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Convenient Phenacene Synthesis by Sequentially Performed Wittig Reaction and Mallory Photocyclization Using Continuous-Flow Techniques

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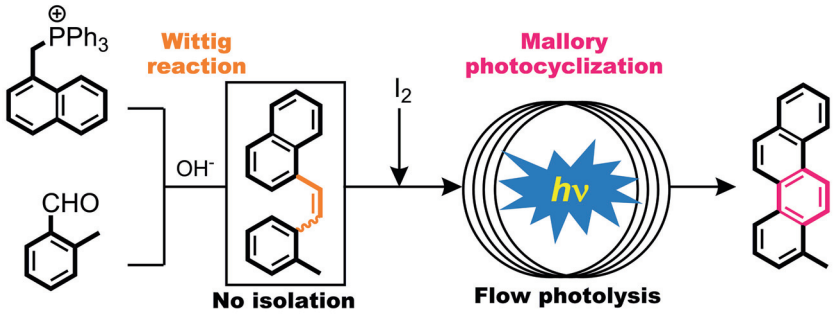

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Abstract Various phenacenes possessing chrysene, picene, and fulminene frameworks were prepared by using a continuous-flow synthetic protocol in which Wittig reaction affording diarylethenes and their Mallory photocyclization producing phenacene skeletons were sequentially performed. The Wittig reaction solution, containing the diarylethene obtained from an arylaldehyde and an arylmethyltriphenylphosphonium salt, was mixed with an iodine solution in the flow system and, subsequently, the solution was subjected to the photoreaction. Desired phenacenes were obtained with high to moderate chemical yield. For the present protocol, isolation of the intermediary diarylethene, which is the key precursor of the phenacene, is unnecessary. The approach provides a convenient method to supply a variety of phenacene samples, which are needed for initial systematic surveys in material science.

Key words phenacene, flow reaction, Mallory photocyclization, Wittig reaction, photochemistry

Aromatic molecules possessing extended π-conjugation are becoming an important class of materials because of their potential applications in organic electronics, such as organic field effect transistors (OFET)[1–4] and organic light-emitting diodes (OLED),[5,6] and even as organic superconductors.[7–10] There are several structural categories of π-extended aromatic compounds, typified by acenes and phenacenes, which consist of, respectively, linear- and zigzag-fusion of benzene rings (Figure 1).

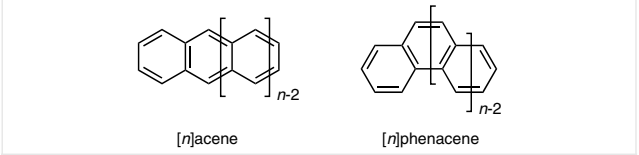


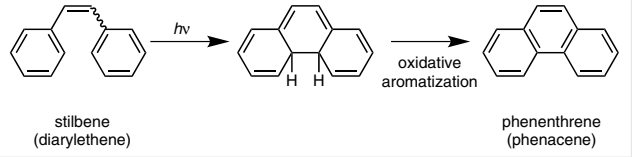
Figure 1 General structures of [*n*]acene and [*n*]phenacene; *n* depicts the number of the benzene rings in the compounds

Acenes have attracted much attention as an active layer of OFET and they have been widely studied[4,6] since the discovery of high-performance p-channel OFET operation of pentacene-based devices.[11] However, the chemical instability of acenes prevents them from being used in practical electronic devices. In contrast, phenacenes have been much less investigated as functional materials in organic electronics. Recently, it has been disclosed that phenacenes are promising materials for the active layer of p-channel OFET.[12–16] It is notable that increasing the number of benzene rings *n* in phenacenes tends to systematically increase in charge mobility of OFET devices fabricated with phenacene single-crystals.[16] Furthermore, upon doping with alkali or alkali-earth metals, picene ([5]phenacene) exhibits superconductivity.[7] Phenacenes are quite stable and robust against exposure to both oxygen and light. Therefore, they are considered to be promising materials for applications in practical organic electronic devices.

Apart from the potential applications, fundamental photophysical features of phenacenes would be of additional interest. Picene fluoresces from the second singlet excited state (S_2) in the gas phase, demonstrating that it has non-Kasha photoluminescence properties.[17]

As for synthesis of phenacene frameworks, since phenacenes are old compounds extracted from coal tar,[18] there are many reported synthetic routes to them. However, little information is available on efficient and systematic phenacene synthesis. Therefore, the development of a facile synthetic protocol for the preparation of various phenacene frameworks is desired to promote phenacene-based material sciences and organic electronics.

One of the most versatile synthetic strategies is photocyclization of diarylethenes followed by oxidative aromatization; the so-called Mallory photocyclization.[19] A general scheme for the reaction is shown in Scheme 1.

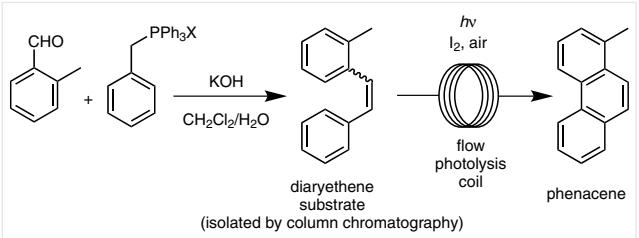


Scheme 1 General reaction scheme for the Mallory photocyclization

Conventionally, batch photolysis has been used for synthetic photoreactions. However, the reaction scale is limited by the size of photolysis vessels, and overreaction forming undesired side products can cause problems. In contrast, continuous-flow photolysis can be used to exclude these drawbacks.[20–22] It has been reported that a continuous-flow photolysis technique was successfully adapted to the Mallory photocyclization for the preparation of phenanthrene and helicene frameworks.[23,24] In our previous study,[15,25] we successfully applied the continuous-flow photolysis to the Mallory photocyclization starting from diarylethenes as the substrates and obtained [*n*]phenacenes possessing benzene rings up to n = 8. Therefore, continuous-flow photolysis has great potential for facile phenacene synthesis.

The diarylethene substrates can be easily prepared by Wittig reaction between arylaldehydes and (arylmethyl)triphenylphosphonium salts in the presence of a base. In our previous phenacene synthesis,[25] we isolated the substrates by column chromatography and subsequently carried out their Mallory photocyclization and it took several hours to complete the two-step synthesis (Scheme 2).

In the present study, we planned to more conveniently synthesize phenacenes by modifying the two-step synthesis. The Wittig diarylethene synthesis and the Mallory photocyclization were sequentially performed without isolation of the diarylethene substrates by using continuous-flow reaction techniques. Various [*n*]phenacenes (n = 4–6)



Scheme 2 Two-step phenacene synthesis by using flow photolysis

were thus obtained in good to moderate chemical yields with shortened overall experimental time.

We first investigated the Wittig–Mallory sequential phenacene synthesis targeting 1-methylchrysene (1MeCH) because methyl-substituted phenacenes serve as building blocks for constructing larger phenacene frameworks.[15,16,26–29] Details of the experimental setup is illustrated in Figure 2. In the Wittig reaction, we chose tetrabutylammonium hydroxide (Bu_4NOH) as the base because it could be used in the homogeneous organic phase and trapped by a silica gel column incorporated in the flow system (see below).

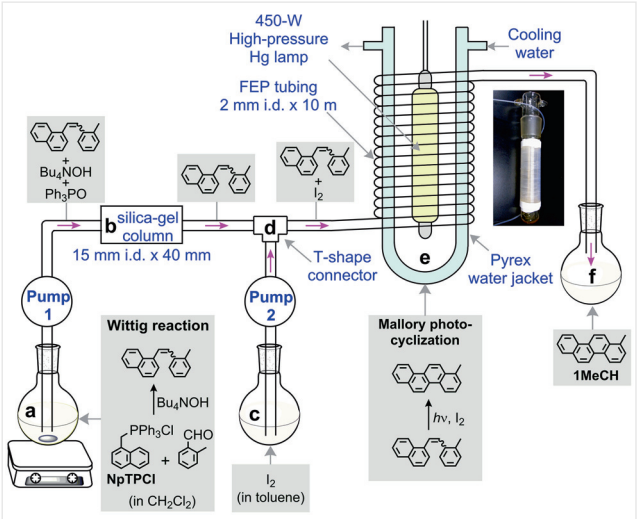


Figure 2 Schematic diagram of the sequentially performed Wittig reaction and Mallory photocyclization for phenacene synthesis. The inserted picture displays the flow photolysis coil part.

A representative experimental procedure is as follows. To a 1.1:1 mixture of tolualdehyde and (1-naphthylmethyl)triphenylphosphonium chloride (NpTPCl) in CH_2Cl_2 was added Bu_4NOH (1.4 equiv) during 12 min and the mixture was stirred at room temperature for an additional 18 min to form 1-(1-naphthyl)-2-(*o*-tolyl)ethene (diarylethene) (Figure 2, a). The resulting mixture was flowed by pump 1 through a silica gel column (**b**) in which excess Bu_4NOH and a part of Ph_3PO, generated in the Wittig reaction, were trapped. The resulting solution containing the diarylethene

was then mixed with a toluene solution of I_2 (**c**) supplied by pump 2 at the 'T'-shaped connector (**d**). The final concentration of I_2 was set to 10 mol% of the initial concentration of NpTPCl. The mixture was photolyzed with a 450 W high-pressure mercury arc lamp while being flowed through the photolysis coil (**e**) made of fluorinated ethylene-propylene copolymer (FEP). The obtained reaction solution (**f**) was concentrated and the residual crude product was washed with MeOH to afford 1MeCH.

The reaction conditions were optimized by modifying two parameters; namely, initial concentration of the reactant NpTPCl (substrate concentration), and residence time (irradiation time) of the flow photolysis. Figure 3 summarizes the results of the product yields as a function of these two parameters. At the same residence time, the yield of 1MeCH increased with a decrease in substrate concentration. Lower substrate concentration is, thus, beneficial for phenacene formation. As for the residence-time dependency, at a high concentration (26 mM), longer residence time resulted in higher product yield; 33% and 50% at 3 min and 9 min residence time, respectively. In contrast, at a lower substrate concentration (6 mM), the product yield reached a maximum at 6 min residence time (78%) and decreased after longer irradiation (9 min, 65%).

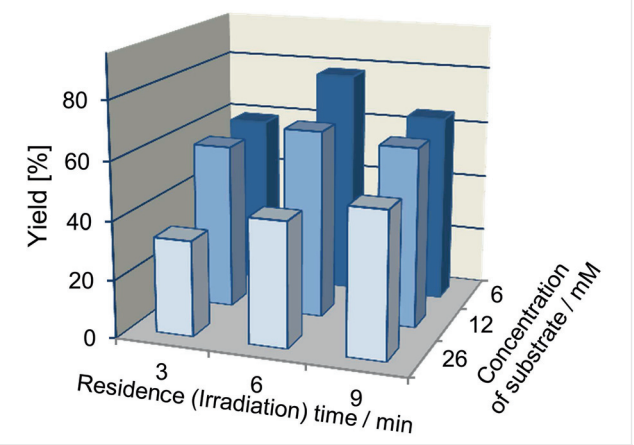


Figure 3 Isolated yields of 1MeCH obtained by the sequential phenacene synthesis plotted as a function of residence time and substrate concentration

We examined the factors decreasing the yield of 1MeCH upon prolonged irradiation, namely at the low substrate concentration, with respect to photodegradation of the photoproduct. A solution of 1MeCH (5 mM in $CDCl_3$) was irradiated under aerated conditions with a small amount of I_2 and the photolysate was analyzed by ^1H NMR spectroscopy. Upon 30 min irradiation, 29% of the initial 1MeCH was consumed, while 1-chrysenecarbaldehyde was observed (7%) as a detectable photoproduct (Figure S1 in the Supporting Information). Photo-oxidative degradation of methyl-substituted aromatics has been observed for photolysis of toluene and xylenes in the presence of oxygen.[30] It is concluded that oxidative photodegradation is partly responsible for the lower yield observed after longer illumination time; thus, prolonged irradiation should be avoided.

Based on the results, we determined to use the optimal conditions for the present phenacene synthesis; namely, 6 min residence time and 6 mM substrate concentration. NpTPCl and (1-phenanthrylmethyl)triphenylphosphonium bromide (PhenTPBr) were used as the Wittig reactants and systematic phenacene synthesis was investigated. The results, together with the product structures and abbreviations, are summarized in Table 1.

Starting from NpTPCl and either benzaldehyde or 1-naphthaldehyde, the parent CH and PIC were obtained in excellent isolated yields, 84% and 86%, respectively (Table 1, entries 1 and 2). Reactions of PhenTPBr with benzaldehyde and 1-naphthaldehyde gave PIC (71%) and FUL (74%), respectively (entries 10 and 11). These chemical yields are comparable to those previously observed for flow photolysis of diarylethenes.[25]

When *o*-substituted benzaldehydes were used as substrates, the corresponding 1-substituted chrysenes and 4-substituted picenes were obtained; thus, the corresponding methyl, bromo, and cyano derivatives could be prepared in moderate to high yields (Table 1, entries 3–5 and 12–14). Furthermore, by using *p*-substituted benzaldehydes, 3-substituted chrysenes (entries 7 and 8) and 2-substituted picenes, respectively, were efficiently prepared (entries 16 and 17).

Nitro derivatives ($1NO_2CH$, $4NO_2PIC$) were not obtained by using the present procedure, and complex reaction mixtures were formed (Table 1, entries 6 and 15). It has been noted that 2-nitrostilbene was photolabile and generates resinous products.[31] π-Extension of the phenyl moiety in 2-nitrostilbene to 1-naphthyl (entry 6) or 1-phenanthryl (entry 15) groups was not effective in promoting the desired Mallory photocyclization.

For the reaction between NpTPCl and *m*-bromobenzaldehyde, two isomeric products, 2BrCH and 4BrCH, are possible through photocyclization of two conformers; that is, *exo*- and *endo*-**A** (Scheme 3). Experimentally, 2BrCH (34%) and unsubstituted CH (34%) were obtained, whereas the expected product 4BrCH was not detected in the present sequential synthesis (Table 1, entry 9). Formation of the dehydrobrominated product CH was unexpected.

For the reaction between PhenTPBr and *m*-bromobenzaldehyde, dehydrobrominated product PIC was detected along with expected cyclization products, 1BrPIC and 3BrPIC (Table 1, entry 18); 3BrPIC/1BrPIC/PIC = 30:21:35%. From the product mixture, 1BrPIC was isolated by extraction with toluene. As PIC and 3BrPIC were not completely separated from each other by chromatography because of their low solubility in common solvents, their yields were determined by the integral ratio of ^1H NMR signals of the product mixture (*cf.* Table 1, entry 18).

Table 1 Synthesis of Phenacenes by Wittig–Mallory Sequential Reactions in the Flow System

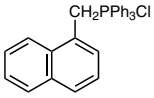
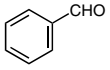
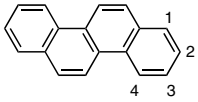
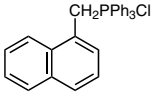
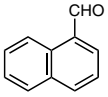
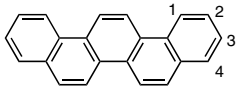
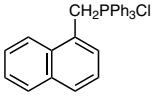
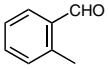
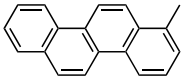
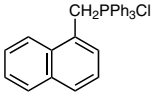
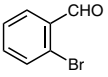
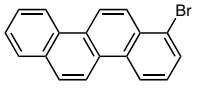
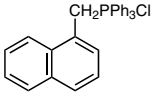
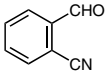
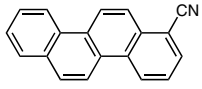
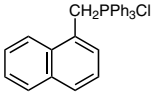
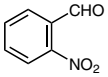
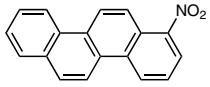
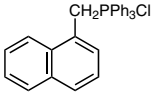
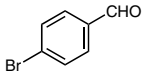
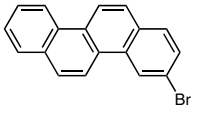
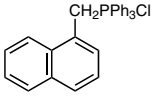
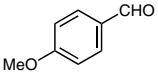
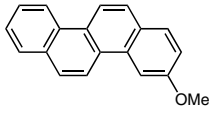
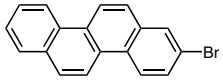
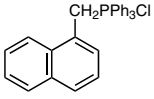
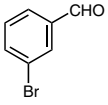
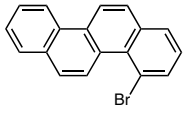
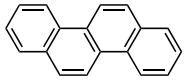
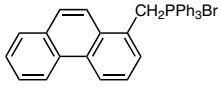
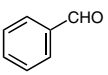
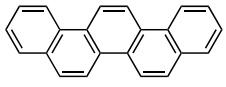
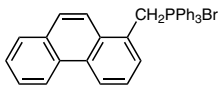
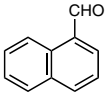
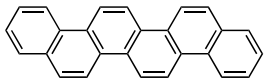
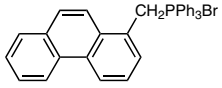
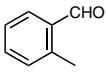
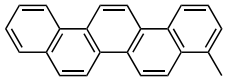
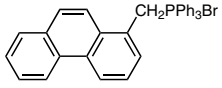
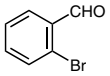
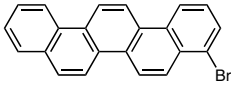
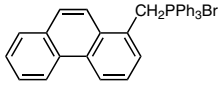
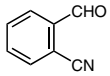
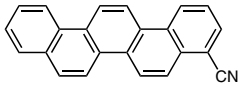
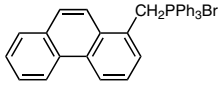
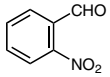
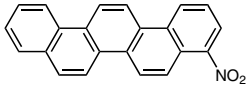
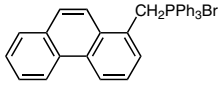
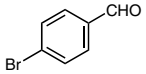
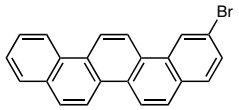
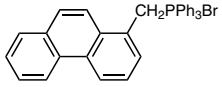
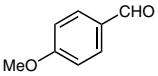
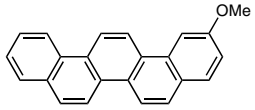
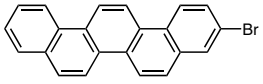
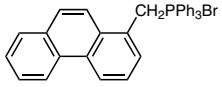
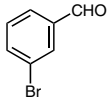
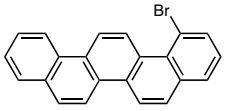
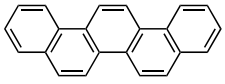
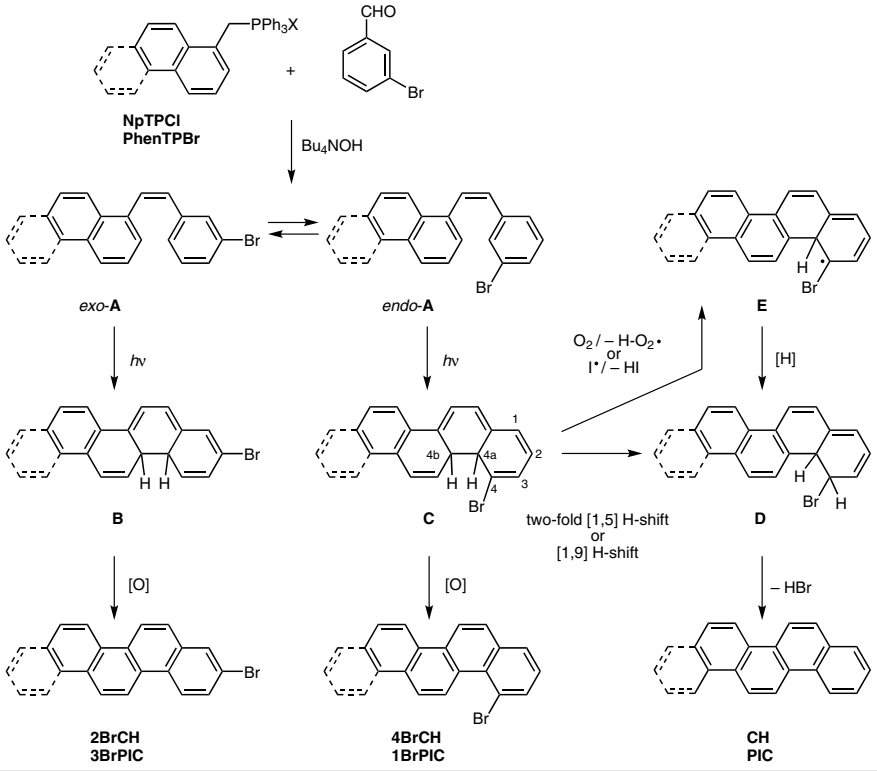
Entry	Substrate				Product	Abbreviation	Isolated yield	
	Phosphonium salt	mg (μmol)	Arylaldehyde	mg (μmol)			mg (μmol)	%
1	 **NpTPCl**	55 (125)		15 (138)		CH	24 (110)	84
2		55 (125)		23 (140)		PIC	30 (110)	86
3		55 (125)		16 (130)		1MeCH	24 (97)	78
4		55 (125)		26 (138)		1BrCH	34 (110)	87
5		55 (125)		19 (142)		1CNCH	20 (79)	63
6		55 (125)		23 (149)		$1NO_2CH$	–[a]	0
7		55 (125)		26 (142)		3BrCH	33 (110)	85
8		55 (125)		19 (141)		3MeOCH	19 (75)	60
						2BrCH	13 (42)	34
9[b]		55 (125)		26 (137)		4BrCH	–[a]	0
						CH	10 (42)	34
10	 **PhenTPBr**	67 (127)		15 (138)		PIC	25 (90)	71

Table 1 (continued)

Entry	Substrate				Product	Abbreviation	Isolated yield	
	Phosphonium salt	mg (μmol)	Arylaldehyde	mg (μmol)			mg (μmol)	%
11		67 (127)		23 (140)		FUL	31 (94)	74
12		67 (127)		16 (130)		4MePIC	28 (96)	75
13		67 (127)		26 (138)		4BrPIC	39 (100)	87
14		67 (127)		19 (142)		4CNPIC	13 (44)	35
15		67 (127)		22 (148)		4NO$_2$PIC	–[a]	0
16		67 (127)		26 (142)		2BrPIC	41 (120)	92
17		67 (127)		19 (141)		2MeOPIC	17 (56)	44
						3BrPIC		3BrPIC/ 1BrPIC/ PIC
18[c]		67 (127)		25 (137)		1BrPIC	36 mg[d] 35 mg[e]	30:21:35 27:45:5
						PIC		

[a] Not detected.
[b] The products were separated by preparative chromatography (reversed-phase silica gel, MeOH).
[c] Product yield was determined by integration of the ^{1}H NMR spectra.
[d] Weight of the crude product mixture and the product ratio obtained under photolysis conditions at r.t.
[e] Weight of the crude product mixture and the product ratio obtained under photolysis conditions at 0 °C.

It was found that the product distribution for the sequential reaction of *m*-bromobenzaldehyde with PhenTPBr was affected by the temperature of the photoreaction step. When the reaction between PhenTPBr and *m*-bromobenzaldehyde was carried out under the ice-cooled photolysis conditions, the product yields were 3BrPIC/1BrPIC/PIC = 27:45:5% at 0 °C. Thus, under the low-temperature photolysis conditions, the yield of PIC decreased while that of 1BrPIC increased (*cf.* Table 1, entry 18). In contrast, for the reaction of NpTPCl and *m*-bromobenzaldehyde, when the sequential synthesis was conducted by cooling the photolysis coil with ice, yields of 2BrCH/CH = 45:34% were comparable to those observed for the reaction performed at r.t. (cf. Table 1, entry 9). These results suggest that a thermal pro-



Scheme 3 Plausible mechanism for formation of CH and PIC in the sequential reaction of *m*-bromobenzaldehyde with NpTPCl and PhenTPBr

cess was involved in the dehydrobromination process and the activation barrier was considered to be higher for the formation of PIC than that for the formation of CH.

Several pathways of thermally occurring dehydrobromination are expected: (1) sigmatropic hydrogen shift of H_{4b} in intermediate **C** *via* two-fold [1,5] shift or direct [1,9] shift[33,34] forming **D**, followed by elimination of HBr, (2) extraction of H_{4b} in intermediate **C** mediated by the dissolved molecular oxygen or iodine radical subsequent to hydrogen re-abstraction of radical **E**, which finally aromatizes to afford the unsubstituted products CH, PIC. It has been noted that [1,5] H-shift is not important in the 4a,4b-dihydrophenanthrene system.[19] Theoretical calculations suggest that a [1,9] H-shift from **C** to **D** is energetically unfavorable compared with the two-fold [1,5] H-shift (Figure S1 in the Supporting Information). Therefore, we deduce that the formation of the dehydrobrominated products might be derived through abstraction of H_{4a} of intermediate **C** followed by hydrogen reabstraction by radical **E** and the final elimination of HBr. During the conversion from **E** into **D**, a C(sp^3)–H bond of 1,3-cyclohexadiene is produced. By considering bond-dissociation energy of the C(sp^3)–H bond in 1,3-cyclohexadiene (73 kcal mol^{-1}),[35] H–I (71 kcal mol^{-1}),[36] and H–$O_2^{\bullet}$ (47 kcal mol^{-1}),[36] the transformation from **E** into **D** is expected to be exothermic. Further experimental and theoretical investigations to reveal the mechanism of HBr elimination are under way.

In summary, various phanacenes were prepared through sequentially performed Wittig reaction and Mallory photocyclization by using continuous-flow photolysis techniques. Isolation of the diarylethene precursors generated in the Wittig reaction was not necessary and drastically shortened total operation time (<1.2 h) was attained for the present reaction scale. The results indicate that several hundred milligrams of phenacenes will be obtained by one-day operation of the flow system. Furthermore, the substituted phenacenes can be converted into various functionalized derivatives through an appropriate functional-group transformation.[32] Therefore, the present synthetic protocol is expected to promote phenacene-based material sciences by rapid supply of various samples needed for initial systematic surveys.

^{1}H and ^{13}C NMR spectra were collected with VARIAN Mercury 300 (300 MHz), VARIAN 400MR (400 MHz) or VARIAN NMR System 600 (600 MHz) spectrometers. IR spectra were measured with a SHIMADZU IR Prestige-21 spectrophotometer. Elemental analyses were performed with a Perkin–Elmer 2400II at the Micro Elemental Analysis Laboratory of Okayama University.

The flow reaction apparatus consisted of two ceramic micro-plunger pumps (Yamazen, MSP-101), a 450 W high-pressure mercury arc lamp (USHIO, UM-452), and FEP tubing (2 mm i.d. × 10 m) (*cf.* Figure

2). A syringe-type disposable silica gel column (Yamazen, W826–02) was incorporated in the flow system (Figure 2, b) and was replaced for each run.

Wittig–Mallory Sequential Phenacene Synthesis; Typical Procedure

To a solution of (1-naphthylmethyl)triphenylphosphonium chloride (55 mg, 125 μmol) and *o*-tolualdehyde (16 mg, 130 μmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of Bu_4NOH (34 mM in CH_2Cl_2, 5 mL, 175 μmol) over 12 min. The solution was diluted with CH_2Cl_2 (5 mL) and stirred at r.t. for 18 min. The resulting Wittig reaction mixture was introduced into the flow reaction apparatus (Figure 2). The excess Bu_4NOH, H_2O, and a part of triphenylphosphine oxide in the reaction mixture were trapped with a silica gel column. The solution that flowed out from the column was mixed with the same volume of solution of I_2 (16 mg, 64 μmol) in toluene (100 mL) through a 'T'-shaped connector and irradiated with a 450 W high-pressure mercury arc lamp. The residence time in the photoreaction coil was set to 6 min (cf. Figure 2). The finally obtained reaction solution was concentrated under reduced pressure and the residual crude product was washed with MeOH to afford 1MeCH (24 mg, 78 %).

In the above protocol, the products were isolated after washing the crude reaction mixture with MeOH. In some cases, the final products were isolated by column chromatography (Table 1, entries 9 and 18) or recrystallization (Table 1, entry 17).

1-Methylchrysene (1MeCH)

[CAS Reg. No. 3351-28-8]

Colorless crystals; mp 252–253 °C (Lit.[37] 250–253 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 8.4 Hz, 1 H), 8.77 (d, *J* = 9.6 Hz, 1 H), 8.75 (d, *J* = 9.2 Hz, 1 H), 8.69 (d, *J* = 8.4 Hz, 1 H), 8.22 (d, *J* = 9.6 Hz, 1 H), 8.01 (d, *J* = 9.2 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.70 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H), 7.68–7.57 (m, 2 H), 7.49 (d, *J* = 7.2 Hz, 2 H), 2.83 (s, 3 H).

Chrysene (CH)

[CAS Reg. No. 218-01-9]

Colorless crystals; mp 259–259.5 °C (Lit.[38] 256 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 8.4 Hz, 1 H), 8.74 (d, *J* = 9.0 Hz, 1 H), 8.02 (d, *J* = 9.0 Hz, 1 H), 8.00 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.72 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.64 (m, *J* = 8.1, 6.9, 1.5 Hz, 1 H).

1-Bromochrysene (1BrCH)

[CAS Reg. No. 76670-38-7]

Colorless crystals; mp 242–243 °C (Lit.[39] 240–241 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 9.3 Hz, 1 H), 8.80 (d, *J* = 8.4 Hz, 1 H), 8.78 (d, *J* = 7.8 Hz, 1 H), 8.69 (d, *J* = 9.0 Hz, 1 H), 8.46 (d, *J* = 9.3 Hz, 1 H), 8.04 (d, *J* = 9.0 Hz, 1 H), 8.01 (d, *J* = 8.1 Hz, 1 H), 7.93 (d, *J* = 7.8 Hz, 1 H), 7.75 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H), 7.70–7.65 (m, 1 H), 7.55 (t, *J* = 7.8 Hz, 1 H).

2-Bromochrysene (2BrCH)

[CAS Reg. No. 55120-48-4]

Colorless crystals; mp 265–265.5 °C (Lit.[39] 261–262 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.83–8.69 (m, 2 H), 8.64 (d, *J* = 9.0 Hz, 1 H), 8.63 (d, *J* = 9.0 Hz, 1 H), 8.14 (d, *J* = 2.1 Hz, 1 H), 8.08–7.96 (m, 2 H), 7.91 (d, *J* = 9.0 Hz, 1 H), 7.77 (dd, *J* = 9.0, 2.1 Hz, 1 H), 7.73 (d, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.66 (d, *J* = 8.1, 6.9, 1.2 Hz, 1 H).

3-Bromochrysene (3BrCH)

[CAS Reg. No. 56158-60-2]

Colorless crystals; mp 182–183 °C (Lit.[39] 182.5–183 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 1.2 Hz, 1 H), 8.76 (d, *J* = 8.0 Hz, 1 H), 8.72 (d, *J* = 9.2 Hz, 1 H), 8.60 (d, *J* = 9.2 Hz, 1 H), 8.45–7.98 (m, 2 H), 7.95 (d, *J* = 9.2 Hz, 1 H), 7.85 (d, *J* = 8.8 Hz, 1 H), 7.76–7.69 (m, 2 H), 7.66 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H).

3-Methoxychrysene (3MeOCH)

[CAS Reg. No. 36288-19-4]

Colorless crystals; mp 147–148 °C (Lit.[40] 145–146 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 8.1 Hz, 1 H), 8.64 (d, *J* = 9.3 Hz, 1 H), 8.60 (d, *J* = 9.0 Hz, 1 H), 8.12 (d, *J* = 2.4 Hz, 1 H), 8.05–7.94 (m, 3 H), 7.91 (d, *J* = 8.7 Hz, 1 H), 7.71 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1 H), 7.67–7.59 (m, 1 H), 7.30 (dd, *J* = 8.7, 2.4 Hz, 1 H), 4.07 (s, 3 H).

1-Cyanochrysene (1CNCH)

[CAS Reg. No. 68723-52-4]

Colorless crystals; mp 232–235 °C (Lit.[41] 228–229 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.04 (d, *J* = 9.0 Hz, 1 H), 8.96 (d, *J* = 9.3 Hz, 1 H), 8.83 (d, *J* = 8.1 Hz, 1 H), 8.70 (d, *J* = 9.3 Hz, 1 H), 8.43 (d, *J* = 9.3 Hz, 1 H), 8.09 (d, *J* = 9.3 Hz, 1 H), 8.05 (dd, *J* = 7.2, 1.2 Hz, 1 H), 8.04 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.82–7.73 (m, 2 H), 7.71 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 1 H).

Picene (PIC)

[CAS Reg. No. 213-46-7]

Colorless crystals; mp >300 °C (Lit.[42] >366–367 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.97 (s, 2 H), 8.87 (d, *J* = 8.4 Hz, 2 H), 8.80 (d, *J* = 9.3 Hz, 2 H), 8.08–7.99 (m, 4 H), 7.75 (ddd, *J* = 8.4, 6.6, 1.5 Hz, 2 H), 7.67 (ddd, *J* = 7.8, 6.6, 1.2 Hz, 2 H).

4-Methylpicene (4MePIC)

[CAS Reg. No. 117868-02-7]

Colorless crystals; mp >300 °C (Lit.[43] >370–372 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, *J* = 9.6 Hz, 1 H), 8.95 (d, *J* = 9.6 Hz, 1 H), 8.87 (d, *J* = 8.4 Hz, 1 H), 8.83 (d, *J* = 9.2 Hz, 1 H), 8.81 (d, *J* = 8.8 Hz, 1 H), 8.76 (d, *J* = 8.4 Hz, 1 H), 8.24 (d, *J* = 9.2 Hz, 1 H), 8.08–7.99 (m, 2 H), 7.75 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H), 7.69 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H), 7.64 (dd, *J* = 8.4, 7.2 Hz, 1 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 2.85 (s, 3 H).

4-Bromopicene (4BrPIC)

Colorless crystals; mp >300 °C.

IR (neat): 3047, 1581, 1427, 1273, 1209, 1051, 797, 766, 748, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, *J* = 9.2 Hz, 1 H), 8.93 (d, *J* = 9.2 Hz, 1 H), 8.90 (d, *J* = 9.6 Hz, 1 H), 8.87 (d, *J* = 8.8 Hz, 1 H), 8.86 (d, *J* = 8.4 Hz, 1 H), 8.80 (d, *J* = 9.2 Hz, 1 H), 8.48 (d, *J* = 9.6 Hz, 1 H), 8.07 (d, *J* = 9.2 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.95 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.61 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1 H), 7.69 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H), 7.58 (dd, *J* = 8.4, 7.6 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_2CDCl_2$, 80 °C): δ = 132.3, 132.2, 130.8, 130.6, 130.5, 129.2, 128.8, 128.7, 128.6, 128.0, 127.2, 127.1, 127.0, 126.0, 123.8, 123.3, 123.2, 123.0, 122.4, 121.7, 121.5, 120.4.

Anal. Calcd for $C_{22}H_{13}Br$: C, 73.96; H, 3.67. Found: C, 73.76; H, 3.55.

3-Bromopicene (3BrPIC)

Colorless crystals; mp >300 °C.

IR (neat): 3051, 1429, 1273, 1263, 880, 806, 752 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.97 (d, *J* = 9.2 Hz, 1 H), 8.92–8.84 (m, 2 H), 8.81 (d, *J* = 9.2 Hz, 1 H), 8.76 (d, *J* = 9.2 Hz, 1 H), 8.71 (d, *J* = 8.8 Hz, 1 H), 8.16 (d, *J* = 2.0 Hz, 1 H), 8.05 (d, *J* = 9.2 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.94 (d, *J* = 9.2 Hz, 1 H), 7.81 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.78–7.72 (m, 1 H), 7.72–7.63 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_2CDCl_2$, 80 °C): δ = 133.4, 132.1, 130.7, 130.5, 130.0, 129.2, 129.0, 128.74, 128.70, 128.6, 128.5, 127.9, 127.1, 126.9, 126.4, 125.0, 123.2, 123.0, 122.3, 121.5, 121.4, 120.8.

Anal. Calcd for $C_{22}H_{13}Br$: C, 73.96; H, 3.67. Found: C, 73.73; H, 3.31.

2-Bromopicene (2BrPIC)

Colorless crystals; mp >300 °C.

IR (neat): 3047, 1431, 1259, 1078, 827, 798, 754 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.02–8.94 (m, 2 H), 8.88 (d, *J* = 8.0 Hz, 1 H), 8.86 (d, *J* = 9.2 Hz, 1 H), 8.81 (d, *J* = 9.2 Hz, 1 H), 8.77 (d, *J* = 9.2 Hz, 1 H), 8.05 (d, *J* = 9.2 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.4 Hz, 1 H), 7.80–7.72 (m, 2 H), 7.68 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_2CDCl_2$, 80 °C): δ = 132.2, 132.0, 130.6, 130.5, 130.1, 130.0, 129.20, 129.16, 128.6, 127.9, 127.8, 127.1, 127.00, 126.95, 126.0, 123.3, 122.3, 122.2, 121.54, 121.50, 121.3, 120.4.

Anal. Calcd for $C_{22}H_{13}Br$: C, 73.96; H, 3.67. Found: C, 73.65; H, 3.51.

1-Bromopicene (1BrPIC)

Colorless crystals; mp 238–239 °C.

IR (neat): 3046, 1429, 1421, 1266, 823, 813, 794, 745 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.13 (d, *J* = 9.6 Hz, 1 H), 8.96–8.84 (m, 2 H), 8.82 (d, *J* = 9.0 Hz, 1 H), 8.76 (d, *J* = 9.3 Hz, 1 H), 8.07 (d, *J* = 9.3 Hz, 1 H), 8.07 (dd, *J* = 7.5, 1.2 Hz, 1 H), 8.03 (d, *J* = 9.3 Hz, 1 H), 8.02 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.99–7.92 (m, 2 H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.68 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 135.0, 132.3, 130.59, 130.57, 129.4, 129.1, 128.8, 128.7, 128.6, 128.4, 127.8, 127.6, 127.06, 127.03, 126.8, 125.5, 123.6, 122.98, 122.97, 121.9, 119.9, 119.8.

Anal. Calcd for $C_{22}H_{13}Br$: C, 73.96; H, 3.67. Found: C, 74.06; H, 3.58.

2-Methoxypicene (2MeOPIC)

Colorless crystals; mp 275–276 °C.

IR (neat): 2994, 1610, 1431, 1221, 1034, 826, 799, 752, 525 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 9.6 Hz, 1 H), 8.87 (d, *J* = 9.6 Hz, 1 H), 8.86 (d, *J* = 8.4 Hz, 1 H), 8.78 (d, *J* = 9.0 Hz, 1 H), 8.66 (d, *J* = 9.0 Hz, 1 H), 8.20 (d, *J* = 2.4 Hz, 1 H), 8.06–8.00 (m, 2 H), 7.98 (d, *J* = 9.0 Hz, 1 H), 7.93 (d, *J* = 9.0 Hz, 1 H), 7.74 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H), 7.70–7.63 (m, 1 H), 4.09 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.8, 132.1, 132.0, 130.6, 130.1, 129.2, 128.9, 128.8, 128.7, 128.1, 127.6, 127.3, 127.0, 126.9, 126.7, 123.3, 121.9, 121.8, 121.3, 119.4, 117.5, 104.0, 55.7.

Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.38; H, 5.23.

4-Cyanopicene (4CNPIC)

Yellow crystals; mp >300 °C.

IR (neat): 2224, 800, 775, 754, 517 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.11 (d, *J* = 8.4 Hz, 1 H), 9.03 (d, *J* = 9.2 Hz, 1 H), 9.01 (d, *J* = 9.2 Hz, 1 H), 8.93 (d, *J* = 9.2 Hz, 1 H), 8.87 (d, *J* = 8.0 Hz, 1 H), 8.80 (d, *J* = 9.2 Hz, 1 H), 8.44 (d, *J* = 9.2 Hz, 1 H), 8.10 (d, *J* = 9.2 Hz, 1 H), 8.08–8.00 (m, 2 H), 7.84 (m, 2 H), 7.71 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_2CDCl_2$, 80 °C): δ = 132.4, 132.3, 131.8, 130.8, 130.4, 129.4, 129.1, 128.7, 128.6, 128.4, 128.3, 128.2, 127.22, 127.18, 126.0, 124.9, 123.7, 123.2, 123.0, 121.3, 121.2, 118.0, 110.9.

Anal. Calcd for $C_{23}H_{13}N$: C, 91.06; H, 4.32; N, 4.62. Found: C, 90.66; H, 4.32; N, 4.62.

Fulminene (FUL)

[CAS Reg. No. 217-37-8]

Colorless crystals; mp >300 °C (Lit.[44] >300 °C).

^1H NMR (600 MHz, $CDCl_2CDCl_2$, 65 °C): δ = 9.05 (d, *J* = 9.6 Hz, 1 H), 9.01 (d, *J* = 9.6 Hz, 1 H), 8.90 (d, *J* = 7.2 Hz, 1 H), 8.89 (d, *J* = 9.0 Hz, 1 H), 8.11 (d, *J* = 9.0 Hz, 1 H), 8.07 (d, *J* = 7.8 Hz, 1 H), 7.79 (t, *J* = 7.2 Hz, 1 H), 7.72 (t, *J* = 7.8 Hz, 1 H).

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Supporting Information

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