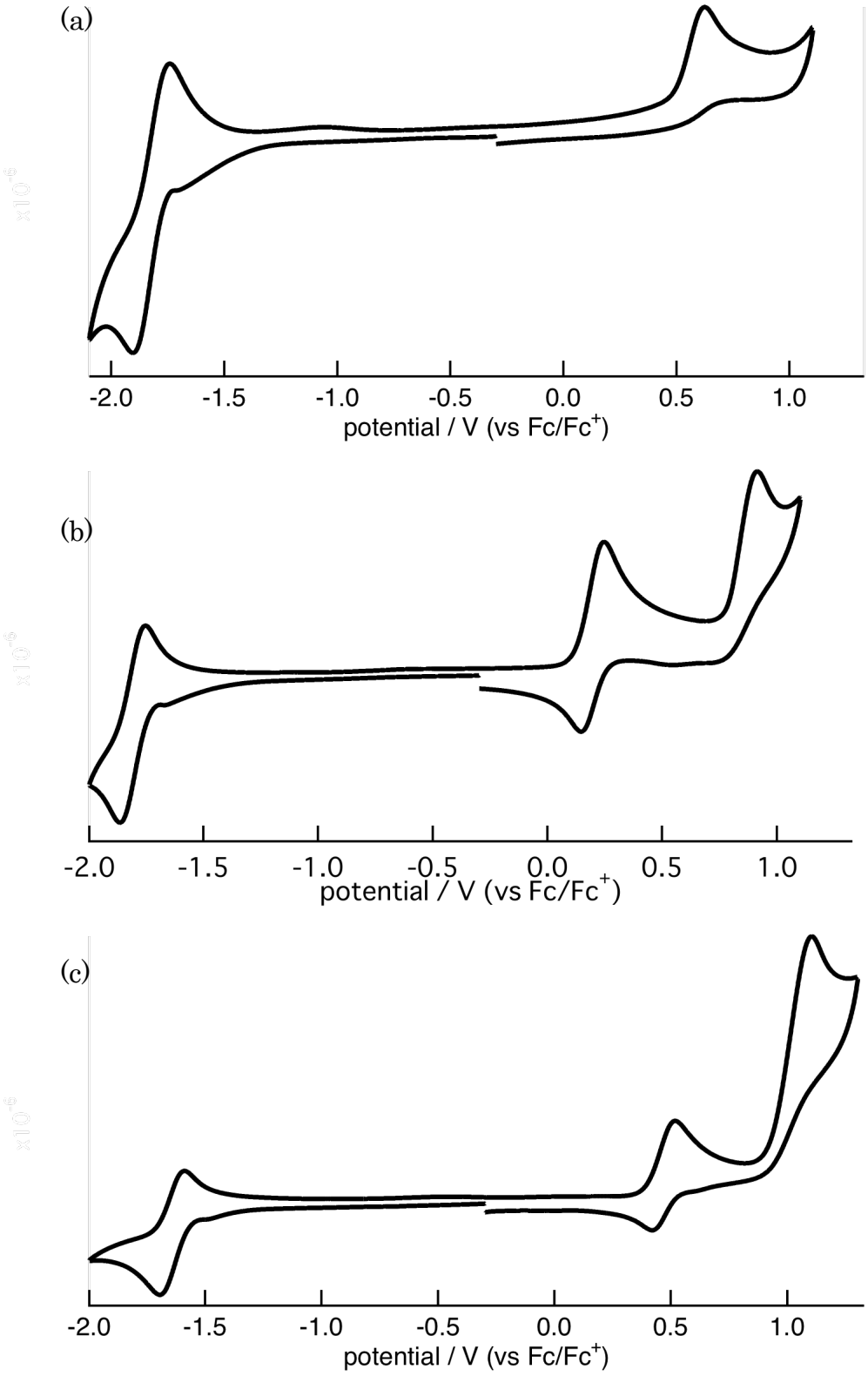

Figure S4. Cyclic voltammogram of (a) **1**, (b) **1-Mn** and (c) **1-Re** in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at rt.

Table S1. Redox potentials of **1**, **1-Mn**, and **1-Re**.

	E^0_{ox} / V vs Fc/Fc^+		E^0_{red} / V vs Fc/Fc^+
1	0.63[a]	-	-1.77
1-Mn	0.20	0.92[a]	-1.81
1-Re	0.47	1.10[a]	-1.64

a: irreversible

Experimental

General Melting points were measured with a Yanaco M-500D melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer using tetramethylsilane as an internal standard. VT NMR spectra were recorded on a JEOL JNM-EX-400. IR spectra were measured on a Hitachi 270-30 as KBr disks. FAB mass spectra were measured on JEOL JMS-MS700 spectrometer. Elemental analyses were performed on Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For spectral measurements, spectral grade of CH_2Cl_2 was purchased from Nacalai tesque co. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

Steady state absorption spectra in the visible region were measured on a Jasco V570. Cyclic voltammetry (CV) measurements were performed on a ALS 612B electrochemical analyzer in deaerated CH_2Cl_2 solution containing 0.1 M $TBAPF_6$ as a supporting electrolyte at rt (100 mV s^{-1}). A platinum electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was platinum wire. The reference electrode was an $Ag/AgNO_3$ (0.1 M $TBAPF_6$, 0.01 M $AgNO_3$ in acetonitrile).

X-ray Analysis. The selected single crystal was mounted in a Lindemann glass capillary with a tiny amount of the mother liquor. Single crystal X-ray diffraction analysis was performed at -173 ºC on a Rigaku VariMax Rapid(Cu) for **1** and Rigaku VariMax Saturn (Mo) for **1-Mn** and **1-Re**. The diffraction data were processed with CrystalStructure, solved with SIR2004 and refined with SHELX-97.[S1]

Synthesis. The synthesis of diformyltripyrrane **3** has been already reported.

Triphyrin 1

$TiCl_4$ (4.1 mL, 37 mmol) was added to a mixture of Zn dust (4.91 g) and CuCl (0.3 g, 3.0 mmol) in THF (150 mL) under an Ar atmosphere. Then the mixture was refluxed for 2 h. A solution of diformyltripyrrane **3** (0.72 g, 1.5 mmol) in THF (150 mL) was added dropwise to a reaction mixture, and refluxed for 1 h. The reaction was quenched with 10% aqueous K_2CO_3 (150 mL). After filtration, the precipitate was washed with $CHCl_3$, the organic layer was dried with Na_2SO_4, and the solvent was

concentrated under a reduce pressure. The residue was purified by alumina column chromatography ($CHCl_3$) and DDQ was added to the eluted solution. After stirring for overnight, the reaction mixture was washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4. The residue was purified by silica gel column chromatography with 20% EtOAc in hexane. Triturated by MeOH gave triphyrin **1** as red solid. Yield: 16% (110 mg, 0.25 mmol). mp: 110.3-111.3 ºC; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 8.88 (s, 2H), 8.87 (s, 2H), 7.25 (br, 1H), 3.47 (t, 4H, J = 7.5 Hz), 3.27 (q, 4H J = 7.6 Hz), 2.98 (s, 6H), 1.95 (m, 4H, J = 7.5 Hz), 1.58 (m, *4H*), 1.51 (t, 6H, J = 7.6 Hz), 1.00 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz; $CDCl_3$): δ = 157.86, 152.48, 145.67, 142.14, 140.19, 133.78, 114.62, 108.08, 34.82, 25.78, 22.81, 19.19, 17.60, 14.21, 10.81; UV (CH_2Cl_2) λ_{max} [nm] (logε) = 336 (4.89), 452 (3.83), 548 (3.90); MS (FAB) m/z: 442 [M^++1]; Anal. Calcd. for $C_{30}H_{39}N_3$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.42; H, 8.81; N, 9.43.

Triphyrin 1-Mn

A solution of triphyrin **1** (7.8 mg, 0.018 mmol), $MnBr(CO)_5$ (9.2 mg, 0.034 mmol) and NaOAc (19.8 mg, 0.24 mmol) in toluene (5 mL) was refluxed for 1 h under an Ar atmosphere. After cooling to rt, the solvent was removed under a reduced pressure. The residue was purified by silica gel chromatography (CH_2Cl_2) and crystallized from MeOH/H_2O to give triphyrin **1-Mn** as brown solid. Yield: 80% (8.3 mg, 0.014 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 2H), 8.79 (s, 2H), 3.33-3.21 (m, 4H), 3.13 (m, 4H), 2.72 (s, 6H), 1.77 (m, 4H), 1.56 (m, 4H), 1.46 (t, 6H, J = 7.6 Hz), 1.01 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) [typical signals]: δ = 161.91, 160.86, 156.19, 140.52, 137.94, 133.09, 118.45, 113.14, 34.44, 25.45, 23.05, 18.69, 17.45, 14.12, 10.85. IR (KBr): [cm^{-1}] = 2007 (C≡O), 1911 (C≡O), 1887 (C≡O); UV (CH_2Cl_2) λ_{max} [nm] (logε) = 342 (4.76), 469 (4.00); HRMS (FAB) m/z calcd. For $[C_{33}H_{42}O_3N_3Mn]^+$: 583.2607, found: 583.2625.

Triphyrin 1-Re

A solution of triphyrin **1** (20 mg, 0.045 mmol), $ReCl(CO)_5$ (82 mg, 0.23 mmol) and NaOAc (41 mg, 0.05 mmol) in toluene (5 mL) was refluxed for 12 h under an Ar atmosphere. After cooling to rt, the solvent was removed under a reduced pressure. The residue was purified by silica gel chromatography ($CHCl_3$) and crystallized from

$CHCl_3$/MeOH to give triphyrin **1-Re** as black solid. Yield: 84% (27 mg, 0.038 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (s, 2H), 8.83 (s, 2H), 3.32-3.04 (m, 8H), 2.70 (s, 6H), 1.76 (m, 4H), 1.56 (m, 4H), 1.46 (t, 6H, J = 7.6 Hz), 1.01 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz; $CDCl_3$): δ = 196.90, 194.27, 161.08, 160.81, 157.20, 139.13, 136.71, 132.43, 119.38, 114.90, 34.26, 25.25, 22.97, 18.52, 17.21, 13.99, 10.76; IR (KBr): [cm^{-1}] = 2000 (C≡O), 1896 (C≡O), 1867 (C≡O); UV (CH_2Cl_2) λ_{max} [nm] (logε) = 270 (4.34), 347 (4.87), 469 (3.94), 550 (3.72); HRMS (FAB) m/z calcd. For $[C_{33}H_{39}O_3N_3Re]^+$: 712.2549, found: 712.2549.

References

S1 G. M. Sheldrick, *Acta Cryst*. 2008, *A64*, 112-122.

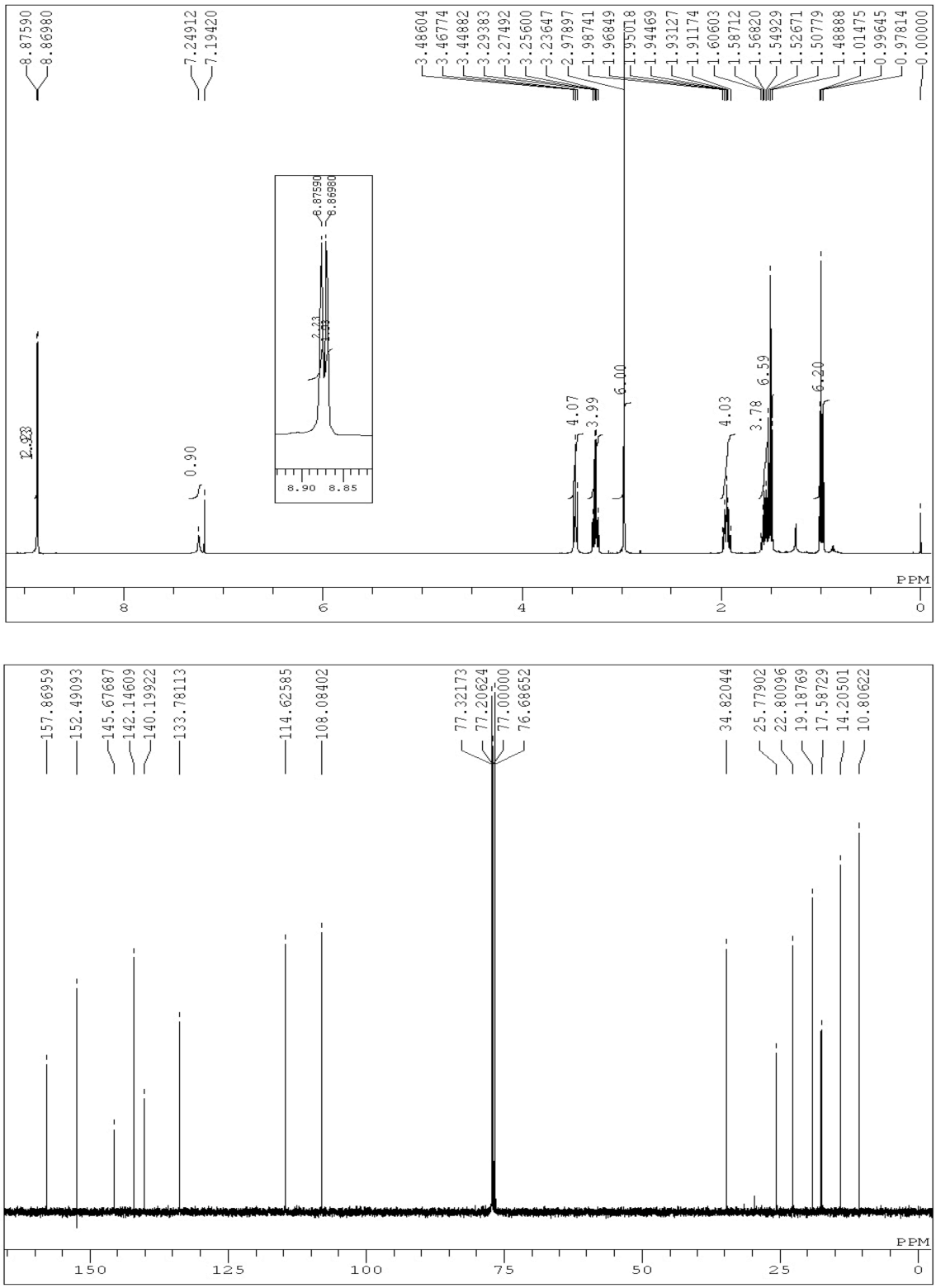

Figure S6. ^{1}H and ^{13}C NMR spectra of triphyrin **1** in $CDCl_3$ at room temperature.

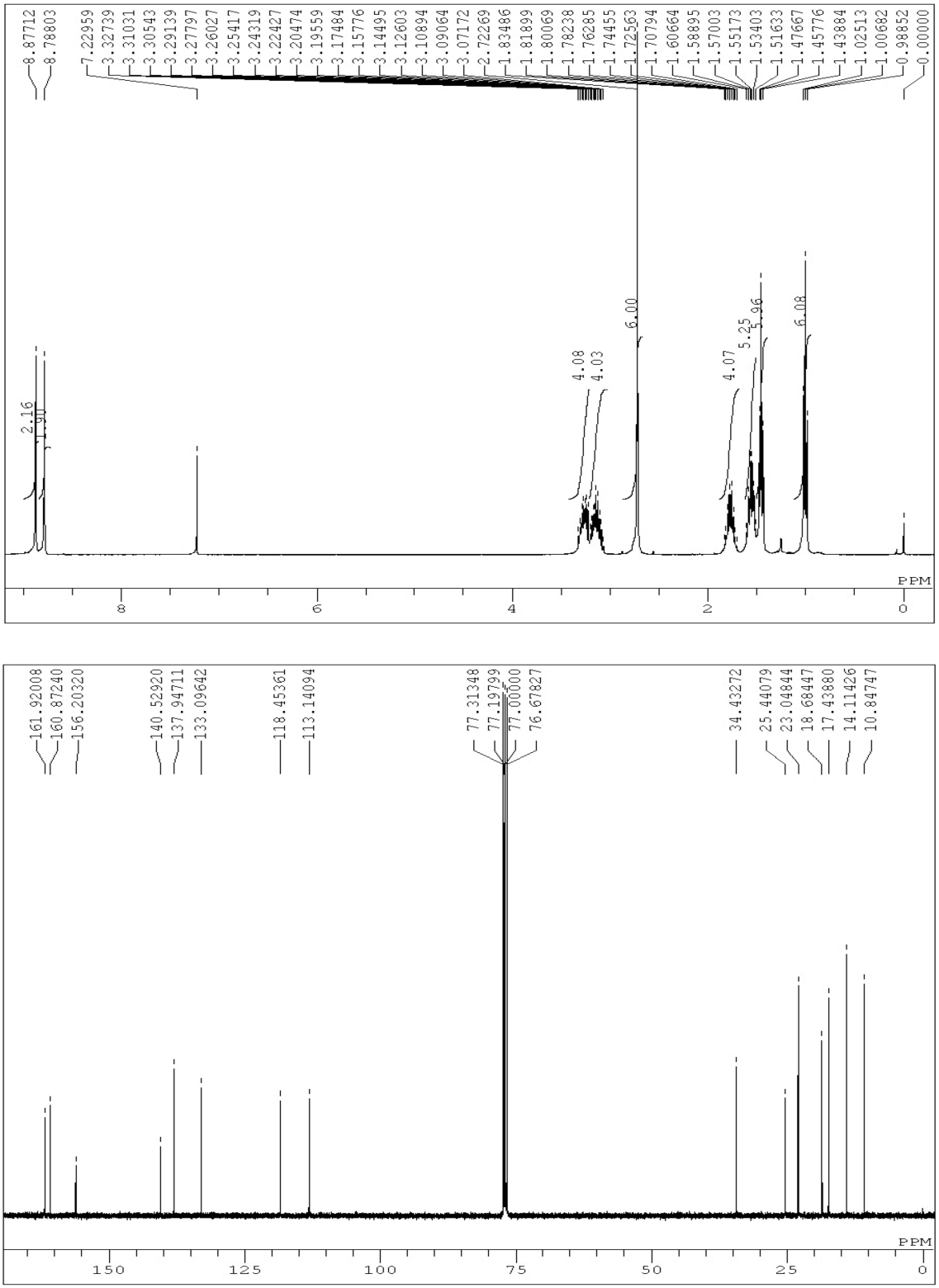

Figure S7. ^{1}H and ^{13}C NMR spectra of triphyrin **Mn-1** in $CDCl_3$ at room temperature.

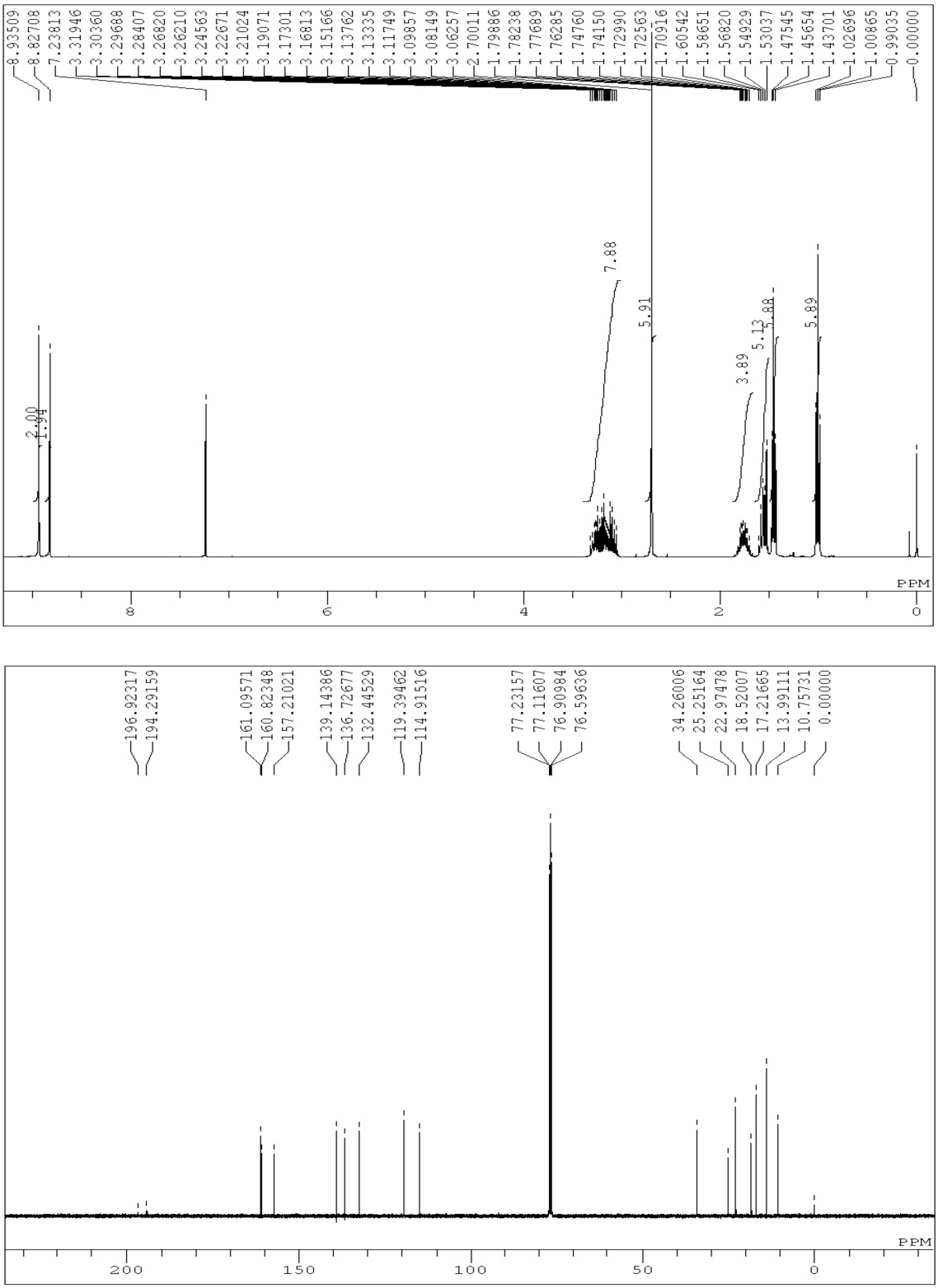

Figure S8. ^{1}H and ^{13}C NMR spectra of triphyrin **Re-1** in $CDCl_3$ at room temperature.

Full author list for ref. (8).

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian 03, R. C., Gaussian, Inc., Wallingford CT, 2004.