Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Transition-Metal Mediated Carbon–Fluorine Bond Formation

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Materials and Methods

All reactions were carried out under an ambient atmosphere unless otherwise mentioned. Except as indicated otherwise, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. In addition, TLC plates were stained using ceric ammonium molybdate or potassium permanganate stain. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluant at 0.3–0.5 bar pressure.[1] Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds. Melting points were measured on a Büchi 510 apparatus. All melting points were measured in open capillaries and are uncorrected. NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 500MHz and 125MHz for ^{1}H and ^{13}C acquisitions, respectively, or on a Varian Mercury 400 spectrometer operating at 375 MHz for ^{19}F acquisition. Chemical shifts (δ) of ^{1}H-NMR and ^{13}C-NMR spectra are reported in ppm with a solvent resonance as an internal standard. Chemical shifts (δ) of ^{19}F-NMR measurements are reported relatively to $CFCl_3$ as the external standard. Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. THF was distilled from sodium/ benzophenone prior to use. Benzo[*h*]quinoline was purchased from TCI America. Iodobenzene diacetate, 4-nitrobenzenesulfonyl amide, phenyllithium (1.6 M in dibutylether), phenylmagnesium bromide (1.0 M in THF), 4-chlorophenylmagnesium bromide (1.0 M in Et_2O), tributylphenyltin, and N-fluorobenzene-sulfonimide were purchased from Aldrich. Palladium acetate and boronic acids were purchased from Frontier Scientific or Boron Molecular. Phenyltrimethylsilane and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) were purchased from VWR and used as received. Phenylzinc chloride[2] and potassium phenyltrifluoroborate[3] were synthesized according to the literature procedures.

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[1] Still, W. C., Kahn, M. & Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **43**, 2923–2925 (1978).

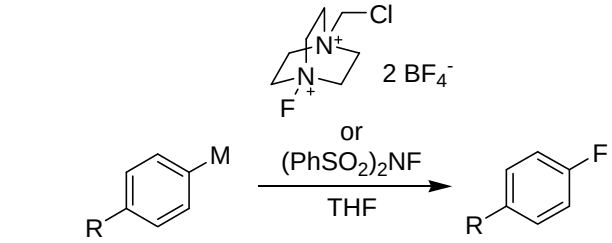
[2] Jansen, A. & Krause, N. Transition metal-promoted synthesis of functionalized and unfunctionalized pyridylallenes. *Synthesis* **14**, 1987–1993 (2002).

[3] Vedejs, E., Chapman, R. W., Fields, S.C., Lin, S & Schrimpf, M. R. Conversion of arylboronic acids into potassium aryltrifluoroborates: convenient precursors of arylboron difluoride lewis acids. *J. Org. Chem.* **60**, 3020–3027 (1995).

Experimental Data

Experimental Procedures and Compound Characterization

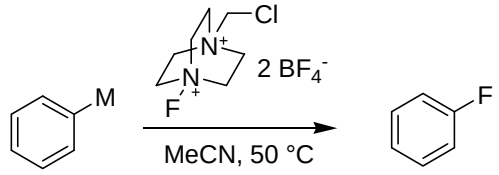
General procedure A for the fluorination of aryllithium, arylmagnesium, and arylzinc substrates:



R = H, Cl; M = Li, MgBr, ZnCl

Under nitrogen atmosphere, the main-group organometallic (0.0400 mmol, 1.00 equiv) is added to 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoro-borate) (14.2 mg, 0.0400 mmol, 1.00 equiv) or N-fluorobenzenesulfoneimide (12.6 mg, 0.0400 mmol, 1.00 equiv) in THF (0.4 mL) at 23 ºC. The reaction mixture is stirred at 23 ºC for 12 hr and to the reaction mixture is added 3-nitrofluorobenzene (4.00 μL, 0.0376 mmol). The yields are determined by comparing integration of the ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC) resonance of fluorobenzene (–115.3 ppm) or 1-chloro-4-fluorobenzene (–116.5 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S1.

General procedure B for the fluorination of arysilane, arylstannate, and arylboronic acid derivatives:



M = $SiMe_3$, $SnBu_3$, $B(OH)_2$, BF_3K

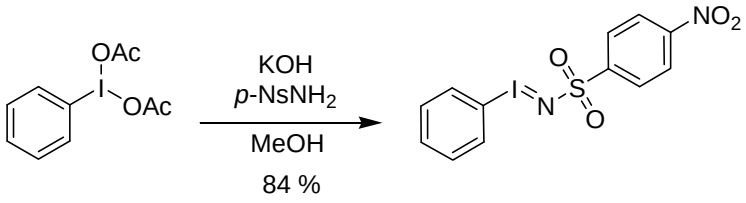
To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (14.2 mg, 0.0400 mmol, 1.00 equiv) in acetonitrile (0.4 mL) at 23 ºC is added the main-group organometallic (0.0400 mmol, 1.00 equiv). The reaction mixture is stirred at 50 ºC for 12 hr and to the reaction mixture is added 3-nitrofluorobenzene (4.00 μL, 0.0376 mmol). The yields are determined by comparing integration of the ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC) resonance of fluorobenzene (–115.3 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S1.

Table S1.: Direct synthesis of fluorobenzene derivatives employing electrophilic fluorine sources:

Organometallic	Reagent	Product	Yield [%] (^{19}F-NMR)
PhLi	$(PhSO_2)_2NF$	PhF[a]	39
PhMgBr	$(PhSO_2)_2NF$	PhF[a]	50
4-Cl-C_6H_4MgBr	$(PhSO_2)_2NF$	4-Cl-C_6H_4F[a]	38
PhZnCl	Selectfluor	PhF[a]	6
$PhB(OH)_2$	Selectfluor	PhF[b]	4
$PhSiMe_3$	Selectfluor	–[b]	0
$PhSnBu_3$	Selectfluor	–[b]	0

[a] following general procedure A
[b] following general procedure B

[{(4-Nitrophenyl)sulfonyl}imino]phenyliodinane[4,5]



To 4-nitrobenzenesulfonyl amide (5.00 g, 24.8 mmol, 1.00 equiv) in methanol (100 mL) at 23 ºC is added potassium hydroxide (3.48 g, 62.0 mmol, 2.50 equiv). The reaction mixture is stirred at 23 ºC for 10 min and cooled to 0 ºC. To the reaction mixture at 0 ºC is added iodobenzene diacetate (7.98 g, 24.8 mmol, 1.00 equiv). The reaction mixture is stirred at 0 ºC for 10 min and further stirred at 23 ºC for 2.0 h. The reaction mixture is poured onto cold water (700 mL) and kept at 0 ºC for 4 h. The suspension is filtered off and the filter cake is washed with water (2 × 200 mL) and methanol (2 × 200 mL) to afford 8.39 g of the title compound as a white solid (84% yield).

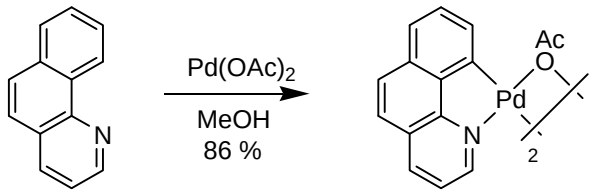
^{1}H-NMR (500 MHz, DMSO-*d*-6, 23 ºC): δ 8.02 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 6.5 Hz, 2H), 7.41 (t, J = 7.0 Hz, 1H), 7.26 (dd, J = 8.0 Hz, J = 7.5 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-*d*-6, 23 ºC): δ 151.7, 148.6, 134.4, 131.4, 130.9, 128.2, 124.3, 117.9. These spectroscopic data correspond to the

[4] Yamada, Y.; Yamamoto, T. & Okawara, M. Synthesis and reaction of new type I-N ylide, N-tosyliminoiodinane. *Chem. Lett.* **4**, 361–362 (1975).

[5] Gullick, J.; Ryan, D.; McMorn, P.; Bethell, D.; King, F.; Hancock, F.; Hutching, G. Catalytic asymmetric heterogeneous aziridination of styrene using Cu^{2+}-exchanged zeolite Y: effect of the counter-cation on enantioselectivity and on the reaction profile. *New J. Chem.* **28**, 1470–1478 (2004).

reported data in reference 5.

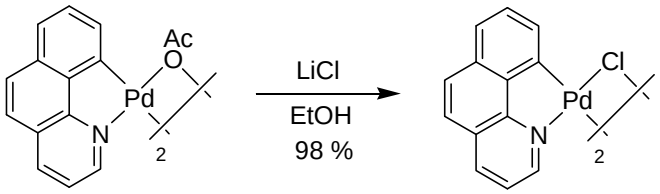
Benzo[*h*]quinolinyl palladium acetate dimer[6]



To benzo[*h*]quinoline (2.60 g, 14.5 mmol, 1.00 equiv) in MeOH (230 mL) at 23 ºC is added palladium acetate (3.26 g, 14.5 mmol, 1.00 equiv). After stirring for 3.0 h, the suspension is filtered off and the filter cake is washed with MeOH (100 mL) and Et_2O (100 mL) to afford 4.27 g of the title compound as a yellow solid (86% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.80 (dd, J = 5.5 Hz, 1.5 Hz, 1H), 7.43 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.24–7.18 (m, 3H), 7.08 (dd, J = 7.0 Hz, J = 1.5 Hz, 1H), 6.97 (d, J = 9.0 Hz, 1H), 6.46 (dd, J = 7.5 Hz, 5.0 Hz, 1H), 2.38 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 182.5, 153.2, 148.9, 148.8, 140.0, 135.3, 132.4, 129.0, 127.9, 127.7, 125.0, 122.9, 122.1, 119.8, 25.2. These spectroscopic data correspond to the reported data in reference 6.

Benzo[*h*]quinolinyl palladium chloro dimer 3[7]



3

To benzo[*h*]quinolinyl palladium acetate dimer (4.27 g, 12.4 mmol, 1.00 equiv) in EtOH (100mL) at 0 ºC is added lithium chloride (10.5 g, 24.8 mmol, 20.0 equiv). The reaction mixture is warmed to 23 ºC and stirred for 1.0 h. The reaction mixture is filtered off and the filter cake is washed with water (3 × 100 mL), MeOH (2 × 100 mL), and Et_2O (100 mL) to afford 3.89 g of the title compound as a pale yellow solid (98% yield).

^{1}H-NMR (500 MHz, DMSO-*d*-6, 23 ºC): δ 9.44 (d, J = 4.5 Hz, 1.0 Hz, 1H), 8.72 (br), 8.67 (d, J = 7.5 Hz,

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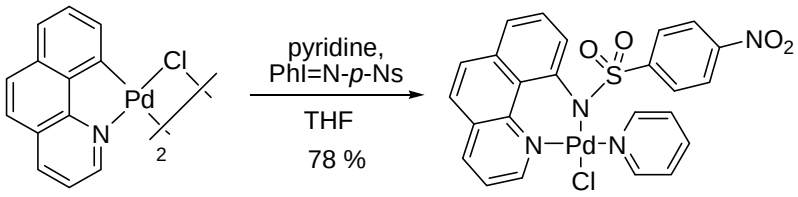
[6] Dick, A. R., Hull , K. L. & Sanford, M. S. A Highly selective catalytic method for the oxidative functionalization of C-H bonds. *J. Am. Chem. Soc.* **126**, 2300–2301(2004).

[7] Hartwell, G. E., Lawrence, R. W. & Smas, M. J. The formation of palladium(II)– and platinum(II)–carbon bonds by proton abstraction from benzo[*h*]quinoline and 8-methylquinoline. *J. Chem. Soc. D.: Chem. Commun.* 912 (1970).

1H), 8.61 (br), 8.22 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.86–7.74 (m, 3H), 7.73 (br), 7.60 (br), 7.53 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz 1H), 7.38 (br); ^{13}C-NMR (125 MHz, DMSO-*d*-6, 23 ºC): δ 153.9, 152.2, 150.7, 150.6, 148.0, 141.7, 139.9, 134.4, 130.8, 129.6, 129.4, .127.5, 125.1, 124.4, 123.0, 122.9. Note: The complicated ^{1}H and ^{13}C-NMR spectra are probably due to the mixture of the title compound and solvent adduct in DMSO-*d*-6. The title compound is not soluble in non-coordinating solvents.

Chloro palladium complex 7[8]

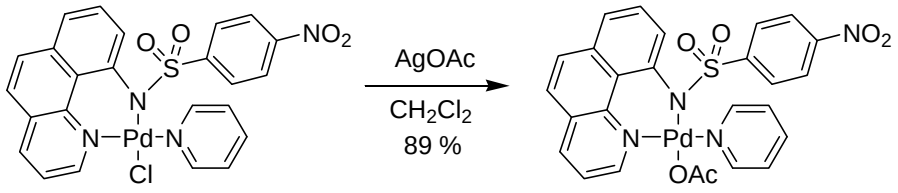


3 **7**

To chloropalladium dimer **3** (1.60 g, 5.00 mmol, 1.00 equiv) in THF (75.0 mL) at 23 ºC is added pyridine (3.20 mL, 40.0 mmol, 8.00 equiv) and PhI=N-*p*-Ns (3.00 g, 7.50 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 17 h. The reaction mixture is filtered off and the filter cake is washed with Et_2O (2 × 10 mL) to afford 2.40 g of the title compound as a light brown solid (78% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.20 (dd, *J* = 4.5 Hz, 1.0 Hz, 1H), 8.97 (d, *J* = 4.5 Hz, 2H), 8.07 (dd, *J* = 6.5 Hz, 1.0 Hz, 1H), 7.92–7.82 (m, 5H), 7.53–7.45 (m, 5H), 7.39 (dd, *J* = 6.5 Hz, 4.5 Hz, 1H), 7.32 (d, *J* = 6.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.1, 152.5, 148.3, 147.3, 141.6, 138.9, 137.8, 137.7, 136.1, 130.7, 130.1, 128.3, 127.1, 126.9, 126.8, 126.2, 125.3, 124.5, 122.5, 122.3. These spectroscopic data correspond to the reported data in reference 6.

Acetato palladium complex 1



7 **1**

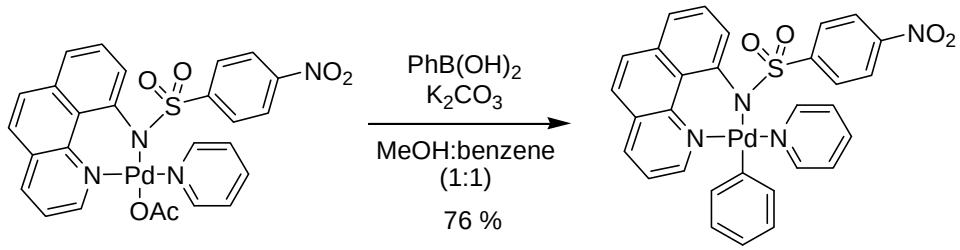
To chloro palladium complex **7** (2.22 g, 3.70 mmol, 1.00 equiv) in CH_2Cl_2 (74.0 mL) at 23 ºC is added AgOAc (3.09 g, 18.5 mmol, 5.00 equiv). The suspension is stirred at 40 ºC for 2.0 h. After cooling to 23 ºC, the suspension is filtered through a plug of celite. The filtrate is concentrated in vacuo and the residue is

[6] Dick, A. R., Remy, M. S., Kampf, J. W. & Sanford, M. S. Carbon-nitrogen bond-forming reactions of palladacycles with hypervalent iodine reagents. *Organometallics* **26**, 1365–1370 (2007).

triturated with Et_2O (50 mL). The solids are filtered off and washed with Et_2O (2 × 50 mL) to afford 2.04 g of the title compound as an orange yellow solid (89% yield).

m.p.: 211 °C (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.93 (d, J = 4.5 Hz, 2H), 8.71 (dd, J = 4.5 Hz, 1.5 Hz, 1H), 8.06 (d, J = 6.5 Hz, 1H), 7.90–7.76 (m, 5H), 7.52 (d, J = 7.0 Hz, 2H) 7.48–7.41 (m, 5H), 7.34 (dd, J = 6.5 Hz, 4.5 Hz, 1H), 1.79 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 177.8, 152.0, 151.4, 148.4, 147.9, 141.8, 139.0, 138.8, 138.1, 136.2, 130.8, 130.5, 129.1, 127.5, 127.0, 126.8, 126.3, 125.3, 124.5, 122.6, 122.2, 24.0; HRMS-FIA (*m/z*): $[M - OAc + MeCN]^+$ calcd for $C_{26}H_{20}N_4O_6PdS$, 604.0265; found, 604.0308. Anal: calcd for $C_{26}H_{20}N_4O_6PdS$: C, 50.13; H, 3.24; N, 9.00; found: C, 49.93; H, 3.44; N, 8.79. Crystal structure is shown in the X-ray Crystallographic Analysis section.

Aryl palladium complex 4a

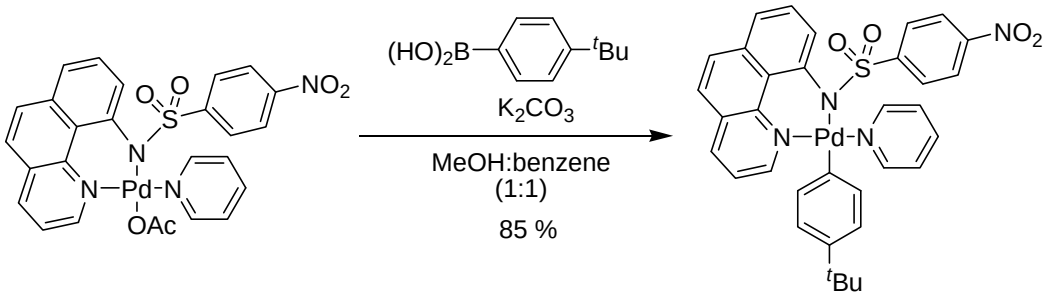


1 **4a**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added phenylboronic acid (86.0 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 2.5 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:1 (v/v) to afford 314 mg of the title compound as a pale yellow solid (76% yield).

TLC (hexane/EtOAc 1:1, v/v): R_F = 0.23; m.p.: 205 °C (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.00 (d, J = 6.5 Hz, 2H), 8.27 (dd, J = 5.5 Hz, 1.5 Hz, 1H), 7.93 (dd, J = 8.0 Hz, 1.5Hz, 1H), 7.79–7.69 (m, 5H), 7.48 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 9.0 Hz, 2H), 7.35–7.28 (m, 4H), 7.03 (dd, J = 8.0 Hz, 6.5 Hz, 1H), 6.84–6.76 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 155.3, 153.9, 153.3, 149.4, 147.8, 144.6, 144.3, 138.0, 137.9, 136.5, 134.8, 130.5, 130.2, 128.5, 127.6, 127.2, 127.0, 126.8, 125.2, 124.7, 124.4, 123.8, 122.4, 121.5; HRMS-FIA (*m/z*): $[M + H]^+$ calcd for $C_{30}H_{22}N_4O_4PdS$, 641.0475; found, 641.0475. Anal: calcd for $C_{30}H_{22}N_4O_4PdS$: C, 56.21; H, 3.46; N, 8.74; found: C, 55.94; H, 3.48; N, 8.40. Crystal structure is shown in the X-ray Crystallographic Analysis section.

Aryl palladium complex 4b

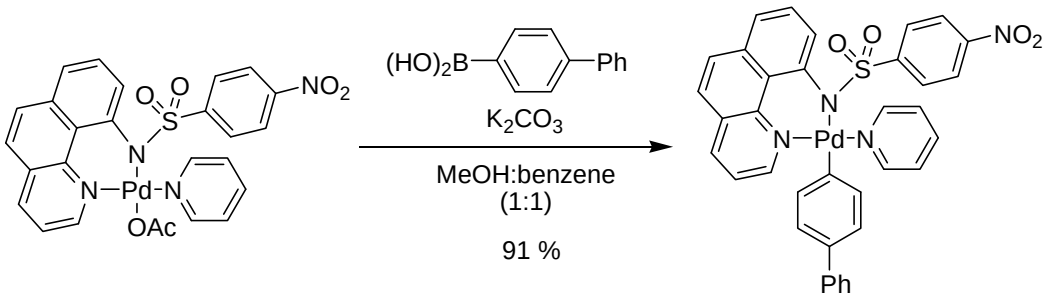


1 **4b**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-tert-butylphenylboronic acid (126 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 13 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 3:2 (v/v) to afford 381 mg of the title compound as a yellow solid (85% yield).

TLC (hexane/EtOAc 1:1, v/v): R_F = 0.49; m.p.: 171 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.00 (d, J = 5.0 Hz, 2H), 8.27 (dd, J = 5.5 Hz 1.5 Hz, 1H), 7.92 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.80–7.70 (m, 5H), 7.48 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 1H), 7.36–7.30 (m, 4H), 7.03 (dd, J = 8.0 Hz, 5.0 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 6.70 (d, J = 8.5 Hz, 2H), 1.19 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.0, 153.4, 150.5, 149.5, 147.8, 146.4, 144.6, 142.3, 137.9, 137.8, 136.4, 134.0, 130.4, 130.1, 128.5, 127.4, 126.9, 126.8, 125.1, 124.6, 124.4, 124.2, 122.4, 121.4, 34.1, 31.7; HRMS-FIA (*m*/*z*): $[M + H]^+$ calcd for $C_{34}H_{30}N_4O_4PdS$, 697.1095; found, 697.1082. Anal: calcd for $C_{34}H_{30}N_4O_4PdS$: C, 58.58; H, 4.34; N, 8.04; found: C, 58.27; H, 4.37; N, 7.84.

Aryl palladium complex 4c



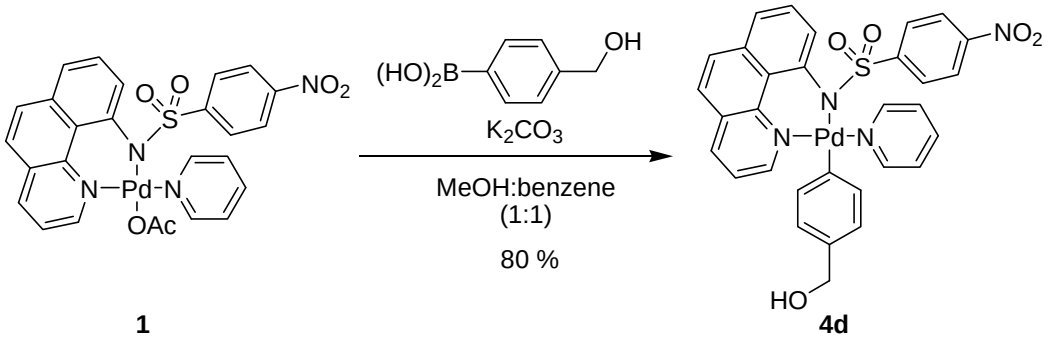
1 **4c**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-biphenyl boronic acid (140 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963

mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 11 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:1 (v/v) to afford 418 mg of the title compound as a yellow solid (91% yield).

TLC (hexane/EtOAc 3:7, v/v): R_F = 0.79; m.p.: 180 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.04 (d, J = 6.5 Hz, 2H), 8.32 (dd, J = 5.0 Hz, 2.0 Hz, 1H), 7.95 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.81–7.71 (m, 5H), 7.50–7.45 (m, 4H), 7.40 (d, J = 9.0 Hz, 1H), 7.38–7.29 (m, 6H), 7.24 (t, J = 7.5 Hz, 1H), 7.09–7.05 (m, 3H), 6.88 (d, J = 8.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.6, 154.1, 153.4, 149.3, 147.8, 144.6, 142.2, 141.4, 138.1, 138.0, 136.5, 135.1, 130.5, 130.2, 128.9, 128.6, 127.6, 127.1, 127.0, 126.9, 126.8, 126.7, 125.6, 125.2, 124.7, 124.4, 122.4, 121.6; HRMS-FIA (m/z): $[M + H]^+$ calcd for $C_{36}H_{26}N_4O_4PdS$, 717.0782; found, 717.0786. Anal: calcd for $C_{36}H_{26}N_4O_4PdS$: C, 60.30; H, 3.65; N, 7.82; found: C, 60.27; H, 3.65; N, 7.60.

Aryl palladium complex 4d



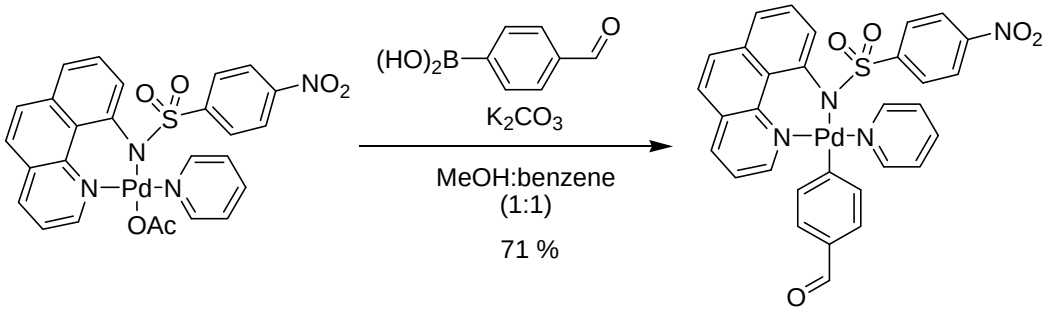
1 **4d**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-(hydroxymethyl)phenylboronic acid (133 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 11 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:4 (v/v) to afford 344 mg of the title compound as a yellow solid (80% yield).

TLC (hexane/EtOAc 3:7, v/v): R_F = 0.37; m.p.: 158 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.99 (d, J = 6.5 Hz, 2H), 8.25 (dd, J = 5.5 Hz, 1.5 Hz, 1H), 7.94 (dd, J = 8.5Hz, 2.0 Hz, 1H), 7.80–7.69 (m, 5H), 7.47 (d, J = 9.0 Hz, 2H), 7,39 (d, J = 9.0 Hz, 1H), 7.36–7.27 (m, 4H), 7.04 (dd, J = 8.5 Hz, 6.5 Hz, 1H), 6.81 (m, 4H), 4.50 (d, J = 4.0 Hz, 2H), 1.49 (t, J = 4.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.6, 153.9, 153.3, 149.3, 147.8, 144.5, 142.2, 138.0, 137.9, 136.5, 136.2, 134.8, 130.5, 130.2, 128.5, 127.5, 126.9, 126.8, 126.2, 125.2, 124.7, 124.4, 121.5, 122.4, 65.5; HRMS-FIA (m/z): $[M + H]^+$ calcd for $C_{31}H_{24}N_4O_5PdS$,

671.0575; found, 617.0598. Anal: calcd for $C_{31}H_{24}N_4O_5PdS$: C, 55.49; H, 3.61; N, 8.35; found: C, 55.10; H, 3.51; N, 7.99.

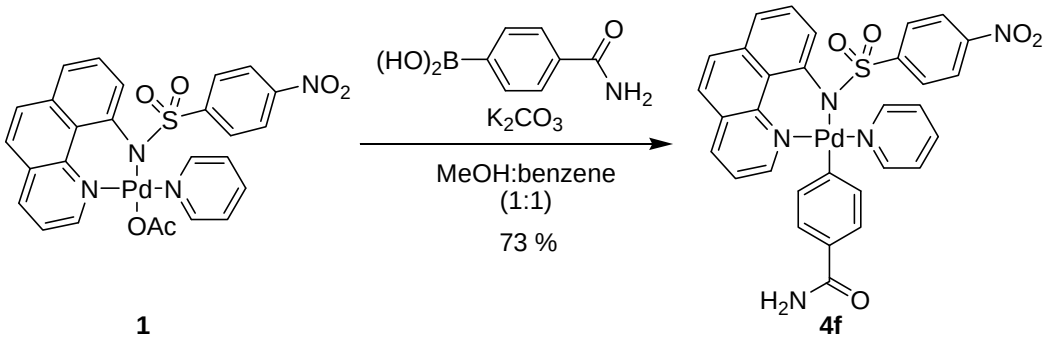
Aryl palladium complex 4e



To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-formylphenylboronic acid (133 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 18 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:1 (v/v) to afford 304 mg of the title compound as a yellow solid (71% yield).

TLC (hexane/EtOAc 3:7, v/v): R_F = 0.40; m.p.: 166 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.77 (s, 1H), 8.97 (d, J = 6.0 Hz, 2H), 8.17 (dd, J = 6.5 Hz, 1.5 Hz, 1H), 7.98 (dd, J = 7.5 Hz, 1.5Hz, 1H), 7.84–7.79 (m, 2H), 7.76–7.71 (m, 3H), 7.48 (d, J = 8.0 Hz, 2H), 7.44–7.36 (m, 3H), 7.31–7.25 (m, 4H), 7.12 (d, J = 7.5 Hz, 2H), 7.07 (dd, J = 8.0 Hz, 5.5 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 192.9, 169.1, 153.7, 153.2, 149.0, 147.9, 144.4, 141.9, 138.4, 138.3, 136.5, 135.5, 133.2, 130.7, 130.4, 128.5, 127.7, 127.6, 126.9, 126.8, 125.4, 124.8, 124.4, 122.4, 121.7; HRMS-FIA (m/z): $[M + H]^+$ calcd for $C_{31}H_{22}N_4O_5PdS$, 669.0419; found, 669.0426. Anal: calcd for $C_{31}H_{22}N_4O_5PdS$: C, 55.65; H, 3.31; N, 8.38; found: C, 55.43; H, 3.58; N, 8.09.

Aryl palladium complex 4f

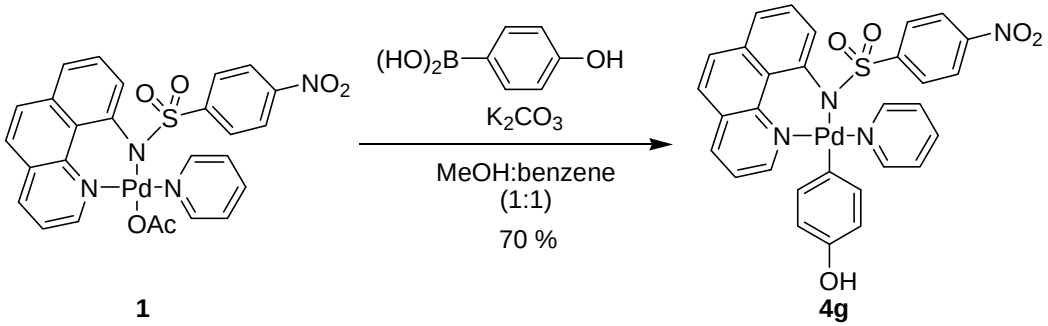


1 **4f**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-aminocarbonylphenylboronic acid (116 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 11 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with EtOAc to afford 319 mg of the title compound as a yellow solid (73% yield).

TLC (EtOAc): R_F = 0.21; m.p.: 175 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.97 (d, J = 5.5 Hz, 2H), 8.19 (dd, J = 6.5 Hz, 1.5 Hz, 1H), 7.97 (dd, J = 7.5 Hz, 1.5Hz, 1H), 7.83–7.70 (m, 5H), 7.47 (d, J = 7.0 Hz, 2H), 7.43–7.30 (m, 3H), 7.28 (dd, J = 9.0 Hz, 1.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.06 (dd, J = 8.5 Hz, 5.5Hz, 1H), 6.89 (d, J = 7.5 Hz, 2H), 5.88 (br, 1H), 5.40 (br, 1H); ^{13}CNMR (125 MHz, $CDCl_3$, 23 ºC): δ 163.3, 153.8, 153.3, 149.0, 144.4, 143.1, 142.0, 138.3, 138.2, 136.5, 135.1, 130.6, 130.3, 129.0, 128.5, 127.6, 126.9, 126.8, 126.0, 125.5, 125.4, 124.8, 124.4, 122.4, 121.6; HRMS-FIA (*m*/*z*): $[M + H]^+$ calcd for $C_{31}H_{23}N_5O_5PdS$, 684.0528; found, 684.0537. Anal: calcd for $C_{31}H_{23}N_5O_5PdS$: C, 54.43; H, 3.39; N, 10.24; found: C, 54.43; H, 3.67; N, 9.95.

Aryl palladium complex 4g



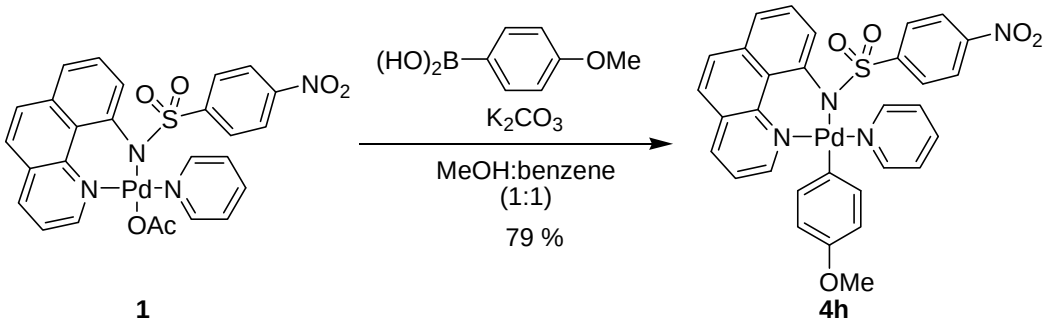
1 **4g**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8

mL) at 23 ºC is added 4-hydroxyphenylboronic acid (97 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 15 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 2:3 (v/v) to afford 295 mg of the title compound as a yellow solid (70%yield).

TLC (hexane/EtOAc, 1:1 v/v): R_F = 0.17; m.p.: 174 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.99 (d, J = 6.5 Hz, 2H), 8.27 (dd, J = 5.0 Hz, 1.5 Hz, 1H), 7.94 (dd, J = 7.5 Hz, 1.5Hz, 1H), 7.79–7.68 (m, 5H), 7.47 (d, J = 9.0 Hz, 2H), 7.40–7.27 (m, 5H), 7.04 (dd, J = 7.5 Hz, 5.5 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 8.0 Hz, 2H), 4.40 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.1, 153.4, 152.7, 149.2, 147.8, 147.4, 144.6, 143.4, 142.2, 137.9, 136.4, 134.8, 130.5, 130.1, 128.5, 127.5, 127.0, 126.8, 125.1, 124.7, 124.3, 122.4, 121.4, 114.5; HRMS-FIA (m/z): $[M + H]^+$ calcd for $C_{30}H_{22}N_4O_5PdS$, 657.0419; found, 657.0433. Anal: calcd for $C_{30}H_{22}N_4O_5PdS$: C, 54.84; H, 3.38; N, 8.53; found: C, 54.56; H, 3.53; N, 8.26.

Aryl palladium complex 4h



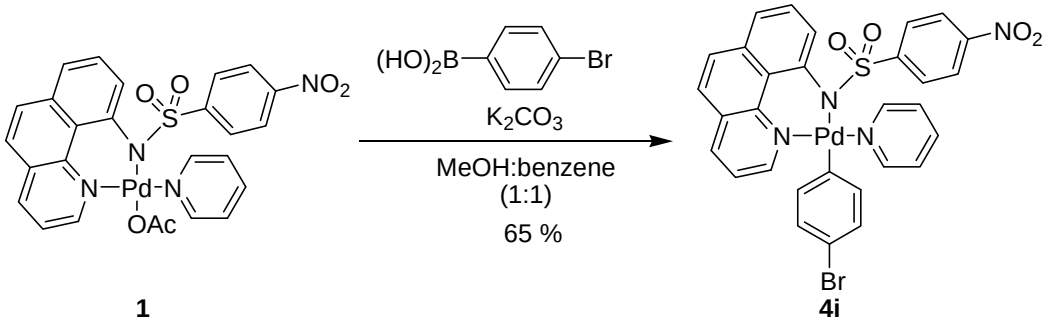
1 **4h**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-methoxyphenylboronic acid (107 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 3.0 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:1 (v/v) to afford 340 mg of the title compound as a yellow solid (79% yield).

TLC (hexane/EtOAc 1:1, v/v): R_F = 0.29; m.p.: 154 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.99 (d, J = 5.5 Hz, 2H), 8.27 (d, J = 5.5 Hz, 1H), 7.94 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 7.80–7.68 (m, 5H), 7.47 (d, J = 6.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 1H), 7.35–7.28 (m, 4H), 7.04 (dd, J = 8.0 Hz, 5.5 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 6.44 (d, J = 8.0 Hz, 2H), 3.65 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 156.9, 154.1, 153.5, 149.3, 147.8, 144.6, 143.5, 142.3, 137.9, 137.9, 136.5, 134.7, 130.5, 130.1, 128.6, 127.5, 127.0, 126.8, 125.1,

124.7, 124.3, 122.4, 121.5, 113.1, 55.1; HRMS-FIA (*m*/*z*): $[M + H]^+$ calcd for $C_{31}H_{24}N_4O_5PdS$, 671.0575; found, 671.0598.

Aryl palladium complex 4i

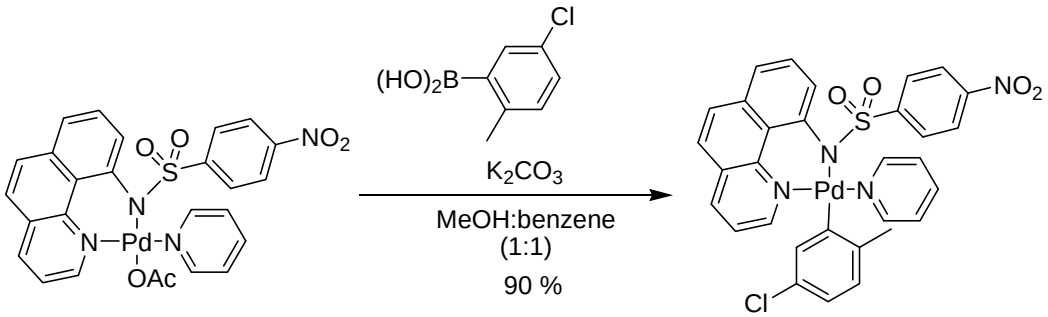


1 **4i**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-bromophenylboronic acid (142 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 3.5 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 3:2 (v/v) to afford 300 mg of the title compound as a yellow solid (65% yield).

TLC (hexane/EtOAc, 1:1 v/v): R_F = 0.79; m.p.: 201 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.96 (d, *J* = 5.0 Hz, 2H), 8.22 (d, *J* = 5.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82–7.68 (m, 5H), 7.47 (d, *J* = 9.0 Hz, 2H) 7.42–7.26 (m, 5H), 7.09 (dd, *J* = 7.5 Hz, 5.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 154.0, 153.5, 153.3, 149.1, 147.9, 142.0, 138.2, 138.1, 136.5, 136.3, 130.6, 130.3, 129.9, 128.5, 127.6, 126.9, 126.8, 125.3, 124.8, 124.4, 122.8, 122.4, 121.7, 118.3; HRMS-FIA (*m*/*z*): $[M + H]^+$ calcd for $C_{30}H_{21}BrN_4O_4PdS$, 718.9575; found, 718.9578. Anal: calcd for $C_{30}H_{21}BrN_4O_4PdS$: C, 50.05; H, 2.94; N, 7.78; found: C, 50.03; H, 2.91; N, 7.51.

Aryl palladium complex 4k

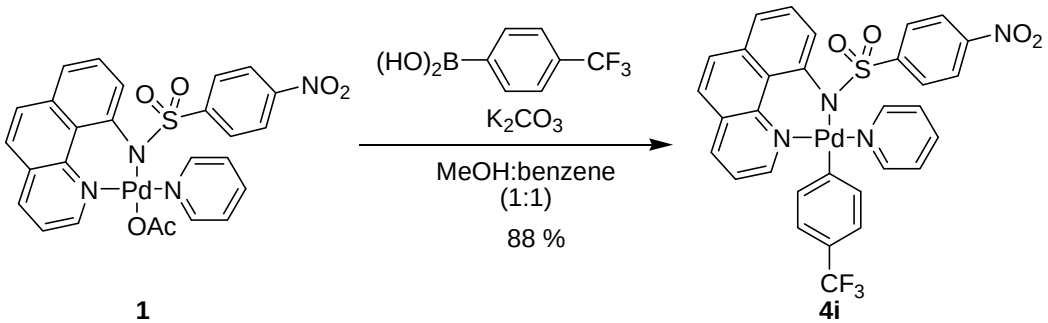


1 **4k**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 5-chloro-2-methylphenylboronic acid (120 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 10 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 3:2 (v/v) to afford 398 mg of the title compound as a yellow solid (90% yield, 1:1.3 atropisomeric mixture with respect to the palladium–carbon bond).

TLC (hexane/EtOAc, 1:1 v/v): R_F = 0.37; m.p.: 178 ºC (decomp.); ^{1}H-NMR, both rotamers (500 MHz, $CDCl_3$, 23 ºC): δ 8.98 (d, J = 5.5 Hz), 8.91 (d, J = 5.5 Hz), 8.28 (d, J = 5.0 Hz), 7.96–7.90 (m), 7.81–7.66 (m), 7.55–7.46 (m), 7.40–7.28 (m), 7.08–6.98 (m), 6.81 (d, J = 8.0 Hz), 6.74 (dd, J = 8.0 Hz, 2.0 Hz), 6.62 (d, J = 2.0 Hz), 6.44 (d, J = 8.0 Hz), 2.99 (s), 1.69 (s); ^{13}C-NMR, both rotamers (125 MHz, $CDCl_3$, 23 ºC): δ 159.6, 159.1, 153.6, 153.4, 152.9, 152.8, 149.4, 147.9, 144.7, 144.6, 142.0, 141.8, 140.1, 139.1, 138.2, 138.1, 138.0, 136.5, 133.4, 132.8, 130.7, 130.6, 130.4, 130.3, 130.2, 129.9, 129.2, 129.0, 128.5, 128.4, 127.8, 127.3, 127.0, 126.8, 126.7, 125.4, 125.2, 125.0, 124.8, 124.5, 124.3, 123.9, 123.8, 122.5, 122.4, 121.6, 24.5, 24.2; HRMS-FIA (*m*/*z*): $[M + H]^+$ calcd for $C_{31}H_{23}ClN_4O_4PdS$, 689.0236; found, 689.0251. Anal: calcd for $C_{31}H_{23}ClN_4O_4PdS$: C, 54.00; H, 3.36; N, 8.13; found: C, 53.72; H, 3.10; N, 8.03.

Aryl palladium complex 4l

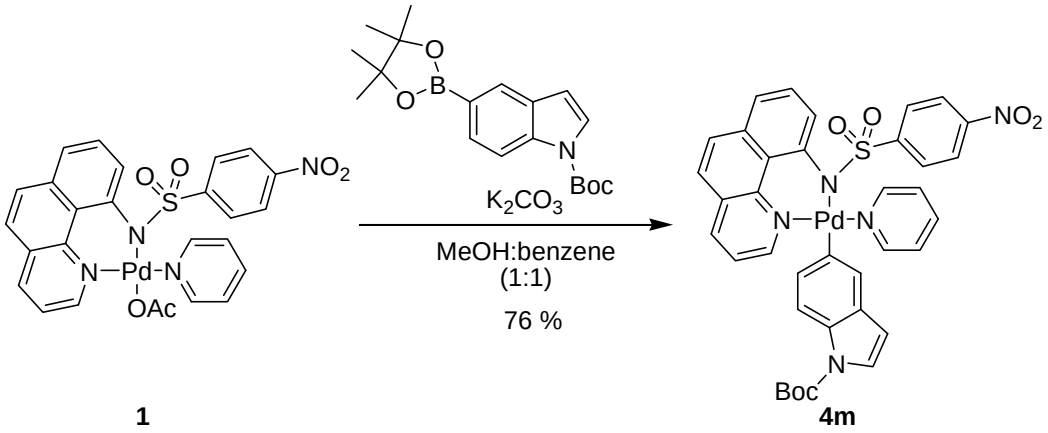


1 **4i**

To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 4-(trifluoromethyl)phenylboronic acid (134 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 10 h, and the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 3:2 (v/v) to afford 400 mg of the title compound as a yellow solid (88% yield).

TLC (hexane/EtOAc, 1:1 v/v): R_F = 0.43; m.p.: 171 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.97 (d, J = 5.5 Hz, 2H), 8.18 (dd, J = 4.5 Hz, 1.5 Hz, 1H), 7.97 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.82–7.70 (m, 5H), 7.48 (d, J = 7.0 Hz, 2H), 7.42–7.26 (m, 5H), 7.09 (dd, J = 8.0 Hz, 5.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 161.3, 153.9, 153.3, 149.0, 147.9, 144.4, 141.9, 138.3, 138.2, 136.5, 135.0, 130.6, 129.5 (q, J = 238 Hz), 127.6, 126.9, 126.8, 126.2 (q, J = 23 Hz), 125.4, 124.8, 124.4, 123.9, 123.2, 122.4, 121.7; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –62.5; HRMS-FIA (*m*/*z*): [M + H]$^+$ calcd for $C_{31}H_{21}F_3N_4O_4PdS$, 709.0343; found, 709.0321. Anal: calcd for $C_{31}H_{21}F_3N_4O_4PdS$: C, 52.51; H, 2.99; N, 7.90; found: C, 52.29; H, 2.98; N, 7.78.

Aryl palladium complex 4m

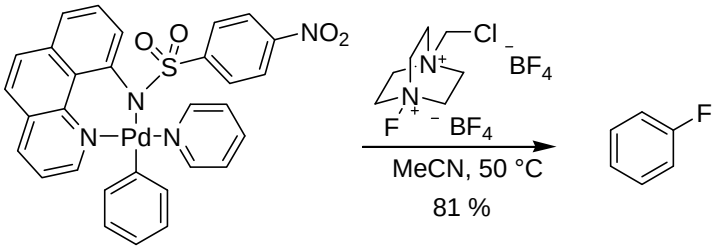


To acetato palladium complex **1** (400 mg, 0.642 mmol, 1.00 equiv) in MeOH (12.8 mL) and benzene (12.8 mL) at 23 ºC is added 1-Boc-indole-5-boronic acid pinacol ester (242 mg, 0.706 mmol, 1.10 equiv) and K_2CO_3 (133 mg, 0.963 mmol, 1.50 equiv). The reaction mixture is stirred at 23 ºC for 6.0 h. After filtered through a plug of celite, the solvent is removed in vacuo. To the solid residue is added $CHCl_3$ (5 mL) and water (5 mL). The phases are separated and the aqueous phase is extracted with $CHCl_3$ (3 × 5 mL). The combined organic phases are washed with brine (5 mL) and dried (Na_2SO_4). The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 1:1 (v/v) to afford 380 mg of the title compound as a yellow solid (76% yield).

TLC (hexane/EtOAc, 3:7 v/v): R_F = 0.26; m.p.: 175 ºC (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 9.01

(d, *J* = 5.0 Hz, 2H), 8.28 (dd, *J* = 5.0 Hz, 1.5 Hz, 1H), 7.91 (dd, *J* = 8.5 Hz, 1.5Hz, 1H), 7.80–7.70 (m, 5H), 7.61 (br, 1H) 7.47 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.33–7.28 (m, 4H), 7.00–6.95 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 1.60 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 153.9, 153.4, 150.1, 149.3, 147.8,147.7, 144.6, 142.3, 137.9, 136.5, 130.5, 130.1, 130.0, 128.6, 127.5, 127.0, 126.8, 126.0, 125.1, 125.0, 124.7, 124.6, 124.4, 122.4, 121.5, 119.9, 113.8, 106.8, 83.4, 28.4; HRMS-FIA (*m*/*z*): [M + Na]$^+$ calcd for $C_{37}H_{31}N_5O_6PdS$, 802.0922; found, 802.0895. Anal: calcd for $C_{37}H_{31}N_5O_6PdS$: C, 56.96; H, 4.01; N, 8.98; found: C, 56.84; H, 3.94; N, 8.65.

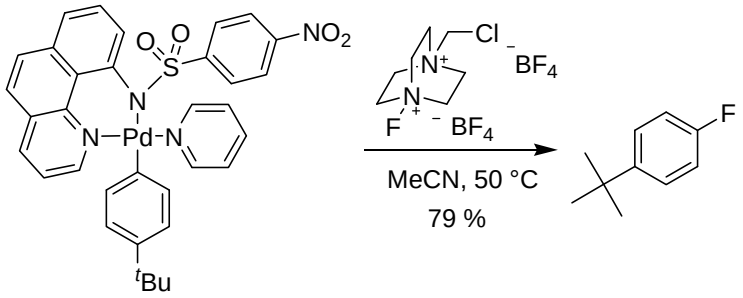
Fluorobenzene 5a



4a **5a**

To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**), (4.3 mg, 0.012 mmol, 1.2 equiv) in acetonitrile-*d*-3 (0.3 mL) at 50 ºC is added aryl palladium complex **4a** (6.4 mg, 0.010 mmol, 1.0 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20min. The reaction mixture is cooled to 23 ºC, and the yield is determined by comparing integration of the ^{19}F-NMR (375 MHz, acetonitrile-*d*-3, 23 ºC) resonance of fluorobenzene (–115.3 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm, 2.00 μL, 0.0188 mmol). (81% yield). The ^{19}F-NMR chemical shift of the product corresponds to that of authentic sample purchased from Aldrich.

1-*tert*-Butyl-4-fluorobenzene 5b

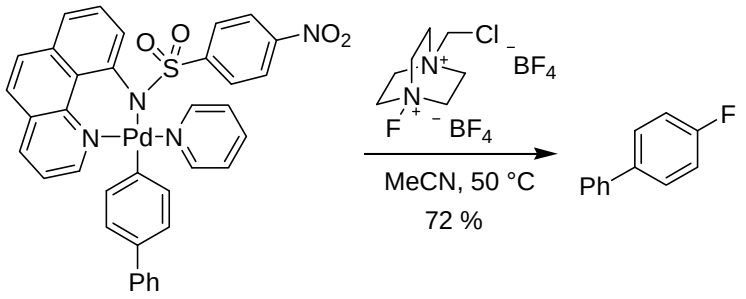


4b **5b**

To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (4.3 mg, 0.012 mmol, 1.2 equiv) in acetonitrile-*d*-3 (0.3 mL) at 50 ºC is added aryl palladium complex **4b** (7.0 mg, 0.010 mmol, 1.0 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. The reaction mixture is cooled to 23 ºC, and the yield is determined by comparing integration of the ^{19}F-NMR (375 MHz,

acetonitrile-*d*-3, 23 ºC) resonance of 1-*tert*-butyl-4-fluorobenzene (–120.7 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm, 2.00 μL, 0.0188 mmol). (79% yield). The ^{19}F-NMR chemical shift of the product corresponds to that of reported data.[9]

4-Fluorobiphenyl 5c

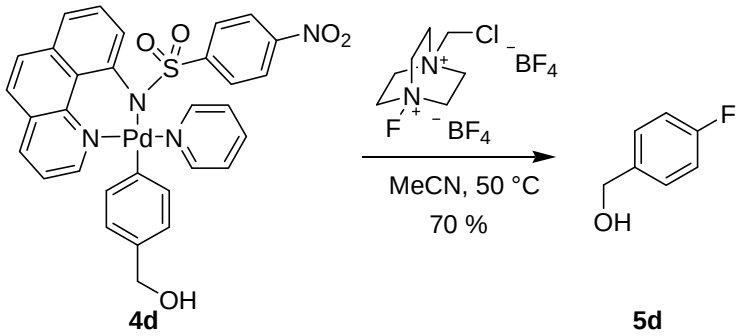


4c **5c**

To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (85.0 mg, 0.240 mmol, 1.20 equiv) in acetonitrile (6.0 mL) at 50 ºC is added aryl palladium complex **4c** (143 mg, 0.200 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv), and filtered through a plug of celite. The filtrate is concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 99:1 (v/v) to afford 24.8 mg of the title compound as a white solid (72% yield). TLC (hexane/EtOAc, 19:1 v/v): R_F = 0.60; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.60–7.54 (m, 4H), 7.47 (dd, J = 7.5 Hz, 7.0 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.14 (dd, J = 8.0 Hz, 7.5 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 162.7 (d, J = 244 Hz), 140.5, 137.6, 129.0, 128.9 (d, J = 8.5 Hz), 127.5, 127.3, 115.8 (d, J = 21 Hz); ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –116.2. These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

[9] Laali, K. K., Okazaki, T. Bunge, S. D. *N*-(Trifluoromethylsulfonyl)aryloxytrifluoromethylsulfoximines [ArO-SO(CF3)=NTf] and *N*-aryltriflimides Ar-N(Tf)2 by thermal and photolytic dediazoniation of [ArN2][BF4] in [BMIM][Tf2N] ionic liquid: exploiting the ambident nucleophilic character of a "nonnucleophilic" anion. *J. Org. Chem.* **72**, 6758–6762 (2007).

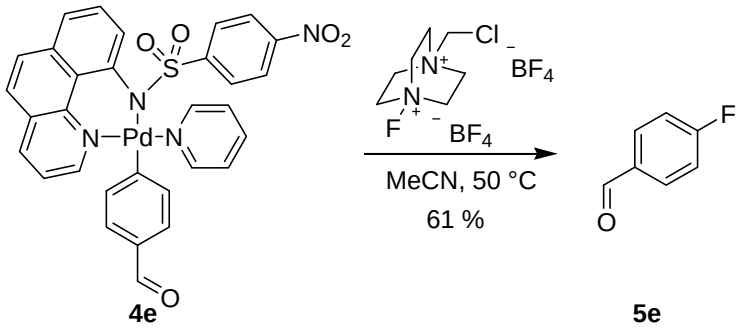
4-Fluorobenzylalcohol 5d



To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120 mmol, 1.20 equiv) in acetonitrile (3.0 mL) at 50 ºC is added aryl palladium complex **4d** (67.1 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with pentane/Et_2O 7:3 (v/v) to afford 8.8 mg of the title compound as colorless oil (70% yield).

TLC (hexane/EtOAc 7:3 v/v): R_F = 0.61; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.29–7.25 (m, 2H), 7.05–7.00 (dd, J = 8.0 Hz, 7.5 Hz, 2H), 4.55 (s, 2H), 3.10 (br, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 162.5 (d, J = 243 Hz), 136.8, 129.0 (d, J = 8.3 Hz), 115.6 (d, J = 21 Hz), 64.5; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –115.4. These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

4-Fluorobenzaldehyde 5e

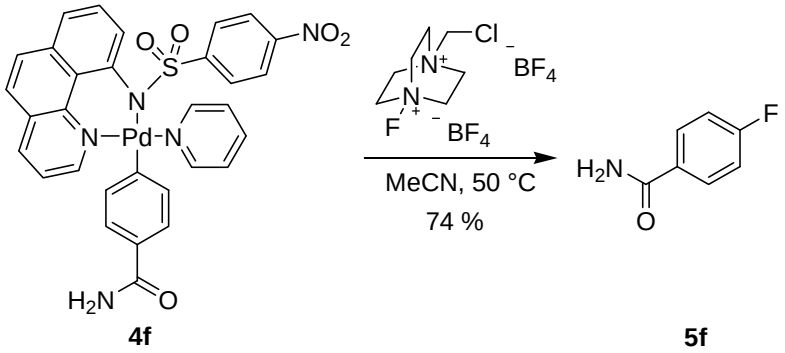


To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120 mmol, 1.20 equiv) in acetonitrile (3.0 mL) at 50 ºC is added aryl palladium complex **4e** (66.9 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with pentane/Et_2O 7:3 (v/v) to afford 8.8 mg of the title compound as colorless oil (61% yield).

TLC (hexane/EtOAc, 7:3 v/v): R_F = 0.77; ^{1}H-NMR (500 MHz, $CDCl_3$ 23 ºC): δ 9.95 (s, 1H), 7.92–7.88 (m, 2H), 7.22–7.18 (dd, J = 8.0 Hz, 7.5 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 190.7, 166.7 (d, J = 255

Hz), 133.2, 132.5 (d, J = 9.9 Hz), 116.6 (d, J = 22 Hz); ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –102.9. These spectroscopic data correspond to those of authentic sample purchased from Aldrich.

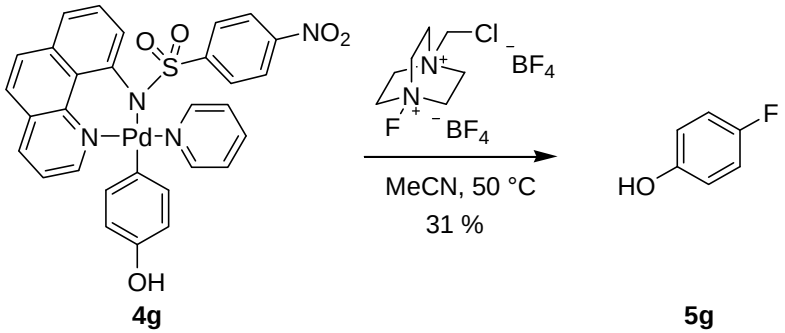
4-Fluorobenzmide 5f



To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120 mmol, 1.20 equiv) in acetonitrile (3.0 mL) at 50 ºC is added aryl palladium complex **4f** (68.4 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with EtOAc to afford 10.3 mg of the title compound as colorless oil (74% yield).

TLC (EtOAc): R_F = 0.40; ^{1}H-NMR (500 MHz, DMSO-*d*-6, 23 ºC): δ 8.02 (br, 1H), 7.95 (dd, J = 9.0 Hz, 6.0Hz, 2H), 7.42 (br, 1H), 7.26 (dd, J = 7.5 Hz, 7.0 Hz, 2H); ^{13}C-NMR (125 MHz, DMSO-*d*-6, 23 ºC): δ 167.6, 164.6 (d, J = 247 Hz), 131.4, 130.8 (d, J = 14 Hz), 115.8 (d, J = 21 Hz); ^{19}F-NMR (375 MHz, DMSO-*d*-6, 23 ºC): δ –110.0. These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

4-Fluorophenol 5g

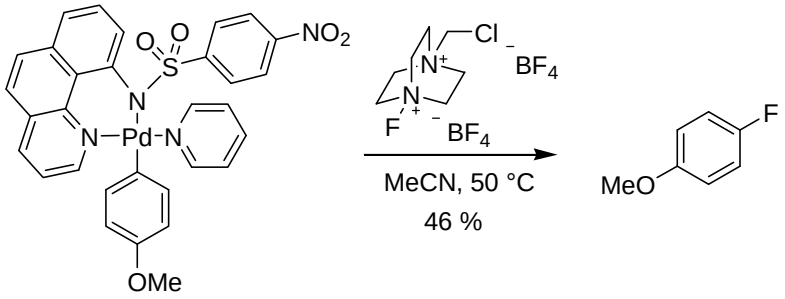


To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (85.0 mg, 0.240 mmol, 1.20 equiv) in acetone (6.0 mL) at 50 ºC is added aryl palladium complex **4g** (131 mg, 0.200 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (16 μL, 0.20 mmol, 1.0 equiv). After concentrated

in vacuo, the residue is purified by preparative TLC eluting with Hexane/EtOAc 7:3 (v/v) to afford 6.9 mg of the title compound as a white solid (31% yield).

TLC (hexane/EtOAc, 7:3 v/v): R_F = 0.58; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 6.95–6.95 (dd, J = 8.0 Hz, 7.5 Hz, 2H), 6.80–6.76 (m, 2H), 5.41 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 157.6 (d, J = 237 Hz), 151.5, 116.5 (d, J = 8.0 Hz), 116.3 (d, J = 21 Hz); ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –124.3. These spectroscopic data correspond to those of authentic sample purchased from Aldrich.

4-Fluoroanisole 5h

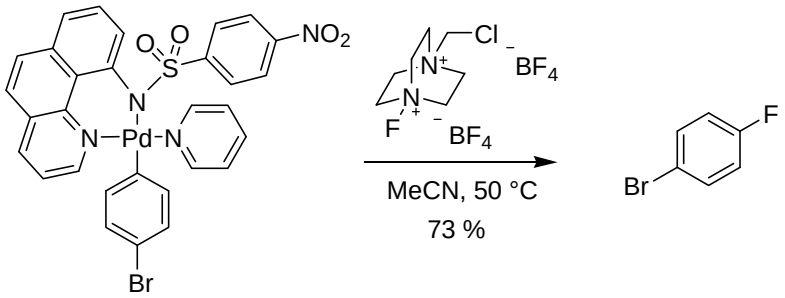


4h **5h**

To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (85.0 mg, 0.240 mmol, 1.20 equiv) in acetone (6.0 mL) at 50 ºC is added aryl palladium complex **4h** (134 mg, 0.200 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (16 μL, 0.20 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with pentane/Et_2O 9:1 (v/v) to afford 11.6 mg of the title compound as colorless oil (46% yield).

TLC (hexane/EtOAc, 9:1 v/v): R_F = 0.55; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.01–6.95 (m, 2H), 6.87–6.81 (m, 2H), 3.79 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 157.4 (d, J = 247 Hz), 155.9, 116.0 (d, J = 23 Hz), 115.0 (d, J = 7.7 Hz), 56.0; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –124.8. These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

1-Bromo-4-fluorobenzene 5i



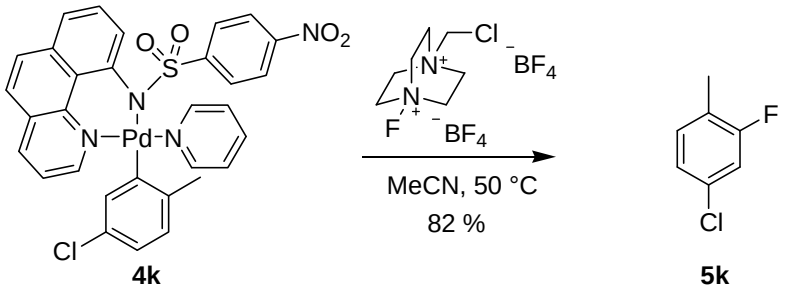
4i **5i**

To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120

mmol, 1.20 equiv) in acetonitrile (3.0 mL) at 50 ºC is added aryl palladium complex **4i** (72.0 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with pentane/Et_2O 19:1 (v/v) to afford 12.8 mg of the title compound as colorless oil (73% yield).

TLC (hexane/EtOAc, 19:1 v/v): R_F = 0.70; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.47–7.42 (m, 2H), 6.98–6.92 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 162.1 (d, J = 245 Hz), 133.2, (d, J = 8.5 Hz), 117.5 (d, J = 23 Hz), 116.8; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –115.7. These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

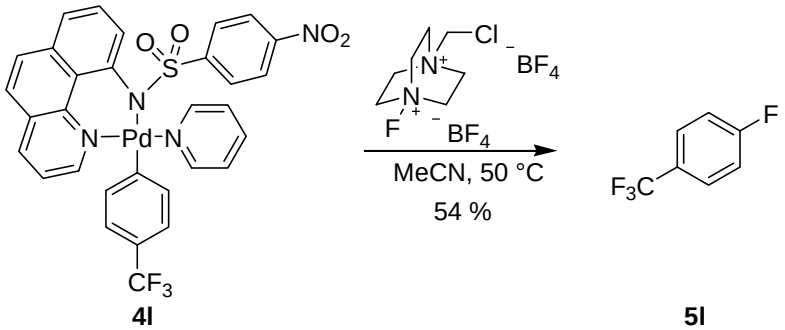
4-Chloro-2-fluorotoluene 5k



To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120 mmol, 1.20 equiv) in acetonitrile (3.0 mL) at 50 ºC is added aryl palladium complex **4k** (68.9 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with pentane/Et_2O 9:1 (v/v) to afford 11.9 mg of the title compound as colorless oil (82% yield).

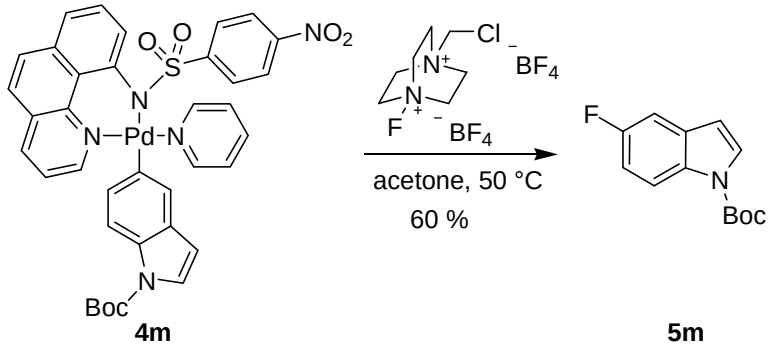
TLC (hexane/EtOAc, 9:1 v/v): R_F = 0.72; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 7.13–7.08 (dd, J = 7.5 Hz, 7.0 Hz, 2H), 7.05–7.01 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 161.3 (d, J = 246 Hz), 132.3, 132.2 (d, J = 5.9 Hz), 124.3, 123.6 (d, J = 17 Hz), 116.0 (d, J = 26 Hz), 14.4; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –115.1; These spectroscopic data correspond to those of authentic sample purchased from Alfa Aesar.

4-Fluorobenzotrifluoride 5l



To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (4.3 mg, 0.012 mmol, 1.2 equiv) in acetonitrile-*d*-3 (0.3 mL) at 50 ºC is added aryl palladium complex **4l** (6.4 mg, 0.010 mmol, 1.0 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. The reaction mixture is cooled to 23 ºC, and the yield is determined by comparing integration of the ^{19}F-NMR (375 MHz, acetonitrile-*d*-3, 23 ºC) resonance of 4-fluorobenzotrifluoride (–109.4 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm, 2.00 μL, 0.0188mmol). (54% yield). The ^{19}F-NMR chemical shift of the product corresponds to that of authentic sample purchased from Alfa Aesar.

N-Boc-5-fluoroindole 5m

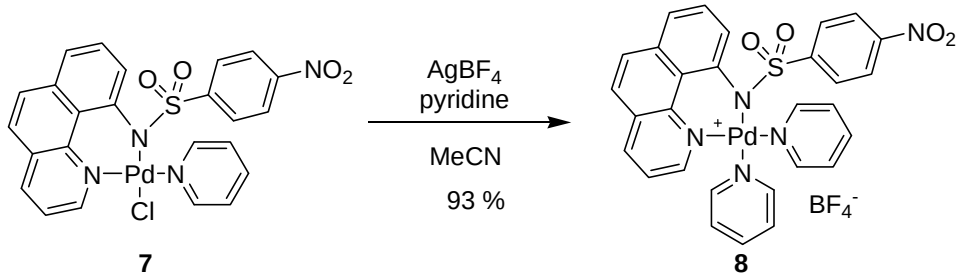


4m **5m**

To 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2**) (42.5 mg, 0.120 mmol, 1.20 equiv) in acetone (3.0 mL) at 50 ºC is added aryl palladium complex **4m** (78.0 mg, 0.100 mmol, 1.00 equiv) as a solid in 10 portions over 10 min. The reaction mixture is stirred at 50 ºC for 20 min. After cooled to 23 ºC, to the reaction mixture is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). After concentrated in vacuo, the residue is purified by preparative TLC eluting with hexane/EtOAc 7:3 (v/v) to afford 14.1 mg of the title compound as colorless oil (60% yield).

TLC (hexane/EtOAc 7:3 v/v): R_F = 0.753; ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC): δ 8.08 (br, 1H), 7.62 (d, J = 4.0 Hz, 1H), 7.20 (dd, J = 6.5 Hz, J = 2.0 Hz, 1H), 7.03 (ddd, J = 7.0 Hz, 6.5 Hz, 2.0 Hz, 1H), 6.52 (d, J = 4.0 Hz, 1H), 1.68 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 159.5 (d, J = 238 Hz), 149.7, 131.8, 131.6 (d, J = 10 Hz), 127.7, 116.3 (d, J = 9.1 Hz), 112.2 (d, J = 24 Hz), 107.2, 106.5 (d, J = 24 Hz), 84.1, 28.4; ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC): δ –121.7. These spectroscopic data correspond to those of authentic sample independently synthesized from 5-fluoroinodole and Boc_2O.

Bispyridine palladium tetrafluoroborate salt 8



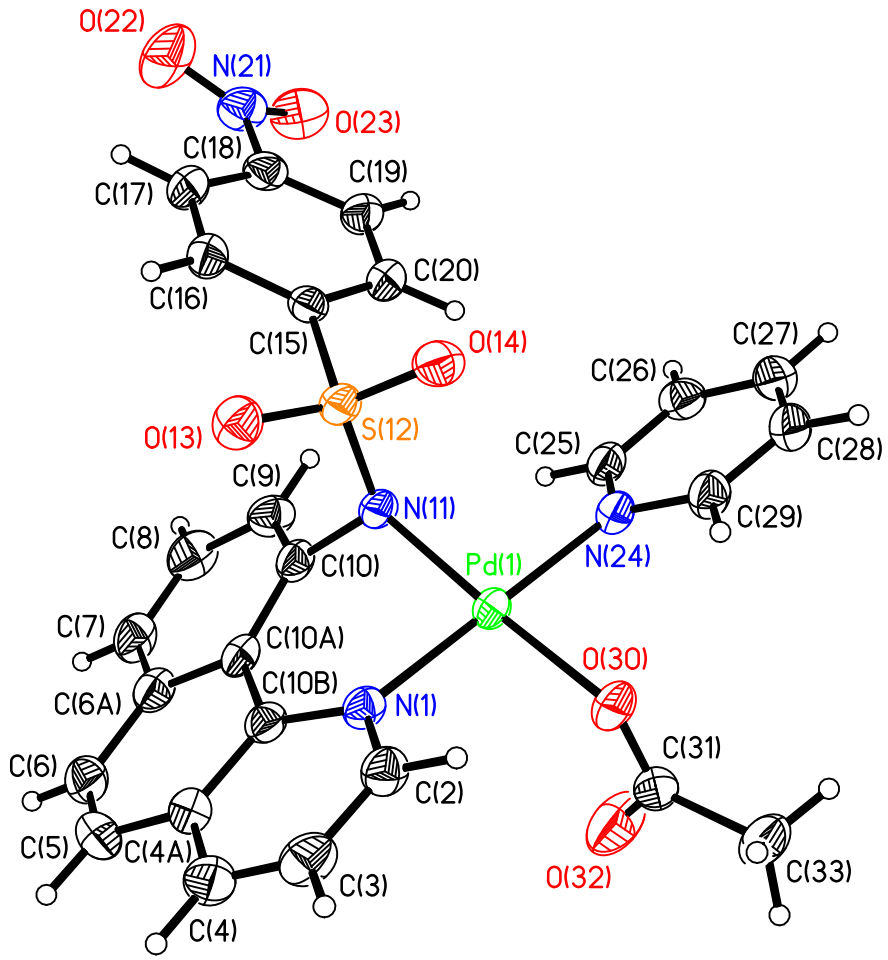
7 **8**

To chloro palladium complex **7** (59.9 mg, 0.100 mmol, 1.00 equiv) in acetonitrile (1.0mL) at 23 ºC is added $AgBF_4$ (38.8 mg, 0.200 mmol, 2.00 equiv). The suspension is stirred at 23 ºC for 1.0 hour and to the suspension is added pyridine (8.1 μL, 0.10 mmol, 1.0 equiv). The suspension is filtered through a plug of celite and the filtrate is concentrated in vacuo to afford 67.9 mg of the title compound as an orange solid (67.9 mg, 93% yield).

^{1}H-NMR (500 MHz, acetone-*d*-6, 23 ºC): δ 9.29 (d, *J* = 5.5 Hz, 2H), 8.99 (d, *J* = 5.5 Hz, 2H), 8.51 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 8.44 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 8.15–8.08 (m, 3H), 8.01 (dd, *J* = 8.0 Hz, 7.5 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.80–7.70 (m, 4H), 7.66 (d, *J* = 9.0 Hz, 2H), 7.59–7.52 (m, 4H), 7.48 (dd, *J* = 8.0 Hz, 5.5 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC): δ 152.6, 152.4, 152.3, 152.2, 152.9, 152.8, 148.7, 147.2, 141.4, 140.8, 140.7, 140.6, 140.5, 140.3, 140.2, 137.7, 136.5, 130.8, 130.6, 130.3, 129.2, 128.8, 127.9, 127.8, 127.4, 127.2, 126.9, 126.8, 126.7, 126.5, 125.2, 124.9, 123.9, 123.8, 123.1, 122.9, 118.4. The complex ^{13}C spectrum is presumably due to pyridine exchange with the NMR solvent acetone. ^{19}F-NMR (375 MHz, acetone-*d*-6, 23 ºC): δ –151.5; HRMS-FIA (*m*/*z*): $[M - C_5H_5N + C_2H_3N - BF_4]^+$ calcd for $C_{31}H_{24}N_4O_5PdS$, 604.0265; found, 604.0228.

X-ray Crystallographic Analysis

Firgure S1.: acetato palladium complex 1 (CCDC 67599)

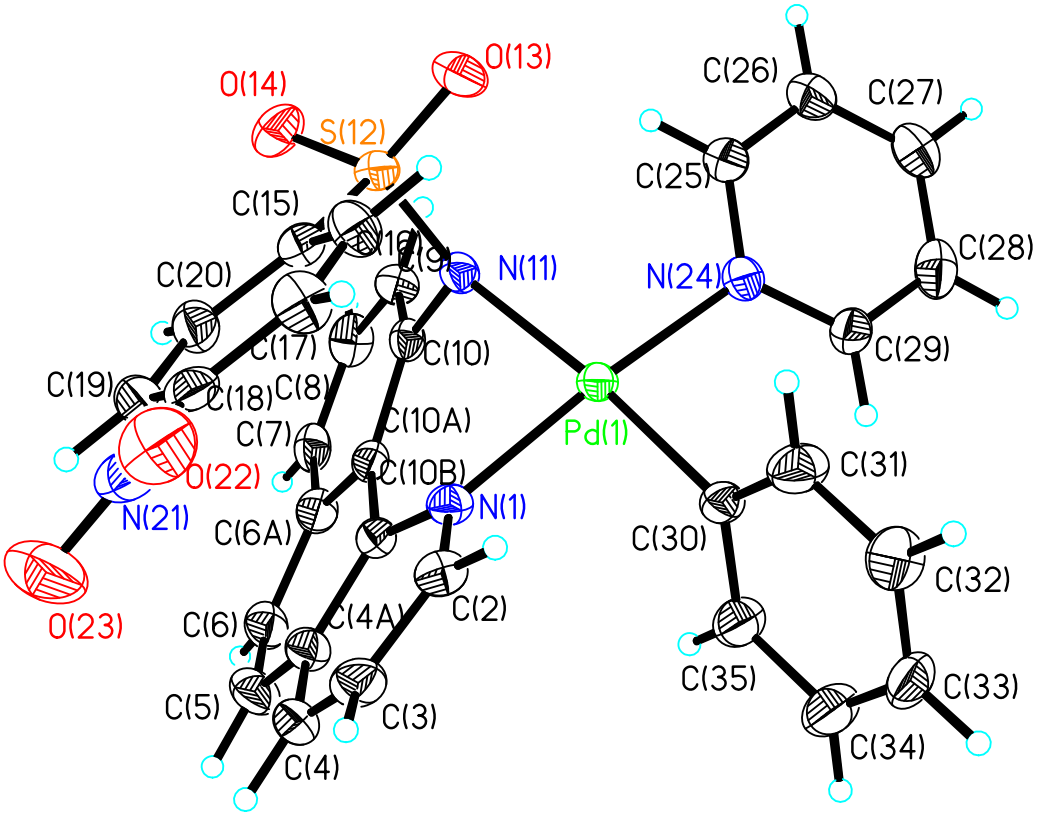


The x-ray structure of acetato palladium complex **1** with hydrogens and with the atom labeling scheme employed. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S2.: Crystal data and structure refinement for acetato palladium complex 1.

Identification code	CCDC 675999 = [Pd(C_5H_5N)($C_2H_3O_2$)($C_{19}H_{12}N_3O_4S$)]	
Formula	C26 H20 N4 O6 Pd S	
Formula weight	622.92	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No. 2)	
Unit cell dimensions	a = 9.1803(2) Å	α= 67.735(1)°
	b = 11.3199(2) Å	β= 87.215(1)°
	c = 12.8456(2) Å	γ = 75.798(1)°
Volume	1196.16(4) $Å^3$	
Z	2	
Density (calculated)	1.730 Mg/m^3	
Absorption coefficient	0.916 mm^{-1}	
F(000)	628	
Crystal size	0.175 x 0.150 x 0.025 mm^3	
Theta range for data collection	1.72 to 27.50°	
Index ranges	-11<=h<=11, -14<=k<=14, -16<=l<=16	
Reflections collected	17370	
Independent reflections	5486 [R(int) = 0.0586]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9775 and 0.8562	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5486 / 0 / 344	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0859	
R indices (all data)	R1 = 0.0518, wR2 = 0.0935	
Largest diff. peak and hole	0.525 and -0.543 e.$Å^{-3}$	

Figure S2.: aryl palladium complex 4a (CCDC 676000)

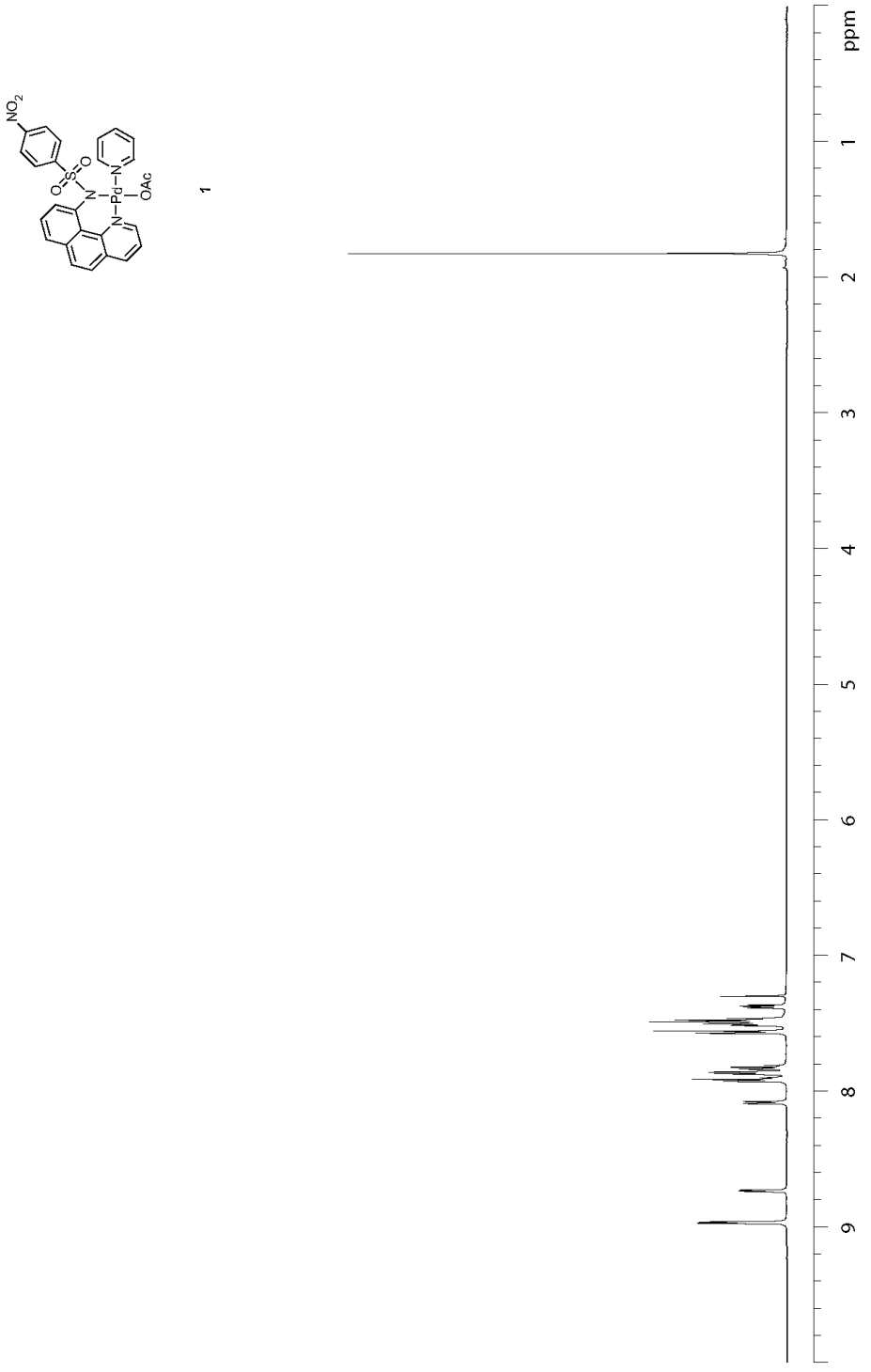


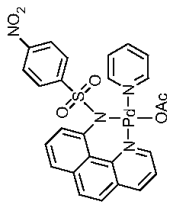
The x-ray structure of aryl palladium complex **4a** with hydrogens and with the atom labeling scheme employed. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S3.: Crystal data and structure refinement for aryl palladium complex 4a.

Identification code	CCDC 676000 = [Pd(C_5H_5N)(C_6H_5)($C_{19}H_{12}N_3O_4S$)]	
Empirical formula	C30 H22 N4 O4 Pd S	
Formula weight	640.98	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$ (No. 19)	
Unit cell dimensions	a = 9.5439(2) Å	α= 90°
	b = 13.8697(2) Å	β= 90°
	c = 19.5047(3) Å	γ = 90°
Volume	2581.86(8) $Å^3$	
Z	4	
Density (calculated)	1.649 Mg/m^3	
Absorption coefficient	0.846 mm^{-1}	
F(000)	1296	
Crystal size	0.125 x 0.075 x 0.050 mm^3	
Theta range for data collection	1.80 to 27.50°	
Index ranges	-12<=h<=12, -18<=k<=18, -25<=l<=25	
Reflections collected	67549	
Independent reflections	5932 [R(int) = 0.1052]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9589 and 0.9016	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5932 / 0 / 361	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0657	
R indices (all data)	R1 = 0.0427, wR2 = 0.0698	
Absolute structure parameter	-0.03(2)	
Largest diff. peak and hole	0.488 and -0.576 e.$Å^{-3}$	

Spectroscopic Data





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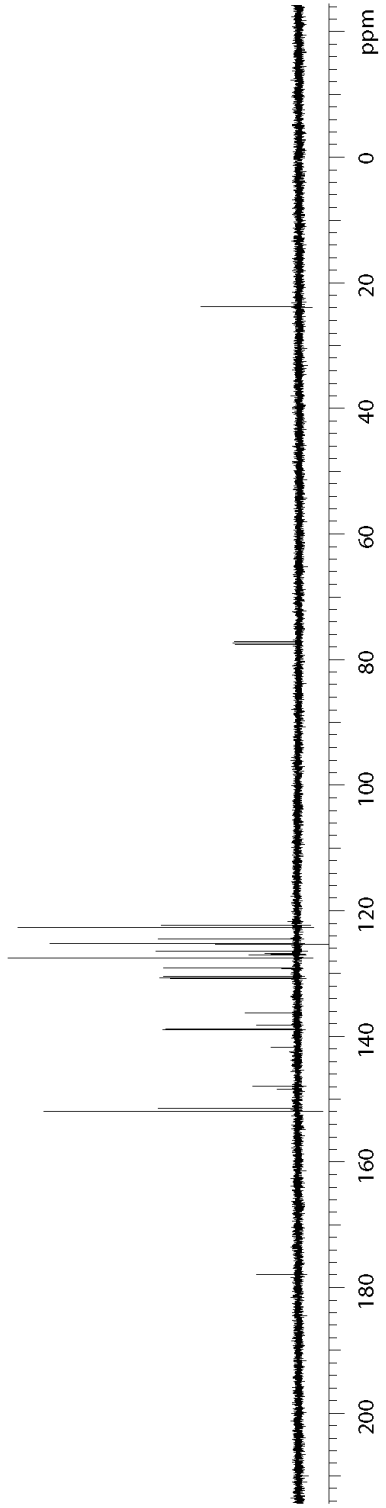

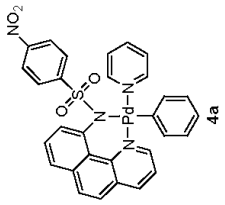

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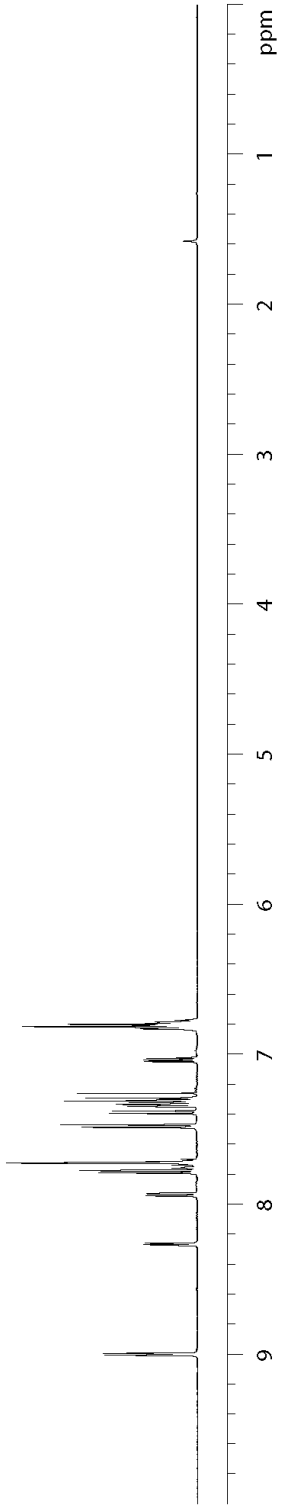

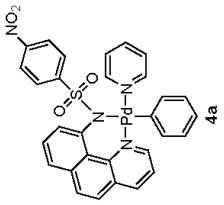

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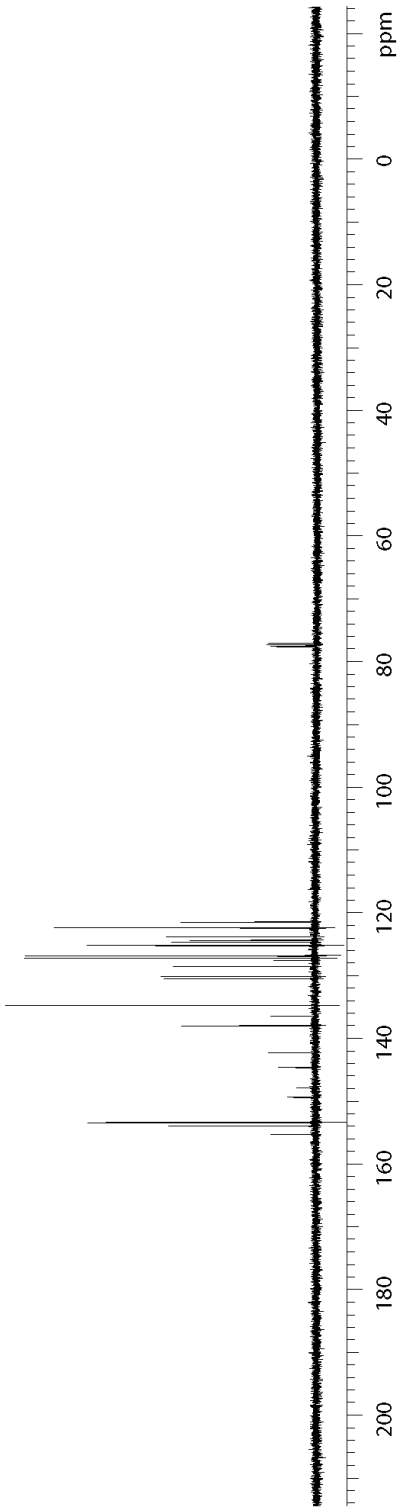

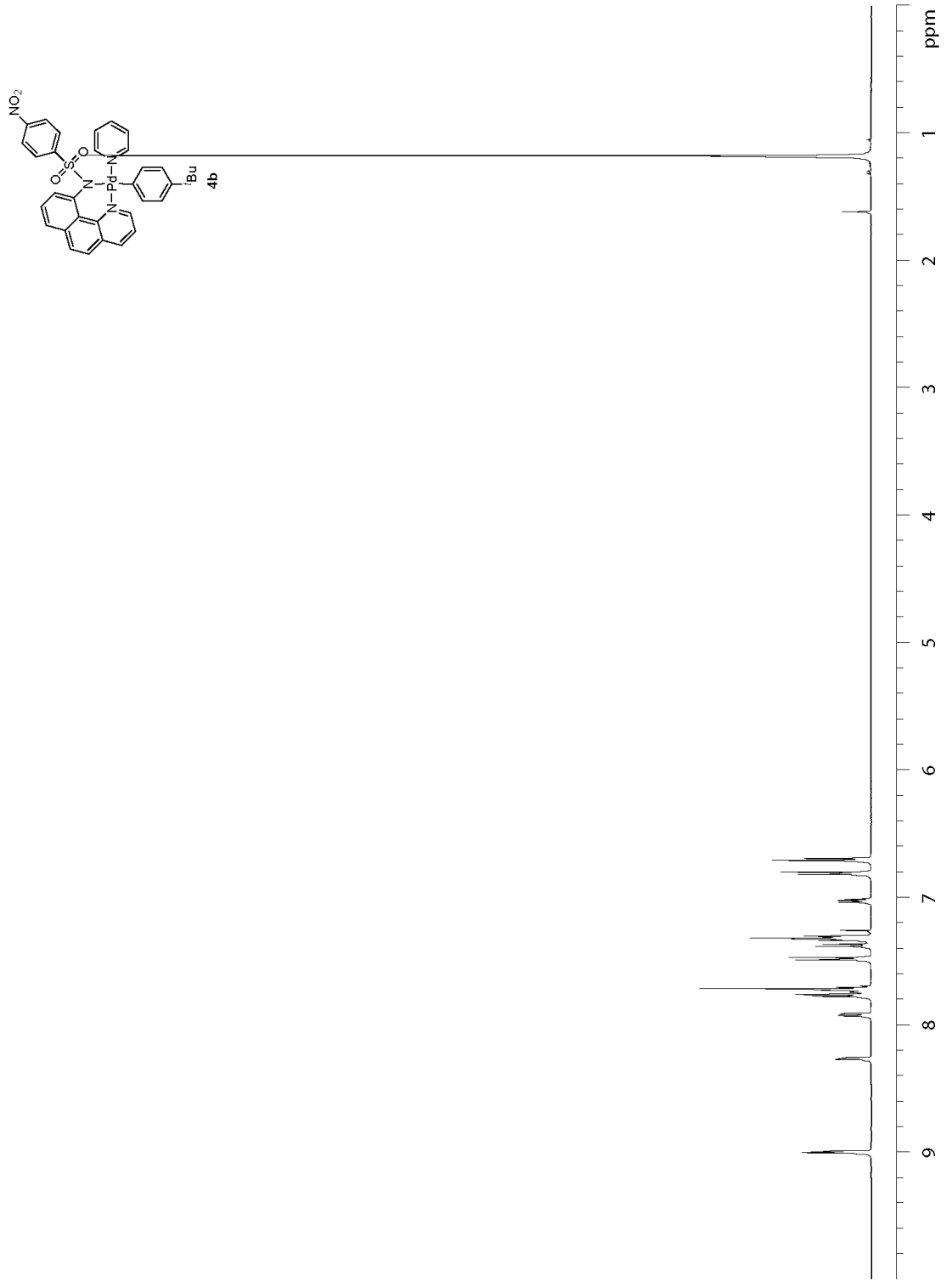
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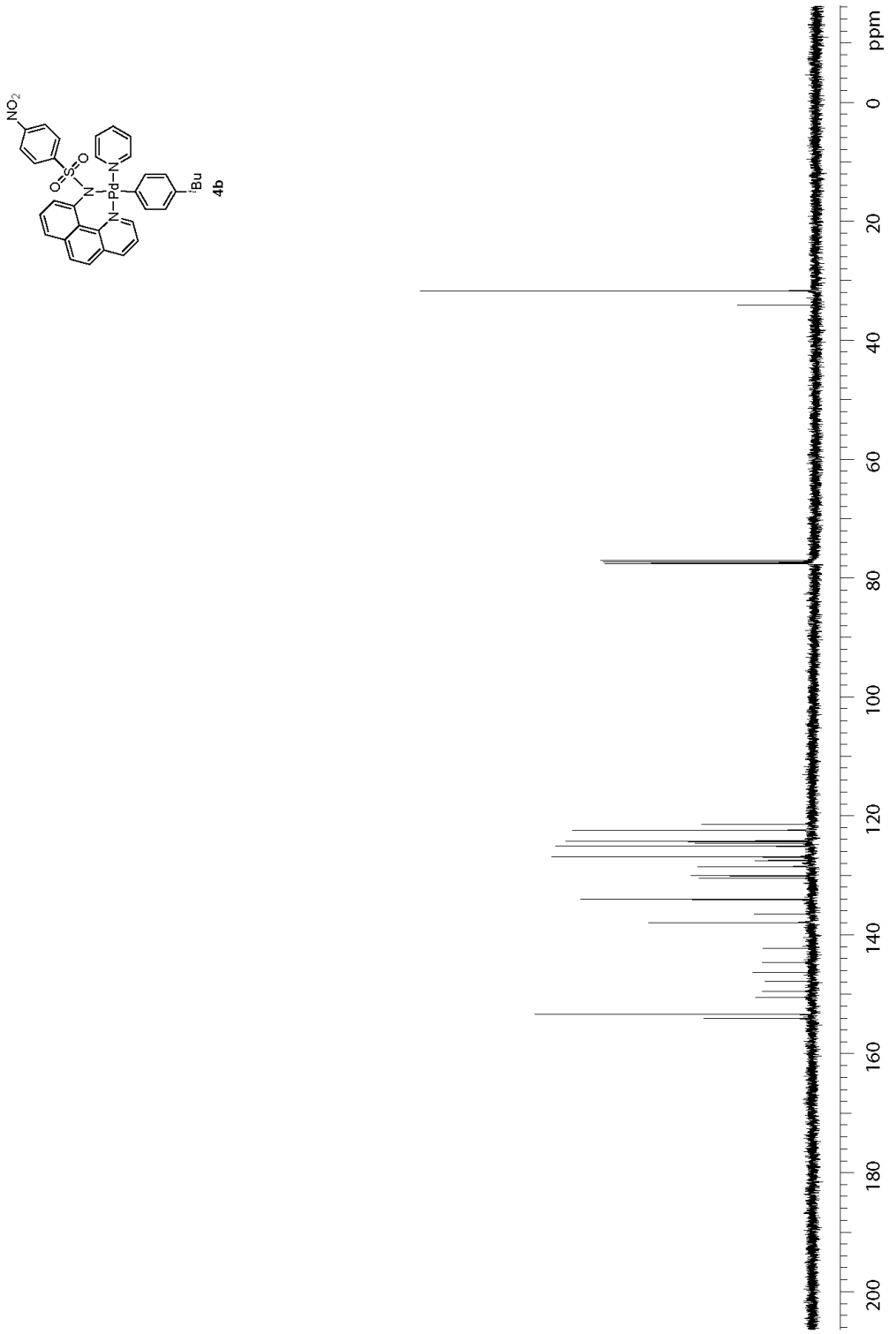
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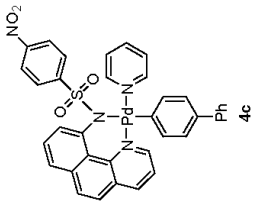

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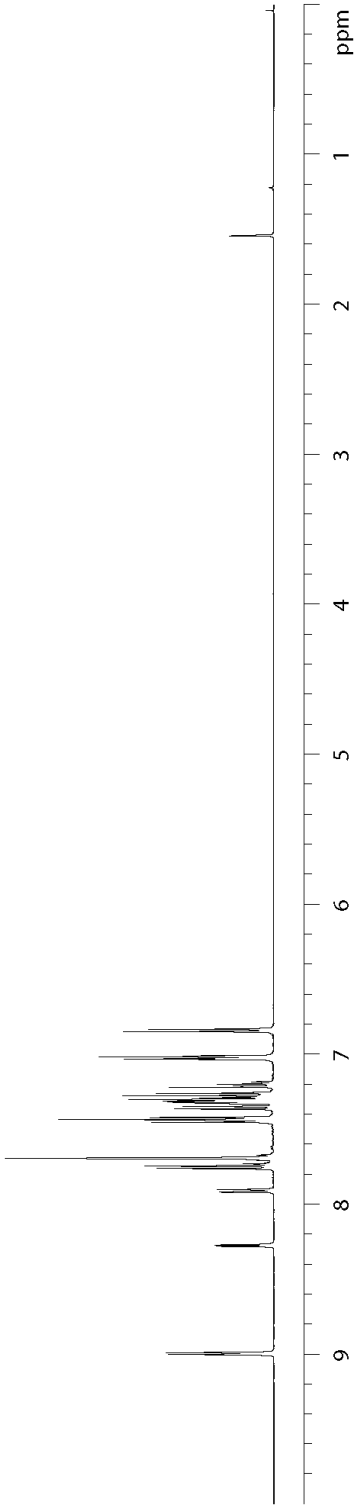

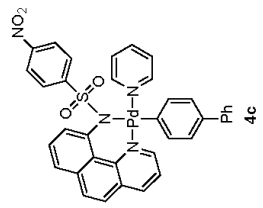

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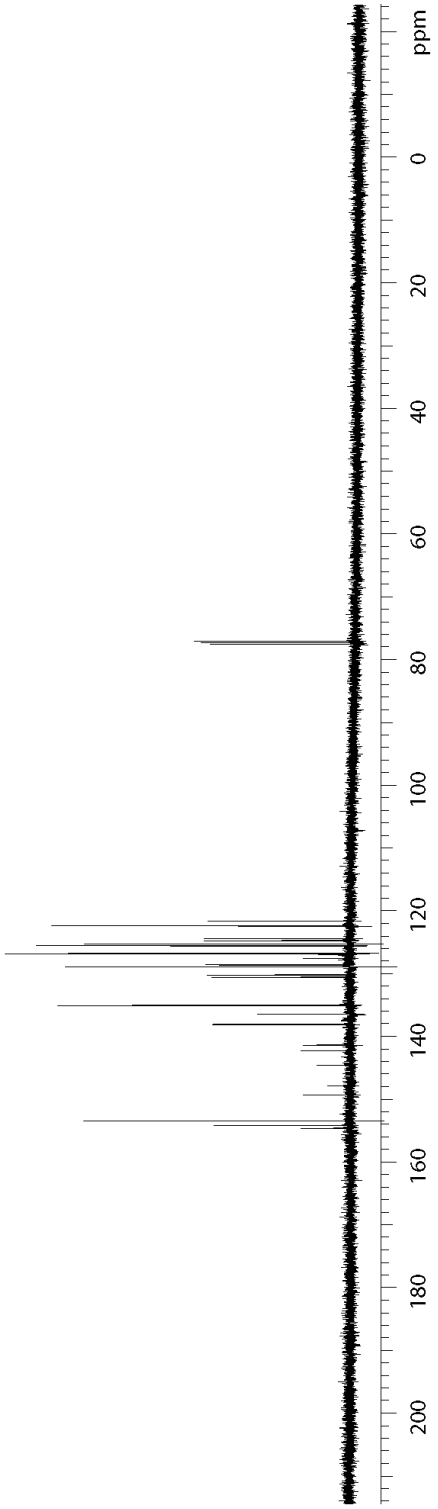

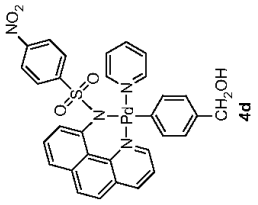

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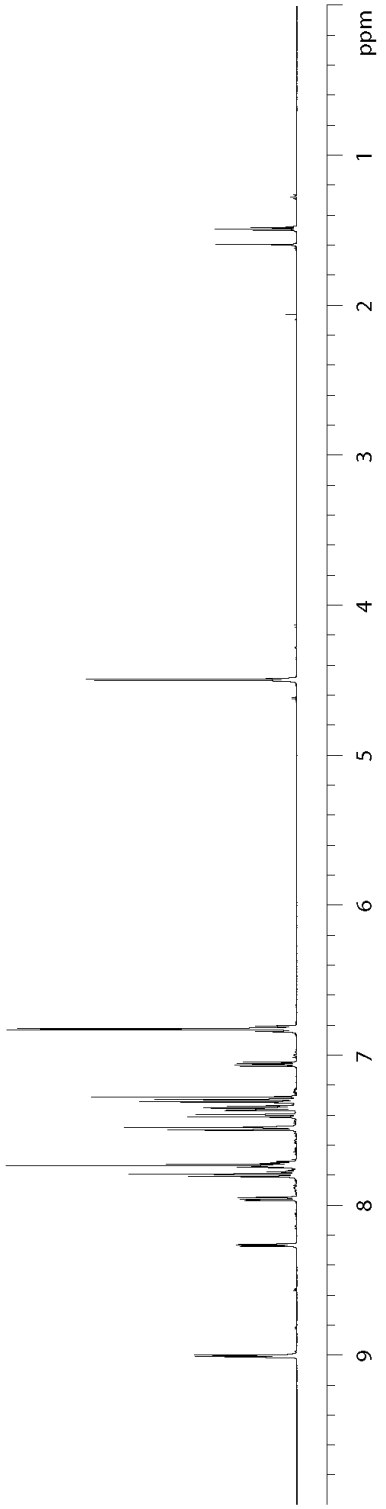

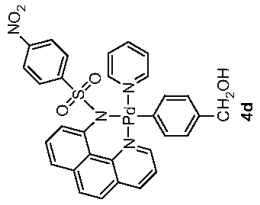

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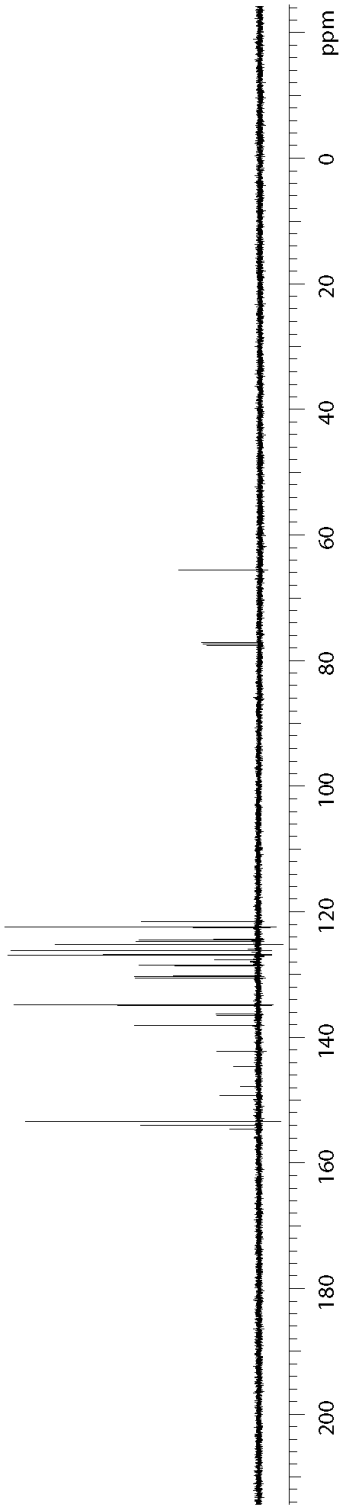

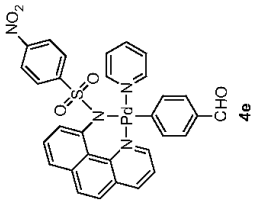

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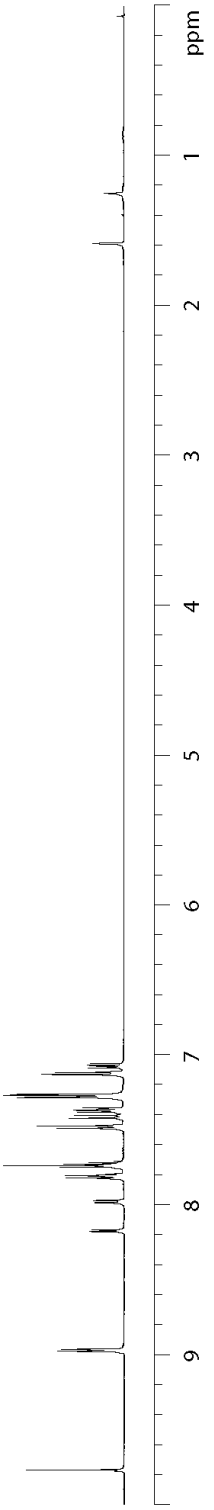

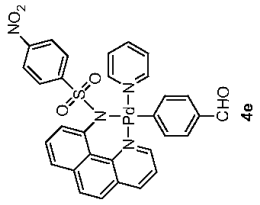

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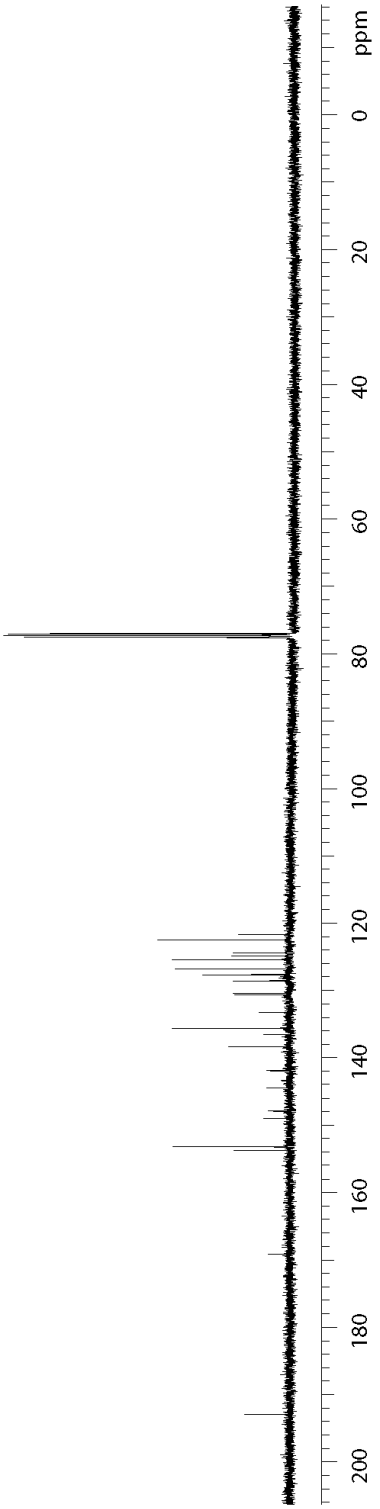

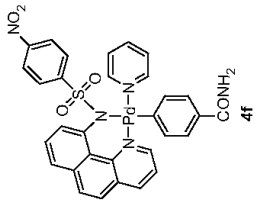

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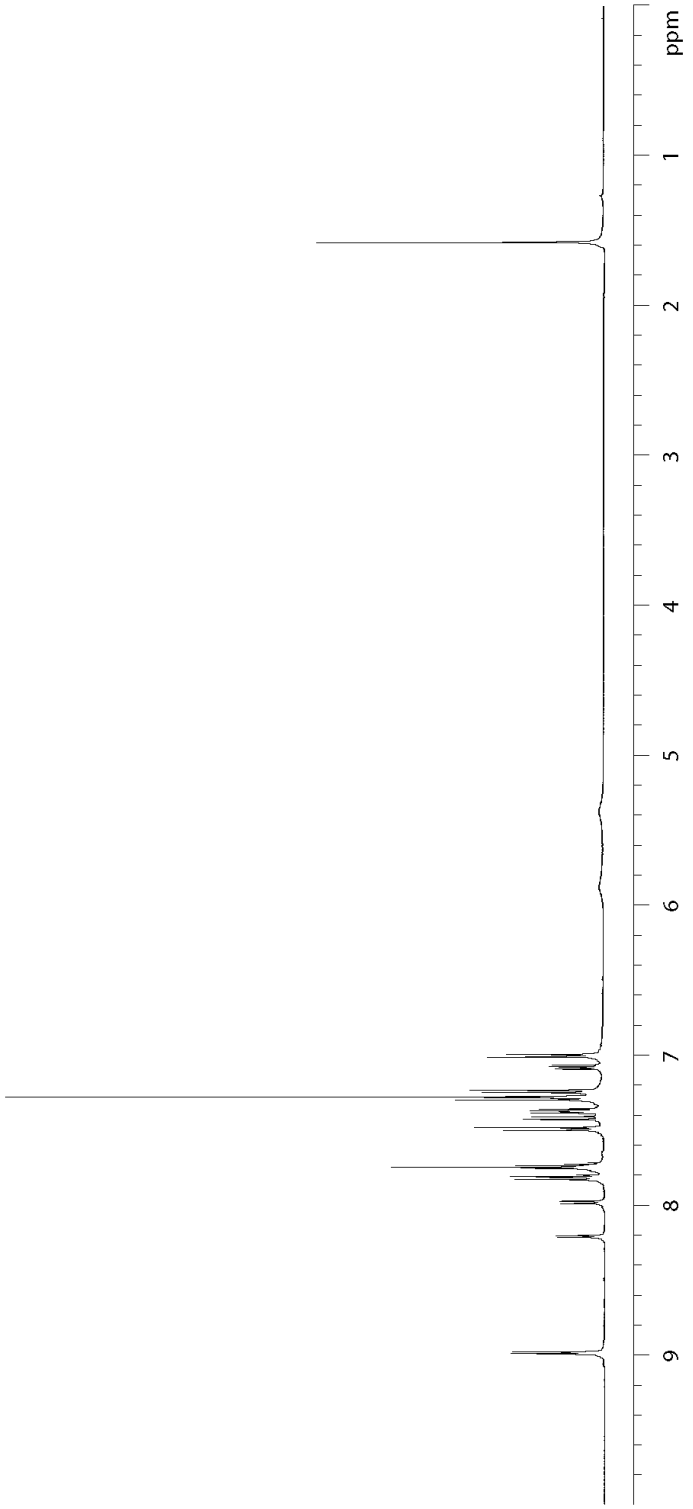

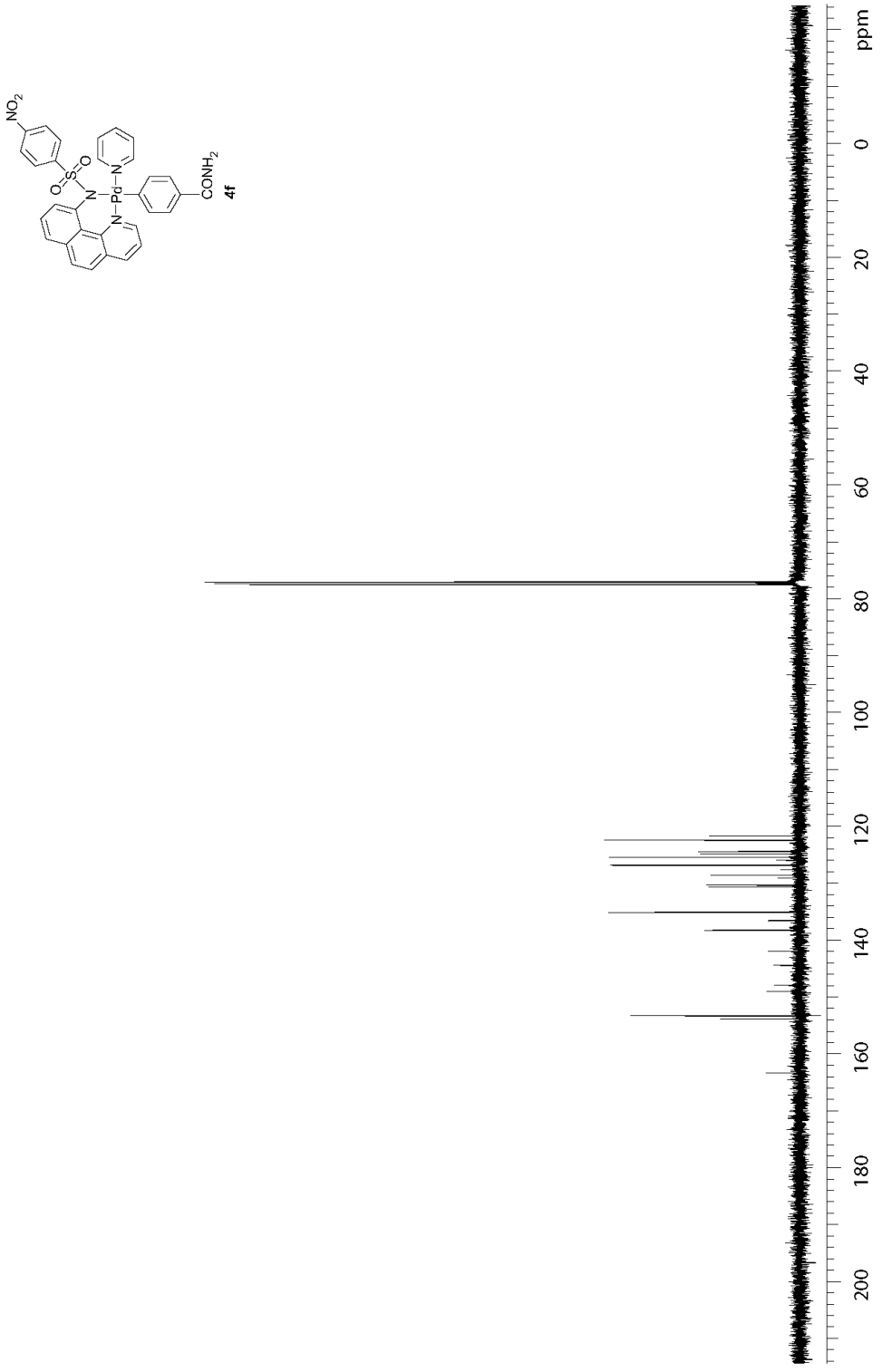
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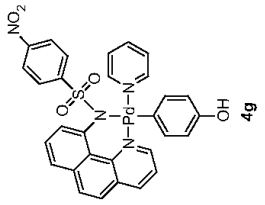

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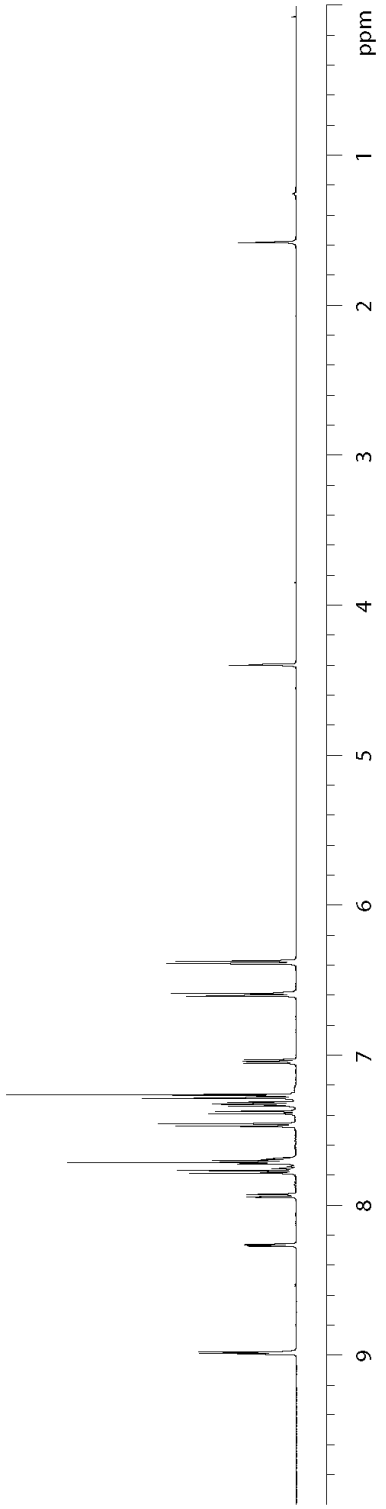

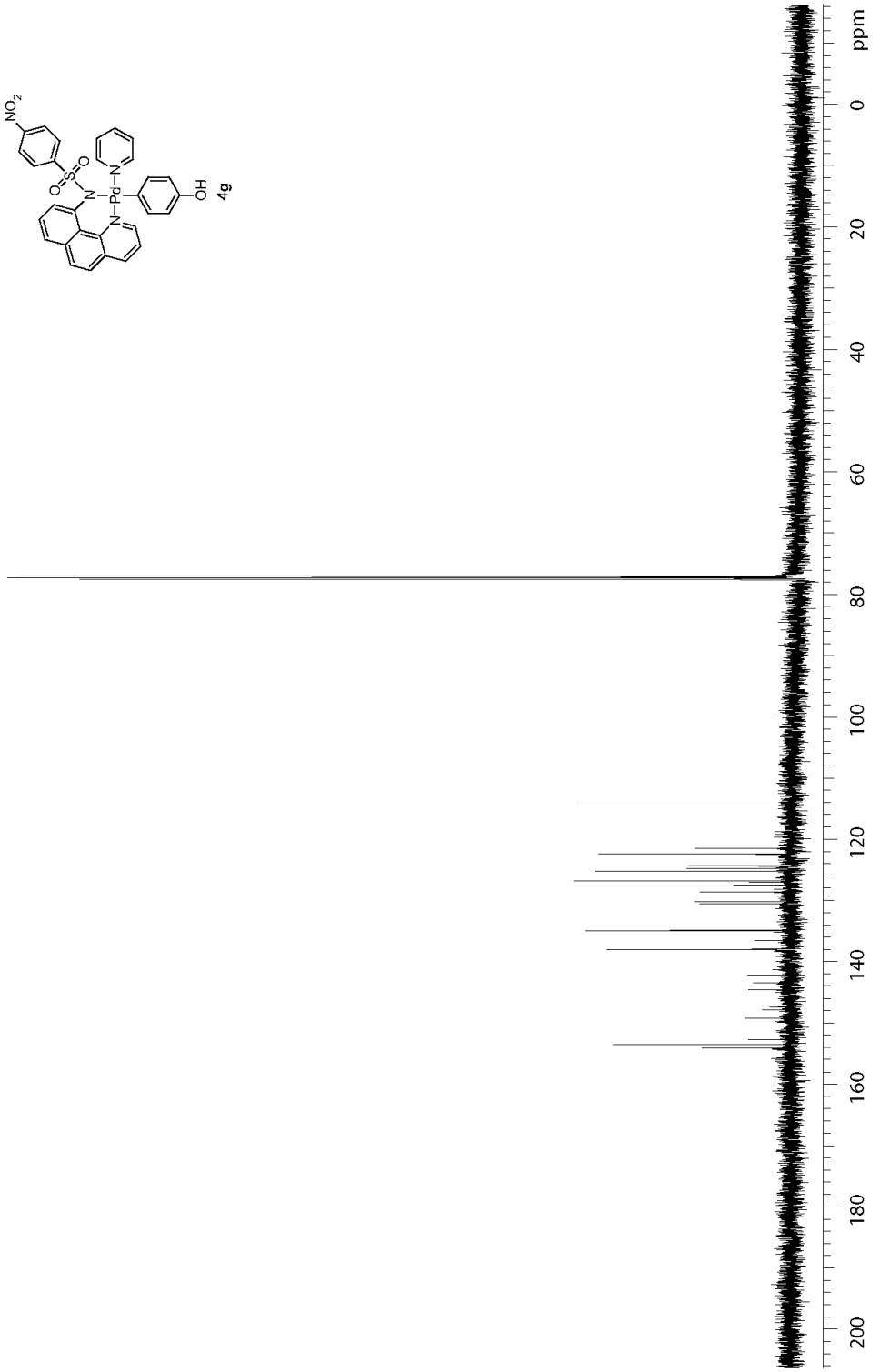
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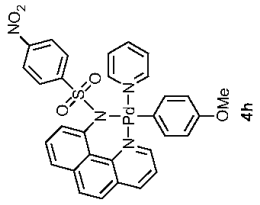

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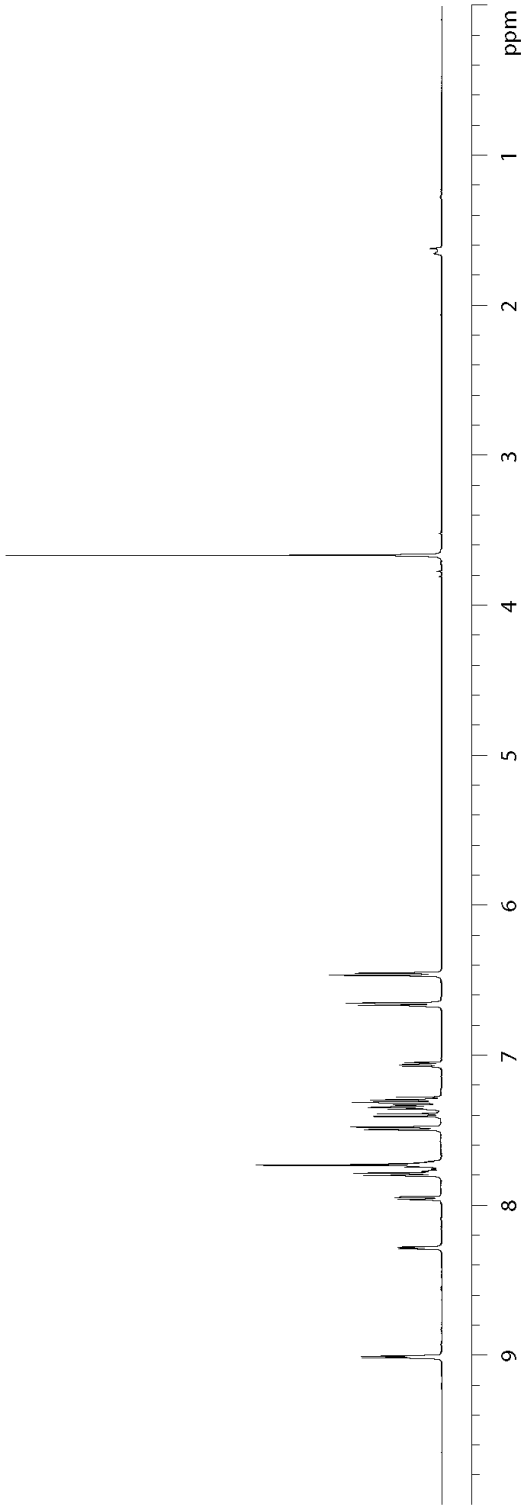

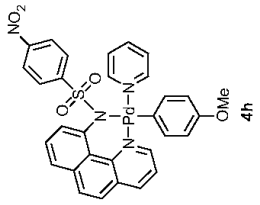

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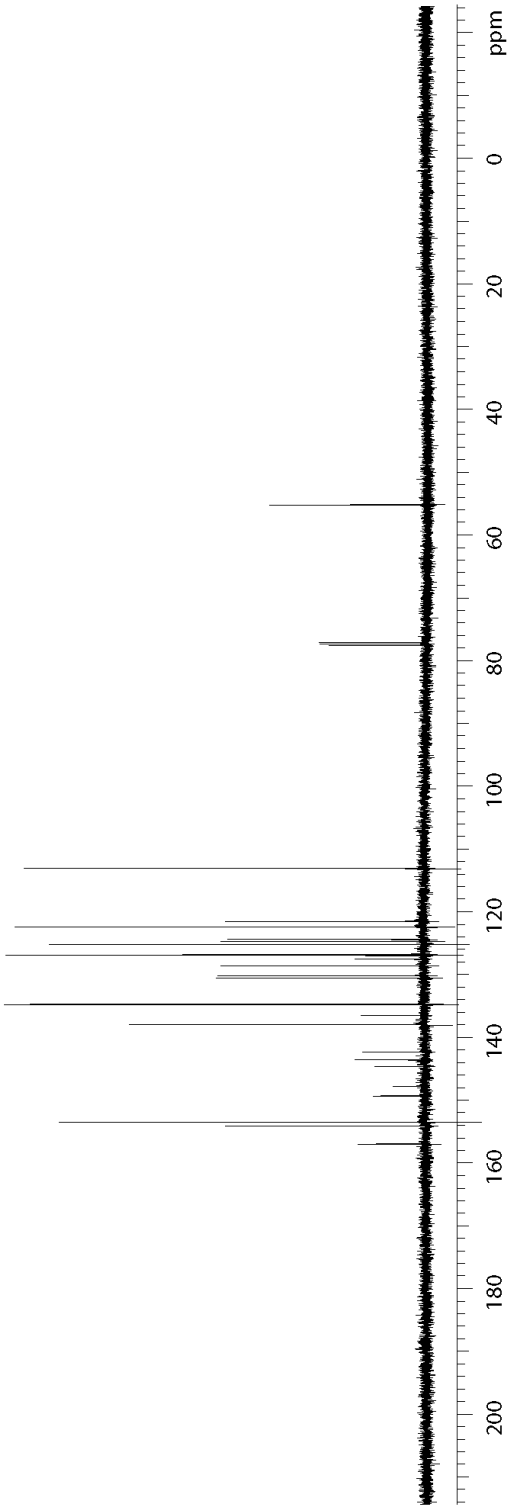

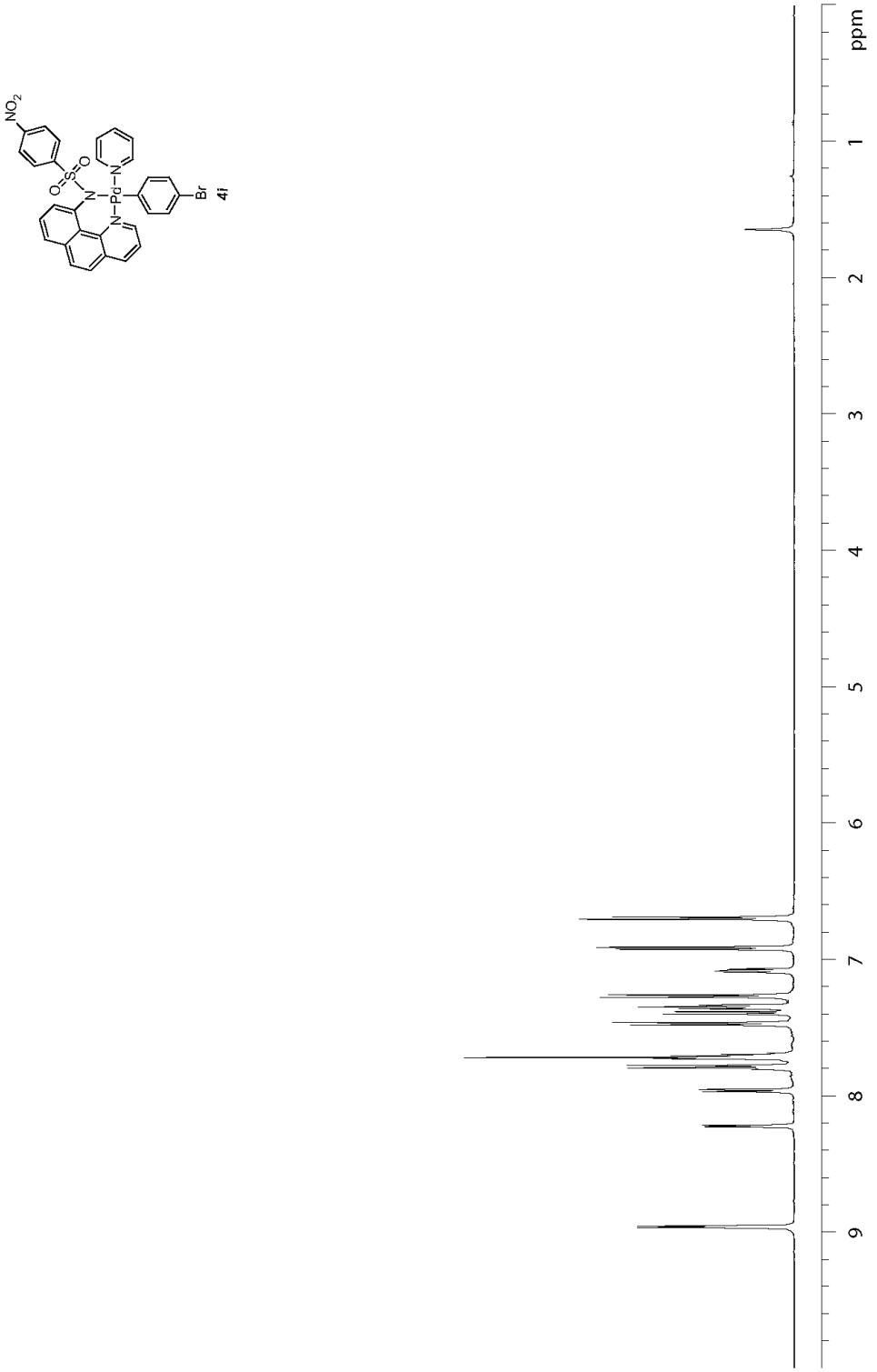
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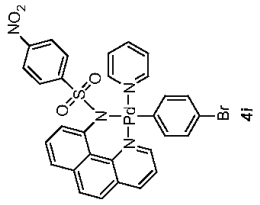

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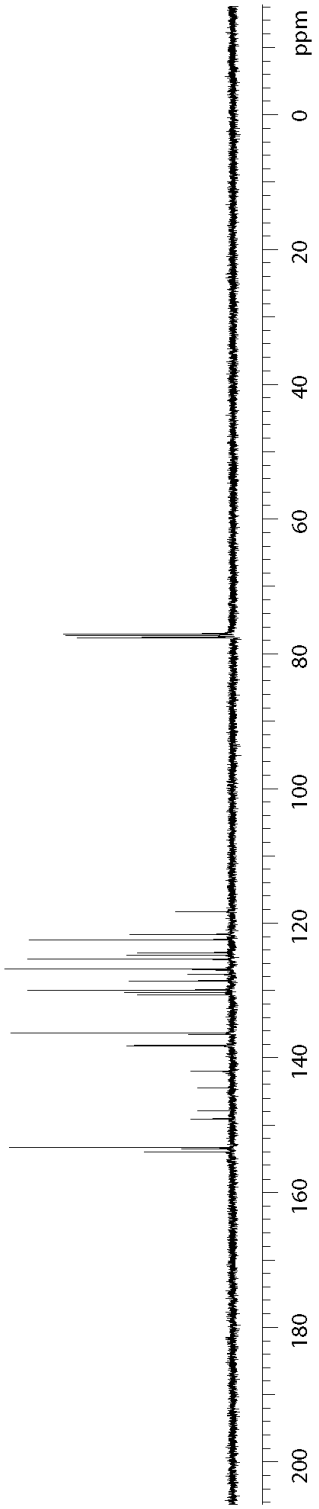

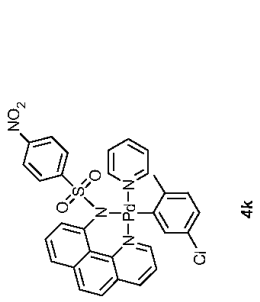

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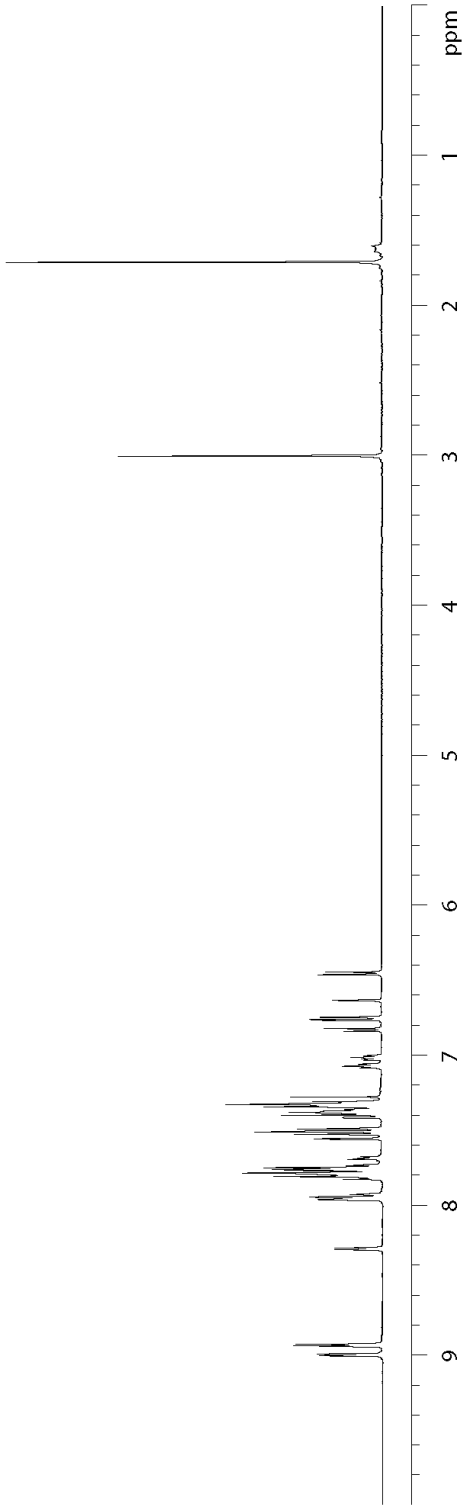

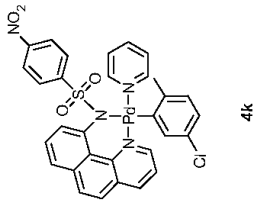

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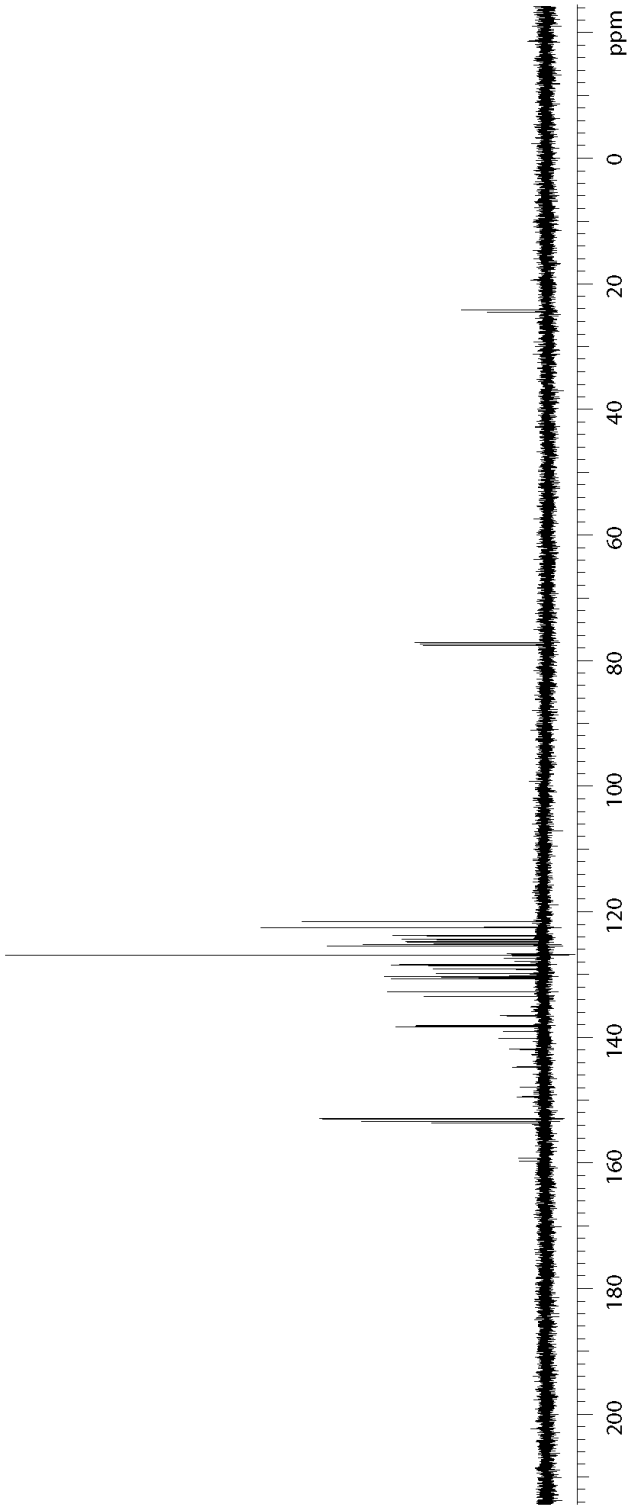

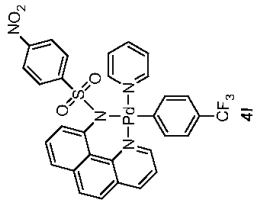

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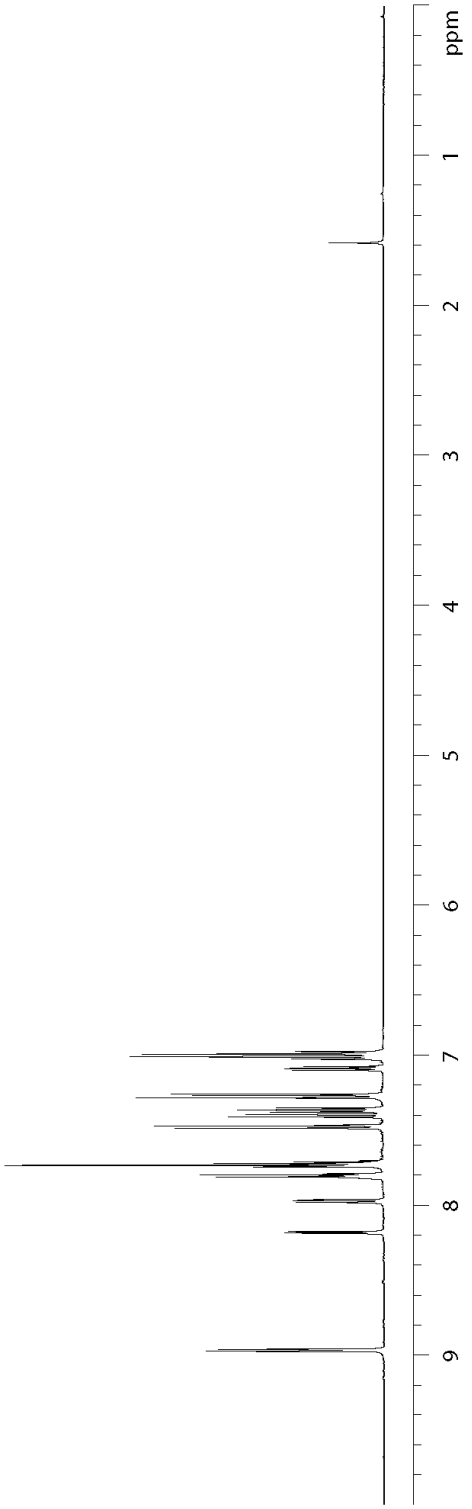

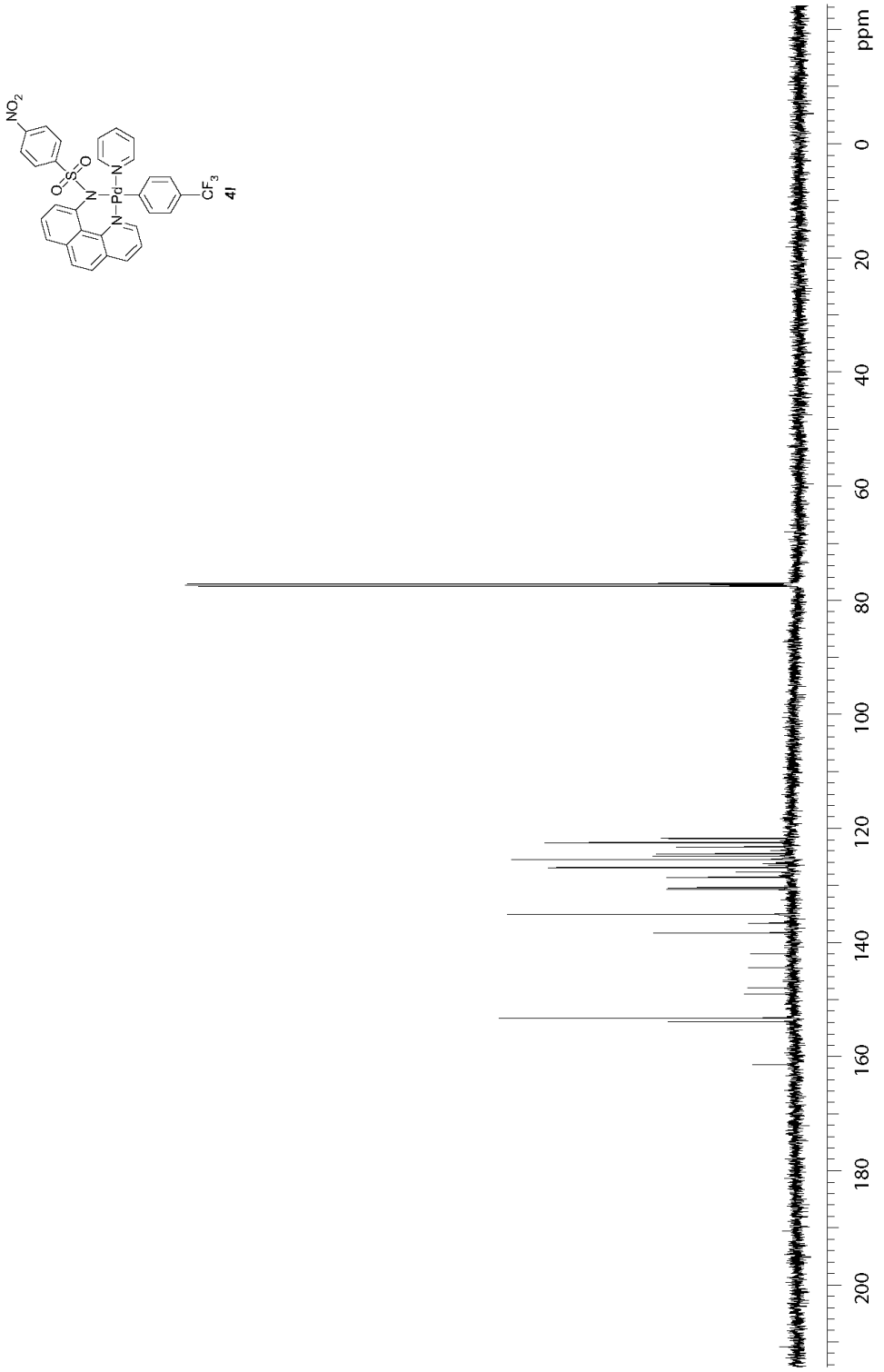
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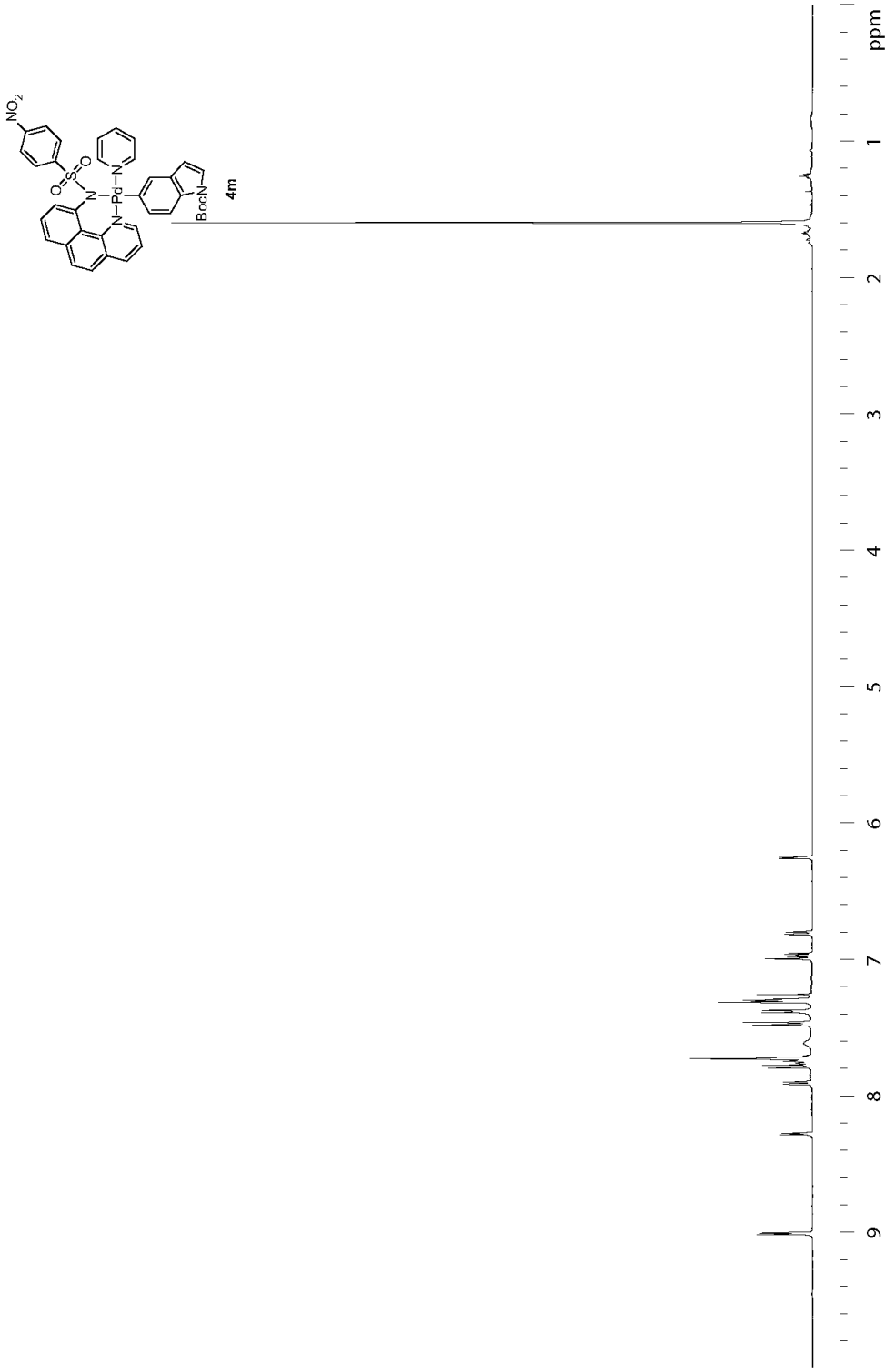
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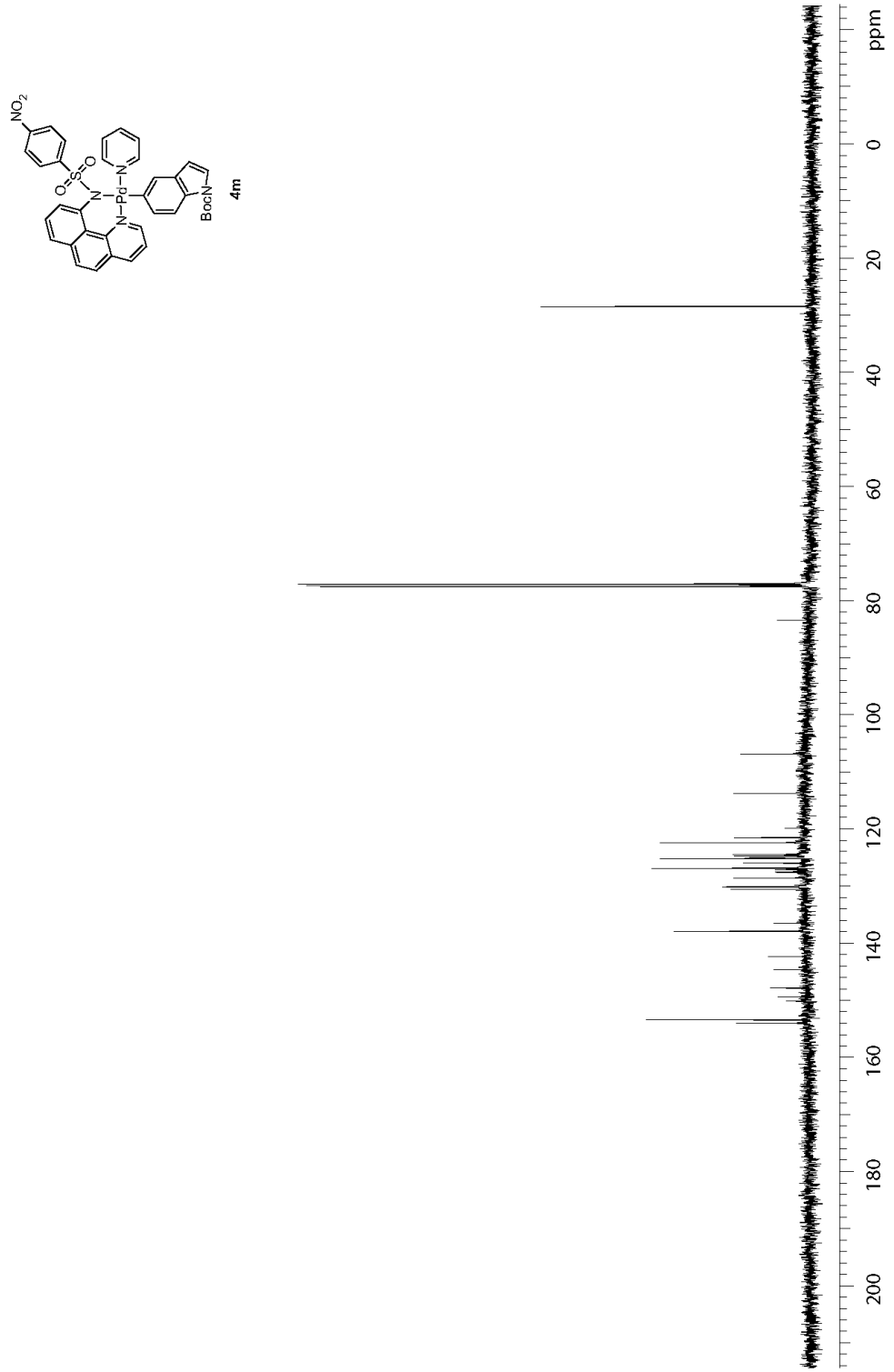
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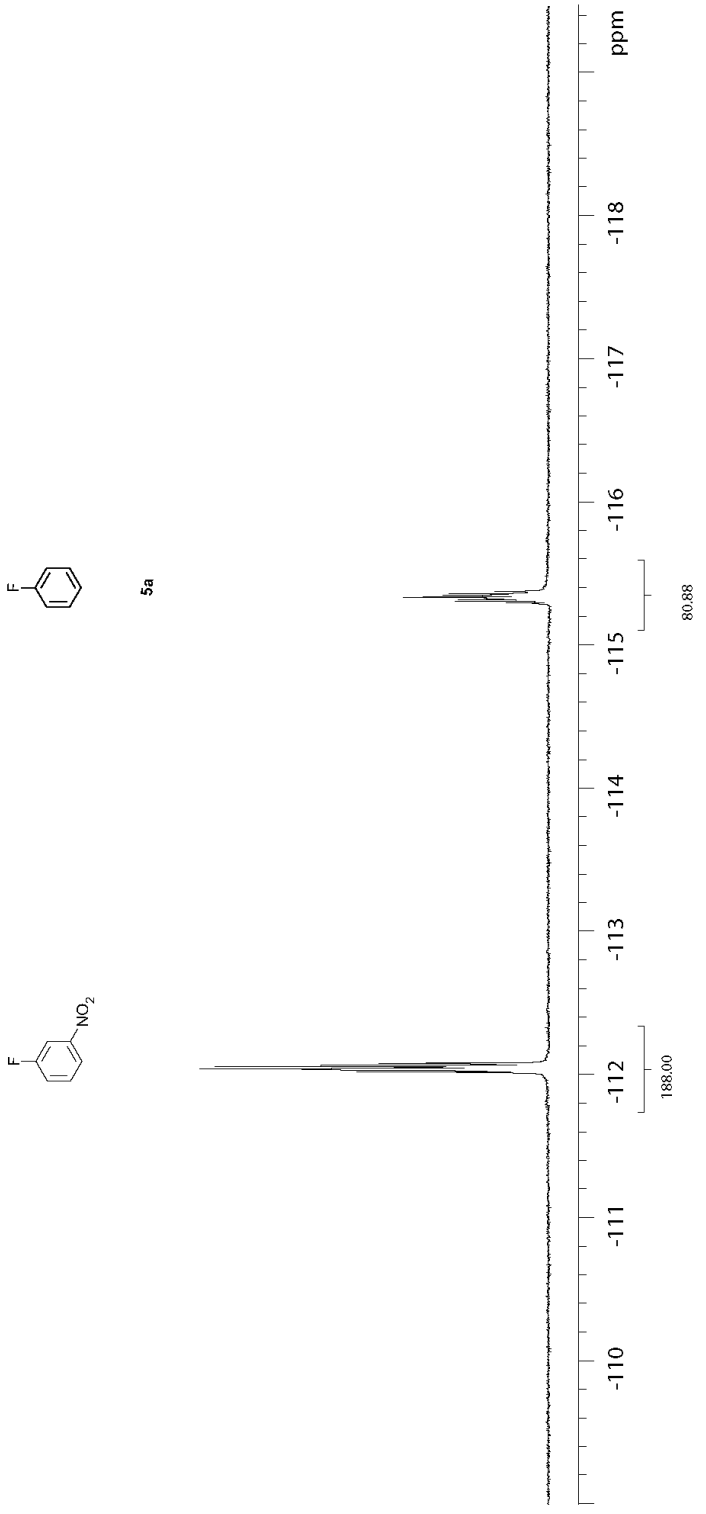
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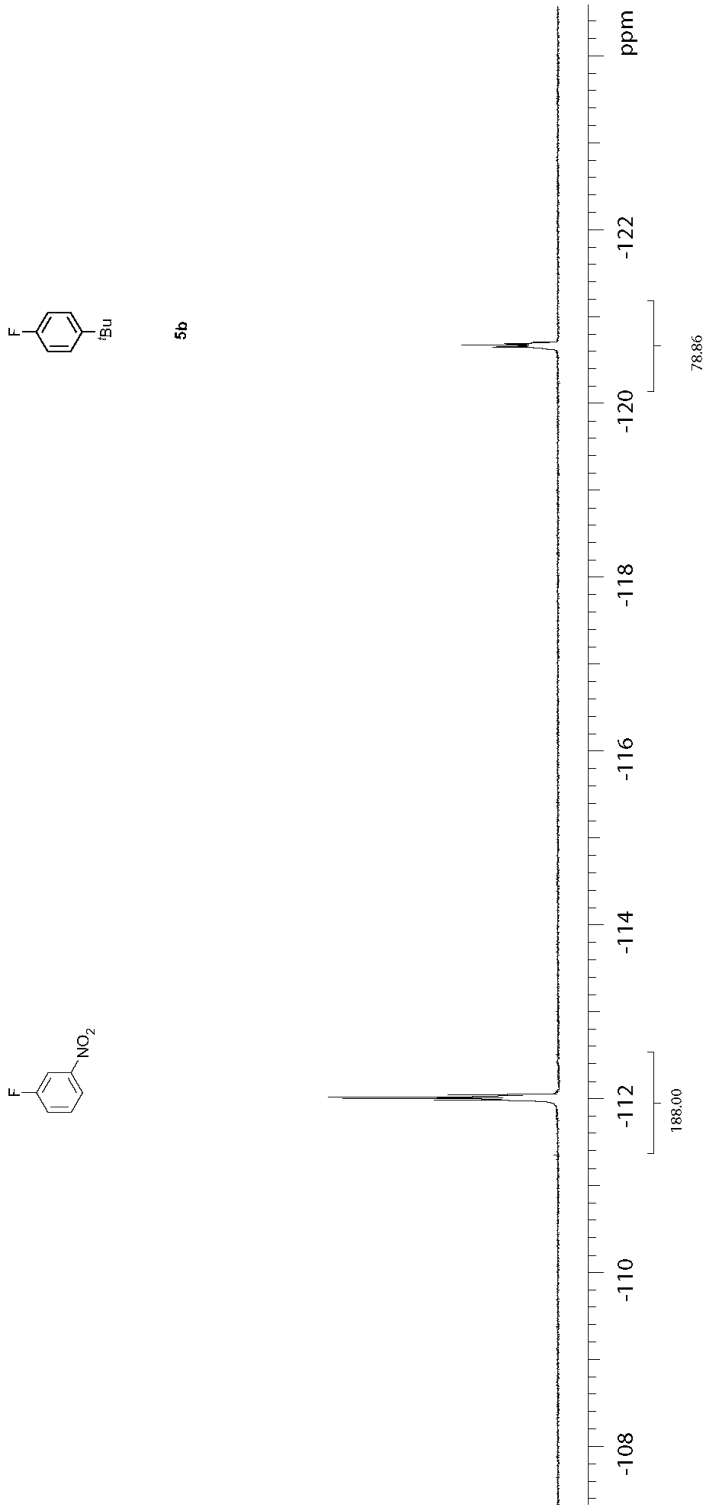
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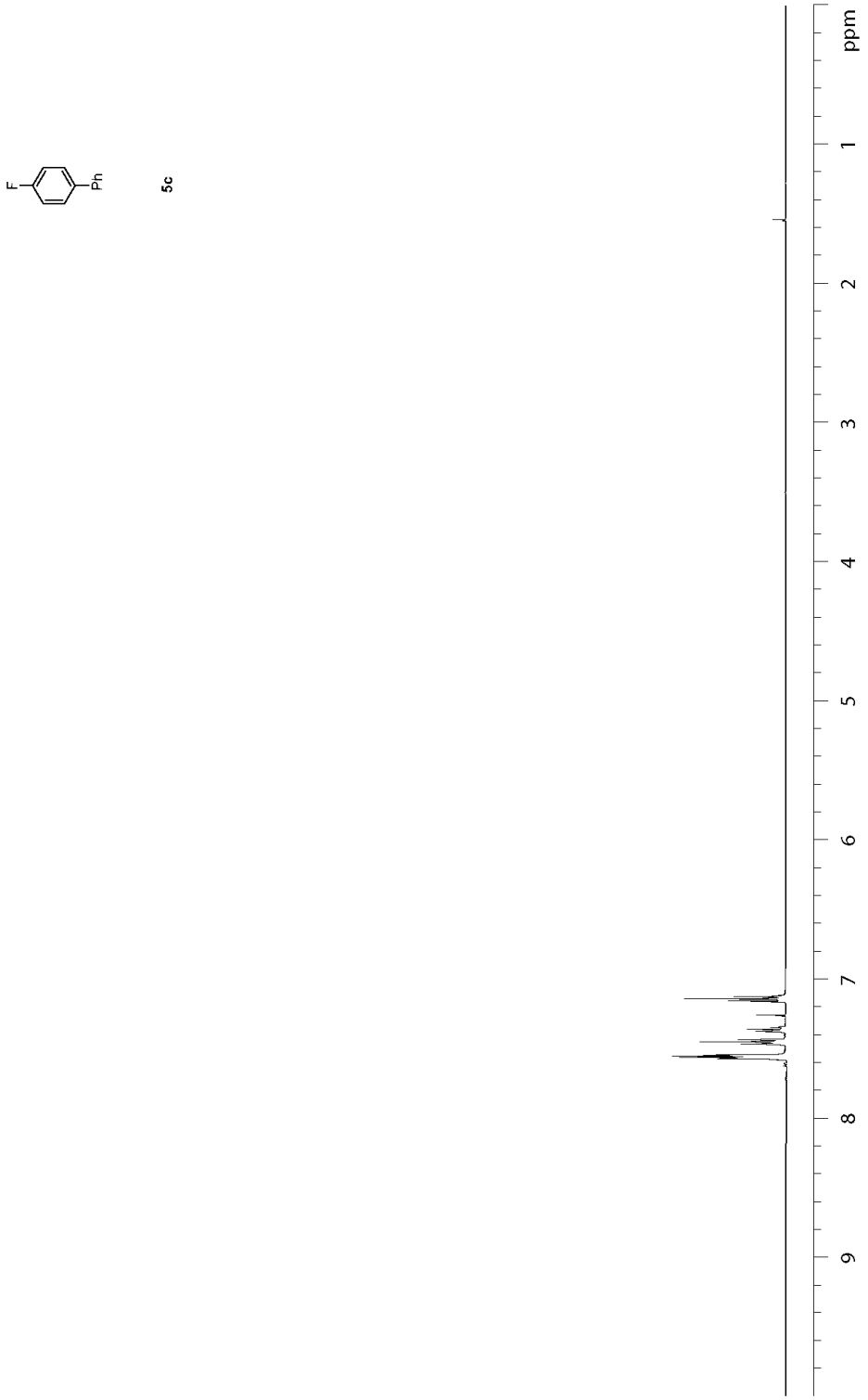
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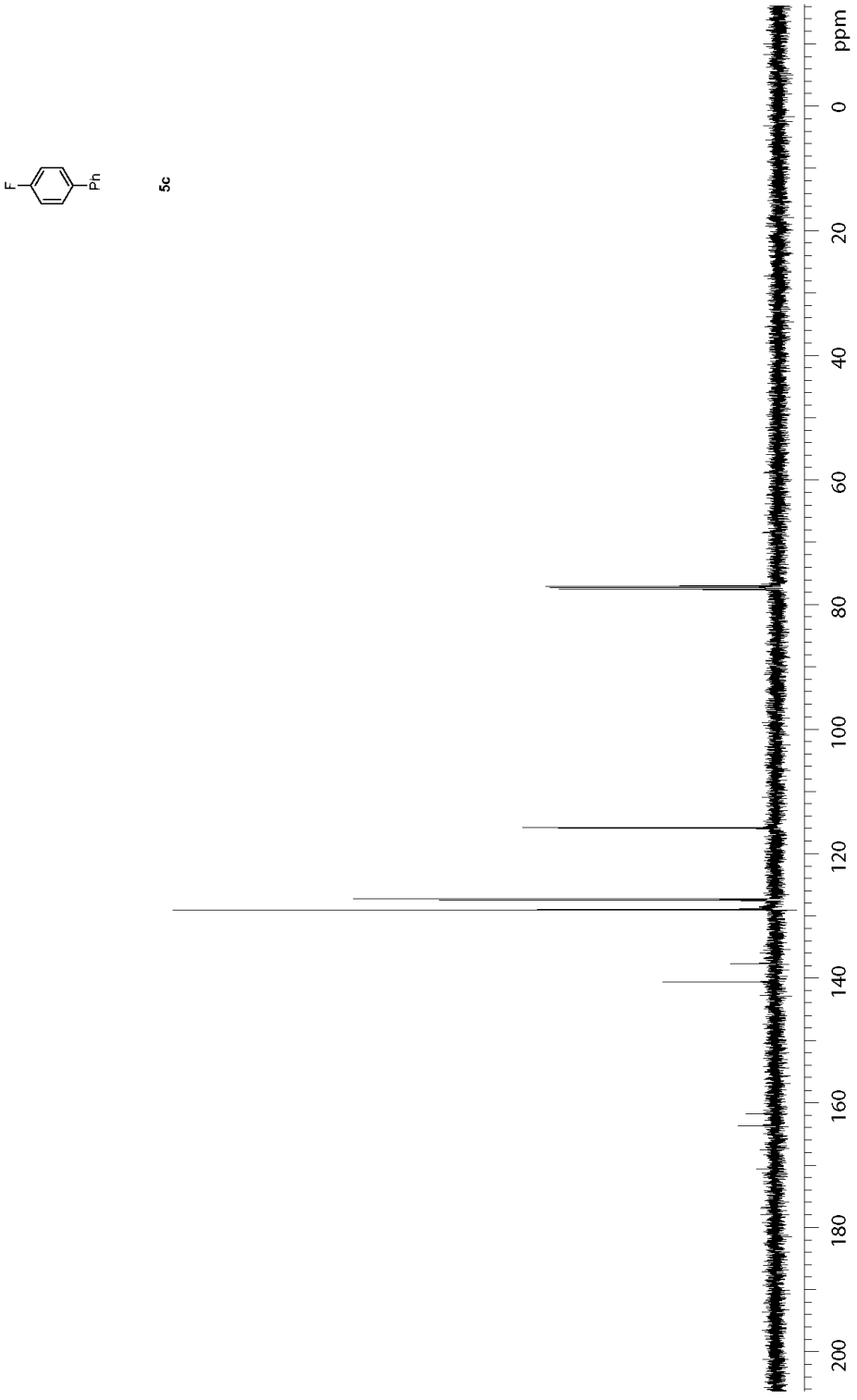
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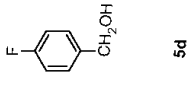

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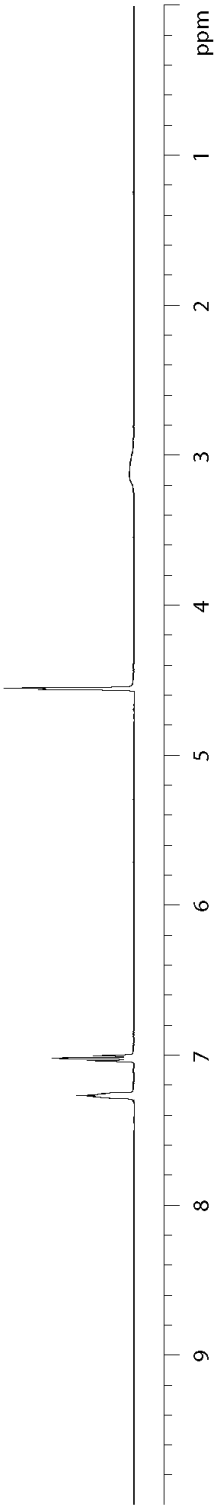

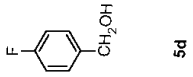

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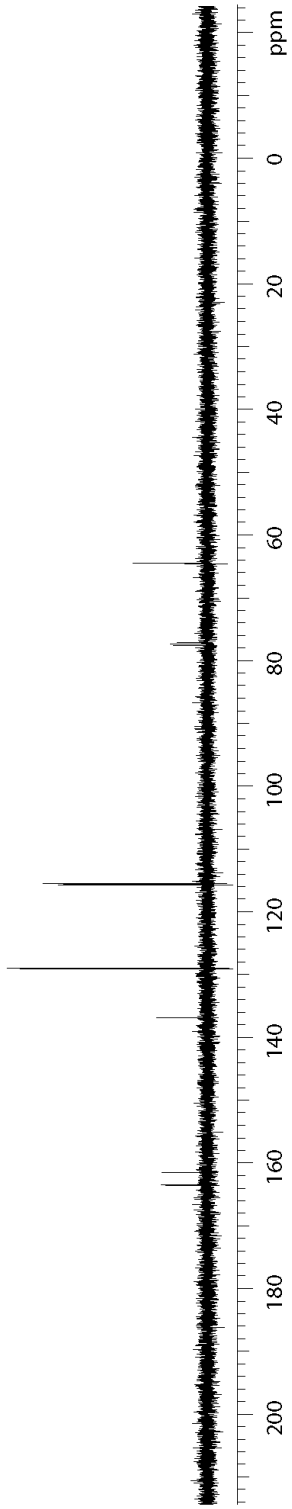

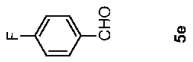

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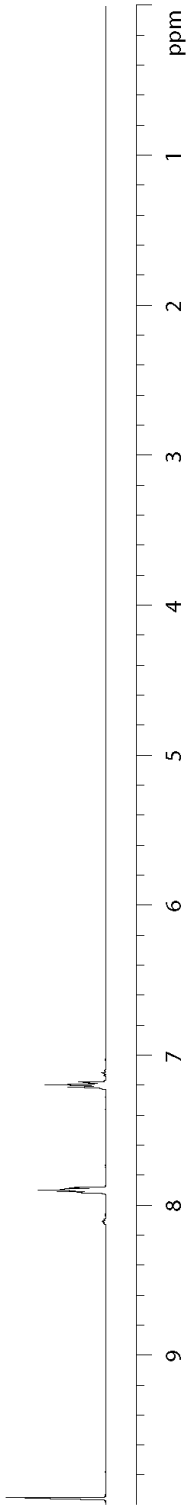

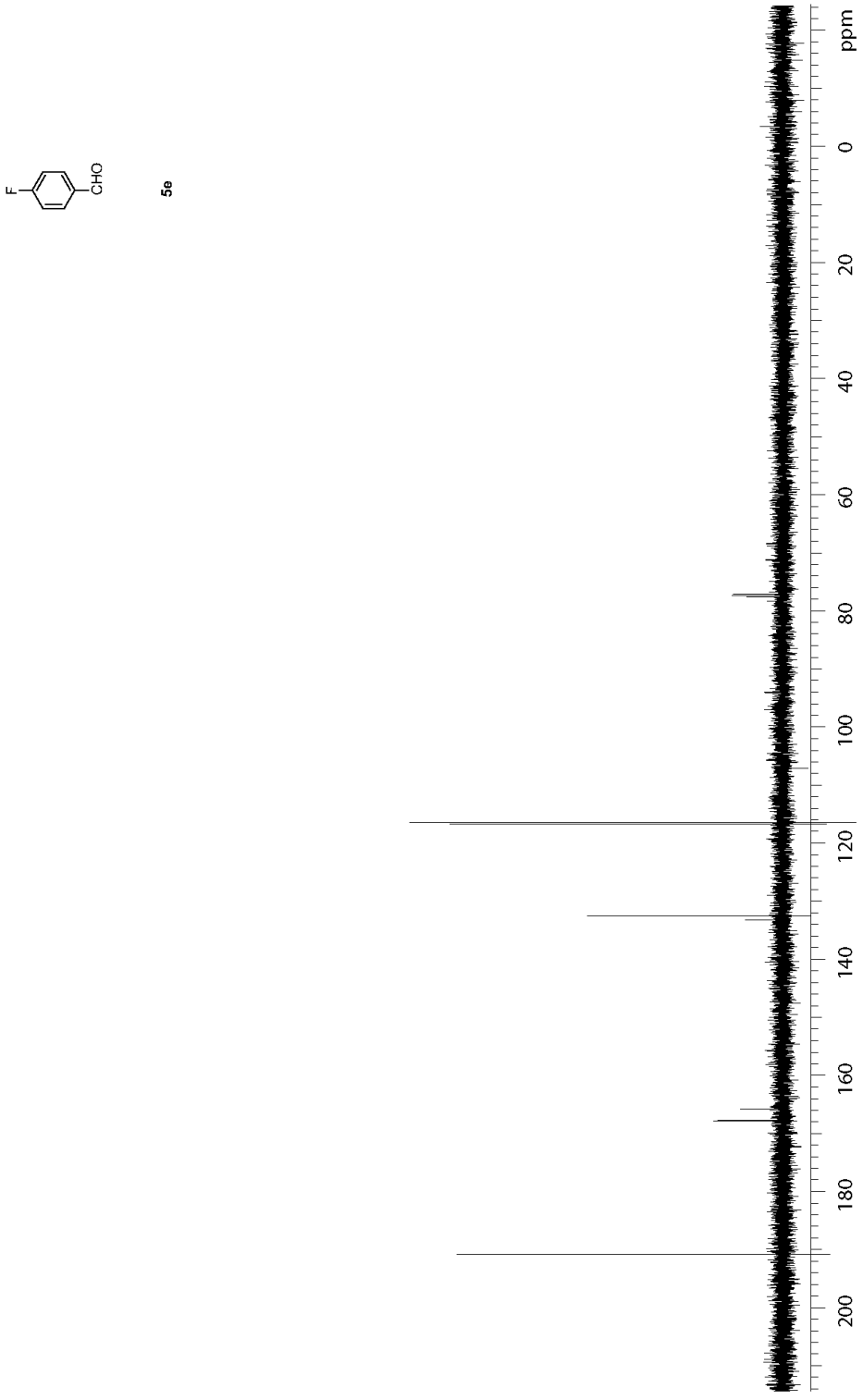
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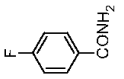

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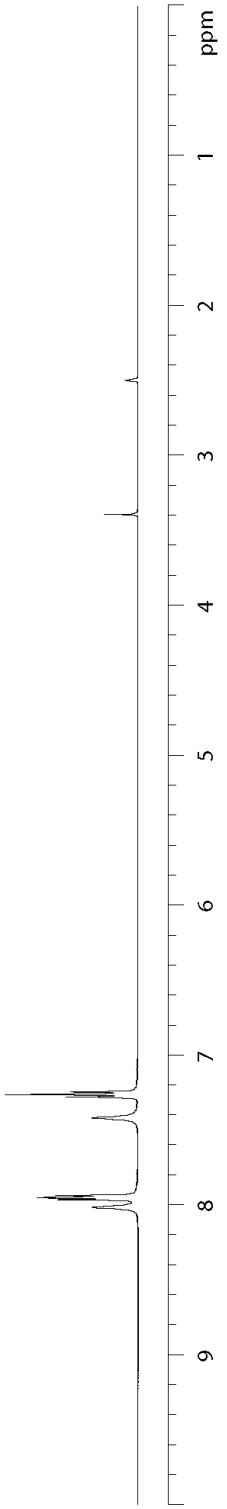

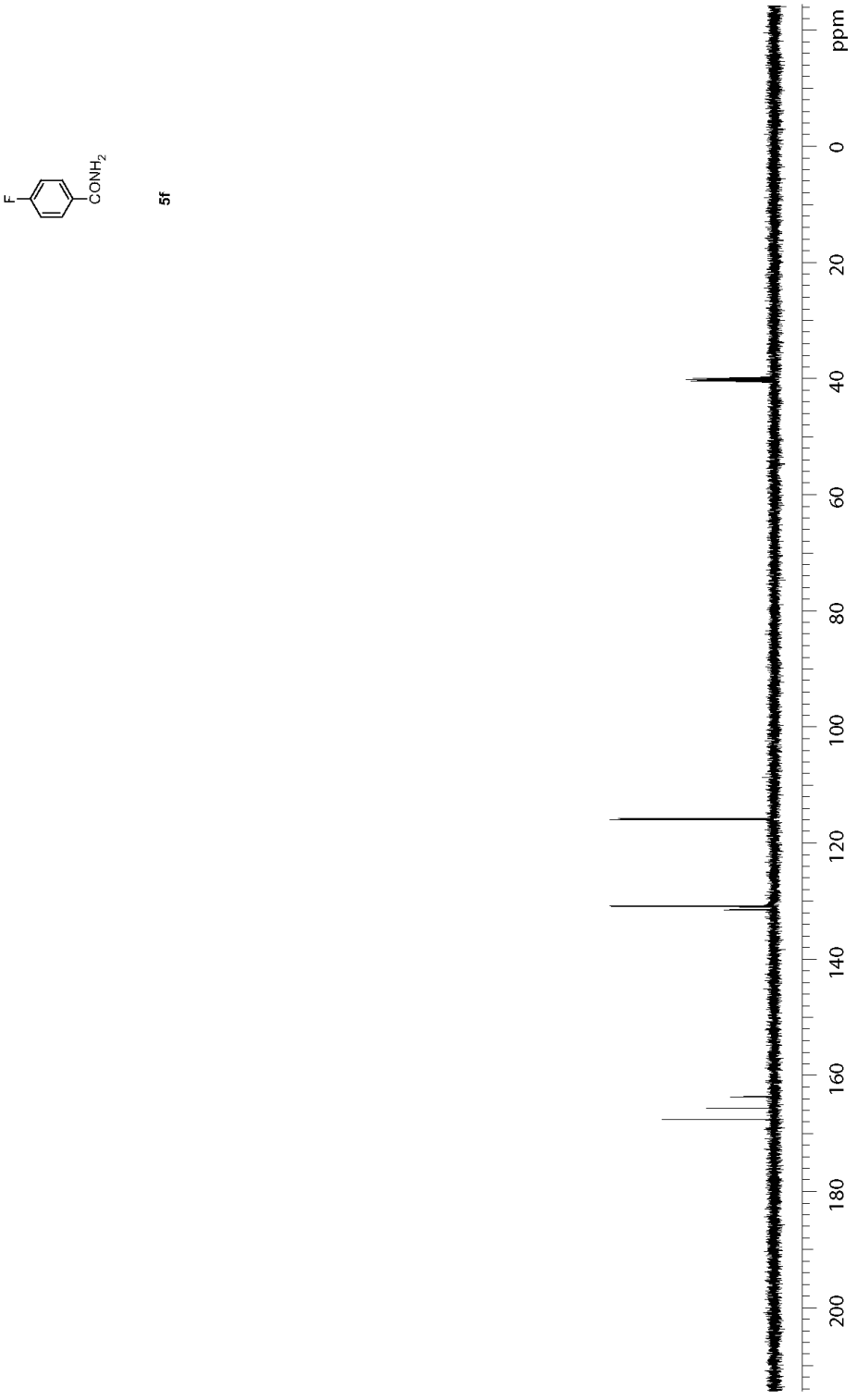
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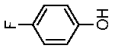

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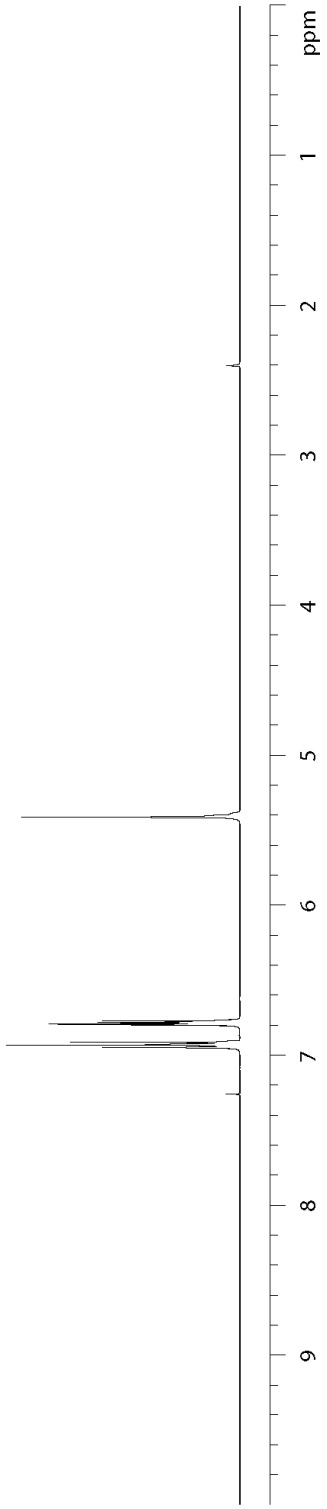

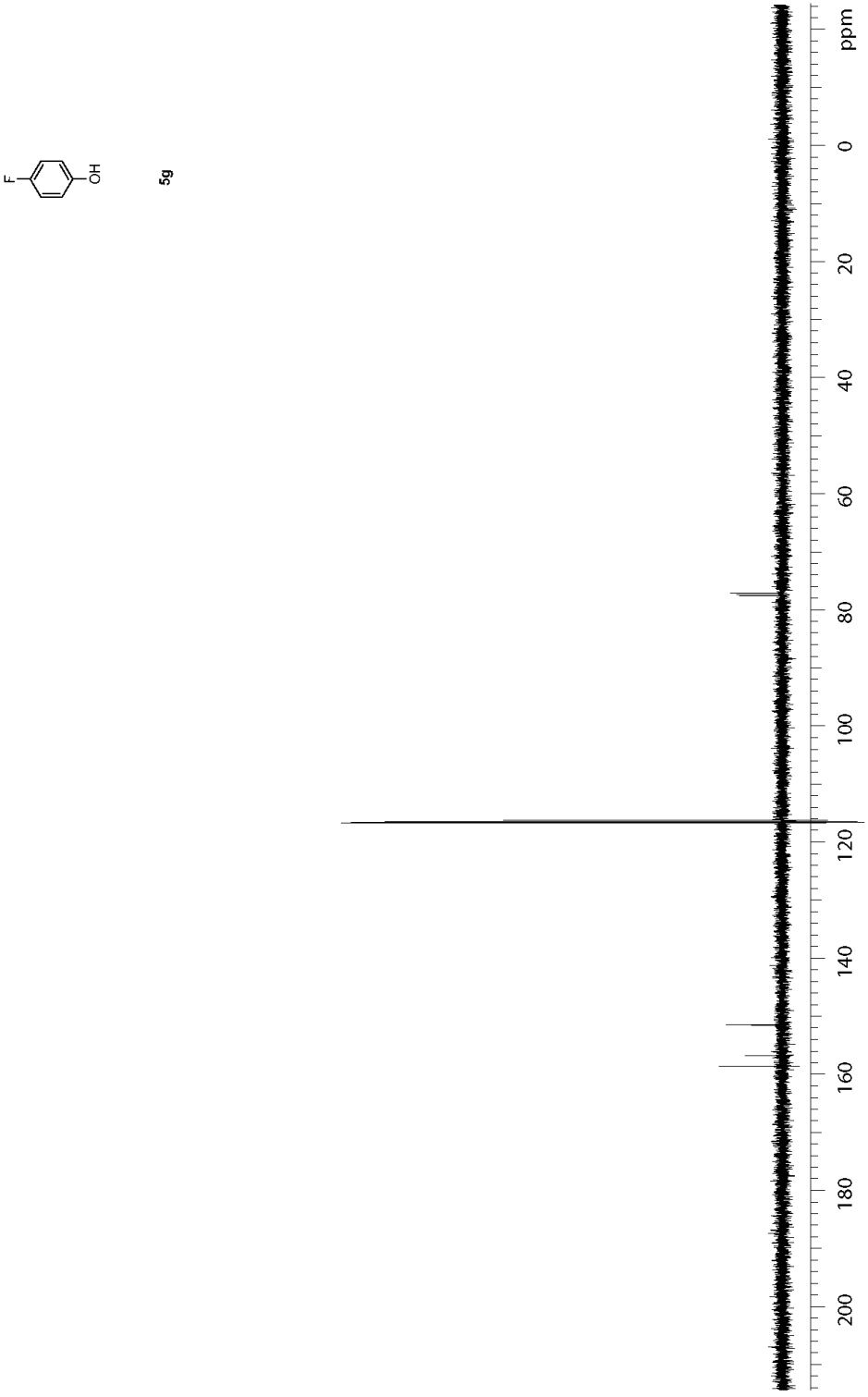
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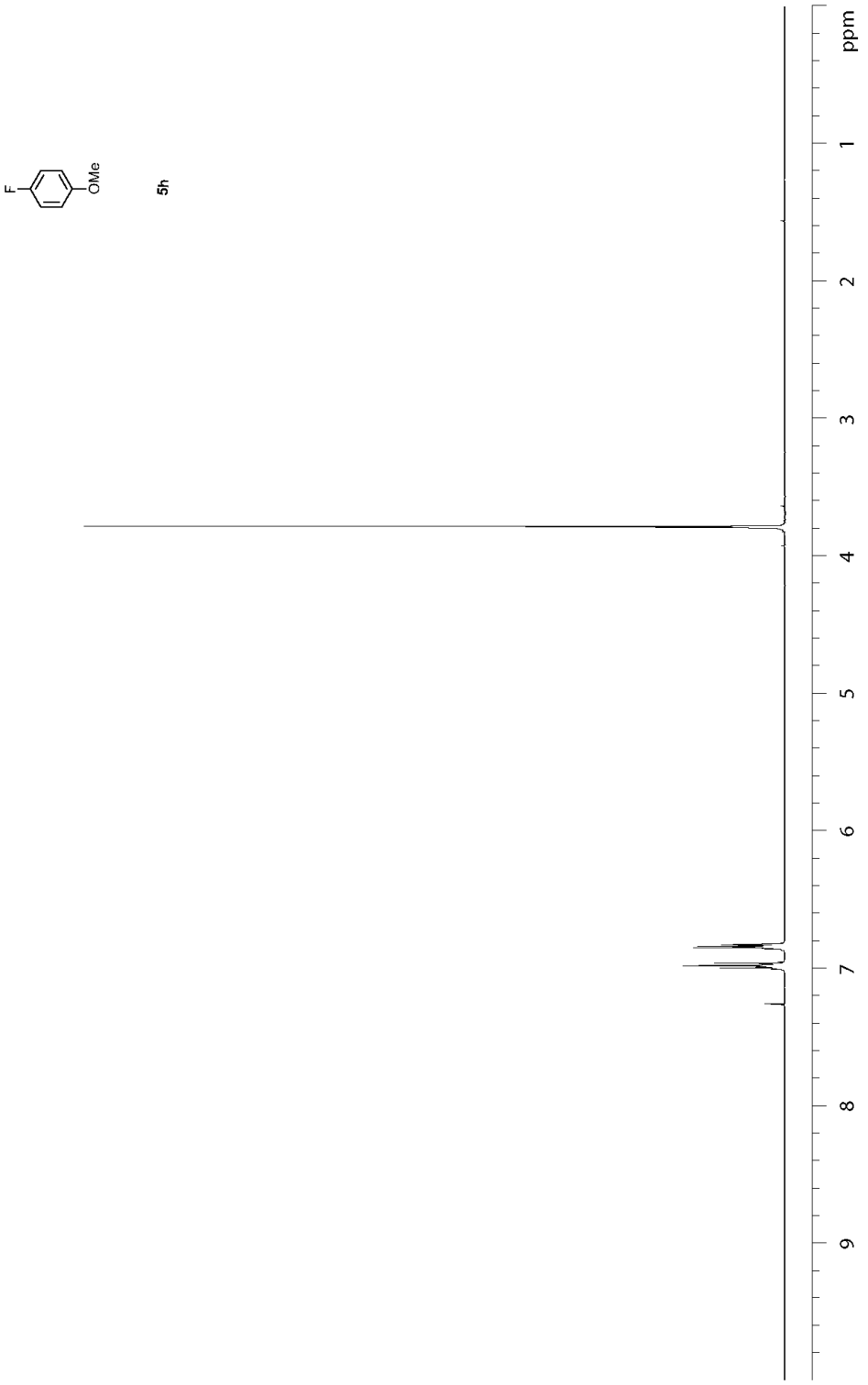
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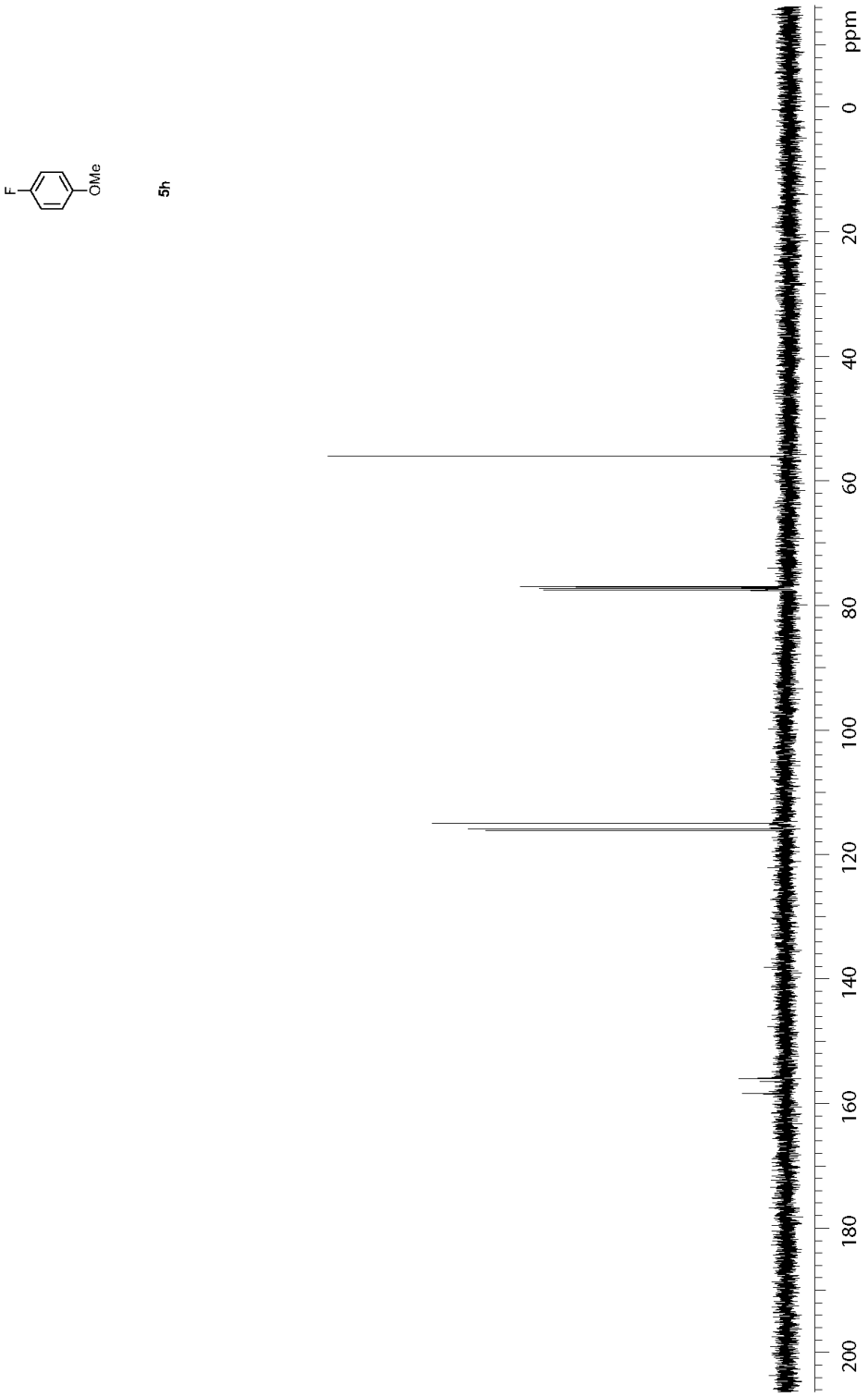
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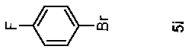

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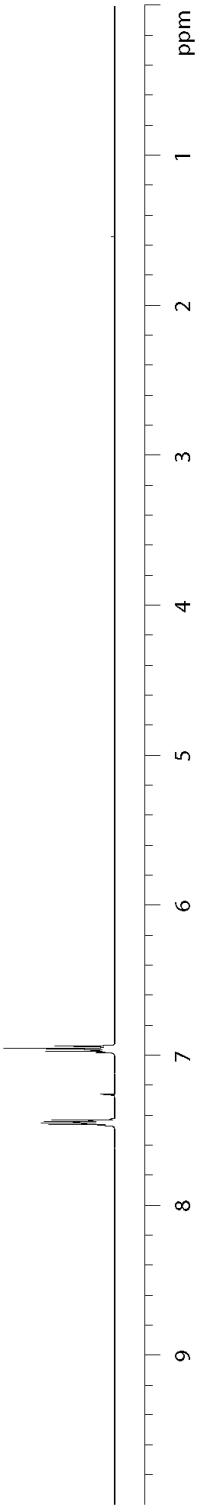

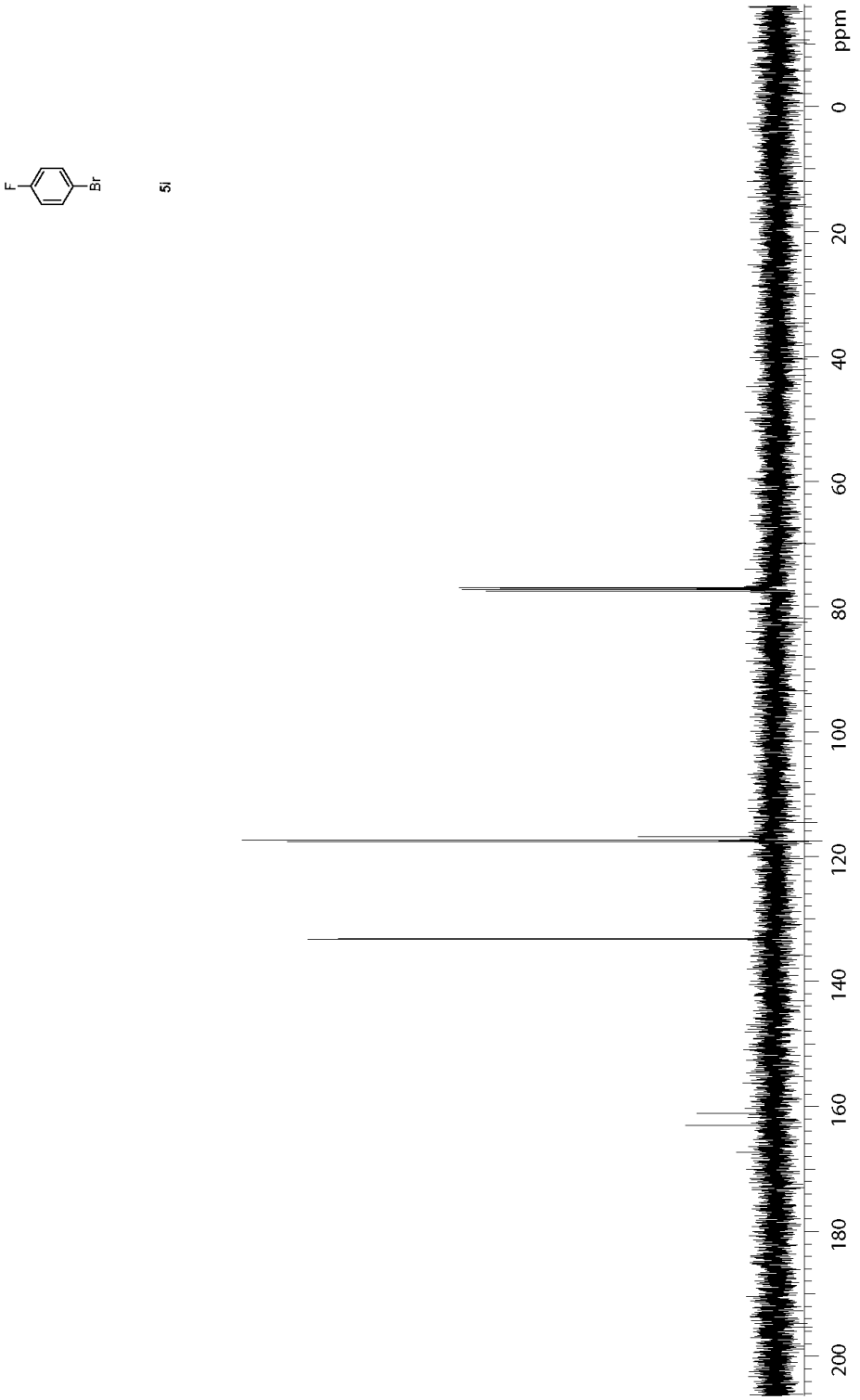
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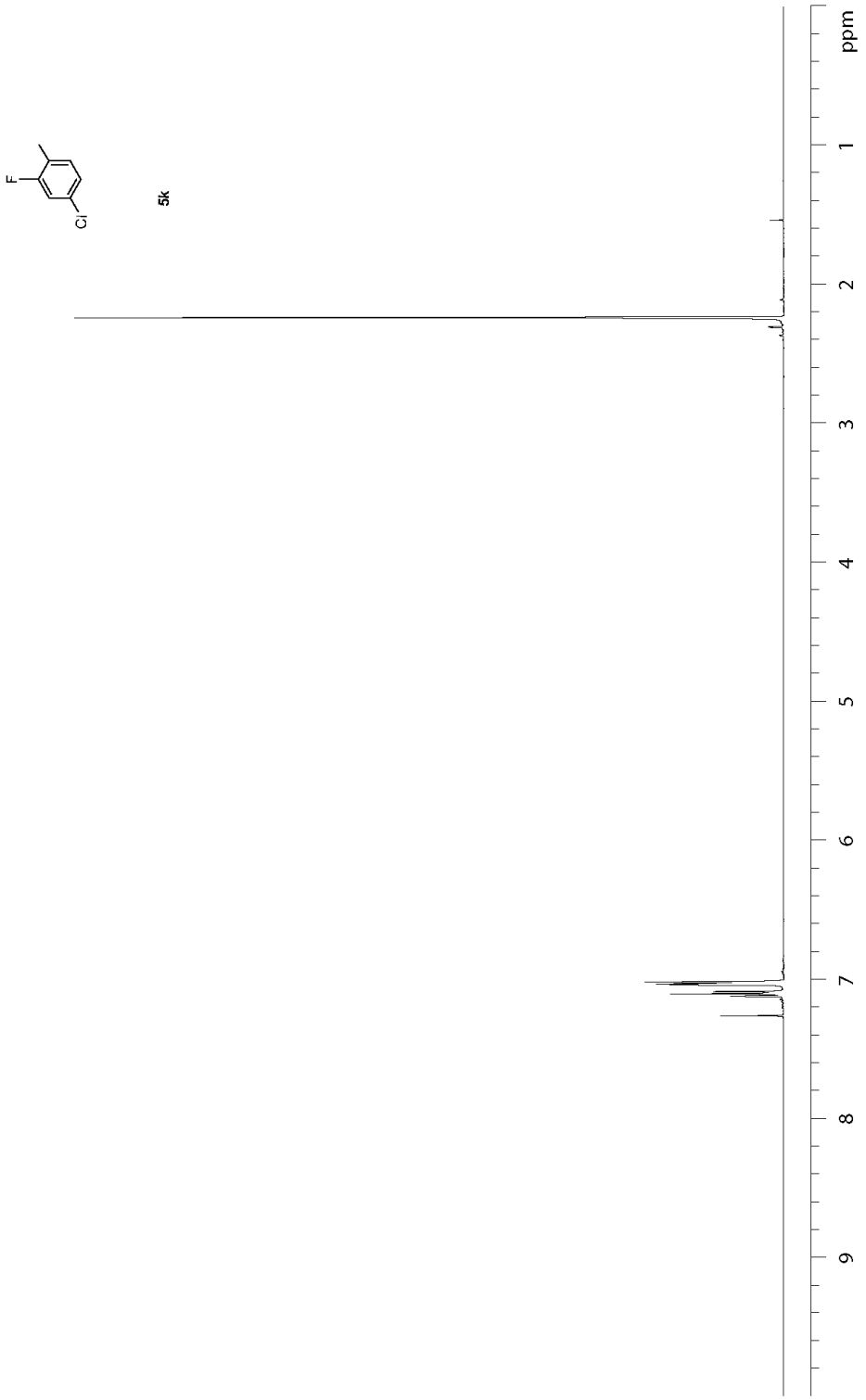
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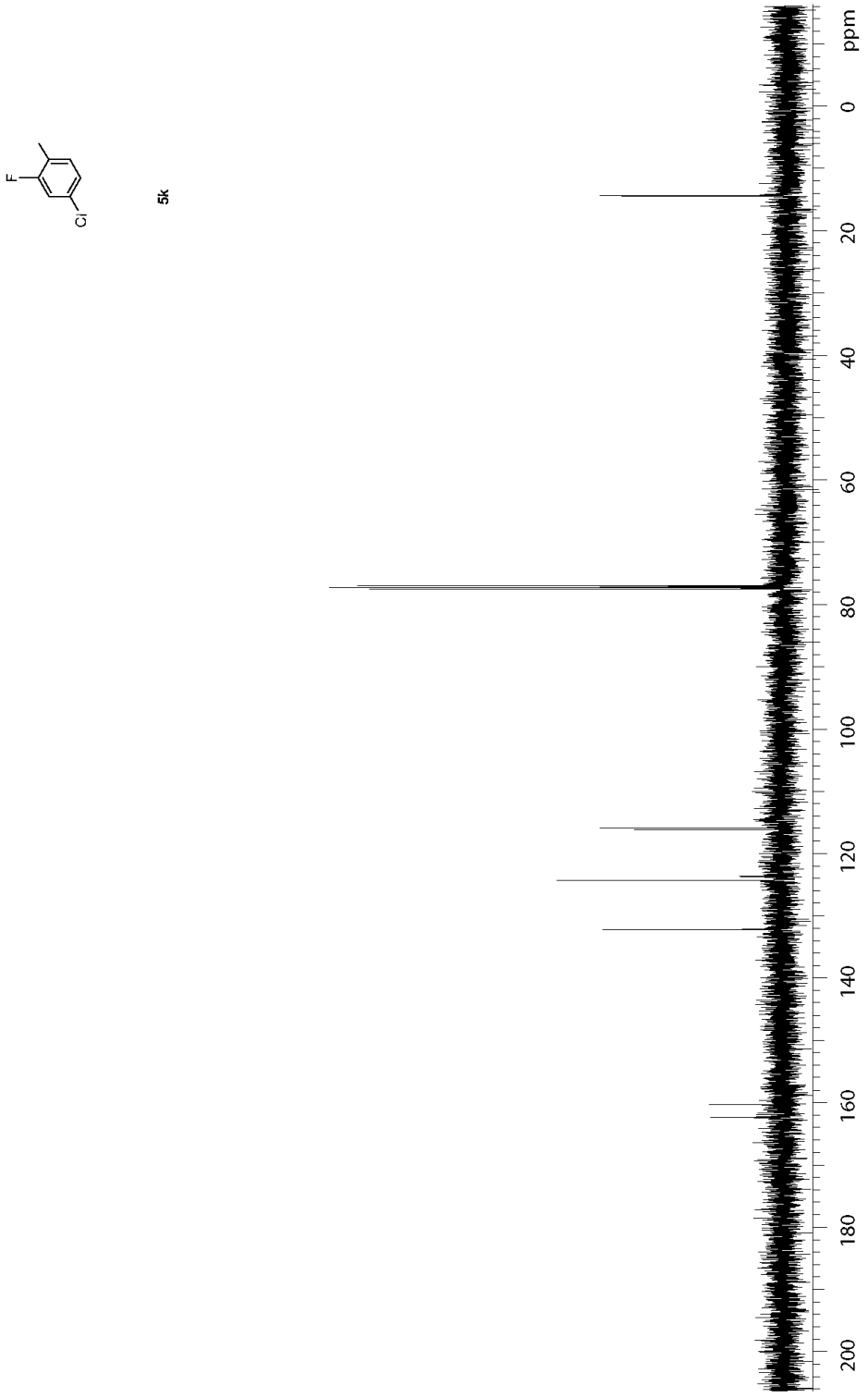
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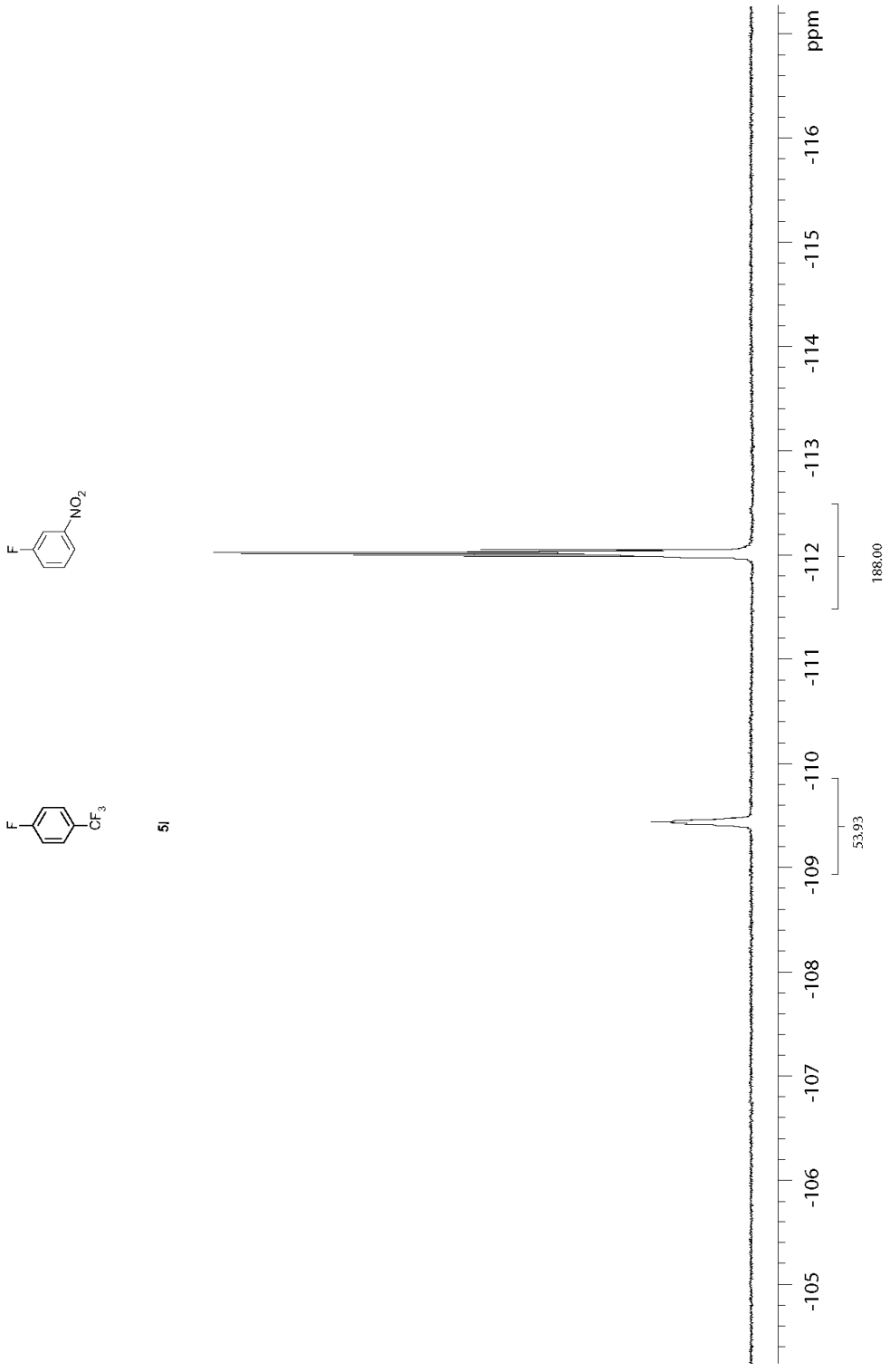
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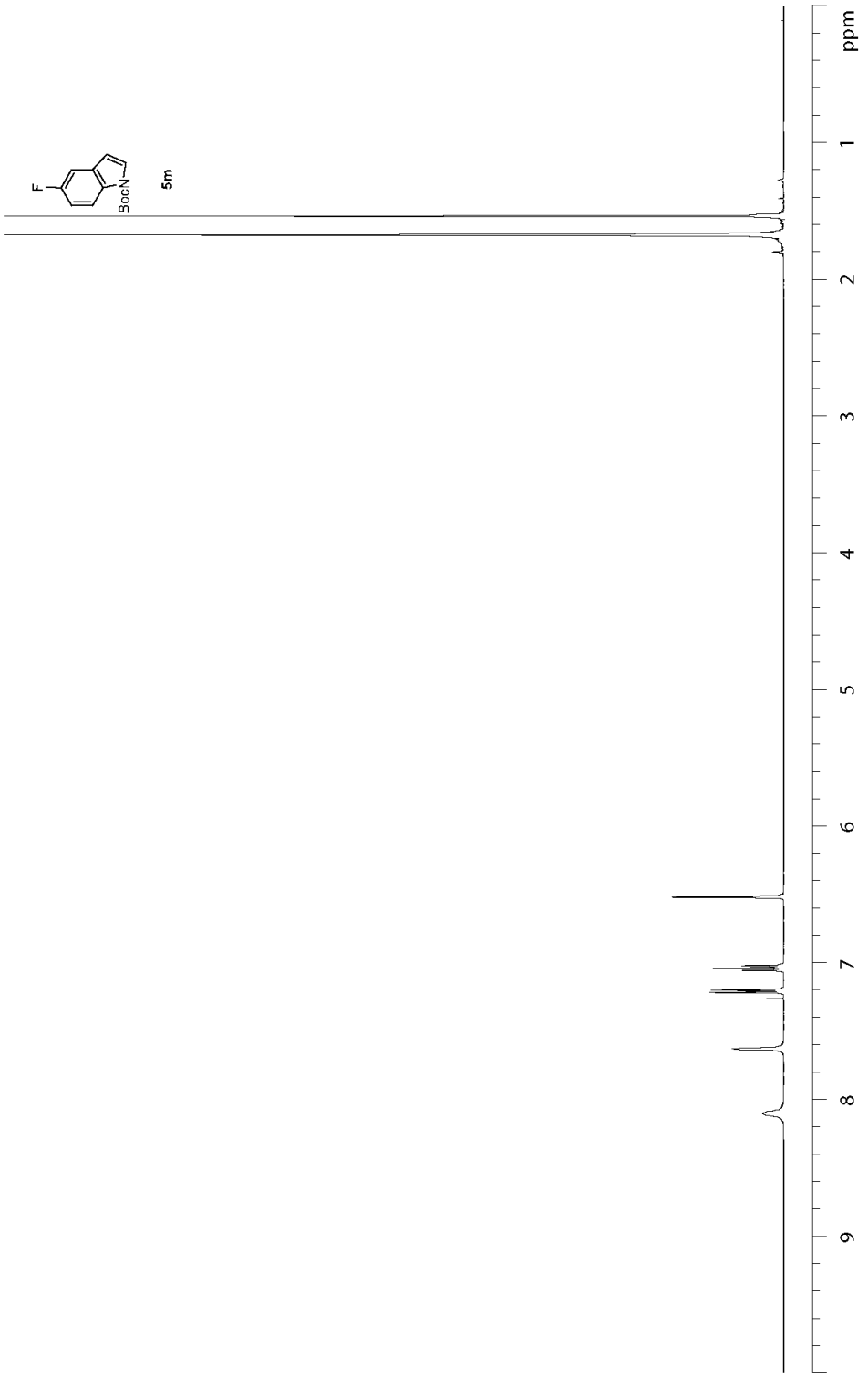
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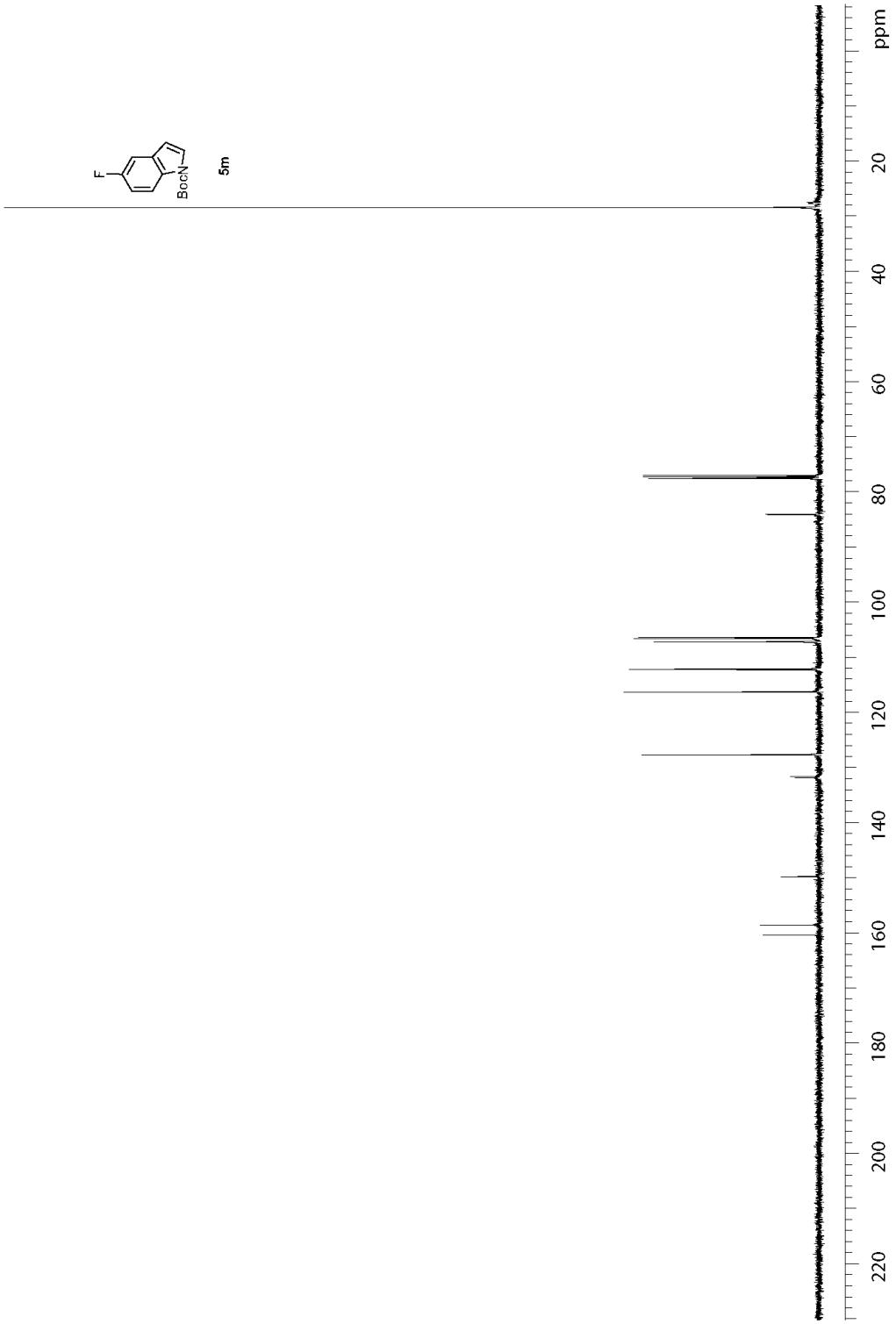
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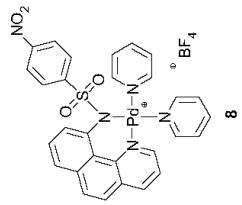

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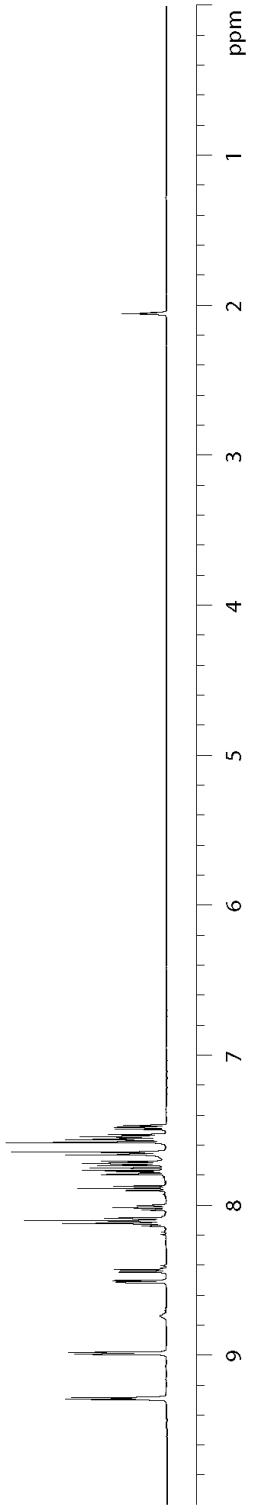

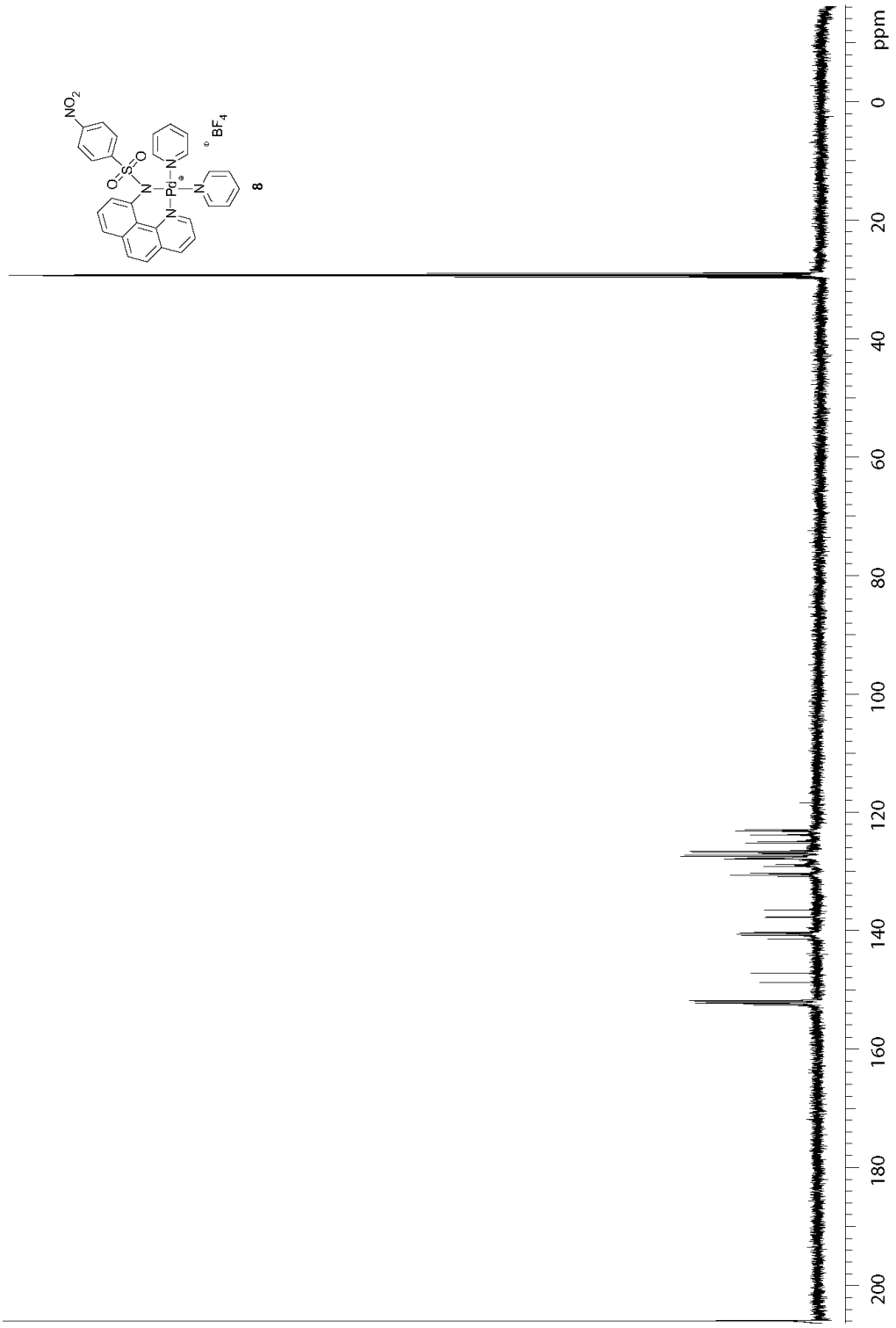
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