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Supporting Information

Synthesis, Structure, Catalytic, and Bio Activity of Some Metal Complexes and Coordination Polymer Featuring Imidazo[1,5-*a*]pyridine and Chromen[4,3-*b*]pyrrole-4-one

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Contents

General Methods and Instrumentation

The solvents were purchased from commercial sources, chemicals used in this report were of reagent grade, obtained from Sigma-Aldrich and TCI, used without any further purification unless otherwise stated. The catalytic products were purified by preparative thin layer chromatography using ethyl acetate and hexane as eluting agents. Fourier Transform Infrared (FT-IR) measurements were recorded by using a Perkin–Elmer attenuated total reflection infrared (ATR-IR) spectrophotometer (4000–400 cm^{-1}). NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker 400MHz, 500 MHz, and 600 MHz instruments. The chemical shift values (δ) (ppm) and the spin–spin coupling constant (J) (Hz) were determined by comparing them to tetramethylsilane (TMS), a standard internal reference with a value of zero ppm. FESEM images of the dry powder sample were taken on a Sigma 300 FESEM instrument (Carl Zeiss). Perkin Elmer Lambda-35 UV–visible spectrometer was used to record absorption spectra with quartz cuvettes of 1 cm path length in the 200-700nm range. Stock solutions of all ligands and complexes were made in DMSO for UV–visible measurement. Emission spectra were recorded in Fluoromax spectrophotometer and varioMACROcube instrument was used for CHN analysis. Electrospray ionization high resolution mass (ESI-HRMS) spectra were recorded on an Agilent MS Model G6546A (Serial Number SG2242E201) Q-TOF mass spectrometer and the simulated spectra were calculated by using MestReNova software. All known compounds were characterized by using NMR spectroscopy and compared with the literature. X-ray crystallographic data were collected using Bruker SMART APEX-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and Agilent XRD diffractometer. The structures were solved by direct methods using APEX4, SHELXT, CrysAlispro, Autochem and refined with Olex2-1.5 using SHELXL program. The crystallographic structures were illustrated by using mercury and ORTEP software. For computational study, all calculations were performed by using Gaussian16 (G16) program and GaussView 5.0 was used for picturization.[1,2]

Synthesis of Ligands

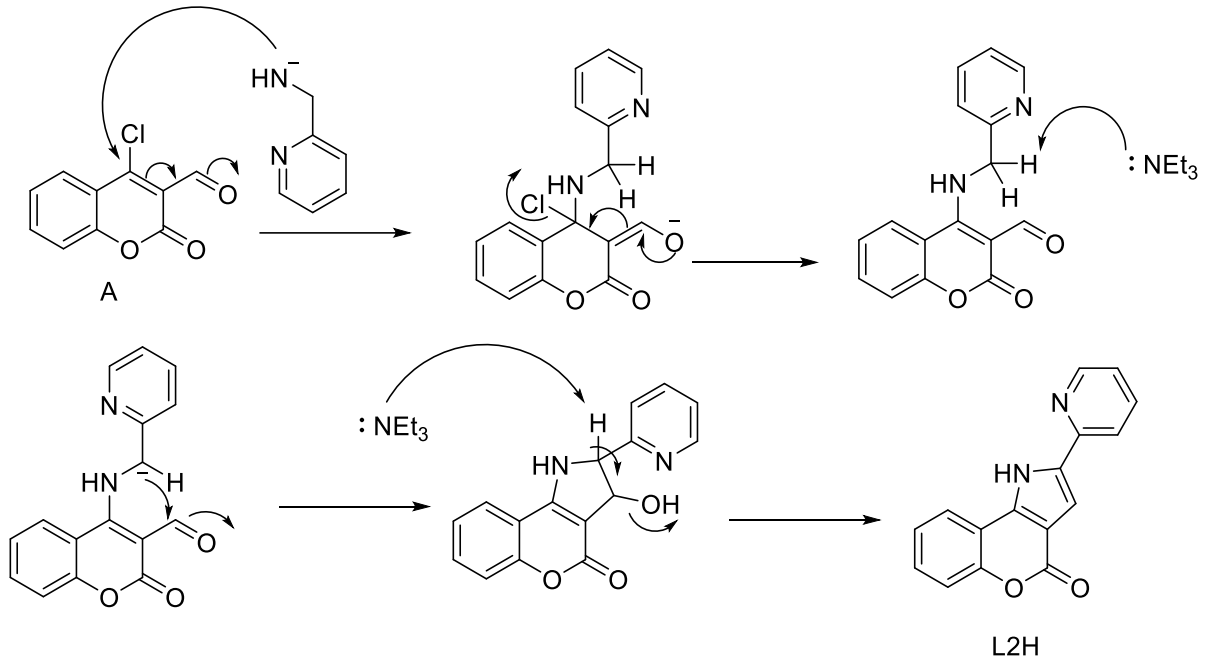
3-(2-bromophenyl)-1-(pyridin-2-yl)imidazo[1,5-a]pyridine (**L1**):

Ligand **L1** was synthesized by following a reported procedure. A mixture consisting of 2,2′-dipyridyl ketone (0.460 g, 2.5 mmol), 2-bromobenzaldehyde (0.925 g, 5 mmol), NH_4OAc (0.965 g, 10 mmol) in 20 mL of glacial acetic acid was stirred at 110 °C for 5 h. Then reaction mixture was cooled to room temperature and poured into 100 mL of ice water. The formed solid was then filtered, dried, and recrystallized from ethanol. Yield: (0.648 g) 74%. Anal. calcd

for $C_{18}H_{12}N_3Br$: C, 61.73%; H, 3.45%; N, 12.00; found: C, 61.58%; H, 3.50%; N, 11.88. ATR-IR (ν, cm^{-1}): 1585, 1523, 1474, 1140, 1006, 790, 776, 743, 706, 618, 422, 438, 403. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 9.2 Hz, 1H), 8.66 – 8.61 (m, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.66 – 7.59 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.7, 1.6 Hz, 1H), 7.14 – 7.06 (m, 1H), 6.97 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.67 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 149.2, 136.9, 136.4, 133.7, 133.3, 131.5, 131.3, 130.3, 129.7, 128.0, 124.6, 122.5, 121.7, 121.4, 120.6, 120.1, 113. UV- Vi s: nm (M^{-1} cm^{-1}) 264 (9150), 294 (9700), 328 (7930), 358 (5810). HRMS (ESI) m/z calcd for [**L1**+H]$^+$: 350.0287, found: 350.0292.

2-(pyridin-2-yl)chromeno[4,3-b]pyrrol-4(1H)-one (**L2H**):

4-chloro-2-oxo-2H-chromene-3-carbaldehyde (**A**) was synthesized by some modification of reported procedure. 4-hydroxy-2-oxo-2H-chromene was taken in dimethylformamide (10 mL) and kept at 273K. In a closed container, $POCl_3$ (2.0 mL) was taken in 5.0 mL DMF and kept at 273K. After few hours, $POCL_3$ solution was added to 4-hydroxy-2-oxo-2H-chromene solution at 273K with constant stirring. After 2 hours of stirring, the reaction mixture was kept at 273K for overnight. Next day, water was added carefully portion wise to the mixture with vigorous stirring at same temperature. Precipitates of **A** were collected by filtration followed by washing with water, dried over fused $CaCl_2$. 2.0 mmol (0.417 mg) of **A** was taken in 10mL absolute ethanol and 2.0 mmol of 2-picolylamine (0.216 g) was added to it followed by few drops of triethylamine. The mixture was stirred at reflux for 12 hours, cooled at room temperature and left undisturbed for few days. Colorless crystals of **L2H** were collected and washed with cold ethanol (20 mL). Yield: (0.377 g) 72%. Anal. calcd for $C_{16}H_{10}N_2O_2$: C, 73.27%; H, 3.84%; N, 10.68; found: C, 73.42%; H, 3.91%; N, 10.51. ATR-IR (neat, cm^{-1}): 3283, 1686, 1450, 1186, 1088, 969, 744, 473. ^{1}H NMR (400 MHz, Chloroform-d) δ 10.92 (s, 1H), 8.49 (d, J = 4.4 Hz, 1H), 7.77 – 7.66 (m, 3H), 7.39 (dd, J = 6.0, 1.3 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 159.3, 152.4, 148.9, 148.9, 137.4, 136.7, 135.8, 129.4, 124.3, 122.6, 120.8, 119.7, 117.8, 113.5, 111.1, 106.2. UV- Vis: nm (M^{-1} cm^{-1}) 340 (28496), 325 (29934), 313 (24877), 290 (14047). HRMS (ESI) *m/z* calculated for [**L2H**+H]$^+$: 263.0815, found 263.0825.



Scheme S1: Synthetic mechanism of **L2H**.

[Ni(**L1**)$_2$(H_2O)$_2$]Cl_2 (**1a**)

Nickel chloride hexahydrate (60 mg, 0.5 mmol) and **L1** (175 mg, 0.5 mmol) were taken in 10 mL ethanol and refluxed for overnight. The solution was left undisturbed for few days to produce cloud green crystals of **1a**. Yield: (147 mg), 68%. Anal. calcd. for [$C_{36}H_{28}N_6Br_2NiO_2$]Cl_2: C, 49.93%; H, 3.26%; N, 9.70; found: C, 50.14%; H, 3.28%; N, 9.64%. ATR-IR (neat, cm^{-1}): 3324 (broad), 1608, 1479, 1369, 1150, 1057, 781, 743, 706, 418. UV-Vis: nm (M^{-1} cm^{-1}) 277 (15860), 285 (16405), 310 (20830), 325(22250), 357 (31200), 371 (33240), 388 (20280). HRMS (ESI) *m/z* calcd for [**1a**-2H_2O]$^{2+}$ 378.9875; found 378.9877.

[Ni(**L1**)$_2$(N_3)$_2$] (**1aa**)

Complex **1a** (43 mg, 0.05 mmol) and sodium azide (7.0 mg, 0.1 mmol) were taken in 10 mL methanol and stirred at room temperature for 12 hours. The solution was left undisturbed for few days to produce greenish white crystals of **1aa**. Yield: (37.0 mg), 88%. Anal. calcd. for [$C_{36}H_{28}N_{12}Br_2Ni$]: C, 51.28%; H, 2.87%; N, 19.93; found: C, 51.37%; H, 2.93%; N, 20.00%. ATR-IR (neat, cm^{-1}): 2924, 2029, 1607, 1549, 1513, 1479, 1366, 1332, 1250, 1056, 1009, 784, 744, 709, 653, 627, 598, 423. UV- Vis: nm (M^{-1} cm^{-1}) 310 (12200), 326 (12750), 356 (16160), 371 (33360), 388 (10300). HRMS (ESI) *m/z* calcd for [**1aa**-2N_3]$^{2+}$ 378.9875; found 378.9857.

[Pd(**L1**)Cl_2] (**1b**)

Solid palladium dichloride (44.5 mg, 0.25 mmol) was taken in 10 mL acetonitrile and was heated till all $PdCl_2$ dissolved. To this solution, 87.5 mg (0.25 mmol) of **L1** was added and the yellow solution was stirred for 24 h at ambient temperature. The precipitates formed were separated by filtration, washed with diethyl ether, and dried in to afford palladium complex **1b**. Yield: (108 mg), 82%. Anal. calcd. for $C_{18}H_{12}BrCl_2N_3Pd$: C, 40.98%; H, 2.29%; N, 7.97; found: C, 41.14%; H, 2.35%; N, 7.93%. ATR-IR (neat, cm^{-1}): 1604, 1557, 1512, 1335, 1244, 1150, 1050, 1022, 1009, 772, 739, 703, 633, 591, 416. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 – 8.96 (m, 1H), 8.44 (d, J = 9.4 Hz, 1H), 8.32 (d, J = 8.1 Hz, 1H), 8.27 ($CHCl_3$), 8.19 (t, J = 8.4 Hz, 1H), 7.79 (dd, J = 5.8, 3.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.63 (dd, J = 6.0, 3.3 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.49 (q, J = 7.1, 6.0 Hz, 2H), 7.11 (s, 1H), 5.72 (CH_2Cl_2). ^{13}C NMR (151 MHz, DMSO-d_6) δ 152.6, 149.2, 140.7, 138.9, 134.1, 133.0, 132.3, 128.3, 128.0, 127.8, 127.2, 127.2, 124.9, 123.7, 122.6, 120.3, 117.2, 116.8, 79.2 ($CHCl_3$), 54.9 (CH_2Cl_2). UV- Vis: nm (M^{-1} cm^{-1}) 268 (9973), 361 (10597), 378 (12333), 396 (8703). HRMS(ESI) *m/z* calcd for [**1b**-Cl]$^+$ 491.8923; found 491.8925.

[Pt(**L1**)Cl_2] (**1c**)

Complex [Pt(**L1**)Cl_2] (**1c**) was prepared using ligand **L1** (35 mg, 0.1 mmol) and $PtCl_2(DMSO)_2$ (42 mg, 0.1 mmol) in acetonitrile. Yield: (46.5 mg), 76%. Anal. calcd. for $C_{18}H_{12}BrCl_2N_3Pt$: C, 35.09%; H, 1.96%; N, 6.82; found: C, 35.20%; H, 2.04%; N, 6.78%. ATR-IR (neat, cm^{-1}): 1642, 1608, 1561, 1513, 1485, 1428, 1338, 1150, 1024, 957, 769, 739, 704, 694, 638, 430, 416. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 – 9.30 (m, 1H), 8.47 (d, J = 9.4 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 8.26 – 8.20 (m, 1H), 7.83 – 7.79 (m, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.67 (dd, J = 5.8, 3.5 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.47 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 5.72 (CH_2Cl_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.46, 148.16, 140.22, 139.62, 134.34, 133.40, 132.60, 129.67, 128.74, 128.18, 128.09, 127.28, 125.06, 124.13, 122.96, 120.28, 116.91, 116.84, 55.08 (CH_2Cl_2), 48.87 (MeOH). UV- Vis: nm (M^{-1} cm^{-1}) 310 (10042), 365 (10498), 383 (10466), 406 (8391). HRMS (ESI): *m/z* calcd for [**1c**+H]$^+$ 579.9524; found 579.9492.

[Cu(**L1**)$_2$Cl]Cl (**1d**)

Copper chloride hexahydrate (60.5 mg, 0.25 mmol) and **L1** (175 mg, 0.5 mmol) were taken in 10 mL ethanol and stirred at 80 °C for 12 hours. The dark blue color solution was left undisturbed for few days to produce crystals of **1d**. Yield: (175 mg), 84%. Anal. calcd. for $[C_{36}H_{24}N_6Br_2CuCl]Cl$: C, 51.79%; H, 2.90%; N, 10.07; found: C, 51.87%; H, 2.94%; N,

10.00%. ATR-IR (neat, cm^{-1}): 1722, 1644, 1602, 1532, 1451, 1239, 1198, 1089, 975, 899, 744, 476, 453, 420. UV- Vis: nm (M^{-1} cm^{-1}) 281 (18100), 360 (25000), 373 (28700), 390 (19980). HRMS (ESI) *m/z* calcd for [**1d**-Cl]$^+$ 797.9390; found 797.9355.

[Cu(**L1**)$_2$Br]Br (**1e**)

Copper bromide (56 mg, 0.25 mmol) and **L1** (175 mg, 0.5 mmol) were taken in 10 mL ethanol and stirred at 80 °C for 12 hours. The light blue color solution was left undisturbed for few days to produce crystals of **1d**. Yield: (166 mg), 72%. Anal. calcd. for [$C_{36}H_{28}N_6Br_3Cu$]Br: C, 46.81%; H, 2.62%; N, 9.10; found: C, 46.92%; H, 2.65%; N, 9.02%. ATR-IR (neat, cm^{-1}): 3418, 1608, 1551, 1530, 1511, 1481, 1440, 1362, 1333, 1249, 1153, 1055, 1011, 784, 743, 702, 652, 594, 423, 412. UV- Vis: nm (M^{-1} cm^{-1}) 309 (19750), 360 (27900), 373 (3200), 390 (21930). HRMS (ESI) *m/z* calcd for [**1e**-Br]$^+$ 843.8868; found 843.8808.

[Ni(**L2**)$_2$(H_2O)$_2$] (**2a**)

Ligand **L2H** (131 mg, 0.5 mmol) was taken in 5.0 mL methanol and stirred under reflux. Nickel chloride hexahydrate (60 mg, 0.25 mmol) in 5.0 mL methanol was added to it followed by few drops of triethylamine. The mixture and was refluxed for 12h, cooled to produce brown precipitate which was then filtered, washed with ether, and dried over fused $CaCl_2$ to produce pure nickel complex **2a**. Yield: (114 mg), 74%. Anal. calcd. for $C_{32}H_{22}N_4NiO_6$: C, 62.27%; H, 3.59%; N, 9.08; found: C, 62.34%; H, 3.61%; N, 8.90. ATR-IR (neat, cm^{-1}): 3281, 1658, 1602, 1446, 1189, 1089, 972, 739, 471, 451. ^{1}H NMR (600 MHz, DMSO-d_6) δ 14.65 (s, 2H), 8.28 (d, J = 6.0 Hz, 3H), 7.65 (s, 4H), 7.47 (s, 4H), 7.43 – 7.34 (m, 4H), 7.27 (s, 2H), 6.97 (s, 3H), 5.22 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.2, 151.6, 131.9, 129.6, 124.3, 122.7, 121.3, 116.1, 113.5, 104.2. UV- Vis: nm (M^{-1} cm^{-1}) 318 (10385), 335 (11425), 361 (14310), 507 (256). HRMS (ESI) *m/z* calcd for (**2a**–2H_2O+H)$^+$ 581.0754; found 581.0754.

[Pd(**L2**)$_2$] (**2b**)

Solid palladium dichloride (44.5 mg, 0.25 mmol) was taken in 10 mL acetonitrile and was refluxed till all palladium dissolved. To the light-yellow color hot solution, Solid **L2H** (131 mg, 0.5 mmol) was added followed by few drops of triethylamine. The resulting deep red color solution were left with continuous stirring for 16 h at ambient temperature. The precipitates formed were separated by filtration, washed with diethyl ether, and dried in vacuo to afford the complex **2b**. Yield: (99 mg), 63%. Anal. calcd. for $C_{32}H_{18}N_4PdO_4$: C, 61.11%; H, 2.88%; N, 8.91; found: C, 61.20%; H, 2.91%; N, 8.82. ATR-IR (neat, cm^{-1}): 1702, 1605, 1539, 1450, 1189, 1085, 955, 743, 447, 422. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (d, J = 6.3 Hz, 2H),

8.54 – 8.49 (m, 2H), 8.04 (d, J = 8.2 Hz, 2H), 7.89 (td, J = 7.8, 1.8 Hz, 2H), 7.64 (s, 2H), 7.46 (dd, J = 11.7, 1.3 Hz, 4H), 7.39 – 7.33 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.22, 151.65, 149.25, 149.15, 137.40, 136.76, 136.67, 129.30, 124.34, 122.65, 120.01, 116.98, 113.71, 113.51, 109.72, 106.43. UV- Vis: nm (M^{-1} cm^{-1}) 294 (8212), 325 (9240), 341 (9282), 352 (7945), 440 (826). HRMS (ESI) *m/z* calcd for (**2b**+H)$^+$ 629.0448; found 629.0405.

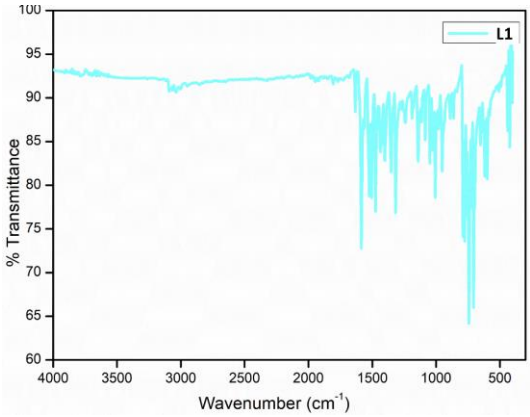
[Pt(**L2**)$_2$] (**2c**)

Cis-dichlorobis(dimethylsulfoxide)platinum(II) (21 mg, 0.05 mmol) and **L2H** (26.4 mg, 0.1 mmol) was mixed in 10 mL acetonitrile along with few drops of triethylamine. The mixture was refluxed with continuous stirring for 24 h. The yellow precipitates formed were separated by filtration, washed with diethyl ether, and dried in vacuo to produce the platinum complex **2c**. Yield: (25.5 mg), 71%. Anal. calcd. for $C_{32}H_{18}N_4PtO_4$: C, 53.56%; H, 2.53%; N, 7.81; found: C, 53.62%; H, 2.50%; N, 7.72. ATR-IR (neat, cm^{-1}): 1702, 1611, 1546, 1454, 1191, 1089, 958, 746, 733, 449, 430. UV- Vis: nm (M^{-1} cm^{-1}) 265 (29804), 292 (25854), 319 (25751), 395 (15429). HRMS (ESI) *m/z* calculated for (**2c**+H)$^+$ 718.1051; found 718.1022.

[Cu(**L2**)$_2$]$_n$ (**2d**)

L2H (131 mg, 0.5 mmol) and copper chloride hexahydrate (60.5 mg, 0.25 mmol) were taken in 10.0 mL methanol along with few drops of triethylamine. The mixture was refluxed with continuous stirring for 12 h. The dark blue precipitates formed were separated by filtration, washed with cold methanol, and dried in vacuo to produce the copper coordination polymer **2d**. Yield (based on monomeric molar mass): (118.5 mg), 81%. Anal. calcd. for monomeric unit $C_{32}H_{18}N_4CuO_4$: C, 65.58%; H, 3.10%; N, 9.56; found: C, 65.67%; H, 3.14%; N, 9.51. ATR-IR (neat, cm^{-1}): 3445, 3335, 1719, 1644, 1601, 1532, 1451, 1198, 1090, 975, 899, 744, 642, 580, 449, 420. UV- Vis: nm (M^{-1} cm^{-1}) 275 (18850), 292 (1680), 317 (20830), 332 (21400), 360 (29260). HRMS (ESI) *m/z* calculated for (Cu(**L2**)$_2$+H)$^+$ 586.0697; found 586.0670 and for (Cu(**L2**)$_2$**L2H**+H)$^+$ 848.1397; found 848.1439.

ATR-IR, NMR, HRMS(ESI) Spectra and FESEM images of all compounds: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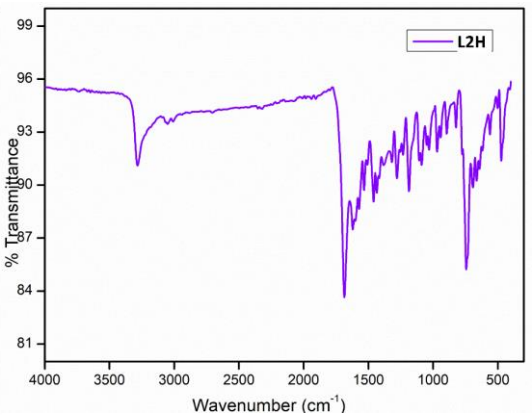
Wavenumber (cm-1)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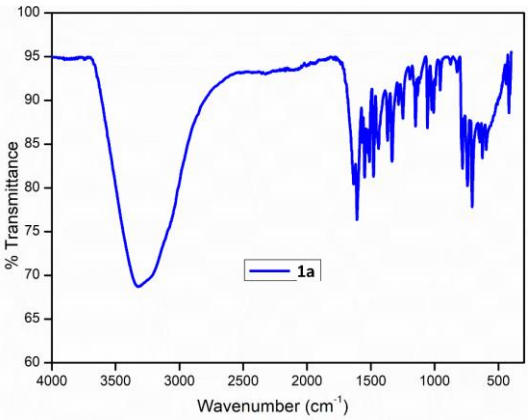
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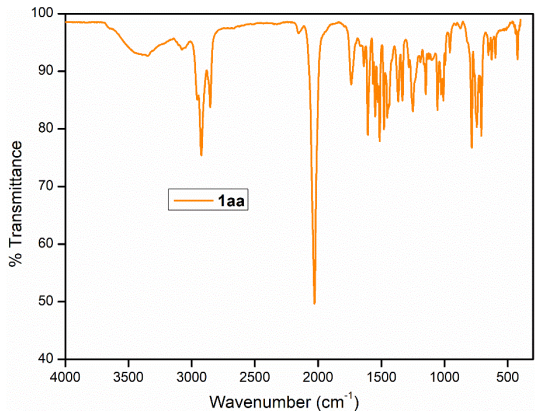
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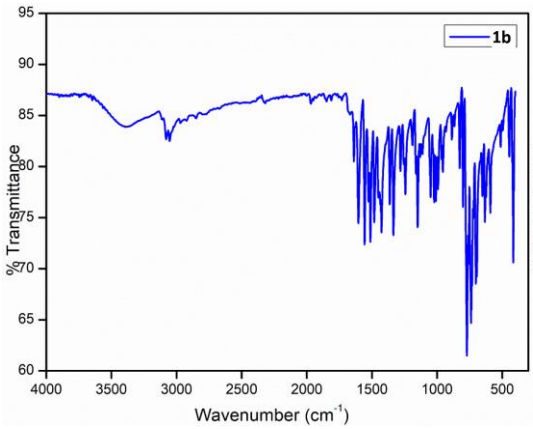
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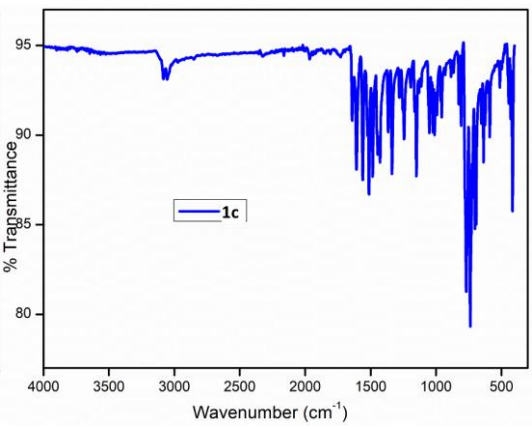
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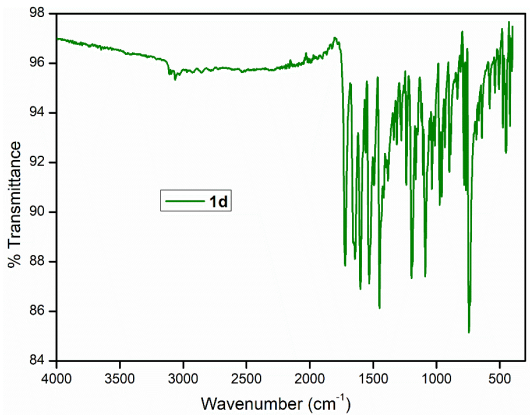
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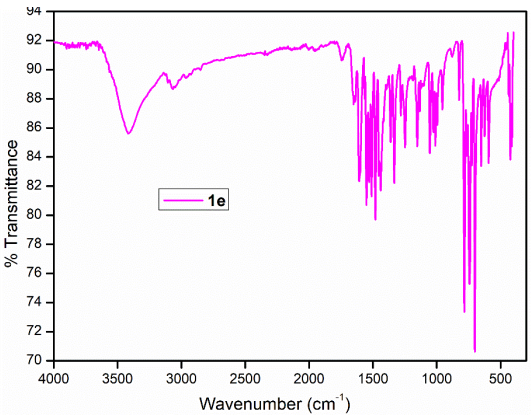
Wavenumber (cm-1)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Wavenumber (cm-1)

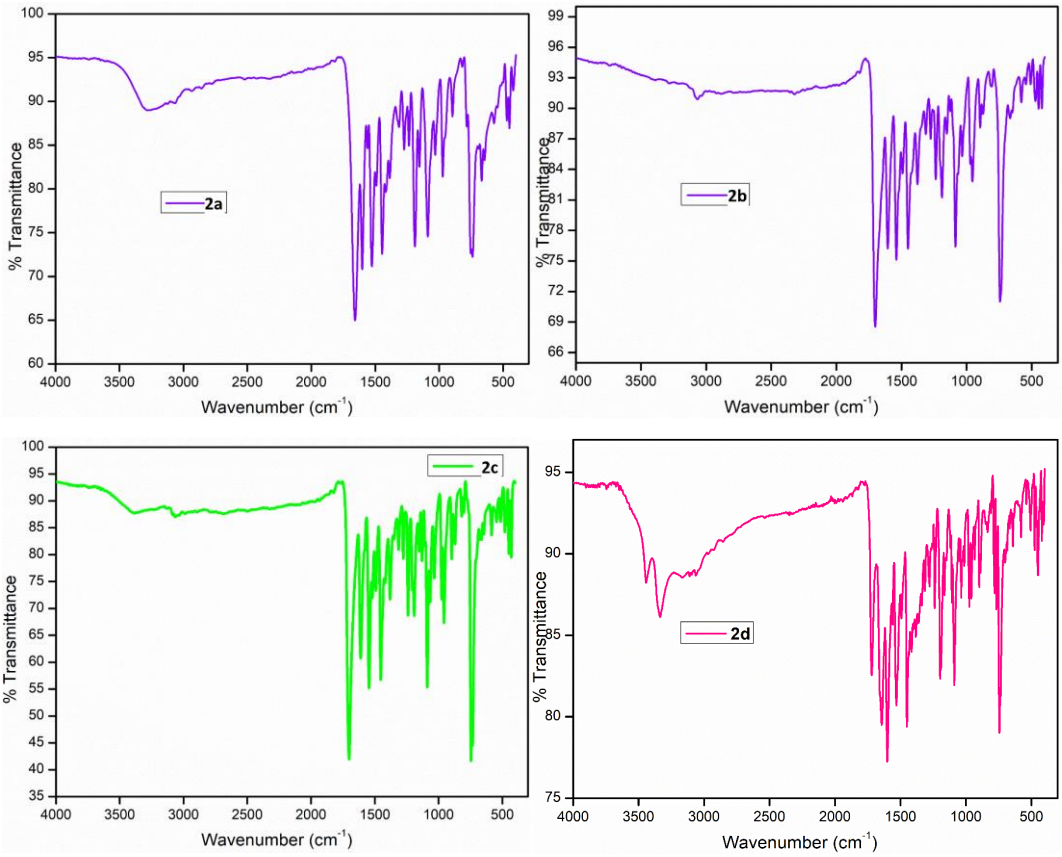
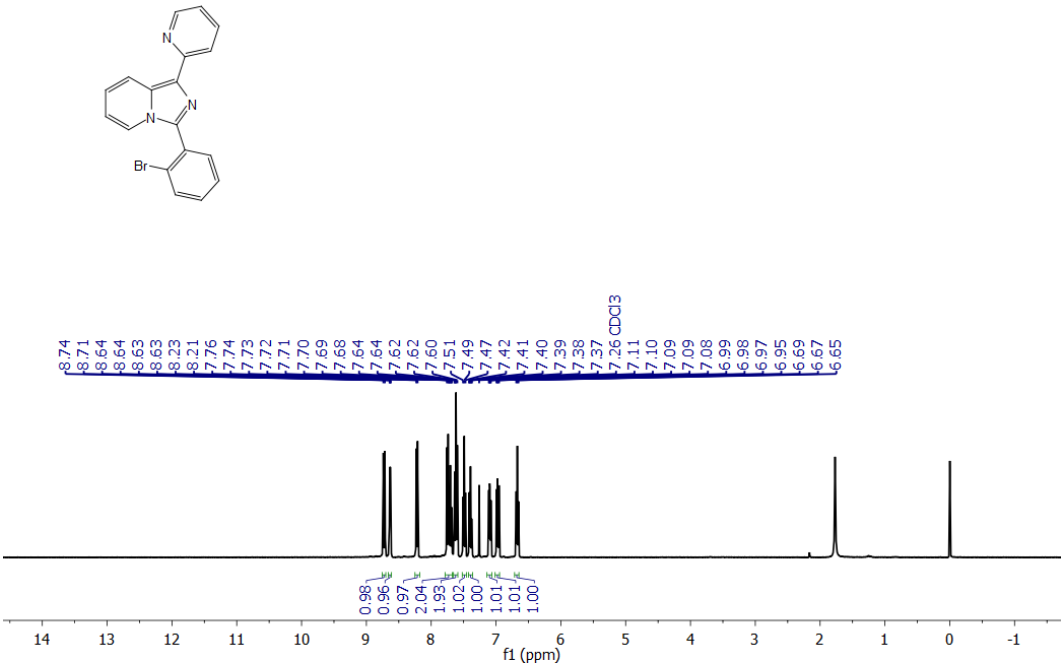


Figure S1: ATR-IR spectra of all ligands and complexes



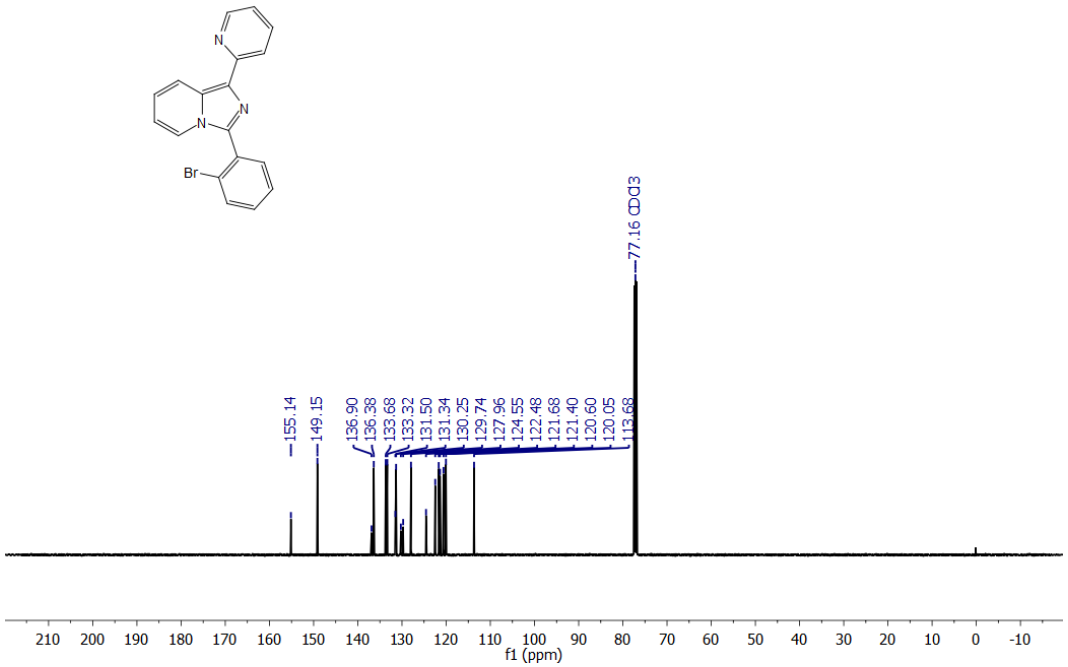
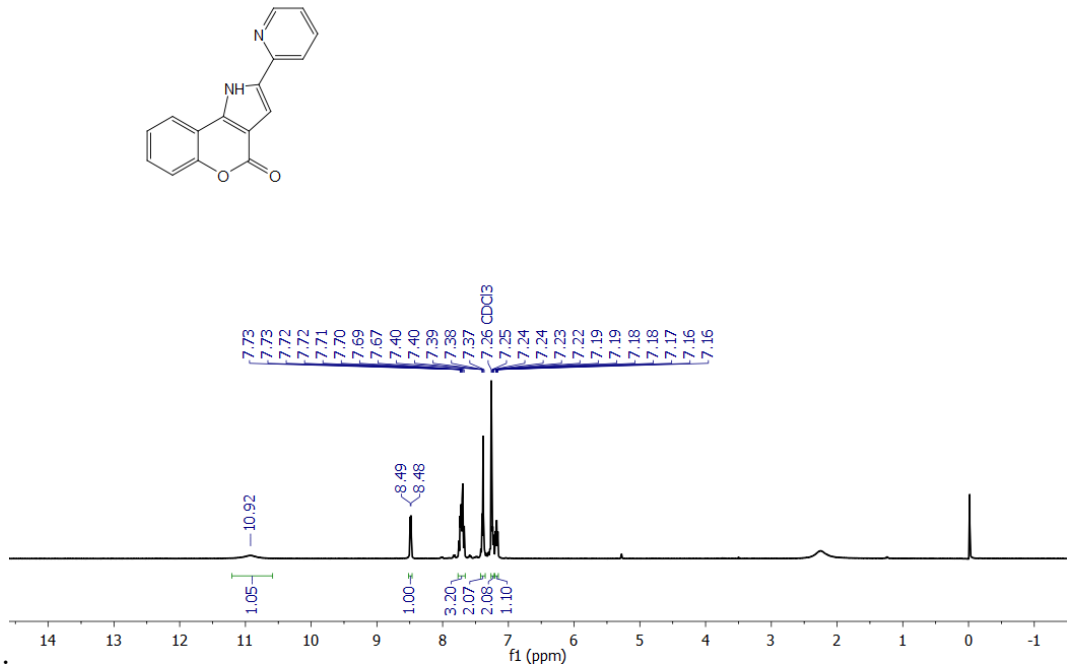


Figure S2A: ^{1}H and ^{13}C NMR spectra of **L1**



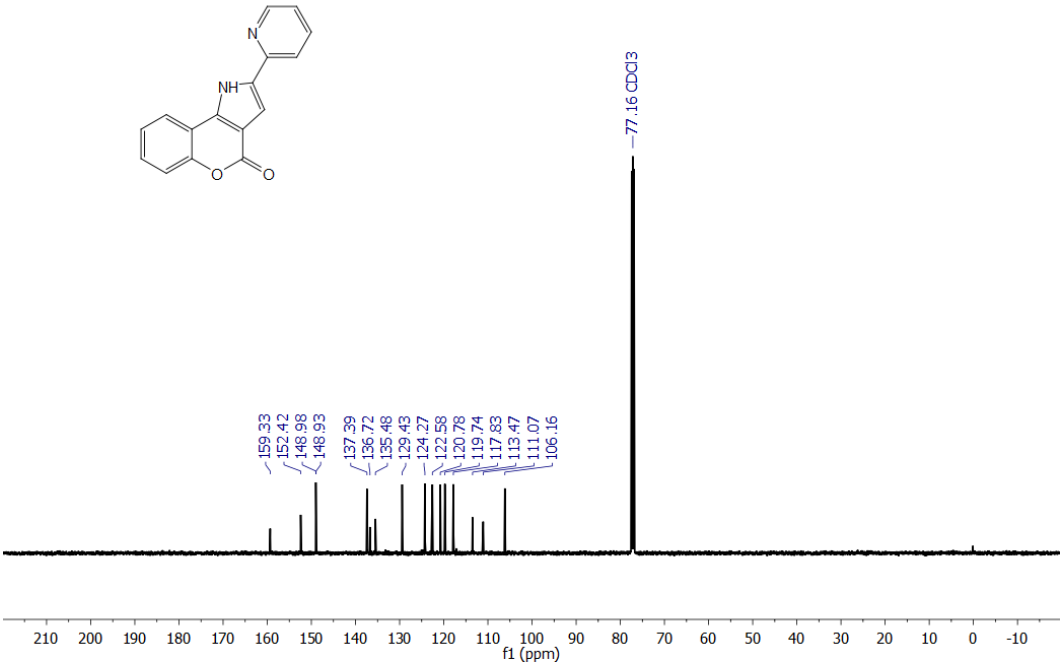
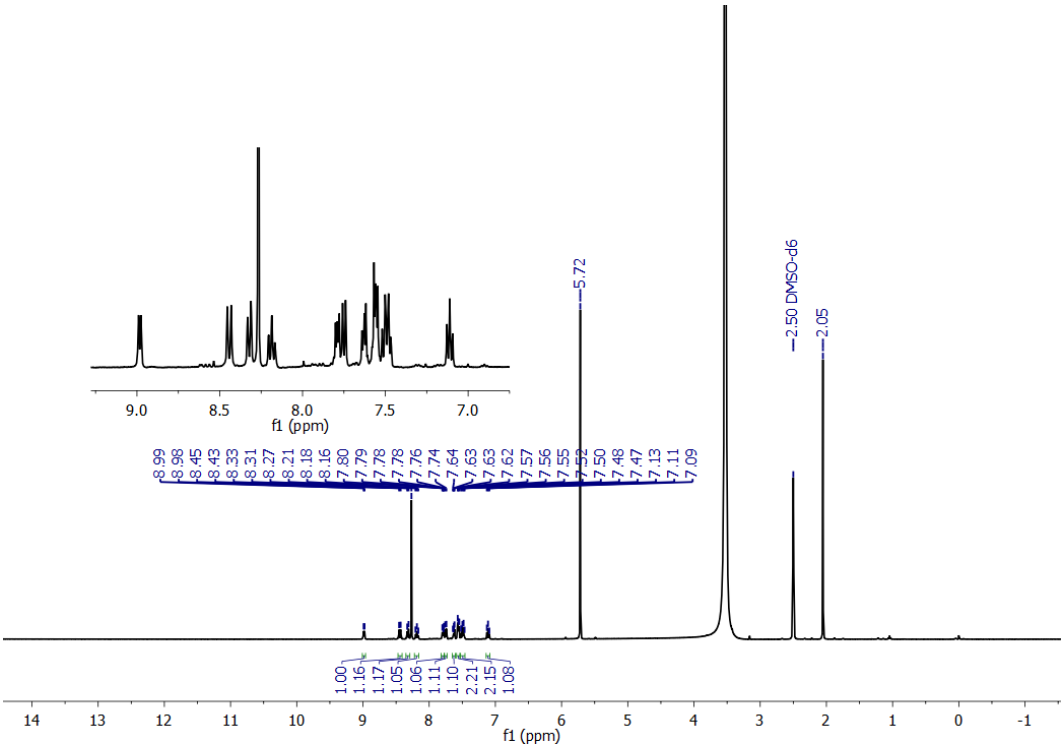


Figure S2B: ^{1}H and ^{13}C NMR spectra of **L2H**



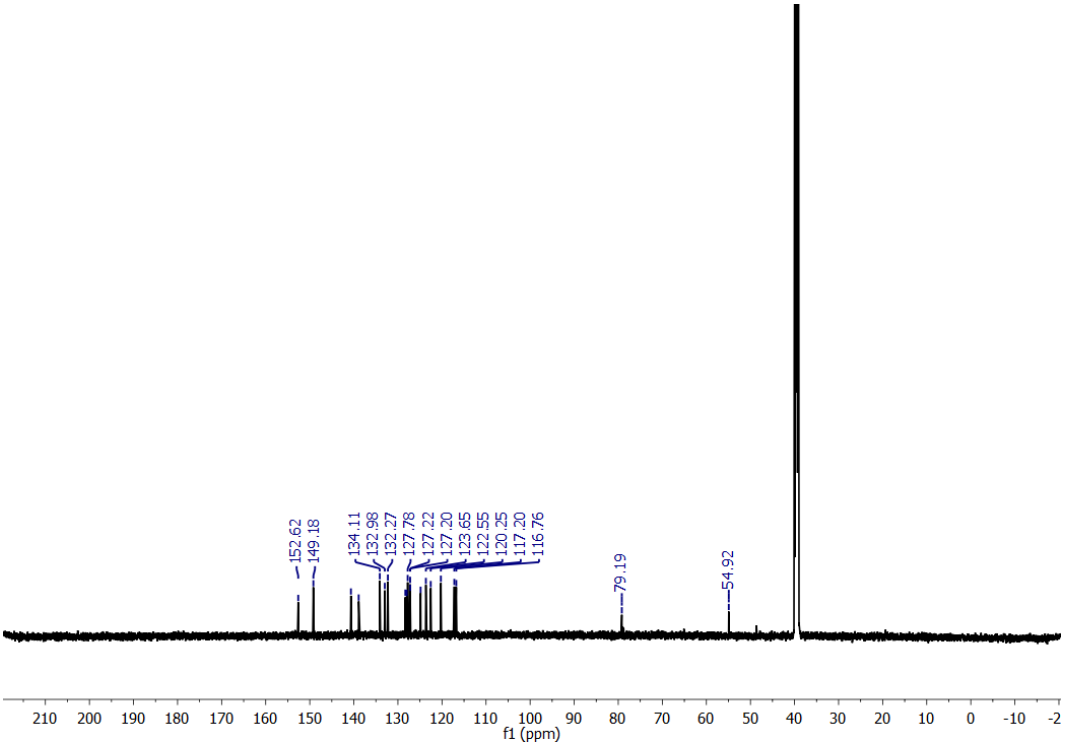
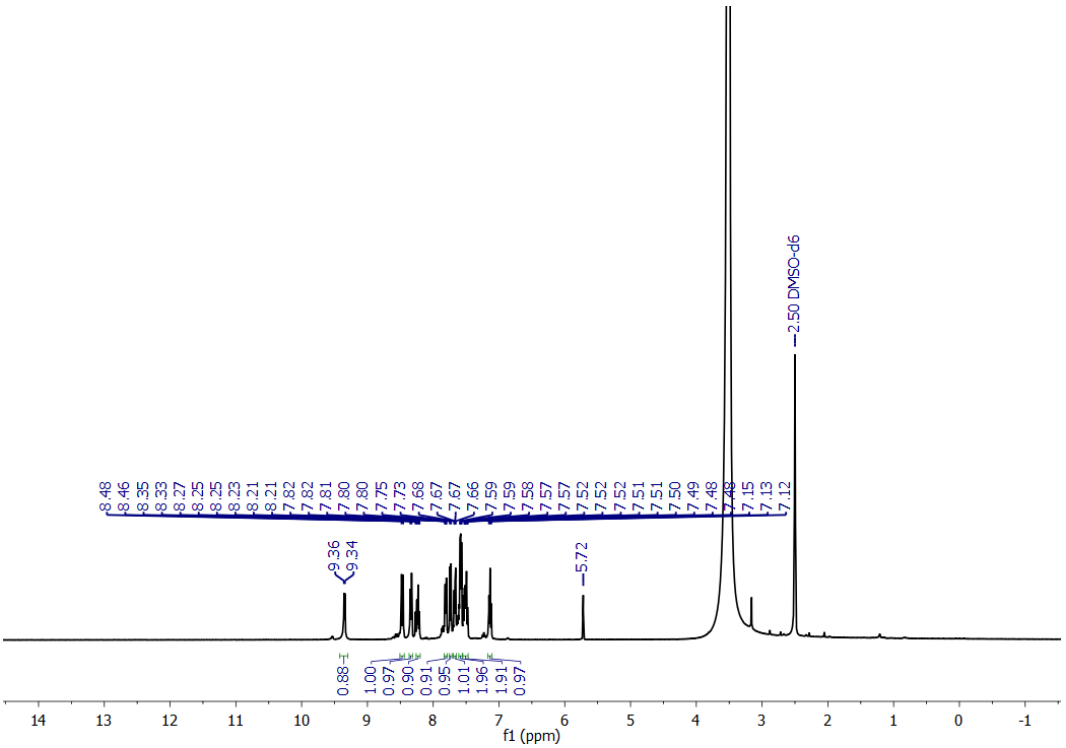


Figure S2C: ^{1}H, and ^{13}C NMR spectra of **1b**



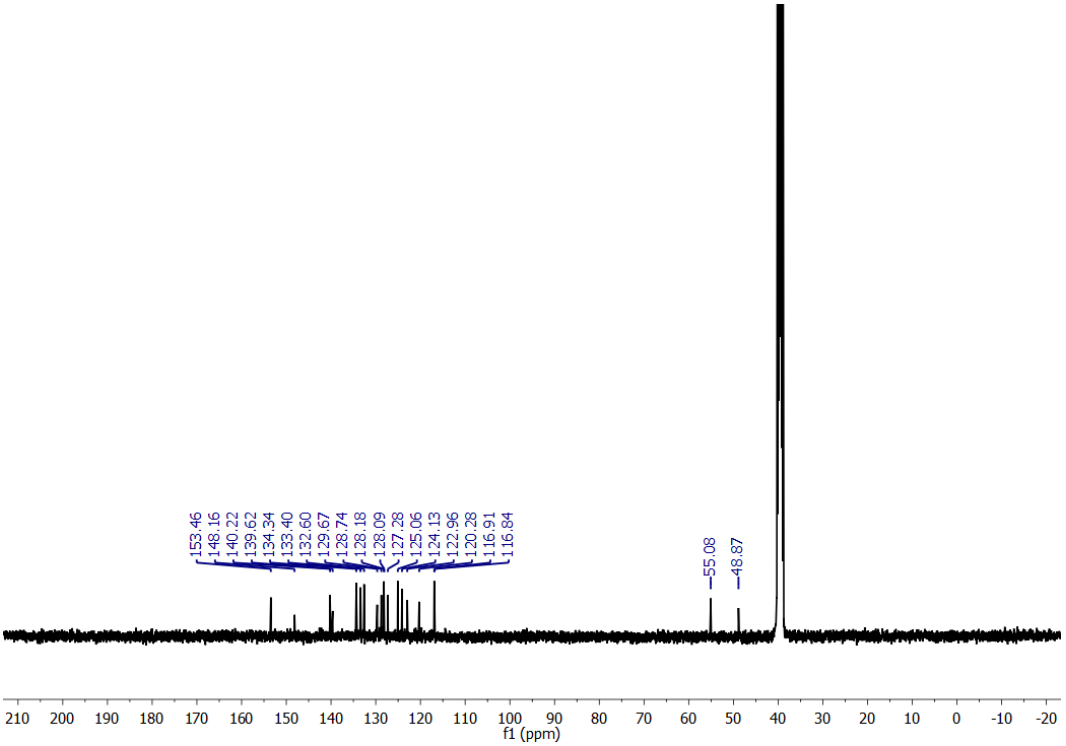
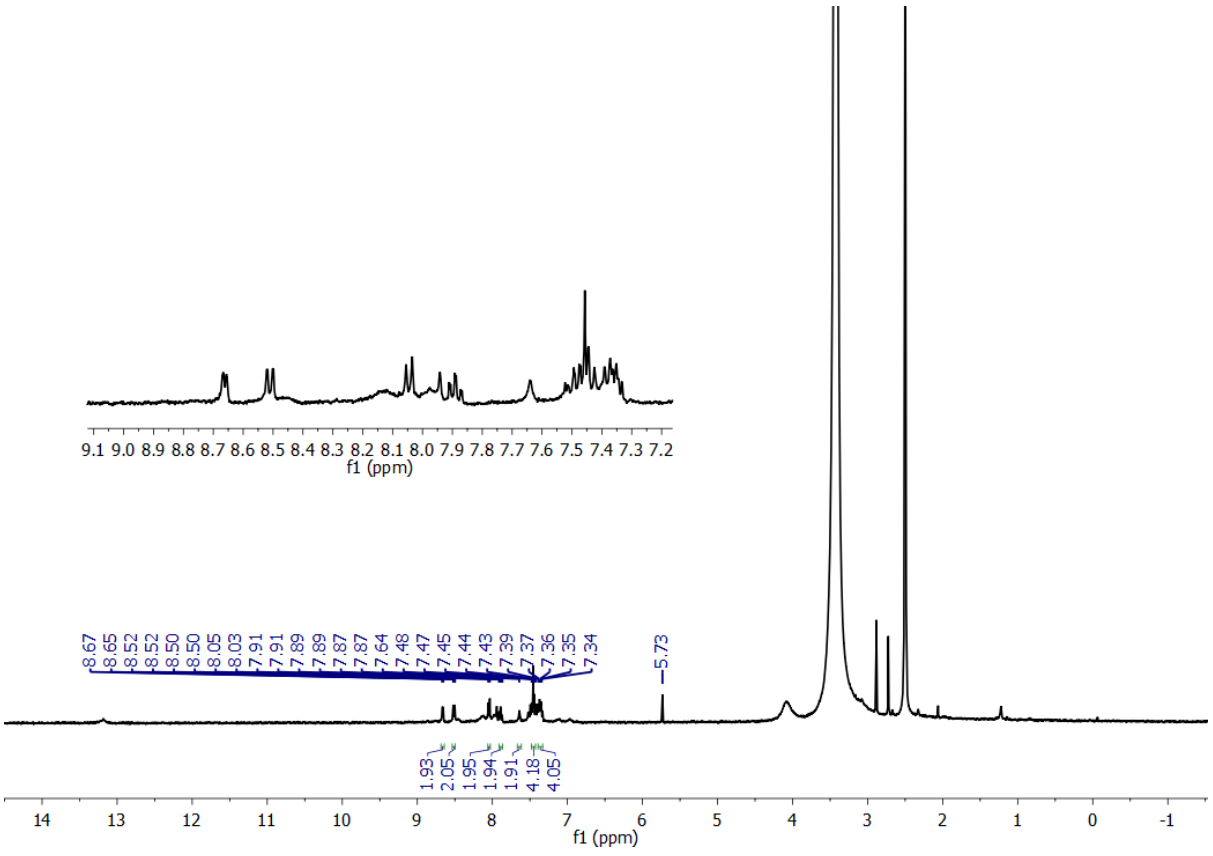


Figure S2D: ^{1}H, and ^{13}C NMR spectra of **1c**



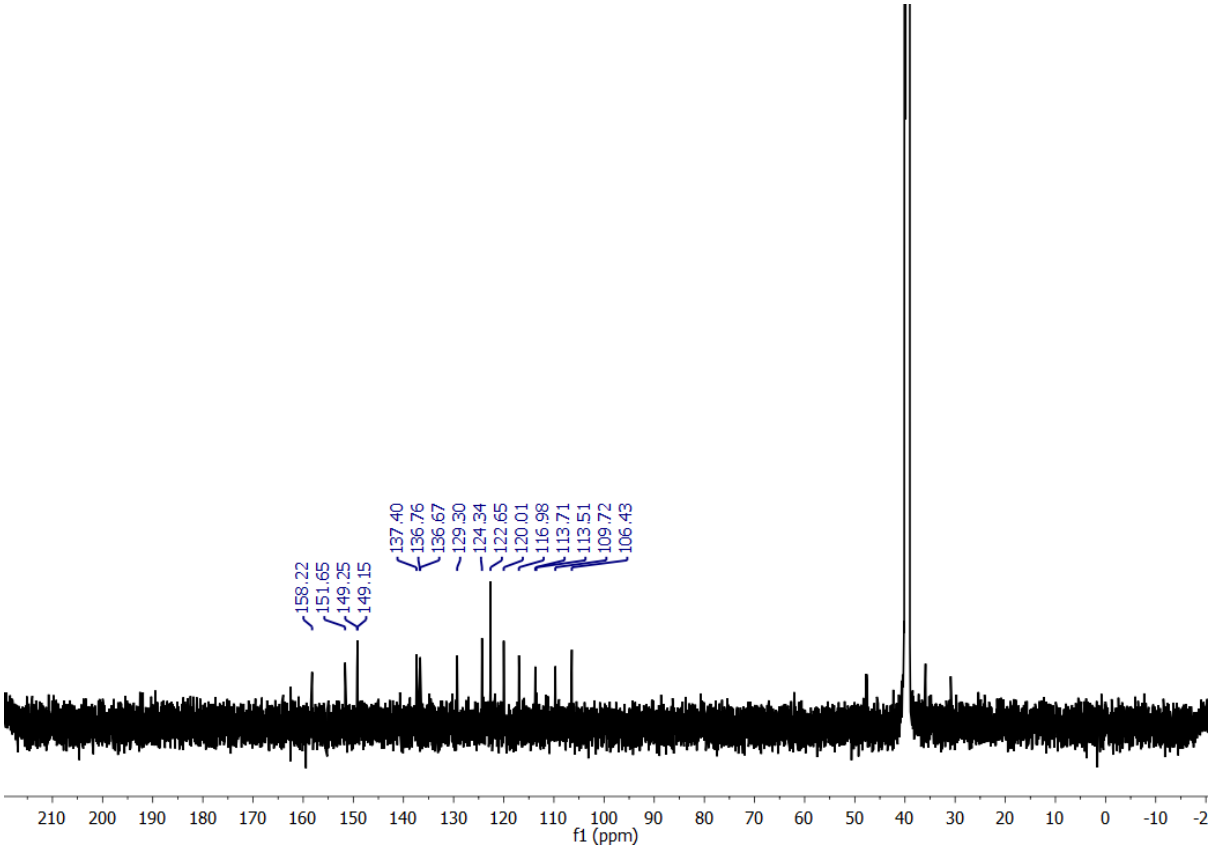
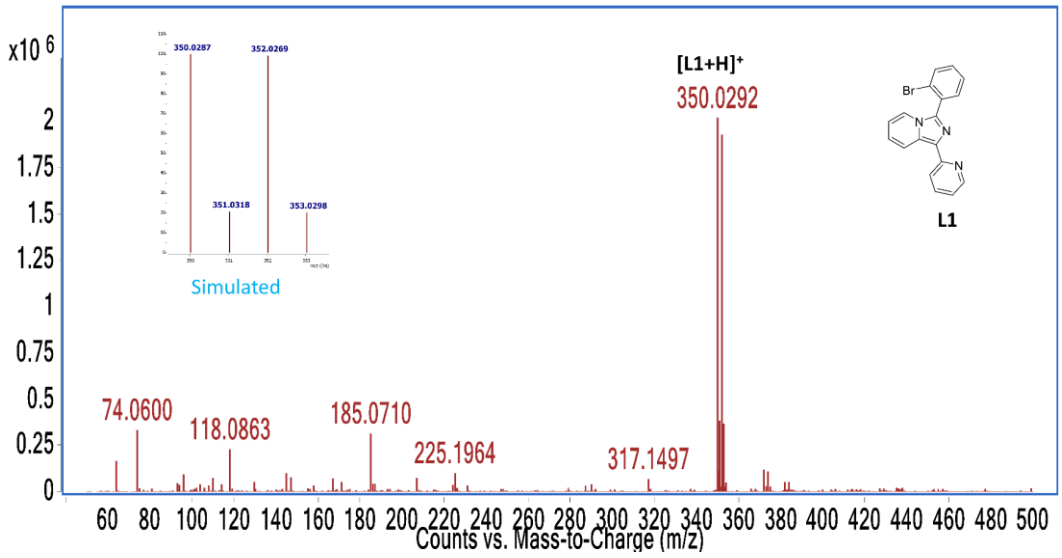


Figure S2E: ^{1}H, and ^{13}C NMR spectra of **2b**



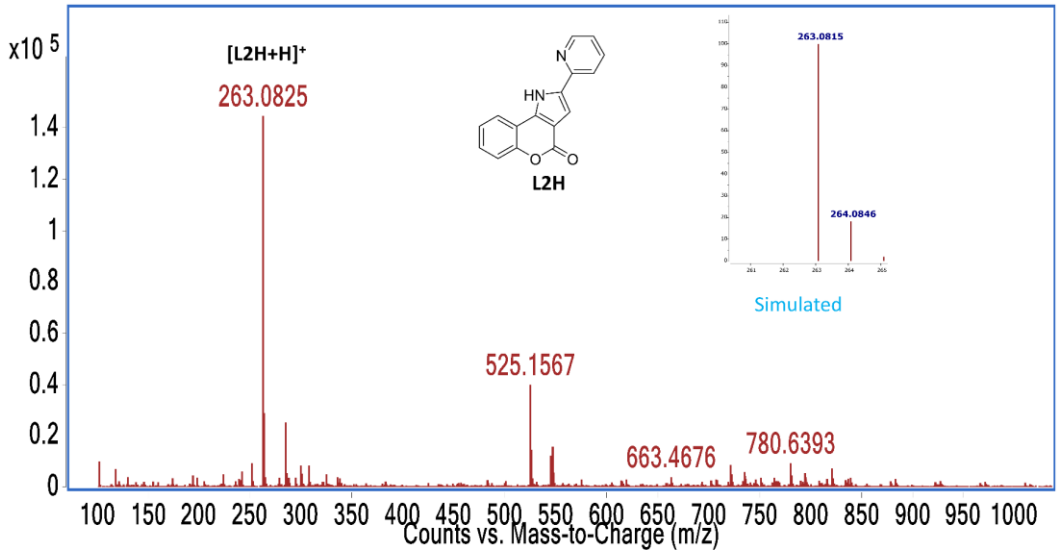
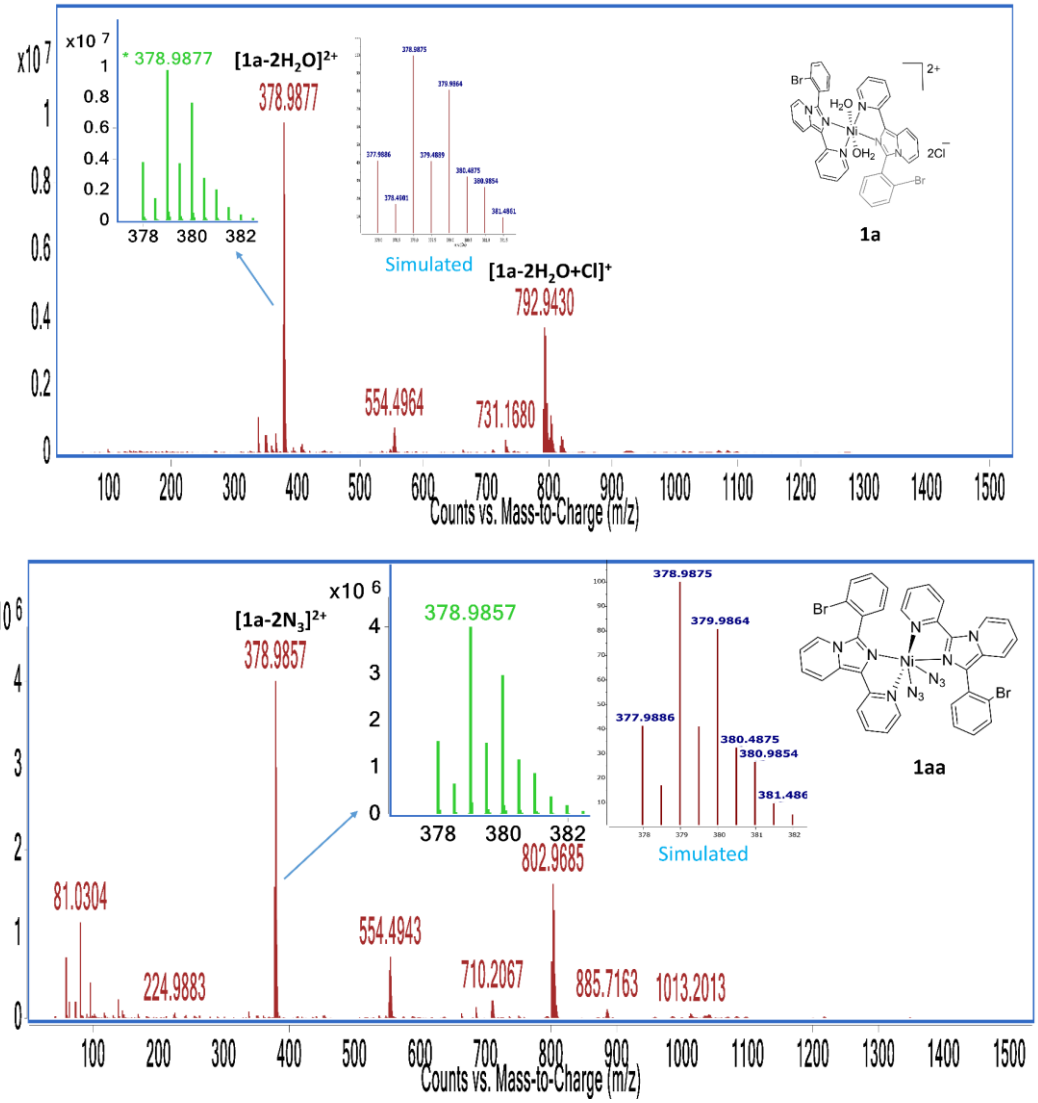
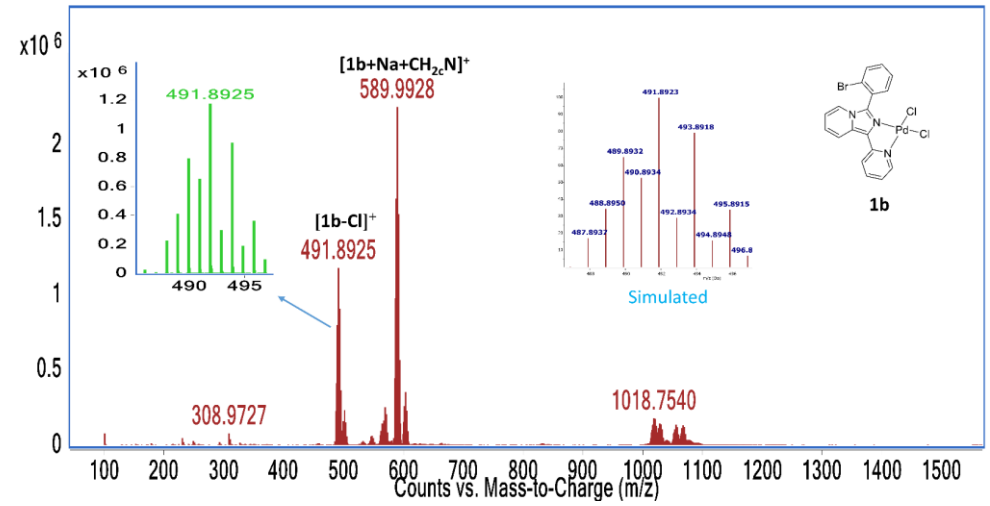
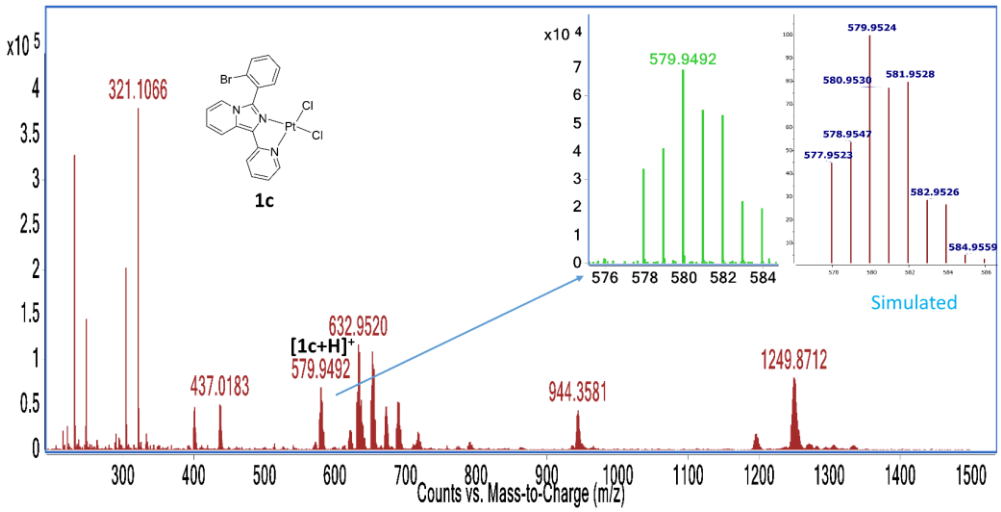
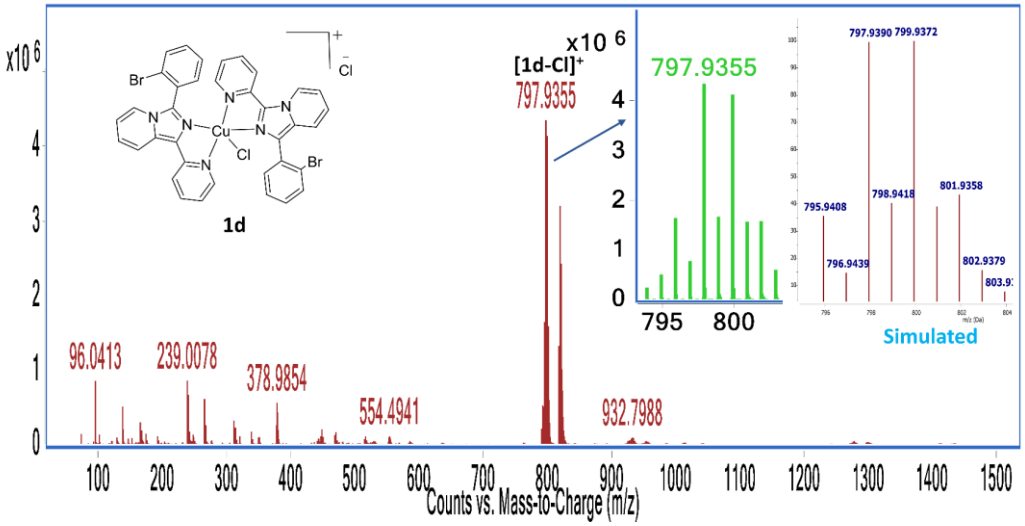


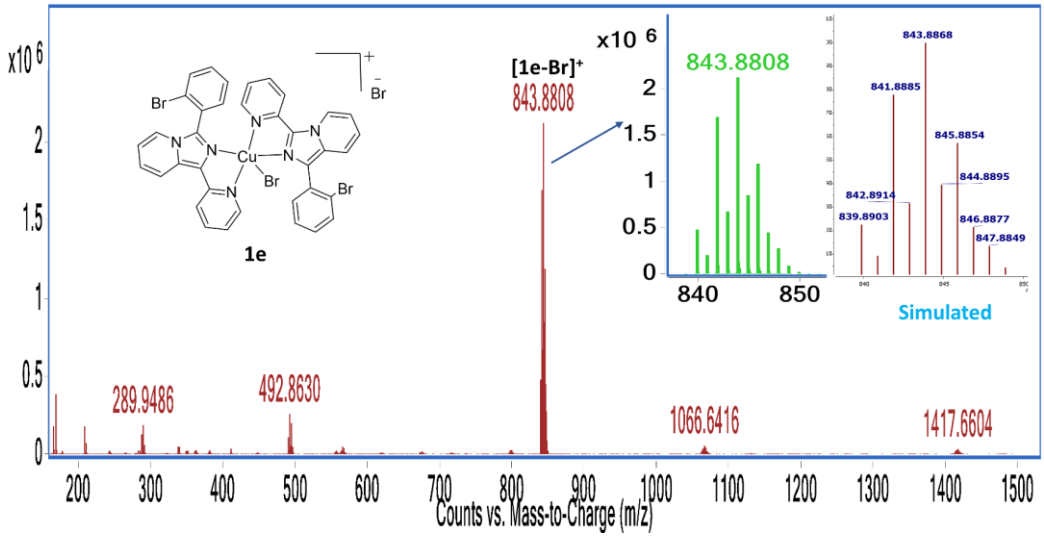
Figure S3A: HRMS spectra of **L1** and **L2H**. Inset simulated spectra.

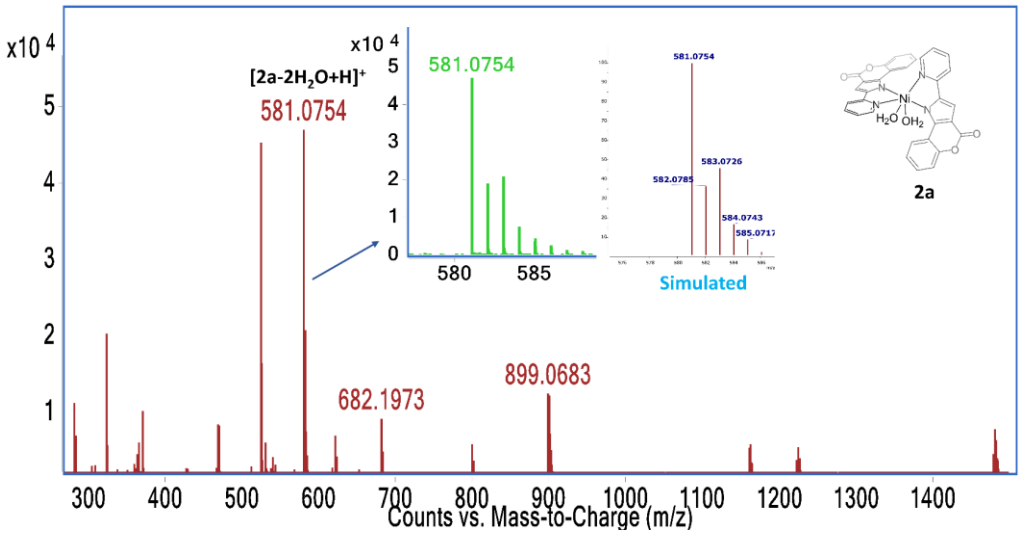


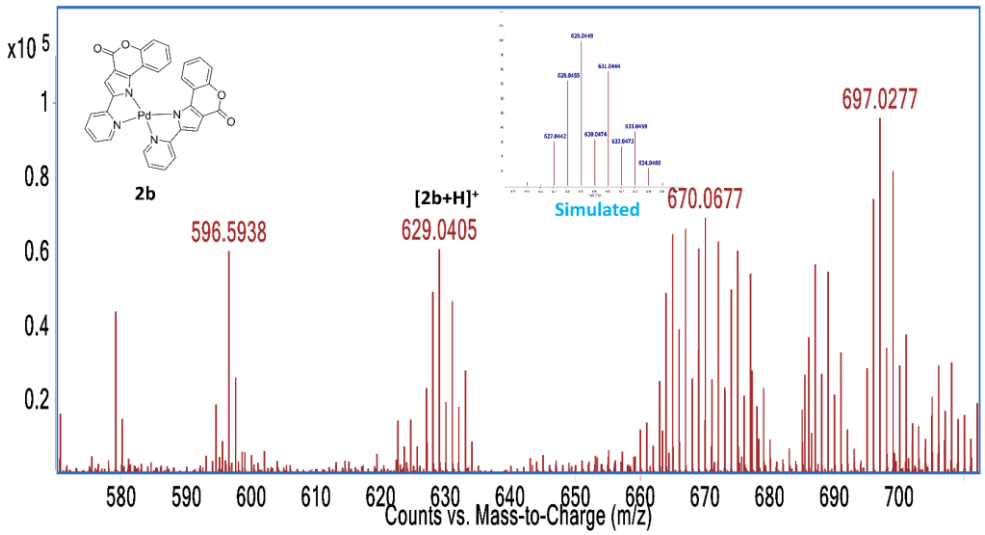

x10 6
[1b+Na+CH2cN]+
589.9928
491.8925
[1b-Cl]+
491.8925
308.9727
1018.7540
Simulated
1b
Counts vs. Mass-to-Charge (m/z)


x10 5
321.1066
1c
579.9492
632.9520
[1c+H]+
579.9492
437.0183
944.3581
1249.8712
Simulated
Counts vs. Mass-to-Charge (m/z)


x10 6
1d
[1d-Cl]+
797.9355
797.9355
96.0413
239.0078
378.9854
554.4941
932.7988
Simulated
Counts vs. Mass-to-Charge (m/z)


x10 6
2
1.5
1
0.5
0
Br
Br
Br
Cu
N
1e
[1e-Br]+
843.8808
289.9486
492.8630
1066.6416
1417.6604
x10 6
843.8808
840
850
843.8868
841.8885
845.8854
844.8895
842.8914
839.8903
846.8877
847.8849
Simulated
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Counts vs. Mass-to-Charge (m/z)


x10 4
5
4
3
2
1
[2a-2H2O+H]+
581.0754
682.1973
899.0683
x10 4
581.0754
580
585
581.0754
583.0726
582.0785
584.0743
585.0717
Simulated
Ni
H2O
OH2
2a
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
Counts vs. Mass-to-Charge (m/z)


x10 5
1
0.8
0.6
0.4
0.2
Pd
2b
[2b+H]+
596.5938
629.0405
670.0677
697.0277
Simulated
580
590
600
610
620
630
640
650
660
670
680
690
700
Counts vs. Mass-to-Charge (m/z)

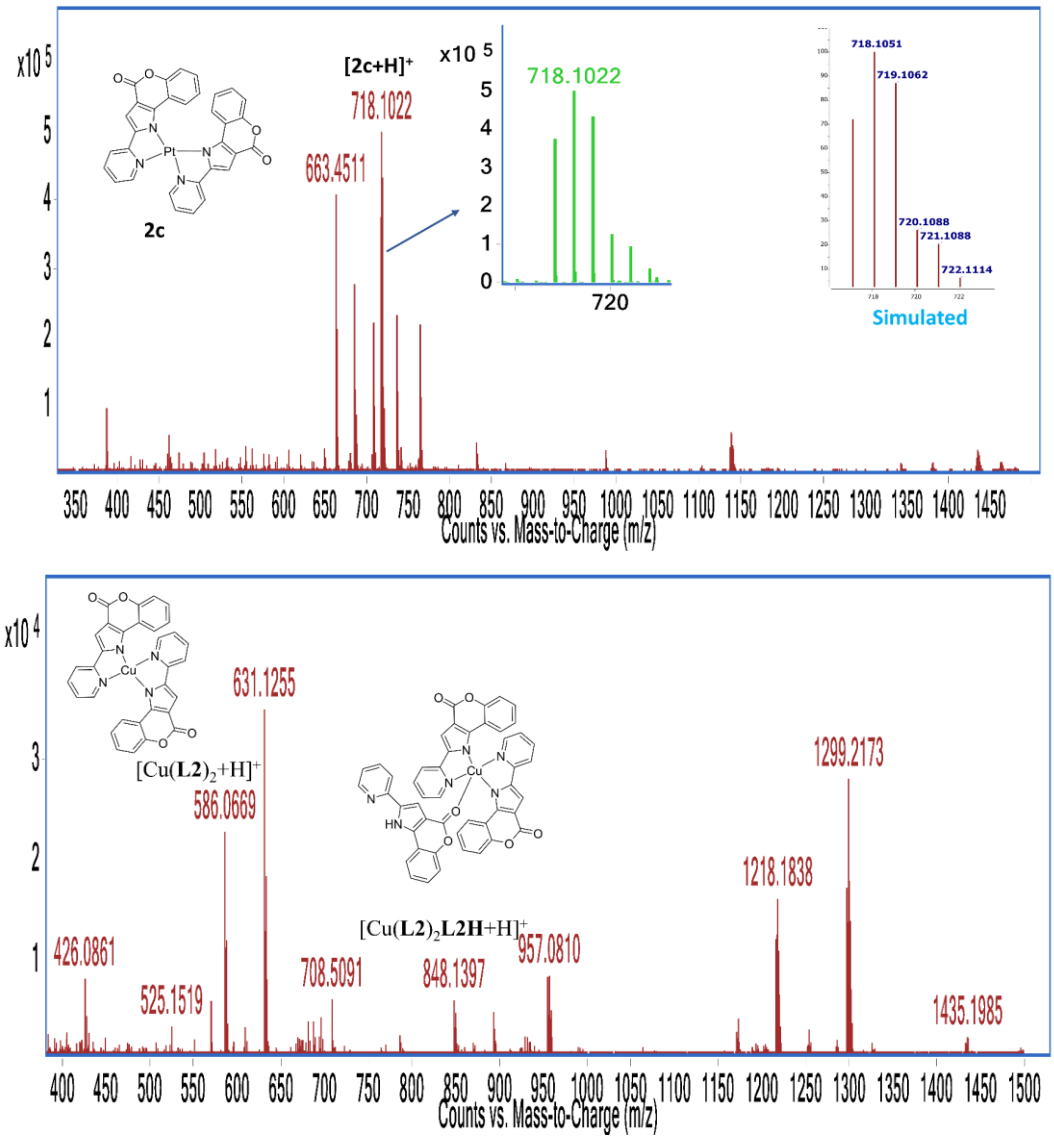
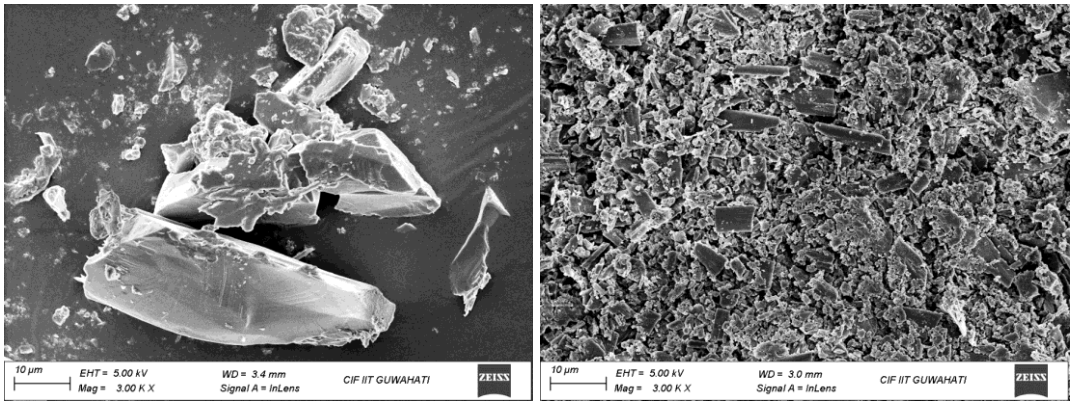
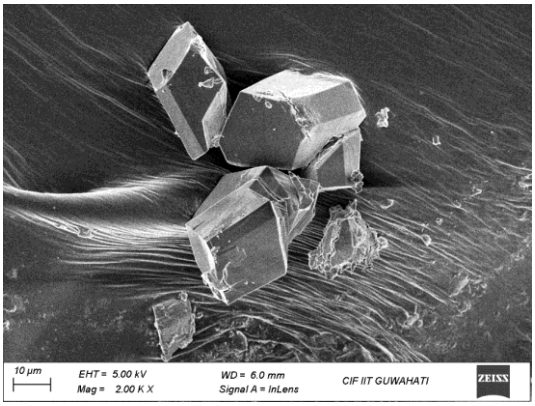


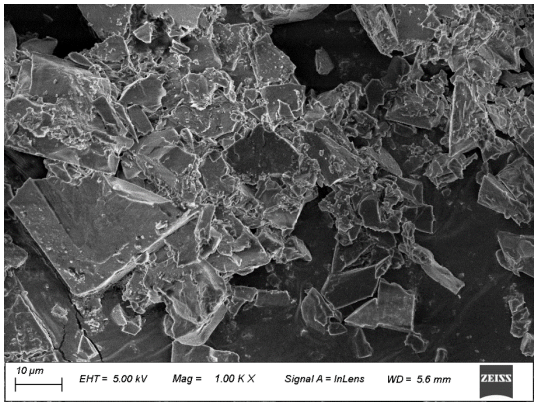
Figure 3B: HRMS spectra of complexes and coordination polymer.



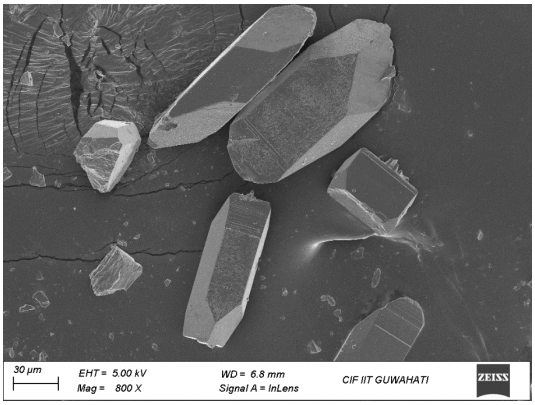
L1 **L2H**



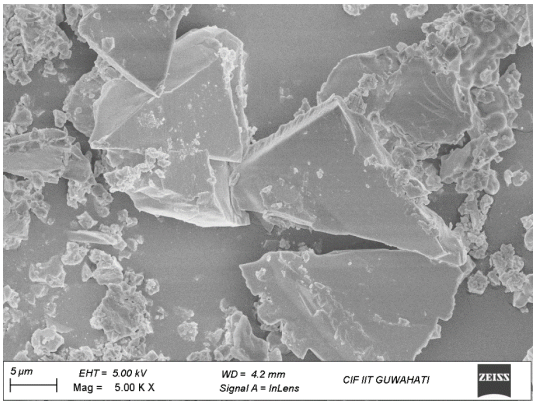
1a



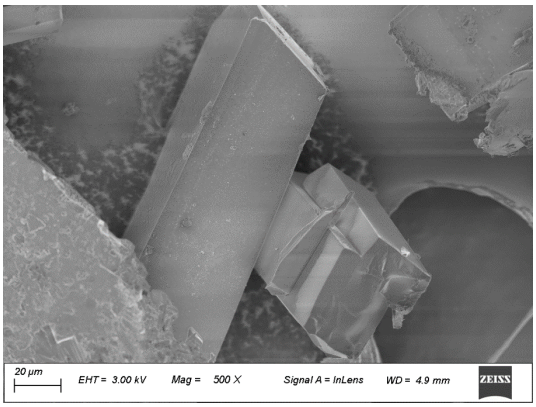
1aa



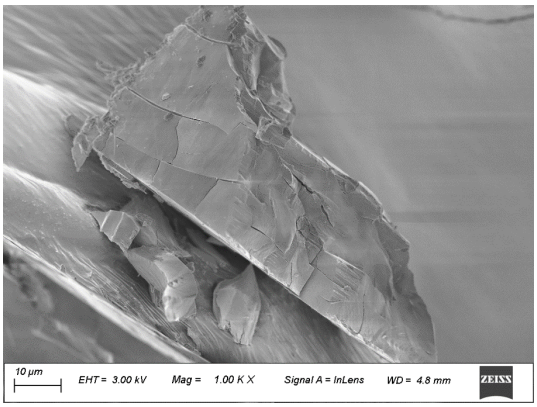
1b



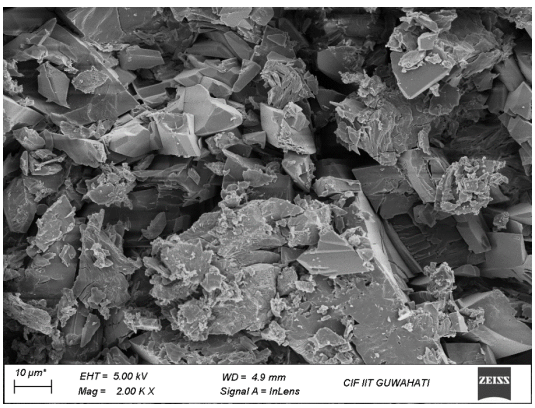
1c

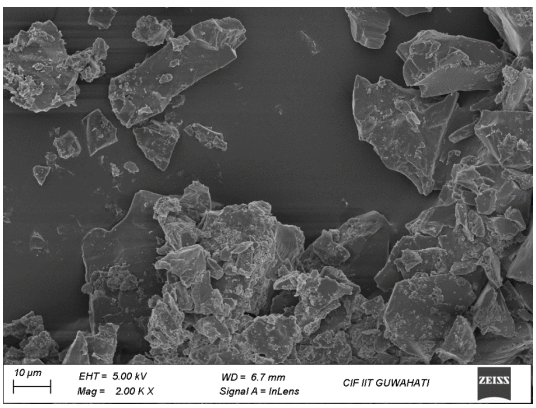


1d

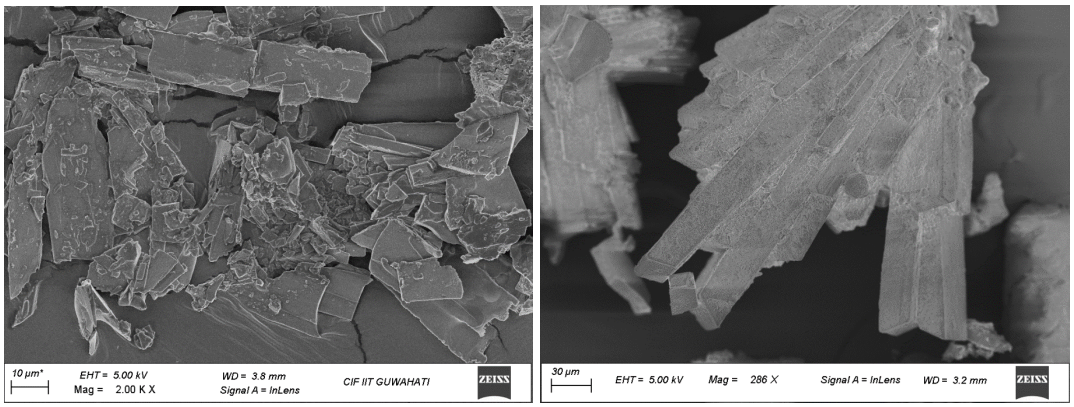


1e





2a **2b**



2c **2d**

Figure S4A: Field Emission Scanning Electron Microscope images of ligands and complexes.

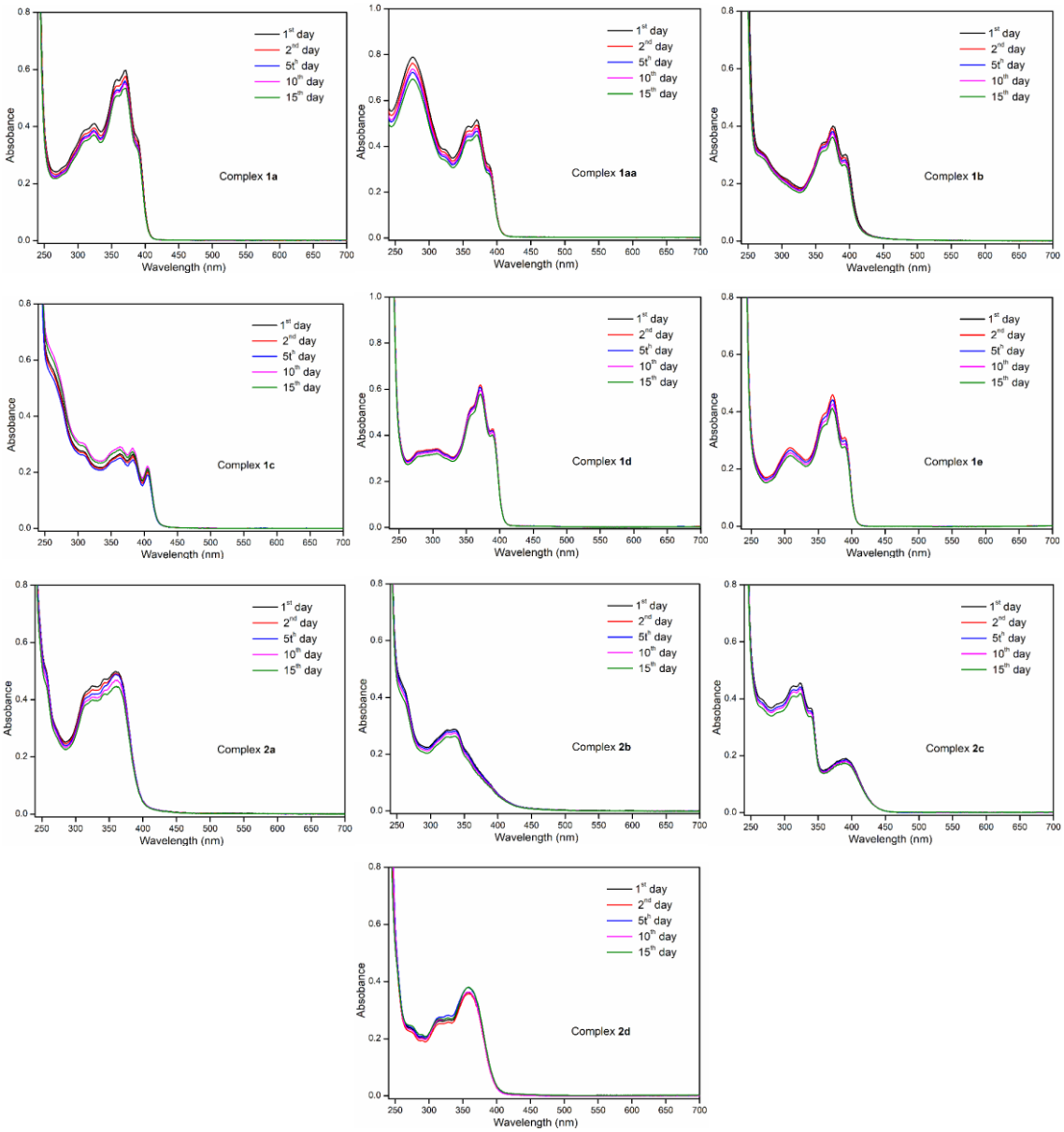
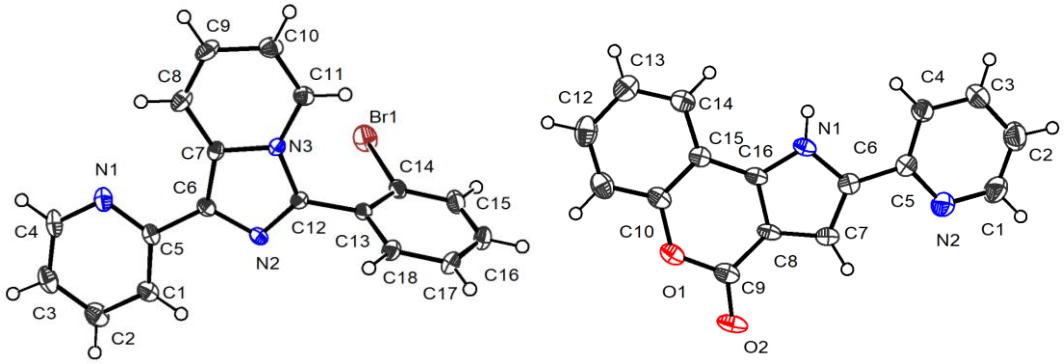


Figure S4B: UV-VIS spectra of all complexes at different time interval.

Crystallographic data, ORTEP diagrams and bond parameters

For the single crystal XRD data collection of the appropriate single crystals of **L1**, **1a**, and **1b**, a single source Super Nova CCD System instrument from Agilent Technologies equipped with a fine focus 1.75 kW sealed tube with Mo-Kα radiation was used at room temperature. The data were reduced using CrysAlisPro and Autochem2.1 software.[4] For rest of the ligand and complexes, data was collected at room temperature using a Bruker SMART APEX CCD diffractometer equipped with fine focus 1.75 kW sealed tube of Mo-Kα (λ = 0.71073 Å) X-ray source, with increasing ω (width of 0.3 ° per frame) at a scan speed of either 3 or 5 s per frame.[5] The SMART software was used for data acquisition and the SAINT software for data extraction. The structure solution and refinement were performed on the Olex2-1.5 using the SHELXT, SHELXL programs.[6,7] All atoms except hydrogen atoms are tuned using anisotropic displacement parameters, whereas hydrogen atoms are tuned using relative isotropic parameters. The disorder in molecular structure of **1a** was fixed using partial occupancies factor, unidentified electron densities were masked using OLEX2 utility.[8] PLATON was used for structure validation and for pictorial depiction linked to X-ray single crystal data, Mercury and ORTEP software was used.[9–11]



L1 **L2H**

Figure S5. ORTEP diagram with 30% ellipsoid probability of ligand (a) **L1H**, (b) **L2H**, (c) **L2H** and (d) **L1** and (3) **L5H**.

Table S1: Crystallographic data and refinement parameters of **L1H**–**L5H**.

Identification code	**L1**	**L2H**
Empirical formula	$C_{18}H_{12}BrN_3$	$C_{16}H_{10}N_2O_2$
Formula weight	350.22	262.26
Temperature/K	293	296.00
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	Pn

a/Å	9.8198(19)	3.8829(5)
b/Å	11.4573(15)	6.2026(7)
c/Å	13.2236(17)	24.973(3)
α/°	90	90
β/°	90	92.208(4)
γ/°	90	90
Volume/Å^3	1487.8(4)	601.00(13)
Z	4	2
ρ_{calc}g/cm^3	1.564	1.449
μ/mm^{-1}	2.762	0.098
F(000)	704.0	272.0
Crystal size/mm^3	0.4 × 0.2 × 0.2	0.08 × 0.05 × 0.02
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.464 to 57.386	6.53 to 51.4
Index ranges	-13 ≤ h ≤ 10, -14 ≤ k ≤ 14, -17 ≤ l ≤ 11	-4 ≤ h ≤ 4, -7 ≤ k ≤ 7, -29 ≤ l ≤ 29
Reflections collected	4246	11830
Independent reflections	3041 [R_{int} = 0.0731, R_{sigma} = 0.1209]	2143 [R_{int} = 0.0496, R_{sigma} = 0.0423]
Data/restraints/ parameters	3041/327/199	2143/2/182
Goodness-of-fit on F^2	1.007	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0708, wR_2 = 0.1563	R_1 = 0.0530, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.1105, wR_2 = 0.1781	R_1 = 0.0768, wR_2 = 0.1136
Largest diff. peak/hole / e Å^{-3}	0.88/-0.98	0.18/-0.16

Table S2: Bond Lengths for **L1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br2	C14	1.918(9)	C6	C7	1.387(12)	C5	C6	1.474(12)
N1	C4	1.322(11)	C7	C8	1.413(13)	C12	C13	1.483(12)
N1	C5	1.364(12)	C8	C9	1.337(14)	C13	C14	1.374(12)
N2	C6	1.378(11)	C9	C10	1.432(13)	C13	C18	1.416(13)
N2	C12	1.293(11)	C10	C11	1.341(13)	C14	C15	1.384(13)

N3	C7	1.398(11)	C1	C5	1.373(13)	C15	C16	1.376(16)
N3	C11	1.375(11)	C2	C3	1.400(15)	C16	C17	1.375(15)
N3	C12	1.377(11)	C3	C4	1.371(15)	C17	C18	1.370(13)
C1	C2	1.367(13)						

Table S3: Bond Angles for **L1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N1	C5	116.5(9)	C9	C8	C7	120.6(9)
C12	N2	C6	107.0(7)	C8	C9	C10	120.6(9)
C11	N3	C7	121.7(8)	C11	C10	C9	119.4(10)
C11	N3	C12	131.7(8)	C10	C11	N3	120.3(9)
C12	N3	C7	106.6(7)	N2	C12	N3	111.8(7)
C2	C1	C5	120.7(10)	N2	C12	C13	126.7(8)
C1	C2	C3	117.8(11)	N3	C12	C13	121.5(8)
C4	C3	C2	118.0(10)	C14	C13	C12	122.3(8)
N1	C4	C3	125.1(10)	C14	C13	C18	116.6(9)
N1	C5	C1	122.0(8)	C18	C13	C12	121.0(8)
N1	C5	C6	116.1(8)	C13	C14	Br2	119.5(7)
C1	C5	C6	122.0(8)	C13	C14	C15	123.0(9)
N2	C6	C5	122.0(8)	C15	C14	Br2	117.5(7)
N2	C6	C7	109.7(7)	C16	C15	C14	118.5(10)
C7	C6	C5	128.2(8)	C17	C16	C15	120.6(10)
N3	C7	C8	117.4(8)	C18	C17	C16	120.2(9)
C6	C7	N3	104.8(7)	C17	C18	C13	121.0(10)
C6	C7	C8	137.7(8)				

Table S4: Bond Lengths for **L2H**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.381(6)	C6	C7	1.370(7)	C8	C16	1.381(6)
O1	C10	1.389(6)	C7	C8	1.405(7)	C10	C11	1.387(8)
O2	C9	1.218(6)	C8	C9	1.422(7)	C10	C15	1.389(6)
N1	C6	1.394(6)	C1	C2	1.384(9)	C11	C12	1.353(8)
N1	C16	1.353(6)	C2	C3	1.356(9)	C12	C13	1.399(9)
N2	C1	1.328(7)	C3	C4	1.378(8)	C13	C14	1.376(8)
N2	C5	1.335(6)	C4	C5	1.384(7)	C14	C15	1.397(7)
C5	C6	1.454(6)				C15	C16	1.427(7)

Table S5: Bond Angles for **L2H**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C10	122.7(4)	O1	C9	C8	116.0(5)
C16	N1	C6	109.3(4)	O2	C9	O1	116.0(5)
C1	N2	C5	117.8(5)	O2	C9	C8	127.9(5)
N2	C1	C2	123.6(6)	O1	C10	C15	122.5(4)
C3	C2	C1	118.4(6)	C11	C10	O1	116.0(5)
C2	C3	C4	119.2(6)	C11	C10	C15	121.5(5)
C3	C4	C5	119.3(5)	C12	C11	C10	119.3(5)
N2	C5	C4	121.8(5)	C11	C12	C13	120.8(6)

N2	C5	C6	115.8(4)	C14	C13	C12	119.8(6)
C4	C5	C6	122.4(4)	C13	C14	C15	120.3(5)
N1	C6	C5	122.6(4)	C10	C15	C14	118.3(4)
C7	C6	N1	107.5(4)	C10	C15	C16	115.0(4)
C7	C6	C5	129.9(4)	C14	C15	C16	126.7(4)
C6	C7	C8	107.4(4)	N1	C16	C8	107.8(4)
C7	C8	C9	130.9(5)	N1	C16	C15	129.7(4)
C16	C8	C7	108.0(4)	C8	C16	C15	122.5(4)
C16	C8	C9	121.0(5)				

Table S6: Crystallographic data and structure refinement parameters of **1a**, **1aa** and **1b**

Identification code	**1a**	**1aa**	**1b**
Empirical formula	$C_{36}H_{30}Br_2Cl_2N_6NiO_3$	$C_{36}H_{26}Br_2N_{12}NiO$	$C_{18}H_{12}BrCl_2N_3Pd$
Formula weight	884.09	861.22	564.06
Temperature/K	295.00	297.00	297.00
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/n$	C2/c
a/Å	11.2189(17)	11.346(4)	26.286(2)
b/Å	12.5312(19)	24.735(8)	11.0439(9)
c/Å	14.612(2)	13.365(5)	15.2328(13)
α/°	94.067(5)	90	90
β/°	109.340(4)	109.158(4)	118.195(2)
γ/°	102.568(4)	90	90
Volume/$Å^3$	1869.0(5)	3543(2)	3897.4(6)
Z	2	4	8
$\rho_{calc}g/cm^3$	1.571	1.615	1.923
μ/mm^{-1}	2.844	2.853	3.291
F(000)	888.0	1728.0	2208.0
Crystal size/mm^3	0.12 × 0.08 × 0.04	0.14 × 0.12 × 0.04	0.14 × 0.08 × 0.075
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.038 to 51.392	5.736 to 52.084	3.516 to 50.33
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	-14 ≤ h ≤ 13, -30 ≤ k ≤ 30, -16 ≤ l ≤ 16	-30 ≤ h ≤ 31, -13 ≤ k ≤ 12, -17 ≤ l ≤ 18
Reflections collected	35819	75433	12662
Independent reflections	6849 [R_{int} = 0.0633, R_{sigma} = 0.0692]	6932 [R_{int} = 0.0715, R_{sigma} = 0.0366]	3476 [R_{int} = 0.0492, R_{sigma} = 0.0619]
Data/restraints/parameters	6849/1244/448	6932/531/534	3476/0/226
Goodness-of-fit on F^2	1.066	1.083	1.160

Final R indexes [I>=2σ (I)]	R_1 = 0.0999, wR_2 = 0.2690	R_1 = 0.0578, wR_2 = 0.1556	R_1 = 0.0662, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.1932, wR_2 = 0.3506	R_1 = 0.0907, wR_2 = 0.1779	R_1 = 0.0929, wR_2 = 0.1199
Largest diff. peak/hole / e Å^{-3}	1.19/-0.75	1.38/-0.93	0.96/-0.57

Table S7: Crystallographic data and structure refinement parameters of **1c**, **1d** and **1e**

Identification code	**1c**	**1d**	**1e**
Empirical formula	$C_{18}H_{12}BrCl_2N_3Pt$	$C_{36}H_{34}Br_2Cl_2CuN_6O_5$	$C_{36}H_{34}Br_4CuN_6O_5$
Formula weight	616.21	924.95	1013.87
Temperature/K	295.00	297.00	297.00
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P-1	P-1
a/Å	25.7953(9)	11.0740(9)	11.1681(11)
b/Å	11.0716(4)	12.8377(10)	12.8349(12)
c/Å	14.8496(5)	14.4872(12)	14.5183(14)
α/°	90	69.906(2)	70.117(3)
β/°	116.0950(10)	76.732(2)	77.736(3)
γ/°	90	85.853(2)	85.953(3)
Volume/Å^3	3808.7(2)	1882.5(3)	1912.4(3)
Z	8	2	2
ρ_{calc}g/cm^3	2.149	1.632	1.761
μ/mm^{-1}	9.752	2.895	4.800
F(000)	2304.0	930.0	1002.0
Crystal size/mm^3	0.18 × 0.14 × 0.12	0.15 × 0.1 × 0.04	0.17 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.608 to 54.194	3.72 to 49.996	4.818 to 49.998
Index ranges	-32 ≤ h ≤ 32, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	47904	45593	49612
Independent reflections	4108 [R_{int} = 0.0389, R_{sigma} = 0.0195]	6522 [R_{int} = 0.0467, R_{sigma} = 0.0312]	6637 [R_{int} = 0.0417, R_{sigma} = 0.0302]
Data/restraints/parameters	4108/0/226	6522/501/497	6637/971/492
Goodness-of-fit on F^2	1.094	1.148	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0607	R_1 = 0.0877, wR_2 = 0.2407	R_1 = 0.0647, wR_2 = 0.1789
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.0682	R_1 = 0.1244, wR_2 = 0.3112	R_1 = 0.0992, wR_2 = 0.2255
Largest diff. peak/hole / e Å^{-3}	2.35/-1.09	1.33/-0.91	1.32/-1.02

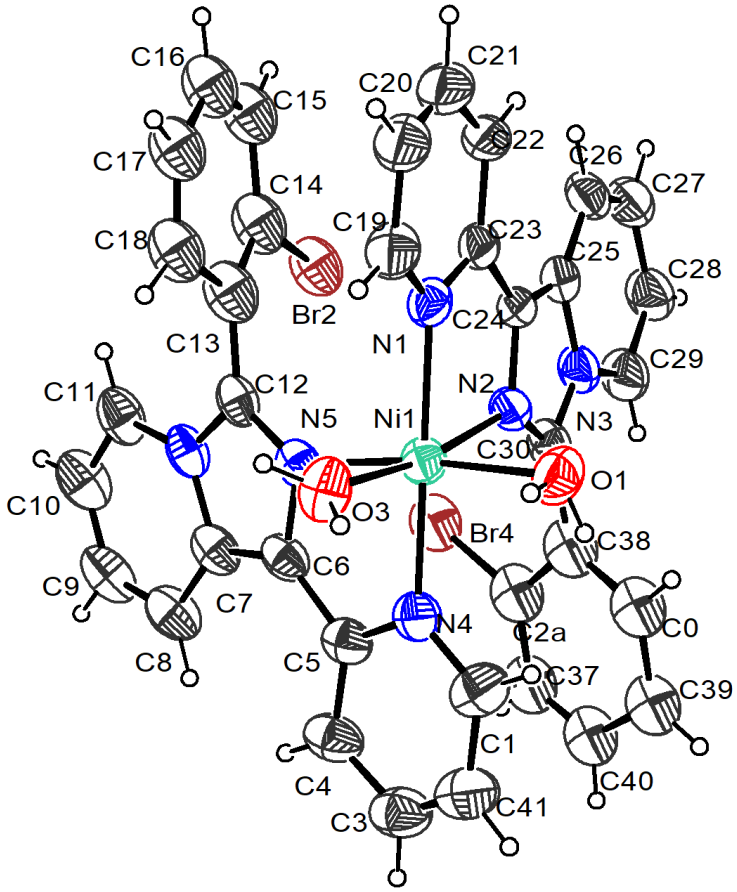


Figure S6. ORTEP diagram of complex **1a** with 30% ellipsoid probability. The molecule was discorded and modelled with partial occupancies factor. Only one part is showing here. Other part and anions were removed for clarity.

Table S8: Bond lengths for **1a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	N1	2.071(7)	C13	C18A	1.59(2)	C3	C2	1.285(18)
Ni1	N5	2.085(7)	C13	C14A	1.26(3)	C32	C33	1.39(2)
Ni1	N2	2.108(7)	C31	C32	1.46(2)	C21	C20	1.286(19)
Ni1	O2	2.095(7)	C31	C36	1.35(2)	C18	C17	1.41(2)
Ni1	O1	2.124(7)	C7	C8	1.392(13)	C14	C15	1.49(2)
Ni1	N4	2.075(8)	C26	C27	1.340(16)	C10	C9	1.383(19)
Br1	C36	1.87(2)	C4	C3	1.431(17)	C15	C16	1.27(2)
Br2	C14	1.898(15)	C11	C10	1.376(16)	C34	C33	1.440(16)
N1	C23	1.380(13)	C19	C20	1.344(16)	C34	C35	1.28(3)
N1	C19	1.333(11)	C27	C28	1.477(16)	C16	C17	1.367(14)
N5	C6	1.376(11)	C1	C2	1.406(17)	C35	C36	1.396(19)
N5	C12	1.352(12)	C28	C29	1.329(15)	Br4	C2A	1.85(2)
N2	C24	1.363(10)	C8	C9	1.373(17)	C2A	C37	1.36(2)
N2	C30	1.344(11)	C30	C31	1.472(17)	C2A	C38	1.34(2)
N4	C5	1.350(12)	C30	C38	1.46(2)	C37	C40	1.26(3)
N4	C1	1.359(13)	C6	C5	1.468(14)	C38	C0	1.45(2)

N3	C25	1.428(12)	C6	C7	1.376(13)	C0	C39	1.40(3)
N3	C30	1.355(12)	Cl3	Cl3[1]	2.33(4)	C39	C40	1.49(2)
N3	C29	1.390(13)	C12	C13	1.485(16)	C18A	C17A	1.40(3)
N6	C12	1.332(11)	C22	C21	1.436(17)	C14A	C15A	1.49(3)
N6	C7	1.416(13)	C5	C4	1.370(13)	C14A	Br2A	1.89(2)
N6	C11	1.362(12)	C13	C18	1.563(18)	C15A	C16A	1.27(3)
C23	C24	1.475(12)	C13	C14	1.286(19)	C16A	C17A	1.36(2)
C23	C22	1.396(13)	C24	C25	1.341(13)	C25	C26	1.430(14)

Table S9: Bond angels for **1a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ni1	N5	100.0(3)	C12	C13	C18A	113.8(17)
N1	Ni1	N2	78.9(3)	C14	C13	C12	128.7(11)
N1	Ni1	O2	91.9(3)	C14	C13	C18	117.9(13)
N1	Ni1	O1	86.5(3)	C14A	C13	C12	130.0(16)
N1	Ni1	N4	179.3(3)	C14A	C13	C18A	116(2)
N5	Ni1	N2	88.7(3)	C32	C31	C30	114.7(13)
N5	Ni1	O2	90.0(3)	C36	C31	C30	126.6(17)
N5	Ni1	O1	173.5(3)	C36	C31	C32	118.7(16)
N2	Ni1	O1	92.9(3)	C6	C7	N6	104.3(8)
O2	Ni1	N2	170.3(3)	C6	C7	C8	135.9(11)
O2	Ni1	O1	89.4(3)	C8	C7	N6	119.7(10)
N4	Ni1	N5	79.6(3)	C27	C26	C25	122.1(11)
N4	Ni1	N2	100.5(3)	C5	C4	C3	114.9(11)
N4	Ni1	O2	88.7(3)	N6	C11	C10	117.1(12)
N4	Ni1	O1	93.9(3)	N1	C19	C20	124.3(13)
C23	N1	Ni1	116.6(6)	C26	C27	C28	119.5(11)
C19	N1	Ni1	126.4(8)	N4	C1	C2	119.0(13)
C19	N1	C23	117.0(9)	C29	C28	C27	120.3(11)
C6	N5	Ni1	112.1(6)	C9	C8	C7	116.6(12)
C12	N5	Ni1	139.3(6)	C2	C3	C4	122.6(12)
C12	N5	C6	107.6(8)	C33	C32	C31	119.0(17)
C24	N2	Ni1	113.1(6)	C20	C21	C22	120.3(12)
C30	N2	Ni1	139.0(6)	C28	C29	N3	119.4(11)
C30	N2	C24	107.2(8)	C21	C20	C19	120.7(13)
C5	N4	Ni1	115.8(6)	C17	C18	C13	114.3(12)
C5	N4	C1	119.4(10)	C13	C14	Br2	118.2(12)
C1	N4	Ni1	124.8(8)	C13	C14	C15	124.6(14)
C30	N3	C25	109.0(8)	C15	C14	Br2	117.2(11)
C30	N3	C29	127.6(9)	C3	C2	C1	120.6(14)
C29	N3	C25	123.3(9)	C11	C10	C9	120.9(12)
C12	N6	C7	109.5(8)	C8	C9	C10	123.1(12)
C12	N6	C11	128.0(10)	C16	C15	C14	114.5(16)
C11	N6	C7	122.6(9)	C35	C34	C33	129.1(19)
N1	C23	C24	112.9(8)	C32	C33	C34	114.4(17)
N1	C23	C22	120.6(9)	C15	C16	C17	128.1(17)
C22	C23	C24	126.4(10)	C34	C35	C36	114.7(19)
N2	C24	C23	117.9(8)	C16	C17	C18	119.9(15)

C25	C24	N2	112.1(8)	C31	C36	Br1	121.8(13)
C25	C24	C23	129.9(9)	C31	C36	C35	124(2)
N3	C25	C26	115.3(9)	C35	C36	Br1	114.0(14)
C24	C25	N3	103.3(8)	C37	C2A	Br4	114(2)
C24	C25	C26	141.3(10)	C38	C2A	Br4	118.3(18)
N2	C30	N3	108.3(8)	C38	C2A	C37	125(3)
N2	C30	C31	128.3(11)	C40	C37	C2A	114(3)
N2	C30	C38	124(2)	C2A	C38	C30	118(2)
N3	C30	C31	122.3(11)	C2A	C38	C0	119(2)
N3	C30	C38	127(2)	C0	C38	C30	122(2)
N5	C6	C5	118.0(8)	C39	C0	C38	117(2)
N5	C6	C7	109.5(9)	C0	C39	C40	115(2)
C7	C6	C5	132.5(9)	C37	C40	C39	127(3)
N5	C12	C13	127.3(9)	C17A	C18A	C13	115(2)
N6	C12	N5	109.1(9)	C13	C14A	C15A	127(2)
N6	C12	C13	123.5(9)	C13	C14A	Br2A	108.3(18)
C23	C22	C21	116.9(12)	C15A	C14A	Br2A	120(2)
N4	C5	C6	113.9(8)	C16A	C15A	C14A	113(3)
N4	C5	C4	123.4(10)	C15A	C16A	C17A	128(3)
C4	C5	C6	122.6(10)	C16A	C17A	C18A	120(3)
C12	C13	C18	113.5(10)				

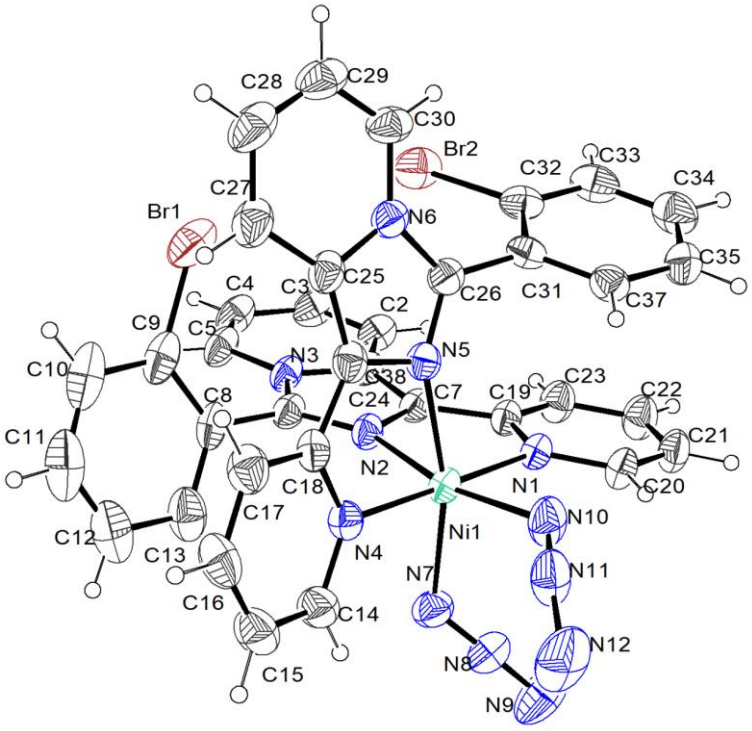


Figure S7. ORTEP diagram of complex **1aa** with 30% ellipsoid probability.

Table S10: Bond lengths for **1aa**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.854(8)	C8	C13	1.430(10)	C27	C28	1.355(10)

Ni1	N2	2.138(4)	C9	C10	1.411(11)	C28	C29	1.380(11)
Ni1	N4	2.112(4)	C10	C11	1.390(14)	C29	C30	1.349(10)
Ni1	N1	2.097(4)	C11	C12	1.341(14)	C31	C32	1.416(10)
Ni1	N10	2.070(5)	C12	C13	1.383(10)	C31	C37	1.385(11)
Ni1	N7	2.089(5)	C14	C15	1.381(9)	C32	C33	1.388(14)
Ni1	N5	2.114(4)	C15	C16	1.368(10)	C33	C34	1.393(13)
Br2	C32	1.870(9)	C16	C17	1.365(9)	C34	C35	1.373(13)
N3	C38	1.406(7)	C17	C18	1.406(8)	C35	C37	1.385(10)
N3	C5	1.392(7)	C18	C24	1.439(8)	N6	C30	1.372(7)
N3	C6	1.364(7)	C19	C23	1.375(8)	C38	C2	1.414(8)
N2	C6	1.316(6)	C20	C21	1.365(8)	C38	C7	1.378(7)
N2	C7	1.379(7)	C21	C22	1.364(9)	C2	C3	1.347(8)
N4	C14	1.346(7)	C22	C23	1.375(8)	C3	C4	1.416(9)
N4	C18	1.346(7)	C24	C25	1.379(8)	C4	C5	1.337(9)
N1	C19	1.348(6)	C25	C27	1.438(8)	C6	C8	1.467(8)
N1	C20	1.356(7)	C26	C31	1.483(9)	C7	C19	1.470(7)
N10	N11	1.102(7)	N7	N8	1.177(7)	C8	C9	1.399(9)
N11	N12	1.259(11)	N8	N9	1.149(7)	N5	C26	1.325(7)
N6	C25	1.398(7)	N5	C24	1.373(7)	N6	C26	1.365(7)

Table S11: Bond angels for **1aa**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N4	Ni1	N2	101.42(17)	C8	C9	C10	119.5(8)
N4	Ni1	N5	77.92(17)	C10	C9	Br1	118.9(6)
N1	Ni1	N2	78.09(16)	C11	C10	C9	118.1(9)
N1	Ni1	N4	179.33(17)	C12	C11	C10	122.9(9)
N1	Ni1	N5	101.55(17)	C11	C12	C13	121.2(10)
N10	Ni1	N2	166.72(19)	C12	C13	C8	118.1(8)
N10	Ni1	N4	90.34(19)	N4	C14	C15	122.3(6)
N10	Ni1	N1	90.09(19)	C16	C15	C14	118.9(6)
N10	Ni1	N7	95.2(2)	C17	C16	C15	119.0(6)
N10	Ni1	N5	92.0(2)	C16	C17	C18	120.9(6)
N7	Ni1	N2	91.03(19)	N4	C18	C17	119.1(5)
N7	Ni1	N4	89.66(19)	N4	C18	C24	115.0(5)
N7	Ni1	N1	90.82(19)	C17	C18	C24	125.8(5)
N7	Ni1	N5	165.69(19)	N1	C19	C7	113.8(5)
N5	Ni1	N2	84.60(16)	N1	C19	C23	121.4(5)
C5	N3	C38	120.7(5)	C23	C19	C7	124.8(5)
C6	N3	C38	108.2(4)	N1	C20	C21	123.1(5)
C6	N3	C5	131.0(5)	C22	C21	C20	118.7(6)
C6	N2	Ni1	140.3(4)	C21	C22	C23	119.3(6)
C6	N2	C7	107.2(4)	C19	C23	C22	119.9(6)

C7	N2	Ni1	112.4(3)	N5	C24	C18	117.5(5)
C14	N4	Ni1	124.5(4)	N5	C24	C25	109.0(5)
C14	N4	C18	119.7(5)	C25	C24	C18	133.5(5)
C18	N4	Ni1	115.5(4)	N6	C25	C27	116.9(6)
C19	N1	Ni1	117.4(3)	C24	C25	N6	105.7(5)
C19	N1	C20	117.6(5)	C24	C25	C27	137.3(6)
C20	N1	Ni1	124.8(4)	N5	C26	N6	110.1(5)
N11	N10	Ni1	129.4(5)	N5	C26	C31	122.8(6)
N10	N11	N12	159.3(12)	C30	C29	C28	120.5(7)
N8	N7	Ni1	127.1(5)	N6	C26	C31	126.5(6)
N9	N8	N7	178.3(7)	C28	C27	C25	118.5(7)
C24	N5	Ni1	112.5(3)	C27	C28	C29	122.3(7)
C26	N5	Ni1	137.8(4)	C29	C30	N6	119.1(7)
C26	N5	C24	107.8(4)	C32	C31	C26	122.3(7)
C26	N6	C25	107.4(4)	C37	C31	C26	119.8(6)
C26	N6	C30	130.1(5)	C37	C31	C32	117.9(7)
C30	N6	C25	122.5(5)	C31	C32	Br2	121.3(6)
N3	C38	C2	118.2(5)	C33	C32	Br2	118.4(6)
C7	C38	N3	104.1(5)	C33	C32	C31	120.3(8)
C7	C38	C2	137.7(5)	C32	C33	C34	120.4(9)
C3	C2	C38	119.3(6)	C35	C34	C33	119.3(9)
C2	C3	C4	121.8(6)	C34	C35	C37	120.8(8)
C5	C4	C3	119.7(5)	C35	C37	C31	121.3(8)
C4	C5	N3	120.2(6)	N2	C7	C38	110.2(4)
N3	C6	C8	123.4(5)	N2	C7	C19	118.3(4)
N2	C6	N3	110.3(5)	C38	C7	C19	131.4(5)
N2	C6	C8	126.3(5)	C9	C8	C6	122.4(6)
C13	C8	C6	117.5(6)	C9	C8	C13	120.2(6)
C8	C9	Br1	121.6(5)				

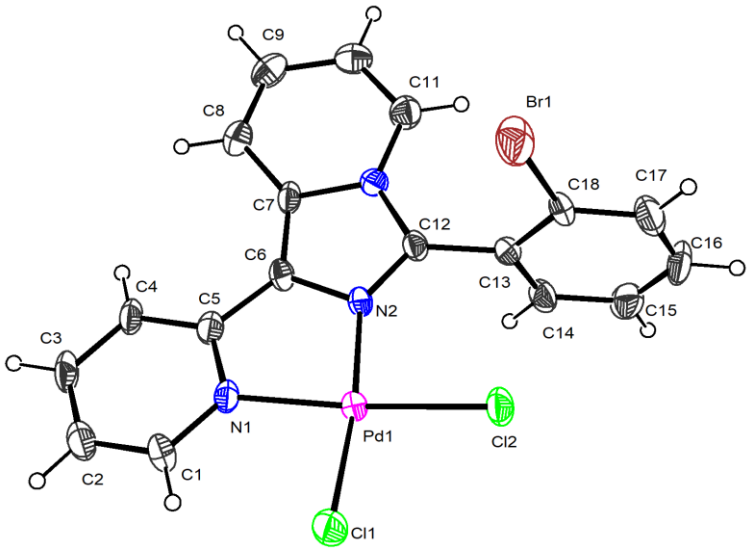


Figure S8. ORTEP diagram of complex **1b** with 30% ellipsoid probability.

Table S12: Bond lengths for **1b**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	Cl1	2.278(2)	C4	C5	1.384(11)	N3	C11	1.379(10)
Pd1	Cl2	2.278(2)	C5	C6	1.441(11)	N3	C12	1.364(10)
Pd1	N1	2.053(6)	C6	C7	1.393(11)	C1	C2	1.366(12)
Pd1	N2	2.040(6)	C7	C8	1.395(11)	C2	C3	1.363(13)
Br1	C18	1.879(9)	C8	C9	1.349(12)	C3	C4	1.372(11)
N1	C1	1.346(10)	C9	C10	1.411(12)	C14	C15	1.386(12)
N1	C5	1.361(10)	C10	C11	1.351(12)	C15	C16	1.352(13)
N2	C6	1.375(9)	C12	C13	1.476(11)	C16	C17	1.360(14)
N2	C12	1.316(9)	C13	C14	1.400(11)	C17	C18	1.384(12)
N3	C7	1.395(9)	C13	C18	1.385(11)			

Table S13: Bond angels for **1b**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Pd1	Cl2	89.80(9)	N2	C6	C7	109.3(7)
N1	Pd1	Cl1	93.2(2)	C7	C6	C5	132.7(7)
N1	Pd1	Cl2	175.9(2)	N3	C7	C8	118.6(8)
N2	Pd1	Cl1	173.53(19)	C6	C7	N3	103.7(7)
N2	Pd1	Cl2	96.08(18)	C6	C7	C8	137.6(8)
N2	Pd1	N1	80.8(3)	C9	C8	C7	119.8(9)
C1	N1	Pd1	126.2(6)	C8	C9	C10	120.5(9)
C1	N1	C5	119.6(7)	C11	C10	C9	120.9(9)
C5	N1	Pd1	114.2(5)	C10	C11	N3	118.5(8)
C6	N2	Pd1	111.8(5)	N2	C12	N3	108.9(7)
C12	N2	Pd1	138.5(5)	N2	C12	C13	128.7(7)
C12	N2	C6	108.4(7)	N3	C12	C13	122.1(7)
C11	N3	C7	121.7(7)	C14	C13	C12	118.4(8)
C12	N3	C7	109.6(7)	C18	C13	C12	123.4(8)
C12	N3	C11	128.6(7)	C18	C13	C14	118.2(8)
N1	C1	C2	121.2(9)	C15	C14	C13	119.7(9)
C3	C2	C1	120.3(9)	C16	C15	C14	120.6(10)
C2	C3	C4	119.0(8)	C15	C16	C17	121.0(9)
C3	C4	C5	120.1(9)	C16	C17	C18	119.6(9)
N1	C5	C4	119.9(8)	C13	C18	Br1	119.3(6)
N1	C5	C6	114.3(7)	C17	C18	Br1	119.7(7)
C4	C5	C6	125.8(8)	C17	C18	C13	121.0(9)
N2	C6	C5	118.0(7)				

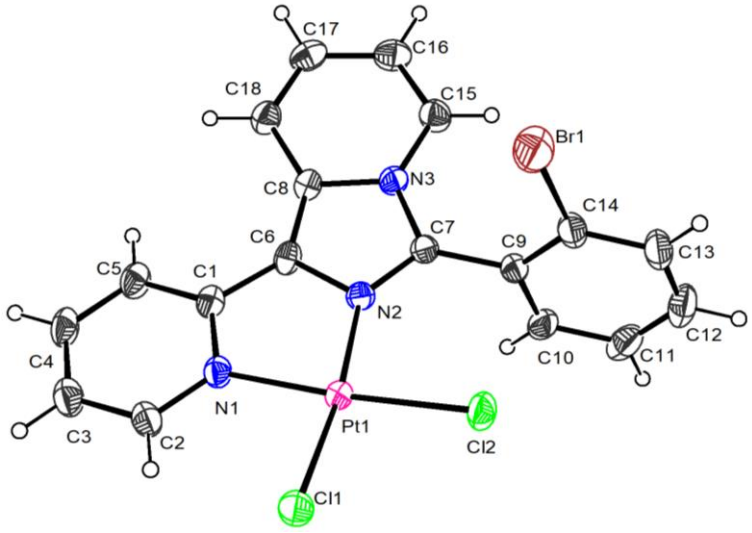


Figure S9. ORTEP diagram of complex **1c** with 30% ellipsoid probability.

Table S14: Bond Lengths for **1c**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl1	2.2951(15)	C3	C4	1.369(10)	C8	C18	1.429(8)
Pt1	Cl2	2.2951(14)	C4	C5	1.374(9)	C9	C10	1.428(9)
Pt1	N1	2.034(4)	C6	C8	1.361(8)	C9	C14	1.377(8)
Pt1	N2	2.024(4)	C7	C9	1.473(7)	C10	C11	1.374(9)
Br1	C14	1.887(7)	N3	C8	1.400(7)	C11	C12	1.391(11)
N1	C1	1.368(7)	N3	C15	1.379(7)	C12	C13	1.350(10)
N1	C2	1.348(7)	C1	C5	1.373(8)	C13	C14	1.385(8)
N2	C6	1.395(7)	C1	C6	1.443(8)	C15	C16	1.346(9)
N2	C7	1.324(7)	C2	C3	1.380(9)	C16	C17	1.406(10)
N3	C7	1.374(7)				C17	C18	1.337(9)

Table S15: Bond Angles for **1c**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Pt1	Cl2	89.05(6)	C8	C6	N2	108.9(5)
N1	Pt1	Cl1	93.76(14)	C8	C6	C1	135.3(5)
N1	Pt1	Cl2	175.83(14)	N2	C7	N3	108.1(5)
N2	Pt1	Cl1	173.15(13)	N2	C7	C9	129.3(5)
N2	Pt1	Cl2	96.75(13)	N3	C7	C9	122.2(5)
N2	Pt1	N1	80.26(18)	N3	C8	C18	117.5(5)
C1	N1	Pt1	115.1(4)	C6	C8	N3	105.3(5)
C2	N1	Pt1	125.8(4)	C6	C8	C18	137.2(5)
C2	N1	C1	119.0(5)	C10	C9	C7	118.2(5)
C6	N2	Pt1	113.2(4)	C14	C9	C7	122.7(5)
C7	N2	Pt1	136.8(4)	C14	C9	C10	119.1(5)
C7	N2	C6	108.5(5)	C11	C10	C9	118.1(7)
C7	N3	C8	109.0(4)	C10	C11	C12	120.8(7)
C7	N3	C15	128.7(5)	C13	C12	C11	121.3(6)
C15	N3	C8	122.2(5)	C12	C13	C14	119.1(7)

N1	C1	C5	120.5(5)	C9	C14	Br1	119.1(4)
N1	C1	C6	114.4(5)	C9	C14	C13	121.5(6)
C5	C1	C6	125.1(6)	C13	C14	Br1	119.4(5)
N1	C2	C3	121.8(6)	C16	C15	N3	118.6(6)
C4	C3	C2	119.0(6)	C15	C16	C17	121.0(6)
C3	C4	C5	119.7(6)	C18	C17	C16	121.4(6)
C1	C5	C4	119.9(6)	C17	C18	C8	119.3(6)
N2	C6	C1	115.7(5)				

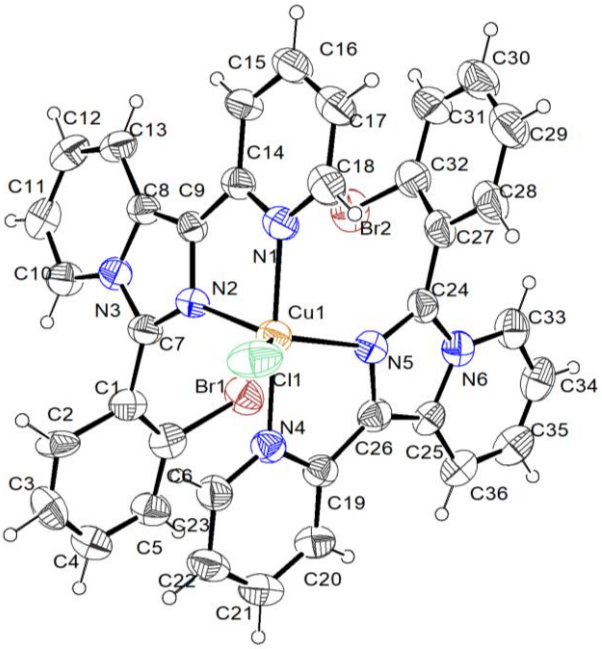


Figure S10. ORTEP diagram of complex **1d** with 30% ellipsoid probability. Counter chloride anion was removed for clarity.

Table S16: Bond Lengths for **1d**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C6	1.891(9)	C11	C12	1.409(15)	C25	C26	1.376(11)
Br2	C32	1.897(11)	C12	C13	1.335(14)	C25	C36	1.431(11)
Cu1	Cl1	2.267(2)	C14	C15	1.403(11)	C27	C28	1.413(15)
Cu1	N2	2.112(7)	C15	C16	1.388(13)	C27	C32	1.378(14)
Cu1	N1	1.991(6)	C16	C17	1.371(15)	C28	C29	1.394(18)
Cu1	N4	1.999(6)	C17	C18	1.360(13)	C29	C30	1.37(2)
Cu1	N5	2.124(6)	C19	C20	1.399(11)	C30	C31	1.362(19)
N3	C7	1.366(10)	C19	C26	1.463(11)	C31	C32	1.390(15)
N3	C8	1.379(10)	C20	C21	1.356(14)	C33	C34	1.355(13)
N3	C10	1.377(11)	C21	C22	1.395(15)	C34	C35	1.348(15)
N2	C7	1.344(10)	C22	C23	1.364(13)	C35	C36	1.381(14)
N2	C9	1.381(9)	C24	C27	1.443(12)	C1	C7	1.458(11)
N1	C14	1.348(11)	N5	C26	1.350(10)	C2	C3	1.239(13)
N1	C18	1.347(11)	N6	C24	1.342(10)	C3	C4	1.382(15)
N4	C19	1.363(10)	N6	C25	1.405(11)	C4	C5	1.378(13)

N4	C23	1.312(10)	N6	C33	1.386(10)	C5	C6	1.384(13)
N5	C24	1.355(10)	C1	C2	1.541(13)	C8	C9	1.376(11)
C9	C14	1.443(11)	C1	C6	1.401(12)	C8	C13	1.421(11)
C10	C11	1.368(13)						

Table S17: Bond Angles for **1d**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Cu1	Cl1	126.18(19)	C12	C13	C8	119.8(9)
N2	Cu1	N5	103.3(2)	N1	C14	C9	115.6(7)
N1	Cu1	Cl1	94.0(2)	N1	C14	C15	119.9(8)
N1	Cu1	N2	80.0(3)	C15	C14	C9	124.4(8)
N1	Cu1	N4	173.9(3)	C16	C15	C14	119.4(9)
N1	Cu1	N5	96.2(2)	C17	C16	C15	119.6(9)
N4	Cu1	Cl1	92.11(19)	C18	C17	C16	118.5(9)
N4	Cu1	N2	96.0(2)	N1	C18	C17	123.4(10)
N4	Cu1	N5	80.3(3)	N4	C19	C20	119.5(7)
N5	Cu1	Cl1	130.5(2)	N4	C19	C26	114.3(7)
C7	N3	C8	109.2(6)	C20	C19	C26	126.1(8)
C7	N3	C10	126.6(7)	C21	C20	C19	120.8(9)
C10	N3	C8	124.2(7)	C20	C21	C22	118.0(9)
C7	N2	Cu1	142.1(5)	C23	C22	C21	118.9(9)
C7	N2	C9	106.8(6)	N4	C23	C22	123.6(9)
C9	N2	Cu1	110.8(5)	N5	C24	C27	127.8(7)
C14	N1	Cu1	116.6(5)	C19	N4	Cu1	116.4(5)
C18	N1	Cu1	124.2(6)	N6	C24	N5	108.2(7)
C18	N1	C14	119.1(7)	N6	C24	C27	124.0(7)
C23	N4	Cu1	124.4(6)	N6	C25	C36	117.1(7)
C23	N4	C19	119.1(7)	C26	C25	N6	103.5(7)
C24	N5	Cu1	140.9(5)	C26	C25	C36	139.4(8)
C26	N5	Cu1	110.7(5)	N5	C26	C19	118.0(7)
C26	N5	C24	107.6(6)	N5	C26	C25	110.8(7)
C24	N6	C25	109.9(6)	C25	C26	C19	131.2(8)
C24	N6	C33	127.2(7)	C28	C27	C24	122.5(10)
C33	N6	C25	122.9(7)	C32	C27	C24	120.1(8)
C6	C1	C2	115.2(7)	C32	C27	C28	117.2(10)
C6	C1	C7	120.3(8)	C29	C28	C27	119.9(14)
C7	C1	C2	123.7(7)	C30	C29	C28	119.8(13)
C3	C2	C1	118.3(8)	C31	C30	C29	122.1(12)
C2	C3	C4	125.4(9)	C30	C31	C32	117.8(12)
C5	C4	C3	119.5(9)	C27	C32	Br2	118.8(7)
C4	C5	C6	119.5(9)	C27	C32	C31	123.1(11)
C1	C6	Br1	119.5(7)	C31	C32	Br2	118.0(9)

C5	C6	Br1	119.3(7)	C34	C33	N6	117.2(9)
C5	C6	C1	121.2(9)	C35	C34	C33	122.9(9)
N3	C7	C1	122.5(7)	C34	C35	C36	121.8(9)
N2	C7	N3	108.9(6)	C35	C36	C25	118.1(9)
N2	C7	C1	128.6(7)	C8	C9	N2	109.9(7)
N3	C8	C13	116.7(8)	C8	C9	C14	133.6(7)
C9	C8	N3	105.2(6)	C11	C10	N3	117.6(8)
C9	C8	C13	138.1(8)	C10	C11	C12	119.8(9)
N2	C9	C14	116.4(7)	C13	C12	C11	121.9(9)

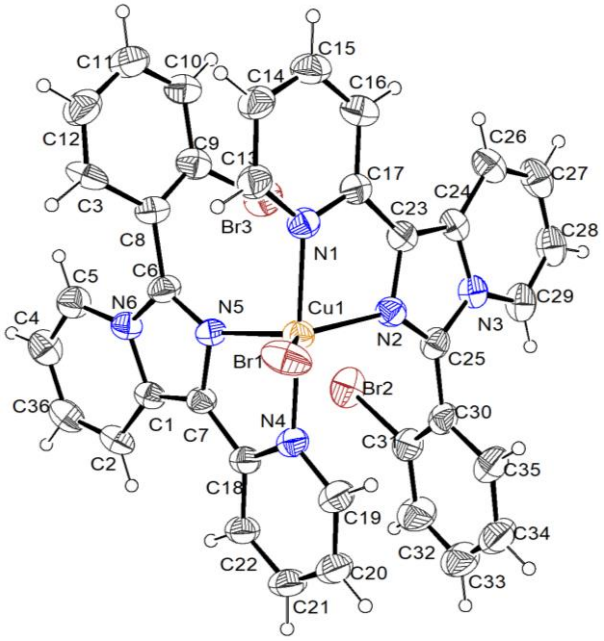


Figure S11. ORTEP diagram of complex **1e** with 30% ellipsoid probability. Counter bromide anion was removed for clarity.

Table S18: Bond Lengths for **1e**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br3	C9	1.894(9)	C10	C11	1.352(13)	N3	C24	1.380(10)
Br1	Cu1	2.4158(12)	C11	C12	1.378(14)	N3	C25	1.368(9)
Br2	C31	1.880(10)	C13	C14	1.379(12)	N3	C29	1.392(10)
Cu1	N5	2.119(6)	C14	C15	1.366(13)	C1	C2	1.427(10)
Cu1	N1	1.996(6)	C15	C16	1.349(13)	C1	C7	1.360(10)
Cu1	N4	1.998(6)	C16	C17	1.409(11)	C2	C36	1.334(12)
Cu1	N2	2.108(6)	C17	C23	1.435(10)	C36	C4	1.393(14)
N6	C1	1.386(9)	C18	C22	1.387(10)	C4	C5	1.351(12)
N6	C5	1.383(10)	C19	C20	1.367(12)	C6	C8	1.485(10)
N6	C6	1.344(9)	C20	C21	1.347(13)	C7	C18	1.459(10)
N5	C6	1.324(10)	C21	C22	1.370(12)	C8	C9	1.367(11)
N5	C7	1.393(9)	C23	C24	1.383(10)	C9	C10	1.407(12)

C3	C8	1.559(11)	C24	C26	1.426(11)	C28	C29	1.343(12)
C3	C12	1.234(12)	C25	C30	1.450(11)	C30	C31	1.388(13)
N1	C13	1.337(10)	N2	C25	1.335(9)	C30	C35	1.414(13)
N1	C17	1.344(9)	C26	C27	1.364(13)	C31	C32	1.414(14)
N4	C18	1.348(9)	C27	C28	1.400(14)	C33	C34	1.380(19)
N4	C19	1.343(10)	C32	C33	1.372(18)	C34	C35	1.409(16)
N2	C23	1.402(9)						

Table S19: Bond Angles for **1e**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N5	Cu1	Br1	125.32(17)	C3	C12	C11	125.2(9)
N1	Cu1	Br1	92.37(18)	N1	C13	C14	121.6(8)
N1	Cu1	N5	95.6(2)	C15	C14	C13	119.0(8)
N1	Cu1	N4	173.8(2)	C16	C15	C14	120.2(8)
N1	Cu1	N2	80.7(2)	C15	C16	C17	119.4(8)
N4	Cu1	Br1	93.72(17)	N1	C17	C16	119.9(7)
N4	Cu1	N5	80.1(2)	N1	C17	C23	115.9(6)
N4	Cu1	N2	96.1(2)	C16	C17	C23	124.1(7)
N2	Cu1	Br1	130.76(17)	N4	C18	C7	114.5(6)
N2	Cu1	N5	103.9(2)	N4	C18	C22	120.7(7)
C5	N6	C1	122.9(6)	C22	C18	C7	124.8(7)
C6	N6	C1	108.6(6)	N4	C19	C20	122.9(8)
C6	N6	C5	128.4(7)	C21	C20	C19	118.6(8)
C6	N5	Cu1	142.7(5)	C20	C21	C22	120.3(8)
C6	N5	C7	106.7(6)	C21	C22	C18	119.1(9)
C7	N5	Cu1	110.5(4)	N2	C23	C17	116.9(6)
C12	C3	C8	117.5(7)	C24	C23	N2	108.2(6)
C13	N1	Cu1	123.7(5)	C24	C23	C17	134.8(7)
C13	N1	C17	119.8(7)	N3	C24	C23	105.7(6)
C17	N1	Cu1	116.3(5)	N3	C24	C26	117.7(7)
C18	N4	Cu1	117.6(5)	C23	C24	C26	136.6(8)
C19	N4	Cu1	124.0(6)	N2	C25	N3	108.6(6)
C19	N4	C18	118.4(7)	N2	C25	C30	128.5(7)
C23	N2	Cu1	109.9(5)	C25	N2	C23	107.9(6)
C25	N2	Cu1	141.5(5)	N3	C25	C30	122.8(7)
C24	N3	C29	123.9(7)	C27	C26	C24	118.4(9)
C25	N3	C24	109.6(6)	C26	C27	C28	121.0(8)
C25	N3	C29	126.5(7)	C29	C28	C27	122.2(8)
N6	C1	C2	116.6(7)	C28	C29	N3	116.7(9)
C7	C1	N6	105.6(6)	C31	C30	C25	119.1(7)
C7	C1	C2	137.8(7)	C31	C30	C35	119.1(9)
C36	C2	C1	120.0(8)	C35	C30	C25	121.7(9)

C2	C36	C4	121.5(8)	C30	C31	Br2	119.8(7)
C5	C4	C36	120.7(9)	C30	C31	C32	121.8(10)
C4	C5	N6	118.2(8)	C32	C31	Br2	118.4(8)
N6	C6	C8	121.1(7)	C33	C32	C31	119.2(12)
N5	C6	N6	110.0(6)	C32	C33	C34	119.3(11)
N5	C6	C8	128.8(7)	C33	C34	C35	123.0(11)
N5	C7	C18	116.9(6)	C34	C35	C30	117.5(12)
C1	C7	N5	109.0(6)	C8	C9	Br3	120.5(6)
C1	C7	C18	133.9(6)	C8	C9	C10	121.2(8)
C6	C8	C3	123.9(7)	C10	C9	Br3	118.2(7)
C9	C8	C3	116.1(7)	C11	C10	C9	118.6(8)
C9	C8	C6	119.7(7)	C10	C11	C12	121.0(9)

Table S20: Crystallographic data and structure refinement parameters of complex **2a – 2d**.

Identification code	**2a**	**2b**	**2c**	**2d**
Empirical formula	$C_{32}H_{22}N_4NiO_6$ [2DMF]	$C_{32}H_{18}N_4O_4Pd$	$C_{32}H_{18}N_4O_4Pt$	$C_{32}H_{18}CuN_4O_4$
Formula weight	763.44	628.90	781.68	586.04
Temperature/K	293(2)	293(2)	296.00	293(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	I2/c	P-1	P-1	$P2_1/c$
a/Å	17.2559(6)	10.7057(6)	13.760(5)	18.832(3)
b/Å	11.6096(3)	11.2188(5)	14.324(5)	8.2583(9)
c/Å	18.5736(7)	12.7019(6)	22.444(8)	18.462(3)
α/°	90	68.128(5)	80.129(11)	90
β/°	107.440(4)	69.582(5)	82.246(11)	118.054(19)
γ/°	90	62.805(5)	75.657(11)	90
Volume/$Å^3$	3549.9(2)	1229.42(13)	4202(3)	2533.9(7)
Z	4	2	6	4
$\rho_{calc}g/cm^3$	1.428	1.699	1.853	1.536
μ/mm^{-1}	0.609	0.805	5.066	0.910
F(000)	1592.0	632.0	2304.0	1196.0
Crystal size/mm^3	0.08 × 0.075 × 0.044	0.18 × 0.08 × 0.065	0.14 × 0.08 × 0.04	0.08 × 0.075 × 0.065
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.294 to 57.54	4.382 to 50	2.966 to 52.772	4.414 to 49.998
Index ranges	-16 ≤ h ≤ 23, -15 ≤ k ≤ 7, -25 ≤ l ≤ 14	-7 ≤ h ≤ 12, -12 ≤ k ≤ 13, -13 ≤ l ≤ 15	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -28 ≤ l ≤ 27	-22 ≤ h ≤ 18, -9 ≤ k ≤ 6, -21 ≤ l ≤ 21
Reflections collected	7783	8408	81649	8541
Independent reflections	4078 [Rint = 0.0239, Rsigma = 0.0340]	4327 [R_{int} = 0.0689,	16862 [R_{int} = 0.0745, R_{sigma} = 0.0869]	4349 [R_{int} = 0.1057, R_{sigma} = 0.2104]

		R_{sigma} = 0.0753]		
Data/restraints/parameters	4078/1/245	4327/0/370	16862/1986/1108	4349/288/370
Goodness-of-fit on F^2	1.095	1.097	1.107	0.983
Final R indexes [I>=2σ (I)]	R1 = 0.0405, wR2 = 0.1154	R_1 = 0.0585, wR_2 = 0.1576	R_1 = 0.0727, wR_2 = 0.1073	R_1 = 0.0887, wR_2 = 0.1615
Final R indexes [all data]	R1 = 0.0487, wR2 = 0.1297	R_1 = 0.0710, wR_2 = 0.1663	R_1 = 0.1325, wR_2 = 0.1301	R_1 = 0.1845, wR_2 = 0.2158
Largest diff. peak/hole / e $Å^{-3}$	0.54/-0.31	1.14/-0.85	3.29/-1.16	0.96/-1.03

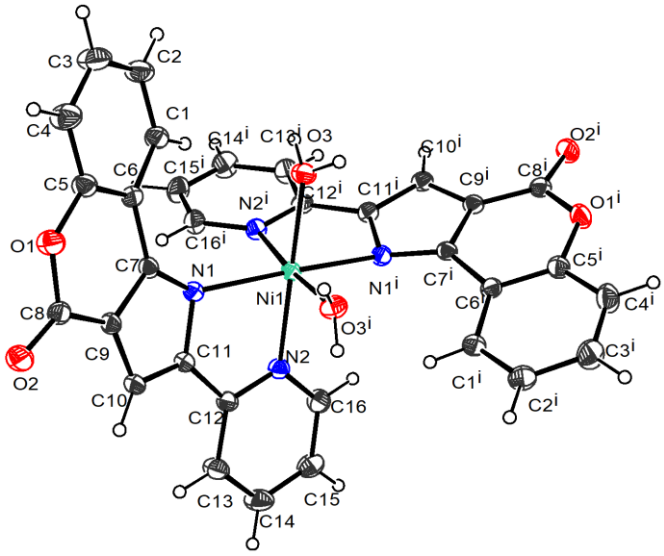


Figure S12. ORTEP diagram of complex **2a** with 30% ellipsoid probability.

Table S21: Bond lengths for **2a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O3 ^{i}	2.0920(17)	C4	C5	1.381(4)	N2	C16	1.338(3)
Ni1	O3	2.0920(17)	C5	C6	1.401(3)	N1	C7	1.346(3)
Ni1	N2 ^{i}	2.0767(19)	C6	C7	1.441(3)	N1	C11	1.394(3)
Ni1	N2	2.0767(19)	C7	C9	1.415(3)	C1	C2	1.370(4)
Ni1	N1	2.1342(18)	C8	C9	1.421(3)	C1	C6	1.404(3)
Ni1	N1 ^{i}	2.1342(18)	C9	C10	1.401(3)	C2	C3	1.386(4)
O1	C5	1.387(3)	C10	C11	1.377(3)	C3	C4	1.381(4)
O1	C8	1.382(3)	C11	C12	1.458(3)	O4	C19	1.229(5)
O2	C8	1.219(3)	C12	C13	1.394(3)	N3	C17	1.446(7)
N2	C12	1.347(3)	C13	C14	1.380(4)	N3	C18	1.418(6)
C15	C16	1.376(4)	C14	C15	1.383(4)	N3	C19	1.299(4)

Table S22: Bond angels for **2a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Ni1	O3 ^{i}	85.88(10)	C4	C5	C6	121.7(2)

O3	Ni1	N1	97.28(7)	C1	C6	C7	126.3(2)
O3 ^{i}	Ni1	N1 ^{i}	97.28(7)	C5	C6	C1	117.0(2)
O3 ^{i}	Ni1	N1	86.91(7)	C5	C6	C7	116.7(2)
O3	Ni1	N1 ^{i}	86.91(7)	N1	C7	C6	129.94(19)
N2	Ni1	O3 ^{i}	88.98(7)	N1	C7	C9	110.79(19)
N2 ^{i}	Ni1	O3 ^{i}	174.45(7)	C9	C7	C6	119.2(2)
N2	Ni1	O3	174.45(7)	O1	C8	C9	116.3(2)
N2 ^{i}	Ni1	O3	88.98(7)	O2	C8	O1	115.4(2)
N2 ^{i}	Ni1	N2	96.22(11)	O2	C8	C9	128.3(2)
N2 ^{i}	Ni1	N1	95.84(7)	C7	C9	C8	122.2(2)
N2	Ni1	N1 ^{i}	95.84(7)	C10	C9	C7	106.87(19)
N2	Ni1	N1	80.32(7)	C10	C9	C8	130.9(2)
N2 ^{i}	Ni1	N1 ^{i}	80.32(7)	C11	C10	C9	105.15(19)
N1	Ni1	N1^{1}	174.29(10)	N1	C11	C12	118.55(19)
C8	O1	C5	122.62(19)	C10	C11	N1	112.3(2)
C12	N2	Ni1	114.06(15)	C10	C11	C12	129.0(2)
C16	N2	Ni1	126.73(16)	N2	C12	C11	115.59(19)
C16	N2	C12	118.9(2)	N2	C12	C13	121.2(2)
C7	N1	Ni1	140.28(15)	C13	C12	C11	123.2(2)
C7	N1	C11	104.86(18)	C14	C13	C12	119.1(2)
C11	N1	Ni1	107.89(14)	C13	C14	C15	119.3(2)
C2	C1	C6	121.1(2)	C16	C15	C14	118.6(2)
C1	C2	C3	120.6(2)	N2	C16	C15	122.9(2)
C4	C3	C2	119.7(3)	C18	N3	C17	119.7(5)
C5	C4	C3	119.7(3)	C19	N3	C17	117.0(5)
O1	C5	C6	122.1(2)	C19	N3	C18	122.9(4)
C4	C5	O1	116.1(2)	O4	C19	N3	122.6(4)

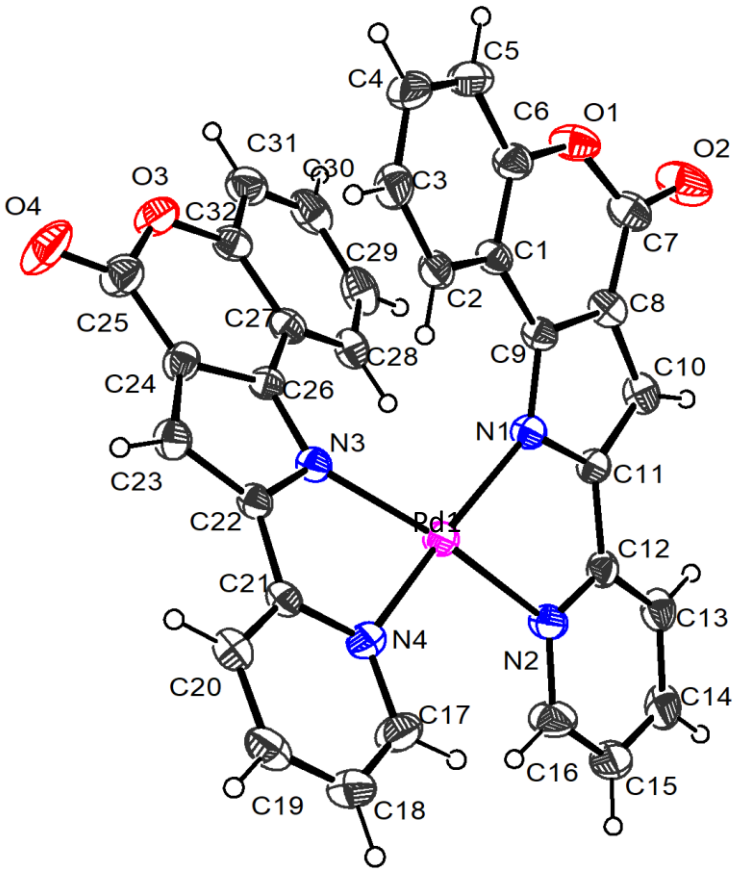


Figure S13. ORTEP diagram of complex **2b** with 30% ellipsoid probability.

Table S23: Bond lengths for **2b**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	N3	2.013(4)	C32	C31	1.384(9)	C8	C7	1.444(9)
Pd1	N1	2.030(4)	C6	C5	1.388(9)	C19	C18	1.336(10)
Pd1	N2	2.100(5)	C9	C8	1.403(8)	C5	C4	1.373(10)
Pd1	N4	2.108(5)	C13	C12	1.381(8)	C31	C30	1.379(10)
O3	C32	1.378(7)	C13	C14	1.381(9)	C28	C29	1.370(9)
O3	C25	1.386(8)	C24	C23	1.418(9)	C29	C30	1.357(11)
O1	C6	1.375(8)	C24	C25	1.428(9)	C14	C15	1.337(11)
O1	C7	1.384(8)	C12	C11	1.453(8)	C17	C18	1.335(10)
N3	C26	1.363(7)	C11	C10	1.372(8)	C15	C16	1.362(10)
N3	C22	1.387(7)	C20	C21	1.374(8)	C26	C27	1.439(8)
N1	C9	1.360(7)	C20	C19	1.387(9)	C26	C24	1.405(8)
N1	C11	1.378(7)	C22	C21	1.443(8)	C1	C6	1.398(8)
N2	C12	1.345(7)	C22	C23	1.372(8)	C1	C9	1.458(7)
N2	C16	1.345(8)	C3	C2	1.383(8)	C1	C2	1.390(8)
N4	C21	1.352(7)	C3	C4	1.379(10)	C27	C32	1.401(8)
N4	C17	1.352(8)	C8	C10	1.403(8)	C27	C28	1.409(8)
O2	C7	1.183(8)				O4	C25	1.193(8)

Table S24: Bond angels for **2b**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

N3	Pd1	N1	101.86(18)	C26	C24	C25	122.9(6)
N3	Pd1	N2	161.52(19)	C23	C24	C25	130.3(6)
N3	Pd1	N4	79.38(18)	N2	C12	C13	122.0(5)
N1	Pd1	N2	79.57(18)	N2	C12	C11	115.1(5)
N1	Pd1	N4	162.34(18)	C13	C12	C11	122.9(5)
N2	Pd1	N4	104.93(18)	N1	C11	C12	116.7(5)
C32	O3	C25	123.2(5)	C10	C11	N1	111.3(5)
C6	O1	C7	124.1(5)	C10	C11	C12	131.9(5)
C26	N3	Pd1	139.8(4)	C21	C20	C19	119.3(6)
C26	N3	C22	106.4(4)	N3	C22	C21	116.9(5)
C22	N3	Pd1	113.6(4)	C23	C22	N3	110.9(5)
C9	N1	Pd1	140.3(4)	C23	C22	C21	132.0(5)
C9	N1	C11	106.2(4)	C4	C3	C2	119.9(6)
C11	N1	Pd1	113.3(3)	N4	C21	C20	121.1(5)
C12	N2	Pd1	113.0(4)	N4	C21	C22	114.5(5)
C16	N2	Pd1	127.8(4)	C20	C21	C22	124.3(5)
C16	N2	C12	117.6(5)	C3	C2	C1	120.8(6)
C21	N4	Pd1	113.0(4)	C9	C8	C10	107.0(5)
C17	N4	Pd1	128.6(4)	C9	C8	C7	122.7(6)
C17	N4	C21	116.8(5)	C10	C8	C7	130.3(6)
N3	C26	C27	130.5(5)	C22	C23	C24	106.1(5)
N3	C26	C24	109.7(5)	C18	C19	C20	119.0(6)
C24	C26	C27	119.8(5)	C11	C10	C8	105.9(5)
C6	C1	C9	115.2(5)	C4	C5	C6	119.3(6)
C2	C1	C6	118.0(5)	C5	C4	C3	120.7(6)
C2	C1	C9	126.7(5)	C30	C31	C32	119.8(7)
C32	C27	C26	115.4(5)	C29	C28	C27	120.5(6)
C32	C27	C28	117.3(5)	C30	C29	C28	121.2(7)
C28	C27	C26	127.2(5)	C15	C14	C13	118.9(6)
O3	C32	C27	122.9(5)	O3	C25	C24	114.7(6)
O3	C32	C31	116.2(6)	O4	C25	O3	116.5(6)
C31	C32	C27	120.9(6)	O4	C25	C24	128.8(7)
O1	C6	C1	122.8(6)	C29	C30	C31	120.2(7)
O1	C6	C5	116.1(6)	O1	C7	C8	114.2(5)
C5	C6	C1	121.1(6)	O2	C7	O1	116.8(6)
N1	C9	C1	130.6(5)	O2	C7	C8	129.1(7)
N1	C9	C8	109.6(5)	C18	C17	N4	123.9(6)
C8	C9	C1	119.7(5)	C17	C18	C19	119.8(7)
C12	C13	C14	118.7(6)	C14	C15	C16	120.7(7)
C26	C24	C23	106.7(5)	N2	C16	C15	122.0(7)

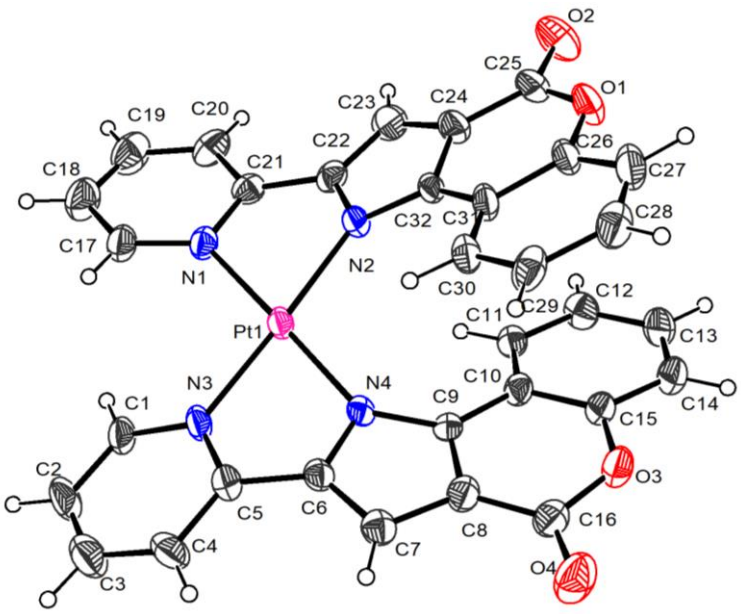


Figure S14. ORTEP diagram of complex **2c** with 30% ellipsoid probability.

Table S25: Bond lengths for **2c**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	N3	2.041(8)	C11	C12	1.389(14)	C8	C7	1.414(15)
Pt1	N4	1.994(8)	C12	C13	1.384(16)	C8	C16	1.418(15)
Pt1	N2	2.015(8)	C13	C14	1.358(17)	C7	C6	1.369(14)
Pt1	N1	2.034(9)	C31	C26	1.413(14)	C32	C24	1.416(15)
N3	C5	1.377(14)	C31	C30	1.373(15)	C32	C31	1.435(15)
N3	C1	1.344(13)	C26	C27	1.399(18)	C24	C23	1.416(16)
N4	C9	1.371(12)	C30	C29	1.384(15)	C24	C25	1.420(16)
N4	C6	1.396(13)	C29	C28	1.388(17)	C23	C22	1.357(15)
N2	C32	1.350(12)	C28	C27	1.375(19)	C22	C21	1.431(15)
N2	C22	1.396(13)	C4	C3	1.341(17)	C21	C20	1.394(15)
N1	C21	1.374(13)	C3	C2	1.375(19)	C20	C19	1.369(17)
N1	C17	1.330(13)	C2	C1	1.371(17)	C19	C18	1.392(19)
O3	C15	1.408(14)	C9	C8	1.408(15)	C10	C15	1.380(14)
O3	C16	1.375(14)	O1	C26	1.359(15)	C10	C11	1.391(14)
O4	C16	1.217(13)	O1	C25	1.367(16)	C5	C4	1.395(15)
O2	C25	1.228(15)	C10	C9	1.434(14)	C5	C6	1.427(14)
C15	C14	1.380(15)				C18	C17	1.378(17)

Table S26: Bond angels for **2c**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N4	Pt1	N3	78.8(3)	C32	C24	C25	121.8(12)
N4	Pt1	N2	102.3(3)	C23	C24	C32	107.5(10)
N4	Pt1	N1	173.7(3)	C23	C24	C25	130.6(12)
N2	Pt1	N3	175.7(4)	C22	C23	C24	104.8(11)

N2	Pt1	N1	78.7(3)	N2	C22	C21	113.6(10)
N1	Pt1	N3	100.6(4)	C23	C22	N2	112.4(10)
C5	N3	Pt1	113.3(7)	C23	C22	C21	133.2(11)
C1	N3	Pt1	129.0(9)	N1	C21	C22	114.9(10)
C1	N3	C5	117.5(10)	N1	C21	C20	120.3(11)
C9	N4	Pt1	141.2(7)	C20	C21	C22	124.6(11)
C9	N4	C6	105.7(8)	C19	C20	C21	120.1(13)
C6	N4	Pt1	112.3(6)	N4	C6	C5	115.5(10)
C32	N2	Pt1	141.5(8)	C7	C6	N4	111.5(9)
C32	N2	C22	105.8(9)	C7	C6	C5	132.4(11)
C22	N2	Pt1	111.8(7)	N2	C32	C24	109.2(10)
C21	N1	Pt1	111.5(7)	N2	C32	C31	131.0(10)
C17	N1	Pt1	130.5(8)	C24	C32	C31	119.7(10)
C17	N1	C21	117.6(10)	C7	C8	C16	130.7(11)
C16	O3	C15	122.3(9)	C6	C7	C8	105.7(10)
C15	C10	C9	116.4(10)	C20	C19	C18	119.2(13)
C15	C10	C11	117.1(10)	C17	C18	C19	117.6(13)
C11	C10	C9	126.4(10)	N1	C17	C18	124.4(13)
N3	C5	C4	120.4(11)	C10	C15	O3	122.0(10)
N3	C5	C6	112.7(10)	C10	C15	C14	123.1(12)
C4	C5	C6	126.4(12)	C14	C15	O3	114.9(10)
C3	C4	C5	120.0(14)	O3	C16	C8	115.8(11)
C4	C3	C2	120.0(13)	O4	C16	O3	116.3(11)
C1	C2	C3	118.8(12)	O4	C16	C8	127.8(12)
N3	C1	C2	122.9(13)	C12	C11	C10	121.1(11)
N4	C9	C10	130.9(10)	C13	C12	C11	118.5(11)
N4	C9	C8	109.2(9)	C14	C13	C12	122.2(12)
C8	C9	C10	119.9(10)	C13	C14	C15	117.8(12)
C9	C8	C7	107.3(10)	C26	C31	C32	114.9(11)
C9	C8	C16	122.0(11)	C30	C31	C32	126.7(10)
O2	C25	O1	116.7(12)	C30	C31	C26	118.4(11)
O2	C25	C24	126.7(15)	O1	C26	C31	123.8(12)
O1	C25	C24	116.6(12)	O1	C26	C27	116.2(11)
C31	C30	C29	122.0(11)	C27	C26	C31	120.0(13)

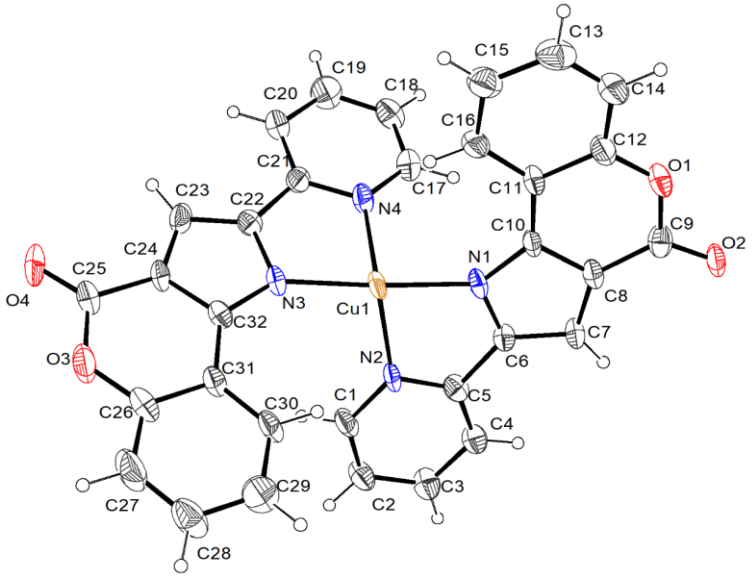


Figure S15. ORTEP diagram of **2d** (monomeric unit) with 30% ellipsoid probability.

Table S27: Bond lengths for **2d**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O2[1]	2.337(5)	C8	C9	1.445(11)	C22	C23	1.354(10)
Cu1	N2	2.055(6)	C8	C10	1.416(9)	C23	C24	1.400(10)
Cu1	N4	2.058(6)	C10	C11	1.412(10)	C24	C25	1.469(11)
Cu1	N1	1.956(6)	C11	C12	1.423(11)	C24	C32	1.383(10)
Cu1	N3	1.966(6)	C11	C16	1.409(10)	C26	C27	1.343(11)
O1	C9	1.363(9)	C12	C14	1.375(11)	C26	C31	1.406(11)
O1	C12	1.347(9)	C13	C14	1.348(11)	C27	C28	1.413(12)
O2	C9	1.227(8)	C13	C15	1.404(13)	C28	C29	1.382(13)
O4	C25	1.187(9)	C15	C16	1.366(11)	C29	C30	1.381(10)
N2	C1	1.351(10)	C17	C18	1.377(10)	C30	C31	1.373(9)
N2	C5	1.349(9)	C18	C19	1.370(12)	C31	C32	1.455(9)
N4	C17	1.359(9)	C19	C20	1.385(11)	C7	C8	1.411(10)
N4	C21	1.345(9)	C20	C21	1.389(9)	C3	C4	1.392(11)
N1	C6	1.355(8)	C21	C22	1.469(10)	C4	C5	1.359(9)
N1	C10	1.371(9)	N3	C32	1.350(8)	C5	C6	1.478(11)
O3	C25	1.392(10)	C1	C2	1.348(10)	C6	C7	1.399(10)
O3	C26	1.380(10)	C2	C3	1.392(10)	N3	C22	1.403(8)

Table S28: Bond angels for **2d**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Cu1	O2[1]	111.8(2)	N1	C10	C11	131.4(7)
N2	Cu1	N4	121.1(2)	C11	C10	C8	121.7(7)
N4	Cu1	O2[1]	126.5(2)	C10	C11	C12	115.7(7)
N1	Cu1	O2[1]	84.8(2)	C16	C11	C10	127.1(7)
N1	Cu1	N2	81.1(2)	C16	C11	C12	117.2(7)
N1	Cu1	N4	95.3(2)	O1	C12	C11	121.1(7)
N1	Cu1	N3	175.8(2)	O1	C12	C14	118.4(8)

N3	Cu1	O2[1]	92.9(2)	C14	C12	C11	120.4(8)
N3	Cu1	N2	103.1(2)	C14	C13	C15	120.2(9)
N3	Cu1	N4	83.1(2)	C13	C14	C12	121.1(9)
C12	O1	C9	126.1(7)	C16	C15	C13	119.9(9)
C1	N2	Cu1	129.5(5)	C15	C16	C11	121.1(9)
C5	N2	Cu1	114.3(5)	N4	C17	C18	121.1(8)
C5	N2	C1	115.8(7)	C19	C18	C17	119.0(9)
C17	N4	Cu1	128.3(5)	C18	C19	C20	121.3(9)
C21	N4	Cu1	113.1(5)	C19	C20	C21	116.2(8)
C21	N4	C17	118.4(7)	N4	C21	C20	123.5(8)
C6	N1	Cu1	114.6(5)	N4	C21	C22	114.2(7)
C6	N1	C10	108.4(6)	C20	C21	C22	122.2(7)
C10	N1	Cu1	136.8(5)	N3	C22	C21	117.5(7)
C26	O3	C25	123.8(7)	C23	C22	N3	110.8(7)
C22	N3	Cu1	112.0(5)	C23	C22	C21	131.7(7)
C32	N3	Cu1	142.1(5)	C22	C23	C24	105.8(7)
C32	N3	C22	105.8(6)	C23	C24	C25	127.9(8)
C2	C1	N2	124.2(8)	C32	C24	C23	108.0(7)
C1	C2	C3	118.6(8)	C32	C24	C25	123.9(8)
C4	C3	C2	118.9(8)	O4	C25	O3	118.3(9)
C5	C4	C3	117.9(8)	O4	C25	C24	128.0(9)
N2	C5	C4	124.5(8)	O3	C25	C24	113.5(8)
N2	C5	C6	111.9(6)	O3	C26	C31	123.2(8)
C4	C5	C6	123.5(8)	C27	C26	O3	115.8(9)
N1	C6	C5	117.3(7)	C27	C26	C31	120.9(9)
N1	C6	C7	111.6(7)	C26	C27	C28	120.7(10)
C7	C6	C5	131.1(7)	C29	C28	C27	118.9(9)
C6	C7	C8	103.9(7)	C30	C29	C28	119.4(9)
C7	C8	C9	130.5(7)	C31	C30	C29	122.0(8)
C7	C8	C10	109.1(7)	C26	C31	C32	115.7(7)
C10	C8	C9	120.3(7)	C30	C31	C26	118.1(7)
O1	C9	C8	114.9(7)	C30	C31	C32	126.1(7)
O2	C9	O1	117.2(8)	N3	C32	C24	109.5(6)
O2	C9	C8	127.9(8)	N3	C32	C31	130.8(7)
N1	C10	C8	106.9(7)	C24	C32	C31	119.7(7)

EPR spectra of 1d, 1e, and 2d

X-band Electron Paramagnetic Resonance (EPR) spectra were recorded in acetonitrile solution at 77 K using a JES-FA200 ESR spectrometer. All measurements were performed under identical instrumental conditions. The microwave frequency was set to 9.1 GHz with a magnetic field centered at 500.00 mT and a sweep width of ±500.00 mT. Spectra were acquired over a sweep time of 30.0 s using a modulation frequency of 100.00 kHz and a modulation amplitude of 2.0 mT. The detection amplitudes were set to 25.0 for CH1 and 2.0 for CH2, and a time constant of 0.03 s was employed.

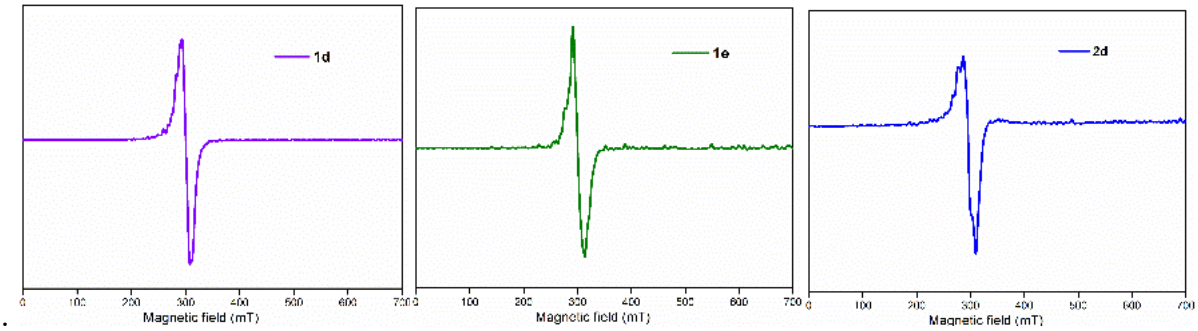


Figure S16: EPR spectra of **1d**, **1e**, and **2d** in acetonitrile.

Optimization of Heck coupling reaction.

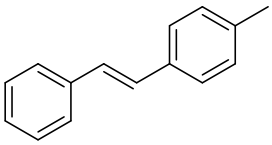
Bromobenzene (0.5 mmol), 4-methylstyrene (0.6 mmol), base (0.75 mmol), and catalyst (x mol%) were mixed in solvent (5.0 mL) and was stirred at specified temperature for a given time. After the completion of the reaction, the mixture was cooled, diluted with ethyl acetate (20.0 mL). Then it was filtered through a short pad of celite and filtrate was removed under reduced pressure; the crude product was purified by column chromatography to produce isolated yields.

General procedure for Heck coupling reaction.

Aryl bromide/iodide (0.5 mmol), 4-methylstyrene/acrylate (0.6 mmol), K_2CO_3 (0.75 mmol), catalyst **1b** (1.0 mol%), and ethanol (5.0 mL) was stirred at 120 ºC for 8 h. After the completion of the reaction, the mixture was cooled, diluted with ethyl acetate (30.0 mL). Then it was filtered through a short pad of celite, filtrate was removed under reduced pressure, and the crude product was purified by column chromatography using mixture of ethylacetate and hexane as eluent.

Specific procedures and characterization data for Heck coupling products 3a-3k

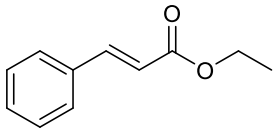
(E)-1-methyl-4-styrylbenzene (3a)



According to the general procedure, the reaction of 4-bromobenzene (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 3.7 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 2.36 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-

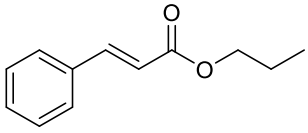
d) δ 137.66, 134.69, 129.54, 128.79, 128.76, 127.84, 127.54, 126.57, 126.53, 21.39. NMR spectroscopic data matched well with literature values.[3]

Ethyl cinnamate (3b)



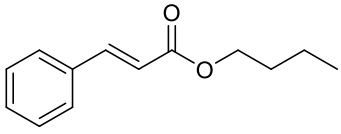
According to the general procedure, the reaction of 4-bromobenzene (0.5 mmol), ethyl acrylate (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.37 (p, *J* = 3.8, 3.1 Hz, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.08, 134.54, 130.29, 128.95, 128.12, 118.35, 60.57, 14.40. NMR spectroscopic data matched well with literature values. [4]

Propyl cinnamate (3c)



According to the general procedure, the reaction of 4-bromobenzene (0.5 mmol), propyl acrylate (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.37 (s, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.17 (td, *J* = 6.9, 1.9 Hz, 2H), 1.73 (q, *J* = 7.0 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.20, 144.67, 134.57, 130.31, 128.15, 118.38, 66.25, 22.20, 10.56. NMR spectroscopic data matched well with literature values.[5]

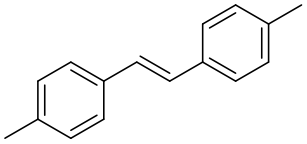
Butyl cinnamate (3d)



According to the general procedure, the reaction of 4-bromobenzene (0.5 mmol), butyl acrylate (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 16.0 Hz, 1H),

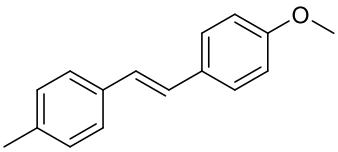
7.52 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.37 (dd, *J* = 5.0, 1.6 Hz, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.69 (p, *J* = 6.8 Hz, 2H), 1.44 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.17, 144.63, 134.55, 128.93, 128.12, 118.36, 64.50, 30.86, 19.28. NMR spectroscopic data matched well with literature values.[5]

1,2-di-p-tolylethene (3e)



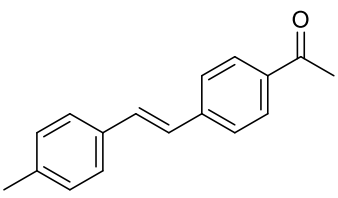
According to the general procedure, the reaction of 4-bromobenzene (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.04 (s, 2H), 2.36 (s, 6H). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.04 (s, 2H), 2.36 (s, 6H). NMR spectroscopic data matched well with literature values.[6]

(E)-1-methoxy-4-(4-methylstyryl)benzene (3f)



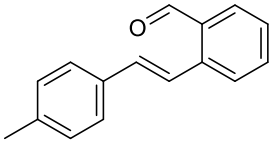
According to the general procedure, the reaction of 4-bromoanisole (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 13.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.28, 137.19, 135.00, 130.48, 129.49, 127.71, 127.36, 126.70, 126.30, 114.25, 55.46, 21.36. NMR spectroscopic data matched well with literature values.[6]

(E)-1-(4-(4-methylstyryl)phenyl)ethan-1-one (3g)



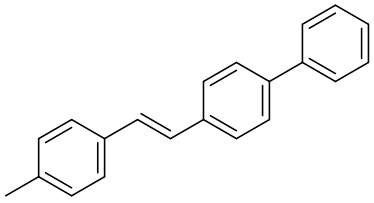
According to the general procedure, the reaction of 4-bromacetophenone (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.08 (d, *J* = 16.3 Hz, 1H), 2.61 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.68, 142.40, 138.53, 135.90, 134.07, 131.58, 129.67, 129.02, 126.90, 126.58, 126.50, 26.72, 21.46. NMR spectroscopic data matched well with literature values.[7]

(E)-2-(4-methylstyryl)benzaldehyde (3h)



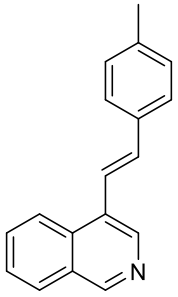
According to the general procedure, the reaction of 2-bromobenzaldehyde (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.33 (s, 1H), 7.99 (d, *J* = 16.2 Hz, 1H), 7.84 (d, *J* = 6.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.84, 140.40, 138.53, 134.29, 134.22, 133.86, 133.01, 132.27, 129.64, 127.57, 127.26, 127.06, 123.77, 21.46. NMR spectroscopic data matched well with literature values.[8]

(E)-4-(4-methylstyryl)-1,1'-biphenyl (3i)



According to the general procedure, the reaction of 1-bromobiphenyl (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 6H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 3.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.86, 140.26, 137.73, 136.73, 134.70, 129.57, 128.84, 127.47, 127.42, 127.34, 127.05, 126.96, 126.59, 21.41. NMR spectroscopic data matched well with literature values.[9]

(E)-4-(4-methylstyryl)isoquinoline (3j)



According to the general procedure, the reaction of 4-bromoisoquinoline (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), and catalyst **2a** (1.0 mol%) afforded the title compound after work-up and chromatography. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 8.85 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.28 (m, 4H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.74, 140.32, 138.41, 134.46, 133.99, 133.39, 130.66, 129.67, 128.33, 127.39, 126.91, 123.13, 121.45, 21.46. NMR spectroscopic data matched well with literature values.[10]

Hot filtration test

Bromobenzene (0.5 mmol), 4-methylstyrene (0.6 mmol), K_2CO_3 (0.75 mmol), catalyst **1b** (1.0 mol%), and ethanol (5.0 mL) was stirred at 120 ºC. After 2 hours, the reaction mixture was filtered through a short pad of celite in hot condition and again stirred for next 6 h. After completion of the reaction, the mixture was cooled, diluted with ethyl acetate (30.0 mL). Then it was filtered through a short pad of celite and filtrate was removed under reduced pressure. The crude product was purified by preparative thin layer chromatography and the yield of product (**3a**) was 82%.

HRMS analysis of Heck coupling reaction mixture

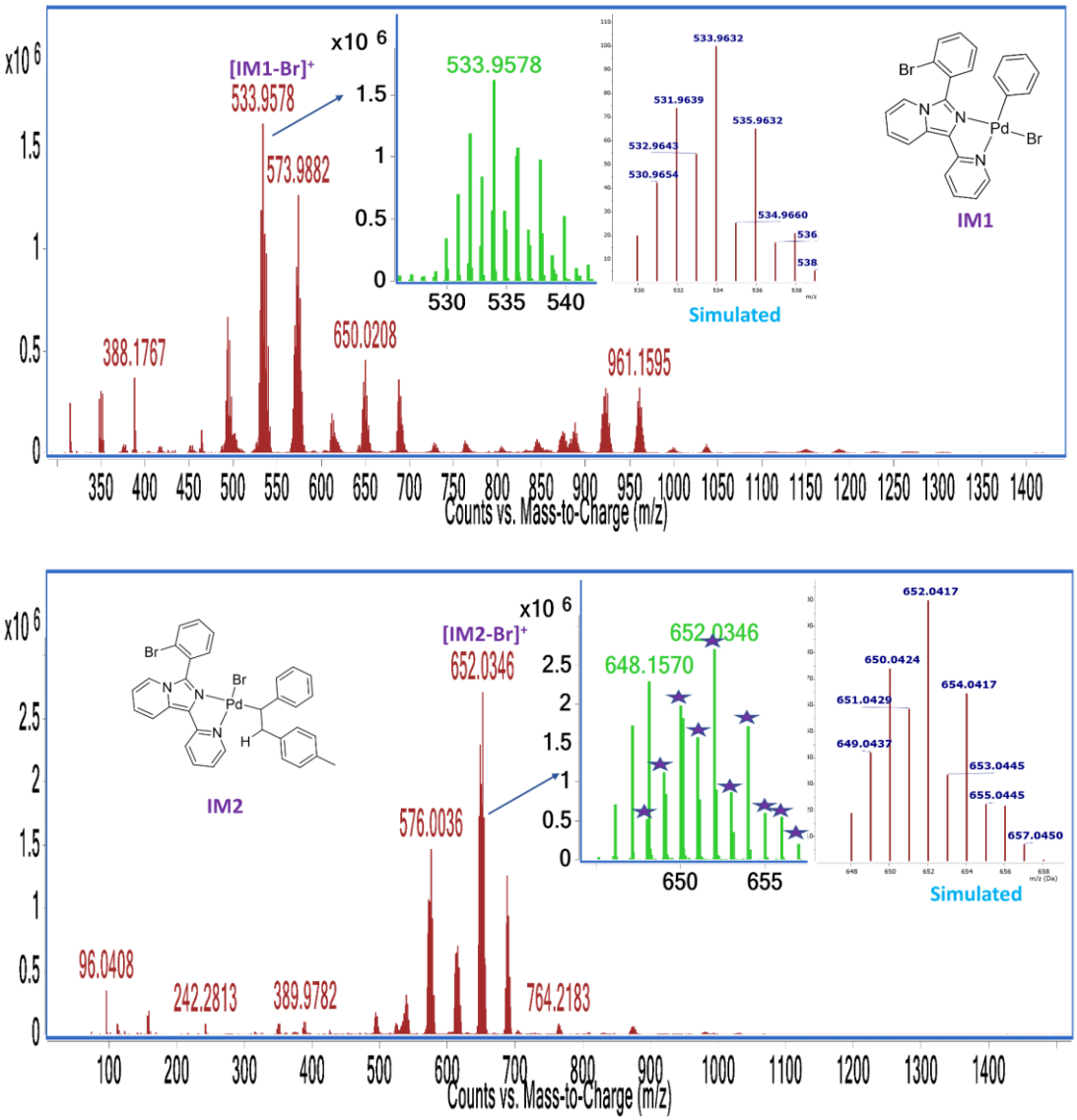
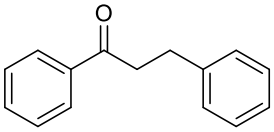


Figure S17: HRMS spectra of Heck coupling reactions mixture. Inset expanded (green) and simulated (red) spectra.

Optimization of α-alkylation of ketone

Under nitrogen atmosphere, acetophenone (0.5 mmol), benzyl alcohol (0.6 mmol), base (0.5 mmol), and catalyst (x mol%) were mixed in solvent (5.0 mL) and was stirred at specified temperature for a given time. After the completion of the reaction, the mixture was cooled, diluted with ethyl acetate (20.0 mL). Then it was filtered through a short pad of celite and filtrate was removed under reduced pressure; the crude product was purified by column chromatography to produce isolated yields.

1,3-Diphenylpropan-1-one (4a)



Acetophenone (1.0 mmol), benzyl alcohol (1.2 mmol), KOH (1.0 mmol), and catalyst **1a** (1.0 mol%) were taken in toluene (5.0 mL) and was stirred at 110 ºC for 12 h under nitrogen atmosphere. After the completion of the reaction, the mixture was cooled, diluted with ethyl acetate (30.0 mL). Then it was filtered through a short pad of celite, filtrate was removed under reduced pressure, and the crude product was purified by column chromatography using a mixture of ethylacetate and hexane as eluent to afford **4a** as white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.47 – 7.43 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.18 (td, *J* = 8.3, 7.7, 5.9 Hz, 4H), 7.14 – 7.10 (m, 1H), 3.24 – 3.16 (m, 2H), 3.01 – 2.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.34, 141.39, 136.95, 133.17, 128.71, 128.63, 128.53, 128.14, 126.24, 40.55, 30.23. NMR spectroscopic data matched well with literature values.[11]

Biomolecule interaction studies

DNA Binding Study:

The interaction of CT-DNA with **1c**–**1e**, **2c** and **2d** was screened by utilizing analytical methods such as UV−Vis and fluorescence spectroscopy. The experiments were performed at room temperature in Tris-HCl buffer (5 mM tris-HCl and 50 mM NaCl, pH = 7.2). The DNA stock solution was prepared in tris-HCl buffer and concentration was determined spectrophotometrically from the absorbance at 260 nm (molar extinction coefficient is 6600 M^{-1} cm^{-1}) and stored at 4 °C in dark. Further, the absorbance of DNA stock solution at 260 and 280 nm gave a ratio of 1.8, signifying that the DNA was adequately protein free. The titration experiment was carried out with fixed complex concentration (15 μM) to which DNA (0−15 μM) was gradually added for absorption measurement. For emission experiments, stock solution of ethidium bromide (EB) was prepared in deionized water. 10.0 μM of EB solution was mixed with 10.0 μM DNA solution and was titrated with variation of complex concentration (0–15 μM).

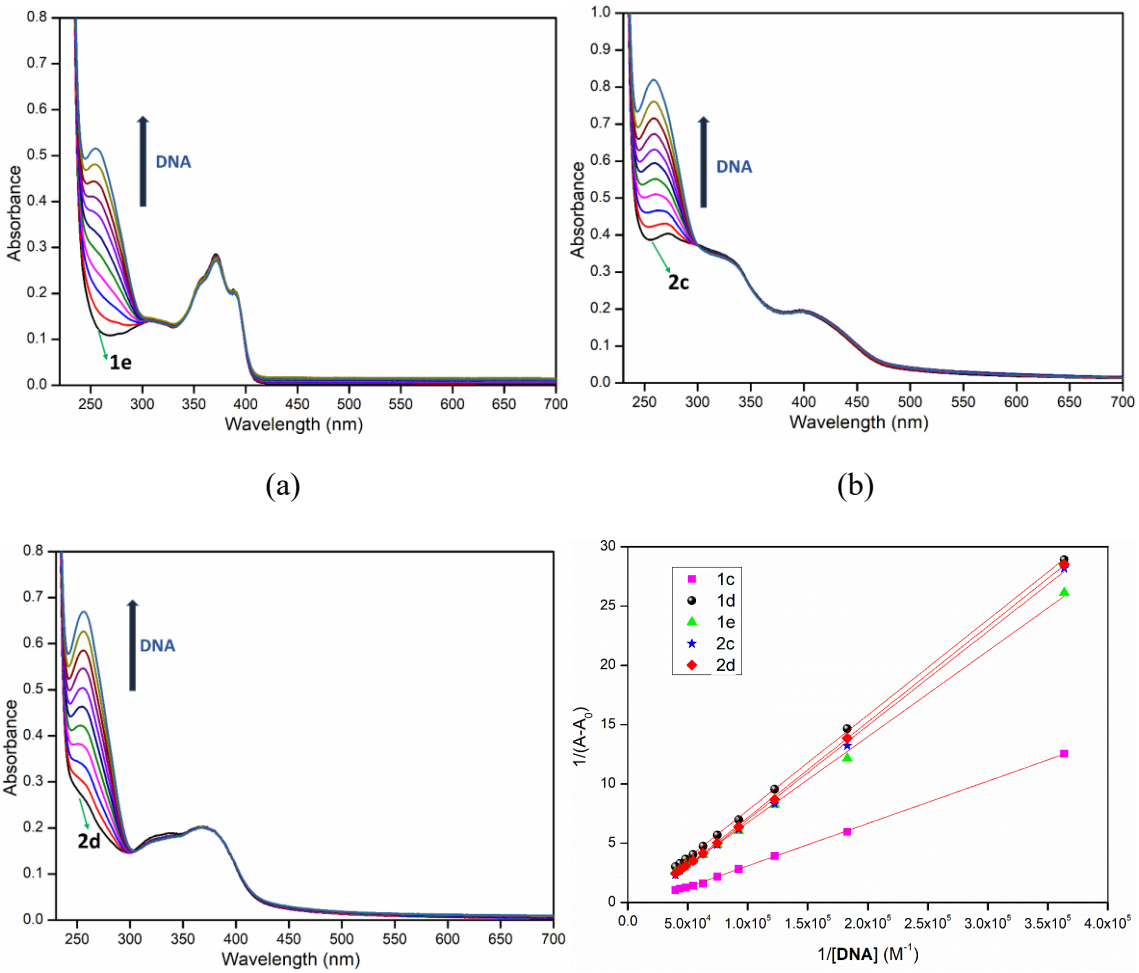


Figure S18: Absorption spectra of CT-DNA in the absence and presence of **1e** (a), **2c** (b), and **2d** (c). The Benesi-Hilderbrand plots for **1c**–**1e**, **2c** and **2d**. Adj. R-Square: 0.99936, 0.99978, 0.99862, 0.99888, and 0.99966 for **1c**–**1e**, **2c** and **2d** respectively.

Equation S1. Benesi-Hilderbrand equation (S1) used to calculate the intrinsic binding constant binding constant K_b in DNA binding study.

$$\frac{1}{A_{obs}-A_0} = \frac{1}{A_{max}-A_0} + \frac{1}{K_b(A_{max}-A_0)[Complex]} \qquad (S1)$$

Where [DNA] is the concentration of DNA in base pairs, A_0, A_{obs}, and A_{obs} are the absorbances of free complex, complex in presence of DNA, and for the complex in the fully bound form respectively. The binding constant K_b can be obtained from the plot $1/(A_{obs} - A_0)$ versus [Complex].

Equation S2. The Gibbs free energy (ΔG) was calculated using equation S2 as given below.

$$\Delta G = -RT \ln Kb \qquad (S2)$$

Equation S3. The Stern−Volmer equation (eq. S3) used to calculate Stern– Volmer quenching constant (K_{SV}) and the biomolecular quenching constant (K_q).

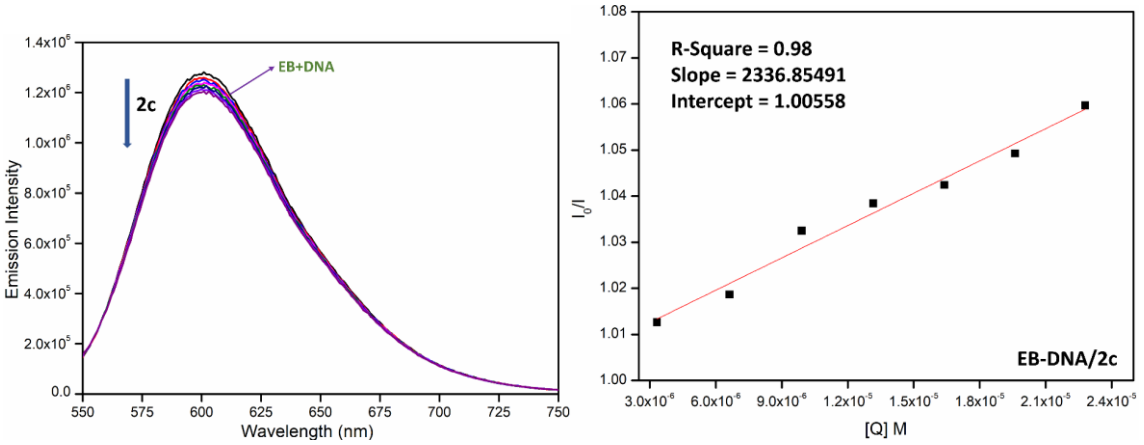
$$\frac{I_0}{I} = 1 + K_{SV}[Q] = 1 + K_q\tau_0[Q] \qquad \text{(S3)}$$

where I_0 and I represent the fluorescence intensities in absence and presence of the quencher 'Q' (here Q is the studied complexes) respectively. [Q] is the quencher concentration, and K_{SV} denotes the Stern– Volmer quenching constant calculated from the plot of I_0/I *vs* [Q], K_q is the biomolecular quenching constant and τ_0 is the mean lifetime of the fluorophore=23ns.

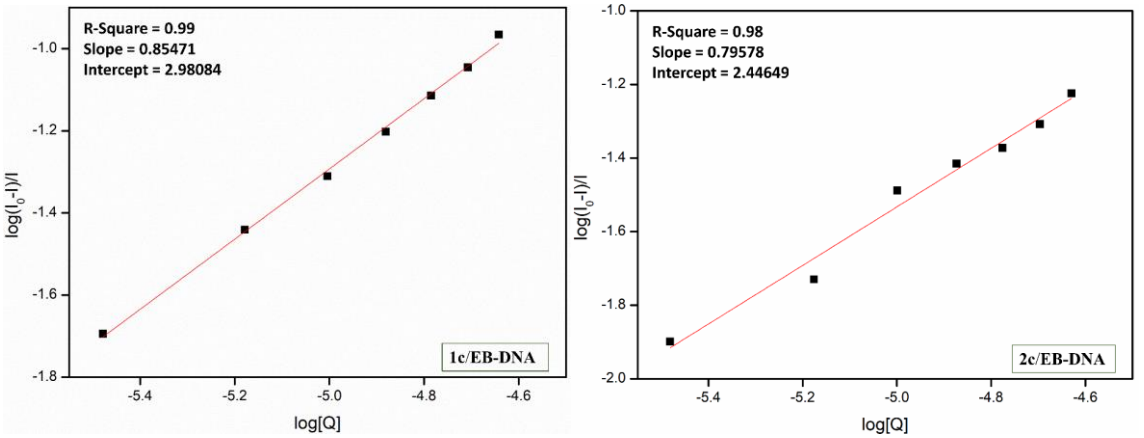
Equation S4. The Scatchard equation (eq. S4) used to find the binding constant (K_b) and the number of binding sites(n)

$$log(\frac{I_0-I}{I}) = logKb + nlog[Q] \qquad \text{(S4)}$$

where I_0, I and Q are the same as in Stern−Volmer equation. The binding constant K_b is the intercept of log $(I_0 - I)/I$ *vs* log [Q] plot. The number of binding sites per nucleotide is n and can be been obtained from the slope.



(a) (b)



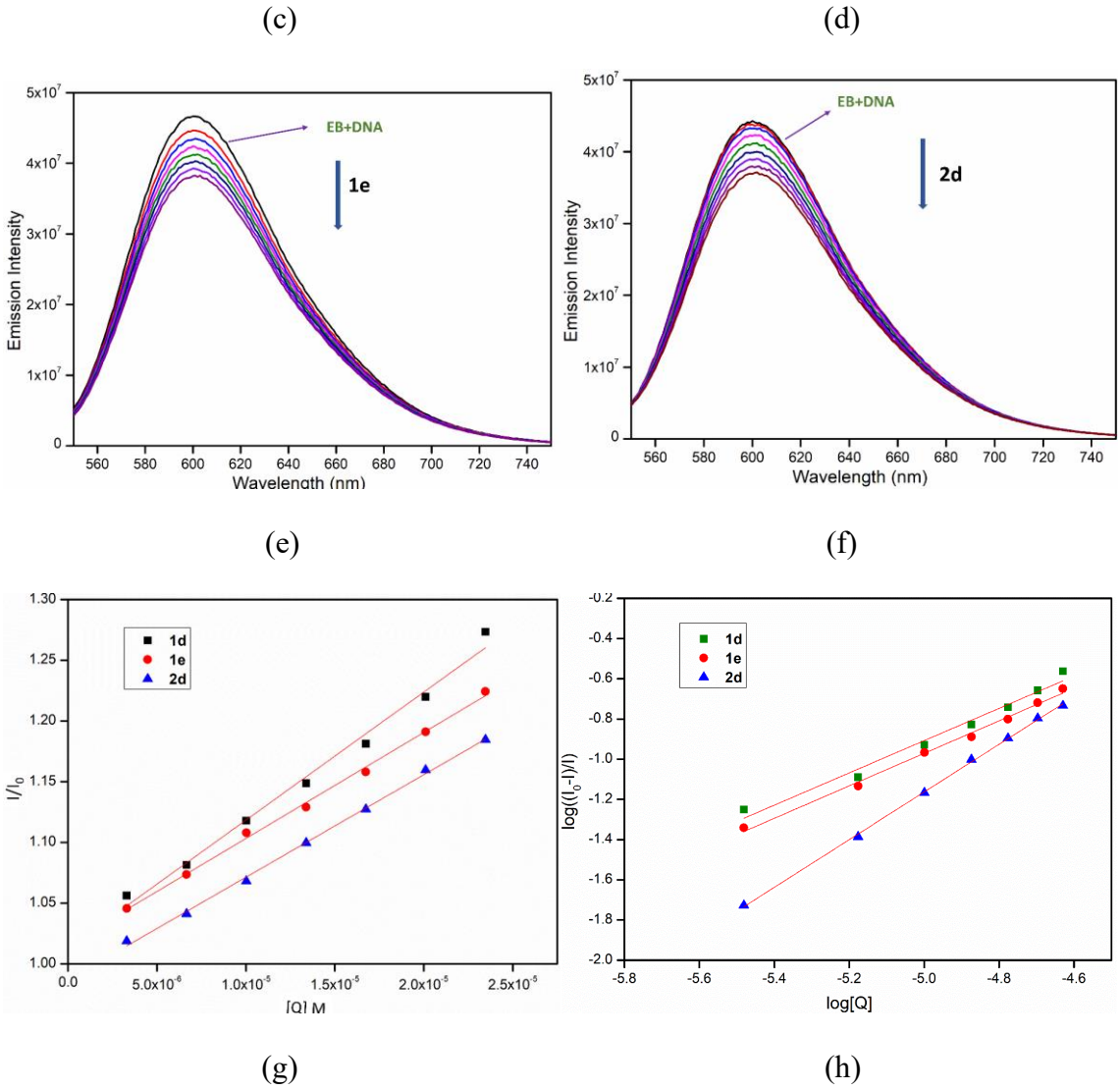


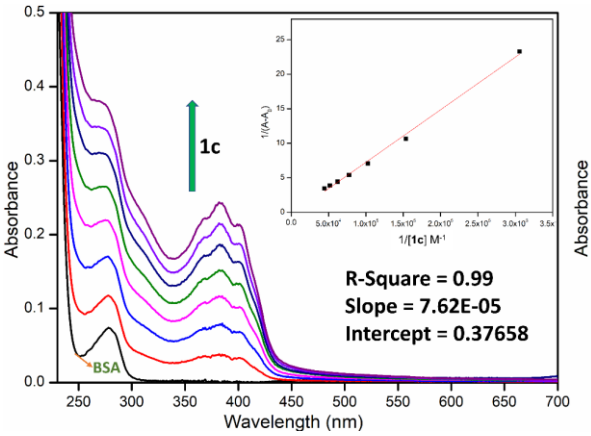
Figure S19: Emission spectra of EB-DNA in the absence and presence of **2c** (a), **1e** (e) and **2d** (f) Stern-Volmer plots for **2c** (b), **1d–2d** (g). R-Square: 0.98755, 0.99685, 0.99776 for **1d–2d**. Scatchard plots for **1c** (c) **2c** (d) and **1d–2d** (h).

Table S29: K_{SV}, K_q, K_b, and n values of EB-DNA interaction with **1c**–**1e**, **2c** and **2d**.

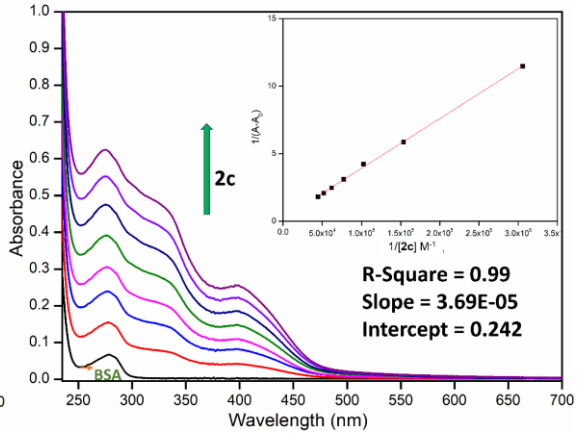
Complexes	K_{SV} (10^4 M^{-1})	K_q (10^{12} M^{-1} s^{-1})	K_b (10^4 M^{-1})	ΔG (kcal mol^{-1})	n
1c	0.44	0.19	0.1	4.06	0.855
2c	0.23	0.10	0.03	3.34	0.80
1d	1.05	0.46	0.13	4.23	0.80
1e	0.87	0.38	0.12	4.19	0.81
2d	0.84	0.37	5.8	6.50	1.18

BSA Binding Study:

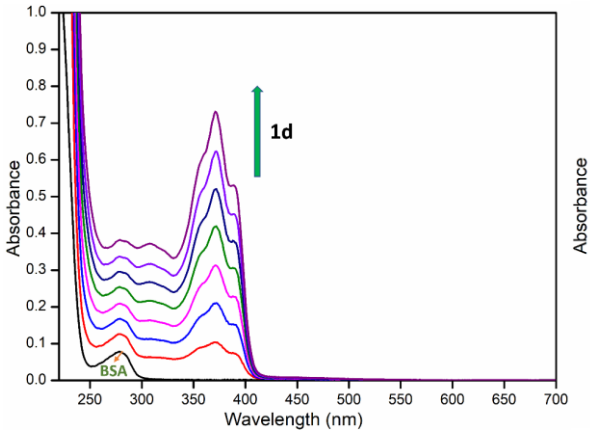
The binding study of **1c**–**1e**, **2c** and **2d** with BSA was performed using fluorescence spectroscopy. BSA stock solution was prepared by dissolving in HEPES buffer (10.0 mM, pH= 7.4) and concentration was determined from the absorbance at 278 nm (molar extinction coefficient 4.4 × 10^4 M^{-1} cm^{-1}). Stock solutions of complexes were prepared in DMSO and diluted in HEPES buffer for analysis. Titration study was carried out with a constant BSA concentration (15 µM) and gradually increasing concentration of complexes (0–16 µM). The excitation was set at 285 nm and emission spectra were collected in the range of 280–500 nm at 25 °C.



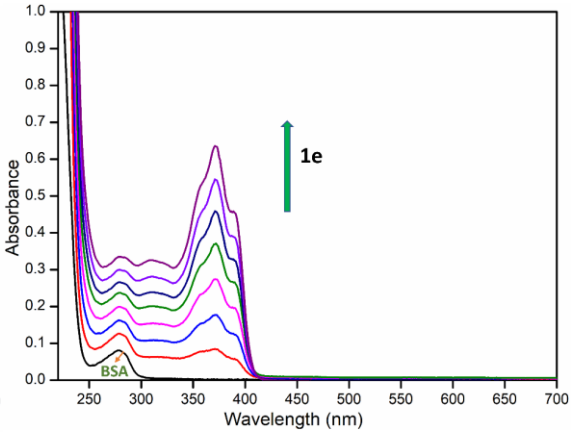
(a)



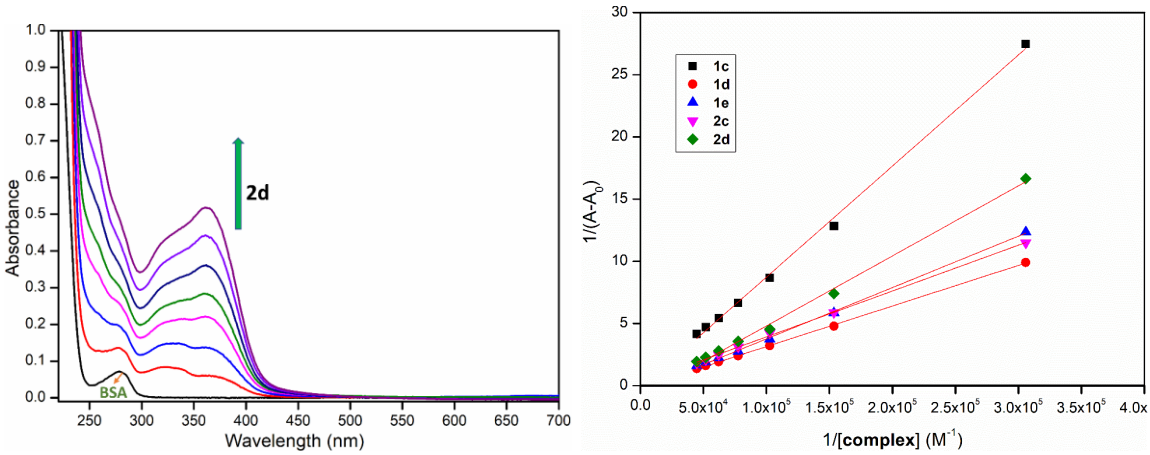
(b)



(c)



(d)

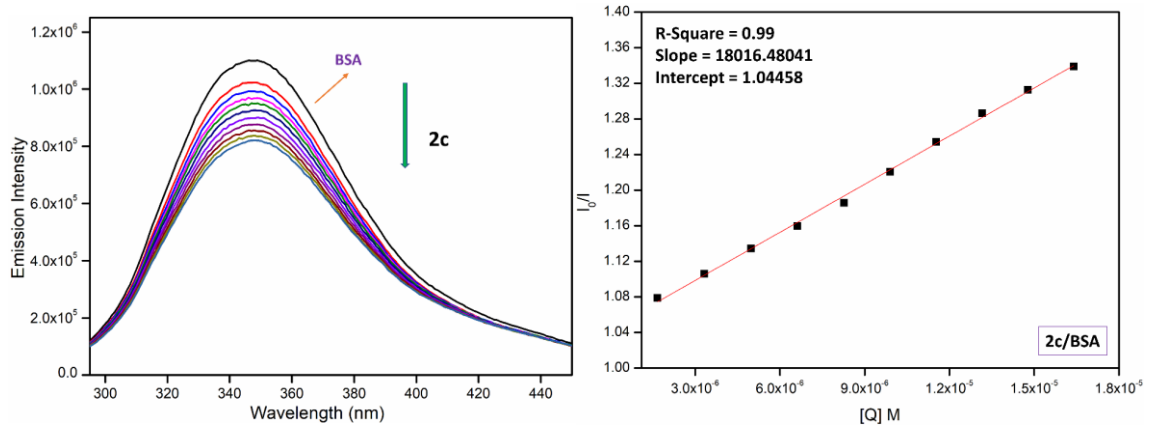


(e) (f)

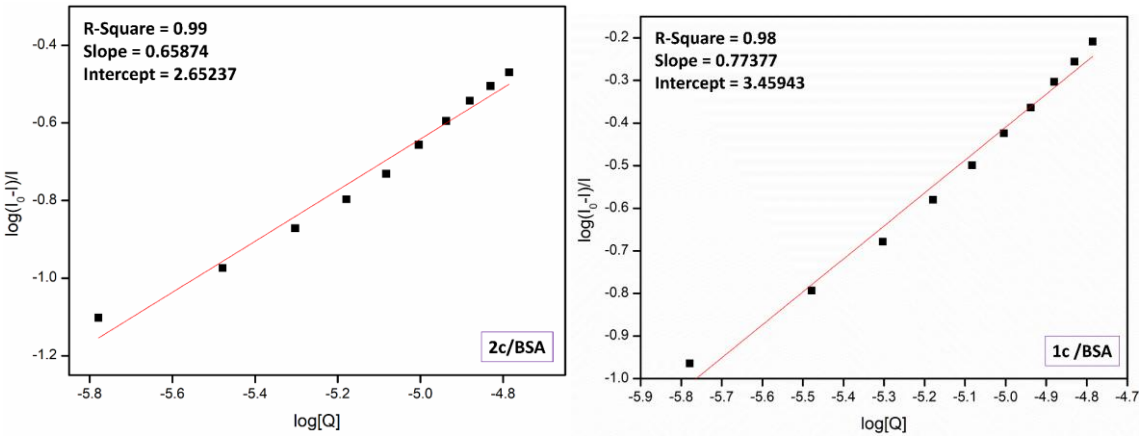
Figure S20: Absorption spectra of BSA in the absence and presence of **1c** (a), **2c** (b), **1d** (c), **1e** (d) and **2d** (e). The Benesi-Hilderbrand plots for **1c**–**1e**, **2c** and **2d**. Adj. R-Square: 0.99732, 0.99957, 0.99894, 0.99898, 0.99615, and 0.99966 for **1c**–**1e**, **2c** and **2d** respectively.

Table S30: K_b and ΔG values from UV-Vis titration of BSA with **1c**–**1e**, **2c** and **2d** individually.

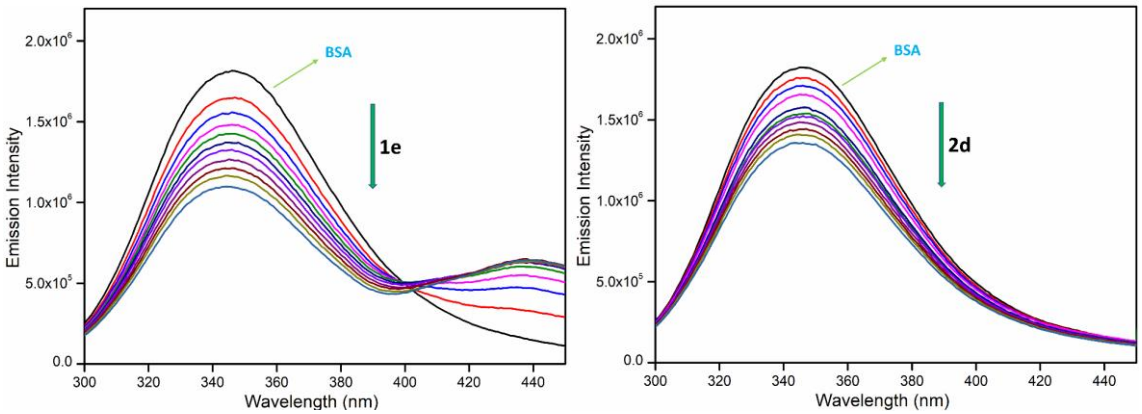
Complexes	**1c**	**2c**	**1d**	**1e**	**2d**
K_b ($\times 10^4\ M^{-1}$)	0.49	0.65	0.37	0.88	1.46
ΔG (Kcal mol^{-1})	5.04	5.21	4.87	5.38	5.69



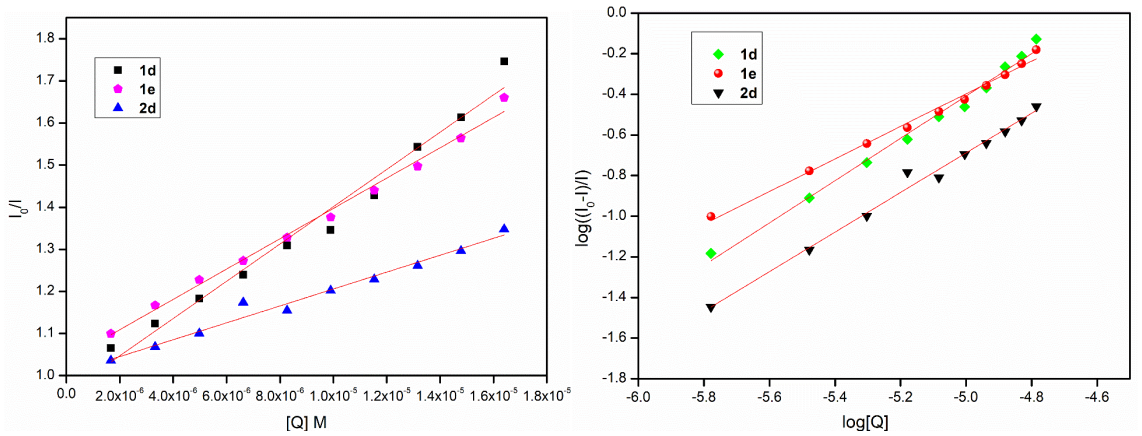
(a) (b)



(c) (d)



(e) (f)

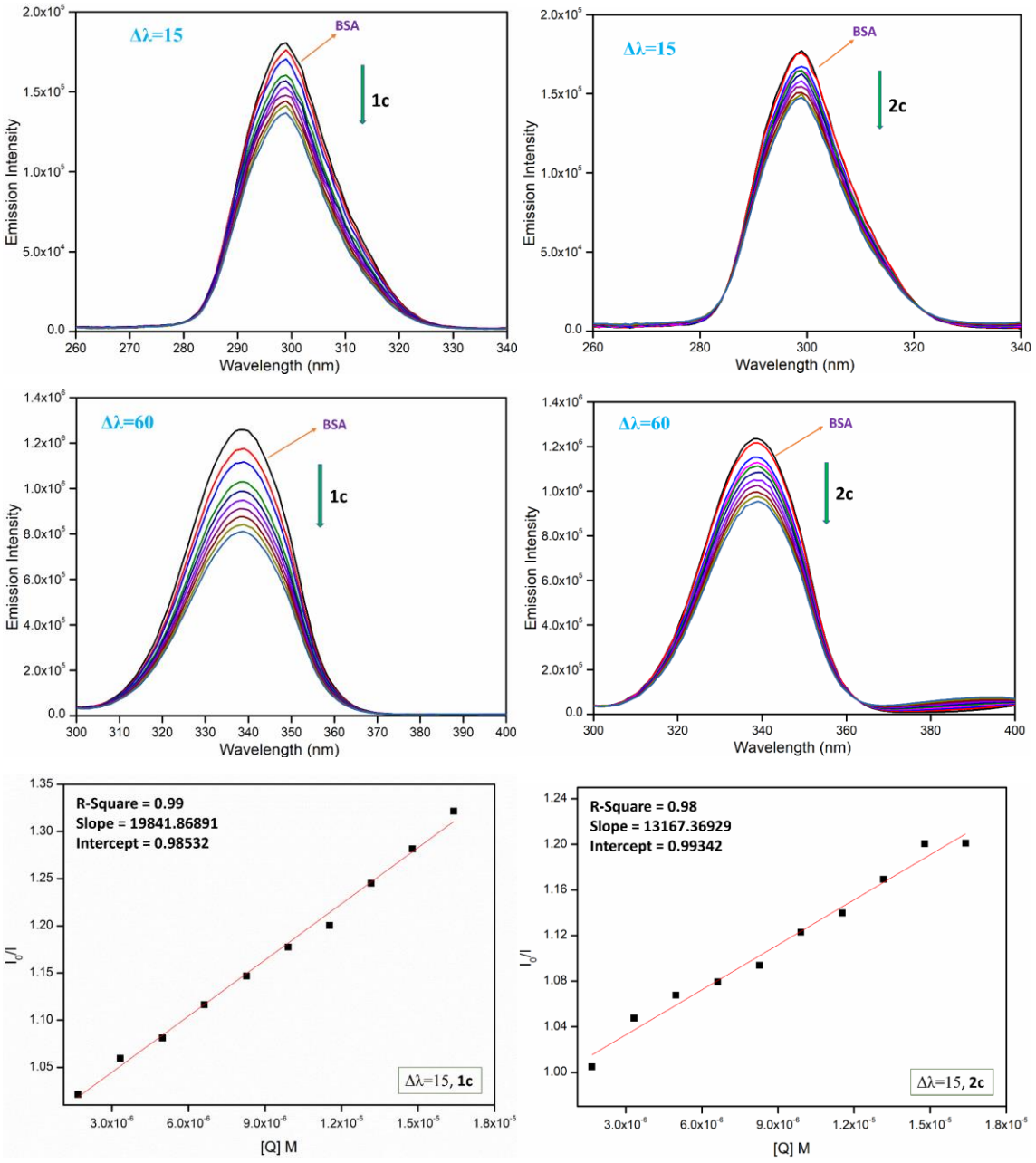


(g) (h)

Figure S21: Emission spectra of BSA in the absence and presence of **2c** (a), **1e** (e), and **2d** (f). The Stern-Volmer plots for **2c** (b), **1d**–**2d** (g), R-Square: 0.994, 0.994, 0.975 for **1c**–**1e**, **2c** and **2d** respectively. Scatchard plots for **1d**–**2d** (h) R-Square: 0.99703, 0.997, 0.95902. for **1c**–**1e**, **2c** and **2d** respectively.

Table 31: K_{SV}, K_q, K_b, and n values of BSA interaction with **1c**–**1e**, **2c** and **2d**.

Complexes	K_{SV} (10^4 M^{-1})	K_q (10^{12} M^{-1} s^{-1})	K_b (10^4 M^{-1})	ΔG (kcal mol^{-1})	n
1c	3.46	1.50	0.29	4.06	0.85
2c	1.80	0.78	0.04	3.34	0.80
1d	4.42	1.92	6.27	6.55	1.04
1e	3.60	1.56	0.41	4.93	0.80
2d	2.00	0.87	1.53	5.71	0.97



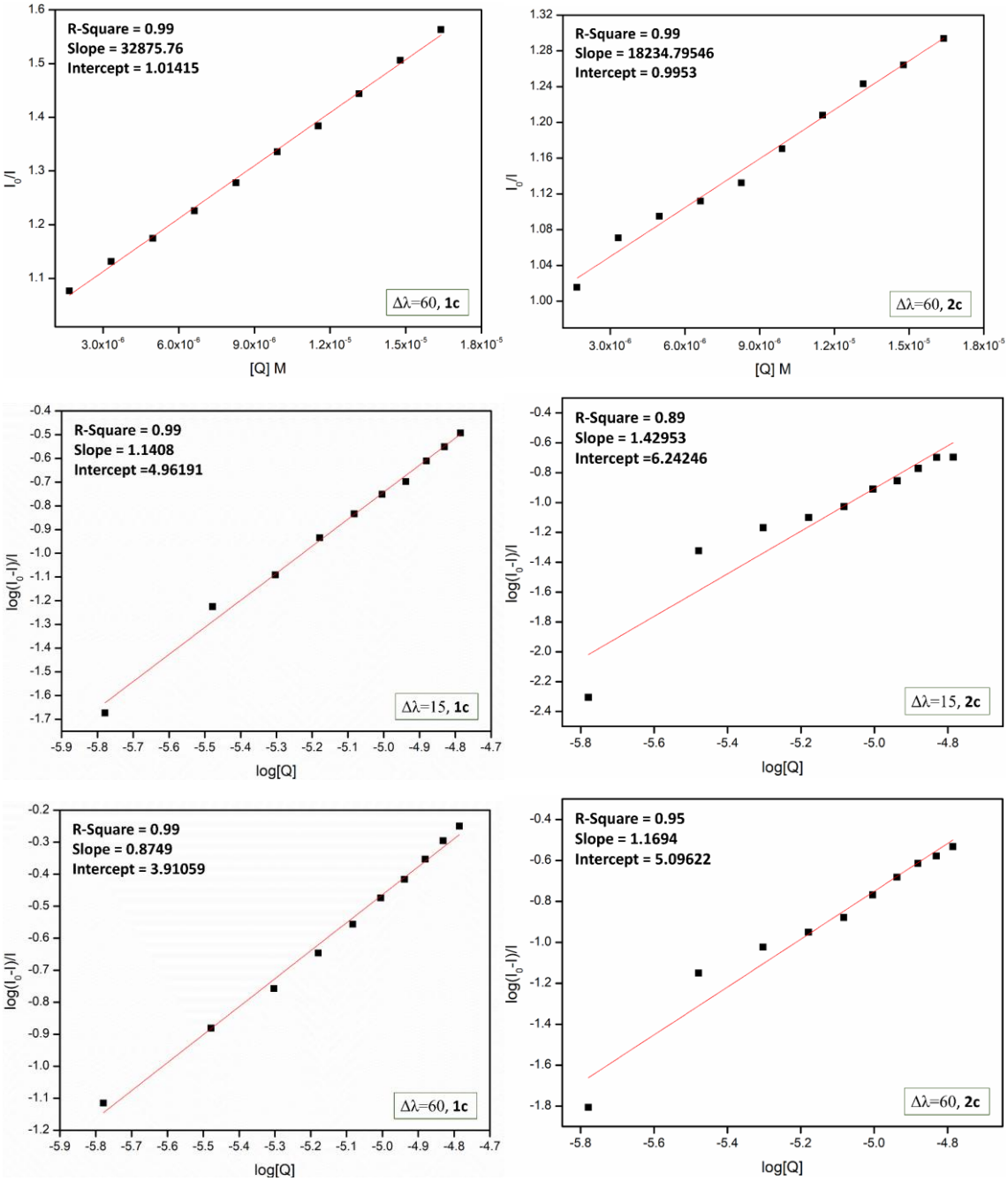


Figure S22: Synchronous emission spectra of BSA at Δλ = 15 and 60 nm in the absence and presence of **1c**, **2c** and their corresponding Stern-Volmer plots and Scatchard plots.

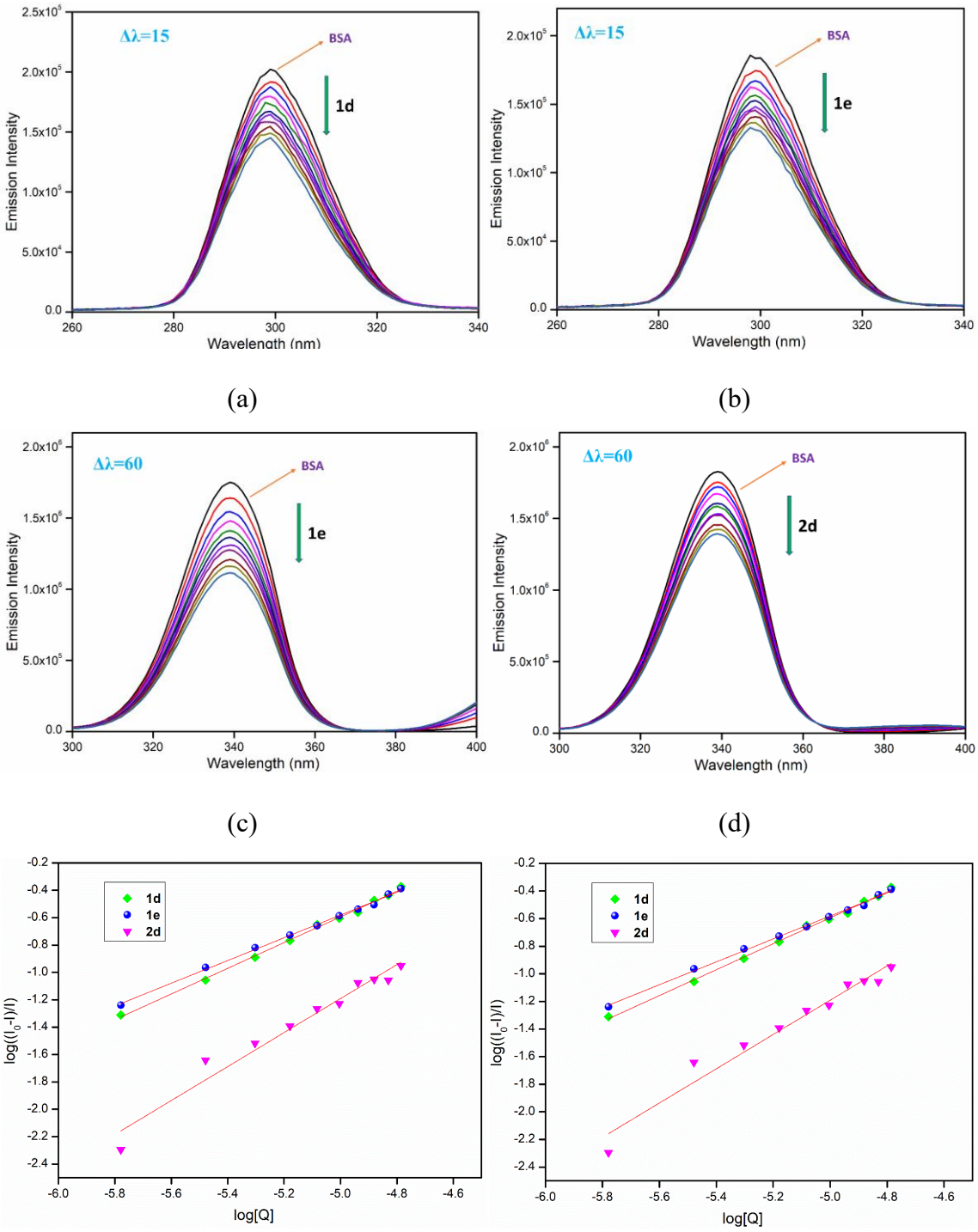


Figure S23: Synchronous emission spectra of BSA in the absence and presence of (a) **1d** at Δλ = 15 nm, (b) **1e** at Δλ = 15 nm, (c) **1e** at Δλ = 60 nm, (d) **2d** at Δλ = 60 nm. Sctachard plots for 1d, 1e, and 2d at Δλ = 15 nm (e) and 60 nm (f).

Table S32: K_{SV}, K_q, K_b, and n values of BSA (synchronous fluorescence data) for **1c**–**1e**, **2c** and **2d**.

Complexes	Δλ (nm)	K_{SV} ($\times 10^4$ M^{-1})	K_q (10^{12} M^{-1} s^{-1})	K_b ($\times 10^4$ M^{-1})	ΔG (kcal mol^{-1})	n
1c	15	1.98	0.86	9.16	6.76	1.14
2c	15	1.32	0.57	175	8.51	1.43
1d	15	2.47	1.07	1.26	5.60	0.94
1e	15	2.28	0.99	0.37	4.87	0.83
2d	15	0.68	0.29	1.04	6.85	1.24
1c	60	3.29	1.43	0.81	5.33	0.87
2c	60	1.82	0.79	12.5	6.95	1.17
1d	60	3.86	1.68	3.87	6.26	1.00
1e	60	3.28	1.43	1.33	5.63	0.92
2d	60	1.83	0.79	0.61	5.17	0.90

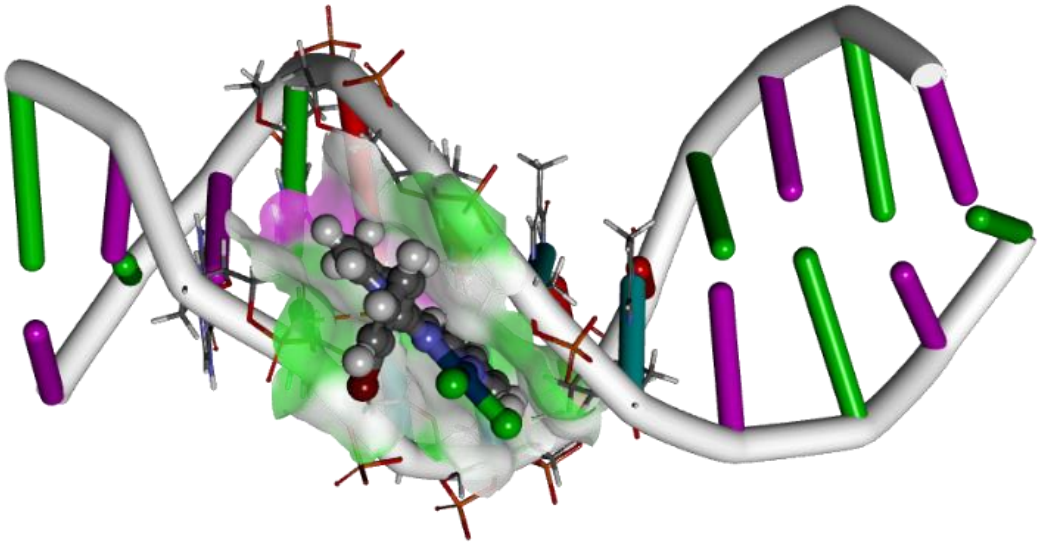
Steady-state fluorescence anisotropy

In HEPES buffer solution at pH 7.4, the fluorescence anisotropy of BSA in the absence and presence of the complexes **1c**–**1e**, **2c** and **2d** were recorded at 25 °C. The excitation slit (5 nm) and emission slit (10 nm) were set for the anisotropy study. The system was excited at 350 nm and emission wavelength was fixed at 533 nm. The following equation was used to determine the steady-state anisotropy (r).

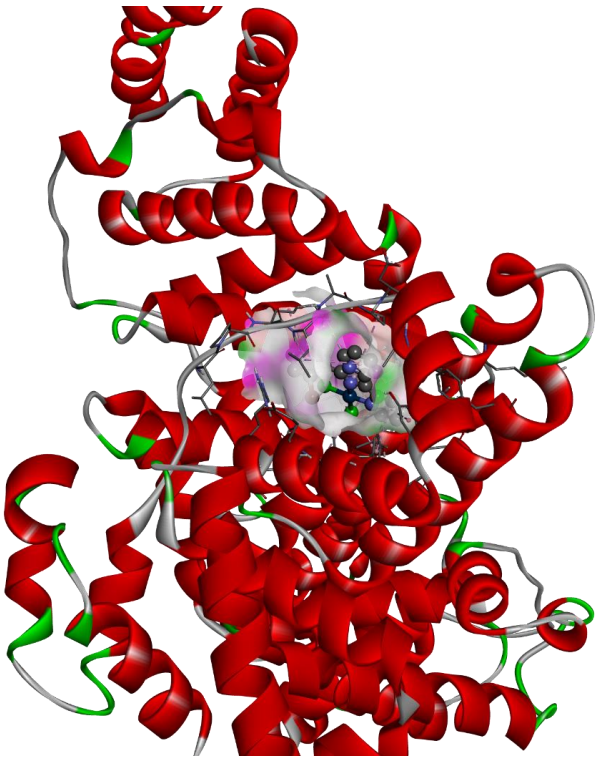
$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH})$$

$$G = I_{VH}/I_{HH}$$

Where G is the instrumental grating factor, I_{VV} and I_{VH} denotes the intensities obtained with the excitation polarizer in the vertical position and the emission polarizer in both the horizontal and vertical positions, respectively.



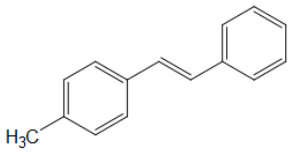
(a)

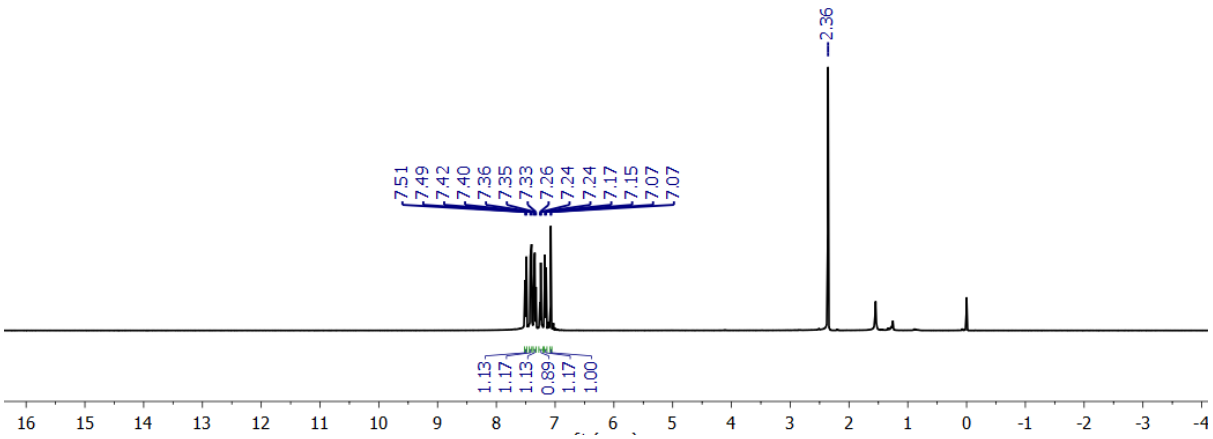


(b)

Figure S24: H-bond interaction of **1c** with (a) DNA (pdb id: 1BNA) and (b) BSA (pdb id-3vo3).

^{1}H and ^{13}C NMR spectra of catalytic products


H3C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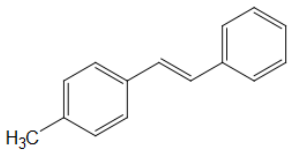
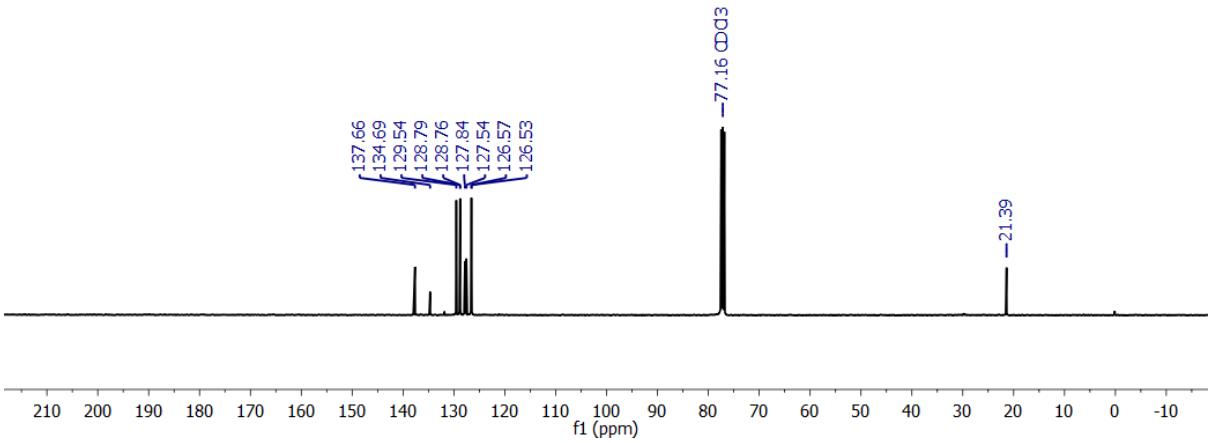
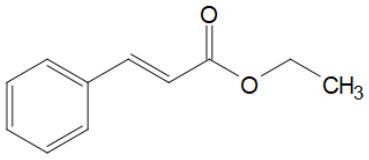
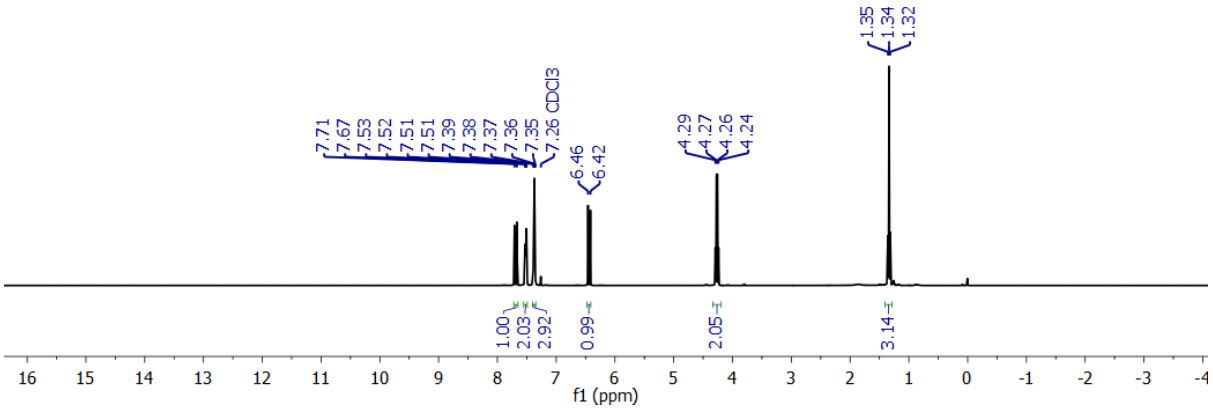
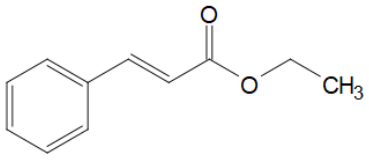
7.49
7.42
7.40
7.36
7.35
7.33
7.26
7.24
7.24
7.17
7.15
7.07
7.07
1.13
1.17
1.13
0.89
1.17
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4

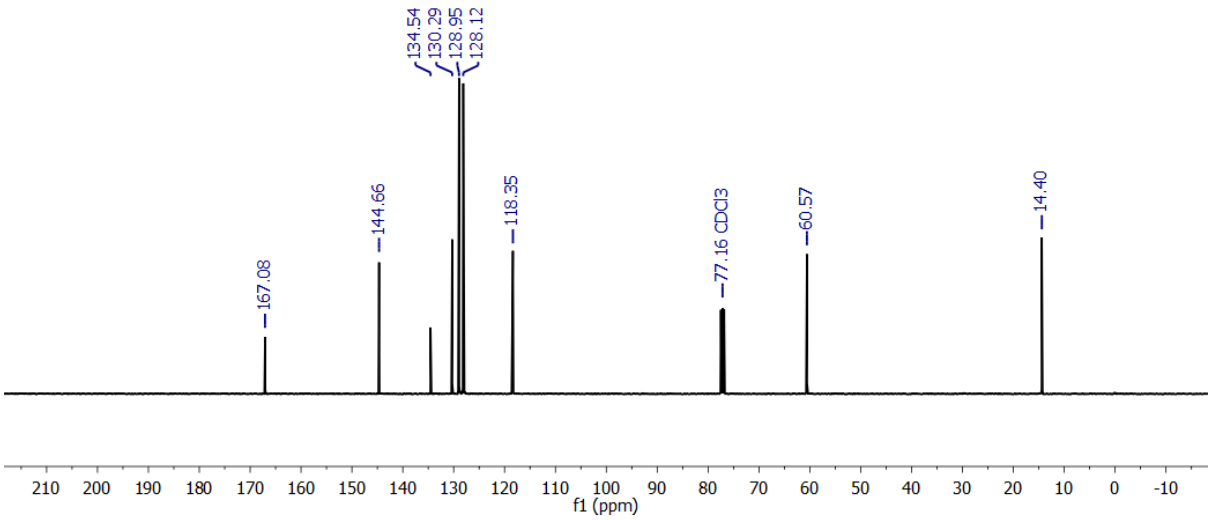

H3C


77.16 CDCl3
137.66
134.69
129.54
128.79
128.76
127.84
127.54
126.57
126.53
21.39
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)


O
O
CH3


7.71
7.67
7.53
7.52
7.51
7.51
7.39
7.38
7.37
7.36
7.35
7.26 CDCl3
6.46
6.42
4.29
4.27
4.26
4.24
1.35
1.34
1.32
1.00
2.03
2.92
0.99
2.05
3.14
f1 (ppm)


O
O
CH3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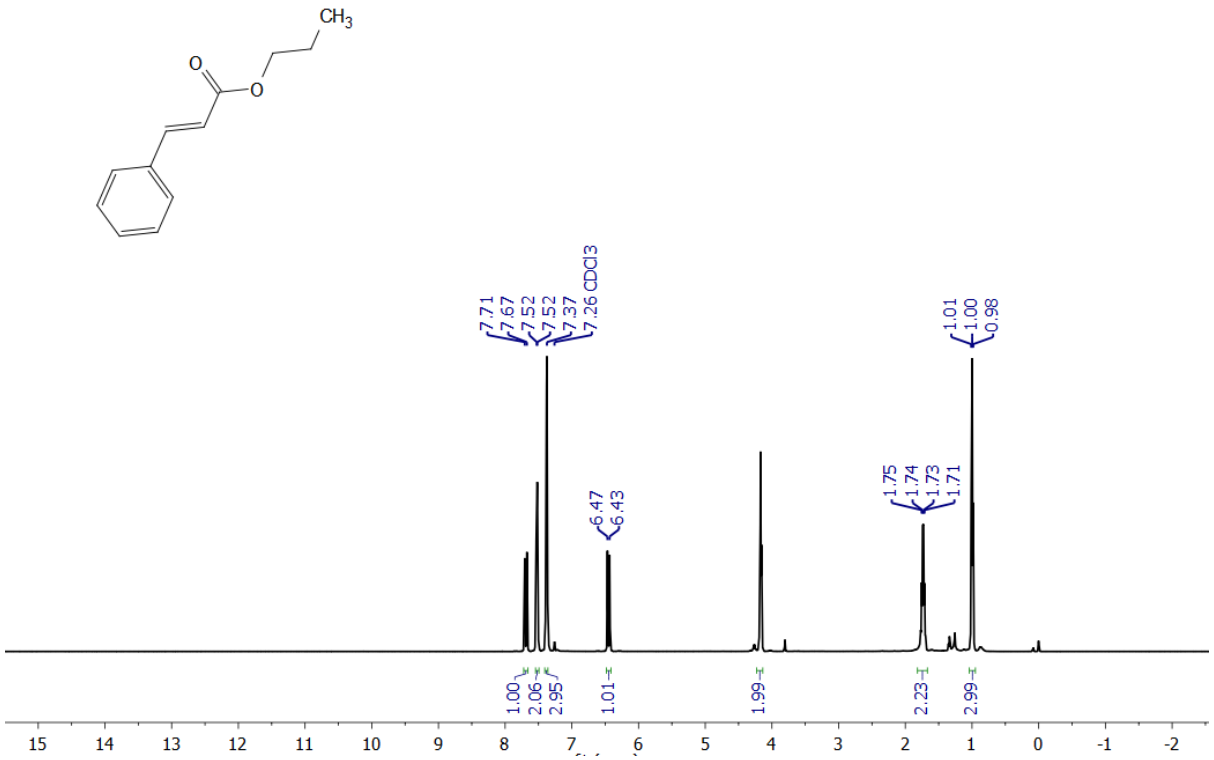
130.29
128.95
128.12
167.08
144.66
118.35
77.16 CDCl3
60.57
14.40
f1 (ppm)


CH3
O
O
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7.67
7.52
7.52
7.37
7.26 CDCl3
6.47
6.43
1.75
1.74
1.73
1.71
1.01
1.00
0.98
1.00
2.06
2.95
1.01
1.99
2.23
2.99
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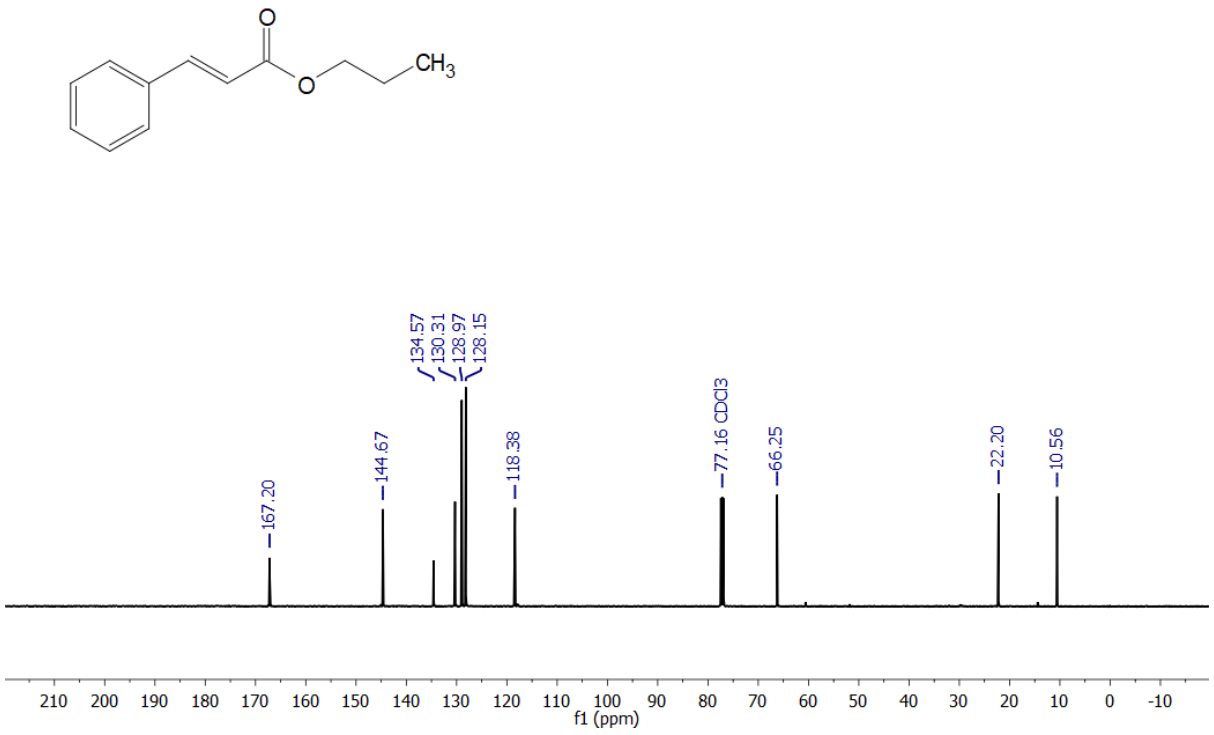
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O
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128.15
144.67
118.38
167.20
77.16 CDCl3
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22.20
10.56
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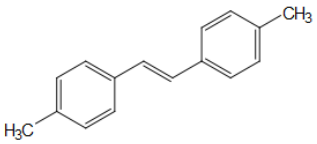
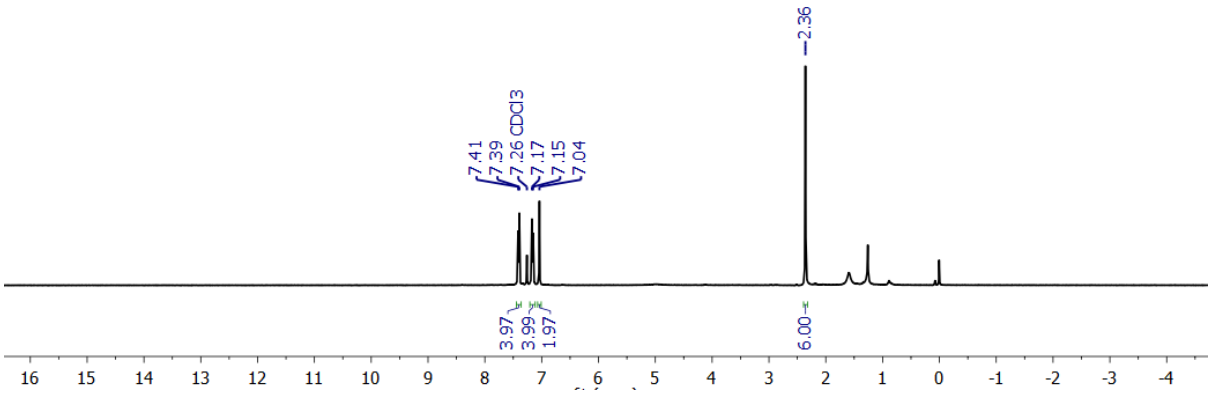
f1 (ppm)


CH3
H3C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7.41
7.39
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3.97
3.99
1.97
6.00
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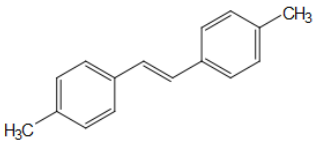
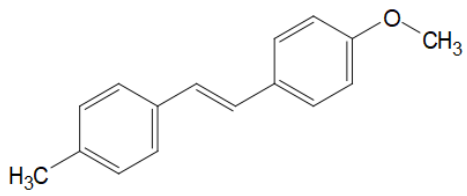
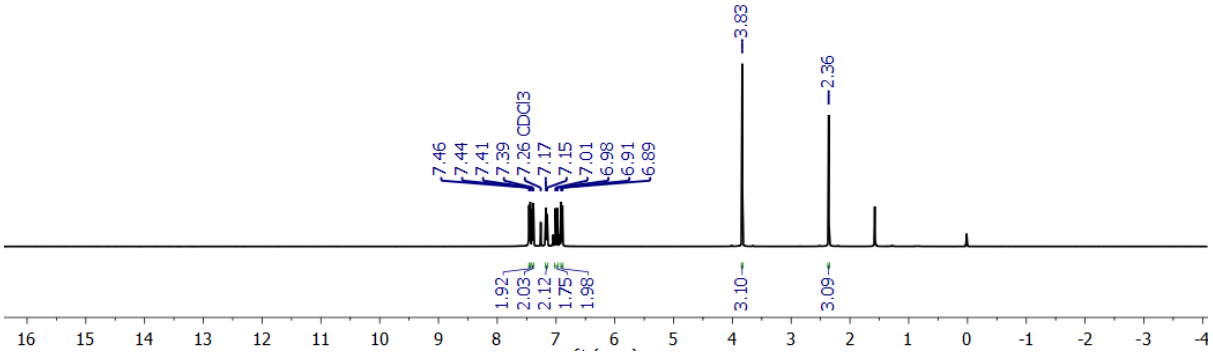

CH3
H3C

77.16 CDCl3
137.42
134.89
129.51
127.79
126.45
21.38
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)


O
CH3
H3C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7.39
7.26 CDCl3
7.17
7.15
7.01
6.98
6.91
6.89
3.83
2.36
1.92
2.03
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1.75
1.98
3.10
3.09
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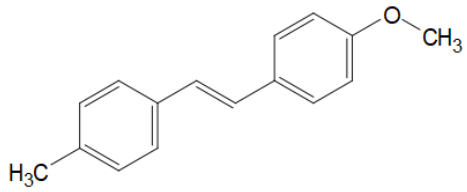
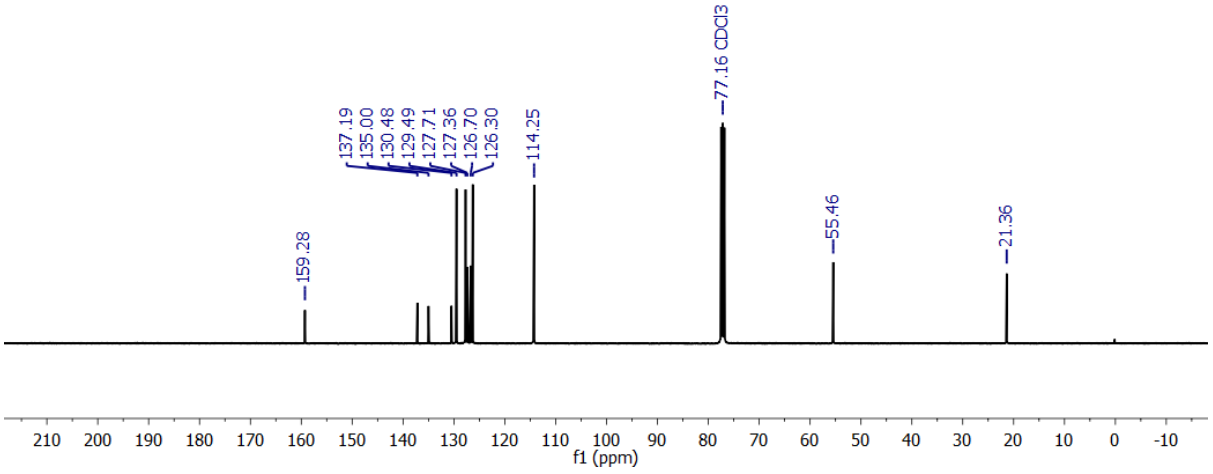

O
CH3
H3C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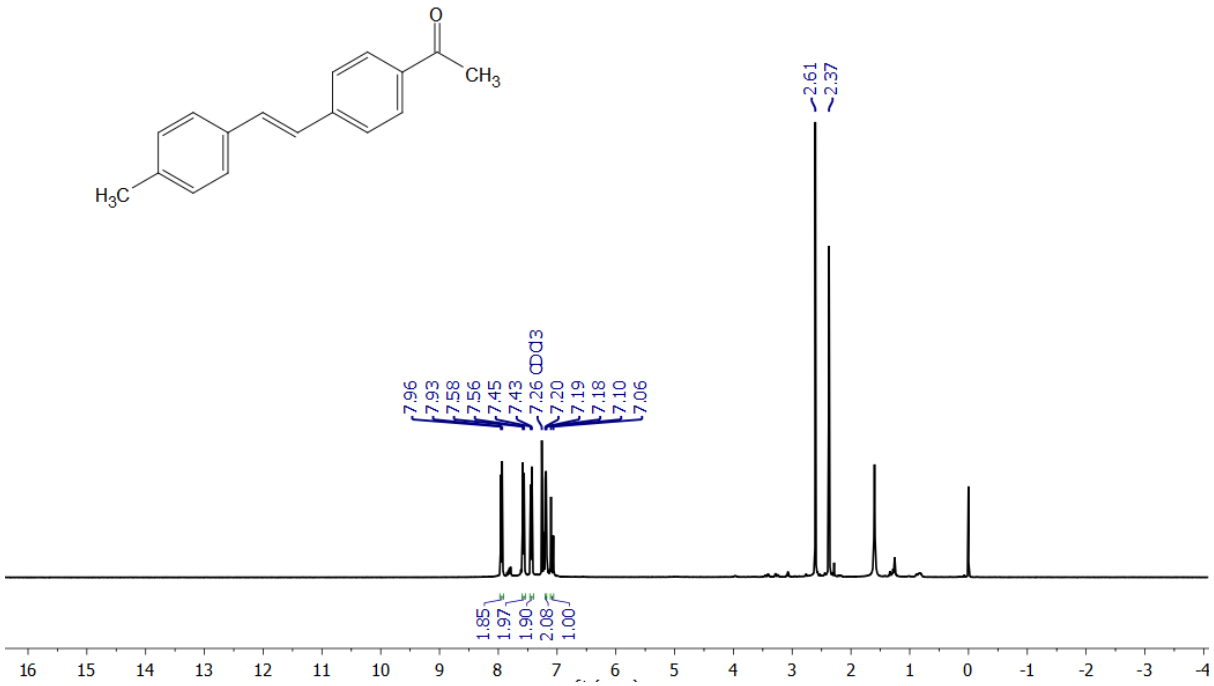
129.49
127.71
127.36
126.70
126.30
114.25
77.16 CDCl3
159.28
55.46
21.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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CH3
H3C
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7.56
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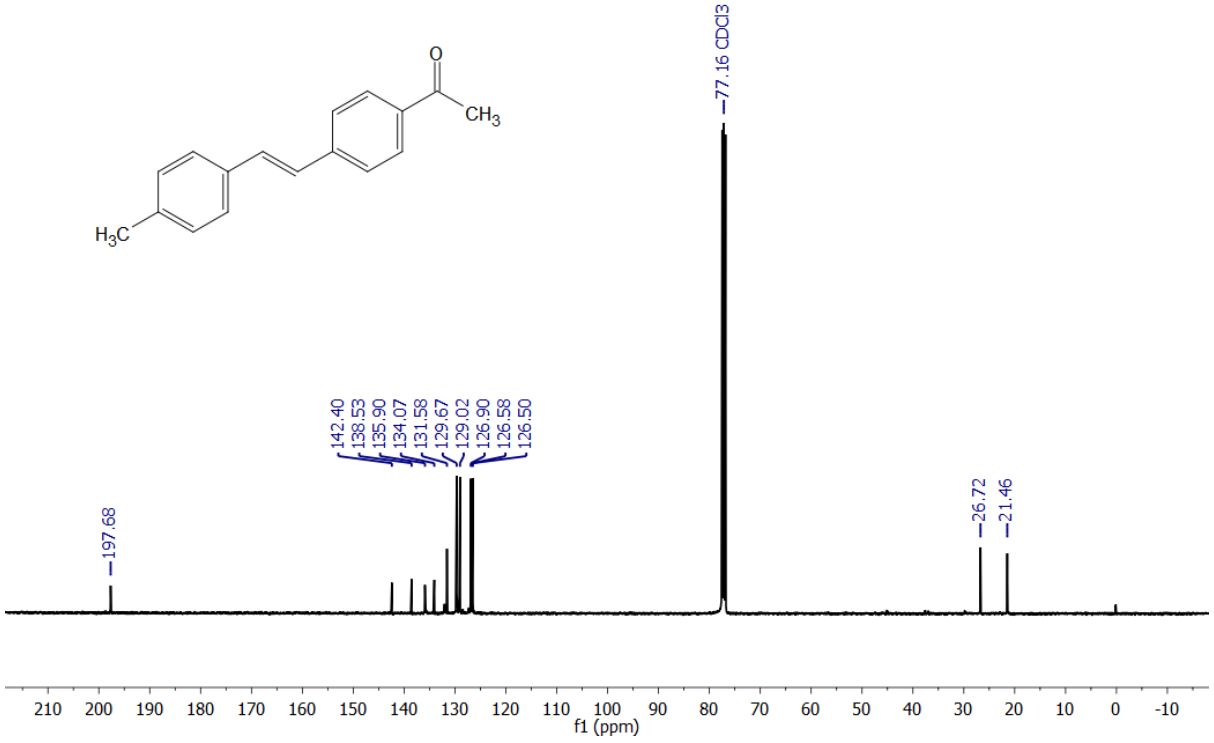
7.43
7.26 CDCl3
7.20
7.19
7.18
7.10
7.06
1.85
1.97
1.90
2.08
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4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CH3
H3C
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135.90
134.07
131.58
129.67
129.02
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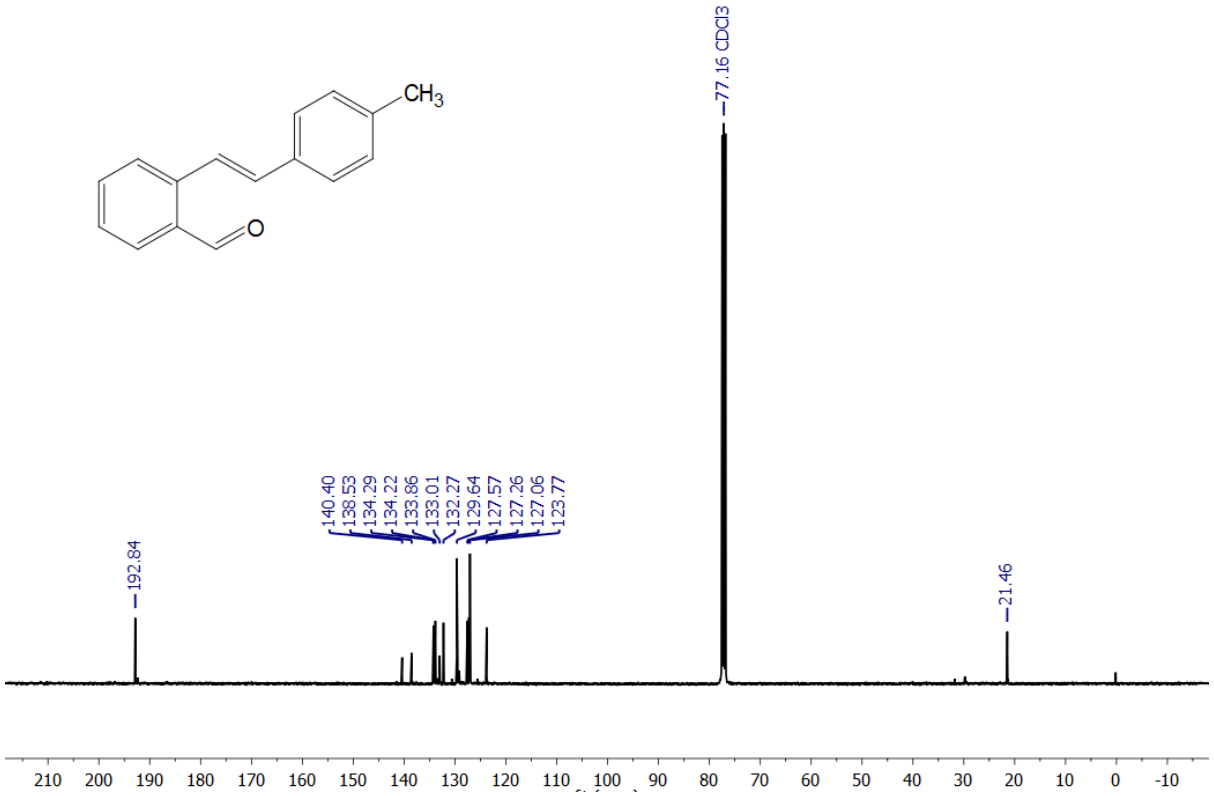
f1 (ppm)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O
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138.53
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134.22
133.86
133.01
132.27
129.64
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127.06
123.77
192.84
21.46
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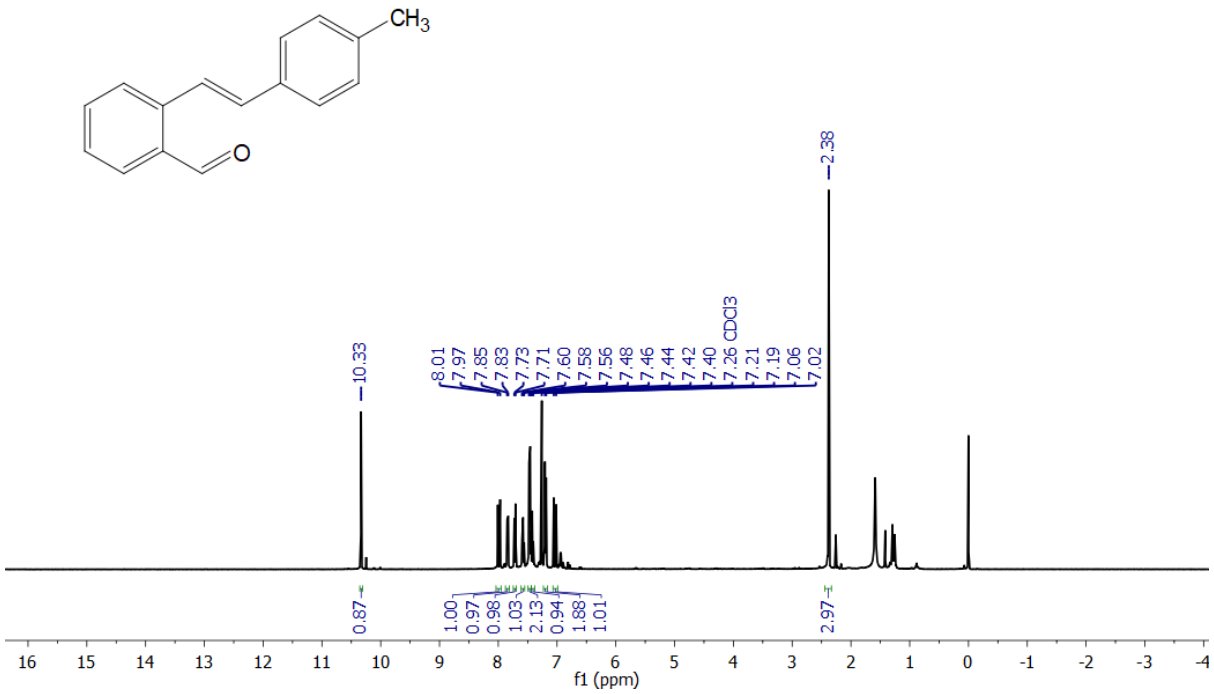
CH3
O
2.38
CDCl3
10.33
8.01
7.97
7.85
7.83
7.73
7.71
7.60
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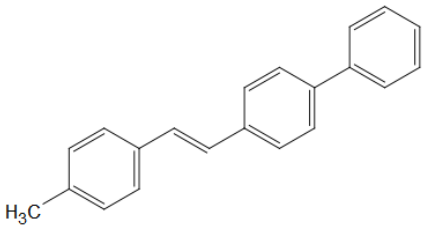
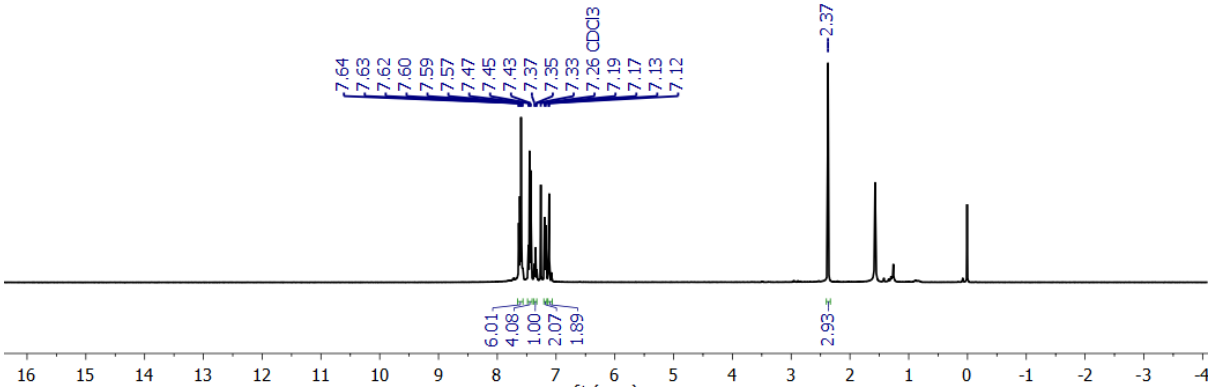
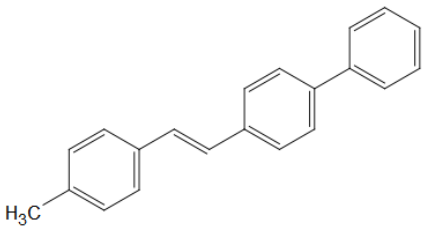
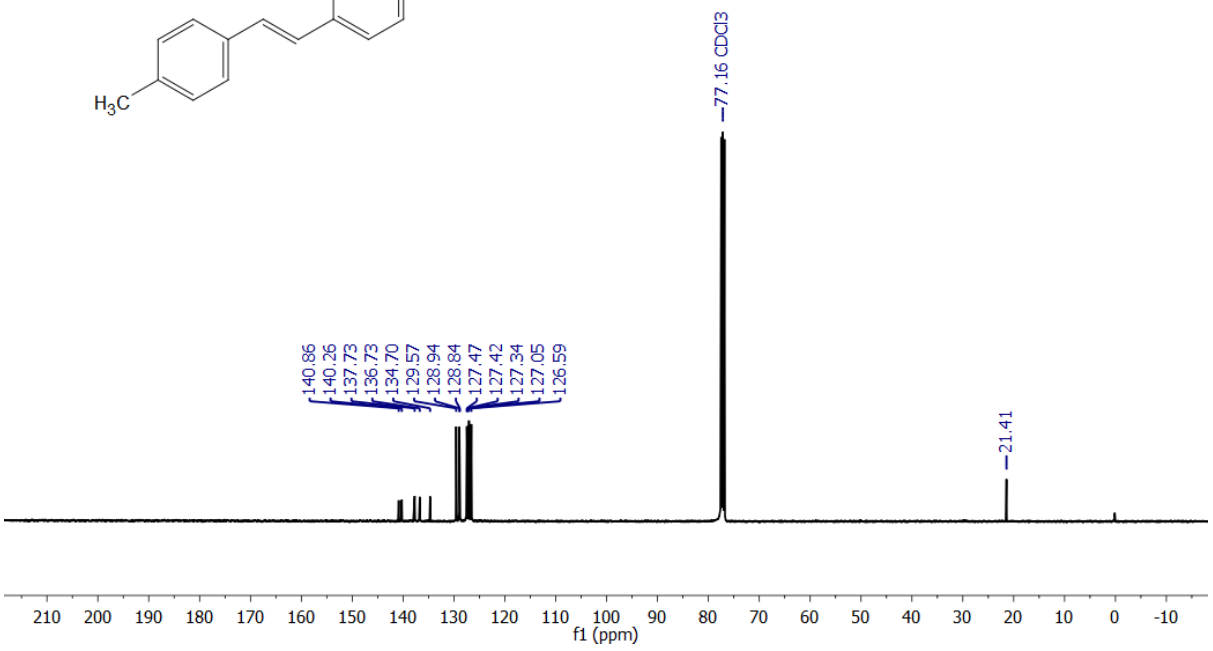
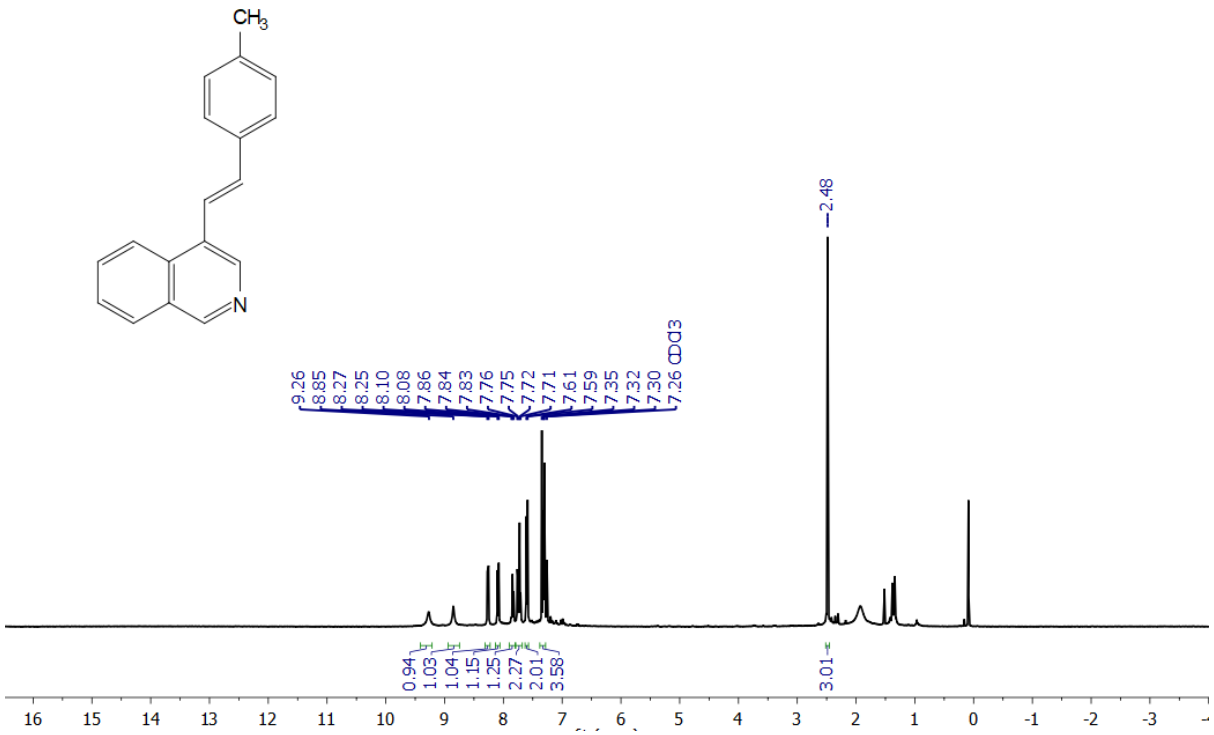
7.56
7.48
7.46
7.44
7.42
7.40
7.26
7.21
7.19
7.06
7.02
0.87
1.00
0.97
0.98
1.03
2.13
0.94
1.88
1.01
2.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

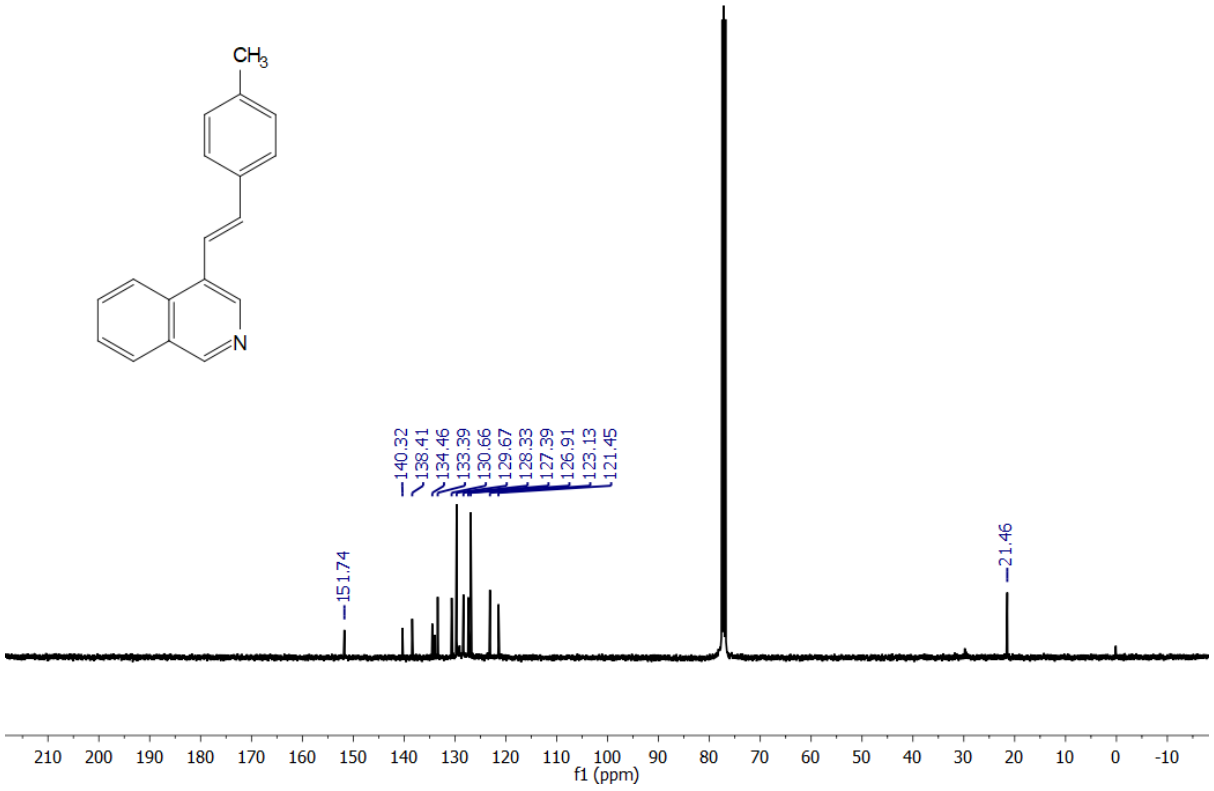

H3C


7.64
7.63
7.62
7.60
7.59
7.57
7.47
7.45
7.43
7.37
7.35
7.33
7.26 CDCl3
7.19
7.17
7.13
7.12
2.37
6.01
4.08
1.00
2.07
1.89
2.93


H3C


140.86
140.26
137.73
136.73
134.70
129.57
128.94
128.84
127.47
127.42
127.34
127.05
126.59
77.16 CDCl3
21.41
f1 (ppm)


CH3
N
9.26
8.85
8.27
8.25
8.10
8.08
7.86
7.84
7.83
7.76
7.75
7.72
7.71
7.61
7.59
7.35
7.32
7.30
7.26 CDCl3
2.48
0.94
1.03
1.04
1.15
1.25
2.27
2.01
3.58
3.01


CH3
N
140.32
138.41
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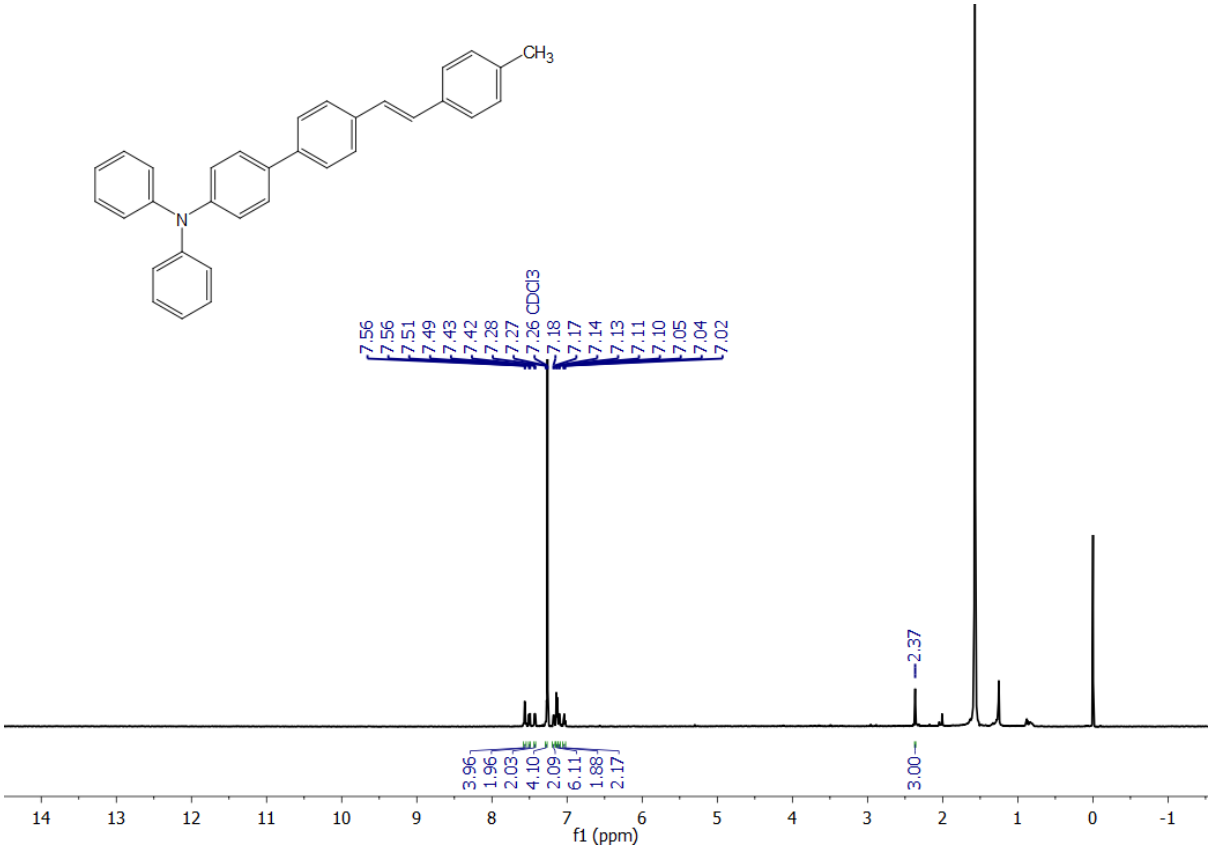
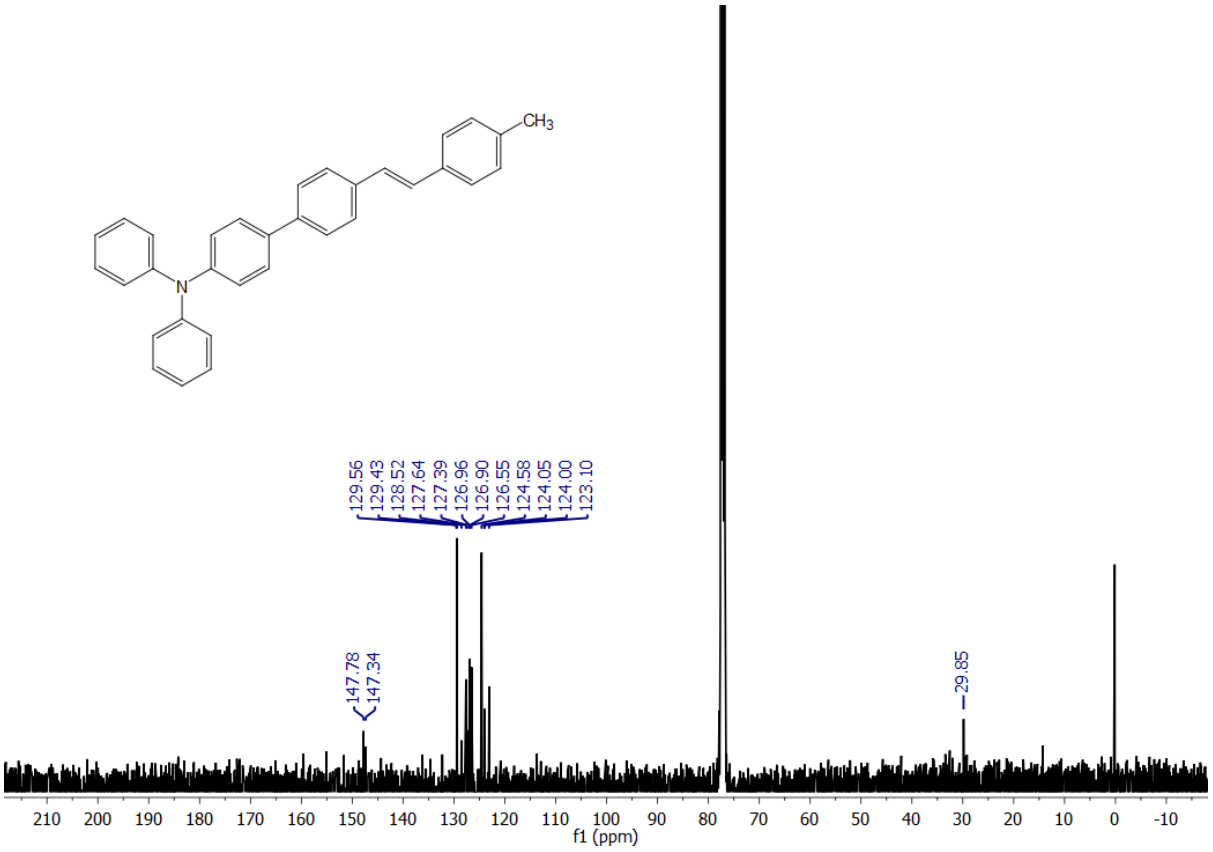
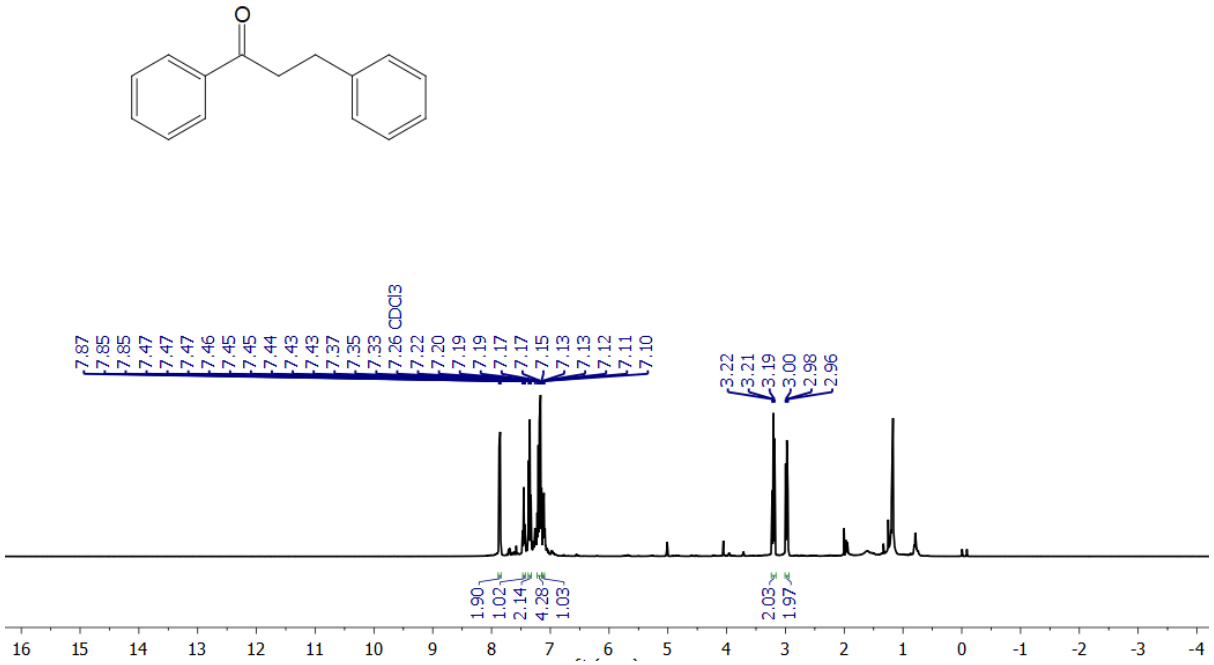
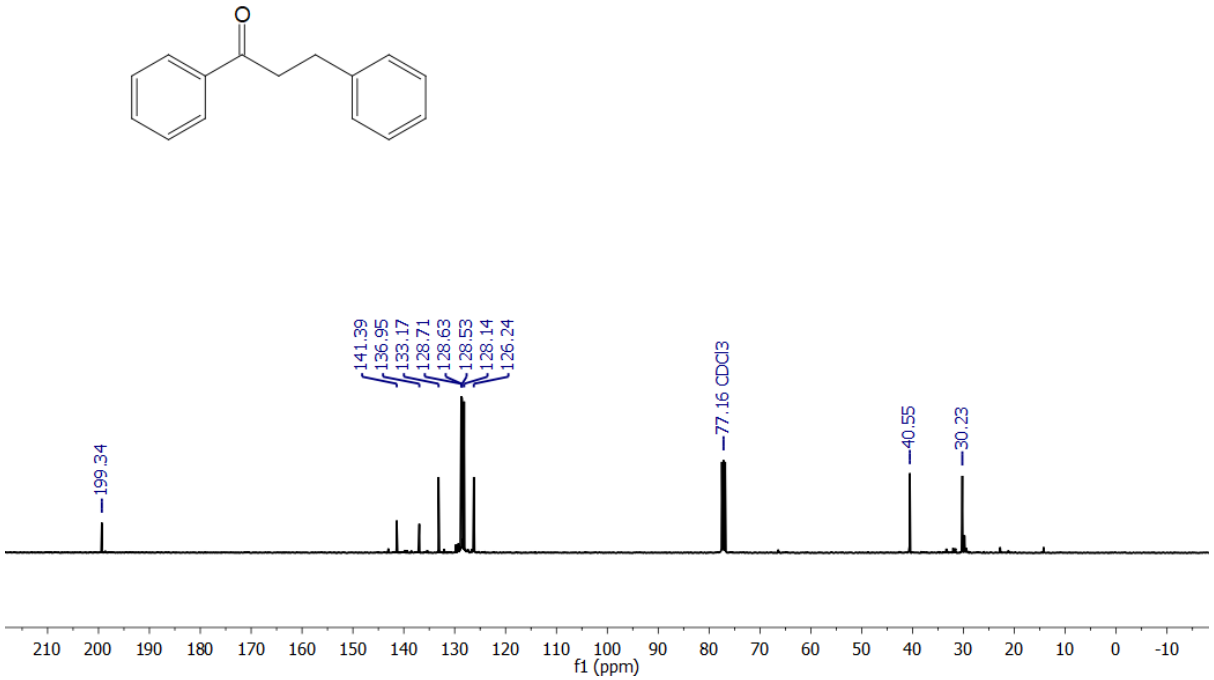
129.67
128.33
127.39
126.91
123.13
121.45
151.74
21.46
f1 (ppm)


CH3
N
7.56
7.56
7.51
7.49
7.43
7.42
7.28
7.27
CDCl3
7.18
7.17
7.14
7.13
7.11
7.10
7.05
7.04
7.02
2.37
3.96
1.96
2.03
4.10
2.09
6.11
1.88
2.17
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


CH3
N
129.56
129.43
128.52
127.64
127.39
126.96
126.90
126.55
124.58
124.05
124.00
123.10
147.78
147.34
29.85
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)


O
7.87
7.85
7.85
7.47
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.37
7.35
7.33
7.26 CDCl3
7.22
7.20
7.19
7.19
7.17
7.17
7.15
7.13
7.13
7.12
7.11
7.10
3.22
3.21
3.19
3.00
2.98
2.96
1.90
1.02
2.14
4.28
1.03
2.03
1.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4


O
141.39
136.95
133.17
128.71
128.63
128.53
128.14
126.24
77.16 CDCl3
40.55
30.23
199.34
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)

Solution state magnetic moment by Evans′ NMR method

Complexes **1a**, **1aa**, **2a**, **1d**, **1e**, and CP **2d** were separately taken in 0.500 mL mixture of DMSO-D6/toluene (95:5 *v/v*) and loaded into a standard NMR tube. Then, a one-end sealed capillary tube filled with same solvent mixture up to the same height as sample and the capillary was carefully inserted into the NMR tube. Evans NMR spectrum was recorded using a 600 MHz operated spectrometer at 296 K as a normal ^{1}H NMR.

From the chemical shift difference, effective magnetic moment (μ_{eff}) was calculated by using the equation (1).

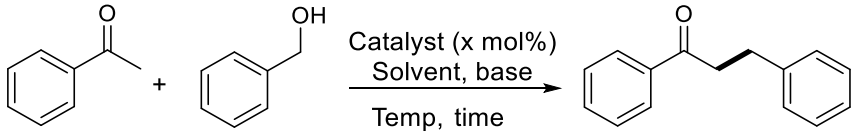
$$\mu_{eff} = 2.828\sqrt{T \cdot \chi_M} \qquad (1)$$

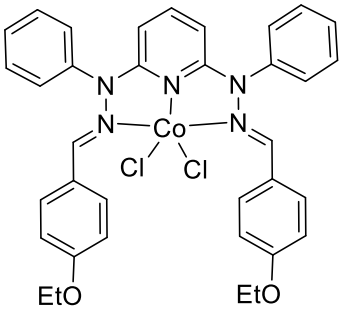
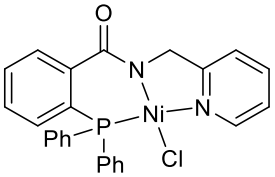
Where, *T* is the temperature in Kelvin and χ_M is the molar magnetic susceptibility of the sample in mL per mole and it was calculated by using the equation (2).

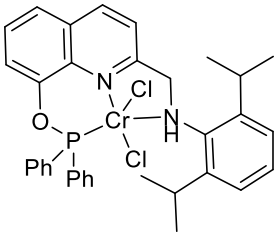
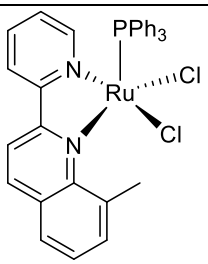
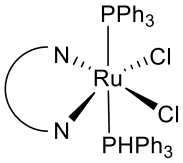
$$\chi_M = \frac{3 \cdot \Delta f}{1000 \cdot f \cdot c} \qquad (2)$$

Δf is the chemical shift difference observed in Hz, f is the spectrometer frequency in Hz, c is the sample concentration in mmol/L.

Table S33: Comparison of catalytic activity for α-alkylation of ketone

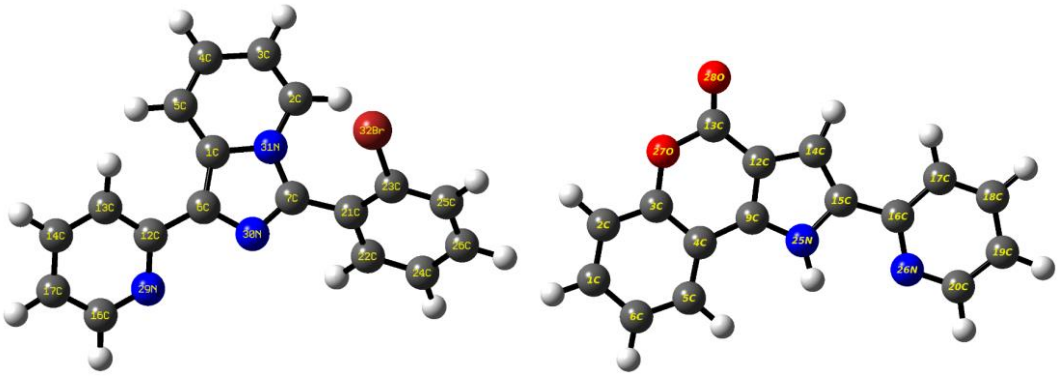


Entry	Catalyst	Cat. mol%	Solvent	Temp (ºC)	Time	Yield (%)	Ref
1.		2	Toluene	110	24 h	91	[12]
2.		0.5	Toluene	110	24 h	99	[13]

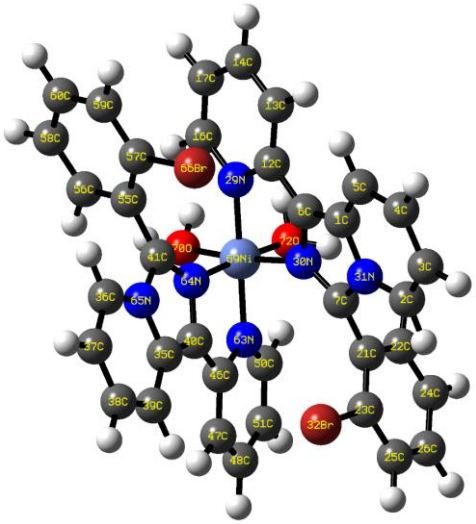
3.		3	Toluene	135	36 h	74 98% for 4-methyl acetophenone	[14]
4.	  N^N = 4-methyl-2,2′-pyridyl-quinoline; 8-methyl-2,2′-pyridyl-quinoline; 6′-methyl-2,2 ′-pyridyl-quinoline; 4,6 ′ -dimethyl-2,2′-pyridyl-quinoline, and 2,2-pyridyl-quinoline.	0.25	Toluene	110	1 h	90-99	[15]
5.	This Work	1	Toluene	110	12 h	91	

Computational study:

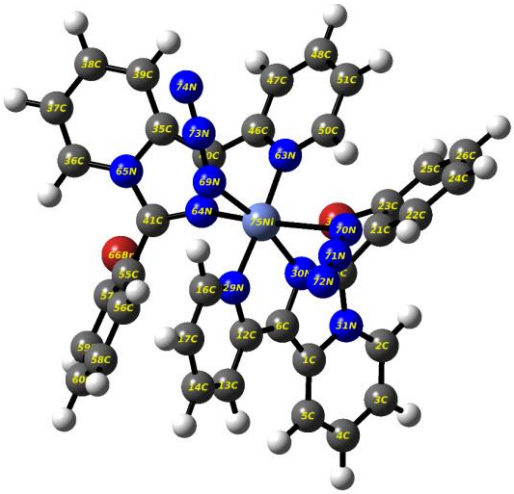
Optimized structures, FMOs, Thermodynamic data, and Cartesian coordinates:



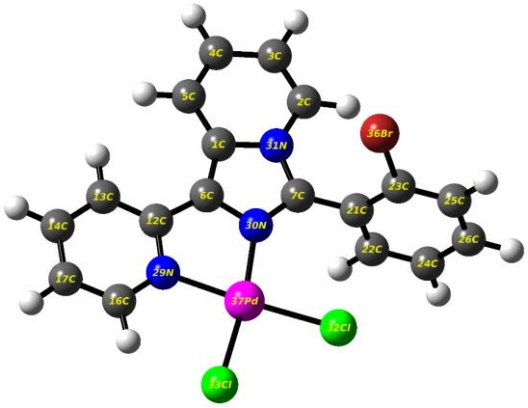
L1 **L2H**



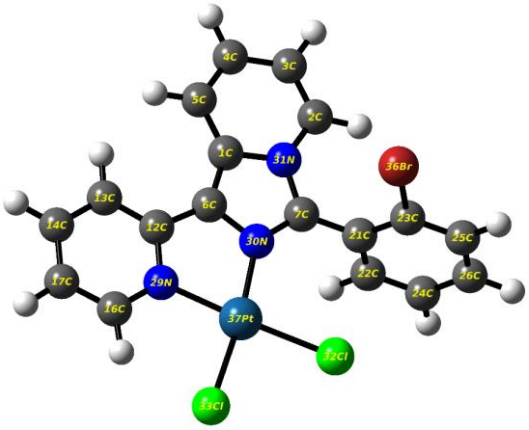
1a



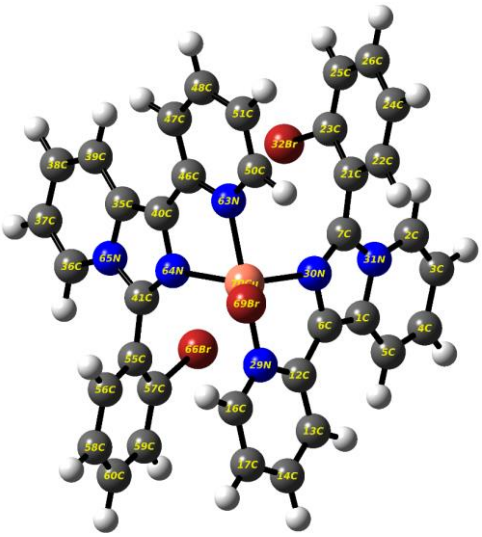
`1aa



1b



1c



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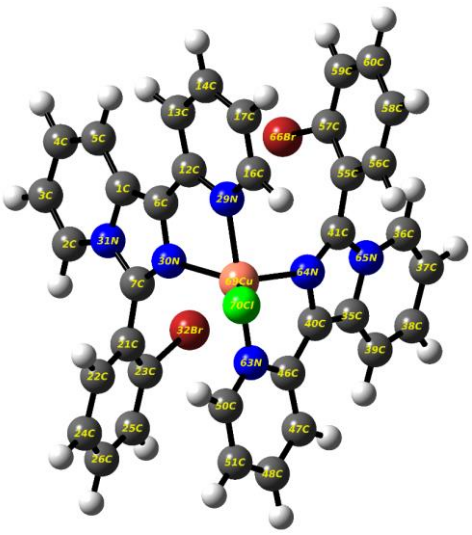
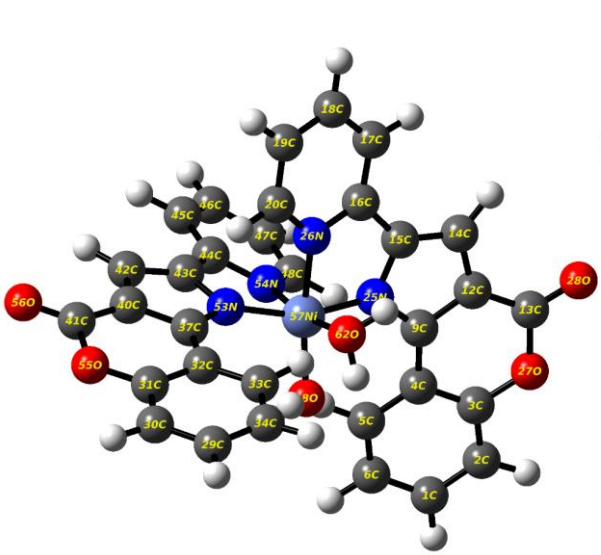
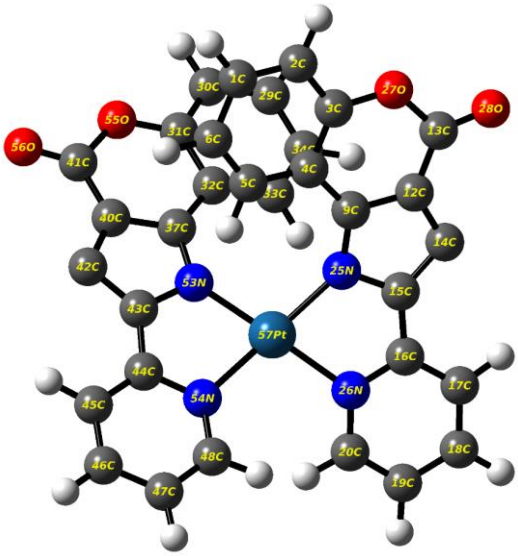


1e



2a



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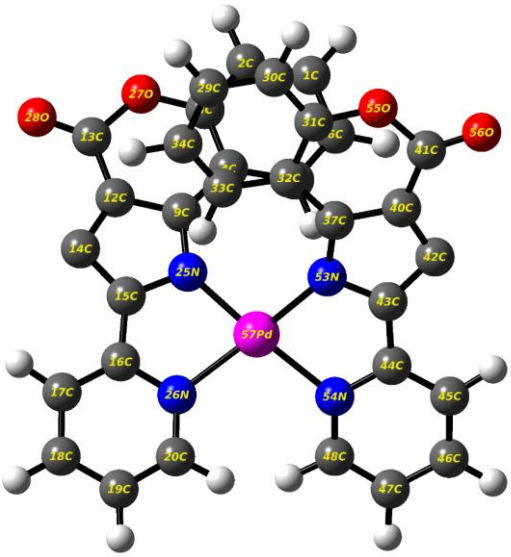

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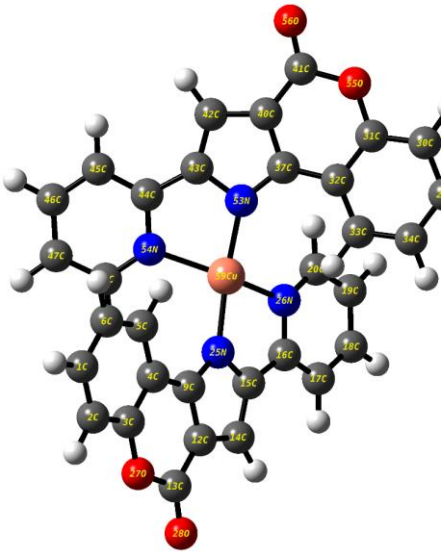
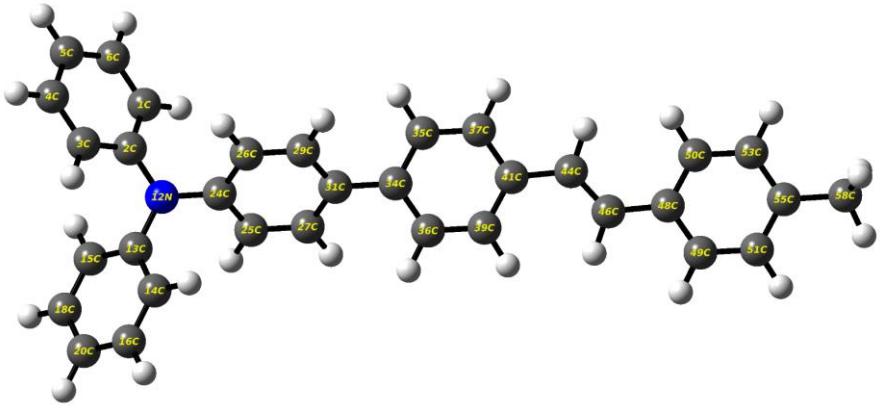


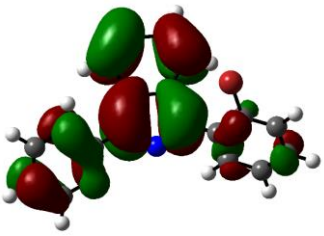
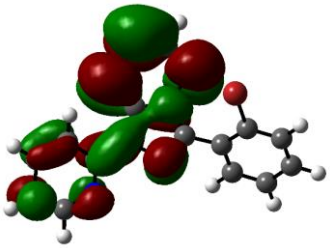
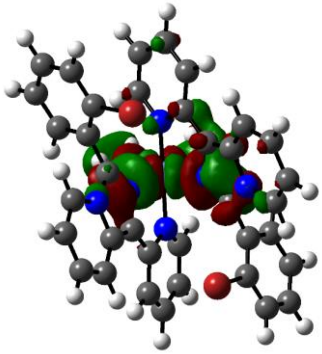
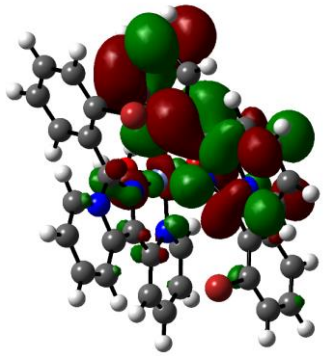
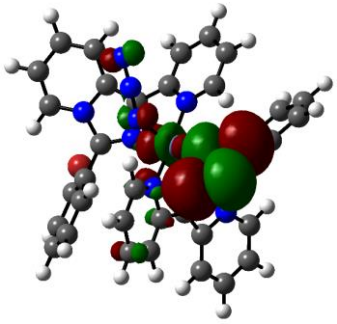
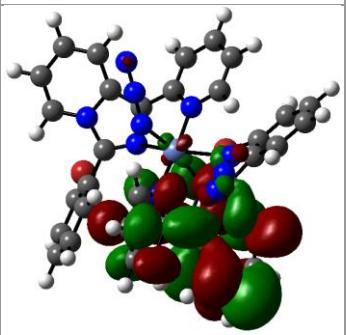
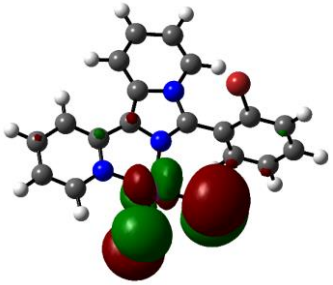
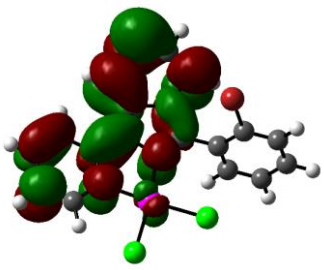
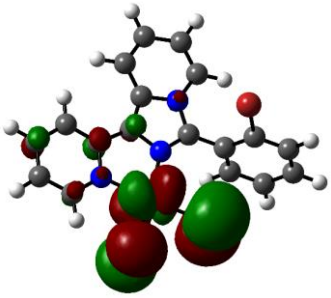
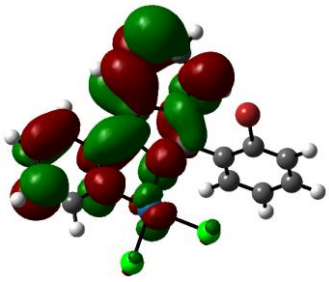
2d

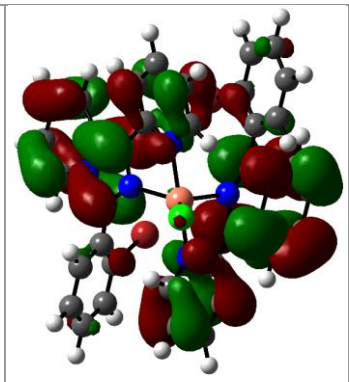
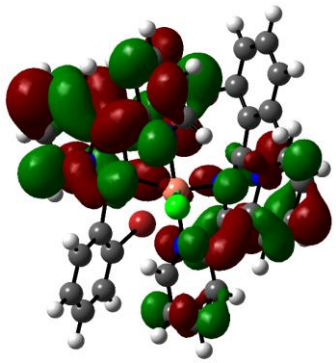
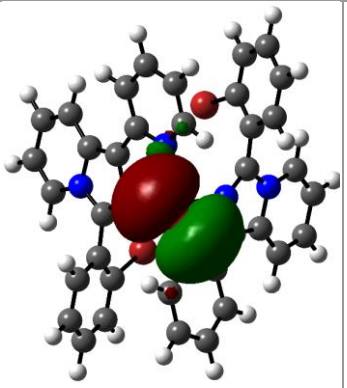
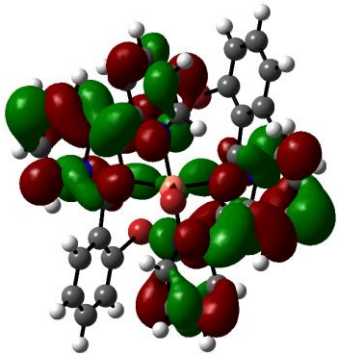
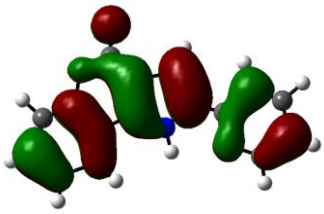
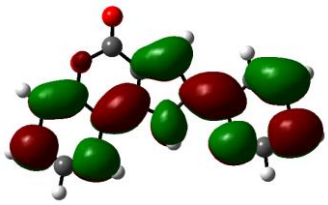
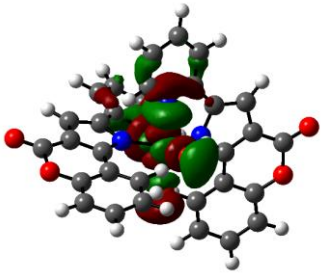
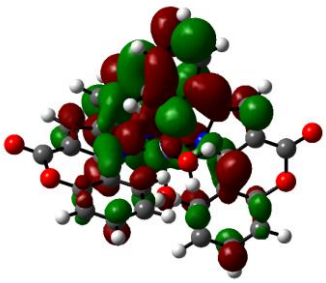
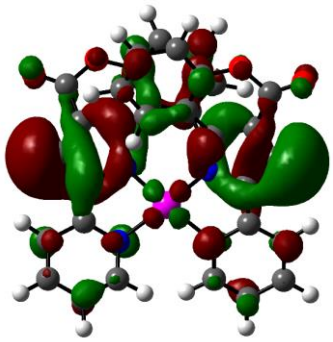
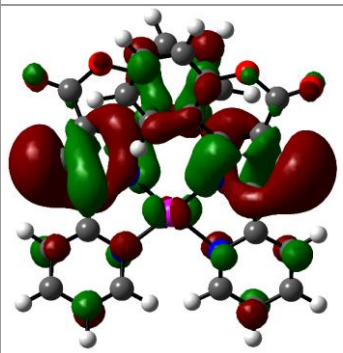


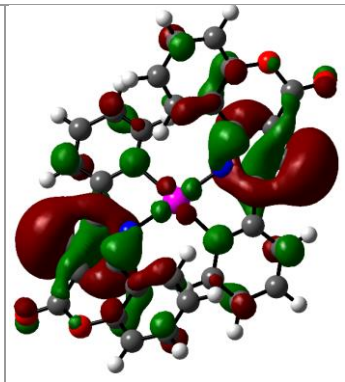
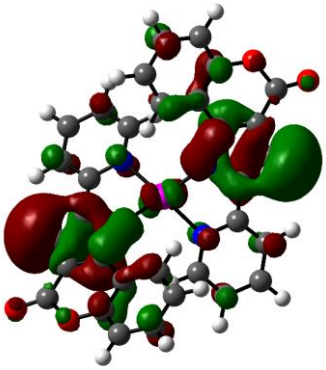
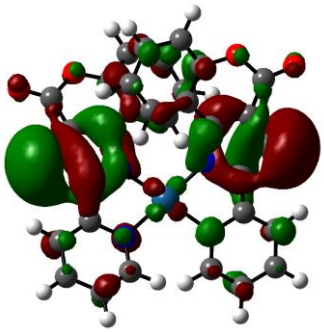
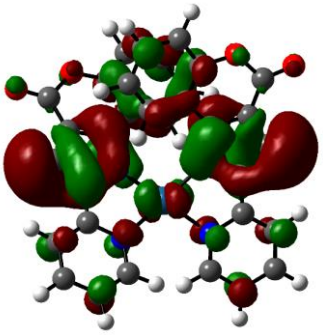
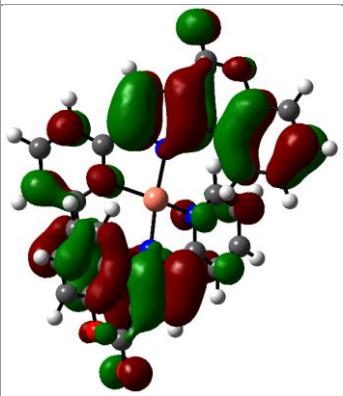
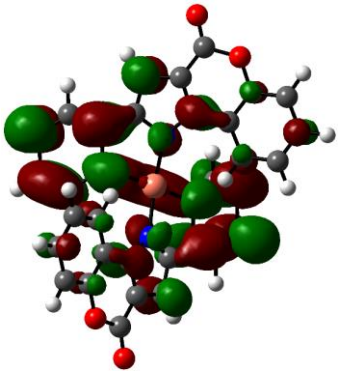
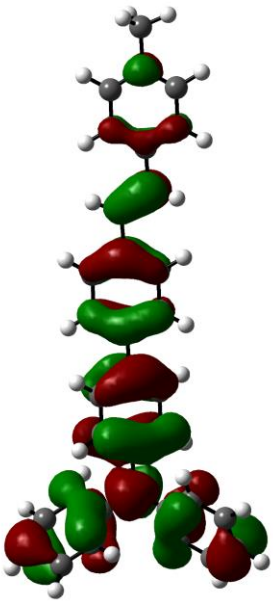
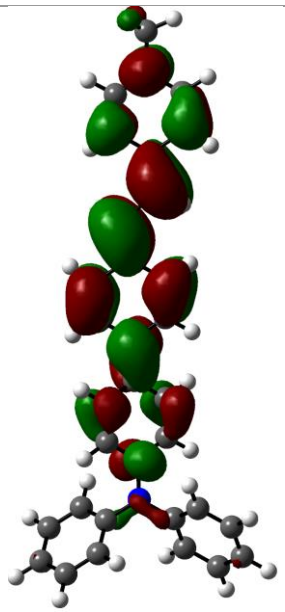
3k

Figure S25: Optimized structure of all compounds

Table S34: FMO diagrams and HOMO–LUMO energy calculations.

Entity	HOMO	LUMO	E_{LUMO} (eV)	E_{HOMO} (eV)	ΔE (eV)
L1			-5.385	-1.392	3.993
1a			-9.187	-7.393	1.794
1aa			-3.912	-2.100	1.812
1b			-5.761	-2.683	3.078
1c			-5.637	-2.706	2.931

1d			-8.335	-4.500	3.835
1e			-8.191	-4.508	3.683
L2H			-5.838	-1.81	4.028
2a			-4.042	-2.118	1.924
2b			-5.583	-4.997	0.586

2b*			-5.714	-5.197	0.517
2c			-5.572	-4.96	0.612
2d monomer			-5.947	-2.478	3.469
3k			-5.104	-1.695	3.409

Thermodynamic properties of **L1**:

Zero-point vibrational energy = 160.79984 Kcal/Mol

Sum of electronic and zero-point Energies = -3431.478782 Hartree

Sum of electronic and thermal Energies = -3431.461881 Hartree

Sum of electronic and thermal Enthalpies = -3431.460937 Hartree

Sum of electronic and thermal Free Energies = -3431.525758 Hartree

Cartesian coordinates of **L1**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.29291	1.106462	-0.54927
2	6	0.906502	1.943734	-1.17914
3	6	0.362424	3.149269	-1.48794
4	6	-1.03919	3.370543	-1.33819
5	6	-1.84767	2.365333	-0.88375
6	6	-1.7702	-0.1469	-0.14465
7	6	0.372531	-0.38162	-0.37756
8	1	1.953063	1.706468	-1.29274
9	1	1.00681	3.934262	-1.86098
10	1	-1.4595	4.332847	-1.60244
11	1	-2.91665	2.504161	-0.79539
12	6	-3.15362	-0.54095	0.159516
13	6	-4.054	0.356497	0.756987
14	6	-5.35431	-0.05818	1.014812
15	1	-3.7266	1.347308	1.046317
16	6	-4.75443	-2.18579	0.119306
17	6	-5.72244	-1.35946	0.687815
18	1	-6.06286	0.618769	1.479475
19	1	-4.99701	-3.2135	-0.14015
20	1	-6.72336	-1.72991	0.873939
21	6	1.700337	-1.01381	-0.46271
22	6	1.824942	-2.15431	-1.27434
23	6	2.839707	-0.60007	0.244098
24	6	3.032749	-2.82568	-1.40422
25	6	4.060388	-1.25726	0.110823
26	6	4.157408	-2.36802	-0.72076
27	1	4.91878	-0.91278	0.672424
28	1	5.10763	-2.88014	-0.81852
29	7	-3.50761	-1.80103	-0.14741
30	7	-0.73562	-1.02915	-0.07307
31	7	0.096454	0.934175	-0.70254
32	35	2.750848	0.839087	1.517383
33	1	0.940948	-2.50086	-1.795
34	1	3.097198	-3.70141	-2.03909

Thermodynamic properties of **1a**:

Zero-point vibrational energy = 317.58758 Kcal/Mol

Sum of electronic and zero-point Energies = -2061.963174 Hartree

Sum of electronic and thermal Energies = -2061.928659 Hartree

Sum of electronic and thermal Enthalpies = -2061.927715 Hartree

Sum of electronic and thermal Free Energies = -2062.033338 Hartree

Cartesian coordinates of **1a**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.02177	-0.95414	2.59114
2	6	2.124925	-2.11203	2.790364
3	6	1.551017	-3.02059	3.649582
4	6	0.157291	-2.93552	3.974433
5	6	-0.62084	-1.91407	3.451412
6	6	-0.42996	0.220507	1.932439
7	6	1.705255	-0.03928	1.395021
8	1	3.169008	-2.13175	2.513369
9	1	2.168296	-3.80354	4.075145
10	1	-0.28278	-3.67209	4.638725
11	1	-1.67452	-1.84407	3.690592
12	6	-1.62791	0.992165	1.91334
13	6	-2.71959	0.848129	2.800884
14	6	-3.79824	1.726086	2.723659
15	1	-2.69281	0.073929	3.556838
16	6	-2.68111	2.824912	0.880662
17	6	-3.77655	2.73693	1.735925
18	1	-4.63367	1.640741	3.411345
19	1	-2.71396	3.58565	0.111098
20	1	-4.59407	3.440763	1.628174
21	6	3.133907	0.25057	1.12472
22	6	3.710877	1.382041	1.757754
23	6	3.998446	-0.58761	0.381668
24	6	5.078137	1.673701	1.642946
25	6	5.369982	-0.31116	0.259606
26	6	5.910877	0.824047	0.890854
27	1	6.011104	-0.97529	-0.31089
28	1	6.974015	1.028706	0.805295
29	7	-1.5932	1.985625	0.945235
30	7	0.621391	0.756568	1.172419
31	7	1.339648	-1.1008	2.244915
32	35	3.319534	-2.20767	-0.51359
33	1	3.086163	2.005098	2.395489
34	1	5.494844	2.537183	2.1528

35	6	0.073475	-1.13761	-2.51764
36	6	-2.08388	-2.28469	-2.72151
37	6	-1.50281	-3.21901	-3.54421
38	6	-0.10259	-3.14774	-3.85904
39	6	0.675266	-2.12064	-3.35359
40	6	0.487842	0.038766	-1.87653
41	6	-1.66552	-0.1818	-1.3787
42	1	-3.13067	-2.29296	-2.45228
43	1	-2.11659	-4.01426	-3.95189
44	1	0.339056	-3.90426	-4.49936
45	1	1.73238	-2.0605	-3.5804
46	6	1.671982	0.85154	-1.92925
47	6	2.777691	0.71201	-2.79047
48	6	3.766462	1.704548	-2.79552
49	1	2.844764	-0.1349	-3.46156
50	6	2.513089	2.902873	-1.10988
51	6	3.62992	2.823767	-1.94823
52	1	4.618503	1.62192	-3.46351
53	1	2.351047	3.751672	-0.45835
54	1	4.362381	3.623056	-1.94572
55	6	-3.09703	0.135145	-1.15607
56	6	-3.65998	1.194237	-1.91577
57	6	-3.97307	-0.62753	-0.35088
58	6	-5.02931	1.495815	-1.8529
59	6	-5.34609	-0.33794	-0.27745
60	6	-5.87418	0.728994	-1.02793
61	1	-5.99903	-0.94514	0.341235
62	1	-6.93879	0.939085	-0.98316
63	7	1.569336	1.927283	-1.08556
64	7	-0.5735	0.598909	-1.14924
65	7	-1.29851	-1.25944	-2.19616
66	35	-3.30628	-2.16983	0.675047
67	1	-3.02427	1.733677	-2.61733
68	1	-5.4393	2.295594	-2.46268
69	28	-0.0173	2.01452	-0.05506
70	8	-0.71988	3.331034	-1.08259
71	1	-1.05355	4.039968	-0.51749
72	8	0.613732	3.339119	0.998009
73	1	-0.1276	3.791574	1.416166
74	1	-1.45713	2.977568	-1.60243
75	1	1.184581	2.967846	1.67158

Thermodynamic properties of **1aa**:

Zero-point vibrational energy = 343.09395 Kcal/Mol

Sum of electronic and zero-point Energies = -2237.950998 Hartree

Sum of electronic and thermal Energies = -2237.907301 Hartree

Sum of electronic and thermal Enthalpies = -2237.906357 Hartree

Sum of electronic and thermal Free Energies = -2238.034482 Hartree

Cartesian coordinates of **1aa**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.421698	-2.47053	-1.85564
2	6	2.064824	-1.13735	-3.81661
3	6	1.898338	-2.24069	-4.61836
4	6	1.469871	-3.4934	-4.05754
5	6	1.240727	-3.60475	-2.6972
6	6	1.331373	-2.19205	-0.48325
7	6	1.929221	-0.27432	-1.44713
8	1	2.384909	-0.17152	-4.18231
9	1	2.093078	-2.15124	-5.68141
10	1	1.330721	-4.35143	-4.70776
11	1	0.919046	-4.54408	-2.26391
12	6	1.175636	-3.00346	0.706063
13	6	1.075896	-4.40512	0.756983
14	6	1.092028	-5.04672	2.007424
15	1	1.023425	-4.98554	-0.15673
16	6	1.287763	-2.87767	3.064966
17	6	1.219861	-4.27588	3.17511
18	1	1.036491	-6.13047	2.063947
19	1	1.357545	-2.22048	3.921558
20	1	1.283697	-4.73593	4.154944
21	6	2.58622	1.027695	-1.6823
22	6	3.880567	1.203868	-1.12852
23	6	2.05976	2.057446	-2.49232
24	6	4.628256	2.357241	-1.41463
25	6	2.796827	3.218223	-2.7769
26	6	4.092943	3.359194	-2.2455
27	1	2.368007	3.998423	-3.39779

28	1	4.668821	4.252448	-2.47435
29	7	1.23634	-2.259	1.861678
30	7	1.62108	-0.84815	-0.2723
31	7	1.813844	-1.2398	-2.45329
32	35	0.230384	1.925244	-3.22023
33	1	4.262253	0.438475	-0.4526
34	1	5.620089	2.470876	-0.98601
35	6	-2.2823	2.147955	1.554673
36	6	-4.55511	1.214699	1.58916
37	6	-4.99491	2.31411	2.286502
38	6	-4.07691	3.356943	2.657513
39	6	-2.74202	3.26934	2.303395
40	6	-1.03694	1.670442	1.082435
41	6	-2.50749	0.104245	0.582535
42	1	-5.19122	0.38531	1.310854
43	1	-6.04005	2.373723	2.570439
44	1	-4.433	4.200539	3.24056
45	1	-2.02738	4.019025	2.621178
46	6	0.263932	2.333464	1.19178
47	6	0.366786	3.741701	1.126272
48	6	1.59986	4.368246	1.34625
49	1	-0.51413	4.325757	0.88427
50	6	2.591442	2.183386	1.623325
51	6	2.729742	3.576294	1.616844
52	1	1.676952	5.451667	1.307795
53	1	3.416676	1.497992	1.808491
54	1	3.702011	4.015958	1.811915
55	6	-3.08792	-1.18457	0.158763
56	6	-2.56266	-2.36407	0.744535
57	6	-4.10921	-1.33526	-0.80701
58	6	-3.05501	-3.63199	0.400167
59	6	-4.61965	-2.59695	-1.15486
60	6	-4.09355	-3.74948	-0.54296

61	1	-5.40352	-2.68011	-1.90097
62	1	-4.48942	-4.72556	-0.81109
63	7	1.390448	1.579231	1.407278
64	7	-1.2057	0.41743	0.516149
65	7	-3.21669	1.129629	1.224364
66	35	-4.8106	0.227771	-1.7903
67	1	-1.76777	-2.259	1.477065
68	1	-2.63597	-4.5178	0.869565
69	7	0.819698	-0.12694	3.451402
70	7	3.913175	-0.53242	1.67843
71	7	4.246336	-1.53204	2.31357
72	7	4.533226	-2.52258	2.934272
73	7	0.50402	0.940936	3.990243
74	7	0.179972	1.928407	4.568497
75	28	1.369167	-0.34204	1.616964

Thermodynamic properties of **1b**:

Zero-point vibrational energy = 165.83537 Kcal/Mol

Sum of electronic and zero-point Energies = -1026.904015 Hartree

Sum of electronic and thermal Energies = -1026.882150 Hartree

Sum of electronic and thermal Enthalpies = -1026.881206 Hartree

Sum of electronic and thermal Free Energies = -1026.958440 Hartree

Cartesian coordinates of **1b**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.032889	2.584801	-0.4099
2	6	2.462557	2.568766	-0.80436
3	6	2.468967	3.941757	-0.82321
4	6	1.248826	4.677211	-0.6278
5	6	0.053286	4.010673	-0.42572
6	6	-0.92977	1.571609	-0.25478
7	6	1.026612	0.521204	-0.54172
8	1	3.342955	1.954506	-0.93944
9	1	3.406441	4.462415	-0.98311
10	1	1.271796	5.762403	-0.63934
11	1	-0.86508	4.564363	-0.27805
12	6	-2.36658	1.582332	-0.04592
13	6	-3.16943	2.738867	0.042438

14	6	-4.55193	2.608489	0.239024
15	1	-2.72429	3.722122	-0.04157
16	6	-4.2739	0.204618	0.251103
17	6	-5.11507	1.323351	0.344273
18	1	-5.17756	3.493934	0.308672
19	1	-4.63605	-0.81547	0.327797
20	1	-6.1793	1.179838	0.496531
21	6	2.100996	-0.46902	-0.75699
22	6	2.161767	-1.16409	-1.98573
23	6	3.090268	-0.74012	0.212156
24	6	3.18009	-2.09483	-2.23759
25	6	4.108773	-1.67551	-0.02088
26	6	4.15283	-2.35126	-1.25447
27	1	4.844635	-1.88553	0.748455
28	1	4.935489	-3.08374	-1.43337
29	7	-2.93678	0.332326	0.061551
30	7	-0.28847	0.330709	-0.33834
31	7	1.262643	1.897566	-0.59819
32	17	0.018668	-2.99237	-0.13225
33	17	-3.30373	-2.8823	0.281281
34	1	1.387469	-0.9884	-2.72667
35	1	3.198736	-2.63287	-3.18063
36	35	3.032719	0.153359	1.968264
37	46	-1.59681	-1.26498	-0.05124

Thermodynamic properties of **1c**:

Zero-point vibrational energy = 166.04174 Kcal/Mol

Sum of electronic and zero-point Energies = -1019.327976 Hartree

Sum of electronic and thermal Energies = -1019.306236 Hartree

Sum of electronic and thermal Enthalpies = -1019.305292 Hartree

Sum of electronic and thermal Free Energies = -1019.382356 Hartree

Cartesian coordinates of **1c**:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	0.390314	2.712655	-0.39569
2	6	2.809105	2.515855	-0.79424
3	6	2.915907	3.885392	-0.81612
4	6	1.754194	4.709253	-0.62172
5	6	0.513005	4.132249	-0.41571
6	6	-0.64406	1.777506	-0.23499
7	6	1.231211	0.579694	-0.52622
8	1	3.642108	1.838642	-0.9284
9	1	3.88917	4.334888	-0.978
10	1	1.856847	5.789743	-0.6367

11	1	-0.36402	4.749859	-0.2682
12	6	-2.07309	1.873876	-0.03
13	6	-2.81477	3.068107	0.063597
14	6	-4.20226	3.009653	0.253744
15	1	-2.31506	4.026021	-0.0113
16	6	-4.05186	0.591765	0.250188
17	6	-4.82914	1.752363	0.346991
18	1	-4.78254	3.924851	0.327762
19	1	-4.46977	-0.40651	0.318894
20	1	-5.89998	1.66233	0.493877
21	6	2.232551	-0.48111	-0.75284
22	6	2.258234	-1.1507	-1.99704
23	6	3.19364	-0.83724	0.217032
24	6	3.213547	-2.14266	-2.26139
25	6	4.148478	-1.83438	-0.02879
26	6	4.157231	-2.48571	-1.27621
27	1	4.862375	-2.10932	0.740786
28	1	4.890113	-3.26566	-1.46508
29	7	-2.70448	0.647393	0.06668
30	7	-0.09748	0.488912	-0.31578
31	7	1.563814	1.934794	-0.58539
32	17	0.038706	-2.85225	-0.12903
33	17	-3.27656	-2.5505	0.280399
34	1	1.504059	-0.90712	-2.73966
35	1	3.205361	-2.6598	-3.21623
36	35	3.184454	0.028137	1.987031
37	78	-1.47407	-0.99581	-0.04871

Thermodynamic properties of **1d**:

Zero-point vibrational energy = 329.10917 Kcal/Mol

Sum of electronic and zero-point Energies = -1951.334270 Hartree

Sum of electronic and thermal Energies = -1951.295687 Hartree

Sum of electronic and thermal Enthalpies = -1951.294743 Hartree

Sum of electronic and thermal Free Energies = -1951.412342 Hartree

Cartesian coordinates of **1d**:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	0.086563	3.132924	-0.72341
2	6	-1.97929	3.435006	-2.02884
3	6	-1.35979	4.398652	-2.78555
4	6	0.014917	4.742032	-2.54261

5	6	0.723916	4.12117	-1.52958
6	6	0.431708	2.313832	0.371366
7	6	-1.67418	1.800541	-0.13031
8	1	-3.00763	3.127807	-2.16575
9	1	-1.91962	4.893033	-3.57141
10	1	0.494009	5.494007	-3.16131
11	1	1.761317	4.374263	-1.35247
12	6	1.631595	2.215823	1.19115
13	6	2.724725	3.107124	1.125942
14	6	3.796959	2.951501	2.015744
15	1	2.723922	3.925395	0.417398
16	6	2.65099	1.062647	2.990516
17	6	3.764106	1.913821	2.965959
18	1	4.636665	3.639799	1.980316
19	1	2.542878	0.276905	3.728177
20	1	4.565011	1.774834	3.68356
21	6	-3.06608	1.30814	-0.05998
22	6	-3.86674	1.708584	1.037616
23	6	-3.66244	0.499555	-1.05375
24	6	-5.21583	1.330158	1.127039
25	6	-5.01045	0.114975	-0.97852
26	6	-5.78975	0.538876	0.11454
27	1	-5.44692	-0.50297	-1.75655
28	1	-6.83569	0.249858	0.16849
29	7	1.622447	1.204913	2.11924
30	7	-0.658	1.511959	0.697515
31	7	-1.26324	2.798976	-1.01924
32	35	-2.59687	-0.15084	-2.57932
33	1	-3.42033	2.331371	1.808464
34	1	-5.81462	1.657456	1.971918
35	6	-0.08482	-3.13194	-0.72783
36	6	1.982714	-3.43438	-2.03054
37	6	1.364388	-4.39858	-2.78753

38	6	-0.01057	-4.742	-2.54616
39	6	-0.72095	-4.12068	-1.53435
40	6	-0.4314	-2.31219	0.366149
41	6	1.674749	-1.79873	-0.13335
42	1	3.011186	-3.12709	-2.16627
43	1	1.92532	-4.89333	-3.57238
44	1	-0.48878	-5.49439	-3.16503
45	1	-1.75854	-4.37387	-1.35848
46	6	-1.63285	-2.21405	1.183706
47	6	-2.7246	-3.10717	1.117914
48	6	-3.79897	-2.95166	2.005054
49	1	-2.72084	-3.92693	0.411128
50	6	-2.65789	-1.05973	2.979138
51	6	-3.7698	-1.9123	2.953621
52	1	-4.63738	-3.6415	1.969214
53	1	-2.55267	-0.27322	3.716352
54	1	-4.57233	-1.77347	3.669421
55	6	3.065982	-1.30469	-0.06187
56	6	3.865464	-1.70214	1.03769
57	6	3.662771	-0.49672	-1.0559
58	6	5.213935	-1.32181	1.1285
59	6	5.010198	-0.11037	-0.97937
60	6	5.788423	-0.53158	0.115497
61	1	5.447009	0.506961	-1.75771
62	1	6.833945	-0.24123	0.170495
63	7	-1.6274	-1.2017	2.110144
64	7	0.657718	-1.50993	0.693141
65	7	1.265266	-2.79788	-1.0223
66	35	2.598359	0.150991	-2.58352
67	1	3.418572	-2.32408	1.808939
68	1	5.811831	-1.64688	1.974868
69	29	-0.00255	0.001163	2.158079
70	17	0.003645	-0.02259	4.51695

Thermodynamic properties of **1e**:

Zero-point vibrational energy = 328.90749 Kcal/Mol

Sum of electronic and zero-point Energies = -1949.550794 Hartree

Sum of electronic and thermal Energies = -1949.511970 Hartree

Sum of electronic and thermal Enthalpies = -1949.511026 Hartree

Sum of electronic and thermal Free Energies = -1949.629969 Hartree

Cartesian coordinates of **1e**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.1475	-0.9432	-3.1699
2	6	-2.25651	-2.1983	-3.37445
3	6	-1.70508	-2.96191	-4.37337
4	6	-0.34445	-2.74783	-4.78532
5	6	0.41921	-1.75647	-4.19494
6	6	0.265192	0.134132	-2.35848
7	6	-1.82337	-0.32221	-1.74403
8	1	-3.27014	-2.31453	-3.01406
9	1	-2.30729	-3.73159	-4.84279
10	1	0.081115	-3.37192	-5.56455
11	1	1.44655	-1.60272	-4.4991
12	6	1.489966	0.920501	-2.31273
13	6	2.530439	0.834933	-3.26367
14	6	3.642329	1.680774	-3.151
15	1	2.458399	0.143765	-4.09343
16	6	2.637634	2.65479	-1.18356
17	6	3.702739	2.606303	-2.09264
18	1	4.441153	1.629746	-3.88538
19	1	2.607933	3.376831	-0.37706
20	1	4.538631	3.287559	-1.97964
21	6	-3.18963	-0.22626	-1.18676
22	6	-4.00046	0.868093	-1.5752
23	6	-3.75462	-1.1977	-0.33052
24	6	-5.33005	0.976527	-1.13687

25	6	-5.08224	-1.1026	0.115873
26	6	-5.87278	-0.01292	-0.29592
27	1	-5.49491	-1.86345	0.770485
28	1	-6.90359	0.055971	0.04047
29	7	1.565668	1.83104	-1.28796
30	7	-0.77316	0.476077	-1.49755
31	7	-1.48543	-1.2099	-2.77038
32	35	-2.67157	-2.72217	0.291769
33	1	-3.57826	1.621906	-2.23471
34	1	-5.93789	1.818171	-1.45574
35	6	0.147214	-0.93437	3.172547
36	6	2.256432	-2.18845	3.381884
37	6	1.705149	-2.94827	4.38377
38	6	0.344572	-2.73261	4.795066
39	6	-0.41925	-1.74364	4.200893
40	6	-0.26558	0.139786	2.356923
41	6	1.823117	-0.31852	1.744496
42	1	3.270013	-2.30599	3.021774
43	1	2.30742	-3.71613	4.856063
44	1	-0.08085	-3.35362	5.576827
45	1	-1.44652	-1.58876	4.504704
46	6	-1.49027	0.926129	2.308221
47	6	-2.53152	0.843109	3.258532
48	6	-3.64312	1.688922	3.142957
49	1	-2.46039	0.153827	4.089935
50	6	-2.63674	2.657888	1.173929
51	6	-3.70251	2.611939	2.082348
52	1	-4.4425	1.639872	3.876882
53	1	-2.60628	3.378001	0.365734
54	1	-4.53811	3.293182	1.967127
55	6	3.189196	-0.22497	1.186334
56	6	4.000665	0.870393	1.570525
57	6	3.753275	-1.19958	0.333089

58	6	5.330007	0.976833	1.130936
59	6	5.08066	-1.10654	-0.11445
60	6	5.871826	-0.01571	0.293055
61	1	5.492641	-1.86981	-0.76666
62	1	6.902458	0.051643	-0.04421
63	7	-1.56508	1.834123	1.281142
64	7	0.772837	0.478583	1.494897
65	7	1.485235	-1.20241	2.774128
66	35	2.669211	-2.72569	-0.28339
67	1	3.579154	1.626653	2.227675
68	1	5.938367	1.81934	1.446505
69	35	0.002911	4.429225	-0.00206
70	29	0.00067	1.895438	-0.00322

Thermodynamic properties of **L2H**:

Zero-point vibrational energy = 141.42775 Kcal/Mol

Sum of electronic and zero-point Energies = -875.696520 Hartree

Sum of electronic and thermal Energies = -875.682260 Hartree

Sum of electronic and thermal Enthalpies = -875.681316 Hartree

Sum of electronic and thermal Free Energies = -875.738578 Hartree

Cartesian coordinates of **L2H**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.66125	-1.66884	-4.3E-05
2	6	-4.43152	-0.29958	-0.00011
3	6	-3.12288	0.180223	-5.4E-05
4	6	-2.03139	-0.71244	0.000077
5	6	-2.2881	-2.093	0.000125
6	6	-3.58965	-2.56866	0.00007
7	1	-5.6797	-2.03911	-9.1E-05
8	1	-5.24416	0.415882	-0.00021
9	6	-0.74017	-0.08663	0.0001
10	1	-1.45821	-2.79123	0.000205
11	1	-3.77589	-3.63584	0.000112
12	6	-0.58476	1.300851	0.000013
13	6	-1.72205	2.193674	-0.0001
14	6	0.804167	1.586404	0.000213
15	6	1.459667	0.369148	0.00008
16	6	2.868955	-0.0061	0.000034

17	6	3.900559	0.94429	0.000112
18	6	5.214626	0.501915	0.000052
19	6	5.471307	-0.86859	-0.00008
20	6	4.384456	-1.73781	-0.00015
21	1	3.670396	2.002266	0.000223
22	1	6.030407	1.215894	0.000112
23	1	6.483064	-1.25443	-0.00013
24	1	4.538525	-2.81318	-0.00025
25	7	0.501982	-0.63222	0.000111
26	7	3.114665	-1.33034	-9.9E-05
27	8	-2.96626	1.539717	-0.00014
28	8	-1.72014	3.393593	-0.00016
29	1	0.769975	-1.60622	0.000067
30	1	1.248517	2.568136	0.000295

Thermodynamic properties of **2a**:

Zero-point vibrational energy = 260.89063 Kcal/Mol

Sum of electronic and zero-point Energies = -2071.543354 Hartree

Sum of electronic and thermal Energies = -2071.514303 Hartree

Sum of electronic and thermal Enthalpies = -2071.513359 Hartree

Sum of electronic and thermal Free Energies = -2071.606738 Hartree

Cartesian coordinates of **2a**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.747403	-3.29796	-2.28242
2	6	5.424274	-2.81904	-1.15304
3	6	4.823901	-1.83796	-0.34772
4	6	3.507448	-1.34902	-0.59761
5	6	2.885376	-1.80306	-1.78951
6	6	3.484173	-2.76164	-2.615
7	1	5.209865	-4.0513	-2.91427
8	1	6.420102	-3.16197	-0.89073
9	6	3.005374	-0.34349	0.33958
10	1	1.944297	-1.36633	-2.08896
11	1	2.979768	-3.08159	-3.52317
12	6	3.939412	0.282113	1.223697
13	6	5.288963	-0.19239	1.448394
14	6	3.284078	1.35679	1.87333
15	6	1.972352	1.323358	1.398592
16	6	0.777308	2.053656	1.69636
17	6	0.739685	3.247371	2.444586
18	6	-0.49659	3.815184	2.76049
19	6	-1.65571	3.142884	2.327061
20	6	-1.53157	1.971878	1.567722

21	1	1.672506	3.696265	2.770652
22	1	-0.5603	4.73459	3.335527
23	1	-2.6483	3.507262	2.57213
24	1	-2.43409	1.461998	1.271282
25	7	1.768277	0.282173	0.487125
26	7	-0.33743	1.406239	1.183709
27	8	5.629339	-1.3554	0.693119
28	8	6.135802	0.257439	2.231578
29	6	-4.78049	-3.69456	1.847465
30	6	-5.49482	-2.96043	0.891774
31	6	-4.90203	-1.84687	0.275221
32	6	-3.55722	-1.44724	0.548974
33	6	-2.89524	-2.16997	1.576124
34	6	-3.48325	-3.27441	2.207606
35	1	-5.23789	-4.55508	2.327645
36	1	-6.51463	-3.21225	0.618187
37	6	-3.03828	-0.32134	-0.23629
38	1	-1.9569	-1.78926	1.943946
39	1	-2.94346	-3.79109	2.99749
40	6	-3.96865	0.409412	-1.04057
41	6	-5.36113	0.06243	-1.22961
42	6	-3.26861	1.438975	-1.70913
43	6	-1.94023	1.282686	-1.32882
44	6	-0.72447	1.871417	-1.79209
45	6	-0.63337	3.031934	-2.58614
46	6	0.61935	3.445595	-3.0458
47	6	1.741384	2.667482	-2.694
48	6	1.569004	1.541728	-1.88025
49	1	-1.53861	3.577291	-2.83322
50	1	0.723302	4.33379	-3.66239
51	1	2.737514	2.917927	-3.04461
52	1	2.436662	0.957714	-1.61879
53	7	-1.75934	0.237464	-0.41225
54	7	0.358651	1.125536	-1.38034
55	8	-5.74789	-1.15442	-0.59868
56	8	-6.21146	0.664676	-1.89828
57	28	0.002744	-0.07141	0.059489
58	8	0.288196	-1.71308	-0.64935
59	1	-0.52893	-2.02575	-0.25424
60	1	-3.68602	2.144736	-2.4115
61	1	3.717056	2.025262	2.602622
62	8	-0.20329	-0.97053	1.618618
63	1	0.418952	-0.63441	2.269065
64	1	-0.03891	-1.90577	1.471609
65	1	-0.05238	-1.9251	-1.52152

Thermodynamic properties of **2b**:

Zero-point vibrational energy = 254.62197 Kcal/Mol

Sum of electronic and zero-point Energies = -1874.850768 Hartree

Sum of electronic and thermal Energies = -1874.820304 Hartree

Sum of electronic and thermal Enthalpies = -1874.819360 Hartree

Sum of electronic and thermal Free Energies = -1874.912865 Hartree

Cartesian coordinates of **2b**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.766893	-0.36801	-3.11855
2	6	4.009671	0.962622	-2.74924
3	6	3.043221	1.661747	-2.01012
4	6	1.823574	1.036558	-1.59957
5	6	1.599389	-0.30849	-2.00706
6	6	2.552316	-0.99969	-2.75762
7	1	4.513018	-0.91226	-3.6912
8	1	4.9252	1.476724	-3.02294
9	6	0.913156	1.868923	-0.85944
10	1	0.664451	-0.78787	-1.7505
11	1	2.361549	-2.02538	-3.05897
12	6	1.203871	3.262206	-0.62069
13	6	2.461099	3.878621	-1.00587
14	6	0.139967	3.823094	0.128378
15	6	-0.83393	2.796846	0.204854
16	6	-2.20715	2.805289	0.60626
17	6	-2.85391	3.942327	1.149196
18	6	-4.1907	3.853084	1.53767
19	6	-4.86446	2.614133	1.410184
20	6	-4.17593	1.522614	0.872826
21	1	-2.27007	4.850214	1.26273
22	1	-4.70196	4.716306	1.953547
23	1	-5.89471	2.494964	1.727878
24	1	-4.65443	0.554763	0.799743
25	7	-0.31759	1.579846	-0.27017
26	7	-2.88605	1.609684	0.446943
27	8	3.356017	2.984155	-1.70479
28	8	2.854038	5.031852	-0.82881
29	6	3.766984	0.367625	3.118424
30	6	4.009582	-0.96305	2.749151
31	6	3.043026	-1.66208	2.010071
32	6	1.823446	-1.03674	1.599515
33	6	1.599451	0.30835	2.006968
34	6	2.55248	0.999451	2.757498

35	1	4.51319	0.911804	3.691033
36	1	4.92505	-1.47726	3.02284
37	6	0.912925	-1.869	0.859431
38	1	0.66457	0.78786	1.75043
39	1	2.361848	2.025166	3.058828
40	6	1.203425	-3.26236	0.620807
41	6	2.460569	-3.87894	1.005986
42	6	0.139421	-3.8232	-0.12816
43	6	-0.83433	-2.79682	-0.20471
44	6	-2.20755	-2.80509	-0.60612
45	6	-2.85452	-3.94207	-1.14893
46	6	-4.19127	-3.85261	-1.53749
47	6	-4.86478	-2.6135	-1.41024
48	6	-4.17607	-1.52204	-0.87301
49	1	-2.27086	-4.85009	-1.2623
50	1	-4.70269	-4.71578	-1.95327
51	1	-5.89499	-2.49418	-1.72802
52	1	-4.65435	-0.55406	-0.8001
53	7	-0.31782	-1.57984	0.270138
54	7	-2.88624	-1.60932	-0.44701
55	8	3.35565	-2.98452	1.704775
56	8	2.853356	-5.03223	0.828977
57	46	-1.58701	0.000075	-6.2E-05

Thermodynamic properties of **2c**:

Zero-point vibrational energy = 255.07902 Kcal/Mol

Sum of electronic and zero-point Energies = -1867.286315 Hartree

Sum of electronic and thermal Energies = -1867.256075 Hartree

Sum of electronic and thermal Enthalpies = -1867.255131 Hartree

Sum of electronic and thermal Free Energies = -1867.348041 Hartree

Cartesian coordinates of **2c**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.900686	-0.42175	-3.08967
2	6	4.159653	0.902277	-2.70893
3	6	3.195132	1.613098	-1.9782
4	6	1.962155	1.003785	-1.5806
5	6	1.719253	-0.33256	-2.00809
6	6	2.669652	-1.0339	-2.75186
7	1	4.645029	-0.97442	-3.6565
8	1	5.085634	1.404331	-2.96942
9	6	1.061241	1.846935	-0.8413
10	1	0.769759	-0.79575	-1.77854
11	1	2.463092	-2.05226	-3.06713

12	6	1.359476	3.238724	-0.61235
13	6	2.624564	3.841684	-0.9942
14	6	0.296493	3.829275	0.12082
15	6	-0.68716	2.809246	0.18948
16	6	-2.06285	2.815082	0.563896
17	6	-2.73645	3.950716	1.075524
18	6	-4.07345	3.846619	1.452863
19	6	-4.71994	2.589539	1.348666
20	6	-4.01151	1.500318	0.841713
21	1	-2.16792	4.869534	1.176785
22	1	-4.60504	4.707841	1.846406
23	1	-5.74859	2.455639	1.665618
24	1	-4.46981	0.522248	0.799803
25	7	-0.18056	1.57749	-0.25469
26	7	-2.71808	1.599671	0.414526
27	8	3.522183	2.929655	-1.67004
28	8	3.026128	4.993036	-0.82855
29	6	3.901205	0.421193	3.088958
30	6	4.159778	-0.90298	2.708459
31	6	3.194939	-1.61367	1.978026
32	6	1.962104	-1.0041	1.580405
33	6	1.719628	0.332418	2.007644
34	6	2.670306	1.033627	2.751173
35	1	4.645767	0.973791	3.655583
36	1	5.085656	-1.4052	2.968971
37	6	1.060874	-1.84716	0.841322
38	1	0.770281	0.795839	1.778054
39	1	2.464121	2.052113	3.066281
40	6	1.358646	-3.23915	0.612683
41	6	2.623535	-3.8424	0.994748
42	6	0.295516	-3.82957	-0.12034
43	6	-0.68781	-2.80912	-0.18918
44	6	-2.06347	-2.81469	-0.56364
45	6	-2.73737	-3.95023	-1.07511
46	6	-4.07432	-3.84585	-1.45247
47	6	-4.72049	-2.58857	-1.34854
48	6	-4.0118	-1.49942	-0.84184
49	1	-2.16903	-4.86919	-1.17627
50	1	-4.60614	-4.70699	-1.84586
51	1	-5.74912	-2.45453	-1.66551
52	1	-4.46976	-0.52118	-0.80023
53	7	-0.18084	-1.57745	0.254643
54	7	-2.71838	-1.59906	-0.41458
55	8	3.521549	-2.93038	1.670147

Thermodynamic properties of **2d**:

Zero-point vibrational energy = 271.81069 Kcal/Mol

Sum of electronic and zero-point Energies = -1945.714942 Hartree

Sum of electronic and thermal Energies = -1945.684304 Hartree

Sum of electronic and thermal Enthalpies = -1945.683360 Hartree

Sum of electronic and thermal Free Energies = -1945.778329 Hartree

Cartesian coordinates of **2d**:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.466228	2.685707	-2.71525
2	6	5.289851	1.615595	-2.33582
3	6	4.751263	0.571838	-1.56646
4	6	3.391907	0.58126	-1.14948
5	6	2.577405	1.665355	-1.55943
6	6	3.105293	2.70718	-2.33104
7	1	4.875608	3.493955	-3.31533
8	1	6.33405	1.563362	-2.62732
9	6	2.961822	-0.55933	-0.36473
10	1	1.52844	1.680772	-1.27924
11	1	2.465986	3.529241	-2.64099
12	6	3.850967	-1.64042	-0.09667
13	6	5.235127	-1.64792	-0.52394
14	6	3.127199	-2.62671	0.627809
15	6	1.832256	-2.11281	0.779839
16	6	0.630009	-2.64672	1.385583
17	6	0.5274	-3.9011	2.032267
18	6	-0.70033	-4.29301	2.577496
19	6	-1.82036	-3.43534	2.477744
20	6	-1.66297	-2.20776	1.824325
21	1	1.400322	-4.54162	2.099502
22	1	-0.79105	-5.25387	3.076635
23	1	-2.7849	-3.71112	2.889339
24	1	-2.48555	-1.51007	1.712901
25	7	1.735094	-0.84126	0.1824
26	7	-0.47307	-1.82864	1.293159

27	8	5.629906	-0.47239	-1.24707
28	8	6.093127	-2.51829	-0.33362
29	6	-4.4666	-2.68537	-2.71527
30	6	-5.29006	-1.6151	-2.33594
31	6	-4.75138	-0.57146	-1.56648
32	6	-3.39208	-0.58116	-1.14931
33	6	-2.57774	-1.66541	-1.55918
34	6	-3.10573	-2.70711	-2.33088
35	1	-4.87606	-3.49353	-3.31542
36	1	-6.33421	-1.56265	-2.62757
37	6	-2.96188	0.559324	-0.36446
38	1	-1.52881	-1.68103	-1.27886
39	1	-2.46654	-3.5293	-2.64074
40	6	-3.8509	1.640529	-0.09643
41	6	-5.23501	1.648284	-0.52386
42	6	-3.12708	2.626658	0.628198
43	6	-1.83223	2.112552	0.780359
44	6	-0.62991	2.646398	1.386026
45	6	-0.52724	3.900719	2.032812
46	6	0.70057	4.292635	2.57785
47	6	1.820612	3.435026	2.477825
48	6	1.663152	2.207485	1.824354
49	1	-1.40018	4.541196	2.100269
50	1	0.791343	5.253461	3.077054
51	1	2.785219	3.71081	2.889262
52	1	2.485737	1.509824	1.712762
53	7	-1.7352	0.841011	0.18289
54	7	0.473173	1.82836	1.293362
55	8	-5.62987	0.472921	-1.2472
56	8	-6.09291	2.518747	-0.3335
57	1	-3.51652	3.574731	0.970243
58	1	3.516731	-3.57476	0.969803
59	29	0.000036	-8.7E-05	0.485823

Table S35: Some selected transitions calculated from TD-DFT calculation.

Sample	State	Transitions		Coefficient (%)	Energy (eV)	Wave Length (nm)	Oscillator strength
		From	To				
L1	S0→S1	HOMO	LUMO	25.60	3.4651	357.8	0.0962
		HOMO	LUMO+1	65.50			
L2H	S0→S1	HOMO	LUMO	70.10	3.708	334.37	0.8441
	S0→S2	HOMO	LUMO+1	68.00	4.1204	300.9	0.1663
1a	S0→S8	HOMO	LUMO+5	24.71	2.1984	563.98	0.0069
		HOMO	LUMO+6	10.09			
		HOMO	LUMO+7	64.75			
	S0→S9	HOMO-4	LUMO+2	11.01	2.3059	537.69	0.0001
		HOMO-3	LUMO	17.75			
		HOMO-3	LUMO+2	62.3			
	S0→S10	HOMO	LUMO+6	12.27	2.3448	528.76	0.0026
		HOMO	LUMO+8	67.98			
1aa	S0→S8	HOMO	LUMO+2	44.36	2.5619	483.95	0.0024
	S0→S9	HOMO	LUMO+1	16.95	2.7049	458.36	0.0016
		HOMO	LUMO	16.79			
		HOMO-5	LUMO+1	14.21			
1b	S0→S1	HOMO-1	LUMO	54.60	2.5032	495.31	0.0001
		HOMO	LUMO	36.30			
	S0→S2	HOMO-4	LUMO	67.70	2.5372	488.67	0.0012
	S0→S3	HOMO-2	LUMO	51.50	2.6537	467.21	0.0004
		HOMO-3	LUMO	32.90			
	S0→S4	HOMO-3	LUMO	55.00	2.703	458.69	0.0009
		HOMO-6	LUMO	32.10			
1c	S0→S1	HOMO-3	LUMO+1	45.80	3.0736	403.39	0.0358
1d	S0→S9	HOMO-32	LUMO	16.88	3.1036	399.49	0.0149
		HOMO-15	LUMO	16.95			
		HOMO-5	LUMO	18.52			
		HOMO-2	LUMO	23.89			
1e	S0→S9	HOMO-32	LUMO	22.10	2.7860	445.03	0.0079
		HOMO-15	LUMO	19.18			
		HOMO-11	LUMO	8.90			
		HOMO-3	LUMO	4.36			
		HOMO-2	LUMO	25.22			
2a	S0→S4	HOMO	LUMO+2	68.57	1.5353	807.57	0.0025
		HOMO	LUMO+4	12.97			
	S0→S5	HOMO	LUMO+3	66.62	1.5767	786.36	0.0044
		HOMO	LUMO+5	19.77			
	S0→S6	HOMO	LUMO+3	20.71	1.7159	722.56	0.0013
		HOMO	LUMO+4	39.26			
		HOMO	LUMO+5	48.73			

		HOMO	LUMO+6	24.28			
	S0→S7	HOMO	LUMO+5	29.97	1.7852	694.5	0.0035
		HOMO	LUMO+6	63.2			
	S0→S8	HOMO-3	LUMO	18.96	2.3127	536.1	0.0006
		HOMO-3	LUMO+4	34.55			
		HOMO-3	LUMO+5	24.51			
		HOMO-3	LUMO+6	11.85			
		HOMO-2	LUMO+4	12.74			
		HOMO	LUMO+7	37.95			
	S0→S9	HOMO-3	LUMO	13.81	2.3264	532.94	0.0029
		HOMO-3	LUMO+4	27.09			
		HOMO-3	LUMO+5	18.8			
		HOMO	LUMO+7	49.43			
	S0→S10	HOMO	LUMO+8	13.6	2.639	469.81	0.0024
		HOMO	LUM+9	68.58			
		HOMO	LUMO+4	13.00			
2b	S0→S8	HOMO-6	LUMO	70.27	1.6441	754.12	0.0002
	S0→S9	HOMO+1	LUMO+1	68.84	2.048	605.39	0.0009
	S0→S10	HOMO-10	LUMO	13.44	2.16	574	0.0625
		HOMO-7	LUMO	67.27			
2c	S0→S9	HOMO-10	LUMO	16.6	2.1716	570.93	0.0735
		HOMO-7	LUMO	67.2			
		HOMO+1	LUMO	11.5			
	S0→S10	HOMO-8	LUMO	46	2.3198	534.46	0.0026
		HOMO+1	LUMO+1	53			
		HOMO	LUMO+8	12.52			
2d	S0→S8	HOMO-2	LUMO	53.29	2.5726	481.94	0.0039
		HOMO-4	LUMO	12.78			

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