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Selective water-based oxychlorination of phenol with hydrogen peroxide catalyzed by manganous sulfate†

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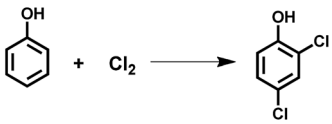
Chlorination of phenols is a key synthetic method because chloro-substituted phenols are essential materials in the synthesis of herbicides, pharmaceuticals, insecticides, dyes, *etc.*[1,2] Among the various chloro-substituted phenols, main products include *p*-chlorophenol, *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, which belong to a group named "light chlorophenols".[3] In this group, 2,4-dichlorophenol is the most important material since it is an intermediate for 2,4-dichlorophenoxyacetic acid, a herbicide that is widely used in crops, rice and other massive productions. Traditional methods for the synthesis of 2,4-dichlorophenol usually involve electrophilic aromatic chlorination of phenol with chlorine gas (Scheme 1).[3–5] However, the utilization of chlorine atoms in these processes is quite low, nearly half of the chlorine is released as waste gas, which results in a waste of material and environmental hazards.[6]



Scheme 1 e e e e , -
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An alternative solution is oxidative chlorination, *i.e.* oxychlorination, which uses chloride anions as a chlorine source in the presence of an oxidant (Scheme 2).[7–12] In these systems, chloride anions are oxidized to chlorine by the oxidant and subsequently incorporated into the products. In general, chlorinating agents, such as sulfuryl chloride,[4,13] *N*-chlorosuccinimide,[11,12] copper chloride,[14–16] trichloroisocyanuric acid[17] and *p*-toluenesulfonyl chloride,[18] are used as chlorine sources, and reagents like sulfuric acid,[19] perchloric acid,[12,20] lithium diisopropylamide,[21] dimethylsulfoxide,[21] *etc.*[22] are employed as oxidants. While the utilization of chlorine atoms in oxychlorination is remarkably increased compared to only half in traditional methods, further research is still required to use cheaper and environmentally friendly reagents.

Compared with most studies focused on the synthesis of monochloro-substituted phenols,[4,23–29] the oxychlorination of phenols to 2,4-dichlorophenols is rather limited so far.[3,20,21] For example, Gustska a *et al.* reported a method for aerobic oxychlorination of phenols over a CuCl$_2$ catalyst, in which metal chlorides were used as chlorinating agents.[30,31] Feng *et al.* found a microwave method for aerobic oxychlorination of phenols catalyzed by CuCl$_2$ with hydrochloric acid as a chlorine source.[23] However, these methods are employed for the synthesis of *p*-chlorophenols. Nobably, Ranasamy *et al.* developed a promising method for the oxychlorination/oxybromination of aromatics including phenols over copper phthalocyanines

Scheme 2 \ e e , - e

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encaps la.ed in eoli.es i.h HCl and alkali chlorides/bromides as halogen so rces and dio gen and h drogen pero ide as o idan.s,[32] b ..he selec.i i. for 2,4-dichloroaroma.ics as lo . Moreo er, VOCs (ola.ile organic compo nds) are s all presen. in .hese s s.ems (Scheme 3).

As for o chlorina.ion, e consider a desirable ro .e for .he chlorina.ion of phenols i.h HCl sing en ironmen.all friendl o idan.s, s ch as dio gen or h drogen pero ide,[23,32,33] in hich chlorine anions are incorpora.ed in.o .he prod c. *via* o ida.ion and a.er is .he onl b -prod c. from .he o idan.s. On .he o.her hand, .he se of a.er as a sol en. is par.ic larl a..rac.i e beca se: (1) a.er is cheaper .han VOC sol en.s; (2) .he risk of e plosions sing a a.er-based s s.em is m ch lo er .han .ha. for s s.ems con.aining VOCs; (3) 2,4-dichlorophenol is almos. insol ble in a.er, and hence .he prod c. can be ob.ained b simple phase separa.ion, hich is con enien. in applica.ion. Ho e er, .his is a challenging .opic, especiall since ca.al .ic me.hods for 2,4-dichlorophenol i.h high ac.i i. and selec.i i. ha e no. been repor.ed pre io sl .

Herein, e presen. an efficien. mangano s(II) s lfa.e-ca.al ed o chlorina.ion of phenol in a.er sing .he o ida-.i e chlorina.ing s s.em HCl/H_2O_2 (Scheme 4). Comple.e con ersion of phenol and high selec.i i. for 2,4-dichlor-ophenol are bo.h achie ed nder mild condi.ions. To .he bes. of o r kno ledge, .his is .he firs. repor. on selec.i e a.er-based o chlorina.ion of phenol in.o 2,4-dichlorophenol in .he liq id phase nder VOC-free condi.ions.

In a . pical reac.ion, phenol (**1**) and a ca.al s. ere added in.o a.er in a glass flask, and gaseo s HCl as in.rod ced .o form a homogeneo s sol .ion. Then, 30% of an aq eo s sol -.ion of H_2O_2 as added .o s.ar. .he reac.ion. In .he ini.ial s. d , .he molar ra.io of $HCl : H_2O_2 : 1$ a. 7.1 : 1.9 : 1 as sed .o screen .he ca.al s.s, and .he res l.s are sho n in Table 1. In .he absence of H_2O_2, no reac.ion occ rred e en i.h a prolonged .ime (Table 1, r n 1). When H_2O_2 as added in .he absence of a ca.al s., con ersion of **1** reached 69% i.h a .o.al ield of 67%, .he prod c.s ere composed of <1% of 2,4-dichlorophenol (**1**), 45% of *p*-chlorophenol (*p*-) and 21% of *o*-chlorophenol (*o*-) (Table 1, r n 2). In .he presence of H_2O_2, me.al sal.s sho ed differen. ac.i i.ies. Among .he .es.ed me.al sal.s, NaCl, $CaCl_2$, $MgCl_2$, $ZnCl_2$, $FeSO_4$, $FeCl_3$, $NiSO_4$, $Co(OAc)_2$, $Co(acac)_2$, LiCl, C $(NO_3)_2$, C $(OAc)_2$ and C Br_2 had a poor effec. (Table 1, r n 3–15), as bo.h .he con ersions and .o.al ields ere lo er .han .hose sing H_2O_2 alone. No.abl , C Cl_2 and $MnSO_4$ indica.ed high ac.i i.ies; .he prod c. dis.rib .ion sho ed a dependence on .he ca.al s.s. A con ersion of 85% for **1** as ob.ained o er C Cl_2, .he .o.al ield as 83%, con.aining <1% of **1** , 54% of *p*- and 29% of *o*- (Table 1, r n 16). Con ersion of **1** o er $MnSO_4$ reached as high as 93% i.h a .o.al ield of 91%, and .he prod c.s ere 16% of **1** , 49% of *p*-, 26% of *o*- and .race 2,6-dichlorophenol (**1**) (Table 1, r n 17). Ob io sl , $MnSO_4$ is more effec.i e in .he forma.ion of **1** . Mean hile, ario s manganese compo nds ere sed, and .he effec. of anions on .he reac.ions as .es.ed (Table 1, r n 188ndMgClB , renfor 2,SO

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Table 2 [a]

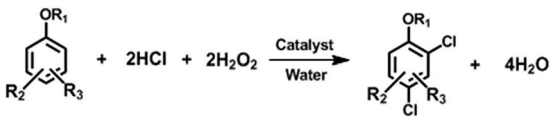
Run	$MnSO_4$ (mol%)	T (°C)	HCl : H_2O_2 : **1** (molar ratio)	Conversion[b] (%)	Total yield[c] (%)	Yield[d] (%)			
						1	*p*-	*o*-	**1**
1	1	25	7.1 : 1.9 : 1	93	91	16	49	26	Trace
2	5	25	7.1 : 1.9 : 1	100	82	55	16	9	Trace
3	10	25	7.1 : 1.9 : 1	100	80	57	15	8	Trace
4	1	25	2.4 : 1.9 : 1	76	74	9	39	25	Trace
5[e]	1	45	2.4 : 1.9 : 1	89	86	25	38	22	1
6[e]	1	60	2.4 : 1.9 : 1	94	92	41	31	18	Trace
7[e]	1	80	2.4 : 1.9 : 1	100	95	72	13	9	3
8[e]	1	90	2.4 : 1.9 : 1	100	83	65	11	5	2
9[f]	1	80	2.4 : 2.8 : 1	100	97	93	1	Trace	3
10[g]	1	80	2.1 : 2.8 : 1	100	95	91	1	Trace	3
11[g]	—	80	2.1 : 2.8 : 1	100	96	34	39	23	Trace
12[h]	—	80	2.0 : 2.0 : 1	94	91	31	35	25	Trace
13[h]	1	80	2.0 : 2.0 : 1	85	83	58	15	10	1
14[g,i]	1	80	2.1 : 2.8 : 1	100	93	89	2	Trace	2
15[j]	1	80	2 : 2.8 : 1	96	92	85	3	2	2
16[k]	1	80	2.1 : 3.7 : 1	100	88	73	4	2	9

[a] Reaction conditions: **1** : 21.3 mmol, HCl: 151.3 mmol, H_2O_2 (30% aq. solution): 4.05 ml, 39.7 mmol, H_2O: 9.8 ml, 3 h. [b] Conversion (%) = [the converted **1** (mol)/initial **1** (mol)] × 100. [c] Total yield (%) = [all products (mol)/initial **1** (mol)] × 100. [d] Yield (%) = [target product (mol)/initial **1** (mol)] × 100. [e] HCl: 50.4 mmol. [f] HCl: 50.4 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol. [g] HCl: 44.7 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol. [h] HCl: 42.6 mmol, H_2O_2 (30% aq. solution): 4.35 ml, 42.6 mmol. [i] Under Ar atmosphere. [j] HCl: 42.6 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol. [k] HCl: 44.7 mmol, H_2O_2 (30% aq. solution): 8.10 ml, 79.4 mmol.

Table 3 [a]

Run time	Conversion[b] (%)	Total yield[c] (%)	Yield[d] (%)			
			1	*p*-	*o*-	**1**
1	100	95	91	1	Trace	3
3	100	94	90	1	Trace	2
6	98	92	88	2	Trace	1

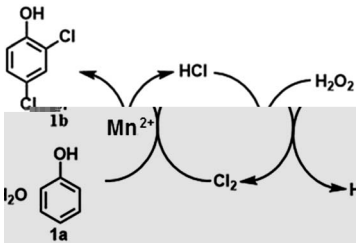
[a] Reaction conditions: **1** : 21.3 mmol, $MnSO_4$: 1 mol%, HCl: 44.7 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol, H_2O: 9.8 ml, 80 °C, 3 h. [b] Conversion (%) = [the converted **1** (mol)/initial **1** (mol)] × 100. [c] Total yield (%) = [all products (mol)/initial **1** (mol)] × 100. [d] Yield (%) = [target product (mol)/initial **1** (mol)] × 100.



Scheme 5

mol% of $MnSO_4$ resulted in lower local yields due to over-oxidation. When the amount of HCl was reduced and HCl : H_2O_2 : **1** was varied to 2.4 : 1.9 : 1, the conversion of **1** was 76% with a total yield of 74%, containing 9% of **1**, 39% of *p*-, 25% of *o*- and trace **1** (Table 2, run 4). A large excess amount of HCl promotes the formation of **1**. The effect of temperature was assessed at a HCl : H_2O_2 : **1** ratio of 2.4 : 1.9 : 1 (Table 2, run 5–8). As the temperature was increased from 45 °C to 90 °C, **1** was completely converted at 80 °C and the total yield was 95%; the yield for **1** reached a maximum of 72% with 13% of *p*-, 9% of *o*- and 3% of **1**. Further increasing the temperature to 90 °C resulted in over-oxidation and the total yield decreased to 83%. Thus, 80 °C is desirable for the reactions.

When we increased the amount of H_2O_2, *i.e.* the ratio of HCl : H_2O_2 : **1** was varied from 2.4 : 1.9 : 1 to 2.4 : 2.8 : 1, the yield of **1** reached as high as 93% with 1% of *p*-, trace *o*- and 3% of **1** (Table 2, run 9). If HCl was further decreased and HCl : H_2O_2 : **1** was tuned to 2.1 : 2.8 : 1, the total yield was 95%, and the yield for **1** was 91% with 1% of *p*-, trace *o*- and 3% of **1** (Table 2, run 10). In the absence of $MnSO_4$, the full conversion of **1** with a total yield of 96% was achieved, and the yield for **1** was 34% with 39% of *p*-, 23% of *o*- and trace **1** (Table 2, run 11). When the reaction was carried out based on the theoretical equation (Scheme 4), *i.e.* HCl : H_2O_2 : **1** was 2.0 : 2.0 : 1, 85% of **1** was converted with a total yield of 83%, and the products were 58% of **1**, 15% of *p*-, 10% of *o*- and 1% of **1** (Table 2, run 13). In the absence of $MnSO_4$, 94% of **1** was converted with a total yield of 91%, containing 31% of **1**, 35% of *p*-, 25% of *o*- and trace **1** (Table 2, run 12). Obviously, the presence of $MnSO_4$ significantly increased the yield of **1**, and hence $MnSO_4$ is key for the selective chlorination of **1** to **1**. When the reaction was performed under an Ar atmosphere (Table 2, run 14), the results were comparable with those in air (Table 2, run 10), so oxygen has no effect on the reactions. If **1** was chlorinated based on a ratio of HCl : **1** as 2.0 : 1, the yield of **1** was 85% with 3% of *p*-, 2% of *o*- and 2% of **1** (Table 2, run 15). As a large excess amount of H_2O_2 was used (HCl : H_2O_2- : **1** = 2.1 : 3.7 : 1), over-oxidation occurred and the total yield decreased to 88% (Table 2, run 16). Because the decomposition of H_2O_2 is inevitable, the used amount of H_2O_2 in the reaction is higher than the theoretical value. The utilization of H_2O_2 and



Scheme 6 A e . . . . . e . . . . . e . . e . . . . . +

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HCl based on .he op.imi ed condi.ions (Table 2, r n 10) is 66% and 87%, respec.i el .

When HCl : H_2O_2 : **1** as 3.1 : 4.2 : 1, f ll con ersion of **1** as achie ed a. 80 °C for 3 h and .he .o.al ield as 91%, .he ield for 2,4,6-.richlorophenol as 73% i.h 11% of **1** , 7% of **1** and .race *p*- and *o*-. If HCl : H_2O_2 : **1** as increased .o 3.5 : 4.2 : 1, f ll con ersion of **1** i.h a .o.al ield of 94% as ob.ained, and 80% of 2,4,6-.richlorophenol i.h 6% of **1** and 8% of **1** ere fo nd as .he prod c.s. Th s, hile .he performance of $MnSO_4$ is be..er in .he s n.hesis of **1** , i. is also ac.i e in .he s n.hesis of 2,4,6-.richlorophenol.

In o r e perimen.s, e fo nd .ha. .he reagen.s formed a homogeneo s sol .ion before reac.ion, and . o discre.e phases ere obser ed a. .he end of .he reac.ion. The .op phase is an aq eo s sol .ion con.aining .he ca.al s., and .he lo er is an organic phase mainl composed of **1** , *p*-, *o*- and **1** . This means .ha. .he prod c.s a .oma.icall come o . from .he aq eo s sol .ion. This proper. is reall con enien. for prod c. collec.ion *via* phase separa.ion. Moreo er, since $MnSO_4$ remains in .he aq eo s sol .ion, rec cling of .he ca.al s. is simple.

In fac., commercial h drochloric acid can be direc.l sed ra.her .han gaseo s HCl in .he reac.ions, as similar res l.s ere also ob.ained nder .he op.imi ed condi.ions. Ho e er, e .hink .ha. .he se of gaseo s HCl is more economical, par.iclarl for large scale prod c.ion. If h drochloric acid is sed, .he prod c.s can be ob.ained b phase separa.ion, b . .he collec.ion of .he ca.al s. req ires .he remo al .he hole aq eo s sol .ion *via* e apora.ion. Then, .he collec.ed ca.al s., **1** and h drochloric acid are mi ed for .he ne . r n. As gaseo s HCl is sed, .he prod c.s ere isola.ed b phase separa.ion, .he remaining aq eo s sol .ion as concen.ra.ed b remo ing e cess a.er from .he sol .ion of H_2O_2 nder red ced press re, and gaseo s HCl as in.rod ced in.o .he concen.ra.ed sol .ion. Then, **1** is added for .he ne . r n. Compared i.h gaseo s HCl, i. is clear .ha. more a.er needs .o be e apora.ed hen sing h drochloric acid.

Based on .he op.imi ed condi.ions, .he rec cle .es. res l.s of .he ca.al s. are sho n in Table 3. After each r n, .he same proced re as performed n.il .he ca.al s. as sed 6 .imes. These res l.s indica.e .ha. .he ca.al s. as rec clable, and no significan. decrease in ac.i i. as obser ed e en after 6 r ns.

Since 2,4-dichloro-s bs.i. .ed phenol deri a.i es presen. a series of al able ma.erials for fine chemicals, .his me.hod as f r.her sed in .he chlorina.ion of ario s phenol deri a.i es (see ESI, Table 1S†). Al.ho gh monochloro-s bs.i. .ed phenols, s ch as *p*- and *o*-, are ndesirable prod c.s in o r reac.ions, .hese compo nds can be efficien.l con er.ed in.o **1** in o r me.hod. Comple.e con ersion of *p*- as ob.ained in a high ield of 96% for **1** , and .he ield of **1** as 94% for .he .o.al con ersion of *o*-. Th s, monochloro-s bs.i. .ed phenols can be effec.i el .ili ed, and .he b -prod c. .ha. remains in o r s s.em is onl **1** . As for bromo- or iodo-s bs.i. .ed phenols, side-reac.ions of debromina.ion/deiodina.ion occ rred and res l.ed in a comple mi . re. This me.hod is effec.i e for alk lphenols, hich ere s ccessf ll chlorina.ed as ario s 2,4-dichlorophenols. A ield of 75% as achie ed for **3** from *o*-cresol (**3**), and an 81% ield for **4** as ob.ained from 2-*tert*-b . lphenol (**4**). Comple.e con ersion of **5** (3,5-dime.h lphenol) as achie ed, and .he ield for **5** as 86%. The chlorina.ion of e.hers of phenol can also be easil performed nder similar condi.ions. Comple.e con ersion of anisole (**6**) led .o a ield of 82% for **6** , and a high ield of 81% for as achie ed from 3,5-dime.h lanisole ( ). Th s, e consider .ha. o r s. d offers a ersa.ile s n.he.ic me.hod in .he man fac. re of ario s 2,4-dichlorophenol deri a.i es (Scheme 5).

The molar ra.io of H_2O_2 : **1** as 2 : 1 according .o .he .heore.ical eq a.ion (Scheme 4), b . i. as 2.8 : 1 nder .he op.imi ed condi.ions (Table 2, r n 10). The sed amo n. of H_2O_2 is higher .han .he .heore.ical al e. I. is ell kno n .ha. .he ca.al .ic decomposi.ion of H_2O_2 o er me.al ions is ine i.able, and .he in.erac.ions of Mn^{2+} i.h H_2O_2 lead .o n mero s reac.i e species, s ch as o gen a.oms, ac.i e o gen species or OH˙/OOH˙ radicals, hich are possible ac.i e species for reac.ions. In o r e perimen.s, hen a free radical sca enger, 2,6-di-*tert*-b . l-4-me.h l phenol, as added in.o .he reac.ions, .he ield of **1** significan.l decreased .o 30%. Al.ho gh .his res l. indica.es .ha. a free radical pa.h a is possibl in ol ed in .he reac.ions, o r a..emp.s .o find o . .he free radicals or ac.i e species failed beca se of .he comple i. of .his s s.em. In con.rolled e perimen.s, e fo nd .ha. .he addi.ion of H_2O_2 in.o an aq eo s sol .ion of HCl immedia.el res l.ed in ligh. ello gas, hich as Cl_2 based on GC-MS anal sis. Th s, hile .he e ac. free radicals or ac.i e species are no. e. clear, .he main pa.h a can be presen.ed as sho n in Scheme 6: HCl is o idi ed b H_2O_2 .o Cl_2; .he genera.ed Cl_2 reac.s i.h **1** .o form **1** i.h .he release of HCl, hich is re-o idi ed and re- sed n.il **1** is e ha s.ed. De.ails of .he reac.ion mechanism are nder in es.iga.ion, and e ill repor. .he res l.s in f . re.

Conclusions

In s mmar , e ha e de eloped a simple, mild and efficien. me.hod for o chlorina.ion of phenol .o 2,4-dichlorophenol ca.al ed b mangano s(II) s lfa.e in .he liq id phase. In .his s s.em, h drogen chloride as sed as a chlorina.ing agen., h drogen pero ide as an o idan. and a.er as a sol en.. We en isage .ha. o r me.hod ill be effec.i e in .he man fac. re of ario s 2,4-dichlorophenol deri a.i es based on .he follo ing

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reasons: (1) high ac.i i. and selec.i i. ; (2) VOC free; (3) simple prod c. separa.ion and rec clable ca.al s..

Experimental section

Phenol and a ca.al s. ere added .o a.er in a .hree-neck flask eq ipped i.h a gas inle., a liq id inle. and a refl condenser (open .o air). Gaseo s HCl as in.rod ced and dissol ed as an aq eo s sol .ion. The flask as immersed in a prehea.ed oil ba.h and igoro sl s.irred i.h a magne.ic s.irrer. Then, H_2O_2 (30% aq. sol .ion) as added drop ise b a channel p mp d ring .he reac.ion. A. .he end of .he reac.ion, .he mi . res ere left .o s.and for 1.5 h, and an isola.ed organic phase from .he aq eo s sol .ion formed a. .he bo..om. The organic phase as collec.ed and dil .ed i.h ace.oni.rile .o prepare .he sample for q an.i.a.i e anal sis. The con ersions and ields ere de.ermined b gas chroma.ograph . Each e perimen. as reprod ced a. leas. .hree .imes. The e perimen.al error in .he de.ermina.ion of .he con ersions and ields normall did no. e ceed 4%. P re prod c.s ere ob.ained b col mn chroma.ograph sing silica gel (pe.role m e.her) and confirmed b GC-MS, ^{1}H and ^{13}C NMR.

^{1} R ^{13} R

2,4-D . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.32 (d, J = 2.4 H , 1H), 7.15 (dd, J = 2.4, 9.6 H , 1H), 6.95 (d, J = 9.0 H , 1H), 5.51 (s, 1H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 150.2, 128.6, 128.56, 125.6, 120.4, 117.1.

4- . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.19 (d, J = 9.0 H , 2H), 6.76 (d, J = 8.4 H , 2H), 4.90 (s, 1H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 154.1, 129.6, 125.7, 116.7.

2- . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.29 (m, 1H), 7.16 (m, 1H), 7.01 (m, 1H), 6.85 (m, 1H), 5.62 (s, 1H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 151.4, 129.1, 128.5, 121.4, 119.9, 116.3.

2,6-D . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.26 (d, J = 7.8 H , 2H), 6.82 (., J = 8.4 H , 1H), 5.85 (s, 1H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 147.9, 128.3, 121.2, 121.1.

2,4,6- . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.28 (s, 2H), 5.81 (s, 1H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 146.9, 128.1, 125.4, 121.6.

2,4-D -6- . ^{1}H-NMR (600 MH , $CDCl_3$) δ: 7.16 (d, J = 2.4 H , 1H), 7.02 (d, J = 2.4 H , 1H), 5.24 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 148.4, 129.6, 127.3, 125.8, 124.7, 119.8, 16.3.

2,4-D -6-*t*- . ^{1}H-NMR (600 MH , $CDCl_3$) δ: 7.20 (d, J = 2.4 H , 1H), 7.15 (d, J = 2.4 H , 1H), 5.80 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 148.5, 138.9, 126.2, 125.9, 124.7, 121.1, 35.5, 29.1.

2,4-D -3,5- . ^{1}H-NMR (600 MH , $CDCl_3$) δ: 6.80 (s, 1H), 5.48 (s, 1H), 2.46 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 149.5, 136.0, 134.2, 126.5, 118.5, 115.1, 20.8, 18.3.

2,4-D . ^{1}H NMR (600 MH , $CDCl_3$) δ: 7.34 (d, J = 2.4 H , 1H), 7.19 (dd, J = 2.4, 9.0 H , 1H), 6.82 (d, J = 9.0 H , 1H), 3.86 (s, 3H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 153.9, 129.9, 127.9, 125.6, 123.2, 112.8, 56.3.

2,4-D -3,5- . ^{1}H NMR (600 MH , $CDCl_3$) δ: 6.67 (s, 1H), 3.86 (s, 3H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MH , $CDCl_3$) δ: 153.2, 136.3, 134.9, 126.8, 120.9, 111.4, 59.3, 21.2, 18.2.

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Notes and references

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