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Butyl lithium (^{n}BuLi)-mediated carboxylation of vinylidenecyclopropanes with CO_2

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ABSTRACT

A novel butyl lithium (^{n}BuLi)-mediated carboxylation of vinylidenecyclopropanes with CO_2 in THF at −78 °C followed by the further transformation has been realized to afford the corresponding carboxylic adducts in moderate to good yields under normal conditions. The scope and limitations as well as the plausible reaction mechanism have been also discussed in this paper.

1. Introduction

As an environmental friendly, abundant and nontoxic natural carbon source, carbon dioxide (CO_2) has received a great concern of organic chemists in recent years.[1] However, due to its high stability in thermodynamics and kinetics, man's industrial and laboratory utilization of carbon dioxide as a chemical feedstock is miniscale. Thus far, the chemical reactions using CO_2 as the starting material and the activation of carbon dioxide by transition metal catalysts are still underdeveloped. On the other hand, organolithium chemistry is of unquestionable importance in organic synthesis and is no longer limited to academia.[2] Owing to the strongly polarized lithium–carbon bond, organolithium compounds are used as highly reactive nucleophiles and strong bases in most of C–C bond forming reactions. Because of the weak Lewis acidity of CO_2, one of the most fundamental processes for CO_2 activation is the reaction of organolithium with CO_2 to form valuable carboxylic acid products and their derivatives.[3] Previously, we reported the lithium diisopropylamide (LDA)-mediated selective carbolithiation reactions of vinylidenecyclopropanes **1**[4] with a variety of electrophiles to give the corresponding adducts in good yields under normal conditions along with the further transformation of these products (Scheme 1).[5] During our ongoing investigation, we found that the butyl lithium (^{n}BuLi)-mediated carboxylation of vinylidenecyclopropanes with CO_2 followed by the further transformation could take place smoothly to afford a variety of novel carboxylic acid products in moderate to good yields under normal conditions. In this paper, we wish to disclose the full details of this interesting reaction.

2. Results and discussion

Initially, the carboxylation of vinylidenecyclopropane **1a** (0.1 mmol) with anhydrous CO_2 was carried out by adding LDA (0.2 mmol) in THF at −78 °C. After treating with $TMSCHN_2$ in methanol, we found that the corresponding carboxylation product **3a** was obtained in 52% yield (Table 1, entry 1). Its structure was determined by ^1H and ^{13}C NMR spectroscopic data and HRMS spectrum (see Supplementary data). Changing the lithiation temperature as −78 °C-room temperature (20 °C) (naturally warming up) did not improve the reaction outcome, affording **3a** in 49% yield (Table 1, entry 2). Other lithiation reagents such as *n*-butyl lithium (^{n}BuLi) were also examined as the lithiation temperature from −78 °C to room temperature, affording **3a** in 63% yield (Table 1, entry 3). Using methyllithium (MeLi) as the lithiation reagent did not produce **3a** under identical conditions (Table 1, entry 4). Further adjusting the employed amounts of **1a** and ^{n}BuLi, adding additive as well as changing the lithiation temperature to examine the reaction outcomes revealed that using 2.5 equiv of ^{n}BuLi as the lithiation reagent and 2.5 equiv of TMEDA as the additive produced **3a** in 72% yield at −78 °C (Table 1, entries 5–8). They are the best conditions for the production of **3a** at the present stage (Table 1, entry 8).

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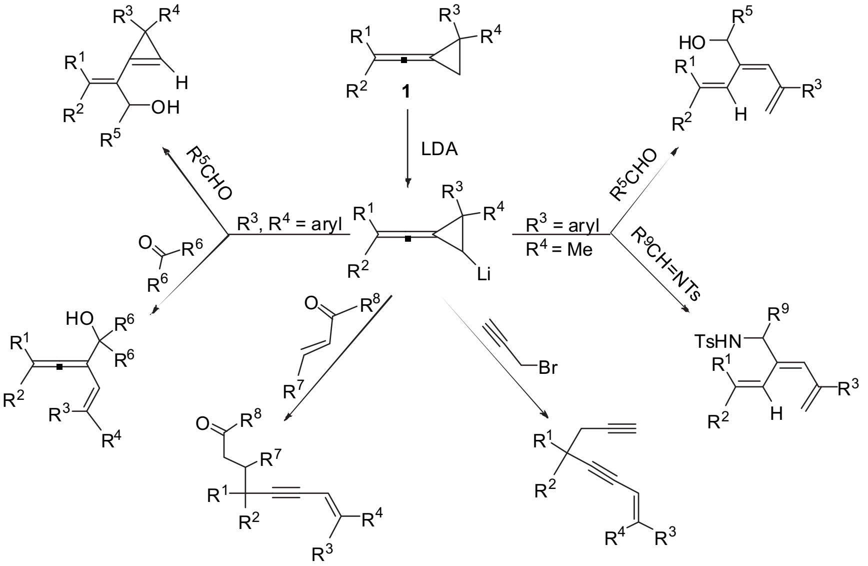
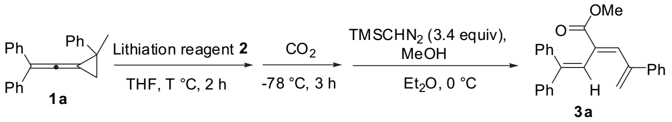


Scheme 1. LDA-mediated carbolithiation reactions of vinylidenecyclopropanes **1** with a variety of electrophiles.

Table 1
Optimize the reaction conditions of ^{n}BuLi-mediated reactions of VDCP **1a** with CO_2



Entry[a]	Lithiation reagent **2**	Molar ratio of **1a** and **2**	T (°C)	Yield[b] (%)
1	LDA	1:2	−78	52
2	LDA	1:2	−78 to rt	49
3	^{n}BuLi	1:2	−78 to rt	63
4	MeLi	1:2	−78	—
5	^{n}BuLi	1:2.5	−78 to rt	68
6	^{n}BuLi	1:3	−78 to rt	67
7	^{n}BuLi	1:2.5	−78	70
8[c]	^{n}*BuLi*	*1:2.5*	*−78*	*72*

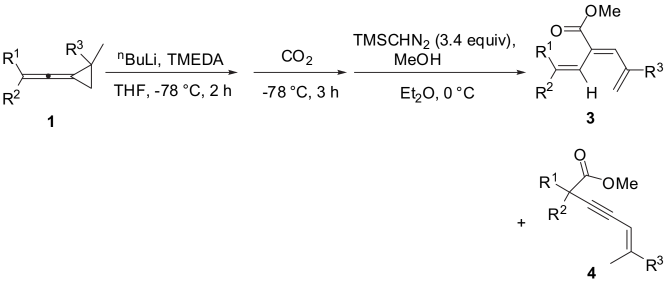
[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by ^{n}BuLi or LDA (0.5 mmol)at −78 °C for 2 h, a CO_2 balloon was attached and the mixture was stirred for 3 h. Next, the reaction was quenched by addition of saturated ammonium chloride solution. Then the resulting mixture was added with MeOH (0.3 mL), $TMSCHN_2$ (3.4 equiv) and Et_2O (2 mL) at 0 °C. After stirring for 2 h, the reactions were quenched by addition of saturated ammonium chloride solution.

[b] Yield of the isolated products.

[c] Addition of 2.5 equiv of TMEDA.

With the optimized reaction conditions in hand, we next examined the carboxylation of an array of vinylidenecyclopropanes **1** (R^1, R^2, R^3=aryl groups, R^4=methyl) with CO_2 followed by the further transformation (esterification). The results of these experiments are summarized in Table 2. As for vinylidenecyclopropanes **1b**, **1c**, and **1d**, in which the aromatic R^1 and R^2 groups bearing electron-withdrawing groups or the aromatic R^3 group bearing electron-withdrawing groups, the reactions with CO_2 proceeded smoothly to furnish the corresponding esterification products **3b**–**3d** in 66%–74% yields after treating with $TMSCHN_2$ in methanol (Table 2, entries 1–3). Adding electron-donating methyl or methoxy groups on the benzene rings (R^1, and R^2 or R^3) of vinylidenecyclopropanes **1g**, **1h**, and **1i**, we found an interesting experimental phenomenon that the corresponding adducts **3g**–**3i** and **4b**–**4d** were both obtained as isomeric mixtures in moderate to good yields and 1.13:1–2.38:1 ratios (Table 2, entries 6–8). In order to understand the influence of the electronic nature of the substituents on the reaction outcomes, we also examined the vinylidenecyclopropanes **1e** (R^1 and R^2 having electron-withdrawing groups and R^3 having electron-donating group) and **1f** (R^1 and R^2 having electron-donating groups and R^3 having electron-withdrawing group) and found that the corresponding carboxylation product **3e** was obtained as the sole product in 51% yield in the case of **1e** and the corresponding carboxylation products **3f**, and **4a** were both formed in 53% yield and in a ratio of 2.44:1 in the case of **1f** (Table 2, entries 4 and 5). These results suggested that introducing the electron-donating substituents such as methyl or methoxy group either at the aromatic rings of R^1 and R^2 or R^3 could change the reaction outcomes. It should be noted that among them, the 1,3-enyne derivatives **4a**–**4d** were produced stereospecifically as *trans*-configuration on the basis of previous results[5] and NMR spectroscopic data (Table 2, entries 5–8).

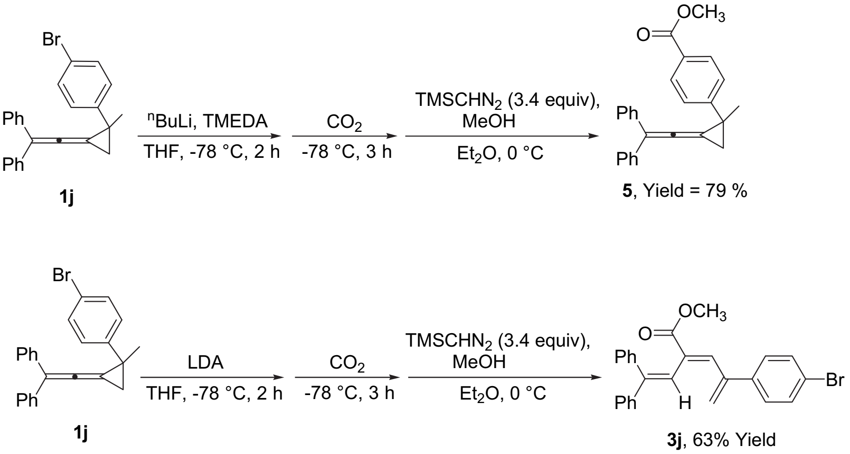
Table 2
^{n}BuLi-mediated reactions of VDCPs **1** with CO_2



Entry[a]	**1** (R^1/R^2/R^3)	Yield[b] (%) (**3**:**4**)
1	**1b** (C_6H_5/C_6H_5/p-FC_6H_4)	**3b**, 74
2	**1c** (C_6H_5/C_6H_5/p-ClC_6H_4)	**3c**, 71
3	**1d** (p-FC_6H_4/p-FC_6H_4/C_6H_5)	**3d**, 66
4	**1e** (p-ClC_6H_4/p-ClC_6H_4/p-MeC_6H_4)	**3e**, 51
5	**1f** (p-MeC_6H_4/p-MeC_6H_4/p-ClC_6H_4)	**3f** and **4a**, 53 (2.44:1)
6	**1g** (C_6H_5/C_6H_5/p-MeC_6H_4)	**3g** and **4b**, 72 (2.38:1)
7	**1h** (C_6H_5/C_6H_5/p-$MeOC_6H_4$)	**3h** and **4c**, 67 (1.13:1)
8	**1i** (p-MeC_6H_4/p-MeC_6H_4/C_6H_5)	**3i** and **4d**, 70 (1.60:1)

[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by ^{n}BuLi or LDA (0.5 mmol) at −78 °C for 2 h, a CO_2 balloon was attached and the mixture was stirred for 3 h. Next, the reaction was quenched by addition of saturated ammonium chloride solution. Then the resulting mixture was added with MeOH (0.3 mL), $TMSCHN_2$ (3.4 equiv) and Et_2O (2 mL) at 0 °C. After stirring for 2 h, the reactions were quenched by addition of saturated ammonium chloride solution.

[b] Yield of the isolated products.



1j

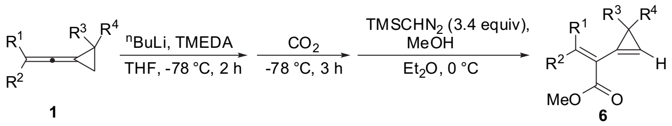
5, Yield = 79 %

1j

3j, 63% Yield

Scheme 2. ^{n}BuLi and LDA-mediated carboxylation reactions of VDCP **1j** with CO$_2$ followed by the further transformation.

Table 3
^{n}BuLi-mediated reactions of VDCPs **1** with CO$_2$



1

6

Entry[a]	**1** ($R^1/R^2/R^3/R^4$)	Yield[b] (%)
1	**1k** $(C_6H_5/C_6H_5/C_6H_5/C_6H_5)$	**6a**, 69
2	**1l** ($C_6H_5/C_6H_5/p$-MeC_6H_4/p-MeC_6H_4)	**6b**, 65
3	**1m** (p-ClC_6H_4/p-$ClC_6H_4/C_6H_5/C_6H_5$)	**6c**, 66
4	**1n** ($C_6H_5/C_6H_5/p$-ClC_6H_4/p-ClC_6H_4)	**6d**, 69
5	**1o** (p-MeC_6H_4/p-$MeC_6H_4/C_6H_5/C_6H_5$)	**6e**, 64
6	**1p** (p-FC_6H_4/p-FC_6H_4/p-FC_6H_4/p-FC_6H_4)	**6f**, 68
7	**1q** (p-FC_6H_4/p-$FC_6H_4/C_6H_5/C_6H_5$)	**6g**, 69

[a] After vinylidenecyclopropane **1a** (0.2 mmol)was lithiated by ^{n}BuLi or LDA (0.5 mmol)at −78 °C for2 h, a CO$_2$ balloon was attached and the mixture was stirred for3 h. Next, the reaction was quenched by addition of saturated ammonium chloride solution. Then the resulting mixture was added with MeOH (0.3 mL), TMSCHN$_2$ (3.4 equiv) and Et$_2$O (2 mL) at 0 °C. After 2 h the reactions were quenched by addition of saturated ammonium chloride solution.

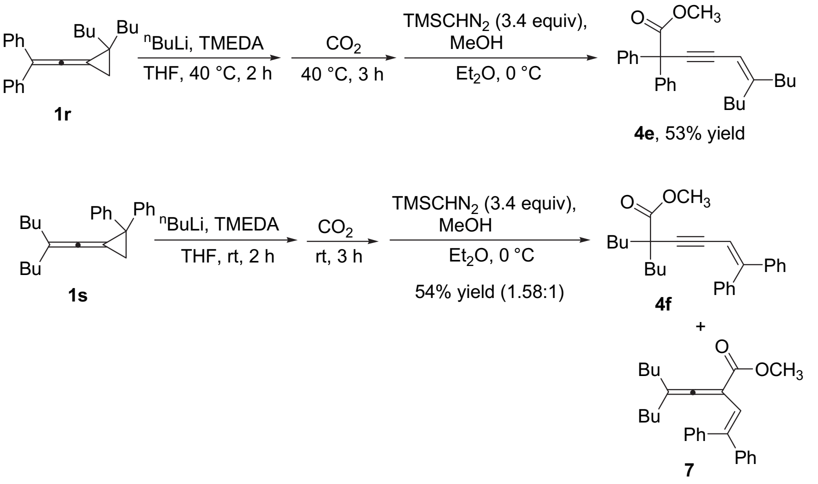
[b] Yield of the isolated products.

More interestingly, using vinylidenecyclopropane **1j**, in which the aromatic R^3 group has a bromine atom, as the substrate, we found that under the standard conditions, the corresponding carboxylation product **5** was obtained in 79% yield rather than the expected product **3j**. Using LDA as the lithiation reagent instead of ^{n}BuLi afforded the expected product **3j** in 63% yield, perhaps due to that the lithium–bromide exchange can more easily take place if the less sterically hindered and stronger base ^{n}BuLi was used as the base in this reaction (Scheme 2).

Encouraged by these results, we further investigated the reactivity of vinylidenecyclopropanes **1k**–**1q** (R^1, R^2, R^3 R^4=aryl groups) with CO$_2$ under the standard conditions and the results of these experiments are summarized in Table 3. It was found that the corresponding carboxylated vinylcyclopropene derivatives **6a**–**6g** were obtained as the sole product in 64–69% yields rather than the carboxylated trienes **3** (Table 3, entries 1–7).[5] Their structures were determined by ^{1}H and ^{13}C NMR spectroscopies and HRMS spectrum (see Supplementary data). The substituents on the aromatic rings did not have significant influence on the reaction outcomes.

Furthermore, we found that using aliphatic vinylidenecyclopropanes **1r** and **1s** as the substrates produced the corresponding carboxylated products in 53% (compound **4e**) and 54% yield (compound **4f** and compound **7**) at 40 °C or at room temperature (20 °C), respectively (Scheme 3).

On the basis of above results, a plausible mechanism for the formation of **3**, **4**, **6**, and **7** is outlined in Scheme 4. Initially, the lithiation of cyclopropyl ring of vinylidenecyclopropanes **1** gives the corresponding cyclopropyl carbanion intermediate **A** by treatment with ^{n}BuLi.[6] Intermediate **A** can be transformed into intermediates **B-1**, **B-2** and **B-3** and there is an equilibrium between all these anionic species as **A**, **B-1**, **B-2** and **B-3**.[7] When R^3 and R^4 are aryl groups and CO$_2$ is used as an electrophile, intermediate **C-1** is



1r

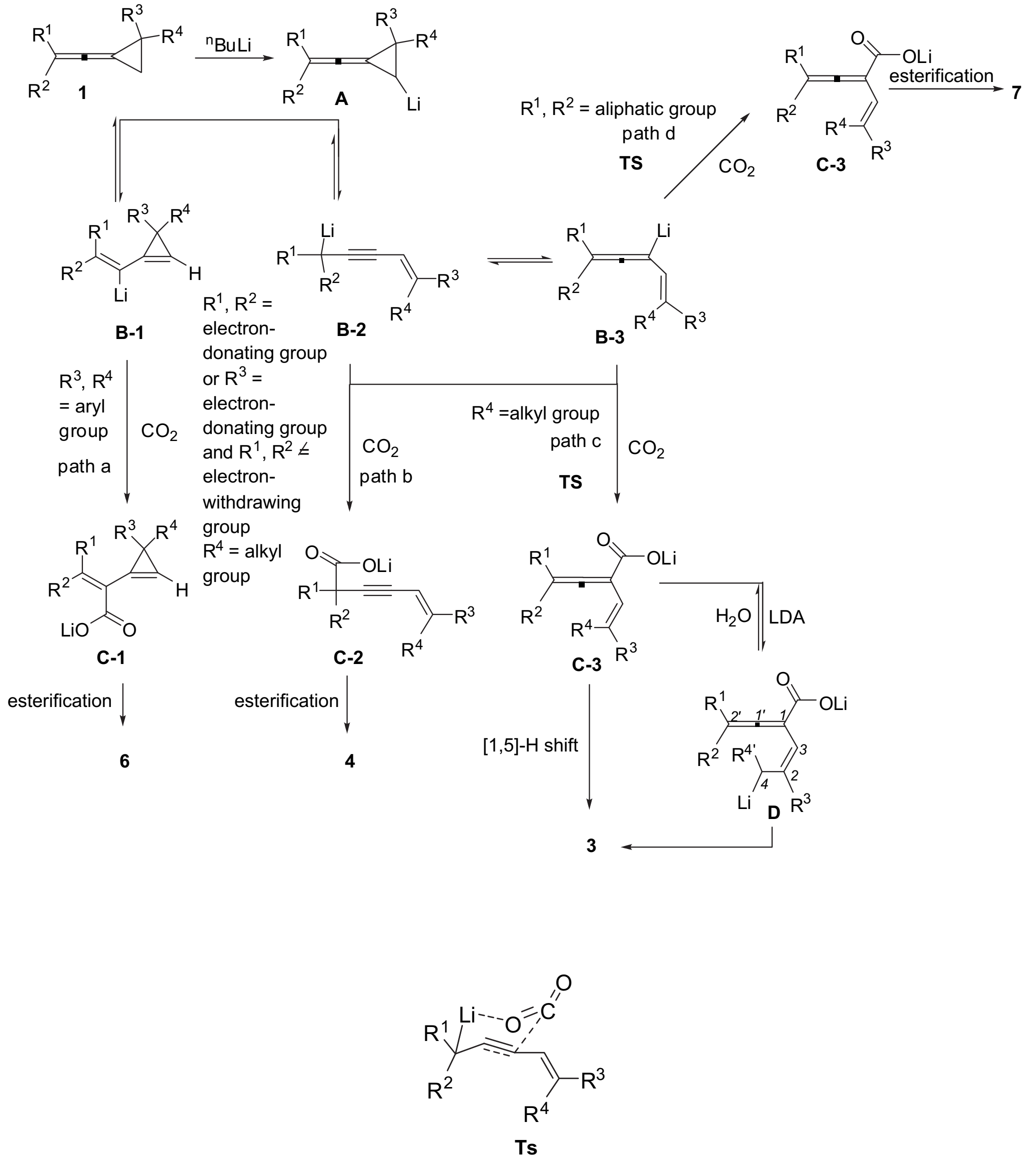
4e, 53% yield

1s

4f

7

Scheme 3. ^{n}BuLi-mediated carboxylation reactions of VDCPs **1r** and **1s** with CO$_2$ followed by the further transformation.



Scheme 4. Plausible reaction mechanism in the carboxylation of vinylidenecyclopropanes **1** with CO_2 followed by the further transformation.

formed by the carboxylation of intermediate **B-1** with CO_2, which subsequently produces carboxylated vinylcyclopropene derivatives **6** after workup (Scheme 4, path a). When R^1, R^2 are aliphatic groups, allene derivatives **7** are obtained by the reaction of intermediate **B-3** with CO_2 through intermediate **C-3** and it is conceivable that a six-membered transition state is concerned in the reaction (**TS**) (Scheme 4, path d). Using vinylidenecyclopropanes **1** in which R^4 is an alkyl group as the substrate, intermediate **C-3** is formed by the reaction of intermediate **B-3** with CO_2 through a six-membered transition state **TS** similarly, which undergoes a [1,5]-H shift to give triene derivatives **3**. On the other hand, intermediate **D** can be formed by lithiation of intermediate **C-3**, which undergoes a [1,5]-lithium shift to give products **3** as well[5b] (Scheme 4, path c). More interestingly, when R^4 is alkyl group and the aromatic groups R^1 and R^2 are electron-donating groups or R^3 is electron-donating group and R^1 and R^2 are not electron-withdrawing groups, except for the products **3**, another products 1,3-enyne derivatives **4** are obtained by the reaction of intermediate **B-2** with CO_2 through intermediate **C-2** (Scheme 4, path b), suggesting that the electronic effect of the substituents on the aromatic rings can significantly affect the reaction outcomes.

3. Conclusions

In conclusion, we have developed an efficient carboxylation of vinylidenecyclopropanes **1** using ^{n}BuLi as the lithiation reagent with CO_2 to produce the corresponding adducts in moderate to good yields under normal conditions. A variety of novel carboxylated products could be formed using CO_2 as the carbon resource. A plausible mechanism has been discussed in this paper on the basis of previously reported literature. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

4. Experimental section

4.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded at 300 or 400 and 75 or 100 MHz, respectively. Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

4.2. General procedure for the synthesis of esters 3, 4, and 5

Under an argon atmosphere, to a solution of vinylidenecyclopropanes **1** (0.2 mmol) in THF (2.0 mL) was added ^{n}BuLi (0.5 mmol) at −78 °C, then the mixture was added 2.5 equiv of TMEDA and was stirred for 2 h. Then the reaction mixture was frozen in a dry ice bath and the atmosphere was pumped off. Then a balloon filled with CO_2 was attached to the reaction flask and the reaction solution was further stirred for 3 h at the same reaction temperature. Then the reaction was quenched by addition of the aqueous solution of ammonium chloride and was warmed to room temperature naturally. The reaction solution was diluted with ether (10.0 mL×3) and extracted by ether. The organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was dissolved in 2 mL of Et_2O, then 0.3 mL of MeOH and 3.4 equiv of $TMSCHN_2$ were added at 0 °C. Then the reaction mixture was quenched by addition of the aqueous solution of ammonium chloride and was warmed to room temperature naturally after 2 h. The reaction solution was diluted with ether (10.0 mL×3) and extracted with ether. The organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

*4.2.1. Compound **1b**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.71 (s, 3H, CH_3), 2.01 (d, J=12.6 Hz, 1H), 2.02 (d, J=12.6 Hz, 1H), 6.93–6.98 (m, 2H, Ar), 7.19–7.36 (m, 10H, Ar), 7.41–7.44 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.8, 25.5, 30.5, 89.3, 112.8, 115.0 (d, J=20.8 Hz), 126.9, 128.25, 128.30, 128.36, 137.6, 137.7, 139.5 (d, J=3.0 Hz), 161.4 (d, J=243.2 Hz), 189.2. IR (CH_2Cl_2) ν 3056, 2967, 2922, 2865, 1995, 1887, 1597, 1510, 1493, 1472, 1442, 1376, 1231, 1157, 1073, 1029, 1015, 902, 836, 767, 695 cm^{-1}. MS (%) (EI) m/z 326 (M^+, 51), 233 (100), 311 (57), 215 (24), 202 (23), 247 (17), 133 (15), 165 (14). HRMS (EI) calcd for $C_{24}H_{19}F$: 326.1471, Found: 326.1472.

*4.2.2. Compound **1e**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.68 (s, 3H, CH_3), 2.01 (d, J=11.2 Hz, 1H), 2.03 (d, J=11.2 Hz, 1H), 2.27 (s, 3H, CH_3), 7.05–7.07 (m, 2H, Ar), 7.18–7.20 (m, 6H, Ar), 7.24–7.29 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 24.6, 25.7, 31.5, 90.0, 110.6, 126.4, 128.46, 128.54, 129.0, 129.41, 129.44, 132.6, 132.7, 135.8, 135.9, 136.0, 140.3, 188.9. IR (CH_2Cl_2) ν 3049, 3026, 2964, 2922, 2867, 1995, 1902, 1714, 1515, 1489, 1092, 1013, 832, 818, 720 cm^{-1}. MS (%) (EI) m/z 390 (M^+, 81), 263 (100), 199 (86), 340 (80), 375 (72), 91 (62), 325 (56), 115 (50). HRMS (EI) calcd for $C_{25}H_{20}Cl_2$: 390.0942, Found: 390.0929.

*4.2.3. Compound **1f**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.65 (s, 3H, CH_3), 1.93 (d, J=16.8 Hz, 1H), 1.94 (d, J=16.8 Hz, 1H), 2.29 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 7.06–7.12 (m, 4H, Ar), 7.16–7.23 (m, 6H, Ar), 7.30–7.32 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.1, 24.1, 25.3, 29.9, 89.3, 112.8, 127.9, 128.2, 128.3, 128.97, 129.01, 131.9, 134.6, 134.7, 136.6, 142.4, 188.7. IR (CH_2Cl_2) ν 3023, 2966, 2921, 2866, 1994, 1713, 1688, 1509, 1492, 1097, 1013, 822, 737 cm^{-1}. MS (%) (EI) m/z 370 (M^+, 81), 222 (100), 355 (92), 263 (91), 243 (82), 305 (77), 179 (75), 320 (74). HRMS (EI) calcd for $C_{26}H_{23}Cl$: 370.1488, Found: 370.1489.

*4.2.4. Compound **1h**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.71 (s, 3H, CH_3), 2.01 (d, J=11.2 Hz, 1H, CH), 2.02 (d, J=11.2 Hz, 1H, CH), 3.77 (s, 3H, OCH_3), 6.81–6.83 (m, 2H, Ar), 7.21–7.36 (m, 10H, Ar), 7.43–7.44 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 25.0, 25.5, 30.8, 55.3, 89.4, 112.4, 113.7, 126.8, 127.8, 127.9, 128.4, 135.9, 137.7, 137.9, 158.1, 189.2. IR (CH_2Cl_2) ν 3903, 3751, 3715, 3648, 3613, 3566, 3524, 2373, 2346, 2323, 1744, 1689, 1680, 1647, 1608, 1550, 1510, 1489, 1339, 984, 698 cm^{-1}. MS (%) (EI) m/z 338 (M^+, 9), 77 (100), 91 (64), 202 (63), 165 (49), 51 (43), 115 (39), 178 (35). HRMS (EI) calcd for $C_{25}H_{22}O$: 338.1671, Found: 338.1680.

*4.2.5. Compound **1p**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 2H, CH_2), 6.95–7.02 (m, 8H, Ar), 7.23–7.29 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 25.6, 38.1, 89.2, 112.4, 115.3 (d, J=20.9 Hz), 115.4 (d, J=21.6 Hz), 129.7 (d, J=8.2 Hz), 129.8 (d, J=7.5 Hz), 133.0 (d, J=3.8 Hz), 138.2 (d, J=3.0 Hz), 161.7 (d, J=244.6 Hz), 162.1 (d, J=245.4 Hz), 189.3. IR (CH_2Cl_2) ν 3042, 2351, 2320, 1997, 1682, 1602, 1557, 1506, 1223, 1157, 1096, 835, 579 cm^{-1}. MS (%) (EI) m/z 442 (M^+, 100), 345 (60), 251 (48), 201 (38), 333 (37), 109 (21), 227 (12), 214 (11). HRMS (EI) calcd for $C_{29}H_{18}F_4$: 442.1345, Found: 442.1348.

*4.2.6. Compound **1j**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.70 (s, 3H, CH_3), 1.99 (d, J=6.8 Hz, 1H, CH), 2.04 (d, J=6.8 Hz, 1H, CH), 7.18 (d, 2H, J=6.0 Hz, Ar), 7.20–7.42 (m, 12H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.2, 25.6, 30.4, 89.3, 113.0, 120.1, 127.0, 128.31, 128.34, 128.4, 131.3, 137.4, 137.5, 142.9, 189.2. IR (CH_2Cl_2) ν 3080, 3056, 2967, 2922, 2865, 1995, 1596, 1491, 1471, 1442, 1393, 1375, 1094, 1074, 1009, 826, 767, 695 cm^{-1}. MS (ESI) m/z 431 (M^++$COOH^-$). HRMS (ESI) calcd for $C_{24}H_{19}{}^{81}Br$: 388.0650, Found: 388.0646.

*4.2.7. Compound **3a**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.30 (s, 3H, OCH_3), 5.51 (t, J=1.2 Hz, 1H), 5.72 (d, J=1.2 Hz, 1H), 6.53 (d, J=1.6 Hz, 1H), 7.13–7.18 (m, 5H, Ar+=CH), 7.25–7.34 (m, 11H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 51.7, 120.3, 122.9, 126.6, 127.6, 127.8, 127.9, 127.98, 128.02, 128.2, 128.4, 129.9, 133.4, 139.2, 139.8, 140.2, 142.3, 143.8, 145.9, 168.6. IR (CH_2Cl_2) ν 3058, 3031, 2951, 2927, 2374, 2346, 2322, 1739, 1724, 1597, 1492, 1447, 1231, 758, 698 cm^{-1}. MS (%) (EI) m/z 366 (M^+, 16), 43 (100), 167 (87), 307 (83), 229 (81), 202 (43), 77 (37), 105 (36), 215 (31). HRMS (EI) calcd for $C_{26}H_{22}O_2$: 366.1620, Found: 366.1622.

*4.2.8. Compound **3b**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.32 (s, 3H, OCH_3), 5.48 (t, J=1.2 Hz, 1H, CH), 5.65 (d, J=1.2 Hz, 1H), 6.50 (d, J=1.6 Hz, 1H), 6.70–7.01 (m, 2H, Ar), 7.08 (d, J=1.2 Hz, 1H), 7.13–7.18 (m, 3H, Ar), 7.24–7.31 (m, 9H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 51.7, 115.2 (d, J=20.9 Hz), 120.1, 122.7, 127.6, 127.7, 127.8, 128.0, 128.16, 128.23, 128.3, 128.4, 129.9, 130.1, 133.6, 135.9 (d, J=3.0 Hz), 138.9, 140.1, 142.2, 142.8, 146.0, 162.6 (d, J=245.4 Hz), 168.5. IR (CH_2Cl_2) ν 3059, 2951, 2928, 2854, 1724, 1660, 1599, 1509, 1446, 1276, 1232, 1159, 1076, 835, 764, 701 cm^{-1}. MS (%) (EI) m/z 384 (M^+, 26), 123 (100), 325 (90), 167 (88), 220 (81), 105 (53), 247 (53), 341 (49), 233 (36). HRMS (EI) calcd for $C_{26}H_{21}FO_2$: 384.1526, Found: 384.1528.

*4.2.9. Compound **3c**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.33 (s, 3H, OCH_3), 5.50 (t, J=1.2 Hz, 1H), 5.67 (d, J=1.2 Hz, 1H), 6.48 (d, J=1.6 Hz, 1H), 7.08 (d, J=1.2 Hz, 1H), 7.09–7.16 (m, 4H, Ar), 7.20–7.23 (m, 2H, Ar), 7.25–7.30 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 51.8, 120.6, 122.6, 127.7, 127.9, 127.96, 128.04, 128.1, 128.3, 128.5, 129.8, 133.6, 133.8, 138.2, 138.6, 140.1, 142.2, 142.7, 146.1, 168.5. IR (CH_2Cl_2) ν 3419, 3058, 3028, 2949, 1720, 1660, 1595, 1492, 1445, 1361, 1235, 1094, 1012, 822, 765, 700 cm^{-1}. MS (%) (EI) m/z 400 (M^+, 15), 167 (100), 341 (50), 236 (47), 263 (31), 139 (30), 368 (28), 105 (25), 291 (22). HRMS (EI) calcd for $C_{26}H_{21}ClO_2$: 400.1230, Found: 400.1232.

*4.2.10. Compound **3d**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.41 (s, 3H, OCH_3), 5.45 (t, J=1.2 Hz, 1H), 5.68 (d, J=1.2 Hz, 1H), 6.39 (d, J=1.6 Hz, 1H), 6.90–7.12 (m, 8H, Ar), 7.17 (d, J=1.2 Hz, 1H), 7.25–7.31 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 51.8, 114.9

(d, *J*=21.6 Hz), 115.1 (d, *J*=20.9 Hz), 120.4, 122.9, 126.6, 128.0, 128.4, 129.7 (d, *J*=8.2 Hz), 131.5 (d, *J*=8.2 Hz), 132.7, 136.0 (d, *J*=3.8 Hz), 138.2 (d, *J*=3.0 Hz), 139.6, 139.7, 143.7, 143.9, 162.2 (d, *J*=246.1 Hz), 162.6 (d, *J*=246.1 Hz), 168.3. IR (CH_2Cl_2) ν 3059, 2953, 1724, 1661, 1600, 1508, 1447, 1435, 1229, 1159, 836, 759, 699 cm^{-1}. MS (%) (EI) *m*/*z* 402 (M$^+$, 5), 203 (100), 43 (23), 109 (18), 77 (17), 343 (16), 91 (13), 123 (12), 183 (11). HRMS (EI) calcd for $C_{26}H_{20}F_2O_2$: 402.1431, Found: 402.1427.

*4.2.11. Compound **3e**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 3.41 (s, 3H, OCH_3), 5.39 (t, *J*=0.3 Hz, 1H), 5.65 (d, *J*=0.3 Hz, 1H), 6.42 (d, *J*=0.4 Hz, 1H), 6.98 (d, *J*=8.8 Hz, 2H, Ar), 7.04 (d, *J*=8.8 Hz, 2H, Ar), 7.11 (d, *J*=7.2 Hz, 2H, Ar), 7.15 (d, *J*=7.2 Hz, 2H, Ar), 7.19 (d, *J*=0.3 Hz, 1H), 7.22 (d, *J*=7.2 Hz, 2H, Ar), 7.25 (d, *J*=7.2 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 51.9, 119.9, 123.8, 126.5, 128.2, 128.4, 129.1, 129.3, 131.1, 132.2, 133.7, 133.8, 136.6, 137.9, 138.2, 140.4, 140.6, 143.2, 143.7, 168.1. IR (CH_2Cl_2) ν 3422, 3028, 2950, 2925, 2858, 1904, 1724, 1664, 1491, 1237, 1091, 1014, 825, 758 cm^{-1}. MS (%) (EI) *m*/*z* 448 (M$^+$, 11), 235 (100), 119 (61), 139 (53), 216 (39), 91 (31), 111 (23), 141 (20), 165 (19). HRMS (EI) calcd for $C_{27}H_{22}Cl_2O_2$: 448.0997, Found: 448.0994.

*4.2.12. Compounds **3f** and **4a**.* A yellow oil. (Compound **3f**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (s, 6H, $2CH_3$), 3.33 (s, 3H, OCH_3), 5.50 (s, 1H, CH), 5.66 (s, 1H, CH), 6.42 (d, *J*=0.3 Hz, 1H), 7.01–7.08 (m, 5H, Ar+=CH), 7.16–7.22 (m, 3H, Ar), 7.26–7.37 (m, 5H, Ar). (Compound **4a**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (d, *J*=0.1 Hz, CH_3), 2.34 (s, 6H, $2CH_3$), 3.82 (s, 3H, OCH_3), 5.99 (d, *J*=0.1 Hz, 1H), 7.01–7.08 (m, 5H, Ar), 7.16–7.22 (m, 3H, Ar), 7.26–7.37 (m, 4H, Ar). (Mixture of compounds **3f** and **4a**) ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.8, 21.1, 21.2, 21.3, 51.7, 53.4, 85.7, 95.1, 106.6, 120.1, 121.9, 125.5, 125.9, 126.7, 127.5, 127.9, 128.06, 128.13, 128.4, 128.5, 128.66, 128.68, 128.7, 128.9, 129.1, 129.2, 129.3, 129.9, 133.8, 137.2, 137.3, 137.6, 137.7, 138.1, 138.6, 139.7, 139.9, 140.9, 143.9, 145.8, 148.8, 168.9, 172.4. IR (CH_2Cl_2) ν 3422, 3026, 2951, 2924, 2855, 2372, 2351, 2346, 2323, 1736, 1730, 1697, 1691, 1509, 1492, 1237, 1093, 1012, 984, 817, 669 cm^{-1}. MS (%) (EI) *m*/*z* 428 (M$^+$, 11), 119 (100), 195 (48), 369 (41), 91 (39), 139 (38), 277 (34), 210 (29), 43 (28). HRMS (EI) calcd for $C_{28}H_{25}ClO_2$: 428.1543, Found: 428.1544.

A yellow oil. (Compound **3g**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.32 (s, 3H, CH_3), 3.28 (s, 3H, OCH_3), 5.47 (d, *J*=1.2 Hz, 1H), 5.69 (d, *J*=1.2 Hz, 1H), 6.52 (d, *J*=1.6 Hz, 1H), 7.11–7.36 (m, 13H, Ar+=CH), 7.45–7.47 (m, 2H, Ar). (Compound **4b**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.31 (d, *J*=1.2 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 5.99 (d, *J*=1.2 Hz, 1H), 7.11–7.36 (m, 12H, Ar), 7.45–7.47 (m, 2H, Ar). (Mixture of compounds **3g** and **4b**) ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.7, 21.1, 51.6, 53.4, 86.2, 94.4, 105.4, 119.6, 123.0, 125.3, 126.5, 127.5, 127.6, 127.7, 127.96, 128.01, 128.18, 128.24, 129.0, 129.1, 129.9, 130.0, 132.4, 133.3, 136.9, 137.8, 137.9, 138.0, 139.5, 140.3, 141.0, 142.3, 143.6, 145.7, 148.9, 168.7, 171.9. IR (CH_2Cl_2) ν 3446, 3057, 3026, 2950, 2923, 2374, 2321, 1738, 1724, 1660, 1599, 1578, 1512, 1492, 1446, 1435, 1362, 1275, 1233, 1016, 812, 764, 699 cm^{-1}. MS (%) (EI) *m*/*z* 380 (M$^+$, 20), 243 (100), 321 (85), 167 (43), 91 (36), 216 (36), 229 (34), 119 (30), 105 (28). HRMS (EI) calcd for $C_{27}H_{24}O_2$: 380.1776, Found: 380.1772.

A yellow oil. (Compound **3h**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.28 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.43 (t, *J*=0.2 Hz, 1H, CH), 5.65 (d, *J*=0.2 Hz, 1H), 6.54 (d, *J*=0.4 Hz, 1H), 6.83–6.88 (m, 4H, Ar+=CH), 7.11–7.24 (m, 4H, Ar), 7.25–7.40 (m, 4H, Ar), 7.45–7.47 (m, 3H, Ar). (Compound **4c**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (d, *J*=0.2 Hz, 3H, CH_3), 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.95 (d, *J*=0.2 Hz, 1H), 6.83–6.88 (m, 4H, Ar), 7.11–7.24 (m, 4H, Ar), 7.25–7.40 (m, 3H, Ar), 7.45–7.47 (m, 3H, Ar). (Mixture of compounds **3h** and **4c**) ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.7, 51.61, 51.63, 53.4, 55.26, 55.29, 86.3, 94.1, 104.5, 113.7, 118.7, 122.9, 126.6, 127.5, 127.6, 127.7, 127.8, 127.96, 128.01, 128.18, 128.23, 129.9, 132.3, 133.2, 133.3, 139.5, 140.3, 141.0, 142.3, 143.1, 145.6, 148.4, 159.5, 159.6, 168.7, 171.9. IR (CH_2Cl_2) ν 3058, 3029, 3002, 2951, 2837, 1738, 1661, 1603, 1576, 1512, 1493, 1446, 1377, 1248, 1181, 1032, 826, 763, 699 cm^{-1}. MS (%) (EI) *m*/*z* 396 (M$^+$, 52), 337 (100), 167 (58), 259 (50), 322 (20), 229 (14), 245 (14), 305 (13), 289 (12). HRMS (EI) calcd for $C_{27}H_{24}O_3$: 396.1725, Found: 396.1726.

A yellow oil. (Compound **3i**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.29 (s, 3H, OCH_3), 5.52 (t, *J*=1.2 Hz, 1H, CH), 5.71 (d, *J*=1.2 Hz, 1H), 6.49 (d, *J*=1.6 Hz, 1H), 7.04–7.16 (m, 7H, Ar+=CH), 7.24–7.34 (m, 6H, Ar), 7.42–7.45 (m, 1H, Ar). (Compound **4d**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 2.34 (s, 6H, $2CH_3$), 3.82 (s, 3H, OCH_3), 6.01 (d, *J*=1.2 Hz, 1H), 7.04–7.16 (m, 6H, Ar), 7.24–7.34 (m, 6H, Ar), 7.42–7.45 (m, 1H, Ar). (Mixture of compounds **3i** and 4**d**) ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.7, 21.0, 21.1, 21.2, 51.6, 53.3, 85.6, 95.0, 106.5, 120.0, 121.8, 125.4, 125.9, 126.6, 127.4, 127.9, 128.06, 128.13, 128.3, 128.4, 128.66, 128.68, 128.74, 128.9, 129.0, 129.1, 129.3, 129.8, 133.8, 137.2, 137.3, 137.5, 137.6, 138.1, 138.6, 139.6, 139.9, 140.9, 143.7, 145.8, 148.8, 168.9, 172.1. IR (CH_2Cl_2) ν 3465, 3056, 3026, 2950, 2922, 2859, 1739, 1655, 1608, 1510, 1447, 1277, 1230, 1021, 817, 758, 696 cm^{-1}. MS (%) (EI) *m*/*z* 394 (M$^+$, 11), 195 (100), 243 (94), 335 (87), 105 (49), 202 (45), 129 (44), 228 (38), 277 (32). HRMS (EI) calcd for $C_{28}H_{26}O_2$: 394.1933, Found: 394.1933.

*4.2.13. Compound **3j**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.34 (s, 3H, OCH_3), 5.50 (d, *J*=1.2 Hz, 1H), 5.67 (d, *J*=1.2 Hz, 1H), 6.46 (d, *J*=2.0 Hz, 1H), 7.08 (d, *J*=1.2 Hz, 1H), 7.12–7.16 (m, 6H, Ar), 7.25–7.30 (m, 6H, Ar), 7.43 (d, *J*=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 51.8, 120.7, 122.0, 122.6, 127.7, 127.9, 128.03, 128.04, 128.1, 128.3, 129.8, 131.4, 133.6, 138.5, 138.7, 140.0, 142.1, 142.7, 146.1, 168.5. IR (CH_2Cl_2) ν 3057, 3027, 2949, 2851, 2374, 2322, 1720, 1659, 1587, 1490, 1444, 1434, 1361, 1238, 1075, 1008, 817, 764, 700 cm^{-1}. MS (%) (EI) *m*/*z* 444 (M$^+$, 10), 167 (100), 414 (21), 280 (19), 249 (18), 306 (17), 385 (17), 228 (16), 105 (11). HRMS (EI) calcd for $C_{26}H_{21}BrO_2$: 444.0725, Found: 444.0722.

*4.2.14. Compound **4e**.* A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.83–0.92 (m, 6H, $2CH_3$), 1.23–1.45 (m, 8H, $4CH_2$), 2.09 (t, 2H, *J*=7.8 Hz, CH_2), 2.29 (t, 2H, *J*=7.8 Hz, CH_2), 3.81 (s, 3H, OCH_3), 5.40 (s, 1H, CH), 7.26–7.35 (m, 6H, Ar), 7.40–7.43 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 14.0, 22.5, 22.7, 29.8, 30.4, 33.2, 35.8, 53.3, 58.6, 85.7, 91.0, 104.0, 127.4, 128.1, 128.2, 128.4, 141.2, 157.7, 172.1. IR (CH_2Cl_2) ν 3061, 2955, 2930, 2871, 2839, 2216, 1742, 1599, 1448, 1433, 1225, 1014, 746, 697 cm^{-1}. MS (%) (EI) *m*/*z* 388 (M$^+$, 5), 329 (100), 249 (10), 91 (9), 167 (9), 217 (6), 215 (6), 191 (5), 202 (4). HRMS (EI) calcd for $C_{27}H_{32}O_2$: 388.2402, Found: 388.2393.

*4.2.15. Compound **5**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.78 (s, 3H, CH_3), 2.08 (d, *J*=7.2 Hz, 1H), 2.12 (d, *J*=7.2 Hz, 1H), 3.90 (s, 3H, OCH_3), 7.25–7.43 (m, 12H, Ar), 7.95 (d, *J*=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.8, 26.0, 30.7, 52.0, 89.7, 113.3, 126.4, 127.0, 127.1, 128.0, 128.3, 128.4, 129.6, 137.4, 137.5, 149.2, 166.9, 189.1. IR (CH_2Cl_2) ν 3481, 2926, 2373, 2346, 2322, 1729, 1689, 1509, 1449, 1278, 1239, 1119, 984, 698, 669 cm^{-1}. MS (%) (EI) *m*/*z* 366 (M$^+$, 7), 194 (100), 165 (99.8), 105 (78), 77 (65), 43 (58), 115 (42), 91 (36). HRMS (EI) calcd for $C_{26}H_{22}O_2$: 366.1620, Found: 366.1618.

*4.2.16. Compound **6a**.* A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.50 (s, 3H, OCH_3), 6.77 (s, 1H, CH), 7.18–7.50 (m, 17H, Ar), 7.58 (s, 1H, Ar), 7.90 (d, *J*=8.4 Hz, 1H, Ar), 8.13 (d, *J*=8.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 51.7, 52.0, 126.15, 126.24, 126.4, 126.7, 126.8, 127.0, 127.5, 127.9, 128.1, 128.3, 128.7, 129.8, 130.0, 131.2, 132.7, 133.2, 138.7, 139.9, 140.0, 142.2, 169.9. IR (CH_2Cl_2) ν 3058, 3025, 2949, 2351, 1727, 1598, 1494, 1453, 1363, 1250, 1224, 1123, 1055, 763, 700 cm^{-1}. MS (%) (EI) *m*/*z* 428 (M$^+$, 6), 396 (100), 289 (24), 291 (24), 369 (9), 319 (8), 165 (7), 276 (6). HRMS (EI) calcd for $C_{31}H_{24}O_2$: 428.1776, Found: 428.1774.

4.2.17. Compound ***6b****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.48 (s, 3H, OCH_3), 6.73 (s, 1H, CH), 7.21–7.30 (m, 14H, Ar), 7.37–7.39 (m, 1H, Ar), 7.47 (s, 1H, Ar), 7.81 (d, J=6.3 Hz, 1H, Ar), 7.89 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 21.9, 51.8, 52.0, 125.6, 126.1, 126.2, 126.7, 127.8, 128.0, 128.6, 128.8, 128.9, 129.0, 129.88, 129.92, 131.3, 131.5, 133.0, 135.7, 137.2, 137.6, 139.8, 142.4, 170.1. IR (CH_2Cl_2) ν 3446, 3057, 3024, 2949, 2921, 2351, 1729, 1717, 1495, 1361, 1250, 1218, 1175, 1124, 827, 699 cm^{-1}. MS (%) (EI) *m*/*z* 456 (M^+, 9), 424 (100), 289 (14), 319 (12), 165 (10), 397 (9), 77 (7), 105 (6). HRMS (EI) calcd for $C_{33}H_{28}O_2$: 456.2089, Found: 456.2094.

4.2.18. Compound ***6c****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.56 (s, 3H, OCH_3), 6.71 (s, 1H, CH), 7.16–7.18 (m, 4H, Ar), 7.25–7.27 (m, 5H, Ar), 7.31–7.51 (m, 8H, Ar), 7.59 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 50.5, 52.2, 126.4, 126.5, 126.6, 126.99, 127.04, 127.7, 128.2, 128.27, 128.34, 130.0, 131.1, 132.3, 132.4, 133.3, 137.8, 139.7, 140.3, 140.5, 169.6. IR (CH_2Cl_2) ν 3057, 2950, 2925, 2854, 1727, 1490, 1250, 1123, 1091, 1056, 1015, 890, 815, 770, 701 cm^{-1}. MS (%) (EI) *m*/*z* 496 (M^+, 7), 464 (100), 429 (37), 289 (25), 365 (18), 182 (10), 325 (9), 394 (9). HRMS (EI) calcd for $C_{31}H_{22}Cl_2O_2$: 496.0997, Found: 496.1001.

4.2.19. Compound ***6d****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.50 (s, 3H, OCH_3), 6.66 (s, 1H, CH), 7.22–7.25 (m, 7H, Ar), 7.28–7.36 (m, 6H, Ar), 7.40 (d, J=8.8 Hz, 2H, Ar), 7.47 (d, J=8.8 Hz, 2H, Ar), 7.51 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 51.8, 52.2, 126.0, 126.5, 126.7, 127.8, 128.1, 128.3, 128.7, 129.7, 129.8, 130.0, 131.1, 131.3, 132.3, 132.6, 133.7, 134.0, 137.8, 138.1, 138.8, 141.6, 169.4. IR (CH_2Cl_2) ν 3060, 3026, 2951, 2926, 2853, 1729, 1600, 1494, 1435, 1358, 1253, 1217, 1100, 1015, 833, 700 cm^{-1}. MS (%) (EI) *m*/*z* 496 (M^+, 8), 464 (100), 289 (31), 437 (24), 165 (14), 182 (14), 359 (14), 429 (12). HRMS (EI) calcd for $C_{31}H_{22}Cl_2O_2$: 496.0997, Found: 496.0994.

4.2.20. Compound ***6e****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.31 (s, 6H, 2CH_3), 3.53 (s, 3H, OCH_3), 6.67 (s, 1H, CH), 7.07–7.09 (m, 3H, Ar), 7.13–7.15 (m, 3H, Ar), 7.28–7.50 (m, 9H, Ar), 7.55 (s, 1H, Ar), 7.89 (dd, J_1=0.8 Hz, J_2=8.0 Hz, 1H, Ar), 8.14 (d, J=8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.0, 51.1, 52.0, 125.2, 126.0, 126.4, 126.66, 126.73, 127.2, 127.5, 128.0, 128.3, 128.7, 129.7, 130.1, 131.1, 132.7, 133.2, 135.6, 139.0, 139.4 139.9, 140.0, 170.0. IR (CH_2Cl_2) ν 3568, 3054, 3023, 2953, 2926, 2859, 1907, 1725, 1511, 1445, 1250, 1123, 1057, 812, 774, 702 cm^{-1}. MS (%) (EI) *m*/*z* 456 (M^+, 4), 424 (100), 289 (15), 305 (14), 43 (13), 397 (12), 91 (10), 235 (8). HRMS (EI) calcd for $C_{33}H_{28}O_2$: 456.2089, Found: 456.2093.

4.2.21. Compound ***6f****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.52 (s, 3H, OCH_3), 6.54 (s, 1H, CH), 6.97–7.02 (m, 4H, Ar), 7.17–7.26 (m, 7H, Ar), 7.42–7.47 (m, 3H, Ar), 7.66 (dd, J_1=2.4 Hz, J_2=11.6 Hz, 1H, Ar), 7.87 (dd, J_1=6.0 Hz, J_2=9.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 50.5, 52.2, 110.4 (d, J=23.1 Hz), 115.1 (d, J=21.6 Hz), 115.5 (d, J=21.6 Hz), 117.3 (d, J=24.5 Hz), 125.8, 129.4, 129.5, 130.2, 131.3 (d, J=8.2 Hz), 131.5 (d, J=8.1 Hz), 132.3, 133.9, 134.0, 135.4 (d, J=2.9 Hz), 137.2 (d, J=3.0 Hz), 137.5, 137.6, 139.3, 161.5 (d, J=244.7 Hz), 162.6 (d, J=246.1 Hz), 169.4. IR (CH_2Cl_2) ν 2953, 2351, 1731, 1604, 1506, 1435, 1357, 1225, 1159, 1016, 841, 729 cm^{-1}. MS (%) (EI) *m*/*z* 500 (M^+, 6), 468 (100), 345 (19), 343 (11), 325 (8), 201 (8), 439 (6), 373 (5). HRMS (EI) calcd for $C_{31}H_{20}F_4O_2$: 500.1399, Found: 500.1400.

4.2.22. Compound ***6g****.* A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.54 (s, 3H, OCH_3), 6.69 (s, 1H, CH), 6.95–7.00 (m, 4H, Ar), 7.19–7.22 (m, 4H, Ar), 7.34–7.45 (m, 5H, Ar), 7.46 (s, 1H, Ar), 7.49 (s, 1H, Ar), 7.56 (s, 1H, Ar), 7.92 (dd, J_1=0.8 Hz, J_2=8.4 Hz, 1H, Ar), 8.05 (d, J=8.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 50.3, 52.1, 115.0 (d, J=20.8 Hz), 126.4, 126.6, 126.9, 127.0, 127.6, 128.3, 130.0, 131.1, 131.3 (d, J=7.5 Hz), 132.5, 133.2, 137.8 (d, J=3.0 Hz), 138.2, 139.7, 140.3, 161.4 (d, J=243.9 Hz), 169.7. IR (CH_2Cl_2) ν 3058, 2951, 1727, 1600, 1507, 1363, 1251, 1226, 1159, 1123, 1057, 826, 756, 702 cm^{-1}. MS (%) (EI) *m*/*z* 464 (M^+, 7), 432 (100), 307 (11), 309 (10), 327 (7), 325 (6), 403 (6), 201 (6). HRMS (EI) calcd for $C_{31}H_{22}F_2O_2$: 464.1588, Found: 464.1587.

A yellow oil. (Compound **4f**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.74–0.78 (m, 6H, 2CH_3), 1.08–1.18 (m, 6H, 3CH_2), 1.40–1.54 (m, 4H, 2CH_2), 1.61–1.71 (m, 2H, CH_2), 3.62 (s, 3H, OCH_3), 6.03 (s, 1H, CH), 7.05–7.08 (m, 1H, Ar), 7.17–7.28 (m, 7H, Ar), 7.36–7.39 (m, 2H, Ar). (Compound **7**) ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.74–0.78 (m, 6H, 2CH_3), 1.08–1.18 (m, 10H, 5CH_2), 1.40–1.54 (m, 2H, CH_2), 3.60 (s, 3H, OCH_3), 6.66 (s, 1H, CH), 7.05–7.08 (m, 1H, Ar), 7.17–7.28 (m, 7H, Ar), 7.36–7.39 (m, 2H, Ar). (Mixture of compounds **4f** and **7**) ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 13.9, 22.2, 22.7, 27.5, 29.2, 29.7, 31.4, 39.4, 49.2, 52.0, 52.3, 83.1, 91.5, 94.2, 99.6, 107.4, 109.4, 119.4, 126.9, 127.2, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 129.6, 130.0, 139.3, 140.1, 141.4, 142.7, 143.1, 147.8, 152.1, 168.4, 174.0, 209.6, 216.0. IR (CH_2Cl_2) ν 3556, 3451, 3079, 3056, 3022, 2957, 2930, 2871, 2236, 1598, 1574, 1494, 1444, 1377, 1318, 1076, 902, 765, 698 cm^{-1}. MS (%) (EI) *m*/*z* 388 (M^+, 62), 217 (100), 229 (94), 271 (73), 329 (58), 202 (56), 91 (56), 262 (55). HRMS (EI) calcd for $C_{27}H_{32}O_2$: 388.2402, Found: 388.2398.

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Supplementary data

Spectroscopic data of all the new compounds and the detailed descriptions of experimental procedures. This material is available free of charge via the Internet. The Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.tet.2009.09.004.

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