ChemPubSoc Europe

DOI: 10.1002/chem.201404463

CHEMISTRY
A European Journal
Full Paper

Synthetic Methods

Metal-Free Oxidative Radical Addition of Carbonyl Compounds to α,α-Diaryl Allylic Alcohols: Synthesis of Highly Functionalized Ketones

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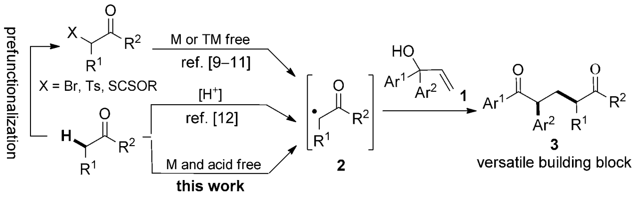
Abstract: A metal-free direct alkylation of simple carbonyl compounds (ketones, esters, and amides) with α,α-diaryl allylic alcohols is described. The protocol provides facile access to highly functionalized dicarbonyl ketones by a radical addition/1,2-aryl migration cascade. The regioselectivity of the reaction was precisely controlled by the nature of the carbonyl compound.

Introduction

Radical chemistry has drawn much attention for new methods of C–C and C–X bond formation in recent decades.[1–3] Among them, significant advances have achieved the free radical initiated $C(sp^3)$–H bond functionalization of ethers, alcohols, amines, alkanes, and activated methylene compounds.[2,3] However, the formation of ketone-derived radicals from readily available materials by C–H bond activation has remained a challenging target (Scheme 1).[4–12] Some earlier studies used UV light[5] or a Mn metal catalyst[6] but were unmanageable or less common for simple ketones. One popular approach was to convert enolates, enol silanes, and enamines into the corresponding radicals with single-electron-transfer reagents (stoichiometric amounts of transition-metal salts combined with other oxidants).[7,8] Zard and co-workers[9] developed powerful chemistry with α-keto-xanthates for building complex molecules. In addition, α-carbonyl alkyl halides[10] and β-ketosulfones[11] have also been applied in C–C bond-forming reactions as radical precursors. Nevertheless, prefunctionalization, narrow substrate scope, and the need for transition-metal catalysts are problematic in these cases. Klussmann[12] has recently discovered a Brønsted acid catalyzed formation of ketone radicals from thermally labile alkenyl peroxides. Clearly, direct utilization of carbonyl compounds as coupling partners would be more atom economical and "greener".



Scheme 1. The formation of ketone-derived radicals. Ts = tosyl, M = metal, TM = transition metal.

1,5-Dicarbonyl compounds are invaluable building blocks for many natural products,[13] such as steroids, alkaloids, and terpenoids. Particularly, 1,5-diketones provide an easy synthetic platform from which to access heterocycles.[14] As such, efficient syntheses of this synthon are much sought-after. However, the conjugate addition of enolates to methyl vinyl ketones in the classical Robinson[15] and Wichterle[16] reactions is limited by inefficiency. Although modifications have been devised (by using silyl enol ethers, enamines, α-silylated ketones) for the Mukaiyama Michael-type reaction,[17] the requirements for catalyst activation, external steps, and additives are unavoidable. The radical process for the construction of 1,5-diketones is less developed.[9c,d] Herein, we communicate our progress in radical pathway transformations[18] and report the oxidative addition of carbonyl compounds to α,α-diaryl allylic alcohols to construct highly functionalized ketones under metal- or acid-free conditions.

Results and Discussion

Initial studies focused on the model reaction of allylic alcohol **1a** and 3,3-dimethylbutan-2-one (**2a**) with various oxidants (Table 1, entries 1–6). To our delight, direct alkylation with concomitant 1,2-migration[18c,d,19,20] of a phenyl group was achieved in the presence of *tert*-butylperoxybenzoate (TBPB) without any redox catalysts,[2,3] and the desired dicarbonyl product **3aa** was obtained in 30 % yield (by GC) after 24 h (Table 1, entry 1). Other radical initiators, such as di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP, 70 % in aqueous solu-

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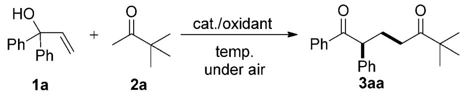
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201404463.

Table 1. Initial discovery and optimization of the reaction conditions.[a]



Entry	Oxidant ([equiv])	Time [h]	T [°C]	GC Yield [%][b]
1	TBPB (3)	24	120	30
2	DTBP (3)	24	120	17
3	TBHP (3)	24	120	trace
4	CHP (3)	24	120	trace
5	$K_2S_2O_8$ (3)	24	120	trace
6	$PhI(OAc)_2$ (3)	24	120	19
7	TBPB (2)	24	120	58
8	TBPB (4)	24	120	49
9	–	24	120	0
10	TBPB (2)	24	120	62[c] (55)[c,d]
11	TBPB (2)	24	120	62[c,e]
12	TBPB (2)	24	150	trace[c]

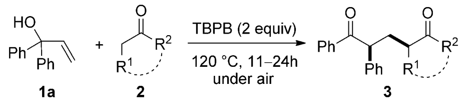
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (1 mL), oxidant (1–3 equiv), 120 °C, under air. [b] Yields were determined by GC analysis with an internal standard. [c] **2a** (3 mL). [d] Isolated yield. [e] Under argon atmosphere.

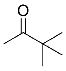
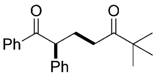
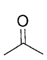
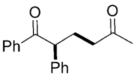
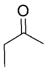
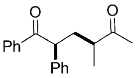
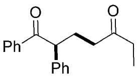
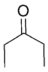
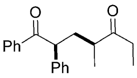
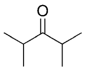
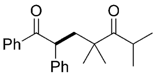
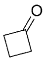
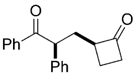
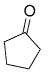
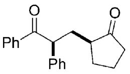
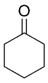
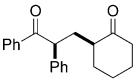
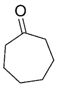
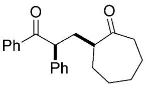
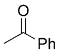
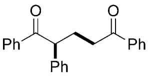
tion), cumyl hydroperoxide (CHP), $K_2S_2O_8$, and $PhI(OAc)_2$ proved to be less efficient (Table 1, entries 2–6). The reaction was dramatically influenced by the amount of oxidant; TBPB (2 equiv) improved the yield of **3aa** to 58 % (Table 1, entries 7 and 8). Furthermore, no product was detected in the absence of TBPB, which suggested the crucial importance of peroxides (Table 1, entry 9). Further screening of the amount of **2a** and reaction temperature established the optimized condition as follows: α,α-diphenyl allylic alcohol **1a** (1 equiv), TBPB (2 equiv) in **2a** (3 mL) at 120 °C for 24 h. The desired product **3aa** could be obtained in 62 % yield (by GC), with an isolated yield of 55 % (Table 1, entry 10). It should be noted that the reaction was not sensitive to air (Table 1, entry 11).[12]

With the optimal conditions in hand, we next evaluated the substrate scope of this radical rearrangement reaction (Table 2). A great drop in yield was observed for the reaction of primary versus secondary versus tertiary ketones (**3ab**–**3ae**; Table 2, entries 2–5). The cleavage of the C–H bond at the terminal methyl moiety of butanone occurred preferentially and **3ac** was isolated as the major product (**3ac**/**3ac′** > 10:1) (Table 2, entry 3). In contrast, tertiary ketone **2e** did not result in the desired product possibly due to negative steric effects (Table 2, entry 5). Other cyclic ketones **2f**–**2i** proceeded smoothly to afford the target alkylation products **3af**–**3ai** in 59–82 % yield (Table 2, entries 6–9). Notably, acetophenone (**2j**) was also a good candidate for the reaction (Table 2, entry 10).

This methodology delivered the corresponding dicarbonyl derivatives when various esters and amides were used (Table 3). *tert*-Butyl acetate (**2k**) coupled with α,α-diphenyl allylic alcohol **1a** to give product **3ak** in 38 % yield, albeit with a slightly lower reactivity than observed with ketones (Table 3, entry 1). Intriguingly, the oxidative functionalization of ethyl acetate was more prone to occur at the C(sp^3)–H bond adjacent to the oxygen atom than carbonyl group, with two isomers **3al** and **4al** (1:1.1) obtained (Table 3, entry 2). Moreover, γ-valerolactone (**2m**) showed excellent regioselectivity; ethyl pivalate (**2n**) and diethyl carbonate (**2o**) also acted successfully in the reaction (Table 3, entries 3–5). A similar selective alkylation occurred at the N-α-position of amides, such as dimethylacetamide (**2p**) and DMF (**2q**) to render the corresponding products **4ap** and **4aq** in 75 and 48 % yield, respectively (Table 3, entries 6 and 7). However, *N*-vinyl-substituted amide **2r** was incompatible with the system, which may be attributed to self-polymerization (Table 3, entry 8). The reaction of *N*-methylpyrrolidine (**2s**) led exclusively to isolation of **4as** (Table 3, entry 9).

Table 2. Substrate scope for the reaction of various ketones with **1a**.

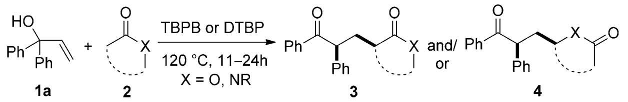


Entry	Ketone	2	Product	3	T [h]	Yield [%][a]
1		**2a**		**3aa**	24	55
2		**2b**		**3ab**	11	93
3		**2c**	 	**3ac** **3ac′**	12	92[b] (>10:1)[c]
4		**2d**		**3ad**	11	76 (1.2:1)[d]
5		**2e**		**3ae**	24	trace
6		**2f**		**3af**	11	80 (1.3:1)[d]
7		**2g**		**3ag**	11	82 (1.1:1)[d]
8		**2h**		**3ah**	11	79 (1.1:1)[d]
9		**2i**		**3ai**	11	59 (1.2:1)[d]
10		**2j**		**3aj**	12	41[e]

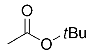
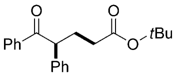
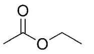
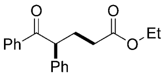
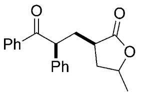
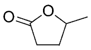
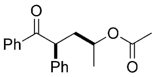
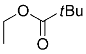
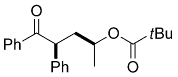
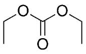
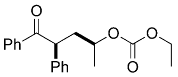
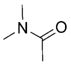
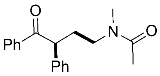
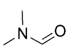
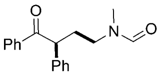
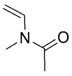
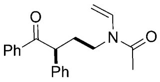
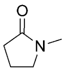
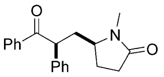
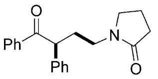
[a] Yield of isolated products under optimal conditions. [b] Combined yield of **3ac** and **3ac′**. [c] Ratio of **3ac**/**3ac′**. [d] Diastereomeric ratio (d.r.) was determined by ^1H NMR spectroscopy of the isolated products. [e] **2j** (1 mL).

Next, a range of α,α-diaryl allylic alcohols were investigated to obtain information about the aryl migration (Tables 4 and 5). Symmetrical substrates **1b**–**1g** with electron-withdrawing (F, Cl, Br, CF_3) or electron-donating groups (Me, OMe) on the ar-

Table 3. Substrate scope for the reaction of carbonyl compounds with **1a**.

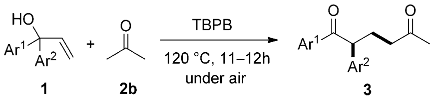


1a **2** **3** **4**

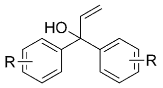
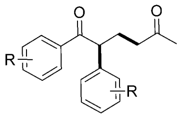
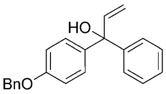
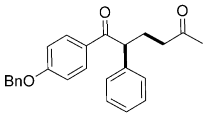
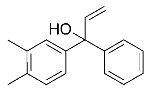
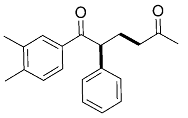
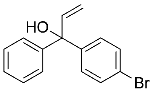
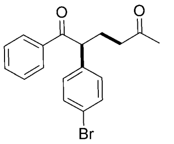
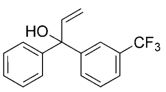
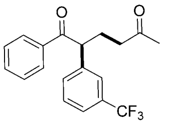
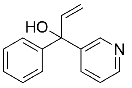
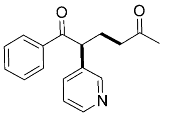
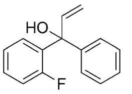
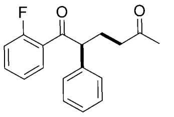
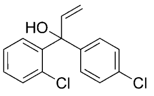
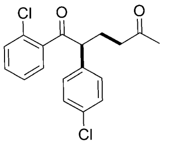
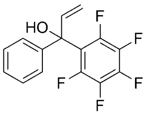
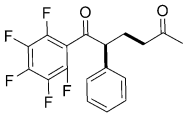
Entry	Carbonyl **2**	Products **3** and/or **4**	*T* [h]	Yield [%][a]
1	 **2k**	 **3ak**	11	38
2	 **2l**	 **3al**	24	32
		 **4al**		35 (1.2:1)[b]
3	 **2m**	 **3am**	12	36
4	 **2n**	 **4an**	20	55 (1:1)[b]
5	 **2o**	 **4ao**	12	43 (1:1)[b]
6	 **2p**	 **4ap**	11	75[c]
7	 **2q**	 **4aq**	11	48[c]
8	 **2r**	 **4ar**	12	0[c]
9	 **2s**	 **4as**	12	65[c]
		 **4as′**		trace[c]

[a] Yield of isolated products under optimal conditions. [b] D.r. determined by ^{1}H NMR spectroscopy of the isolated product. [c] DTBP (3 equiv) as oxidant in **2** (1 mL).

Table 4. Substrate scope for the reaction of various α,α-diaryl allylic alcohols with acetone.



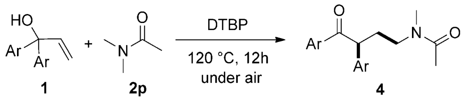
1 **2b** **3**

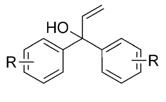
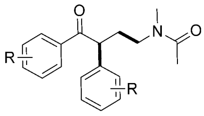
Entry	Compound **1**	Product **3**	*T* [h]	Yield [%][a]
1	 **1b** (R=4-F)	 **3bb**	12	78
2	**1c** (R=4-Cl)	**3cb**	11	89
3	**1d** (R=4-Br)	**3db**	11	83
4	**1e** (R=4-Me)	**3eb**	12	74
5	**1f** (R=4-OMe)	**3fb**	10	48
6	**1g** (R=3-CF$_3$)	**3gb**	11	75
7	**1h** 	**3hb** 	11	84 (4.5:1)[b]
8	**1i** 	**3ib** 	11	95 (2:1)[b]
9	**1j** 	**3jb** 	12	87 (3.6:1)[b]
10	**1k** 	**3kb** 	11	94 (4.8:1)[b]
11	**1l** 	**3lb** 	11	64 (>20:1)[b]
12	**1m** 	**3mb** 	12	85 (2.5:1)[b]
13	**1n** 	**3nb** 	11	59 (>30:1)[b]
14	**1o** 	**3ob** 	12	trace

[a] Yields of isolated products under optimal conditions. [b] Ratio of **3** and its isomer **3′** determined by ^{1}H NMR spectroscopy of the isolated product; only the major products are shown. Total yield of both isomers. Bn = benzyl.

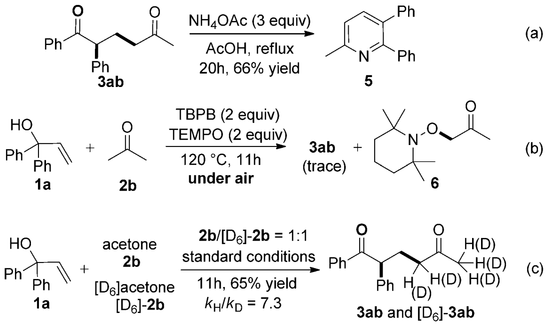
omatic ring were well tolerated and furnished the α-aryl-γ-acetyl compounds **3bb**–**3gb** in moderate-to-good yields (Table 4, entries 1–6). Application of unymmetric alcohol **1h** in the reaction with acetone provided an inseparable mixture of isomers in 84% total yield with a ratio of 4.5:1 (Table 4, entry 7). Clearly, both the electronic character and steric demand of the substituents affected the rearrangement. For substrates **1i**–**1k** and heterocyclic alcohol **1l**, preferential migration of the more-electron-poor aryl group was detected (Table 4, entries 8–11). On the other hand, *ortho*-substituted aryl rings **1m**–**1n** migrated less effectively, which indicated that steric hindrance was unfavorable for the migration procedure (Table 4, entries 12 and 13). This chemoselectivity suggested that the reaction might involve a radical process.[19,20] However, pentafluorophenyl substrate **1o** was almost inert under our conditions (Table 4, entry 14). Apart from ketones, a series of pharmaceutically relevant amide derivatives[21] were

Table 5. Substrate scope for the reaction of various α,α-diaryl allylic alcohols with **2 p**.



Entry	1	Product 4	Yield [%][a]
			
1	**1 b** (R=4-F)	**4 bp**	74
2	**1 c** (R=4-Cl)	**4 cp**	53
3	**1 d** (R=4-Br)	**4 db**	29
4	**1 e** (R=4-Me)	**4 eb**	50
5	**1 f** (R=4-OMe)	**4 fb**	48
6	**1 g** (R=3-CF_3)	**4 gb**	39

[a] DTBP (3 equiv) as oxidant in **2** (1 mL) for 12 h; yield of isolated product.

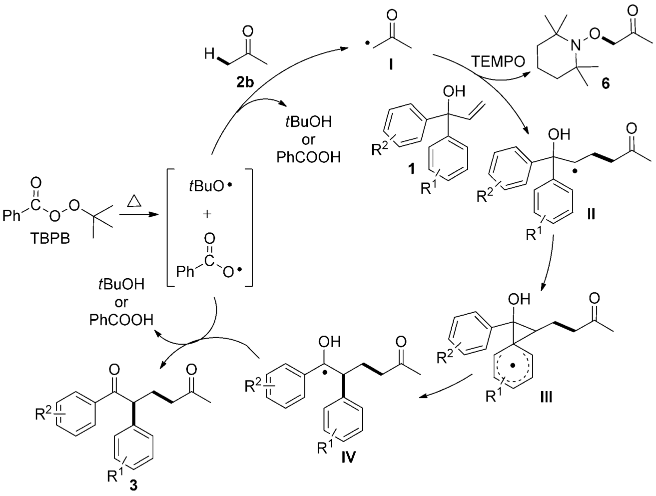


Scheme 2. AcOH = acetic acid.

synthesized in moderate-to-good yields (Table 5). This chemistry was applied in the synthesis of complicated heterocycle **5** (Scheme 2 a).

Some control experiments were carried out to understand the details of the mechanism. The reaction was completely suppressed in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), only TEMPO–acetone adduct **6** was observed (determined by LC-MS analysis; Scheme 2 b). These results suggested that an acetone radical was involved. Moreover, the intermolecular kinetic isotope effects (KIEs) were investigated ($k_H/k_D = 7.3$), which indicated that C(sp^3)–H bond cleavage of acetone may be the rate-determining step (Scheme 2 c).

On the basis of recent publications[12, 18c, d, 20] and the results above, a possible mechanism was proposed (Scheme 3). At high temperature, TBPB decomposed to a *tert*-butoxy radical and benzoate radical. Hydrogen abstraction from acetone with a *tert*-butoxyl radical (or benzoate radical) provided the radical species **I**, which added to allylic alcohol to produce alkyl intermediate **II**. Subsequently, an intramolecular 5-*ipso* cyclization led to the spiro[2.5]octadienyl radical **III**, which was followed by migration of an aryl group to form a new C(sp^3)-centered radical intermediate **IV**.[18c, d, 20] Finally, the desired product **3** was delivered after further oxidation and deprotonation steps.[2]



Scheme 3. Possible mechanism.

Conclusion

We have developed a powerful and convergent alkylation reaction of diaryl allylic alcohols with carbonyl compounds that involves C(sp^3)–H bond functionalization and a radical addition/1,2-aryl migration cascade. 1,5-Diketones were synthesized by using simple ketones. Ester substrates provided both 1,5-diketones and γ-acyloxy ketones. Amide substrates led exclusively to the formation of γ-amido ketones. Rewardingly, the utilization of simple carbonyl derivatives as radical precursors complements the set of mostly metal-mediated reactions that employ activated or prefunctionalized compounds. Future work will be focused on further exploration of the reaction mechanism.

Experimental Section

General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried without precautions to exclude air and moisture, unless otherwise noted. Melting points were recorded with an Electrothermal digital melting point apparatus. IR spectra were recorded with a FTIR spectrophotometer by using KBr optics. ^1H and ^{13}C NMR spectra were recorded in solution in $CDCl_3$ with a 400 MHz spectometer. Tetramethylsilane (TMS) served as internal standard. HRMS (ESI or EI) were obtained by using commercial apparatus.

General procedure for oxidative addition of ketones or esters to α,α-diaryl allylic alcohols

α,α-Diaryl allylic alcohol **1** (0.3 mmol), **2** (3 mL), and TBPB (0.6 mmol) were stirred at 120 °C under air for 11–24 h. Upon completion of the reaction (indicated by TLC), the solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate) to afford pure product **3** and/or **4**.

Compound 3aa: White solid (55%); m.p. 69.2–71.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.00–7.94 (m, 2H), 7.51–7.44 (m, 1H), 7.41–7.35 (m, 2H), 7.30–7.25 (m, 4H), 7.23–7.16 (m, 1H), 4.70 (t, J = 7.4 Hz, 1H), 2.51–2.45 (m, 2H), 2.43–2.32 (m, 1H), 2.16–2.05 (m, 1H), 1.06 ppm (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 216.0, 200.1, 139.4, 136.9, 133.1, 129.2, 128.9, 128.7, 128.6, 127.4, 52.3, 44.4, 33.9, 28.1, 26.7 ppm; IR (KBr): $\tilde{\nu}$ = 2958, 2931, 1699, 1671, 1596, 1579, 1447, 1366, 1283, 1246, 1176, 1088, 1004, 770, 756, 696, 682 cm^{-1}; HRMS: m/z calcd for C$_{21}$H$_{25}$O$_2$: 309.1855 [M+H]$^+$; found: 309.1865.

Compound 3ab: White solid; 93%; m.p. 60.5–63.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.98–7.92 (m, 2H), 7.50–7.44 (m, 1H), 7.41–7.35 (m, 2H), 7.32–7.26 (m, 4H), 7.23–7.18 (m, 1H), 4.69–4.61 (m, 1H), 2.46–2.34 (m, 3H), 2.17–2.10 (m, 1H), 2.08 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 208.7, 199.7, 139.2, 136.8, 133.2, 129.2, 128.9, 128.7, 128.5, 127.4, 52.4, 41.2, 30.2, 27.8 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 2922, 2852, 1709, 1668, 1594, 1490, 1368, 1268, 1160, 1003, 753, 695 cm^{-1}; HRMS: m/z calcd for C$_{18}$H$_{19}$O$_2$: 267.1385 [M+H]$^+$, found: 267.1390.

Compounds 3ac and 3ac′: White solid; 92%; **3ac**/**3ac′** > 10:1; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.01–7.89 (m, 2H), 7.50–7.45 (m, 1H), 7.41–7.35 (m, 2H), 7.35–7.32 (m, 4H), 7.23–7.19 (m, 1H), 4.70–4.58 (m, 1H), 2.50–2.36 (m, 1.5H), 2.23–2.16 (m, 0.5H), 2.08 (d, J = 40.1 Hz, 3H), 1.91–1.83 (m, 1H), 1.13 ppm (dd, J = 26.2, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 212.5, 212.4, 199.7, 199.6, 139.4, 139.3, 139.1, 136.9, 136.8, 136.7, 133.22, 133.17, 129.27, 129.25, 129.2, 128.94, 128.87, 128.78, 128.75, 128.7, 128.6, 128.5, 128.3, 127.5, 127.5, 126.0, 52.5, 51.3, 51.1, 45.3, 44.6, 39.8, 37.0, 36.5, 36.1, 28.6, 28.4, 27.9, 17.4 ppm; IR (KBr): $\tilde{\nu}$ = 2962, 2923, 1705, 1695, 1670, 1595, 1579, 1491, 1447, 1433, 1346, 1238, 1212, 1175, 968, 755, 698, 663 cm^{-1}; HRMS: m/z calcd for C$_{19}$H$_{21}$O$_2$: 281.1542 [M+H]$^+$; found: 281.1554.

Compound 3ad: Colorless oil; 76%; d.r. = 1.2:1; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.00–7.89 (m, 2H), 7.51–7.44 (m, 1H), 7.42–7.34 (m, 3H), 7.29–7.20 (m, 4H), 4.66–4.57 (m, 1H), 2.60–2.14 (m, 5H), 1.94–1.83 (m, 1H), 1.11 (dd, J = 24.9, 7.0 Hz, 3H), 1.06–0.91 ppm (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 215.10, 215.08, 199.8, 199.7, 139.5, 139.1, 136.9, 136.7, 133.21, 133.15, 129.23, 129.19, 128.9, 128.84, 128.77, 128.7, 128.6, 128.34, 128.33, 127.44, 127.40, 127.1, 51.3, 51.0, 44.2, 43.6, 37.2, 36.6, 34.5, 17.7, 17.5, 8.04, 7.96 ppm; IR (KBr): $\tilde{\nu}$ = 2971, 2935, 2876, 1707, 1679, 1597, 1579, 1492, 1447, 1264, 1208, 1176, 1028, 1001, 970, 756, 697 cm^{-1}; HRMS: m/z calcd for C$_{20}$H$_{23}$O$_2$: 295.1698 [M+H]$^+$; found: 295.1703.

Compound 3af: Colorless oil; 80%; d.r. = 1.3:1; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.00–7.93 (m, 2H), 7.51–7.43 (m, 1H), 7.41–7.27 (m, 6H), 7.23–7.16 (m, 1H), 4.93–4.86 (m, 1H), 3.27–3.08 (m, 1H), 3.05–2.84 (m, 2H), 2.50–2.33 (m, 1H), 2.26–1.97 (m, 2H), 1.72–1.54 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 212.1, 211.9, 199.6, 199.5, 139.2, 138.8, 136.9, 136.5, 133.2, 133.1, 129.3, 129.2, 128.99, 128.96, 128.77, 128.75, 128.7, 128.3, 127.5, 58.5, 57.7, 51.14, 51.08, 44.72, 44.70, 34.4, 34.1, 17.5, 17.4 ppm; IR (KBr): $\tilde{\nu}$ = 2950, 2923, 2855, 1771, 1678, 1596, 1579, 1447, 1391, 1212, 1176, 1081, 1024, 1001, 965, 758, 696, 651 cm^{-1}; HRMS: m/z calcd for C$_{19}$H$_{19}$O$_2$: 279.1385 [M+H]$^+$; found: 279.1397.

Compound 3ag: White solid; 82%; d.r. = 1.1:1; m.p. 53.2–55.8 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02–7.95 (m, 2H), 7.51–7.44 (m, 1H), 7.41–7.26 (m, 6H), 7.23–7.16 (m, 1H), 5.09–4.94 (m, 1H), 2.44–2.06 (m, 4H), 2.03–1.90 (m, 3H), 1.78–1.63 (m, 1H), 1.61–1.47 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 221.5, 221.4, 199.90, 199.89, 139.34, 139.28, 137.0, 136.7, 133.17, 133.07, 129.22, 129.16, 128.98, 128.95,, 128.8, 128.74, 128.71, 128.4, 127.40, 127.37, 51.3, 50.8, 47.1, 46.1, 38.4, 38.4, 34.6, 34.3, 30.9, 30.7, 20.9 ppm; IR (KBr): $\tilde{\nu}$ = 2956, 2921, 2854, 1731, 1672, 1595, 1491, 1446, 1290, 1256, 1213, 1155, 1001, 973, 758, 748, 697 cm^{-1}; HRMS: m/z calcd for C$_{20}$H$_{21}$O$_2$: 293.1542 [M+H]$^+$; found: 293.1547.

Compound 3ah: White solid; 79%; d.r. = 1.1:1; m.p. 100.9–102.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02 (d, J = 7.4 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.47 (dd, J = 12.9, 7.1 Hz, 1H), 7.41–7.35 (m, 2H), 7.32–7.19 (m, 5H), 4.92–4.84 (m, 1H), 2.44–2.14 (m, 4H), 2.05–1.93 (m, 1.5H), 1.86–1.75 (m, 1.5H), 1.70–1.40 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 213.8, 213.7, 200.3, 200.2, 140.3, 139.2, 137.0, 136.8, 133.1, 133.0, 129.2, 129.1, 129.02, 128.95, 128.73, 128.71, 128.68, 128.2, 127.3, 127.2, 51.4, 50.8, 49.1, 47.9, 42.6, 42.5, 35.5, 35.4, 35.1, 34.2, 28.4, 28.3, 25.3 ppm; IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1706, 1672, 1594, 1445, 1232, 1130, 1069, 980, 756, 697 cm^{-1}; HRMS: m/z calcd for C$_{21}$H$_{23}$O$_2$: 307.1698 [M+H]$^+$; found: 307.1695.

Compound 3ai: Colorless oil; 59%; d.r. = 1.2:1; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.99–7.90 (m, 2H), 7.50–7.44 (m, 1H), 7.40–7.35 (m, 2H), 7.32–7.26 (m, 4H), 7.23–7.16 (m, 1H), 4.74–4.62 (m, 1H), 2.55–2.28 (m, 4H), 2.10–1.88 (m, 2H), 1.84–1.71 (m, 3H), 1.51–1.25 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 216.5, 216.4, 200.2, 200.0, 139.9, 139.1, 137.1, 136.8, 133.2, 133.1, 129.18, 129.17, 129.0, 128.9, 128.80, 128.76, 128.7, 128.3, 127.4, 127.3, 51.1, 51.0, 50.4, 49.1, 43.2, 43.0, 37.1, 36.3, 32.7, 32.5, 29.5, 29.3, 28.7, 28.6, 24.5, 24.3 ppm; IR (KBr): $\tilde{\nu}$ = 2926, 2854, 1709, 1680, 1597, 1579, 1447, 1261, 1234, 1209, 1175, 933, 756, 697, 669 cm^{-1}; HRMS: m/z calcd for C$_{22}$H$_{25}$O$_2$: 321.1855 [M+H]$^+$; found: 321.1864.

Compound 3aj: White solid; 41%; m.p. 74.6–76.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.97 (dd, J = 5.2, 3.3 Hz, 2H), 7.89 (dd, J = 5.2, 3.3 Hz, 2H), 7.56–7.35 (m, 7H), 7.31–7.28 (m, 3H), 7.23–7.18 (m, 1H), 4.77 (t, J = 7.3 Hz, 1H), 3.07–2.87 (m, 2H), 2.64–2.54 (m, 1H), 2.34–2.23 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 200.1, 199.8, 139.4, 137.0, 136.9, 133.3, 133.2, 129.3, 129.0, 128.8, 128.7, 128.6, 128.3, 127.4, 52.7, 36.2, 28.5 ppm; IR (KBr): $\tilde{\nu}$ = 2967, 2895, 1682, 1674, 1596, 1578, 1490, 1416, 1372, 1279, 1249, 1188, 1176, 983, 762, 730, 691 cm^{-1}; HRMS: m/z calcd for C$_{23}$H$_{21}$O$_2$: 329.1542 [M+H]$^+$; found: 329.1546.

Compound 3ak: White solid; 38%; m.p. 54.5–55.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.98–7.92 (m, 2H), 7.50–7.44 (m, 1H), 7.41–7.34 (m, 2H), 7.31–7.27 (m, 4H), 7.24–7.18 (m, 1H), 4.67 (t, J = 7.3 Hz, 1H), 2.47–2.36 (m, 1H), 2.21 (dd, J = 10.5, 4.0 Hz, 2H), 2.17–2.07 (m, 1H), 1.43 ppm (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 199.7, 172.8, 139.1, 136.9, 133.1, 129.2, 128.9, 128.7, 128.5, 127.4, 80.5, 52.6, 33.3, 29.2, 28.3 ppm; IR (KBr): $\tilde{\nu}$ = 2968, 2870, 1726, 1677, 1597, 1579, 1449, 1367, 1279, 1254, 1156, 1143, 1000, 986, 849, 759, 741, 696, 683, 663 cm^{-1}; HRMS: m/z calcd for C$_{21}$H$_{25}$O$_3$: 325.1804 [M+H]$^+$; found: 325.1788.

Compound 3al: Colorless oil; 32%; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.98–7.93 (m, 2H), 7.50–7.45 (m, 1H), 7.41–7.35 (m, 2H), 7.30–7.26 (m, 4H), 7.24–7.18 (m, 1H), 4.68 (t, J = 7.3 Hz, 1H), 4.14–4.07 (m, 2H), 2.51–2.40 (m, 1H), 2.32–2.26 (m, 2H), 2.22–2.12 (m, 1H), 1.23 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 199.5, 173.5, 139.0, 136.8, 133.2, 129.3, 129.0, 128.7, 128.5, 127.5, 60.6, 52.6, 32.1, 29.0, 14.4 ppm; IR (KBr): $\tilde{\nu}$ = 2979, 2934, 1728, 1679, 1597, 1492, 1447, 1374, 1235, 1211, 1176, 1028, 756, 697 cm^{-1}; HRMS: m/z calcd for C$_{19}$H$_{21}$O$_3$: 297.1491 [M+H]$^+$; found: 297.1480.

Compound 4al: Colorless oil; 35%; d.r. = 1.2:1; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.00–7.90 (m, 2H), 7.51–7.45 (m, 1H), 7.42–7.34 (m, 2H), 7.31–7.26 (m, 4H), 7.23–7.17 (m, 1H), 4.97–4.88 (m, 0.55H), 4.83–4.74 (m, 0.45H), 4.72–4.63 (m, 1H), 2.58–2.46 (m, 1H), 2.13–1.99 (m, 1H), 1.92 (s, 1.3H), 1.87 (s, 1.7H), 1.26 (d, J = 6.3 Hz, 1.7H), 1.20 ppm (d, J = 6.2 Hz, 1.3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 199.3, 199.2, 170.83, 170.77, 139.4, 138.9, 136.8, 136.6, 133.2, 129.32, 129.26, 128.92, 128.85, 128.77, 128.75, 128.5, 128.3, 127.5, 127.4, 69.9, 69.6, 50.3, 50.2, 40.3, 40.1, 21.4, 21.3, 20.8 ppm; IR (KBr): $\tilde{\nu}=$ 2977, 2931, 1731, 1680, 1597, 1494, 1448, 1372, 1240, 1177, 1028, 949, 758, 697 cm^{-1}; HRMS: *m/z* calcd for $C_{19}H_{21}O_3$: 297.1491 [*M*+H]$^+$; found: 297.1497.

Compound 3am: Colorless oil; 36%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 8.03–7.94 (m, 2H), 7.51–7.44 (m, 1H), 7.42–7.34 (m, 3H), 7.33–7.27 (m, 3H), 7.25–7.18 (m, 1H), 5.24–5.08 (m, 1H), 4.71–4.40 (m, 1H), 2.60–2.40 (m, 2H), 2.25–1.87 (m, 3H), 1.54–1.42 (m, 1H), 1.41–1.28 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$199.62, 199.58, 199.5, 179.3, 179.1, 179.0, 139.12, 139.09, 138.64, 138.60, 136.79, 136.75, 136.44, 136.37, 133.3, 133.2, 129.4, 129.3, 129.09, 128.99, 128.9, 128.80, 128.77, 128.74, 128.72, 128.32, 128.27, 127.61, 127.57, 75.4, 75.21, 75.18, 51.0, 50.8, 50.4, 39.6, 38.5, 38.01, 37.99, 37.4, 36.4, 36.2, 35.5, 35.1, 21.29, 21.27, 21.1, 21.0 ppm; IR (KBr): $\tilde{\nu}=$ 2975, 2931, 2872, 1760, 1679, 1596, 1490, 1448, 1303, 1197, 1175, 1090, 956, 806, 759, 741, 698 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{21}O_3$: 309.1491 [*M*+H]$^+$; found: 309.1495.

Compound 4an: White solid; 55%; d.r.=1:1; m.p. 50.2–53.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$7.98–7.88 (m, 2H), 7.51–7.43 (m, 1H), 7.41–7.34 (m, 2H), 7.31–7.24 (m, 4H), 7.23–7.17 (m, 1H), 4.92–4.72 (m, 1H), 4.71–4.64 (m, 1H), 2.64–2.43 (m, 1H), 2.14–1.94 (m, 1H), 1.24 (d, *J*=6.2 Hz, 1.5H), 1.20 (s, 4.5H), 1.17 (d, *J*=6.2 Hz, 1.5H), 1.13 ppm (s, 4.5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$199.3, 199.1, 178.1, 178.0, 139.6, 138.9, 136.9, 136.6, 133.2, 133.1, 129.3, 128.9, 128.84, 128.76, 128.7, 128.5, 128.2, 127.5, 127.4, 69.5, 69.0, 50.2, 50.1, 40.7, 40.0, 39.0, 38.9, 27.4, 27.3, 20.64, 20.58 ppm; IR (KBr): $\tilde{\nu}=$ 2971, 2930, 2871, 1722, 1673, 1596, 1448, 1279, 1266, 1162, 1138, 1067, 1032, 979, 760, 744, 706, 691 cm^{-1}; HRMS: *m/z* calcd for $C_{22}H_{27}O_3$: 339.1960 [*M*+H]$^+$; found: 339.1973.

Compound 4ao: Colorless oil; 43%; d.r.=1:1; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$7.99–7.91 (m, 2H), 7.51–7.43 (m, 1H), 7.41–7.33 (m, 2H), 7.33–7.26 (m, 4H), 7.24–7.16 (m, 1H), 4.84–4.52 (m, 2H), 4.21–4.01 (m, 2H), 2.62–2.40 (m, 1H), 2.22–1.99 (m, 1H), 1.36–1.18 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$199.3, 199.2, 154.81, 154.80, 139.3, 138.7, 136.9, 136.5, 133.2, 133.1, 129.4, 129.3, 129.0, 128.9, 128.70, 128.67, 128.6, 128.4, 128.3, 127.6, 127.4, 127.1, 73.8, 73.1, 64.0, 63.9, 50.1, 49.8, 40.6, 39.8, 20.77, 20.75, 14.5, 14.4 ppm; IR (KBr): $\tilde{\nu}=$2980, 2933, 1738, 1680, 1597, 1447, 1372, 1255, 1208, 1138, 1023, 1003, 790, 758, 696 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{23}O_4$: 327.1596 [*M*+H]$^+$; found: 327.1602.

Compound 3bb: White solid; 78%; m.p. 79.4–81.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$8.01–7.94 (m, 2H), 7.26–7.20 (m, 2H), 7.10–7.03 (m, 2H), 7.03–6.96 (m, 2H), 4.63 (t, *J*=7.1 Hz, 1H), 2.44–2.40 (m, 2H), 2.39–2.31 (m, 1H), 2.09 (s, 3H), 2.09–2.01 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.6, 198.1, 167.1, 164.6, 163.5, 161.0, 134.8, 134.7, 132.99, 132.96, 131.6, 131.5, 130.03, 129.95, 116.3, 116.1, 116.0, 115.8, 51.4, 40.9, 30.2, 27.8 ppm; IR (KBr): $\tilde{\nu}=$ 2963, 2925, 2855, 1714, 1672, 1592, 1504, 1409, 1369, 1270, 1255, 1181, 1151, 1097, 991, 850, 829, 819, 790, 777, 662 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{17}F_2O_2$: 303.1197 [*M*+H]$^+$; found: 303.1201.

Compound 3cb: White solid; 89%; m.p. 54.5–56.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$7.90–7.85 (m, 2H), 7.39–7.34 (m, 2H), 7.29–7.25 (m, 2H), 7.21–7.16 (m, 2H), 4.61 (t, *J*=7.1 Hz, 1H), 2.44–2.39 (m, 2H), 2.39–2.31 (m, 1H), 2.09 (s, 3H), 2.08–2.01 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.4, 198.2, 139.8, 137.3, 134.8, 133.5, 130.3, 129.8, 129.5, 129.1, 51.5, 40.8, 30.2, 27.6 ppm; IR (KBr): $\tilde{\nu}=$2932, 1712, 1680, 1587, 1570, 1489, 1399, 1364, 1263, 1209, 1173, 1160, 1091, 1013, 816, 744, 688 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{17}Cl_2O_2$: 335.0606 [*M*+H]$^+$; found: 335.0605.

Compound 3db: Colorless oil; 83%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.82–7.76 (m, 2H), 7.53 (d, *J*=8.6 Hz, 2H), 7.42 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.4 Hz, 2H), 4.59 (t, *J*=7.1 Hz, 1H), 2.43–2.39 (m, 2H), 2.38–2.30 (m, 1H), 2.09 (s, 3H), 2.08–2.00 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.4, 198.3, 137.8, 135.2, 132.5, 132.2, 130.4, 130.1, 128.6, 121.7, 77.6, 77.2, 76.9, 51.6, 40.7, 30.3, 27.5 ppm; IR (KBr): $\tilde{\nu}=$2927, 2854, 1712, 1680, 1584, 1567, 1486, 1396, 1363, 1270, 1208, 1173, 1159, 1070, 1009, 926, 808, 792, 734, 682 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{17}Br_2O_2$: 422.9595 [*M*+H]$^+$; found: 422.9602.

Compound 3eb: Colorless oil; 74%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.85 (d, *J*=8.2 Hz, 2H), 7.16 (dd, *J*=7.9, 6.2 Hz, 4H), 7.08 (d, *J*= 8.0 Hz, 2H), 4.58 (t, *J*=6.9 Hz, 1H), 2.45–2.38 (m, 2H), 2.36 (dd, *J*= 5.1, 3.0 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 2.12–2.09 (m, 1H), 2.08 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.8, 199.4, 143.9, 137.0, 136.4, 134.3, 129.9, 129.4, 129.1, 128.3, 51.9, 41.3, 30.2, 27.8, 21.8, 21.2 ppm; IR (KBr): $\tilde{\nu}=$2923, 2858, 1713, 1674, 1605, 1511, 1363, 1265, 1207, 1175, 1160, 813, 778, 736 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{23}O_2$: 295.1698 [*M*+H]$^+$; found: 295.1699.

Compound 3fb: Colorless oil; 48%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.98–7.91 (m, 2H), 7.21–7.15 (m, 2H), 6.89–6.79 (m, 4H), 4.54 (t, *J*= 7.1 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.45–2.38 (m, 2H), 2.38–2.29 (m, 1H), 2.08 (s 3H), 2.08–2.05 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.9, 198.5, 163.5, 158.9, 131.6, 131.2, 129.8, 129.5, 114.6, 113.9, 77.6, 77.2, 76.9, 55.6, 55.4, 51.2, 41.3, 30.2, 27.9 ppm; IR (KBr): $\tilde{\nu}=$2956, 2838, 1711, 1669, 1598, 1574, 1509, 1458, 1441, 1419, 1361, 1247, 1166, 1111, 1028, 832, 771, 710 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{23}O_4$: 327.1596 [*M*+H]$^+$; found: 327.1603.

Compound 3gb: Colorless oil; 75%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 8.24 (s, 1H), 8.13 (d, *J*=8.0 Hz, 1H), 7.77 (d, *J*=7.8 Hz, 1H), 7.59–7.43 (m, 5H), 4.82–4.76 (m, 1H), 2.50–2.39 (m, 3H), 2.18–2.11 (m, 1H), 2.11 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.3, 197.9, 139.5, 136.9, 132.02, 132.01, 131.92, 131.88, 131.87, 131.8, 131.6, 131.4, 130.4, 130.0, 129.91, 129.89, 129.86, 129.6, 128.7, 125.84, 125.80, 125.76, 125.7, 125.34, 125.30, 125.26, 125.2, 124.79, 124.75, 124.71, 124.67, 52.1, 40.6, 30.2, 27.8 ppm; IR (KBr): $\tilde{\nu}=$2934, 1714, 1688, 1611, 1327, 1162, 1120, 1099, 1072, 805, 703, 693, 658 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{17}F_6O_2$: 403.1133 [*M*+H]$^+$; found: 403.1141.

Compounds 3hb and 3hb′ (only the structure of the main product is **3hb** is shown in the main text): White solid; 84%; 4.5:1 **3hb**/**3hb′**; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$7.94 (d, *J*=8.9 Hz, 2H), 7.41–7.29 (m, 6H), 7.29–7.25 (m, 3H), 7.22–7.16 (m, 1H), 6.96–6.86 (m, 2H), 5.03 (d, *J*=31.0 Hz, 2H), 4.62–4.56 (m, 1H), 2.46–2.32 (m, 3H), 2.15–2.08 (m, 1H), 2.07 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major product **3hb**): $\delta=$208.8, 198.2, 162.7, 139.6, 136.3, 133.1, 131.3, 129.2, 128.9, 128.42, 128.41, 127.6, 127.3, 114.7, 70.3, 52.0, 41.3, 30.2, 27.9 ppm; IR (KBr): $\tilde{\nu}=$2956, 2924, 2869, 1708, 1676, 1655, 1597, 1572, 1507, 1453, 1363, 1271, 1243, 1205, 1167, 1019, 988, 838, 740, 697 cm^{-1}; HRMS: *m/z* calcd for $C_{25}H_{25}O_3$: 373.1804 [*M*+H]$^+$; found: 373.1813.

Compounds 3ib and 3ib′: Colorless oil; 95%; 2:1 **3ib**/**3ib′**; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$7.98–7.93 (m, 0.63H), 7.74 (s, 0.66H), 7.71–7.66 (m, 0.68H), 7.48–7.43 (m, 0.38H), 7.40–7.34 (m, 0.74H), 7.29–7.26 (m, 2.49H), 7.22–7.16 (m, 0.71H), 7.14–7.09 (m, 1H), 7.06–6.97 (m, 1H), 4.66–4.54 (m, 1H), 2.48–2.32 (m, 3H), 2.25 (d, *J*=2.0 Hz, 4H), 2.19 (d, *J*=7.8 Hz, 2H), 2.13–2.08 (m, 1H), 2.08–2.07 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$208.81, 208.75, 199.9, 199.5, 142.8, 139.5, 137.5, 137.1, 136.9, 136.5, 135.8, 134.7, 133.0, 130.4, 130.0, 129.9, 129.4, 129.1, 128.9, 128.7, 128.4, 127.3, 126.7, 126.0, 52.2, 52.0, 41.3, 31.6, 30.2, 27.9, 27.8, 20.1, 19.99, 19.96, 19.5 ppm; IR (KBr): $\tilde{\nu}=$2923, 2867, 1712, 1674, 1604, 1493, 1448, 1363, 1264, 1159, 1132, 965, 758, 730, 701 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{23}O_2$: 295.1698 $[M+H]^+$; found: 295.1703.

Compounds 3 jb and 3 jb′: Colorless oil; 87%; 3.6:1 **3 jb**/**3 jb′**; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.12$–7.89 (m, 2H), 7.53–7.45 (m, 1H), 7.45–7.35 (m, 3H), 7.31–7.21 (m, 1H), 7.18–7.14 (m, 2H), 4.69–4.55 (m, 1H), 2.45–2.31 (m, 3H), 2.09 (s, 3H), 2.08–2.02 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, major product **3 jb**): $\delta = 208.4$, 199.3, 138.2, 136.5, 133.4, 132.3, 130.2, 128.9, 128.8, 121.5, 51.6, 40.9, 30.2, 27.7 ppm; IR (KBr): $\tilde{\nu} = 2956$, 2927, 2854, 1712, 1679, 1582, 1487, 1447, 1355, 1271, 1175, 1159, 1072, 1009, 813, 701, 687 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{18}BrO_2$: 345.0490 $[M+H]^+$; found: 345.0491.

Compounds 3 kb and 3 kb′: Colorless oil; 94%; 4.8:1 **3 kb**/**3 kb′**; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.14$–7.89 (m, 2H), 7.74–7.47 (m, 4H), 7.45–7.39 (m, 2H), 7.29–7.11 (m, 1H), 4.82–4.61 (m, 1H), 2.49–2.36 (m, 3H), 2.14–2.10 (m, 1H), 2.11–2.07 ppm (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 208.6$, 208.3, 199.2, 140.2, 136.5, 133.6, 131.9, 129.7, 129.5, 128.94, 128.90, 128.5, 125.3, 125.2, 124.5, 124.4, 52.7, 51.8, 40.92, 40.87, 31.6, 30.2, 28.0, 27.6 ppm; IR (KBr): $\tilde{\nu} = 2958$, 2928, 1714, 1682, 1447, 1364, 1161, 1122, 1073, 965, 799, 701, 687, 658 cm^{-1}; HRMS: *m/z* calcd for $C_{19}H_{18}F_3O_2$: 335.1259 $[M+H]^+$; found: 335.1263.

Compound 3 lb: White solid; 64%; m.p. 99.3–101.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.58$ (s, 1H), 8.49 (d, $J = 3.6$ Hz, 1H), 7.97 (d, $J = 7.4$ Hz, 2H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.24 (dd, $J = 7.8$, 4.7 Hz, 1H), 4.75 (t, $J = 7.0$ Hz, 1H), 2.51–2.37 (m, 3H), 2.16–2.04 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 208.1$, 199.1, 150.1, 148.9, 136.3, 135.7, 134.9, 133.6, 128.94, 128.87, 124.1, 49.3, 40.8, 30.2, 27.8 ppm; IR (KBr): $\tilde{\nu} = 2957$, 2925, 2854, 1704, 1679, 1581, 1427, 1368, 1264, 1211, 1177, 1025, 987, 796, 766, 716, 702, 687 cm^{-1}; HRMS: *m/z* calcd for $C_{17}H_{18}NO_2$: 268.1338 $[M+H]^+$; found: 268.1340.

Compounds 3 mb and 3 mb′: Colorless oil; 85%; 2.5:1 **3 mb**/**3 mb′**; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.98$–7.93 (m, 0.6H), 7.73–7.66 (m, 0.6H), 7.51–7.45 (m, 0.4H), 7.44–7.36 (m, 1.4H), 7.29–7.17 (m, 4H), 7.15–6.98 (m, 2H), 5.02–4.48 (m, 1H), 2.52–2.33 (m, 3H), 2.09 (d, $J = 4.9$ Hz, 3H), 2.08–2.05 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 208.5$, 208.2, 199.07, 199.05, 198.93, 198.89, 138.2, 136.3, 134.4, 134.3, 133.4, 131.2, 131.1, 129.2, 129.0, 128.8, 128.7, 127.5, 126.2, 125.0, 124.6, 124.6, 116.9, 116.6, 116.0, 115.8, 56.7, 56.6, 41.3, 41.0, 30.1, 27.4, 26.8 ppm; IR (KBr): $\tilde{\nu} = 2958$, 2931, 2854, 1713, 1682, 1608, 1580, 1489, 1481, 1449, 1358, 1275, 1225, 1158, 1103, 757, 740, 699 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{18}FO_2$: 285.1291 $[M+H]^+$; found: 285.1299.

Compound 3 nb: Colorless oil; 59%; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$–7.28 (m, 2H), 7.28–7.23 (m, 2H), 7.21–7.15 (m, 1H), 7.14–7.08 (m, 3H), 4.51–4.45 (m, 1H), 2.48–2.40 (m, 3H), 2.10 (s, 3H), 2.09–2.05 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 208.2$, 202.7, 139.4, 136.0, 133.7, 131.7, 130.6, 130.5, 130.2, 129.3, 129.1, 126.9, 56.0, 40.9, 30.2, 26.5 ppm; IR (KBr): $\tilde{\nu} = 2931$, 2856, 1702, 1589, 1490, 1432, 1409, 1366, 1270, 1160, 1091, 1014, 814, 765, 742, 645 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{17}Cl_2O_2$: 335.0606 $[M+H]^+$; found: 335.0619.

General procedure for oxidative addition of amides to α,α-diaryl allylic alcohols

α,α-Diaryl allylic alcohol **1** (0.3 mmol), **2** amide (1 mL), and DTBP (0.9 mmol) was stirred at 120 °C under air for 11–12 h. Upon completion of the reaction (indicated by TLC), a saturated aqueous solution of NaCl (15 mL) was added and the mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried with sodium sulfate and concentrated. The pure product **4** was obtained after purification of the residue by column chromatography (silica gel; ethyl acetate/petroleum ether).

Compound 4 ap: Colorless oil; 75%; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.98$–7.92 (m, 2H), 7.52–7.45 (m, 1H), 7.42–7.35 (m, 2H), 7.34–7.26 (m, 3H), 7.25–7.15 (m, 1H), 4.75–4.47 (m, 1H), 3.61–3.21 (m, 2H), 2.90 (d, $J = 6.3$ Hz, 3H), 2.57–2.42 (m, 1H), 2.11–1.97 (m, 1H), 1.96–1.88 ppm (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 199.4$, 198.8, 170.9, 170.8, 139.5, 138.9, 136.6, 136.4, 133.5, 133.1, 129.5, 129.2, 128.94, 128.92, 128.86, 128.7, 128.3, 128.2, 127.7, 127.3, 51.4, 50.9, 49.1, 46.1, 36.1, 33.3, 32.5, 31.7, 21.9, 21.3 ppm; IR (KBr): $\tilde{\nu} = 2930$, 2869, 1709, 1677, 1629, 1491, 1447, 1402, 1260, 1236, 1203, 1175, 1014, 1001, 959, 755, 697, 653 cm^{-1}; HRMS: *m/z* calcd for $C_{19}H_{22}NO_2$: 296.1651 $[M+H]^+$; found: 296.1660.

Compound 4 aq: Colorless oil; 48%; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.90$–7.81 (m, 2H), 7.45–7.38 (m, 1H), 7.35–7.28 (m, 3H), 7.27–7.20 (m, 4H), 7.17–7.10 (m, 1H), 4.59–4.40 (m, 1H), 3.42–3.12 (m, 2H), 2.82 (d, $J = 9.3$ Hz, 3H), 2.48–2.34 (m, 1H), 2.07–1.88 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 199.3$, 198.8, 163.01, 162.95, 139.2, 138.5, 136.6, 136.3, 133.5, 133.2, 129.5, 129.3, 129.0, 128.92, 128.89, 128.8, 128.4, 128.3, 127.8, 127.5, 51.5, 50.4, 47.7, 43.0, 34.7, 32.0, 29.9, 29.6 ppm; IR (KBr): $\tilde{\nu} = 2924$, 2854, 1667, 1597, 1447, 1395, 1313, 1259, 1234, 1209, 1175, 1071, 1029, 961, 757, 697 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{20}NO_2$: 282.1494 $[M+H]^+$; found: 282.1498.

Compound 4 as: Colorless oil; 65%; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.98$–7.92 (m, 2H), 7.55–7.45 (m, 1H), 7.43–7.37 (m, 2H), 7.35–7.28 (m, 4H), 7.26–7.16 (m, 1H), 4.68–4.57 (m, 1H), 3.49–3.24 (m, 2H), 3.01–2.87 (m, 1H), 2.88–2.71 (m, 3H), 2.43–2.11 (m, 3H), 1.91–1.61 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 199.3$, 198.7, 198.6, 175.3, 175.01, 174.99, 139.3, 139.2, 138.2, 136.43, 136.40, 136.3, 133.5, 133.4, 133.2, 129.8, 129.51, 129.48, 129.2, 128.92, 128.88, 128.86, 128.8, 128.7, 128.30, 128.27, 128.0, 127.8, 127.6, 127.4, 126.2, 126.1, 58.7, 58.2, 51.6, 50.0, 49.8, 49.6, 47.1, 41.4, 38.0, 37.2, 31.6, 31.0, 30.8, 30.1, 29.8, 28.1, 28.0, 24.6, 24.5, 17.8, 17.8 ppm; IR (KBr): $\tilde{\nu} = 2925$, 2856, 1674, 1596, 1492, 1447, 1423, 1282, 1176, 1115, 1071, 1001, 940, 758, 698, 667 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{22}NO_2$: 308.1651 $[M+H]^+$; found: 308.1653.

Compound 4 bp: Colorless oil; 74%; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.00$–7.92 (m, 2H), 7.37–7.25 (m, 2H), 7.10–6.94 (m, 4H), 4.66–4.42 (m, 1H), 3.61–3.20 (m, 2H), 2.90 (s, 3H), 2.56–2.42 (m, 1H), 2.07–1.96 (m, 1H), 1.96–1.89 ppm (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 197.6$, 196.9, 170.8, 170.5, 134.90, 134.87, 132.59, 132.57, 131.4, 131.3, 129.6, 129.63, 129.55, 129.4, 127.7, 127.6, 116.5, 116.3, 116.1, 116.0, 115.84, 115.82, 115.6, 114.9, 114.7, 50.3, 49.8, 48.7, 45.8, 35.9, 33.1, 32.4, 31.6, 21.7, 21.1 ppm; IR (KBr): $\tilde{\nu} = 2931$, 2859, 1679, 1634, 1595, 1506, 1407, 1224, 1155, 1013, 833, 801 cm^{-1}; HRMS: *m/z* calcd for $C_{19}H_{20}F_2NO_2$: 332.1462 $[M+H]^+$; found: 332.1467.

Compound 4 cp: White solid; 53%; m.p. 87.6–91.7 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.88$–7.82 (m, 2H), 7.39–7.42 (m, 2H), 7.27–7.17 (m, 4H), 4.64–4.38 (m, 1H), 3.64–3.16 (m, 2H), 2.90 (s, 3H), 2.57–2.40 (m, 1H), 2.08–1.96 (m, 1H), 1.97–1.89 ppm (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 197.9$, 197.2, 171.1, 170.7, 140.2, 139.8, 137.7, 137.0, 134.6, 134.4, 133.9, 133.4, 130.31, 130.27, 129.8, 129.6, 129.5, 129.4, 129.3, 129.1, 50.8, 50.3, 48.9, 46.0, 36.1, 33.4, 32.4, 31.7, 21.9, 21.3 ppm; IR (KBr): $\tilde{\nu} = 2927$, 2855, 1681, 1630, 1588, 1488, 1456, 1402, 1278, 1263, 1238, 1208, 1089, 1014, 993, 841, 807, 741, 687 cm^{-1}; HRMS: *m/z* calcd for $C_{19}H_{20}Cl_2NO_2$ 364.0871 $[M+H]^+$; found: 364.0876.

Compound 4 dp: White solid; 29%; m.p. 121.2–122.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.80$–7.73 (m, 2H), 7.56–7.52 (m, 2H), 7.47–7.38 (m, 2H), 7.19–7.10 (m, 2H), 4.60–4.38 (m, 1H), 3.64–3.17 (m, 2H), 2.90 (s, 3H), 2.57–2.43 (m, 1H), 2.08–1.97 (m, 1H), 1.94 ppm (d, $J=27.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=198.0$, 197.3, 171.1, 170.7, 138.2, 137.5, 135.0, 134.8, 132.8, 132.4, 132.3, 132.1, 130.41, 130.35, 130.0, 129.8, 129.0, 128.6, 122.0, 121.6, 50.8, 50.3, 48.9, 46.0, 36.1, 33.4, 32.3, 31.6, 21.9, 21.3 ppm; IR (KBr): $\tilde{\nu}=2957$, 2925, 2853, 1681, 1630, 1584, 1485, 1456, 1405, 1276, 1261, 1240, 1069, 1010, 994, 804, 731, 678 cm^{-1}; HRMS: m/z calcd for $C_{19}H_{20}Br_2NO_2$: 451.9861 $[M+H]^+$; found: 451.9860.

Compound 4ep: Colorless oil; 50%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.87–7.81 (m, 2H), 7.20–7.13 (m, 4H), 7.12–7.05 (m, 2H), 4.63–4.41 (m, 1H), 3.57–3.20 (m, 2H), 2.90 (d, $J=2.9$ Hz, 3H), 2.53–2.39 (m, 1H), 2.34 (d, $J=4.2$ Hz, 3H), 2.27 (d, $J=8.2$ Hz, 3H), 2.08–1.96 (m, 1H), 1.96–1.90 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=199.1$, 198.5, 170.9, 170.8, 144.3, 143.9, 137.3, 136.9, 136.6, 136.1, 134.1, 133.9, 130.1, 129.8, 129.5, 129.4, 129.07, 129.05, 128.1, 128.0, 50.8, 50.3, 49.1, 46.1, 36.1, 33.3, 32.5, 31.7, 21.9, 21.79, 21.77, 21.3, 21.20, 21.19 ppm; IR (KBr): $\tilde{\nu}=2923$, 2861, 1673, 1635, 1605, 1511, 1444, 1405, 1263, 1237, 1176, 1017, 960, 842, 812, 781, 757 cm^{-1}; HRMS: m/z calcd for $C_{21}H_{26}NO_2$: 324.1964 $[M+H]^+$; found: 324.1970.

Compound 4fp: Colorless oil; 48%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.98–7.89 (m, 2H), 7.25–7.16 (m, 2H), 6.88–6.79 (m, 4H), 4.62–4.38 (m, 1H), 3.82 (d, $J=2.6$ Hz, 3H), 3.75 (d, $J=6.0$ Hz, 3H), 3.60–3.18 (m, 2H), 2.90 (d, $J=3.9$ Hz, 3H), 2.52–2.38 (m, 1H), 2.07–1.97 (m, 1H), 1.93 ppm (d, $J=20.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 198.1, 197.5, 170.9, 170.8, 163.7, 163.5, 159.0, 158.8, 131.9, 131.3, 131.2, 129.6, 129.4, 129.3, 129.2, 127.4, 114.8, 114.5, 114.0, 113.9, 55.7, 55.6, 55.44, 55.40, 50.1, 49.6, 49.1, 46.1, 36.1, 33.3, 32.6, 31.7, 21.9, 21.3 ppm; IR (KBr): $\tilde{\nu}=2932$, 2837, 1667, 1634, 1598, 1574, 1509, 1460, 1441, 1418, 1303, 1245, 1167, 1027, 960, 823, 788, 763 cm^{-1}; HRMS: m/z calcd for $C_{21}H_{26}NO_4$: 356.1862 $[M+H]^+$; found: 356.1864.

Compound 4gp: Colorless oil; 39%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 8.20 (s, 1H), 8.14–8.05 (m, 1H), 7.81–7.73 (m, 1H), 7.61–7.38 (m, 5H), 4.80–4.55 (m, 1H), 3.63–3.19 (m, 2H), 2.92 (s, 3H), 2.66–2.48 (m, 1H), 2.14–2.00 (m, 1H), 1.99–1.88 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=197.3$, 196.6, 171.0, 170.5, 139.7, 139.0, 136.5, 136.2, 131.86, 131.85, 131.72, 131.71, 131.54, 131.53, 131.50, 131.4, 131.21, 131.20, 130.09, 130.05, 129.68, 129.65, 129.4, 125.6, 125.53, 125.50, 125.46, 124.81, 124.77, 124.74, 124.70, 124.43, 124.40, 124.36, 124.3, 122.5, 122.2, 51.1, 50.7, 48.7, 45.8, 35.9, 33.2, 32.3, 31.7, 21.6, 21.0 ppm; IR (KBr): $\tilde{\nu}=2930$, 2856, 1687, 1636, 1490, 1326, 1164, 1120, 1097, 1072, 804, 703, 694 cm^{-1}; HRMS: m/z calcd for $C_{21}H_{20}F_6NO_2$ 432.1398 $[M+H]^+$; found: 432.1398.

Compound 5

1,2-Diphenylhexane-1,5-dione (**3ab**, 0.5 mmol) and NH_4OAc (1.5 mmol) in glacial acetic acid (3 mL) was stirred at 120°C overnight. Upon completion of the reaction (indicated by TLC), a saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried with sodium sulfate and concentrated under vacuum. The pure product **5** was obtained as a colorless solid (66%) after purification of the residue by column chromatography (silica gel; ethyl acetate/petroleum ether). M.p. 84.0–85.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.61$ (d, $J=7.8$ Hz, 1H), 7.36–7.32 (m, 2H), 7.25–7.17 (m, 7H), 7.16–7.17 (m, 2H), 2.66 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=157.3$, 156.7, 140.6, 140.3, 139.0, 133.3, 130.1, 129.8, 128.4, 128.1, 127.8, 127.1, 121.9, 24.6 ppm; IR (KBr): $\tilde{\nu}=2957$, 2922, 2853, 1587, 1556, 1455, 1434, 1375, 1066, 1005, 833, 795, 762, 694 cm^{-1}; HRMS: m/z calcd for $C_{18}H_{16}N$: 246.1283 $[M+H]^+$; found: 246.1286.

Acknowledgements

We gratefully acknowledge the Natural Science Foundation of China (21172162, 21372174), the Young National Natural Science Foundation of China (21202113), the PhD Programs Foundation of Ministry of Education of China (2013201130004), and the Key Laboratory of Organic Synthesis of Jiangsu Province (KJS1211), PAPD.

Keywords: allylic compounds · 1,2-aryl migration · dicarbonyl compounds · domino reactions · radical reactions

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Received: July 18, 2014