Supporting Information for
Improved Synthesis of Aryl-Substituted Anthracenes and Heteroacenes

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Experimental section

General Methods. All reactions were carried out under nitrogen. CH₂Cl₂ was
distilled over P₂O₅. Unless noted, all commercial reagents were used without further
purification. ¹H and ¹³C NMR spectra were recorded at 300 and 75.4 MHz,
respectively, and in CDCl₃ (containing 0.03% TMS) solutions. ¹H NMR spectra was
recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ¹³C NMR
spectra was recorded with CDCl₃ (δ = 77.00 ppm) as internal reference. NMR yields
were determined using mesitylene or dibromomethane as an internal standard.

1a,¹ 1b (S,S-isomer),² 2a,³ 3a,⁴ 3c,⁵ 3g,⁶ 3j,⁷ 3k⁸ and 4a⁹ are known compounds.
A typical procedure for the preparation of diacetate 2f.

To a solution of *o*-phthalaldehyde (5 mmol, 670 mg) in THF (10 mL) was added 3,5-dimethylphenyl magnesium bromide (prepared from 3,5-dimethylbromobenzene (20 mmol in 10 mL THF) and turning Magnesium (20 mmol, 480 mg) in THF (40 mL). The reaction mixture was stirred for 1 hour at room temperature. Then the reaction was quenched with a saturated aqueous solution of NH₄Cl and extracted with EtOAc. The extract was washed with brine and dried over Na₂SO₄. The solvent was evaporated *in vacuo* and the residue was used directly for the next step.

To a solution of the above residue in dry CH₂Cl₂ were added triethylamine (30 mmol, 5 mL), Ac₂O (20 mmol, 2 mL) and DMAP (1 mmol, 122 mg), the resulting solution was stirred at room temperature for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ and extracted with CH₂Cl₂. The extract was washed with brine and dried over Na₂SO₄. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 5:1) to yield the desired diacetate of acetic acid {2-[acetoxy-(3,5-dimethyl-phenyl)-methyl]-phenyl}-(3,5-dimethyl-phenyl)-methyl ester (2f). The compound was obtained as a mixture of two diastereomers with a ratio of 1.71:1 as a colorless sticky liquid in 99% yield (overall yield from *o*-phthalaldehyde). ¹H NMR (CDCl₃, Me₄Si) two isomers: δ 1.98 (s), 2.09 (s), 2.19 (s), 2.25 (s), 6.67 (s), 6.79 (s), 6.83 (s), 6.87 (s), 7.14 (s), 7.20 (s), 7.29-7.38 (m), 7.45-7.48 (m); ¹³C NMR (CDCl₃, Me₄Si) two isomers: δ 20.9, 21.1, 21.2, 21.2, 73.0, 73.6, 124.8, 125.1, 127.8, 128.1, 128.2, 128.7, 129.4, 137.6, 137.8, 137.9, 139.1, 139.4, 169.6, 169.7; IR (neat): 3009, 2919, 2865, 1743, 1607, 1454, 1370, 1231, 1158, 1021, 974, 855, 816, 766, 662 cm⁻¹; HRMS (ESI) for C₂₈H₃₀O₄Na [M+Na]⁺: calcd 453.2036, found 453.2032; Anal. Calcd. for C₂₈H₃₀O₄: C, 78.11, H, 7.02; Found: C, 78.10; H, 6.84.
1,2-Phenylenebis(phenylmethanol) (1a)\(^1\) Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=3:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.23:1 as a colorless sticky liquid in 97% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 3.67 (bs), 5.86 (s), 6.10 (bs), 7.06-7.07 (m), 7.16-7.28 (m); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 71.9, 73.5, 126.2, 126.8, 127.3, 127.4, 128.0, 128.1, 128.3, 129.3, 141.4, 141.5, 142.4, 142.6.

1,2-Phenylenebis(p-tolylmethanol) (1b)\(^2\) Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=3:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.39:1 as a light green sticky liquid in 92% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 2.29 (s), 2.31 (s), 3.70 (bs), 3.83 (bs), 5.78 (s), 6.00 (s), 7.01-7.10 (m), 7.11-7.14 (m), 7.17-7.22 (m); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 21.0, 21.1, 71.6, 73.1, 126.3, 126.7, 127.77, 127.8, 128.0, 128.8, 128.9, 136.76, 136.79, 139.5, 139.7, 141.4, 141.6. HRMS (EI) for C\(_{22}\)H\(_{20}\)O [M-H\(_2\)O]\(^+\): calcld 300.1514, found 300.1506.
Acetic acid [2-(acetoxy-phenyl-methyl)-phenyl]-phenyl-methyl ester (2a). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.55:1 as a colorless sticky liquid in 88% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: δ 1.93 (s), 2.00 (s), 7.09-7.12 (m), 7.19-7.36 (m), 7.42-7.44 (m); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: δ 20.7, 20.8, 73.1, 73.2, 127.0, 127.1, 127.6, 127.7, 128.18, 128.19, 128.20, 128.23, 128.3, 137.5, 137.7, 139.0, 139.3, 169.4, 169.6.

Acetic acid [2-(acetoxy-p-tolyl-methyl)-phenyl]-p-tolyl-methyl ester (2b). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.53:1 as a colorless sticky liquid in 99% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: δ 1.93 (s), 2.03 (s), 2.26 (s), 2.29 (s), 6.98-7.20 (m), 7.27-7.31 (m), 7.36-7.39 (m), 7.42-7.45 (m); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: δ 20.8, 20.85, 20.89, 20.9, 73.0, 73.2, 127.2, 128.0, 128.85, 128.9, 136.1, 136.4, 137.3, 137.4, 137.6, 137.7, 169.5, 169.6; IR (neat):3027, 2923, 1742, 1514 1453, 1370, 1232, 1018, 970, 797, 755 cm\(^{-1}\); HRMS (ESI) for C\(_{26}\)H\(_{26}\)O\(_4\)Na [M+Na\(^+\)]: calcd 425.1723, found 425.1721; Anal. Calcd. for C\(_{26}\)H\(_{26}\)O\(_4\): C, 77.59, H, 6.51; Found: C, 77.63; H, 6.33.

Acetic acid [2-[acetoxy-(4-methoxy-phenyl)-methyl]-phenyl]-(4-methoxy-phenyl)
-methyl ester (2c). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.99:1 as a yellow green sticky liquid in 74% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.93 (s), 2.04 (s), 3.69 (s), 3.73 (s), 6.73 (d, $J = 8.4$ Hz), 6.83 (d, $J = 8.4$ Hz), 7.01 (d, $J = 9.0$ Hz), 7.10 (s) 7.15-7.19 (m), 7.30-7.34 (m), 7.40-7.43 (m), 7.45-7.48 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.8, 20.9, 54.9, 72.7, 72.9, 113.5, 113.6, 127.7, 127.9, 128.6, 128.7, 130.9, 131.3, 137.4, 137.5, 158.9, 159.1, 169.5, 169.7; IR (neat): 3066, 3002, 2958, 2936, 2838, 1739, 1611, 1585, 1513, 1463, 1370, 1304, 1233, 1174, 1022, 969, 829, 806, 783, 756 cm$^{-1}$; HRMS (ESI) for C$_{26}$H$_{26}$O$_6$Na [M+Na]$^+$: calcd 457.1622, found 457.1624.

[Diagram of compound 2d]

Acetic acid {2-[acetoxy-(4-tert-butyl-phenyl)-methyl]-phenyl}- (4-tert-butyl-phenyl)-methyl ester (2d). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.14:1 as a sticky liquid in 64% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.26 (s), 1.29 (s), 1.93 (s), 2.06 (s), 6.99 (s), 7.02 (s), 7.12 (s), 7.15 (s), 7.21-7.47 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.9, 21.0, 31.2, 31.3, 34.40, 34.44, 73.0, 73.3, 125.2, 125.3, 126.8, 127.0, 128.0, 128.1, 128.2, 128.6, 136.3, 136.6, 137.7, 137.9, 150.6, 169.7, 169.8; IR (neat): 3060, 3032, 2963, 2904, 2869, 1742, 1512, 1462, 1411, 1369, 1231, 1109, 1018, 971, 806, 760 cm$^{-1}$; HRMS (ESI) for C$_{32}$H$_{38}$O$_4$Na [M+Na]$^+$: calcd 509.2662, found 509.2660.
Acetic acid \([2-(acetoxy-o-tolyl-methyl)-phenyl]-o-tolyl-methyl ester\) (2e).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 4.64:1 as a light yellow solid in 81% yield. \(^1\H\)NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 1.71 (s), 1.96 (s), 2.17 (s), 2.31 (s), 7.04-7.24 (m), 7.25-7.34 (m); \(^1\C\)NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 18.9, 18.9, 20.2, 20.9, 70.6, 70.7, 125.7, 127.2, 127.4, 127.91, 127.99, 128.2, 128.3, 128.4, 130.6, 136.4, 136.6, 136.9, 137.1, 137.2, 169.6, 170.0; IR (neat): 3068, 3026, 2957, 1739, 1490, 1462, 1370, 1233, 1018, 970, 931, 870, 753 cm\(^{-1}\); HRMS (ESI) for C\(_{26}\)H\(_{26}\)O\(_4\)Na \([M+Na]^+\): calcd 425.1723, found 425.1722; Anal. Calcd. for C\(_{26}\)H\(_{26}\)O\(_4\): C, 77.59, H, 6.51; Found: C, 77.69; H, 6.50.

Acetic acid \([2-(acetoxy-p-tolyl-methyl)-4,5-dimethyl-phenyl]-p-tolyl-methyl ester\) (2g).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.42:1 as a colorless sticky liquid in 63% yield. \(^1\H\)NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 1.96 (s), 2.02 (s), 2.19 (s), 2.21 (s), 2.26 (s), 2.28 (s), 7.02-7.17 (m); \(^1\C\)NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 19.5, 20.84, 20.88, 20.9, 73.1, 73.2, 126.8, 126.9, 128.79, 128.8, 129.3, 129.5, 134.9, 135.1, 136.47, 136.52, 136.7, 137.1, 169.5, 169.7; IR (neat): 3025, 2922, 2865, 1742, 1514, 1450, 1369, 1231, 1180, 1112, 1019, 967, 808, 606 cm\(^{-1}\); HRMS (ESI) for C\(_{28}\)H\(_{30}\)O\(_4\)Na \([M+Na]^+\):
Acetic acid [2-(acetoxy-biphenyl-4-yl-methyl)-phenyl]-biphenyl-4-yl-methyl ester (2h). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 2.15:1 as a white solid in 90% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 2.01 (s), 2.08 (s), 7.15-7.51 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.9, 21.0, 73.0, 73.4, 126.9, 127.3, 127.5, 127.9, 128.1, 128.3, 128.4, 128.7, 128.8, 137.4, 137.7, 138.1, 138.2, 140.40, 140.44, 140.6, 140.7, 169.7, 169.8; IR (neat): 3058, 3030, 1741, 1709, 1600, 1519, 1487, 1408, 1370, 1231, 1184, 1019, 972, 856, 761, 736, 698 cm$^{-1}$; HRMS (ESI) for C$_{36}$H$_{30}$O$_4$Na [M+Na]$^+$: calcd 549.2036, found 549.2029.

Acetic acid {2-[acetoxy-(4-tert-butyl-phenyl)-methyl]-4,5-dimethyl-phenyl}-(4-tert-butyl-phenyl)-methyl ester (2i). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.44:1 as a sticky liquid in 66% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.26 (s), 1.28 (s), 1.29 (s), 1.97 (s), 2.05 (s), 2.21 (s), 2.23 (s), 7.00-7.42 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 19.6, 21.0, 21.1, 73.1, 73.4, 125.2, 126.4, 126.9, 127.2, 129.3, 130.0, 130.9, 135.0, 135.2, 136.6, 136.76, 136.79, 136.9, 150.3, 150.4. 169.7, 169.8; IR (neat): 3053, 3032, 2963, 2897, 2868, 1744, 1614, 1570, 1512, 1462, 1368, 1231, 1109, 1020,
967, 822, 732 cm\(^{-1}\); HRMS (ESI) for C\(_{34}\)H\(_{42}\)O\(_{4}\)Na [M+Na]\(^+\): calcd 537.2975, found 537.2968.

Acetic acid [2-(acetoxy-naphthalen-1-yl-methyl)-phenyl]-naphthalen-1-yl-methyl ester (2j). The title compound was prepared analogously to the procedure described for 2f except that the reaction of \(o\)-phthalaldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded one of the two diastereomers as a white solid in 51% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 2.13 (s, 6H), 7.20-7.36 (m, 10H), 7.42-7.45 (m, 2H), 7.51 (d, \(J = 8.4\) Hz, 2H), 7.68-7.72 (m, 4H), 7.89 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 20.9, 70.2, 123.2, 124.6, 125.7, 126.3, 126.4, 128.1, 128.5, 129.0, 130.8, 133.6, 133.8, 137.3, 169.9; IR (neat): 3054, 3057, 2941, 1739, 1599, 1511, 1487, 1434, 1367, 1233, 1163, 1079, 1046, 1014, 965, 800, 799, 730 cm\(^{-1}\); HRMS (MALDI/DHB) for C\(_{32}\)H\(_{26}\)O\(_{4}\)Na [M+Na]\(^+\): calcd 497.1723, found 497.1725; Anal. Calcd. for C\(_{32}\)H\(_{26}\)O\(_{4}\): C, 80.99; H, 5.52; Found: C, 81.07; H, 5.55.

Acetic acid [2-(acetoxy-naphthalen-2-yl-methyl)-phenyl]-naphthalen-2-yl-methyl ester (2k). The title compound was prepared analogously to the procedure described for 2f except that the reaction of \(o\)-phthalaldehyde with arylmagnesium bromide was
done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (elucent: petroleum ether/ethyl acetate=5:1) afforded one of the two diastereomers with a ratio of 1.84:1 as a light yellow solid in 85% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 1.94 (s), 2.05 (s), 7.23-7.44 (m), 7.49-7.54 (m), 7.60-7.72 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 20.8, 20.9, 73.3, 73.5, 124.8, 124.9, 125.9, 126.1, 126.1, 126.4, 127.3, 127.4, 127.8, 127.9, 128.1, 128.3, 128.4, 128.8, 132.6, 132.7, 132.8, 132.8, 136.5, 136.6, 137.5, 137.8, 169.6, 169.7; IR (neat): 3058, 3022, 1741, 1601, 1508, 1434, 1369, 1229, 1021, 812, 749 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{32}$H$_{26}$O$_4$Na [M+Na]$^+$: calcd 497.1723, found 497.1725.

Acetic acid [2-(acetoxy-phenanthren-9-yl-methyl)-phenyl]-phenanthren-9-yl-methyl ester (2l). The title compound was prepared analogously to the procedure described for 2f except that the reaction of $\alpha$-phthalaldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel afforded one of the two diastereomers as a white solid in 15% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 2.18 (s, 6H), 7.08-7.13 (m, 2H), 7.38-7.63 (m, 16H), 7.91 (s, 2H), 8.44 ($t$, $J$ = 8.4 Hz, 4H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 21.1, 70.5, 122.3, 122.9, 123.9, 126.4, 126.5, 126.7, 127.1, 128.0, 128.1, 128.7, 128.8, 129.6, 130.3, 130.4, 130.5, 132.3, 137.2, 170.1; IR (neat): 3065, 2918, 1739, 1712, 1497, 1451, 1434, 1368, 1230, 1018, 967, 897, 750, 726 cm$^{-1}$; HRMS (ESI) for C$_{40}$H$_{30}$O$_4$Na [M+Na]$^+$:
The title compound was prepared analogously to the procedure described for 2f except that the reaction of aldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 3:1 as a white solid in 86% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 1.75 (s), 1.76 (s), 2.21 (s), 2.22 (s), 2.24 (s), 2.28 (s), 7.18-7.55 (m), 7.62-7.66 (m), 7.80 (s), 7.82 (s), 7.88-8.02 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 19.6, 20.3, 20.9, 70.3, 70.4, 123.3, 123.5, 124.6, 124.8, 125.4, 125.6, 125.8, 126.2, 126.3, 126.6, 128.4, 128.9, 129.4, 130.9, 131.0, 133.6, 134.2, 134.5, 134.6, 134.8, 134.9, 169.5, 170.0; IR (neat): 3051, 2922, 1714, 1599, 1510, 1436, 1367, 1226, 1022, 963, 808, 777, 733 cm$^{-1}$; HRMS (ESI) for C$_{34}$H$_{30}$O$_4$Na [M+Na]$^+$: calcd 525.2036, found 525.2037.
-1-yl-methyl ester (2n). The title compound was prepared analogously to the procedure described for 2f except that the reaction of aldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 3.33:1 as a white solid in 39% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.71 (s), 1.99 (s), 2.10 (s), 2.21 (s), 7.16-7.50 (m), 7.71-7.86 (m), 7.96 (s); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.4, 21.1, 70.3, 70.6, 123.3, 123.4, 124.6, 124.9, 125.7, 125.8, 125.9, 126.4, 126.5, 126.7, 127.80, 127.84, 128.49, 128.5, 129.18, 129.22, 130.9, 131.2, 132.6, 132.8, 133.6, 133.85, 133.92, 135.2, 135.2, 169.6, 170.0; IR (neat): 3054, 3014, 2961, 1741, 1599, 1511, 1432, 1399, 1366, 1229, 1020, 968, 896, 802, 779 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{36}$H$_{28}$O$_4$Na [M+Na]$^+$: calcd 547.1880, found 547.1882.

Acetic acid [3-(acetoxy-naphthalen-2-yl-methyl)-naphthalen-2-yl]-naphthalen-2-yl-methyl ester (2o). The title compound was prepared analogously to the procedure described for 2f except that the reaction of aldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 2.15:1 as a white solid in 57% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.97 (s), 2.10 (s), 7.22-7.57 (m), 7.63-7.74 (m), 7.79-7.83 (m), 7.91 (s), 7.98 (s); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.9, 21.1, 73.7, 74.1, 125.1, 125.2, 126.2, 126.3, 126.6, 126.7, 127.4, 127.5, 127.9, 128.0, 128.2, 128.3, 128.8, 132.7, 132.8, 132.9, 132.9, 135.4, 135.6, 136.5, 136.6, 169.8, 169.9; IR

![Acetic acid [3-(acetoxy-naphthalen-2-yl-methyl)-naphthalen-2-yl]-naphthalen-2-yl-methyl ester (2o).](image)
Acetic acid [3-(acetoxy-phenanthren-9-yl-methyl)-naphthalen-2-yl]-phenanthren-9-yl-methyl ester (2p). The title compound was prepared analogously to the procedure described for 2f except that the reaction of aldehyde with arylmagnesium bromide was done at room temperature for overnight and then at refluxing temperature for 2 h. Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded one of the diastereomers as a sticky colorless liquid in 15% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 2.28 (s, 6H), 7.05 (t, $J$ = 7.8 Hz, 2H), 7.40-7.79 (m, 16H), 7.98 (s, 4H), 8.47-8.51 (m, 4H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 21.2, 70.5, 122.3, 122.9, 124.0, 126.5, 126.5, 126.7, 126.8, 127.1, 127.8, 127.9, 127.9, 128.9, 129.6, 130.4, 130.5, 130.6, 132.4, 132.9, 135.1, 170.1; IR (neat): 3059, 3015, 2929, 1741, 1712, 1496, 1449, 1366, 1228, 1018, 968, 898, 751, 725 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{44}$H$_{32}$O$_4$Na [M+Na]$^+$: calcd 647.2193, found 647.2169.

Acetic acid {2-[acetoxy-(5-chloro-thien-2-yl)-methyl]-phenyl}-(5-chloro-thien-2-yl)
-methyl ester (2r). Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 5.84:1 as a yellow sticky liquid in 92% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 2.03 (s), 2.06 (s), 6.40 (dd, $J = 3.9$, 0.6 Hz), 6.56 (dd, $J = 3.9$, 0.9 Hz), 6.61 (d, $J = 3.9$ Hz), 6.69 (d, $J = 3.6$ Hz), 7.14 (d, $J = 0.6$ Hz), 7.20 (s), 7.39-7.45 (m), 7.54-7.63 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): major isomer: $\delta$ 20.9, 69.5, 125.6, 126.6, 127.4, 128.9, 131.0, 136.2, 140.6, 169.4; minor isomer: 20.8, 69.2, 125.4, 126.6, 128.7, 131.2, 136.1, 141.1, 169.5; IR (neat): 3065, 2930, 2847, 1744, 1489, 1448, 1370, 1226, 1063, 1018, 998, 966, 925, 795, 746 cm$^{-1}$; HRMS (ESI) for C$_{20}$H$_{16}$O$_4$S$_2$Cl$_2$Na [M+Na]$^+$: calcd 476.9759, found 476.9752.

Benzo[b]thiophen-3-yl-[2-(benzo[b]thiophen-3-yl-hydroxy-methyl)-phenyl]-methanol (1s). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=4:1) afforded the title compound as one of the two diastereomers in 41 % yield. $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 4.14 (br, 2H), 6.41 (s, 2H), 7.06 (s, 4H), 7.18-7.33 (m, 8H), 7.90 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 67.9, 122.2, 122.6, 123.8, 124.17, 124.2, 127.6, 128.4, 136.9, 136.9, 139.6, 140.6. HRMS (EI) for C$_{24}$H$_{16}$O$_5$S$_2$ [M-H$_2$O]$^+$: calcd 384.0643, found 384.0633.
Acetic acid [2-(acetoxy-benzo[b]thiophen-3-yl-methyl)-phenyl]-benzo[b]thiophen-3-yl-methyl ester (2s). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as one of the two diastereomers as a sticky colorless liquid in 88% yield (one step from 1s). $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 1.98 (s, 6H), 7.01 (s, 2H), 7.20-7.25 (m, 4H), 7.40-7.47 (m, 4H), 7.55 (s, 2H), 7.59-7.62 (m, 2H), 7.70-7.73 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 20.7, 68.6, 121.9, 122.6, 124.3, 124.5, 127.0, 127.8, 128.6, 133.9, 136.6, 137.1, 140.4, 169.9. HRMS (MALDI/DHB) for C$_{28}$H$_{22}$O$_4$S$_2$Na [M+Na]$^+$: calcd 509.0852, found 509.0847.

Acetic acid [2-(acetoxy-thien-2-yl-methyl)-4,5-dimethyl-phenyl]-thien-2-yl-methyl ester (2t). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 4.23:1 as a brown sticky liquid in 93% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 1.97 (s), 2.03 (s), 2.27 (s), 2.29 (s), 6.66-6.89 (m), 7.18-7.36 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: $\delta$ 19.6, 20.8, 20.9, 69.6, 69.7, 125.9, 126.4, 126.5, 126.7, 128.6, 129.1, 134.2, 134.3, 137.2, 142.6, 143.2, 169.5, 169.6; IR (neat): 3103, 3072, 3009, 2970, 2938, 2916, 2856, 1710, 1692, 1607, 1559, 1482, 1446, 1411, 1370, 1292, 1226, 1021, 890, 832, 700 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{22}$H$_{22}$O$_4$Na [M+Na]$^+$: calcd
Acetic acid \((3\text{-}[\text{acetoxy-(5-chloro-thien-2-yl)-methyl}]\text{-naphthalen-2-yl})\text{-} (5\text{-chloro-thien-2-yl})\text{-methyl ester (2v).}\) Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 4.59:1 as a yellow sticky liquid in 93% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 2.06 (s), 2.10 (s), 6.45 (dd, \(J = 3.6, 0.9\) Hz), 6.58 (dd, \(J = 3.9, 0.9\) Hz), 6.62 (d, \(J = 3.6\) Hz), 6.68 (d, \(J = 3.9\) Hz), 7.22 (d, \(J = 1.2\) Hz), 7.30 (s), 7.51-7.55 (m), 7.87-7.90 (m), 8.06 (s), 8.09 (s); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si): two isomers: \(\delta\) 20.8, 20.9, 125.5, 125.7, 126.8, 126.9, 127.0, 127.1, 127.5, 127.3, 131.3, 132.7, 133.7, 133.8, 140.7, 141.2, 169.4, 169.6; IR (neat): 3058, 2933, 1745, 1599, 1541, 1502, 1466, 1370, 1227, 1062, 1018, 997, 959, 902, 799, 748 cm\(^{-1}\); HRMS (MALDI/DHB) for C\(_{24}\)H\(_{18}\)O\(_4\)S\(_2\)Cl\(_2\)Na [M+Na]\(^+\): calcd 526.9916, found 526.9932.

Acetic acid \((3\text{-}[\text{acetoxy-benzo[b]thien-3-yl-methyl}]\text{-naphthalen-2-yl})\text{-} (benzo[b])text{-thien-3-yl-methyl ester (2w).}\) Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 4.70:1 as a sticky brown liquid in 63% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 1.88 (s), 2.05 (s),
6.94-7.33 (m), 7.44-7.53 (m), 7.56-7.72 (m), 7.78-8.10 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 20.6, 20.8, 68.6, 69.1, 122.1, 122.6, 122.7, 124.4, 124.5, 124.6, 126.3, 126.8, 127.4, 127.6, 127.9, 132.7, 133.7, 134.0, 134.4, 134.6, 137.0, 137.2, 140.3, 140.4, 169.7, 169.9; IR (neat): 3058, 1742, 1712, 1459, 1429, 1368, 1227, 1018, 962, 906, 757, 732 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{32}$H$_{24}$O$_4$S$_2$Na [M+Na]$^+$: calcd 559.1008, found 559.0995.

A typical procedure for the preparation of diester 2q.

The diol was prepared analogously to the procedure described for 2f.

To a solution of the above residue in dry CH$_2$Cl$_2$ were added triethylamine (100 mmol, 16.7 ml), PivCl (20 mmol, 2.47 ml) and catalytic amount of DMAP, the resulting solution was stirred at refluxing temperature for 30 min before being diluted with hexanes. The solid precipitates were filtered off and the filtrate obtained was concentrated. The residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate = 40:1) to yield the desired ester.

2,2-Dimethyl-propionic acid \{2-[(2,2-dimethyl-propionyloxy)-thien-2-yl-methyl]-phenyl]-thien-2-yl-methyl ester (2q).\] Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=40:1) afforded two diastereomers with a ratio of 2.18:1 as a light yellow sticky liquid in 95% yield.

$^1$H NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 1.16 (s), 1.19 (s), 6.51 (d, $J = 3.6$ Hz ), 6.72-6.74 (m), 6.80 (t, $J = 3.6$ Hz ), 6.86-6.89 (m), 7.15 (dd, $J = 5.1, 1.5$ Hz), 7.23 (dd, $J = 5.4, 1.2$ Hz), 7.32 (s), 7.38-7.42 (m), 7.57-7.64 (m); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two isomers: δ 26.9, 38.7, 68.9, 69.2, 125.9, 126.2, 126.6, 126.8, 126.9, 127.2, 128.5,
137.2, 137.3, 142.8, 143.2, 176.6, 176.7; IR (neat): 3104, 3059, 2963, 1697, 1482,
1406, 1373, 1258, 1219, 1199, 1149, 1084, 999, 852, 829, 793, 739, 700, 681
cm\(^{-1}\); HRMS (MALDI/DHB) for C\(_{26}\)H\(_{30}\)O\(_4\)S\(_2\)Na [M+Na]\(^+\): calcd 493.1478, found 493.1476.

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\text{PivO} \\
\text{S} \\
\text{PivO} \\
\text{2u}
\end{array}
\]

2,2-Dimethyl-propionic acid \{3-[(2,2-dimethyl-propionyloxy)-thien-2-yl-methyl]-
naphthalen-2-yl]-thien-2-yl-methyl ester (2u). Purification of the crude product by
flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=40:1)
afforded two diastereomers with a ratio of 1.6:1 as a light yellow sticky liquid in 72%
yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 1.19 (s), 1.21 (s), 6.58 (d, \(J = 3.6\) Hz ),
6.75 (dd, \(J = 5.1, 3.6\) Hz ), 6.82 (d, \(J = 3.3\) Hz ), 6.89 (dd, \(J = 5.1, 3.6\) Hz ), 7.18 (dd, \(J =
5.1, 1.2\) Hz ), 7.26-7.28 (m), 7.34 (s), 7.46 (s), 7.51-7.54 (m), 7.86-7.89 (m), 8.07 (s),
8.09 (s); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \(\delta\) 26.94, 26.98, 38.8, 69.3, 126.2,
126.3, 126.7, 126.7, 126.8, 127.1, 127.2, 127.5, 127.9, 132.8, 132.9, 135.2, 135.4,
142.7, 143.3, 176.7, 176.9; IR (neat): 3105, 3058, 2973, 2933, 2907, 2872, 1733,
1478, 1460, 1396, 1366, 1275, 1233, 1139, 1074, 1031, 898, 836, 705 cm\(^{-1}\); HRMS
(MALDI/DHB) for C\(_{30}\)H\(_{32}\)O\(_4\)S\(_2\)Na [M+Na]\(^+\): calcd 543.1634, found 543.1636.

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\begin{array}{c}
\text{3a}
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9-Phenylanthracene (3a) \(^4\) \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 7.31-7.36 (m, 2H), 7.41-7.47
(m, 4H), 7.52-7.60 (m, 3H), 7.66 (d, \(J = 8.4\) Hz, 2H), 8.03 (d, \(J = 8.4\) Hz, 2H), 8.49 (s,
1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 125.1, 125.3, 126.5, 126.8, 127.4, 128.3, 128.3,
130.1, 131.2, 131.3, 136.9, 138.7.
1,3-Diphenyl-1,3-dihydroisobenzofuran (4a).\(^9\) (Table 1, entry 1). \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \( \delta \) 6.20 (s), 6.44 (s), 7.00-7.03 (m), 7.10-7.13 (m), 7.22-7.44 (m); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si) two isomers: \( \delta \) 85.5, 85.9, 122.1, 122.3, 126.9, 127.8, 127.9, 128.0, 128.2, 128.5, 128.6, 141.2, 141.7, 142.1, 142.5.

2-Methyl-9-\(p\)-tolylanthracene (3b). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 83% yield as a sticky liquid (anthracene:phthalan derivative =96:4). \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): \( \delta \) 2.39 (s, 3H), 2.60 (s, 3H), 7.25-7.43 (m, 8H), 7.63 (d, \( J = 8.4 \text{ Hz}, 1 \text{H} \)), 7.91 (d, \( J = 8.4 \text{ Hz}, 1 \text{H} \)), 7.97(d, \( J = 8.1 \text{Hz}, 1 \text{H} \)), 8.39 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si): \( \delta \) 21.4, 22.2, 124.6, 124.9, 125.1, 126.1, 126.8, 127.9, 128.2, 128.3, 129.0, 129.9, 130.5, 130.8, 131.1, 134.8, 135.8, 136.0, 136.9; IR (neat): 3028, 2918, 2852, 1739, 1714, 1632, 1571, 1514, 1450, 1415, 1365, 1219, 1022, 883, 817, 744 cm\(^{-1}\); HRMS (EI) for C\(_{22}\)H\(_{18}\) [M]\(^+\): calcd 282.1409, found 282.1404.
2-Methoxy-9-(4-methoxyphenyl)anthracene (3c). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 74% yield as a yellow green solid (anthracene:phthalan derivative =99:1). M.p. 163-165 °C (lit. 175-176 °C); $^1$H NMR (CDCl$_3$, Me$_4$Si): δ 3.71 (s, 3H), 3.93 (s, 3H), 6.87 (d, $J$ = 2.1 Hz, 1H), 7.09-7.16 (m, 3H), 7.32-7.39 (m, 4H), 7.63 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 8.7 Hz, 1H), 7.99(d, $J$ = 8.4 Hz, 1H), 8.38 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): δ 55.0, 55.3, 102.6, 113.9, 120.0, 124.1, 125.4, 126.3, 126.4, 127.9, 128.4, 129.9, 130.0, 130.9, 131.1, 131.5, 132.2, 134.6, 156.9, 158.8; IR (neat): 3005, 2955, 2930, 2903, 2832, 1629, 1609, 1575, 1512, 1483, 1464, 1435, 1415, 1367, 1348, 1264, 1268, 1227, 1176, 1207, 889, 857, 836, 809, 785, 753 cm$^{-1}$; HRMS (EI) for C$_{22}$H$_{18}$O$_2$: calcd 314.1307, found 314.1305; Anal. Calcd. for C$_{22}$H$_{18}$O$_2$: C, 84.05, H, 5.77; Found: C, 84.32; H, 5.86.

2-tert-Butyl-9-(4-tert-butylphenyl)anthracene (3d). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 83% yield as a yellow solid (anthracene:phthalan derivative =94:6). $^1$H NMR (CDCl$_3$, Me$_4$Si): δ 1.27 (s, 9H), 1.45 (s, 9H), 7.29-7.39 (m, 4H), 7.51-7.59 (m, 4H), 7.71 (d, $J$ = 9.0 Hz, 1H), 7.96 (t, $J$ = 9.0 Hz, 2H), 8.39 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): δ 30.8, 31.5, 34.7, 35.0, 121.1,
124.6, 124.9, 125.0, 125.7, 126.9, 127.9, 128.3, 129.9, 130.3, 130.4, 130.9, 131.1, 135.7, 136.9, 147.4, 150.1; IR (neat): 3052, 3032, 2962, 2903, 2867, 1765, 1742, 1715, 1628, 1511, 1477, 1460, 1415, 1393, 1362, 1268, 1202, 1107, 1022, 936, 909, 888, 821, 742 cm⁻¹; HRMS (EI) for C₂₈H₃₀: calcd 366.2348, found 366.2346; Anal. Calcd. for C₂₈H₃₀: C, 91.75, H, 8.25; Found: C, 91.76; H, 8.07.

1-Methyl-10-o-tolylanthracene (3e). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product (60 mg, 99% yield) as a yellow solid (anthracene:phthalan derivative =95:5). ¹H NMR (CDCl₃, Me₄Si): δ 1.84 (s, 3H), 2.84 (s, 3H), 7.11-7.49 (m, 10H), 8.07 (d, J = 8.7 Hz, 1H), 8.61 (s, 1H); ¹³C NMR (CDCl₃, Me₄Si): δ 19.7, 19.9, 122.8, 124.9, 125.1, 125.2, 125.45, 125.48, 125.8, 126.3, 127.7, 128.8, 129.6, 129.9, 130.0, 131.0, 131.1, 131.2, 134.3, 136.8, 137.7, 138.5; IR (neat): 3055, 3015, 2922, 2852, 1739, 1622, 1456, 1377, 1333, 1236, 1033, 1015, 877, 846, 809, 749, 734 cm⁻¹; HRMS (EI) for C₂₂H₁₈ [M]⁺: calcd 282.1409, found 282.1410.

9-(3,5-Dimethylphenyl)-1,3-dimethylanthracene (3f). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 84% yield as a yellow green sticky liquid (anthracene:phthalan derivative >99:1). ¹H NMR (CDCl₃, Me₄Si): δ 2.03 (s,
3H), 2.36 (s, 6H), 2.42 (s, 3H), 6.99 (s, 2H), 7.01 (s, 1H), 7.08 (s, 1H), 7.15-7.25 (m, 1H), 7.33-7.38 (m, 1H), 7.48 (d, J = 8.7 Hz, 1H), 7.61 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.30 (s, 1H); 13C NMR (CDCl₃, Me₄Si) : δ 21.3, 25.4, 124.6, 124.9, 126.2, 126.7, 127.4, 127.6, 128.0, 128.6, 129.3, 130.7, 131.2, 131.9, 133.1, 133.9, 135.6, 136.6, 137.1, 142.1; IR (neat): 3024, 2967, 2915, 2860, 1714, 1632, 1599, 1560, 1460, 1382, 1363, 1257, 1219, 1066. 1031, 897, 873, 839, 796, 737, 713 cm⁻¹; HRMS (EI) for C₂₄H₂₂ [M]⁺: calcd 310.1722, found 310.1721.

2,3,7-Trimethyl-9-p-tolylanthracene (3g).⁶ Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 84% yield as a yellow green solid (anthracene:phthalan derivative =93:7). ¹H NMR (CDCl₃, Me₄Si): δ 2.31 (s, 3H), 2.38 (s, 3H), 2.42 (s, 3H), 2.52 (s, 3H), 7.21-7.37 (m, 7H), 7.73 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 8.27 (s, 1H); ¹³C NMR (CDCl₃, Me₄Si) : δ 20.2, 20.6, 21.4, 22.2, 124.7, 124.8, 125.5, 127.1, 127.3, 128.1, 129.0, 129.2, 129.6, 129.8, 130.1, 130.3, 131.1, 134.2, 134.7, 135.3, 136.1, 136.7; IR (neat): 3017, 2919, 2859, 1740, 1715, 1661, 1626, 1608, 1513, 1449, 1351, 1299, 1238, 1179, 1110, 1018, 891, 817 cm⁻¹; HRMS (EI) for C₂₄H₂₂ [M]⁺: calcd 310.1722, found 310.1729.
9-(Biphenyl-4-yl)-2-phenylanthracene (3h). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 86% yield as a yellow solid (anthracene:phthalan derivative = 89:11). \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 7.25-7.58 (m, 12H), 7.69-7.79 (m, 6H), 7.94 (s, 1H), 8.00 (d, \(J = 8.4\) Hz, 1H), 8.07 (d, \(J = 9.0\) Hz, 1H), 8.46 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si): \(\delta\) 124.4, 125.2, 125.3, 125.5, 126.4, 126.8, 127.0, 127.1, 127.3, 127.4, 127.4, 128.4, 128.8, 128.9, 129.0, 130.3, 130.5, 130.6, 131.4, 131.7, 136.9, 137.6, 137.8, 140.1, 140.7, 141.2; IR (neat): 3053, 5029, 1713, 1599, 1487, 1453, 1414, 1351, 1219, 1007, 889, 830, 762, 744, 697 cm\(^{-1}\); HRMS (EI) for C\(_{32}\)H\(_{22}\): calcd 406.1722, found 406.1722.

7-tert-Butyl-9-(4-tert-butylphenyl)-2,3-dimethylantracene (3i) and 1,3-Bis(4-tert-butylphenyl)-5,6-dimethyl-1,3-dihydroisobenzofuran (4i).

Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded 3i and 4i in 87% yield with a ratio of 76:34 as a yellow sticky liquid. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) two compounds: \(\delta\) 1.26 (s), 1.30 (s), 1.31 (s), 1.46 (s), 2.19 (s), 2.20 (s), 2.32 (s), 2.42 (s), 6.11 (s), 6.34
(s), 6.81 (s), 6.90 (s), 7.19-7.58 (m), 7.73 (s), 7.90 (s), 7.92 (s), 8.26 (s); $^{13}$C NMR (CDCl$_3$, Me$_4$Si) two compounds: δ 19.89, 19.95, 20.2, 20.7, 30.8, 31.4, 31.5, 34.5, 34.6, 34.7, 34.9, 85.2, 85.5, 120.8, 120.9, 123.0, 123.1, 124.0, 124.4, 124.9, 125.4, 125.5, 125.6, 126.3, 126.7, 127.2, 127.6, 127.8, 129.6, 129.7, 129.9, 130.6, 130.9, 134.7, 135.1, 135.6, 135.9, 136.2, 136.3, 138.7, 139.5, 139.7, 140.4, 146.7, 149.8, 150.7, 150.9; IR (neat) two compounds: 3013, 2962, 2904, 2867, 1715, 1624, 1510, 1460, 1394, 1364, 1267, 1202, 1119, 1107, 1017, 908, 891, 830, 802, 734 cm$^{-1}$; HRMS (EI) for 3i C$_{30}$H$_{34}$ [M]$^+$: calcd 394.2661, found 394.2666; HRMS (MALDI/DHB) for 4i C$_{30}$H$_{36}$ONa [M+Na]$^+$: calcd 435.2658, found 435.2642 (The HRMS data for the individual components of the mixture of 3i and 4i could be obtained because the substances behaved differently under different mass spectroscopic ionization conditions).

7-Naphthalen-1-yl-benzo[a]anthracene (3j). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 99% yield as a yellow solid. M.p. 182-183 ºC (lit. 186 ºC); $^1$H NMR (CDCl$_3$, Me$_4$Si): δ 7.08-7.58 (m, 10H), 7.61-7.74 (m, 3H), 7.96 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 8.89 (d, $J = 8.1$ Hz, 1H), 9.31 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): δ 121.9, 123.0, 125.5, 125.6, 125.86, 125.9, 126.3, 126.5, 126.7, 126.9, 127.1, 127.2, 128.1, 128.2, 128.51, 128.55, 128.6, 129.0, 129.5, 130.5, 131.5, 131.6, 133.4, 133.6, 135.4, 136.6; IR (neat): 3055, 1712, 1504, 1354, 1250, 1221, 1143, 1016, 884, 824, 797, 777, 749 cm$^{-1}$; HRMS (EI) for C$_{28}$H$_{18}$ [M]$^+$: calcd 354.1409, found 354.1400.
12-Naphthalen-2-yl-benzo[a]anthracene (3k). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 99% yield as a white solid. M.p. 140-142 °C (lit7 153 °C); ¹H NMR (CDCl₃, Me₄Si): δ 6.88 (td, J = 8.4, 1.5 Hz, 1H), 7.26-7.33 (m, 2H), 7.43-7.57 (m, 7H), 7.67-7.79 (m, 3H), 7.84 (s 1H), 7.97-8.06 (m, 3H), 8.37 (s, 1H); ¹³C NMR (CDCl₃, Me₄Si): δ 125.50, 125.56, 125.6, 126.2, 126.3, 126.4, 127.0, 127.1, 127.57, 127.62, 127.8, 127.9, 128.1, 128.2, 128.5, 128.7, 128.9, 129.1, 129.2, 131.1, 131.3, 131.4, 132.4, 132.7, 133.7, 134.0, 137.0, 139.9; IR (neat): 3051, 2925, 1712, 1628, 1597, 1491, 1358, 1299, 1241, 1142, 1026, 889, 765, 747 cm⁻¹; HRMS (EI) for C₂₈H₁₈ [M]⁺: calcd 354.1409, found 354.1415; Calcd. for C₂₈H₁₈: C, 94.88, H, 5.12; Found: C, 94.72; H, 5.36.

9,10-Dimethyl-7-(naphthalen-1-yl)benzo[a]anthracene (3m) Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) to afforded the desired product in 93% yield as a yellow solid. M.p. 94-96 °C; ¹H NMR (CDCl₃, Me₄Si): δ 2.26 (s, 3H), 2.50 (s, 3H), 7.22-7.63 (m, 8H), 7.72-7.80 (m, 3H), 7.99-8.11 (m, 3H), 8.94 (d, J = 7.5 Hz, 1H), 9.27 (s, 1H); ¹³C NMR (CDCl₃, Me₄Si): δ 20.3, 20.5, 120.7, 122.9, 125.6, 125.7, 125.9, 126.2, 126.5, 126.6, 126.75, 126.82, 127.8, 127.9, 128.2, 128.4, 128.9, 130.6, 130.7, 130.8,
7-(Naphthalen-1-yl)benzo[a]naphthacene (3n) Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 95% yield as a yellow solid. M.p. 124-126 °C; $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 7.13-7.86 (m, 13H), 8.01-8.13 (m, 4H), 8.83 (s, 1H), 8.93 (d, $J = 7.8$ Hz, 1H), 9.51 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 122.1, 123.1, 125.1, 125.4, 125.5, 125.7, 125.8, 126.0, 126.3, 126.5, 126.9, 127.1, 127.2, 127.4, 127.9, 128.2, 128.4, 128.50, 128.54, 129.2, 129.3, 129.9, 130.3, 130.6, 131.3, 131.6, 133.5, 133.7, 135.1, 136.7; IR (neat): 3052, 2948, 2904, 1712, 1592, 1505, 1435, 1360, 1221, 1156, 1089, 1015, 896, 821, 802, 782, 752 cm$^{-1}$; HRMS (EI) for C$_{30}$H$_{22}$ [M]$^+$: calcd 382.1722, found 382.1719.

14-Naphthalen-2-yl-benzo[a]naphthacene (3o) Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 83% yield as a yellow solid. M.p. 112-114 °C; $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 6.86 (t, $J = 7.8$ Hz, 1H), 7.25-7.70 (m, 11H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.89 (s, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 8.11 (d, $J =
8.4 Hz, 2H), 8.47 (s, 1H), 8.56 (s, 1H); 13C NMR (CDCl3, Me4Si): δ 124.9, 125.6, 125.6, 126.2, 126.4, 126.6, 126.8, 127.4, 127.6, 127.8, 128.0, 128.30, 128.31, 128.4, 128.9, 129.1, 129.19, 129.22, 129.3, 129.8, 131.2, 131.2, 131.35, 131.39, 132.8, 133.8, 134.2, 136.9, 139.9; IR (neat): 3051, 2924, 2853, 1712, 1628, 1597, 1501, 1452, 1432, 1359, 1220, 897, 859, 822, 805, 741 cm⁻¹; HRMS (EI) for C32H20 [M]+: calcd 404.1565, found 404.1570.

9-Phenanthren-9-yl-dibenzo[a,c]naphthacene (3p). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 97% yield as a yellow solid. M.p. 182-185°C; 1H NMR (CDCl3, Me4Si): δ 6.65 (t, J = 8.4 Hz, 1H), 7.19-7.77 (m, 14H), 7.86 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 8.69 (s, 1H), 8.77 (d, J = 7.8 Hz, 1H), 8.89 (t, J = 8.1 Hz, 2H), 9.36 (s, 1H); 13C NMR (CDCl3, Me4Si): δ 122.7, 122.9, 123.1, 123.2, 123.3, 124.1, 125.1, 125.7, 126.1, 126.4, 126.6, 126.9, 126.9, 127.1, 127.3, 127.55, 127.58, 127.7, 127.9, 128.3, 128.8, 128.9, 129.2, 129.9, 130.1, 130.3, 130.5, 130.7, 130.8, 131.5, 131.6, 131.7, 131.7, 132.3, 132.7, 134.8, 139.1; IR (neat): 3060, 2957, 2925, 2854, 1711, 1601, 1493, 1447, 1358, 1220, 896, 752, 724 cm⁻¹; HRMS (MALDI/DHB) for C40H25 [M+H]+: calcd 505.1951, found 505.1932.
**4-Thien-2-yl-naphtho[2,3-b]thiophene (5a).** Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/CHCl$_3$=3:1) afforded the desired product in 83% yield as a sticky liquid. $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 7.19-7.29 (m, 3H), 7.38-7.48 (m,3H), 7.52 (dd, $J$ = 4.8, 1.2 Hz, 1H), 7.90 (d, $J$ = 8.4 Hz, 1H), 8.00 (d, $J$ = 48.1 Hz, 1H), 8.38 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 121.5, 123.7, 125.2, 125.4, 126.2, 126.3, 126.4, 127.1, 127.5, 128.3, 128.7, 130.3, 130.9, 137.5, 138.9, 139.5; IR (neat): 3103, 3068, 1711, 1503, 1482, 1437, 1404, 1373, 1353, 1322, 1258, 1219, 1168, 1150, 1112, 1085, 1039, 1023, 999, 874, 852, 828, 819, 793, 779, 738, 700, 680 cm$^{-1}$; HRMS (EI) for C$_{16}$H$_{10}$S$_2$: calcd 266.0222, found 266.0224.

**6-Benzob[b]thiophen-3-yl-benzo[b]naphtho[2,3-d]thiophene (5c).** Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) afforded the desired product in 79% yield as a yellow solid. M.p.191-193°C; $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 7.21 (s, 1H), 7.23 (s, 1H), 7.35-7.52 (m, 5H), 7.61-7.69 (m, 3H), 8.00 (d, $J$ = 7.8 Hz, 1H), 8.09 (d, $J$ = 8.1 Hz, 1H), 8.26-8.28 (m, 1H), 8.68 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 120.3, 121.9, 122.7, 122.8, 123.4, 124.3, 124.5, 124.7, 125.11, 125.14, 126.1, 126.6, 127.7, 128.7, 131.3, 131.5, 134.2, 134.7, 135.4, 138.3, 139.9, 140.21, 140.23; IR (neat): 3060, 2955, 2923, 1712, 1588, 1490, 1451, 1428, 1360, 1313, 1251, 1219, 1156, 1066, 1020, 954, 881, 851, 779, 758, 731 cm$^{-1}$; HRMS (EI) for C$_{24}$H$_{14}$: calcd 366.0537, found 366.0537.
6,7-Dimethyl-4-thien-2-yl-naphtho[2,3-b]thiophene (5d). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 88% yield as a white solid. M.p. 122-123 °C; \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): δ 2.34 (s, 3H), 2.39 (s, 3H), 7.16-7.24 (m, 3H), 7.33 (d, \(J = 5.4\) Hz, 1H), 7.50 (d, \(J = 5.4\) Hz, 1H), 7.60 (s, 1H), 7.72 (s, 1H), 8.22 (s, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si): δ 20.1, 20.5, 120.4, 123.7, 125.1, 126.2, 126.6, 127.1, 127.41, 128.5, 129.4, 130.2, 135.2, 135.4, 136.6, 138.8, 139.4; IR (neat): 3102, 3079, 3004, 2967, 2915, 1713, 1480, 1407, 1372, 1353, 1222, 1107, 1084, 1025, 1004, 887, 832, 698, 681 cm\(^{-1}\); HRMS (EI) for C\(_{18}\)H\(_{14}\)S\(_2\) [M]+: calcd 294.0537, found 294.0543.

4-Thien-2-yl-anthra[2,3-b]thiophene (5e). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/CHCl\(_3\)=3:1) afforded the desired product in 79% yield as a yellow solid. M.p. 120-122 °C; \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si): δ 7.25-7.30 (m, 3H), 7.32-7.41 (m, 3H), 7.57 (dd, \(J = 4.8\) Hz, \(J = 1.2\) Hz, 1H), 7.87 (d, \(J = 7.8\) Hz, 1H), 7.93 (d, \(J = 7.8\) Hz, 1H), 8.44 (s, 1H), 8.49 (s, 1H), 8.59 (s, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si): δ 121.4, 123.6, 125.0, 125.1, 125.4, 125.9, 126.5, 127.2, 127.8, 128.6, 128.9, 129.2, 129.5, 131.1, 131.2, 137.2, 139.2, 139.5; IR (neat): 3081, 3050, 2970, 1738, 1708, 1431, 1363, 1287, 1229, 1198, 1139, 1080, 995, 889, 828, 741, 699, 665 cm\(^{-1}\); HRMS (EI) for C\(_{20}\)H\(_{12}\)S\(_2\) [M]+: calcd 316.0380, found 316.0384.
2-Chloro-4-(5-chloro-thien-2-yl)-anthra[2,3-b]thiophene (5f). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the desired product in 87% yield as a yellow solid. M.p. 115-117°C; $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 6.97 (dd, $J$ = 3.9, 0.9 Hz, 1H), 7.09-7.12 (m, 2H), 7.36-7.43 (m, 2H), 7.87-7.93 (m, 2H), 8.24 (s, 1H), 8.35 (s, 1H), 8.52 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 121.2, 122.0, 123.9, 124.6, 125.5, 125.6, 125.7, 126.5, 127.8, 128.4, 128.5, 129.1, 129.1, 130.9, 131.2, 131.5, 134.8, 136.2, 137.3, 138.5; IR (neat): 3051, 2924, 1713, 1512, 1450, 1394, 1359, 1333, 1295, 1217, 1061, 992, 888, 800, 739 cm$^{-1}$; HRMS (EI) for C$_{20}$H$_{10}$Cl$_2$S$_2$: calcd 383.9601, found 383.9595.

12-Benzothienyl3-yl-13-thia-indeno[1,2-b]anthracene (5g). Purification of the crude product by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1) and then recrystallization afforded the desired product in 56% yield as a yellow solid. M.p. 149-151°C; $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta$ 7.18-7.26 (m, 2H), 7.34-7.48 (m, 5H), 7.63-7.78 (m, 3H), 8.04 (t, $J$ = 8.4 Hz, 2H), 8.19 (s, 1H), 8.26-8.29 (m, 1H), 8.70 (s, 1H), 8.83 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta$ 120.3, 122.1, 122.7, 122.9, 123.4, 123.5, 124.3, 124.7, 124.8, 125.3, 125.5, 125.9, 126.8, 127.2, 127.9, 128.2, 128.5, 129.9, 130.1, 130.9, 131.8, 134.4, 134.9, 135.3, 138.4, 139.7, 140.3; IR (neat): 3054, 1710, 1607, 1582, 1451, 1430, 1358, 1328, 1287, 1252, 1219, 1098, 893, 743 cm$^{-1}$; HRMS (MALDI/DHB) for C$_{28}$H$_{17}$S$_2$ [M+H]$^+$: calcd 417.0766, found 417.0758.
Formation of anthracenes from diol 1b.

To a solution of 1,2-phenylenebis(p-tolylmethanol) 1b (0.4 mmol, 127 mg) in ClCH₂CH₂Cl (4 mL) was added TfOH (0.04 mmol, 3.6 µL). The reaction mixture was stirred for 3 h at 80 °C. After the reaction mixture was cooled down to room temperature, an appropriate amount of silica gel was added to the mixture and the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (eluent: chloroform) to afford a mixture of anthracene 3b and one isomer (the structure of which was unknown, it was suggested to be an alkyl-group migration product derived from 3b) with a ratio of 1:1 as a sticky liquid in 94% combined yield.

¹H NMR (CDCl₃, Me₄Si) containing a mixture of 3b and one unknown isomer: δ 2.36 (s), 2.45 (s), 2.47 (s), 2.07 (s), 7.09-7.11 (m), 7.21-7.43 (m), 7.57-7.68 (m), 7.85-7.95 (m), 8.27 (s), 8.35 (s). ¹³C NMR (CDCl₃, Me₄Si) containing a mixture of 3b and one unknown isomer: δ 21.35, 21.37, 21.7, 22.2, 124.6, 124.8, 124.90, 124.93, 125.1, 125.3, 126.1, 126.5, 126.7, 126.8, 126.9, 127.9, 128.1, 128.2, 128.3, 128.90, 128.99, 129.0, 129.8, 129.9, 130.5, 130.8, 131.1, 131.1, 131.5, 131.6, 134.5, 134.8, 135.7, 135.8, 135.9, 136.8, 136.9, 136.9.

References:


Figure 1. The X-ray Crystal Structure of Compound 3c (structure of one of the two crystallographically independent 3c).

Figure 2. The X-ray Crystal Structure of Compound 5c.