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PAPER

A novel ketone olefination *via* organozinc reagents in the presence of diphenyl phosphite†

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Carbonyl compounds react with organozinc reagents in the presence of diphenyl phosphite to give the corresponding olefins. A variety of 1,3-dienes and unsaturated esters were obtained in moderate to excellent yields under mild conditions.

Introduction

The olefination of carbonyl compounds is a very important transformation in organic synthesis. The Wittig reaction,[1] Julia reaction[2] and Peterson reaction,[3] as well as their variants[4] provide a highly effective and general method. These reactions need ylides which are generated by a stepwise procedure under basic conditions. Several systems employing stoichiometric amounts of organometallic reagents based on Ti or Cr have been researched in the olefination reaction and some achieved great success.[5] Another catalytic alternative which is based on Re,[6] Fe,[7] Ru,[8] Co,[9] Rh,[10] or Cu[11] carbene complexes also has been reported. Recently, our group developed a new one-pot method for the olefination of carbonyl compounds with Grignard reagents in the presence of diethyl phosphite,[12] which opens up the possibility of olefination by organometallic reagents in the presence of phosphite (Scheme 1).

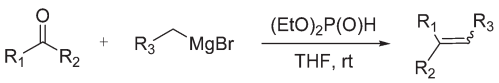
Zinc is a relatively non-toxic and inexpensive metal. Although ignored for many years, today organozinc reagents are one of the most useful classes of organometallic reagents for organic synthesis.[13] Compared with Grignard reagents, organozinc reagents are relatively stable, more selective, and tolerant to ester and amide functional groups.[14] On the other hand, allylic magnesium reagents are difficult to prepare and are unstable, while allylic zinc reagents are much more readily available. Therefore, the attempt to introduce organozinc reagents to carbonyl olefination is meaningful.

Herein, we present a convenient method for the olefination of ketones, *via* organozinc reagents in the presence of diphenyl phosphite.

Results and discussion

Initially, we investigated the reaction of benzophenone with allylzinc bromide in the presence of different additives to optimize the reaction. First, we use diethyl phosphate as the additive. Strangely, the employment of diethyl phosphate affords only 10% of **3a** after a reaction time of 24 h (Table 1, entry 1). Even if the temperature was elevated to 50 °C, the yield remained poor (Table 1, entry 2). Therefore, we investigated the effect of other additives on the carbonyl olefination reaction. Triphenylphosphine, triethylphosphite, triethylphosphate, and 2-(diethoxyphosphoryl) acetate did not promote the reaction (Table 1, entries 3–6). When diisopropyl phosphite was used as the additive, the desired product was detected, but the yield was very low (Table 1, entry 7). To our delight, when diphenyl phosphite was employed as the additive at 50 °C, 87% yield was obtained in 5 h (Table 1, entry 8). Performing the reaction at room temperature caused a slight decrease of the yield (Table 1, entry 9). Then we tested the amount of allylzinc bromide and additive (Table 1, entries 10–14). After some investigations, we concluded that the use of 1.2 equiv. of diphenyl phosphite and 3 equiv. of allylzinc bromide was found to be optimal. Encouraged by these efficient experimental results, we further explored the scope of carbonyl compounds and organozinc reagents. A selection of pertinent results are collected in Tables 2–4.

As shown in Table 2, benzophenone and substituted benzophenones are all workable substrates to react with allylzinc bromide, giving a range of conjugated dienes with good to excellent yields, and no obvious electronic effect was observed (Table 2, entries 1–3, 6–10). Aliphatic ketone such as 2-adamantanone reacting with allylzinc bromide in the same conditions affords the corresponding diene in 85% yield (Table 2, entry 5).



Scheme 1 Olefination of carbonyl compounds with Grignard reagents.

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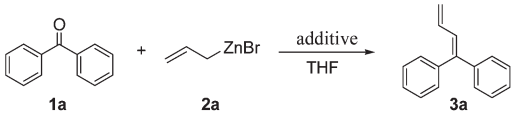
Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	Additive (equiv.)	2a (equiv.)	Time (h)	Yield[b] (%)
1	$(EtO)_2P(O)H$ (1.2)	3	24	10[c]
2	$(EtO)_2P(O)H$ (1.2)	3	24	31
3	Ph_3P (1.2)	3	24	—
4	$(EtO)_3P$ (1.2)	3	24	—
5	$(EtO)_3PO$ (1.2)	3	24	—
6	$(EtO)_2P(O)CH_2COOEt$(1.2)	3	24	—
7	$(i\text{-}PrO)_2P(O)H$ (1.2)	3	24	22
8	$(PhO)_2P(O)H$ (1.2)	3	5	87
9	$(PhO)_2P(O)H$ (1.2)	3	5	79[c]
10	$(PhO)_2P(O)H$ (1.5)	3	5	75
11	$(PhO)_2P(O)H$ (1)	3	5	74
12	$(PhO)_2P(O)H$ (0.8)	3	5	65
13	$(PhO)_2P(O)H$ (1.2)	4	5	45
14	$(PhO)_2P(O)H$ (1.2)	2	5	31

[a] To a solution of **1a** (0.5 mmol) in THF (3 mL) was added **2a** (1.5 mmol) in THF under a nitrogen atmosphere at room temperature, and the mixture was stirred for 30 minutes, then the additive (0.6 mmol) was added to this mixture and stirred at 50 °C. [b] Isolated yield based on **1a** after silica gel chromatography. [c] At room temperature.

When 9-fluorenone was applied, a slightly lower yield was obtained (Table 2, entry 4). Acetophenone gave a mixture of conjugated diene and 1,4-diene with a ratio of 63 : 37 (Table 2, entry 11). When the reaction was performed with aldehyde as substrate, (*E*)-alkenes were obtained as the only product, however the yield was poor (Table 2, entry 12). Then, we tested other two organozinc reagents **2b** and **2c**, corresponding dienes and diyne were obtained at an acceptable yield accompanied by corresponding alcohols (Table 2, entries 13–15). However, when aliphatic and aromatic organozinc reagents **2d** and **2e** react with benzaldehyde and acetophenone respectively, desired products were not detected (Table 2, entries 16, 17).

Moreover, we were pleased to find that the reaction was successfully extended to Reformatsky reagents. A range of α,β-unsaturated esters were obtained at good to excellent yields (Table 3, entries 1–6). When the two aryl groups of ketones are not symmetrical, a modest (*E*)/(*Z*) ratio was found (Table 3, entry 5). When the reaction of **4a** with acetophenone was investigated, a mixture of conjugated and unconjugated products was obtained at a ratio of 58 : 42 with 76% total yield (Table 3, entry 7). Aldehyde such as piperonal only gave a 44% yield in the reaction. But the selectivity was very good, only the thermodynamically more stable (*E*)-isomer was observed (Table 3, entry 8).

Then we tested two other Reformatsky regents **4b** and **4c**. Acetophenone and substituted acetophenones react with **4b** to give unconjugated esters with fair to good yields (Table 4, entries 1–4). Otherwise, when **4c** was used in this reaction, only the unconjugated product **5kd** was obtained with medium yield (Table 4, entry 5).

According to our previous work,[12] a similar mechanism was proposed (Scheme 2). It revealed that the six-centered transition state was formed in the reaction. The P anion abstracts the H of the methylene group and the –ZnBr of **7** was the assistant.

Conclusions

In summary, we have developed a novel olefination of carbonyl compounds with organozinc reagents. A range of conjugated dienes and unsaturated esters could be readily obtained under mild conditions. Further investigation of the usage of other organometallic reagents in olefination reactions is under way in our group.

Experimental section

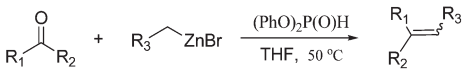
General methods

All chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 60–90 °C boiling point fraction of petroleum. THF was distilled from sodium benzophenone under nitrogen. All reactions were conducted under a nitrogen atmosphere. Metallic zinc and all solvents were purchased from commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300–400 mesh). The IR spectra was measured on a varian 1000 FT-IR spectrometer as KBr disks (4000–400 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 or 300 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.50 ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

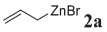
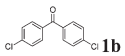
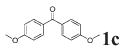
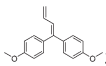
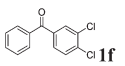
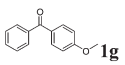
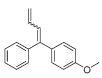
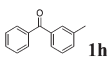
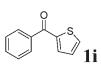
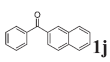
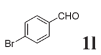
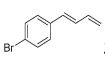
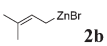
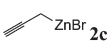
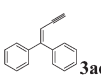
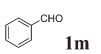
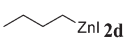
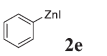
General procedure for the synthesis of organozinc reagents. Alkyl bromide (128 μL, 1.5 mmol) and zinc powder (0.1170 g, 1.8 mmol) in dry THF (3 mL) under a nitrogen atmosphere at room temperature (for **4b** and **4c**, 5% I_2 was added to trigger the reaction). The mixture was stirred for about 15 minutes, and zinc powder disappeared. The stirring was continued to 0.5 h. **2d** and **2e** were prepared according to Knochel's method.[16] The concentration of organozinc reagents was determined by titration with I_2.[17]

General procedure for the olefination reaction. A solution of organozinc reagent in THF (1.5 mmol) was added to a solution of carbonyl compounds (0.5 mmol) in dry THF (3 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 30 minutes. Then diphenyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred for 5 h at 50 °C and then was quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3 × 10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300–400 mesh, petroleum ether and ethyl acetate as eluent).

Table 2 Olefination of carbonyl compounds with organozinc reagents[a]



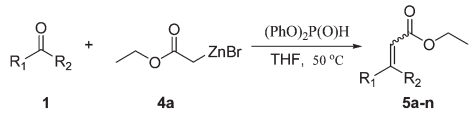
1 2 3

Entry	Substrate	Zinc reagent	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	87
2	 **1b**	**2a**	 **3b**	85
3	 **1c**	**2a**	 **3c**	92
4	 **1d**	**2a**	 **3d**	71
5	 **1e**	**2a**	 **3e**	85
6	 **1f**	**2a**	 **3f**	86[c]
7	 **1g**	**2a**	 **3g**	78[c]
8	 **1h**	**2a**	 **3h**	88[c]
9	 **1i**	**2a**	 **3i**	82[c]
10	 **1j**	**2a**	 **3j**	86[c]
11	 **1k**	**2a**	 **3ka** **3kb**	82 (63 : 37)
12	 **1l**	**2a**	 **3l**	31
13	**1a**	 **2b**	 **3ab**	41
14	**1b**	**2b**	 **3bb**	33
15	**1a**	 **2c**	 **3ac**	35
16	 **1m**	 **2d**		—
17	**1k**	 **2e**		—

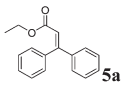
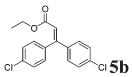
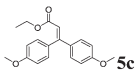
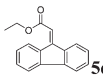
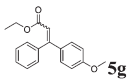
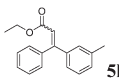
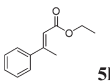
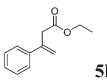
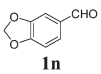
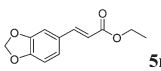
[a] To a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added organozinc reagent (1.5 mmol) in THF under a nitrogen atmosphere at room temperature, and the mixture was stirred for 30 minutes, then diphenyl phosphite (0.6 mmol) was added to this mixture and stirred at 50 °C for 5 h. [b] Isolated yield based on carbonyl compounds after silica gel chromatography. [c] Whether it is a *Z* or *E* configuration can not be determined by ^{1}H NMR.

1,1-Diphenylbuta-1,3-diene (3a).[12] The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; IR (KBr): 3080, 3056, 3026, 1666, 1619, 1598, 1493, 1445, 905, 765, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.16 (m, 10H), 6.71 (d, J = 11.0 Hz, 1H), 6.44 (td, J = 10.5 Hz, J = 16.9 Hz, 1H), 5.38 (d, J = 16.8 Hz, 1H), 5.11 (d, J = 10.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.64, 142.58, 140.14, 135.46, 130.93, 129.03, 128.71, 128.68, 128.10,

Table 3 Olefination of carbonyl compounds with Reformatsky reagent **4a**[a]

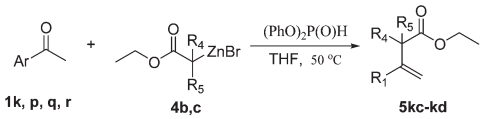


1 **4a** **5a-n**

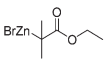
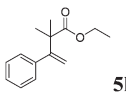
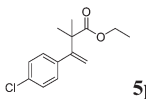
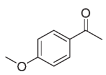
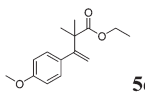
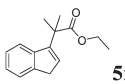
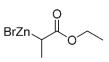
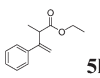
Entry	Substrate	Product	Yield (%)[b]
1	**1a**	 **5a**	89
2	**1b**	 **5b**	80
3	**1c**	 **5c**	82
4	**1d**	 **5d**	65
5	**1g**	 **5g**	68 *E*/*Z* = 61 : 39[c]
6	**1h**	 **5h**	88[d]
7	**1k**	 **5ka**  **5kb**	76 (58 : 42)
8	 **1n**	 **5n**	43

[a] To a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added **4a** (1.5 mmol) in THF under a nitrogen atmosphere, and the mixture was stirred for 30 minutes at 50 °C, then diphenyl phosphite (0.6 mmol) was added to this mixture and stirred at 50 °C for 5 h. [b] Isolated yield based on carbonyl compounds after silica gel chromatography. [c] The ratio *Z*/*E* was obtained from ^{1}H NMR spectroscopy.[15] [d] Whether it is a *Z* or *E* configuration can not be determined from ^{1}H NMR spectroscopy.

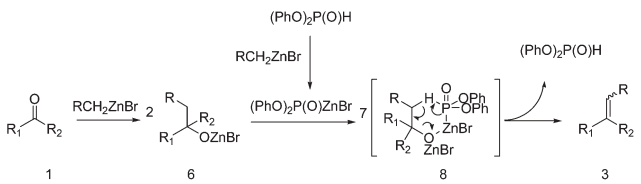
Table 4 Olefination of carbonyl compounds with Reformatsky reagents **4b** and **4c**[a]



1k, p, q, r **4b,c** **5kc-kd**

Entry	Substrate	Reformatsky reagent	Product	Yield (%)[b]
1	**1k**	 **4b**	 **5kc**	73
2	 **1p**	**4b**	 **5p**	61
3	 **1q**	**4b**	 **5q**	82
4	 **1r**	**4b**	 **5r**	87
5	**1k**	 **4c**	 **5kd**	45

[a] To a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added **4b** or **4c** (1.5 mmol) in THF under a nitrogen atmosphere, and the mixture was stirred for 30 minutes at 50 °C, then diphenyl phosphite (0.6 mmol) was added to this mixture and stirred at 50 °C for 5 h. [b] Isolated yield based on carbonyl compounds after silica gel chromatography.



Scheme 2 Possible mechanism for olefination of carbonyl compounds.

128.02, 127.90, 119.15. HRMS (EI$^+$) calcd for $C_{16}H_{14}$ (M^+): 206.1096; found: 206.1096.

1,1-bis(4-Chlorophenyl)buta-1,3-diene (3b).[12] The title compound was obtained according to the general procedure. Colourless oil; Yield: 85%; IR (KBr): 3033, 1668, 1590, 1488, 1401, 908, 765, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 11.0 Hz, 1H), 6.38 (td, J = 10.5 Hz, J = 16.9 Hz, 1H), 5.42 (d, J = 16.7 Hz, 1H), 5.18 (d, J = 10.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.06, 140.59, 137.99, 134.75, 134.02, 132.16, 129.74, 129.66, 129.22, 129.03, 128.91, 120.35. HRMS (EI$^+$) calcd for $C_{16}H_{12}{}^{35}Cl_2$ (M^+): 274.0316; found: 274.0316; HRMS(EI$^+$) calcd for $C_{16}H_{12}{}^{37}Cl_2$ (M^+): 276.0287; found: 276.0280.

1,1-bis(4-Methoxyphenyl)buta-1,3-diene (3c).[12] The title compound was obtained according to the general procedure. Colourless oil; Yield: 92%; IR (KBr): 3035, 3002, 1659, 1605, 1505, 1463, 1287, 908, 831, 780 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.21 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.4, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 11.0 Hz, 1H), 6.46 (td, J = 10.4 Hz, J = 16.7 Hz, 1H), 5.33 (d, J = 16.6 Hz, 1H), 5.07 (d, J = 9.9 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.51, 159.21, 142.72, 135.60, 135.42, 132.46, 131.95, 129.19, 127.04, 117.64, 113.87, 113.81, 55.59. HRMS (EI$^+$) calcd for $C_{18}H_{18}O_2$ (M^+): 266.1307; found: 266.1306.

9-Allylidene-9H-fluorene (3d).[18] The title compound was obtained according to the general procedure. Yellow oil; Yield: 71%; IR (KBr): 3061, 1659, 1609, 1476, 1448, 938, 917, 760, 730 cm^{-1}; ^{1}H NMR (300 MHz $CDCl_3$): δ 7.94 (d, J = 7.4 Hz,

1H), 7.73–7.67 (m, 3H), 7.60–7.47 (m, 1H), 7.37–7.22 (m, 4H), 7.15 (d, J = 11.7 Hz, 1H), 5.68 (d, J = 16.5 Hz, 1H), 5.56 (d, J = 9.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.28, 139.68, 139.45, 137.39, 135.65, 133.09, 128.35, 128.28, 127.42, 127.25, 127.20, 125.45, 123.84, 120.43, 120.17, 119.87. HRMS (EI^+) calcd for $C_{16}H_{12}$ (M^+): 204.0939; found: 204.0942.

Tricyclo[3.3.1.13,7]decane, 2-(2-propen-1-ylidene) (3e).[19] The title compound was obtained according to the general procedure. Colourless oil; Yield: 85%; IR (KBr): 3042, 2908, 1674, 987, 968, 951, 890 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (td, J = 10.6 Hz, J = 16.8 Hz, 1H), 5.78 (d, J = 11.0 Hz, 1H), 5.10 (d, J = 16.8 Hz, 1H), 4.93 (d, J = 9.1 Hz, 1H), 3.03 (s, 1H), 3.38 (s, 1H), 1.96–1.74 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.70, 132.63, 118.25, 114.14, 40.89, 40.03, 39.19, 37.40, 33.04, 28.75. HRMS (EI^+) calcd for $C_{13}H_{18}$ (M^+): 174.1409; found: 174.1410.

1,2-Dichloro-4-(1-phenylbuta-1,3-dienyl)benzene (3f). The title compound was obtained according to the general procedure. Colourless oil; Yield: 86%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3058, 1549, 1493, 1469, 1445, 945, 908, 765, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.05 (m, 8H), 6.70 (t, J = 10.7 Hz, 1H), 6.47–6.32 (m, 1H), 5.44 (d, J = 16.8 Hz, 1H), 5.20 (dd, J = 5.4 Hz, J = 9.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.44, 141.34, 141.04, 140.79,139.92, 138.74, 134.70, 134.32, 132.68, 132.38, 131.81, 131.55, 130.49, 130.30, 130.10, 129.99, 129.77, 129.44, 128.65, 128.15,128.09, 127.72, 127.03, 120.33, 120.27. HRMS (EI^+) calcd for $C_{16}H_{12}{}^{35}Cl_2$ (M^+): 274.0316; found: 274.0316; HRMS (EI^+) calcd for $C_{16}H_{12}{}^{37}Cl_2$ (M^+): 276.0287; found: 276.0280.

1-Methoxy-4-(1-phenylbuta-1,3-dienyl)benzene (3g).[20] The title compound was obtained according to the general procedure. Colourless oil; Yield: 72%; IR (KBr): 3055, 1604, 1510, 1462, 1442, 1290, 966, 904, 832 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.13 (m, 7H), 6.93–6.80 (m, 2H), 6.65 (dd, J = 4.9, J = 10.9 Hz, 1H), 6.47–6.34 (m, 1H), 5.36 (dd, J = 9.0 Hz, J = 16.4 Hz, 1H), 5.10 (t, J = 11.9 Hz, 1H), 3.84–3.79 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.47, 159.19, 143.09, 142.94, 142.75, 140.11, 135.36, 134.94, 131.90, 130.63, 129.96, 128.98, 128.51, 128.37, 127.95, 127.71, 127.57, 127.18, 121.02, 120.93, 118.47, 117.92,133.85, 133.78, 55.52, 55.50. HRMS (EI^+) calcd for $C_{17}H_{16}O$ (M^+): 236.1201; found: 236.1201.

1-Methyl-3-(1-phenylbuta-1,3-dienyl)benzene (3h).[21] The title compound was obtained according to the general procedure. Colourless oil; Yield: 88%; IR (KBr): 3055, 3025, 1666, 1601, 1492, 1445, 904, 787, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.03 (m, 9H), 6.70 (d, J = 10.9 Hz, 1H), 6.49–6.39 (m, 1H), 5.38 (d, J = 16.8 Hz, 1H), 5.12 (d, J = 9.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.72, 143.69, 142.58, 142.53, 140.17, 139.99, 138.19, 138.16, 135.52, 135.44, 131.38, 130.86, 128.87, 128.83, 128.78, 128.66, 128.62, 128.57, 128.53, 128.48, 128.02, 127.97, 127.90, 127.79, 125.32, 118.92, 118.89, 21.93, 21.90. HRMS (EI^+) calcd for $C_{17}H_{16}$ (M^+): 220.1252; found: 220.1253.

2-(1-Phenylbuta-1,3-dienyl)thiophene (3i). The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3048, 1609, 1596, 1490, 1444, 860, 840, 770, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.28 (m, 5H), 7.18 (d, J = 4.8 Hz, 1H), 6.91–6.89 (m, 1H), 6.76–6.62 (m, 2H), 6.30 (td, J = 10.5 Hz, J = 17.1 Hz, 1H), 5.36 (d, J = 16.9 Hz, 1H), 5.08 (d, J = 10.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.08, 139.04, 137.49, 137.74, 130.43, 128.67, 128.22, 127.94, 127.54, 126.75, 125.26, 118.87. HRMS (EI^+) calcd for $C_{14}H_{12}S$ (M^+): 212.0660, found: 212.0662.

2-(1-Phenylbuta-1,3-dienyl)naphthalene (3j). The title compound was obtained according to the general procedure. White solid; Yield: 86%; Compound purity: 98% (confirmed by HPLC); IR (KBr): 3055, 1627, 1597, 1504, 1444, 899, 818, 763, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87–7.21 (m, 12H), 6.83 (dd, J = 11.0 Hz, J = 17.4 Hz, 1H), 6.55–6.43 (m, 1H), 5.43 (d, J = 16.8 Hz, 1H), 5.14 (t, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.37, 143.32, 142.28, 139.88, 139.68, 137.37, 135.27, 133.57, 133.46, 133.08, 132.95, 130.77, 129.71, 129.30, 129.19, 128.72, 128.51, 128.30, 127.97, 127.85, 127.77, 127.27, 126.42, 126.37, 126.25, 125.63, 119.13, 119.05. HRMS (EI^+) calcd for $C_{20}H_{16}$ (M^+): 256.1252, found: 256.1252.

1-(Penta-2,4-dien-2-yl)benzene (3ka), 1-(penta-1,4-dien-2-yl) benzene (3kb).[12] The title compound was obtained according to the general procedure. Colourless solid; Yield; 82%; IR (KBr): 3081, 3057, 1599, 1494, 1445, 912, 863, 758, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.21 (m, 5H), 5.90 (tdd, J = 6.6 Hz, J = 10.1 Hz, J = 16.7 Hz, 1H), 5.39 (s, 1H), 5.14–5.05 (m, 3H), 3.25 (d, J = 6.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.77, 141.39, 136.66, 128.74, 127.92, 126.46, 116.95, 113.63, 39.97. HRMS (EI^+): calcd. for $C_{11}H_{12}$ (M^+): 144.0939; found: 144.0938.

(E)-1-Bromo-4-(buta-1,3-dienyl)benzene (3l).[22] The title compound was obtained according to the general procedure. Colourless oil; Yield: 31%; IR (KBr): 3051, 2962, 1638, 1501, 1407, 807, 680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J = 8.3 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 6.75 (dd, J = 10.7 Hz, J = 15.1 Hz, 1H), 6.54–6.41 (m, 2H), 5.34 (d, J = 17.0 Hz, 1H), 5.20 (d, J = 10.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.30, 133.49, 129.14, 128.95, 127.72, 125.21, 118.76, 115.80. HRMS (EI^+): calcd for $C1_1H_{10}O_2$ (M^+): 207.9888; found: 208.9612.

4-Methyl-1,1-diphenylpenta-1,3-diene (3ab).[23] The title compound was obtained according to the general procedure. Colourless oil; Yield: 41%; IR (KBr): 3045, 2973, 1614, 1505, 1463, 908, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.26 (m, 10H), 6.87 (d, J = 11.2 Hz, 1H), 5.92 (d, J = 10.5 Hz, 1H), 1.89 (s, 3H), 1.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.39, 140.49, 140.01, 137.95, 130.87, 130.43, 128.41, 127.72, 127.30, 127.19, 124.78, 123.49, 26.79, 18.92. HRMS (EI^+) calcd for $C_{18}H_{18}$ (M^+): 234.1409; found: 234.1412.

1,1-bis(4-Chlorophenyl)buta-1,3-diene (3bb). The title compound was obtained according to the general procedure. Colourless oil; Yield: 33%; Compound purity: 99% (confirmed by HPLC); IR (KBr): 3032, 1593, 1492, 1440, 915, 863, 765, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.17–7.11 (m, 4H), 6.83 (d, J = 11.4 Hz, 1H), 5.85 (d, J = 11.4 Hz, 1H), 1.88 (s, 3H), 1.77

(s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.36, 139.37, 138.38, 137.39, 133.34, 133.10, 132.09, 128.80, 128.71, 128.58, 125.51, 122.93, 26.76, 18.91. HRMS (EI^+) calcd for $C_{18}H_{16}{}^{35}Cl_2$ (M^+): 302.0629; found: 302.0630; HRMS (EI^+) calcd for $C_{18}H_{16}{}^{37}Cl_2$ (M^+): 304.0600; found: 304.0642.

1,1-Diphenylbut-1-en-3-yne (3ac).[24] The title compound was obtained according to the general procedure. Colourless oil; Yield: 35%; IR (KBr): 3287, 3057, 3025, 1598, 1495, 1443, 849, 774, 763, 729, 697 cm^{-1}; ^{1}H NMR (300 MHz $CDCl_3$): δ 7.44–7.30 (m, 10H), 6.02 (s, 1H), 3.00 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.72, 141.35, 139.10, 130.17, 128.78, 128.56, 128.22, 106.25, 82.69, 81.76. HRMS (EI^+) calcd for $C_{16}H_{12}$ (M^+): 204.0939; found: 204.0938.

Ethyl 3,3-diphenylacrylate (5a).[25] The title compound was obtained according to the general procedure. Colourless oil; Yield: 89%; IR (KBr): 3057, 3026, 1723, 1617, 1575, 1492, 1445, 875, 771, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.21 (m, 10H), 6.36 (s, 1H), 4.04 (q, J = 6.9 Hz, 2H), 1.10 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.36, 156.74, 141.05, 139.25, 129.64, 129.37, 128.62, 128.54, 128.35, 128.12, 117.73, 60.30, 14.26. HRMS (EI^+) calcd for $C_{17}H_{16}O_2$ (M^+): 252.1150; found: 252.1152.

Ethyl 3,3-bis(4-chlorophenyl)acrylate (5b).[26] The title compound was obtained according to the general procedure. Colourless oil; Yield: 80%; IR (KBr): 3025, 1721, 1619, 1589, 1491, 1402, 880, 830, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.34 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.85, 154.26, 139.08, 137.06, 136.00, 134.66, 130.79, 129.72, 128.96, 128.52, 118.38, 60.54, 14.26. HRMS (EI^+) calcd for $C_{17}H_{14}{}^{35}Cl_2O_2$ (M^+): 320.0371; found: 320.0371; HRMS (EI^+) calcd for $C_{17}H_{14}{}^{37}Cl_2O_2$ (M^+): 322.0341; found: 322.0350.

Ethyl 3,3-diphenylacrylate (5c).[27] The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; IR (KBr): 3039, 2969, 1688, 1592, 1495, 752, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.84 (d, J = 7.9 Hz, 2H), 6.23 (s, 1H), 4.07 (q, J = 6.9 Hz, 2H), 3.82 (d, J = 8.2 Hz, 6H), 1.16 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.39, 155.65, 154.57, 151.38, 128.73, 126.17, 125.79, 124.94, 109.79, 108.61, 108.12, 54.82, 50.29, 50.17, 9.12. HRMS (EI^+) calcd for $C_{19}H_{20}O_4$ (M^+): 312.1362; found: 312.1408.

Ethyl 2-(9H-fluoren-9-ylidene)acetate (5d).[28] The title compound was obtained according to the general procedure. Yellow solid; Yield: 65%; IR (KBr): 3062, 2980, 1713, 1600, 1450, 869, 780, 730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (d, J = 7.8 Hz, 1H), 7.62 (dd, J = 7.5 Hz, J = 15.5 Hz, 3H), 7.42–7.22 (m, 4H), 6.74 (s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.52, 148.46, 142.71, 140.94, 139.05, 135.39, 131.07, 130.75, 129.41, 128.25, 127.66, 121.44, 119.97, 119.77, 114.14, 60.90, 14.58. HRMS (EI^+) calcd for $C_{17}H_{14}O_2$ (M^+): 250.0994; found: 250.0991.

Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (5g).[29] The title compound was obtained according to the general procedure. Colourless oil; Yield: 68%; IR (KBr): 3058, 2980, 1720, 1604, 1511, 1462, 1251, 874, 833, 774, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.15 (m, 7H), 6.90 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.31 (s, 1H; E isomer), 6.27 (s, 1H; Z isomer), 4.06 (dq, J = 7.0 Hz, J = 14.2 Hz , 2H), 3.82 (d, J = 9.9 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H; Z isomer), 1.10 (t, J = 7.1 Hz, 3H; E isomer). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.50, 161.00, 159.98, 156.82, 156.52, 141.78, 139.51, 133.34, 131.26, 131.18, 129.99, 129.57, 129.32, 128.80, 128.54, 128.23, 128.08, 117.12, 115.60, 114.00, 113.46, 60.24, 60.12, 55.56, 55.45, 14.40, 14.28. HRMS (EI^+) calcd for $C_{18}H_{18}O_3$ (M^+): 282.1256; found: 282.1256.

Ethyl 3-phenyl-3-*m*-tolylacrylate (5h).[30] The title compound was obtained according to the general procedure. Colourless oil; Yield: 88%; IR (KBr): 3048, 2979, 1720, 1603, 1511, 1493, 1444, 833, 774, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.00 (m, 9H), 6.35 (s, 1H), 4.05 (dq, J = 2.3 Hz, J = 7.0 Hz , 2H), 2.35–2.32 (m, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.62, 157.19, 157.07, 141.37, 141.29, 139.56, 139.41, 138.45, 137.84, 130.66, 130.10, 129.78, 129.58, 129.31, 128.80, 128.75, 128.51, 128.29, 128.21, 126.75, 126.06, 117.85, 117.79, 60.46, 21.86, 14.47. HRMS (EI^+) calcd for $C_{18}H_{18}O_2$ (M^+): 266.1307; found: 266.1305.

(E)-ethyl 3-phenylbut-2-enoate (5ka).[31] The title compound was obtained according to the general procedure. Colourless oil; Yield: 32%; IR (KBr): 3024, 1714, 1629, 1446, 1273, 873, 767, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.26 (m, 5H), 6.13 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.58 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.21, 155.74, 142.46, 129.19, 128.71, 126.52, 117.40, 60.08, 18.18, 14.58. HRMS (EI^+) calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994; found: 190.0993.

Ethyl 3-phenylbut-3-enoate (5kb).[31] The title compound was obtained according to the general procedure. Colourless oil; Yield: 44%; IR (KBr): 3085, 1734, 1627, 1495, 1445, 906, 860, 776, 733, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.25 (m, 5H), 5.54 (s, 1H), 5.23 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.51 (s, 2H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.77, 141.42, 140.26, 128.80, 128.19, 126.24, 116.60, 61.21, 41.77, 14.52. HRMS (EI^+) calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994; found: 190.0995.

(E)-ethyl 3-(benzo[d][1,3]dioxol-5-yl)acrylate (5n).[32] The title compound was obtained according to the general procedure. White solid; Yield: 67%; IR (KBr): 3062, 2980, 1709, 1604, 1503, 1447, 1250, 980, 931, 853, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 15.9 Hz, 1H), 7.03–6.79 (m, 2H), 6.80 (d, J = 7.9 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 6.00 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.39, 149.76, 148.54, 144.49, 129.11, 124.59, 116.42, 108.74, 106.69, 101.76, 60.61, 14.56. HRMS (EI^+) calcd for $C_{12}H_{12}O_4$ (M^+): 220.0736; found: 220.0740.

Ethyl 2,2-dimethyl-3-phenylbut-3-enoate (5kc).[33] The title compound was obtained according to the general procedure.

Colourless oil; Yield: 73%; IR (KBr): 3083, 3056, 1731, 1626, 1493, 1444, 1255, 909, 776, 703 cm^{-1}; ^1H NMR (300 MHz, CDC_{l3}): δ 7.27–7.15 (m, 5H), 5.32 (s, 1H), 5.15 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 1.39 (s, 6H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.69, 153.44, 142.02, 128.18, 128.04, 127.27, 114.66, 60.78, 47.80, 26.14, 14.21. HRMS (EI^+) calcd for $C_{14}H_{18}O_2$ (M^+): 218.1307; found: 218.1315.

Ethyl 3-(4-chlorophenyl)-2,2-dimethylbut-3-enoate (5p). The title compound was obtained according to the general procedure. Colourless oil; Yield: 61%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3024, 2980, 1729, 1630, 1489, 1399, 1253, 908, 908, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 5.33 (s, 1H), 5.14 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 1.38 (s, 6H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.42, 152.30, 140.43, 133.21, 129.56, 128.19, 115.29, 61.07, 47.71, 26.03, 14.22. HRMS (EI^+) calcd for $C_{14}H_{17}{}^{35}ClO_2$ (M^+): 252.0917; found: 252.0916; HRMS ($EI+^+$) calcd for $C_{14}H_{17}{}^{37}ClO_2$ (M^+): 254.0888; found: 254.0888.

Ethyl 3-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (5q). The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; Compound purity: 99% (confirmed by HPLC); IR (KBr): 3024, 1729, 1609, 1511, 1464, 1247, 909, 836 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 5.27 (s, 1H), 5.12 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.38 (s, 6H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.79, 158.88, 152.88, 134.38, 129.22, 114.05, 113.39, 60.91, 55.37, 47.84, 26.12, 14.23. HRMS (EI^+) calcd for $C_{16}H_{20}O_3$ (M^+): 248.1412; found: 248.1414.

Ethyl 2-(3H-inden-1-yl)-2-methylpropanoate (5r). The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; Compound purity: 98% (confirmed by HPLC); IR (KBr): 3073, 2975, 1736, 1636, 1399, 907, 776, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J = 7.1 Hz, 1H), 7.32 (d, J = 7.3 Hz, 1H), 7.25–7.15 (m, 2H), 6.36 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.35 (s, 2H), 1.59 (s, 6H), 1.13 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.08, 148.21, 145.24, 143.74, 127.98, 126.29, 124.86, 124.34, 120.88, 61.30, 43.87, 37.76, 25.76, 14.54. HRMS (EI^+) calcd for $C_{15}H_{18}O_2$ (M^+): 230.1307; found: 230.1308.

Ethyl 2-methyl-3-phenylbut-3-enoate (5kd).[34] The title compound was obtained according to the general procedure. Colourless oil; Yield: 45%; IR (KBr): 3073, 2977, 1733, 1628, 1503, 1446, 767, 701 cm^{-1}; ^1H NMR 300 MHz, $CDCl_3$): δ 7.40–7.25 (m, 5H), 5.39 (s, 1H), 5.23 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.67 (q, J = 7.1 Hz, 1H), 1.39 (d, J = 7.08 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.66, 148.29, 141.29, 128.51, 127.82, 126.70, 114.11, 60.87, 44.77, 17.22, 14.26. HRMS (EI^+) calcd for $C_{13}H_{16}O_2$ (M^+): 204.1150; found: 204.1151.

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