Supplementary Information For:

# Luminescent Pt(2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine)$X^+$: A comparison with the spectroscopic and electrochemical properties of Pt(tpy)$X^+$ (X = Cl, CCPh, Ph, or $CH_3$)

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**Experimental.**

**Materials and Methods.** $K_2PtCl_4$ was purchased from Pressure Chemical Company. 2,2′:6′,2′′-terpyridine (tpy), phenylacetylene, trimethyl(phenyl)tin, dimethyl sulfide, 1.4 M solution of methyllithium (halide content ca. 0.05 M) in diethyl ether, and tetrabutylammonium hexafluorophosphate (TBAH) were obtained from Sigma-Aldrich, whereas N-methyl-1,2-phenylenediamine and 2,6-pyridinedicarboxylic acid were obtained from Acros Organics and used as received. Commercial reagent grade solvents such as dichloromethane, diethyl ether, and acetonitrile were further purified using standard procedures.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories. 2,6-bis(N-methylbenzimidazol-2-yl)pyridine[2] (mbzimpy) and platinum synthons such as $Pt(COD)Cl_2$, $Pt(COD)(Ph)Cl$, and $Pt(SMe_2)(Me)Cl$ {obtained by the following synthetic route: $Pt(SMe_2)_2Cl_2 \rightarrow [PtMe_2(\mu\text{-}SMe_2)]_2 \rightarrow Pt(SMe_2)(Me)Cl$}[3] (where, COD = 1,5-Cyclooctadiene, Ph = Phenyl, Me = Methyl) were synthesized in highly pure form according to published procedures.[3-6] Syntheses of the aforementioned compounds were carried out under an argon atmosphere using standard Schlenk techniques. Argon was pre-dried using activated sieves, and trace oxygen was removed with activated R3-11 catalyst from Schweizerhall. **1(a-d)** were synthesized following the procedures for the corresponding **2(a-d)** (vide Infra, Scheme 1S) and substituting tpy with mbzimpy. Characterization data for **2(a-d)** summarized in the main text. Elemental analyses of **1(a-d)**, **2(a-d)**, and $[Zn(mbzimpy)_2](PF_6)$ **(3)** were performed by Atlantic Microlab, Norcross, GA. The 1D ($^1H$, $^{13}C$, and $^{195}Pt$) and in several instances 2D (COSY, HSQC, and/or NOE) NMR spectra were recorded at room temperature (20-25 °C). In the case of **1b**, a series of $^1H$ NMR spectra were also recorded over the temperature range of 25-70 °C. 2D NOE experiments were run with mixing time, $\tau_m$, of 75 ms. Spectra are reported in parts per millions (ppm) relative to TMS ($\delta$ = 0 ppm), or the residual internal standard (~ the protic solvent impurity) [($CD_3CN$, $\delta_H$ = 1.94 ppm; and $\delta_C$ = 1.32 ppm for $CD_2HCN$) or ($(CD_3)_2SO$, $\delta_H$ = 2.50 ppm; and $\delta_C$ = 39.52 ppm for $CD_3SOCD_2H$)], or relative to a saturated solution of $Na_2[PtCl_6]$ in $D_2O$ in the case of $^{195}Pt$ NMR.

**Instrumentation**. The $^1H$, $^{13}C$, COSY, and HSQC NMR spectra were recorded using Bruker AC 400 MHz instrument, whereas NOE and $^{195}Pt$ NMR spectra were recorded using a Bruker DMX 500 MHz and a Bruker AMX 400 MHz instruments, respectively. Mass spectra were obtained by electrospray ionization using either an Ionspec HiRes ESI-FTICRMS instrument or a Micromass Q-TOF-II instrument. The instrument conditions were optimized and calibrated in positive ion mode using poly-alanine (Sigma) and in negative ion mode using sodium iodide (Fisher Scientific). The observed isotope patterns agreed well with those predicted based on natural isotopic abundances (only monoisotopic masses are provided here). Infrared spectra were collected using a Nicolet 6700 FTIR spectrometer.

**Synthesis and characterization.**

**2,6-bis(N-methylbenzimidazol-2-yl)pyridine, (mbzimpy).** Synthesis of mbzimpy was adapted from Addison *et al.,*[2] and optimized for reaction conditions. N-methyl-1,2-phenylenediamine (0.73 g, 6.0 mmol) was added to 10 ml of aqueous orthophosphoric acid (85 %) under vigorous magnetic stirring, followed by addition of 2,6-

pyridinedicarboxylic acid (0.50 g, 3.0 mmol). The reaction mixture was refluxed under argon at 250 °C (using a sand bath) for 24 h. The resulting solution, upon cooling down to room temperature, was added drop-wise to an ice-cold aqueous solution of potassium hydroxide (~1 M, 100 mL). The flask was then chilled in an ice-water-bath for at least 2 h. The mbzimpy precipitate filtered off and washed with ice-cold distilled water. The product was further purified by recrystallization from acetone: water (~ 90:10 v/v) solution. Glassy-white needles with a light-bluish-hue were obtained by slow evaporation of the solvent mixture. Yield: 0.91 g, 90 %. MS-ESI (m/z): 340.15 ($C_{21}H_{17}N_5H^+$), Calcd., 340.16. $^1$H NMR (400 MHz, 3 mM, $(CD_3)_2SO$, 298 K, δ/ppm) $\delta_H$ 8.41 (2H, d, $^3J$ = 7.6 Hz, $H_3$ and $H_5$), 8.23 (1H, t, $^3J$ = 7.4 Hz, $H_4$), 7.78 (2H, d, $^3J$ = 8.0 Hz, $H_{4'}$ and $H_{4''}$), 7.71 (2H, d, $^3J$ = 8.0 Hz, $H_{7'}$ and $H_{7''}$), 7.38 (2H, dd, $^3J$ = 7.2 Hz, $H_{6'}$ and $H_{6''}$), 7.32 (2H, dd, $^3J$ = 7.2 Hz, $H_{5'}$ and $H_{5''}$), 4.27 (6H, s, N-$CH_3$). $^{13}$C NMR (400 MHz, 54 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δc 149.7, 149.2, 141.9, 138.6 ($C_4$), 137.1, 125.1 ($C_3$ and $C_5$), 123.4 ($C_{6'}$ and $C_{6''}$), 122.6 ($C_{5'}$ and $C_{5''}$), 119.5 ($C_{4'}$ and $C_{4''}$), 111.0 ($C_{7'}$ and $C_{7''}$), 32.6 (N-$CH_3$).

**[Pt(tpy)Cl](PF$_6$) (2a).** A mixture of Pt(COD)$Cl_2$ (100 mg, 0.27 mmol) and tpy (63 mg, 0.27 mmol) in 50 mL of water was refluxed for 24 h. After cooling to room temperature, the resultant mixture was filtered to rid excess of Pt(COD)$Cl_2$. The red filtrate was then reduced in volume by roto-evaporation, followed by the addition of acetone (~100 ml) until a precipitate was formed. Red **2a(**Cl) was filtered off and then washed with acetone. Metathesis of the chloride salt using a saturated aqueous solution of $NH_4PF_6$ yielded the orange-red $(PF_6)^-$ salt of **2a**. The solid was filtered, and washed successively with water and diethyl ether, and then vacuum dried. MS-ESI (m/z): 464.03($PtC_{15}H_{11}N_3Cl)^+$**.** Anal. Calcd. for $C_{15}H_{11}N_3ClF_6PPt$: C, 29.60; H, 1.82; N, 6.90. Found: C, 29.70; H, 1.75; N, 6.91. $^1$H NMR (400 MHz, $CD_3CN$, 298K, δ/ppm) δ 9.0 (2H, d, $^3J_{H\text{-}H}$ = 8.0 Hz, $^3J_{Pt\text{-}H}$ = 36.2 Hz), 8.45 (1H, t, $^3J$ = 8.0 Hz) ; 8.36 (2H, dd, $^3J$ = 8.0 Hz, $^5J$ = 1.2 Hz); 8.20 - 8.30 (4H, m), 7.83 (2H, dd, $^3J$ = 6.0 Hz, $^5J$ = 1.2 Hz).

**[Pt(tpy)CCPh](PF$_6$) (2b).** To a solution of **2a** (125 mg, 0.25 mmol) in DMF (100 mL) were added 2 equivalents of phenyl acetylene (55 μl, 0.5 mmol), CuI (10 mg), and triethylamine (5 mL). The reaction mixture was stirred under argon for 24 h at room temperature. The resultant solution was filtered and to the filtrate added in excess triethylamine, which yielded a yellow (and sometimes orange-brown) precipitate of the chloride salt of **2b**. The solid was filtered off and washed with diethyl ether. Metathesis of the chloride salt using a saturated aqueous solution of $NH_4PF_6$ yielded a red $(PF_6)^-$ salt of **2b**. MS-ESI (m/z): 529.11 $(C_{23}H_{16}N_3Pt)^+$, 144.98 $(PF_6)^-$. Anal. Calcd. for $C_{23}H_{16}F_6N_3PPt$: C, 40.96; H, 2.39; N, 6.23. Found: C, 41.07; H, 2.26; N, 6.36. FT-IR, $\nu_{(C\equiv C)}$ = 2124.6cm$^{-1}$. $^1$H NMR (400 MHz, 1.2 mM in $(CD_3)_2SO$, 298K, δ/ppm) $\delta_H$ 9.2 (2H, d, $J_{H\text{-}H}$ = 5.6 Hz, $J_{Pt\text{-}H}$ = 40 Hz, $H_6$ and $H_{6''}$), 8.70 (2H, d, $J$ = 8.0 Hz) and 8.68 (2H, d, $J$ = 8.0 Hz) ($H_{3'}$; $H_{5'}$, and $H_3$; $H_{3''}$), 8.62 (1H, t, $J$ = 5.6 Hz, $H_{4'}$), 8.53 (2H, dd, $J$ = 7.8 Hz, $H_4$ and $H_{4''}$), 7.96 (2H, dd, $J$ = 6.6 Hz, $H_5$ and

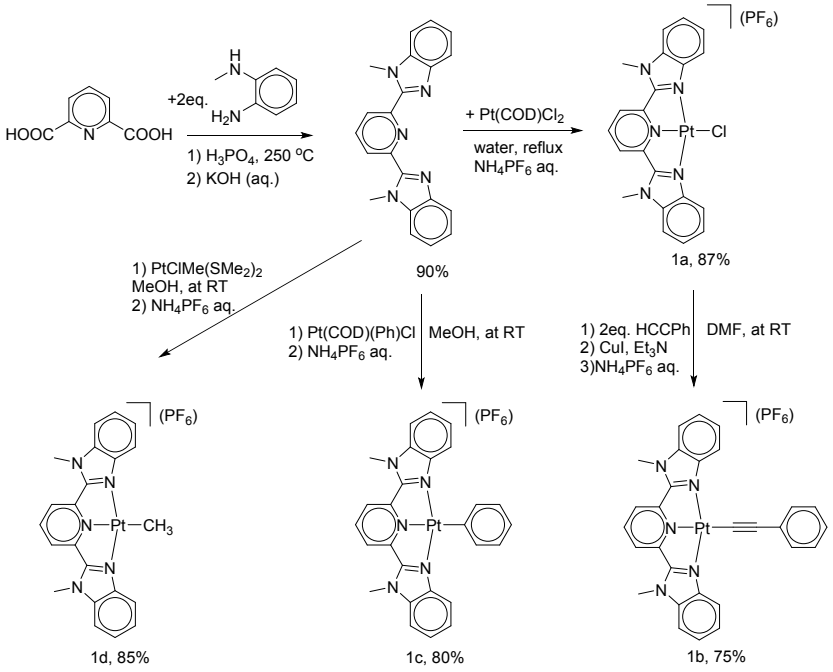
$H_{5''}$), 7.53 (2H, d, *J* = 8.0 Hz, $H_{2'''}$ and $H_{6'''}$), 7.37 (2H, dd, *J* = 7.6 Hz, $H_{3'''}$ and $H_{5'''}$), 7.29 (1H, t, *J* = 7.4 Hz, $H_{4'''}$). $^1$H NMR (400 MHz, 26.5 mM in $(CD_3)_2SO$, 298K, δ/ppm) $\delta_H$ 8.71 (2H, d, *J* = 5.6 Hz, $H_6$ and $H_{6''}$), 8.25-8.45 (7H, m, $H_{3'}$,$H_{5'}$, $H_{4'}$, $H_3$, $H_{3''}$, $H_4$, $H_{4''}$) , 7.72 (2H, dd, *J* = 6.2 Hz, $H_5$ and $H_{5''}$), 7.25-7.40 (5H, m, $H_{2'''}$, $H_{3'''}$, $H_{4'''}$, $H_{5'''}$, and $H_{6'''}$, ). $^{13}$C NMR (400 MHz, 26.5 mM in $(CD_3)_2SO$, 298 K, δ/ppm) $\delta_c$ 158.3; 153.5 ($C_{2'}$,$C_{6'}$; and $C_2$, $C_{2''}$), 153.6 ($C_6$ and $C_{6''}$), 141.9; 141.8; 125.8; 124.1 ($C_{3'}$, $C_{5'}$; $C_{4'}$; $C_3$, $C_{3''}$; and $C_4$, $C_{4''}$), 131.7; 128.2; 126.6 ($C_{2'''}$, $C_{6'''}$; $C_{3'''}$, $C_{5'''}$; and $C_{4'''}$), 129.5 ($C_5$ and $C_{5''}$), 126.5 ($C_{1'''}$), 103.1; 98.3 ($C_{1''''}$, $C_{2''''}$ ). $^{195}$Pt NMR (400 MHz, 60.9 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δ -3127.5

**[Pt(tpy)Ph](PF$_6$) (2c).** A mixture of Pt(COD)(Ph)Cl (150 mg, 0.36 mmol) and tpy (84 mg, 0.36 mmol) was stirred in methanol for 24 h at room temperature. The resultant orange mixture was filtered. The filtrate was then reduced in volume under vacuum. The addition of a saturated aqueous solution of $NH_4PF_6$ to the filtrate led to an orange precipitate of the $(PF_6)^-$ salt of **2c**. The precipitate filtered off and washed with diethyl ether. MS-ESI (m/z): 505.09 $(PtC_{21}N_3H_{16})^+$, 144.91 $(PF_6)^-$. Anal. Calcd. for $C_{21}H_{16}F_6N_3PPt$: C, 38.78; H, 2.48; N, 6.46. Found: C, 38.52; H, 2.61; N, 6.21. $^1$H NMR (400 MHz, $(CD_3)_2SO$, 298 K, δ/ppm) δ 8.73 (2H, d,$^3J$ = 8.0 Hz), 8.68 (2H, d, $^3J$ = 8.0 Hz), 8.60 (1H, t, $^3J$ = 8.0 Hz), 8.47 (2H, dd, $^3J$ =7.8 Hz), 8.34 (2H, d, $^3J_{H\text{-}H}$ = 5.2, $^3J_{Pt\text{-}H}$ = 44 Hz), 7.84 (2H, dd, $^3J$ = 6.4 Hz), 7.51 (2H, d, $^3J$ = 7.2 Hz), 7.34 (2H, dd, $^3J$ = 7.4 Hz), 7.11 (1H, t, $^3J$ = 7.2). $^{195}$Pt NMR (400 MHz, 49.5 mM in $(CD_3)_2SO$, 298 K, relative to $Na_2[PtCl_6]$ in $D_2O$ as an external reference, δ/ppm) δ -3130.5 (s).

**[Pt(tpy)CH$_3$](PF$_6$) (2d).** Synthesis of $PtClMe(SMe_2)_2$ was adapted from Hill *et al*.[3] A mixture of tpy (0.11 g, 0.47 mmol) and $PtClMe(SMe_2)_2$ (0.2 g, 0.47 mmol ) in 50 mL methanol was sonicated for 6 h at room temperature to give a red solution. The resultant solution was filtered, and the filtrate was reduced in volume to 2 mL under vacuum. Upon addition of 25 mL of diethyl ether, the mixture was chilled in a dry-ice/acetone bath for 1 hour. The resultant red precipitate was isolated by filtration, and then washed successively with dichloromethane and diethyl ether. $(PF_6)^-$ salt of **2d** was prepared by metathesis using a saturated aqueous solution of $NH_4PF_6$. An orange-red crystals were obtained upon slow evaporation from acetone: water (90:10) solution. Yield: 0.26, 84%. Anal. Calcd. for $C_{16}H_{14}F_6N_3PPt$: C, 32.66; H, 2.40; N, 7.14. Found: C, 32.88; H, 2.28; N, 7.33.$^1$H NMR (400 MHz, 1.5 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δ 8.91 (2H, d, $^3J$ = 5.6 Hz, $J_{Pt\text{-}H}$ = 49.6 Hz, $H_6$ and $H_{6''}$), 8.62-8.67 (4H, d, $^3J$ = 8.4 Hz), 8.55 (1H, t, $^3J$ = 8.4 Hz), 8.47 (2H, dd, $^3J$ = 7.8 Hz), 7.87 (2H, dd, $^3J$ = 6.4 Hz), 1.10 (3H, s, $^2J_{Pt\text{-}H}$ = 73.2 Hz, Pt-$CH_3$). $^1$H NMR (400 MHz, 240 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δ 7.96 (2H, dd), 7.85-7.65 (7H, m), 7.30 (2H, dd), -0.08 (3H, s). $^{13}$C NMR (400 MHz, 240 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δ 157.9, 150.5, 150.1, 140.7, 139.8, 128.5, 125.0, 123.05, -5.14. $^{195}$Pt NMR (400 MHz, 79.8 mM in $(CD_3)_2SO$, 298 K, δ/ppm) δ -3198.4 (RT); -3194.0 (50 °C); -3189.0 (70 °C).

**[Zn(mbzimpy)$_2$](PF$_6$)$_2$ (3).** A mixture of $ZnCl_2$ (0.1 g, 0.73 mmol) and mbzimpy (0.50 g, 1.47 mmol) in 30 ml methanol was refluxed for 24 h. After cooling the resultant solution down to a room temperature, a white precipitate of [Zn(mbzimpy)$_2$]$Cl_2$ was isolated and washed with methanol. Metathesis of [Zn(mbzimpy)$_2$]$Cl_2$ using a saturated aqueous solution of $NH_4PF_6$ yielded **3** as a white solid which was filtered off and washed with water. Shiny white crystals of **3** were obtained upon slow evaporation from acetone: water (90:10) solution. Yield, 0.66 g, 87%. MS-ESI (m/z) = $(C_{42}H_{34}N_{10}Zn)^{2+}$/2, 371.03 (100%). Anal. Calcd. for $C_{42}H_{34}F_{12}N_{10}P_2Zn$: C, 48.78 ; H, 3.31; N, 13.54. Found: C, 48.67; H, 3.22; N, 13.56. $^1$H NMR (400 MHz, $(CD_3)_2SO$, 298 K, δ/ppm) δ 8.44 (4H, d, $H_{py}$), 8.26 (2H, t, $H_{py}$), 7.78 (4H, d, $H_{bzim}$), 7.73 (4H, d, $H_{bzim}$), 7.40 (4H, dd, $H_{bzim}$), 7.33 (4H, d, $H_{bzim}$), 4.29 (12H, s, N-$CH_3$).

(*Note*: py = pyridine, bzim = benzimidazole)




**Scheme S1.** Syntheses of Pt(mbzimpy)X$^+$, **1(a-d)**, complexes.

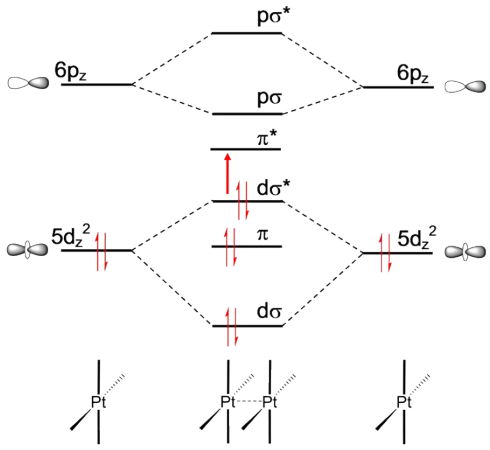



**Figure S1.** Qualitative molecular orbital diagram showing the origin of the MMLCT for two closely interacting square planar platinum (II) complexes.

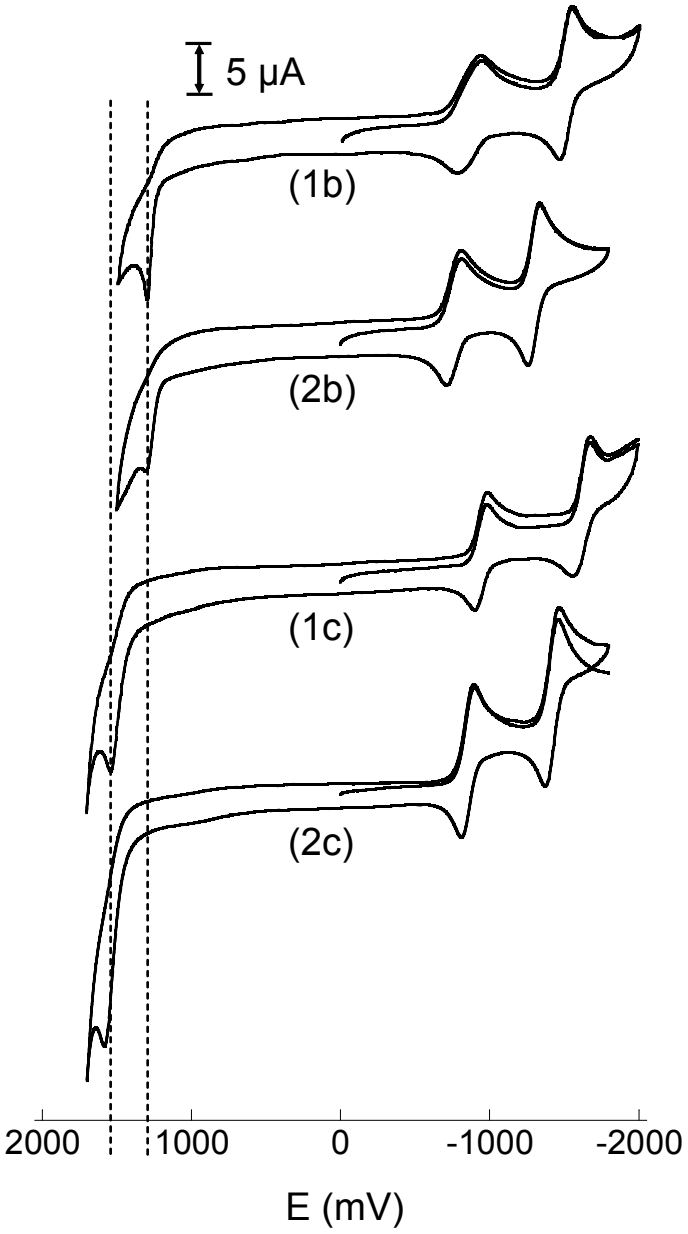



**Figure S2.** Cyclic voltammograms of **1b, 1c** and **2b, 2c** in 0.1 M TBAH/DMF at a scan rate of 100 mV/s. (Conditions are the following: The working electrode was a glassy carbon, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl in 3.0 M NaCl).

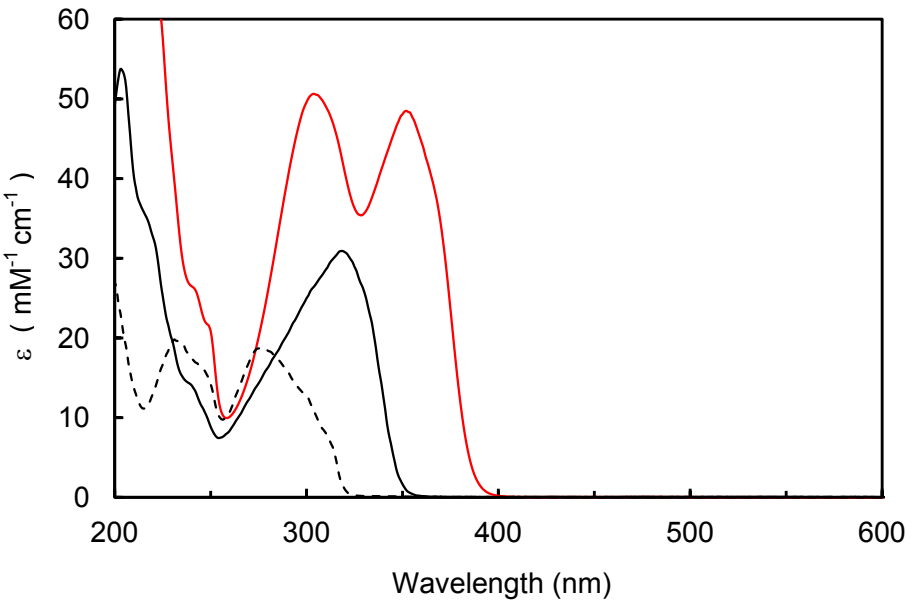



**Figure S3.** Electronic absorption spectra of **3** (—), mbzimpy (—), and tpy (····· ) in acetonitrile at room temperature.

**Table S1.** Electronic absorption data in acetonitrile at room temperature. (Absorption data in other solvents are specified with superscripts).

| **Compound** | **Absorbance $\lambda_{max}$ nm (ε, $M^{-1}$ $cm^{-1}$)** |
|---|---|
| **1a** | 217 (48 064), 246 (18 779), 309 (24 538), 339 (23 693), 355sh (21 671), 371 (19 186), 428 (1 524), 452 (1 209) |
| **1a**[a] | 315 (23 735), 336 (24 176), 356sh (22 043), 371sh (20 195), 428sh (1 494), 452sh (1 189) |
| **1b** | 214sh (47 774), 245 (26 271), 271 (19 183), 325 (22 638), 351 (23 524), 367sh (20 608), 435br (3 841) |
| **1b**[a] | 329 (23 234), 352 (24 458), 367sh (21 783), 435 (4 150) |

| | |
|---|---|
| **1c** | 218sh (44 890), 242sh (26 829), 314 (26 305), 349 (25 373), 368 (20 077), 433 (1 324), 468 (581) |
| **1c**[a] | 315 (26 330), 350 (25 435), 368sh (21 291), 433sh (1 373), 468 (650) |
| **1d** | 219 (39 573), 229 (32 680), 242 (27 970), 312 (26 570), 346 (26 808), 365sh (20 664), 468 (650) |
| **1d**[a] | 314 (26 261), 346 (25 401), 367sh (19 792), 468sh (561) |
| **3** | 216(68 340), 241sh (26 343), 249sh (21 556), 304 (50 636), 352 (48 507) |
| mbzimpy | 203 (53 724), 216sh (35 376), 240sh (14 069), 318 (30 905) |
| mbzimpy[a] | 307sh (29 722), 324 (35 058) |
| mbzimpy[b] | 312sh (28 926), 327(34 214), 339sh (28 818) |
| **2a** | 210 (21 570), 231 (17 155), 254 (26 996), 271sh (19 729), 281 (26 471), 305 (9 495), 318 (10 528), 331 (15 128), 348 (8 653), 378 (2 285), 392sh(2 078), 471 (77) |
| **2b** | 244 (39 364), 262 (38 744), 269sh (37 405), 284sh (24 832), 312 (12 867), 328 (12 657), 343 (14 514), 432 (4, 466) |
| **2c** | 231sh (28 002), 242 (26 868), 270 (28 202), 276 (26 933), 316 (13 153), 338 (10 719), 406 (2 245), 419 (2 338), 476 (328) |
| **2d** | 219sh (22 140), 235 (19 769), 244 (19 505), 270 (29 178),278sh (26 481), 313 (12 768), 324 (10 463), 337 (11 912), 384sh (1 707), 406 (2 255), 424sh (1 755) |
| $Zn(tpy)_2^+$ | 282, 308sh, 321, 334 …(Aldridge *et al.*)[7] |
| Terpyridine | 231 (19 800), 246sh (16 147), 277 (18 779), 300sh (12 760), 310sh (8 052) |

[a]: in DMSO, [b]: in cyclohexane, sh: shoulder, br: broad

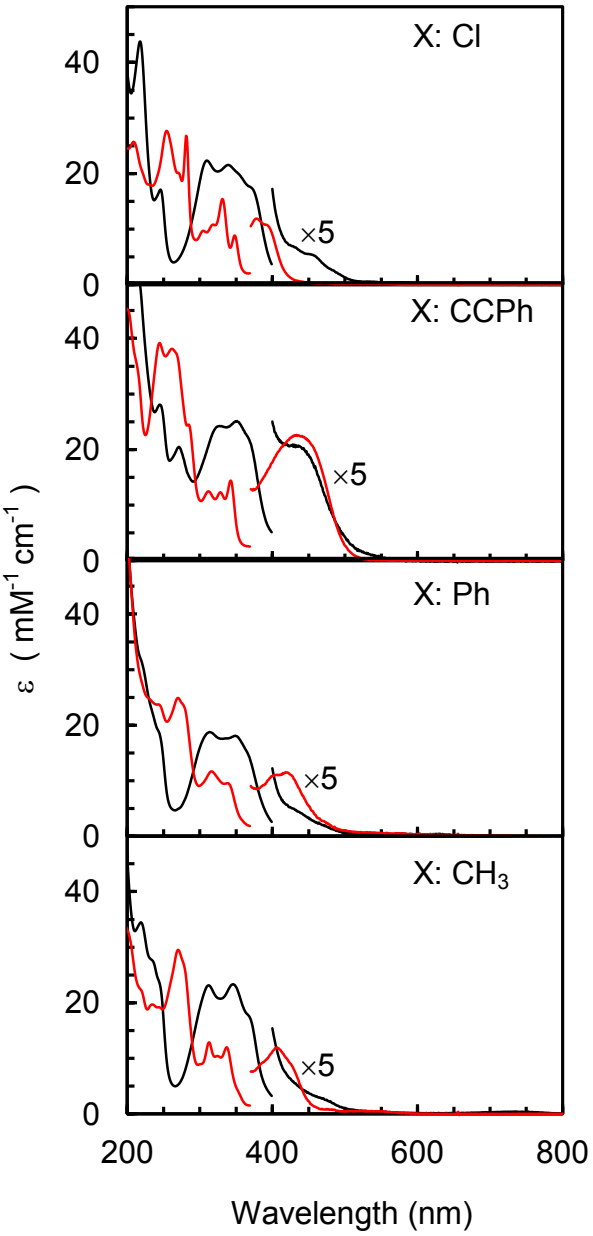



**Figure S4.** Overlays of electronic absorption spectra of [Pt(mbzimpy)X]($PF_6$) (black lines) and [Pt(tpy)X]($PF_6$) (red lines) in acetonitrile at RT. (where X = Cl, CCPh, Ph, or $CH_3$ ).

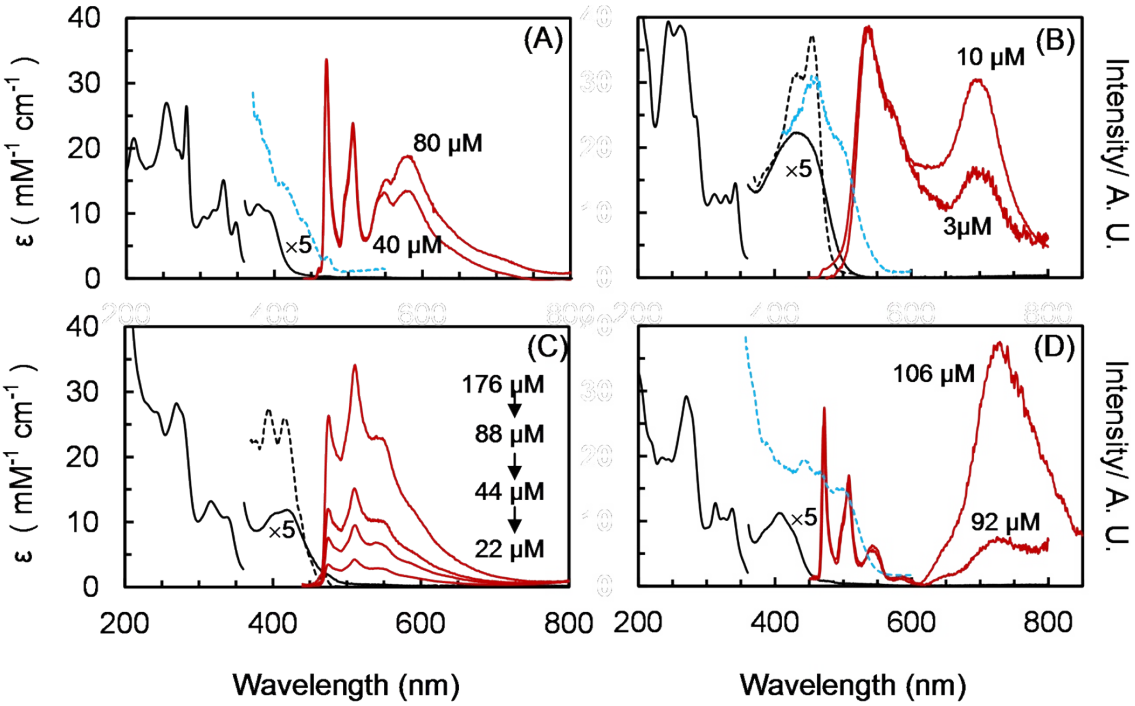



**Figure S5.** Room temperature electronic absorption spectrum in acetonitrile (—). 77K glassy solution emission ($\lambda_{ex}$ = 350 nm , —) and excitation spectra for A) **2a** in butyronitrile, ($\lambda_{em}$ = 581 nm, ---- ) B) **2b** in EMD, ($\lambda_{em}$ = 535 nm , ---- ; $\lambda_{em}$= 700 nm , ----) C) **2c** in butyronitrile; ($\lambda_{em}$ = 471 nm, ----) D) **2d** in butyronitrile ($\lambda_{em}$ = 706 nm, ----) spectra. Excepting for **2c**, the emission spectra at various concentrations are normalized at $\lambda_{max}$ of the first vibronic feature.

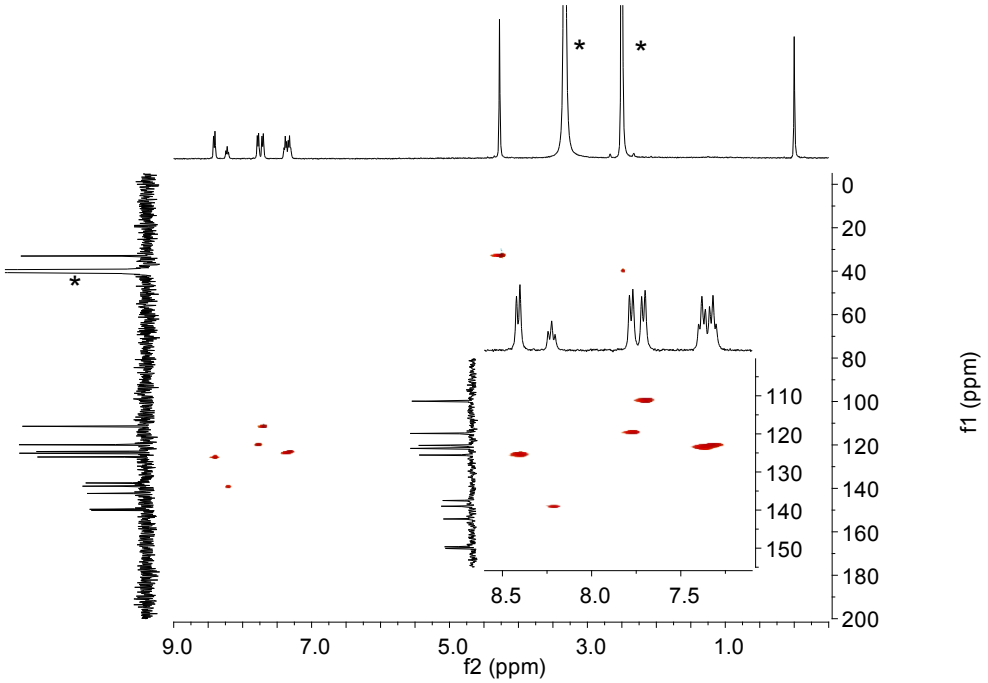



**Figure S6.** $^{1}$H-$^{13}$C HSQC NMR spectrum of mbzimpy in dmso-$d_6$ at rt.

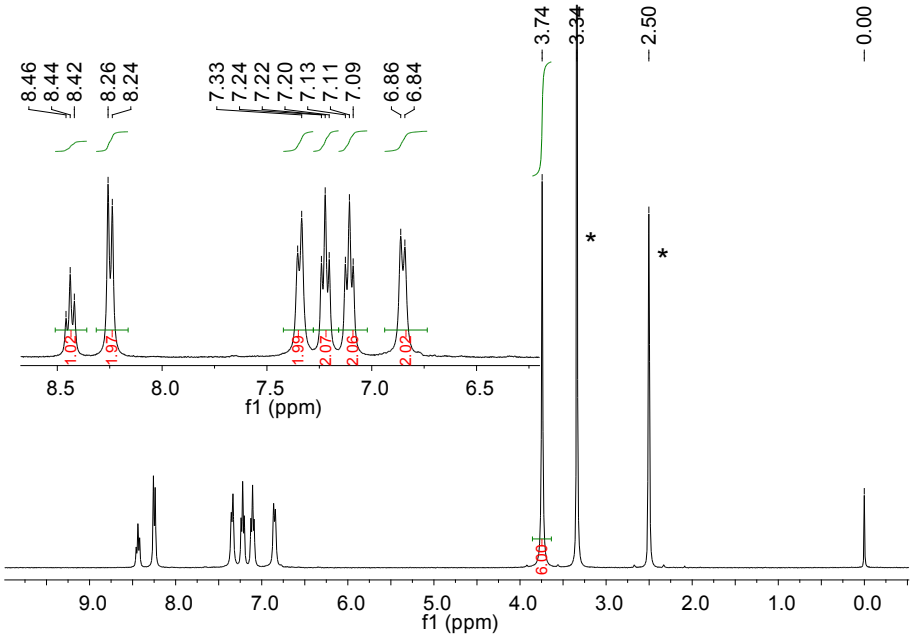



**Figure S7.** $^{1}$H-NMR spectrum of 23.2 mM solution of **1a** in dmso-$d_6$ at rt.

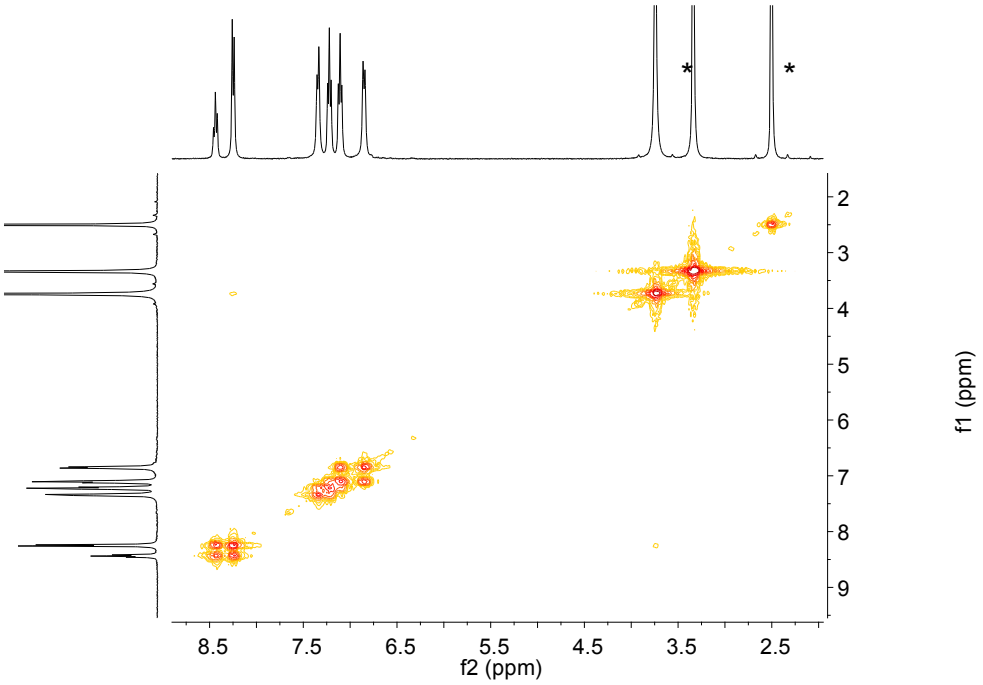



**Figure S8.** $^{1}$H-$^{1}$H COSY spectrum of 23.2 mM solution of **1a** in dmso-$d_6$ at rt.

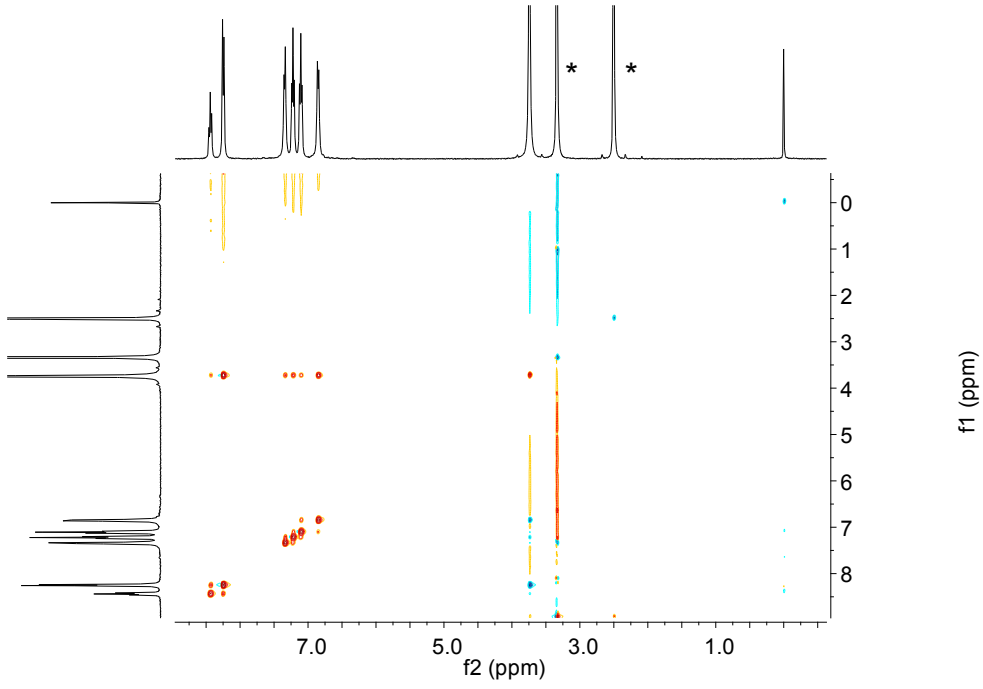



**Figure S9.** 2D $^{1}$H-$^{1}$H NOESY spectrum of 23.2 mM solution of **1a** in dmso-$d_6$ at rt.

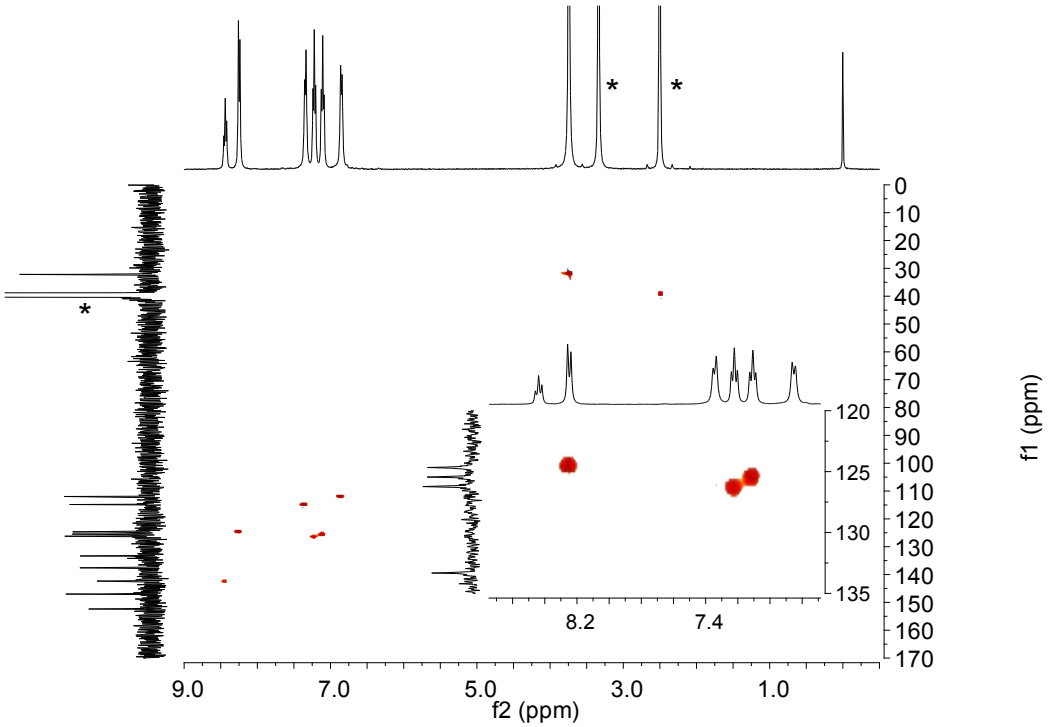



**Figure S10.** $^{1}H$-$^{13}C$ HSQC spectrum of 23.2 mM solution of **1a** in dmso-$d_6$ at rt.

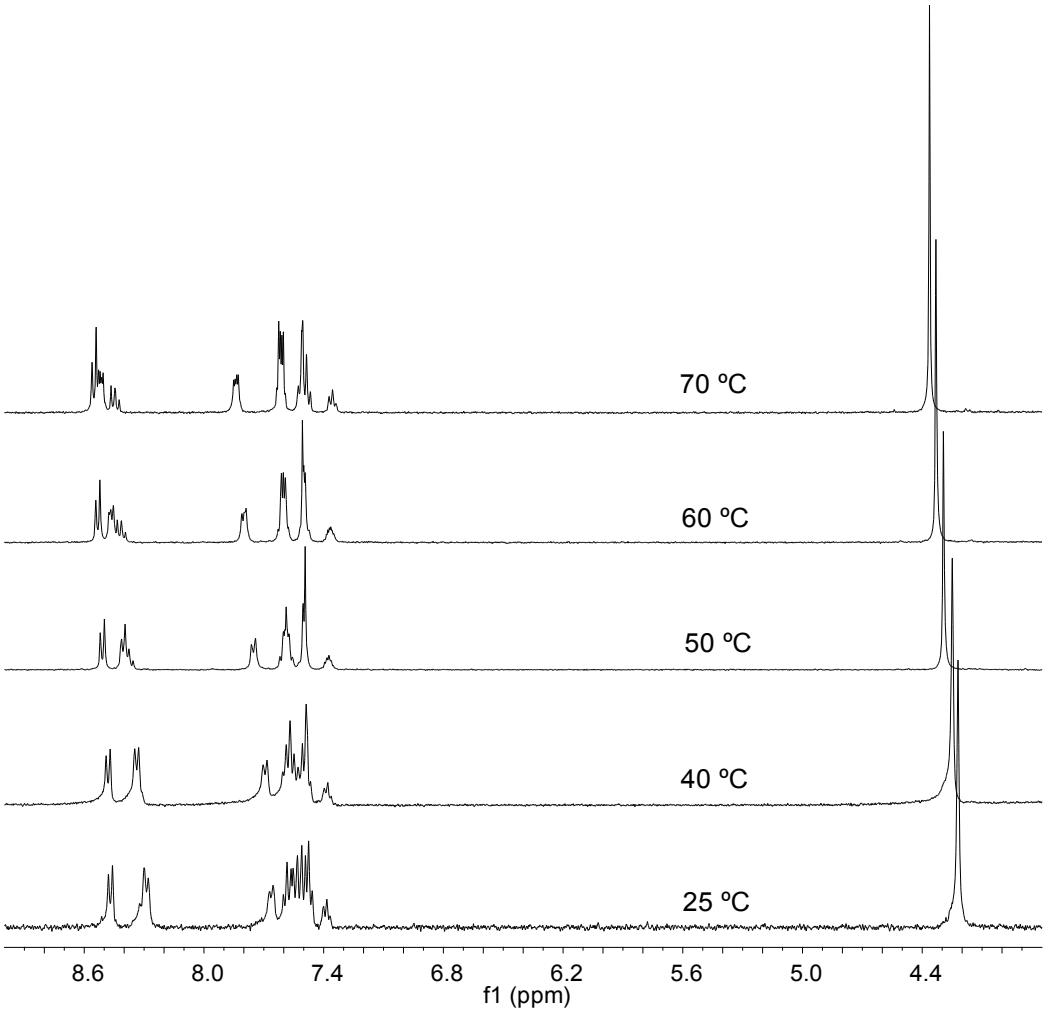



**Figure S11.** An overlay of $^{1}$H NMR spectra of 0.017 mM solution of **1b** in dmso-$d_6$ at temperatures ranged from 25-70 °C.

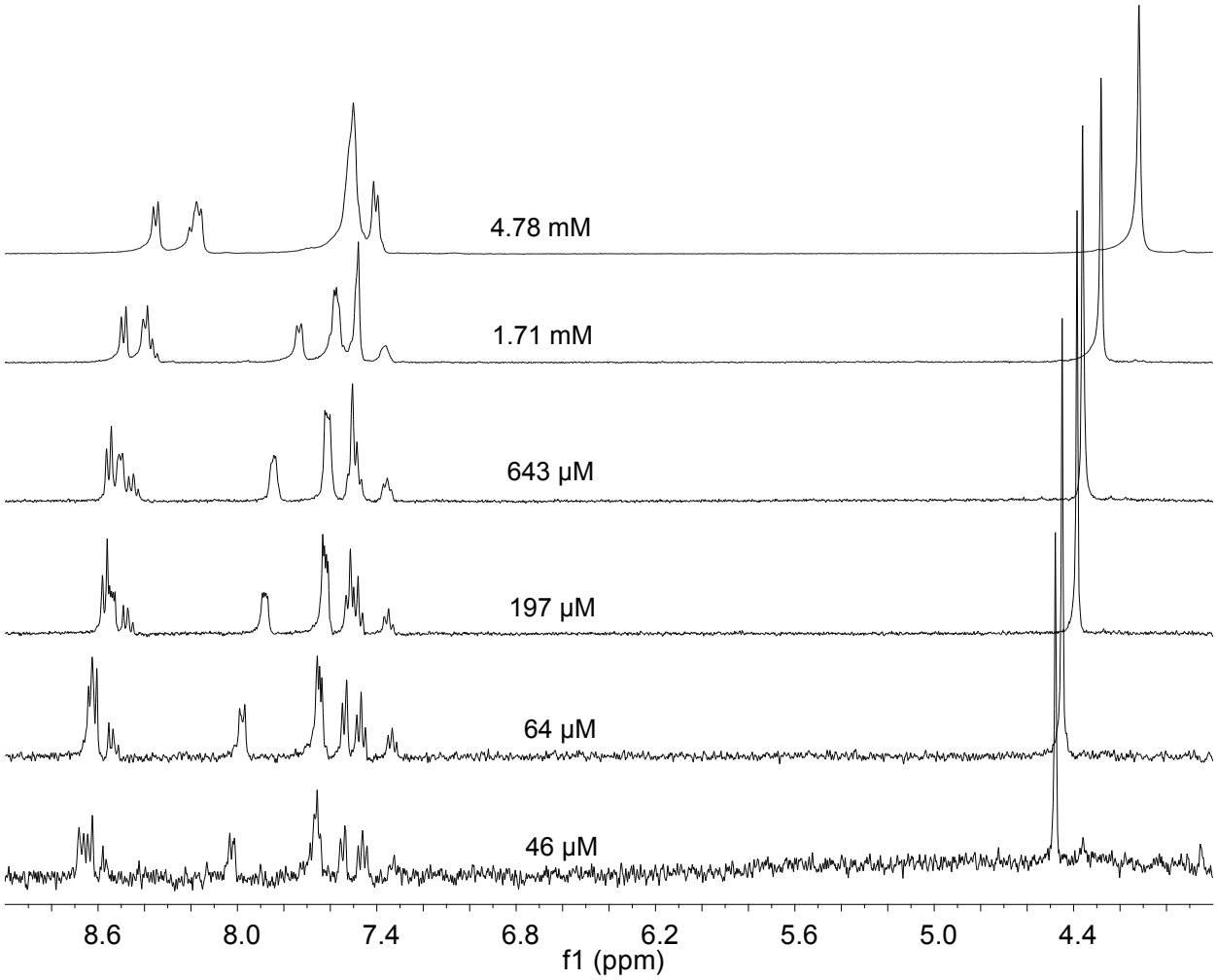



**Figure S12.** An overlay of $^{1}$H NMR spectra of **1b** at concentrations ranged from 0.05-5.0 mM in DMSO-$d_6$ at 60 °C

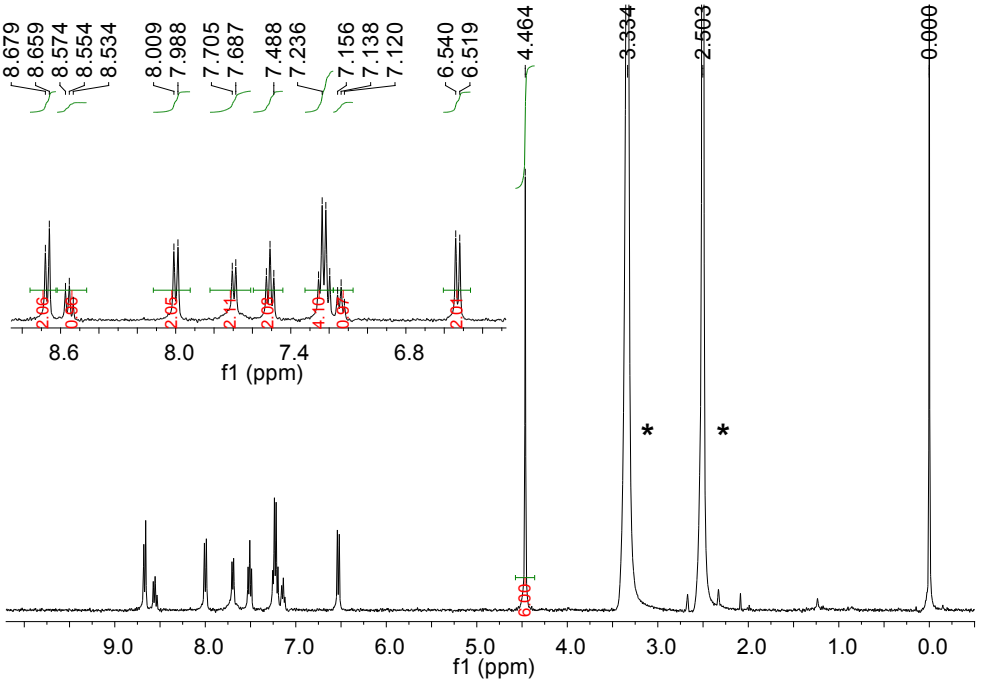



**Figure S13.** $^{1}$H NMR spectrum of 2.1 mM solution of **1c** in dmso-$d_6$ at rt.

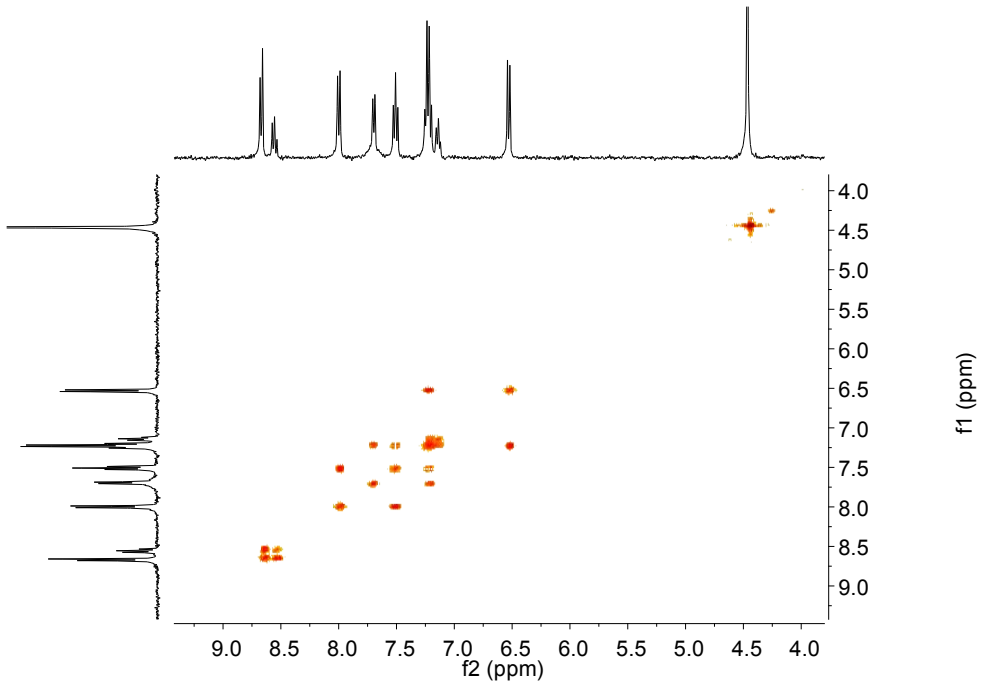



**Figure S14.** $^{1}$H-$^{1}$H COSY NMR spectrum of **1c** in dmso-$d_6$ at rt.

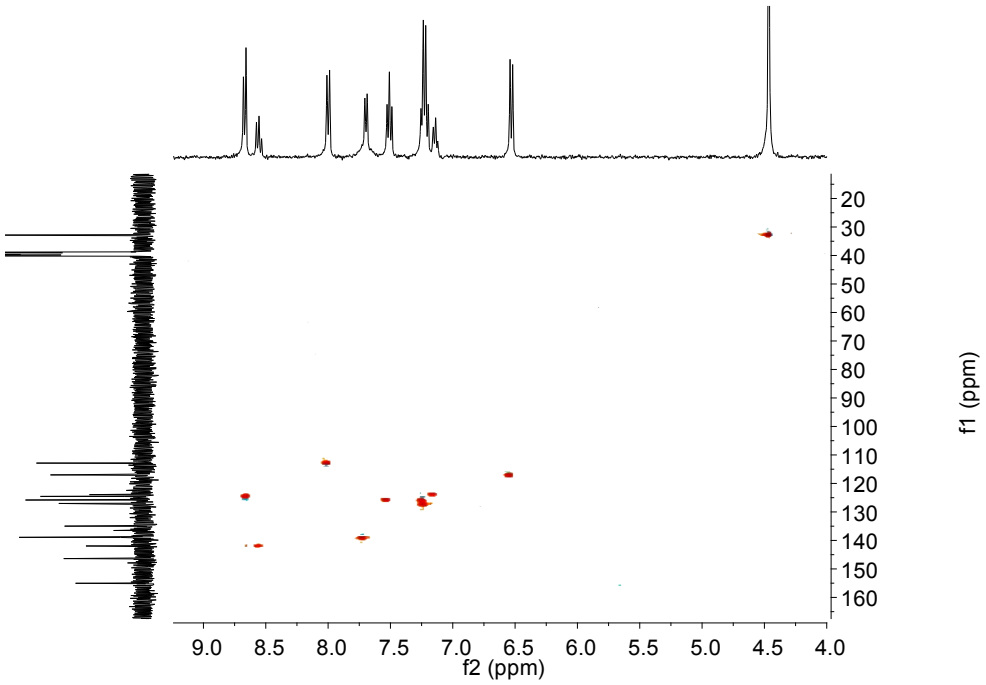



**Figure S15.** $^{1}H$-$^{13}C$ HSQC spectrum of 12 mM solution of **1c** in dmso-$d_6$ at rt.

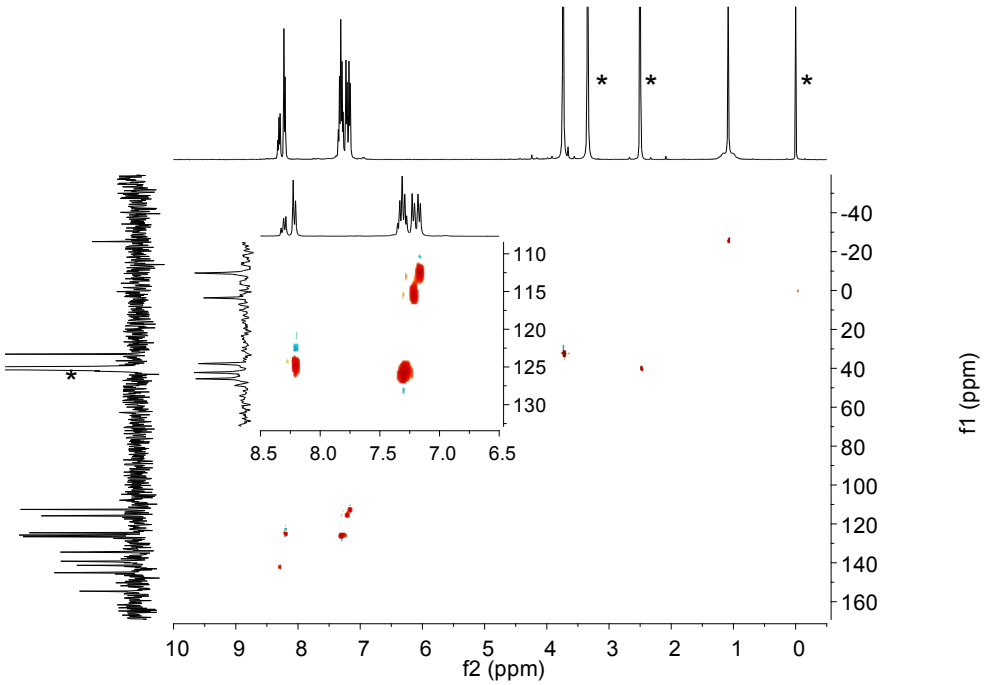



**Figure S16.** $^{1}H$-$^{13}C$ HSQC spectrum of 29.4 mM solution of **1d** in dmso-$d_6$ at rt

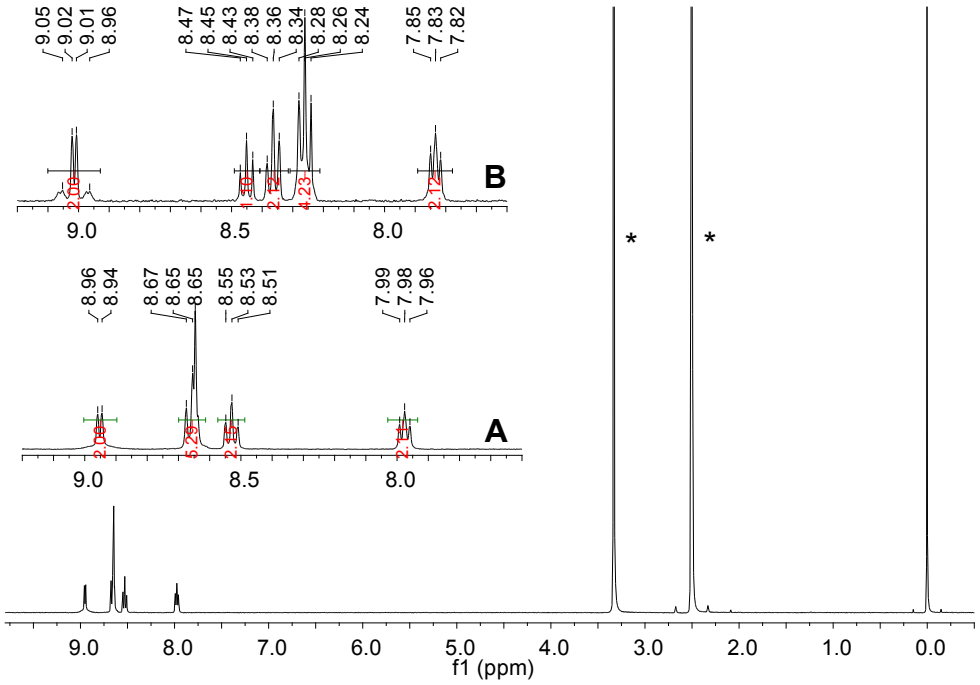



**Figure S17.** $^{1}$H NMR spectrum of **2a** in dmso-$d_6$ at rt. (Inset: A partial view of $^{1}$H NMR spectrum A) in dmso-$d_6$, and B) acetonitrile-$d_3$)

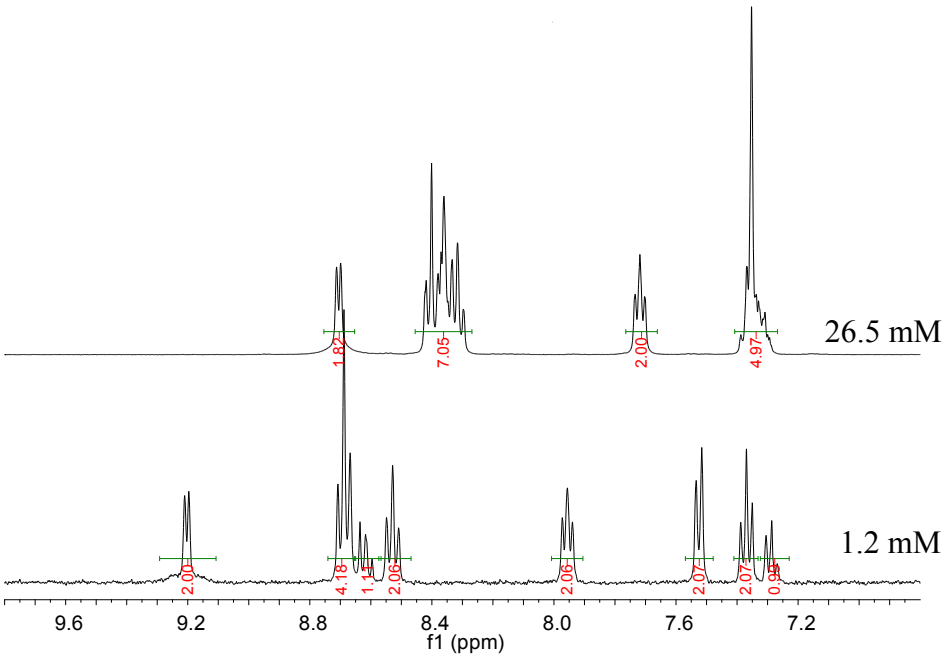



**Figure S18.** An overlay of $^{1}$H NMR spectra of **2b** in dmso-$d_6$ at two different concentrations at rt.

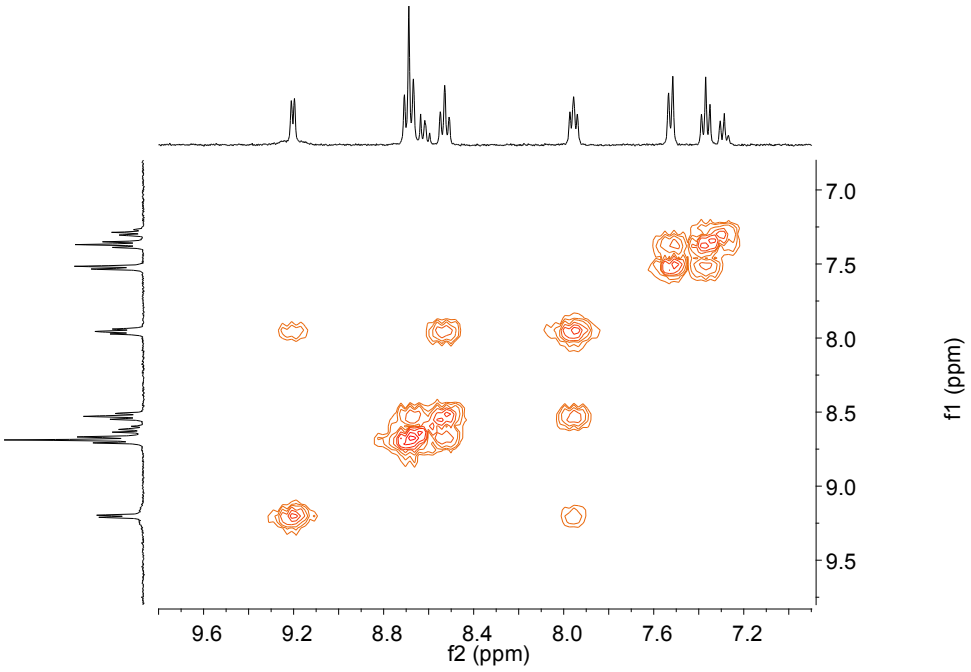



**Figure S19.** $^{1}$H-$^{1}$H COSY spectrum of 1.2 mM solution of **2b** in dmso-$d_6$ at rt.

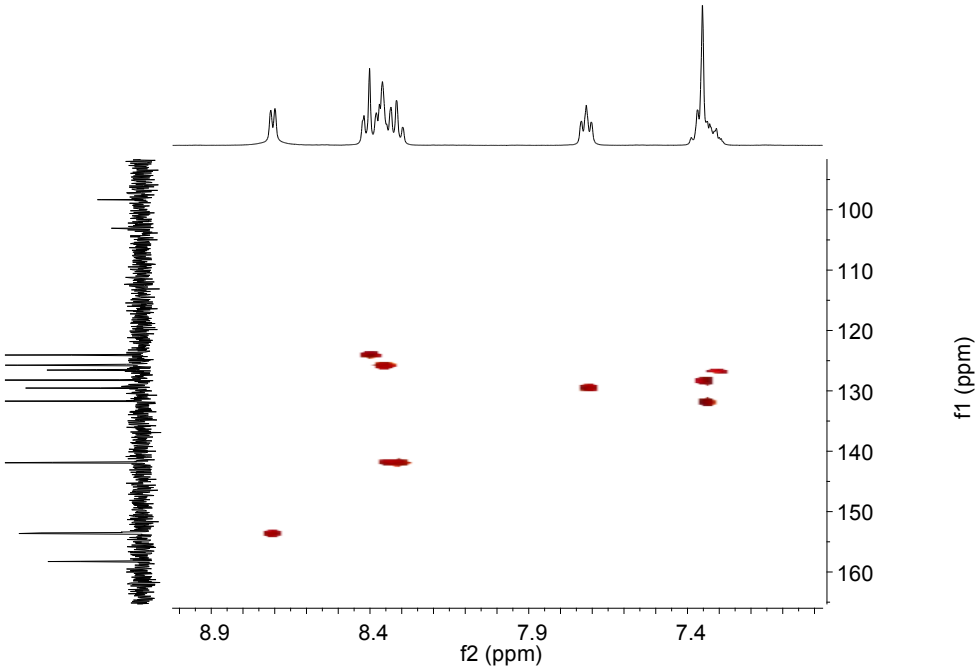



**Figure S20.** $^{1}$H-$^{13}$C HSQC spectrum of 26.5 mM solution of **2b** in dmso-$d_6$ at rt.

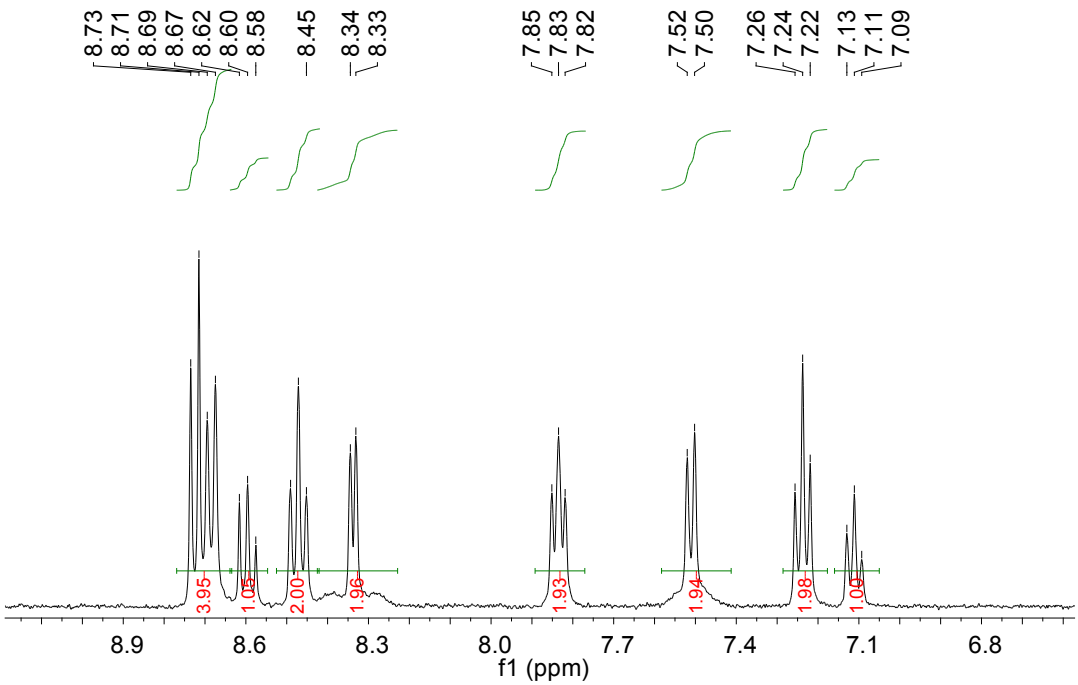



**Figure S21.** $^{1}$H NMR spectrum of **2c** in dmso-$d_6$ at rt.

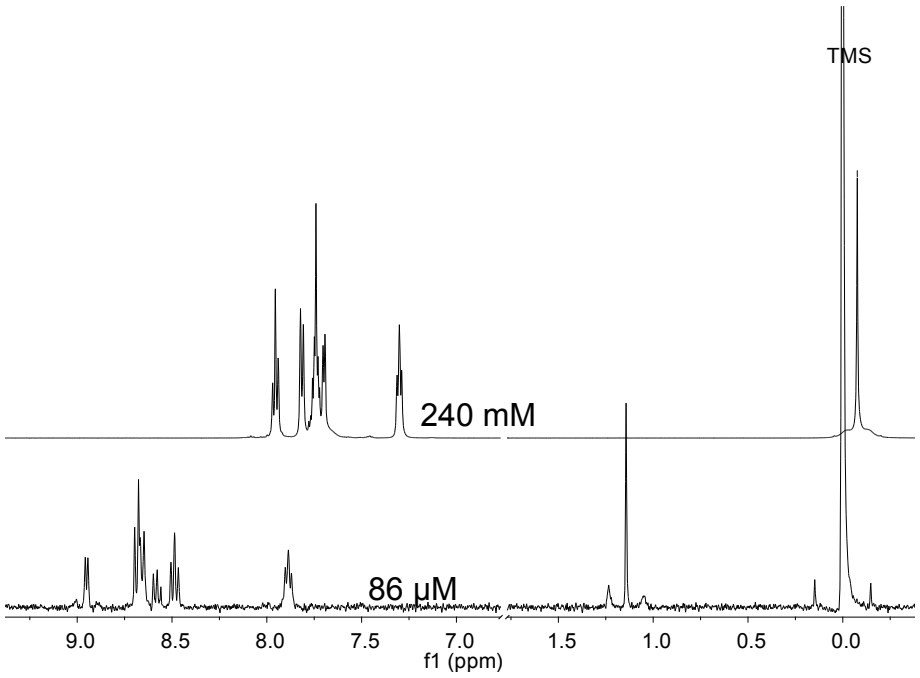



**Figure S22.** An overlay of $^{1}$H NMR spectra of **2d** in dmso-$d_6$ and dmso-$d_6$ at rt.

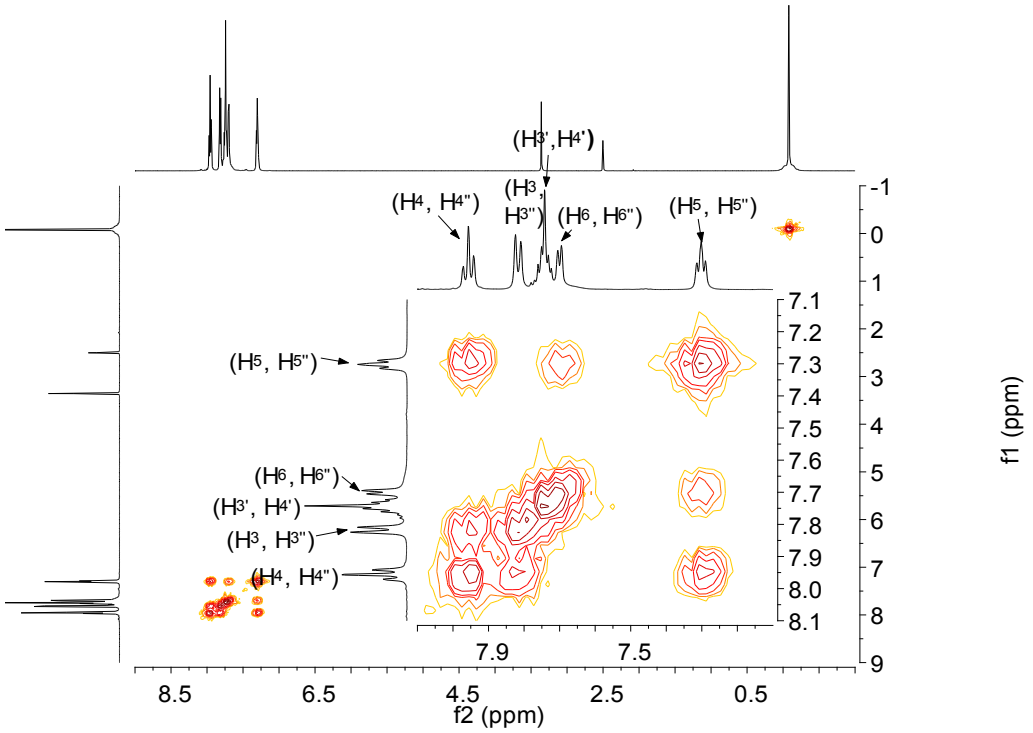



**Figure S23.** $^{1}$H-$^{1}$H COSY spectrum of 240 mM solution of **2d** in dmso-$d_6$ at rt.

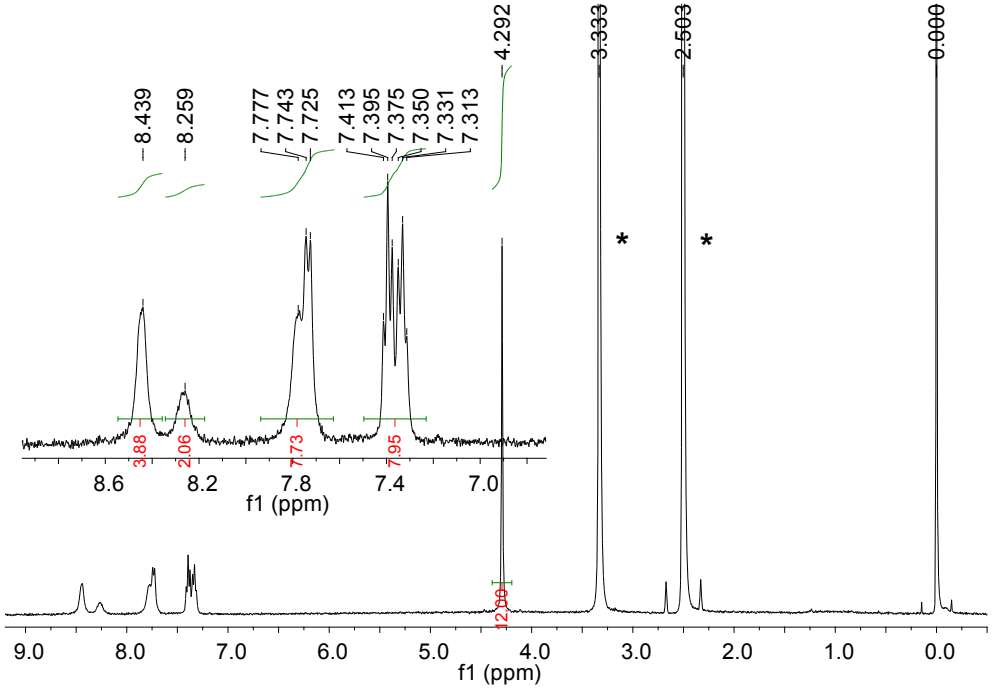



**Figure S24.** $^{1}$H NMR spectrum of **3** in dmso-$d_6$ at rt.

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