Supplementary material (ESI) for *Chemical Communications*
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Direct C-H Arylation of Arenes with Aryltin Reagents Catalyzed by Palladium Complexes

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General. Infrared (IR) spectra were recorded on a JASCO FT/IR-350 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 spectrometer. High resolution mass spectra (HRMS) were obtained on a HITACH M2500S. All reactions were performed in Vial tubes under a N_2 atmosphere. Aryltintrichlorides (**2b–2e**) were prepared as described in the literatures.[1] $CuCl_2$ was dried at 150 °C under reduced pressure and stored under N_2. Flash chromatographies were performed using spherical silica gel (40-100 μm, Kanto Chemical).

Reaction of Phenanthrene (1b) with Phenyltintrichloride (2a). A mixture of **1b** (89.1 mg, 0.50 mmol), **2a** (302.2 mg, 1.00 mmol), $CuCl_2$ (269.0 mg, 2.0 mmol) and $PdCl_2$ (4.4 mg, 0.025 mmol) in 1 mL of dried 1.2-dichloroethane was stirred at 80 °C for 16 h. The reaction mixture was quenched with water (1 mL). The organic layer was separated with 30 mL of Et_2O. After the solvent was removed in *vacuo*, the residue was purified by silica gel flash chromatography (hexane) to give **3ba** (101.6 mg, 0.40 mmol).

Reaction of Tetraline (1d) with Phenyltintrichloride (2a). To a mixture of **1d** (66.1 mg, 0.50 mmol), $CuCl_2$ (538.0 mg, 4.0 mmol) and $PdCl_2$ (4.4 mg, 0.025 mmol) in 1 mL of dried 1.2-dichloroethane, **2a** (604.4 mg, 2.00 mmol) was added dropwise over 11 h at 80 °C with stirring. After 5 h of additional stirring, the reaction mixture was quenched with water (1 mL). The organic layer was separated with 30 ml of Et_2O. After the solvent was removed in *vacuo*, the residue was purified by silica gel flash chromatography (hexane) and preparative GPC to give **3da** (48.9 mg,

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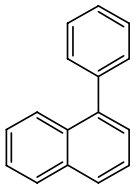
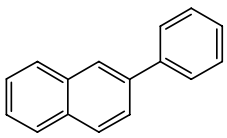
0.23 mmol) and **4da** (21.2 mg, 0.05 mmol).

1-Phenylnaphthalene (3aa-α).[2]



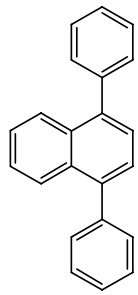
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.91-7.88 (m, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.52-7.46 (m, 6H), 7.43-7.40 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 140.7, 140.2, 133.8, 131.6, 130.0, 128.7, 128.2, 127.6, 127.2, 127.1, 126.9, 126.0, 125.7, 125.4. IR (neat): 3055, 1949, 1393, 777, 701 cm^{-1}.

2-Phenylnaphthalene (3aa-β).[3]



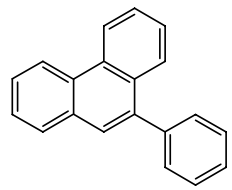
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05 (d, *J* = 1.7 Hz, 1H), 7.93-7.86 (m, 3H), 7.75 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.74-7.72 (m, 2H), 7.52-7.47 (m, 4H), 7.40-7.37 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 141.1, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6. IR (KBr): 3057, 1949, 1495, 1454, 822, 763, 690 cm^{-1}.

1,4-Diphenylnaphthalene (4aa-1,4-Ph).[4]



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.99-7.95 (m, 2H), 7.55-7.49 (m, 8H), 7.47 (s, 2H), 7.46-7.42 (m, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 140.8, 139.8, 131.9, 130.1, 128.3, 127.3, 126.4, 126.4, 125.8. IR (KBr): 3052, 1949, 1491, 1384, 774, 770 cm^{-1}. Although other regioisomers of **4aa** were also obtained, substitution patterns of these isomers could not be determined. HRMS spectra for a mixture of these isomers were in agreement with the molecular formula of **4aa**.

9-Phenylphenanthrene (3ba).[5]



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.75 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.66-7.63 (m, 2H), 7.61-7.57 (m, 1H), 7.55-7.48 (m, 5H), 7.46-7.42 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 140.8, 138.8, 131.5, 131.1, 130.6,

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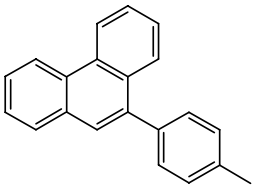
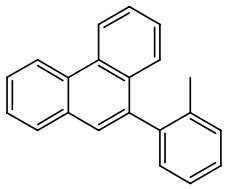
130.0, 129.9, 128.6, 128.3, 127.5, 127.3, 126.9, 126.8, 126.6, 126.5, 126.4, 122.9, 122.5. IR (KBr): 3071, 1487, 1445, 698 cm^{-1}.

9-(4-Tolyl)phenanthrene (3bb).



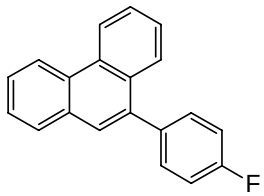
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.76 (d, *J* = 8.2 Hz, 1H), 8.70 (d, *J* = 8.1 Hz, 1H), 7.95-7.93 (m, 1H), 7.88-7.86 (m, 1H), 7.66-7.63 (m, 3H), 7.61-7.58 (m, 1H), 7.54-7.50 (m, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 138.7, 137.8, 137.0, 131.6, 131.2, 130.6, 129.9, 129.9, 129.0, 128.6, 127.4, 126.9, 126.8, 126.4, 126.4, 126.4, 122.9, 122.5, 21.3. IR (KBr): 3021, 1507, 1448, 820, 771 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{16}$: 268.1252; found: 268.1251.

9-(2-Tolyl)phenanthrene (3bc).



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.74 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.67-7.58 (m, 4H), 7.50-7.45 (m, 2H), 7.38-7.30 (m, 4H), 2.05 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 140.2, 138.4, 137.0, 131.6, 131.3, 130.3, 130.3, 130.0, 129.9, 128.6, 127.7, 127.1, 126.8, 126.8, 126.6, 126.5, 126.4, 125.7, 122.8, 122.5, 20.0. IR (KBr): 3060, 1489, 1449, 753, 728 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{16}$: 268.1252; found: 268.1250.

9-(4-Fluorophenyl)phenanthrene (3bd).



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.75 (d, *J* = 8.2 Hz, 1H), 8.69 (d, *J* = 8.3 Hz, 1H), 7.86-7.83 (m, 2H), 7.66-7.63 (m, 3H), 7.61-7.59 (m, 1H), 7.54-7.51 (m, 1H), 7.50-7.46 (m, 2H), 7.21-7.15(m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 162.3 (d, $J_{C\text{-}F}$ = 244.6 Hz), 137.7, 136.7 (d, $J_{C\text{-}F}$ = 3.6 Hz), 131.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 131.4, 131.1, 130.6, 130.0, 128.6, 127.7, 126.9, 126.7, 126.7, 126.6, 126.5, 123.0, 122.5, 115.2 (d, $J_{C\text{-}F}$ = 21.1 Hz). IR (KBr): 3061, 1501, 1213, 834, 752 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{13}F$: 272.1001; found: 272.0999.

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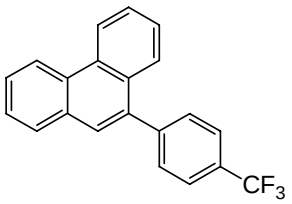
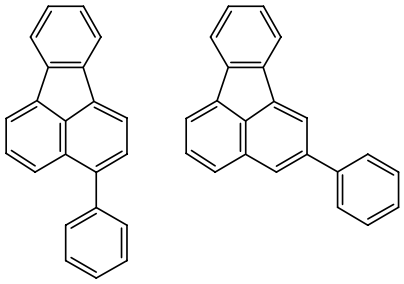
9-(4-Trifluoromethylphenyl)phenanthrene (3be).



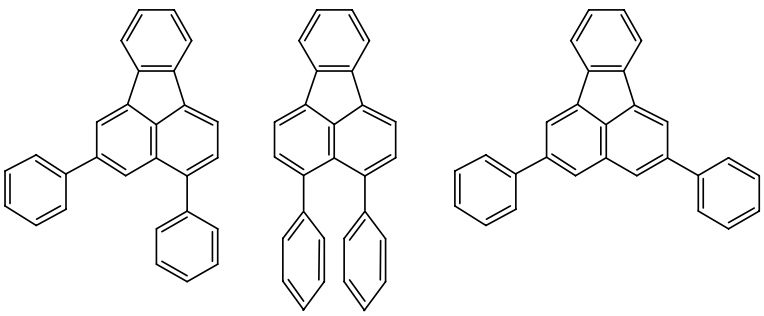
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.77 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 8.3 Hz, 1H), 7.88-7.87 (m, 1H), 7.81-7.79 (m, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.69-7.61 (m, 6H), 7.55-7.52 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 144.5, 137.3, 131.2, 130.6, 130.5, 130.4, 130.1, 129.6 (q, J_{C-F} = 32.3 Hz), 128.8, 127.8, 127.0, 127.0, 126.7, 126.7, 126.4, 125.3 (q, J_{C-F} = 3.8 Hz), 124.3 (q, J_{C-F} = 270.5 Hz), 123.0, 122.6. IR (KBr): 3061, 1615, 1325, 1117, 842 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{13}F_3$: 322.0969; found: 322.0966.

Mixture of 3-phenylfluoranthene and 2-phenylfluoranthene (3ca).



^{1}H-NMR (500 MHz, $CDCl_3$) Peaks for **3-Ph**: δ (ppm) 7.95 (d, J = 7.1 Hz, 1H), 7.94-7.89 (m, 4H), 7.61-7.57 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 2H). Peaks for **2-Ph**: 8.16 (d, J = 1.1 Hz, 0.20 H), 7.99 (d, J = 1.1 Hz, 0.20 H), 7,85-7.84 (m, 0.20H), 7.76-7.75 (m, 0.40H), 7.64-7.62 (m, 0.2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.0, 141.6, 140.2, 139.8, 139.7, 139.5, 139.3, 139.1, 137.5, 137.0, 136.8, 136.3, 132.7, 131.8, 130.3, 130.0, 129.8, 128.9, 128.6, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 126.8, 125.6, 125.1, 121.6, 121.6, 121.5, 121.4, 120.2, 120.0. IR (KBr): 3055, 1444, 761, 700 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{14}$: 278.1096; found: 278.1093.

Mixture of 2,4-diphenylfluoranthene , 3,4-diphenylfluoranthene and 2,5-diphenylfluoranthene (4ca).



^{1}H-NMR (500 MHz, $CDCl_3$) Peaks for **2,4-Ph**: δ (ppm) 8.17 (d, J = 1.0 Hz, 1H), 8.09 (d, J = 1.0 Hz, 1H), 7.93 (d, J = 7.1 Hz, 1H), 7.91-7.89 (m, 2H), 7.68-7.66 (m, 2H), 7.63-7.61

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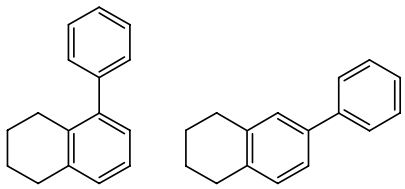
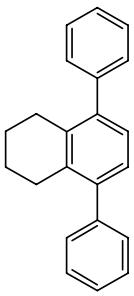
(m, 2H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.52-7.50 (m, 2H), 7.50-7.42 (m, 3H), 7.41-7.35 (m, 3H). Peaks for **3.4-Ph**: 7.96 (d, *J* = 7.1 Hz, 1.84H), 7.95-7.92 (m, 1.84H), 7.52 (d, *J* = 7.1 Hz, 1.84H), 7.41-7.37 (m, 1.84H), 7.02-7.00 (m, 3.68H), 6.97-6.90 (m, 5.52H). Peaks for **2,5-Ph**: 8.13 (d, *J* = 0.9 Hz, 0.18H), 8.02 (d, *J* = 0.9 Hz, 0.18H), 7.78-7.75 (m, 0.36H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ(ppm) 142.1, 141.8, 141.2, 140.4, 139.7, 139.5, 139.4, 139.2, 137.7, 136.6, 136.1, 133.6, 132.0, 130.3, 129.9, 129.1, 128.9, 128.8, 128.4, 128.3, 127.8, 127.7, 127.5, 127.4, 127.4, 127.1, 126.5, 125.9, 125.2, 124.0, 121.7, 121.5, 121.5, 121.2, 120.1, 112.0, 119.8. IR (KBr): 3053, 1445, 842, 756, 700 cm^{-1}. HRMS (EI) calcd for $C_{28}H_{18}$: 354.1409; found: 354.1403.

Mixture of 5-phenyl-1,2,3,4-tetrahydronaphthalene[6] and 6-phenyl-1,2,3,4-tetrahydronaphthalene (3da).[7]



^{1}H-NMR (500 MHz, $CDCl_3$) Peaks for **5-Ph**: δ (ppm) 7.41-7.38 (m, 2H), 7.34-7.25 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 2H), 1.81-1.77 (m, 2H), 1.73-1.68 (m, 2H). Peaks for **6-Ph**: 7.58-7.56 (m, 0.32H), 7.43-7.40 (m, 0.32H), 7.15-7.13 (m, 0.16H), 2.82-2.80 (m, 0.64H), 1.84-1.81 (m, 0.64H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.1, 142.0, 141.3, 138.5, 137.4, 136.3, 134.8, 129.5, 129.2, 128.6, 128.4, 127.9, 127.8, 127.1, 127.0, 126.9, 126.6, 125.2, 124.3, 29.9, 29.5, 29.1, 28.2, 23.3, 23.2, 22.9. IR (neat): 3051, 2928, 1454, 759, 701 cm^{-1}.

5,8-Diphenyl-1,2,3,4-tetrahydronaphthalene (4da).



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43-7.40 (m, 4H), 7.36-7.33 (m, 6H), 7.11 (s, 2H), 2.67 (s, 4H), 1.69 (s, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.1, 142.3, 135.1, 129.3, 128.0, 126.8, 126.7, 28.6, 22.9. IR (KBr): 3056, 2930, 2858, 1460, 763, 702 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}$: 284.1565; found: 284.1562.

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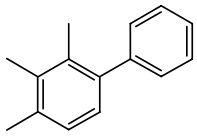
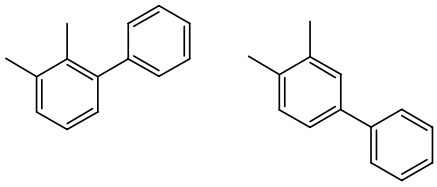
2,3,4-Trimethylbiphenyl (3ea).[8]



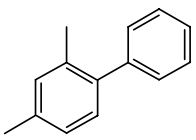
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.39-7.36 (m, 2H), 7.32-7.27 (m, 3H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.9, 140.2, 135.6, 135.4, 133.8, 129.5, 127.9, 127.0, 126.4, 126.4, 20.8, 17.6, 16.0. IR (neat): 2921, 1602, 1474, 764, 703 cm^{-1}.

Mixture of 2,3-dimethylbiphenyl and 3,4-dimethylbiphenyl (3fa).[9]



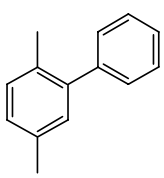
^{1}H-NMR (500 MHz, $CDCl_3$) Peaks for **3-Ph**: δ (ppm) 7.41-7.37 (m, 2H), 7.34-7.29 (3H), 7.17-7.12 (m, 2H), 7.09-7.08 (m, 1H), 2.34 (s, 3H), 2.15 (s, 3H). Peaks for **4-Ph**: 7.59-7.56 (m, 0.64H), 7.43-7.40 (m, 0.64H), 7.21-7.19 (m, 0.32H), 2.33 (s, 0.96H), 2.30 (s, 0.96H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.5, 142.2, 141.3, 138.9, 137.2, 136.9, 135.7, 134.0, 130.0, 129.4, 128.8, 128.7, 128.4, 127.9, 127.6, 127.0, 126.9, 126.6, 125.2, 124.5, 20.7, 19.9, 19.4, 17.0. IR (neat): 3056, 2939, 1464, 760, 701 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{14}$: 182.1096; found: 182.1094.

2,4-Dimethylbiphenyl (3ga).[10]



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.41-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 2.37 (s, 3H), 2.25 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 141.9, 139.1, 136.9, 135.1, 131.1, 129.7, 129.3, 128.0, 126.6, 126.4, 21.0, 20.4. IR (neat): 2921, 1482, 765, 703 cm^{-1}.

2,5-Dimethylbiphenyl (3ha).[11]



^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.41-7.38 (m, 2H), 7.34-7.30 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 2.35 (s, 3H), 2.23 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 142.1, 141.7, 135.1, 132.1, 130.5, 130.2, 129.1, 128.0, 127.9, 126.6, 20.9, 19.9. IR (neat): 3024, 2922,

1487, 1444, 811, 702 cm^{-1}.

References

1 (*a*) K. Fugami, K. Kawata, T. Enokido, Y. Mishiba, S. Hagiwara, Y. Hirunuma, D. Koyama, M. Kameyama and M. Kosugi, *J. Organomet. Chem.*, 2000, **611**, 433; (*b*) D. A. Powell, T. Maki and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 516.

2 S. Riggleman and P. DeShong, *J. Org. Chem.*, 2003, **68**, 8106.

3 Z.-Y. Tang and Q.-S. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 3058.

4 G. W. Kabalka, Y. Ju and Z. Wu, *J. Org. Chem.*, 2003, **68**, 7915.

5 K. Kanno, Y. Liu, A. Iesato, K. Nakajima and T. Takahashi, *Org. Lett.*, 2005, **7**. 5453.

6 V. B. Kurteva, A. G. Santos and C. A. M. Afonso, *Org. Biomol. Chem.*, 2004, **2**, 514.

7 N. Asao, T. Nogami, S. Lee and Y. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 10921.

8 M. P. Hartshorn, M. P. Judd, R. J. Martyn, W. T. Robinson, G. J. Wright and R. W. Vannoort, *Aust. J. Chem.*, 1990, **43**, 1519.

9 K. W. Anderson and S. W. Buchwald, *Angew. Chem. Int. Ed.*, 2005, **44**, 6173.

10 A. K. Sahoo, T. Oda, Y. Nakao and T. Hiyama, *Adv. Synth. Catal.*, 2004, **346**. 1715.

11 D. Liu, W. Gao, Q. Dai and X. Zhang, *Org. Lett.*, 2005, **7**. 4907.