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Fluorinated Johnson Reagent for Transfer-Trifluoromethylation to Carbon Nucleophiles

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A novel reagent, [(oxido)phenyl(trifluoromethyl)-λ^4-sulfanylidene]dimethylammonium tetrafluoroborate has been developed for the electrophilic trifluoromethylation of carbon nucleophiles. The reagent was designed as a trifluorinated version of a Johnson-type methyl-transfer reagent. The first example of vinylogous trifluoromethylation of dicyanoalkylidenes is also demonstrated.

Introduction

Since the discovery by Yagupolskii and co-workers that diaryl(trifluoromethyl)sulfonium salts are effective for the trifluoromethylation of thiophenolates,[1] the design and synthesis of electrophilic trifluoromethylating reagents have been extensively researched in both academic and industrial fields, due to the significant unique features that trifluoromethylated compounds have in pharmaceuticals, agricultural chemicals,[2] and functional materials. Among the several reagents developed,[3,4] *S*-(trifluoromethyl)dibenzothiophenium salts designed by Umemoto et al. have emerged as one of the most powerful tools for this purpose.[3a–3d] A series of Umemoto reagents are commercially available and are effective for the trifluoromethylation of hetero-nucleophiles, however, yields for the trifluoromethylation of carbon nucleophiles are not satisfactory, with the exception of the Cahard's modification protocol.[5] Recently, Togni et al. reported that the hypervalent iodine(III)–CF_3 reagent is a mild electrophilic trifluoromethylating reagent of carbon- and heteroatom-centered nucleophiles (Figure 1).[4e–4g] This new reagent has wide generality for effecting trifluoromethylation of a range of nucleophiles; however, more effective reagents are required for the trifluoromethylation of carbon nucleophiles, in particular β-keto esters.

In connection with our interest in the enantiocontrolled synthesis of organo-fluorine compounds,[6,7] we required new reagents for the electrophilic trifluoromethylation of carbon nucleophiles, in order to further develop the enantioselective electrophilic trifluoromethylation reaction.[2,8] We herein disclose the design, synthesis and evaluation of [(oxido)phenyl(trifluoromethyl)-λ^4-sulfanylidene]dimethylammonium tetrafluoroborate (**1**) for the electrophilic trifluoromethylation of β-keto esters **2**. We also demonstrate the first *vinylogous* trifluoromethylation of dicyanoalkylidenes **4** using **1** (Scheme 1).

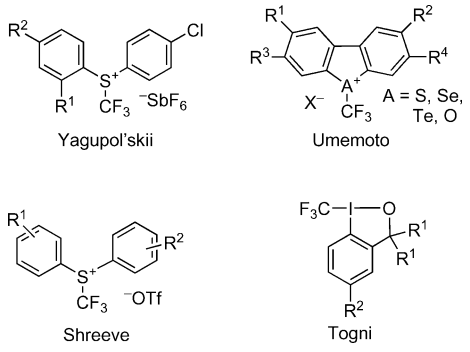
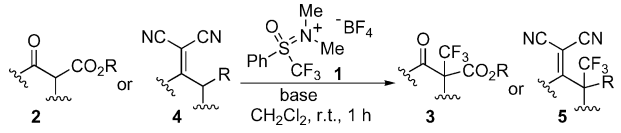


Figure 1. Electrophilic trifluoromethylating reagents.



Scheme 1. A novel reagent **1** for trifluoromethylation of carbon nucleophiles.

Results and Discussion

Forty years ago, Johnson and co-workers introduced [methyl(oxido)phenyl-λ^4-sulfanylidene]dimethylammonium tetrafluoroborate (**6**) for methylene transfer reactions such

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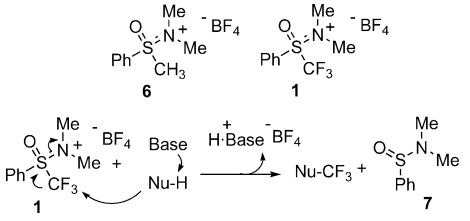
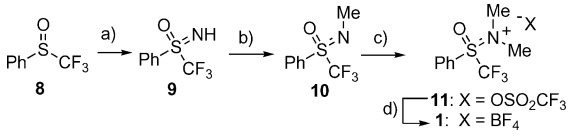
as cyclopropanation and aziridine formation.[9] The methylene transfer from **6** over a wide range of substrates is promoted by the cleavage of the good leaving group, *N*,*N*-dimethylbenzenesulfinamide (**7**). Since then, **6** and related compounds have gained substantial synthetic significance as immensely powerful tools for methylene transfer.[9d,9e] This success led us to investigate the synthesis of the trifluorinated version of **6** (salt **1**) as a novel electrophilic reagent for trifluoromethylation. Transfer of the CF_3 group from **1** to the substrates should proceed via the reaction with the nucleophiles to give the trifluoromethylated adducts, displacing **7** (Scheme 2).



Scheme 2. Johnson's reagent **6** and the newly designed reagent **1**.

The salt **1** was synthesized by the procedure shown in Scheme 3. Phenyl trifluoromethyl sulfoxide **8** was synthesized from the nucleophilic trifluoromethylation of methyl phenylsulfinate with $TMSCF_3$, the Friedel–Crafts reaction of benzene with sodium trifluoromethanesulfinate or the oxidation of trifluoromethyl phenyl sulfide.[1,3,10] Conversion of sulfoxide **8** to sulfoximine **9** was done under conventional NaN_3/H_2SO_4 conditions.[11] The stepwise methylation of **9** with MeI/K_2CO_3 followed by the treatment with methyl trifluoromethansulfonate gave the trifluoromethanesulfonate **11** as a viscous oil. Finally, **11** was successively transformed into **1** by $NaBF_4$ in MeOH to give colourless crystals in high yield (Scheme 3). The salt **1** is a relatively stable, easy to handle solid, and was characterized by single-crystal X-ray crystallography, which shows that N1 adopts a nearly planar, sp^2-like structure, as evidenced by the sum of the dihedral angles (350.83°) between S–N1–C8 (119.6°), S–N1–C9 (117.29°) and C8–N1–C9 (113.94°). In addition, the N1–S bond length is 1.5810 Å which is shorter than the typical length of an N–S bond (1.656 Å)[12] and similar to the length of a typical N=S double bond (1.541 Å).[12] Therefore, a cation is presumed to be located on N1 rather than on the sulfur atom (Figure 2).



Scheme 3. a) NaN_3, 25% fuming H_2SO_4, 70 °C, 3 h, 81%; b) CH_3I, K_2CO_3, THF, reflux, 7 h, 97%; c) methyl trifluoromethansulfonate, neat, room temp., 6 h, 93%; d) sat. $NaBF_4$ aq., MeOH, room temp., 13 h, 92%.

To optimize the trifluoromethylation of carbon nucleophiles, we first examined the reaction of β-keto ester **2a** with **1**. The solvent and base were varied, and the results are summarized in Table 1.

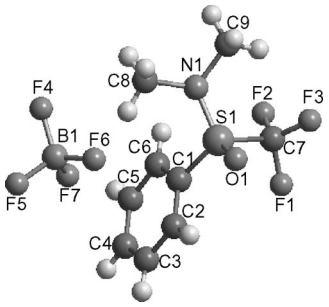
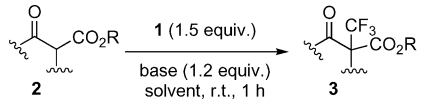
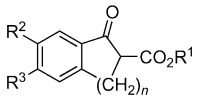
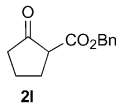


Figure 2. X-ray crystallographic structure of **1**.

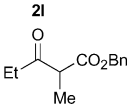
Table 1. Trifluoromethylation of β-keto esters **2** with **1**.[a]







2a: R^1 = Me, R^2 = R^3 = H, *n* = 1
2b: R^1 = Et, R^2 = R^3 = H, *n* = 1
2c: R^1 = *i*Pr, R^2 = R^3 = H, *n* = 1
2d: R^1 = Bn, R^2 = R^3 = H, *n* = 1
2e: R^1 = *t*Bu, R^2 = R^3 = H, *n* = 1
2f: R^1 = 2-adamantyl, R^2 = R^3 = H, *n* = 1
2g: R^1 = Me, R^2 = R^3 = OMe, *n* = 1
2h: R^1 = *t*Bu, R^2 = R^3 = OMe, *n* = 1
2i: R^1 = *t*Bu, R^2 = H, R^3 = Br, *n* = 1
2j: R^1 = Me, R^2 = R^3 = H, *n* = 2
2k: R^1 = *t*Bu, R^2 = R^3 = H, *n* = 2



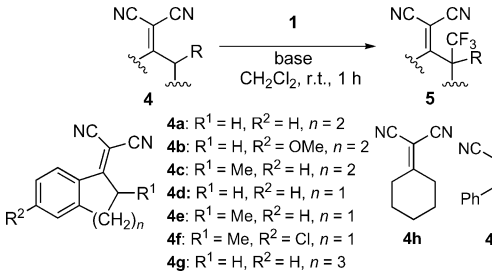
Entry	2	Base[b]	Solvent	3	Yield[c] (%)
1	**2a**	DBU	CH_2Cl_2	**3a**	93
2	**2a**	TMG	CH_2Cl_2	**3a**	87
3	**2a**	TBD	CH_2Cl_2	**3a**	71
4	**2a**	P_1	CH_2Cl_2	**3a**	88
5	**2a**	P_2	CH_2Cl_2	**3a**	77
6	**2a**	DBU	DMF	**3a**	80
7[d]	**2a**	DBU	toluene	**3a**	49
8	**2a**	DBU	MeCN	**3a**	74
9	**2a**	DBU	THF	**3a**	81
10[e]	**2a**	pyridine	CH_2Cl_2	**3a**	0
11	**2a**	Et_3N	CH_2Cl_2	**3a**	13
12	**2b**	DBU	CH_2Cl_2	**3b**	74
13	**2c**	DBU	CH_2Cl_2	**3c**	89
14	**2d**	DBU	CH_2Cl_2	**3d**	90
15	**2e**	DBU	CH_2Cl_2	**3e**	65
16	**2f**	DBU	CH_2Cl_2	**3f**	80
17	**2g**	DBU	CH_2Cl_2	**3g**	86
18	**2h**	DBU	CH_2Cl_2	**3h**	76
19	**2i**	DBU	CH_2Cl_2	**3i**	79
20	**2j**	P_1	CH_2Cl_2	**3j**	63
21	**2k**	DBU	CH_2Cl_2	**3k**	37
22	**2l**	DBU	CH_2Cl_2	**3l**	60
23[f]	**2l**	DBU	$CHCl_3$	**3l**	71
24	**2m**	P_1	CH_2Cl_2	**3m**	24
25	**2m**	P_2	CH_2Cl_2	**3m**	54
26[g]	**2a**	DBU	CH_2Cl_2	**3a**	75

[a] The reaction of **2** with **1** (1.5 equiv.) was carried out in the presence base (1.2 equiv.) in solvent at room temp. For detailed reaction conditions, see the Supporting Information. [b] TMG: tetramethylguanidine; TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene; P_1: phosphazene base P_1-*t*Bu; P_2: phosphazene base P_2-Et. [c] Isolated yield. [d] The reaction time: 2 h. [e] The reaction time: 16 h. [f] The reagent **1** (3.0 equiv.) was used. [g] The reaction was carried out in the presence of nitrobenzene (1.0 equiv.).

We found that salt **1** reacts with indanone carboxylate **2a** in the presence of DBU in CH_2Cl_2 to yield the trifluoromethylated compound **3a** in a good yield of 93% (Table 1, entry 1). Guanidine bases, such as TMG and TBD, and phosphazene bases such as P_1-*t*Bu and P_2-Et, were also equally effective for the transfer trifluoromethylation from **1** to **2a** in good to high yields (entries 2–5). The reaction proceeded in a variety of solvents in the presence of DBU (entries 6–9). On the other hand, no reaction was observed in the case of weak bases such as triethylamine and pyridine (entries 10 and 11). This finding is of interest because the transfer trifluoromethylation was not hampered under strong base conditions. Further studies focused on the variation of the substrates. Under similar conditions, β-keto esters such as indanone, tetralone, and oxocyclopentancarboxylates **2b**–**l** were examined to investigate the scope of the reaction. The substitutions on the benzene ring and the variation of ester moiety did not effect the yield and reaction time, and were indeed good substrates to afford the corresponding trifluoromethylated compounds **3b**–**l** in good to high yields within an hour (entries 12–23). Although the yield of the trifluoromethylation of acyclic ester **2m** was low in the presence of P_1 base; it was improved to 54% when the reaction was carried out using the phosphazene base, P_2 (entries 24 and 25). To understand the mechanism of this trifluoromethylation, we attempted the trifluoromethylation of **2a** in the presence of nitrobenzene (entry 26). Nitrobenzene is known to act as a radical scavenger resulting in the inhibition of a radical reaction.[13] However, in our experiment, the desired product was obtained independent of the presence of nitrobenzene. Therefore, under typical conditions, the reaction would be classified as an electrophilic trifluoromethylation. A free radical or single electron transfer (SET) mechanism might be ruled out, although a detailed study is required.

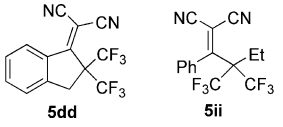
We were next interested in the *vinylogous* trifluoromethylation of dicyanoalkylidenes **4** under the same trifluoromethylation conditions, since a number of C–C bond formation reactions has been developed for activated alkylidenes,[14] with the exception of trifluoromethylation. To start our investigation, we examined the reaction of the tetralone-derived dicyanoalkylidene **4a** with **1** in CH_2Cl_2 using DBU or P_1 as the base at room temperature. The corresponding trifluoromethylated dicyanoalkylidene **5a** was obtained with both bases, but the P_1 base showed a better yield of **5a** (Table 2, entries 1–4). The scope of the vinylogous electrophilic trifluoromethylation reaction is shown in Table 2. The reaction generally proceeded nicely to provide the desired products in good to high yields (entries 3–12). Substitution at the allylic position influenced the reaction slightly. While mono-trifluoromethyaltion was observed for the reaction of the tetralone-type (n = 2, six-membered ring) and benzosuberone-type (n = 3, seven-membered ring) dicyanoalkylidenes **4a**, **4b** and **4g**, a mixture of mono- and di-trifluoromethylated products (**5d** and **5dd**) was obtained in the reaction of the indanone-type **4d** (n = 1, five-membered ring).

Table 2. Vinylogous trifluoromethylation of dicyanoalkylidenes **4**.[a]



Entry	**4**	Base (equiv.)	**1** (equiv.)	**5**	Yield[b] (%)
1	**4a**	DBU (1.2)	1.5	**5a**	53
2	**4a**	DBU (2.0)	2.2	**5a**	52
3	**4a**	P_1 (1.2)	1.5	**5a**	77
4[c]	**4a**	P_1 (2.0)	2.2	**5a**	92
5	**4b**	P_1 (2.0)	2.2	**5b**	86
6[d]	**4c**	P_1 (2.0)	1.0	**5c**	63
7	**4d**	P_1 (2.0)	2.2	**5d**	77[e]
8	**4e**	P_1 (1.2)	1.5	**5e**	84
9	**4f**	P_1 (1.2)	1.5	**5f**	88
10	**4g**	P_1 (2.0)	2.2	**5g**	68
11	**4h**	P_1 (1.2)	1.5	**5h**	50 (79)[f]
12	**4i**	P_1 (2.0)	2.2	**5i**	79[g]

[a] The reaction of **4** with **1** (1.5–2.2 equiv.) was carried out in the presence base (1.2–2.0 equiv.) in CH_2Cl_2 at room temp. For detailed reaction conditions, see the Supporting Information. [b] Isolated yield. [c] Reaction time: 15 min. [d] The reaction was carried out using 2.0 equiv. of **4c**. The yield was calculated from the reagent **1**. [e] A mixture of **5d** and bis(trifluoromethylated) compound **5dd** (**5d**/**5dd** = 54:46). [f] Based on recovered **4h**. [g] A mixture of **5i** and bis(trifluoromethylated) compound **5ii** (**5i**/**5ii** = 76:24).



Conclusions

We have fathomed the potential of the newly synthesized [(oxido)phenyl(trifluoromethyl)-λ⁴-sulfanylidene]dimethylammonium tetrafluoroborate (**1**) as a reagent for the trifluoromethylation of carbon nucleophiles, including the first example of *vinylogous* trifluoromethylation of dicyanoalkylidenes. The enantioselective trifluoromethylation of carbon nucleophiles using **1** is under investigation.

Experimental Section

Typical Procedure for the Trifluoromethylation of β-Keto Esters: To a stirred solution of β-keto ester **2a** (20 mg, 0.105 mmol) in CH_2Cl_2 (0.5 mL, 0.2 M) was added DBU (18.8 μL, 0.126 mmol), and stirred for 15 min at room temperature. The reagent **1** (51.4 mg, 0.158 mmol) was added, and stirred for 15 min at room temperature. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (benzene) to give **3a** (25.1 mg, 93%) as a pale yellow solid.

Methyl 2-(Trifluoromethyl)-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (3a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.4 Hz, 1 H), 7.73–7.65 (m, 1 H), 7.54–7.41 (m, 2 H), 3.78 (s, 3 H), 3.75,

3.59 (AB quartet, J = 17.5 Hz, 2 H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –69.2 (s, 3 F) ppm. ^{13}C NMR (150.9 Hz, $CDCl_3$): δ = 192.82, 165.60, 151.65, 136.28, 134.36, 128.50, 126.30, 125.60, 123.47 (q, J = 282 Hz), 63.05 (q, J = 26.3 Hz), 53.56, 34.16 ppm. IR (KBr): $\tilde{\nu}$ = 2968 (C–H), 1756 (COOMe), 1719 (CO), 1316–1163 (CF_3) cm^{-1}. MS (APCI) m/z 257 (M^- – H). HRMS (EI) Calcd for $C_{12}H_9F_3O_3[M]^+$: 258.0504, found: 258.0504.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and spectroscopic data for all compounds.

Acknowledgments

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[1] L. M. Yagupol'skii, N. V. Kondratenko, G. N. Timofeeva, *J. Org. Chem. USSR* **1984**, *20*, 103–106.

[2] a) P. Kirsch, *Modern Fluoroorganic Chemistry*; Wiley-VCH, Weinheim, Germany, **2004**; b) T. Umemoto, *Chem. Rev.* **1996**, *96*, 1757–1777; c) J.-A. Ma, D. Cahard, *Chem. Rev.* **2004**, *104*, 6119–6146; d) J.-A. Ma, D. Cahard, *J. Fluorine Chem.* **2007**, *9*, 975–996; e) N. Shibata, S. Mizuta, T. Toru, *J. Synth. Org. Chem. Jpn.* **2008**, *66*, 215–218.

[3] a) T. Umemoto, S. Ishihara, *Tetrahedron Lett.* **1990**, *31*, 3579–3582; b) T. Umemoto, S. Ishihara, *J. Am. Chem. Soc.* **1993**, *115*, 2156–2164; c) T. Umemoto, K. Adachi, *J. Org. Chem.* **1994**, *59*, 5692–5699; d) T. Umemoto, S. Ishihara, *J. Fluorine Chem.* **1998**, *92*, 181–187; e) J.-J. Yang, R. L. Kirchmeier, J. M. Shreeve, *J. Org. Chem.* **1998**, *63*, 2656–2660; f) T. Umemoto, S. Ishihara, *J. Fluorine Chem.* **1999**, *98*, 75–81; g) E. Magnier, J. C. Blazejewski, M. Tordeux, C. Wakselman, *Angew. Chem.* **2006**, *118* 1301–1304; *Angew. Chem. Int. Ed.* **2006**, *45*, 1279–1282; h) T. Umemoto, K. Adachi, S. Ishihara, *J. Org. Chem.* **2007**, *72*, 6905–6917; i) L. M. Yagupol'skii, V. A. Matsnev, R. K. Orlova, B. G. Deryabkin, Y. L. Yagupol′skii, *J. Fluorine Chem.* **2008**, *129*, 131–136; j) T. Umemoto, U. S. Patent 6,239,289 (**2001**); k) J. M. Shreeve, U. S. Patent 6,215,021 (**2001**); l) K. Adachi, S. Ishihara, Japanese Patent, 20030388769.

[4] a) L. M. Yagupol'skii, I. I. Maletina, N. V. Kondratenko, V. V. Orda, *Synthesis* **1978**, 835–837; b) T. Umemoto, Y. Kuriu, H. Shuyama, O. Miyano, S.-I. Nakayama, *J. Fluorine Chem.* **1982**, *20*, 695–698; c) T. Umemoto, Y. Kuriu, S. Nakayama, *Tetrahedron Lett.* **1982**, *23*, 4101–4102; d) T. Umemoto, A. Ando, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 447–452; e) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579–2586; f) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem.* **2007**, *119*, 768–771; *Angew. Chem. Int. Ed.* **2007**, *46*, 754–757; g) P. Eisenberger, I. Kieltsch, N. Armanino, A. Togni, *Chem. Commun.* **2008**, 1575–1577; h) G. K. S. Prakash, I. Ledneczki, S. Chacko, G. A. Olah, *Org. Lett.* **2008**, *10*, 557–560; i) G. K. S. Prakash, C. Weber, S. Chacko, G. A. Olah, *Org. Lett.* **2007**, *9*, 1863–1866.

[5] J.-A. Ma, D. Cahard, *J. Org. Chem.* **2003**, *68*, 8726–8729.

[6] a) N. Shibata, *J. Synth. Org. Chem. Jpn.* **2006**, *64*, 14–24; b) N. Shibata, T. Ishimaru, S. Nakamura, T. Toru, *J. Fluorine Chem.* **2007**, *128*, 469–483; c) N. Shibata, E. Suzuki, Y. Takeuchi, *J. Am. Chem. Soc.* **2000**, *122*, 10728–10729; d) N. Shibata, E. Suzuki, T. Asahi, M. Shiro, *J. Am. Chem. Soc.* **2001**, *123*, 7001–7009; e) N. Shibata, T. Ishimaru, E. Suzuki, K. L. Kirk, *J. Org. Chem.* **2003**, *68*, 2494–2497; f) N. Shibata, T. Ishimaru, T. Nagai, J. Kohno, T. Toru, *Synlett* **2004**, 1703–1706; g) N. Shibata, T. Ishimaru, M. Nakamura, T. Toru, *Synlett* **2004**, 2509–2512; h) N. Shibata, J. Kohno, K. Takai, T. Ishimaru, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem.* **2005**, *117*, 4276–4279; *Angew. Chem. Int. Ed.* **2005**, *44*, 4204–4207; i) T. Fukuzumi, N. Shibata, M. Sugiura, S. Nakamura, T. Toru, *J. Fluorine Chem.* **2006**, *127*, 548–551; j) N. Shibata, H. Yasui, S. Nakamura, T. Toru, *Synlett* **2007**, 1153–1157; k) D. S. Reddy, N. Shibata, J. Nagai, S. Nakamura, T. Toru, *Angew. Chem.* **2008**, *120*, 170–174; *Angew. Chem. Int. Ed.* **2008**, *47*, 164–168; l) T. Ishimaru, N. Shibata, T. Horikawa, N. Yasuda, S. Nakamura, T. Toru, M. Shiro, *Angew. Chem.* **2008**, *120*, 4225–4229; *Angew. Chem. Int. Ed.* **2008**, *47*, 4157–4161.

[7] a) T. Fukuzumi, N. Shibata, M. Sugiura, H. Yasui, S. Nakamura, T. Toru, *Angew. Chem.* **2006**, *118*, 5095–5099; *Angew. Chem. Int. Ed.* **2006**, *45*, 4973–4977; b) S. Mizuta, N. Shibata, Y. Goto, T. Furukawa, S. Nakamura, T. Toru, *J. Am. Chem. Soc.* **2007**, *129*, 6394–6395; c) S. Mizuta, N. Shibata, M. Hibino, S. Nagano, S. Nakamura, T. Toru, *Tetrahedron* **2007**, *63*, 8521–8528; d) S. Mizuta, N. Shibata, S. Akiti, H. Fujimoto, S. Nakamura, T. Toru, *Org. Lett.* **2007**, *9*, 3707–3710.

[8] a) T. Umemoto, K. Adachi, *J. Org. Chem.* **1994**, *59*, 5692–5699; b) V. Petrik, J.-A. Ma, D. Cahard, Proceedings of ECSOC-10, *International Electronic Conference on Synthetic Organic Chemistry*, 10th, Nov. 1–30, **2006**, a034/1–a034/10.

[9] a) C. R. Johnson, E. R. Janiga, M. Haake, *J. Am. Chem. Soc.* **1968**, *90*, 3890–3891; b) C. R. Johnson, M. Haake, C. W. Schroeck, *J. Am. Chem. Soc.* **1970**, *92*, 6594–6598; c) C. R. Johnson, E. R. Janiga, *J. Am. Chem. Soc.* **1973**, *95*, 7692–7700; d) A. W. Johnson, *Ylide Chemistry*; Academic Press, New York, **1966**; e) B. M. Trost, L. S. Melvin Jr, *Sulfur Ylides: Emerging Synthetic Intermediates*, Academic Press, New York, **1975**.

[10] a) L. M. Yagupol'skii, M. S. Marenets, N. V. Kondratenko, *Zh. Obshch. Khim.* **1965**, *35*, 377–387; b) N. V. Kondratenko, V. N. Movchun, L. M. Yagupol'skii, *Zh. Org. Khim.* **1989**, *25*, 1116–1117; c) V. N. Movchun, A. A. Kolomeitsev, Y. L. Yagupol'skii, *J. Fluorine Chem.* **1995**, *70*, 255–257; d) R. P. Singh, G. Cao, R. L. Kirchmeier, J. M. Shreeve, *J. Org. Chem.* **1999**, *64*, 2873–2876; e) C. Wakselman, M. Tordeux, C. Freslon, L. Saint-Jalmes, *Synlett* **2001**, *4*, 550–552.

[11] a) N. V. Kondratenko, O. A. Radchenko, L. M. Yagupol'skii, *Zh. Org. Khim.* **1984**, *20*, 2250–2251; b) E. Magnier, C. Wakselman, *Synthesis* **2003**, 565–569.

[12] *Handbook of Chemistry, Pure Chemistry*, 5th ed., Marzene, Japan, **2004**, II–886.

[13] a) W. Zhang, L. Zhu, J. Hu, *Tetrahedron* **2007**, *63*, 10569–10575; b) S. Staver, M. Zupan, *Tetrahedron Lett.* **1996**, *37*, 3591–3594.

[14] Examples: a) D. Xue, Y.-C. Chen, Q.-W. Wang, L.-F. Cun, J. Zhu, J.-G. Deng, *Org. Lett.* **2005**, *7*, 5293–5296; b) T. B. Poulsen, C. Alemparte, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 11614–11615; c) T. B. Poulsen, M. Bell, K. A. Jørgensen, *Org. Biomol. Chem.* **2006**, *4*, 63–70; d) M. Bell, K. Frisch, K. A. Jørgensen, *J. Org. Chem.* **2006**, *71*, 5407–5410; e) J.-W. Xie, L. Yue, D. Xue, X.-L. Ma, Y.-C. Chen, Y. Wu, J. Zhu, J.-G. Deng, *Chem. Commun.* **2006**, 1563–1565; f) B. Niess, K. A. Jørgensen, *Chem. Commun.* **2007**, *16*, 1620–1622; g) J.-W. Xie, W. Chen, R. Li, M. Zeng, W. Du, L. Yue, Y.-C. Chen, Y. Wu, J. Zhu, J.-G. Deng, *Angew. Chem.* **2007**, *119*, 393–396; *Angew. Chem. Int. Ed.* **2007**, *46*, 389–392; h) T.-Y. Liu, H.-L. Cui, J. Long, B.-J. Li, Y. Wu, L.-S. Ding, Y.-C. Chen, *J. Am. Chem. Soc.* **2005**, *129*, 1878–1879.

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