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# Functionalized $\alpha$ -keto stabilized sulfonium ylides as highly active ligand precursors for palladium catalyzed Suzuki–Miyaura cross-couplings



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### A R T I C L E I N F O

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## ABSTRACT

Five  $\alpha$ -keto stabilized sulfonium ylides as type (Me)<sub>2</sub>SCHC(O)C<sub>6</sub>H<sub>4</sub>-*p*-X (X = H, Br, NO<sub>2</sub>, CH<sub>3</sub> and OCH<sub>3</sub>) {L<sub>1</sub>-L<sub>5</sub>} were used as ligand precursors in the Suzuki–Miyaura cross-coupling reaction. The best catalytic performance was obtained by using a sulfonium ylide/Pd ratio of 2:1. The catalytic systems displayed high activities, which increased in the order R = NO<sub>2</sub> (L<sub>3</sub>) < Br (L<sub>2</sub>) < H (L<sub>1</sub>) < CH<sub>3</sub> (L<sub>4</sub>) < OCH<sub>3</sub> (L<sub>5</sub>). The coupling reactions proceeded smoothly with 0.05 mol% PdCl<sub>2</sub> and 0.1 mol% L<sub>5</sub> in DMF at 130 °C between varieties of electronically activated, deactivated and neutral aryl halides and aryl boronic acids within short reaction times and without the need for exclusion of air which gave good to high yields of the corresponding products. All the studied ligands demonstrated very high activity in the Suzuki–Miyaura cross-coupling, which yielded turnover numbers up to 1940. Comparative studies showed that the performance of sulfonium ylide L<sub>5</sub> is significantly superior to that of related phosphine-free ligands.

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Palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with aryl boronic acids is a powerful method for the formation of C-C bonds and generation of unsymmetrical biaryls [1–3]. Among the common protocols, aryl iodides and bromides have been found to be the more reactive than aryl chlorides [4,5]. However, more economic aryl chlorides have been partly employed in cross-coupling reactions [6,7]. On the other hand, wide varieties of aryl boronic acids with various substituents were used to the synthesis of a desired biphenyl product [8,9]. The traditional Suzuki reaction proceeds using a palladium complex with a ligand (usually a phosphine) [10–12] and there has been much recent attention attracted on employing new catalysts that are environmentally benign and efficient [13]. Also, it is a well-known fact that in Suzuki reactions, the activity of the catalyst depends on the nature of the ligand structure attached to the Pd metal [14]. Bulky electron-rich phosphine ligands are prominent in the palladium catalyzed Suzuki cross-coupling reaction, resulting from their superior donor capability and stabilization effects [15-17]. Though these catalysts exhibited excellent catalytic properties, most of them are sensitive to air and/or moisture besides expensive and therefore require oxygen-free handling to minimize ligand oxidation [18,19]. These drawbacks place a significant limitation on their synthetic applications. In contrast, phosphinefree ligands, containing N, O and S atoms, are typically inexpensive, easily prepared and stable toward heat, moisture and air [20-24]. Therefore, these advantages encourage us to use sulfonium ylide as ideal alternatives to tertiary phosphines in transition-metal based homogeneous catalysts. Sulfonium ylides  $R_2S = C(R')CO(R'')$  can behave

http://dx.doi.org/10.1016/j.inoche.2014.07.027 1387-7003/© 2014 Published by Elsevier B.V. as ligands, because the carbanion located at the C $\alpha$  of the ylide or the enolate oxygen is able to donate electron density to a transition metal [25–28]. Furthermore, the rich coordination modes of these ylides in bonding and use of these compounds in organic and organometallic reactions can provide a variety of information [29]. Thus, using a combination of ligands with metal precursors, providing in-situ formation of catalytic species, has seemed to be not only practical but also more efficient than the isolated ligand-metal complexes. In some cases, this fact arises from the low efficiency of complexation stages and/or aiming to operational simplicity. The recent review published by Kumar and coworkers shows a comparative study on organosulfur and related ligands in the Suzuki–Miyaura C–C coupling reaction [30]. During the last review reported in 2013, there has been no report on using of sulfonium ylides as ligand precursor in the Suzuki-Miyaura coupling reaction. Therefore, investigation of catalytic activity of  $\alpha$ -keto stabilized sulfonium ylides can establish a new field in organosulfur and related ligands used in catalytic systems. In this communication, we attempted to use sulfonium ylides that we recently developed [31,32] accompanied by Pd precursors in the Suzuki-Miyaura cross-coupling reaction (Scheme 1).

As shown in Scheme 2, all sulfonium ylides were synthesized as described previously [31]. At first, 1 equiv. of 2-bromoacetophenone, 2-bromo-4'-bromoacetophenone, 2-bromo-4'-methylacetophenone, 2-bromo-4'-methylacetophenone was reacted with 3 equiv. of dimethyl sulfide in acetone to form the respective sulfonium salts. Subsequent treatment with aqueous 10% NaOH solution led to eliminate HBr, giving the  $L_1-L_5$  ligands.

The catalytic activity of  $L_1-L_5$  in Suzuki cross-coupling reactions was then examined. Initially, we carried out a model reaction to optimizing

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Scheme 1. Suzuki-Miyaura cross-coupling reaction using sulfonium ylide ligands.



Scheme 2. Synthetic route of ligands L1-L5

the reaction conditions. Reaction of phenyl boronic acid with 4bromobenzene was chosen as a model reaction. At the first stage of optimization, we studied the catalyst loading effect on the reaction at four different catalyst concentrations. As expected, various catalyst loadings showed a significant effect on the performance of the catalyst systems. When the loading of PdCl<sub>2</sub> was reduced to 0.005 mol% from 0.05 mol%, the yield of the corresponding product (or biphenyl) was decreased (Table 1, entries 3 (50%) and 2 (75%)). Also, excessive amount of catalyst did not increase the yields significantly (Table 1, entry 4). Therefore, with respect to the economic aspect, low catalyst loading of 0.05 mol% was chosen as the best concentration of catalyst (Table 1, entry 2).

We then examined the effect of the ligand:metal (L:M) mole ratio on yield of reaction. The L:M mole ratio shows a dramatic influence on the Suzuki reaction. When L:M mole ratio was changed to 1:1 (both at 0.05 mol%), the yield was lowered to 42% (Table 1, entry 5). At the 1:4 palladium to ligand ratio, the yield was not significantly changed (Table 1, entry 7 (76%)). Also when no ligand was used, the yield was greatly decreased and trace amount of biphenyl was formed (Table 1, entry 6). This result shows that in the absence of ligand, catalysis of the reaction encounters with uphill. Finally, at the 2:1 palladium to ligand ratio, the yield decreased to 45% (Table 1, entry 8), that it is similar

to the result obtained in entry 5 and indicates that excess amount of
PdCl <sub>2</sub> cannot significantly increase catalyst performance. Therefore in
seems that the complex coordination is 1:2 palladium to ligand
(Table 1, entry 2).

to the regult obtained in entry E and indicates that ever

In the next step, we investigated the influence of various bases on the Suzuki–Miyaura cross-coupling reaction. The organic and inorganic bases were investigated, as shown in Table 1. Addition of proper bases has a remarkable accelerating effect on the reaction time. Thus, we investigated a series of reactions to screening influence of base on the catalytic system. Among the tested bases,  $Cs_2CO_3$  was the most effective base for the coupled product with 90% yield (Table 1, entry 9), while other bases, such as  $K_2CO_3$ ,  $Na_2CO_3$  and NaOAc proved to be less active and gave lower yields (Table 1, entries 2 (75%), 10 (62%) and 11 (55%)). Use of organic base Et<sub>3</sub>N gave inferior result and showed slow reaction rates compared to inorganic bases (Table 1, entry 12 (40%)).

Finally, the model reaction was carried out in the presence of different solvents and temperatures. It was found that the polarity of the solvent had a considerable effect. For instance, a non-polar solvent like toluene and *n*-hexane gave poor yields (Table 1, entries 14 (51%) and 15 (44%)), whereas polar solvents such as DMF and NMP were the most productive solvents and were more efficient for the yield of biaryl compounds up to 80% (Table 1, entries 9 and 13). Other polar aprotic

Table	1
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Optimization of reaction conditions.<sup>a</sup>

$\langle \rangle$	Br + (HO) <sub>2</sub> B	PdCl <sub>2</sub> , L <sub>1</sub>					
Entry	PdCl <sub>2</sub> mol%	PdCl <sub>2</sub> :L	Base	Solvent	Temperature	Yield <sup>b</sup>	TON <sup>c</sup>
1	0.5	1:2	K <sub>2</sub> CO <sub>3</sub>	DMF	130	78	156
2	0.05	1:2	K <sub>2</sub> CO <sub>3</sub>	DMF	130	75	1500
3	0.005	1:2	K <sub>2</sub> CO <sub>3</sub>	DMF	130	50	10,000
4	1.0	1:2	K <sub>2</sub> CO <sub>3</sub>	DMF	130	80	80
5	0.05	1:1	K <sub>2</sub> CO <sub>3</sub>	DMF	130	42	840
6	0.05	1:0	K <sub>2</sub> CO <sub>3</sub>	DMF	130	Trace	0
7	0.05	1:4	K <sub>2</sub> CO <sub>3</sub>	DMF	130	76	1520
8	0.05	2:1	K <sub>2</sub> CO <sub>3</sub>	DMF	130	45	900
9	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	DMF	130	80	1600
10	0.05	1:2	Na <sub>2</sub> CO <sub>3</sub>	DMF	130	62	1240
11	0.05	1:2	NaOAc	DMF	130	55	1100
12	0.05	1:2	NEt <sub>3</sub>	DMF	130	40	800
13	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	NMP	130	75	1500
14	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	100	51	1000
15	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	n-Hexane	60	44	880
16	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	Methanol	60	62	1240
17	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	100	67	1340
18	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	DMF	60	56	1120
19	0.05	1:2	Cs <sub>2</sub> CO <sub>3</sub>	DMF	80	67	1340
20	0.05	1:2	$Cs_2CO_3$	DMF	100	74	1480

<sup>a</sup> Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (2.4 mmol), PdCl<sub>2</sub>, L<sub>1</sub>, base (4.0 mmol), solvent (3 ml) and 2 h.

<sup>b</sup> Isolated yield based on aryl halide.

<sup>c</sup> Mole of product per mole of catalyst.

#### Table 2

Evaluation of catalytic activity of the ligands in Suzuki cross-coupling reaction.<sup>a</sup>

Br	+ (HO) <sub>2</sub> B	PdCl <sub>2</sub> , L <sub>n</sub> DMF, Cs <sub>2</sub> CO <sub>3</sub>				
Entry	Ligand	R	PdCl <sub>2</sub> mol%	PdCl <sub>2</sub> :L	Yield <sup>b</sup>	TON <sup>c</sup>
1	None	-	0.05	1:2	Trace	0
2	L <sub>1</sub>	- H	0.05	1:2	80	1600
3	L <sub>2</sub>	-Br	0.05	1:2	73	1460
4	L <sub>3</sub>	$-NO_2$	0.05	1:2	70	1400
5	L <sub>4</sub>	- CH <sub>3</sub>	0.05	1:1	81	1620
6	L <sub>5</sub>	$-OCH_3$	0.05	1:2	89	1780

<sup>a</sup> Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (2.4 mmol), PdCl<sub>2</sub>, L<sub>n</sub>, Cs<sub>2</sub>CO<sub>3</sub> (4.0 mmol), DMF (3 ml) and 2 h.

<sup>b</sup> Isolated yield based on aryl halide.

<sup>c</sup> Mole of product per mole of catalyst.

solvents including methanol and water gave comparatively low yields (Table 1, entries 16 (62%) and 17 (67%)). Also, effect of temperature on catalytic activity was investigated. Results showed that at a lower temperature, the reaction was not completed and yield of product was decreased (Table 1, entries 18 (56%), 19 (67%) and 20 (74%)). Best efficiency was observed at reflux temperature (130 °C), so this temperature was chosen as the default reaction temperature.

After the optimization stage, we employed these reaction conditions including  $Cs_2CO_3$  (1 mmol), 0.05 mol% of PdCl<sub>2</sub>, 0.1 mol% of ligand and 2 ml DMF at reflux temperature to evaluate the catalytic activity of  $L_1-L_5$  in the Suzuki cross-coupling reactions. To verify how the ligands would promote this coupling reaction most efficiently, we investigated a series

of reactions by taking the model reaction in different ligands (see Table 1).

Among the presented sulfonium ylides, ligand  $L_1$  has no any electron-donating or electron-withdrawing substituent on benzene ring and showed moderate efficiency and yielded the coupling product at 80% (Table 2, entry 2). Substitution of electron withdrawing groups such as -Br or  $-NO_2$  in the benzene ring led to lower yields of 73% and 70% in  $L_2$  and  $L_3$  ligands (Table 2, entries 3 and 4). These results suggested that the decrease of the electron density on the donor atoms of ligand plays an important role in the catalytic activity of ligands. On the other hand, electron-donating groups such as  $-CH_3$  and  $-OCH_3$ , activate the benzene ring and cause the increase in electron-donating

#### Table 3

Suzuki cross-coupling reaction of aryl halides with aryl boronic acids.<sup>a</sup>

Ar-X + Ar '-B(OH)<sub>2</sub> 
$$\xrightarrow{\text{PdCl}_2, \text{L}_5}$$
 Ar-Ar '  
Cs<sub>2</sub>CO<sub>3</sub>, DMF

	2	h			
Entry	Ar-X	$Ar'-B(OH)_2$	Product (Ar–Ar')	Yield <sup>b</sup>	TON <sup>c</sup>
1	Ph–I	Ph-B(OH) <sub>2</sub>	Ph-Ph	95	1900
2	Ph–Br	Ph-B(OH) <sub>2</sub>	Ph-Ph	89	1780
3	Ph-Cl	Ph-B(OH) <sub>2</sub>	Ph-Ph	80	1600
4	p-Me-Ph-I	Ph-B(OH) <sub>2</sub>	p-Me-Ph-Ph	85	1700
5	p-Me-Ph-Br	Ph-B(OH) <sub>2</sub>	p-Me-Ph-Ph	78	1560
6	p-OHC-Ph-Br	Ph-B(OH) <sub>2</sub>	p-OHC-Ph-Ph	94	1880
7	p-OHC-Ph-Cl	Ph-B(OH) <sub>2</sub>	p-OHC-Ph-Ph	88	1760
8	p-CH₃OC–Ph–Br	Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> OC–Ph–Ph	92	1840
9	p-CH <sub>3</sub> OC-Ph-Cl	Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> OC-Ph-Ph	81	1620
10	p-O <sub>2</sub> N-Ph-Br	Ph-B(OH) <sub>2</sub>	p-O <sub>2</sub> N-Ph-Ph	97	1940
11	p-CH <sub>3</sub> O-Ph-I	Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> O-Ph-Ph	92	1840
12	p-CH <sub>3</sub> O-Ph-Br	Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> O-Ph-Ph	82	1640
13	1-naphthyl–Br	Ph-B(OH) <sub>2</sub>	C <sub>10</sub> H <sub>7</sub> -Ph	77	1540
14	Ph–I	p-Et-Ph-B(OH) <sub>2</sub>	Ph-Ph-Et	92	1840
15	Ph–Br	p-Et-Ph-B(OH) <sub>2</sub>	Ph-Ph-Et	85	1700
16	Ph–Cl	p-Et-Ph-B(OH) <sub>2</sub>	Ph-Ph-Et	74	1480
17	p-Me-Ph-I	p-Et-Ph-B(OH) <sub>2</sub>	p-Me-Ph-Ph-p-Et	81	1620
18	p-Me-Ph-Br	p-Et-Ph-B(OH) <sub>2</sub>	p-Me-Ph-Ph-p-Et	72	1440
19	p-OHC-Ph-Br	p-Et-Ph-B(OH) <sub>2</sub>	p-OHC-Ph-Ph-p-Et	90	1800
20	p-OHC-Ph-Cl	p-Et-Ph-B(OH) <sub>2</sub>	p-OHC-Ph-Ph-p-Et	81	1620
21	p-CH <sub>3</sub> OC-Ph-Br	p-Et-Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> OC-Ph-Ph-p-Et	86	1720
22	p-CH <sub>3</sub> OC−Ph−Cl	p-Et-Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> OC-Ph-Ph-p-Et	75	1500
23	p-O <sub>2</sub> N-Ph-Br	p-Et-Ph-B(OH) <sub>2</sub>	p-O <sub>2</sub> N-Ph-Ph-p-Et	94	1880
24	p-CH <sub>3</sub> O-Ph-I	p-Et-Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> O-Ph-Ph-p-Et	89	1780
25	p-CH <sub>3</sub> O-Ph-Br	p-Et-Ph-B(OH) <sub>2</sub>	p-CH <sub>3</sub> O-Ph-Ph-p-Et	80	1600
26	1-naphthyl-Br	<i>p</i> -Et-Ph-B(OH) <sub>2</sub>	C <sub>10</sub> H <sub>7</sub> -Ph-p-Et	72	1440

<sup>a</sup> Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (2.4 mmol), PdCl<sub>2</sub> (0.05 mol%), L<sub>5</sub> (0.1 mol%), Cs<sub>2</sub>CO<sub>3</sub> (4.0 mmol), DMF (3 ml) and 2 h.

<sup>b</sup> Isolated yield based on aryl halide.

<sup>c</sup> Mole of product per mole of catalyst.

## Table 4

Comparison with other catalytic systems.

	├───Br + (HO)₂B───	Catalyst	$\rightarrow$					
Entry	Pd source	Ligand	mol%	Condition		Yield <sup>a</sup>	TON <sup>b</sup>	Ref.
1	PdCl <sub>2</sub>	β-ketoamine	0.5	Na <sub>2</sub> CO <sub>3</sub> , DMF, 60 °C, 6 h		67	134	[24]
2	$Pd(OAc)_2$	-	1.0	Na2CO3, PEG/DMF, 50 °C, 0.5 h		24	24	[33]
3	Pd(dba) <sub>2</sub>	P,S-heterodonor	1.0	<sup>t</sup> BuOK, DMF, 80 °C, 10 h		69	69	[34]
4	PdCl <sub>2</sub>	Benzimidazolium salt	0.01	K <sub>2</sub> CO <sub>3</sub> , DMF, 110 °C, 3 h		12	1200	[35]
5	$Pd(OAc)_2$	1,4-Diaza-bicyclo-[2.2.2]octane	3	Na <sub>2</sub> CO <sub>3</sub> , DMF, 40 °C, 16 h		94	31	[9]
6	PdCl <sub>2</sub>	Sulfonium ylide	0.05	Cs <sub>2</sub> CO <sub>3</sub> , DMF, 60 °C, 2 h	(	56	1120	This work
		-		80 °C	J	67	1340	
				110 °C	٦ ١	74	1480	
				130 °C	l	80	1600	

<sup>a</sup> Isolated yield based on aryl halide.

<sup>b</sup> Mole of product per mole of catalyst.

ability of both the carbanion and the enolate moieties of the ligand. The conversion of the biphenyl product reached 81% and 89% for **L**<sub>4</sub> and **L**<sub>5</sub>, respectively (Table 2, entries 5 and 6). Therefore, sulfonium ylide **L**<sub>5</sub> was chosen as proper ligand with high efficient activity toward the Suzuki cross-coupling reaction.

Under optimized conditions, we examined the scope of the reaction of phenyl boronic acid with various aryl halides bearing electrondonating and electron-withdrawing groups in the presence of 0.05 mol% of Pd catalyst to give Suzuki products in good to excellent yields. The results are summarized in Table 3. Conversely, increasing electron density on the aryl halides lowered the catalyst activity. That is, better yields are achieved for aryl halides with electron-withdrawing rather than electrondonating substituents. The electronic properties of aryl iodides did not affect significantly the catalyst performance, so the reactions proceeded very fast and resulted in excellent yields for both electron-deficient and electron-rich aryl iodides (Table 3, entries 1 (95%), 11 (90%), 14 (92%) and 24 (89%)). It was found that the cross-coupling reaction of aryl boronic acid with aryl bromides including electron-donating substituents such as the  $-CH_3$  and  $-OCH_3$  group and electron withdrawing substituents such as the -NO2 and -CHO group was transformed efficiently to the biaryl products. The reaction of electronically neutral bromobenzene with boronic acid derivatives showed good yields (Table 3, entries 2 (89%) and 15 (85%)). In electron rich or deactivated *p*-bromotoluene and *p*-bromoanisole, the reaction gave yields around 80% and this indicated that the coupling was sensitive to the electron density on the aryl halides due to the methyl and methoxy groups, respectively (Table 3, entries 4 (85%), 12 (82%), 17 (81%) and 25 (89%)). As expected, coupling reaction of the electron-poor or activated 4bromobenzaldehyde and 4-bromonitrobenzene with aryl boronic acids leads to relatively excellent yields (Table 3, entries 6 (94%), 10 (97%), 19 (90%) and 23 (94%)). To extend the scope of our work, we next investigated the coupling of various electron rich and deficient aryl chloride substrates coupled to organoboron compounds. While aryl bromides or iodides react readily, less expensive aryl chlorides are inert and have slower reaction rate due to the stronger C-Cl bond. Aryl chlorides with electron withdrawing substituents (Table 3, entries 7, 9. 20 and 22) react more easily than aryl chlorides with electron donating groups (Table 3, entries 5 and 18). For instance, the -CHO substituted chlorobenzene showed moderate reactivity with 88% and 81% yields (Table 3, entries 7 and 20), while for the -CH<sub>3</sub> substituted chlorobenzene yields reduce (Table 3, entries 5 (78%) and 18 (72%)).

Overall, the observed catalytic efficiency of these ligands in the presence of PdCl<sub>2</sub> was proven to be remarkably high and the Suzuki corresponding products were obtained with reasonable yields in most reactions. Also, results indicate that this catalytic system can be comparable to those found in the literature for similar palladium (II)-catalyzed Suzuki coupling reactions. Although several in-situ generated catalyst

systems have been reported to support Suzuki C – C coupling reactions, phosphine free catalytic system of this sulfur ylide ligand is novel. A comparison of catalytic efficiency among the most active in-situ Pd complexes that catalyze the Suzuki cross coupling reaction under the same conditions was also undertaken and presented in Table 4. Low catalyst loading, high reactivity with bromobenzene in short reaction time and stability toward air make it a superb complex for Suzuki cross-coupling reactions.

In summary, we have developed a novel protocol for Suzuki– Miyaura cross-coupling reactions in a phosphine-free environment. We have introduced basic new  $\alpha$ -keto stabilized sulfonium ylide ligand used in Suzuki–Miyaura reactions. Results showed that  $L_5$ , with an electron-donating structure, was most efficient and enabled the coupling of various aryl halides with aryl boronic acid in good to excellent yields. The ease of preparation of the ylidic ligand, its high solubility in organic solvents, very low catalyst loading and stability toward air and moisture make it an ideal catalytic system for the Suzuki crosscoupling reaction.

#### Appendix A. Supplementary material

Materials, physical measurements and selected <sup>13</sup>C and <sup>1</sup>H NMR spectra of some compounds can be found in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.07.027.

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