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A synthesis of diketones from carbonyl compounds and α,ω-dichloro-α,ω-disulfinylalkanes with two carbon–carbon bond-formation via bis-sulfinyloxiranes

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Abstract—Bis-sulfinyloxiranes were synthesized in two steps from carbonyl compounds and α,ω-dichloro-α,ω-disulfinylalkanes, which were synthesized from α,ω-dibromoalkanes in three steps, in good yields. Treatment of the bis-sulfinyloxiranes with sodium benzenethiolate and piperidine gave α,α′-di(phenylthio) diketones and α,α′-diamino diketones, respectively, in high yields. From these products, some kinds of diketones were synthesized in good to high yields.

Ketones and their derivatives are obviously among the most important and fundamental compounds in organic and synthetic organic chemistry.[1] Innumerable studies on the chemistry and synthesis of monoketones and their derivatives have already been reported; however, good method for preparation of diketones is quite limited.[1h] In view of the importance of diketones in organic chemistry, new synthetic methods are eagerly sought.

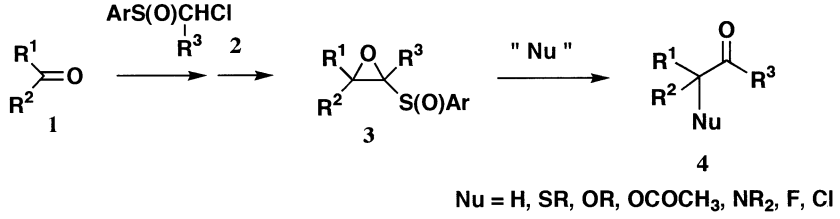
We previously reported a versatile procedure for a synthesis of homologated α-substituted carbonyl compounds **4** from carbonyl compounds **1** by the use of aryl 1-chloroalkyl sulfoxides **2** as the homologating agent via sulfinyloxiranes **3** (Scheme 1).[2] In continuation of our study for homologation of carbonyl compounds[3] by using aryl 1-chloroalkyl sulfoxides as the homologating agent, we report herein a procedure for a synthesis of diketones, including α,α′-disubstituted dikentones **7** and unsaturated diketones **8**, from carbonyl compounds **1** and α,ω-dichloro-α,ω-disulfinylalkanes **5** via bis-sulfinyloxiranes **6** (Scheme 2).

1. Results and discussion

1.1. Synthesis of bis-sulfinyloxiranes from acetone and reactions with some nucleophiles

As mentioned above, we previously reported a versatile procedure for the synthesis of α-substituted carbonyl compounds **4** from carbonyl compounds **1** through sulfinyloxiranes **3** (Scheme 1). We expected that if we could easily synthesize the compounds having two sulfinyloxirane groups in a molecule, we could obtain a diketone having two α-substituents. We examined the feasibility of this methodology and developed a new procedure for synthesis of various kinds of diketones. The scope and limitation of this method are also described.

At first, 1,4-dichloro-1,4-di(tolylsulfinyl)butane **9** was synthesized from 1,4-dibromobutane by the procedure described before.[4] Sulfoxide **9** was treated with slight excess of LDA at −60°C for 10 min followed by acetone. The



Scheme 1.

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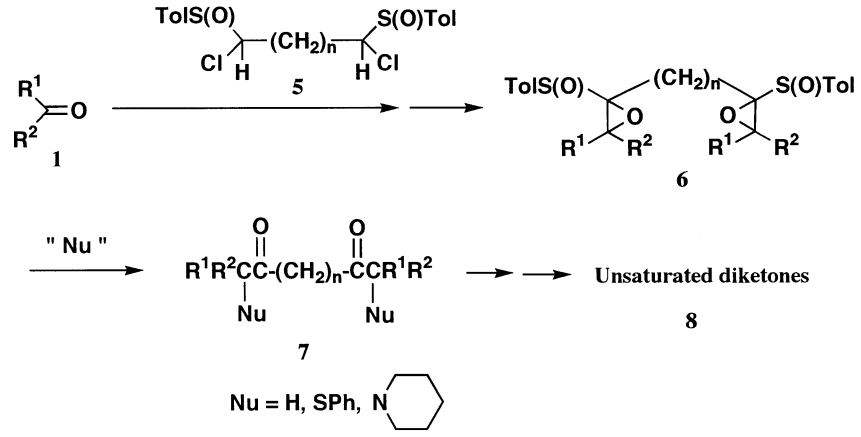
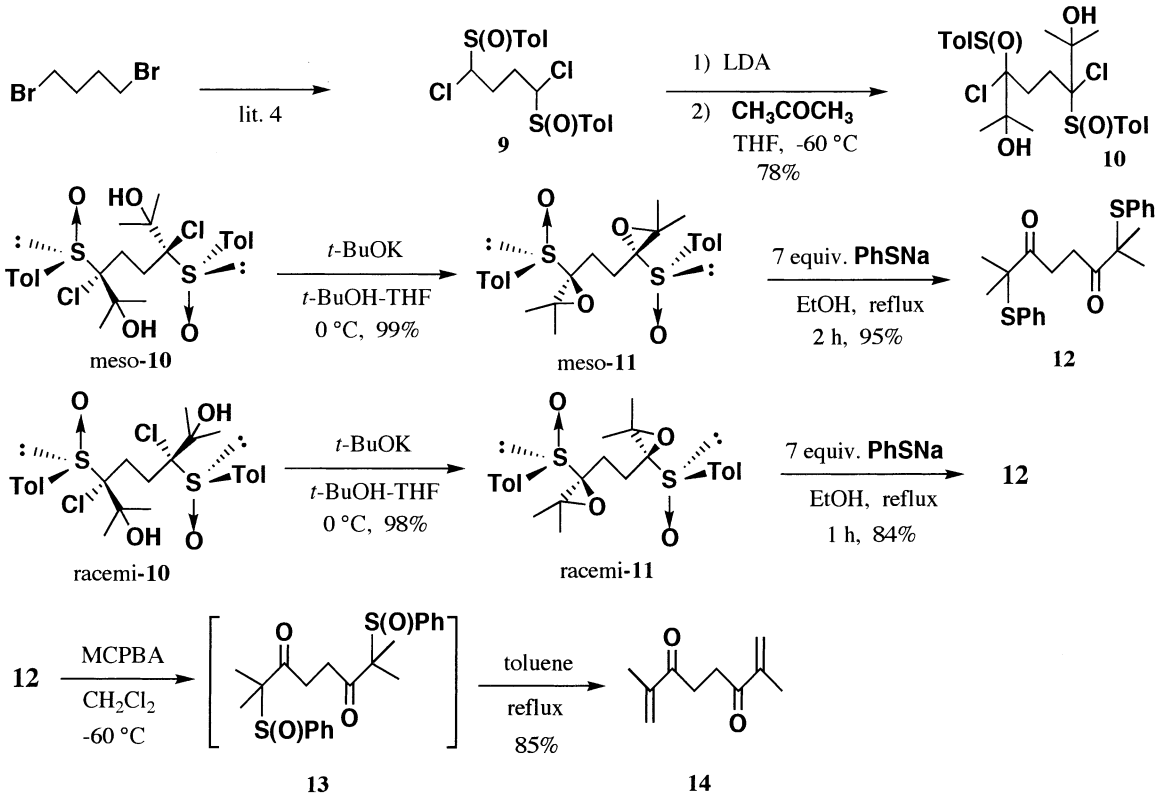


Scheme 2.

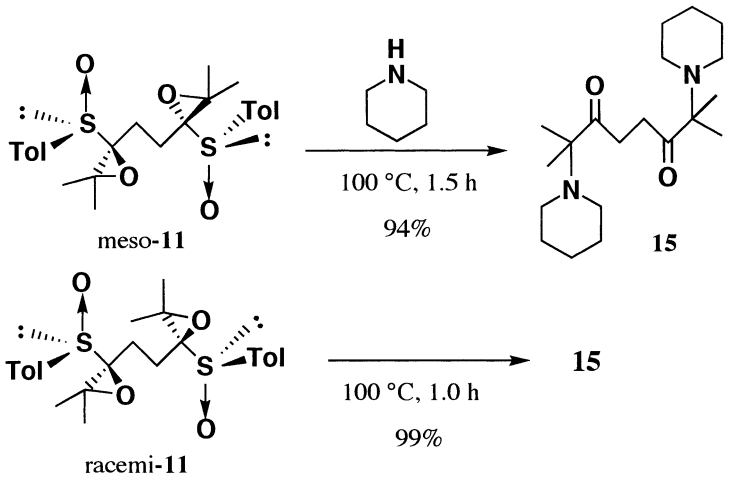
reaction worked, and the desired adduct **10** was obtained in 78% yield (Scheme 3). The adduct **10** has four chiral centers, and theoretically the production of eight diastereomers is possible; however, only two diastereomers (expressed as less polar product (49%) and more polar product (29%) on silica gel TLC) were obtained.

We have already observed that the reaction of the carbanion having a chlorine and a sulfinyl group to carbonyl compounds takes place with complete chiral induction from the sulfur chiral center.[5] So, the diastereomers must be a *meso*- and a *racemi*-compound, respectively. In order to know which is which, the products were analyzed by HPLC on a chiral stationary column (CHIRALCEL OD, Daicel) and we found that only the more polar product is separated in two peaks. By this investigation, we were able to determine the less polar product and the more polar product are the *meso*-compound and the *racemi*-compound, respectively. The relative configurations are shown in Scheme 3.

Next, the adducts **10** were treated with potassium *tert*-butoxide in a mixture of *tert*-butanol and THF at 0°C. Quite clean reaction took place to afford the desired bis-sulfinyloxiranes **11** in quantitative yields. The bis-sulfinyloxiranes, *meso*-**11** and *racemi*-**11**, are both good crystalline compounds and quite stable at room temperature. Finally,



Scheme 3. Synthesis of bis-sulfinyloxiranes **11** from acetone and **9**, and reaction with benzenthiolate to give bis(phenylthio)diketone **12**.



Scheme 4. Treatment of the bis-sulfinyloxiranes **11** with piperidine without a solvent.

these bis-sulfinyloxiranes were treated with excess sodium benzenethiolate in refluxing ethanol to give the desired diketone having two phenylthio groups on its α position **12** in good to high yield.[6] As shown in Scheme 3, both **11** showed somewhat different reactivity toward the thiolate; however, no problem was observed in the use of this reaction for a practical preparation of the diketone **12**.

As an extension of this procedure, transformation of **12** to α,β-unsaturated diketone **14** was investigated.[7] Sulfide **12** was oxidized in the usual way with *m*-chloroperbenzoic acid (MCPBA) to give sulfoxide **13** as a mixture of diastereomers. Without further purification, a mixture of sulfoxide **13** was heated in refluxing toluene for 1 h. Enone **14** was obtained in 85% yield and we found that **14** was a somewhat unstable compound and decomposed slowly on standing at room temperature.

In our previous study, we found that a sulfinyloxirane reacted with amines to give α-amino ketones.[5b,8] We applied this reaction to the bis-sulfinyloxiranes, *meso*-**11** and *racemi*-**11** (Scheme 4). The reaction was simply conducted by heating **11** in piperidine without a solvent for 1–1.5 h. This reaction worked quite smoothly to afford the desired diketone having two piperidines on its α-position **15** in a quantitative yield. Again some difference in the reaction of *meso*-**11** and *racemi*-**11** was observed; however, it was smaller than in the case of the reaction with benzenethiolate.

We previously investigated some reactions of sulfinyloxiranes **3** with sodium benzeneselenolate.[9] This reaction gave good yields of the ketones without α-substituents (**4**, Nu=H). We applied this reaction to bis-sulfinyloxiranes **11**; however, only a complex mixture was obtained.

1.2. Synthesis of bis-sulfinyloxiranes from 3-phenylpropanal and reaction with benzenethiolate and piperidine

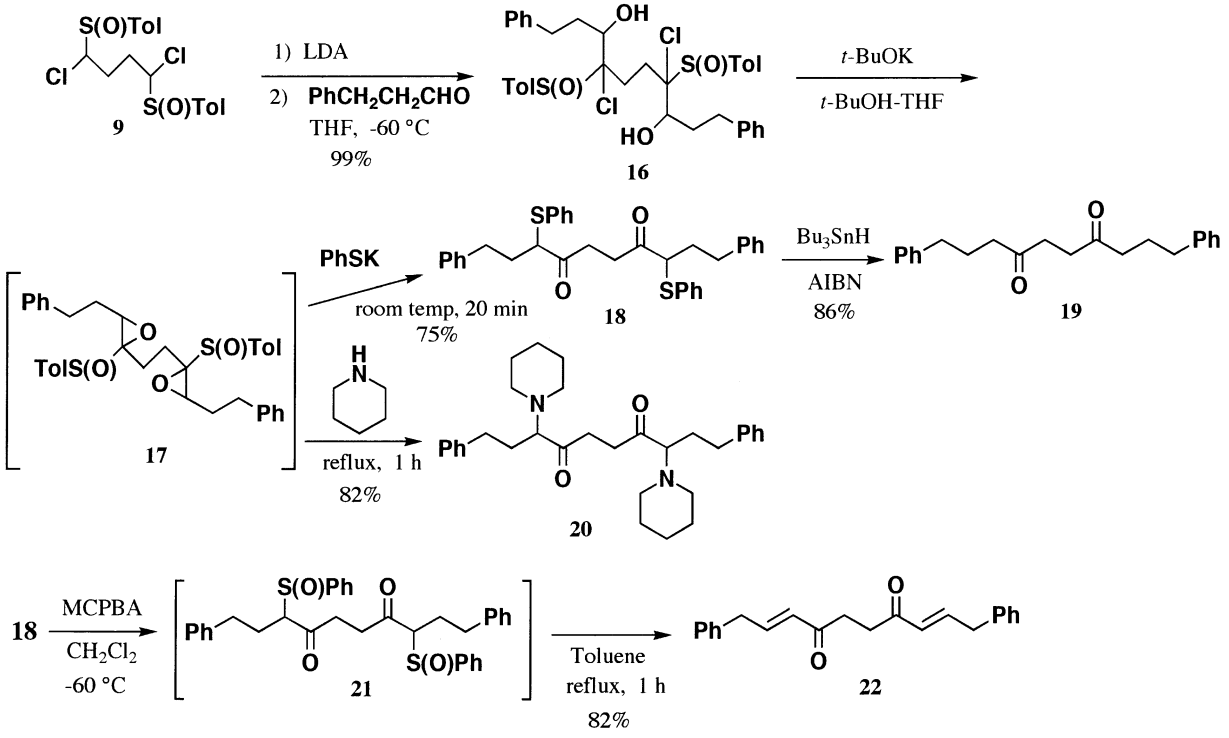
Next, we tried to synthesize the bis-sulfinyloxirane from an aldehyde and investigated if the bis-sulfinyloxirane could be used in a syntheis of diketones. 3-Phenylpropanal was used as a representative example of the aldehydes (Scheme 5).

In a similar manner as described above, the dianion of **9** was reacted with 3-phenylpropanal to give the adduct **16**. The adduct has six chiral centers and the product **16** was found to be a mixture of several diastereomers. After rough purification by silica gel column chromatography (the yield of **16** was quantitative), the mixture was treated with *tert*-BuOK at room temperature for 30 min, then excess benzenethiol was added to the reaction mixture. The thiolate reacted quite fast with the intermediate, bis-sulfinyloxirane **17**, at room temperature, and a rather clean reaction mixture was obtained, from which the desired diphenylthio diketone **18** was obtained in 75% yield from the adduct **16**.

In the case of the synthesis of α-amino diketone, a mixture of sulfinyloxiranes **17** was isolated from the reaction mixture by extraction. After the solvent was evaporated under vacuum, the residue was heated in piperidine without a solvent to give the desired diketone **20** having two piperidine moieties at both α-positions. As described above, although the adduct **16** and bis-sulfinyloxirane **17** were a mixture of several diastereomers, the method presented in this paper was found to be very useful for a synthesis of diketones from aldehyde with almost no problem.

In order to confirm the utility of this method, bis(phenylthio) diketone **18** was converted to 1,10-diphenyl-4,7-decanedione **19** and 1,10-diphenyl-2,8-decadiene-4,7-dione **22**. Thus, bis(phenylthio) diketone **18** was treated with tributyltin hydride in the presence of 2,2′-azobisisobutyronitrile (AIBN) in refluxing benzene to afford desulfurized 1,10-diphenyl-4,7-decanedione **19** in 86% yield.[10] It is worth noting that this interesting diketone **19** was synthesized from **9** and 3-phenylpropanal in only three operations.

α,β-Unsaturated diketone **22** was also synthesized in a similar way as described above. The sulfur of **18** was oxidized with MCPBA at −60°C, and the produced mixture of the sulfoxides was roughly purified and heated under reflux in toluene to give the enone **22** in 82% yield from **18**. The α,β-unsaturated diketone **22** was found to be quite stable at room temperature.

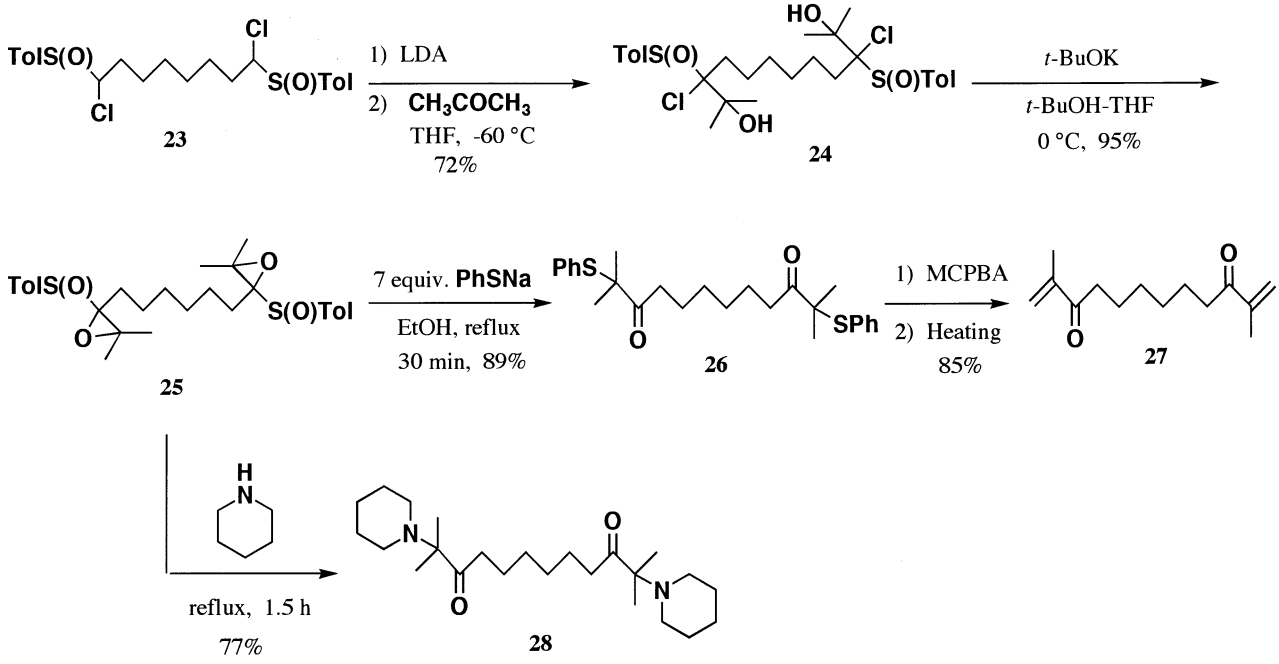


Scheme 5. Synthesis of bis-sulfinyloxiranes **17** from 3-penylpropanal and **9**, and some reactions.

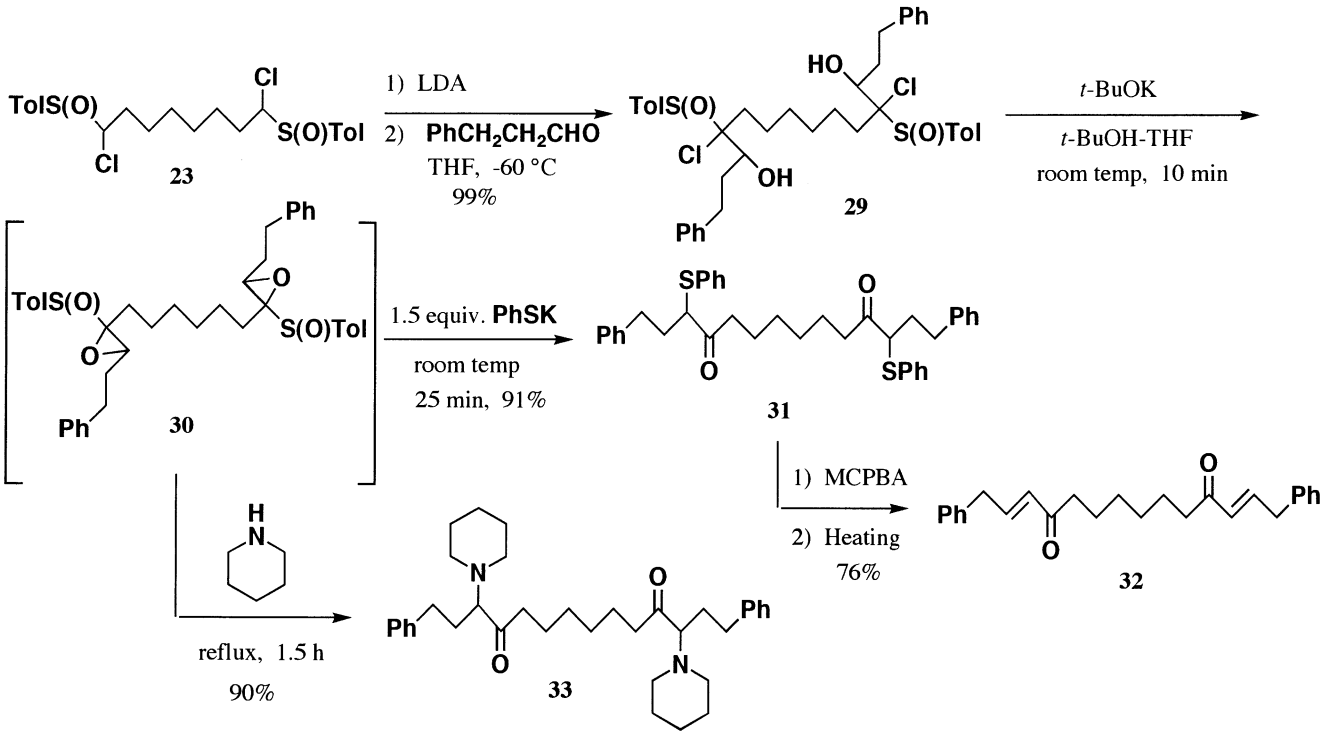
1.3. Prolonging and shortening of the methylene chain of the α,ω-dichloro-α,ω-disulfinylalkane; the scope and limitation of this procedure

In order to know the scope and limitation of this procedure we studied these reactions starting from the α,ω-dichloro-α,ω-disulfinyl alkanes having a longer or a shorter methylene chain. At first, 1,8-dichloro-1,8-disulfinyloctane **23** was synthesized from 1,8-dibromooctane. The methylene carbon chain in **23** is four-carbon longer than that in **9**.

Generation of the dianion of **23** and reaction with acetone was carried out under similar conditions as described for **9** to give the adduct **24** in 72% yield (Scheme 6). Again, the product was a mixture of only two diastereomers, which were difficult to separate. This time we used this mixture



Scheme 6. Synthesis of bis-sulfinyloxiranes **25** from acetone and **23**, and reaction with benzenthiolate and piperidine.

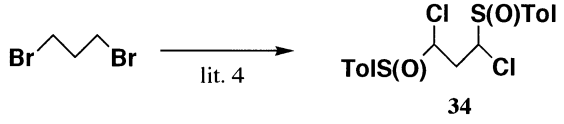


Scheme 7. Synthesis of bis-sulfinyloxiranes **30** from 3-phenylpropanal and **23**, and reaction with benzenthiolate and piperidine.

in the following experiments without isolation. In a similar manner as described above, the mixture of the adducts **24** was treated with *tert*-BuOK to afford a mixture of bis-sulfinyloxiranes **25** in a quantitative yield after silica gel column chromatography.

Treatment of **25** with sodium benzenethiolate and piperidine was carried out under similar conditions as in the case with **11** to give α-thio diketone **26** and α-amino diketone **28** in good yields. The yields and the reaction time were found to be slightly different from the reaction with **11**; however, we concluded that there is no essential difference between **11** and **25** in chemical reactivity. The dithio diketone **26** was converted to α,β-unsaturated diketone **27** in 85% yield in two steps without problem.

Scheme 7 shows the results of this procedure starting from **23** and 3-phenylpropanal. The reaction of the dianion of **23** with the aldehyde gave the adducts **29** as a mixture of several diastereomers in quantitative yield after rough chromatography. The adduct **29** was treated with excess *tert*-BuOK at room temperature for 10 min, then benzenethiol was added to the reaction mixture. This treatment gave the desired dithio diketone **31** in 91% yield. Synthesis of α-amino diketone **23** was carried out in a similar way as described for the synthesis of **20** to give **33** in 90% yield. α,β-Unsaturated diketone **32** was synthesized from **31** in 76% yield in two steps (Scheme 8).



Scheme 8.

Finally, we synthesized 1,3-dichloro-1,3-disulfinylpropane **34** from 1,3-dibromopropane. The synthesized **34** was found to be stable at room temperature; however, **34** decomposed quickly upon treatment with LDA at −78°C. In consequence, we could not synthesize 1,3-diketones by this method.

In conclusion, we have established a new procedure for the synthesis of several diketones from ketones and aldehydes with α,ω-dichloro-α,ω-disulfinylalkanes with two carbon-carbon bond-formation. α,α′-Dithio diketones, α,α′-diamino diketones were synthesized in good overall yields by this method. From the α,α′-dithio diketones, α,β-unsaturated diketones and diketones having no α-substituent can be obtained in good yields. A limitation of this procedure is that we can not synthesize the diketones having one methylene between the two carbonyl carbons.

2. Experimental

2.1. General

All melting points are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silical gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, diisopropylamine, piperidine, and benzene were distilled from CaH_2 and THF was distilled from diphenylketyl. Acetone was dried over $CaSO_4$ and distilled before

use. Methanol and liquid N_2 were used for the cooling bath at −100°C.

2.1.1. α,ω-Dichloro-α,ω-disulfinylalkanes (9, 23, and 34). These compounds were synthesized from α,ω-dibromoalkanes and *p*-toluenethiol in a similar way as described before.[4]

*1,4-Dichloro-1,4-di(p-tolylsulfinyl)butane (**9**).* *N*-Chlorosuccinimide (recrystallized from benzene; 2.98 g; 22 mmol) was added to a solution of 1,4-di(*p*-tolylthio)-butane (3.03 g; 10 mmol) in carbontetrachloride (50 ml). The suspension was stirred at room temperature for 1.5 h. The precipitates were filtered off and the solvent of the filtrate was evaporated under vacuum. The residue was dissolved with CH_2Cl_2 (50 ml) and the solution was cooled to −60°C. To the solution was added *m*-CPBA (5.43 g; 22 mmol) in one portion with stirring and the reaction mixture was stirred at −60°C for 2.5 h. The solution was washed twice with 5% NaOH followed by sat. aq. NH_4Cl. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 3.58 g (89%) of **9** (diastereomeric mixture) as a mixture of crystals and oil. IR (neat) 2923, 1596, 1448, 1179, 1044 (SO), 754 cm^{-1}; ^1H NMR δ 2.18–2.69 (4H, m), 2.44 (6H, s, CH_3), 4.34–4.60 (2H, m), 7.34–7.36 (4H, m), 7.56–7.65 (4H, m). MS *m/z* (%) 402 (M^+, trace), 263 (48), 140 (100), 92 (63). Calcd for $C_{18}H_{20}Cl_2O_2S_2$: M, 402.0282. Found: *m/z* 402.0272.

*1,8-Dichloro-1,8-di(p-tolylsulfinyl)octane (**23**).* Colorless oil (diasteromeric mixture); IR (neat) 2924, 2856, 1087, 1047 (SO), 810 cm^{-1}; ^1H NMR δ 1.36–1.71 (8H, m), 1.88–1.97 (2H, m), 2.19–2.24 (2H, m), 2.43 (6H, s, CH_3), 4.36–4.41 (1.6H, m), 4.49–4.53 (0.4H, m), 7.33–7.64 (8H, m). MS *m/z* (%) 458 (M^+, trace), 140 (100), 92 (32). Calcd for $C_{22}H_{28}Cl_2O_2S_2$: M, 458.0908. Found: *m/z* 458.0912.

*1,3-Dichloro-1,3-di(p-tolylsulfinyl)propane (**34**).* Colorless oil (diastereomeric mixture). IR (neat) 3004, 2953, 1087, 1058 (SO), 812, 755 cm^{-1}; ^1H NMR δ 2.43–3.04 (2H, CH_2), 2.43, 2.44, 2.45, 2.46 (CH_3), 4.61–4.66 (0.6H, m), 4.82–5.06 (1.4H, m), 7.29–7.63 (8H, m). MS *m/z* (%) 388 (M^+, trace), 249 (56), 139 (100), 123 (82), 91 (64). Calcd for $C_{17}H_{18}Cl_2O_2S_2$: M, 388.0125. Found: *m/z* 388.0134.

2.1.2. 3,6-Dichloro-2,7-dimethyl-3,6-di(*p*-tolylsulfinyl)-octane-2,7-diol (10). To a solution of LDA (5 mmol) in 12 ml of THF at −60°C was added dropwise with stirring a solution of **9** (804 mg; 2 mmol) in THF. The reaction mixture was stirred for 10 min, then acetone (0.44 ml; 6 mmol) was added and the solution was stirred for 10 min. The reaction was quenched by sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by recrystallization and silica gel column chromatography to give less polar product (meso-**10**; 507 mg; 49%) and more polar product (racemi-**10**; 300 mg; 29%). *Meso*-**10**; mp 157–158°C ($CHCl_3$–hexane). IR (KBr) 3304 (OH), 1490, 1145, 1068, 1032 (SO), 809 cm^{-1}; ^1H NMR δ 1.19 (6H, s), 1.55 (6H, s), 1.99 (4H, m), 2.43 (6H, s), 7.33 (4H, d, *J*=8.6 Hz), 7.60 (4H, d, *J*=8.6 Hz). MS *m/z* (%) 246 (52), 140 (68), 139 (65), 123 (74), 91 (100); Anal. Calcd for $C_{24}H_{32}Cl_2O_4S_2$: C, 55.48; H, 6.21; Cl, 13.65; S, 12.34. Found: C, 55.64; H, 6.13; Cl, 14.06; S, 12.24. Racemi-**10**; mp 126–128°C ($CHCl_3$–hexane). IR (KBr) 3319 (OH), 1182, 1079, 1039 (SO), 756 cm^{-1}; ^1H NMR δ 1.35 (6H, s), 1.52 (6H, s), 1.77–1.85 (2H, m), 2.16–2.21 (2H, m), 2.43 (6H, s), 7.31 (4H, d, *J*=8.0 Hz), 7.60 (4H, d, *J*=8.0 Hz). MS *m/z* (%) 276 (20), 246 (77), 214 (64), 185 (88), 139 (100), 91 (100). Anal. Calcd for $C_{24}H_{32}Cl_2O_4S_2$: C, 55.48; H, 6.21; Cl, 13.65; S, 12.34. Found: C, 55.23; H, 6.21; Cl, 13.31; S, 12.41.

2.1.3. 2,6-Diepoxy-2,7-dimethyl-3,6-di(*p*-tolylsulfinyl)-octane (11). To a solution of *tert*-BuOK (280 mg; 2.4 mmol) in *tert*-BuOH (6 ml) and THF (6 ml) at 0°C was added dropwise with stirring a solution of *Meso*-**10** (520 mg; 1 mmol) in THF. The reaction mixture was stirred for 40 min. The reaction was quenched by sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 442 mg (99%) of *Meso*-**11** as colorless crystals. *Meso*-**11**; mp 194–195°C ($CHCl_3$–hexane). IR (KBr) 1378, 1080, 1048 (SO), 810 cm^{-1}; ^1H NMR δ 1.15 (6H, s), 1.27–1.33 (2H, m), 1.70 (6H, s), 2.06–2.13 (2H, m), 2.41 (6H, s), 7.28 (4H, d, *J*=8.2 Hz), 7.49 (4H, d, *J*=8.2 Hz). MS *m/z* (%) 246 (trace), 167 (100), 139 (52), 91 (65), 69 (79); Anal. Calcd for $C_{24}H_{30}O_4S_2$: C, 64.54; H, 6.77; S, 14.36. Found: C, 64.26; H, 6.68; S, 14.39. Racemi-**11**; mp 159–160°C ($CHCl_3$–hexane). IR (KBr) 1492, 1451, 1092, 1047 (SO), 808 cm^{-1}; ^1H NMR δ 1.35–1.47 (2H, m), 1.38 (6H, s), 1.74 (6H, s), 1.88–1.98 (2H, m), 2.38 (6H, s), 7.28 (4H, d, *J*=8.0 Hz), 7.48 (4H, d, *J*=8.0 Hz). MS *m/z* (%) 447 ($[M+H]^+$, trace), 167 (100), 139 (40), 123 (46), 69 (76). Calcd for $C_{24}H_{31}O_4S_2$: [M+H], 447.1664. Found: *m/z* 447.1649. Anal. Calcd for $C_{24}H_{30}O_4S_2$: C, 64.54; H, 6.77; S, 14.36. Found: C, 64.17; H, 6.69; S, 14.41.

2.1.4. 2,7-Dimethyl-2,7-di(phenylsulfenyl)octane-3,6-dione (12). To a solution of NaH (60% oil suspension; 360 mg; 9 mmol) in EtOH (9 ml) at 0°C was added dropwise with stirring a solution of PhSH (0.86 ml; 8.4 mmol). The reaction mixture was stirred for 10 min, then *Meso*-**11** (268.0 mg; 0.6 mmol) in EtOH at rt was added and the solution was heated under reflux for 2 h. The reaction was quenched by sat. aq. NH_4Cl and 5% NaOH and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 220 mg (95%) of **12** as colorless crystals. Mp 88–89°C (AcOEt–hexane). IR (KBr) 2924, 1692 (CO), 1437, 1301, 1048 cm^{-1}; ^1H NMR δ 1.46 (12H, s), 3.11 (4H, s), 7.29–7.37 (10H, m). MS *m/z* (%) 386 (M^+, 3), 235 (10), 151 (100), 110 (8). Calcd for $C_{22}H_{26}O_2S_2$: M, 386.1374. Found: *m/z* 386.1369. Anal. Calcd: C, 68.36; H, 6.78; S, 16.59. Found: C, 68.09; H, 6.68; S, 16.76.

2.1.5. 2,7-Dimethyl-1,7-octadiene-3,6-dione (14). The thioketone **12** (39 mg; 0.1 mmol) was dissolved with CH_2Cl_2 (50 ml) and the solution was cooled to −60°C. To the solution was added *m*-CPBA (66 mg; 0.27 mmol) in one portion with stirring and the reaction mixture was stirred at −60°C for 1 h. The solution was washed twice with 5% NaOH followed by sat. aq. NH_4Cl. The solution was dried

over $MgSO_4$. The solvent was evaporated to give a residue, which was used in the next reaction without further purification. Toluene (2 ml) was added to the residue and the reaction mixture was heated under reflux for 2.5 h. Sat. aq. NH_4Cl was added to the reaction mixture and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 14 mg (85%) of the enone **14** as a colorless oil. IR (neat) 2925, 1673 (CO), 1368, 1070, 935 cm^{-1}; ^1H NMR δ 1.89 (6H, s), 3.04 (4H, s), 5.80 (2H, s), 6.07 (2H, s). MS *m/z* (%) 166 (M^+, 5), 138 (25), 125 (20), 97 (21), 69 (100), 41 (85). Calcd for $C_{10}H_{14}O_2$: M, 166.0993. Found: *m/z* 166.0999.

2.1.6. 2,7-Dimethyl-2,7-di(*N*-piperidinyl)octane-3,6-dione (15). A solution of *meso*-**11** (45 mg; 0.1 mmol) in piperidine (2 ml) was heated at 100°C for 1.5 h. The excess piperidine was evaporated under vacuum. The product was purified by silica gel column chromatography to give 32 mg (94%) of **15** as colorless crystals. Mp 105–106°C (EtOH–H_2O). IR (KBr) 2920, 2804, 1708 (CO), 1360, 1199, 1044 cm^{-1}; ^1H NMR δ 1.11 (12H, s), 1.43–1.53 (4H, m), 1.57 (8H, m), 2.37 (8H, t, *J*=4.9 Hz), 2.91 (4H, s). MS *m/z* (%) 336 (M^+, trace), 127 (10), 126 (100). Calcd for $C_{20}H_{36}O_2N_2$: M, 336.2777. Found: *m/z* 336.2799. Anal. Calcd: C, 71.38; H, 10.78; N, 8.32. Found: C, 71.48; H, 10.98; N, 8.23.

2.1.7. 4,7-Dichloro-1,10-diphenyl-4,7-di(*p*-tolylsulfinyl)-decane-3,8-diol (16). A mixture of colorless crystals and oil (a mixture of several diastereomers); IR (neat) 3370 (OH), 1494, 1454, 1081, 1032 (SO), 752 cm^{-1}; ^1H NMR δ 1.55–3.10 (18H, m), 3.65–4.0 (2H, m), 7.0–7.7 (18H, m).

2.1.8. 1,10-Diphenyl-3,8-di(phenylsulfenyl)octane-4,7-dione (18). To a solution of *tert*-BuOK (50 mg; 0.4 mmol) in *tert*-BuOH (2 ml) and THF (2 ml) at 0°C was added dropwise with stirring a solution of **16** (67 mg; 0.1 mmol) in THF. The mixture was stirred for 10 min, then benzenethiol (0.03 ml; 0.3 mmol) was added to the reaction mixture. After 20 min, the reactions were quenched by sat. aq. NH_4Cl and 5% NaOH and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 54 mg (75%) of **18** as a colorless oil. IR (neat) 2922, 1705 (CO), 1439, 748 cm^{-1}; ^1H NMR δ 1.94–2.04 (2H, m), 2.13–2.30 (2H, m), 2.70–2.82 (6H, m), 2.93–3.02 (2H, m), 3.64 (2H, m), 7.16–7.34 (20H, m). MS *m/z* (%) 538 (M^+, 21), 434 (14), 117 (86), 91 (100). Calcd for $C_{34}H_{34}O_2S_2$: M, 538.2000. Found: *m/z* 538.1998.

2.1.9. 1,10-Diphenyldecane-4,7-dione (19). To a solution of tributyltin hydride (0.22 ml; 0.8 mmol) and AIBN (16 mg; 0.1 mmol) in distilled benzene (4 ml) was added dropwise with stirring a solution of **18** (54 mg; 0.1 mmol) in benzene. The reaction mixture was heated under reflux for 10 min. The solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography to give **19** (28 mg; 86%) as a low melting solid. IR (KBr) 2947, 1702 (CO), 1497, 1410, 1357, 1072 cm^{-1}; ^1H NMR δ 1.91 (4H, quint, *J*=7.4 Hz), 2.46 (4H, t, *J*=7.4 Hz), 2.59–2.64 (8H, m), 7.15–7.30 (10H, m). MS *m/z* (%) 322 (M^+, 17), 218 (62), 147 (34), 114 (100), 91 (92). Calcd for $C_{22}H_{26}O_2$: M, 322.1931. Found: *m/z* 322.1934.

2.1.10. 1,10-Diphenyl-3,8-di(*N*-piperidinyl)decane-4,7-dione (20). To a solution of *tert*-BuOK (33.7 mg; 0.3 mmol) in *tert*-BuOH (2 ml) and THF (2 ml) at 0°C was added dropwise with stirring a solution of **16** (67 mg; 0.1 mmol) in THF. The reaction mixture was stirred for 10 min. The reaction was quenched by sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent was evaporated. The residue (**16**) was heated at 100°C in piperidine for 1 h. The excess piperidine was evaporated under vacuum. The product was purified by silica gel column chromatography to give 32 mg (94%) of **20** as a colorless oil. IR (neat) 2933, 1713 (CO), 1454, 1115, 788 cm^{-1}; ^1H NMR δ 1.42 (4H, m), 1.57 (8H, m), 1.89–2.04 (4H, m), 2.50 (8H, m), 2.62–2.91 (8H, m), 3.15 (2H, m), 7.16–7.29 (10H, m). MS *m/z* (%) 488 (M^+, trace), 203 (16), 202 (100), 91 (10). Calcd for $C_{32}H_{44}N_2O_2$: M, 488.3402. Found: 488.3388.

2.1.11. (*E*)-1,10-Diphenyl-2,8-decadiene-4,7-dione (22). Colorless crystals; mp 57.5–58°C (AcOEt–hexane). IR (KBr) 3027, 1673 (CO), 1146, 1101, 981 cm^{-1}; ^1H NMR δ 2.87 (4H, s), 3.54 (4H, d, *J*=6.7 Hz), 6.11 (2H, dt, *J*=15.8, 1.5 Hz), 7.00 (2H, dt, *J*=15.8, 6.8 Hz), 7.20–7.40 (10H, m). MS *m/z* (%) 318 (M^+, 45), 201 (100), 145 (91), 117 (67), 91 (71). Calcd for $C_{22}H_{22}O_2$: M, 318,1618. Found: *m/z* 318.1609. Anal. Calcd: C, 82.99; H, 6.96. Found: C, 82.64; H, 6.58.

2.1.12. 3,10-Dichloro-2,11-dimethyl-3,10-di(*p*-tolylsulfinyl)dodecane-2,11-diol (24). Colorless oil (a mixture of two diastereomers); IR (neat) 3348 (OH), 2937, 1081, 1042 (SO), 809 cm^{-1}; ^1H NMR δ 1.04–2.25 (12H, m, CH_2), 1.40, 1.60, 2.43 (CH_3), 7.32–7.35 (4H, m), 7.54–7.67 (4H, m).

2.1.13. 2,10-Diepoxy-2,11-dimethyl-3,10-di(*p*-tolylsulfinyl)dodecane (25). A mixture of light yellow oil and crystals (a mixture of two diastereomers); IR (neat) 2927, 1494, 1378, 1085, 1054 (SO), 813 cm^{-1}; ^1H NMR δ 0.76–0.90 (4H, m), 1.05–1.12 (2H, m), 1.36 (6H, s), 1.52–1.63 (4H, m), 1.79 (6H, s), 1.83–1.91 (2H, m), 2.42 (6H, s), 7.30 (4H, d, *J*=7.9 Hz), 7.52–7.54 (4H, m). MS *m/z* (%) 341 (4), 246 (25), 223 (77), 140 (100), 123 (44), 69 (66).

2.1.14. 2,11-Dimethyl-2,11-di(phenylsulfenyl)dodecane-3,10-dione (26). Colorless crystals; mp 86.5–87.5°C (Hexane). IR (KBr) 2929, 1696 (CO), 1465, 1368, 1075, 759 cm^{-1}; ^1H NMR δ 1.36–1.39 (4H, m), 1.41 (12H, s), 1.61–1.64 (4H, m), 2.77 (4H, t, *J*=7.5 Hz), 7.24–7.35 (10H, m). MS *m/z* (%) 442 (M^+, 3), 165 (10), 151 (100). Calcd for: $C_{26}H_{34}O_2S_2$: M, 442.2001. Found: *m/z* 422.2007. Anal. Calcd: C, 70.55; H, 7.74; S, 14.48. Found: C, 70.80; H, 7.75; S, 14.62.

2.1.15. 2,11-Dimethyl-1,11-dodecadiene-3,10-dione (27). Colorless oil; IR (neat) 2929, 2852, 1678 (CO), 1451, 1371, 1059, 932 cm^{-1}; ^1H NMR δ 1.33 (4H, quint, *J*=3.6 Hz), 1.61 (4H, m), 1.87 (6H, s), 2.67 (6H, t, *J*=7.3 Hz), 5.75 (2H, s), 5.95 (2H, s). MS *m/z* (%) 222

(M^+, 9), 139 (22), 97 (10), 84 (28), 69 (100). Calcd for $C_{14}H_{22}O_2$: M, 222.1619. Found: *m/z* 222.1621.

2.1.16. 2,11-Dimethyl-2,11-di(*N*-piperidinyl)dodecane-3,10-dione (28). Colorless oil; IR (neat) 2933, 1713 (CO), 1362, 1197, 1033, 755 cm^{-1}; ^1H NMR δ 1.07 (12H, s), 1.25–1.31 (4H, m), 1.51–1.58 (12H, m), 2.32 (8H, t, *J*=4.9 Hz), 2.65 (4H, t, *J*=7.6 Hz). MS *m/z* (%) 392 (M^+, trace), 250 (4), 218 (8), 161 (6), 126 (100), 109 (8). Calcd for $C_{24}H_{44}O_2N_2$: M, 392.3403. Found: *m/z* 392.3398.

2.1.17. 4,11-Dichloro-1,14-diphenyl-4,11-di(*p*-tolylsulfinyl)tetradecane-3,12-diol (29). Colorless oil (a mixture of several diastereomers); IR (neat) 3376 (OH), 1495, 1455, 1080, 1033 (SO), 753 cm^{-1}; ^1H NMR δ 1.07–3.16 (20H, m), 2.41, 2.45 (CH_3), 3.51–4.14 (2H, m), 7.08–7.66 (18H, m). MS *m/z* (%) 428 (10), 396 (16), 357 (14), 223 (25), 140 (100), 105 (100).

2.1.18. 1,14-Diphenyl-3,12-di(phenylsulfenyl)tetradecane-4,11-dione (31). Light yellow oil; IR (neat) 2931, 1705 (CO), 1455, 1439, 748, 670 cm^{-1}; ^1H NMR δ 1.19–1.25 (4H, m), 1.47–1.58 (4H, m), 1.99 (2H, quint, *J*=7.1 Hz), 2.15 (2H, quint, *J*=7.1 Hz), 2.47 (2H, dt, *J*=17.1, 7.3 Hz), 2.60 (2H, dt, *J*=17.1, 7.4 Hz), 2.67–2.79 (4H, m), 3.56 (2H, t, *J*=7.3 Hz), 7.14–7.34 (20H, m). MS *m/z* (%) 594 (M^+, 7), 490 (20), 149 (12), 117 (100), 91 (70) Calcd for: $C_{38}H_{42}O_2S_2$: M, 594.2627. Found: *m/z* 594.2642.

2.1.19. (*E*)-1,14-Diphenyl-2,12-tetradecadiene-4,11-dione (32). Light yellow oil; IR (neat) 2933, 1695 (CO), 1669, 1627, 1496, 1454, 982, 750, 700 cm^{-1}; ^1H NMR δ 1.29 (4H, m), 1.59 (4H, m), 2.51 (4H, t, *J*=7.4 Hz), 3.53 (4H, d, *J*=6.8 Hz), 6.08 (2H, dt, *J*=15.9, 1.7 Hz), 6.93 (2H, dt, *J*=15.9, 6.6 Hz), 7.16–7.38 (10H, m). MS *m/z* (%) 374 (M^+, 39), 257 (16), 231 (7), 211 (16), 145 (70), 117 (100), 91 (47). Calcd for $C_{26}H_{30}O_2$: M, 374.2244. Found: *m/z* 374.2227.

2.1.20. 1,14-Diphenyl-3,12-di(*N*-piperidinyl)tetradecane-4,11-dione (33). Colorless oil; IR (neat) 2933, 1712 (CO), 1454, 1115, 751, 670 cm^{-1}; ^1H NMR δ 1.28–1.57 (20H, m), 1.87–1.99 (4H, m), 2.40–2.64 (16H, m), 3.07–3.10 (2H, m), 7.16–7.29 (10H, m). MS *m/z* (%) 544 (M^+, trace), 202 (100), 110 (5), 91 (10). Calcd for $C_{36}H_{52}O_2N_2$: M, 544.4029. Found: *m/z* 544.4026.

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