Intermolecular sequential [4 + 2]-cycloaddition–aromatization reaction of aryl-substituted allenes with DMAD affording phenanthrene and naphthalene derivatives†

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An efficient entry to phenanthrene and naphthalene derivatives through intermolecular sequential [4 + 2]-cycloaddition–aromatization reactions of aryl-substituted allenes with DMAD in the absence of any catalyst was discovered. In this reaction the aromatic ring and the adjacent carbon–carbon double bond of the allene unit acted as the 1,3-diene.

Introduction

Phenanthrene is a very important structural unit responsible for various biological effects.[1] Many naturally occurring compounds of biological and therapeutic interest contain a phenanthrene or reduced phenanthrene nucleus.[2–9] Thus, many synthetic routes have been developed for the preparation of phenanthrene derivatives.[10]

On the one hand, Diels–Alder reactions involving allene units are well documented.[11–13] For example, electron-deficient allenes participate in the Diels–Alder-type [4 + 2]-cycloaddition mostly as a dienophile, in which the electron-deficient internal C=C bond of the allene reacts highly selectively;[12] [4 + 2]-cycloadditions of alkynes with the 1,3-diene unit in conjugated allenenes are also known processes.[13] However, only scattered reports have appeared in which an aryl group and the conjugated C=C bond of an allene were incorporated as the 1,3-diene unit: Pasto and Yang reported an intermolecular cycloaddition reaction between phenylpropadiene and maleimide, affording [4 + 2]-cycloaddition–aromatization products together with [2 + 2]-cycloaddition adducts as minor products;[14] Ollis and Laird discovered the intramolecular [4 + 2]-cycloaddition–aromatization of phenylallene activated by heteroatoms with an acetylene moiety.[15] Recently, Brummond and Chen,[16a] Ohno *et al.*,[16b] Mukai *et al.*,[17] and ourselves[18] observed intramolecular [2 + 2]-cycloadditions involving alkynes and the conjugated C=C bond of an aryl allene unit. In the studies by Mukai *et al.*[17] and us,[18a] it is interesting to observe the formation of Diels–Alder products of the alkyne with the vinyl arene unit in 1-aryl-1,2-allenes as the minor products. In trying to obtain solely the Diels–Alder reaction between the alkyne and the vinyl arene unit in 1-aryl-1,2-allenes, we observed intermolecular [4 + 2]-cycloaddition reactions of 1-aryl-1,2-allenes with DMAD (dimethyl acetylenedicarboxylate) affording phenanthrene and naphthalene derivatives efficiently.

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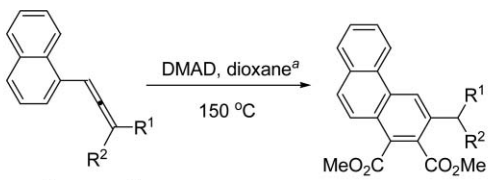
Results and discussion

We started our study by mixing α-allenyl naphthalenes **1a** and **1b** with DMAD, however, no reaction occurred. When we introduced an electron-withdrawing ethoxycarbonyl group to the allene moiety, *i.e.*, **1c**, the corresponding reaction afforded phenanthrene derivative **2c** in 50% yield (Scheme 1).



1a R^1 = H, R^2 = H
1b R^1 = Me, R^2 = CH_2OH
1c R^1 = Me, R^2 = COOEt

2a NR
2b NR
2c 50 %

[a] The reaction was conducted in a reaction tube with a screw cap.

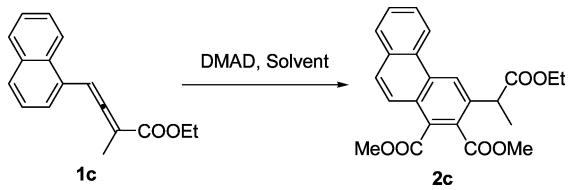
Scheme 1

With these primary results in hand, we screened the reaction conditions by changing the solvents. The results in Table 1 indicated that dioxane is the best solvent, affording **2c** in 72% yield (entry 12, Table 1). At a lower temperature, the yield of **2c** dropped dramatically (entries 13–15, Table 1). The structure of **2** was confirmed by an X-ray diffraction study of **2c**[19] (Fig. 1)†.

With the optimized reaction conditions, we investigated the scope of the intermolecular [4 + 2]-cycloaddition–aromatization reactions of α-naphthyl allenes. From the results presented in Table 2, the following items should be noted: (1) the electron-withdrawing group of the α-allenyl naphthalenes could be CO_2Et (entries 1–5, Table 2) and $P(O)Ph_2$ (entries 6–10, Table 2); (2) the stability of the 4-naphthyl-2,3-allenoate **1g** is low under the standard conditions, which may explain the low-yielding nature of this reaction (entry 5, Table 2); (3) other alkynes, such as diphenylalkyne, bis(trimethylsilyl)acetylene and dec-5-yne, are not effective.

When we used an allene with a phenyl group and a $P(O)Ph_2$ group on the same end, *i.e.*, **3**, the [4 + 2]-cycloaddition–aromatization reaction could also proceed to afford naphthalene derivative **4** (Scheme 2). An X-ray diffraction study confirmed the

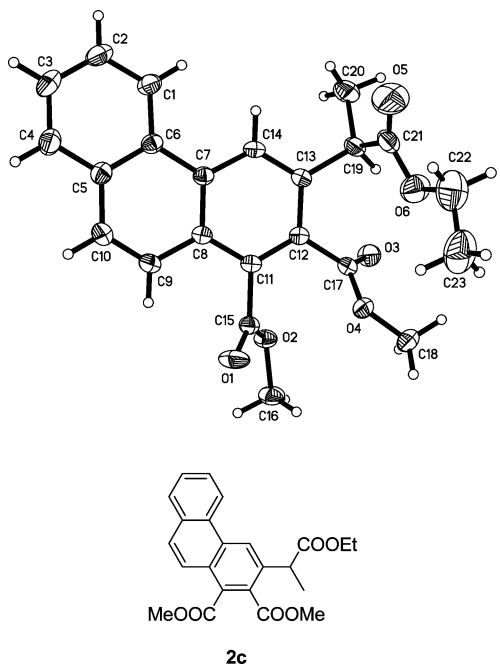
Table 1 Intermolecular [4 + 2]-cycloaddition–aromatization reactions of ethyl 4-(α-naphthyl)-2-methylbutadienoate **1c** with DMAD under different conditions[a]



1c **2c**

Entry	Solvent	Temperature/°C	Time/h	Isolated yield of **2c** (%)
1	Toluene	150	14	54
2	DMF	150	3	39
3	i-C_8H_{18}	150	12	43
4	DME	150	12	30
5	THF	150	13	46
6	t-BuOMe	150	13	39
7	n-Bu_2O	150	12	46
8	Anisole	150	12	45
9	CH_3CN	150	15	60
10	CCl_3CH_3	150	10	66
11	Xylene	150	15	52
12	*Dioxane*	*150*	*10*	*72*
13	Dioxane	130	10	33
14	Dioxane	110	10	35
15	Dioxane	90	12	18

[a] The reaction was conducted using 1.5 equiv. of **1c** and 1 equiv. of DMAD in a reaction tube with a screw cap.



2c

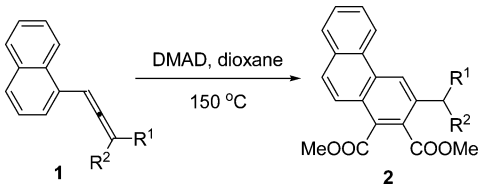
Fig. 1 ORTEP drawing of **2c**.

structure of **4**[20] (Fig. 2)†. This reaction could potentially be used to establish a new library of phosphine ligands.[21]

Conclusions

In conclusion, we have developed an efficient entry to phenanthrene and naphthalene derivatives through intermolecular [4 + 2]-cycloaddition–aromatization reactions of aryl-substituted allenes with DMAD in the absence of any catalyst. Due to the potential utility of these compounds, this method will be useful in organic

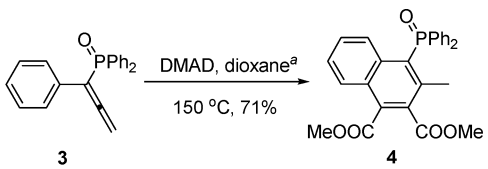
Table 2 Intermolecular [4 + 2]-cycloaddition–aromatization reactions of electron-deficient α-naphthyl allenes **1** with DMAD[a]



1 **2**

Entry	**1** R^1	R^2		Time/h	**2**	Isolated yield of **2** (%)
1	Me	CO_2Et	**1c**	10	**2c**	72
2	n-Pr	CO_2Et	**1d**	24	**2d**	64
3	n-Bu	CO_2Et	**1e**	24	**2e**	58
4	i-Bu	CO_2Et	**1f**	24	**2f**	40
5	Allyl	CO_2Et	**1g**	19	**2g**	40
6[b]	n-Pr	$P(O)Ph_2$	**1h**	72	**2h**	76
7[b]	n-Bu	$P(O)Ph_2$	**1i**	72	**2i**	80
8[b]	n-C_5H_{11}	$P(O)Ph_2$	**1j**	72	**2j**	70
9[b]	n-C_6H_{13}	$P(O)Ph_2$	**1k**	72	**2k**	73
10[b]	$PhCH_2CH_2$	$P(O)Ph_2$	**1l**	72	**2l**	65

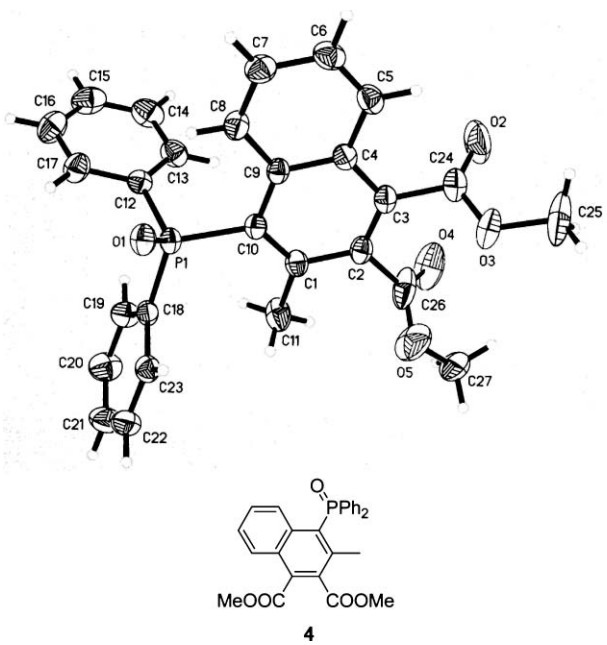
[a] The reaction was conducted using 1.5 equiv. of **1** and 1 equiv. of DMAD in a reaction tube with a screw cap. [b] The reaction was conducted using 1 equiv. of **1** and 2 equiv. of DMAD.



3 **4**

[a] The reaction was conducted in a reaction tube with a screw cap.

Scheme 2



4

Fig. 2 ORTEP drawing of **4**.

synthesis and medicinal chemistry. Further studies in this area are being pursued in our group.

Experimental section

Starting materials

2,3-Allenoic esters **1c–g** were prepared according to the published procedure by treatment of the acyl chlorides with ethyl 2-(triphenylphosphoranylidene)alkanoates.[22] 1,2-Allenyl phosphine oxides **1h–l** and **3** were prepared according to the known method by the reaction of chlorodiphenylphosphine with propargylic alcohols in the presence of Et_3N.[23]

^{31}P NMR (121.5 MHz, $CDCl_3$) spectra were recorded using 85% H_3PO_4 as the external standard.

General procedure

To a solution of α-naphthyl allene **1** (0.375 mmol) in 1 mL of 1,4-dioxane were added DMAD (34 mg, 0.25 mmol) and 1 mL of 1,4-dioxane. The mixture was heated to 150 °C in a reaction tube with a screw cap. After complete conversion of the starting material (monitored by TLC, eluent: petroleum ether–ethyl acetate = 5 : 1), the reaction mixture was concentrated and purified by flash chromatography on silica gel (eluent: petroleum ether–ethyl ether = 10 : 1) to afford the product **2**.

The following compounds were prepared according to the *General procedure*:

(1) 1,2-Bis(methoxycarbonyl)-3-(1-ethoxycarbonyl-ethyl)phenanthrene (2c)

A solution of **1c** (187 mg, 0.74 mmol) and DMAD (69 mg, 0.49 mmol) in 3 mL of dry 1,4-dioxane was heated to 150 °C for 10 hours to afford 111 mg (72%) of **2c**: R_f (petroleum ether–ethyl acetate, 5 : 1) = 0.33; solid, mp 94–95 °C (petroleum ether–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 1 H), 8.67 (d, J = 8.1 Hz, 1 H), 7.92 (d, J = 9 Hz, 1 H), 7.87 (dd, J = 8.1, 1.5 Hz, 1 H), 7.79 (d, J = 9 Hz, 1 H), 7.72–7.60 (m, 2 H), 4.38 (q, J = 7.2 Hz, 1 H), 4.22–4.07 (m, 2 H), 4.02 (s, 3 H), 3.96 (s, 3 H), 1.71 (d, J = 7.5 Hz, 3 H), 1.19 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 174.0, 168.5, 168.1, 136.2, 132.1, 131.73, 131.67, 129.8, 129.1, 129.0, 128.6, 127.8, 127.4, 127.2, 124.0, 122.9, 122.8, 61.0, 52.8, 52.6, 42.2, 18.7, 14.0; MS (EI) m/z (%) 394 (M^+, 2.53), 41 (100); IR (neat) ν 2982, 2952, 2925, 1732, 1593, 1441, 1294, 1223, 1210, 1195, 1176, 1106 cm^{-1}; anal. calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.11; H, 5.91.

(2) 1,2-Bis(methoxycarbonyl)-3-(1-ethoxycarbonyl-butyl)phenanthrene (2d)

A solution of **1d** (105 mg, 0.375 mmol) and DMAD (34 mg, 0.25 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 24 hours to afford 65 mg (64%) of **2d**: R_f (petroleum ether–ethyl acetate, 5 : 1) = 0.33; solid, mp 87–88 °C (petroleum ether–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1 H), 8.71 (d, J = 8.1 Hz, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.80 (d, J = 9.6 Hz, 1 H), 7.73–7.62 (m, 2 H), 4.25–4.02 (m, 3 H), 4.02 (s, 3 H), 3.97 (s, 3 H), 2.30–2.21 (m, 1 H), 2.00–1.91 (m, 1 H), 1.50–1.32 (m, 2 H), 1.20 (t, J = 7.5 Hz, 3 H), 0.96 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.7, 168.5, 168.3, 134.9, 132.1, 131.6, 131.3, 130.6, 129.2, 129.1, 128.6, 127.9, 127.5, 127.3, 124.3, 123.1, 122.9, 60.9, 52.8, 52.7, 47.3, 36.2, 20.9, 14.0, 13.8; MS (ESI) m/z (%) 440 ($M + NH_4^+$, 100), 423 ($M + H^+$, 14); IR (neat) ν 2955, 2873, 1732, 1592, 1440, 1349, 1292, 1224, 1176, 1116 cm^{-1}; anal. calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 70.93; H, 6.17.

(3) 1,2-Bis(methoxycarbonyl)-3-(1-ethoxycarbonyl-pentyl)phenanthrene (2e)

A solution of **1e** (100 mg, 0.340 mmol) and DMAD (35 mg, 0.25 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 24 hours to afford 62 mg (58%) of **2e**: R_f (petroleum ether–ethyl acetate, 5 : 1) = 0.33; liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1 H), 8.71 (d, J = 8.1 Hz, 1 H), 7.94 (d, J = 9.3 Hz, 1 H), 7.88 (dd, J = 7.5, 0.9 Hz, 1 H), 7.80 (d, J = 9.3 Hz, 1 H), 7.73–7.62 (m, 2 H), 4.24–4.02 (m, 3 H), 4.02 (s, 3 H), 3.97 (s, 3 H), 2.32–2.20 (m, 1 H), 2.05–1.92 (m, 1 H), 1.50–1.27 (m, 4 H), 1.20 (t, J = 6.9 Hz, 3 H), 0.90 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.7, 168.5, 168.3, 134.9, 132.1, 131.6, 131.3, 130.6, 129.2, 129.0, 128.6, 127.9, 127.5, 127.3, 124.3, 123.1, 122.9, 60.9, 52.8, 52.6, 47.6, 33.8, 29.8, 22.4, 14.1, 13.8; MS (ESI) m/z (%) 475 ($M + K^+$, 8), 459 ($M + Na^+$, 15), 454 ($M + NH_4^+$, 100), 437 ($M + H^+$, 18), 405 ($M^+ - OMe$, 35); IR (neat) ν 2954, 2931, 2872, 1732, 1592, 1516, 1440, 1349, 1293, 1260, 1222, 1176, 1117, 1024, 1007 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{28}O_6Na$ ($M + Na^+$) 459.1778. Found 459.1778.

(4) 1,2-Bis(methoxycarbonyl)-3-(1-ethoxycarbonyl-3-methylbutyl)phenanthrene (2f)

A solution of **1f** (115 mg, 0.391 mmol) and DMAD (36 mg, 0.25 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 24 hours to afford 44 mg (40%) of **2f**: R_f (petroleum ether–ethyl acetate, 5 : 1) = 0.33; liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1 H), 8.71 (d, J = 7.8 Hz, 1 H), 7.94 (d, J = 9.3 Hz, 1 H), 7.89 (dd, J = 7.2, 0.9 Hz, 1 H), 7.81 (d, J = 9.0 Hz, 1 H), 7.74–7.65 (m, 2 H), 4.32 (dd, J = 8.7, 6.3 Hz, 1 H), 4.25–4.02 (m, 2 H), 4.02 (s, 3 H), 3.97 (s, 3 H), 2.25–2.13 (m, 1 H), 1.85–1.75 (m, 1 H), 1.68–1.57 (m, 1 H), 1.20 (q, J = 7.2 Hz, 3 H), 0.96 (d, J = 6.6 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.8, 168.5, 168.4, 135.0, 132.2, 131.7, 131.3, 130.6, 129.3, 129.1, 128.6, 127.9, 127.5, 127.3, 124.4, 123.2, 122.9, 61.0, 52.9, 52.7, 45.5, 43.2, 26.3, 22.6, 22.4, 14.1; MS (EI) m/z (%) 437 ($M + H^+$, 12.95), 346 (100); IR (neat) ν 2954, 1732, 1463, 1455, 1435, 1292, 1222, 1176, 1005 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{28}O_6$ (M^+) 436.1886. Found 436.1878.

(5) 1,2-Bis(methoxycarbonyl)-3-(1-ethoxycarbonylbut-3-enyl)phenanthrene (2g)

A solution of **1g** (106 mg, 0.375 mmol) and DMAD (37 mg, 0.25 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 19 hours to afford 44 mg (40%) of **2g** together with an unidentified product (34 mg). **2g**: R_f (petroleum ether–ethyl acetate, 5 : 1) = 0.33; liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 1 H), 8.69 (d, J = 8.1 Hz, 1 H), 7.94 (d, J = 9.0 Hz, 1 H), 7.89 (dd, J = 9.0, 1.2 Hz, 1 H), 7.81 (d, J = 9.3 Hz, 1 H), 7.74–7.62 (m, 2 H), 5.89–5.74 (m, 1 H), 5.15 (d, J = 17.1 Hz, 1 H), 5.05 (d, J = 10.5 Hz, 1 H), 4.33 (dd, J = 8.4, 6.9 Hz, 1 H), 4.24–4.06 (m,

2 H), 4.02 (s, 3 H), 3.97 (s, 3 H), 3.08–2.96 (m, 1 H), 2.80–2.70 (m, 1 H), 1.20 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.0, 168.5, 168.1, 134.9, 134.1, 132.2, 131.6, 130.3, 129.21, 129.16, 128.6, 127.9, 127.6, 127.3, 124.4, 123.1, 122.9, 117.4, 61.1, 52.8, 52.7, 47.5, 37.9, 14.1; MS (EI) m/z (%) 420 (M^+, 16.51), 291 (100); IR (neat) ν 2952, 1732, 1441, 1350, 1293, 1261, 1224, 1176 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{24}O_6Na$ (M + Na$^+$) 443.1465. Found 443.1473.

(6) 1,2-Bis(methoxycarbonyl)-3-(1-diphenylphosphinoylbutyl)phenanthrene (2h)

A solution of **1h** (99 mg, 0.24 mmol) and DMAD (68 mg, 0.48 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 72 hours to afford 102 mg (76%) of **2h**: R_f (petroleum ether–ethyl acetate, 1 : 1) = 0.67; solid, mp 170–171 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.52 (d, $J =$ 2.4 Hz, 1 H), 8.85 (d, $J = 8.1$ Hz, 1 H), 8.06–7.97 (m, 2 H), 7.86–7.50 (m, 10 H), 7.17–7.08 (m, 3 H), 4.65–4.54 (m, 1 H), 3.96 (s, 3 H), 3.82 (s, 3 H), 2.32–2.20 (m, 1 H), 2.02–1.92 (m, 1 H), 1.26–1.16 (m, 2 H), 0.76 (t, $J = 7.5$ Hz, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.5; MS (ESI) m/z (%) 551 (M + H$^+$, 100); IR (neat) ν 2955, 1724, 1589, 1437, 1350, 1296, 1229, 1197, 1163, 1117 cm^{-1}; anal. calcd for $C_{34}H_{31}O_5P$: C 74.17; H 5.68. Found: C 74.00; H 5.73.

(7) 1,2-Bis(methoxycarbonyl)-3-(1-diphenylphosphinoylpentyl)phenanthrene (2i)

A solution of **1i** (107 mg, 0.25 mmol) and DMAD (72 mg, 0.51 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 72 hours to afford 114 mg (80%) of **2i**: R_f (petroleum ether–ethyl acetate, 1 : 1) = 0.67; solid, mp 181–182 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.53 (s, 1 H), 8.85 (d, $J =$ 8.4 Hz, 1 H), 8.05–7.96 (m, 2 H), 7.86–7.77 (m, 2 H), 7.75–7.66 (m, 2 H), 7.66–7.50 (m, 6 H), 7.17–7.05 (m, 3 H), 4.63–4.55 (m, 1 H), 3.93 (s, 3 H), 3.81 (s, 3 H), 2.45–2.20 (m, 1 H), 2.12–1.95 (m, 1 H), 1.25–1.02 (m, 4 H), 0.67 (t, $J = 7.2$ Hz, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.6; MS (ESI) m/z (%) 565 (M + H$^+$, 100); IR (neat) ν 2953, 1727, 1590, 1514, 1438, 1294, 1226, 1210, 1187, 1172, 1117 cm^{-1}; anal. calcd for $C_{35}H_{33}O_5P$: C 74.45; H 5.89. Found: C 74.57; H 6.00.

(8) 1,2-Bis(methoxycarbonyl)-3-(1-diphenylphosphinoylhexyl)phenanthrene (2j)

A solution of **1j** (102 mg, 0.23 mmol) and DMAD (76 mg, 0.53 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 72 hours to afford 94 mg (70%) of **2j**: R_f (petroleum ether–ethyl acetate, 1 : 1) = 0.67; solid, mp 138–140 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (s, 1 H), 8.86 (d, $J =$ 8.4 Hz, 1 H), 8.05–7.96 (m, 2 H), 7.88–7.50 (m, 10 H), 7.20–7.06 (m, 3 H), 4.64–4.54 (m, 1 H), 3.93 (s, 3 H), 3.81 (s, 3 H), 2.35–2.22 (m, 1 H), 2.06–1.90 (m, 1 H), 1.25–1.00 (m, 6 H), 0.70 (t, $J =$ 5.7 Hz, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.8; MS (ESI) m/z (%) 579 (M + H$^+$, 100); IR (neat) ν 3423, 3053, 2951, 2928, 2856, 1737, 1719, 1590, 1439, 1352, 1295, 1223, 1211, 1187, 1163, 1150, 1116, 1008 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{35}PO_5Na$ (M + Na$^+$) 601.2114. Found 601.2093.

(9) 1,2-Bis(methoxycarbonyl)-3-(1-diphenylphosphinoylheptyl)phenanthrene (2k)

A solution of **1k** (111 mg, 0.25 mmol) and DMAD (70 mg, 0.49 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 72 hours to afford 107 mg (73%) of **2k**: R_f (petroleum ether–ethyl acetate, 1 : 1) = 0.67; solid, mp 99–101 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (d, $J = 2.1$ Hz, 1 H), 8.85 (d, $J = 8.4$ Hz, 1 H), 8.05–7.95 (m, 2 H), 7.89–7.63 (m, 5 H), 7.63–7.45 (m, 5 H), 7.26–7.16 (m, 1 H), 7.16–7.08 (m, 2 H), 4.61–4.50 (m, 1 H), 3.96 (s, 3 H), 3.81 (s, 3 H), 2.35–2.20 (m, 1 H), 2.15–1.90 (m, 1 H), 1.30–0.98 (m, 8 H), 0.74 (t, $J = 7.2$ Hz, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.8; MS (ESI) m/z (%) 615 (M + Na$^+$, 20), 593 (M + H$^+$, 100); IR (neat) ν 3610, 3405, 2951, 2930, 1729, 1712, 1658, 1588, 1437, 1294, 1224, 1178, 1163, 1116 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{37}PO_5Na$ (M + Na$^+$) 615.2271. Found 615.2273.

(10) 1,2-Bis(methoxycarbonyl)-3-(3-phenyl-1-diphenylphosphinoylpropyl)phenanthrene (2l)

A solution of **1l** (120 mg, 0.26 mmol) and DMAD (70 mg, 0.49 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 72 hours to afford 101 mg (65%) of **2l**: R_f (petroleum ether–ethyl acetate, 1 : 1) = 0.67; solid, mp 182–183 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (s, 1 H), 8.88 (d, $J =$ 8.4 Hz, 1 H), 8.02–7.92 (m, 2 H), 7.92–7.64 (m, 5 H), 7.64–7.45 (m, 5 H), 7.25–7.05 (m, 6 H), 6.93 (d, $J = 7.8$ Hz, 2 H), 4.70–4.62 (m, 1 H), 3.97 (s, 3 H), 3.76 (s, 3 H), 2.69–2.34 (m, 4 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.5; MS (ESI) m/z (%) 613 (M + H$^+$, 100); IR (neat) ν 3058, 2945, 1734, 1718, 1589, 1454, 1437, 1296, 1224, 1190, 1170, 1116 cm^{-1}; anal. calcd for $C_{39}H_{33}O_5P$: C 76.46; H 5.43. Found: C 76.35; H 5.41.

(11) 1,2-Bis(methoxycarbonyl)-4-(diphenylphosphino-yl)-3-methylnaphthalene (4)

A solution of **3** (125 mg, 0.40 mmol) and DMAD (37 mg, 0.26 mmol) in 2 mL of dry 1,4-dioxane was heated to 150 °C for 36 hours to afford 85 mg (71%) of **4**: R_f (ethyl ether) = 0.25; solid, mp 169–170 °C (petroleum ether–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, $J = 8.7$ Hz, 1 H), 8.05 (d, $J = 8.7$ Hz, 1 H), 7.70–7.60 (m, 4 H), 7.55–7.38 (m, 7 H), 7.35–7.24 (m, 1 H), 4.01 (s, 3 H), 3.88 (s, 3 H), 2.29 (s, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 31.9; MS (ESI) m/z (%) 458 (M + H$^+$, 100); IR (neat) ν 3058, 2945, 1734, 1437, 1339, 1301, 1251, 1183 cm^{-1}; anal. calcd for $C_{27}H_{23}O_5P$: C 70.74; H 5.06. Found: C 70.54; H 5.20.

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19 Crystal data for compound **2c**: $C_{23}H_{22}O_6$, MW = 394.41, triclinic, *P*–1, $a = 7.7495(7)$ Å, $b = 10.1805(9)$ Å, $c = 13.3793(12)$ Å, $\alpha = 93.494(2)°$, $\beta = 91.931\ (2)°$, $\gamma = 109.458\ (2)°$, $V = 991.77\ (15)$ Å^3, $T = 293(2)$ K, $Z = 2$, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.0525$, w$R2 = 0.1429$, reflections collected/unique: 5856/4188 ($R_{int} = 0.0382$). CCDC: 648596.

20 Crystal data for compound **4**: $C_{27}H_{23}O_5P$, MW = 458.42, monoclinic, $P2_1/c$, $a = 11.330(10)$ Å, $b = 22.000(19)$ Å, $c = 9.420(8)$ Å, $\alpha = 90°$, $\beta = 98.108(15)°$, $\gamma = 90°$, $V = 2324(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.0560$, w$R2 = 0.1453$, reflections collected/unique: 13454/5044 ($R_{int} = 0.0786$). CCDC: 648597.

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