DOI: 10.1002/asia.200800155

Tin-Free Radical Carbonylation of Alkylsulfonyl Derivatives into Alkylcarbonyl Derivatives

Sangmo Kim, Kyoung-Chan Lim, and Sunggak Kim*[a]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

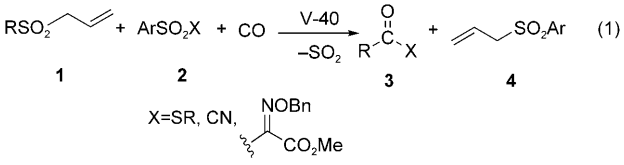
Abstract: A simple radical approach based on tin-free radical carbonylation is devised for the direct conversion of alkylthiosulfonates, alkylsulfonyl cyanides, and alkylsulfonyl oxime ethers into the corresponding alkyl thiol esters, acyl cyanides, and acylated oxime ethers in a single step. The present approach is very simple, highly efficient, and minimizes the formation of byproducts.

Keywords: acylation · C–C coupling · carbonylation · radical reactions · synthetic methods

Introduction

The use of radicals in organic synthesis has been increased dramatically in the last 30 years arising from the increased understanding of the factors governing reactivity, regio- and stereoselectivity.[1] Radical reactions proceed under very mild conditions with a very high synthetic efficiency, but most radical reactions suffer from a major drawback mainly associated with problems of high toxicity of organotin compounds. Therefore, much attention has been given to the development of tin-free radical reactions in recent years.[2] In connection with our continued effort for the development of tin-free radical-mediated carbon–carbon bond formation,[3] we reported tin-free radical carbonylation reactions using alkyl allyl sulfone radical precursors.[4] Recently, we have reported a highly selective, atom economical, and environmentally benign radical reaction for the conversion of alkylsulfonyl derivatives into alkylcarbonyl derivatives.[5]

According to our previous studies,[4b] reaction of alkyl allyl sulfone precursor **1** with arylsulfonyl derivatives **2** in heptane under pressurized carbon monoxide using V-40 [1,1′-azobis(cyclohexane-1-carbonitrile)] initiator affords alkylcarbonyl derivatives **3** in high yields under tin-free conditions [Eq. (1)]. Although this approach is highly efficient and useful for the preparation of several carbonyl compounds under mild conditions, the reaction yields allyl aryl sulfone side-product **4**. To increase the synthetic efficiency by both maximizing atom utilization and minimizing byproducts or waste, we have come up with a new type of radical reaction in which a substrate could be utilized, not only as a radical precursor, but also as a radical acceptor. Similar types of radical reactions using Barton's thiohydroxamate esters[6] and xanthate derivatives[7] have been reported previously.

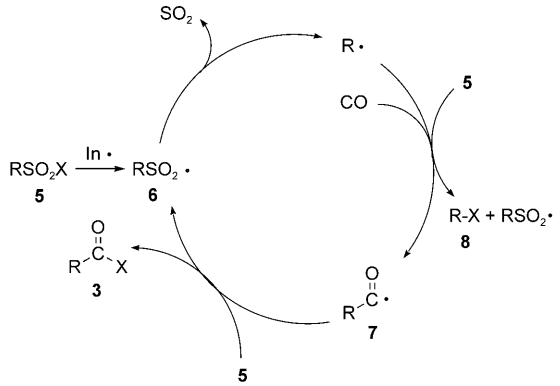


(1)

Results and Discussion

To obviate the problem of the formation of allyl aryl sulfone **4**, we have studied the feasibility of using alkylsulfonyl derivatives as radical precursors as well as acceptors. This idea is based on the previously known thermal desulfonylation of alkylsulfonyl radicals to liberate alkyl radicals along with sulfur dioxide.[8] Scheme 1 shows a plausible rationale for the direct conversion of alkylsulfonyl derivative **5** into alkylcarbonyl derivative **3**. The reaction is initiated by the reaction of **5** with radical initiator to generate alkylsulfonyl radical **6**. The success of the present approach depends critically on the preferential formation of acyl radical **7** through radical carbonylation rather than direct reaction with **5** to afford

[a] S. Kim, K.-C. Lim, S. Kim
Center for Molecular Design & Synthesis and
Department of Chemistry
School of Molecular Sciences
Korea Advanced Institute of Science and Technology (KAIST)
Daejeon 305-701 (Korea)
Fax: (+82) 42-869-8370
E-mail: skim@kaist.ac.kr

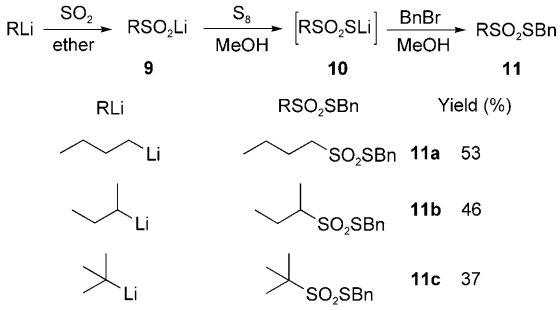


Scheme 1. Plausible mechanism for the direct conversion of RSO_2X into RCOX.

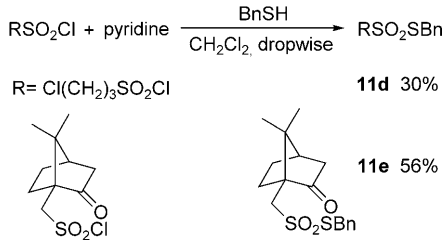
byproduct **8**, which should depend very much on the nature of alkyl radicals.[9,10] Primary alkyl radicals are expected to be more favorable than secondary and tertiary alkyl radicals for radical carbonylation because of their high reactivity toward carbon monoxide. According to our previous studies,[4] alkylthiosulfonates, alkylsufonyl cyanides and alkylsulfonyl oxime ethers were very promising in their ability to quench the corresponding acyl radicals for the direct conversion into the corresponding carbonyl derivatives under tin-free conditions.

Radical Carbonylation of *S*-Benzyl Alkylthiosulfonates

S-Benzyl alkylthiosulfonates **11** can be prepared from alkyllithiums and alkylsulfonyl chlorides by previously reported methods.[11–13] First, alkyllithium was treated with sulfur dioxide to give alkyl sulfinate salt **9**. Further treatment of **9** with sulfur followed by addition of benzyl bromide in methanol provided *S*-benzyl alkylthiosulfonates **11** via **10** (Scheme 2).[11] Second, treatment of an alkylsulfonyl chloride with benzyl mercaptan in the presence of pyridine in dichloromethane gave **11** in low yields (Scheme 3).[12] The present procedure was not efficient, usually yielding some unreacted starting alkylsulfonyl chlorides. The alkylsulfonyl chloride was first converted into thiosulfonic acid sodium salt **12** with anhydrous sodium hydrosulfide in anhydrous methanol and **12** was further treated with benzyl bromide in methanol to afford *S*-benzyl alkylthiosulfonate **11**.[13] The

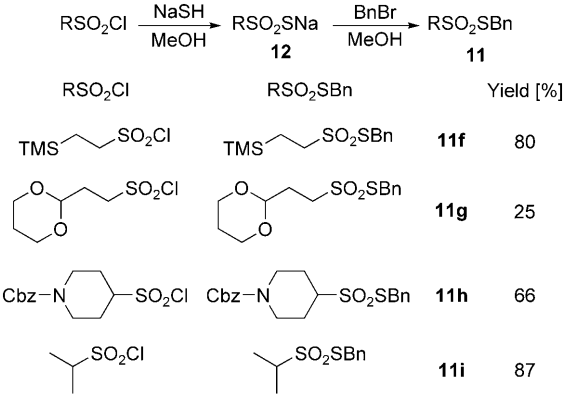


Scheme 2. Preparation of RSO_2SBn from RLi.



Scheme 3. Preparation of RSO_2SBn from RSO_2Cl.

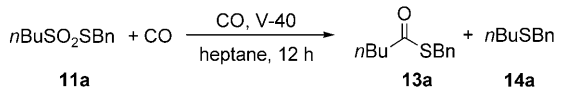
present procedure was reliable and worked with structurally different alkylsulfonyl chlorides as shown in Scheme 4.



Scheme 4. Preparation of RSO_2SBn from RSO_2Cl.

To find out an optimum condition for the conversion of alkyl thiosulfonates into the corresponding thiol esters [Eq. (2)], we briefly examined the effect of CO pressure and concentration of the substrate. When *S*-benzyl *n*-butanethiosulfonate **11a** was subjected to the pressurized CO (95 atm) in heptane (0.01 M) using V-40 at 100 °C for 12 h, *S*-benzyl thiobutanoate (**13a**) was isolated in 82 % yield along with starting material (15 %) (Table 1, entry 3). Several noteworthy features are indicated from Table 1. First, there was no indication of the formation of benzyl *n*-butyl sulfide (**14a**). Second, the starting material was not completely consumed at 100 °C under a high pressure of CO (95 atm) (Table 1, en-

Table 1. The effect of CO pressure and concentration of **11a**.

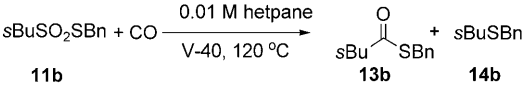


Entry	Conc. (**11a**) [M]	CO [atm]	Temp. [°C]	Yield[a] **13a** [%]	**11a** [%]
1	0.10	95	100	35	64
2	0.05	95	100	57	42
3	0.01	95	100	82	15
4	0.01	95	120	91	–
5	0.01	50	120	97	–
6	0.01	30	120	84	15
7	0.01	10	120	77	18

[a] **14a** was not obtained.

tries 1–3). By increasing the reaction temperature to 120 °C, the reaction was complete. Finally, the CO pressure could be lowered to 50 atm at 120 °C (Table 1, entry 5). Further lowering the CO pressure to 30 atm and 10 atm gave the recovery of the starting material to some extent (Table 1, entries 6 and 7). In the case of *S*-benzyl secondary alkylthiosulfonates, they are less reactive than primary alkylthiosulfonates. As shown in Table 2, *S*-benzyl *sec*-butanethiosulfonate

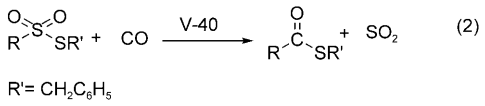
Table 2. The effect of CO pressure for **11b**.



Entry	CO [atm]	Time [h]	**13b** [%]	Yield **14b** [%]	**11b** [%]
1	95	24	86	–	9
2	95	12	69	–	27
3	50	12	57	trace	31
4	30	12	42	11	35

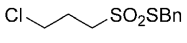
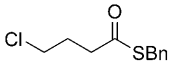
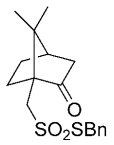
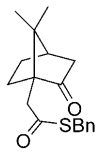
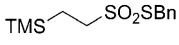
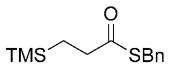
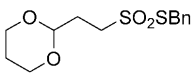
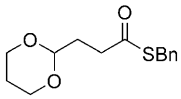
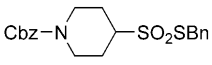
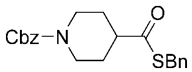
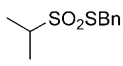
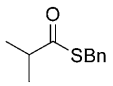
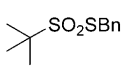
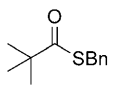
11b required a higher pressure of CO (95 atm) to obviate the formation of the corresponding sulfide by-product **14b** (Table 2, entries 1 and 2). In addition, a longer reaction time (24 h) was needed to consume the starting material. Thus, remaining reactions were carried out at 120 °C under pressurized CO (50 atm for primary substrates and 95 atm for secondary and tertiary).

The experimental results are summarized in Table 3. Primary *S*-benzyl alkylthiosulfonates underwent clean conversion into the corresponding thiol esters in high yields (Table 3, entries 1–4). Secondary *S*-benzyl alkylthiosulfonates worked well under a higher pressure (95 atm), yielding the corresponding thiol esters (Table 3, entries 5 and 6). In several cases, a small amount of the starting *S*-benzyl alkylthiosulfonates was recovered (Table 3, entries 2–4, 6). As we expected, the present method reaches a limit with tertiary alkylthiosulfonates (Table 3, entry 7). Radical reaction of *S*-benzyl *tert*-butylthiosulfonate (**11c**) under the same condition afforded a small amount of 2,2-dimethyl-thiopropionic acid *S*-benzyl ester (**13c**; 19%) along with 67% recovery of the starting material and some sulfide byproduct (**14c**; 9%). This result arises from the low reactivity of the *tert*-butyl radical toward *S*-benzyl *tert*-butylthiosulfonate and an unfavorable equilibrium toward the carbonylation process relative to primary and secondary alkyl radicals.



Sequential radical reactions involving cyclization and thioalkoxycarbonylation were briefly studied, although the present approach is not the direct substitution of SO_2 into CO (Scheme 5). The first example consists of a five-step sequence involving desulfonylation, 5-exo cyclization, and carbonylation as major reactions. When a solution of alkylthiosulfonate **15** and V-40 initiator at pressurized CO (50 atm) was treated in heptane at 120 °C for 24 h, the desired thiol ester **16** was isolated in 71% yield along with some starting material (19%). In the case of alkylthiosulfonate **17** under the similar condition, since the initial 4-exo cyclization is disfavored, carbonylation occurred. As shown in Scheme 5, radical cyclization of acyl radical was followed by the second carbonylation to afford the desired thiol ester **18** in 47% yield along with some starting material (18%). It is noteworthy that the cyclization of the sufonyl radical generated from **17** was not observed, probably arising from the facile β-elimination of the resulting cyclized radical intermediate.

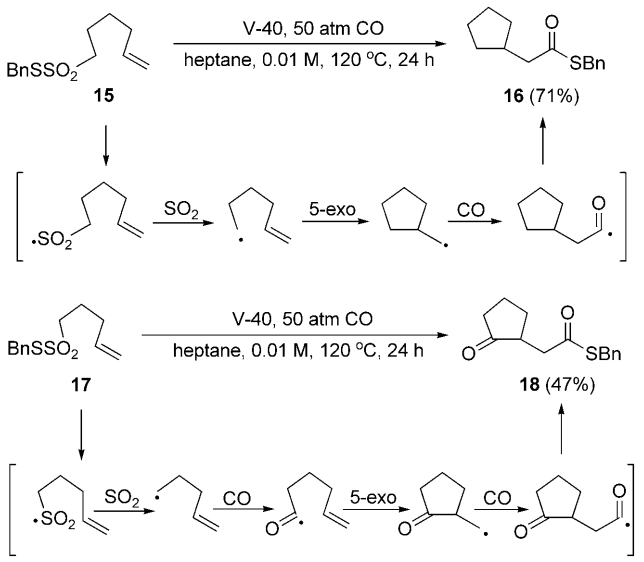
Table 3. Direct conversion of RSO_2SBn into RCOSBn.

Entry	Substrate	CO [atm]	Product	Yield [%][a]
1		50		91
2		50		84 (5)
3		50		80 (6)
4		50		78 (7)
5		95		87
6		95		80 (18)
7		95		19 (67)[b]

[a] The numbers in the parentheses indicate the recovered starting material. [b] *tert*-Butylsulfanylmethyl-benzene (9%) was also isolated.

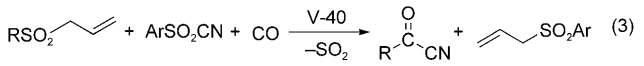
Radical Carbonylation of RSO_2CN into RCOCN

Acyl cyanides are valuable synthetic intermediates for various functional group conversions and the synthesis of *N*-heterocyclic compounds.[14,15]



Scheme 5. Sequential radical reactions.

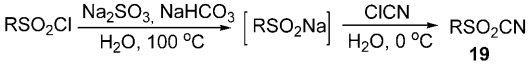
Among various methods available for the synthesis of acyl cyanides, treatment of carboxylic acid chlorides with heavy metal cyanides is most convenient.[16] Another approach involving Pd-catalyzed cyanocarbonylation of aryl iodides is also attractive,[17] but this approach is not applicable to the synthesis of aliphatic acyl cyanides. Recently, we have reported a new radical approach for the synthesis of aliphatic acyl cyanides based on tin-free radical cyanocarbonylation using alkyl allyl sulfone, *p*-toluenesulfonyl cyanide and CO [Eq. (3)].[4c]



Several alkylsulfonyl cyanides tested in this study were prepared from alkylsulfinic acid sodium salts and cyanogen chloride by the literature method.[18] Alkylsulfonyl chlorides were treated with sodium sulfite and sodium bicarbonate to yield alkylsulfinic acid sodium salts, which were further reacted with cyanogen chloride to afford alkylsulfonyl cyanides **19** (Table 4).

The present approach follows the same guiding principle of the direct conversion of *S*-benzyl alkylthiosulfonates into the thiol esters and is based on thermal desulfonylation and preferential reaction of alkyl radicals with carbon monoxide rather than with alkylsulfonyl cyanides [Eq. (4)]. To search for the optimum condition, we briefly studied the effect of CO and concentration. As shown in Table 5, the best result was obtained when the reaction was carried out with **19a** under 95 atm of CO using V-40 initiator (0.2 equiv) in refluxing heptane (0.01 M) at 120 °C for 24 h (Table 5, entry 2). Cyanide byproduct **22a** was formed at the lower pressure of CO (50 atm and 30 atm; Table 5, entries 3 and 4) and/or at a higher concentration (0.05 M) of **19a** (Table 5, entry 1). Since aliphatic acyl cyanides **20** are sensitive to hydrolysis, they were quenched with methanol or aniline to yield the corresponding methyl esters or amides for isolation.[19]

Table 4. Preparation of RSO_2CN from RSO_2Cl.



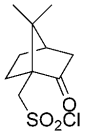
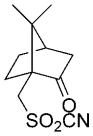
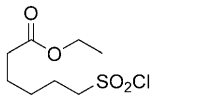
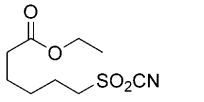
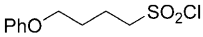
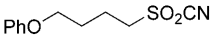
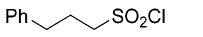
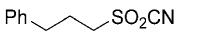
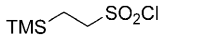
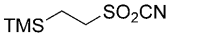
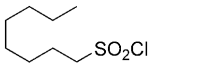
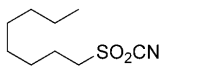
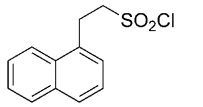
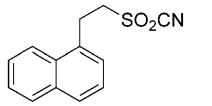
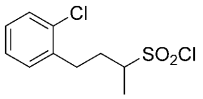
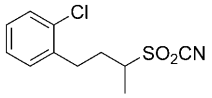
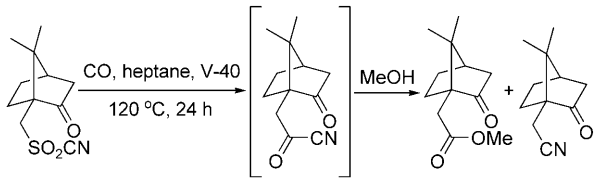
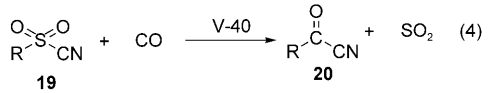
RSO_2Cl	RSO_2SBn	Yield [%]
		89
		85
		86
		85
		65
		57
		70
		72

Table 5. Effect of concentration of **19a** and pressure of CO.

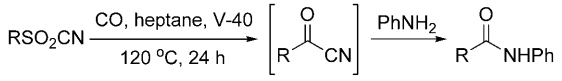


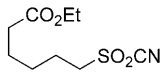
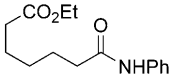
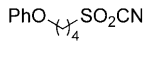
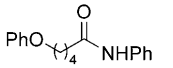
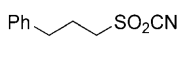
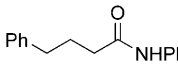
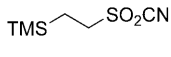
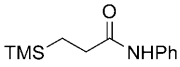
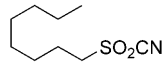
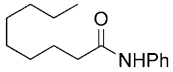
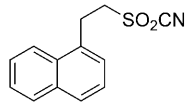
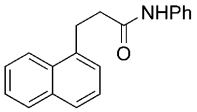
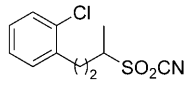
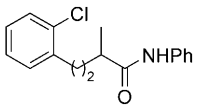
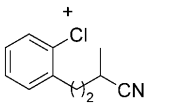
Entry	Conc. (**19a**) [M]	CO [atm]	Yield **21a** [%]	Yield **22a** [%]
1	0.05	95	81	12
2	0.01	95	84	-
3	0.01	50	77	7
4	0.01	30	73	14



As shown in Table 6, when several primary alkylsulfonyl cyanides were subjected to the standard condition (95 atm of CO, 120 °C, 24 h), the corresponding amides were isolated

Table 6. Direct conversion of RSO_2CN into RCOCN.



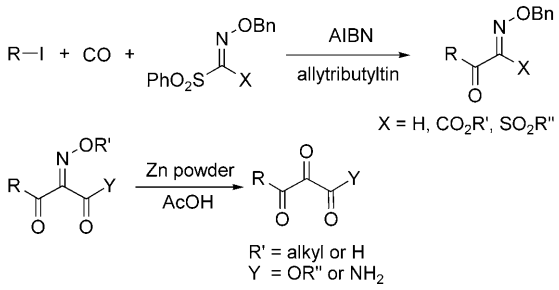
Entry	Substrate	CO [atm]	Product	Yield [%]
1		95		21 b (70
2		95		86 (6)[a]
3		95		81
4		95		53
5		95		73
6		95		68
7		95		33:51[b]
8		130		43:41[b]

[a] The numbers in the parentheses indicate the recovered starting material. [b]The ratio indicates **21h**/**22b**.

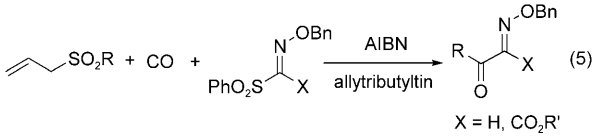
in good yields after quenching the reaction mixture with aniline (Table 6, entries 1–6). The cyanide byproduct was not produced. However, the present approach reaches a limit to secondary alkyl sulfonyl cyanides. When **19h** was subjected to the similar condition, nitrile **22b** was isolated in 51% yield along with the desired product **21h** in 33% yield (Table 6, entry 7). To reduce the formation of nitrile byproduct, when the reaction was carried out at 130 atm of CO, the yield of **21h** was improved to some extent but was not good enough (Table 6, entry 8).

Radical Carbonylation of Alkylsulfonyl Oxime Ethers into Acylated Oxime Ethers

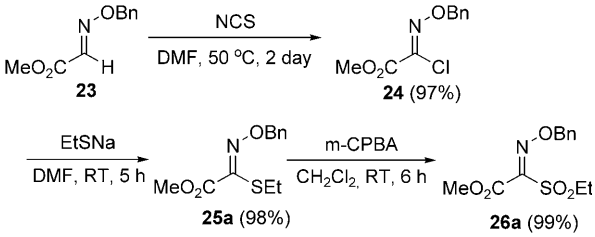
An allyltin mediated tandem radical approach using carbon monoxide and phenylsulfonyl oxime ether as multiple radical one-carbon synthons was reported previously (Scheme 6).[20] This strategy is promising and permits the synthesis of several types of vicinal singly and doubly acylated oxime ethers, which would be precursors of vicinal di- and tricarbonyl compounds. Recently, we have developed the tin-free version of the present approach using alkyl allyl sulfone precursors [Eq. (5)].[4d]



Scheme 6. Radical carbonylation of phenylsulfonyl oxime ethers.



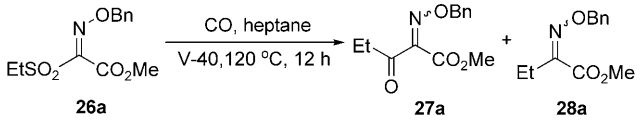
Ethanesulfonyl oxime ether **26a** was prepared from oxime ester **23** by a three-step sequence. After chlorination of **23** with *N*-chlorosuccinimide, **24** was treated with sodium thioethoxide to give **25a**, which was further oxidized to **26a** (Scheme 7).



Scheme 7. Preparation of ethanesulfonyl oxime ether **26a**.

The same guiding principle as we observed in this study could be further applied to the direct conversion of alkylsulfonyl oxime ethers into the acylated oxime ethers. When ethanesulfonyl oxime ether **26a** was subjected to pressurized CO (30 atm) in heptane (0.01 M) using V-40 at 120°C for 12 h, acylated oxime ether **27a** was isolated in 83% yield along with some starting material (15%; Table 7, entry 2). When the reaction was repeated at higher concentration of **26a** (0.05 M), byproduct **28a** was isolated in 6% yield along with the desired product (64%) and the starting material (27%) (Table 7, entry 5). By performing the reaction under 50 atm of CO, the starting material was completely consumed without the formation of the oxime ether byproduct (entry 1) (Table 7). The remaining reactions were carried out in heptane at pressurized CO (50 atm for primary alkyl sulfonyl oxime ether and 95 atm for secondary alkyl sulfonyl oxime ethers) at 120°C for 12 h. Additional experimental results are included in Table 8. Alkylsulfonyl oxime ethers bearing an ester group were converted into the corresponding acylated oxime ethers in high yields (Table 8, entries 1–4). Unactivated ethanesulfonyl oxime ether underwent a

Table 7. Effect of concentration of **26a** and pressure of CO.



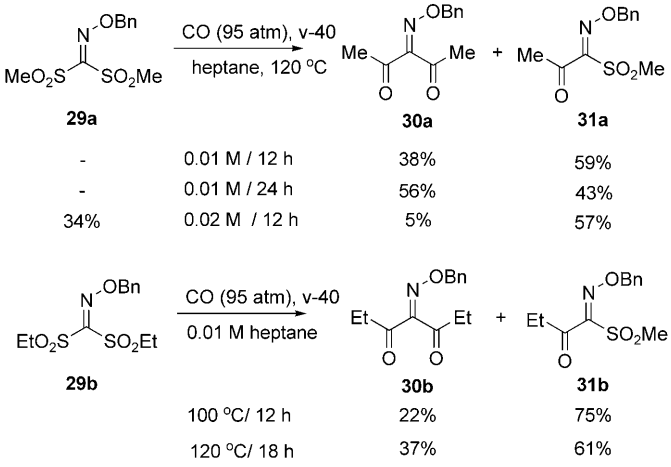
26a **27a** **28a**

Entry	Conc. (**26a**) [M]	CO [atm]	Yield **27a** [%]	**28a** [%]	**26a** [%]
1	0.01	50	96	–	–
2	0.01	30	83	–	15
3[a]	0.01	30	87	–	9
4	0.03	30	84	–	14
5	0.05	30	64	6	27

[a] Reaction time: 24 h.

clean carbonylation (Table 8, entry 5) but cyclohexylsulfonyl oxime ether yielded a small amount of cyclohexyl oxime ether byproduct under the same condition. However, the by-product was not formed when the reaction was performed under 95 atm of CO (Table 8, entry 6).

Our attention turned to vicinal double carbonylation using bis-alkylsulfonyl oxime ether **29**. The similar allyltin mediated approach was reported previously using carbon monoxide and phenylsulfonyl oxime ether. When bis-methanesulfonyl oxime ether (**29a**) was subjected under 95 atm CO in 0.01 M heptane at 120 °C for 12 h, mono acylated oxime ether **31a** was obtained in 59% yield along with the desired bis-acylated oxime ether **30a** in 38% yield. The longer reaction time (24 h) gave a slightly better result. Furthermore, when the solution was concentrated to 0.02 M, the reaction slowed down and the yield of the bis-carbonylated product was dramatically reduced as shown in Scheme 8. When the reaction was repeated with bis-ethanesulfonyl oxime ether **29b** under similar conditions, similar results were obtained, yielding mono-acylated oxime ether **31b** as a major product.

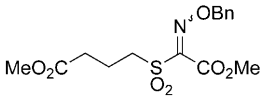
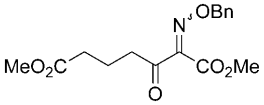
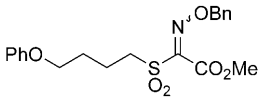
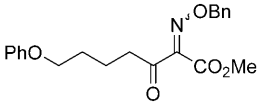
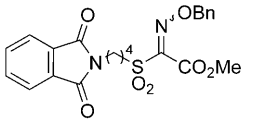
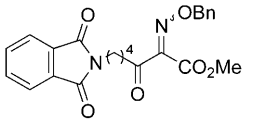
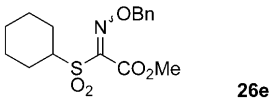
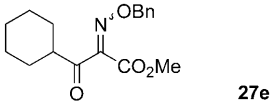
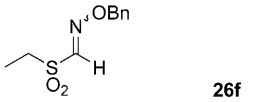
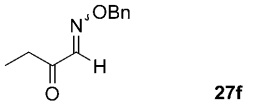
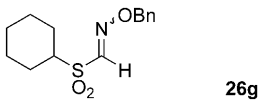
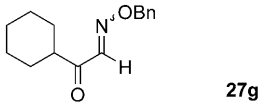


Scheme 8. Radical carbonylation of bis-alkylsulfonyl oxime ether **29**.

Conclusions

We have discovered the first simple and highly efficient way to convert alkylsulfonyl derivatives into the corresponding carbonyl compounds in high yields using tin-free radical car-

Table 8. Direct conversion of sulfonyl oxime ethers into acylated oxime ethers.

Entry	Substrate	CO [atm]	Product	Yield [%][a]
1	 **26b**	50	 **27b**	94
2	 **26c**	50	 **27c**	93
3	 **26d**	50	 **27d**	94
4	 **26e**	95	 **27e**	92
5	 **26f**	50	 **27f**	85
6	 **26g**	95	 **27g**	69 (15)

[a] The numbers in the parentheses indicate the recovered starting material.

bonylation. The present approach is based on thermal desulfonylation and the preferential formation of an acyl radical through radical carbonylation rather than the direct reaction with alkylsufonyl derivatives. Alkylthiosulfonates, alkylsulfonyl cyanides and alkylsulfonyl oxime ethers were very effective in their ability to quench the corresponding acyl radicals for the direct conversion into the corresponding carbonyl derivatives under tin-free conditions. Furthermore, the present approach would be applicable to similar types of radical reactions using alkyl allyl sulfones and alkyl vinyl sulfones.

Experimental Section

Typical Procedure for the Preparation of S-benzyl Alkylthiosulfonates from Alkyllithiums

11a: *S*-Benzyl butane-1-sulfonothioate: Sulfur dioxide (4.4 mL, 100 mmol) was condensed in a dry flask at −78 °C, and cold ether (16 mL) was added. A 2.5 M hexane solution of *n*-butyllithium (4.0 mL, 10 mmol) was added dropwise over 10 min. The reaction mixture was stirred for another 30 min at −78 °C, and then was allowed to warm up to room temperature for 24 h. All volatile materials were removed under reduced pressure to give lithium butane-1-sulfinate (**9a**, 1.27 g, 99 %). A mixture of lithium butane-1-sulfinate (1.27 g, 9.9 mmol) and sulfur (3.17 g, 9.9 mmol) in MeOH (60 mL) was heated under reflux for 2 h. Removal of solvent gave crude lithium butane-1-sulfonothioate (**10a**, 1.59 g, 100 %). MW: $C_4H_9LiO_2S_2$ = 160.18; ^{1}H NMR (D_2O, 400 MHz) δ = 0.76 (t, J = 7.4 Hz, 3H), 1.23–1.41 (m, 4H), 2.22 ppm (t, J = 7.5 Hz, 2H); ^{13}C NMR (D_2O, 100 MHz) δ = 13.5, 22.0, 24.2, 61.0 ppm.

A mixture of lithium butane-1-sulfonothioate (**10a**, 1.59 g, 9.9 mmol) and benzyl bromide (1.69 g, 9.9 mmol) in MeOH (50 mL) was refluxed for 3 h. After removal of solvent under reduced pressure, the mixture was diluted with CH_2Cl_2 (100 mL), washed with brine (100 mL), dried over $MgSO_4$, and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give *S*-benzyl butane-1-sulfonothioate (**11a**) (1.28 g, 53 %). MW: $C_{11}H_{16}O_2S_2$ = 244.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.80 (t, J = 7.3, 3H), 1.20–1.27 (m, 2H), 1.67–1.71 (m, 2H), 2.82–2.86 (m, 2H), 4.31 (s, 2H), 7.28–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 13.3, 21.0, 25.2, 40.5, 62.7, 128.1, 129.0, 129.1, 135.3 ppm; IR (polymer) $\tilde{\nu}$ = 2962, 1496, 1454, 1325, 1127, 701 cm^{-1}; HRMS [M^+] calcd for $C_{11}H_{16}O_2S_2$: 244.0592, found 244.0596.

11b: Butanethiosulfonic acid *S*-benzyl ester: MW: $C_{11}H_{16}O_2S_2$ = 244.37; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.90 (t, J = 7.5, 3H), 1.39 (d, J = 6.84 Hz, 3H), 1.48–1.56 (m, 1H), 1.98–2.06 (m, 1H), 2.64–2.68 (m, 1H), 4.31 (s, 2H), 7.28–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 11.1, 13.1, 23.1, 40.5, 69.5, 128.1, 128.9, 129.1, 135.4 ppm.

11c: 2-Methyl-propanethiosulfonic acid *S*-benzyl ester: MW: $C_{11}H_{16}O_2S_2$ = 244.37; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (s, 9H), 4.36 (s, 2H), 7.28–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.8, 41.0, 69.1, 128.1, 128.9, 129.3, 135.2 ppm.

11d: 3-Chloro-propanethiosulfonic acid *S*-benzyl ester: MW: $C_1H_{13}ClO_2S_2$ = 264.79; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.08–2.12 (m, 2H), 2.96 (t, J = 7.3 Hz, 2H), 3.41 (t, J = 6.2 Hz, 2H), 4.27 (s, 2H), 7.28–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 26.5, 40.6, 42.1, 59.9, 128.1, 128.9, 129.3, 135.2 ppm.

11e: 7,7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-methanethiosulfonic acid *S*-benzyl ester: MW: $C_{17}H_{22}O_3S_2$ = 338.49; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.69 (s, 3H), 0.98 (s, 3H), 1.37–1.41 (m, 1H), 1.65–1.69 (m, 1H), 1.88 (d, J = 13.9, 1H), 1.98–2.05 (m, 2H), 2.28–2.43 (m, 2H), 2.83 (d, J = 10.9 Hz, 1H), 3.57 (d, J = 10.9 Hz, 1H), 4.41 (dd, J = 15.1, 10.1 Hz, 2H), 7.24–7.41 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 19.5, 19.7, 24.8, 26.9, 40.9, 42.4, 42.5, 47.9, 59.3, 60.9, 128.1, 128.9, 129.2, 135.0, 213.7 ppm.

Typical Procedure for the Preparation of S-Benzyl Alkylthiosulfonates from Alkylsulfonyl Chlorides

11f: S-benzyl 2-(trimethylsilyl)ethanesulfonothioate: A mixture of 2-(trimethylsilyl)ethanesulfonyl chloride (1.0 g, 5 mmol) and sodium hydrosulfide (1.4 g, 25 mmol) in MeOH (10 mL) was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the excess sodium hydrosulfide was removed by passing through a silica gel column using acetone and methanol as eluant to give crude sodium 2-(trimethylsilyl)ethanesulfinate (**12f**, 1.10 g, 100 %). MW: $C_5H_{13}NaO_2S_2Si$ = 220.36; ^{1}H NMR (D_2O, 400 MHz) δ = −0.07 (s, 9H), 0.94–0.98 (m, 2H), 3.07–3.21 ppm (m, 2H); ^{13}C NMR (D_2O, 100 MHz) δ = −3.0, 11.5, 62.1 ppm.

A solution of sodium 2-(trimethylsilyl)ethanesulfinate (**12f**, 1.1 g, 5 mmol) and benzyl bromide (1.28 g, 7.5 mmol) in MeOH (10 mL) was refluxed overnight. After removal of solvent under reduced pressure, the mixture was diluted with CH_2Cl_2 (50 mL), washed with brine (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:20) as eluant to give *S*-benzyl 2-(trimethylsilyl)ethanesulfonothioate (**11f**) (1.15 g, 80 %). MW: $C_{12}H_{20}O_2S_2Si$ = 288.50; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = −0.11 (t, J = 3.4, 9H), 0.91–0.96 (m, 2H), 2.71–2.75 (m, 2H), 4.30 (s, 2H), 7.28–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = −2.1, 10.4, 40.5, 60.2, 128.2, 129.0, 129.1, 135.8 ppm; IR (polymer) $\tilde{\nu}$ = 2951, 1454, 1417, 1314, 1249, 1124, 699 cm^{-1}; HRMS [M^+] calcd for $C_{12}H_{20}O_2S_2Si$: 288.0674, found 288.0644.

11g: 2-[1,3]Dioxan-2-yl-ethanethiosulfonic acid *S*-benzyl ester: MW: $C_{15}H_{16}O_3S_2$ = 292.42; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.21–1.28 (m, 2H), 1.99–2.05 (m, 2H), 3.11–3.14 (m, 2H), 3.67–3.71 (m, 2H), 3.99–4.03 (m, 2H), 4.32 (s, 2H), 4.55 (t, J = 4.6 Hz, 1H), 7.24–7.37 ppm (m, 5H).

11h: 4-Benzylsulfanylthiosulfonyl-piperidine-1-carboxylic acid benzyl ester: MW: $C_{20}H_{23}NO_4S_2$ = 405.53; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.63–1.69 (m, 2H), 1.97–2.02 (m, 3H), 2.47–2.54 (m, 3H), 4.22–4.26 (m, 1H), 4.30 (s, 2H), 5.08 (s, 2H), 7.28–7.37 ppm (m, 10H).

11i: Isopropanethiosulfonic acid *S*-benzyl ester: MW: $C_{10}H_{14}O_2S_2$ = 230.35; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.33 (d, J = 5.2 Hz, 6H), 2.96–3.02 (m, 1H), 4.32 (s, 2H), 7.24–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.1, 40.4, 63.2, 128.2, 129.0, 129.1, 135.8 ppm.

Typical procedure for direct conversion of RSO_2SBn into $RCOSBn$

Dried heptane (20 mL), *S*-benzyl *n*-butylthiosulfonate (**11a**) (49 mg, 0.2 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was sealed, purged three times with 10 atm of CO, pressurized with 50 atm of CO, and then heated at 120 °C with stirring for 12 h. After excess CO was discharged at room temperature, the solvent was removed under reduced pressure. The residue was purified by passing through a silica gel column using ethyl acetate and *n*-hexane (1:50) as eluant to give *S*-benzyl thiobutanoate (**13a**) (40 mg, 97 %).

13d: 4-Chloro-thiobutyric acid *S*-benzyl ester: MW: $C_{11}H_{13}ClOS$ = 228.04; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.13 (m, 2H), 2.75 (t, 2H, J = 7.2 Hz), 3.56 (t, 2H, J = 6.3 Hz), 4.13 (s, 2H), 7.23–7.29 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 28.0, 33.2, 40.5, 43.7, 127.3, 128.6, 128.7, 137.3, 197.5 ppm; IR (polymer) $\tilde{\nu}$ = 2962, 1695, 1495, 1454, 1411, 1090, 1003, 701 cm^{-1}; HRMS [M^+] calcd for $C_{11}H_{13}ClOS$: 228.0376, found 228.0374.

13e: 7, 7-Dimethyl-2-oxo-bicyclo[2.2.1]hept-1-yl)-thioacetic acid *S*-benzyl ester: MW: $C_{18}H_{22}O_2S$ = 302.43; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.87 (s, 3H), 0.94 (s, 3H), 1.32–1.39 (m, 1H), 1.62–1.71 (m, 1H), 1.85 (d, J = 18.3 Hz, 1H), 1.91–1.99 (m, 1H), 2.02–2.12 (m, 2H), 2.30–2.37 (m, 1H), 2.45 (d, J = 15.2 Hz, 1H), 2.80 (d, J = 15.2 Hz, 1H), 4.10 (dd, J = 17.1, 18.3 Hz, 2H), 7.19–7.27 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 19.7, 19.9, 26.8, 26.9, 33.5, 39.5, 42.7, 43.1, 47.5, 60.1, 127.1, 128.5, 128.8, 137.5, 196.6, 216.2 ppm; IR (polymer) $\tilde{\nu}$ = 2961, 1745, 1696, 1496, 1455, 1056, 750 cm^{-1}; HRMS [M^+] calcd for $C_{18}H_{22}O_2S$: 302.1340, found 302.1345.

13f: 3-Trimethylsilanyl-thiopropionic acid *S*-benzyl ester: MW: $C_{13}H_{20}OSSi$ = 252.45; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = −0.03–0.00 (m, 9H), 0.86–0.90 (m, 2H), 2.49–2.53 (m, 2H), 4.10 (s, 2H), 7.22–7.28 ppm

(m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = -1.8$, 12.4, 33.2, 38.5, 127.2, 128.6, 128.8, 137.8, 200.3 ppm; IR (polymer) 2954, 1695, 1496, 1455, 1250, 1178, 862 cm^{-1}; HRMS [M^+] calcd for $C_{13}H_{20}OSSi$: 252.1004, found 252.1006.

13g: 3-[1, 3]Dioxan-2-yl-thiopropionic acid *S*-benzyl ester: MW: 3-[1, 3]Dioxan-2-yl-thiopropionic acid *S*-benzyl ester: $C_{14}H_{18}O_3S = 266.36$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.28$–1.31 (m, 1H), 1.91–2.04 (m, 3H), 2.68 (t, $J = 7.4$ Hz, 2H), 3.68 −3.74 (td, $J = 12.4$, 2.3 Hz, 2H), 4.02–4.07 (dd, $J = 10.9$, 5.0 Hz, 2H), 4.10 (s, 2H), 4.55 (t, $J = 4.9$ Hz, 1H), 7.20–7.28 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 25.6$, 30.4, 33.1, 37.9, 66.8, 100.5, 127.2, 128.5,128.8, 137.7, 198.2 ppm; IR (polymer) $\tilde{\nu} = 2968$, 2854, 1690, 1496, 1455, 1242, 1147, 1012, 705 cm^{-1}; HRMS [M^+] calcd for $C_{14}H_{18}O_3S$: 266.0977, found 266.0997.

13h: 4-Benzylsulfanylcarbonyl-piperidine-1-carboxylic acid benzyl ester: MW: $C_{21}H_{23}NO_3S = 369.48$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.63$–1.73 (m, 2H), 1.87 (br, 2H), 2.60–2.67 (m, 1H), 2.83–2.89 (br, 2H), 4.22 (s, 2H), 4.12–4.15 (br, 2H), 5.11 (s, 2H), 7.22–7.35 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 28.4$, 32.9, 43.2, 49.8, 67.1, 127.3, 127.8, 128.0, 128.4, 128.6, 128.7, 136.6, 137.3, 155.0, 200.5 ppm; IR (polymer) $\tilde{\nu} = 2947$, 2859, 1695, 1497, 1431, 1225, 968, 699 cm^{-1}; HRMS [M^+] calcd for $C_{21}H_{23}NO_3S$: 369.1399, found 369.1393.

16: Cyclopentyl-thioacetic acid *S*-benzyl ester: MW: $C_{14}H_{18}O = 202.29$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.11$–1.20 (m, 2H), 1.48–1.63 (m, 4H), 1.76–1.84 (m, 2H), 2.23–2.31 (m, 1H), 2.56 (d, $J = 7.4$ Hz, 2H), 4.10 (s, 2H), 7.19–7.29 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 4.8$, 32.3, 33.1, 37.1, 49.7, 127.1, 128.6, 128.7, 137.8, 198.4 ppm; IR (polymer) $\tilde{\nu} =$ 2958, 1694, 1495, 1453, 972, 699 cm^{-1}; HRMS [M^+] calcd for $C_{14}H_{18}O$: 202.1358, found 234.1073.

18: 2-Oxo-cyclopentyl-thioacetic acid *S*-benzyl ester: MW: $C_{14}H_{16}O_2S =$ 248.34; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.53$–1.58 (m, 1H), 1.70–1.81 (m, 1H), 1.92–2.07 (m, 1H), 2.09–2.19 (m, 1H), 2.27–2.32 (m, 2H), 2.41–2.50 (m, 1H), 2.56–2.62 (m, 1H), 3.03 (dd, $J = 9.1$, 3.7 Hz, 1H), 4.11 (s. 2H), 7.21–7.29 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 20.5$, 29.2, 33.2, 37.2, 43.2, 45.9, 127.2, 128.6, 128.7, 137.3, 197.0, 218.6 ppm.

Typical Procedure for Preparation of Alkylsulfonyl Cyanides

19a: (+)-camphor-10-sulfonyl cyanide: A mixture of (+)-camphor-10-sulfonyl chloride (1.25 g, 5 mmol), Na_2SO_3 (630 mg, 5 mmol), and $NaHCO_3$ (840 mg, 10 mmol) in H_2O (10 mL) was stirred at room temperature for 4 h. After the organic impurities in the reaction mixture was removed by washing with ether (10 mL x 2), cyanogen chloride (615 mg, 10 mmol) was added to the reaction mixture in one portion and then the reaction mixture was stirred at 0 °C for 4 h. The mixture was extracted with CH_2Cl_2 (20 mL), and the organic extracts were washed with brine (10 mL x 2), dried over Na_2SO_4, filtered, and concentrated to give an analytically pure (+)-camphor-10-sulfonyl cyanide (**19a**, 1.07 g, 89%). MW: $C_{11}H_{15}NO_3S = 241.31$; ^{1}H NMR ($C_6D_6$, 400 MHz) $\delta = 0.24$ (s, 3H), 0.39 (s, 3H), 0.72–0.77 (m, 1H), 1.29–1.35 (m, 3H), 1.49–1.59 (m, 1H), 1.71–1.84 (m, 2H), 2.67 (d, $J = 15.4$ Hz, 1H), 3.40 ppm(d, $J = 15.4$ Hz, 1H); ^{13}C NMR (C_6D_6, 100 MHz) $\delta = 18.8$, 19.0, 25.4, 26.7, 41.8, 42.6, 47.9, 57.6, 59.1, 114.6, 211.4 ppm; IR (polymer) $\tilde{\nu} = 2977$, 2186, 1736, 1648, 1372, 1182 cm^{-1}; HRMS [M^+] calcd for $C_{11}H_{15}NO_3S$: 241.0773, found 215.0740.

19b: Ethyl 6-(cyanosulfonyl)hexanoate: MW: $C_9H_{15}NO_4S = 233.28$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.23$ (t, $J = 7.1$ Hz, 3H), 1.51–1.57 (m, 2H), 1.64–1.69 (m, 2H), 1.93–2.01 (m, 2H), 2.31 (t, $J = 7.1$ Hz, 2H), 3.36–3.40 (m, 2H), 4.07–4.13 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta =$ 14.1, 22.0, 23.9, 27.0, 33.4, 57.9, 60.4, 112.4, 172.9 ppm.

19c: 4-Phenoxybutane-1-sulfonyl cyanide: MW: $C_{11}H_{13}NO_3S = 239.29$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.97$–2.04 (m, 2H), 2.17–2.25 (m, 2H), 3.49–3.53 (m, 2H), 4.01–4.04 (m, 2H), 6.86–6.98 (m, 3H), 7.26–7.30 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 19.9$, 27.1, 58.1, 66.4, 112.4, 114.3, 121.2, 129.5, 158.2 ppm.

19d: 3-Phenylpropane-1-sulfonyl cyanide: MW: $C_{10}H_{11}NO_2S = 209.26$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 2.27$–2.34 (m, 2H), 2.82–2.85 (m, 2H), 3.30–3.34 (m, 2H), 7.16–7.35 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 23.7$, 33.2, 57.3, 112.4, 127.0, 128.3, 128.9, 138.3 ppm.

19e: 2-(Trimethylsilyl)ethanesulfonyl cyanide: MW: $C_6H_{13}NO_2SSi =$ 191.32; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 0.10$ (s, 9H), 1.13–1.17 (m, 2H), 3.25–3.30 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = -2.0$, 9.1, 55.7, 112.3 ppm.

19f: Octane-1-sulfonyl cyanide: MW: $C_9H_{17}NO_2S = 203.30$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 0.86$ (t, $J = 7.0$ Hz, 3H), 1.26–1.36 (m, 8H), 1.47–1.50 (m, 2H), 1.91–1.99 (m, 2H), 3.35 ppm (t, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 13.9$, 22.2, 22.4, 27.6, 28.7, 28.7, 31.5, 58.3, 112.6 ppm.

19g: 2-(Naphthalen-1-yl)ethanesulfonyl cyanide: MW: $C_{13}H_{11}NO_2S =$ 245.30; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 3.68$–3.74 (m, 4H), 7.38–7.45 (m, 2H), 7.51–7.62 (m, 2H), 7.82–7.91 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 25.7$, 58.5, 112.4, 122.0, 125.5, 126.2, 127.1, 127.1, 128.8, 129.3, 130.6, 130.8, 134.0 ppm.

19h: 4-(2-Chlorophenyl)butane-2-sulfonyl cyanide: MW: $C_{12}H_{15}ClNO_2S =$ 257.74; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.56$–1.63 (m, 3H), 1.96–2.00 (m, 1H), 2.43–2.46 (m, 1H), 2.88–2.99 (m, 2H), 3.25–3.29 (m, 1H), 7.17–7.24 (m, 3H), 7.36–7.37 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 213.0$, 28.8, 30.0, 62.7, 111.5, 127.3, 128.5, 129.9, 130.4, 136.6 ppm.

Typical Procedure for the Direct Conversion of RSO_2CN into RCOCN

Dried heptane (20 mL), (+)-camphor-10-sulfonyl cyanide (**19a**) (48 mg, 0.2 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was sealed, purged three times with 10 atm of CO, pressurized with 95 atm of CO, and then heated at 120 °C with stirring for 24 h. After excess CO was discharged at room temperature, the reaction mixture was poured into a 100 mL round-bottom flask, quenched with excess MeOH at room temperature for 4 h with stirring. After the solvent and MeOH were removed under reduced pressure, the residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (1:50) as eluant to give **21a** (40 mg, 84%).

MW: $C_{12}H_{18}O_3 = 210.27$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 0.85$ (s, 3H), 0.93 (s, 3H), 1.32–1.37 (m, 1H), 1.69–1.75 (m, 1H), 1.83 (d, $J = 18.3$ Hz, 1H), 1.92–2.05 (m, 3H), 2.18 (d, $J = 15.0$ Hz, 1H), 2.28–2.36 (m, 1H), 2.46 (d, $J = 15.0$ Hz, 1H), 3.63 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 19.4$, 19.8, 26.8, 26.9, 30.5, 42.7, 43.1, 47.2, 51.4, 58.9, 172.4, 216.4 ppm; IR (polymer) $\tilde{\nu} = 2954$, 1743, 1417, 1315, 1279, 1196, 1171 cm^{-1}; HRMS [M^+] calcd for $C_{12}H_{18}O_3$: 210.1256, found 210.1240.

21b: 6-Phenylcarbamoyl-hexanoic acid ethyl ester: MW: $C_{15}H_{21}NO_3 =$ 263.33; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.22$ (t, $J = 7.2$ Hz, 3H), 1.34–1.58 (m, 2H), 1.60–1.74 (m, 4H), 2.26–2.34 (m, 4H), 4.09 (q, $J = 7.1$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 1H), 7.25–7.29 (m, 2H), 7.5 (d, $J = 7.9$ Hz, 2H), 7.64 ppm (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 14.2$, 24.4, 25.1, 28.5, 34.0, 37.2, 60.2, 119.8, 124.0, 128.8, 138.0, 171.3, 173.7 ppm; IR (polymer) $\tilde{\nu} = 3319$, 2941, 1734, 1669, 1601, 1541, 1444, 758 cm^{-1}; HRMS [M^+] calcd for $C_{15}H_{21}NO_3$: 263.1521, found 263.1521.

21c: 5-Phenoxy-pentanoic acid phenylamide: MW: $C_{17}H_{19}NO_2 = 269.34$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.86$–1.94 (m, 4H), 2.43 (t, 2H, $J =$ 6.9 Hz), 4.00 (t, 2H, $J = 5.9$ Hz), 6.87–6.95 (m, 3H), 7.06–7.10 (m, 1H), 7.24–7.32 (m, 5H), 7.48–7.50 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 2.5$, 28.6, 37.2, 67.5, 114.4, 119.8, 120.7, 124.2, 129.0, 129.5, 137.9, 158.9, 170.9 ppm; IR (polymer) $\tilde{\nu} = 3314$, 2920, 1667, 1601, 1541, 1499, 1246, 755 cm^{-1}; HRMS [M^+] calcd for $C_{17}H_{19}NO_2$:269.1416:, found 269.1412.

21d: 4,*N*-Diphenyl-butyramide: MW: $C_{16}H_{17}NO = 239.31$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 2.04$ (m, 2H), 2.32 (t, 2H, $J = 7.6$ Hz), 2.68 (t, 2H, $J = 7.4$ Hz), 7.07–7.10 (m, 1H), 7.16–7.21 (m, 3H), 7.24–7.31 (m, 4H), 7.40 (br, 1H), 7.48–7.50 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta =$ 26.8, 35.0, 36.7, 119.8, 124.2, 126.0, 128.4, 128.5, 128.9, 137.9, 141.3, 171.1 ppm; IR (polymer) $\tilde{\nu} = 3325$, 1698, 1600, 1553, 1499, 1443, 756, 698 cm^{-1}; HRMS [M^+] calcd for $C_{16}H_{17}NO$: 239.1310, found 239.1295.

21h: 4-(2-Chloro-phenyl)-2-methyl-*N*-phenyl-butyramide: MW: $C_{17}H_{18}ClNO = 287.78$; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.28$ (d, $J = 6.9$ Hz, 3H), 1.76–1.83 (m, 1H), 2.02–2.12 (m, 1H), 2.34–2.39 (m, 1H), 2.79 (dis, t, 2H), 7.09–7.21 (m, 5H), 7.28–7.32 (m, 3H), 7.52 ppm (d, $J = 7.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 18.1$, 31.3, 34.1, 42.1, 119.9, 124.5, 126.9, 127.5, 129.0, 129.5, 130.4, 133.9, 137.9, 139.2, 174.3 ppm; IR (poly-

mer) $\tilde{\nu}$ = 3303, 2934, 1662, 1601, 1540, 1442, 753 cm^{-1}; HRMS [M^+] calcd for $C_{17}H_{18}ClNO$: 287.1077, found 287.1073.

Typical Procedure for the Preparation of Alkylsulfonyl Oxime Ethers

A mixture of methyl 2-(benzyloxyimino)acetate (**23**, 1.36 g, 7 mmol), and *N*-chlorosuccinimide (2.82 g, 21 mmol) in DMF (15 mL) was stirred at 50 °C for 2 days. The mixture was diluted with Et_2O (60 mL), washed with brine (30 mL x 2), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give methyl 2-(benzyloxyimino)-2-chloroacetate (**24**, 1.55 g, 97 %). MW: $C_{10}H_{10}ClNO_3$ = 227.64; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.89 (s, 3H), 5.36 (s, 2H), 7.35–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 53.9, 78.8, 128.5, 128.6, 128.6, 130.9, 135.4, 159.0 ppm.

Ethanethiol (342 mg, 5.5 mmol) was added to a slurry of NaH (200 mg, 5 mmol) in DMF (10 mL) at 0 °C. After being stirred at 0 °C for 30 min, **24** (1.25 g, 5.5 mmol) was added to the reaction mixture at 0 °C. The resulting reaction mixture was stirred at room temperature for 5 h, treated with NH_4Cl (aq), diluted with Et_2O (50 mL), washed with brine (30 mL x 2), dried over $MgSO_4$, and concentrated. The residue was purified by a column chromatography on silica gel using ethyl acetate and *n*-hexane (1:10) as eluant to give **25** (1.24 g, 98 %). MW: $C_{12}H_{15}NO_3S$ = 253.32; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.24 (t, J = 7.4 Hz, 3H), 2.99 (q, J = 7.4 Hz, 2H), 3.85 (s, 3H), 5.27 (s, 2H), 7.26–7.35 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 15.2, 25.8, 53.1, 77.8, 128.0, 128.1, 128.4, 136.5, 147.0, 161.3 ppm.

A solution of **25** (1.24 g, 4.9 mmol) in CH_2Cl_2 (25 mL) was treated with $NaHCO_3$ (1.23 g, 14.7 mmol), and *m*-CPBA (3.29 g, 14.7 mmol) at 0 °C successively. After being stirred at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2 (25 mL), washed with 10 % $Na_2S_2O_3$ (aq, 50 mL), $NaHCO_3$ (aq, 50 mL), and brine (30 mL x 2), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:3) as eluant to give methyl 2-(benzyloxyimino)-2-(ethylsulfonyl)acetate (**26a**, 1.38 g, 99 %). MW: $C_{12}H_{15}NO_5S$ = 285.32; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.25 (t, J = 7.5 Hz, 3H), 3.27 (q, J = 7.5 Hz, 2H), 3.87 (s, 3H), 5.35 (s. 2H), 7.35–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 6.3, 51.0, 53.7, 80.2, 128.4, 128.7, 128.9, 134.6, 145.8, 159.0 ppm; IR (polymer) $\tilde{\nu}$ = 2957, 1751, 1600, 1455, 1336, 1151, 997 cm^{-1}; HRMS [M^+] calcd for $C_{12}H_{15}NO_5S$: 285.0671, found 285.0664.

Typical Procedure for the Direct Conversion of Alkylsulfonyl Oxime Ethers into Acylated Oxime Ethers

Dried heptane (20 mL), **23a** (57 mg, 0.2 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was sealed, purged triple with 10 atm of CO, pressurized with 50 atm of CO, and then heated at 120 °C with stirring for 18 h. After excess CO was discharged at room temperature, the solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (1:50) as eluant to give 2-Benzyloxyimino-3-oxo-pentanoic acid methyl ester (**27a**) (48 mg, 96 %).

MW: $C_{13}H_{15}NO_4$ = 249.26; major : minor = 4.13:1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ = 1.08 (t, J = 7.3 Hz, 3H), 2.76 (q, J = 7.3 Hz, 2H), 3.84 (s, 3H), 5.28 (s, 2H), 7.31–7.35 ppm (m, 5H); minor: δ = 1.09 (t, J = 7.3 Hz, 3H), 2.61 (q, J = 7.3 Hz, 2H), 3.84 (s, 3H), 5.27 (s, 2H), 7.31–7.35 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ = 7.5, 31.0, 52.6, 78.5, 128.2, 128.4, 128.5, 135.9, 149.6, 161.6, 195.7 ppm; minor: δ = 6.6, 36.0, 53.0, 78.8, 128.3, 128.5, 128.6, 135.6, 150.2, 160.7, 199.7 ppm; IR (polymer) $\tilde{\nu}$ = 2943, 1751, 1696, 1457, 1296, 1218, 1007, 700 cm^{-1}; HRMS [M^+] calcd for $C_{13}H_{15}NO_4$: 249.1001, found 249.0999.

26b: 4-(Benzyloxyimino-methoxycarbonyl-methanesulfonyl)-butyric acid methyl ester: MW: $C_{15}H_{19}NO_7S$ = 357.38; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.99–2.05 (m, 2H), 2.37 (t, 2H, J = 7.0 Hz), 3.33–3.37 (m, 2H), 3.64 (s, 3H), 3.89 (s, 3H), 5.37 (s, 2H), 7.36 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 17.5, 31.7, 51.8, 53.8, 55.5, 80.5, 128.6, 128.8, 129.1, 134.6, 145.9, 159.1, 172.2 ppm; IR (polymer) $\tilde{\nu}$ = 2923, 1756, 1456, 1371, 1323, 1092, 985, 757 cm^{-1}; HRMS [M^+] calcd for $C_{15}H_{19}NO_7S$: 357.0882, found 357.0881.

26c: Benzyloxyimino-(4-phenoxy-butane-1-sulfonyl)-acetic acid methyl ester: MW: $C_{20}H_{23}NO_6S$ = 405.47; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.77–1.82 (m, 2H), 1.88–1.94 (m, 2H), 3.35 (t, 2H, J = 7.7 Hz), 3.87 (t, 2H, J = 5.87), 3.89 (s, 3H), 5.34 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 19.1, 27.7, 53.8, 56.3, 66.6, 80.5, 144.4, 120.9, 128.6, 128.8, 129.1, 129.5, 134.7, 146.2, 158.6, 159.1 ppm; IR (polymer) $\tilde{\nu}$ = 1773, 1336, 1291, 1279, 1143, 1010, 758, 696 cm^{-1}; HRMS [M^+] calcd for $C_{20}H_{23}NO_6S$: 405.1246, found 405.1270.

26d: Benzyloxyimino-[4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-butane-1-sulfonyl]-acetic acid methyl ester: MW: $C_{22}H_{22}N_2O_7S$ = 458.49; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.66–1.77 (m, 4H), 3.30 (t, 2H, J = 8.0 Hz), 3.57 (t, 2H, J = 6.9 Hz), 3.87 (s, 3H), 5.37 (s, 2H), 7.32–7.36 (m, 5H), 7.68–7.71 (m, 2H), 7.80–7.82 ppm(m 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 19.3, 27.0, 36.8, 53.8, 55.7, 80.4, 123.2, 128.6, 128.8, 129.0, 131.9, 134.2, 134.6, 146.0, 159.0, 168.1; IR (polymer) $\tilde{\nu}$ = 2956, 1772, 1747, 1437, 1332, 1279, 1034, 745 cm^{-1}; HRMS [M^+] calcd for $C_{22}H_{22}N_2O_7S$: 458.1148, found 458.1181.

26e: Benzyloxyimino-cyclohexanesulfonyl-acetic acid methyl ester: MW: $C_{16}H_{21}NO_5S$ = 339.41; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.04–1.17 (m, 3H), 1.50–1.53 (m, 2H), 1.61–1.64 (m, 1H), 1.80–1.84 (m, 2H), 1.94–1.97 (m, 2H), 3.27–3.33 (m, 1H), 3.88 (s, 3H), 5.36 (s, 2H), 7.34–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.1, 24.8, 25.0, 53.8, 64.2, 80.3, 128.6, 128.8, 129.0, 134.9, 146.0, 159.4 ppm; IR (polymer) $\tilde{\nu}$ = 2938, 2859, 1794, 1351, 1283, 1092, 1011, 741 cm^{-1}; HRMS [M^+] calcd for $C_{16}H_{21}NO_5S$: 339.1140, found 339.1163.

26g: Cyclohexyldulfonylmethanal *O*-benzyl oxime: MW: $C_{14}H_{19}NO_3S$ = 281.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.11–1.15 (m, 3H), 1.46–1.50 (m, 2H), 1.61–1.64 (m, 1H), 1.80–1.84 (m, 2H), 1.91–1.95 (m, 2H), 3.26 (m, 1H), 5.29 (s, 2H), 7.17 (s, 1H), 7.33–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.1, 24.8, 25.1, 63.2, 79.1, 128.5, 128.7, 128.8, 135.6, 142.6 ppm; IR (polymer) $\tilde{\nu}$ = 2938, 2858, 1452, 1369, 1115, 1015, 757, 699 cm^{-1}; HRMS [M^+] calcd for $C_{14}H_{19}NO_3S$: 281.1086, found 281.1082.

27b: 2-Benzyloxyimino-3-oxo-heptanedioic acid dimethyl ester: MW: $C_{16}H_{19}NO_6$ = 321.33; major : minor = 2.54:1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ = 1.88–1.95 (m, 2H), 2.34 (t, J = 7.3 Hz, 2H), 2.81 (t, J = 7.2 Hz, 2H), 3.64 (s, 3H), 3.84 (s, 3H), 5.28 (s, 2H), 7.31–7.37 ppm (m, 5H); minor: δ = 1.89–1.97 (m, 2H), 2.31 (t, J = 7.3 Hz, 2H), 2.67 (t, J = 7.0 Hz, 2H), 3.62 (s, 3H), 3.84 (s, 3H), 5.26 (s, 2H), 7.29–7.36 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ = 18.7, 32.9, 36.6, 51.2, 52.6, 78.7, 128.2, 128.5, 128.6, 135.8, 149.7, 161.5, 173.4, 194.3 ppm; minor: δ = 17.8, 32.6, 41.5, 51.5, 53.1, 78.9, 128.4, 128.6, 128.6, 135.5, 150.0, 160.6, 173.3, 198.3 ppm; IR (polymer) $\tilde{\nu}$ = 2955, 1748, 1695, 1456, 1302, 1213, 1000, 700 cm^{-1}; HRMS [M^+] calcd for $C_{16}H_{19}NO_6$: 321.1212, found 321.1218.

27c: 2-Benzyloxyimino-3-oxo-7-phenoxy-heptanoic acid methyl ester: MW: $C_{21}H_{23}NO_5$ = 369.41; major : minor = 2.96:1; ^{1}H NMR ($CDCl_3$, 400 MHz) major: δ = 1.78–1.81 (m, 4H), 2.82–2.85 (m, 2H), 3.85 (s, 3H), 3.92–3.95 (m, 2H), 5.29 (s, 2H), 6.85–6.94 (m, 3H), 7.24–7.28 (m, 2H), 7.32–7.36 ppm (m,5H); minor: δ = 1.73–1.81 (m, 4H), 2.67 (dis, t, 2H), 3.84 (s, 3H), 3.87 (dis, t, 2H), 5.27 (s, 2H), 6.83–6.93 (m, 3H), 7.23–7.25 (m, 2H), 7.27–7.32 ppm (m,5H); ^{13}C NMR ($CDCl_3$, 100 MHz) major: δ = 20.4, 28.5, 37.1, 52.6, 67.2, 78.5, 114.4, 120.6, 128.2, 128.5, 128.5, 129.4, 135.8, 149.8, 158.9, 161.6, 194.9 ppm; minor: δ = 19.2, 28.4, 42.1, 53.1, 67.1, 78.9, 114.4, 120.6, 128.4, 129.6, 129.4, 135.5, 150.2, 158.9, 160.7, 198.8 ppm; IR (polymer) $\tilde{\nu}$ = 2953, 1748, 1694, 1601, 1498, 1245, 1000, 755, 694 cm^{-1}; HRMS [M^+] calcd for $C_{21}H_{23}NO_5$: 369.1576, found 369.1575.

27f: 2-Oxo-butyraldehyde *O*-benzyl-oxime: MW: $C_{11}H_{13}NO_2$ = 191.23; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.09 (t, 3H, J = 7.4 Hz), 2.77 (q, 2H, J = 7.4 Hz), 5.23 (s, 2H), 7.33–7.37 (m, 5H), 7.49 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 7.6, 31.2, 77.7, 128.4, 128.5, 128.5, 136.2, 147.7, 198.9 ppm; IR (polymer) $\tilde{\nu}$ = 2940, 1695, 1587, 1368, 1187, 1020, 924, 699 cm^{-1}; HRMS [M^+] calcd for $C_{11}H_{13}NO_2$:191.0946, found 191.0949.

30a: Pentane-2,3,4-trione 3-(*O*-benzyl-oxime): MW: $C_{12}H_{13}NO_3$ = 219.24; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.27 (s, 3H), 2.35 (s, 3H), 5.25 (s, 2H),

7.31–7.36 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=25.6 (30.5), 78.6, 128.4, 128.6, 128.6, 156.1, 194.3 ppm (198.3); IR (polymer) $\tilde{\nu}$=2928, 1795, 1651, 1366, 1300, 998, 731, 700 cm^{-1}; HRMS [M^+] calcd for $C_{12}H_{13}NO_3$:219.0895, found 219.0896.

31a: 1-Methanesulfonyl-propane-1,2-dione 1-(*O*-benzyl-oxime): MW: $C_{11}H_{13}NO_4S$=255.29; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.46 (s, 3H), 3.14 (s, 3H), 5.31 (s, 2H), 7.33–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=31.4, 42.9, 79.9, 128.6, 128.8, 129.0, 134.7, 155.5, 193.0 ppm; IR (polymer) $\tilde{\nu}$=1729, 1335, 1214, 1009, 938, 764, 700, 526 cm^{-1}; HRMS [M^+] calcd for $C_{11}H_{13}NO_4S$: 255.0565, found 255.0551.

29b: Bis-ethanesulfonyl-methanone *O*-benzyl-oxime: MW: $C_{12}H_{17}NO_5S_2$=319.40, ^{1}H NMR ($CDCl_3$, 400 MHz) : δ=1.27–1.36 (m, 6H), 3.29 (q, 2H, J=9.9 Hz), 3.44 (q, 2H, J=9.9 Hz), 5.48 (s, 2H), 7.36 ppm (m, 5H), ^{13}C NMR ($CDCl_3$, 100 MHz) : δ=6.1 (6.8), 49.9 (51.4), 81.7, 128.8, 128.9, 129.3, 134.0, 150.2 ppm; IR (polymer) : $\tilde{\nu}$=2985, 1538, 1456, 1346, 1162, 1046, 994, 701 cm^{-1}; HRMS [M^+] calcd for $C_{12}H_{17}NO_5S_2$:319.0548, found 319.0543.

30b: Heptane-3,4,5-trione 4-(*O*-benzyl-oxime): MW: $C_{14}H_{17}NO_3$=247.29, ^{1}H NMR ($CDCl_3$, 400 MHz) : δ=1.04–1.09 (m, 6H), 2.52 (q, 2H, J=7.2 Hz), 2.77 (q, 2H, J=7.2 Hz), 5.22 (s, 2H), 7.29–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ=6.5 (7.5), 31.4 (36.5), 78.4, 128.2, 128.5, 128.6, 136.0, 155.8, 197.4 ppm, (201.8); IR (polymer) : $\tilde{\nu}$=2981, 1688, 1458, 1407, 1364, 1087, 749, 700 cm^{-1}; HRMS [M^+] calcd for $C_{14}H_{17}NO_3$:247.1208, found 247.1202.

31b: 1-Ethanesulfonyl-butane-1,2-dione 1-(*O*-benzyl-oxime): MW: $C_{13}H_{17}NO_4S$=283.34, ^{1}H NMR ($CDCl_3$, 400 MHz) : δ=1.09 (t, 3H, J=7.2 Hz), 1.29 (t, 3H, J=7.4 Hz), 2.74 (q, 2H, J=7.2 Hz), 3.23 (q, 2H, J=7.4 Hz), 5.28 (s, 2H), 7.29–7.38 ppm (m, 5H), ^{13}C NMR ($CDCl_3$, 100 MHz) : δ=6.6, 6.6, 37.3, 49.5, 79.5, 128.6, 128.7, 128.9, 135.0, 155.0, 197.1 ppm; IR (polymer): $\tilde{\nu}$=2983, 1772, 1591, 1367, 1090, 980, 922, 742 cm^{-1}; HRMS [M^+] calcd for $C_{13}H_{17}NO_4S$: 283.0878, found 283.0878.

Acknowledgements

We thank Korea Science and Engineering Foundation (R01-2007-000-21315-0), the Center for Molecular Design & Synthesis, KEPCO, and BK21 for financial support.

[1] a) C. P. Jasperse, D. P. Curran, T. L. Fevig, *Chem. Rev.* **1991**, *91*, 1237; b) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon, New York, **1986**; c) M. Ramaiah, *Tetrahedron* **1987**, *43*, 3542; d) D. P. Curran, *Synthesis* **1988**, 417 (part 1); D. P. Curran, *Synthesis* **1988**, 489 (part 2); e) C. Thebtaranonth, Y. Thebtaranonth, *Tetrahedron* **1990**, *46*, 1412; f) E. R. Laird, W. L. J. Jorgenson, *J. Org. Chem.* **1990**, *55*, 9; g) "Radical Addition Reactions" and "Radical Cyclization Reactions and Sequential Radical Reactions": D. P. Curran in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**; h) C. H. Schiesser, L. M. Wild, *Tetrahedron* **1996**, *52*, 13265.

[2] For reviews, a) P. A. Baguley, J. C. Walton, *Angew. Chem.* **1998**, *110*, 3272; *Angew. Chem. Int. Ed.* **1998**, *37*, 3072; b) C. Ollivier, P. Renaud, *Chem. Rev.* **2001**, *101*, 3415; c) F. Bertrand, F. L. Guyader, L. Liguori, G. Ouvry, B. Quiclet-Sire, S. Seguin, S. Z. Zard, *C. R. Acad. Sci. Ser. IIc* **2001**, *4*, 547; d) A. Studer, S. Amrein, *Synthesis* **2002**, 835.

[3] a) S. Kim, H.-J. Song, T.-L. Choi, J.-Y. Yoon, *Angew. Chem.* **2001**, *113*, 2592; *Angew. Chem. Int. Ed.* **2001**, *40*, 2524; b) S. Kim, C. J. Lim, C. Song, W.-J. Chung, *J. Am. Chem. Soc.* **2002**, *124*, 14306; c) S. Lee, C. J. Lim, S. Kim, *Bull. Korean Chem. Soc.* **2004**, *25*, 1611; d) S. Kim, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 809.

[4] a) S. Kim, C. J. Lim, *Bull. Korean Chem. Soc.* **2003**, *24*, 1219; b) S. Kim, S. Kim, N. Otsuka, I. Ryu, *Angew. Chem.* **2005**, *117*, 6339; *Angew. Chem. Int. Ed.* **2005**, *44*, 6183; c) S. Kim, C. H. Cho, S. Kim, Y. Uenoyama, I. Ryu, *Synlett* **2005**, 3160; d) S. Kim, K.-C. Lim, S. Kim, I. Ryu, *Adv. Synth. Catal.* **2007**, *349*, 527.

[5] S. Kim, K.-C. Lim, S. Kim, *Chem. Commun.* **2007**, 4507.

[6] For a review, D. Crich, L. Quintero, *Chem. Rev.* **1989**, *89*, 1413.

[7] For reviews, a) S. Z. Zard, *Angew. Chem.* **1997**, *109*, 724; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 672; b) S. Z. Zard, *Chem. Eur. J.* **2006**, *12*, 6002.

[8] a) C. Chatgilialoglu in *The Chemistry of Sulfones and Sulfoxides* (Eds.: S. Patai, Z. Rappoport, C. J. M. Stirling), Wiley, New York, **1988**, p. 1089; b) M. Bertrand, *Org. Prep. Proced. Int.* **1994**, *26*, 257.

[9] For reviews on radical carbonylation, a) I. Ryu, N. Sonoda, *Angew. Chem.* **1996**, *108*, 1140–1157; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1050–1066; b) I. Ryu, N. Sonoda, D. P. Curran, *Chem. Rev.* **1996**, *96*, 177–194; c) I. Ryu, *Chem. Soc. Rev.* **2001**, *30*, 16–25; d) I. Ryu, *Chem. Rec.* **2002**, 249–258.

[10] a) K. W. Watkins, W. W. Word, *Int. J. Chem. Kinet.* **1974**, *6*, 855; b) A. Bakac, J. H. Espenson, *J. Chem. Soc. Chem. Commun.* **1991**, 1497; c) A. Bakac, J. H. Espenson, V. G. Young, Jr., *Inorg. Chem.* **1992**, *31*, 4959; d) K. W. Watkins, W. W. Thompson, *Int. J. Chem. Kinet.* **1973**, *5*, 791; e) K. Nagahara, I. Ryu, N. Kambe, M. Komatsu, N. Sonoda, *J. Org. Chem.* **1995**, *60*, 7384; f) W. T. Boese, A. S. Goldman, *Tetrahedron Lett.* **1992**, *33*, 2119.

[11] a) H. W. Pinnick, M. A. Reynolds, *J. Org. Chem.* **1979**, *44*, 160; b) J. D. Macke, L. Field, *J. Org. Chem.* **1988**, *53*, 396.

[12] J.-P. Mahieu, M. Gosselet, B. Sebille, Y. Beuzard, *Synth. Commun.* **1986**, *16*, 1709.

[13] M. Kita, M. Watanabe, N. Takada, K. Suenaga, K. Yamada, D. Uemura, *Tetrahedron* **2002**, *58*, 6405.

[14] For a review on acyl cyanides, a) J. Thesing, D. Witzel, A. Brehm, *Angew. Chem.* **1956**, *68*, 425; b) S. Hünig, R. Schaller, *Angew. Chem.* **1982**, *94*, 1; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 36.

[15] For recent reports on acyl cyanides a) Y. Yamamoto, K. Kinpara, T. Saigoku, H. Takagishi, S. Okuda, H. Nishiyama, K. Itoh, *J. Am. Chem. Soc.* **2005**, *127*, 605; b) C. Duplais, F. Bures, I. Sapountzis, T. J. Tobias, G. Cahiez, P. Knochel, *Angew. Chem.* **2004**, *116*, 3028; *Angew. Chem. Int. Ed.* **2004**, *43*, 2968; c) T. Watahiki, S. Ohba, T. Oriyama, *Org. Lett.* **2003**, *5*, 2679; d) B. W. Yoo, D. Y. Kim, J. W. Choi, S. K. Hwang, K. I. Choi, J. H. Kim, *Bull. Korean Chem. Soc.* **2003**, *24*, 263; e) P. Saikia, D. D. Laskar, D. Prajapati, J. S. Sandhu, *Tetrahedron Lett.* **2002**, *43*, 7525; f) B. W. Yoo, S. K. Hwang, D. Y. Kim, J. W. Choi, J. J. Ko, K. I. Choi, J. H. Kim, *Tetrahedron Lett.* **2002**, *43*, 4813.

[16] a) Y.-Q. Cao, Y.-F. Du, B.-H. Chen, J.-T. Li, *Synth. Commun.* **2004**, *34*, 2951; b) G. A. Olah, M. Arvanaghi, G. K. S. Prakash, *Synthesis* **1983**, 636; c) T. Ando, T. Kawate, J. Tamawaki, T. Hanafusa, *Synthesis* **1983**, 637.

[17] M. Tanaka, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 637.

[18] a) G. H. Coleman, R. W. Leeper, C. C. Schulze, *Inorg. Synth.* **1946**, *2*, 90; b) M. S. A. Vrijland, *Org. Synth.* **1977**, *57*, 88.

[19] a) E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1980**, *21*, 731; b) B. S. Bal, W. E. Childers, H. W. Pinnick, Jr., *Tetrahedron* **1981**, *37*, 2091.

[20] a) I. Ryu, H. Kuriyama, S. Minakata, M. Komatsu, J.-Y. Yoon, S. Kim, *J. Am. Chem. Soc.* **1999**, *121*, 12190; b) I. Ryu, H. Kuriyama, H. Miyazato, S. Minakata, M. Komatsu, J.-Y. Yoon, S. Kim, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1407.

Received: April 3, 2008
Published online: July 30, 2008

