Organic & Biomolecular Chemistry

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Cite this: *Org. Biomol. Chem.*, 2011, **9**, 2258

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PAPER

Effective oxidation of benzylic and alkane C–H bonds catalyzed by sodium *o*-iodobenzenesulfonate with Oxone as a terminal oxidant under phase-transfer conditions†

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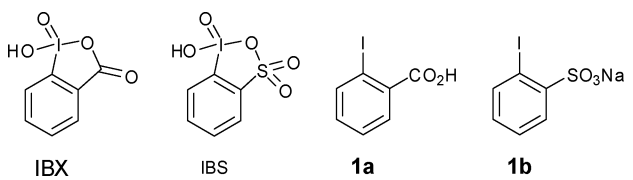
Received 15th September 2010, Accepted 16th December 2010
DOI: 10.1039/c0ob00722f

Catalytic oxidation of benzylic C–H bonds could be efficiently realized using IBS as a catalyst which was generated *in situ* from the oxidation of sodium 2-iodobenzenesulfonate (**1b**) by Oxone in the presence of a phase-transfer catalyst, tetra-*n*-butylammonium hydrogen sulfate, in anhydrous acetonitrile at 60 °C. Various alkylbenzenes, including toluenes and ethylbenzenes, several oxygen-containing functionalities substituted alkylbenzenes, and a cyclic benzyl ether could be efficiently oxidized. And, the same reagent system of cat. **1b**/Oxone/cat. *n*-Bu_4NHSO_4 could be applied to the effective oxidation of alkanes as well.

Introduction

Benzylic C–H bond oxidation is one of the key transformations in organic synthesis.[1] Usually, various metal-based oxidizing agents, especially chromium- and manganese-based ones, are used to enable such transformations either in stoichiometric or in catalytic quantities.[2] Noticeably, *o*-iodoxybenzoic acid (IBX, Chart 1), that is a mild and low toxic oxidant, can effect a number of synthetic transformations[3] including the efficient oxidation of benzylic C–H bonds reported by Nicolaou *et al.*.[4] And very recently, Vinod *et al.* described a catalytic benzylic C–H oxidation protocol using IBX generated *in situ* from 2-iodobenzoic acid (**1a**) and Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in aqueous acetonitrile.[5] Zhdankin *et al.* first reported a thia-analogue of IBX, 2-iodoxybenzenesulfonic acid (IBS), which could be prepared from the oxidation of 2-iodobenzenesulfonic acid by Oxone in water.[6] However, because of the low stability of IBS toward organic solvents such as acetonitrile, DMSO, and methanol, oxidative reactivity of preformed IBS toward organic substrates was therefore not investigated. Very recently, Ishihara *et al.* described the catalytic use of IBS which was generated *in situ* from the oxidation of 2-iodobenzenesulfonic acid or its sodium salt (**1b**) for the effective oxidation of alcohols to the corresponding carbonyl compounds.[7a] And, the same research group also reported an IBS-catalyzed oxidative rearrangement of tertiary allylic alcohols to enones in the presence of a phase-transfer catalyst, *n*-Bu_4NHSO_4.[7b] Moreover, Giannis *et al.* reported the acceleration effect of *n*-Bu_4NHSO_4 in the IBX-catalyzed alcohol oxidation under aqueous conditions.[7c] In the course of our research program for exploration of reactions involving hypervalent iodine reagents,[8] we observed that catalytic oxidation of benzylic C–H bonds could be efficiently realized using IBS as a catalyst which was generated *in situ* from the oxidation of sodium 2-iodobenzenesulfonate (**1b**) by Oxone in the presence of a phase-transfer catalyst tetra-*n*-butylammonium hydrogen sulfate in anhydrous acetonitrile. And, the same system of cat. **1b**/Oxone/cat. *n*-Bu_4NHSO_4 was found to be capable of oxidizing alkane C–H bonds efficiently as well.



IBX IBS **1a** **1b**

Chart 1 IBX and its thia-analogue IBS and their respective precursors.

Results and discussion

Initially, the oxidative transformation of 1,1-dimethyltetralin (**2**) to 4,4-dimethyltetralone (**3**) catalyzed by 2-iodobenzoic acid (**1a**, 0.3 equiv.) which would produce IBX *in situ*,[9] was accomplished in a yield of 70% in the presence of *n*-Bu_4NHSO_4 (0.6 equiv.) and Oxone (3 equiv.) in dry acetonitrile at 60 °C after 4.5 h (Table 1, entry 1). When decreasing the amount of catalyst **1a** to 0.2 equiv., a comparable yield was still obtained (entry 2). Further reducing the loading of **1a** to 0.05 equiv. and that of *n*-Bu_4NHSO_4 to 0.2 equiv. only afforded a trace amount of 4,4-dimethyltetralone (**3**) after 3 h (entry 3). However, when the catalyst sodium 2-iodobenzenesulfonate (**1b**) was employed to replace **1a**, the full conversion of **2** was observed in 3 h with the yield of **3** being 71% under the otherwise same reaction conditions (entry 4 *vs.* entry 3), clearly indicating that IBS, which would be formed

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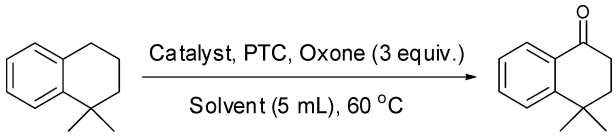
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0ob00722f

Table 1 Optimization for the benzylic oxidation of 1,1-dimethyltetralin[a]



2 **3**

Entry	Catalyst (equiv.)	PTC (equiv.)	Solvent	Time/h	Conv. (%)	Yield (%)
1	**1a** (0.3)	*n*-Bu_4NHSO_4 (0.6)	CH_3CN	4.5	100	70
2	**1a** (0.2)	*n*-Bu_4NHSO_4 (0.6)	CH_3CN	6	100	75
3	**1a** (0.05)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN	3	10	5
4	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN	3	100	71
5	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	EtOAc	18	80	62
6	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	DMF	16	5	2
7	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	DMSO	16	9	1
8	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	PhCN	16	80	52
9	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN–H_2O (4 : 1)[b]	18	30	7
10	**1b** (0.05)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN–H_2O (9 : 1)[b]	18	40	9
11	**1b** (0.05)	*n*-Bu_4NPF_6 (0.2)	CH_3CN	10	96	65
12	**1b** (0.05)	*n*-Bu_4NCl (0.2)	CH_3CN	7	100	70
13	**1b** (0.05)	$C_{16}H_{33}N(CH_3)_3Cl$ (0.2)	CH_3CN	8	100	64
14	**1b** (0.01)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN	4	100	69
15[c]	**1b** (0.002)	*n*-Bu_4NHSO_4 (0.2)	CH_3CN	16	75	57

[a] The conversion of 1,1-dimethyltetralin (0.5 mmol) and the chemical yield of 4,4-dimethyltetralone were determined by GC. [b] Volume ratio. [c] 5 mmol scale.

in situ from **1b** and Oxone, was a more powerful oxidant than IBX. With this promising result in hand, various solvents and three other commonly used phase-transfer catalysts were screened to establish the optimal reaction conditions. The solvent screening study showed that acetonitrile was still the best one among all tested solvents (entries 5–8). It was apparent that the presence of water retarded the reaction judged by the reaction rate and chemical yield (entries 9 and 10). Comparing with other phase-transfer catalysts (entries 11–13), *n*-Bu_4NHSO_4 proved to be the best one for this transformation. The study on the efficacy of catalyst **1b** indicated that the oxidation of **2** can be completed in 4 h in the yield of 69% with 1 mol% of catalyst **1b** (entry 14). Moreover, 0.2 mol% of **1b** was enough for the oxidation of **2** (5 mmol scale) to **3**, the turn-over number was up to 285 in this case (entry 15). But, for the sake of fast reaction rate, the loading of catalyst **1b** (5 mol%) and other parameters shown in entry 4 were used in the following study.

To test the scope and generality of this IBS-catalyzed benzylic C–H oxidation protocol, various alkylbenzenes, including toluenes and ethylbenzenes, several oxygen-containing functionalities substituted alkylbenzenes, and a cyclic benzyl ether were tried and results are summarized in Table 2. Diphenylmethane (**4a**) and fluorene (**4b**) were efficiently oxidized to benzophenone and 9*H*-fluoren-9-one in 73% and 93% yield, respectively (Table 2, entries 1–2). It was worth noting that fluorene could not be oxidized at all using a catalytic amount of **1a** (20 mol%) together with Oxone in aqueous acetonitrile at 70 °C.[5] Like substrate **2**, oxidation of other benzo-fused alkylbenzenes including 1,1-dimethylindane (**4c**), indane (**4d**), and tetralin (**4e**) proceeded smoothly to yield their corresponding ketones in good to high yields (entries 3–5).

The oxidation of toluene to benzoic acid, which is one of the most important transformations in industry, could be efficiently accomplished under our anhydrous benzylic oxidation conditions (Table 2, entry 6). Various toluene derivatives were also tested and their corresponding acid products were obtained in high yields (entries 7–12). Oxidation rates for toluene derivatives with strong electron-withdrawing groups like nitro and cyano group were slower and more catalyst **1b** (10 mol%) and Oxone were required (entries 11 and 12). As for *p*-xylene (**4m**), terephthalic acid, which is used chiefly in the manufacture of resins and textile fibers, could be obtained in good yield (65%) with the present non-metal IBS-catalyzed procedure (entry 13). Moreover, ethylbenzene and its four derivatives could be converted into their corresponding ketones in moderate to good yields along with the formation of various benzoic acids as minor products except for 4-ethylbenzoic acid (entry 17). Like 4-nitrotoluene, 1-ethyl-4-nitrobenzene (**4r**) having the strong electron-withdrawing nitro group reacted slowly which required more catalyst **1b** (10 mol%) and Oxone (entry 18). An acetate group was well tolerated under the present conditions, affording 4-acetoxy-1-tetralone (**5t**) in 71% yield (entry 20). It should be mentioned that under our anhydrous conditions, the cyclic ketal moiety which is extremely sensitive to acid remained intact, resulting in the formation of corresponding ketone **5u** in good yield (entry 21). A cyclic ether, 1,3-dihydroisobenzofuran (**4v**), was smoothly oxidized to its corresponding lactone in 80% yield (entry 22).

And, it was found that the same reaction system of cat. **1b**/Oxone/cat. *n*-Bu_4NHSO_4 could efficiently oxidize cyclohexane (**6a**) to cyclohexanone (**7a**) and cyclohex-2-enone (**8a**) in acetonitrile (Scheme 1). Other organic solvents such as acetic acid, chlorobenzene and benzene only gave trace amounts of oxygenated products. The reaction run in benzonitrile produced the two products in the total yield of 36% with roughly the same ratio of **7a** to **8a**. More loading of catalyst **1b** (0.1 mmol) did not improve the total yield of **7a** and **8a**. Just as in the case of benzylic C–H oxidation, the use of 2-iodobenzoic acid (**1a**) as the

Table 2 IBS-catalyzed oxidation of benzylic methylenes with Oxone in the presence of *n*-Bu_4NHSO_4[a]

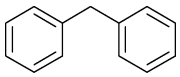
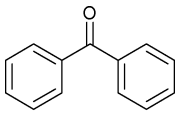
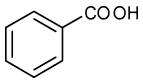
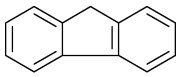
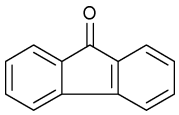
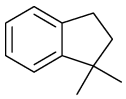
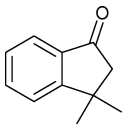
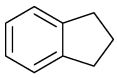
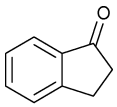
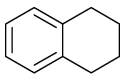
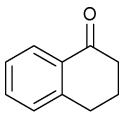
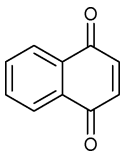
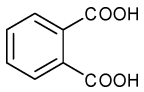
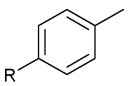
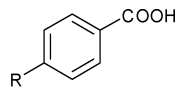
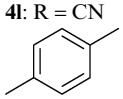
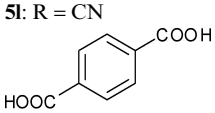
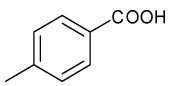
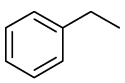
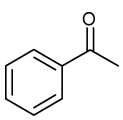
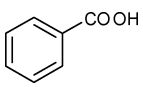
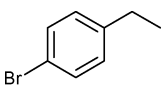
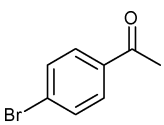
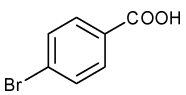
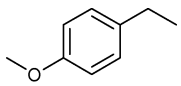
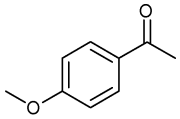
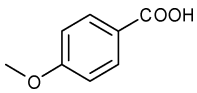
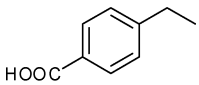
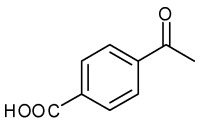
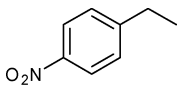
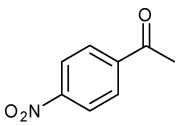
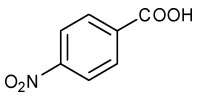
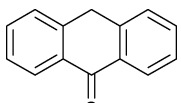
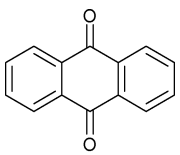
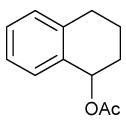
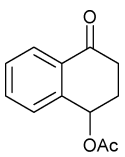
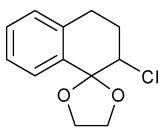
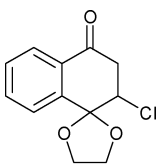
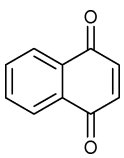
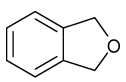
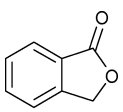
Entry	Substrates	Time/h	Conv. (%)	Products and yields (%)					
1	 **4a**	11	100	 **5a**	73		17		
2	 **4b**	10	100	 **5b**	93				
3	 **4c**	5	100	 **5c**	81				
4	 **4d**	5	100	 **5d**	60				
5	 **4e**	4	100	 **5e**	52		11		4
6	 **4f**: R = H	24	80[b]	 **5f**: R = H	73				
7[c]	**4g**: R = *t*Bu	24	88[b]	**5g**: R = *t*Bu	64				
8	**4h**: R = Cl	24	74[b]	**5h**: R = Cl	70				
9	**4i**: R = Br	24	81[b]	**5i**: R = Br	68				
10	**4j**: R = Ac	24	80[b]	**5j**: R = Ac	65				
11[d,e]	**4k**: R = NO_2	36	80	**5k**: R = NO_2	70				
12[d,f]	**4l**: R = CN	36	88	**5l**: R = CN	75				
13[g]	 **4m**	24	100	 **5m**	65		32		
14	 **4n**	6	100[b]	 **5n**	50[b]		38		
15	 **4o**	6	100	 **5o**	52		37		

Table 2 *(Contd.)*

Entry	Substrates	Time/h	Conv. (%)	Products and yields (%)			
16	 **4p**	5	100	 **5p**	72		22
17	 **4q**	12	87	 **5q**	79		
18[h]	 **4r**	24	100	 **5r**	70		24
19	 **4s**	12	100	 **5s**	90		
20	 **4t**	12	100	 **5t**	71		
21[i]	 **4u**	24	83	 **5u**	56		17
22	 **4v**	5	100	 **5v**	80		

[a] Unless otherwise indicated, the reaction conditions used were those shown in entry 4 of Table 1; 4 equiv. of Oxone was used for entries 6–10. [b] GC analysis. [c] *p-tert*-Butylbenzaldehyde was also obtained in 15% yield. [d] 10 mol% of **1b** and 9 equiv. of Oxone were used. [e] 6% of *p*-nitrobenzaldehyde was also observed. [f] 8% of *p*-cyanobenzaldehyde was also observed. [g] 12 equiv. of Oxone were used. [h] 10 mol% of **1b** and 6 equiv. of Oxone were used. [i] The reaction was carried out under N_2 atmosphere in the presence of 4 Å MS.

pre-catalyst would reduce the efficacy of the reaction with the total yield of **7a** and **8a** being only 17%.

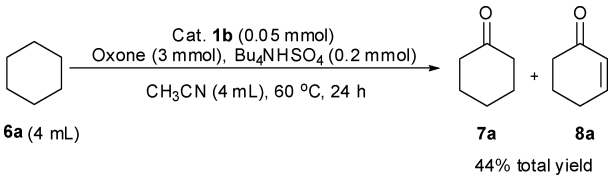
Some alkanes, including cyclic and acyclic ones, were tried and the results are summarized in Table 3. Like **6a**, cycloheptane and cyclooctane were smoothly oxidized to the corresponding oxygenated products in good yields (Table 3, entries 2 and 3). Adamantane (**6d**), a polycyclic alkane, was also a good substrate under the present conditions (entry 4). Acyclic alkane *n*-hexane (**6e**) was oxidized to 2-hexanone and 3-hexanone in the total yield of 22% (entry 5).

To explore the mechanism of this IBS-catalyzed benzylic and alkane C–H bond oxidation, the trapping experiments of the carbocation, which was believed to be a key intermediate, were conducted firstly. 1-Acetamidoadamantane was obtained when

Table 3 IBS-catalyzed oxidation of alkanes with Oxone in the presence of *n*-Bu_4NHSO_4[a]

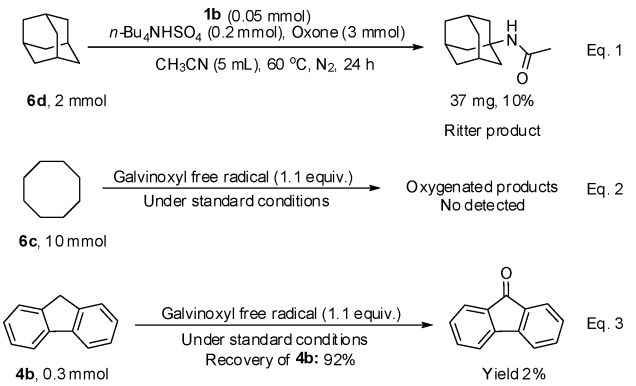
Entry	Substrates	Oxygenated products (% yield)[b]	Total yield (%)[b]
1	cyclohexane (**6a**)	cyclohexanone (**7a**, 25), cyclohex-2-enone (**8a**, 19)	44
2	cycloheptane (**6b**)	cycloheptanone (53), cyclohept-2-enone (6), cyclohepta-2,6-dienone (2)	61
3	cyclooctane (**6c**)	cyclooctanone (42), (*Z*)-cyclooct-2-enone (14), cycloocta-2,7-dienone (6)	62
4[c]	adamantane (**6d**)	1-adamantanol (16), 2-adamantanone (10) adamantane-1,3-diol (17)	43
5	*n*-hexane (**6e**)	hexan-2-one (11), hexan-3-one (11)	22

[a] Unless otherwise indicated, reaction conditions employed were those shown in Scheme 1. [b] GC yield based on the amount of Oxone. [c] 10 mmol of **6d** and 10 mL of CH_3CN were used.



Scheme 1 Oxidation of cyclohexane catalyzed by **1b** with Oxone.

the oxidation of adamantane was carried out under N_2 (Scheme 2, Eq. 1). Since the carbocation of adamantane was known to undergo Ritter reaction with acetonitrile leading to the formation of 1-acetamidoadamantane,[10] this observation confirmed the presence of carbocation in the oxidation of adamantane. However, the detection of benzylic cation failed in the oxidation of indane under N_2 since no Ritter product *N*-(2,3-dihydro-1*H*-inden-1-yl)acetamide (**9**) was observed. One control experiment showed that compound **9** was unstable to oxidation to 2,3-dihydro-1*H*-inden-1-one and *N*-(3-oxo-2,3-dihydro-1*H*-inden-1-yl)acetamide under the reaction conditions, and this might be the reason for the failure of its detection. Furthermore, the complete and almost complete inhibition of oxidation of cyclooctane and fluorene, respectively, by the addition of Galvinoxyl free radical as an efficient radical inhibitor suggested that radical species are involved in both reactions (Scheme 2, Eq. 2 and 3). These initial experimental proofs implied that the carbocation and radical species might be the key intermediates in the alkane and benzylic oxidation. In addition, the function of the phase-transfer catalyst *n*-Bu_4NHSO_4 was its capability to increase the solubility of Oxone and catalyst **1b** in anhydrous acetonitrile.[11]



Scheme 2 Three experiments to verify intermediates in the IBS-catalyzed benzylic and alkane C–H bond oxidation.

Conclusions

In summary, an efficient IBS-catalyzed benzylic methylene oxidation reaction has been developed along with the use of Oxone as a terminal oxidant and a catalytic amount of *n*-Bu_4NHSO_4 to improve the solubility of pre-catalyst **1b** and Oxone in dry acetonitrile. And, the same combination of cat. **1b**/Oxone/cat. *n*-Bu_4NHSO_4 is also efficient for the alkane C–H bond oxidation. The isolation of the Ritter product 1-acetamidoadamantane indicated that the carbocation intermediate undoubtedly existed in the adamantane oxidation. The high efficacy and wide substrate scope of this non-metal protocol, ready availability of **1b** and Oxone, which is a non-toxic solid and easy to store and handle, and environmentally benign nature made the present catalytic IBS/Oxone/cat. *n*-Bu_4NHSO_4 system an attractive way to oxidize benzylic and alkane C–H bonds.

Experimental

The sodium 2-iodobenzenesulfonate was prepared from commercially available 2-aminobenzenesulfonic acid following the reported procedure.[6,7a] 1,1-Dimethyltetralin, 1,1-dimethylindane, 1-acetoxytetralin, cyclohept-2-enone, cyclooct-2-enone, cyclohepta-2,6-dienone, cycloocta-2,7-dienone and adamantane-1,3-diol were synthesized according to the known methods; the rest of the substrates and Oxone® were commercially available from *Alfa Aesar*® or *Acros*, and were used as received. The quaternary ammomium salts from *Alfa Aesar*® were stored in a desiccator. The solvent CH_3CN was distilled from anhydrous CaH_2. The ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were measured at 100 MHz using a Bruker AV 400 instrument; $CDCl_3$ or DMSO-d_6 was used as the solvent. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, multiplicities, coupling constants (Hz) and integration. ^{13}C NMR spectra are reported in ppm (δ) relative to the central line of triplet of $CDCl_3$ at 77.00 ppm. GC analysis was carried out on a Shimadzu 2014 series GC system equipped with Rtx-5 column (30 m, ID 0.25 mm) and a FID.

The typical procedure for the IBS-catalyzed benzylic C–H oxidation

To a solution of 1,1-dimethyltetralin (80 mg, 0.5 mmol) in CH_3CN (5 mL) in a two necked round-bottom flask equipped with a condenser and a stirrer bar was added sodium 2-iodobenzenesulfonate (**1b**) (7.7 mg, 0.025 mmol), *n*-Bu_4NHSO_4 (33.9 mg, 0.1 mmol) and Oxone® (923 mg, 1.5 mmol). The suspension was stirred vigorously at 60 °C. After the reaction was complete as determined

by TLC, the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (40 mL × 3). Then the combined organic layer was washed with brine (10 mL) and dried with anhydrous $MgSO_4$. The solvent was evaporated off *in vacuo*, and the residue was purified by column chromatography on silica gel (hexane–EtOAc = 50/1 as eluent) to give the product 4,4-dimethyltetralone as a white solid.[12] (62 mg, 71%). mp 12–14 °C;^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.22 (dd, J = 1.2 Hz, 8 Hz, 1H), 7.53 (m, 1H), 7.43 (d, J = 8 Hz, 1H), 7.30 (m, 1H), 2.74 (t, J = 6.8 Hz, 2H), 2.03 (t, J = 6.8 Hz, 2H), 1.40 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 198.47, 152.23, 133.84, 131.08, 127.26, 126.24, 125.80, 37.00, 35.89, 33.88, 29.70.

Diphenylmethanone (5a)[12]. White solid; mp 47–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.6 Hz, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.55, 137.41, 132.28, 129.89, 128.13.

9-Fluorenone (5b)[12]. Yellow solid; mp 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.6 Hz, 2H), 7.46–7.53 (m, 4H), 7.29 (dt, J = 1.2, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.84, 144.34, 134.61, 134.05, 128.99, 124.21, 120.24.

3-Dimethyl-1-indenone (5c)[13]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 2.50 (s, 2H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.84, 163.73, 135.16, 134.86, 127.28, 123.42, 123.19, 52.80, 38.41, 29.87.

1-Indanone (5d)[12]. White solid; mp 40–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 3.15 (t, J = 5.2 Hz, 2H), 2.69 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.92, 155.04, 136.93, 134.46, 127.13, 126.58, 123.52, 36.07, 25.66.

1-Tetralone (5e)[12]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, J = 0.8 Hz, 7.6 Hz, 1H), 7.47 (td, J = 1.6 Hz, 7.6 Hz, 1H), 7.24–7.32 (m, 2H); 2.97 (t, J = 6 Hz, 2H), 2.65 (t, J = 6.4 Hz, 2H), 2.10–2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.28, 144.38, 133.28, 132.48, 128.67, 127.01, 126.50, 39.05, 29.58, 23.17.

Naphthalene-1,4-dione[15]. Yellow solid; mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, J = 3.6 Hz, 6 Hz, 2H), 7.69 (dd, J = 3.6 Hz, 6 Hz, 2H), 6.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.00, 138.64, 133.90, 131.87, 126.38.

Phthalic acid[16]. White solid; mp 206–208 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.28 (s, 2H), 7.69 (dd, J = 3.2 Hz, 5.6 Hz, 2H), 7.58 (dd, J = 3.2 Hz, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.62, 132.87, 130.71, 128.46.

Benzoic acid (5f)[14]. White solid; mp 122–124 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.97 (s, 1H), 7.96 (d, J = 6.8 Hz, 2H), 7.60 (d, J = 6.0 Hz, 1H), 7.49 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.30, 132.80, 130.71, 129.23, 128.50.

4-*tert*-Butylbenzoic acid (5g)[17]. White solid; mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.51, 157.58, 130.11, 126.53, 125.46, 35.16, 31.07.

4-*tert*-Butylbenzaldehyde[16]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.01, 158.43, 134.01, 129.67, 125.96, 35.33, 31.04.

4-Chlorobenzoic acid (5h)[14]. White solid; mp 236–237 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.19 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.43, 137.76, 131.09, 129.58, 128.69.

4-Bromobenzoic acid (5i)[14]. White solid; mp 249–250 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.19 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.58, 131.68, 131.26, 129.95, 126.86.

4-Acetylbenzoic acid (5j)[12]. White solid; mp 205–207 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.31 (s, 1H), 8.04 (s, 4H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.68, 166.61, 139.79, 134.45, 129.51, 128.27, 26.95.

4-Nitrobenzoic acid (5k)[14]. Slightly yellow solid; mp 238–239 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.72 (s, 1H), 8.34 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.75, 149.95, 136.31, 130.64, 123.65.

4-Cyanobenzoic acid (5l)[18]. White solid; mp 209–211 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.57 (s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.02, 134.78, 132.63, 129.88, 118.15, 115.03.

4-Cyanobenzenealdehyde[18]. White solid; mp 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 7.93 (d, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.56, 138.72, 132.88, 129.87, 117.67, 117.61.

Tetrephthalic acid (5m)[19]. White solid; mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.28 (s, 2H), 8.04 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.64, 134.39, 129.40

4-Methylbenzoic acid[14]. White solid; mp 177–179 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.81 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.31, 142.92, 129.28, 129.01, 128.00, 21.00.

Acetophenone (5n)[14]. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.82, 136.78, 132.83, 128.29, 128.01, 26.29.

4-Bromophenyl methyl ketone (5o)[20]. White solid; mp 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.83, 135.78, 131.79, 129.75, 128.18, 26.41.

4-Methoxyphenyl methyl ketone (5p)[20]. White solid; mp 38–39 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.62, 163.36, 130.45, 130.19, 113.55, 55.32, 26.20.

4-Methoxybenzoic acid[14]. White solid; mp 181–183 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.60 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.96, 162.81, 131.31, 122.93, 113.78, 55.41.

4-Nitrophenyl methyl ketone (5r)[20]. Yellow solid; mp 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.31, 150.31, 141.32, 129.27, 123.92, 26.95.

9,10-Anthraquinone (5s)[12]. Yellow solid; mp 275–277 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32–8.34 (m, 4H), 7.81–7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.15, 134.11, 133.52, 127.23.

4-Acetoxy-1-tetralone (5t)[12]. Slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.40–7.44 (m, 2H), 6.10 (t, J = 4.6 Hz, 1H), 2.86–2.94 (m, 1H), 2.60–2.67 (m, 1H), 2.23–2.41 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.55, 170.22, 140.52, 133.71, 131.77, 128.81, 128.12, 126.94, 68.86, 34.18, 28.26, 21.00.

2′-Chloro-3′,4′-dihydro-2′*H*-spiro[[1,3]dioxolane-2,1′-naphthalene] (5u). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.6 Hz, 1H), 7.64–7.68 (m, 2H), 7.50–7.53 (m, 1H), 4.56–4.59 (m, 1H), 4.25–4.33 (m, 4H), 3.40 (dd, J = 3.6 Hz, 17.6 Hz, 1H), 3.24 (dd, J = 3.6 Hz, 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.24, 140.42, 134.42, 131.34, 129.70, 127.14, 125.48, 105.92, 67.00, 64.40, 59.14, 45.13; IR (KBr): $\tilde{\nu}$ = 2958, 2923, 2871, 2852, 1733, 1697, 1601, 1490, 1456, 1435, 1288, 1079, 969, 767 cm^{-1}. HRMS (ESI): m/z: calcd. for $C_{12}H_{11}ClO_3H$ $[M + H]^+$ 239.0469; found: 239.0474.

Isobenzofuran-1-one (5v)[12]. White solid; mp 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.43–7.47 (m, 2H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.03, 146.43, 133.93, 128.90, 125.54, 122.05, 69.58.

The typical procedure for the IBS-catalyzed alkane C–H oxidation

To the suspension of **1b** (0.05 mmol, 15.3 mg), Bu_4NHSO_4 (0.2 mmol, 67.8 mg), and Oxone® (3 mmol, 1.84 g) in CH_3CN (4 mL) in a two necked round-bottom flask equipped with condenser and magnetic stirrer bar was added cyclohexane (4 mL, 33 mmol). The mixture was heated at 60 °C in an oil bath for 24 h. After cooling to room temperature, the resulting mixture was filtered to remove the undissolved solid. The filtrates were washed with water (5 mL × 2) and brine (5 mL), dried with anhydrous $MgSO_4$. Then the solution was subjected to GC analysis.

Cyclohept-2-enone[21]. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52–6.58 (m, 1H), 5.96–5.99 (d, J = 12 Hz, 1H), 2.57–2.59 (m, 2H), 2.41–2.44 (m, 2H), 1.77–1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.26, 146.35, 132.46, 43.46, 30.16, 26.06, 21.65.

Cyclohepta-2,6-dienone[22]. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57–6.61 (m, 2H), 6.06 (d, J = 11.6 Hz, 2H), 2.42 (t, J = 3.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.03, 143.94, 133.74, 27.26.

Cyclooct-2-enone[23]. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30–6.36 (td, J = 12.8 Hz, 6.2 Hz, 1H), 5.97–6.00 (d, J = 12.8 Hz, 1H), 2.61–2.65 (t, J = 6.8 Hz, 2H), 2.47–2.51 (m, 2H), 1.76–1.83 (m, 2H), 1.52–1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.04, 141.63, 132.32, 42.63, 28.47, 25.00, 23.00, 23.49.

Cycloocta-2,7-dienone[22]. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23–6.37 (m, 4H), 2.31–2.37 (m, 4H), 1.69–1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.40, 141.57, 135.79, 27.06, 24.90.

Adamantane-1,3-diol[24]. White solid; mp 298–300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.49 (s, 2H), 2.12 (s, 2H), 1.46–1.90 (m, 10H), 1.37 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 68.49, 53.21, 44.01, 34.67, 30.62.

1-Acetamidoadamantane[25]. White solid; mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (s, 1H), 2.04 (s, 3H), 1.97 (s, 6H), 1.90 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.44, 51.86, 41.49, 36.25, 29.32, 24.57. IR (KBr): ν = 3278, 3079, 2906, 2847, 1643, 1559, 1373, 1361, 1342, 1304, 1138 cm^{-1}. HRMS (ESI): m/z: calcd. for $C_{12}H_{19}ONa$ $[M + Na]^+$: 216.1359; found: 216.1363.

Acknowledgements

This work was financially supported by The National Natural Science Foundation of China (No. 20572046 and No. 20872064), Program for New Century Excellent Talents in University (NCET-07-0461), and the Tianjin Natural Science Foundation (09JCY-BJC05900).

Notes and references

1 M. Hudlicky, *Oxidations in Organic Chemistry*, ACS Monograph No. 186, American Chemical Society, Washington DC, 1990.
2 For Cr-catalyzed oxidation, see: (*a*) J. Muzart, *Tetrahedron Lett.*, 1987, **28**, 2131; (*b*) S. Yamazaki, *Org. Lett.*, 1999, **1**, 2129. For Mn-catalyzed oxidation, see: (*c*) N. H. Lee, C.-S. Lee and D. S. Jung, *Tetrahedron Lett.*, 1998, **39**, 1385. For Ru-catalyzed oxidation, see: (*d*) S-I. Murahashi, Y. Oda, T. Naota and T. Kuwabara, *Tetrahedron Lett.*, 1993, **34**, 1299; (*e*) S. I. Murahashi, N. Komiya, Y. Oda, T. Kuwabara and T. Naota, *J. Org. Chem.*, 2000, **65**, 9186. For Rh-catalyzed oxidation, see: (*f*) A. J. Catino, J. M. Nichols, H. Choi, S. Gottipamula and M. P. Doyle, *Org. Lett.*, 2005, **7**, 5167. For Fe-catalyzed oxidation, see: (*g*) C. Pavan, J. Legros and C. Bolm, *Adv. Synth. Catal.*, 2005, **347**, 703; (*h*) M. Nakanishi and C. Bolm, *Adv. Synth. Catal.*, 2007, **349**, 861. For Bi-catalyzed oxidation, see: (*i*) J. Oldham, A. J. Burton and A. G. Barrett, *Org. Lett.*, 2005, **7**, 4549. For Ni-catalyzed oxidation, see: (*j*) S. Yamazaki, *Synth. Commun.*, 1999, **29**, 2211. For Cu-catalyzed oxidation, see: (*k*) S. Velusamy and T. Punniyamurthy, *Tetrahedron Lett.*, 2003, **44**, 8955. For Co-catalyzed oxidation, see: (*l*) T. Punniyamurthy and J. Iqbal, *Tetrahedron Lett.*, 1994, **35**, 4003; (*m*) P. Li and H. Alper, *J. Mol. Catal.*, 1990, **61**, 51. For Au-catalyzed oxidation, see: (*n*) H.-R. Li, Z.-P. Li and Z.-J. Shi, *Tetrahedron*, 2009, **65**, 1856. For Mo-catalyzed oxidation, see: (*o*) S. Das, T. Bhowmick, T. Punniyamurthy, D. Dey, J. Nath and M. K. Chaudhuri, *Tetrahedron Lett.*, 2003, **44**, 4915.
3 (*a*) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (*b*) A. Varvoglis, *Hypervalent Iodine in Organic Synthesis*, Academic Press: London, 1997; (*c*) A. Varvoglis, *Tetrahedron*, 1997, **53**, 1179; (*d*) T. Wirth, *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*; Topics in Current Chemistry Series 224; Springer: Berlin-Tokyo, 2003; (*e*) T. Wirth, *Angew. Chem., Int. Ed.*, 2005, **44**, 3656; (*f*) R. D. Richardson and T. Wirth, *Angew. Chem.*, 2006, **118**, 4510, (*Angew. Chem., Int. Ed.*, 2006, **45**, 4402); (*g*) V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299–5358; (*h*) V. V. Zhdankin, *Arkivoc*, 2009, **i**, 1–62; (*i*) M. Ochiai and K. Miyamoto, *Eur. J. Org. Chem.*, 2008, 4229; (*j*) T. Dohi and Y. Kita, *Chem. Commun.*, 2009, 2073; (*k*) M. Uyanik and K. Ishihara, *Chem. Commun.*, 2009, 2086.
4 (*a*) K. C. Nicolaou, P. S. Baran and Y.-L. Zhong, *J. Am. Chem. Soc.*, 2001, **123**, 3183; (*b*) K. C. Nicolaou, T. Montagnon, P. S. Baran and Y.-L. Zhong, *J. Am. Chem. Soc.*, 2002, **124**, 2245.

5 L. R. Ojha, S. Kudugunti, P. P. Maddukuri, A. Kommareddy, M. R. Gunna, P. Dokuparthi, H. B. Gottam, K. K. Botha, D. R. Parapati and T. K. Vinod, *Synlett*, 2009, 117.
6 A. Y. Koposov, D. N. Litvinov, V. V. Zhdankin, M. J. Ferguson, R. McDonald and R. R. Tykwinski, *Eur. J. Org. Chem.*, 2006, 4791.
7 (*a*) M. Uyanik, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **131**, 251; (*b*) M. Uyanik, R. Fukatsu and K. Ishihara, *Org. Lett.*, 2009, **11**, 3470; (*c*) A. Schulze and A. Giannis, *Synthesis*, 2006, 257.
8 (*a*) X.-F. Zhao and C. Zhang, *Synthesis*, 2007, 551; (*b*) X.-Q. Li, X.-F. Zhao and C. Zhang, *Synthesis*, 2008, 2589; (*c*) X.-Q. Li and C. Zhang, *Synthesis*, 2009, 1163; (*d*) J. Yu and C. Zhang, *Synthesis*, 2009, 2324; (*e*) X.-Q. Li, W.-K. Wang and C. Zhang, *Adv. Synth. Catal.*, 2009, **351**, 2342; (*f*) J. Yu, J. Tian and C. Zhang, *Adv. Synth. Catal.*, 2010, **352**, 531; (*g*) X.-Q. Li, W.-K. Wang, Y.-X. Han and C. Zhang, *Adv. Synth. Catal.*, 2010, **352**, 2588.
9 M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537.
10 S. Sakaguchi, T. Hirabayashi and Y. Ishii, *Chem. Commun.*, 2002, 516.
11 B. M. Trost and R. Braslau, *J. Org. Chem.*, 1988, **53**, 532.
12 T. Dohi, N. Takenaga, A. Goto, H. Fujioka and Y. Kita, *J. Org. Chem.*, 2008, **73**, 7365.
13 T. Nagano and S. Kobayashi, *Chem. Lett.*, 2008, **37**, 1042.
14 K. Sato, M. Aoki, J. Takage, K. Zimmerrnann and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2287.
15 O. Suchard, R. Kane, B. J. Roe, E. Zimmermann, C. Jung, P. A. Waske, J. Mattay and M. Oelgemöller, *Tetrahedron*, 2006, **62**, 1467.
16 H. Tanaka, J. Chou, M. Mine and M. Kuroboshi, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1745.
17 T. M. A. Shaikh, L. Emmanuvel and A. Sudalai, *J. Org. Chem.*, 2006, **71**, 5043.
18 R. K. Arvela and N. E. Leadbeater, *J. Org. Chem.*, 2003, **68**, 9122.
19 P. Berger, A. Bessmernykh, J.-C. Caille and S. Mignonac, *Synthesis*, 2006, 3106.
20 K. Fujita, N. Tanino and R. Yamaguchi, *Org. Lett.*, 2007, **9**, 109.
21 A. R. Pinder, *J. Org. Chem.*, 1982, **47**, 3607.
22 H. O. Krabbenhoft, *J. Org. Chem.*, 1979, **44**, 4285.
23 D. Crich and Y. Zou, *Org. Lett.*, 2004, **6**, 775.
24 R. W. Murray and H. Gu, *J. Org. Chem.*, 1995, **60**, 5673.
25 R. D. Chambers, A. M. Kenwright, M. Parsons, G. Sandford and J. S. Moilliet, *J. Chem. Soc., Perkin Trans. 1*, 2002, 2190.