Electronic Supplementary Information

Pyramidalization/Twisting of the Amide Functionality via Remote Steric Congestion Triggered by Metal–Coordination

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1. General Methods

1-1. Reactions and purifications

Unless otherwise noted, all reactions were carried out in an oven-dried flask fitted with a septum under an argon atmosphere with magnetically stirred chips. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Thin layer chromatography (TLC) was performed on Merck TLC plates (0.25 mm) with silica gel 60 F254 and visualized by UV quenching and staining with $KMnO_4$. Flash column chromatography was performed using SiO_2 [Kanto Chemical 60N (neutral, spherical, 50–60 μm)] or CombiFlash systems with a Redisep column..

1-2. Characterizations

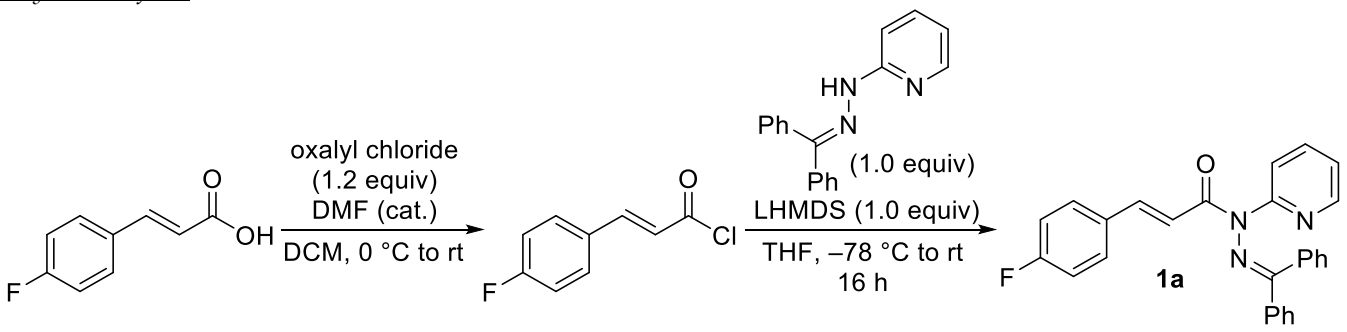
Infrared (IR) spectra were recorded on a HORIBA FT210 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a Bruker AVANCE III HD400, Bruker AVANCE III 500, or a JEOL ECZ-600R. Chemical shifts (δ) are given in ppm relative to residual solvent peaks.[1] Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), q (quartet), m (multiplet), br (broad). For ^{19}F NMR, chemical shifts were reported in the scale relative to $PhCF_3$ (δ –62.7680 ppm in $CDCl_3$) as an external reference. High-resolution mass spectra were measured on a Thermo Fisher Scientific LTQ Orbitrap XL.

1-3. Solvents and reagents

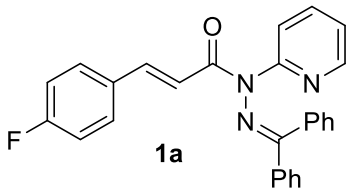
THF, toluene, hexane, and CH_3CN were purified by passing through a solvent purification system (Glass Contour). All other materials were used as supplied by commercial vendors or prepared by the method described in the corresponding references.

2. General Procedures

*2-1. Synthesis of **1a**.*



(*E*)-*N*'-(Diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide (1a)

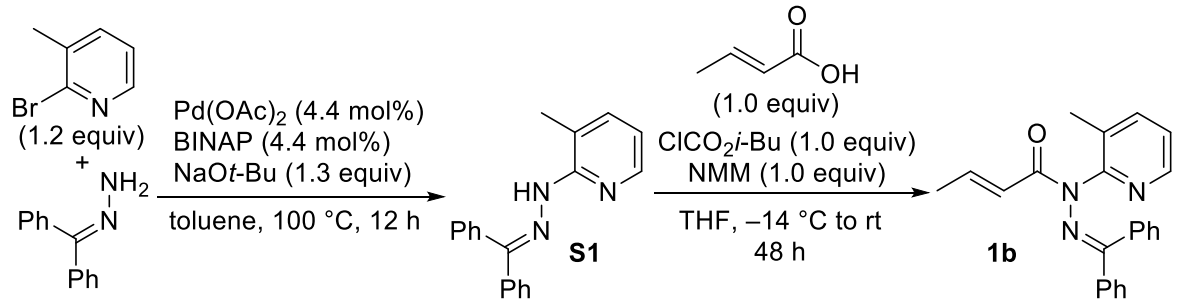


To a solution of *p*-fluorocinnamic acid (166 mg, 1.0 mmol, 1.0 equiv) in 2 mL of dichloromethane at 0 °C, under argon, was added oxalyl chloride (152 mg, 1.2 mmol, 1.2 equiv) followed by one drop of DMF. After 10 minutes the solution was allowed to warm to room temperature and stirred for 2 h. The solvent and excess oxalyl chloride was removed *in vacuo* to yield the corresponding crude acid chloride, which was used without further purification.

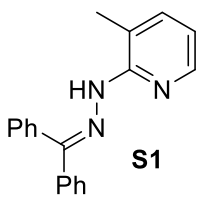
To a stirred solution of LHMDS (1.0 M in THF, 1.0 mmol) at –78 °C was slowly added 2-(2-(diphenylmethylene)hydrazinyl)pyridine[2] (273.3 mg, 1.0 mmol, 1.0 equiv) in anhydrous THF (2.0 mL). After 1 h, the crude acid chloride (1.0 mmol, 1.0 equiv) in anhydrous THF (2.5 mL) was then added dropwise and the mixture was allowed to stir for 30 minitues at –78 °C and then allowed to warm to room temperature over 4 h and stirred for 12 h. The reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic layer was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel flash column chromatography (hexane/EtOAc, 100:0 –4:1 –2:1) gave title compound **1a** (307 mg, 73% yield).

Yellow solid, m.p.: 127–129 °C; ^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.29–8.27 (m, 1H), 7.67–7.65 (m, 2H), 7.63–7.59 (m, 3H), 7.55–7.48 (m, 2H), 7.46–7.42 (m, 2H), 7.28–7.20 (m, 4H), 7.15–7.11 (m, 2H), 7.07–7.01 (m, 4H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ 170.5, 166.2, 164.6 (d, J = 248.3 Hz), 155.4, 149.1, 141.8, 138.4, 138.0, 136.7, 132.7 (d, J = 3.2 Hz), 132.1, 131.2 (d, J = 8.8 Hz), 129.9, 129.7, 129.4, 129.1, 129.0, 122.8, 122.3, 120.6 (d, J = 2.5 Hz), 116.8 (d, J = 22.1 Hz); ^{19}F NMR (376 MHz, 343 K, $CDCl_3$): –112.4 (m); IR (KBr): $\tilde{\nu}$ = 3049, 1662, 1615, 1599, 1508, 1357, 1230, 994, 828, 699 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{27}H_{21}ON_3F$ $[M+H]^+$: 422.1663, found: 422.1661.

*2-2. Synthesis of **1b**.*



2-(2-(Diphenylmethylene)hydrazinyl)-3-methylpyridine (S1)



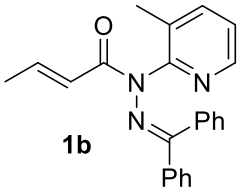
Following the procedure of J. B. Arterburn, et al.,[2] a flask was charged with benzophenone hydrazone (762 mg, 3.9 mmol, 1.0 equiv), $Pd(OAc)_2$ (38.3 mg, 0.17 mmol, 4.4 mol%), racemic 2,2′-bis(diphenylphosphanyl)-1,1′-binaphtyl (BINAP) (106.4 mg, 0.17 mmol, 4.4 mol%), and NaO*t*-Bu (653 mg, 6.8 mmol, 1.75 equiv) in a glove box. The flask was purged with argon, then anhydrous toluene (10 mL) and 2-bromo-3-methylpyridine (828 mg, 4.8 mmol, 1.24 equiv) were added. The reaction mixture was heated at 100 °C and stirred for 12 h. The reaction mixture was cooled, diluted with EtOAc, washed with water and concentrated under vacuum. The residue was purified by flash column chromatography (hexane/EtOAc, 100:0 – 6:1 – 4:1) to yield title compound **S1** (706 mg, 63% yield).

Brown solid, m.p.: 79–80 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.11 (dd, J = 5.0, 1.7 Hz, 1H), 7.94 (s, 1H), 7.67–7.56 (m, 4H), 7.55–7.48 (m, 1H), 7.39–7.28 (m, 6H), 6.72 (dd, J = 7.2, 4.9 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 153.5, 147.4, 145.9, 139.4, 138.0, 132.9, 129.9, 129.5, 129.0, 128.5, 128.2, 127.0, 117.9, 116.1, 18.4; IR (KBr): $\tilde{\nu}$ = 3314, 3042,

2965, 1586, 1556, 1488, 1452, 1292, 1116, 785, 690 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495, found: 288.1497.

(*E*)-*N*'-(Diphenylmethylene)-*N*-(3-methylpyridin-2-yl)but-2-enehydrazide (1b)

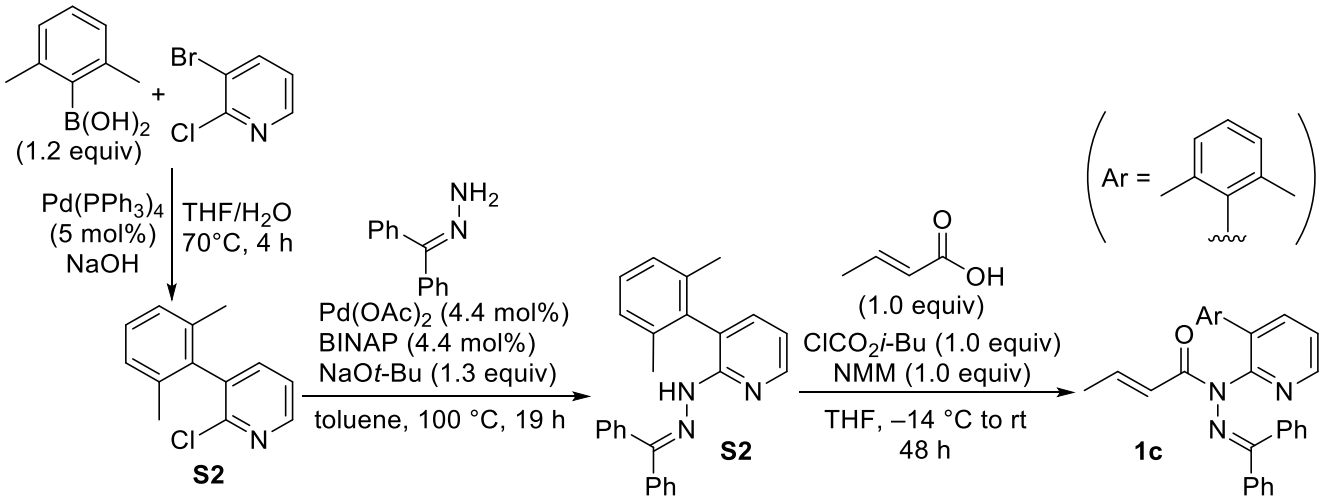
A solution of crotonic acid (86.1 mg, 1.0 mmol, 1.0 equiv) and *N*-methylmorpholine (202 mg, 2.0 mmol, 2.0 equiv) in anhydrous THF (7.0 mL) was cooled to –14 °C and treated dropwise with isobutyl chloroformate (137 mg, 1.0 mmol, 1.0 equiv). After 1 h, a solution of 2-(2-(diphenylmethylene)hydrazinyl)-3-methylpyridine **S1** (287 mg, 1.0 mmol, 1.0 equiv) in anhydrous THF (7.0 mL) was added dropwise. The reaction mixture was warmed to room temperature over 2 h and stirred for 46 h. The resulting mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 100:0 – 4:1 – 2:1) to yield title compound **1b** (89.8 mg, 25% yield).



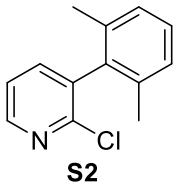
*Note that the NMR spectra of title compound **1a** was recorded at elevated temperature (50 °C), as peaks were broadened at room temperature.*

Brown solid, m.p.: 154–156 °C; ^{1}H NMR (500 MHz, 323 K, CD_3CN): δ 8.14 (br d, *J* = *ca*. 4 Hz, 1H), 7.57–7.51 (m, 2H), 7.48–7.42 (m, 1H), 7.39–7.36 (m, 2H), 7.24–7.09 (m, 4H), 7.04–6.80 (m, 5H), 1.94 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, 323 K, CD_3CN): δ 168.1, 161.9, 155.2, 147.3, 143.9, 139.7, 139.6, 137.4, 133.3, 131.3, 129.4, 129.3, 129.2, 128.9, 128.8, 124.2, 124.1, 18.5, 18.3; IR (KBr): $\tilde{\nu}$ = 2962, 2910, 1676, 1638, 1445, 1343, 1204, 967, 784, 698 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{23}H_{22}ON_3$ $[M+H]^+$: 356.1757, found: 356.1760.

*2-3. Synthesis of **1c**.*

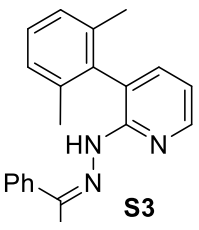


2-Chloro-3-(2,6-dimethylphenyl)pyridine (S2)



Following the procedure of P. Langer et al.,[3] the flask charged with 3-bromo-2-chloropyridine (1.89 g, 9.8 mmol, 1.0 equiv), 2,6-dimethylphenyl boronic acid (1.77 g, 11.8 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (568 mg, 0.49 mmol, 5.0 mol%), and NaOH (1.18 g, 29.6 mmol, 3.0 equiv) were evacuated and back filled with argon. To the mixture, THF (132 mL) and water (19 mL) were added, and then the reaction flask was evacuated and back filed several times with argon. The reaction was heated at 70 °C and stirred for 4 h. The solvent was evaporated *in vacuo*. The residue was extracted with EtOAc and water. The organic layer was dried over Na_2SO_4 and filtered and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc, 100:0 – 19:1) to yield title compound **S2** (1.79 g, 84% yield).

White solid, m.p.: 94–96 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.36 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.26 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.20–7.13 (m, 1H), 7.11–7.03 (m, 2H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 151.0, 148.8, 139.8, 136.9, 136.12, 136.09, 128.4, 127.6, 122.8, 20.4; IR (KBr): $\tilde{\nu}$ = 3047, 2911, 1554, 1446, 1386, 1085, 998, 778, 725 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{13}H_{13}NCl$ $[M+H]^+$: 218.0731, found: 218.0730.



2-(2-(Diphenylmethylene)hydrazinyl)-3-(2,6-dimethylphenyl)pyridine (S3)

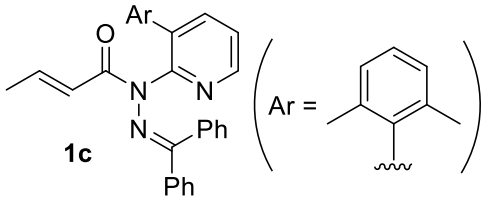
Following the procedure of J. B. Arterburn, et al.,[2] a flask was charged with benzophenone

hydrazone (295 mg, 1.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (14.9 mg, 0.066 mmol, 4.4 mol%), racemic 2,2′-bis(diphenylphosphanyl)-1,1′-binaphtyl (BINAP) (41.2 mg, 0.066 mmol, 4.4 mol%), and NaO*t*-Bu (253 mg, 2.6 mmol, 1.75 equiv) in a glove box. The flask was purged with argon, then anhydrous toluene (3.8 mL), and 2-chloro-3-(2,6-dimethylphenyl)pyridine **S2** (410 mg, 1.9 mmol, 1.25 equiv) were added. The reaction mixture was heated at 100 °C and stirred for 19 h. The reaction mixture was cooled, diluted with EtOAc, washed with water and concentrated under vacuum. The residue was purified by flash column chromatography (hexane/EtOAc, 100:0 – 6:1–4:1) to yield title compound **S3** (461 mg, 81% yield).

Brown solid, m.p.: 119–121 °C; ^{1}H NMR (400 MHz, 298 K, CD_3CN): δ 8.26 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.51 (s, 1H), 7.43–7.33 (m, 5H), 7.32–7.27 (m, 3H), 7.25 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.08 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.05–7.00 (m, 2H), 7.00–6.96 (m, 2H), 6.91 (dd, *J* = 7.3, 4.9 Hz, 1H), 1.86 (s, 6H); ^{13}C NMR (100 MHz, 298 K, CD_3CN): δ 152.5, 148.5, 148.4, 139.0, 138.8, 137.2, 135.8, 133.1, 130.5, 130.1, 129.4, 129.2, 129.1, 128.9, 128.8, 127.4, 121.5, 116.8, 20.3; IR (KBr): $\tilde{\nu}$ = 3319, 3021, 2913, 1575, 1503, 1488, 1395, 1235, 1217, 1128, 769, 705, 691 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{26}H_{24}N_3$ $[M+H]^+$: 378.1965, found: 378.1961.

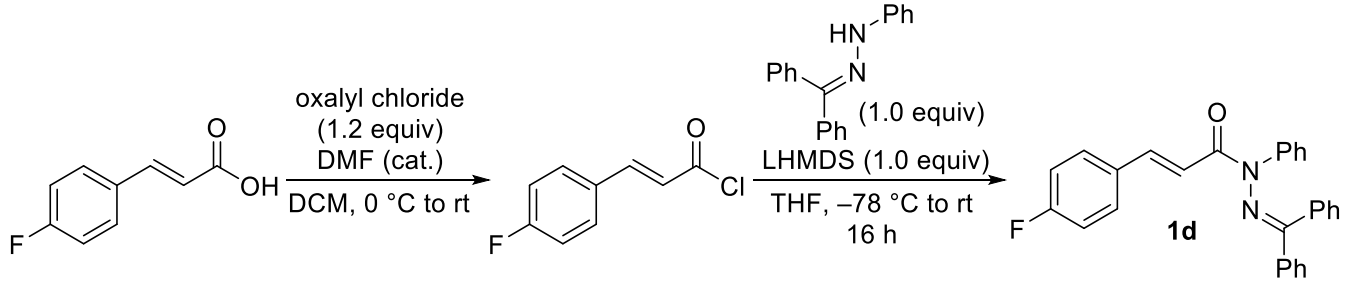
(*E*)-*N*'-(Diphenylmethylene)-*N*-[3-(2,6-dimethylphenyl)pyridin-2-yl]but-2-enehydrazide (1c)

Following the above described reaction for the preparation of amide **1b**, amide **1c** was obtained in 28% yield (72.3 mg) from 2-(2-(diphenylmethylene)hydrazinyl)-3-(2,6-dimethylphenyl)pyridine **S3** (218 mg, 0.58 mmol) after purification by flash column chromatography (hexane/EtOAc, 100:0 – 4:1 – 2:1).

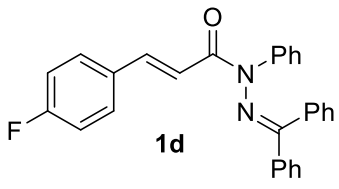


White solid, m.p.: 139–141 °C; ^{1}H NMR (400 MHz, 298 K, CD_3CN): δ 8.49 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.52–7.38 (m, 2H), 7.36–7.24 (m, 5H), 7.22–717 (m, 3H), 7.09 (br s, 2H), 6.60 (br s, 2H), 6.44 (dq, *J* = 14.1, 6.9 Hz, 1H), 5.65 (dq, *J* = 15.1, 1.8 Hz, 1H), 1.92 (s, 6H), 1.62 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, 298 K, CD_3CN): δ 169.8, 163.8, 155.4, 148.9, 142.0, 141.0, 139.0, 137.93, 137.92, 137.0, 135.4, 131.5, 129.6, 129.1, 129.0 (3C), 128.43, 128.38, 125.8, 124.5, 21.2, 17.9; ^{1}H NMR (400 MHz, 298 K, d_6-acetone): δ 8.52 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.67 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.53 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.47–7.39 (m, 1H), 7.36–7.28 (m, 4H), 7.27–7.14 (m, 4H), 7.08 (br s, 2H), 6.62 (br s, 2H), 6.40 (dq, *J* = 14.1, 6.9 Hz, 1H), 5.67 (dq, *J* = 15.0, 1.7 Hz, 1H), 1.96 (s, 6H), 1.61 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, 298 K, d_6-acetone): δ 169.0, 163.4, 155.8, 148.7, 141.6, 139.8, 139.2, 138.1, 137.7, 137.2, 135.3, 131.1, 129.5, 129.1, 129.0, 128.9, 128.7, 128.3, 128.1, 126.2, 124.2, 21.2, 17.8; IR (KBr): $\tilde{\nu}$ = 3051, 2912, 1683, 1645, 1561, 1415, 1319, 1176, 965, 771, 695 cm^{-1}; HRMS (ESI) *m*/*z* calculated for $C_{30}H_{28}ON_3$ $[M+H]^+$: 446.2227, found: 446.2222.

*2-4. Synthesis of **1d**.*



(*E*)-*N*'-(Diphenylmethylene)-3-(4-fluorophenyl)-*N*-phenylacrylohydrazide (1d)



Following the above described reaction for the preparation of amide **1a**, amide **1d** was obtained in 29% yield (122 mg) from 1-(diphenylmethylene)-2-phenylhydrazine[4] (272 mg, 1.0 mmol) after purification by flash column chromatography (hexane/EtOAc, 100:0 – 4:1).

*Note that the NMR spectra of title compound **1d** was recorded at elevated temperature (70 °C), as peaks were broadened at room temperature.*

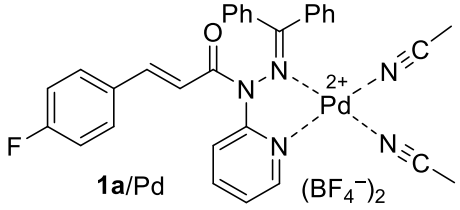
Yellow solid, m.p.: 134–136 °C; ^{1}H NMR (500 MHz, 343 K, DMSO-d_6): δ 7.79–7.50 (m, 6H), 7.47–7.44 (m, 2H), 7.39–7.25 (m, 3H), 7.22–7.17 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.07–6.77 (m, 5H); ^{13}C NMR (125 MHz, 343 K, DMSO-d_6): δ 170.2, 163.5, 162.7 (d, *J* = 248.2 Hz), 141.7, 140.2, 136.7, 134.9, 131.1 (d, *J* = 3.3 Hz), 130.8, 129.8 (d, *J* = 8.5 Hz), 128.7, 128.3, 128.14, 128.09, 127.7, 127.4, 126.0, 125.7, 118.8 (d, *J* = 2.3 Hz), 115.5 (d, *J* = 21.9 Hz); ^{19}F NMR (376 MHz, 343 K, DMSO-d_6): –110.9 (m); IR (KBr): $\tilde{\nu}$ = 3056, 3036, 1652, 1615, 1600, 1591, 1507, 1489, 1372, 1225, 1157, 1003, 991, 824, 698 cm^{-1}; HRMS (ESI)

m/*z* calculated for $C_{28}H_{22}ON_2F$ [M+H]$^+$: 421.1711 found: 421.1708.

*2-5. Preparation and characterization of metal complexes with amides **1a–c***

(*E*)-*N*'-(Diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide·*Pd* (1:1) Complex (1a/Pd)

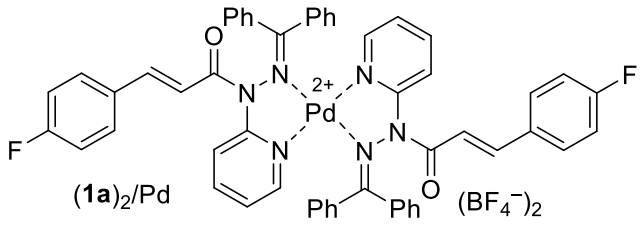
Complex **1a**/Pd was formed immediately after the addition of CD_3CN (550 μL) into an NMR tube containing (*E*)-*N*'-(diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide (**1a**) (4.9 mg, 0.0117 mmol, 1.0 equiv) and $[Pd(CH_3CN)_4](BF_4)_2$ (5.2 mg, 0.0117 mmol, 1 equiv).



^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.40 (td, J = 7.9, 1.5 Hz, 1H), 8.36 (dd, *J* = 6.1, 1.4 Hz, 1H), 7.98–7.92 (m, 2H), 7.91–7.86 (m, 1H), 7.82–7.74 (m, 2H), 7.73–7.65 (m, 5H), 7.63–7.58 (m, 1H), 7.51–7.43 (m, 2H), 7.35–7.27 (m, 2H), 7.23–7.14 (m, 2H), 6.73 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ 191.6, 165.60 (d, *J* = 251.2 Hz), 163.6, 152.7, 152.1, 149.0, 146.4, 136.7, 134.7, 134.54, 134.50, 132.4 (d, *J* = 8.9 Hz), 131.2 (d, *J* = 3.2 Hz), 130.8, 130.00, 129.97, 129.9, 126.3, 119.6, 117.2 (d, *J* = 22.3 Hz), 114.2 (d, *J* = 2.5 Hz); ^{19}F NMR (376 MHz, 298 K, CD_3CN): –109.1 (m), –151.5 (s, $^{10}BF_4$), –151.6 (s, $^{11}BF_4$); HRMS (ESI) *m*/*z* calculated for $C_{27}H_{20}ON_3F_2Pd$ [M–$(CH_3CN)_2$– BF_4^-– BF_3]$^+$: 546.0604 found: 546.0620.

(*E*)-*N*'-(Diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide·*Pd* (2:1) Complex [(1a)$_2$/Pd]

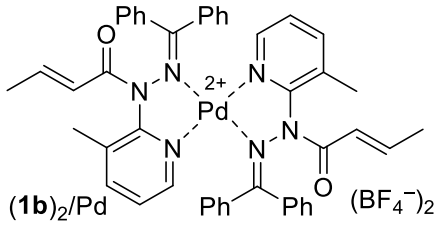
Complex (**1a**)$_2$/Pd was formed immediately after the addition of CD_3CN (550 μL) into an NMR tube containing (*E*)-*N*'-(diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide (**1a**) (4.9 mg, 0.0117 mmol, 1.0 equiv) and $[Pd(CH_3CN)_4](BF_4)_2$ (2.6 mg, 0.00585 mmol, 0.5 equiv).



^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.39 (d, *J* = 15.4 Hz, 2H), 8.16–8.06 (m, 4H), 8.01 (d, J = 7.1 Hz, 4H), 7.87 (m, 4H), 7.74–7.64 (m, 4H), 7.53 (t, *J* = 7.9 Hz, 4H), 7.39 (d, *J* = 7.8 Hz, 4H), 7.35 (m, 2H), 7.30 (t, *J* = 8.6 Hz, 4H), 7.15–7.09 (m, 6H), 6.77 (d, *J* = 15.4 Hz, 2H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ 189.6, 169.4, 166.0 (d, *J* = 252.4 Hz), 153.3, 152.1, 150.7, 145.6, 136.0, 134.8, 134.5, 133.3, 132.9 (d, *J* = 9.1 Hz), 131.5, 131.1 (d, *J* = 3.2 Hz), 129.8 (3Cx2), 127.0, 121.0, 117.4 (d, *J* = 22.3 Hz), 113.6; ^{19}F NMR (376 MHz, 343 K, CD_3CN): –108.2 (m), –151.7 (s, $^{10}BF_4$), –151.8 (s, $^{11}BF_4$); HRMS (ESI) *m*/*z* calculated for $C_{54}H_{40}O_2N_6F_2Pd$ [M–$(BF_4^-)_2$]$^{2+}$: 474.1102 found: 474.1113.

(*E*)-*N*'-(Diphenylmethylene)-*N*-(3-methylpyridin-2-yl)but-2-enehydrazide·*Pd* (2:1) Complex [(1b)$_2$/Pd]

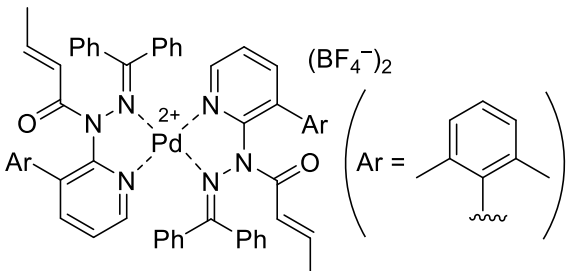
Complex (**1b**)$_2$/Pd was formed immediately after the addition of CD_3CN (550 μL) into an NMR tube containing (*E*)-*N*'-(diphenylmethylene)-*N*-(3-methylpyridin-2-yl)but-2-enehydrazide (**1b**) (4.2 mg, 0.0117 mmol, 1.0 equiv) and $[Pd(CH_3CN)_4](BF_4)_2$ (2.6 mg, 0.00585 mmol, 0.5 equiv).



^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.04–7.94 (m, 4H), 7.89–7.88 (m, 2H), 7.84–7.83 (m, 2H), 7.81–7.72 (m, 2H), 7.72–7.65 (m, 2H), 7.57–7.51 (m, 4H), 7.44–7.37 (m, 6H), 7.25–7.20 (m, 6H), 5.99 (d, *J* = 14.9 Hz, 2H), 2.15 (dd, *J* = 7.0, 1.7 Hz, 6H), 1.82 (s, 6H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ; 189.8, 169.0, 155.2, 152.1, 149.8, 147.1, 135.2, 135.0, 134.4, 133.7, 132.4, 131.4, 129.8, 129.7, 129.6, 127.3, 119.3, 19.0, 18.4; HRMS (ESI) *m*/*z* calculated for $C_{46}H_{42}O_2N_6Pd$ [M–$(BF_4^-)_2$]$^{2+}$: 408.1197 found: 408.1206.

(*E*)-*N*'-(Diphenylmethylene)-*N*-[3-(2,6-dimethylphenyl)pyridin-2-yl]but-2-enehydrazide·*Pd* (2:1) Complex [(1c)$_2$/Pd]

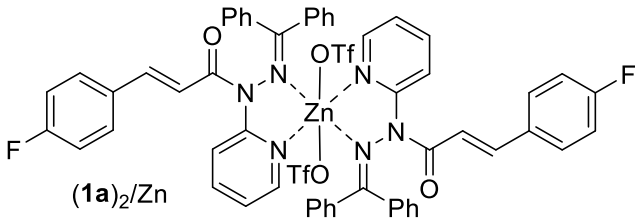
Complex (**1c**)$_2$/Pd was formed immediately after the addition of CD_3CN (550 μL) into an NMR tube containing (*E*)-*N*'-(diphenylmethylene)-*N*-[3-(2,6-dimethylphenyl)pyridin-2-yl]but-2-enehydrazide (**1c**) (5.2 mg, 0.0117 mmol, 1.0 equiv) and $[Pd(CH_3CN)_4](BF_4)_2$ (2.6 mg, 0.00585 mmol, 0.5 equiv).



^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.88 (br s, 2H), 7.98 (dd, *J* = 5.7, 1.5 Hz, 2H), 7.88–7.74 (m, 6H), 7.51–7.41 (m, 6H), 7.39–7.27 (m, 8H), 7.28–7.23 (m, 4H), 7.22–7.15 (m, 4H), 6.59 (d, *J* = 7.0 Hz, 2H), 6.36 (d, *J*

= 15.0 Hz, 2H), 2.16 (dd, *J* = 7.0, 1.6 Hz, 6H), 2.14 (s, 6H), 0.79 (s, 6H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ 187.9, 171.0, 156.6, 153.2, 151.5, 147.8, 137.8, 137.1, 136.6, 136.4, 134.9, 134.5, 134.1 (br), 133.8, 133.5, 132.7, 130.3 (br), 130.2, 130.05, 130.02, 129.0, 128.5, 127.0, 119.8, 21.3, 20.3, 19.3; HRMS (ESI) *m*/*z* calculated for $C_{60}H_{54}O_2N_6Pd$ $[M–(BF_4^-)_2]^{2+}$: 498.1666 found: 498.1670.

(*E*)-*N*'-(Diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide·*Zn* (2:1) Complex [(1a)$_2$/Zn]

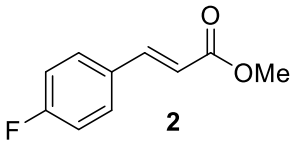


Complex (**1a**)$_2$/Zn was formed immediately after the addition of CD_3CN (550 μL) into an NMR tube containing (*E*)-*N*'-(diphenylmethylene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide (**1a**) (4.9 mg, 0.0117 mmol, 1.0 equiv) and $Zn(OTf)_2$ (2.1 mg, 0.00585 mmol, 0.5 equiv).

^{1}H NMR (500 MHz, 298 K, CD_3CN): δ 8.24 (br s, 2H), 7.99 (s, 2H), 7.62–7.35 (m, 22H), 7.29 (t, *J* = 7.7 Hz, 4H), 7.11 (t, *J* = 8.7 Hz, 4H), 7.09–6.94 (m, 6H); ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ 181.1, 166.4, 165.2 (d, *J* = 248.8 Hz), 154.1, 148.2, 146.5, 142.6, 136.6, 135.4, 134.0, 132.0 (d, *J* = 8.8 Hz), 131.8, 131.6 (d, *J* = 3.8 Hz), 131.0, 129.6, 129.4, 129.3, 123.8, 121.9 (d, *J* = 318.8 Hz), 121.1, 117.3, 117.0 (d, *J* = 22.5 Hz); ^{19}F NMR (376 MHz, 343 K, CD_3CN):–78.3 (s), –110.2 (br s); HRMS (ESI) *m*/*z* calculated for $C_{55}H_{40}O_5N_6F_5SZn$ $[M–(OTf^-)]^+$: 1055.1987 found: 1055.1993.

*2-6. Synthesis of ester **2***

Methyl (*E*)-3-(4-fluorophenyl)acrylate (2)



*Note that ester **2** is known compound.*[5]

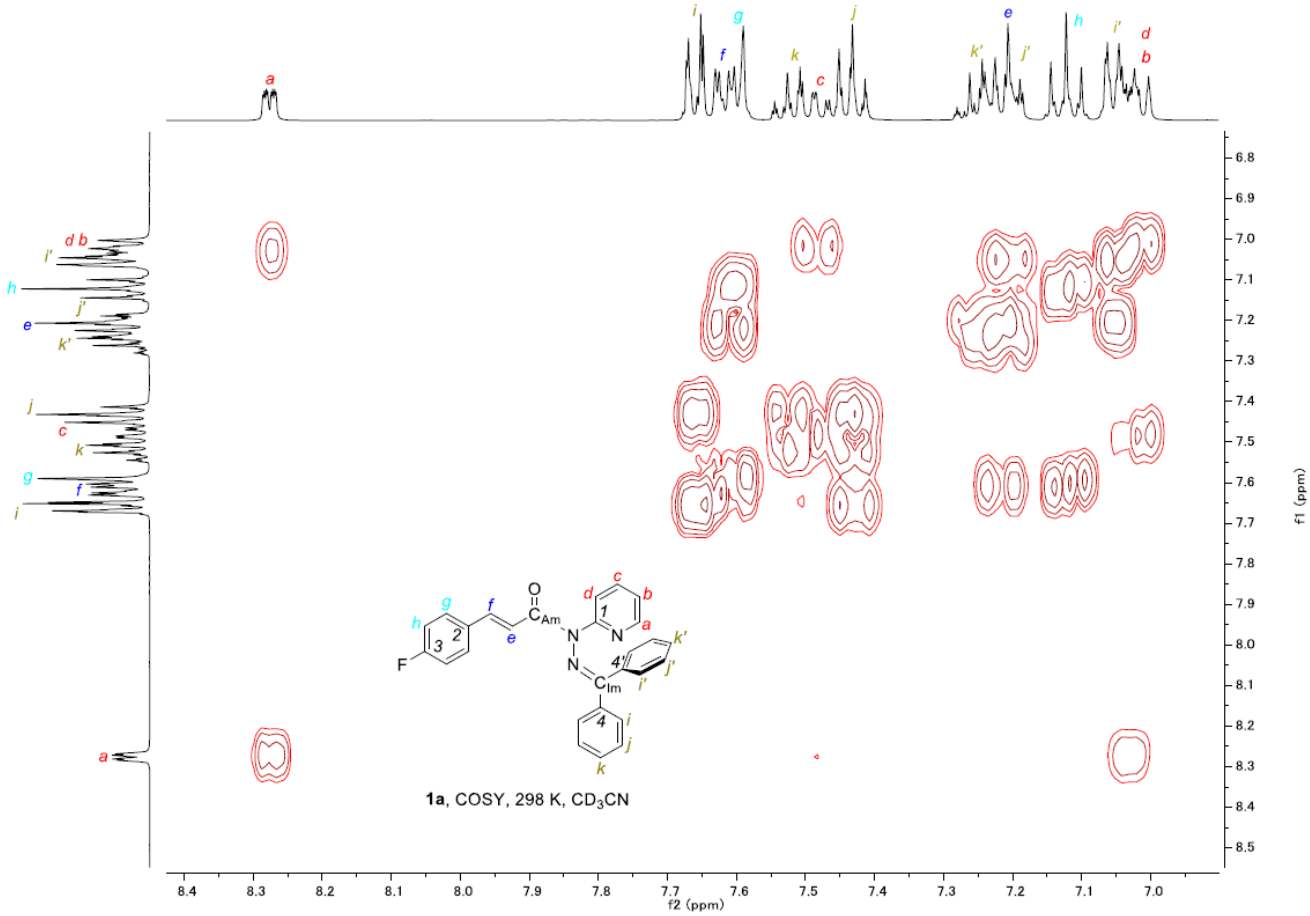
To a mixture of (*E*)-*N*'-((*E*)-benzylidene)-3-(4-fluorophenyl)-*N*-(pyridin-2-yl)acrylohydrazide (**1a**) (42.1 mg, 0.10 mmol 1.0 equiv) and $Zn(OTf)_2$ (1.8 mg, 0.005 mmol, 5 mol%) was added MeOH (9.4 mL) at room temperature. After stirred for 24 h, the reaction mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography (hexane/EtOAc, 19:1) gave title compound **2** (16.5 mg, 92% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.57–7.42 (m, 2H), 7.16–6.96 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ .167.5, 164.05 (d, *J* = 251.5 Hz), 143.7, 130.8 (d, J = 3.3 Hz), 130.08 (d, *J* = 8.5 Hz), 117.69 (d, *J* = 2.4 Hz), 116.20 (d, *J* = 22.0 Hz), 51.9; ^{19}F NMR (376 MHz, 298 K, $CDCl_3$): –109.6 (m).

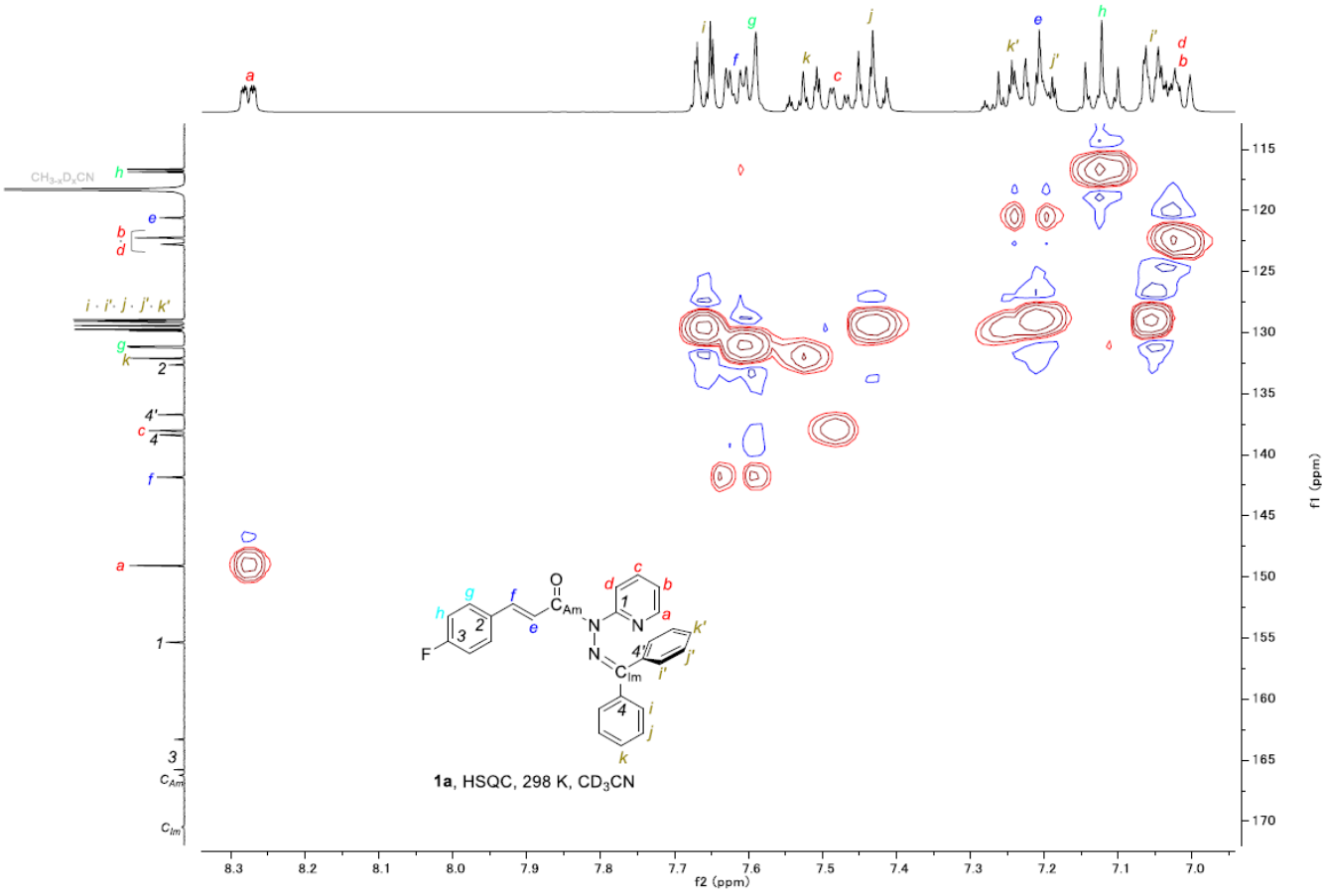
3. NMR Analyses of Amide–Metal Complexes

*3-1. **1a**–Pd Complexes*

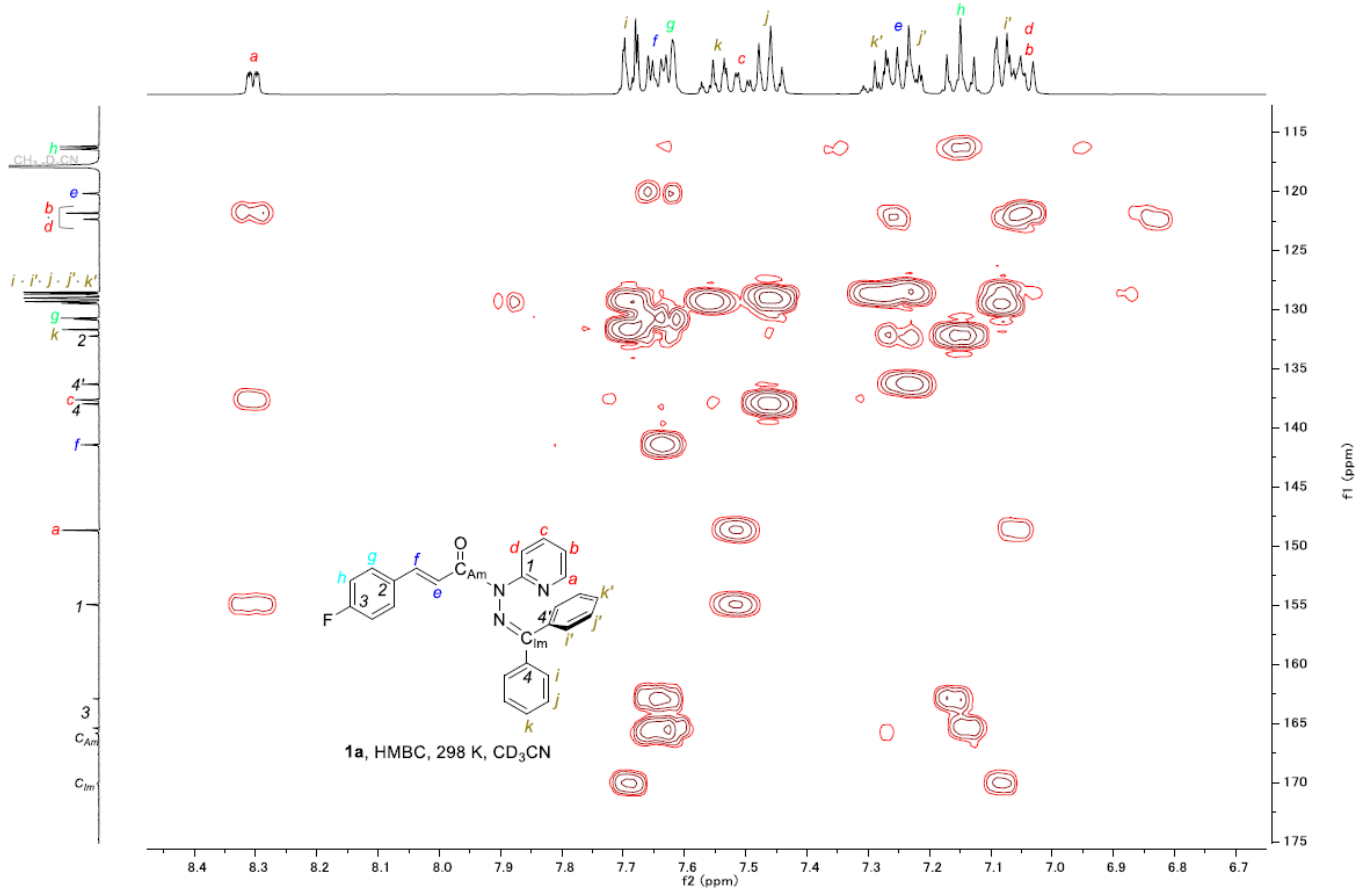
*3-1-1. Detailed NMR of **1a** for peak assignments*

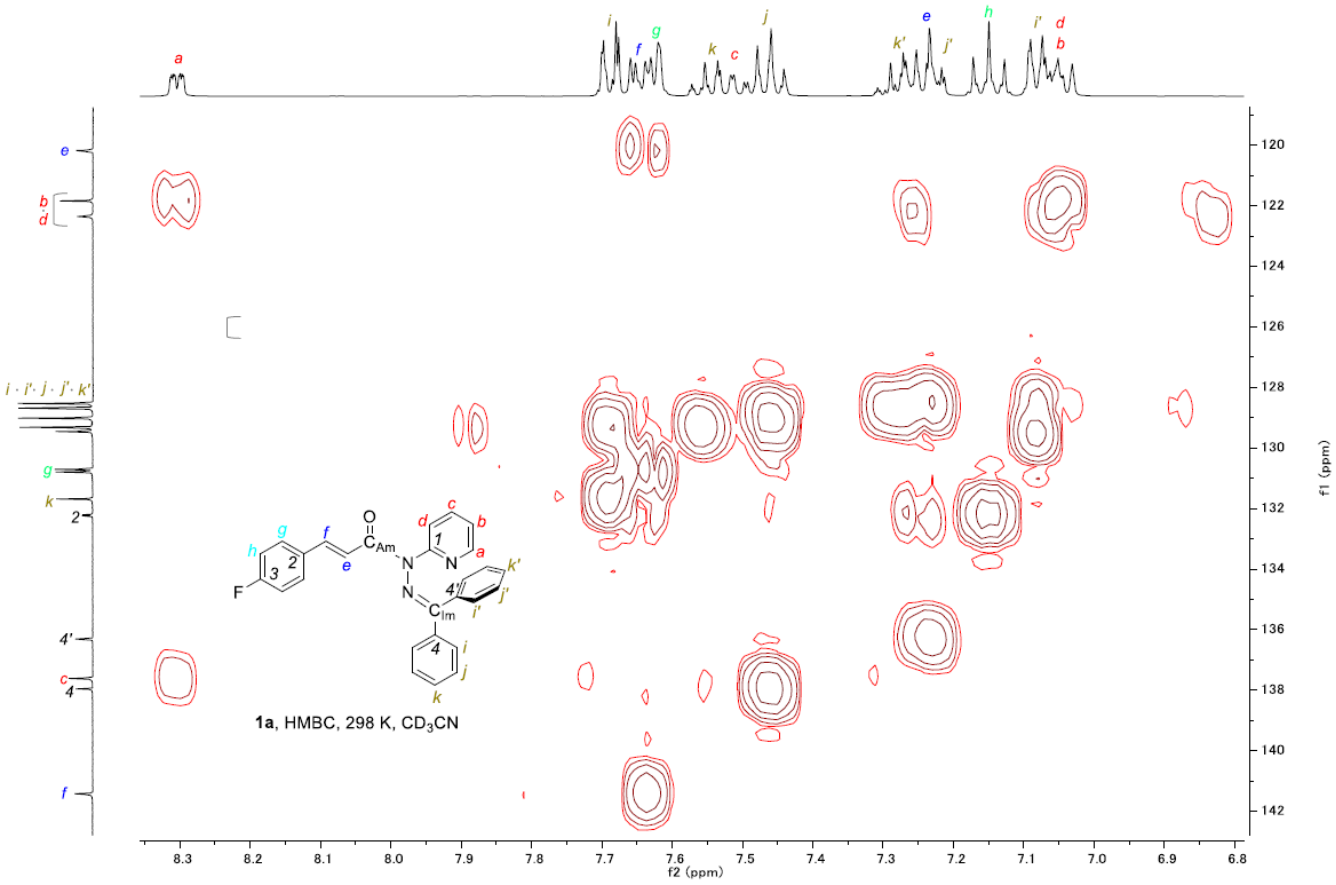


1a, COSY, 298 K, CD_3CN

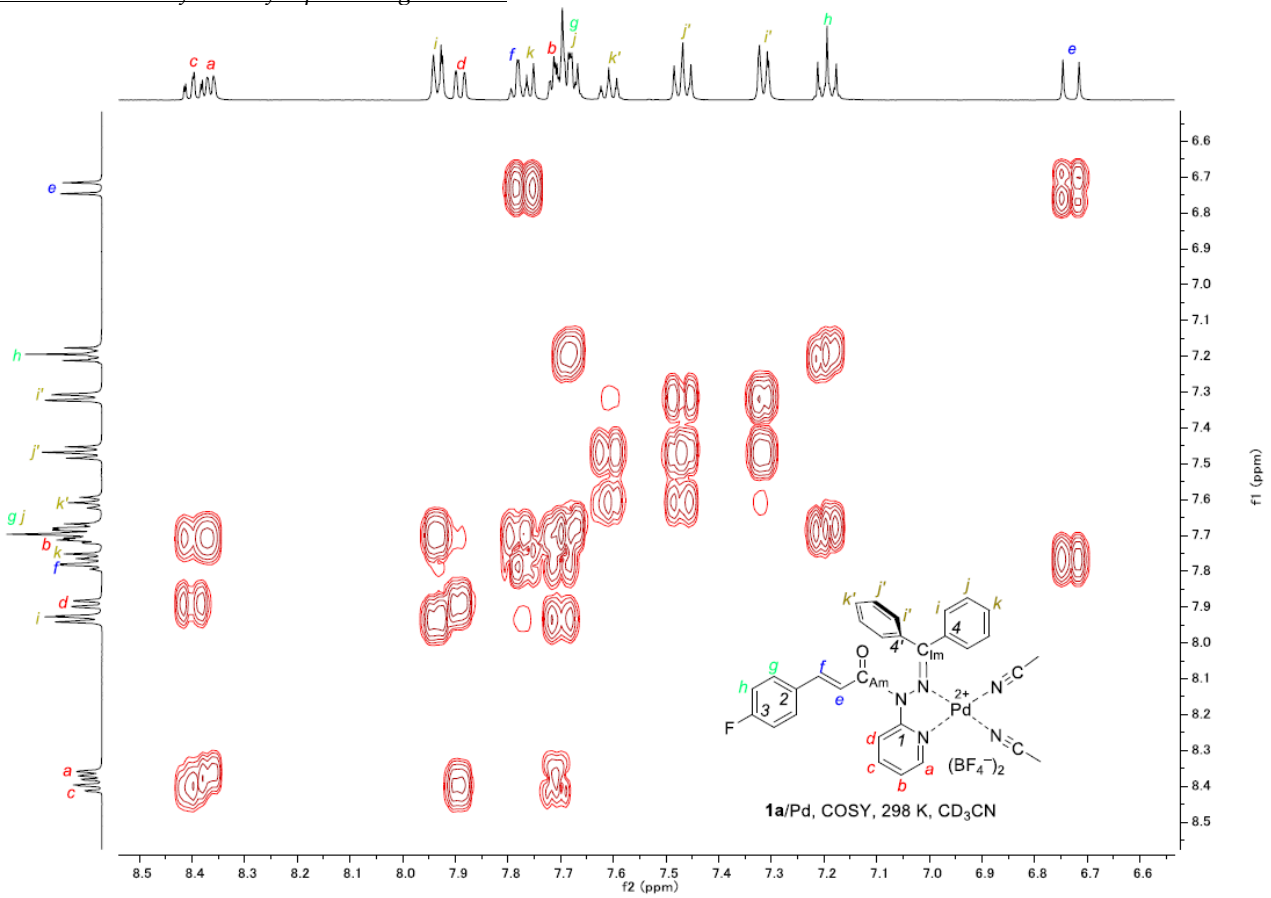


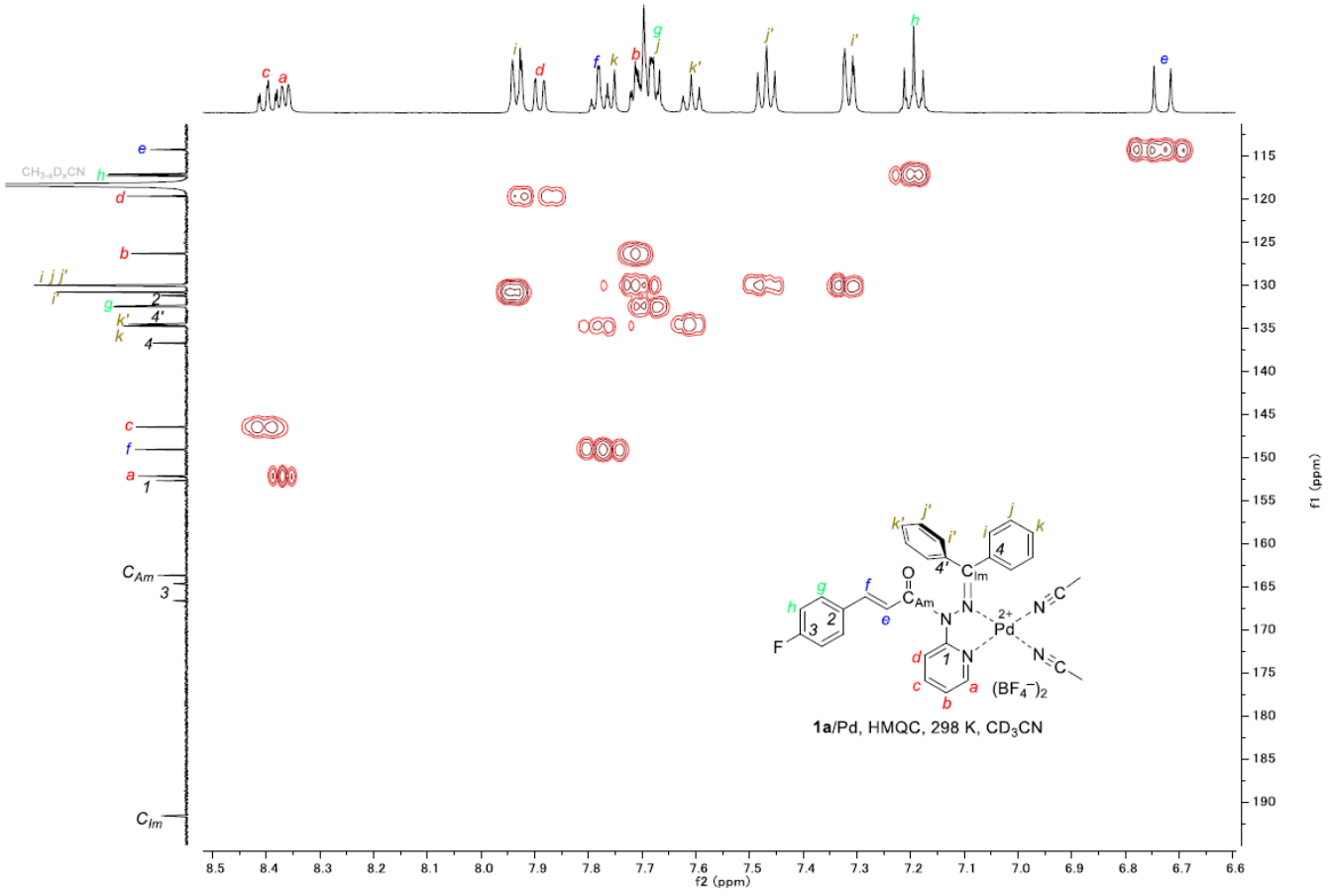
1a, HSQC, 298 K, CD_3CN

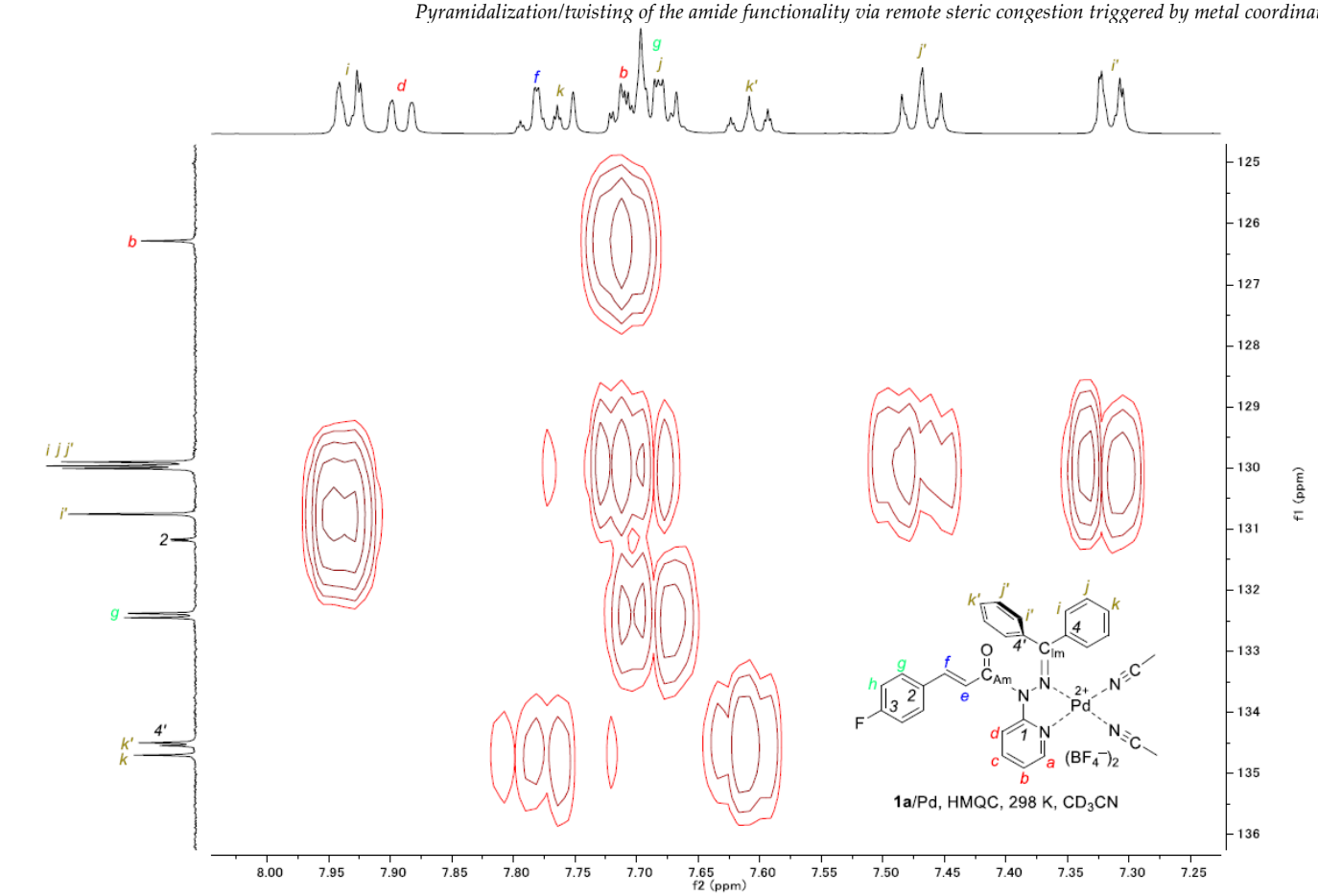

f2 (ppm)
f1 (ppm)
1a, HMBC, 298 K, CD3CN

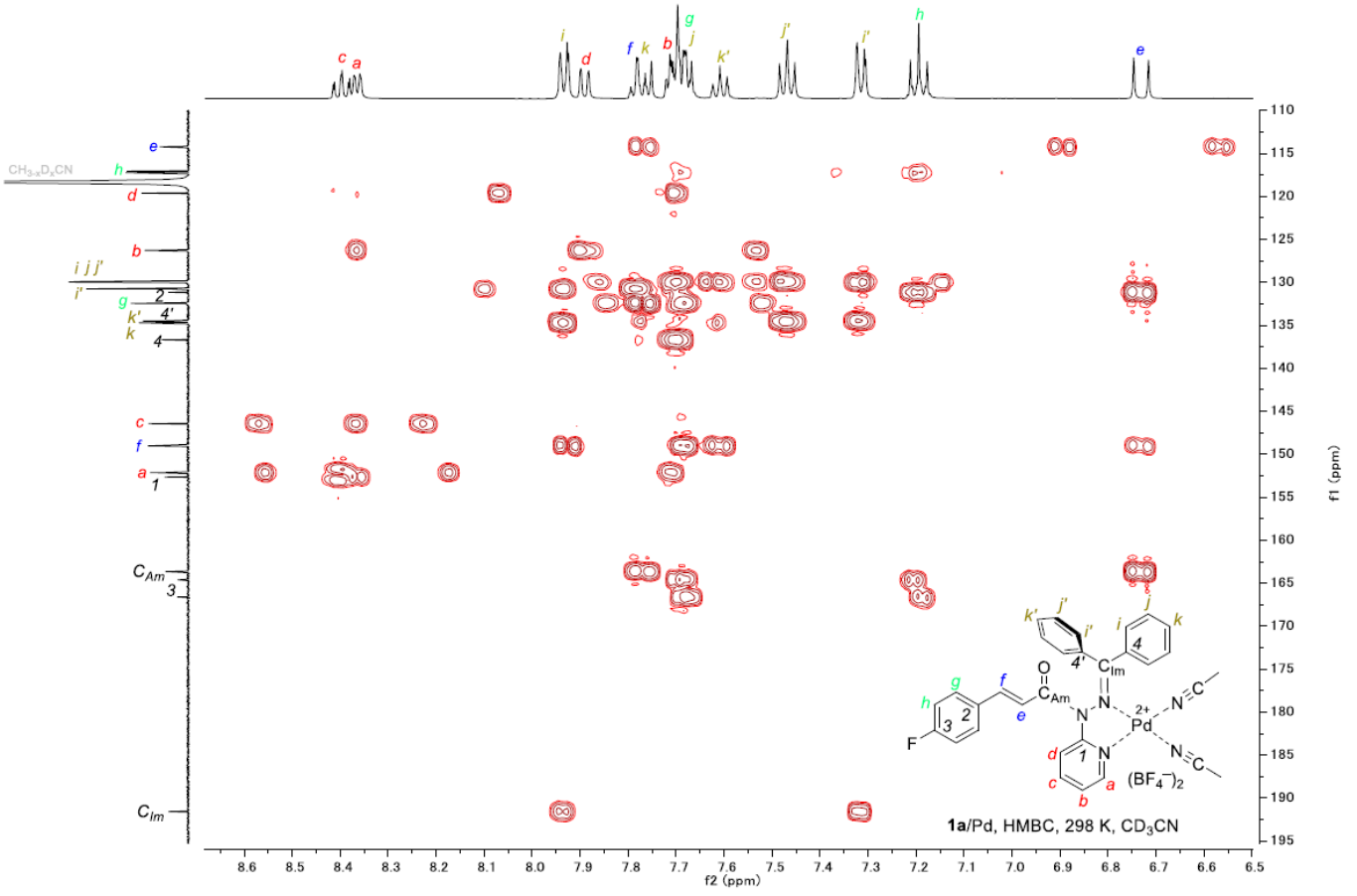

f2 (ppm)
f1 (ppm)
1a, HMBC, 298 K, CD3CN

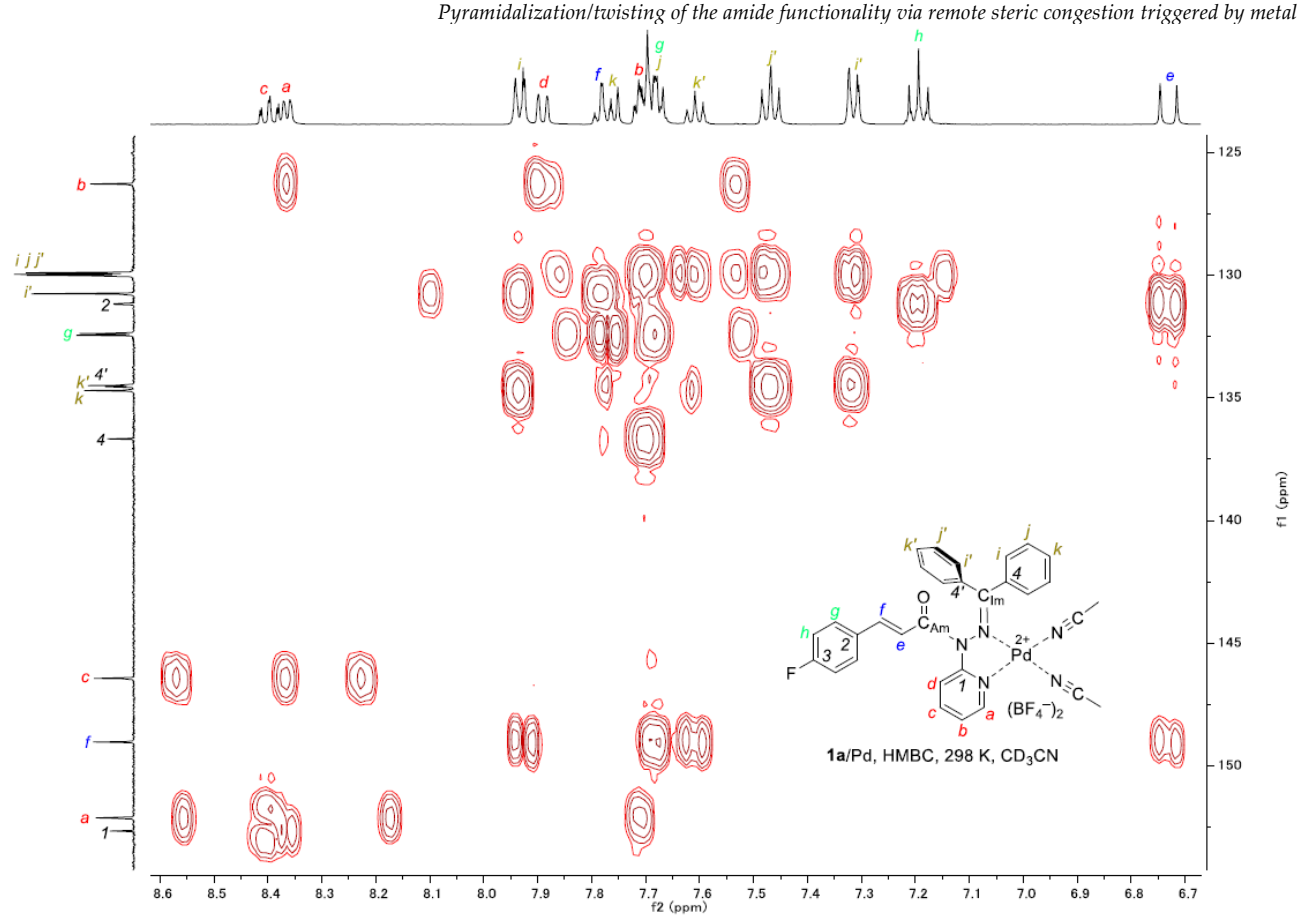
*3-1-2. Detailed NMR of **1a**/Pd for peak assignments*

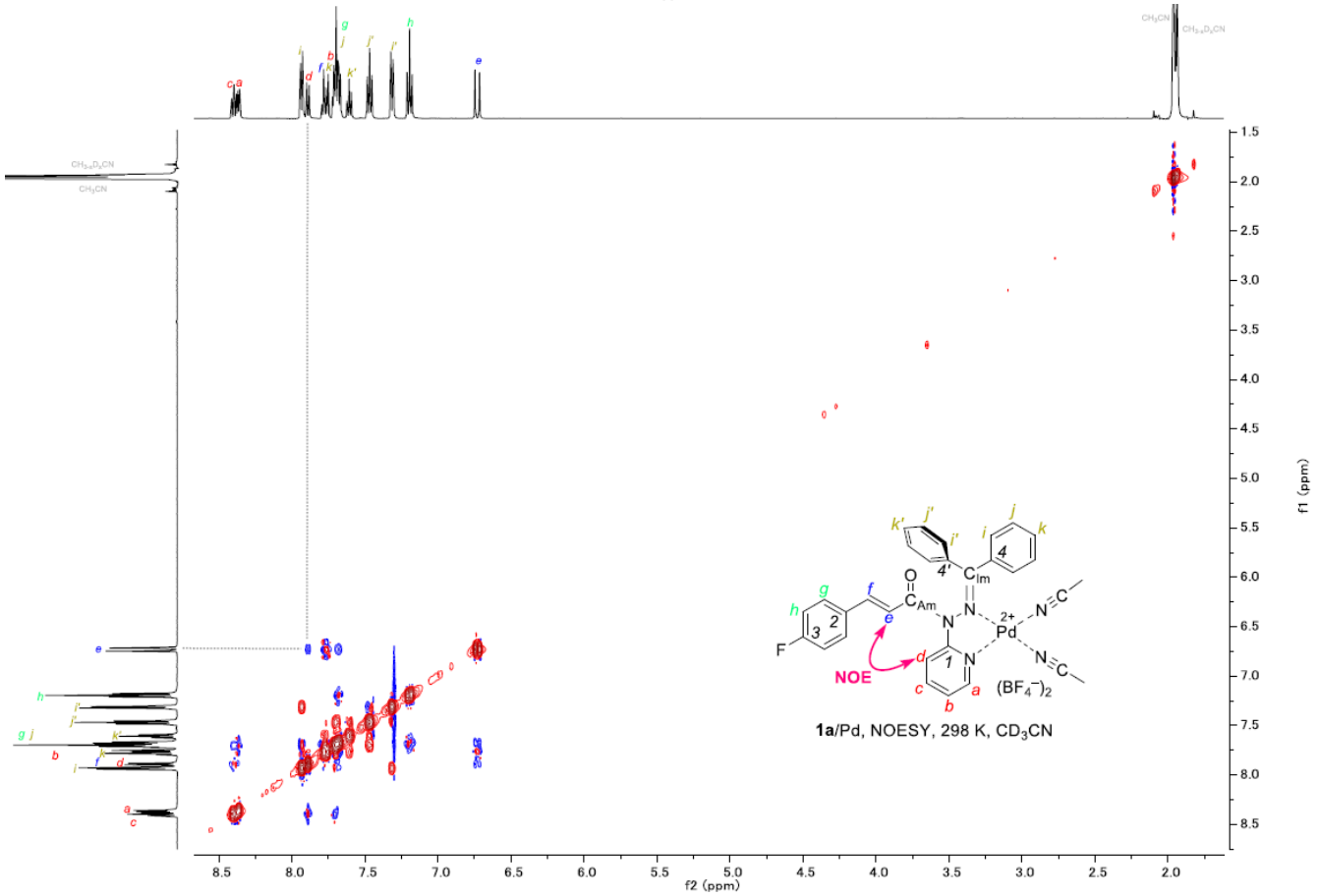




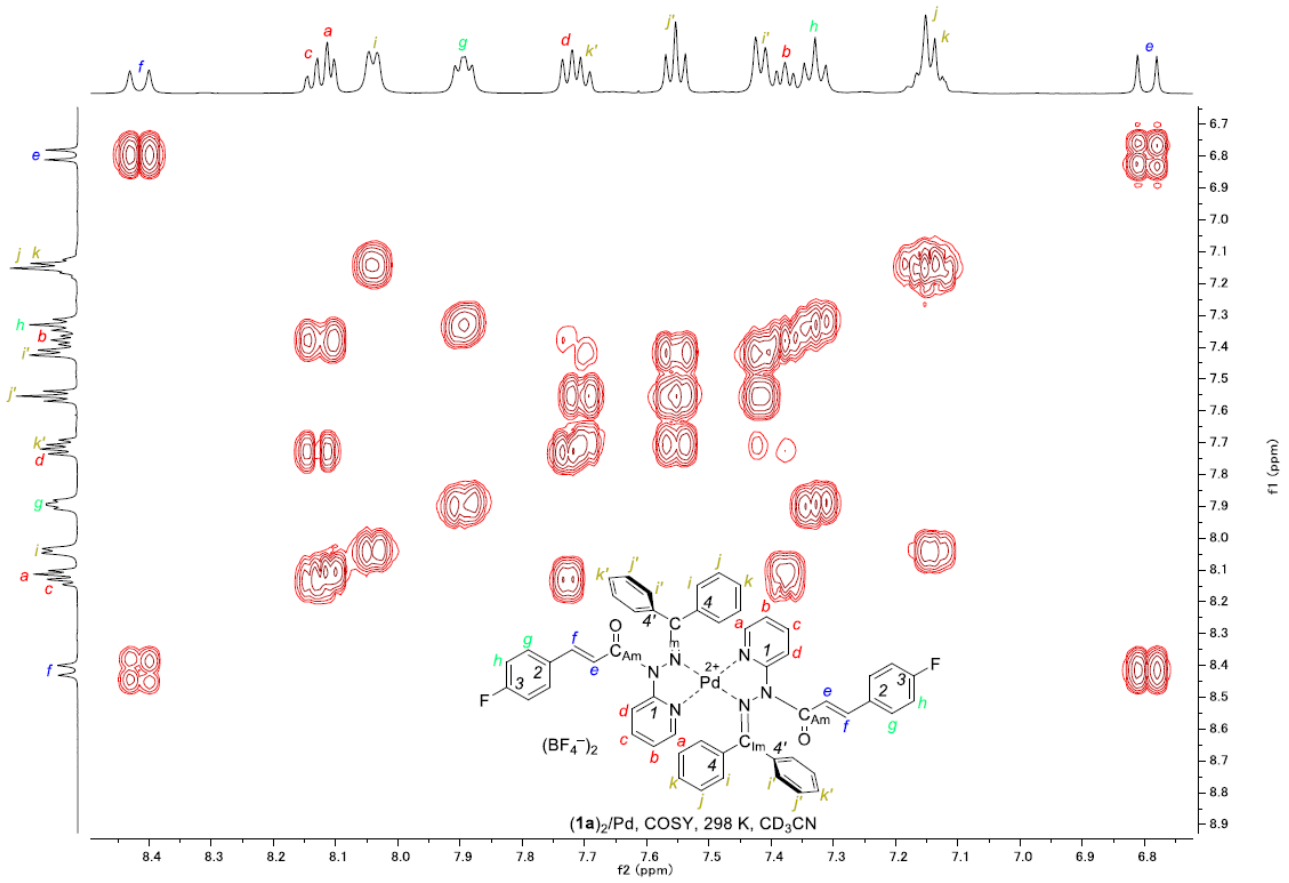

f2 (ppm)
f1 (ppm)
1a/Pd, HMQC, 298 K, CD3CN

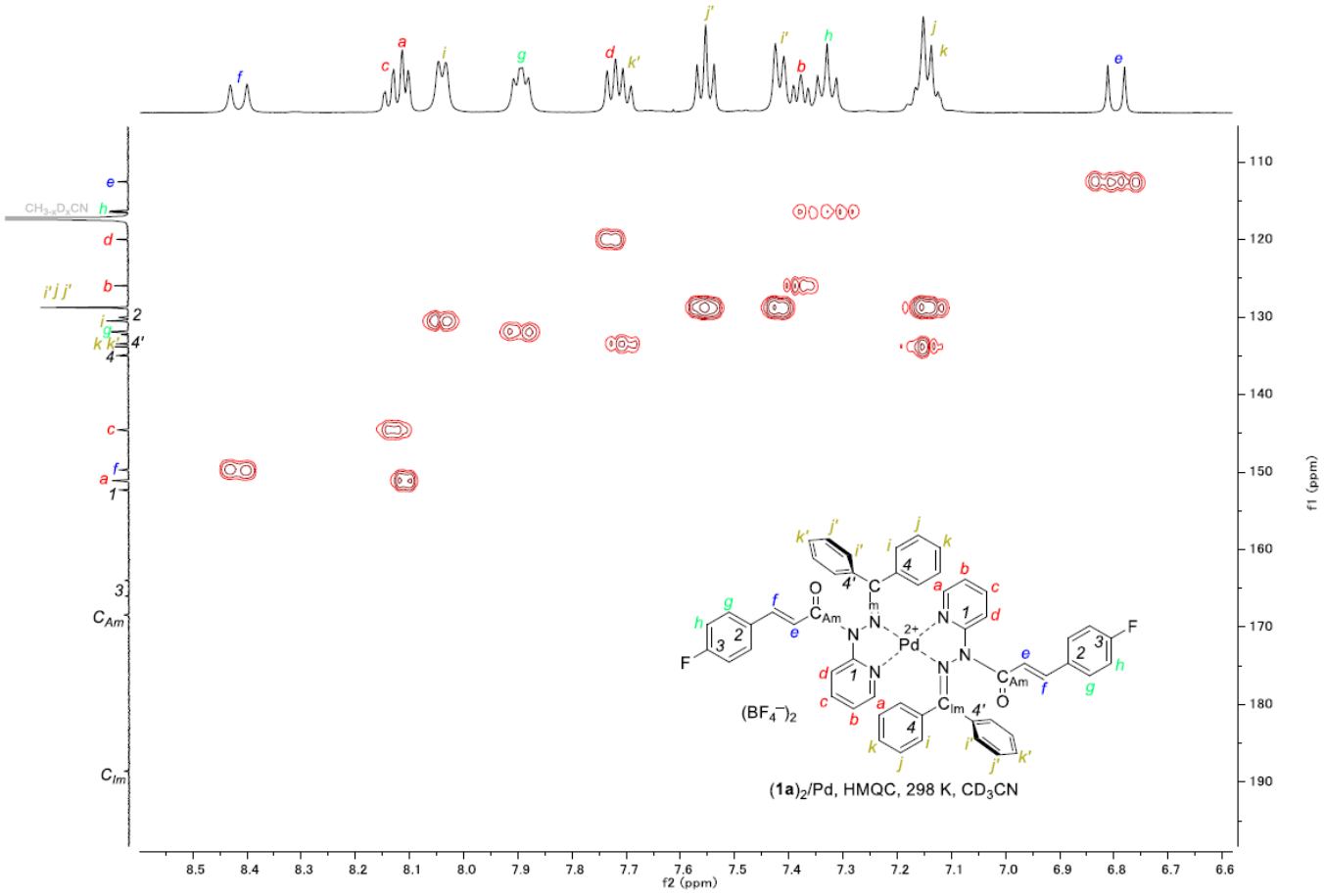

f2 (ppm)
f1 (ppm)
1a/Pd, HMBC, 298 K, CD3CN

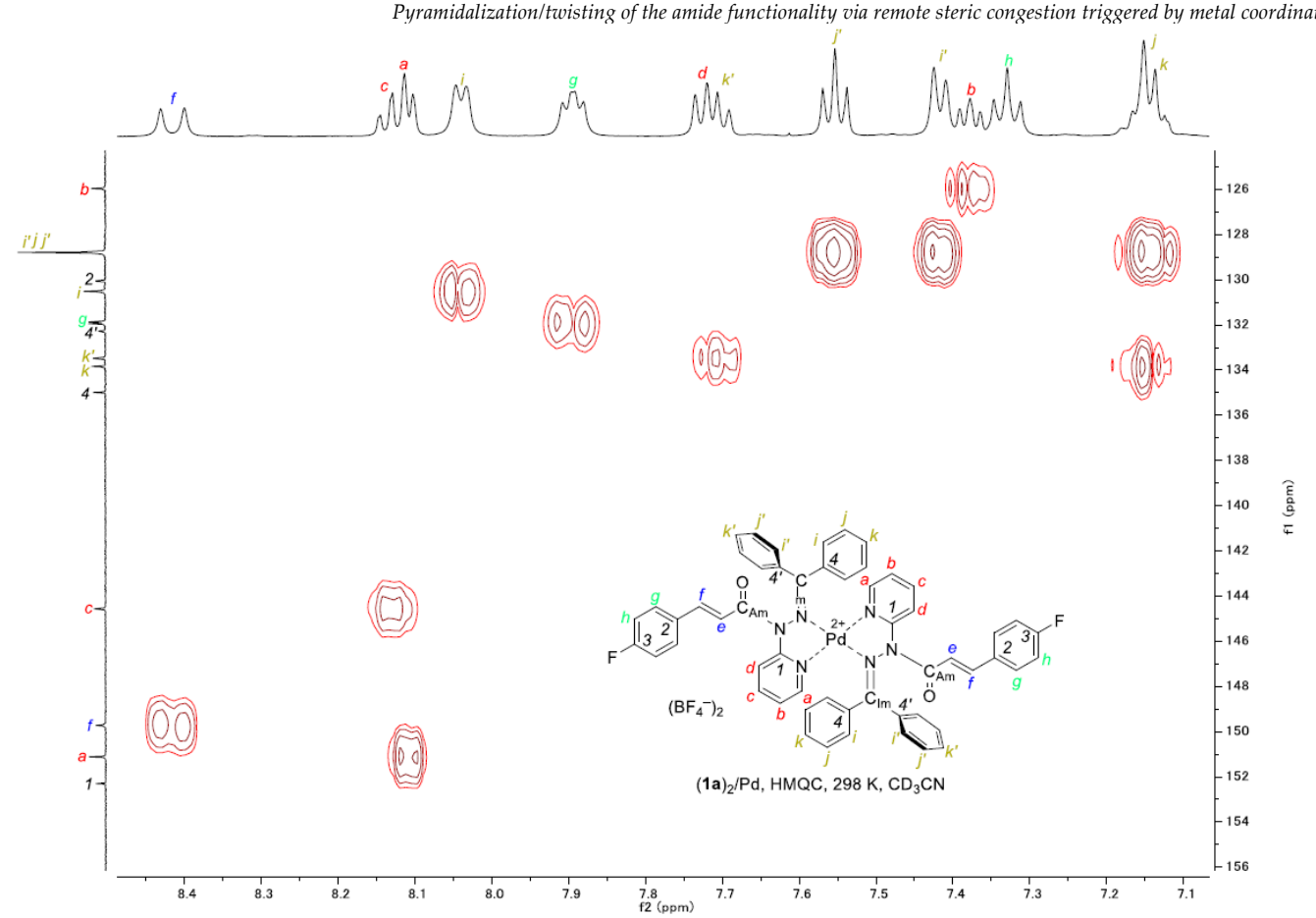

f2 (ppm)
f1 (ppm)
1a/Pd, HMBC, 298 K, CD3CN

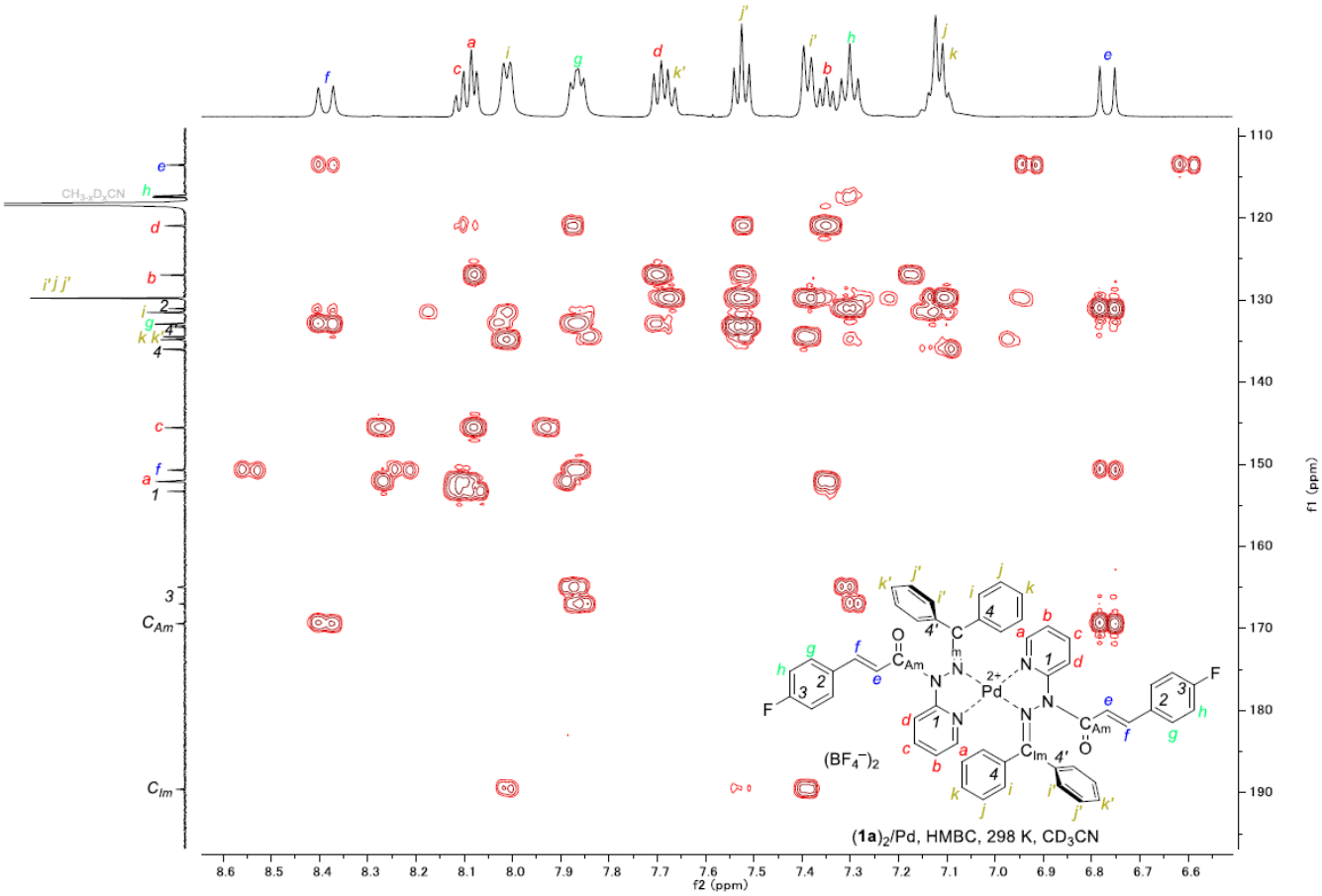

f2 (ppm)
f1 (ppm)
NOE
1a/Pd, NOESY, 298 K, CD3CN

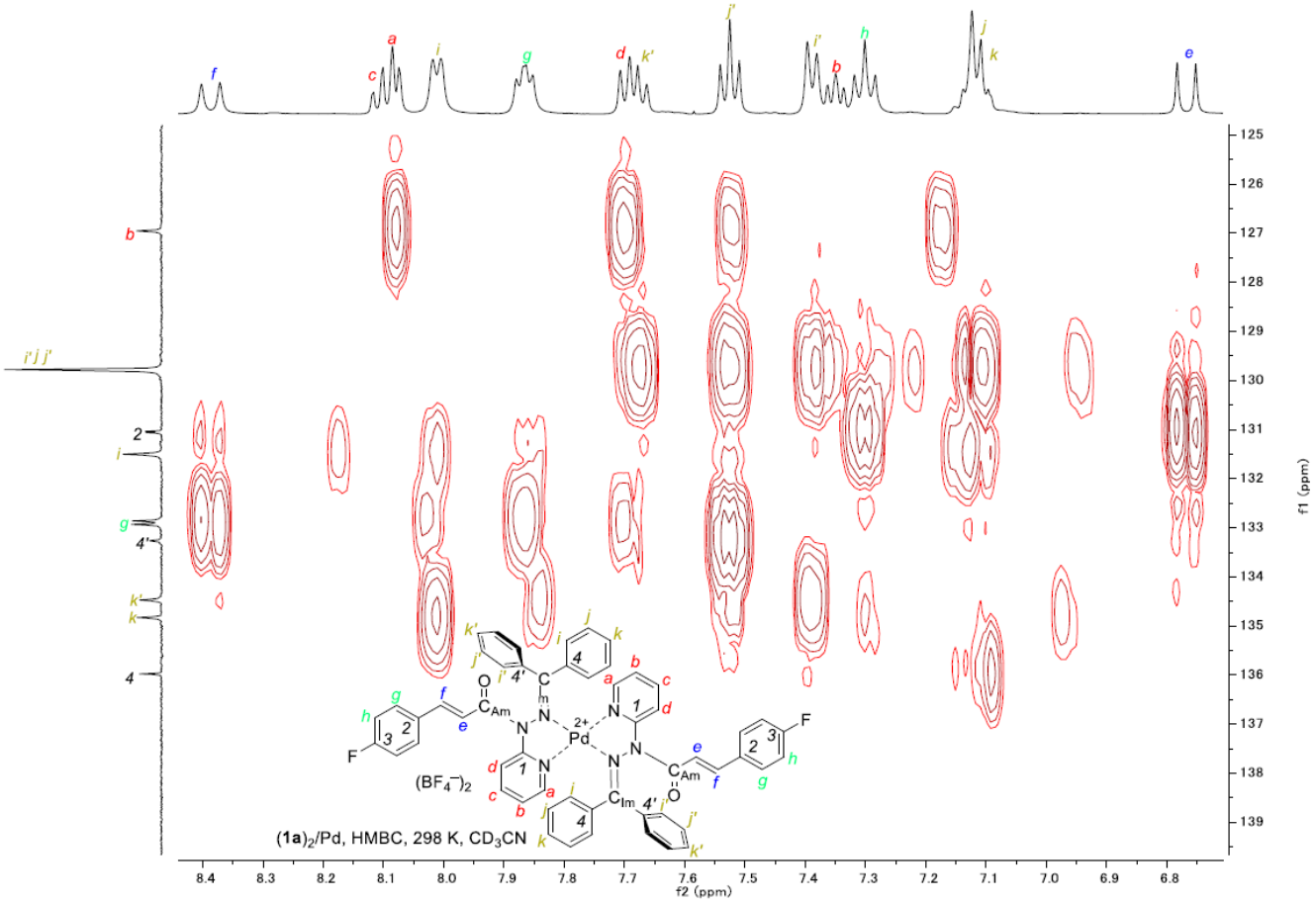
*3-1-3. Detailed NMR of (**1a**)₂/Pd for peak assignments*

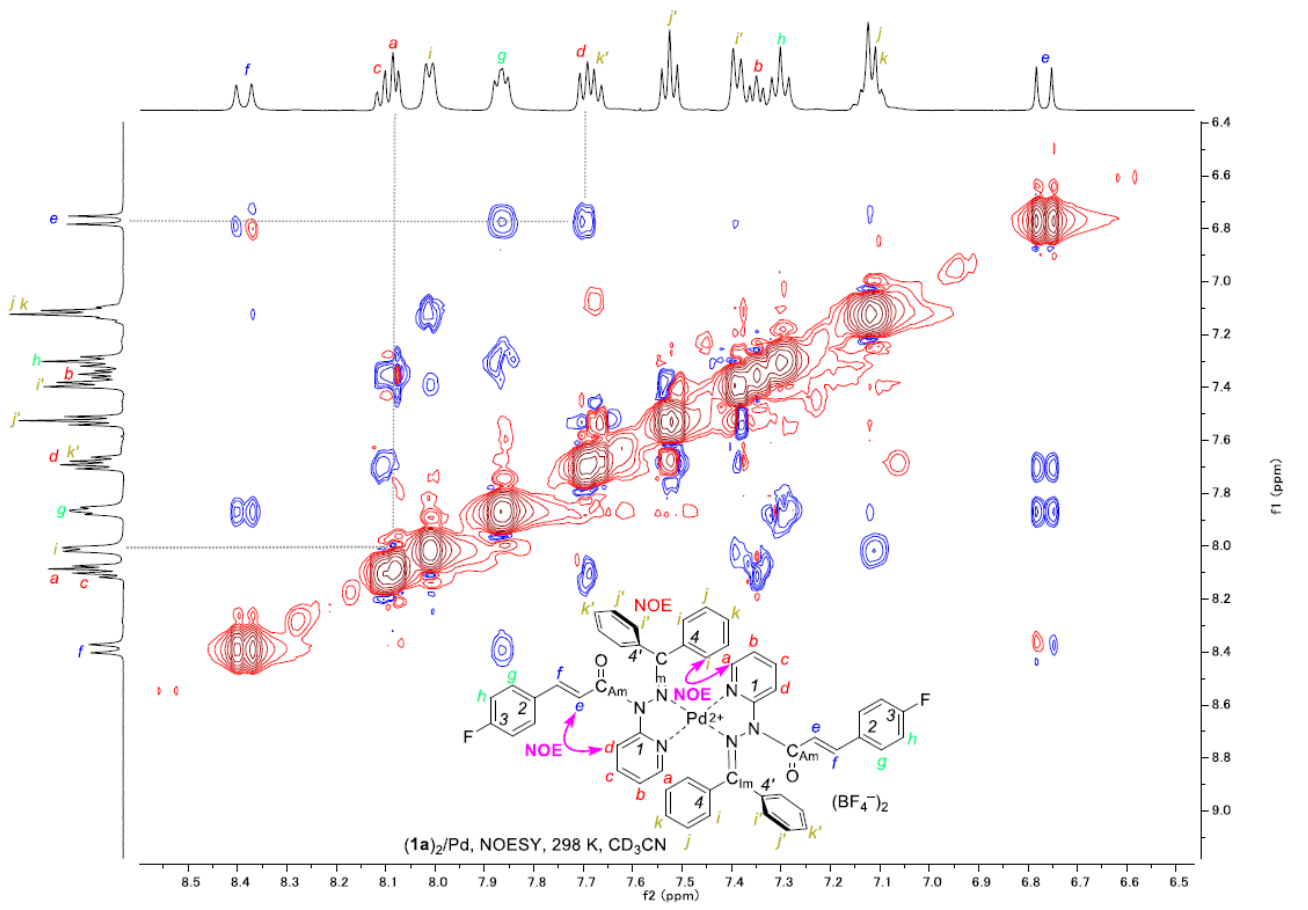


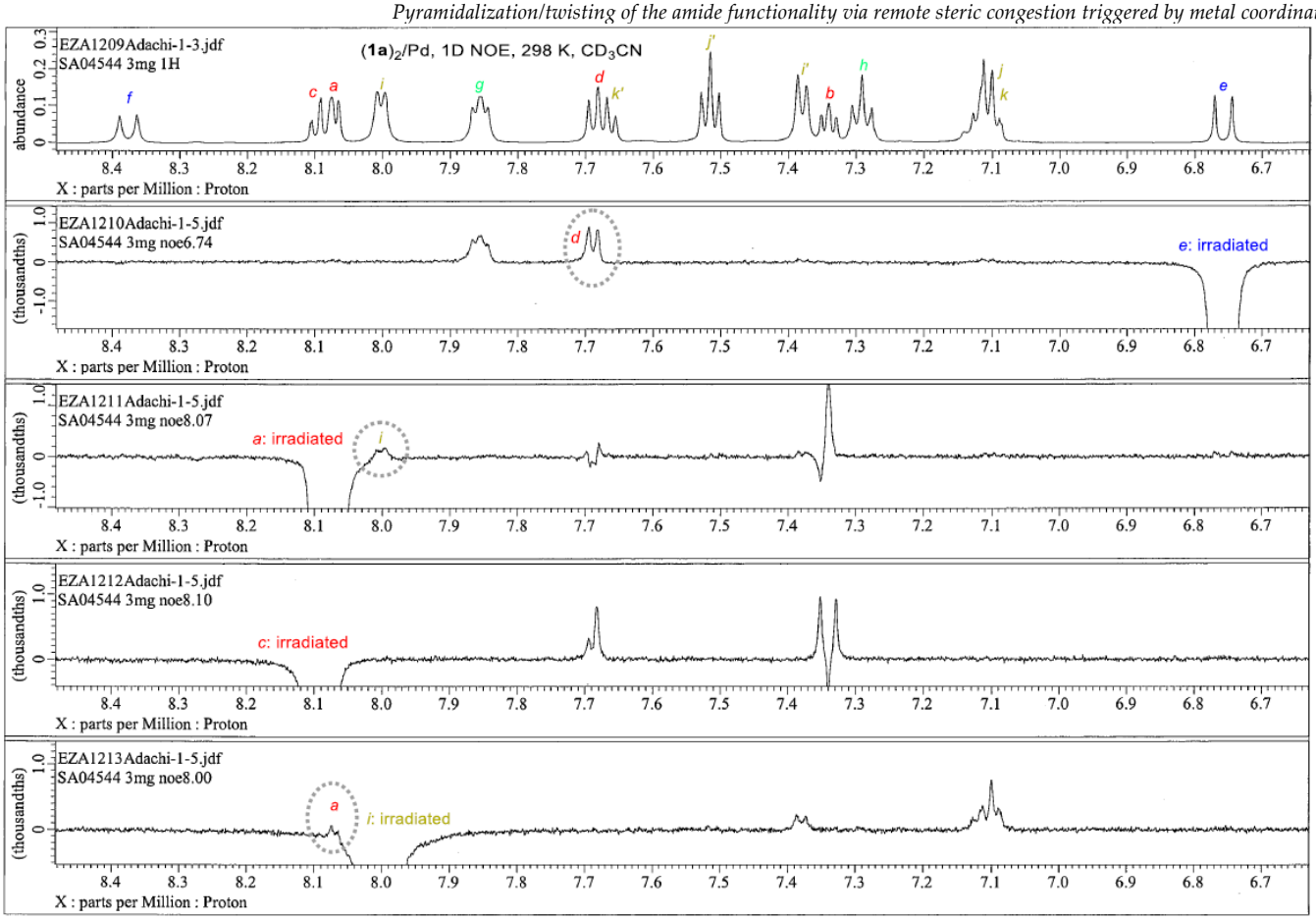



f2 (ppm)
f1 (ppm)
(BF4−)2
(1a)2/Pd, HMQC, 298 K, CD3CN


f2 (ppm)
f1 (ppm)
(BF4−)2
(1a)2/Pd, HMBC, 298 K, CD3CN


(1a)2/Pd, HMBC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)


NOE
(1a)2/Pd, NOESY, 298 K, CD3CN
f2 (ppm)
f1 (ppm)


EZA1209Adachi-1-3.jdf
SA04544 3mg 1H
(1a)2/Pd, 1D NOE, 298 K, CD3CN
abundance
X : parts per Million : Proton
EZA1210Adachi-1-5.jdf
SA04544 3mg noe6.74
e: irradiated
EZA1211Adachi-1-5.jdf
SA04544 3mg noe8.07
a: irradiated
EZA1212Adachi-1-5.jdf
SA04544 3mg noe8.10
c: irradiated
EZA1213Adachi-1-5.jdf
SA04544 3mg noe8.00
i: irradiated
(thousandths)

*3-1-4. Stacked ^{1}H and ^{13}C NMR of **1a**, **1a**/Pd, and (**1a**)$_2$/Pd*

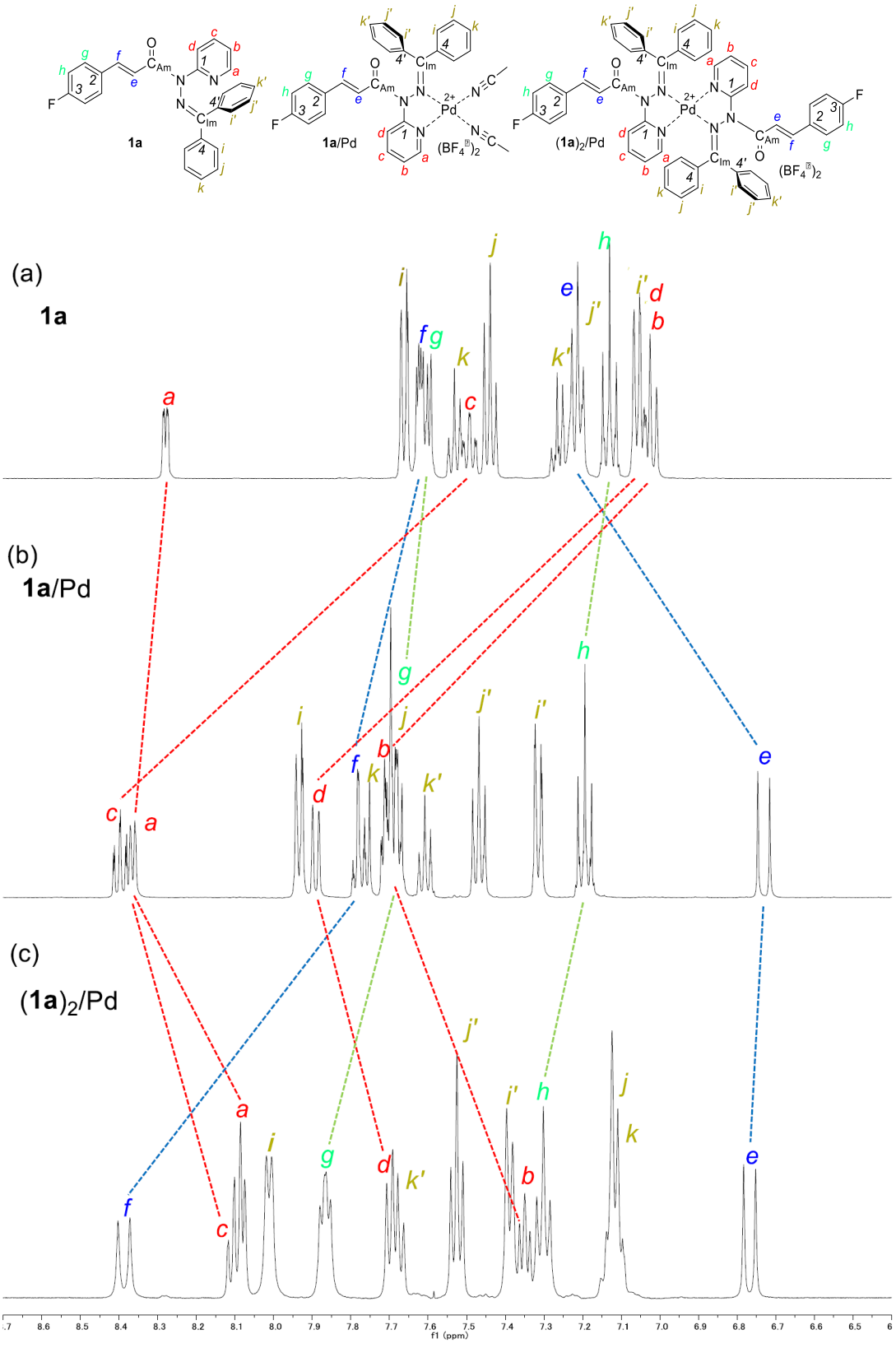


Figure S1. (a) ^{1}H NMR of **1a** in CD_3CN. (b) ^{1}H NMR of **1a**/$[Pd(CH_3CN)_4](BF_4)_2$ = 1/1 in CD_3CN. (c) ^{1}H NMR of **1a**/$[Pd(CH_3CN)_4](BF_4)_2$ = 2/1 in CD_3CN. *i*▪*j*▪*k* and *i*′▪*j*′▪*k*′ are not distinguished in (a) and (b).

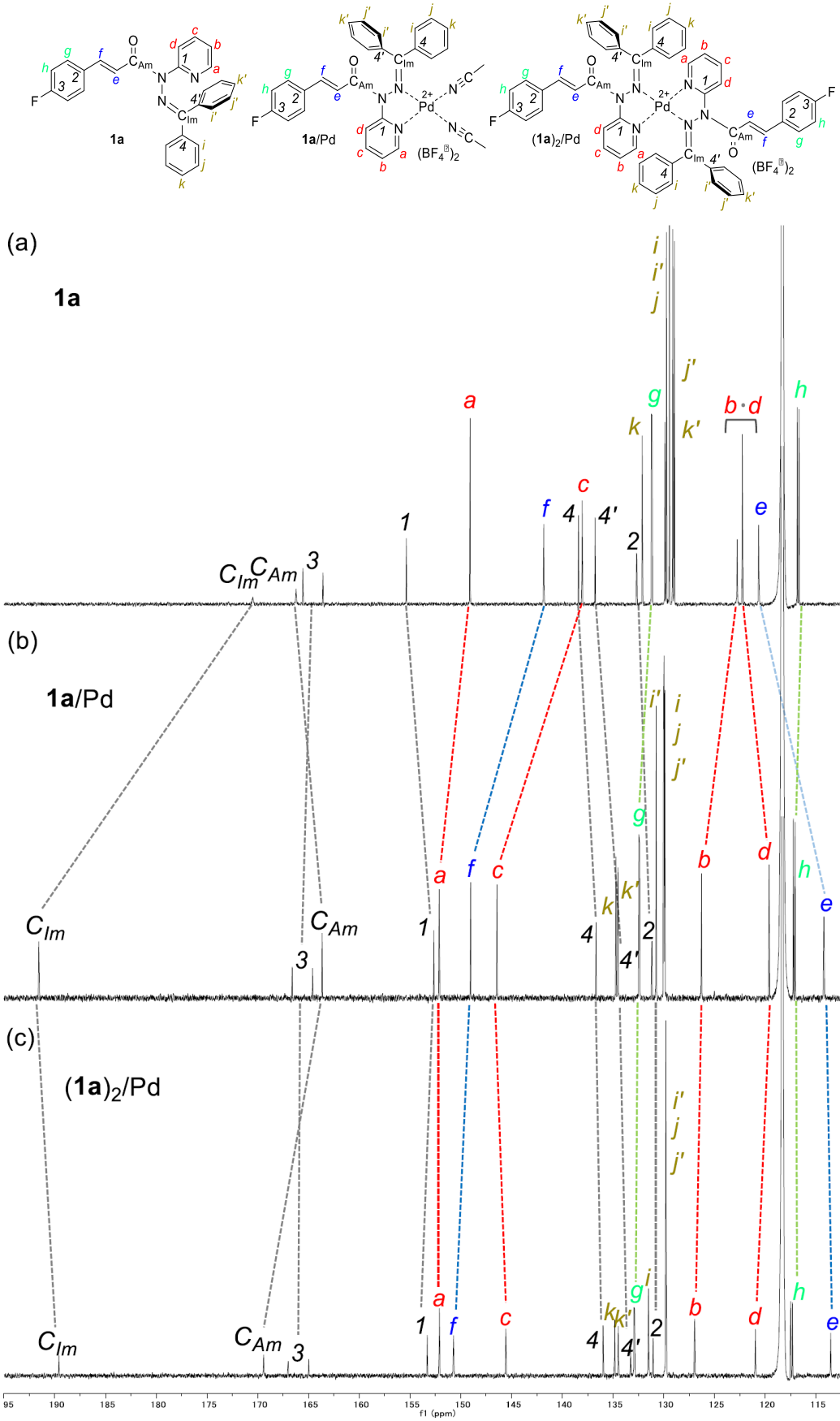
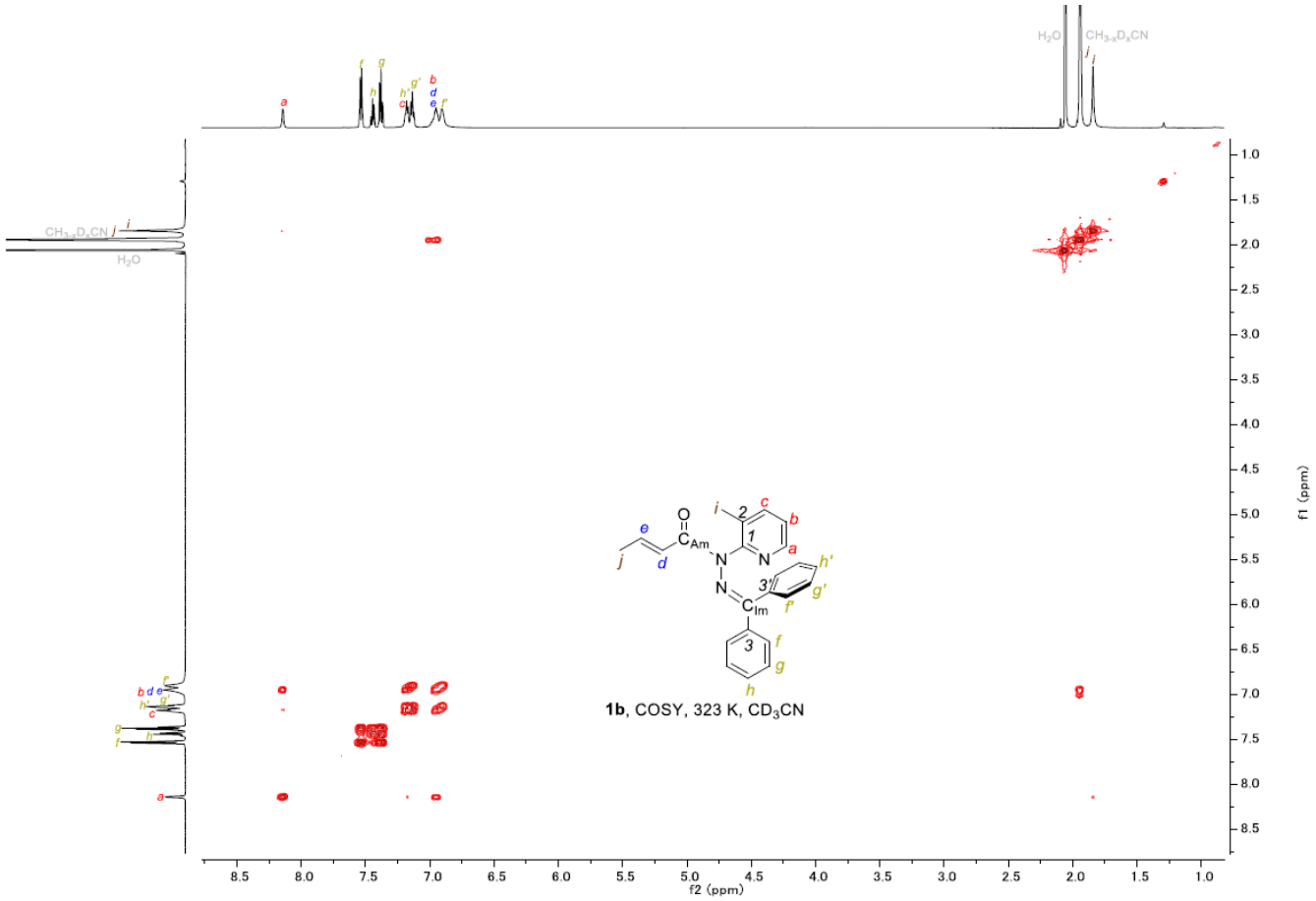
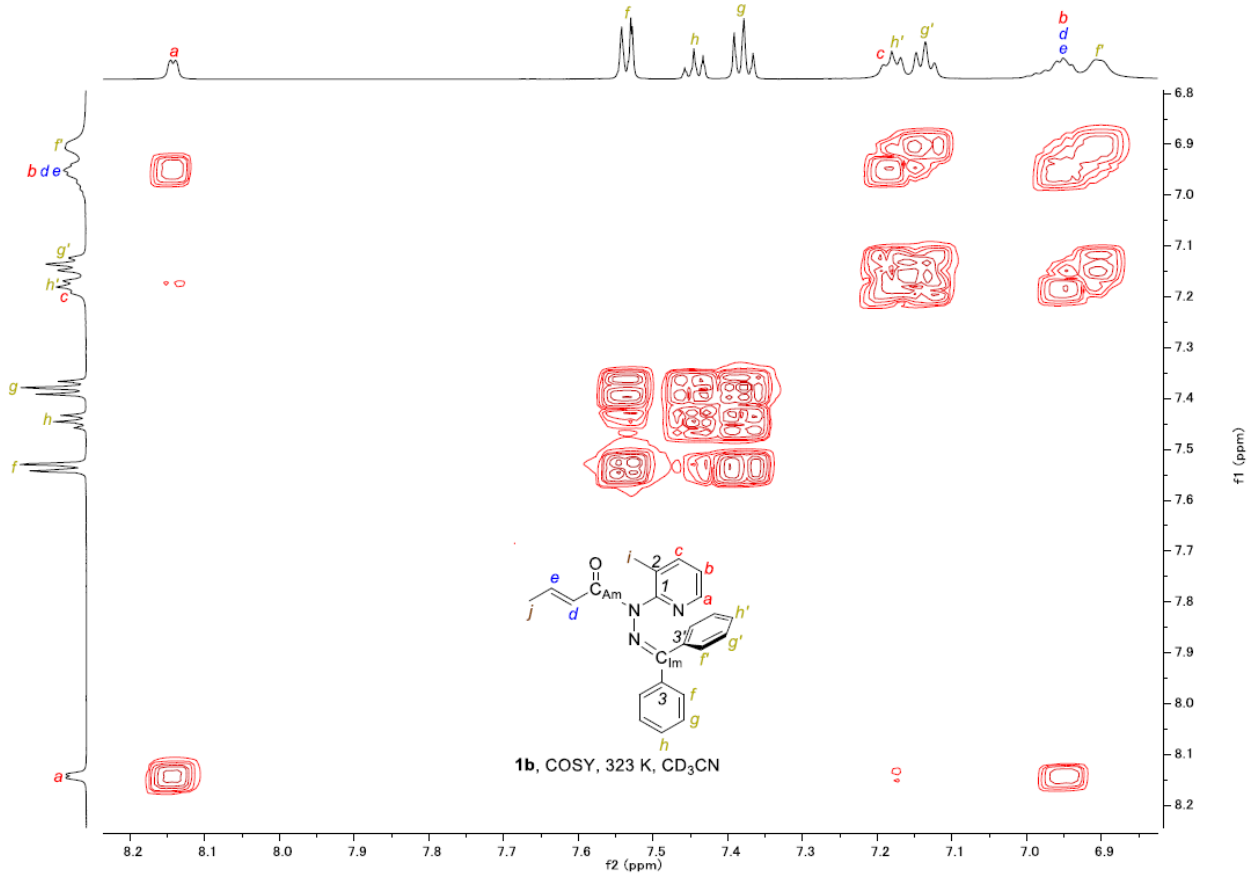


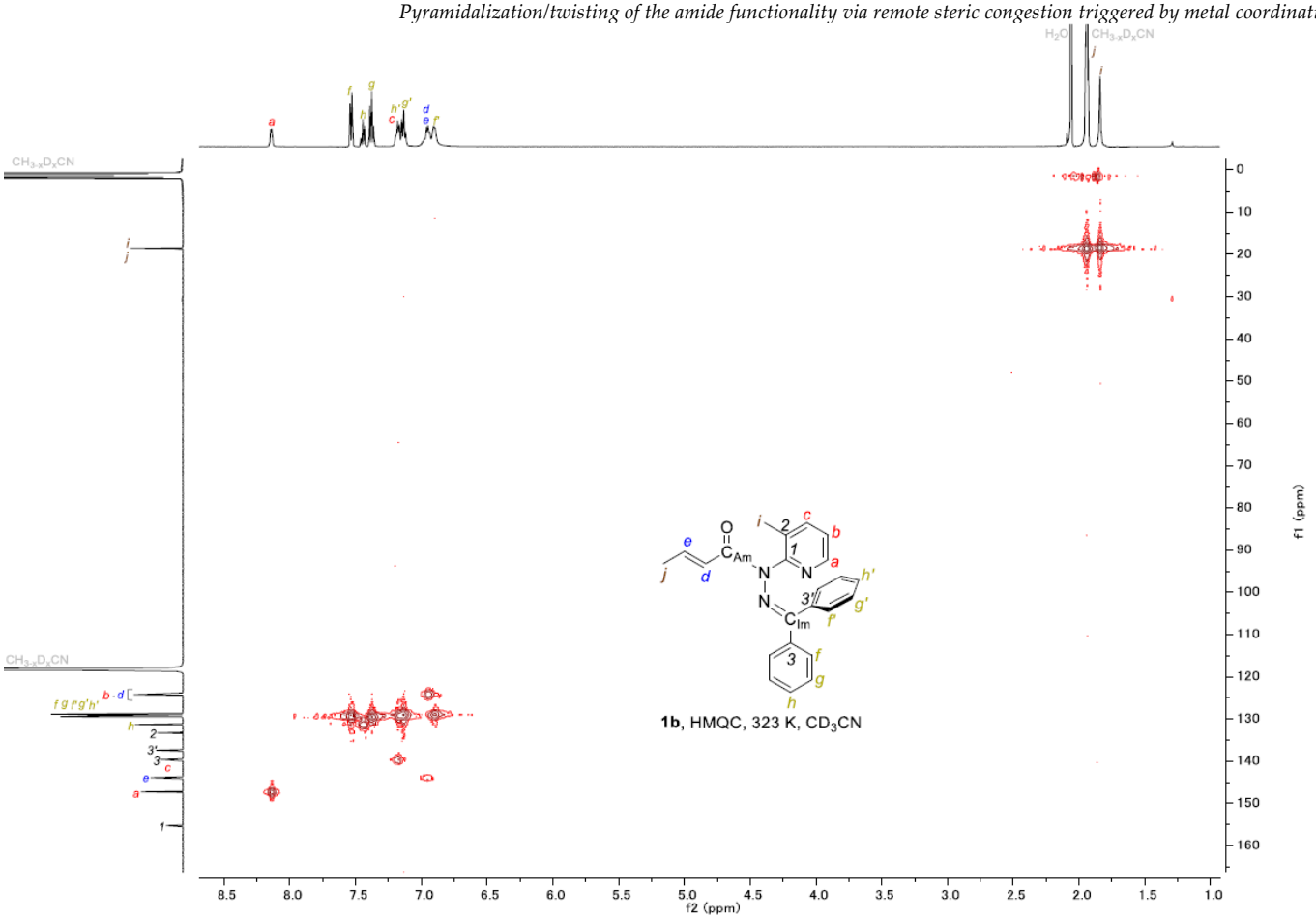
Figure S2. (a) ^{13}C NMR of **1a** in CD_3CN. (b) ^{13}C NMR of **1a**/$[Pd(CH_3CN)_4](BF_4)_2$ = 1/1 in CD_3CN. (c) ^{13}C NMR of **1a**/$[Pd(CH_3CN)_4](BF_4)_2$ = 2/1 in CD_3CN. *i*▪*j*▪*k*▪*4* and *i′*▪*j′*▪*k′*▪*4′* are not distinguished in (a) and (b).

*3-2. **1b**–Pd Complex*

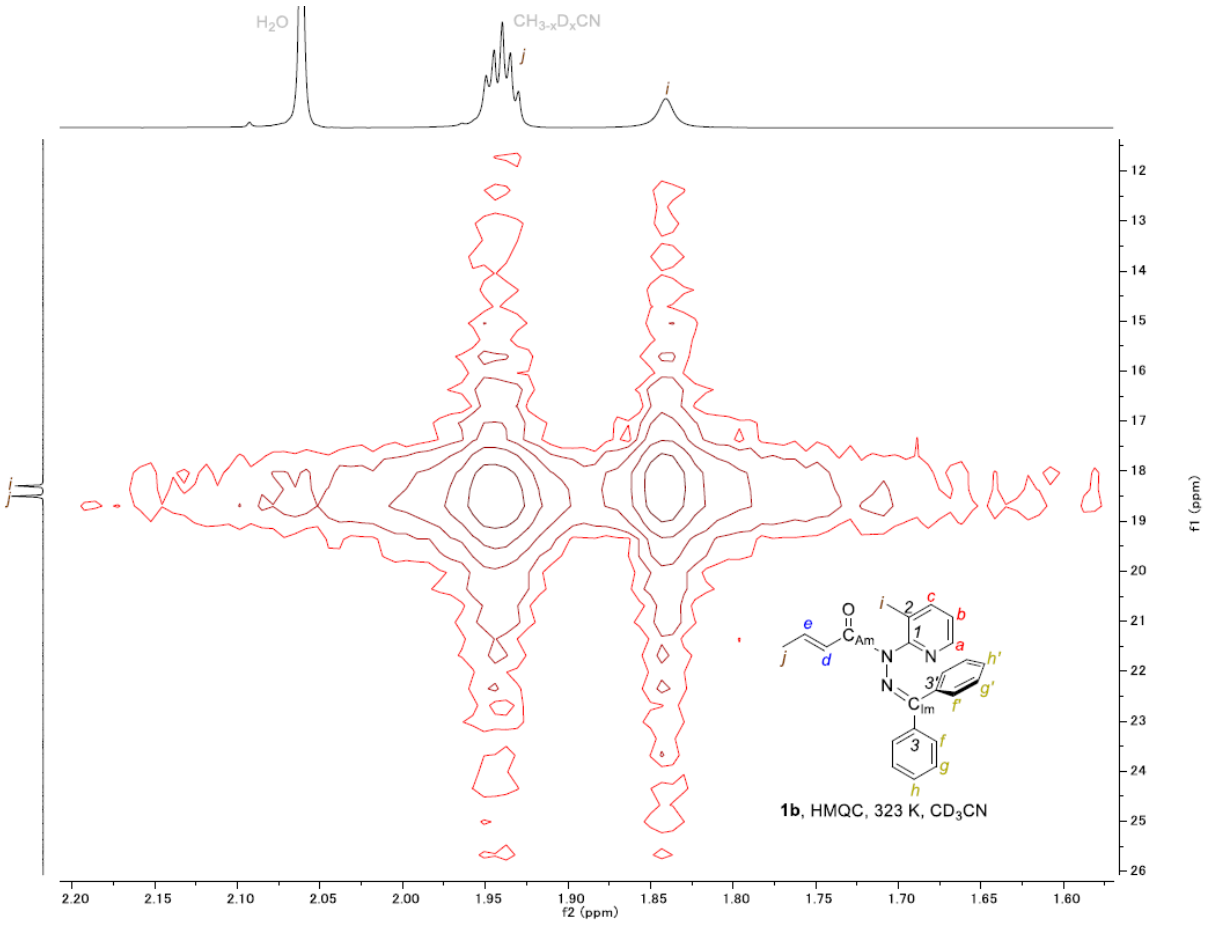
*3-2-1. Detailed NMR of **1b** for peak assignments*



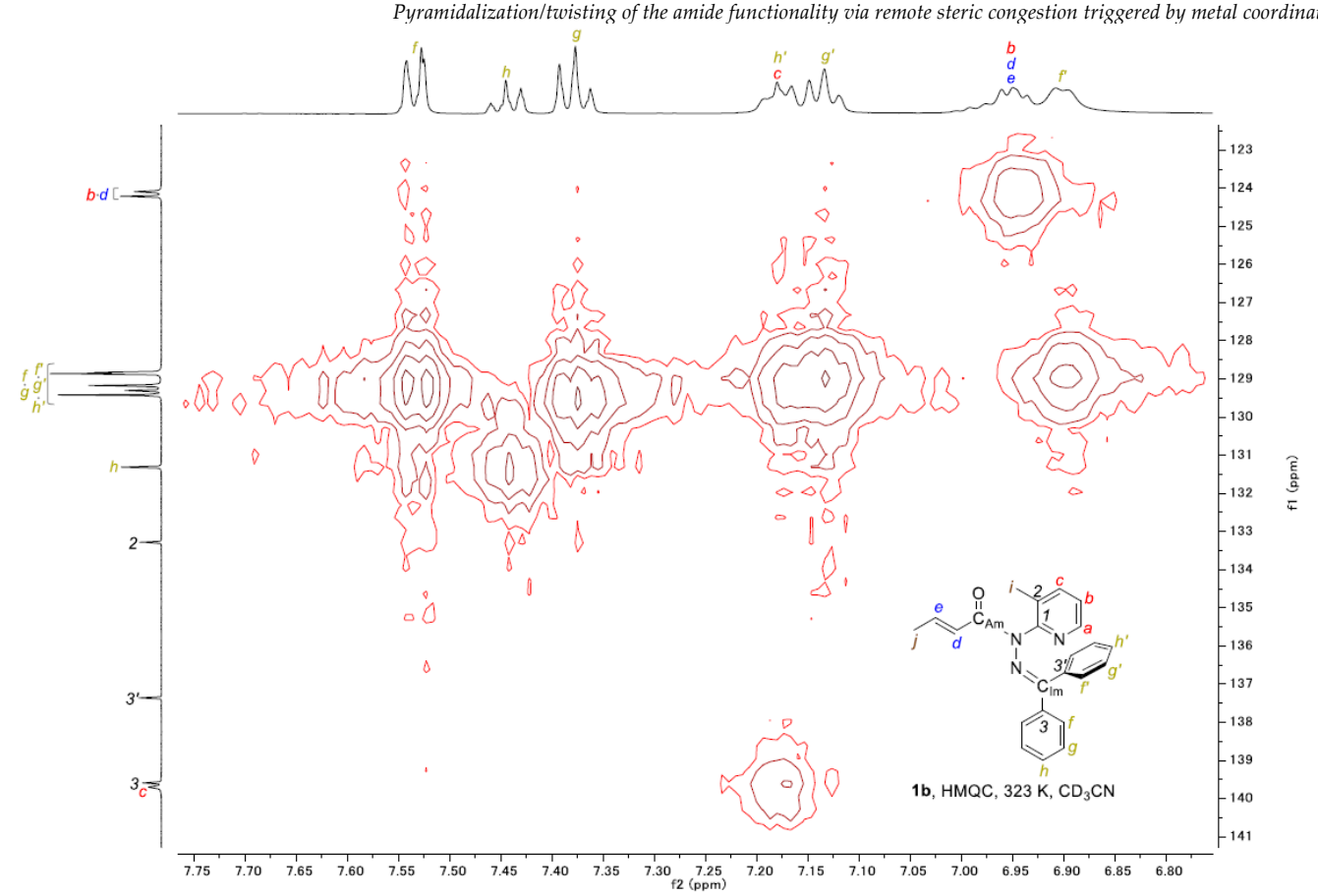




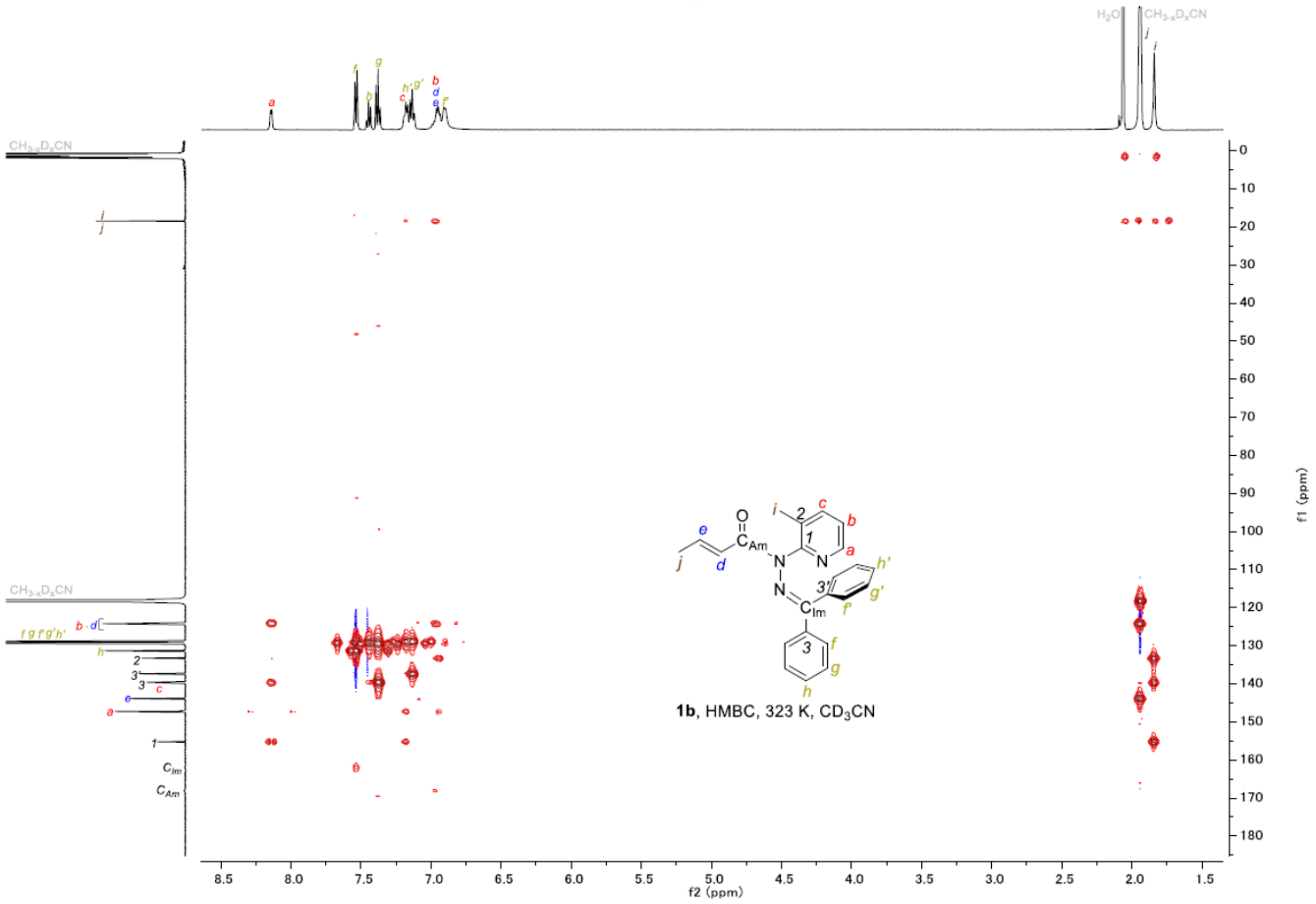
1b, HMQC, 323 K, CD_3CN



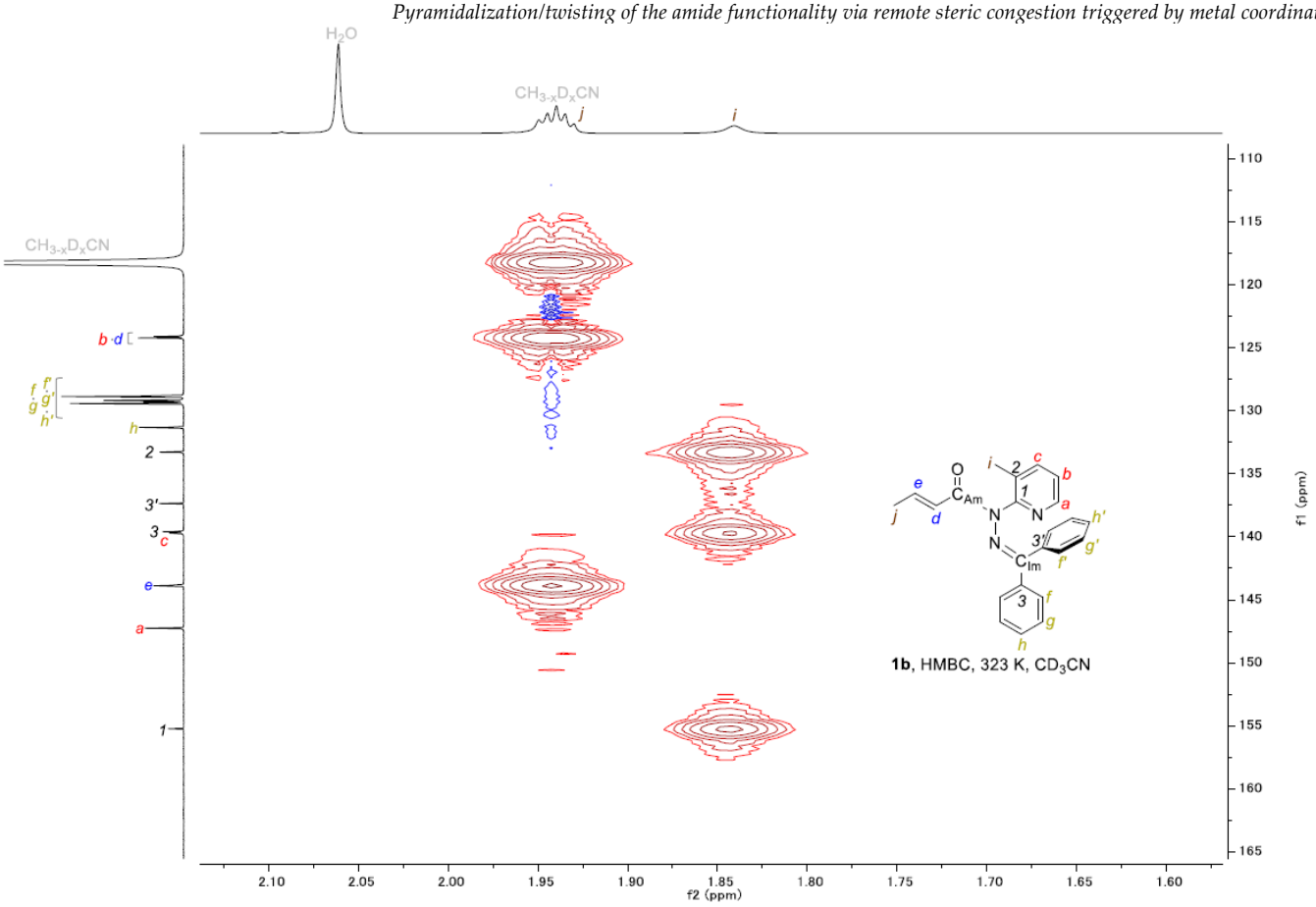
1b, HMQC, 323 K, CD_3CN

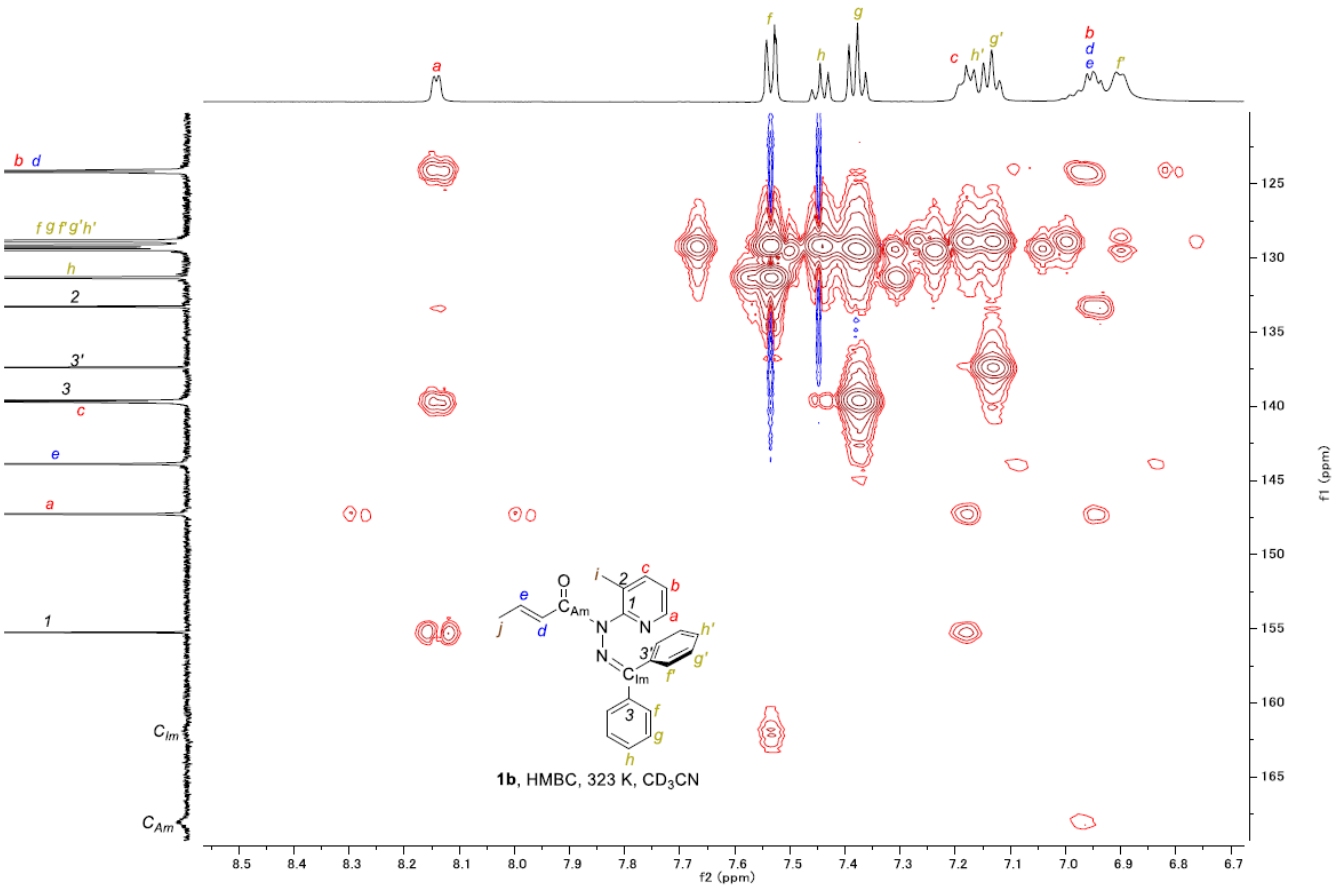


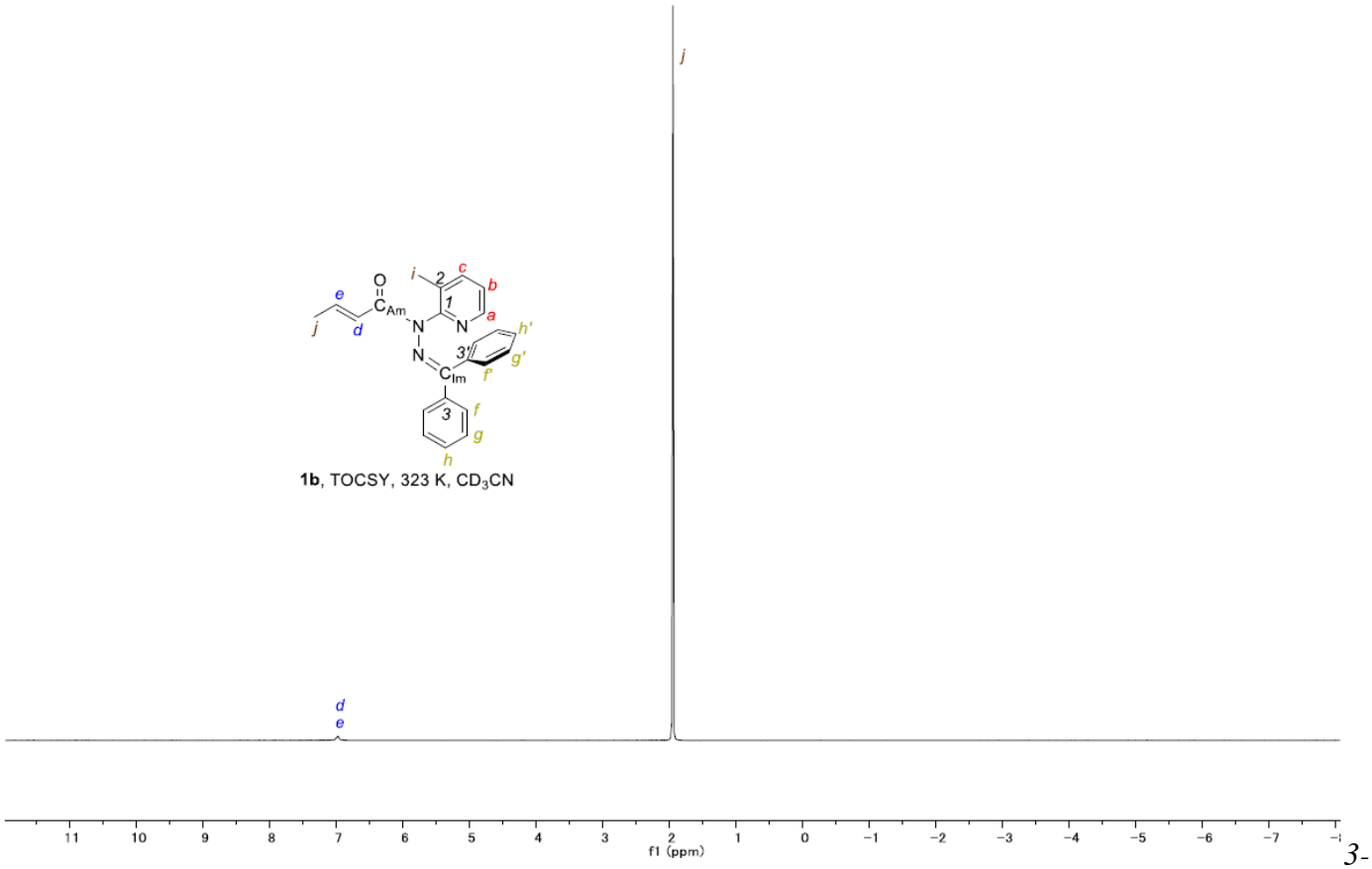
1b, HMQC, 323 K, CD_3CN



1b, HMBC, 323 K, CD_3CN


H2O
CH3-xDxCN
j
i
CH3-xDxCN
b d
f f'
g g'
h'
h
2
3'
3
c
e
a
1
f1 (ppm)
f2 (ppm)
1b, HMBC, 323 K, CD3CN

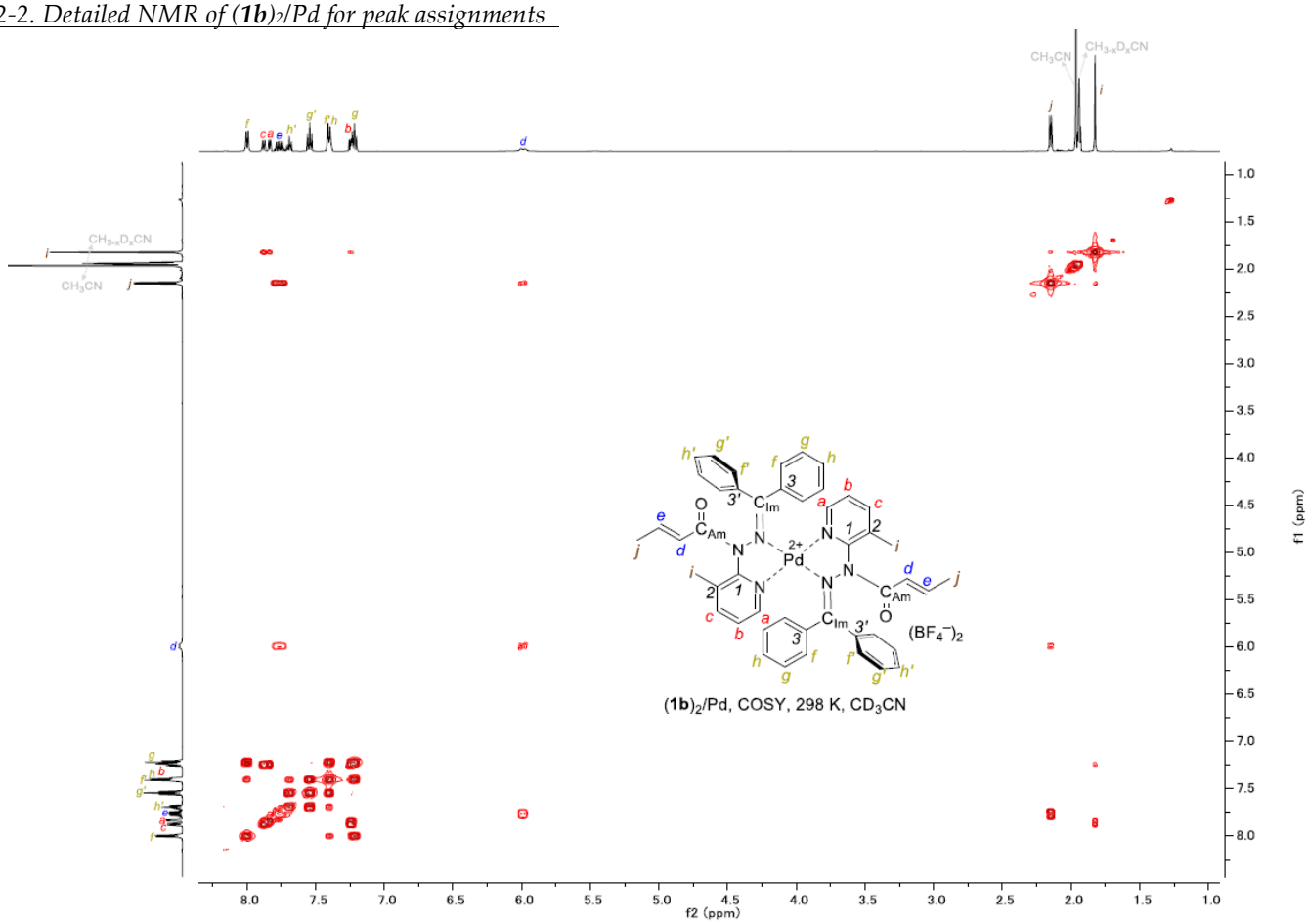

a
f
h
g
c
h'
g'
b
d
e
f'
b d
f g f' g' h'
h
2
3'
3
c
e
a
1
CIm
CAm
f1 (ppm)
f2 (ppm)
1b, HMBC, 323 K, CD3CN



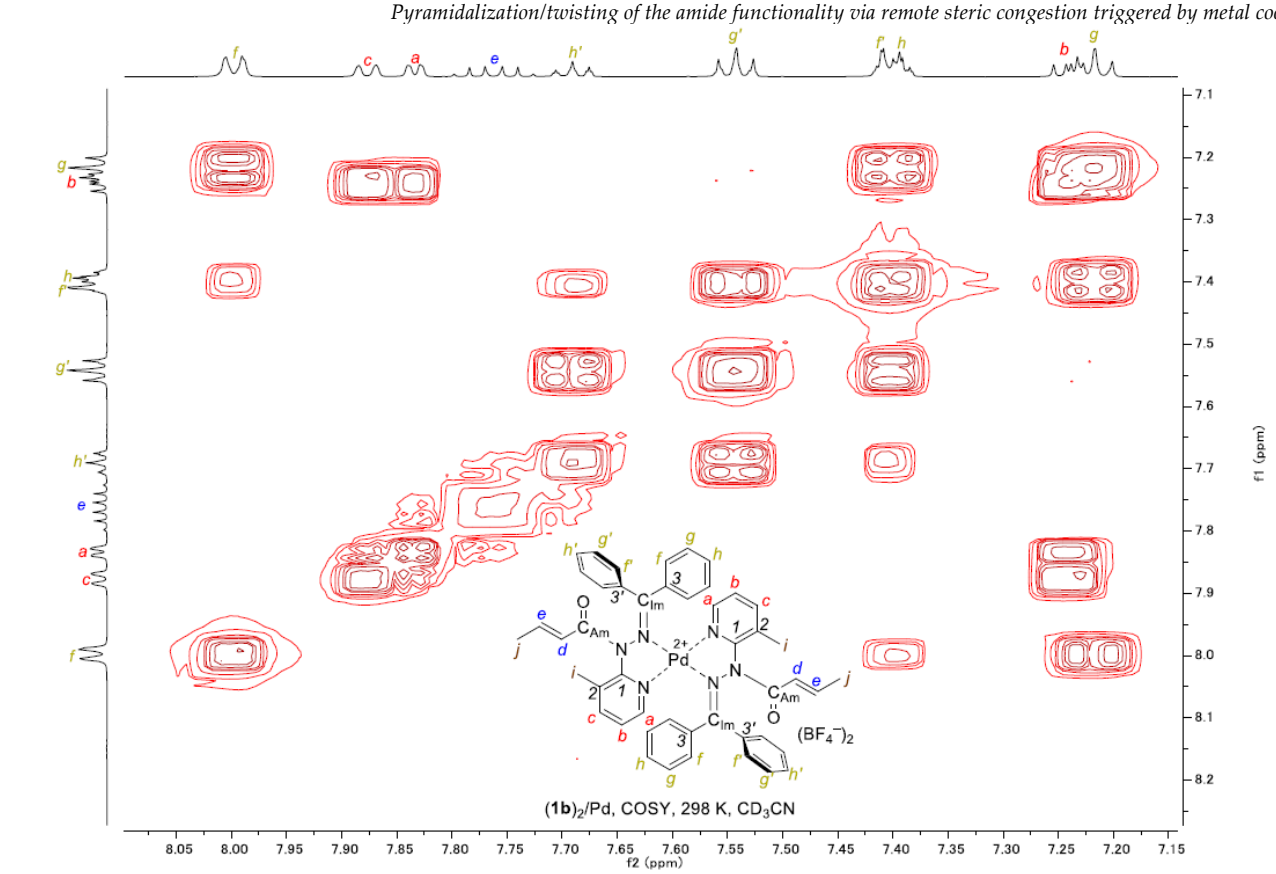
1b, TOCSY, 323 K, CD_3CN

3-

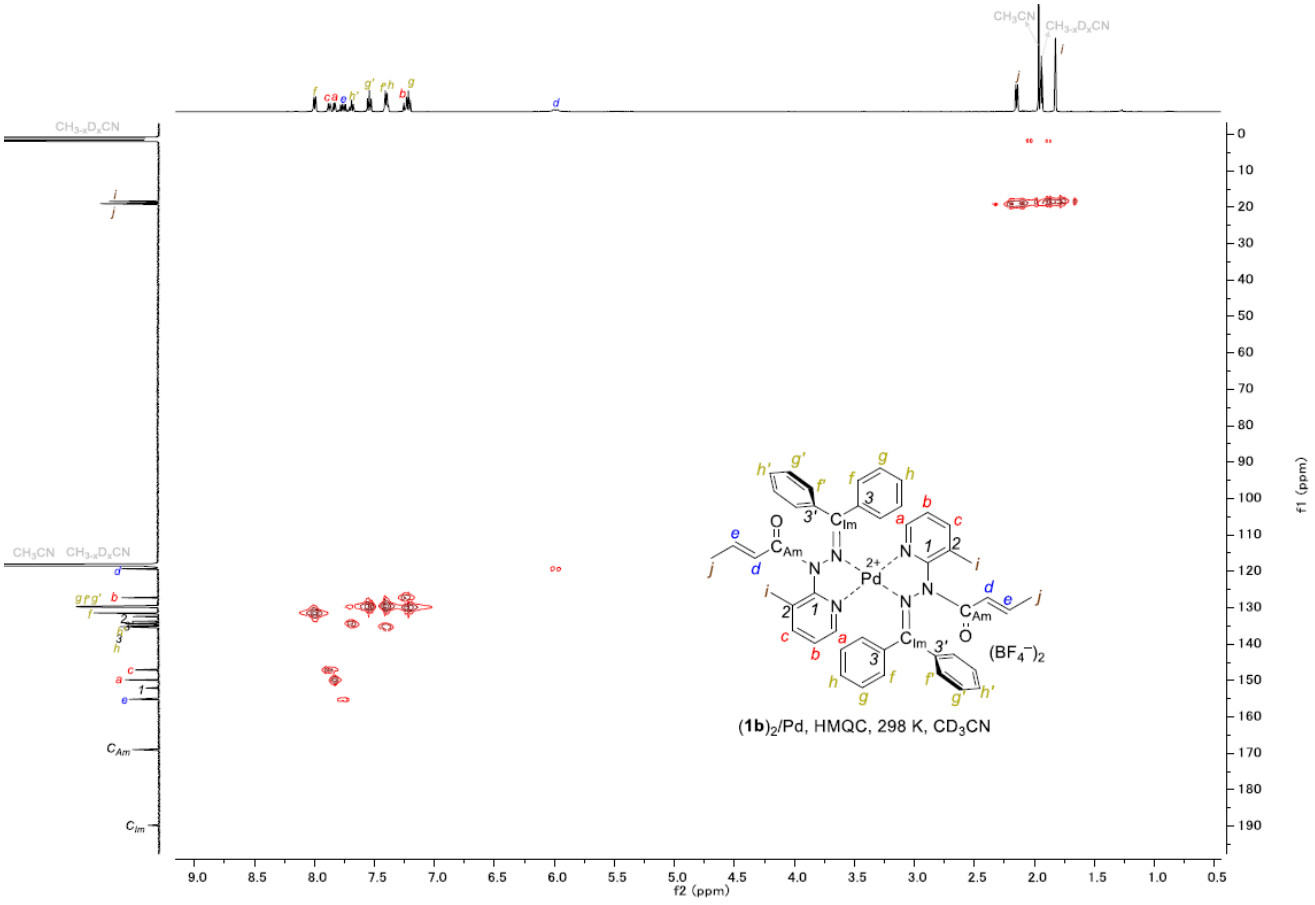
*3-2-2. Detailed NMR of (**1b**)₂/Pd for peak assignments*



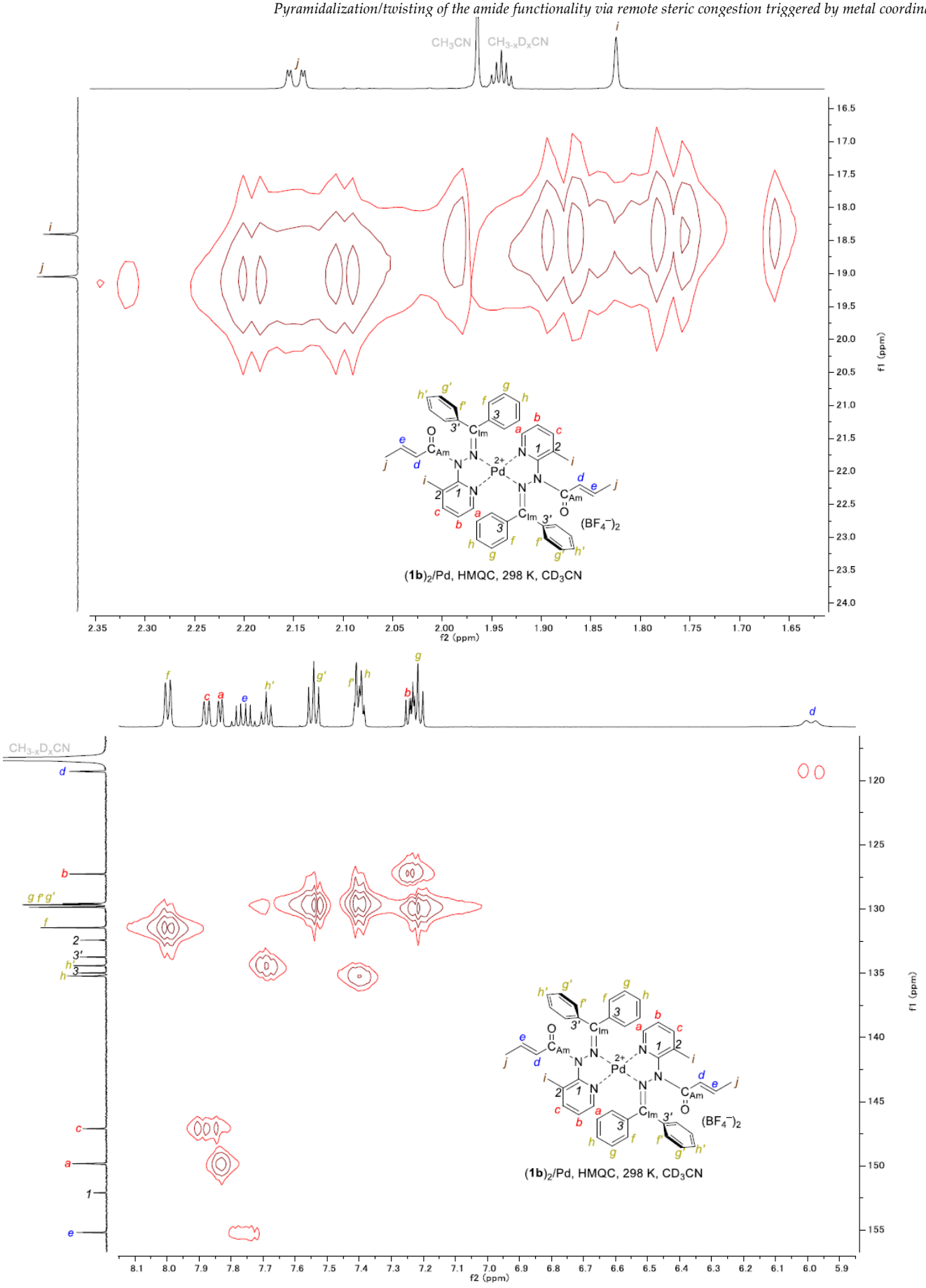
(**1b**)$_2$/Pd, COSY, 298 K, CD_3CN

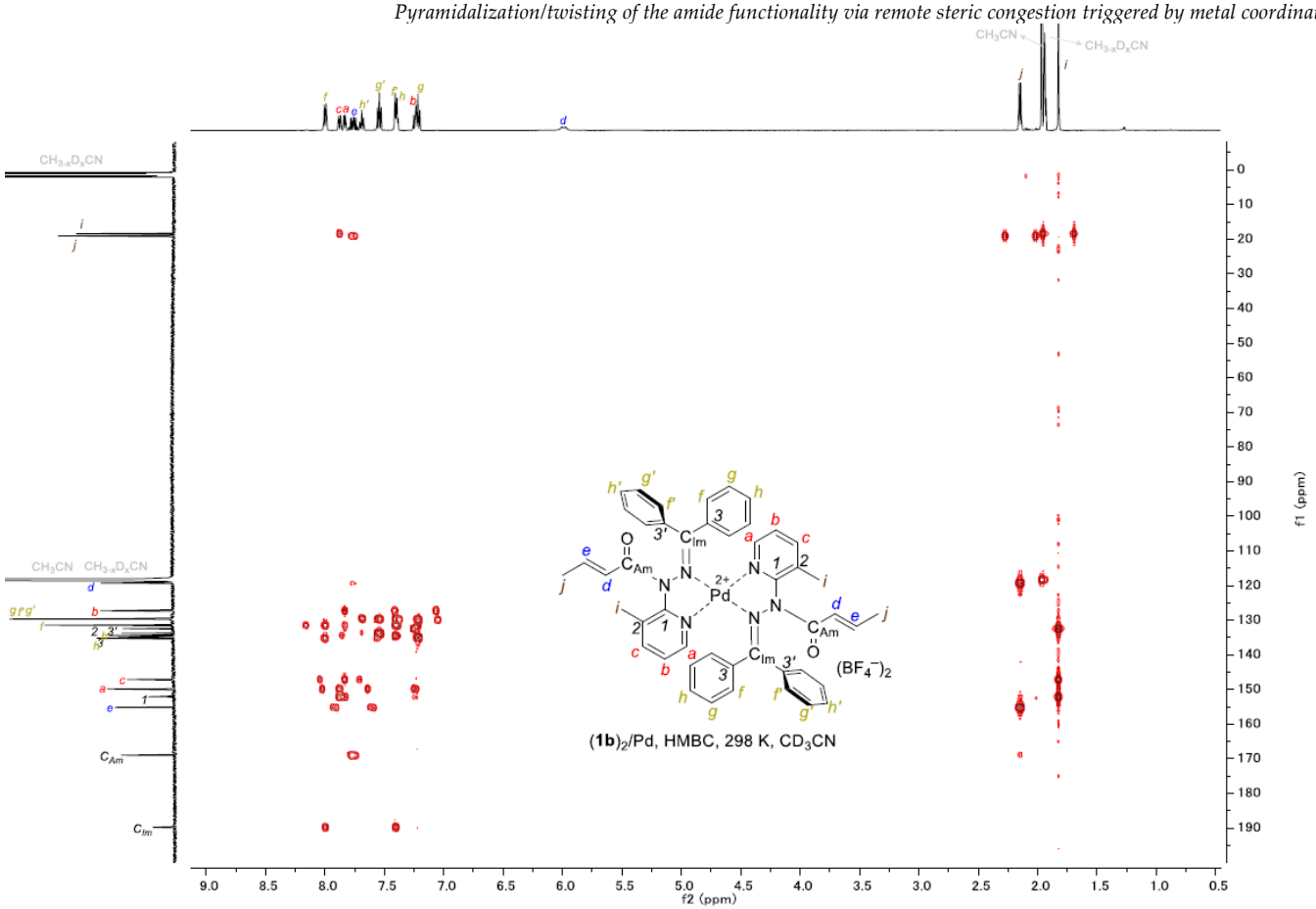


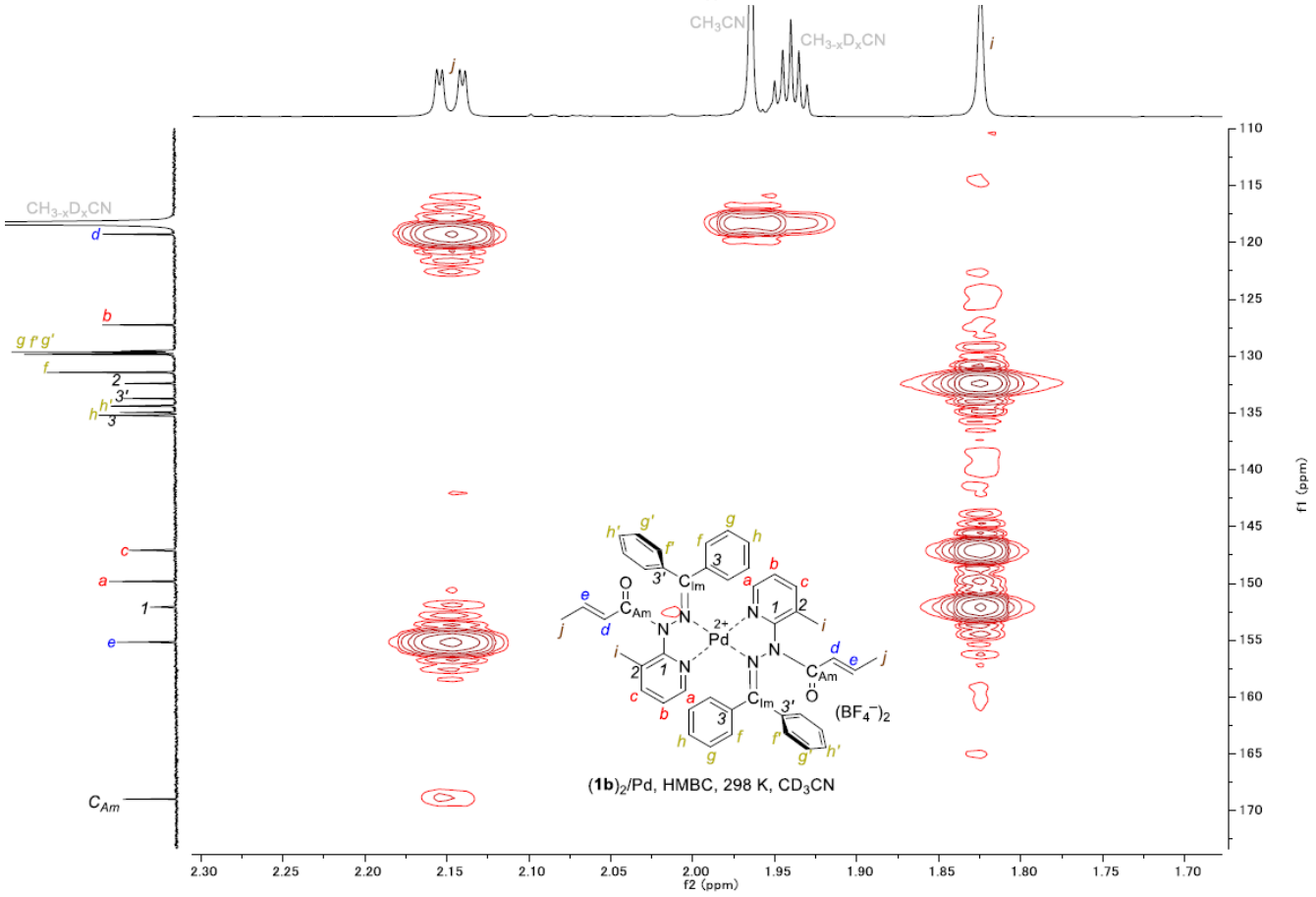
(1b)$_2$/Pd, COSY, 298 K, CD$_3$CN

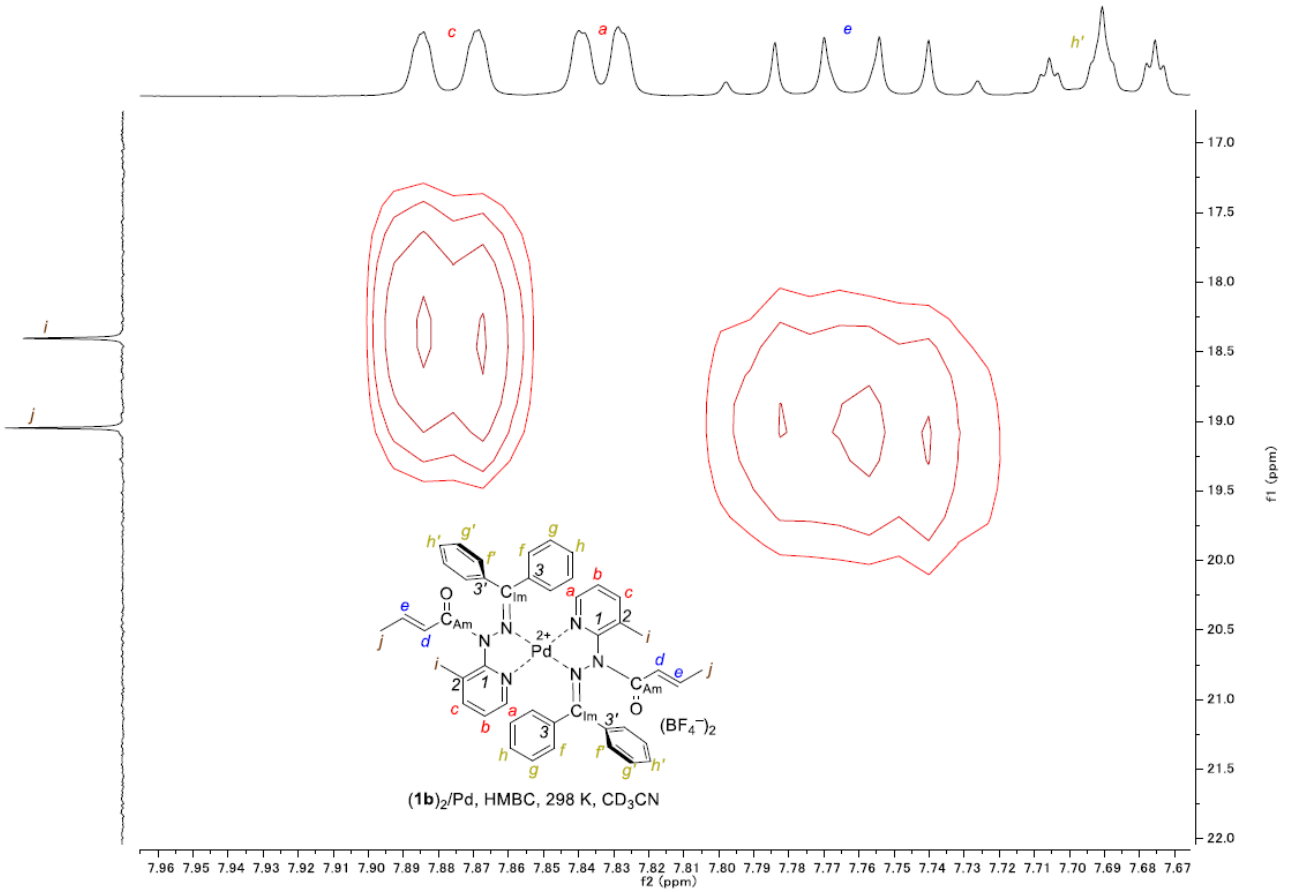


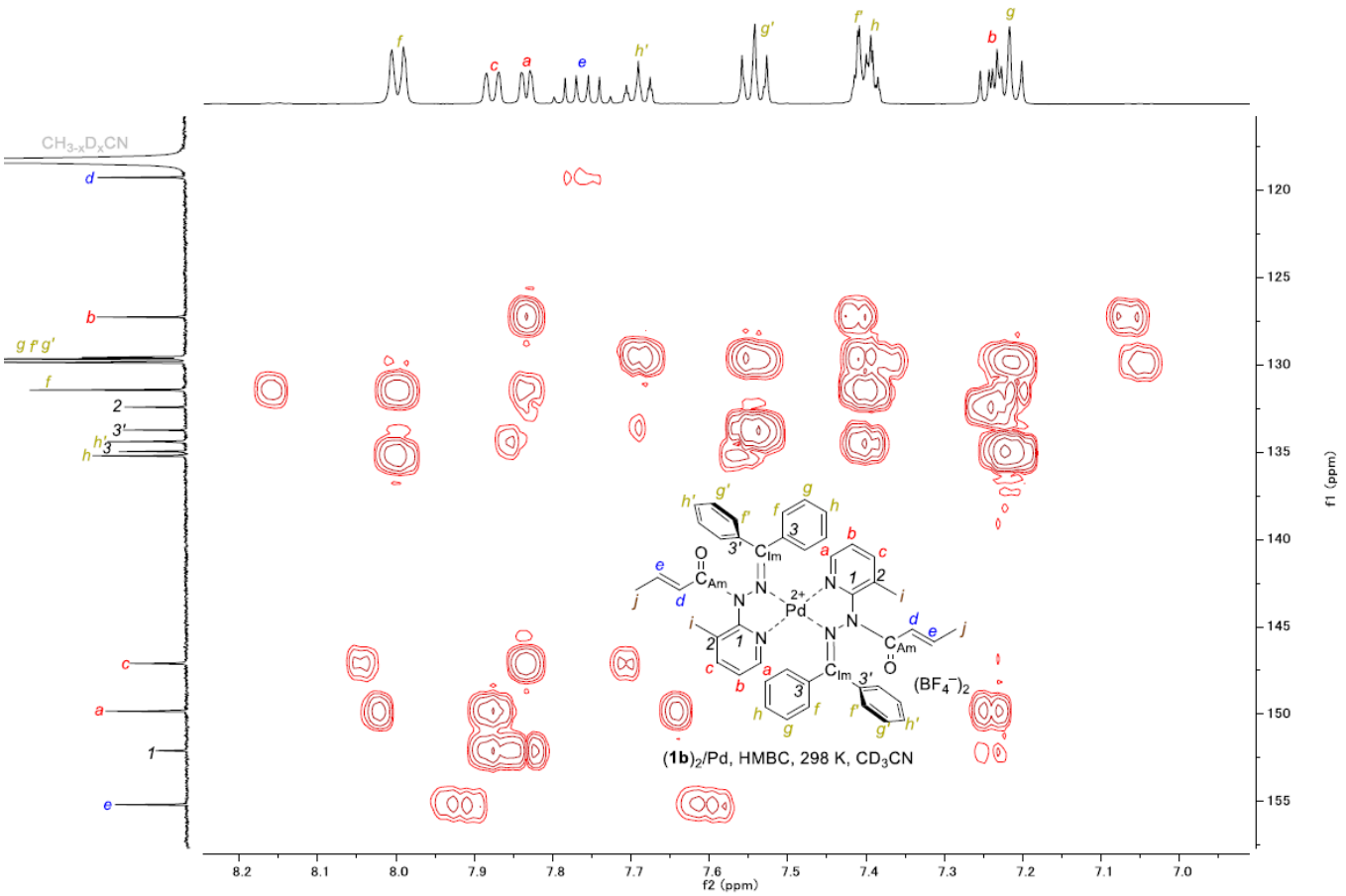
(1b)$_2$/Pd, HMQC, 298 K, CD$_3$CN

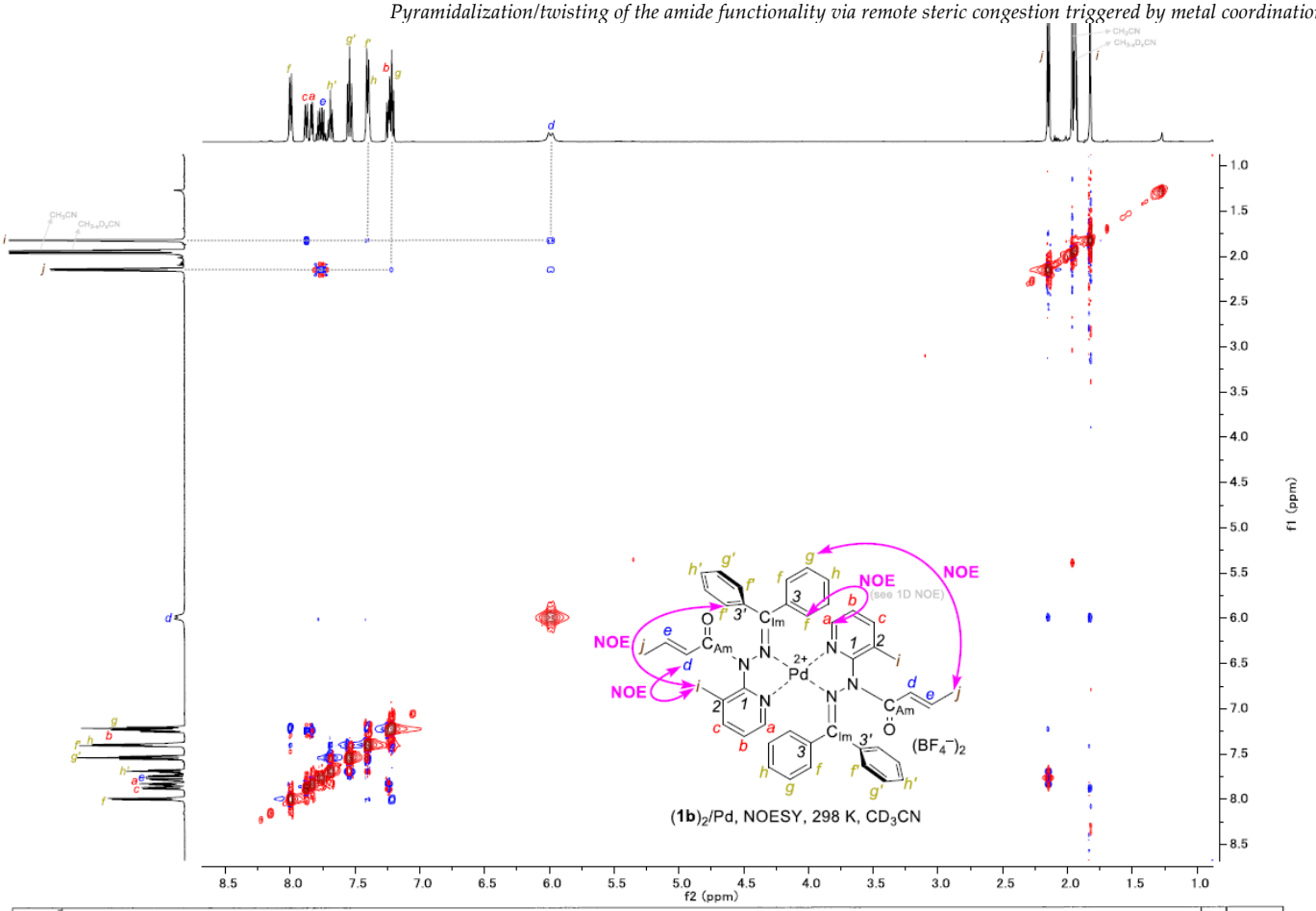

CH3CN
CH3-xDxCN
(1b)2/Pd, HMQC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)
(BF4−)2

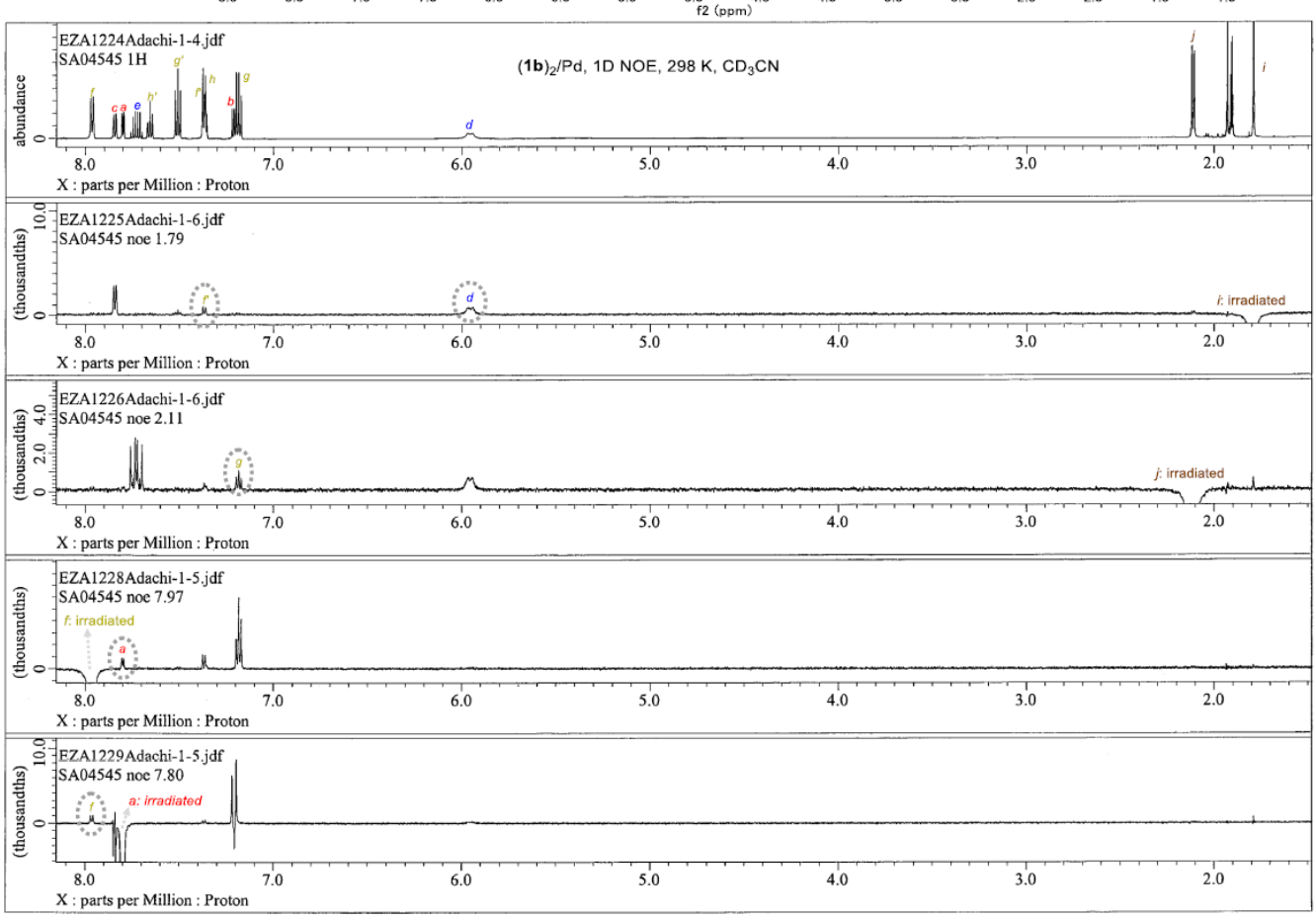

CH3CN
CH3-xDxCN
(1b)2/Pd, HMBC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

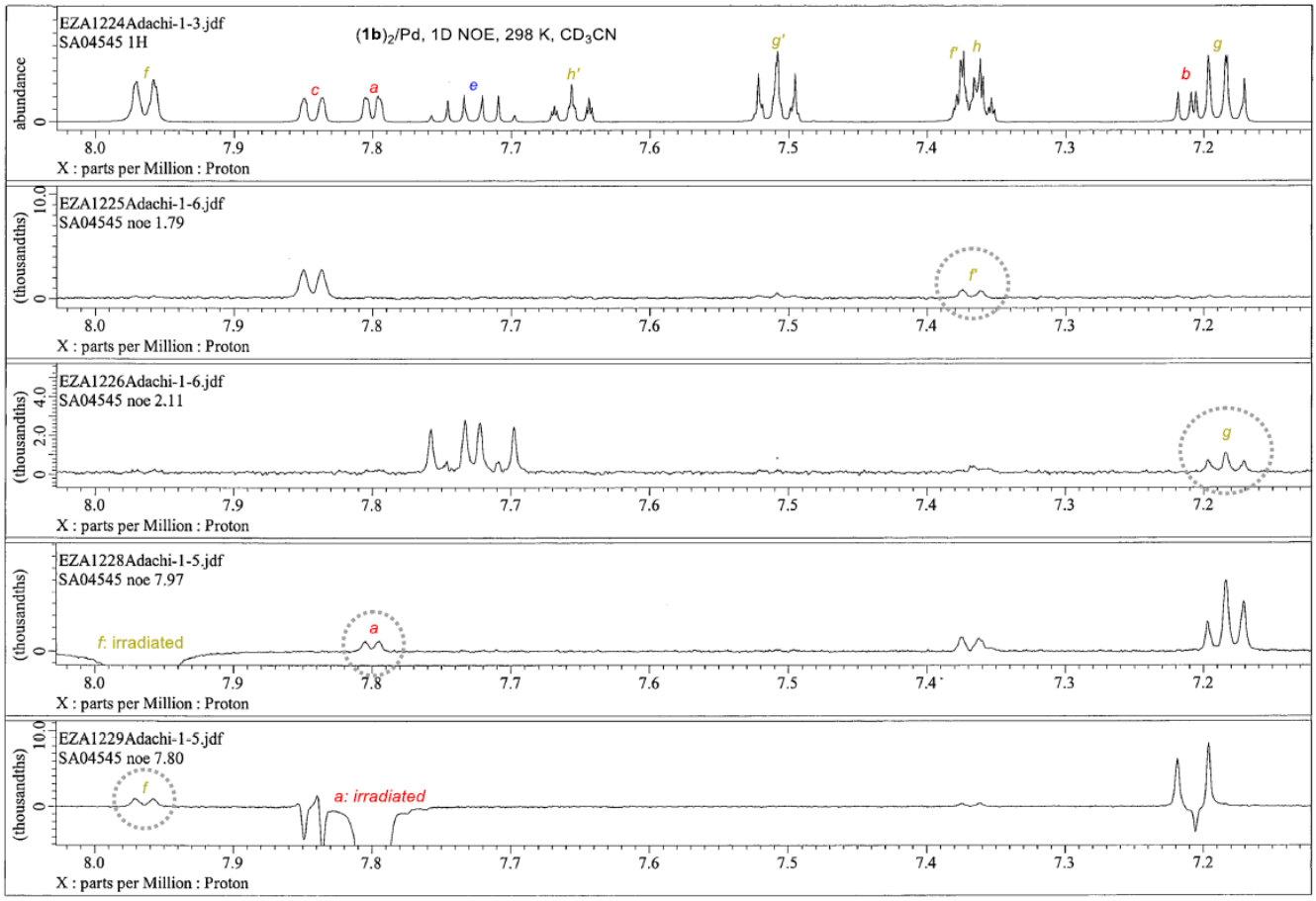

CH3CN
CH3-xDxCN
(1b)2/Pd, HMBC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)


c
a
e
h'
i
j
f2 (ppm)
f1 (ppm)
(1b)2/Pd, HMBC, 298 K, CD3CN


CH3-xDxCN
d
b
g f' g'
f
2
3'
h'
3
h
c
a
1
e
f2 (ppm)
f1 (ppm)
(1b)2/Pd, HMBC, 298 K, CD3CN


NOE
NOE
NOE
(see 1D NOE)
(1b)2/Pd, NOESY, 298 K, CD3CN
f2 (ppm)
f1 (ppm)


EZA1224Adachi-1-4.jdf
SA04545 1H
(1b)2/Pd, 1D NOE, 298 K, CD3CN
abundance
X : parts per Million : Proton
EZA1225Adachi-1-6.jdf
SA04545 noe 1.79
i: irradiated
EZA1226Adachi-1-6.jdf
SA04545 noe 2.11
j: irradiated
EZA1228Adachi-1-5.jdf
SA04545 noe 7.97
f: irradiated
EZA1229Adachi-1-5.jdf
SA04545 noe 7.80
a: irradiated
(thousandths)


EZA1224Adachi-1-3.jdf
SA04545 1H
(1b)2/Pd, 1D NOE, 298 K, CD3CN
abundance
f
c
a
e
h'
g'
f'
h
b
g
X : parts per Million : Proton
EZA1225Adachi-1-6.jdf
SA04545 noe 1.79
(thousandths)
f'
EZA1226Adachi-1-6.jdf
SA04545 noe 2.11
g
EZA1228Adachi-1-5.jdf
SA04545 noe 7.97
f: irradiated
a
EZA1229Adachi-1-5.jdf
SA04545 noe 7.80
f
a: irradiated
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2

*3-2-3. Stacked ^{1}H and ^{13}C NMR of **1b** and (**1b**)$_2$/Pd*

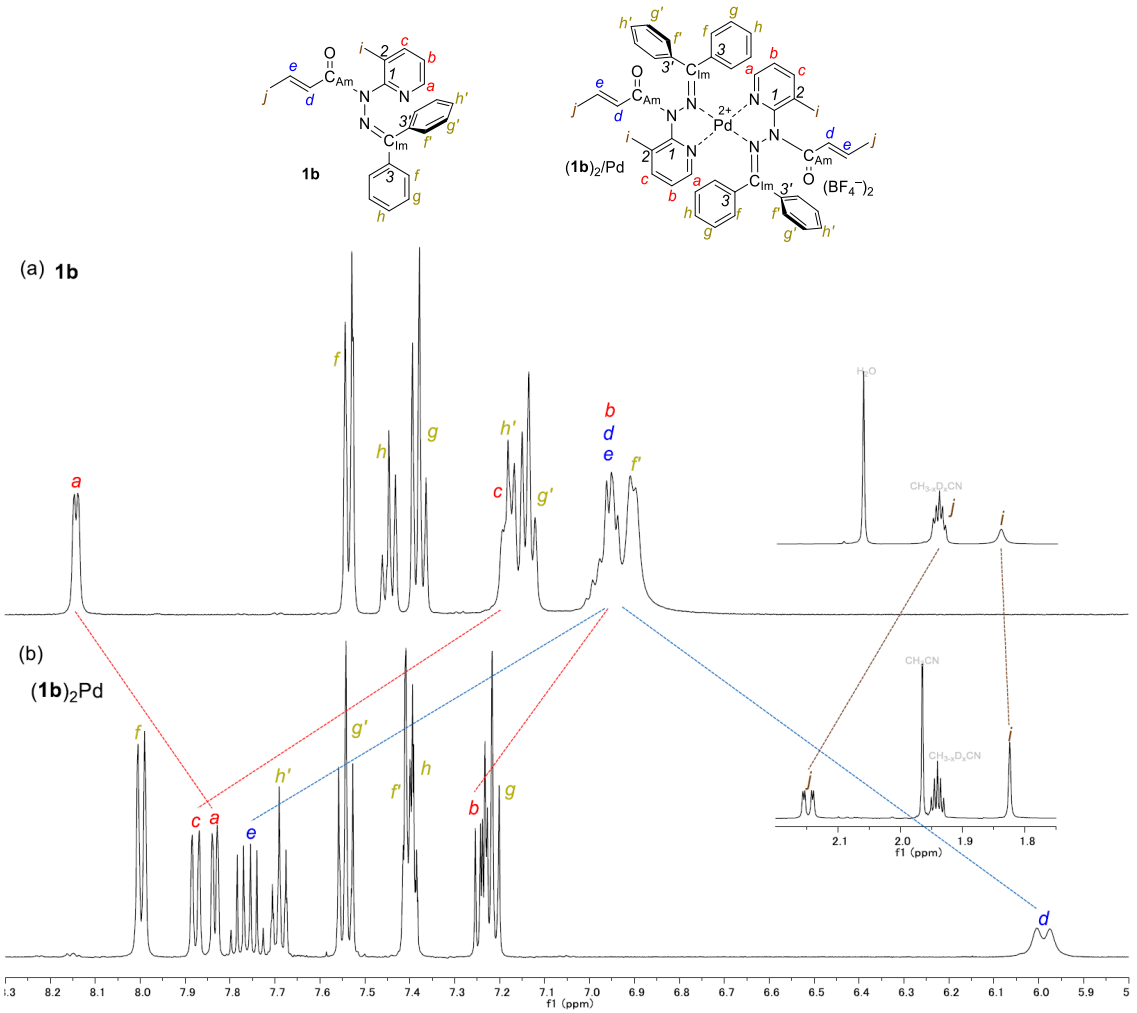


Figure S3. (a) ^{1}H NMR of **1b** in CD_3CN. (b) ^{1}H NMR of **1b**/$[Pd(CH_3CN)_4](BF_4)_2$ = 2/1 in CD_3CN. *f*▪*g*▪*h* and *f*′▪*g*′▪*h*′ are not distinguished in (a).

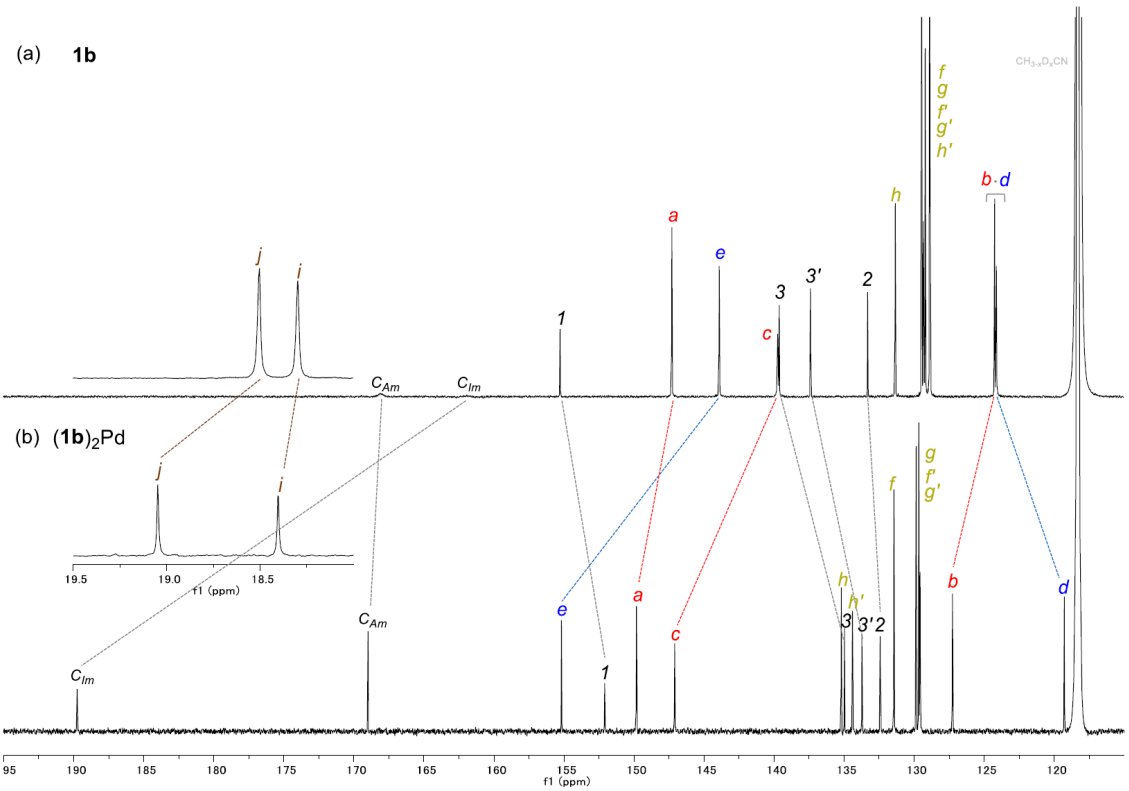
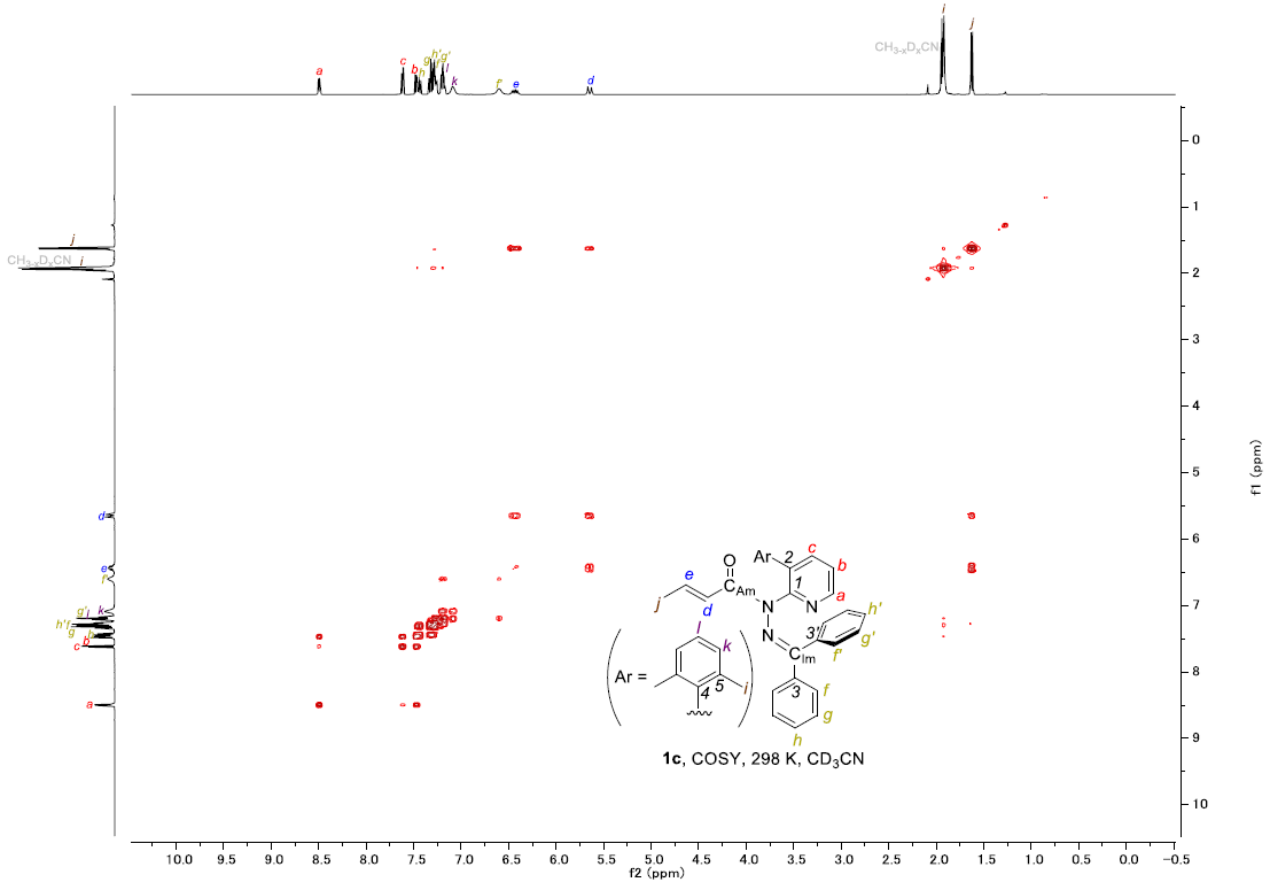
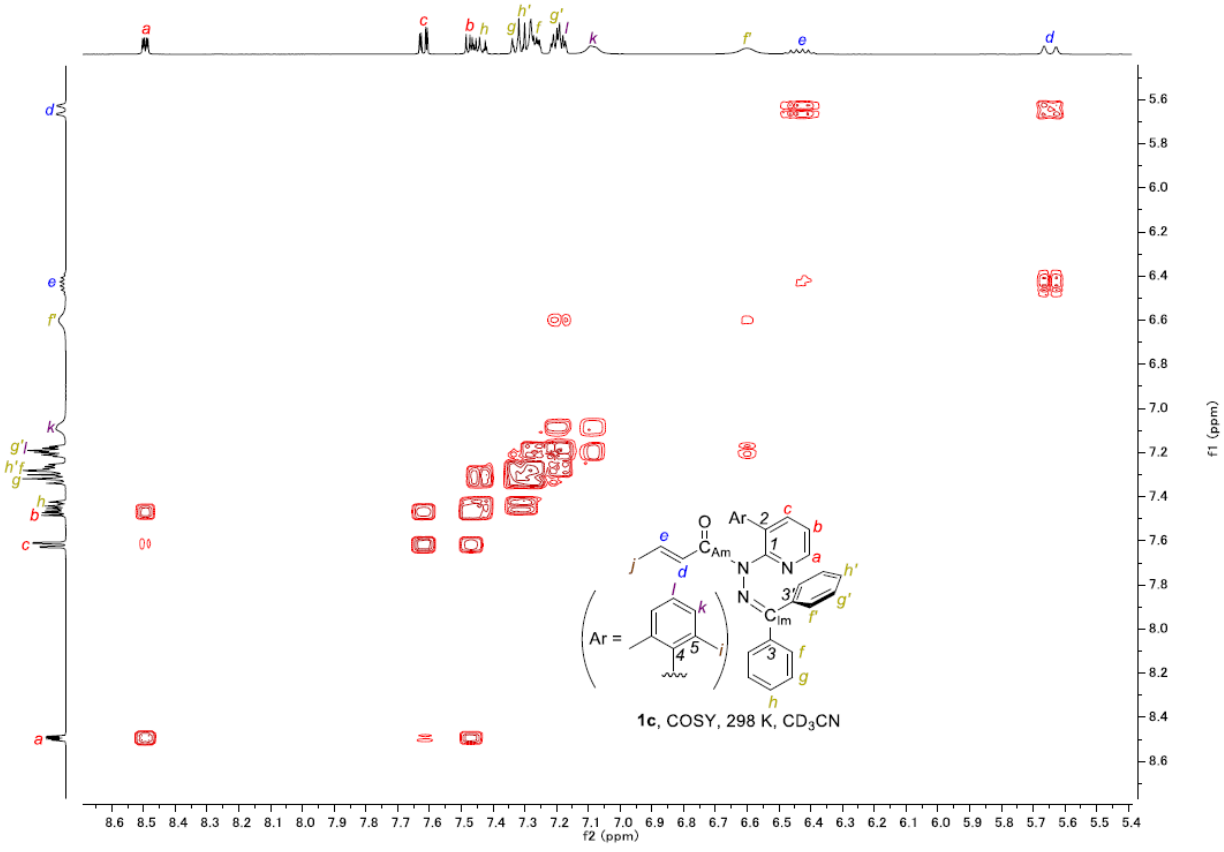


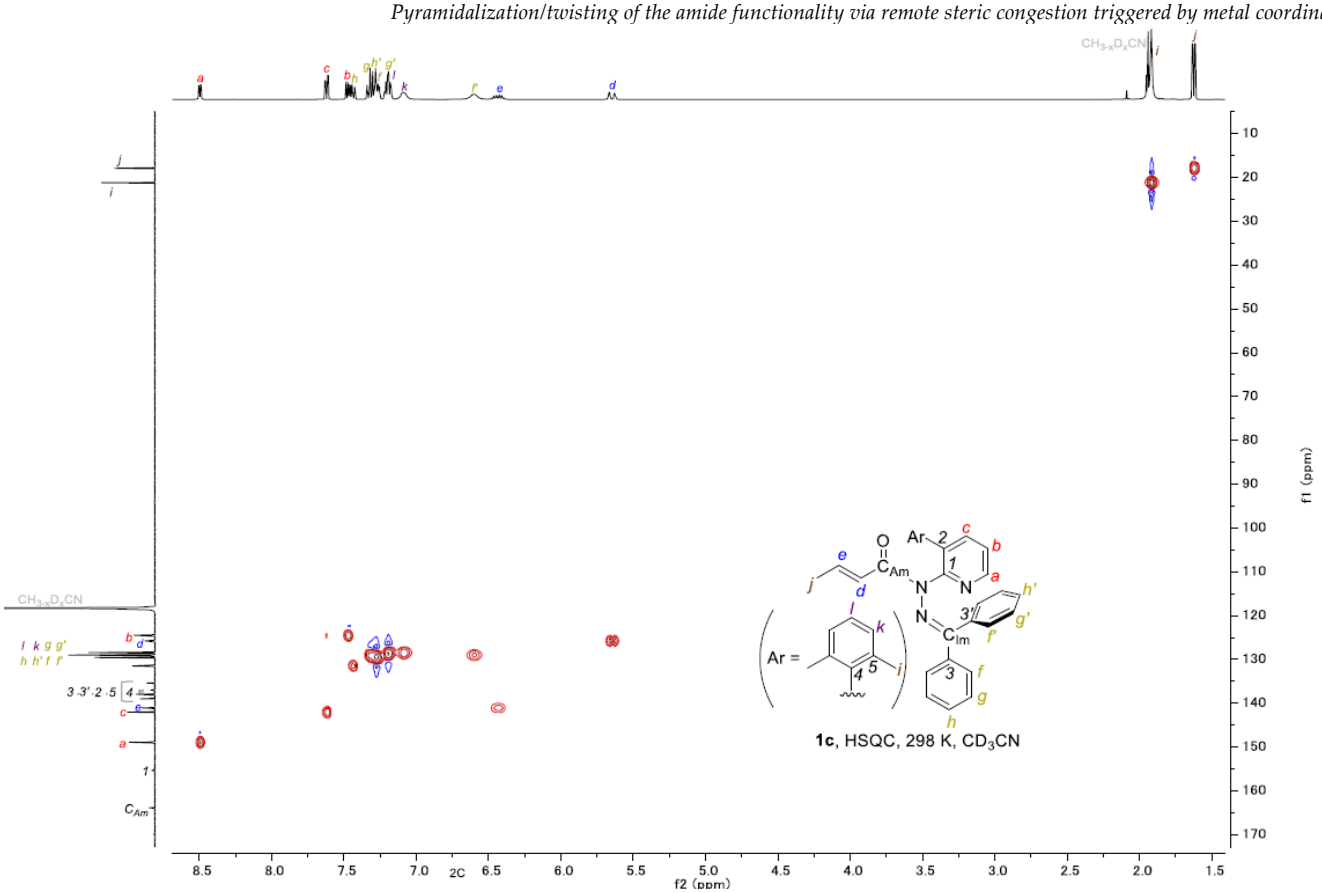
Figure S4. (a) ^{13}C NMR of **1b** in CD_3CN. (b) ^{13}C NMR of **1b**/$[Pd(CH_3CN)_4](BF_4)_2$ = 2/1 in CD_3CN. *f*▪*g*▪*h*▪3 and *f*′▪*g*′▪*h*′▪3′ are not distinguished in (a).

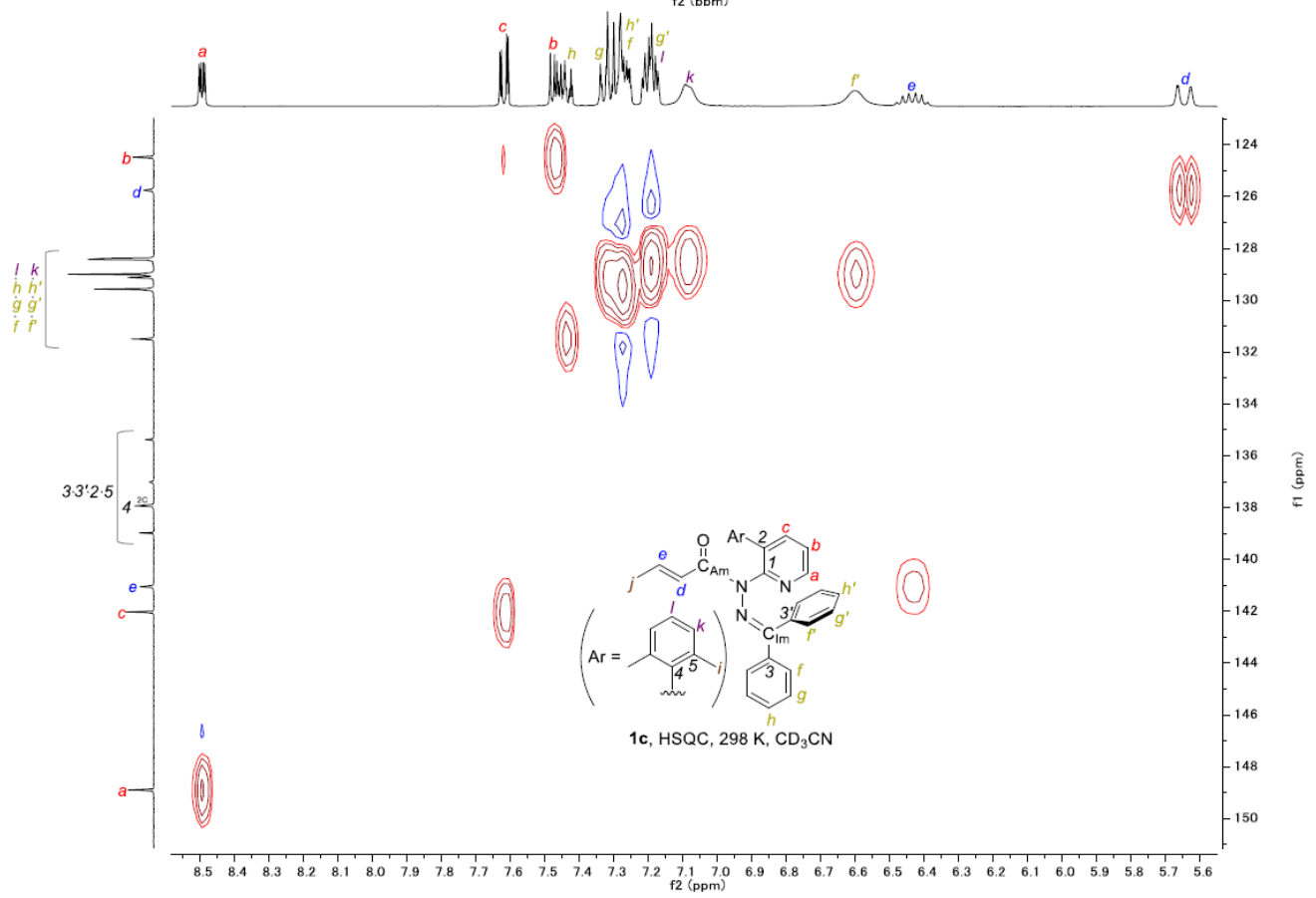
*3-1. **1c**–Pd Complex*

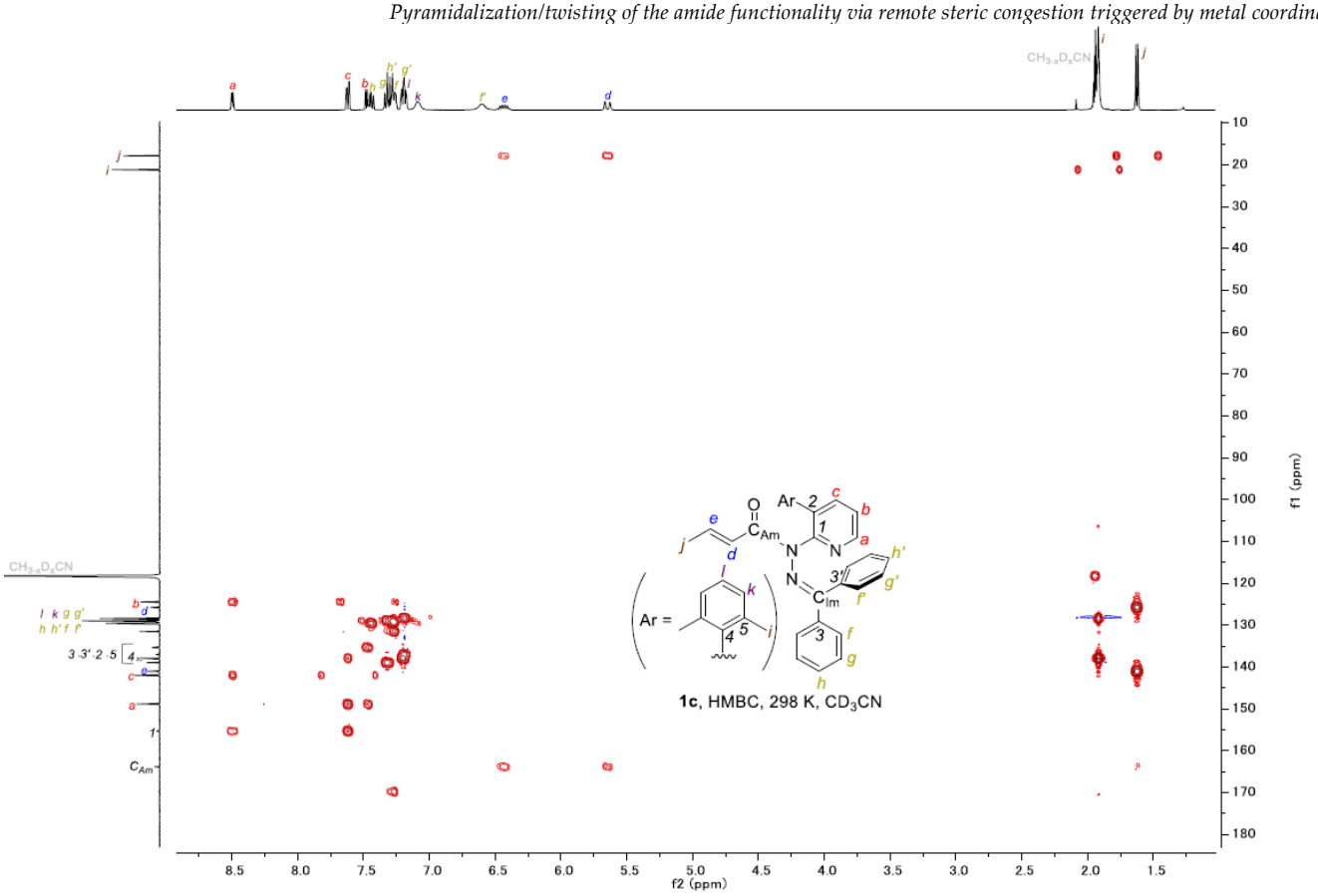
*3-3-1. Detailed NMR of **1c** for peak assignments*

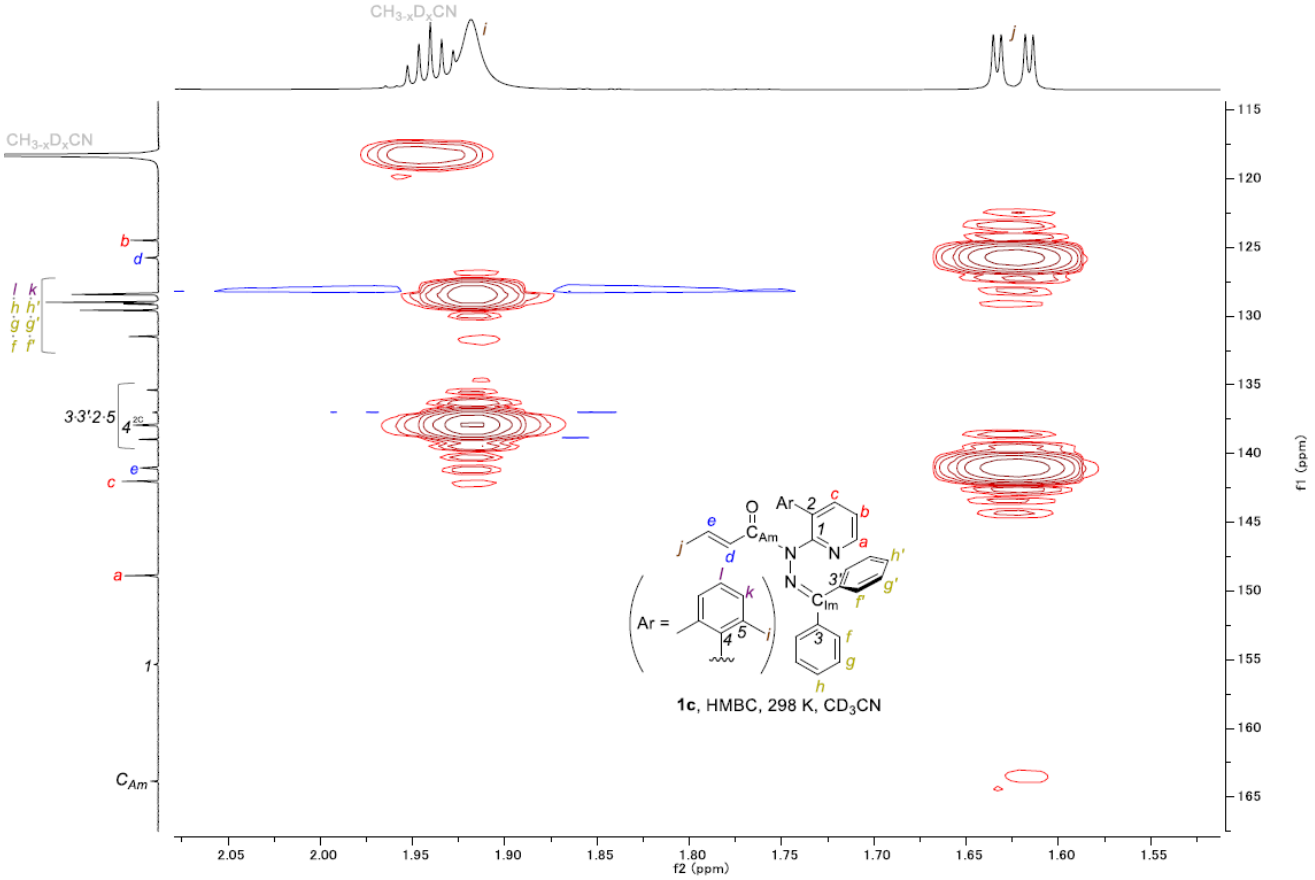


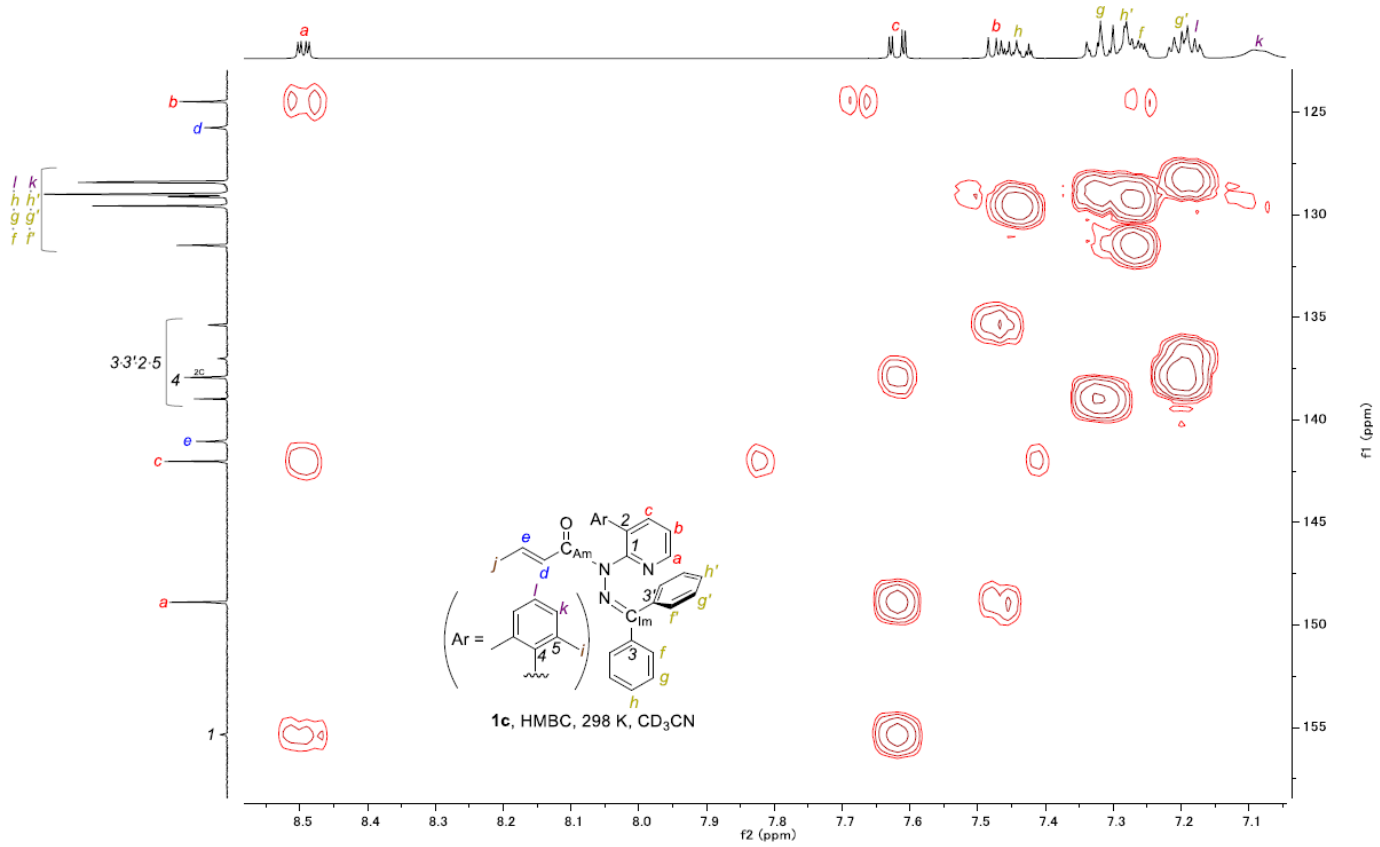



f2 (ppm)
f1 (ppm)
Ar =
1c, HSQC, 298 K, CD3CN

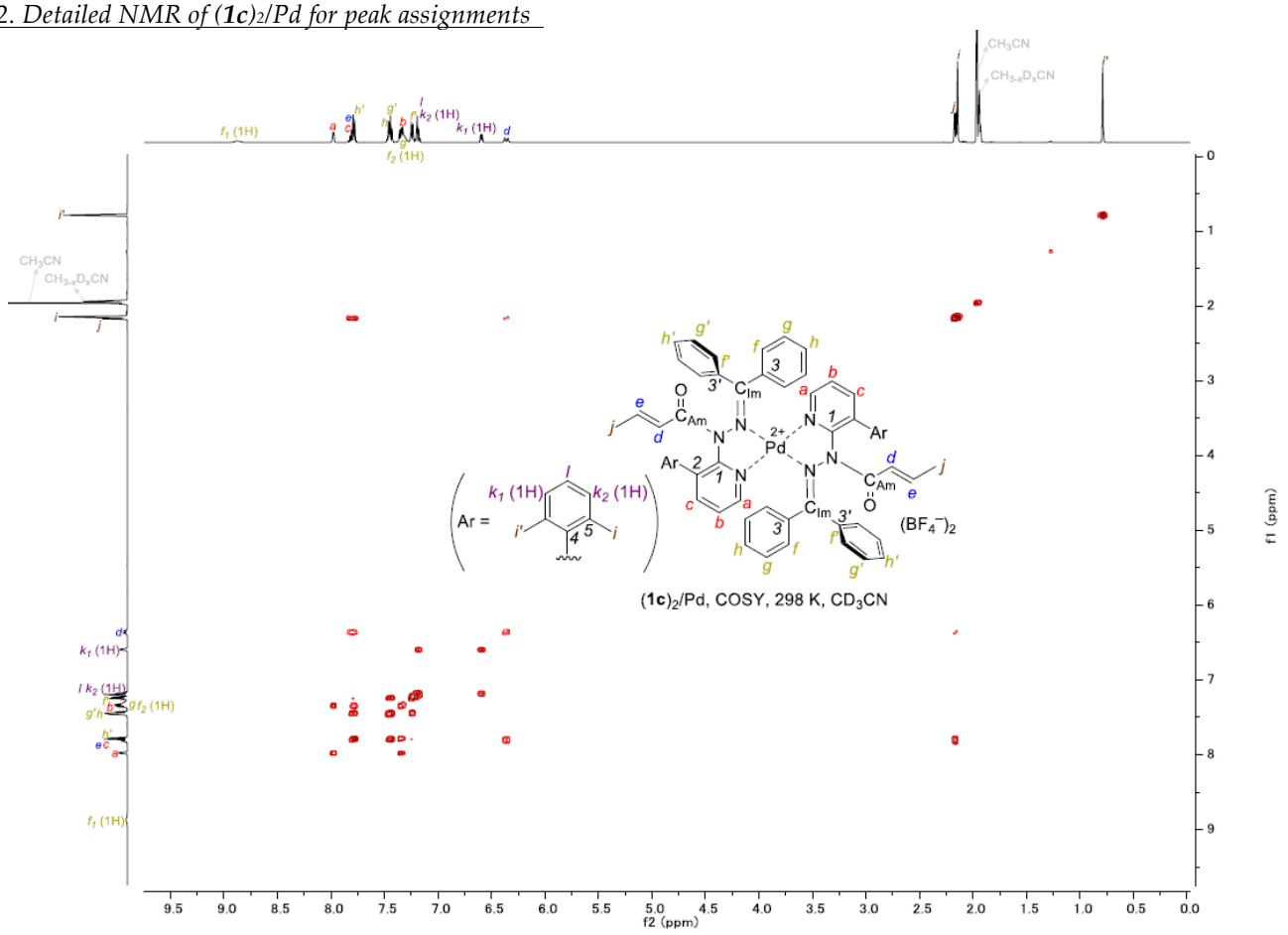

f2 (ppm)
f1 (ppm)
Ar =
1c, HSQC, 298 K, CD3CN

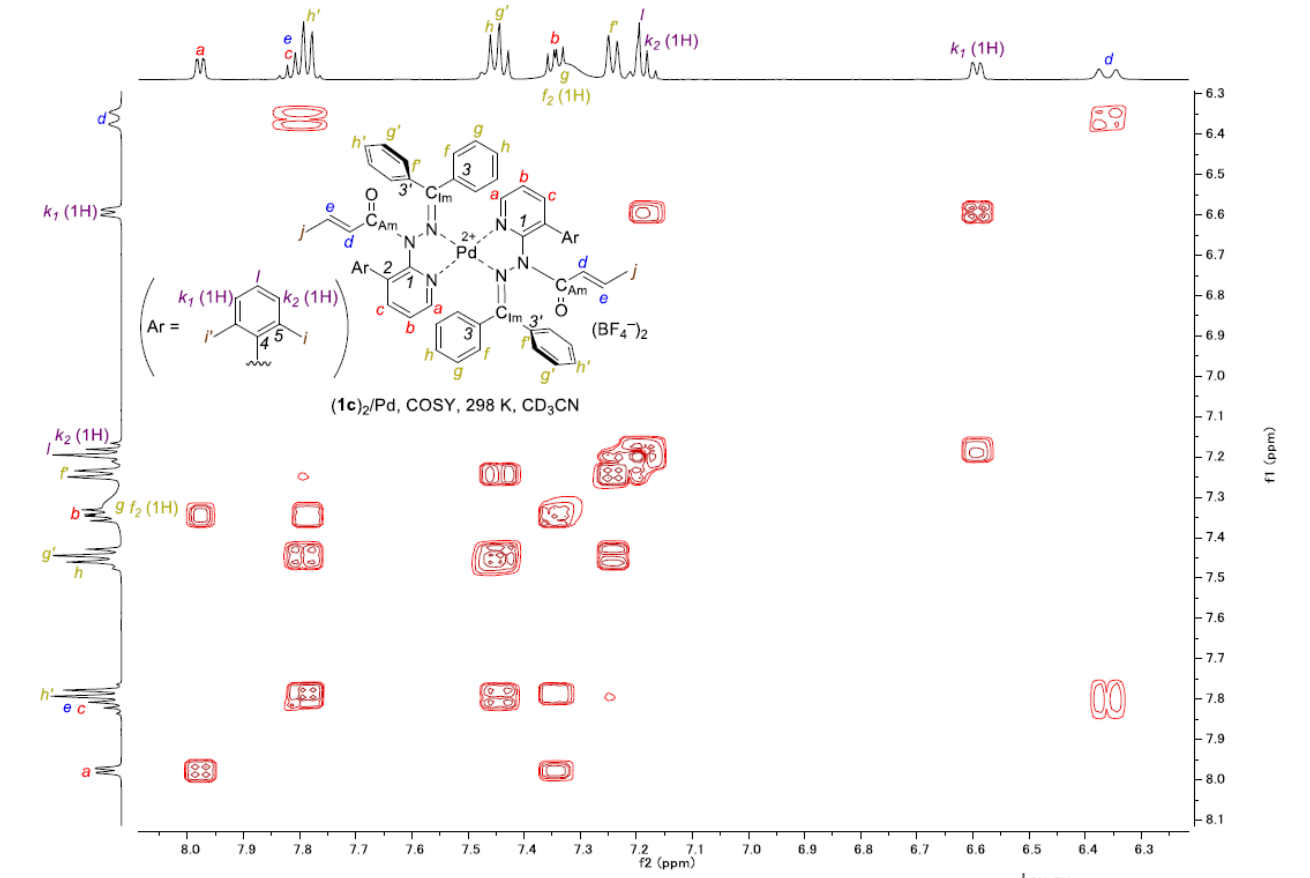

f2 (ppm)
f1 (ppm)
Ar =
1c, HMBC, 298 K, CD3CN

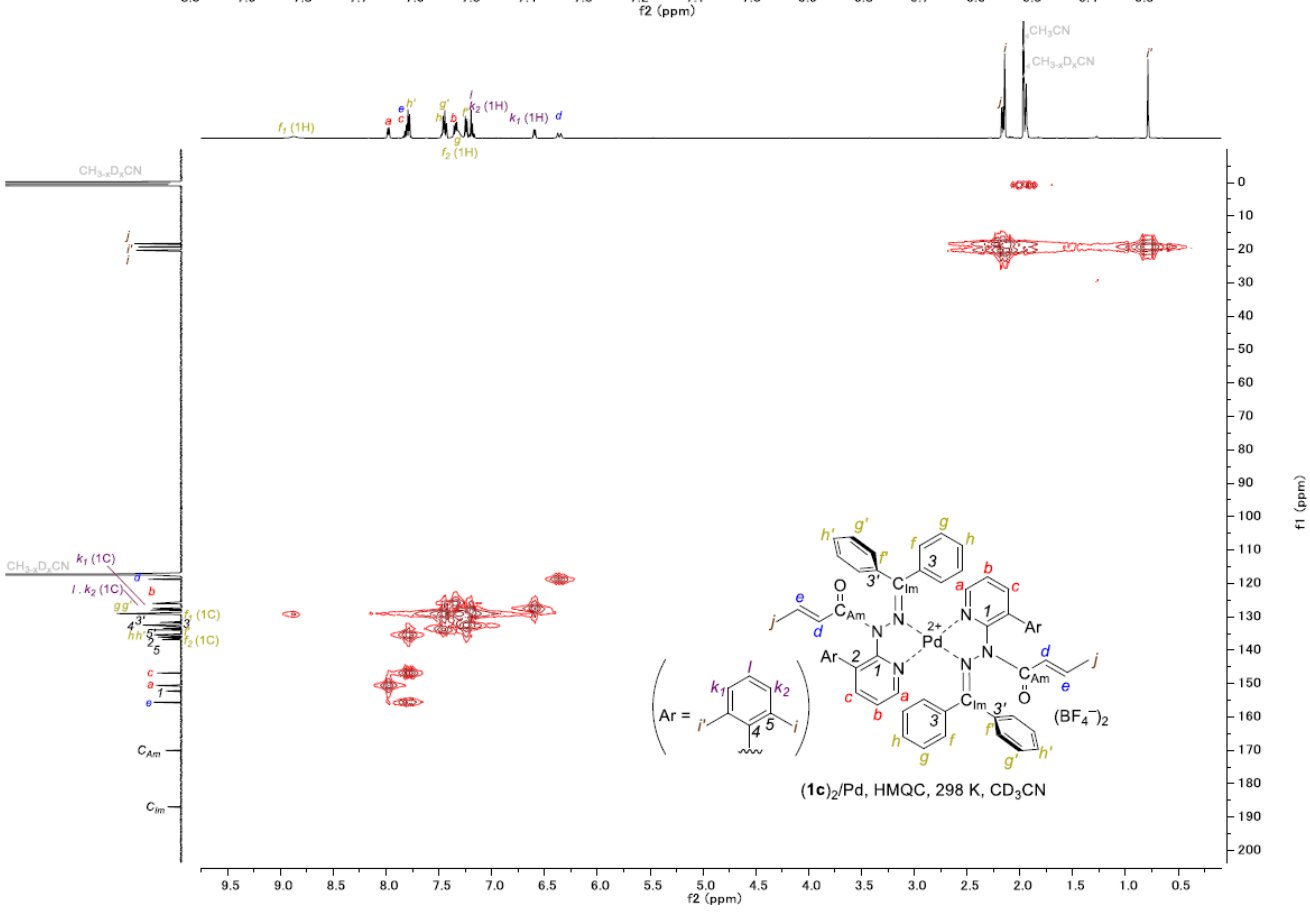

f2 (ppm)
f1 (ppm)
Ar =
1c, HMBC, 298 K, CD3CN

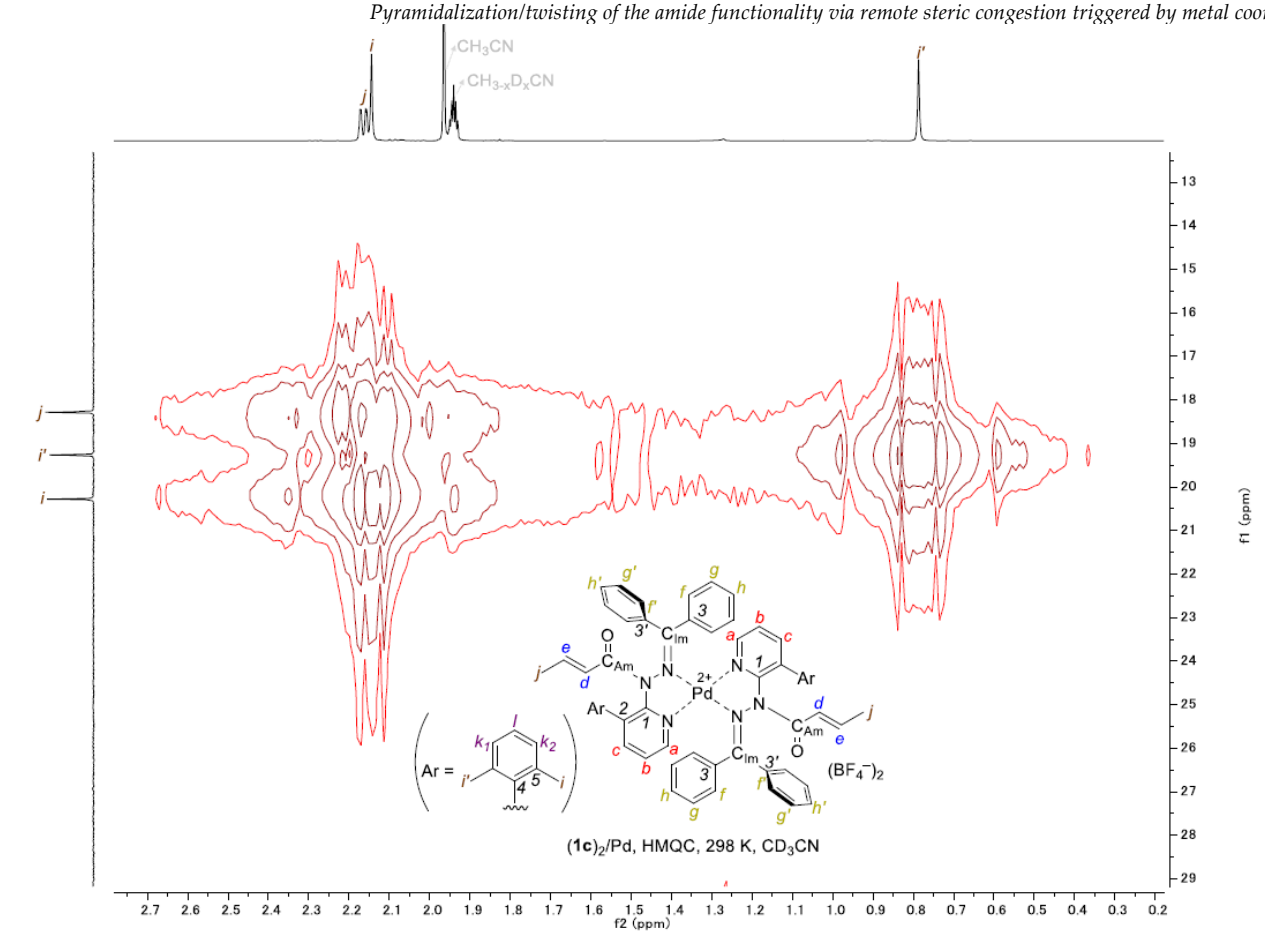


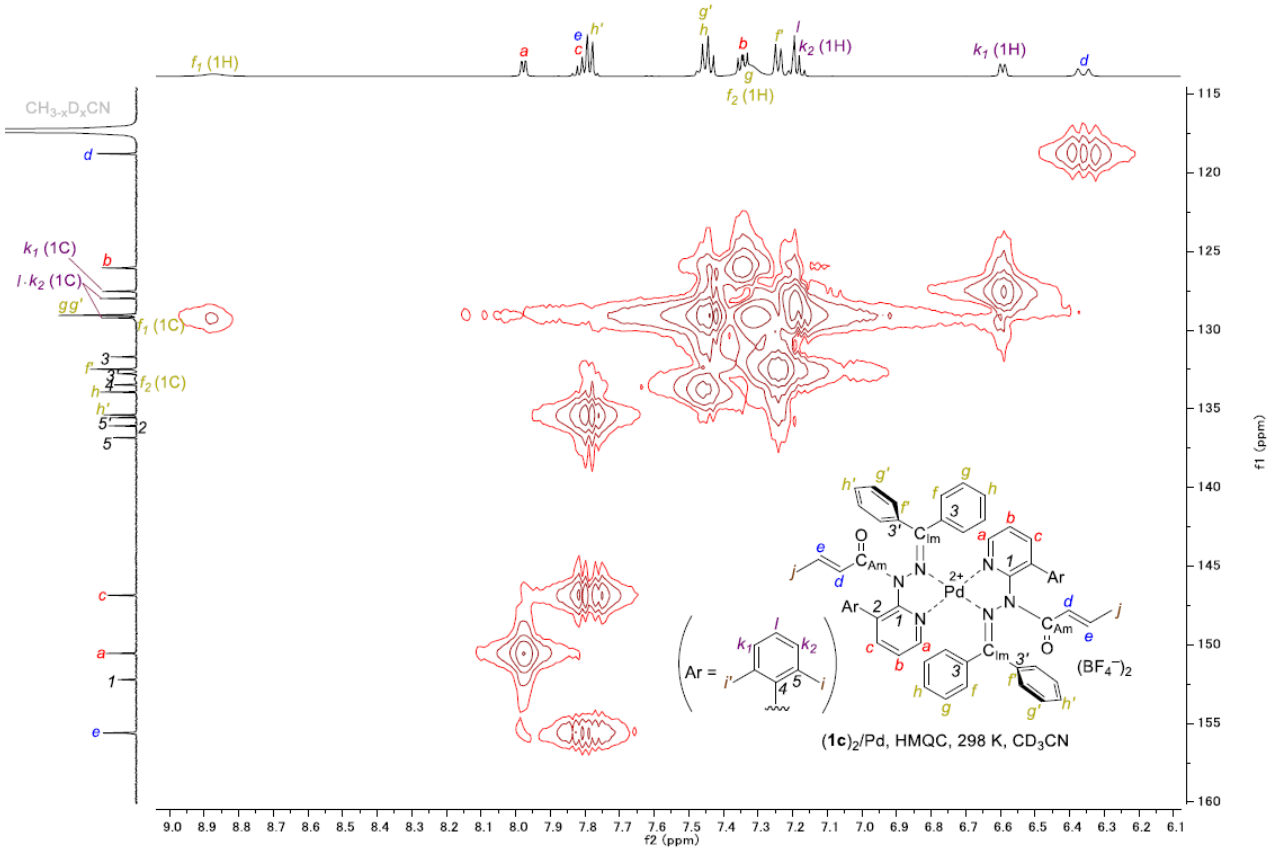
*3-3-2. Detailed NMR of (**1c**)$_2$/Pd for peak assignments*

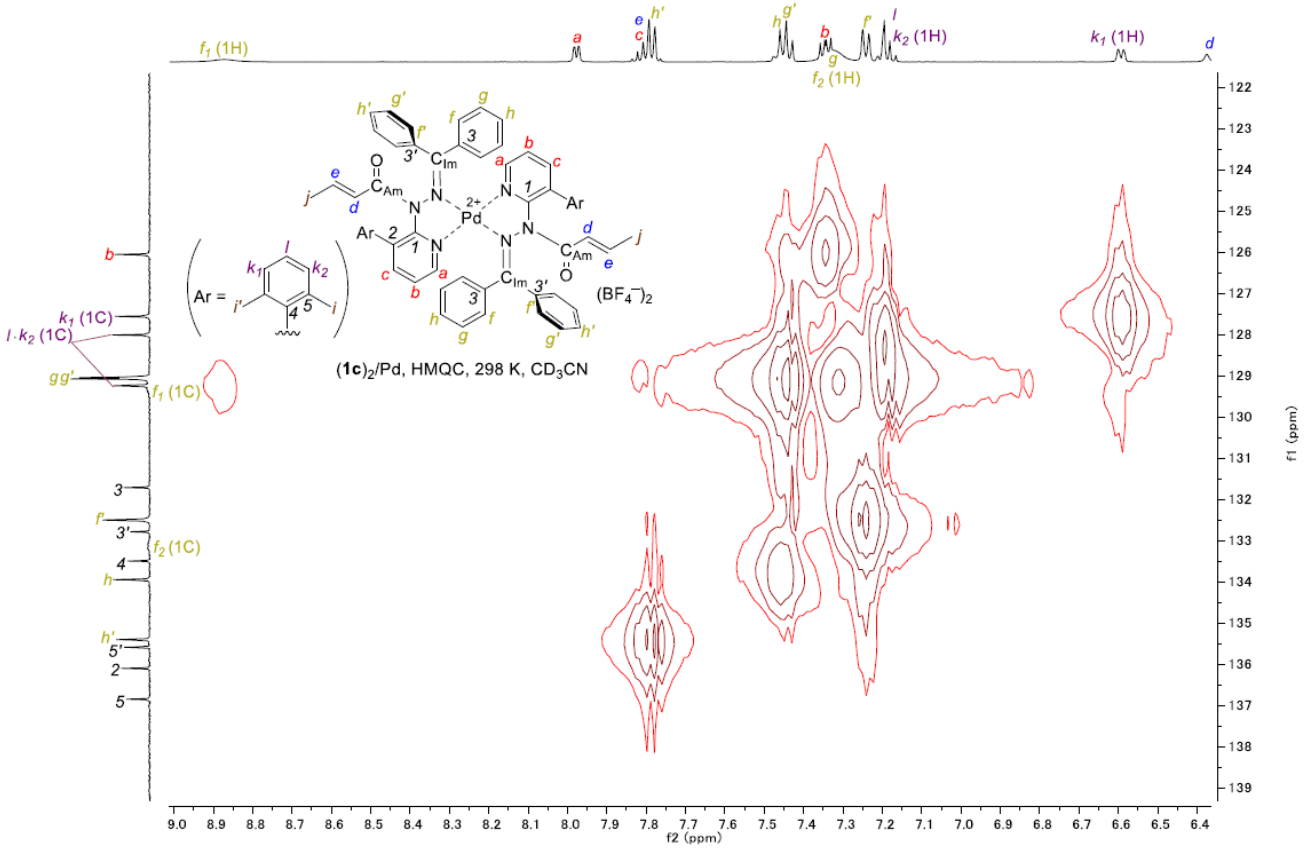


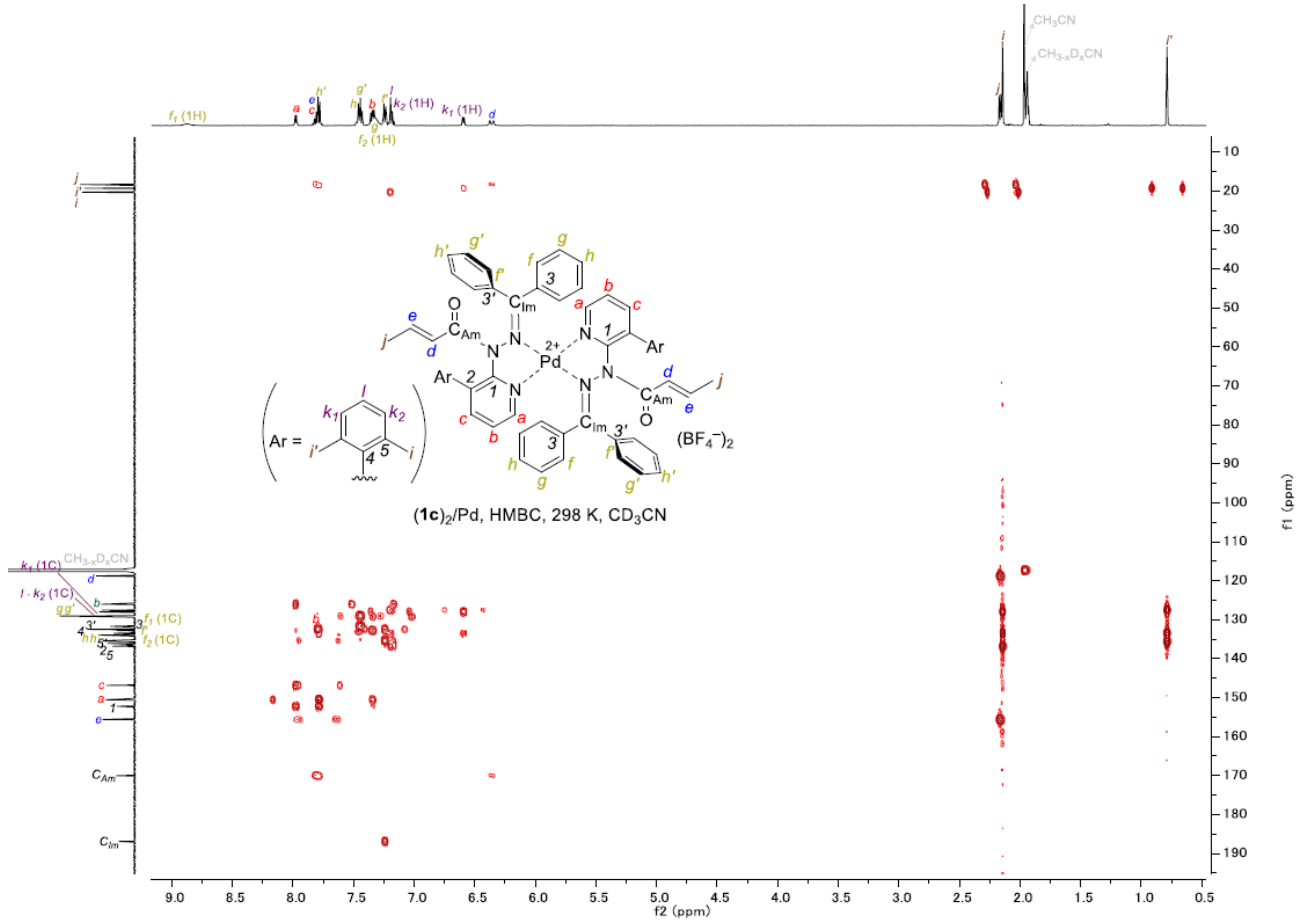

k1 (1H)
k2 (1H)
f2 (1H)
Ar =
(BF4−)2
(1c)2/Pd, COSY, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

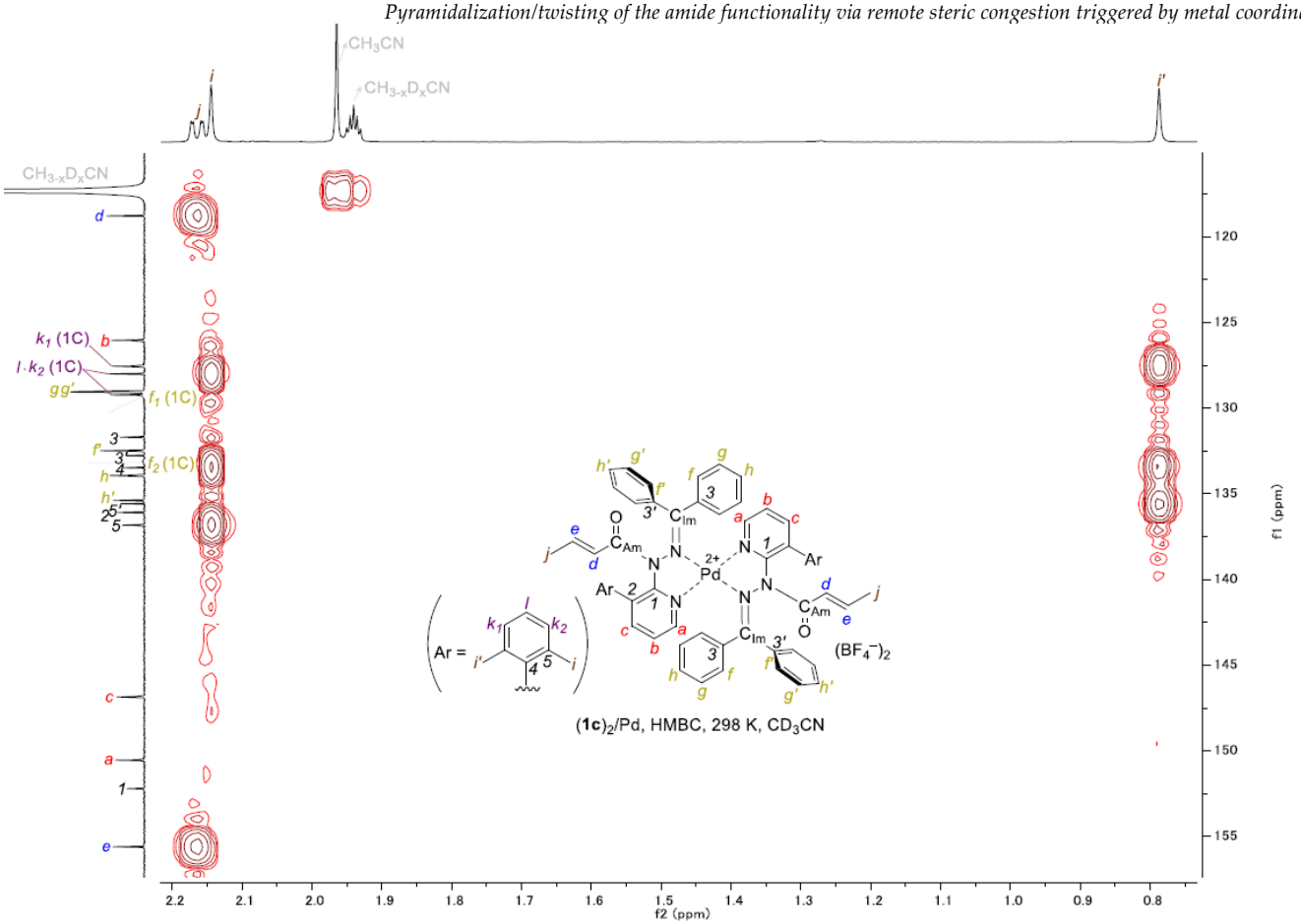

CH3-xDxCN
k1 (1C)
k2 (1C)
f1 (1C)
f2 (1C)
CAm
CIm
Ar =
(BF4−)2
(1c)2/Pd, HMQC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

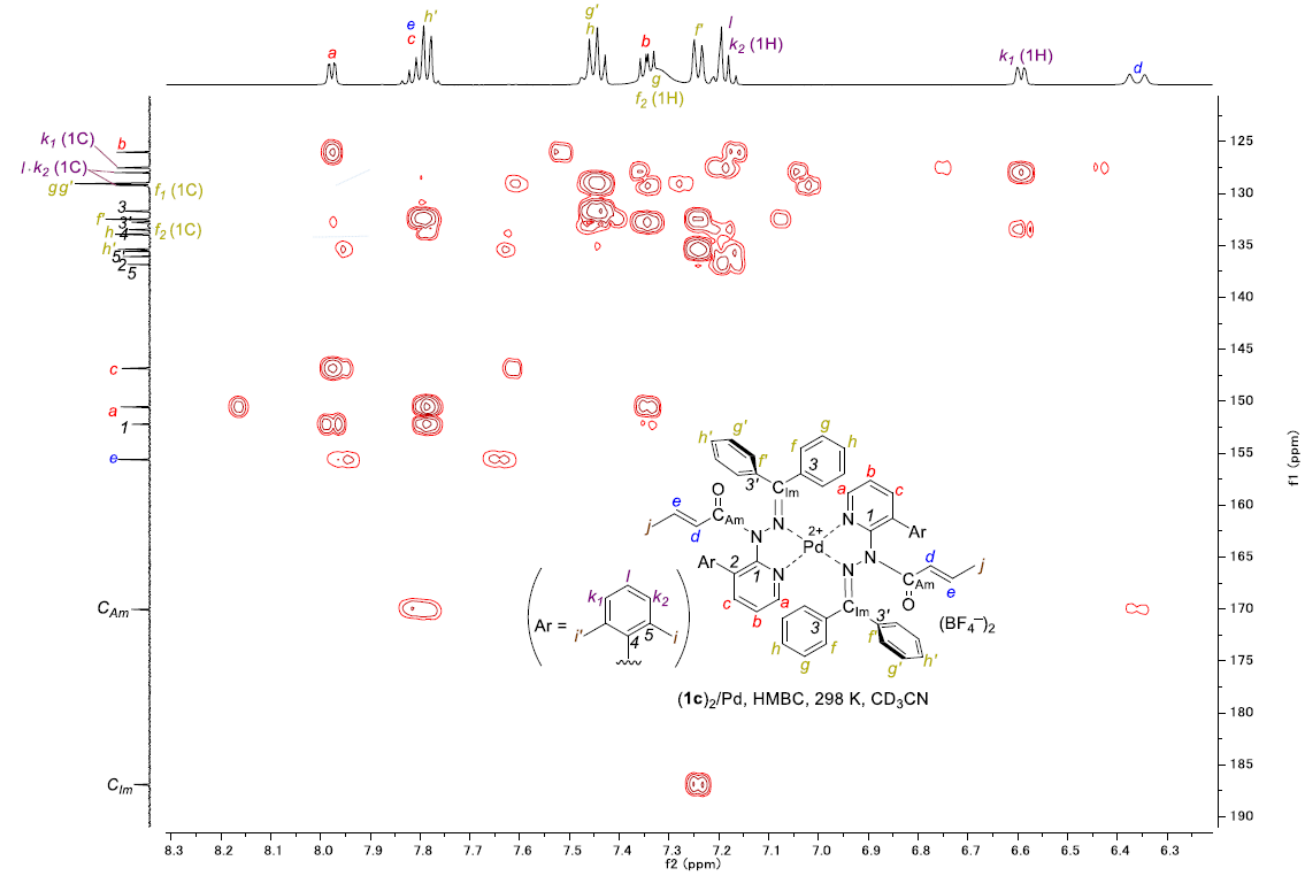

i
i'
j
CH3CN
CH3-xDxCN
f1 (ppm)
f2 (ppm)
Ar =
(BF4−)2
(1c)2/Pd, HMQC, 298 K, CD3CN

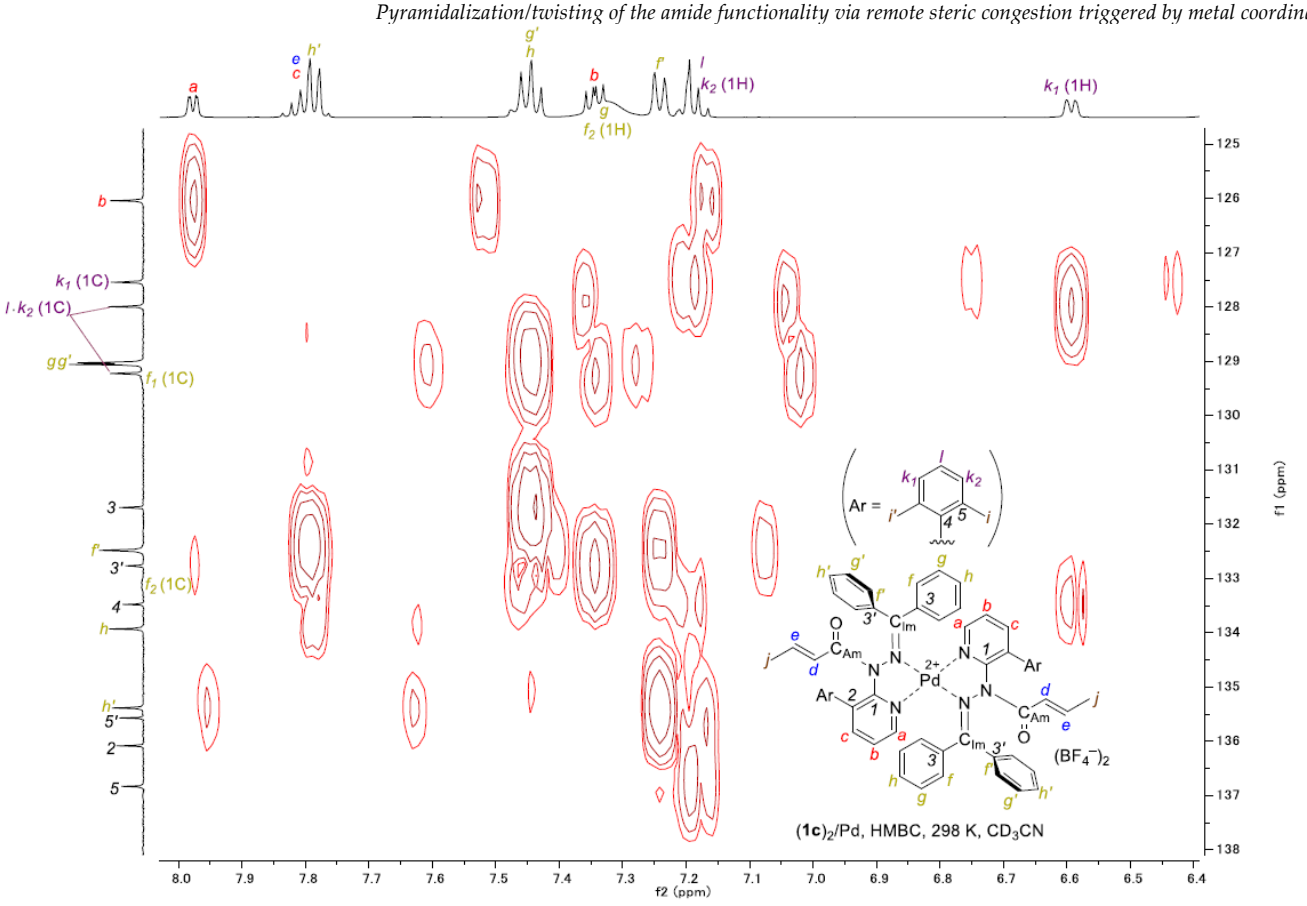

f1 (1H)
f2 (1H)
k1 (1H)
k2 (1H)
CH3-xDxCN
k1 (1C)
l·k2 (1C)
gg'
f1 (1C)
f2 (1C)
f1 (ppm)
f2 (ppm)
Ar =
(BF4−)2
(1c)2/Pd, HMQC, 298 K, CD3CN

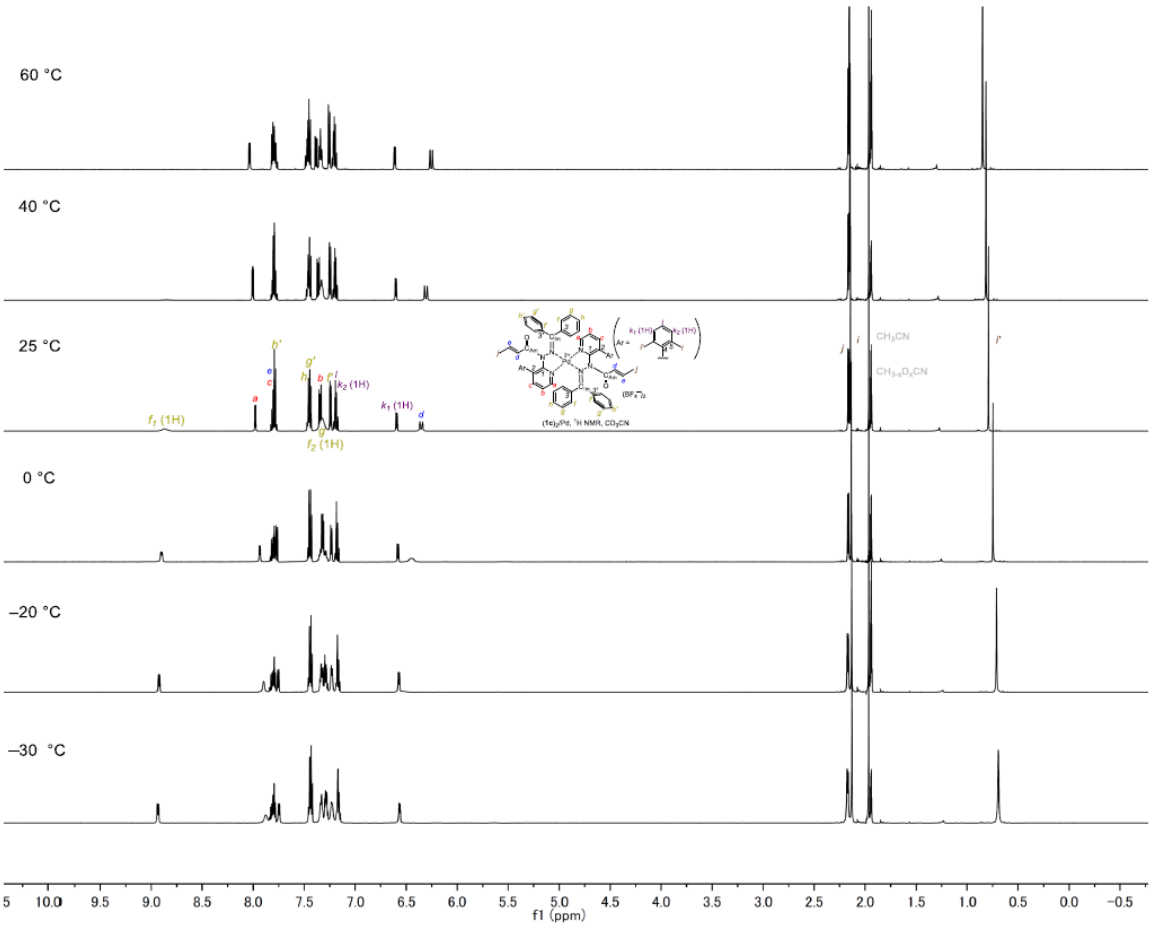

(1c)2/Pd, HMQC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

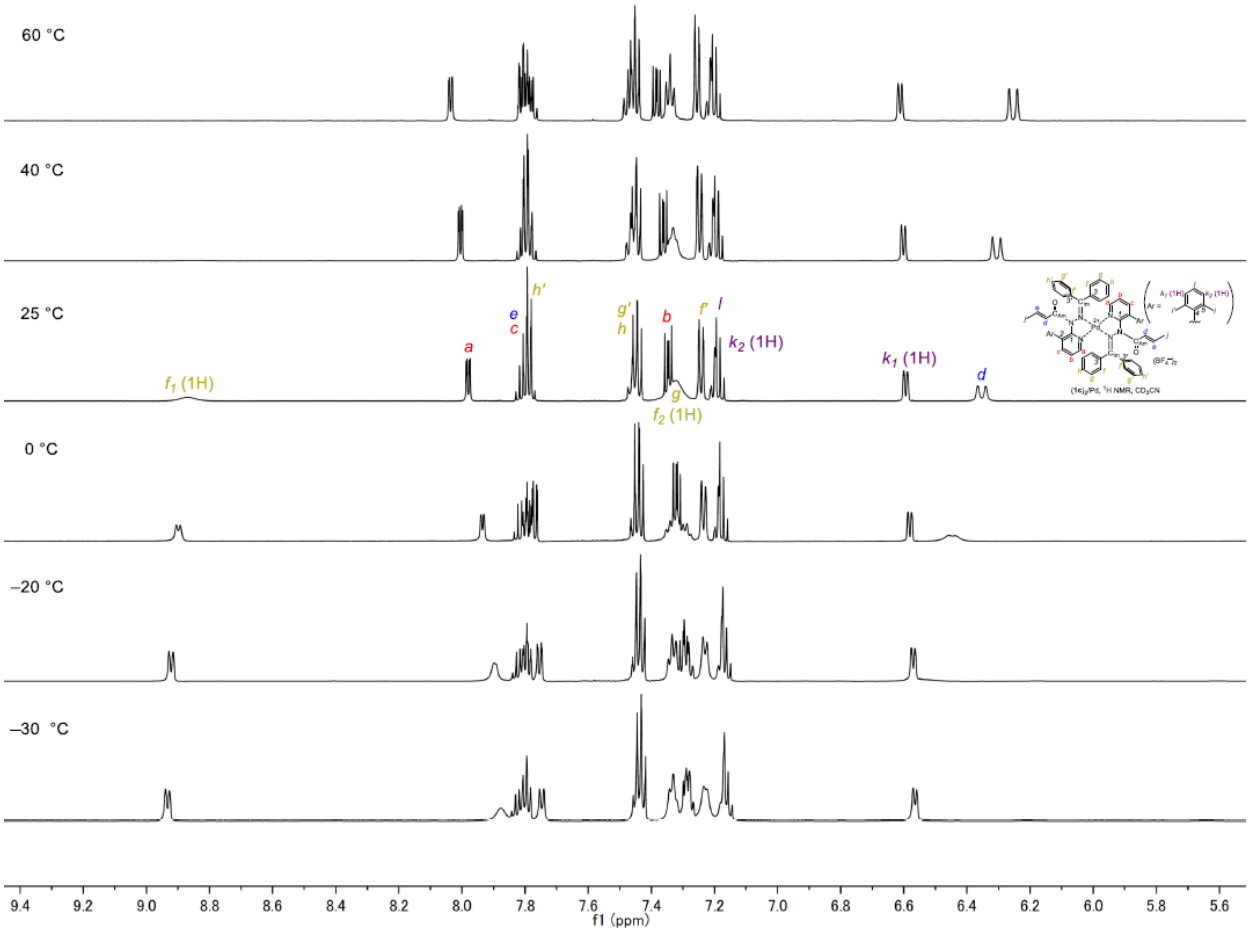

(1c)2/Pd, HMBC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

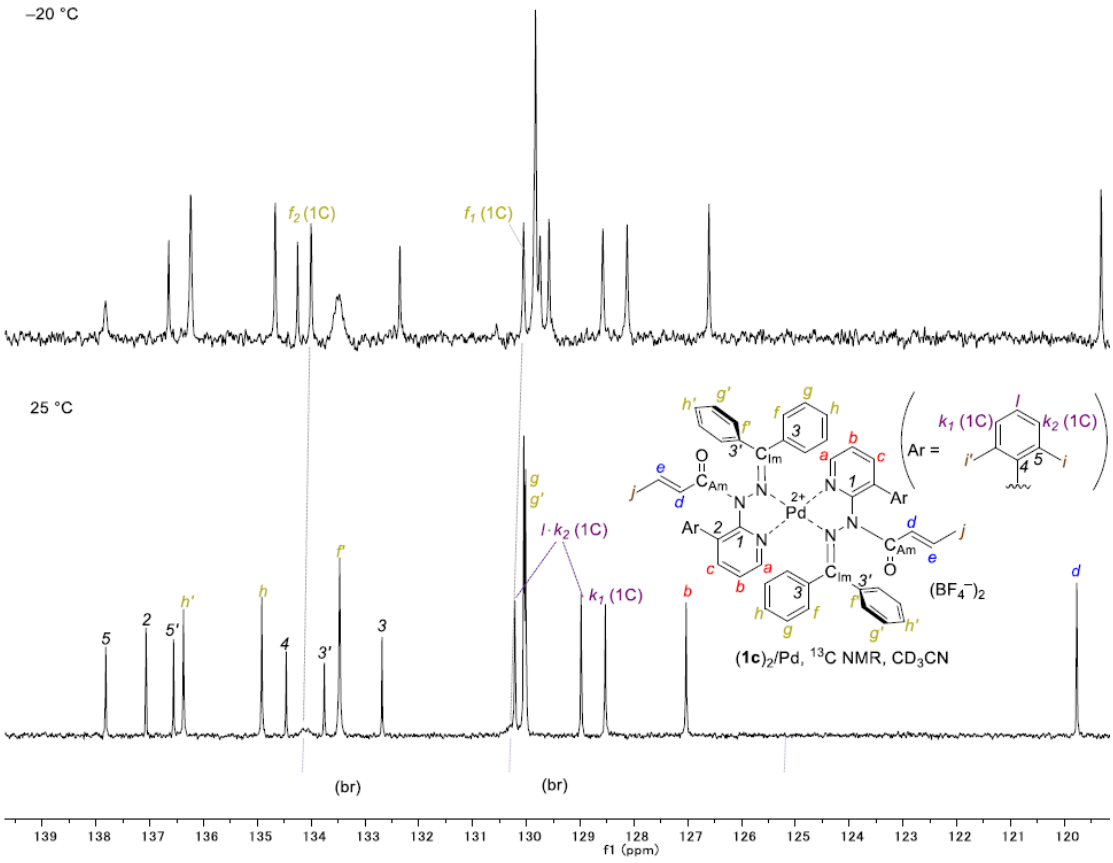

CH3CN
CH3-xDxCN
f2 (ppm)
f1 (ppm)
(1c)2/Pd, HMBC, 298 K, CD3CN

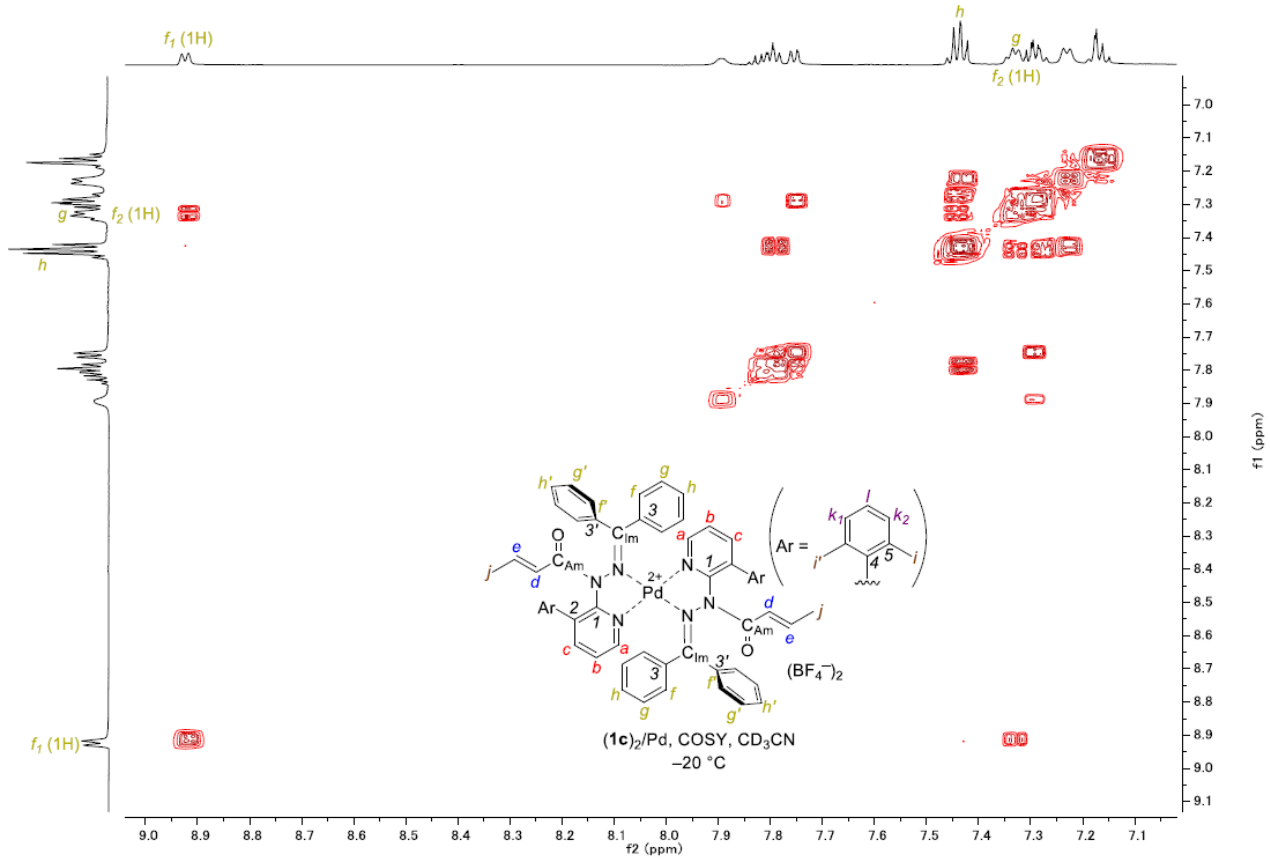

f2 (1H)
f2 (ppm)
f1 (ppm)
(1c)2/Pd, HMBC, 298 K, CD3CN

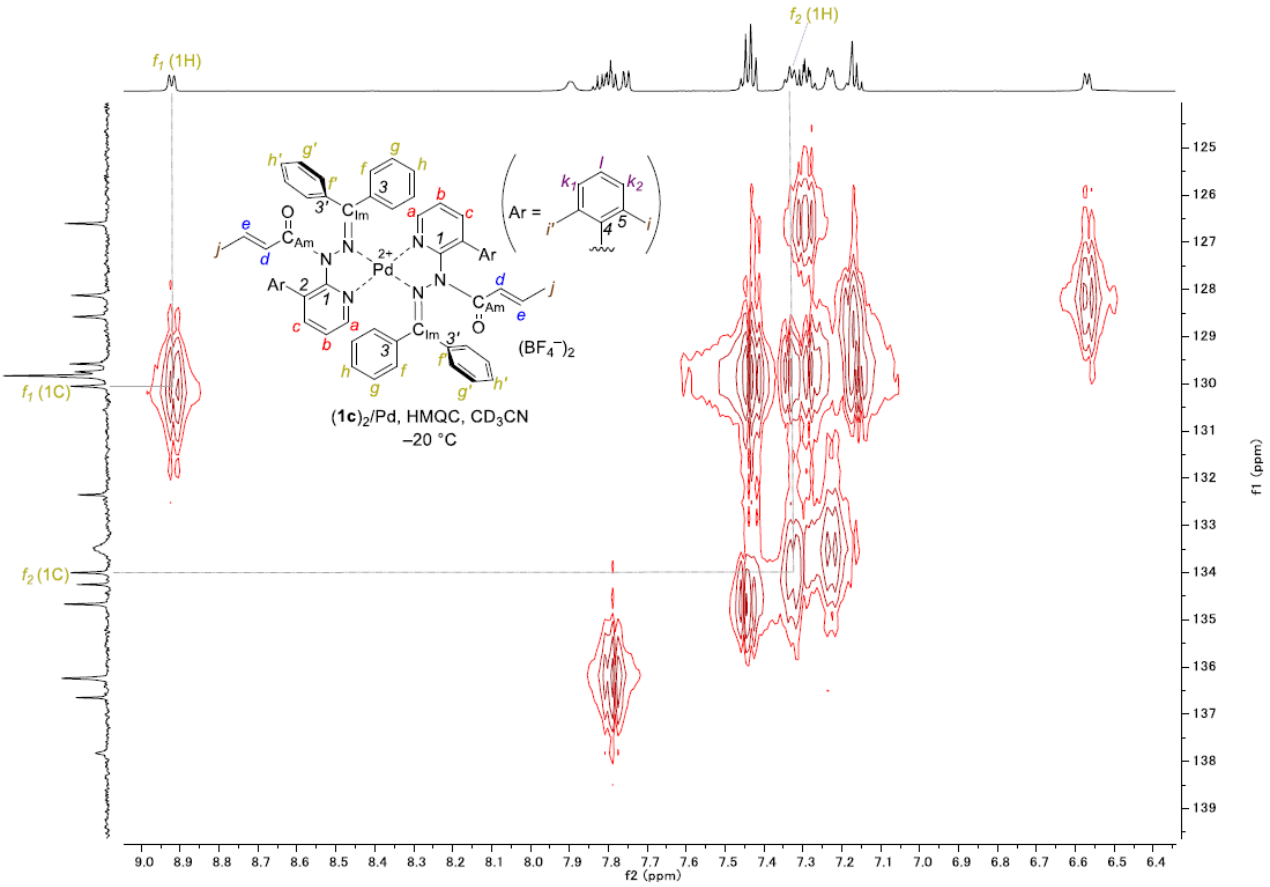

(1c)2/Pd, HMBC, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

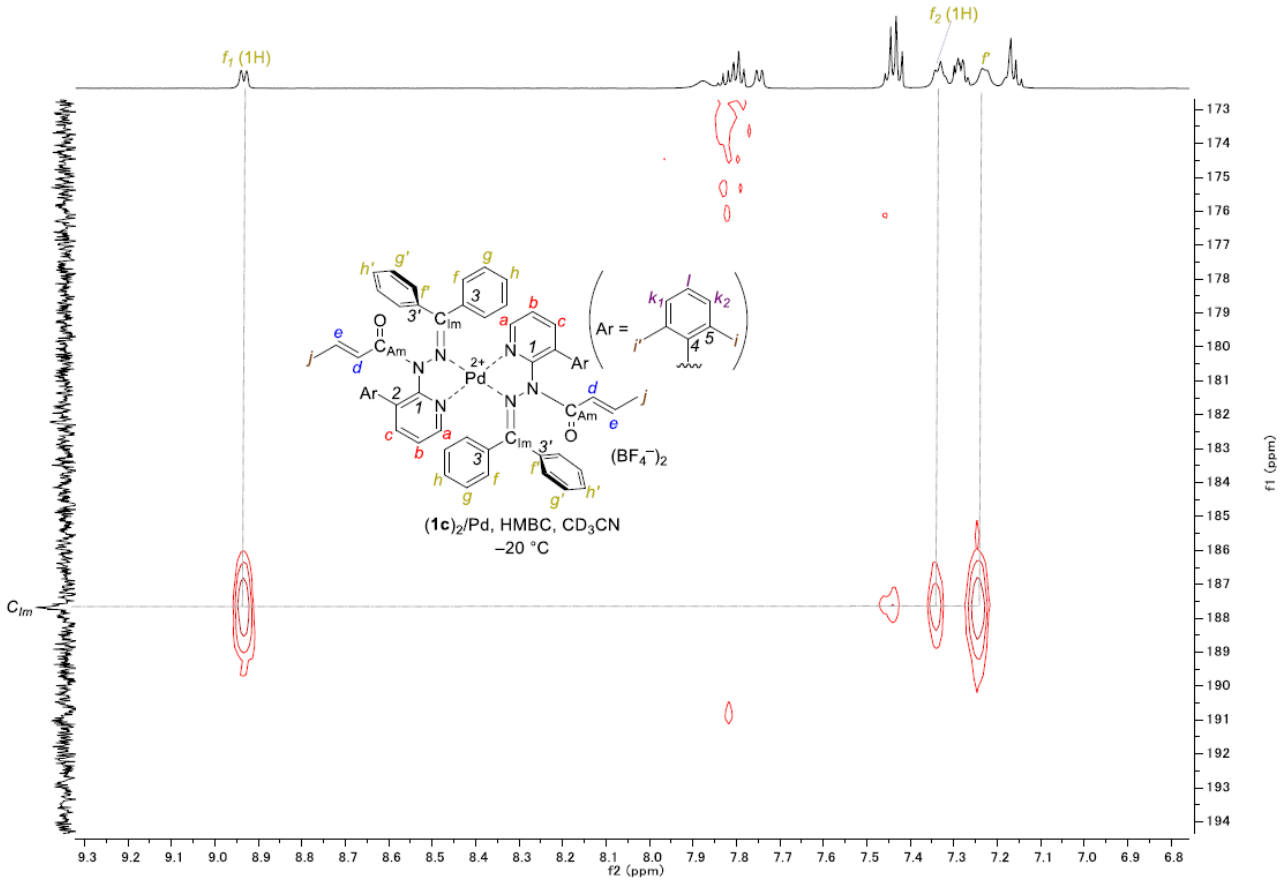

60 °C
40 °C
25 °C
0 °C
–20 °C
–30 °C
f1 (ppm)

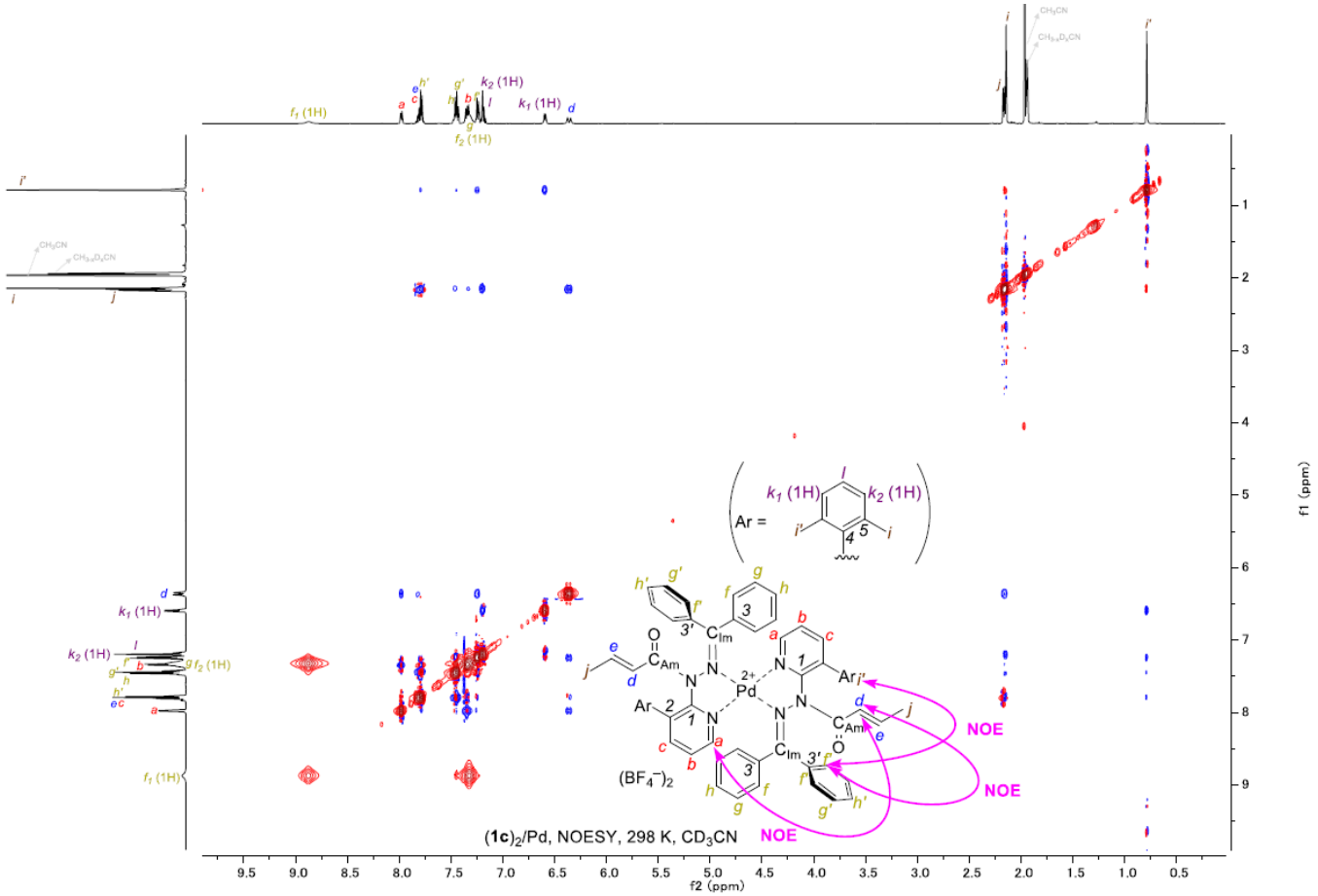

60 °C
40 °C
25 °C
0 °C
–20 °C
–30 °C
f1 (1H)
a
e
c
h'
g'
h
b
g
f'
l
k2 (1H)
f2 (1H)
k1 (1H)
d
(1c)2Pd, 1H NMR, CD3CN
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6
f1 (ppm)

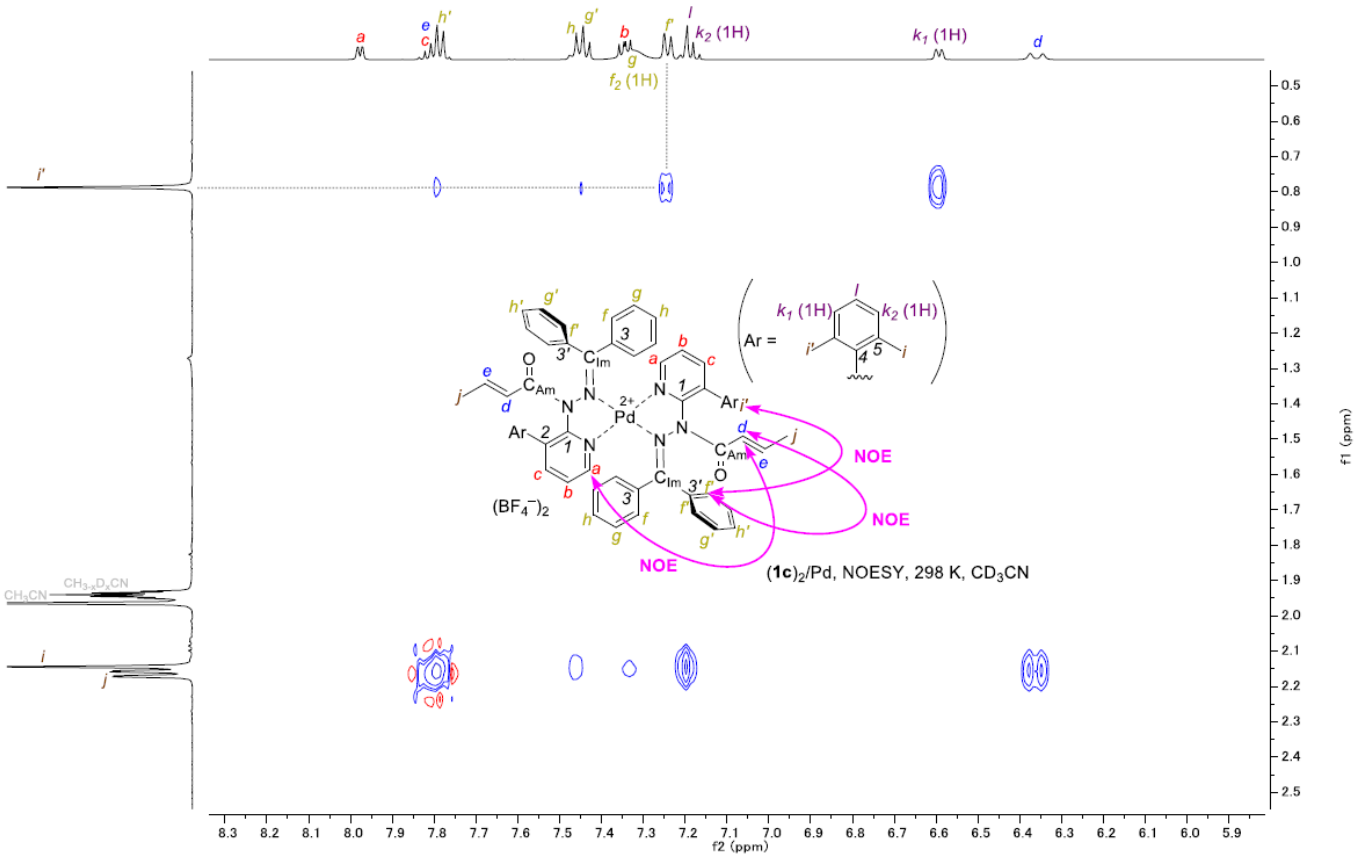

–20 °C
f2 (1C)
f1 (1C)
25 °C
l·k2 (1C)
k1 (1C)
5
2
5'
h'
h
4
3'
f'
3
(br)
(br)
k1 (1C)
k2 (1C)
Ar =
i'
i
(BF4–)2
(1c)2/Pd, 13C NMR, CD3CN
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)

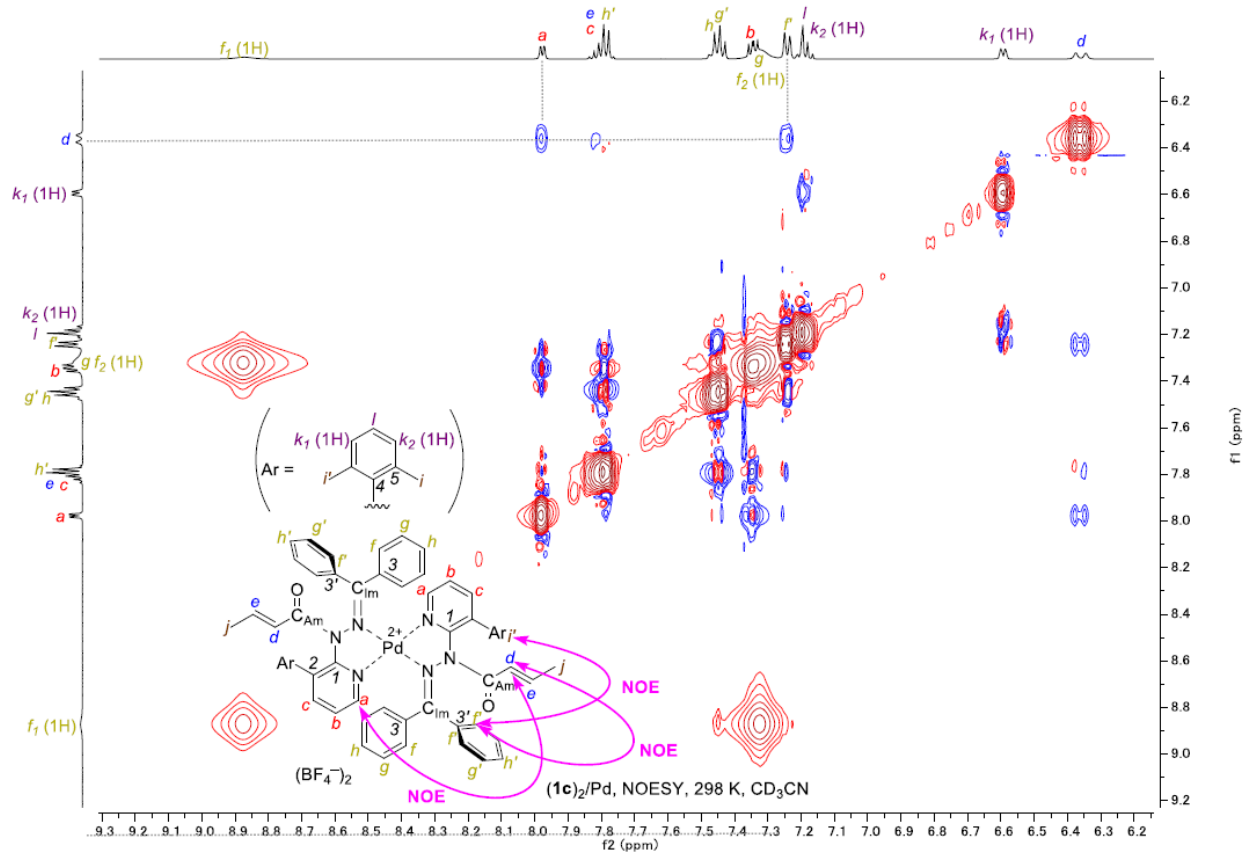

f1 (1H)
f2 (1H)
g
h
f2 (1H)
f1 (1H)
f2 (ppm)
f1 (ppm)
Ar =
(BF4−)2
(1c)2/Pd, COSY, CD3CN
–20 °C


f2 (1H)
f1 (1H)
f1 (1C)
f2 (1C)
f2 (ppm)
f1 (ppm)
Ar =
(BF4−)2
(1c)2/Pd, HMQC, CD3CN
–20 °C


f2 (1H)
f1 (1H)
Ar =
(1c)2/Pd, HMBC, CD3CN
–20 °C
(BF4−)2
CIm
f2 (ppm)
f1 (ppm)


k1 (1H)
k2 (1H)
Ar =
NOE
NOE
NOE
(1c)2/Pd, NOESY, 298 K, CD3CN
(BF4−)2
f2 (ppm)
f1 (ppm)


NOE
NOE
NOE
(1c)2/Pd, NOESY, 298 K, CD3CN
f2 (ppm)
f1 (ppm)


NOE
NOE
NOE
(1c)2/Pd, NOESY, 298 K, CD3CN
f2 (ppm)
f1 (ppm)

*3-3-3. Stacked ^{1}H and ^{13}C NMR of **1c** and (**1c**)$_2$/Pd*

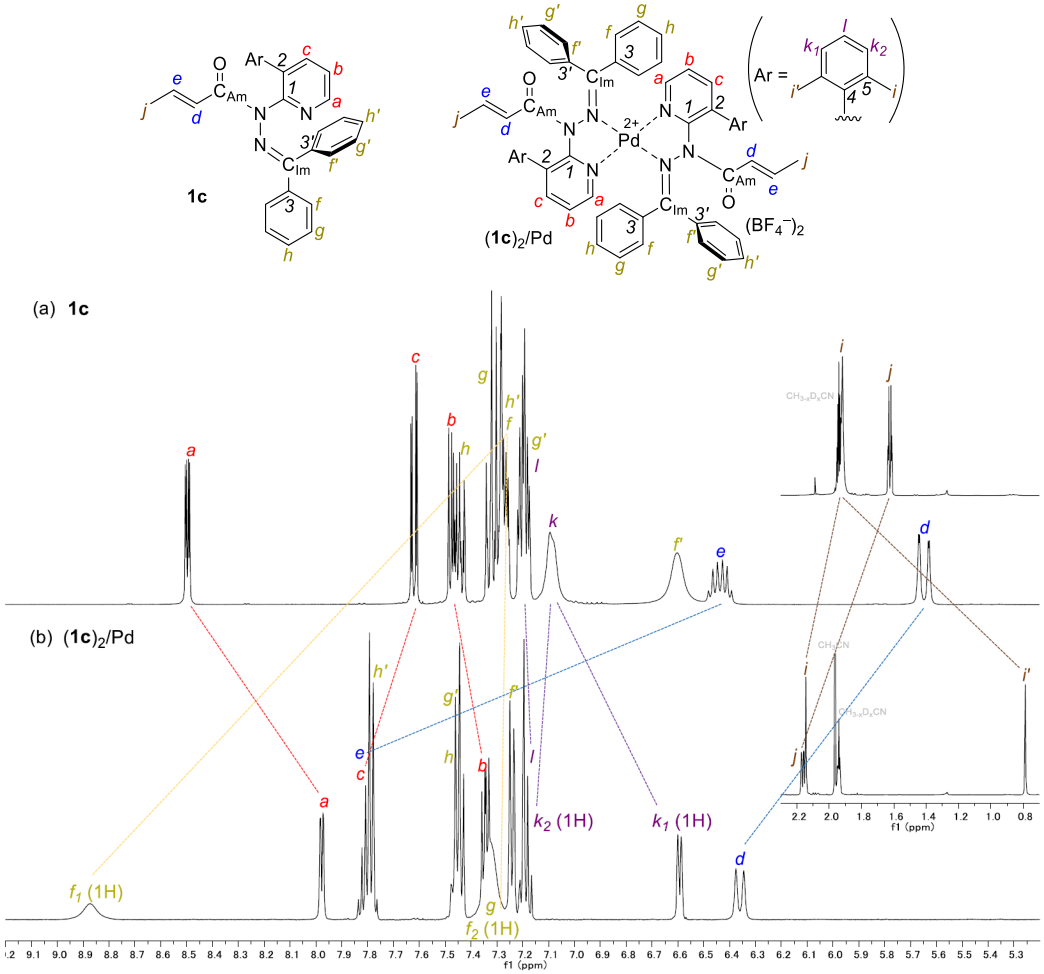


Figure S5. (a) ^{1}H NMR of **1c** in CD_3CN. (b) ^{1}H NMR of **1c**/[$Pd(CH_3CN)_4$](BF_4)$_2$ = 2/1 in CD_3CN. *f*▪*g*▪*h* and *f′*▪*g′*▪*h′* are not distinguished in (a).

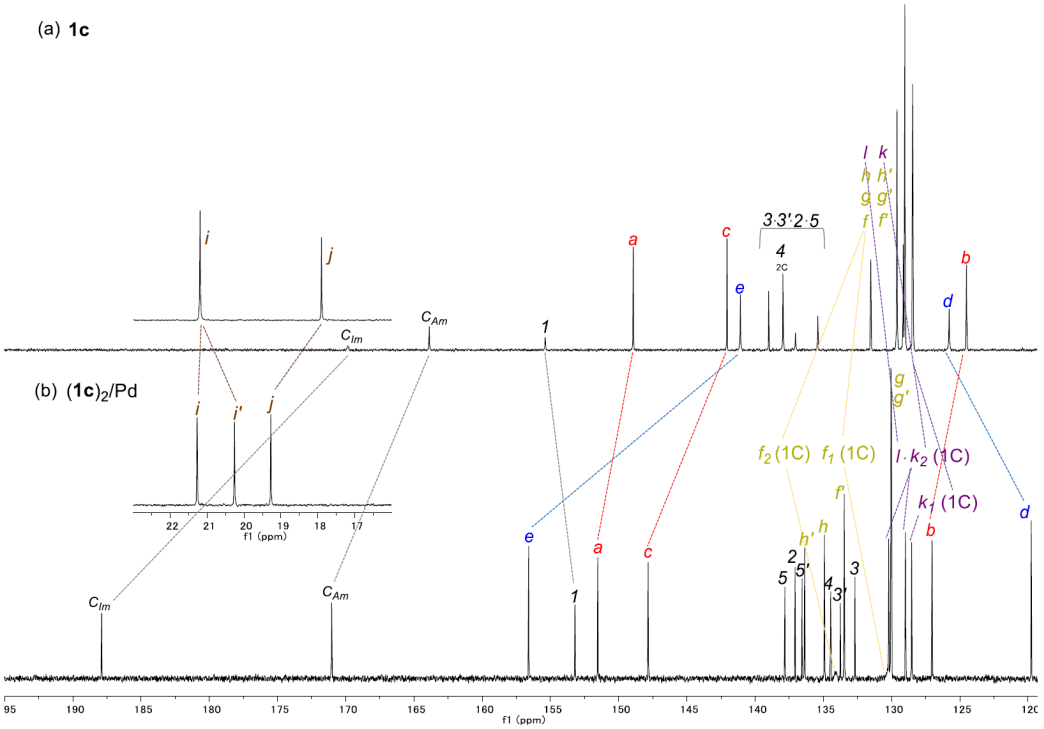


Figure S6. (a) ^{13}C NMR of **1c** in CD_3CN. (b) ^{13}C NMR of **1c**/[$Pd(CH_3CN)_4$](BF_4)$_2$ = 2/1 in CD_3CN. *f*▪*g*▪*h* 3 and *f′*▪*g′*▪*h′*▪3′ are not distinguished in (a)

*3-4-1. ^{1}H NMR of a 1:1 mixture of amide **1b** or **1c** with [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$*

Although ^{1}H NMR of the mixture of **1a**:[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ = 1:1 in CD$_3$CN showed clean formation of **1a**/Pd (**1a**:Pd^{2+} = 1:1) (Figure S1b), **1b** and **1c** in NMR analysis under otherwise identical conditions gave two species, one of which is (**1**)$_2$/Pd (amide **1b** or **1c**: Pd^{2+} = 2:1) and another is assumed to be **1**/Pd (amide **1b** or **1c**: Pd^{2+} = 1:1) (Figure S7 and S8).

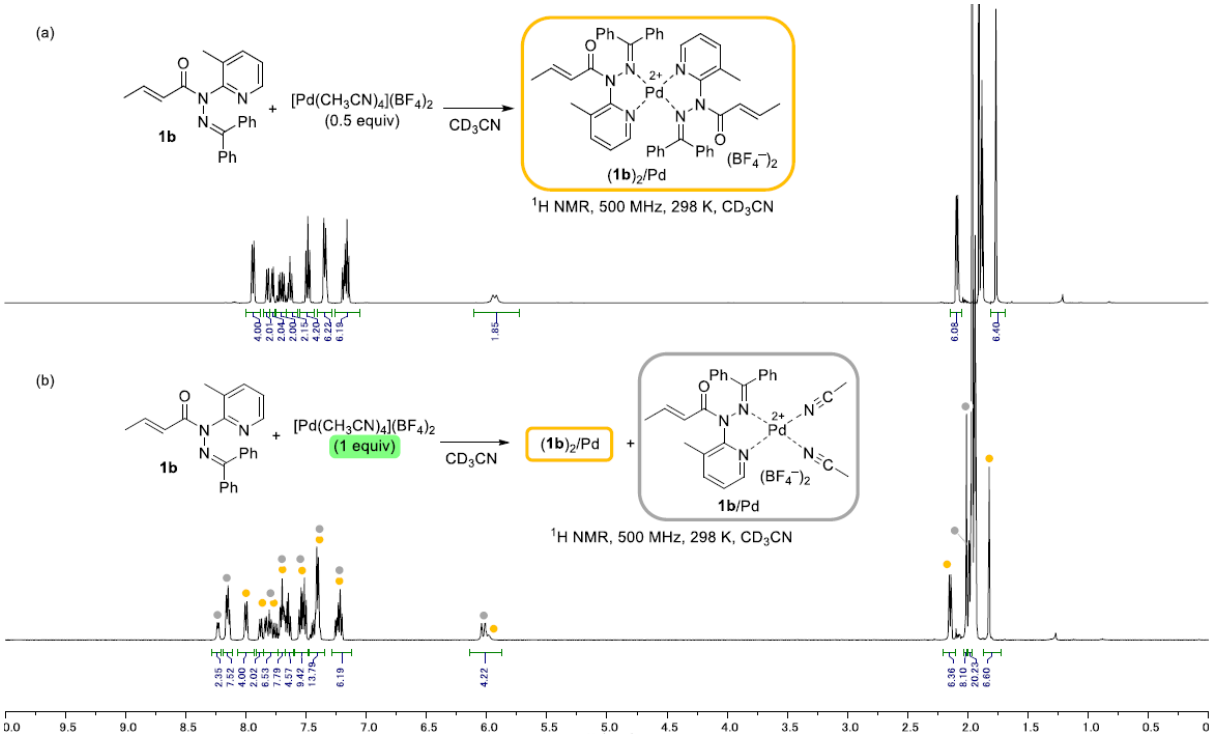


Figure S7. (a) ^{1}H NMR of **1c**/[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ = 2/1 in CD$_3$CN. (b) ^{1}H NMR of **1c**/[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ = 1/1 in CD$_3$CN.

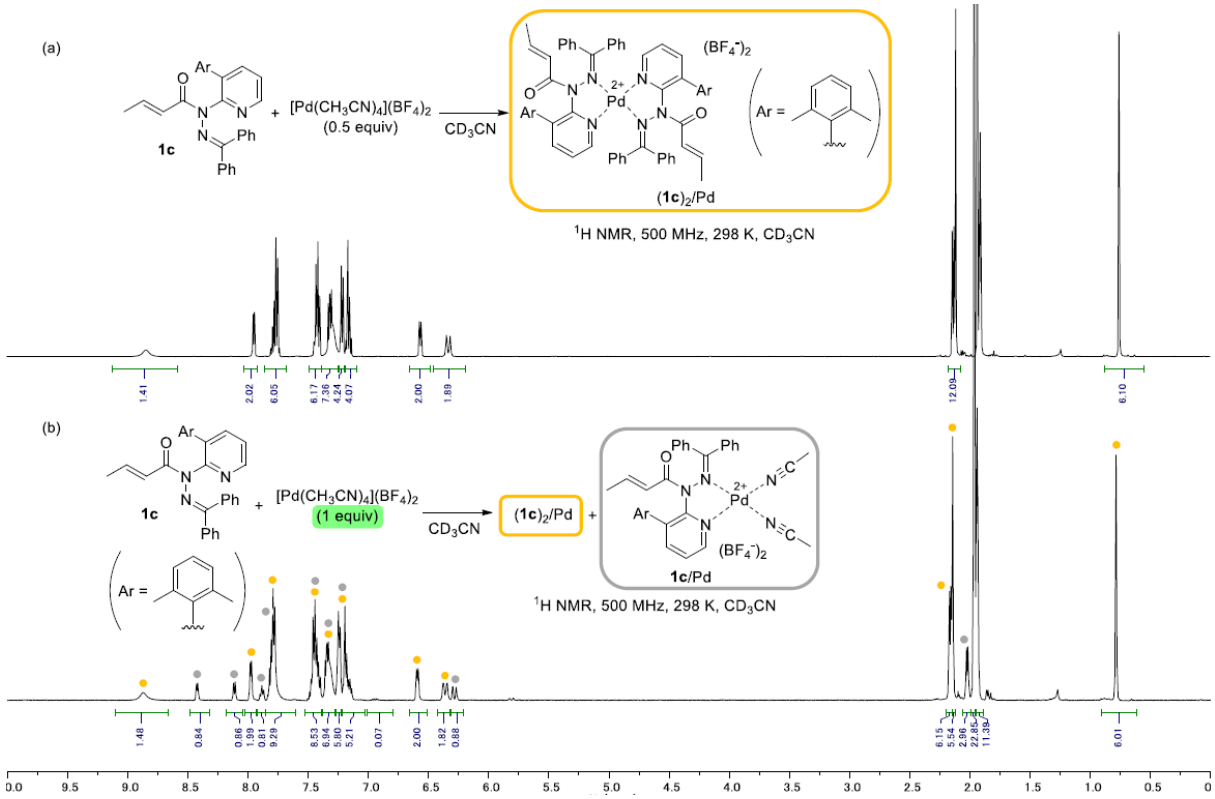


Figure S8. (a) ^{1}H NMR of **1c**/[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ = 2/1 in CD$_3$CN. (b) ^{1}H NMR of **1c**/[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ = 1/1 in CD$_3$CN.

*3-5-1. ^{1}H NMR of **1a**-metal complexes with variable stoichiometry*

The ^{1}H NMR of a mixture of (**1a**)$_2$/Pd with **1a** or **1a**/Pd showed the sum of the two individual spectra rather than an averaged spectrum (Figure S9). In contrast, ^{1}H NMR signals of a mixture of **1a** and Zn(OTf)$_2$ were averaged (Figure S10).

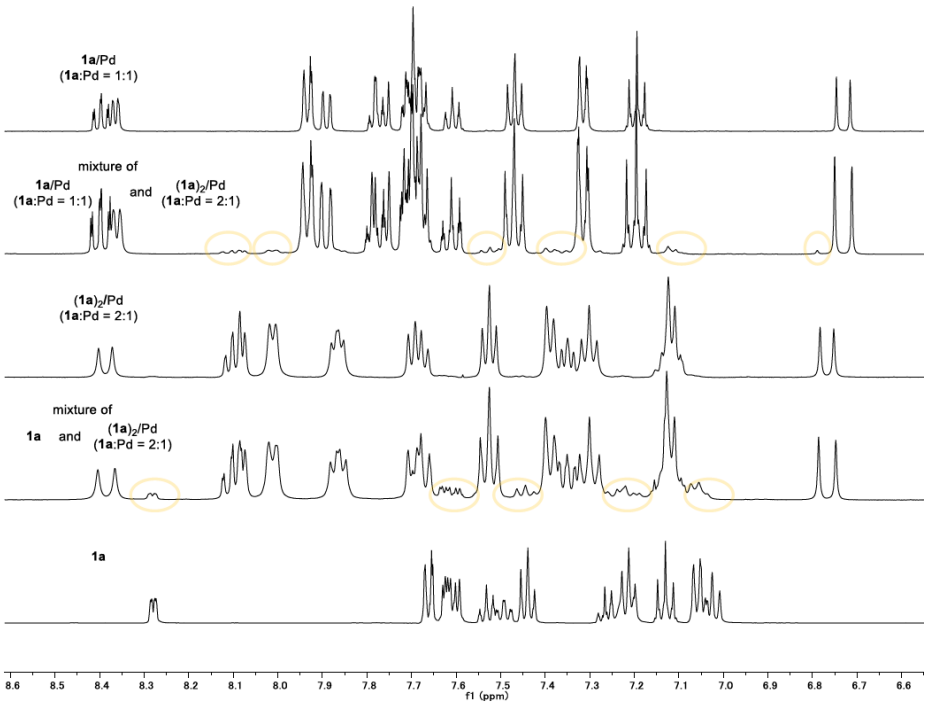


Figure S9. ^{1}H NMR of a mixture of (**1a**)$_2$Pd with **1a** or **1a**/Pd.

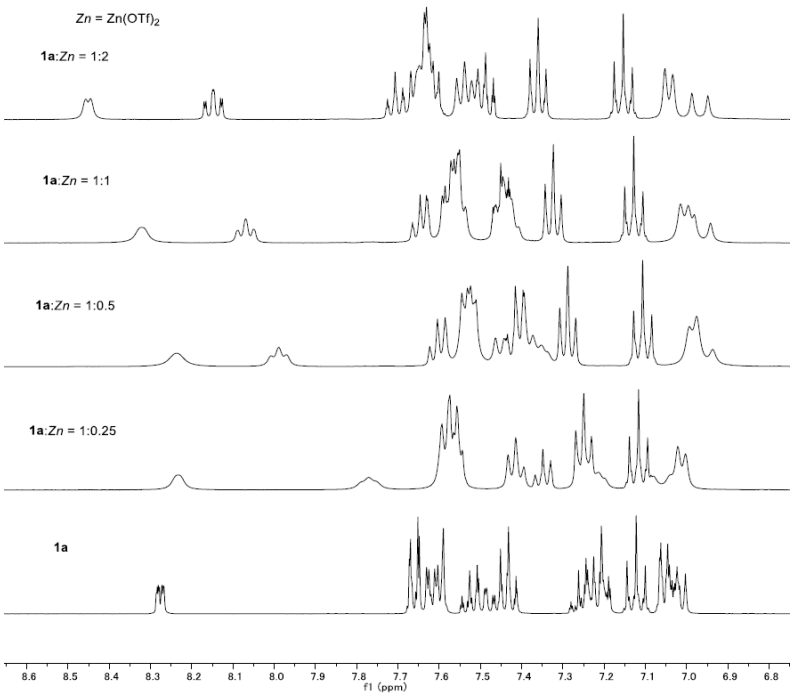


Figure S10. (a) Averaged ^{1}H NMR of a mixture of **1a** and Zn(OTf)$_2$

4. Crystal Structures of Amides 1a–c and Their Pd Complexes

*4-1. Crystal structures of amides **1a–c***

A crystal of **1a** was obtained by vapor diffusion of hexane into an acetone solution of **1a**. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S11 and Table S1. CCDC 1495002 contains the supplementary crystallographic data for **1a**.

(a) **(b)**

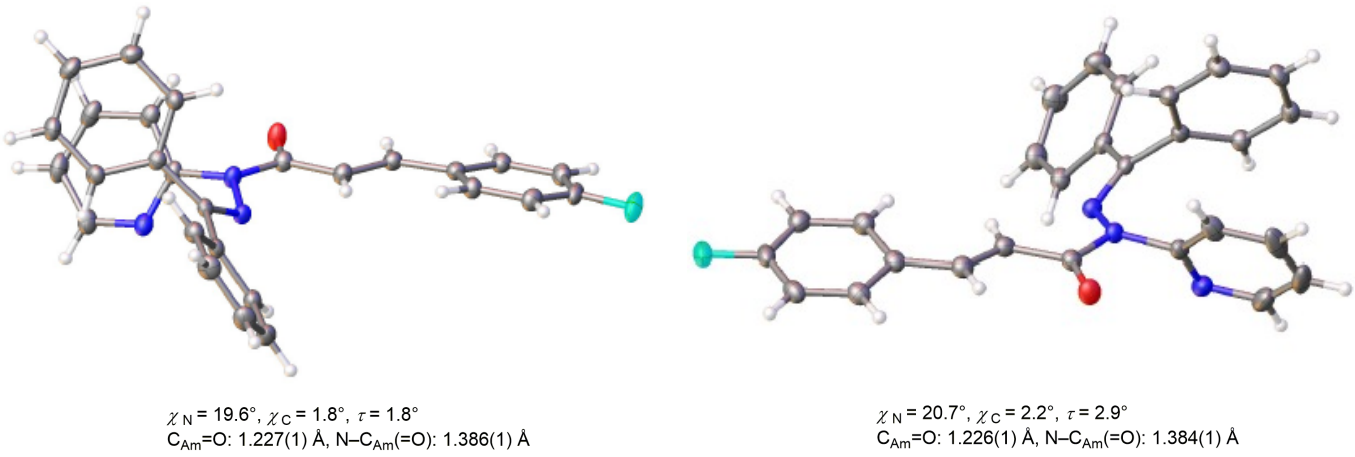


Figure S11. Structure of 1a. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, skyblue: F

(Two structures were found per unit cell.)

Table S1. Selected crystal data of 1a

Empirical Formula	$C_{54}H_{40}F_2N_6O_2$
Formula Weight	842.95
Temperature/°C	–180.0
Crystal Color, Habit	colourless, prism
Crystal Dimensions	0.259 x 0.117 x 0.067 mm
Crystal System	triclinic
Cell constants	
a	12.2208(5) Å
b	12.9781(4) Å
c	15.6515(3) Å
V	2184.84(13) Å^3
Space Group	*P*–1 (#2)
Z value	2
D_{calc}	1.281 g/cm^3
F_{000}	880.00
No. of Reflections Measured	Total: 26191
	Unique: 7535 (R_{int} = 0.0825)
R_1 (I>2.00σ(I))	0.0358
R (All reflections)	0.0398
wR_2 (All reflections)	0.1020

A crystal of **1b** was obtained by vapor diffusion of *i*-Pr_2O into an CH_3CN solution of **1b**. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S12 and Table S2. CCDC 1495001 contains the supplementary crystallographic data for **1b**.

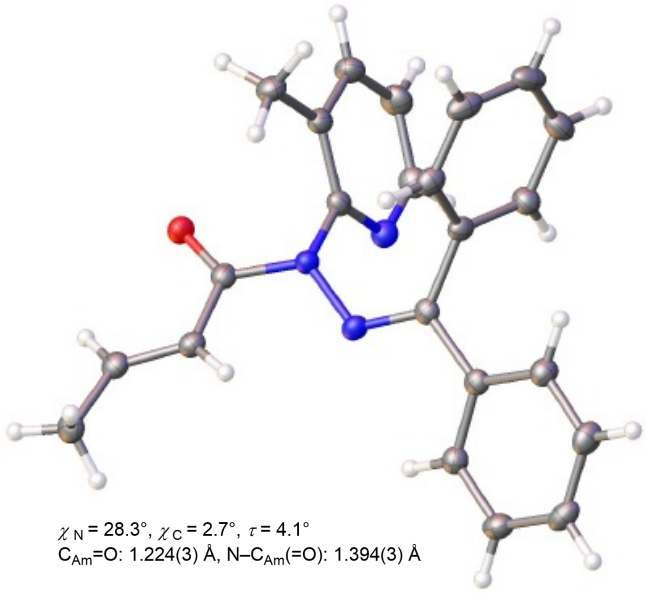


Figure S12. Structure of 1b. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O

Table S2. Selected crystal data of 1b

Empirical Formula	$C_{23}H_{21}N_3O$
Formula Weight	355.44
Temperature/°C	–180.0
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.200 x 0.200 x 0.200 mm
Crystal System	monoclinic
Cell constants	
a	11.3565(2) Å
b	11.5389(2) Å
c	15.0221(3) Å
V	1878.76(10) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.257 g/cm^3
F_{000}	752.00
No. of Reflections Measured	Total: 21297
	Unique: 3434 (R_{int} = 0.0330)
R_1 (I>2.00σ(I))	0.0575
R (All reflections)	0.0636
wR_2 (All reflections)	0.1613

A crystal of **1c** was obtained by vapor diffusion of *i*-Pr_2O into an CH_3CN solution of **1c**. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S13 and Table S3. CCDC 1495003 contains the supplementary crystallographic data for **1c**.

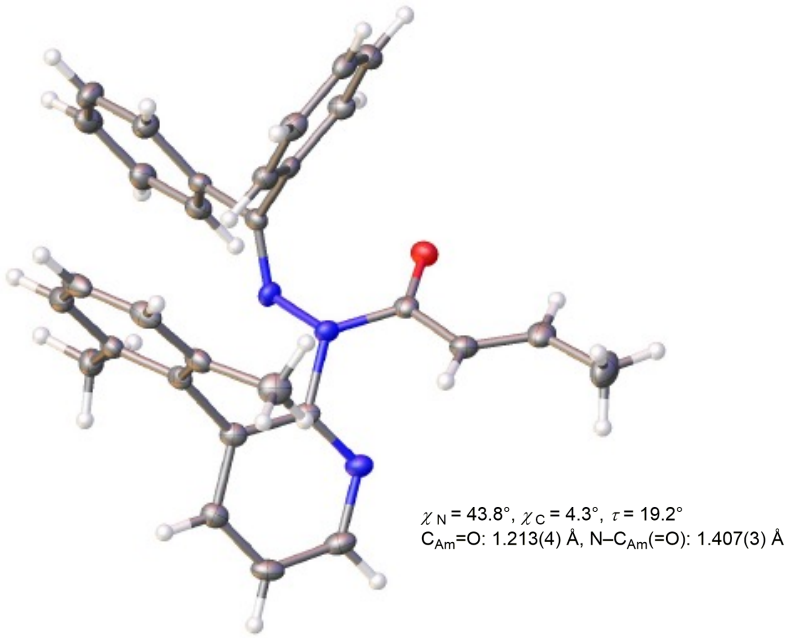


Figure S13. Structure of 1c. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O

Table S3. Selected crystal data of 1c

Empirical Formula	$C_{30}H_{27}N_3O$
Formula Weight	445.56
Temperature/°C	–180.0
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 x 0.200 x 0.200 mm
Crystal System	monoclinic
Cell constants	
a	18.8592(4) Å
b	7.68843(16) Å
c	18.4442(3) Å
V	2438.13(17) $Å^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.214 g/cm^3
F_{000}	944.00
No. of Reflections Measured	Total: 25572
	Unique: 4459 (R_{int} = 0.0902)
R_1 (I>2.00σ(I))	0.0550
R (All reflections)	0.1009
wR_2 (All reflections)	0.1747

4-2. Crystal structures of metal complexes with amides ***1a–c***

A crystal of (**1a**)$_2$/Pd was obtained by vapor diffusion of hexane into an acetone solution of (**1a**)$_2$/Pd. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S14 and Table S4. CCDC 1495004 contains the supplementary crystallographic data for (**1a**)$_2$/Pd.

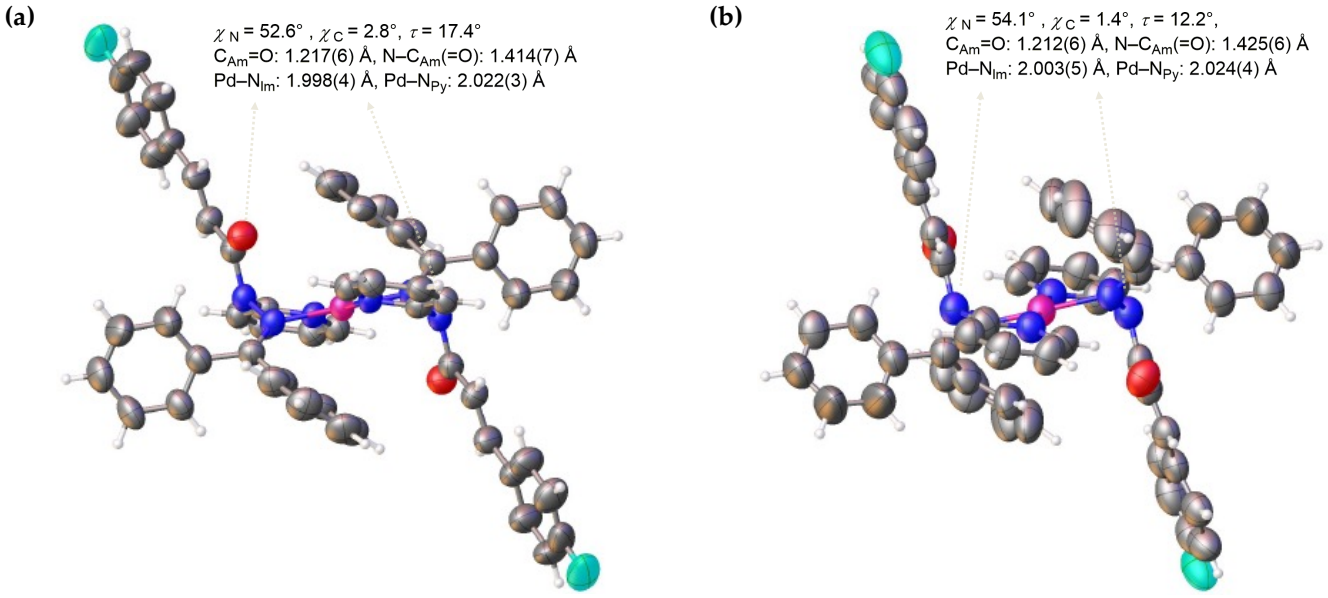


Figure S14. Structure of (1a)$_2$/Pd. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, skyblue: F, yellow: S, pink: Pd
(Two structures were found per unit cell.)

Table S4. Selected crystal data of (1a)$_2$/Pd.

Empirical Formula	$C_{54}H_{40}F_2N_6O_2Pd$
Formula Weight	949.35
Temperature/°C	–180.0
Crystal Color, Habit	yellow, platelet
Crystal Dimensions	0.200 x 0.200 x 0.050 mm
Crystal System	triclinic
Cell constants	
a	10.7056(3) Å
b	16.7664(4) Å
c	18.6108(5) Å
V	3174.3(2) Å^3
Space Group	*P*–1 (#2)
Z value	2
D_{calc}	0.993 g/cm^3
F_{000}	972.00
No. of Reflections Measured	Total: 37622
	Unique: 11413 (R_{int} = 0.0884)
R_1 (I>2.00σ(I))	0.0659
R (All reflections)	0.0797
wR_2 (All reflections)	0.2041

A crystal of (**1b**)$_2$/Pd was obtained by vapor diffusion of *i*-Pr$_2$O into an CH$_3$CN solution of (**1b**)$_2$/Pd. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S15 and Table S5. CCDC 1494999 contains the supplementary crystallographic data for (**1b**)$_2$/Pd.

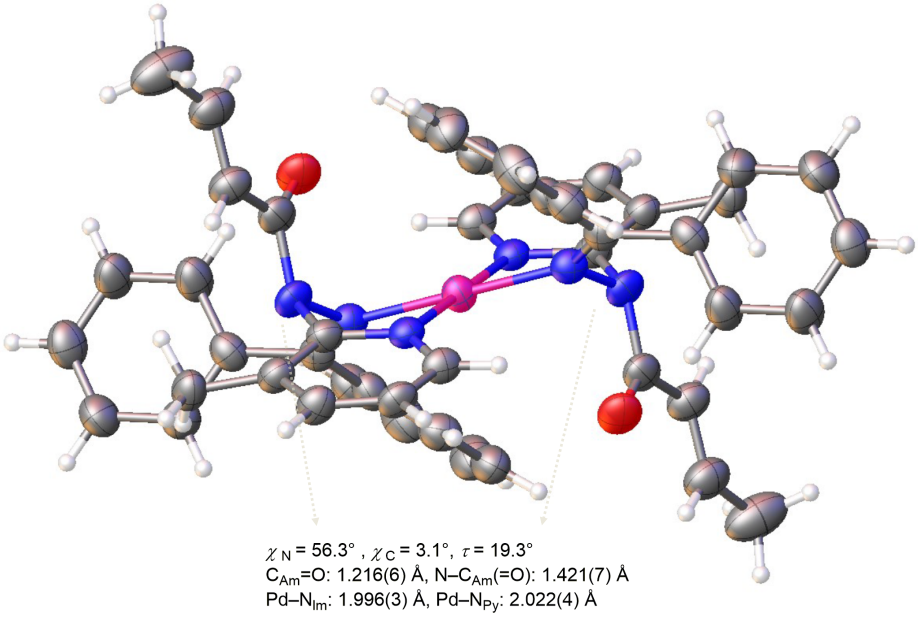


Figure S15. Structure of (1b)$_2$/Pd. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, pink: Pd

Table S5. Selected crystal data of (1b)$_2$/Pd

Empirical Formula	$C_{46}H_{42}N_6O_2Pd$
Formula Weight	817.28
Temperature/°C	–180.0
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 x 0.200 x 0.200 mm
Crystal System	triclinic
Cell constants	
a	8.88787(16) Å
b	10.65997(19)
c	12.1038(2) Å
V	1069.19(7) Å^3
Space Group	*P*–1 (#2)
Z value	1
D_{calc}	1.269 g/cm^3
F_{000}	422.00
No. of Reflections Measured	Total: 12558
	Unique: 3851 (R_{int} = 0.0638)
R_1 (I>2.00σ(I))	0.0541
R (All reflections)	0.0617
wR_2 (All reflections)	0.1453

A crystal of (**1c**)$_2$/Pd was obtained by vapor diffusion of *i*-Pr$_2$O into an CH$_3$CN solution of (**1c**)$_2$/Pd. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S16 and Table S6. CCDC 1495000 contains the supplementary crystallographic data for (**1c**)$_2$/Pd.

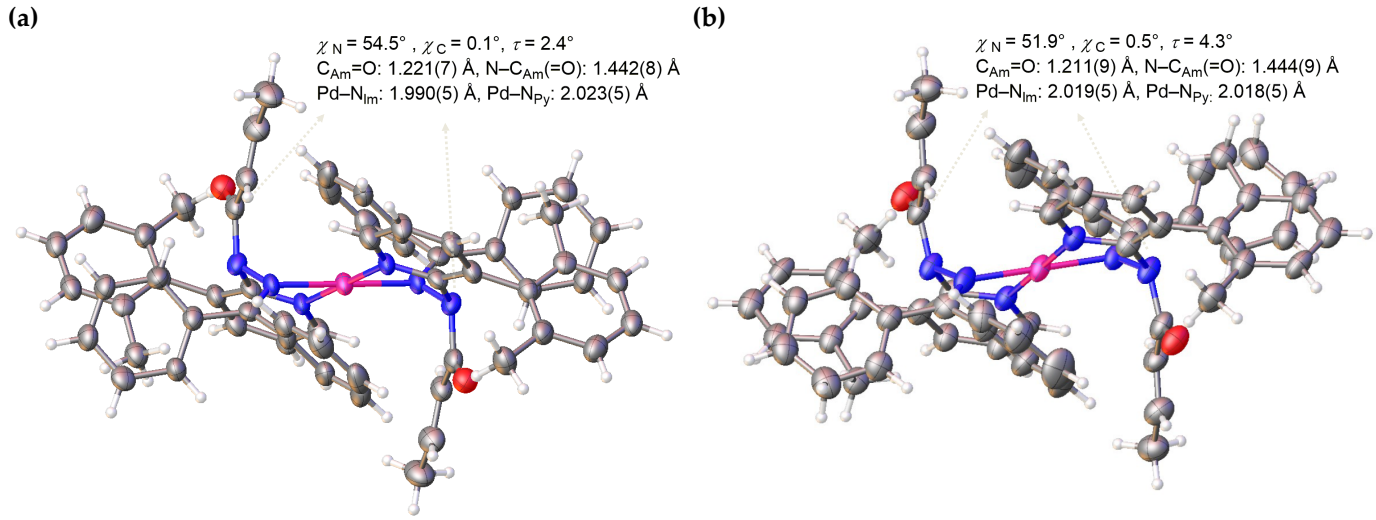


Figure S16. Structure of (1c)$_2$/Pd. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, pink: Pd (Two structures were found per unit cell.)

Table S6. Selected crystal data of (1c)$_2$/Pd.

Empirical Formula	$C_{60}H_{55}B_2F_8N_6O_2Pd$
Formula Weight	1172.14
Temperature/°C	–180.0
Crystal Color, Habit	yellow, platelet
Crystal Dimensions	0.300 x 0.200 x 0.020 mm
Crystal System	triclinic
Cell constants	
a	13.2547(2) Å
b	14.2678(3) Å
c	15.5271(3) Å
V	2805.98(15) Å^3
Space Group	*P*–1 (#2)
Z value	2
D_{calc}	1.387 g/cm^3
F_{000}	1202.00
No. of Reflections Measured	Total: 33116
	Unique: 10068 (R_{int} = 0.0714)
R_1 (I>2.00σ(I))	0.0858
R (All reflections)	0.1110
wR_2 (All reflections)	0.2542

A crystal of **1c**/Pd was obtained by vapor diffusion of *i*-Pr_2O into an CH_3CN solution of **1c**/Pd. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Cu-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S17 and Table S7. CCDC 1494998 contains the supplementary crystallographic data for **1c**/Pd.

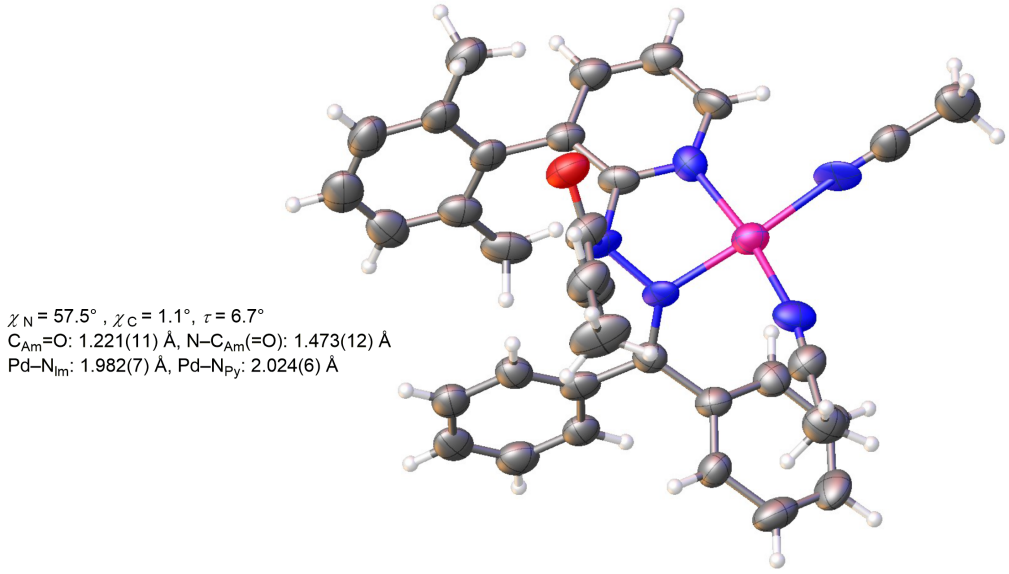


Figure S17. Structure of 1c/Pd. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, pink: Pd

Table S7. Selected crystal data of 1c/Pd

Empirical Formula	$C_{34}H_{33}B_2F_8N_5OPd$
Formula Weight	807.67
Temperature/°C	–180.0
Crystal Color, Habit	yellow, platelet
Crystal Dimensions	0.200 x 0.200 x 0.050 mm
Crystal System	triclinic
Cell constants	
a	9.1646(3) Å
b	10.8129(4) Å
c	17.3580(8) Å
V	1703.87(11) $Å^3$
Space Group	*P*–1 (#2)
Z value	2
D_{calc}	1.574 g/cm^3
F_{000}	816.00
No. of Reflections Measured	Total: 20068
	Unique: 6102 (R_{int} = 0.1098)
R_1 (I>2.00σ(I))	0.0954
R (All reflections)	0.1223
wR_2 (All reflections)	0.2774

A crystal of (**1a**)$_2$/Zn was obtained by vapor diffusion of diisoporpyl ether into an CH_3CN solution of (**1a**)$_2$/Zn. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα radiation. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined structure and crystallographic parameters are summarized in Figure S18 and Table S8. CCDC 1495005 contains the supplementary crystallographic data for (**1a**)$_2$/Zn.

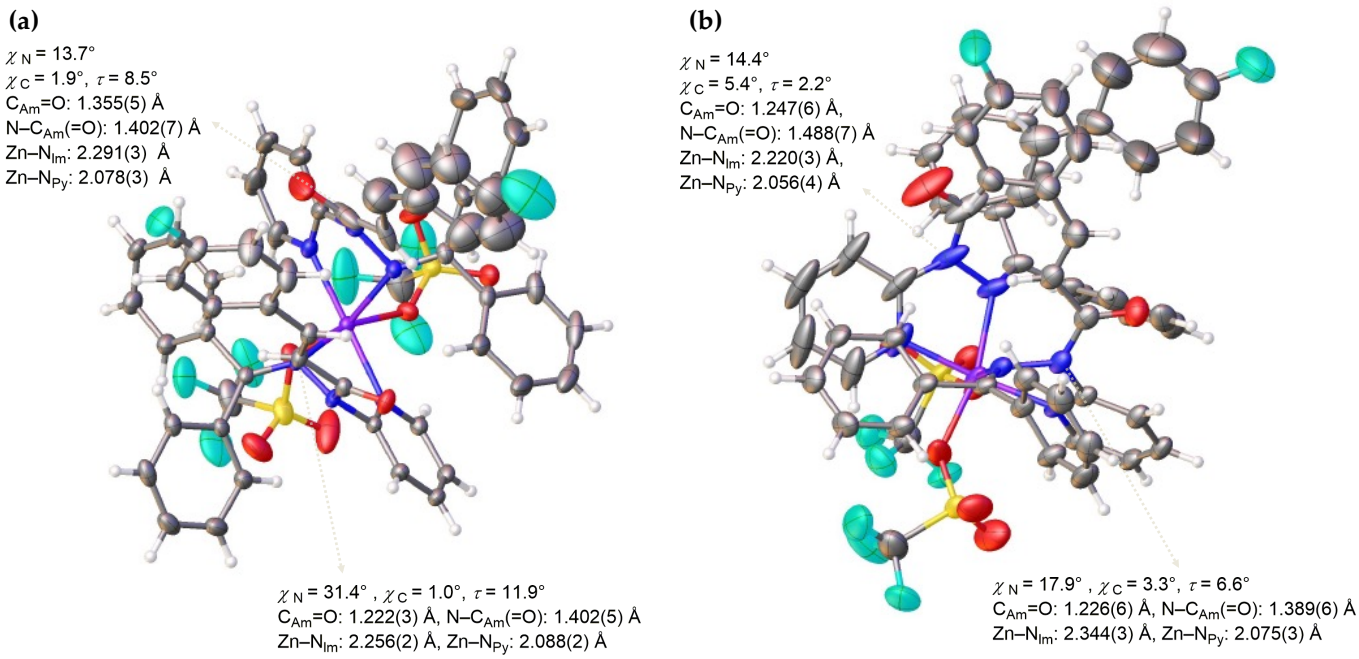


Figure S18. Structure of (1a)$_2$/Zn. [ORTEP plot (50% ellipsoids)], Color code; gray: C, white: H, blue: N, red: O, skyblue: F, yellow: S, purple: Zn
(Two structures were found per unit cell.)

Table S8. Selected crystal data of (1a)$_2$/Zn.

Empirical Formula	$C_{57}H_{41.5}F_8N_{6.5}O_8S_2Zn$
Formula Weight	1226.98
Temperature/°C	–180.0
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.175 x 0.159 x 0.120 mm
Crystal System	triclinic
Cell constants	
a	15.7265(3) Å
b	20.4033(4) Å
c	21.0479(3) Å
V	6230.5(2) Å^3
Space Group	*P*–1 (#2)
Z value	4
D_{calc}	1.308 g/cm^3
F_{000}	2508.00
No. of Reflections Measured	Total: 122871
	Unique: 28530 (R_{int} = 0.0255)
R_1 (I>2.00σ(I))	0.0721
R (All reflections)	0.0818
wR_2 (All reflections)	0.2052

5. References

1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
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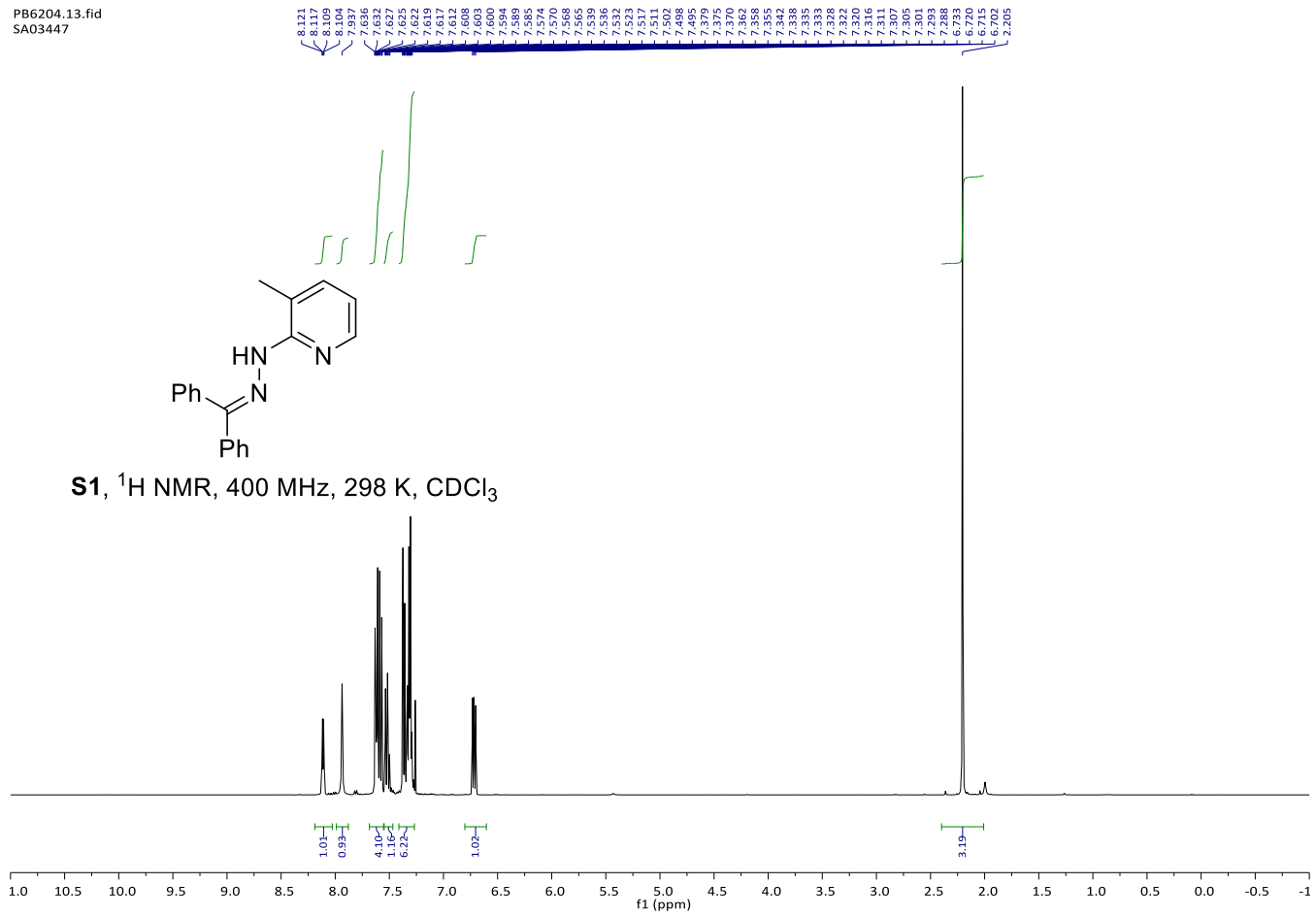
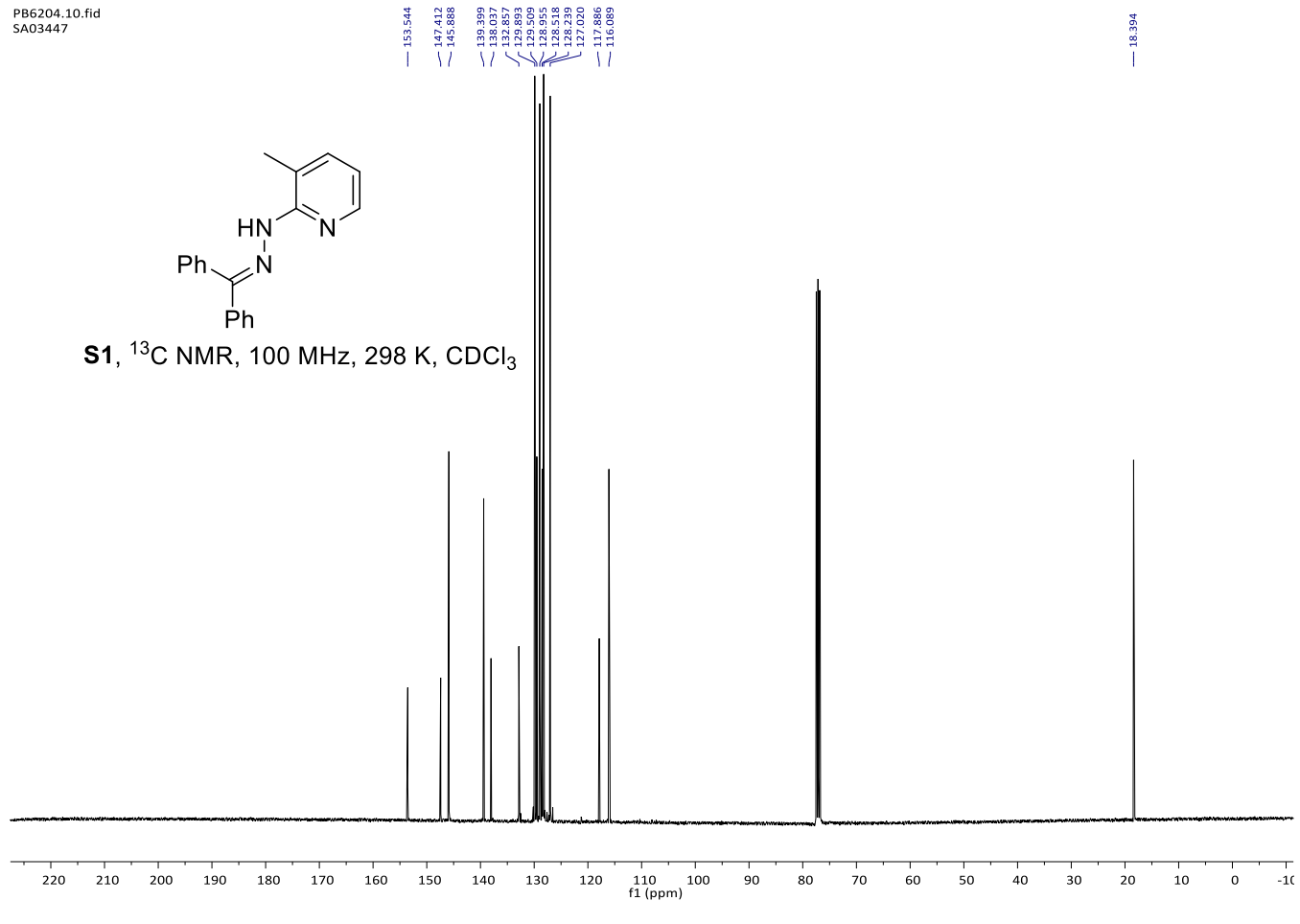
6. NMR Spectra of New Compounds (¹H, ¹³C, and ¹⁹F NMR spectra)

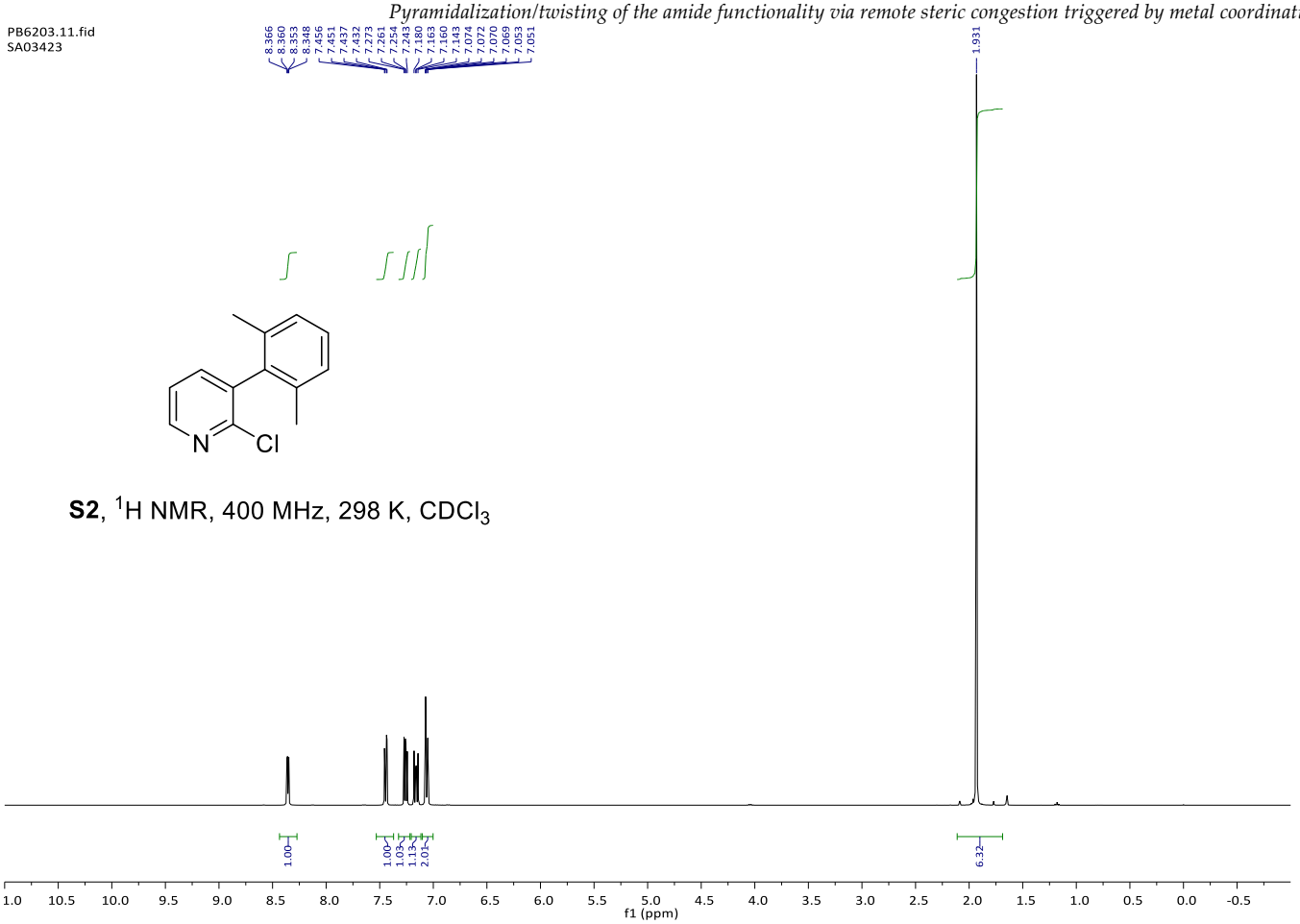


S1, ^{1}H NMR, 400 MHz, 298 K, $CDCl_3$



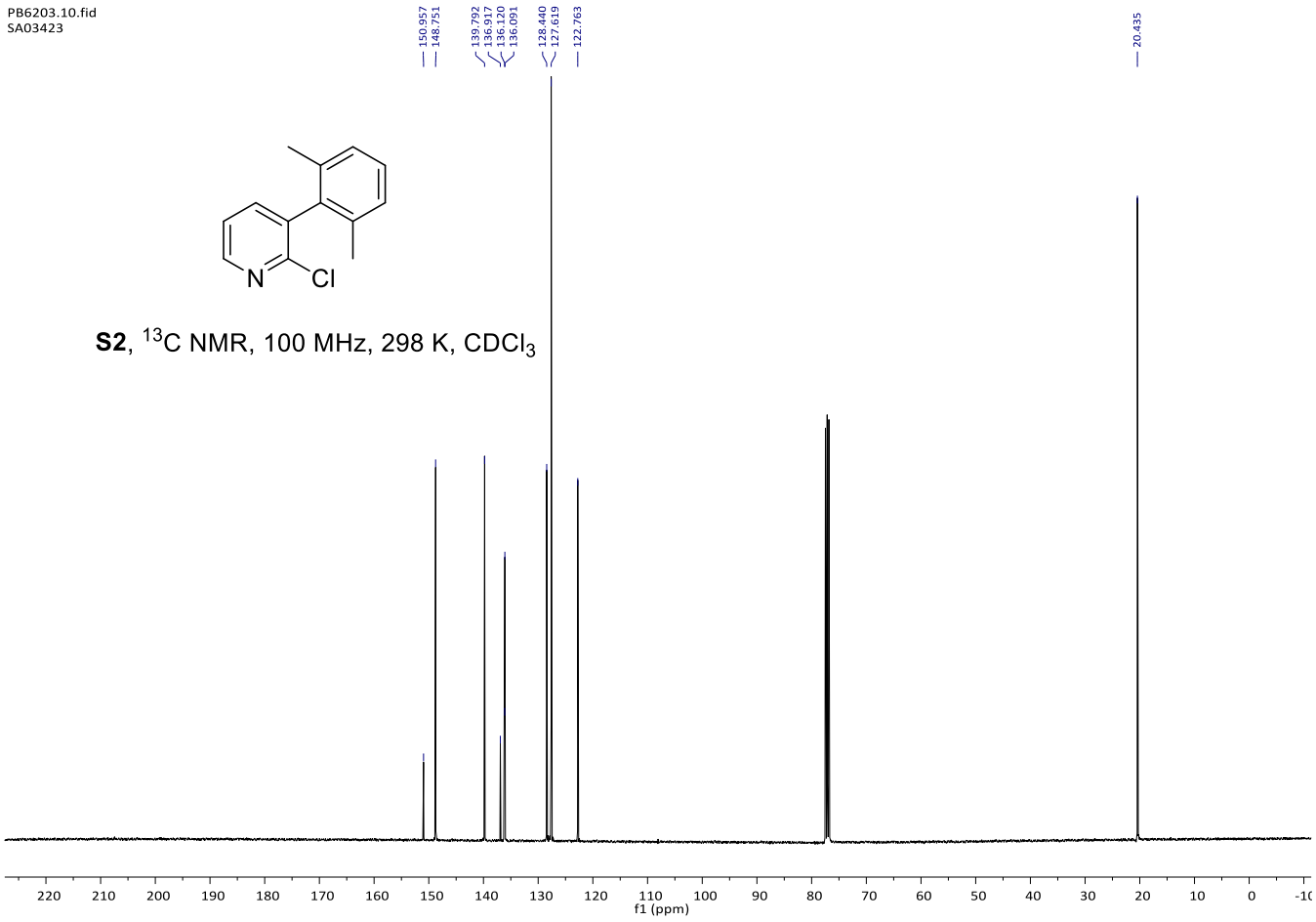
S1, ^{13}C NMR, 100 MHz, 298 K, $CDCl_3$

PB6203.11.fid
SA03423



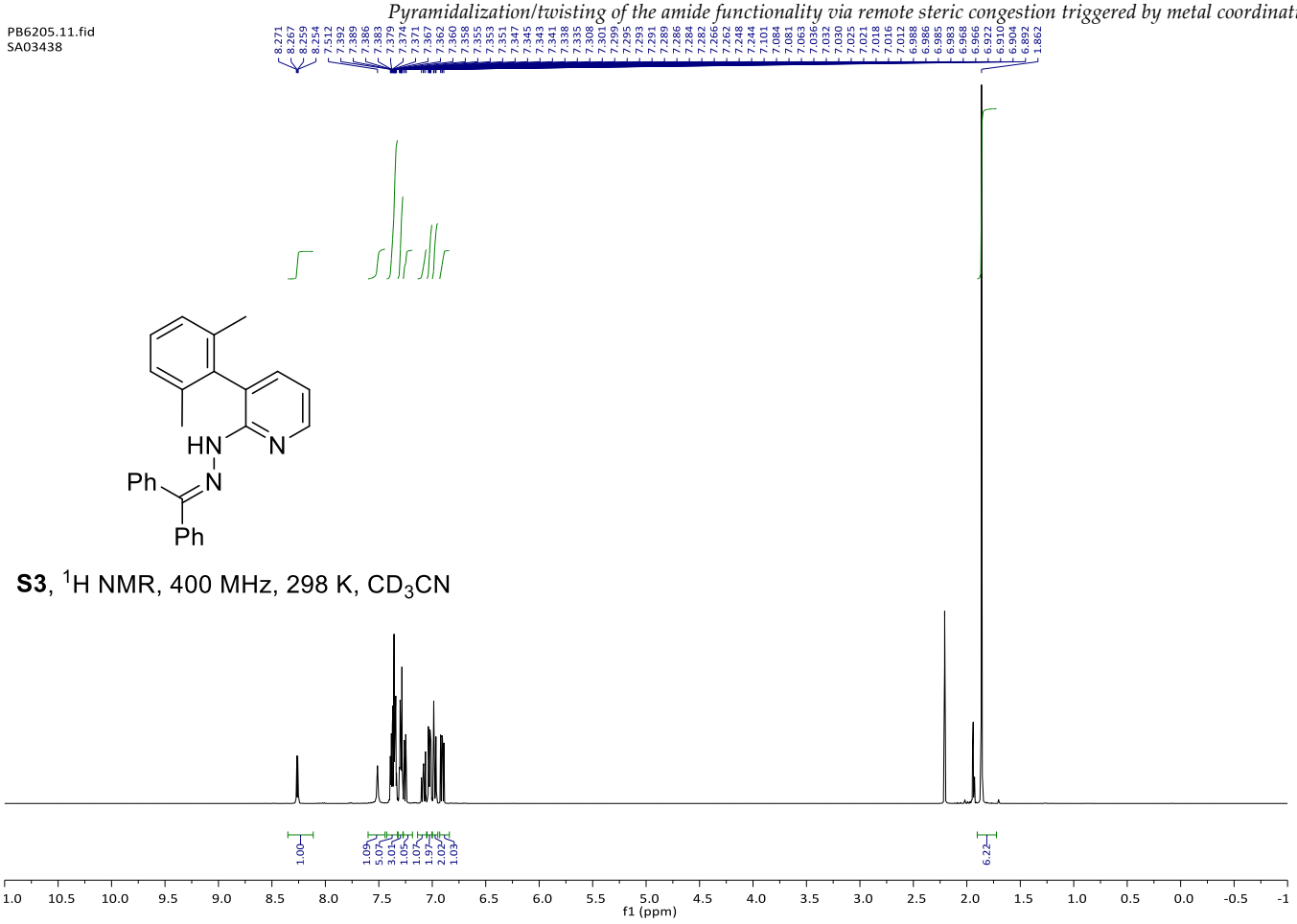
S2, ^{1}H NMR, 400 MHz, 298 K, $CDCl_3$

PB6203.10.fid
SA03423



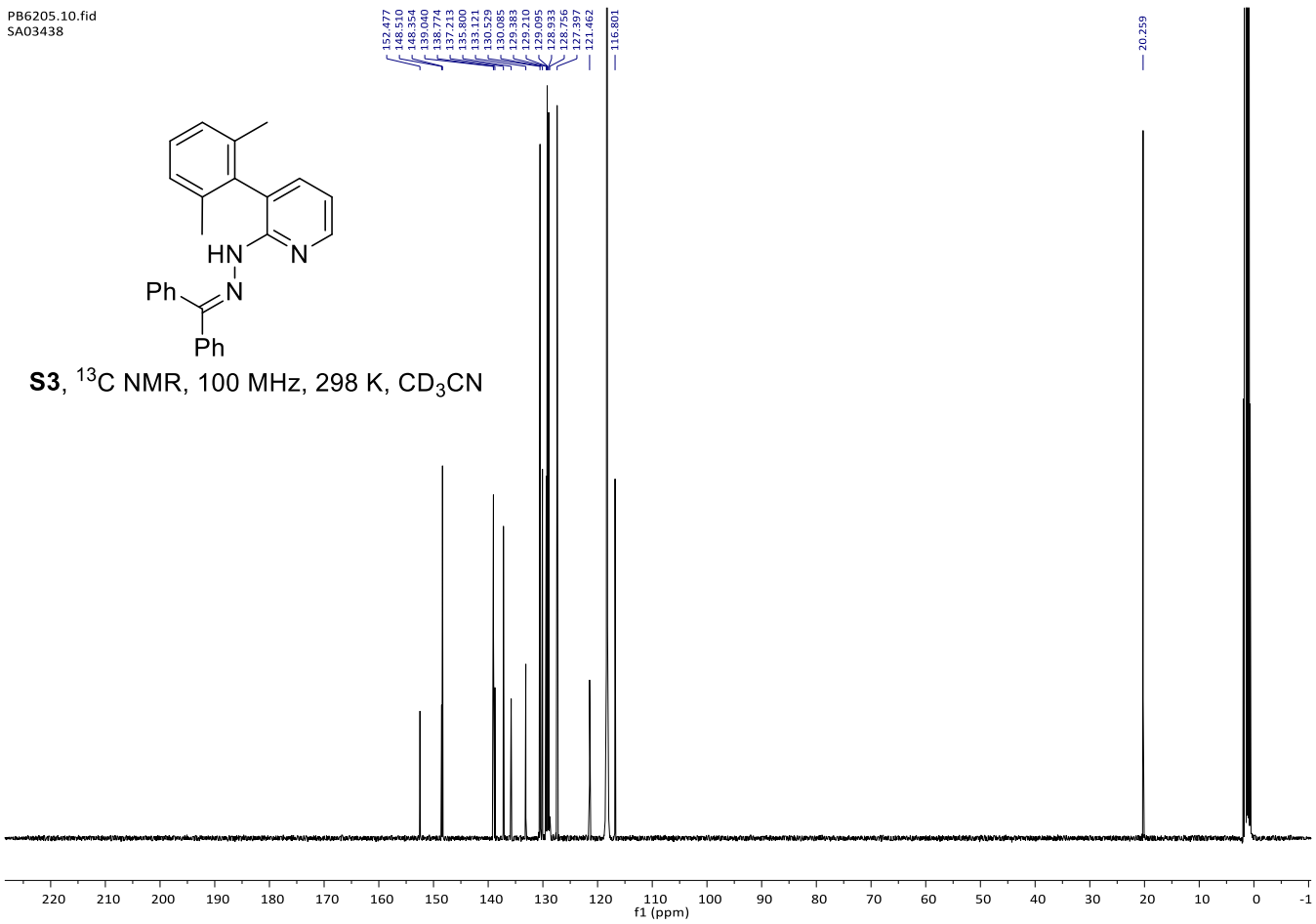
S2, ^{13}C NMR, 100 MHz, 298 K, $CDCl_3$

PB6205.11.fid
SA03438



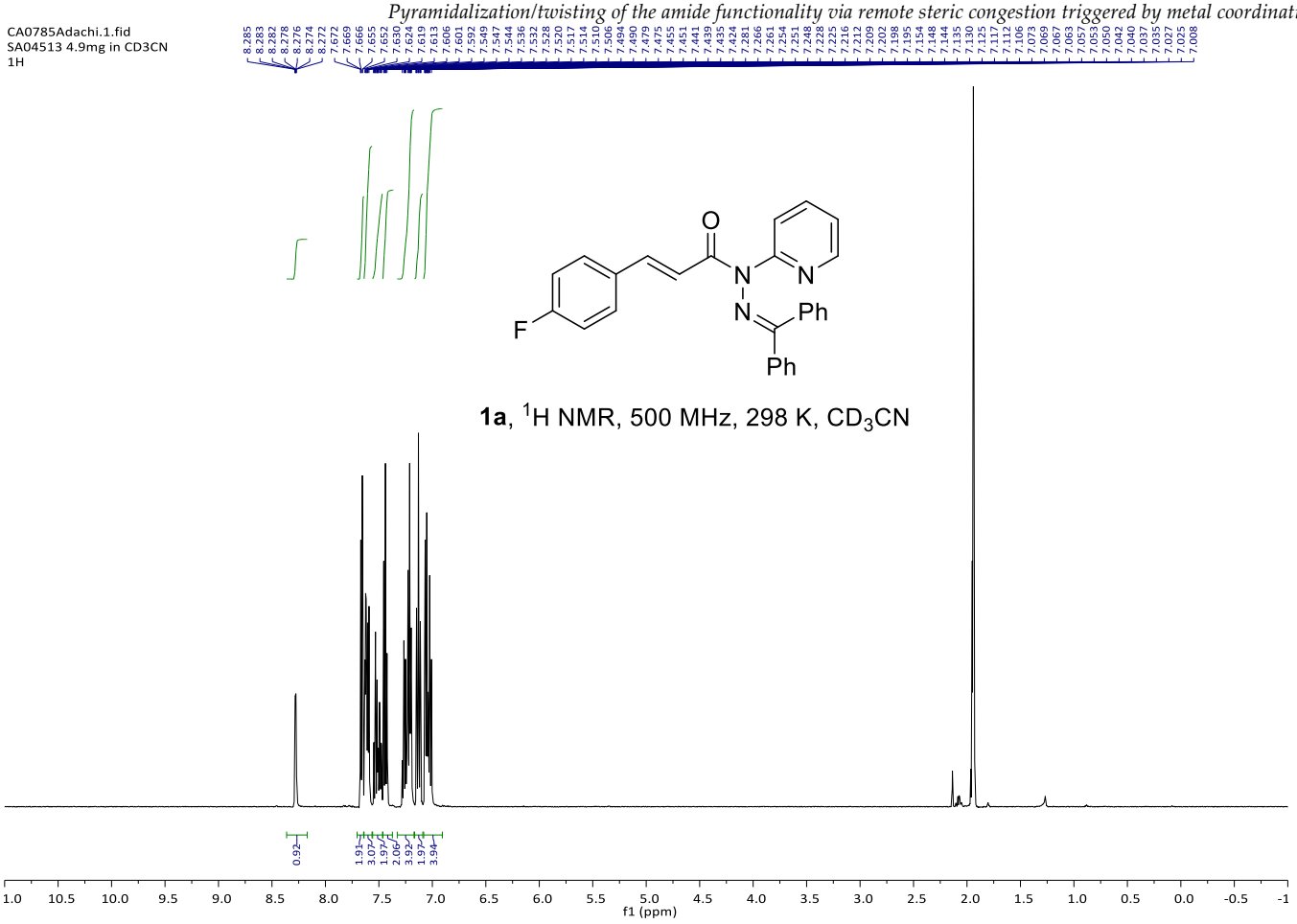
S3, ^{1}H NMR, 400 MHz, 298 K, CD_3CN

PB6205.10.fid
SA03438



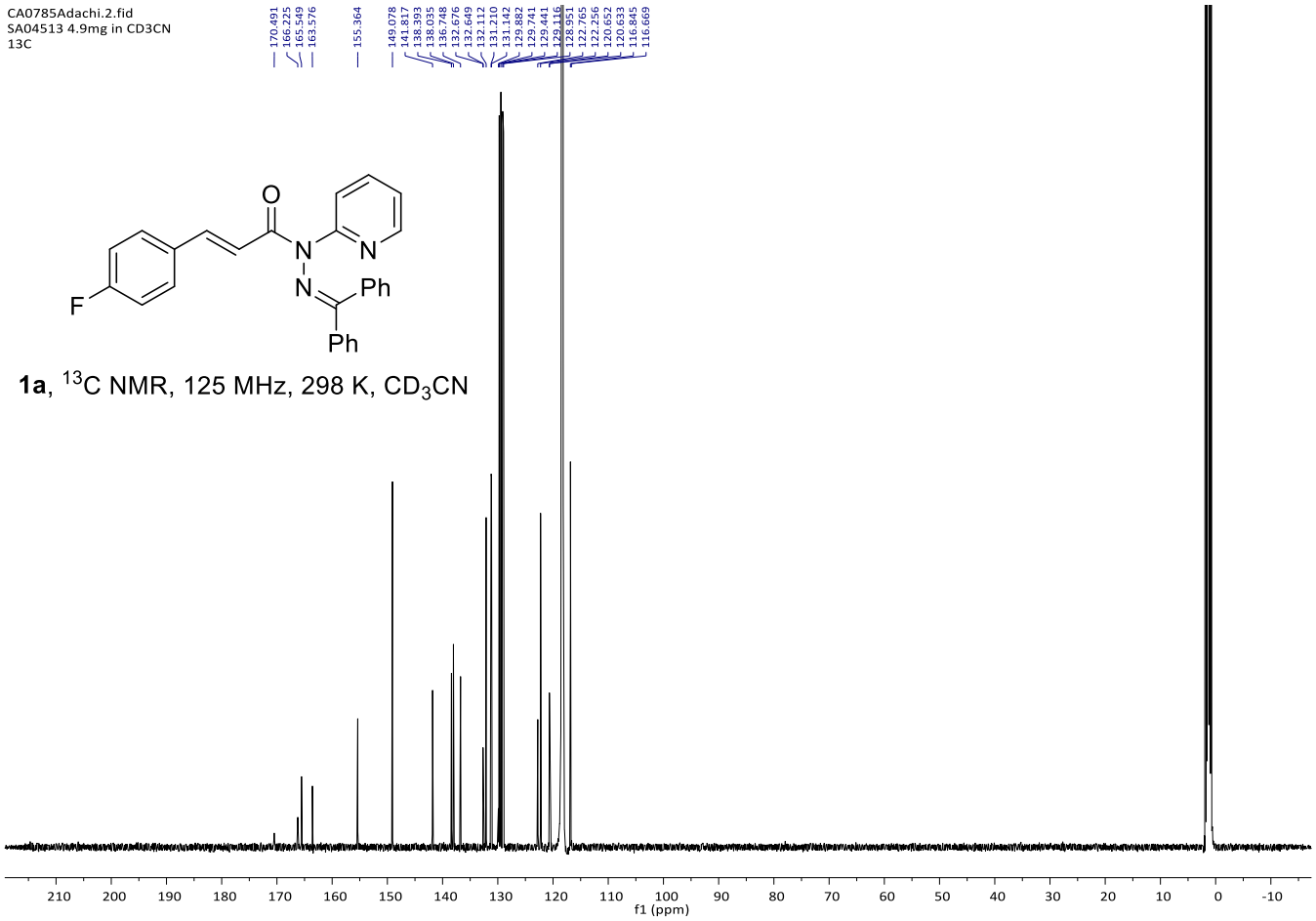
S3, ^{13}C NMR, 100 MHz, 298 K, CD_3CN

CA0785Adachi.1.fid
SA04513 4.9mg in CD3CN
1H



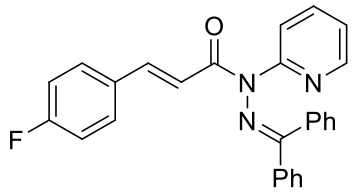
1a, ^{1}H NMR, 500 MHz, 298 K, CD_3CN

CA0785Adachi.2.fid
SA04513 4.9mg in CD3CN
13C



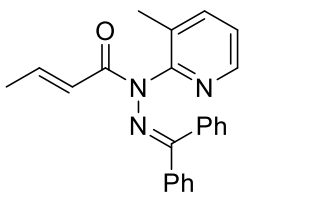
1a, ^{13}C NMR, 125 MHz, 298 K, CD_3CN

PB7851.10.fid
SA04513

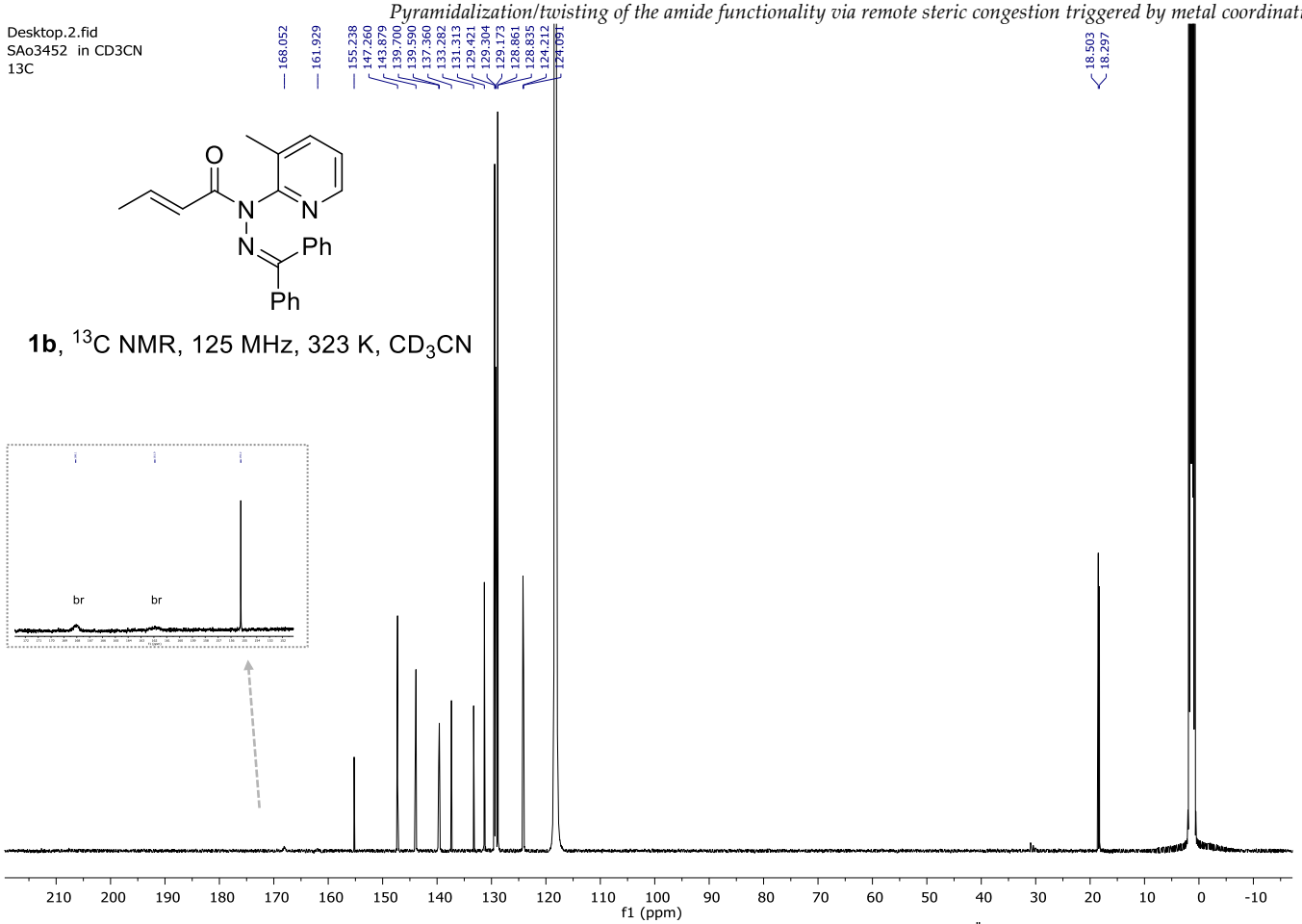


1a, ^{19}F NMR, 376 MHz, 298 K, CD_3CN

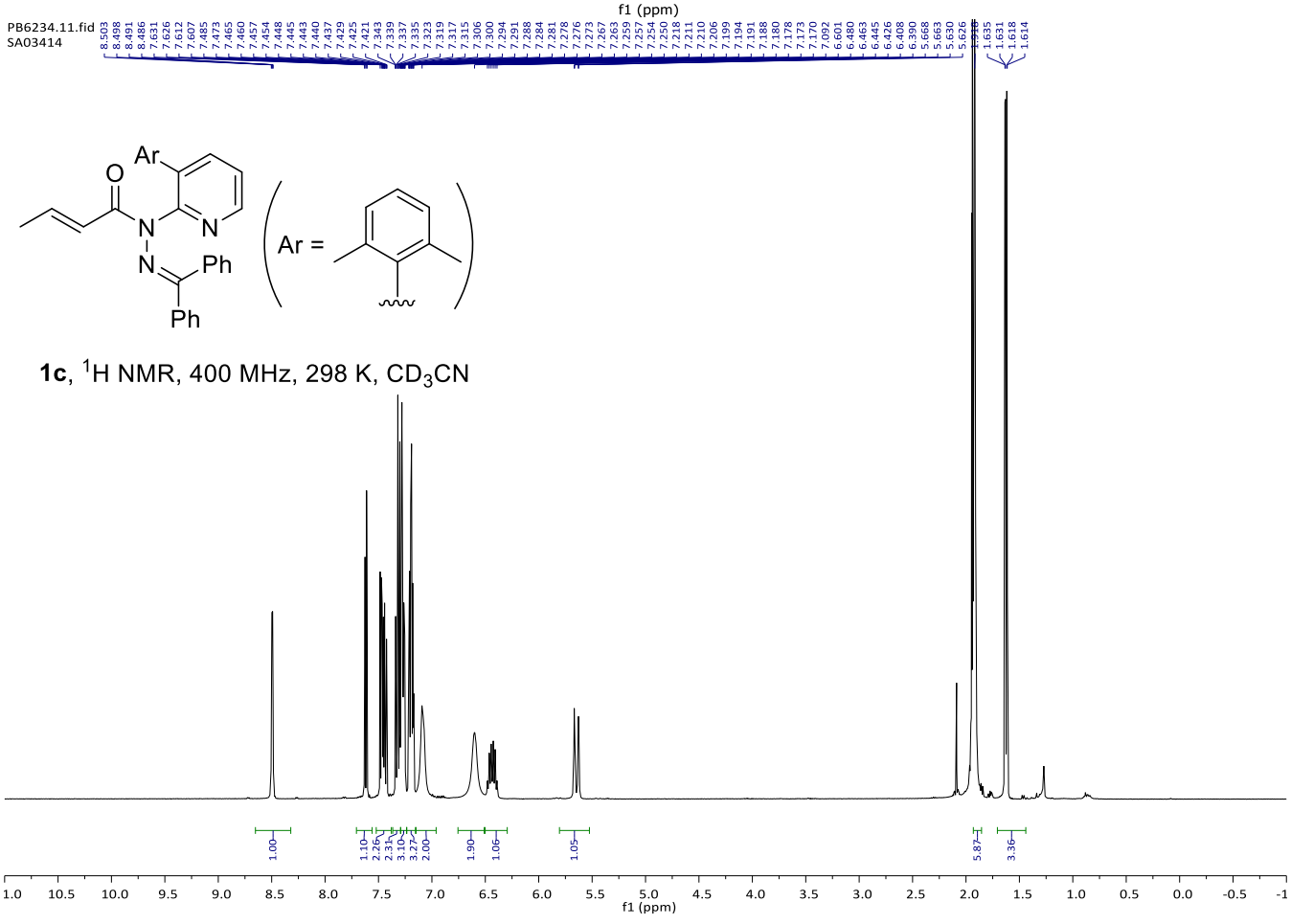
CA0717Adachi.1.fid
SAo3452 in CD3CN
1H



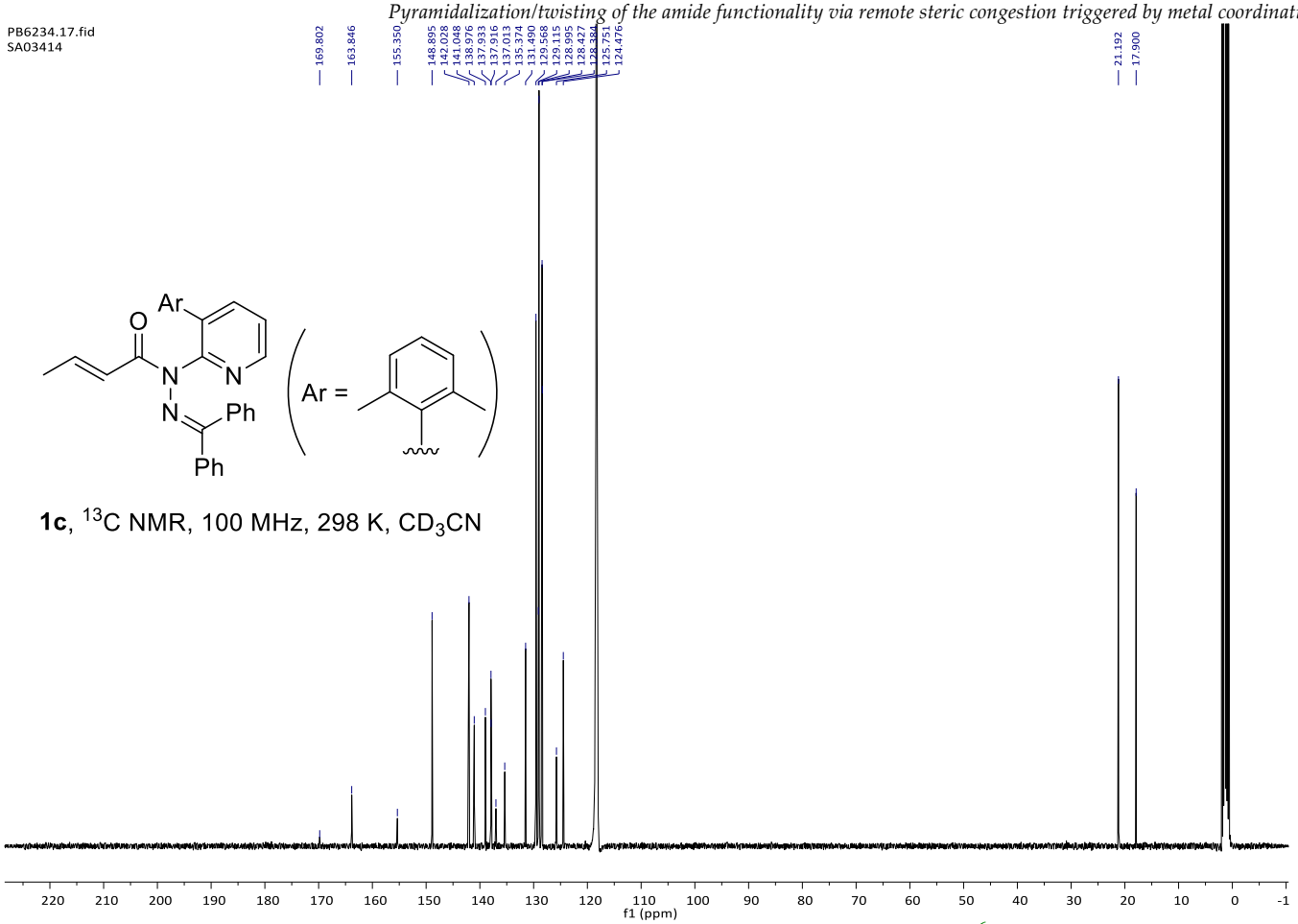
1b, ^{1}H NMR, 500 MHz, 323 K, CD_3CN



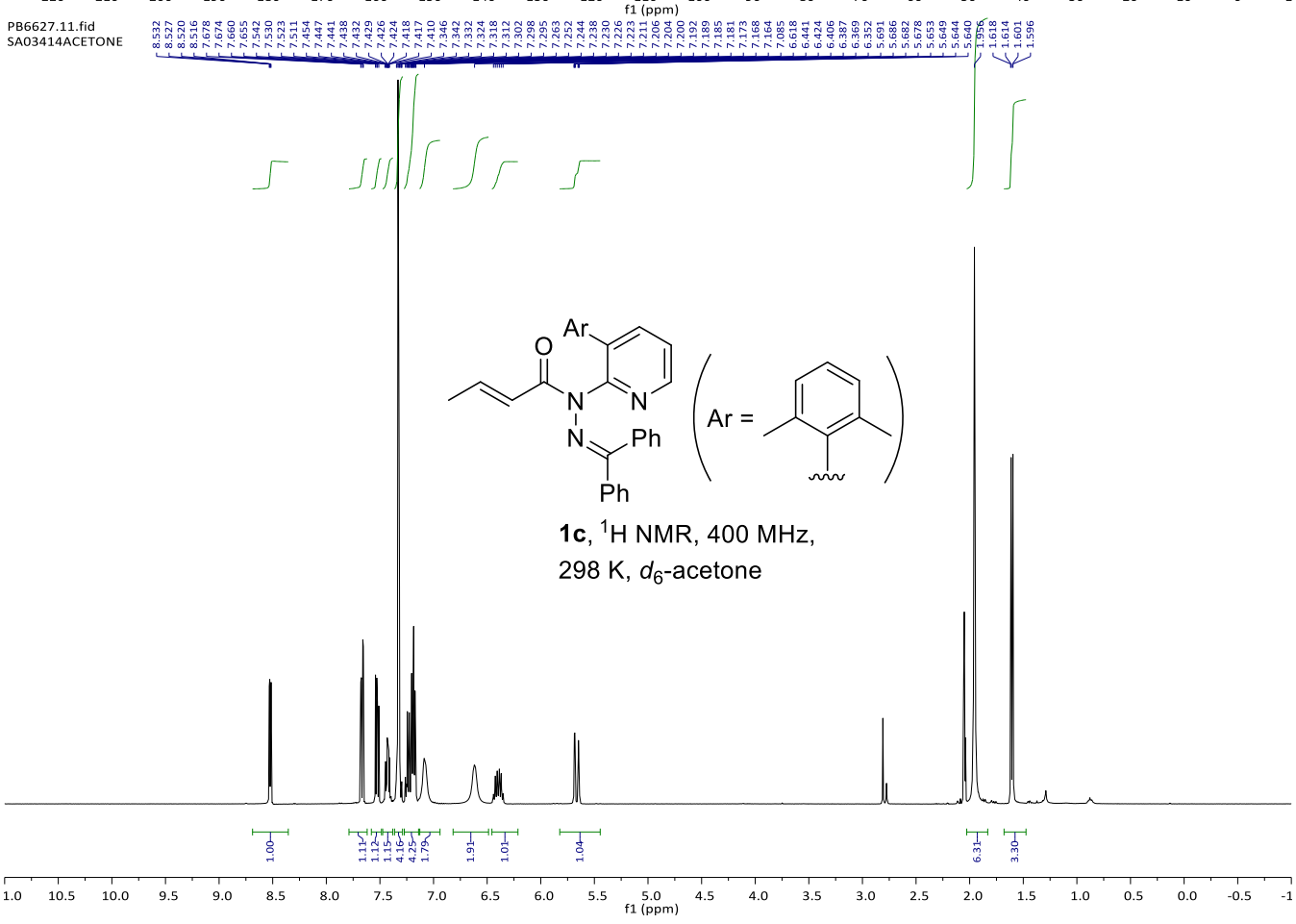
1b, ^{13}C NMR, 125 MHz, 323 K, CD_3CN



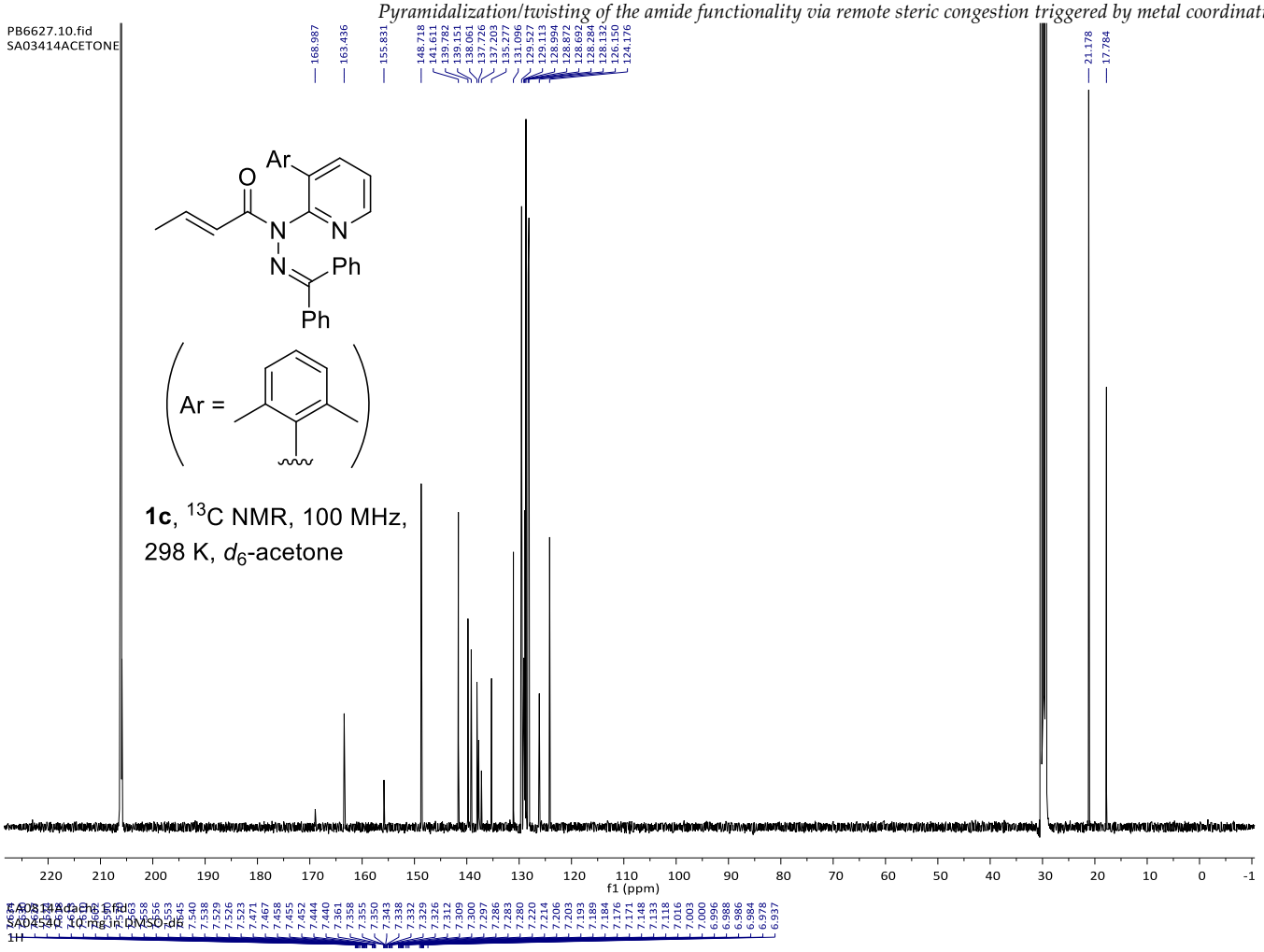
1c, ^{1}H NMR, 400 MHz, 298 K, CD_3CN

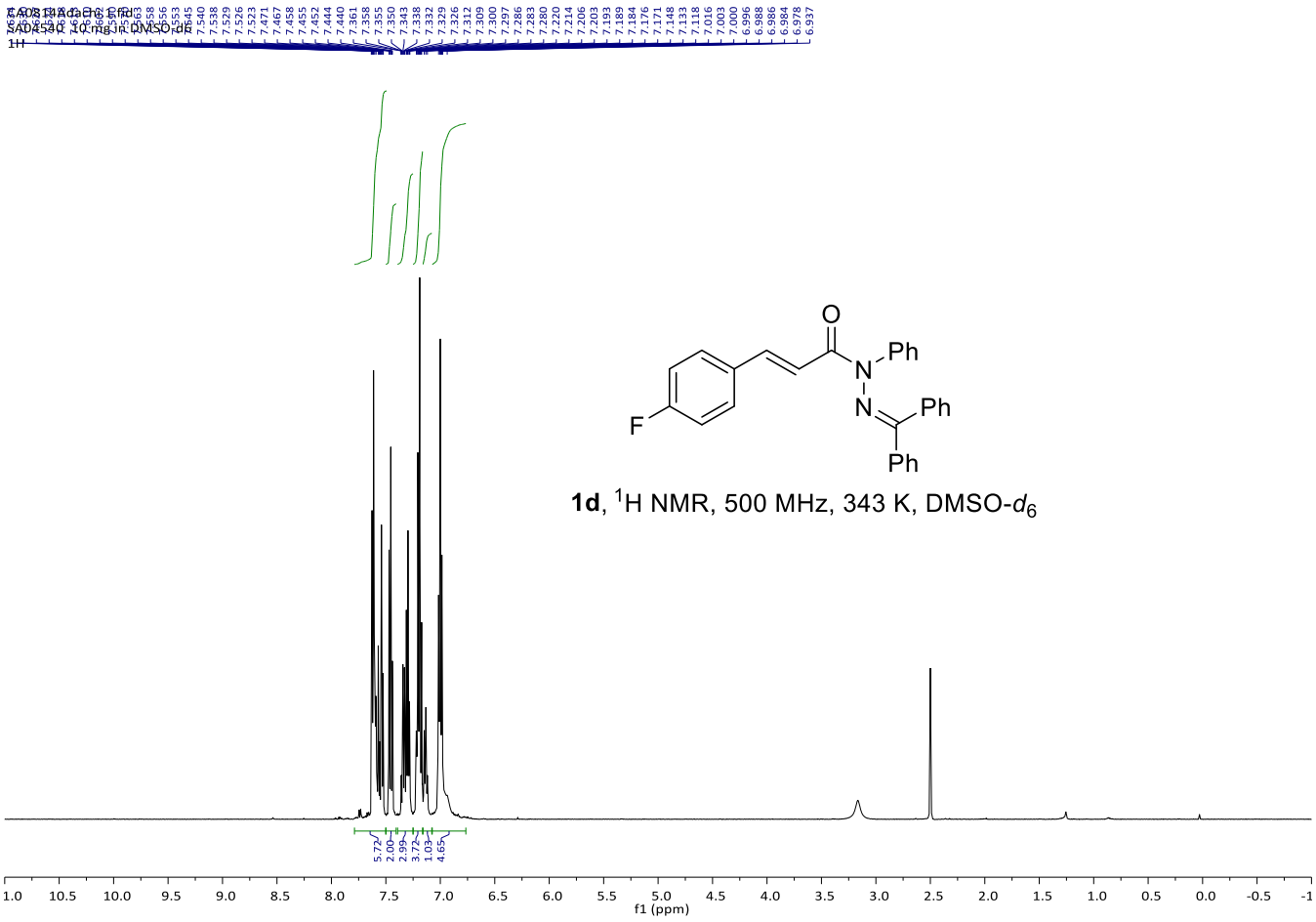


1c, ^{13}C NMR, 100 MHz, 298 K, CD_3CN

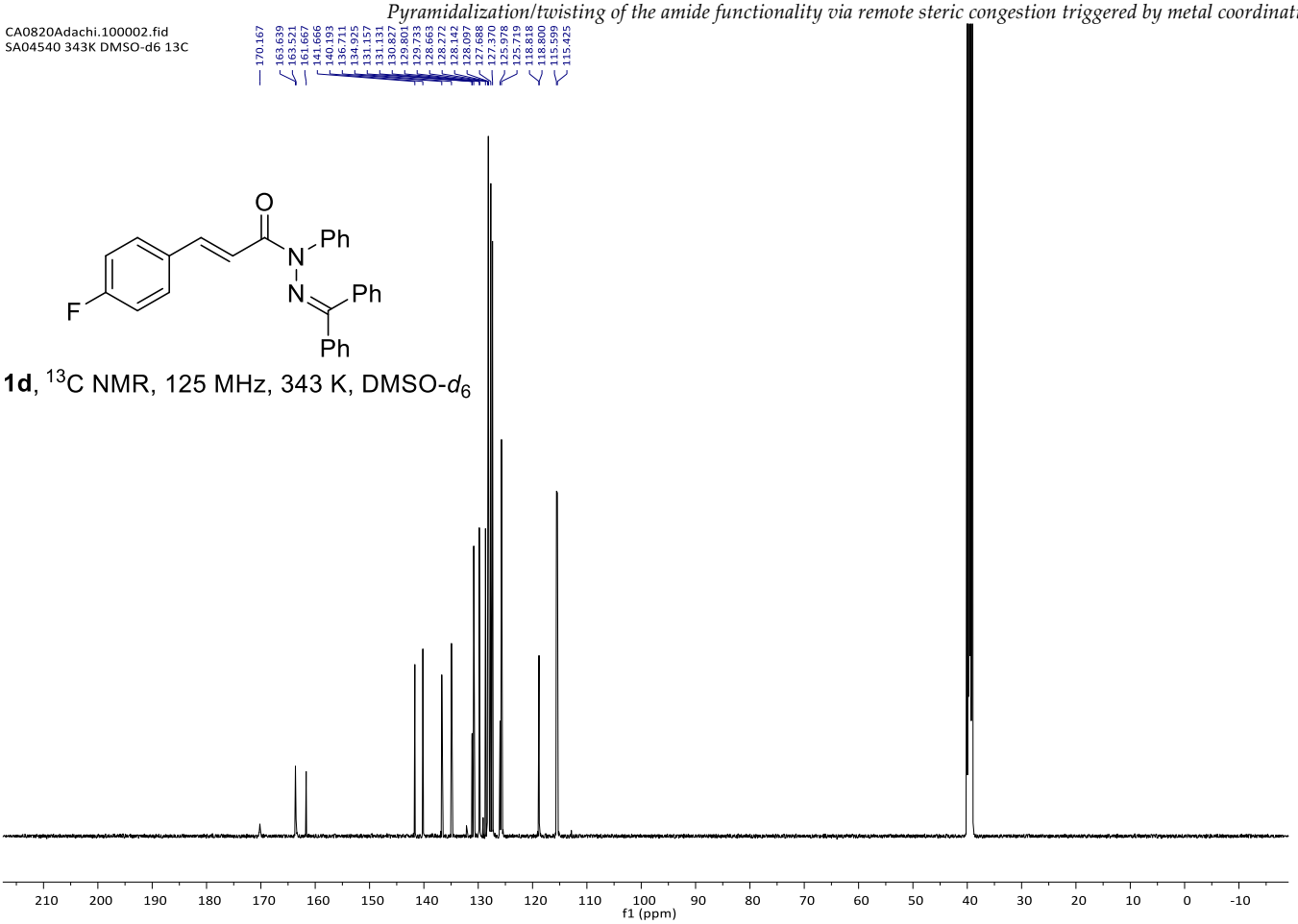


1c, ^{1}H NMR, 400 MHz,
298 K, d_6-acetone


PB6627.10.fid
SA03414ACETONE
168.987
163.436
155.831
148.718
141.611
139.782
139.151
138.061
137.726
137.203
135.277
131.096
129.527
129.133
128.994
128.872
128.692
128.284
128.132
126.150
124.176
21.178
17.784
Ar
O
N
N
N
Ph
Ph
Ar =
1c, ^{13}C NMR, 100 MHz,
298 K, d_6-acetone
f1 (ppm)

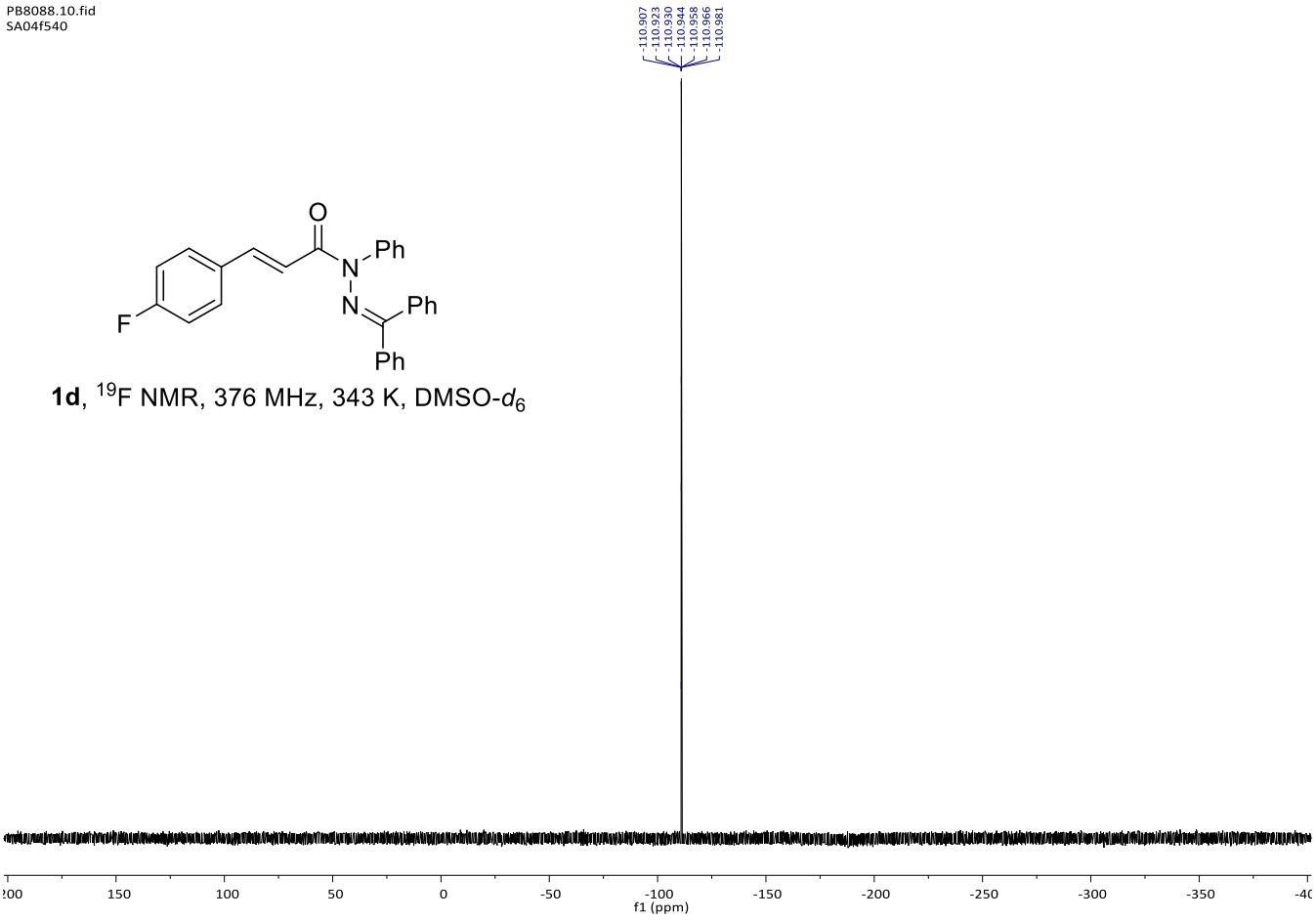

SA03414AD-01
SA03414AD-01
SA02540_10.mg.n.DMSO-d6
1H
O
Ph
N
N
Ph
F
Ph
1d, ^{1}H NMR, 500 MHz, 343 K, DMSO-d_6
5.72
2.00
2.99
2.73
1.03
4.65
f1 (ppm)

CA0820Adachi.100002.fid
SA04540 343K DMSO-d6 13C

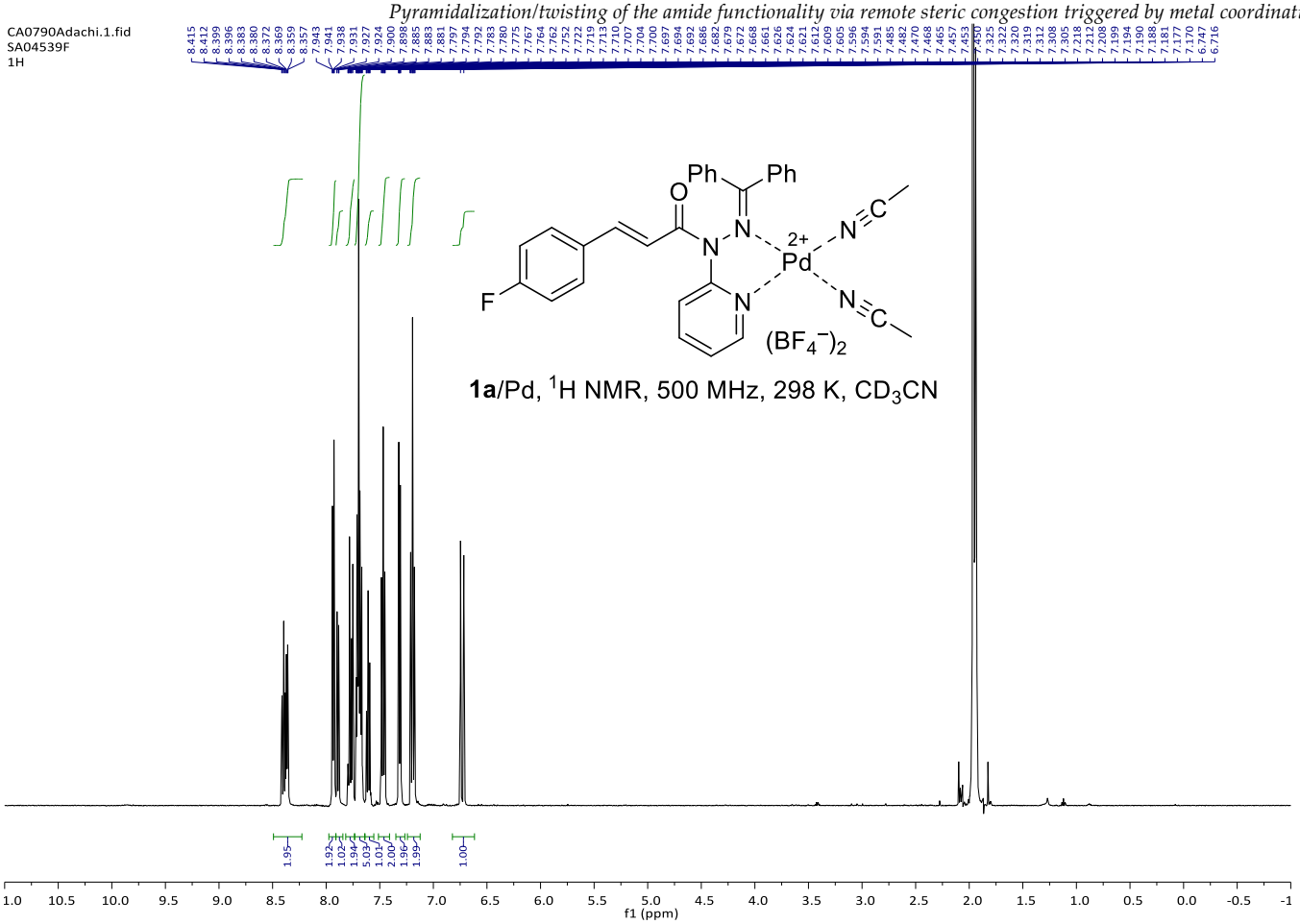


1d, ^{13}C NMR, 125 MHz, 343 K, DMSO-d_6

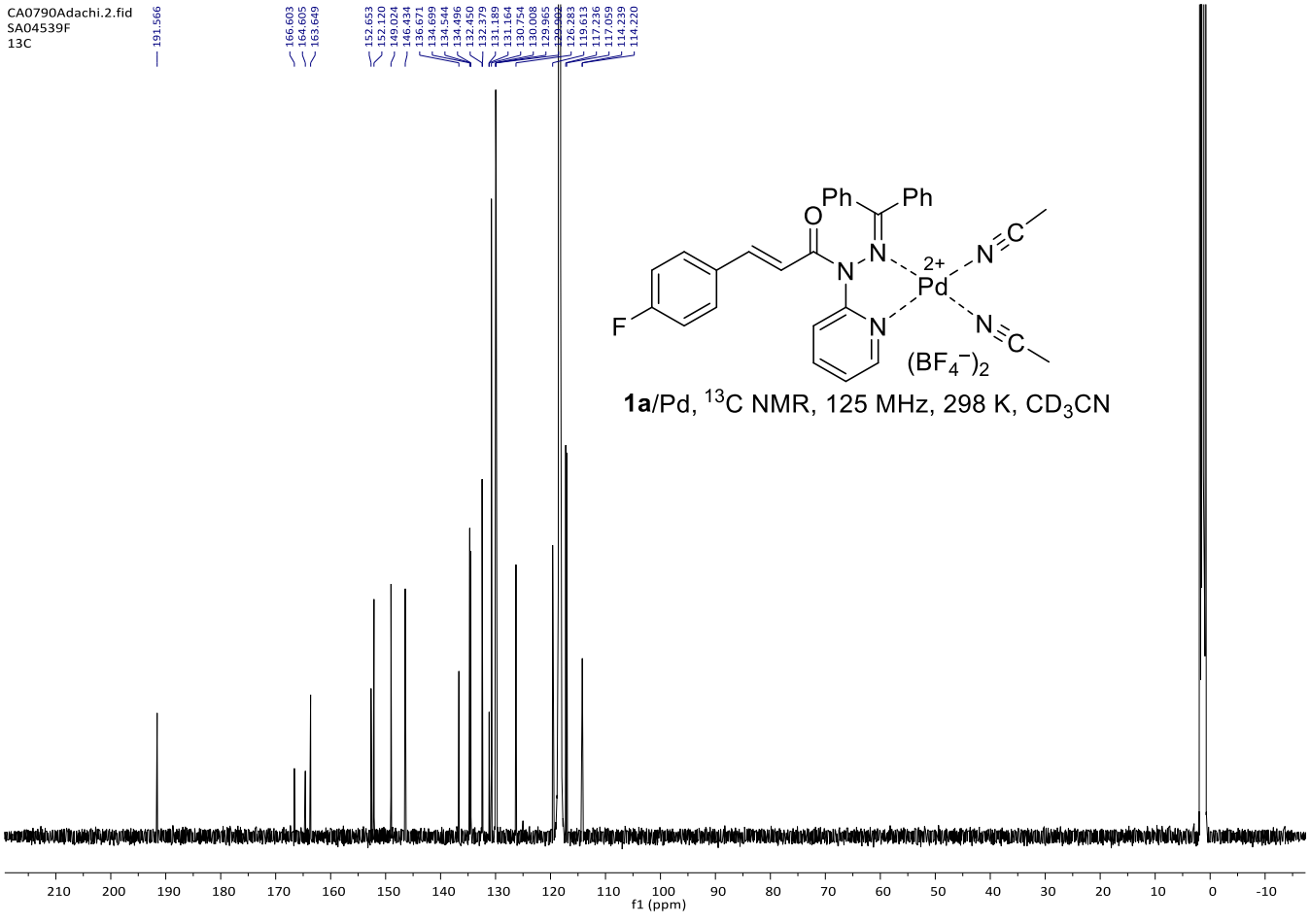
PB8088.10.fid
SA04f540



1d, ^{19}F NMR, 376 MHz, 343 K, DMSO-d_6

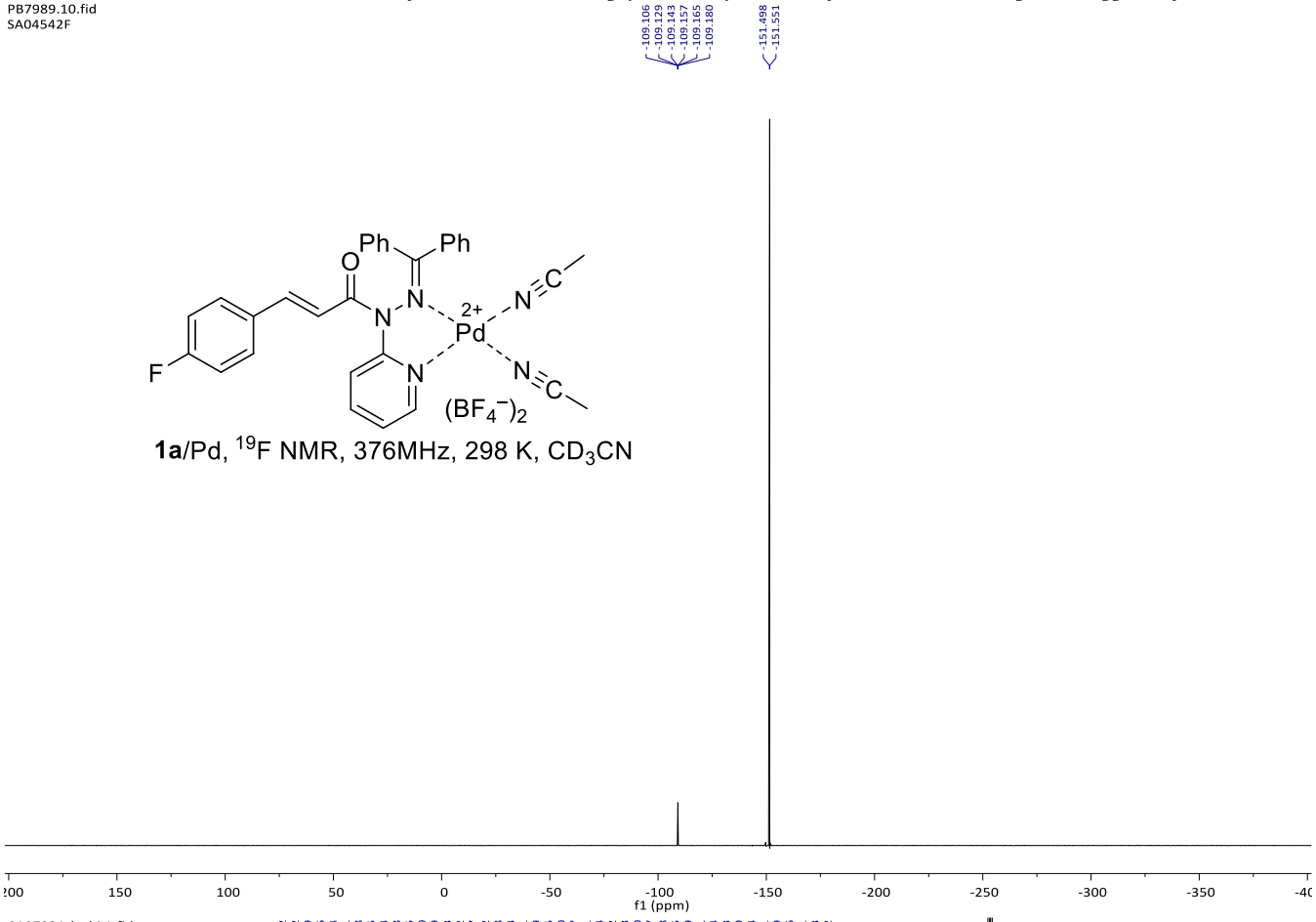


1a/Pd, ^{1}H NMR, 500 MHz, 298 K, CD_3CN



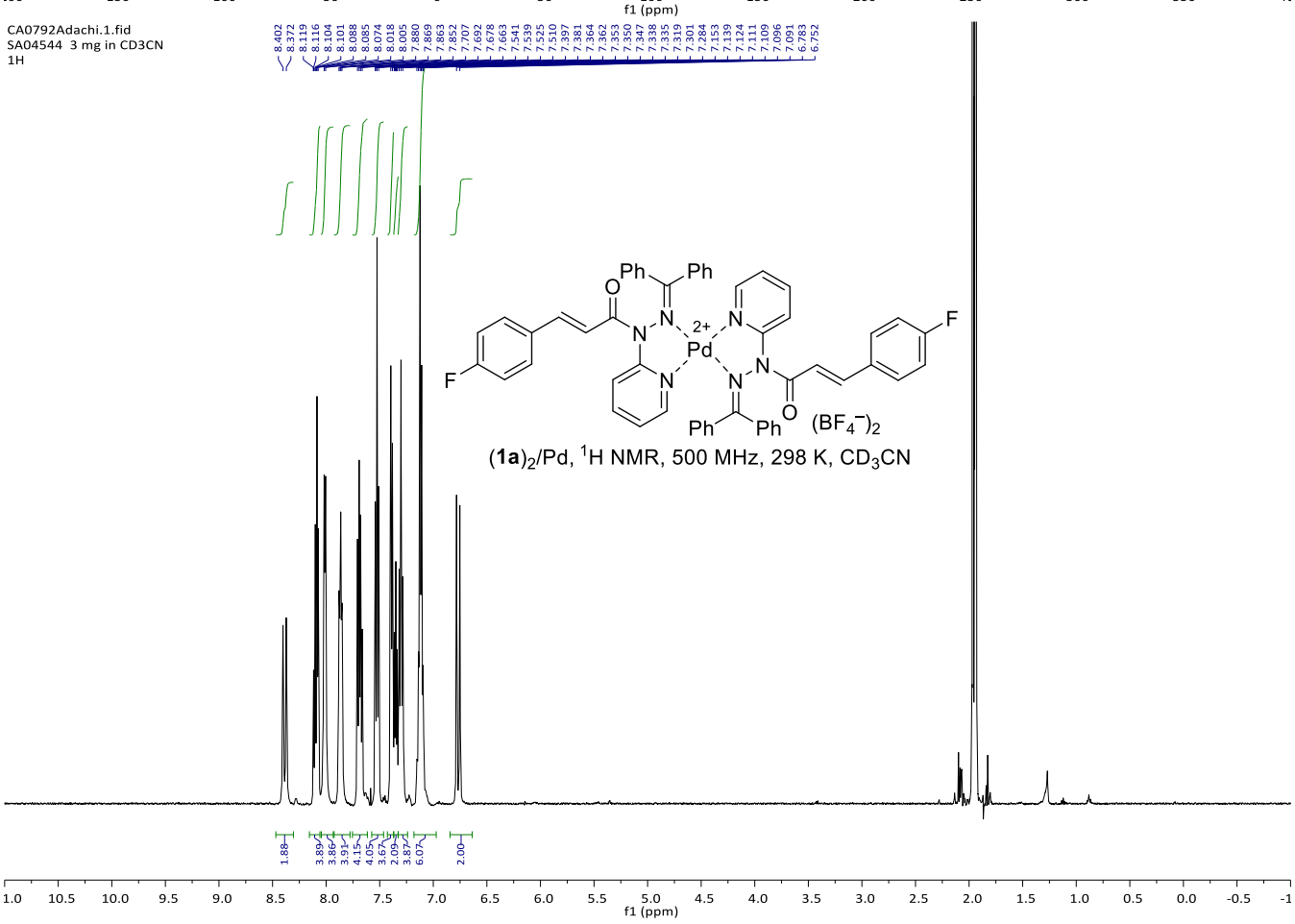
1a/Pd, ^{13}C NMR, 125 MHz, 298 K, CD_3CN

PB7989.10.fid
SA04542F



1a/Pd, ^{19}F NMR, 376MHz, 298 K, CD_3CN

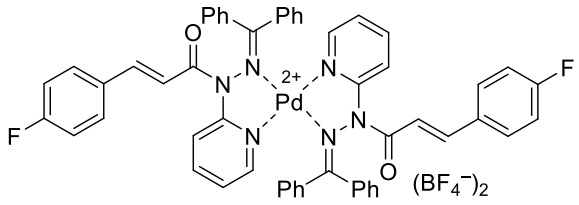
CA0792Adachi.1.fid
SA04544 3 mg in CD3CN
1H



(**1a**)$_2$/Pd, ^{1}H NMR, 500 MHz, 298 K, CD_3CN

CA0792Adachi.2.fid
SA04544 in CD3CN
13C

189.591
169.420
166.993
164.986
153.292
152.104
150.714
145.555
135.977
134.829
134.472
133.264
132.933
132.861
131.503
131.063
131.037
129.777
126.954
120.973
117.501
117.323
113.554

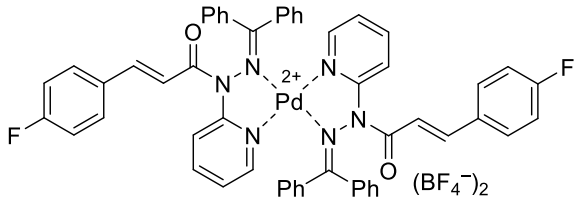


$(\mathbf{1a})_2$/Pd, ^{13}C NMR, 125 MHz, 298 K, CD_3CN

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

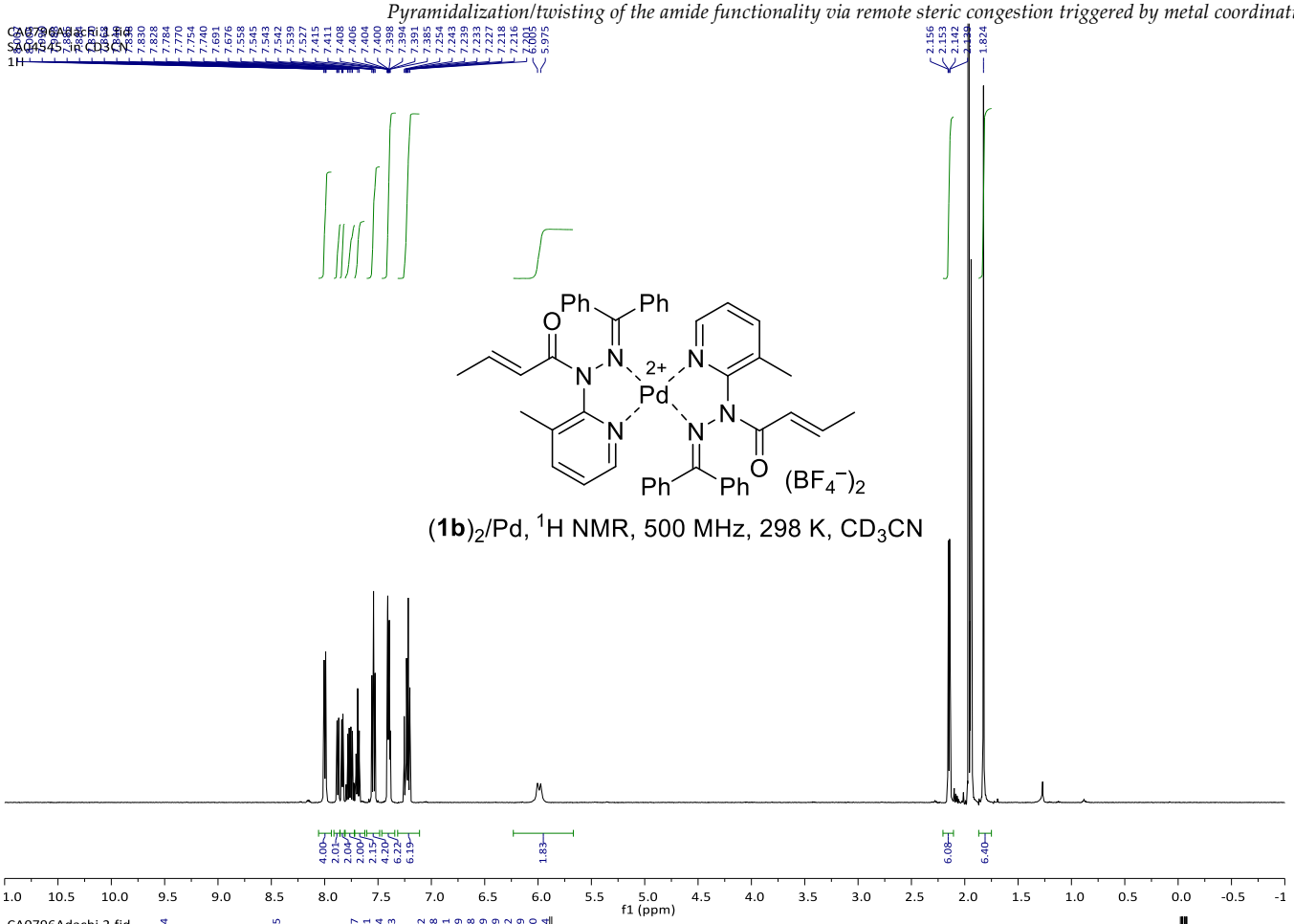
PB8056.12.fid
SA04544

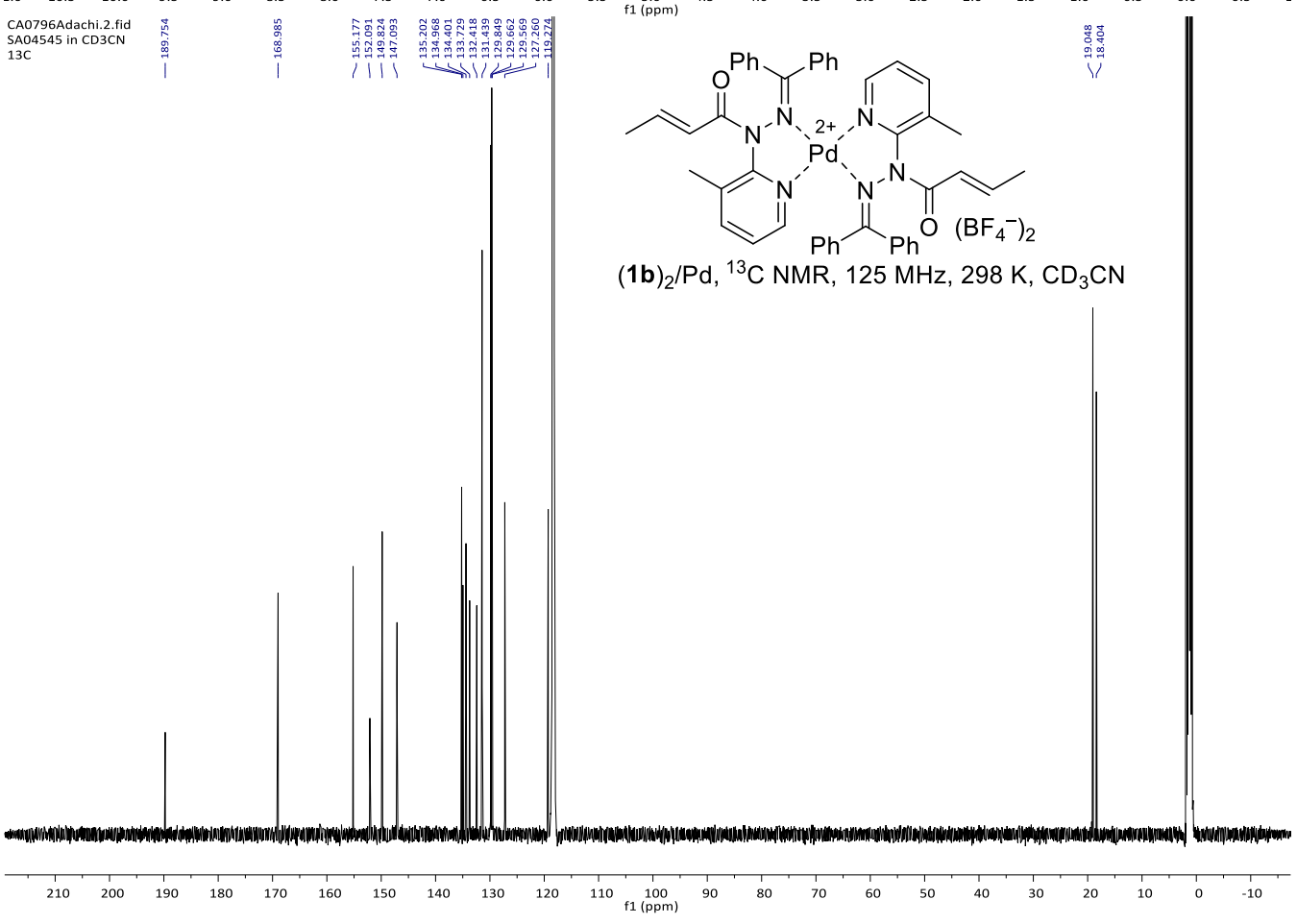
-108.204
-108.226
-108.245
-108.262
-151.716
-151.766

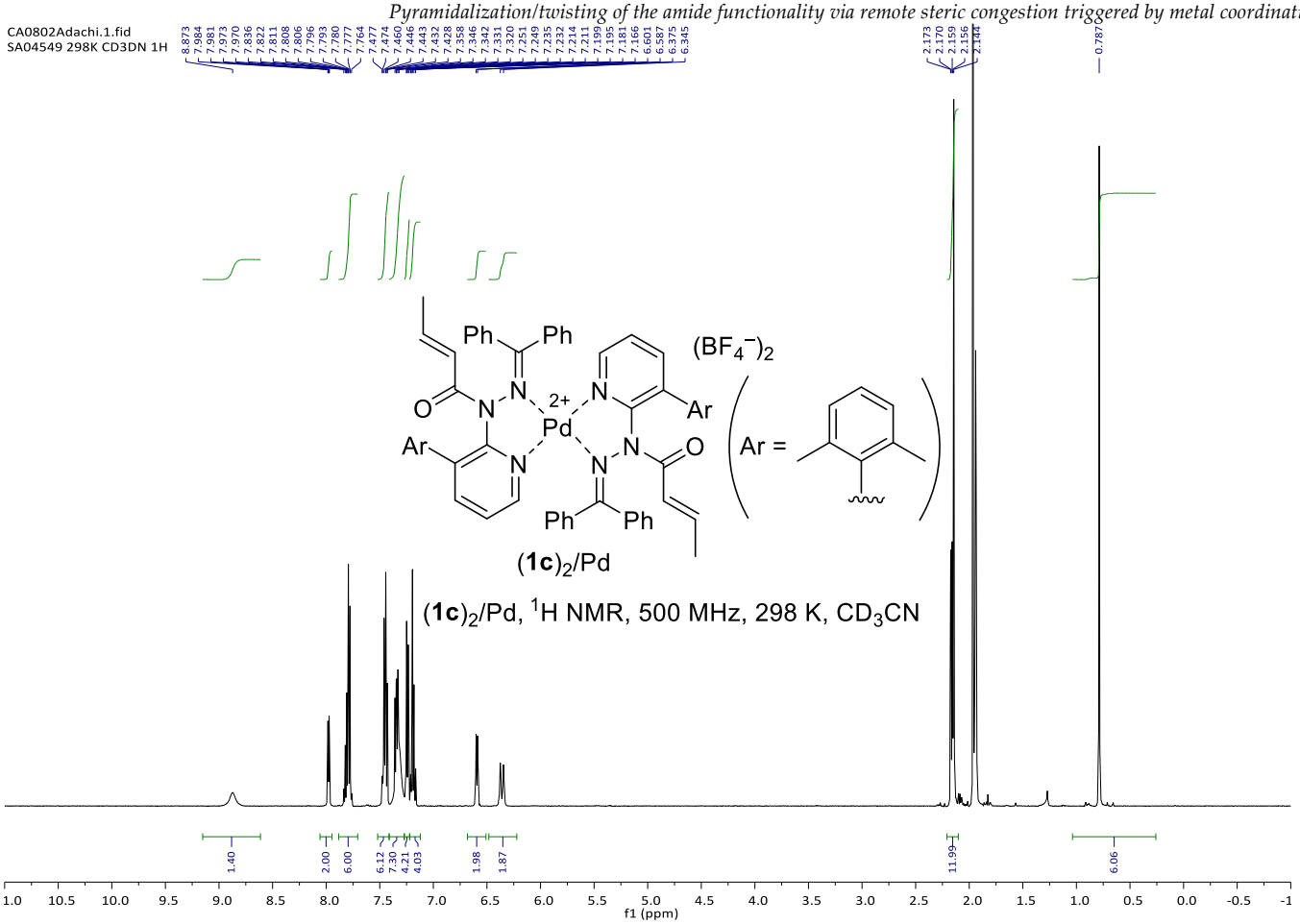


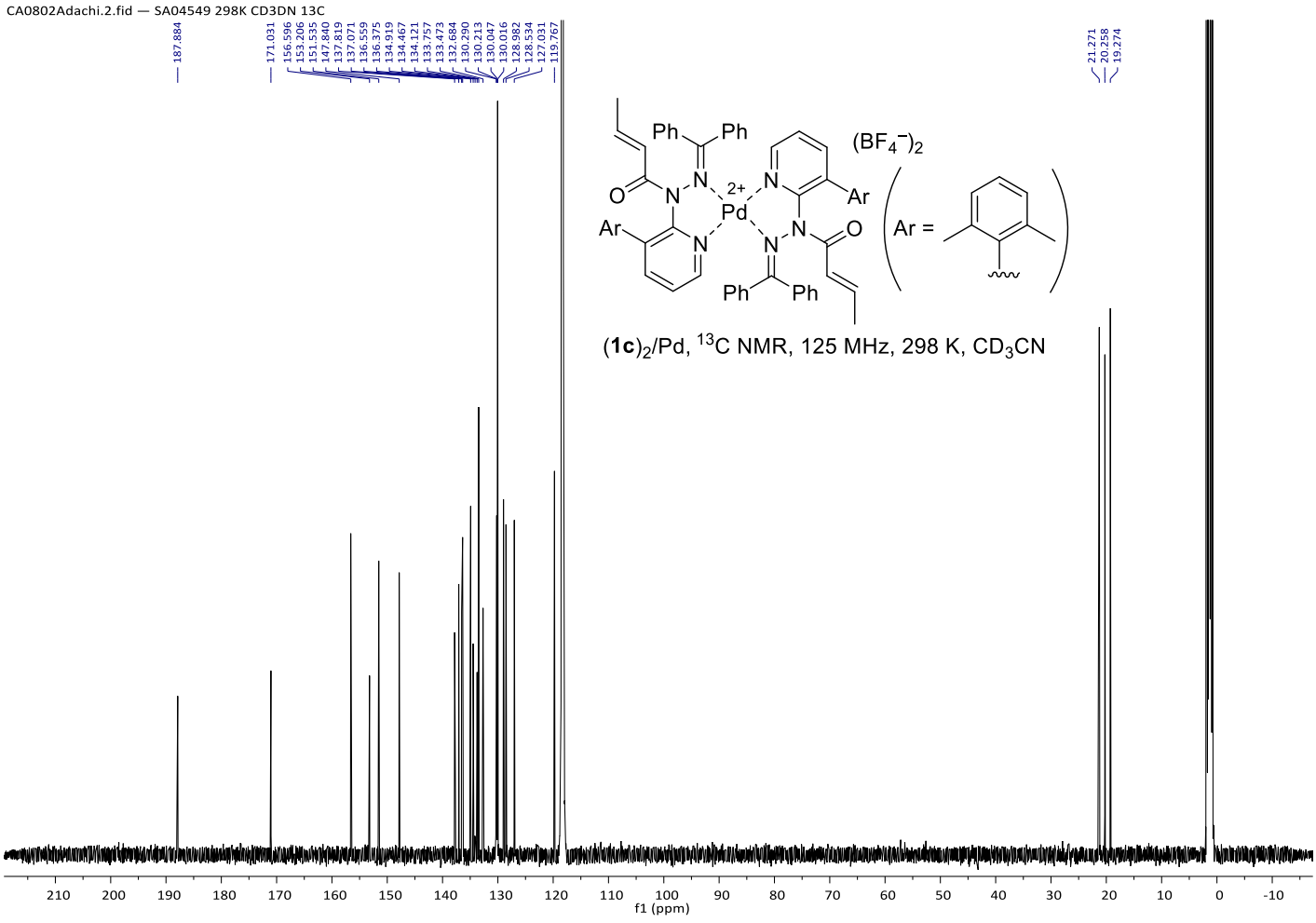
$(\mathbf{1a})_2$/Pd, ^{19}F NMR, 376MHz, 298 K, CD_3CN

200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -40
f1 (ppm)

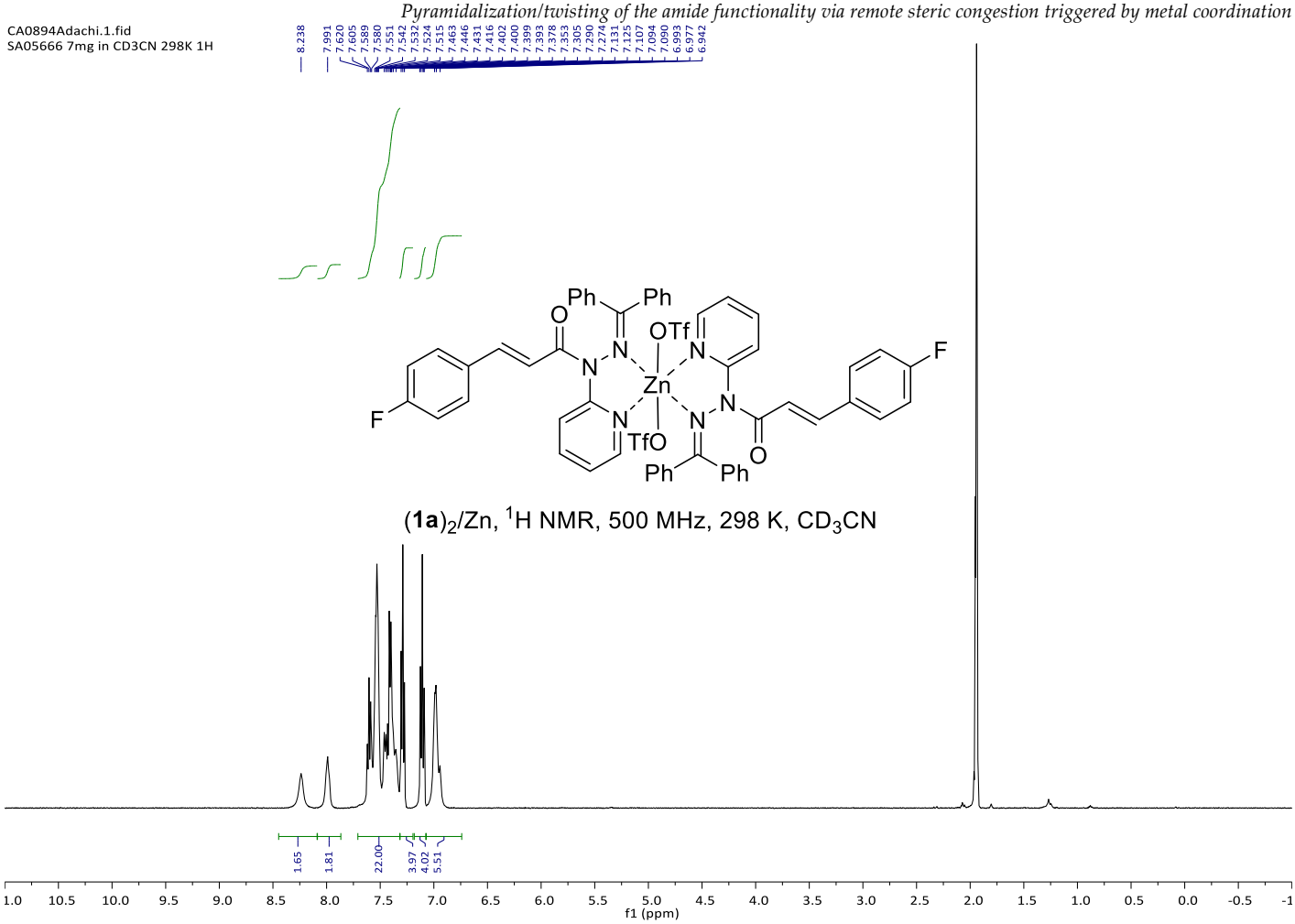

CA0796Adachi.2.fid
SA04545 in CD3CN
1H
(1b)2/Pd, 1H NMR, 500 MHz, 298 K, CD3CN
f1 (ppm)


CA0796Adachi.2.fid
SA04545 in CD3CN
13C
(1b)2/Pd, 13C NMR, 125 MHz, 298 K, CD3CN
f1 (ppm)


CA0802Adachi.1.fid
SA04549 298K CD3DN 1H
(1c)2/Pd
(1c)2/Pd, 1H NMR, 500 MHz, 298 K, CD3CN
f1 (ppm)

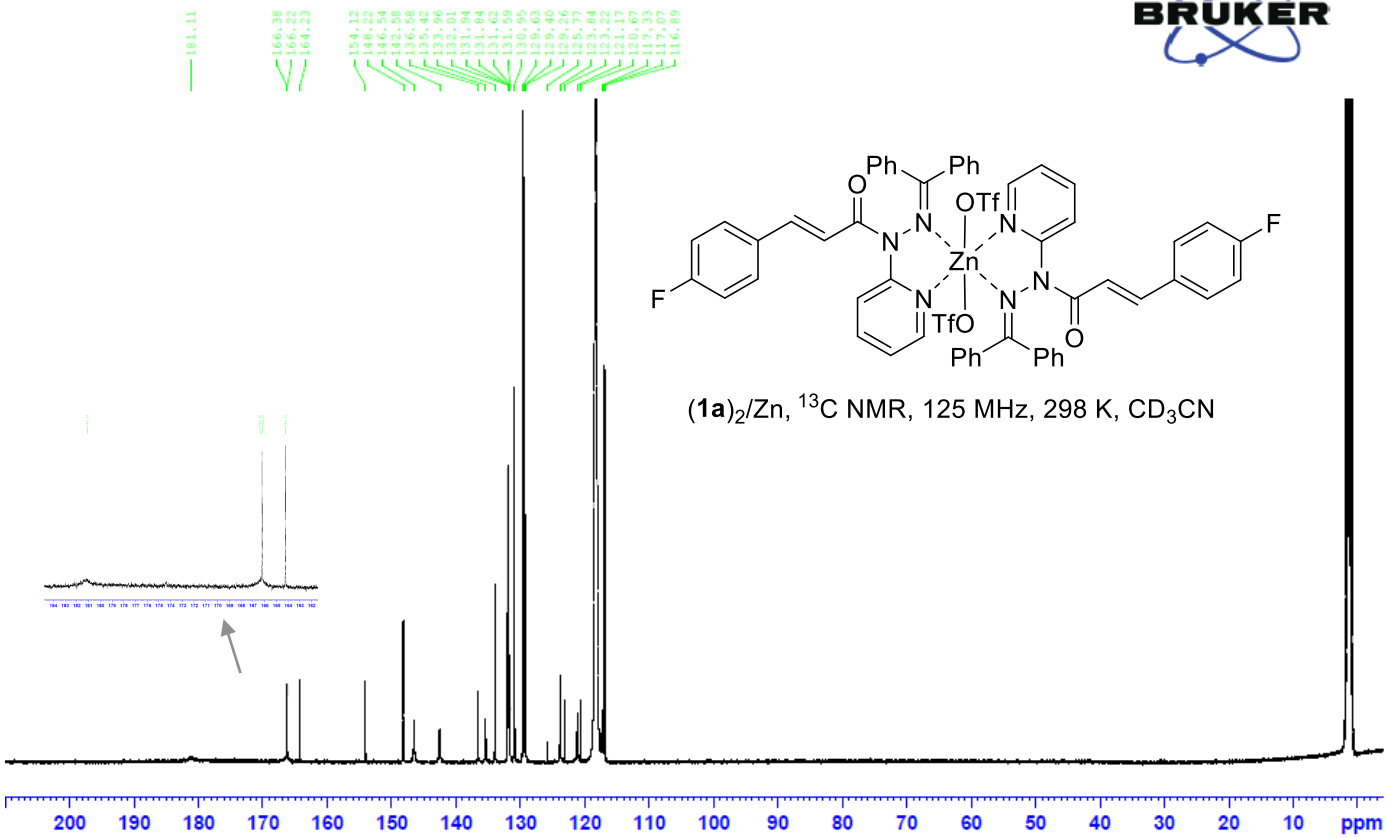

CA0802Adachi.2.fid — SA04549 298K CD3DN 13C
(1c)2/Pd, 13C NMR, 125 MHz, 298 K, CD3CN
f1 (ppm)

CA0894Adachi.1.fid
SA05666 7mg in CD3CN 298K 1H



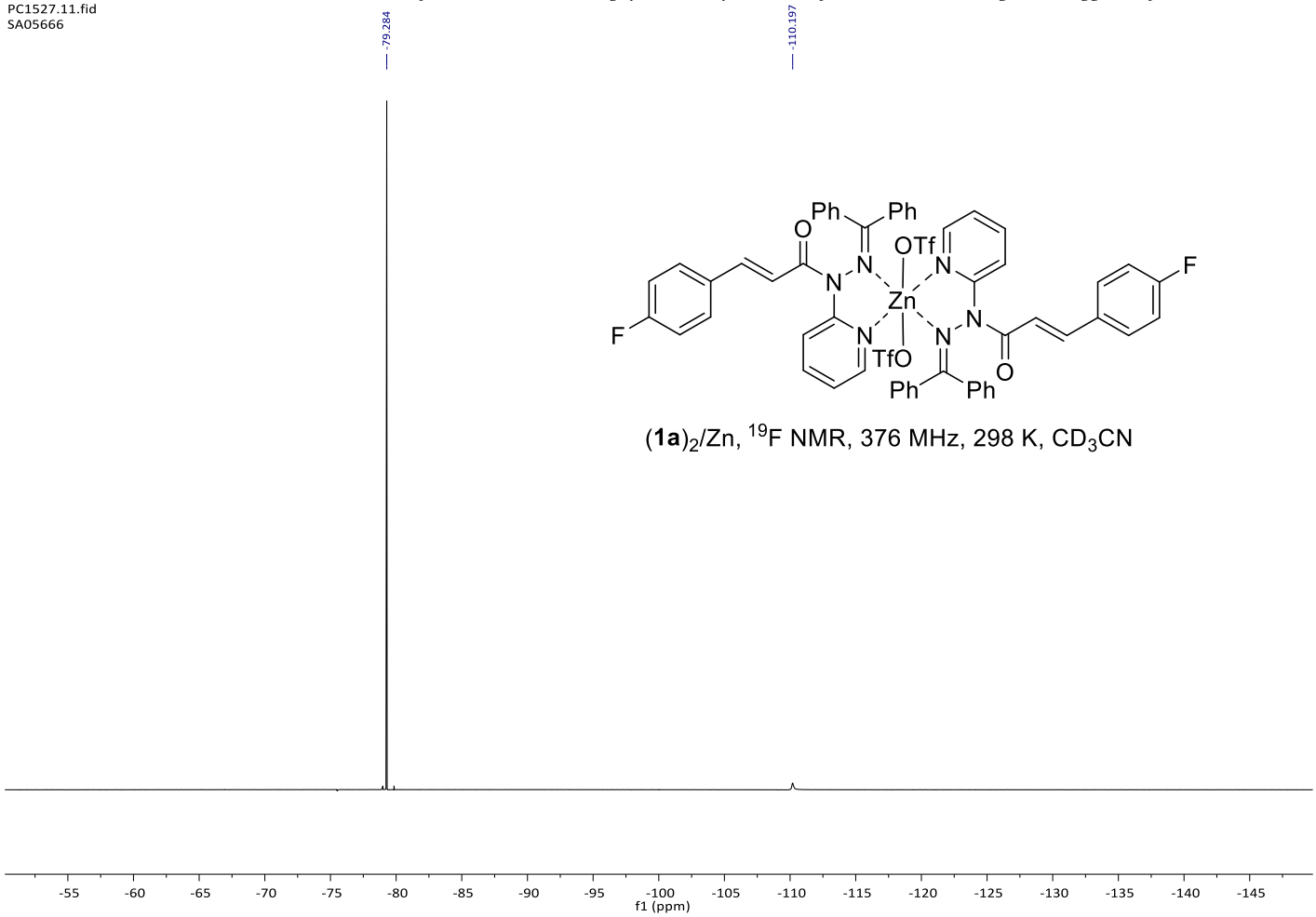
(**1a**)$_2$/Zn, ^{1}H NMR, 500 MHz, 298 K, CD_3CN

SA05666 7mg in CD3CN 298K 13C



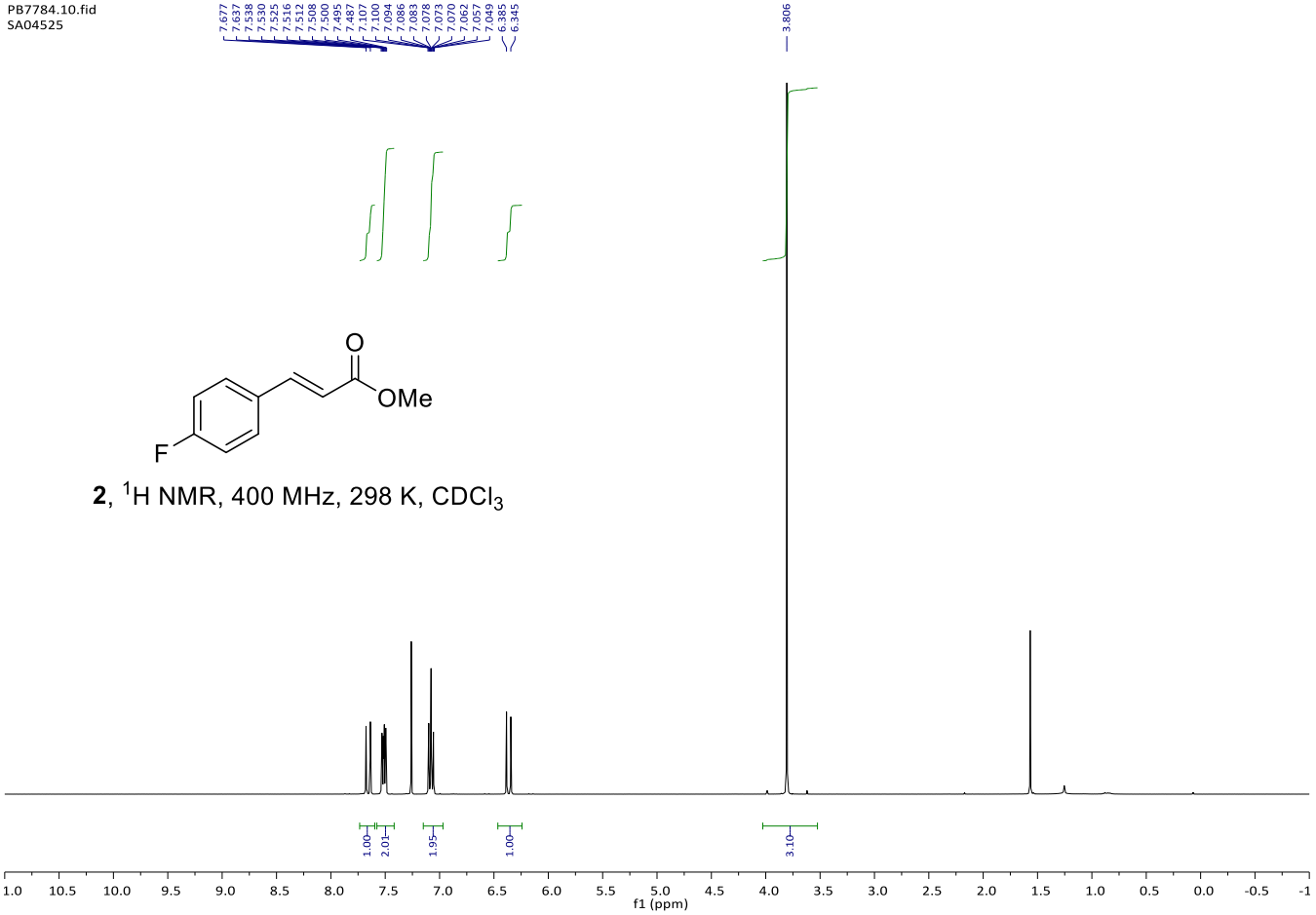
(**1a**)$_2$/Zn, ^{13}C NMR, 125 MHz, 298 K, CD_3CN

PC1527.11.fid
SA05666



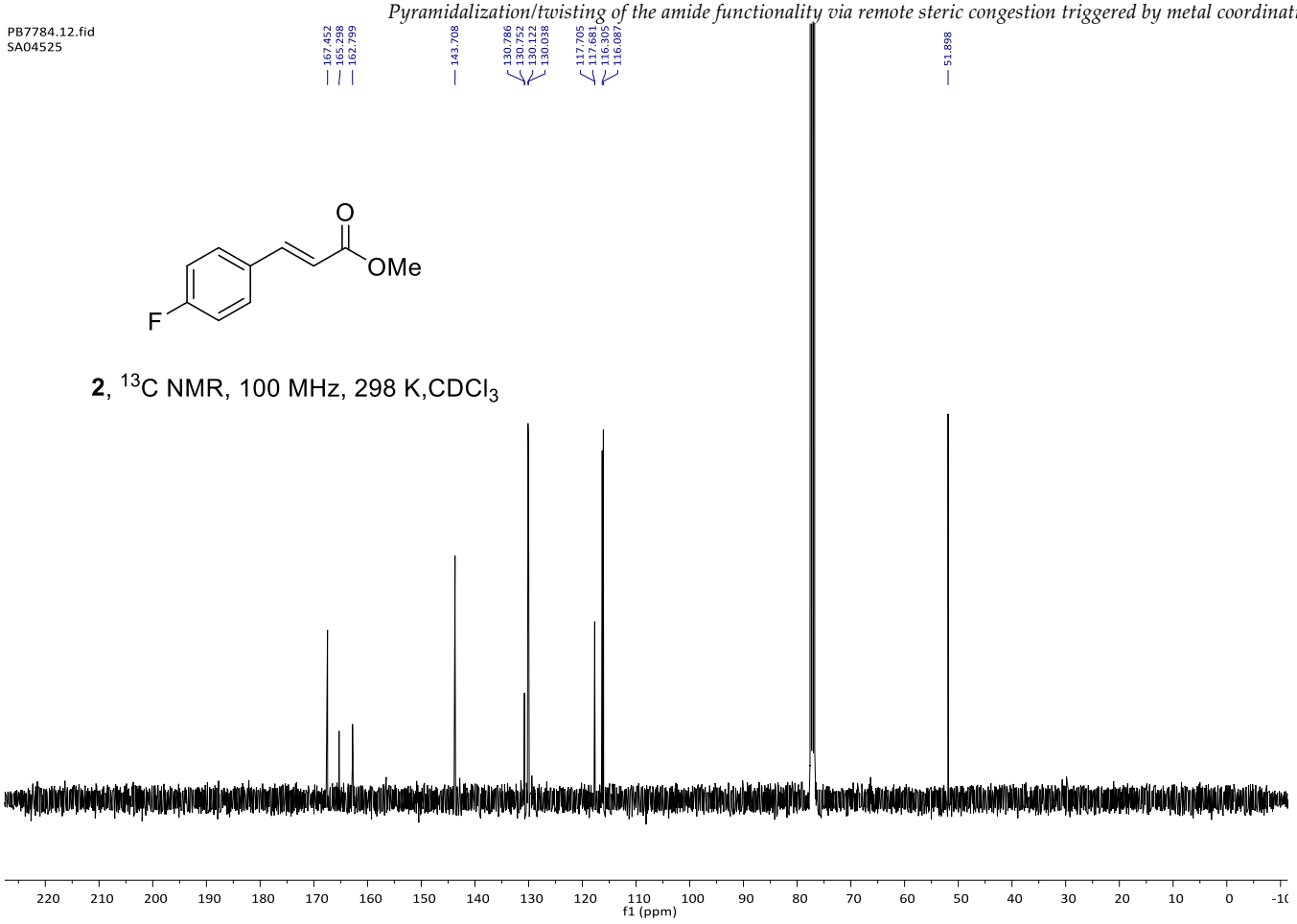
(**1a**)$_2$/Zn, ^{19}F NMR, 376 MHz, 298 K, CD_3CN

PB7784.10.fid
SA04525



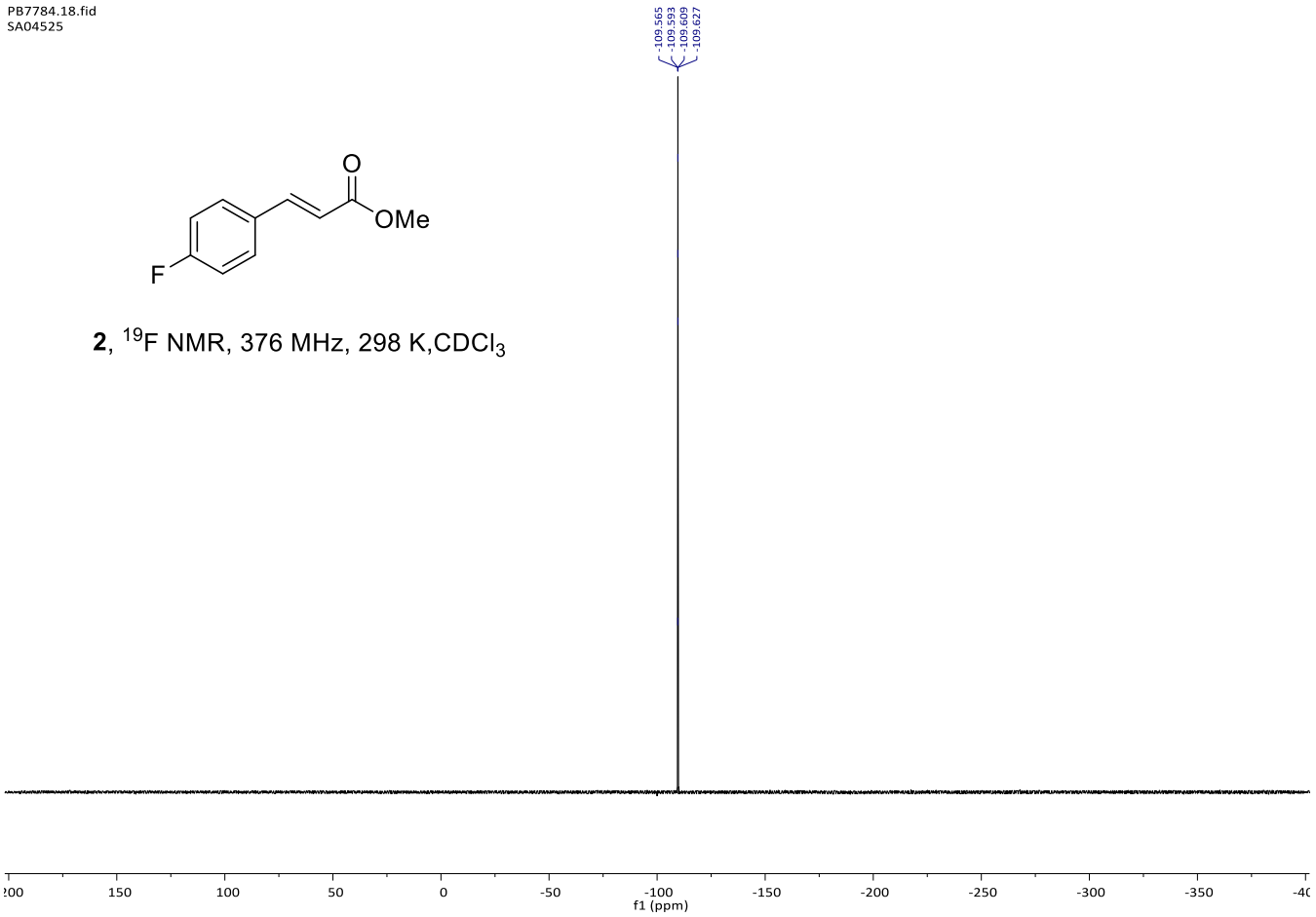
2, ^{1}H NMR, 400 MHz, 298 K, $CDCl_3$

PB7784.12.fid
SA04525



2, ^{13}C NMR, 100 MHz, 298 K,$CDCl_3$

PB7784.18.fid
SA04525



2, ^{19}F NMR, 376 MHz, 298 K,$CDCl_3$