
Supporting Information for

CuCl-Catalyzed Hydroxylation of *N*-heteroarylcarbazole Bromide: Approach for the Preparation of *N*-heteroarylcarbazolyl Phenols and Its Application in the Synthesis of Phosphorescent Emitters

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General Information. ^1H NMR spectra were recorded at 400 or 500 MHz, and ^{13}C NMR spectra were recorded at 100 or 126 MHz NMR instruments in CDCl_3 or $\text{DMSO-}d_6$ solutions and chemical shifts were referenced to tetramethylsilane (TMS) or residual protiated solvent. If CDCl_3 was used as solvent, ^1H NMR spectra were recorded with TMS ($\delta = 0.00$ ppm) as internal reference; ^{13}C NMR spectra were recorded with CDCl_3 ($\delta = 77.00$ ppm) as internal reference. If $\text{DMSO-}d_6$ was used as solvent, ^1H NMR spectra were recorded with TMS ($\delta = 0.00$ ppm) or residual H_2O ($\delta = 3.33$ ppm) as internal reference; ^{13}C NMR spectra were recorded with $\text{DMSO-}d_6$ ($\delta = 39.52$ ppm) as internal reference. All of the new compounds were analyzed for HRMS on an ESI-QTOF mass spectrometer using electrospray ionization in positive ion mode. Steady state emission experiments were performed on a Horiba Jobin Yvon FluoroLog-3 spectrometer. The following abbreviations (or combinations thereof) were used to explain ^1H NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad. Mass spectra were recorded on Voyager DE-STR MALDI-TOF mass spectrometer from Applied Biosystems. The Microanalysis Laboratory at Shanghai Institute of Organic Chemistry performed the elemental analysis.

The samples of compounds **2a-1l** for the ^1H NMR spectra in this supporting information were provided from method of "Condition C" except **2g** which was provided from method of "Condition A". IR spectra were tested in solid state in KBr thin films. UV spectra were tested in CH_2Cl_2 solutions.

Ligands **L1-L12** were purchased and used as received without further purification. Ligands N^1 -(benzyl)- N^2 -(4-methyl-2-phenylphenyl)oxalamide **L13** and N^1 -(4-hydroxy-2,6-dimethylphenyl)- N^2 -(4-hydroxy-3,5-dimethylphenyl)oxalamide **L14** were synthesized according the reported literature.¹ All the starting materials **1a-1p** were synthesized according our previous reported method.²

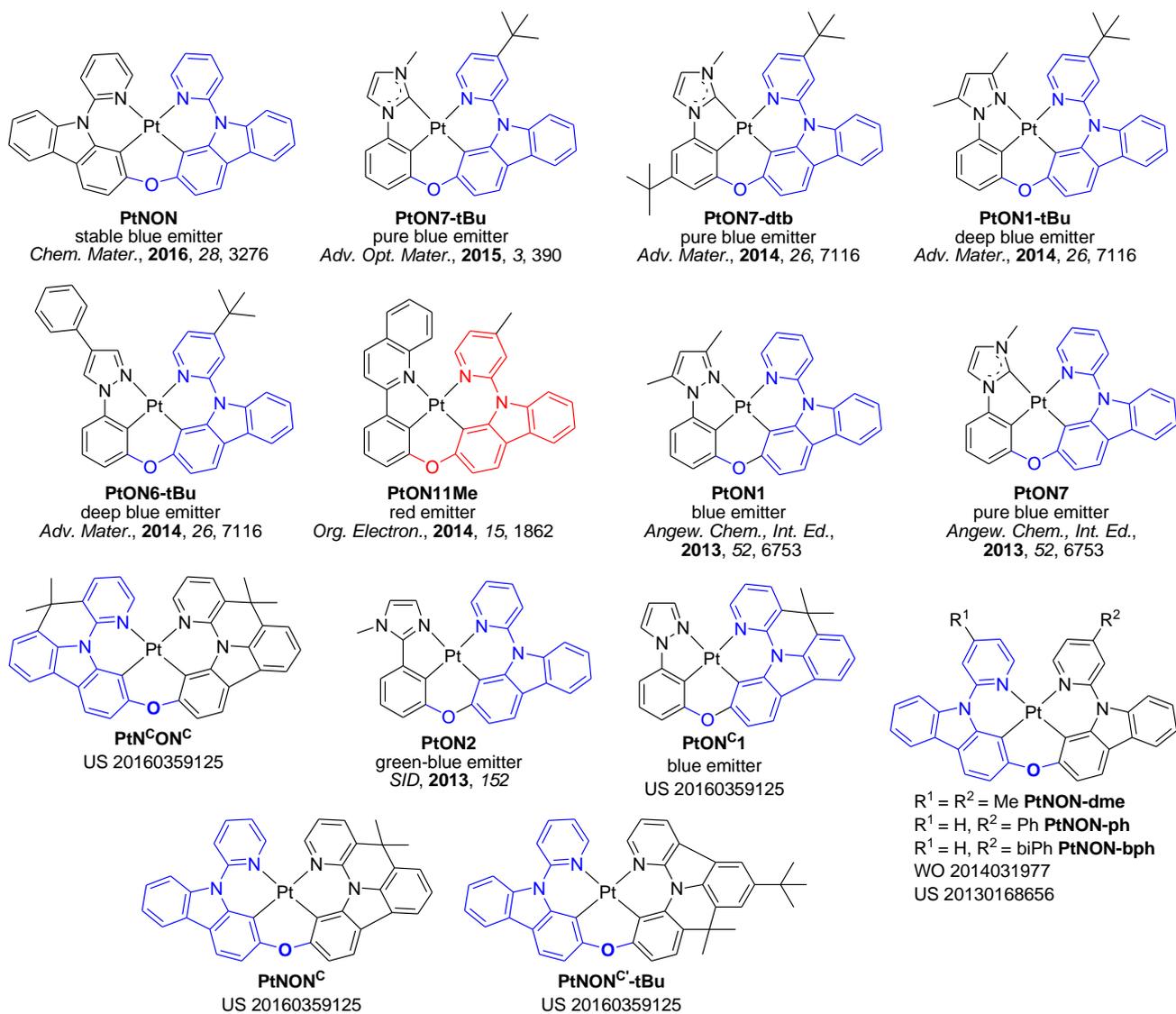
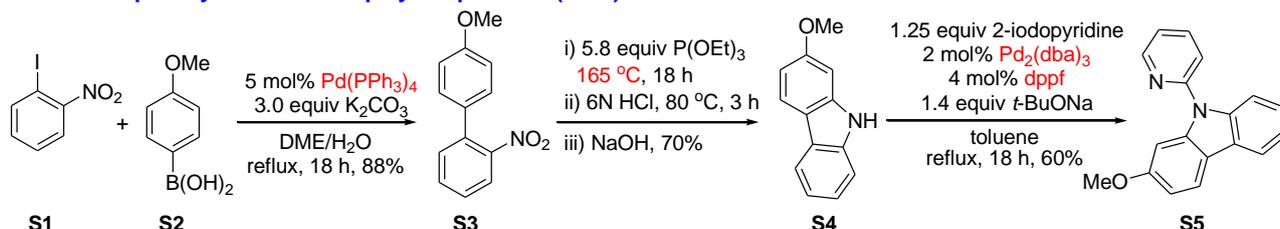


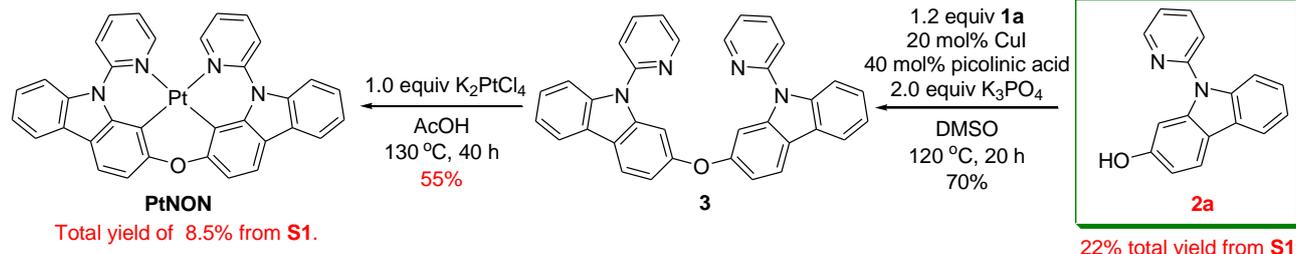
Figure S1. Selected tetradentate platinum-based phosphorescent emitters containing 2-oxy-9-(pyridin-2-yl)-9H-carbazole skeleton

Previous report by Universal Display Corporation (UDC): US 20130168656

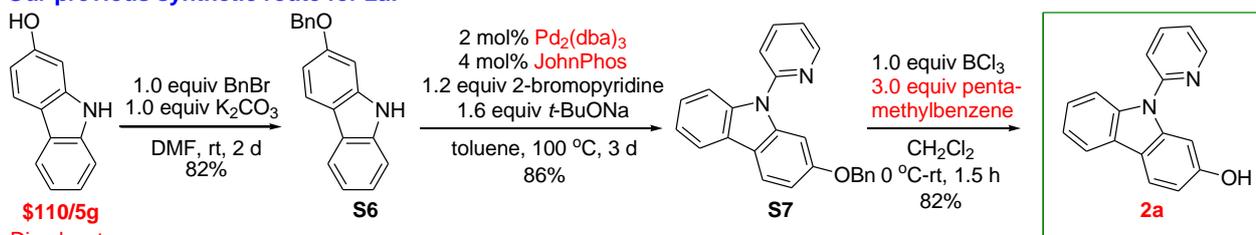


Disadvantages:

- (I) Expensive Pd catalysts and phosphine ligands;
- (II) High reaction temperature;
- (III) Low total yield.



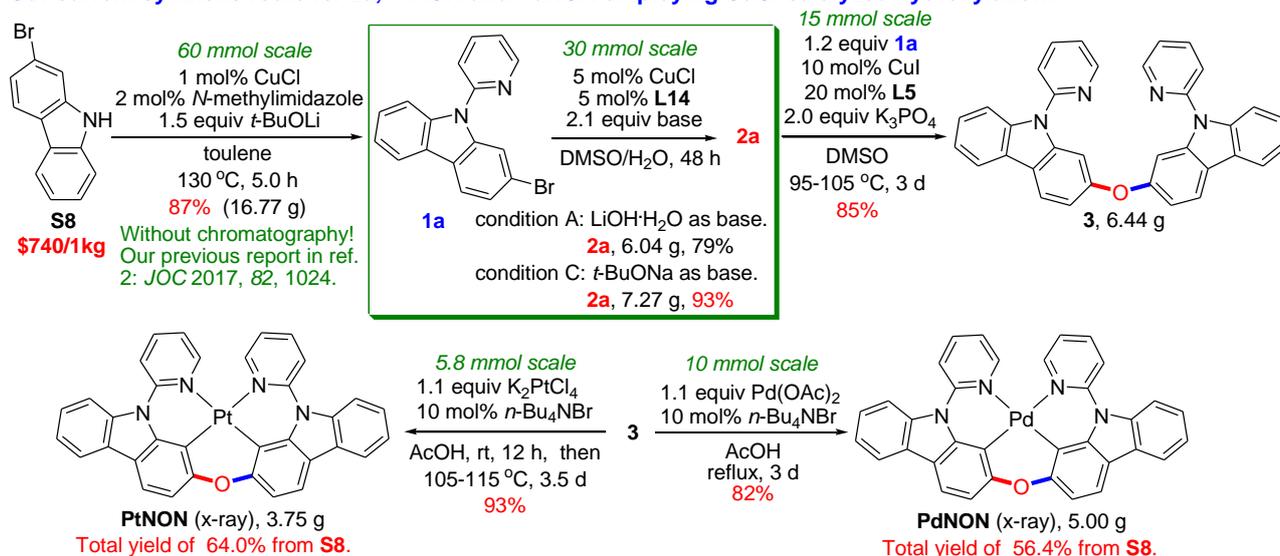
Our previous synthetic route for 2a:



Disadvantages:

- (I) Starting material is very expensive;
- (II) Expensive Pd catalyst and phosphine ligand;
- (III) Consuming a plenty of penta-methylbenzene.

Our current synthetic route for 2a, PtNON and PdNON employing CuCl-catalyzed hydroxylation:



Advantages:

- (I) Inexpensive starting material;
- (II) Expensive Pd catalysts and phosphine ligands free;
- (III) Large-scale synthesis;
- (IV) High total yield.

Figure S2. Comparison of synthetic route for critical intermediate 2a and PtNON

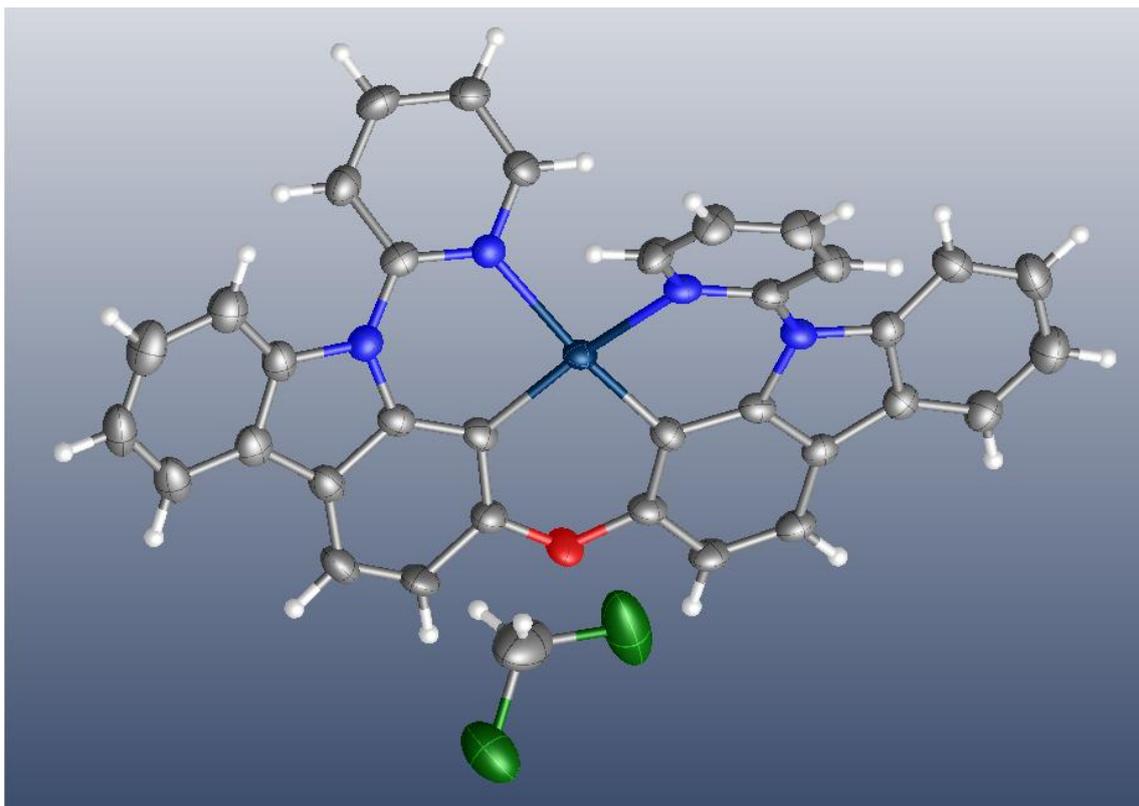


Figure S3. X-ray structure of **PtNON** with a molecule of CH_2Cl_2 . Ellipsoids are shown at the 50% probability level.

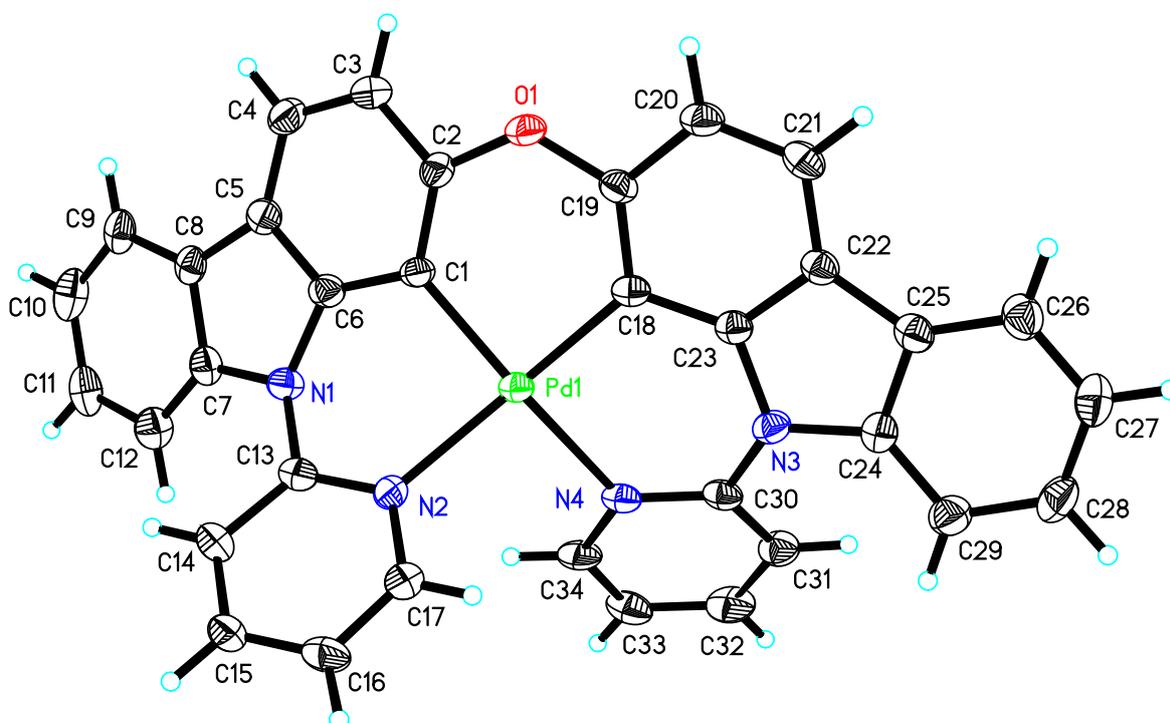
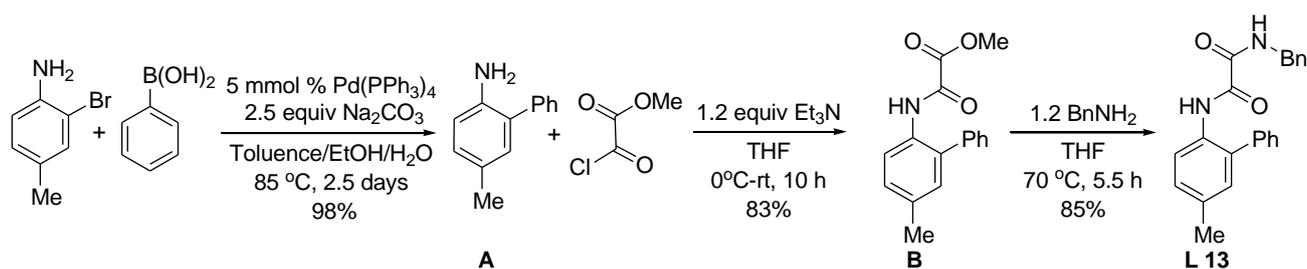


Figure S4. X-ray structure of **PdNON**. Ellipsoids are shown at the 50% probability level.

Synthesis of Ligand L13.¹



Phenylboronic acid (3.72 mL, 30.0 mmol, 1.0 equiv), $\text{Pd(PPh}_3)_4$ (1.73 g, 1.5 mmol, 0.05 equiv) and Na_2CO_3 (7.95 g, 75.0 mmol, 2.5 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then 2-bromo-4-methylaniline (3.72 mL, 30.0 mmol, 1.0 equiv) and solvent toluene/EtOH/ H_2O (100 mL/100 mL/100 mL) were added under nitrogen. Then the mixture was bubbled with nitrogen for 20 minutes and was stirred under reflux at 80°C for 2.5 days. The reaction mixture was allowed to cool to room temperature and concentrated under reduced pressure, diluted with EtOAc. The organic layer was then separated and aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 40:1-5:1) to afford **A** as a colourless liquid 5.4 g in 98% yield.

$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ 2.18 (s, 3H), 4.54 (s, 2H), 6.68 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 1.5$ Hz, 1H), 6.87 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.30-7.34 (m, 1H), 7.39-7.45 (m, 4H)

4-Methyl-2-phenylaniline (5.5 g, 30.0 mmol, 1.0 equiv) in THF (60 mL) was added to a dry three-necked flask with magnetic stir bar under nitrogen. After adding Et_3N (5.0 mL, 36.0 mmol, 1.2 equiv), the mixture was cooled to 0°C , then mono-methyl oxalyl chloride (3.04 mL, 33.0 mmol, 1.1 equiv) was added to the solution slowly. After the resulting mixture was stirred at room temperature for 10 h. The mixture was washed with the same volume of water. The organic phase was dried over Na_2SO_4 , filtered and the filtrate was concentrated under reduced pressure. The crude product was purified through chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1-3:1) to afford **B** as a white solid 6.7 g in 83% yield.

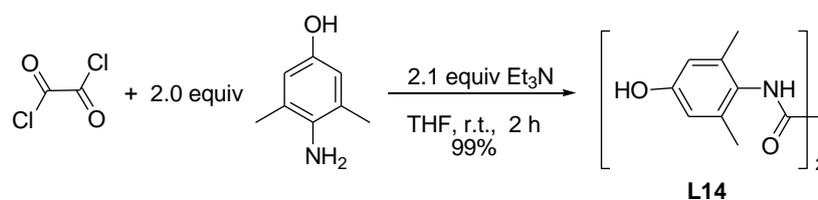
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ 2.39 (s, 3H), 3.89 (s, 3H), 7.15 (d, $J = 2.0$ Hz, 1H), 7.25 (dd, $J = 8.5,$

2.0 Hz, 1H), 7.38-7.40 (m, 2H), 7.44-7.47 (m, 1H), 7.51-7.54 (m, 2H), 8.33 (d, $J = 8.0$ Hz, 1H), 9.02 (s, 1H).

A solution of the above monoamide **B** (2.7 g, 10 mmol, 1.0 equiv) and BnNH_2 (1.3 mL, 12 mmol, 1.2 eq.) in THF (10 mL) was stirred at 70 °C for 5.5 h, then it was cooled to room temperature and then to -10 °C in refrigerator. The products precipitated out as crystals. The mixture was filtered, and the collected solid was washed with small amount of cold diethyl ether to afford **L13** as a white solid 2.9 g in 85% yield.

^1H NMR (500 MHz, CDCl_3): δ 2.37 (s, 3H), 4.48 (d, $J = 6.5$ Hz, 2H), 7.13 (d, $J = 2.0$ Hz, 1H), 7.21 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.25-7.35 (m, 5H), 7.38-7.40 (m, 2H), 7.43 (tt, $J = 7.5, 1.5$ Hz, 1H), 7.51 (dd, $J = 5.5, 1.5$ Hz, 2H), 7.81 (br, 1H), 8.29 (d, $J = 8.5$ Hz, 1H), 9.46 (s, 1H).

Synthesis of Ligand **L14**.¹



4-Amino-3,5-dimethylphenol (8.23 g, 60.0 mmol, 2.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then solvent THF (200 mL) was added under nitrogen. The mixture was then stirred until the solid was dissolved. After adding Et_3N (8.73 mL, 63.0 mmol, 2.1 equiv), the mixture was cooled to 0 °C, and oxalyl chloride (2.36 mL, 30.0 mmol, 1.0 equiv) was then added to the solution slowly at that temperature. After the resulting mixture was stirred at room temperature for 2 h, it was concentrated under reduced pressure to remove the solvent. Water was added to the resulting residue to dissolve $\text{Et}_3\text{N}\cdot\text{HCl}$. The slurry was filtered and the solid was washed with water and cold diethyl ether, then dried under vacuum to afford **L14** as a gray solid 10.2 g in 99% yield.

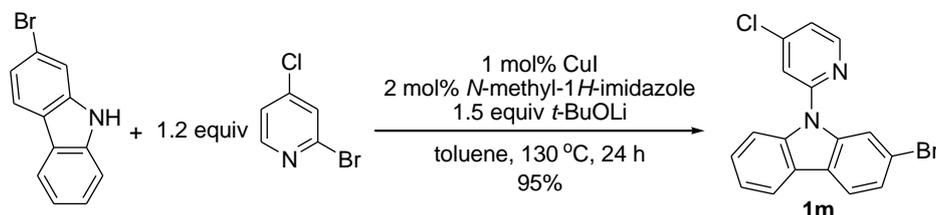
^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 2.06 (s, 12H), 6.49 (s, 4H), 9.25 (s, 2H), 9.95 (s, 2H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 18.1, 114.3, 125.5, 136.1, 155.9, 159.3.

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 351.1315, found 351.1322.

Synthesis of Starting Materials of 2-Bromo-9-(pyridin-2-yl)-9H-carbazole and Its Analogues. Three new compounds were made as following procedure.²

Synthesis of 2-bromo-9-(4-chloropyridin-2-yl)-9H-carbazole **1m**:



2-Bromocarbazole (1.23 g, 5.00 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), *t*-BuOLi (0.60 g, 7.5 mmol, 1.5 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then ligand *N*-methyl-1*H*-imidazole (7.9 μ L, 0.10 mmol, 0.02 equiv), 2-bromo-4-chloropyridine (0.66 mL, 6.00 mmol, 1.2 equiv) and the solvent toluene (20 mL) were added under nitrogen. The mixture was then stirred at 130 °C for 24 hours until the 2-bromocarbazole was consumed completely monitored by TLC. The reaction mixture was cooled to room temperature and quenched with a solution of Na₂SO₃, diluted with EtOAc, filtered through a pad of celite and washed with EtOAc. The organic layer was then separated, dried over Na₂SO₄, filtered, and the filtrate was concentrated, the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 5:1-3:2 as eluent to afford **1m** as a white solid 1.70 g in 95% yield.

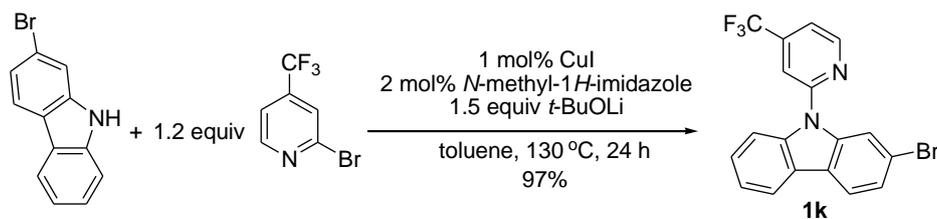
mp: 231.5-232.7 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 7.38 (t, *J* = 7.5 Hz, 1H), 7.50-7.54 (m, 2H), 7.66 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 1.0 Hz, 1H), 8.02 (d, *J* = 1.5 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.73 (d, *J* = 5.5 Hz, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 111.3, 114.3, 119.1, 119.2, 120.7, 121.7, 122.1, 122.5, 122.8, 123.0, 124.1, 127.1, 138.8, 139.6, 145.3, 150.8, 151.3.

HRMS (ESI): calcd for C₁₇H₁₁BrClN₂ [M + H]⁺ 356.9789, found 356.9800.

Synthesis of 2-bromo-9-(4-(trifluoromethyl)pyridin-2-yl)-9H-carbazole **1k**:



2-Bromocarbazole (1.23 g, 5.00 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), *t*-BuOLi (0.60 g, 7.5 mmol, 1.5 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then ligand *N*-methyl-1*H*-imidazole (7.9 μ L, 0.10 mmol, 0.02 equiv), 2-bromo-4- trifluoromethyl pyridine (0.79 mL, 6.00 mmol, 1.2 equiv) and the solvent toluene (20 mL) were added under nitrogen. The mixture was then stirred at 130 °C until the 2-bromocarbazole was consumed completely monitored by TLC. The reaction mixture was cooled to room temperature and quenched with a solution of Na₂SO₃, diluted with EtOAc, filtered through a pad of celite and washed with EtOAc. The organic layer was then separated, dried over Na₂SO₄, filtered, the filtrate was concentrated, and the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 3:1-1:1 as eluent to afford **1k** as a white solid 1.90 g in 97% yield.

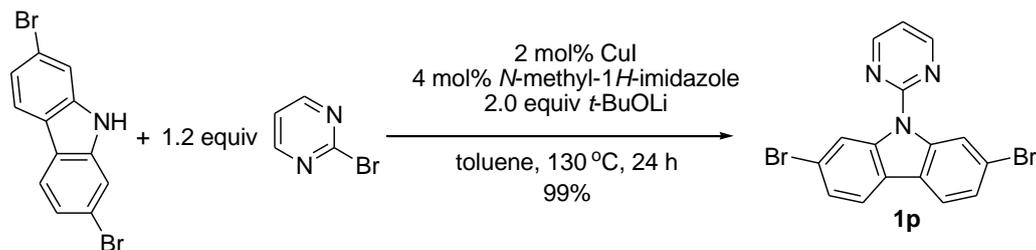
mp: 90.7-91.5 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 7.38-7.41 (m, 1H), 7.53 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.04 (d, *J* = 1.5 Hz, 1H), 8.16 (d, *J* = 0.5 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 9.02 (d, *J* = 5.0 Hz, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 111.1, 114.3, 115.1 (d, *J* = 4.0 Hz, 1C), 117.8, 119.2, 120.8, 121.9, 122.2, 122.6 (q, *J* = 272.0 Hz, 1C), 122.9, 123.1, 124.3, 127.2, 138.9, 139.6, 139.7 (q, *J* = 33.0 Hz, 1C), 151.3, 151.5.

HRMS (ESI): calcd for C₁₈H₁₁BrF₃N₂ [M+H]⁺ 391.0052, found 391.0041.

Synthesis of 2,7-dibromo-9-(pyrimidin-2-yl)-9*H*-carbazole **1p**:



2,7-Dibromocarbazole (1.66 g, 5.10 mmol, 1.0 equiv), 2-bromopyrimidine (0.97 g, 6.10 mmol, 1.2 equiv), CuI (19.4 mg, 0.10 mmol, 0.02 equiv), *t*-BuOLi (0.82 g, 10.2 mmol, 2.0 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then ligand *N*-methyl-1*H*-imidazole (16.0 μ L, 0.20 mmol, 0.04 equiv) and solvent toluene (20 mL) were added under nitrogen. The mixture was then stirred at 130 °C for 24 hours until the 2-bromocarbazole was consumed completely monitored by TLC. The reaction mixture was cooled to room temperature and quenched with a solution of Na₂SO₃, diluted with EtOAc, filtered through a pad of celite and washed with EtOAc. The organic layer was then separated, dried over Na₂SO₄, filtered, the filtrate was concentrated, and the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 5:1-3:2 as eluent to afford **1p** as a white solid 2.03 g in 99% yield.

mp: 213.5-214.1 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 7.47 (t, *J* = 4.5 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.5 Hz, 2H), 8.22 (d, *J* = 3.0 Hz, 2H), 9.02 (d, *J* = 1.5 Hz, 2H), 9.05 (d, *J* = 5.0 Hz, 2H).

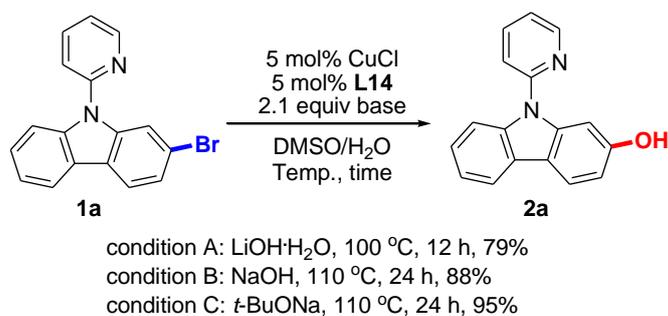
¹³C NMR (100 MHz, CDCl₃): δ 116.7, 119.8, 120.5, 120.6, 124.0, 125.8, 139.8, 158.0, 158.6.

HRMS (EI): calcd for C₁₆H₉N₃Br₂ [M]⁺ 400.9163, found 400.9178.

General Experimental Procedure for Hydroxylation of 2-Bromo-9-(pyridin-2-yl)-9*H*-carbazole and Its Analogues. 2-Bromo-9-(pyridin-2-yl)-9*H*-carbazole or its analogues, CuCl, ligand and base were added to a dry Schlenk tube equipped with a magnetic stir bar. The tube was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then DMSO and H₂O were added into the tube under nitrogen atmosphere. The tube was placed in oil bath (100 or 110 °C) and stirred for 12-48 h until the starting material was consumed completely monitoring by TLC. Then the mixture was cooled down, diluted with ethyl acetate. The organic layer was then

separated, and aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product.

9-(Pyridin-2-yl)-9H-carbazol-2-ol (**2a**):



Condition A: Following the general procedure, the reaction of **1a** (323.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (88.1 mg, 2.1 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 100 °C for 12 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 206.9 mg in 79% yield.

Condition B: Following the general procedure, the reaction of **1a** (161.1 mg, 0.5 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and NaOH (42.0 mg, 1.1 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 114.5 mg in 88% yield.

Condition C: Following the general procedure, the reaction of **1a** (161.1 mg, 0.5 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and $t\text{-BuONa}$ (100.9 mg, 1.1 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 123.5 mg in 95% yield.

mp: 191.1-192.4 °C.

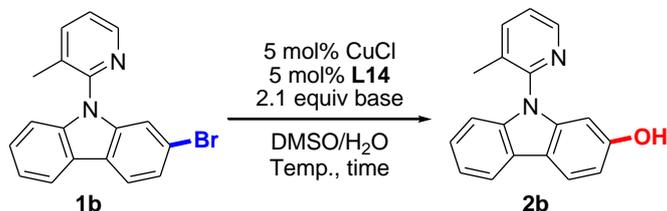
^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 6.79 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.18 (d, $J = 2.0$ Hz, 1H), 7.23-7.26 (m, 1H), 7.32 (td, $J = 8.5, 1.0$ Hz, 1H), 7.47 (ddd, $J = 7.5, 5.0, 1.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.5$ Hz, 1H), 8.06 (d, $J = 7.5$ Hz, 1H), 8.11 (td, $J = 8.0, 2.0$ Hz, 1H), 8.72 (ddd, $J = 5.0, 2.0, 0.5$ Hz, 1H), 9.61 (s, 1H).

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ 97.1, 110.3, 110.8, 115.9, 119.0, 119.1, 120.78, 121.1, 121.8, 124.0,

124.5, 138.8, 139.3, 140.5, 149.5, 150.9, 157.0.

HRMS (ESI): calcd for $C_{17}H_{13}N_2O$ $[M + H]^+$ 261.1022, found 261.1028.

9-(3-Methylpyridin-2-yl)-9H-carbazol-2-ol (**2b**):



condition A: LiOH·H₂O, 100 °C, 24 h, 89%

condition B: NaOH, 110 °C, 24 h, 91%

condition C: *t*-BuONa, 110 °C, 24 h, 98%

Condition A: Following the general procedure, the reaction of **1b** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and LiOH·H₂O (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2b** (eluent: petroleum ether/ethyl acetate = 10:1-3:1) as a brown solid 245.2 mg in 89% yield.

Condition B: Following the general procedure, the reaction of **1b** (84.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2b** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 65.2 mg in 91% yield.

Condition C: Following the general procedure, the reaction of **1b** (212.9 mg, 0.63 mmol, 1.0 eq), CuCl (3.1 mg, 0.03 mmol, 0.05 eq), ligand **L14** (10.3 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (127.1 mg, 1.32 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2b** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 168.9 mg in 98% yield.

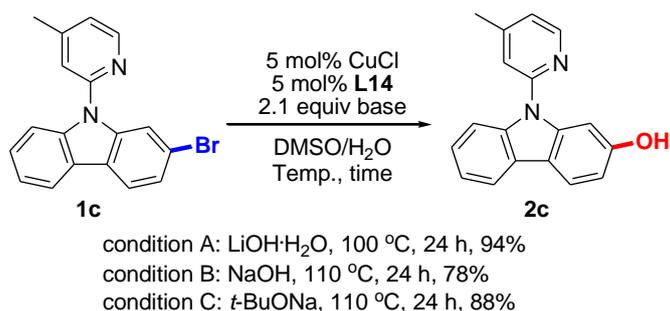
mp: 242.8-244.4 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 2.01 (s, 3H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.27 (td, *J* = 7.0, 1.0 Hz, 1H), 7.57 (dd, *J* = 8.0, 5.0 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 8.04-8.07 (m, 2H), 8.57 (dd, *J* = 4.5, 1.0 Hz, 1H), 9.50 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 16.9, 95.8, 109.6, 109.8, 115.1, 119.4, 112.0, 121.4, 123.2, 124.2, 124.4, 131.0, 139.6, 141.0, 141.4, 147.8, 148.8, 157.0.

HRMS (ESI): calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1179, found 275.1191.

9-(4-Methylpyridin-2-yl)-9H-carbazol-2-ol (**2c**):



Condition A: Following the general procedure, the reaction of **1c** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and LiOH·H₂O (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 258.4 mg in 94% yield.

Condition B: Following the general procedure, the reaction of **1c** (84.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 53.8 mg in 78% yield.

Condition C: Following the general procedure, the reaction of **1c** (210.0 mg, 0.62 mmol, 1.0 eq), CuCl (3.1 mg, 0.03 mmol, 0.05 eq), ligand **L14** (10.2 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (124.9 mg, 1.30 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 150.1 mg in 88% yield.

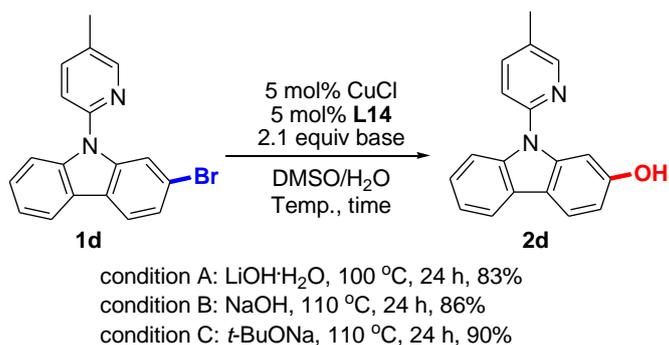
mp: 178.4-179.2 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 2.48 (s, 3H), 6.78 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 7.23-7.26 (m, 1H), 7.30-7.33 (m, 2H), 7.57 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 8.57 (d, *J* = 5.0 Hz, 1H), 9.59 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 20.7, 97.2, 110.3, 110.9, 115.8, 119.2, 119.5, 120.7, 121.1, 122.9, 124.0, 124.5, 138.9, 140.6, 149.1, 150.5, 151.0, 157.0.

HRMS (ESI): calcd for C₁₈H₁₅N₂O [M + H]⁺ 275.1179, found 275.1190.

9-(5-Methylpyridin-2-yl)-9H-carbazol-2-ol (**2d**):



Condition A: Following the general procedure, the reaction of **1d** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and LiOH·H₂O (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 226.6 mg in 83% yield.

Condition B: Following the general procedure, the reaction of **1d** (55.7 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.01 mmol, 0.05 eq), ligand **L14** (2.6 mg, 0.01 mmol, 0.05 eq) and NaOH (13.9 mg, 0.35 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 39.0 mg in 86% yield.

Condition C: Following the general procedure, the reaction of **1d** (183.2 mg, 0.54 mmol, 1.0 eq), CuCl (2.7 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.9 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (109.0 mg, 1.13 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 133.9 mg in 90% yield.

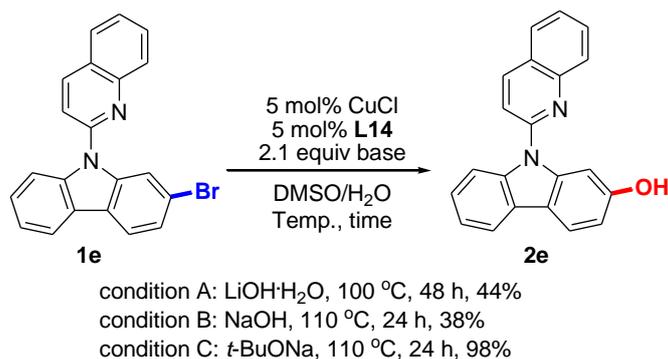
mp: 201.3-202.6 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 2.43 (s, 3H), 6.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.22-7.25 (m, 1H), 7.29-7.32 (m, 1H), 7.62-7.64 (m, 2H), 7.93 (ddd, *J* = 8.5, 2.5, 0.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.04-8.06 (m, 1H), 8.55 (dd, *J* = 2.0, 1.0 Hz, 1H), 9.59 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 17.5, 97.0, 110.2, 110.7, 115.8, 118.6, 119.2, 120.6, 121.1, 123.9, 124.5, 131.3, 139.0, 139.6, 140.7, 148.6, 149.5, 157.0.

HRMS (ESI): calcd for C₁₈H₁₅N₂O [M + H]⁺ 275.1179, found 275.1180.

9- (Quinolin-2-yl)-9H-carbazol-2-ol (**2e**):



Condition A: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and LiOH·H₂O (22.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 48 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 33.8 mg in 44% yield.

Condition B: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 29.4 mg in 38% yield and **1e** was recycled 18.5 mg in 20% yield.

Condition C: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 76.4 mg in 98% yield.

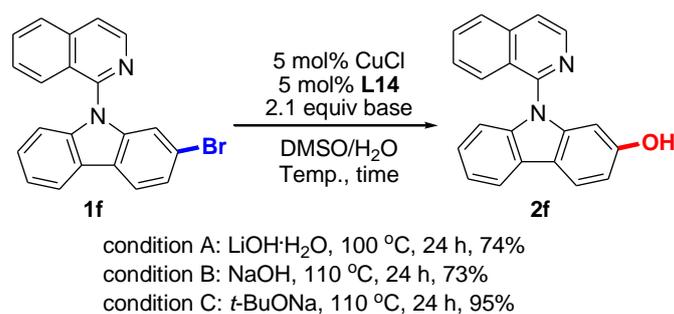
mp: 217.3- 218.7 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 6.83 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.28-7.31 (m, 1H), 7.37 (td, *J* = 8.0, 1.0 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.67-7.70 (m, 1H), 7.86-7.89 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.09 (t, *J* = 8.5 Hz, 2H), 8.12-8.13 (m, 1H), 8.66 (d, *J* = 8.5 Hz, 1H), 9.67 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 97.7, 110.7, 111.3, 116.2, 117.7, 119.3, 121.2, 121.3, 124.4, 124.7, 126.3, 126.5, 128.1(2C), 130.6, 138.8, 139.5, 140.5, 147.0, 150.4, 157.2.

HRMS (ESI): calcd for C₂₁H₁₅N₂O [M + H]⁺ 311.1179, found 311.1170.

9- (Isoquinolin-2-yl)-9*H*-carbazol-2-ol (**2f**):



Condition A: Following the general procedure, the reaction of **1f** (186.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and LiOH·H₂O (44.1 mg, 1.05 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 114.5 mg in 74% yield.

Condition B: Following the general procedure, the reaction of **1f** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 56.3 mg in 73% yield.

Condition C: Following the general procedure, the reaction of **1f** (186.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 147.9 mg in 95% yield.

mp: 247.5-248.2 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 6.37 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.96-6.98 (m, 1H), 7.21-7.26 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.62-7.66 (m, 1H), 7.88-7.92 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.12-8.13 (m, 2H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 5.5 Hz, 1H), 9.49 (s, 1H).

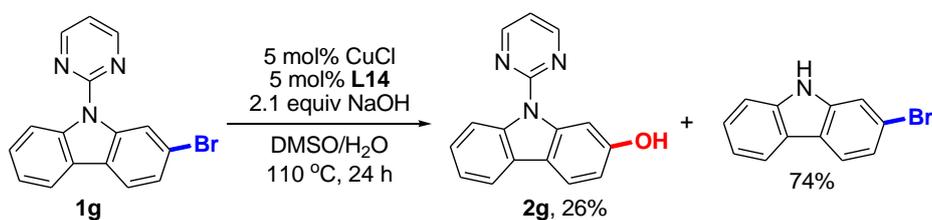
¹³C NMR (100 MHz, DMSO-*d*₆): δ 96.4, 110.1, 110.4, 115.5, 119.4, 120.4, 121.5, 121.8, 123.6, 124.4, 124.4, 124.8, 127.6, 128.7, 131.4, 138.3, 140.8, 142.2, 142.4, 149.3, 157.0.

HRMS (ESI): calcd for C₂₁H₁₅N₂O [M + H]⁺ 311.1179, found 311.1186.

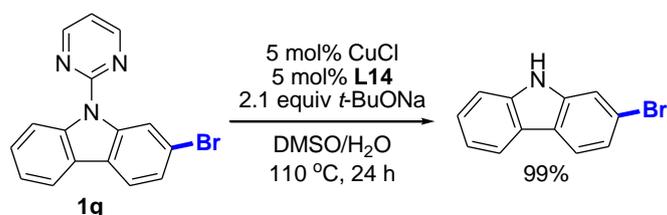
9- (Pyrimidin-2-yl)-9*H*-carbazol-2-ol (**2g**):



Condition A: Following the general procedure, the reaction of **1g** (54.3 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.008 mmol, 0.05 eq), ligand **L14** (2.8 mg, 0.008 mmol, 0.05 eq) and LiOH·H₂O (15.0 mg, 0.36 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2g** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 33.2 mg in 75% yield.



Condition B: Following the general procedure, the reaction of **1g** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours using petroleum ether/ethyl acetate = 5:1-3:1 as eluent afforded 2-bromocarbazole 46.6 mg in 74% yield and **2g** as a brown solid 17.1 mg in 26% yield.



Condition C: Following the general procedure, the reaction of **1g** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded 2-bromocarbazole (eluent: petroleum ether/ethyl acetate = 5:1-3:1) 61.7 mg in 99% yield.

2g: mp: 157.1-158.8 °C.

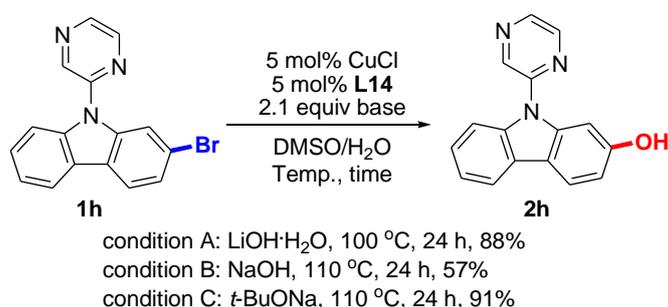
¹H NMR (500 MHz, DMSO-*d*₆): δ 6.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.32 (td, *J* = 7.5, 1.0 Hz, 1H), 7.37-7.40 (m, 1H), 7.41 (t, *J* = 4.5, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.05 (dd, *J* = 7.5, 0.5 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.99 (d, *J* = 4.5 Hz, 2H), 9.69 (s, 1H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 102.5, 111.3, 115.9, 116.9, 117.2, 118.7, 120.5, 122.3, 124.9, 125.5, 138.3, 139.9, 157.2, 158.3, 158.6 (2C).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$ 262.0975, found 262.0977.

2-Bromocarbazole: ^1H NMR (500 MHz, DMSO- d_6): δ 7.17-7.20 (m, 1H), 7.29 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.40-7.43 (m, 1H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.67 (d, $J = 2.0$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.0$ Hz, 1H), 11.40 (s, 1H). The structure was confirmed by comparison of ^1H NMR spectrum with that of purchased sample.

9- (Pyrazin-2-yl)-9H-carbazol-2-ol (**2h**):



Condition A: Following the general procedure, the reaction of **1h** (54.3 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.008 mmol, 0.05 eq), ligand **L14** (2.8 mg, 0.008 mmol, 0.05 eq) and LiOH·H₂O (15.0 mg, 0.36 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 39.2 mg in 88% yield.

Condition B: Following the general procedure, the reaction of **1h** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 37.7 mg in 57% yield.

Condition C: Following the general procedure, the reaction of **1h** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 59.6 mg in 91% yield.

mp: 204.9-206.1 °C.

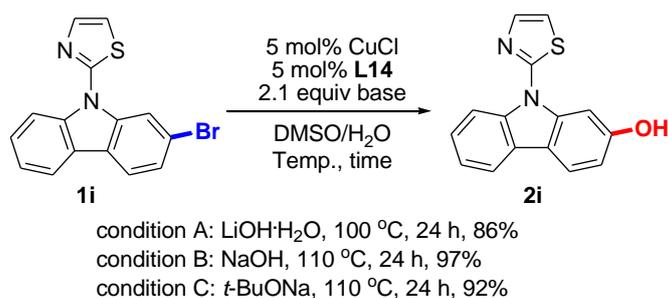
^1H NMR (500 MHz, DMSO- d_6): δ 6.83 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.23 (d, $J = 2.0$ Hz, 1H), 7.29 (td, $J = 7.5, 1.0$ Hz, 1H), 7.33-7.37 (m, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 8.07-8.09 (m, 1H),

8.71 (d, $J = 3.0$ Hz, 1H), 8.81 (dd, $J = 2.5, 1.5$ Hz, 1H), 9.12 (d, $J = 1.0$ Hz, 1H), 9.70 (s, 1H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 97.2, 110.9, 111.0, 116.2, 119.3, 121.3, 121.6, 124.5, 124.8, 138.5, 140.3, 140.7, 142.0, 143.8, 147.8, 157.3.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$ 262.0975, found 262.0981.

9- (Thiazol-2-yl)-9*H*-carbazol-2-ol (**2i**):



Condition A: Following the general procedure, the reaction of **1i** (164.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (44.1 mg, 1.05 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 113.9 mg in 86% yield.

Condition B: Following the general procedure, the reaction of **1i** (82.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 64.7 mg in 97% yield.

Condition C: Following the general procedure, the reaction of **1i** (164.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and $t\text{-BuONa}$ (100.9 mg, 1.05 mmol, 2.1 eq) in $\text{DMSO}/\text{H}_2\text{O}$ (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 122.8 mg in 92% yield.

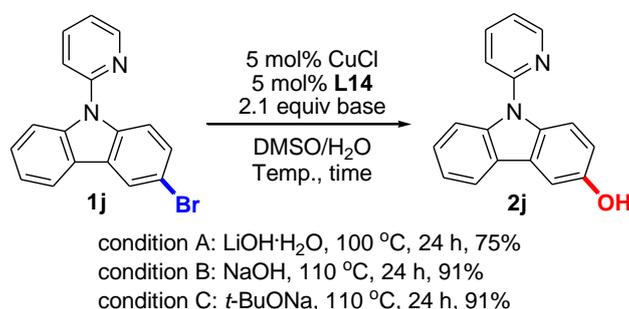
mp: 152.6- 154.5 °C.

^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.86 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.35 (td, $J = 7.5, 1.0$ Hz, 1H), 7.42-7.45 (m, 1H), 7.66 (d, $J = 2.0$ Hz, 1H), 7.76 (d, $J = 3.5$ Hz, 1H), 7.88 (d, $J = 3.5$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 8.08-8.10 (m, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 9.87 (s, 1H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 99.6, 111.5, 112.0, 116.2, 116.3, 119.4, 121.4, 122.3, 124.7, 125.3, 138.4, 139.7, 140.1, 157.7, 158.3.

HRMS (ESI): calcd for C₁₅H₁₁N₂OS [M + H]⁺ 267.0587, found 267.0575.

9-(Pyridin-2-yl)-9H-carbazol-3-ol (**2j**):



Condition A: Following the general procedure, the reaction of **1j** (61.9 mg, 0.19 mmol, 1.0 eq), CuCl (1.0 mg, 0.010 mmol, 0.05 eq), ligand **L14** (3.1 mg, 0.010 mmol, 0.05 eq) and LiOH·H₂O (16.7 mg, 0.40 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 37.1 mg in 75% yield.

Condition B: Following the general procedure, the reaction of **1j** (80.8 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 59.0 mg in 91% yield.

Condition C: Following the general procedure, the reaction of **1j** (80.8 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 59.1 mg in 91% yield.

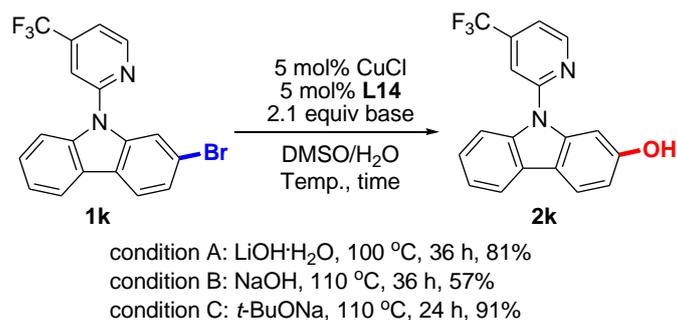
mp: 163.9-164.8 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 6.95 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.25-7.29 (m, 1H), 7.40-7.44 (m, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 8.06-8.09 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.70 (ddd, *J* = 5.0, 2.0, 0.5 Hz, 1H), 9.26 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 105.1, 111.3, 112.1, 115.3, 118.4, 120.3, 120.4, 121.3, 123.5, 124.5, 126.2, 132.7, 139.2 (2 C), 149.3, 151.1, 152.2.

HRMS (ESI): calcd for C₁₇H₁₃N₂O [M + H]⁺ 261.1022, found 261.1033.

9-(4-Trifluoromethylpyridin-2-yl)-9H-carbazol-3-ol (**2k**):



Condition A: Following the general procedure, the reaction of **1k** (106.0 mg, 0.27 mmol, 1.0 eq), CuCl (1.4 mg, 0.014 mmol, 0.05 eq), ligand **L14** (4.5 mg, 0.014 mmol, 0.05 eq) and LiOH·H₂O (23.8 mg, 0.57 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 36 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 72.1 mg in 81% yield.

Condition B: Following the general procedure, the reaction of **1k** (99.5 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 36 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 47.2 mg in 57% yield.

Condition C: Following the general procedure, the reaction of **1k** (96.0 mg, 0.245 mmol, 1.0 eq), CuCl (1.2 mg, 0.012 mmol, 0.05 eq), ligand **L14** (4.0 mg, 0.012 mmol, 0.05 eq) and *t*-BuONa (73.0 mg, 0.22 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 73.0 mg in 91% yield.

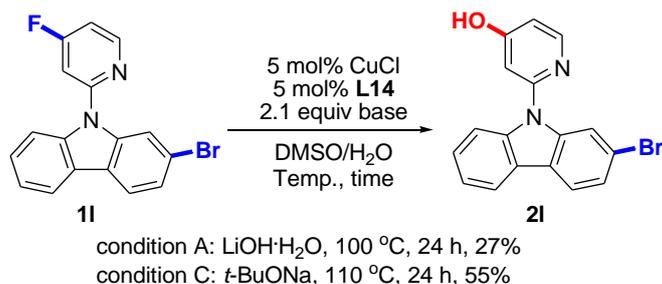
mp: 155.1-156.7 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 6.83 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.28 (t, *J* = 2.5 Hz, 1H), 7.35 (t, *J* = 3.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 5.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 6.5 Hz, 2H), 9.00 (d, *J* = 5.0 Hz, 1H), 9.71 (s, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆): δ 97.2, 110.9, 110.9, 114.4 (d, *J* = 3.8 Hz, 1C), 116.2, 117.0 (q, *J* = 3.2 Hz, 1C), 119.2, 121.2, 121.6, 122.6 (q, *J* = 274.1 Hz, 1C), 124.4, 124.7, 138.5, 139.4 (q, *J* = 31.2 Hz, 1C), 140.2, 151.3, 152.0, 157.2.

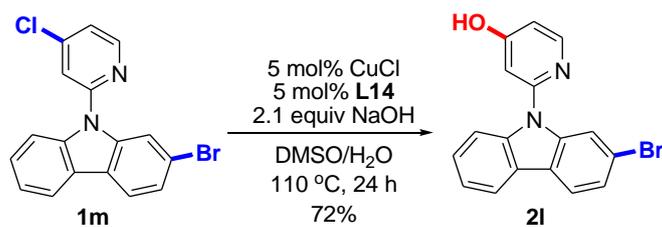
HRMS (ESI): calcd for C₁₈H₁₂F₃N₂O [M + H]⁺ 329.0896, found 329.0906.

2-Bromo -9-(4-hydroxypyridin-2-yl)- 9H-carbazole (**2l**) (Scheme 1, eqs 1-3):

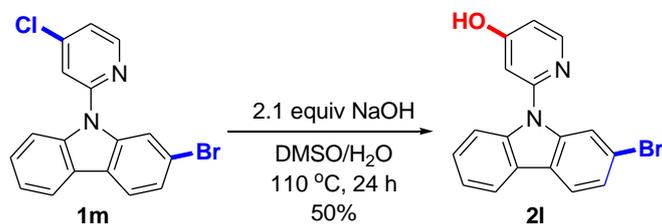


Condition A: Following the general procedure, the reaction of **1l** (343.2 mg, 1.0 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and LiOH·H₂O (88.1 mg, 2.10 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 93.0 mg in 27% yield.

Condition C: Following the general procedure, the reaction of **1l** (168.4 mg, 0.49 mmol, 1.0 eq), CuCl (2.4 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (98.9 mg, 1.03 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 74.3 mg in 55% yield.



Condition B: Following the general procedure, the reaction of **1m** (89.4 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 52.9 mg in 72% yield.



Condition B (without CuCl and **L14**): Following the general procedure, the reaction of **1m** (89.4 mg, 0.25 mmol, 1.0 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 42.7 mg in

50% yield.

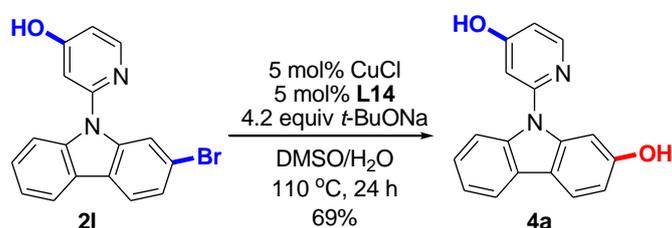
mp: 125.7-126.1 °C.

^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.90 (dd, $J = 5.5, 2.0$ Hz, 1H), 7.10 (d, $J = 2.0$ Hz, 1H), 7.33-7.36 (m, 1H), 7.48 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.49-7.52 (m, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 1.5$ Hz, 1H), 8.21 (d, $J = 7.5$ Hz, 1H), 8.27 (d, $J = 2.5$ Hz, 1H), 8.44 (d, $J = 5.5$ Hz, 1H), 11.89 (s, 1H).

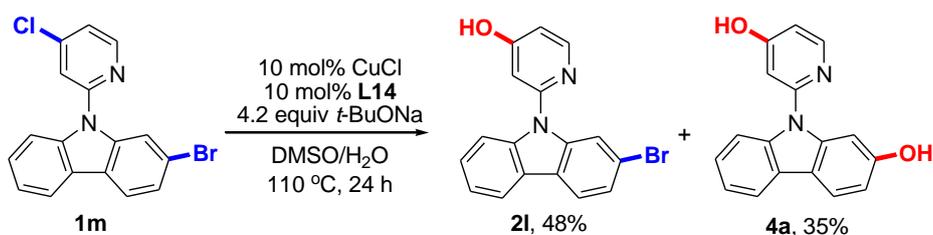
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 106.1, 110.6, 111.4, 114.2, 118.9, 120.6, 121.2, 122.1, 122.5, 122.7, 123.5, 126.8, 139.0, 139.8, 150.5, 151.6, 166.2.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{12}\text{BrN}_2\text{O}$ $[\text{M} + \text{H}]^+$ 339.0128, found 339.0138.

9-(4-Hydroxypyridin-2-yl)-9H-carbazol-2-ol (**4a**) (Scheme 1, eqs 3, 4):



Condition C: Following the general procedure, the reaction of **2I** (48.7 mg, 0.14 mmol, 1.0 eq), CuCl (0.7 mg, 0.007 mmol, 0.05 eq), ligand **L14** (2.3 mg, 0.007 mmol, 0.05 eq) and *t*-BuONa (56.5 mg, 0.59 mmol, 4.2 eq) in DMSO/ H_2O (2.0 mL/0.5 mL) at 110 °C for 24 hours afforded **4a** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 26.7 mg in 69% yield.



Condition C: Following the general procedure, the reaction of **1m** (89.4 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/ H_2O (2.0 mL/1.0 mL) at 110 °C for 24 hours afforded **2I** (eluent: petroleum ether/ethyl acetate = 3:1-1:1) as a white solid: 40.4 mg in 48% yield and **4a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 23.9 mg in 35% yield.

mp: 298.3-299.7 °C.

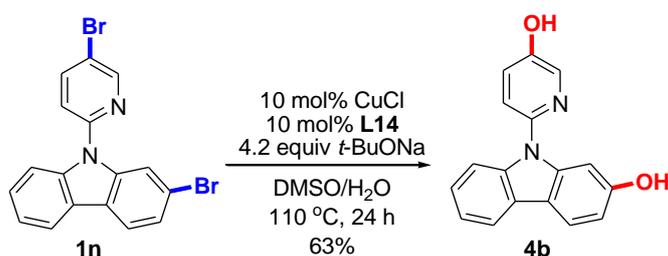
^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.77 (dd, $J = 8.5, 2.0$ Hz, 1H), 6.86 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.03 (d, J

= 2.0 Hz, 1H), 7.18 (d, $J = 2.0$ Hz, 1H), 7.21-7.24 (m, 1H), 7.31 (td, $J = 7.5, 1.5$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.5$ Hz, 1H), 8.04 (d, $J = 7.5$ Hz, 1H), 8.40 (d, $J = 6.0$ Hz, 1H), 9.58 (s, 1H), 11.08 (s, 1H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 97.3, 105.8, 110.1, 110.2, 111.0, 115.8, 119.0, 120.6, 121.0, 123.9, 124.4, 138.9, 140.6, 150.3, 152.3, 156.9, 166.0.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 277.0972, found 277.0973.

9-(5-Hydroxypyridin-2-yl)- 9H- carbazol-2-ol (**4b**) (Scheme 1, eq 5):



Condition C: Following the general procedure, the reaction of **1n** (100.5 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/H₂O (2.0 mL/1.0 mL) at 110 °C for 24 hours afforded **4b** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 43.8 mg in 63% yield.

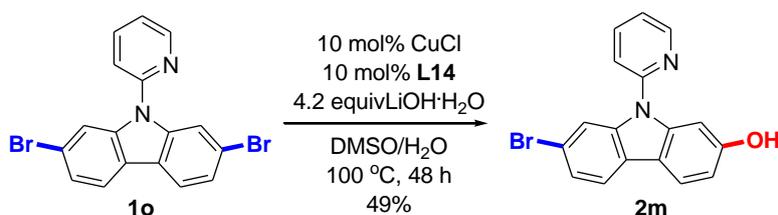
mp: 257.0-258.3 °C.

^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.75 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.95 (d, $J = 2.0$ Hz, 1H), 7.19-7.22 (m, 1H), 7.29 (td, $J = 7.0, 1.0$ Hz, 1H), 7.47-7.49 (m, 2H), 7.53 (d, $J = 8.5$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 8.03 (d, $J = 7.5$ Hz, 1H), 8.24-8.25 (m, 1H), 9.54 (s, 1H), 10.26 (s, 1H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 96.4, 109.8, 110.2, 115.4, 119.1, 120.1, 120.5, 121.0, 123.4, 124.3, 125.2, 137.0, 139.4, 141.2, 142.2, 152.6, 156.9.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 277.0972, found 277.0983.

7- Bromo -9-(pyridin-2-yl)- 9H- carbazol-2-ol (**2m**) (Scheme 1, eq 6):



Condition A: Following the general procedure, the reaction of **1o** (61.3 mg, 0.15 mmol, 1.0 eq), CuCl (1.5 mg, 0.015 mmol, 0.10 eq), ligand **L14** (4.9 mg, 0.015 mmol, 0.10 eq) and LiOH·H₂O (26.4 mg, 0.63 mmol, 4.2 eq) in DMSO/H₂O (2.0 mL/0.5 mL) at 100 °C for 48 hours afforded **2m** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 24.5 mg in 49% yield.

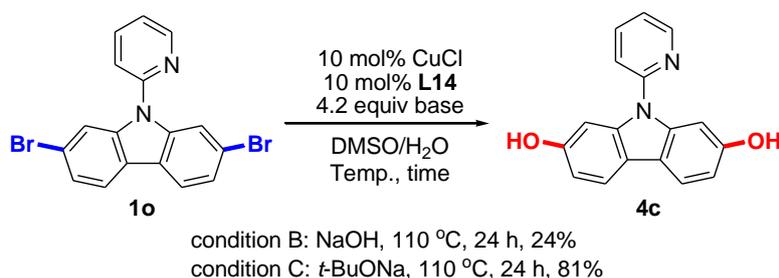
mp: 196.0-196.7 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 6.82 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.41 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.51 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 8.04 (dd, *J* = 8.0, 2.5 Hz, 1H), 8.14 (td, *J* = 8.0, 2.0 Hz, 1H), 8.74-8.76 (m, 1H), 9.74 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ 97.0, 110.9, 113.6, 115.2, 117.0, 119.2, 120.9, 121.6, 122.3, 123.3, 123.6, 139.7, 139.7, 140.8, 149.7, 150.4, 157.6.

HRMS (ESI): calcd for C₁₇H₁₂BrN₂O [M + H]⁺ 339.0128, found 339.0128.

9-(Pyridin-2-yl)- 9H- carbazol-2,7-diol (**4c**) (Scheme 1, eqs 7, 8):



Condition B: Following the general procedure, the reaction of **1o** (80.4 mg, 0.20 mmol, 1.0 eq), CuCl (2.0 mg, 0.02 mmol, 0.10 eq), ligand **L14** (6.5 mg, 0.02 mmol, 0.10 eq) and NaOH (33.6 mg, 0.84 mmol, 4.2 eq) in DMSO/H₂O (2.0 mL/1.0 mL) at 110 °C for 24 hours afforded **4c** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 16.5 mg in 24% yield.

Condition C: Following the general procedure, the reaction of **1o** (100.5 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/H₂O (2.0 mL/1.0 mL) at 110 °C for 24 hours afforded **4c** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 55.8 mg in 81% yield.

mp: 266.1-267.6 °C.

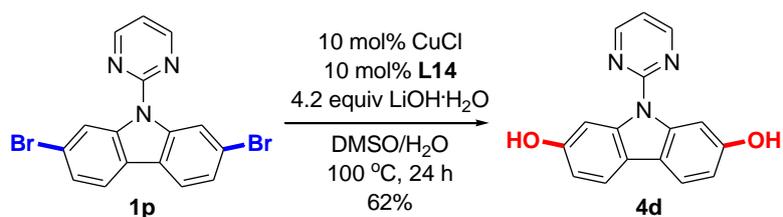
¹H NMR (500 MHz, DMSO-*d*₆): δ 6.71 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.09 (d, *J* = 2.0 Hz, 2H), 7.45 (ddd, *J* =

7.5, 5.0, 1.0 Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 8.10 (td, $J = 8.0, 2.0$ Hz, 1H), 8.72 (ddd, $J = 5.0, 2.0, 0.5$ Hz, 1H), 9.37 (s, 2H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 97.2, 109.9, 116.5, 118.9, 119.8, 121.8, 139.3, 140.3, 149.5, 151.1, 155.6.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 277.0972, found 277.0961.

9-(pyrimidin-2-yl)-9H-carbazol-2,7-diol (**4d**) (Scheme 1, eq 9):



Condition A: Following the general procedure, the reaction of **1p** (100.8 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and LiOH·H₂O (44.1 mg, 1.05 mmol, 4.2 eq) in DMSO/H₂O (2.0 mL/1.0 mL) at 100 °C for 24 hours afforded **4d** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 42.8 mg in 62% yield.

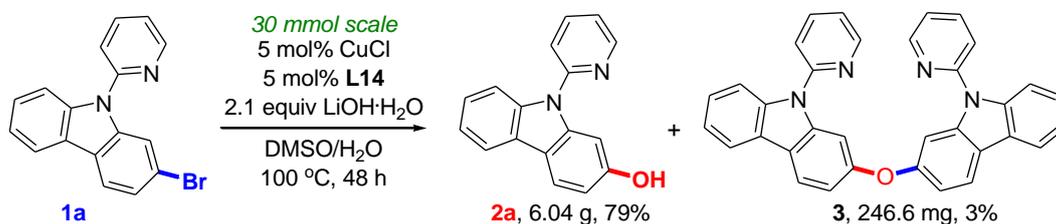
mp: 267.3-268.9 °C.

^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.77 (dd, $J = 8.5, 2.0$ Hz, 2H), 7.38 (t, $J = 5.0$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 2H), 8.19 (d, $J = 2.0$ Hz, 2H), 8.97 (d, $J = 5.0$ Hz, 2H), 9.46 (s, 2H).

^{13}C NMR (126 MHz, $\text{DMSO-}d_6$): δ 102.8, 110.9, 116.7, 117.8, 119.0, 139.6, 115.7, 158.3, 158.4.

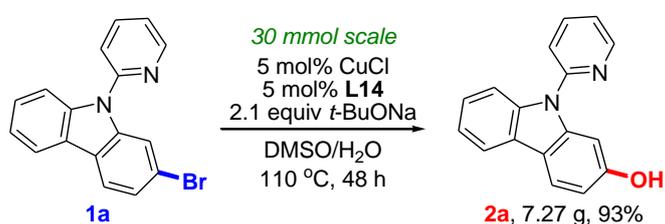
HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 278.0924, found 278.0916.

Large-scale Synthesis and Its application:

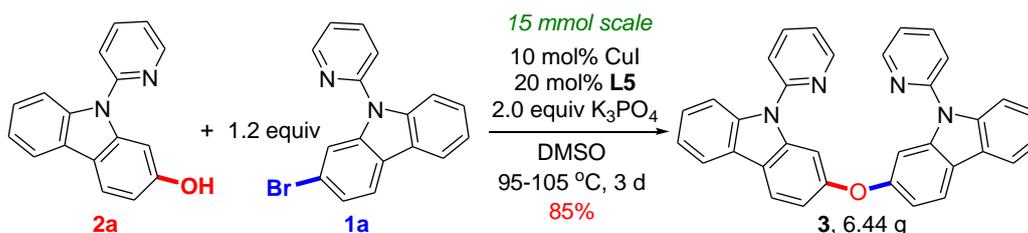


Condition A: Following the general procedure, the reaction of **1a** (9.70 g, 30.00 mmol, 1.0 eq), CuCl (148.5 mg, 1.50 mmol, 0.05 eq), ligand **L14** (493.0 mg, 1.50 mmol, 0.05 eq) and LiOH·H₂O (2.64 g, 63.0 mmol, 2.1 eq) in DMSO/H₂O (37.5 mL/9.5 mL) at 100 °C for 48 hours. Then the mixture was cooled to room temperature, then H₂O (100 mL) and EtOAc (100 mL) were added, filtered through a

pad of celite, and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (100 mL × 5). The combined organic layer was washed with water (50 mL) and then dried over Na₂SO₄, filtered, and the filtrate was concentrated in vacuum. The residue was recrystallized in PE/EtOAc (20 mL/20 mL) to afford the desired product **2a** as a white solid 5.61 g. The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 5:1–3:1 as eluent to afford **3** 246.6 mg in 3% yield and the product **2a** as a white solid 425.5 mg. The total yield of **2a** was 79%. The structure of **3** was confirmed by ¹H NMR.

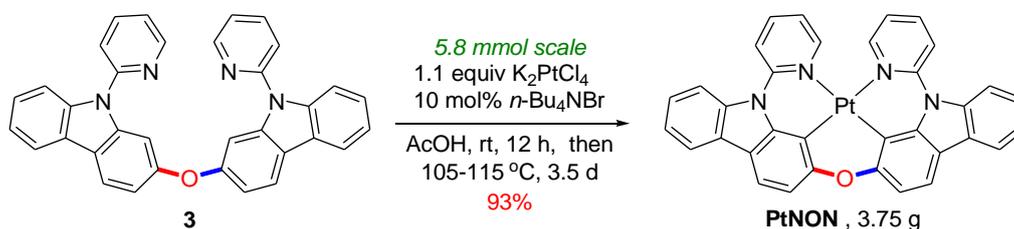


Condition C: Following the general procedure, the reaction of **1a** (9.70 g, 30.00 mmol, 1.0 eq), CuCl (148.5 mg, 1.50 mmol, 0.05 eq), ligand **L14** (493.0 mg, 1.50 mmol, 0.05 eq) and *t*-BuONa (6.05 g, 63.0 mmol, 2.1 eq) in DMSO/H₂O (37.5 mL/9.5 mL) at 110 °C for 48 hours. Then the mixture was cooled to room temperature, and H₂O (100 mL) and EtOAc (100 mL) were added, filtered through a pad of celite, and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (100 mL × 5). The combined organic layer was washed with water (50 mL) and then dried over Na₂SO₄ and filtered, and the filtrate was concentrated in vacuum. The residue was recrystallized in PE/EtOAc (10 mL/10 mL) to afford the desired product as a white solid 5.77 g. The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 5:1–3:1 as eluent to afford the product as a white solid 1.5 g. The total yield was 93%. The structure of **2a** was confirmed by ¹H NMR.



To a dry three-necked flask equipped with a magnetic stir bar, added **2a** (3.90 g, 15.00 mmol, 1.0 eq), **1a** (5.82 g, 18.00 mmol, 1.2 eq), CuI (0.29 g, 1.50 mmol, 0.1 eq), picolinic acid **L5** (0.37 g, 3.00 mmol, 0.2 eq), K₃PO₄ (6.37 g, 30.00 mmol, 2.0 eq). The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then DMSO (60 mL) was added under nitrogen and the mixture was stirred at 95-105 °C for 3 days. The mixture was then cooled down to ambient temperature and diluted with ethyl acetate, filtered and washed with a plenty of ethyl acetate. The filtrate was then washed with water for three time and then dried over sodium sulfate. Filtered and the solvent was removed under reduced pressure, the residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate (10:1-3:1) as eluent to obtain the desired product as a brown solid 6.44 g in 85% yield.

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.06 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.41-7.45 (m, 4H), 7.51 (d, *J* = 2.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 4H), 8.06 (td, *J* = 7.6, 2.0 Hz, 2H), 8.20 (d, *J* = 7.6 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.64 (dd, *J* = 5.6, 2.4 Hz, 2H). The spectroscopic data is in agreement with that previously reported.³

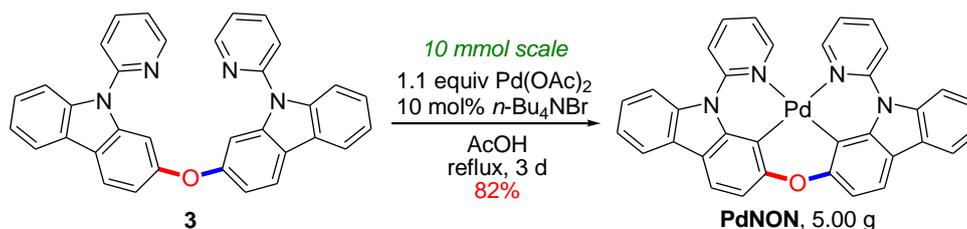


Ligand **3** (2.92 g, 5.81 mmol, 1.00 eq), K₂PtCl₄ (2.65 g, 6.39 mmol, 1.10 eq), *n*Bu₄NBr (0.19 g, 0.58 mmol, 0.10 eq) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then AcOH (350 mL) was added under nitrogen. The mixture was stirred at room temperature for 12 hours, then at 105-115 °C for 3.5 days. The mixture was then cooled down to ambient temperature and the solvent was evaporated under reduced pressure, the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent to obtain the desired product as a yellow solid 3.75 g in 93% yield.

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.20 (d, *J* = 10.0 Hz, 2H), 7.31 (td, *J* = 7.0, 3.5 Hz, 2H), 7.42 (t, *J* = 9.0

Hz, 2H), 7.48-7.52 (m, 2H), 7.93 (d, $J = 10.0$ Hz, 2H), 8.08 (d, $J = 10.0$ Hz, 2H), 8.17-8.20 (m, 6H), 9.03 (d, $J = 7.0$ Hz, 2H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 93.9, 111.7, 114.2, 115.2, 115.9, 116.4, 119.6, 120.3, 122.7, 124.2, 127.7, 137.4, 139.7, 142.2, 147.7, 151.3, 152.0. The spectroscopic data is in agreement with that previously reported.³



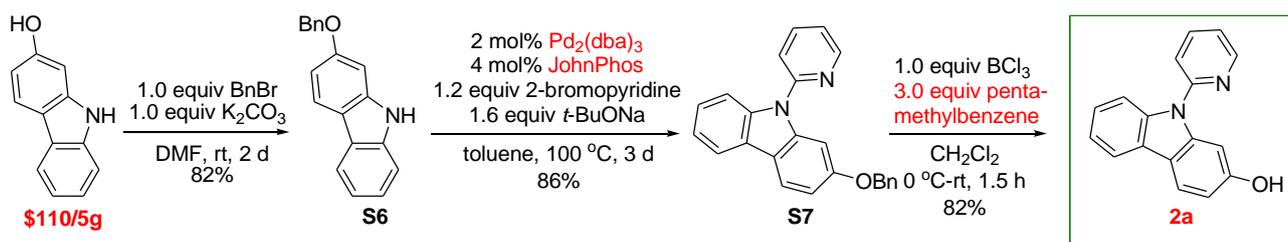
Ligand **3** (5.03 g, 10.00 mmol, 1.00 eq), Pd(OAc)₂ (2.47 g, 11.00 mmol, 1.10 eq), *n*Bu₄NBr (0.32 g, 1.00 mmol, 0.10 eq) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then AcOH (500 mL) was added under nitrogen and the mixture was refluxed for 3 days. The mixture was then cooled down to ambient temperature and the solvent was evaporated under reduced pressure, the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane (2:1-3:2-1:1) as eluent to obtain the desired product as a yellow solid 5.00 g in 82% yield.

^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 7.21 (d, $J = 8.4$ Hz, 2H), 7.33-7.37 (m, 2H), 7.40 (td, $J = 7.6$ Hz, 2H), 7.46-7.51 (m, 2H), 7.80 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H), 8.14 (d, $J = 3.6$ Hz, 4H), 8.19 (d, $J = 7.2$ Hz, 2H), 8.90 (d, $J = 5.6$ Hz, 2H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 107.8, 111.7, 114.0, 116.1, 116.3, 117.0, 119.6, 120.2, 122.5, 124.3, 127.6, 137.5, 140.4, 142.9, 148.5, 150.9, 151.0.

HRMS (MALDI-FT_DHB): for $\text{C}_{34}\text{H}_{21}\text{N}_4\text{O}^{102}\text{Pd}$ [M+H]⁺: calcd 603.0766, found 603.0763.

Our previous synthetic route for 2a:



A mixture of 9H-carbazol-2-ol (5.00 g, 27.30 mmol, 1.00 eq), BnBr (3.25 mL, 27.30 mmol, 1.00 eq), K₂CO₃ (3.77 g, 27.30 mmol, 1.00 eq) in DMF (40 mL) was stirred for 2 days. Then quenched by H₂O (150 mL) and the mixture was stirred for 10 minutes. The precipitate was filtered off and washed with water three times and ethyl acetate once. The collect solid was dried under vacuum to afford the desired product **S6** as a white solid 6.13 g in 82% yield.

¹H NMR (400 MHz, DMSO-*d*₆): δ 5.20 (s, 2H), 6.86 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.40-7.44 (m, 3H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 11.12 (bs, 1H).

2-Benzyloxy-9H-carbazole **S6** (4.01 g, 15.00 mmol, 1.0 eq), Pd₂(dba)₃ (0.28 g, 0.30 mmol, 0.02 eq), JohnPhos (0.18 g, 0.60 mmol, 0.04 eq), *t*-BuONa (2.31 g, 24.00 mmol, 1.6 eq) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then 2-bromopyridine (1.72 mL, 18.00 mmol, 1.2 eq) and the solvent toluene (45.0 mL) were added under nitrogen. The mixture was then stirred under reflux at 100 °C for three days. The reaction mixture was allowed to cool to room temperature and concentrated, and the residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 10:1-5:1 as eluent to afford **S7** as a white solid 4.55 g in 86% yield.

mp: 89.6-90.8 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ 5.18 (s, 2H), 7.04 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.27-7.30 (m, 1H), 7.32-7.42 (m, 5H), 7.47-7.50 (m, 3H), 7.72-7.76 (m, 2H), 8.09-8.14 (m, 3H), 8.73-8.74 (m, 1H).

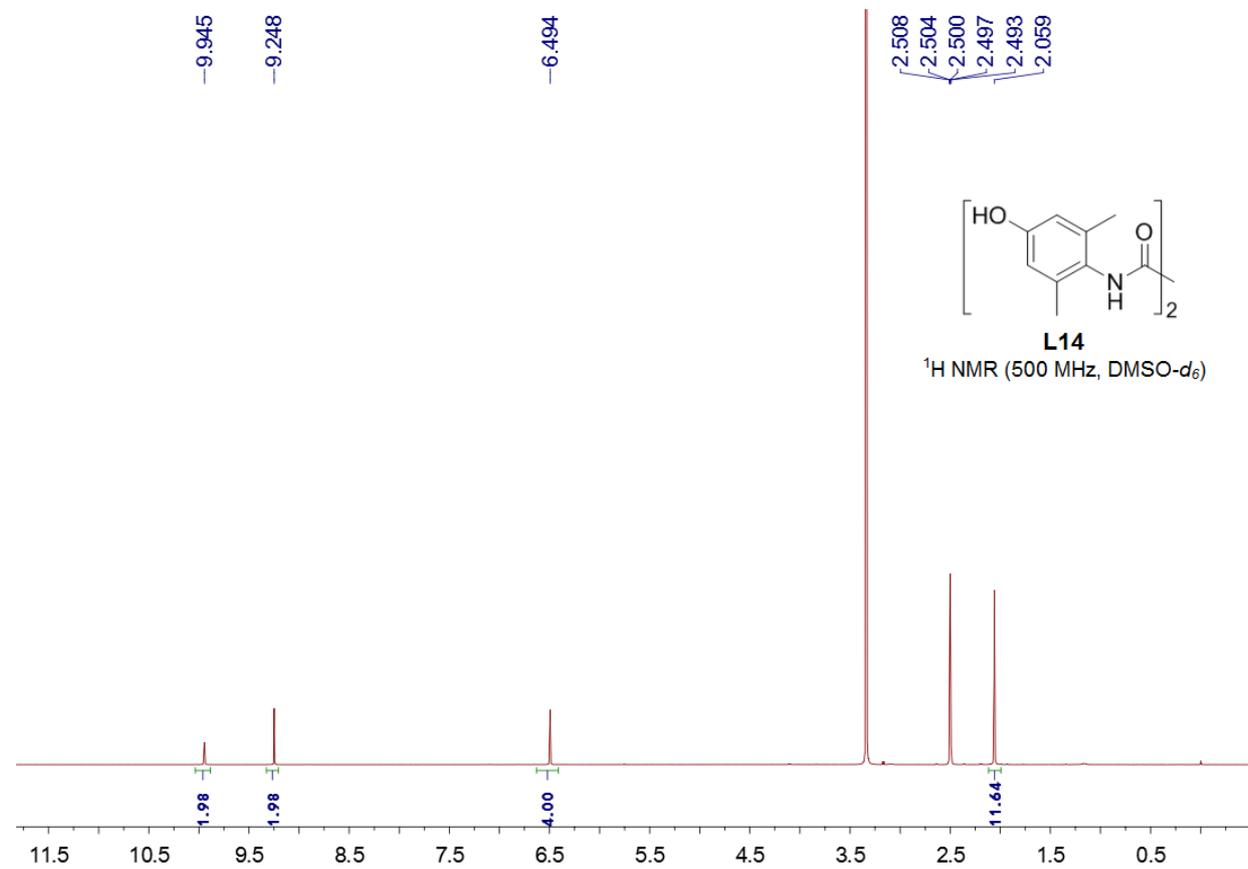
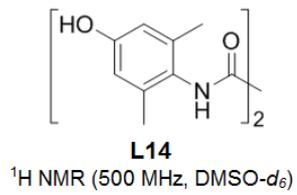
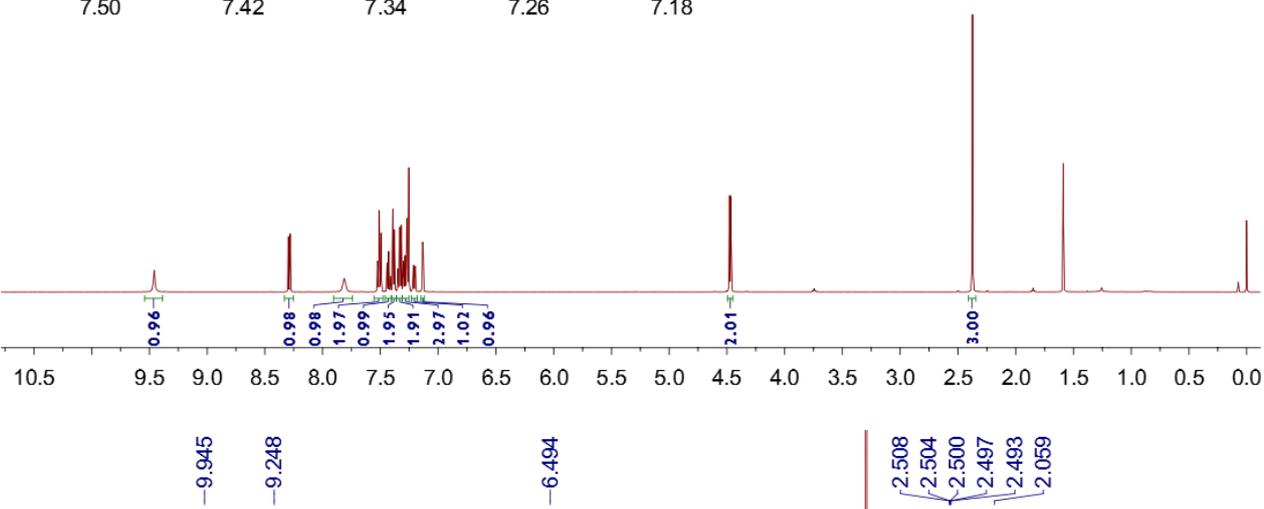
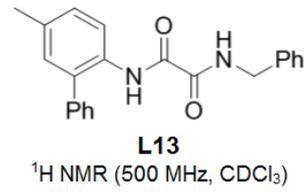
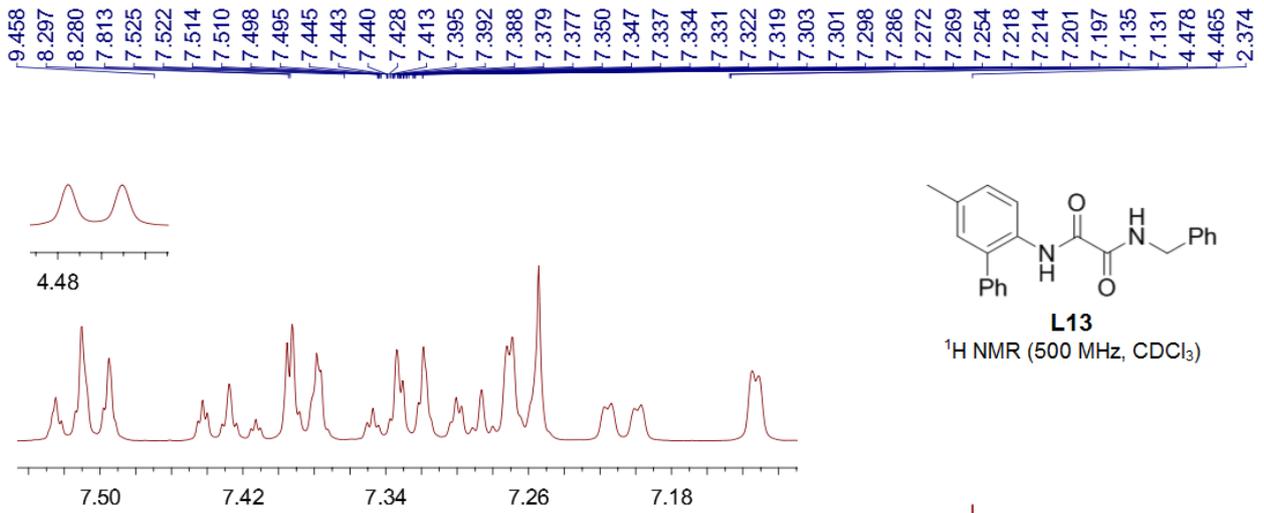
¹³C NMR (100 MHz, DMSO-*d*₆): δ 69.7, 96.8, 110.1, 111.1, 117.3, 119.0, 119.6, 121.0, 121.2, 122.0, 123.7, 125.1, 127.9, 127.9, 128.5, 137.1, 139.0, 139.5, 140.1, 149.6, 150.8, 157.9.

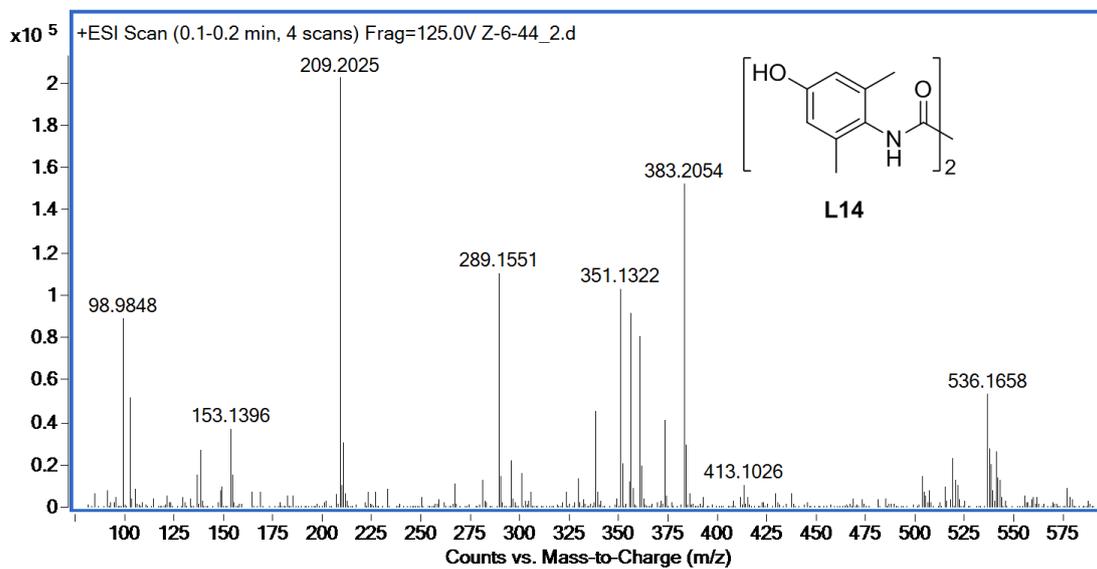
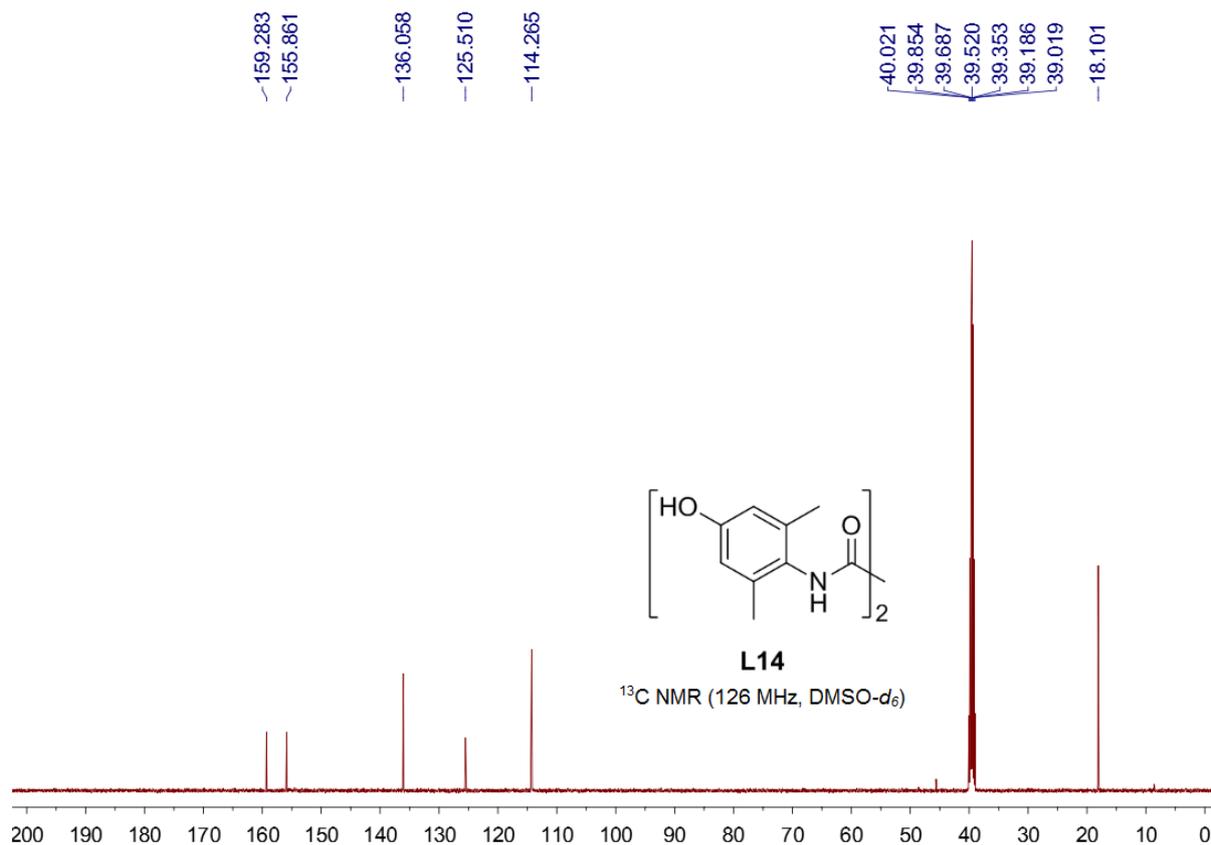
HRMS (ESI): calcd for C₂₄H₁₉N₂O [M + H]⁺ 351.1492, found 351.1509.

A solution of BCl₃ (32.5 mL, 32.5 mmol, 1.0 M in CH₂Cl₂, 2.5 eq) was added slowly to a solution of **S7** (4.55 g, 13.00 mmol, 1.0 eq) and pentamethylbenzene (5.78 g, 39.0 mmol, 3.0 eq) in CH₂Cl₂ (100 mL) at 0 °C. Then the mixture was stirred at 0 °C for 1.5 hours until the starting material **S7** was consumed completely monitored by TLC. Then quenched by water and diluted with CH₂Cl₂, neutralized with a solution of NaHCO₃ until there was no gas to generate. The organic layer was separated and dried over sodium sulphate, filtered and the filtrate was concentrated. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 10:1-3:1 as eluent to afford the desired product **2a** as a brown solid 2.79 g in 82% yield. The structure of the product was confirmed by ¹H NMR.

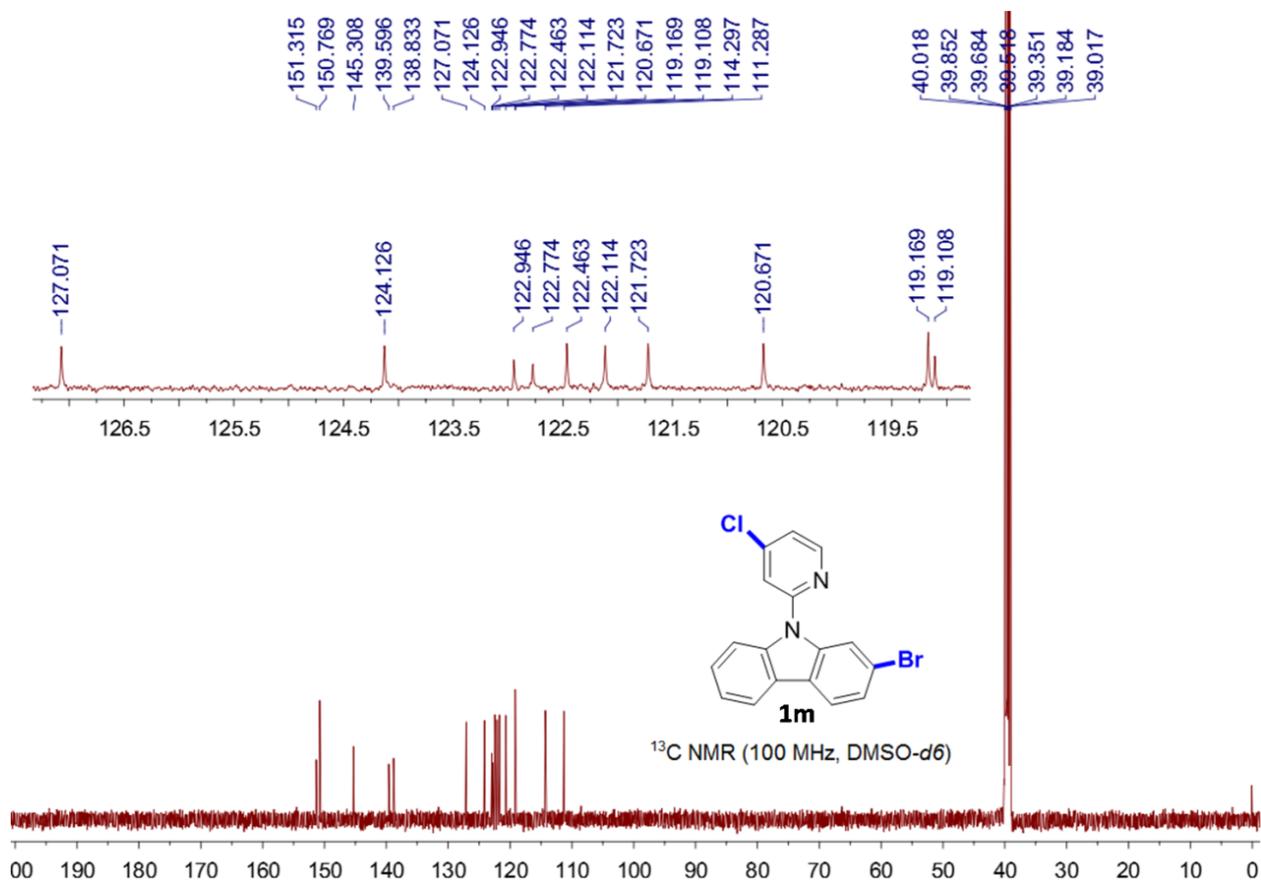
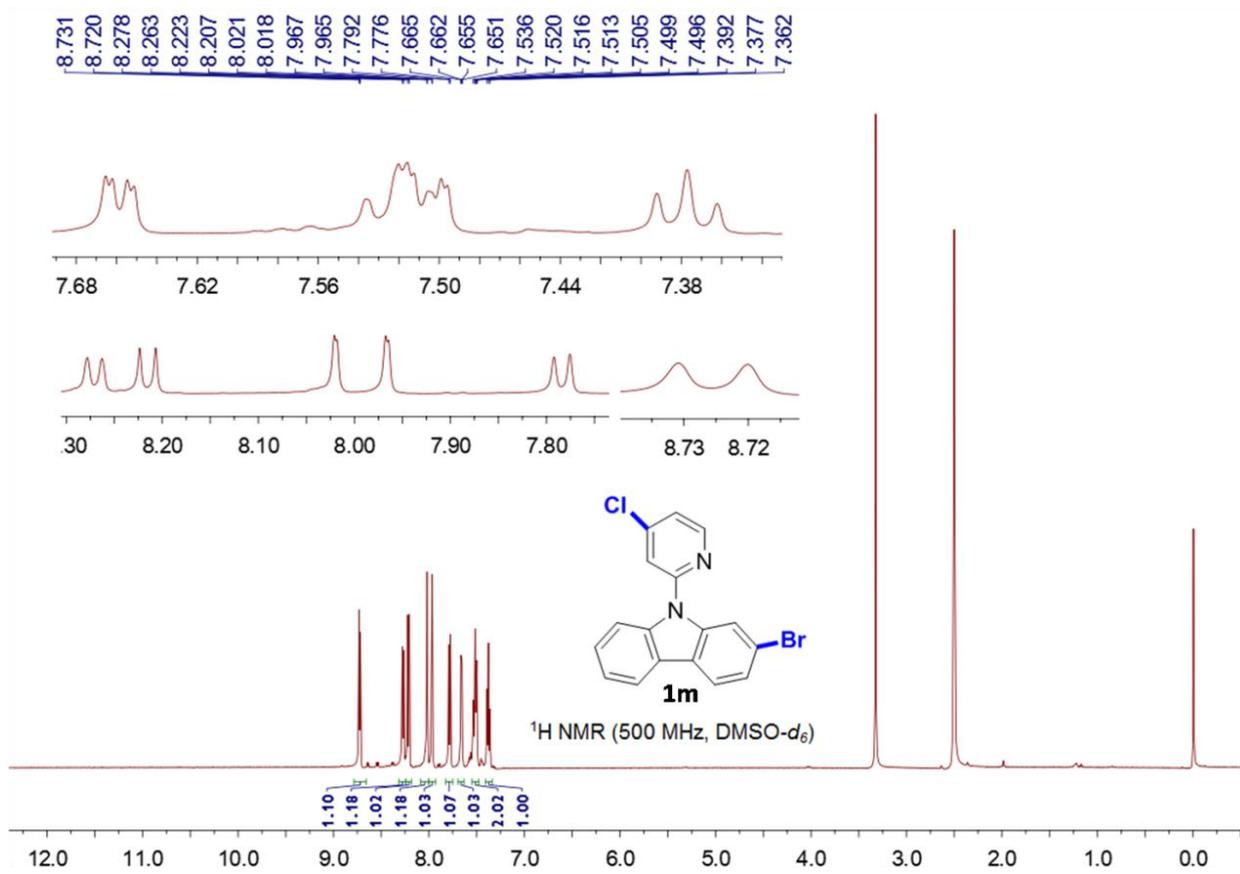
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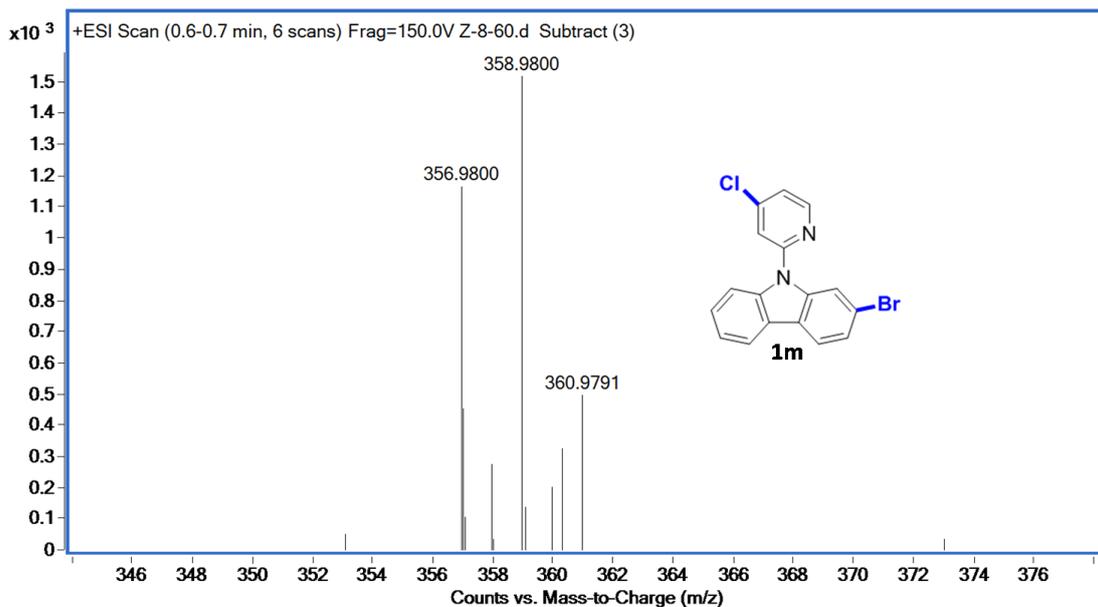
- [1] S. Xia, L. Gan, K. Wang, Z. Li and D. Ma, *J. Am. Chem. Soc.*, 2016, **138**, 13493.
- [2] X. Zhao, Y. She, K. Fang and G. Li, *J. Org. Chem.*, 2017, **82**, 1024.
- [3] T. B. Fleetham, L. Huang, K. Klimes, J. Brooks and J. Li, *Chem. Mater.*, 2016, **28**, 3276.



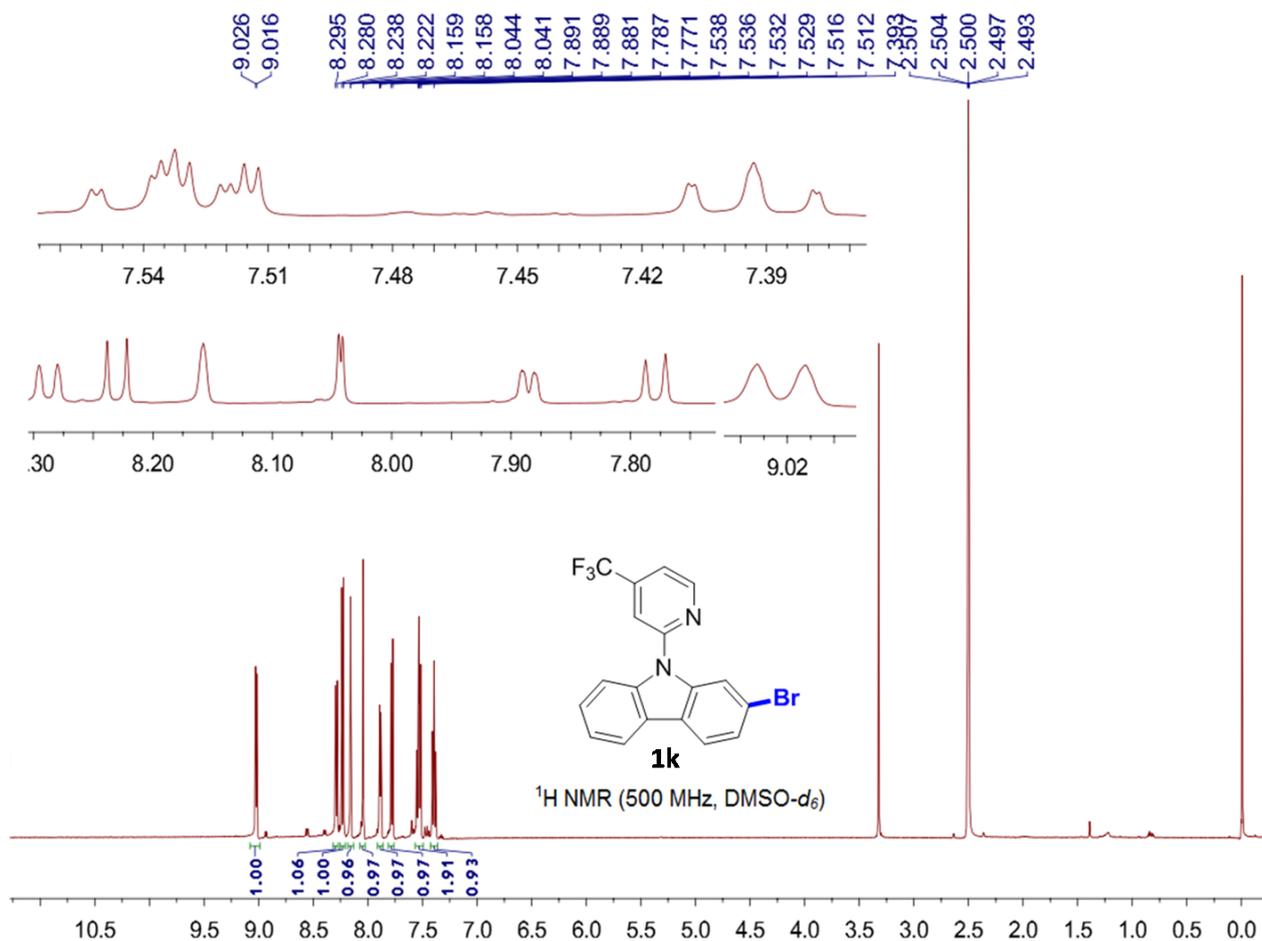


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
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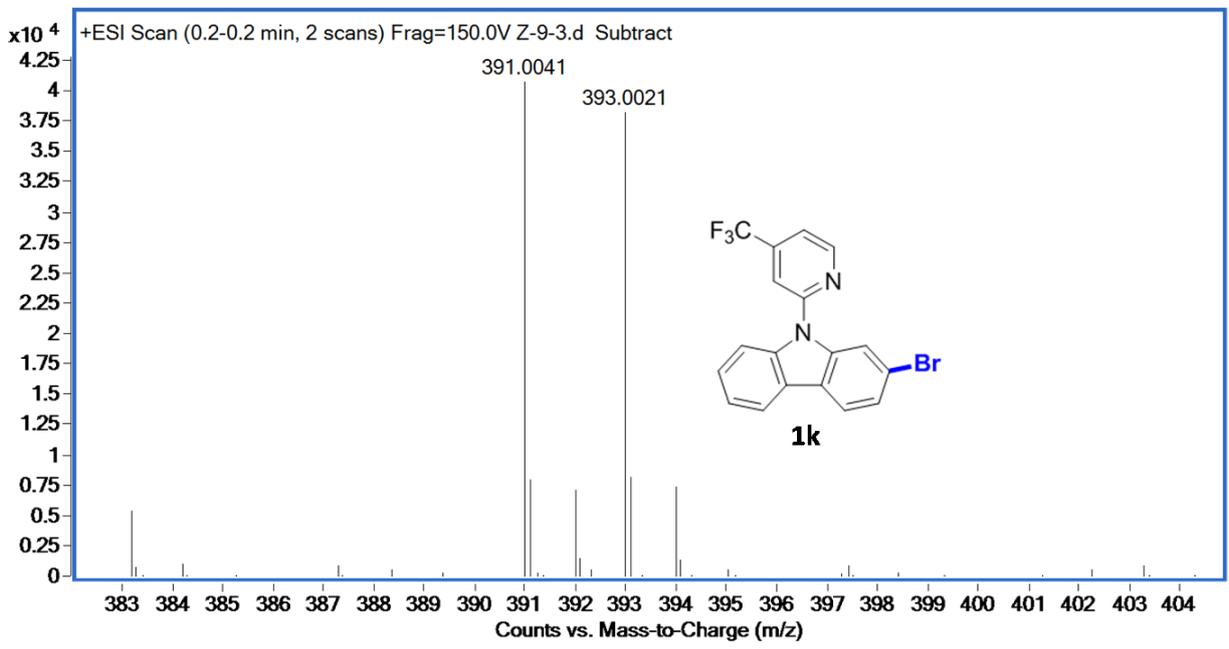
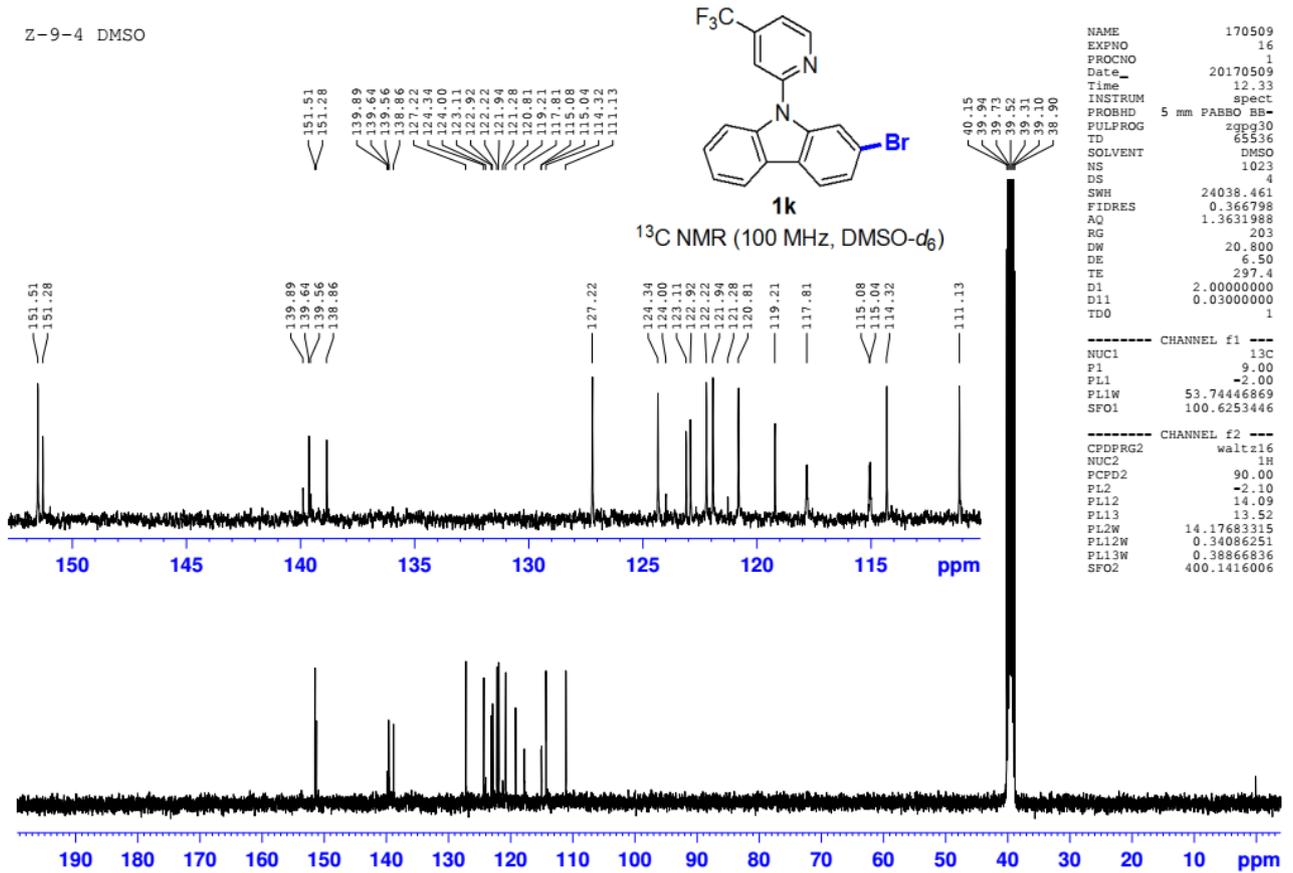




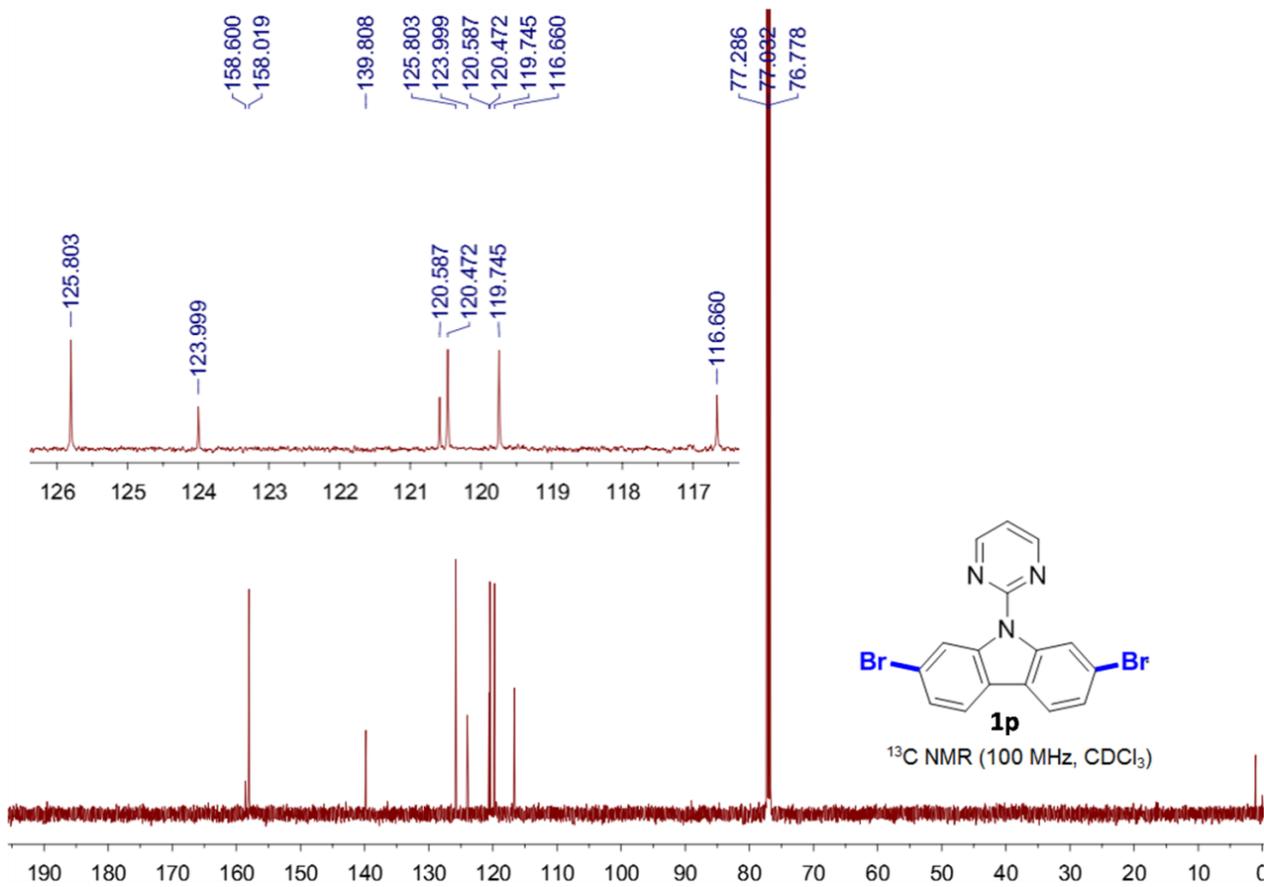
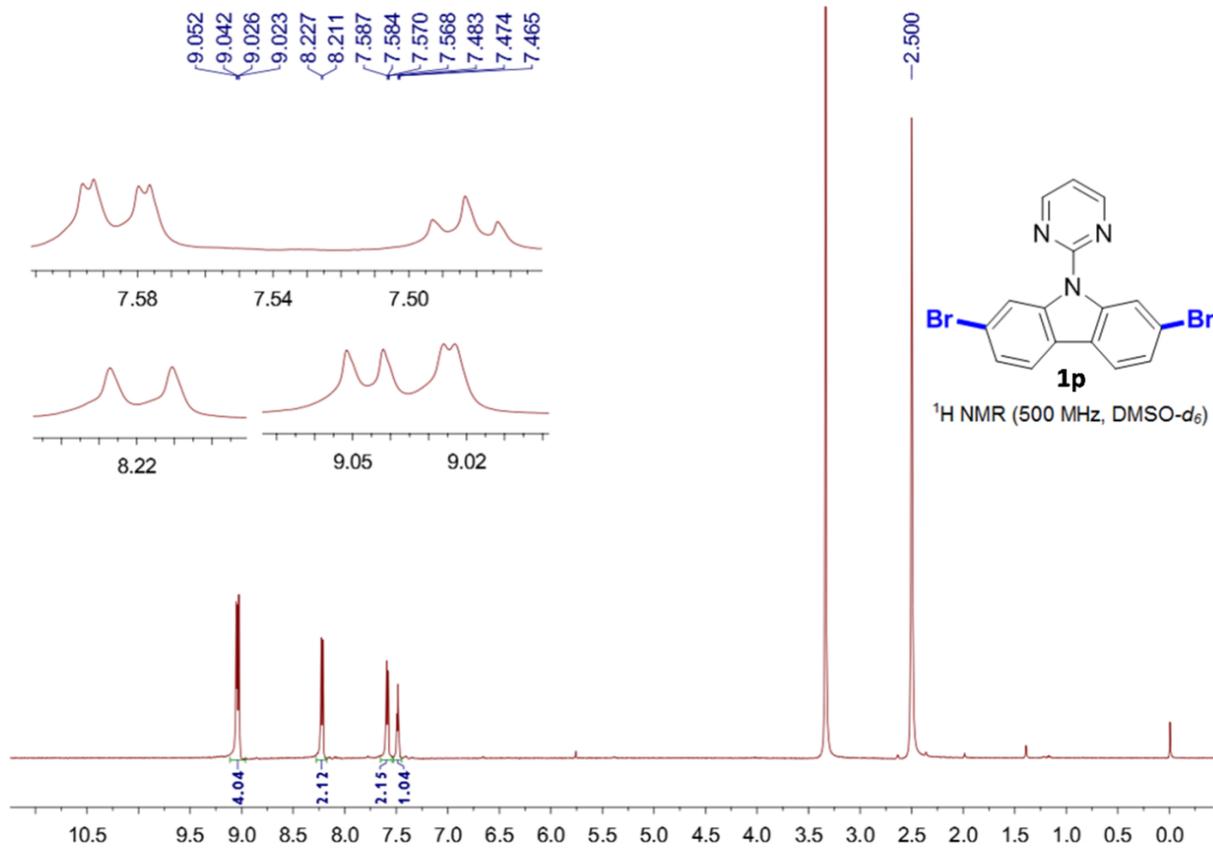
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₀ BrClN ₂	C ₁₇ H ₁₁ BrClN ₂	356.9800	356.9789	-3.19



Z-9-4 DMSO

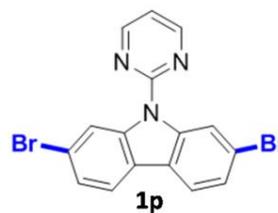
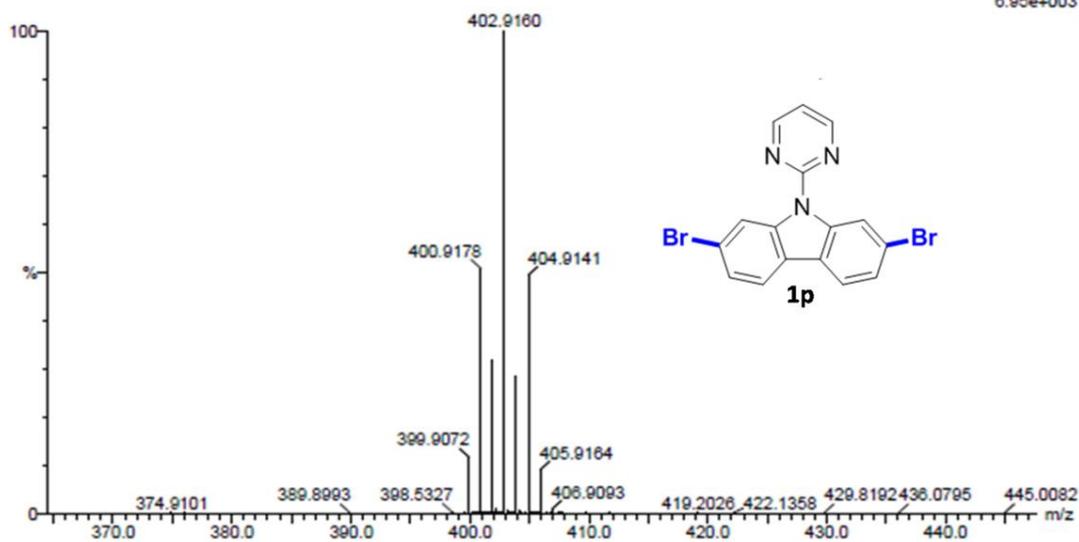


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
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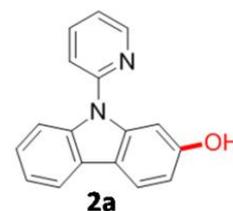
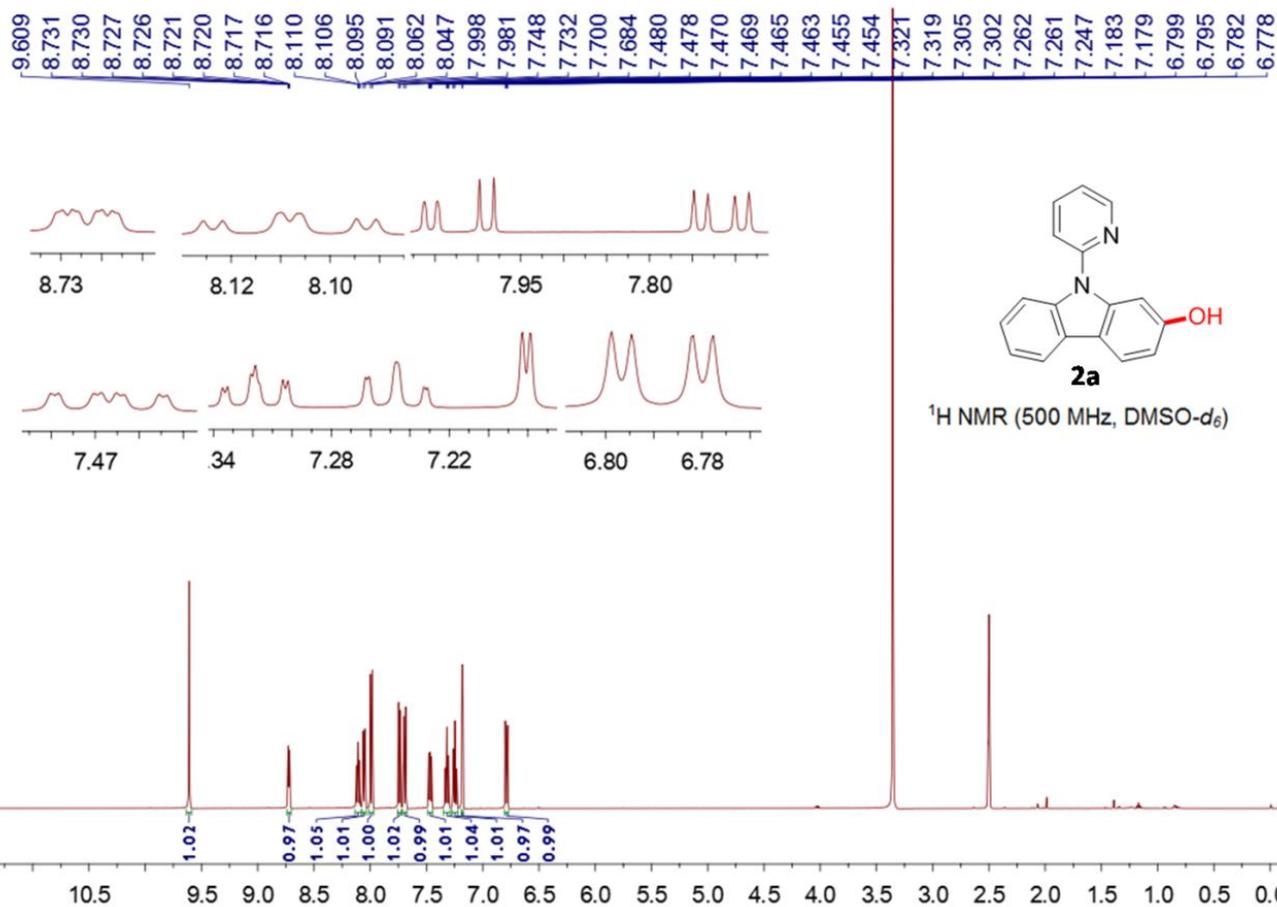


default file
Z-6-34 2207 (18.510) Cm (2201:2214-(2163:2183+2246:2275))

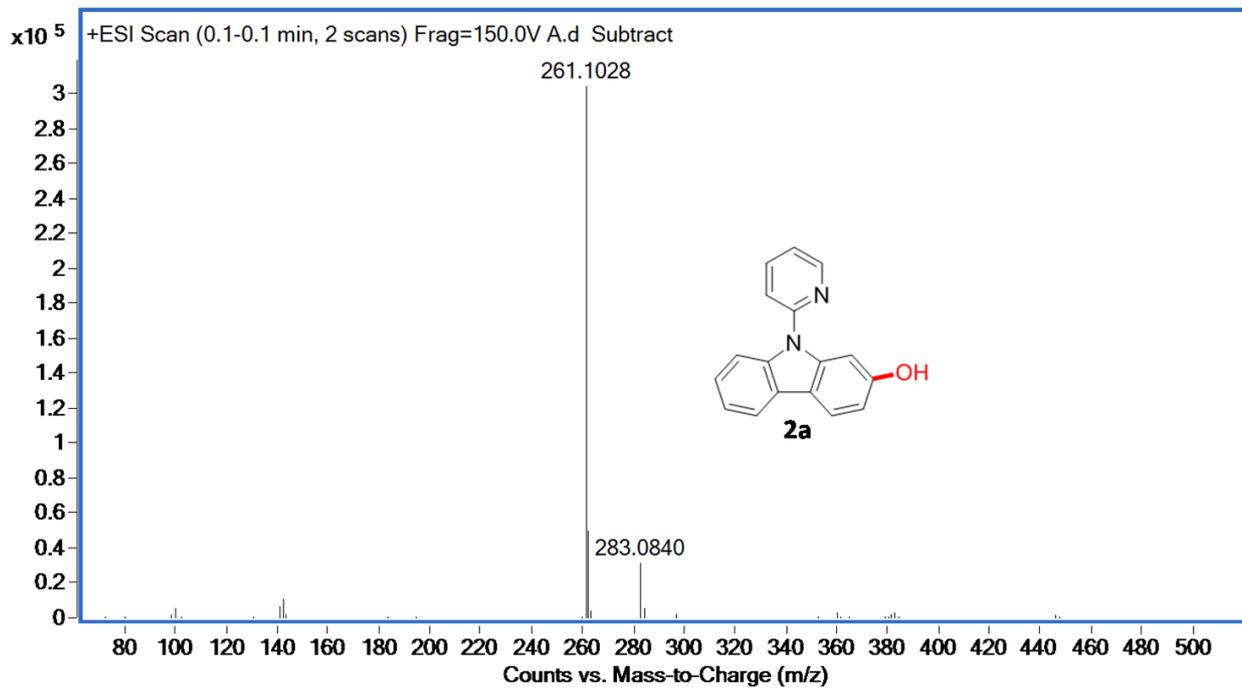
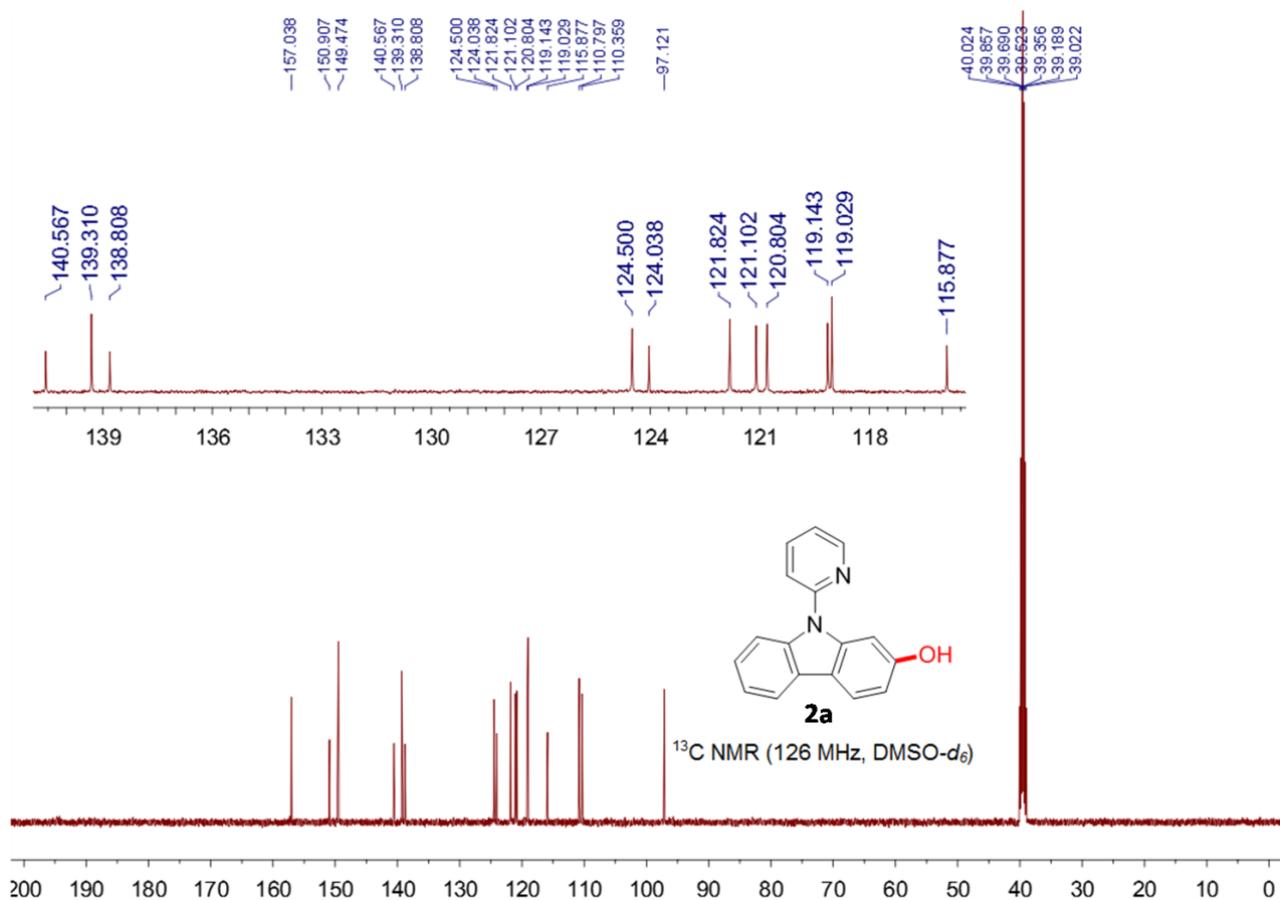
TOF MS EI+
6.95e+003



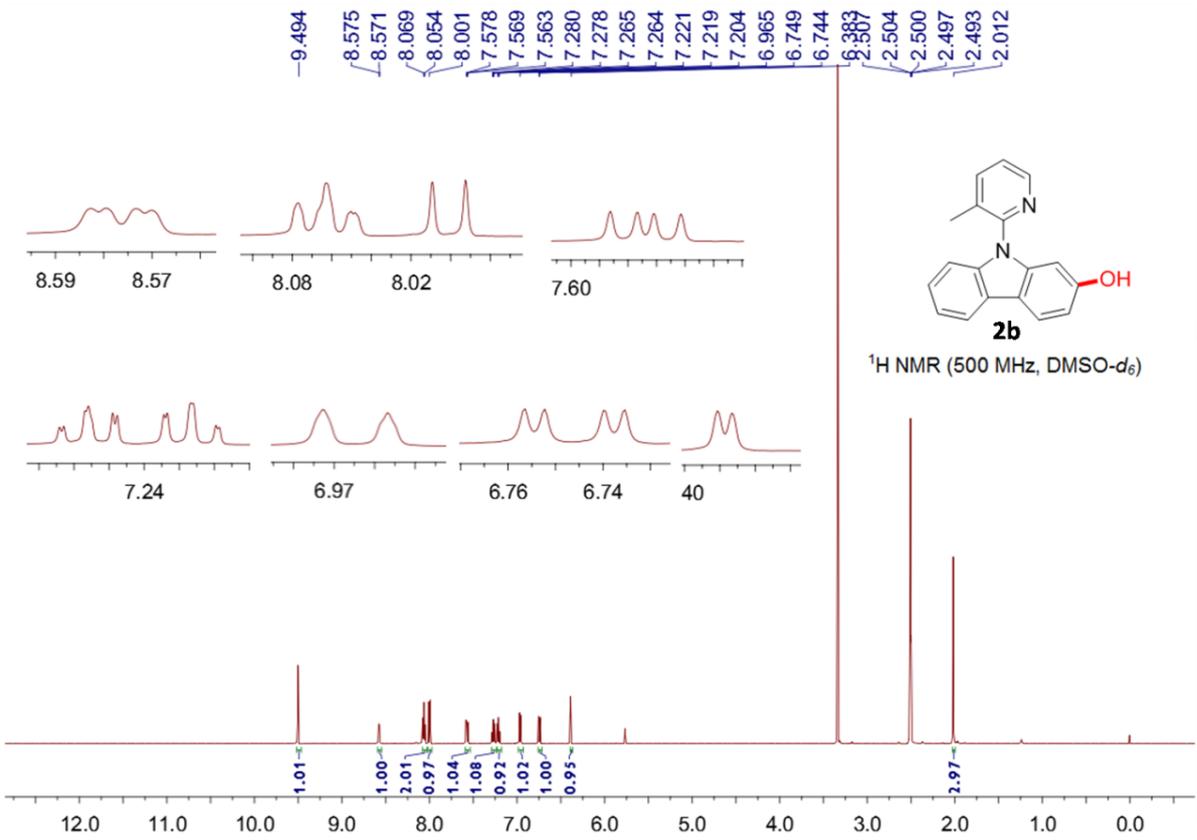
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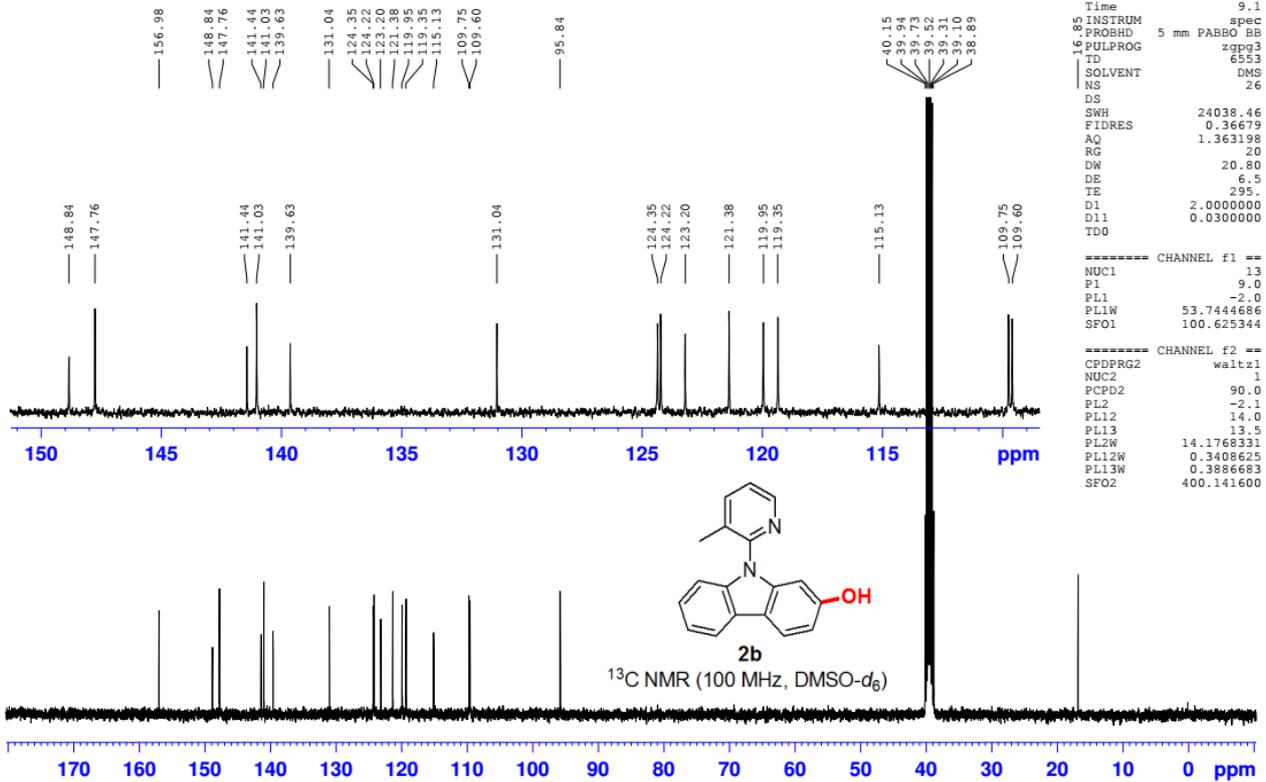
¹H NMR (500 MHz, DMSO-d₆)



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₂ N ₂ O	C ₁₇ H ₁₃ N ₂ O	261.1028	261.1022	-2.16

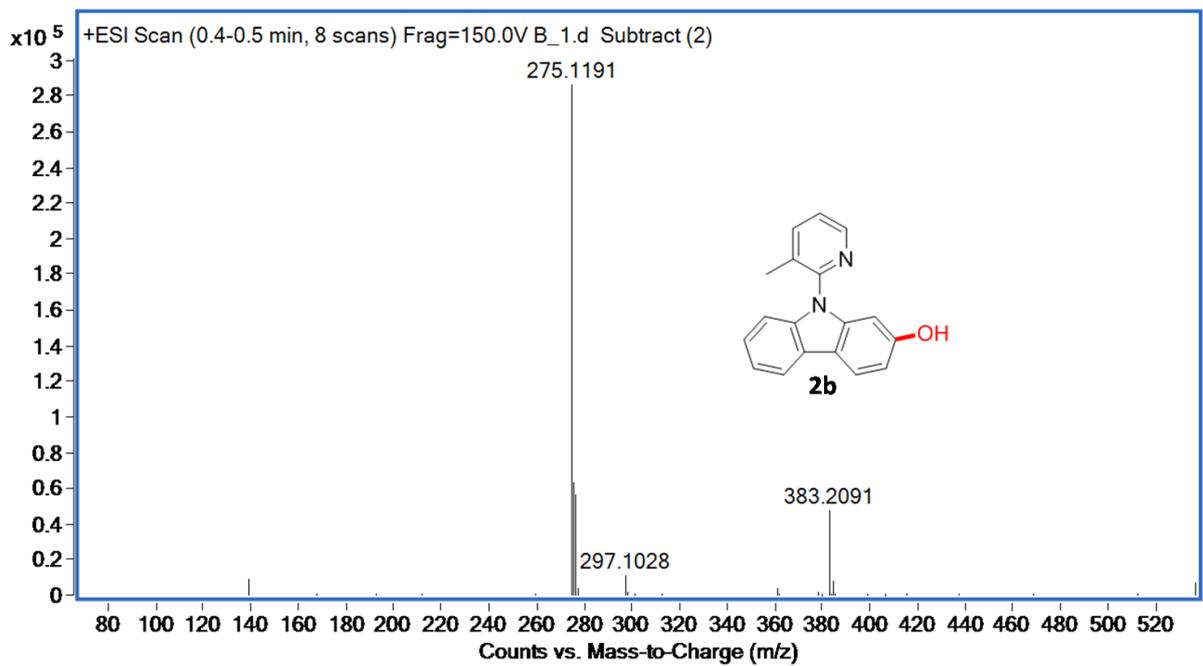


Z-7-17-1 DMSO

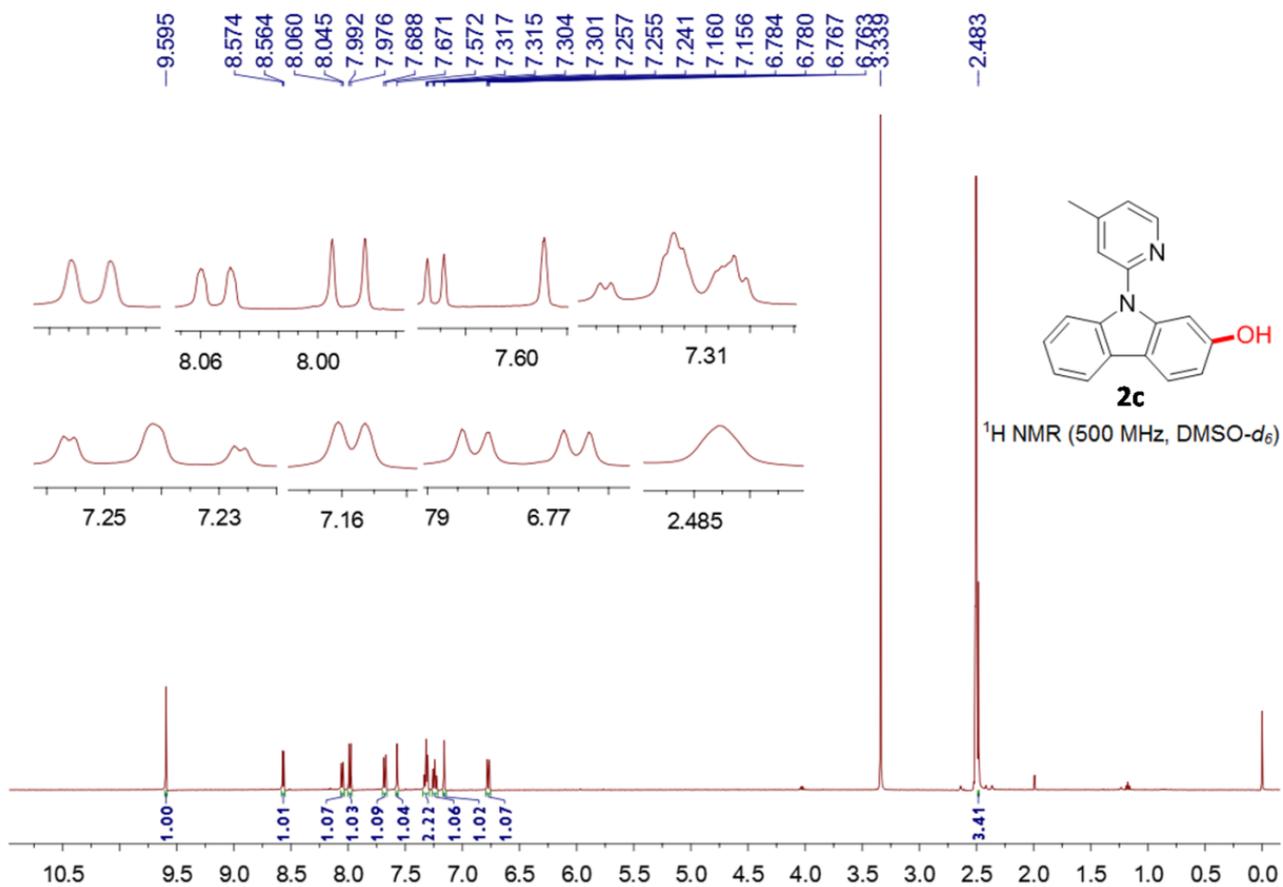


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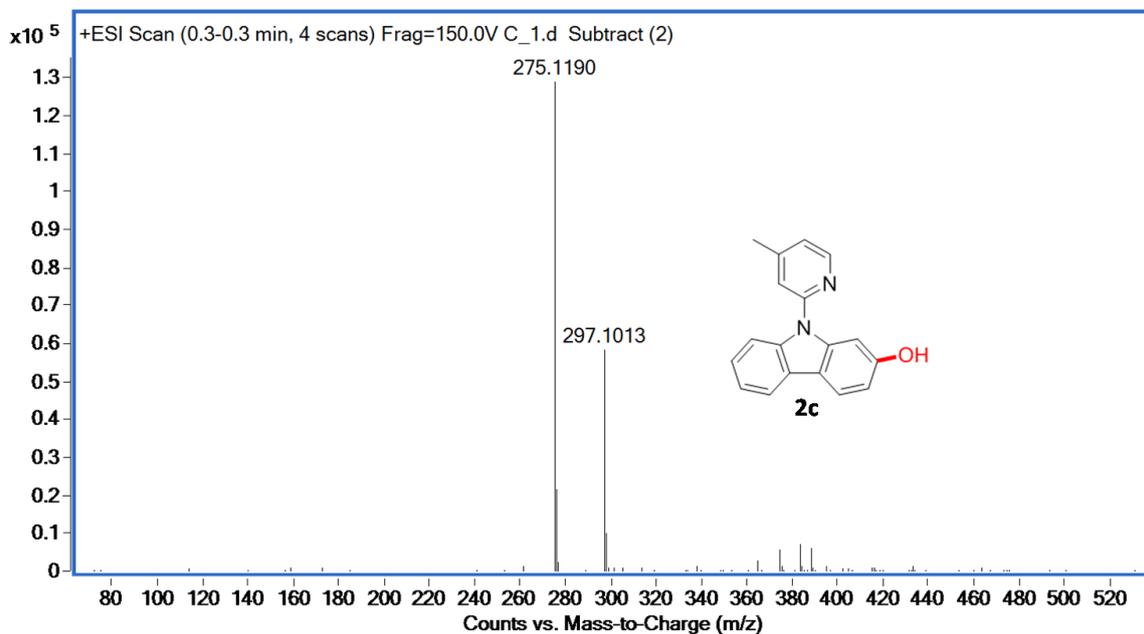
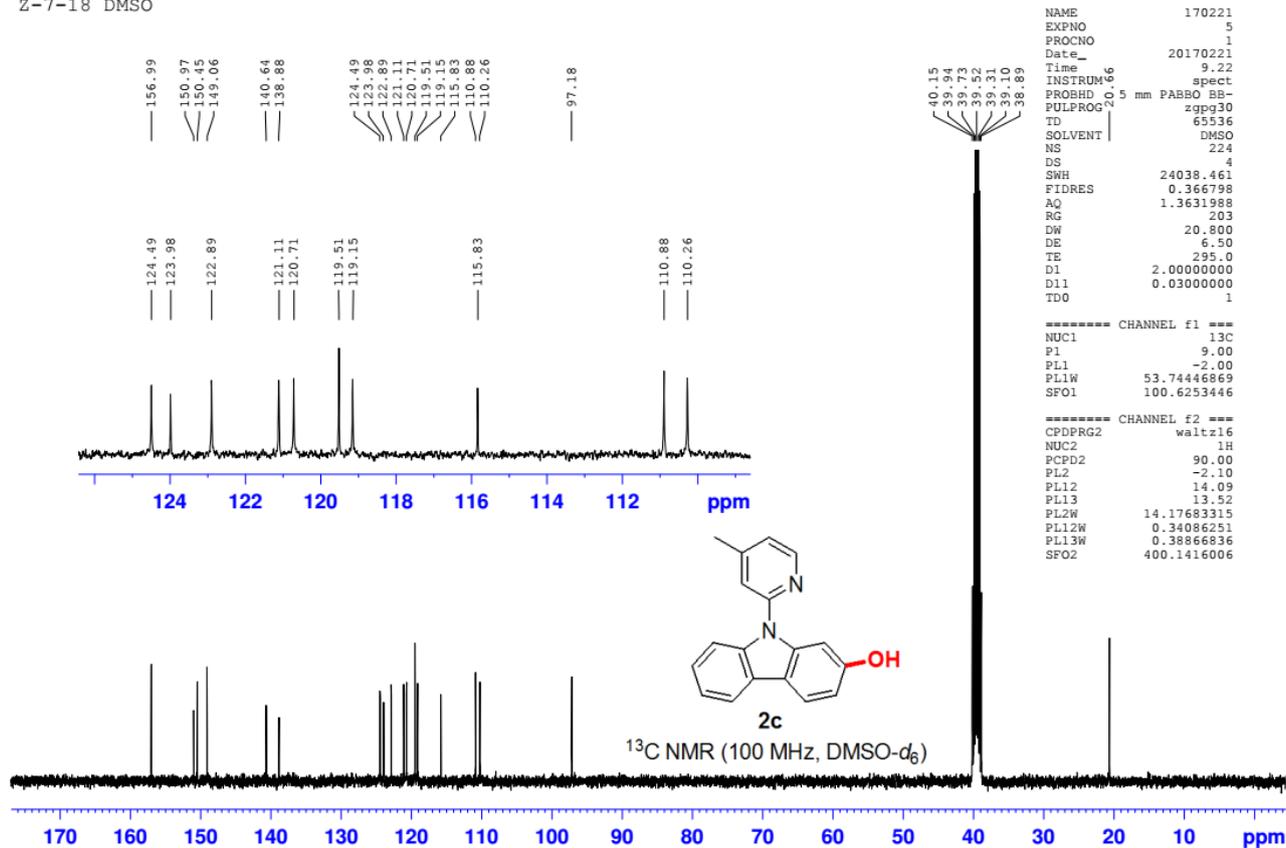
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PROCNO
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SOLVENT      DMS
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FIDRES      0.36679
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RG           2.0
DW          20.80
DE           6.5
TE           295.
D1          2.0000000
D11         0.0300000
TD0
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NUC1         13
P1           9.0
PL1         -2.0
PL1W        53.7444686
SFO1        100.625344
===== CHANNEL f2 =====
CPDPRG2     waltz16
NUC2         1
PCPD2       90.0
PL2         -2.1
PL12        14.0
PL13        13.5
PLZW        14.1768331
PL12W       0.3408625
PL13W       0.3886683
SFO2        400.141600
  
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Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
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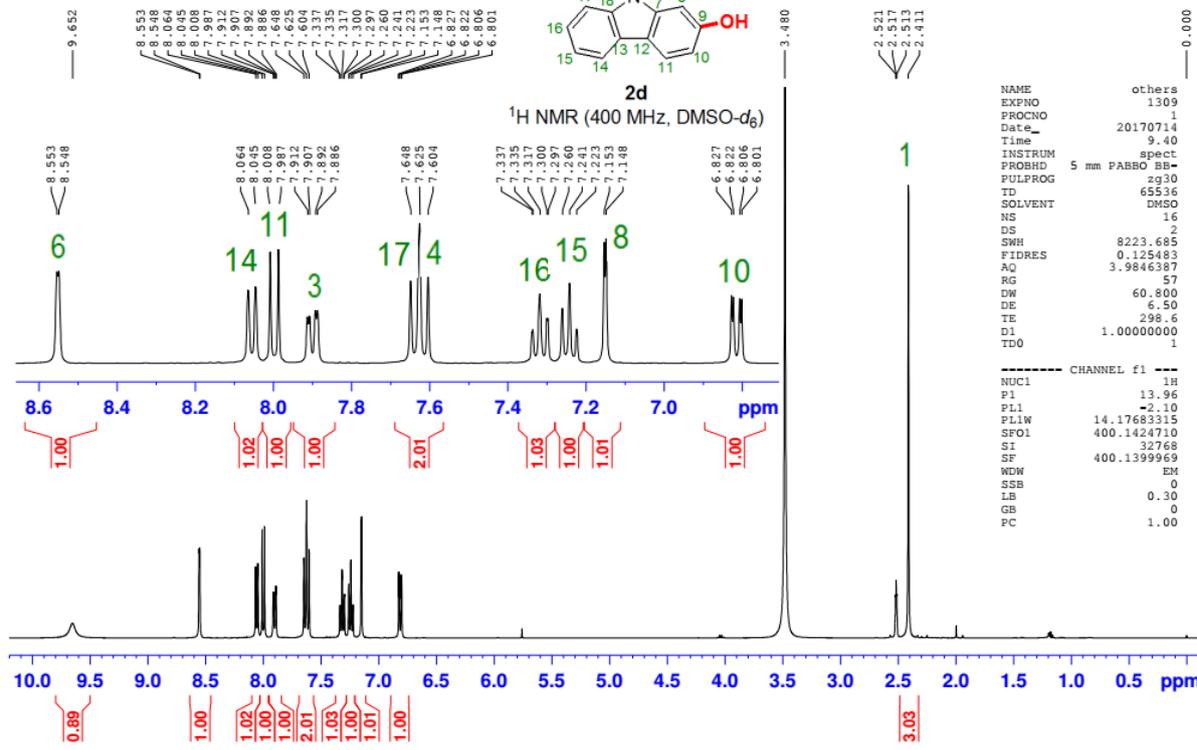


Z-7-18 DMSO



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
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Z-7-19 DMSO

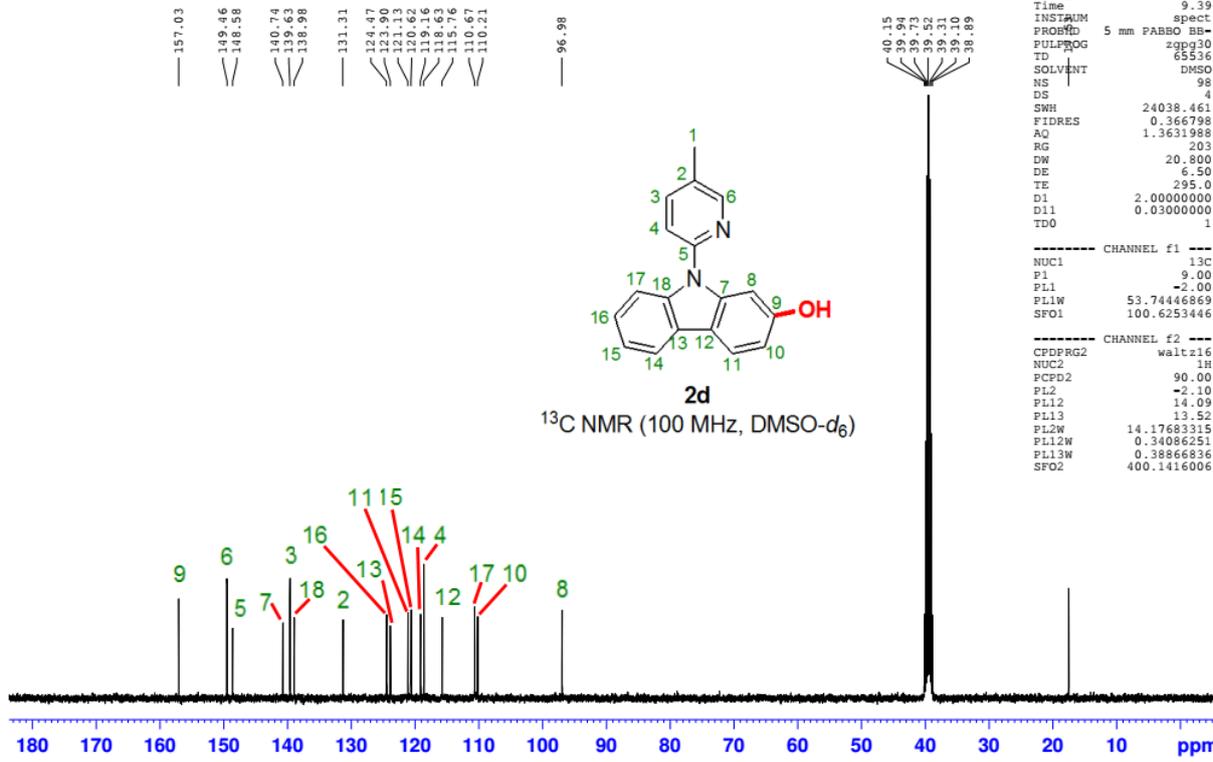


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FIDRES   0.125483
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RG         57
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TE        298.6
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TD0       1

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PL1       -2.10
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Z-7-19 DMSO



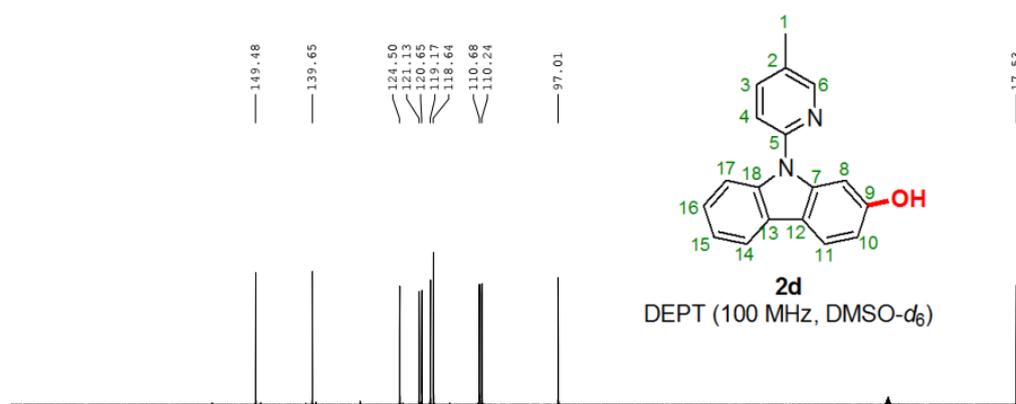
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D11       0.03000000
TD0       1

----- CHANNEL f1 -----
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P1        9.00
PL1       -2.00
PL1W     53.74446869
SF01     100.6253446

----- CHANNEL f2 -----
CPDPRG2  waltz16
NUC2      1H
PCPD2    90.00
PL2       -2.10
PL12     14.09
PL13     13.52
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PL12W    0.34086251
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Z-7-19 DMSO



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PROCNO    1
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Time      10.10
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DS         4
SWH        24038.461
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AQ         1.3631988
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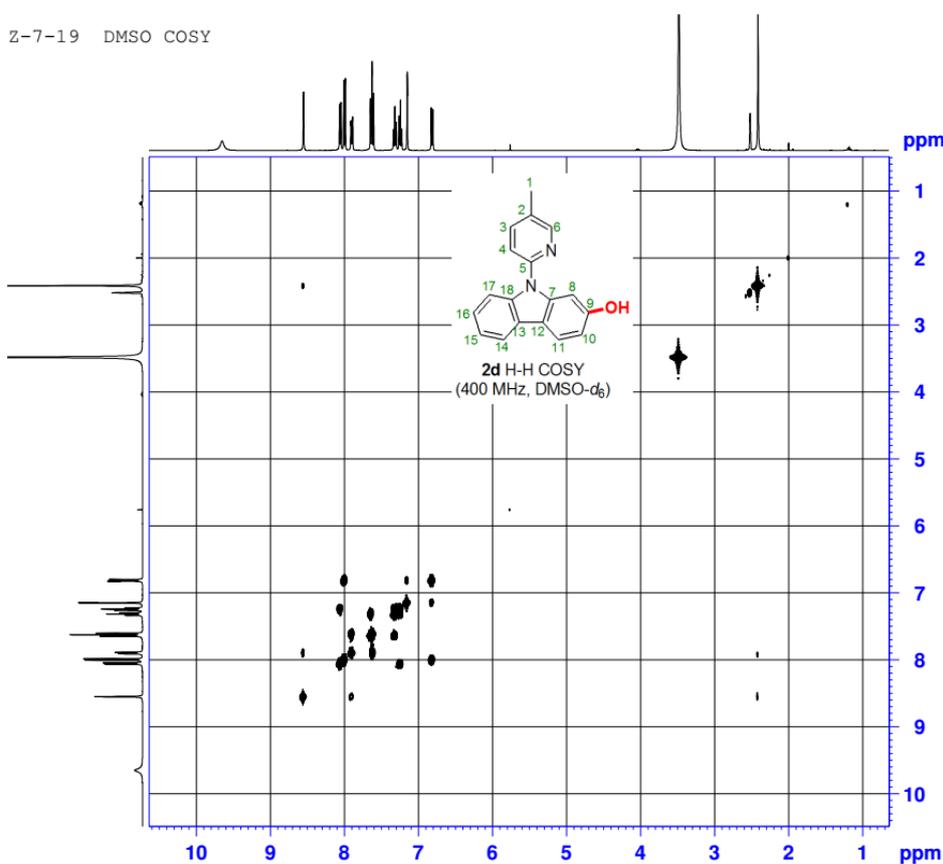
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===== CHANNEL f1 =====
NUC1      13C
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P2        18.00
PL1        -2.00
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SFO1     100.6253446

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
P3         13.96
P4         27.92
PCPD2     90.00
PL2        -2.10
PL12      14.09
  
```



Z-7-19 DMSO COSY



```

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PROCNO    1
Date_     20170714
Time      11.17
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SWH        4000.000
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AQ         0.2560500
RG         128
DW         125.000
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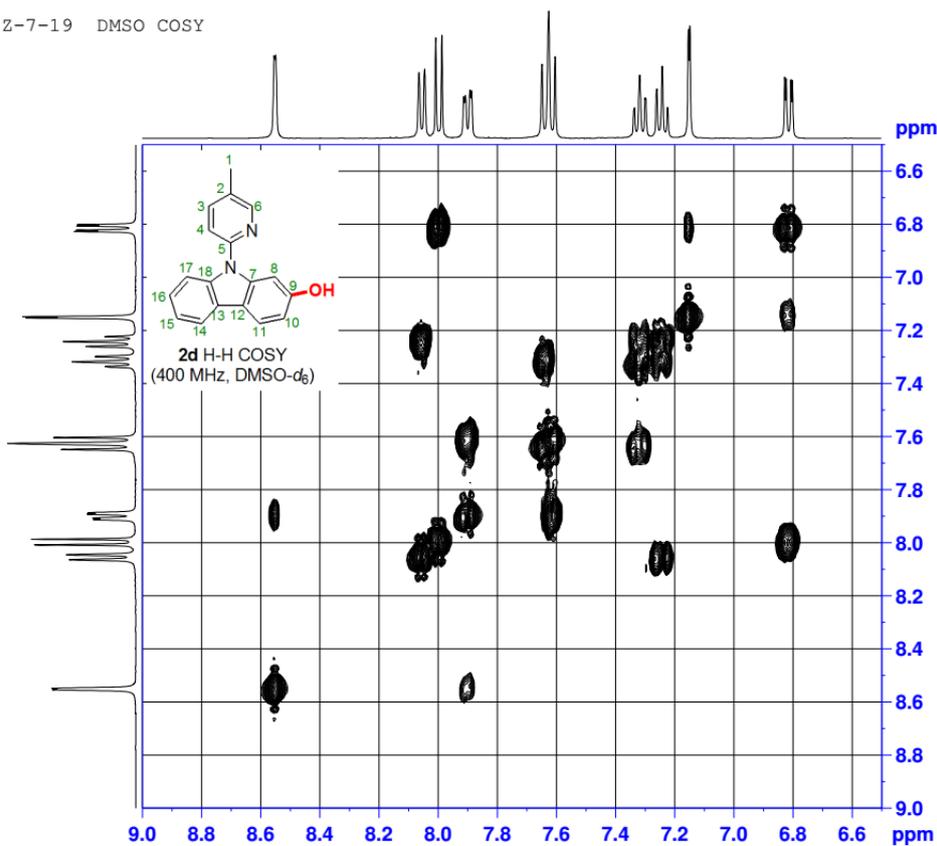
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===== CHANNEL f1 =====
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PL1        -2.10
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SFO1     400.1420007
  
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===== GRADIENT CHANNEL =====
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GPZ1       10.00
P16        1000.00
ND0        1
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SFO1       400.142
FIDRES     31.261093
SW         10.000
FMODE      QF
SI         1024
SF         400.1399940
WDW        SINE
SSB        0
LB         0.00
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SI         1024
MC2        QF
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Z-7-19 DMSO COSY



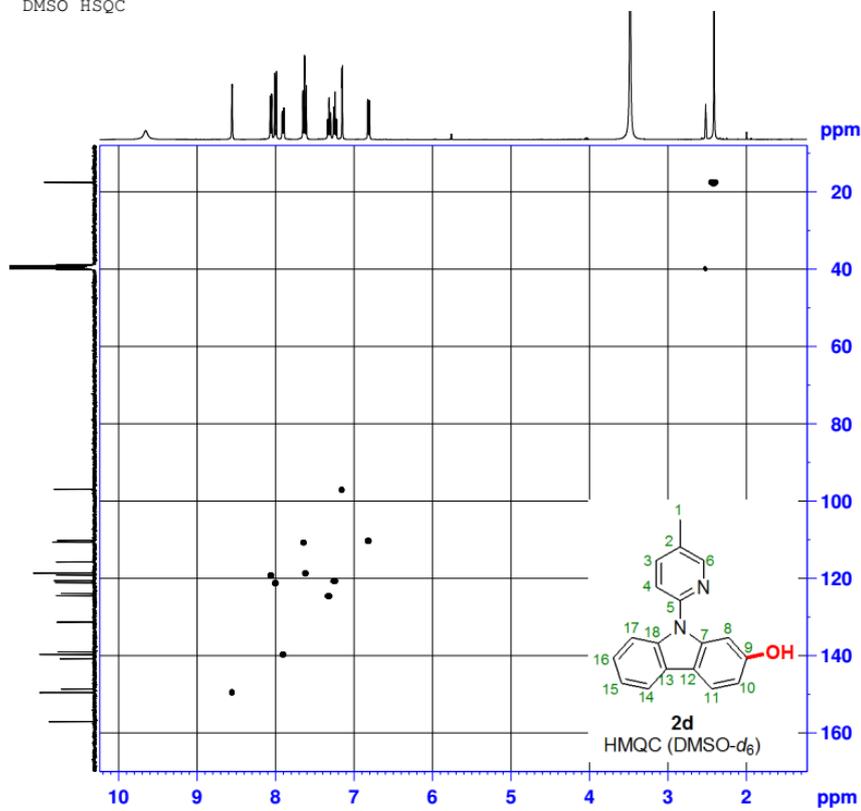
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TD        2048
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D16       0.00020000
INO       0.00024990

===== CHANNEL f1 =====
NUC1      1H
P0        13.96
P1        13.96
PL1       -2.10
PL1W      14.17683315
SFO1      400.1420007

===== GRADIENT CHANNEL =====
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SFO2      n
  
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Z-7-19 DMSO HSQC



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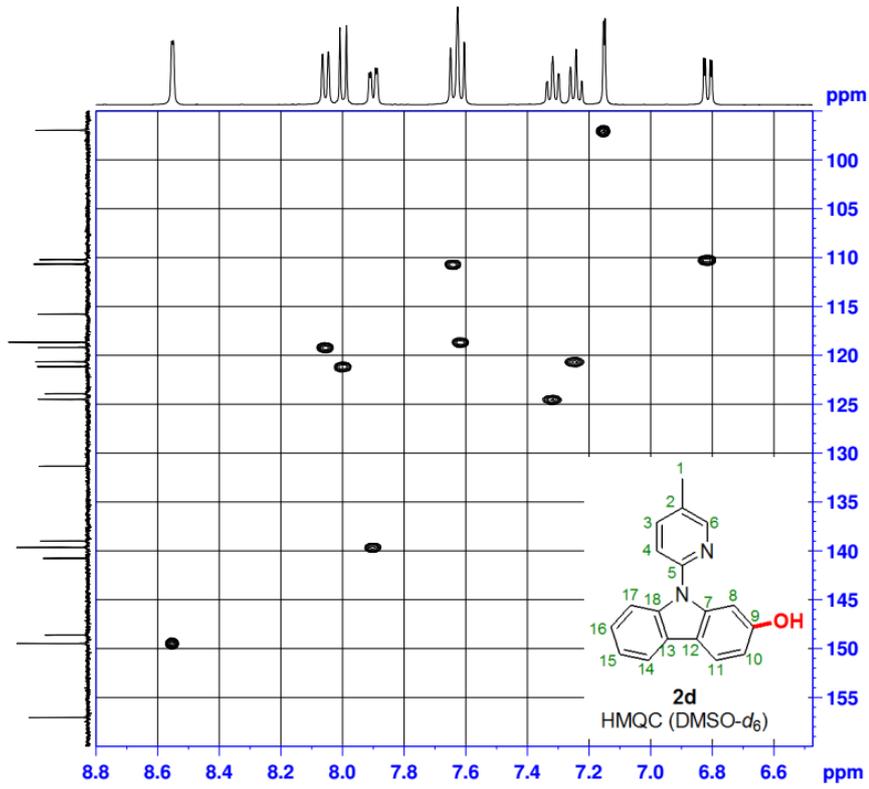
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D4        0.00172414
D11       0.03000000
D13       0.00000400
D16       0.00020000
INO       0.0002485
ZGPTNS

===== CHANNEL f1 =====
NUC1      1H
P1        13.96
P2        27.92
P28       1.00
PL1       -2.10
PL1W      14.17683315
SFO1      400.1420007

===== CHANNEL f2 =====
CPDPRG2   garp
NUC2      13C
P3        9.70
P4        19.40
PCPD2     80.00
PL2       -2.00
PL12      16.30
PL2W      53.74446869
PL12W     0.79493910
SFO2      100.6253445

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPNAM2    SINE.100
GPZ1      80.00
GPZ2      20.10
P16       1000.00
  
```

Z-7-19 DMSO HSQC



```

NAME      others
EXPNO     1312
PROCNO    1
Date_     20170714
Time      11.25
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   hsqcetgp
TD         1024
SOLVENT   DMSO
NS         1
DS         16
SWH        4000.000
FIDRES    3.906250
AQ         0.1280500
RG         203
DW         125.000
DE         6.50
TE         298.7
CNST2     145.0000000
D0         0.0000300
D1         1.48586798
D4         0.00172414
D11        0.03000000
D13        0.00000400
D16        0.00020000
INO        0.00002485
ZGOPTNS
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.96
P2        27.92
P28       1.00
PL1       -2.10
PL1W      14.17683315
SFO1      400.1420007
  
```

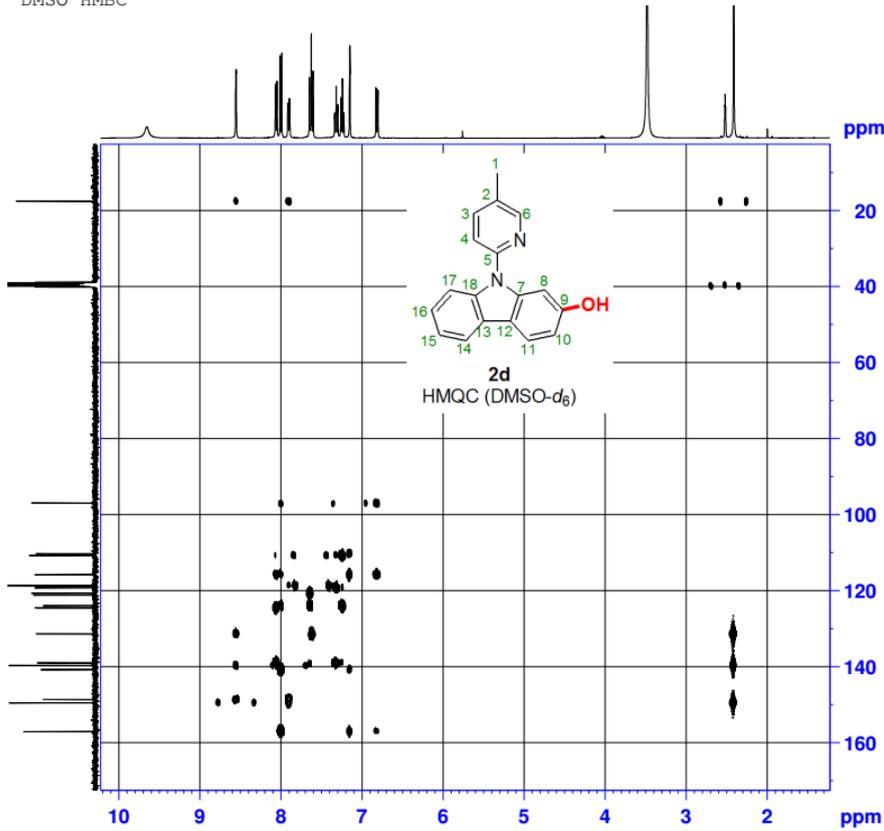
```

===== CHANNEL f2 =====
CPDPRG2   garp
NUC2      13C
P3         9.70
P4         19.40
PCPD2     80.00
PL2        -2.00
PL12       16.30
PL2W      53.74446869
PL12W     0.79493910
SFO2      100.6253445
  
```

```

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPNAM2    SINE.100
GPZ1      80.00
GPZ2      20.10
P16       1000.00
  
```

Z-7-19 DMSO HMBC



```

NAME      others
EXPNO     1313
PROCNO    1
Date_     20170714
Time      11.32
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   hmbcgpndgf
TD         4096
SOLVENT   DMSO
NS         4
DS         16
SWH        4000.000
FIDRES    0.976563
AQ         0.5120500
RG         203
DW         125.000
DE         6.50
TE         298.7
CNST13    8.00000000
D0         0.00000300
D1         1.50000000
D6         0.06250000
D16        0.00020000
INO        0.00002485
  
```

```

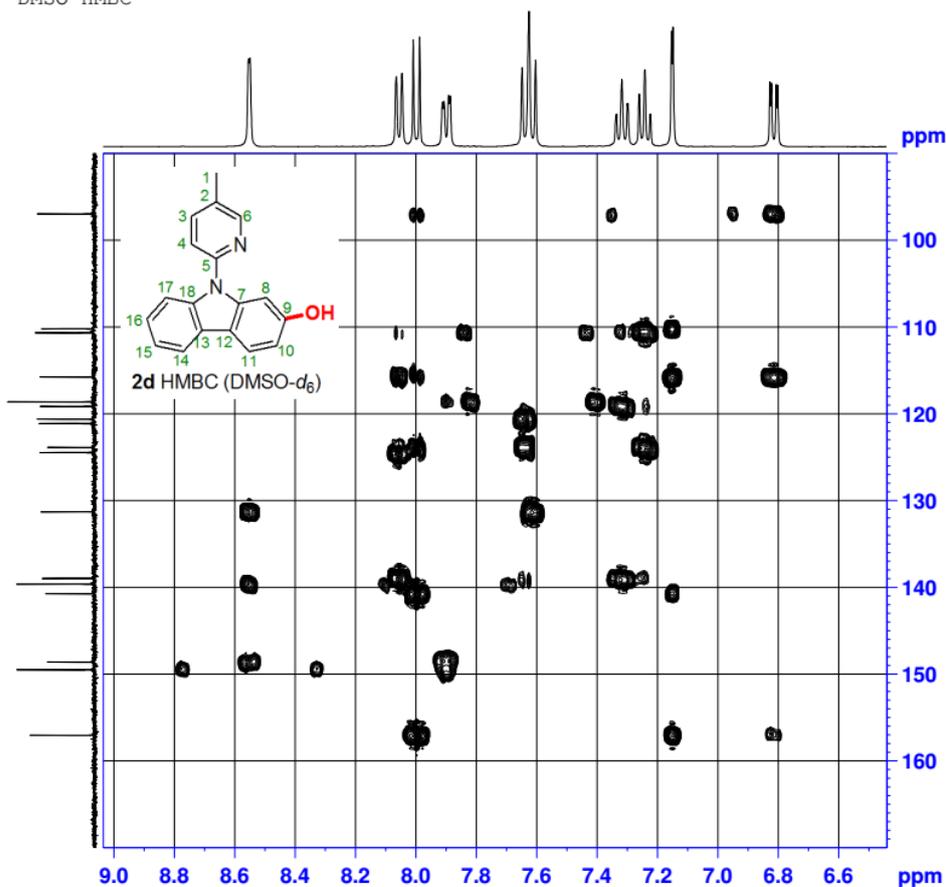
===== CHANNEL f1 =====
NUC1      1H
P1        13.96
P2        27.92
PL1       -2.10
PL1W      14.17683315
SFO1      400.1420007
  
```

```

===== CHANNEL f2 =====
NUC2      13C
P3         9.70
P4         19.40
PL2        -2.00
PL2W      53.74446869
SFO2      100.6253445
  
```

```

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPNAM2    SINE.100
GPNAM3    SINE.100
GPZ1      50.00
GPZ2      30.00
GPZ3      40.10
P16       1000.00
ND0        2
TD         128
SFO1      100.6253
FIDRES    157.227097
SW         200.000
FnMODE    QF
SI         1024
  
```



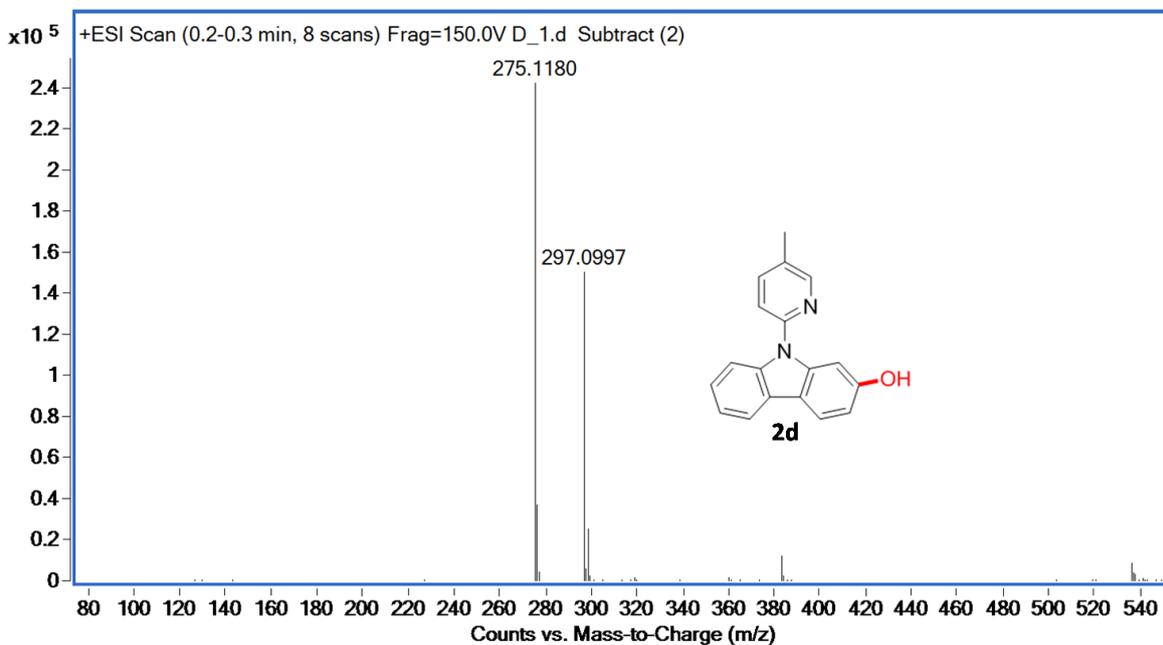
```

NAME      others
EXPNO     1313
PROCNO    1
Date_     20170714
Time      11.32
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   hmbcgpndqf
TD         4096
SOLVENT   DMSO
NS         4
DS         16
SWH        4000.000
FIDRES     0.976563
AQ         0.5120500
RG         203
DW         125.000
DE         6.50
TE         298.7
CNST13    8.0000000
D0         0.00000300
D1         1.50000000
D6         0.06250000
D16        0.00020000
IN0        0.00002485

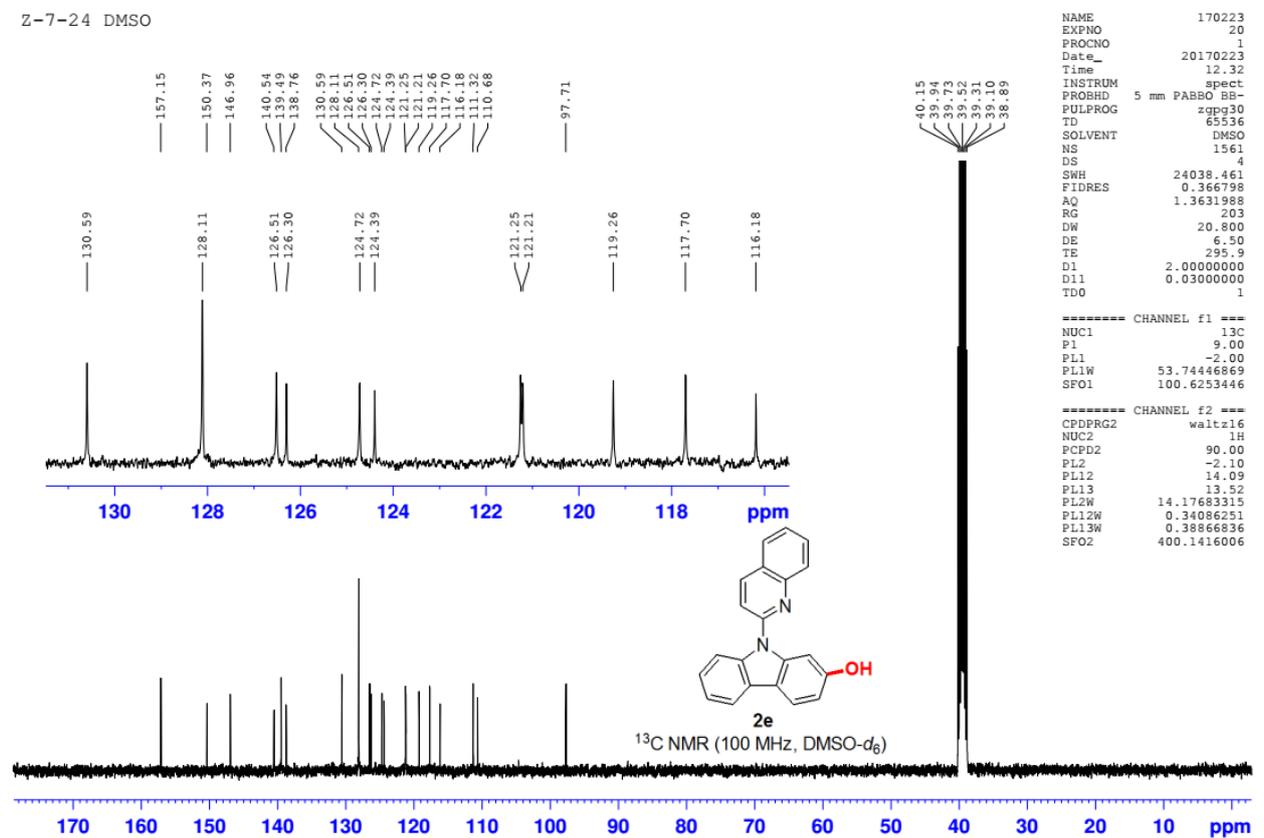
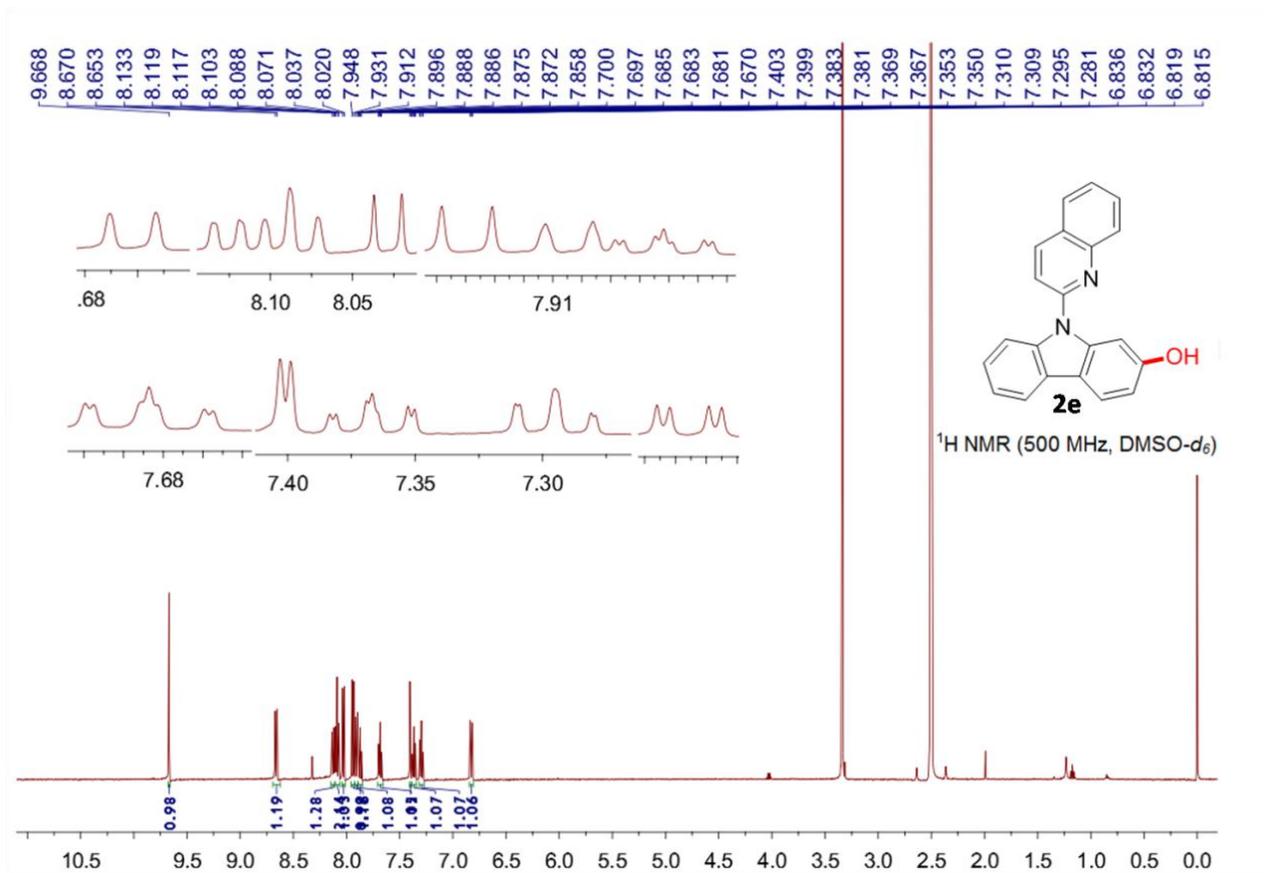
===== CHANNEL f1 =====
NUC1       1H
P1         13.96
P2         27.92
PL1        -2.10
PL1W       14.17683315
SFO1       400.1420007

===== CHANNEL f2 =====
NUC2       13C
P3         9.70
P2         -2.00
PL2W       53.74446869
SFO2       100.6253445

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPNAM2    SINE.100
GPNAM3    SINE.100
GPZ1      50.00
GPZ2      30.00
GPZ3      40.10
P16       1000.00
ND0        2
TD         128
SFO1       100.6253
FIDRES     157.227097
SW         200.000
FnMODE    OF
SI         1024
  
```



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₈ H ₁₄ N ₂ O	C ₁₈ H ₁₅ N ₂ O	275.1180	275.1179	-0.4



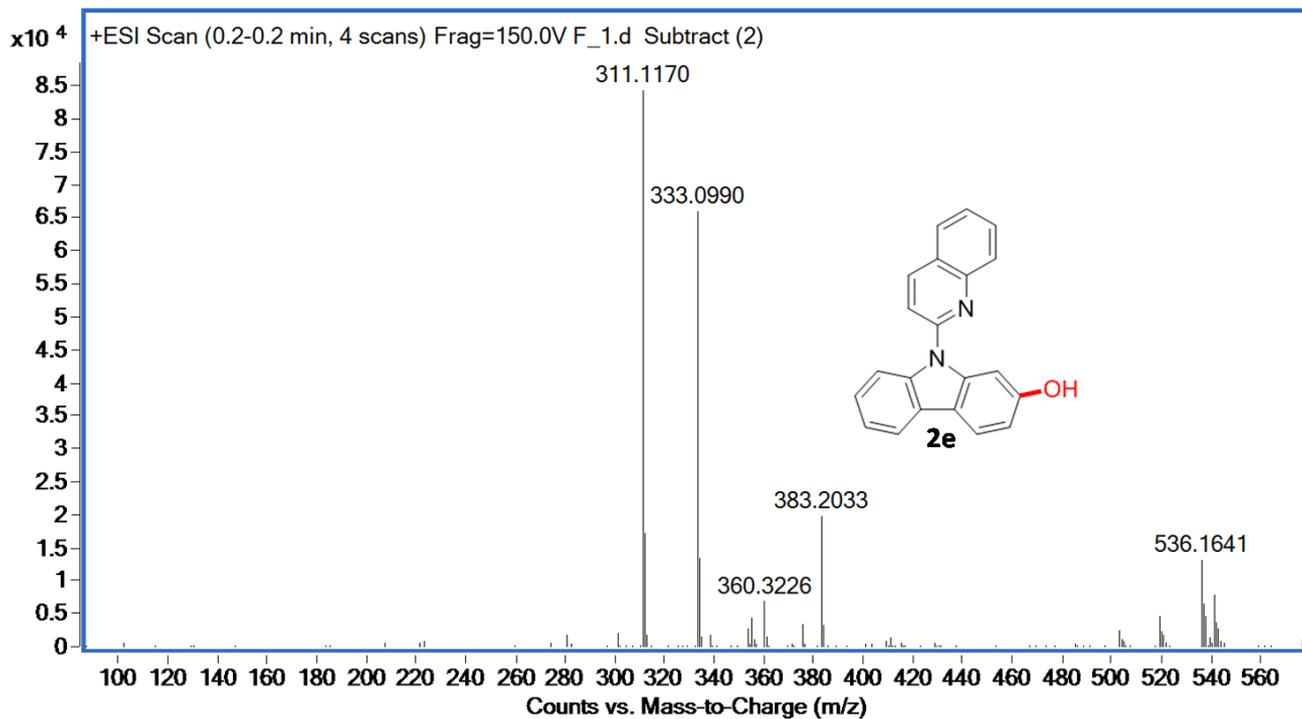
```

NAME 170223
EXPNO 20
PROCNO 1
Date_ 20170223
Time 12.32
INSTRUM spect
PROBHD 5 mm PABBO BP-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1561
DS 4
SWH 24038.461
FIDRES 0.366798
AQ 1.3631988
RG 203
DW 20.800
DE 6.50
TE 295.9
D1 2.00000000
D11 0.03000000
TDO 1

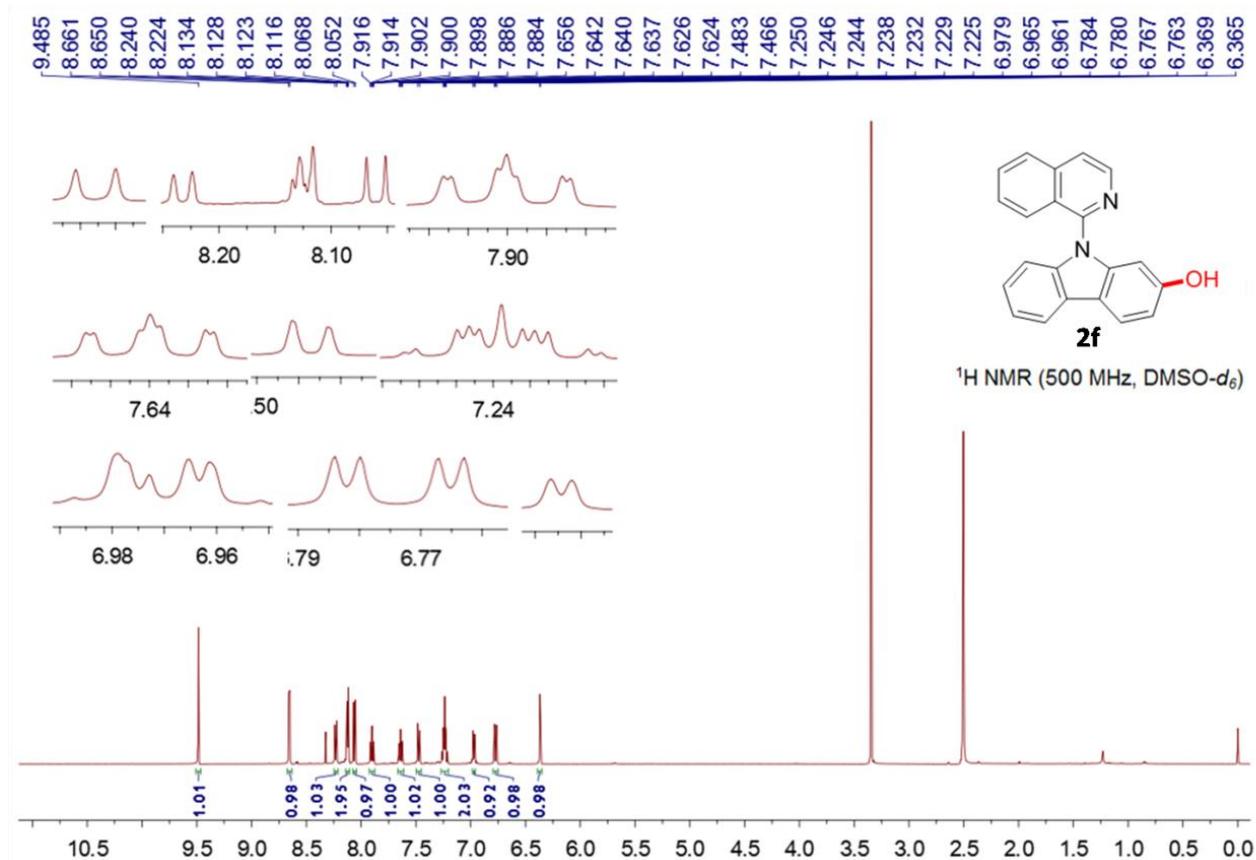
----- CHANNEL f1 -----
NUC1 13C
P1 9.00
PL1 -2.00
PL1W 53.74446869
SFO1 100.6253446

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00
PL2 -2.10
PL12 14.09
PL13 13.52
PL2W 14.17683315
PL12W 0.34086251
PL13W 0.38866836
SFO2 400.1416006

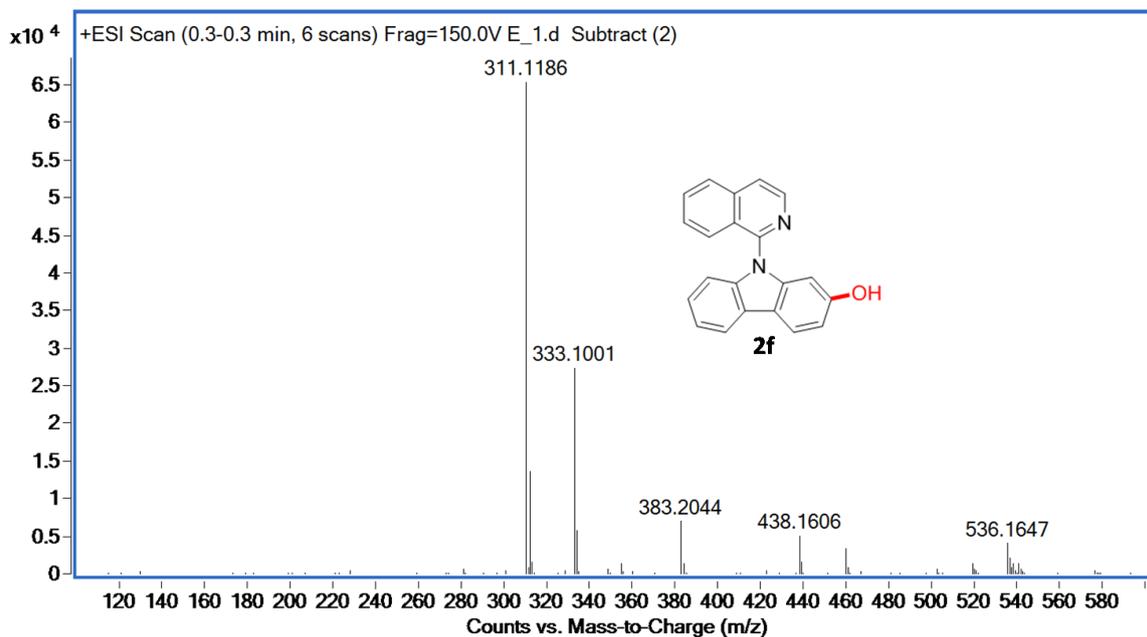
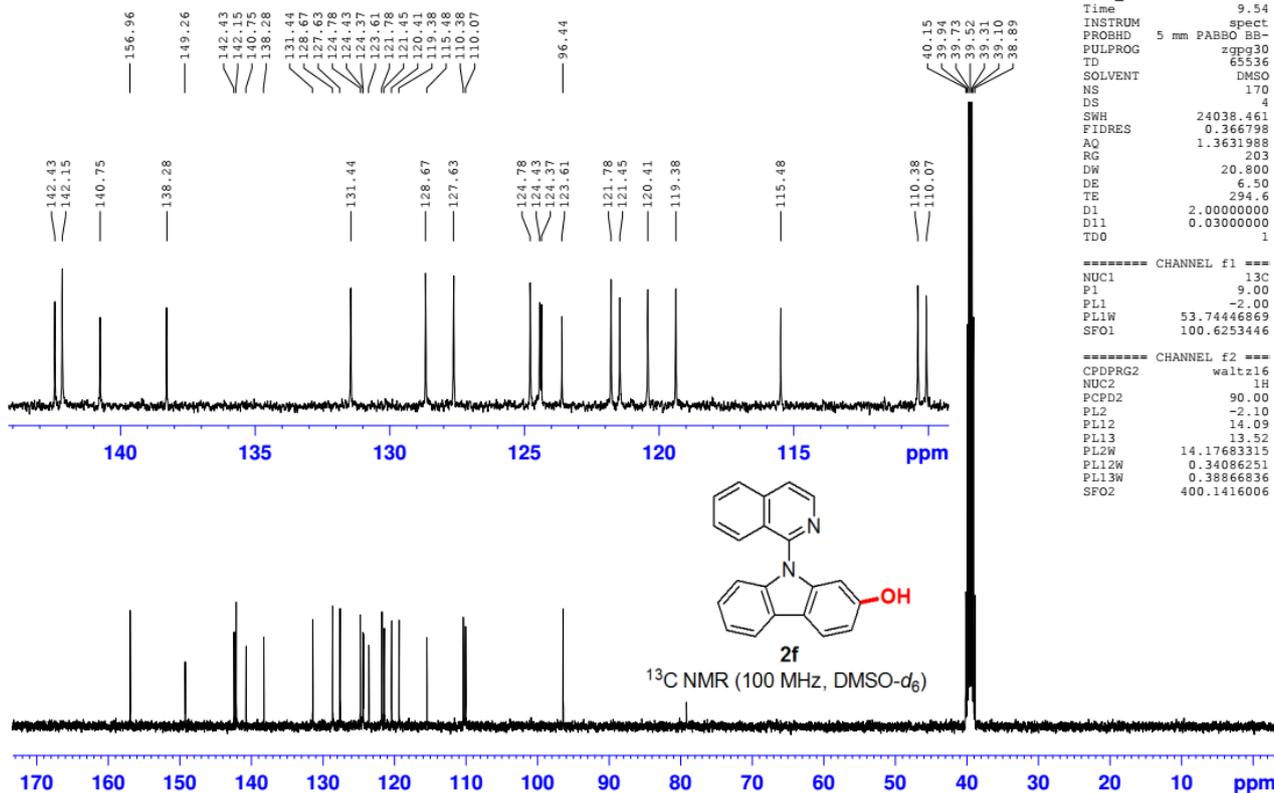
```



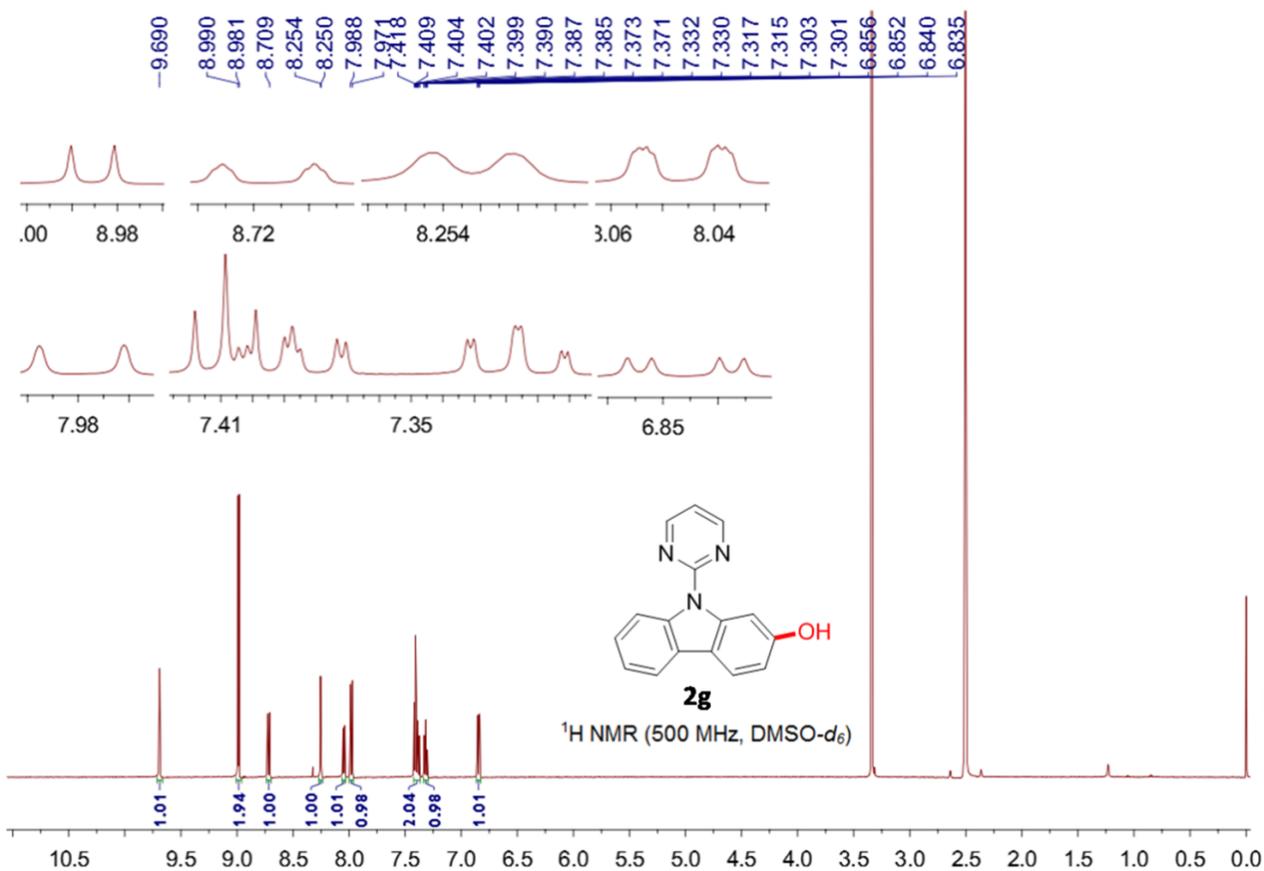
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₂₁ H ₁₄ N ₂ O	C ₂₁ H ₁₅ N ₂ O	311.1170	311.1179	2.87



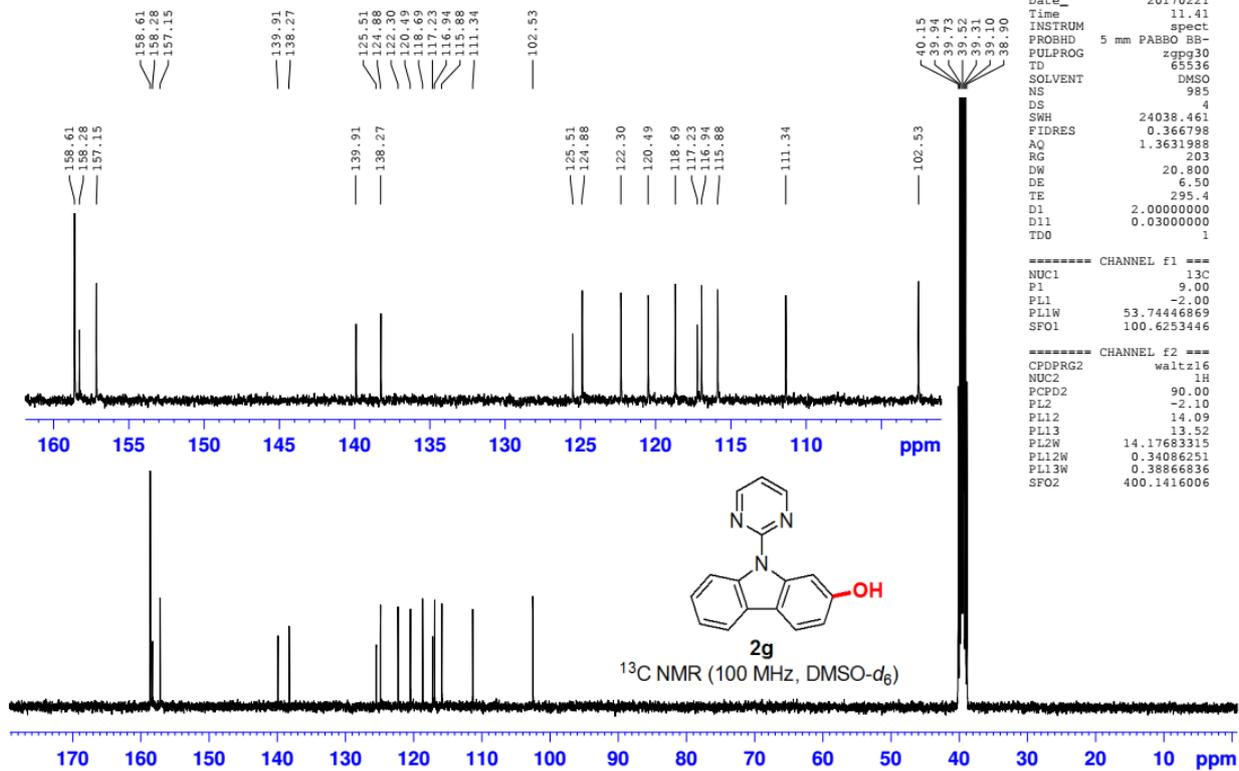
Z-7-23 DMSO



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₂₁ H ₁₄ N ₂ O	C ₂₁ H ₁₅ N ₂ O	311.1186	311.1179	-2.29



Z-7-25 DMSO



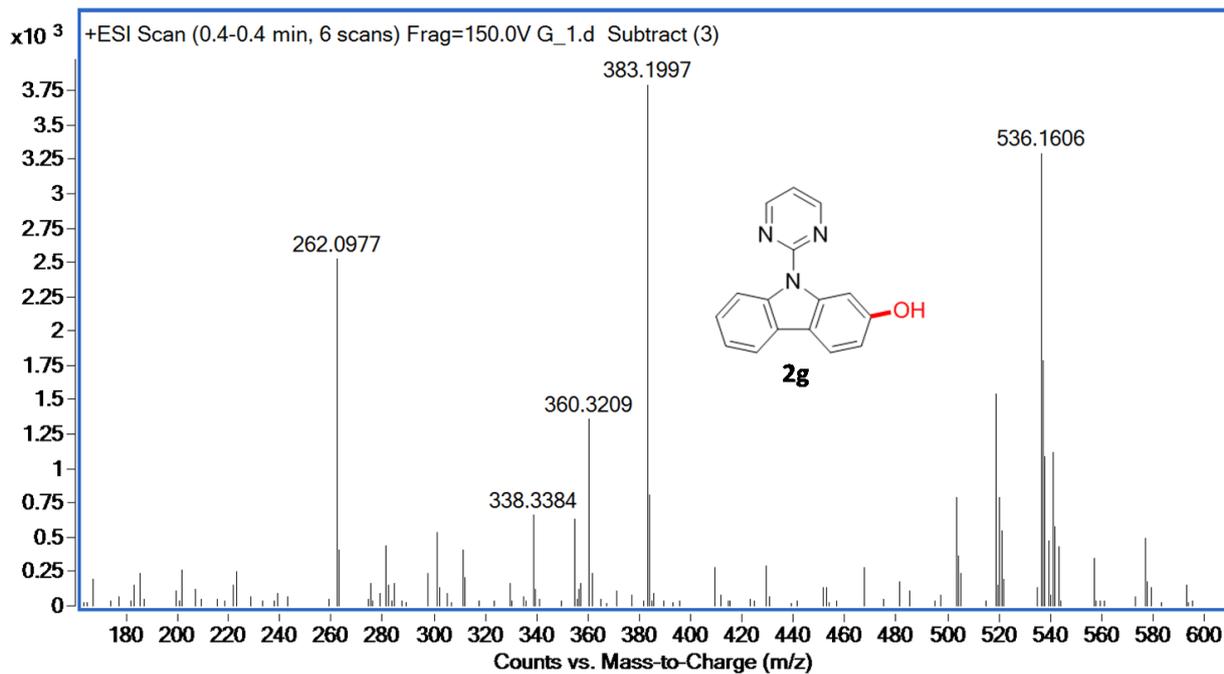
```

NAME 170221
EXPNO 18
PROCNO 1
Date_ 20170221
Time 11.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 985
DS 4
SWH 24038.461
FIDRES 0.366798
AQ 1.3631988
RG 203
DW 20.800
DE 6.50
TE 295.4
D1 2.00000000
D11 0.03000000
TDO 1

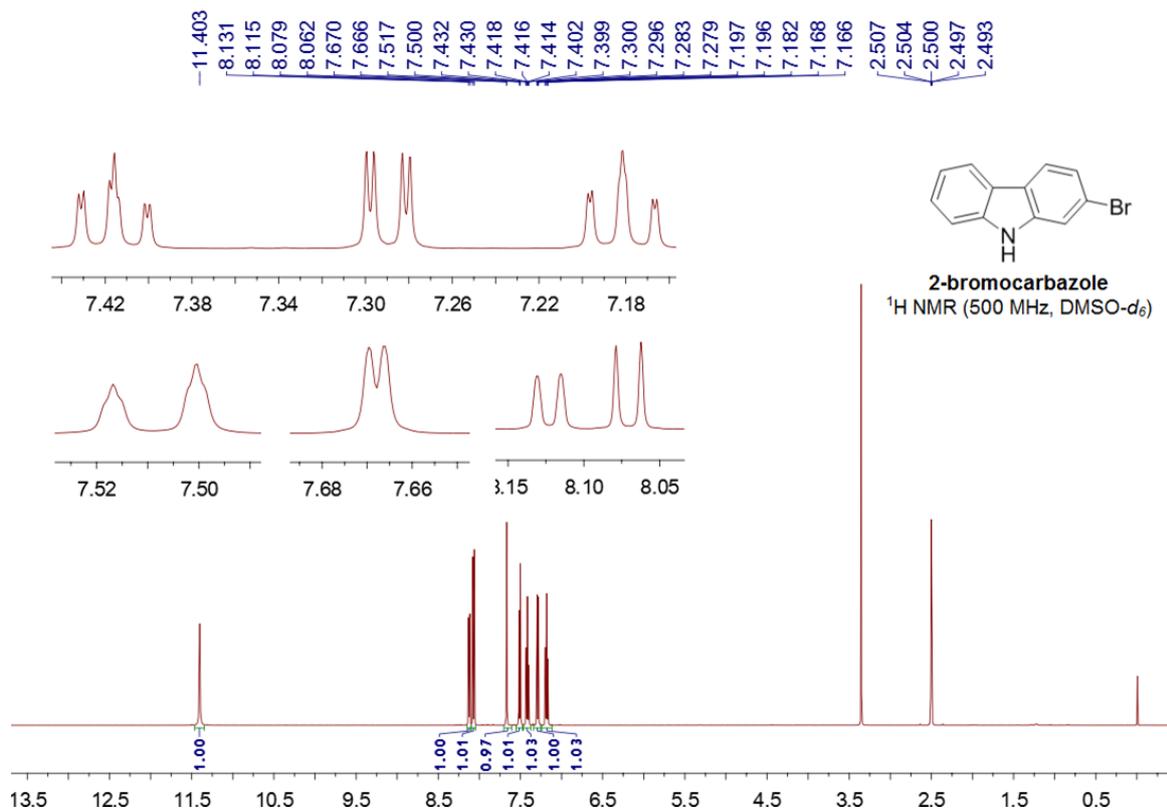
===== CHANNEL f1 =====
NUC1 13C
P1 9.00
PL1 -2.00
PL1W 53.74446869
SFO1 100.6253446

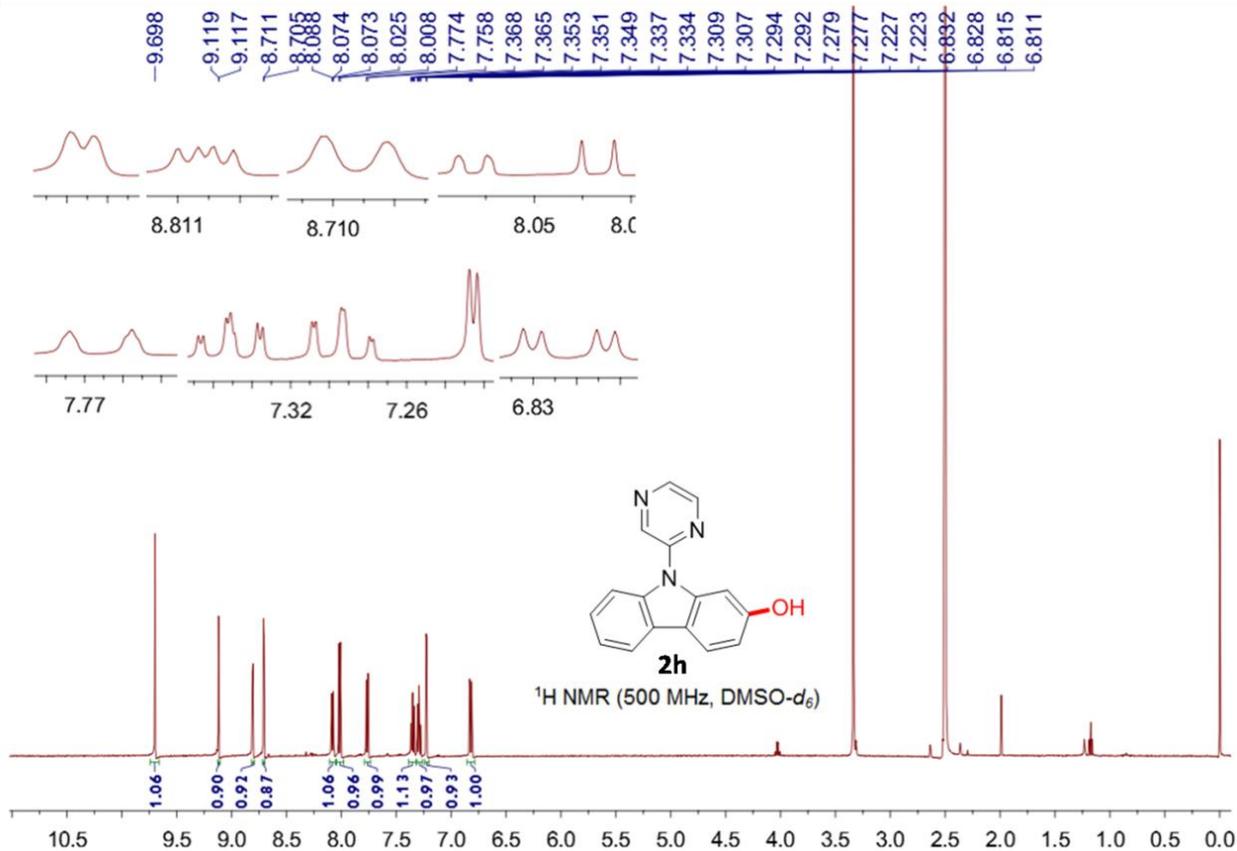
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00
PL2 -2.10
PL12 14.09
PL13 13.52
PL1W 14.17683315
PL12W 0.34086251
PL13W 0.38866836
SFO2 400.1416006

```

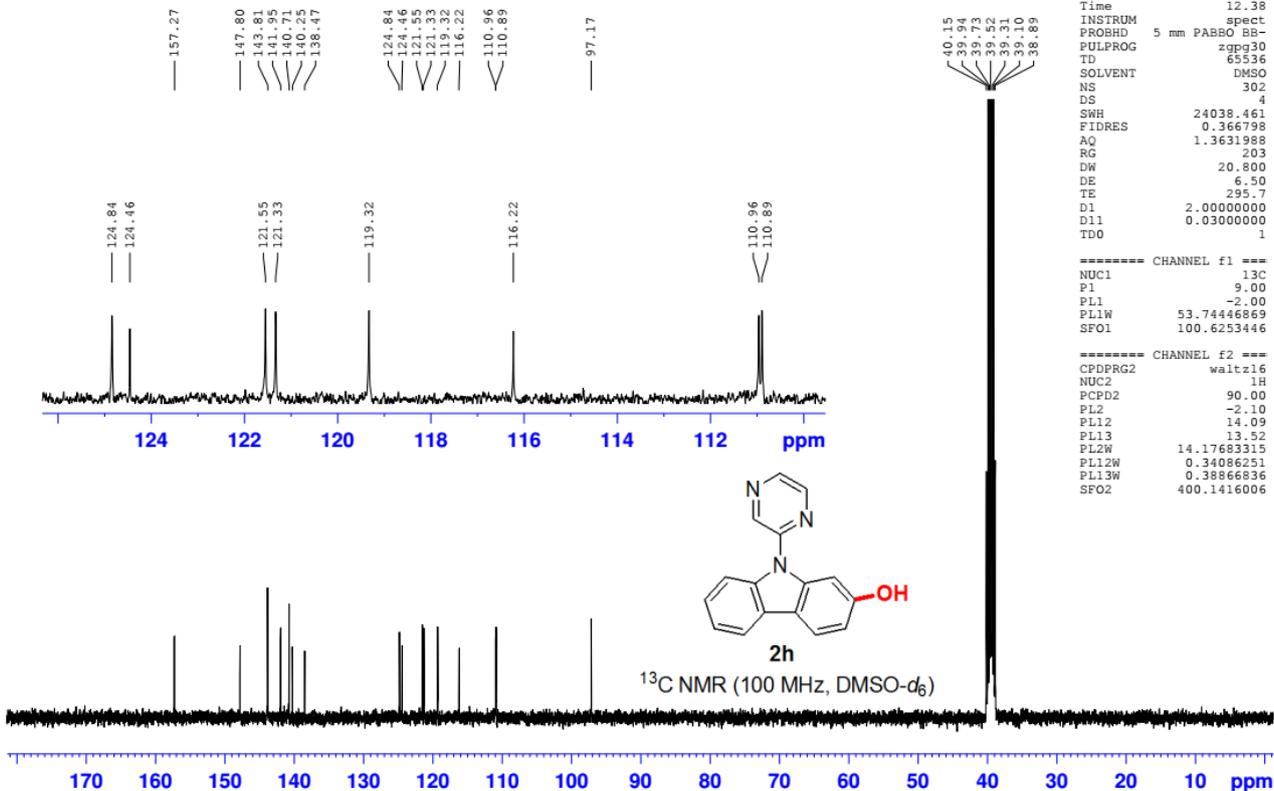


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₆ H ₁₁ N ₃ O	C ₁₆ H ₁₂ N ₃ O	262.0977	262.0975	-0.81





Z-7-26 DMSO



```

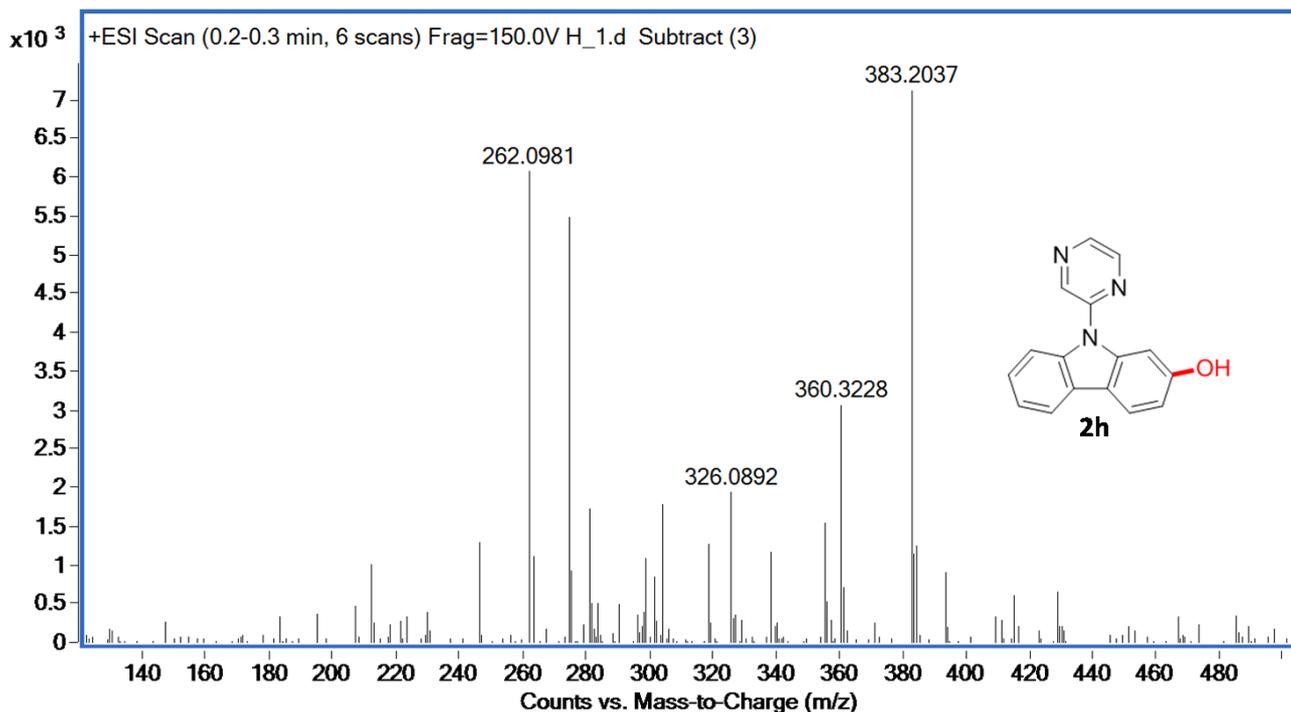
NAME          170221
EXPNO         19
PROCNO        1
Date_         20170221
Time          12.38
INSTRUM      spect
PROBHD       5 mm PABBO BB-
PULPROG      zgpg30
TD            65536
SOLVENT      DMSO
NS            302
DS            4
SWH           24038.461
FIDRES       0.366798
AQ            1.3631988
RG            203
DW            20.800
DE            6.50
TE            295.7
D1            2.00000000
D11           0.03000000
TD0           1
  
```

```

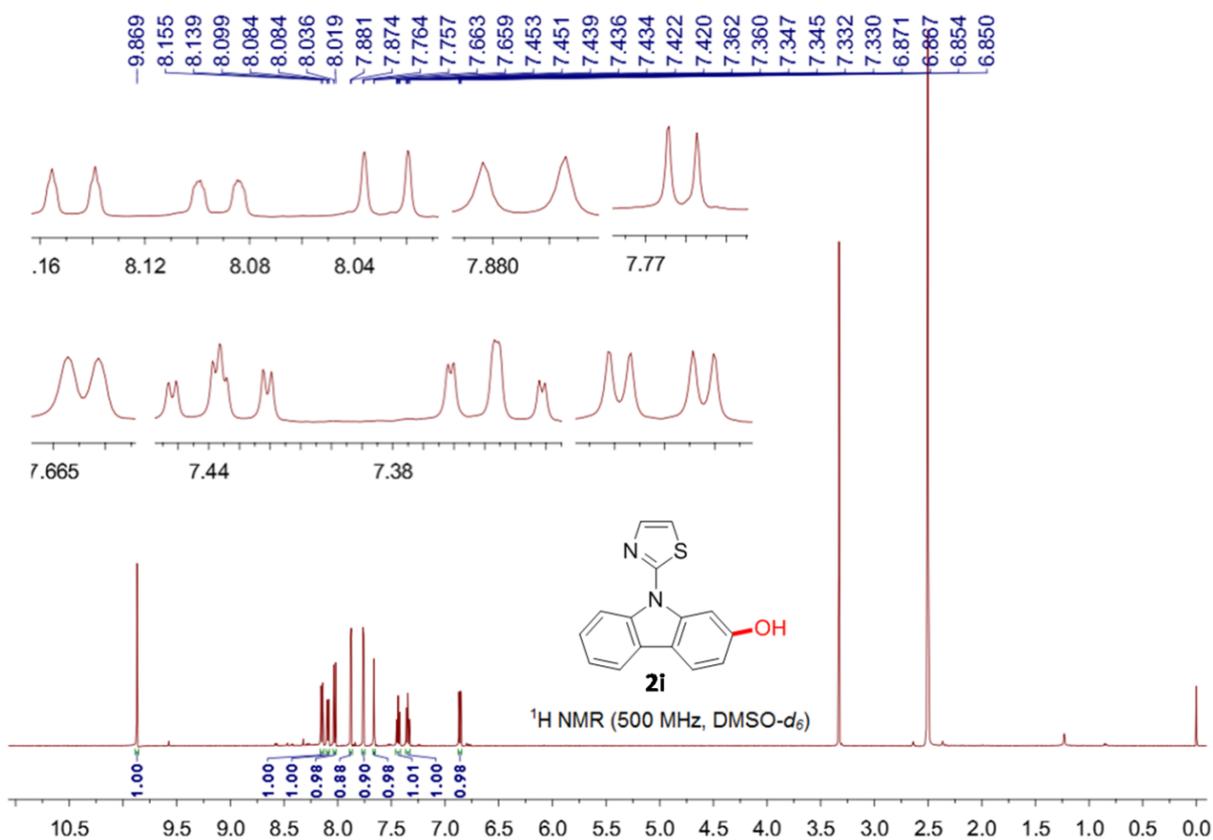
===== CHANNEL f1 =====
NUC1          13C
P1             9.00
PL1           -2.00
PL1W          53.74446869
SF01          100.6253446
  
```

```

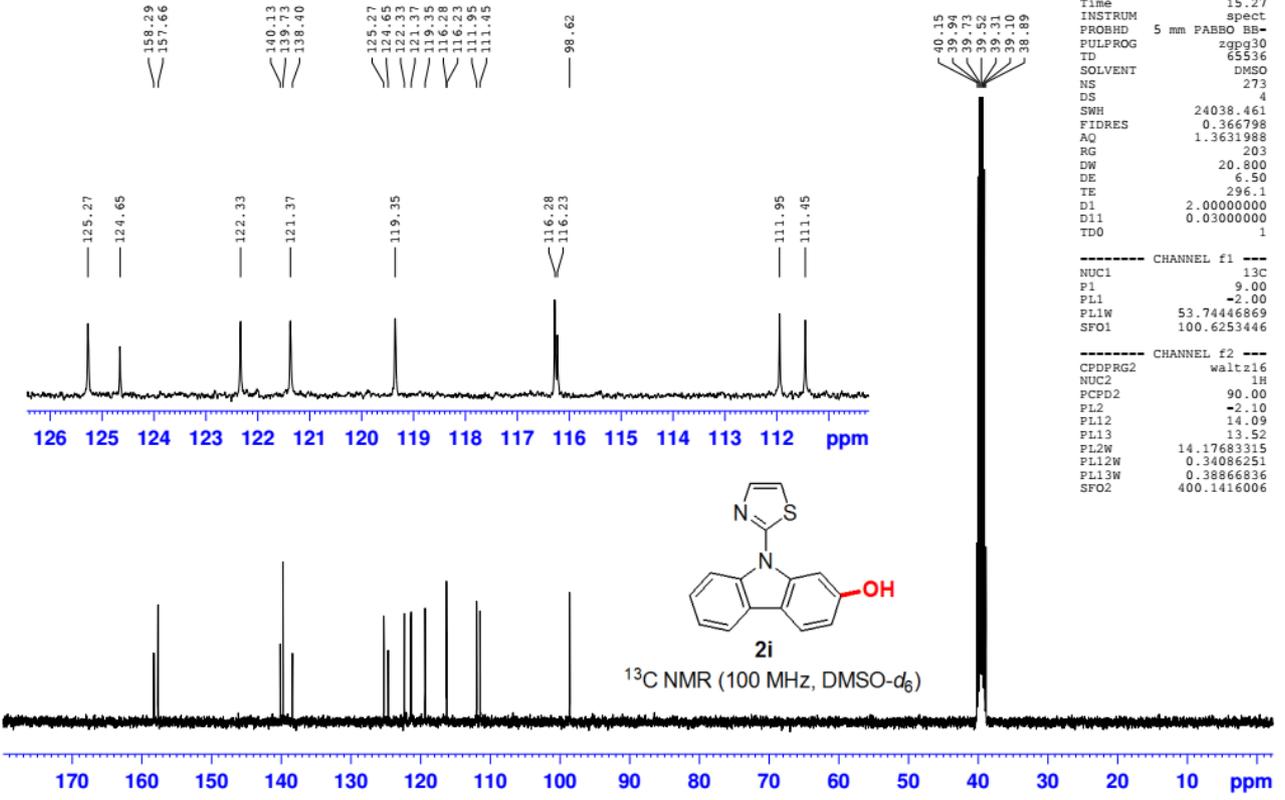
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        90.00
PL2           -2.10
PL12         14.09
PL13         13.52
PL2W         14.17683315
PL12W        0.34086251
PL13W        0.38866836
SF02          400.1416006
  
```



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₆ H ₁₁ N ₃ O	C ₁₆ H ₁₂ N ₃ O	262.0981	262.0975	-2.34



Z-7-27 DMSO

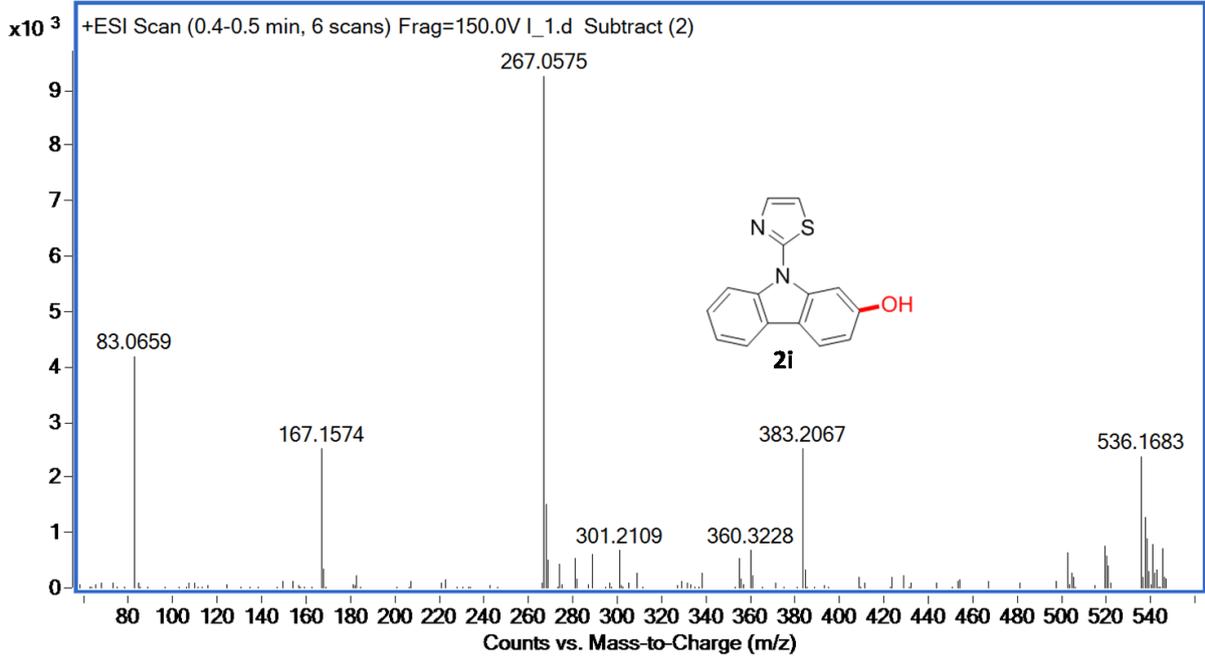


```

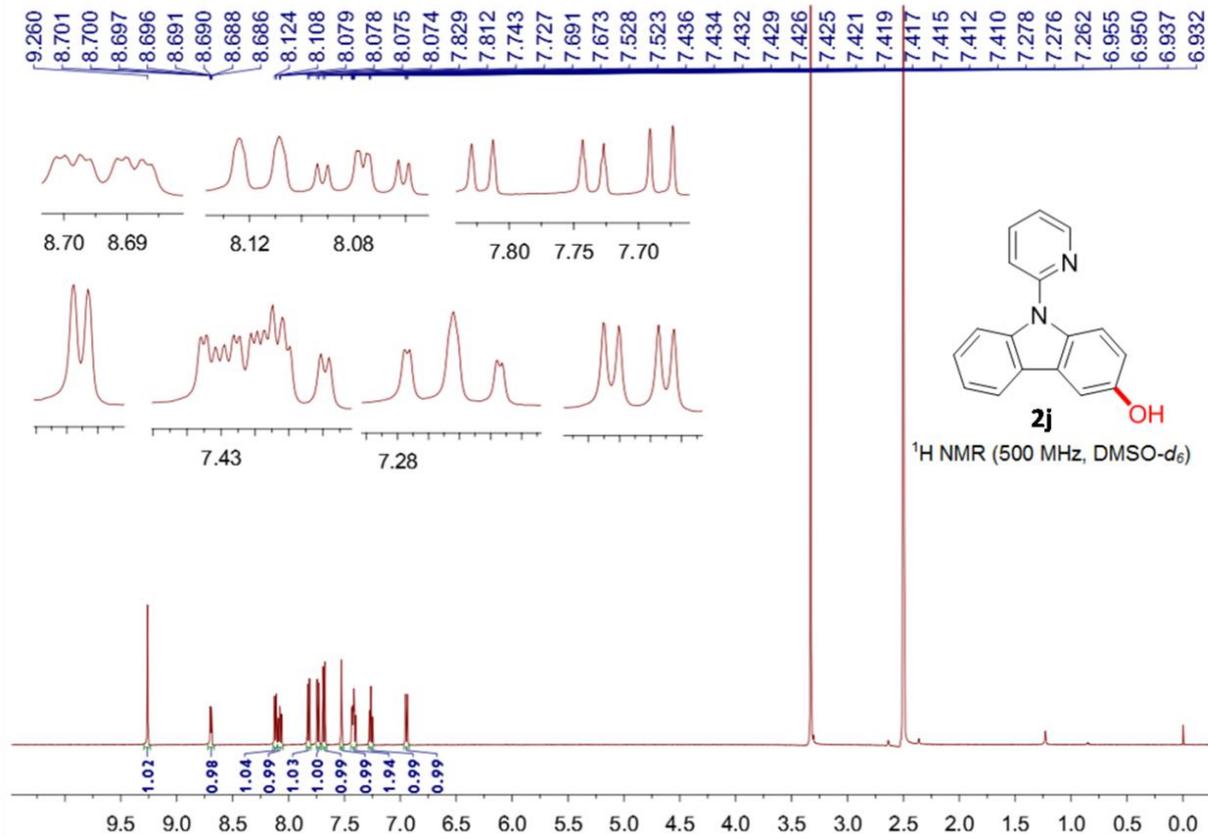
NAME          170221
EXPNO         31
PROCNO        1
Date_         20170221
Time          15.27
INSTRUM       spect
PROBHD        5 mm FAPBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            273
DS            4
SWH           24038.461
FIDRES        0.366798
AQ            1.3631988
RG            203
DW            20.800
DE            6.50
TE            296.1
D1            2.00000000
D11           0.03000000
TD0           1

----- CHANNEL f1 -----
NUC1          13C
P1            9.00
PL1          -2.00
PL1W         53.74446869
SFO1         100.6253446

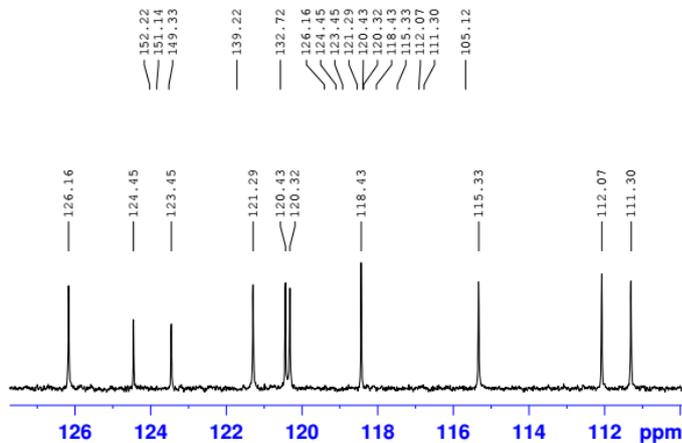
----- CHANNEL f2 -----
CPDPRG2      waltz16
NUC2          1H
PCPD2        90.00
PL2          -2.10
PL12         14.09
PL13         13.52
PL2W         14.17683315
PL12W        0.34086251
PL13W        0.38866836
SFO2         400.1416006
    
```



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₅ H ₁₀ N ₂ OS	C ₁₅ H ₁₁ N ₂ OS	267.0575	267.0587	4.36



Z-7-38 DMSO



40.15
39.94
39.73
39.52
39.31
39.10
38.89

```

NAME 170222
EXPNO 28
PROCNO 1
Date_ 20170222
Time 19.55
INSTRUM spect
PROBHD 5 PABBO BE-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 3200
DS 4
SWH 24038.461
FIDRES 0.366798
AQ 1.3631988
RG 203
DW 20.800
DE 6.50
TE 295.8
D1 2.00000000
D11 0.03000000
TDO 1

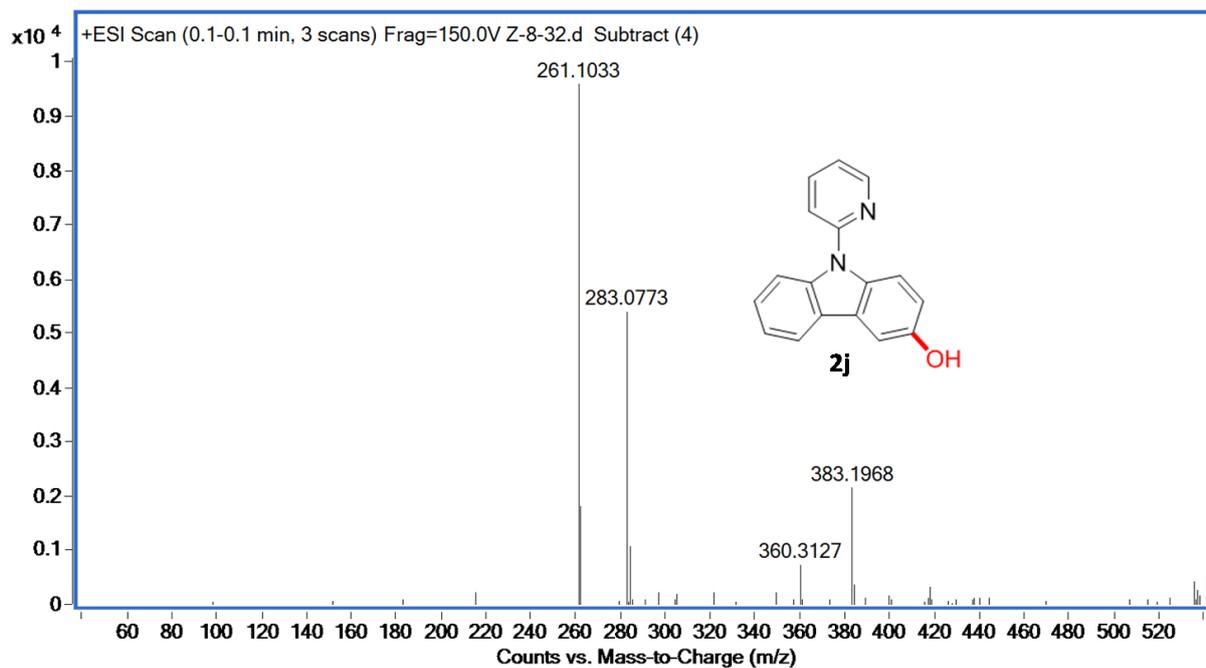
----- CHANNEL f1 -----
NUC1 13C
P1 9.00
PL1 -2.00
PL1W 53.74446869
SFO1 100.6253446

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00
PL2 -2.10
PL12 14.09
PL13 13.52
PL2W 14.17683315
PL12W 0.34086251
PL13W 0.38866836
SFO2 400.1416006

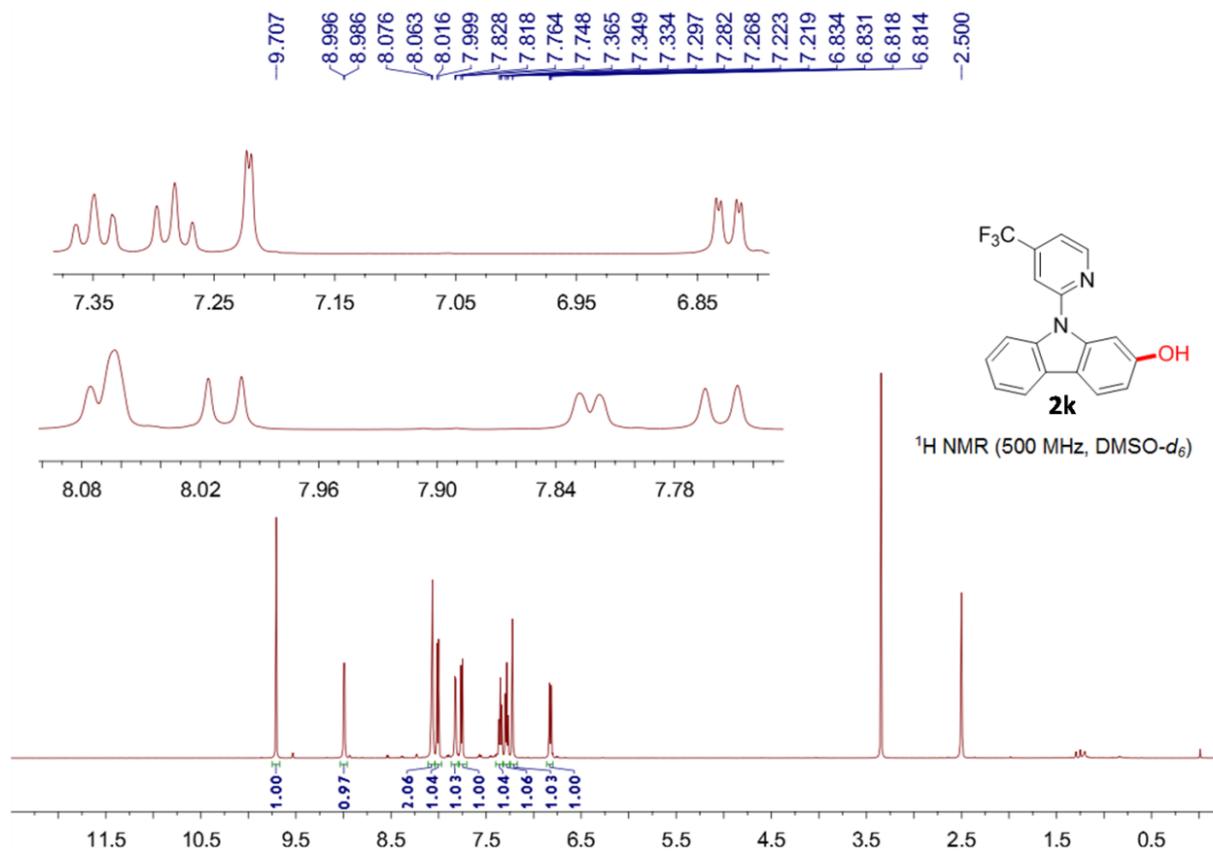
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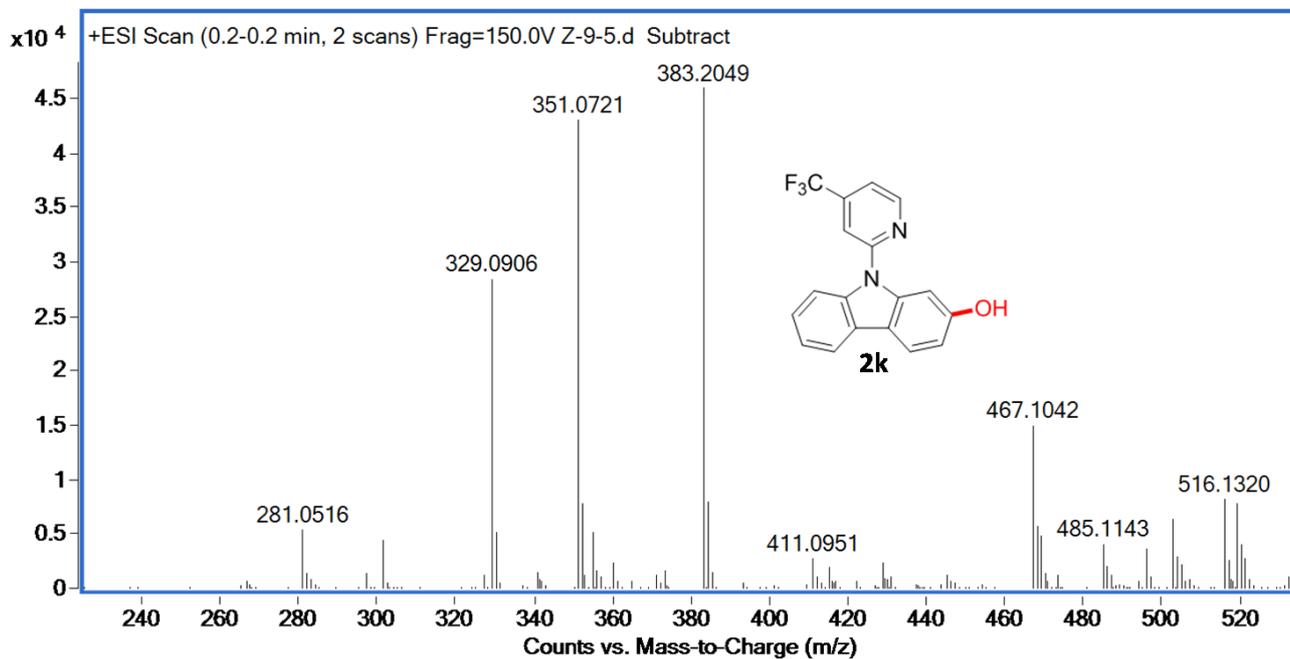
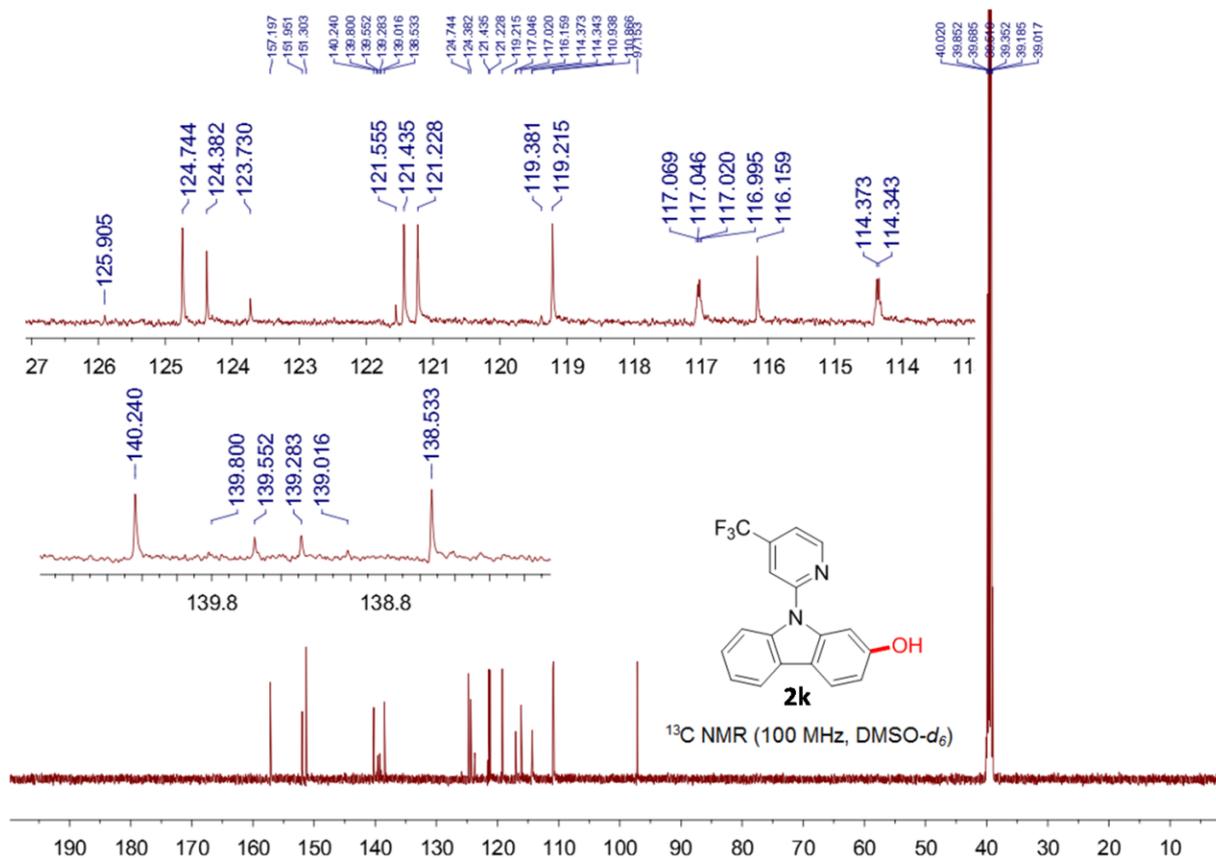
13C NMR (100 MHz, DMSO-*d*₆)

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

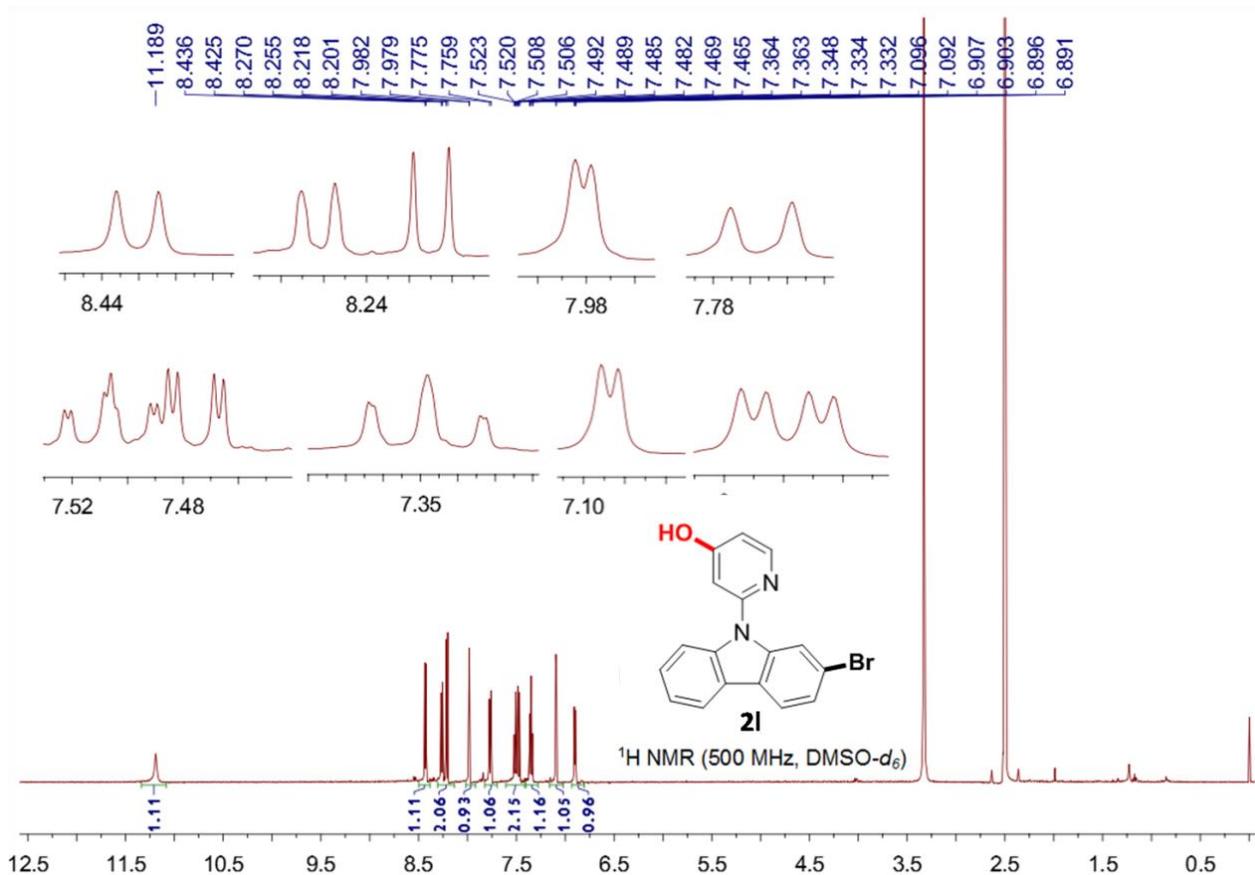


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₂ N ₂ O	C ₁₇ H ₁₂ N ₂ O	261.1033	261.1022	-4.08

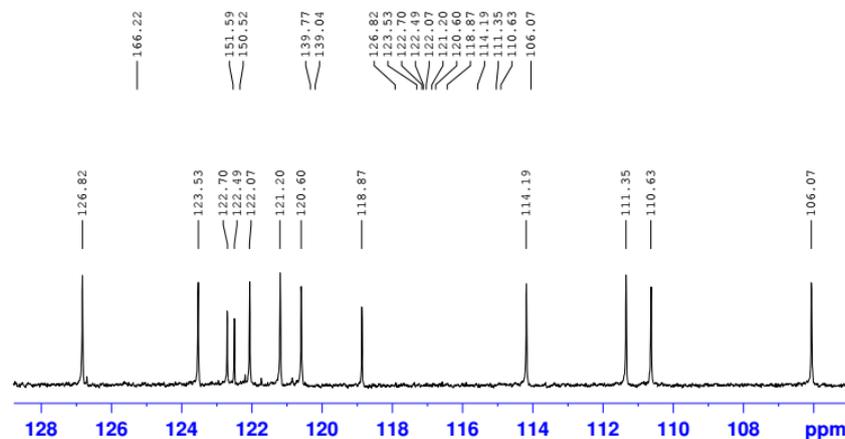




Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₈ H ₁₁ F ₃ N ₂ O	C ₁₈ H ₁₂ F ₃ N ₂ O	329.0	329.0896	-2.97



Z-7-21-P3 DMSO

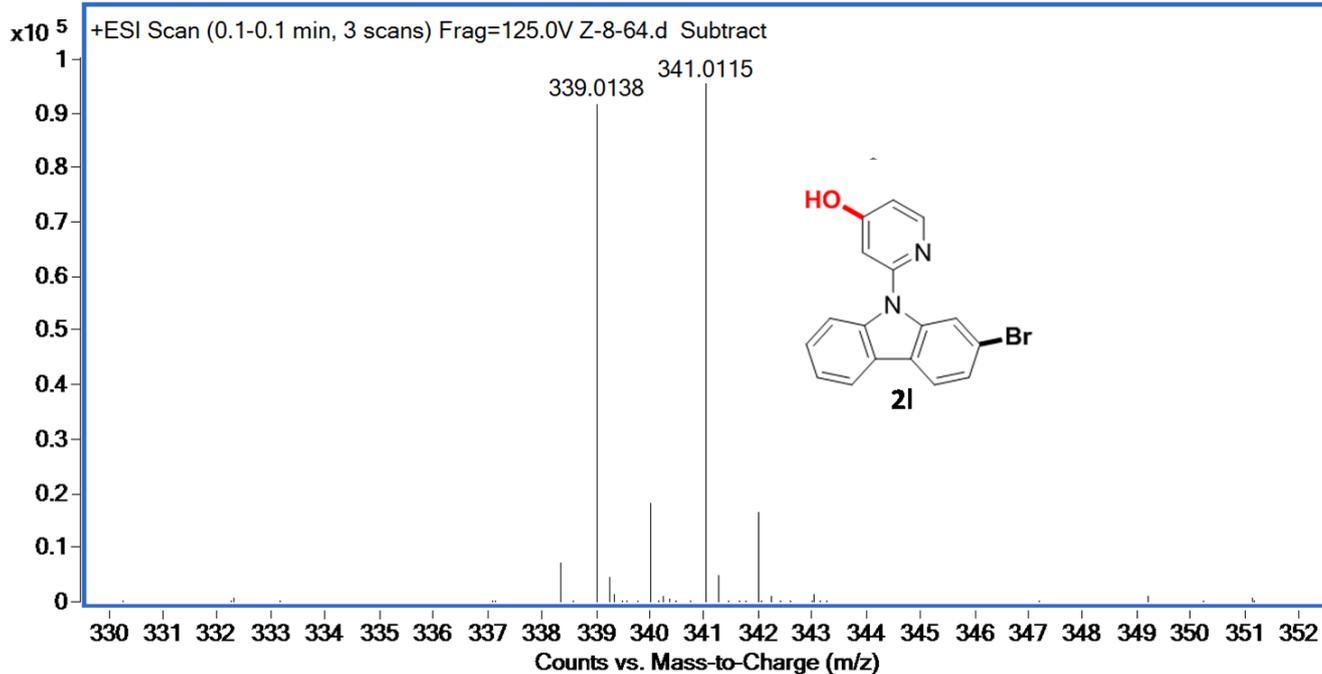


```

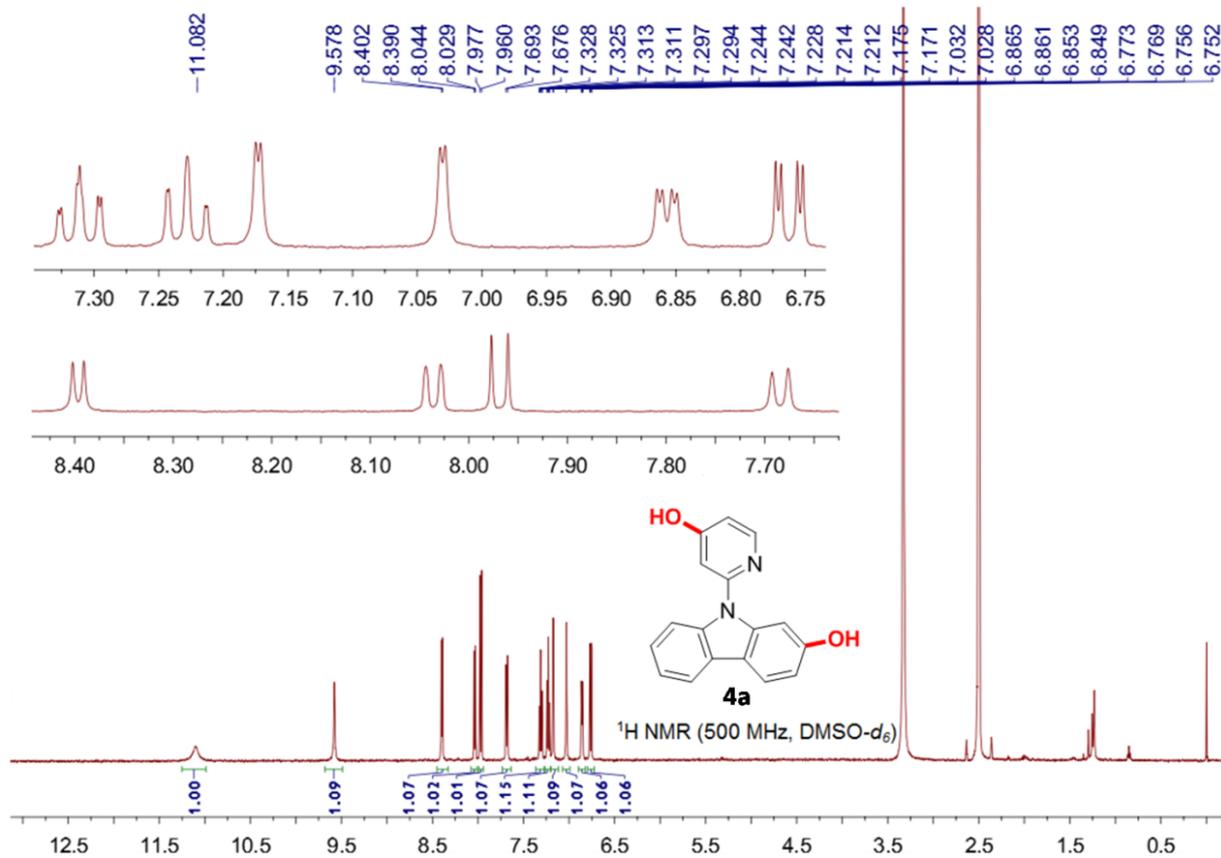
NAME          170221
EXPNO         43
PROCNO        1
Date_         20170222
Time          0.35
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            8000
DS            4
SWH           24038.461
FIDRES        0.366798
AQ            1.3631988
RG            203
DW            20.800
DE            6.50
TE            298.2
D1            2.0000000
D11           0.0300000
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.00
PL1          -2.00
PL1W         53.74446869
SFO1         100.6253446

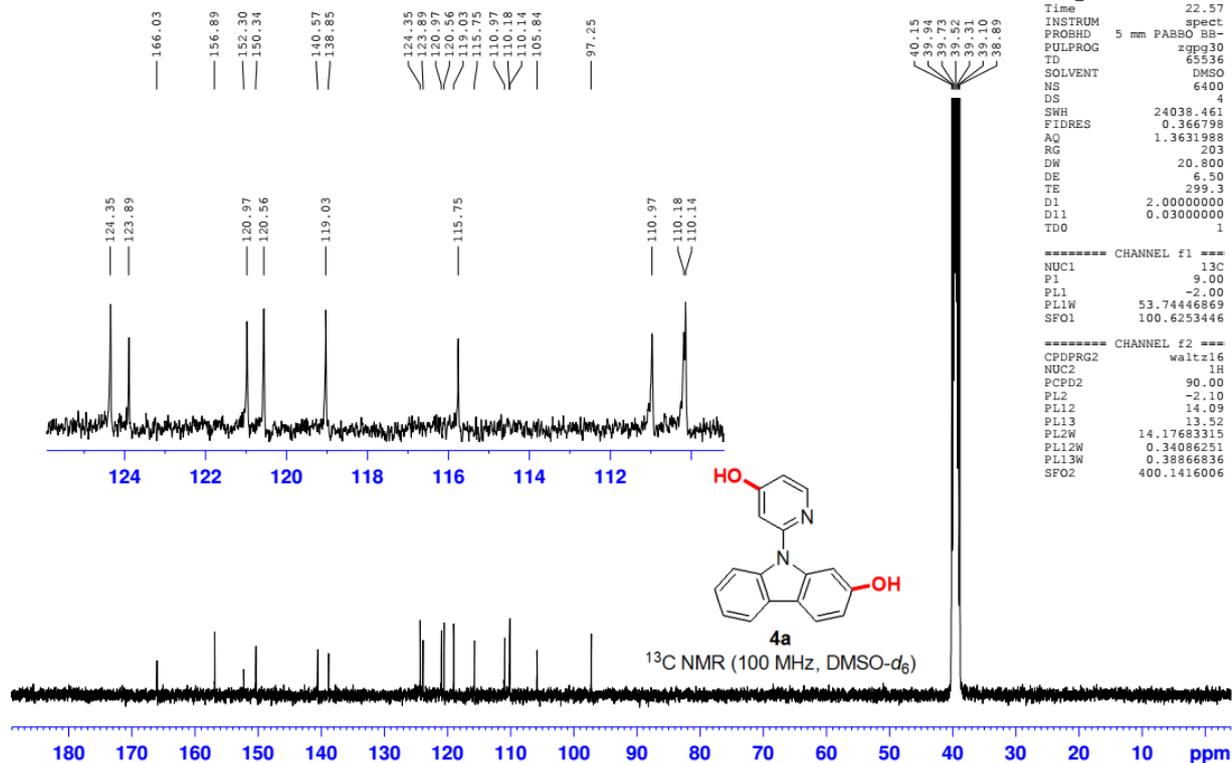
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        90.00
PL2          -2.10
PL12         14.09
PL13         13.52
PL2W         14.17683315
PL12W        0.34086251
PL13W        0.38866836
SFO2         400.1416006
  
```



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₁ BrN ₂ O	C ₁₇ H ₁₂ BrN ₂ O	339.0138	339.0128	-3.1



Z-9-3 (4-2OH) DMSO

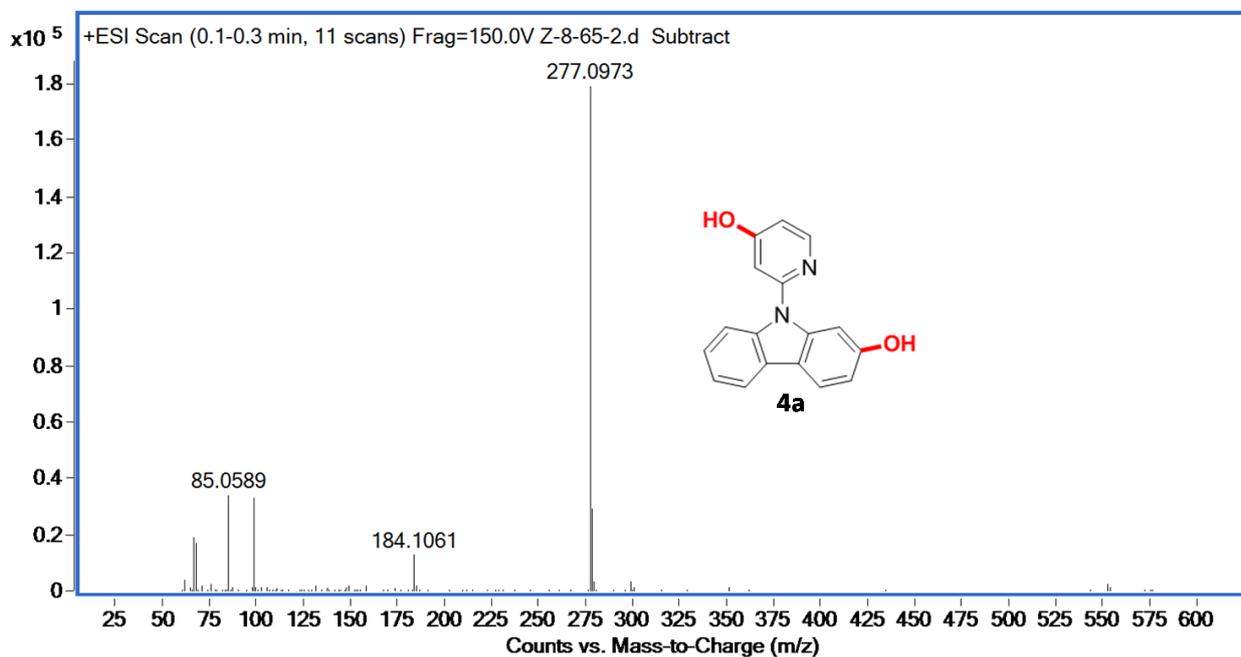


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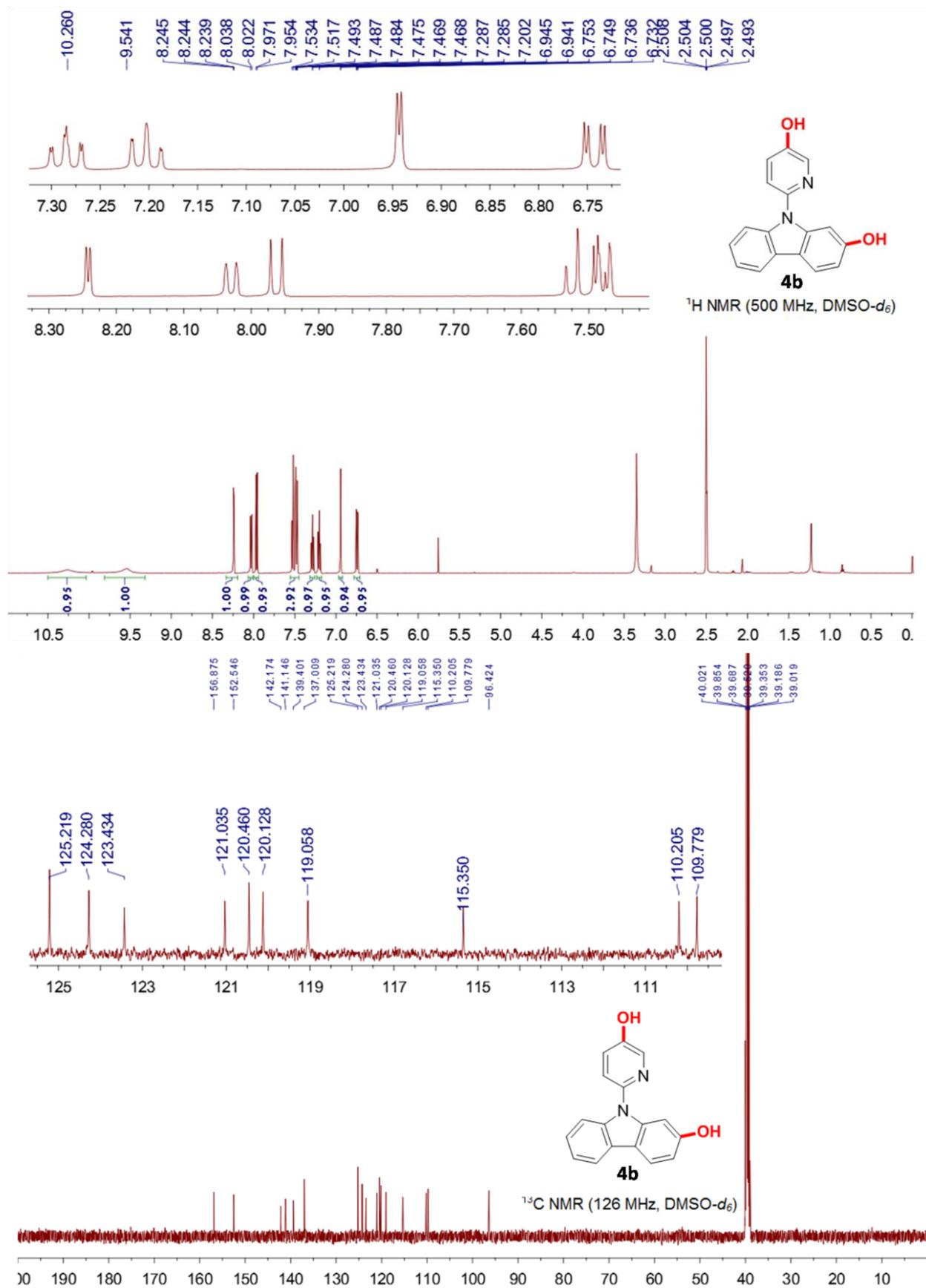
NAME          170510
EXPNO         44
PROCNO        1
Date_         20170510
Time          22.57
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            6400
DS            4
SWH           24038.461
FIDRES        0.366798
AQ            1.3631988
RG            203
DW            20.800
DE            6.50
TE            299.3
D1            2.00000000
D11           0.03000000
TD0           1

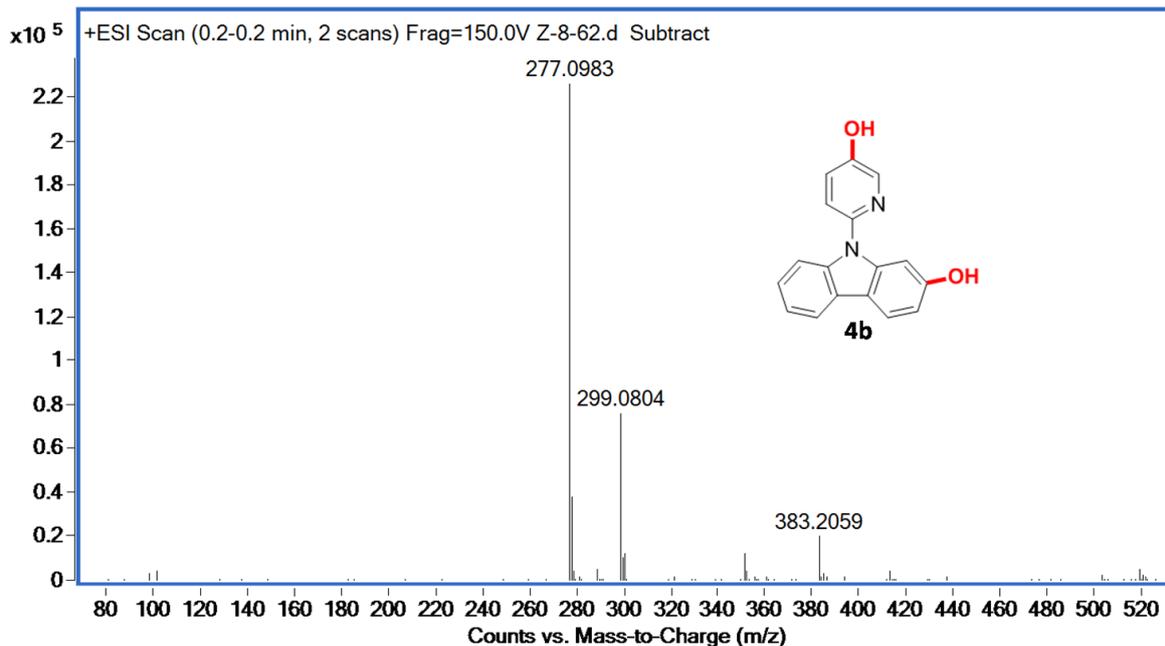
===== CHANNEL f1 =====
NUC1          13C
P1            9.00
PL1          -2.00
PL1W         53.74446669
SFO1         100.6253446

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         90.00
PL2           -2.10
PL12         14.09
PL13         13.52
PL2W         14.17683315
PL12W        0.34086251
PL13W        0.38866836
SFO2         400.1416006
    
```

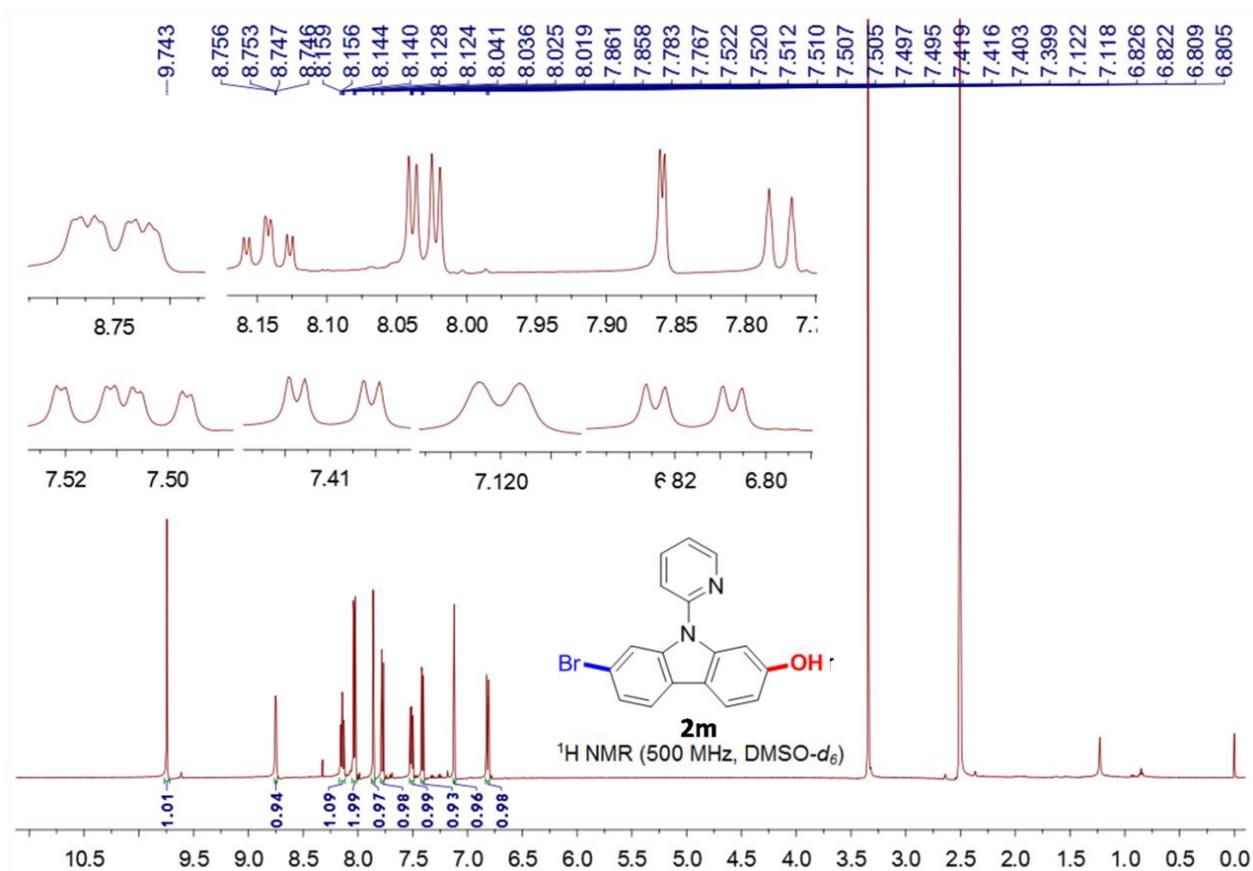


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₂ N ₂ O ₂	C ₁₇ H ₁₃ N ₂ O ₂	277.0973	277.0972	-0.53

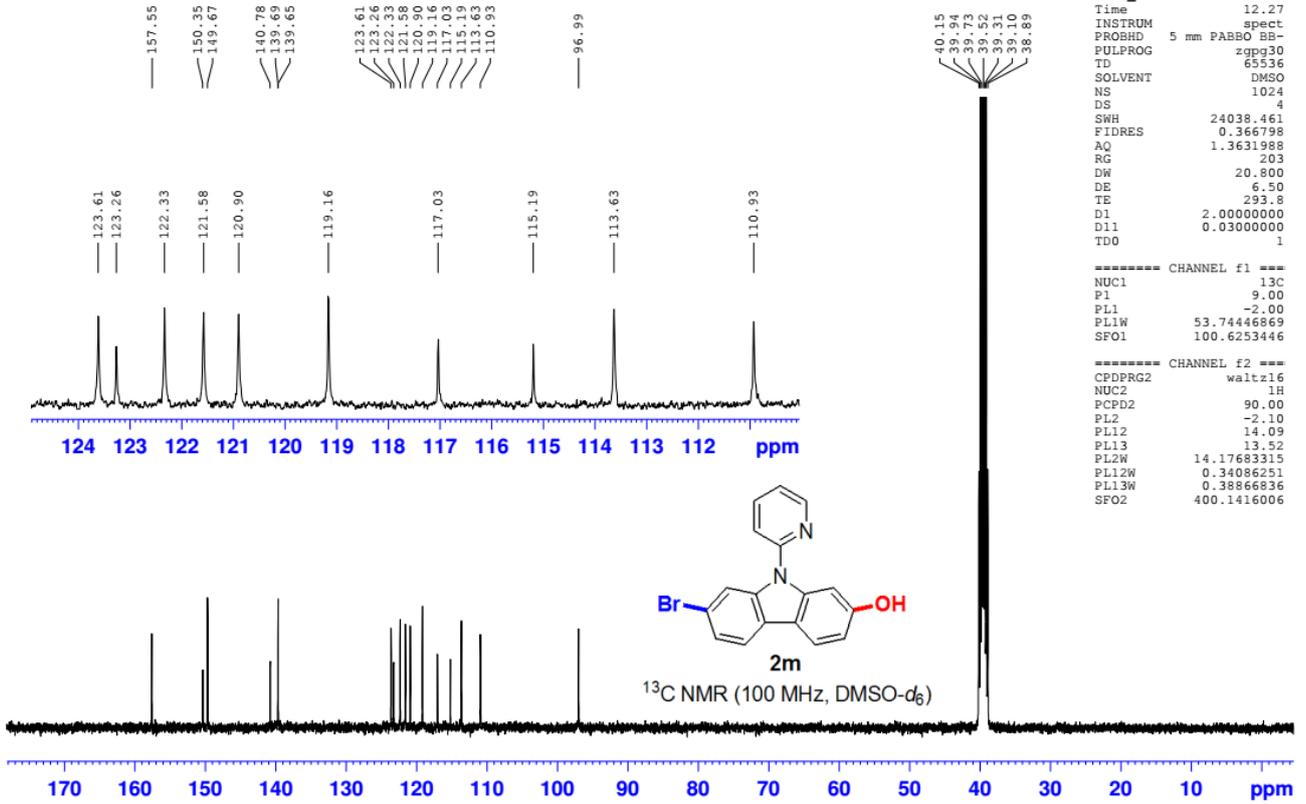




Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₇ H ₁₂ N ₂ O ₂	C ₁₇ H ₁₃ N ₂ O ₂	277.0983	277.0972	-4.15



Z-7-29 DMSO

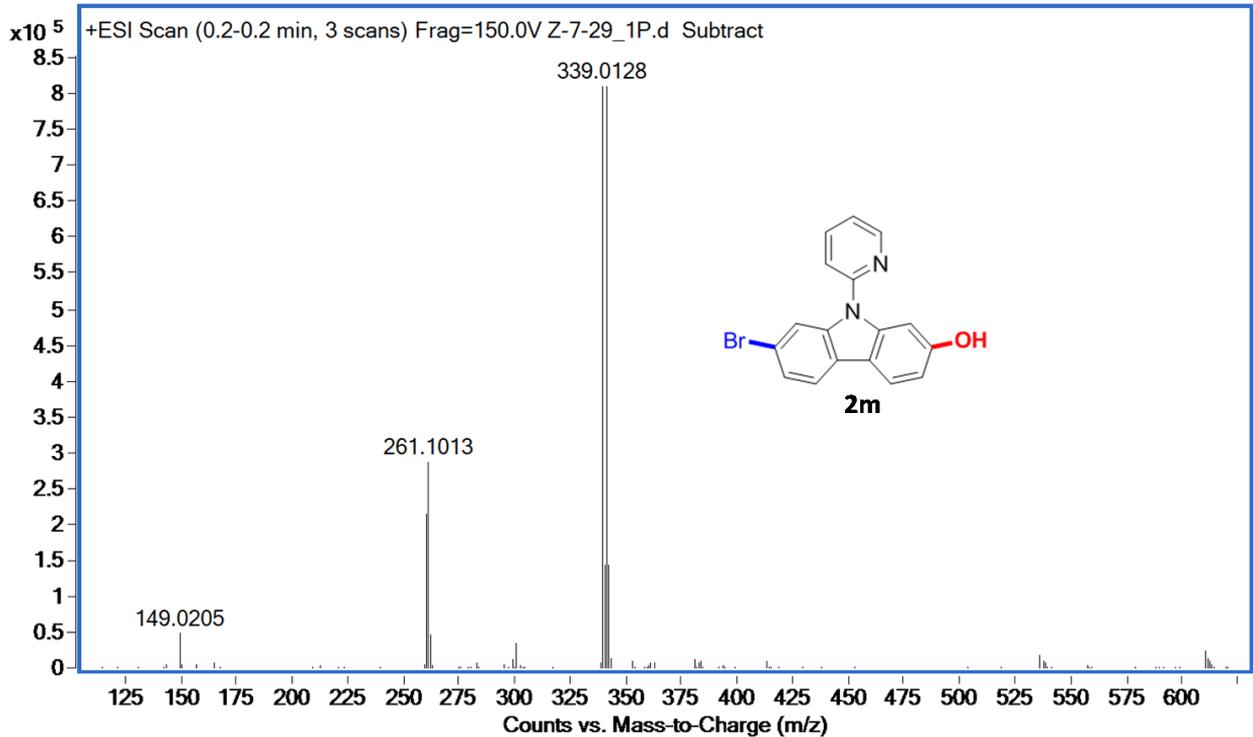


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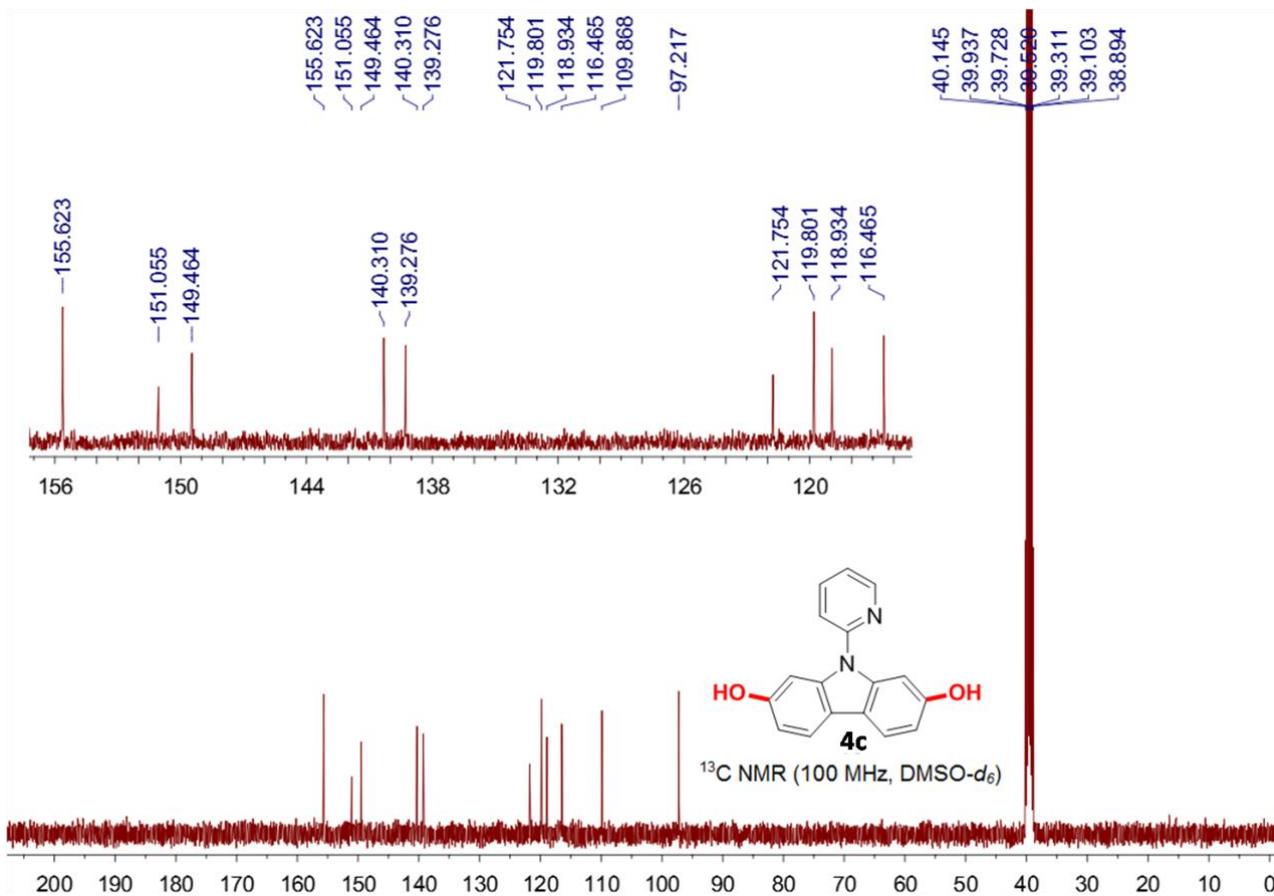
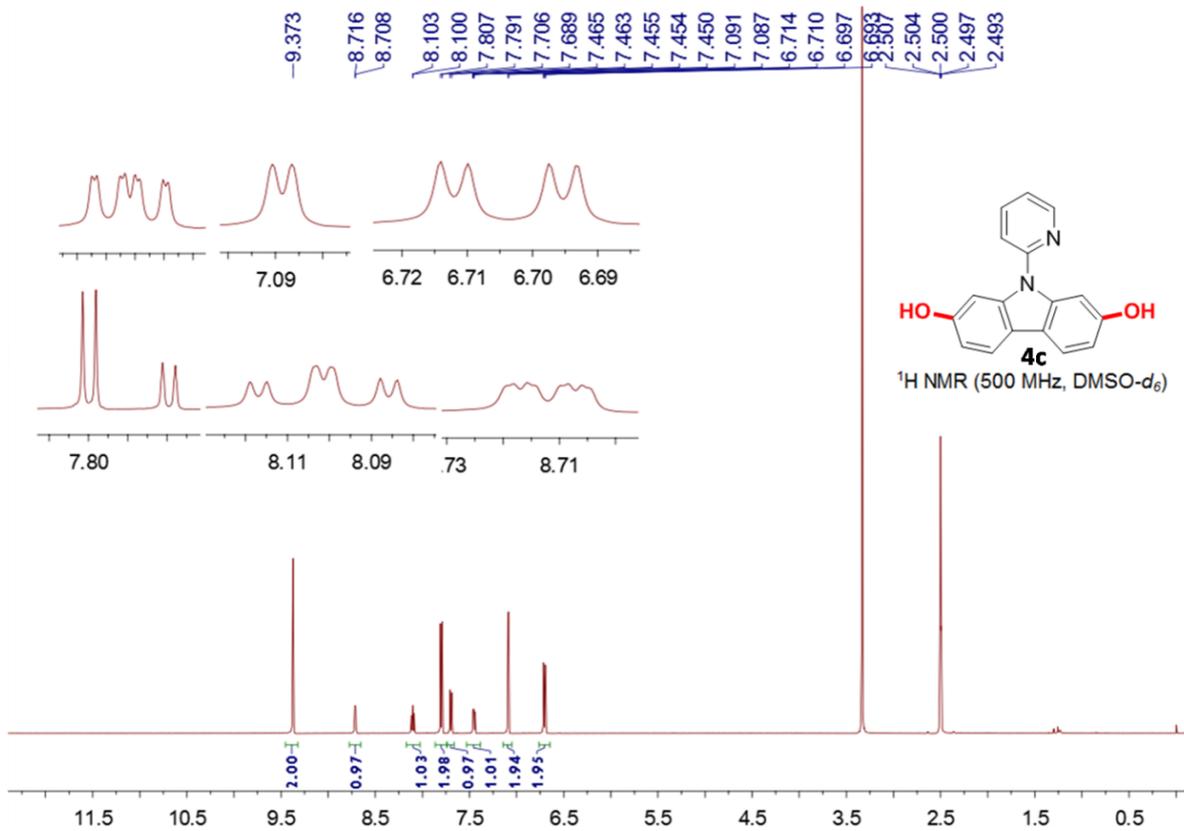
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PROCNO        1
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TD            65536
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NS            1024
DS            4
SWH           24038.461
FIDRES       0.366798
AQ           1.3631988
RG            203
DW           20.800
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TE           293.8
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TD0           1

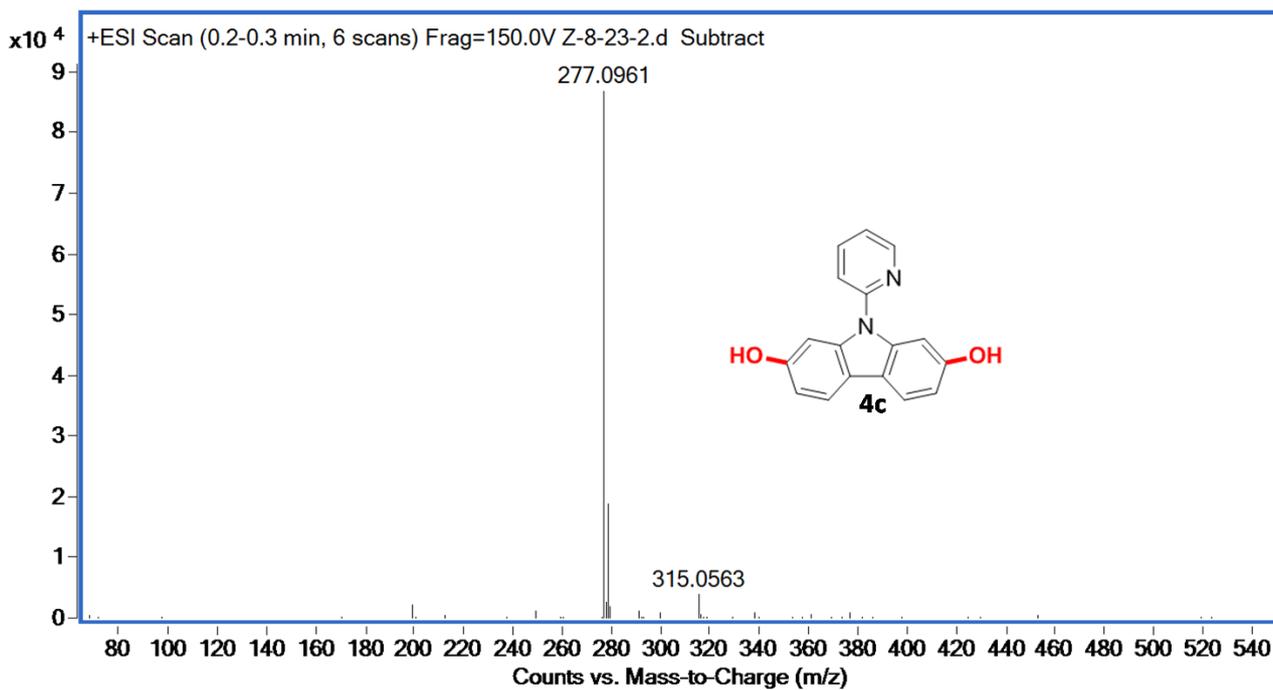
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P1            9.00
PL1          -2.00
PL1W         53.74446869
SFO1         100.6253446

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         90.00
PL2          -2.10
PL12         14.09
PL13         13.52
PL12W        14.17683315
PL12W        0.34086251
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SFO2         400.1416006
    
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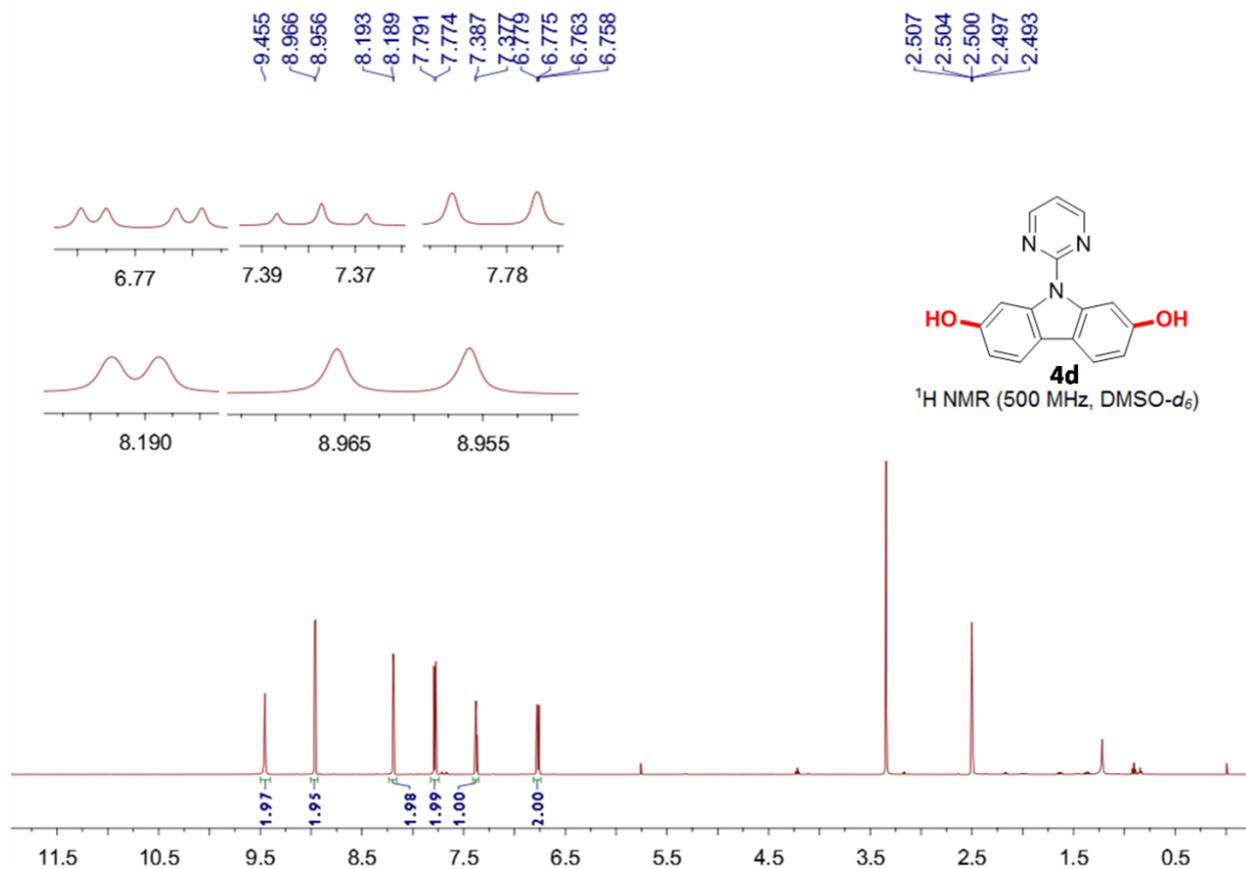


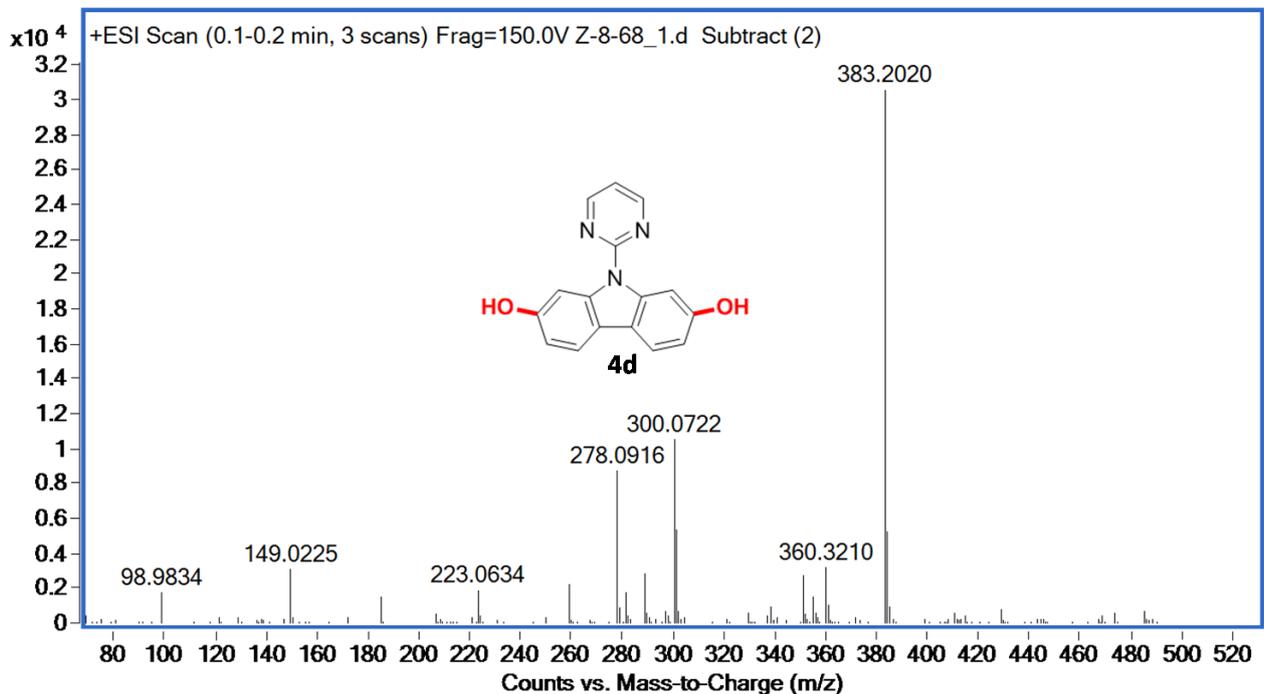
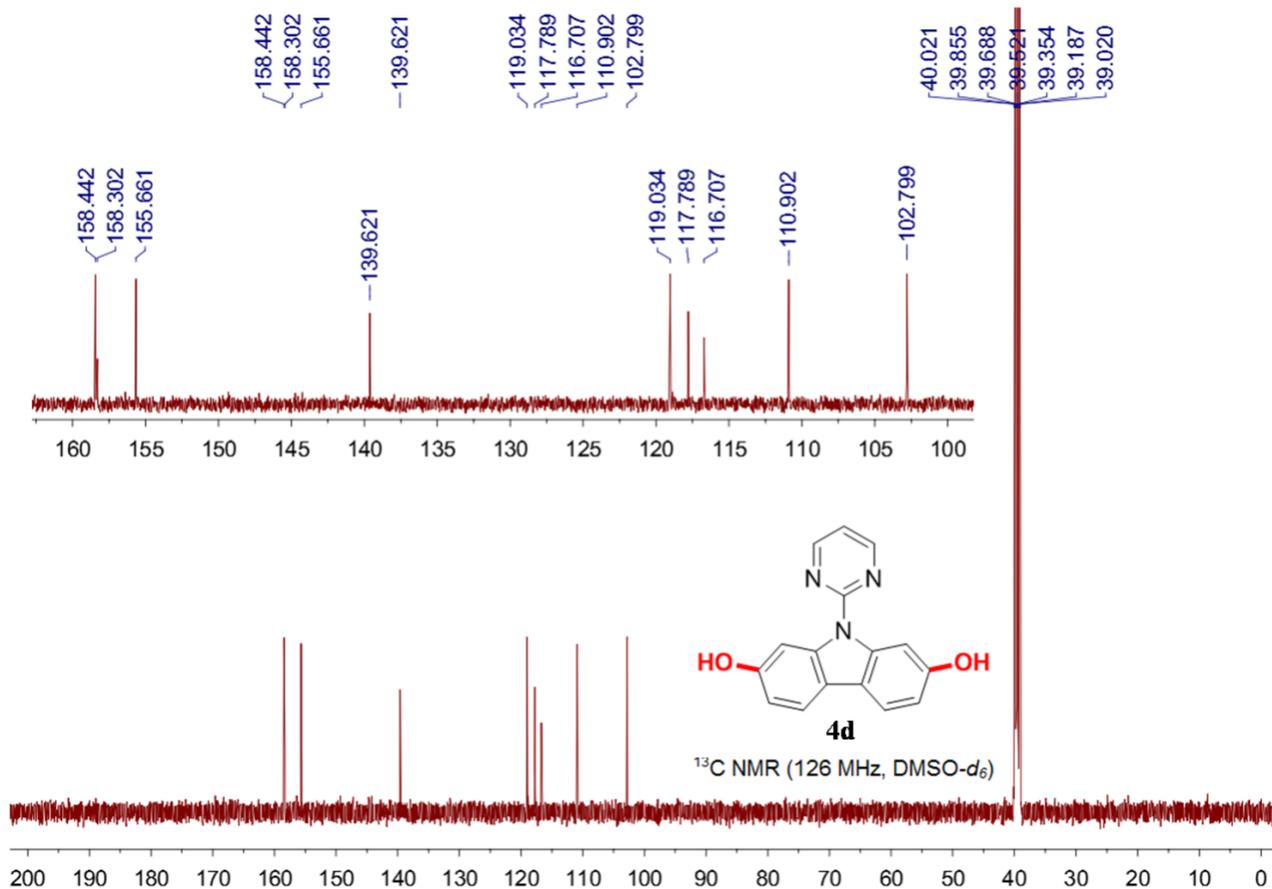
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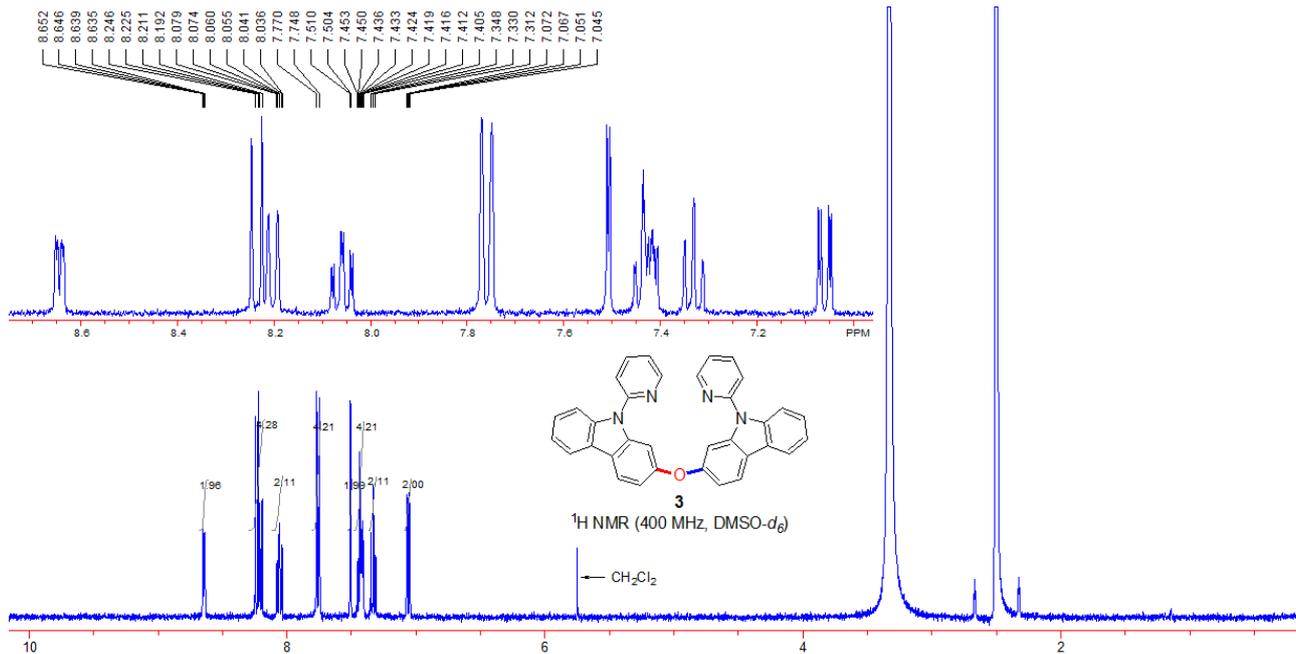


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
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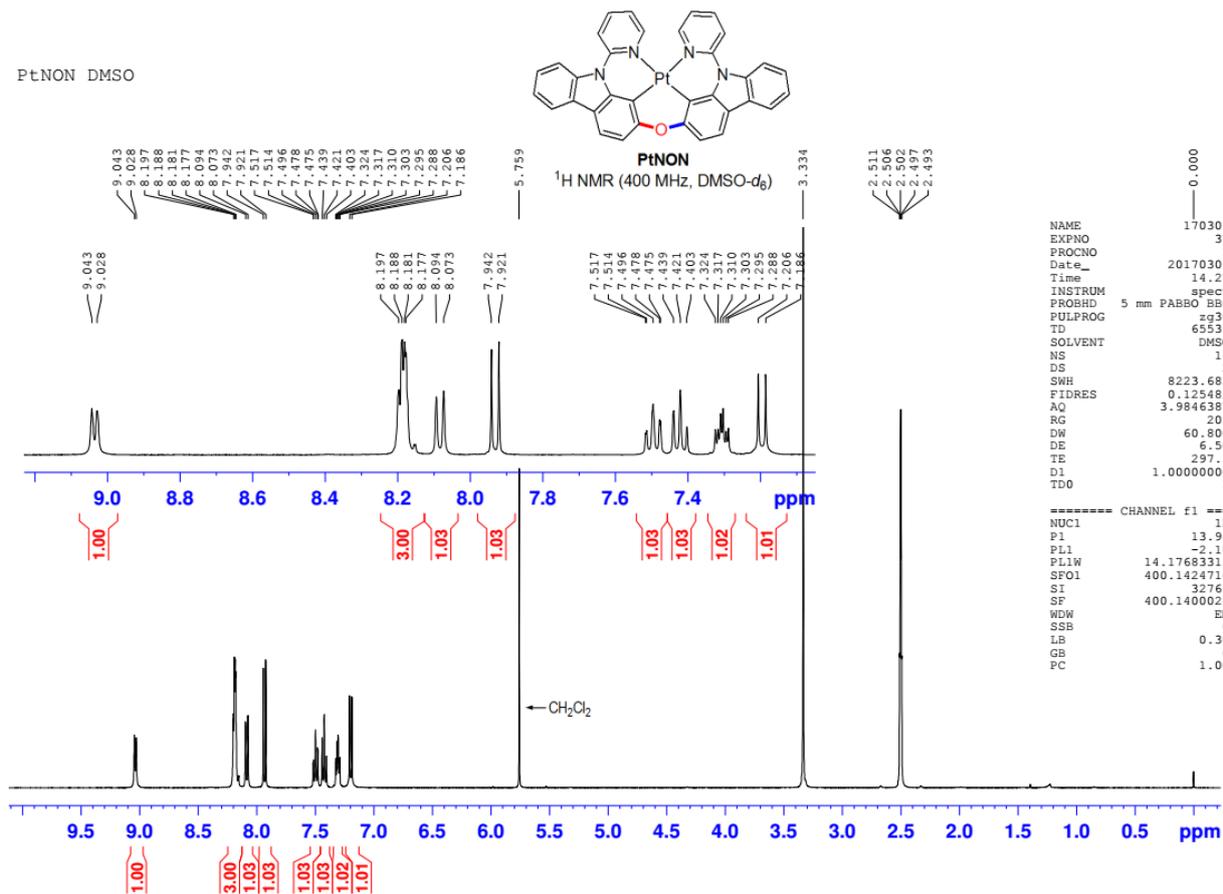




Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C ₁₆ H ₁₁ N ₃ O ₂	C ₁₆ H ₁₂ N ₃ O ₂	278.0916	278.0924	2.9



PtNON DMSO



PtNON DMSO

151.95
151.27
147.72
142.21
139.70
137.43

127.70
124.18
122.70
120.33
119.64
116.41
115.86
115.23
114.73
111.73

93.93

54.83

40.14
39.94
39.73
39.52
39.31
39.10
38.89

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Time_ 1.07
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FIDRES 0.366798
AQ 1.3631988
RG 203
DW 20.800
DE 6.50
TE 300.2
D1 2.0000000
D11 0.03000000
TD0 1

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PL1 -2.00
PL1W 53.74446869
SFO1 100.6253446

==== CHANNEL f2 ===
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NUC2 1H
PCPD2 90.00
PL2 -2.10
PL12 14.09
PL13 13.52
PL2W 14.17683315
PL12W 0.34086251
PL13W 0.38866836
SFO2 400.1416006



PdNON DMSO

150.97
150.90
148.54
142.94
140.40
137.47
127.60
124.30
122.54
120.18
119.63
116.98
116.38
116.08
113.98
111.72
107.79

54.84

40.15
39.94
39.73
39.52
39.31
39.10
38.90

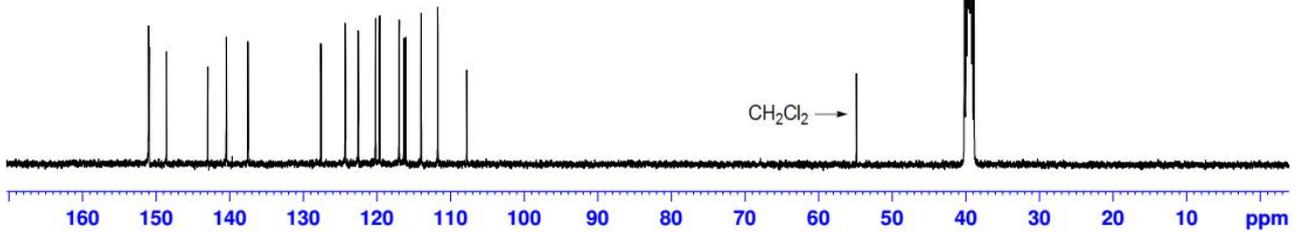


¹³C NMR (100 MHz, DMSO-d₆)

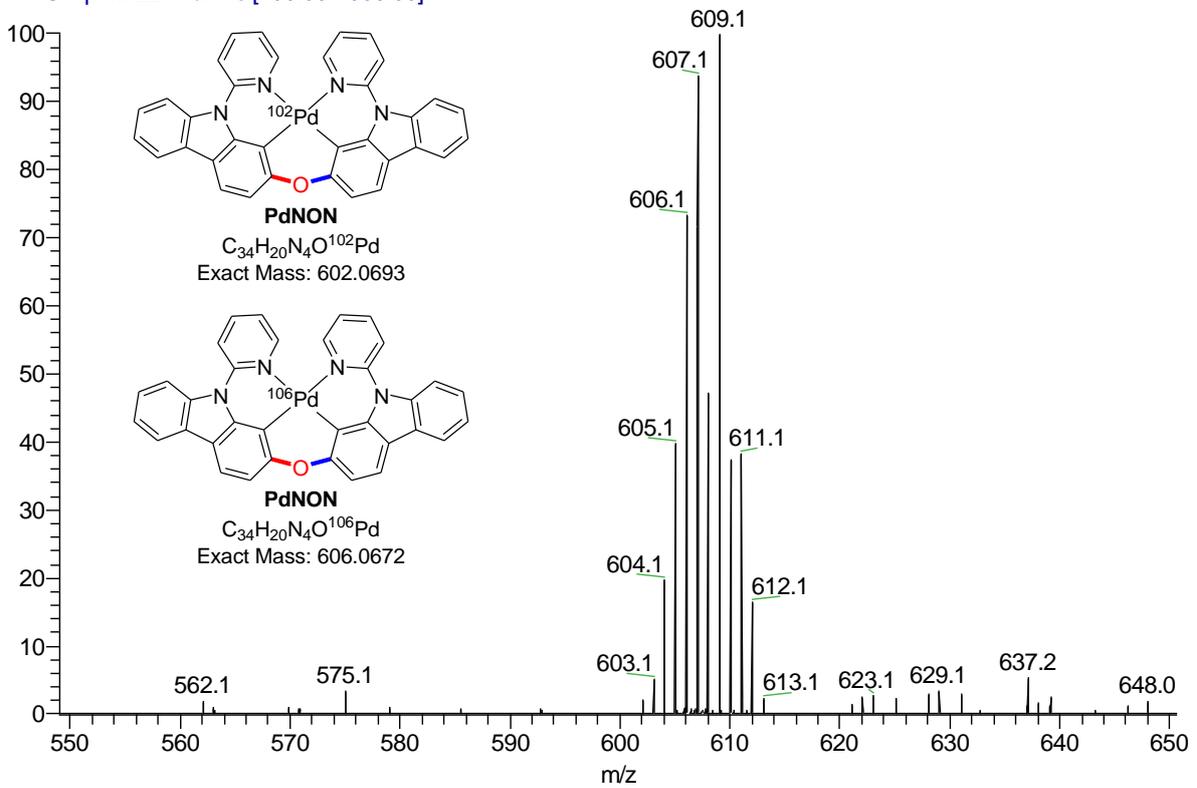
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FIDRES 0.366798
AQ 1.3631988
RG 203
DW 20.800
DE 6.50
TE 299.7
D1 2.0000000
D11 0.0300000
TDO 1

===== CHANNEL f1 ===
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P1 9.00
PL1 -2.00
PL1W 53.74446869
SFO1 100.6253446

===== CHANNEL f2 ===
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NUC2 1H
PCPD2 90.00
PL2 -2.10
PL12 14.09
PL13 13.52
PL2W 14.17683315
PL12W 0.34086251
PL13W 0.38866836
SFO2 400.1416006



M170425 #5 RT: 0.2887 AV: 1 NL: 7.81E3
T: FTMS + p MALDI Full ms [100.00-1000.00]



S70

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

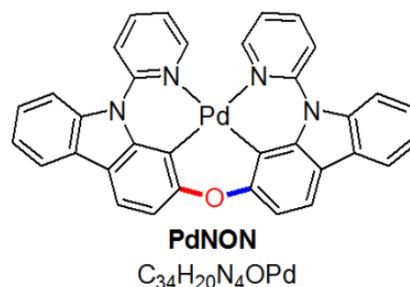
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M170426

Sample Serial Number: PdNON

Operator : HUAQIN Date: 2017/03/10

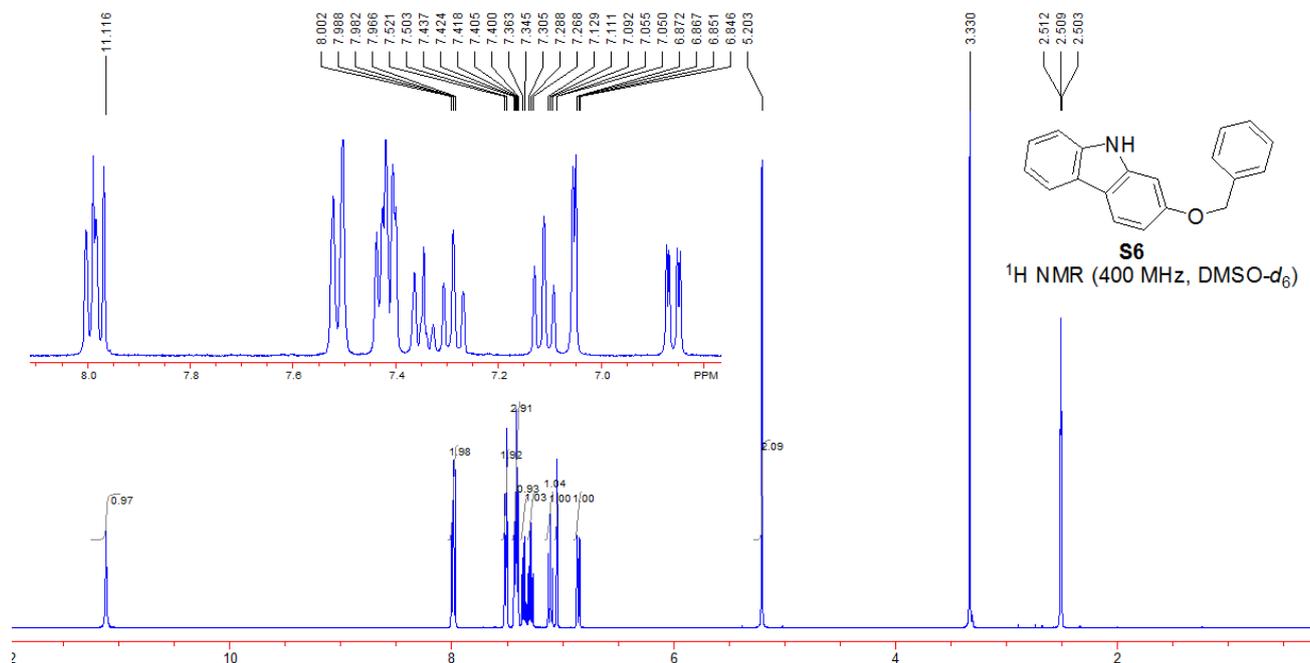
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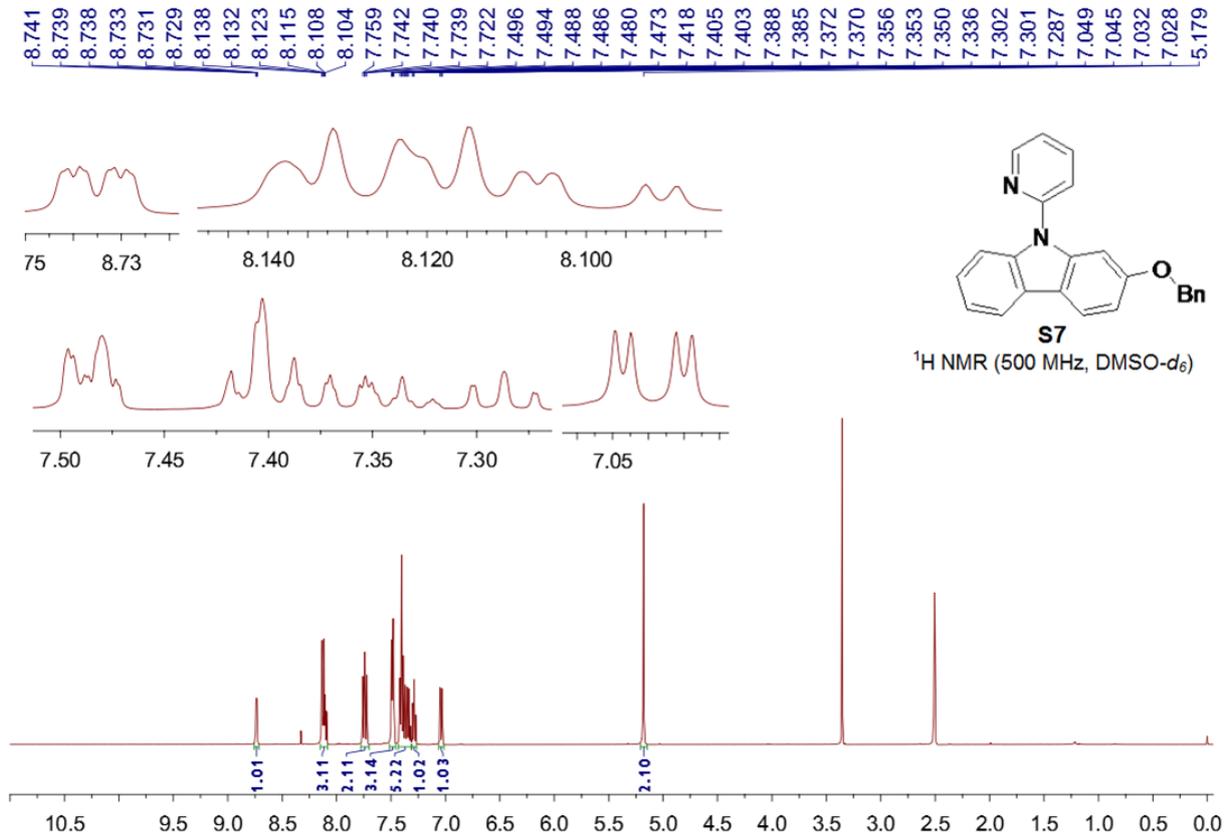


Elemental composition search on mass 603.08

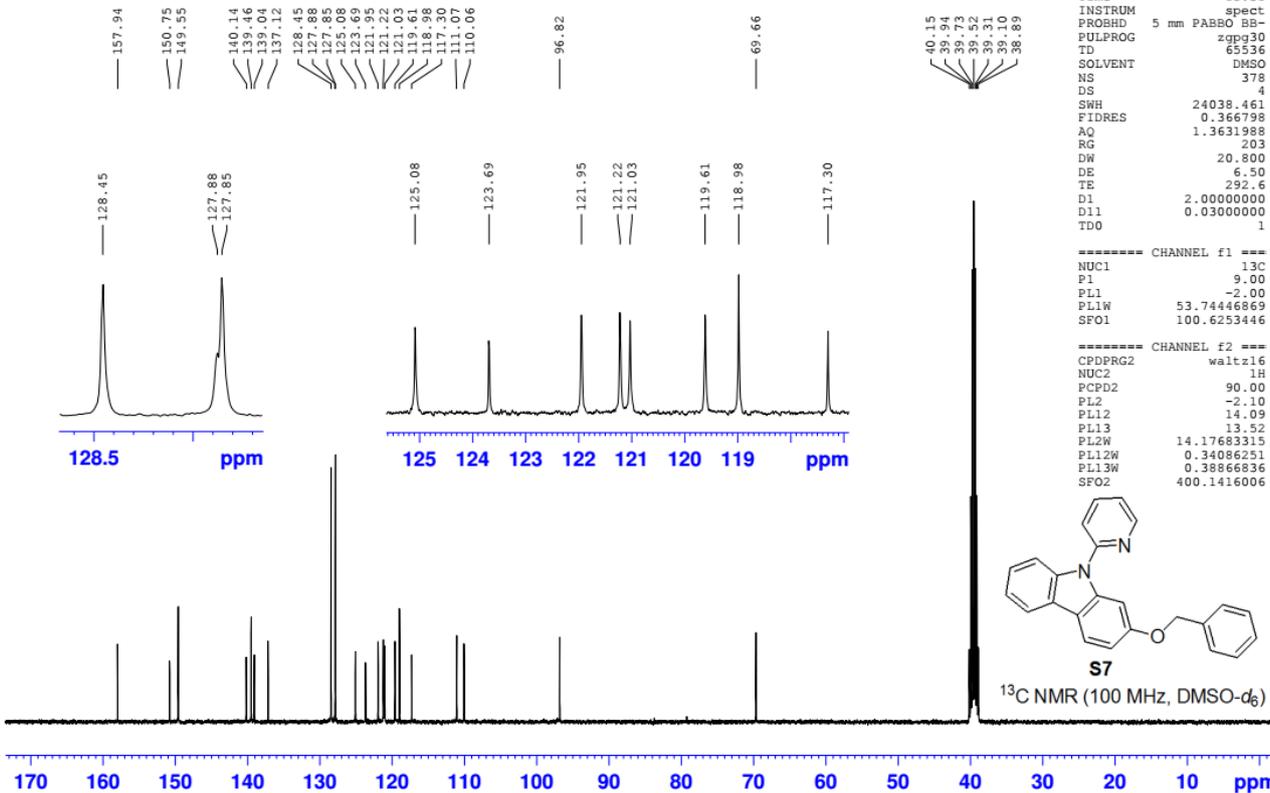
m/z= 598.08–608.08

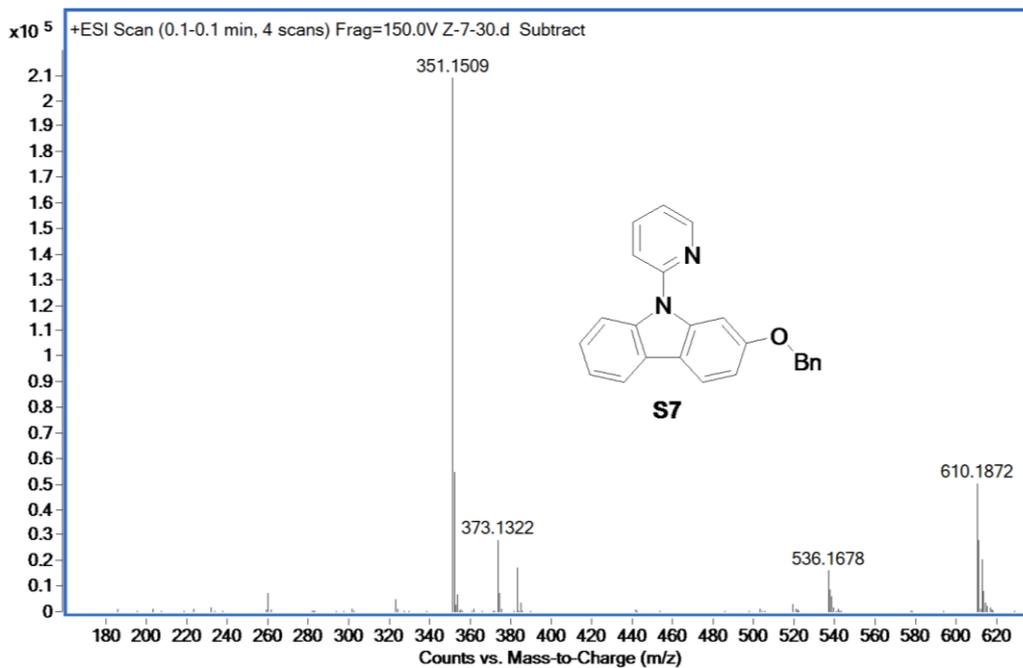
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
603.0763	603.0766	-0.52	26.5	C ₃₄ H ₂₁ O N ₄ ¹⁰² Pd
	603.0753	1.69	21.5	C ₃₃ H ₂₅ O ₅ ¹⁰² Pd
	603.0779	-2.75	26.0	C ₃₆ H ₂₃ O ₂ N ¹⁰² Pd
	603.0739	3.92	22.0	C ₃₁ H ₂₃ O ₄ N ₃ ¹⁰² Pd



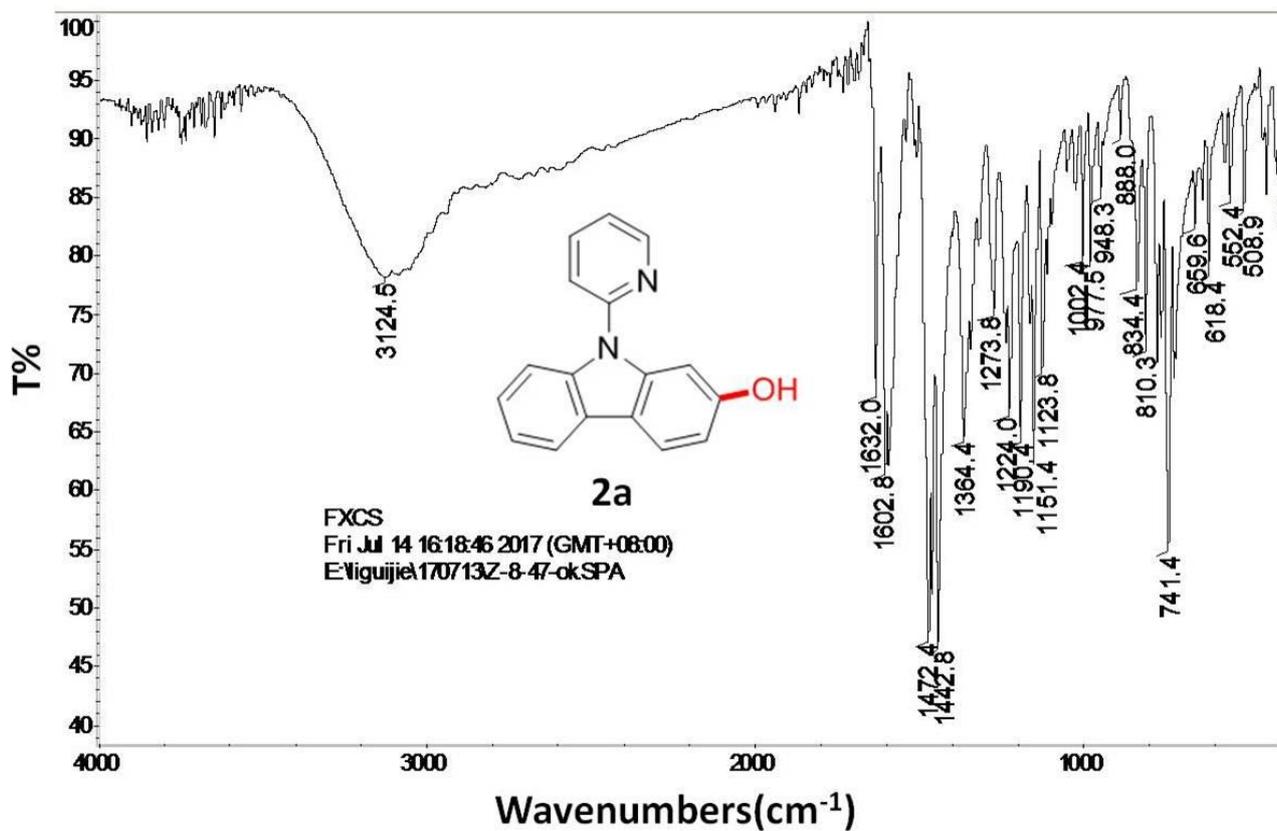


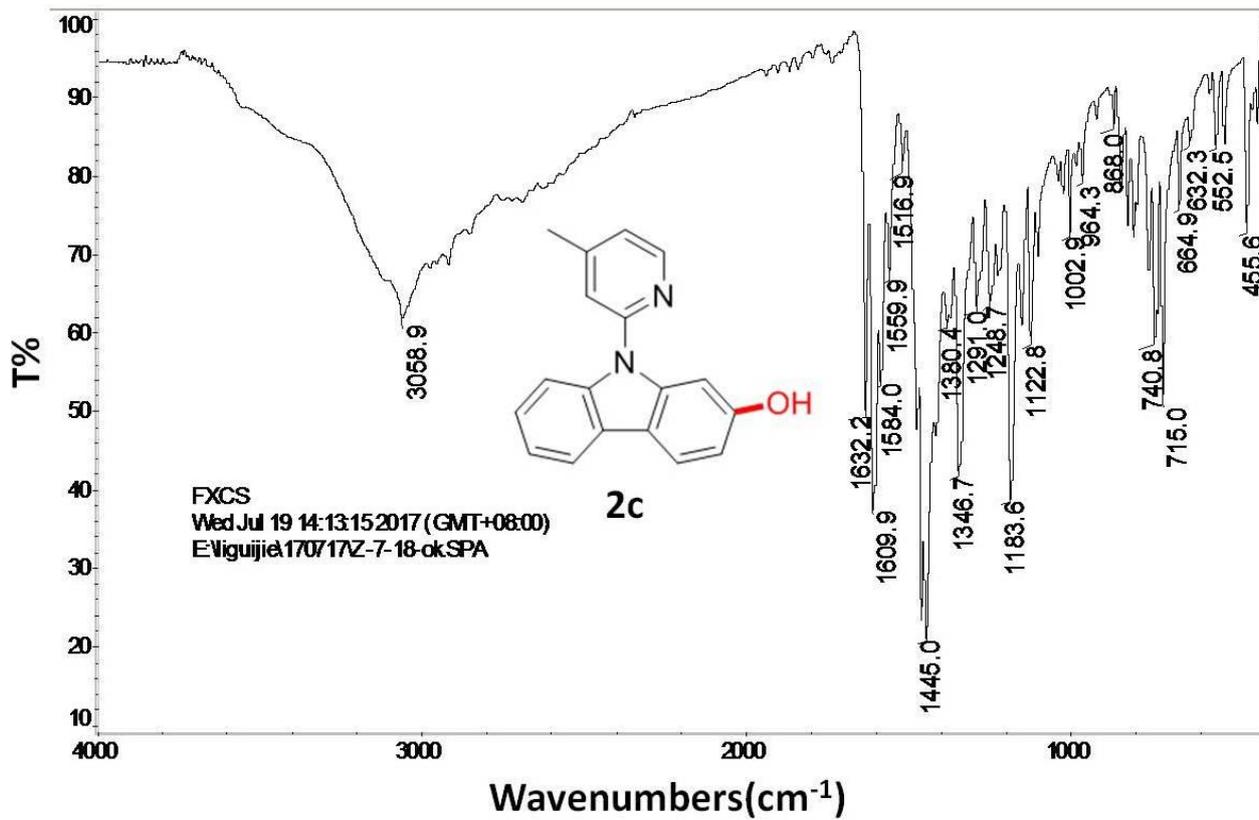
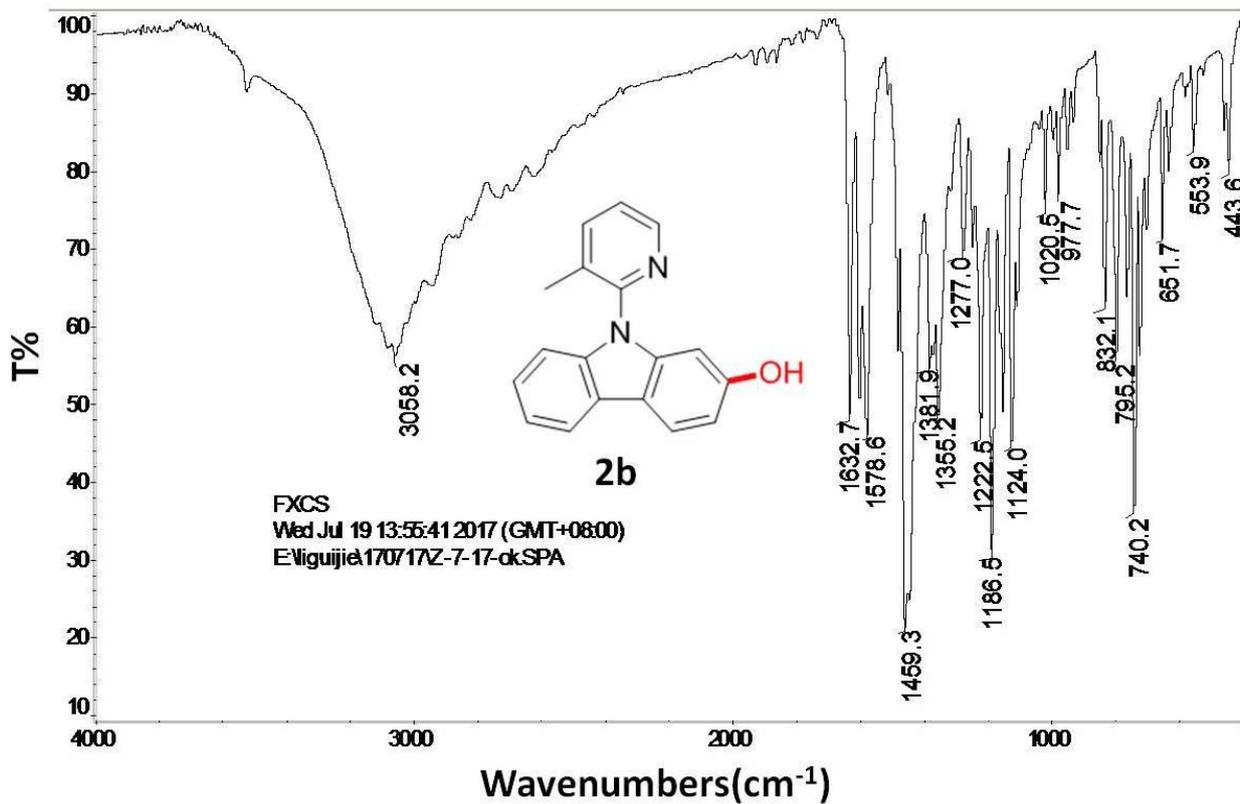
Z-7-30 DMSO

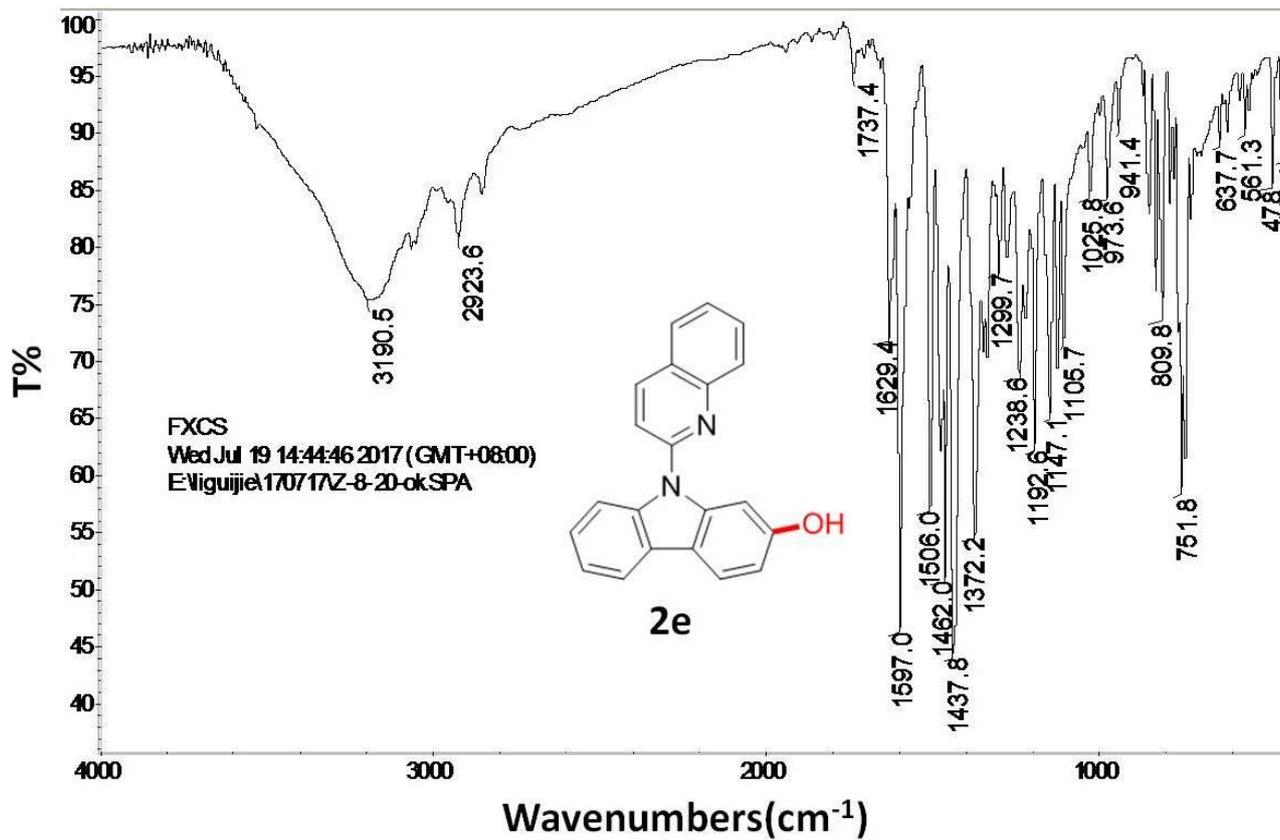
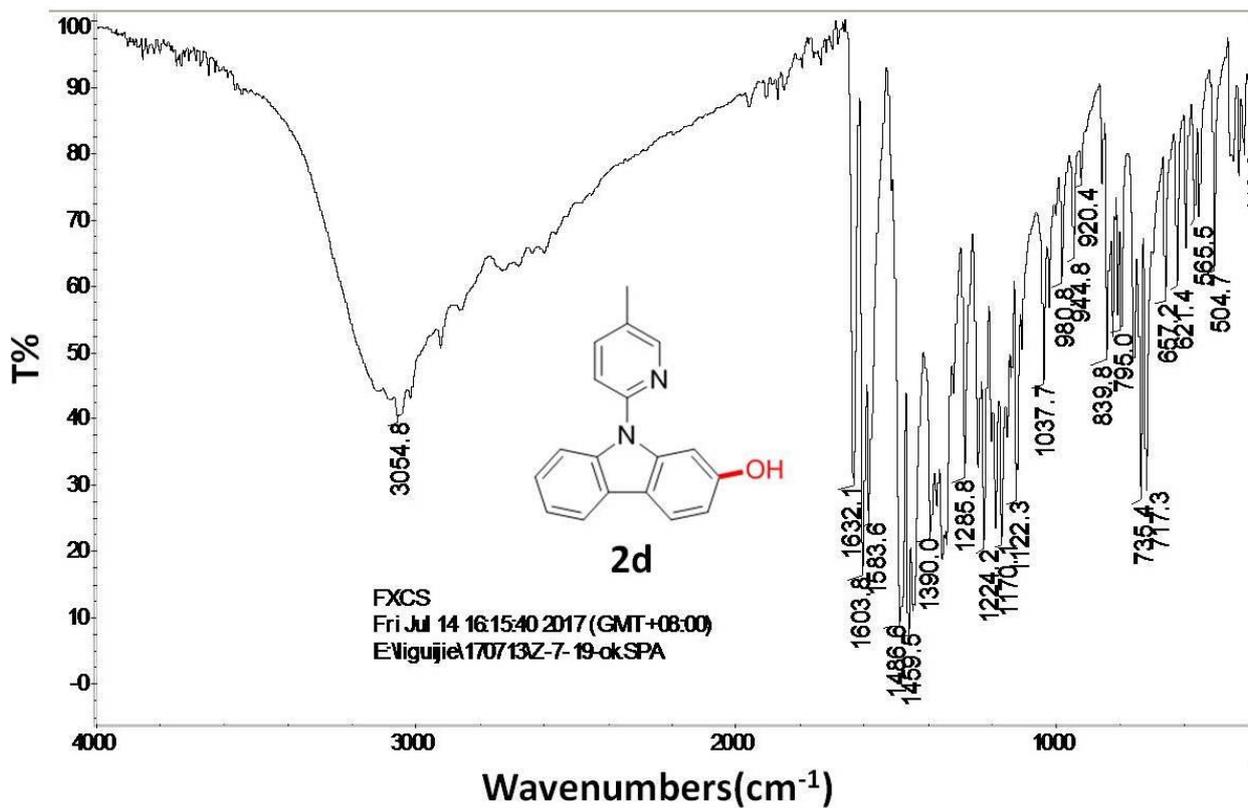


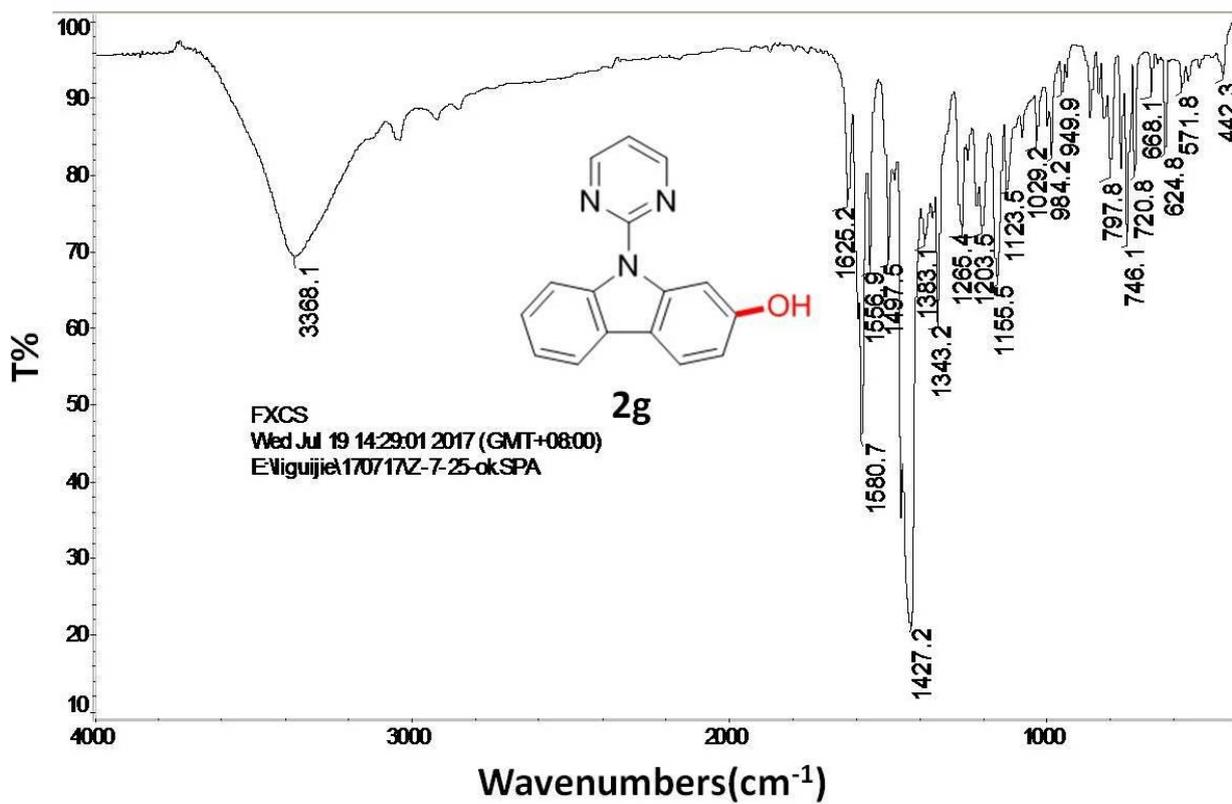
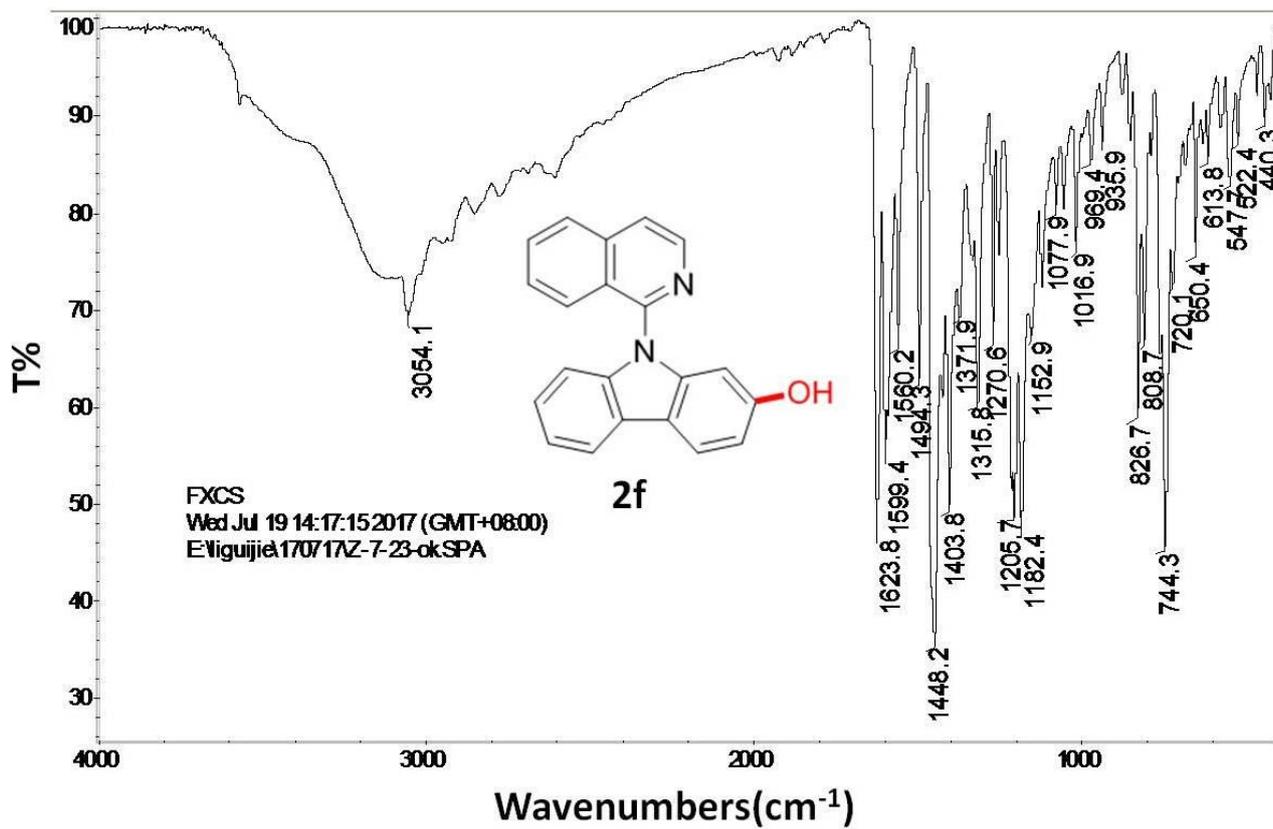


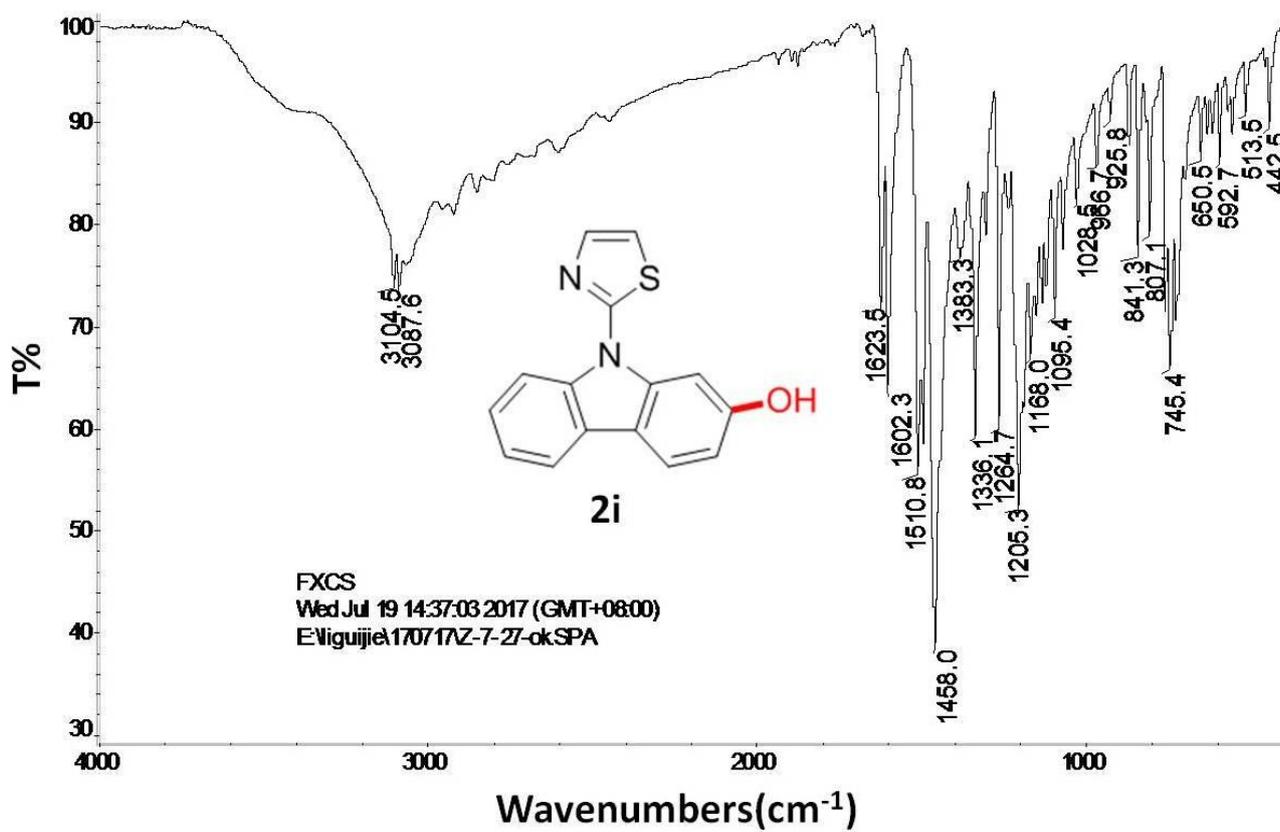
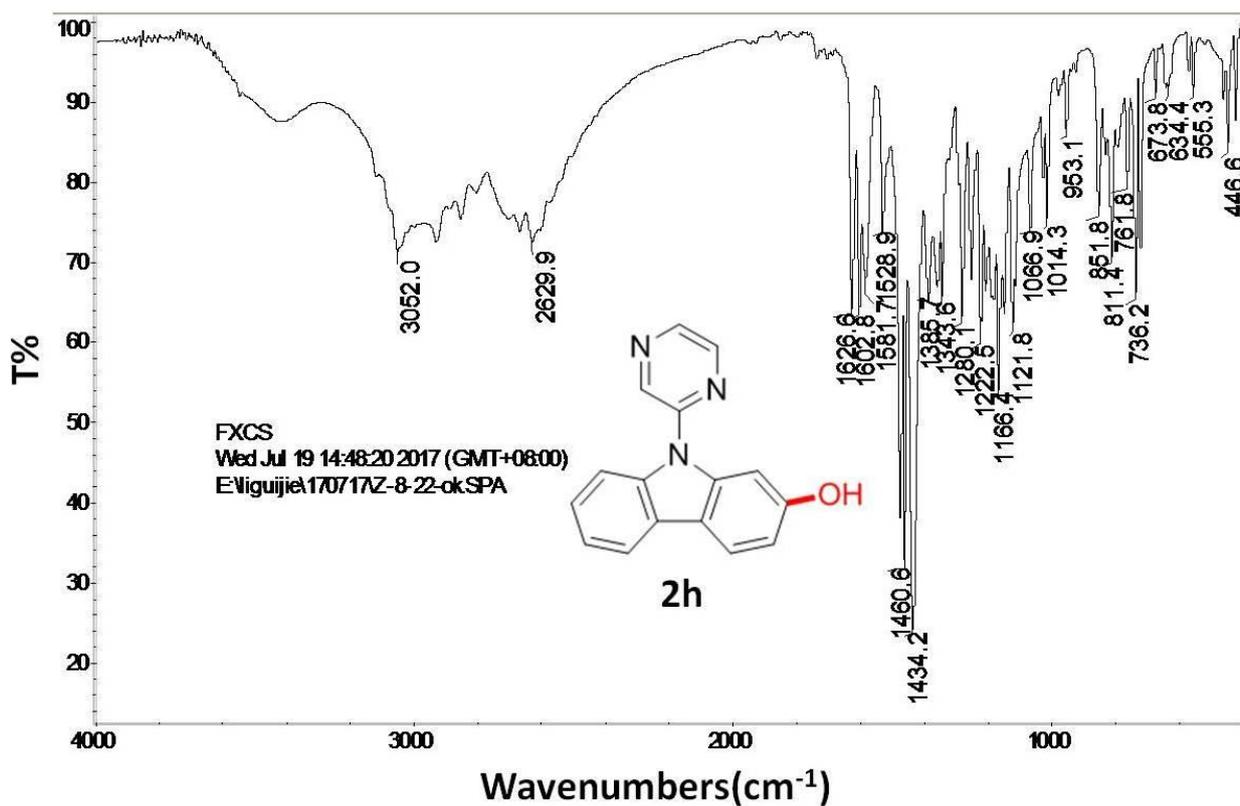
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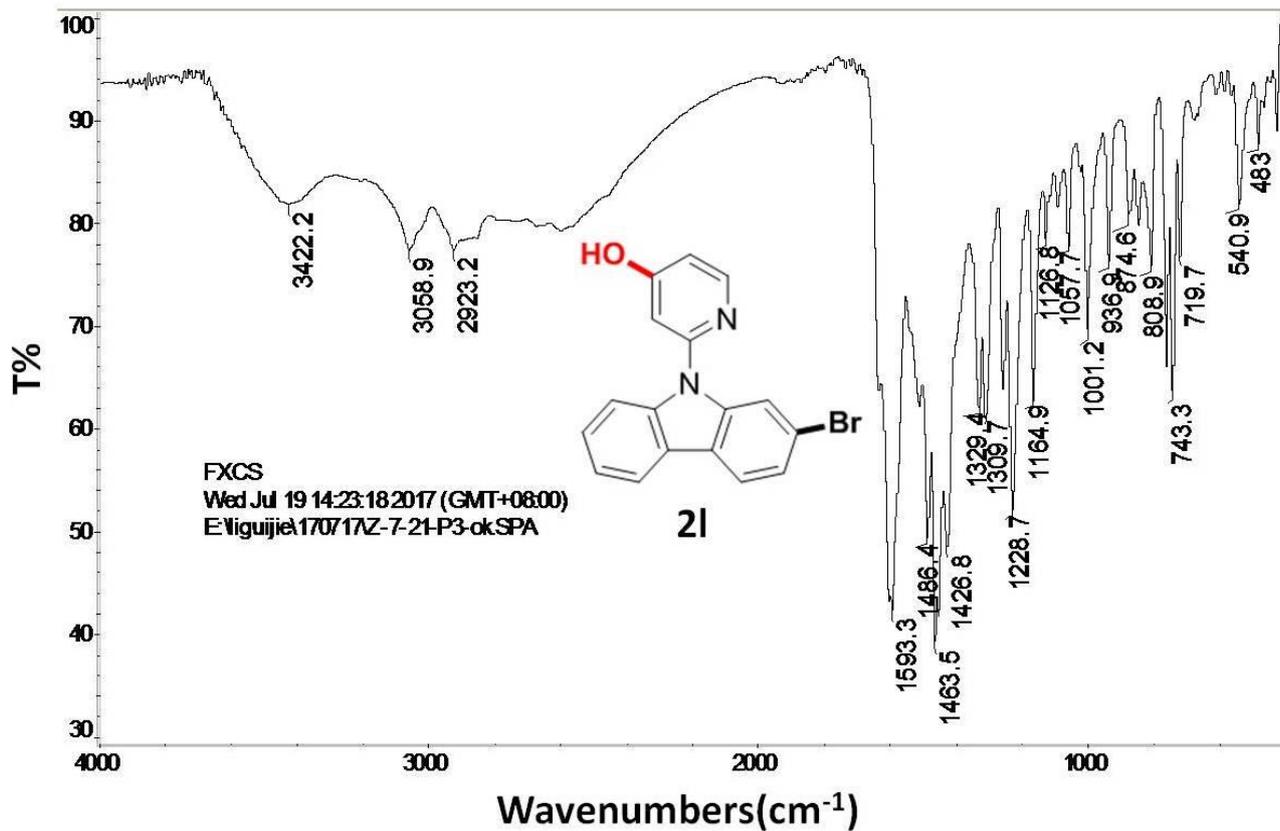
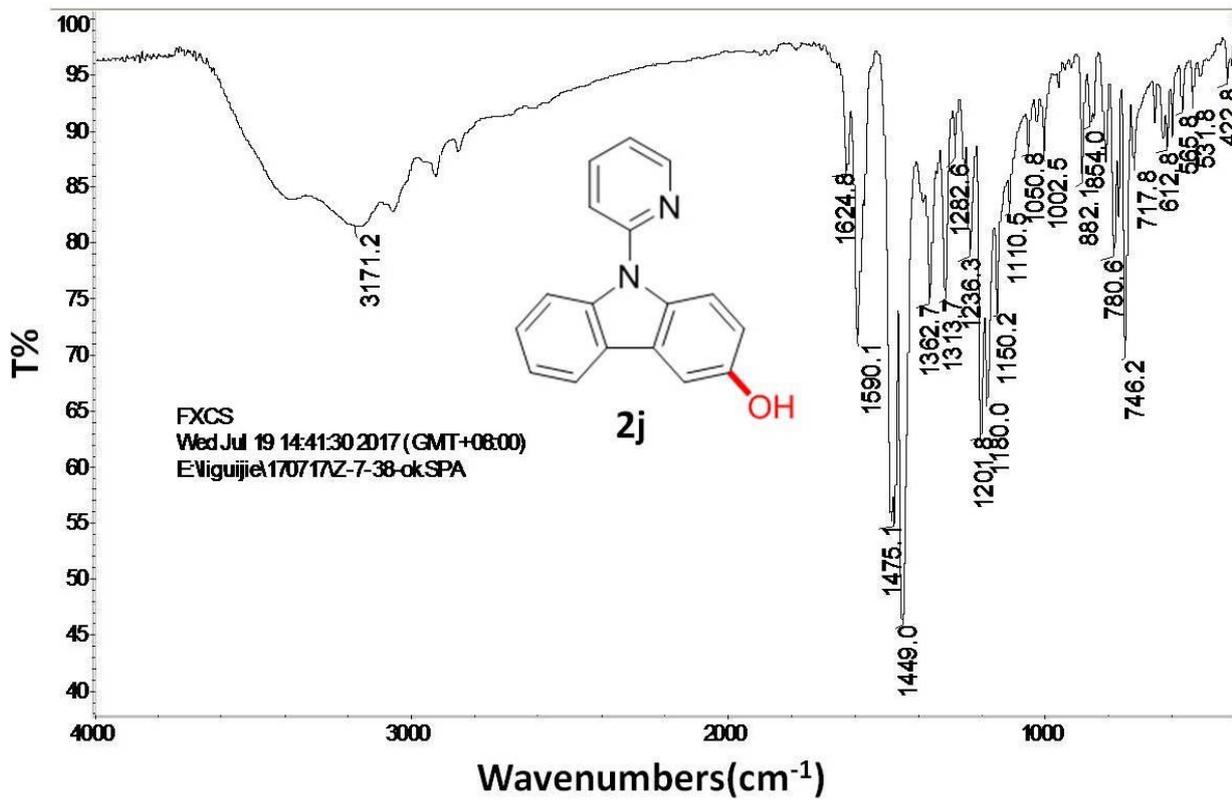


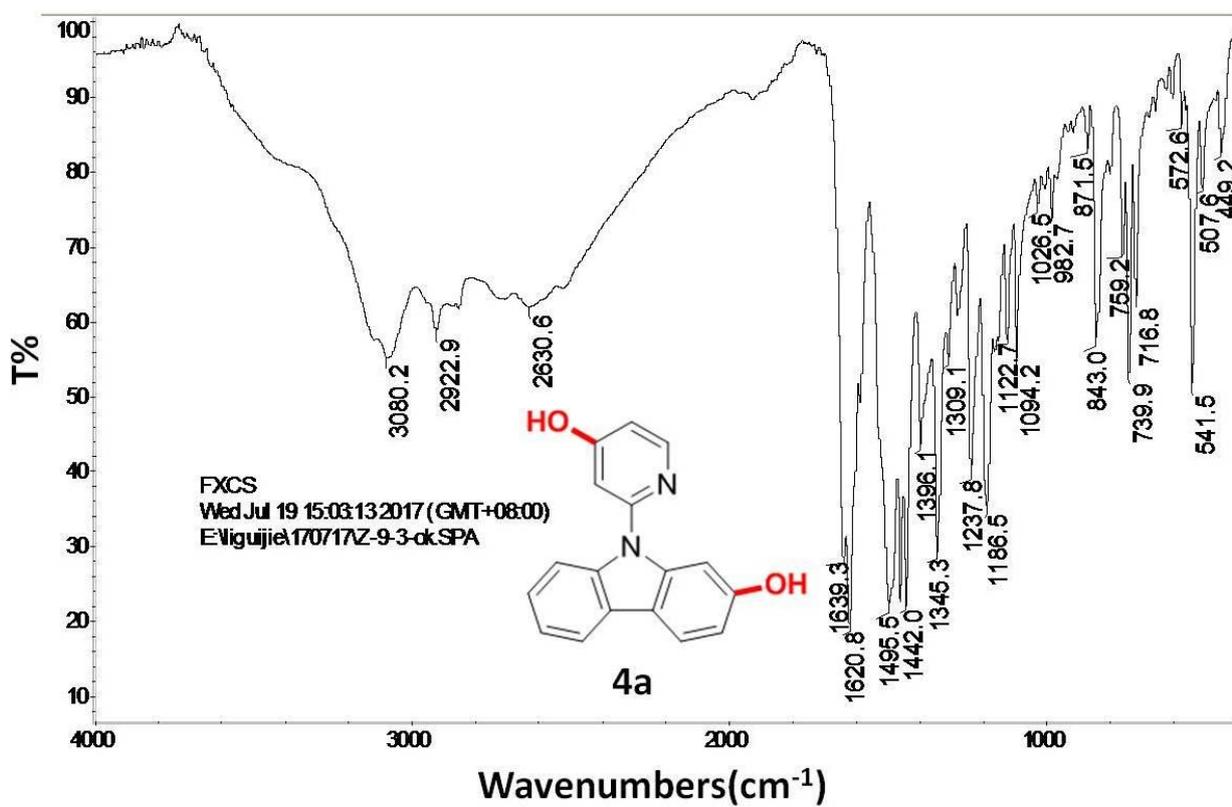
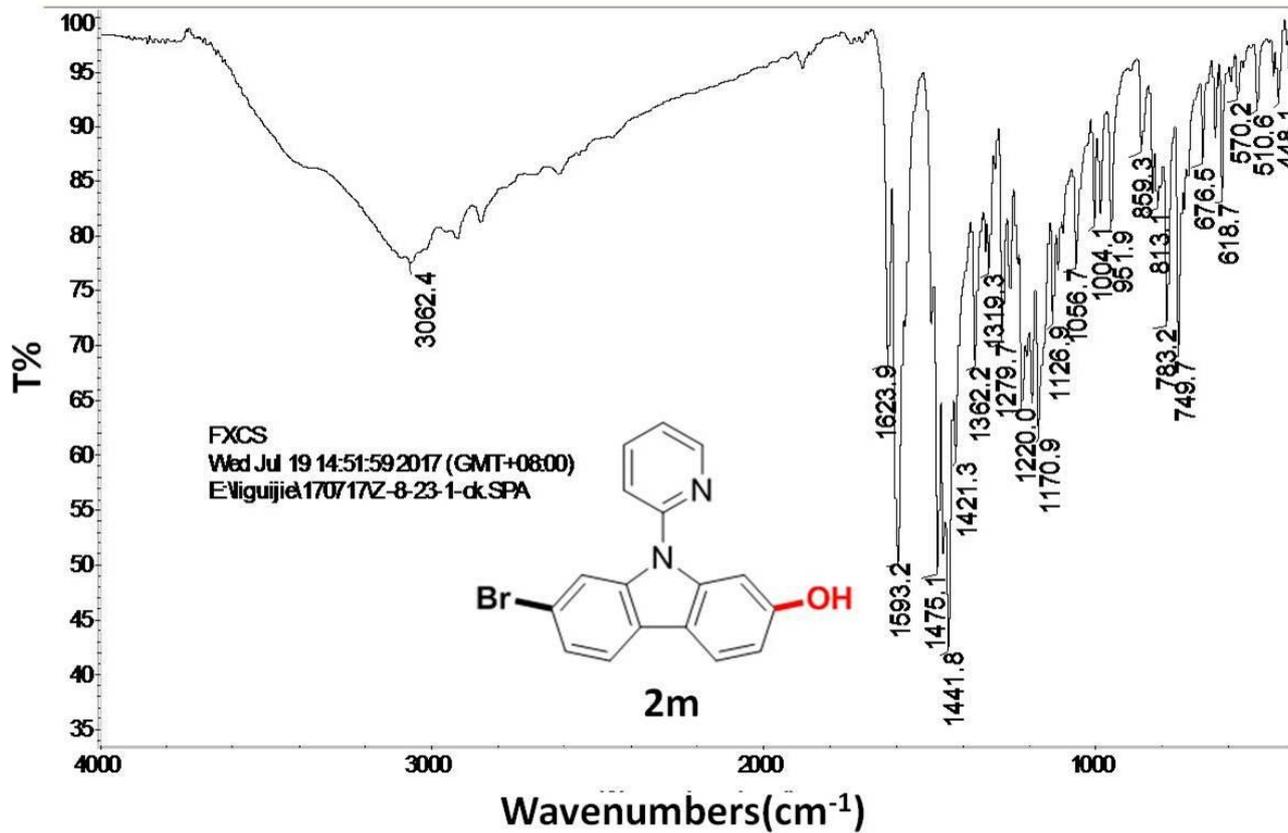


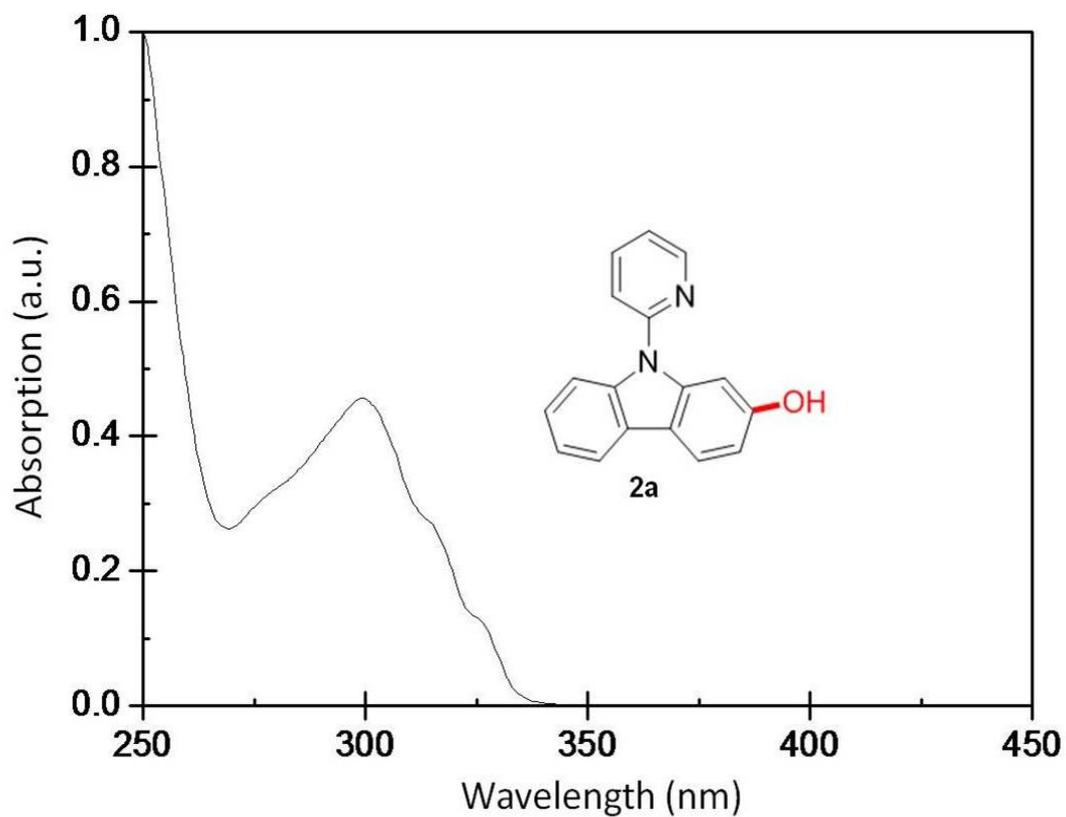
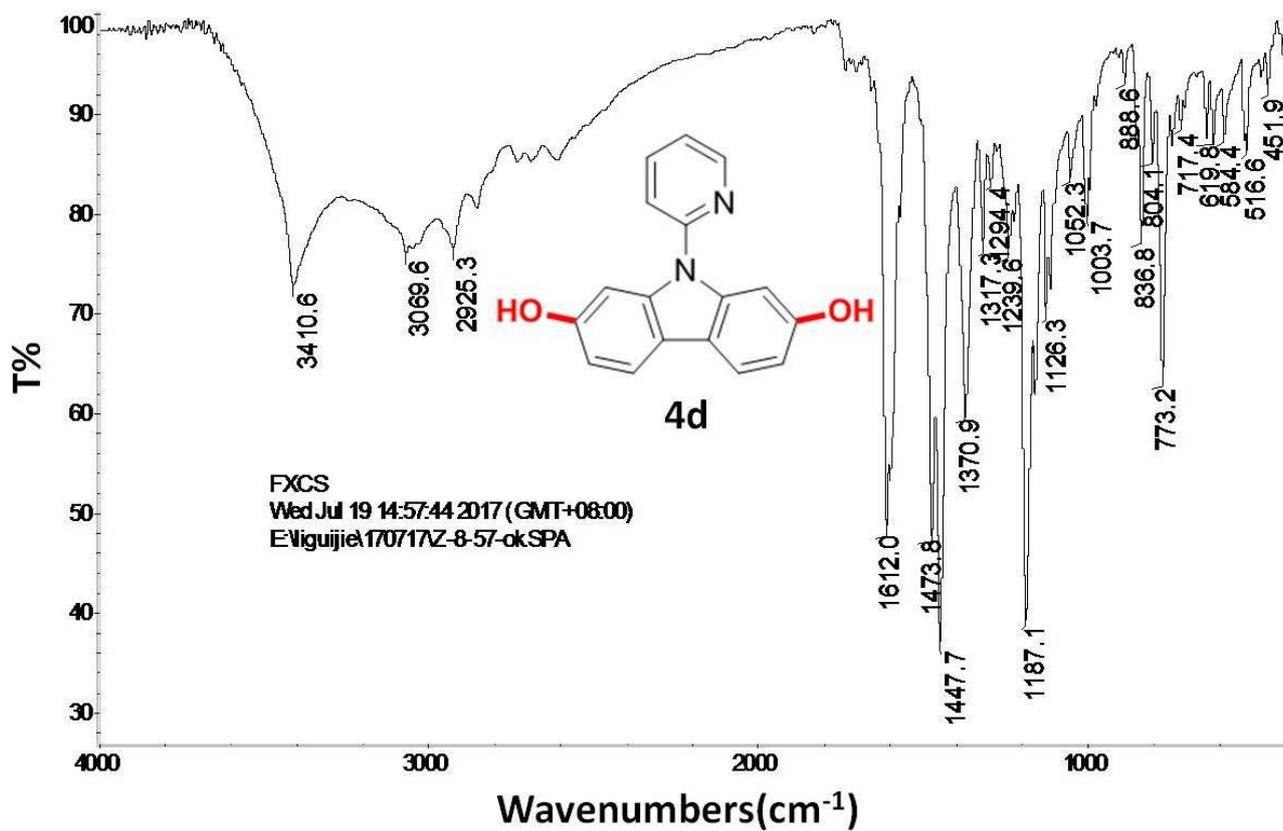


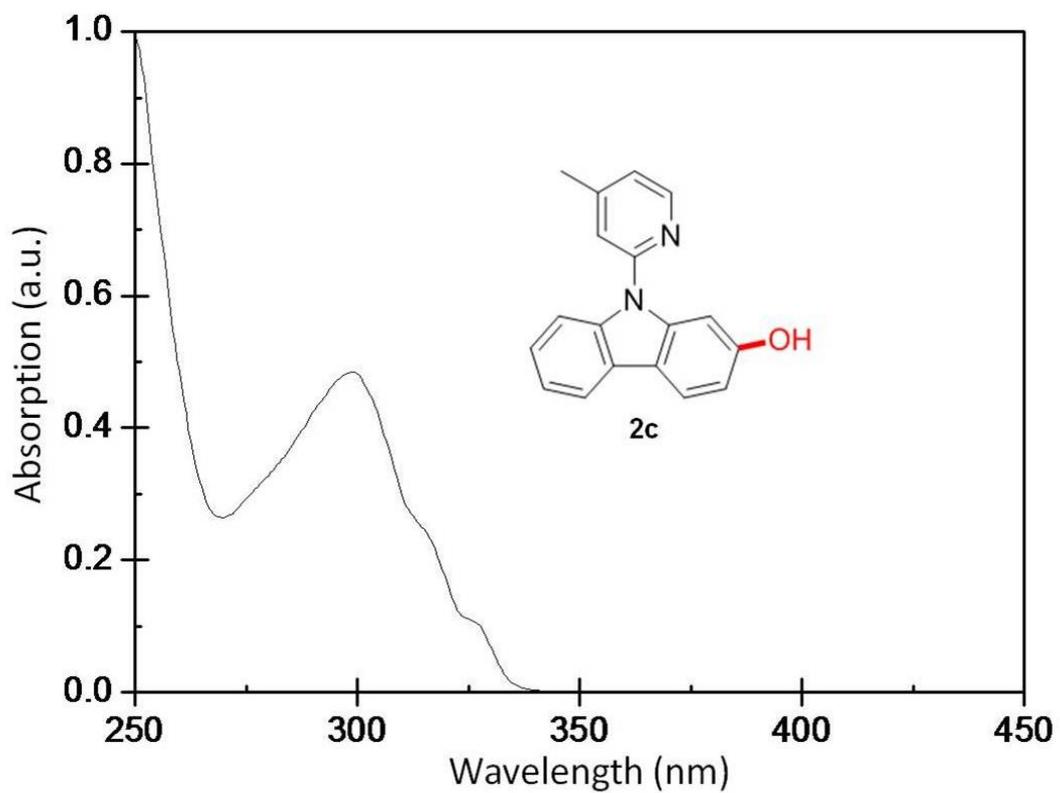
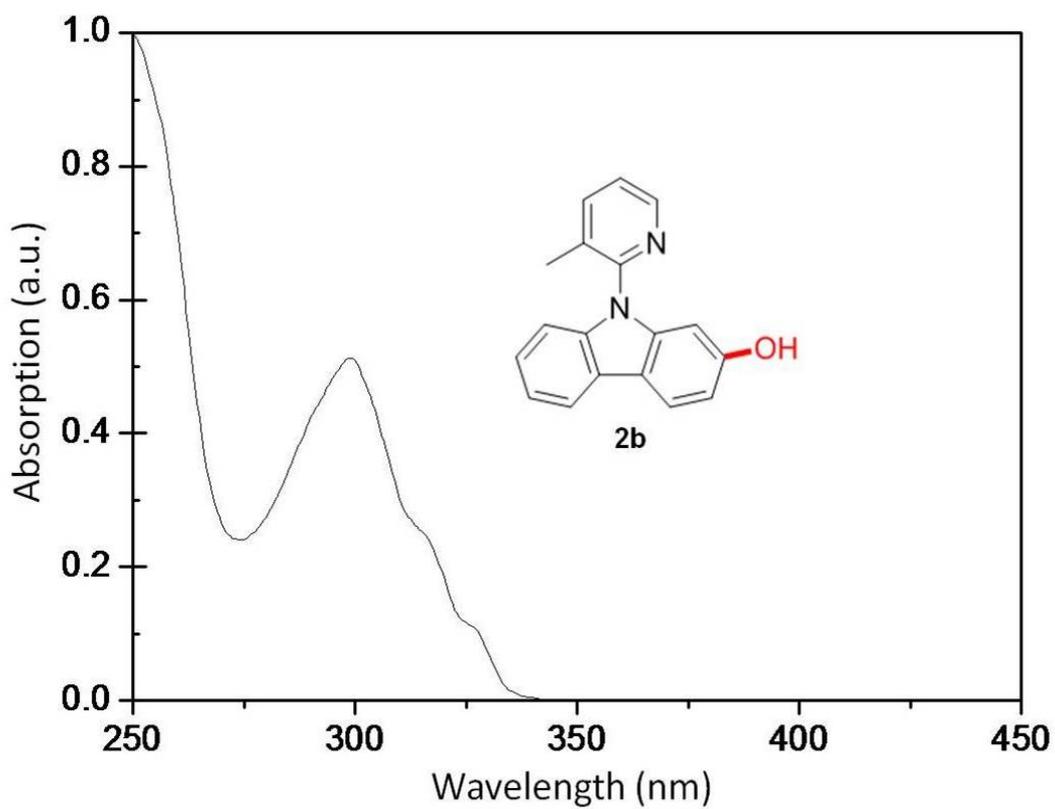


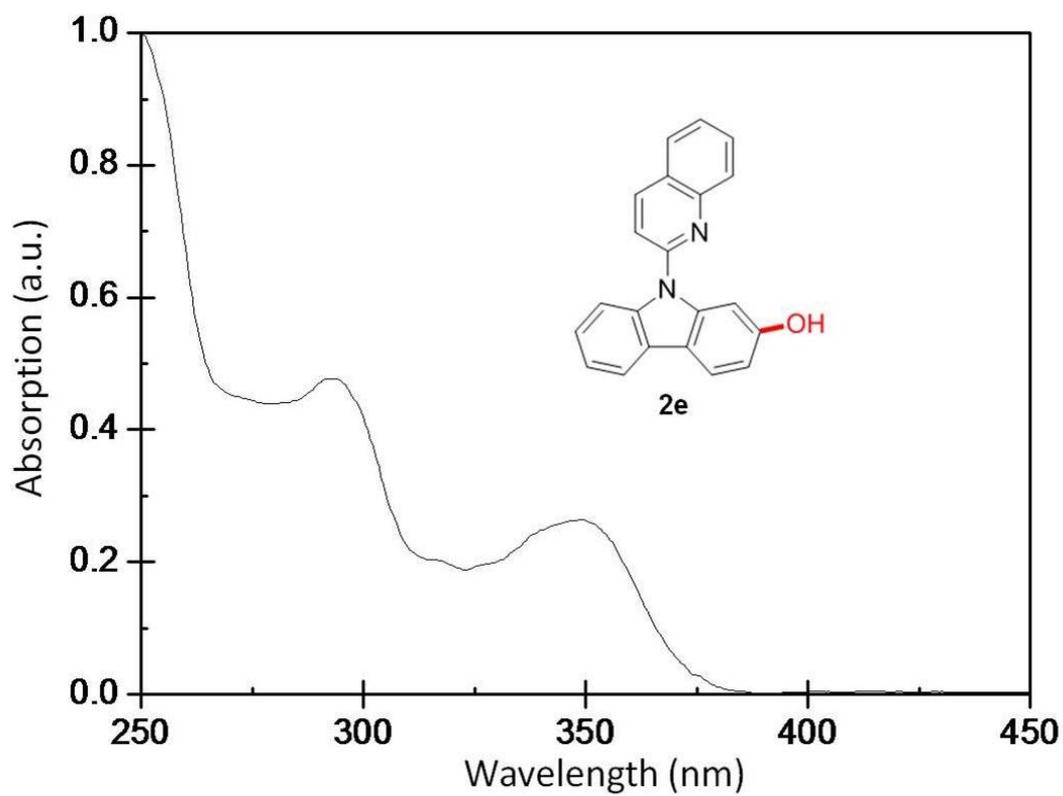
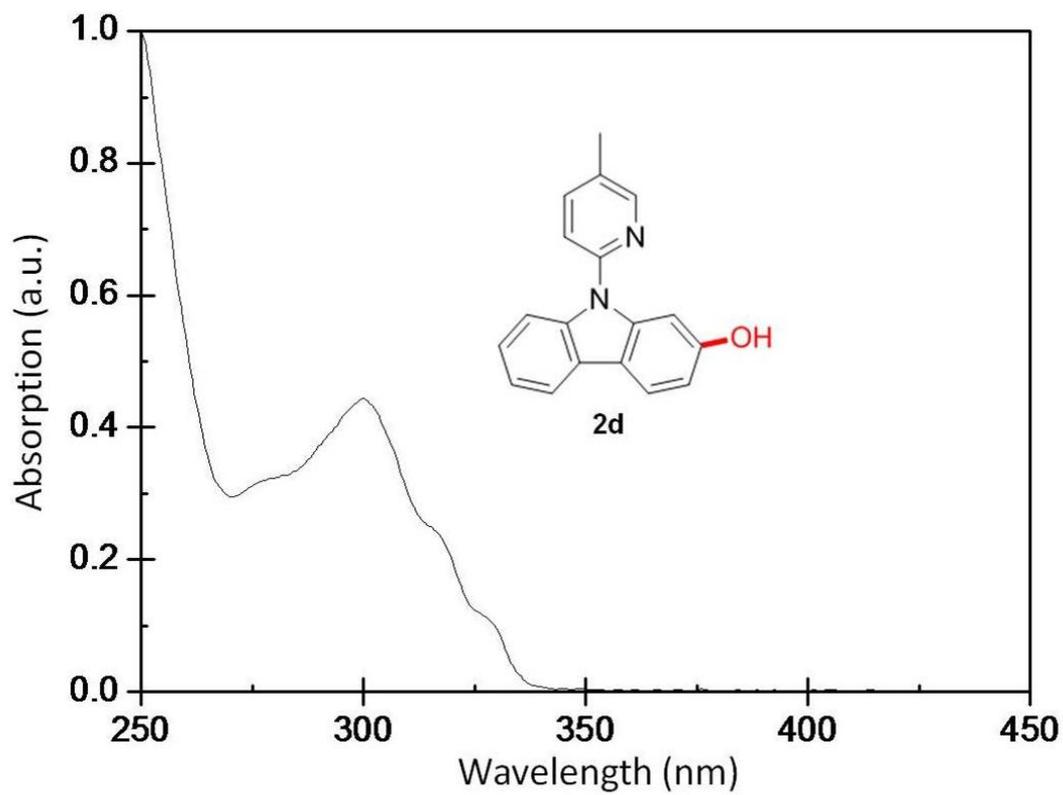


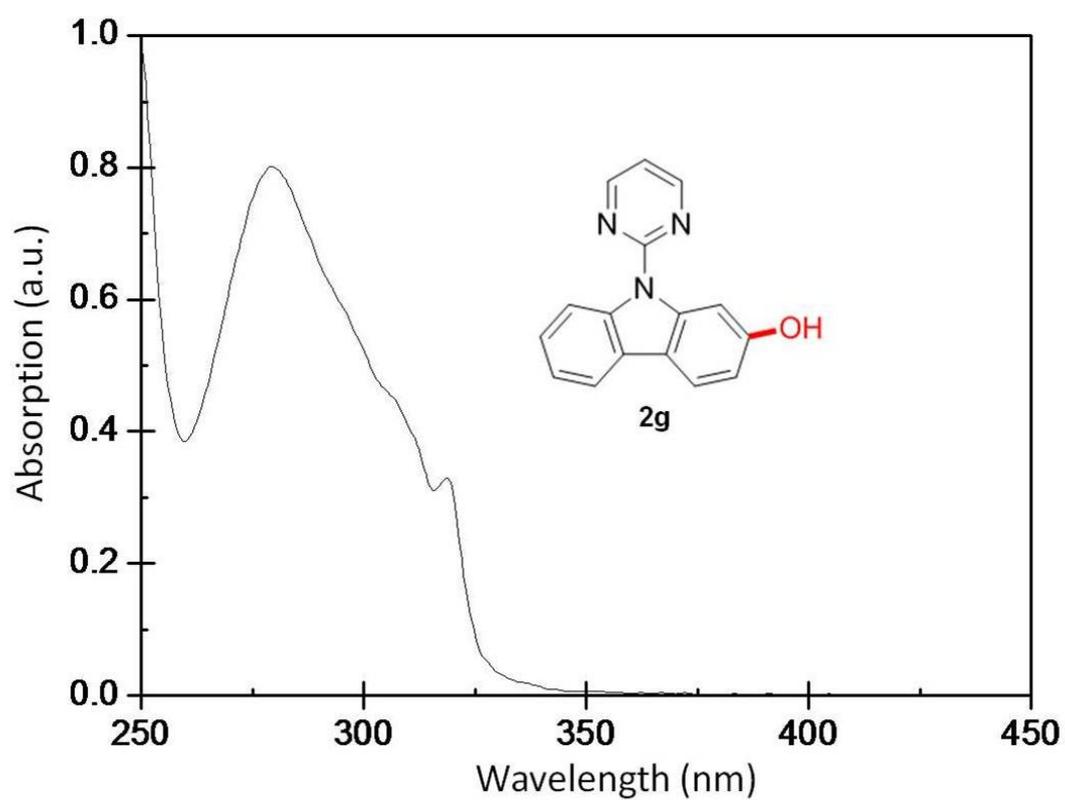
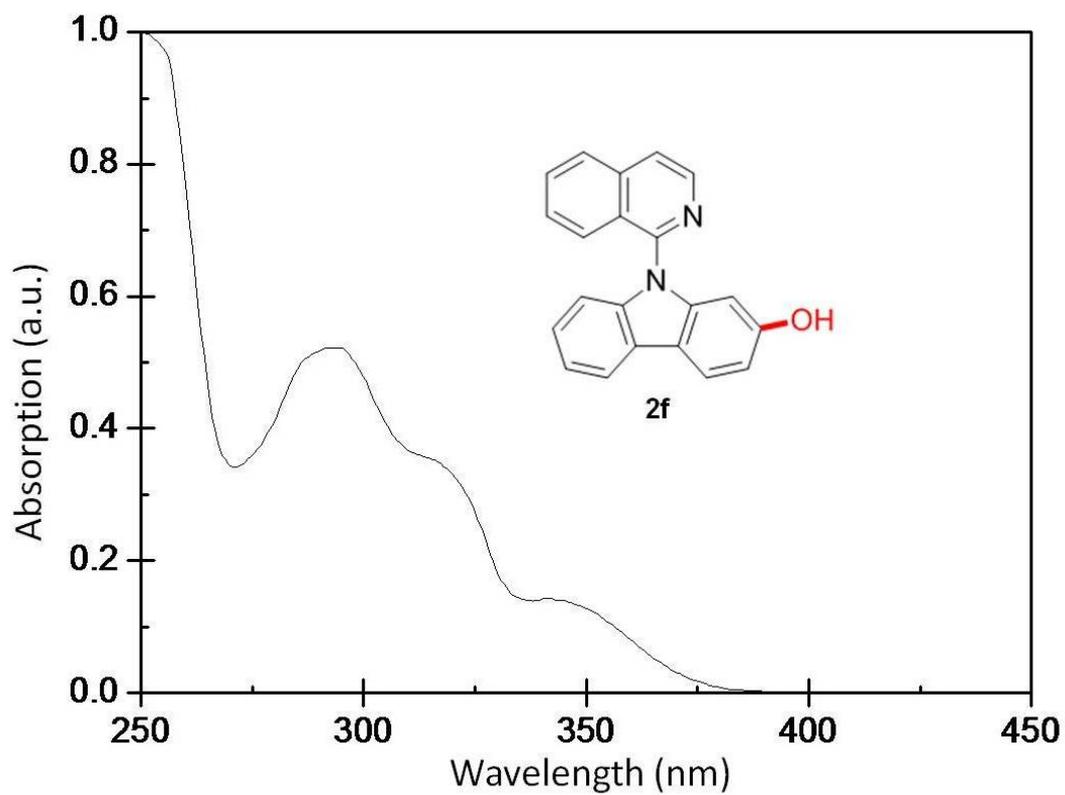


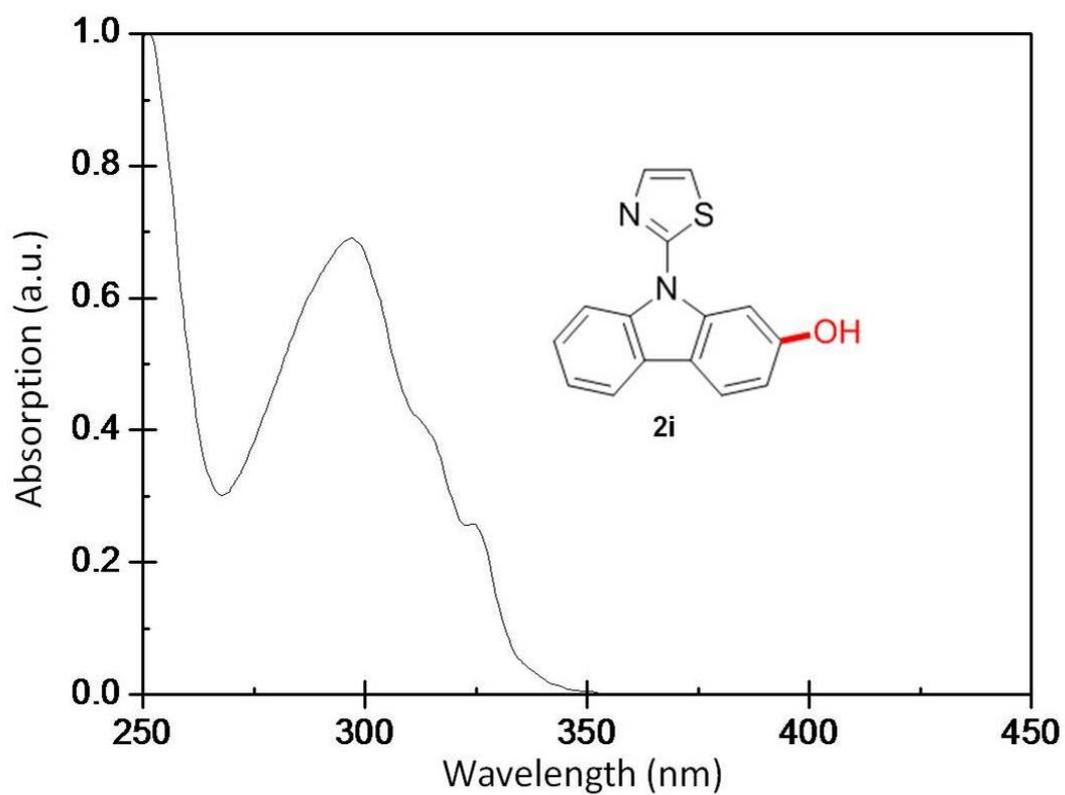
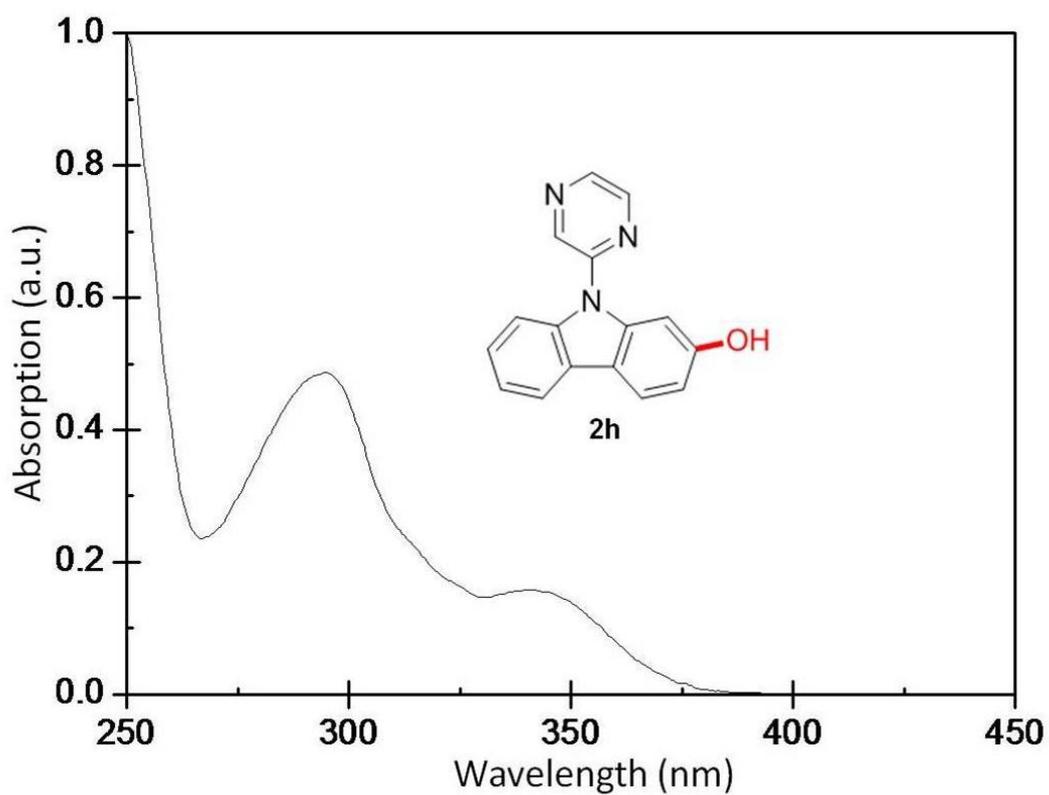


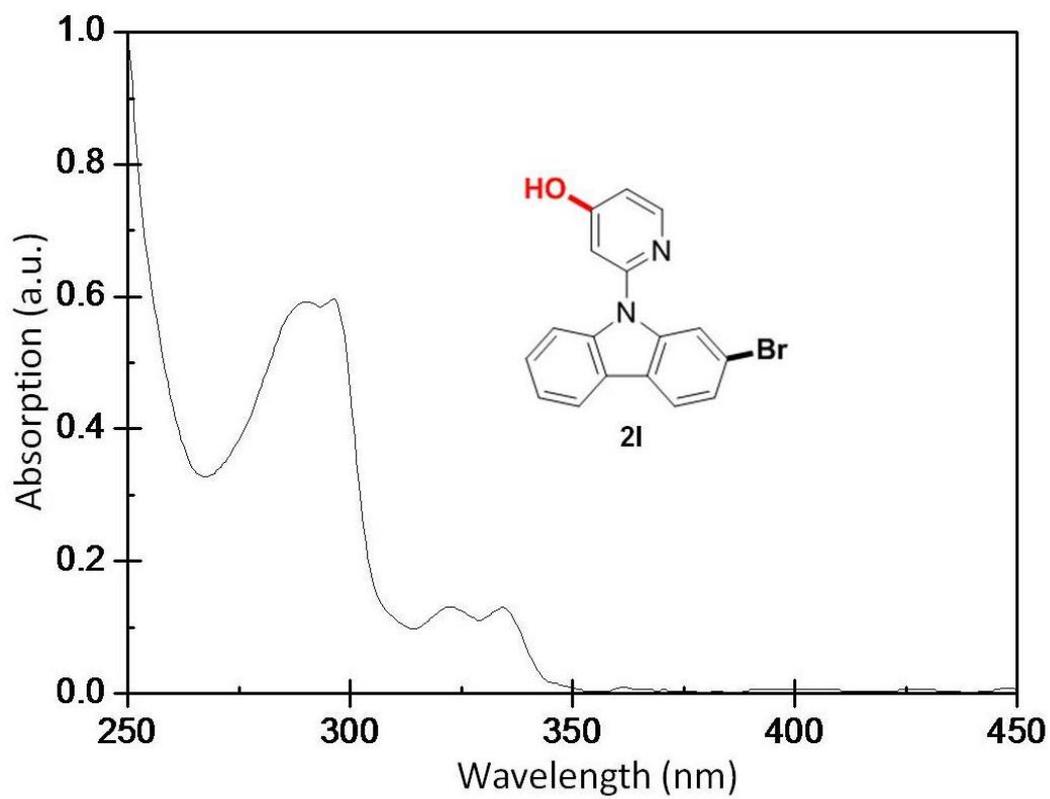
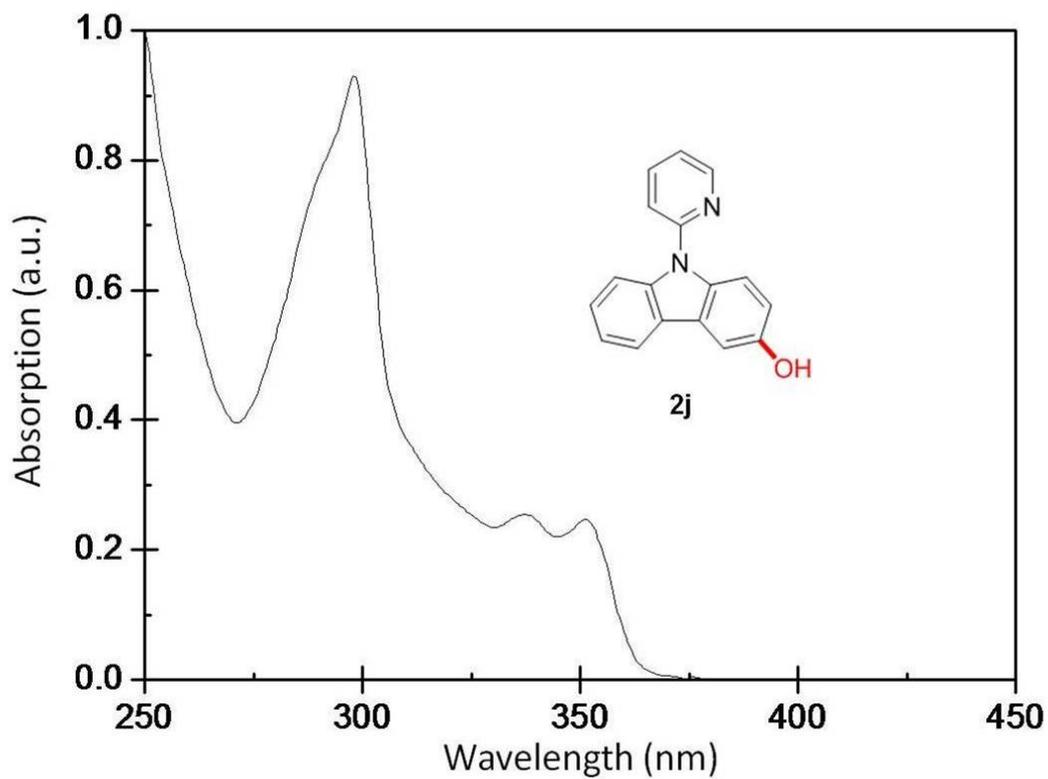


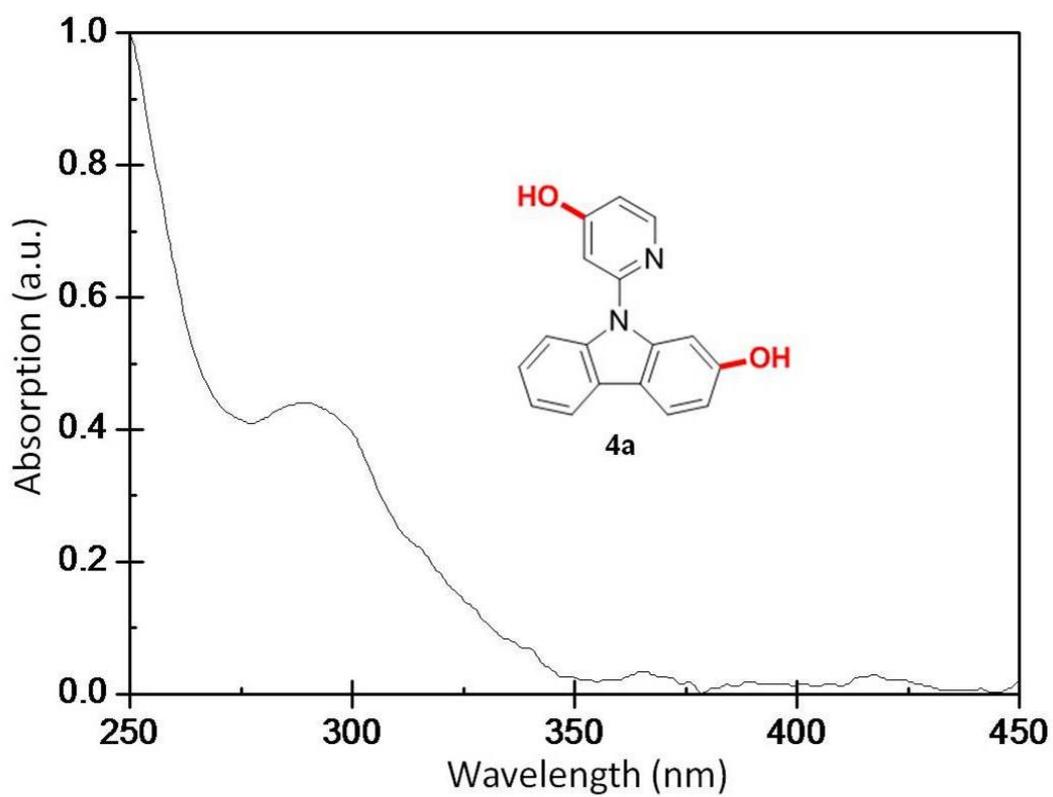
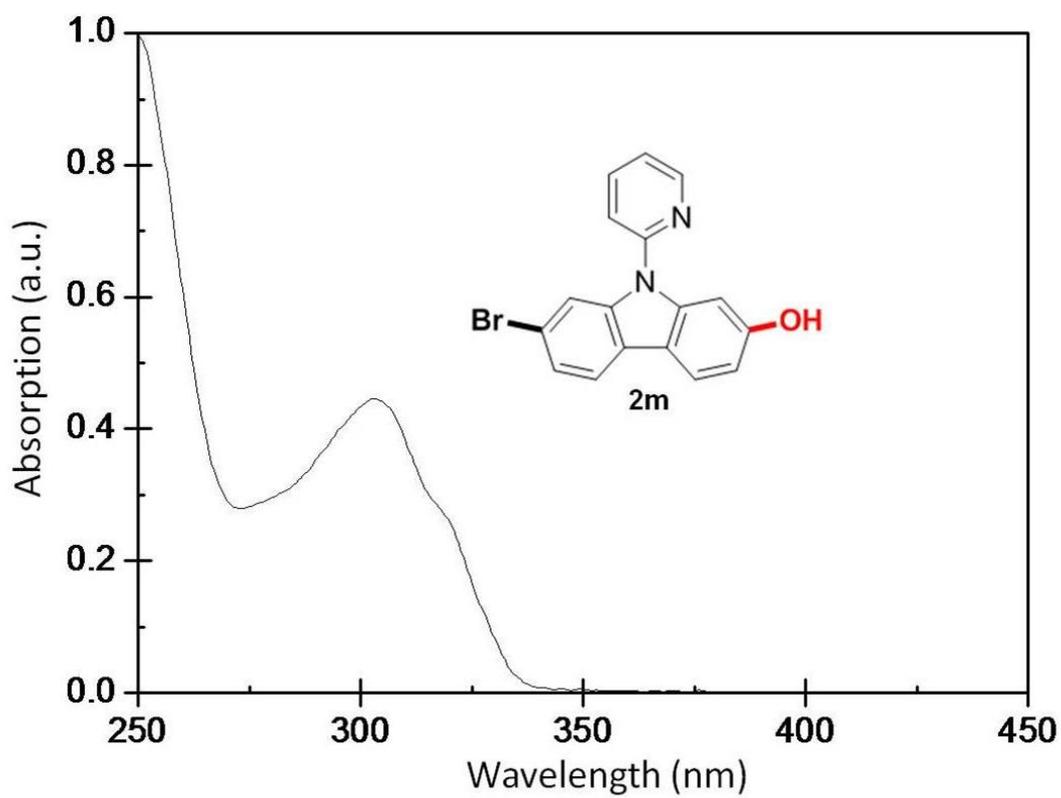


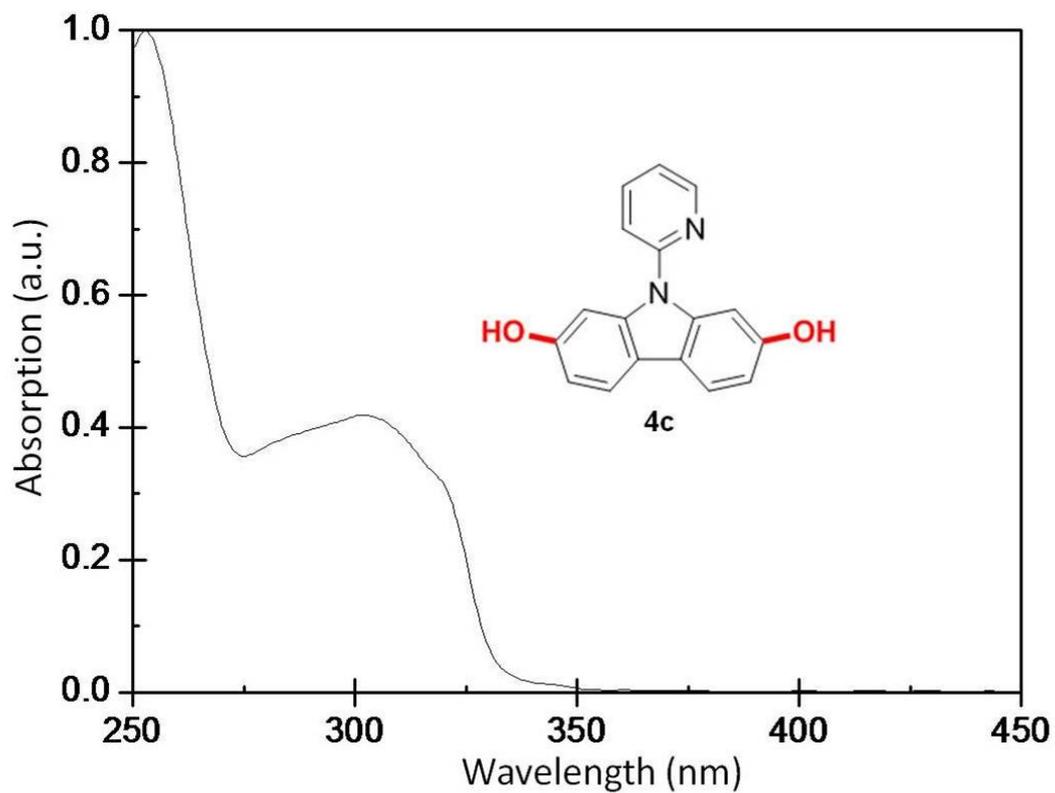












X-ray Structure of PtNON and its Crystal Data:

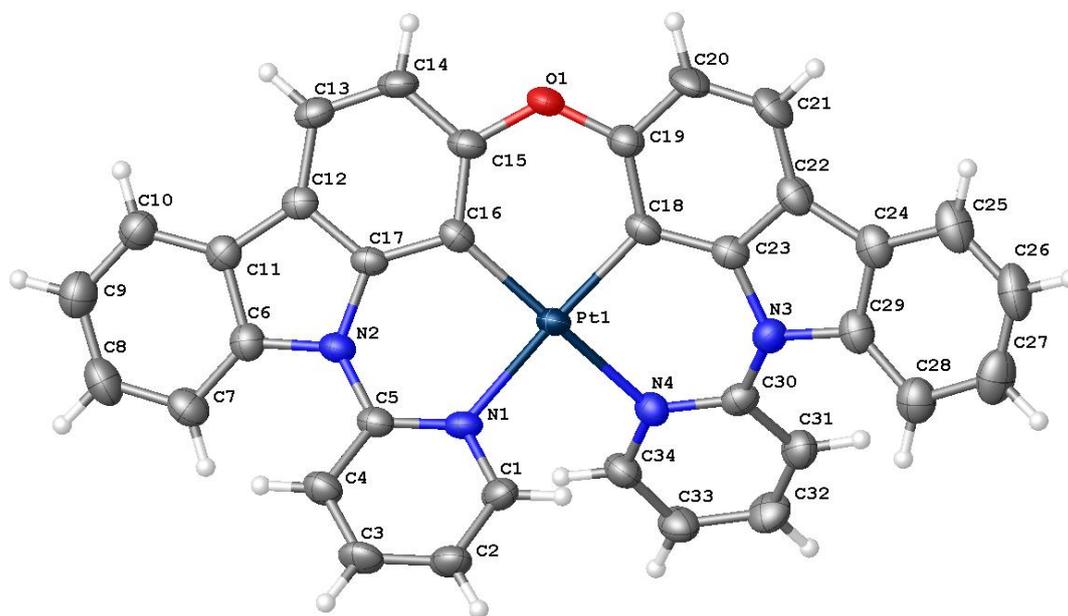


Figure S5. X-ray structure of **PtNON** with a molecule of CH_2Cl_2 . Ellipsoids are shown at the 50% probability level.

Table 1. Crystal data and structure refinement for mo_dm17076_0m.

Identification code	mo_dm17076_0m	
Empirical formula	C35 H22 Cl2 N4 O Pt	
Formula weight	780.55	
Temperature	190 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.8556(15) Å	$\alpha = 90^\circ$
	b = 10.2243(11) Å	$\beta = 97.000(2)^\circ$
	c = 21.102(2) Å	$\gamma = 90^\circ$
Volume	2967.1(5) Å ³	
Z	4	
Density (calculated)	1.747 Mg/m ³	
Absorption coefficient	4.945 mm ⁻¹	
F(000)	1520	
Crystal size	0.1 x 0.08 x 0.02 mm ³	
Theta range for data collection	1.481 to 30.757 °	
Index ranges	-16<=h<=19, -14<=k<=14, -30<=l<=28	
Reflections collected	29441	
Independent reflections	9188 [R(int) = 0.0710]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5522	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9188 / 0 / 388	
Goodness-of-fit on F ²	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.0843	
R indices (all data)	R1 = 0.0904, wR2 = 0.0982	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.558 and -2.043 e.Å ⁻³	

X-ray structure of PdNON and its Crystal Data:

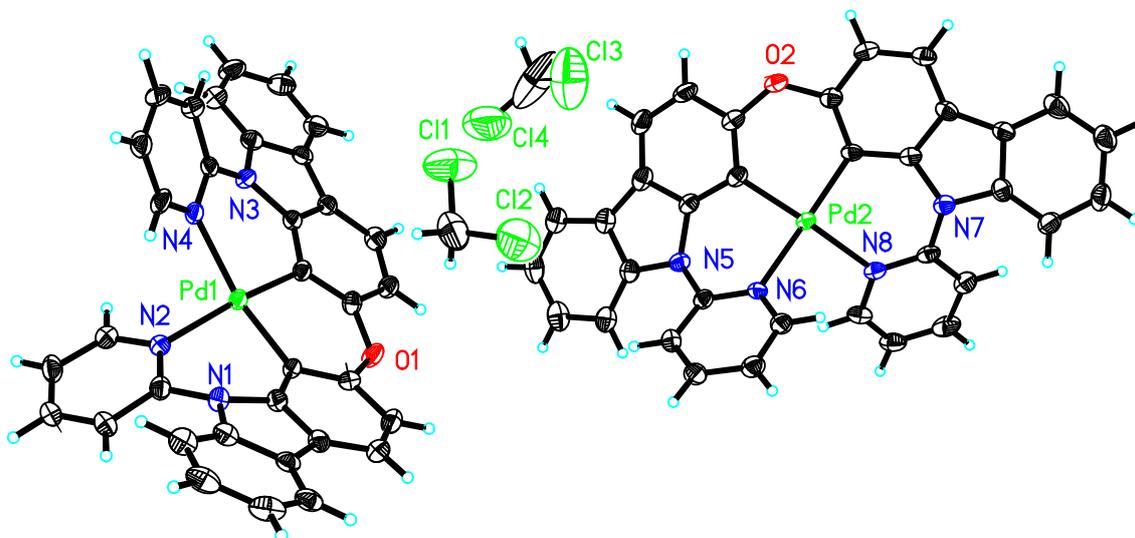


Figure S6. X-ray structure of PdNON with CH₂Cl₂ molecules. Ellipsoids are shown at the 50% probability level.

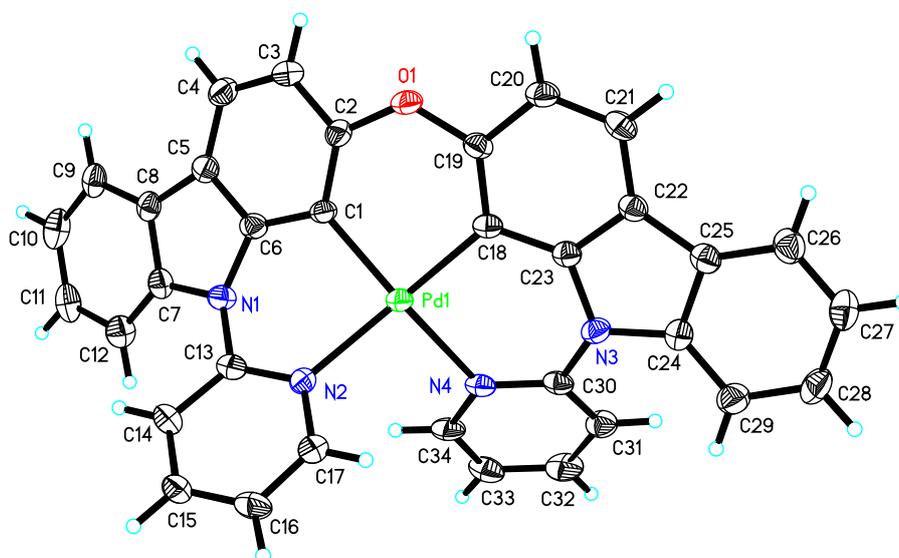


Figure S7. X-ray structure of PdNON. Ellipsoids are shown at the 50% probability level.

Table 2. Crystal data and structure refinement for cd17063.

Identification code	cd17063	
Empirical formula	C ₃₅ H ₂₂ Cl ₂ N ₄ O Pd	
Formula weight	691.86	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.6518(12) Å	α = 90 °
	b = 10.0242(10) Å	β = 103.209(2) °
	c = 24.692(3) Å	γ = 90 °
Volume	2807.7(5) Å ³	
Z	4	
Density (calculated)	1.637 Mg/m ³	
Absorption coefficient	0.889 mm ⁻¹	
F(000)	1392	
Crystal size	0.180 x 0.150 x 0.100 mm ³	
Theta range for data collection	1.694 to 25.497 °	
Index ranges	-9 ≤ h ≤ 14, -12 ≤ k ≤ 12, -29 ≤ l ≤ 29	
Reflections collected	16248	
Independent reflections	10196 [R(int) = 0.0298]	
Completeness to theta = 25.242 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6433	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10196 / 1 / 775	
Goodness-of-fit on F ²	1.007	
Final R indices [I > 2σ(I)]	R1 = 0.0426, wR2 = 0.1034	
R indices (all data)	R1 = 0.0481, wR2 = 0.1075	
Absolute structure parameter	0.003(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.645 and -0.521 e.Å ⁻³	

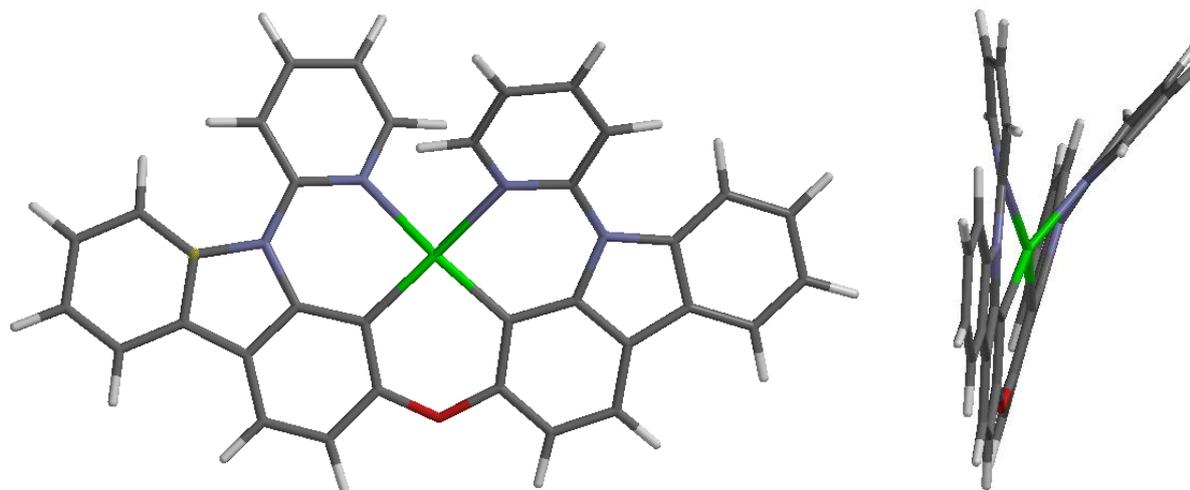


Figure S10. Optimized molecular structure of **PtNON** based on the DFT calculation, top-view (left) and side-view (right)

Job WF22290 started on ARIZONA-50E3BCF at Wed Dec 14 11:38:50 2016

Jaguar version 3.5, release 42

Job name: WF22290

Task: Geometry optimization

Stoichiometry: PtC34N4H200

Molecular weight: 695.13 amu

Molecular charge: 0

Spin multiplicity: 1

Point Group: C1

SCF method: B3LYP

Basis set: LACVP**

Basis functions: 668

Total electrons: 278
Alpha electrons: 139
Beta electrons: 139
Total orbitals: 710
Core orbitals: 139
Open-shell orbitals: 0
Occupied orbitals: 139
Shells: 1

Non-default options chosen:

SCF calculation type: DFT

DFT=Becke_3_Parameter/HF+Slater+Becke88+VWN+LYP (B3LYP)

Geometry will be optimized in redundant internal coordinates

Initial Hessian: from previous calculation

Iter	Energy	Gmax	Grms	Dmax	Drms
1	-1720.951289 *	0.17908	0.01544	0.08962	0.01456
2	-1720.953299 .	0.17353	0.01511	0.08599	0.01178
3	-1720.955662 .	0.16641	0.01492	0.07932	0.01167
4	-1720.952492 .	0.17641	0.01540	0.07800	0.01357
5	-1720.956788 .	0.16751	0.01516	0.09560	0.01816
6	-1720.961976 .	0.17672	0.01515	0.09232	0.01815
7	-1720.972560 .	0.17019	0.01440	0.07818	0.01815
8	-1720.984474 .	0.15407	0.01363	0.08973	0.01815
9	-1721.003493 .	0.12708	0.01186	0.15711	0.01817
10	-1721.032386 .	0.09634	0.00980	0.09942	0.01816
11	-1721.048700 .	0.08378	0.00798	0.16355	0.01816
12	-1721.069541 .	0.06242	0.00712	0.14748	0.01817

```

13 -1721.088927 . 0.04681 . 0.00495 . 0.17486 . 0.01819 .
14 -1721.104974 . 0.03298 . 0.00366 . 0.17430 . 0.01817 .
15 -1721.116004 . 0.02316 . 0.00246 . 0.18770 . 0.01817 .
16 -1721.122983 . 0.01612 . 0.00241 . 0.15769 . 0.01819 .
17 -1721.127522 . 0.01150 . 0.00217 . 0.14637 . 0.01816 .
18 -1721.129841 . 0.01132 . 0.00205 . 0.11115 . 0.01816 .
19 -1721.131593 . 0.01087 . 0.00184 . 0.10459 . 0.01816 .
** restarting optimization from step 19 **
19 -1721.129622 . 0.01087 . 0.00184 . 0.08667 . 0.01817 .
** restarting optimization from step 19 **
19 -1721.130122 . 0.01087 . 0.00184 . 0.03876 . 0.00912 .
22 -1721.131991 . 0.00948 . 0.00170 . 0.02436 . 0.00456 .
23 -1721.132675 . 0.00470 . 0.00064 . 0.01199 . 0.00232 .
24 -1721.132966 . 0.00440 . 0.00042 . 0.01768 . 0.00230 .
25 -1721.132986 * 0.00439 . 0.00043 . 0.00783 . 0.00115 *
26 -1721.133065 . 0.00430 . 0.00038 . 0.00619 . 0.00166 .
** restarting optimization from step 26 **
26 -1721.132992 . 0.00430 . 0.00038 . 0.00614 . 0.00082 *
28 -1721.133073 * 0.00429 . 0.00037 . 0.03362 . 0.00390 .
29 -1721.133283 . 0.00415 . 0.00039 . 0.00951 . 0.00230 .
** restarting optimization from step 29 **
29 -1721.133136 . 0.00415 . 0.00039 . 0.01003 . 0.00118 *
31 -1721.133383 . 0.00409 . 0.00037 . 0.01163 . 0.00162 .
32 -1721.133517 . 0.00410 . 0.00038 . 0.02087 . 0.00228 .
33 -1721.133617 . 0.00399 . 0.00041 . 0.01981 . 0.00457 .
** restarting optimization from step 33 **
33 -1721.132849 . 0.00399 . 0.00041 . 0.02238 . 0.00227 .
35 -1721.133601 * 0.00414 . 0.00046 . 0.01013 . 0.00119 *
36 -1721.133737 . 0.00413 . 0.00042 . 0.01663 . 0.00163 .

```

```

37 -1721.133812 . 0.00408 . 0.00037 . 0.01971 . 0.00321 .
** restarting optimization from step 37 **
37 -1721.133753 . 0.00408 . 0.00037 . 0.01570 . 0.00165 .
39 -1721.133956 . 0.00403 . 0.00041 . 0.02258 . 0.00228 .
40 -1721.134095 . 0.00403 . 0.00043 . 0.03379 . 0.00322 .
41 -1721.134248 . 0.00401 . 0.00043 . 0.04761 . 0.00454 .

42 -1721.134508 . 0.00404 . 0.00053 . 0.02640 . 0.00645 .
** restarting optimization from step 42 **
42 -1721.133879 . 0.00404 . 0.00053 . 0.01657 . 0.00321 .
** restarting optimization from step 42 **
42 -1721.134036 . 0.00404 . 0.00053 . 0.01380 . 0.00162 .
45 -1721.134609 . 0.00395 . 0.00043 . 0.02278 . 0.00228 .
46 -1721.134747 . 0.00397 . 0.00040 . 0.01886 . 0.00321 .
** restarting optimization from step 46 **
46 -1721.134685 . 0.00397 . 0.00040 . 0.01491 . 0.00164 .
48 -1721.134986 . 0.00375 . 0.00037 . 0.02310 . 0.00228 .
49 -1721.135178 . 0.00362 . 0.00036 . 0.03359 . 0.00323 .
50 -1721.135305 . 0.00276 . 0.00058 . 0.01387 . 0.00161 .
51 -1721.135405 . 0.00255 . 0.00039 . 0.01940 . 0.00229 .
52 -1721.135637 . 0.00227 . 0.00030 . 0.04071 . 0.00456 .
53 -1721.136055 . 0.00237 . 0.00029 * 0.09162 . 0.00911 .
54 -1721.136679 . 0.00253 . 0.00032 . 0.06423 . 0.01289 .
** restarting optimization from step 54 **
54 -1721.132167 . 0.00253 . 0.00032 . 0.06540 . 0.00642 .
56 -1721.137238 . 0.00266 . 0.00030 * 0.09350 . 0.00911 .
57 -1721.137953 . 0.00267 . 0.00036 . 0.07511 . 0.01284 .
** restarting optimization from step 57 **

```

WARNING: Hessian has too many zero eigenvalues

Some coordinates may be inadvertently frozen

57 -1721.135899 . 0.00267 . 0.00036 . 0.01689 . 0.00334 .

** stopping now - optimization seems to be stuck **

59 -1721.137207 ! 0.00000 # 0.00000 # 0.00000 # 0.00000 #

** Geometry optimization complete **

Final energy -1721.1372066777

Job WF22290 completed on ARIZONA-50E3BCF at Thu Dec 15 13:41:39 2016

Reason for exit: Successful completion

Titan Program CPU Time : 025:34:19.1

Titan Program Wall Time: 026:02:48.8

TITAN Properties Program: (PC/x86)
6.0.6

Release

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 278

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
-----	-----	-----	-----
1 C C02	-4.6368950	-3.7100679	0.6481290
2 C C03	-4.3901202	-0.6108380	0.7131852
3 C C04	0.4404129	3.5124433	3.2087283

4	C	C05	-0.2660028	2.3365110	3.4369753
5	C	C10	-3.4711708	-3.3666805	-0.0637516
6	C	C08	1.2631750	3.6131635	2.0990652
7	C	C09	-0.2155401	1.3779693	2.4447552
8	C	C36	-3.0669282	-0.9045055	0.3007321
9	C	C11	1.4066194	2.5194741	1.2073634
10	N	N12	0.5361387	1.4840152	1.3193004
11	N	N3	-2.6753150	-2.1744356	-0.1158341
12	N	N1	2.3900833	2.4722774	0.2225897
13	Pt	Pt15	-0.0126004	0.0097696	-0.2046844
14	C	C16	-1.5386412	-2.4439259	-0.9702282
15	C	C17	2.5629514	1.4314114	-0.7686423
16	C	C18	-1.6867859	-3.7539798	-1.4759623
17	C	C19	-0.4171993	-1.6310486	-1.2526800
18	C	C20	1.7697946	0.2934910	-1.0341927
19	C	C21	3.7138210	1.7518816	-1.5201678
20	C	C22	-0.7449822	-4.2914956	-2.3604620
21	C	C23	0.5009578	-2.2260386	-2.1379375
22	C	C24	2.2419181	-0.4891115	-2.1064442
23	C	C25	4.1360838	0.9387704	-2.5761484
24	C	C26	0.3445978	-3.5131053	-2.6995727
25	C	C27	3.3914395	-0.1872423	-2.8653073
26	O	O1	1.6641615	-1.6444024	-2.5585654
27	H	H5	0.3539925	4.3597861	3.8885771
28	H	H6	-0.8786521	2.1901841	4.3158296
29	H	H11	-0.8153057	0.4773699	2.5027481
30	H	H14	-0.8638464	-5.2940721	-2.7596566
31	H	H15	5.0237308	1.1886002	-3.1511878
32	H	H17	3.6569483	-0.8628280	-3.6729039

33	C	C1	4.2880824	2.9607853	-1.0008019
34	C	C2	3.4910634	3.3879909	0.0854681
35	C	C3	3.9107067	4.5028093	0.8295984
36	C	C4	5.0692215	5.1912328	0.4426240
37	H	H18	5.3746258	6.0573046	1.0267564
38	C	C5	5.8306481	4.7858694	-0.6621719
39	H	H20	6.7239620	5.3420999	-0.9426470
40	C	C6	5.4431310	3.6565943	-1.3825634
41	H	H23	6.0349349	3.3031407	-2.2245891
42	C	C28	-2.8692367	-4.3389025	-0.8990097
43	C	C29	-3.4134258	-5.6233221	-1.0280753
44	H	H19	-2.9297125	-6.3523081	-1.6756258
45	C	C30	-4.5689878	-5.9493095	-0.3141343
46	H	H26	-5.0057423	-6.9398855	-0.3998036
47	C	C31	-5.1695609	-4.9948183	0.5188149
48	H	H27	-6.0692257	-5.2378812	1.0822806
49	C	C32	-4.7831018	0.6958250	0.9397793
50	H	H4	-5.8052400	0.8977037	1.2460947
51	C	C33	-3.8642589	1.7360094	0.7577843
52	H	H13	-4.1307820	2.7789369	0.8833760
53	C	C34	-2.5719507	1.3811013	0.4458872
54	H	H2	-1.8016083	2.1332006	0.3331604
55	N	N2	-2.1527194	0.1001705	0.2677705
56	H	H41	1.1179029	-3.8692430	-3.3742553
57	H	H9	-5.1653224	-3.0179899	1.2964779
58	H	H16	-5.0931137	-1.3940914	0.9161182
59	H	H24	3.4051494	4.8624079	1.7102846
60	H	H25	1.7832947	4.5300452	1.8986182

Point Group = C1 Order = 1 Nsymop = 1

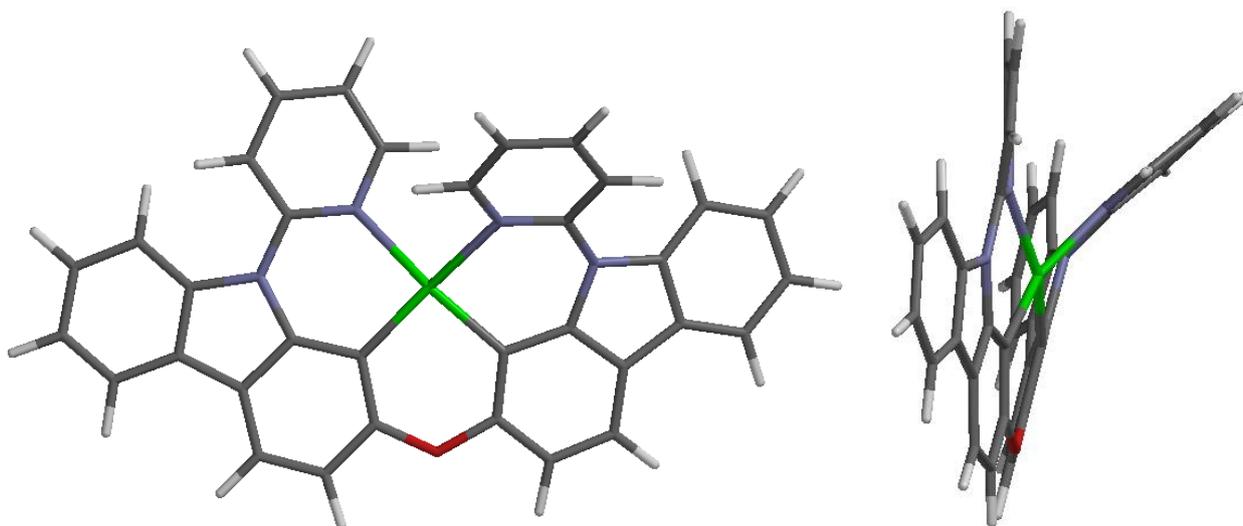


Figure S11. Optimized molecular structure of **PdNON** based on the DFT calculation, top-view (left) and side-view (right)

Job WF32422 started on GUIJIELI at Thu Jun 22 04:12:24 2017

Jaguar version 3.5, release 42

Job name: WF32422
Task: Geometry optimization
Stoichiometry: PdC34N4H200
Molecular weight: 606.07 amu
Molecular charge: 0
Spin multiplicity: 1
Point Group: C1
SCF method: B3LYP
Basis set: LACVP**
Basis functions: 668
Total electrons: 278
Alpha electrons: 139
Beta electrons: 139
Total orbitals: 710

Core orbitals: 139
Open-shell orbitals: 0
Occupied orbitals: 139
Shells: 1

Non-default options chosen:

SCF calculation type: DFT

DFT=Becke_3_Parameter/HF+Slater+Becke88+VWN+LYP (B3LYP)

Geometry will be optimized in redundant internal coordinates

Initial Hessian: from previous calculation

Iter	Energy	Gmax	Grms	Dmax	Drms
1	-1728.681314 *	0.02607 .	0.00350 .	0.10309 .	0.01906 .
2	-1728.691578 .	0.01668 .	0.00219 .	0.11244 .	0.01907 .
3	-1728.694855 .	0.01146 .	0.00211 .	0.11593 .	0.01907 .
** restarting optimization from step 3 **					
3	-1728.681547 .	0.01146 .	0.00211 .	0.15257 .	0.01905 .
5	-1728.698280 .	0.00822 .	0.00167 .	0.10117 .	0.01905 .
6	-1728.698206 .	0.01611 .	0.00286 .	0.12162 .	0.01904 .
7	-1728.699978 .	0.00844 .	0.00196 .	0.07924 .	0.01905 .
** restarting optimization from step 7 **					
7	-1728.695283 .	0.00844 .	0.00196 .	0.11389 .	0.01911 .
** restarting optimization from step 7 **					
7	-1728.684949 .	0.00844 .	0.00196 .	0.03927 .	0.00957 .
** restarting optimization from step 7 **					
7	-1728.696049 .	0.00844 .	0.00196 .	0.02316 .	0.00477 .
** stopping now - optimization seems to be stuck **					
11	-1728.699767 !	0.00000 #	0.00000 #	0.00000 #	0.00000 #

** Geometry optimization complete **

Final energy -1728.69976652055

Job WF32422 completed on GUIJIELI at Thu Jun 22 06:21:43 2017

Reason for exit: Successful completion

Titan Program CPU Time : 002:05:20.9

Titan Program Wall Time: 002:09:19.2

TITAN Properties Program: (PC/x86)
6.0.6

Release

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 278

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
1 C C02	-4.1481074	1.2548823	3.7715263
2 C C03	-4.4626483	0.5096204	0.7259867
3 C C04	0.4310345	3.2020204	-3.5183961
4 C C05	-0.3676527	3.4113736	-2.3898763
5 C C10	-3.2177009	0.2696986	3.4294212
6 C C08	1.3279074	2.1471926	-3.5365636
7 C C09	-0.3185183	2.4390293	-1.4111030
8 C C36	-3.0790410	0.2983577	0.9367842
9 C C11	1.4363101	1.3029971	-2.4113707

10	N	N12	0.5056714	1.3659403	-1.4412911
11	N	N3	-2.5521776	0.0372316	2.2002735
12	N	N1	2.4471676	0.3680805	-2.3087764
13	C	C16	-1.5021939	-0.9154939	2.4350297
14	C	C17	2.5437219	-0.7285626	-1.3775027
15	C	C18	-1.6363767	-1.3763703	3.7654654
16	C	C19	-0.4739273	-1.3154697	1.5676208
17	C	C20	1.6735186	-1.1165742	-0.3391410
18	C	C21	3.7170331	-1.4462853	-1.7110623
19	C	C22	-0.7684441	-2.3669699	4.2419819
20	C	C23	0.3692009	-2.2983407	2.0945128
21	C	C24	2.0784534	-2.2767125	0.3434583
22	C	C25	4.0579536	-2.6111975	-1.0158072
23	C	C26	0.2197503	-2.8401280	3.3911026
24	C	C27	3.2277486	-3.0251975	0.0104529
25	O	O1	1.4420795	-2.8336693	1.4272400
26	H	H6	-1.0484990	4.2517678	-2.3033335
27	H	H11	-0.9787374	2.4778407	-0.5567005
28	H	H14	-0.8596716	-2.7491853	5.2545046
29	H	H15	4.9518979	-3.1705630	-1.2736546
30	H	H17	3.4397257	-3.9150552	0.5973549
31	C	C1	4.4021225	-0.7564450	-2.7818124
32	C	C2	3.6199289	0.3687531	-3.1201500
33	C	C3	4.0965598	1.3130896	-4.0348168
34	C	C4	5.3305243	1.0735046	-4.6446941
35	H	H18	5.7033168	1.8028739	-5.3562459
36	C	C5	6.0896143	-0.0656881	-4.3497261
37	H	H20	7.0425041	-0.2285923	-4.8406998
38	C	C6	5.6326066	-0.9775418	-3.4048815

39	H	H23	6.2345889	-1.8358557	-3.1201088
40	C	C28	-2.6918401	-0.6155385	4.3992527
41	C	C29	-3.1640799	-0.5643659	5.7122780
42	H	H19	-2.7651585	-1.2422315	6.4619560
43	C	C30	-4.1299143	0.3848151	6.0492035
44	H	H26	-4.5003860	0.4372436	7.0671698
45	C	C31	-4.6019230	1.2957114	5.0907165
46	H	H27	-5.3156748	2.0630610	5.3779304
47	C	C32	-4.9395090	0.6903624	-0.5587751
48	H	H4	-6.0005950	0.8459657	-0.7208145
49	C	C33	-4.0493913	0.6419770	-1.6378766
50	H	H13	-4.3796392	0.7590851	-2.6621019
51	C	C34	-2.7128107	0.4286971	-1.3537115
52	H	H2	-1.9731546	0.3683140	-2.1430151
53	N	N2	-2.2229029	0.2891573	-0.1020010
54	H	H41	0.9287221	-3.6005223	3.7068160
55	H	H9	-4.4683887	2.0135203	3.0563869
56	H	H16	-5.1469265	0.4771809	1.5587456
57	H	H24	3.5833761	2.2429953	-4.2261021
58	H	H25	1.8934126	1.9289481	-4.4227257
59	H	H10	0.3570212	3.8593975	-4.3763904
60	Pd	Pd1	-0.0820745	-0.2236405	-0.0549663

Point Group = C1 Order = 1 Nsymop = 1