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Synthesis of Oxatricyclooctanes via Photoinduced Intramolecular Oxa-[4+2] Cycloaddition of Substituted *o*-Divinylbenzenes

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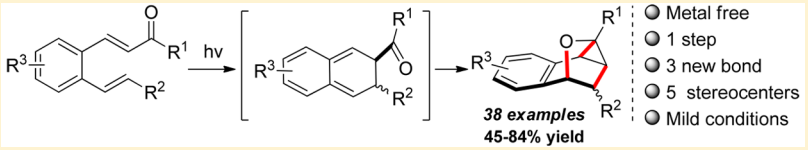
Supporting Information



ABSTRACT: The photolysis of substituted *o*-divinylbenzenes promotes a one-step and metal-free conversion to oxatricycles at room temperature. Irradiation *o*-divinylbenzenes results in an pericyclic reaction to form cyclic *o*-quinodiemthane intermediates, which subsequently undergo intramolecular oxa-[4+2] cycloaddition to form oxacyclic derivatives.

INTRODUCTION

Photoinduced organic reaction is a significant and powerful tool for the generation of carbo- and heterocyclic frameworks in the synthesis of complex polycyclic compounds[1] or natural products[2] possessing a broad range of significant biological activities, which, however, would be difficult to access with the classical methods in the ground state. More specifically, photochemical reaction is an environmentally friendly way for syntheses of various natural products and unnatural compounds because it often does not require activation reagents, such as acids, bases, metals, or enzymes.[3]

The complicated oxacyclic compounds are widely present in numerous biologically active natural products, such as przewalskin and carnosol (Figure 1).[4] For example, compound **A** (Figure 1) which was reported by Chao et al. exhibits significant anti-HCV (antihepatitis C virus) activity (EC_{50} = 7.5 μM) with nontoxicity (IC_{50} = 419.2 μM) and has a higher therapeutic index (TI) value (TI = 55.9).[5] However, current synthetic examples often need multiple steps to build the oxa-skeletons and only a few methods that use transition metals, e.g., Rh, Pt ,or Au as catalysts, are reported (Scheme 1).[6] For instance, Adams and co-worker have developed a cyclopropanation reaction promoted by $[Rh(OAc)_2]_2$ to generate such tricyclic compound (Scheme 1a).[6a] Subsequently, Oh's group developed the $PtCl_2$ catalyzed cyclization reaction to afford fused cyclopropanes (Scheme 1b).[6b] Besides, Liu et al. have demonstrated tandem oxacyclization/[4+2]-cycloaddition cascade reaction for the synthesis of highly substituted oxacyclic compounds catalyzed by Au (Scheme 1c).[6c] With our continues on the photochemical methodologies,[7] especially the work for construction of benzobicyclo[2.2.2]octane skeletons using *o*-divinylbenzenes and olefins,[7d] we found that such *o*-divinylbenzenes can generate oxatricyclooctanes under UV light when there was no dienophile in the reaction system. It is a convenient, transition-metal-free and step-economical approach for the rapid construction of such bridged-ring compounds through photoinduced intramolecular oxa-[4+2] reactions of substituted *o*-divinylbenzenes (Scheme 1d).

RESULTS AND DISCUSSION

Our investigation was initially carried out by the irradiation of substituted *ortho*-divinylbenzene **a1** in MeCN under air using 350 nm wavelength as light source at room temperature. The desired product **b1** containing *cis*/*trans* stereoisomers were obtained in 80% isolated yield (Table 1, entry 1). Subsequently, light source was screened, and it indicated that the suitable wavelength was proven to be 350 nm or 500 W medium pressure mercury lamp with a Pyrex filter (Table 1, entries 1−4). The reaction did not take place in the blue LEDs (Table 1, entry 5). Further, a set of solvents was examined and the reaction performed in MeCN provided the best result (Table 1, entries 1, 6−12). Other strong polar solvents, such as MeOH and DMF were proven to be ineffective for this transformation (Table 1, entries 8−9). Wet MeCN also proceeded smoothly with a decreased yield, which meant that this reaction was not sensitive to moisture (Table 1, entry 13). Further investigation showed that higher yield could be obtained when the reaction was carried out under a N_2 atmosphere (Table 1, entry 14).

To investigate the scope of this protocol, a variety of substituted *o*-divinylbenzenes derivatives were prepared and subjected to the optimized reaction conditions, and the representative results are listed in Table 2. As expected, the reaction worked well in the cases of alkyl ketones to afford the target products in good to excellent yields (Table 2, **b1**, **b2**). Sterically bulky groups, such as butyl or phenyl, on substrate could also furnish the corresponding products but in lower yields as 52% and 45%, respectively (Table 2, **b3**, **b4**), which

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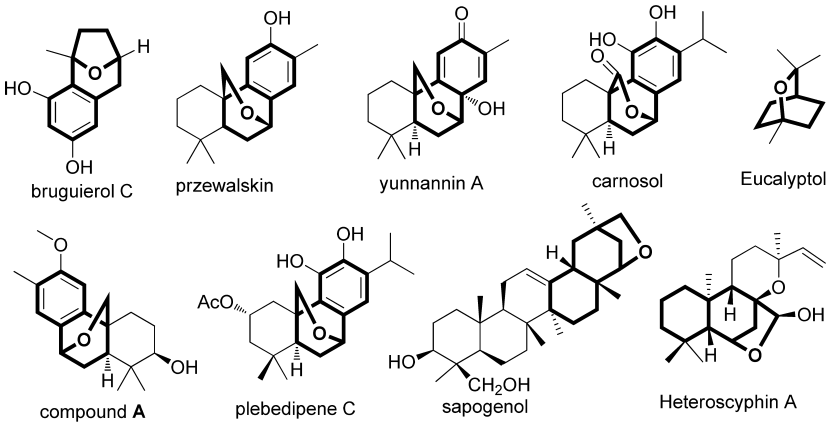
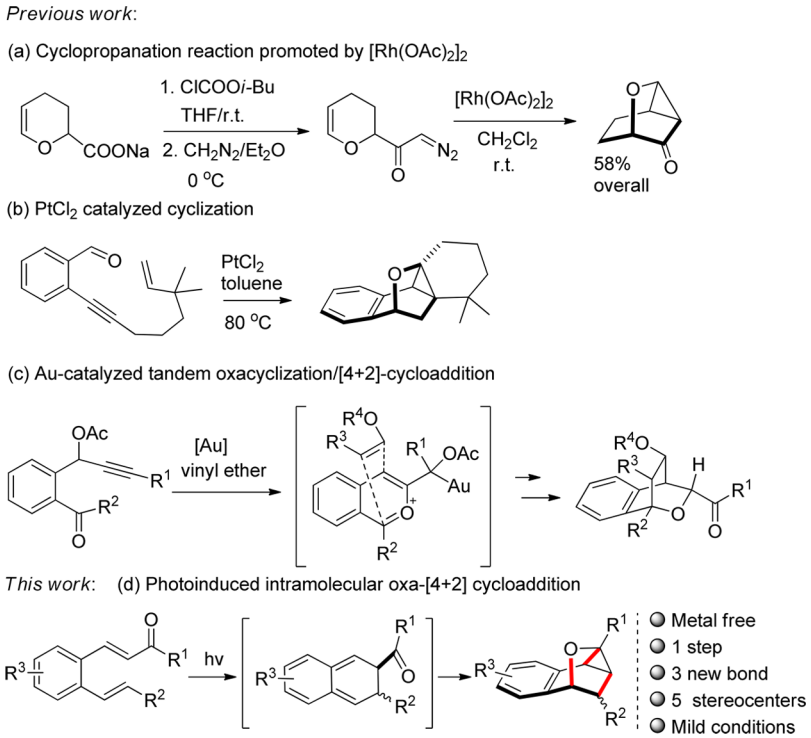


Figure 1. Natural products with complicated oxacyclic skeletons.

Scheme 1. Approaches for the Complicated Oxacyclic Skeletons



might be due to the groups that had large steric hindrance and might cause other side reactions, e.g. Norrish type I/II reaction.[8]

Then we examined the substrates containing ester groups which, as expected, led to the corresponding products in good yields (Table 2, **b5**−**b14**). The aryl groups with different groups were also tolerated under the reaction conditions. For example, both electron-donating substituents (MeO, Me) and electron-withdrawing substituents (F, Cl) on the phenyl ring were suitable for this reaction, leading to the corresponding products in moderate to good yields (Table 2, **b15**−**b20**, **b33**−**b37**). Substituted 1,2-divinylnaphthalene also worked well under the reaction conditions to afford the desired product in 53% yield (Table 2, **b21**). Next we turned our attention to the investigation of substrate containing a cyano group, which worked smoothly to get the product in 78% yield (Table 2, **b22**). We examined the substrates with aldehyde groups, and it was found that the reactions were completed within shorter reaction time, which was probably due to the aldehyde group that was easy to be excited by UV light (Table 2, **b23**−**b37**). Furthermore, the substrate containing two ester groups could furnish the corresponding products with lower yield, probably due to the fact that the carbon−oxygen double bond of ester group was not a good dienophile compared with carbonyl group or aldehyde group in this reaction (Table 2, **b38**). The structure of all obtained photoproducts was assigned on the basis of ^{1}H, ^{13}C, 2D NMR, and mass spectrometry analysis. Two of the products **b6′** and **b22′** (Table 2) were suitable for X-ray single-crystal structure analysis (X-ray crystallography data see SI), allowing unambiguous determination of the structure and relative configuration.[9]

Before the mechanism was proposed, a survey of literatures was conducted and showed that the photochemistry of stilbene-like compound trended to form the benzobicyclo[2.1.1]hexene photoproduct via a free-radical process.[10] However, Marija Šindler-Kulyk group did not observe such a product, but

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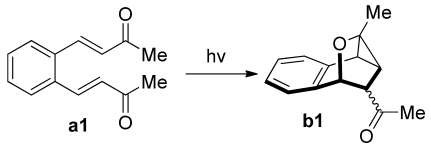
Table 1. Optimization of Reaction Conditions[a]



entry	solvent (anhydrous)	light source	time (h)	yield (%)[b] (dr)[c]
1	MeCN	350 nm	4.0	80 (2.0:1)
2	MeCN	300 nm	4.0	70 (2.9:1)
3	MeCN	500 W medium pressure mercury lamp	3.0	72 (1.9:1)
4	MeCN	500 W medium pressure mercury lamp with Pyrex	3.0	77 (2.3:1)
5	MeCN	blue LEDs	24.0	0
6	benzene	350 nm	4.0	80 (2.3:1)
7	toluene	350 nm	4.0	72 (2.1:1)
8	MeOH	350 nm	8.0	39 (> 10:1)
9	DMF	350 nm	8.0	26 (> 10:1)
10	CH_2Cl_2	350 nm	4.0	70 (2.0:1)
11	THF	350 nm	6.0	60 (2.4:1)
12	acetone	350 nm	4.0	72 (2.6:1)
13[d]	MeCN	350 nm	6.0	70 (2.2:1)
14[e]	MeCN	350 nm	4.0	84 (2.1:1)

[a]Reaction conditions: a1 (0.5 mmol), solvent (anhydrous, 50 mL), air atmosphere, rt. [b]Isolated yield. [c]Diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture. [d]Wet solvent. [e]N_2 atmosphere.

benzo[*f*]quinolone derivatives instead when they studied the photochemistry of stilbene-like compound with a different substituted group.[11] The study from Škorić's group on the photochemistry of butadiene derivatives showed that a six-membered ring closure followed by a sigmatropic 1,5-H shift was involved in the reaction and the cyclic *o*-quinodimethane (*o*-QDM) was the key intermediate (Scheme 2, eq 1),[12] which might be helpful for us to map out the reaction mechanism. To collect more information, we then carried out a few control experiments. At first, a radical scavenger, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), was added to the reaction of **1a** in order to determine whether the process of the formation of oxatricyclootanes is a radical pathway or not. Consequently, compound **b1′** was obtained as a single product which meant this process of the formation photoproduct is not a radical pathway, and its stereoisomer **b1″** was vanished (Scheme 2, eq 2) which was owing to TEMPO that could prevent the photochemical *cis*/*trans* isomerization. Another control experiment was conducted by adding excess amount of butylated hydroxytoluene (BHT) to the reaction of **1a** which afforded the products smoothly (Scheme 2, eq 3) which also meant the process of the formation oxatricyclooctanes is not a radical pathway. The above experimental results indicated that a radical pathway could be excluded in this photoinduced reaction. To add more credence, four more control experiments were conducted by addition of cyclohexa-1,3-diene, *trans*-stilbene, phenylacetylene, anthracene as a triplet quencher in the solution of **a1** in MeCN, which had no effects on this reaction efficiency. In addition, we successfully obtained the benzobicyclo[2.2.2]octane derivative **c1** and **c5** in good yield when we added dienophile, such as maleic anhydride and *N*-methylmaleimide, into the system to trap the reactive intermediate cyclic *o*-QDM (Scheme 2, eq 4,5). Such a result revealed that a highly reactive intermediate cyclic *o*-QDM might be formed via a conrotatory six-membered ring closure process according to Woodword–Hoffmann rules[13] which was consistent with the work of Škorić's group (Scheme 2, eq 1).

Based upon these observations, we propose the mechanism depicted in Scheme 3. Under the irradiation of UV light, the double bond of ***trans,trans*-a** was excited to cause a pericyclic reaction to form a highly reactive intermediate cyclic-*o*-QDM. As a highly reactive intermediate, the intermediate *o*-QDM can react with carbon–oxygen double bond via a Diels–Alder reaction to form the final product.[14] In addition, carbon–carbon double bond can undergo photochemical *cis/trans* isomerization reaction to form ***cis,trans*-a** which could furnish the minor stereoisomer product in same manner.

The synthetic application of the products has been demonstrated by catalytic hydrogenation of the product **b10** as a representative compound which led to the oxa-bicyclic product **d10** in 90% yield via opening of the cyclopropane ring (Scheme 4).

To demonstrate the potential utility of this methodology, a gram scale reaction of **a1** was carried out. The desired product was isolated in 78% yield under the standard reaction conditions (Scheme 5).

CONCLUSION

In summary, we have developed a facile and metal-free procedure for the syntheses of complicated oxacyclic skeleton compounds via photoinduced intramolecular oxa-[4+2] reactions of substituted o-divinylbenzenes under mild condition. This reaction undergoes a pericyclic reaction through a conrotatory six-membered ring closure process to form *o*-quinodimethane as the key intermediate. In addition, the gram scale reaction demonstrated the synthetic value and utility of this protocol.

EXPERIMENTAL SECTION

General Information. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Flash column chromatography was performed using 200–300 mesh silica gel. ^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were obtained in $CDCl_3$ or DMSO-d^6 with TMS as internal standard. High-resolution mass spectra (HRMS) were recorded on a Q-TOF (ESI) mass spectrometer. Low-resolution mass spectra were obtained from GC-MS system. The 350 nm light is from the phosphor-coated lamps (emission centered at 350 nm). The 500 W medium pressure mercury lamp is a mercury arc lamp. A Pyrex filter works as a filter for a shorter wavelength of UV (~<280 nm). The wavelength of the blue LED is 450 nm and its intensity is 6 W.

General Procedure for Preparation of Substrates. *General Procedure for Syntheses of Compound **a1–a4**.* A solution of the 1-bromopropan-2-one (1.0 g, 7.3 mmol) and triphenylphosphine (1.9 g, 7.3 mmol) were refluxed in toluene (50 mL) for 4 h. After completion, the reaction mixture was allowed to cool to room temperature and the phosphonium salt was filtered and washed with Et_2O (3 × 50 mL). The phosponium salt was then dissolved in H_2O: DCM (1:1) 150 mL and 4 M. aq. NaOH (50 mL) was added. The mixture was stirred for 2 h and then extracted with DCM (3 × 100 mL). The combined organic phases were washed with brine, dried (Na_2SO4) and concentrated in vacuo to afford 1-(triphenylphosphoranylidene)propan-2-one as a white solid.[15] To a solution of phthaldialdehyde (402 mg, 3.0 mmol) in THF (30 mL) was added the 1-(triphenylphosphoranylidene)-propan-2-one (7.2 mmol). The mixture was stirred at room temperature for 16 h and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/EtOAc = 5/1)

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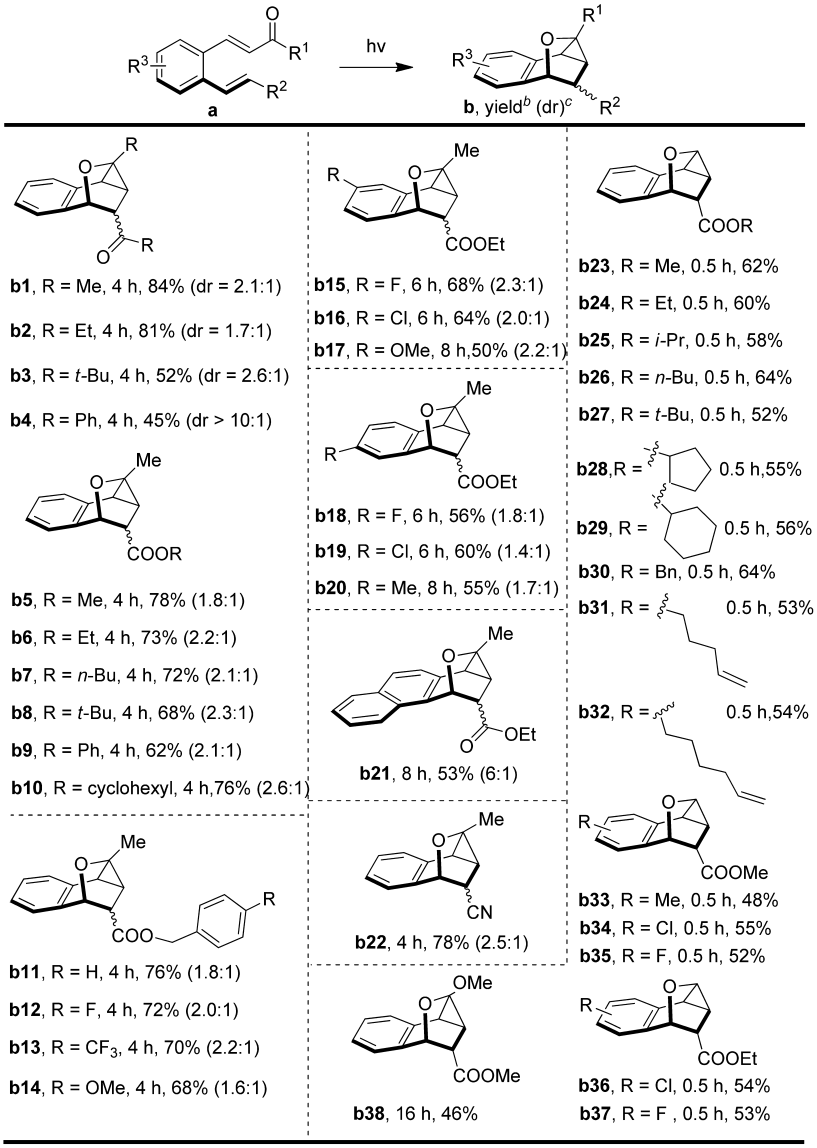
Table 2. Study of Reaction Scope[a]



[a]Reaction condition: a (0.5 mmol), solvent (anhyrous, 50 mL), N_2 atmosphere, rt. [b]Isolated yield. [c]Diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture.

afforded the compound **a1** as a white solid.[16] Yield 79% (based on phthaldialdehyde). Compounds **a2**–**a4** are prepared following the general procedure above.

*General Procedure for Syntheses of Compound **a5**–**a14**.* To a solution of phthaldialdehyde (5.0 mmol) in THF (60 mL) was added the ethyl 2-(triphenylphosphoranylidene)acetate (5.0 mmol). The mixture was stirred at room temperature for 16 h and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/EtOAc: 9/1) afforded the (*E*)-ethyl 3-(2-formylphenyl)acrylate.[16] To a solution of (*E*)-ethyl 3-(2-formylphenyl)acrylate (4.0 mmol) in THF (60 mL) was added the 1-(triphenylphosphoranylidene)propan-2-one (5.0 mmol). The mixture was stirred at room temperature for 16 h and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/EtOAc: 5/1) afforded the compound **a6**.[16] Yield 64% (based on phthaldialdehyde for two steps). Compounds **a5**, **a7**–**a14** are prepared following the general procedure above.

*General Procedure for Syntheses of Compound **a15**–**a22**.* To a solution of the 2-bromo-5-fluorobenzaldehyde (10.0 mmol) in anhydrous toluene (100 mL) were successively added $Pd(OAc)_2$ (0.2 mmol), triphenylphosphine (0.4 mmol), ethyl acrylate (20 mmol), and triethylamine (25 mmol) at room temperature. The reaction mixture was heated at reflux for 24 h, cooled to r.t., diluted with ether, and filtered through a thin pad of Celite. The filtrate was diluted with water and extracted with ether. The organic layers were combined, dried over $MgSO_4$, and concentrated under vacuum. The dark thick oil obtained was purified by flash silica chromatography employing mixtures of *n*-hexane and ethyl acetate as eluents to get the (*E*)-ethyl 3-(4-fluoro-2-formylphenyl)acrylate.[17] To a solution of (*E*)-ethyl 3-(4-fluoro-2-formylphenyl)acrylate (5.0 mmol) in THF (60 mL) was added 1-(triphenylphosphoranylidene)propan-2-one (6.0 mmol). The mixture was stirred at room temperature for 16 h and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/EtOAc: 9/1) afforded the compound **a15**.[16] Yield 45% (based on 2-bromo-5-fluorobenzaldehyde for two steps). Compounds **a16**–**a22** are prepared following the general procedure above (for Compounds **a16**–**a22** the starting material 5.0 mmol).

*General Procedure for Syntheses of Compound **a23**–**a38**.* To a solution of phthaldialdehyde (5.0 mmol) in THF (60 mL) was added the ethyl 2-(triphenylphosphoranylidene)acetate (11.0 mmol). The mixture was stirred at room temperature for 16 h and concentrated in

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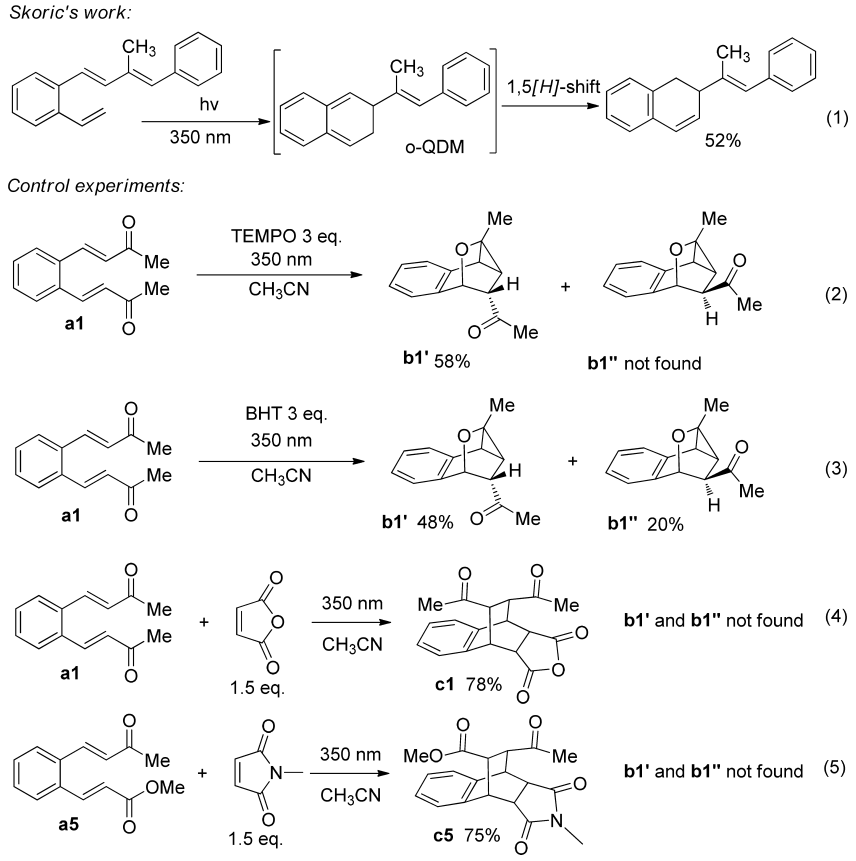
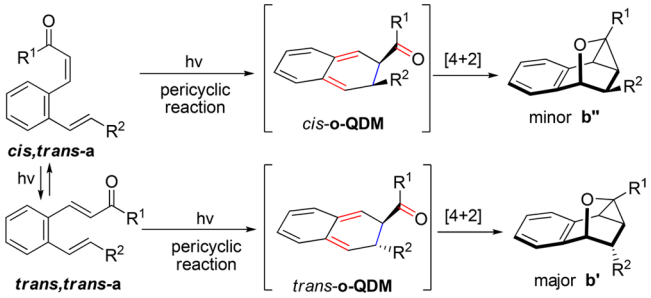
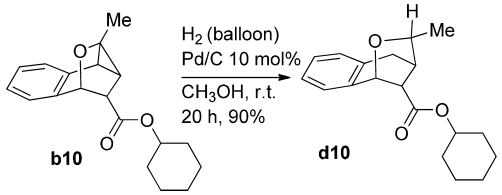
Scheme 2. Previous Work and Control Experiments



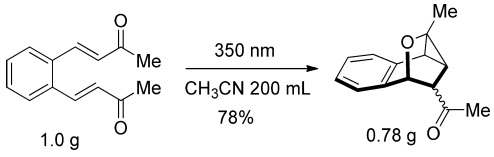
Scheme 3. Plausible Mechanism



Scheme 4. Synthetic Transformation of Compound b10



Scheme 5. Reaction of a1 at Gram Scale



vacuo. Purification of the residue by column chromatography (petroleum ether/EtOAc: 9/1) afforded the (*E*)-3-[2-{(*E*)-2-Ethoxycarbonylvinyl}phenyl]acrylic acid ethyl ester.[16] To a solution of the (*E*)-3-[2-{(*E*)-2-ethoxycarbonylvinyl}phenyl]acrylic acid ethyl ester (3 mmol) in dry THF (20 mL) at −78 °C was added DIBAL-H (6.2 mL of a 1.0 M solution in toluene, 6.2 mmol) slowly. After stirring for 1 h, the reaction mixture was allowed to return to 0 °C. Four hours later, the reaction was quenched with methanol (3 mL). Then 20 mL aqueous solution of 0.5 M HCl was added. One hour later, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by chromatography on silica gel (EtOAc/hexane, 1/3) gave the (*E*)-ethyl 3-(2-((*E*)-3-hydroxyprop-1-en-1-yl)phenyl)acrylate as a clear oil.[18] To a solution of oxalyl chloride (2.4 mmol) in dry CH_2Cl_2 (10 mL) cooled at −78 °C was added dropwise a solution of dimethyl sulfoxide (DMSO 2.3 mmol) in CH_2Cl_2 (10 mL). After 5 min, a solution of the (*E*)-ethyl 3-(2-((*E*)-3-hydroxyprop-1-en-1-yl)phenyl)acrylate (2 mmol) in CH_2Cl_2 (10 mL) was added. The reaction mixture was then stirred for 15 min at −78 °C and triethylamine (10 mmol) was added in one portion. After 10 min at −78 °C, the mixture was allowed to warm to room temperature and diluted with CH_2Cl_2 (40 mL). The organic layer was successively washed with a saturated aqueous solution of NH_4Cl (20 mL) and brine (20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/EtOAc: 9/1) afforded the aldehyde **a24**. Yield 36% (based on phthaldialdehyde for three steps). Compounds **a23**, **a25**−**a38** are prepared following the general procedure above.

General Procedures for Preparation of Products. A quartz glass tube was charged with substrate **a** (0.5 mmol) and then charged with N_2 three times. Then anhydrous MeCN (50 mL) was added. The mixture was allowed to expose to 350 nm mercury lamp for 0.5−18 h (monitored by TLC). After the substrate was consumed. The reaction was cooled to room temperature. Then, the solvent was removed in

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vacuo, the residue was purified by column chromatography to give the product **b**.

Gram scale reactions: A quartz glass tube was charged with substrate **a1** (1.0 g) and then charged with N_2 three times. Then anhydrous MeCN (200 mL) was added. The mixture was allowed to expose to 300 nm mercury lamp with Pyrex filter for 8 h (monitored by TLC). After the substrate **a1** was consumed. The reaction was cooled to room temperature. Then, the solvent was removed in vacuo, the residue was purified by column chromatography to give the product **b1**.

(3E,3′E)-4,4′-(1,2-Phenylene)bis(but-3-en-2-one) ***a1***.[16] White solid. 507 mg. Yield 79%. Mp. 89−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 16.0 Hz, 2H), 7.60 (dd, J = 5.7, 3.5 Hz, 2H), 7.43 (dd, J = 5.8, 3.3 Hz, 2H), 6.64 (d, J = 16.0 Hz, 2H), 2.41 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 139.8, 134.6, 130.4, 130.3, 127.8, 28.1. HRMS (ESI): calcd for $C_{14}H_{15}O_2$, $[M+H]^+$, 215.1067; found, 215.1069.

(1E,1′E)-1,1′-(1,2-Phenylene)bis(pent-1-en-3-one) ***a2***. White solid. 544 mg. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 16.0 Hz, 2H), 7.59 (dd, J = 5.7, 3.5 Hz, 2H), 7.41 (dd, J = 5.8, 3.3 Hz, 2H), 6.65 (d, J = 16.0 Hz, 2H), 2.72 (q, J = 7.3 Hz, 4H), 1.19 (t, J = 7.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 138.7, 134.7, 130.1, 129.4, 127.7, 34.5, 8.1. HRMS (ESI): calcd for $C_{16}H_{19}O_2$, $[M+H]^+$, 243.1380; found, 243.1387.

(1E,1′E)-1,1′-(1,2-Phenylene)bis(4,4-dimethylpent-1-en-3-one) ***a3***. White solid. 625 mg. Yield 70%. Mp. 92−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 15.5 Hz, 2H), 7.75−7.52 (m, 2H), 7.40 (dd, J = 5.6, 3.4 Hz, 2H), 6.98 (d, J = 15.5 Hz, 2H), 1.23 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.7, 140.2, 135.48, 129.78, 128.28, 124.8, 43.2, 26.3. HRMS (ESI): calcd for $C_{20}H_{27}O_2$, $[M+H]^+$, 299.2006; found, 299.2010.

(2E,2′E)-3,3′-(1,2-Phenylene)bis(1-phenylprop-2-en-1-one) ***a4***.[16] Yellow solid. 578 mg. Yield 57%. Mp 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 15.6 Hz, 2H), 8.03 (d, J = 7.6 Hz, 4H), 7.72 (dd, J = 5.5, 3.5 Hz, 2H), 7.59 (t, J = 7.3 Hz, 2H), 7.55−7.46 (m, 4H), 7.43 (d, J = 15.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.11, 141.75, 137.94, 135.44, 132.99, 130.15, 128.72, 128.63, 128.22, 126.14. HRMS (ESI): calcd for $C_{24}H_{19}O_2$, $[M+H]^+$, 339.1380; found, 339.1375.

(E)-Methyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a5***. White solid. 782 mg. Yield 68%. Mp. 46−47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 15.8 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.58 (dd, J = 9.0, 5.1 Hz, 2H), 7.42 (ddd, J = 6.1, 4.0, 2.1 Hz, 2H), 6.63 (d, J = 16.1 Hz, 1H), 6.36 (dd, J = 15.8, 0.7 Hz, 1H), 3.83 (d, J = 0.7 Hz, 3H), 2.41 (d, J = 0.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 161.5, 136.1, 134.5, 129.1, 128.9, 125.1, 124.9, 124.8, 122.4, 122.3, 116.3, 46.6, 22.6. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1020.

(E)-Ethyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a6***. White solid. 780 mg. Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 15.8 Hz, 1H), 7.87 (d, J = 16.1 Hz, 1H), 7.70−7.52 (m, 2H), 7.52−7.33 (m, 2H), 6.62 (d, J = 16.1 Hz, 1H), 6.36 (dd, J = 15.8, 0.8 Hz, 1H), 4.29 (qd, J = 7.1, 0.7 Hz, 2H), 2.41 (d, J = 0.8 Hz, 3H), 1.35 (td, J = 7.1, 0.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 161.1, 135.9, 134.6, 129.2, 128.9, 125.1, 124.9, 124.8, 122.4, 122.3, 116.8, 55.4, 22.5, 9.0. HRMS (ESI): calcd for $C_{15}H_{17}O_3$, $[M+H]^+$, 245.1172; found, 245.1177.

(E)-Butyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a7***. White solid. 816 mg. Yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 15.8 Hz, 1H), 7.87 (d, J = 16.1 Hz, 1H), 7.58 (dd, J = 6.1, 2.7 Hz, 2H), 7.41 (dd, J = 5.7, 3.5 Hz, 2H), 6.62 (d, J = 16.1 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 4.24 (t, J = 6.7 Hz, 2H), 2.41 (s, 3H), 1.80−1.62 (m, 2H), 1.58−1.35 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 161.2, 135.8, 134.6, 129.2, 128.9, 125.1, 124.94, 124.79, 122.46, 122.36, 116.7, 59.3, 25.4, 22.3, 13.9, 8.46. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1490.

(E)-tert-Butyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a8***. White solid. 788 mg. Yield 58%. Mp. 85−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 15.8 Hz, 1H), 7.87 (d, J = 16.1 Hz, 1H), 7.65−7.48 (m, 2H), 7.48−7.11 (m, 2H), 6.60 (d, J = 16.1 Hz, 1H), 6.29 (d, J = 15.8 Hz, 1H), 2.40 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 165.6, 139.98, 139.96, 134.56, 134.1, 130.3, 130.2, 129.8, 127.6, 127.5, 123.8, 80.8, 28.1, 27.6. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1489.

(E)-Phenyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a9***. White solid. 730 mg. Yield 50%. Mp. 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 15.8 Hz, 1H), 7.90 (d, J = 16.1 Hz, 1H), 7.67 (dd, J = 5.4, 3.7 Hz, 1H), 7.62 (dd, J = 5.5, 3.7 Hz, 1H), 7.49−7.43 (m, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.31−7.23 (m, 1H), 7.22−7.09 (m, 2H), 6.65 (d, J = 16.1 Hz, 1H), 6.57 (d, J = 15.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 164.8, 150.6, 143.1, 139.7, 134.5, 134.1, 130.7, 130.5, 130.3, 129.5, 127.9, 127.8, 125.9, 121.6, 121.0, 27.8. HRMS (ESI): calcd for $C_{19}H_{17}O_3$, $[M+H]^+$, 293.1172; found, 293.1173.

(E)-Cyclohexyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a10***. White solid. 774 mg. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 15.8 Hz, 1H), 7.87 (d, J = 16.1 Hz, 1H), 7.59 (dd, J = 5.4, 3.8 Hz, 2H), 7.47−7.35 (m, 2H), 6.62 (d, J = 16.1 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 5.13−4.73 (m, 1H), 2.41 (s, 3H), 1.93 (m 2H), 1.77 (m, 2H), 1.62−1.16 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 160.5, 135.5, 134.7, 129.2, 128.9, 125.1, 124.9, 124.7 122.4, 122.3, 117.3, 67.7, 26.4, 22.3, 20.1, 18.5. HRMS (ESI): calcd for $C_{19}H_{23}O_3$, $[M+H]^+$, 299.1642; found, 299.1644.

(E)-Benzyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a11***. White solid. 765 mg. Yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 15.8 Hz, 1H), 7.85 (d, J = 16.1 Hz, 1H), 7.68−7.49 (m, 2H), 7.49−7.31 (m, 7H), 6.61 (d, J = 16.1 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 5.27 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 166.2, 141.8, 139.9, 135.8, 134.3, 130.6, 130.27, 130.25, 128.6, 128.39, 128.35, 127.76, 127.74, 121.6, 66.6, 27.7. HRMS (ESI): calcd for $C_{20}H_{19}O_3$, $[M+H]^+$, 307.1329; found, 307.1330.

(E)-4-Fluorobenzyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylate ***a12***. White solid. 842 mg. Yield 52%. Mp. 79−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 15.8 Hz, 1H), 7.85 (d, J = 16.1 Hz, 1H), 7.71−7.48 (m, 2H), 7.41 (dt, J = 5.8, 4.0 Hz, 4H), 7.18−6.95 (m, 2H), 6.61 (d, J = 16.1 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 5.23 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 166.1, 162.72 (d, J = 247.1 Hz), 141.9, 139.8, 134.34 (d, J = 11.8 Hz), 131.74 (d, J = 3.2 Hz), 130.5, 130.4, 130.3, 130.29, 130.27, 127.76, 127.74, 121.45, 115.59 (d, J = 21.6 Hz), 65.87, 27.8. HRMS (ESI): calcd for $C_{20}H_{18}FO_3$, $[M+H]^+$, 325.1234; found, 325.1233.

(E)-4-(Trifluoromethyl)benzyl 3-(2-((E)-3-Oxobut-1-en-1-yl)-phenyl)acrylate ***a13***. White solid. 991 mg. Yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 15.8 Hz, 1H), 7.86 (d, J = 16.1 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.62−7.57 (m, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.46−7.40 (m, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 5.32 (s, 1H), 2.39 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.5, 160.7, 137.0, 134.6, 134.51 (q, J = 27.7 Hz), 134.4, 129.1, 128.8, 125.2, 125.0, 125.0, 124.9, 122.9, 122.4, 120.3 (q, J = 3.5 Hz), 118.7 (d, J = 272.0 Hz), 115.7, 60.2, 22.5. HRMS (ESI): calcd for $C_{21}H_{18}F_3O_3$, $[M+H]^+$, 375.1203; found, 375.1204.

(E)-4-Methoxybenzyl 3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)-acrylate ***a14***. White solid. 789 mg. Yield 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.8 Hz, 1H), 7.85 (d, J = 16.1 Hz, 1H), 7.70−7.50 (m, 2H), 7.47−7.32 (m, 4H), 6.92 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 16.1 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 5.21 (s, 2H), 3.82 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 166.3, 159.7, 141.6, 139.9, 134.4, 134.3, 130.5, 130.2, 130.1, 127.9, 127.75, 127.71, 121.8, 114.0, 66.4, 55.3, 27.7. HRMS (ESI): calcd for $C_{21}H_{21}O_4$, $[M+H]^+$, 337.1434; found, 337.1435.

(E)-Ethyl 3-(4-Fluoro-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a15***. White solid. 1179 mg. Yield 45%. Mp. 64−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 15.8 Hz, 1H), 7.81 (d, J = 16.0 Hz, 1H), 7.58 (dd, J = 8.7, 5.7 Hz, 1H), 7.27 (dd, J = 9.3, 2.6 Hz, 1H), 7.12 (td, J = 8.4, 2.5 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.31 (d, J = 15.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 166.2, 163.4 (d, J = 251.6 Hz), 139.9, 138.5 (d, J = 1.8 Hz), 136.4 (d, J = 8.2 Hz), 131.0, 130.7 (d, J = 3.0 Hz), 129.8 (d, J = 8.3 Hz), 121.9, 117.5 (d, J = 22.0 Hz),

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114.1 (d, J = 22.8 Hz), 60.8, 28.1, 14.3. HRMS (ESI): calcd for $C_{15}H_{16}O_3F$, $[M+H]^+$, 263.1078; found, 263.1076.

(E)-Ethyl 3-(4-Chloro-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a16***. White solid. 695 mg. Yield 50%. Mp. 101−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 15.8 Hz, 1H), 7.78 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.37 (dd, J = 8.4, 1.7 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.34 (d, J = 15.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 166.2, 139.9, 138.3, 136.1, 135.8, 132.8, 131.1, 130.2, 129.0, 127.5, 122.5, 60.9, 28.2, 14.3. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0785.

(E)-Ethyl 3-(4-Methoxy-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a17***. Yellow solid. 643 mg. Yield 47%. Mp. 74−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 15.7 Hz, 1H), 7.87 (d, J = 16.1 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 6.96 (dd, J = 8.7, 2.6 Hz, 1H), 6.60 (d, J = 16.1 Hz, 1H), 6.27 (d, J = 15.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 166.8, 160.9, 140.6, 139.9, 135.9, 130.7, 129.2, 127.1, 119.6, 116.7, 111.9, 60.6, 55.5, 27.7, 14.3. HRMS (ESI): calcd for $C_{16}H_{19}O_4$, $[M+H]^+$, 275.1278; found, 275.1280.

(E)-Ethyl 3-(5-Fluoro-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a18***. White solid. 641 mg. Yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 15.8 Hz, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.59 (dd, J = 8.7, 5.6 Hz, 1H), 7.31−7.22 (m, 1H), 7.12 (td, J = 8.3, 2.6 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 166.0, 163.56 (d, J = 251.3 Hz), 139.9, 138.6, 136.70 (d, J = 7.9 Hz), 130.46 (d, J = 3.2 Hz), 130.1, 129.7 (d, J = 8.7 Hz), 123.1, 117.43 (d, J = 22.0 Hz), 114.21 (d, J = 22.8 Hz), 60.9, 27.9, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}O_3F$, $[M+H]^+$, 263.1078; found, 263.1079.

(E)-Ethyl 3-(5-Chloro-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a19***. White solid. 583 mg. Yield 42%. Mp. 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 15.8 Hz, 1H), 7.78 (d, J = 16.1 Hz, 1H), 7.54 (dd, J = 8.3, 5.1 Hz, 2H), 7.37 (dd, J = 8.4, 1.7 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 166.0, 139.7, 138.5, 136.2, 136.0, 132.6, 130.5, 130.0, 128.9, 127.6, 123.2, 60.9, 27.9, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0784.

(E)-Ethyl 3-(5-Methyl-2-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate ***a20***. White solid. 670 mg. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 15.8 Hz, 1H), 7.84 (d, J = 16.1 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 6.34 (d, J = 15.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 166.4, 141.2, 140.6, 139.8, 134.4, 131.4, 131.1, 129.4, 128.3, 127.5, 121.8, 60.7, 27.7, 21.3, 14.3. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1330.

(E)-Ethyl 3-(2-((E)-3-Oxobut-1-en-1-yl)naphthalen-1-yl)acrylate ***a21***. White solid. 588 mg. Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 16.1 Hz, 1H), 8.13−8.01 (m, 1H), 7.92 (d, J = 16.2 Hz, 1H), 7.85 (dd, J = 9.2, 3.8 Hz, 2H), 7.71 (d, J = 8.7 Hz, 1H), 7.56 (dd, J = 6.3, 3.3 Hz, 2H), 6.76 (d, J = 16.2 Hz, 1H), 6.15 (d, J = 16.1 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 165.8, 141.6, 140.7, 134.2, 133.8, 131.4, 130.5, 129.4, 129.3, 128.5, 128.4, 127.4, 127.3, 125.4, 123.6, 61.0, 27.6, 14.3. HRMS (ESI): calcd for $C_{19}H_{19}O_3$, $[M+H]^+$, 295.1329; found, 295.1325.

(E)-3-(2-((E)-3-Oxobut-1-en-1-yl)phenyl)acrylonitrile ***a22***. White solid. 364 mg. Yield 37%. Mp. 149−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 16.2, 4.2 Hz, 2H), 7.60 (d, J = 7.3 Hz, 1H), 7.54−7.34 (m, 3H), 6.63 (d, J = 16.0 Hz, 1H), 5.85 (d, J = 16.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 147.4, 138.7, 134.8, 134.1, 133.3, 131.1, 130.9, 130.4, 127.9, 126.9, 99.9, 28.2. HRMS (ESI): calcd for $C_{13}H_{12}NO$, $[M+H]^+$, 198.0913; found, 198.0914.

(E)-Methyl 3-(2-((E)-3-Oxoprop-1-enyl)phenyl)acrylate. ***a23***.[19] Yellow solid. 367 mg. Yield 34%. Mp. 82−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 15.8 Hz, 1H), 7.90 (d, J = 15.8 Hz, 1H), 7.72−7.58 (m, 2H), 7.55−7.43 (m, 2H), 6.69 (dd, J = 15.8, 7.7 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 166.8, 148.8, 141.0, 134.5, 133.5, 131.4, 131.0, 130.3, 127.9, 127.7, 122.1, 52.0. LRMS (EI): 216[M+], 201, 184, 157, 143, 128, 115, 102, 89. HRMS (ESI): calcd for $C_{13}H_{13}O_3$, $[M+H]^+$, 217.0859; found, 217.0866.

(E)-Ethyl 3-(2-((E)-3-Oxoprop-1-enyl)phenyl)acrylate. ***a24***.[20] Yellow solid. 414 mg. Yield 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 15.8 Hz, 1H), 7.88 (d, J = 15.8 Hz, 1H), 7.69−7.57 (m, 2H), 7.55−7.38 (m, 2H), 6.67 (dd, J = 15.8, 7.7 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 166.3, 148.8, 140.7, 134.7, 133.5, 131.4, 131.0, 130.2, 127.9, 127.6, 122.6, 60.9, 14.3.

(E)-Isopropyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a25***. Colorless oil. 402 mg. Yield 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 15.8 Hz, 1H), 7.91 (d, J = 15.8 Hz, 1H), 7.74−7.59 (m, 2H), 7.55−7.35 (m, 2H), 6.69 (dd, J = 15.8, 7.7 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 5.48−4.96 (m, 1H), 1.35 (d, J = 6.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 165.9, 148.9, 140.4, 134.7, 133.4, 131.3, 131.0, 130.1, 127.8, 127.6, 123.0, 68.3, 21.9. LRMS (EI): 244[M+], 215, 202, 184, 173, 157, 129, 115, 102, 89. HRMS (ESI): calcd for $C_{15}H_{17}O_3$, $[M+H]^+$, 245.1172; found, 245.1170.

(E)-Cutyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a26***. White solid. 516 mg. Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, J = 7.7 Hz, 1H), 8.08 (d, J = 15.8 Hz, 1H), 7.90 (d, J = 15.8 Hz, 1H), 7.74−7.58 (m, 2H), 7.55−7.41 (m, 2H), 6.69 (dd, J = 15.8, 7.7 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 1.72 (dd, J = 14.7, 6.7 Hz, 2H), 1.47 (dd, J = 14.7, 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 166.5, 148.8, 140.7, 134.6, 133.4, 131.4, 131.0, 130.2, 127.8, 127.6, 122.5, 64.8, 30.7, 19.22, 13.7. LRMS (EI): 258[M+], 229, 201, 184, 173, 157, 129, 115, 102, 89. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1328.

(E)-tert-Butyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a27***. White solid. 464 mg. Yield 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 15.7 Hz, 1H), 7.91 (d, J = 15.8 Hz, 1H), 7.69−7.58 (m, 2H), 7.56−7.41 (m, 2H), 6.69 (dd, J = 15.8, 7.7 Hz, 1H), 6.34 (d, J = 15.7 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 165.7, 149.0, 139.6, 134.8, 133.3, 131.2, 131.0, 130.0, 127.8, 127.5, 124.3, 81.1, 28.2. LRMS (EI): 258[M+], 202, 184, 173, 157, 145, 129, 115, 102, 89. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1334.

(E)-Cyclopentyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a28***. Colorless oil. 513 mg. Yield 38%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, J = 7.7 Hz, 1H), 8.04 (d, J = 15.8 Hz, 1H), 7.88 (d, J = 15.8 Hz, 1H), 7.73−7.52 (m, 2H), 7.45 (dd, J = 6.3, 2.7 Hz, 2H), 6.67 (dd, J = 15.8, 7.7 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 5.32 (ddd, J = 8.6, 6.1, 2.7 Hz, 1H), 2.03−1.88 (m, 2H), 1.85−1.50 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 166.2, 148.9, 140.4, 134.7, 133.4, 131.3, 131.0, 130.1, 127.8, 127.6, 123.0, 77.6, 32.7, 23.8. LRMS (EI): 270[M+], 202, 184, 173, 157, 129, 115. HRMS (ESI): calcd for $C_{17}H_{19}O_3$, $[M+H]^+$, 271.3304; found, 271.3306.

(E)-Cyclohexyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a29***. White solid. 482 mg. Yield 34%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 15.8 Hz, 1H), 7.90 (d, J = 15.8 Hz, 1H), 7.71−7.61 (m, 2H), 7.51−7.43 (m, 2H), 6.68 (dd, J = 15.8, 7.7 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 4.99−4.88 (m, 1H), 2.01−1.91 (m, 2H), 1.83−1.75 (m, 2H), 1.61−1.27 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 165.8, 148.9, 140.4, 134.7, 133.3, 131.3, 131.0, 130.1, 127.8, 127.6, 123.1, 73.2, 31.7, 25.3, 23.8. LRMS (EI): 284[M+], 202, 184, 157, 129, 115, 102, 83. HRMS (ESI): calcd for $C_{18}H_{21}O_3$, $[M+H]^+$, 285.1485; found, 285.1489.

(E)-Benzyl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a30***. White solid. 613 mg. Yield 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 15.8 Hz, 1H), 7.89 (d, J = 15.8 Hz, 1H), 7.67−7.62 (m, 2H), 7.49−7.38 (m, 7H), 6.69 (dd, J = 15.8, 7.6 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H), 5.31 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 166.2, 148.7, 141.3, 135.7, 134.4, 133.5, 131.4,

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131.0, 130.3, 128.6, 128.4, 128.4, 127.8, 127.6, 122.1, 66.7. LRMS (EI): 292[M+], 201, 186, 157, 141, 128, 115, 91. HRMS (ESI): calcd for $C_{19}H_{17}O_3$, $[M+H]^+$, 293.1172; found, 293.1180.

(E)-Pent-4-en-1-yl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a31***. Colorless oil. 405 mg. Yield 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 15.8 Hz, 1H), 7.88 (d, J = 15.8 Hz, 1H), 7.74−7.56 (m, 2H), 7.46 (dd, J = 8.9, 5.3 Hz, 2H), 6.67 (dd, J = 15.8, 7.6 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.02−5.64 (m, 1H), 5.07 (dd, J = 17.1, 1.5 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.26 (t, J = 6.6 Hz, 2H), 2.19 (dd, J = 14.3, 7.2 Hz, 2H), 1.89−1.70 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 166.4, 148.8, 140.8, 137.4, 134.5, 133.4, 131.4, 131.0, 130.2, 127.8, 127.6, 122.4, 115.4, 64.3, 30.0, 27.8. LRMS (EI): 270[M+], 201, 184, 157, 129, 28. HRMS (ESI): calcd for $C_{17}H_{19}O_3$, $[M+H]^+$, 271.1329; found, 271.1330.

(E)-Hex-5-en-1-yl 3-(2-((E)-3-Oxoprop-1-en-1-yl)phenyl)acrylate ***a32***. Colorless oil. 498 mg. Yield 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 15.8 Hz, 1H), 7.88 (d, J = 15.8 Hz, 1H), 7.63 (dd, J = 10.4, 7.0 Hz, 2H), 7.46 (dd, J = 8.9, 5.3 Hz, 2H), 6.67 (dd, J = 15.8, 7.7 Hz, 1H), 6.39 (d, J = 15.7 Hz, 1H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.04 (dd, J = 17.1, 1.6 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.25 (t, J = 6.6 Hz, 2H), 2.13 (q, J = 7.1 Hz, 2H), 1.81−1.68 (m, 2H), 1.62−1.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 166.4, 148.8, 140.7, 138.3, 134.6, 133.4, 131.4, 131.0, 130.2, 127.8, 127.6, 122.4, 114.9, 64.8, 33.3, 28.1, 25.2. LRMS (EI): 284[M+], 172, 157, 128, 115. HRMS (ESI): calcd for $C_{18}H_{21}O_3$, $[M+H]^+$, 285.1485; found, 285.1487.

(E)-Methyl 3-(4 or 5-Methyl-2-((E)-3-oxoprop-1-en-1-yl)phenyl)-acrylate. ***a33***. White solid. 369 mg. Yield 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, J = 7.1 Hz, 1H), 8.05 (dd, J = 15.8, 7.2 Hz, 1H), 7.86 (dd, J = 15.7, 10.7 Hz, 1H), 7.69−7.49 (m, 1H), 7.43 (d, J = 9.8 Hz, 1H), 7.35−7.14 (m, 1H), 6.80−6.55 (m, 1H), 6.38 (dd, J = 15.8, 7.6 Hz, 1H), 3.84 (d, J = 2.7 Hz, 3H), 2.41 (d, J = 9.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 193.5, 166.9, 166.8, 148.9, 148.8, 141.6, 141.1, 140.8, 140.6, 134.5, 133.4, 132.0, 131.7, 131.2, 130.7, 130.4, 128.3, 128.1, 127.7, 127.6, 121.8, 120.9, 51.97, 51.93, 21.49, 21.38. LRMS (EI): 230[M+], 215, 198, 185, 171, 157, 142, 128, 115, 102, 89. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1017.

(E)-Methyl 3-(4 or 5-Chloro-2-((E)-3-oxoprop-1-en-1-yl)phenyl)-acrylate ***a34***. White solid. 375 mg. Yield 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91−9.73 (d, J = 7.0 Hz, 1H), 8.00 (d, J = 15.8 Hz, 1H), 7.80 (d, J = 15.8 Hz, 1H), 7.59 (m, 2H), 7.44 (d, J = 8.4 Hz, 1H), 6.66 (dd, J = 15.8, 7.5 Hz, 1H), 6.40 (dd, J = 15.8, 7.0 Hz, 1H), 3.86 (d, J = 1.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.1, 192.9, 166.5, 166.4, 147.2, 147.0, 139.7, 139.64, 137.1, 136.4, 136.03, 135.0, 132.7, 132.2, 131.8, 131.6, 130.9, 130.3, 129.12 128.9, 127.7, 127.5, 123.2, 122.4, 52.1, 52.0. LRMS (EI): 250[M+], 235, 221, 207, 191, 183, 162, 151, 142, 127, 115, 101, 87. HRMS (ESI): calcd for $C_{13}H_{11}O_3ClNa$, $[M + Na]^+$, 273.0289; found, 273.0296.

(E)-Methyl 3-(4 or 5-Fluoro-2-((E)-3-oxoprop-1-en-1-yl)phenyl)-acrylate ***a35***. White solid. 387 mg. Yield 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (dd, J = 12.2, 7.6 Hz, 1H), 8.01 (dd, J = 15.7, 5.5 Hz, 1H), 7.82 (dd, J = 15.8, 9.1 Hz, 1H), 7.71−7.51 (m, 1H), 7.32 (dd, J = 14.4, 5.8 Hz, 1H), 7.18 (dd, J = 10.5, 5.9 Hz, 1H), 6.64 (dt, J = 15.8, 7.9 Hz, 1H), 6.38 (t, J = 16.3 Hz, 1H), 3.85 (d, J = 3.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 193.0, 166.6, 166.4, 164.0 (d, J = 253.1 Hz), 163.5 (d, J = 252.0 Hz), 147.4, 147.1, 139.7 (d, J = 11.0 Hz), 136.8 (d, J = 8.4 Hz), 135.5, 132.1, 131.17 (d, J = 1.4 Hz), 130.71 (d, J = 3.3 Hz), 129.9, 129.9, 129.8, 129.75 (d, J = 3.1 Hz), 123.1, 121.8, 118.38 (d, J = 22.0 Hz), 117.70 (d, J = 22.1 Hz), 114.40 (d, J = 22.3 Hz), 114.10 (d, J = 22.3 Hz), 52.1, 52.0. HRMS (ESI): calcd for $C_{13}H_{12}O_3F$, $[M+H]^+$, 235.0765; found, 235.0766.

(E)-Ethyl 3-(4 or 5-Chloro-2-((E)-3-oxoprop-1-en-1-yl)phenyl)-acrylate ***a36***. Colorless oil. 463 mg. Yield 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 7.6, 1H), 7.99 (d, J = 15.8, 1H), 7.81 (d, J = 15.8, 1H), 7.64−7.54 (m, 2H), 7.47−7.40 (m, 1H), 6.66 (dd, J = 15.8, 7.6 Hz, 1H), 6.40 (d, J = 15.7, 1H), 4.36−4.29 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 193.0, 166.2, 166.0, 147.3, 147.1, 139.5, 139.3, 137.1, 136.3, 136.1, 134.9, 132.9, 132.2, 131.8, 131.5, 130.9, 130.2, 129.1, 128.9, 127.7, 127.4, 123.7, 122.9, 61.10 61.0, 14.30, 14.31. LRMS (EI): 264[M+], 235, 218, 207, 191, 163, 155, 128, 115, 101, 87. HRMS (ESI): calcd for $C_{14}H_{14}O_3Cl$, $[M+H]^+$, 265.0626; found, 265.0628.

(E)-Ethyl 3-(4 or 5-Fluoro-2-((E)-3-oxoprop-1-en-1-yl)phenyl)-acrylate ***a37***. Colorless oil. 396 mg. Yield 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (dd, J = 12.2, 7.6 Hz, 1H), 8.01 (dd, J = 15.7, 5.5 Hz, 1H), 7.83 (dd, J = 15.8, 9.0 Hz, 1H), 7.73−7.57 (m, 1H), 7.44−7.25 (m, 1H), 7.24−7.10 (m, 1H), 6.64 (dt, J = 15.7, 7.8 Hz, 1H), 6.37 (t, J = 16.5 Hz, 1H), 4.72−3.79 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.27 (s), 193.0, 166.2, 166.0, 164.01 (d, J = 253.1 Hz), 163.46 (d, J = 251.5 Hz), 147.5, 147.2, 139.5, 139.4, 136.9 (d, J = 8.1 Hz), 135.5 (d, J = 8.0 Hz), 132.1, 131.1, 129.96 (d, J = 9.0 Hz), 129.9, 129.8, 129.71 (d, J = 2.9 Hz), 123.6, 122.3, 118.38 (d, J = 22.0 Hz), 117.63 (d, J = 22.1 Hz), 114.4 (d, J = 22.7 Hz), 114.07 (d, J = 22.5 Hz), 61.0, 60.9, 14.2. HRMS (ESI): calcd for $C_{14}H_{14}O_3F$, $[M+H]^+$, 249.0921; found, 249.0923.

(E)-3-[2-{(E)-2-Methoxycarbonylvinyl}phenyl]acrylic Acid Methyl Ester a38.[16] White solid. 984 mg. Yield 80%. Mp. 64−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 15.8 Hz, 2H), 7.57 (dd, J = 5.7, 3.5 Hz, 2H), 7.40 (dd, J = 5.8, 3.4 Hz, 2H), 6.36 (d, J = 15.8 Hz, 2H), 3.83 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.84, 141.46, 134.23, 130.11, 127.62, 121.45, 51.83. LRMS (EI): 246[M+], 231, 215, 199, 186, 171, 155, 143, 128, 115, 102, 92, 77. HRMS (ESI): calcd for $C_{14}H_{15}O_4$, $[M+H]^+$, 247.0965; found, 247.0967.

Compound ***b1′***. White solid. 61 mg. Yield 57%. Mp. 79−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.4 Hz, 1H), 7.27 (td, J = 7.4, 1.3 Hz, 1H), 7.16 (td, J = 7.3, 1.3 Hz, 1H), 7.10 (d, J = 7.0 Hz, 1H), 5.24 (d, J = 6.2 Hz, 1H), 3.38 (dd, J = 6.2, 2.8 Hz, 1H), 2.34 (d, J = 7.8 Hz, 1H), 1.95 (dd, J = 7.8, 2.7 Hz, 1H), 1.82 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.6, 133.6, 131.0, 128.4, 126.5, 125.0, 123.5, 75.7, 61.7, 52.8, 29.4, 23.9, 20.2, 16.8. HRMS (ESI): calcd for $C_{14}H_{15}O_2$, $[M+H]^+$, 215.1067; found, 215.1069.

Compound ***b1″***. Colorless oil. Twenty-nine mg. Yield 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.22 (t, J = 6.9 Hz, 1H), 7.18 (d, J = 7.3 Hz, 1H), 5.17 (s, 1H), 2.34 (d, J = 9.3 Hz, 4H), 2.27 (s, 1H), 1.94 (d, J = 8.0 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.1, 134.5, 132.5, 128.2, 126.6, 125.0, 122.2, 77.5, 60.4, 53.9, 28.5, 25.0, 20.8, 16.5. HRMS (ESI): calcd for $C_{14}H_{15}O_2$, $[M+H]^+$, 215.1067; found, 215.1074.

Compound ***b2′***. White solid. 61 mg. Yield 51%. Mp. 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.4 Hz, 1H), 7.27−7.20 (m, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 5.26 (d, J = 6.2 Hz, 1H), 3.35 (dd, J = 6.2, 2.6 Hz, 1H), 2.21 (dq, J = 17.7, 7.2 Hz, 1H), 2.12−1.91 (m, 4H), 1.05 (t, J = 7.4 Hz, 3H), 0.73 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.2, 133.7, 131.4, 128.2, 126.3, 124.9, 123.5, 75.7, 66.4, 52.0, 35.2, 23.9, 22.6, 18.7, 10.4, 7.1. HRMS (ESI): calcd for $C_{16}H_{19}O_2$, $[M+H]^+$, 243.1380; found, 243.1381.

Compound ***b2″***. Colorless oil. 36 mg. Yield 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.1 Hz, 1H), 5.16 (s, 1H), 2.83−2.49 (m, 2H), 2.34 (d, J = 8.1 Hz, 1H), 2.26 (s, 1H), 2.19−1.98 (m, 2H), 1.93 (d, J = 8.1 Hz, 1H), 1.11 (t, J = 7.3 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.0, 134.9, 132.7, 128.1, 126.5, 124.9, 122.1, 77.4, 65.2, 52.7, 34.3, 23.6, 23.5, 19.6, 10.5, 7.6. HRMS (ESI): calcd for $C_{16}H_{19}O_2$, $[M+H]^+$, 243.1380; found, 243.1383

Compound ***b3***. Colorless oil. 77 mg. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−6.85 (m, 4H), 5.02 (s, 1H), 2.64 (s, 1H), 2.48 (d, J = 8.2 Hz, 1H), 1.88 (d, J = 8.2 Hz, 1H), 1.18 (s, 9H), 1.09 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.8, 135.8, 133.2, 127.9, 126.6, 124.7, 121.6, 78.0, 72.4, 46.4, 44.8, 31.1, 27.4, 26.5, 21.4, 20.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−6.74 (m, 4H), 5.30 (d, J = 5.9 Hz, 1H), 3.64 (dd, J = 5.8, 2.2 Hz, 1H), 2.56 (d, J = 8.2 Hz, 1H), 1.88 (d, J = 8.2 Hz, 1H), 1.05 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.7, 134.8, 131.3, 128.1, 125.8, 124.5, 122.6, 76.1, 71.0, 46.7, 44.22, 31.1, 27.0, 26.55, 20.37, 20.1. HRMS (ESI): calcd for $C_{20}H_{27}O_2$, $[M+H]^+$, 299.2006; found, 299.2007.

Compound ***b4***. Yellow oil. 76 mg. Yield 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.92 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.55−7.51 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 7.4 Hz, 1H), 7.38−7.32 (m, 3H), 7.27 (t, J = 5.8 Hz, 3H), 5.42 (s, 1H), 3.34 (s, 1H), 2.89 (d, J =

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8.1 Hz, 1H), 2.53 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 136.4, 135.8, 135.0, 133.4, 132.5, 128.8, 128.4, 128.4, 128.3, 127.5, 127.0, 126.6, 125.4, 122.3, 78.1, 65.8, 48.4, 27.3, 23.2. HRMS (ESI): calcd for $C_{24}H_{19}O_2$, $[M+H]^+$, 339.1380; found, 339.1384.

Compound ***b5′***. White solid. 57 mg. Yield 50%. Mp. 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.4 Hz, 1H), 7.26 (td, J = 7.4, 1.4 Hz, 1H), 7.14 (td, J = 7.3, 1.3 Hz, 1H), 7.09 (d, J = 7.0 Hz, 1H), 5.20 (d, J = 6.2 Hz, 1H), 3.43 (dd, J = 6.2, 2.9 Hz, 1H), 3.32 (s, 3H), 2.30 (d, J = 7.9 Hz, 1H), 1.94 (dd, J = 7.9, 2.9 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 128.0, 126.2, 122.9, 121.1, 119.5, 118.2, 70.4, 56.2, 46.2, 39.4, 18.5, 14.4, 11.5. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1018.

Compound ***b5″***. Colorless oil. 32 mg. Yield 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.23 (m, 2H), 7.23−6.98 (m, 2H), 5.25 (s, 1H), 3.78 (s, 3H), 2.29 (s, 1H), 2.27 (d, J = 8.1 Hz, 1H), 1.99 (d, J = 8.0 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 129.0, 127.3, 122.9, 121.2, 119.6, 117.1, 72.8, 55.1, 46.9, 40.7, 19.3, 14.9, 11.2. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1014.

Compound ***b6′***. White solid. 61 mg. Yield 50%. Mp. 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.4 Hz, 1H), 7.29−7.21 (m, 1H), 7.14 (td, J = 7.3, 1.2 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.20 (d, J = 6.3 Hz, 1H), 3.96−3.57 (m, 2H), 3.41 (dd, J = 6.2, 2.9 Hz, 1H), 2.31 (d, J = 7.9 Hz, 1H), 1.94 (dd, J = 7.9, 2.9 Hz, 1H), 1.68 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 133.5, 131.4, 128.2, 126.3, 124.6, 123.7, 75.8, 61.5, 60.3, 44.8, 23.8, 19.8, 16.8, 13.8. HRMS (ESI): calcd for $C_{15}H_{17}O_3$, $[M+H]^+$, 245.1172; found, 245.1173.

Compound ***b6″***. Colorless oil. Twenty-seven mg. Yield 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.23 (m, 2H), 7.23−6.94 (m, 2H), 5.24 (s, 1H), 4.23 (qd, J = 7.1, 1.1 Hz, 2H), 2.36−2.12 (m, 2H), 1.99 (d, J = 8.0 Hz, 1H), 1.74 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 134.3, 132.7, 128.1, 126.5, 124.9, 122.4, 78.2, 61.1, 60.4, 46.2, 24.7, 20.3, 16.5, 14.2. HRMS (ESI): calcd for $C_{15}H_{17}O_3$, $[M+H]^+$, 245.1172; found, 245.1174.

Compound ***b7′***. White solid. 66 mg. Yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.2 Hz, 1H), 7.29−7.23 (m, 1H), 7.14 (td, J = 7.3, 1.2 Hz, 1H), 7.09 (d, J = 6.6 Hz, 1H), 5.20 (d, J = 6.2 Hz, 1H), 3.72 (qt, J = 10.8, 6.5 Hz, 2H), 3.42 (dd, J = 6.2, 2.9 Hz, 1H), 2.30 (d, J = 7.9 Hz, 1H), 1.94 (dd, J = 7.9, 2.9 Hz, 1H), 1.68 (s, 3H), 1.38−1.20 (m, 2H), 1.20−1.07 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 133.4, 131.4, 128.1, 126.4, 124.7, 123.7, 75.7, 64.2, 61.4, 44.8, 30.4, 23.8, 19.8, 18.9, 16.8, 13.6. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1489.

Compound ***b7″***. Colorless oil. 31 mg. Yield 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.19 (m, 2H), 7.22−6.81 (m, 2H), 5.23 (s, 1H), 4.47−3.77 (m, 2H), 2.27 (d, J = 8.0 Hz, 2H), 1.99 (d, J = 8.0 Hz, 1H), 1.73 (s, 3H), 1.70−1.59 (m, 2H), 1.54−1.31 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 134.4, 132.7, 128.1, 126.5, 124.9, 122.4, 78.2, 64.9, 60.3, 46.2, 30.6, 24.7, 20.3, 19.1, 16.5, 13.7. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1486.

Compound ***b8′***. White solid. 64 mg. Yield 48%. Mp. 105−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.4 Hz, 1H), 7.28−7.21 (m, 1H), 7.15 (td, J = 7.2, 1.2 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 5.13 (d, J = 6.3 Hz, 1H), 3.35 (dd, J = 6.3, 2.9 Hz, 1H), 2.27 (d, J = 7.9 Hz, 1H), 1.90 (dd, J = 7.9, 2.9 Hz, 1H), 1.67 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 133.7, 131.6, 128.1, 126.4, 124.5, 124.1, 80.7, 75.9, 61.5, 45.7, 27.5, 23.8, 20.0, 16.8. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1483.

Compound ***b8″***. Colorless oil. Twenty-eight mg. Yield 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.24 (m, 2H), 7.16 (dd, J = 4.5, 2.1 Hz, 2H), 5.19 (s, 1H), 2.24 (d, J = 8.0 Hz, 1H), 2.17 (s, 1H), 1.93 (d, J = 8.0 Hz, 1H), 1.73 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 134.6, 132.8, 128.0, 126.4, 124.8, 122.4, 81.2, 78.4, 60.3, 47.1, 28.1, 24.7, 20.5, 16.6. HRMS (ESI): calcd for $C_{17}H_{21}O_3$, $[M+H]^+$, 273.1485; found, 273.1484.

Compound ***b9′***. Colorless oil. 61 mg. Yield 42%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.29 (m, 2H), 7.24−7.16 (m, 4H), 7.13−7.06 (m, 1H), 6.45 (dd, J = 5.5, 3.7 Hz, 2H), 5.36 (d, J = 6.3 Hz, 1H), 3.67 (dd, J = 6.3, 2.9 Hz, 1H), 2.37 (d, J = 7.9 Hz, 1H), 2.05 (dd, J = 7.9, 2.9 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 150.2, 133.6, 131.4, 129.2, 128.5, 126.7, 125.8, 124.9, 124.0, 121.2, 75.9, 61.9, 45.0, 24.1, 19.8, 16.8. HRMS (ESI): calcd for $C_{19}H_{17}O_3$, $[M+H]^+$, 293.1172; found, 293.1179.

Compound ***b9″***. Colorless oil. Twenty-nine mg. Yield 20%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.36 (m, 2H), 7.35−7.27 (m, 2H), 7.27−7.18 (m, 3H), 7.18−7.12 (m, 2H), 5.41 (s, 1H), 2.52 (s, 1H), 2.33 (d, J = 8.0 Hz, 1H), 2.11 (d, J = 8.0 Hz, 1H), 1.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 150.7, 134.2, 132.6, 129.5, 128.3, 126.6, 126.0, 125.1, 122.6, 121.5, 78.3, 60.6, 46.5, 24.8, 20.3, 16.5. HRMS (ESI): calcd for $C_{19}H_{17}O_3$, $[M+H]^+$, 293.1172; found, 293.1176.

Compound ***b10′***. White solid. 81 mg. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.4 Hz, 1H), 7.29−7.22 (m, 1H), 7.14 (td, J = 7.3, 1.2 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.19 (d, J = 6.3 Hz, 1H), 4.77−4.23 (m, 1H), 3.40 (dd, J = 6.2, 2.9 Hz, 1H), 2.30 (d, J = 7.9 Hz, 1H), 1.94 (dd, J = 7.9, 2.9 Hz, 1H), 1.68 (s, 3H), 1.61−1.52 (m, 2H), 1.49−1.34 (m, 3H), 1.26−0.85 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 133.5, 131.4, 128.1, 126.3, 124.6, 123.9, 75.8, 72.5, 61.4, 45.0, 31.29, 31.20, 25.2, 23.8, 23.6, 19.8, 16.8. HRMS (ESI): calcd for $C_{19}H_{23}O_3$, $[M+H]^+$, 299.1642; found, 299.1643.

Compound ***b10″***. Colorless oil. 31 mg. Yield 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.23 (m, 2H), 7.23−6.95 (m, 2H), 5.22 (s, 1H), 5.02−4.45 (m, 1H), 2.26 (d, J = 7.8 Hz, 2H), 1.98 (d, J = 8.0 Hz, 1H), 1.93−1.82 (m, 2H), 1.81−1.70 (m, 5H), 1.57−1.21 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 134.4, 132.8, 128.1, 126.4, 124.8, 122.4, 78.3, 73.2, 60.3, 46.4, 31.59, 31.54, 25.4, 24.7, 23.6, 20.3, 16.5. HRMS (ESI): calcd for $C_{19}H_{23}O_3$, $[M+H]^+$, 299.1642; found, 299.1644.

Compound ***b11′***. White solid. 80 mg. Yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.22 (m, 5H), 7.12−6.76 (m, 4H), 5.20 (d, J = 6.2 Hz, 1H), 4.74 (q, J = 12.3 Hz, 2H), 3.46 (dd, J = 6.2, 2.9 Hz, 1H), 2.30 (d, J = 7.9 Hz, 1H), 1.96 (dd, J = 7.9, 2.9 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 135.4, 133.4, 131.3, 128.4, 128.3, 128.2, 128.1, 126.4, 124.8, 123.7, 75.7, 66.3, 61.5, 44.8, 23.9, 19.8, 16.8. HRMS (ESI): calcd for $C_{20}H_{18}O_3Na$, $[M + Na]^+$, 329.1148; found, 329.1143.

Compound ***b11″***. Colorless oil. 44 mg. Yield 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.31 (m, 5H), 7.30−7.23 (m, 2H), 7.20−7.11 (m, 2H), 5.27 (s, 1H), 5.22 (q, J = 12.4 Hz, 2H), 2.33 (s, 1H), 2.27 (d, J = 8.1 Hz, 1H), 2.01 (d, J = 8.0 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 135.8, 134.2, 132.6, 128.6, 128.3, 128.2, 128.1, 126.5, 124.9, 122.5, 78.1, 66.8, 60.4, 46.2, 24.7, 20.3, 16.5. HRMS (ESI): calcd for $C_{20}H_{18}O_3Na$, $[M + Na]^+$, 329.1148; found, 329.1146.

Compound ***b12′***. White solid. 77 mg. Yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.3 Hz, 1H), 7.24 (td, J = 7.4, 1.1 Hz, 1H), 7.06 (td, J = 7.4, 1.2 Hz, 1H), 7.02−6.87 (m, 5H), 5.19 (d, J = 6.2 Hz, 1H), 4.72 (s, 2H), 3.45 (dd, J = 6.2, 2.9 Hz, 1H), 2.30 (d, J = 7.9 Hz, 1H), 1.96 (dd, J = 7.9, 2.9 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) 169.8, 162.58 (d, J = 246.7 Hz), 133.3, 131.32 (d, J = 3.2 Hz), 131.2, 130.3, 130.3, 128.2, 126.4, 124.8, 123.7, 115.34 (d, J = 21.4 Hz), 75.6, 65.5, 61.5, 44.8, 23.8, 19.8, 16.7. HRMS (ESI): calcd for $C_{20}H_{18}FO_3$, $[M+H]^+$, 325.1234; found, 325.1233.

Compound ***b12″***. Colorless oil. 38 mg. Yield 24%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.33 (m, 2H), 7.31−7.25 (m, 2H), 7.20−7.14 (m, 2H), 7.10−7.03 (m, 2H), 5.25 (s, 1H), 5.18 (q, J = 12.3 Hz, 2H), 2.32 (s, 1H), 2.27 (d, J = 8.1 Hz, 1H), 1.99 (d, J = 8.1 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 162.71 (d, J = 247.4 Hz), 134.2, 132.6, 131.67 (d, J = 3.2 Hz), 130.2, 130.1, 128.2, 126.5, 125.0, 122.4, 115.59 (d, J = 21.9 Hz), 78.1, 66.1, 60.4, 46.2, 24.7, 20.3, 16.4. HRMS (ESI): calcd for $C_{20}H_{18}FO_3$, $[M+H]^+$, 325.1234; found, 325.1232.

Compound ***b13′***. White solid. 90 mg. Yield 48%. H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.3 Hz, 1H), 7.26−7.19 (m, 1H), 7.07 (d, J = 8.1 Hz, 2H), 7.06−7.00 (m, 1H), 6.95 (d, J = 7.3 Hz, 1H), 5.21 (d, J = 6.2 Hz, 1H), 4.93−4.47 (m, 2H), 3.49 (dd, J = 6.2, 2.9 Hz, 1H), 2.31 (d, J = 7.8 Hz, 1H), 1.98 (dd, J = 7.9, 2.9 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 139.3, 133.3, 131.1, 130.2 (q, J = 32.2 Hz), 128.3, 126.4, 125.3 (q, J =

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3.6 Hz), 125.38, 124.8, 124.04 (q, J = 280.5 Hz), 123.7, 75.6, 65.3, 61.5, 44.7, 23.8, 19.7, 16.7. HRMS (ESI): calcd for $C_{21}H_{18}O_3F_3$, $[M+H]^+$, 375.1203; found, 375.1210.

Compound ***b13″***. White solid. 41 mg. Yield 22%^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.37−7.29 (m, 2H), 7.26−6.91 (m, 2H), 5.30 (m, 3H), 2.39 (s, 1H), 2.33 (d, J = 8.1 Hz, 1H), 2.05 (d, J = 8.1 Hz, 1H), 1.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 139.8, 134.1, 132.5, 130.4 (q, J = 32.2 Hz), 128.3, 128.0, 126.5, 125.6 (q, J = 3.6 Hz), 125.0, 124.0 (q, J = 272.0 Hz), 122.4, 78.15, 65.8, 60.4, 46.2, 24.7, 20.3, 16.5. HRMS (ESI): calcd for $C_{21}H_{18}O_3F_3$, $[M+H]^+$, 375.1203; found, 375.1206.

Compound ***b14***. Colorless oil. 114 mg. Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 7.18−7.11 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.0 Hz, 3H), 5.24 (s, 1H), 5.14 (m, 2H), 3.78 (s, 3H), 2.29 (s, 1H), 2.28 (d, J = 6.5 Hz, 1H), 1.98 (d, J = 8.1 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 159.7, 134.3, 132.7, 130.2, 128.1, 127.9, 126.4, 124.9, 122.5, 114.0, 78.2, 66.7, 60.4, 55.3, 46.2, 24.7, 20.3, 16.5.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.21 (m, 4H), 6.89 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 5.17 (d, J = 6.4 Hz, 1H), 4.67 (s, 2H), 3.79 (s, 3H), 3.43 (dd, J = 6.2, 2.8 Hz, 1H), 2.25 (d, J = 8.1 Hz, 1H), 1.94 (dd, J = 7.8, 2.8 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 159.6, 133.4, 131.3, 130.1, 128.1, 127.6, 126.5, 124.8, 123.7, 113.8, 75.7, 66.1, 60.4, 55.3, 44.8, 23.9, 19.9, 16.8. HRMS (ESI): calcd for $C_{21}H_{20}NaO_4$, $[M+Na]^+$, 359.1254; found, 359.1261.

Compound ***b15′***. White solid. 62 mg. Yield 48%. Mp. 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−6.96 (m, 2H), 6.83 (td, J = 9.2, 2.4 Hz, 1H), 5.19 (d, J = 6.2 Hz, 1H), 4.10−3.63 (m, 2H), 3.42 (dd, J = 6.2, 2.8 Hz, 1H), 2.29 (d, J = 7.9 Hz, 1H), 1.98 (dd, J = 7.9, 2.8 Hz, 1H), 1.68 (s, 3H), 0.93 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.76, 162.7 (d, J = 245.0 Hz), 135.8 (d, J = 8.9 Hz), 127.3, 125.3 (d, J = 8.9 Hz), 113.4 (d, J = 22.7 Hz), 111.5 (d, J = 22.1 Hz), 75.1, 61.6, 60.4, 44.8, 24.1 (d, J = 1.6 Hz), 20.1, 16.7, 13.9. HRMS (ESI): calcd for $C_{15}H_{16}FO_3$, $[M+H]^+$, 263.1078; found, 263.1072.

Compound ***b15″***. Colorless oil. Twenty-seven mg. Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.1, 5.5 Hz, 1H), 7.01 (dd, J = 9.1, 2.2 Hz, 1H), 6.94−6.85 (m, 1H), 5.23 (s, 1H), 4.23 (q, J = 7.0 Hz, 2H), 2.25 (d, J = 8.3 Hz, 2H), 2.02 (d, J = 8.0 Hz, 1H), 1.74 (d, J = 4.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 162.7 (d, J = 244.5 Hz), 135.0 (d, J = 8.8 Hz), 130.2 (d, J = 2.2 Hz), 124.0 (d, J = 8.8 Hz), 113.5 (d, J = 22.4 Hz), 111.5 (d, J = 22.0 Hz), 77.6, 61.1, 60.4, 46.3, 24.9, 20.5, 16.4, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}FO_3$, $[M+H]^+$, 263.1078; found, 263.1077.

Compound ***b16′***. White solid. 59 mg. Yield 43%. Mp. 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.4 Hz, 1H), 7.13 (dd, J = 7.9, 1.8 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 5.19 (d, J = 6.2 Hz, 1H), 3.99−3.68 (m, 2H), 3.42 (dd, J = 6.2, 2.9 Hz, 1H), 2.27 (d, J = 7.9 Hz, 1H), 1.99 (dd, J = 7.9, 2.8 Hz, 1H), 1.67 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 135.4, 133.7, 129.8, 126.4, 125.0, 124.8, 75.1, 61.7, 60.5, 44.7, 23.8, 20.1, 16.6, 13.9. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0780.

Compound ***b16″***. Colorless oil. Twenty-nine mg. Yield 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 10.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 5.23 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.24 (d, J = 10.8 Hz, 2H), 2.03 (d, J = 8.0 Hz, 1H), 1.73 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 134.7, 133.7, 132.7, 126.5, 124.9, 123.7, 77.5, 61.2, 60.6, 46.1, 24.5, 20.5, 16.3, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0781.

Compound ***b17′***. White solid. 47 mg. Yield 34%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.67 (dd, J = 8.2, 2.5 Hz, 1H), 5.16 (d, J = 6.2 Hz, 1H), 3.89−3.66 (m, 5H), 3.39 (dd, J = 6.2, 2.9 Hz, 1H), 2.26 (d, J = 7.9 Hz, 1H), 1.93 (dd, J = 7.9, 2.9 Hz, 1H), 1.67 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 159.6, 134.9, 124.8, 124.2, 111.6, 110.4, 75.3, 61.4, 60.3, 55.2, 45.1, 24.3, 20.1, 16.8, 14.0. HRMS (ESI): calcd for $C_{16}H_{19}O_4$, $[M+H]^+$, 275.1278; found, 275.1274.

Compound ***b17″***. Colorless oil. Twenty-one mg. Yield 16%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.2, 2.5 Hz, 1H), 5.20 (s, 1H), 4.22 (qd, J = 7.1, 1.1 Hz, 2H), 3.80 (s, 3H), 2.28 (s, 1H), 2.22 (d, J = 8.0 Hz, 1H), 1.98 (d, J = 8.0 Hz, 1H), 1.73 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 159.7, 134.2, 127.2, 123.5, 112.2, 110.1, 77.8, 61.0, 60.2, 55.3, 46.6, 25.1, 20.6, 16.5, 14.2. HRMS (ESI): calcd for $C_{16}H_{19}O_4$, $[M+H]^+$, 275.1278; found, 275.1274.

Compound ***b18′***. White solid. 47 mg. Yield 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 6.6 Hz, 1H), 6.97 (t, J = 8.9 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.17 (d, J = 6.2 Hz, 1H), 3.83 (q, J = 6.9 Hz, 2H), 3.55−3.15 (m, 1H), 2.30 (d, J = 7.9 Hz, 1H), 1.94 (dd, J = 7.8, 2.4 Hz, 1H), 1.67 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 160.70 (d, J = 243.3 Hz), 132.91 (d, J = 7.5 Hz), 129.1, 127.67 (d, J = 7.7 Hz), 114.99 (d, J = 21.8 Hz), 111.13 (d, J = 22.6 Hz), 75.2, 61.4, 60.5, 44.7, 23.1, 19.6, 16.6, 13.9. HRMS (ESI): calcd for $C_{15}H_{16}FO_3$, $[M+H]^+$, 263.1078; found, 263.1080.

Compound ***b18″***. Colorless oil. 26 mg. Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.17 (m, 1H), 6.98 (td, J = 8.9, 2.5 Hz, 1H), 6.92 (dd, J = 8.2, 2.4 Hz, 1H), 5.20 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.35−2.18 (m, 2H), 1.98 (d, J = 8.1 Hz, 1H), 1.73 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 160.73 (d, J = 243.9 Hz), 135.71 (d, J = 7.3 Hz), 128.34 (d, J = 2.8 Hz), 127.74 (d, J = 7.8 Hz), 114.81 (d, J = 21.5 Hz), 110.00 (d, J = 22.6 Hz), 77.69 (d, J = 1.8 Hz), 61.2, 60.3, 46.0, 24.0, 20.0, 16.3, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}FO_3$, $[M+H]^+$, 263.1078; found, 263.1076.

Compound ***b19′***. White solid. 49 mg. Yield 35%. Mp. 123−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.3 Hz, 2H), 7.11 (s, 1H), 5.16 (d, J = 6.3 Hz, 1H), 4.13−3.74 (m, 2H), 3.42 (dd, J = 6.2, 2.9 Hz, 1H), 2.29 (d, J = 7.9 Hz, 1H), 1.97 (dd, J = 7.9, 2.8 Hz, 1H), 1.67 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 132.8, 132.0, 130.5, 128.1, 127.7, 124.0, 75.1, 61.8, 60.5, 44.6, 23.4, 19.9, 16.6, 13.9. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0783.

Compound ***b19″***. Yellow solid. 34 mg. Yield 25%. Mp. 75−76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 8.1, 1.9 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 1.5 Hz, 1H), 5.21 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.32−2.22 (m, 2H), 2.03 (d, J = 8.1 Hz, 1H), 1.74 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 135.6, 131.3, 130.6, 128.1, 127.8, 122.8, 77.6, 61.2, 60.6, 45.9, 24.2, 20.3, 16.3, 14.2. HRMS (ESI): calcd for $C_{15}H_{16}ClO_3$, $[M+H]^+$, 279.0782; found, 279.0784.

Compound ***b20′***. White solid. 44 mg. Yield 35%. Mp. 85−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.92 (s, 1H), 5.15 (d, J = 6.2 Hz, 1H), 3.81 (q, J = 7.1 Hz, 2H), 3.39 (dd, J = 6.2, 2.9 Hz, 1H), 2.30 (s, 3H), 2.26 (d, J = 7.9 Hz, 1H), 1.90 (dd, J = 7.9, 2.8 Hz, 1H), 1.66 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 134.1, 131.3, 130.3, 128.8, 126.1, 124.5, 75.8, 61.4, 60.2, 44.9, 23.5, 21.1, 19.7, 16.8, 13.8. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1330.

Compound ***b20″***. Colorless oil. Twenty-six mg. Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.99 (s, 1H), 5.18 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 2.26 (s, 1H), 2.22 (d, J = 8.0 Hz, 1H), 1.95 (d, J = 8.0 Hz, 1H), 1.72 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 134.5, 134.3, 129.6, 128.7, 126.3, 123.2, 78.3, 61.0, 60.3, 46.3, 24.3, 21.1, 20.2, 16.5, 14.2. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1332.

Compound ***b21***. Colorless oil. 67 mg. Yield 53%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 6.12 (s, 1H), 4.99 (d, J = 6.6 Hz, 1H), 4.41−4.15 (m, 2H), 3.86−3.56 (m, 1H), 3.38 (s, 1H), 1.51 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 148.4, 148.2, 132.6, 131.6, 129.6, 129.2, 128.7, 126.9, 124.9, 123.7, 119.4, 99.6, 76.4, 60.6, 51.6, 39.2, 19.8, 14.3. HRMS (ESI): calcd for $C_{19}H_{19}O_3$, $[M+H]^+$, 295.1329; found, 295.1321.

Compound ***b22′***. White solid. 55 mg. Yield 56%. Mp. 147−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 4.0 Hz, 2H), 7.32−7.02 (m, 2H), 5.22 (d, J = 5.6 Hz, 1H), 3.30 (dd, J = 5.5, 2.9 Hz, 1H), 2.37 (d, J = 7.8 Hz, 1H), 2.06 (dd, J = 7.7, 2.8 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 131.5, 130.9, 129.1, 126.9, 125.7, 123.9,

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117.3, 75.7, 61.2, 29.7, 23.7, 20.9, 16.3. HRMS (ESI): calcd for $C_{13}H_{12}NO$, $[M+H]^+$, 198.0913; found, 198.0916.

Compound ***b22″***. Colorless oil. 22 mg. Yield 22%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.25−7.20 (m, 1H), 7.16 (d, J = 7.4 Hz, 1H), 5.25 (s, 1H), 2.34 (d, J = 6.1 Hz, 2H), 2.08 (d, J = 8.1 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.5, 131.3, 129.0, 126.8, 125.6, 122.7, 119.5, 77.6, 60.5, 31.9, 24.5, 21.1, 16.3. HRMS (ESI): calcd for $C_{13}H_{12}NO$, $[M+H]^+$, 198.0913; found, 198.0915.

Compound ***b23***. White solid. 67 mg. Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.3 Hz, 1H), 7.34−7.27 (m, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 5.24 (d, J = 5.9 Hz, 1H), 4.22 (m, 1H), 3.37 (s, 4H), 2.43 (m, 1H), 2.18 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 132.4, 131.7, 128.3, 126.5, 124.9, 123.6, 74.6, 54.5, 51.6, 43.9, 17.72, 14.4. LRMS (EI): 216[M+], 201, 187, 172, 155, 143, 129, 115, 102. HRMS (ESI): calcd for $C_{13}H_{13}O_3$, $[M+H]^+$, 217.0859; found, 217.0860.

Compound ***b24***. White solid. 69 mg. Yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.4 Hz, 1H), 7.28 (dd, J = 7.4, 1.3 Hz, 1H), 7.16 (td, J = 7.4, 1.1 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 5.21 (d, J = 6.3 Hz, 1H), 4.51−4.08 (m, 1H), 3.92−3.67 (m, 2H), 3.33 (dd, J = 6.3, 3.0 Hz, 1H), 2.40 (dd, J = 8.0, 5.2 Hz, 1H), 2.26−2.00 (m, 1H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 132.5, 131.7, 128.2, 126.5, 124.8, 123.7, 74.7, 60.4, 54.5, 44.0, 17.7, 14.4, 13.8. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1018

Compound ***b25***. White solid. 70 mg. Yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 7.27 (t, J = 6.5 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.20 (d, J = 6.2 Hz, 1H), 4.63 (dt, J = 12.5, 6.2 Hz, 1H), 4.17 (t, J = 4.1 Hz, 1H), 3.43−3.25 (m, 1H), 2.47−2.29 (m, 1H), 2.21−2.06 (m, 1H), 0.90 (d, J = 6.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 132.6, 131.6, 128.3, 126.5, 124.7, 124.0, 74.7, 67.8, 54.6, 44.1, 21.4, 17.7, 14.4. LRMS (EI): 244[M+], 215, 201, 186, 173, 157, 129, 102. HRMS (ESI): calcd for $C_{15}H_{17}O_3$, $[M+H]^+$, 245.1172, found, 245.1178.

Compound ***b26***. White solid. 82 mg. Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.21 (d, J = 6.2 Hz, 1H), 4.18 (t, J = 4.5 Hz, 1H), 3.74 (dtd, J = 17.4, 11.1, 6.3 Hz, 2H), 3.43−3.24 (m, 1H), 2.50−2.30 (m, 1H), 2.20−2.06 (m, 1H), 1.34−1.25 (m, 2H), 1.17 (dt, J = 20.9, 7.1 Hz, 2H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 132.5, 131.7, 128.3, 126.5, 124.8, 123.7, 74.7, 64.3, 54.5, 44.0, 30.4, 18.9, 17.7, 14.5, 13.6. LRMS (EI): 258[M+], 242, 229, 205, 184, 173, 157, 129, 102. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1330.

Compound ***b27***. White solid. 67 mg. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 5.14 (d, J = 6.2 Hz, 1H), 4.16 (s, 1H), 3.45−3.09 (m, 1H), 2.55−2.28 (m, 1H), 2.11 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 132.7, 131.9, 128.2, 126.5, 124.6, 124.1, 80.8, 74.8, 54.5, 44.8, 27.5, 17.6, 14.6. LRMS (EI): 258[M+], 228, 214, 202, 185, 173, 157, 129, 102. HRMS (ESI): calcd for $C_{16}H_{19}O_3$, $[M+H]^+$, 259.1329; found, 259.1332.

Compound ***b28***. White solid. 74 mg. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 7.28 (dd, J = 7.4, 6.6 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 5.18 (d, J = 6.3 Hz, 1H), 4.80 (dt, J = 8.3, 2.9 Hz, 1H), 4.17 (t, J = 4.6 Hz, 1H), 3.30 (dd, J = 6.3, 3.0 Hz, 1H), 2.38 (dd, J = 8.0, 5.2 Hz, 1H), 2.20−2.07 (m, 1H), 1.63−1.09 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.68, 132.66, 131.73, 128.32, 126.54, 124.76, 123.82, 77.30, 74.75, 54.55, 44.12, 32.34, 32.23, 23.76, 23.70, 17.69, 14.52. LRMS (EI): 270[M+], 199, 173, 155, 129. HRMS (ESI): calcd for $C_{17}H_{19}O_3$, $[M+H]^+$, 271.1329; found, 271.1330.

Compound ***b29***. White solid. 79 mg. Yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 7.27 (t, J = 5.9 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.20 (d, J = 6.2 Hz, 1H), 4.48−4.35 (m, 1H), 4.17 (t, J = 4.5 Hz, 1H), 3.46−3.19 (m, 1H), 2.49−2.32 (m, 1H), 2.24−2.08 (m, 1H), 1.56 (d, J = 12.8 Hz, 2H), 1.44 (d, J = 5.0 Hz, 3H), 1.25−1.03 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 132.6, 131.6, 128.3, 126.5, 124.7, 123.9, 74.7, 72.6, 54.5, 44.2, 31.2, 25.2, 23.6, 17.7, 14.5. LRMS (EI): 284[M+], 255, 202, 173, 157, 129, 102. HRMS (ESI): calcd for $C_{18}H_{21}O_3$, $[M+H]^+$, 285.1485; found, 285.1490.

Compound ***b30***. White solid. 93 mg. Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 7.28 (dd, J = 6.4, 2.6 Hz, 4H), 7.11 (t, J = 7.4 Hz, 1H), 7.05 (dd, J = 6.3, 2.7 Hz, 2H), 7.00 (d, J = 7.3 Hz, 1H), 5.21 (d, J = 6.2 Hz, 1H), 4.77 (q, J = 12.2 Hz, 2H), 4.18 (t, J = 4.6 Hz, 1H), 3.38 (dd, J = 6.2, 2.9 Hz, 1H), 2.40 (dd, J = 7.9, 5.2 Hz, 1H), 2.22−2.11 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 135.4, 132.4, 131.6, 128.4, 128.3, 128.3, 128.1, 126.5, 125.0, 123.7, 74.6, 66.4, 54.5, 44.07, 17.7, 14.5. LRMS (EI): 292[M+], 262, 244, 217, 199, 173, 155, 129, 91. HRMS (ESI): calcd for $C_{19}H_{17}O_3$, $[M+H]^+$, 293.1172; found, 293.1176.

Compound ***b31***. White solid. 72 mg. Yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.4 Hz, 1H), 7.30−7.23 (m, 1H), 7.16 (td, J = 7.4, 0.9 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 5.69 (ddt, J = 16.3, 9.7, 6.6 Hz, 1H), 5.22 (d, J = 6.3 Hz, 1H), 4.97 (dd, J = 3.2, 1.4 Hz, 1H), 4.93 (d, J = 0.9 Hz, 1H), 4.30−4.02 (m, 1H), 3.75 (qt, J = 10.9, 6.6 Hz, 2H), 3.34 (dd, J = 6.2, 2.9 Hz, 1H), 2.40 (dd, J = 8.0, 5.2 Hz, 1H), 2.26−2.07 (m, 1H), 2.01−1.80 (m, 2H), 1.48 ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 137.4, 132.5, 131.7, 128.3, 126.5, 124.9, 123.7, 115.1, 74.7, 63.9, 54.5, 44.0, 29.8, 27.5, 17.7, 14.5. LRMS (EI): 270[M+], 241, 193, 155, 129. HRMS (ESI): calcd for $C_{17}H_{19}O_3$, $[M+H]^+$, 271.1329; found, 271.1334.

Compound ***b32***. White solid. 76 mg. Yield 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 1H), 7.31−7.24 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 5.75 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.21 (d, J = 6.3 Hz, 1H), 5.05−4.92 (m, 2H), 4.18 (t, J = 4.6 Hz, 1H), 3.90−3.54 (m, 2H), 3.34 (dd, J = 6.2, 2.9 Hz, 1H), 2.40 (dd, J = 7.9, 5.2 Hz, 1H), 2.27−2.08 (m, 1H), 1.96 (q, J = 6.8 Hz, 2H), 1.39−1.12 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 138.3, 132.5, 131.7, 128.3, 126.5, 124.8, 123.7, 114.8, 74.7, 64.4, 54.5, 44.0, 33.2, 27.8, 24.9, 17.7, 14.5. LRMS (EI): 284[M+], 199, 184, 172, 155, 129. HRMS (ESI): calcd for $C_{18}H_{20}O_3Na$, $[M + Na]^+$, 307.1305; found, 307.1308.

Compound ***b33***. White solid. 55 mg. Yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−6.90 (m, 3H), 5.17 (t, J = 6.6 Hz, 1H), 4.16 (s, 1H), 3.37 (s, 3H), 3.34−3.23 (m, 1H), 2.44−2.28 (m, 4H), 2.18−2.03 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 138.0, 132.2, 129.1, 127.1, 125.7, 123.4, 74.4, 54.5, 51.6, 44.1, 21.2, 17.4, 14.5. LRMS (EI): 230[M+], 213, 201, 186, 169, 157, 142, 128, 115, 102. HRMS (ESI): calcd for $C_{14}H_{15}O_3$, $[M+H]^+$, 231.1016; found, 231.1019.

Compound ***b34***. White solid. 68 mg. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.14 (t, J = 8.2 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 5.20 (d, J = 6.0 Hz, 1H), 4.29−4.12 (m, 1H), 3.58−3.29 (m, 4H), 2.38 (m, 1H), 2.24−2.10 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major: δ 170.0, 134.3, 131.0, 130.1, 127.9, 125.1, 123.8, 74.0, 54.6, 51.8, 43.8, 17.6, 14.8, minor: δ 170.0, 133.9, 130.8, 128.4, 127.9, 126.6, 124.9, 74.0, 54.6, 51.8, 43.8, 17.6, 14.8. LRMS (EI): 250[M+], 235, 221, 207, 191, 177, 162, 142, 127, 101. HRMS (ESI): calcd for $C_{13}H_{12}ClO_3$, $[M+H]^+$, 251.0469; found, 251.0470.

Compound ***b35***. White solid. 60 mg. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 7.6 Hz, 2H), 6.86 (t, J = 8.6 Hz, 1H), 5.21 (d, J = 6.0 Hz, 1H), 4.19 (s, 1H), 3.54−3.19 (m, 4H), 2.47−2.32 (m, 1H), 2.28−2.06 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 162.77 (d, J = 245.0 Hz), 134.74 (d, J = 8.9 Hz), 134.74 (d, J = 8.9 Hz), 127.7, 125.22 (d, J = 8.8 Hz), 113.62 (d, J = 22.7 Hz), 111.94 (d, J = 22.1 Hz), 74.0, 54.5, 51.7, 44.0, 18.0, 14.8. LRMS (EI): 234[M+], 219, 205, 190, 175, 161, 146, 135, 127, 115. HRMS (ESI): calcd for $C_{13}H_{12}O_3F$, $[M+H]^+$, 235.0765; found, 235.0769.

Compound ***b36***. White solid. 70 mg. Yield 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.10 (m, 2H), 5.20 (d, J = 6.1 Hz, 1H), 4.20 (m, 1H), 3.99−3.65 (m, 2H), 3.34 (m, 1H), 2.52−2.28 (m, 1H), 2.25−2.04 (m, 1H), 0.95 (t, J = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 134.5, 133.8, 130.1, 126.6, 125.1, 125.0, 74.1, 60.6, 54.6, 43.9, 17.6, 14.8, 13.9. LRMS (EI): 264[M+], 248, 235, 218, 207, 191, 163, 127, 115, 101. HRMS (ESI): calcd for $C_{14}H_{14}O_3Cl$, $[M+H]^+$, 265.0626; found, 265.0628.

Compound ***b37***. White solid. 65 mg. Yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.27 (m, 1H), 7.07 (d, J = 8.5 Hz, 2H), 6.85 (t, J = 8.6 Hz, 1H), 5.20 (d, J = 6.2 Hz, 1H), 4.36−4.08 (m, 1H), 3.90−

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3.67 (m, 2H), 3.50−3.11 (m, 1H), 2.52−2.31 (m, 1H), 2.21−2.06 (m, 1H), 0.94 (t, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6 (s), 162.79 (d, J = 245.1 Hz), 134.91 (d, J = 8.8 Hz), 127.68 (d, J = 3.0 Hz), 125.39 (d, J = 9.0 Hz), 113.58 (d, J = 22.6 Hz), 111.76 (d, J = 22.0 Hz), 74.1, 60.5, 54.5, 44.0, 18.0, 14.8, 13.9. LRMS (EI): 248[M+], 229, 219, 202, 191, 175, 159, 147, 127, 115. HRMS (ESI): calcd for $C_{14}H_{14}O_3F$, $[M+H]^+$, 249.0921; found, 249.0923.

Compound ***b38***. Colorless oil. 56 mg. Yield 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.4 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 5.27 (d, J = 6.1 Hz, 1H), 3.55 (s, 4H), 3.32 (s, 3H), 2.80 (d, J = 8.4 Hz, 1H), 2.36 (dd, J = 8.3, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 132.8, 131.5, 128.4, 126.1, 125.3, 123.7, 95.5, 75.7, 57.0, 51.5, 43.8, 24.9, 19.4. HRMS (ESI): calcd for $C_{14}H_{15}O_4$, $[M+H]^+$, 247.0965; found, 247.0967.

Compound ***c1***. White solid. 244 mg. Yield 78%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.24 (m, 3H), 7.16 (d, J = 7.1 Hz, 1H), 4.07 (s, 1H), 3.91 (s, 1H), 3.54 (dd, J = 9.3, 2.0 Hz, 1H), 3.43 (s, 1H), 3.39 (d, J = 5.1 Hz, 1H), 3.32 (dd, J = 9.3, 2.0 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.5, 204.5, 171.3, 171.0, 136.0, 133.6, 129.1, 128.9, 126.1, 125.4, 50.6, 49.6, 45.0, 41.4, 38.5, 38.0, 29.4, 28.0. HRMS (ESI): calcd for $C_{18}H_{17}O_5$, $[M+H]^+$, 313.1071; found, 313.1078.

Compound ***c5***. Colorless oil. 256 mg. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (m, 3H), 7.12−6.94 (m, 1H), 4.09−4.00 (m, 1H), 3.97 (t, J = 3.1 Hz, 1H), 3.81 (s, 3H), 3.44 (dd, J = 5.4, 2.2 Hz, 1H), 3.33 (dd, J = 5.4, 2.9 Hz, 1H), 3.29 (dd, J = 8.5, 3.2 Hz, 1H), 3.15 (dd, J = 8.5, 3.3 Hz, 1H), 2.49 (s, 3H), 2.23 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 204.6, 177.3, 177.0, 173.5, 136.3, 133.8, 128.4, 128.2, 125.7, 125.3, 52.7, 52.5, 44.4, 42.4, 41.0, 38.7, 38.6, 28.1, 24.3. HRMS (ESI): calcd for $C_{19}H_{20}O_5N$, $[M+H]^+$, 342.1336; found, 342.1339.

Compound ***d10***. Colorless oil. 63 mg. Yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.16 (m, 1H), 7.15−7.10 (m, 2H), 7.07 (d, J = 7.4 Hz, 1H), 4.97 (d, J = 4.9 Hz, 1H), 4.66−4.45 (m, 1H), 4.08 (q, J = 6.3 Hz, 1H), 3.39 (t, J = 5.0 Hz, 1H), 3.34 (dd, J = 17.5, 4.1 Hz, 1H), 2.78 (d, J = 17.4 Hz, 1H), 2.62 (s, 1H), 1.72−1.51 (m, 2H), 1.44−1.31 (m, 4H), 1.27 (d, J = 6.3 Hz, 4H), 1.20−1.07 (m, 2H), 1.05−0.83 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 138.0, 133.5, 129.1, 128.3, 127.9, 126.1, 80.7, 77.7, 72.5, 47.3, 41.3, 33.5, 31.3, 30.8, 25.2, 23.4, 23.2, 21.8. HRMS (ESI): calcd for $C_{19}H_{25}O_3$, $[M+H]^+$, 301.1798; found, 301.1794.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01055.

^{1}H and ^{13}C NMR spectra, NOE spectra, and 2D spectra of starting materials and products (DOCX)

X-ray crystallographic data for **b6′** (CIF)

X-ray crystallographic data for **b22′** (CIF)

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Notes

The authors declare no competing financial interest.

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