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$FeCl_3$-Mediated Synthesis of β-Alkynyl Ketones via Domino Nucleophilic-Substitution/Intramolecular-Cyclization/Reverse Claisen Condensation of *N*-Cyclohexyl Propargylamines and 1,3-Diketones

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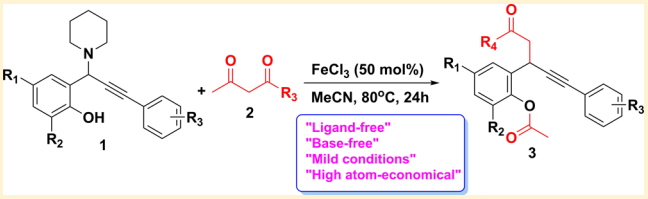
Supporting Information

ABSTRACT: The synthesis of β-alkynyl ketones was achieved in good to excellent yields by an iron-catalyzed domino reaction of *N*-cyclohexyl propargylamines and 1,3-diketones. A plausible mechanism involving nucleophilic substitution, intramolecular cyclization, and reverse Claisen condensation for this process is proposed.

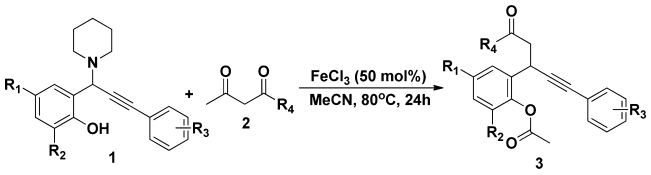


Because β-alkynyl carbonyl derivatives are versatile intermediates that lead to various useful structures, such as pyran, furan, and pyrrole derivatives,[1] many research efforts have been focused on the efficient synthesis of these derivatives. An efficient route to β-alkynyl carbonyl derivatives is the classic Nicholas reaction, using propargylic ethers and a stoichiometric amount of $Co_2(CO)_8$, which unavoidably leads to the generation of a significant amount of metallic waste.[2] In this context, the development of alternative, atom-economical approaches to β-alkynyl carbonyl derivatives is a highly desired goal. One common strategy to achieve this goal is the catalytic direct conjugate addition reaction of terminal alkynes to electron-deficient alkenes under the catalysis of various metal catalysts, including palladium,[3] copper,[4] rhodium,[5] ruthenium,[6] zinc,[7] and cobalt[8] complexes. Another strategy to access β-alkynyl carbonyl derivatives is the intramolecular nucleophilic substitution of propargylic substrates with an enolate-type nucleophile. However, examples with this strategy are rare.

In recent years, iron salts, being effective, alternative, and promising transition-metal catalysts, have received much more attention because of their low cost, abundance, and environmentally benign properties.[9] In particular, $FeCl_3$ has been widely applied as a Lewis acid catalyst for the catalytic synthesis of heterocyclic compounds,[10,9a] multicomponent reactions,[11] cross-coupling reactions,[12] and cyclization reactions.[13] Previously, we developed an efficient synthesis approach for coumarins and polysubstituted pyridines using $FeCl_3$-catalyzed cascade and multicomponent reactions.[14] As part of our ongoing efforts devoted to iron-catalyzed organic reactions, herein, we report a novel synthetic pathway to β-alkynyl ketones involving an $FeCl_3$-catalyzed domino process of nucleophilic-substitution/intramolecular-cyclization/reverse Claisen condensation catalyzed by $FeCl_3$ under mild conditions in good to excellent yields (Scheme 1).

In a preliminary study, *N*-cyclohexyl propargylamines **1** were prepared via the A^3-coupling reaction of salicylaldehydes, piperidine, and terminal alkynes using CuI as the catalyst, according to the literature procedure.[15] As an exploratory experiment, **1a** and **2a** were chosen as model substrates to optimize the reaction conditions, with results presented in Table 1.

Scheme 1. Synthesis of β-Alkynyl Ketones via $FeCl_3$-Catalyzed Domino Reactions of *N*-Cyclohexyl Propargylamines and 1,3-Diketones



Neither reducing the catalyst loading nor increasing the catalyst loading of $FeCl_3$ increased the yield further (Table 1, entries 1, 2, and 4). Replacing $FeCl_3$ with other Lewis acids, such as $CuBr_2$, CuI, $Sc(OTf)_3$, or Brønsted acid (H_2SO_4), all led to inferior results (Table 1, entries 5−8). No reaction occurred in the absence of the catalyst (Table 1, entry 9). Changing the solvent to CH_2Cl_2, THF, DMF, and DMSO reduced the yields to 30, 31, 15, and 27%, respectively (Table 1, entries 17−19, 21). When H_2O or 1,4-dioxane was used as the solvent, the desired product was obtained in very low yield (Table 1, entries 20 and 22). Interestingly, when EtOH was used as the solvent, only the compound 2-(1-ethoxy-3-phenylprop-2-yn-1-yl)phenol was isolated in 92% yield (Table 1, entry 15). Thus, the optimal reaction conditions were found to be 50 mol % catalyst $FeCl_3$ with CH_3CN as the solvent at 80 °C for 24 h (Table 1, entry 3).

With the optimal reaction conditions in hand, various aromatic propargylic amines **1** and 1,3-diketones **2** were

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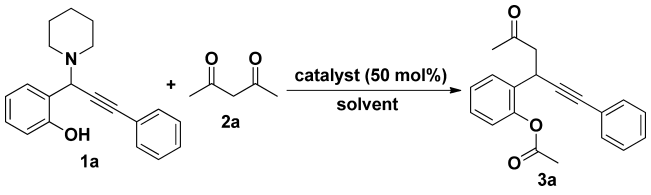
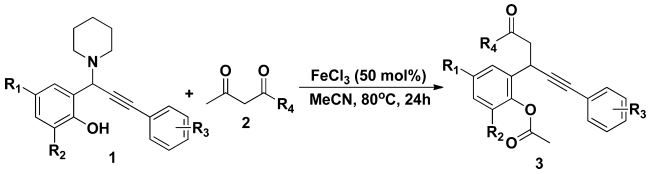
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	temp/°C	time/h	yield/%
1[b]	$FeCl_3$	CH_3CN	80	24	45
2[c]	$FeCl_3$	CH_3CN	80	24	80
3	$FeCl_3$	CH_3CN	80	24	89
4[d]	$FeCl_3$	CH_3CN	80	24	87
5	$CuBr_2$	CH_3CN	80	24	trace
6	H_2SO_4	CH_3CN	80	24	trace
7	$Sc(OTf)_3$	CH_3CN	80	24	63
8	CuI	CH_3CN	80	24	10
9		CH_3CN	80	24	0
10	$FeCl_3$	CH_3CN	r.t.	24	trace
11	$FeCl_3$	CH_3CN	60	24	67
12	$FeCl_3$	CH_3CN	100	24	89
13	$FeCl_3$	CH_3CN	80	5	10
14	$FeCl_3$	CH_3CN	80	12	72
15	$FeCl_3$	CH_3CH_2OH	80	24	trace[e]
16	$FeCl_3$	CH_3OH	80	24	trace
17	$FeCl_3$	CH_2Cl_2	60	24	30
18	$FeCl_3$	THF	80	24	31
19	$FeCl_3$	DMF	80	24	15
20	$FeCl_3$	H_2O	80	24	trace
21	$FeCl_3$	DMSO	80	24	27
22	$FeCl_3$	1,4-dioxane	80	24	trace

[a]Reaction conditions: 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)-phenol **1a** (1.0 mmol), acetylacetone **2a** (1.0 mmol), catalyst, solvent (5 mL). [b]20 mol % of catalyst was used. [c]40 mol % of catalyst was used. [d]1.0 equiv of catalyst was used. [e]2-(1-Ethoxy-3-phenylprop-2-yn-1-yl)phenol was obtained in 92% yield as the main product after 24 h.

Table 2. $FeCl_3$-Catalyzed Domino Reaction for the Formation of β-Alkynyl Ketones[a]



entry	R_1, R_2, R_3	R_4	product	yield (%)
1	**1a** (H, H, H)	**2a** (CH_3)	**3a**	89
2	**1b** (H, H, 4-CH_3)	**2a**	**3b**	91
3	**1c** (H, H, 4-Cl)	**2a**	**3c**	87
4	**1d** (H, H, 2-F)	**2a**	**3d**	86
5	**1e** (H, H, 4-F)	**2a**	**3e**	89
6	**1f** (CH_3, H, H)	**2a**	**3f**	93
7	**1g** (CH_3, H, 4-CH_3)	**2a**	**3g**	92
8	**1h** (Cl, H, 4-CH_3)	**2a**	**3h**	89
9	**1i** (Br, H, 4-CH_3)	**2a**	**3i**	87
10	**1m** (*tert*-butyl, *tert*-butyl, H)	**2a**		NR[b]
11	**1a** (H, H, H)	**2b** (Ph)	**3j**	86
12	**1b** (H, H, 4-CH_3)	**2b**	**3k**	85
13	**1c** (H, H, 4-Cl)	**2b**	**3l**	79
14	**1d** (H, H, 2-F)	**2b**	**3m**	82
15	**1e** (H, H, 4-F)	**2b**	**3n**	83
16	**1f** (CH_3, H, H)	**2b**	**3o**	84
17	**1g** (CH_3, H, 4-CH_3)	**2b**	**3p**	85
18	**1h** (Cl, H, 4-CH_3)	**2b**	**3q**	77
19	**1i** (Br, H, 4-CH_3)	**2b**	**3r**	78
20	**1j** (H, H, 4-OCH_3)	**2b**	**3s**	68
21	**1k** (Cl, H, H)	**2b**	**3t**	78
22	**1l** (Br, H, H)	**2b**	**3u**	75
23	**1m** (*tert*-butyl, *tert*-butyl, H)	**2b**		NR[b]

[a]Reaction conditions: aromatic propargylic amines **1** (1.0 mmol), 1,3-diketones **2** (1.0 mmol), $FeCl_3$ (0.5 mmol), CH_3CN (10 mL), 80 °C, 24 h. [b]No reaction.

examined to test the scope and limitation of this cascade reaction; the results are summarized in Table 2. In most cases, the desired β-alkynyl ketones were smoothly generated in good to excellent yields. Both acetylacetone (**2a**) and benzoylacetone (**2b**) were found to yield the desired products, with the former providing relatively higher yields of the products. Among the various *N*-cyclohexyl propargylamines **1** that were examined, electron-donating R_1 groups ($-CH_3$) resulted in higher yields than when R_1 was an electron-withdrawing group ($-Cl$, $-Br$) (Table 2, entries 6, 7, 17, 18). The reaction was affected significantly by the steric effect. No product was detected with a *tert*-butyl group at the *ortho* and *para* positions of the hydroxyl of *N*-cyclohexyl propargylamines (**1m**) (Table 2, entries 10, 23). The structure of product **3j** was unambiguously confirmed by the X-ray crystallographic analysis, as shown in Figure 1 in the Supporting Information.

A plausible mechanism was proposed for this domino process based on our experimental results and literature reports (Scheme 2).[16] First, *N*-cyclohexyl of **1a** obtained a proton from the phenol hydroxyl group to become the phenoxide intermediate **A**. Subsequently, intermediate **A** attacks the carbonyl of intermediate **B**, the complex form of diketone **2a** and Fe(III) ion, to form the intermediate **C**. Next, intermediate **E** results from intramolecular nucleophilic substitution and releases piperidine. Finally, a reverse Claisen condensation reaction of intermediate **E** in the presence of $FeCl_3$ as a Lewis acid, followed by a proton transfer process, generates the desired product **3a**.

To support the reaction mechanism, the substrate of 2-(phenyl(piperidin-1-yl)methyl)phenol (**1n**) was synthesized by the Petasis boronic Mannich reaction of salicylaldehyde, phenylboronic acid, and piperidine, according to the literature procedure,[17] which then reacted with acetylacetone (**2a**) under the optimized reaction condition (Scheme 3). As expected, the desired product 2-(3-oxo-1-phenylbutyl)phenyl acetate was obtained in 80% yield.

In conclusion, we have developed an iron-promoted method for the synthesis of β-alkynyl ketones in good to excellent yields through the nucleophilic-substitution/intramolecular-cyclization/reverse Claisen condensation of *N*-cyclohexyl propargylamines and 1,3-diketones. The notable advantages of this method are the mild reaction conditions, the inexpensive and efficient eco-friendly catalyst, and use of base-free and ligand-free conditions, under air. This methodology is highly facile and efficient and can be a useful basis for the synthesis of other interesting alkynyl ketone compounds. The resulting β-alkynyl ketones are versatile building blocks in the construction of heterocyclic architectures prevalent in natural products.

EXPERIMENTAL SECTION

General Comments. Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used

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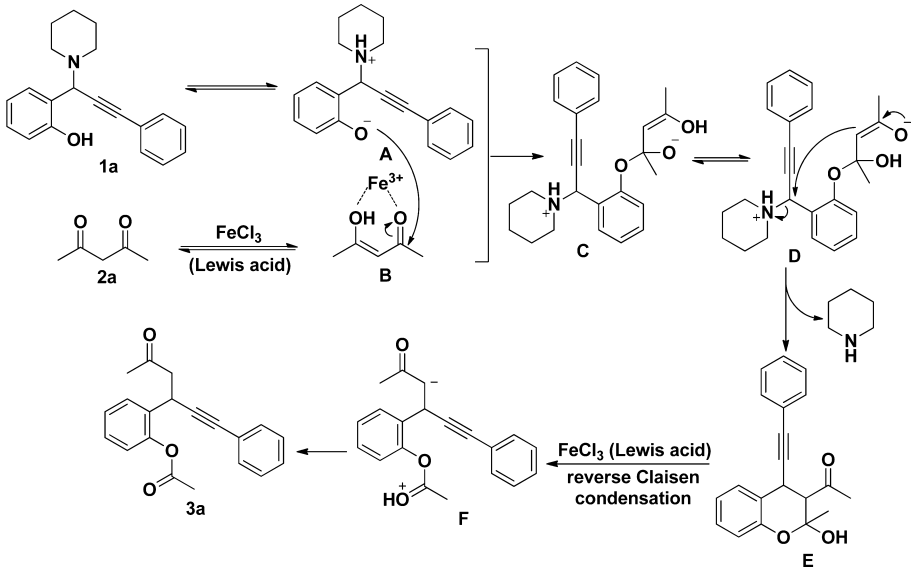
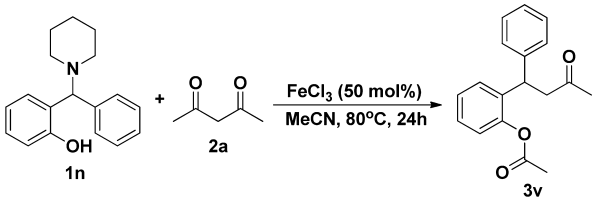
Scheme 2. Proposed Mechanism for the Formation of β-Alkynyl Ketones via $FeCl_3$-Catalyzed Domino Process of *N*-Cyclohexyl Propargylamines and 1,3-Diketones



Scheme 3. Synthesis of 2-(3-Oxo-1-phenylbutyl)phenyl Acetate via $FeCl_3$-Catalyzed Domino Reactions of 2-(Phenyl(piperidin-1-yl)methyl)phenol (1n) and Acetylacetone (2a)



as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. Flash chromatography was performed using 200−300 mesh silica gel with the indicated solvent system according to standard techniques. The ^1H and ^{13}C NMR data were recorded on 300 MHz NMR spectrometers, unless otherwise specified. Chemical shifts (δ) in parts per million are reported relative to the residual signals of chloroform (7.26 ppm for ^1H and 77.16 ppm for ^{13}C), and all ^{13}C NMR were recorded with proton broad-band decoupling and indicated as $^{13}C\{^1H\}$NMR. Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet), and the coupling constants (J) are reported in hertz. HRMS analysis with a quadrupole time-of-flight mass spectrometer yielded ion mass/charge (m/z) ratios in atomic mass units. IR spectra were measured as dry films (KBr), and the peaks are reported in terms of wavenumber (cm^{-1}).

General Procedure for the Synthesis of 2-(5-Oxo-1-phenylhex-1-yn-3-yl)phenyl Acetate (3a). Anhydrous $FeCl_3$ (0.50 mmol, 81 mg) was added to a stirred solution of *N*-cyclohexyl propargylamines **1a** (1 mmol, 306 mg) and acetylacetone **2a** (1 mmol, 100 mg) in acetonitrile (5 mL). The mixture was heated at 80 °C for 24 h in an oil bath and then cooled down to room temperature. The mixture was washed with water and diluted with CH_2Cl_2 (3 × 10 mL). Organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated in vacuum. The residue was further purified by flash column chromatography on silica gel with ethyl acetate and petroleum ether as the eluting solvent to afford the product **3a** in 89% yield.

*2-(5-Oxo-1-phenylhex-1-yn-3-yl)phenyl Acetate (**3a**).* Petroleum ether/ethyl acetate 16:1, 89% yield (272 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$,) δ 7.60 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H), 7.38−7.41 (m, 2H), 7.24−7.31 (m, 5H), 7.06 (dd, J = 1.5 Hz, J = 8.1 Hz, 1H), 4.53 (dd, J = 5.1 Hz, J = 8.4 Hz, 1H), 3.02 (dd, J = 8.4 Hz, J = 16.2 Hz, 1H), 2.81 (dd, J = 5.1 Hz, J = 16.8 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 169.5, 147.8, 132.6, 131.7, 129.3, 128.3, 128.1, 126.5, 123.1, 89.6, 82.7, 50.2, 30.6, 28.4, 21.0 ppm; IR (KBr) ν 1763, 1717, 1597, 1489, 1443, 1368, 1200, 1169, 1096, 1011, 912, 820, 758, 692, 667, 590, 496 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{18}O_3 + H]^+$ 307.1329, found 307.1333.

*2-(5-Oxo-1-(p-tolyl)hex-1-yn-3-yl)phenyl Acetate (**3b**).* Petroleum ether/ethyl acetate 16:1, 91% yield (291 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, J = 1.8 Hz, J = 7.2 Hz, 3H), 7.20−7.28 (m, 4H), 7.02−7.18 (m, 3H), 4.48 (dd, J = 4.8 Hz, J = 8.4 Hz, 1H), 2.98 (dd, J = 8.7 Hz, J = 16.8 Hz, 1H), 2.77 (dd, J = 5.1 Hz, J = 16.5 Hz, 1H),2.29 (s, 6H), 2.15 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ205.6, 169.4, 147.8, 138.1, 132.7, 131.5, 129.3, 129.0, 128.2, 126.4, 123.0, 120.1, 88.8, 82.8, 50.3, 30.6, 28.5, 21.4, 21.0 ppm; IR (KBr) ν 1767, 1717, 1609, 1510, 1487, 1368, 1202, 1169, 1096, 1011, 947, 912, 818, 756, 664, 532, cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{20}O_3 + Na]^+$ 343.1305, found 343.1309.

*2-(1-(4-Chlorophenyl)-5-oxohex-1-yn-3-yl)phenyl Acetate (**3c**).* Petroleum ether/ethyl acetate 16:1, 87% yield (295 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, J = 2.4 Hz, J = 7.5 Hz, 1H), 7.05 (dd, J = 1.5 Hz, J = 7.5 Hz, 1H), 7.22−7.33 (m, 7H), 4.51 (dd, J = 5.1 Hz, J = 8.4 Hz, 1H), 3.02 (dd, J = 8.4 Hz, J = 16.8 Hz, 1H), 2.81 (dd, J = 5.1 Hz, J = 17.1 Hz, 1H), 2.32 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 169.4, 147.8, 134.0, 132.9, 132.4, 129.2, 128.6, 128.4, 126.5, 123.1, 121.6, 90.7, 81.5, 50.0, 30.5, 28.3, 21.0 ppm; IR (KBr) ν 1765, 1717, 1489, 1368, 1202, 1169, 1092, 1042, 1013, 912, 829, 758, 667, 559, 527, cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{17}O_3Cl + H]^+$ 341.0939, found 341.0945.

*2-(1-(2-Fluorophenyl)-5-oxohex-1-yn-3-yl)phenyl Acetate (**3d**).* Petroleum ether/ethyl acetate 16:1, 86% yield (278 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, J = 2.1 Hz, J = 7.2 Hz, 1H), 7.22−7.40 (m, 4H), 7.01−7.10 (m, 3H), 4.58 (dd, J = 5.1 Hz, J = 8.7 Hz, 1H), 3.04 (dd, J = 8.7 Hz, J = 16.5 Hz, 1H), 2.81 (dd, J = 5.1, J = 16.8 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 169.5, 164.5($^1J_{CF}$ = 249 Hz), 161.2, 147.8, 133.5, 132.3, 129.8, 129.7, 129.3, 128.4, 126.5, 123.9, 123.0, 115.5, 115.2, 95.0, 76.2, 50.1, 30.6, 28.5, 21.0 ppm; IR (KBr) ν 1765, 1716, 1574, 1491, 1450, 1369, 1202, 1094, 1042, 1011, 947, 912, 758, 667, 554 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{17}O_3F + H]^+$ 325.1235, found 325.1236.

*2-(1-(4-Fluorophenyl)-5-oxohex-1-yn-3-yl)phenyl Acetate (**3e**).* Petroleum ether/ethyl acetate 16:1, 89% yield (288 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, J = 1.5 Hz, J = 7.2 Hz, 1H), 7.22−7.39 (m, 4H), 7.06 (dd, J = 1.5 Hz, J = 8.1 Hz, 1H), 6.94 (t, J =

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8.7 Hz, 2H), 4.52 (dd, J = 5.1 Hz, J = 8.7 Hz, 1H), 3.02(dd, J = 8.4 Hz, J = 16.5 Hz, 1H), 2.81 (dd, J = 5.4 Hz, J = 17.1 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 169.5, 164.0($^1J_{CF}$ = 247 Hz), 160.7, 147.8, 133.6, 133.4, 132.5, 129.2, 128.3, 126.5, 123.1, 115.6, 115.3, 89.3, 81.5, 50.1, 30.5, 28.3, 21.0 ppm; IR (KBr) ν 1767, 1717, 1601, 1506, 1369, 1202, 1169, 1094, 1013, 912, 839, 756, 662, 561, 492 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{17}FO_3 + H]^+$ 325.1235, found 325.1238.

*4-Methyl-2-(5-oxo-1-phenylhex-1-yn-3-yl)phenyl Acetate (**3f**).* Petroleum ether/ethyl acetate 16:1, 93% yield (297 mg), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.41 (m, 3H), 7.25−7.28 (m, 3H), 7.07−7.10 (m, 1H), 6.93 (d, J = 8.1 Hz, 1H), 4.48 (dd, J = 5.4 Hz, J = 9.0 Hz, 1H), 3.01 (dd, J = 8.7 Hz, J = 16.5 Hz, 1H), 2.80 (dd, J = 4.8 Hz, J = 16.2 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 169.7, 136.1, 132.1, 131.7, 129.7, 128.9, 128.2, 128.0, 122.7, 89.7, 82.6, 50.2, 30.5, 28.4, 21.0 ppm; IR (KBr) ν 1763, 1719, 1597, 1491, 1423, 1368, 1190, 1101, 1011, 905, 829, 758, 692, 544 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{20}O_3 + Na]^+$ 343.1305, found 343.1309.

*4-Methyl-2-(5-oxo-1-(p-tolyl)hex-1-yn-3-yl)phenyl Acetate (**3g**).* Petroleum ether/ethyl acetate 16:1, 92% yield (307 mg), saffron yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.28 (d, J = 7.5 Hz, 2H), 7.07 (d, J = 6.9 Hz, 3H), 6.93 (d, J = 8.7 Hz, 1H), 4.47 (dd, J = 5.1 Hz, J = 8.4 Hz, 1H), 3.00 (dd, J = 8.7 Hz, J = 7.8 Hz, 1H), 2.79 (dd, J = 4.5 Hz, J = 16.5 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 169.7, 145.5, 138.0, 136.1, 132.2, 131.5, 129.7, 128.9, 128.8, 122.7, 120.1, 88.8, 82.7, 50.3, 30.6, 28.5, 21.4, 21.0 ppm; IR (KBr) ν 1763, 1717, 1510, 1497, 1418, 1368, 1192, 1101, 1042, 1011, 905, 818, 635, 538 cm^{-1}; HRMS (ESI) calcd for $[C_{22}H_{22}O_3 + H]^+$ 335.1642, found 335.1644.

*4-Chloro-2-(5-oxo-1-(p-tolyl)hex-1-yn-3-yl)phenyl Acetate (**3h**).* Petroleum ether/ethyl acetate 16:1, 89% yield (315 mg), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 2.7 Hz, 1H), 7.23−7.30 (m, 3H), 7.08 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 9.0 Hz, 1H), 4.53 (dd, J = 5.1 Hz, J = 9.0 Hz, 1H), 3.00 (dd, J = 8.7 Hz, J = 16.8 Hz, 1H), 2.77 (dd, J = 5.4 Hz, J = 16.5 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.2, 169.2, 146.3, 138.3, 134.7, 131.7, 131.6, 129.2, 129.0, 128.2, 124.4, 119.7, 88.0, 83.3, 50.0, 30.5, 28.2, 21.5, 20.9 ppm; IR (KBr) ν 1765, 1717, 1601, 1510, 1481, 1404, 1368, 1196, 1165, 1109, 1042, 1011, 897, 818, 692, 529 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{19}O_3Cl + H]^+$ 355.1096, found 355.1097.

*4-Bromo-2-(5-oxo-1-(p-tolyl)hex-1-yn-3-yl)phenyl Acetate (**3i**).* Petroleum ether/ethyl acetate 16:1, 87% yield (346 mg), saffron yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 2.1 Hz, 1H), 7.39−7.42 (m, 1H), 7.26−7.30 (m, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 8.7 Hz, 1H), 4.49 (dd, J = 5.1 Hz, J = 8.4 Hz, 1H), 3.01 (dd, J = 8.7 Hz, J = 16.8 Hz, 1H), 2.78 (dd, J = 5.1 Hz, J = 16.8 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.2, 169.2, 146.8, 138.3, 135.1, 132.2, 132.5, 131.2, 131.1, 129.0, 124.8, 119.7, 119.4, 87.9, 83.3, 50.0, 30.6, 28.1, 21.5, 21.0 ppm; IR (KBr) ν 1763, 1717, 1510, 1497, 1418, 1368, 1192, 1101, 1042, 1011, 908, 818, 681, 596, 536 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{19}O_3Br + H]^+$399.0590, found 399.0581.

*2-(5-Oxo-1,5-diphenylpent-1-yn-3-yl)phenyl Acetate (**3j**).* Petroleum ether/ethyl acetate 16:1, 86% yield (316 mg), white solid; mp = 111−113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97−8.00 (m, 2H), 7.68 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H), 7.54−7.60 (m, 1H), 7.43−7.49 (m, 2H), 7.23−7.35 (m, 7H), 7.08 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H), 4.75 (dd, J = 4.8 Hz, J = 9.0 Hz, 1H), 3.63 (dd, J = 8.7 Hz, J = 16.2 Hz, 1H), 3.30 (dd, J = 4.8 Hz, J = 16.5 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 169.5, 147.9, 136.8, 133.3, 132.9, 131.6, 129.4, 128.7, 128.3, 128.2, 128.0, 126.5, 123.2, 123.1, 89.8, 82.9, 45.6, 28.9, 21.1, ppm; IR (KBr) ν 1761, 1688, 1489, 1369, 1196, 1094, 910, 760, 691, 503 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{20}O_3 + H]^+$ 369.1485, found 369.1485.

*2-(5-Oxo-5-phenyl-1-(p-tolyl)pent-1-yn-3-yl)phenyl Acetate (**3k**).* Petroleum ether/ethyl acetate 16:1, 85% yield (324 mg), white solid; mp = 101−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 1.5 Hz, J = 6.6 Hz, 2H), 7.63 (dd, J = 2.1 Hz, J = 7.5 Hz, 1H), 7.50−7.56 (m, 1H), 7.40−7.45 (m, 2H), 7.17−7.28 (m, 4H), 7.00−7.07 (m, 3H), 4.70 (dd, J = 4.5 Hz, J = 8.4 Hz, 1H), 3.59 (dd, J = 8.4 Hz, J = 13.8 Hz, 1H), 3.26 (dd, J = 4.8 Hz, J = 16.5 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 169.5, 147.9, 138.0, 136.8, 133.3, 133.0, 131.5, 129.4, 128.9, 128.7, 128.3, 126.4, 123.1, 120.1, 89.0, 83.0, 45.6, 29.0, 21.4, 21.1 ppm; IR (KBr) ν 1761, 1686, 1595, 1508, 1489, 1450, 1366, 1198, 1094, 1011, 912, 822, 756, 691, 584, 530 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{22}O_3 + H]^+$ 383.1642, found 383.1642.

*2-(1-(4-Chlorophenyl)-5-oxo-5-phenylpent-1-yn-3-yl)phenyl Acetate (**3l**).* Petroleum ether/ethyl acetate 16:1, 79% yield (317 mg), white solid; mp = 115−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.99 (m, 2H), 7.63 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H), 7.55−7.60 (m, 1H), 7.44−7.49 (m, 2H), 7.19−7.34 (m, 7H), 7.08 (dd, J = 1.5 Hz, J = 7.5 Hz, 1H), 4.72 (dd, J = 5.4 Hz, J = 9.0 Hz, 1H), 3.62 (dd, J = 9.0 Hz, J = 16.8 Hz, 1H), 3.30 (dd, J = 5.1 Hz, J = 16.5 Hz, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 169.5, 147.9, 136.7, 133.9, 133.4, 132.9, 132.6, 129.3, 128.7, 128.5, 128.4, 128.2, 126.5, 123.1, 121.7, 90.8, 81.8, 45.4, 28.8, 21.1 ppm; IR (KBr) ν 1751, 1690, 1585, 1580, 1489, 1447, 1369, 1356, 1207, 1092, 1013, 916, 827, 760, 689, 594, 525 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}O_3Cl + H]^+$ 403.1096, found 403.1095.

*2-(1-(2-Fluorophenyl)-5-oxo-5-phenylpent-1-yn-3-yl)phenyl Acetate (**3m**).* Petroleum ether/ethyl acetate 16:1, 82% yield (316 mg), white solid; mp = 77−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.98 (m, 2H), 7.71 (dd, J = 2.1 Hz, 6.9 Hz, 1H), 7.54−7.56 (m, 1H), 7.43−7.48 (m, 2H), 7.19−7.35 (m, 4H), 7.08 (dd, J = 2.1 Hz, J = 7.2 Hz, 1H), 6.98−7.04 (m, 2H), 4.80 (dd, J = 4.5 Hz, J = 8.1 Hz, 1H), 3.64 (dd, J = 8.7 Hz, J = 17.1 Hz, 1H), 3.32 (dd, J = 5.4 Hz, J = 16.8 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 169.4, 164.5 ($^1J_{CF}$ = 249 Hz), 161.3, 147.9, 136.7, 133.6, 133.3, 132.6, 129.7, 129.6, 129.4, 128.6, 128.4, 128.2, 126.5, 123.8, 123.0, 115.5, 115.2, 95.2, 76.3, 45.6, 28.9, 21.0 ppm; IR (KBr) ν 1757, 1686, 1595, 1580, 1489, 1445, 1371, 1252, 1200, 1094, 912, 814, 734 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}O_3F + H]^+$ 387.1391, found 387.1390.

*2-(1-(4-Fluorophenyl)-5-oxo-5-phenylpent-1-yn-3-yl)phenyl Acetate (**3n**).* Petroleum ether/ethyl acetate 16:1, 83% yield (320 mg), pale yellow solid; mp = 80−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97−8.00 (m, 2H), 7.66 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H), 7.56−7.58 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.24−7.35 (m, 4H), 7.08 (dd, J = 1.5 Hz, J = 7.8 Hz, 1H), 6.91−6.97 (m, 2H), 4.73 (dd, J = 4.5 Hz, J = 8.7 Hz, 1H), 3.62 (dd, J = 9.0 Hz, J = 16.8 Hz, 1H), 3.31 (dd, J = 4.8 Hz, J = 16.5 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 169.5, 163.9 ($^1J_{CF}$ = 248 Hz), 160.6, 147.9, 136.7, 133.5, 133.4, 132.7, 129.4, 128.7, 128.4, 128.2, 126.5, 123.1, 115.5, 115.3, 89.5, 81.8, 45.4, 28.8, 21.0 ppm; IR (KBr) ν, 1763, 1688, 1597, 1504, 1449, 1368, 1223, 1198, 501, 1096, 910, 843, 758, 691, 532 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}O_3F + H]^+$ 387.1391, found 387.1393.

*4-Methyl-2-(5-oxo-1,5-diphenylpent-1-yn-3-yl)phenyl Acetate (**3o**).* Petroleum ether/ethyl acetate 16:1, 84% yield (320 mg), white solid; mp = 88−90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.98 (d, J = 1.2 Hz, 1H), 7.56−7.58 (m, 1H), 7.45−7.50 (m, 3H), 7.32−7.36 (m, 2H), 7.24−7.26 (m, 3H), 7.10 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 4.70 (dd, J = 4.8 Hz, J = 8.7 Hz, 1H), 3.63 (dd, J = 9.0 Hz, J = 16.8 Hz, 1H), 3.29 (dd, J = 5.1 Hz, J = 16.5 Hz, 1H), 2,37 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 169.7, 145.7, 136.8, 136.2, 133.3, 132.4, 131.7, 129.9, 128.9, 128.7, 128.3, 128.2, 127.9, 123.3, 122.8, 89.9, 82.8, 45.6, 28.9, 21.1 ppm; IR (KBr) ν 1763, 1686, 1595, 1489, 1449, 1366, 1213, 1188, 1099, 1009, 899, 766, 689, 530, 505 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{22}O_3 + H]^+$ 383.1642, found 383.1643.

*4-Methyl-2-(5-oxo-5-phenyl-1-(p-tolyl)pent-1-yn-3-yl)phenyl Acetate (**3p**).* Petroleum ether/ethyl acetate 16:1, 85% yield (336 mg), white solid; mp = 87−89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97−8.00 (m, 2H), 7.44−7.58 (m, 4H), 7.24 (d, J = 7.2 Hz, 1H), 7.21 (s, 1H), 7.04−7.12 (m, 3H), 6.96 (d, J = 7.8 Hz, 1H), 4.69 (dd, J = 4.5 Hz, J = 8.4 Hz, 1H), 3.62 (dd, J = 9.0 Hz, J = 16.8 Hz, 1H), 3.28 (dd, J = 4.5 Hz, J = 16.5 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 169.7, 145.7, 137.9, 136.9, 136.1, 133.3, 132.5, 131.5, 129.9, 128.9, 128.7, 128.3, 122.8, 120.2, 89.1, 82.9, 45.7,

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28.9, 21.4, 21.1 ppm; IR (KBr) ν 1748, 1690, 1508, 1447, 1356, 1221, 1207, 1196, 818, 758, 690 cm^{-1}; HRMS (ESI) calcd for $[C_{27}H_{24}O_3 + H]^+$ 397.1798, found 397.1799.

*4-Chloro-2-(5-oxo-5-phenyl-1-(p-tolyl)pent-1-yn-3-yl)phenyl Acetate (**3q**).* Petroleum ether/ethyl acetate 16:1, 77% yield (320 mg), saffron yellow solid; mp = 97−99 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97−8.00 (m, 2H), 7.68 (d, J = 2.4 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.22−7.29 (m, 3H), 7.03−7.08 (m, 3H), 4.73 (dd, J = 4.8 Hz, J = 8.7 Hz, 1H), 3.63 (dd, J = 8.7 Hz, J = 16.8 Hz, 1H), 3.27(dd, J = 5. One Hz, J = 16.5 Hz, 1H), 2.32 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 169.2, 146.4, 138.2, 136.6, 135.0, 133.4, 131.7, 131.6, 129.4, 129.0, 128.7, 128.3, 124.5, 119.8, 88.2, 83.5, 45.4, 28.7, 21.5, 21.0 ppm; IR (KBr) ν 1751, 1692, 1597, 1508, 1477, 1447, 1371, 1204, 1163, 1107, 1007, 901, 816, 760, 692, 498 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{21}O_3Cl + H]^+$ 417.1252, found 417.1251.

*4-Bromo-2-(5-oxo-5-phenyl-1-(p-tolyl)pent-1-yn-3-yl)phenyl Acetate (**3r**).* Petroleum ether/ethyl acetate 16:1, 78% yield (358 mg), pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 2.4 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.44−7.54 (m, 3H), 7.28 (d, J = 4.5 Hz, 1H), 7.26 (s, 1H), 7.02 (dd, J = 7.8 Hz, 22.8 Hz, 3H), 4.76 (dd, J = 4.8 Hz, J = 8.4 Hz, 1H), 3.67 (dd, J = 8.4 Hz, 16.2 Hz, 1H), 3.30 (dd, J = 4.8 Hz, J = 16.5 Hz, 1H), 2.36 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 169.1, 147.0, 138.2, 136.7, 135.3, 133.4, 132.3, 131.5, 131.2, 129.0, 128.7, 128.3, 124.8, 119.8, 119.4, 88.2, 83.5, 45.5, 28.7, 21.4, 20.9 ppm; IR (KBr) ν 1767, 1684, 1597, 1510, 1477, 1449, 1368, 1120, 1161, 1103, 1009, 816, 689, 754, 592, 529 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{21}O_3Br + H]^+$ 461.0747, found 461.0752.

*2-(1-(4-Methoxyphenyl)-5-oxo-5-phenylpent-1-yn-3-yl)phenyl Acetate (**3s**).* Petroleum ether/ethyl acetate 16:1, 68% yield (270 mg), white oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96−7.99 (m, 2H), 7.66−7.69 (m, 1H), 7.54−7.57 (m, 1H), 7.43−7.48 (m, 2H), 7.24−7.31 (m, 4H), 7.07−7.10 (m, 1H), 6.77 (t, J = 2.4 Hz, 1H), 6.75 (d, J = 2.1 Hz, 1H), 4.72 (dd, J = 5.4 Hz, J = 9.0 Hz, 1H), 3.77 (s, 3H), 3.61 (dd, J = 8.7 Hz, J = 16.5 Hz, 1H), 3.28 (dd, J = 5.1 Hz, J = 16.5 Hz, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 169.5, 159.3, 147.9, 136.8, 133.3, 133.0, 129.4, 128.6, 125.3, 128.2, 126.4, 123.1, 115.3, 113.8, 88.2, 82.7, 55.2, 45.6, 28.9, 21.1 ppm; IR (KBr) ν 1769, 1682, 1607, 1508, 1449, 1248, 1202, 1173, 1049, 831, 750 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{22}O_4 + H]^+$ 399.1591, found 399.1590.

*4-Chloro-2-(5-oxo-1,5-diphenylpent-1-yn-3-yl)phenyl Acetate (**3t**).* Petroleum ether/ethyl acetate 16:1, 78% yield (313 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 2H), 7.68−7.68 (m, 1H), 7.56−7.61 (m, 1H), 7.45 (s, 2H), 7.27−7.36 (m, 6H), 7.04 (dd, J = 1.5 Hz, J = 8.4 Hz, 1H), 4.69 (dd, J = 5.1 Hz, J = 7.5 Hz, 1H), 3.63 (dd, J = 8.4 Hz, J = 16.5 Hz, 1H), 3.28 (dd, J = 4.5 Hz, J = 16.8 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 169.2, 146.4, 136.6, 134.8, 133.5, 131.7, 129.4, 128.7, 128.3, 128.2, 124.4, 122.9, 89.0, 83.4, 45.4, 28.6, 21.0 ppm; IR (KBr) ν 1761, 1684, 1597, 1489, 1368, 1200, 1163, 1109, 1011, 758, 691 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}O_3Cl + H]^+$ 403.1096, found 403.1096.

*4-Bromo-2-(5-oxo-1,5-diphenylpent-1-yn-3-yl)phenyl Acetate (**3u**).* Petroleum ether/ethyl acetate 16:1, 75% yield (334 mg), brown oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 2.1 Hz, 1H), 7.37−7.57 (m, 4H), 7.23−7.32 (m, 5H), 6.94 (d, J = 8.1 Hz, 1H), 4.69 (dd, J = 4.8 Hz, J = 8.4 Hz, 1H), 3.59 (dd, J = 8.7 Hz, J = 16.8 Hz, 1H), 3.23 (dd, J = 5.1 Hz, J = 17.1 Hz, 1H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 169.2, 146.9, 136.6, 135.2, 133.5, 132.3, 131.7, 131.3, 128.7, 128.3, 128.2, 124.8, 122.9, 119.5, 89.0, 83.4, 45.4, 28.6, 21.0 ppm; IR (KBr) ν 1767, 1684, 1597, 1479, 1449, 1368, 1198, 1161, 1103, 1009, 910, 756, 691 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}O_3Br + H]^+$ 447.0590, found 447.0593.

*2-(3-Oxo-1-phenylbutyl)phenyl Acetate (**3v**).* Petroleum ether/ethyl acetate 12:1, 80% yield (225 mg), yellow oil; ^1H NMR (300 MHz, $CDCl_3$,) δ 7.14−7.28 (m, 8H), 7.04 (d, J = 7.5 Hz, 2H), 4.77 (t, J = 7.5 Hz, 1H), 3.24, 3.18 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 3.10, 3.04 (dd, J = 6.6 Hz, J = 6.6 Hz, 1H), 2.22 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 169.1, 148.3, 142.6, 135.6, 128.5, 128.2, 127.7, 127.5, 126.5, 126.1, 123.0, 48.7, 39.6, 30.5, 20.9 ppm; IR (KBr) ν 1759, 1708, 1489, 1448, 1371, 1207, 1112, 1014, 916, 823, 771, 756, 702, 667 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{19}O_3 + H]^+$ 283.1334, found 283.1328.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all compounds and crystallographic data of compound **3j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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