Supplementary Information

Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

Kazuya Yamaguchi,[a] Hiroki Kondo,[a] Junichiro Yamaguchi,*[a] and Kenichiro Itami*[a,b]

[a] *Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan*

[b] *Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan*

E-mail: junichiro@chem.nagoya-u.ac.jp, itami.kenichiro@a.mbox.nagoya-u.ac.jp

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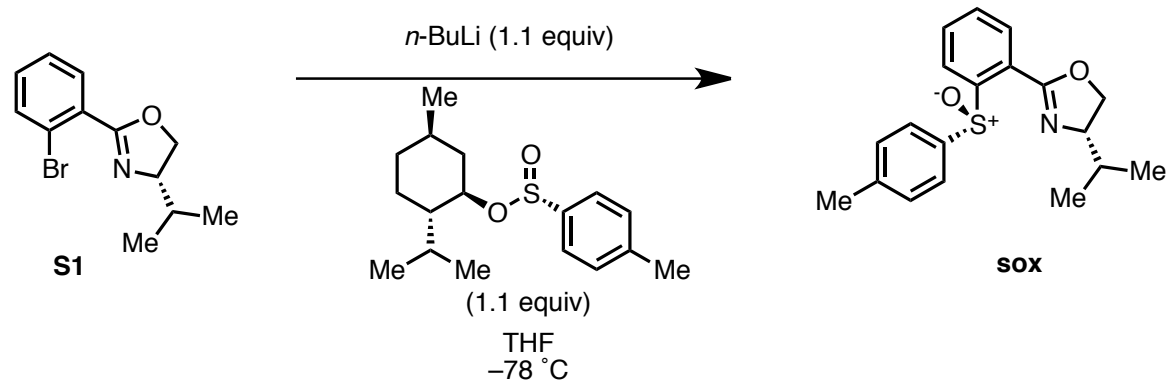
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used as received. 1-methyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (**1J**),[1] 2-methylnaphthalen-1-ylboronic acid (**2b**),[2] 2-isopropylnaphthalen-1-ylboronic acid (**2d**),[3] and **L4,**[4] **L5,**[5] **L10 (sox)**[6] were synthesized according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware using standard vacuum-line techniques. All C–H bond arylation reactions were performed in screw cap 20 mL glass vessel tubes and heated in an 8-well reaction block (heater + magnetic stirrer) unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative high performance liquid chromatography (preparative HPLC) was performed with a Biotage Isolera®, one equipped with Biotage SNAP Cartridge KP-C18-HS columns using acetonitrile/water as an eluent. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). High-resolution mass spectra (HRMS) were obtained from JMS-T100TD (DART) or JMS-700 (FAB) instruments. Chiral HPLC analysis was conducted on a Shimadzu Prominence 2000 instrument equipped with DAICEL Chiracel OD-H (4.6 mm x 250 mm). Nuclear magnetic resonance (NMR) spectra were recorded on JEOL ECS-400 (^{1}H 400 MHz, ^{13}C 100 MHz) or JEOL ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometers. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

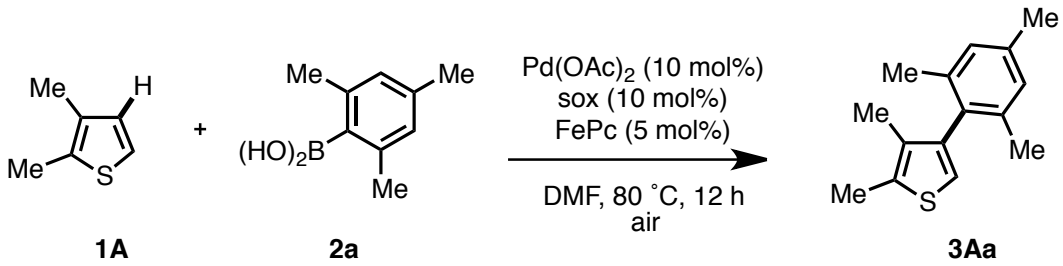
2. Preparation of Ligand (sox)



To a solution of (*S*)-2-(2-bromophenyl)-4-isopropyl-4,5-dihydrooxazole[7] (**S1**: 678 mg, 3.0 mmol) in THF (15 mL) was slowly added *n*-BuLi (1.6 M in hexane, 2.1 mL, 3.3 mmol) at –78 ˚C under nitrogen atmosphere. After stirring at –78 ˚C for 1 h, a solution of (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-*p*-toluenesulfinate (971 mg, 3.3 mmol) in THF (15 m L) was added dropwise, stirred at –78 ˚C for 30 min, then room temperature for 30 min. To the mixture was added saturated aqueous NH_4Cl and the mixture was extracted with EtOAc. The organic layer was washed with water, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 3:1) to give the desired product (**sox**) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75–7.68 (m, 1H), 7.58–7.48 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.34 (dd, *J* = 9.2, 7.3 Hz, 1H), 4.15–4.01 (m, 2H), 2.32 (s, 3H), 1.82–1.70 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.65, 146.19, 143.62, 140.85, 131.79, 130.19, 129.68, 129.47, 126.45, 125.56, 125.28, 73.29, 69.84, 32.44, 21.28, 18.93, 17.85; HRMS (DART) *m/z* calcd for $C_{19}H_{22}NO_2S$ $[M+H]^+$: 328.1371, found: 328.1373.

Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

3-1. General Procedure for C–H Coupling with Hindered Arylboronic Acid

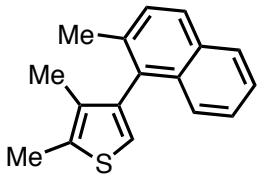


1A **2a** **3Aa**

To a screw cap 20 mL glass vessel containing a magnetic stirring bar were added 2,3-dimethyl thiophene (**1A**: 28 mg, 0.25 mmol), mesitylboronic acid (**2a**: 164 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), sox (8.2 mg, 0.025 mmol), FePc (7.1 mg, 0.0125 mmol) and DMF (0.2 mL). The mixture was stirred at 80 ˚C for 12 h under air, cooled to room temperature, passed through a short pad of silica gel (EtOAc) and the filtrate was evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give **3Aa** (50 mg, 86%, C4/C5 = 99:1) as a colorless oil. The yield was as isolated yield, and C4/C5 ratio was determined by ^{1}H NMR.

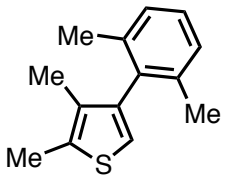
2,3-Dimethyl-4-(2-methylnaphthalen-1-yl)thiophene[3] **(3Aa):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.68 (s, 1H), 2.40 (s, 3H), 2.32 (s, 3H), 1.97 (s, 6H), 1.76 (s, 3H).

3-2. Compound Data of Coupling Product.



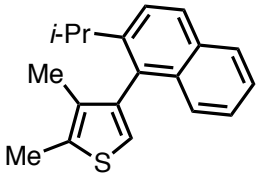
3Ab

2,3-Dimethyl-4-(2-methylnaphthalen-1-yl)thiophene[3] **(3Ab):** Following the general procedure with 2,3-dimethylthiophene (**1A**: 28 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **3Ab** (58 mg, 92%, C4/C5 = 98:2) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.73 (m, 2H), 7.44–7.31 (m, 4H), 6.84 (s, 1H), 2.47 (s, 3H), 2.22 (s, 3H), 1.71 (s, 3H).



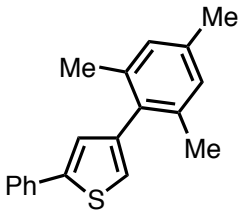
3Ac

4-(2,6-dimethylphenyl)-2,3-dimethylthiophene[3] **(3Ac):** Following the general procedure with 2,3-dimethylthiophene (**1A**: 28 mg) and (2,6-dimethylphenyl)boronic acid (**2c**: 150 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give the coupling product **3Ac** (37 mg, 69%, C4/C5 = 97:3) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18–7.12 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (s, 1H), 2.41 (s, 3H), 2.01 (s, 6H), 1.76 (s, 3H).



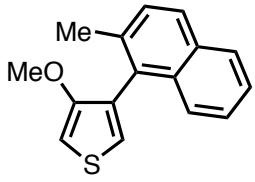
3Ad

4-(2-Isopropylnaphthalen-1-yl)-2,3-dimethylthiophene[3] **(3Ad):** Following the general procedure with 2,3-dimethylthiophene (**1A**: 28 mg) and (2-isopropylnaphthalene-1-yl)boronic acid (**2d**: 214 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give the coupling product **3Ad** (49 mg, 70%, C4/C5 = 90:10) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.43–7.29 (m, 3H), 6.85 (s, 1H), 2.97–2.85 (m, 1H), 2.47 (s, 3H), 1.71 (s, 3H), 1.20 (d, *J* = 7.3 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H).



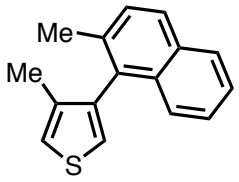
3Ba

4-Mesityl-2-phenylthiophene (3Ba): Following the general procedure with 2-phenylthiophene (**1B**: 40 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **3Ba** (37 mg, 53%, C4/C5 = 99:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.32–7.25 (m, 1H), 7.15 (d, *J* = 1.2 Hz, 1H), 6.96–6.94 (m, 3H), 2.33 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.97, 141.69, 136.96, 136.91, 134.41, 133.90, 128.89, 128.05, 127.44, 125.67, 125.05, 121.89, 21.03, 20.71; HRMS (DART) *m/z* calcd for $C_{19}H_{19}S$ $[M+H]^+$: 279.1207, found: 279.1209.



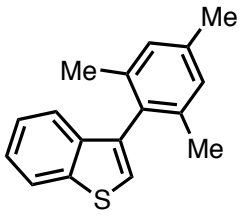
3Cb

3-Methoxy-4-(2-methylnaphthalen-1-yl)thiophene (3Cb): Following the general procedure with 3-methoxylthiophene (**1C**: 29 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 50:1) to give **3Cb** (40 mg, 63%, C4/C5 = >99:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.76 (m, 2H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.41–7.33 (m, 3H), 7.08 (d, *J* = 3.4 Hz, 1H), 6.43 (d, *J* = 3.4 Hz, 1H), 3.74 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.96, 135.07, 133.37, 131.93, 130.97, 130.59, 128.45, 127.78, 127.72, 125.88, 125.77, 124.72, 123.39, 96.59, 57.48, 20.51; HRMS (DART) *m/z* calcd for $C_{16}H_{15}OS$ $[M+H]^+$: 255.0844, found: 255.0845.



3Db

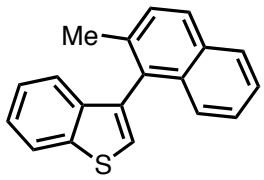
3-Methyl-4-(2-methylnaphthalen-1-yl)thiophene[3] **(3Db):** Following the general procedure with 3-methylthiophene (**3D**: 25 mg) and 2-methylnaphthalene-1-lyboronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **3Db** (40 mg, 67%, C4/C5 = >99:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.42–7.34 (m, 4H), 7.13–7.12 (m, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 2.22 (s, 3H), 1.86 (s, 3H).



3Ea

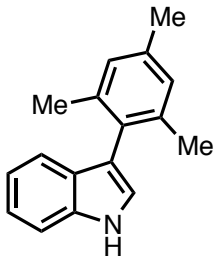
3-Mesitylbenzo[*b*]thiophene (3Ea): Following the general procedure with benzo[*b*]thiophene (**1E**: 34 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **3Ea** (46 mg, 73%, C4/C5 = >99:1) as a colorless oil. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.39–7.33 (m, 1H), 7.32–7.25 (m, 2H), 7.18 (s, 1H), 6.99 (s, 2H), 2.37 (s, 3H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.00, 138.89, 137.71, 137.30, 136.40, 131.91, 128.12, 124.23, 124.08, 123.30, 122.74, 122.67, 21.11, 20.24; HRMS (DART) *m/z* calcd for $C_{17}H_{17}S$ $[M+H]^+$: 253.1051, found: 253.1051.



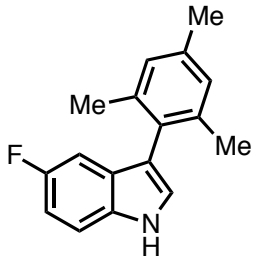
3Eb

3-(2-Methylnaphthalen-1-yl)benzo[*b*]thiophene[3] **(3Eb):** Following the general procedure with benzo[*b*]thiophene (**1E**: 34 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **3Eb** (55 mg, 80%, C4/C5 = >99:1) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.42–7.32 (m, 4H), 7.30–7.19 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 2.21 (s, 3H).



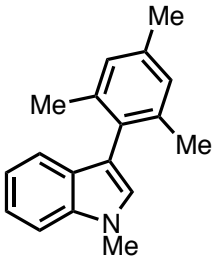
3Fa

3-Mesityl-1*H*-indole (3Fa): Following the general procedure with indole (**1F**: 29 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 5:1) to give **3Fa** (34 mg, 57%, C3/C2 = 88:12) as a orange oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (brs, 1H), 7.45–7.41 (m, 1H), 7.26–7.18 (m, 2H), 7.10–7.01 (m, 2H), 6.99 (s, 2H), 2.36 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.41, 136.52, 135.97, 130.86, 127.96, 127.37, 122.40, 121.93, 119.89, 119.55, 115.82, 111.02, 21.06, 20.77; HRMS (DART) *m/z* calcd for $C_{17}H_{18}N$ $[M+H]^+$: 236.1439, found: 236.1439.



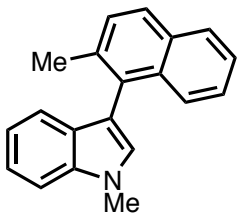
3Ga

5-Fluoro-3-mesityl-1*H*-indole (3Ga): Following the general procedure with 5-fluoro-1*H*-indole (**1G**: 34 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 5:1) to give **3Ga** (29 mg, 47%, C3/C2 = 87:13) as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.36–7.32 (m, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.98–6.93 (m, 3H), 6.90–6.78 (m, 1H), 2.35 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ156.56 (d, J_{FC} = 236 Hz), 138.31, 136.78, 132.47, 130.28, 128.04, 127.88 (d, J_{FC} = 15 Hz), 124.19, 116.07 (d, J_{FC} = 4.8 Hz), 111.61 (d, J_{FC} = 9.6 Hz), 110.39 (d, J_{FC} = 27 Hz), 104.58 (J_{FC} = 23 Hz), 21.06, 20.71; HRMS (DART) *m/z* calcd for $C_{17}H_{17}FN$ $[M+H]^+$: 254.1345, found: 254.1345.



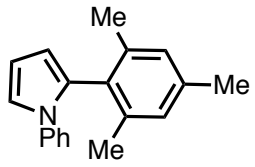
3Ha

3-Mesityl-1-methyl-1*H*-indole (3Ha): Following the general procedure with *N*-methylindole (**1H:** 33 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 5:1) to give **3Ha** (31mg, 49%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.35 (m, 1H), 7.27–7.22 (m, 2H), 7.09–7.04 (m, 1H), 6.98 (s, 2H), 6.87 (s, 1H), 3.85 (s, 3H), 2.35 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.39, 136.83, 136.35, 130.99, 127.95, 127.85, 127.09, 121.43, 120.04, 118.98, 114.27, 109.10, 32.77, 21.06, 20.87; HRMS (DART) *m/z* calcd for $C_{18}H_{20}N$ $[M+H]^+$: 250.1596, found: 250.1596.



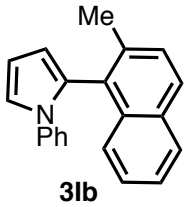
3Hb

1-Methyl-3-(2-methylnaphthalen-1-yl)-1*H*-indole (3Hb): Following the general procedure with *N*-methylindole (**1H**: 33 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 7:1) to give **3Hb** (53mg, 86%, C3/C2= 87:13) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.46 (t, *J* = 9.2 Hz, 2H), 7.41–7.37 (m, 1H), 7.31–7.25 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.08–7.04 (m, 2H), 3.93 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.82, 135.46, 134.24, 132.08, 130.62, 128.67, 128.53, 128.26, 127.68, 127.04, 126.61, 125.53, 124.60, 121.64, 120.35, 119.24, 112.84, 109.22, 32.88, 21.15; HRMS (DART) *m/z* calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439, found: 272.1439.



3Ia

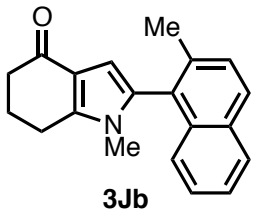
2-Mesityl-1-phenyl-1*H*-pyrrole (3Ia): Following the general procedure with 1-phenyl-1*H*-pyrrole (**1I**: 36 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 20:1) and reverse phase HPLC using Isolera® to give **3Ia** (27 mg, 41%) as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 2H), 7.15–7.13 (m, 1H), 7.04–6.99 (m, 3H), 6.81 (s, 2H), 6.38 (t, *J* = 3.2 Hz, 1H), 6.14–6.11 (m, 1H), 2.26 (s, 3H), 1.98 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.60, 138.57, 137.48, 131.18, 130.23, 128.70, 127.94, 125.76, 123.75, 121.03, 110.72, 108.87, 21.08, 20.54; HRMS (DART) *m/z* calcd for $C_{19}H_{20}N$ $[M+H]^+$: 262.1596, found: 262.1597.



3Ib

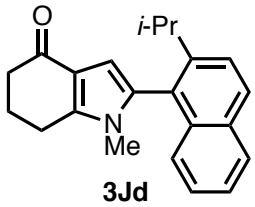
2-(2-Methylnaphthalen-1-yl)-1-phenyl-1*H*-pyrrole (3Ib): Following the general procedure with 1-phenyl-1*H*-pyrrole (**1I**: 36 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 20:1) and reverse phase HPLC using Isolera® to give **3Ib** (35 mg, 49%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.43–7.37 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.13–7.01 (m, 4H), 6.98–6.93 (m, 2H), 6.50 (t, *J* = 4.0 Hz, 1H), 6.33–6.29 (m, 1H), 2.05 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 140.34, 136.57, 134.45, 131.82, 129.46, 128.61, 128.24, 128.07, 127.72, 126.16, 125.93, 124.81, 123.91, 121.69, 112.05, 109.05, 20.56; HRMS (DART) *m/z* calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1439, found: 284.1437.



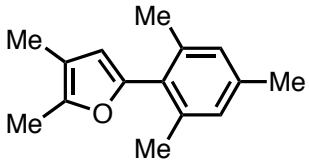
3Jb

1-Methyl-2-(2-methylnaphthalen-1-yl)-6,7-dihydro-1*H*-indol-4(5*H*)-one (3Jb): Following the general procedure with 1-methyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (**1J**: 37 mg) and (2-methylnaphthalene-1-yl)boronic acid (**2b**: 186 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 1:1) to give **3Jb** (60 mg, 89%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.7, 2.8 Hz, 2H), 7.47–7.33 (m, 4H), 6.55 (s, 1H), 3.11 (s, 3H), 2.91–2.84 (m, 2H), 2.62–2.53 (m, 2H), 2.33–2.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.25, 143.86, 137.02, 134.06, 131.84, 131.79, 128.80, 128.31, 127.87, 127.82, 126.54, 125.47, 125.15, 120.36, 106.22, 37.84, 30.80, 23.64, 22.16, 20.56; HRMS (DART) *m/z* calcd for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1545, found: 290.1547.



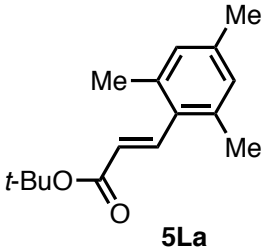
3Jd

2-(2-Isopropylnaphthalen-1-yl)-1-methyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (3Jd): Following the general procedure with 1-methyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (**1J**: 37 mg) and (2-isopropylnaphthalene-1-yl)boronic acid (**2d**: 214 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 1:1) to give **3Jd** (43 mg, 55%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.45–7.38 (m, 2H), 7.31–7.24 (m, 1H), 6.57 (s, 1H), 3.10 (s, 3H), 3.03–2.92 (m, 1H), 2.90–2.81 (m, 2H), 2.62–2.51 (m, 2H), 2.31–2.21 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.22, 147.40, 143.77, 134.00, 131.78, 131.37, 129.48, 127.80, 126.51, 126.16, 125.78, 125.25, 123.59, 120.28, 106.51, 37.81, 30.89, 30.83, 24.51, 23.60, 23.11, 22.14; HRMS (DART) *m/z* calcd for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1858, found: 318.1857.



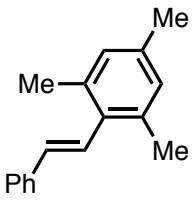
3Ka

5-Mesityl-2,3-dimethylfuran (3Ka): To a screw cap 20 mL glass vessel containing a magnetic stirring bar were added 2,3-dimethylfuran (**1K**: 24 mg, 0.25 mmol), mesitylboronic acid (**2a**: 164 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), FePc (7.1 mg, 0.0125 mmol) and DMSO (0.2 mL). The mixture was stirred at 80 ˚C for 12 h under air, cooled to room temperature, passed through a short pad of silica gel (EtOAc) and the filtrate was evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give the product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 6.00 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.19 (s, 6H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.00, 146.16, 138.05, 137.78, 128.63, 128.24, 114.46, 112.34, 21.06, 20.64, 11.33, 10.01; HRMS (DART) *m/z* calcd for $C_{15}H_{19}O$ $[M+H]^+$: 215.1436, found: 215.1438.



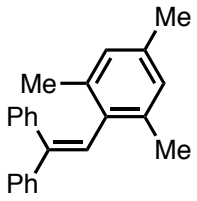
5La

(*E*)-*tert*-Butyl 3-mesitylacrylate (5La): Following the general procedure with *tert*-butyl acrylate (**4L**: 32 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane/EtOAc = 20:1) to give **5La** (55 mg, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.5 Hz, 1H), 6.88 (s, 2H), 5.97 (d, J = 16.5 Hz, 1H), 2.33 (s, 6H), 2.28 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.41, 142.01, 138.02, 136.80, 131.07, 129.06, 124.85, 80.42, 28.23, 21.13, 21.01; HRMS (DART) *m/z* calcd for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1698, found: 247.1698.



5Ma

(*E*)-1,3,5-Trimethyl-2-styrylbenzene (5Ma): To a screw cap 20 mL glass vessel containing a magnetic stirring bar were added styrene (**4M**: 26 mg, 0.25 mmol), mesitylboronic acid (**2a**: 164 mg, 1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), FePc (7.1 mg, 0.0125 mmol) and DMSO (0.2 mL). The mixture was stirred at 80 ˚C for 12 h under air, cooled to room temperature, passed through a short pad of silica gel (EtOAc) and the filtrate was evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give **5Ma** (54 mg, 98%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.30–7.25 (m, 1H), 7.10 (d, J = 16.4 Hz, 1H), 6.91 (s, 2H), 6.59 (d, J = 16.4 Hz, 1H), 2.34 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.71, 136.30, 136.15, 133.96, 133.62, 128.69, 128.63, 127.43, 126.88, 126.20, 21.00, 20.96; HRMS (DART) *m/z* calcd for $C_{17}H_{19}$ $[M+H]^+$: 223.1487, found: 223.1482.

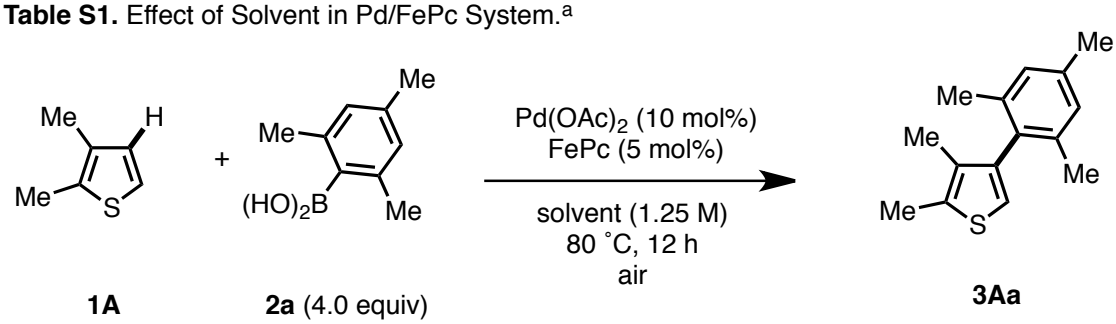


5Na

(2-Mesitylethene-1,1-diyl)dibenzene (5Na): Following the general procedure with ethene-1,1-diyldibenzene (**4N**: 45 mg) and mesitylboronic acid (**2a**: 164 mg), the crude product was purified by preparative thin-layer chromatography (hexane) to give **5Na** (49 mg, 65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 7.17–7.08 (m, 3H), 7.00–6.93 (m, 2H), 6.80 (s, 1H), 6.75 (s, 2H), 2.23 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.17, 143.56, 140.38, 136.14, 135.94, 133.91, 129.80, 128.40, 128.09, 128.03, 127.66, 127.52, 127.40, 127.05, 20.98, 20.45; HRMS (DART) *m/z* calcd for $C_{23}H_{23}$ $[M+H]^+$: 299.1800, found: 299.1801.

4. Investigation of Reaction Parameters.

Table S1. Effect of Solvent in Pd/FePc System.[a]

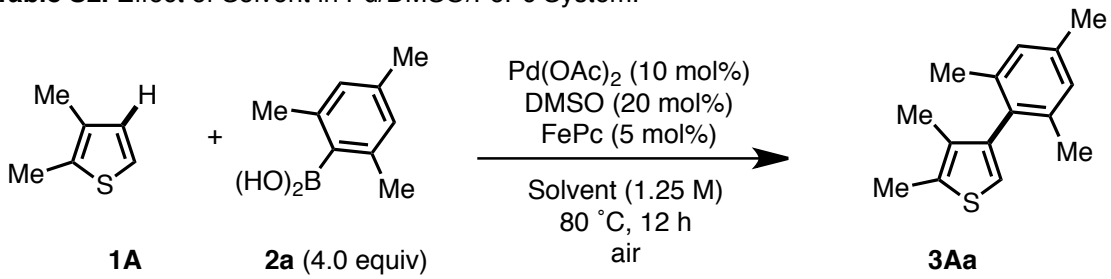


1A **2a** (4.0 equiv) **3Aa**

Entry	Solvent	Yield/%	C4/C5[b]
1	DMSO	83	95/5
2	*i*-PrOH	ND	—
3	DMSO/*i*-PrOH (1:1)	92	95/5
4	CH_3CN	trace	—
5	toluene	trace	—
6	DMF	32	98/2
7	DMAc	7	97/3
8	NMP	12	97/3

a: Conditions: **1A** (0.25 mmol), **2a** (1.0 mmol), $Pd(OAc)_2$ (0.025 mmol), FePc (0.0125 mmol) in solvent (0.2 mL), 80 ˚C, under air. b: Determined by ^1H NMR.

Table S2. Effect of Solvent in Pd/DMSO/FePc System.[a]

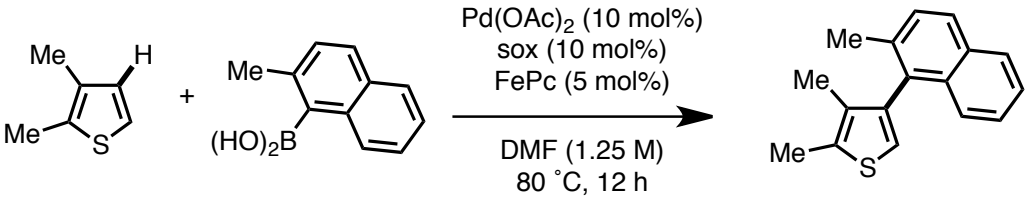


1A **2a** (4.0 equiv) **3Aa**

Entry	Solvent	Yield/%	C4/C5[b]
1	DMF	86	99/1
2	DMAc	67	98/2
3	NMP	23	98/2
4	DME	23	98/2
5	toluene	trace	—
6	DCE	trace	—
7	*i*-PrOH	trace	—
8	AmylOH	11	98/2

a: Conditions: **1A** (0.25 mmol), **2a** (1.0 mmol), $Pd(OAc)_2$ (0.025 mmol), DMSO (0.050 mmol), FePc (0.0125 mmol) in solvent (0.2 mL), 80 ˚C, under air. b: Determined by ^{1}H NMR.

Table S3. Effect of Arylboronic Acid.[a]

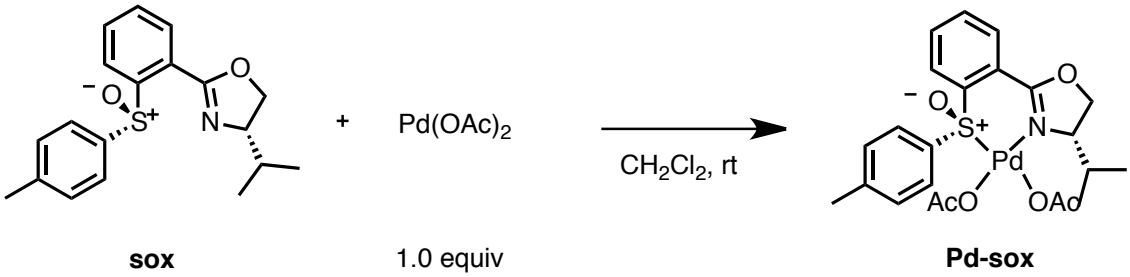


1A **2b** (X equiv) **3Ab**

Entry	**2b**/equiv	Yield/%	C4/C5[b]
1	4.0	92	96/4
2	2.0	89	97/3
3	1.5	77	98/2
4	1.0	61	98/2

a: Conditions: **1A** (0.25 mmol), **2b** (X equiv), $Pd(OAc)_2$ (0.025 mmol), sox (0.025 mmol), FePc (0.0125 mmol) in DMF (0.2 mL), 80 ˚C, under air. b: Determined by ^{1}H NMR.

5. Preparation of $Pd(OAc)_2$/sox complex.



sox 1.0 equiv **Pd-sox**

Crystals of $Pd(OAc)_2$/sox (**Pd-sox**) were obtained by vapor diffusion of pentane into a $CHCl_3$ solution of $Pd(OAc)_2$ and **sox** (1.0 equiv) at room temperature. $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) and **sox** (16.4 mg, 0.050 mmol) were dissolved with dichloromethane (1.0 mL). The solution was evaporated under reduced pressure. The residue was dissolved with $CHCl_3$ and then transferred into a vial containing pentane. The vial was sealed with a Teflon cap and maintained at room temperature. Yellow crystalline plate formed. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 8.08–7.97 (m, 2H), 7.88–7.81 (m, 1H), 7.30 (d, J = 8.7 Hz, 2H), 4.46 (t, J = 9.6 Hz, 1H), 4.36–4.24 (m, 2H), 2.54–2.41 (m, 1H), 2.39 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 0.85 (d, J = 6.9 Hz, 3H), 0.09 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.02, 160.54, 145.39, 140.46, 136.93, 134,66, 133.60, 132.38, 130.50, 130.32, 128.31, 127.18, 120.90, 69.97, 69.61, 29.95, 22.19, 21.56, 19.35, 13.78; HRMS (FAB) *m/z* calcd for $C_{21}H_{24}NO_4PdS$ $[M–OAc]^+$: 492.0461, found: 492.0457.

6. X-ray Crystal Structure Analysis of Pd-sox.

A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) was used. The structures were solved by direct methods with (SIR-97)[8] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[9] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. Details of the crystal data and a summary of the intensity data collection parameters for **Pd-sox** are listed in Table S4.

Table S4. Crystallographic data and structure refinement details for **Pd-sox**.

	Pd-sox
Formula	$C_{24}H_{28}Cl_3NO_6PdS$
Fw	671.28
T (K)	103(2)
λ (Å)	0.71070
cryst syst	Monoclinic
space group	$P2_1$
a, (Å)	9.3736(10)
b, (Å)	15.1780(11)
c, (Å)	10.1053(9)
α, (deg)	90
β, (deg)	107.302(4)
γ, (deg)	90
V, (Å^3)	1372.7(2)
Z	2
D_{calc}, (g / cm^3)	1.642
m (mm^{-1})	1.083
F(000)	680
cryst size (mm)	0.15 × 0.15 × 0.15
2θ range, (deg)	3.54–25.00
reflns collected	8294
indep reflns/R_{int}	4743/0.0287
params	330
GOF on F^2	1.024
R_1, wR_2 [I>2σ(I)]	0.0261, 0.0686
R_1, wR_2 (all data)	0.0289, 0.0696
abs struct param	-0.02(2)

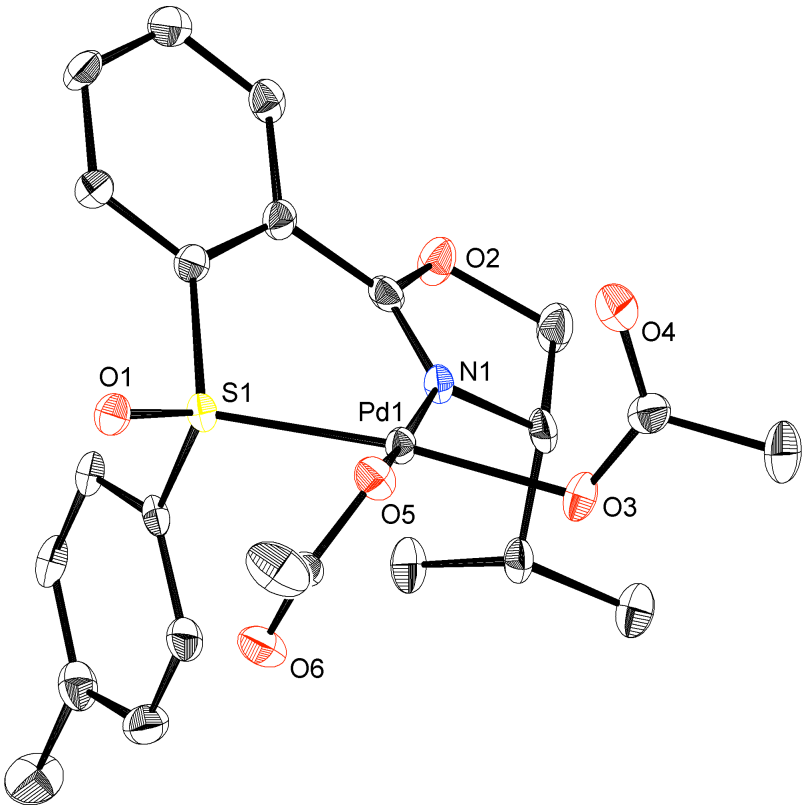
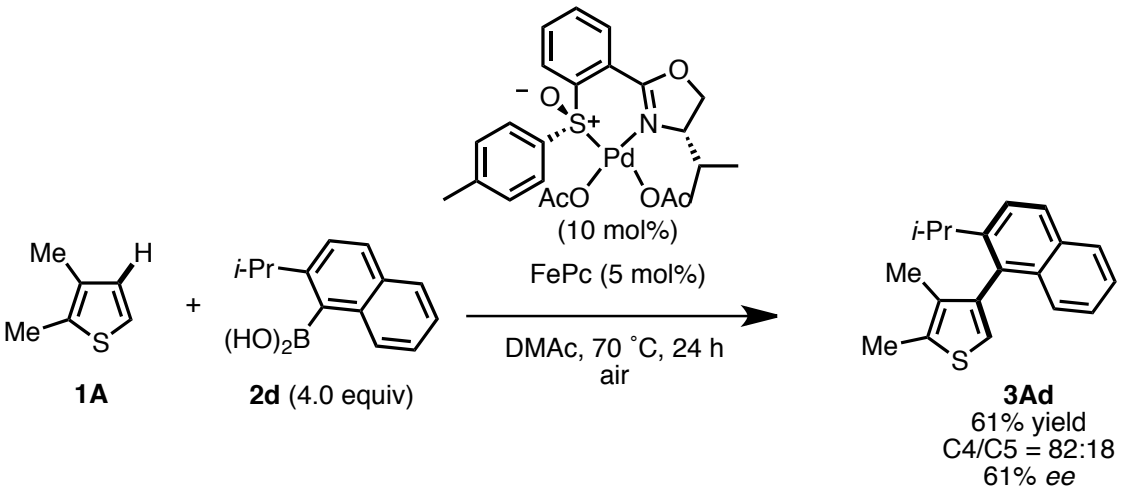


Figure S1. ORTEP drawing of **Pd-sox** with 50% thermal ellipsoid. All hydrogen atoms and solvent molecule are omitted for clarity.

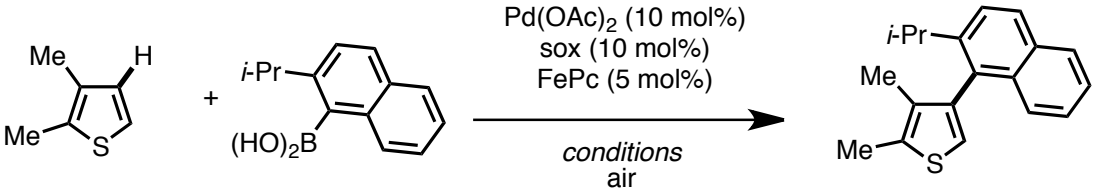
7-1. Enantioselective C–H Coupling



Scheme S1. Enantioselective C–H coupling.

To a screw cap 20 mL glass vessel containing a magnetic stirring bar were added 2,3-dimethylthiophene (**1A**: 28 mg, 0.25 mmol), (2-isopropylnaphtalene-1-yl)boronic acid (**2d**: 214 mg, 1.0 mmol), **Pd-sox** (13.8 mg, 0.025 mmol), FePc (7.1 mg, 0.0125 mmol) and DMAc (0.5 mL). The mixture was stirred at 70 ˚C for 24 h under air, cooled to room temperature, passed through a short pad of silica gel (EtOAc) and the filtrate was evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give (*S*)-**3Ad** (43 mg, 61%, C4/C5 = 82:18, 61% *ee*) as a colorless oil. The enantiomeric excess was determined by HPLC with a Chiracel OD–H column, UV detected at 254 nm, flow rate 1.0 mL/min (hexane). Retention times (tr); major enantiomer tr = 9.6 min, minor enantiomer tr = 7.8 min (HPLC chart is shown in p. S20). According to the literature value[3], the absolute configuration was determined as *S*-configuration.

7-2. Reaction Optimization of Enantioselective C–H Coupling



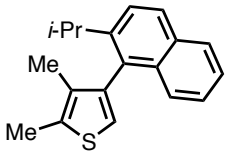
1A **2d** (4.0 equiv) **3Ad**

Entry	Solvent	Conc/ M	Temp/ ˚C	Time/ h	Yield/ %	C4/C5	ee/ %
1	DMF	1.25	80	12	70	90/10	45
2	DMAc	1.25	80	12	57	86/14	55
3	DMAc	0.5	80	24	54	85/15	58
4	DMAc	0.5	70	24	61	82/18	61
5[a]	DMAc	0.5	70	12	57	85/15	58
6[a]	DMAc	0.5	70	24	77	85/15	59
7	DMAc	0.5	60	24	52	87/13	54

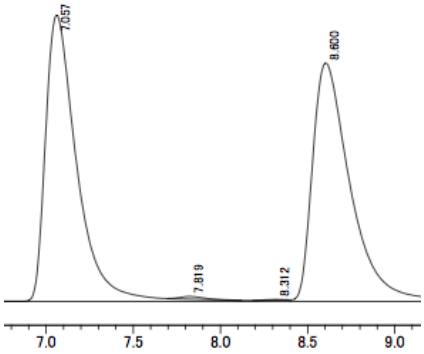
a: 20 mol% of ligand (sox) was used.

8. HPLC Chart of 3Ad

racemate



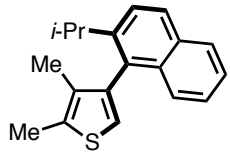
(±)-**3Ad**



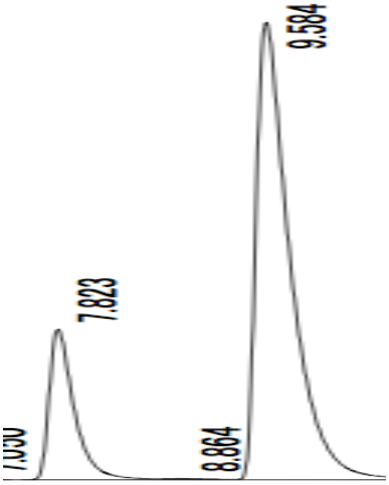
OD-H ®
254 nm
hexane
1.0 mL/min

retention time	area
7.057	13491841
7.819	94676
8.312	15780
8.600	13263610

enantiomeric enriched



(*S*)-**3Ad**



retention time	area
7.823	4493284
8.864	13356
9.584	18635546

9. References

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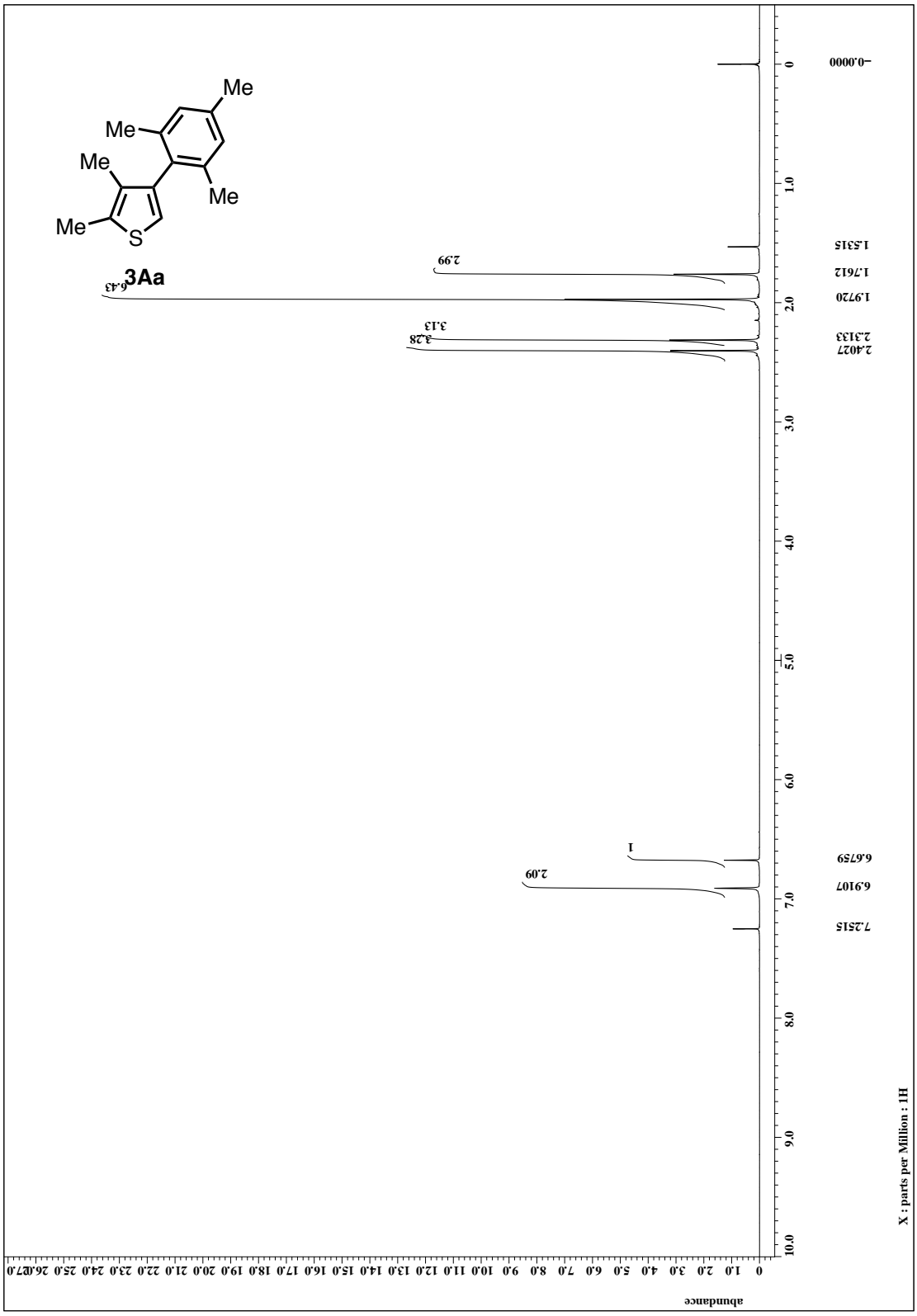
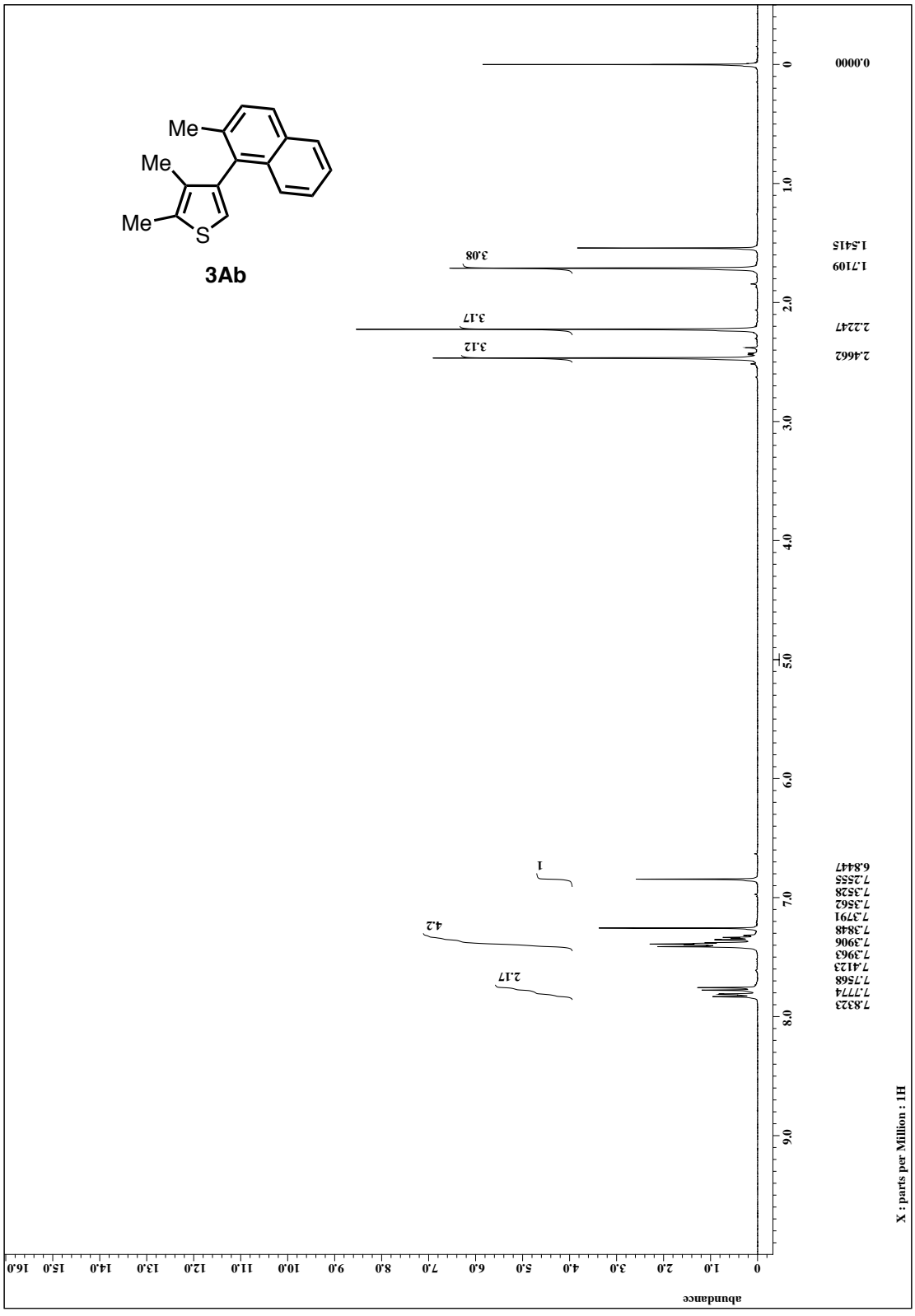
10. ^{1}H NMR and ^{13}C NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$) of 3Aa:

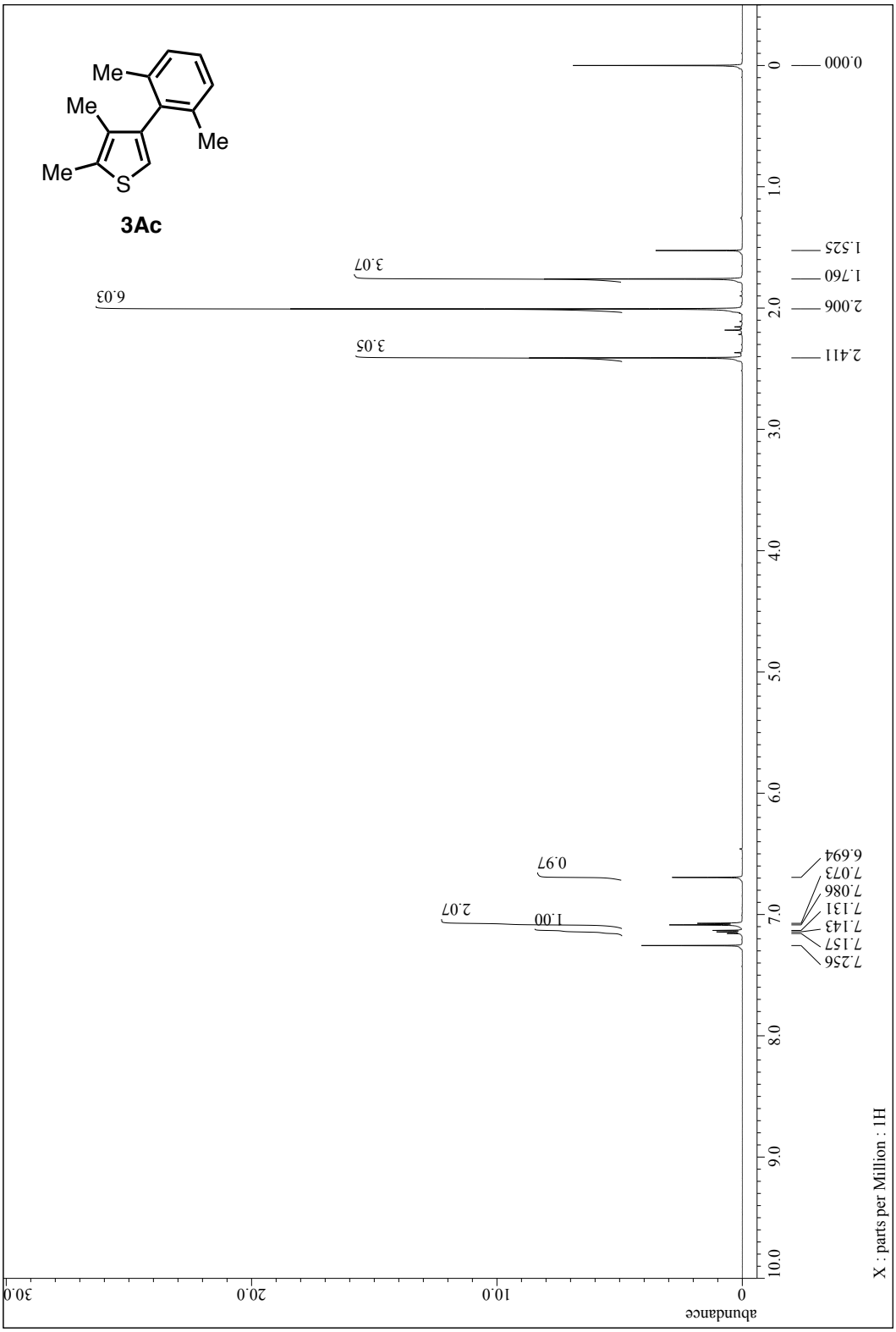


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

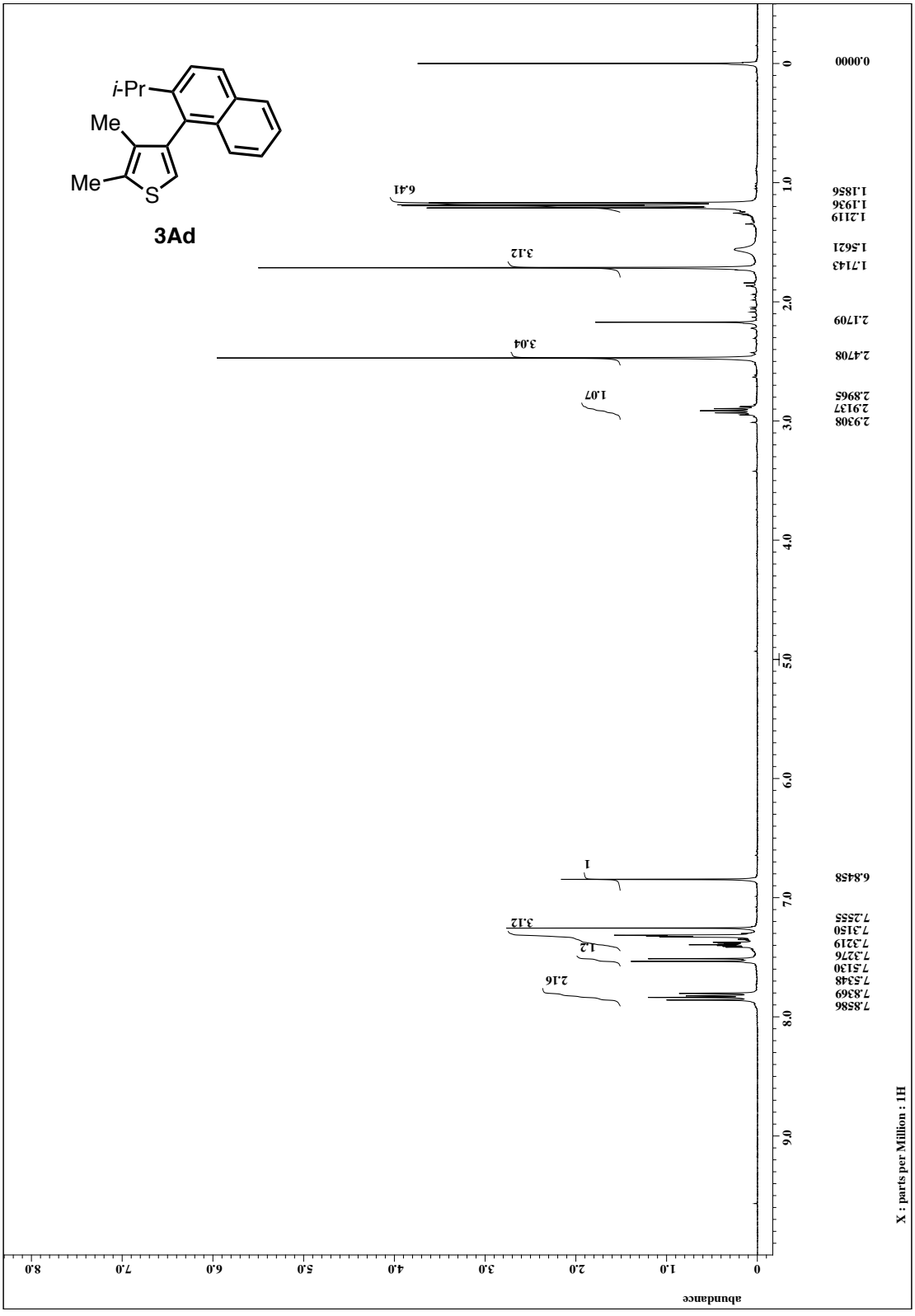
^{1}H NMR (400 MHz, $CDCl_3$) of 3Ab:



^{1}H NMR (600 MHz, $CDCl_3$) of 3Ac:

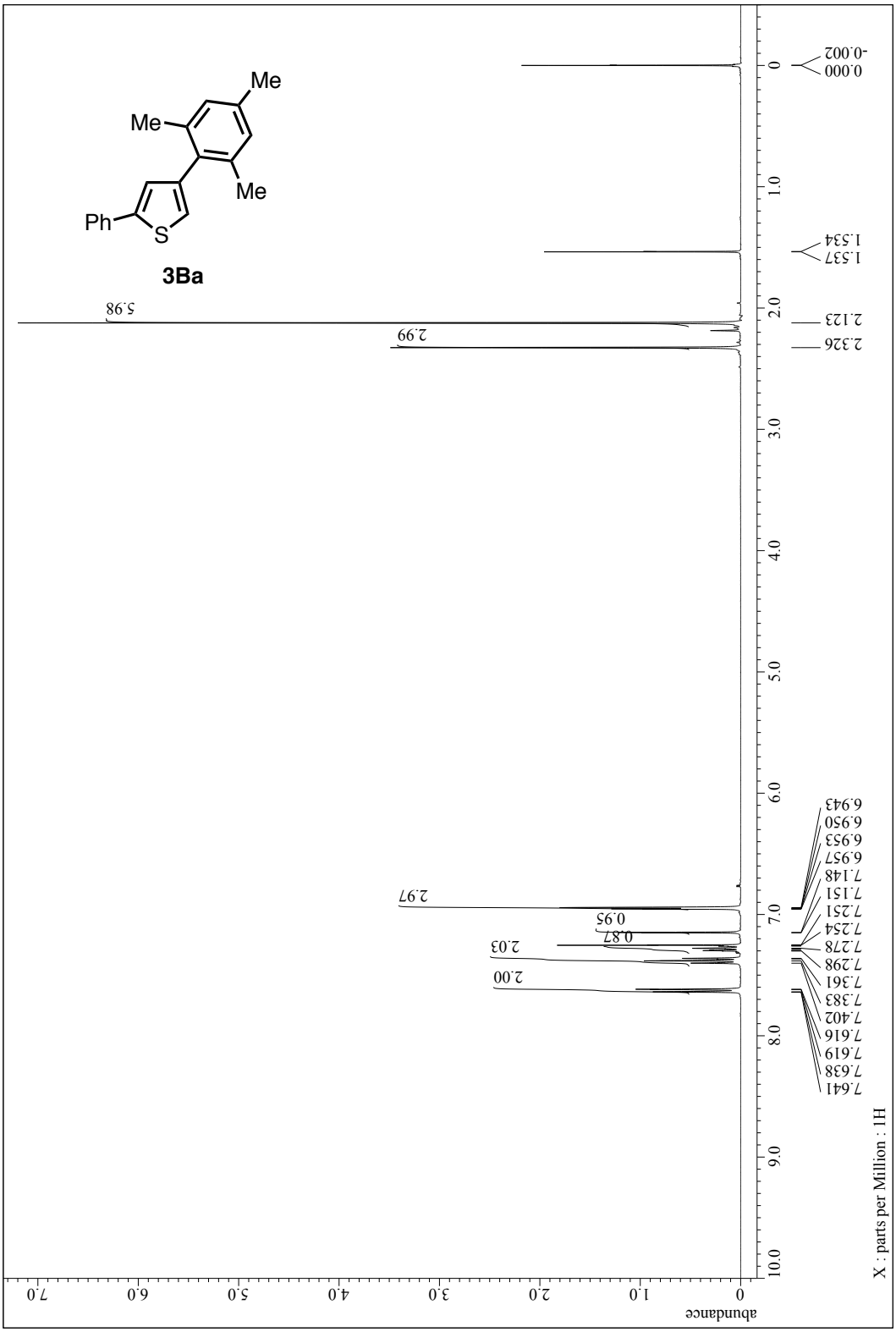


^{1}H NMR (400 MHz, $CDCl_3$) of 3Ad:

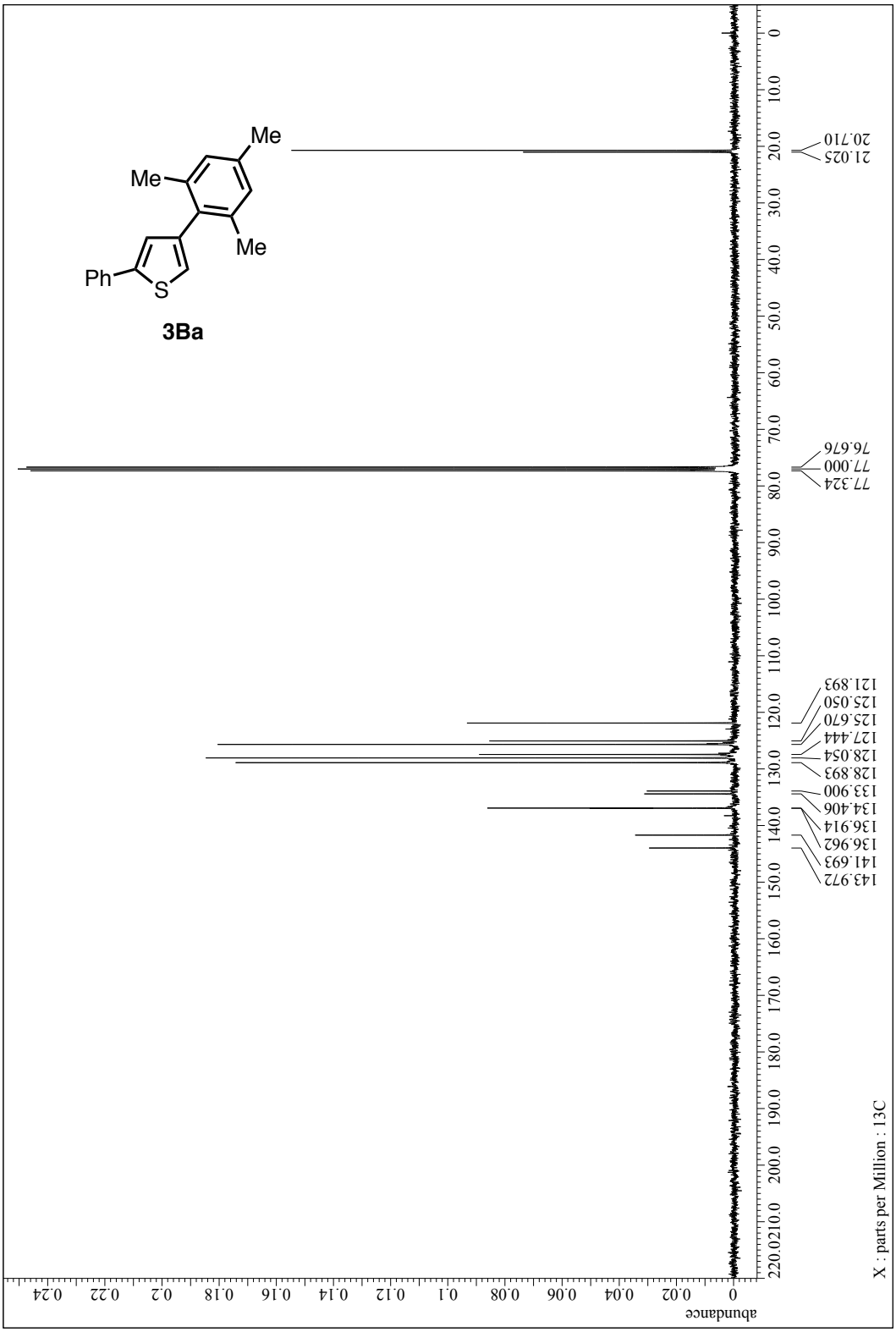


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Ba:

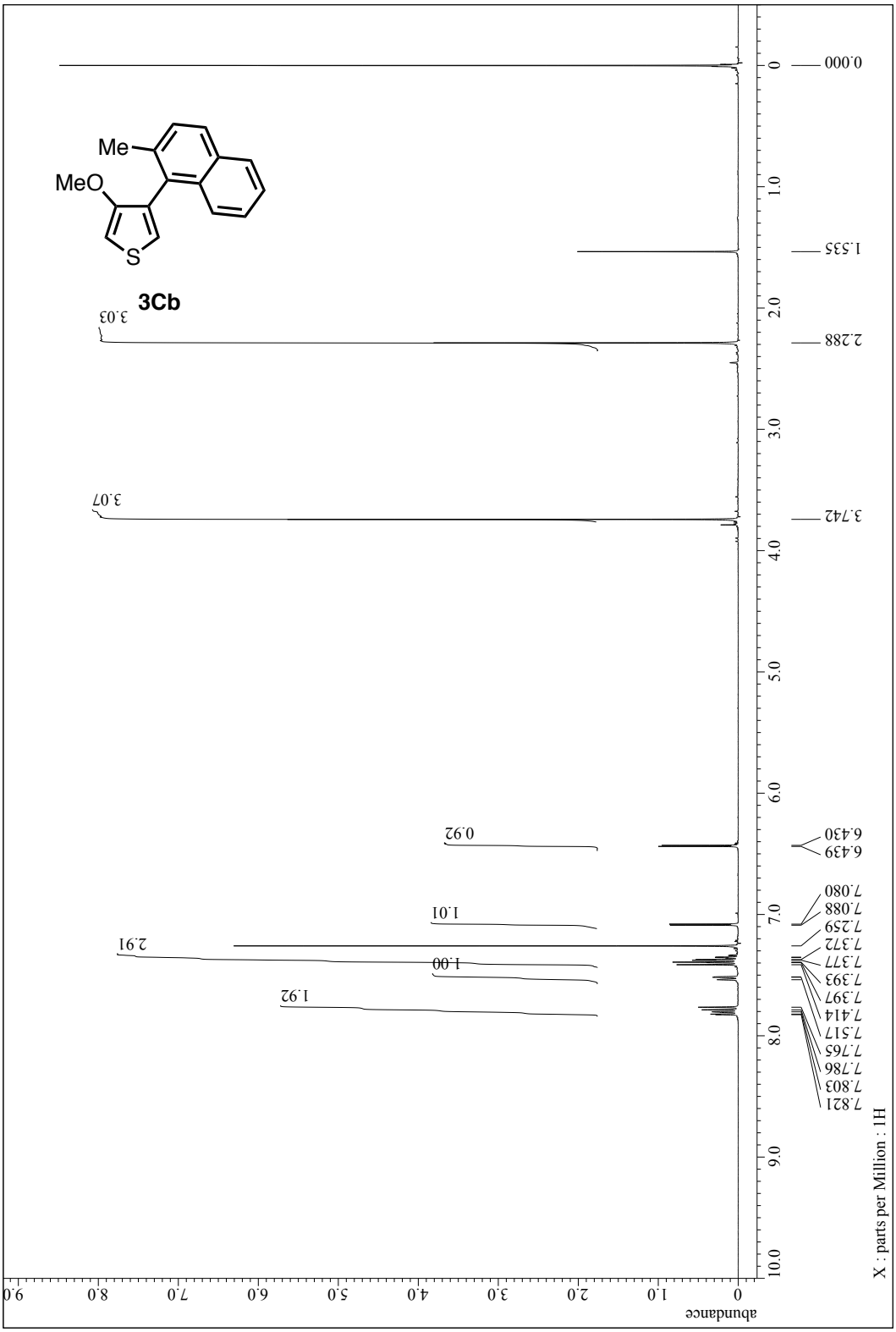


^{13}C NMR (100 MHz, $CDCl_3$) of 3Ba:

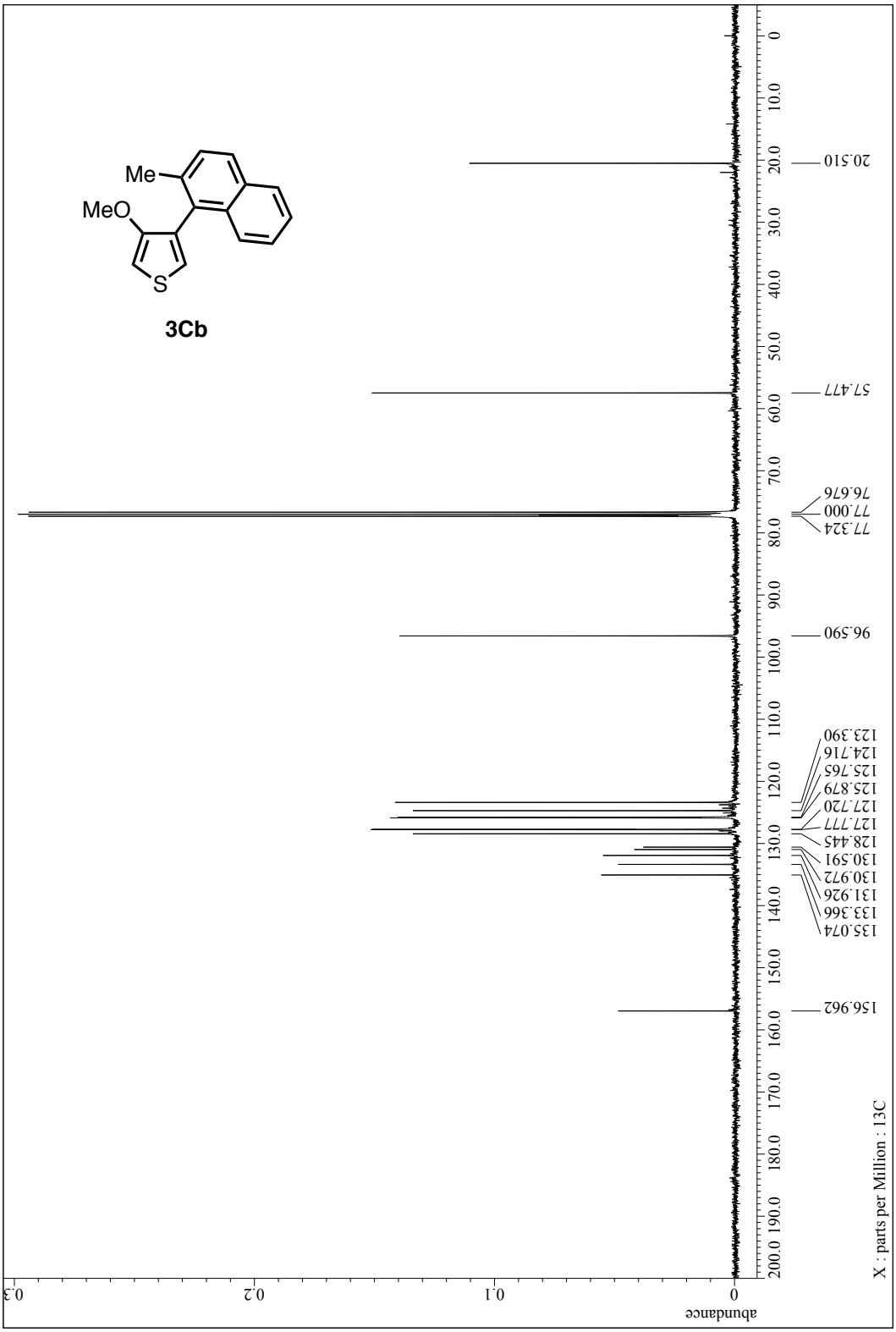


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Cb:

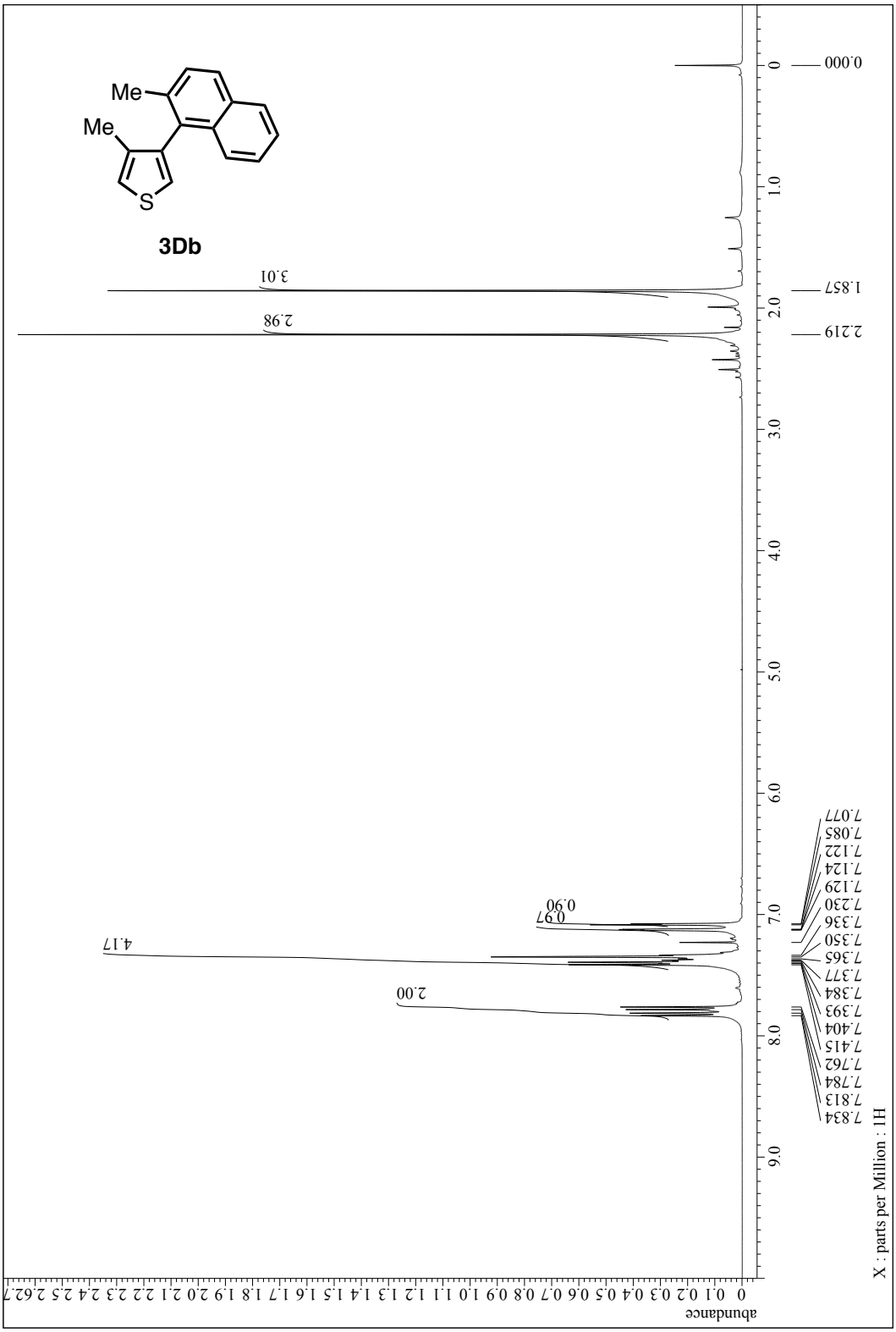


^{13}C NMR (100 MHz, $CDCl_3$) of 3Cb:



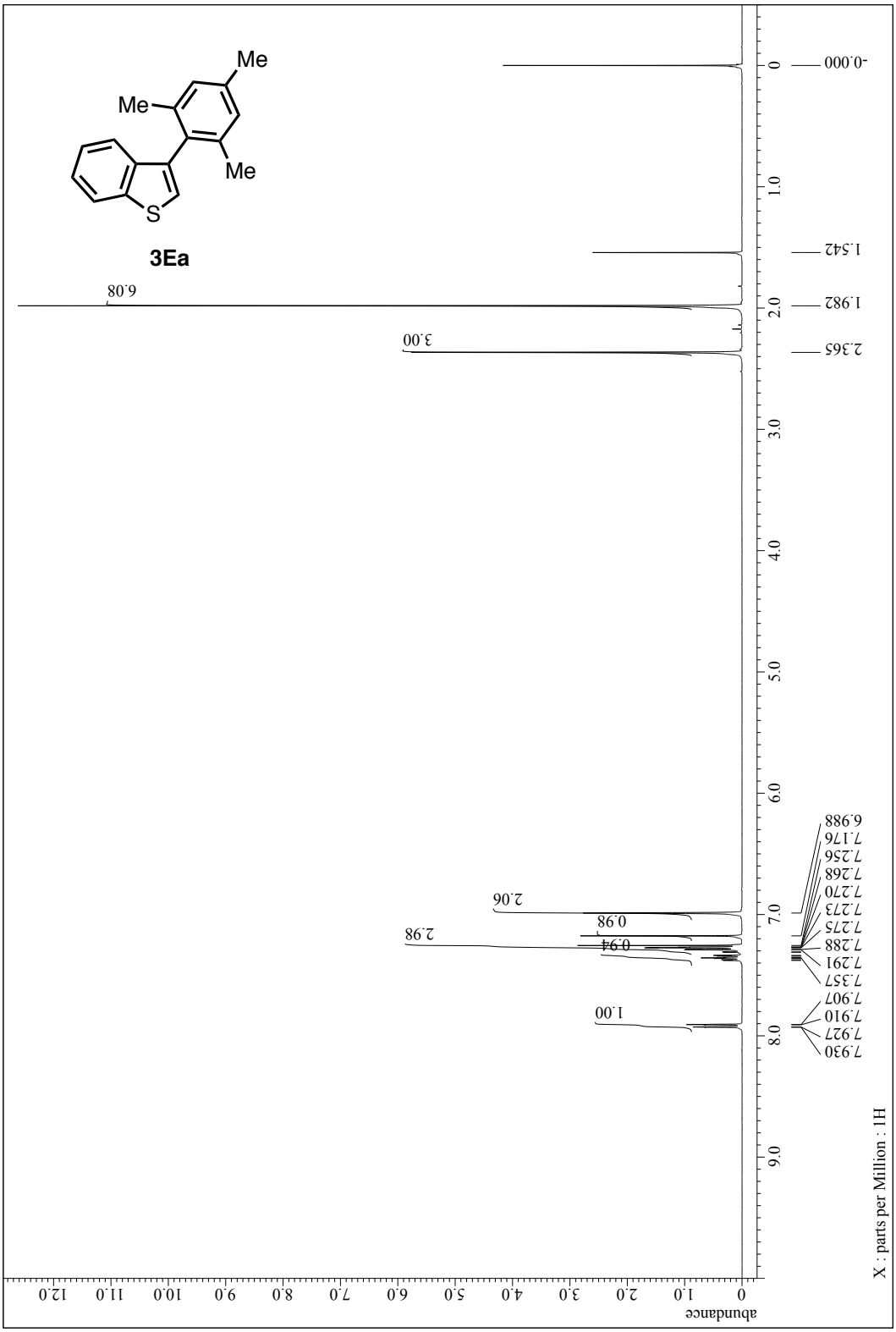
Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Db:

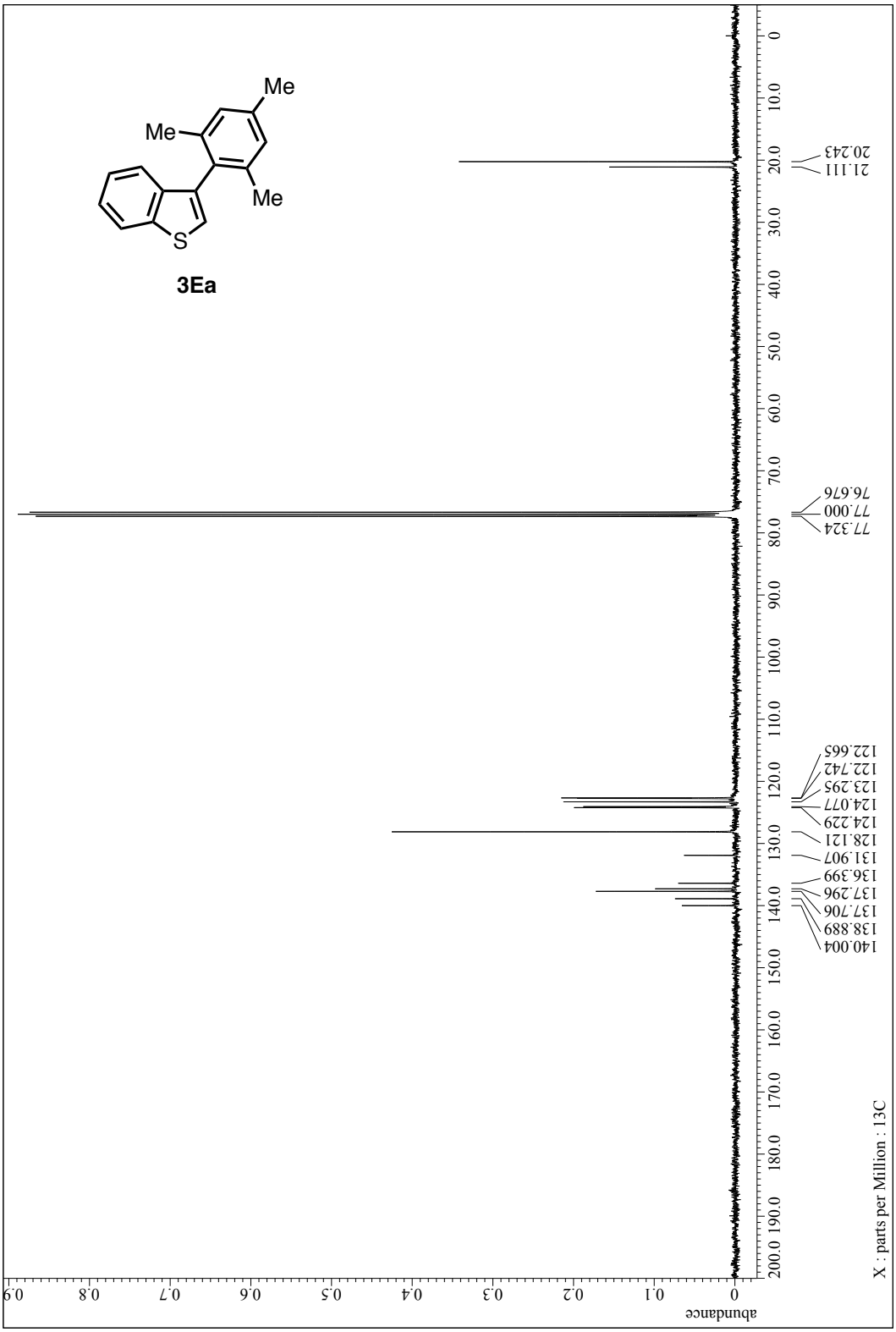


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Ea:

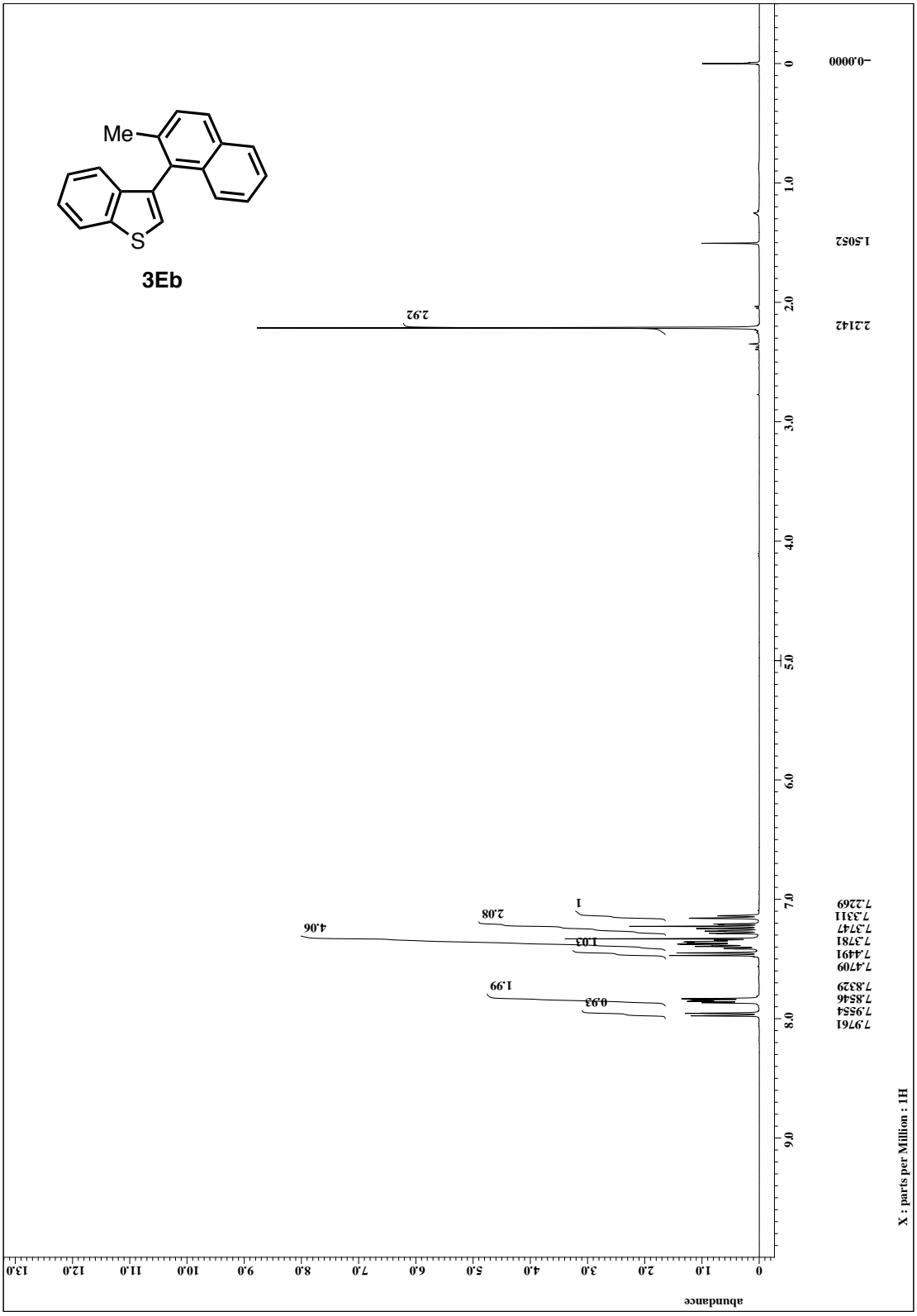


^{13}C NMR (100 MHz, $CDCl_3$) of 3Ea:



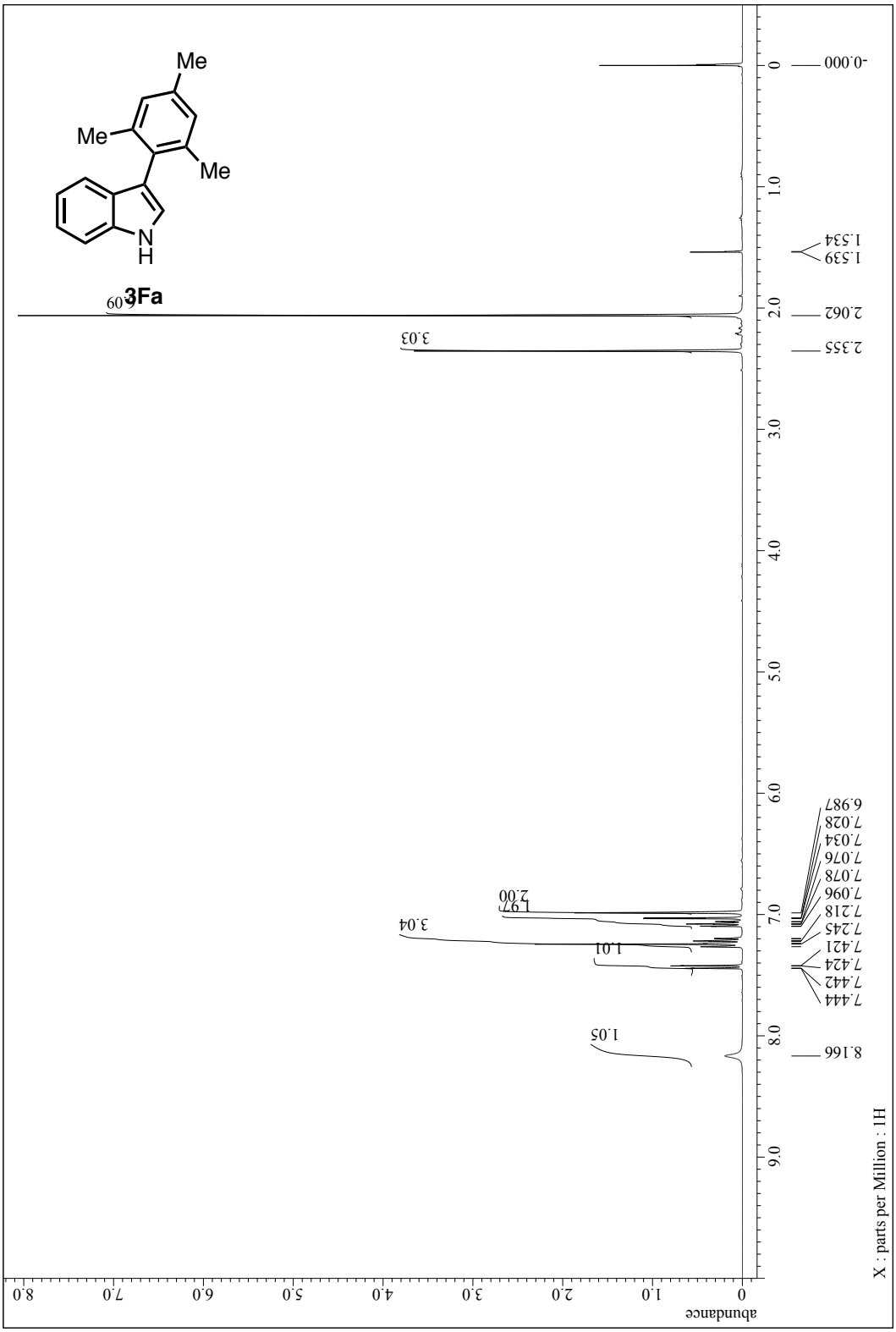
Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Eb:

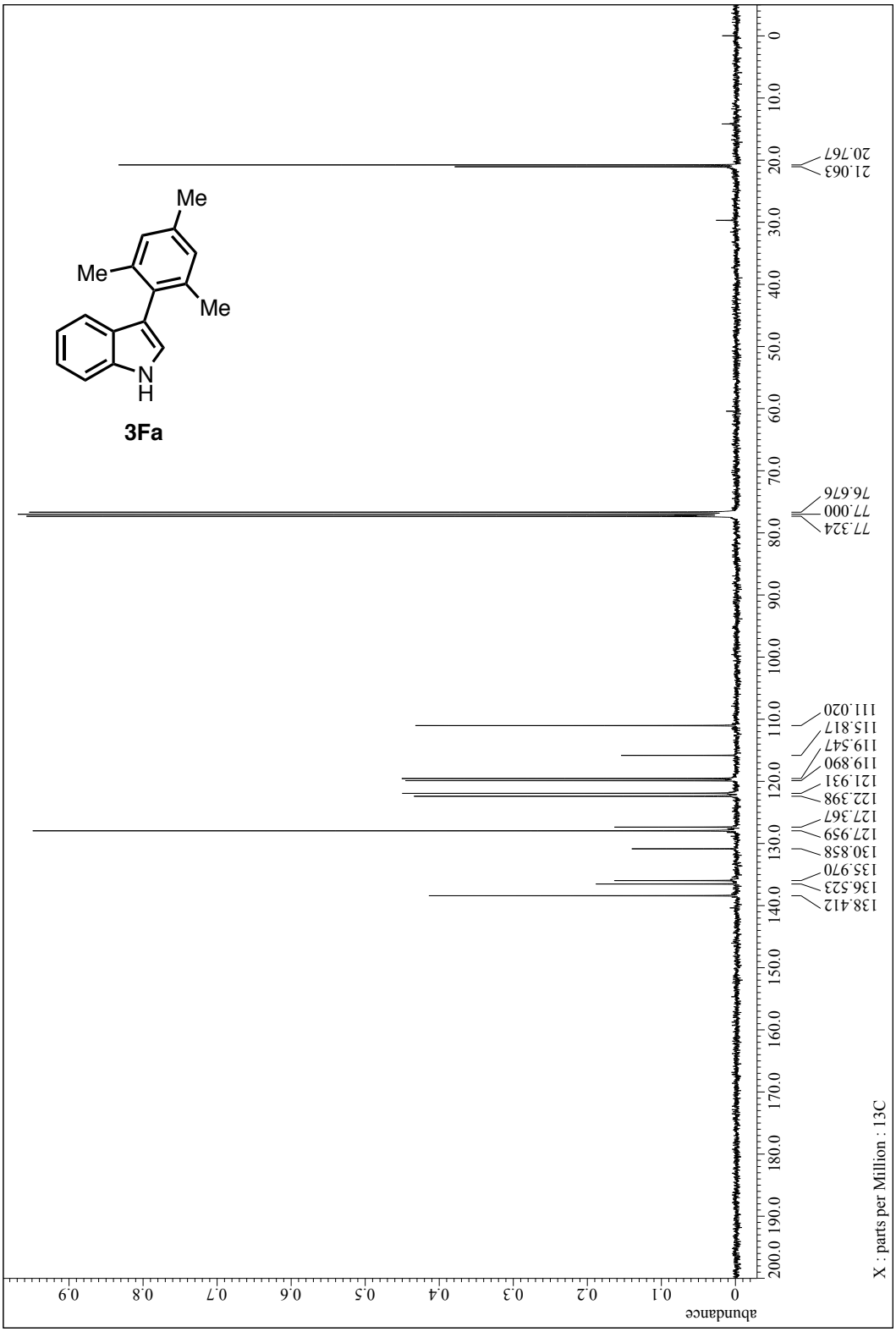


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Fa:

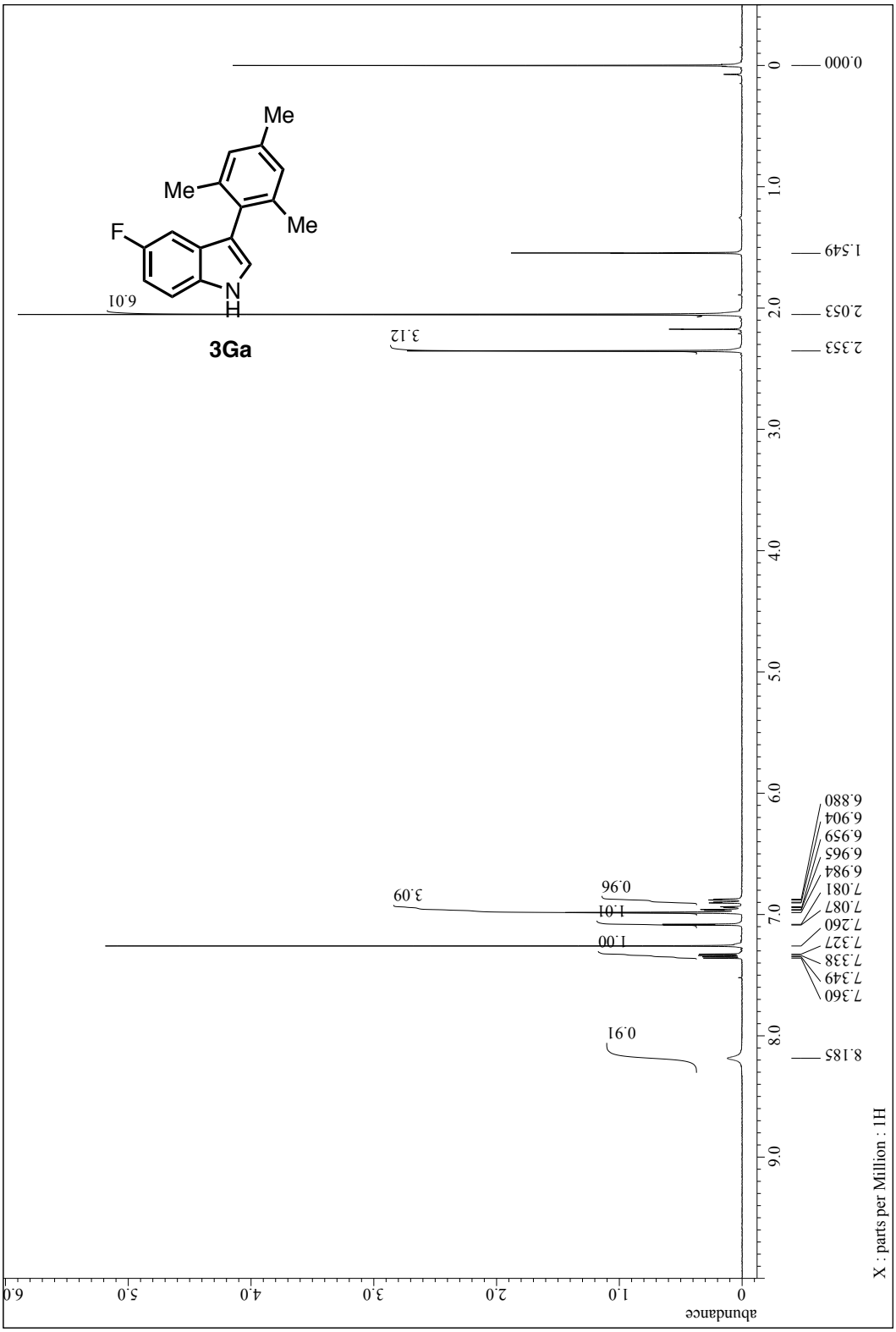


^{13}C NMR (100 MHz, $CDCl_3$) of 3Fa:

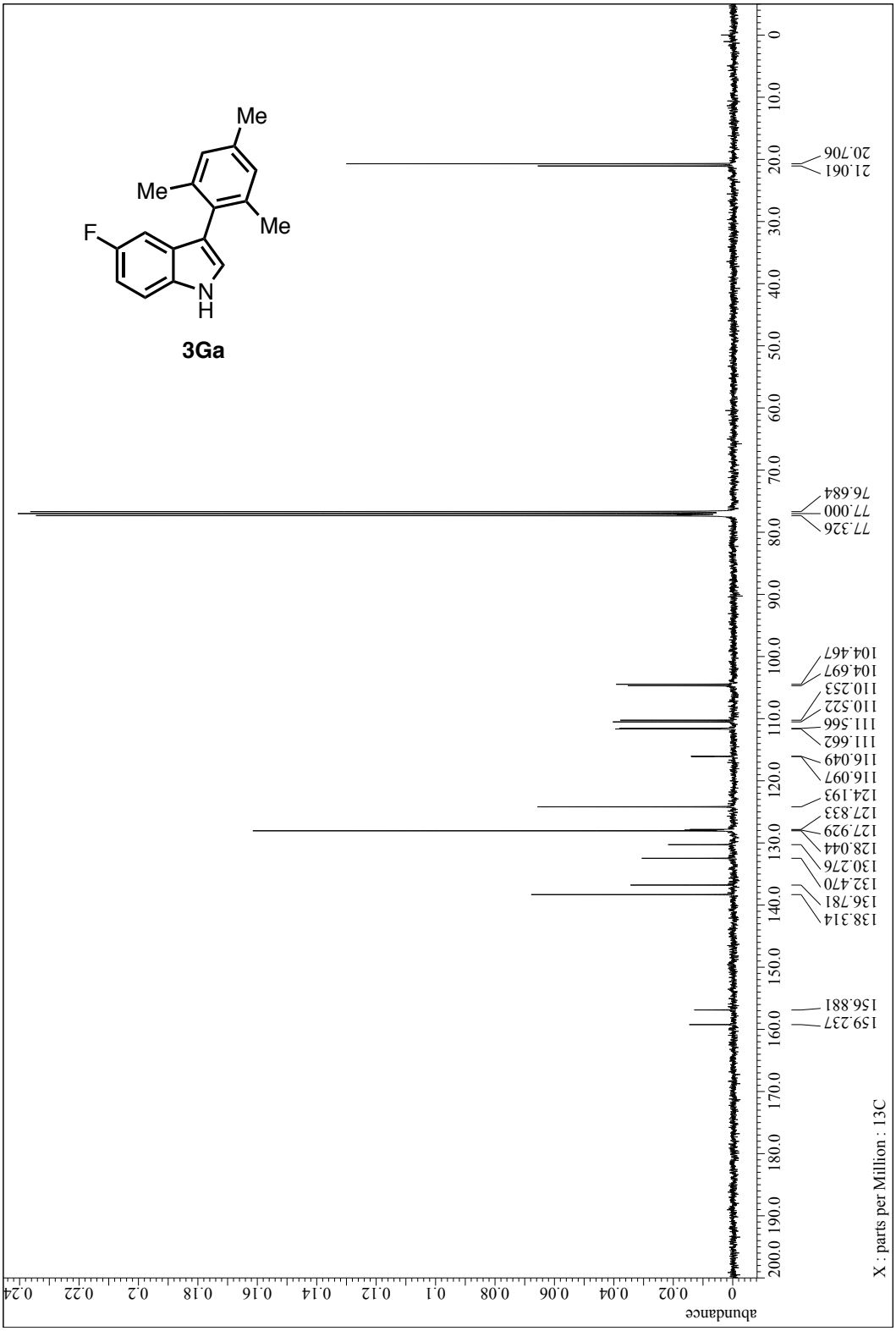


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Ga:

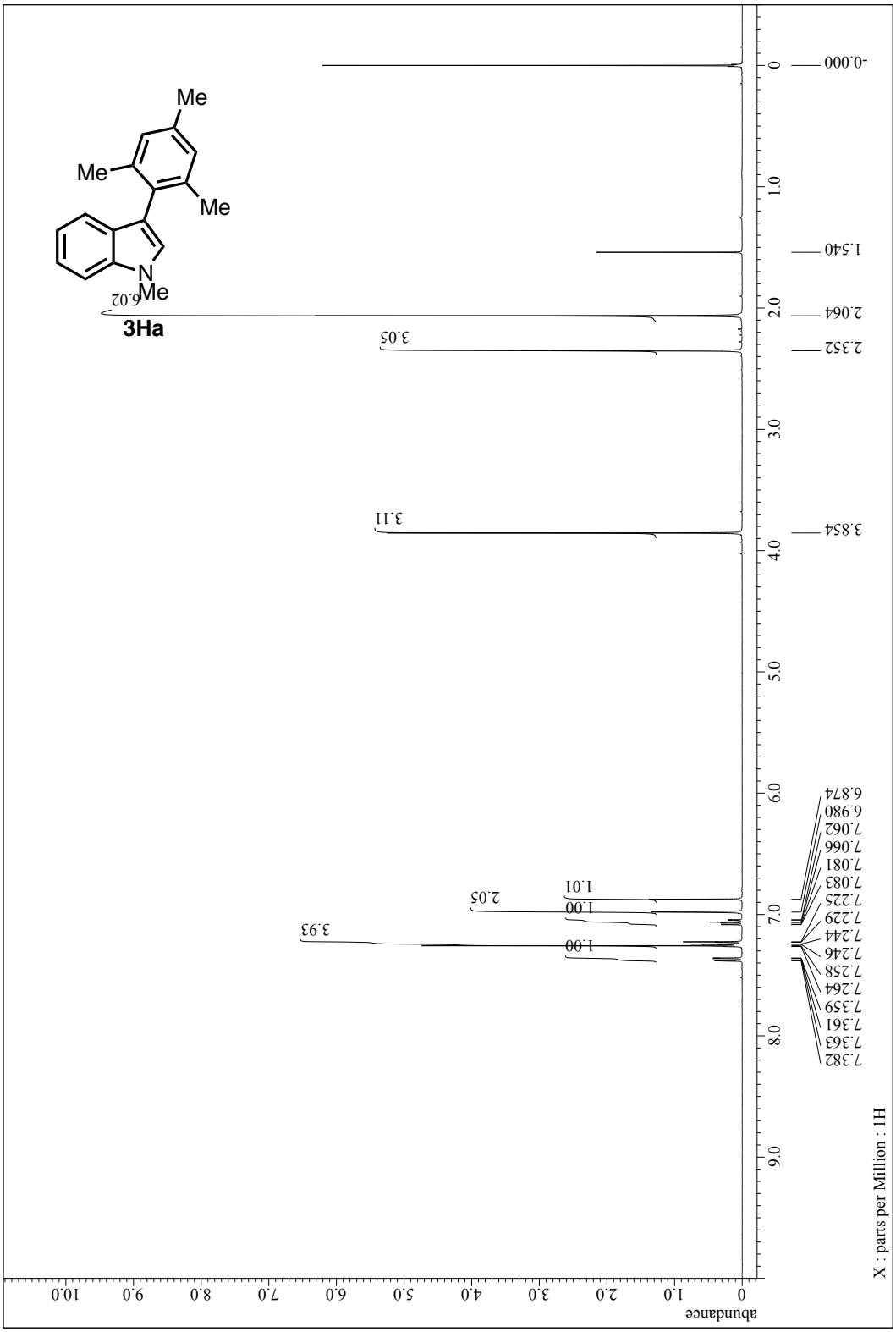


^{13}C NMR (100 MHz, $CDCl_3$) of 3Ga:

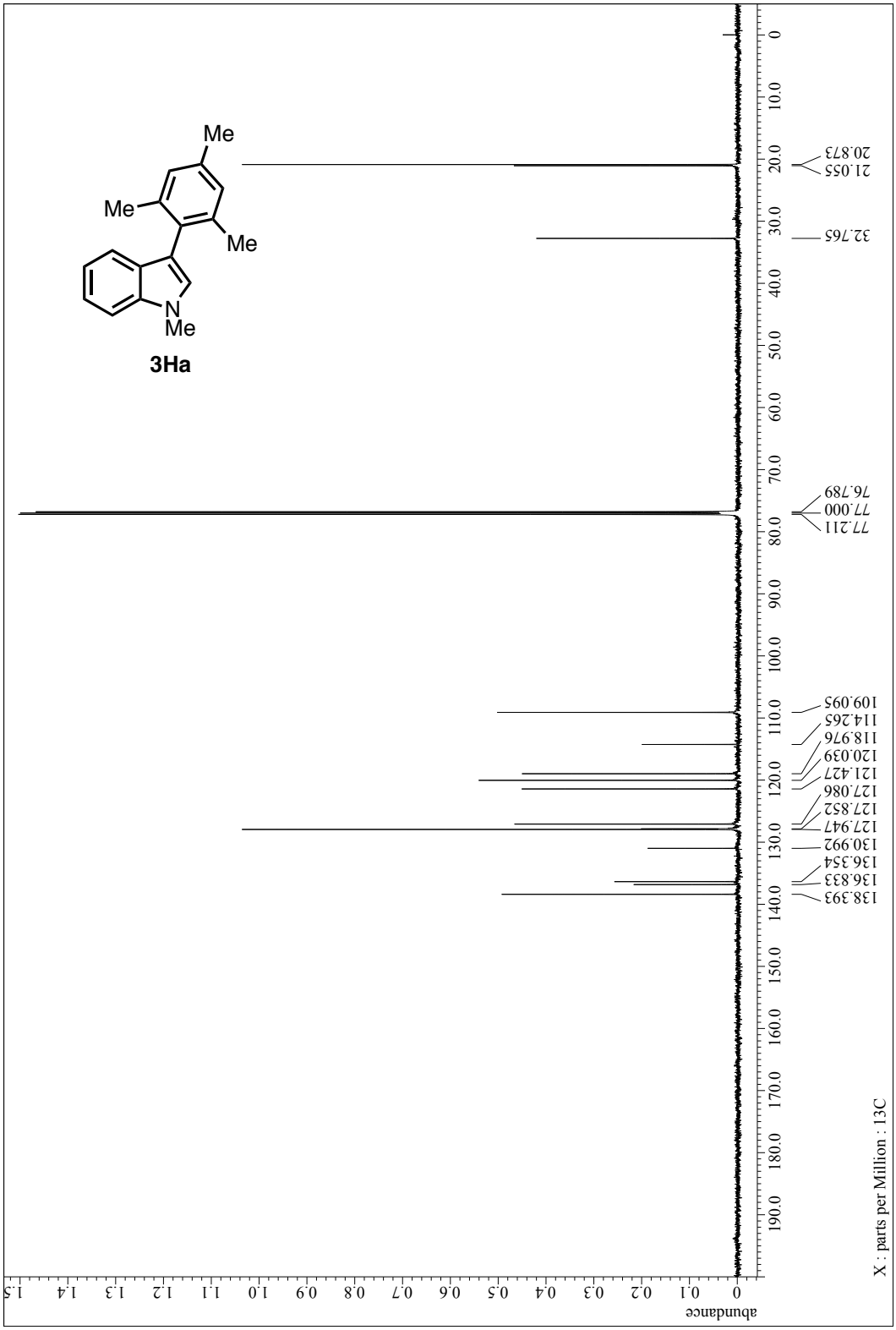


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 3Ha:

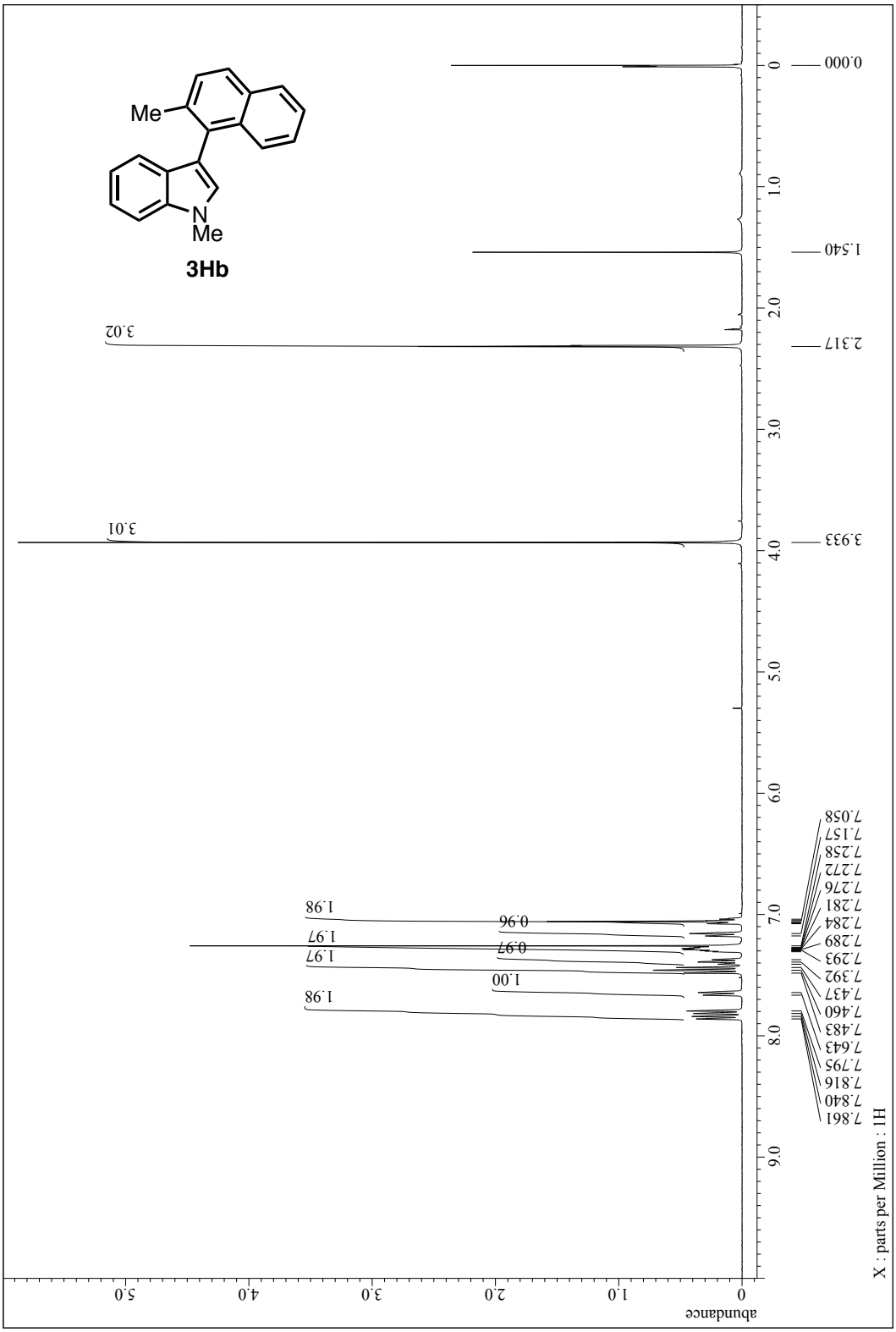


^{13}C NMR (150 MHz, $CDCl_3$) of 3Ha:

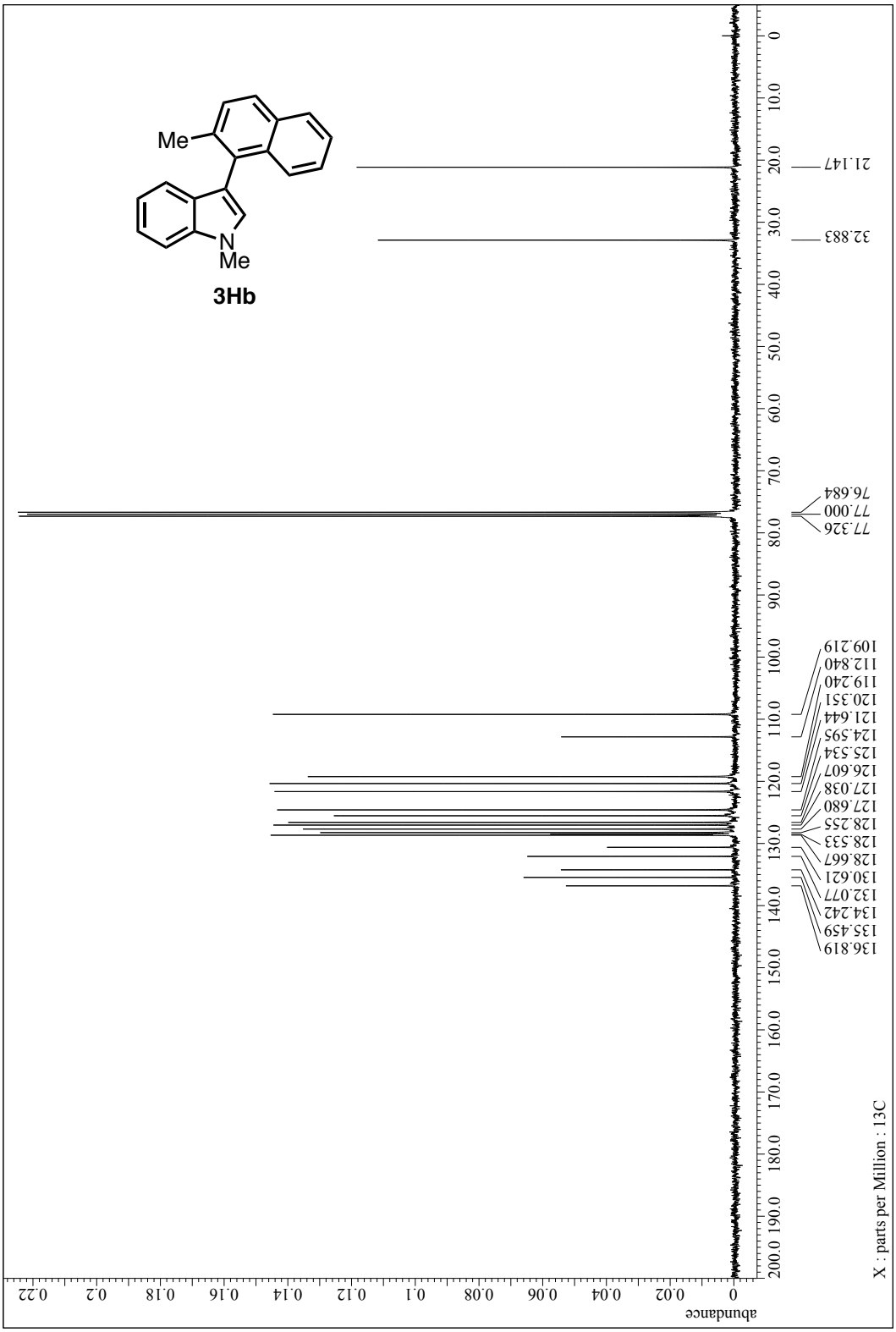


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

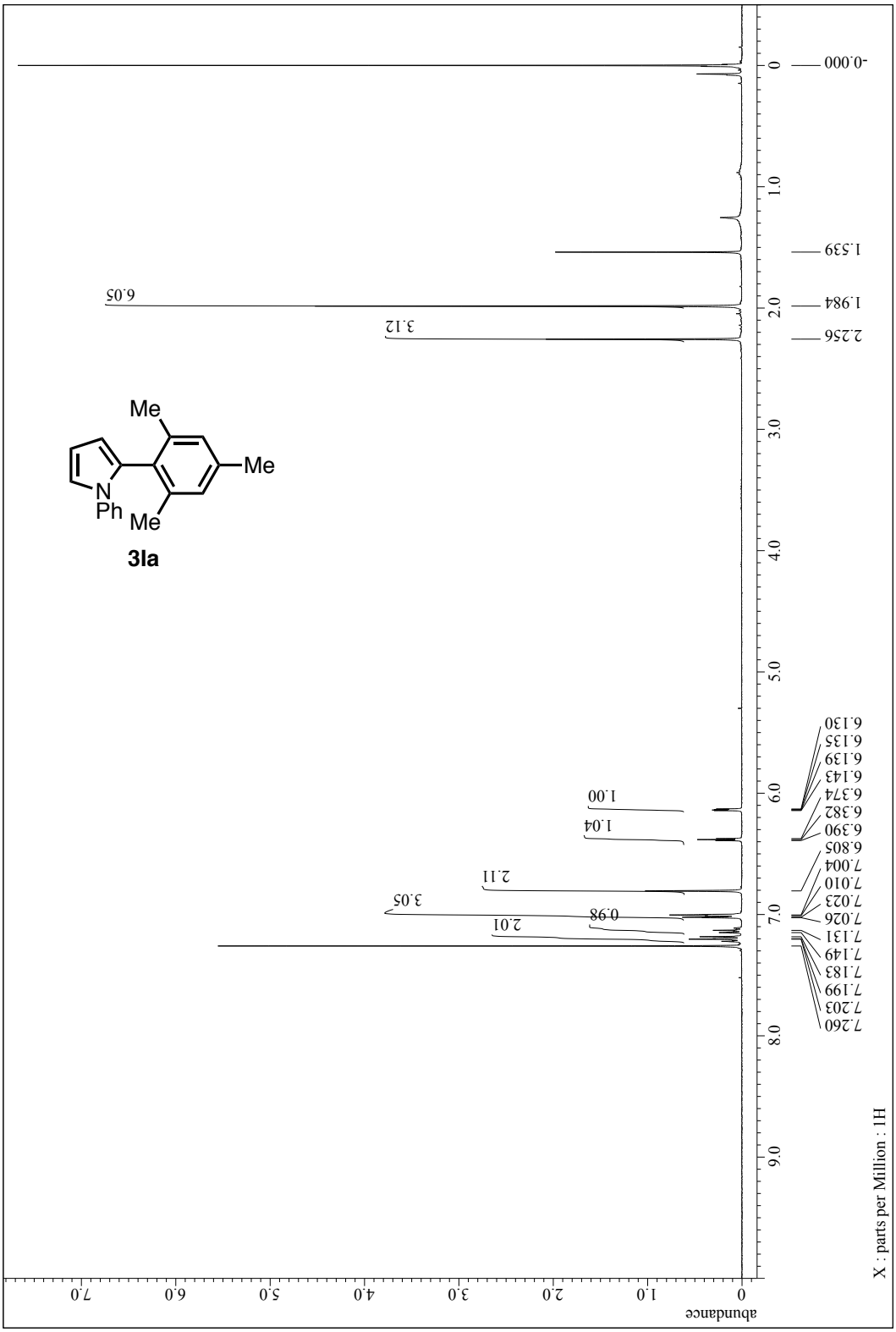
^{1}H NMR (400 MHz, $CDCl_3$) of 3Hb:



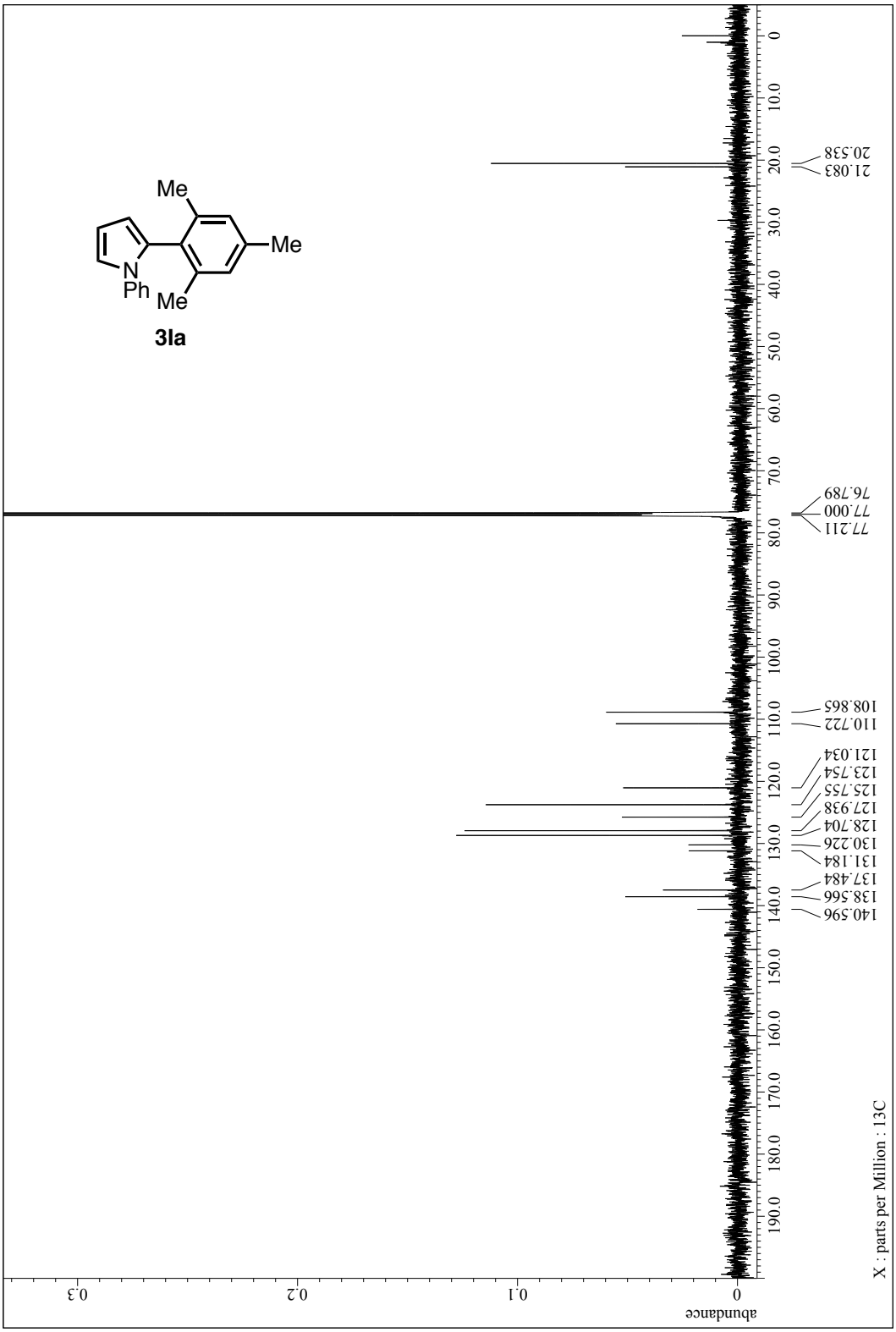
^{13}C NMR (100 MHz, $CDCl_3$) of 3Hb:



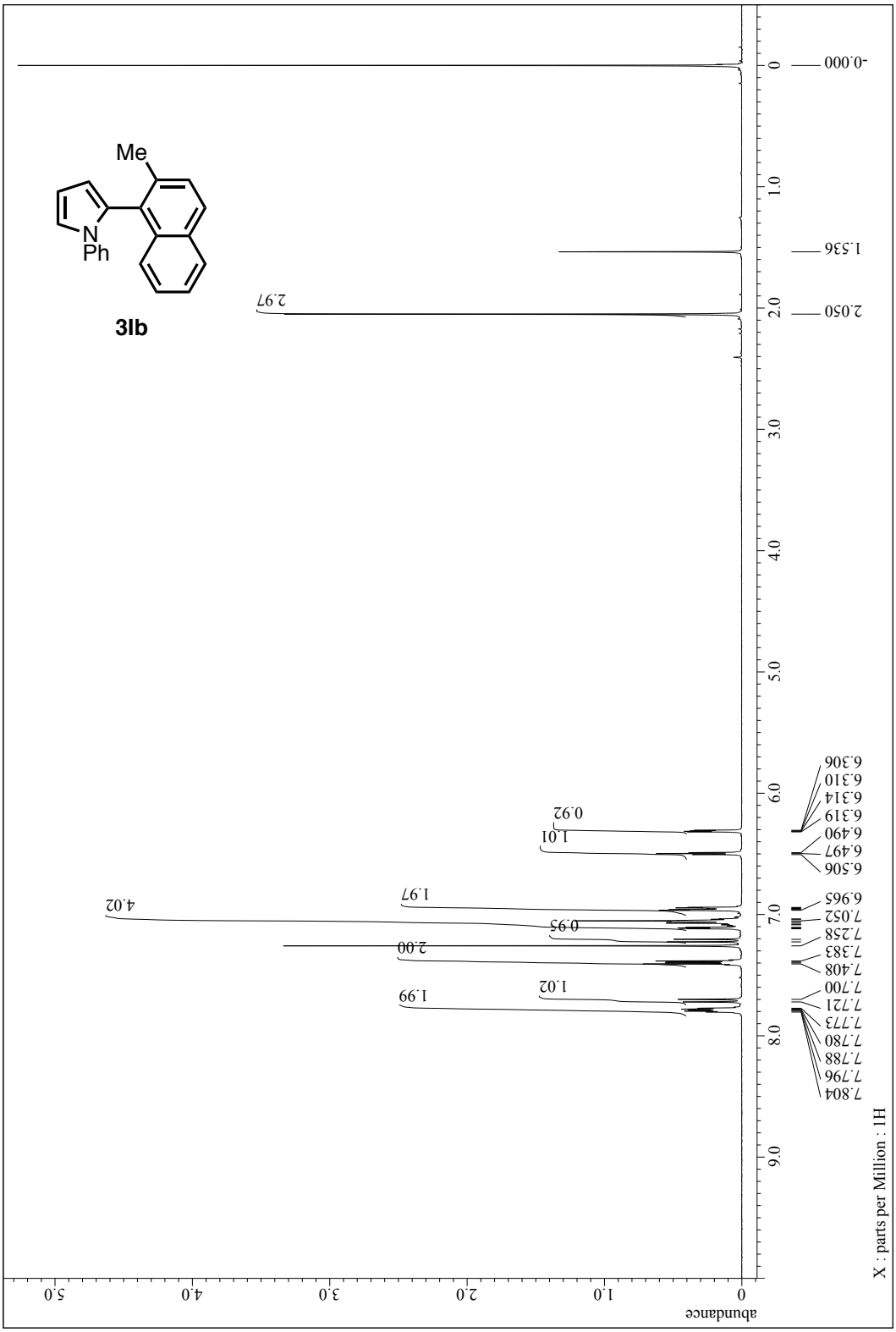
^{1}H NMR (400 MHz, $CDCl_3$) of 3Ia:



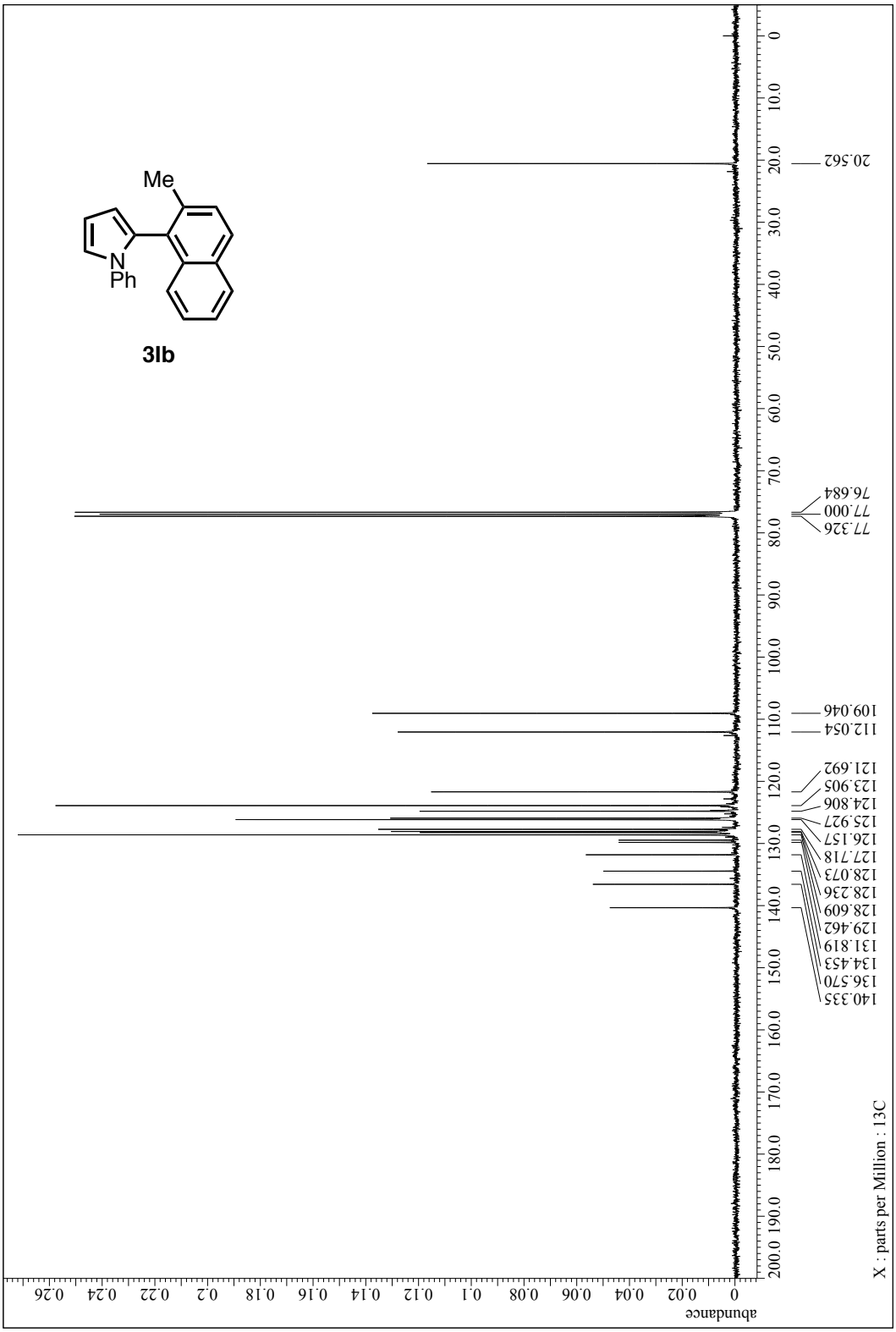
^{13}C NMR (150 MHz, $CDCl_3$) of 3Ia:



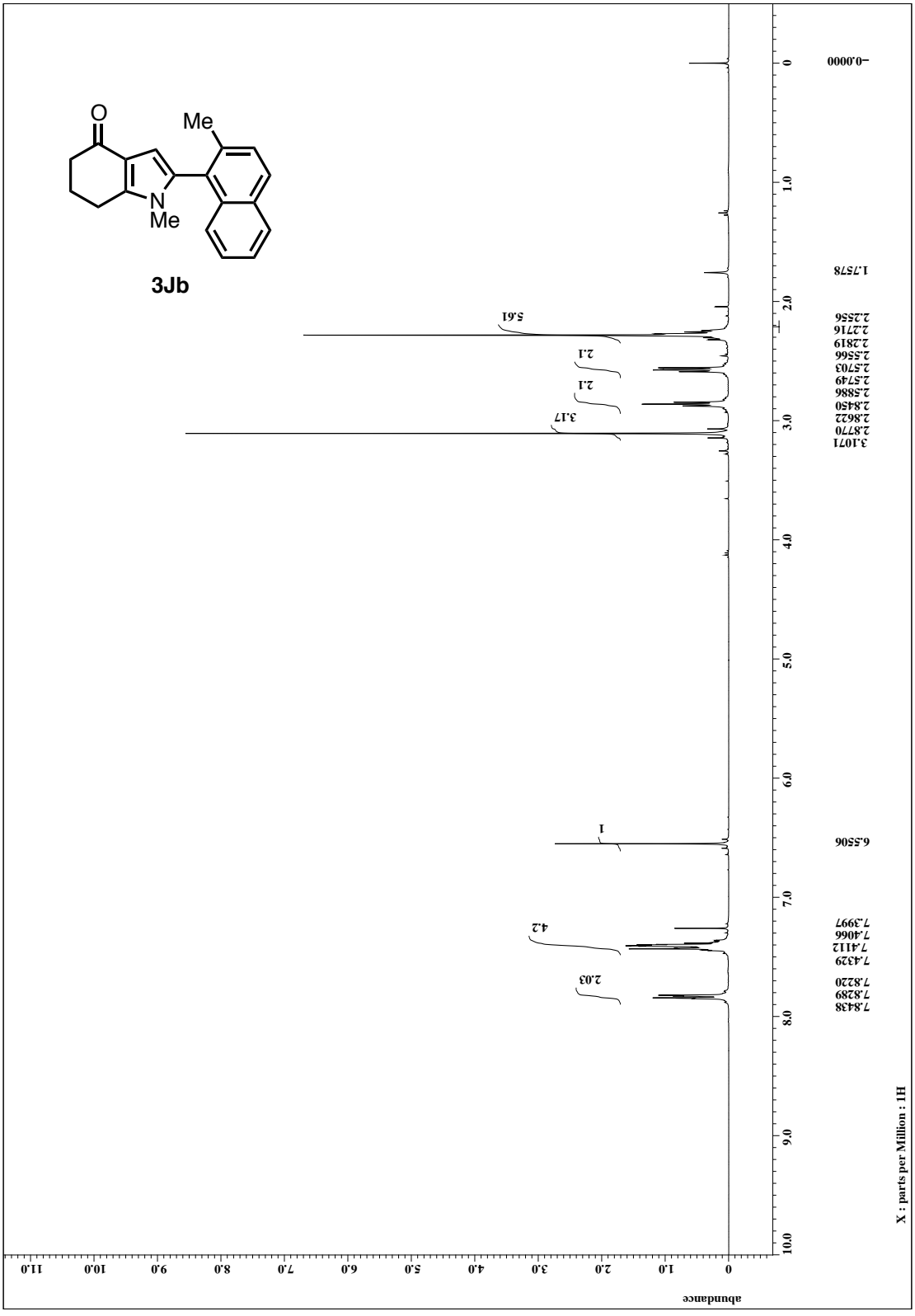
^{1}H NMR (400 MHz, $CDCl_3$) of 3Ib:



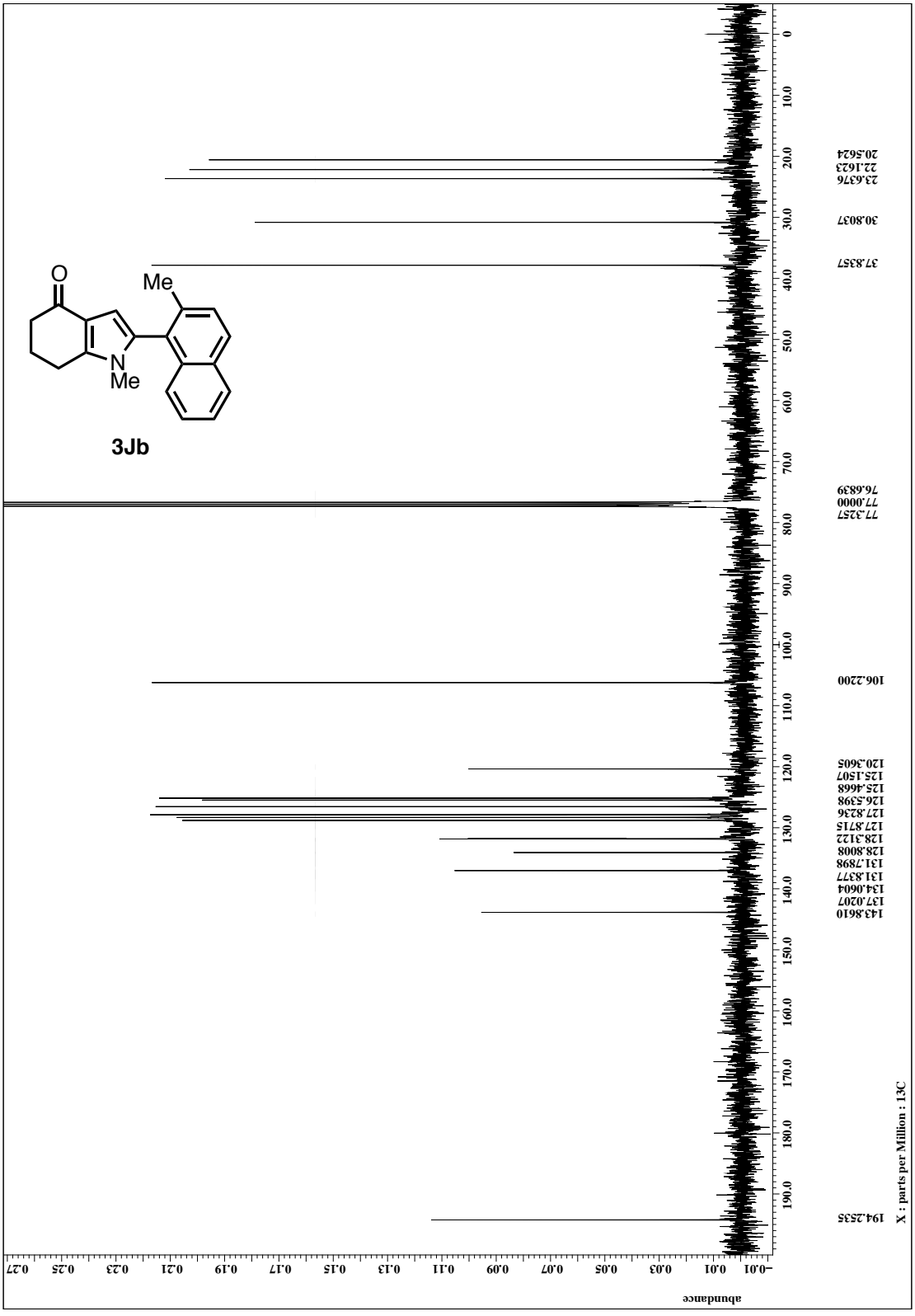
^{13}C NMR (100 MHz, $CDCl_3$) of 3Ib:



^{1}H NMR (400 MHz, $CDCl_3$) of 3 Jb:

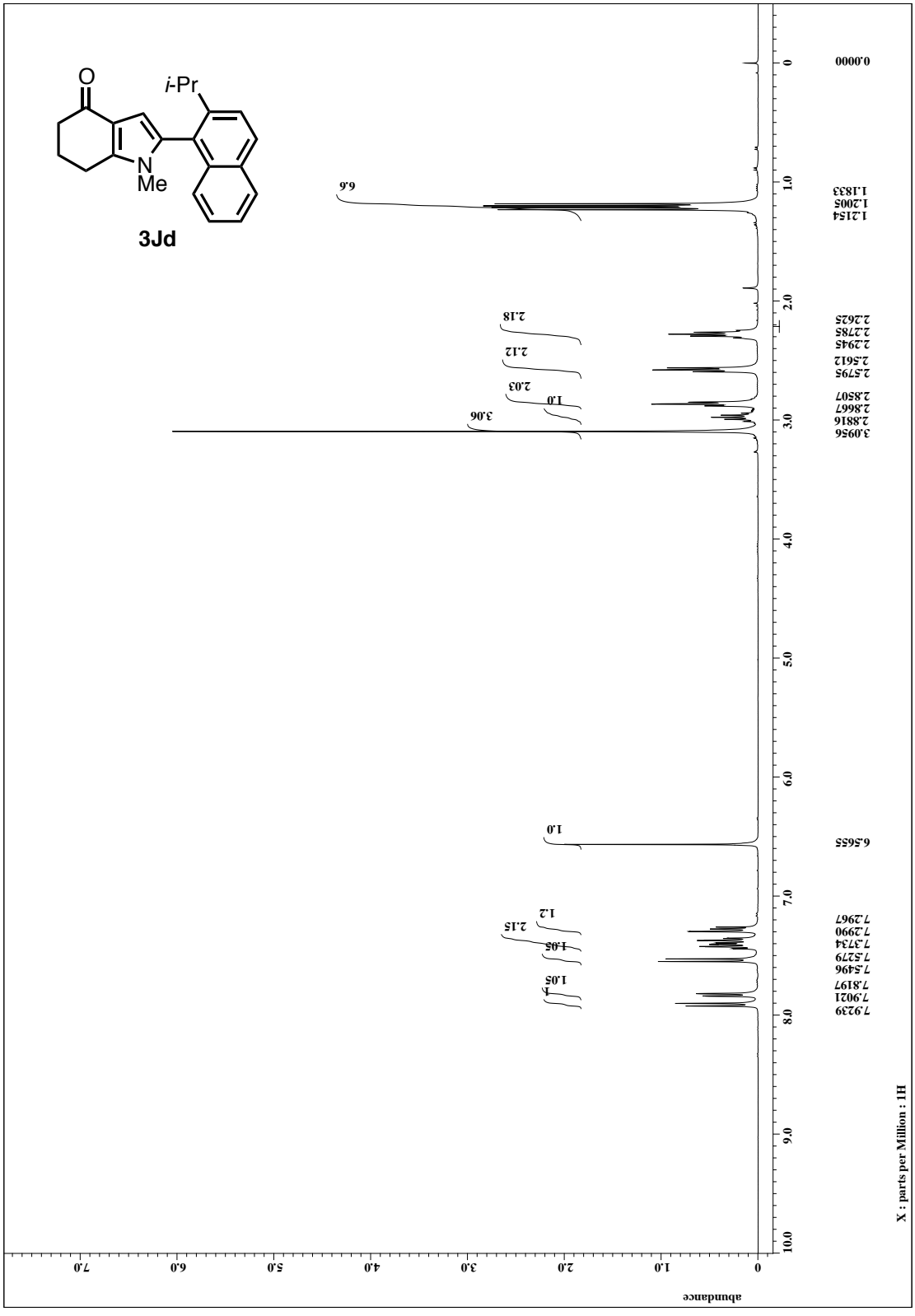


^{13}C NMR (100 MHz, $CDCl_3$) of 3Jb:

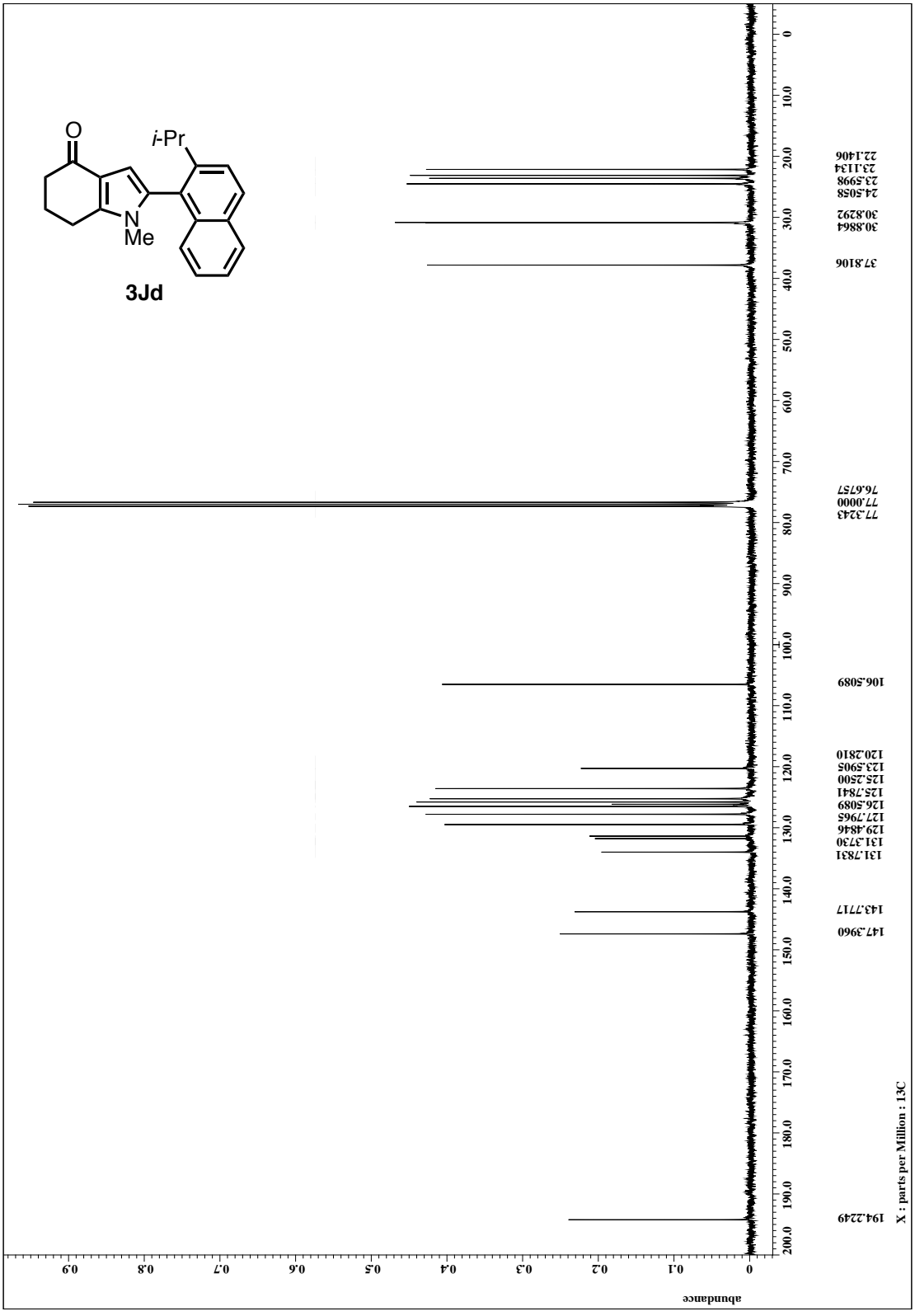


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

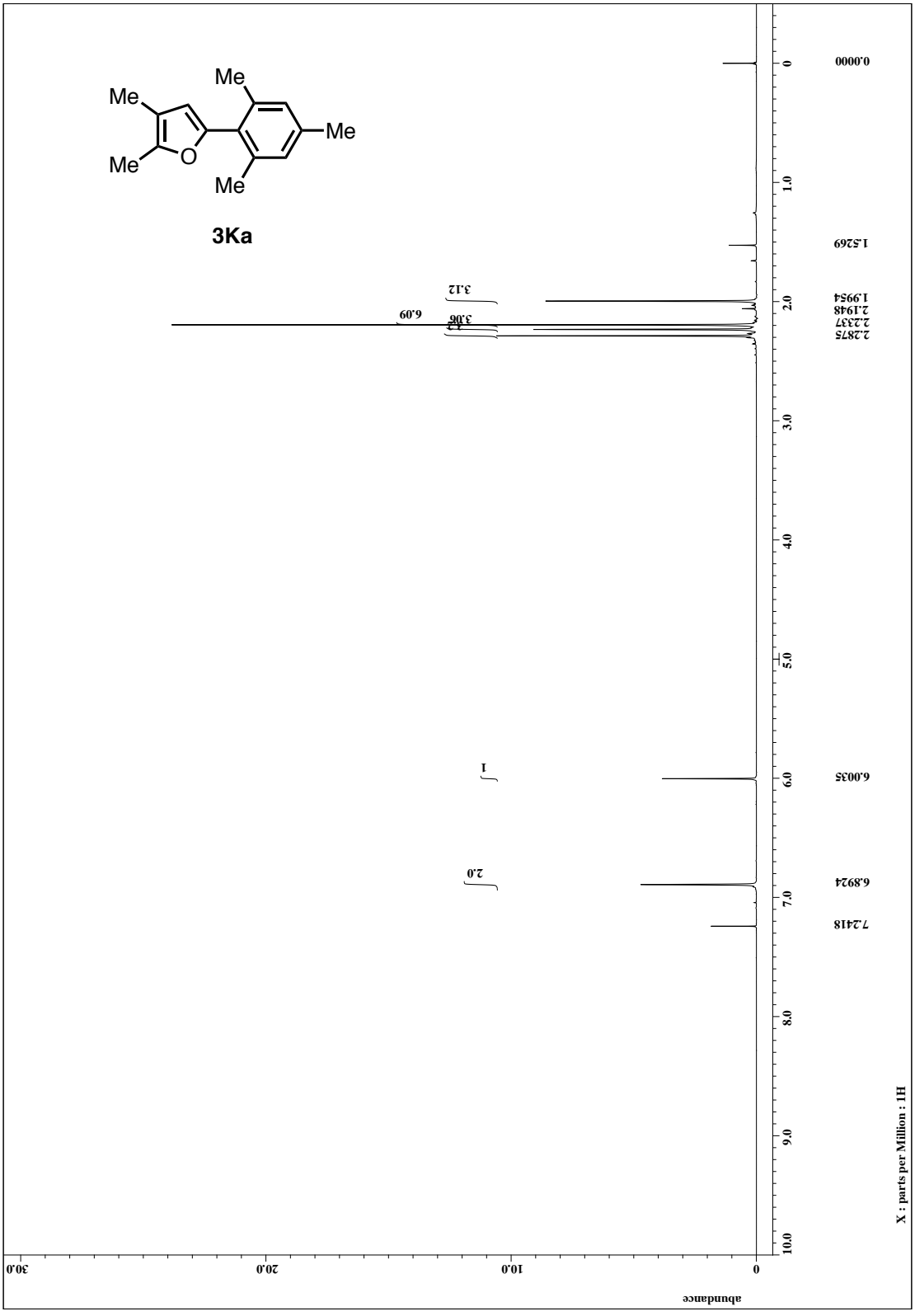
^{1}H NMR (400 MHz, $CDCl_3$) of 3Jd:



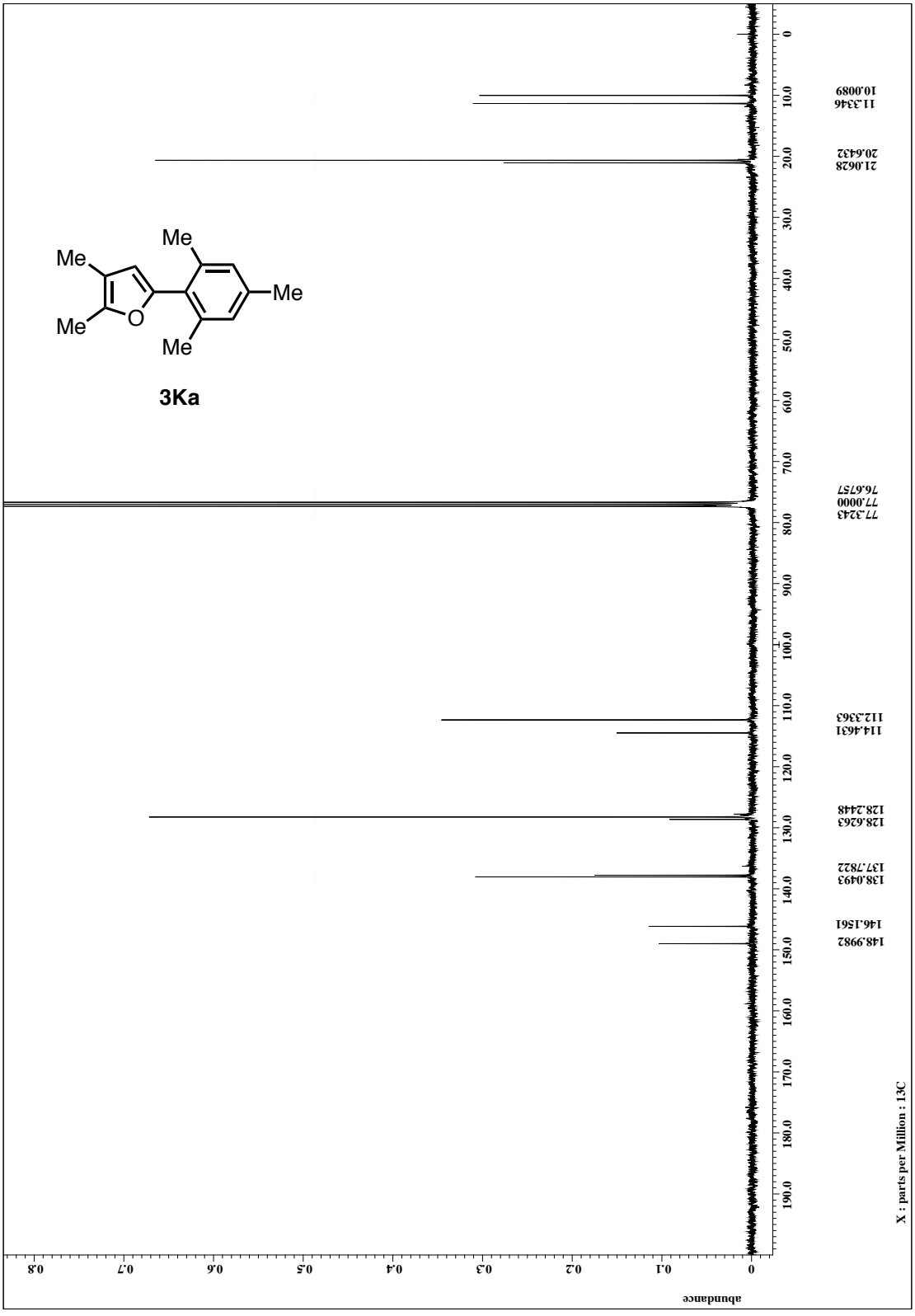
^{13}C NMR (100 MHz, $CDCl_3$) of 3Jd



^{1}H NMR (400 MHz, $CDCl_3$) of 3Ka:

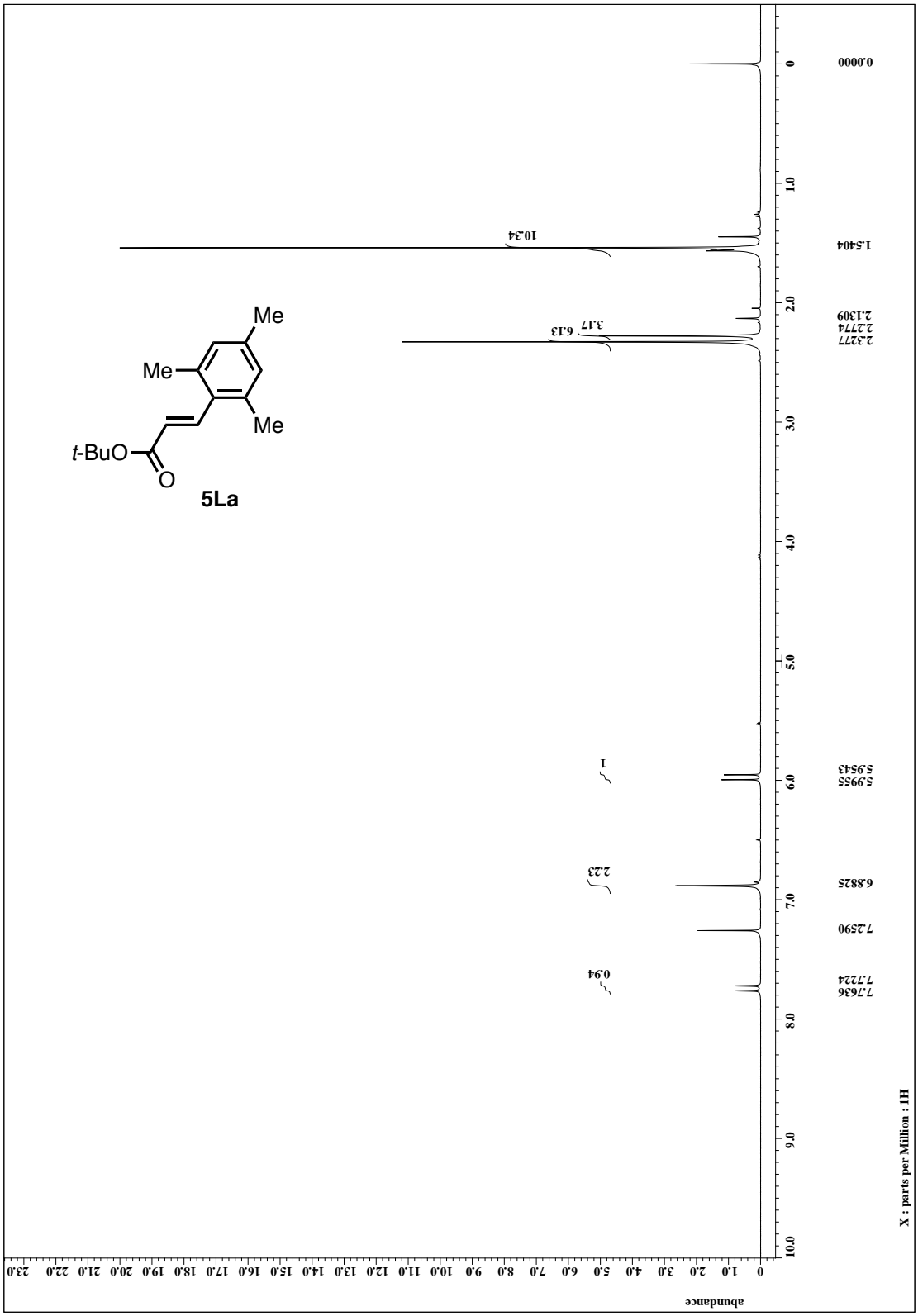


^{13}C NMR (100 MHz, $CDCl_3$) of 3Ka:

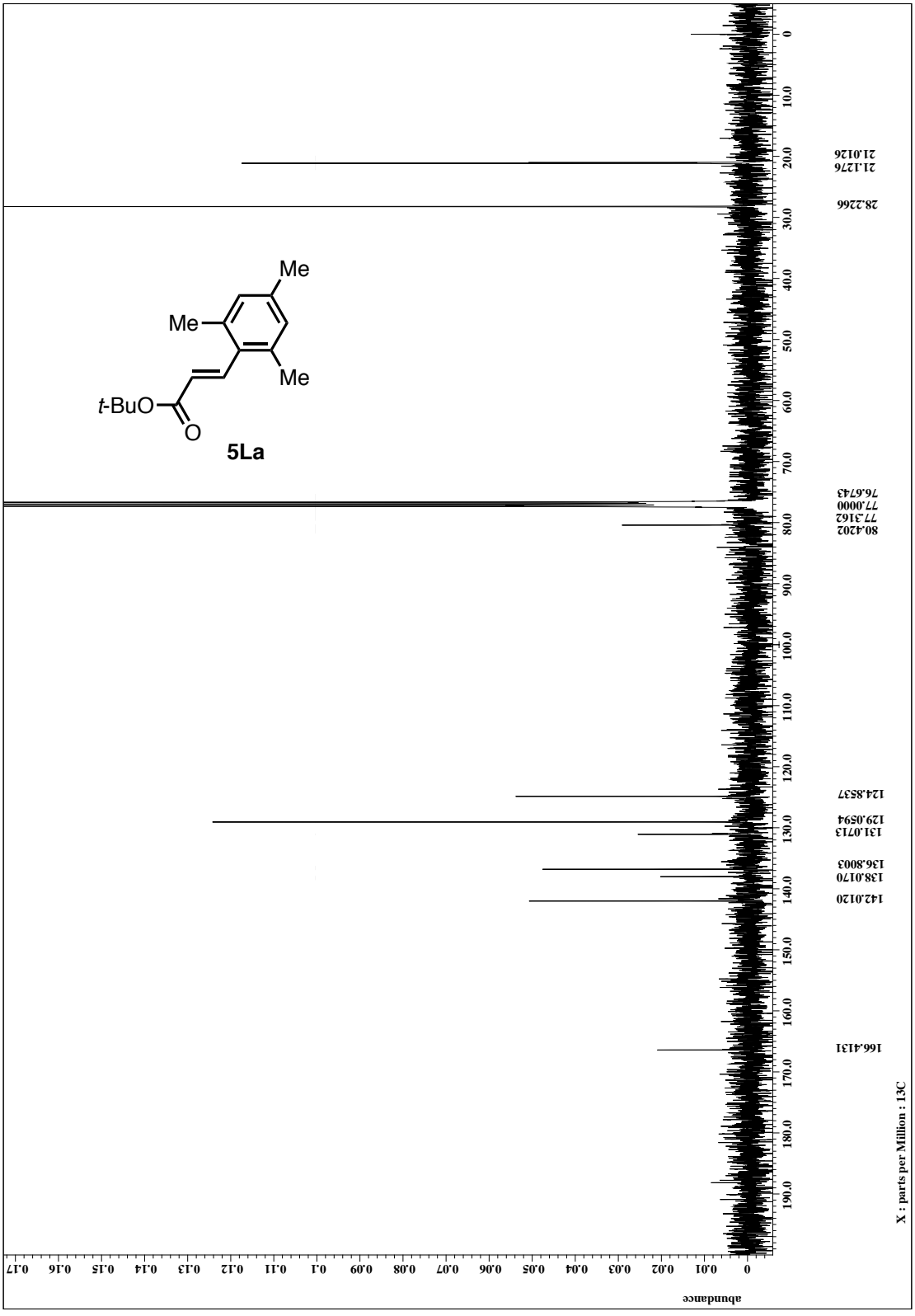


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

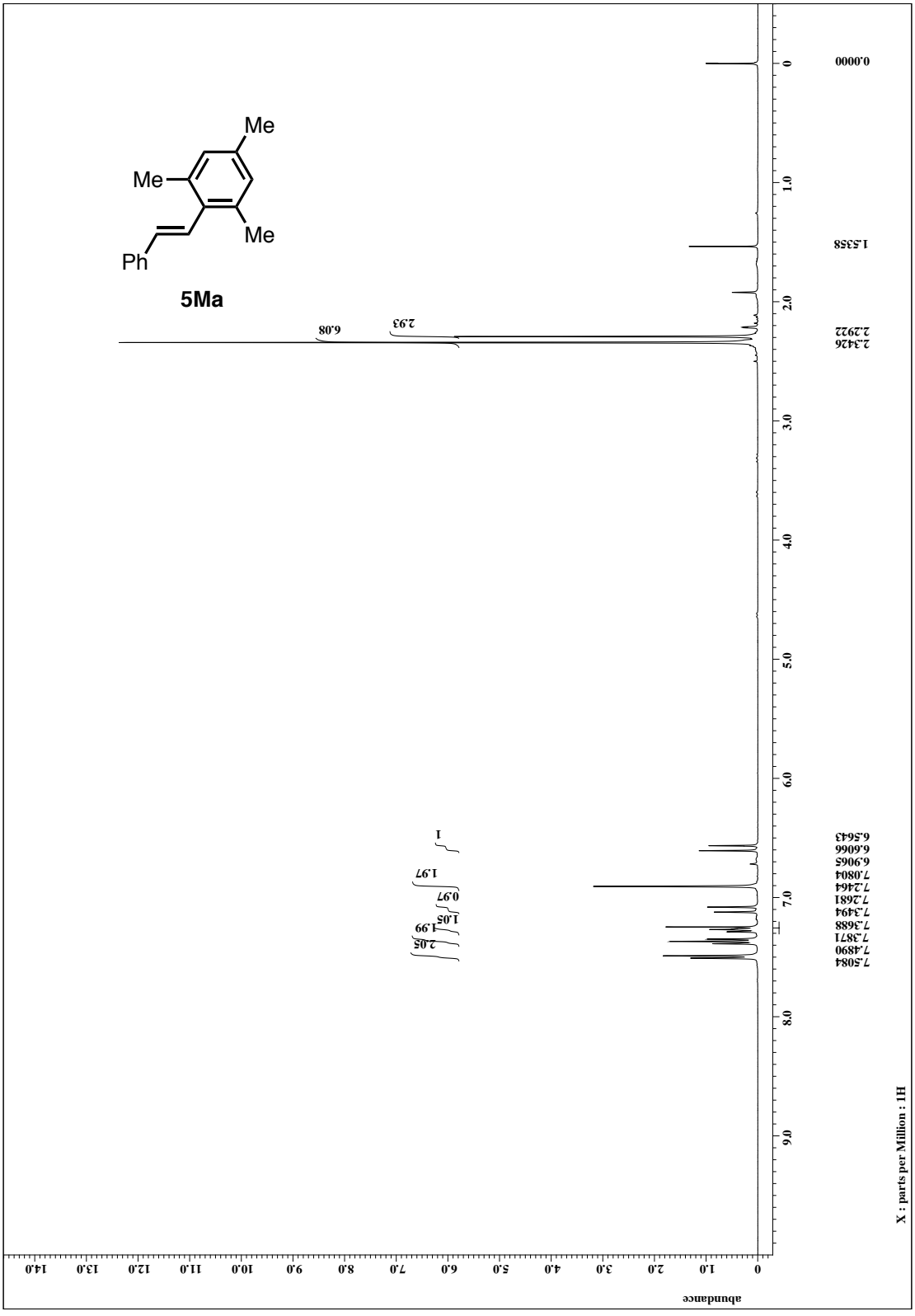
^{1}H NMR (400 MHz, $CDCl_3$) of 5La:



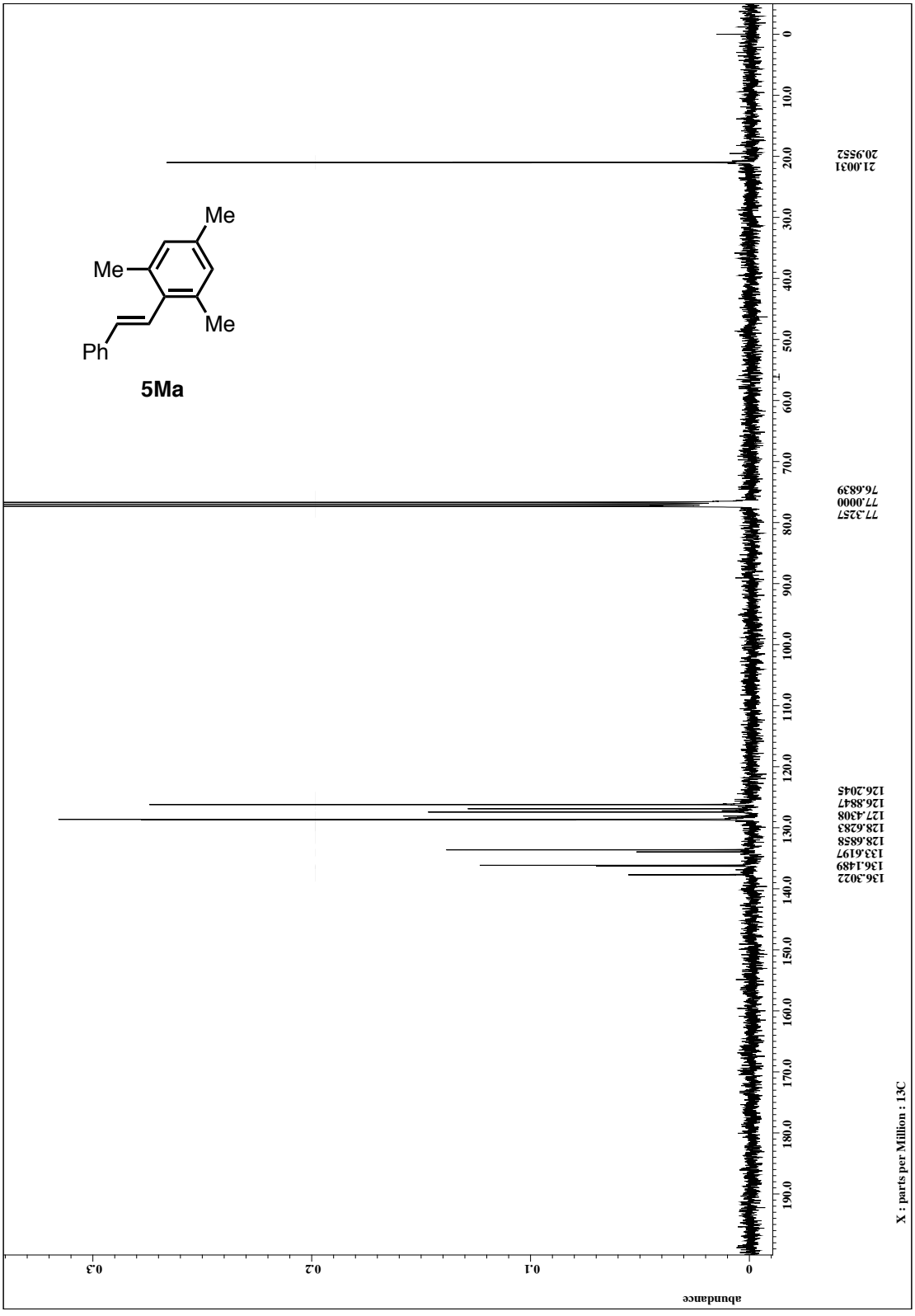
^{13}C NMR (100 MHz, $CDCl_3$) of 5La:



^{1}H NMR (400 MHz, $CDCl_3$) of 5Ma:

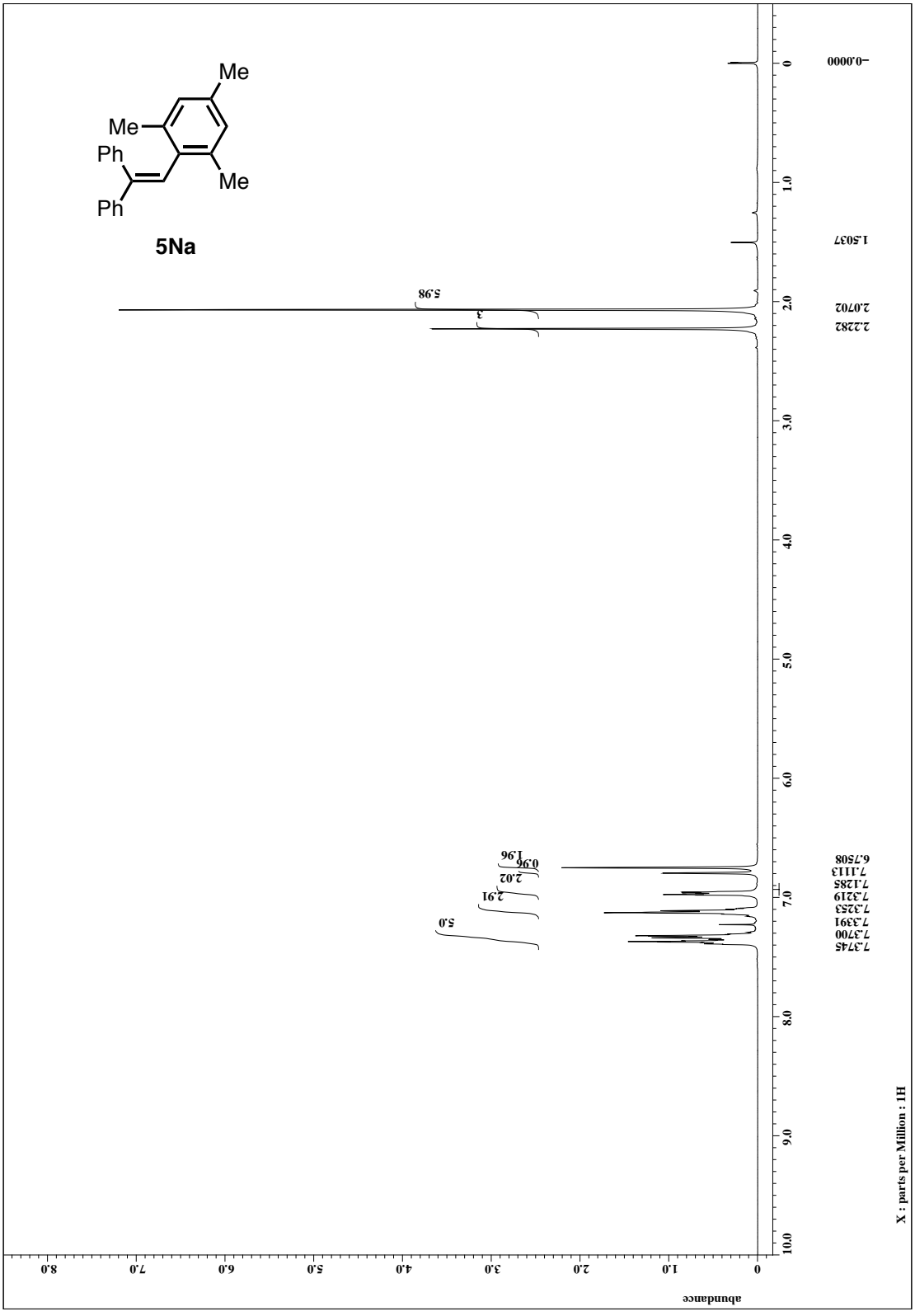


^{13}C NMR (100 MHz, $CDCl_3$) of 5Ma:

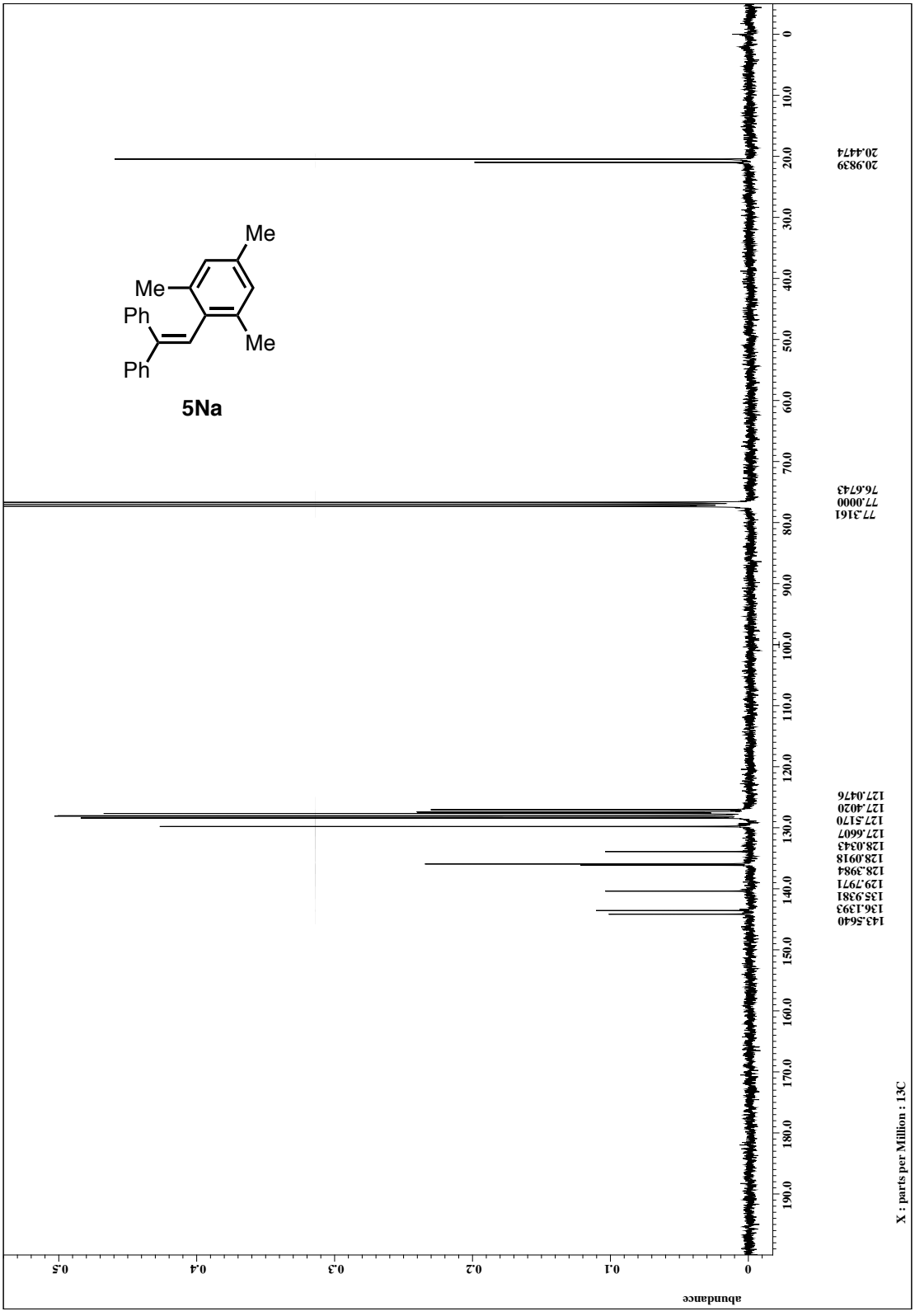


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of 5Na:

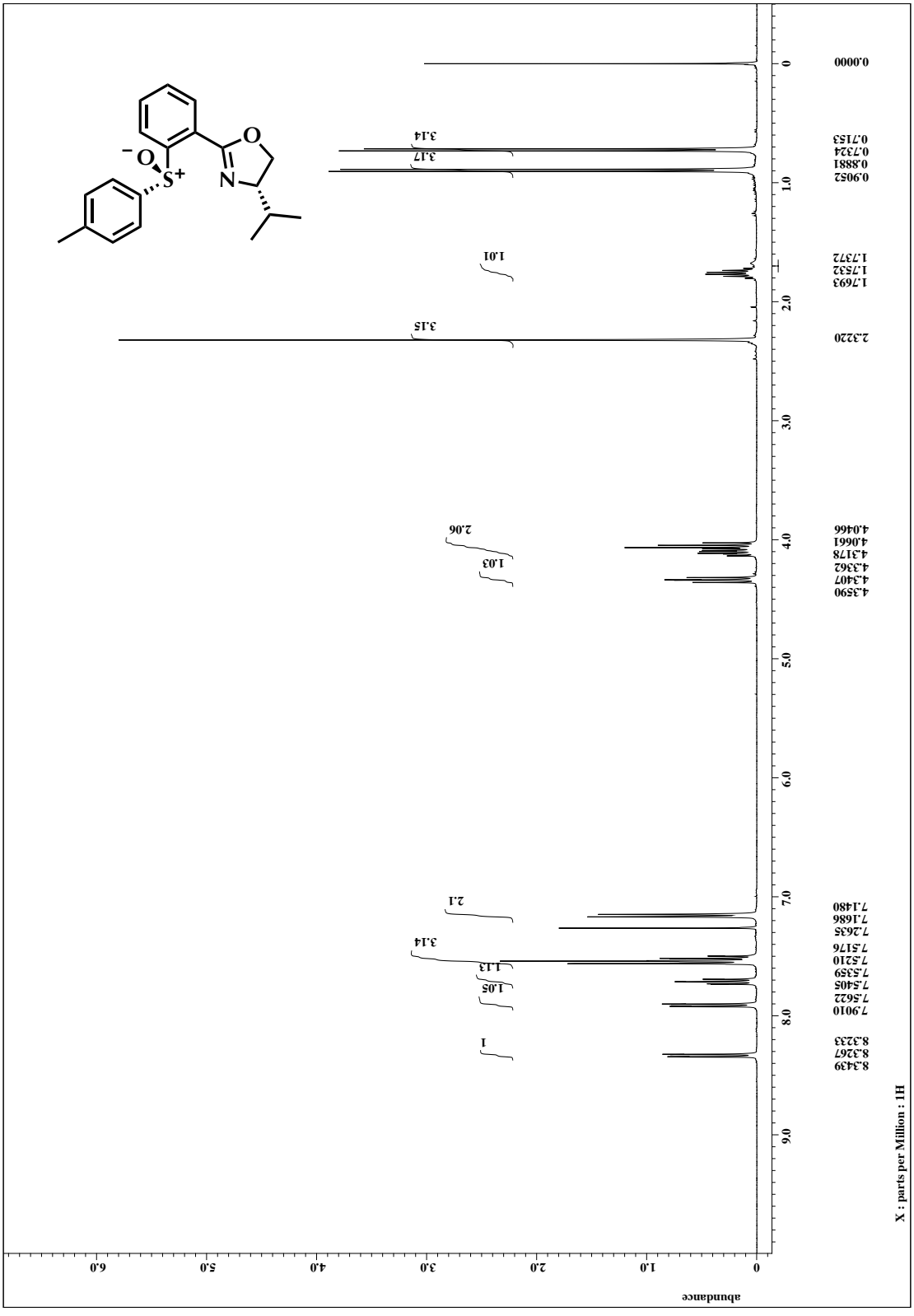


^{13}C NMR (100 MHz, $CDCl_3$) of 5Na:

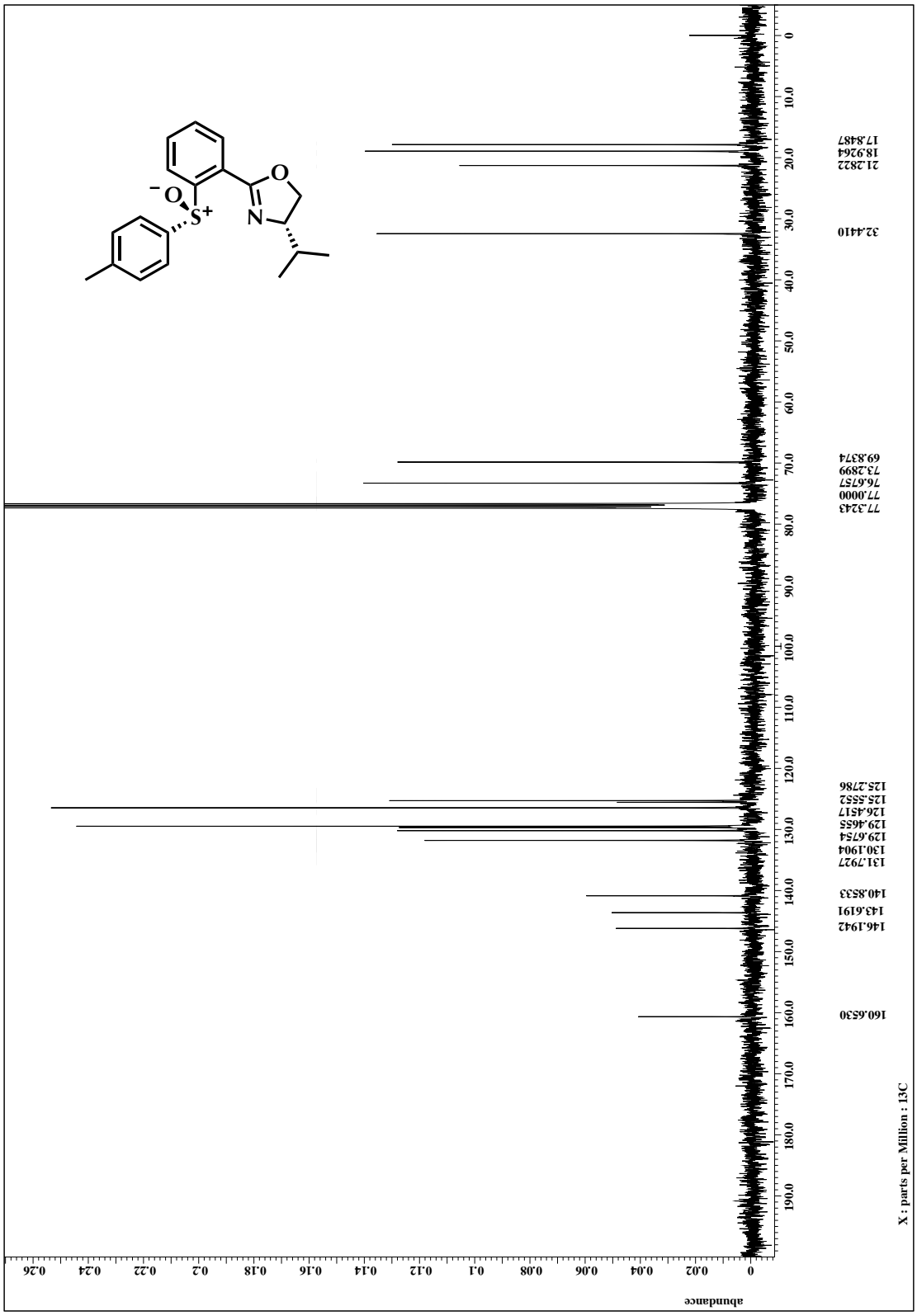


Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of sox ligand:

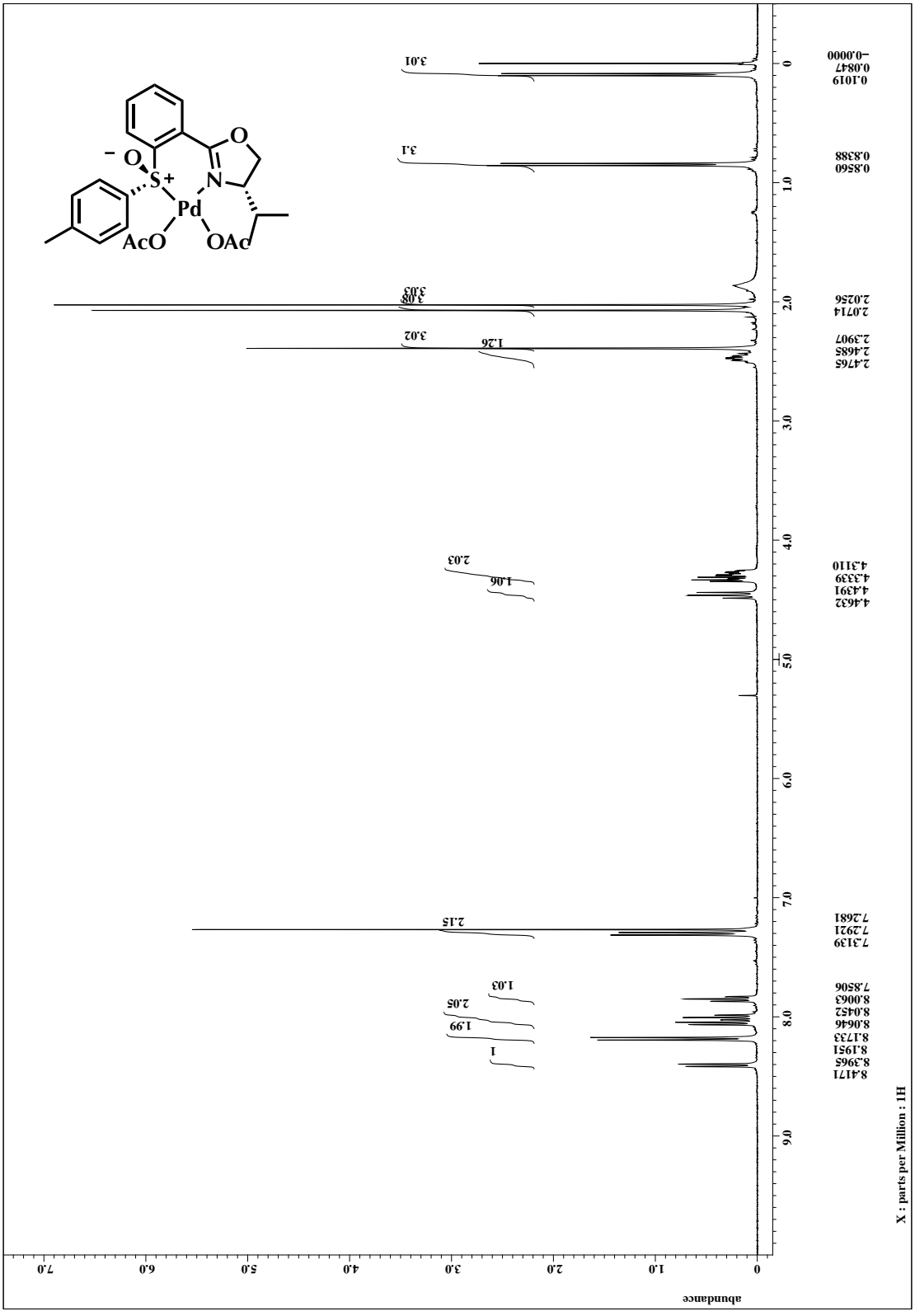


^{13}C NMR (100 MHz, $CDCl_3$) of sox ligand



Aromatic C–H Coupling with Hindered Arylboronic Acids by Pd/Fe Dual Catalysts

^{1}H NMR (400 MHz, $CDCl_3$) of Pd-sox complex:



^{13}C NMR (100 MHz, $CDCl_3$) of Pd-sox complex: