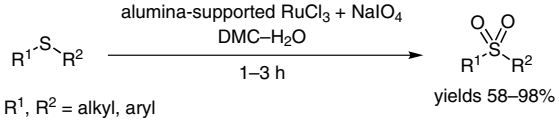
Synthesis M. H. Ali et al. Paper

Oxidation of Aryl Sulfides to Sulfones with Alumina-Supported Ruthenium Catalyst in Dimethyl Carbonate–Water Media

Mohammed Hashmat Ali*[a]
Bjorn Olesen[a]
Brindaban Ranu[b]
Luke Clippard[a]
Jacqueline Heath[a]
Garrett Meyer[a]
Tawanika Williams[a]

[a] Chemistry Department, Southeast Missouri State University, Cape Girardeau, Missouri 63701, USA
mhali@semo.edu
[b] Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India



Received: 02.08.2015
Accepted after revision: 06.10.2015
Published online: 03.12.2015
DOI: 10.1055/s-0035-1560834; Art ID: ss-2015-m0253-op

Abstract A new procedure for the oxidation of sulfides to sulfones utilizing heterogeneous ruthenium reagent has been developed. A small amount of ruthenium trichloride ($RuCl_3$) supported on alumina and excess sodium metaperiodate ($NaIO_4$) was used to produce the ruthenium oxidizing catalyst in the reaction mixture. Sodium metaperiodate oxidized the pre-catalyst $RuCl_3$ to RuO_4 and also maintained a constant supply of RuO_4 by oxidizing lower valent ruthenium ions during the course of the reaction. An environmentally friendly solvent mixture of dimethyl carbonate (DMC) and water was employed. A wide variety of aromatic sulfides were oxidized to sulfones in good to excellent yields by utilizing this procedure.

Key words sulfides, sulfones, RuO_4, dimethyl carbonate, green chemistry

Since Djerassi and Engle introduced ruthenium tetroxide (RuO_4) as an oxidizing reagent in 1953, the chemistry of RuO_4-promoted oxidation reactions has expanded greatly[1–6] to the point where RuO_4 is now a commonly used, versatile oxidizing reagent. Oxidation of C–H bonds of saturated hydrocarbons, oxygen transfer to alkenes in epoxidation, dihydroxylation, ketohydroxylation, cleavage of carbon–carbon and carbon–heteroatom multiple bonds, oxidation of aromatic compounds, oxidation of a carbon adjacent to a heteroatom such as alcohol oxidation, and oxidation of heteroatoms have all been successfully carried out with RuO_4.[3,4] RuO_4 can be used as either a stoichiometric or a catalytic reagent. However, since RuO_4 is expensive, most often a small amount of $RuCl_3$ or RuO_2 is used to generate RuO_4 and the reduced form of the ruthenium produced in the reaction is re-oxidized with a less expensive co-oxidant. A wide variety of oxidants are capable of re-oxidizing lower valent ruthenium compounds such as $RuCl_3$ and RuO_2 to RuO_4. Trichloroisocyanuric acid,[7] bromate salts,[8–10] peroxydisulfates,[10] hypochlorites,[10–13] N-bromo salts,[14] hypervalent iodine compounds,[15] peroxides,[10,11,16–19] peracids,[20,21] oxygen or air,[22–26] bromamine-T,[27,28] oxone,[10,11,29,30] N-oxide compounds,[31,32] periodic acid,[33,34] and periodates[10,35–52] effectively convert lower valent ruthenium compounds into RuO_4. Introduction of a co-oxidant makes it possible to use ruthenium in organic transformations more economically. Given that RuO_4 is a very powerful oxidant, selectivity in ruthenium-promoted oxidation reactions is often an issue. To improve selectivity and yield, a number of modifications to the original RuO_4-promoted reaction have been reported. These include oxidation reactions under phase-transfer conditions,[48–50] under solvent-free ultrasonic radiation,[51] and through the use of Ru–Ce bimetallic oxidant.[52]

In terms of environmental benefits, heterogeneous rather than homogeneous reactions are generally a better choice. Heterogeneous reagents are more environmentally friendly than homogeneous reagents, and a solid support renders heterogeneous reagents safer by anchoring them and not allowing them to become airborne. Furthermore, heterogeneous reagents generate less waste and often reduce reaction times by spreading reagents on the large surface area provided by the solid substrate particles. In general, heterogeneous systems also allow reactions to be carried out in a safer manner.

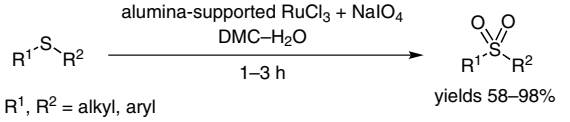
As an extension of our interest in developing green procedures for the transformation of organic functional groups,[53–58] we became interested in the possibility of developing a simple, effective, and environmentally friendly heterogeneous ruthenium reagent for sulfide oxidation in biodegradable dimethyl carbonate reaction media.

Ruthenium reagents anchored on solids using linkers have been reported.[59–69] Linkers are generally attached to solids using multistep procedures. However, these preparative methods are not as environmentally friendly as desired. Cheung reported the preparation of a heterogeneous

ruthenium reagent by impregnating [(1,4,7-trimethyl-1,4,7-triazacyclononane)Ru($CF_3COO)_2(H_2O)$]CF_3COO^- complex on silica gel for the oxidation of secondary alcohols to ketones and for the epoxidation of alkenes using *tert*-butyl hydroperoxide (TBHP) as the stoichiometric oxidant.[59] Preparation of this ruthenium complex involves multiple steps and requires expensive and/or corrosive reagents such as silver trifluoromethane sulfonate and trifluoroacetic acid. RuO_2 supported on V_2O_5-Al_2O_3,[60] TiO_2,[61,69] zeolite,[62,63] Al_2O_3,[64,65,67] hydroxyapatite,[66] and ZSM-5[68] have also been used in the oxidation of various functional groups. RuO_2 on V_2O_5-Al_2O_3 was used in the oxidation of cyclohexane and alkenes with peroxide as co-oxidant. This reagent produced low to moderate yield of the products.[60] RuO_2 on zeolite was also found to be active towards cyclohexane oxidation.[62] Ruthenium reagents on Al_2O_3, zeolite, hydroxylapatite, and ZSM-5 were found to be effective in aerobic oxidation of alcohols.[63,64,66,68] Alumina-supported ruthenium reagents oxidize primary amines to nitriles and secondary amines to imines in the presence of dioxygen.[65,67]

RuO_4-promoted reactions generally employ water–halogenated hydrocarbon biphasic media. The role of the organic solvent in the biphasic media is to dissolve organic substrates and water is necessary because the stoichiometric oxidants usually have low solubility in organic solvents. Low-valent ruthenium compounds are also insoluble in most organic solvents. Historically, CCl_4–H_2O has been used in RuO_4-promoted reactions because this biphasic media produced better yields of product. Recently, biphasic media of water and nonhalogenated solvents, such as, acetonitrile–water,[70] acetonitrile–hexane–water,[71] ethyl acetate–water,[50,72,73] ethyl acetate–acetonitrile–water,[8–11,74–79] cyclohexane–acetonitrile–water,[75] acetone–acetonitrile–water,[75] and dimethyl carbonate–water[80] were found to work well in ruthenium-promoted oxidation reactions. Dimethyl carbonate (DMC) is a biodegradable solvent and has very low or no toxicity.[81–82] It has received federal VOC exemption in 2009 in the USA. Introduction of DMC in the ruthenium oxidation procedure is thus a step closer toward developing a green reaction.

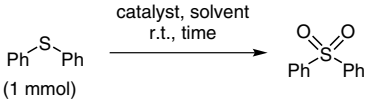
We report herein a heterogeneous procedure for the oxidation of sulfides with $RuCl_3$ and $NaIO_4$ using DMC–H_2O media (Scheme 1). This procedure can be used to oxidize sulfides carrying various functional groups and offers several benefits of green chemistry.



Scheme 1 General reaction scheme for oxidation of sulfides to sulfones with alumina-supported ruthenium catalyst

Our interest in green chemistry prompted us to investigate the use of solid-supported ruthenium reagents in DMC–H_2O media. Oxidation of diphenyl sulfide was explored as the model reaction, and the results obtained under various conditions are reported in Table 1. We found that both Ru/Al_2O_3 and Ru/SiO_2 are capable of oxidizing diphenyl sulfide to diphenyl sulfone in aqueous media, albeit in lower yield and requiring longer reaction time (entries 1–5). We believe that the limited solubility of diphenyl sulfide in water led to the lower yields in this reaction. Ru/SiO_2 and Ru/Al_2O_3 reactions in water for 24 hours produced 42 and 10% yields of diphenyl sulfones respectively (entries 1 and 4). Yields improved to 81 and 44%, respectively, when these reactions were allowed to continue for 48 hours (entries 2 and 5). However, ruthenium on Al_2O_3 in DMC–H_2O produced 96% yield of product in just one hour (entry 6), and ruthenium on SiO_2 under a similar conditions produced 75% yield of product in three hours (entry 7). Ruthenium on Al_2O_3 produced lower yield when the reaction time was shorter than one hour (entry 8). The use of either $RuCl_3$ alone on silica gel (entry 3) or $FeCl_3$ instead of $NaIO_4$ as co-oxidant (entry 9), failed to produce the oxidation product.

Table 1 Standardization of Reaction Conditions for the Oxidation of Diphenyl Sulfide with γ-Alumina-Supported Ruthenium Catalyst



catalyst: Ru (0.0005 mmol) + co-catalyst (3 mmol)

Entry	Catalyst	Co-oxidant	Solvent	Time (h)	Yield (%)[a]
1	Ru/SiO_2	$NaIO_4$	H_2O	24	42
2	Ru/SiO_2	$NaIO_4$	H_2O	48	81
3	Ru/SiO_2	–	H_2O	24	0
4	Ru/Al_2O_3	$NaIO_4$	H_2O	24	10
5	Ru/Al_2O_3	$NaIO_4$	H_2O	48	44
6	Ru/Al_2O_3	$NaIO_4$	DMC–H_2O (8:1)	1	96
7	Ru/SiO_2	$NaIO_4$	DMC–H_2O (8:1)	3	75
8	Ru/Al_2O_3	$NaIO_4$	DMC–H_2O (8:1)	0.5	57
9	Ru/Al_2O_3	$FeCl_3$	DMC–H_2O (8:1)	12	0

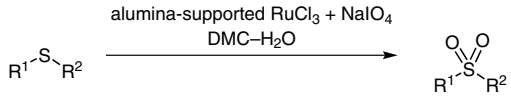
[a] Yield of purified product.

Given that the use of ruthenium on Al_2O_3 in DMC–H_2O produced the best results in our model study (Table 1, entry 6), we used these reaction conditions for the oxidation of a wide variety of sulfides; the results are presented in Table 2.

A large number of aromatic sulfides were oxidized by using our newly developed procedure. The presence of activating groups (Table 2, entries 9, 11, and 13) or deactivating groups (entries 3, 5–8, 10, 14, and 15) did not affect the reaction time or yields significantly. The results indicate that

a large number of functional groups can tolerate the reaction conditions. The survival of nitrile (entry 3), nitro (entry 6), ketone (entries 7 and 17), aldehyde (entry 8), ester (entry 10), methoxy group (entries 11 and 13), and hetero aromatics (entries 9 and 17) is significant. Aromatic rings also survived during these reactions. Notably, aromatic compounds are known to undergo oxidation with ruthenium reagents.[33,78] The use of thiazole produced a brown tar that we were unable to purify (entry 18).

Table 2 Oxidation of Aryl Sulfides to the Corresponding Sulfones Using γ-Alumina-Supported Ruthenium Catalyst



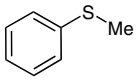
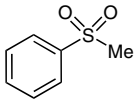
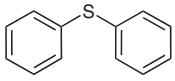
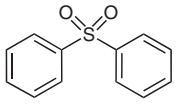
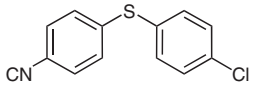
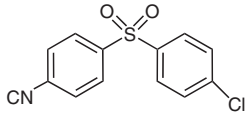
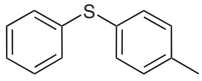
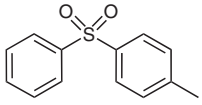
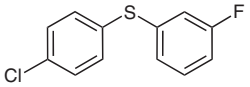
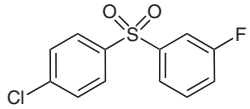
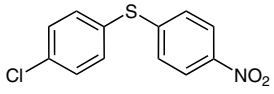
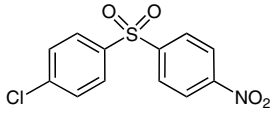
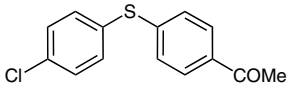
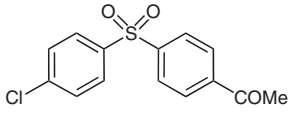
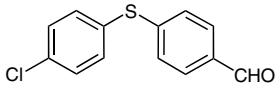
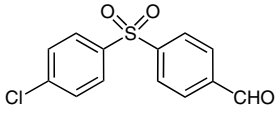
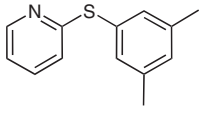
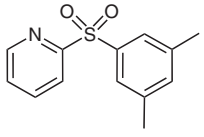
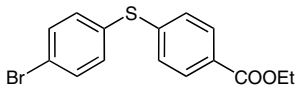
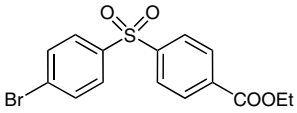
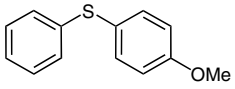
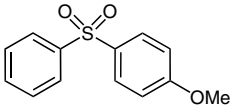
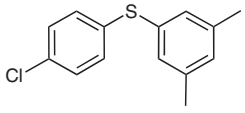
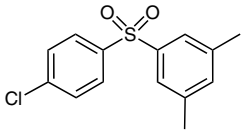
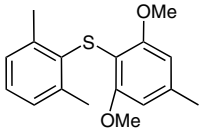
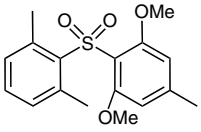
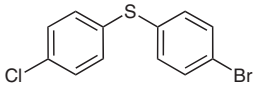
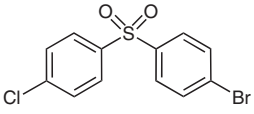
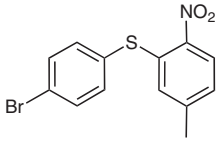
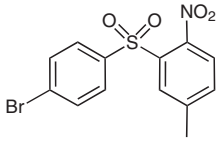
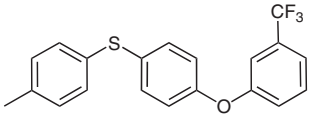
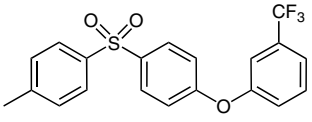
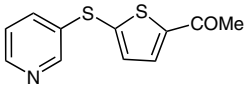
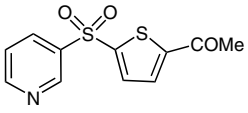
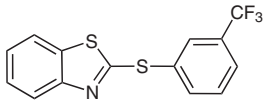
Entry	Sulfide	Time (h)	Sulfone	Yield (%)[a]
1		1		91
2		2		96
3		2		98
4		2		78
5		2		82
6		2		96
7		3		71
8		2		95
9		2		97

Table 2 (continued)

Entry	Sulfide	Time (h)	Sulfone	Yield (%)[a]
10		1.5		78
11		1		97
12		1		64
13		2		89
14		1		91
15		2		58
16		3		90
17		2		90
18			unidentified product mixture	

[a] Yield of purified product. All products were characterized by ^{1}H, ^{13}C NMR and HRMS/elemental analysis data.

In conclusion, the ruthenium-catalyzed oxidation procedure described herein is simple and can be used to oxidize a wide variety of aromatic sulfides to sulfones under environmentally friendly conditions. A wide variety of functional groups are tolerated under the reaction conditions. This procedure has the potential to be accepted as a green chemistry procedure.

Sulfides were purchased from Sigma–Aldrich Chemical Company, India, or prepared in the laboratory. All other chemicals and solvents were purchased from Sigma–Aldrich Chemical Company, India.

All products listed in the Table 2 were characterized by IR, NMR (^{1}H, ^{13}C, and DEPT135), mp and HRMS data. IR spectra were recorded on a Thermo-Nicolet Nexus 670 spectrophotometer. NMR spectra were recorded on a Bruker 500 MHz spectrometer. Melting points were de-

termined using a MeltTemp apparatus. HRMS data were collected on a QToF Mass Analyzer. Spectral data of known compounds were compared with published data, and references are listed accordingly.

Preparation of the Solid-Supported Reagent

$RuCl_3$–Al_2O_3 reagent was prepared by stirring a mixture of $RuCl_3$ (10 mg) and anhydrous γ-alumina (Al_2O_3; 2 g) in anhydrous acetone (10 mL), overnight in a round-bottom flask followed by removal of acetone under vacuum.

Oxidation of Diphenylsulphide to Diphenyl Sulfone; General Procedure (Table 2, Entry 2)[83]

Basic γ-alumina (2 g) and sodium metaperiodate (3 mmol) were placed in a small, round-bottom flask. The basic γ-alumina added above provided support to the metaperiodate. To the well-stirred mixture, H_2O (1 mL) was added followed by Ru–Al_2O_3 catalyst (20 mg, 0.0005 mmol $RuCl_3$). After 2–3 min, DMC (6 mL) was added followed by a solution of diphenylsulphide (1 mmol) in DMC (2 mL). The reaction mixture was stirred at r.t. and the progress of the reaction was monitored by thin-layer chromatography (TLC). When the reaction was complete (ca. 2 h), the mixture was filtered, the solid was rinsed with EtOAc (3 × 6 mL), and the combined filtrate was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the organic solvent gave the crude product, which was purified by column chromatography over silica gel (petroleum ether–EtOAc, 75:25) to provide the corresponding sulfone.

Yield: 209.5 mg (96%); white solid; mp 123 °C.

IR (KBr): 3080, 3066, 2781, 2459, 2330, 1969, 1898, 1770, 1579, 1475, 1448, 1309, 1155 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 7.5 Hz, 4 H), 7.56 (t, *J* = 7 Hz, 2 H), 7.95 (d, *J* = 7.5 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.80 (4 CH), 129.41 (4 CH), 133.31 (2 CH), 141.76 (2 C).

DEPT 135: 127.66 (CH), 129.27 (CH), 133.17 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{10}O_2S$: 241.029922; found: 241.0288.

Methylphenyl Sulfone (Table 2, Entry 1)[83]

Yield: 142 mg (91%); white solid; mp 86 °C.

IR (KBr): 528, 689, 748, 789, 963, 1086, 1148, 1287, 1329, 2896, 2969, 3009 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.06 (s, 3 H), 7.48–7.60 (t, *J* = 7 Hz, 2 H), 7.63–7.70 (t, *J* = 7 Hz, 1 H), 7.90–7.95 (d, *J* = 7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.63 (CH_3), 127.50 (CH), 129.5 (CH), 133.8 (2 C), 140.8 (2 C); DEPT 135: 44.50 (CH_3), 127.36 (CH), 129.37 (CH), 133.69 (CH).

1-(4-Chlorophenylsulfonyl)-4-cyanobenzene (Table 2, Entry 3)

Yield: 272 mg (98%); gummy solid.

IR (KBr): 552, 590, 640, 704, 754, 798, 837, 849, 1013, 1071, 1090, 1155, 1289, 1323, 1396, 1478, 1580, 2236, 3042, 3065, 3090 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (*J* = 8.6 Hz, 2 H), 7.83 (d, *J* = 8.6 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 8.06 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.09, 138.78, 133.31, 130.14, 129.56 (2 C),128.41 (2 C), 117.34 (2 C), 117.14 (2 C).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_8NClO_2S$: 299.986199; found: 299.9862.

Phenyl-4-methylphenyl Sulfone (Table 2, Entry 4)

Yield of sulfone: 181.5 mg (78%); gummy solid. Yield of sulfoxide: 37 mg (17%).

IR (KBr): 548, 654, 687, 729, 818, 1107, 1157, 1296, 1306, 1319, 1447, 1593, 2986, 2970, 3057 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.30 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.83 (d, *J* = 7 Hz, 2 H), 7.93 (d, *J* = 7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.66 (CH_3), 127.62 (C), 127.84 (2 CH), 129.33 (2 CH), 129.91 (2 C), 133.09 (2 CH), 137.15 (C), 138.80 (C), 142.13 (C).

DEPT 135: 21.55 (CH_3), 127.51 (CH), 127.72 (CH), 129.21 (CH), 129.92 (CH), 132.98 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_2S$: 255.045572; found: 255.0462.

1-(4-Chlorophenylsulfonyl)-3-fluorobenzene (Table 2, Entry 5)

Yield: 222 mg (82%), the remainder was a mixture of unidentified products; white solid; mp 175–178 °C.

IR (KBr): 573, 631, 675, 691, 708, 758, 787, 827, 885, 1009, 1080, 1148, 1217, 1323, 1393, 1431, 1476, 1576, 1593, 3067, 3094 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.30 (t, *J* = 6.5 Hz, 1 H), 7.50–7.55 (m, 3 H), 7.62–7.63 (d, *J* = 6.5 Hz, 1 H), 7.72 (d, *J* = 6.5 Hz, 1 H), 7.90 (d, *J* = 6.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.10 (CH), 120.88 (CH), 123.52 (CH), 129.31 (2 CH), 129.98 (2 CH), 131.44 (CH), 140.41 (C), 143.37 (C), 161.56 (C), 163.57 (C).

DEPT 135: 115.04 (CH), 120.82 (CH), 123.46 (CH), 129.25 (CH), 129.92 (CH), 131.38 (CH).

Anal. Calcd for $C_{12}H_8ClFO_2S$: C, 53.24; H, 2.98. Found: C, 52.98; H, 2.64.

1-(4-Chlorophenylsulfonyl)-4-nitrobenzene (Table 2, Entry 6)

Yield: 286 mg (96%); yellowish solid; mp 173–174 °C.

IR (KBr): 3107, 3034, 1909, 1605, 1531, 1477, 1402, 1352, 1325, 1157, 1089, 1013, 856, 768, 735 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 9 Hz, 2 H), 7.90 (dd, *J* = 2, 9 Hz, 2 H), 8.11 (dd, *J* = 2, 9 Hz, 2 H), 8.35 (d, *J* = 9 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.77 (2 CH), 129.13 (2 CH), 129.62 (2 CH), 130.20 (2 CH), 138.70 (CH), 141.20 (CH), 147.11 (CH), 150.65 (CH).

DEPT 135: 124.65 (CH), 129.00 (CH), 129.49 (CH), 130.08 (CH).

Anal. Calcd for $C_{12}H_8ClNO_4S$: C, 48.41; H, 2.71; N, 4.70. Found: C, 48.83; H, 2.68; N, 4.74.

1-[4-(4-Chlorophenylsulfonyl)phenyl]ethanone (Table 2, Entry 7)

Yield: 209 mg (71%), the remainder was a mixture of unidentified products; white solid; mp 128–129 °C.

IR (KBr): 3092, 3040, 1697, 1576, 1474, 1396, 1321, 1259, 1153, 1127, 1012, 962 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 7.88 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 8.5 Hz, 2 H), 8.06 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.99 (CH_3), 128.13 (2 CH), 129.31 (2 CH), 129.46 (2 CH), 129.97 (2 CH), 139.49 (CH), 140.62 (CH), 140.71 (CH), 145.17 (CH), 196.77 (C=O).

DEPT 135: 26.86 (CH_3), 128.00 (CH), 129.17 (CH), 129.31 (CH), 129.83 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}ClO_3S$: 317.0015; found: 317.0015.

1-[4-(4-Chlorophenylsulfonyl)phenyl]ethanal (Table 2, Entry 8)

Yield: 267 mg (95%); gummy solid.

IR (KBr): 3078, 3020, 1687, 1672, 1587, 1387, 1285, 1169, 1082, 1011, 820 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 7 Hz, 2 H), 7.39 (d, *J* = 7 Hz, 2 H), 7.44 (d, *J* = 7 Hz, 2 H), 7.74 (d, *J* = 7 Hz, 2 H), 9.92 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.72 (2 CH), 130.19 (C), 130.30 (2 CH), 130.38 (2 CH), 134.20 (C), 135.54 (2 CH), 135.61 (C), 146.46 (C),191.24 (COH).

DEPT 135: 127.55 (CH), 130.04 (CH), 130.24 (CH), 135.41 (CH), 191.11 (CHO).

2-(3,5-Dimethylphenylsulfonyl)pyridine (Table 2, Entry 9)

Yield: 240 mg (97%); white solid; mp 97 °C.

IR (KBr): 3053, 2953, 1607, 1574, 1454, 1323, 1271, 1165, 1149, 1120, 987 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 6 H), 7.21 (s, 1 H), 7.40–7.46 (m, 1 H), 7.66 (s, 2 H), 7.90–7.93 (m, 1 H), 8.19 (d, *J* = 8 Hz, 1 H), 8.68 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.33, 122.35, 126.50, 126.93, 135.67, 138.18, 139.05, 139.36, 150.60, 159.40.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{13}NO_2S$: 270.056471; found: 270.0566.

Ethyl 4-(4-Bromophenylsulfonyl)ethylbenzoate (Table 2, Entry 10)

Yield: 288 mg (78%), the remainder was a mixture of unidentified products; white solid; mp 125–126 °C.

IR (KBr): 3097, 2980, 1722, 1574, 1400, 1325, 1273, 1155, 1099, 1009 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.5 Hz, 3 H), 4.37–4.42 (q, *J* = 7.5 Hz, 2 H), 7.66 (d, *J* = 7.5 Hz, 2 H), 7.80 (d, *J* = 7.5 Hz, 2 H), 7.98 (d, *J* = 7.5 Hz, 2 H), 8.16 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.37 (CH_3), 61.94 (CH_2), 127.81 (2 CH), 129.14 (C), 129.49 (2 CH), 130.68 (2CH), 132.93 (2 CH), 135.08 (C), 140.12 (C), 145.05 (C), 165.04 (C=O).

DEPT 135: 14.36 (CH_3), 61.80 (CH_2), 127.66 (CH), 129.34 (CH), 130.54 (CH), 132.79 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}BrO_4S$: 390.961563; found: 390.9614.

Phenyl-4-methoxyphenyl Sulfone (Table 2, Entry 11)

Yield: 245 mg (97%); gummy solid.

IR (KBr): 558, 687, 731, 804, 835, 1018, 1107, 1152, 1265, 1298, 1317, 1447, 1497, 1576, 1591, 2845, 2945, 2999, 3077 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.96–6.99 (d, *J* = 8.5 Hz, 2 H), 7.48–7.55 (m, 3 H), 7.88 (d, *J* = 8.5 Hz, 2 H), 7.93 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.78 (CH_3), 114.66 (2 CH), 127.46 (2 CH), 129.34 (2 CH), 130.04 (2 CH), 132.96 (2 CH), 133.31 (C), 142.55 (C), 163.54 (C).

DEPT 135: 55.63 (CH_3), 114.51 (CH), 127.32 (CH), 129.19 (CH), 129.89 (CH), 132.83 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}O_3S$: 271.040487; found: 270.9596.

1-(4-Chlorophenylsulfonyl)-3,5-dimethylbenzene (Table 2, Entry 12)

Yield: 180 mg (64%), the remainder was a mixture of unidentified products; white solid; mp 137–139 °C.

IR (KBr): 3084, 2955, 2916, 1908, 1764, 1607, 1578, 1472, 1391, 1321, 1151, 1084 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 6 H), 7.26 (s, 1 H), 7.54 (d, *J* = 8 Hz, 2 H), 7.60 (s, 2 H), 7.94 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.36 (2 CH_3), 125.30 (2 CH), 129.22 (2 CH), 129.68 (2 CH), 135.30 (2 CH), 139.69 (C), 139.83 (C), 140.63 (C), 141.05 (C).

DEPT 135: 21.21 (CH_3), 125.15 (CH), 129.07 (CH), 129.54 (CH), 135.16 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{13}ClO_2S$: 303.022250; found: 303.0221.

Anal. Calcd for $C_{14}H_{13}ClO_2S$: C, 59.89; H 4.67. Found: C, 60.21; H 3.95.

2-(2,6-Dimethylphenylsulfonyl)-1,3-dimethoxybenzene (Table 2, Entry 13)

Yield: 317 mg (89%); white solid; mp 153–155 °C.

IR (KBr): 2972, 2941, 2837, 1584, 1474, 1429, 1310, 1254, 1155, 1107, 779 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.59 (s, 6 H), 3.69 (s, 6 H), 6.55 (d, *J* = 8.5 Hz, 2 H), 7.04 (d, *J* = 7.5 Hz, 2 H), 7.21 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.69 (2 CH_3), 56.40 (2 C), 105.34 (2 C), 130.73 (2 C), 131.33 (2 C), 134.49 (2 C), 139.07 (2 C), 159.43 (2 C).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}O_4S$: 329.082352; found: 329.0824.

1-(4-Chlorophenylsulfonyl)-4-bromobenzene (Table 2, Entry 14)

Yield: 302 mg (91%); white solid; mp 139–140 °C.

IR (KBr): 3092, 1574, 1474, 1393, 1327, 1281, 1159, 1009, 824 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.78 (d, *J* = 8.5 Hz, 2 H), 7.86 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 128.93 (C), 129.27 (2 CH), 129.32 (2 CH), 129.92 (2 CH), 132.91 (2 CH), 139.87 (C), 140.41 (C), 140.48 (C).

DEPT 135: 129.12 (CH), 129.17 (CH), 129.77 (CH), 132.75 (CH).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_8BrClO_2S$: 352.901461; found: 352.8960.

3-(4-Bromophenylsulfonyl)-1-methyl-4-nitrobenzene (Table 2, Entry 15)

Yield: 206.5 mg (58%), the remainder was a mixture of unidentified products; white solid; mp 190–192 °C.

IR (KBr): 3091, 2951, 2879, 1933, 1568, 1535, 1475, 1389, 1358, 1313, 1153, 1066, 887 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 7.54 (d, *J* = 7 Hz, 1 H), 7.68–7.71 (m, 3 H), 7.83 (d, *J* = 7.5 Hz, 2 H), 8.17 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.69 (CH_3), 123.46 (C), 125.37 (CH), 127.10 (C), 129.17 (C), 129.89 (CH), 132.14 (CH), 132.51 (CH), 134.37 (C), 135.15 (CH), 139.87 (C), 144.53 (C).

DEPT 135: 21.54 (CH_3), 125.23 (CH), 129.74 (CH), 132.00 (CH), 132.36 (CH), 135.01 (CH).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}BrNO_4S$: 355.9592; found: 355.9492.

1-(4-Tosylphenoxy)-3-(trifluoromethyl)benzene (Table 2, Entry 16)

Yield: 353 mg (90%); yellow viscous liquid.

IR (neat): 3099, 3057, 1857, 1679, 1578, 1518, 1429, 1362, 1323, 1261, 1167, 1119, 1018 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.04 (d, *J* = 7 Hz, 2 H), 7.21 (d, *J* = 8 Hz, 1 H), 7.30 (m, 3 H), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 8 Hz, 1 H), 7.83 (d, *J* = 8 Hz, 2 H), 7.92 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6 (CH_3), 60.45 (CF_3), 117.10 (CH), 117.13 (2 CH), 118.34 (CH), 121.57 (CH), 123.36 (CH), 127.67 (2 CH), 130.07 (2 CH), 130.16 (C), 130.92 (2 CH), 136.75 (C), 138.94 (C), 144.27 (C), 155.64 (C), 16.91 (C).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}F_3O_3S$: 393.0772; found: 393.0766.

1-[5-(Pyridin-3-ylsulfonyl)thiophen-2-yl]ethanone (Table 2, Entry 17)

Yield: 244 mg (90%); white solid; mp 149–150 °C.

IR (KBr): 2998, 1975, 1684, 1601, 1568, 1422, 1357, 1258, 1178 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.57 (s, 3 H), 7.50–7.54 (m, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.83 (d, *J* = 7.5 Hz, 1 H), 7.94–7.98 (m, 1 H), 8.20 (d, *J* = 8 Hz, 1 H), 8.71–8.2 (br d, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.11 (CH_3), 122.20 (CH), 127.59 (CH), 131.42 (CH), 135.13 (CH), 138.51 (CH), 146.16 (C), 150.75 (CH), 151.60 (C), 158.19 (C), 190.41 (C=O).

DEPT 135: 26.99 (CH_3), 122.07 (CH), 127.47 (CH), 131.13 (CH), 135.01 (CH), 138.38 (CH), 150.63 (CH).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{11}H_9NO_3S_2$: 268.0102; found: 268.0098.

Acknowledgment

The authors are grateful for the financial support from the National Science Foundation (NSF)-IRES grant number OISE-0966395.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560834.

References

(1) Djerrasi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *I75*, 3838.
(2) Naota, T.; Takaya, H.; Murahasi, S.-I. *Chem. Rev.* **1998**, *98*, 2599.
(3) Plietker, B. *Synthesis* **2005**, 2453.
(4) Pagliaro, M.; Campestrini, S.; Ciriminna, R. *Chem. Soc. Rev.* **2005**, *34*, 837.
(5) Carlson, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.
(6) Gore, E. S. *Platinum Met. Rev.* **1983**, *27*, 111.
(7) Yamaoka, H.; Moriya, N.; Ikunaka, M. *Org. Process Res. Dev.* **2004**, *8*, 931.
(8) Desai, S. M.; Halligudi, N. N.; Nandibewoor, S. T. *Transition Met. Chem. (Dordrecht, Neth.)* **2002**, *27*, 207.
(9) Giddings, S.; Mills, A. *J. Org. Chem.* **1988**, *53*, 1103.
(10) Plietker, B.; Niggemann, M. *Org. Biomol. Chem.* **2004**, *2*, 2403.
(11) Plietker, B. *J. Org. Chem.* **2004**, *69*, 8287.
(12) Spitzer, U. A.; Lee, D. G. *J. Org. Chem.* **1975**, *40*, 2539.
(13) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *Chem. Commun.* **1970**, 1420.
(14) Rangaswami, M.; Anand, S.; Gowda, N. M. M. *Synth. React. Inorg. Met.-Org. Chem.* **2001**, *31*, 1479.
(15) Yusubov, M. S.; Chi, K.-W.; Park, J. Y.; Karimov, R.; Zhdankin, V. V. *Tetrahedron Lett.* **2006**, *47*, 6305.
(16) Barak, G.; Dakka, A.; Sasson, Y. *J. Org. Chem.* **1988**, *53*, 3553.
(17) Shingate, B. B.; Hazra, B. G.; Salunke, D. B.; Pore, V. S. *Tetrahedron Lett.* **2011**, *52*, 6007.
(18) Murahashi, S.-I.; Naota, T.; Miyaguchi, N.; Noda, S. *J. Am. Chem. Soc.* **1996**, *118*, 2509.
(19) Cheung, W.-H.; Yip, W.-P.; Yu, W.-Y.; Che, C.-M. *Can. J. Chem.* **2005**, *83*, 521.
(20) Murahashi, S.-I.; Saito, T.; Hanaoka, H.; Murakami, Y.; Naota, T.; Kumobayashi, H.; Akutagawa, S. *J. Org. Chem.* **1993**, *58*, 2929.
(21) Komiya, N.; Noji, S.; Murahasi, S.-I. *Chem. Commun.* **2001**, 65.
(22) Jain, S. L.; Sain, B. *Chem. Commun.* **2002**, 1040.
(23) Ragagnin, G.; Knochel, P. *Synlett* **2004**, 951.
(24) Shiroishi, H.; Nukaga, M.; Yamashita, S.; Kaneko, M. *Chem. Lett.* **2002**, 488.
(25) Chang, S.; Lee, M.; Ko, S.; Lee, P. *Synth. Commun.* **2002**, *32*, 1279.
(26) Matsumoto, M.; Watanabe, N. *J. Org. Chem.* **1984**, *49*, 3435.
(27) Jain, S. L.; Sharma, V. B.; Sain, B. *Synth. Commun.* **2005**, *35*, 465.
(28) Sharma, V. B.; Jain, S. L.; Sain, B. *Tetrahedron Lett.* **2004**, *45*, 4281.
(29) Yang, D.; Zhang, C. *J. Org. Chem.* **2001**, *66*, 4815.
(30) Plietker, B. *J. Org. Chem.* **2003**, *68*, 7123.
(31) Gross, Z.; Ini, S. *Org. Lett.* **1999**, *1*, 2077.
(32) Zhang, R.; Yu, W.-Y.; Wong, K.-Y.; Che, C.-M. *J. Org. Chem.* **2001**, *66*, 8145.
(33) Nunez, M. T.; Martin, V. S. *J. Org. Chem.* **1990**, *55*, 1928.
(34) Shoair, A. G.; Mohamed, R. H. *Synth. Commun.* **2006**, *36*, 59.
(35) Kraft, P.; Eichenberger, W. *Eur. J. Org. Chem.* **2003**, 3735.
(36) Webster, F. X.; Rivas-Enterrios, J.; Silverstein, R. M. *J. Org. Chem.* **1987**, *52*, 689.
(37) Mazoir, N.; Auhmani, A.; Daubi, M. *Synth. Commun.* **2007**, *37*, 1289.
(38) Akbutina, F. A.; Torosyan, S. A.; Vostrikov, N. S.; Spririkhin, L. V.; Miftakhov, M. S. *Russ. Chem. Bull.* **1996**, *45*, 2813.
(39) Ziyat, H.; Ali, M. A.; Karim, A.; Meliet, C.; Castanet, Y.; Mortreux, A. *Acta Chim. Slov.* **2004**, *51*, 223.
(40) Parikh, V. M.; Jones, J. K. N. *Can. J. Chem.* **1965**, *43*, 3452.
(41) Phukan, P.; Sudalai, A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3015.
(42) Hjelmencrantz, A.; Berg, U. *J. Org. Chem.* **2002**, *67*, 3585.
(43) Han, J.-S.; Lowary, T. L. *J. Org. Chem.* **2003**, *68*, 3735.
(44) Sarker, T. K.; Basak, S. *Org. Lett.* **2004**, *6*, 2925.
(45) Ferraz, H. M.; Longo, L. S. *Org. Lett.* **2003**, *5*, 1337.
(46) Alcaide, B.; Almendros, P.; Alonso, J. M. *Tetrahedron Lett.* **2003**, *44*, 8693.
(47) Torii, S.; Inokuchi, T.; Kondo, K. *J. Org. Chem.* **1985**, *50*, 4980.
(48) Yuasa, Y.; Tsuruta, H. *J. Essent. Oil Res.* **1998**, *10*, 39.
(49) Morris, P. E.; Kiely, D. E. *J. Org. Chem.* **1987**, *52*, 1149.

(50) Yuasa, Y.; Shibuya, S.; Yuasa, Y. *Synth. Commun.* **2003**, *33*, 3947.
(51) Rup, S.; Sindt, M.; Oget, N. *Tetrahedron Lett.* **2010**, *51*, 3123.
(52) Plietker, B.; Niggemann, M. *J. Org. Chem.* **2005**, *70*, 2402.
(53) Ali, M. H.; Niedbalsky, M.; Bohnert, G.; Bryant, D. *Synth. Commun.* **2006**, *36*, 1751.
(54) Ali, M. H.; Wiggin, C. J. *Synth. Commun.* **2001**, 3383.
(55) Ali, M. H.; Wiggin, C. J. *Synth. Commun.* **2001**, 1389.
(56) Ali, M. H.; Leach, D. R.; Schmitz, C. E. *Synth. Commun.* **1998**, 2969.
(57) Ali, M. H.; Bohnert, G. J. *Synth. Commun.* **1998**, 2983.
(58) Ali, M. H.; Bohnert, G. J. *Synthesis* **1997**, 764.
(59) Cheung, W.-H.; Yu, W.-Y.; Yip, W.-P.; Zhu, N.-Y.; Che, C.-M. *J. Org. Chem.* **2002**, *67*, 7716.
(60) Tchener, Y. N.; Choukchou-Braham, A.; Bachir, R. *Bull. Mater. Sci.* **2012**, *35*, 673.
(61) Amama, P. B.; Itoh, K.; Murabayashi, M. *J. Mater. Sci.* **2004**, *39*, 4349.
(62) Zhan, B.-Z.; White, M. A.; Pincock, J. A.; Robertson, K. N.; Cameron, T. S.; Sham, T.-K. *Can. J. Chem.* **2003**, 764.
(63) Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Rao, K. V. R.; Robertson, K. N.; Cameron, T. S. *J. Am. Chem. Soc.* **2003**, *125*, 2195.
(64) Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2002**, *41*, 4538.
(65) Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2003**, *42*, 1480.
(66) Ho, C.-M.; Yu, W.-Y.; Che, C.-M. *Angew. Chem. Int. Ed.* **2004**, *43*, 3303.
(67) Yamaguchi, K.; Mizuno, N. *Angew. Chem.* **2003**, *115*, 1518.
(68) Qian, G.; Zhao, R.; Lu, G.; Qi, Y.; Suo, J. *Synth. Commun.* **2004**, *34*, 1753.
(69) Gallagher, L. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 5308.
(70) Arini, G. A.; Szeto, P.; Hughes, D. L.; Stockman, R. A. *Tetrahedron Lett.* **2004**, *45*, 8371.
(71) Kimberley, M. *ChemSpider SyntheticPage* **2002**, 186; DOI: 10.1039/SP186.
(72) Rinner, U.; Siengalewicz, P.; Hudlicky, T. *Org. Lett.* **2002**, *4*, 115.
(73) Sharma, N. K.; Ganesh, K. N. *Tetrahedron Lett.* **2004**, *45*, 1403.
(74) Plietker, B.; Niggemann, M. *Org. Lett.* **2003**, *5*, 3353.
(75) Griffith, P.; Kwong, E. *Synth. Commun.* **2003**, *33*, 2945.
(76) Paquette, L. A.; Kahane, A. L.; Seekamp, C. K. *J. Org. Chem.* **2004**, *69*, 5555.
(77) Zimmermann, F.; Meux, E.; Mieloszynski, J.-L.; Lecuire, J.-M.; Oget, N. *Tetrahedron Lett.* **2005**, *46*, 3201.
(78) Moutevelis-Minakakis, P.; Sinanoglou, C.; Loukas, V.; Kokotos, G. *Synthesis* **2005**, 933.
(79) Yang, D.; Chen, F.; Dong, Z.-M.; Zhang, D.-W. *J. Org. Chem.* **2004**, *69*, 2221.
(80) Cornely, J.; Ham, L. M. S.; Meade, D. E.; Dragojlovic, V. *Green Chem.* **2003**, *5*, 34.
(81) Tundo, P.; Avico, F.; Anthony, E. R.; Grego-Rossi, S. *Dimethyl Carbonate: Green Solvent and Ambient Reagent*, In *Green Chemical Reactions, NATO Science for Peace and Security Series*; Tundo, P.; Esposito, V., Eds.; Springer: Dordrecht, **2008**, 213–232.
(82) Yu, B.; Liu, A.-H.; He, L.-N.; Li, B.; Diazo, Z.-F.; Li, Y.-N. *Green Chem.* **2012**, *14*, 957.
(83) Kim, S. S.; Nehru, K.; Kim, S. S.; Kim, D. W.; Jung, H. C. *Synthesis* **2002**, 2484.