Metallophthalocyanine Complex, Cr(TBPC)OTf: An Efficient, Recyclable Lewis Acid Catalyst in the Regio- and Stereoselective Rearrangement of Epoxides to Aldehydes

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SUPPORTING INFORMATION

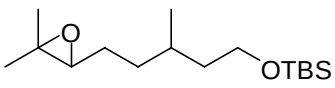
General: ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX270, JNM-AL300, and JNM-GSX400 spectrometer. The chemical shifts were reported in ppm relative to $CHCl_3$ (δ = 7.24) for ^{1}H-NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C-NMR. IR spectra were recorded on a JASCO FT/IR-7000 spectrophotometer. UV–visible absorption spectra were measured with a Hitachi U-3210 spectrophotometer using dichloromethane as a solvent and reference in 1.0-cm quartz cells. Optical rotation was measured on a JASCO DIP-4 polarimeter. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer. Chiral HPLC analysis was performed on a JASCO GULLIVER-series instrument. Merck kiesel-gel 60 and Merck kiesel-gel 60 F_{254} were employed for silica gel column and thin layer chromatography, respectively. 1,2-Dichloroethane was distilled from P_2O_5. Free base 2,9,16,23-tetra-*tert*-butylphthalocyanin, H_2(TBPC), was purchased from Aldrich. All other commercially available reagents were used without further purification unless otherwise stated.

Preparation of [2,9,16,23-tetra-*tert*-butylphthalocyaninato]chromium(III) chloride, Cr(TBPC)Cl: The corresponding free base 2,9,16,23-phthalocyanine H_2(TBPC) (2.22 g, 3.3 mmol) was dissolved in 150 mL of refluxing DMF. After waiting for several hours (1–2 h) for the phthalocyanine to dissolve, $CrCl_2$ (2 g) was added to the refluxing solution. The reaction mixture was refluxed for 5 h under Ar, and then allowed to cool to room temperature. The volume of the solvent was reduced to ca. 50 mL under a reduced pressure, poured into brine (1 L), and allowed to stand for 12 h at room temperature. The resulting precipitate was collected by filtration, and washed with water (20 mL × 3) to give crude Cr(TBPC)Cl. The crude Cr(TBPC)Cl was dissolved in $CHCl_3$ (50 mL), and then filtered. The filtrate was concentrated under a reduced pressure. The residue was applied to an aluminum column (Merck Aluminum oxide 90 active basic, activity stage I) and eluted with $CHCl_3$. The remaining H_2(TBPC) was eluted as a blue band with the solvent front. This was followed by a slow-moving green band of Cr(TBPC)Cl. After the Cr(TBPC)Cl was eluted from the column,

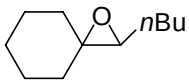
the volume of $CHCl_3$ was reduced to ca. 50 mL under a reduced pressure. The solution containing the Cr(TBPC)Cl was washed with 1 M HCl, (100 mL × 2), dried over $MgSO_4$, and concentrated in vacuo. The resulting solid was purified by recrystallization from CH_2Cl_2 / hexane and dried at 100 °C under a reduced pressure (< 1 mmHg) for 12 h to give purified Cr(TBPC)OTf (1.50 g, 61 %). UV-visible spectrum and IR spectrum are shown in Fig. 1 and Fig. 2, respectively, on page S8. HRFAB-MS: calcd for $[C_{48}H_{48}ClCrN_8]^+$ 823.3096, found 823.3098.

Preparation of [2,9,16,23-tetra-*tert*-butylphthalocyaninato]chromium (III) triflate, Cr(TBPC)OTf: Cr(TBPC)Cl (165 mg, 0.2 mmol) and AgOTf (62 mg, 0.24 mmol) were added to a flame-dried, argon-purged two-necked 100 mL round-bottom flask equipped with a condenser. Absolute THF (30 mL) was added, and the mixture was refluxed under Ar for 5 h. The reaction mixture was allowed to cool to room temperature, and concentrated in vacuo. The resulting residue was dissolved in dry dry CH_2Cl_2 (ca. 30 mL). The solution was filtered through a pad of Celite, and the filter cake was washed with dry CH_2Cl_2 (ca. 10 mL × 3). The combined filtrate was concentrated under a reduced pressure to give crude Cr(TPP)OTf as a dark greenish solid. The crude Cr(TBPC)OTf was dissolved in dry CH_2Cl_2 (ca. 50 mL), and the solution was filtered through a membrane filter (Millipore Durapore HVLP02500) under Ar. At this point, Ag salts can be completely removed. The volume of CH_2Cl_2 was reduced to ca. 30 mL under a reduced pressure. Hexane (100 mL) was added, and the mixture was allowed to stand at room temperature for 5 h under Ar. The resulting solid was collected by filtration with a membrane filter (Millipore Durapore HVLP02500), and dried under a reduced pressure (< 1 mmHg) at 100°C for 12 h to give purified Cr(TBPC)OTf (168 mg, 90 %). UV-visible spectrum and IR spectrum are shown in Fig. 3 and Fig. 4, respectively, on page S9. HRFAB-MS: calcd for $[C_{49}H_{48}N_8O_3F_3SCr]^+$ 937.2927, found 937.2944.

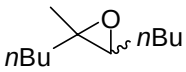
Preparation of epoxides: Optical active epoxy silyl ethers **1d**,[1] **1e**,[2] **1f**,[2] **1g**,[3] and **1h**[3] were prepared by the reported methods. Other epoxides were prepared by simple epoxidation of olefins with MCPBA. The absolute configuration of epoxides **1d**−**h** was determined by comparison of the optical rotations with those of authentic samples.[1–3]



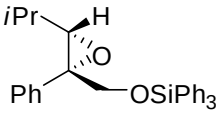
8-(*tert*-Butyldimethylsiloxy)-2,6-dimethyl-2-octene oxide (1a)[3]: ^{1}H-NMR (300 MHz, $CDCl_3$), δ 3.71–3.59 (2H, m), 2.69 (1H, br t), 1.27 (3H, s), 1.31 (3H, s), 1.61−1.21 (7H, m), 0.90 (3H, d, *J* = 6.3 Hz), 0.89 (9H, s), 0.05 (6H, s).



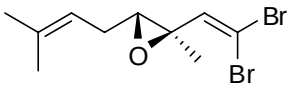
1-Cyclohexyliden-1-hexene oxide (1b): ^{1}H-NMR (300 MHz, $CDCl_3$), δ 2.70 (1H, t, *J* = 6.0 Hz), 1.78–1.34 (16H, m), 0.92 (3H, t, *J* = 7.0 Hz); ^{13}C-NMR (100.4 MHz, $CDCl_3$), δ 64.92, 62.73, 35.82, 29.45, 28.94, 27.96, 25.91, 25.08, 24.99, 22.76, 14.17.



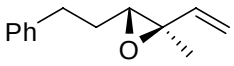
5-Methyl-5-decene oxide (1c) (*cis* / *trans* = 1:1): ^{1}H-NMR (300 MHz, $CDCl_3$), δ 2.69 (1H, br t, *J* = 6.0 Hz), 1.65–1.32 (12H, m), 1.27 (3H×0.5, s, for *cis*-isomer), 1.23 (3H × 0.5, s, for *E*-isomer), 0.87-0.99 (6H, m); ^{13}C-NMR (100.4 MHz, $CDCl_3$), δ 65.0 (for *cis*-isomer), 63.7 (for *trans*-isomer), 61.0 (for *cis*-isomer), 60.9 (for *trans*-isomer), 38.7 (for *trans*-isomer), 32.7 (for *cis*-isomer), 29.0 (for *cis*-isomer), 28.8 (for *trans*-isomer), 28.6 (for *trans*-isomer), 28.3 (for *cis*-isomer), 27.8 (for *cis*-isomer), 27.6 (for *trans*-isomer), 23.2 (for *trans*-isomer), 22.9 (for *cis*-isomer), 22.8 (for *trans*-isomer), 22.7 (for *cis*-isomer), 22.5 (for *cis*-isomer), 16.7 (for *trans*-isomer), 14.2, 14.2.



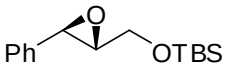
(2*S*,3*S*)-3-Isopropyl-2-phenyl-2,3-epoxypropan-1-triphenylsilyl ether (1d)[1]: $[\alpha]_D^{23}$ = –24.8° (*c* 1.04, $CHCl_3$, >99% *ee*), [lit.[1] $[\alpha]_D^{26}$ = –24.8° (*c* 1.83, $CHCl_3$, >99% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.59–7.27 (20H, m), 4.08 (2H, s), 2.94 (1H, d, *J* = 8.6 Hz), 0.99–0.92 (4H, m), 0.74 (3H, d, *J* = 6.6 Hz). The *ee* was determined by ^{1}H-NMR analysis of the Mosher's ester derived from the corresponding epoxy alcohol with (–)-MTPA chloride.



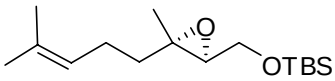
(2*R*,3*R*)-2-(2,2-Dibromoethenyl)-2-methyl-3-(3-methyl-2-butenyl) oxirane (1e)[2]: $[\alpha]_D^{25}$ = –48.3° (*c* 0.85, CH_2Cl_2, >99% *ee*), [lit.[2] $[\alpha]_D^{25}$ = –47.1° (*c* 0.675, CH_2Cl_2, >95% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 6.72 (1H, s), 5.24 (1H, br t, *J* = 7.2 Hz), 3.01 (1H, t, *J* = 6.3 Hz), 2.18–2.40 (2H, m), 1.65 (3H, s), 1.73 (3H, s), 1.43 (3H, s). The *ee* was determined by ^{1}H-NMR analysis of the Mosher's ester derived from the corresponding epoxyalcohol with (+)-MTPA chloride.



(2*R*,3*R*)-2-Ethenyl-2-methyl-3-(2-phenylethyl)oxirane (1f)[2]: $[\alpha]_D^{25}$ = +15.9° (*c* 1.20, CH_2Cl_2, >99% *ee*), [lit.[2] $[\alpha]_D^{25}$ = +15.3° (*c* 1.15, CH_2Cl_2, 96% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.32–7.28 (2H, m), 7.22–7.18 (3H, m), 5.63 (1H, dd, *J* = 10.8 and 17.4 Hz), 5.27 (1H, dd, *J* = 1.1 and 17.4 Hz), 5.16 (1H, dd, *J* = 1.1 and 10.8 Hz), 2.93–2.81 (1H, m), 2.85 (1H, t, *J* = 6.2 Hz), 2.73 (1H, dt, *J* = 8.1 and 13.9 Hz), 2.03–1.80 (2H, m), 1.26 (3H, s). The *ee* was determined by ^{1}H-NMR analysis of the Mosher's ester derived from the corresponding epoxyalcohol with (+)-MTPA chloride.



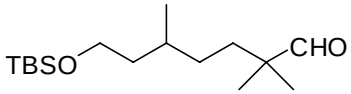
(2*R*,3*R*)-1-(*tert*-butyldimethylsilyloxy)-3-phenyl-2,3-epoxypropane (1g)[4]: $[\alpha]_D^{23}$ = +27.9° (*c* 1.12, $CHCl_3$, >99% ee), [lit.[3] $[\alpha]_D^{24}$ = +27.6° (*c* 1.10, $CHCl_3$, 98% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.39–7.27 (5H, m, Ph), 3.97 (1H, dd, *J* = 3.1 and 12.1 Hz, CHOSi), 3.83 (1H, dd, *J* = 4.4 and 12.1 Hz, CHOSi), 3.81 (1H, d, *J* = 2.4 Hz, PhC<u>H</u>), 3.17–3.13 (1H, m, $CH_2C\underline{H}$-O), 0.93 (9H, s, ^{t}Bu), 0.12 (3H, s, $(CH_3)_2Si$), 0.11 (3H, s, $(CH_3)_2Si$). The ee was determined by ^{1}H-NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (–)-MTPA chloride.



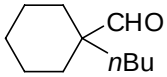
(2*S*,3*S*)-1-(*tert*-butyldimethylsilyloxy)-3,7-dimethyl-2,3-epoxyoct- 6-ene (1h)[4]: $[\alpha]_D^{23}$ = –4.80 ° (*c* 1.04, $CHCl_3$, >99% ee), [lit.[3] $[\alpha]_D^{24}$ = –4.57 ° (*c* 1.00, $CHCl_3$, 95% ee)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 5.10 (1H, br t), 3.73 (2H, dd, *J* = 1.2 and 5.3 Hz), 2.90 (1H, t, *J* = 5.3 Hz), 2.08 (2H, q, *J* = 7.2 Hz), 1.68(3H, s, $(C\underline{H}_3)_2C$=CH), 1.61 (3H, s, $(C\underline{H}_3)_2C$=CH), 1.65–1.40 (2H, m, CH_2C-O), 1.27 (3H, s, CH_3C-O), 0.91 (9H, s, ^{t}Bu), 0.09 (3H, s, $(CH_3)_2Si$), 0.08 (3H, s, $(CH_3)_2Si$). The ee was determined by ^{1}H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (+)-MTPA chloride.

General procedure for the catalytic rearrangement of epoxides to aldehydes: The phthalocyanine catalyst Cr(TBPC)OTf was dried over silica gel for 10 h under a reduced pressure (1 mmHg) at 100 °C just before its use. To a solution of epoxides **1** (1.0 mmol) in freshly distilled 1,2-dichloroethane (5 mL) was added Cr(TBPC)OTf (9.4 mg, 0.01 mmol). The mixture was heated to reflux under Ar until shown to be complete by TLC analysis. The reaction mixture was concentrated under a reduced pressure, and hexane (10 mL) was added. The mixture was allowed to stand for 12 h, and then filtered through a membrane filter

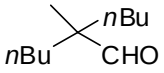
(Millipore Durapore HVLP02500) to remove the catalyst. The filtrate was concentrated under a reduced pressure, and the residue was purified by flush chromatography on silica-gel (1:10 AcOEt / hexane) to afford the title product **3**.



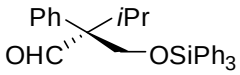
7-(*tert*-Butyldimethylsiloxy)-2,2,5-trimethylheptanal (3a)[3]: ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.44 (1H, s, CHO), 3.69–3.56 (2H, m, CH_2OSi), 1.60–1.07 (7H, m, C<u>H</u>CH_3 and $3CH_2$), 1.04 ($(CH_3)_2C$), 0.89 (9H, s, ^{t}Bu), 0.88 (3H, d, J = 7.2 Hz, C<u>H</u>$_3$-CH), 0.02 (6H, s, $(CH_3)_2Si$); Anal. Calcd for $C_{16}H_{34}O_2Si$: C, 67.07; H, 11.96. Found: C, 66.98; H, 11.98.



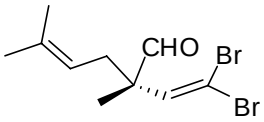
1-Butylcyclohexanecarbaldehyde (3b)[1]: ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.41 (1H, s, CHO), 1.91–1.85 (2H, m, CH_2), 1.56–1.07 (14H, m, $7CH_2$), 0.87 (3H, t, J = 7.0 Hz, CH_3); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 207.4, 49.7, 36.3, 31.1, 25.9, 25.6, 23.4, 22.64, 13.9.



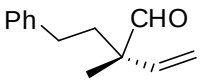
2-Butyl-2-methylhexanal (3c): ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.43 (1H, s, CHO), 1.54–1.05 (12H, m, $6CH_2$), 1.00 (3H, s, CH_3-C), 0.89 (6H, t, J = 7.1 Hz, $2CH_3$); ^{13}C-NMR (100.4 MHz, $CDCl_3$), δ 206.7, 49.1, 35.4, 26.3, 23.5, 18.3, 14.1.



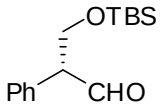
(*S*)-3-Methyl-2-phenyl-2-((triphenylsilyloxy)methyl)butanal (3d)[1]: $[\alpha]_D^{23}$ = –28.1° (*c* 1.05, $CHCl_3$, 98% *ee*), [lit.[1] $[\alpha]_D^{26}$ = –28.5° (*c* 0.29, $CHCl_3$, >99% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.80 (1H, s, CHO), 7.66–7.07 (20H, m, Ph), 4.28 (1H, d, J = 10.5 Hz, CHOSi), 4.25 (1H, d, J = 10.5 Hz, CHOSi), 2.74 (1H, septet, J = 6.8 Hz, C<u>H</u>$(CH_3)_2$), 0.89 (3H, d, J = 6.8 Hz, CH_3), 0.81 (3H, d, J = 6.8 Hz, CH_3). The *ee* was determined by HPLC analysis after the conversion of the aldehyde, **3d**, to the corresponding alcohol with $NaBH_4$ [DAICEL CHIRACEL OD-H, 2-propanol/hexane = 0.2:500, flow rate 0.5 mL/min, t_R = 13.5 min (minor isomer) and 14.0 min (major isomer), detection at 220nm].



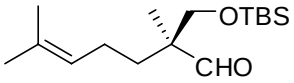
(*S*)-2-(2,2-Dibromovinyl)-2,5-dimethylhex-4-enal (3e)[2]: $[\alpha]_D^{25}$ = +23.1° (*c* 1.05, CH_2Cl_2, 99% *ee*), [lit.[2] $[\alpha]_D^{25}$ = +22.3° (*c* 0.99, CH_2Cl_2, >95% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.59 (1H, s, CHO), 6.68 (1H, s, CH=CBr_2), 5.06 (1H, tq, *J* = 1.5 and 7.5 Hz, C<u>H</u>=$C(CH_3)_2$), 2.43 (1H, dd, *J* = 7.5 and 14.5 Hz, C<u>H_2</u>-C-CHO), 2.34 (1H, dd, *J* = 7.5 and 14.5 Hz, C<u>H_2</u>-C-CHO),1.73 (3H, d, *J* = 1.1 Hz, CH_3), 1.62 (3H, s, CH_3), 1.29 (3H, s, C<u>H_3</u>-C-CHO). The *ee* was determined by HPLC analysis after the conversion of the aldehyde, **3e**, to the corresponding alcohol with $NaBH_4$ [DAICEL CHIRACEL OD-H, 2-propanol/hexane = 1:100, flow rate 1.5 mL/min, t_R = 11.3 min (minor isomer) and 12.6 min (major isomer), detection at 220nm].



(S)-2-Methyl-2-phenethylbut-3-enal (3f)[2]: $[\alpha]_D^{25}$ = +26.7° (*c* 1.15, CH_2Cl_2, >99% *ee*), [lit.[2] $[\alpha]_D^{25}$ = +25.8° (*c* 0.41, CH_2Cl_2, 96% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.43 (1H, s, CHO), 7.32–7.26 (2H, m, Ph), 7.22–7.17 (3H, m, Ph), 5.86 (1H, dd, *J* = 10.8 and 17.6 Hz, C<u>H</u>=CH_2), 5.34 (1H, dd, *J* = 0.7 and 10.8 Hz, CH=C<u>H_2</u>), 5.20 (1H, dd, *J* = 0.7 and 17.6 Hz, CH=C<u>H_2</u>), 2.64–2.47 (2H, m, CH_2-C), 1.94–1.89 (2H, m, Ph-C<u>H_2</u>), 1.27 (3H, s, CH_3). The *ee* was determined by HPLC analysis after the conversion of the aldehyde, **3g**, to the corresponding alcohol with $NaBH_4$ [Daicel CHIRACEL OD-H, 2-propanol/hexane = 10:90, flow rate 0.5 mL/min, t_R = 21.2 min (major isomer) and 22.8 min (minor isomer), detection at 254nm].

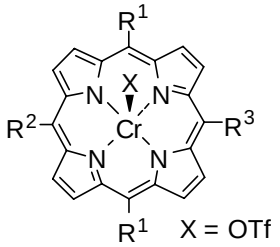


(*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-phenylpropanal (3g)[4]**:** $[\alpha]_D^{23}$ = +32.8° (*c* 1.15, $CHCl_3$, >99% ee), [lit.[3] $[\alpha]_D^{22}$ = +32.3° (*c* 1.00, $CHCl_3$, 98% *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.84 (1H, d, *J* = 2.0 Hz, CHO), 7.41–7.22 (5H, m, Ph), 4.25 (1H, dd, *J* = 7.3 and 10.1 Hz, CHOSi), 3.98 (1H, dd, *J* = 5.7 and 10.1 Hz, CHOSi), 3.75 (1H, br t, *J* = 6.6 Hz, PhC<u>H</u>), 0.85 (9H, s, ^{t}Bu), 0.01 (3H, s, (CH_3)Si), -0.01 (3H, s, (CH_3)Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3h** to the corresponding alcohol with $NaBH_4$ and then to the benzoic ester with PhCOCl, DMAP, and Et_3N [DAICEL CHIRALPAK AD-H, 2-propanol/hexane = 1:500, flow rate 0.5 mL/min, t_R 18.3 min (minor isomer) and 19.6 min (major isomer), detection at 220 nm].



(*S*)-2-((*tert*-Butyldimethylsilyloxy)methyl)-2,6-dimethylhept-5-enal (3h)[4]: $[\alpha]_D^{23}$ = +6.80° (*c* 1.12, $CHCl_3$, > 99 % ee), [lit.[3] $[\alpha]_D^{24}$ = +6.45° (*c* 1.00, $CHCl_3$, 95 % *ee*)]; ^{1}H-NMR (300 MHz, $CDCl_3$), δ 9.56 (1H, s, CHO), 5.06 (1H, br t, CH=C), 3.68 (1H, d, *J* = 9.9 Hz, CHOSi), 3.57 (1H, d, *J* = 9.9 Hz, CHOSi), 1.96–1.85 (2H, m, C$\underline{H}_2$-CH=C), 1.67 (3H, s, C$\underline{H}_3$-C=CH), 1.58 (3H, s, C$\underline{H}_3$-C=CH), 1.63–1.41 (2H, m, C$\underline{H}_2$-C-CHO), 1.04 (3H, s, CH_3), 0.87 (9H, s, ^{t}Bu), 0.03 (6H, s, $(CH_3)_2$Si). The ee was determined by HPLC analysis after the conversion of the aldehyde, **3j**, to the corresponding alcohol with $NaBH_4$ and then to the *p*-nitrobenzoic ester with *p*-NO_2-PhCOCl, DMAP, and Et_3N [DAICEL CHIRALPAK OD-H, 2-propanol/hexane = 1:500, flow rate 0.4 mL/min, t_R 19.3 min (major isomer), detection at 250nm].

Molecular structures of *meso*-substituted porphyrins given in Table 1:



Cr(TPFP)OTf: $R^1 = R^2 = R^3 = C_6F_5$
Cr(DPP-Br)OTf: R^1 = Ph, R^2 = H, R^3 = Br
Cr(DPP-2Br)OTf: R^1 = Ph, $R^2 = R^3$ = Br
Cr(DPP-CN)OTf: R^1 = Ph, R^2 = H, R^3 = CN
Cr(DPP-2CN)OTf: R^1 = Ph, $R^2 = R^3$ = CN

These porphyrin catalysts can be prepared from metal insertion reaction of the corresponding free base porphyrins with $CrCl_2$ followed by axial ligand exchange with AgOTf. The starting free base porphyrins were prepared by the literature methods.[5]

References

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5 (a) H_2(DPP-Br) and H_2(DPP-2Br): S. G. DiMagno, V. S. Y. Lin and M. J. Therien, *J. Org. Chem.*, 1993, **58**, 5983–5993; (b) H_2(DPP-CN) and H_2(DPP-2CN): T. Takanami, M. Hayashi, H. Chijimatsu, W. Inoue and K. Suda, *Org. Lett.*, 2005, **7**, 3937–3940; (c) H_2(TPFP): commercially available.

Fig. 1. UV-vis spectrum of Cr(TBPC)Cl in CH_2Cl_2.

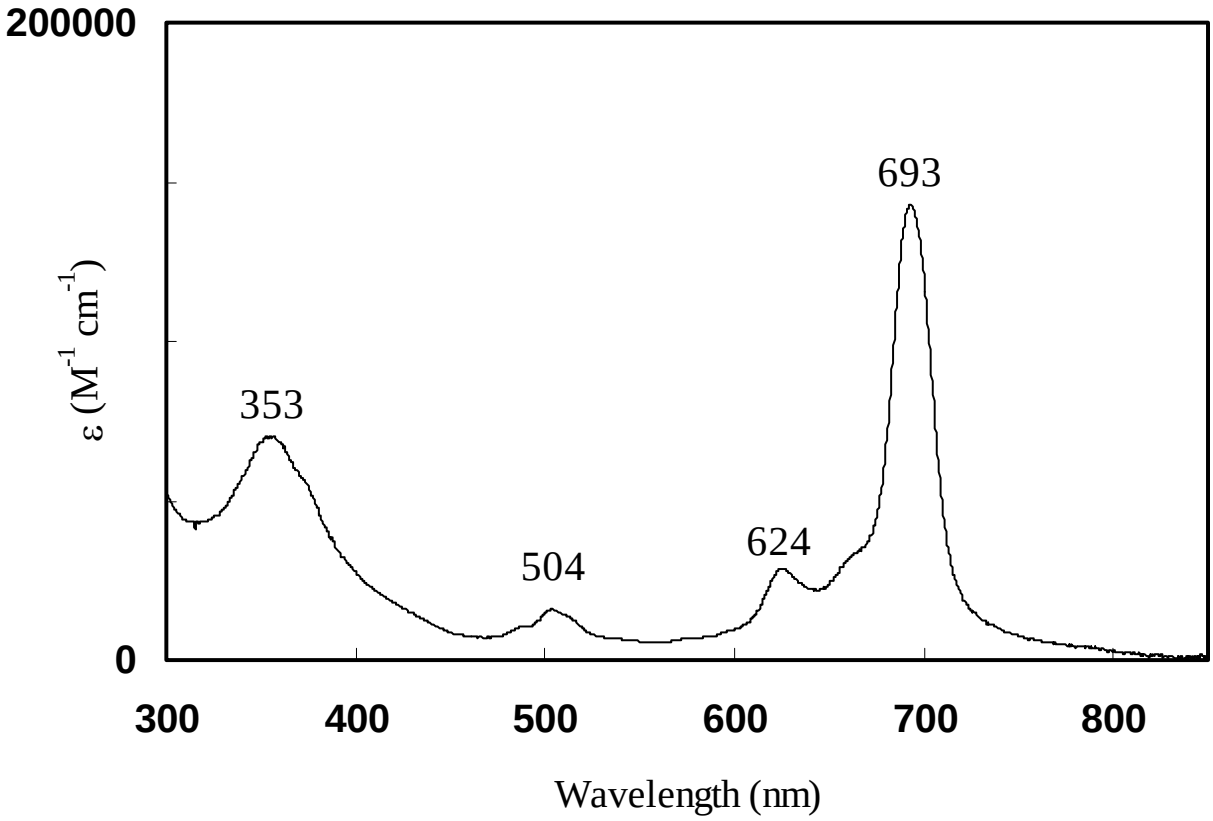

Fig. 2. IR spectrum of Cr(TBPC)Cl

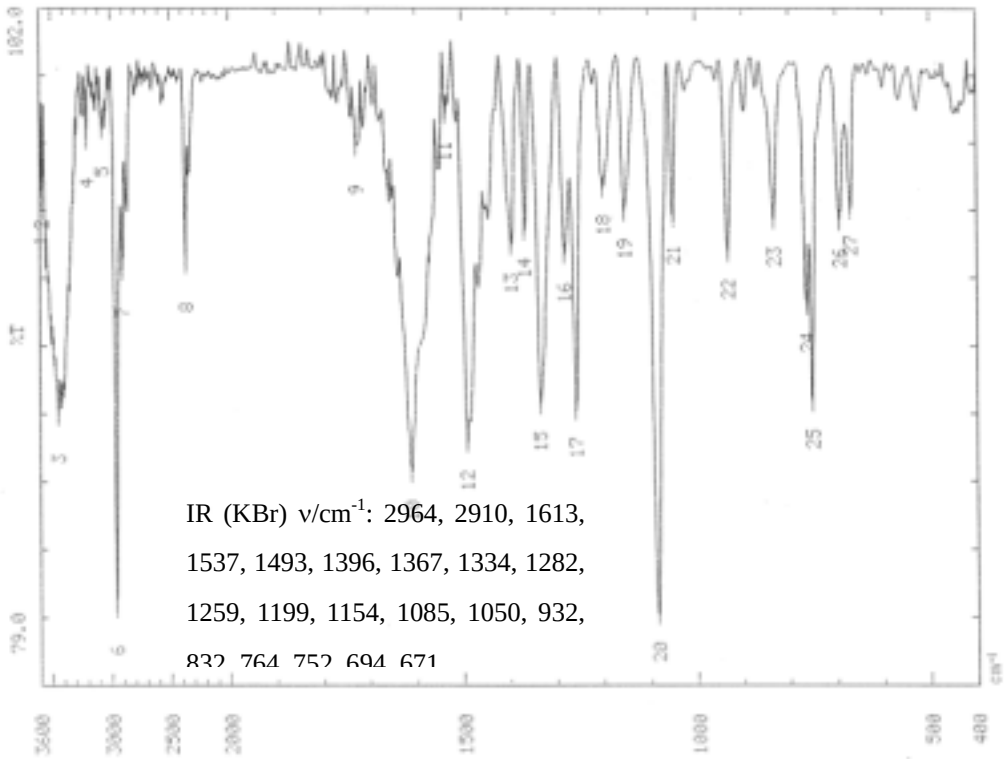

Fig. 3 UV-vis spectrum of Cr(TBPC)OTf in CH_2Cl_2.

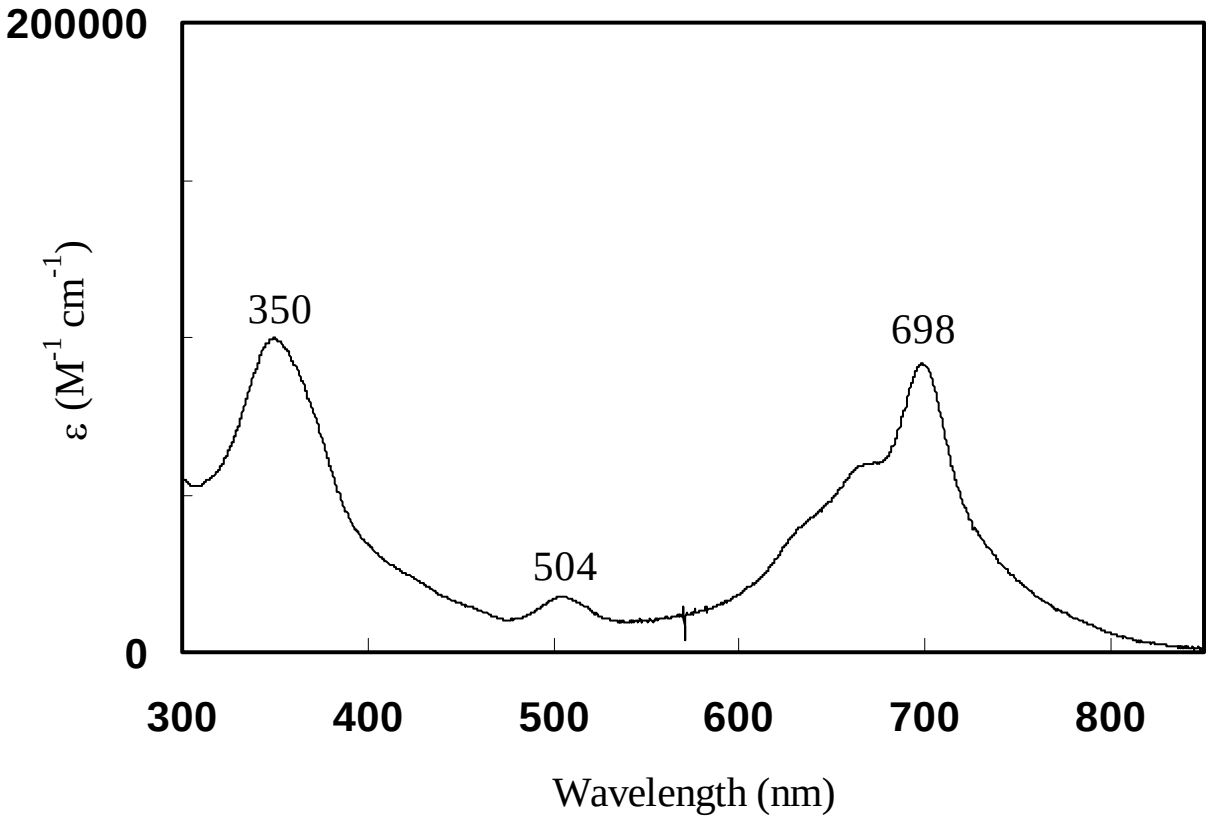

Fig. 4. IR spectrum of Cr(TBPC)OTf.