



Supporting Information

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Supporting Information
of
Nickel-Catalyzed Cross-Coupling of Aryl Methyl Ethers with Aryl Boronic Esters

Mamoru Tobisu,* Toshiaki Shimasaki, Naoto Chatani*[†]

*Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University,
Suita, Osaka 565-0871, Japan*

[†]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871,
Japan*

tobisu@chem.eng.osaka-u.ac.jp; chatani@chem.eng.osaka-u.ac.jp

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1. General Information.

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

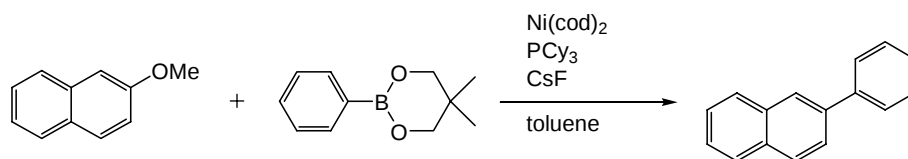
Materials. Toluene and dioxane were purchased from Wako Chemicals and used as received. $\text{Ni}(\text{cod})_2$ (CAS 1295-35-8) was purchased from Strem Chemicals and used as received. Tricyclohexylphosphine (CAS 2622-14-2) and CsF (CAS 13400-13-0) were purchased from Aldrich and used as received. 2-Phenyl-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 5123-13-7), 2-(4-trifluoromethylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 501374-30-7), 2-(4-methoxycarbonylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 905966-40-7), 2-(4-acetylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 460088-33-9), 2-(4-trimethylsilylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 574755-28-5), 2-(4-dimethylaminophenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 95752-87-7), 2-(2-methylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 91994-11-5), 2-(4-methoxyphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 213596-33-9) and 2-(2-fluorophenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 346656-39-1) were prepared from phenylboronic acid, 4-trifluoromethylphenylboronic acid (CAS 128796-39-4), 4-methoxycarbonylphenyl boronic acid (CAS 99768-12-4), 4-acetylphenylboronic acid (CAS 149104-90-5), 4-trimethylsilylphenylboronic acid (CAS 17865-11-1), 4-dimethylaminophenylboronic acid (CAS 28611-39-4), 2-methylphenylboronic acid (CAS 16419-60-6), 4-methoxyphenylboronic acid (CAS 5720-07-0) and 2-fluorophenylboronic acid (CAS 1993-03-9) with 2, 2'-Dimethyl-1, 3-propanediol (CAS 126-30-7).¹ 9-Methoxyphenanthrene (5085-74-5), *trans*-4-methoxystyrene (CAS 1694-19-5) and 2-acetyl-6-methoxynaphthalene (CAS 3900-45-6) were prepared from 9-hydroxyphenanthrene (CAS 484-17-3), 4-hydroxystyrene (CAS 3839-46-1) and 2-acetyl-6-hydroxynaphthalene (CAS 10441-41-5) with iodomethane (CAS 74-88-4).² 2-Methoxy-6-methoxycarbonylnaphthalene (CAS 5043-02-7) was prepared from 2-methoxy-6-naphthoic acid (CAS 2471-70-7) and methanol by the esterification with H_2SO_4 .³ 2-(4-fluorophenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (CAS 225916-39-2) were purchased from Aldrich and used as received. 1-Methoxynaphthalene (CAS 2216-69-5), 2-acetyl-6-methoxynaphthalene (CAS 320-77461), 4'-Methoxyacetophenone (CAS 100-06-1), 2-methoxynaphthalene (CAS 93-04-9) and 2-bromo-6-methoxynaphthalene (CAS 5111-65-9) were purchased from Wako Chemicals and TCI and used as received.

References

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- (2) L. I. Kruse, C. W. DeBrosse, C. H. Kruse, *J. Am. Chem. Soc.* **1985**, *107*, 5435.
- (3) F. X. Tavares, K. A. Al-Barazani, M. J. Bishop, C. S. Britt, D. L. Carlton, J. P. Cooper, P. L. Feldman, D. M. Garrido, A. S. Goetz, M. K. Grizzle, D. L. Hertzog, D. M. Ignar, D. G. Lang, M. S. McIntyre, R. J. Ott, A. J. Peat, H.-Q. Zhou, *J. Med. Chem.* **2006**, *49*, 7108.

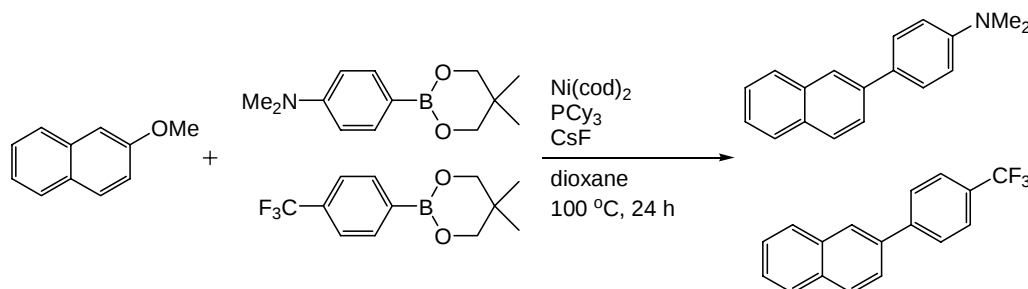
2. Typical procedure

Nickel-catalyzed reaction of 2-methoxynaphthalene with organoboronates: preparation of 2-phenylnaphthalene.



All reactions were carried out in 10-mL sample vials with a teflon-sealed screwcap in a glovebox under nitrogen atmosphere. To the orange mixture of Ni(cod)_2 (13.8 mg, 0.05 mmol), PCy_3 (56.0 mg, 0.2 mmol) and CsF (341.8 mg, 2.25 mmol) in toluene (1.5 mL) was added 2-methoxynaphthalene (79.1 mg, 0.5 mmol) and 2-Phenyl-5, 5-dimethyl-1, 3, 2-dioxaborinane (142.5 mg, 0.75 mmol) at room temperature, followed by heating at 120 °C for 12 h. After cooling to room temperature, the crude mixture was purified by flash column chromatography on silica gel (hexane) to give the desired 2-phenylnaphthalene (94.7 mg, 93 %) as a white powder.

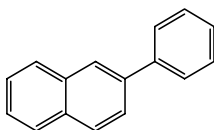
Competitive experiment



To the orange mixture of Ni(cod)_2 (13.8 mg, 0.05 mmol), PCy_3 (56.0 mg, 0.2 mmol) and CsF (380.0 mg, 2.5 mmol) in dioxane (5 mL) was added 2-methoxynaphthalene (79.1 mg, 0.5 mmol) and 2-(4-dimethylaminophenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (582.8 mg, 2.5 mmol) and 2-(4-trifluoromethylphenyl)-5, 5-dimethyl-1, 3, 2-dioxaborinane (645.1 mg, 2.5 mmol) at room temperature, followed by heating at 100 °C for 24 h. After cooling to room temperature, the crude mixture was purified by flash column chromatography on silica gel (hexane to hexane / CH_2Cl_2 = 1 / 1) to give the desired 2-(4-trifluoromethylphenyl)naphthalene (54.9 mg, 40 %), 2-(4-dimethylaminophenyl)naphthalene (58.2 mg, 47 %) and unconverted 2-methoxynaphthalene (< 10 %) as a white powder.

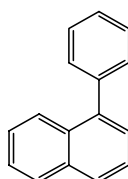
3. Data of products

2-Phenylnaphthalene [612-94-2].



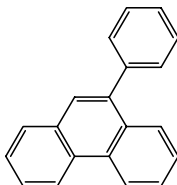
^1H NMR (CDCl_3 , 270 MHz): δ 7.40 (t, $J = 7.3$ Hz, 1H), 7.48-7.56 (m, 3H), 7.74-7.79 (m, 3H), 7.87-8.00 (m, 3H), 8.07 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 125.5, 125.7, 125.8, 126.2, 127.2, 127.3, 127.5, 128.1, 128.3, 128.7, 132.5, 133.5, 138.4, 141.0.

1-Phenylnaphthalene [605-02-7].



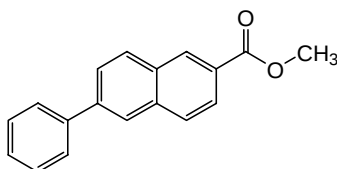
^1H NMR (CDCl_3 , 270 MHz): δ 7.51-7.64 (m, 9H), 7.93-8.03 (m, 3H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 125.3, 125.7, 126.0, 126.9, 127.2, 127.6, 128.2, 130.0, 131.6, 133.8, 140.2, 140.7.

9-Phenylphenanthrene [844-20-2].



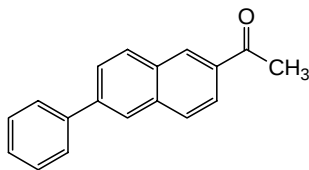
^1H NMR (CDCl_3 , 270 MHz): δ 7.48-7.72 (m, 10 H), 7.93 (d, $J = 7.9$ Hz, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 8.75 (d, $J = 7.9$ Hz, 1H), 8.81 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 122.5, 122.9, 126.4, 126.5, 126.6, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.0, 130.6, 131.1, 131.5, 138.7, 140.8.

2-Methoxycarbonyl-6-phenylnaphthalene [904688-59-1].



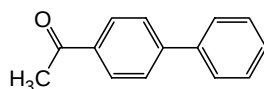
^1H NMR (CDCl_3 , 270 MHz): δ 4.00 (s, 3H), 7.42-7.54 (m, 3H), 7.73 (d, $J = 6.8$ Hz, 1H), 7.80 (dd, $J = 1.6$ and 8.6 Hz, 1H), 7.90-8.12 (m, 5H), 8.63 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 52.2, 125.1, 125.5, 125.6, 126.3, 127.4, 127.8, 128.3, 128.9, 129.8, 130.7, 131.5, 135.7, 140.4, 140.8, 167.1.

2-Acetyl-6-phenylnaphthalene.



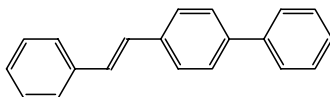
mp 141–143 °C; ^1H NMR (CDCl_3 , 270 MHz): δ 2.73 (s, 3H), 7.42–7.58 (m, 3H), 7.71–8.08 (m, 7H), 8.46 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 26.6, 124.2, 125.4, 126.4, 127.3, 127.8, 128.5, 128.9, 129.8, 130.0, 131.5, 134.3, 135.7, 140.3, 141.0, 197.8; IR(KBr): 3066 w, 2997 w, 2962 w, 2924 w, 2852 w, 1676 s, 1625.7 m, 1468 w, 1448 w, 1358 m, 1282 m, 1219 w, 1194 w, 1128 w, 1066 w, 1016 w, 964 w, 941 w, 891 m, 870 w, 829 m, 758 s, 687 m, 665 m, 577 w, 474 m cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}$: 246.1045, found 246.1043.

4-Phenylacetophenone [92-91-1].



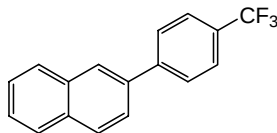
^1H NMR (CDCl_3 , 270 MHz): δ 2.65 (s, 3H), 7.41–7.51 (m, 3H), 7.62–7.65 (m, 2H), 7.69 (d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 26.7, 127.1, 127.2, 128.1, 128.79, 128.83, 135.7, 139.7, 145.6, 197.5.

4-Phenyl-*trans*-stilbene [21175-18-8].



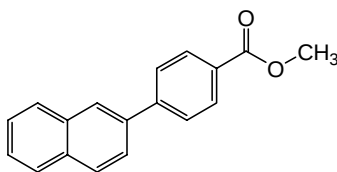
^1H NMR (CDCl_3 , 270 MHz): δ 7.17 (s, 2H), 7.26–7.49 (m, 7H), 7.54–7.65 (m, 7H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 126.5, 126.9, 127.3, 127.7, 128.2, 128.7, 128.8, 136.4, 137.3, 140.3, 140.6.

2-(4-Trifluoromethylphenyl)naphthalene [460743-71-9].



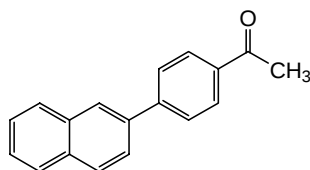
^1H NMR (CDCl_3 , 270 MHz): δ 7.52–7.55 (m, 2H), 7.72–7.76 (m, 3H), 7.81–7.97 (m, 5H), 8.07 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 124.3 (q, J = 269.4 Hz), 125.0, 125.7 (q, J = 3.8 Hz), 126.2, 126.4, 126.5, 127.5, 127.6, 128.2, 128.6, 129.2 (q, J = 32.2 Hz), 132.9, 133.4, 144.4, 144.5.

2-(4-Methoxycarbonylphenyl)naphthalene [205823-29-6].



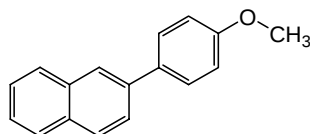
^1H NMR (CDCl_3 , 270 MHz): δ 3.92 (s, 3H), 7.46 (d, J = 7.5 Hz, 1H), 7.51-7.56 (m, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.93 (t, J = 6.9 Hz, 2H), 8.05 (d, J = 7.2 Hz, 1H), 8.09 (s, 1H), 8.16 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 52.2, 125.1, 126.2, 126.3, 127.16, 127.22, 127.6, 128.2, 128.5, 129.4, 130.1, 132.8, 133.4, 145.4, 166.8.

2-(4-Acetylphenyl)naphthalene [150988-77-5].



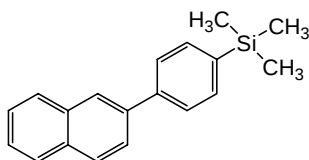
^1H NMR (CDCl_3 , 270 MHz): δ 2.67 (s, 3H), 7.51-7.55 (m, 2H), 7.75-7.97 (m, 6H), 8.08 (d, J = 8.3 Hz, 2H), 8.10 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 26.6, 125.1, 126.3, 126.4, 126.5, 127.4, 127.6, 128.3, 128.7, 128.9, 132.9, 133.5, 135.8, 137.0, 145.6, 197.7.

2-(4-Methoxyphenyl)naphthalene [59115-45-6].



^1H NMR (CDCl_3 , 270 MHz): δ 4.00 (s, 3H), 7.06 (d, J = 8.9 Hz, 2H), 7.48-7.57 (m, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.76 (dd, J = 2.0 and 8.6 Hz, 1H), 7.88-7.95 (m, 3H), 8.04 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 55.3, 114.3, 125.0, 125.4, 125.6, 126.2, 127.6, 128.0, 128.3, 128.4, 132.2, 133.5, 133.7, 138.1, 159.2.

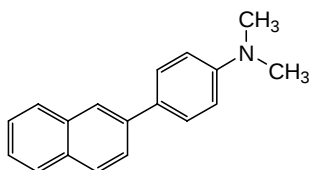
2-(4-Trimethylsilylphenyl)naphthalene.



mp 108–109 °C; ^1H NMR (CDCl_3 , 270 MHz): δ 7.50-7.53 (m, 2H), 7.66-7.80 (m, 5H), 7.87-7.96 (m, 3H), 8.08 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 0.17, 126.4, 126.6, 126.8, 127.1, 127.6, 128.5, 129.0, 129.2, 133.5, 134.5, 134.7, 139.3, 140.2, 142.3; IR(KBr): 3055 w, 3016 w, 2947 w, 2893 w, 1923 w, 1628 w, 1595 m, 1542 w, 1496 w, 1435 w, 1390 w, 1342 w, 1246 s, 1194 w, 1130 w, 1111 s, 1028 w, 1018 w, 964 w, 951 w, 901 w, 868 s, 841 s, 812 s, 758 s, 744 s, 721 s, 690 m, 633 m, 621 m, 580 w, 550 m, 511

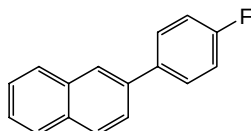
m, 480 s, 444, m cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{Si}$ 276.1334, found 276.1328.

2-(4-Dimethylaminophenyl)naphthalene [359653-43-3].



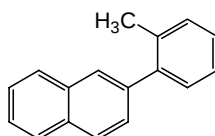
^1H NMR (CDCl_3 , 270 MHz): δ 3.03 (s, 6H), 6.87 (d, J = 8.1 Hz, 2H), 7.43 (t, J = 6.9 Hz, 1H), 7.48 (t, J = 6.6 Hz, 1H), 7.66 (d, J = 8.9 Hz, 2H), 7.75 (dd, J = 1.6 and 8.6 Hz, 1H), 7.83-7.89 (m, 3H), 7.99 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 40.6, 112.8, 124.0, 125.1, 125.2, 125.9, 127.5, 127.8, 128.1 (br-s), 128.9, 131.9, 133.8, 138.4, 149.8.

2-(4-Fluorophenyl)naphthalene [28396-55-6].



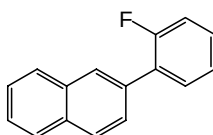
^1H NMR (CDCl_3 , 270 MHz): δ 7.24 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.58-7.60 (m, 3H), 7.73-7.86 (m, 3H), 7.98-8.07 (m, 3H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 115.7 (d, $J_{\text{C-F}}$ = 21.6 Hz), 125.3, 125.6, 125.8, 126.0, 126.4, 127.6, 128.1, 128.5, 128.9, 132.5, 133.6, 137.2, 137.5, 162.5 (d, $J_{\text{C-F}}$ = 244.8 Hz).

2-(2-Methylphenyl)naphthalene [66778-24-3].



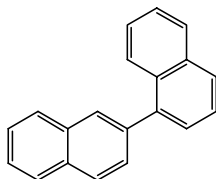
^1H NMR (CDCl_3 , 270 MHz): δ 2.43 (s, 3H), 7.41-7.45 (m, 4H), 7.58-7.62 (m, 3H), 7.89 (s, 1H), 7.94-7.99 (m, 2H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 20.5, 125.8 (br-s), 126.1, 127.3, 127.5, 127.6, 127.69, 127.75, 128.0, 130.0, 130.3, 132.2, 133.3, 135.5, 139.5, 141.8.

2-(2-Fluorophenyl)naphthalene [22082-95-7].



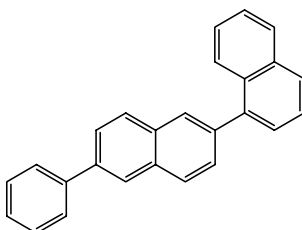
^1H NMR (CDCl_3 , 270 MHz): δ 7.18-7.60 (m, 6H), 7.71 (d, J = 8.6 Hz, 1H), 7.89-7.95 (m, 3H), 8.04 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 116.1 (d, $J_{\text{C-F}}$ = 22.8 Hz), 126.2 (d, $J_{\text{C-F}}$ = 3.3 Hz), 126.21, 126.22, 127.0 (d, $J_{\text{C-F}}$ = 2.8 Hz), 127.4, 127.6, 128.1 (d, $J_{\text{C-F}}$ = 19.4 Hz), 128.1 (d, $J_{\text{C-F}}$ = 2.8 Hz), 128.8, 129.0, 130.0, 131.0 (d, $J_{\text{C-F}}$ = 3.3 Hz), 132.6, 133.3, 159.9 (d, $J_{\text{C-F}}$ = 245.9 Hz).

1-(2-Naphthyl)naphthalene [4325-74-0].



^1H NMR (CDCl_3 , 270 MHz): δ 7.54-7.70 (m, 6H), 7.77 (dd, $J = 1.6$ and 6.5 Hz, 1H), 7.98-8.11 (m, 5H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 125.3, 125.7, 125.91, 125.96, 126.0, 126.2, 127.1, 127.5, 127.61, 127.63, 127.9, 128.2, 128.3, 128.6, 131.6, 132.4, 133.3, 133.7, 138.2, 140.0.

2-(1-Naphthyl)-6-phenylnaphthalene.



mp 156–157 °C; ^1H NMR (CDCl_3 , 270 MHz): δ 7.49-7.67 (m, 7H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.84-7.90 (m, 3H), 8.98-8.09 (m, 6H), 8.22 (s, 1H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 125.4, 125.6, 125.8, 126.00, 126.02, 126.1, 127.2, 127.4, 127.8, 127.9, 128.3, 128.5, 128.6, 128.9, 131.7, 132.5, 132.8, 133.8, 138.4, 138.7, 140.1, 141.0; IR (KBr): 3055 m, 3024 m, 1589 m, 1574 w, 1506 m, 1489 m, 1475 m, 1444 m, 1396 m, 1363 m, 1321 w, 1246 w, 1205 w, 1180 w, 1157 w, 1138 w, 1074 w, 1018 m, 966 m, 953 w, 887 s, 864 w, 825 s, 804 s, 773 s, 756 s, 715 w, 698 s, 683 s, 667 s, 644 w, 625 w, 600 w, 584 w, 567 w, 530 w, 511 m, 482 s, 434 m cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{26}\text{H}_{18}$ 330.1409, found 330.1411.

