Synthesis H.-C. Tai et al. Special Topic

Nucleophilic Conjugate 1,5-Addition of Gilman Reagents to (*E*)-Hex-2-en-4-ynedioates: An Access to β(γ′)-Substituted Muconates

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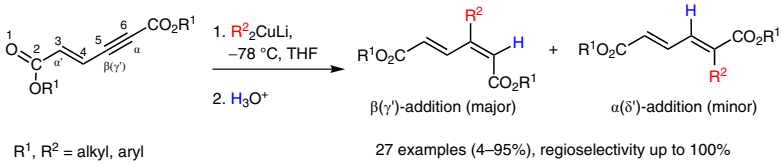

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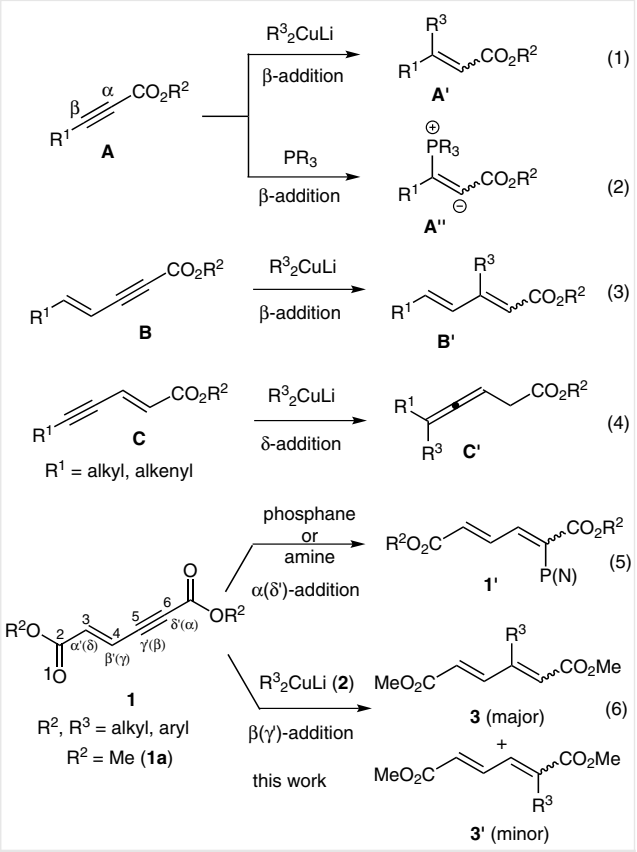
Abstract An unusual nucleophilic conjugate addition of organocuprates to enynedioates resulted in chemo- and regioselective formation of β(γ′)-addition products, rather than α(δ′)-addition products, in moderate to good yields. This addition pattern is different from that with organophosphanes or alkyl amines, and presents a short and efficient method for the preparation of various β(γ′)-alkyl- or -aryl-substituted muconates compared with other synthetic approaches.

Key words addition reactions, alkynes, cuprates, multicomponent reactions, regioselectivity

Nucleophilic conjugate addition is a powerful method for the formation of C–C bonds.[1] Nucleophiles are known to undergo regioselective addition to π-conjugated systems.[2] Since their discovery in 1952 by Gilman et al.,[3] the coinage transition-metal-based reagents organocuprates have played a significant role in selective organic transformations through conjugate addition.[4] Because of their nucleophilic character, organocuprates are widely used in conjugate additions with various electrophilic substrates for syntheses of biologically active natural or synthetic products.[5] Organocuprates generally show high regio- and stereoselectivity toward Michael acceptors in 1,4-conjugate addition reactions. They also show an unusual reactivity towards various highly conjugated alkenoates and alkynoates that depends on the nature and the position of the activating group on the activated conjugate system.[6] For example, alkynoates **A** give the corresponding 1,4-conjugate addition products **A′** with organocuprates $R^3{}_2CuLi$ through carbocupration and subsequent protonation (Scheme 1, path 1).[7] In a similar fashion, phosphanes also undergo a similar 1,4-conjugate addition with alkynoates **A** and form the zwitterions **A″** (path 2).[8] Interestingly, enynoates **B** with an electron-withdrawing alkenyl substituent on the alkynoate triple bond react with organocuprates by chemoselective 1,4-addition to give conjugated dienes **B′** (path 3),[9] whereas those with the reversed enyne moiety, namely the ynenoates **C**, give allenes **C′** through 1,6-addition (path 4).[10] Gilman reagents show chemoselective reactivity toward enynes **B** and **C**, reacting at the alkynyl carbon. However, to the best of our knowledge, there is no direct experimental evidence that explains the nucleophilic conjugate addition patterns of enynes **B** and **C** with Gilman and phosphane reagents. In a recent report, we could only suggest a putative β-addition mechanism for the addition of phosphanes to enynes **C**,[11] because it was not possible to isolate any intermediates of the reaction.

We and others have observed that phosphane nucleophiles attack the α(δ′)-carbon of dimethyl (2*E*)-hex-2-en-4-ynedioate (**1a**)[12] (Scheme 1, path 5) and diynedioates,[13] as well as undergoing α-addition to oligoynoates.[14] The addition to enynedioates **1** can be considered as a 1,6-addition because the alkenoate ester has a higher numbering priority in IUPAC nomenclature. On the basis of a previous study, we predicted that reactions of enynedioates **1** with Gilman nucleophiles should provide allenes through 1,6-addition as that of **C** to give **C′** – the same addition pattern of **1** with phosphanes and amines (path 5). To our surprise, the chemical reactivity of enynedioates **1** toward Gilman nucleophiles differed from that of **C**. Here, we report that with enynedioates **1** predominantly undergo nucleophilic attack by organocuprates at the β(γ′)-carbon rather than the α(δ′)-carbon, in contrast with the addition pattern with phosphanes or amines. This reaction results in direct regioselective formation of β(γ′)-alkyl- or -aryl-substituted muconates (Scheme 1, path 6). According to the IUPAC nomenclature system, the addition pattern is 1,5-addition, because the numbering starts with the higher priority on the alke-



Scheme 1 Addition patterns of nucleophilic reagents to alkynoates (**A**), eneynoates (**B**), ynenoates (**C**), and enynedioates (**1**)

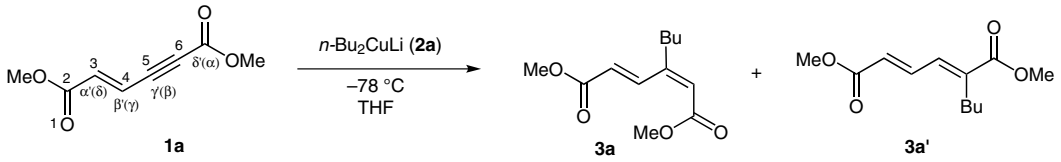
nyl moiety. The 1,5-addition terminology that is used corresponds to nucleophilic attack at C5 for the carbon numbering of enynedioates **1**, although it is a 1,4-addition with respect to the proximate alkynoate moiety. Because the resulting 1,3-diene muconates are important building blocks for the synthesis of various natural or synthetic products,[15] and the related muconic acids and their derivatives are important chemical intermediates in the polymer industry,[16] the unusual β(γ′)-alkyl or -aryl-substituted muconates are valuable synthetic intermediates for our conjugate 1,5-addition method. Previous methods for the synthesis of relevant alkyl- or aryl-substituted muconate derivatives include oxidation of catechol derivatives,[17] ruthenium-catalyzed addition of carbenes to alkynes,[18] ruthenium-catalyzed hydrovinylation of alkynes by acrylates,[19] rhodium-catalyzed codimerization of alkenes and electron-deficient internal alkynes,[20] halogenation/dehydrohalogenation of adipic acid derivatives,[21] and metal-catalyzed cross-coupling of acrylates.[22]

To optimize the conditions for the reaction, we choose dimethyl (2*E*)-hex-2-en-4-ynedioate (**1a**) as a model substrate and lithium dibutylcuprate (**2a**) as an organocuprate reagent. Tuning the conditions to achieve an addition reaction of enynedioate **1a** with Gilman reagents is not a trivial matter, because **1a** is quite reactive toward nucleophiles. We examined the effects of the stoichiometric ratio of the organocuprate, the concentration of the reaction mixture, and the reaction time on the regio- and chemoselectivity of the reaction. In a preliminary study in which enynedioate **1a** (0.040 M) was treated with 0.5 equivalents of Gilman reagent **2a** in tetrahydrofuran at –78 °C for one hour (Table 1, entry 1), we obtained a 12% yield of a 1:1 mixture of the 1,5-addition [β(γ′)-addition] and 1,6-addition [α(δ′)-addition] products **3a** and **4a**, respectively, with no regioselectivity. When we prolonged the reaction time to two hours (entry 2), the combined yield of the addition products improved to 18%. Under these reaction conditions, however, we observed a slight shift in the regioselectivity from β(γ′)-addition to α(δ′)-addition. Next, we carried out the reaction for 16 hours until the enynedioate **1a** was completely consumed (entry 3). This produced no improvement in the yield of the products, but the β(γ′)-addition product **3a** was formed in larger amounts than the α(δ′)-addition product **4a**. Having obtained these anomalous results, we performed other experiments with 0.7 or 1.0 equivalent of Gilman reagent **2a** under identical conditions for two hours (entries 4 and 5). This resulted in an increase in the yield to 33% with a small change in regioselectivity. The low yield of the reaction and the negligible recovery of the starting material prompted us to reduce the concentration of the reaction mixture, because dark materials, probably formed by polymerization, were observed in entries 1–5. The reaction of 1.19 mmol of enynedioate **1a** (0.024 M) with one equivalent of Gilman reagent **2a** in tetrahydrofuran (50 mL) for two hours gave a 50% yield in several experiments and provided products **3a** and **4a** in a ratio of 73:27 (entry 6). Further dilution of the reaction mixture resulted in poor product formation, with recovery of the starting material (entry 7). To our delight, however, we isolated a 58% yield of products with a low recovery of **1a** when we reduced the reaction time to 30 minutes (entry 8). We then examined the effects of further increases in the amount of the organocuprate and of reductions in the reaction time (entries 9–11, 13, and 15). With 1.5 equivalents of the organocuprate and a reaction time of ten minutes, we obtained a 75% yield of products with predominant formation of the β(γ′)-addition product **3a**. Prolonging the reaction with 1.5–2 equivalents of organocuprate resulted in the formation of the β(γ′)-addition product **3a**, but the overall yield was comparatively low (entries 12, 14, and 16). Addition of hexamethylphosphoramide was not effective in increasing the yield, as it gave the β(γ′)-addition product **3a** in only 29% yield (entry 17). We also carried out the reaction with 1.2 equivalents of the Grignard reagent methylmagnesium bromide in the presence of lithium and copper salts (entry 18). In this experiment, the β(γ′)-addition product **3a** was obtained, but in a very low yield (13%). In summary, therefore, we found that the yield of the reaction was highly dependent on the

concentration of the enynedioate and the reaction time. The best yield of the β(γ′)-addition product was obtained with 1.19 mmol of enynedioate **1a** and 1.5 equiv of organocuprate reagent in 50 mL of THF (0.024 M concentration with respect to the enyne) at –78 °C for 10 min. We therefore chose these reaction conditions to examine the scope of the reaction. The β(γ′)- and α(δ′)-addition products, **3a** and **3a′**, were fully characterized by means of ^{1}H and NOE NMR spectroscopic techniques (see Supporting Information, Figure S1).

Next, we prepared a series of propiolate esters by *N*,*N*′-dicyclohexylcarbodiimide-induced coupling of propiolic acid and the appropriate alcohols, and we used the products to synthesize the conjugated enynedioates **1c**–**i** by means of 1,4-diazabicyclo[2.2.2]octane-catalyzed dimerization.[23] We then examined the scope of the 1,5-addition reaction of organocuprates **2** to enynedioates **1** under the optimized conditions (Table 2). Product yields were found to be highly dependent on the size of the Gilman reagent. When dimethyl (2*E*)-hex-2-en-4-ynedioate (**1a**) was treated with the methyl or phenyl Gilman reagents **2b** and **2c**, respectively, under the optimized reaction conditions, the corresponding β(γ′)-addition products **3b** and **3c** were obtained in 77% and 54% yield, respectively. In these two cases, no α(δ′)-addition product was formed (Table 2, entries 2 and 3). The stereochemistry of the methyl addition product was consistent with that of the butyl addition product (2*Z*,4*E*), whereas with in the case of the phenyl addition product, it changed to (2*E*,4*E*) because of the higher priority of the phenyl moiety over the alkenyl moiety in the product structure. We observed a decrease in the yield as the length of the alkyl chain in the ester was increased. The

Table 1 Optimization of the Reaction Conditions[a]

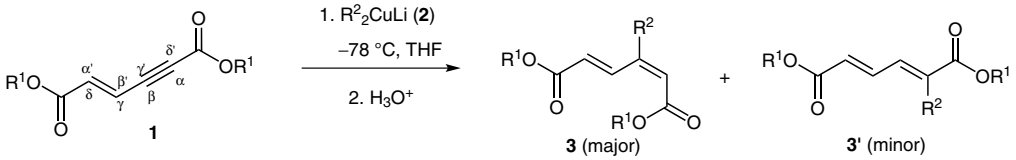


1a **3a** **3a'**

Entry	**2a** (equiv)	THF[b] (mL)	Concentration[c] (M) of **1a**	Time (h)	Yield[d,e] (%) of (**3a** + **3a′**)	Selectivity[f] [β(γ′)/α(δ′)]
1	0.5	30	0.040	1	12 (29)	50:50
2	0.5	30	0.040	2	18 (28)	44:56
3	0.5	30	0.040	16	14	64:36
4	0.7	30	0.040	2	31 (32)	56:45
5	1.0	30	0.040	2	33 (34)	62:38
6	1.0	50	0.024	2	50 (55)	73:27
7	1.0	100	0.012	2	27 (49)	44:56
8	1.0	50	0.024	0.5	58 (62)	66:34
9	1.25	50	0.024	0.5	59	82:18
10	**1.5**	**50**	0.024	**1/6**	**75**	**71:29**
11	1.5	50	0.024	0.5	75	88:12
12	1.5	50	0.024	1	59	100:0
13	1.75	50	0.024	0.5	67	85:15
14	1.75	50	0.024	1	61	100:0
15	2.0	50	0.024	0.5	69	92:8
16	2.0	50	0.024	1	68	100:0
17[g]	1.0	30	0.040	2	29	100:0
18[h]	1.2	50	0.024	1/6	13 (19)	100:0

[a] Reaction conditions: enynedioate **1a** (200 mg, 1.19 mmol), Bu_2CuLi (**2a**; 0.5–2.0 equiv) [prepared in situ from BuLi and CuI (2:1.1) in THF at –20 °C], THF, –78 °C.
[b] Total amount of solvent in the reaction mixture.
[c] Final molar concentration of enynedioate **1a** in the reaction mixture.
[d] Determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard.
[e] Yields in parentheses are based on the conversion of the starting materials.
[f] Determined spectroscopically by proton integration.
[g] HMPA (1.5 equiv) was added.
[h] Instead of Bu_2CuLi, a mixture of MeMgBr, LiBr/LiCl (1 equiv), and CuI (0.5 equiv) was added.

Table 2 Scope of the Reaction of Enynedioates **1** with Gilman Reagents **2**[a]



Entry	**1**; R^1	**2**; R^2	**3**	Yield[b,c] (%) of **3** + **3**′	Selectivity[d] (**3**/**3**′)
1	**1a**; Me	**2a**; Bu	**3a**	75	71:29
2	**1a**; Me	**2b**; Me	**3b**	77	100:0
3	**1a**; Me	**2c**; Ph	**3c**	54	100:0
4	**1b**; Et	**2a**	**3d**	52 (58)	67:33
5	**1b**; Et	**2b**	**3e**	81	100:0
6	**1b**; Et	**2c**	**3f**	31 (51)	100:0
7	**1c**; *n*-Bu	**2a**	**3g**	42	95:5[e]
8	**1c**; *n*-Bu	**2b**	**3h**	80	100:0
9	**1c**; *n*-Bu	**2c**	**3i**	11	100:0
10	**1d**; *n*-Hex	**2a**	**3j**	38	100:0
11	**1d**; *n*-Hex	**2b**	**3k**	80	100:0
12	**1d**; *n*-Hex	**2c**	**3l**	10	100:0
13	**1e**; *c*-Pent	**2a**	**3m**	56	100:0
14	**1e**; *c*-Pent	**2b**	**3n**	73 (84)	100:0
15	**1e**; *c*-Pent	**2c**	**3o**	11 (13)	100:0
16	**1f**; *c*-Hex	**2a**	**3p**	70	100:0
17	**1f**; *c*-Hex	**2b**	**3q**	63 (67)	100:0
18	**1f**; *c*-Hex	**2c**	**3r**	8 (9)	100:0
19	**1g**; Bz	**2a**	**3s**	30	100:0
20	**1g**; Bz	**2b**	**3t**	95	100:0
21	**1g**; Bz	**2c**	**3u**	4	100:0
22	**1h**; Ph	**2a**	**3v**	10	100:0
23	**1h**; Ph	**2b**	**3w**	69	100:0
24	**1h**; Ph	**2c**	**3x**	22	100:0
25	**1i**; 2-thienylmethyl	**2a**	**3y**	41	100:0
26	**1i**; 2-thienylmethyl	**2b**	**3z**	80	100:0
27	**1i**; 2-thienylmethyl	**2c**	**3aa**	14 (43)	100:0

[a] Reaction conditions: enynedioate **1** (1.19 mmol), THF (25 mL), R^2_2CuLi [1.5 equiv; prepared in situ from R^2Li and CuI (2:1.1) in THF (25 mL) at –20 °C], –78 °C, 10 min.
[b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard.
[c] Yields in parentheses are based on the conversion of the starting material.
[d] Determined spectroscopically by proton integration.
[e] The α(δ′)-addition product **3g**′ was not isolated because of its low yield.

methyl, ethyl, butyl, and hexyl esters **1a**, **1b**, **1c** and **1d**, respectively reacted with the butyl Gilman reagent **2a** to give the corresponding major β(γ′)-addition products **3a**, **3d**, **3g**, and **3j** in 75, 52, 42% and 38% yields, respectively (entries 1, 4, 7, and 10). Likewise, each enynedioate showed a similar reactivity trend toward the Gilman reagents **2a**–**c**; the yields decreased in the order Me > Bu > Ph for the substituent on the Gilman reagent (entries 1–3, 4–6, 7–9, and 10–12). Furthermore, the cycloalkyl enynedioates **1e** and **1f** showed similar reactivities toward Gilman reagents **2a**–**c** (entries 13–18); however, the methyl Gilman reagent **2b** gave the 1,5-addition product in a 70% yield (entry 16). The 1,5-addition pattern also occurred with the benzyl enynedioate **1g** and the phenyl enynedioate **1h** (entries 19–24); with Gilman reagent **2b**, these gave good addition yields of up to 95%. The thienylmethyl analogue **1i**, also underwent

addition in up to 80% yield (entries 25–27).The α(δ′)-addition products **3a′**, **3d′**, and **3g′** were obtained as byproducts when the butyl Gilman reagent **2a** was used (entries 1, 4 and 7, respectively), although the β(γ′)-addition products predominated in these cases.

According to the scope study, the methyl Gilman reagent **2b** and the phenyl Gilman reagent **2c** show high chemo- and regioselectivities toward β(γ′)-addition with enynedioates. The products were characterized by means of IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and their structures were confirmed by means of high-resolution mass spectrometry. The configuration of the C_α=C_β double bond was confirmed by nuclear Overhauser effect (NOE) experiments. Overall, the observed addition at C5 might be governed by a chelation-controlled process involving interaction of the proximate carbonyl group of the alkynoate with the copper ion; this mode of coordination could activate the 5-position to nucleophilic attack.

In conclusion, we have demonstrated a 1,5-addition [or β(γ′)-addition] of alkyl or aryl nucleophiles to dialkyl or diaryl (2*E*)-hex-2-en-4-ynedioates by using Gilman reagents. The conjugated enynedioates showed an unusual reactivity towards organocuprate reagents in comparison with organophosphane or alkyl amine nucleophiles. The results provide a short, efficient, three-component route for the synthesis of β(γ′)-alkyl or -aryl-substituted muconates for possible use in polymer chemistry

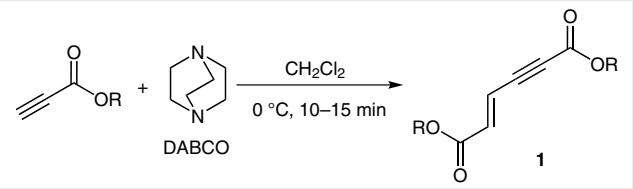
All reactions were performed under N_2. Anhydrous THF and benzene were distilled over Na/benzophenone under argon. IR spectra were recorded on an Excalibur HE series FTS 3100 spectrophotometer from Digilab. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DRX-300 NMR or an Agilent 400-MR DD2 400 NMR spectrometer at 300 (400) or 75 (100) MHz, respectively. The chemical shifts in the ^{1}H and ^{13}C NMR spectra are referenced to TMS or residual $CHCl_3$. The high-resolution mass spectra (HRMS) were recorded on a Finnigan MAT-95XL or a Varian 901-MS magnetic-sector mass spectrometer operated in the EI, ESI, or APCI mode.

Organocopper Reagents 2a–c (Gilman Reagents); General Procedure

The alkyl- or aryllithium R^2Li (3.56 mmol) was added to a suspension of CuI (373 mg, 1.96 mmol) in anhydrous THF (25 mL) in a 50 mL double-necked flask at –20 °C, and the resulting mixture was stirred for 30 min at –20 °C. The mixture was then slowly cooled to –78 °C with continuous stirring, and the resulting Gilman reagent (1.78 mmol) was used directly in the subsequent reaction.

(*E*)-Enynedioates 1a–g; General Procedure

A 50 mL round-bottomed flask was charged with a solution of the appropriate alkyl propiolate (5 mmol) in CH_2Cl_2 (10 mL) at 0 °C. DABCO (5.61 mg, 0.05 mmol) was added, and the solution was stirred for 10–15 min. When the reaction was complete, the mixture was separated by column chromatography (silica gel, EtOAc–hexanes) to give the pure product (Scheme 2). Spectroscopic and physical data for compounds **1a**[24], **1b**[23], and **1h**[23] have been previously reported.



Scheme 2

Dibutyl (2*E*)-Hex-2-en-4-ynedioate (1c)

Yellow liquid; isolated yield: 1.008 g (80%); R_f = 0.35 (CH_2Cl_2–hexanes, 1:1).

FTIR (KBr): 749, 1467, 1623, 1730, 2224, 2874, 2973 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.95 (m, 6 H), 1.36–1.41 (m, 4 H), 1.63–1.66 (m, 4 H), 4.14–4.22 (m, 4 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 6.76 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (2 C), 19.4, 19.5, 30.7, 30.9, 65.6, 66.7, 81.9, 87.4, 121.9, 135.8, 153.6, 165.2.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{14}H_{20}O_4$: 252.1356; found: 252.1361.

Dihexyl (2*E*)-Hex-2-en-4-ynedioate (1d)

Yellow liquid; isolated yield: 1.279 g (83%); R_f = 0.38 (CH_2Cl_2–hexanes, 1:1).

FTIR (KBr): 963, 1116, 1388, 1468, 1608, 1732, 2222, 2857, 2962 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.89 (m, 6 H), 1.27 (br s, 12 H), 1.63–1.69 (m, 4 H), 4.14–4.21 (m, 4 H), 6.45 (d, *J* = 16.0 Hz, 1 H), 6.76 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (2 C), 22.4 (2 C), 25.3, 25.4, 28.2, 28.4, 31.2, 31.3, 65.4, 66.5, 81.4, 87.0, 121.4, 135.3, 153.1, 164.7.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{18}H_{28}O_4$: 308.1982; found: 308.1989.

Dicyclopentyl (2*E*)-Hex-2-en-4-ynedioate (1e)

Colorless liquid; isolated yield: 0.832 g (80%); R_f = 0.35 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1619, 1717, 2222, 2869, 2969 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58–1.91 (m, 16 H), 5.24–5.27 (m, 2 H), 6.42 (d, *J* = 15.9 Hz, 1 H), 6.73 (d, *J* = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.6 (4 C), 32.5 (2 C), 32.6 (2 C), 78.1, 79.6, 81.0, 87.3, 121.2, 135.6, 152.8, 164.4.

HRMS (EI$^+$): *m*/*z* [M – 69 + 1]$^+$ calcd for $C_{11}H_{12}O_4$: 208.0736; found: 208.0741.

Dicyclohexyl (*E*)-Hex-2-en-4-ynedioate (1f)

Colorless liquid; isolated yield: 0.843 g (76%); R_f = 0.33 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1452, 1619, 1714, 2222, 2783, 2860, 2941 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.57 (m, 12 H), 1.72–1.77 (m, 4 H), 1.85–1.92 (m, 4 H), 4.80–4.93 (m, 2 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 6.76 (d, *J* = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.8 (4 C), 25.3, 25.4, 31.5 (2 C), 31.6 (2 C), 73.9, 75.6, 81.4, 87.5, 121.5, 136.0, 152.9, 164.3.

HRMS (EI$^+$): *m*/*z* [M – 83 + 1]$^+$ calcd for $C_{12}H_{14}O_4$: 222.0892; found: 222.0895.

Dibenzyl (2*E*)-Hex-2-en-4-ynedioate (1g)

Colorless liquid; isolated yield: 1.296 g (81%); R_f = 0.18 (EtOAc–hexanes, 1:20).

FTIR (KBr): 1099, 1497, 1621, 1720, 2220, 2957, 3034 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.25 (s, 2 H), 5.26 (s, 2 H), 6.50 (d, *J* = 15.9 Hz, 1 H), 6.83 (d, *J* = 15.9 Hz, 1 H), 7.40–7.41 (m, 10 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.7, 67.7, 81.7, 86.9, 121.6, 128.1, 128.2, 128.4 (8 C), 134.3, 134.9, 135.0, 152.6, 164.1.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{20}H_{16}O_4$: 320.1049; found: 320.1044.

Bis(2-thienylmethyl) (2*E*)-Hex-2-en-4-ynedioate (1i)

Colorless liquid; isolated yield: 1.245 g (75%); R_f = 0.15 (EtOAc–hexanes, 1:20).

FTIR (KBr): 835, 1442, 1608, 1714, 2218, 2956 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 2 H), 5.38 (s, 2 H), 6.45 (d, *J* = 16.2 Hz, 1 H), 6.79 (d, *J* = 16.2 Hz, 1 H), 6.98–7.02 (m, 2 H), 7.11–7.15 (m, 2 H), 7.33–7.35 (m, 2 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 61.1, 61.9, 82.0, 86.9, 122.1, 126.8, 126.9, 127.2, 127.6, 128.6, 129.2, 134.9, 136.0, 136.9, 152.6, 164.2.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{16}H_{12}O_4S_2$: 332.0177; found: 332.0176.

Alkyl- and Aryldienedioates 3a–3aa; General Procedure

A solution of the appropriate enynedioate **1** (1.19 mmol) in benzene (10 mL) was distilled at 120 °C in a Dean–Stark apparatus to remove any residual moisture as an azeotropic mixture; this procedure was repeated twice more. THF (25 mL) was added, and the resulting mixture was cooled to –78 °C. The freshly prepared Gilman reagent **2** (1.78 mmol, 1.5 equiv) was added from a syringe, and the mixture was stirred for 10 min at –78 °C. The reaction was quenched with sat. aq NH_4Cl (5 mL) and the mixture was warmed to r.t. and stirred for 10 min. The product was extracted with EtOAc (10 × 3 mL), and the extracts were washed with successively with H_2O (5 × 1 mL) and brine (5 × 2 mL) then dried (Na_2SO_4) and concentrated under vacuum. The crude product was purified by flash chromatography (silica gel, hexanes–EtOAc).

Dimethyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3a)

Colorless liquid; isolated yield: 0.142 g (53%); R_f = 0.23 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1155, 1435, 1601, 1633, 1720, 2873, 2932, 2955 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, *J* = 6.9 Hz, 3 H), 1.23–1.52 (m, 4 H), 2.34 (t, *J* = 7.8 Hz, 2 H), 3.73 (s, 3 H), 3.78 (s, 3 H), 5.90 (s, 1 H), 6.17 (d, *J* = 16.2 Hz, 1 H), 8.54 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 13.8, 22.4, 30.8, 33.6, 51.5, 51.9, 122.1, 123.4, 139.8, 151.9, 161.9, 167.0.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{12}H_{18}O_4$: 226.1205; found: 226.1198.

Dimethyl (2*E*,4*E*)-2-Butylhexa-2,4-dienedioate (3a')

Colorless liquid; isolated yield: 0.060 g (22%); R_f = 0.30 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1155, 1436, 1458, 1601, 1633, 1722, 2874, 2932, 2955 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 3 H), 1.21–1.40 (m, 4 H), 2.44 (t, *J* = 7.4 Hz, 2 H), 3.72 (s, 6 H), 6.09 (d, *J* = 15.3 Hz, 1 H), 7.13 (d, *J* = 12.0 Hz, 1 H), 7.49 (dd, *J* = 12.0, 15.3 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3, 23.0, 27.7, 32.4, 52.3, 52.6, 127.1, 135.0, 138.9, 140.4, 167.2, 168.2.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{12}H_{18}O_4$: 226.1205; found: 226.1198.

Dimethyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3b)

Colorless liquid; isolated yield: 0.168 g (77%); R_f = 0.43 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1056, 1244, 1436, 1603, 1634, 1730, 2359, 2846, 2953, 2994, 3086 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.88 (s, 1 H), 6.11 (d, *J* = 16.1 Hz, 1 H), 8.55 (d, *J* = 16.1 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3, 51.3, 51.7, 123.0, 124.0, 140.1, 147.4, 165.5, 166.7.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_9H_{12}O_4$: 184.0736; found: 184.0738.

Dimethyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3c)

Colorless liquid; isolated yield: 0.159 g (54%); R_f = 0.18 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1434, 1493, 1593, 1628, 1732, 2952, 2998, 3026, 3058 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 3.77 (s, 3 H), 5.89 (d, *J* = 16.2 Hz, 1 H), 6.01 (s, 1 H), 7.24–7.28 (m, 2 H), 7.34–7.39 (m, 3 H), 8.74 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.6, 51.7, 122.7, 127.7, 128.4 (2 C), 128.5 (2 C), 128.9, 138.3, 140.2, 152.4, 165.6, 166.6.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{14}H_{14}O_4$: 246.0892; found: 246.0897.

Diethyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3d)

Colorless liquid; isolated yield: 0.107 g (35%; 39% based on recovered starting materials); R_f = 0.33 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1037, 1467, 1599, 1633, 1726, 2874, 2935, 2959 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.2 Hz, 3 H), 1.15–1.44 (m, 8 H), 1.37–1.44 (m, 2 H), 2.25 (t, *J* = 7.8 Hz, 2 H), 4.06–4.19 (m, 4 H), 5.80 (s, 1 H), 6.07 (d, *J* = 16.2 Hz, 1 H), 8.46 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.5, 13.9, 14.0, 22.2, 30.6, 33.4, 60.0, 60.4, 122.3, 123.4, 139.5, 151.3, 165.2, 166.3.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{14}H_{22}O_4$: 254.1518; found: 254.1523.

Diethyl (2*E*,4*E*)-2-Butylhexa-2,4-dienedioate (3d')

Colorless liquid; isolated yield: 0.050 g (17%; 19% based on recovered starting materials); R_f = 0.38 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1466, 1603, 1632, 1713, 2874, 2934, 2960 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, *J* = 6.9 Hz, 3 H), 1.28–1.44 (m, 10 H), 2.5 (t, *J* = 7.8 Hz, 2 H), 4.22 (q, *J* = 6.9 Hz, 4 H), 6.14 (d, *J* = 15.0 Hz, 1 H), 7.12 (d, *J* = 12.0 Hz, 1 H), 7.54 (dd, *J* = 12.0, 15.0 Hz, 1 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 13.8, 14.2 (2 C), 22.5, 27.2, 32.0, 60.7, 60.9, 127.0, 134.3, 138.3, 140.2, 166.4, 167.3.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{14}H_{22}O_4$: 254.1518; found: 254.1523.

Diethyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3e)

Colorless liquid; isolated yield: 0.205 g (81%); R_f = 0.25 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1036, 1449, 1603, 1633, 1728, 2906, 2939, 2983 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20–1.26 (m, 6 H) 1.96 (s, 3 H), 4.09–4.20 (m, 4 H), 5.86 (s, 1 H), 6.08 (d, *J* = 16.2 Hz, 1 H), 8.54 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (2 C), 20.3, 60.1, 60.5, 123.4, 124.2, 140.0, 147.0, 165.1, 166.3.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{11}H_{16}O_4$: 212.1049; found: 212.1045.

Diethyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3f)

Colorless liquid; isolated yield: 0.101 g (31%; 51% based on recovered starting materials); R_f = 0.25 (EtOAc–hexanes, 1:11).

FTIR (KBr): 881, 1034, 1165, 1593, 1628, 1717, 2905, 2937, 2982 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.35 (m, 6 H), 4.18–4.29 (m, 4 H), 5.89 (d, *J* = 16.2 Hz, 1 H), 6.01 (s, 1 H), 7.26–7.29 (m, 2 H), 7.37–7.39 (m, 3 H), 8.73 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1 (2 C), 60.6, 60.7, 123.3, 128.0, 128.4 (2 C), 128.6 (2 C), 128.9, 138.5, 140.2, 152.2, 165.3, 166.3.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{16}H_{18}O_4$: 274.1205; found: 274.1212.

Dibutyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3g)

Colorless liquid; isolated yield: 0.153 g (42%); R_f = 0.43 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1467, 1600, 1631, 1721, 2781, 2873, 2961 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 9 H), 1.27–1.50 (m, 6 H), 1.56–1.68 (m, 6 H), 2.31 (t, *J* = 7.8 Hz, 2 H), 4.08–4.16 (m, 4 H), 5.86 (s, 1 H), 6.12 (d, *J* = 16.2 Hz, 1 H), 8.50 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (2 C), 13.7, 19.0 (2 C), 22.4, 30.5, 30.6, 30.7, 33.5, 64.1, 64.5, 122.5, 123.5, 139.6, 151.4, 165.5, 166.6.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{18}H_{30}O_4$: 310.2144; found: 310.2144.

Dibutyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3h)

Colorless liquid; isolated yield: 0.255 g (80%); R_f = 0.35 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1149, 1282, 1456, 1603, 1726, 2875, 2935, 2961 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.2 Hz, 6 H) 1.31–1.40 (m, 4 H), 1.57–1.64 (m, 4 H), 1.98 (s, 3 H), 4.07–4.16 (m, 4 H), 5.87 (s, 1 H), 6.10 (d, *J* = 16.0 Hz, 1 H), 8.55 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.5 (2 C), 18.9, 19.0, 20.4, 30.5, 30.6, 64.1, 64.4, 123.5, 124.2, 140.0, 146.9, 165.2, 166.4.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{15}H_{24}O_4$: 268.1675; found: 268.1668.

Dibutyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3i)

Colorless liquid; isolated yield: 0.044 g (11%); R_f = 0.40 (EtOAc–hexanes, 1:11).

FTIR (KBr): 1167, 1260, 1466, 1492, 1593, 1626, 1719, 2874, 2960 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.98 (m, 6 H), 1.35–1.49 (m, 4 H), 1.60–1.73 (m, 4 H), 4.15–4.23 (m, 4 H), 5.90 (d, *J* = 16.1 Hz, 1 H), 6.02 (s, 1 H), 7.26–7.30 (m, 2 H), 7.36–7.42 (m, 3 H), 8.73 (d, *J* = 16.1 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (2 C), 19.0, 19.1, 30.6 (2 C), 64.5, 64.6, 123.4, 128.0, 128.4 (2 C), 128.6 (2 C), 128.9, 138.5, 140.1, 152.1, 165.4, 166.4.

HRMS (ESI$^+$): *m*/*z* [M$^+$] for $C_{20}H_{26}O_4$: 330.1831; found: 330.1825.

Dihexyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3j)

Colorless liquid; isolated yield: 0.164 g (38%); R_f = 0.40 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1153, 1468, 1600, 1631, 1721, 2861, 2931, 2958 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88–0.91 (m, 9 H), 1.22–1.49 (m, 14 H), 1.59–1.68 (m, 6 H), 2.32 (t, *J* = 7.7 Hz, 2 H), 4.08–4.17 (m, 4 H), 5.87 (s, 1 H), 6.14 (d, *J* = 16.2 Hz, 1 H), 8.52 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 13.9 (2 C), 22.4 (3 C), 25.5 (2 C), 28.5 (2 C), 30.7, 31.4 (2 C), 33.6, 64.5, 64.8, 122.5, 123.6, 139.7, 151.4, 165.6, 166.6.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{22}H_{38}O_4$: 366.2770; found: 366.2764.

Dihexyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3k)

Colorless liquid; isolated yield: 0.310 g (80%); R_f = 0.33 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1153, 1281. 1307, 1381, 1603, 1633, 1718, 2860, 2932, 2957 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 6 H), 1.24–1.41 (m, 12 H), 1.60–1.71 (m, 4 H), 2.02 (s, 3 H), 4.10–4.19 (m, 4 H), 5.92 (s, 1 H), 6.14 (d, *J* = 15.9 Hz, 1 H), 8.60 (d, *J* = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.9 (2 C), 20.5, 22.5 (2 C), 25.5 (2 C), 28.5, 28.6, 31.4 (2 C), 64.5, 64.8, 123.6, 124.3, 140.1, 147.0, 165.3, 166.5.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{19}H_{32}O_4$: 324.2301; found: 324.2302.

Dihexyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3l)

Colorless liquid; isolated yield: 0.046 g (10%); R_f = 0.34 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1167, 1264, 1462, 1628, 1719, 2860, 2927 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 6 H), 1.24–1.36 (m, 12 H), 1.62–1.71 (m, 4 H), 4.13–4.21 (m, 4 H), 5.89 (d, *J* = 16.2 Hz, 1 H), 6.02 (s, 1 H), 7.27–7.30 (m, 2 H), 7.37–7.39 (m, 3 H), 8.71 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 14.0 (2 C), 22.5 (2 C), 25.5, 25.6, 28.6 (2 C), 31.4 (2 C), 64.9, 65.0, 123.5, 128.1, 128.5 (2 C), 128.7 (2 C), 128.9, 138.6, 140.2, 152.2, 165.5, 166.5.

HRMS (APCI$^+$): *m*/*z* [M + 1]$^+$ calcd for $C_{24}H_{35}O_4$: 387.2530; found: 387.2534.

Dicyclopentyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3m)

Colorless liquid; isolated yield: 0.221 g (56%); R_f = 0.40 (EtOAc–hexanes, 1:9).

FTIR (KBr): 995, 1097, 1152, 1229, 1277, 1462, 1600, 1628, 1715, 2868, 2962 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3 H), 1.25–1.53 (m, 4 H), 1.60–1.76 (m, 12 H), 1.86–1.95 (m, 4 H), 2.33 (t, *J* = 7.7 Hz, 2 H), 5.22–5.27 (m, 2 H), 5.86 (s, 1 H), 6.13 (d, *J* = 16.2 Hz, 1 H), 8.47 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0, 22.7, 23.9 (4 C), 31.0, 32.8 (2 C), 32.9 (2 C), 33.8, 77.3, 77.5, 123.3, 124.1, 139.7, 151.1, 165.6, 166.6.

HRMS (APCI$^+$): *m*/*z* [M + 1]$^+$ calcd for $C_{20}H_{31}O_4$: 335.2217; found: 335.2231.

Dicyclopentyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3n)

Colorless liquid; isolated yield: 0.255 g (73%; 84% based on recovered starting materials); R_f = 0.32 (EtOAc–hexanes, 1:9).

FTIR (KBr): 881, 990, 1045, 1153, 1242, 1281, 1313, 1446, 1603, 1627, 1715, 2868, 2967 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (m, 4 H), 1.74 (m, 8 H), 1.89 (m, 4 H), 2.05 (d, *J* = 1.2 Hz, 3 H), 5.21–5.28 (m, 2 H), 5.89 (s, 1 H), 6.11 (d, *J* = 16.2 Hz, 1 H), 8.52 (dd, *J* = 0.6, 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7, 23.8 (4 C), 32.7 (2 C), 32.8 (2 C), 77.2, 77.5, 124.2, 124.8, 140.0, 146.6, 165.2, 165.4.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{17}H_{24}O_4$: 292.1675; found: 292.1675.

Dicyclopentyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3o)

Colorless liquid; isolated yield: 0.047 g (11%; 13% based on recovered starting materials); R_f = 0.34 (EtOAc–hexanes, 1:9).

FTIR (KBr): 703, 990, 1031, 1161, 1265, 1365, 1460, 1594, 1624, 2867, 2965 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.58–1.95 (m, 16 H), 5.21–5.26 (m, 1 H), 5.29–5.32 (m, 1 H), 5.86 (d, *J* = 16.2 Hz, 1 H), 5.97 (d, *J* = 0.3 Hz, 1 H), 7.27–7.29 (m, 2 H), 7.36–7.39 (m, 3 H), 8.67 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.9 (4 C), 32.8 (2 C), 32.9 (2 C), 77.6, 77.7, 124.2, 128.6 (3 C), 128.9 (2 C), 129.0, 138.9, 140.2, 151.9, 165.4, 166.5.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{22}H_{26}O_4$: 354.1831; found: 354.1818.

Dicyclohexyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3p)

Colorless liquid; isolated yield: 0.302 g (70%); R_f = 0.42 (EtOAc–hexanes, 1:9).

FTIR (KBr): 883, 1024, 1156, 1226, 1275, 1457, 1598, 1628, 1717, 2862, 2934 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3 H), 1.25–1.56 (m, 16 H), 1.76 (m, 4 H), 1.90 (m, 4 H), 2.34 (t, *J* = 7.2 Hz, 2 H), 4.82–4.87 (m, 2 H), 5.88 (d, *J* = 0.9 Hz, 1 H), 6.15 (dd, *J* = 0.9, 16.2 Hz, 1 H), 8.50 (dd, *J* = 0.9, 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.8, 22.5, 23.8 (4 C), 25.4 (2 C), 30.8, 31.6 (4 C), 33.6, 72.6, 72.9, 123.2, 124.0, 139.6, 150.9, 164.9, 165.9.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{22}H_{34}O_4$: 362.2457; found: 362.2460.

Dicyclohexyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3q)

Colorless liquid; isolated yield: 0.241 g (63%; 67% based on recovered starting materials); R_f = 0.21 (EtOAc–hexanes, 0.5:9).

FTIR (KBr): 884, 1044, 1158, 1240, 1277, 1449, 1603, 1630, 1716, 2860, 2935 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.58 (m, 12 H), 1.76 (m, 4 H), 1.89 (m, 4 H), 2.02 (d, *J* = 1.2 Hz, 3 H), 4.82–4.89 (m, 2 H), 5.92 (d, *J* = 0.6 Hz, 1 H), 6.13 (dd, *J* = 0.6, 16.2 Hz, 1 H), 8.57 (dd, *J* = 0.6, 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.5, 23.7 (2 C), 23.8 (2 C), 25.4 (2 C), 31.6 (4 C), 72.7, 72.9, 124.2, 124.7, 140.0, 146.5, 164.7, 165.9.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{19}H_{28}O_4$: 320.1988; found: 320.2000.

Dicyclohexyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3r)

Colorless liquid; isolated yield: 0.035 g (8%; 9% based on recovered starting materials); R_f = 0.40 (EtOAc–hexanes, 1:9).

FTIR (KBr): 707, 1020, 1172, 1261, 1453, 1595, 1626, 1714, 2858, 2936 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.59 (m, 12 H), 1.74 (m, 4 H), 1.90 (m, 4 H), 4.82–4.94 (m, 2 H), 5.88 (dd, *J* = 0.6, 16.2 Hz, 1 H), 6.00 (s, 1 H), 7.27–7.31 (m, 2 H), 7.37–7.39 (m, 3 H), 8.71 (dd, *J* = 0.6, 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.9 (2 C), 24.0 (2 C), 25.5 (2 C), 31.8 (2 C), 31.9 (2 C), 73.3 (2 C), 124.4, 128.6 (3 C), 128.9 (2 C), 129.0, 138.9, 140.3, 151.9, 165.1, 166.1.

HRMS (APCI$^+$): *m*/*z* [M + 1]$^+$ calcd for $C_{24}H_{31}O_4$: 383.2217; found: 383.2229.

Dibenzyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3s)

Colorless liquid; isolated yield: 0.134 g (30%); R_f = 0.25 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1378, 1456, 1498, 1599, 1631, 1725, 2873, 2933, 2957 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.5 Hz, 3 H), 1.29–1.42 (m, 2 H), 1.45–1.55 (m, 2 H), 2.36 (t, *J* = 8.1 Hz, 2 H), 5.21 (s, 2 H), 5.26 (s, 2 H), 5.98 (s, 1 H), 6.26 (d, *J* = 16.4 Hz, 1 H), 7.36–7.41 (m, 10 H), 8.69 (d, *J* = 16.4 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 22.4, 30.7, 33.6, 66.1, 66.4, 122.3, 123.4, 128.2 (4 C), 128.3 (2 C), 128.5 (4 C), 135.8 (2 C), 140.2, 152.1, 165.1, 166.3.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{24}H_{26}O_4$: 378.1831; found: 378.1843.

Dibenzyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3t)

Colorless liquid; isolated yield: 0.380 g (95%); R_f = 0.15 (EtOAc–hexanes, 1:20).

FTIR (KBr): 1380, 1450, 1496, 1600, 1723, 2886, 2952 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 5.21 (s, 2 H), 5.26 (s, 2 H), 6.01 (s, 1 H), 6.24 (d, *J* = 16.3 Hz, 1 H), 7.34–7.44 (m, 10 H), 8.76 (d, *J* = 16.3 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.4, 66.0, 66.3, 123.2, 124.1, 128.1 (4 C), 128.2 (2 C), 128.4 (4 C), 135.7, 135.8, 140.5, 147.6, 164.8, 166.0.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{21}H_{20}O_4$: 336.1362; found: 336.1359.

Dibenzyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3u)

Colorless liquid; isolated yield: 0.020 g (4%); R_f = 0.30 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1592, 1627, 1714, 2890, 2954, 3034, 3064 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.29 (s, 2 H), 5.31 (s, 2 H), 6.06 (d, *J* = 15.9 Hz, 1 H), 6.14 (s, 1 H), 7.31–7.49 (m, 15 H), 8.97 (d, *J* = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.2, 66.3, 122.9, 127.7, 128.1 (4 C), 128.2 (2 C), 128.4 (6 C), 128.5 (2 C), 128.9, 135.6 (2 C), 138.2, 140.6, 152.6, 164.8, 165.9.

HRMS (APCI$^+$): *m*/*z* [M + 1]$^+$ calcd for $C_{26}H_{23}O_4$: 399.1591; found: 399.1606.

Diphenyl (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3v)

Colorless liquid; isolated yield: 0.043 g (10%); R_f = 0.18 (EtOAc–hexanes, 1:20).

FTIR (KBr): 1589, 1633, 1733, 2872, 2931, 2958 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 6.9 Hz, 3 H), 1.38–1.48 (m, 2 H), 1.60–1.65 (m, 2 H), 2.51 (t, *J* = 8.1 Hz, 2 H), 6.20 (s, 1 H), 6.43 (d, *J* = 16.2 Hz, 1 H), 7.11–7.15 (m, 4 H), 7.21–7.26 (m, 2 H), 7.35–7.42 (m, 4 H), 8.82 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.8, 22.6, 30.9, 33.9, 121.5 (4 C), 121.9, 123.7, 125.8, 125.9, 129.4 (4 C), 141.0, 150.4, 150.6, 154.1, 163.8, 164.8.

HRMS (APCI$^+$): m/z [M + 1]$^+$ calcd for $C_{22}H_{23}O_4$: 351.1591; found: 351.1599.

Diphenyl (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate(3w)

Colorless liquid; isolated yield: 0.254 g (69%); R_f = 0.13 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1368, 1383, 1457, 1494, 1590, 1633, 1748, 2924, 2955, 3065 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 6.24 (s, 1 H), 6.43 (d, J = 16.2 Hz, 1 H), 7.12–7.16 (m, 4 H), 7.20–7.27 (m, 2 H), 7.36–7.39 (m, 4 H), 8.90 (d, J = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7, 121.4 (4 C), 122.9, 124.4, 125.8, 125.9, 129.3 (4 C), 141.3, 149.5, 150.3, 150.6, 163.5, 164.7.

HRMS (EI$^+$): m/z [M$^+$] calcd for $C_{19}H_{16}O_4$: 308.1049; found: 308.1051.

Diphenyl (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3x)

Colorless liquid; isolated yield: 0.094 g (22%); R_f = 0.20 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1127, 1360, 1492, 1587, 1627, 1731, 2851, 2928, 3062 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (d, J = 15.9 Hz, 1 H), 6.35 (s, 1 H), 7.12–7.30 (m, 5 H), 7.36–7.50 (m, 10 H), 9.04 (d, J = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 121.4 (4 C), 122.4, 125.8, 125.9, 128.1, 128.6 (4 C), 129.3, 129.4 (4 C), 138.0, 141.5, 150.3, 150.5, 154.3, 163.5, 164.4.

HRMS (EI$^+$): m/z [M$^+$] calcd for $C_{24}H_{18}O_4$: 370.1205; found: 370.1212.

Bis(2-thienylmethyl) (2*Z*,4*E*)-3-Butylhexa-2,4-dienedioate (3y)

Colorless liquid; isolated yield: 0.189 g (41%); R_f = 0.18 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1140, 1378, 1441, 1457, 1598, 1631, 1717, 2872, 2931, 2957 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3 H), 1.26–1.36 (m, 2 H), 1.40–1.51 (m, 2 H), 2.32 (t, J = 7.8 Hz, 2 H), 5.33 (s, 2 H), 5.38 (s, 2 H), 5.92 (s, 1 H), 6.20 (d, J = 16.2 Hz, 1 H), 6.97–7.01 (m, 2 H), 7.12–7.15 (m, 2 H), 7.31–7.34 (m, 2 H), 8.61 (d, J = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 22.4, 30.7, 33.6, 60.3, 60.7, 122.1, 123.3, 126.8 (2 C), 126.9 (2 C), 128.3 (2 C), 137.7 (2 C), 140.4, 152.4, 164.9, 166.1.

HRMS (EI$^+$): m/z [M$^+$] calcd for $C_{20}H_{22}O_4S_2$: 390.0960; found: 390.0891.

Bis(2-thienylmethyl) (2*Z*,4*E*)-3-Methylhexa-2,4-dienedioate (3z)

Colorless liquid; isolated yield: 0.332 g (80%); R_f = 0.20 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1382, 1441, 1540, 1602, 1634, 1714, 2857, 2924, 2954 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 5.33 (s, 2 H), 5.39 (s, 2 H), 5.95 (s, 1 H), 6.19 (d, J = 15.9 Hz, 1 H), 6.97–7.01 (m, 2 H), 7.12–7.15 (m, 2 H), 7.31–7.34 (m, 2 H), 8.67 (d, J = 15.9 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.5, 60.3, 60.6, 123.1, 124.1, 126.8 (2 C), 126.9 (2 C), 128.3 (2 C), 137.7 (2 C), 140.7, 147.9, 164.6, 166.0.

HRMS (EI$^+$): m/z [M – C_5H_5S]$^+$ calcd for $C_{12}H_{11}O_4S$: 251.0378; found: 251.0372.

Bis(2-thienylmethyl) (2*E*,4*E*)-3-Phenylhexa-2,4-dienedioate (3aa)

Colorless liquid; isolated yield: 0.066 g (14%; 43% based on recovered starting materials); R_f = 0.13 (EtOAc–hexanes, 1:10).

FTIR (KBr): 1591, 1624, 1716, 2854, 2925, 2955 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.38 (s, 2 H), 5.40 (s, 2 H), 5.94 (d, J = 16.2 Hz, 1 H), 6.05 (s, 1 H), 6.98–7.02 (m, 2 H), 7.13–7.17 (m, 2 H), 7.24–7.29 (m, 2 H), 7.31–7.38 (m, 5 H), 8.82 (d, J = 16.2 Hz, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 60.5, 60.6, 122.8, 126.8 (2 C), 126.9 (2 C), 127.7, 128.4 (5 C), 128.6 (2 C), 129.0, 137.6, 138.2, 140.8, 152.8, 164.7, 165.8.

HRMS (APCI$^+$): m/z [M + 1]$^+$ calcd for $C_{22}H_{19}O_4S_2$: 411.0719; found: 411.0725.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378856.

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