

The Electronic Supplementary Information for

Systematic investigations on fused π -system compounds of seven benzene rings prepared by photocyclization of diphenanthrylenes

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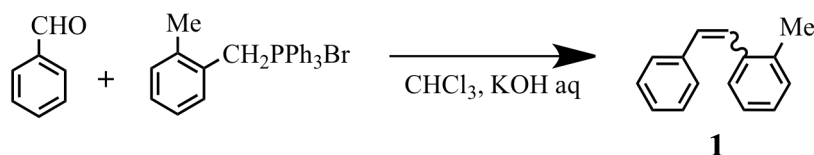
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1. Synthesis of phenanthrene derivatives.

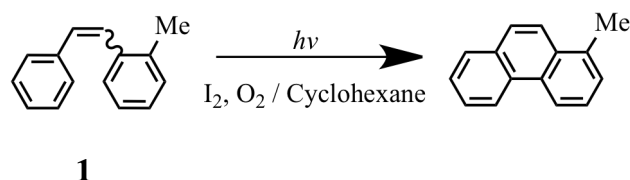
1-1. Synthesis of (phenanthrylmethyl)triphenyl phosphonium salts

1-1-1. Preparation of compound 1



To a chloroform solution (130 ml) of (*o*-methylbenzyl)triphenylphosphonium bromide (4.5 g, 10.1 mmol) and benzaldehyde (1.0 ml, 9.8 mmol), aqueous KOH (50 %, 20 ml) was dropwise added. The mixture was stirred at 65 °C for 1h. After cooling to room temperature, the organic layer was separated, washed with water and brine, and evaporated under reduced pressure. The product was purified by silica gel chromatography with hexane as the eluent to obtain compound **1** (1.73 g, 91%). The compound obtained was used in the following photoreaction without further purification.

1-1-2. Preparation of 1-methylphenanthrene



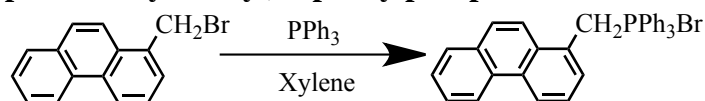
A cyclohexane solution (2000 ml) of compound **1** (1.78 g, 9.16 mmol) and 50 mg I₂ was photolyzed using with a home-made micro-flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate and brine. After usual work-up, the product was purified by silica gel chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-methyl phenanthrene (1.69 g, 96 %). Mp 118–120 °C (lit 121–123 °C)² ¹H NMR (300 MHz, CDCl₃) δ_H = 8.71 (d, 1H, *J* = 8.0 Hz), 8.60 (d, 1H, *J* = 8.2 Hz), 7.96 (d, 1H, *J* = 9.1 Hz), 7.90 (dd, 1H, *J* = 7.4, 1.4 Hz), 7.79 (d, 1H, *J* = 9.1 Hz), 7.51–7.69 (m, 3H), 7.45 (d, 1H, *J* = 7.4 Hz), 2.76 (s, 3H).

1-1-3. Preparation of 1-bromomethylphenanthrene



A CCl₄ solution (90 ml) of 1-methylphenanthrene (1.68 g, 8.7 mmol), *N*-bromosuccinimide (NBS, 2.18 g, 12.2 mmol) and benzoyl peroxide (BPO, 0.20 g, 0.60 mmol) was refluxed under N₂ atmosphere for 3 h. After cooling to room temperature, the filtrated solution was washed with water and brine. The product was purified by silica gel chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-(bromomethyl)phenanthrene (1.65 g, 70 %). Mp 96–97 °C (lit 97 °C)³ ¹H NMR (300 MHz, CDCl₃) δ_H = 8.72 (d, 1H, *J* = 8.2 Hz), 8.70 (d, 1H, *J* = 8.4 Hz), 8.10 (d, 1H, *J* = 9.1 Hz), 7.88–7.96 (a doublet and a dd signals overlap, 2H), 7.56–7.96 (m, 4H), 5.02 (s, 2H).

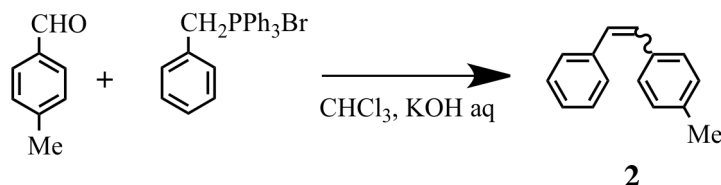
1-1-4. Preparation of (1-phenanthrylmethyl)triphenylphosphonium bromide



A xylene (30 ml) solution of 1-bromomethylphenanthrene (810 mg, 3.0 mmol) and triphenylphosphine (1.21 g, 4.5 mmol) was refluxed for 12 h under N₂ atmosphere. The precipitate was filtrated and washed

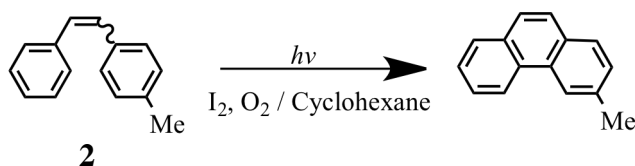
with benzene, providing the desired phosphonium salt (1.0 g, 75 %). Mp >300 °C. ¹H NMR (600 MHz, CDCl₃): δ_H = 8.51 (d, 1H, *J* = 8.2 Hz), 8.64 (d, 1H, *J* = 7.9 Hz), 7.71–7.62 (m, 10H), 7.61–7.56 (m, 2H), 7.53 (t, 1H, *J* = 7.3 Hz), 7.51–7.46 (m, 6H), 7.33–7.26 (m, 2H), 7.21 (d, 1H, *J* = 9.2 Hz), 5.86 (d, 2H, *J*_{PH} = 13.9 Hz) ¹³C NMR (151 MHz, CDCl₃): δ_C = 135.0 (*J*_{PH} = 3.8 Hz), 134.6 (*J*_{PH} = 9.8 Hz), 131.3 (*J*_{PH} = 6.4 Hz), 131.2 (*J*_{PH} = 4.6 Hz), 131.1, 130.6 (*J*_{PH} = 3.4 Hz), 130.13 (*J*_{PH} = 12.4 Hz), 130.05, 128.5, 127.3, 126.9 (*J*_{PH} = 5.5 Hz), 126.1 (*J*_{PH} = 9.8 Hz), 123.8 (*J*_{PH} = 9.0 Hz), 123.5 (*J*_{PH} = 9.8 Hz), 122.8, 121.6 (*J*_{PH} = 1.7 Hz), 117.8 (*J*_{PH} = 85.3 Hz), 28.1 (*J*_{PH} = 45.7 Hz).

1-1-5. Preparation of compound 2 (4-methylstilbene)



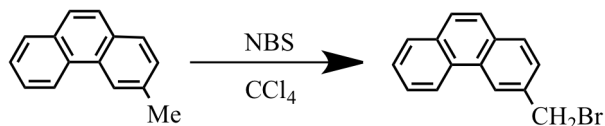
To a chloroform solution (50 ml) of benzyltriphenylphosphonium bromide (2.86 g, 6.6 mmol) and *p*-tolualdehyde (0.65 ml, 5.5 mmol), aqueous KOH (50 %, 25 ml) was dropwise added. The mixture was stirred at 65 °C for 1h. After cooling to room temperature, the organic layer was separated, washed with water and brine, and concentrated under reduced pressure. The product was purified by silica gel chromatography with a hexane/chloroform mixture (10:1, v/v) to obtain compound 2 (1.04 g, 99%). The compound obtained was used in the following photoreaction without further purification.

1-1-6. Preparation of 3-methylphenanthrene



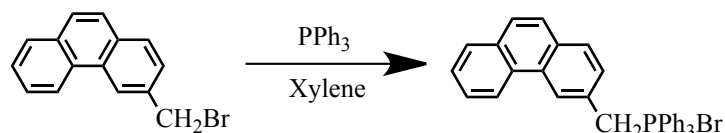
A cyclohexane solution (1000 ml) of compound 2 (1.04 g, 5.4 mmol) and 50 mg I₂ was photolyzed using with a home-made flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate and brine. After usual work-up, the product was purified by silica gel chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 3-methylphenanthrene (900 mg, 90 %). Mp 62–63 °C (lit 63–65 °C)² ¹H NMR (400 MHz CDCl₃): δ_H = 8.67 (d, 1H, *J* = 8.24 Hz) 8.47 (s, 1H) 7.86 (dd, 1H, *J* = 1.37, 7.79 Hz) 7.78 (d, 1H, *J* = 8.01) 7.71–7.55 (m, 4H) 7.42 (dd, 1H, *J* = 1.49, 8.13 Hz) 2.62 (s, 3H).

1-1-7. Preparation of 3-(bromomethyl)phenanthrene



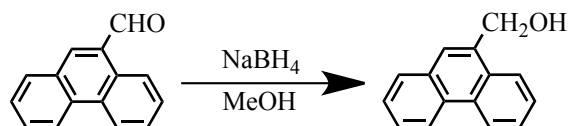
A CCl₄ solution (100 ml) of 3-methylphenanthrene (1.92 g, 10.0 mmol), *N*-bromosuccinimide (NBS, 2.31g, 12.0 mmol) and benzoyl peroxide (BPO, 0.20 g, 0.50 mmol) was refluxed under N₂ atmosphere for 3 h. After cooling to room temperature, the filtrated solution was washed with water and brine. The product was purified by silica gel chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 3-(bromomethyl)phenanthrene (1.28 g, 48 %). Mp 117–118 °C (lit 95–96 °C)⁴ ¹H NMR (400 MHz CDCl₃): δ_H = 8.67 (d, 2H, *J* = 6.18 Hz) 7.92–7.86 (m, 2H) 7.76–7.59 (m, 5H) 4.78 (s, 2H). The ¹H NMR data were consistent with those reported ones.⁵

1-1-8. Preparation of (3-phenanthryl)methylphosphonium bromide



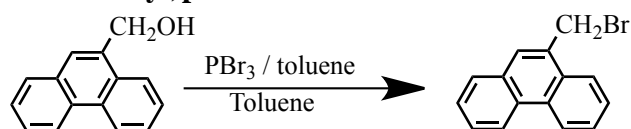
A xylene (70 ml) solution of 3-(bromomethyl)phenanthrene (1.52 g, 7.0 mmol) and triphenylphosphine (2.75 g, 10.5 mmol) was refluxed for 12 h under N₂ atmosphere. The precipitate was filtrated and washed with benzene, providing the desired phosphonium salt (2.74 g, 73 %). Mp 297–298.5 °C (lit. 270–272 °C) ⁴ ¹H NMR (600 MHz, CDCl₃): δ_H = 8.51 (d, 1H, *J* = 8.2 Hz), 8.46 (d, 1H, *J* = 7.9 Hz), 7.71–7.62 (m, 10H), 7.61–7.56 (m, 2H), 7.53 (t, 1H, *J* = 7.3 Hz), 7.51–7.46 (m, 6H), 7.33–7.26 (m, 2H, *J* = 9.2 Hz), 5.86 (d, 2H, *J*_{PH} = 13.9 Hz). ¹³C NMR (151 MHz, CDCl₃): δ_C = 134.9 (*J*_{PH} = 2.9 Hz), 134.7 (*J*_{PH} = 9.8 Hz), 131.9, 131.3, 130.1, (*J*_{PH} = 12.4 Hz), 130.0 (br), 129.8, 129.5 (br), 128.7, 128.3, 127.6, 126.9 (*J*_{PH} = 10.1 Hz), 126.4 (*J*_{PH} = 6.7 Hz), 126.2 (*J*_{PH} = 2.0 Hz), 125.3 (*J*_{PH} = 9.0 Hz), 123.2, 118.0 (*J*_{PH} = 8.4 Hz), 31.1 (*J*_{PH} = 46.6 Hz).

1-1-9. Preparation of 9-phenanthrene methanol



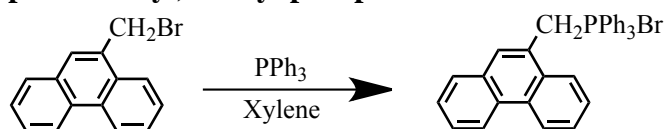
A methanol solution (40 ml) of phenanthrene-9-carbaldehyde (930 mg, 4.5 mmol), NaBH₄ (260 mg, 6.8 mmol) was stirred for 1 h at room temperature. The solvent was evaporated, and the product was extracted with 100 ml benzene. The solution was washed with water and brine. The product was purified by silica gel chromatography with a hexane/ethyl acetate mixture (5:1, v/v) as the eluent to obtain 9-phenanthrene methanol (920 mg, 98 %). Mp 153-154 °C (lit. 150–152 °C)⁶. ¹H NMR (600 MHz, CDCl₃): δ_H = 8.75 (dd, 1H, *J* = 7.9, 1.3 Hz), 8.68 (d, 1H, *J* = 8.3 Hz), 8.18 (dd, 1H, *J* = 7.6, 1.7 Hz), 7.89 (dd, *J* = 7.8, 1.0 Hz), 7.81 (s, 1H), 7.71–7.64, m, 2H), 7.60 (ddd, 1H, *J* = 8.1, 6.9, 1.2 Hz), 5.22 (d, 2H, *J* = 6.0 Hz), 1.80 (t, 1H, *J* = 6.0 Hz). ¹³C NMR (151 MHz, CDCl₃): δ_C = 134.7, 131.6, 130.9, 130.6, 130.3, 128.8, 127.00, 126.97, 126.9, 126.7, 126.1, 124.4, 123.3, 122.7, 64.2.

1-1-10. Preparation of 9-(bromomethyl)phenanthrene



To a toluene solution (30 ml) of 9-phenanthrene methanol (580 mg, 2.8 mmol), a toluene solution (6 ml) of PBr₃ (0.30 ml, 3.1 mmol) was added dropwise at 0 °C. After warming up to the room temperature, the mixture was stirred for 4 h, and washed with water and brine. The product was purified by silica gel chromatography with a hexane/chloroform mixture (3:1, v/v) as the eluent to obtain 9-(bromomethyl)phenanthrene (430 mg, 57 %). Mp 118-120 °C. (lit. 120 °C)⁷ ¹H NMR (600 MHz, CDCl₃): δ_H = 8.75 (m, 1H), 8.67 (d, 1H, *J* = 8.3 Hz), 8.23 (m, 1H), 7.87 (d, 1H, *J* = 7.8 Hz), 7.86 (s, 1H), 7.75–7.70 (m, 2H), 7.68 (ddd, 1H, *J* = 8.3, 7.2, 1.4 Hz), 7.61 (ddd, 1H, *J* = 8.1, 7.2, 1.1 Hz), 5.03(s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ_C = 131.8, 131.3, 131.2, 131.1, 129.7, 129.1, 128.9, 127.6, 127.13, 127.08, 127.06, 124.7, 123.4, 122.8, 32.6.

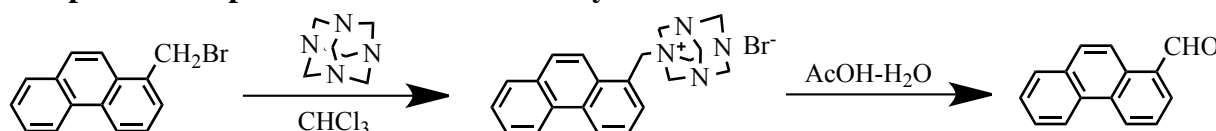
1-1-11. Preparation of (9-phenanthryl)methyl phosphonium bromide



A xylene (30 ml) solution of 9-(bromomethyl)phenanthrene (430 mg, 1.58 mmol) and triphenylphosphine (900 mg, 3.4 mmol) was refluxed for 12 h under N₂ atmosphere. The precipitate was filtrated and washed with benzene, providing the desired phosphonium salt (650 mg, 77 %). Mp > 300 °C. ¹H NMR (600 MHz, CDCl₃): δ_H = 8.54 (d, 1H, *J* = 8.3 Hz), 8.51 (d, 1H, *J* = 8.3 Hz), 7.81 (d, 1H, *J* = 4.5 Hz), 7.78–7.71 (m, 6H), 7.68–7.64 (m, 3H), 7.63–7.50 (m, 2H), 7.52–7.47 (m, 7H), 7.45 (d, 1H, *J* = 8.2 Hz), 7.39 (t, 1H, *J* = 7.5 Hz), 7.08 (ddd, 1H, *J* = 8.1, 7.1, 1.0 Hz), 6.92 (d, 2H, *J*_{PH} = 14.2 Hz). ¹³C NMR (151 MHz, CDCl₃): δ_C = 134.9 (*J*_{PH} = 2.9 Hz), 134.5 (*J*_{PH} = 9.8 Hz), 132.2 (*J*_{PH} = 7.8 Hz), 130.7 (*J*_{PH} = 4.1 Hz), 130.3, 130.10, 130.08 (*J*_{PH} = 12.4 Hz), 128.9, 127.5 (*J*_{PH} = 1.7 Hz), 126.8, 126.4, 124.3, 122.8, 122.3 (*J*_{PH} = 1.7 Hz), 121.7, (*J*_{PH} = 9.5 Hz), 117.8 (*J*_{PH} = 86.1 Hz), 27.8 (*J*_{PH} = 47.1 Hz).

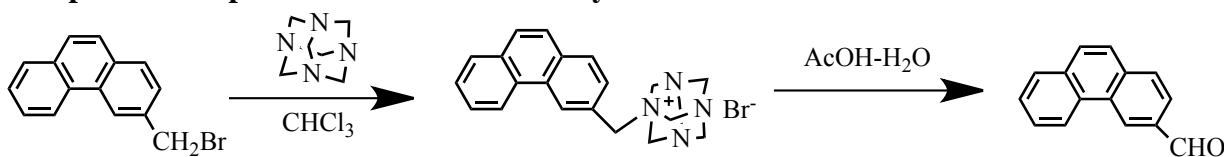
1-2. Synthesis of phenanthrenecarbaldehydes

1-2-1. Preparation of phenanthrene-1-carbaldehyde



A chloroform solution (60 ml) of 1-(bromomethyl)phenanthrene (1.65 g, 6.1 mmol) and hexamethylenetetramine (1.30 g, 9.3 mmol) was refluxed under N₂ atmosphere for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. A mixture of acetic acid and water (1:1 v/v, 50 ml) was added to the residue. The solution was stirred under N₂ atmosphere at 100 °C for 1 h. After cooling to room temperature, the solution was washed successively with aqueous NaHCO₃, water and brine. The product was purified by silica gel chromatography with hexane/ethyl acetate (5:1, v/v) as the eluent to obtain phenanthrene-1-carbaldehyde (0.51 g, 41 %). Mp 101–103 °C. (lit. 110–111 °C)⁸ ¹H NMR (400 MHz, CDCl₃) δ_H = 10.53 (s, 1H), 9.15 (d, 1H, *J* = 9.1 Hz), 9.01 (d, 1H, *J* = 8.4 Hz), 8.70 (d, 1H, *J* = 8.4 Hz), 8.10 (dd, 1H, *J* = 7.7, 1.2 Hz), 7.94–7.99 (a doublet and a dd signals overlap, 2H), 7.82 (dd, 1H, *J* = 7.2, 8.4 Hz), 7.72 (ddd, 1H, *J* = 8.4, 7.0, 1.4 Hz), 7.67 (ddd, 1H, *J* = 7.8, 7.0, 1.4 Hz).

1-2-2. Preparation of phenanthrene-3-carbaldehyde

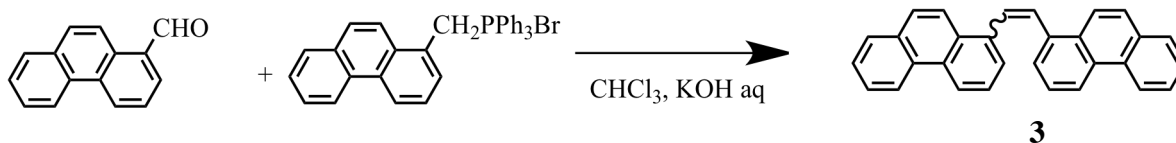


A chloroform solution (80 ml) of 3-(bromomethyl)phenanthrene (2.28 g, 8.4 mmol) and hexamethylenetetramine (1.80 g, 12.6 mmol) was refluxed under N₂ atmosphere for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. A mixture of acetic acid and water (1:1 v/v, 50 ml) was added to the residue. The solution was stirred under N₂ atmosphere at 100 °C for 1 h. After cooling to room temperature, the solution was washed successively with aqueous NaHCO₃, water and brine. The product was purified by silica gel chromatography with hexane/ethyl acetate (5:1, v/v) as the eluent to obtain phenanthrene-3-carbaldehyde (1.25 g, 72 %). Mp 80–81 °C. (lit. 79.5–80 °C)⁹ ¹H NMR (400 MHz CDCl₃): δ_H = 10.26 (s, 1H) 9.17 (s, 1H) 8.78 (d, 1H, *J* = 8.2 Hz) 8.07 (dd, 1H, *J* = 1.6, 8.2 Hz) 7.99 (d, 1H, *J* = 8.2 Hz) 7.95–7.87 (m, 2H) 7.79–7.72 (m, 2H) 7.69–7.63 (m, 1H).

2. Synthesis of condensed compounds

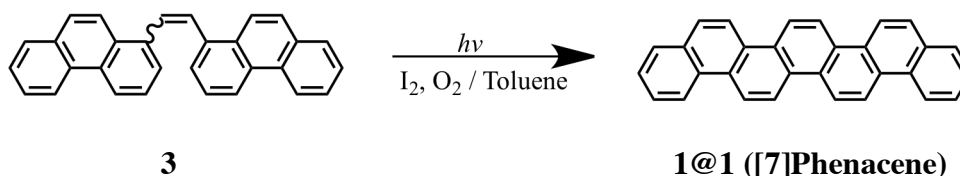
2-1. Synthesis of 1@1 ([7]phenacene)

2-1-1. Preparation of Compound 3



To a solution of (1-phenanthrylmethyl)triphenylphosphonium bromide (103 mg, 0.50 mmol) and phenanthrene-1-carbaldehyde (266 mg, 0.50 mmol) in 30 ml of CH_2Cl_2 was added a solution of KOH (0.4 g) in H_2O (0.4 ml). The mixture was stirred at r.t. for 2 h. The precipitate formed was collected and washed with MeOH (A). The filtrate and the washings were combined and concentrated under reduced pressure. The residue was chromatographed on silica-gel (hexane) to afford pale yellow solid (B). The obtained crude compound **3** (A and B, 183 mg, 96%) were used in the following photoreaction without further purification.

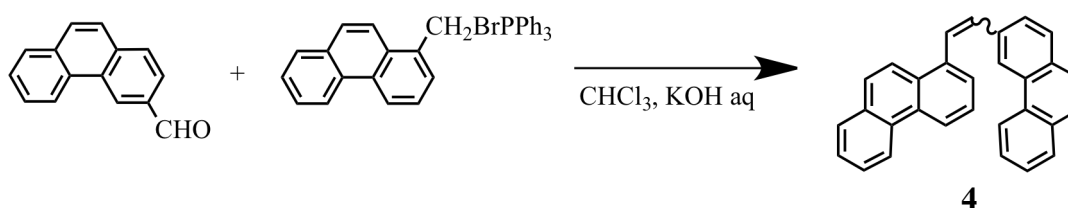
2-1-2. Synthesis of 1@1 ([7]phenacene)



The crude compound **3** (95 mg, 0.25 mmol) was dissolved in toluene (500 ml) and I_2 (6 mg) was added to the solution. The resulting solution was irradiated by using a home-made flow photoreactor.¹ The solvent was removed under reduced pressure and the residue was collected and washed in boiling $\text{CHCl}_2\text{CHCl}_2$ to afford 1@1([7]phenacene) as colorless fine plates (58 mg, 59%). Mp > 300 °C (lit. 565 °C)¹⁰. ^1H NMR (600 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) δ_{H} = 9.13 (d, 2H, J = 9.4 Hz), 9.08 (s, 2H), 9.05 (d, 2H, J = 9.4 Hz), 8.94–8.89 (two doublets overlap, 4H), 8.12 (d, 2H, J = 8.1 Hz), 8.08 (d, 2H, J = 8.1 Hz), 7.81 (t, 2H, J = 7.8 Hz), 7.23 (t, 2H, J = 7.8 Hz).

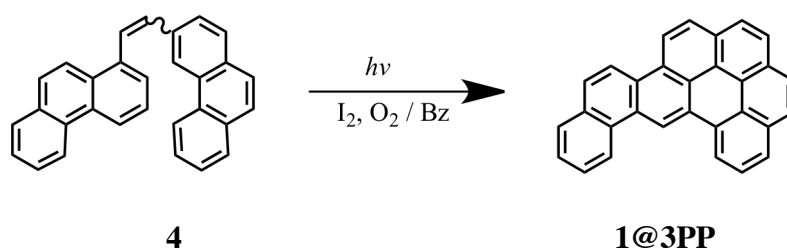
2-2. Synthesis of 1@3PP

2-2-1. Preparation of Compound 4



To a chloroform solution (10 ml) of (1-phenanthrylmethyl)triphenylphosphonium bromide (590 mg, 1.1 mmol) and phenanthrene-3-carbaldehyde (210 mg, 1.0 mmol), aqueous KOH (50 %, 10 ml) was added dropwise. The solution was refluxed for 1 h under N_2 atmosphere, and washed with water and brine. The organic solution was separated, dried with Na_2SO_4 and concentrated. The product was separated by silica-gel chromatography with a hexane/chloroform (4:1, v/v) mixture as the eluent to obtain of compound **4** (250 mg, 66 %). The compound obtained was used in the following photoreaction without further purification.

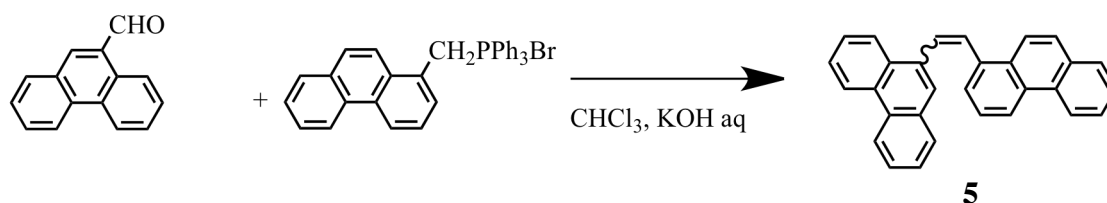
2-2-2. Synthesis of 1@3PP



A benzene solution (150 ml) of compound **4** (90 mg, 0.2 mmol) and 50 mg I₂ was photolyzed with the flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na₂SO₄. The product was purified by silica-gel chromatography with a hexane/chloroform mixture (4:1, v/v) as the eluent to obtain 1@3PP (20 mg, 22 %). Mp 287–288 °C (lit. 290-292 °C)¹¹. ¹H NMR (600 MHz, CDCl₂CDCl₂) δ_H = 10.09 (s, 1H), 9.06–9.12 (two doublets overlap, 2H), 8.93 (d, 1H, *J* = 8.8 Hz), 8.81 (d, 1H, *J* = 8.8 Hz), 8.33 (d, 1H *J* = 8.1 Hz), 8.25–8.3 (two doublets overlap, 2H), 8.17 (d, 1H, *J* = 7.5 Hz), 7.98–8.12 (m, 5H), 7.85 (t, 1H, *J* = 7.2 Hz), 7.76 (t, 1H, *J* = 7.2 Hz). ¹³C NMR (151 MHz, CDCl₂CDCl₂, 60 °C) δ_C = 132.3, 132.1, 130.81, 130.77, 129.33, 129.31, 128.82, 128.77, 128.6, 128.1, 127.7, 127.6, 127.49, 127.47, 127.2, 127.04, 127.02, 126.95, 126.5, 126.2, 126.0, 125.9, 124.7, 124.2, 123.2, 122.4, 121.5, 120.9, 115.3. HRMS (FAB) *m/z* calcd. for C₃₀H₁₆ 376.1252 [M⁺], found 376.1252.

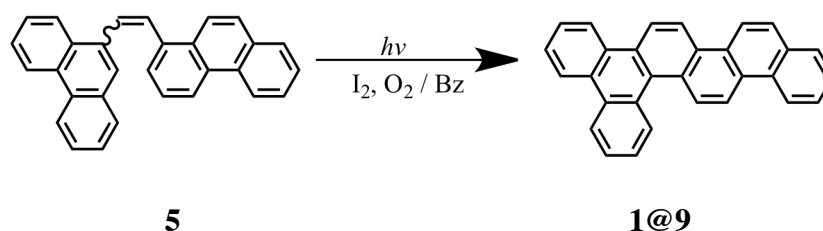
2-3. Synthesis of 1@9

2-3-1. Preparation of Compound 5



To a chloroform solution (10 ml) of (1-phenanthrylmethyl)triphenylphosphonium bromide (550 mg, 1.0 mmol) and phenanthrene-9-carbaldehyde (210 mg, 1.0 mmol), aqueous KOH (50 %, 8 ml) was added dropwise. The solution was refluxed for 1 h under N₂ atmosphere, and washed with water and brine. The organic solution was separated, dried with Na₂SO₄ and concentrated. The product was separated by silica-gel chromatography with a hexane/chloroform (4:1, v/v) mixture as the eluent to obtain of compound **5** (360 mg, 95 %). The compound obtained was used in the following photoreaction without further purification.

2-3-2. Synthesis of 1@9

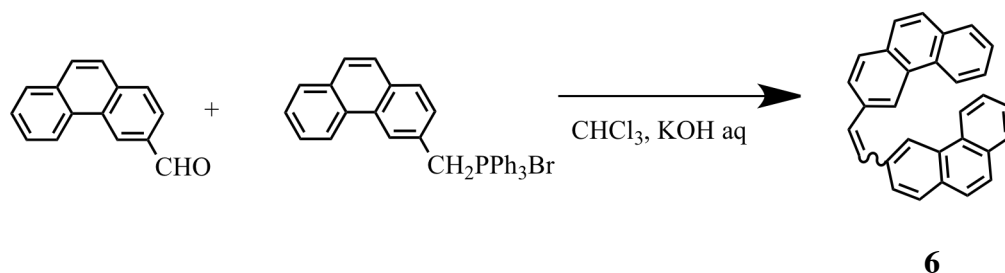


A benzene solution (150 ml) of compound **5** (110 mg, 0.3 mmol) and 50 mg I₂ was photolyzed with the flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na₂SO₄. The product was purified by silica-gel chromatography with a hexane/chloroform mixture (4:1, v/v) as the eluent to obtain 1@9 (60 mg, 55 %).

Mp 288–289 °C. ^1H NMR (600 MHz, CDCl_3) δ_{H} = 9.11 (d, 1H, J = 9.2 Hz), 8.99 (d, 1H, J = 9.1 Hz), 8.93 (dd, 1H, J = 8.0, 1.0 Hz), 8.89–8.80 (m, 4H), 7.79–8.72 (m, 3H), 8.08 (d, 1H, J = 9.0 Hz), 8.04 (d, 1H, J = 7.7 Hz), 7.78–7.60 (m, 6H). ^{13}C NMR (151 MHz, $\text{CDCl}_2\text{CDCl}_2$) δ_{C} = 132.1, 131.0, 130.5, 130.3, 130.0, 130.0, 129.5, 129.4, 128.8, 128.7, 128.2, 128.2, 128.0, 127.9, 127.8, 127.71, 127.65, 127.5, 127.2, 127.1, 126.9, 126.4, 123.8, 123.7, 123.4, 123.3, 122.8, 121.7, 121.4, 120.9. HRMS (FAB) m/z calcd. for $\text{C}_{30}\text{H}_{18}$ 378.1409 [M^+], found 378.1415.

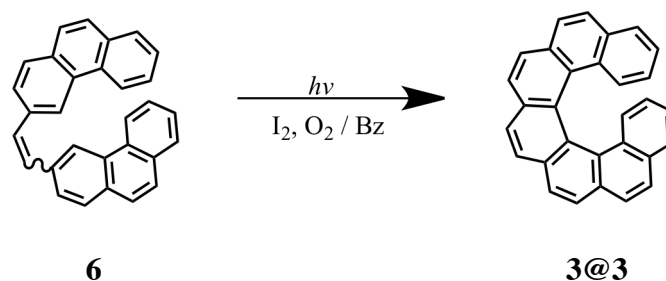
2-4. Synthesis of 3@3

2-4-1. Preparation of Compound 6



To a chloroform solution (15 ml) of (3-phenanthrylmethyl)triphenylphosphonium bromide (650 mg, 1.2 mmol) and phenanthrene-3-carbaldehyde (210 mg, 1.0 mmol), aqueous KOH (50 %, 8 ml) was added dropwise. The solution was refluxed for 1 h under N_2 atmosphere, and washed with water and brine. The organic solution was separated, dried with Na_2SO_4 and concentrated. The product was separated by silica-gel chromatography with a hexane/chloroform (5:1, v/v) mixture as the eluent to obtain compound **6** (350 mg, 92 %). The compound obtained was used in the following photoreaction without further purification.

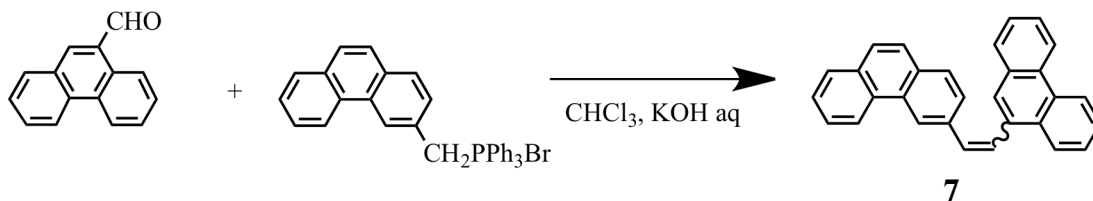
2-4-2. Synthesis of 3@3



A benzene solution (500 ml) of compound **6** (350 mg, 0.9 mmol) and 50 mg I_2 was photolyzed with the flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na_2SO_4 . The product was purified by silica-gel chromatography with a hexane/chloroform mixture (5:1, v/v) as the eluent to obtain **3@3** (90 mg, 25 %). Mp 255–256 °C (lit. 254–256 °C)¹². ^1H NMR (600 MHz, CDCl_3) δ_{H} = 8.04 (s, 2H), 8.01 (d, 2H, J = 8.1 Hz), 7.93 (d, 2H, J = 8.1), 7.75 (d, 2H, J = 8.4 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.31 (brd, 2H, J = 7.9 Hz), 7.17 (brd, 2H, J = 8.5 Hz), 6.91 (m, 2H), 6.41 (m, 2H). These data are similar to ^1H NMR (300 MHz, CDCl_3) data reported in the literature.¹³ HRMS (FAB) m/z calcd. for $\text{C}_{30}\text{H}_{18}$ 378.1409 [M^+], found 378.1370.

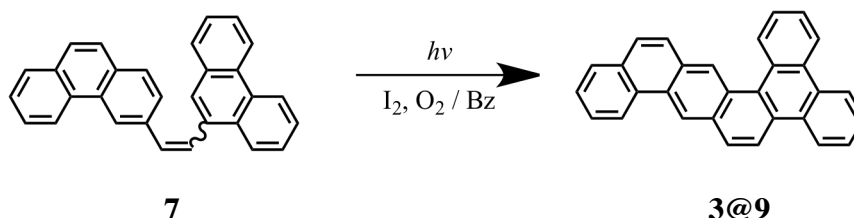
2-5. Synthesis of 3@9

2-5-1. Preparation of Compound 7



To a chloroform solution (10 ml) of (3-phenanthrylmethyl)triphenylphosphonium bromide (530 mg, 1.0 mmol) and phenanthrene-9-carbaldehyde (210 mg, 1.0 mmol), aqueous KOH (50 %, 8 ml) was added dropwise. The solution was refluxed for 1 h under N_2 atmosphere, and washed with water and brine. The organic solution was separated, dried with Na_2SO_4 and concentrated. The product was separated by silica-gel chromatography with a hexane/chloroform (3:1, v/v) mixture as the eluent to obtain of compound 7 (320 mg, 84 %). The compound obtained was used in the following photoreaction without further purification.

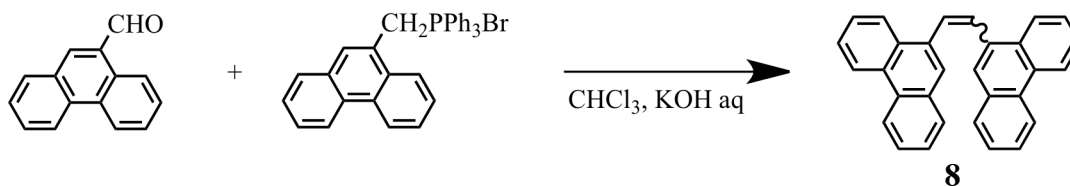
2-5-2. Synthesis of 3@9



A benzene solution (150 ml) of compound 7 (100 mg, 0.26 mmol) and 50 mg I_2 was photolyzed with the flow photoreactor.¹ The photolyzed solution was washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na_2SO_4 . The product was purified by silica-gel chromatography with a hexane/chloroform mixture (2:1, v/v) as the eluent to obtain 3@9 (40 mg, 40 %). Mp 212–213 °C (lit. 210-212 °C)¹¹. ^1H NMR (600 MHz, CDCl_3) δ_{H} = 9.43 (s, 1H), 9.23 (s, 1H), 9.08 (dd, 1H, J = 7.6, 1.7 Hz), 8.89 (d, 1H, J = 8.0 Hz), 8.79 (dd, 1H, J = 8.0, 1.7 Hz), 8.76 (m, 1H), 8.69 (m, 1H), 8.63 (d, 1H, J = 9.1 Hz), 8.22 (d, 1H, J = 8.9 Hz), 7.91 (m, 1H), 7.89 (d, 1H, J = 9.0 Hz), 7.77–7.70 (m, 6H), 7.67 (ddd, 1H, J = 7.9, 7.2, 1.2 Hz). ^{13}C NMR (151 MHz, CDCl_3) δ_{C} = 132.3, 132.2, 131.0, 130.8, 130.5, 130.2, 129.9, 129.7, 129.3, 129.0, 128.8, 128.4, 128.3, 128.0, 127.9, 127.5, 127.3, 127.0, 126.8, 126.5, 124.0, 123.7, 123.3, 123.2, 121.8, 121.2. HRMS (FAB) m/z calcd. for $\text{C}_{30}\text{H}_{18}$ 378.1409 [M^+], found 378.1410.

2-6. Synthesis of 9@9PP

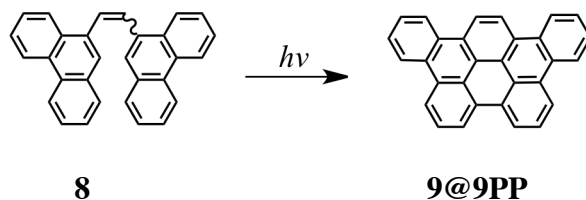
2-6-1. Preparation of Compound 8



To a chloroform solution (10 ml) of (9-phenanthrylmethyl)triphenylphosphonium bromide (630 mg, 1.2 mmol) and phenanthrene-9-carbaldehyde (230 mg, 1.1 mmol), aqueous KOH (50 %, 8 ml) was added dropwise. The solution was refluxed for 1 h under N_2 atmosphere, and washed with water and brine. The

organic solution was separated, dried with Na_2SO_4 and concentrated. The product was separated by silica-gel chromatography with a hexane/chloroform (5:1, v/v) mixture as the eluent to obtain of compound **8** (260 mg, 68 %). The compound obtained was used in the following photoreaction without further purification.

2-6-2. Synthesis of 9@9PP



A benzene solution (400 ml) of compound **8** (150 mg, 0.39 mmol) and 50 mg I_2 was photolyzed with the microflow photoreactor.¹ The precipitate was filtrated and washed with cyclohexane. The crude product was purified by recrystallization from toluene, providing 9@9PP (133 mg, 89 %). Mp 408–409 °C (lit. 380 °C)¹⁴. $^1\text{H NMR}$ (600 MHz, $\text{CDCl}_2\text{CDCl}_2$) δ_{H} = 9.29 (s, 2H), 9.13 (d, 2H, $J = 7.9$ Hz), 9.03 (d, 2H $J = 7.9$ Hz), 8.99 (d, 2H $J = 7.6$ Hz), 8.91 (d, 2H $J = 7.7$ Hz), 8.15 (t, 2H $J = 7.8$ Hz), 7.81 (m, 4H). HRMS (FAB) m/z calcd. for $\text{C}_{30}\text{H}_{16}$ 376.1252 [M^+], found 376.1277.

2. X-ray crystallographic data

The X-ray diffraction data of the single crystals were collected on a VariMax DW with Saturn CCD diffractometer with Mo-K α X-rays ($\lambda = 0.71075 \text{ \AA}$) at 93 K. The structures were solved by direct methods (SHELXS-2013)¹⁵ and refined on F² by full-matrix least-squares techniques (SHELXL-2013).¹⁵ The crystallographic data have been deposited to the Cambridge Crystallographic Data Centre: the deposition numbers CCDC 1521684–1521686 for 3@9, 3@3 and 1@9. The copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data and structure refinement summary.^a

Compound	1@9	3@3	3@9
CCDC number ^b	1521686	1521685	1521684
Molecular formula	C ₃₀ H ₁₈	C ₃₀ H ₁₈	C ₃₀ H ₁₈
Molecular weight	378.44	378.44	378.44
Crystal size / mm ³	0.29 × 0.26 × 0.01	0.30 × 0.14 × 0.09	0.47 × 0.04 × 0.04
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁</i>
<i>a</i> / Å	7.560(4)	8.001(4)	12.778(11)
<i>b</i> / Å	20.153(11)	11.525(6)	5.158(4)
<i>c</i> / Å	23.743(12)	20.641(10)	14.363(12)
β / deg.	-	96.436(9)	98.059(13)
<i>V</i> / Å ³	3673(3)	1891.3(16)	937.3(13)
<i>Z</i>	8	4	2
<i>d</i> _{calc.} / g cm ⁻³	1.390	1.329	1.341
μ / mm ⁻¹ .	0.079	0.075	0.076
λ / nm	0.71075	0.71075	0.71075
Temperature / K	93(2)	93(2)	93(2)
$2\theta_{\max}$ / deg.	54.88	55.07	55.02
<i>F</i> ₀₀₀	1584	792	396
Measured/independent reflections	33379/4121	21737/4350	11168/4279
<i>N</i> _{para}	271	271	271
GOF	0.938	1.109	1.011
<i>R</i> _{int}	0.0684	0.0552	0.0632
<i>R</i> ₁	0.0775	0.0518	0.0703
<i>wR</i> ₂ (all data)	0.1627	0.1291	0.1354
Max/min residual electron density	0.199/-0.287	0.293/-0.197	0.221/-0.251

^{a,b} These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

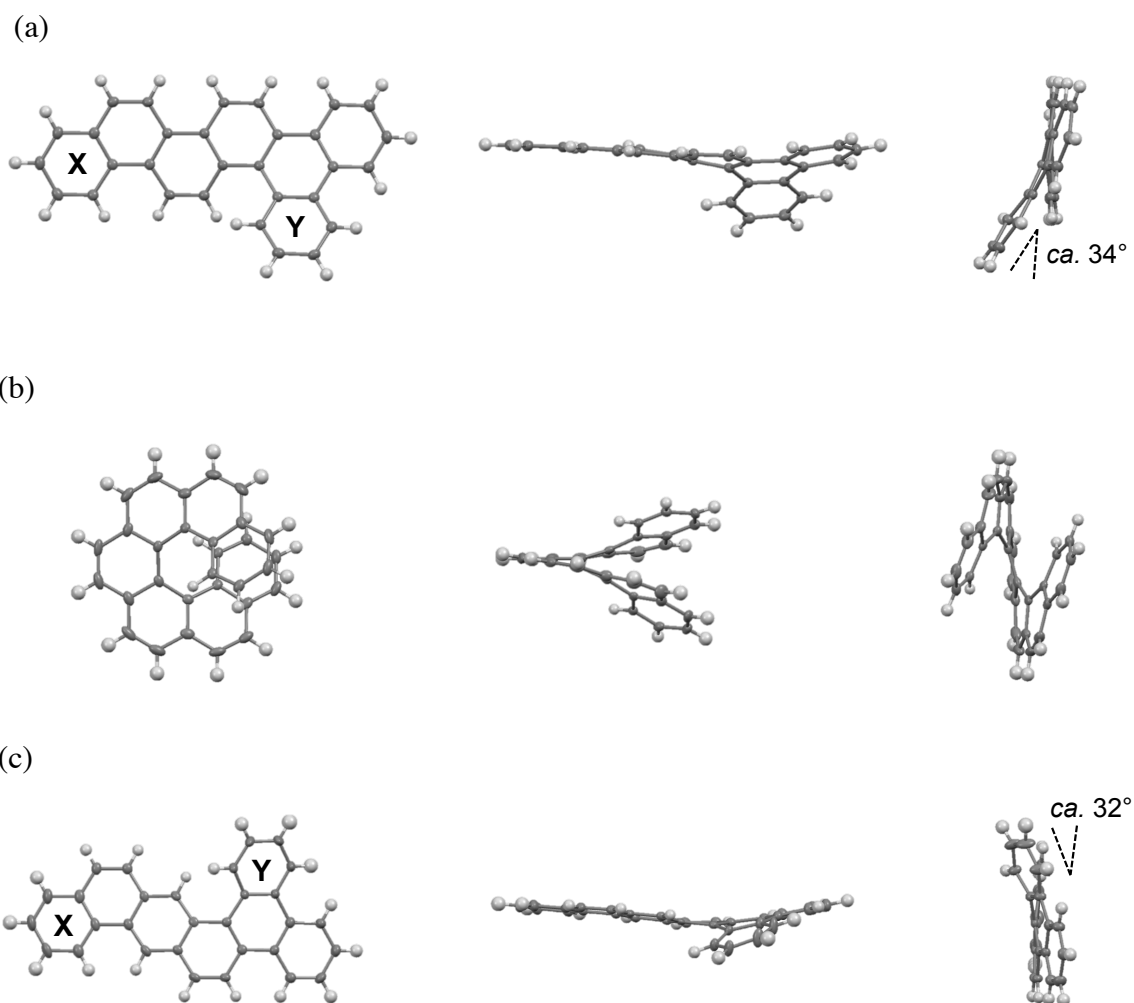


Figure S1. ORTEP drawings of 1@9 (a) and 3@3 (b) and 3@9 (c). From left to right: front, top and side views. For 1@9 and 3@9, the dihedral angle between ring X and Y is indicated in the side view.

3. Decay profiles of fluorescence.

Figure S2 shows decay profiles of fluorescence of the compounds studied in this work.

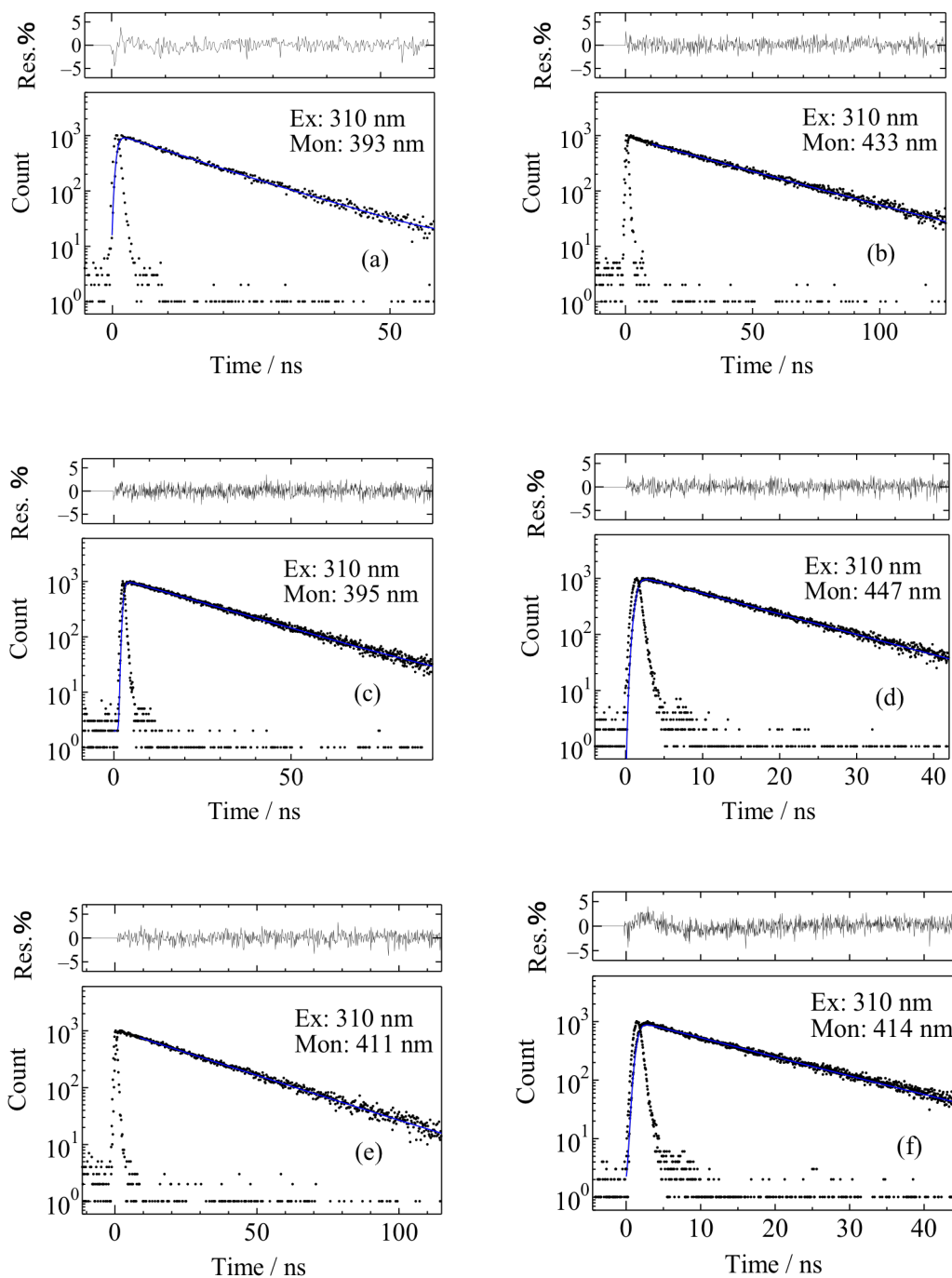


Figure S2. Decay profiles of fluorescence of 1@1 (a), 1@3PP (b), 1@9 (c), 3@3 (d), 3@9 (e) and 9@9PP (f) at 295 K. CHCl₃ was used for 1@1 and 9@9PP whereas cyclohexane was for the others. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.

4. Results of DFT calculations (molecular structures, atom coordinates, sum of electronic and zero-point energies)

The calculation was carried out at the DFT level, using the Gaussian 09 software package.¹⁶ The geometries of the studied compounds were fully optimized by using the 6-31+G(d) base set at the B3LYP method. Atom coordinates for the optimized geometries of the studied compounds in vacuum are as follows.

Figure S3 shows molecular geometries of 9@9 and 9@9PP in the ground state optimized by DFT calculations.

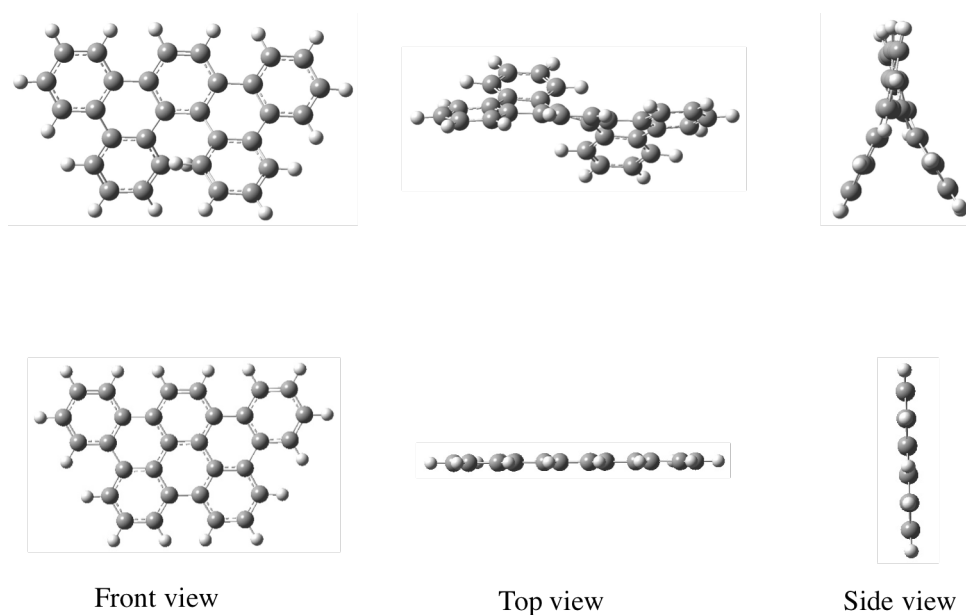


Figure S3. Molecular geometries of 9@9 (upper) and 9@9PP (lower) in the ground state optimized by DFT calculations.

Figure S4 shows molecular geometry of 1@3 and 1@3PP in the ground state optimized by DFT calculations.

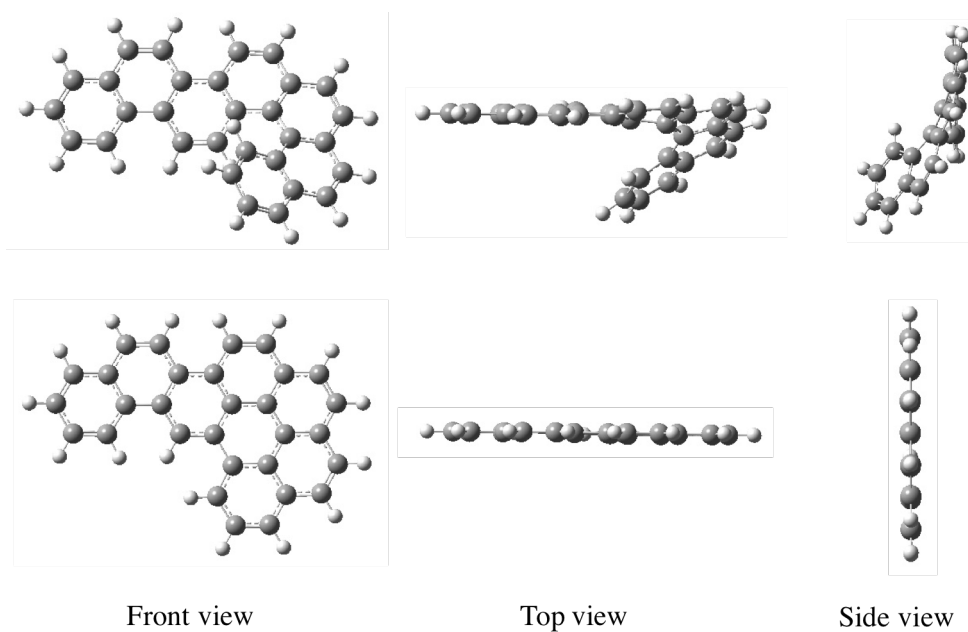


Figure S4. Molecular geometries of 1@3 (upper) and 1@3PP (lower) in the ground state optimized by DFT calculations.

Figure S5 shows molecular geometry of 3@3 and 3@9 in the ground state optimized by DFT calculations.

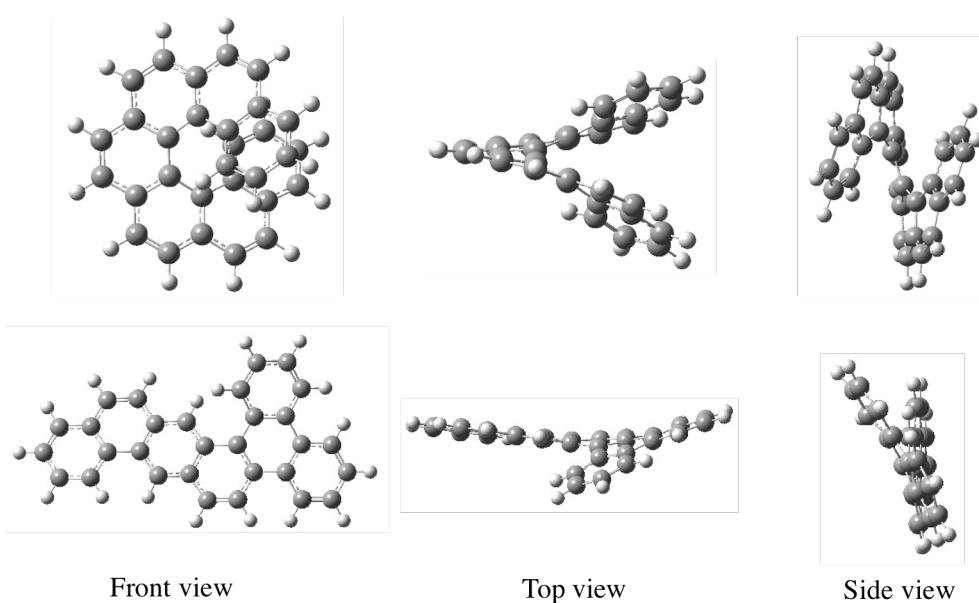


Figure S5. Molecular geometries of 3@3 ([7]helicene, upper) and 3@9 (lower) in the ground state optimized by DFT calculations.

Table S2. Atom coordinates for the optimized geometry of 1@1.

	X	Y	Z
C	7.78100	-0.42301	0.01960
C	7.10472	-1.66698	0.02935
C	5.69251	-1.69802	0.01711
C	4.96158	-0.48338	-0.00485
C	5.64158	0.76108	-0.01439
C	7.04023	0.78206	-0.00228
C	3.54157	-0.49656	-0.00509
C	2.83072	0.72934	-0.00483
C	3.54605	1.95857	-0.01655
C	4.89703	1.97278	-0.02404
C	2.84102	-1.73166	-0.01904
C	1.42859	-1.74068	0.00587
C	0.71445	-0.51473	-0.00359
C	1.40846	0.72481	-0.00501
C	-0.70729	-0.51483	-0.00341
C	-1.41306	0.71534	-0.00034
C	-0.69465	1.94149	-0.00928
C	0.69103	1.95216	0.00700
C	-1.41966	-1.74319	-0.01856
C	-2.83169	-1.73721	0.00658
C	-3.53071	-0.50311	-0.00177
C	-2.83576	0.71720	-0.00015
C	-4.95221	-0.48446	-0.00128
C	-5.64599	0.75003	0.00317
C	-4.91716	1.97042	0.00733
C	-3.54850	1.94794	0.01490
C	-5.68566	-1.69615	-0.01658
C	-7.09786	-1.65832	-0.02893
C	-7.77018	-0.40973	0.02259
C	-7.06567	0.76168	0.01625
H	8.88008	-0.39482	0.01961
H	7.67854	-2.60442	0.05583
H	5.16356	-2.66214	0.03411
H	7.56347	1.74912	-0.00040

H	2.99938	2.91299	-0.00935
H	5.42084	2.93963	-0.02906
H	3.39799	-2.67981	-0.03914
H	0.88526	-2.69621	0.04256
H	-1.23840	2.89746	-0.02590
H	1.23570	-2.68694	0.04239
H	-5.45295	2.93066	0.01080
H	-2.99965	2.90072	0.04538
H	-5.15579	-2.65989	-0.00998
H	-7.67284	-2.59455	-0.06926
H	-8.86776	-0.37810	0.07955
H	-7.60736	1.71852	0.02929

Sum of electronic and zero-point energies = -1154.00170256 Hartree

Table S3. Atom coordinates for the optimized geometry of 1@3.

	X	Y	Z
C	-5.67045	-1.40608	-0.00901
C	-5.76324	-2.70524	-0.46029
C	-4.59893	-3.37135	-0.89975
C	-3.37870	-2.72505	-0.89138
C	-3.25034	-1.37735	-0.44907
C	-4.41648	-0.73797	0.00713
C	-1.99068	-0.65396	-0.42259
C	-1.92674	0.65827	0.07003
C	-3.14293	1.26125	0.55274
C	-4.33671	0.60268	0.51413
C	-0.78905	-1.22577	-0.94910
C	0.41305	-0.57967	-0.84938
C	0.52283	0.69285	-0.20768
C	-0.66628	1.36640	0.10408
C	1.81473	1.32560	-0.04861
C	1.83868	2.72103	0.02288
C	0.62349	3.43686	0.27329
C	-0.56924	2.77512	0.37551
C	3.07225	0.61574	-0.04125
C	4.22924	1.31310	-0.40113
C	4.20823	2.74138	-0.48313
C	3.06223	3.43047	-0.18961
C	3.22796	-0.76279	0.38798
C	4.42033	-1.45162	0.10126
C	5.52473	-0.74672	-0.49146
C	5.44999	0.60316	-0.67363
C	2.27242	-1.42293	1.20977
C	2.42067	-2.74998	1.56109
C	3.56166	-3.47065	1.14616
C	4.55925	-2.82228	0.44800
H	-6.58022	-0.89609	0.34744
H	-6.73419	-3.22623	-0.46521
H	-4.66768	-4.41740	-1.24174

H	-2.51226	-3.31167	-1.22959
H	-3.15568	2.27075	0.98857
H	-5.24191	1.10122	0.8992
H	-0.78405	-2.19589	-1.46647
H	1.29467	-1.05332	-1.31075
H	0.64511	4.53392	0.38475
H	-1.45909	3.39311	0.56552
H	5.12858	3.30001	-0.71903
H	3.07410	4.53259	-0.18999
H	6.46799	-1.27282	-0.71022
H	6.33801	1.14607	-1.03613
H	1.40072	-0.88254	1.61103
H	1.66266	-3.24233	2.19207
H	3.68263	-4.52642	1.43826
H	5.48122	-3.37102	0.19526

Sum of electronic and zero-point energies = - 1154.12086247 Hartree

Table S4. Atom coordinates for the optimized geometry of 1@3PP.

	X	Y	Z
C	-3.34789	3.47837	0.00029
C	-2.02996	3.90911	0.00060
C	-0.98031	2.98283	0.00058
C	-1.21660	1.60203	0.00023
C	-2.57186	1.15196	0.00002
C	-3.64250	2.10064	0.00005
C	-2.87592	-0.24936	-0.00008
C	-4.22790	-0.68281	-0.00027
C	-5.27695	0.29257	-0.00029
C	-4.99647	1.62764	-0.00015
C	-1.81954	-1.21495	-0.00004
C	-2.14042	-2.59831	-0.00008
C	-3.50237	-3.00369	-0.00027
C	-4.51432	-2.07475	-0.00037
C	-0.44929	-0.79217	0.00012
C	0.59606	-1.76023	0.00014
C	0.23042	-3.14555	0.00005
C	-1.07644	-3.54665	-0.00004
C	-0.12905	0.60780	0.00006
C	1.20720	0.97938	-0.00015
C	2.27400	0.05388	-0.00008
C	1.97289	-1.33724	0.00023
C	3.66629	0.49715	-0.00021
C	4.70629	-0.47920	0.00016
C	4.35911	-1.86767	0.00059
C	3.05773	-2.27577	0.00061
C	4.04803	1.86191	-0.00070
C	5.37969	2.24210	-0.00075
C	6.40053	1.27059	-0.00034
C	6.06182	-0.06901	0.00012

H	-4.16455	4.19656	0.00029
H	-1.80328	4.97215	0.00087
H	0.03412	3.36561	0.00090
H	-6.30797	-0.05415	-0.00040
H	-5.80010	2.36049	-0.00013
H	-3.73183	-4.06690	-0.00035
H	-5.55367	-2.39548	-0.00053
H	1.00130	-3.90666	-0.00003
H	-1.32058	-4.60664	-0.00012
H	1.44934	2.03247	-0.00039
H	5.16052	-2.60310	0.00093
H	2.85174	-3.33941	0.00104
H	3.29386	2.64103	-0.00105
H	5.63638	3.29837	-0.00118
H	7.44401	1.57447	-0.00033
H	6.83686	-0.83246	0.00044

Sum of electronic and zero-point energies = -1152.86449704 Hartree

Table S5. Atom coordinates for the optimized geometry of 1@9.

	X	Y	Z
C	6.18012	-1.50496	0.73813
C	5.58768	-0.25962	0.60671
C	4.22967	-0.11876	0.24079
C	3.44925	-1.29096	0.04528
C	4.08158	-2.55058	0.17162
C	5.42159	-2.66259	0.50458
C	3.62129	1.18923	-0.00496
C	2.21743	1.28392	-0.23176
C	1.37902	0.08581	-0.12703
C	2.00771	-1.17480	-0.18539
C	-0.06263	0.13847	0.00016
C	-0.85096	-1.01819	-0.27261
C	-0.16609	-2.23773	-0.52748
C	1.19838	-2.32072	-0.42267
C	-0.74590	1.28578	0.51179
C	-2.10990	1.32985	0.61989
C	-2.93661	0.24740	0.19870
C	-2.29955	-0.94370	-0.23260
C	-4.38739	0.32788	0.23797
C	-5.15857	-0.81002	-0.14780
C	-4.48109	-1.99383	-0.57382
C	-3.11774	-2.05742	-0.61463
C	-5.08823	1.49540	0.63659
C	-6.47098	1.53306	0.66366
C	-7.22570	0.40150	0.28851
C	-6.57401	-0.74822	-0.11200
C	4.40804	2.35876	-0.11251
C	3.86057	3.57675	-0.48149
C	2.49682	3.65155	-0.80094

C	1.70016	2.52403	-0.68329
H	7.22596	-1.58126	1.02391
H	6.18869	0.62190	0.80067
H	3.51035	-3.46103	0.03254
H	5.87518	-3.64552	0.60162
H	-0.71919	-3.14319	-0.74737
H	1.66203	-3.29148	-0.55286
H	-0.16975	2.12099	0.89048
H	-2.55933	2.21387	1.05836
H	-5.07545	-2.85295	-0.87709
H	-2.65450	-2.97342	-0.96203
H	-4.54160	2.38734	0.92261
H	-6.97795	2.44329	0.97364
H	-8.31169	0.43799	0.31211
H	-7.14150	-1.62763	-0.40915
H	5.47779	2.30476	0.05522
H	4.49576	4.45467	-0.56578
H	2.06650	4.58195	-1.16250
H	0.66489	2.58598	-0.99487

Sum of electronic and zero-point energies = -1154.01244715 Hartree

Table S6. Atom coordinates for the optimized geometry of 3@3.

	X	Y	Z
C	2.98564	1.72962	1.83944
C	2.95279	0.64157	2.68820
C	1.77172	-0.12313	2.78215
C	0.67934	0.16945	1.98612
C	0.69964	1.23925	1.05343
C	1.86373	2.07272	1.04335
C	-0.43911	1.59137	0.21336
C	-0.46450	2.90512	-0.33012
C	0.71455	3.71805	-0.31274
C	1.85758	3.29185	0.29522
C	-1.58354	0.72963	-0.03529
C	-2.82183	1.36467	-0.35496
C	-2.83661	2.72403	-0.78752
C	-1.67509	3.43923	-0.86444
C	-1.58439	-0.72782	0.03534
C	-2.82341	-1.36144	0.35501
C	-4.04940	-0.64238	0.22513
C	-4.04865	0.64705	-0.22505
C	-0.44098	-1.59089	-0.21336
C	-0.46788	-2.90463	0.33007
C	-1.67907	-3.43735	0.86440
C	-2.83977	-2.72079	0.78753
C	0.69817	-1.24005	-1.05343
C	1.86130	-2.07485	-1.04337
C	1.85375	-3.29400	-0.29528
C	0.71023	-3.71892	0.31265

C	0.67908	-0.17021	-1.98610
C	1.77179	0.12115	-2.78212
C	2.95199	-0.64489	-2.68818
C	2.98360	-1.73302	-1.83946
H	3.86777	2.36470	1.79206
H	3.81500	0.39601	3.30287
H	1.71179	-0.94436	3.49176
H	-0.22196	-0.41763	2.10510
H	0.67550	4.68970	-0.80032
H	2.75651	3.90406	0.28259
H	-3.78559	3.16571	-1.08265
H	-1.66931	4.45245	-1.25963
H	-4.98206	-1.16219	0.43143
H	-4.98072	1.16793	-0.43134
H	-1.67448	-4.45059	1.25955
H	-3.78925	-3.16138	1.08265
H	2.75198	-3.90723	-0.28266
H	0.67007	-4.69053	0.80021
H	-0.22156	0.41789	-2.10507
H	1.71280	0.94246	-3.49170
H	3.81449	-0.40030	-3.30283
H	3.86500	-2.36911	-1.79210

Sum of electronic and zero-point energies = -1153.99965696 Hartree

Table S7. Atom coordinates for the optimized geometry of 3@9.

	X	Y	Z
C	-1.53443	2.36768	0.78694
C	-2.24636	3.55055	0.89529
C	-3.60305	3.58328	0.53769
C	-4.23073	2.41448	0.14096
C	-3.53279	1.18839	0.04307
C	-2.13201	1.17251	0.31052
C	-4.22799	-0.06451	-0.24328
C	-3.53975	-1.29540	-0.05381
C	-2.10455	-1.29157	0.22692
C	-1.38612	-0.08248	0.21441
C	-5.58159	-0.09762	-0.65095
C	-6.25723	-1.29242	-0.83407
C	-5.59004	-2.50809	-0.61359
C	-4.25763	-2.50268	-0.23698
C	-1.40180	-2.51579	0.48823
C	-0.04704	-2.55039	0.64187
C	0.74004	-1.38060	0.41532
C	0.06890	-0.13940	0.13664
C	2.14327	-1.44984	0.39467
C	2.94352	-0.36275	0.03957
C	2.27294	0.84129	-0.36590
C	0.87655	0.92418	-0.30394
C	4.40580	-0.40910	0.01245

C	5.12542	0.72682	-0.46190
C	4.40695	1.89948	-0.89374
C	3.04984	1.95569	-0.84459
C	5.14665	-1.53273	0.44281
C	6.53305	-1.54552	0.3992
C	7.23820	-0.42579	-0.07834
C	6.53797	0.69224	-0.49981
H	-0.50718	2.34800	1.12791
H	-1.75722	4.44220	1.27906
H	-4.17115	4.50679	0.61293
H	-5.29585	2.44406	-0.05891
H	-6.11160	0.82977	-0.83724
H	-7.29678	-1.28558	-1.15113
H	-6.10888	-3.45269	-0.75449
H	-3.75782	-3.45589	-0.11132
H	-1.95977	-3.43687	0.60723
H	0.45538	-3.48408	0.88424
H	2.59474	-2.40944	0.62846
H	0.41611	1.83686	-0.66418
H	4.98063	2.74944	-1.25653
H	2.52235	2.85108	-1.16586
H	4.63063	-2.40726	0.82567
H	7.07439	-2.42471	0.73905
H	8.32446	-0.43743	-0.11217
H	7.07171	1.56640	-0.86679

Sum of electronic and zero-point energies = -1154.02277529 Hartree

Table S8. Atom coordinates for the optimized geometry of 9@9.

	X	Y	Z
C	3.59752	2.08470	-1.00044
C	2.94309	3.13773	-1.61765
C	1.54779	3.09187	-1.76871
C	0.83571	2.02000	-1.25860
C	1.47346	0.96032	-0.56846
C	2.89339	0.97166	-0.48493
C	0.71582	-0.20652	-0.09416
C	1.42145	-1.42293	0.06066
C	2.87714	-1.40675	0.22954
C	3.59663	-0.19475	0.05055
C	3.58512	-2.55646	0.65012
C	4.94624	-2.51763	0.90881
C	5.64903	-1.31165	0.76312
C	4.97891	-0.17402	0.34135
C	-0.71582	-0.20652	0.09419
C	-1.42144	-1.42294	-0.06062
C	-0.68306	-2.63249	-0.07509
C	0.68307	-2.63249	0.07517
C	-1.47347	0.96032	0.56847
C	-2.89341	0.97165	0.48493

C	-3.59663	-0.19477	-0.05054
C	-2.87712	-1.40676	-0.22953
C	-0.83573	2.02002	1.25860
C	-1.54783	3.09188	1.76870
C	-2.94312	3.13773	1.61763
C	-3.59754	2.08469	1.00043
C	-4.97891	-0.17405	-0.34136
C	-5.64901	-1.31169	-0.76315
C	-4.94620	-2.51765	-0.90887
C	-3.58508	-2.55647	-0.65015
H	4.68081	2.10296	-0.95414
H	3.51288	3.97357	-2.01531
H	1.02572	3.88393	-2.29921
H	-0.23631	1.98373	-1.40952
H	3.05684	-3.48968	0.80953
H	5.45968	-3.41557	1.24258
H	6.71188	-1.26484	0.98552
H	5.53552	0.75236	0.24809
H	-1.19705	-3.58444	-0.14277
H	1.19705	-3.58444	0.14289
H	0.23628	1.98377	1.40952
H	-1.02577	3.88395	2.29919
H	-3.51294	3.97356	2.01529
H	-4.68083	2.10294	0.95412
H	-5.53554	0.75231	-0.24809
H	-6.71186	-1.26489	-0.98556
H	-5.45962	-3.41560	-1.24267
H	-3.05678	-3.48968	-0.80958

Sum of electronic and zero-point energies = -1154.00378226 Hartree

Table S9. Atom coordinates for the optimized geometry of 9@9PP.

	X	Y	Z
C	-5.71858	-1.49390	-0.00154
C	-5.02330	-0.29660	-0.00085
C	-3.60905	-0.25448	-0.00011
C	-2.89404	-1.48002	-0.00029
C	-3.62750	-2.69097	-0.00100
C	-5.01169	-2.70612	-0.00158
C	-2.87398	1.01359	0.00069
C	-1.44426	1.01155	0.00036
C	-0.71804	-0.23980	0.00006
C	-1.43058	-1.46734	0.00016
C	0.71804	-0.23980	0.00021
C	1.43058	-1.46734	0.00046
C	0.68862	-2.66492	0.00071
C	-0.68861	-2.66492	0.00053
C	1.44426	1.01156	-0.00032
C	2.87397	1.01360	-0.00076
C	3.60905	-0.25448	-0.00022

C	2.89404	-1.48002	0.00052
C	5.02330	-0.29659	-0.00028
C	5.71858	-1.49389	0.00035
C	5.01169	-2.70612	0.00112
C	3.62750	-2.69097	0.00120
C	0.73366	2.24843	-0.00044
C	1.46222	3.44831	-0.00164
C	2.85189	3.44638	-0.00229
C	3.54891	2.24492	-0.00174
C	-3.54891	2.24492	0.00187
C	-2.85189	3.44638	0.00255
C	-1.46222	3.44831	0.00183
C	-0.73367	2.24843	0.00054
H	-6.80542	-1.49000	-0.00213
H	-5.59445	0.62417	-0.00100
H	-3.10750	-3.64142	-0.00121
H	-5.54367	-3.65389	-0.00211
H	1.19356	-3.62315	0.00097
H	-1.19355	-3.62316	0.00075
H	5.59445	0.62417	-0.00080
H	6.80542	-1.48999	0.00029
H	5.54368	-3.65389	0.00167
H	3.10751	-3.64142	0.00188
H	0.95187	4.40347	-0.00221
H	3.39464	4.38806	-0.00326
H	4.63146	2.27846	-0.00216
H	-4.63146	2.27845	0.00244
H	-3.39464	4.38806	0.00370
H	-0.95186	4.40346	0.00247

Sum of electronic and zero-point energies = -1152.84832277 Hartree

5. ^1H and ^{13}C NMR spectra

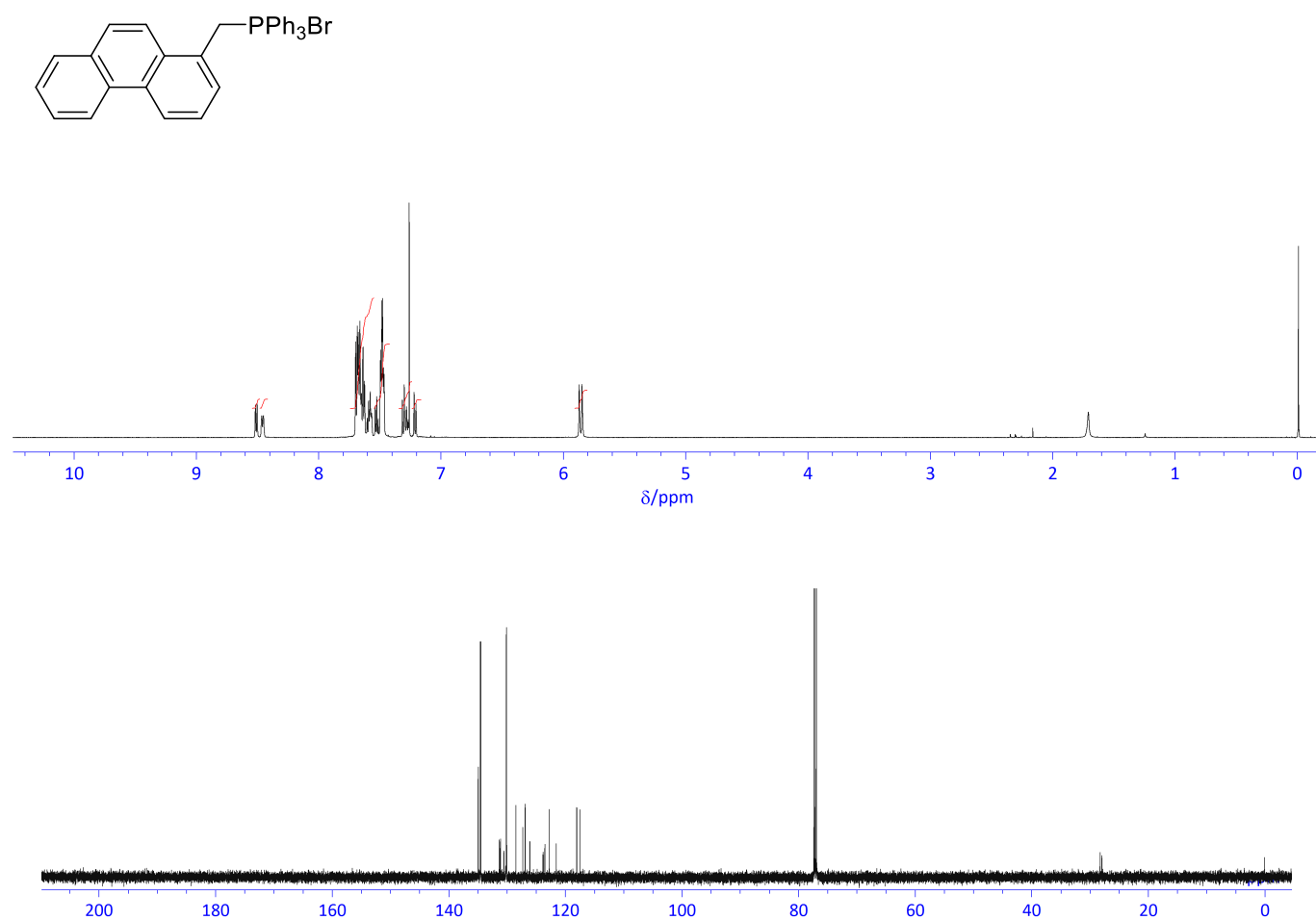


Figure S3. ^1H NMR (600 MHz, CDCl_3 , upper) and ^{13}C NMR (151 MHz, CDCl_3 , lower) spectra of (1-phenanthrylmethyl)triphenylphosphonium bromide.

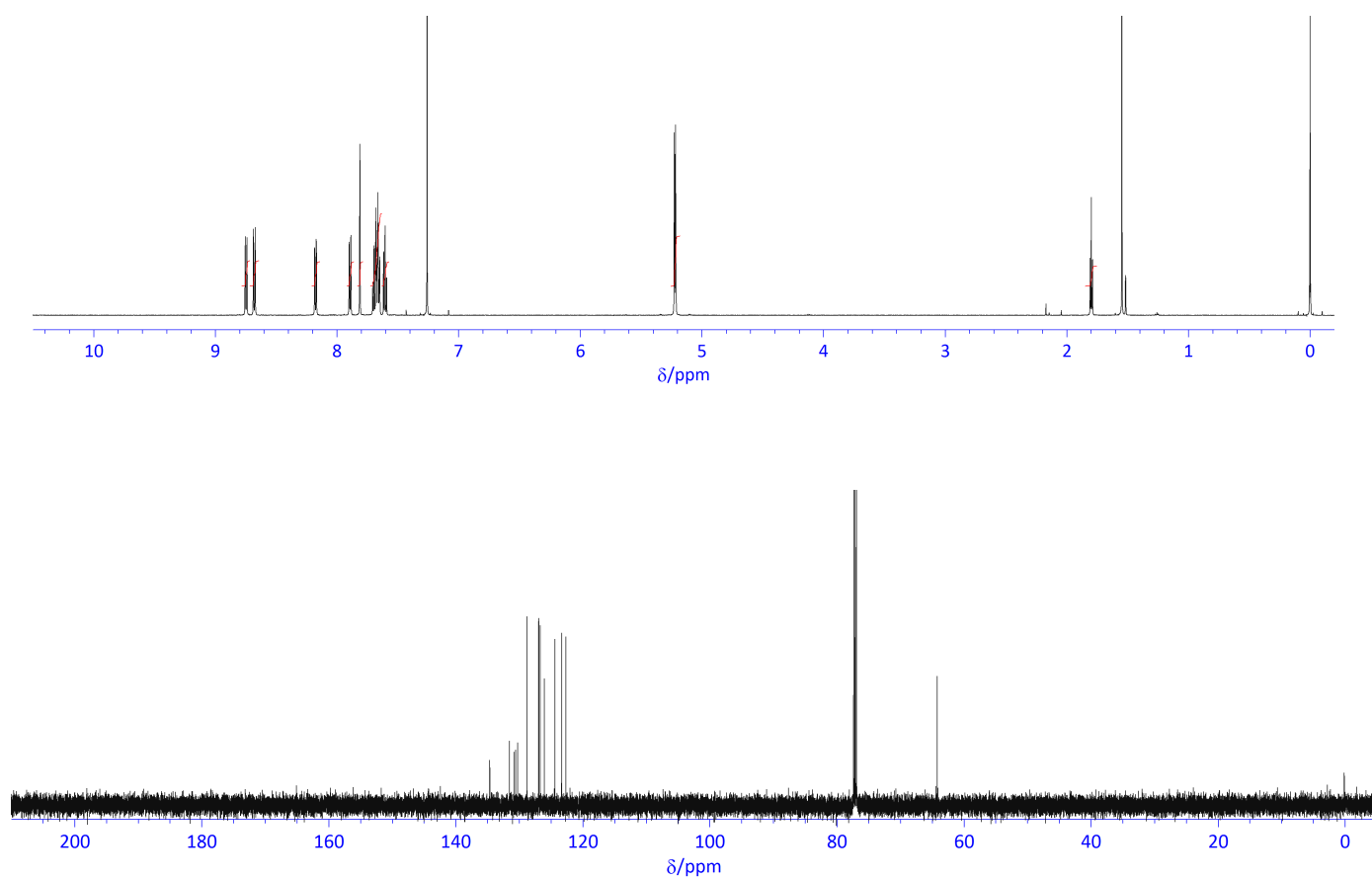
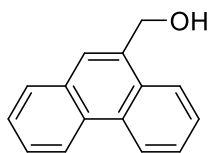


Figure S5. ^1H NMR (600 MHz, CDCl_3 , upper) and ^{13}C NMR (151 MHz, CDCl_3 , lower) spectra of 9-phenanthrene methanol.

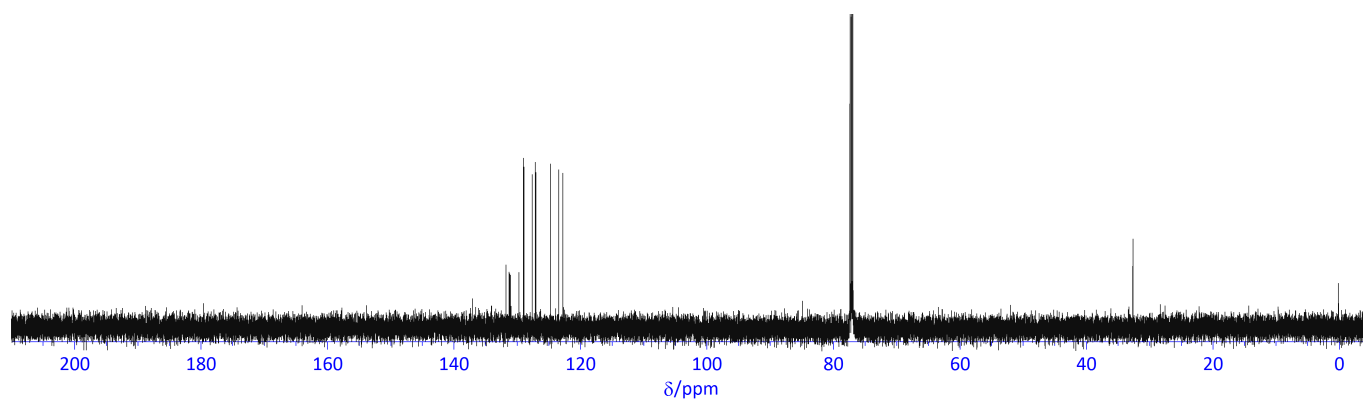
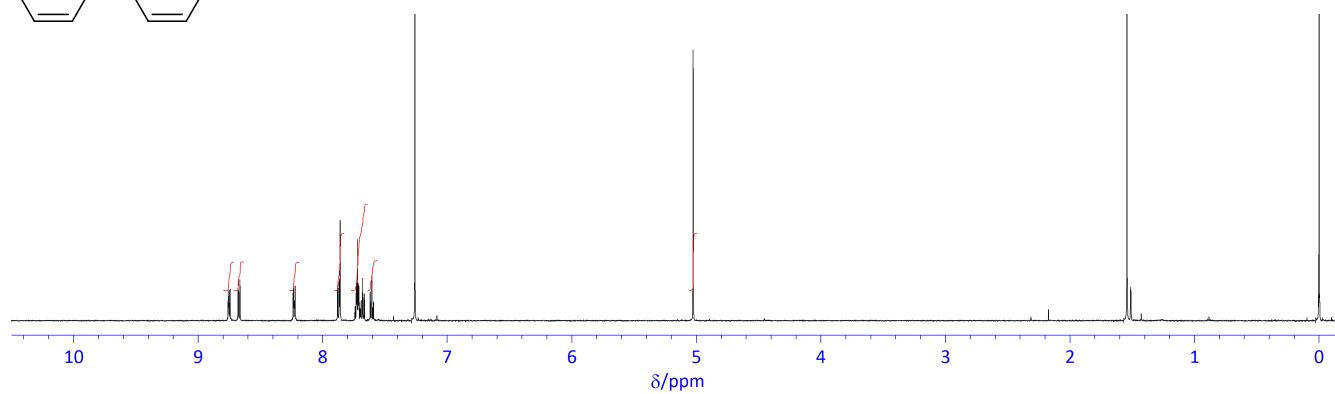
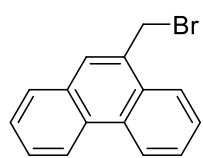


Figure S6. ^1H NMR (600 MHz, CDCl_3 , upper) and ^{13}C NMR (151 MHz, CDCl_3 , lower) spectra of 9-(bromomethyl)phenanthrene.

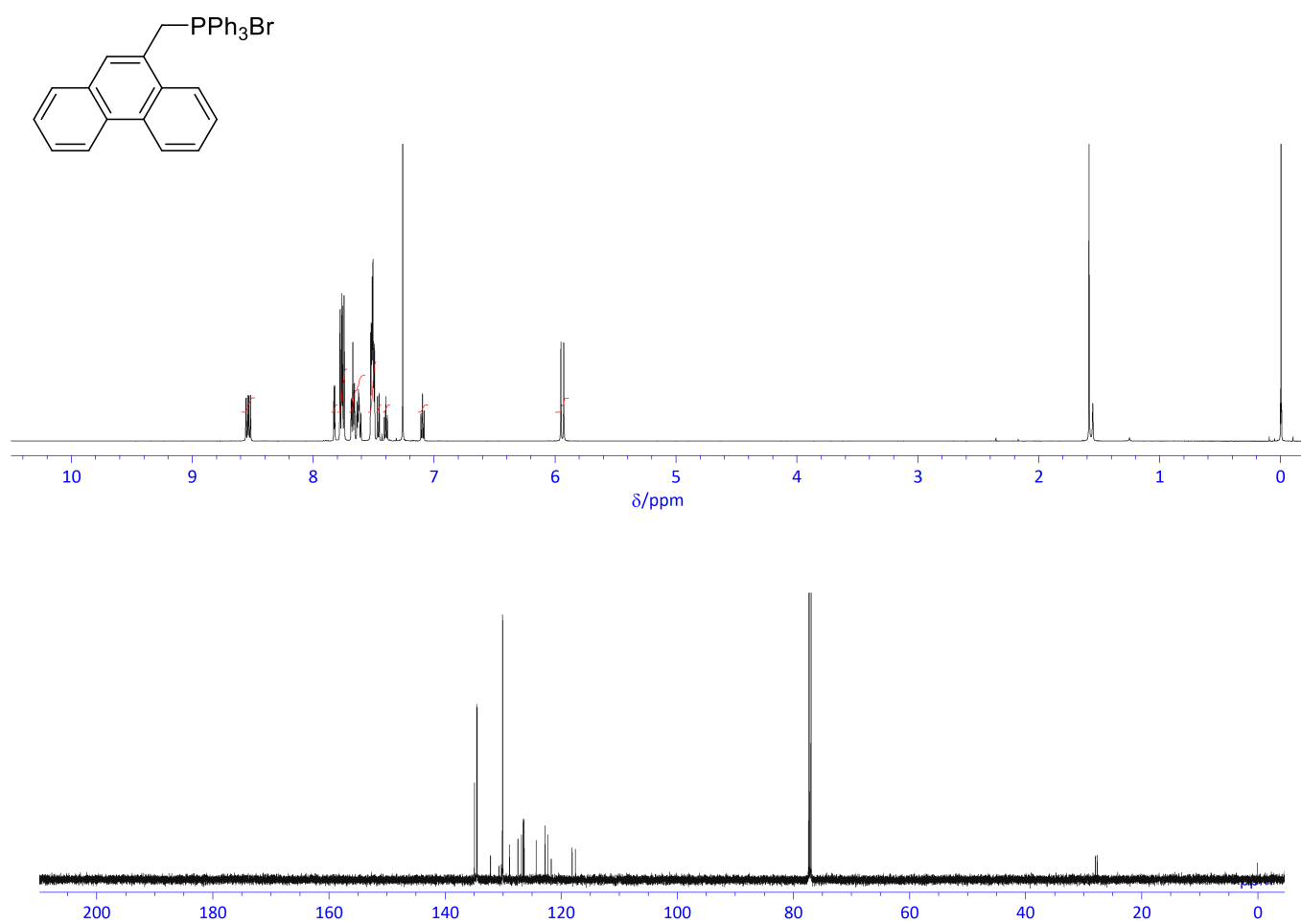


Figure S7. ^1H NMR (600 MHz, CDCl_3 , upper) and ^{13}C NMR (151 MHz, CDCl_3 , lower) spectra of (9-phenanthrylmethyl)triphenylphosphonium bromide.

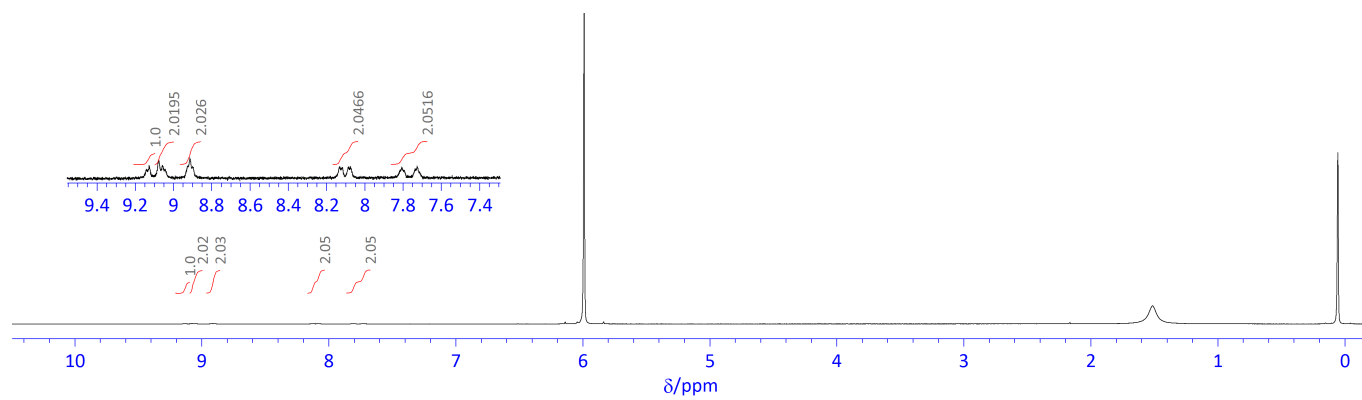
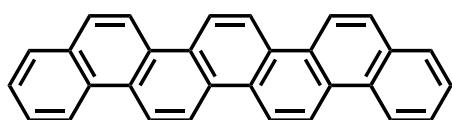


Figure S8. ^1H NMR (600 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) spectra of 1@1 ([7]phencene).

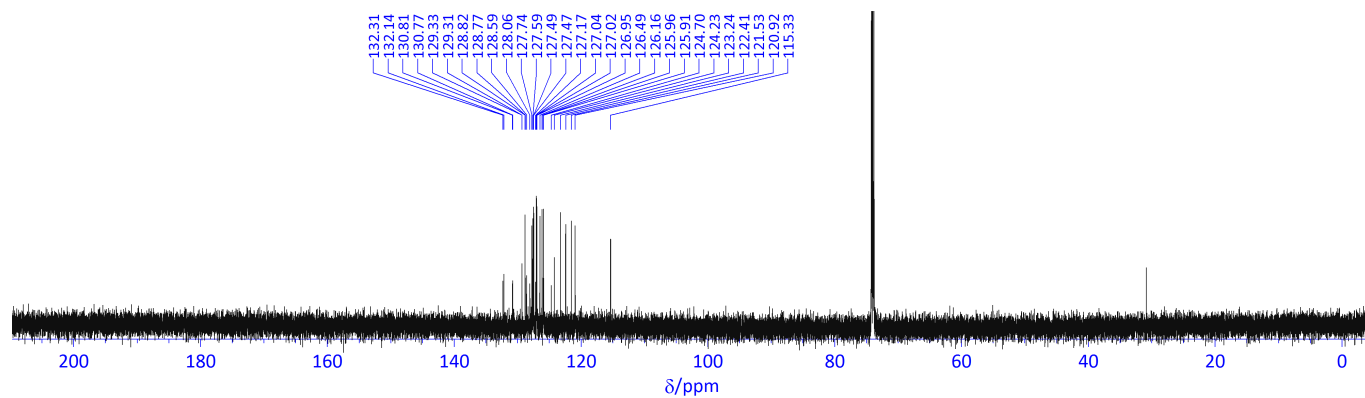
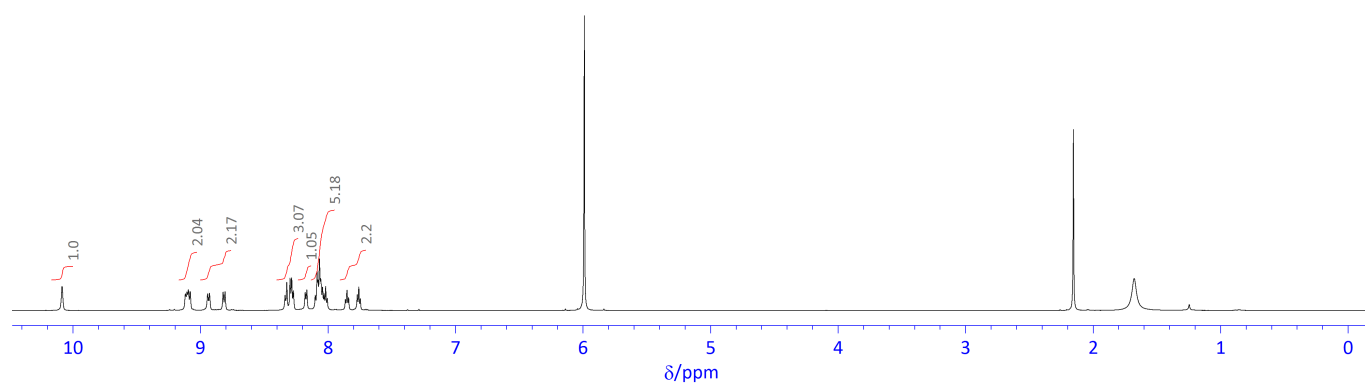
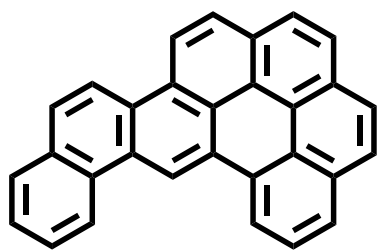


Figure S9. ¹H (600 MHz, CDCl₂CDCl₂, r.t., upper) and ¹³C (151 MHz, CDCl₂CDCl₂, 60°C, lower) NMR spectra of 1@3PP.

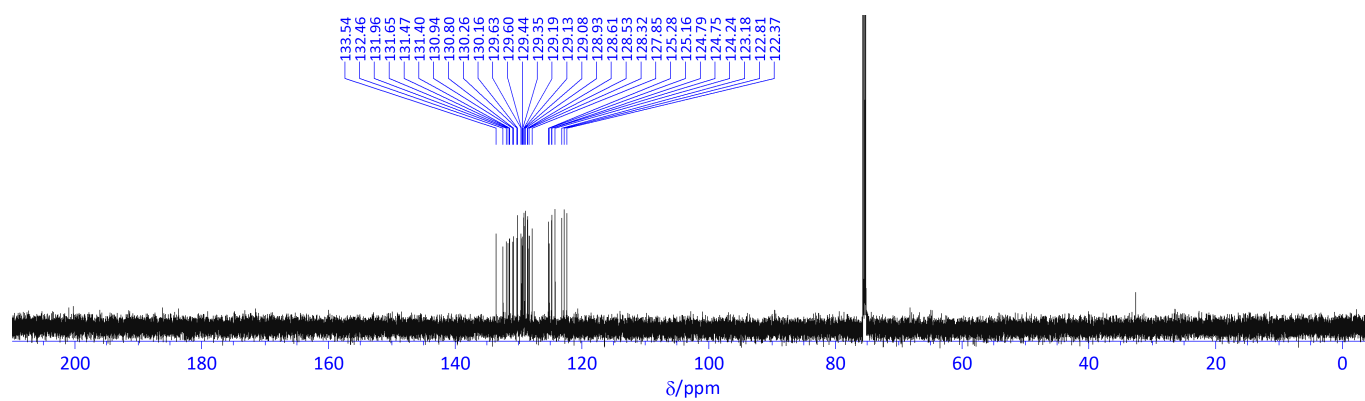
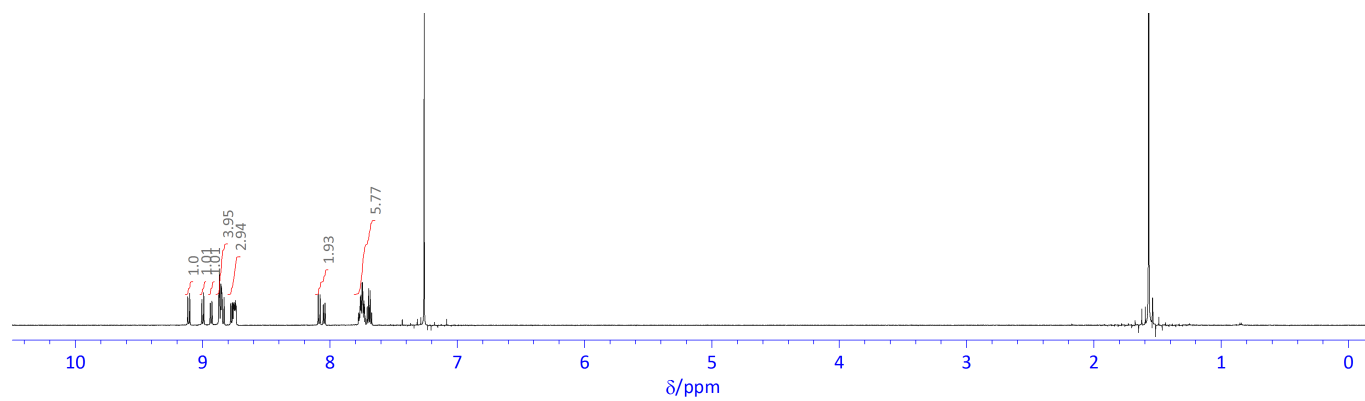
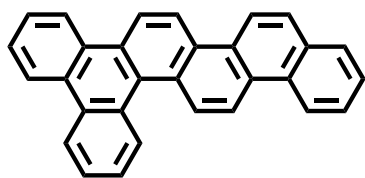


Figure S10. ¹H (600 MHz, CDCl₃, upper) and ¹³C (151 MHz, CDCl₂CDCl₂, lower) NMR spectra of 1@9.

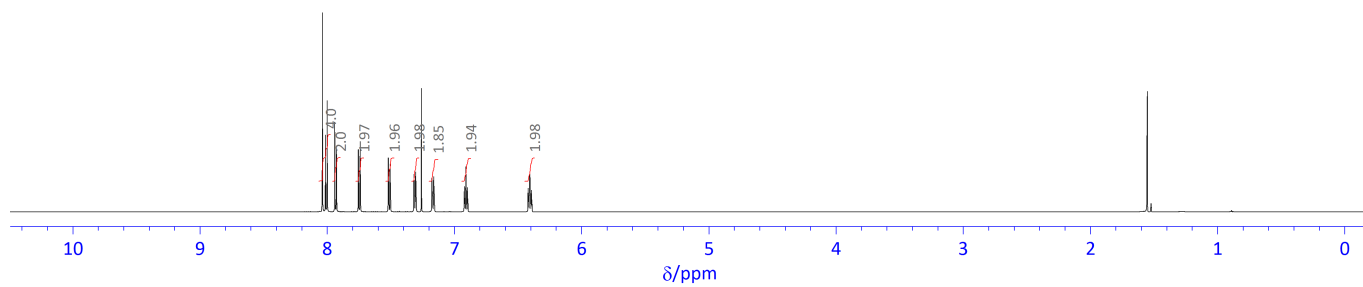
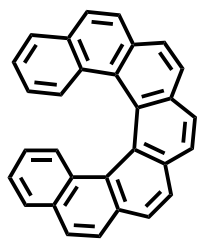


Figure S11. ^1H NMR spectrum (600 MHz, CDCl_3) of 3@3.

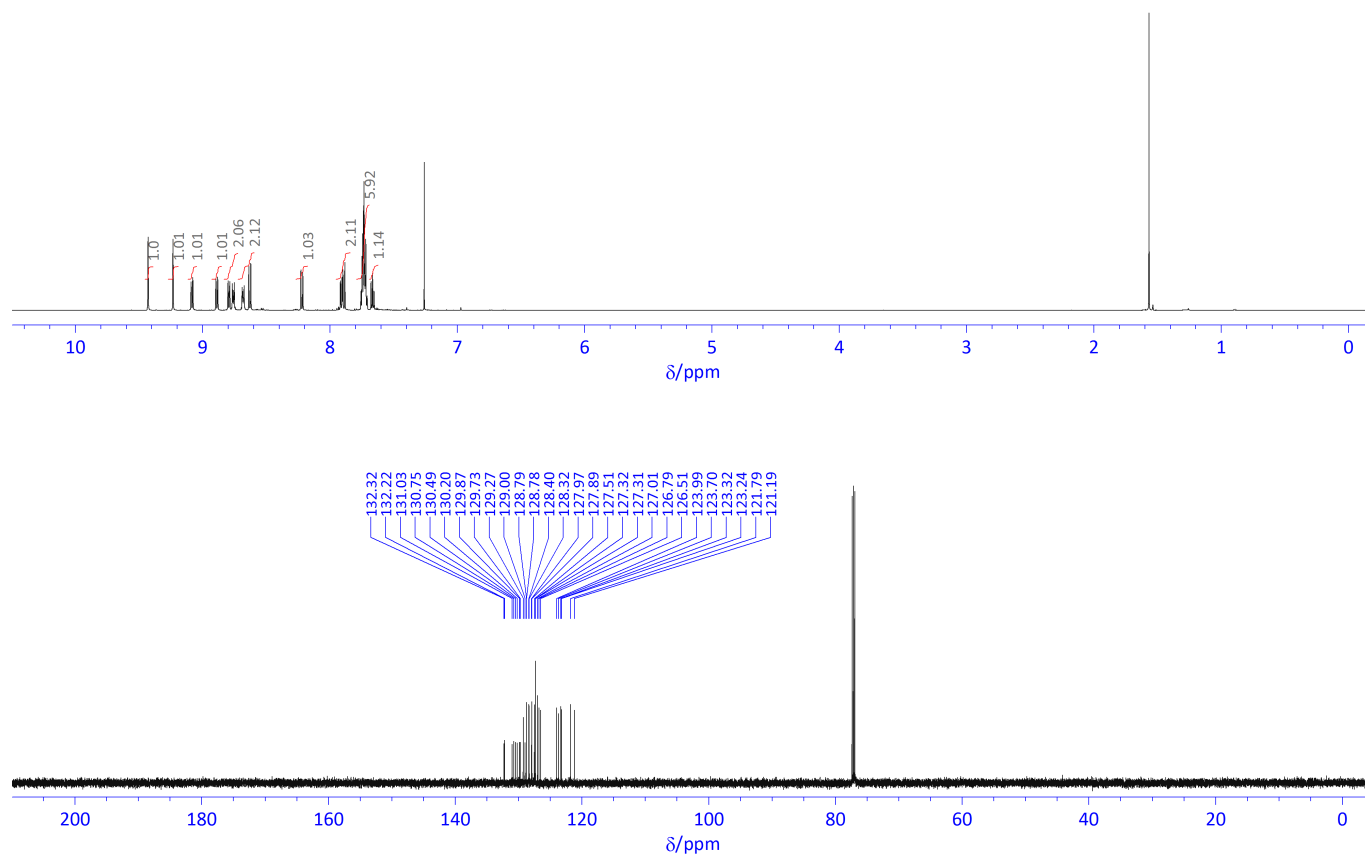
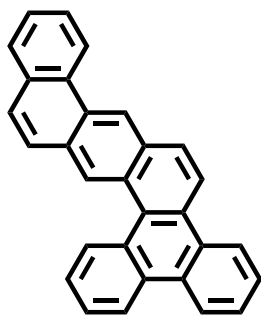


Figure S12. ¹H (600 MHz, CDCl₃, upper) and ¹³C (151 MHz, CDCl₃, lower) NMR spectra of 3@9.

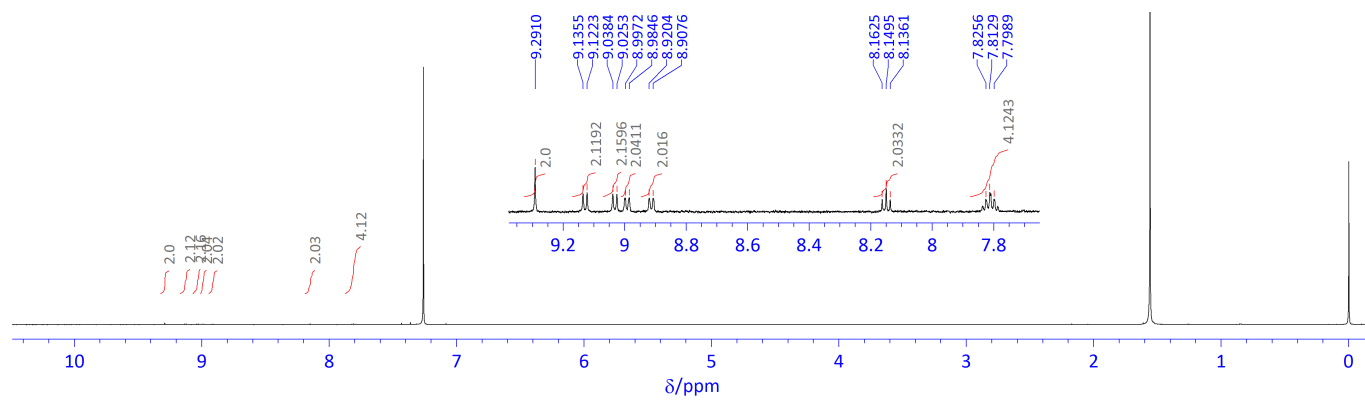
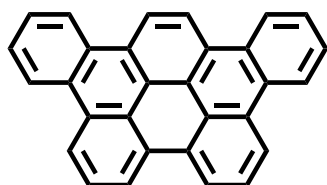


Figure S13. ^1H (600 MHz, CDCl_3) NMR spectra of 9@9PP.

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