catalysts

MDPI

Supplementary information

Expanding the Family of Octahedral Chiral-at-Metal Cobalt(III) Catalysts by Introducing Tertiary Amine Moiety Into the Ligand

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Characterization of the complex Λ(*R*,*R*)-2

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.57 (s, 2H, *CH=N*), 7.43–7.32 (m, 8H, *ArH*), 7.31–7.27 (m, 2H, *ArH*), 7.17 (d, *J* = 2.5 Hz, 2H, *ArH*), 7.09 (br.s, 2H, *NH*), 6.91 (d, *J* = 2.5 Hz, 2H, *ArH*), 5.10–4.90 (m, 2H, *CH-N*), 4.07–3.78 (m, 6H, *CH$_2$-Ph, CH-N*), 3.47 (t, *J* = 9.0 Hz, 2H, *CH$_2$*), 3.37 (t, *J* = 9.01 Hz, 2H, *CH$_2$*), 3.31 (t, *J* = 8.0 Hz, 2H, *CH$_2$*), 3.01 (t, *J* = 8.0 Hz, 2H, *CH$_2$*), 1.87 (br.s, 2H, *NH*), 1.20 (s, 18H, *t*Bu), 0.95 (s, 18H, *t*Bu) ppm.

^{13}C-NMR (101 MHz, CDCl$_3$): δ = 163.4, 161.4, 143.0, 138.9, 137.2, 130.3, 128.6, 128.5, 128.2, 127.4, 117.8, 75.6, 61.6, 60.6, 50.8, 49.9, 35.3, 33.9, 31.4, 29.8 ppm.

Elem. anal. calcd. for $C_{52}H_{72}CoN_6O_2Cl$ x $1.2H_2O$ (%): C, 67.22; H, 8.07; N, 9.04, found: C, 67.07; H, 8.04; N, 8.48.

$[\alpha]_D^{25}$= –2292° (c=0.02 in MeOH).

Characterization of the complex Δ(*S*,*S*)-2

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.57 (s, 2H, *CH=N*), 7.43–7.32 (m, 8H, *ArH*), 7.31–7.27 (m, 2H, *ArH*), 7.17 (d, *J* = 2.5 Hz, 2H, *ArH*), 7.09 (br.s, 2H, *NH*), 6.91 (d, *J* = 2.5 Hz, 2H, *ArH*), 5.10–4.90 (m, 2H, *CH-N*), 4.07–3.78 (m, 6H, *CH$_2$-Ph, CH-N*), 3.47 (t, *J* = 9.0 Hz, 2H, *CH$_2$*), 3.37 (t, *J* = 9.01 Hz, 2H, *CH$_2$*), 3.31 (t, *J* = 8.0 Hz, 2H, *CH$_2$*), 3.01 (t, *J* = 8.0 Hz, 2H, *CH$_2$*), 1.87 (br.s, 2H, *NH*), 1.20 (s, 18H, *t*Bu), 0.95 (s, 18H, *t*Bu) ppm.

^{13}C-NMR (101 MHz, CDCl$_3$): δ = 163.4, 161.4, 143.0, 138.9, 137.2, 130.3, 128.6, 128.5, 128.2, 127.4, 117.8, 75.6, 61.6, 60.6, 50.8, 49.9, 35.3, 33.9, 31.4, 29.8 ppm.

Elem. anal. calcd. for $C_{52}H_{72}CoN_6O_2Cl$ x $0.8H_2O$ (%): C, 67.74; H, 8.05; N, 9.12, found: C, 67.73; H, 8.13; N, 8.79.

$[\alpha]_D^{25}$= +2103° (c=0.04 in MeOH).

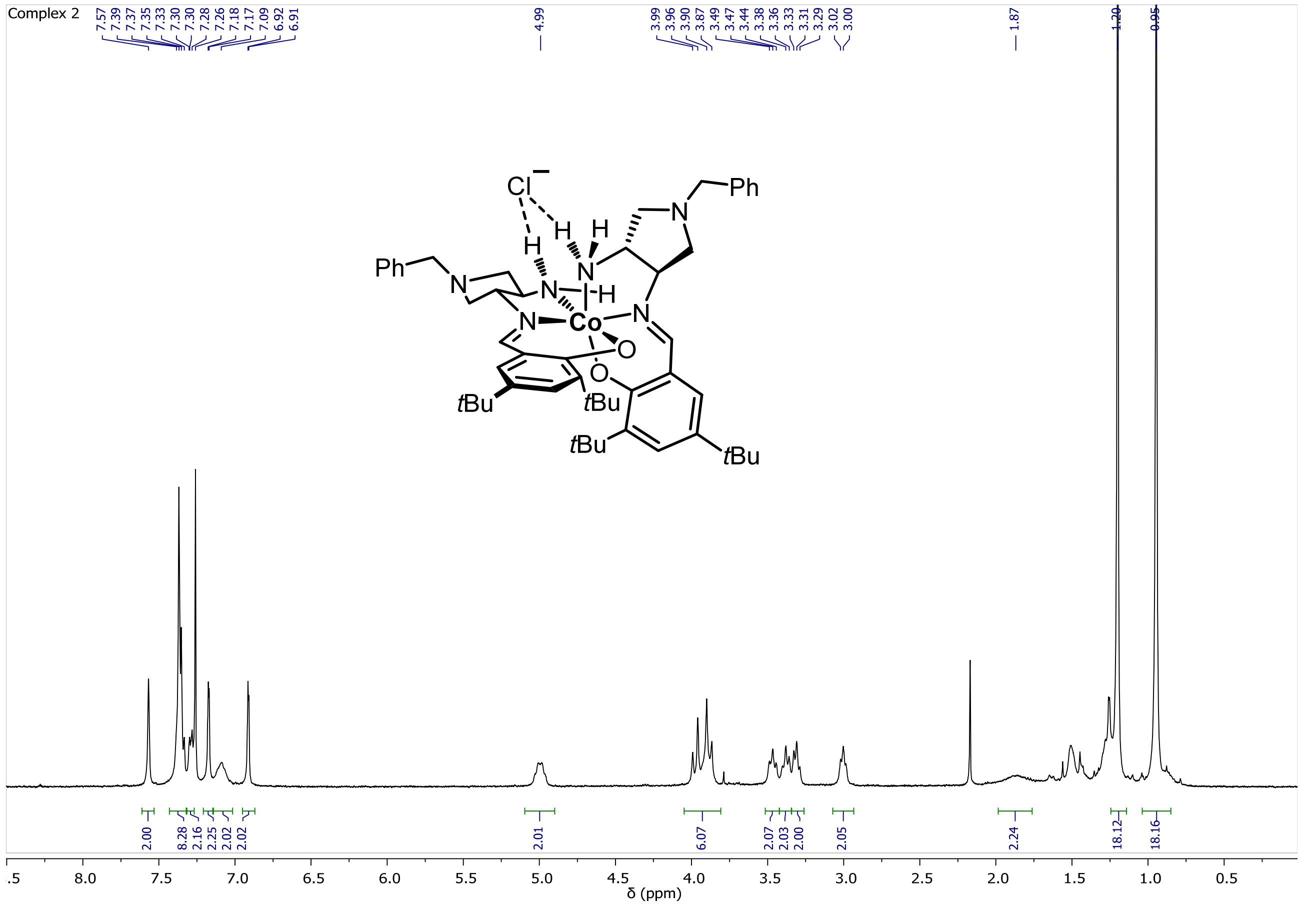


Figure S1. ^{1}H NMR spectrum of the complex **2.**

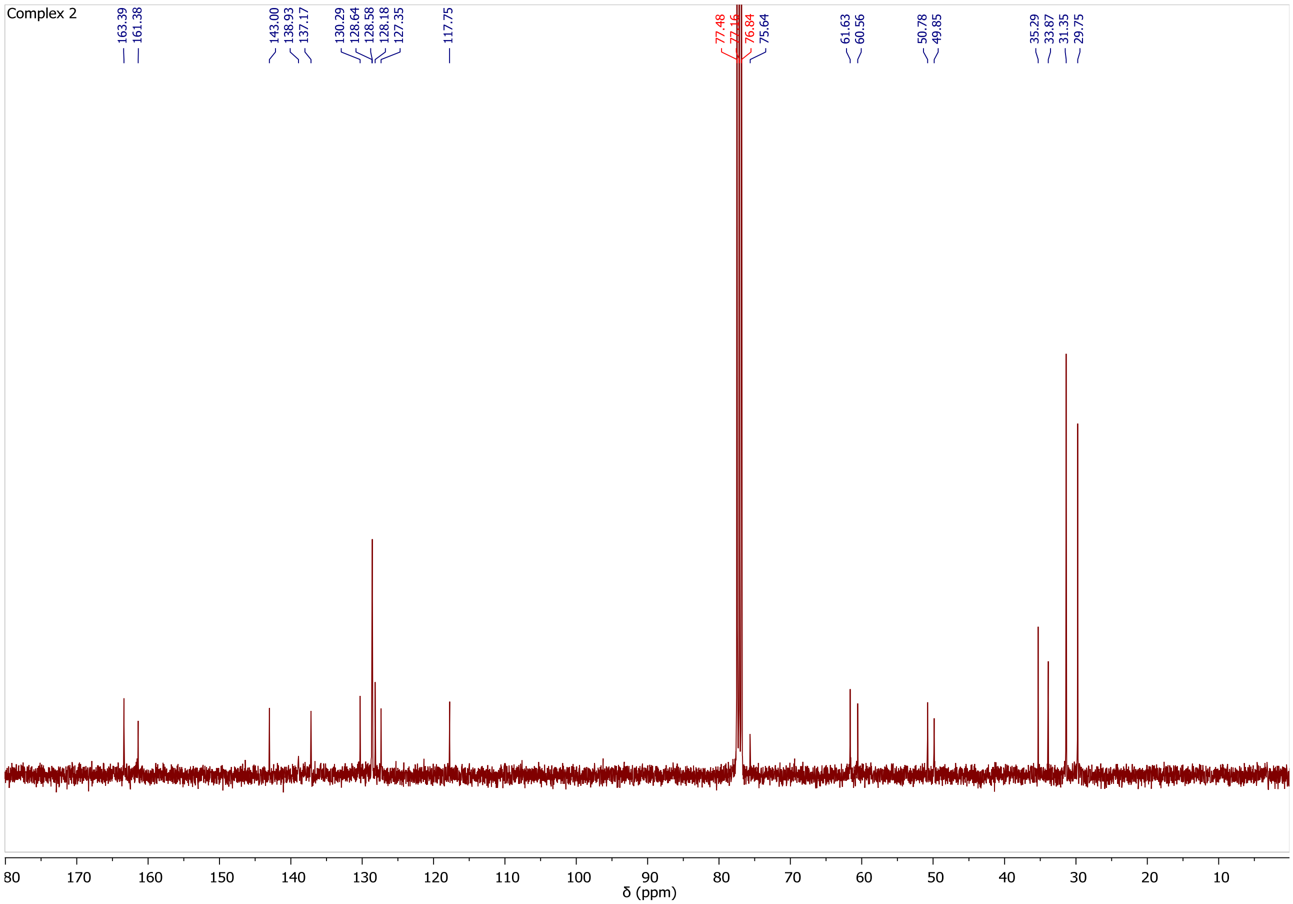


Figure S2. ^{13}C NMR spectrum of the complex **2.**

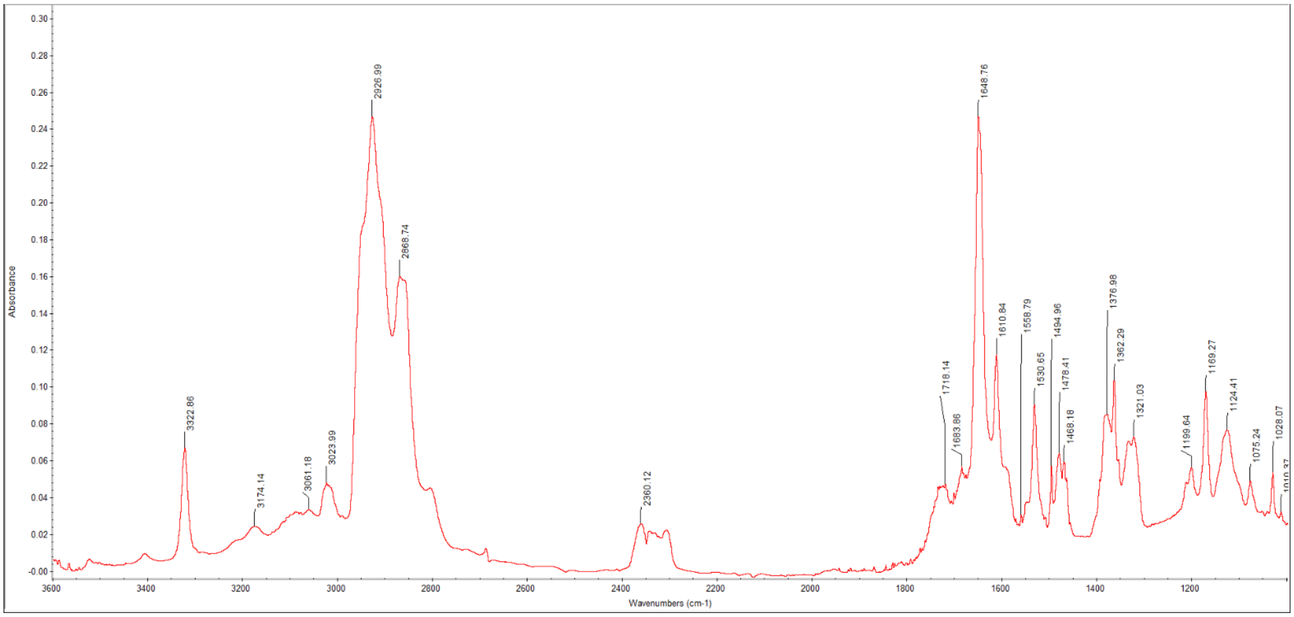


Figure S3. IR spectrum of the complex Λ(*R*,*R*)-**2** recorded in CH_2Cl_2 (c = 4.4 × 10^{-3} M).

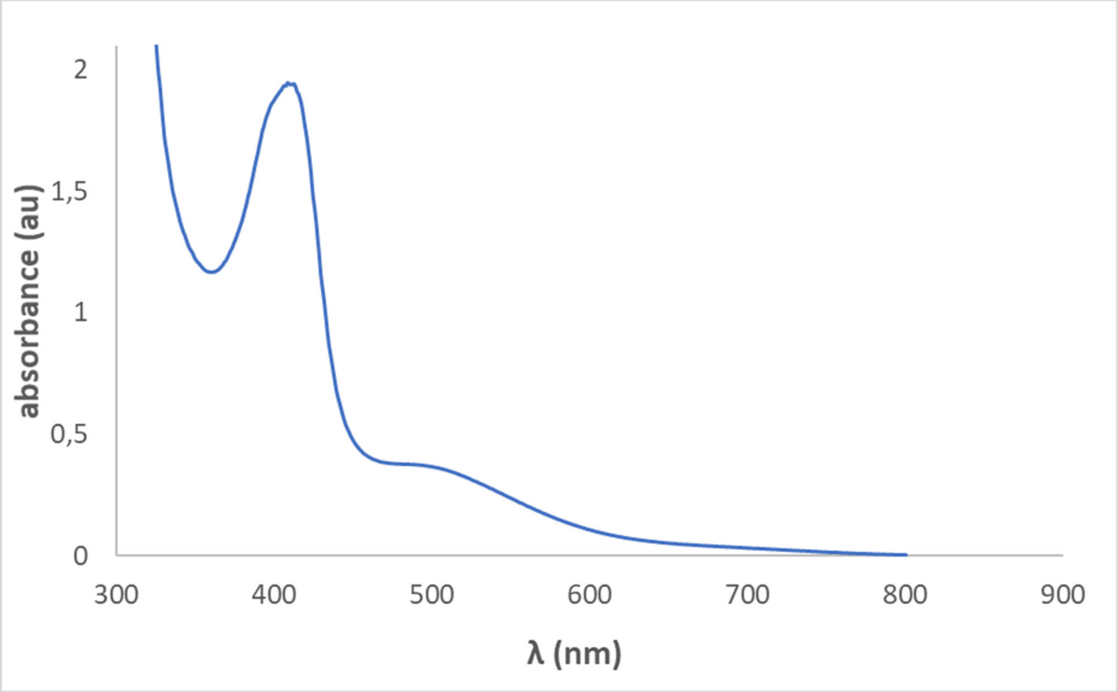


Figure S4. UV-vis spectrum of the complex Λ(*R*,*R*)-**2** recorded in CH_2Cl_2 (c = 4.4 × 10^{-3} M).

X-ray diffraction study of the Co(III) complex 2

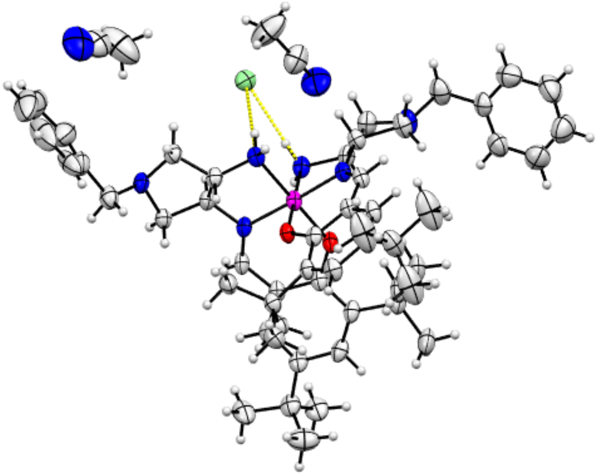


Figure S5. X-ray structure of the Co(III) complex **2** of Δ-configuration with co-crystallized acetonitrile molecules.

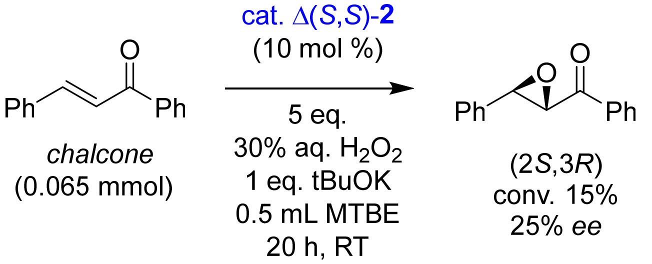
Table S1. Crystallographic data for the complex **2.**

Data block	Complex 2
Brutto formula	$C_{56}H_{78}ClCoN_8O_2$
Formula weight	989.64
Diffractometer	Bruker SMART APEX CCD area detector
Scan mode	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube
Crystal Dimensions, mm	0.02 × 0.18 × 0.25
Crystal colour	brown
Crystal system	*triclinic*
a, Å	11.6512(15)
b, Å	14.7315(18)
c, Å	17.205(2)
α, °	90.658(3)
β, °	99.107(3)
γ, °	104.433(2)
Volume, Å^3	2819.7(6)
Density, gcm^{-3}	1.166
Temperature, K	120
T_{min}/T_{max}	0.6437/0.7461
μ, mm^{-1}	0.397
Space group	$P\bar{1}$
Z	2
F(000)	1060
Reflections collected	27067
Independent reflections	11086
Reflections (I>2σ(I))	6491
Parameters	628
R_{int}	0.0595
$2\theta_{min}$ - $2\theta_{max}$, °	3.634 - 52.000
wR_2 (all reflections)	0.1858
R_1(I>σ(I))	0.0624
GOF	1.024
ρ_{min}/ρ_{max}, eÅ^{-3}	-0.467/0.835

Table S2. Selected bond distances and angles for the complex **2**.

Distance	Å	Angle	°	Hydrogen Bond	Å
Co1-O1	1.888(3)	O1-Co1-N2	179.2(1)	H2B…Cl1	2.336
Co1-O2	1.888(2)	O2-Co1-N5	179.4(1)	H5B…Cl1	2.384
Co1-N1	1.903(3)	N1-Co1-N4	177.5(1)		
Co1-N2	1.993(3)	N2-Co1-N5	91.9(1)		
Co1-N4	1.905(3)				
Co1-N5	1.987(3)				

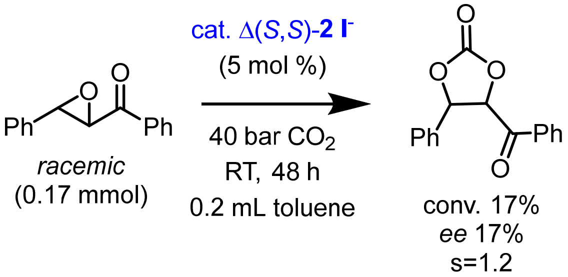
Evaluation of catalytic activity of the enantiopure complexes 2



Scheme S1. Epoxidation of chalcone.

The reaction was performed under our previously published conditions (ref. [13]).

(2*S*,3*R*)-Phenyl-3-phenyloxiran-2-yl)methanone: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J*=7.5 Hz, 2H), 7.62 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.7 Hz, 2H), 7.46–7.31 (m, 5H), 4.31 (d, *J*=1.8 Hz, 1H), 4.08 (d, *J*=1.6 Hz, 1H) ppm. HPLC Kromasil 3-AmyCoat column; 25 °C, hexane/isopropanol 95:5, λ = 254 nm, 1 mL/min, t_R = 10.1 (major), 10.9 min.

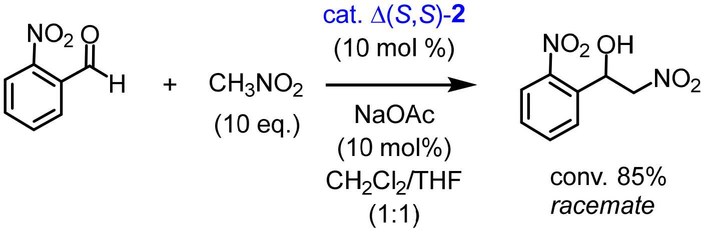


Scheme S2. Kinetic resolution of chalcone epoxide with CO_2.

The reaction was performed under our previously published conditions (ref. [13]).

4-Benzoyl-5-phenyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J*=7.5 Hz, 2H), 7.66 (t, *J*=7.5 Hz, 1H), 7.55–7.43 (m, 7H), 5.98 (d, *J*=6.2 Hz, 1H), 5.60 (d, *J*=6.2 Hz, 1H) ppm. HPLC CHIRALCEL OD-H column; 25 °C, heptane/isopropanol 90:10, λ = 220 nm, 1 mL/min, t_R = 18.0, 33.1 (major) min. The iodide complex **2** was obtained according to our published procedure (*ChemSusChem* **2016**, *9*, 216) and used without further purification and characterization.

S factor calculated as (ln[1–c(1+ee)])/(ln[1–c(1–ee)]) where c is the conversion and *ee* is the enantiomeric excess of the cyclic carbonate product.

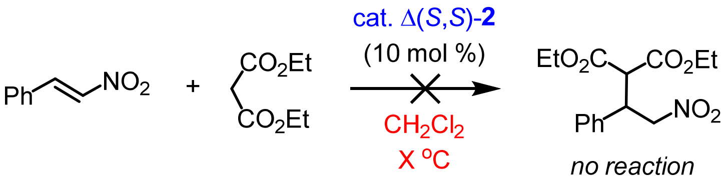


Scheme S3. Asymmetric Henry reaction of the o-nitrobenzaldehyde with the nitromethane.

The reaction was performed under our previously published conditions (*Inorg. Chem.* **2019**, *58*, 11051).

2-Nitro-1-(2-nitrophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11–8.08 (m, 1H), 7.98–7.96 (m, 1H), 7.78–7.74 (m, 1H), 7.59–7.55 (m, 1H), 6.07 (ddd, *J*=8.8, 4.2, 2.2 Hz, 1H), 4.89 (dd, *J*=13.9, 2.2 Hz, 1H), 4.57 (dd, *J*=13.9, 8.8 Hz, 1H), 3.15 (d, *J*=4.2 Hz, 1H) ppm. HPLC

Kromasil 3-AmyCoat column; 25 °C, heptane/isopropanol 90:10, λ = 254 nm, 1 mL/min, t_R = 11.0, 12.7 min.



Scheme S4. Michael addition of dimethyl malonate to *trans*-β-nitrostyrene.

The reaction was performed under published conditions (ref. [24]).