Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2013

Electronic Supplementary Information

Hydrogel Formed by a Simple Squaric Acid Derivative

Yutaka Ohsedo,[*a] Misao Miyamoto,[a, b, c]
Masashi Oono,[b] Kazuaki Shikii[b] and Akihiro Tanaka[b]

[a] *Advanced Materials Research Laboratory, Collaborative Research Division, Art, Science and Technology Center for Cooperative Research, Kyushu University 203-1 Motooka Nishi-ku Fukuoka 819-0385 (Japan). Fax: (+81) 92-400-4382; Tel: (+81) 92-400-4381; E-mail: ohsedo@astec.kyushu-u.ac.jp*
[b] *Nissan Chemical Industries, Ltd., 2-10-1 Tsuboi-cho Funabashi Chiba 274-8507 (Japan).*
[c] *Current affiliation; Nippon Phosphoric acid Co., JP, 14 Kitasode, Sodegaura, Chiba (Japan).*

Table of Contents

Materials and Methods

All reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K).

The gelation tests were performed using the vial inversion method. **PhSQ** was place in a 2.2 cc vial with water in set concentration (wt%) and capped. The vial was heated in a water bath at 60 °C until **PhSQ** was dissolved. **PhSQ** aqueous solution was left for 30 min at room temperature; gelation was checked with the naked eye by inverting the vial.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on AVANCE 500 (500 MHz, Bruker BioSpin K.K.) and ECP-500 (500MHz, JEOL Ltd.) spectrometers, respectively. Mass spectra were recorded on an LTQ Orbitrap spectrometer (ESI FTMS, Thermo Fisher Scientific K.K). Elemental analysis was performed with a JM10 elemental analyzer (J-SCIENCE LAB CO., Ltd.). SEM images were recorded with a JSM-7400 scanning electron microscope (JEOL Ltd.) at 1.0 kV; SEM samples (**PhSQ**) were dried on the SEM sample stages and used without conductive material coating. TEM images were recorded with an H-8000 transmission electron microscope (Hitachi High-Technologies Corporation) at 200kV; TEM samples (**PhSQ**) were dried on the TEM sample stages and used without staining. Thermal analysis was performed with an EXSTAR6000 differential scanning calorimeter DSC (Seiko Instruments Inc.) using an SUS-made closable sample pan. Rheological measurements of frequency sweep were performed with an MCR-101 rheometer (Anton Paar Japan K.K.) with a parallel plate (8 mm diameter) at a gap of 0.50 mm and strain of 0.10% (measurement temperature: 24 °C). Rheological measurements of strain sweep were performed with an MCR-101 rheometer with a parallel plate (8 mm diameter) at a gap of 0.50 mm and constant angular frequqncy 1 rad s^{-1} (measurement temperature: 24 °C). The hydrogel sample for rheological measurements was melted at 60°C on a sample stage; the plate was set (the overflow sol was swept), and then, the temperature of the sample stage was cooled to 25 °C to form the hydrogel. Infrared spectroscopy was performed with an FT/IR-620 (JASCO Corporation) using the ATR method (ZnSe prism). Single-crystal X-ray diffraction data were recorded on a SMART APEX II Ultra X-ray diffractometer（Bruker AXS K.K.）with CuKα at −100 °C. Synchrotron X-ray powder diffraction data of **PhSQ** hydrogel and anhydrous **PhSQ** crystal were recorded on a Debye–Scherrer camera on the BL19B2 beamline (λ = 1.00 Å) at the SPring-8 synchrotron radiation facility, Japan.

PhSQ Synthesis

Under N_2 atmosphere, dichloromethane (5 mL), benzene (2.07 g, 31.7 mmol) and squaric dichloride (4.00 g, 31.7 mmol) were combined and immersed in an ice bath. Squaric dichloride was synthesised as reported in the literature.[1] **CAUTION**: squaric dichloride is corrosive, harmful if inhaled and causes skin irritation.[2] To this mixture, $AlCl_3$ (5.31 g, 44.7 mmol) was added gradually. The mixture was stirred at 35 °C for 2h, quenched with water and washed with brine. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was hydrolysed with acetic acid/water (v/v=1/1, 20 mL) at 70 °C for 1h. The solvent was removed in vacuo. The residue was dissolved in hot water and filtered to remove water-insoluble impurities; this step was repeated two times. Water was removed from the solution in vacuo to yield **PhSQ** (2.82 g, yield 60.6%) as a pale yellow powder.

^{1}H-NMR (500 MHz, DMSO-d_6, TMS, δ, ppm): 7.99 (m, 2H), 7.47 (dt, 2H, J = 7.6 Hz, J = 1.3 Hz), 7.40 (tt, 1H, J = 7.4 Hz, J = 1.3 Hz). ^{13}C-NMR (125 MHz, DMSO-d_6, δ, ppm): 205.37, 196.76, 173.65, 130.74, 130.69, 129.47, 129.47, 125.72.

ESI MS:calcd for $C_{10}H_6O_3$ (MW = 174.03): m/z = 173.02 [M+−H]. Elemental anal. calcd for $C_{10}H_6O_3$: C, 68.97%; H, 3.47%; Found: C, 69.08%; H, 3.33%.

Crystallographic Analysis

A **PhSQ**·H_2O single crystal sample for crystallographic analysis was prepared by recrystallisation from acetonitrile. An anhydrous **PhSQ** crystal was prepared by drying a **PhSQ** single crystal in vacuo at 40 °C. Tables S1 and S2 list the unit-cell and crystal data for **PhSQ** in various states.

Samples of synchrotron X-ray powder diffraction were packed in Lindenman glass capillaries (diameter 0.3 mm). The data collection times were 20 min. The powder diffraction data was indexed with the N-TREOR auto-indexing program. Peak intensities were extracted by the Le Bail method. Crystal structure was determined by the direct-space method (parallel tempering algorithm) with the FOX program. Rietveld refinement was performed with the TOPAS program. Crystal structures were visualised from CIF data using two programs: Mercury (Cambridge Crystallographic Data Centre) and Diamond 3.2 (demonstration version, Crystal Impact GbR, Bonn, Germany).

Table S1 Unit-cell and crystal data of **PhSQ**·H_2O single crystal.

Chemical formula	C10H6O3·H_2O
Crystal system	Triclinic
Space group	P-1
Unit-cell parameters	a (Å) = 6.9284 (4), b (Å) = 8.1002 (5), c (Å) = 9.1236 (5)
	α (°) = 75.226 (3), β (°) = 85.617 (3), γ (°) = 66.772 (3)
	V (Å^3) = 454.80 (5)
Z	2
Temperature	173 K
Number of reflections measured	4039
Number of independent reflections	1571
Rint	0.0176
Final R values(I > 2sigma(I))	0.0362
Final wR values(I > 2sigma(I))	0.0980
Number of independent reflections	1571
R / *wR*	0.04 / 0.11

Table S2 Unit-cell and crystal data of 30 wt% **PhSQ** hydrogel.

Chemical formula	C10H6O3·$2H_2O$
Crystal system	Trigonal
Space group	R-3
Unit-cell parameters	a (Å) = 38.6546 (8), c (Å) = 3.8342 (1), c / a = 0.0992, *V* (Å^3) = 4960.21 (22)
Temperature	300 K

Table S3 Unit-cell and crystal data of anhydrous **PhSQ** crystal.

Chemical formula	C10H6O3
Crystal system	Triclinic
Space group	P-1
Unit-cell parameters	a (Å) = 6.4589 (3), b (Å) = 7.1658 (4), c (Å) = 9.3191 (9)
	α (°) = 105.6977(62), β (°) = 101.6720 (35), γ (°) = 102.4815 (65), *V* (Å^3) = 391.12 (1)
Temperature	300 K

Table 1 (full version) Transition temperatures of **PhSQ**/water systems at different **PhSQ** concentrations.

Sample (heating and cooling rate)	$T_{gel\rightarrow sol}$ /°C (ΔH/mJ mg^{-1})	$T_{sol\rightarrow gel}$ /°C (ΔH/mJ mg^{-1})
PhSQ 25 wt%/H_2O (5 °C/min)	49 (16.8)	9 (16.8)
PhSQ 25 wt%/H_2O (1 °C/min)	49 (41.7)	No peak
PhSQ 30 wt%/H_2O (5 °C/min)	54 (39.2)	16 (32.6)
PhSQ 30 wt%/H_2O (1 °C/min)	51 (35.0)	19 (34.8)
PhSQ 50 wt%/H_2O (5 °C/min)	57 (41.9)	41 (34.9,shoulder)
PhSQ 50 wt%/H_2O (1 °C/min)	54 (48.4)	41 (16.0), 38 (31.8)

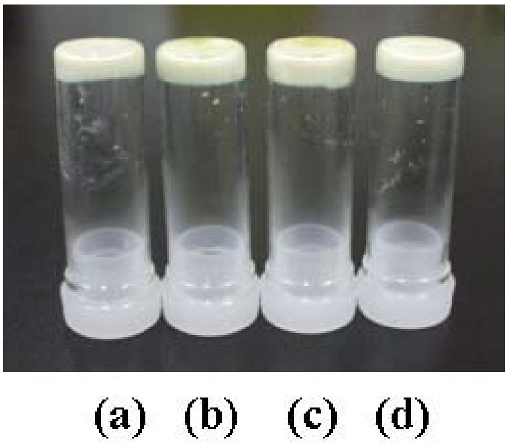

Fig. S1 Images of **PhSQ**/buffer solution of 20 wt% **PhSQ** at 25 °C after gelation test: (a) oxalate pH solution (pH 1.68), (b) phthalate pH solution (pH 4.01), (c) phosphate pH solution (pH 7.41) and (d) carbonate pH solution (pH 10.01).

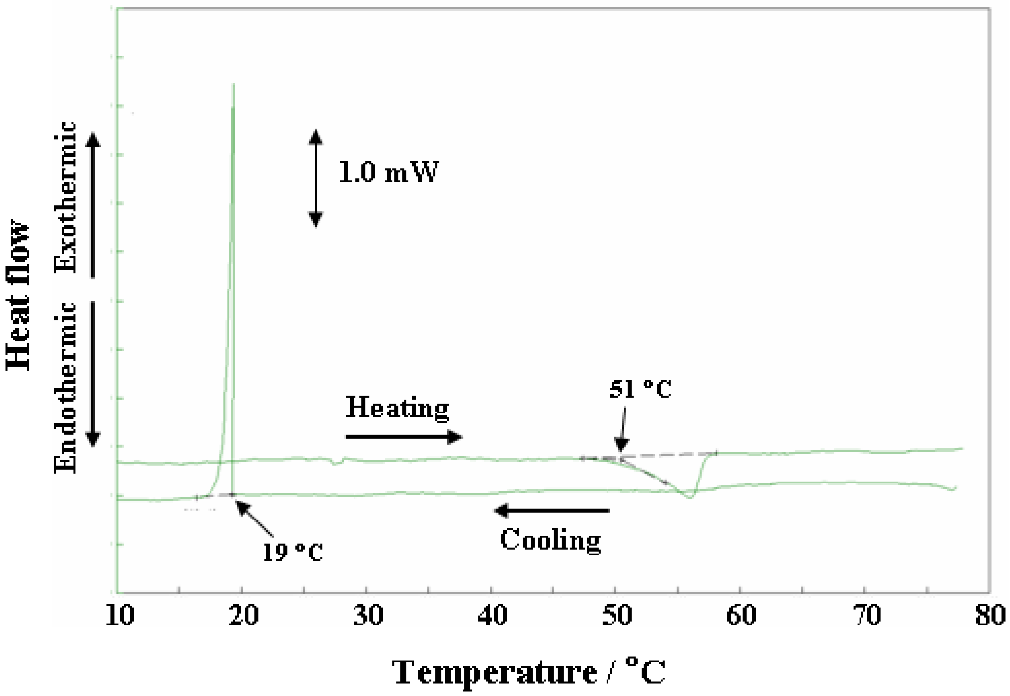

Fig. S2 DSC curves of 30 wt% **PhSQ**/water system (heating and cooling rate was 1 min/°C).

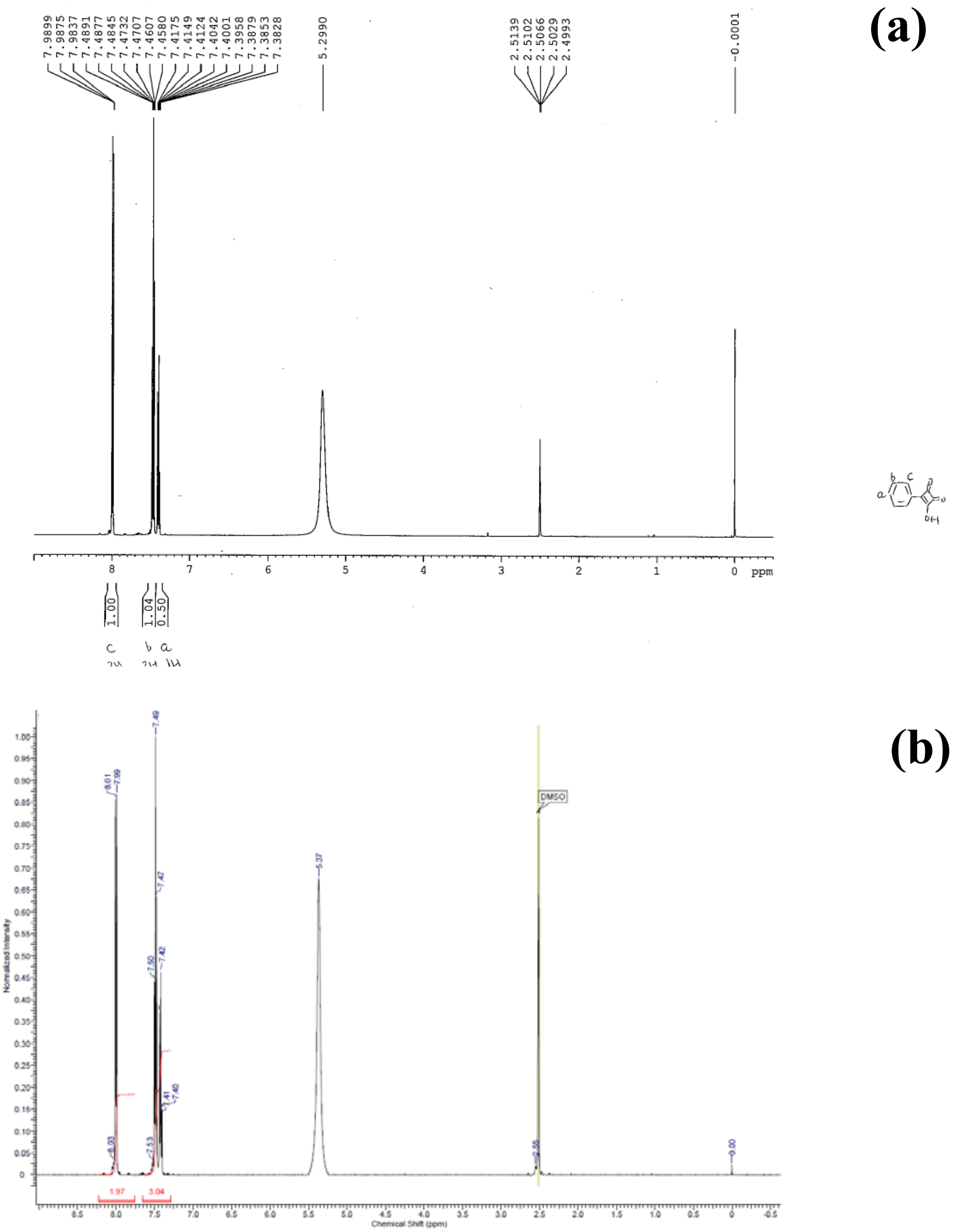

Fig. S3 ^{1}H-NMR spectra of **PhSQ** before and after gelation test ((a) and (b), respectively). Sample after gelation test (20 wt% **PhSQ**/water system) was vacuum dried and dissolved in DMSO-d_6 (^{1}H-NMR spectra (b) was created by ACD/NMR Processor Academic Edition).

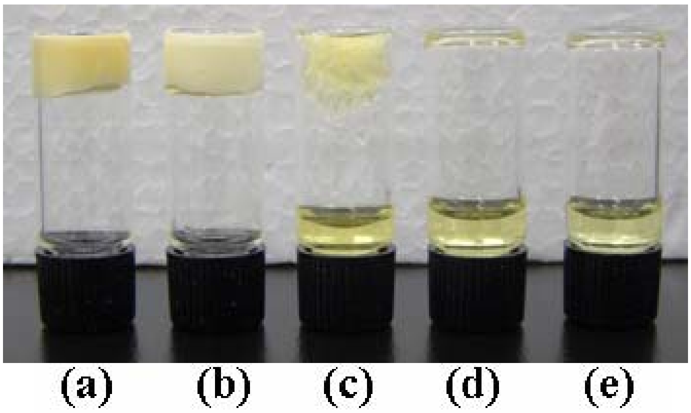

Fig. S4 Images of **PhSQ**/oxalate pH solution of different concentration of **PhSQ** at 25 °C (pH 1.68) after gelation test: (a) 20 wt% (gel), (b) 10 wt% (gel), (c) 5 wt% (crystal), (d) 2 wt% (solution) and (e) 1 wt% (solution).

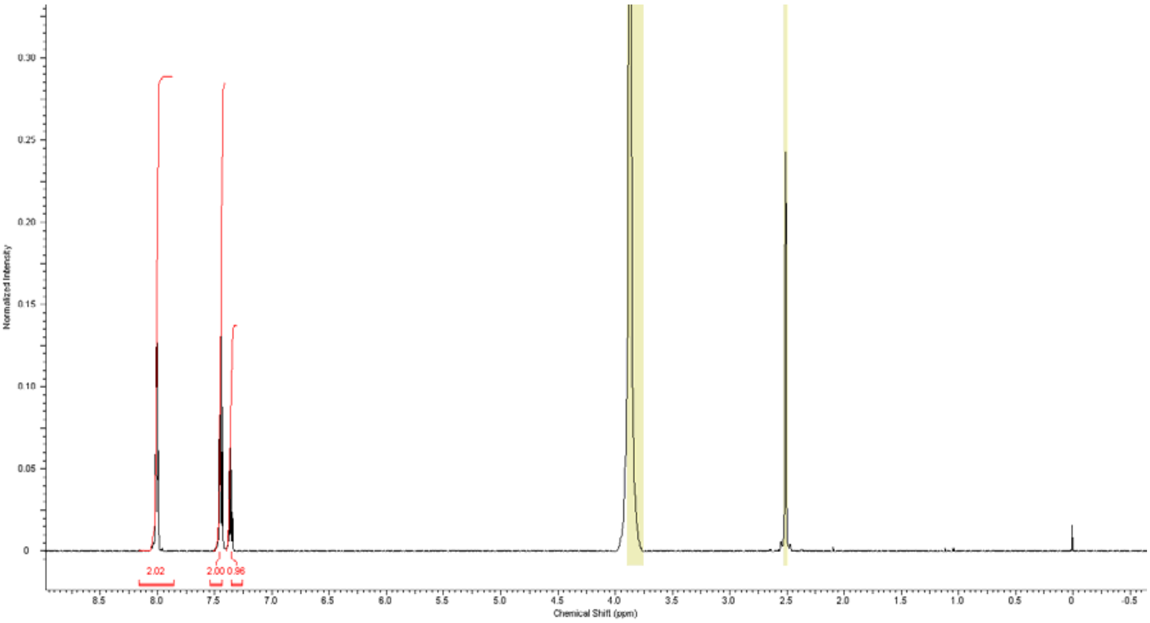

Fig. S5 ^{1}H-NMR spectra of **PhSQ**/1M HCl aq. after gelation test. Sample after gelation test (20 wt% **PhSQ**/1M HCl aq. system) was vacuum dried and dissolved in DMSO-d_6 (^{1}H-NMR spectra was created by ACD/NMR Processor Academic Edition).

Figs. S6 and S7

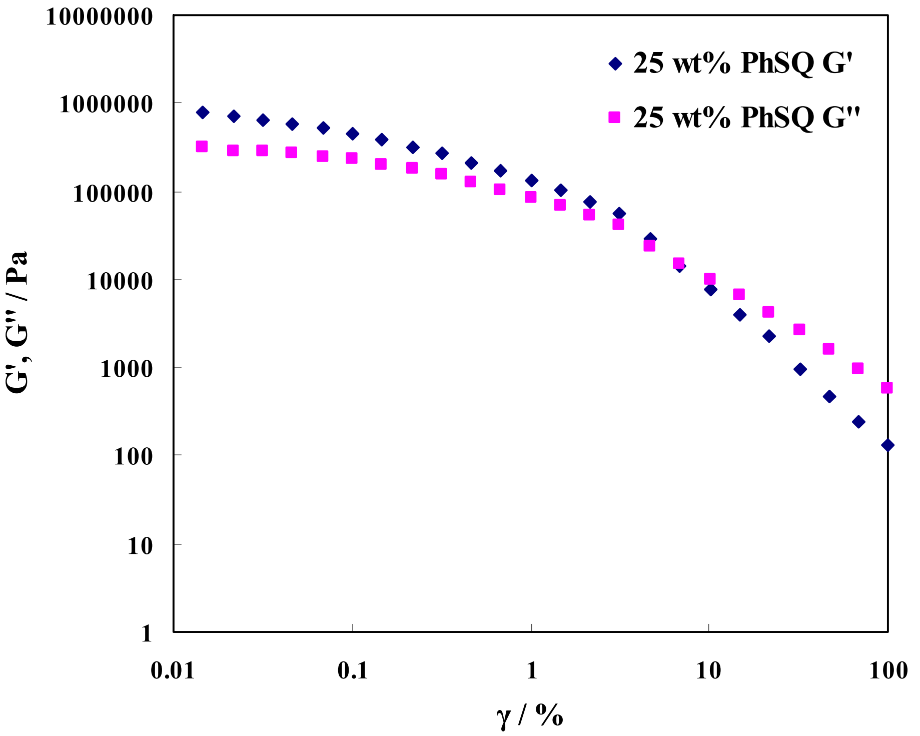

Figure S6. Dynamic rheological properties of strain sweep of 25 wt% **PhSQ**/water system on G', G'' versus strain measured using a rheometer with a parallel plate.

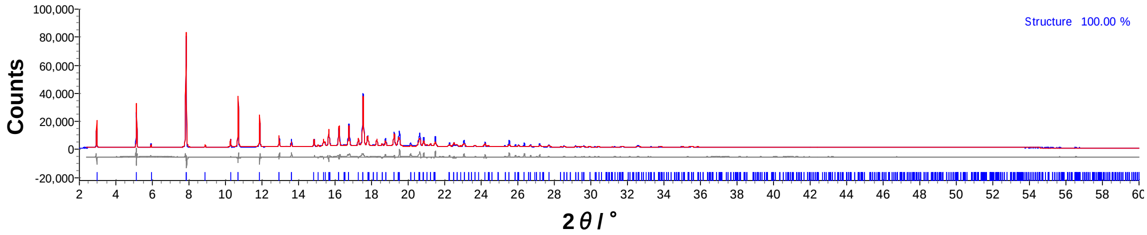

Fig. S7 Powder X-ray diffraction patterns of 30 wt% **PhSQ** hydrogel. Red lines = experimental patterns, blue lines = calculated patterns, grey lines = difference between experimental and calculated patterns and blue marks = peak positions.

.

Acknowledgements

We would like to thank Nissan Chemical Industries for financial and technical support and Dr. Osamu Hirata for his helpful discussions and comments. A part of this work was supported by the Nanotechnology Network Project (Kyushu-area Nanotechnology Network) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Synchrotron experiments were performed on the BL19B2 at SPring-8 under the auspices of the Japan Synchrotron Radiation Research Institute (JASRI), Proposal No. 2010B1914. We would also like to thank the Industrial Technology Center of SAGA and Mr. Keisuke Tsuge for asistance with rheological measurements. We would like to thank Enago (www.enago.jp) for the English language review.

References

1 R. C. De Selms, C. J. Fox, R. C. Riordan, *Tetrahedron Lett*., 1970, **11**, 781.

2 B. Lunelli, *Tetrahedron Lett*., 2007, **48**, 3595.