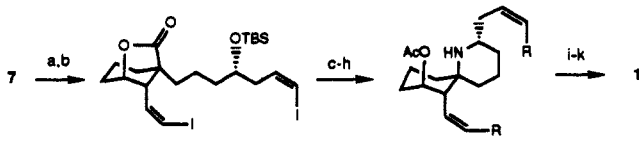
Scheme II. Synthesis of Histrionicotoxin[a]



[a] (a) O_3, then Ph_3P; (b) $(Ph_3P^+CH_2I)I^-$, $NaN(TMS)_2$, HMPA, THF, 52%; (c) 5% HCl, THF; (d) Ph_3P, CBr_4, ether, 2 h, 53%; NH_4Cl, $AlMe_3$, PhH, 40 °C, 18 h; (f) Ac_2O, Py, DMAP, 70%; (g) $(CF_3CO_2)_2IPh$, CH_3CN, H_2O, 3 days; (h) Et_3N, $ClCH_2CH_2Cl$, 65–70 °C, 2 h, 31% (A small quantity of the 2-epimer was undoubtedly formed in step d (cf. footnote 12) and was removed during the silica gel purification of **12**); (i) $Pd(PPh_3)_4$, CuI, PhH, (trimethylsilyl)-acetylene; (j) $Bu_4N^+F^-$; (k) aqueous K_2CO_3, MeOH, 40%.

9. Protection of the alcohol functionality was essential to prevent carbamate formation during the Hoffman-like rearrangement of amide **9** to amine **10**. The latter reaction could be accomplished satisfactorily by treatment of **9** with phenyliodonium bistrifluoroacetate in aqueous acetonitrile.[10] Cyclization of the amine **10** thus obtained was carried out at 55 °C with triethylamine in 1,2-dichloroethane to give, after deprotection, histrionicotoxin 235A (**2**) ($[\alpha]^{25}_D$ −102°, c = 1.82, EtOH)[11,12] in 10 steps (1.8% overall yield) from the readily available ester **3**.

We considered first an approach to the synthesis of histrionicotoxin itself which simply involved elaboration of histrionicotoxin 235A. This approach was abandoned when it became clear that protection of the very hindered secondary amine was going to be very difficult: acylating agents, for instance, only acylated the secondary hydroxyl group. Another approach was abandoned when a known method for the introduction of a (*Z*)-enyne chain proved unsuitable.[13]

The successful route to histrionicotoxin involved the assumption that an effective assembly of the required (*Z*)-enyne system should result from the palladium-catalyzed coupling of a (*Z*)-vinyl iodide with a suitable derivative of acetylene. We further assumed that the vinyl iodide system would prove compatible with the chemical transformations that would have to follow its early introduction in a histrionicotoxin precursor. Both assumptions proved to be correct.

The most direct application of this strategy to the systems readily available to us required an effective method for the synthesis of (*Z*)-vinyl iodides from aldehydes. This problem, in fact, provided the motivation for designing the method we recently reported to achieve this transformation.[14] Its application to the dialdehyde obtained by ozonolysis of lactone **7**, itself an early intermediate on the route (vide supra) to histrionicotoxin 235A, successfully led to the bis((*Z*)-vinyl iodide) **11** (Scheme II). In a similar manner as described above for the synthesis of histrionicotoxin 235A, **11** was converted to the spiropiperidine **12**, which was then coupled with (trimethylsilyl)acetylene[15] to give the dienyne **13**. Deprotection of **13** proceeded smoothly to give (−)-histonicotoxin ($[\alpha]^{25}_D$ −114°, c = 1.06, EtOH) (11 steps, 2.4% overall yield, from **7**). The spectroscopic data (IR, MS (CI), NMR) for the synthetic (−)-histrionicotoxin coincided with those obtained with authentic natural (−)-histrionicotoxin.

The two total syntheses just described are the first recorded syntheses of naturally occurring members of the histrionicotoxin family in the proper absolute stereochemistry. They illustrate important features of the "allylic epoxide cyclization": brevity, as well as regio-, stereo-, and enantioselectivity.

Acknowledgment. We thank Dr. J. W. Daly of the National Institutes of Health for a sample of natural (−)-histrionicotoxin, Dr. A. Srikrishna for his valuable studies of earlier routes to histrionicotoxin, and the National Science Foundation and the National Institutes of Health for their support.

(9) Levin, J. I.; Turos, E.; Weinreb, S. M. *Synth. Commun.* **1982**, *12*, 989.
(10) Boutin, R. H.; Loudon, G. M. *J. Org. Chem.* **1984**, *49*, 4277.
(11) Histrionicotoxin 235A has the following characteristics: IR ($CHCl_3$) 3681, 3601, 3350 (br), 3068, 3020, 2978, 2939, 2872, 1640, 1602, 1524, 1429, 1336, 1128, 1074, 995, 970, 923 cm^{-1}; MS (CI) 235 (M^+), 220, 218, 194, 192, 176, 166, 150, 110, 108, 96, 93, 85, 83; ^{13}C NMR (67.5 MHz; $CDCl_3$, 78.13) 137.3, 135.5, 119.0, 118.9, 73.97, 55.80, 50.92, 46.45, 42.34, 37.87, 37.49, 32.86, 29.41, 19.84, 16.28; ^1H NMR (400 MHz; $CHCl_3$, 7.27) δ 5.81 (dtq, J = 0.8, 10, 7.6 Hz), 5.68 (ddt, J = 0.8, 17, 10 Hz), 5.07–5.21 (m), 3.80 (m), 3.07 (m), 2.99 (d, J = 10 Hz), 2.18 (dt, J = 0.8, 6.8 Hz), 2.05 (qt, J = 14, 4 Hz).
(12) Some 2-epihistrionicotoxin 235A (11%) was also obtained (eluted first from silica gel). This arises mainly from the 7% (*R*)-**5** formed in the enantioselective synthesis of **5** and possibly from a small amount of racemization in the formation of bromide **8**.
(13) The reaction of aldehyde **14** with the titanium tetraisopropoxide complex of the anion of bis(trimethylsilyl)propyne led to a 1:1 mixture of the *Z* and *E* olefins **15**, even though these are the same conditions that convert

cyclohexanecarboxaldehyde almost entirely to (*Z*)-1-cyclohexyl-4-(trimethylsilyl)-1-buten-3-yne, the correct geometric isomer in the context of histrionicotoxin synthesis. Cf.: Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.
(14) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173.
(15) Descoins, C.; Lettere, M.; Linstrumelle, G.; Michelot, D.; Ratovelomanana, V. *Synth. Commun.* **1984**, *14*, 761.

Highly Efficient Asymmetric Hydrogenation of Amino Ketone Derivatives Leading to Practical Syntheses of (*S*)-Propranolol and Related Compounds†

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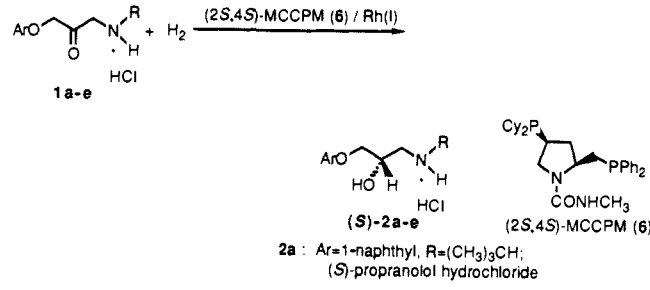
We report here an unprecedented and highly efficient asymmetric hydrogenation of the 3-(aryloxy)-2-oxo-1-propylamine derivatives **1a–e** leading to the practical synthesis of the (*S*)-1-amino-3-(aryloxy)-2-propanol derivatives **2a–e**, chiral β-adrenergic blocking agents, e.g., (*S*)-propranolol hydrochloride (**2a**).[1-3]



The demonstrated synthesis of (*S*)-propranolol hydrochloride (**2a**) is shown in Scheme I. After conversion of 1-naphthol (**3**)

† Asymmetric Reactions Catalyzed by Chiral Metal Complexes. 41.
(1) For recently reported preparations of (*S*)-propranolol and related compounds by nonenzymatic asymmetric synthesis, see: (a) Klunder, J. M.; Ko, S. Y.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 3710. (b) Miyano, S.; Lu, L. D.-L.; Viti, S. M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 4350. (c) Katsuki, T. *Tetrahedron Lett.* **1984**, *25*, 2821. (d) Bäckvall, J. E.; Björkman, E. E.; Bystrom, S. E. *Tetrahedron Lett.* **1982**, *23*, 943.
(2) For the synthesis of homochiral β-blockers utilizing enzyme technology, see: (a) Terao, Y.; Murata, M.; Achiwa, K.; Nishino, T.; Akamatsu, M.; Kamimura, M. *Tetrahedron Lett.* **1988**, *29*, 5173. (b) Matsuo, N.; Ohno, N. *Tetrahedron Lett.* **1985**, *26*, 5533. (c) Hamaguchi, S.; Hasegawa, J.; Kawaharada, H.; Watanabe, K. *Agric. Biol. Chem.* **1984**, *48*, 2055. (d) Iriuchijima, S.; Kojima, N. *Agric. Biol. Chem.* **1982**, *46*, 1153. (e) Iriuchijima, S.; Keiyu, A.; Kojima, N. *Agric. Biol. Chem.* **1982**, *46*, 1953.
(3) For the synthesis of homochiral β-blockers using chiral building blocks, e.g., D-mannitol, see: (a) Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447 and references cited therein. (b) Bouzoubaa, M.; Leclerc, G.; Rakhit, S.; Andermann, G. *J. Med. Chem.* **1985**, *28*, 896.

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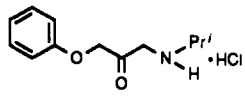
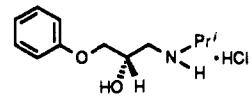
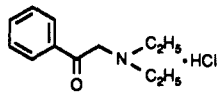
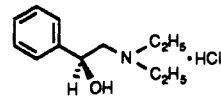
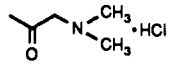
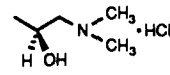
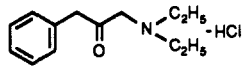
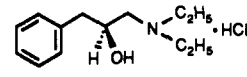
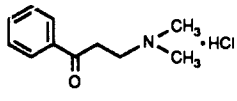
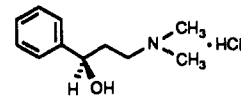
Table I. Asymmetric Hydrogenation of 3-(Aryloxy)-2-oxo-1-propylamine Derivatives (**1**) Catalyzed by the (2*S*,4*S*)-MCCPM–Rhodium(I) Complex[a]

	substrate				product			
entry	no.	Ar	R	conversn,[b] %	no.	$[\alpha]^{21}_D$, deg (*c* 1.1, ethanol)	% ee[c]	confign[d]
1	**1a**	1-naphthyl	$(CH_3)_2CH$	100	**2a**	−23.2	90.8	*S*
2	**1b**	$CH_3O(CH_2)_2C_6H_4$	$(CH_3)_2CH$	100	**2b**	−19.0	93.1	*S*
3	**1c**	C_6H_5	$(CH_3)_2CH$	100	**2c**	−23.5	86.6	*S*
4	**1d**	C_6H_5	Bn	100	**2d**	−14.1	97.4	*S*
5	**1e**	3,5-$(CH_3)_2C_6H_3$	Bn	100	**2e**	−19.1	94.9	*S*

[a] Reaction was carried out by using 0.01 mol % rhodium catalyst. The chemical yields were quantitative. [b] Determined by ^{1}H NMR analysis. [c] Determined by HPLC analysis of their free amines with a chiral column (Chiralcel OD). [d] Assignment based on the optical rotations of the authentic samples prepared from (2*S*)-glycidyl tosylate: Klunder, J. M.; Ko, S. Y.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 3710.

Table II. Asymmetric Hydrogenation of Amino Ketone Derivatives Catalyzed by the (2*S*,4*S*)-MCCPM–Rhodium(I) Complex[a]

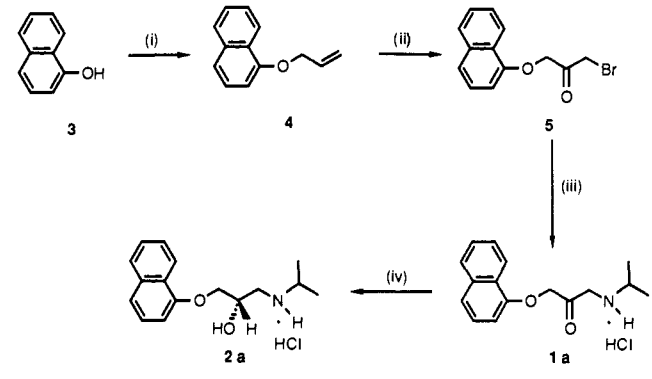
	substrate		product			
no.		conversn,[b] %	no.		% ee	confign
1c		100	**2c**		86.6	*S*
7		100	**8**		96[c]	*S*
9		100	**10**		85.7[d]	*S*[f]
11		100	**12**		91.2[d]	*S*[g]
13		100	**14**		63.6[e]	*R*[h]

[a] Reaction was carried out by using 0.01 mol % rhodium catalyst in methanol at 50 °C for 20 h under an initial hydrogen pressure of 20 kg/cm^2. The chemical yields were quantitative. [b] Determined by ^{1}H NMR analysis. [c] Reported result; see ref 6c. [d] Determined by HPLC analysis of phenylcarbamate derivatives with a chiral column (Ultron ES-OVM). [e] Determined by HPLC analysis of its free amine. [f] Determined by sign of the rotation; see: Sullivan, H. R.; Beck, J. R.; Pohland, A. *J. Org. Chem.* **1963**, *28*, 2381. [g] Assignment based on the optical rotation of the authentic sample prepared from (2*R*)-1-*O*-acetyl-2-*O*-benzylglycerol. [h] Determined by the sign of the rotation of its free amine; see: Yamaguchi, S.; Kabuto, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3033.

to the allyl naphthyl ether **4**, oxidative bromination of the olefinic part of **4** with excess sodium bromite in aqueous acetic acid[4] gave the α-bromo ketone **5**. Amination of **5** with isopropylamine was followed by treatment with hydrogen chloride[5] to give *N*-isopropyl-3-(naphthyloxy)-2-oxo-1-propylamine hydrochloride (**1a**; mp 249–255 °C dec). Asymmetric hydrogenation of **1a** (2.00 g, 6.8 mmol) proceeded smoothly in the presence of 0.01 mol % of rhodium catalyst prepared in situ by [Rh(1,5-cyclooctadiene)Cl]$_2$ and (2*S*,4*S*)-MCCPM (**6**)[6] in a ratio of 1:2.4 and 0.25 mmol of triethylamine in methanol (10 mL) at 50 °C for 20 h under an initial hydrogen pressure of 20 kg/cm^2. Usual workup gave colorless crystals of (*S*)-propranolol hydrochloride (**2a**; 1.97 g, 98%); $[\alpha]^{21}_D$ −23.2° (*c* 1.08, ethanol). Optically pure **2a** was obtained by single recrystallization from methanol–diethyl ether: mp 199–202 °C; $[\alpha]^{21}_D$ −25.9° (*c* 1.06, ethanol);[1a] 26% overall yield from 1-naphthol (**3**).

Asymmetric hydrogenation of a series of 3-(aryloxy)-2-oxo-1-propylamine derivatives (**1b–e**) catalyzed by the (2*S*,4*S*)-MCCPM–Rh(I) complex gave smoothly (*S*)-methoprolol hydrochloride (**2b**) and the synthetic intermediates **2d** and **2e** for 5-[(aryloxy)methyl]-2-oxazolidinones (centrally acting muscle relaxants) such as (*S*)-mephenoxalone and (*S*)-metaxalone (Table I).[7]

Scheme I[a]



[a] Reagents and conditions: (i) NaH, KI, allyl bromide, *N*,*N*-dimethylformamide, 0–25 °C, 6 h, 91%; (ii) 5 equiv of sodium bromite, AcOH–H_2O, 0–25 °C, argon, 6 h, 62%; (iii) $(CH_3)_2CHNH_2$, $(CH_3)_2$-$CHOH$–H_2O, 40 °C, 1 h; then HCl gas, 0 °C, 51%; (iv) H_2 (20 kg/cm^2), $[Rh(COD)Cl]_2$, (2*S*,4*S*)-MCCPM, Et_3N, methanol, 50 °C, 20 h, 98% (90.8% ee); then recrystallization from methanol–ether, 92% (~100% ee).

In addition to the high stereoselectivity (≥86.6% ee) and catalytic efficiency ([substrate]/[Rh] = 10.000), the absolute

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(5) Goto, T. *Yakugaku Zasshi* **1954**, *74*, 318.
(6) (a) Takahashi, H.; Hattori, M.; Chiba, M.; Morimoto, T.; Achiwa, K. *Tetrahedron Lett.* **1986**, *27*, 4477. (b) Takahashi, H.; Morimoto, T.; Achiwa, K. *Chem. Lett.* **1987**, 855. (c) Takeda, H.; Tachinami, T.; Aburatani, M.; Takahashi, H.; Morimoto, T.; Achiwa, K. *Tetrahedron Lett.* **1989**, *30*, 363. (d) Takeda, H.; Tachinami, T.; Aburatani, M.; Takahashi, H.; Morimoto, T.; Achiwa, K. *Tetrahedron Lett.* **1989**, *30*, 367.
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configuration of the newly formed hydroxyl group of the products is noteworthy. Thus, the asymmetric hydrogenation of the 3-(aryloxy)-2-oxo-1-propylamine hydrochloride (**1b–e**) catalyzed by the (2*S*,4*S*)-MCCPM–Rh(I) complex gave the *S* product (**2b–e**) in 86.6–97.4% ee, whereas the same hydrogenation of 2-(*N*,*N*-diethylamino)acetophenone hydrochloride (**7**)[6c] yielded (*S*)-2-(*N*,*N*-diethylamino)-1-phenylethanol hydrochloride (**8**) in 97% ee. Therefore, the hydroxyl groups of **2a–e** have dramatically the opposite configuration to that of **8**.

For an understanding of the reason for the opposite stereoselectivity, the asymmetric hydrogenation of several types of amino ketones catalyzed by the (2*S*,4*S*)-MCCPM–Rh(I) complex was carried out. The results, listed in Table II, show that the α-amino ketone derivatives **1c**, **7**, **9**, and **11** are hydrogenated with higher enantioselectivities (86–97% ee) than the β-amino ketone derivatives [3-(*N*,*N*-dimethylamino)propiophenone hydrochloride, **13**] (63.6% ee) and that the asymmetric hydrogenations of (*N*,*N*-dimethylamino)acetone hydrochloride (**9**) and 1-phenyl-3-(*N*,*N*-diethylamino)-2-propanone hydrochloride (**11**)[8] bearing an alkyl group adjacent to the prochiral carbonyl group proceed with high enantioselectivities (85.7% ee and 91.2% ee, respectively) as well as 2-(*N*,*N*-diethylamino)acetophenone hydrochloride (**7**) having a phenyl ring (97% ee). With respect to the absolute stereochemistry of the hydroxyl groups of the hydrogenated products, all of them, except **2c**, have the same configuration. Because the 3-(aryloxy)-2-oxo-1-propylamine derivatives (**1**) contain an oxygen atom substituting on the α-position of the prochiral carbonyl group, the lone pair of electrons of the oxygen atom may play an important role in the stereoselectivity of these asymmetric hydrogenations.

The (2*S*,4*S*)-MCCPM–Rh(I) complex is a very efficient catalyst for the asymmetric hydrogenation of a variety of amino ketone derivatives leading to practical syntheses of chiral medicines such as (*S*)-propranolol, (*S*)-methoprolol, (*S*)-mephenoxalone, and (*S*)-metaxalone.

Acknowledgment. This work was partially supported by a Grant-in-Aid (No. 01470139) for Scientific Research for the Ministry of Education, Science, and Culture of Japan.

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Photochemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in Phosphine Solutions: Evidence for an Associative Photosubstitution Mechanism

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Over the past few years there has been much interest in the photochemistry of $(\eta^5\text{-}C_5R_5)ML_2$ and $(\eta^5\text{-}C_5R_5)ML(H)_2$ (M = Rh, Ir; R = H, CH_3; L = CO, PR_3, olefin) complexes leading to intermolecular activation of hydrocarbon C–H bonds.[1] Extensive matrix isolation, flash photolysis, and low-temperature solution studies have been performed on these systems, and they indicate that their C–H activation and photosubstitutional reactions proceed initially via ligand dissociation to yield a 16-electron species.[2] Recently, theoretical models of methane C–H bond activation have arisen based on this premise, i.e., that a coordinatively unsaturated 16-electron $(\eta^5\text{-}C_5R_5)ML$ complex is the key reactive intermediate.[3]

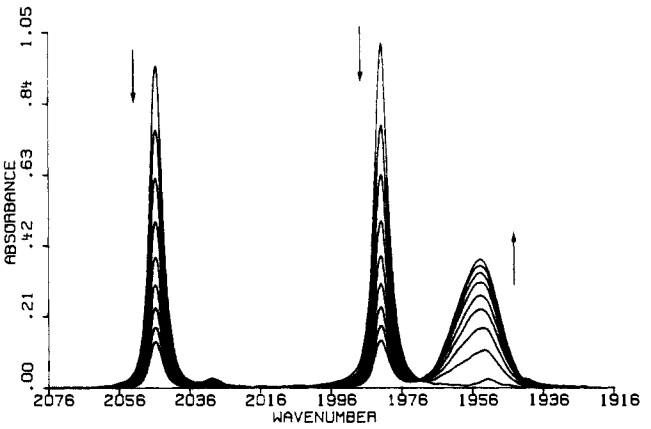

Figure 1. FTIR absorption spectral changes accompanying the 458-nm laser photolysis of 2.5×10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in deoxygenated decalin solution containing 0.05 M PPh_3 at 10 °C. Spectra are depicted following 0, 1, 2, 3, 4, 5, 6, 7, and 8 h irradiation time intervals.

In contrast, scant support has been given to the idea that associative processes play a role in these C–H bond activation mechanisms.[4] Although matrix isolation studies of $(\eta^5\text{-}C_5R_5)M(CO)_2$ (M = Rh, Ir) have provided preliminary evidence[5] for a ring slippage ($\eta^5 \rightarrow \eta^3$) step, this argument was later dropped in favor of a photochemically generated $(\eta^5\text{-}C_5R_5)M(CO)$ intermediate again.[6] Throughout these interpretations, however, many of which involve simple photosubstitution, there appears to be little weight attached to the known thermal reactivity of these molecules which have implicated ring slippage processes.[7] Our interest in the photoprocesses of $(\eta^5\text{-}C_5R_5)M(CO)_2$ has been stimulated by this apparent dichotomy. We present here a study of the solution photochemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in the presence of excess scavenging PPh_3 ligand; the results show unequivocally that this photoreaction proceeds via an *associative mechanism*.

Solutions (4 mL) of 2.5×10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in decalin containing excess PPh_3 (0.05–0.3 M) were rigorously deoxygenated, cooled to 10 °C, and then irradiated with the 458-nm line of an Ar ion laser. During photolysis the samples were rapidly stirred to ensure a uniform optical density throughout the solution. Laser powers of 50–200 mW were employed and accurately determined by means of a calibrated external power meter. Reactions were monitored throughout photolysis by UV–visible and FTIR spectroscopy; spectra were also recorded from solutions kept in the dark at 10 °C to assess the extent of thermal processes.

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