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Supporting Information

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SET-Induced Oxidative Cross-Coupling of Arenes Leading to Biaryls by Use of Organoiodine(III) Oxidants

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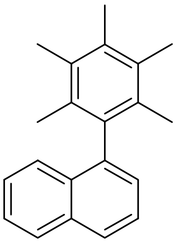
General Information ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-300 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad singlet, m = multiplet), coupling constant (Hz), interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses and high resolution mass spectra were performed by the Elemental Analysis Section of Osaka University. Column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh)).

Materials Phenyliodine bis(trifluoroacetate) (PIFA) was prepared from commercial phenyliodine diacetate (PIDA) and trifluoroacetic acid.$^{1)}$ Absolute dichloromethane, $BF_3 \cdot Et_2O$ and arenes (**1a**,**b**, **1e**-**j**, **2a-c**) are commercially available and used as received. Other 2-Bromo-7-methylnaphthalene (**1c**) and 2-Bromo-6-methylnaphthalene (**1d**) were prepared from corresponding naphthalenediols according to the literature.$^{2)}$ 2,4,6-trimethylbiphenyl (**2d**) was obtained from commercially available 2-Bromomesitylene and Phenyl boronic acid by the known method.$^{3)}$

Typical Experimantal Procedure for Large-Scale Preparation

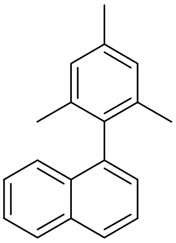
To a stirred solution of **1b** (1.04 g, 5 mmol) and nucleophile **2b** (1.80 g, 15 mmol, 3 equiv.) in CH_2Cl_2 (0.1 M of **1b**) was added successively $BF_3 \cdot Et_2O$ (1.27 mL, 10 mmol, 2 equiv.) and PIFA (2.15 g, 5 mmol, 1 equiv.) under nitrogen atmosphere at -78 ^oC. The reaction mixture was stirred at -78 ^oC for 3 h, then quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was analyzed by GC to confirm the absence of homodimers of **1b** and **2b**, and then it was dried over solid Na_2SO_4. After removal of the solvent *in vacuo*, the residue was subjected to column chromatography on silica gel with *n*-hexane as an eluent to give the cross-coupling biaryl **3bb**.

1-(Pentamethylphenyl)naphthalene (3aa)$^{4)}$



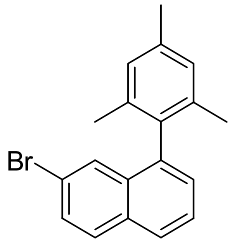
Colorless crystals; m.p. 119-121 ^oC; ^1H NMR (270MHz, $CDCl_3$): δ = 1.80 (s, 6H), 2.28 (s, 6H), 2.35 (s, 3H), 7.23 (d, J = 9.0 Hz, 1H), 7.31-7.34 (m, 2H), 7.42-7.55 (m, 2H), 7.84 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 16.7, 17.0, 18.2, 125.6, 125.7, 125.9, 126.7, 126.8, 128.0, 132.2, 132.3, 132.3, 133.5, 134.0, 137.1, 140.7 ppm; IR (KBr): 3043, 2995, 2923, 1506, 1456, 1388, 1016, 912, 79, 779, 740, 650 cm^{-1}.

1-(2,4,6-Trimethylphenyl)naphthalene (3ab)$^{5)}$



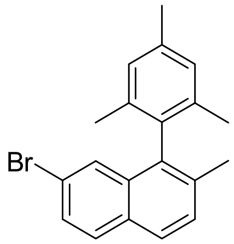
Colorless crystals; m.p. 72-75 ^oC; ^1H NMR (300MHz, $CDCl_3$): δ = 1.87 (s, 6H), 2.39 (s, 3H), 7.00 (s, 2H), 7.25 (d, J = 6.9 Hz, 1H), 7.34 (m, 2H), 7.45-7.55 (m, 2H) 7.83-7.90 (m, 2H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.3, 21.1, 125.5, 125.7, 126.0, 126.7, 127.1, 128.0, 128.2, 132.0, 133.7, 136.7, 136.8, 136.9, 138.8 ppm; IR (KBr): 2916, 1490, 1448, 1039, 850, 769, 748, 727 cm^{-1}.

7-Bromo-1-(2,4,6-trimethylphenyl)naphthalene (3bb)



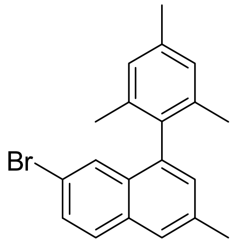
Colorless crystals; m.p. 129-131 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.86 (s, 6H), 2.39 (s, 3H), 7.01 (s, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.50-7.57 (m, 3H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.3, 21.1, 120.4, 126.2, 127.0, 127.5, 127.8, 128.2, 129.2, 130.0, 132.2, 133.2, 135.8, 136.7, 137.1, 138.2 ppm; IR (KBr): 3042, 2916, 1612, 1583, 1489, 1431, 1356, 1065, 970, 829, 752, 582 cm^{-1}; HRMS (FAB): calcd for $C_{19}H_{17}Br$ $[M - H]^+$: 324.0514, found 324.0534.

7-Bromo-2-methyl-1-(2,4,6-trimethylphenyl)naphthalene (3cb)



Colorless crystals; m.p. 118-120 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.77 (s, 6H), 2.10 (s, 3H), 2.39 (s, 3H), 7.01 (s, 2H), 7.36 (s, 1H), 7.44 (m, 2H), 7.71 (m, 2H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 19.8, 19.9, 21.2, 120.4, 126.8, 127.1, 128.2, 128.4, 129.2, 129.7, 130.6, 133.5, 134.5, 134.6, 136.0, 136.3, 136.9 ppm; IR (KBr): 3044, 2916, 2856, 2731, 1897, 1730, 1612, 1587, 1494, 1434, 1377, 1353, 1211, 1116, 1066, 1014, 921, 835, 734, 673, 584 cm^{-1}; HRMS (FAB): calcd for $C_{20}H_{19}Br$ $[M - H]^+$: 338.0670, found 338.0662.

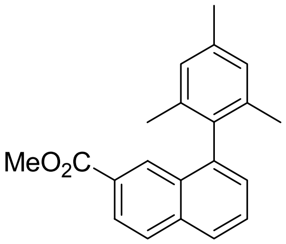
7-Bromo-3-methyl-1-(2,4,6-trimethylphenyl)naphthalene (3db)



Colorless crystals; m.p. 131-132 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.86 (s, 6H), 2.38 (s, 3H), 2.50 (s, 3H), 6.99 (s, 2H), 7.12 (d, *J* = 1.5 Hz, 1H), 7.44 (s, 1H), 7.48 (dd, *J* = 1.5, 8.4 Hz, 1H), 7.57 (s, 1H), 7.66 (d, *J* = 8.4Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.3, 21.1, 21.7, 119.3, 126.0, 127.3, 128.2, 129.2, 129.3, 129.3, 130.0, 131.5, 132.4, 135.8, 136.6, 137.0, 138.0 ppm; IR (KBr): 2918, 2858, 2732, 1903, 1764, 1591, 1479, 1444, 1365, 1315, 1234, 1122, 1068, 912, 742, 650, 596 cm^{-1}; HRMS (FAB): calcd for $C_{20}H_{19}Br$ $[M - H]^+$: 338.0670, found 338.0661.

8-(2,4,6-Trimethylphenyl)naphthalene-2-carboxylic acid methyl ester (3eb)

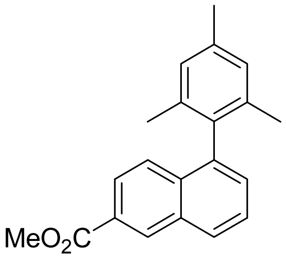
(*minor product*)



Colorless oil; ^{1}H NMR (270MHz, $CDCl_3$): δ = 1.85 (s, 6H), 2.40 (s, 3H), 3.87 (s, 3H), 7.00 (s, 2H), 7.31 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.63 (dd, *J* = 8.1, 9.3 Hz, 1H), 7.87 (d, *J* = 9.3 Hz, 1H), 7.93 (d, *J* = 9.6 Hz, 1H), 8.04 (dd, *J* = 1.8, 9.6 Hz, 1H), 8.10 (d, *J* = 1.2 Hz, 1H) ppm.

5-(2,4,6-Trimethylphenyl)naphthalene-2-carboxylic acid methyl ester (3eb')

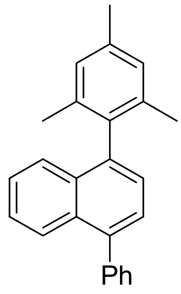
(*major product*)



Colorless oil; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.85 (s, 6H), 2.40 (s, 3H), 3.97 (s, 3H), 7.02 (s, 2H), 7.39 (m, 2H), 7.60 (t, *J* = 8.1, 1H), 7.91 (dd, *J* = 1.5, 9.0 Hz, 1H), 7.96 (d, 8.1 Hz, 1H), 8.67 (d, *J* = 1.5 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.3, 21.1, 52.2, 125.3, 125.8, 126.6, 127.3, 128.2, 128.5, 129.1, 131.5, 132.8, 134.1, 136.0, 136.7, 137.1, 138.9, 167.3 ppm; IR (KBr): 2949, 2916, 2854, 1722, 1614, 1433, 1332, 1274, 1236, 1193, 1114, 1093, 977, 850, 779, 742, 669 cm^{-1}.

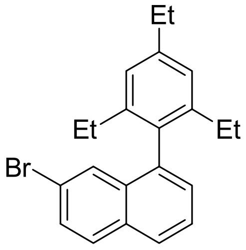
1-Phenyl-4-(2,4,6-trimethylphenyl)naphthalene (3fb)

The regioselectivity of **3fb** was determined by comparing the coupling product to an authentic sample, which was prepared from 1-bromo-4-phenylnaphthalene and mesitylboronic acid by Suzuki coupling.$^{6)}$



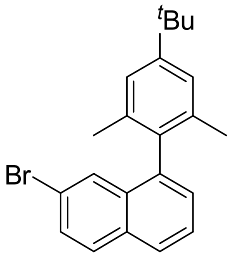
Colorless amorphous; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.93 (s, 6H), 2.40 (s, 3H), 7.03 (s, 2H), 7.29-7.59 (m, 10H), 7.97 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.4, 21.1, 125.7, 125.8, 125.8, 126.3, 126.4, 126.8, 127.1, 128.1, 128.2, 130.2, 131.8, 132.2, 136.8, 136.9, 137.0, 138.3, 139.3, 140.9 ppm; IR (KBr): 3022, 2916, 2731, 2245, 1951, 1886, 1822, 1728, 1610, 1492, 1442, 1384, 1157, 1029, 910, 848, 769, 734, 704, 646 cm^{-1}.

7-Bromo-1-(2,4,6-triethylphenyl)naphthalene (3bc)



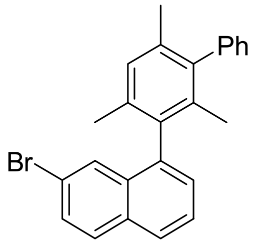
Colorless crystals; m.p. 77-79 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.8 Hz, 6H), 1.35 (t, *J* = 7.8 Hz, 3H), 2.05-2.22 (m, 4H), 2.74 (q, *J* = 7.8 Hz, 2H), 7.06 (s, 2H), 7.32 (dd, *J* = 1.2, 6.9 Hz, 1H), 7.50-7.55 (m, 3H), 7.75 (d, *J* = 9.6 Hz, 1H), 7.80 (d, *J* = 9.6 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 15.4, 15.6, 26.7, 28.8, 120.2, 125.3, 125.8, 127.0, 128.0, 128.5, 129.2, 129.9, 131.9, 134.0, 134.8, 137.6, 142.7, 143.8 ppm; IR (KBr): 3049, 2972, 2869, 1942, 1759, 1606, 1583, 1490, 1458, 1355, 1315, 1180, 1110, 1064, 964, 873, 829, 754, 582 cm^{-1}.

7-Bromo-1-(4-*tert*-butyl-2,6-dimethylphenyl)naphthalene (3bd)



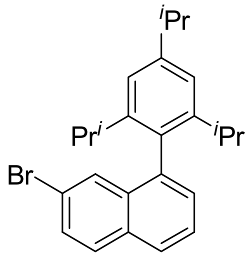
Colorless crystals; m.p. 147-149 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.40 (s, 9H), 1.89 (s, 6H), 7.18 (s, 2H), 7.29 (dd, *J* = 0.9, 7.2 Hz, 1H), 7.51-7.56 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.1, 31.5, 34.4, 120.3, 124.5, 126.2, 126.9, 127.5, 127.8, 129.2, 130.0, 132.2, 133.2, 135.8, 136.2, 138.4, 150.3 ppm; IR (KBr): 3043, 2962, 2866, 1608, 1583, 1487, 1355, 1303, 1263, 1224, 1180, 1141, 1105, 1064, 966, 883, 869, 829, 750, 646, 605, 584 cm^{-1}; HRMS (FAB): calcd for $C_{22}H_{23}Br$ $[M - H]^+$: 366.0983, found 366.0974.

7-Bromo-1-[2,4,6-trimethyl(biphenyl)-3-yl]naphthalene (3be)



Colorless crystals; m.p. 194-197 ^{o}C; ^{1}H NMR (300MHz, CDCl$_3$): δ = 1.59 (s, 3H), 1.92 (s, 3H), 2.13 (s, 3H), 7.15 (s, 1H), 7.22-7.46 (m, 6H), 7.560-7.63 (m, 3H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 18.6, 20.4, 20.9, 120.4, 126.2, 126.5, 127.0, 127.5, 127.9, 128.4, 128.4, 128.8, 129.2, 129.3, 129.5, 130.0, 132.2, 133.2, 134.8, 135.4, 135.6, 136.5, 138.6, 139.9, 141.4 ppm; IR (KBr): 3046, 2918, 2856, 2732, 2245, 1944, 1876, 1811, 1733, 1583, 1440, 1353, 1311, 1193, 1105, 1064, 948, 912, 829, 740, 704, 650, 596 cm^{-1}; HRMS (FAB): calcd for C$_{25}$H$_{21}$Br [M - H]$^{+}$: 400.0827 found 400.0800.

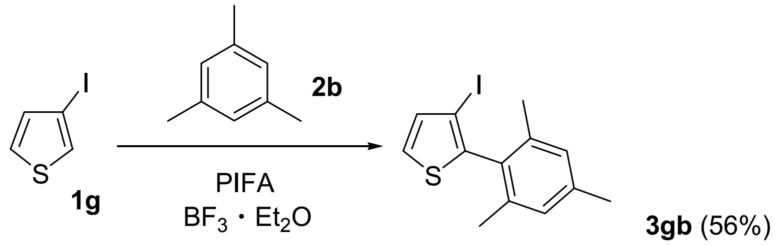
7-Bromo-1-(2,4,6-triisopropylphenyl)naphthalene (3bf)



Colorless crystals; m.p. 176-179 ^{o}C; ^{1}H NMR (300MHz, CDCl$_3$): δ = 0.97 (d, *J* = 6.9 Hz, 6H), 1.03 (d, *J* = 6.9 Hz, 6H), 1.36 (d, *J* = 6.9Hz, 6H), 2.29 (sep, *J* = 6.9Hz, 2H), 3.00 (sep, *J* = 6.9 Hz, 1H), 7.13 (s, 2H), 7.31 (dd, *J* = 1.2, 6.9 Hz, 1H), 7.49-7.56 (m, 3H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 23.9, 24.1, 24.7, 30.6, 34.3, 120.0, 120.9, 125.7, 126.9, 128.3, 128.4, 129.2, 129.8, 131.8, 133.4, 134.5, 138.0, 147.2, 148.5 ppm; IR (KBr): 3053, 2960, 2866, 1768, 1606, 1581, 1490, 1461, 1359, 1317, 1263, 1172, 1095, 1066, 966, 877, 831, 742, 651, 611, 569 cm^{-1}; HRMS (FAB): calcd for C$_{25}$H$_{29}$Br [M - H]$^{+}$: 408.1453, found 408.1456.

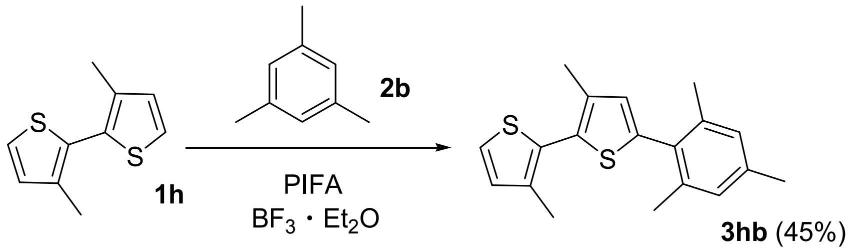
Cross-Coupling Using Other Types of Substrates

These products were obtained according to the general procedure.



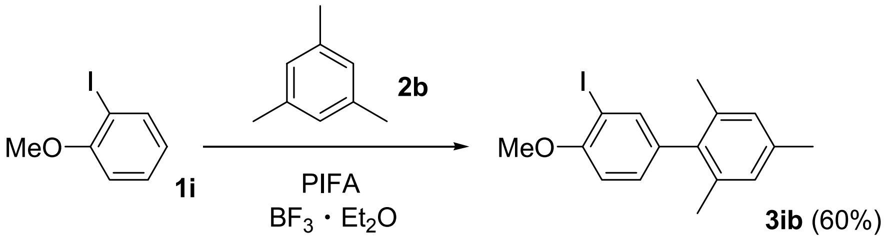
3-Iodo-2-(2,4,6-trimethylphenyl)thiophene (3gb)

Colorless crystals; m.p. 120-122 °C; ^{1}H NMR (300MHz, CDCl$_3$): $\delta = 2.04$ (s, 6H), 2.33 (s, 3H), 6.95 (s, 2H), 7.14 (d, $J = 5.1$ Hz, 1H), 7.33 (d, $J = 5.1$ Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 20.3, 21.2, 81.7, 127.4, 128.2, 130.5, 134.9, 138.2, 138.6, 142.1 ppm; IR (KBr): 3101, 2914, 2729, 1735, 1608, 1473, 1440, 1373, 1334, 1224, 1136, 1031, 968, 910, 852, 790, 734, 715, 640, 553 cm^{-1}; HRMS (FAB): calcd for $C_{13}H_{13}IS$ [M - H]$^+$: 327.9783, found 327.9794.



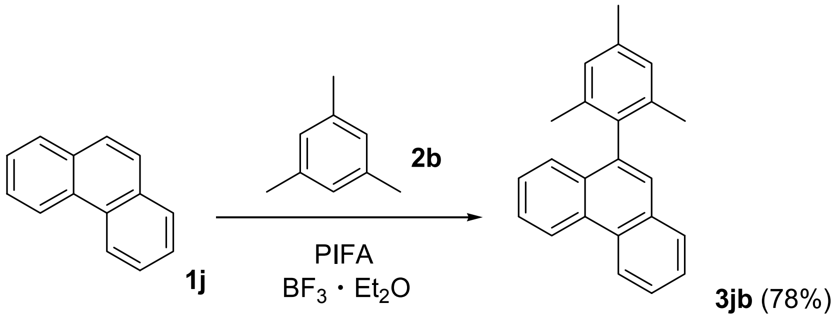
3,3'-Dimethyl-5-(2,4,6-trimethylphenyl)-[2,2']bithiophenyl (3hb)

Colorless oil; ^{1}H NMR (300MHz, CDCl$_3$): $\delta = 2.19$ (m, 9H), 2.22 (s, 3H), 2.31 (s, 3H), 6.60 (s, 1H), 6.91 (d, $J = 4.8$ Hz, 1H), 6.93 (s, 2H), 7.26 (d, $J = 4.8$ Hz, 1H) ppm; IR (KBr): 2920, 2856, 1446, 1377, 848, 833, 709 cm^{-1}; Anal: calcd for $C_{19}H_{20}S_2$: C, 73.03; H, 6.45, found C, 73.20; H, 6.65.



3'-Iodo-4'-methoxy-2,4,6-trimethylbiphenyl (3ib)

Colorless crystals; m.p. 131-133 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 2.01 (s, 6H), 2.31 (s, 3H), 3.92 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 2H), 7.08 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.57 (d, *J* = 2.1 Hz, 1H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.8, 21.0, 56.3, 85.8, 110.7, 128.0, 130.4, 135.3, 136.2, 136.8, 137.1, 140.0, 156.7 ppm; IR (KBr): 3010, 2916, 2837, 1595, 1469, 1377, 1278, 1253, 1180, 1141, 1053, 1020, 910, 850, 813, 736, 677, 651, 580, 547 cm^{-1}; HRMS (FAB): calcd for $C_{16}H_{17}IO$ $[M - H]^+$: 352.0324, found 352.0322.



9-(2,4,6-Trimethyl-phenyl)-phenanthrene (3jb)$^{7)}$

Colorless crystals; m.p. 158-161 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.93 (s, 6H), 2.45 (s, 3H), 7.02 (s, 2H), 7.24-7.67 (m, 6H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.75 (t, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.2, 21.1, 122.5, 122.8, 126.1, 126.3, 126.4, 126.6, 126.7, 127.2, 128.1, 128.5, 129.9, 130.5, 131.3, 132.0, 136.6, 136.9, 137.0, 137.3 ppm; IR (KBr): 3039, 2916, 1847, 1506, 1483, 1390, 1016, 850, 800, 779 cm^{-1}; Anal. calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80, found: C, 93.37; H, 6.96.

References

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