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

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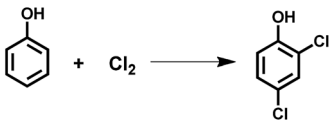
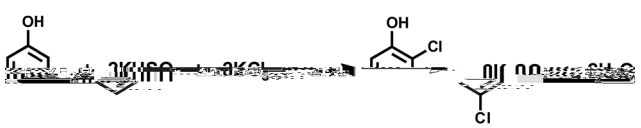
Chlorina ion of phenols is a ke s n he ic me hod beca se chloro-s bs i ed phenols are essen ial ma erials in he s n hesis of herbicides, pharmace icals, insec icides, d es, *etc.*[1,2] Among he ario s chloro-s bs i ed phenols, main prod c s incl de *p*-chlorophenol, *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6- richlorophenol, hich belong o a gro p named "ligh chlorophenols".[3] In his gro p, 2,4-dichlorophenol is he mos impor an ma erial since i is an in ermedia e for 2,4-dichloropheno ace ic acid, a herbicide ha is idel sed in crops, rice and o her massi e c l i a ions. Tradi ional me hods for he s n hesis of 2,4-dichlorophenol s all in ol e elec rophilic aroma ic chlorina ion of phenol i h chlorine gas (Scheme 1).[3–5] Ho e er, he ili a ion of chlorine a oms in hese processes is q i e lo , nearl half of he chlorine is released as as e gas, hich res l s in a as e of ma erial and en ironmen ha ards.



Scheme 1

An al erna i e sol ion is o ida i e chlorina ion, *i.e.* o - chlorina ion, hich ses chloride anions as a chlorine so rce in he presence of an o idan (Scheme 2).[–12] In hese s s ems, chloride anions are o idi ed o chlorine b he o idan and s bseq en l incorpora ed in o he prod c s. In general, chlorina ing agen s, s ch as s lf r l chloride,[4,13] *N*-chloros ccinimide,[11,12] copper chloride,[14–1] i ani m e rachloride[1] and *p*- ol ene s lfon l chloride,[1] are sed as chlorine so rces, and reagen s like s lf ric acid,[1] perchloric acid,[12,20] li hi m diisoprop lamide,[1] dime h ls lfo ide,[21] *etc.*[22] are emplo ed as o idan s. While he ili a ion of chlorine a oms in o - chlorina ion is remarkabl increased compared o onl half in radi ional me hods, f r her research is s ill req ired o se cheaper and en ironmen all friendl reagen s.

Compared i h mos s dies foc sed on he s n hesis of monochloro-s bs i ed phenols,[4,23–2] he o chlorina ion of phenols o 2,4-dichlorophenols is ra her limi ed so far.[3,20,2] For e ample, G se ska a *et al.* repor ed a me hod for aerobic o - chlorina ion of phenols o er a C Cl_2 ca al s , in hich me al chlorides ere sed as chlorina ing agen s.[30,31] Feng *et al.* fo nd a micro a e me hod for aerobic o chlorina ion of phenols ca al ed b C Cl_2 i h h drochloric acid as a chlorine so rce.[23] Ho e er, hese me hods are e ploi ed for he s n hesis of *p*-chlorophenols. No abl , Ra nasam *et al.* de eloped a promising me hod for he o chlorina ion/o bromina ion of aroma ics incl ding phenols o er copper ph haloc anines



Scheme 2

[a]Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, China. E-mail: anzj@qibebt.ac.cn
[b]School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China. E-mail: bgan@ustl.edu.cn

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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 18–

Table 2 [a]

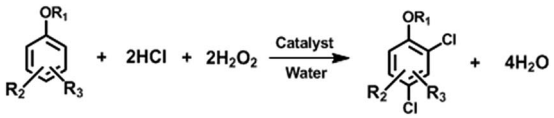
Run	$MnSO_4$ (mol%)	T (°C)	HCl : H_2O_2 : 1 (molar ratio)	Conversion[b] (%)	Total yield[c] (%)	Yield[d] (%) 1	*p*-	*o*-	1
1	1	25	7.1 : 1.9 : 1	93	91	16	49	26	Trace
2	5	25	7.1 : 1.9 : 1	100	82	55	16	9	Trace
3	10	25	7.1 : 1.9 : 1	100	80	57	15	8	Trace
4	1	25	2.4 : 1.9 : 1	76	74	9	39	25	Trace
5[e]	1	45	2.4 : 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 (%) = [(reacted **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

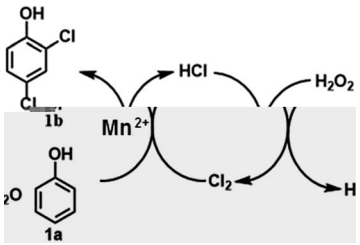
[a] Reaction conditions: **1** : 21.3 mmol, $MnSO_4$: 1 mol%, HCl: 44.7 mmol, H_2O_2 (30% aq. solution): 6.08 ml, 58.8 mmol, H_2O: 9.8 ml, 80 °C, 3 h. [b] Conversion (%) = [(reacted **1** (mol)/initial **1** (mol)] × 100. [c] Total yield (%) = [(all products (mol)/initial **1** (mol)] × 100. [d] Yield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



Scheme 5

mol% of $MnSO_4$ resulted in lower total 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 tested 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 consumed 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** at 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

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 icularl 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 ( ) led o a ield of 82% for , 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 $OH^{\bullet}$/$OOH^{\bullet}$ 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

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

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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.

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2,4- . ^{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, - . ^{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, - . ^{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- - - t . ^{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- - *t*- 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- -3,5- t . ^{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- . ^{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- -3,5- t . ^{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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