A Room-Temperature, Copper-Catalyzed Cascade Process for Diethyl 2-Aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylate

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Abstract: A room-temperature cascade process for the formation of diethyl 2-aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylate is described by using a combination of Michael addition and copper-catalyzed α-arylation of malonic acid derivatives. The protocol worked well for a variety of 1-(2-iodoaryl)enones and displayed great functional group compatibility.

Key words: Michael addition, copper, catalysis, cascade reactions, α-arylation

3-Aryl-3,4-dihydronaphthalen-1(2*H*)-ones, also known as γ-aryl-α-tetralones, are important intermediates for the synthesis of the rodenticide flocoumafen and many other bioactive dihydro- or tetrahydronaphthalenic compounds.[1] Intramolecular Friedel–Crafts acylation is the classical method for synthesizing this class of compounds.[1,2] However, this approach is only suitable for a limited range of precursors and/or gives low yields.

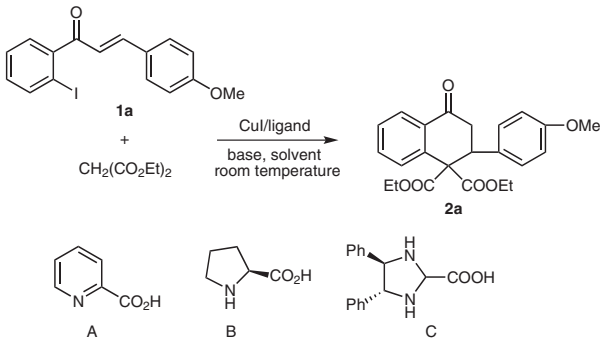
Copper-catalyzed arylation of malonates and their derivatives represents one of the most efficient methods available for the construction of C–C bonds. However, the original protocol shares similar deficiencies to those found with Ullmann chemistry, in that high temperatures and stoichiometric amounts of copper complex are required, and the reactions are sometimes difficult to reproduce.[3,4] In recent years, great advances have been achieved in copper-catalyzed Ullmann-type reactions[5] and the optimized processes under mild conditions have been successfully applied to the synthesis of α-aryl malonates.[6,7] More significantly, the reaction had been reported to proceed at room temperature.[7d]

In this paper, we would like to report a feasible method for the synthesis of 3-aryl-3,4-dihydronaphthalen-1(2*H*)-one derivatives by using a one-pot cascade process that combines a Michael addition reaction[8] and room-temperature, copper-catalyzed C–C bond formation.

The study was initiated by an investigation into the potential cascade reaction of unsaturated ketone **1a** with diethyl malonate under the catalysis of copper(I) iodide (Table 1).

Although no desired product was detected in the absence of copper salts, we were pleased to find that product **2a** was obtained with 5% yield under the catalysis of 10 mol% CuI at room temperature using sodium hydroxide as the necessary base (Table 1, entry 1). Further investigation revealed that supporting ligands, such as picolinic acid[7d] and L-proline[7c] could significantly improve the reaction efficiency (Table 1, entries 2 and 3). When *trans*-

Table 1 A Copper-Catalyzed Cascade Process for the Formation of Diethyl 2-Aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylates[a]



Entry	Ligand	Base	Solvent	Yield (%)[b]
1	–[c]	NaOH	DMSO	5
2	A	NaOH	DMSO	50
3	B	NaOH	DMSO	45
4	C	NaOH	DMSO	85
5	C	NaOH	dioxane	75
6	C	NaOH	DMF	20
7	C	NaOH	toluene	n.d.[d]
8	C	K_2CO_3	DMSO	n.d.[d]
9	C	K_3PO_4	DMSO	40
10	C	Cs_2CO_3	DMSO	76

[a] Reaction conditions: **1** (0.5 mmol), diethyl malonate (0.6 mmol), CuI (0.05 mmol), ligand (0.1 mmol), base (1.25 mmol), r.t., 3 h.
[b] Isolated yield.
[c] No ligand.
[d] No desired product was detected.

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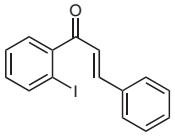
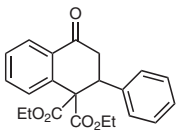
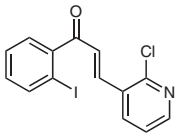
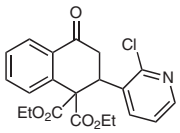
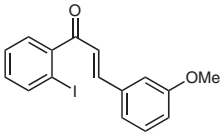
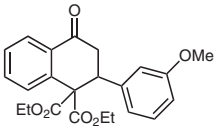
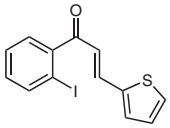
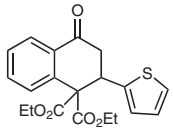
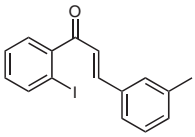
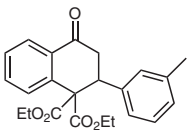
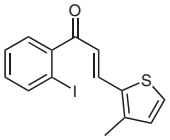
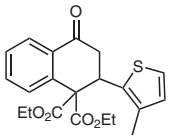
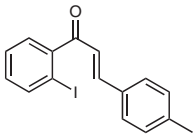
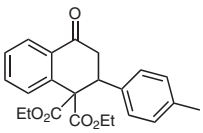
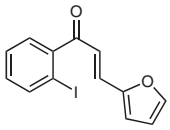
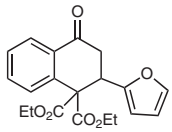
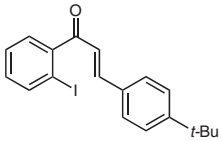
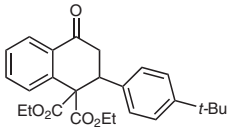
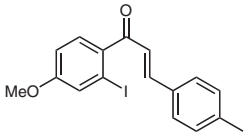
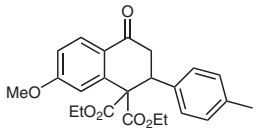
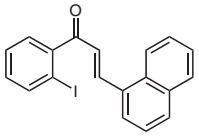
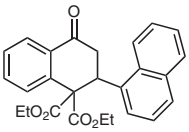
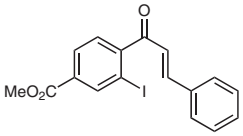
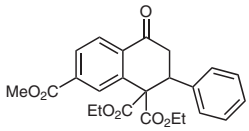
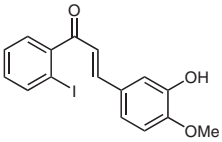
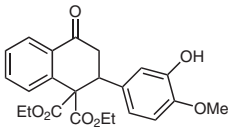
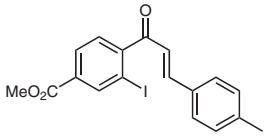
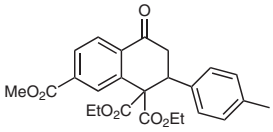
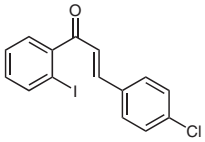
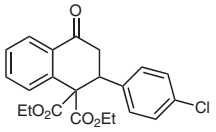
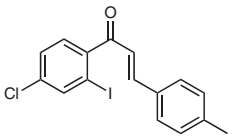
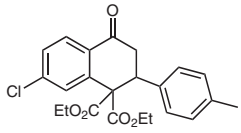
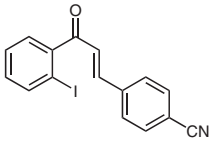
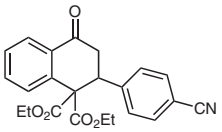
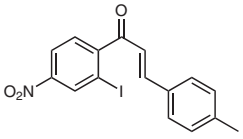
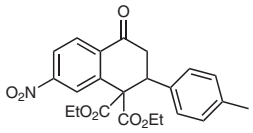
Table 2 Scope of 1-(2-Iodoaryl)enone Substrates for the Formation of Diethyl 2-Aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylate[a]

Entry	Aryl iodide	Product	Yield (%)[b]	Entry	Aryl iodide	Product	Yield (%)
1	 **1b**	 **2b**	68	10	 **1k**	 **2k**	50[c]
2	 **1c**	 **2c**	62	11	 **1l**	 **2l**	87
3	 **1d**	 **2d**	65	12	 **1m**	 **2m**	67
4	 **1e**	 **2e**	82	13	 **1n**	 **2n**	63
5	 **1f**	 **2f**	87	14	 1o	 **2o**	68
6	 **1g**	 **2g**	40[c]	15	 **1p**	 **2p**	75
7	 **1h**	 **2h**	42[c]	16	 **1q**	 **2q**	82
8	 **1i**	 **2i**	75	17	 **1r**	 **2r**	73
9	 **1j**	 **2j**	32	18	 **1s**	 **2s**	60

[a] Reaction conditions: **1** (0.5 mmol), diethyl malonate (0.6 mmol), CuI (0.05 mmol), ligand C (0.1 mmol), NaOH (1.25 mmol), r.t., 3 h.
[b] Isolated yield.
[c] Reaction time 10 h.

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4,5-diphenylimidazolidine-2-carboxylic acid (ligand **C**) was used as the supporting ligand, about 85% of the desired product was isolated when the reaction was performed at room temperature for three hours (Table 1, entry 4). Ligand **C** was also recognized as an efficient organocatalyst for the Michael addition reaction.[9] A screening of the reaction medium suggested that dimethylsulfoxide (DMSO) was the optimal solvent for the new cascade reaction. Other solvents, such as 1,4-dioxane and *N*,*N*-dimethylformamide (DMF), gave significantly lower isolated yields (Table 1, entries 5 and 6). When the reaction was carried out in the nonpolar solvent toluene, almost no desired product was detected (Table 1, entry 7). When a range of bases were also evaluated, it was found that Cs_2CO_3 was also a suitable base for the cascade reaction (Table 1, entries 4 and 8–10), however, sodium hydroxide was chosen as the optimal base for further studies because of its economic efficiency.

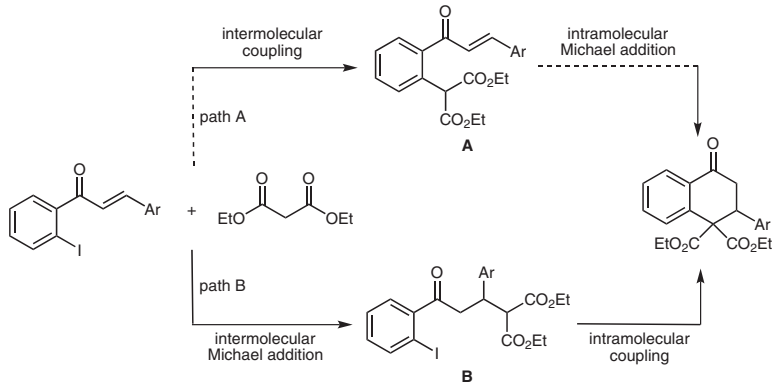
The scope of this new protocol was further explored by combining diethyl malonate with a variety of 1-(2-iodoaryl)enones under the optimized conditions. As shown in Table 2, almost all the tested combinations successfully produced the desired products with moderate to excellent isolated yields. However, the substrate bearing a free hydroxy group on the phenyl ring delivered the corresponding product with significantly lower yield (Table 2, entry 7), which might be due to the acidity of the hydroxy group. The results indicated that the electronic nature of the aromatic ring directly linked to the double bond had a clear influence on the cascade reaction. When the aromatic ring carried an electron-donating group, such as methyl, methoxy or *tert*-butyl group etc, the desired product was produced with excellent to good yields (Table 2, entries 1–5). However, when the phenyl ring possessed an electron-withdrawing nitrile group, only 32% of the corresponding product was isolated (Table 2, entry 9). The steric effect of the aromatic ring directly linked to the double bond also had some influence on the reaction. For instance, substrates with greater steric hindrance (Table 2, entry 6 and 10) gave significantly lower isolated yield. The results also showed that the electronic density of the iodo-substituted phenyl ring had little effect on the cascade process. Almost all of the tested substrates bearing electron-donating or electron-withdrawing groups produced the desired products with excellent or good yields (Table 2, entries 14–18).

It is worth noting that the reactions also performed well for enones with heteroaryl substituents (Table 2, entries 10–13). All the substrates possessing heteroaryl substitutions produced the desired products with good or moderate yields under similar conditions.

A mechanism of this copper-catalyzed cascade reaction is proposed in Scheme 1. 1-(2-Iodoaryl)enones may react with diethyl malonate to produce the diethyl 2-aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylate product through two different pathways. One is through copper-catalyzed intermolecular C–C coupling between the diethyl malonate and aryl iodides first, followed by an intramolecular Michael addition. The second possibility is that diethyl malonate first reacts with the enone to produce the Michael addition product **B**, and subsequent copper-catalyzed intramolecular C–C coupling reaction yields the desired product. Since Michael addition is more favored under mild conditions than the copper-catalyzed C–C coupling reactions, we propose that pathway B might be more reasonable; this hypothesis was confirmed by the isolation of the intermediate **B**, which can be obtained either under ligand-free conditions as the major product in our model reaction, or by quenching the CuI/ligand supporting system before the reaction had reached completion. The isolated intermediate **B** can be further transformed into the final product under the CuI/ligand supporting conditions.

In summary, we have demonstrated a simple and flexible cascade process for preparing diethyl 2-aryl-3,4-dihydro-4-oxo-1,1(2*H*)-naphthalenedicarboxylates from easily available 1-(2-iodoaryl)enones and diethyl malonate. The protocol worked well for a variety of 1-(2-iodoaryl)enones and displayed great functional group compatibility. Our new protocol will greatly facilitate the synthesis of γ-aryl-α-tetralone-derivatives and should find many applications in the future.

All the 2-iodoaryl enones were made from 2-iodoaryl ketones and corresponding aryl aldehydes, which were commercially available from Aldrich, TCI and ACROS. The starting materials and products were confirmed by NMR and mass spectral analysis.



Scheme 1 The proposed mechanism of the copper-catalyzed cascade reaction

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Synthesis of Substrate 1; General Procedure

2-Iodoaryl acetone (10 mmol), aryl aldehyde (10 mmol), 15% NaOH (20 mL) and MeOH (20 mL) were added together and stirred at r.t. for 3 h. After the reaction was complete, EtOAc (20 mL) and H_2O (10 mL) were added. The organic phase was separated, dried over Na_2SO_4 and evaporated under vacuum. The substrate **1** was separated by silica gel column chromatography (EtOAc–PE, 1:50).

Synthesis of 2a–s; General Procedure

1-(2-Iodoaryl) enone **1** (0.5 mmol), base (1.0 mmol), CuI (0.05 mmol) and solvent (1 mL) were added together into a reacting tube. Diethyl malonate (0.6 mmol) was slowly added and the mixtures were stirred at r.t. under the protection of a nitrogen atmosphere. The reaction was monitored by TLC. Upon completion, EtOAc (10 mL) and H_2O (5 mL) were added to the reaction mixture and the organic phase was separated, dried over Na_2SO_4 and evaporated in vacuum. The residues were loaded onto a silica gel column and purified (EtOAc–PE, 1:15) to obtain the final products **2**.

Diethyl 2-(4-Methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2a)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 4.27 (t, *J* = 6.0 Hz, 1 H), 4.22–4.10 (m, 2 H), 4.01–3.93 (m, 2 H), 3.92 (s, 3 H), 3.52 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.15 (dd, *J* = 6.0, 17.2 Hz, 1 H), 1.21 (t, *J* = 6.8 Hz, 3 H), 1.06 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.1, 169.6, 168.5, 159.0, 137.9, 133.2, 132.6, 131.9, 131.8, 129.9, 128.5, 126.6, 113.7, 62.6, 62.1, 61.6, 55.1, 45.9, 42.4, 13.8, 13.7.

ESI-MS: *m*/*z* = 397.1 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{25}O_6$: 397.1651; found: 397.1650.

Diethyl 4-Oxo-2-phenyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2b)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 8.4 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.19–7.16 (m, 3 H), 7.09–7.06 (m, 2 H), 4.32 (t, *J* = 5.6 Hz, 1 H), 4.23–4.10 (m, 2 H), 3.98–3.92 (m, 2 H), 3.56 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.19 (dd, *J* = 6.4, 17.2 Hz, 1 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 1.03 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.0, 169.6, 168.5, 139.8, 137.8, 133.3, 132.6, 131.9, 128.8, 128.5, 128.3, 127.6, 126.6, 62.3, 62.2, 61.6, 46.7, 42.2, 13.7, 13.6.

ESI-MS: *m*/*z* = 367.1 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{23}O_5$: 367.1545; found: 367.1540.

Diethyl 2-(3-Methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2c)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 6.65–6.62 (m, 2 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.23–4.10 (m, 2 H), 4.00–3.94 (m, 2 H), 3.65 (s, 3 H), 3.55 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.17 (dd, *J* = 6.0, 17.2 Hz, 1 H), 1.20 (t, *J* = 6.8 Hz, 3 H), 1.04 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.9, 169.5, 168.4, 159.4, 141.3, 137.7, 133.2, 132.6, 131.9, 129.3, 128.5, 126.6, 121.0, 114.8, 112.9, 62.2, 61.6, 55.0, 46.7, 42.2, 13.7, 13.6.

ESI-MS: *m*/*z* = 397.0 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{25}O_6$: 397.1651; found: 397.1650.

Diethyl 4-Oxo-2-*m*-tolyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2d)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, *J* = 7.6 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.06–6.98 (m, 2 H), 6.91 (s, 1 H), 6.86 (d, *J* = 7.6 Hz, 1 H), 4.28 (t, *J* = 6.0 Hz, 1 H), 4.23–4.12 (m, 2 H), 3.99–3.93 (m, 2 H), 3.53 (dd, *J* = 6.0, 17.2 Hz, 1 H), 3.19 (dd, *J* = 6.0, 17.2 Hz, 1 H), 2.23 (s, 3 H), 1.20 (t, *J* = 6.8 Hz, 3 H), 1.04 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.0, 169.6, 168.4, 139.7, 137.9, 137.7, 133.2, 132.6, 131.8, 129.7, 128.5, 128.3, 128.2, 126.6, 125.7, 62.4, 62.1, 61.5, 46.6, 42.1, 21.3, 13.7, 13.6.

ESI-MS: *m*/*z* = 381.1 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{25}O_5$: 381.1702; found: 381.1699.

Diethyl 4-Oxo-2-*p*-tolyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2e)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 6.99–6.94 (m, 4 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.23–4.12 (m, 2 H), 4.01–3.92 (m, 2 H), 3.54 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.17 (dd, *J* = 6.4, 17.2 Hz, 1 H), 2.21 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.06 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.1, 169.6, 168.5, 137.8, 137.2, 136.7, 133.2, 132.7, 131.8, 128.9, 128.6, 128.5, 126.6, 62.5, 62.1, 61.6, 46.3, 42.2, 20.9, 13.7, 13.6.

ESI-MS: *m*/*z* = 381.1 $[M + H]^+$.

HR-MS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{25}O_5$: 381.1702; found: 381.1703.

Diethyl 2-(4-*t*-Butylphenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2f)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.50 (t, *J* = 7.2 Hz, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 4.29 (t, *J* = 5.6 Hz, 1 H), 4.23–4.11 (m, 2 H), 3.96 (q, *J* = 7.2 Hz, 1 H), 3.53 (dd, *J* = 6.0, 17.2 Hz, 1 H), 3.19 (dd, *J* = 6.4, 17.2 Hz, 1 H), 1.23 (s, 9 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 0.98 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.2, 169.6, 168.6, 150.4, 137.8, 136.6, 133.2, 132.7, 131.9, 128.5, 128.4, 126.6, 125.2, 62.4, 62.1, 61.6, 46.3, 42.2, 34.3, 14.0, 13.7, 13.5.

ESI-MS: *m*/*z* = 423.1 $[M + H]^+$.

HR-MS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{31}O_5$: 423.2171; found: 423.2165.

Diethyl 4′-Oxo-3′,4′-dihydro-1,2′-binaphthyl-1′,1′(2′*H*)-dicarboxylate (2g)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.19–8.13 (m, 2 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.72–7.64 (m, 2 H), 7.58–7.48 (m, 3 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 5.42–5.39 (m, 1 H), 4.24–4.13 (m, 2 H), 3.88 (dd, *J* = 6.4, 16.8 Hz, 1 H), 3.72–3.63 (m, 2 H), 3.10 (dd, *J* = 3.2, 16.8 Hz, 1 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 0.56 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 197.9, 171.8, 170.8, 139.1, 138.0, 136.2, 135.4, 134.7, 133.4, 131.3, 130.7, 130.1, 128.8, 128.5, 127.7, 127.3, 127.2, 124.7, 64.6, 63.7, 63.3, 44.5, 41.9, 15.9, 15.2.

ESI-MS: *m*/*z* = 417.1 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{25}O_5$: 417.1702; found: 417.1706.

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Diethyl 2-(3-Hydroxy-4-methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2h)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.4 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 6.69 (s, 1 H), 6.63 (d, *J* = 8.4 Hz, 1 H), 6.53 (d, *J* = 8.4 Hz, 1 H), 5.53 (s, 1 H), 4.24–4.11 (m, 3 H), 4.03–3.81 (m, 2 H), 3.80 (s, 3 H), 3.52 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.14 (dd, *J* = 6.0, 17.2 Hz, 1 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.0, 169.6, 168.4, 145.9, 145.3, 137.8, 133.2, 133.0, 132.6, 131.8, 128.5, 126.6, 120.2, 115.5, 110.5, 62.5, 62.1, 61.6, 55.8, 46.1, 42.3, 13.7, 13.6.

ESI-MS: *m*/*z* = 413.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{25}O_7$: 413.1600; found: 413.1591.

Diethyl 2-(4-Chlorophenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2i)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.22–4.13 (m, 2 H), 4.02–3.94 (m, 2 H), 3.51 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.17 (dd, *J* = 6.4, 17.2 Hz, 1 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.07 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.5, 169.4, 168.3, 138.2, 137.7, 133.6, 133.4, 132.5, 131.7, 130.2, 128.6, 128.5, 126.8, 62.3, 62.2, 61.7, 46.2, 41.9, 13.7, 13.6.

ESI-MS: *m*/*z* = 401.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{22}ClO_5$: 401.1156; found: 401.1150.

Diethyl 2-(4-Cyanophenyl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2j)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.70–7.63 (m, 2 H), 7.54–7.49 (m, 3 H), 7.25–7.24 (m, 2 H), 4.36 (t, *J* = 6.0 Hz, 1 H), 4.22–4.16 (m, 2 H), 4.01–3.95 (m, 2 H), 3.51 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.19 (dd, *J* = 6.8, 17.2 Hz, 1 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.05 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.9, 169.2, 168.1, 145.0, 137.5, 133.6, 132.3, 131.6, 130.0, 128.9, 126.9, 118.3, 111.8, 62.4, 62.2, 61.9, 46.7, 41.6, 13.7, 13.6.

ESI-MS: *m*/*z* = 392.0 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{22}NO_5$: 392.1498; found: 392.1491.

Diethyl 2-(2-Chloropyridin-3-yl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2k)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.21 (s, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.70 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 6.94–6.91 (m, 1 H), 5.01–4.99 (m, 1 H), 4.29–3.74 (m, 2 H), 4.01 (q, *J* = 7.2 Hz, 2 H), 3.74 (dd, *J* = 5.6, 16.8 Hz, 1 H), 3.02 (dd, *J* = 2.8, 17.2 Hz, 1 H), 1.09 (t, *J* = 7.2 Hz, 3 H), 0.97 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.9, 168.7, 168.4, 151.4, 148.3, 137.5, 136.4, 134.3, 133.5, 132.9, 132.3, 128.9, 126.7, 122.3, 62.6, 62.1, 60.4, 41.9, 41.1, 13.7, 13.5.

ESI-MS: *m*/*z* = 402.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}ClNO_5$: 402.1108; found: 402.1103.

Diethyl 4-Oxo-2-(thiophen-2-yl)-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2l)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.14–7.12 (m, 1 H), 6.91 (s, 1 H), 6.79 (d, *J* = 5.2 Hz, 1 H), 4.48 (t, *J* = 6.0 Hz, 1 H), 4.27–4.12 (m, 2 H), 4.04 (q, *J* = 7.2 Hz, 2 H), 3.51 (dd, *J* = 5.2, 17.2 Hz, 1 H), 3.14 (dd, *J* = 5.2, 17.2 Hz, 1 H), 1.22 (t, *J* = 6.8 Hz, 1 H), 1.08 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.9, 169.5, 168.4, 139.9, 137.6, 133.3, 132.4, 131.8, 128.6, 128.0, 126.7, 125.3, 123.3, 62.4, 62.2, 61.7, 42.1, 42.0, 13.8, 13.7.

ESI-MS: *m*/*z* = 373.0 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}O_5S$: 373.1110; found: 373.1108.

Diethyl 2-(3-Methylthiophen-2-yl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2m)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 4.8 Hz, 1 H), 6.68 (d, *J* = 4.8 Hz, 1 H), 4.77 (t, *J* = 5.2 Hz, 1 H), 4.27–3.95 (m, 4 H), 3.61 (dd, *J* = 5.6, 17.6 Hz, 1 H), 3.04 (dd, *J* = 4.4, 17.6 Hz, 1 H), 2.19 (s, 3 H), 1.94 (t, *J* = 7.2 Hz, 3 H), 1.12 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.2, 169.3, 168.4, 136.8, 135.6, 134.9, 133.3, 132.7, 132.4, 128.7, 126.7, 123.8, 62.2, 62.0, 61.8, 42.9, 40.0, 13.8, 13.7, 13.6.

ESI-MS: *m*/*z* = 387.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}O_5S$: 387.1266; found: 387.1267.

Diethyl 2-(Furan-2-yl)-4-oxo-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2n)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, *J* = 7.6 Hz, 1 H), 7.62–7.56 (m, 2 H), 7.48–7.44 (m, 1 H), 7.21 (s, 1 H), 6.21–6.19 (m, 1 H), 6.00 (s, 1 H), 4.47 (t, *J* = 5.6 Hz, 1 H), 4.33–4.17 (m, 2 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 3.46 (dd, *J* = 5.2, 17.6 Hz, 1 H), 3.06 (dd, *J* = 6.8, 17.6 Hz, 1 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.1, 169.2, 168.3, 153.0, 141.8, 137.4, 133.2, 132.1, 131.2, 128.5, 126.7, 110.2, 107.8, 62.3, 62.0, 61.9, 40.0, 39.7, 13.8, 13.7.

ESI-MS: *m*/*z* = 357.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}O_6$: 357.1338; found: 357.1336.

Diethyl 7-Methoxy-4-oxo-2-*p*-tolyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2o)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, *J* = 8.8 Hz, 1 H), 7.20 (s, 1 H), 7.03–6.97 (m, 5 H), 4.28–4.15 (m, 3 H), 4.05–3.95 (m, 2 H), 3.91 (s, 3 H), 3.51 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.11 (dd, *J* = 6.0, 17.2 Hz, 1 H), 2.27 (s, 3 H), 1.25 (t, *J* = 6.8 Hz, 3 H), 1.10 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.9, 169.5, 168.4, 163.4, 139.8, 137.1, 136.8, 129.0, 128.9, 128.6, 126.4, 116.5, 114.7, 62.6, 62.1, 61.6, 55.5, 46.3, 41.9, 20.9, 13.8, 13.6.

ESI-MS: *m*/*z* = 411.1 [M + H]$^+$.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}O_6$: 411.1808; found: 411.1804.

1,1-Diethyl 7-Methyl 4-Oxo-2-phenyl-3,4-dihydronaphthalene-1,1,7(2*H*)-tricarboxylate (2p)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.42 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.18–7.16 (m, 3 H), 7.05–7.03 (m, 2 H), 4.35 (t, *J* = 5.6 Hz, 1 H), 4.26–4.13 (m, 2 H), 3.99–3.93 (m, 5 H), 3.58 (dd, *J* = 5.6, 17.2 Hz, 1 H), 3.20 (dd, *J* = 6.0, 17.2 Hz, 1 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.02 (t, *J* = 7.2 Hz, 3 H).

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^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.4, 169.2, 168.1, 166.0, 139.4, 137.9, 135.4, 134.2, 133.5, 129.2, 128.7, 128.4, 127.7, 126.7, 62.4, 62.2, 61.8, 52.4, 46.5, 42.3, 13.7, 13.5.

ESI-MS: *m/z* = 425.1 $[M + H]^+$.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{24}H_{25}O_7$: 425.1600; found: 425.1602.

1,1-Diethyl 7-Methyl 4-oxo-2-*p*-tolyl-3,4-dihydronaphthalene-1,1,7(2*H*)-tricarboxylate (2q)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.41 (s, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 8.98 (d, *J* = 8.0 Hz, 2 H), 8.93 (d, *J* = 8.0 Hz, 2 H), 4.32 (t, *J* = 6.0 Hz, 1 H), 4.25–4.15 (m, 2 H), 4.02–3.92 (m, 5 H), 3.56 (dd, *J* = 5.6, 17.6 Hz, 1 H), 3.17 (dd, *J* = 6.0, 17.2 Hz, 1 H), 2.24 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.06 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.5, 169.2, 168.1, 166.0, 138.0, 137.3, 136.3, 135.4, 134.2, 133.5, 129.2, 129.1, 128.5, 126.7, 62.3, 61.8, 52.4, 46.1, 42.4, 20.8, 13.7, 13.6.

ESI-MS: *m/z* = 439.1 $[M + H]^+$.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{27}O_7$: 439.1757; found: 439.1749.

Diethyl 7-Chloro-4-oxo-2-*p*-tolyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2r)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.09 (d, *J* = 8.4 Hz, 1 H), 7.73 (s, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 7.6 Hz, 2 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 4.29 (t, *J* = 6.0 Hz, 1 H), 4.24–4.15 (m, 2 H), 4.03–3.93 (m, 2 H), 3.54 (dd, *J* = 6.0, 17.2 Hz, 1 H), 3.12 (dd, *J* = 6.0, 17.2 Hz, 1 H), 2.25 (s, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.08 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.9, 169.0, 167.9, 139.7, 139.2, 137.4, 136.4, 132.0, 131.1, 129.1, 129.0, 128.5, 128.1, 62.4, 62.2, 61.8, 46.2, 42.1, 20.9, 13.7, 13.6.

ESI-MS: *m/z* = 415.0 $[M + H]^+$.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{24}ClO_5$: 415.1312; found: 415.1307.

Diethyl 7-Nitro-4-oxo-2-*p*-tolyl-3,4-dihydronaphthalene-1,1(2*H*)-dicarboxylate (2s)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.66 (s, 1 H), 8.29 (s, 1 H), 6.98 (d, *J* = 7.6 Hz, 2 H), 6.87 (d, *J* = 7.6 Hz, 2 H), 4.37 (t, *J* = 7.2 Hz, 1 H), 4.28–4.14 (m, 2 H), 4.05–3.95 (m, 2 H), 3.64 (dd, *J* = 6.0, 17.2 Hz, 1 H), 3.16 (dd, *J* = 6.0, 17.2 Hz, 1 H), 2.24 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.08 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.5, 168.5, 167.7, 150.4, 139.2, 137.7, 136.5, 135.9, 129.2, 128.4, 127.9, 127.8, 123.1, 62.8, 62.2, 62.1, 45.9, 42.4, 20.8, 13.7, 13.6.

ESI-MS: *m/z* = 426.1 $[M + H]^+$.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{24}NO_7$: 426.1553; found: 426.1545.

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