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Palladium-catalyzed benzylic direct arylation of benzyl sulfones with aryl halides

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ABSTRACT

An effective palladium catalyst system for the direct arylation of benzyl sulfones with aryl halides has been developed. The catalytic reaction provides a facile route to diarylmethyl sulfones. The products can be transformed further via desulfonylative functionalization mediated by aluminum compounds.

1. Introduction

Transition-metal-catalyzed direct arylations at sp^3-hybridized carbons having acidic hydrogens have been attracting attention in the modern cross-coupling reaction.[1–5] In light of the importance of this transformation, we thus envisioned a new application of the direct arylation, specifically, intermolecular benzylic arylation of benzyl sulfones (Table 1).[6] Benzyl sulfone **1**, readily prepared from benzyl halide and sodium arenesulfinate, has benzylic hydrogens of satisfactory acidity for deprotonation.[7] Palladium-catalyzed arylation of **1** with aryl halide **2** would afford diarylmethyl sulfone **3**.

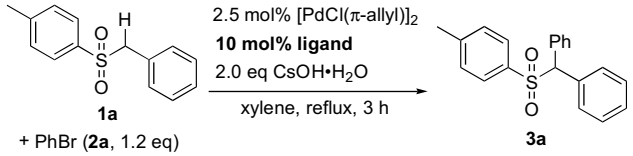
2. Results and discussion

Treatment of benzyl sulfone **1a** with bromobenzene (**2a**) in the presence of cesium hydroxide and catalytic amounts of π-allylpalladium chloride dimer and tricyclohexylphosphine ($P(^cC_6H_{11})_3$) in refluxing xylene provided the corresponding arylated product **3a** in moderate yield (Table 1, entry 1). A plausible reaction mechanism includes deprotonation of **1a** with cesium hydroxide followed by transmetalation of α-tosylbenzylcesium with an arylpalladium bromide intermediate. Although the product should have the more acidic hydrogen,[8] we could not observe *p*-tolyl triphenylmethyl sulfone, which could be derived from second arylation.[9]

The effect of the phosphine ligand is summarized in Table 1. Although a number of phosphine ligands showed poor to moderate activity for the reaction, the use of $P(^cC_6H_{11})_3$ and P^tBu_3 resulted in high efficiency (entries 1 and 12). Other ligands such as triarylphosphines and bidentate phosphine ligands were much less effective.

By using $P(^cC_6H_{11})_3$ as the optimal ligand, the effect of bases was examined (Table 2). Cesium carbonate showed no activity (entry 7) while alkali metal hydroxides and ^{t}BuOK acted as effective bases (entries 1–6 and 8). Finally, we found that the desired product **3a** was obtained in 90% yield by a similar reaction in refluxing toluene

Table 1
Optimization of ligand for direct phenylation of benzyl sulfone **1a**



Entry	Ligand	^{1}H NMR yield (%)
1	$P(^cC_6H_{11})_3$	68
2	PPh_3	19
3	$P(o\text{-tol})_3$	Trace
4	$P(p\text{-MeOC}_6H_4)_3$	24
5	$P(p\text{-FC}_6H_4)_3$	35
6	DPPE (2.5 mol %)	Trace
7	*rac*-BINAP (2.5 mol %)	6
8	DPEphos (2.5 mol %)	8
9	Xantphos (2.5 mol %)	31
10	PMe_3	0
11	P^nBu_3	0
12	P^tBu_3 (2.5 mol %)	52

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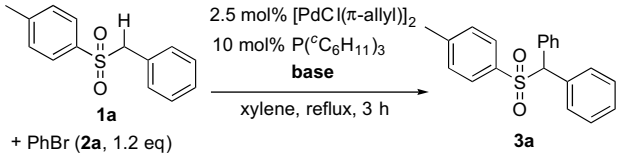
Table 2
Optimization of base for direct phenylation of benzyl sulfone **1a**



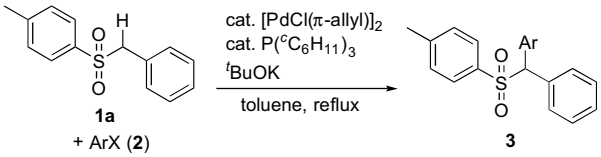
Entry	Base (equiv)	^{1}H NMR yield (%)
1	CsOH·H$_2$O (1.2)	24
2	CsOH·H$_2$O (2.0)	68
3	CsOH·H$_2$O (3.0)	41
4	KOH (2.0)	50
5	KOH (3.0)	30
6	NaOH (2.0)	37
7	Cs_2CO_3 (2.0)	0
8	^{t}BuOK (2.0)	61
9	^{t}BuOK (2.0)[a]	90[b]
10	^{t}BuOK (2.0)[c]	39
11	^{t}BuOK (2.0)[d]	0

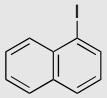
[a] Toluene was used as a solvent.
[b] Isolated yield.
[c] Performed in toluene at 80 °C for 15 h.
[d] Performed in toluene at 50 °C at 15 h.

(entry 9). The reaction at 80 °C or lower resulted in incomplete conversion even after 15 h (entries 10 and 11).

With the optimal conditions, we performed the direct arylation of a variety of aryl halides (Table 3). Iodobenzene (**2b**) reacted smoothly (entry 2), although chlorobenzene (**2c**) gave **3a** in lower yield (entry 3). Aryl iodides having chloro- (entry 4), trifluoromethyl- (entry 5), and ester groups (entry 6) could be employed. Unfortunately, attempts on the reaction with electron-rich aryl iodides resulted in incomplete conversions. For such reactions, it was effective to use an *N*-heterocyclic carbene (NHC) precursor IPr·HCl[10] instead of tricyclohexylphosphine to obtain the corresponding product in high yield (entries 7–10). Sterically demanding aryl iodides **2k** and **2l** also participated in the reaction by using the NHC ligand (entries 11 and 12).

Table 3
Pd-catalyzed arylation of benzyl sulfone **1a**



Entry	ArX **2**				Time (h)	**3**	Isolated yield[a] (%)
1		**2a**	X=	Br	3	**3a**	90
2		**2b**		I	2		99
3		**2c**		Cl	3		31[a]
4		**2d**	R=	*p*-Cl	2	**3d**	76
5		**2e**		*m*-CF$_3$	3	**3e**	75
6		**2f**		*p*-CO$_2$^{t}Bu	5	**3f**	75
7		**2g**		*p*-Me	2	**3g**	80[b]
8		**2h**		*p*-F	4	**3h**	64[b]
9		**2i**		*p*-MeO	7	**3i**	67[b]
10		**2j**		*m*-Me	2	**3j**	84[b]
11		**2k**		*o*-Me	5	**3k**	67[b]
12		**2l**			5	**3l**	69[b]

[a] The yield was determined by ^{1}H NMR analysis.
[b] IPr·HCl (0.030 mmol) was used as a ligand.

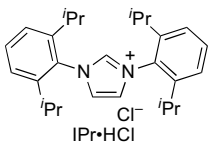
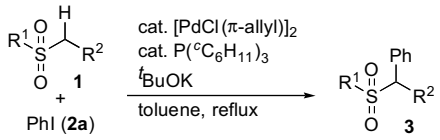


Table 4
Pd-catalyzed phenylation of other sulfones



Entry	R^1	R^2	**1**	Time (h)	**3**	Isolated yield/%
1	*p*-MeC$_6$H$_4$	*p*-FC$_6$H$_4$	**1b**	3	**3h**	77[a]
2		*p*-MeOC$_6$H$_4$	**1c**	3	**3i**	73[a]
3		2-Naphthyl	**1d**	4	**3m**	62
4	*p*-CF$_3$C$_6$H$_4$	Ph	**1e**	2	**3n**	77
5	*p*-MeOC$_6$H$_4$		**1f**	2	**3o**	83
6	Morpholinyl	Ph	**1g**	1	**3p**	75
7	NMePh		**1h**	1	**3q**	71

[a] IPr·HCl (0.030 mmol) was used as a ligand.

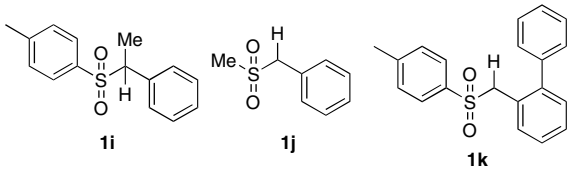
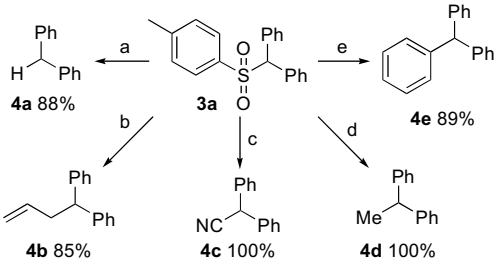


Figure 1. Other sulfones.

Other sulfones were subjected to the arylation reaction (Table 4). The reactions of *p*-substituted benzyl sulfones **1b**, **1c** and 2-naphthylmethyl sulfone **1d** proceeded smoothly (entries 1–3). The *p*-trifluoromethyl- and the *p*-methoxy groups of the arenesulfonyl moieties did not interfere with the arylation (entries 4 and 5). Benzylic sulfonamides **1g** and **1h** could be employed to afford the corresponding diarylmethanesulfonamides (entries 6 and 7).[11] Unfortunately, the reactions of 1-phenylethyl sulfone **1i** and benzyl methyl sulfone **1j** resulted in no conversions, because of the low acidity of the benzylic protons (Fig. 1). The reaction of 2-biphenylylmethyl sulfone **1k** also afforded no arylated product, due to the steric hindrance.

Finally, desulfonylative transformations of the product **3a** were investigated (Scheme 1). Treatment of diphenylmethyl sulfone **3a**



Scheme 1. Desulfonylative transformations of diphenylmethyl sulfone **3a** in the presence of aluminum compounds: (a) $AlCl_3$ (1.5 equiv), Et_3SiH (1.5 equiv), CH_2Cl_2, 25 °C, 1 h; (b) $AlCl_3$ (1.5 equiv), $Me_3SiCH_2CH{=}CH_2$ (1.5 equiv), CH_2Cl_2, 25 °C, 1 h; (c) $AlCl_3$ (1.5 equiv), Me_3SiCN (1.5 equiv), CH_2Cl_2, 25 °C, 1 h; (d) $AlMe_3$ (1.5 equiv), CH_2Cl_2, 25 °C, 2 h; (e) $AlCl_3$ (1.5 equiv), C_6H_6, 25 °C, 1 h.

with hydrosilane, allylsilane, or silyl cyanide in the presence of aluminum chloride provided the corresponding desulfonylative product in high yield.[12] Methylation of **3a** with trimethylaluminum proceeded smoothly.[13] Friedel–Crafts alkylation of benzene with diphenylmethyl sulfone **3a** was facile to yield triphenylmethane (**4e**).

3. Conclusion

In summary, we have developed an effective palladium catalyst system for the direct arylation of benzyl sulfones with aryl halides. The catalytic reaction provides a facile route to diarylmethane derivatives.

4. Experimental

4.1. General

4.1.1. Instrumentation

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on a Varian Unity INOVA 500 spectrometer and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

4.1.2. Materials

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Tricyclohexylphosphine and imidazolinium salt IPr·HCl were purchased from Strem. Preparations of sulfones (**1a**–**1i**) are shown below. Preparations of sulfones **1j**[14] and **1k**[15] were carried out according to the literature. All reactions were carried out under argon atmosphere.

4.2. Experimental procedures

*4.2.1. Synthesis of benzyl aryl sulfones (**1a**–**1d**, **1i**)*

Synthesis of sulfone **1a** is representative. Benzyl chloride (4.6 mL, 40 mmol) was added to a suspension of sodium *p*-toluenesulfinate tetrahydrate (11.0 g, 44 mmol) and tetrabutylammonium bromide (0.64 g, 2.0 mmol) in 1,2-dimethoxyethane (40 mL) at room temperature. The resulting mixture was heated at reflux for 3 h. The mixture was poured into water and insoluble materials were collected by filtration to yield benzyl *p*-tolyl sulfone (**1a**, 8.9 g, 36 mmol, 82%).

*4.2.2. Synthesis of benzyl aryl sulfones (**1e** and **1f**)*

Synthesis of sulfone **1e** is representative. A solution of butyllithium (1.6 M in hexane, 6.3 mL, 10 mmol) was slowly added to a solution of *p*-trifluoromethylbromobenzene (1.4 mL, 10 mmol) in tetrahydrofuran (50 mL) at −78 °C and the reaction mixture was stirred for 15 min at −78 °C. Sulfur (0.32 g, 10 mmol) was added to the reaction mixture. After the reaction mixture was stirred for 10 min at −78 °C, benzyl bromide (1.2 mL, 10 mmol) was slowly added. After being stirred for 1 h at room temperature, the reaction mixture was quenched with a saturated ammonium chloride solution. The product was extracted with ethyl acetate three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. The residue containing benzyl 4-trifluoromethylphenyl sulfide was used for the next step without further purification.

Aqueous H_2O_2 (30%, 4.5 mL, 40 mmol) was slowly added to a solution of the crude sulfide and molybdenum dichloride dioxide (0.30 g, 1.5 mmol) in acetonitrile (10 mL). After being stirred for 18 h at room temperature, the resulting mixture was poured into aqueous sodium thiosulfate. Extraction with ethyl acetate followed by silica gel column purification furnished benzyl *p*-trifluoromethylphenyl sulfone (**1e**, 0.97 g, 3.2 mmol) in 32% yield in two steps.

*4.2.3. Synthesis of benzylic sulfonamides (**1g** and **1h**)*

Synthesis of sulfonamide **1g** is representative. A solution of phenylmethanesulfonyl chloride (1.9 g, 10 mmol) in tetrahydrofuran (5 mL) was slowly added to a solution of morpholine (0.44 mL, 5.0 mmol) and diisopropylethylamine (2.1 mL, 12 mmol) in tetrahydrofuran (10 mL) at 0 °C. After the reaction mixture was stirred for 8 h at room temperature, the reaction mixture was quenched with a saturated ammonium chloride solution. Extraction with ethyl acetate followed by silica gel column purification furnished *N*-benzylsulfonylmorpholine (**1g**, 0.97 g, 4.0 mmol) in 80% yield.

4.2.4. Typical procedure for palladium-catalyzed direct arylation of aryl benzyl sulfones

Synthesis of sulfone **3a** is representative (Table 3, entry 2). ^{t}BuOK (449 mg, 4.0 mmol) and π-allylpalladium chloride dimer (18 mg, 0.05 mmol) were placed in a 20-mL two-necked reaction flask equipped with a Dimroth condenser under Ar atmosphere. Tricyclohexylphosphine (0.5 M in toluene, 0.4 mL, 0.2 mmol), toluene (10 mL), benzyl *p*-tolyl sulfone (**1a**, 493 mg, 2.0 mmol), and iodobenzene (**2a**, 0.27 mL, 2.4 mmol) were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 2 h. After the mixture was cooled to room temperature, a saturated aqueous ammonium chloride solution (10 mL) was added. The product was extracted with ethyl acetate three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification (hexane/ethyl acetate=5:1) gave diphenylmethyl *p*-tolyl sulfone (**3a**, 637 mg, 1.97 mmol) in 99% yield.

*4.2.5. Synthesis of **4a**, **4b**, and **4c***

Synthesis of diphenylmethane (**4a**) is representative. Aluminum trichloride (40 mg, 0.3 mmol) was added to a solution of diphenylmethyl *p*-tolyl sulfone (**3a**, 65 mg, 0.2 mmol) and triethylsilane (48 μL, 0.3 mmol) in dichloromethane (2.0 mL). After being stirred for 1 h at room temperature, the reaction mixture was quenched with aqueous sodium hydroxide (1 M, 3 mL). The product was extracted with ethyl acetate three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification yielded diphenylmethane (**4a**, 30 mg, 0.18 mmol) in 88% yield.

*4.2.6. Synthesis of **4d***

A solution of trimethylaluminum (1.0 M in toluene, 0.4 mL, 0.4 mmol) was added to a solution of diphenylmethyl *p*-tolyl sulfone (**3a**, 65 mg, 0.2 mmol) in dichloromethane (2.0 mL). After being stirred for 2 h at room temperature, the reaction mixture was quenched with aqueous sodium hydroxide (1 M, 3 mL). The product was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Chromatographic purification on silica gel gave 1,1-diphenylethane (**4d**, 26 mg, 0.20 mmol) in quantitative yield.

*4.2.7. Synthesis of **4e***

Aluminum trichloride (40 mg, 0.3 mmol) was added to a solution of diphenylmethyl *p*-tolyl sulfone (**3a**, 65 mg, 0.2 mmol) in benzene (2.0 mL). After being stirred for 1 h at room temperature, the reaction mixture was quenched with aqueous sodium hydroxide (1 M,

3 mL). Extractive workup followed by silica gel column purification afforded triphenylmethane (**4e**, 43 mg, 0.18 mmol) in 89% yield.

4.3. Characterization data

*4.3.1. Benzyl p-tolyl sulfone (**1a**)*[13]

^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 4.29 (s, 2H), 7.08–7.10 (m, 2H), 7.22–7.28 (m, 4H), 7.30–7.33 (m, 1H), 7.49–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 63.1, 128.5, 128.7, 128.8, 128.9, 129.7, 131.0, 135.2, 144.8. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73%. Found: C, 68.51; H, 5.71%.

*4.3.2. p-Fluorophenylmethyl p-tolyl sulfone (**1b**)*

IR (Nujol) 2923, 2854, 1460, 1377, 1126, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 4.26 (s, 2H), 6.94–6.98 (m, 2H), 7.06–7.08 (m, 2H), 7.25–7.27 (m, 2H), 7.50–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 62.2, 115.8 (d, J_{C-F}=21.5 Hz), 124.3 (d, J_{C-F}=3.9 Hz), 129.3 (d, J_{C-F}=127 Hz), 132.7 (d, J_{C-F}=8.6 Hz), 134.9, 145.0, 162.2, 164.2. HRMS (DI-EI$^+$) (m/z) observed: 264.0620 (Δ=1.9 ppm), calcd for $C_{14}H_{13}O_2FS$ [M$^+$]: 264.0620. Mp 161–164 °C.

*4.3.3. p-Methoxyphenylmethyl p-tolyl sulfone (**1c**)*[15]

^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.79 (s, 3H), 4.23 (s, 2H), 6.79 (d, J=8.5 Hz, 2H), 7.00 (d, J=8.5 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 7.51 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 55.4, 62.4, 114.2, 120.3, 128.8, 129.7, 132.2, 135.2, 144.8, 160.1.

*4.3.4. 2-Naphthylmethyl p-tolyl sulfone (**1d**)*

IR (Nujol) 2923, 2854, 1654, 1507, 1465, 1151 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 4.45 (s, 2H), 7.19–7.22 (m, 3H), 7.46–7.52 (m, 4H), 7.56 (s, 1H), 7.72–7.75 (m, 2H), 7.81–7.83 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.8, 63.3, 125.9, 126.6, 126.8, 127.9, 128.05, 128.14, 128.5, 128.8, 129.7, 130.7, 133.21, 133.25, 135.2, 144.9. Mp 135–137 °C.

*4.3.5. Benzyl p-trifluoromethylphenyl sulfone (**1e**)*

IR (Nujol) 2922, 2854, 1655, 1457, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 2H), 7.08–7.10 (m, 2H), 7.26–7.30 (m, 2H), 7.35 (tt, J=7.0, 2.0 Hz, 1H), 7.70–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 63.0, 123.3 (q, J_{C-F}=272 Hz), 126.2 (q, J_{C-F}=3.8 Hz), 127.7, 129.0, 129.3, 129.5, 131.0, 135.6 (q, J_{C-F}=33.0 Hz), 141.5. Anal. Calcd for $C_{14}H_{11}F_3O_2S$: C, 55.99; H, 3.69%. Found: C, 55.73; H, 3.81%. Mp 163–165 °C.

*4.3.6. Benzyl p-methoxyphenyl sulfone (**1f**)*[16]

^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H), 4.28 (s, 2H), 6.88–6.91 (m, 2H), 7.08–7.10 (m, 2H), 7.25–7.29 (m, 2H), 7.30–7.34 (m, 1H), 7.51–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.8, 63.3, 109.9, 114.2, 128.68, 128.72, 128.8, 129.6, 131.0, 163.9.

*4.3.7. N-Benzylsulfonylmorpholine (**1g**)*[6e]

^{1}H NMR ($CDCl_3$) δ 3.10 (dd, J=4.5, 4.5 Hz, 4H), 3.62 (dd, J=4.5, 4.5 Hz, 4H), 4.24 (s, 2H), 7.39–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 46.3, 56.9, 66.9, 128.7, 129.0, 129.1, 130.9.

*4.3.8. N-Benzylsulfonyl-N-methylaniline (**1h**)*[6e]

^{1}H NMR ($CDCl_3$) δ 3.13 (s, 3H), 4.27 (s, 2H), 7.23–7.28 (m, 3H), 7.33–7.41 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 39.1, 56.5, 126.1, 127.0, 128.8, 128.93, 128.94, 129.4, 131.0, 141.6.

*4.3.9. 1-Phenylethyl p-tolyl sulfone (**1i**)*

IR (Nujol) 2923, 2854, 1654, 1645, 1457, 1373 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.76 (d, J=7.0 Hz, 3H), 2.40 (s, 3H), 4.21 (q, J=7.0 Hz, 1H), 7.14–7.15 (m, 2H), 7.18–7.20 (m, 2H), 7.23–7.31 (m, 3H), 7.40–7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.3, 21.8, 66.2, 128.5, 128.9, 129.40, 129.44, 129.6, 134.07, 134.08, 144.6. HRMS (DI-EI$^+$) (m/z) observed: 260.0867 (Δ=1.4 ppm), calcd for $C_{15}H_{16}O_2S$ [M$^+$]: 260.0871. Mp 114–117 °C.

*4.3.10. Benzyl methyl sulfone (**1j**)*[14]

^{1}H NMR ($CDCl_3$) δ 2.75 (s, 3H), 4.25 (s, 2H), 7.42 (br, 5H); ^{13}C NMR ($CDCl_3$) δ 39.2, 61.5, 128.5, 129.3 (×2C), 129.3, 130.7.

*4.3.11. 2-Biphenylylmethyl p-tolyl sulfone (**1k**)*[15]

^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 4.39 (s, 2H), 6.84–6.86 (m, 2H), 7.12–7.14 (m, 3H), 7.23–7.29 (m, 5H), 7.35–7.37 (m, 2H), 7.60–7.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.7, 59.1, 125.8, 127.3, 127.7, 128.2, 128.6, 128.7, 129.2, 129.6, 130.4, 131.7, 135.8, 139.9, 143.8, 144.6.

*4.3.12. Diphenylmethyl p-tolyl sulfone (**3a**)*

IR (Nujol) 2925, 2854, 1457, 1377, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 5.26 (s, 1H), 7.15 (d, J=8.0 Hz, 2H), 7.30–7.33 (m, 6H), 7.49 (d, J=8.0 Hz, 2H), 7.52–7.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.8, 76.7, 128.76, 128.85, 129.2, 129.4, 130.2, 133.3, 135.5, 144.6. Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63%. Found: C, 74.20; H, 5.67%. Mp 181–185 °C.

*4.3.13. p-Chlorophenyl(phenyl)methyl p-tolyl sulfone (**3d**)*

IR (Nujol) 2924, 2854, 1655, 1457, 1377 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 5.24 (s, 1H), 7.17–7.18 (m, 2H), 7.29–7.32 (m, 5H), 7.47–7.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 21.8, 75.8, 129.0 (×2C), 129.1, 129.2, 129.6, 130.0, 131.4, 131.8, 132.9, 135.0, 135.2, 144.9. Anal. Calcd for $C_{20}H_{17}ClO_2S$: C, 67.31; H, 4.80%. Found: C, 67.10; H, 4.90%. Mp 131–135 °C.

*4.3.14. Phenyl(m-trifluoromethylphenyl)methyl p-tolyl sulfone (**3e**)*

IR (Nujol) 2923, 2854, 1692, 1654, 1465, 1451, 1373 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 5.33 (s, 1H), 7.15–7.17 (m, 2H), 7.32–7.33 (m, 3H), 7.45–7.52 (m, 5H), 7.56–7.57 (m, 1H), 7.66 (s, 1H), 7.84 (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.7, 76.0, 123.9 (q, J_{C-F}=271 Hz), 125.5 (q, J_{C-F}=3.8 Hz), 127.1 (q, J_{C-F}=3.8 Hz), 129.0, 129.08, 129.14, 129.4, 129.6, 130.0, 131.1 (q, J_{C-F}=32.5 Hz), 132.5, 133.3, 134.4, 134.9, 145.1. Anal. Calcd for $C_{21}H_{17}F_3O_2S$: C, 64.60; H, 4.39%. Found: C, 64.61; H, 4.53%. Mp 92–95 °C.

*4.3.15. tert-Butyl p-[p-tolylsulfonyl(phenyl)methyl]benzoate (**3f**)*

IR (Nujol) 2923, 2854, 1654, 1507, 1457, 1151 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 9H), 2.39 (s, 3H), 5.31 (s, 1H), 7.17 (d, J=8.0 Hz, 2H), 7.31–7.32 (m, 3H), 7.49–7.51 (m, 4H), 7.59–7.60 (m, 2H), 7.92–7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 28.3, 76.3, 81.5, 128.96, 128.97, 129.2, 129.6, 129.86, 129.94, 130.1, 132.3, 132.8, 135.3, 137.8, 144.9, 165.4. Mp 104–107 °C.

*4.3.16. Phenyl(p-tolyl)methyl p-tolyl sulfone (**3g**)*

IR (Nujol) 2923, 2854, 1457, 1383, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.37 (s, 3H), 5.23 (s, 1H), 7.12–7.16 (m, 4H), 7.29–7.31 (m, 3H), 7.41–7.43 (m, 2H), 7.48–7.52 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.3, 22.0, 76.4, 128.7, 128.8, 129.2, 129.4, 129.6, 130.0, 130.1, 130.2, 133.5, 135.6, 138.7, 144.5. Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%. Found: C, 74.93; H, 6.05%. Mp 145–148 °C.

*4.3.17. p-Fluorophenyl(phenyl)methyl p-tolyl sulfone (**3h**)*

IR (Nujol) 2923, 2854, 1655, 1457, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 5.26 (s, 1H), 6.99–7.03 (m, 2H), 7.16 (d, J=8.0 Hz, 2H), 7.30–7.33 (m, 3H), 7.47–7.53 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 21.8, 75.7, 115.8 (d, J_{C-F}=21.5 Hz), 128.88, 128.93, 129.1 (d, J_{C-F}=3.4 Hz), 129.2, 129.5, 130.0, 131.9 (d, J_{C-F}=8.1 Hz), 134.2 (d, J_{C-F}=269 Hz), 144.8, 162.0, 164.0. Anal. Calcd for $C_{20}H_{17}FO_2S$: C, 70.57; H, 5.03%. Found: C, 70.31; H, 5.20%. Mp 159–162 °C.

*4.3.18. p-Methoxyphenyl(phenyl)methyl p-tolyl sulfone (**3i**)*

IR (Nujol) 2923, 2854, 1457, 1377, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 3.78 (s, 3H), 5.22 (s, 1H), 6.84 (d, J=8.5 Hz, 2H), 7.15 (d, J=8.5 Hz,

2H), 7.29–7.43 (m, 3H), 7.43–7.46 (m, 2H), 7.48–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.8, 55.5, 76.0, 114.2, 125.1, 128.7, 128.8, 129.2, 129.4, 130.0, 131.4, 133.6, 135.6, 144.5, 159.9. Anal. Calcd for $C_{21}H_{20}O_3S$: C, 71.56; H, 5.72%. Found: C, 71.56; H, 5.77%. Mp 155–158 °C.

*4.3.19. Phenyl(m-tolyl)methyl p-tolyl sulfone (**3j**)*

IR (Nujol) 2923, 2854, 1655, 1457, 1379 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H), 2.38 (s, 3H), 5.26 (s, 1H), 7.13–7.18 (m, 3H), 7.23 (dd, J=7.5, 7.5 Hz, 1H), 7.31–7.39 (m, 5H), 7.50–7.55 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.6, 21.7, 76.6, 127.1, 128.7 (×2C), 128.8, 129.2, 129.4, 129.5, 130.1, 130.8, 133.1, 133.4, 135.5, 138.5, 144.5. Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%. Found: C, 74.96; H, 6.06%. Mp 120–122 °C.

*4.3.20. Phenyl(o-tolyl)methyl p-tolyl sulfone (**3k**)*

IR (Nujol) 2923, 2854, 1655, 1457, 1375 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3H), 2.38 (s, 3H), 5.57 (s, 1H), 7.06 (d, J=8.0 Hz, 1H), 7.15–7.21 (m, 3H), 7.28–7.31 (m, 4H), 7.47–7.51 (m, 4H), 8.16 (dd, J=8.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.9, 21.8, 71.5, 126.6, 128.6, 128.7, 128.8, 129.1 (×2C), 129.5, 130.5, 130.9, 132.2, 133.1, 135.9, 137.0, 144.6. Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%. Found: C, 74.73; H, 6.09%. Mp 125–127 °C.

*4.3.21. 1-Naphthyl(phenyl)methyl p-tolyl sulfone (**3l**)*

IR (neat) 3068, 2930, 2861, 2247, 1507 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 6.20 (s, 1H), 7.07 (d, J=7.0 Hz, 2H), 7.22–7.26 (m, 3H), 7.35–7.39 (m, 2H), 7.48–7.56 (m, 5H), 7.76–7.81 (m, 3H), 8.48 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 70.9, 122.2, 125.4, 125.7, 126.8, 127.3, 128.3, 128.66, 128.72, 129.1, 129.2, 129.3, 129.4, 130.5, 131.6, 133.3, 134.1, 135.7, 144.6. HRMS (DI-EI$^+$) (m/z) observed: 372.1180 (Δ=1.2 ppm), calcd for $C_{24}H_{20}O_2S$ [M$^+$]: 372.1184.

*4.3.22. 2-Naphthyl(phenyl)methyl p-tolyl sulfone (**3m**)*

IR (Nujol) 2923, 2854, 1654, 1465, 1375 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 5.45 (s, 1H), 7.12 (d, J=7.5 Hz, 2H), 7.30–7.34 (m, 3H), 7.46–7.48 (m, 2H), 7.52 (d, J=6.5 Hz, 2H), 7.57–7.59 (m, 2H), 7.66 (dd, J=9.0, 2.0 Hz, 1H), 7.79–7.80 (m, 3H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.8, 76.7, 126.5, 126.8, 127.2, 127.7, 128.4, 128.6, 128.8, 128.9, 129.2, 129.5, 129.7, 130.2, 130.8, 133.2, 133.3, 133.4, 135.5, 144.7. HRMS (DI-EI$^+$) (m/z) observed: 372.1181 (Δ=0.8 ppm), calcd for $C_{24}H_{20}O_2S$ [M$^+$]: 372.1184. Mp 141–145 °C.

*4.3.23. Diphenylmethyl p-trifluoromethylphenyl sulfone (**3n**)*

IR (Nujol) 2922, 2954, 1462, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 1H), 7.31–7.34 (m, 6H), 7.53–7.55 (m, 4H), 7.61 (d, J=8.0 Hz, 2H), 7.75 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 76.7, 123.2 (q, J_{C-F}= 272 Hz), 125.9 (q, J_{C-F}=3.9 Hz), 129.0, 129.2, 129.8, 130.1, 132.4, 135.2 (q, J_{C-F}=33.0 Hz), 142.0. Anal. Calcd for $C_{20}H_{15}F_3O_2S$: C, 63.82; H, 4.02%. Found: C, 63.73; H, 4.10%. Mp 130–133 °C.

*4.3.24. Diphenylmethyl p-methoxyphenyl sulfone (**3o**)*

IR (Nujol) 2910, 2852, 1472, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 5.26 (s, 1H), 6.80 (d, J=7.0 Hz, 2H), 7.29–7.33 (m, 6H), 7.50–7.54 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 55.7, 76.8, 113.9, 128.7, 128.8, 129.9, 130.1, 131.3, 133.4, 163.7. Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.98; H, 5.36%. Found: C, 70.91; H, 5.40%. Mp 145–149 °C.

*4.3.25. N-(Diphenylmethyl)sulfonylmorpholine (**3p**)*

IR (Nujol) 2924, 2854, 1465, 1458, 1339 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.02 (dd, J=4.5, 4.5 Hz, 4H), 3.53 (dd, J=4.5, 4.5 Hz, 4H), 5.29 (s, 1H), 7.33–7.41 (m, 6H), 7.63–7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 46.5, 66.9, 72.8, 128.9, 129.1, 129.7, 134.2. Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03%. Found: C, 64.54; H, 6.02. Mp 152–154 °C.

*4.3.26. N-Methyl-N,1,1-triphenylmethanesulfonamide (**3q**)*

IR (Nujol) 2923, 2854, 1654, 1457, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 3H), 5.35 (s, 1H), 7.14–7.16 (m, 2H), 7.21–7.24 (m, 1H), 7.28–7.38 (m, 8H), 7.58–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 39.7, 72.2, 126.2, 126.9, 128.8, 128.9, 129.2, 129.9, 134.2, 141.6. Anal. Calcd for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68%. Found: C, 71.22; H, 5.78%. Mp 115–117 °C.

*4.3.27. Diphenylmethane (**4a**)[17]*

^{1}H NMR ($CDCl_3$) δ 3.98 (s, 2H), 7.18–7.21 (m, 6H), 7.26–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 42.1, 126.3, 128.7, 129.1, 141.3.

*4.3.28. 4,4-Diphenyl-1-butene (**4b**)[18]*

^{1}H NMR ($CDCl_3$) δ 2.81 (dd, J=7.5, 7.5 Hz, 2H), 4.00 (t, J=7.5 Hz, 1H), 4.94 (d, J=10.5 Hz, 1H), 5.02 (d, J=17.0 Hz, 1H), 5.71 (ddt, J=7.5, 10.5, 17.0 Hz, 1H), 7.16 (dd, J=7.0, 7.0 Hz, 2H), 7.21–7.28 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 40.1, 51.4, 116.5, 126.4, 128.1, 128.6, 137.0, 144.7.

*4.3.29. Diphenylacetonitrile (**4c**)[19]*

^{1}H NMR ($CDCl_3$) δ 5.13 (s, 1H), 7.30–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 42.8, 119.8, 127.9, 128.4, 129.4, 136.2.

*4.3.30. 1,1-Diphenylethane (**4d**)[20]*

^{1}H NMR ($CDCl_3$) δ 1.64 (d, J=7.0 Hz, 3H), 4.14 (q, J=7.0 Hz, 1H), 7.15–7.19 (m, 2H), 7.21–7.24 (m, 4H), 7.25–7.29 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.0, 44.9, 126.2, 127.8, 128.5, 146.5.

*4.3.31. Triphenylmethane (**4e**)[21]*

^{1}H NMR ($CDCl_3$) δ 5.55 (s, 1H), 7.11–7.12 (m, 6H), 7.19–7.22 (m, 3H), 7.27–7.30 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 57.0, 126.5, 128.5, 129.6, 144.1.

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References and notes

1. α-Arylation of carbonyls: (a) Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234–245; (b) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382–12383; (c) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108–11109; (d) Gaertzen, O.; Buchwald, S. L. *J. Org. Chem.* **2002**, *67*, 465–475; (e) Satoh, T.; Inoh, J.; Kawamura, Y.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2239–2246; γ-Arylations of α,β-unsaturated carbonyl compounds: (f) Terao, Y.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **1998**, *39*, 6203–6206; (g) Muratake, H.; Natsume, M. *Tetrahedron Lett.* **1997**, *38*, 7581–7582.
2. Intermolecular arylation at activated benzylic or allylic positions: (a) Inoh, J.; Satoh, T.; Pivsa-Art, S.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **1998**, *39*, 4673–4676; (b) Dyker, G.; Heiermann, J.; Miura, M.; Inoh, J.; Pivsa-Art, S.; Satoh, T.; Nomura, M. *Chem.—Eur. J.* **2000**, *6*, 3426–3433; (c) Dyker, G.; Heiermann, J.; Miura, M. *Adv. Synth. Catal.* **2003**, *345*, 1127–1132; (d) Niwa, T.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 2373–2375; (e) Mousseau, J. J.; Larivée, A.; Charette, A. B. *Org. Lett.* **2008**, *10*, 1641–1643; (f) Campeau, L.-C.; Schipper, D. J.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 3266–3267; (g) Niwa, T.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 4689–4691.
3. Intramolecular arylative cyclization at benzylic positions: (a) Ren, H.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3462–3465; (b) Ren, H.; Li, Z.; Knochel, P. *Chem. Asian J.* **2007**, *2*, 416–433; (c) Dong, C.-G.; Hu, Q.-S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2289–2292; (d) Hu, Q.-S. *Synlett* **2007**, 1331–1345; (e) Catellani, M.; Motti, E.; Ghelli, S. *Chem. Commun.* **2000**, 2003–2004; (f) Salcedo, A.; Neuville, L.; Zhu, J. *J. Org. Chem.* **2008**, *73*, 3600–3603.
4. Arylation of *N*-*tert*-butylhydrazones as an acyl anion equivalent: Takemiya, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 14800–14801.
5. Other C(sp^3)–H arylation involving cleavage of less acidic hydrogens: (a) Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154–13155; (b) Shabashov, D.; Daugulis, O. *Org. Lett.* **2005**, *7*, 3657–3659; (c) Reddy, B. V. S.; Reddy, L. R.; Corey, E. J. *Org. Lett.* **2006**, *8*, 3391–3394; (d) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330–7331; (e) Giri, R.; Maugel, N.; Li, J.-J.; Wang, D.-H.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510–3511; (f) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696; (g) Pastine, S. J.; Gribkov, D. V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220–14221; (h) Lafrance, M.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 14570–14571; (i) Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2008**, *10*, 1759–1762.
6. α-Arylation of α-sulfonyl carbonyl compounds: (a) Grimm, J. B.; Katcher, M. H.; Witter, D. J.; Northrup, A. B. *J. Org. Chem.* **2007**, *72*, 8135–8138; (b) Kashin, A. N.; Mitin, A. V.; Beletskaya, I. P.; Wife, R. *Tetrahedron Lett.* **2002**, *43*, 2539–2542;

(c) Mitin, A. V.; Kashin, A. N.; Beletskaya, I. P. *J. Organomet. Chem.* **2004**, *689*, 1085–1090; (d) Zeevaart, J. G.; Parkinson, C. J.; de Koning, C. B. *Tetrahedron Lett.* **2005**, *46*, 1597–1599; For α-arylation of methanesulfonamides, see Ref. 6d. Synthesis of benzylic sulfonamides by Pd-catalyzed Negishi coupling of sulfonylmethylzinc chlorides with aryl halides: (e) Zhou, G.; Ting, P.; Aslanian, R.; Piwinski, J. J. *Org. Lett.* **2008**, *10*, 2517–2520.

7. The pK_a value of the benzylic protons of $PhSO_2CH_2Ph$ was reported to be 23.4 in dimethyl sulfoxide at 25 °C. See: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *1*, 456–463.
8. The pK_a value of the benzylic proton of $PhSO_2CHPh_2$ was reported to be 22.3 in dimethyl sulfoxide at 25 °C. See Ref. 7.
9. The second arylation was observed in direct arylation of phenyl(4-pyridyl)-methane providing the corresponding tetraarylmethane. See Ref. 2d.
10. (a) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534; (b) Jafarpour, L.; Steven, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49–54.
11. Diarylmethanesulfonamide skeletons are found in biologically active compounds. See: St-Denis, Y.; Levesque, S.; Bachand, B.; Edmunds, J. J.; Leblond, L.; Preville, P.; Tarazi, M.; Winocour, P. D.; Siddiqui, M. A. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1181–1184.
12. Substitution reactions of sulfones with carbon nucleophiles in the presence of aluminum chloride: Brown, D. S.; Bruno, M.; Davenport, R. J.; Ley, S. V. *Tetrahedron* **1989**, *45*, 4293–4308.
13. Nicolaou, K. C.; Duggan, M. E.; Hwang, C.-K. *J. Am. Chem. Soc.* **1986**, *108*, 2468–2469.
14. Ju, Y.; Kumar, D.; Varma, R. S. *J. Org. Chem.* **2006**, *71*, 6697–6700.
15. Kuwano, R.; Kondo, Y.; Shirahama, T. *Org. Lett.* **2005**, *7*, 2973–2975.
16. Gupta, B. D.; Roy, M.; Roy, S.; Kumar, M.; Das, I. *J. Chem. Soc., Perkin Trans. 2* **1990**, 537–543.
17. Sun, H.-B.; Li, B.; Chen, S.; Li, J.; Hua, R. *Tetrahedron* **2007**, *63*, 10185–10188.
18. Yasuda, M.; Saito, T.; Ueda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414–1416.
19. Yoshida, H.; Watanabe, M.; Morishita, T.; Ohshita, J.; Kunai, A. *Chem. Commun.* **2007**, 1505–1507.
20. Chasssaing, S.; Kumarraja, M.; Pale, P.; Sommer, J. *Org. Lett.* **2007**, *9*, 3889–3892.
21. Podder, S.; Roy, S. *Tetrahedron* **2007**, *63*, 9146–9152.