One-Pot Sequential Acylation/Alkylation Reactions of 3-Sulfolenes

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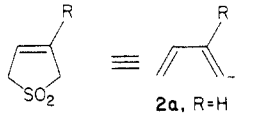
3-Sulfolene 2-anion and 3-methyl-3-sulfolene 2-anion have been generated at −105 °C and are stable in the absence of electrophiles for at least 15 min at this temperature. These anions were used in sequential reactions with acyl chlorides and alkyl halides to yield the corresponding 2-acyl-2-alkyl-3-sulfolenes.

Recently, we[1] and others[2] reported the success of direct deprotonation/alkylation of 3-sulfolenes **1** without formation of the ring-opened side products. The combination of direct alkylation and thermal extrusion of sulfur dioxide provides an ideal route for the preparation of terminally substituted conjugated dienes. In this manner, the commercially available 3-sulfolene **1a** acts as a butadiene 1-anion equivalent. The potential synthetic value of the route has been exemplified by the selective one-step syntheses of β-ocimene and α-farnesene[3] as well as the facile construction of hydroindan and hydronaphthalene skeletons.[4]

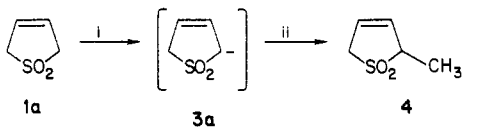


1a, R=H
1b, R=CH_3

Application of this reaction has been limited to the syntheses of hydrocarbons, because the unstable sulfolene 2-anions **3** undergo ring-opening reactions[5] in the absence of electrophiles even at −78 °C. In order to achieve the alkylation reactions without the ring-opening of the sulfolenes, an alkyl halide was first mixed with the 3-sulfolene before treatment with base.[1,2,4] It appeared that complexity would arise if electrophiles bearing acidic protons were used in these substitution reactions. One solution to the problem of ring-opening of the 3-sulfolene anion was reported by Bloch[6] who used a masked 3-sulfolene as the key intermediate. However, multistep reactions are required. We have found that this problem can be solved more easily by lowering the reaction temperature for the direct deprotonation of 3-sulfolenes.

When 3-sulfolene **1a** or **1b** is treated with *n*-BuLi in THF/HMPA at −105 °C, the brown anion **3a** or **3b** is formed and remains stable for at least 15 min at this temperature. Treatment of **3a** with MeI gives 2-methyl-3-sulfolene (**4**) in 81% yield (Scheme I). This is the first report of a sulfolene anion not opening if generated in the absence of electrophiles. The regioselective deprotonations of **1b** and other similar systems at the 2-position have been established in the study of deprotonation/methylation reaction[1] and the syntheses of some natural products.[3,7]

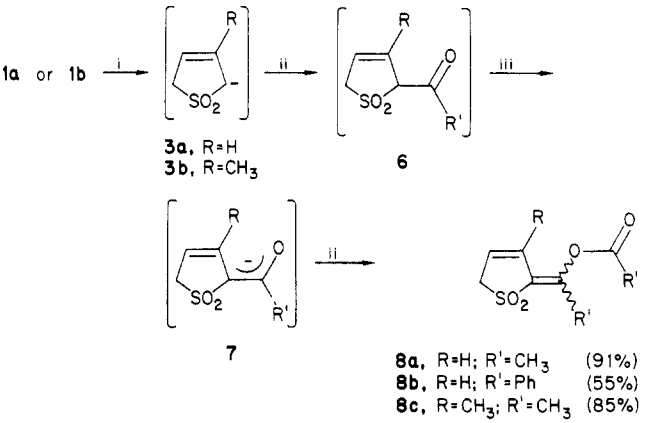
Scheme I[a]



1a **3a** **4**

[a] (i) *n*-BuLi, −105 °C; (ii) CH_3I.

Scheme II[a]



3a, R=H
3b, R=CH_3

6

7

8a, R=H; R'=CH_3 (91%)
8b, R=H; R'=Ph (55%)
8c, R=CH_3; R'=CH_3 (85%)

[a] (i) *n*-BuLi, −105 °C; (ii) R'COCl (**5a**, R' = CH_3; **5b**, R' = Ph); (iii) **3a** or **3b**, anion exchange.

The conditions were then used for the direct deprotonation/acylation sequence. Thus, sulfolenes **1a** and **1b** (2 mmol) were deprotonated with *n*-BuLi (2 mmol) followed by treatment with acyl chlorides **5a** or **5b** (2 mmol) in an attempt to prepare 2-acyl-3-sulfolenes **6**. Although the acylation occurred as expected, the final products obtained were compounds **8a–c** (Scheme II). These products must have been formed by further acylation of the acylated sulfolene anions **7** which arose from the anion exchange process between **3** and **6**. The yields shown in Scheme II are based on the consumed 3-sulfolenes. The actual configurations of **8a–c** are not determined; however, HPLC and NMR analyses indicate that only a single isomer was obtained in each case.

The above results indicate that the deprotonations of acylated 3-sulfolenes **6** are very rapid. It was therefore thought that an alkyl group should be easily introduced at the 2-position of **6** via C-alkylation of the anions **7**. Indeed, when **1** (3 mmol) was treated with *n*-BuLi (3 mmol) and then with acyl chlorides **5a** or **5c** (1 mmol) and alkyl halides (3 mmol) sequentially, the expected 2-acyl-2-alkyl-3-sulfolenes **9a–l** were obtained in fair to good yields (eq 1 and Table I) and the side reactions of O-acylation as shown in Scheme II were not observed. The structural assignments of **9g–l** are based on the regioselective deprotonation of **1b**. Compounds **9** are potential

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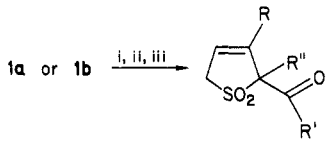
0022-3263/86/1951-1000$01.50/0

Table I. Preparation of 2-Acyl-2-alkyl-3-sulfolenes 9a–l

starting material	acyl chlorides	alkyl halides	products 9	yields, %
1a	5a	MeI	9a, R = H; R′ = R″ = Me	51
1a	5a	CH_2CHCH_2Br	9b, R = H; R′ = Me; R″ = allyl	50
1a	5a	$PhCH_2Br$	9c, R = H; R′ = Me; R″ = benzyl	60
1a	5c	MeI	9d, R = H; R′ = isobutyl; R″ = Me	65
1a	5c	CH_2CHCH_2Br	9e, R = H; R′ = isobutyl; R″ = allyl	65
1a	5c	$PhCH_2Br$	9f, R = H; R′ = isobutyl; R″ = benzyl	43
1b	5a	MeI	9g, R = R′ = R″ = Me	56
1b	5a	CH_2CHCH_2Br	9h, R = R′ = Me; R″ = allyl	66
1b	5a	$PhCH_2Br$	9i, R = R′ = Me; R″ = benzyl	64
1b	5c	MeI	9j, R = R″ = Me; R′ = isobutyl	87
1b	5c	CH_2CHCH_2Br	9k, R = Me; R′ = isobutyl; R″ = allyl	92
1b	5c	$PhCH_2Br$	9l, R = Me; R′ = isobutyl; R″ = benzyl	52

insecticides and fungicides[8] which have been prepared by another reaction sequence from 2-acylthiophenes.[9] Our one-pot procedure provides a more efficient and versatile route for these materials.

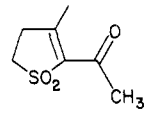


(1)

9a-l

(i) *n*-BuLi, −105 °C; (ii) R′COCl (**5a** or **5c**, R′=isobutyl); (iii) R″X

When the reaction mixture of **3b** with acetyl chloride **5a** was treated with water at various pH ranges instead of an alkyl halide, 2-acetyl-3-methyl-3-sulfolene (**6**, R = R′ = Me) was not isolated. The only product obtained was the double-bond isomer **10**. This result is in agreement with the known base-induced double-bond migration of the 2-substituted sulfolene systems.[10] The formation of **10** represents another example confirming the regioselectivity of the deprotonation of **1b** as well as the structure assignments of **9g–l**.



10

Since 3-sulfolenes have been demonstrated to serve as butadiene anion equivalents in a regioselective and stereospecific manner,[1-4] the success of the one-pot acylation/alkylation reactions, which leads to 3-sulfolenes with oxygenated substituents, extends the usefulness of this methodology in organic synthesis.

Experimental Section

General Methods. ^1H NMR spectra were determined on a JEOL FX-100 NMR spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Perkin-Elmer 290 IR spectrophotometer. Mass spectra were recorded on a JEOL JMS-D-100 mass spectrometer. Elemental analyses were performed at the National Taiwan University, Taipei. All reactions were carried out under an atmosphere of dry nitrogen. All anhydrous solvents were freshly distilled before use.

Generation of 3-Sulfolene-2-carbanions 3a and 3b. To a mixture of 3-sulfolene **1a** or **1b** (2.54 mmol) in THF–HMPA (10 mL–0.8 mL) was added *n*-BuLi (2.5 mmol) dropwise at −105 °C (in an ethanol/liquid nitrogen cooling bath). The solution was stirred for 10 min during which time it gradually turned to red-brown, indicating the formation of the sulfolene carbanion. The carbanions **3a** and **3b** thus generated remained unchanged for at least 15 min.

Preparation of 2-Methyl-3-sulfolene (4). Method A. This is the general procedure used before for alkylation reactions of 3-sulfolenes.[3,4] To a mixture of 3-sulfolene (4.93 mmol), MeI (2.4 mmol), and HMPA (9.6 mmol) in dry THF (15 mL) at −78 °C was added LiHMDS (2.4 mmol) dropwise. The resulting mixture was stirred for 30 min and an excess of EtOAc (20 mL) was added to cause precipitation. The cooling bath was then removed and the mixture was allowed to warm up to room temperature gradually. The precipitate was filtered off and the excess of solvent was evaporated under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and further purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give **4** in 80% yield. The spectral data were identical with those reported earlier.[1]

Method B. To a solution of carbanion **3a** (2 mmol) at −105 °C was added MeI (3 mmol) in one shot, and then the cooling bath was allowed to warm up gradually. When the temperature reached −20 °C, EtOAc (5 mL) was added to cause precipitation. The precipitate was filtered off and the solvent removed under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and was further purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give pure **4** in 81% yield.

Preparations of 2-[(Acyloxy)alkylidene]-3-sulfolenes 8a–c. To a solution of the sulfolene carbanion **3a** or **3b** (2 mmol) at −105 °C was added acyl chloride **5a** or **5b** (2 mmol) dropwise, and the reaction mixture was stirred for 30 min at −105 °C. The reaction temperature was allowed to warm up gradually to room temperature whereupon EtOAc (5 mL) was added to cause precipitation. The precipitate was filtered off and the solvent removed under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and was further purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give the pure product **8a–c**.

2-[1-(Acetyloxy)ethylidene]-2,5-dihydrothiophene 1,1-dioxide (8a): IR (liquid) 2980, 2940, 1700, 1670, 1380, 1310, 1010 cm^{-1}; ^1H NMR δ 2.20 (s, 3 H), 2.35 (s, 3 H), 3.85 (br s, 2 H), 5.90–6.10 (m, 1 H), 6.40–6.70 (m, 1 H); MS, *m/e* 202 (M^+), 160, 145, 96, 81, 53, 43 (base).

Anal. Calcd for $C_8H_{10}O_4S$: C, 47.51; H, 4.98. Found: C, 47.51; H, 4.96.

2-[1-(Benzoyloxy)benzylidene]-2,5-dihydrothiophene 1,1-dioxide (8b): mp 135–137 °C; IR (KBr) 3080, 3000, 2930, 1760, 1640, 1620, 1320, 1200, 1120 cm^{-1}; ^1H NMR δ 3.90 (br s, 2 H), 6.00–6.20 (m, 1 H), 6.55–6.75 (m, 1 H), 7.30–8.22 (m, 10 H); MS, *m/e* 326 (M^+), 262, 128, 115, 105, 77 (base), 51.

Anal. Calcd for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.32. Found: C, 66.31; H, 4.39.

2-[1-(Acetyloxy)ethylidene]-3-methyl-2,5-dihydrothiophene 1,1-dioxide (8c): IR (liquid) 2980, 2950, 1780, 1670, 1380, 1310, 1200, 1170, 1140, 1020 cm^{-1}; ^1H NMR δ 2.00 (br s, 3 H), 2.20 (s, 3 H), 2.35 (s, 3 H), 3.80 (br s, 2 H), 5.71 (br s, 1 H); MS, *m/e* 216 (M^+), 174, 159, 110, 95, 67, 43 (base).

Anal. Calcd for $C_9H_{12}O_4S$: C, 49.99; H, 5.59. Found: C, 49.83; H, 5.55.

Preparations of 2-Acyl-2-alkyl-3-sulfolenes 9a–l. To a solution of the sulfolene carbanion **3a** or **3b** (3 mmol) at −105 °C was added acyl chloride **5a** or **5c** (1 mmol) dropwise. The reaction

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mixture was stirred at −105 °C for 30 min, and the temperature of the cooling bath was allowed to come up gradually to −90 °C whereupon an alkyl halide (2 mmol) was added in one shot. The reaction mixture was stirred and the cooling bath was removed when it came up to −50 °C, and the stirring was continued at room temperature for 3.5 h. Chloroform (5 mL) was added to the mixture to cause precipitation. The precipitate was filtered off and the solvent removed under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and was further purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give the pure product **9a**–**l**.

2-Acetyl-2-methyl-2,5-dihydrothiophene 1,1-dioxide (9a): IR (liquid) 3100, 3000, 2900, 1730, 1630, 1370, 1320, 1140 cm^{-1}; ^1H NMR δ 1.65 (s, 3 H), 2.35 (s, 3 H), 3.82 (s, 2 H), 6.13 (br s, 2 H); MS, m/e 174 (M^+), 132, 110, 95, 67, 43 (base).

Anal. Calcd for $C_7H_{10}O_3S$: C, 48.26; H, 5.79. Found: C, 48.24; H, 5.97.

2-Acetyl-2-allyl-2,5-dihydrothiophene 1,1-dioxide (9b): IR (liquid) 3100, 3000, 2900, 1730, 1655, 1370, 1320, 1140, 1000, 930 cm^{-1}; ^1H NMR δ 2.33 (s, 3 H), 2.50–3.20 (m, 2 H), 3.80 (br s, 2 H), 5.05–5.30 (m, 2 H), 5.40–5.80 (m, 1 H), 6.20 (br s, 2 H); MS, m/e 200 (M^+), 158, 136, 109, 91, 79, 65, 51, 43 (base), 39.

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04. Found: C, 53.99; H, 6.10.

2-Acetyl-2-benzyl-2,5-dihydrothiophene 1,1-dioxide (9c): mp 139–140 °C dec; IR (KBr) 3080, 2980, 2940, 1715, 1360, 1300, 1120 cm^{-1}; ^1H NMR δ 2.30 (s, 3 H), 3.15 (d, 1 H, J = 14 Hz), 3.62–3.82 (m, 3 H), 6.16 (s, 2 H), 7.10–7.35 (m, 5 H); MS, m/e 250 (M^+), 208, 186, 171, 143, 128, 115, 91 (base), 65, 43.

Anal. Calcd for $C_{13}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.82; H, 5.62.

2-Isovaleroyl-2-methyl-2,5-dihydrothiophene 1,1-dioxide (9d): IR (liquid) 3080, 2950, 2870, 1720, 1370, 1315, 1135 cm^{-1}; ^1H NMR δ 0.90 (d, 6 H, J = 7 Hz), 1.60 (s, 3 H), 1.90–2.41 (m, 1 H), 2.50 (d, 2 H, J = 7 Hz), 3.80 (br s, 2 H), 6.20 (br s, 2 H); MS, m/e 216 (M^+), 152, 132, 109, 95, 85, 67, 57, 43, 41 (base), 39.

Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46. Found: C, 55.59; H, 7.47.

2-Isovaleroyl-2-allyl-2,5-dihydrothiophene 1,1-dioxide (9e): IR (liquid) 3080, 2950, 2870, 1720, 1370, 1320, 1130, 1000, 920 cm^{-1}; ^1H NMR δ 0.95 (d, 6 H, J = 7 Hz), 1.62–2.19 (m, 1 H), 2.51–3.10 (m, 4 H), 3.80 (br s, 2 H), 5.00–5.20 (m, 2 H), 5.41–5.78 (m, 1 H), 6.20 (br s, 2 H); MS, m/e 242 (M^+), 178, 121, 91, 77, 65, 57, 43, 41 (base), 39.

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49. Found: C, 59.08; H, 7.35.

2-Isovaleroyl-2-benzyl-2,5-dihydrothiophene 1,1-dioxide (9f): mp 125–126.5 °C; IR (KBr) 3080, 2940, 1720, 1365, 1305, 1260, 1130 cm^{-1}; ^1H NMR δ 0.83 (d, 3 H, J = 7 Hz), 0.86 (d, 3 H, J = 7 Hz), 1.90–2.70 (m, 3 H), 3.11 (d, 1 H, J = 14 Hz), 3.72 (d, 1 H, J = 14 Hz), 3.65–3.80 (m, 2 H), 6.20 (br s, 2 H), 7.05–7.35 (m, 5 H); MS, m/e 292 (M^+), 228, 171, 143, 128, 115, 91, 85, 65, 57 (base), 41.

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.51; H, 7.07.

2-Acetyl-2,3-dimethyl-2,5-dihydrothiophene 1,1-dioxide (9g): IR (liquid) 3080, 3000, 2950, 1730, 1320, 1150 cm^{-1}; ^1H NMR δ 1.60 (s, 3 H), 1.75 (br s, 3 H), 2.30 (s, 3 H), 3.80 (br s, 2 H), 5.90 (br s, 1 H); MS, m/e 188 (M^+), 146, 124, 109, 81, 53, 43 (base), 41, 39.

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.05; H, 6.43. Found: C, 51.28; H, 6.50.

2-Acetyl-2-allyl-3-methyl-2,5-dihydrothiophene 1,1-dioxide (9h): IR (liquid) 3100, 3000, 2950, 1730, 1650, 1370, 1320, 1140, 1000 cm^{-1}; ^1H NMR δ 1.75 (br s, 3 H), 2.25 (s, 3 H), 2.40–3.00 (m, 2 H), 3.62 (br s, 2 H), 5.00–5.30 (m, 2 H), 5.40–5.70 (m, 1 H), 5.80 (br s, 1 H); MS, m/e 214 (M^+), 172, 150, 107, 91, 79, 65, 53, 43 (base).

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59. Found: C, 55.93; H, 6.56.

2-Acetyl-2-benzyl-3-methyl-2,5-dihydrothiophene 1,1-dioxide (9i): mp 116–117 °C; IR (in chloroform) 3050, 3000, 2950, 1725, 1370, 1320, 1140 cm^{-1}; ^1H NMR δ 1.75 (br s, 3 H), 2.31 (s, 3 H), 3.20–3.80 (m, 4 H), 5.75 (br s, 1 H), 7.20 (br s, 5 H); MS, m/e 264 (M^+), 222, 200, 157, 141, 129, 115, 91, 77, 65, 51, 43 (base).

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.66; H, 6.12.

2-Isovaleroyl-2,3-dimethyl-2,5-dihydrothiophene 1,1-dioxide (9j): IR (liquid) 3050, 2950, 2870, 1720, 1315, 1140 cm^{-1}; ^1H NMR δ 0.95 (d, 6 H, J = 7 Hz), 1.63 (s, 3 H), 1.75 (br s, 3 H), 2.00–2.40 (m, 1 H), 2.50 (d, 2 H, J = 7 Hz), 3.75 (br s, 2 H), 5.80 (br s, 1 H); MS, m/e 230 (M^+), 166, 151, 146, 123, 109, 85, 81, 57, 41 (base), and 39.

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88. Found: 57.09; H, 7.81.

2-Isovaleroyl-2-allyl-3-methyl-2,5-dihydrothiophene 1,1-dioxide (9k): IR (liquid) 3080, 2950, 2860, 1720, 1640, 1365, 1310, 1140, 1000 cm^{-1}; ^1H NMR δ 0.95 (d, 6 H, J = 7 Hz), 1.85 (br s, 3 H), 2.00–3.30 (m, 5 H), 3.80 (br s, 2 H), 5.00–5.40 (m, 2 H), 5.40–5.70 (m, 1 H), 5.90 (br s, 1 H); MS, m/e 256 (M^+), 212, 192, 151, 107, 91, 85, 79, 57 (base), 41, 39.

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.91; H, 7.86. Found: C, 60.91; H, 7.85.

2-Isovaleroyl-2-benzyl-3-methyl-2,5-dihydrothiophene 1,1-dioxide (9l): IR (liquid) 3050, 3020, 2950, 2850, 1720, 1360, 1305, 1130 cm^{-1}; ^1H NMR δ 0.92 (d, 3 H, J = 7 Hz), 0.95 (d, 3 H, J = 7 Hz), 1.85 (br s, 3 H), 2.00–3.70 (complex, 5 H), 3.30 (d, 1 H, J = 14 Hz), 3.60 (d, 1 H, J = 14 Hz), 5.70 (br s, 1 H), 7.20 (br s, 5 H); MS, m/e 306 (M^+), 242, 222, 185, 174, 157, 141, 129, 115, 91, 85, 57 (base), 41.

Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24. Found: 66.77; H, 7.29.

Preparation of 2-Acetyl-3-methyl-2-sulfolene (10). To a solution of the sulfolene carbanion **3b** (3 mmol) was added acetyl chloride (1 mmol) dropwise and the reaction mixture was stirred at −105 °C for 30 min whereupon water (0.5 mL) and chloroform (20 mL) were added. The mixture was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was eluted through a silica gel column (hexane/EtOAc, 2:1) to remove HMPA and was further purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give the pure product in 60% yield: mp 59–60 °C; IR (neat) 2950, 2850, 1700, 1620, 1370, 1300, 1140 cm^{-1}; ^1H NMR δ 2.30 (s, 3 H), 2.50 (s, 3 H), 2.78–3.10 (m, 2 H), 3.22–3.45 (m, 2 H); MS, m/e 174 (M^+), 159, 97, 85, 67, 43 (base).

Anal. Calcd for $C_7H_{10}O_3S$: C, 48.26; H, 5.79. Found: C, 48.17; H, 5.82.

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Registry No. **1a**, 77-79-2; **1b**, 1193-10-8; **4**, 6007-71-2; **5a**, 75-36-5; **5b**, 98-88-4; **5c**, 108-12-3; **8a**, 100206-91-5; **8b**, 100206-92-6; **8c**, 100206-93-7; **9a**, 100206-94-8; **9b**, 100206-95-9; **9c**, 100206-96-0; **9d**, 100206-97-1; **9e**, 100206-98-2; **9f**, 100206-99-3; **9g**, 100207-00-9; **9h**, 100228-84-0; **9i**, 100207-01-0; **9j**, 100207-02-1; **9k**, 100207-03-2; **9l**, 100207-04-3; **10**, 100207-05-4.