Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dual Stimuli-Responsive Interconvertible Heteroleptic Platinum Coordination Modes

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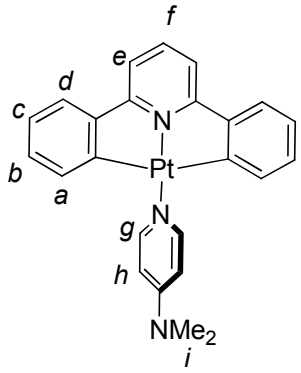
General Experimental Section

Unless otherwise stated, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. Dichloromethane and acetone were dried using an Innovative Technologies SPS-400-7 Solvent Purification System. Unless stated otherwise, all reactions were carried out under an atmosphere of nitrogen. Column chromatography on silica was carried out using Kiesegel C69 (Merck, Germany) as the stationary phase and TLC was performed on precoated silica 60 gel plates (0.20 mm thick, $60F_{254}$. Merck Germany) and observed under UV light. Column chromatography on alumina was carried out using Brockmann activity II, basic; pH 10 ± 0.5 (Fluka) as the stationary phase and TLC was performed on precoated aluminium oxide 60 gel plates (0.25 mm thick, $60F_{254}$. Merck Germany) and observed under UV light. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz instrument at a constant temperature of 300 K. Chemical shifts are reported in parts per million from low to high field. Coupling constants (*J*) are reported in hertz (Hz) and refer to coupling through three bonds i.e. ^{3}J, unless otherwise stated. Standard abbreviations indicating multiplicity were used as follows: m = multiplet, br = broad, d = doublet, t = triplet, s = singlet. Other abbreviations used in the Supporting Information, include; DCM = dichloromethane; $PyNMe_2$ = *N,N*-dimethyl-4-aminopyridine; DMSO = dimethylsulfoxide; Et_2O = diethyl ether; EtOAc = ethyl acetate; MeOH = methanol; NEt_3 = triethylamine; P_1-^{t}Bu = *tert*-butylamino-tris(dimethylamino)phosphazene; PyH = pyridine, $PyCF_3$ = 4-trifluoromethylpyridine, RT = room temperature; TLC = thin layer chromatography; TsOH = *p*-toluenesulfonic acid. [**L**Pt(DMSO)] was prepared according to literature procedures.[1] All melting points (m.p.) were determined using Sanyo Gallenkamp apparatus. MS FAB and EI

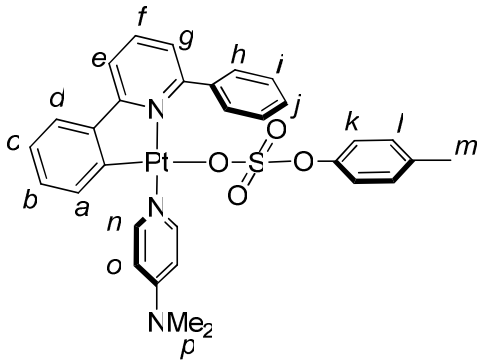
mass spectrometry was carried out by the services at the University of Edinburgh. The absorption spectra were recorded using a PerkinElmer Lambda 9 spectrometer controlled using UV/Winlab software. Photochemical reactions were carried out in quartz NMR tubes using a multilamp photoreactor (model MLU18, manufactured by Photochemical Reactors Ltd, Reading, UK) and monitored using ^{1}H NMR spectroscopy.

Synthetic Details



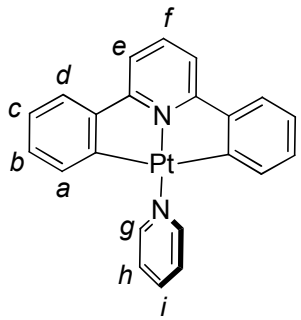
[**L**Pt(PyNMe$_2$)]

To a yellow solution of [**L**Pt(DMSO)] (0.094 g, 0.187 mmol) in CH_2Cl_2 (4 mL) was added PyNMe$_2$ (0.028 g, 0.187 mmol), which resulted in a darkening of the solution colour to orange within 5 mins. The reaction was monitored by TLC (alumina, 90.5:9:0.5 EtOAc:CH_2Cl_2:NEt_3) until complete (1.5 h), after which time the excess solvent was removed under reduced pressure. Purification of the crude product using column chromatography on alumina (90.5:9:0.5 EtOAc:CH_2Cl_2:NEt_3) and subsequent recrystallisation (CH_2Cl_2/hexane) gave an orange solid (0.102 g, 98%). m.p. 292 ºC (dec.); ^{1}H NMR (400 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 8.58 (2H, d, J = 7.2 Hz, J (^{195}Pt) = 42.0 Hz, H$_g$), 7.69 – 7.65 (1H, m, H$_f$), 7.55 (2H, d, J = 7.2 Hz, H$_d$), 7.43 – 7.40 (2H, m, H$_e$), 7.20 – 7.17 (2H, m, H$_h$), 7.10 – 7.02 (4H, m, H$_{b+c}$), 6.81 – 6.79 (2H, m, H$_a$), 3.26 (6H, s, H$_i$); ^{13}C NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 172.8, 167.6, 151.7, 148.9, 138.8, 133.1, 129.5, 123.1, 122.4, 121.9, 113.7, 107.9, 38.4; UV/Vis ([D_7]DMF:CD_2Cl_2; 1:1): λ_{max} / nm (ε / M^{-1} cm^{-1}): 386 (2944), 285 (33618), 336 (8939); LR-FABMS (3-NOBA matrix): *m/z* = 547 $[MH]^+$; HR-FABMS (3-NOBA matrix); *m/z* = 547.1457 (calc. for $C_{24}H_{22}N_3Pt$, 547.1461).



[*cis*-H**L**Pt(PyNMe$_2$)OTs]

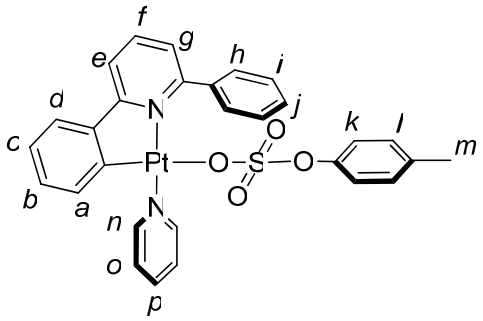
To a solution of [**L**Pt(PyNMe$_2$)] (10.0 mg, 0.018 mmol) in 1:1 CH_2Cl_2/acetone (2 mL) was added TsOH·H_2O (3.5 mg, 0.018 mmol). After stirring for 5 min. the excess solvent was removed under reduced pressure to give the product as a pale yellow solid (9.7 mg, 72%). ^{1}H NMR (400 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 8.32 – 8.17 (4H, m, H_{e+f+n}), 8.09 – 8.07 (1H, d, H_g), 7.76 – 7.71 (3H, m, H_{d+k}), 7.60 – 7.59 (4H, m, H_{h+i}), 7.55 (1H, m, H_j), 7.21 – 7.18 (3H, m, H_{c+l}), 7.04 – 7.00 (1H, m, H_b), 6.73 (2H, d, J = 7.2 Hz, H_o), 6.53 – 6.41 (1H, m, H_a), 3.17 (6H, s, H_p), 2.38 (3H, s, H_m); ^{13}C NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 166.0, 161.5, 161.4, 157.1, 157.0, 153.8, 150.4, 145.0, 143.3, 138.9, 138.4, 131.2, 128.4, 128.3, 128.2, 127.6, 127.4, 125.1, 123.5, 123.3, 116.7, 107.5, 38.2, 20.0; LR-FABMS (3-NOBA matrix): *m/z* = 547 [M-OTs]$^+$; HR-FABMS (3-NOBA matrix); *m/z* = 547.1457 (calc. for $C_{24}H_{22}N_3Pt$, 547.1461).



[**L**Pt(PyH)]

To a yellow solution of [**L**Pt(DMSO)] (0.050 g, 0.10 mmol) in CH_2Cl_2 (20 mL) was added PyH (0.008 mL, 0.10 mmol). The reaction was monitored by TLC (alumina,

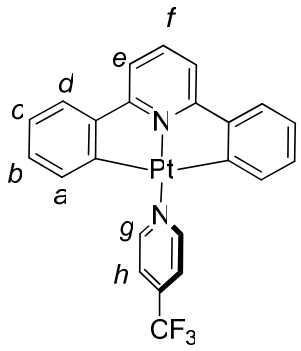
90.5:9:0.5 EtOAc:CH_2Cl_2:NEt_3) until complete (3 h), after which time the excess solvent was removed under reduced pressure. Purification of the crude product using column chromatography on alumina (90.5:9:0.5 EtOAc:CH_2Cl_2:NEt_3) and subsequent recrystallisation (CH_2Cl_2/hexane) gave an orange solid (0.042 g, 84%). m.p. 201-203 ºC; ^{1}H NMR (400 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 9.16 (2H, d, J = 6.8 Hz, J (^{195}Pt) = 43.6 Hz, H_g), 8.12 – 8.08 (1H, m, H_i), 7.72 – 7.65 (3H, m, H_{f+h}), 7.57 (2H, d, J = 6.8 Hz, H_d), 7.45 – 7.43 (2H, m, H_e), 7.19 – 7.16 (2H, m, H_b), 7.08 – 7.03 (2H, m, H_c), 6.94 – 6.89 (2H, m, H_a); ^{13}C NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 172.1, 167.5, 153.2, 148.8, 139.4, 136.3, 132.5, 129.7, 126.2, 123.3, 122.7, 113.9; UV/Vis ([D_7]DMF:CD_2Cl_2; 1:1); λ_{max} / nm (ε / M^{-1} cm^{-1}): 393 (999), 344 (3237), 280 (7266), 251 (8953); LR-FABMS (3-NOBA matrix); *m/z* = 504 $[M]^+$; HR-FABMS (3-NOBA matrix); *m/z* = 504.10469 (calc. for $C_{22}H_{17}N_2Pt$, 504.10340).



[H**L**Pt(PyH)OTs]

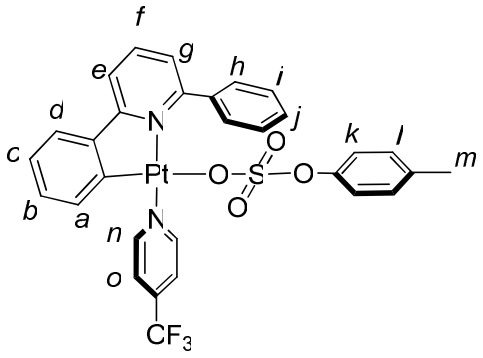
To a solution of [**L**Pt(PyH)] (20 mg, 0.040 mmol) in 1:1 CH_2Cl_2/acetone (3/1 mL) was added TsOH.H_2O (7.6 mg, 0.040 mmol). After stirring for 5 min. the excess solvent was removed under reduced pressure to give the product as a pale yellow solid and the desired product was recrystallised from hexane and $CHCl_3$ (19 mg, 71%). ^{1}H NMR (400 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 9.01 (2H, J = 6.4 Hz, J (^{195}Pt) = 38.8 Hz, H_n), 8.23 – 8.10 (3H, m, H_{e+h}), 7.78 – 7.55 (10H, m, $H_{d+f+g+i+k+o+p}$), 7.24 – 7.16 (4H, m, H_{c+j+l}), 7.03 – 6.99 (1H, m, H_b), 6.38 – 6.22 (1H, m, H_a), 2.34 (3H, s, H_m); ^{13}C

NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 176.9, 157.6, 157.6, 153.5, 140.0, 139.7, 139.3, 135.6, 132.1, 131.6, 129.4, 129.3, 128.5 (2C), 128.3, 127.0, 125.9 (2C), 124.5, 117.6, 115.9, 114.9, 107.9; LR-FABMS (3-NOBA matrix): *m/z* = 504 $[M\text{-}OTs]^+$; HR-FABMS (3-NOBA matrix); *m/z* = 504.10397 (calc. for $C_{22}H_{17}N_2Pt$, 504.10340).



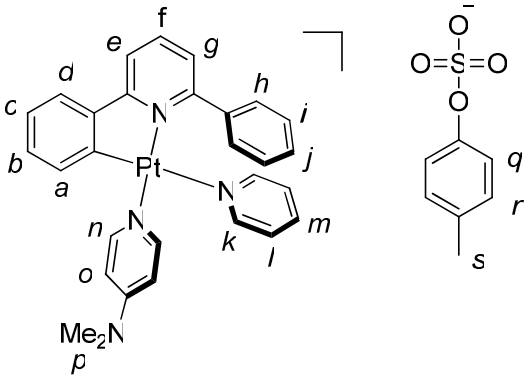
[**L**Pt($PyCF_3$)]

To a yellow solution of [**L**Pt(DMSO)] (0.067 g, 0.13 mmol) in CH_2Cl_2 (10 mL) was added $PyCF_3$ (0.020 g, 0.13 mmol), which resulted in a darkening of the solution to orange. The reaction was stirred overnight at room temperature and the excess solvent was removed under reduced pressure. Purification of the crude product using column chromatography on alumina (90.5:9:0.5 EtOAc:CH_2Cl_2:NEt_3) and subsequent recrystallisation (CH_2Cl_2/hexane) gave an orange solid (0.062 g, 83%). m.p. 228-232 ºC (dec); ^{1}H NMR (400 MHz,[D_7]DMF:CD_2Cl_2; 1:1): 9.48 (2H, d, *J* = 6.0 Hz, *J* (^{195}Pt) = 45.6 Hz, H_g), 8.02 – 7.99 (2H, m, H_h), 7.74 (1H, t, *J* = 8.0 Hz, H_f), 7.58 (2H, d, *J* = 6.8 Hz, H_d), 7.47 (2H, d, *J* = 8.0 Hz, H_e), 7.23 – 7.18 (2H, m, H_b), 7.13 – 7.07 (2H, m, H_c), 6.95 – 6.86 (2H, m, H_a); ^{13}C NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 171.6, 167.5, 154.5, 148.7, 139.7, 132.3, 129.8, 127.9, 125.0, 123.5, 123.0, 122.3, 114.1; UV/Vis ([D_7]DMF:CD_2Cl_2; 1:1); λ_{max} / nm (ε / M^{-1} cm^{-1}): 392 (2717), 340 (6584), 270 (18991); LR-FABMS (3-NOBA matrix): *m/z* = 572 $[MH]^+$; HR-FABMS (3-NOBA matrix); *m/z* = 572.0916 (calc. for $C_{23}H_{16}N_2F_3Pt$, 572.09078).



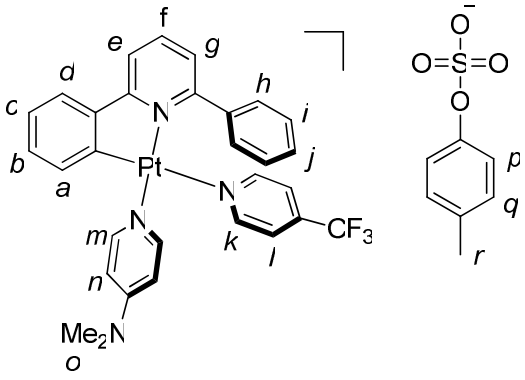
[*cis*-H**L**Pt(PyCF$_3$)OTs]

To a solution of [**L**Pt(PyCF$_3$)] (12.4 mg, 0.022 mmol) in 1:1 CH_2Cl_2/acetone (4 mL) was added TsOH.H_2O (4.1 mg, 0.022 mmol). After stirring for 5 min. the excess solvent was removed under reduced pressure to give the product as a pale yellow solid (16.1 mg, 98%). ^{1}H NMR (400 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 9.39 – 9.22 (2H, m, H_n), 8.20 (1H, t, J = 7.6 Hz, H_f), 8.10 (1H, d, J = 7.6 Hz, H_e), 7.97-7.92 (2H, m, H_o), 7.78 – 7.54 (8H, m, $H_{d+k+h+i+j}$), 7.25 – 7.22 (2H, m, H_{c+g}), 7.13 (2H, d, J = 6.4 Hz, H_l), 7.04 – 7.00 (1H, m, H_b), 6.36 – 6.25 (1H, m, H_a), 2.35 (3H, s, H_m); ^{13}C NMR (100 MHz, [D_7]DMF:CD_2Cl_2; 1:1): 171.4, 167.7, 161.5, 155.7, 154.7, 152.4, 142.7, 142.2, 139.6, 131.3, 128.8, 128.7, 128.4, 127.7, 127.5, 125.2, 124.6, 124.0, 123.9, 122.4, 122.3, 115.1, 20.1; LR-FABMS (3-NOBA matrix): *m/z* = 572[M-OTs]$^+$; HR-FABMS (3-NOBA matrix); *m/z* = 572.08949 (calc. for $C_{23}H_{16}N_2F_3Pt$, 572.09078).



[*trans*-H**L**Pt(PyNMe$_2$)(PyH)]OTs

To a bright yellow solution of [**L**Pt(PyNMe$_2$)] (7.3 mg, 0.013 mmol) in 1:1 CH_2Cl_2/acetone (6 mL) was added pyridinium tosylate (3.3 mg, 0.013 mmol) and the pale yellow solution was stirred at RT for 5 mins. The excess solvent was removed under reduced pressure to give the product as a bright yellow solid (10.4 mg, 90%). ^{1}H NMR (400 MHz, [D$_7$]DMF:CD_2Cl_2; 1:1): 8.31 – 8.14 (6H, m, H$_{e+f+k+n}$), 7.85 (1H, d, J = 7.6 Hz, H$_d$), 7.74 – 7.66 (3H, m, H$_{m+q}$), 7.60 – 7.58 (2H, m, H$_h$), 7.46 (1H, dd, J = 7.6 Hz, ^4J = 1.2 Hz, H$_g$), 7.27 – 7.20 (4H, m, H$_{c+j+l}$), 7.17 – 7.13 (4H, m, H$_{i+r}$), 7.09 – 7.05 (1H, m, H$_b$), 6.66 – 6.65 (2H, d, J = 7.2 Hz, H$_o$), 6.55 – 6.45 (1H, m, H$_a$), 3.12 (6H, s, H$_p$), 2.35 (3H, s, H$_s$); ^{13}C NMR (100 MHz, [D$_7$]DMF:CD_2Cl_2; 1:1): 167.1, 161.5, 153.7, 150.0, 149.5, 145.8, 145.5, 139.8, 139.1, 139.0, 137.2, 137.0, 136.8, 132.1, 128.7, 128.3, 127.9, 127.7, 127.4, 125.2, 124.9, 123.7, 116.9, 108.1, 102.2, 38.3, 20.0; UV/Vis ([D$_7$]DMF:CD_2Cl_2; 1:1); λ_{max} / nm (ε / M^{-1} cm^{-1}): 342 (2407), 285 (7897); LR-FABMS (3-NOBA matrix): *m/z* = 547 [M-PyH]$^+$; HR-FABMS (3-NOBA matrix); *m/z* = 547.14537 (calc. for $C_{24}H_{22}N_3Pt$, 547.14560).

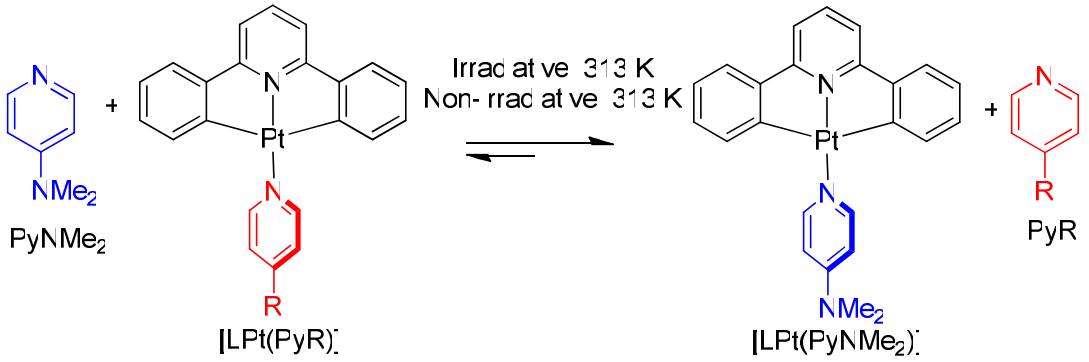


[*trans*-H**L**Pt(PyNMe$_2$)(PyCF$_3$)]OTs

To a bright yellow solution of [**L**Pt(PyNMe$_2$)] (8.4 mg, 0.015 mmol) in 1:1 CH_2Cl_2/acetone (6 mL) was added trifluoromethylpyridinium tosylate (5.2 mg, 0.015 mmol) and the pale yellow solution was stirred at RT for 5 mins. The excess solvent was removed under reduced pressure to give the product as a bright yellow solid (11.5

mg, 81%). ^{1}H NMR (400 MHz, CD_2Cl_2): 8.36 (2H, d, J = 6.4 Hz, H_k), 8.20 (2H, d, J = 7.2 Hz, H_m), 8.10 (1H, t, J = 8.0 Hz, H_f), 7.94 (1H, d, J = 8.0 Hz, H_e), 7.71 (2H, d, J = 7.6 Hz, H_{d+j}), 7.53 – 7.50 (2H, m, H_h), 7.31 – 7.23 (8H, m, $H_{c+g+i+l+q}$), 7.13 – 7.06 (3H, m, H_{b+p}), 6.52 – 6.44 (3H, m, H_{a+n}), 3.07 (6H, s, H_o), 2.36 (3H, s, H_r); ^{13}C NMR (100 MHz,[D_7]DMF:CD_2Cl_2; 1:1): 167.07, 153.9, 151.4, 150.2, 150.1, 145.8, 144.5, 139.4, 139.1, 138.7, 137.9, 132.2, 129.0, 128.5, 128.2, 127.9, 127.6, 125.3, 124.1, 124.0, 123.9, 120.9, 120.9, 118.8, 117.1, 108.3, 38.4, 20.1; UV/Vis ([D_7]DMF:CD_2Cl_2; 1:1); λ_{max} / nm (ε / M^{-1} cm^{-1}): 386 (2943), 336 (8939), 285 (33618); LR-FABMS (3-NOBA matrix): *m/z* = 548 [MH-$PyCF_3$]$^+$; HR-FABMS (3-NOBA matrix); *m/z* = 548.15420 (calc. for $C_{24}H_{23}N_3Pt$, 548.15452).

Ligand Exchange Reactions



Scheme S1. Equilibrium between $PyNMe_2$ + [**L**Pt(PyR)] $\rightleftharpoons$ [**L**Pt($PyNMe_2$)] + PyR

Experimental procedure under irradiative and non-irradiative conditions

(i) Irradiative conditions

To a 0.01 M solution of [**L**Pt(PyR)] (7.95 μmol) in 1:1 v/v [D_7]DMF:CD_2Cl_2 (0.35 mL:0.35 mL) was added $PyNMe_2$ (0.97 mg, 7.95 μmol). The mixture was agitated for one minute to give a clear solution and then placed in a quartz NMR tube. The sample was irradiated with broad band 275-375 nm light at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy.

(ii) Non-irradiative conditions

To a 0.01 M solution of [**L**Pt(PyR)] (7.95 μmol) in 1:1 v/v [D_7]DMF:CD_2Cl_2 (0.35 mL:0.35 mL) was added $PyNMe_2$ (0.97 mg, 7.95 μmol). The mixture was agitated for one minute to give a clear solution and then placed in a darkened NMR tube and wrapped in aluminium foil. The sample was maintained at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy.

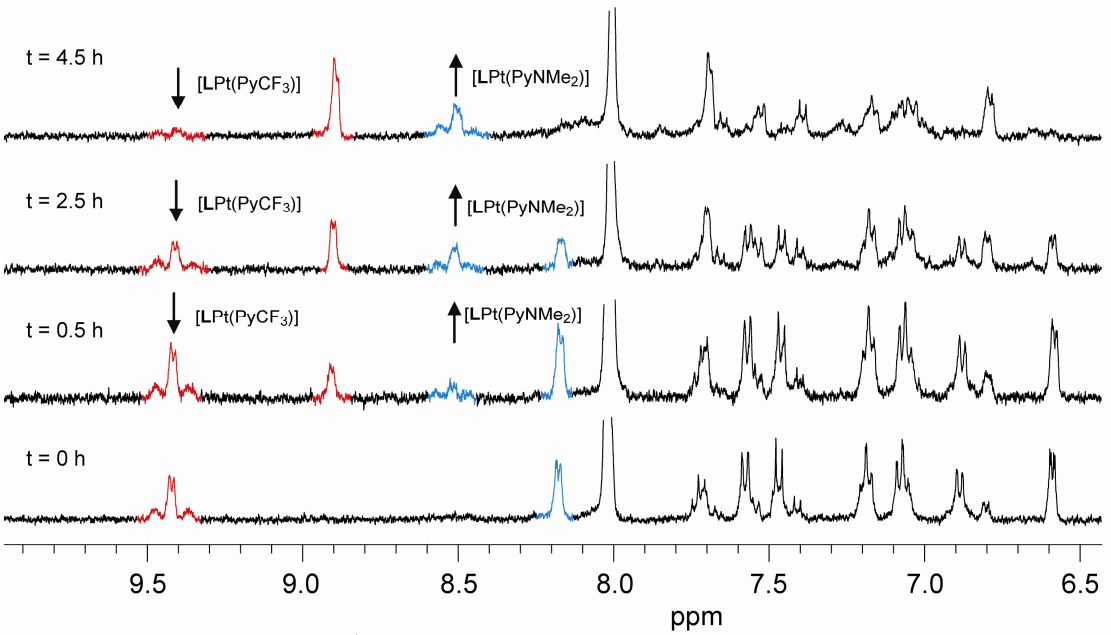
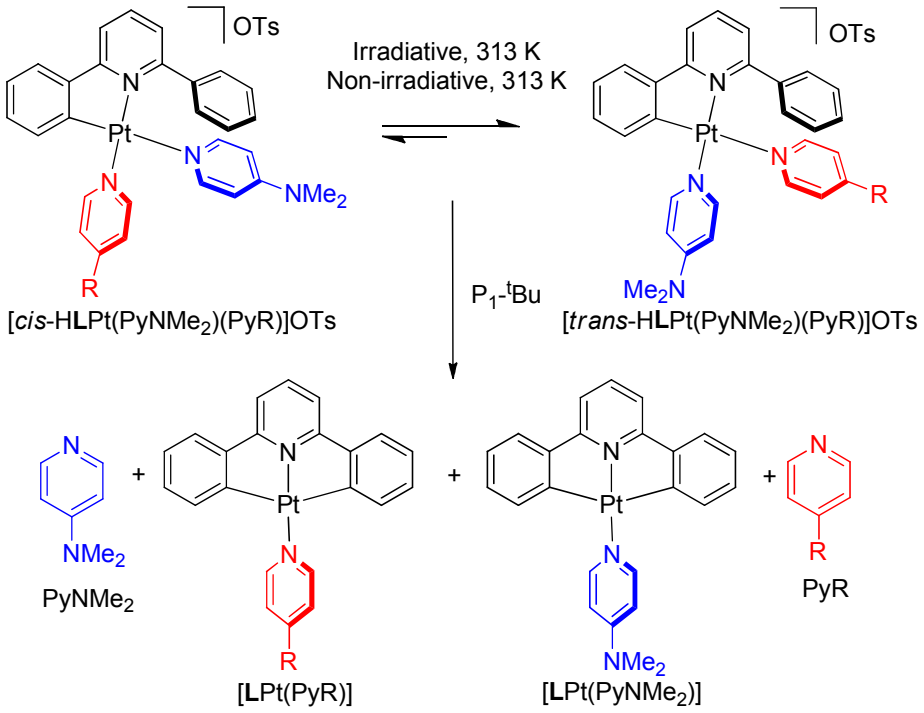


Figure S1. Representative ^{1}H NMR spectra showing the equilibration of $PyNMe_2$ + [**L**Pt($PyCF_3$)] $\rightleftharpoons$ [**L**Pt($PyNMe_2$)] + $PyCF_3$ under irradiative conditions.

Entry	Starting Complex	Pt(PyR): Pt($PyNMe_2$)	Time (h)	Conditions
1	[**L**Pt(PyH)]	17:83	10.5	Irradiative
2	[**L**Pt(PyH)]	28:72	264	Non-irradiative
3	[**L**Pt($PyCF_3$)]	11:89	4	Irradiative
4	[**L**Pt($PyCF_3$)]	15:85	44	Non-irradiative

Table S1. Equilibrium ratios and equilibration times for $PyNMe_2$ + [**L**Pt(PyR)] $\rightleftharpoons$ [**L**Pt($PyNMe_2$)] + PyR under irradiative and non-irradiative conditions.



Scheme S2. [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs $\rightleftharpoons$ [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs followed by base mediated cyclometallation to aid analysis.

Experimental procedure under irradiative and non-irradiative conditions

(i) Irradiative conditions

To a 0.01 M solution of [H**L**Pt(PyR)OTs] (7.95 μmol) in 1:1 v/v [D$_7$]DMF:CD$_2$Cl$_2$ (0.35 mL:0.35 mL) was added PyNMe$_2$ (0.97 mg, 7.95 μmol). The mixture was agitated for one minute to give a clear solution and then placed in a quartz NMR tube. The sample was irradiated with broad band 275-375 nm light at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy. P$_1$-^{t}Bu (10.1 μL, 39.75 μmol) was added directly to the NMR tube and then the sample was vigorously shaken for 30 seconds before a final ^{1}H NMR spectrum was recorded.

(ii) Non-irradiative conditions

To a 0.01 M solution of [H**L**Pt(PyR)OTs] (7.95 μmol) in 1:1 v/v [D$_7$]DMF:CD$_2$Cl$_2$ (0.35 mL:0.35 mL) was added PyNMe$_2$ (0.97 mg, 7.95 μmol). The mixture was agitated for one minute to give a clear solution and then placed in a darkened NMR tube and wrapped in aluminium foil. The sample was maintained at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy. P$_1$-^{t}Bu (10.1 μL, 39.75

μmol) was added directly to the NMR tube and then the sample was vigorously shaken for 30 seconds before a final ^{1}H NMR spectrum was recorded.

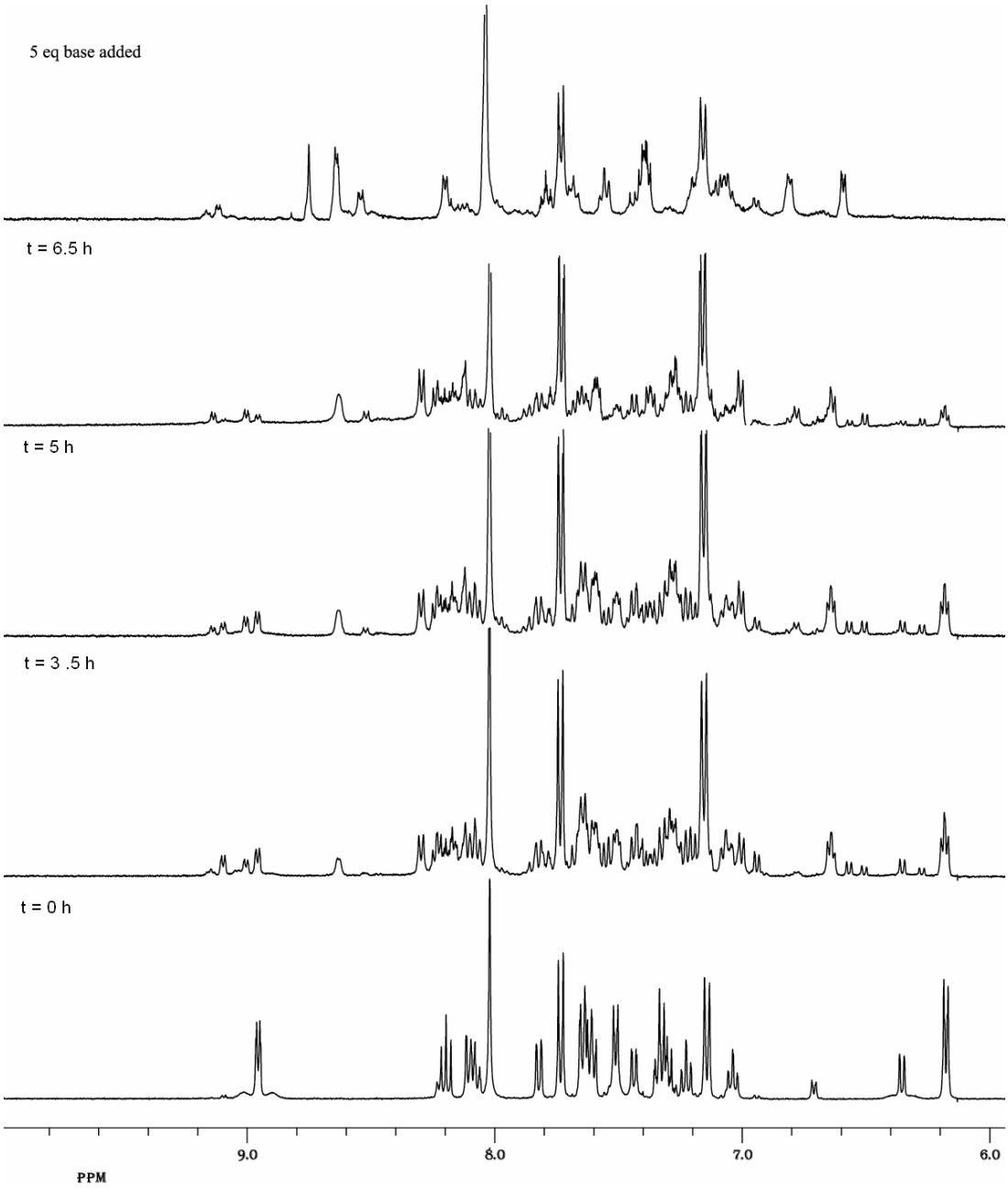
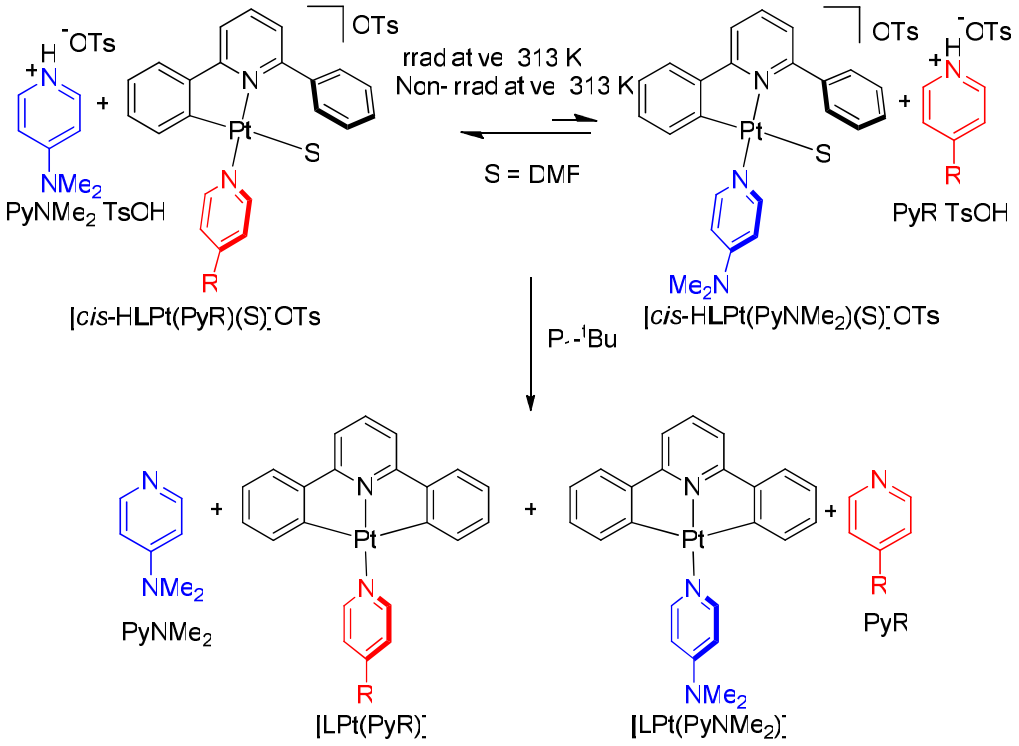


Figure S2. Representative ^{1}H NMR spectra to show the equilibration of [*cis*-H**L**Pt(PyH)(PyNMe$_2$)]OTs $\rightleftharpoons$ [*trans*-H**L**Pt(PyNMe$_2$)(PyH)]OTs under irradiative conditions, followed by base mediated cyclometallation to aid analysis. .

Entry	Starting Complex	*cis*:*trans*[a]	Time (h)	Conditions
1	[*cis*-H**L**Pt(PyH)($PyNMe_2$)]OTs	26:74	6.5	Irradiative
2	[*cis*-H**L**Pt(PyH)($PyNMe_2$)]OTs	49:51	528[b]	Non-irradiative
3	[*cis*-H**L**Pt($PyCF_3$)($PyNMe_2$)]OTs	20:80	4	Irradiative
4	[*cis*-H**L**Pt($PyCF_3$)($PyNMe_2$)]OTs	30:70	528[b]	Non-irradiative

Table S2. Equilibrium ratios and equilibration times for [*cis*-H**L**Pt(PyR)($PyNMe_2$)]OTs $\rightleftharpoons$ [*trans*-H**L**Pt($PyNMe_2$)(PyR)]OTs under irradiative and non-irradiative conditions. [a]The ratio of *cis:trans* was indirectly measured by converting the corresponding C^N complexes to C^N^C complexes using the base P_1-^{t}Bu, and then by integration of the resultant [**L**Pt(PyR)] and [**L**Pt($PyNMe_2$)] complexes. [b]264 h at 313 K + 264 h at 333 K.



Scheme S3. $PyNMe_2.TsOH$ + [*cis*-H**L**Pt(PyR)(S)]OTs ⇌ PyR.TsOH + [*cis* -H**L**Pt($PyNMe_2$)(S)]OTs followed by base mediated cyclometallation to aid analysis.

Experimental procedure under irradiative and non-irradiative conditions

(i) Irradiative conditions

To a 0.01 M solution of [H**L**Pt($PyNMe_2$)OTs] (5.84 mg, 7.95 µmol) in 1:1 v/v [D_7]DMF:CD_2Cl_2 (0.35 mL:0.35 mL) was added PyR.TsOH (7.95 µmol). The mixture was agitated for one minute to give a clear solution and then placed in a quartz NMR tube. The sample was irradiated with broad band 275-375 nm light at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy. P_1-^{t}Bu (10.1 µL, 39.75 mmol) was added directly to the NMR tube and then the sample was vigorously shaken for 30 seconds before a final ^{1}H NMR spectrum was recorded.

(i) Non-rradiative conditions

To a 0.01 M solution of [H**L**Pt($PyNMe_2$)OTs] (5.84 mg, 7.95 µmol) in 1:1 v/v [D_7]DMF:CD_2Cl_2 (0.35 mL:0.35 mL) was added PyR.TsOH (7.95 µmol). The mixture was agitated for one minute to give a clear solution and then placed in a darkened NMR tube and wrapped in aluminium foil. The sample was maintained at 313 K until no further changes could be detected by ^{1}H NMR spectroscopy. P_1-^{t}Bu

(10.1 μL, 39.75 mmol) was added directly to the NMR tube and then the sample was vigorously shaken for 30 seconds before a final ^{1}H NMR spectrum was recorded.

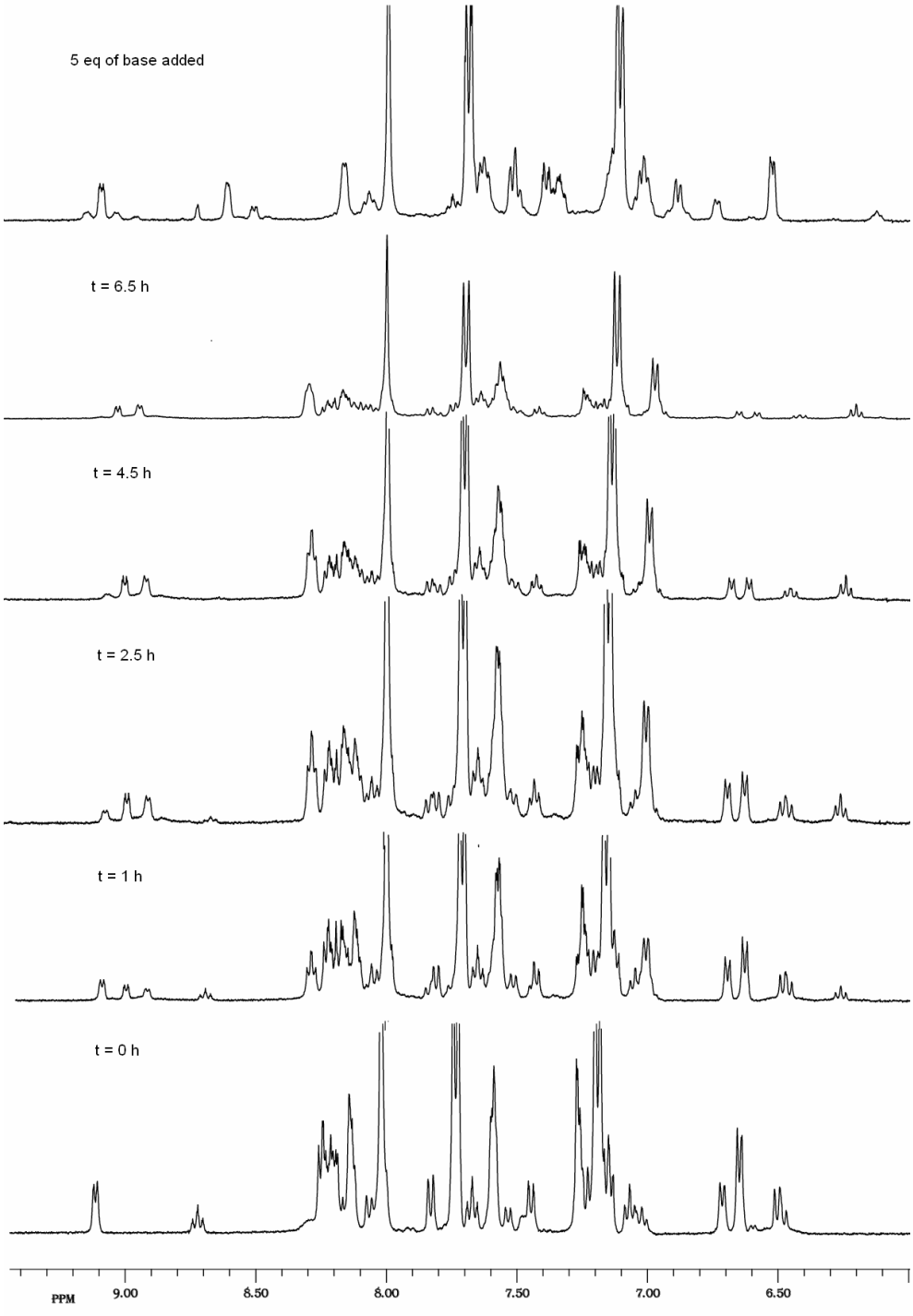


Figure S3. Representative ^{1}H NMR spectra to show the equilibration of $PyNMe_2$.TsOH + [*cis*-H**L**Pt(PyH)(S)]OTs $\rightleftharpoons$ $PyCF_3$.TsOH + [*cis*-H**L**Pt($PyNMe_2$)(S)]OTs under irradiative conditions, followed by base mediated cyclometallation to aid analysis..

Entry	Starting PyR.TsOH	Pt(PyR): Pt(PyNMe$_2$)^a	Time (h)	Conditions
1	PyH.TsOH	70:30	6.5	Irradiative
2	PyH.TsOH	41:59	576^b	Non-irradiative
3	PyCF$_3$.TsOH	85:15	5.5	Irradiative
4	PyCF$_3$.TsOH	63:37	576^b	Non-irradiative

Table S3. Equilibrium ratios and equilibration times for PyNMe$_2$.TsOH + [*cis*-H**L**Pt(PyR(S)]OTs $\rightleftharpoons$ PyR.TsOH + [*cis*-H**L**Pt(PyNMe$_2$)(S)]OTs under irradiative and non-irradiative conditions. ^{a}The ratio of [*cis*-H**L**Pt(PyR(S)]OTs:[*cis*-H**L**Pt(PyNMe$_2$)(S)]OTs was indirectly measured by converting the C^N complexes to the corresponding C^N^C complexes using the base P$_1$-^{t}Bu, and then by integration of the resultant [**L**Pt(PyR)] and [**L**Pt(PyNMe$_2$)] complexes. ^{b}312 h at 313 K + 264 h at 333 K.

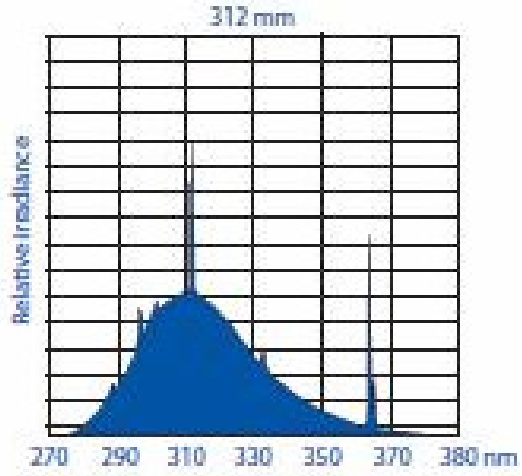


Figure S4. Emission spectrum for the broad band 275-375 nm light used for the irradiative studies.

References

1. (a) G. W. Cave, F. P. Fanizzi, R. J. Deeth, W. Errington and J. P. Rourke, *Organometallics*, 2000, **19**, 1355; (b) J. D. Crowley, I. M. Steele and B. Bosnich, *Inorg. Chem.*, 2005**, 44,** 2989.

Appendix A: ^{1}H and ^{13}C NMR spectra

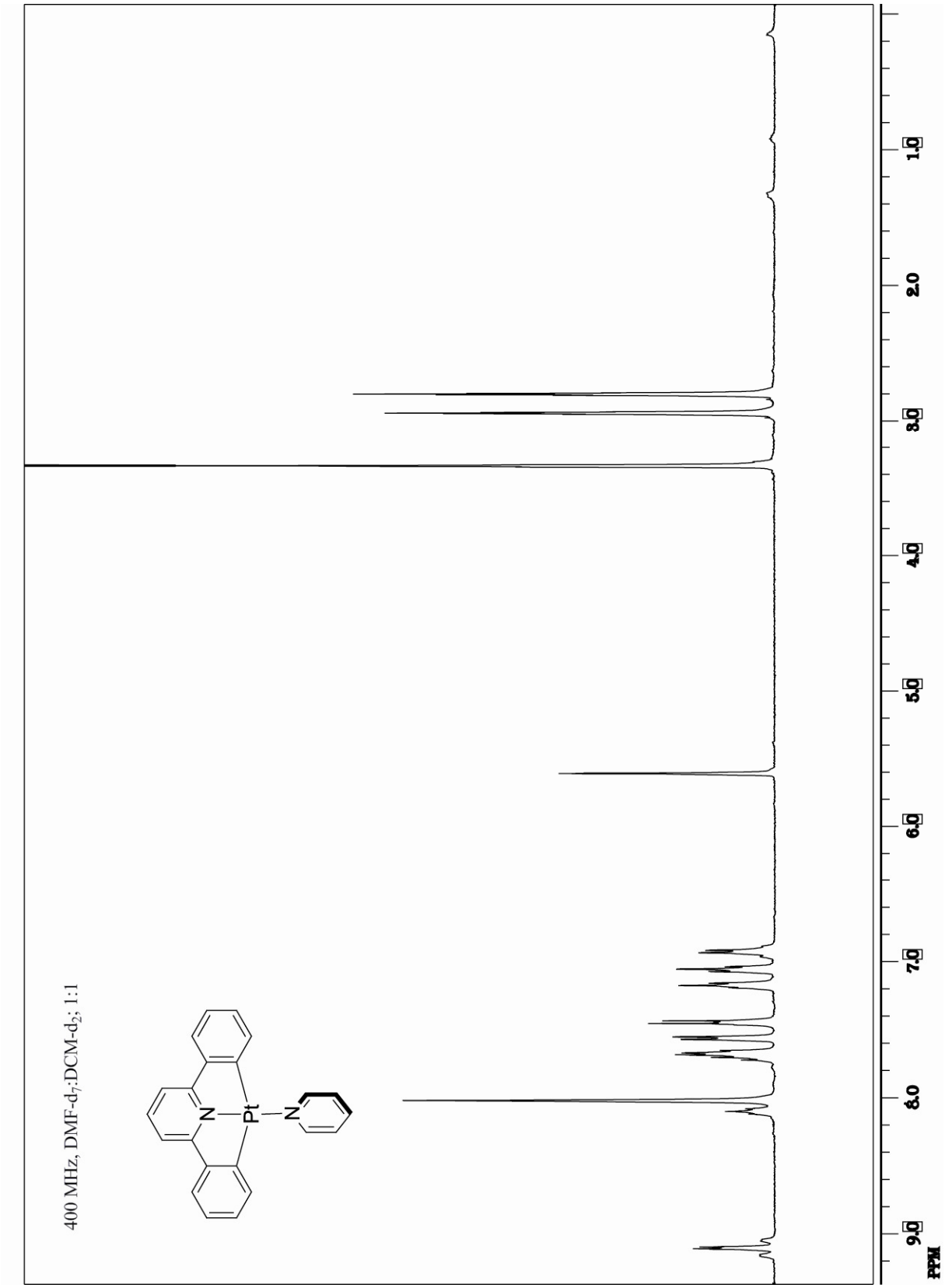


Figure S5: ^{1}H NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt(Py)].

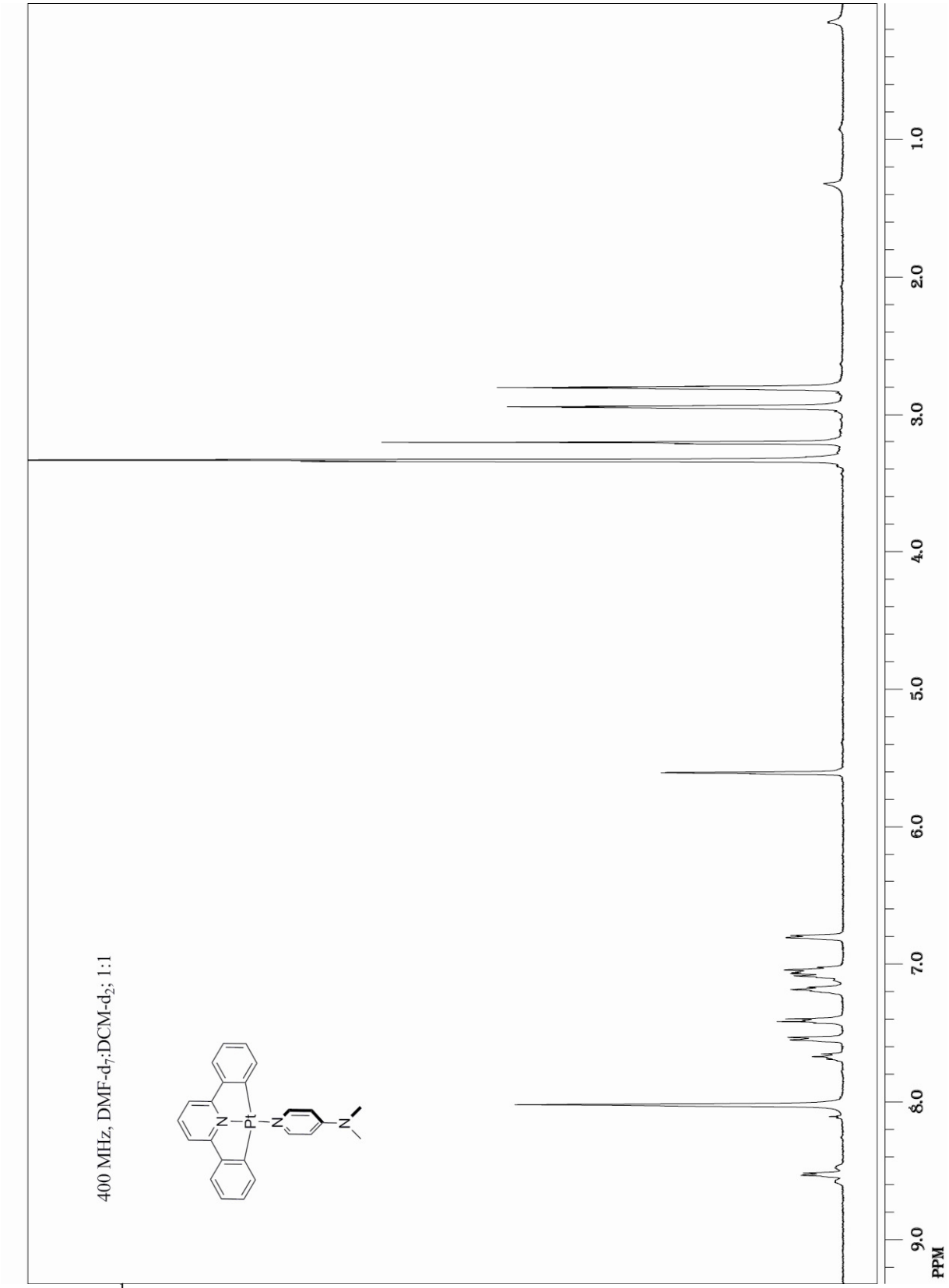


Figure S6: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [**L**Pt(PyNMe$_2$)].

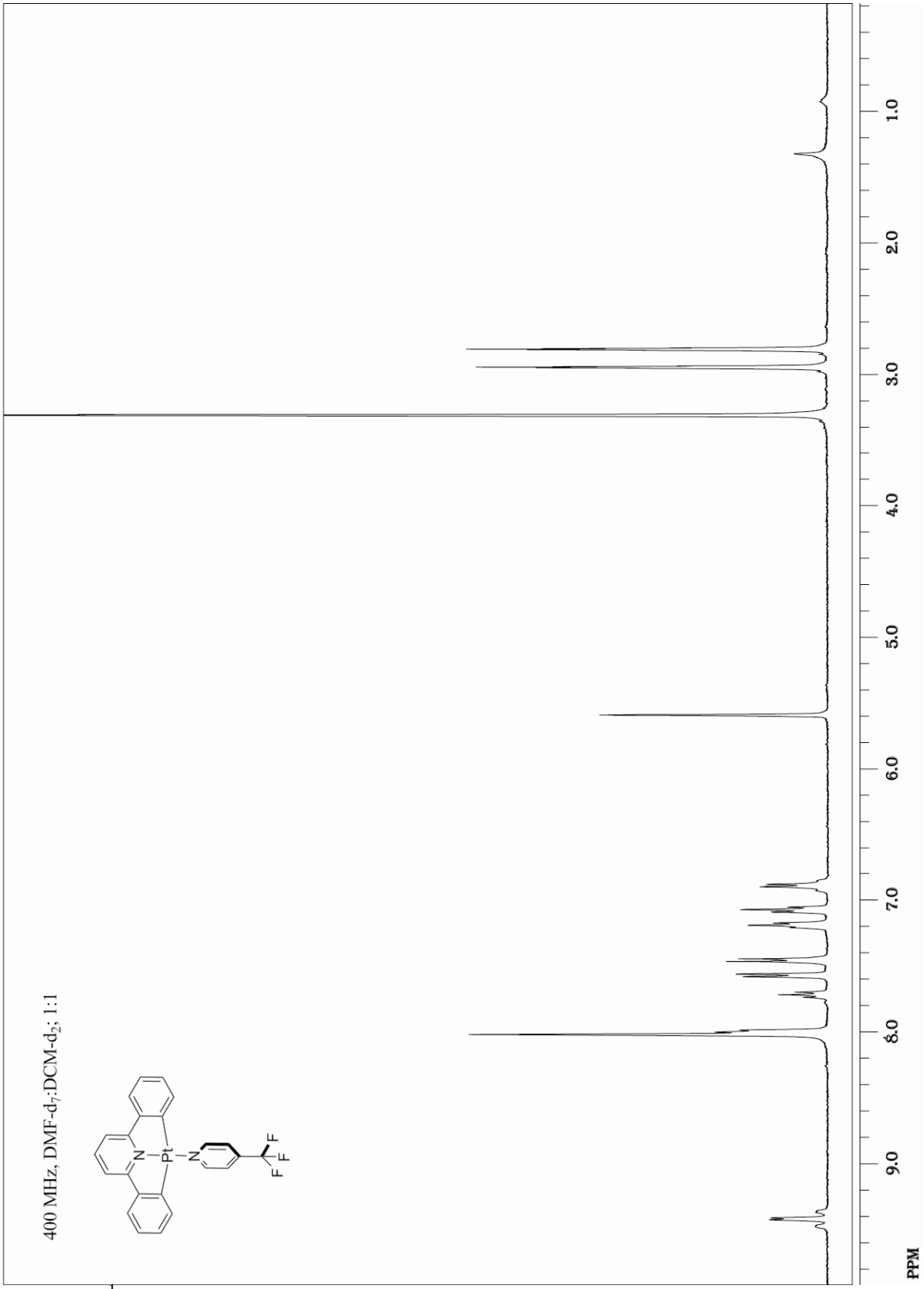


Figure S7: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [**L**Pt($PyCF_3$)].

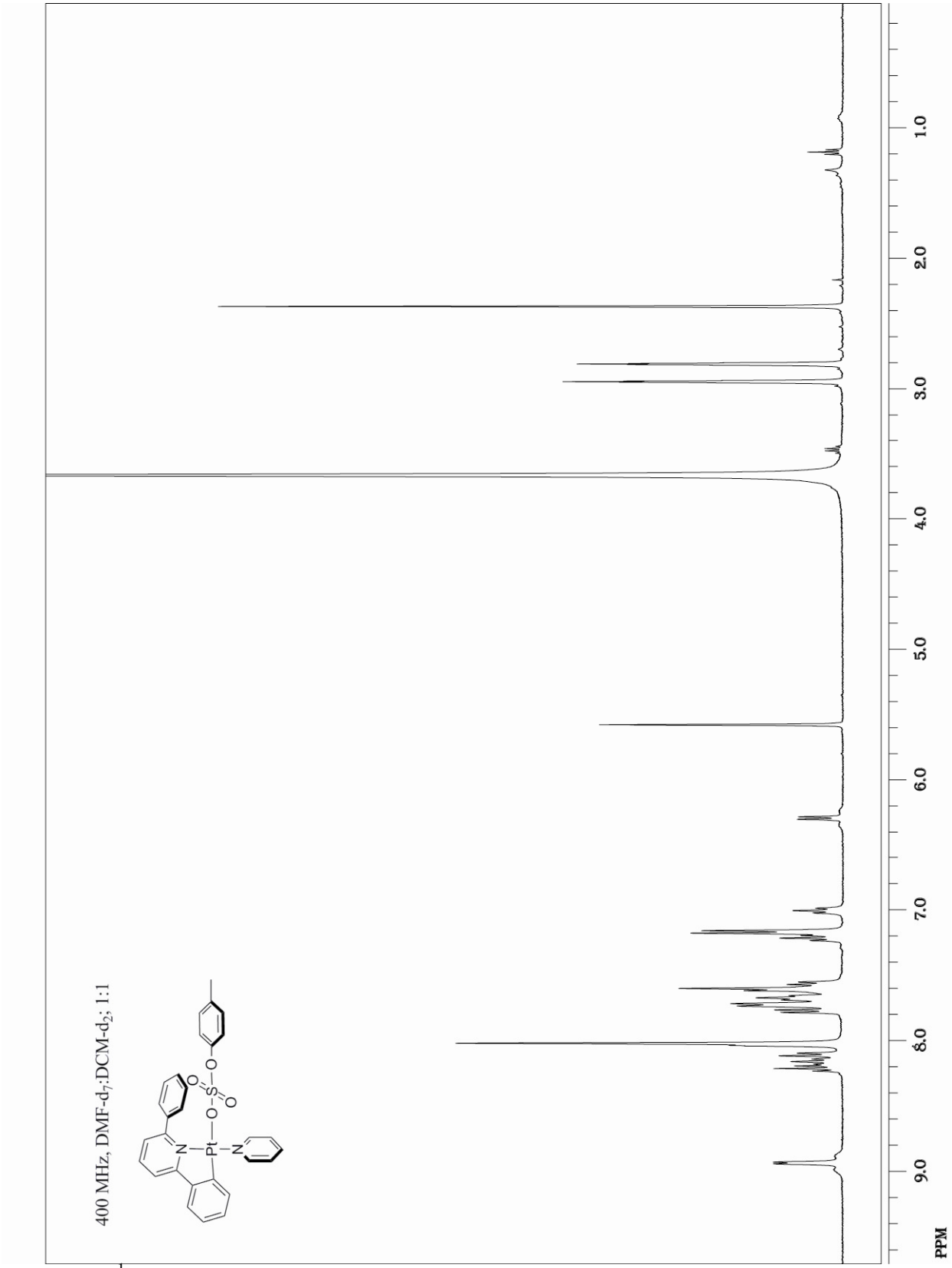


Figure S8: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [H**L**Pt(Py)(OTs].

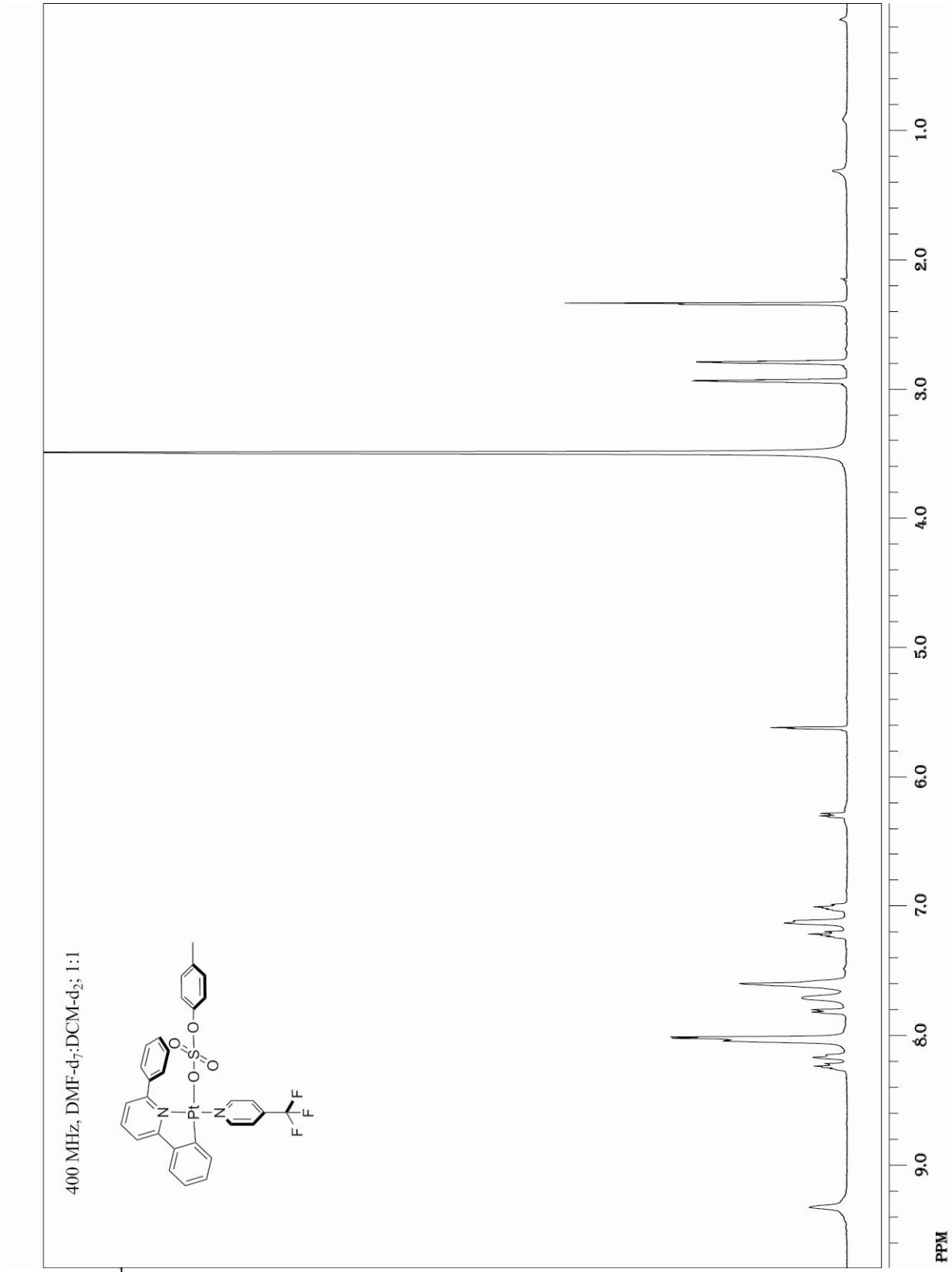


Figure S9: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [**HL**Pt($PyCF_3$)(OTs)].

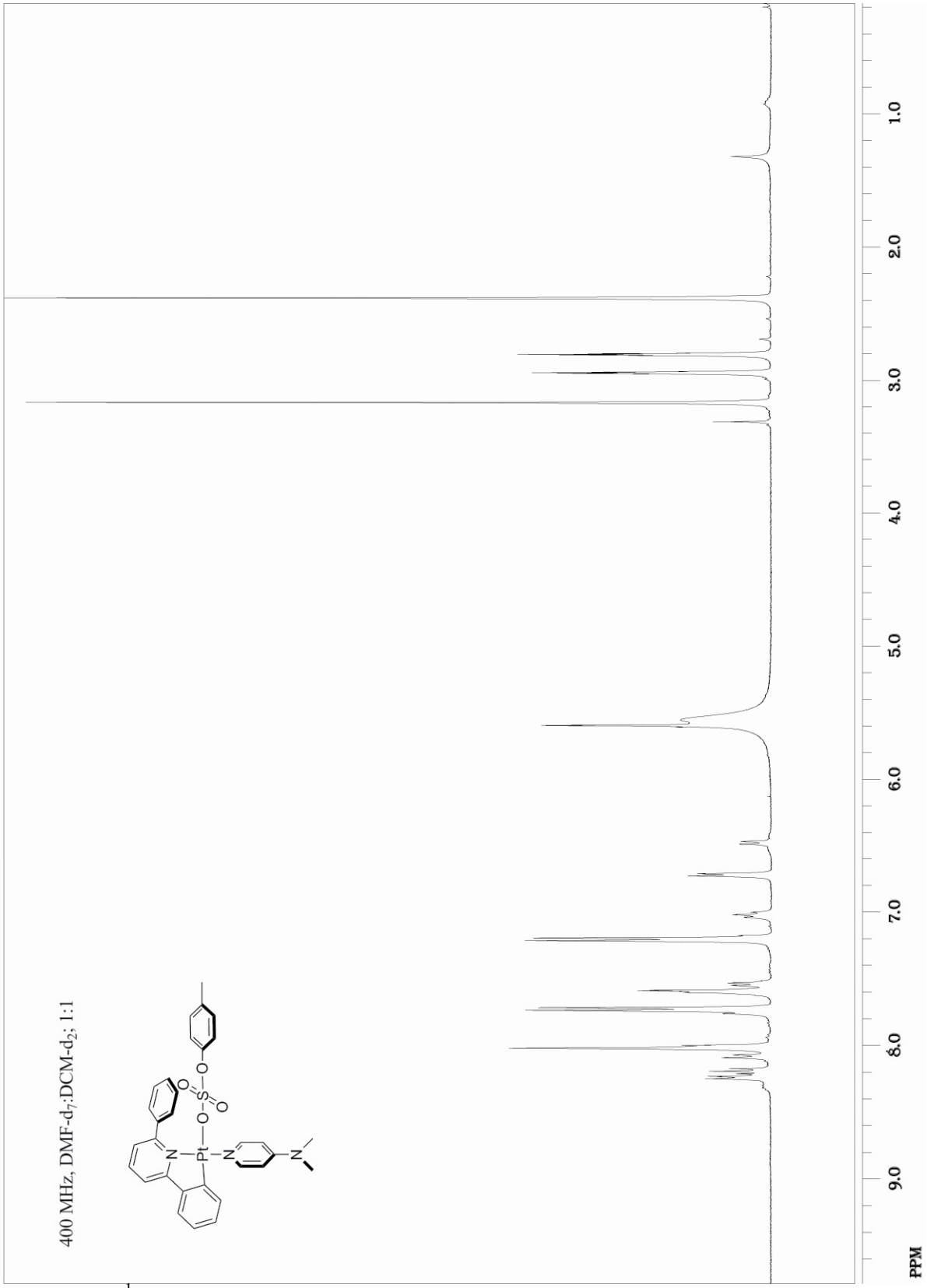


Figure S10: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [H**L**Pt(PyNMe_2)(OTs)].

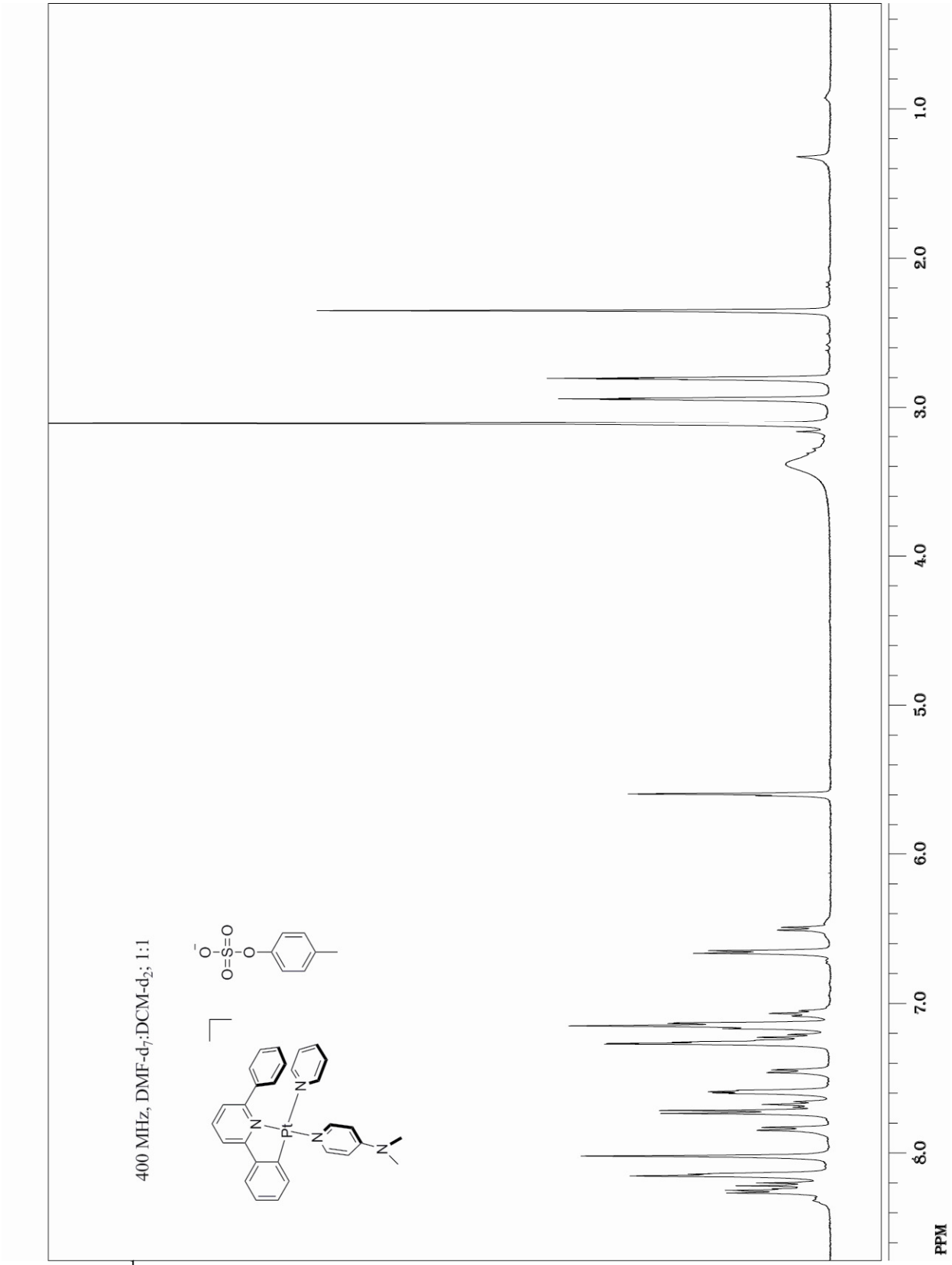


Figure S11: ^{1}H NMR spectrum (400 MHz, 1:1 [D_7]DMF:CD_2Cl_2, 300 K) of [H**L**Pt($PyNMe_2$)(Py)]OTs.

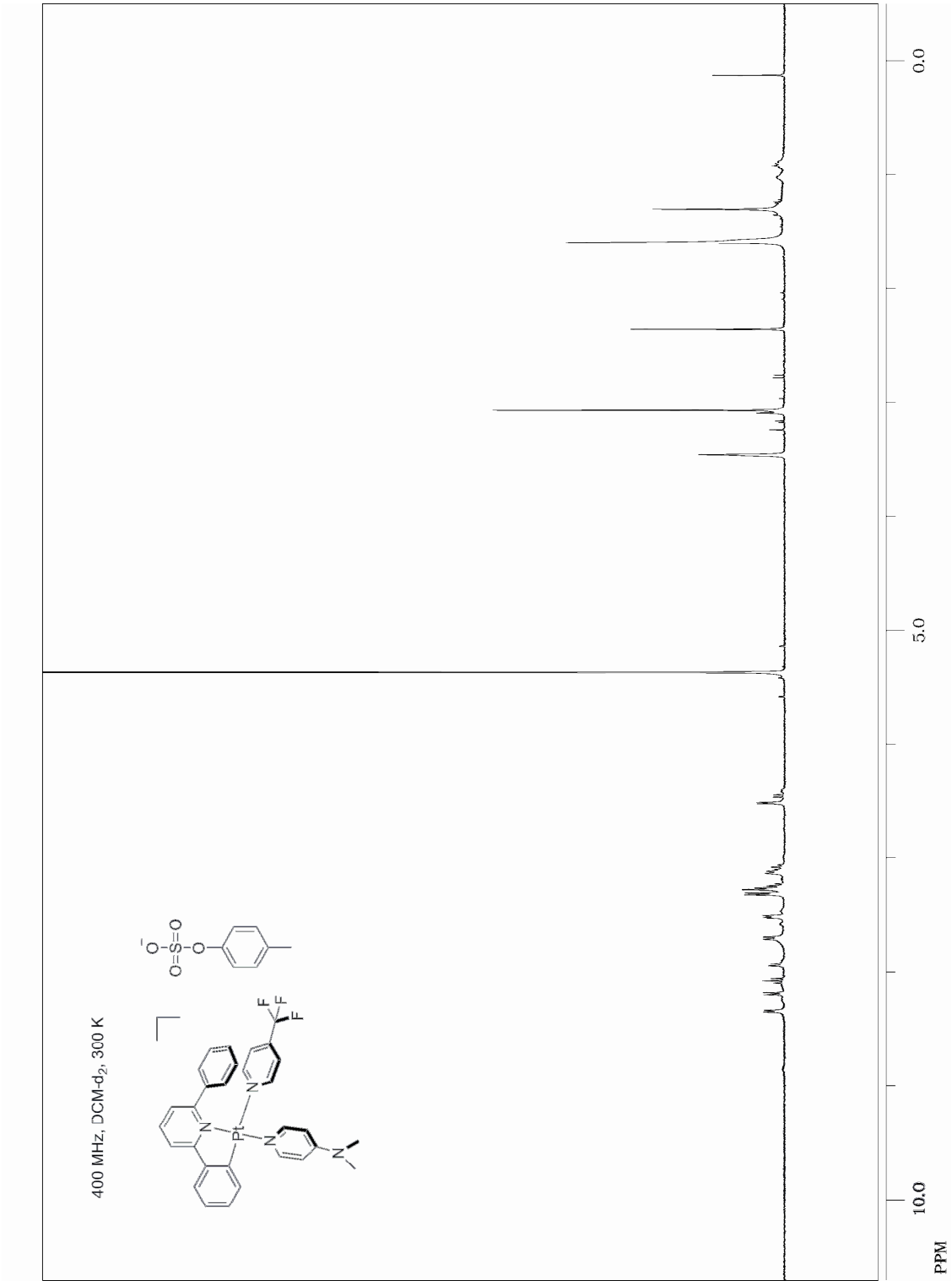


Figure S12: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 300 K) of [H**L**Pt(PyNMe$_2$)(PyCF$_3$)]OTs.

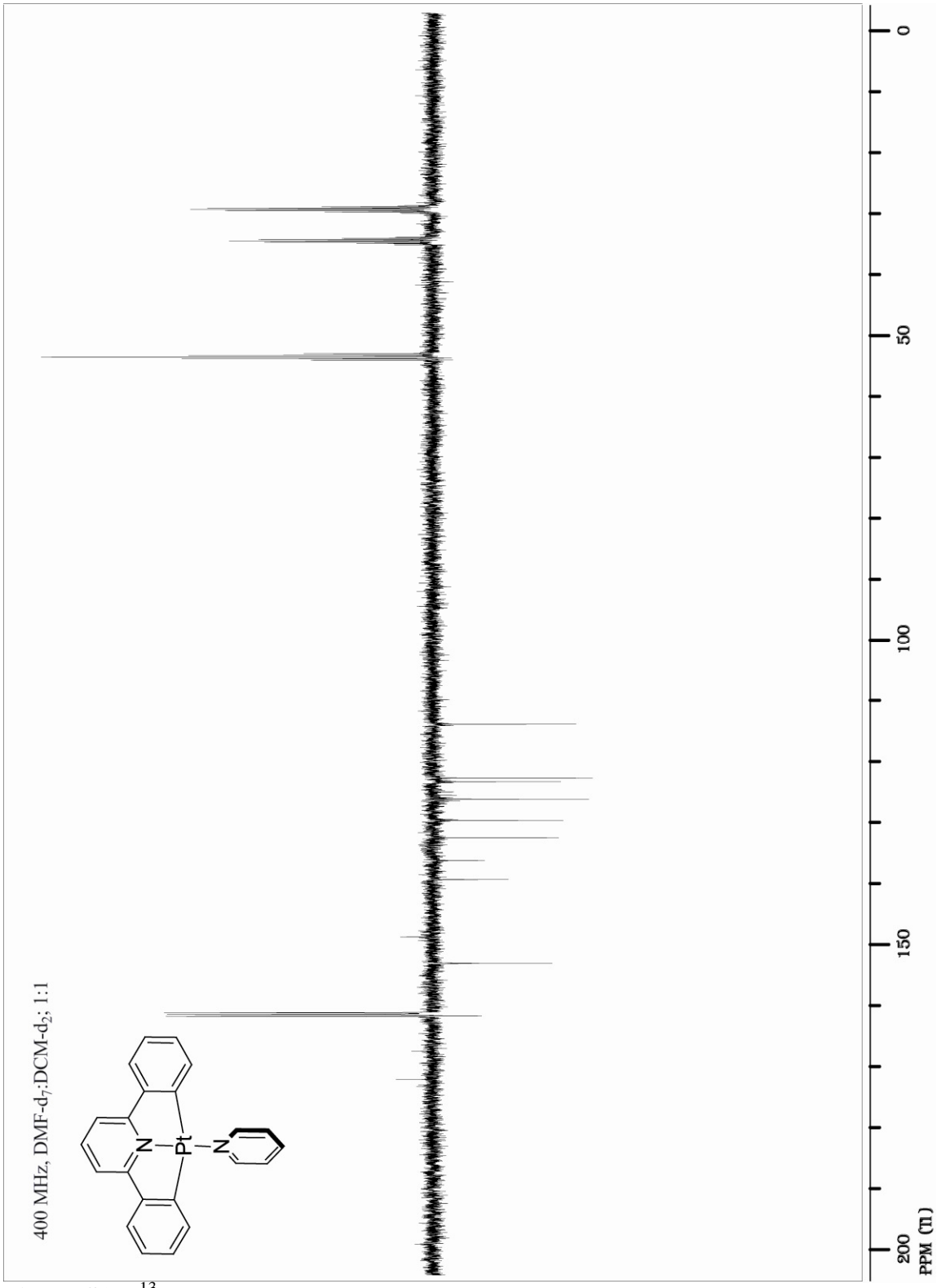


Figure S13: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt(Py)].

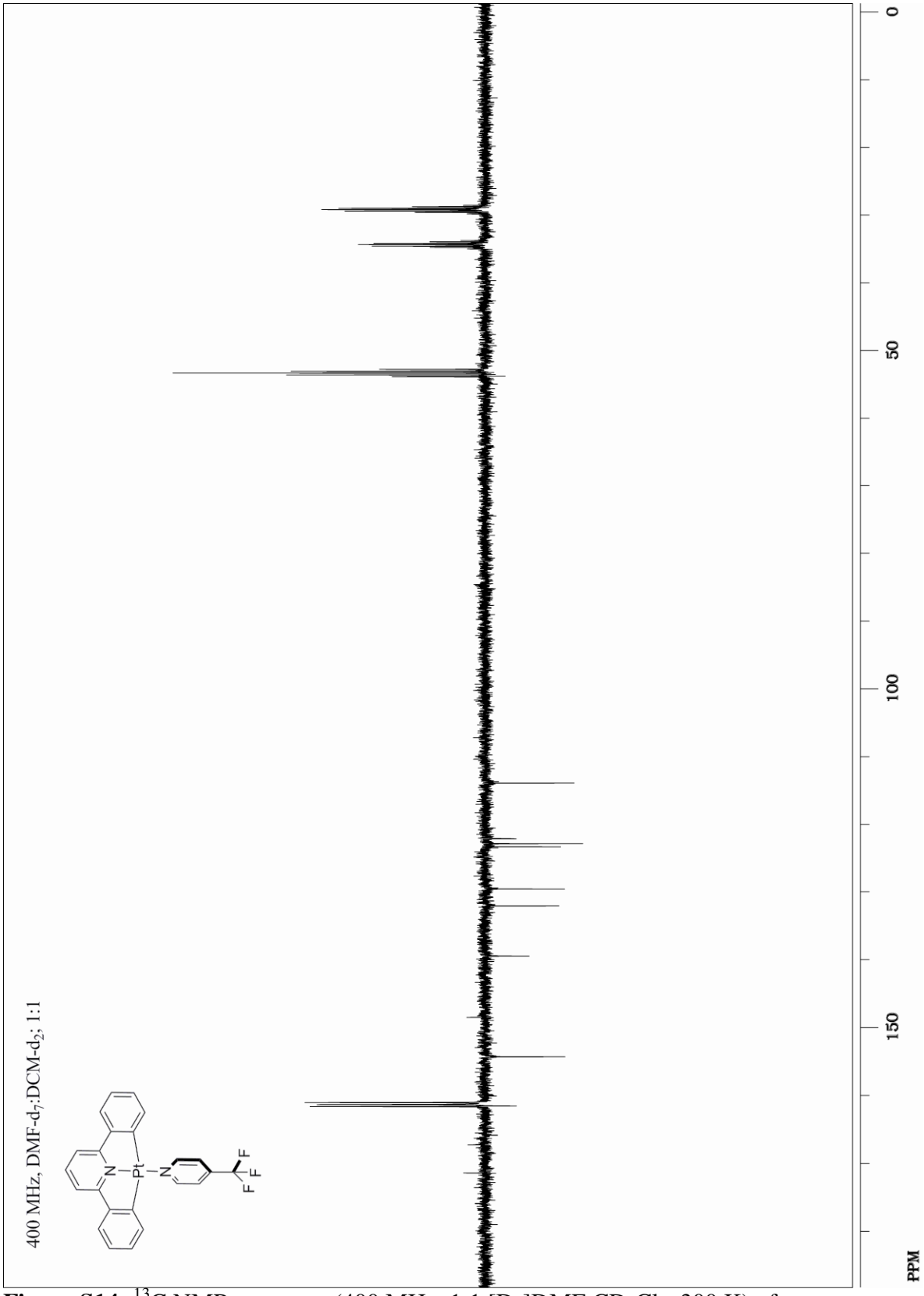


Figure S14: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt($PyCF_3$)].

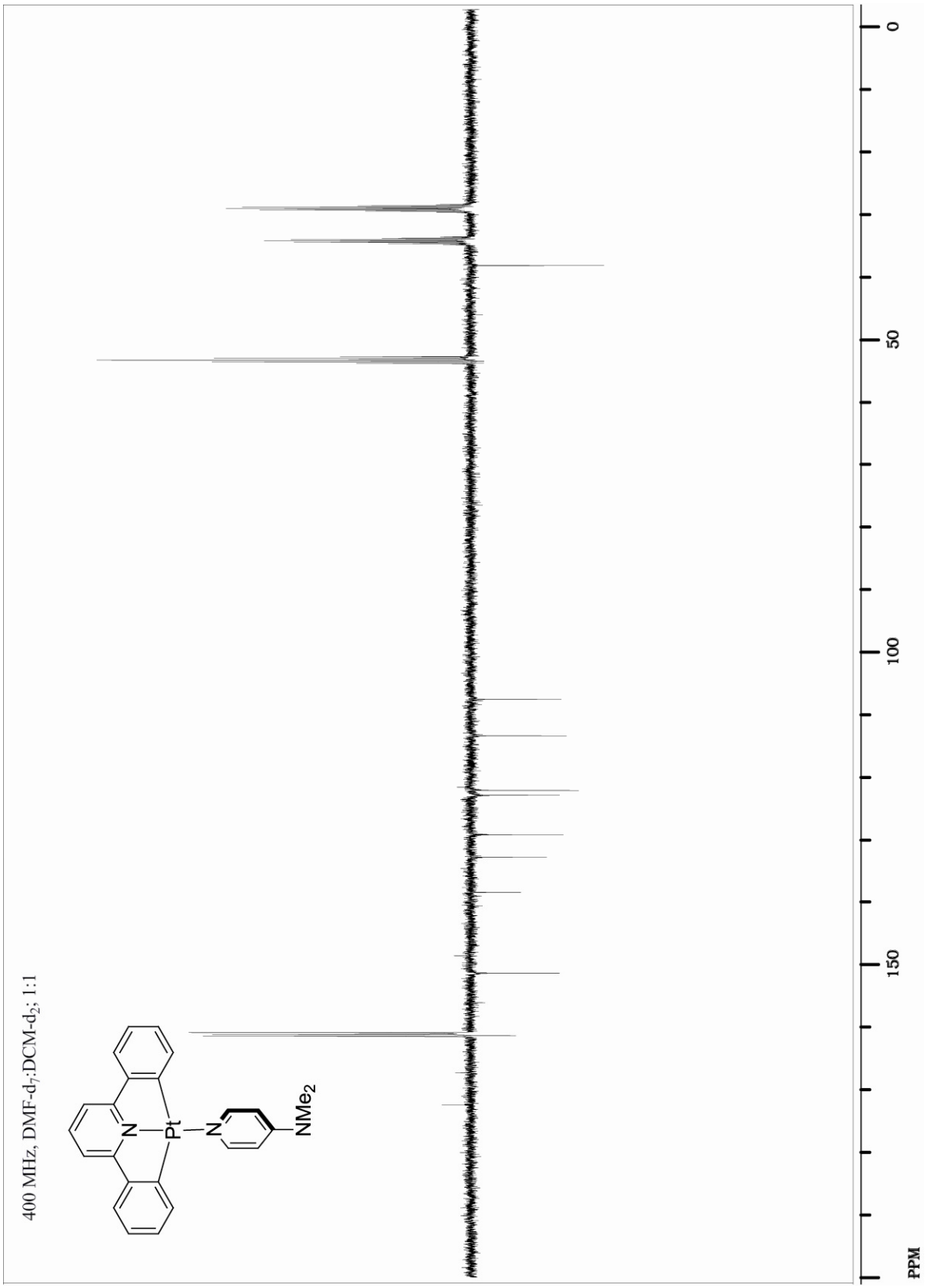


Figure S15: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt($PyNMe_2$)].

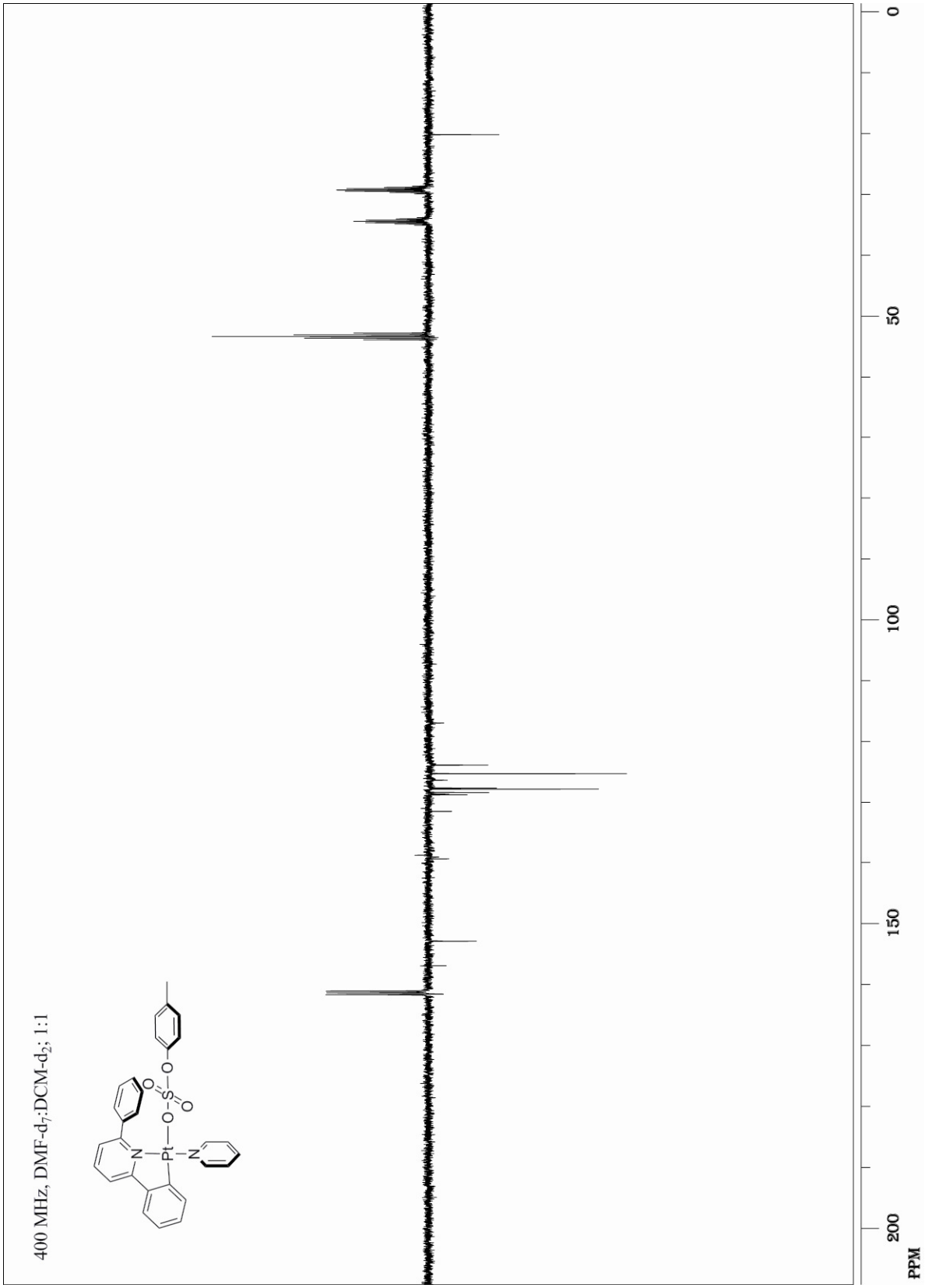


Figure S16: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [H**L**Pt(Py)(OTs].

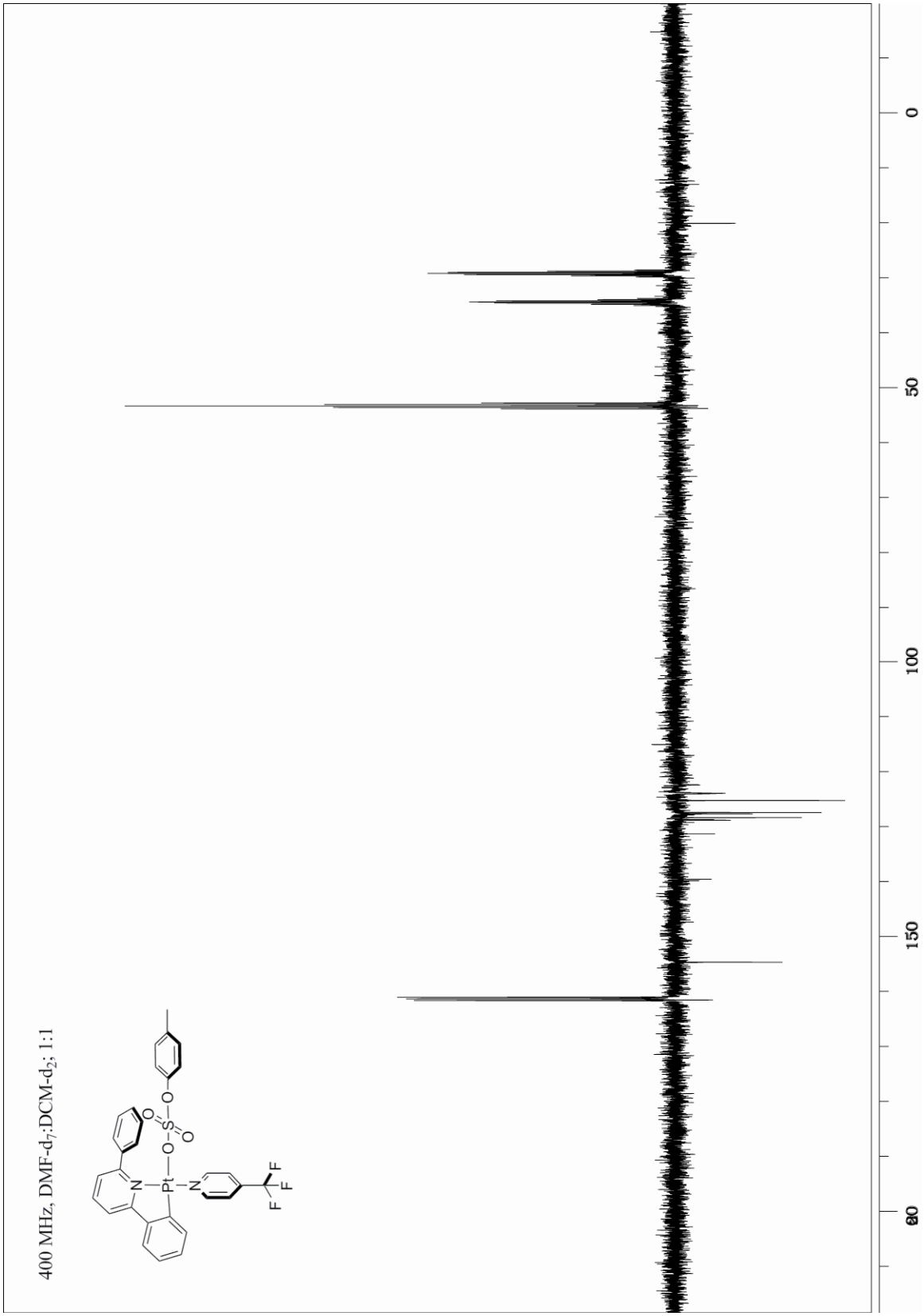


Figure S17: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [H**L**Pt(CF_3)(OTs)].

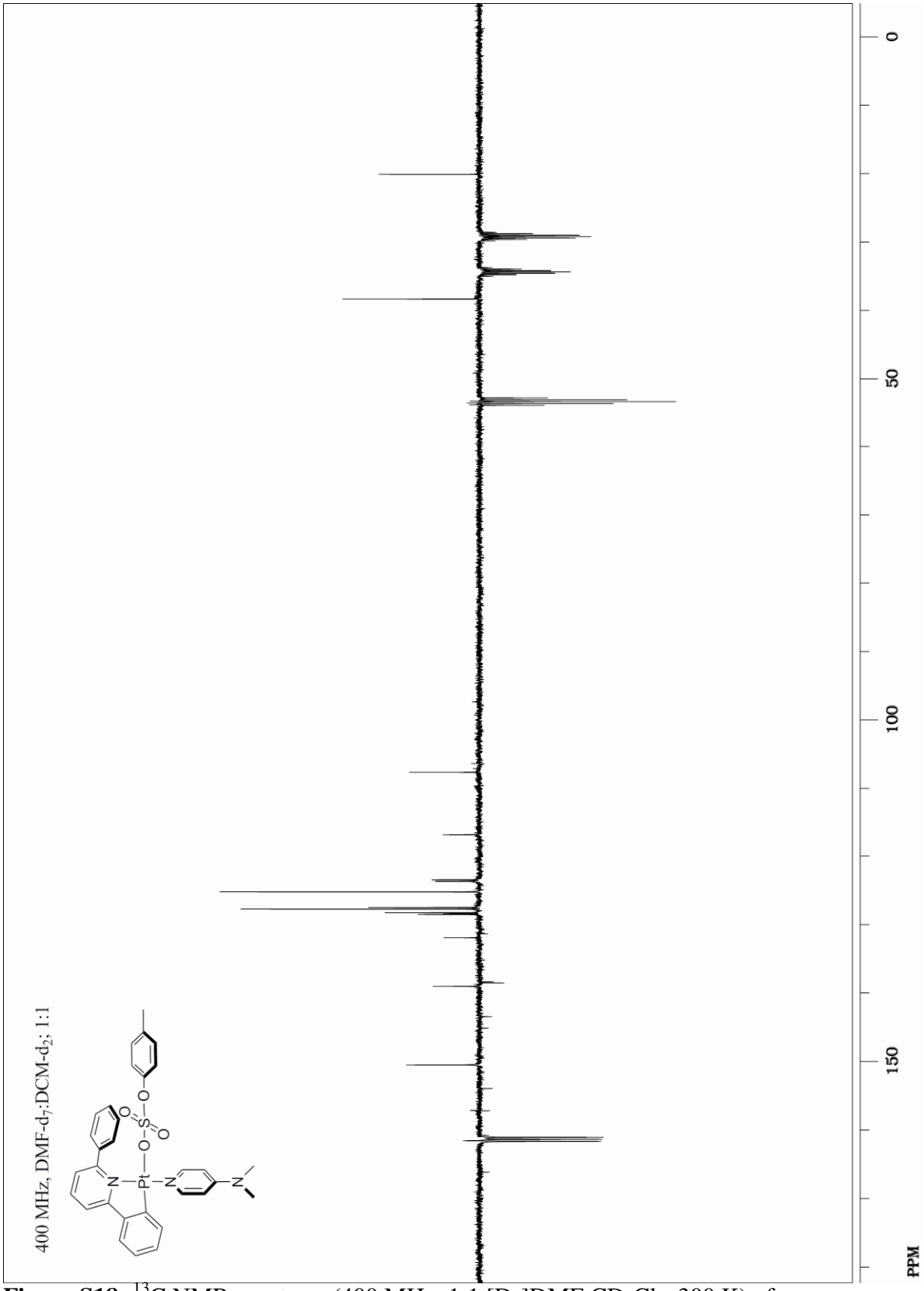


Figure S18: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [H**L**Pt($PyNMe_2$)(OTs)].

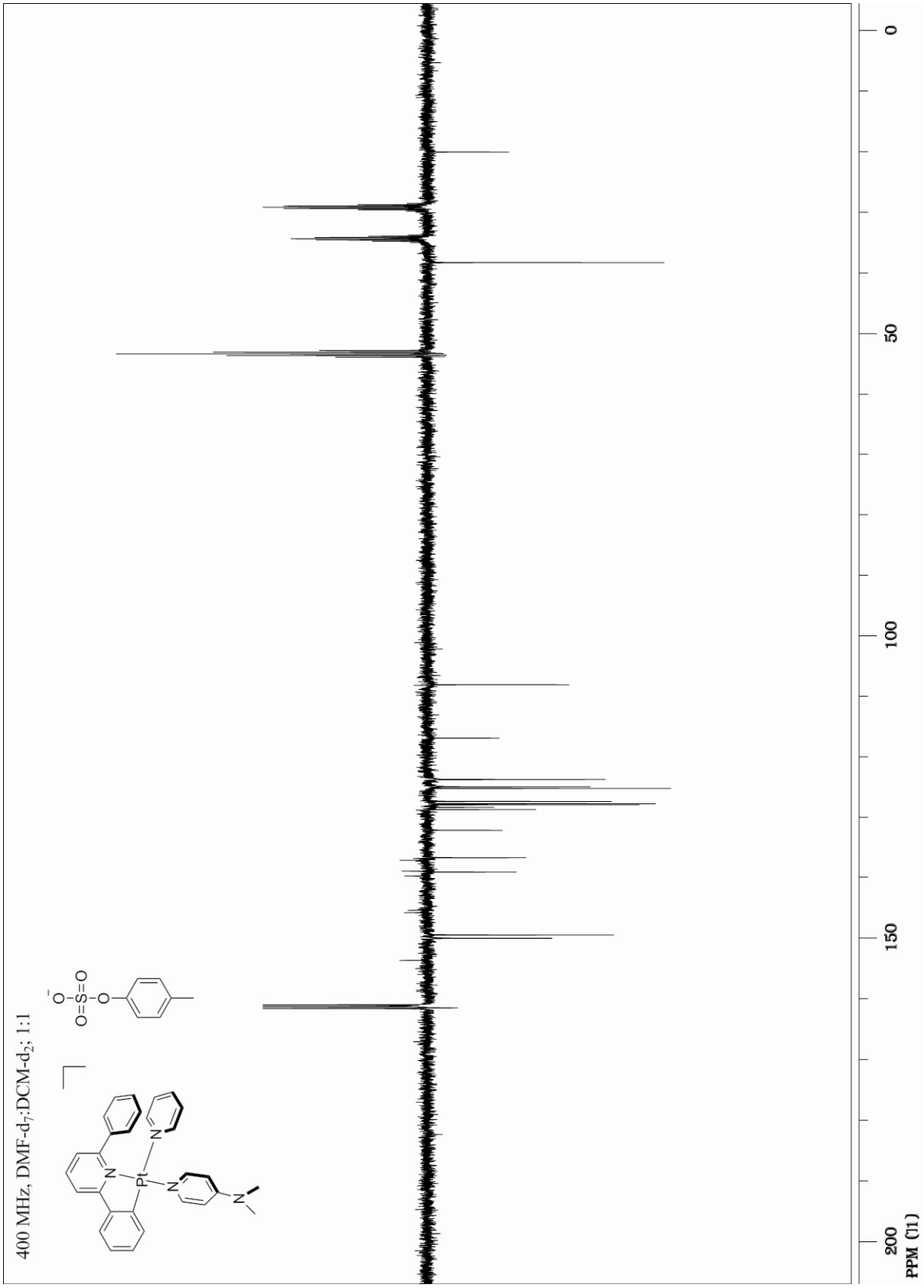


Figure S19: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt($PyNMe_2$)(Py)]OTs.

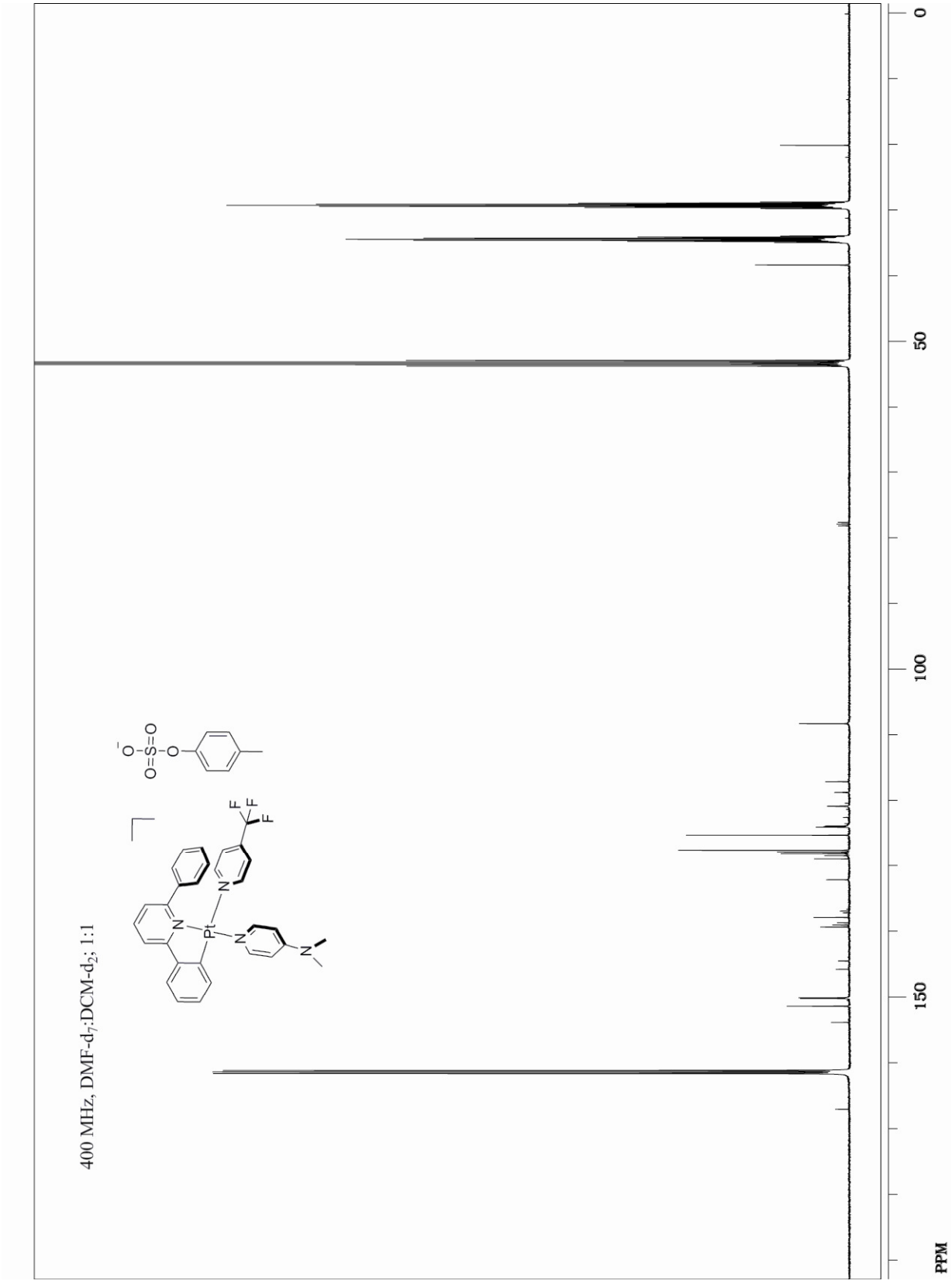


Figure S20: ^{13}C NMR spectrum (400 MHz, 1:1 $[D_7]DMF:CD_2Cl_2$, 300 K) of [**L**Pt($PyNMe_2$)($PyCF_3$)]OTs.