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Supporting Information

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Platinum and Palladium Complexes Containing Cationic Ligands as Catalysts for Arene H/D Exchange and Oxidation**

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Table of Contents

General Procedures

NMR spectra were recorded on Varian Inova 500 or 400 MHz NMR spectrometers with the residual solvent peak ([D_6]acetone: ^{1}H: δ=2.05 ppm, ^{13}C: δ=206.68, 29.92 ppm; [D_4]AcOH: ^{1}H: δ=11.65, 2.04 ppm, ^{13}C: δ=178.99, 20.0 ppm; [D_3]acetonitrile: ^{1}H: δ=1.94 ppm, ^{13}C: δ=118.69, 1.39 ppm; [D_6]benzene: ^{1}H: δ=7.16 ppm, ^{13}C: δ=128.39 ppm; [D_1]chloroform: ^{1}H: δ=7.24 ppm, ^{13}C: δ=77.23 ppm) as the internal reference unless otherwise noted. Chemical shifts are reported in parts per million (ppm) (δ). Multiplicities are reported as follows: br (broad resonance), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (*J*) are reported in Hz. Infrared (IR) spectroscopy was performed on a Perkin Elmer FTIR. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67-100 %), m (medium, 40-67 %), w (weak, 20-40 %), and br (broad). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

All reactions were conducted without rigorous exclusion of air and moisture unless noted otherwise. [D_4]AcOH and [D_1]TFA were purchased from Cambridge Isotopes Lab and stored in Schlenk tubes under N_2. [D_6]Acetone, [D_3]acetonitrile, [D_6]benzene and [D_1]chloroform were purchased from Cambridge Isotopes Lab and used as received. Dichloromethane (CH_2Cl_2), diethylether (Et_2O), methanol (MeOH), pentane, acetonitrile (MeCN), toluene, acetone and ethyl acetate (EtOAc) were obtained from Fisher Scientific or Aldrich and used as purchased. Benzene for H/D exchange and acetoxylation was obtained from Aldrich and stored over 4 Å molecular sieves. Ethanol

(EtOH), 200 proof, was obtained from Deacon Labs, Inc., and used as received. Celite and acetic anhydride were purchased from EM Science. Sodium acetate (anhydrous), Ag_2CO_3, AgOTf, bromobenzene, and 1,2-dimethoxybenzene (veratrol) were purchased from Acros Organics. PhCl, glacial acetic acid (AcOH), $MgSO_4$, K_2CO_3, Ag_2SO_4 and naphthalene were purchased from Fisher Scientific. Deuterium chloride (DCl 35% in D_2O) was purchased from Cambridge Isotope Laboratories. Chlorobenzene was purchased from Burdick & Jackson. 1,2-Dichlorobenzene and α,α,α-trifluorotoluene were purchased from TCI America. $Pd(OAc)_2$ was purchased from Pressure Chemical Company. Iodosobenzene diacetate ($PhI(OAc)_2$) was obtained from Alfa Aesar. AgCl, $AgBF_4$, $AgPF_6$, $AgNO_3$, silver trifluoroacetate (AgTFA), AgOTs, ethyl benzoate, 2,2'-bipyridine (bpy), and 1,1,2-trichloroethane were purchased from Aldrich. (bpym)$PtCl_2$ **1**[1], (4,4'-di-*tert*-butylbipyridine)$PtCl_2$,[2] $(DMSO)_2PtCl_2$,[3] 2,4,6-tris(4-*tert*-butylphenyl)pyrilium tetrafluoroborate,[4] 4,4'-diaminobipyridine,[5] (4,4'-di-*tert*-butylbipyridine)$PdCl_2$[6], (COD)$PdCl_2$[7] and ligand **2a**[8] were prepared according to literature procedures. Stock solutions of silver salts and bpy were prepared using volumetric glassware and all liquid reagents were dispensed by difference using gas-tight Hamilton syringes.

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[1] I. Bar-Nahum, A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 10236-10237.
[2] J. Vicente, P. Gonzalez-Herrero, M. Perez-Cadenas, P. G. Jones, D. Bautista, *Inorg. Chem.* **2007**, *46*, 4718-4732.
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[4] K. Dimroth, W. Tüncher, H. Kaletsch, *Chem. Ber.* **1978**, *111*, 264-271.
[5] a) G. Maerker, F. H. Case, *J. Am. Chem. Soc.* **1958**, *80*, 2745-2748; b) D. S. C. Back, N. E. Rothnie, *Aust. J. Chem.* **1983**, *36*, 1141-1147; c) R.-A. Fallahpour, M. Neuburger, M. Zehnder, *New J. Chem.* **1999**, *23*, 53-61; d) R. A. Fallahpour, *Eur. J. Inorg. Chem.* **1998**, 1205-1207.
[6] S. R. Foley, H. Shen, U. A. Qadeer, R. F. Jordan, *Organometallics* **2004**, *23*, 600-609.
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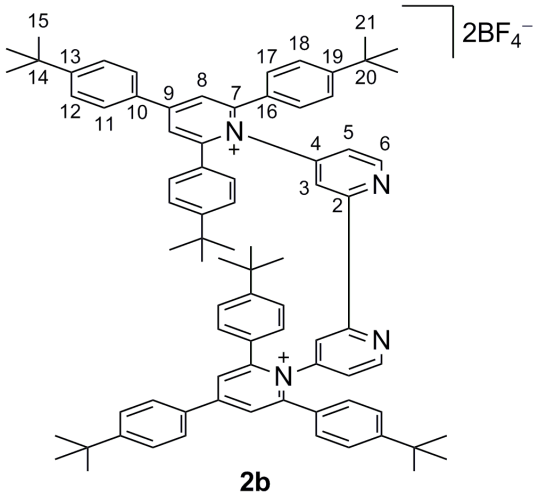
[8] P. P. Lainé, I. Ciofini, P. Ochsenbein, E. Amouyal, C. Adamo, F. Bedioui, *Chem. Eur. J.* **2005**, *11*, 3711-3727.

H/D exchange data for benzene was measured on a Shimadzu GC-MS Q5000 using a xTi®-5 (serial # 790776) column obtained from RESTEK. All raw data were deconvoluted using Periana's benzene H/D exchange worksheet with a reported error of 5%.[9] An assumption in the worksheet is that the fragmentation pattern of each isotopolog is identical. To obtain the most accurate analysis, pure samples of each isotopolog must be analyzed to determine the exact coefficients of the polynomial expansion for the given instrument. This treatment confirmed that the calculated percents of each isotopolog were within the reported error of the worksheet.

Gas chromatography was carried out on a Shimadzu 17A instrument using a Restek Rtx-5 (crossbond 5% diphenyl−95% dimethyl polysiloxane; 15 m, 0.25 mm i.d., 0.25 μm df) column. GC-MS investigations were carried out on a Shimadzu GCMS-QP2010S instrument using a Shimadzu SHRXI-5MS (serial # 936407; 30 m, 0.25 mm i.d., 0.25 μm df) column. Retention times were verified using isolated material. Yields were calculated by calibrating isolated material and standard to the response of the instrument.

[9] K. H. J. Young, S. K. Meier, J. M. Gonzales, J. Oxgaard, W. A. Goddard, R. A. Periana, *Organometallics* **2006**, *25*, 4734-4737.

Preparation of Pt and Pd catalysts



2b

Synthesis of ligand 2b

A mixture of 2,4,6-tris(4-*tert*-butylphenyl)pyrilium tetrafluoroborate (6.06 g, 10.7 mmol, 4.00 equiv), 4,4'-diaminobipyridine (500 mg, 2.69 mmol, 1.00 equiv), and anhydrous sodium acetate (3.17 g, 38.7 mmol, 14.4 equiv) in EtOH (100 mL) was heated under reflux for 24 h. The solvent was removed by rotary evaporation, and the resulting residue was stirred in water (40 mL) for 20 min, which produced a light yellow suspension. The solids were collected on a frit and washed with water (5 x 25 mL). The solid material was then dissolved in CH_2Cl_2 (50 mL), this solution was dried over $MgSO_4$, filtered, and the filter plug was rinsed with CH_2Cl_2 (2 x 25 mL). Pentane (200 mL) was added to the combined filtrates and the resulting mixture was stirred for 10 min. The formed precipitate was collected by filtration, washed with cold pentane (2 x 25 mL) and dried under vacuum, affording ligand **2b** as a white solid (2.92 g, 85%). m.p. 372°C (decomp.); ^{1}H NMR (500 MHz, [D_3]acetonitrile, 25 °C): δ=8.38 (s, 4H; H^8), 8.35 (d, ^3J(H,H)=5.4 Hz, 2H; H^6), 8.07 (m, 4H; H^{11}), 7.98 (d, ^4J(H,H)=1.7 Hz, 2H; H^3), 7.69

(m, 4H; H^{12}), 7.36 (m, 8H; H^{18}), 7.28 (m, 8H; H^{17}), 7.24 (dd, ^{3}J(H,H)=5.4 Hz, ^{4}J(H,H)=1.7 Hz, 2H; H^{5}), 1.38 (s, 18H; H^{15}), 1.22 ppm (s, 36H; H^{21}); ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C): δ=158.1, 157.9, 157.1 (2 x C), 156.7, 155.2, 151.3, 148.5, 131.6, 130.7, 129.6, 127.9, 126.5, 126.5, 125.2, 121.5, 35.9, 35.6, 31.3, 31.2 ppm; ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C): δ=–151.77 ($^{10}BF_4^-$), –151.83 ppm ($^{11}BF_4^-$); IR (KBr): $\tilde{\nu}$ =575 (m), 837 (s), 1065 (br), 1246 (m), 1270 (s), 1365 (s), 1396 (m), 1459 (s), 1510 (s), 1582 (s), 1625 (s), 2963 (s), 3059 (m) cm^{-1}; HRMS (ESI): *m/z* calcd. 1191.7038 $[M–BF_4]^+$, found 1191.7046; elemental analysis calcd. (%) for $C_{80}H_{88}B_2F_8N_4 \cdot 0.8\ H_2O$: C, 74.28; H, 6.98; N, 4.33, found (%): C, 74.34; H, 6.89; N, 4.31.

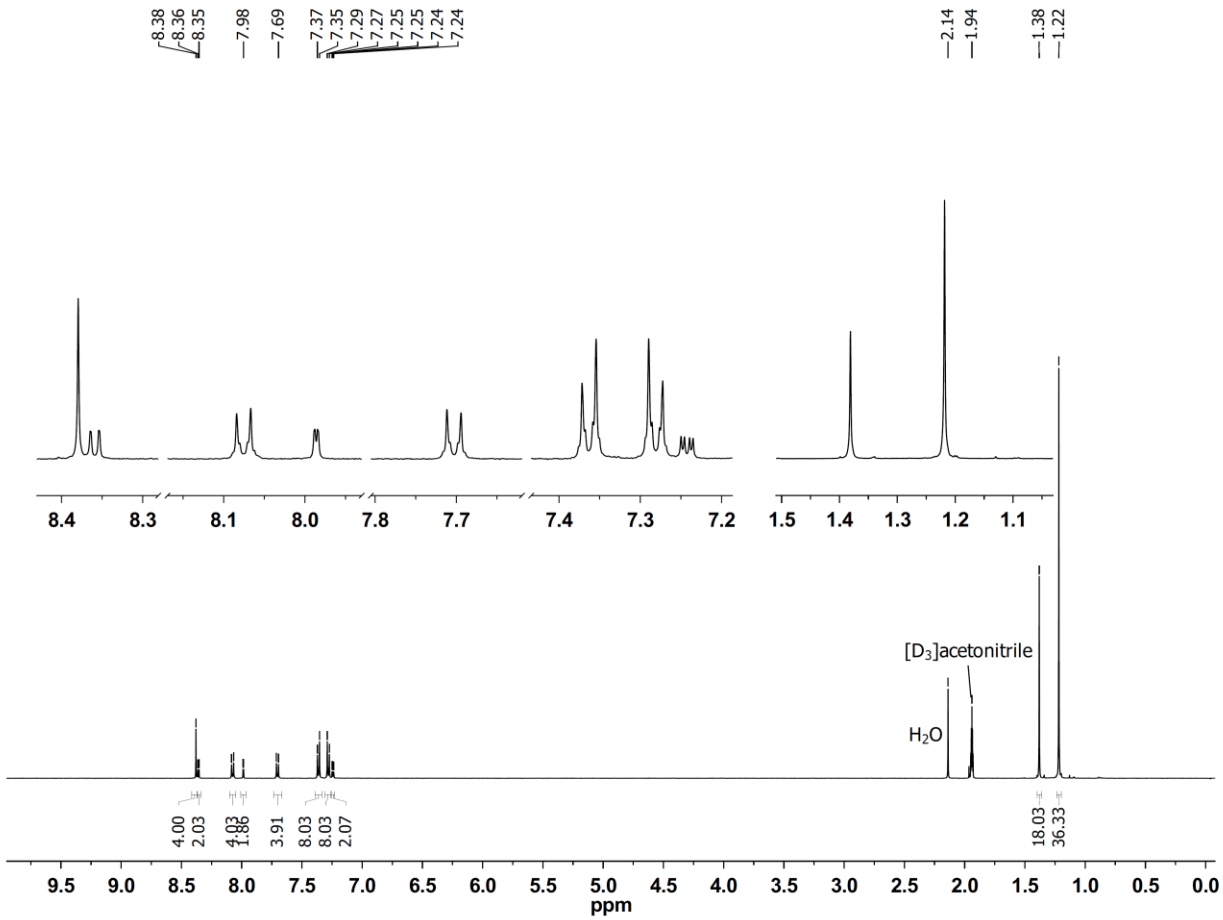


Figure 1. ^{1}H NMR (500 MHz, [D_3]acetonitrile, 25 °C) of ligand **2b**

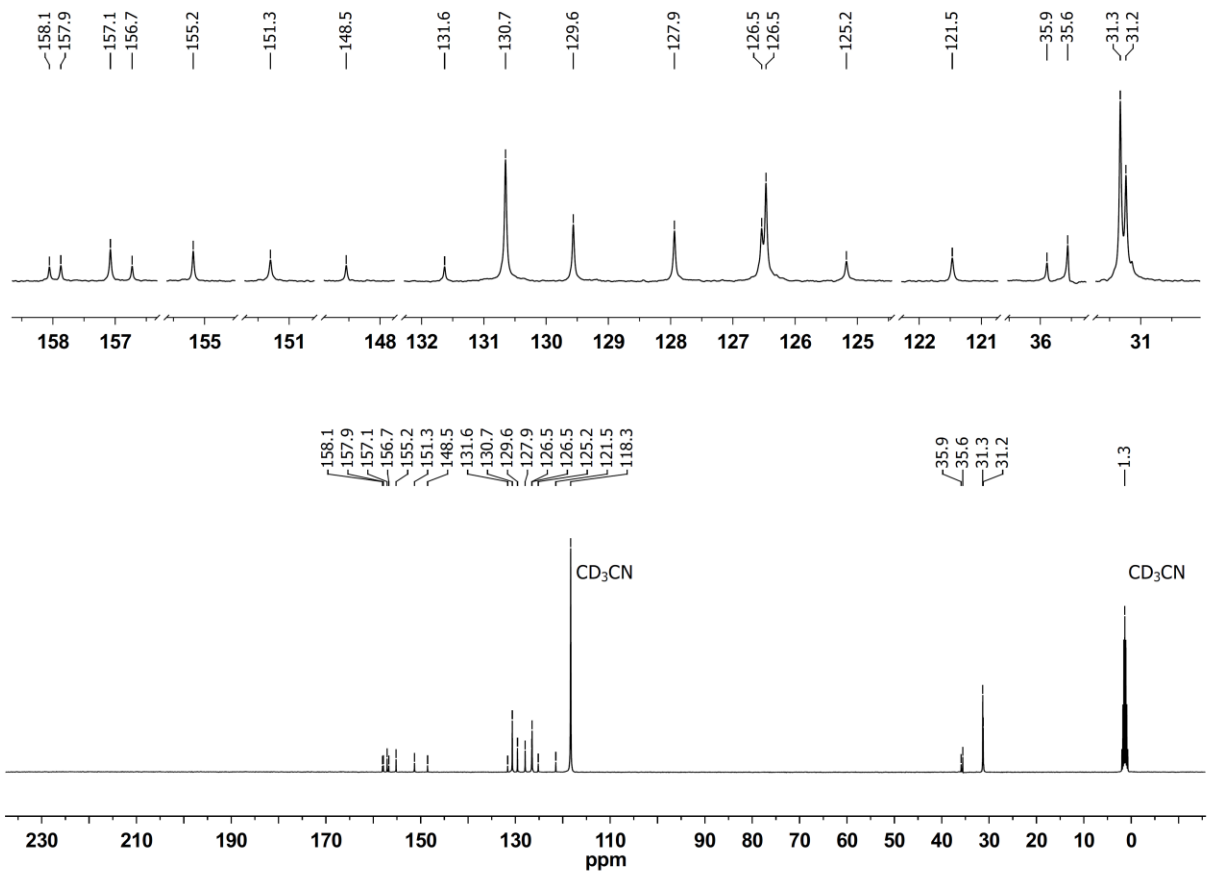


Figure 2. ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C) of ligand **2b**

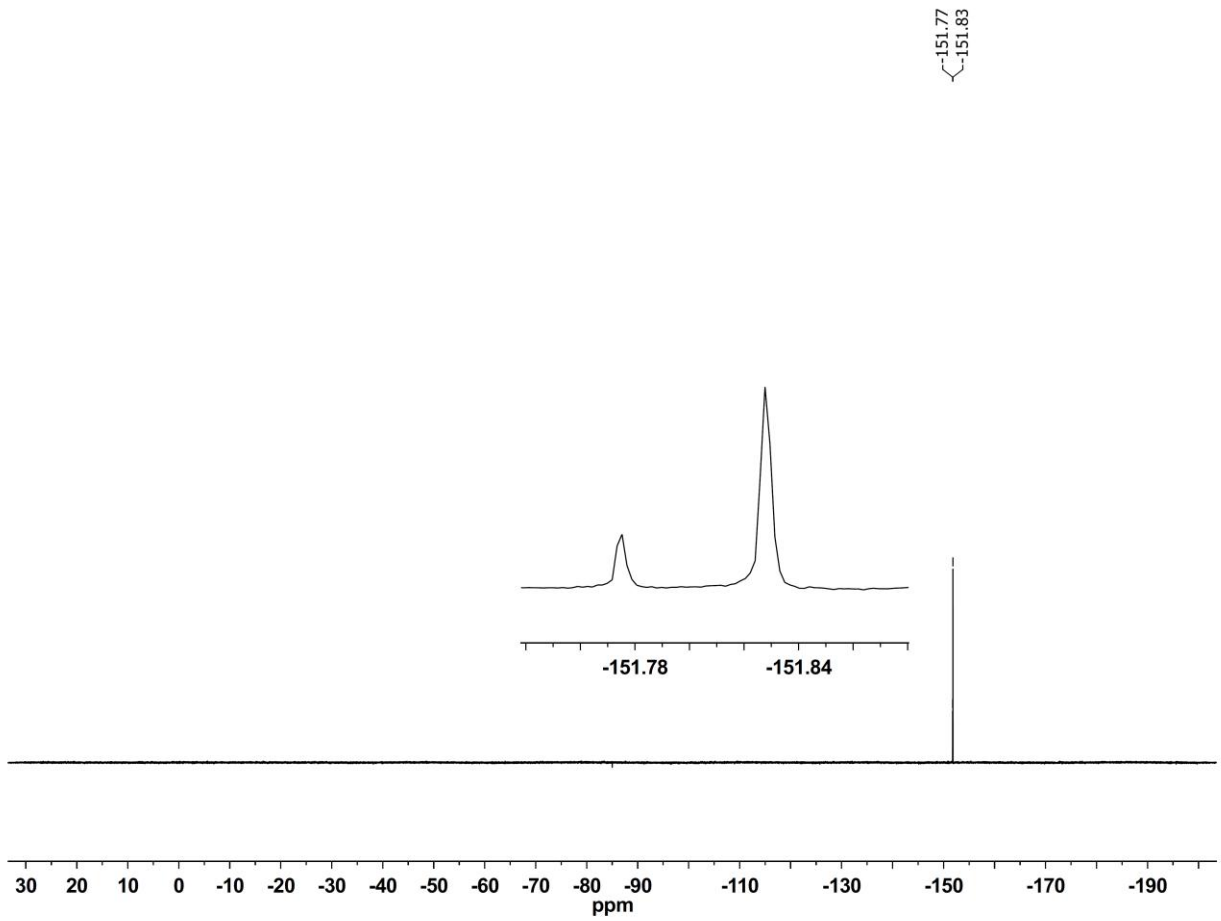


Figure 3. ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C) of ligand **2b**

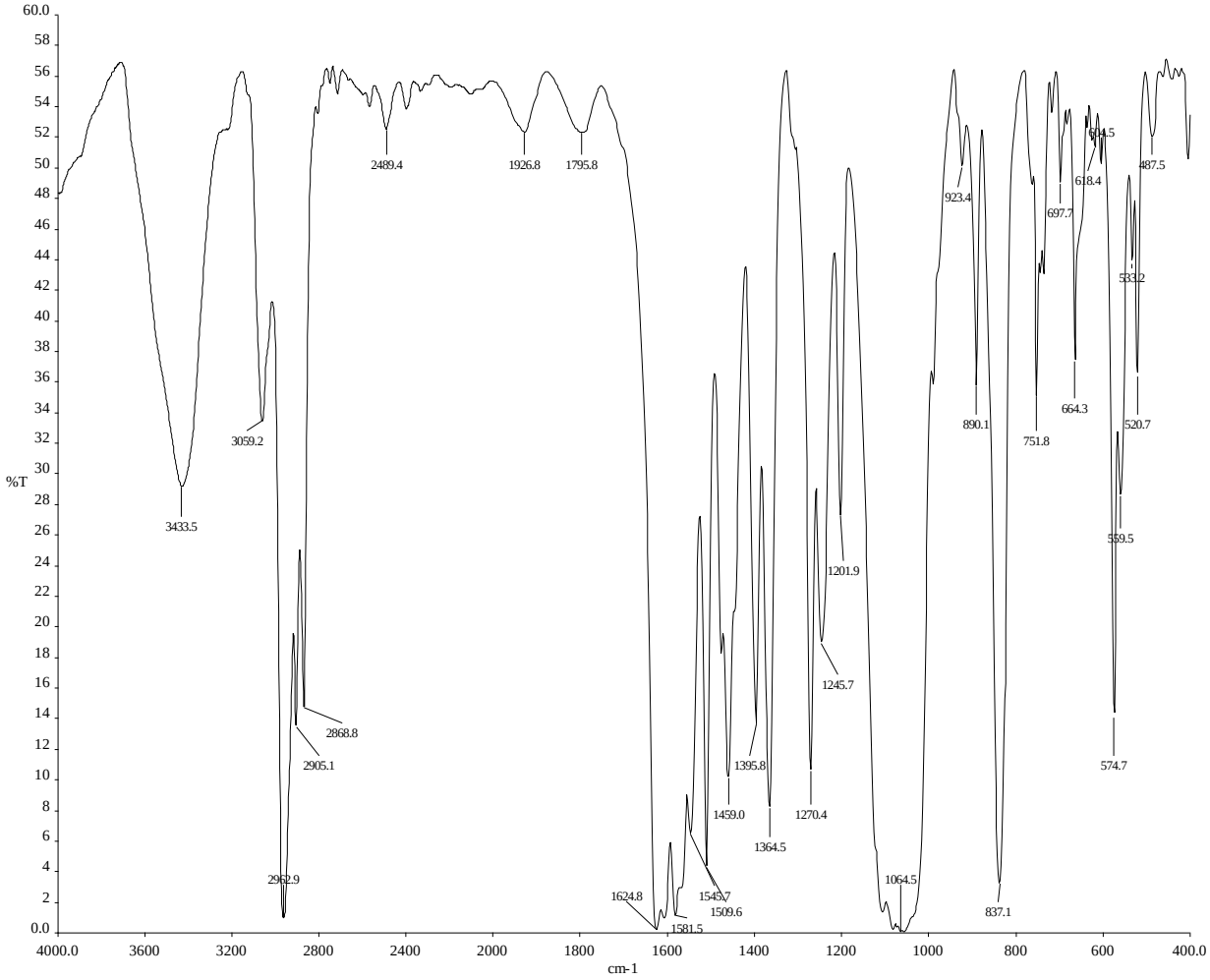
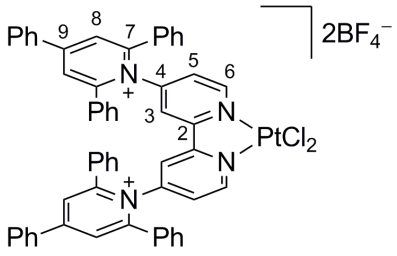


Figure 4. IR (KBr) of ligand **2b**



3a

Synthesis of Pt complex 3a

A mixture of ligand **2a** (530 mg, 0.562 mmol, 1.05 equiv) and $(DMSO)_2PtCl_2$ (225 mg, 0.533 mmol, 1.00 equiv) in MeOH (66 mL) was heated under reflux for 10 h. The mixture was cooled to RT, and the solvent was removed under vacuum. The resulting solid residue was recrystallized from a mixture of acetonitrile (6 mL) and toluene (15 mL) and was then isolated by filtration and dried under vacuum to afford the title complex **3a** as a yellow solid (422 mg, 66%). m.p. 348°C (decomp.); ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C): δ=9.45 (d, ^{3}J(H,H)=6.3 Hz, 2H; H^{6}), 8.51 (s, 4H; H^{8}), 8.18-8.13 (m, 4H; Ph), 7.94 (m, 2H; H^{3}), 7.77-7.66 (m, 6H; Ph), 7.61 (dd, ^{3}J(H,H)=6.3 Hz, ^{4}J(H,H)=2.3 Hz, 2H; H^{5}), 7.52 (m, 4H; Ph), 7.44 ppm (m, 16H, Ph); ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C): δ=159.4, 158.0, 156.8, 151.6, 149.7, 134.4, 134.3, 132.5, 132.1, 131.0, 130.9, 130.2, 129.9, 128.9, 127.1, 124.4 ppm; ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C): δ=–148.58 ($^{10}BF_4^-$), –148.63 ppm ($^{11}BF_4^-$); IR (KBr): $\tilde{\nu}$ =499 (w), 534 (w), 617 (w), 699 (s), 767 (s), 866 (w), 892 (m), 1060 (br), 1185 (w), 1231 (m), 1360 (m), 1418 (w), 1438 (w), 1460 (m), 1483 (m), 1495 (m), 1546 (s), 1625 (s), 3058 (m) cm^{-1}; elemental analysis calcd. (%) for $C_{56}H_{40}B_2Cl_2F_8N_4Pt$: C, 55.65; H, 3.34; N, 4.64, found (%): C, 55.94; H, 3.35; N, 4.60.

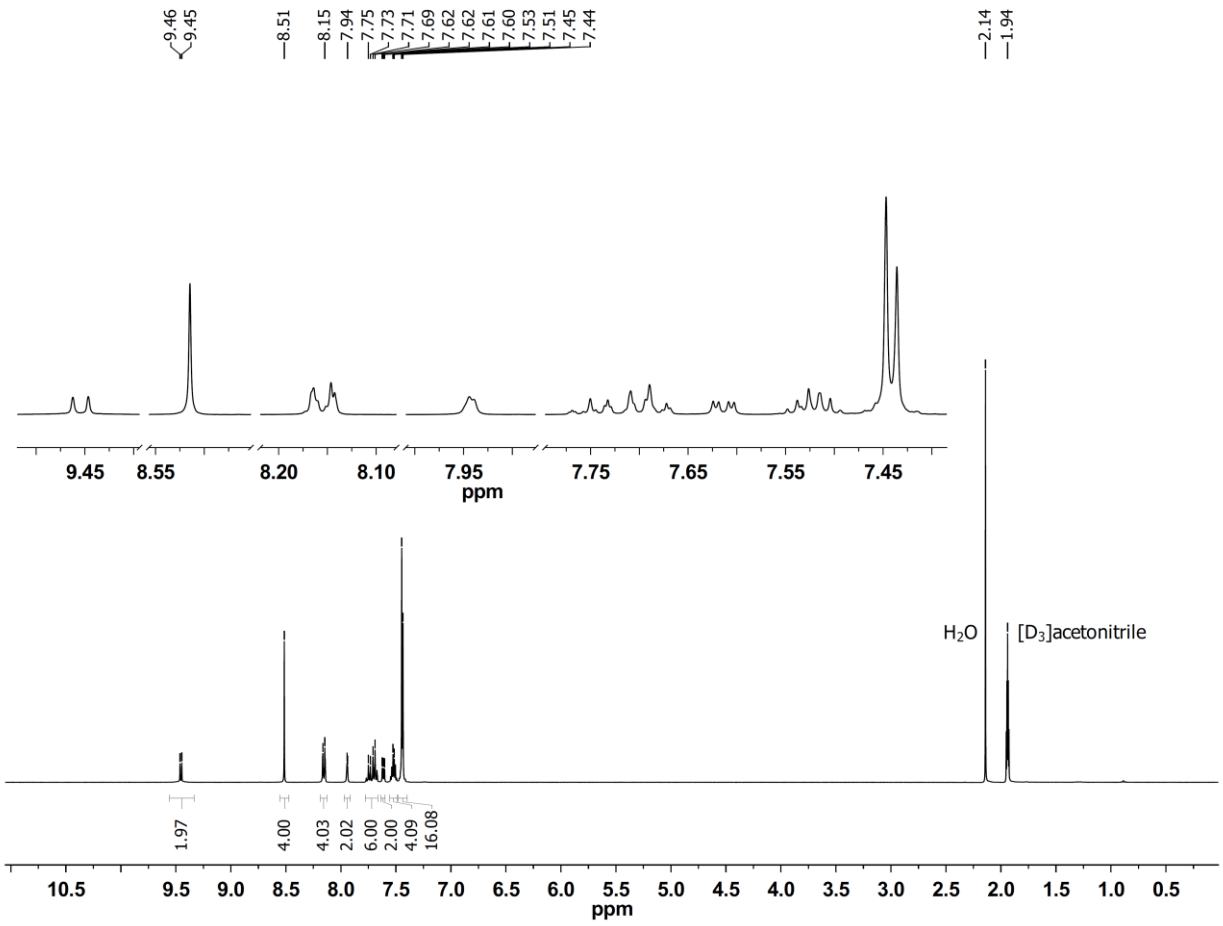


Figure 5. ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C) of complex **3a**

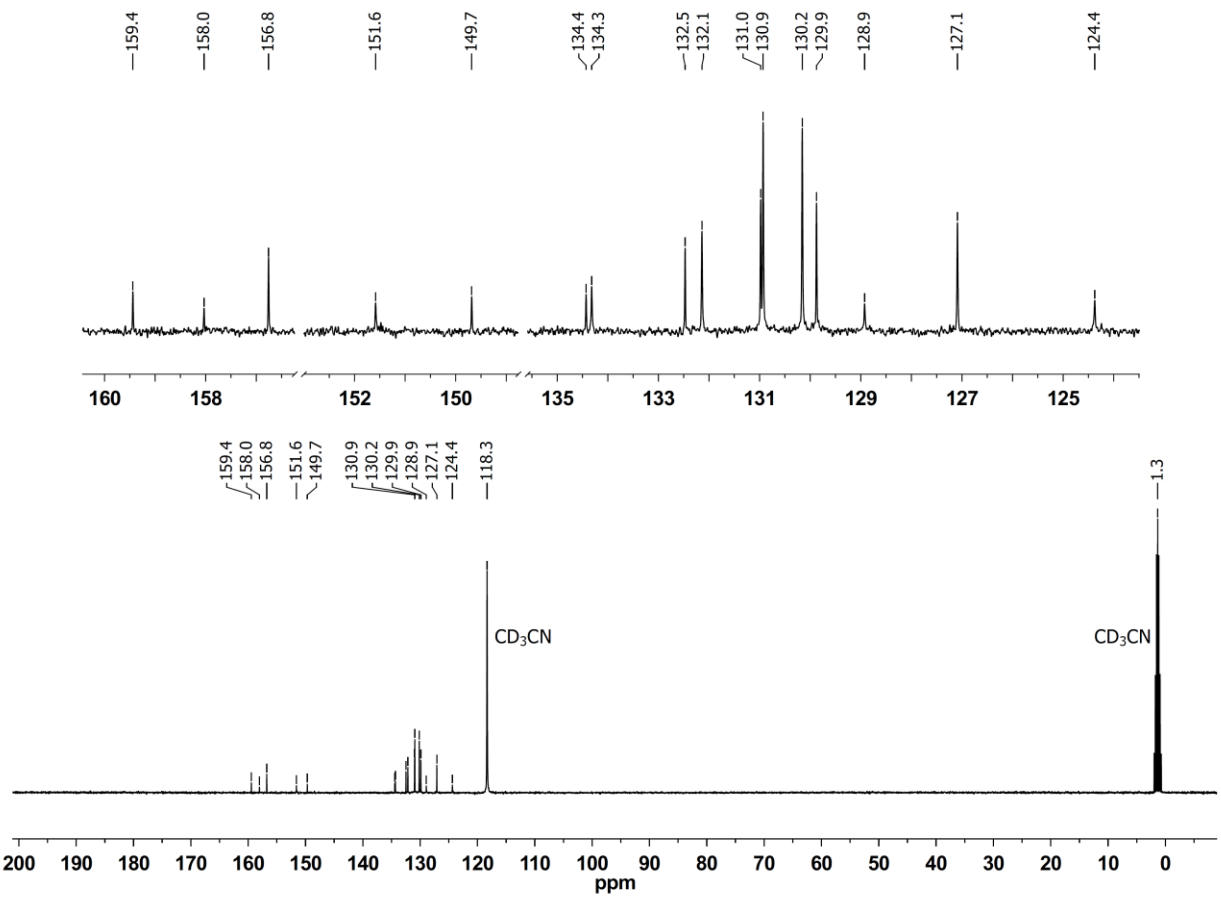


Figure 6. ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C) of complex **3a**

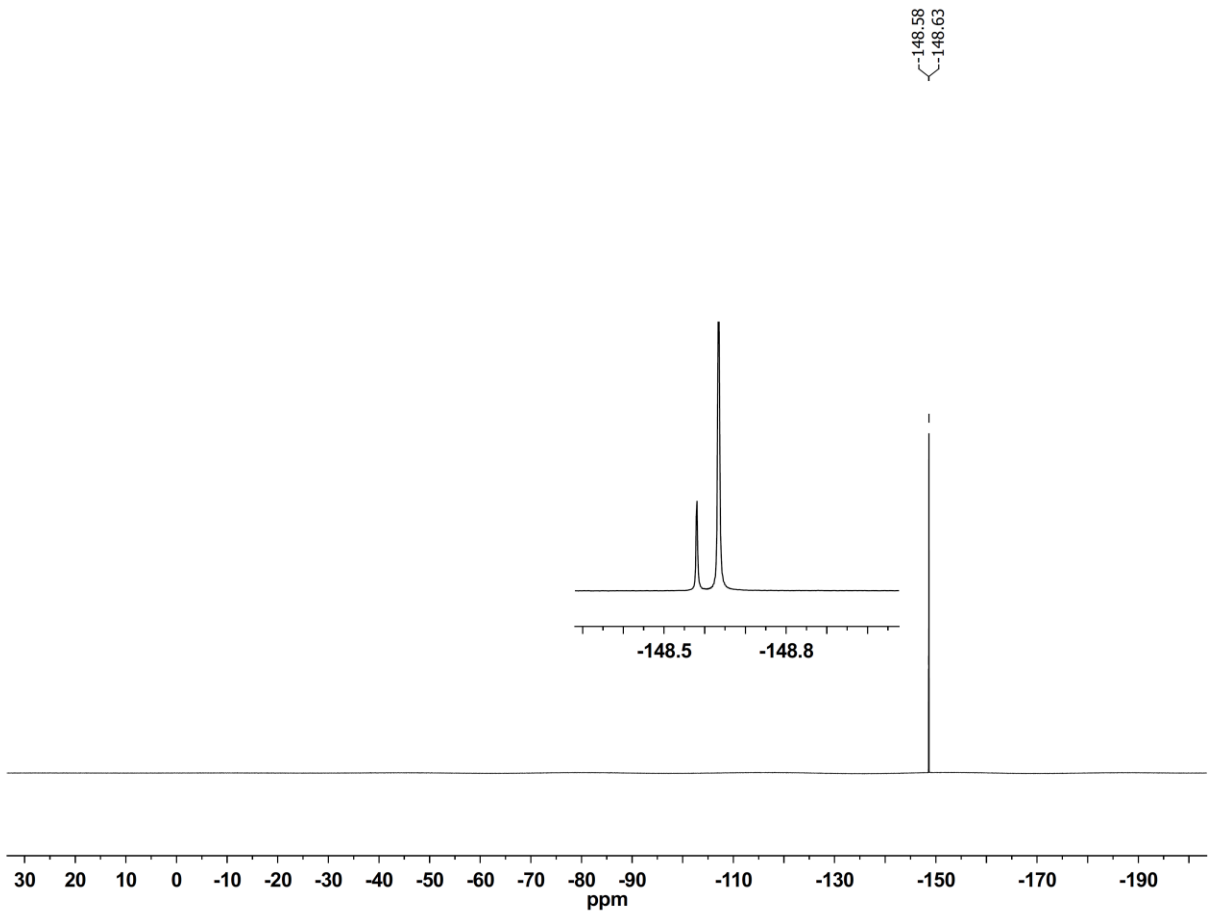


Figure 7. ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C) of complex **3a**

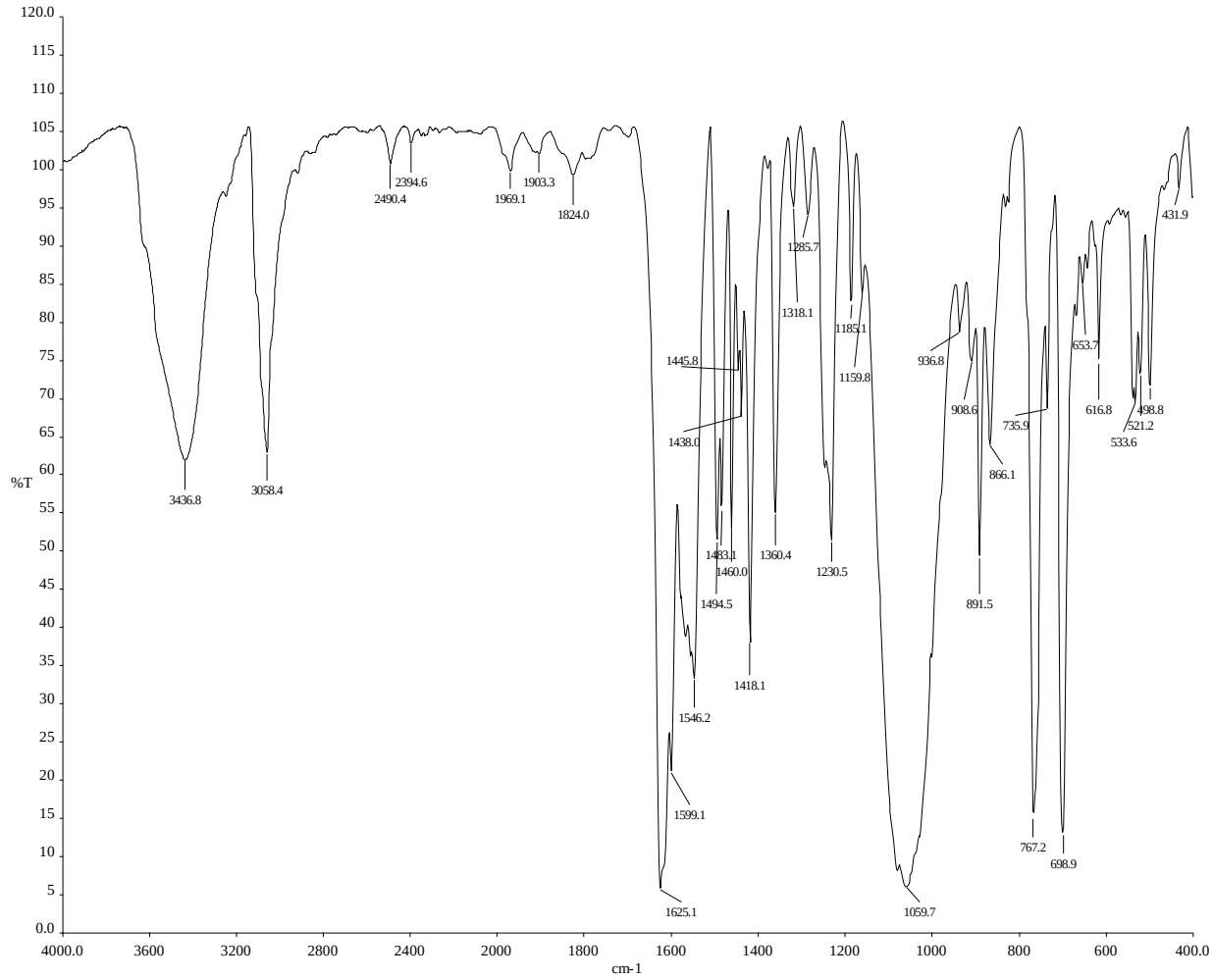
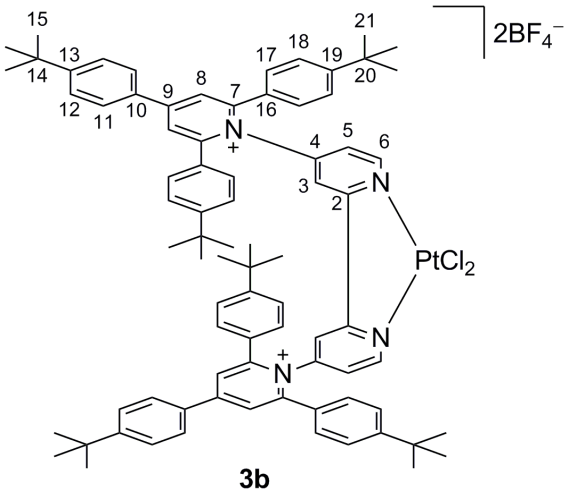


Figure 8. IR (KBr) of complex **3a**



3b

Synthesis of Pt complex 3b

A mixture of ligand **2b** (763 mg, 0.596 mmol, 1.05 equiv) and $(DMSO)_2PtCl_2$ (240 mg, 0.568 mmol, 1.00 equiv) in MeOH (60 mL) was heated under reflux for 15 h. The mixture was cooled to RT, and the solvent was removed under vacuum. The residue was recrystallized at 8 ºC from a mixture of acetonitrile (1 mL) and toluene (10 mL) and was then isolated by filtration and dried under vacuum to afford the title complex **3b** as an orange solid (457 mg, 52%). m.p. 317°C (decomp.); ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C): δ=9.32 (d, ^3J(H,H)=6.3 Hz, 2H; H^6), 8.39 (s, 4H; H^8), 8.09 (m, 4H; H^{11}), 8.03 (d, ^4J(H,H)=2.2 Hz, 2H; H^3), 7.71 (m, 4H; H^{12}), 7.51 (dd, ^3J(H,H)=6.3 Hz, ^4J(H,H)=2.2 Hz, 2H; H^5), 7.42 (m, 8H; H^{18}), 7.34 (m, 8H; H^{17}), 1.39 (s, 18H; H^{15}), 1.27 ppm (s, 36H; H^{21}); ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C): δ=158.7, 158.5, 158.3, 156.8, 155.4, 149.9, 131.6, 130.8, 129.9, 129.7, 128.5, 128.0, 127.1, 126.6, 126.5, 124.6, 35.9, 35.6, 31.4, 31.2 ppm; ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C): δ=–148.40 ($^{10}BF_4^-$), –148.46 ppm ($^{11}BF_4^-$); IR (KBr): $\tilde{\nu}$ =562 (w), 583 (w), 838 (s), 1084 (br), 1203 (w), 1231 (w), 1271 (w), 1364 (m), 1398 (w), 1422 (w), 1442 (w), 1479 (m), 1509 (m), 1543 (m), 1569 (m), 1603 (s), 1624 (s), 2870 (w), 2907 (w), 2964 (s), 3074

(w) cm^{-1}; elemental analysis calcd. (%) for $C_{80}H_{88}B_2Cl_2F_8N_4Pt$: C, 62.18; H, 5.74; N, 3.63, found (%): C, 62.39; H, 5.69; N, 3.64.

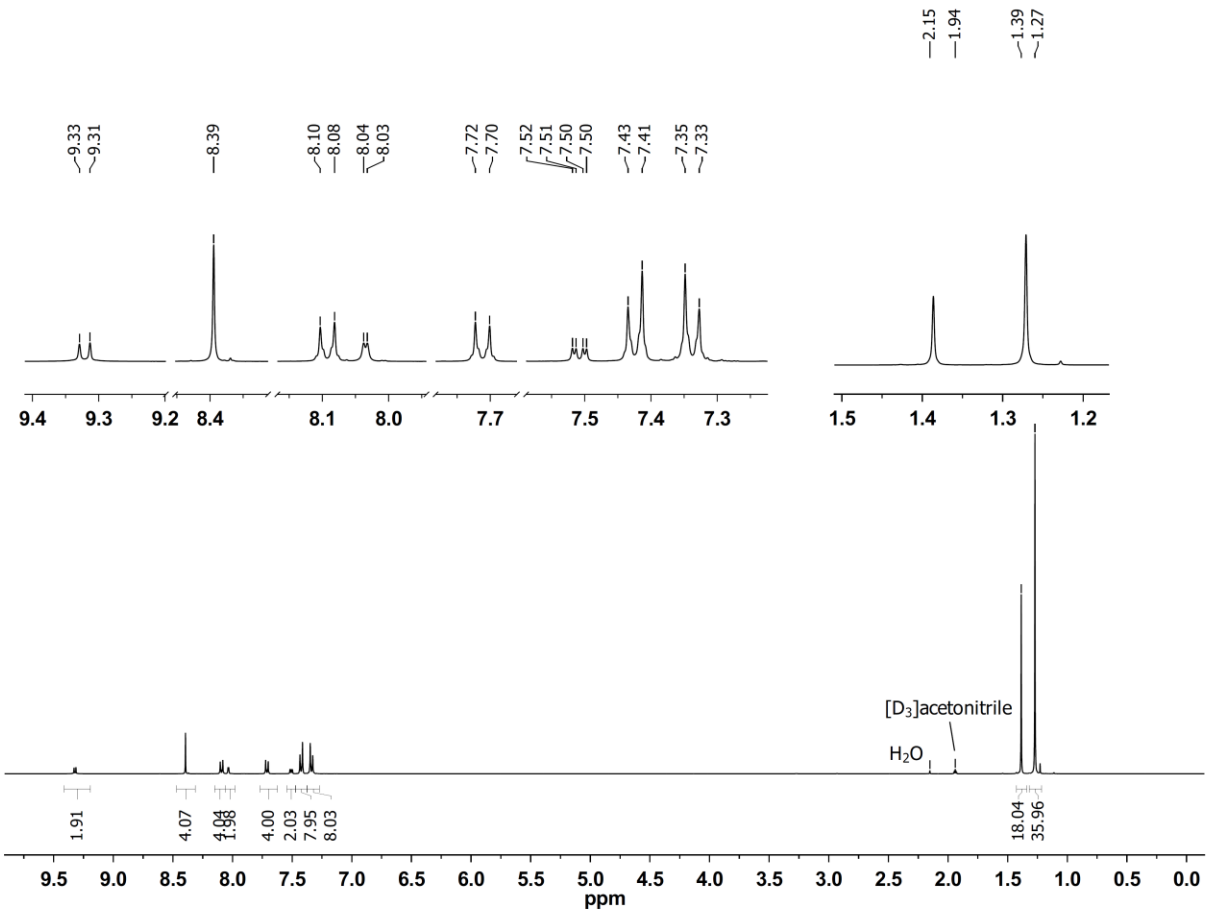


Figure 9. ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C) of complex **3b**

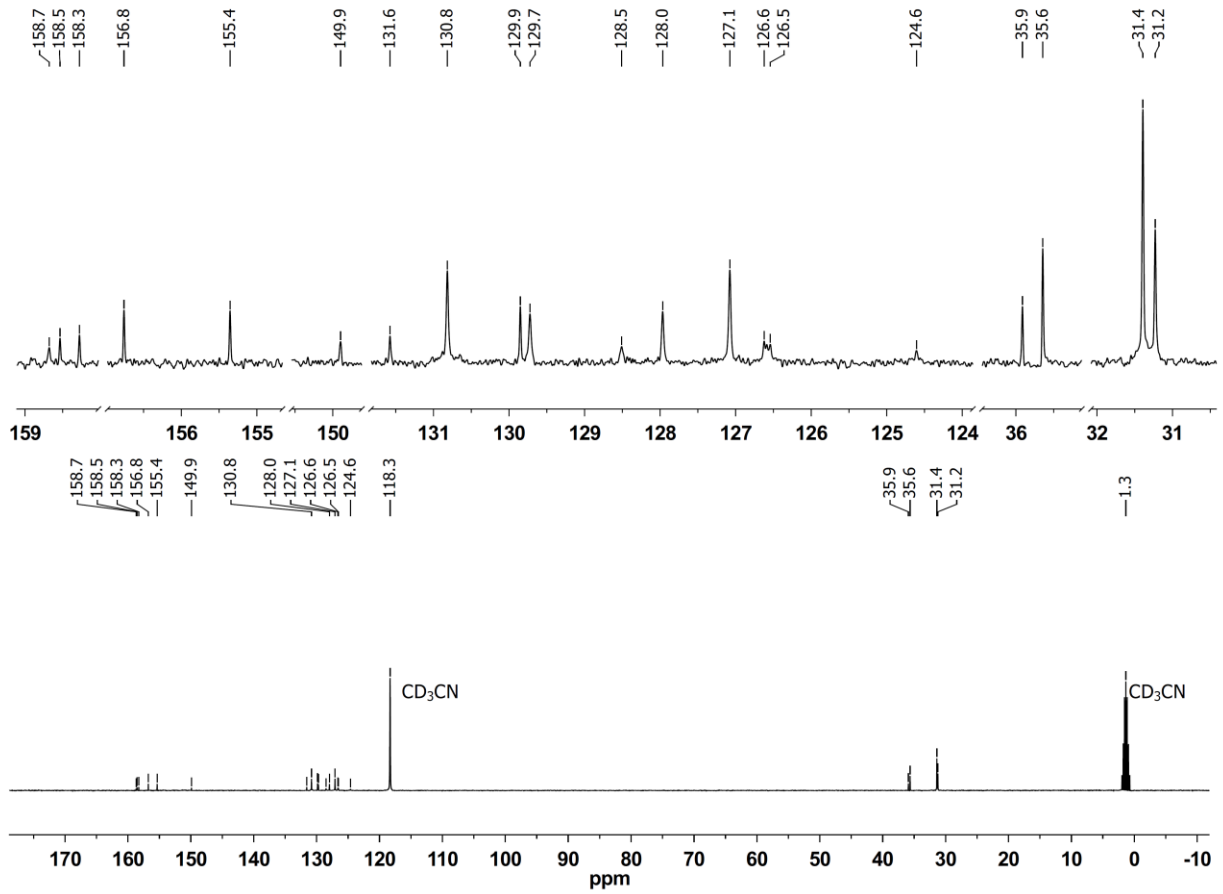


Figure 10. ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C) of complex **3b**

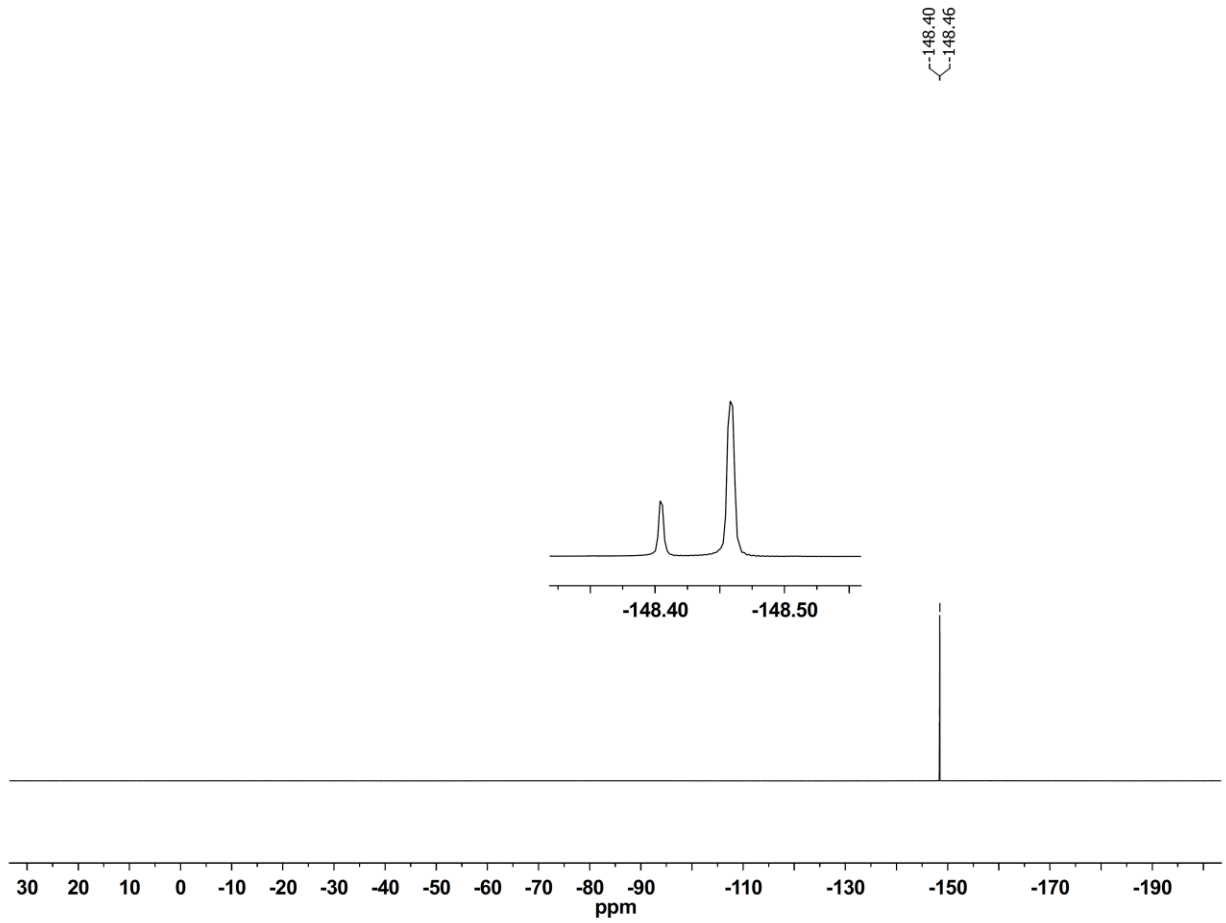


Figure 11. ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C) of complex **3b**

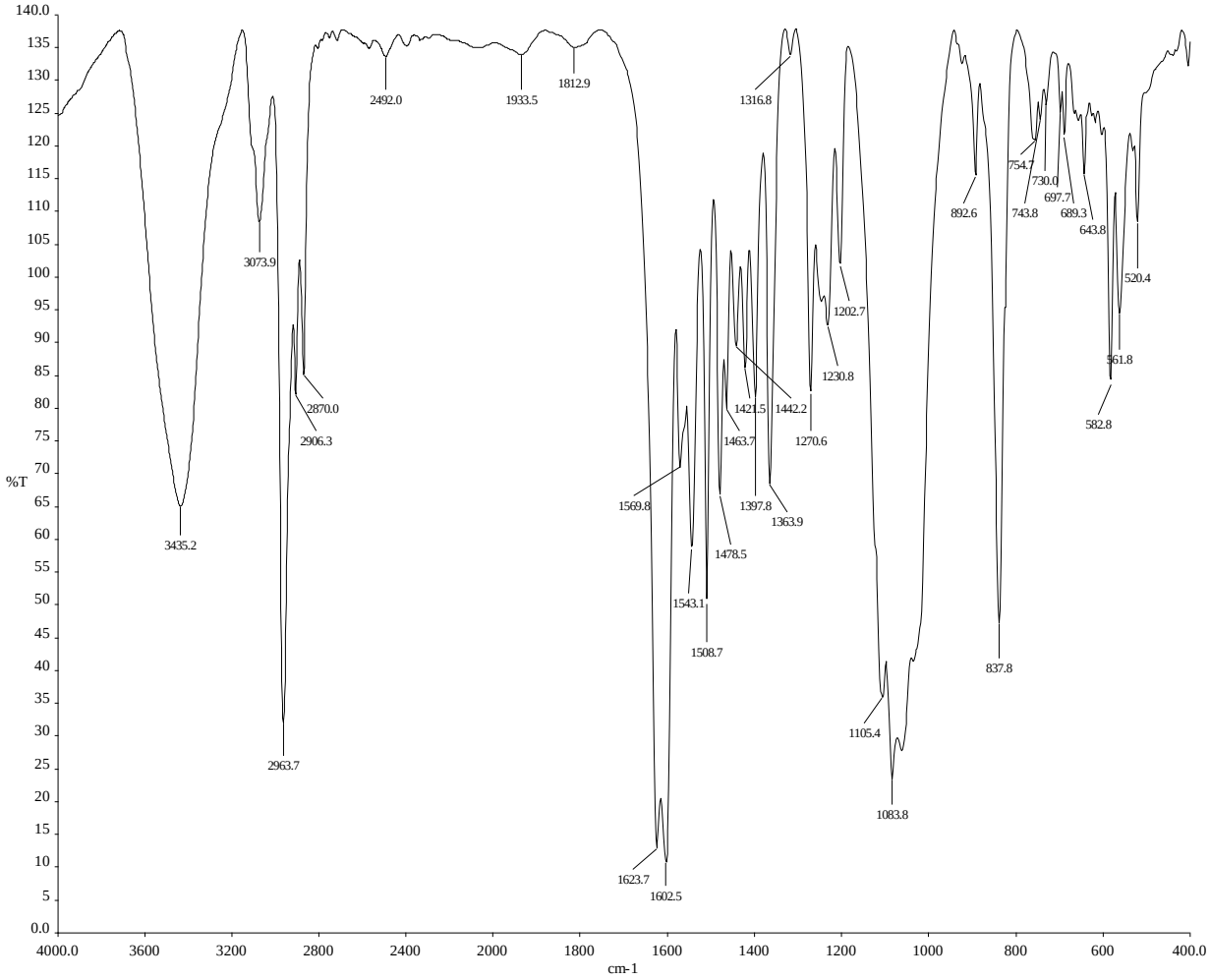
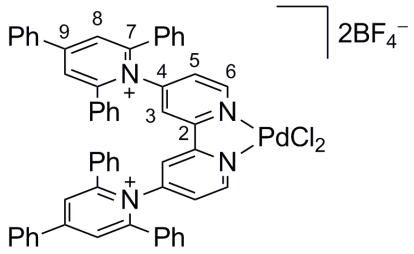


Figure 12. IR (KBr) of complex **3b**



3c

Synthesis of Pd complex 3c

A mixture of ligand **2a** (900 mg, 0.955 mmol, 1.00 equiv) and (COD)$PdCl_2$ (273 mg, 0.956 mmol, 1.00 equiv) in CH_2Cl_2 (250 mL) was stirred at RT for 22 h. The solvent was removed under vacuum. The residue was suspended in acetonitrile (5 mL) and the resulting suspension was filtered. The filter plug was rinsed with acetonitrile (2 x 2 mL). Diffusion of a mixture of pentane and diethyl ether (1 : 1) into the filtrate over a period of 24 h resulted in formation of a crystalline precipitate, which was collected and dried under vacuum to afford the title complex **3c** as a yellow solid (902 mg, 84%). m.p. 292°C (decomp.); ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C): δ=9.01 (d, ^{3}J(H,H)=6.2 Hz, 2H; H^{6}), 8.51 (s, 4H; H^{8}), 8.17-8.12 (m, 4H; Ph), 7.89 (d, ^{4}J(H,H)=2.2 Hz, 2H; H^{3}), 7.76-7.65 (m, 6H; Ph), 7.62 (dd, ^{3}J(H,H)=6.2 Hz, ^{4}J(H,H)=2.2 Hz, 2H; H^{5}), 7.56-7.40 (m, 20H; Ph); ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C): δ=159.8, 157.5, 157.3, 153.2, 150.9, 134.8, 134.6, 132.8, 132.5, 131.3, 131.3, 130.5, 130.2, 128.6, 127.4, 124.2 ppm; ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C): δ=−145.97 ($^{10}BF_4^-$), −146.01 ppm ($^{11}BF_4^-$); IR (KBr): $\tilde{\nu}$ =503 (w), 522 (w), 533 (m), 614 (w), 619 (w), 701 (s), 765 (s), 871 (w), 889 (m), 931 (w), 1083 (br), 1185 (w), 1230 (s), 1282 (w), 1318 (w), 1357 (s), 1414 (s), 1445 (w), 1461 (w), 1494 (s), 1549 (s), 1568 (s), 1621 (s), 3058 (m) cm^{-1}; elemental analysis calcd. (%) for $C_{56}H_{40}B_2Cl_2F_8N_4Pd$: C, 60.06; H, 3.60; N, 5.00, found (%): C, 59.10; H, 3.76; N, 4.92.

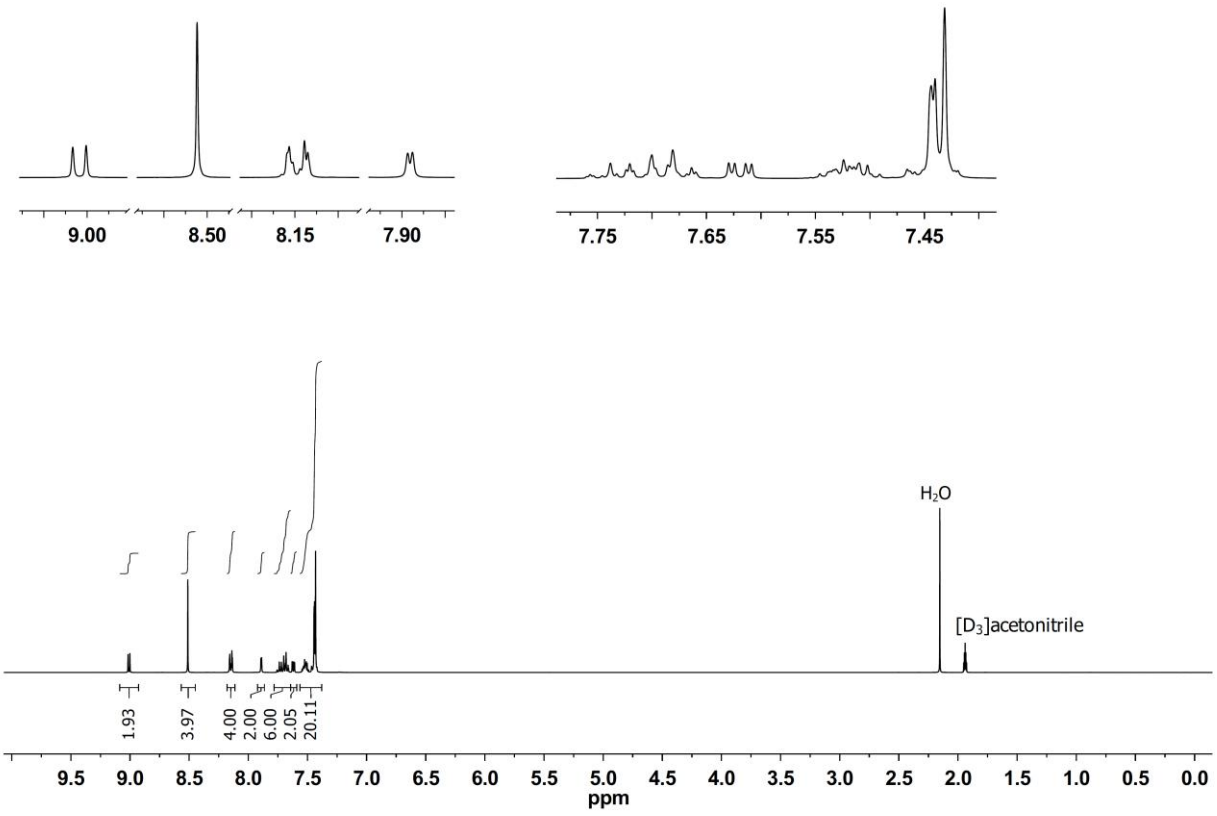


Figure 13. ^{1}H NMR (400 MHz, [D_3]acetonitrile, 25 °C) of complex **3c**

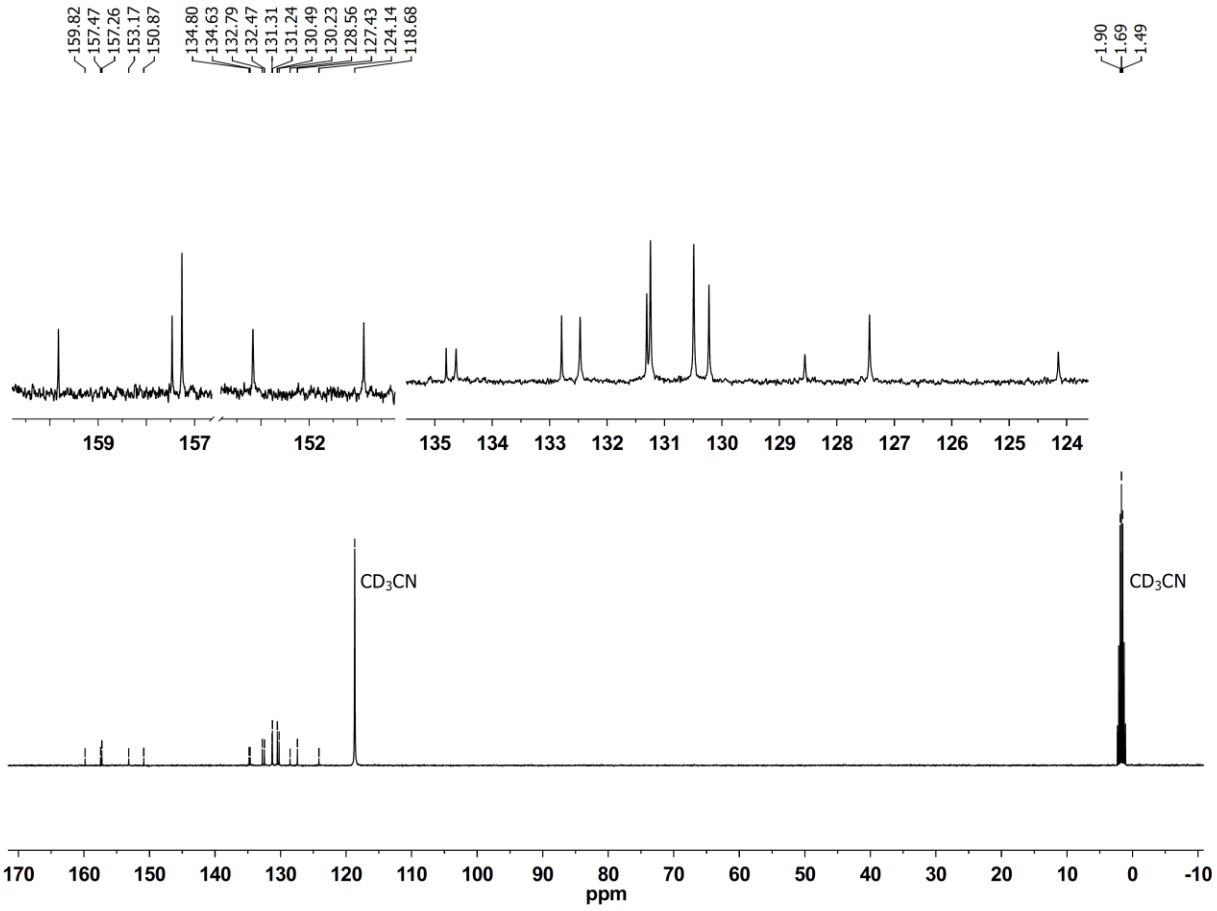


Figure 14. ^{13}C NMR (101 MHz, [D_3]acetonitrile, 25 °C) of complex **3c**

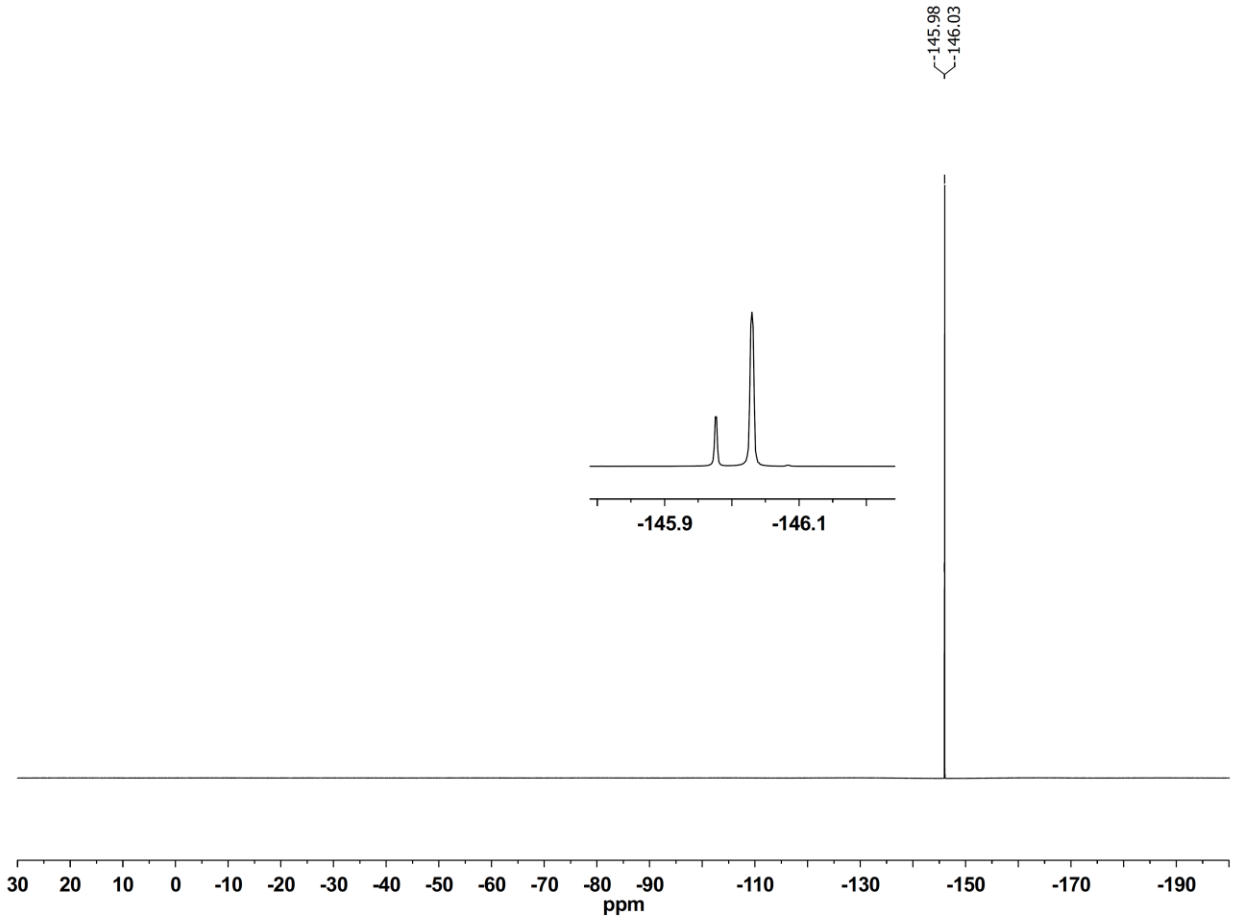


Figure 15. ^{19}F NMR (377 MHz, [D_3]acetonitrile, 25 °C) of complex **3c**

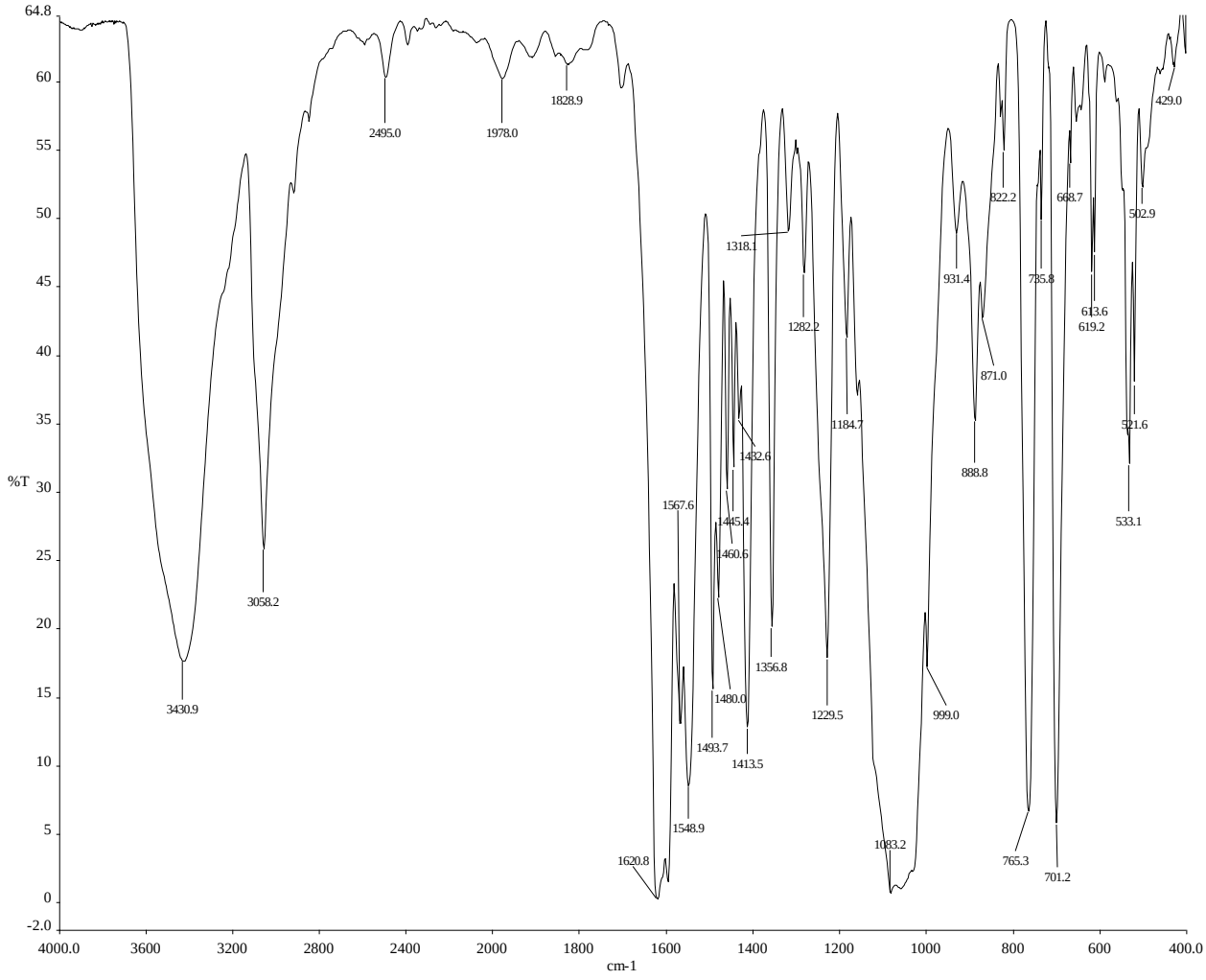


Figure 16. IR (KBr) of complex **3c**

H/D Exchange Reactions[10]

All glassware and stir bars were treated with aqua regia, washed with copious water and acetone, and dried before each use.

General Procedure For H/D Exchange Reactions Between C_6H_6 and $[D_4]$AcOH at 2 mol % Catalyst Loading.

To a 4 mL resealable Schlenk tube was added catalyst (5.0 μmol, 2.0 mol %) and 0.10 mL (10 μmol, 4.0 mol %) of a stock solution of $AgBF_4$ (19.5 mg, 100 μmol) in 1.0 mL $[D_4]$AcOH, which had been prepared immediately prior to use. An additional 0.27 mL of $[D_4]$AcOH was added, and the mixture was stirred for 1 min. Benzene (22.3 μL, 19.5 mg, 0.250 mmol, 1.00 equiv), was added to the reaction vessel, which was subsequently sealed. The vessel was completely submerged in a preheated oil bath. At the end of the reaction, the vessel was cooled to RT. The reaction mixture was then filtered over a plug of Celite to remove any particulates and rinsed with EtOAc (1 x 2 mL) into a 20 mL scintillation vial. A saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 1 mL) was added to the vial to quench and separate the acid. The organic layer was carefully separated and diluted with additional EtOAc to give a 12.8 mM solution of benzene (~1 mg/mL) for analysis by GC-MS.

The % deuterium incorporation was defined as the percent of C–H bonds converted to C–D bonds. The background reaction (in the absence of the Pt catalyst) at 150 °C is minimal with $[D_4]$AcOH and is described in detail in reference [10]. Investigations at 100

[10] H/D exchange was conducted using a standard procedure developed in our group: A. J. Hickman, J. M. Villalobos, M. S. Sanford, *Organometallics* **2009**, *28*, 5316-5322.

°C (see Table 1 below) in [D_4]AcOH revealed even lower background activity without platinum catalyst than had been observed at 150 °C.[11]

Turnover numbers (TONs) are calculated as mol deuterium incorporated per mol of catalyst. Reported values have been corrected for the background reaction in the presence of AgCl, which is formed in situ. The reported error is the standard deviation of at least two replicate trials.

Table 1. Turnover numbers for background H/D exchange between benzene and [D_4]AcOH at 100 °C after 2 and 24 h. Conditions: Benzene (22.3 μl, 0.25 mmol, 1.00 equiv), Ag additive (10 μmol, 4.0 mol %), [D_4]AcOH (0.37 ml, 6.5 mmol, 25 equiv).

Additive	TON 2 h	TON 24 h
$AgBF_4$	0.19 ± 0.22	0.01 ± 0.00
AgOTf	0.06 ± 0.00	0.09 ± 0.10
AgCl	0.04 ± 0.05	0.03 ± 0.01

[11] Stock solutions of AgCl in [D_4]AcOH could not be made due to low solubility. Therefore, AgCl was weighed out independently.

Table 2. Turnover numbers and turnover frequencies for H/D exchange between benzene and $[D_4]$AcOH at 150 °C catalyzed by **1**, **3a**, **3b**, **3c**, dtbpyPtCl$_2$ (dtbpy = 4,4'-di-*tert*-butylbipyridine) and dtbpyPdCl$_2$ after 15 min, 2 h and 24 h. Conditions: Pt^{II} catalyst (5 μmol, 2 mol %), benzene (22.3 μl, 0.25 mmol, 1.00 equiv), $AgBF_4$ (1.9 mg, 10 μmol), $[D_4]$AcOH (0.37 ml, 6.5 mmol, 25 equiv).

Catalyst	TON 15 min	TOF 15 min	TON 2 h	TON 24 h
1	nd[a]	0.01 s^{-1}[b]	3 ± 0	94 ± 13[b]
3a	92 ± 10	0.1024 s^{-1}	217 ± 6	255 ± 2
3b	89 ± 1	0.0983 s^{-1}	230 ± 2	249 ± 0
3c	45 ± 0	0.0501 s^{-1}	168 ± 1	249 ± 1
dtbpyPtCl$_2$	3 ± 1[b]	0.003 s^{-1}[b]	17 ± 1[a]	144 ± 12[b]
dtbpyPdCl$_2$	2 ± 0	0.0021 s^{-1}	13 ± 0	90 ± 18

[a] not determined. [b] see ref. [10].

Table 3. Turnover numbers for H/D exchange between benzene and $[D_4]$AcOH at 100 °C catalyzed by **1**, **3a**, **3b**, **3c**, dtbpyPtCl$_2$ and dtbpyPdCl$_2$ after 2, 24 and 48 h. Conditions: catalyst (5 μmol, 2 mol %), benzene (22.3 μl, 0.25 mmol, 1.00 equiv), $AgBF_4$ (1.9 mg, 10 μmol), $[D_4]$AcOH (0.37 ml, 6.5 mmol, 25 equiv).

Catalyst	TON 2 h	TON 24 h	TON 48 h
1	0 ± 0	0 ± 0	1 ± 0
3a	25 ± 9	136 ± 14	197 ± 15
3b	30 ± 0	167 ± 8	220 ± 3
3c	10 ± 0	57 ± 8	60 ± 11
dtbpyPtCl$_2$	0 ± 0	1 ± 0	2 ± 0
dtbpyPdCl$_2$	0 ± 0	2 ± 1	2 ± 1

Catalyst Loading Study 3a (150 °C)

H/D Exchange Between C_6H_6 and $[D_4]$AcOH at 1.0 mol % Catalyst Loading of 3a.

By analogy to the general procedure for H/D exchange (see above), **3a** (6.3 mg, 5.2 μmol, 1.0 mol %), $AgBF_4$ (10.4 μmol, 2.0 mol %), $[D_4]$AcOH (0.74 mL, 0.83 g, 12.9 mmol, 25 equiv), and benzene (46.5 μL, 40.6 mg, 0.520 mmol, 1.00 equiv) were reacted at 150 °C in a resealable Schlenk tube. Workup and analysis were performed according to the general procedure.

H/D Exchange Between C_6H_6 and $[D_4]$AcOH at 0.5 mol % Catalyst Loading of 3a.

By analogy to the general procedure for H/D exchange (see above), **3a** (5.0 mg, 4.1 μmol, 0.5 mol %), $AgBF_4$ (8.2 μmol, 1.0 mol %), $[D_4]$AcOH (1.17 mL, 1.31 g, 20.4 mmol, 25 equiv), and benzene (73.3 μL, 64.1 mg, 0.82 mmol, 1.00 equiv) were reacted at 150 °C in a resealable Schlenk tube. Workup and analysis were performed according to the general procedure.

H/D Exchange Between C_6H_6 and $[D_4]$AcOH at 0.25 mol % Catalyst Loading of 3a.

By analogy to the general procedure for H/D exchange (see above), **3a** (2.5 mg, 2.1 μmol, 0.25 mol %), $AgBF_4$ (4.2 μmol, 0.50 mol %), $[D_4]$AcOH (1.20 mL, 1.34 g, 21.0 mmol, 25 equiv), and benzene (75.1 μL, 65.6 mg, 0.84 mmol, 1.00 equiv) were reacted at 150 °C in a resealable Schlenk tube. Workup and analysis were performed according to the general procedure.

H/D Exchange Between C_6H_6 and $[D_4]$AcOH at 0.1 mol % Catalyst Loading of 3a.

By analogy to the general procedure for H/D exchange (see above), **3a** (2.5 mg, 2.1 μmol, 0.1 mol %), $AgBF_4$ (4.2 μmol, 0.2 mol %), $[D_4]$AcOH (3.00 mL, 3.36 g, 52.4 mmol, 25 equiv) and benzene (185 μL, 162 mg, 2.10 mmol, 1.00 equiv) were reacted at 150 °C in a resealable Schlenk tube. Workup and analysis were performed according to the general procedure.

Table 4. Turnover numbers for H/D exchange between benzene and $[D_4]$AcOH at 150 °C catalyzed by **3a** at different catalyst loadings after 2, 24 and 48 h. Conditions see above.

Catalyst Loading **3a** [mol %]	$TON_{stat\ max}$[a]	TON 2 h	TON 24 h	TON 48 h
2.0	242	217 ± 6	255 ± 2[b]	nd[c]
1.0	484	424 ± 6	513 ± 1[b]	nd[c]
0.50	968	650 ± 15	1011 ± 6[b]	nd[c]
0.25	1935	606 ± 7	1728 ± 25	nd[c]
0.10	4839	635 ± 23	2384 ± 60	3273 ± 110

[a] maximum statistical turnover number [$TON_{stat\ max} = TON_{max}*25/(25+6)$].[12] [b] The TONs under these conditions level off at ~4-6% above the value for the $TON_{stat\ max}$. This may be due to an isotope effect. [c] Not determined.

[12] The maximum theoretical turnover number (TON_{max}) was calculated considering the case of complete D incorporation (600%) for C_6H_6 as substrate. Thus, for a catalyst loading of 2.0 mol %, a TON_{max} of 300 was reached, if only C_6D_6 would be observed after the reaction. In analogy, at a catalyst loading of 0.1 mol %, the TON_{max} would account to 6000.

Silver Additive Study 100 °C

By analogy to the general procedure for H/D exchange (see above), **3b** (4.0 mg, 2.6 μmol, 2.0 mol %), Ag additive[13,14] (5.2 μmol, 4.0 mol %), [D_4]AcOH (0.19 mL, 0.21 g, 3.3 mmol, 25 equiv), and benzene (11.6 μL, 10.1 mg, 0.130 mmol, 1.00 equiv) were reacted at 100 °C in a resealable Schlenk tube.

Table 5. Turnover numbers for H/D exchange between benzene and [D_4]AcOH at 100 °C catalyzed by **3b** after 24 h. Conditions: **3b** (4.0 mg, 2.6 μmol, 2.0 mol %), benzene (11.6 μl, 0.13 mmol, 1.00 equiv), Ag additive[13,14] (5.2 μmol, 4.0 mol %), [D_4]AcOH (0.19 ml, 3.3 mmol, 25 equiv)

Additive	TON 24 h	Additive	TON 24 h
$AgBF_4$	167 ± 8	Ag_2CO_3	1 ± 0
$AgPF_6$	79 ± 9	$AgNO_3$	0 ± 0
AgOTf	209 ± 1	AgTFA	17 ± 8
AgOTs	144 ± 8	none	0 ± 0
Ag_2SO_4	163 ± 10		

[13] Stock solutions of Ag_2SO_4, AgOTs, $AgNO_3$ and Ag_2CO_3 in [D_4]AcOH could not be made due to low solubility. Therefore, these additives were weighed out independently.

[14] In the case of the additives Ag_2CO_3 and Ag_2SO_4, only 2.6 μmol (2.0 mol %) of the respective salts were used. Workup and analysis were performed according to the general procedure.

H/D Exchange Reactions Between Liquid Aromatic Substrates and [D_4]AcOH at 2 mol % Catalyst Loading.

By analogy to the general procedure for H/D exchange between benzene and [D_4]AcOH (see above), **3a** (3.0 mg, 2.5 μmol, 2.0 mol %), AgOTf (5.0 μmol, 4.0 mol %), [D_4]AcOH (0.36 mL, 0.40 g, 6.25 mmol, 50 equiv), and the aromatic substrate (0.125 mmol, 1.00 equiv; see Figure 13 below) were reacted at 150 °C in a resealable Schlenk tube. At the end of the reaction, the vessel was cooled to RT and $CH_2ClCHCl_2$ (11.6 μL, 16.7 mg, 0.125 mmol, 1.00 equiv) was added as internal standard for ^{1}H NMR spectroscopy.

Workup for ethyl benzoate. 0.3 mL of the reaction mixture was filtered through a plug of celite and was rinsed with [D_6]acetone (0.6 mL). The resulting filtrate was analyzed by ^{1}H NMR spectroscopy.

Workup for bromobenzene. 0.3 mL of the reaction mixture was filtered through a plug of celite and rinsed with [D_6]benzene (0.6 mL). The resulting filtrate was analyzed by ^{1}H NMR spectroscopy.

Workup for *sec*-butylbenzene. 0.3 mL of the reaction mixture was filtered through a plug of celite and rinsed with [D_3]acetonitrile (0.6 mL). The resulting filtrate was analyzed by ^{1}H NMR spectroscopy.

Workup for neopentylbenzene and *iso*-propylbenzene. 0.3 mL of the reaction mixture was filtered through a plug of celite and rinsed with $CDCl_3$ (0.6 mL). The resulting filtrate was analyzed by ^1H NMR spectroscopy.

Workup for α,α,α-trifluorotoluene and 1,2-dimethoxybenzene (veratrole). The reaction mixture was diluted with [D_6]benzene (1 mL) and extracted with a saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 1 mL) to quench and separate the acid. The organic layer was carefully separated and filtered through $MgSO_4$. The resulting filtrate was analyzed by ^1H NMR spectroscopy.

Workup for 1,2-dichlorobenzene. The reaction mixture was diluted with [D_1]chloroform (1 mL) and extracted with saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 1 mL) to quench and separate the acid. The organic layer was carefully separated and filtered through $MgSO_4$. The resulting filtrate was analyzed by ^1H NMR spectroscopy.

H/D Exchange Reactions Between Naphthalene and [D_4]AcOH.

To a 4 mL resealable Schlenk tube was added catalyst **3a** (3.0 mg, 2.5 μmol, 2.0 mol %), naphthalene (16.0 mg, 0.125 mmol, 1.00 equiv), and 0.10 mL (5.0 μmol, 4.0 mol %) of a stock solution of AgOTf (50 μmol) in 1.0 mL [D_4]AcOH, which had been prepared immediately prior to use. An additional 0.26 mL of [D_4]AcOH was added, and the reaction vessel was subsequently sealed. The vessel was completely submerged in an oil bath preheated to 150 °C. At the end of the reaction, the vessel was cooled to RT and $CH_2ClCHCl_2$ (11.6 μL, 16.7 mg, 0.125 mmol, 1.00 equiv) was added as internal

standard. 0.3 mL of the reaction mixture was filtered through a plug of celite and was rinsed with [D_6]acetone (0.6 mL). The resulting filtrate was analyzed by ^{1}H NMR spectroscopy.

In all cases, the % deuterium incorporation was calculated from the loss of signal intensity in single scan ^{1}H NMR spectra as referenced to integration from a sample containing standard (1,1,2-trichloroethane) and non-deuterated substrate in an equimolar ratio. The reported error is the standard deviation of at least two replicate trials.

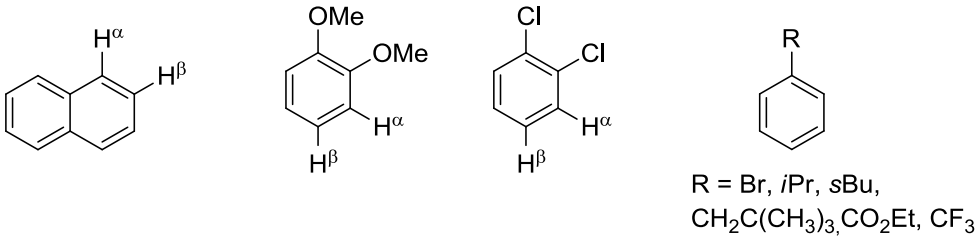


Figure 17. Aromatic substrates examined for H/D exchange with [D_4]AcOH.

Table 6. Arene D incorporation[a] after H/D exchange reaction at 150 °C between $[D_4]$AcOH and monosubstituted aromatic substrates. Conditions: **3a** (3.0 mg, 2.5 μmol, 2.0 mol %), substrate (0.125 mmol, 1.00 equiv), AgOTf (5.0 μmol, 4.0 mol %), $[D_4]$AcOH (0.36 mL, 0.40 g, 6.25 mmol, 50 equiv).

Substrate	Reaction Time [h]	D incorporation [%]			
		Ar-H average	*ortho*	*meta*	*para*
$(H_3C)_3CCH_2Ph$[a]	168	94 ± 0	93 ± 1	95 ± 1	96 ± 1
*s*BuPh[a]	168	93 ± 1	93 ± 1[b]	93 ± 1	93 ± 1[b]
*i*PrPh[a]	168	95 ± 1	95 ± 0	95 ± 1	96 ± 1
BrPh	48	90 ± 1	93 ± 0	87 ± 1	92 ± 2
$PhCO_2Et$	168	88 ± 2	85 ± 2	93 ± 2	87 ± 1
$PhCF_3$	168	61 ± 1	55 ± 2	71 ± 1	52 ± 1

[a] See table 8 below for quantification of alkyl D incorporation. [b] Average values, due to overlapping ^{1}H NMR signals.

Table 7. D incorporation after H/D exchange reaction at 150 °C between $[D_4]$AcOH and monosubstituted aromatic substrates. Conditions: **3a** (3.0 mg, 2.5 μmol, 2.0 mol %), substrate (0.125 mmol, 1.00 equiv), AgOTf (5.0 μmol, 4.0 mol %), $[D_4]$AcOH (0.36 mL, 0.40 g, 6.25 mmol, 50 equiv).

Substrate	Reaction Time [h]	D incorporation [%]		
		Ar-H average	H^{α}	H^{β}
naphthalene	48	91 ± 1	92 ± 1	91 ± 1
1,2-dimethoxybenzene	48	97 ± 0	97 ± 0	98 ± 0
1,2-dichlorobenzene	168	49 ± 1	50 ± 3	48 ± 0

Direct Quantification of D Incorporation in sp^3 C-H Bonds of Alkyl Substituted Arenes

H/D exchange experiments were performed as described above. The reaction mixture was diluted with chloroform (1.5 mL) and extracted with saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 3 x 1 mL) to quench and separate the acid. The organic layer was carefully separated and filtered through $MgSO_4$. The resulting filtrate was analyzed by ^2H NMR spectroscopy (relaxation delay 10 s). Since the amount of aromatic D incorporation has been calculated from the loss of signal intensity against 1,1,2-trichloroethane as internal standard (see above) in ^1H NMR spectra of analogous samples, the % D incorporation into the alkyl groups can be calculated from the relative integration of alkyl and aryl signals in the ^2H NMR spectra.

Table 8. Alkyl D incorporation after H/D exchange reaction between $[D_4]$AcOH and alkyl substituted aromatic substrates. Conditions: **3a** (3.0 mg, 2.5 μmol, 2.0 mol %), substrate (0.125 mmol, 1.00 equiv), AgOTf (5.0 μmol, 4.0 mol %), $[D_4]$AcOH (0.36 mL, 0.40 g, 6.25 mmol, 50 equiv), 168 h, 150 °C.

Substrate	D incorporation [%]	
	Ar-H average	alkyl-H
$(H_3C)_3CCH_2Ph$	94 ± 0	3 (CH_3)
*s*BuPh	93 ± 1	8 (CH_2), 7 ($CHC\underline{H}_3$), 2 ($CH_2C\underline{H}_3$)
*i*PrPh	95 ± 1	7 (CH_3)

Regioselectivity Study - [Pt] catalyzed H/D Exchange

By analogy to the general procedure for H/D exchange between benzene and $[D_4]$AcOH (see above), catalyst (2.5 μmol, 0.5 mol %), $AgBF_4$ (5.0 μmol, 1.0 mol %), $[D_4]$AcOH (0.71 mL, 0.80 g, 12.4 mmol, 25 equiv), and the aromatic substrate (0.500 mmol, 1.00 equiv) were reacted at 150 °C in a resealable Schlenk tube. At the end of the reaction, the vessel was cooled to RT and $CH_2ClCHCl_2$ (46.3 μL, 66.7 mg, 0.500 mmol, 1.00 equiv) was added as internal standard for ^{1}H NMR spectroscopy. Workup, analysis and calculation of the % D incorporation for ethylbenzoate and bromobenzene were performed as described above.

Workup for ethylbenzene. At the end of the reaction, the reaction mixture was cooled to 0 °C and $CH_2ClCHCl_2$ (46.3 μL, 66.7 mg, 0.500 mmol, 1.00 equiv) was added as internal standard for ^{1}H NMR spectroscopy. 0.3 mL of the reaction mixture was filtered through a plug of celite and was rinsed with $[D_6]$acetone (0.6 mL). The resulting filtrate was analyzed by ^{1}H NMR spectroscopy. Calculation of the % D incorporation was performed as described above

Table 9. D incorporation after H/D exchange reaction at 150 °C between $[D_4]$AcOH and EtPh, BrPh and $PhCO_2Et$, respectively. Conditions: catalyst (2.5 μmol, 0.5 mol %), substrate (0.500 mmol, 1.00 equiv), $AgBF_4$ (5.0 μmol), $[D_4]$AcOH (0.71 ml, 12.4 mmol, 25 equiv).

Substrate	Catalyst	Reaction Time	D incorporation [%]			
			Ar-H average	*ortho*	*meta*	*para*
EtPh	**3a**	10 min	24 ± 2	26 ± 1	20 ± 4	30 ± 1
BrPh	**3a**	4 h	25 ± 2	35 ± 3	14 ± 2	24 ± 0
BrPh	**1**	141 h	25 ± 3	27 ± 3	19 ± 3	30 ± 3
$PhCO_2Et$	**3a**	18 h	26 ± 2	21 ± 2	33 ± 2	22 ± 1

Regioselectivity Study - D^+ catalyzed H/D Exchange

A mixture of bromobenzene (26.3 μL, 39.3 mg, 0.250 mmol, 1.00 equiv), $[D_1]$TFA (0.51 mL, 0.719 g, 6.25 mmol, 25.0 equiv) and 0.05 mL DCl solution in D_2O (35%) was reacted at 150 °C in a resealable Schlenk tube. At the end of the reaction, the vessel was cooled to RT and $CH_2ClCHCl_2$ (23.1 μL, 33.3 mg, 0.250 mmol, 1.00 equiv) was added as internal standard for ^{1}H NMR spectroscopy. The reaction mixture was diluted with $[D_6]$benzene (0.5 mL) and extracted with a saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 2 mL) to quench and separate the acid. The organic layer was carefully separated and filtered through $MgSO_4$. The resulting filtrate was analyzed by ^{1}H NMR spectroscopy.

Table 10. D incorporation after H/D exchange reaction at 150 °C between [D_1]TFA, DCl in D_2O and BrPh. Conditions: PhBr (26.3 μL, 39.3 mg, 0.250 mmol, 1.00 equiv), [D_1]TFA (0.51 mL, 0.719 g, 6.25 mmol, 25.0 equiv), DCl in D_2O (35%, 0.05 mL).

Substrate	Catalyst	Reaction Time	D incorporation [%]			
			Ar-H average	*ortho*	*meta*	*para*
BrPh	DCl/D_2O	38 h	26 ± 2	31 ± 3	5 ± 2	58 ± 0

Pd catalyzed Acetoxylation

$Pd(OAc)_2$ catalyzed Acetoxylation of Benzene - General Procedure[15]

To a mixture of $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv) and $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %) in a pressure resistant vial with a screw cap, glacial acetic acid (0.90 mL) and acetic anhydride (0.10 mL) were added. The suspension was stirred at RT for 1 min, before benzene (1.00 mL, 875 mg, 11.2 mmol, 10.0 equiv) was added. The vial was sealed and heated to 100 °C using a preheated hotplate. At the end of the reaction, the vessel was cooled to RT and PhCl (50 μL) was added as an internal standard for quantitative GC analysis. The mixture was diluted with Et_2O (2 mL) and filtered through a plug of celite. The filtrate was extracted with a saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 2 mL) to quench and separate the acid. The organic layer was carefully separated and diluted with additional Et_2O to a total volume of 20 mL. The resulting solution was analyzed by GC.

$Pd(OAc)_2$ catalyzed Acetoxylation of Benzene - Addition of Bipyridine

By analogy to the general procedure for acetoxylation of benzene (see above), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), 0.50 mL (11.2 μmol, 1.0 mol %) of a stock solution of bipyridine (35.0 mg, 224 μmol) in 10 mL AcOH, AcOH (0.40 mL), acetic anhydride (0.10 mL) and benzene (1.00 mL, 875 mg, 11.2 mmol, 10.0 equiv) were reacted at 100 °C. Workup and analysis were performed as described above.

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[15] Adapted from: T. Yoneyama, R. H. Crabtree, *J. Mol Catal. A* **1996**, *108*, 35-40.

$Pd(OAc)_2$ catalyzed Acetoxylation of Benzene - Addition of Dicationic Ligand 2a

By analogy to the general procedure for acetoxylation of benzene (see above), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), **2a** (10.6 mg, 11.2 μmol, 1.0 mol %), AcOH (0.90 mL), acetic anhydride (0.10 mL) and benzene (1.00 mL, 875 mg, 11.2 mmol, 10.0 equiv) were reacted at 100 °C. Workup and analysis were performed as described above.

Table 11. Calibrated GC yields of phenyl acetate (PhOAc) and biphenyl (PhPh). Conditions: Benzene (1.00 mL, 875 mg, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C.[16]

	Catalyst system							
	$Pd(OAc)_2$		$Pd(OAc)_2$/bpy 2:1		$Pd(OAc)_2$/**2a** 2:1		$Pd(OAc)_2$/bpym 2:1	
Reaction Time [h]	PhOAc	PhPh	PhOAc	PhPh	PhOAc	PhPh	PhOAc	PhPh
2	6.2 ± 0.0	0.0 ± 0.0	9.1 ± 0.4	0.7 ± 0.0	12.5 ± 0.1	0.7 ± 0.0	1.4 ± 0.2	0.3 ± 0.0
4	12.0 ± 0.1	0.7 ± 0.0	17.6 ± 0.1	0.7 ± 0.0	29.0 ± 2.0	0.7 ± 0.0	1.2 ± 0.4	0.3 ± 0.0
6	17.3 ± 2.5	0.7 ± 0.0	25.4 ± 0.6	0.8 ± 0.0	44.1 ± 3.3	1.0 ± 0.0	3.4 ± 0.9	0.3 ± 0.0
8	24.2 ± 3.7	0.7 ± 0.0	36.8 ± 1.1	0.9 ± 0.0	58.8 ± 1.9	1.1 ± 0.0	3.2 ± 1.2	0.3 ± 0.0
12	33.0 ± 1.8	0.7 ± 0.0	47.4 ± 0.1	0.8 ± 0.0	66.8 ± 0.2	1.5 ± 0.4	3.2 ± 1.2	0.3 ± 0.0
16	50.5 ± 4.2	0.7 ± 0.0	62.1 ± 1.4	0.9 ± 0.2	68.4 ± 1.3	2.6 ± 0.0	3.1 ± 3.0	0.3 ± 0.0
20	57.2 ± 3.2	1.1 ± 0.3	70.1 ± 0.3	1.9 ± 0.3	68.0 ± 0.5	2.4 ± 0.0	5.9 ± 4.9	0.3 ± 0.0
24	66.2 ± 0.2	1.7 ± 0.5	70.3 ± 0.9	1.8 ± 0.1	68.1 ± 0.4	2.5 ± 0.0	13.8 ± 1.8	0.3 ± 0.0

[16] The reported error is the standard deviation of at least two replicate trials. The observation that all reactions level off around 70% yield could be due to the formation of by-products as well as the stability of the oxidant under the reaction conditions. Other than biphenyl, also IC_6H_4OAc and $C_6H_4(OAc)_2$ isomers could be identified as by-products using GC-MS analysis. Since the above shown yields are calculated on the amount of oxidant, an excess of $PhI(OAc)_2$ as in directed acetoxylation reactions could not be used.

$Pd(OAc)_2$ catalyzed Acetoxylation of Liquid Arenes[15]

By analogy to the general procedure for acetoxylation of benzene, $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), glacial acetic acid (0.90 mL), acetic anhydride (0.10 mL) and the arene (10.0 equiv) were reacted at 100 °C. At the end of the reaction, the vessel was cooled to RT and GC standard (20 μL; PhCl in the case of trifluoromethylbenzene as substrate, neopentylbenzene in the case of the other substrates) was added. The mixture was diluted with EtOAc (2 mL) and filtered through a plug of celite. The filtrate was extracted with a saturated aqueous solution of K_2CO_3 (9 M in deionized H_2O, 2 x 2 mL) to quench and separate the acid. The organic layer was carefully separated and diluted with additional EtOAc to a total volume of 20 mL. The resulting solution was analyzed by GC or GC-MS.

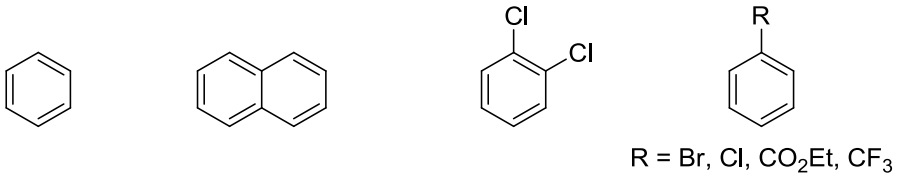

Figure 18. Aromatic substrates examined for acetoxylation with $PhI(OAc)_2$.

$Pd(OAc)_2$ catalyzed Acetoxylation of Naphthalene[15]

$PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %) and naphthalene (1.44 g, 11.2 mmol, 10.0 equiv) were suspended in glacial acetic acid (0.90 mL) and acetic anhydride (0.10 mL). The vial was sealed and the mixture was reacted at 100 °C. At the end of the reaction, the vessel was cooled to RT and 20 μL

neopentylbenzene were added as an internal standard for quantitative GC analysis. Workup and analysis were performed as described above.

$Pd(OAc)_2$ catalyzed Acetoxylation of Arenes - Addition of Bipyridine

By analogy to the general procedures for acetoxylation (see above), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), 0.50 mL (11.2 μmol, 1.0 mol %) of a stock solution of bipyridine (35.0 mg, 224 μmol) in 10 mL AcOH, AcOH (0.40 mL), acetic anhydride (0.10 mL) and arene (10.0 equiv) were reacted at 100 °C. Workup and analysis were performed as described above.

$Pd(OAc)_2$ catalyzed Acetoxylation of Arenes - Addition of Dicationic Ligand 2a

By analogy to the general procedures for acetoxylation (see above), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), **2a** (10.6 mg, 11.2 μmol, 1.0 mol %), AcOH (0.90 mL), acetic anhydride (0.10 mL) and arene (10.0 equiv) were reacted at 100 °C. Workup and analysis were performed as described above.

Table 12. Calibrated combined GC yields and site-selectivity (α:β) of naphthylacetate regioisomers. Conditions: Naphthalene (1.44 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
4	51.9 ± 2.5 (1.46:1)	60.2 ± 1.8 (0.97:1)	76.6 ± 2.6 (0.89:1)
24	73.3 ± 1.4 (1.43:1)	78.6 ± 0.7 (0.93:1)	79.5 ± 1.8 (0.85:1)
48	80.4 ± 1.5 (1.39:1)	79.8 ± 0.9 (0.94:1)	78.2 ± 0.8 (0.87:1)

Table 13. Calibrated combined GC yields and site-selectivity (o:m:p) of ClC_6H_4OAc regioisomers. Conditions: PhCl (1.14 mL, 1.26 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
4	4.0 ± 0.1 (0.70:0.02:1)	6.4 ± 0.3 (0.56:0.17:1)	13.0 ± 0.2 (0.91:0.31:1)
24	38.4 ± 0.2 (0.82:0.51:1)	48.2 ± 1.3 (0.63:0.58:1)	83.7 ± 0.5 (0.81:0.72:1)
48	57.7 ± 1.6 (0.92:0.69:1)	78.0 ± 0.5 (0.67:0.74:1)	89.0 ± 0.3 (0.86:0.75:1)

Table 14. Calibrated combined GC yields and site-selectivity (o:m:p) of BrC_6H_4OAc regioisomers. Conditions: PhBr (1.18 mL, 1.76 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
4	7.9 ± 0.0 (1.16:1.10:1)	9.9 ± 0.3 (0.76:1.00:1)	17.0 ± 0.5 (1.06:1.06:1)
24	38.1 ± 3.5 (1.19:1.17:1)	50.3 ± 4.6 (0.80:1.08:1)	83.1 ± 1.1 (0.89:1.12:1)
48	41.4 ± 0.8 (1.21:1.15:1)	55.7 ± 2.0 (0.77:1.06:1)	84.9 ± 0.9 (0.89:1.09:1)

Table 15. Calibrated combined GC yields and site-selectivity (o:m:p) of $EtO_2CC_6H_4OAc$ regioisomers. Conditions: $PhCO_2Et$ (1.60 mL, 1.68 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
4	2.8 ± 0.2 (0.97:2.13:1)	5.5 ± 0.2 (0.62:3.11:1)	8.8 ± 0.4 (0.62:3.49:1)
24	8.6 ± 0.5 (0.82:3.44:1)	18.9 ± 0.9 (0.49:3.83:1)	34.2 ± 1.8 (0.59:3.87:1)
48	31.3 ± 2.4 (0.71:3.58:1)	60.3 ± 2.4 (0.52:3.92:1)	75.7 ± 2.6 (0.51:3.84:1)

Table 16. Calibrated combined GC yields and site-selectivity (o:m:p) of $CF_3C_6H_4OAc$ regioisomers. Conditions: $PhCF_3$ (1.38 mL, 1.64 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
24	8.9 ± 0.3 (0.65:3.20:1)	11.6 ± 0.3 (0.45:3.19:1)	17.7± 0.6 (0.27:2.67:1)
48	12.6 ± 0.9 (0.46:3.03:1)	21.8 ± 0.3 (0.29:3.19:1)	43.2 ± 1.2 (0.14:2.81:1)
72	17.2 ± 0.2 (0.37:3.20:1)	30.6 ± 2.1 (0.22:3.25:1)	49.3 ± 1.2 (0.14:2.76:1)

Table 17. Calibrated combined GC yields and site-selectivity (α:β) of $Cl_2C_6H_3OAc$ regioisomers. Conditions: 1,2-Dichlorobenzene (1.26 mL, 1.65 g, 11.2 mmol, 10.0 equiv), AcOH (0.90 mL), Ac_2O (0.10 mL), $PhI(OAc)_2$ (361 mg, 1.12 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.0 mg, 22.4 μmol, 2.0 mol %), ligand (11.2 μmol, 1.0 mol %), 100 °C. The reported error is the standard deviation of at least two replicate trials.

	Catalyst system		
Reaction Time [h]	$Pd(OAc)_2$	$Pd(OAc)_2$/bpy 2:1	$Pd(OAc)_2$/**2a** 2:1
24	10.5 ± 1.1 (0.65:1)	23.7 ± 0.0 (0.38:1)	32.9 ± 0.6 (0.40:1)
48	25.9 ± 0.7 (0.61:1)	42.5 ± 3.1 (0.38:1)	51.7 ± 0.1 (0.39:1)
72	46.5 ± 0.2 (0.62:1)	76.0 ± 1.0 (0.37:1)	70.5 ± 0.6 (0.36:1)