An Economical Approach to the Synthesis of Unsaturated Thiacrown Ethers

Dong-Qing Sun, Jing-Kui Yang*

College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing, 100049, P. R. of China
Fax +86(10)88256092; E-mail: jkyang@gucas.ac.cn

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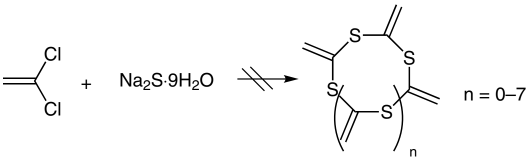
Abstract: The inexpensive starting material, 1,1-dichloroethylene, was used as a substitute for 1,2-dichloroethylene to synthesize unsaturated thiacrown ethers through the reaction of 1,1-dichloroethylene with sodium sulfide in the presence of a 15-crown-5 catalyst. Besides the compounds containing *cis*-carbon–carbon double bonds, two unsaturated thiacrown ethers each containing one *trans*-carbon–carbon double bond were also isolated.

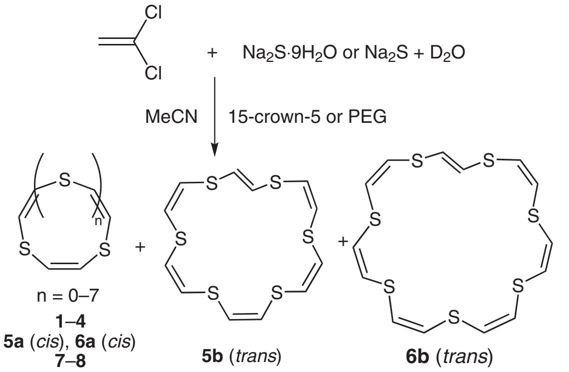
Key words: unsaturated thiacrown ether, 1,1-dichloroethylene, economical approach, macrocyclic compounds, hydrogen anion transfer

Unsaturated thiacrown ethers are a class of multifunctional molecules that have received increasing attention in the fields of organic and analytical chemistry. Their special cavity sizes and restricted conformations determine the high selectivity towards transition metals[1,2] and metallofullerene.[3] Because the carbon–carbon double bonds of unsaturated thiacrown ethers are more active than the corresponding saturated systems, their oxidation and photochemical behavior naturally became the focus of interest.[4] After the first unsaturated benzothiacrown ether was obtained by Nakayama et al.,[5] *cis*-1,2-dichloroethylene was introduced to the synthesis of unsaturated thiacrown ethers. In 2001, large-ring unsaturated thiacrown ethers without substituents were synthesized for the first time by Kamigata's group by treating *cis*-1,2-dichloroethylene with sodium sulfide.[1] Soon afterwards, unsaturated selenacrown ethers and their complexations with silver were reported.[6] In addition, some analogues containing similar unsaturated segments also aroused the attention of a number of chemists.[7] The elegant work reported by these authors stimulated us to do further studies. However, *cis*-1,2-dichloroethylene, the key reactant for preparing unsaturated thiacrown ethers is very expensive. Fortunately, 1,1-dichloroethylene, which was used to construct carbon–carbon double bonds,[8] was found to be a convenient substitute in our experiments. This starting material could be used with almost the same effect as *cis*-1,2-dichloroethylene, while being sixteen to fifty times cheaper than the latter (prices quoted by Sigma–Aldrich in the Chinese mainland in April, 2011).

We originally expected that the product shown in Scheme 1 would be generated in this reaction, but, unexpectedly, the experiment resulted in the formation of the well-known unsaturated thiacrown ethers **1**–**8** (Scheme 2). Moreover, we also obtained (*E*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (**5b**), which was mentioned in one of Kamigata's reports,[4] and a new thiaheterocycle, (*E*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19-heptathiacyclo-heneicosa-2,5,8,11,14,17,20-heptaene (**6b**) was identified at the same time; no other products were isolated except for some polymeric material.



Scheme 1 The originally expected reaction



Scheme 2 Reaction of 1,1-dichloroethylene with $Na_2S\cdot 9H_2O$, or Na_2S and D_2O and catalysts; no deuterated product was detected

The best total yield of unsaturated thiacrown ethers was almost the same as that obtained by Kamigata et al.,[1] nevertheless, the price of 1,1-dichloroethylene is approximately 2 to 6% that of *cis*-1,2-dichloroethylene, which reduces the cost greatly. Therefore, it is still an economically viable method for the preparation of unsaturated thiacrown ethers. Most importantly, the total yields were slightly better at higher temperature than those at room temperature; the reactions were accelerated to completion in only two hours at 80 °C (Table 1). In addition, some studies with phase-transfer catalysts were also made in an attempt to find less expensive and non- or low-toxic substitutes, such as polyethylene glycol, to replace 15-crown-5. Experiments demonstrated that some polyethylene glycols did indeed show a certain amount catalytic activity, although the effect was not as good as with crown ether

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(Table 1). A comparison of the catalytic efficiency could be ordered as: 15-crown-5 > PEG2000 > MPEG750 > PEG300 > tetraethylene glycol dimethyl ether. Moreover, total yields increased with an increase in the amount of catalyst. However, when the amount of 15-crown-5 was increased to more than 0.4 equiv, no apparent improvement was observed. Additionally, increasing the concentration of the reactants decreased the total yields of the products due to the formation of more polymeric material.[1,9]

To explore methods to synthesize halogenated unsaturated thiacrown ethers, trichloroethylene and tetrachloroethylene were treated, respectively, with sodium sulfide nonahydrate, which produced a polymerization product nearly completely. This polymer was slightly soluble in tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF), and partially dissolved even in dimethylsulfoxide (DMSO), which indicated the possible existence of cross-linked structures. Ikeda and co-workers have reported the synthesis of poly(vinylene sulfide) from *trans*-1,2-dichloroethylene and sodium sulfide nonahydrate in high con-

Table 1 Reactions of 1,1-Dichloroethylene with Sodium Sulfide Nonahydrate or Sodium Sulfide and Deuterium Oxide in Acetonitrile

Entry	Conc. (M)[a]	Time (h)	Temp (°C)	Cat. (equiv)[b]	Total yield (%)	Ratio[c]									
						1	**2**	**3**	**4**	**5a**	**6a**	**7**	**8**	**5b**	**6b**
1[d]	10^{-3}	45	r.t.	A (0.4)	40	44	3	~0	4	18	16	10	5	–	–
2	10^{-3}	48	r.t.	–	~0	NA									
3	10^{-3}	48	r.t.	A (0.4)	36 (33)[e]	39	4	~0	6	21	13	8	5	2	2
4	10^{-3}	48	r.t.	A 0.5	37	35	4	~0	6	22	13	9	5	4	2
5	2×10^{-3}	48	r.t.	A (0.4)	20	30	5	~0	8	24	16	8	4	3	2
6	3×10^{-3}	48	r.t.	A (0.4)	14	11	7	~0	3	23	25	18	8	3	2
7[f]	10^{-3}	72	r.t.	A (0.4)	29	38	4	~0	6	20	12	10	6	2	2
8	10^{-3}	72	r.t.	B (0.05)	3	trace for some									
9	10^{-3}	72	r.t.	B (0.1)	11	35	3	~0	17	19	10	7	3	3	3
10	10^{-3}	72	r.t.	B (0.2)	15	40	3	~0	12	18	9	10	4	2	2
11	2×10^{-3}	72	r.t.	B (0.2)	10	33	3	~0	12	22	12	8	4	4	2
12	10^{-3}	72	r.t.	C (0.15)	3	trace for some									
13	10^{-3}	72	r.t.	C (0.4)	10	38	4	~0	13	20	10	8	4	2	1
14	10^{-3}	72	r.t.	C (0.5)	10	38	4	~0	11	19	9	10	4	3	2
15	10^{-3}	72	r.t.	D (0.5)	6	34	3	~0	6	22	15	14	4	2	1
16	10^{-3}	72	r.t.	E (0.4)	2	trace for some									
17	10^{-3}	2	50	A (0.4)	19	31	4	~0	6	21	15	12	6	3	2
18	10^{-3}	12	50	A (0.4)	28	24	4	~0	6	26	16	11	6	4	3
19	10^{-3}	24	50	A (0.4)	40	31	4	~0	7	24	12	10	6	3	3
20	10^{-3}	48	50	A (0.4)	40	30	4	~0	7	23	13	10	6	4	3
21	10^{-3}	2	80	A (0.4)	40	32	4	~0	6	20	16	11	5	3	3
22	10^{-3}	12	80	A (0.4)	41	29	4	~0	7	21	15	12	6	4	2
23	10^{-3}	24	80	A (0.4)	41	29	5	~0	7	20	14	12	7	4	2

[a] The concentration of sodium sulfide, assuming sodium sulfide dissolved completely in MeCN.

[b] Catalysts: 15-crown-5 (A), PEG2000 (B), MPEG750 (C), PEG300 (D), tetraethylene glycol dimethyl ether (E).

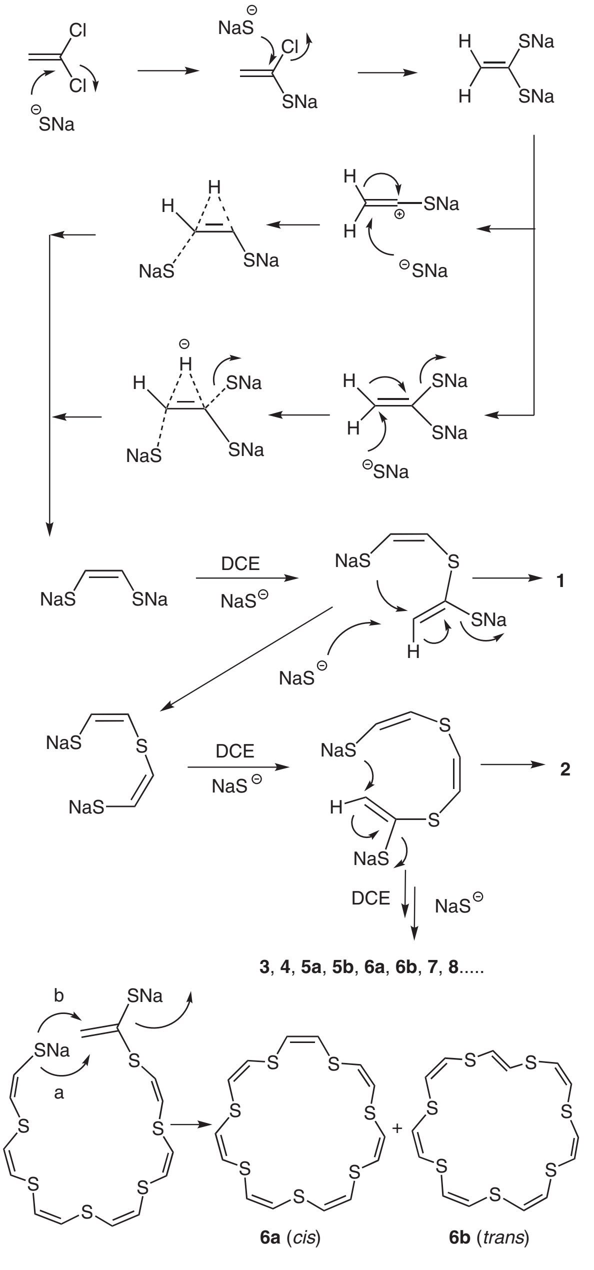
[c] Total yields and ratios of **1**–**4**, **5a**, **6a**, **7**, and **8** were determined by integration of the ^{1}H NMR spectra based on the amount of added catalyst; yields of **5b** and **6b** were isolated. Compounds **2** and **3** were identified by ^{1}H NMR, ^{13}C NMR, and MS analysis of the mixture of **2** and **3**.

[d] The *cis*-1,2-dichloroethylene reacted with sodium sulfide nonahydrate (see Tsuchiya et al.[1]).

[e] Isolated total yield in parentheses.

[f] Reaction of 1,1-dichloroethylene with Na$_2$S and D$_2$O in anhydrous MeCN.

centration with *N*-methyl-2-pyrrolidone as solvent.[9,10] Accordingly, we attempted to synthesize unsaturated thiacrown ethers containing *trans*-carbon–carbon double bonds by treating *trans*-1,2-dichloroethylene with sodium sulfide in low concentration in the presence of 15-crown-5 in acetonitrile, but discovered that, even at a temperature of 60 °C, the reaction only generated a small amount of thioacetamide derived from the reaction of acetonitrile with hydrogen sulfide, which was produced by the hydrolysis of sodium sulfide.



Scheme 3 Plausible stepwise reaction mechanism

A plausible mechanism is depicted in Scheme 3. The reaction might occur in a stepwise way as described. When a sodium ion is captured by either crown ether or PEG, the NaS^- anion can be actively liberated from the $Na_2S\cdot9H_2O$ unit. Acting as nucleophile, two NaS^- anions can attack the positive center of 1,1-dichloroethylene, which leads to the formation of sodium ethene-1,1-bis(thiolate) with fractional charge transfer through the double bond.[11] One of the NaS^- anions dissociates from sodium ethene-1,1-bis(thiolate) and recombines with another carbon atom with the hydrogen anion transferring simultaneously. Alternatively, there is a possibility that the third NaS^- anion attacks the terminal carbon and initiates the expulsion of one NaS^- from the ethene-1,1-bis(thiolate) unit, which delivers sodium ethene-1,2-bis(thiolate). In both cases, after subsequent substitution reaction with the reactant, the following sulfur ions come from the *syn*-direction, resulting in the formation of a series of *cis*-products. It is difficult to produce ring compounds (six- to fifteen-membered rings) containing *trans*-double bonds because of the high strain force, but both kinds of double bonds (*cis* and *trans*) could be furnished by attack of the sulfur ion in two different directions when the chain intermediate achieves a certain length (usually containing six to seven sulfur atoms). Moreover, the corresponding larger ring compounds with *trans*-double bonds might also be generated in small amounts in the reaction, but were difficult to isolate because of the very low yields. To probe the hydrogen anion transfer mechanism, deuterium oxide and anhydrous Na_2S were added to the reaction in anhydrous acetonitrile instead of $Na_2S\cdot9H_2O$. Under these conditions, no deuterated thiacrown ether was detected, which suggests the intramolecular hydrogen anion transfer theory operates.

In summary, an economical approach to the synthesis of unsaturated thiacrown ethers, starting from 1,1-dichloroethylene and sodium sulfide nonahydrate in the presence of a phase-transfer catalyst has been developed. However, the synthesis of specific large-membered unsaturated thiacrown ethers in high yields and efforts to improve the catalytic efficiency of the PEG series are still challenges for us. Other heteroatomic unsaturated crown ethers may also be obtained in the same way and will be the focus of one of our further explorations.

All reactions were carried out under an atmosphere of nitrogen or argon with magnetic stirring. Anhydrous MeCN was distilled from CaH_2 prior to use. Other reagents were used as obtained from commercial sources unless otherwise noted. Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.20 mm silica gel 60 with 254 nm fluorescent indicator. Compounds were visualized under ultraviolet light at 254 nm and by putting the plate in an atmosphere of iodine. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer or with a Bruker Avance 300 spectrometer in $CDCl_3$ at r.t. Chemical shifts are reported in ppm (δ) with TMS as internal standard. High resolution mass spectra were recorded with a Waters Micromass GCT mass spectrometer. Melting points are uncorrected. IR data were recorded with a Thermo Nicolet AVATAR 360 FTIR spectrometer.

General Procedure: Method 1

Ground $Na_2S\cdot9H_2O$ (7.35 g, 98%, 30 mmol) and 15-crown-5 (2.69 g, 98%, 12 mmol) were suspended in commercially available MeCN (270 mL, AR, undried). A solution of 1,1-dichloroethylene (4.94 g, 51 mmol) in MeCN (30 mL) was added dropwise to the suspension with stirring over about 30 min. After additional stirring for

48 h at r.t., the reaction mixture was filtered, and the filtrate was evaporated in vacuo and extracted with EtOAc (4 × 30 mL), washed with H_2O (2 × 15 mL) and dried over Na_2SO_4. After removal of solvent, the residue was purified by chromatography on a silica gel column (300–400; petroleum ether–EtOAc, 3:1) to give the products (33% total yield). R_f = 0.9 (**1**), 0.82 (**2**), 0.53 (**4**), 0.30 (**5b**), 0.27 (**5a**), 0.21 (**6b**), 0.13 (**6a**), 0.06 (**7**), 0.04 (**8**). The ratio of yields was 39:4:6:2:21:2:13:8:5.

General Procedure: Method 2

Ground Na_2S (2.6 g, 90%, 30 mmol), 15-crown-5 (2.69 g, 98%, 12 mmol) and D_2O (5.4 g, 270 mmol) were suspended in anhydrous MeCN (270 mL). A solution of 1,1-dichloroethylene (4.94 g, 51 mmol) in anhydrous MeCN (30 mL) was added dropwise to the suspension with stirring over about 30 min. After additional stirring for 72 h at r.t., the reaction mixture was filtered, and the filtrate was evaporated in vacuo and extracted with EtOAc (4 × 30 mL), washed with D_2O (2 × 15 mL) and dried over Na_2SO_4. The products were purified as described in Method 1.

General Procedure: Method 3

Ground $Na_2S{\cdot}9H_2O$ (7.35 g, 98%, 30 mmol) and 15-crown-5 (2.69 g, 98%, 12 mmol) were suspended in commercially available MeCN (300 mL, AR, undried). 1,1-Dichloroethylene (4.94 g, 51 mmol) was injected quickly into the suspension with stirring. After additional stirring for 2 h at 80 °C, the reaction mixture was processed as described in Method 1.

The characterization data for all known compounds match the data given in Kamigata's article.[1]

1,4-Dithiin (1)

Light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.21 (s, 4 H).

MS (EI): *m*/*z* (%) = 116 (100) [M]$^+$, 71 (15), 58 (11).

(*Z*,*Z*,*Z*)-1,4,7-Propathiacyclopropadeca-2,5,8-propaene (9-UT-3) (2)

Colorless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.27 (s, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.8.

MS (EI): *m*/*z* = 174 [M]$^+$.

(*Z*,*Z*,*Z*,*Z*)-1,4,7,10-Butathiacyclobutadeca-2,5,8,11-butaene (12-UT-4) (3)

Colorless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.43 (s, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.1.

MS (EI): *m*/*z* = 232 [M]$^+$.

(*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13-Pentathiacyclopentadeca-2,5,8,11,14-pentaene (15-UT-5) (4)

Colorless crystals; mp 125–127 °C.

IR (KBr): 3024, 3009, 2998, 1556, 1524, 1292, 1282, 853, 809, 706, 679, 658, 649 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (s, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.9.

MS (EI): *m*/*z* (%) = 290 [M]$^+$ (12), 116 (100), 103 (65), 97 (16), 71 (28), 58 (25).

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (18-UT-6) (5a)

Colorless solid; mp 162–164 °C.

IR (KBr): 3011, 1546, 1525, 1282, 1053, 821, 810, 720, 665, 640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.4.

MS (EI): *m*/*z* (%) = 348 (12) [M]$^+$, 116 (100), 103 (78), 97 (18), 71 (47), 58 (22), 45 (40).

(*E*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (5b)

Colorless solid; mp 129–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (d, *J* = 8.4 Hz, 2 H), 6.30 (s, 2 H), 6.35 (d, *J* = 8.0 Hz, 2 H), 6.42 (s, 2 H), 6.43 (d, *J* = 8.4 Hz, 2 H), 6.51 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.3, 121.5, 122.4, 124.5, 129.7, 131.1.

MS (EI): *m*/*z* (%) = 348 (10) [M]$^+$, 116 (100), 103 (32), 71 (20), 58 (8).

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19-Heptathiacycloheneicosa-2,5,8,11,14,17,20-heptaene (21-UT-7) (6a)

Colorless solid; mp 192–194 °C.

IR (KBr): 3026, 1557, 1539, 1277, 810, 716, 672, 636, 536 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.33 (s, 14 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.7.

MS (EI): *m*/*z* (%) = 406 (4) [M]$^+$, 116 (100), 103 (25), 71 (26).

(*E*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19-Heptathiacycloheneicosa-2,5,8,11,14,17,20-heptaene (6b)

Colorless solid; mp 110–112 °C.

IR (KBr): 3015, 1541, 1281, 913, 800 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.30 (d, *J* = 8.4 Hz, 2 H), 6.31 (d, *J* = 8.4 Hz, 2 H), 6.32 (s, 2 H), 6.33 (d, *J* = 8.0 Hz, 2 H), 6.37 (d, *J* = 8.40 Hz, 2 H), 6.38 (d, *J* = 8.4 Hz, 2 H), 6.50 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.2, 121.5, 121.6, 122.3, 125.0, 128.1, 129.9.

MS (EI): *m*/*z* (%) = 406 (6) [M]$^+$, 116 (100), 103 (38), 71 (24), 58 (8).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{14}S_7$: 405.9141; found: 405.9144.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19,22-Octathiacyclotetracosa-2,5,8,11,14,17,20,23-octaene (24-UT-8) (7)

Colorless crystals; mp 188–189 °C.

IR (KBr): 3026, 1558, 1272, 807, 725, 657, 624 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.31 (s, 16 H).

MS (EI): *m*/*z* (%) = 464 (2) [M]$^+$, 116 (100).

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19,22,25-Nonathiacycloheptacosa-2,5,8,11,14,17,20,23,26-nonaene (27-UT-9) (8)

Colorless solid; mp 199–201 °C.

IR (KBr): 3034, 1604, 1562, 1271, 870, 719, 656, 624 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (s, 18 H).

MS (EI): *m*/*z* (%) = 522 (2) [M]$^+$, 116 (100), 103 (20), 71 (32), 58 (12).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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