Supporting Information

Selective C-H functionalizations of arenes catalyzed by poly NHC-Pd in flow

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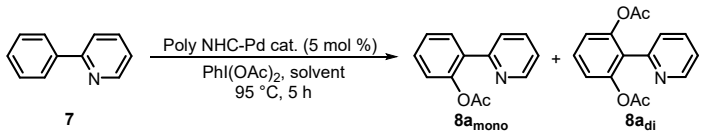
Table of Contents

1. Supporting Tables

Table S1. Optimizations of selective acetoxylation in batch



7 **8a**$_{mono}$ **8a**$_{di}$

Entry	Poly cat.	Solvent	$PhI(OAc)_2$ (equiv.)	Yield (%) [a]	
				8a$_{mono}$	**8a**$_{di}$
1	**4**	DCE	1.5	21	4
2	**4**	DCM	1.5	26	32
3	**5**	DCM	1.5	31	40
4	**6**	DCM	1.5	28	35
5	**5**	CH_3CN	1.5	1.1	0
6	**5**	THF	1.5	0	0
7	**5**	1,4-dioxane	1.5	0	0
8	**5**	DMF	1.5	0	0
9	**5**	AcOH	1.5	0	0
10	**5**	Ac_2O	1.5	32	46
11	**5**	Toluene	1.5	9	61
12	**5**	HFIP	1.5	4	0
13	**5**	DCM/Ac_2O [b]	1.5	32	48
14	**5**	AcOH/Ac_2O [b]	1.5	31	54
15	**5**	AcOH/Ac_2O [b]	1.4	33	49
16	**5**	AcOH/Ac_2O [b]	1.3	38	30
17 [c]	**5**	AcOH/Ac_2O [b]	1.5	0	0

[a] Yields were determined by LC-MS internal standard method with mesitylene. [b] The volume ratio of co-solvent was 1:1. [c] No catalyst was added.

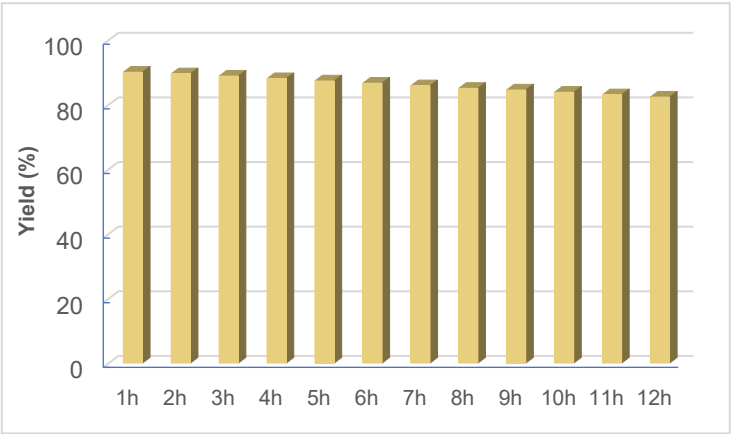
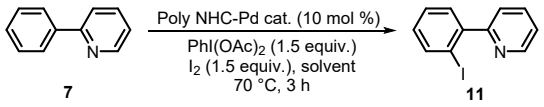


Fig. S1 The continuous operation of flow acetoxylation.

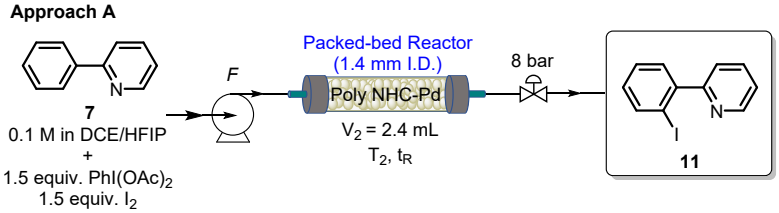
Table S2. Optimizations of selective iodination in batch



Entry	Poly cat.	Solvent	Time (h)	Yield (%) [a]
1	**5**	DCE	3	81
2	**5**	DCM	3	29
3	**4**	DCE	3	65
4	**6**	DCE	3	70
5	**5**	CH_3CN	3	55
6	**5**	NMP	3	71
7	**5**	1,4-dioxane	3	83
8	**5**	DMF	3	84
9	**5**	AcOH	3	0
10	**5**	HFIP	3	52
11	**5**	DCE/HFIP (v:v = 2:1)	3	70
12	**5**	DCE/HFIP (v:v = 4:1)	3	88
13	**5**	DCE/HFIP (v:v = 6:1)	3	82
14	**5**	DCE/HFIP (v:v = 4:1)	1	91
15 [b]	**5**	DCE/HFIP (v:v = 4:1)	1	0
16 [c]	**5**	DCE/HFIP (v:v = 4:1)	1	0

[a] Yields were determined by LC-MS internal standard method with mesitylene. [b] The reaction was carried out in the absence of catalyst. [c] The reaction was carried out in the absence of I_2.

Table S3. Optimizations of selective iodination in flow using packed-bed reactor.

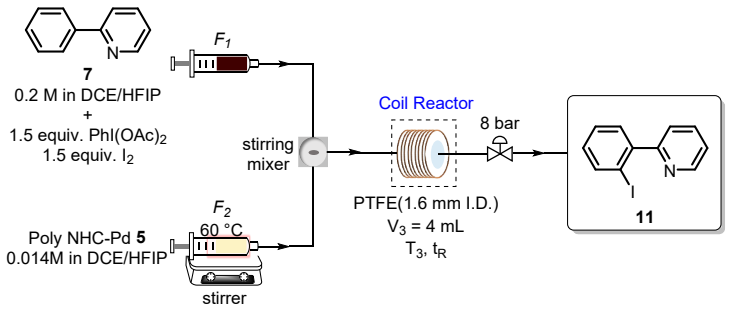


Entry	T (°C)	t_R (min)	*F* (mL/min)	Yield (%)[a]
1	70	15	0.16	38
2	80	15	0.16	50
3	90	15	0.16	61

4	100	15	0.16	69(60)[b]
5	105	15	0.16	66
6	100	10	0.24	64

[a] Yields were determined by LC-MS internal standard method with mesitylene. [b] Isolated yield.

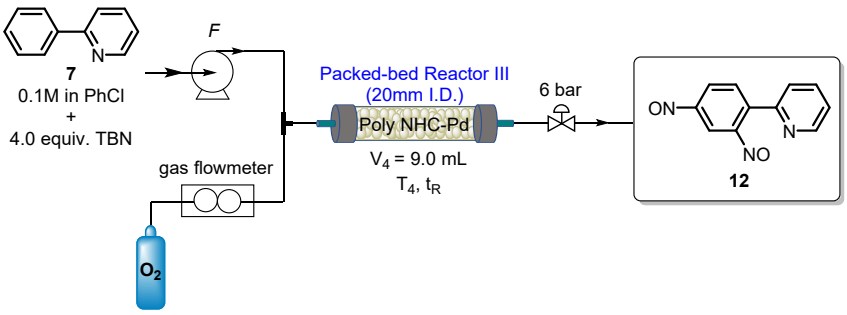
Table S4. Optimizations of selective iodination in flow using PTFE coil reactor.



Entry	T_3 (°C)	t_R (min)	F_1 (mL/min)	F_2 (mL/min)	Yield (%)[a]
1	80	15	0.13	0.13	61
2	90	15	0.13	0.13	73
3	100	15	0.13	0.13	79
4	105	15	0.13	0.13	78
5	105	10	0.2	0.2	88(80)[b]
6	105	8	0.25	0.25	75

[a] Yields were determined by LC-MS internal standard method with mesitylene. [b] Isolated yield.

Table S5. Optimizations of selective nitrosation in flow using packed-bed reactor.



Entry	T_4 (°C)	t_R (min)	O_2 (sccm)	F (mL/min)	Yield (%)[a]
1	90	6	5.0	0.6	57
2	100	6	5.0	0.6	69
3	105	6	5.0	0.6	85(78)[b]
4	110	6	5.0	0.6	79
5	105	9	3.4	0.4	68
6	105	4	7.6	0.9	72

[a] Yields were determined by LC-MS internal standard method with mesitylene. [b] Isolated yield.

2. General Information

Unless otherwise noted, solvents were purified according to standard methods prior to use. All the reactions were monitored by thin-layer chromatography (TLC) and LC-MS (Agilent 1260 Infinity II with an Agilent InfinityLab LC/MSD series, Agilent ProsheII120 EC-C18, RRHD 2.7 μm, 2.1 × 50 mm). The column chromatography characterization was performed with silica gel (200-300 mesh). All new compounds were characterized by NMR spectroscopy, high resolution mass spectroscopy (HRMS). ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance 400). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), and CD_3OD (δ = 3.31 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16 ppm), the central DMSO-d_6 resonance (δ = 39.50 ppm), and the central CD_3OD resonance (δ = 49.00 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. HRMS spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). X-Ray crystallographic structure was recorded on a Bruker D8 VENTURE MetalJet X-ray single crystal diffractometer. SEM was recorded on ZEISS Sigma 300. TEM was recorded on JEOL JEM-2100Plus. ICP-OES was recorded on Agilent 720ES.

3. Flow Experimental Equipment Information

The continuous flow system was established, which include commercial available feeding equipments, continuous reactors and process control unit etc.

The main devices information is as follows:

Feeding equipments: syringe pump (Fusion 4000, CHEMYX), plunger pump (AP0010, SANOTAC).

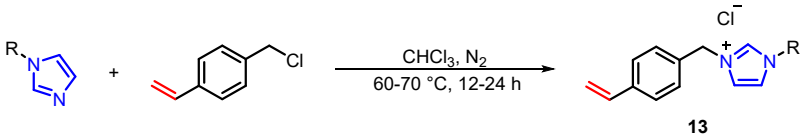
Continuous reactors: stainless steel (SS) packed bed (MF200, Shen zhen E-Zheng tech Co., Ltd), PTFE coil reactor (0.8 mm I.D. and 1.6 mm I.D.) and PTFE fittings (Run Ze Fluid), stainless steel (SS) coil reactor (0.6 mm I.D.) and stainless steel fittings (Shang hai Xitai Fluid Technology Co.,

Ltd) and High-precision temperature chamber(Jiangsu Hengmin Instrument Manufacturing Co., Ltd).

Process control unit: back-pressure valve (0-300 psi, FAV-300B, Shen zhen insftech), heating tapes (L = 250mm, W =10 mm, U = 220 v, P = 120 w).

4. Synthesis of NHCs

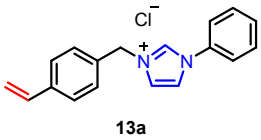
4.1 Experimental procedures



To a 25 mL round bottom flask, imidazole (10.0 mmol, 1.0 equiv.) was added. The flask was evacuated and backfilled with N_2 (3 cycles), then a solution of 4-vinylbenzyl chloride (11.0 mmol, 1.1 equiv.) in 15 mL dry chloroform were added. The mixture was stirred at 60-70 ℃ for 12-24 h. Then the reation mixture was removed in vacuum. The resulting residue was purified by short silica column flash chromatography (DCM/MeOH = 30:1) to give the corresponding NHCs (**13**).[1]

4.2 Characterization data of NHCs

1-phenyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13a**) [2]



2.8 g, 95% yield

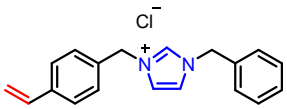
Physical State: pale yellow solid

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.38 (s, 1H), 8.09 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.6 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.54 (s, 4H), 6.75 (dd, J = 11.2, 6.8 Hz, 1H), 5.88 (d, J = 17.6 Hz, 1H), 5.53 (s, 2H), 5.30 (d, J = 11.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 137.6, 135.0, 135.7, 134.7, 134.1, 130.1, 129.7, 129.1, 126.6, 123.2, 121.7, 121.4, 115.3, 51.9.

HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2^+$ [M-Cl]$^+$: 261.1386, found: 261.1386.

1-benzyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13b**) [3]



13b

2.9 g, 93% yield

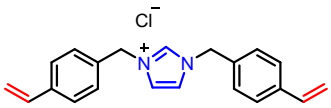
Physical State: pale yellow viscous liquid

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 7.87 (s, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.43 (m, 7H), 6.74 (dd, J = 11.2, 6.8 Hz, 1H), 5.87 (d, J = 18.0 Hz, 1H), 5.45 (d, J = 5.2 Hz, 4H), 5.30 (d, J = 11.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 137.6, 136.4, 135.0, 134.0, 134.4, 129.1, 128.9, 128.8, 128.4, 126.7, 122.9, 115.4, 51.0, 51.7.

HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2^+$ [M-Cl]$^+$: 275.1543, found: 275.1543.

1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13c**)



13c

3.0 g, 90% yield

Physical State: yellow viscous liquid

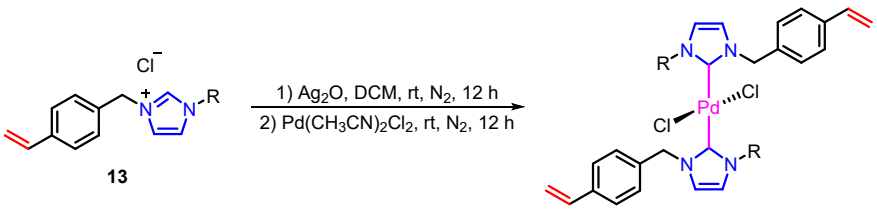
^{1}H NMR (400 MHz, CD_3OD) δ 7.64 (s, 2H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 6.75 (dd, *J* = 17.6, 10.8 Hz, 2H), 5.83 (dd, *J* = 18.4, 0.8 Hz, 2H), 5.41 (s, 4H), 5.29 (dd, *J* = 10.8, 0.8 Hz, 2H).

^{13}C NMR (100 MHz, CD_3OD) δ 140.1, 137.2, 134.5, 129.0, 128.1, 124.0, 115.5.

HRMS (ESI) m/z calcd for $C_{21}H_{21}N_2^+$ [M-Cl]$^+$: 301.1699, found: 301.1699.

5. Synthesis of NHC-Pds

5.1 Experimental procedures [4]



Step 1: synthesis of NHC-Ags

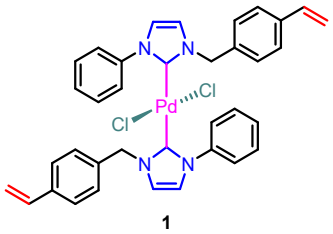
To a 250 mL round bottom flask, Ag_2O (5.5 mmol, 0.55 equiv.) was added. The flask was evacuated and backfilled with N_2 (3 cycles), then a solution of NHCs **13** (10.0 mmol, 1.0 equiv.) in 100 mL dry dichloromethane were added. The mixture was stirred at room temperature for 12 h for transmetalation.

Step 2: synthesis of NHC-Pds

Under N_2 atmosphere, $Pd(CH_3CN)_2Cl_2$(5.0 mmol, 0.5 equiv.) was added to the flask containing NHC-Ags solution obtained in the previous step. The mixture was stirred at room temperature for 12 h. Then the reaction mixture was filtered, and the filtrate is decolorized by activated carbon. The filtrate was removed in vacuum to afford the crude product of NHC-Pds, which was washed with methanol (3 cycles) to afford NHC-Pds.

5.2 Characterization data of NHC-Pds

bis(1-phenyl-3-(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**1**)



1

2.8 g, 80% yield

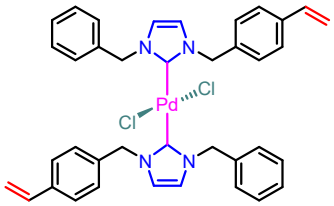
Physical State: golden yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 4H), 7.50 (d, J = 8.4 Hz, 4H), 7.46 (d, J = 8.3 Hz, 4H), 7.21 – 7.16 (m, 6H), 7.09 (d, J = 2.0 Hz, 2H), 6.79 – 6.72 (m, 4H), 5.80 (dd, J = 17.6, 1.2 Hz, 2H), 5.61 (s, 4H), 5.29 (dd, J = 10.8, 0.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 140.1, 137.7, 136.5, 135.7, 129.1, 129.0, 128.2, 126.9, 125.52, 122.3, 120.8, 114.5, 54.3.

HRMS (ESI) m/z calcd for $C_{36}H_{32}ClN_4Pd^+$ $[M\text{-}Cl]^+$: 661.1345, found: 661.1339.

bis(1-benzyl-3-(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**2**)



2

2.3 g, 65% yield

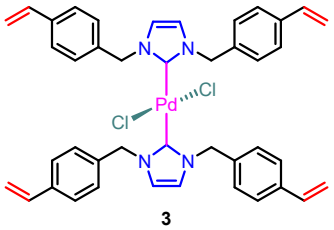
Physical State: Pale yellowish white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 8H), 7.35 – 7.26 (m, 10H), 6.70 – 6.61 (m, 6H), 5.73 – 5.65 (m, 10H), 5.22 (d, *J* = 10.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 137.4, 136.5, 136.3, 135.9, 128.9, 128.8, 128.8, 128.7, 128.68, 128.2, 128.2, 126.7, 121.1, 121.0, 114.3, 114.2, 54.4, 54.4, 54.1, 54.1.

HRMS (ESI) m/z calcd for $C_{38}H_{36}ClN_4Pd^+$ $[M\text{-}Cl]^+$: 689.1658, found: 689.1661.

bis(1,3-bis(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**3**)



3

2.3 g, 60% yield

Physical State: golden yellow solid

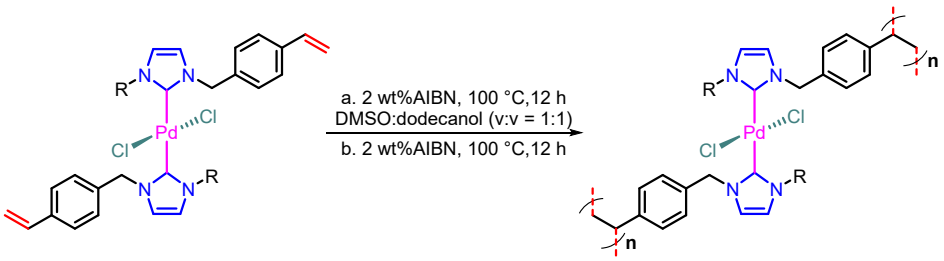
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 8H), 7.32 (d, *J* = 8.0 Hz, 8H), 6.72 – 6.58 (m, 8H), 5.70 (d, *J* = 19.6 Hz, 12H), 5.22 (d, *J* = 10.8 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 137.4, 136.4, 135.9, 128.8, 126.7, 121.1, 114.2, 54.1.

HRMS (ESI) m/z calcd for $C_{42}H_{40}ClN_4Pd^+$ $[M\text{-}Cl]^+$: 741.1971, found: 741.1669.

6. Synthesis of Poly NHC-Pd Catalysts

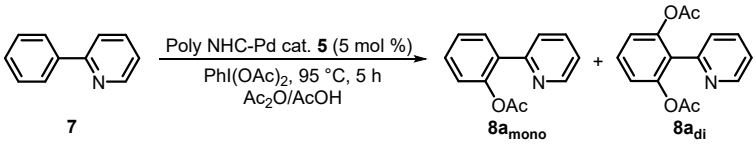
6.1 Experimental procedures



To a 50 mL reaction tube, NHC-Pd (1.0 g) and AIBN (20 mg, 2 wt%) in 10 mL dimethyl sulfoxide and 10 mL 1-Dodecanol were added. The mixture was stirred at 100 ℃ for 12 h. [5] Afterward, AIBN (20 mg, 2 wt%) was added before being heated at 100 ℃ for a further 12 h. Then 200 ml of methanol was added to the reaction solution to precipitate the polymers. The mixture was filtered and the solid was washed with methanol (3 cycles) to afford poly NHC-Pd catalysts.

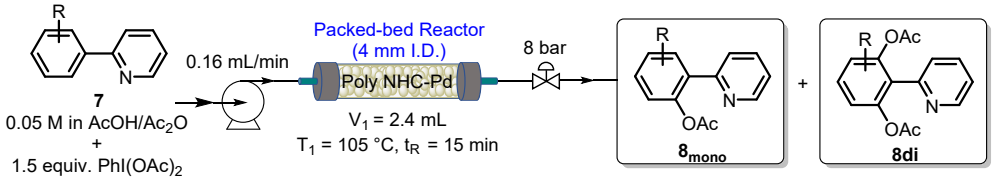
7. C-H acetoxylation of 2-Phenylpyridine compounds

7.1 Experimental procedures in batch



To a 10 mL reaction tube, **7** (0.6 mmol, 1 equiv.), diacetoxyiodo benzene (0.9 mmol, 1.5 equiv.) and poly NHC-Pd catalyst **5** (0.03 mmol, 5 mol%) in acetic acid (3 mL) and acetic anhydride (3 mL) were added. The reaction mixture was heated to 95 ℃ for 5 h. Then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / EtOAc = 2:1) to give the product $\mathbf{8}_{\mathbf{mono}}$ and $\mathbf{8}_{\mathbf{di}}$. [6]

7.2 Experimental procedure in flow

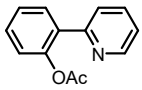


One flow stream was delivered into the flow reactor by the plunger pump (AP0010, SANOTAC). The stream contained a solution of **7** (1.0 mmol, 1.0 equiv.) and diacetoxyiodo benzene (1.5 mmol,

1.5 equiv.) in acetic acid (10 mL) and acetic anhydride (10 mL). This stream was pumped through the packed-bed reactor (2.4 mL internal volume, t_R = 15 min, 300 mg poly NHC-Pd catalyst **5** and 1.5 g 60-80 mesh silica gel powder were packed in it) at 105 ℃ at a flow rate of 0.16 mL/min. A 8.0 bar back-pressure regulator (BPR) was connected at the outlet of packed-bed reactor. The output from the packed-bed reactor was collected for 63 minutes (10 mL), then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / EtOAc = 2:1) to give the product $\mathbf{8}_{\mathbf{mono}}$ and $\mathbf{8}_{\mathbf{di}}$.

7.3 Characterization data of product $\mathbf{8}_{\mathbf{mono}}$ and $\mathbf{8}_{\mathbf{di}}$

2-(pyridin-2-yl)phenyl acetate ($\mathbf{8a}_{\mathbf{mono}}$) [7]



$\mathbf{8a}_{\mathbf{mono}}$

33.0 mg, 31% yield

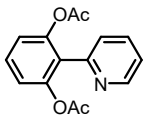
Physical State: light red oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.36 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29 (td, *J* = 7.6, 1.6 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.10 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 155.8, 149.6, 148.2, 136.6, 133.1, 130.9, 129.9, 126.6, 123.8, 123.3, 122.4, 21.1.

HRMS (ESI) m/z calcd for $C_{13}H_{12}NO_2^+$ $[M+H]^+$: 214.0863, found: 214.0863.

2-(pyridin-2-yl)-1,3-phenylene diacetate ($\mathbf{8a}_{\mathbf{di}}$) [8]



$\mathbf{8a}_{\mathbf{di}}$

63.7 mg, 47% yield

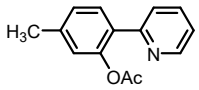
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.66 (td, *J* = 7.6, 2.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.25 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 1.95 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.98, 151.16, 148.38, 148.03, 135.06, 128.41, 126.40, 124.11, 121.55, 119.67, 19.59.

HRMS (ESI) m/z calcd for $C_{15}H_{14}NO_4^+$ $[M+H]^+$: 272.0917, found: 272.0917.

5-methyl-2-(pyridin-2-yl)phenyl acetate (**8b$_{mono}$**) [7]



8b$_{mono}$

42.0 mg, 37% yield

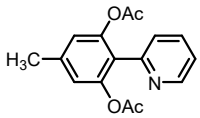
Physical State: light orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.63 (td, *J* = 7.6, 2.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.08 (ddd, *J* = 8.0, 1.6, 0.8 Hz, 1H), 6.90 (d, *J* = 0.8 Hz, 1H), 2.32 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 154.8, 148.5, 146.9, 139.2, 135.2, 129.5, 129.2, 126.2, 122.7, 122.4, 120.9, 20.1, 20.0.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

5-methyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8b$_{di}$**) [9]



8b$_{di}$

68.4 mg, 48% yield

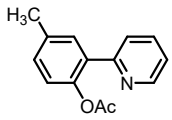
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.61 (td, *J* = 7.6, 1.6 Hz, 1H), 7.22 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.85 – 6.80 (m, 2H), 2.31 (s, 3H), 1.93 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 152.4, 149.4, 148.8, 140.1, 135.9, 125.1, 124.7, 122.4, 121.3, 21.3, 20.6.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$: 286.1074, found: 286.1074.

4-methyl-2-(pyridin-2-yl)phenyl acetate (**8c$_{mono}$**) [7]



8c$_{mono}$

57.9 mg, 51% yield

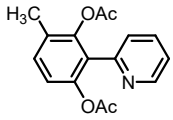
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.66 (td, *J* = 7.6, 2.0 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 2.34 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 155.9, 149.6, 145.9, 136.5, 136.3, 132.7, 131.4, 130.5, 123.8, 123.0, 122.3, 21.1, 21.6.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

4-methyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8c$_{di}$**)



8c$_{di}$

25.6 mg, 18% yield

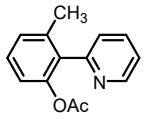
Physical State: bright yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.64 (td, *J* = 7.6, 2.0 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 2.13 (s, 3H), 1.93 (d, *J* = 2.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.5, 152.8, 149.5, 147.6, 147.0, 136.0, 130.98, 129.1, 127.6, 125.1, 122.5, 120.5, 20.7, 20.3, 16.3.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$: 286.1074, found: 286.1074.

3-methyl-2-(pyridin-2-yl)phenyl acetate (**8d$_{mono}$**) [7]



8d$_{mono}$

86.3 mg, 76% yield

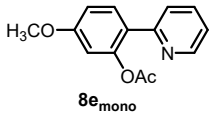
Physical State: orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.63 (td, *J* = 7.6, 1.6 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 2.07 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 155.7, 149.4, 148.3, 138.0, 135.9, 133.5, 128.7, 127.9, 124.6, 122.0, 119.9, 20.40, 19.8.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

5-methoxy-2-(pyridin-2-yl)phenyl acetate (**8e$_{mono}$**) [7]



8e$_{mono}$

54.7 mg, 45% yield

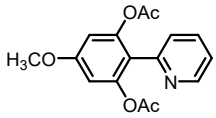
Physical State: orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.62 (td, *J* = 7.6, 2.0 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.42 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.11 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 3.75 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 160.8, 155.7, 149.4, 149.1, 136.4, 131.5, 125.6, 123.3, 121.8, 112.4, 108.8, 55.6, 21.1.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_3^+$ $[M+H]^+$: 244.0968, found: 244.0968.

5-methoxy-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8e$_{di}$**) [9]



8e$_{di}$

24.1 mg, 16% yield

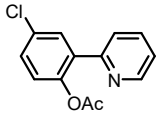
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.70 (td, *J* = 7.6, 2.0 Hz, 1H), 7.30 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.23 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.66 (s, 2H), 3.82 (s, 3H), 2.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 160.2, 152.4, 149.8, 149.4, 136.0, 125.3, 122.3, 120.2, 106.9, 55.7, 20.7.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_5^+$ $[M+H]^+$: 302.1023, found: 302.1023.

4-chloro-2-(pyridin-2-yl)phenyl acetate (**8f$_{mono}$**)



8f$_{mono}$

66.7 mg, 54% yield

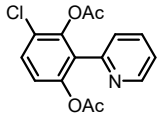
Physical State: brown oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 2.0, 1.2 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.65 (d, *J* = 2.6 Hz, 1H), 7.47 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 154.6, 149.8, 146.7, 136.7, 134.6, 131.9, 130.8, 129.8, 124.8, 123.8, 122.9, 21.1.

HRMS (ESI) m/z calcd for $C_{13}H_{10}ClNO_2^+$ $[M+H]^+$: 248.0473, found: 248.0473.

4-chloro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8f$_{di}$**)



8f$_{di}$

10.7 mg, 7% yield

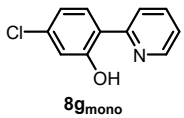
Physical State: brown solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (ddd, *J* = 4.8, 2.0, 1.2 Hz, 1H), 7.74 (td, *J* = 7.6, 2.0 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 2.08 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 167.9, 151.8, 149.7, 147.6, 145.8, 136.3, 130.0, 129.7, 125.6, 125.0, 123.0, 121.8, 20.7, 20.3.

HRMS (ESI) m/z calcd for $C_{15}H_{12}ClNO_4^+$ $[M+H]^+$: 306.0528, found: 306.0528.

5-chloro-2-(pyridin-2-yl)phenol (**8g$_{mono}$**) [9]



8g$_{mono}$

32.8 mg, 32% yield

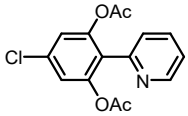
Physical State: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 14.43 (s, 1H), 8.36 (dt, *J* = 5.2, 1.6 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.0, 145.8, 138.1, 136.7, 127.1, 121.9, 119.1, 119.1, 118.6, 117.4.

HRMS (ESI) m/z calcd for $C_{11}H_9ClNO^+$ $[M+H]^+$: 206.0367, found: 206.0367.

5-chloro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8g$_{di}$**) [9]



8g$_{di}$

16.8 mg, 11% yield

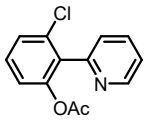
Physical State: red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.73 (td, *J* = 8.0, 1.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.13 (s, 2H), 2.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 151.6, 149.7, 149.5, 136.2, 134.5, 126.5, 125.2, 122.9, 121.5, 20.7.

HRMS (ESI) m/z calcd for $C_{15}H_{13}ClNO_4^+$ $[M+H]^+$: 306.0528, found: 306.0528.

3-chloro-2-(pyridin-2-yl)phenyl acetate (**8h$_{mono}$**) [10]



8h$_{mono}$

107.4 mg, 87% yield

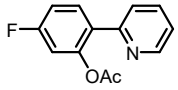
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.22 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 1.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 153.6, 149.4, 149.4, 136.1, 133.9, 133.2, 129.7, 127.4, 125.4, 122.8, 121.6, 20.4.

HRMS (ESI) m/z calcd for $C_{13}H_{11}ClNO_2^+$ $[M+H]^+$: 248.0473, found: 248.0473.

5-fluoro-2-(pyridin-2-yl)phenyl acetate (**8i$_{mono}$**) [9]



8i$_{mono}$

61.2 mg, 53% yield

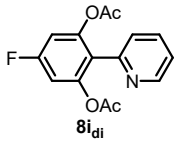
Physical State: light orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.62 – 7.59 (m, 1H), 7.42 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.98 (td, *J* = 8.4, 2.8 Hz, 1H), 6.85 (dd, *J* = 9.2, 2.8 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 161.7 (d, *J* = 250.1 Hz), 153.9, 148.6, 147.8 (d, *J* = 11.0 Hz), 135.4, 130.9 (d, J = 9.2 Hz), 128.4 (d, *J* = 3.7 Hz), 122.4, 121.2, 112.5 (d, *J* = 21.0 Hz), 110.0 (d, *J* = 24.2 Hz), 19.9.

HRMS (ESI) m/z calcd for $C_{13}H_{11}FNO_2^+$ $[M+H]^+$: 232.0768, found: 233.0768.

5-fluoro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8i$_{di}$**) [9]



8i$_{di}$

30.3 mg, 21% yield

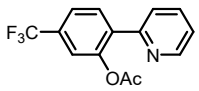
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.66 (td, *J* = 7.6, 1.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 1.96 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.0 (d, *J* = 249.9 Hz), 150.5, 148.7 (d, *J* = 12.9 Hz), 148.4, 135.3, 124.3, 122.7 (d, *J* = 4.5 Hz), 121.7, 107.8 (d, *J* = 24.3 Hz), 19.5.

HRMS (ESI) m/z calcd for $C_{15}H_{13}FNO_4^+$ $[M+H]^+$: 290.0823, found: 290.0823.

2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl acetate (**8j$_{mono}$**) [9]



8j$_{mono}$

59.0 mg, 42% yield

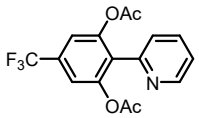
Physical State: light yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.71 (td, *J* = 7.6, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.0, 1.6, 0.8 Hz, 1H), 7.50 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.24 (ddd, *J* = 7.2, 2.4, 1.2 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 153.4, 148.7, 147.1, 135.6, 135.4, 130.80 (q, *J* = 33.2 Hz), 130.5, 123.8, 122.7, 122.12 (q, *J* = 3.7 Hz), 121.9, 121.1, 119.7 (q, *J* = 3.9 Hz), 19.8.

HRMS (ESI) m/z calcd for $C_{14}H_{11}F_3NO_2^+$ $[M+H]^+$: 282.0736, found: 282.0736.

2-(pyridin-2-yl)-5-(trifluoromethyl)-1,3-phenylene diacetate (**8j$_{di}$**) [9]



8j$_{di}$

40.7 mg, 24% yield

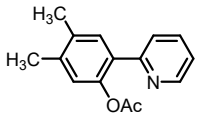
Physical State: light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.4 Hz, 1H), 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.38 (d, *J* = 0.8 Hz, 2H), 7.34 – 7.29 (m, 2H), 2.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 151.2, 149.8, 149.6, 136.4, 131.73 (q, *J* = 34.1 Hz), 125.2, 123.2, 118.1 (q, *J* = 3.7 Hz), 20.6.

HRMS (ESI) m/z calcd for $C_{16}H_{13}F_3NO_4^+$ $[M+H]^+$: 340.0791, found: 340.0791.

4,5-dimethyl-2-(pyridin-2-yl)phenyl acetate (**8k$_{mono}$**)



8k$_{mono}$

80.7 mg, 67% yield

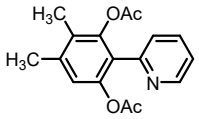
Physical State: orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.8, 2.0, 1.2 Hz, 1H), 7.58 (td, *J* = 7.6, 2.0 Hz, 1H), 7.42 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.40 (s, 1H), 7.09 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.83 (s, 1H), 2.19 (s, 6H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 154.8, 148.5, 144.8, 137.6, 135.1, 133.8, 130.5, 129.1, 123.0, 122.4, 120.8, 19.9, 18.6, 18.2.

HRMS (ESI) m/z calcd for $C_{15}H_{15}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1176.

4,5-dimethyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8k$_{di}$**)



8k$_{di}$

19.4 mg, 13% yield

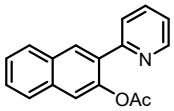
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.62 (td, *J* = 7.6, 2.0 Hz, 1H), 7.21 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.16 (ddd, *J* = 7.2, 2.4, 1.2 Hz, 1H), 6.85 (s, 1H), 2.27 (s, 3H), 2.01 (s, 3H), 1.92 (d, *J* = 2.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 167.6, 151.9, 148.3, 146.3, 145.1, 138.0, 134.9, 126.6, 124.1, 121.3, 120.7, 19.6, 19.3, 11.6.

HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_4^+$ $[M+H]^+$: 300.1230, found: 300.1230.

3-(pyridin-2-yl)naphthalen-2-yl acetate (**8l$_{mono}$**)[11]



8l$_{mono}$

59.2 mg, 45% yield

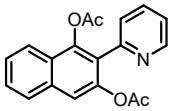
Physical State: orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 2.0, 1.2 Hz, 1H), 8.06 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.62 (td, *J* = 7.6, 2.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.41 – 7.34 (m, 2H), 7.15 – 7.11 (m, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 154.9, 148.5, 144.9, 135.3, 132.6, 131.4, 130.6, 129.6, 127.2, 126.2, 126.0, 125.1, 122.7, 121.2, 119.5, 19.9.

HRMS (ESI) m/z calcd for $C_{17}H_{13}NO_2^+$ $[M+H]^+$: 264.1019, found: 264.1019.

2-(pyridin-2-yl)naphthalene-1,3-diyl diacetate (**8l$_{di}$**)



8l$_{di}$

33.7 mg, 21% yield

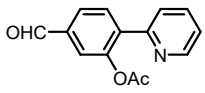
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.69 (td, *J* = 7.6, 1.6 Hz, 1H), 7.54 (s, 1H), 7.50 – 7.42 (m, 2H), 7.35 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 2.09 (s, 3H), 1.97 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.0, 152.9, 149.7, 146.0, 145.5, 136.1, 133.8, 127.9, 127.7, 126.8, 125.8, 125.7, 125.5, 122.7, 122.1, 118.6, 20.8, 20.6.

HRMS (ESI) m/z calcd for $C_{19}H_{15}NO_4^+$ $[M+H]^+$: 322.1074, found: 322.1074.

5-formyl-2-(pyridin-2-yl)phenyl acetate (**8m$_{mono}$**) [7]



8m$_{mono}$

44.6 mg, 37% yield

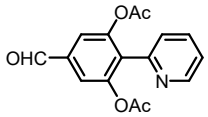
Physical State: orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.66 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.53 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 168.1, 153.5, 148.8, 147.6, 137.7, 136.4, 135.5, 130.7, 126.4, 123.3, 122.8, 122.0, 19.9.

HRMS (ESI) m/z calcd for $C_{14}H_{12}NO_3^+$ $[M+H]^+$: 242.0812, found: 242.0812.

5-formyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8m$_{di}$**)



8m$_{di}$

35.9 mg, 24% yield

Physical State: yellow solid

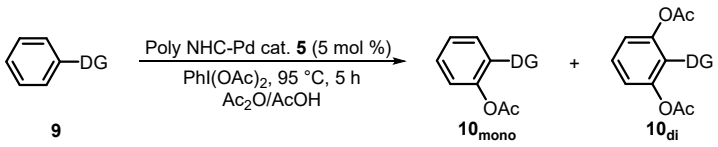
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.65 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.70 (td, *J* = 7.6, 1.6 Hz, 1H), 7.56 (s, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 1.98 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 168.7, 151.3, 149.9, 149.8, 137.2, 136.3, 125.1, 123.2, 121.8, 20.6.

HRMS (ESI) m/z calcd for $C_{16}H_{14}NO_5^+$ $[M+H]^+$: 300.0866, found: 300.0866.

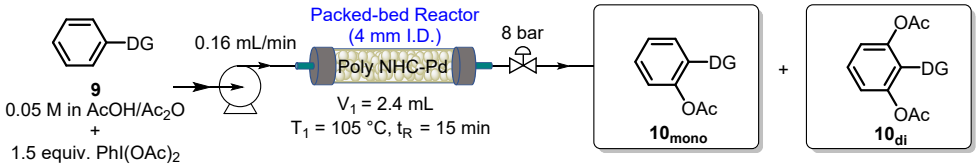
8. C-H acetoxylation of arenes using different directing groups

8.1 Experimental procedures in batch



To a 10 mL reaction tube, **9** (0.6 mmol, 1.0 equiv.), diacetoxyiodo benzene (0.9 mmol, 1.5 equiv.) and poly NHC-Pd catalyst **5** (0.03 mmol, 5 mol%) in acetic acid (3 mL) and acetic anhydride (3 mL) were added. The reaction mixture was heated to 95 °C for 5 h. Then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / EtOAc = 2:1) to give the product $\mathbf{10}_{\mathbf{mono}}$ and $\mathbf{10}_{\mathbf{di}}$.

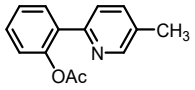
8.2 Experimental procedures in flow



One flow stream was delivered into the flow reactor by the plunger pump (AP0010, SANOTAC). The stream contained a solution of **9** (1.0 mmol, 1.0 equiv.) and diacetoxyiodo benzene (1.5 mmol, 1.5 equiv.) in acetic acid (10 mL) and acetic anhydride (10 mL). This stream was pumped through packed-bed reactor (2.4 mL internal volume, t_R = 15 min, 300 mg poly NHC-Pd catalyst **5** and 1.5 g 60-80 mesh silica gel powder were packed in it) at 105 °C at a flow rate of 0.16 mL/ min. A 8.0 bar back-pressure regulator (BPR) was connected at the outlet of packed-bed reactor. The output from the packed-bed reactor was collected for 63 minutes (10 mL), then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / EtOAc = 2:1) to give the product $\mathbf{10}_{\mathbf{mono}}$ and $\mathbf{10}_{\mathbf{di}}$.

8.3 Characterization data of product $\mathbf{10}_{\mathbf{mono}}$ and $\mathbf{10}_{\mathbf{di}}$

2-(5-methylpyridin-2-yl)phenyl acetate ($\mathbf{10a}_{\mathbf{mono}}$)



10a$_{mono}$

32.9 mg, 29% yield

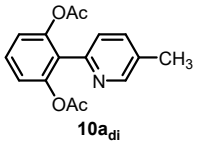
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.54 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.34 (td, *J* = 7.6, 1.6 Hz, 1H), 7.15 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.37 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 151.9, 148.9, 147.0, 135.8, 130.7, 129.7, 128.4, 125.3, 122.1, 121.9, 76.3, 76.0, 75.7, 19.9, 17.1.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

2-(5-methylpyridin-2-yl)-1,3-phenylene diacetate (**10a$_{di}$**)



10a$_{di}$

65.5 mg, 46% yield

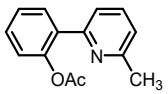
Physical State: yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 1.94 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.8, 149.2, 149.1, 136.6, 132.1, 129.1, 127.4, 124.5, 120.6, 20.6, 18.3.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$: 286.1074, found: 286.1074.

2-(6-methylpyridin-2-yl)phenyl acetate (**10b$_{mono}$**)



10b$_{mono}$

44.3 mg, 39% yield

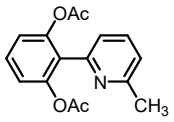
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 2.53 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 157.1, 154.1, 147.0, 135.6, 132.2, 129.9, 128.5, 125.3, 122.2, 120.8, 119.6, 23.6, 20.0.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

2-(6-methylpyridin-2-yl)-1,3-phenylene diacetate (**10b$_{di}$**)



10b$_{di}$

7.1 mg, 5% yield

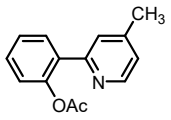
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.0, 4.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.54 (s, 3H), 1.96 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 160.1, 155.6, 154.2, 149.0, 137.9, 130.4, 121.7, 121.0, 116.1, 113.7, 23.9, 21.4.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$: 286.1074, found: 286.1074.

2-(4-methylpyridin-2-yl)phenyl acetate (**10c$_{mono}$**)



10c$_{mono}$

45.4 mg, 40% yield

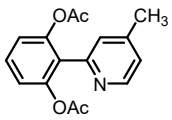
Physical State: light orange oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.8 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 (td, *J* = 7.6, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.02 (ddd, *J* = 5.2, 1.6, 0.8 Hz, 1H), 2.33 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.46, 154.72, 148.24, 147.08, 146.35, 132.23, 129.74, 128.56, 125.31, 123.45, 122.17, 20.13, 19.93.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

2-(4-methylpyridin-2-yl)-1,3-phenylene diacetate (**10c$_{di}$**)



10c$_{di}$

57.0 mg, 40% yield

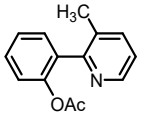
Physical State: light orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.13 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 3H), 2.37 (s, 3H), 2.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 152.0, 149.2, 149.1, 147.4, 129.4, 127.5, 126.0, 123.7, 120.8, 21.2, 20.7.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$: 286.1074, found: 286.1074.

2-(3-methylpyridin-2-yl)phenyl acetate (**10d$_{mono}$**) [7]



10d$_{mono}$

89.7 mg, 79% yield

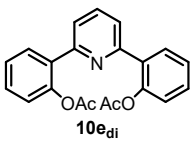
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.4 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.32 (td, *J* = 7.2, 1.2 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.06 (m, 2H), 2.11 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 154.5, 147.1, 145.6, 136.9, 132.5, 131.2, 129.4, 128.2, 124.8, 121.7, 121.5, 19.5, 18.0.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$: 228.1019, found: 228.1019.

pyridine-2,6-diylbis(2,1-phenylene) diacetate (**10e$_{di}$**)



10e$_{di}$

69.4 mg, 40% yield

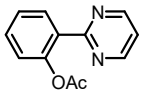
Physical State: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.33 (td, *J* = 7.6, 1.6 Hz, 2H), 7.25 (td, *J* = 7.6, 1.6 Hz, 2H), 7.06 (dd, *J* = 8.0, 1.2 Hz, 2H), 1.96 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 155.4, 148.3, 136.6, 132.9, 131.1, 129.8, 126.4, 123.5, 121.9, 20.9.

HRMS (ESI) m/z calcd for $C_{21}H_{18}NO_4^+$ $[M+H]^+$: 348.1230, found: 348.1230.

2-(pyrimidin-2-yl)phenyl acetate (**10f$_{mono}$**) [7]



10f$_{mono}$

28.9 mg, 27% yield

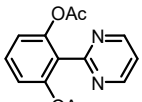
Physical State: bright yellow soild

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (td, *J* = 7.6, 1.6 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.16 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 164.0, 157.1, 149.5, 131.7, 131.5, 130.6, 126.4, 124.0, 119.2, 21.3.

HRMS (ESI) m/z calcd for $C_{12}H_{11}N_2O_2^+$ $[M+H]^+$: 215.0815, found: 215.0815.

2-(pyrimidin-2-yl)-1,3-phenylene diacetate (**10f$_{di}$**) [6]



10f$_{di}$

74.8 mg, 55% yield

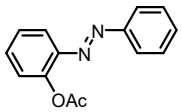
Physical State: orange solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.07 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 161.9, 156.9, 149.7, 130.2, 121.4, 119.5, 20.9.

HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_4^+$ $[M+H]^+$: 273.0870, found: 273.0870.

(E)-2-(phenyldiazenyl)phenyl acetate (**10g$_{mono}$**) [7]



10g$_{mono}$

72.0 mg, 60% yield

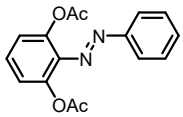
Physical State: red oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.23 (td, *J* = 8.0, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 151.7, 147.9, 142.9, 131.0, 130.3, 128.0, 125.5, 122.3, 121.9, 116.6, 19.7.

HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_2^+$ $[M+H]^+$: 241.0972, found: 241.0972.

(E)-2-(phenyldiazenyl)-1,3-phenylene diacetate (**10g$_{di}$**)



10g$_{di}$

10.4 mg, 7% yield

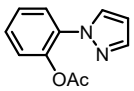
Physical State: red solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 143.7, 130.7, 129.5, 128.2, 121.6, 120.6, 19.8.

HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2O_4^+$ $[M+H]^+$: 299.1026, found: 299.1026.

2-(1H-pyrazol-1-yl)phenyl acetate (**10h$_{mono}$**) [7]



10h$_{mono}$

62.6 mg, 62% yield

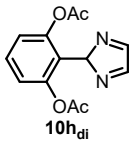
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 10.8, 1.6 Hz, 2H), 7.52 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.12 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.34 (t, *J* = 2.4 Hz, 1H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 142.2, 140.0, 132.1, 129.1, 127.3, 125.7, 124.6, 123.0, 106.0, 19.7.

HRMS (ESI) m/z calcd for $C_{11}H_{11}N_2O_2^+$ $[M+H]^+$: 203.0815, found: 203.0815.

2-(2H-imidazol-2-yl)-1,3-phenylene diacetate (**10h$_{di}$**)



10h$_{di}$

26.0 mg, 20% yield

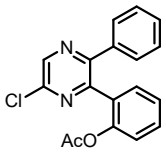
Physical State: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.32 (t, *J* = 2.4 Hz, 1H), 1.99 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.9, 141.1, 131.9, 129.4, 121.2, 106.4, 20.4.

HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O_4^+$ $[M+H]^+$: 261.0870, found: 261.0870.

2-(6-chloro-3-phenylpyrazin-2-yl)phenyl acetate (**10i$_{mono}$**)



10i$_{mono}$

113.4 mg, 70% yield

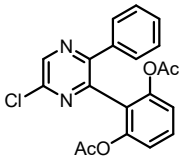
Physical State: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.41 – 7.38 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.15 (m, 2H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 153.0, 148.0, 147.6, 147.1, 141.5, 136.6, 131.5, 130.5, 130.2, 129.6, 129.2, 128.3, 126.1, 123.1, 20.9.

HRMS (ESI) m/z calcd for $C_{18}H_{14}ClN_2O_2^+$ $[M+H]^+$: 325.0738, found: 325.0738.

2-(6-chloro-3-phenylpyrazin-2-yl)-1,3-phenylene diacetate (**10i$_{di}$**)



10i$_{di}$

40.1 mg, 21% yield

Physical State: pale yellow solid

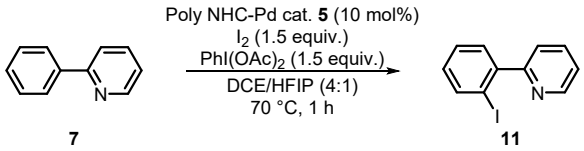
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.48 – 7.45 (m, 2H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 1.90 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 154.0, 149.0, 147.8, 143.7, 141.6, 136.2, 130.1, 130.0, 128.8, 128.5, 120.6, 20.8.

HRMS (ESI) m/z calcd for $C_{20}H_{16}ClN_2O_4^+$ $[M+H]^+$: 383.0793, found: 383.0793.

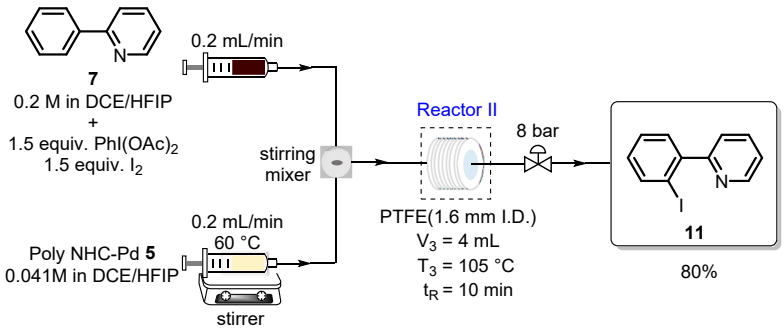
9. C-H Iodination of 2-Phenylpyridine

9.1 Experimental procedures in batch



To a reaction tube was added **7** (0.4 mmol, 1.0 equiv.), diacetoxyiodo benzene (0.6 mmol, 1.5 equiv), iodine (0.6 mmol, 1.5 equiv.) and poly NHC-Pd catalyst **5** (0.04 mmol, 10 mol%) in DCE (3.2 mL) and HFIP (0.8 mL). The reaction mixture was heated to 70 ℃ for 1 h. Then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / DCM = 1:1) to give the product **11**. [12]

9.2 Experimental procedures in flow

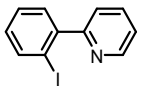


Two flow streams were delivered into the flow reactor by the syringe pump (Fusion 4000, CHEMYX). Stream 1 contained a solution of **7** (1.0 mmol, 1.0 equiv.), diacetoxyiodo benzene (1.5 mmol, 1.5 equiv.) and iodine (1.5 mmol, 1.5 equiv.) in DCE (4 mL) and HFIP (1 mL) premixed at 60 ℃. Stream 2 contained a solution of poly NHC-Pd catalyst **5** (0.207 mml) in DCE (4 mL) and

HFIP (1 mL). The glass syringe containing stream 2 wrapped with heating tapes set at 60 °C due to higher temperature is beneficial for the suspension of catalyst. In addition, a magnetic stirrer was beneath the heated glass syringe which prior filled with a magnetic stir bar to maintain the catalyst suspended evenly at 100 rpm.These stream were pumped each at a flow rate of 0.2 mL/min and mixed through a stainless steel CSTR and passed through a PTFE coil reactor (4 mL internal volume, t_R = 10 min) at 105 °C. A 8.0 bar back-pressure regulator (BPR) was connected at the outlet of coil reactor. The output from the coil reactor was collected for 15 minutes (6 mL), then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / DCM = 1:1) to give the product **11**.

9.3 Characterization data of product 11

2-(2-iodophenyl)pyridine (**11**) [8]



11

134.9 mg, 80% yield

Physical State: orange oil

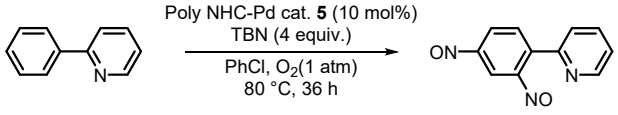
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69 (td, *J* = 7.6, 1.6 Hz, 1H), 7.43 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.25 – 7.20 (m, 1H), 7.03 – 6.98 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 148.2, 144.0, 138.7, 135.0, 129.3, 128.7, 127.2, 123.4, 121.5, 95.7.

HRMS (ESI) m/z calcd for $C_{11}H_9IN^+$ $[M+H]^+$: 281.9774, found: 281.9774.

10. C-H Nitrosation of 2-Phenylpyridine

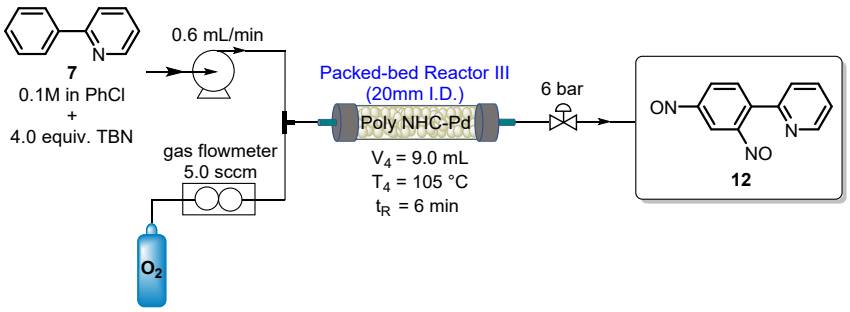
10.1 Experimental procedures in batch



7 **12**

To a 10 mL Shlenk tube, poly NHC-Pd catalyst **5** (0.04 mmol, 10 mol%) was added. The flask was evacuated and backfilled with O_2 (3 cycles), then a solution of **7** (0.4 mmol, 1.0 equiv.), *tert*-butyl nitrite (1.6 mmol, 4.0 equiv) in 4 mL PhCl were added. The reaction mixture was heated to 80 ℃ for 36 h. Then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / EtOAc = 1:1) to give the product **12**. [13]

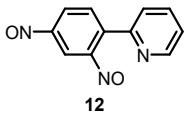
10.2 Experimental procedures in flow



Two flow streams were delivered into the Packed-bed Reactor. Stream 1 contained a solution of **7** (1.5 mmol, 1.0 equiv.) and *tert*-butyl nitrite (6.0 mmol, 4.0 equiv) in PhCl (15 mL). Stream 1 was pumped at a flow rate of 0.6 mL/min by the plunger pump (AP0010, SANOTAC). Oxygen as stream 2 was pumped through a gas flow meter at a flow rate of 5.0 sccm. These stream were pumped through a packed-bed reactor (9.0 mL internal volume, t_R = 6 min, 500 mg poly NHC-Pd catalyst **5** and 2.5 g 60-80 mesh silica gel powder were packed in it) at 105 ℃. A 6.0 bar back-pressure regulator (BPR) was connected at the outlet of packed-bed reactor. The output from the packed-bed reactor was collected for 15 minutes (9.0 mL), then the reaction mixture was removed in vacuum to afford the crude product, which was purified by short silica column flash chromatography (PE / DCM = 1:1) to give the product **12**.

10.3 Characterization data of product 12

2-(2,4-dinitrosophenyl)pyridine (**12**)



149.6 mg, 78% yield

Physical State: bright yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, J = 2.0, 0.8 Hz, 1H), 8.90 (dt, J = 6.8, 0.8 Hz, 1H), 8.41 (dd, J = 9.6, 2.0 Hz, 1H), 8.28 (dt, J = 8.4, 1.2 Hz, 1H), 7.83 (dd, J = 9.2, 0.8 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.42 (td, J = 6.8, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl3) δ 151.49, 140.77, 137.74, 129.26, 125.42, 123.40, 118.96, 118.51, 118.40, 115.88, 114.14.

HRMS (ESI) m/z calcd for $C_{11}H_8N_3O_2^+$ $[M+H]^+$: 214.0611, found: 214.0611.

11. X-Ray Crystallography of NHC-Pds

11.1 Single crystal X-Ray Diffraction data of 1

Compound **1** (10.0 mg) was dissolved in DCM (5.0 mL) and filtered to remove insoluble materials. The solution was added acetone (5.0 mL) and kept at room temperature until a single crystal was obtained. The crystals were subjected for single crystal XRD to determine the absolute configuration of **1**.

CCDC number : 2328748

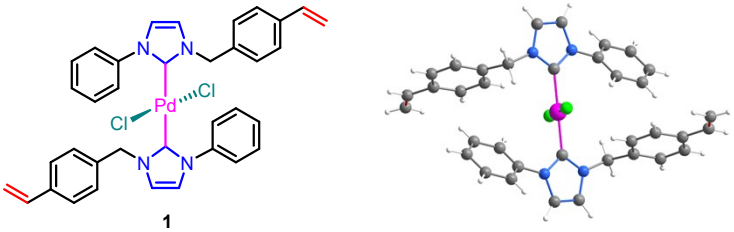


Figure S1. The X-Ray Crystallographic Structure of **1**

Table S5 Crystal data and stmicture refinement for **1**

Identification code	Compound **1**
Empirical formula	$C_{36}H_{32}Cl_2N_4Pd$
Formula weight	697.95
Temperature	173(2) K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.9658(6) Å a= 90°.

	b = 8.7755(4) Å	b= 107.5090(10)°.
	c = 14.1054(7) Å	g= 90°.
Volume	1530.57(13) Å^3	
Z	2	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	4.547 mm^{-1}	
F(000)	712	
Crystal size	0.190 x 0.170 x 0.160 mm^3	
Theta range for data collection	5.378 to 54.941°.	
Index ranges	-15<=h<=15, -10<=k<=10, -17<=l<=17	
Reflections collected	21030	
Independent reflections	2897 [R(int) = 0.0366]	
Completeness to theta = 53.594°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2897 / 0 / 196	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0517	
R indices (all data)	R1 = 0.0232, wR2 = 0.0533	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.359 and -0.449 e.Å^{-3}	

11.2 Single crystal X-Ray Diffraction data of 2

Compound **2** (10.0 mg) was dissolved in DCM (5.0 mL) and filtered to remove insoluble materials. The solution was added CH_3CN (5.0 mL) and kept at room temperature until a single crystal was obtained. The crystals were subjected for single crystal XRD to determine the absolute configuration of **2**.

CCDC number : 2328770

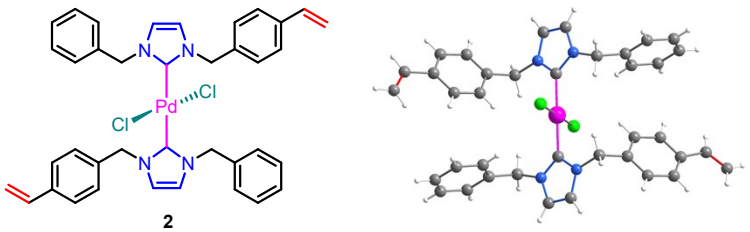


Figure S2. The X-Ray Crystallographic Structure of **2**

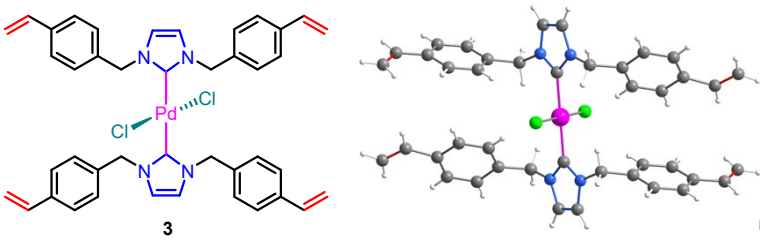
Table S6 Crystal data and stmicture refinement for **2**

Identification code	Compound **2**
Empirical formula	$C_{38}H_{36}Cl_2N_4Pd$
Formula weight	726.01
Temperature	258(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.665(3) Å a= 90°.
	b = 8.580(3) Å b= 102.789(7)°.
	c = 18.918(6) Å g= 90°.
Volume	1688.1(8) $Å^3$
Z	2
Density (calculated)	1.428 Mg/m^3
Absorption coefficient	0.741 mm^{-1}
F(000)	744
Crystal size	0.180 x 0.150 x 0.040 mm^3
Theta range for data collection	2.452 to 27.546°.
Index ranges	-12<=h<=13, -11<=k<=11, -24<=l<=24
Reflections collected	13726
Independent reflections	3888 [R(int) = 0.0584]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.688
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3888 / 31 / 224
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0719
R indices (all data)	R1 = 0.0611, wR2 = 0.0826
Extinction coefficient	n/a
Largest diff. peak and hole	0.276 and -0.419 $e.Å^{-3}$

11.3 Single crystal X-Ray Diffraction data of 3

Compound **3** (10.0 mg) was dissolved in DCM (5.0 mL) and filtered to remove insoluble materials. The solution was added acetone (5.0 mL) and kept at room temperature until a single crystal was obtained. The crystals were subjected for single crystal XRD to determine the absolute configuration of **3**.

CCDC number : 2328769



3

Figure S3. The X-Ray Crystallographic Structure of **3**

Table S7 Crystal data and stmicture refinement for **3**

Identification code	Compound **3**	
Empirical formula	$C_{45}H_{46}Cl_2N_4OPd$	
Formula weight	836.16	
Temperature	173(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.7181(12) Å	a= 90°.
	b = 8.3216(3) Å	b= 121.915(2)°.
	c = 20.0167(10) Å	g= 90°.
Volume	4060.5(3) $Å^3$	
Z	4	
Density (calculated)	1.368 Mg/m^3	
Absorption coefficient	3.499 mm^{-1}	
F(000)	1728	
Crystal size	0.320 x 0.260 x 0.250 mm^3	
Theta range for data collection	4.528 to 54.981°.	
Index ranges	-34<=h<=34, -10<=k<=9, -23<=l<=24	
Reflections collected	23210	
Independent reflections	3865 [R(int) = 0.0667]	
Completeness to theta = 53.594°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.334	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3865 / 38 / 272	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0978	
R indices (all data)	R1 = 0.0397, wR2 = 0.0997	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.424 and -1.336 $e.Å^{-3}$	

12. Image of the Flow System

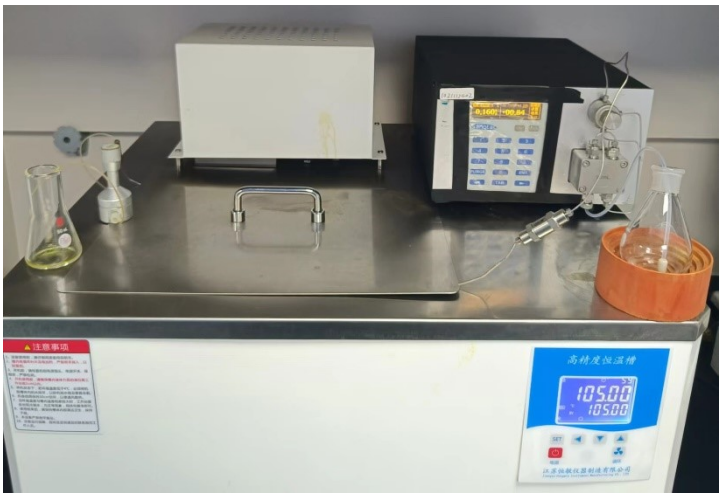


Figure S4. Continuous Packed-bed Reactor I setup
(C-H acetoxylation of arenes step)

Figure S5. Continuous coil reactor II setup
(C-H iodination of 2-phenylpyridine step)

Figure S6. Continuous Packed-bed Reactor III setup
(C-H nitrosation of 2-phenylpyridine step)

13. References

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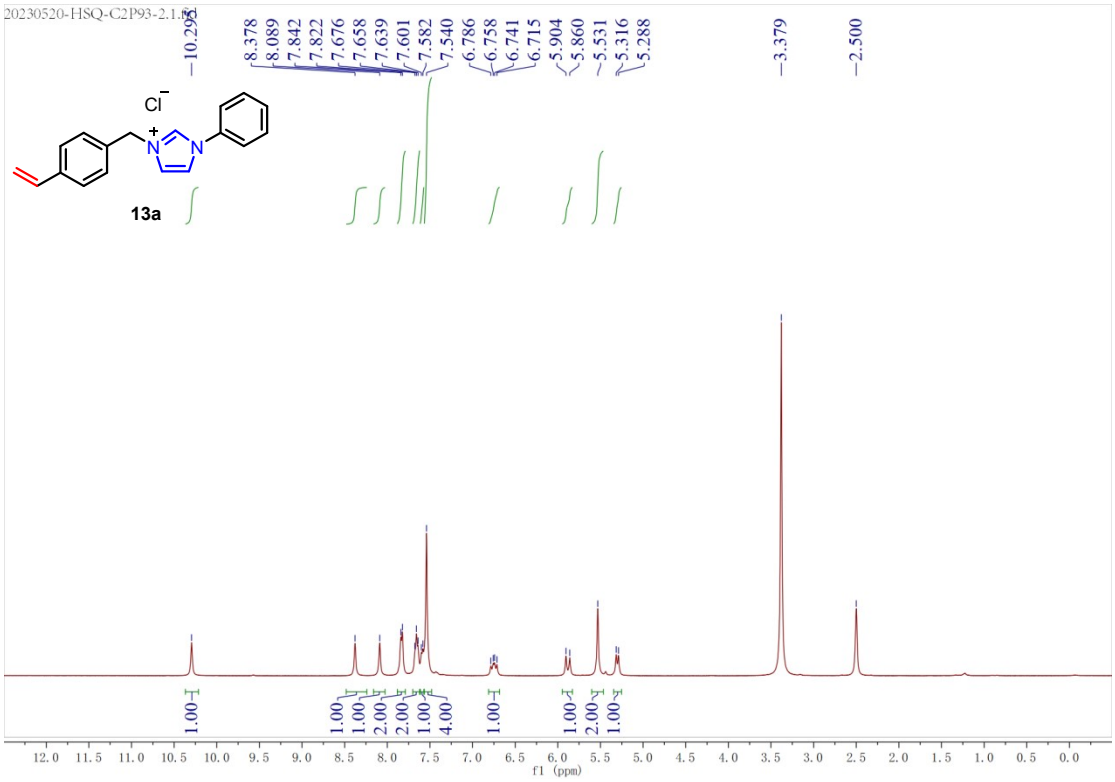
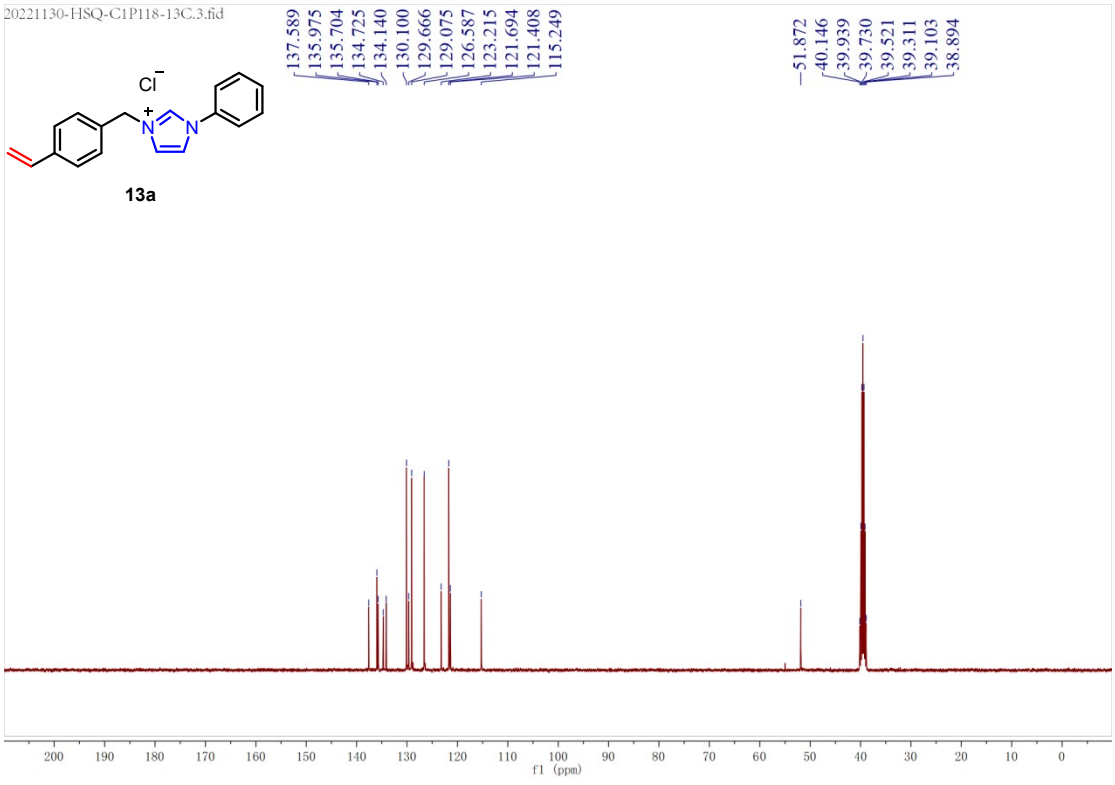
14. NMR Spectra

1-phenyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13a**)

^{1}H NMR (400 MHz, DMSO-d_6)

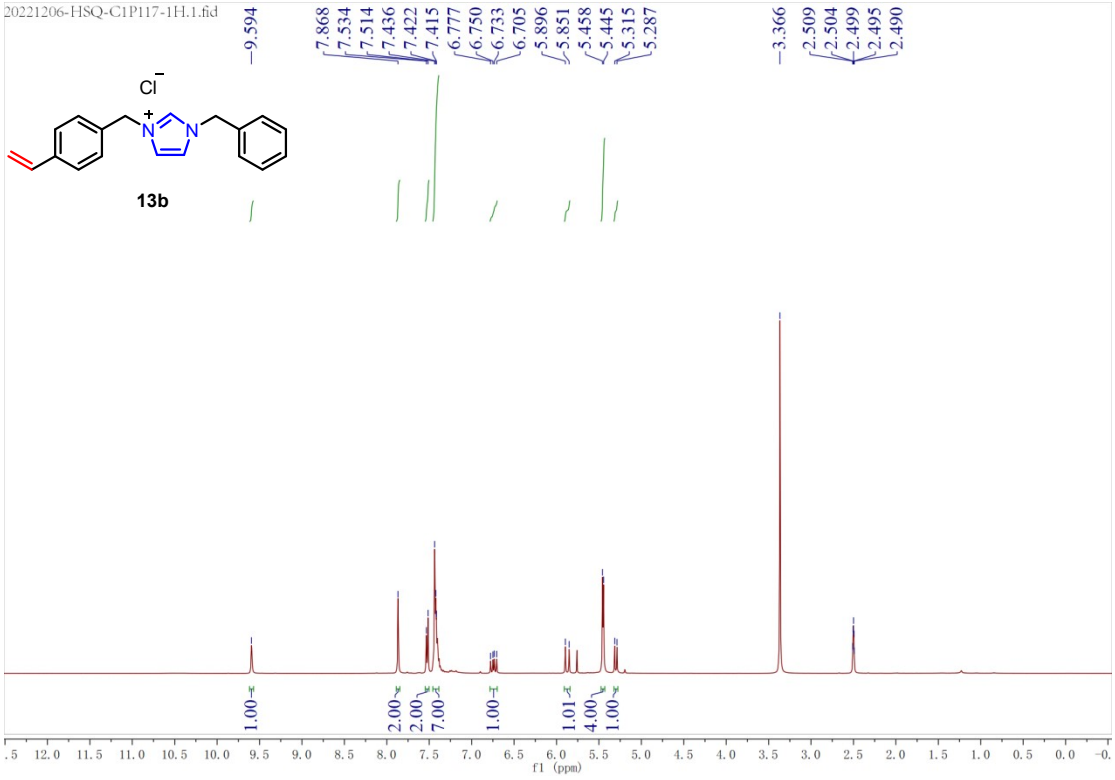


^{13}C NMR (100 MHz, DMSO-d_6)

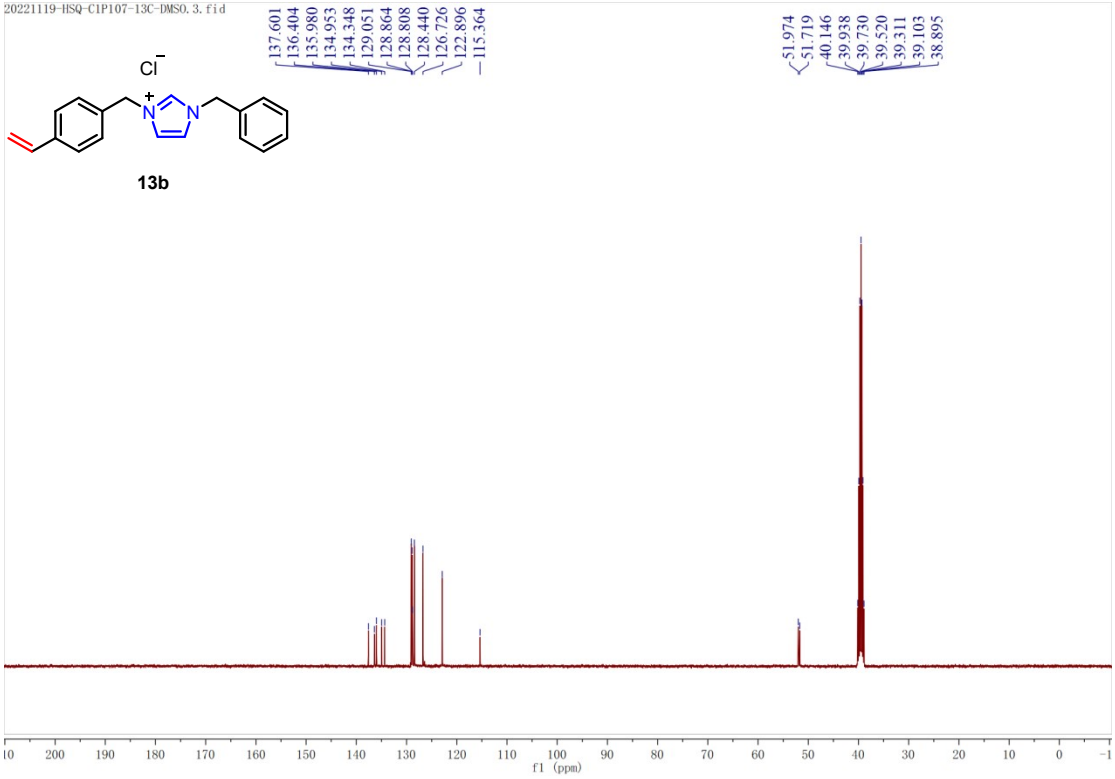


1-benzyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13b**)

^{1}H NMR (400 MHz, DMSO-d_6)

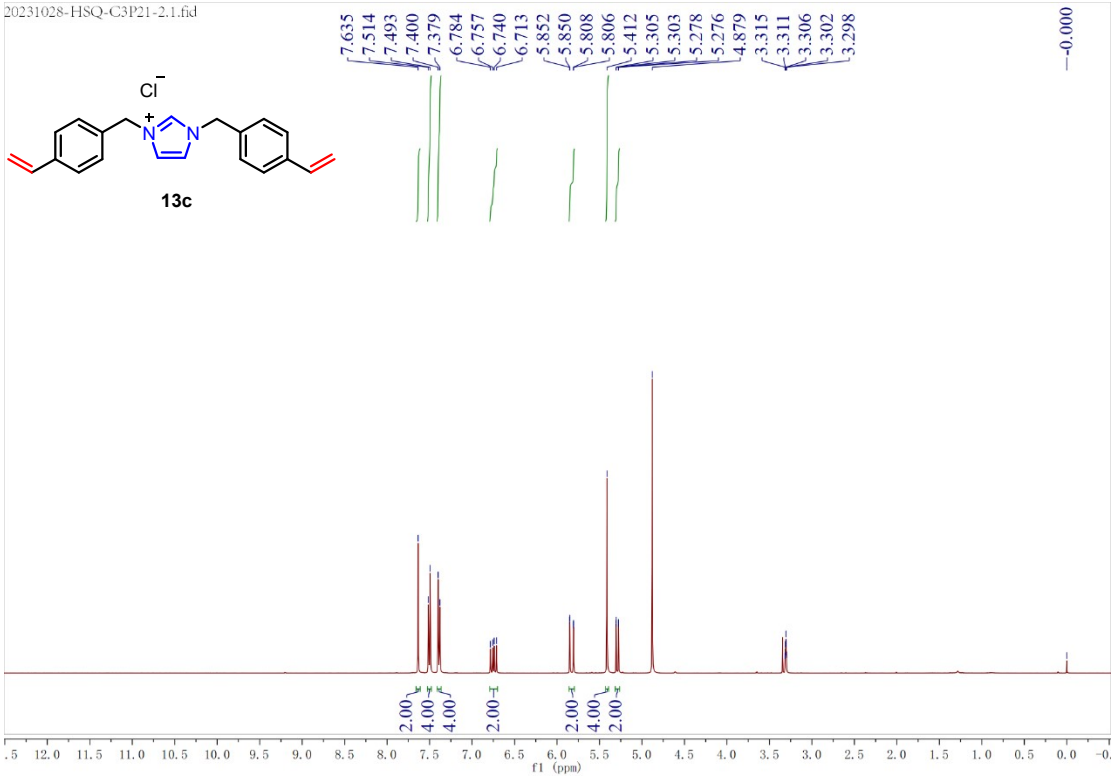


^{13}C NMR (100 MHz, DMSO-d_6)

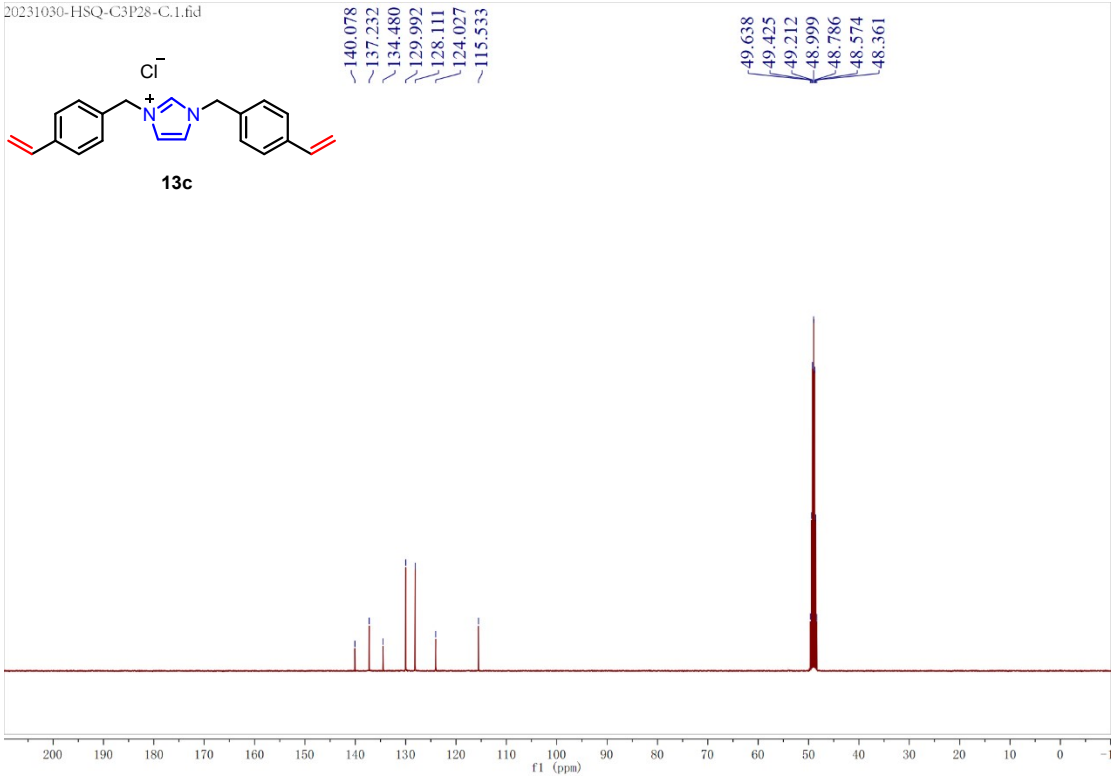


1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**13c**)

^{1}H NMR (400 MHz, CD_3OD)

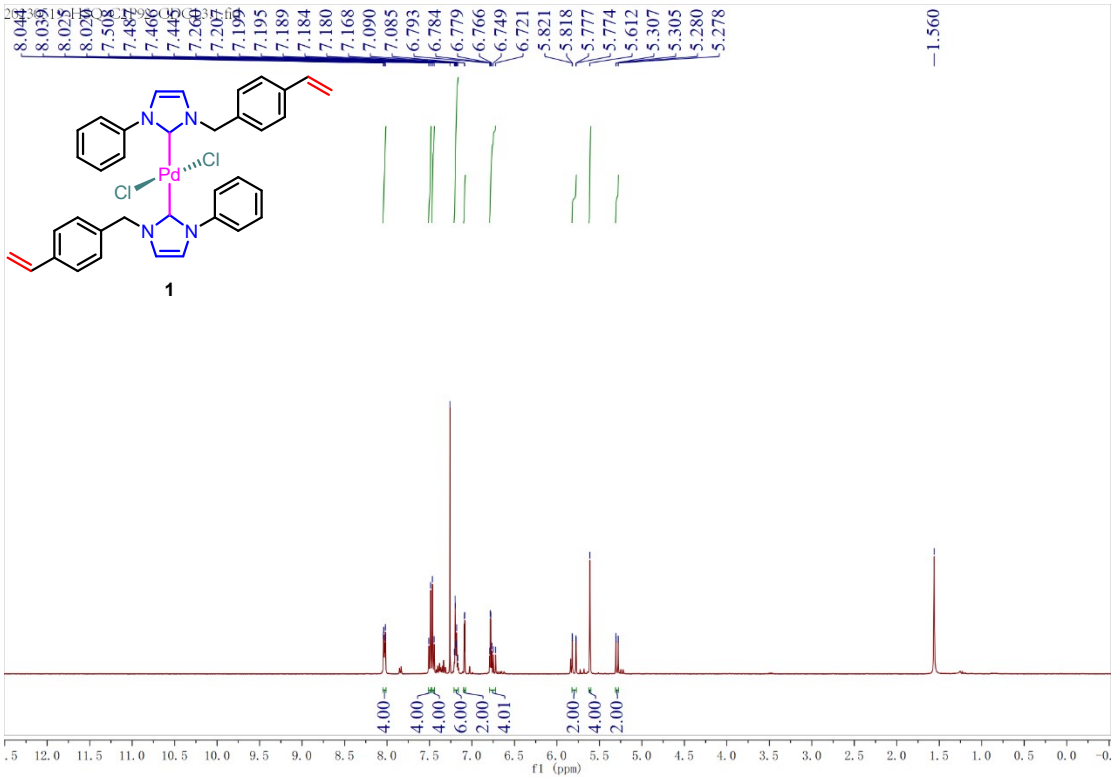


^{13}C NMR (100 MHz, CD_3OD)

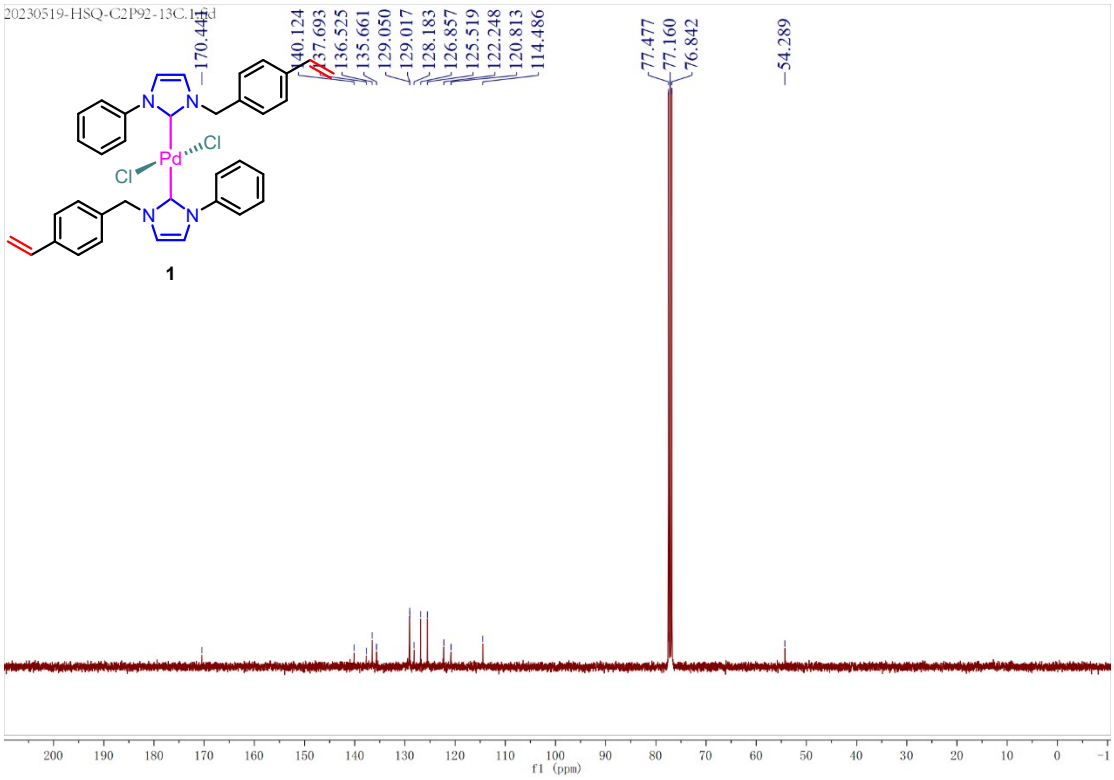


bis(1-phenyl-3-(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**1**)

^{1}H NMR (400 MHz, $CDCl_3$)

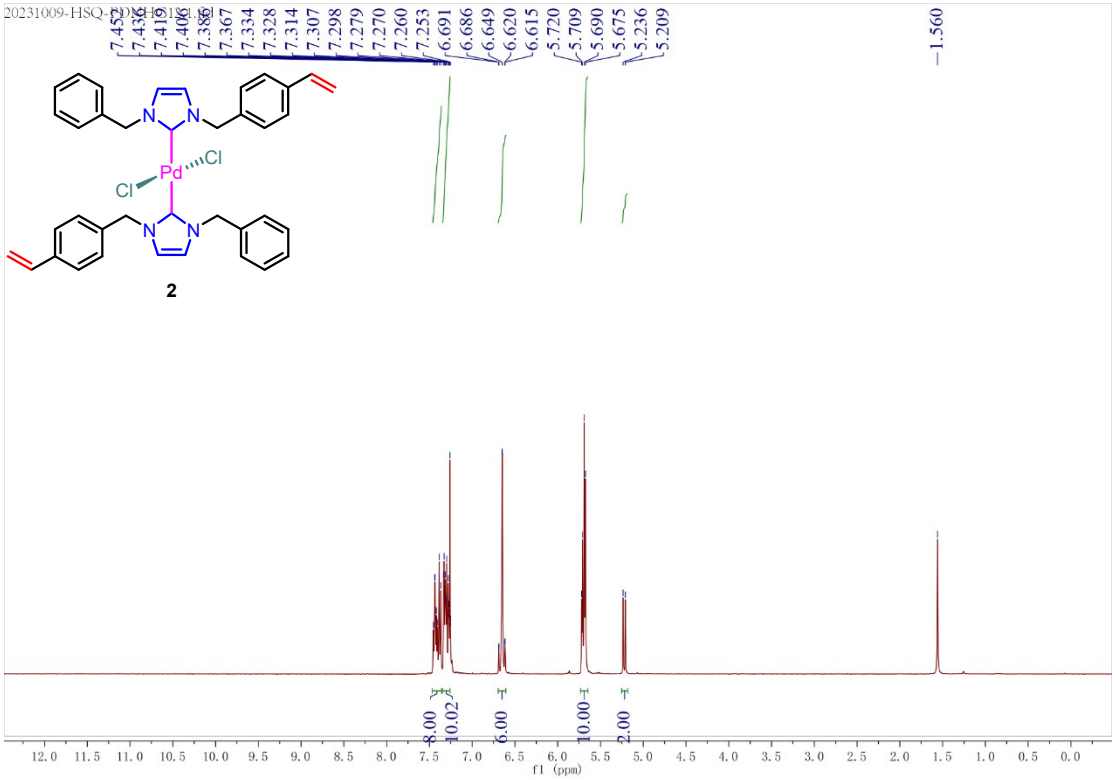


^{13}C NMR (100 MHz, $CDCl_3$)

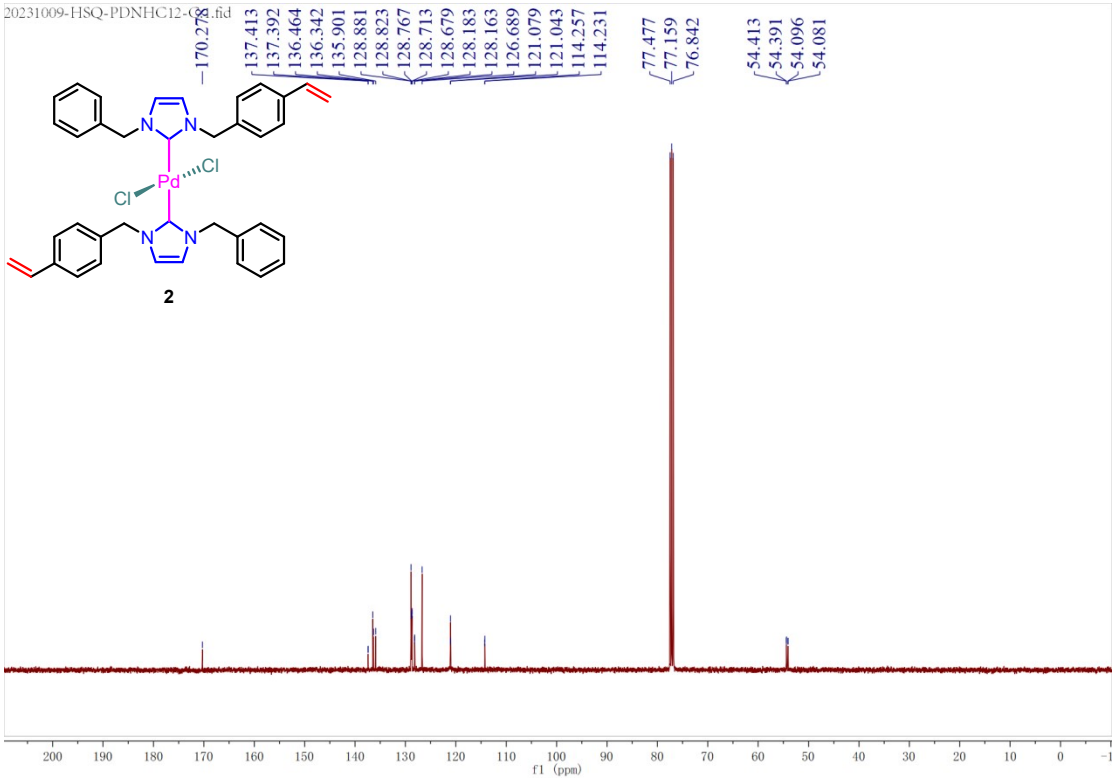


bis(1-benzyl-3-(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**2**)

^{1}H NMR (400 MHz, $CDCl_3$)

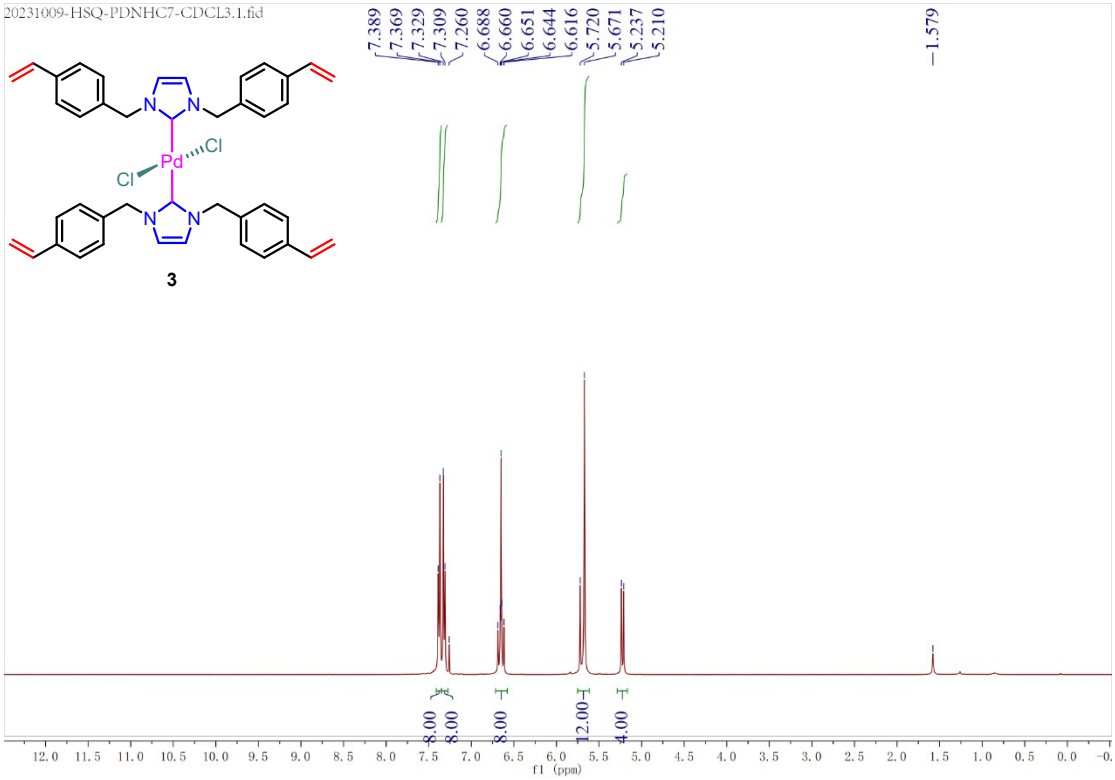


^{13}C NMR (100 MHz, $CDCl_3$)

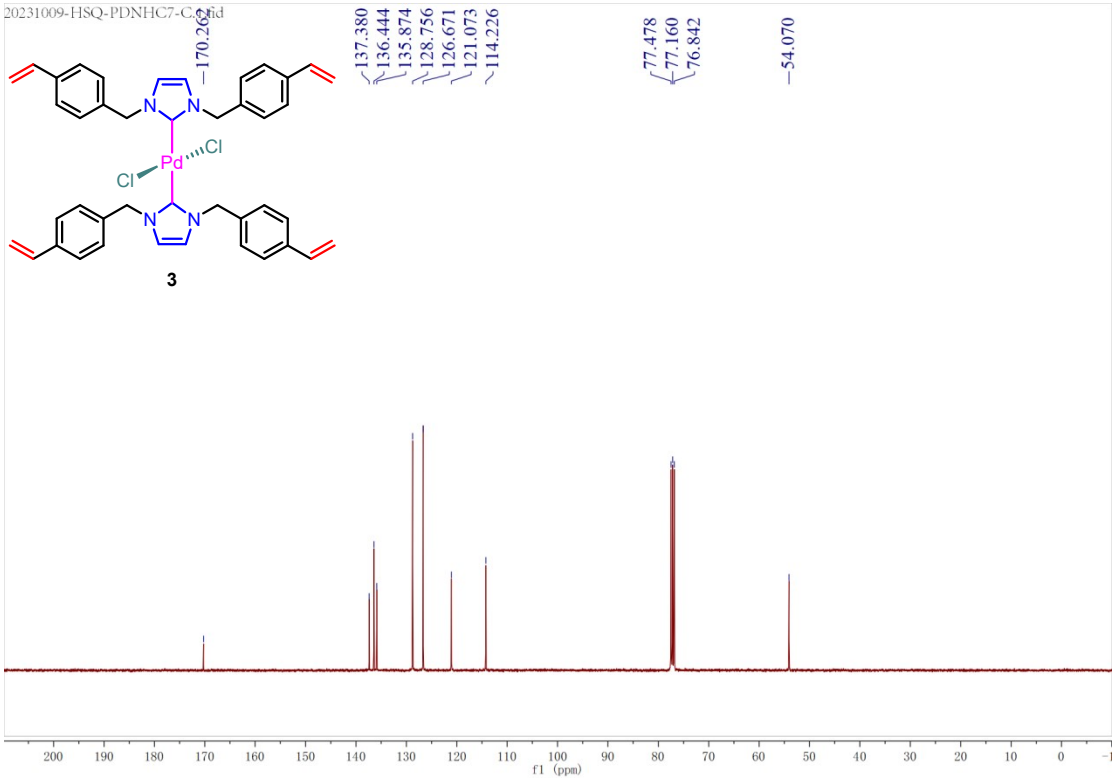


bis(1,3-bis(4-vinylbenzyl)-2,3-dihydro-1H-imidazol-2-yl)palladium(IV) chloride (**3**)

^{1}H NMR (400 MHz, $CDCl_3$)

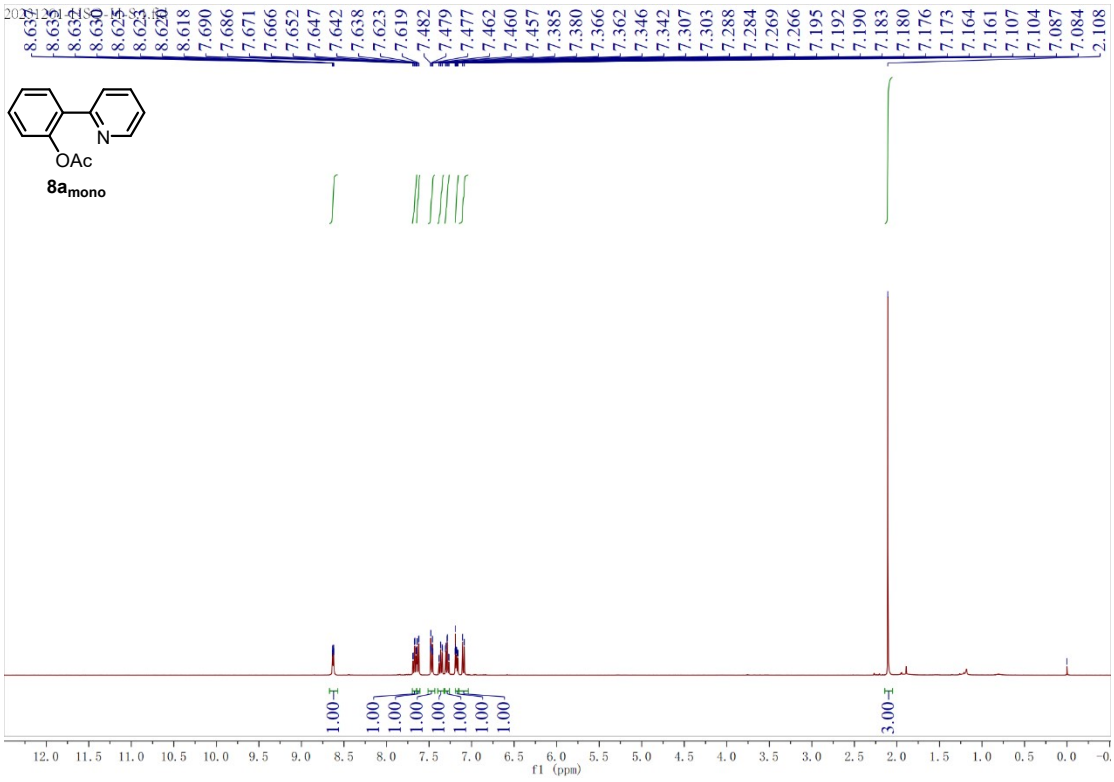


^{13}C NMR (100 MHz, $CDCl_3$)

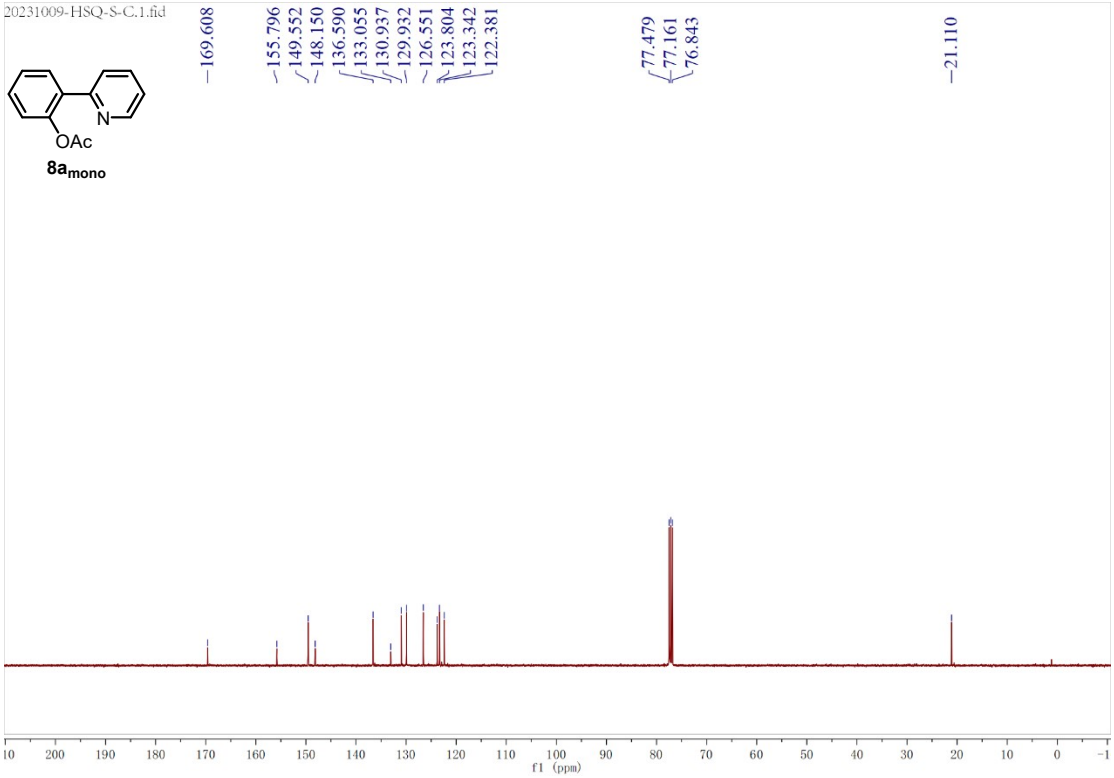


2-(pyridin-2-yl)phenyl acetate (**8a$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

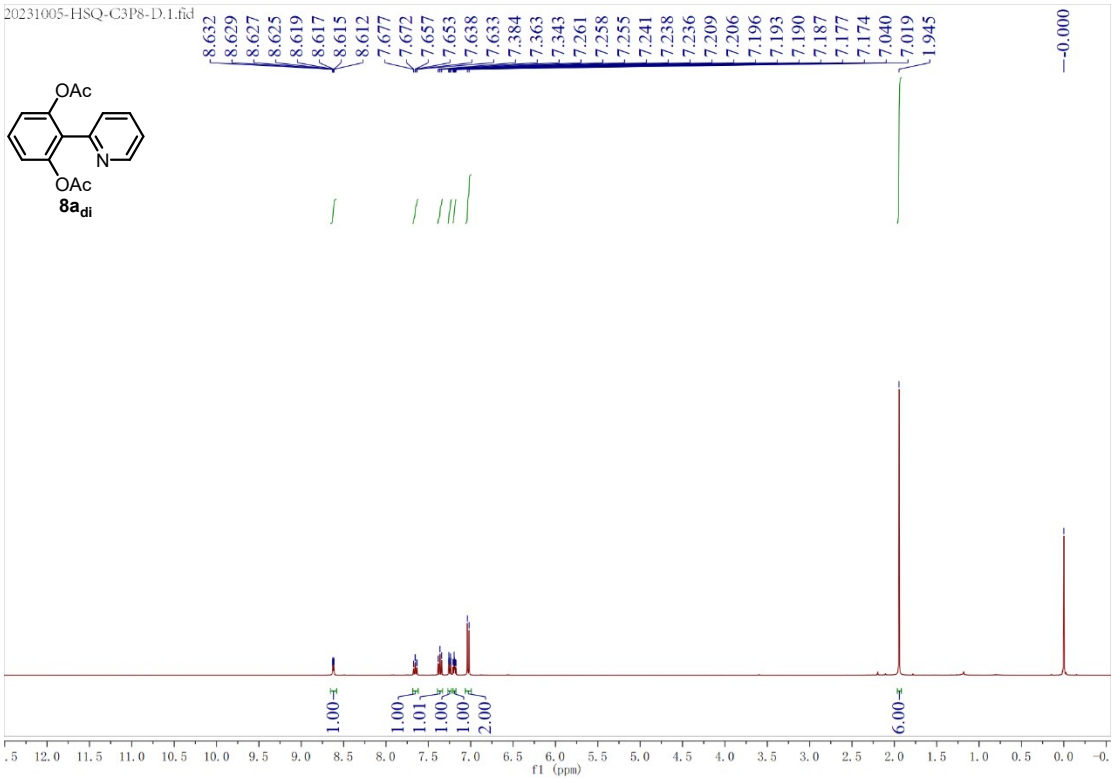


^{13}C NMR (100 MHz, $CDCl_3$)

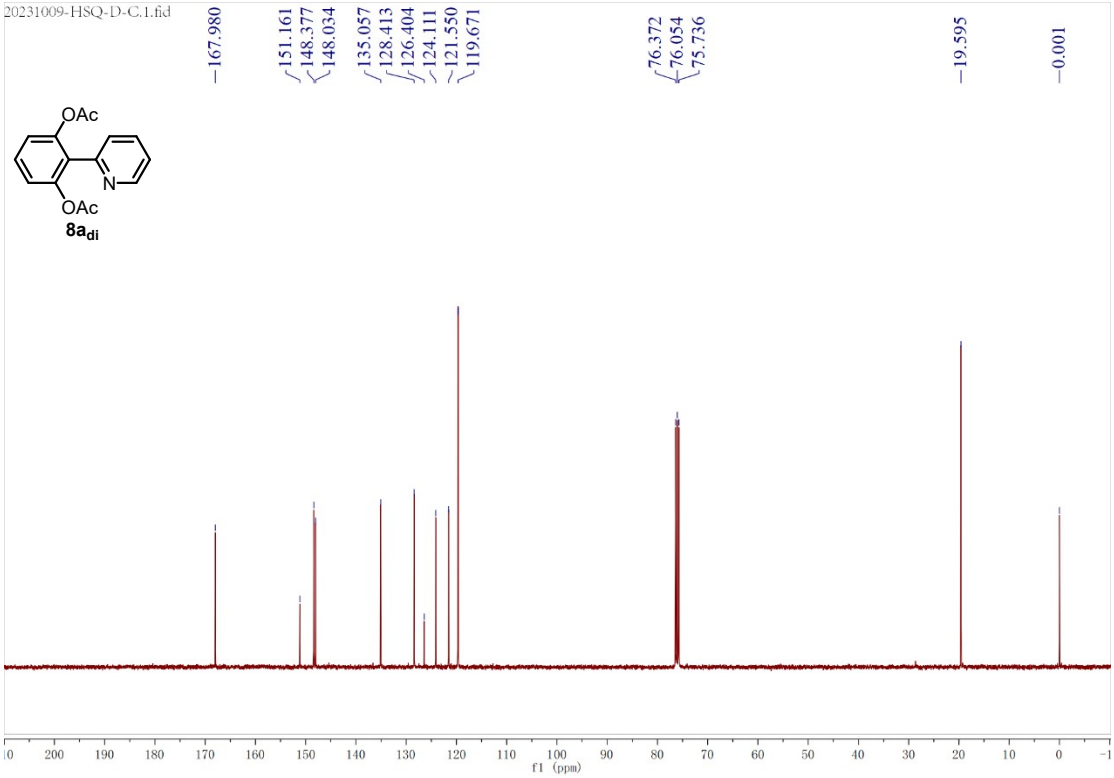


2-(pyridin-2-yl)-1,3-phenylene diacetate (**8a$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

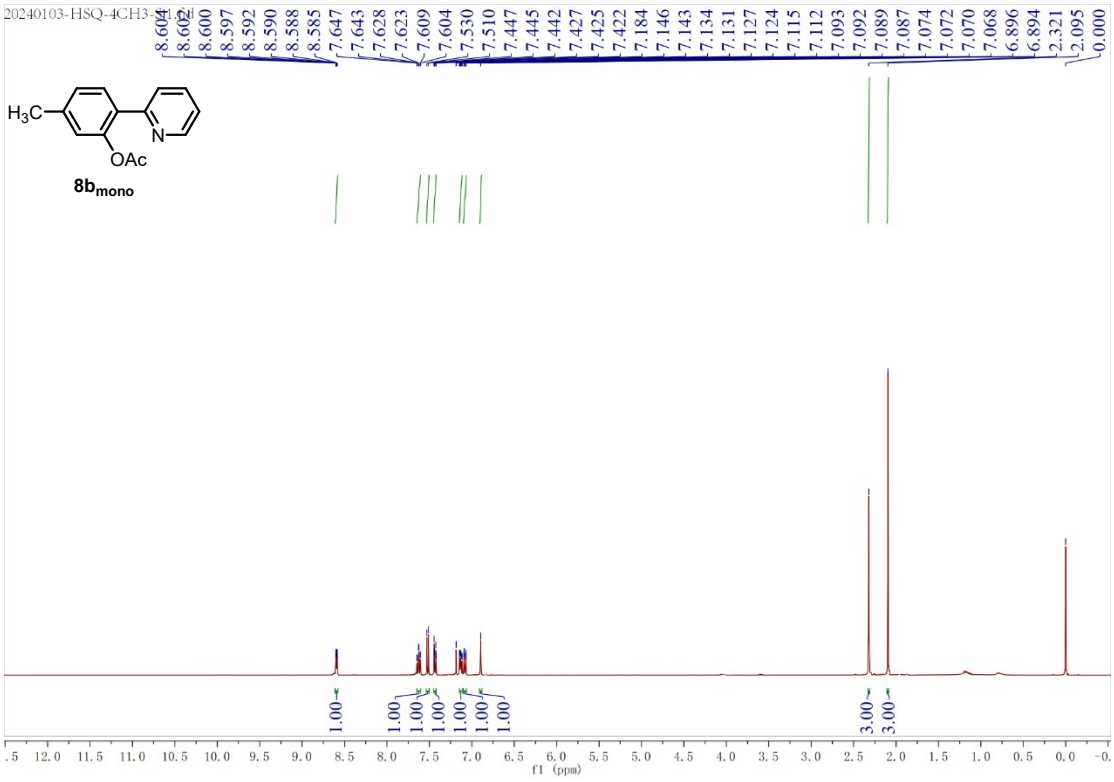


^{13}C NMR (100 MHz, $CDCl_3$)

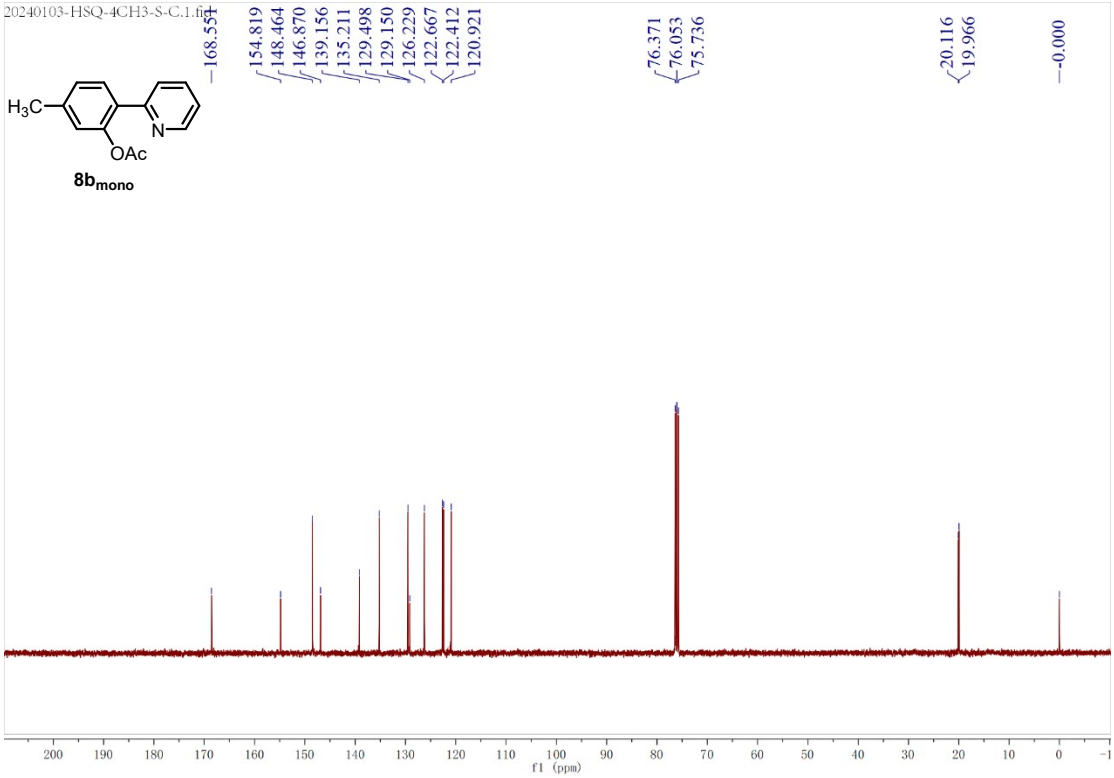


5-methyl-2-(pyridin-2-yl)phenyl acetate (**8b$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

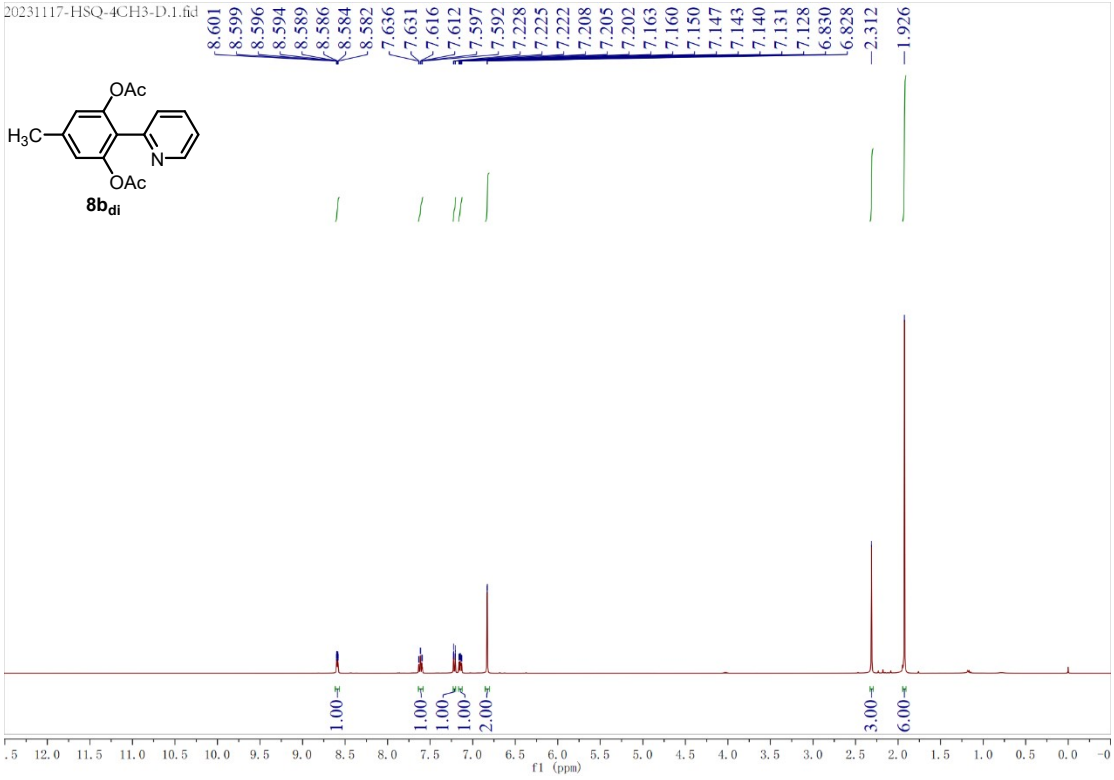


^{13}C NMR (100 MHz, $CDCl_3$)

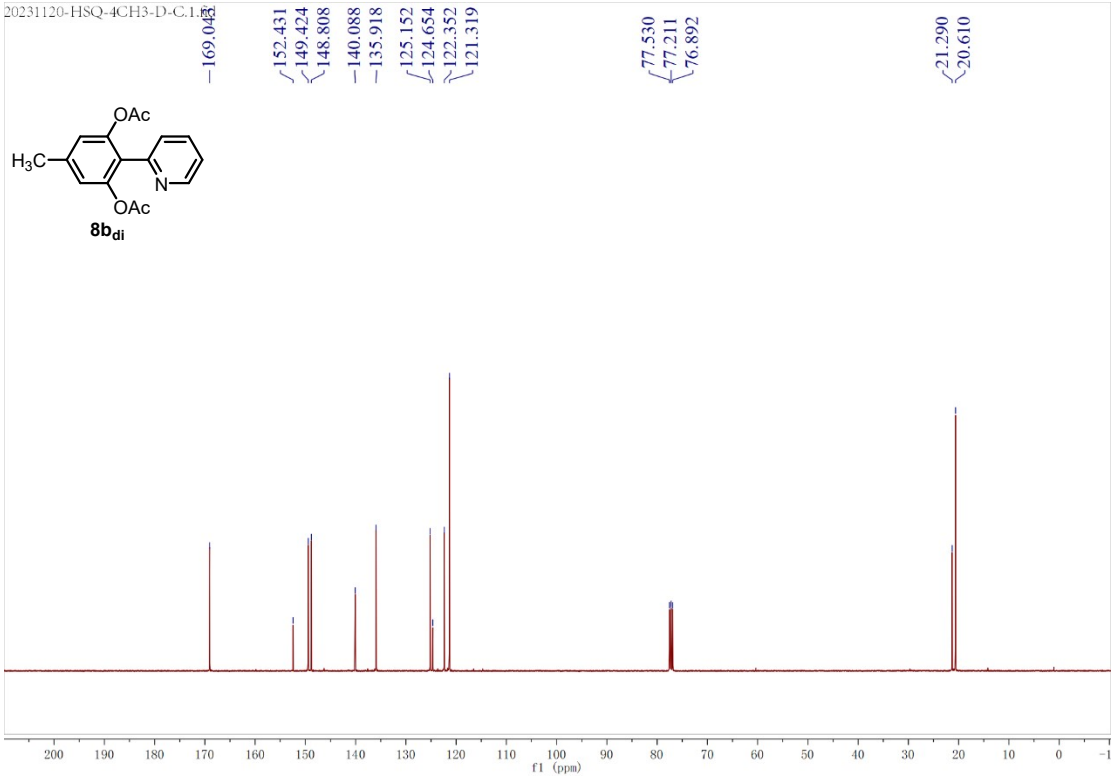


5-methyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8b$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

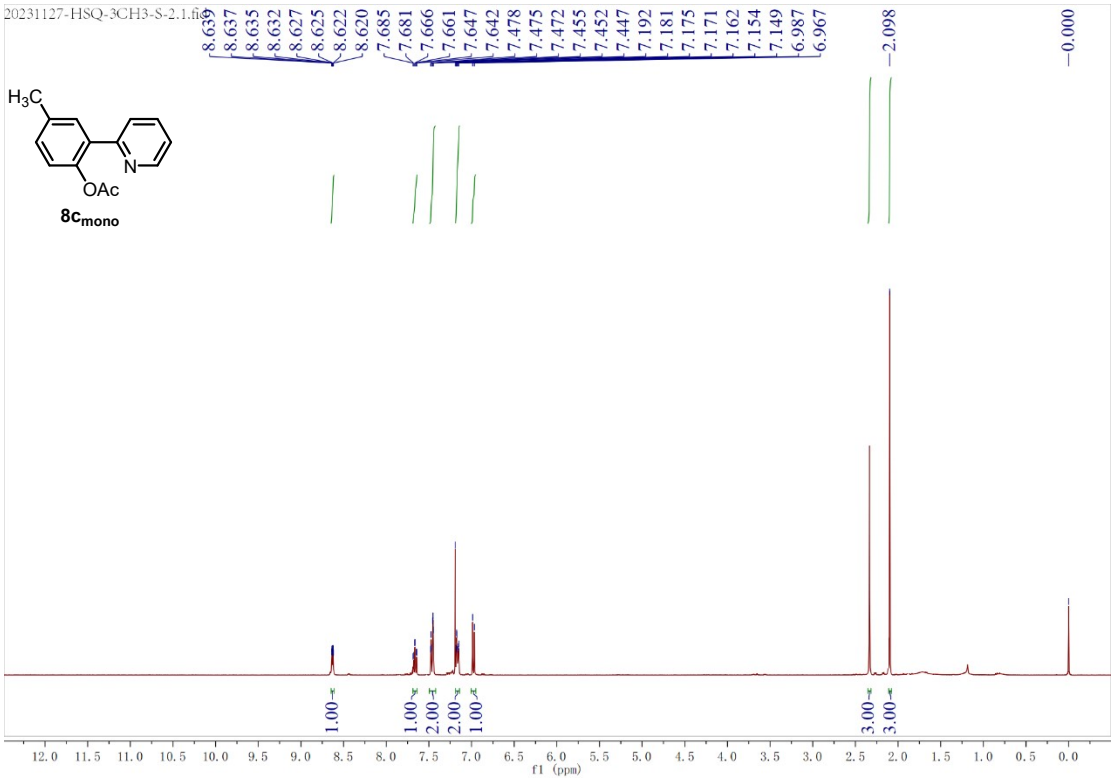


^{13}C NMR (100 MHz, $CDCl_3$)

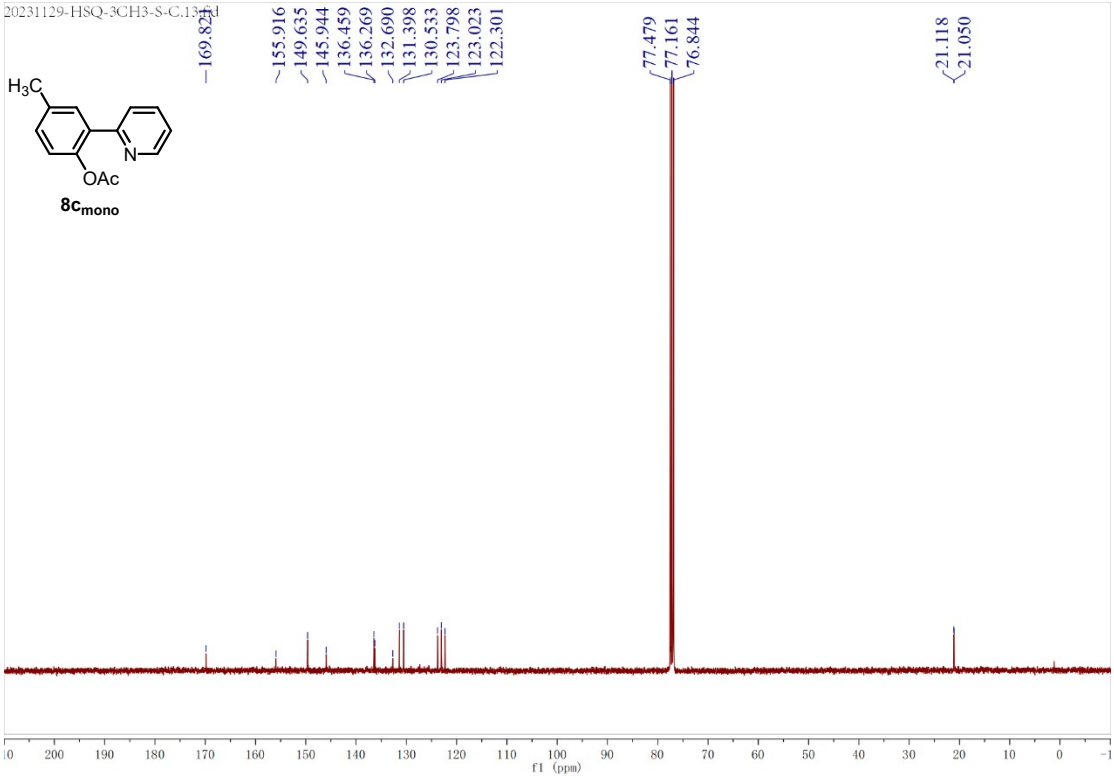


4-methyl-2-(pyridin-2-yl)phenyl acetate (**8c$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

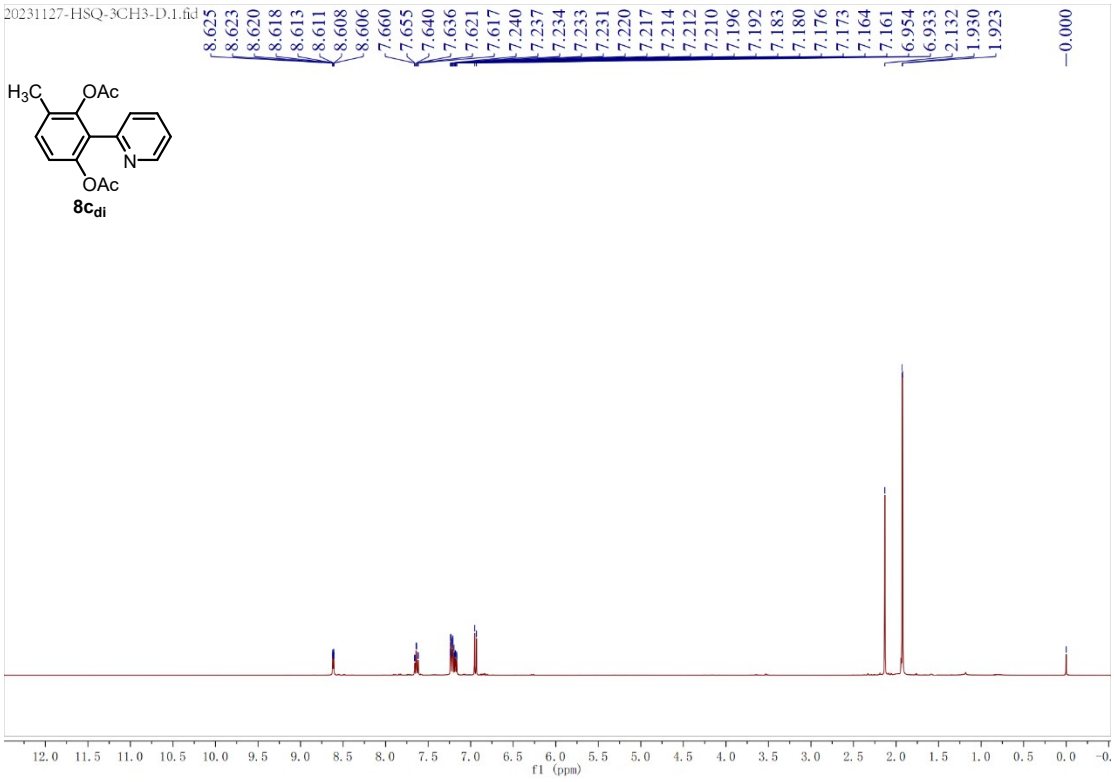


^{13}C NMR (100 MHz, $CDCl_3$)

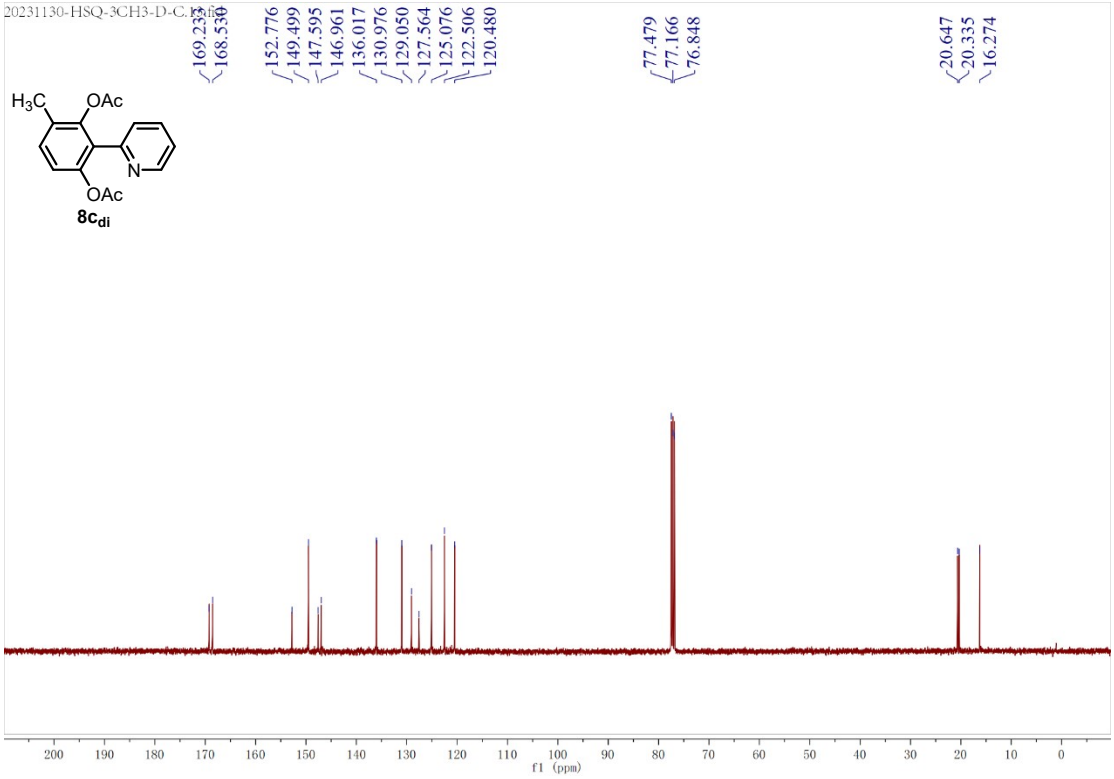


4-methyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8c$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

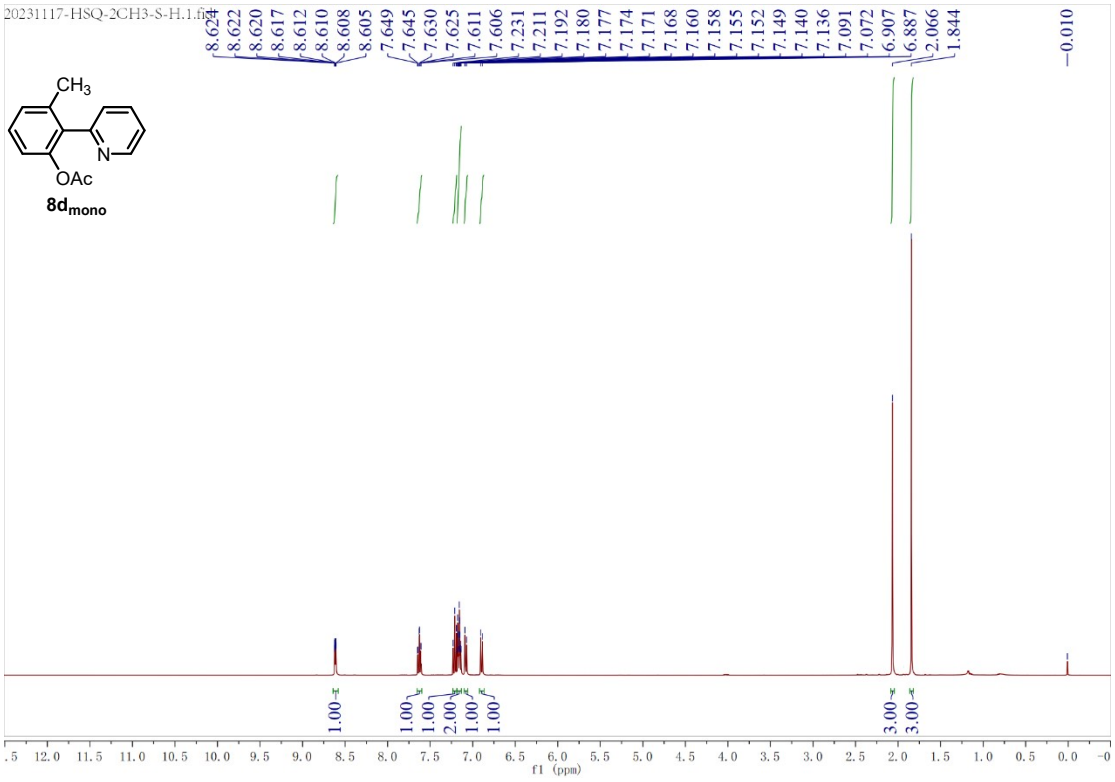


^{13}C NMR (100 MHz, $CDCl_3$)

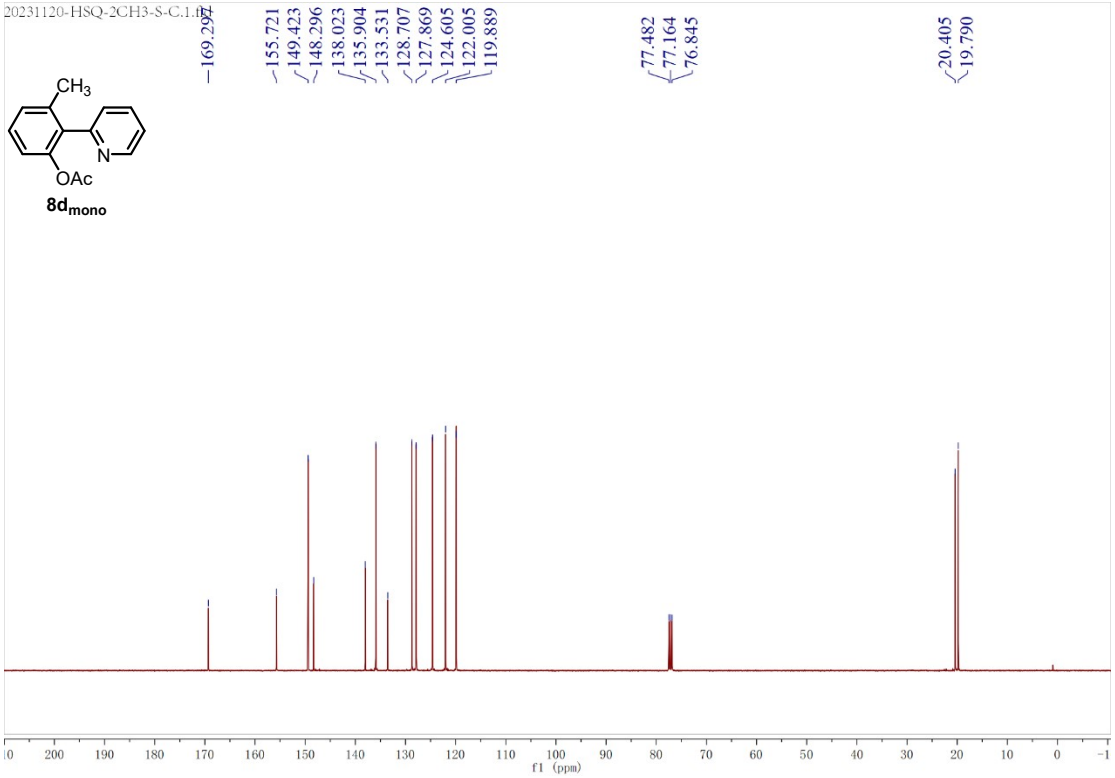


3-methyl-2-(pyridin-2-yl)phenyl acetate (**8d$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

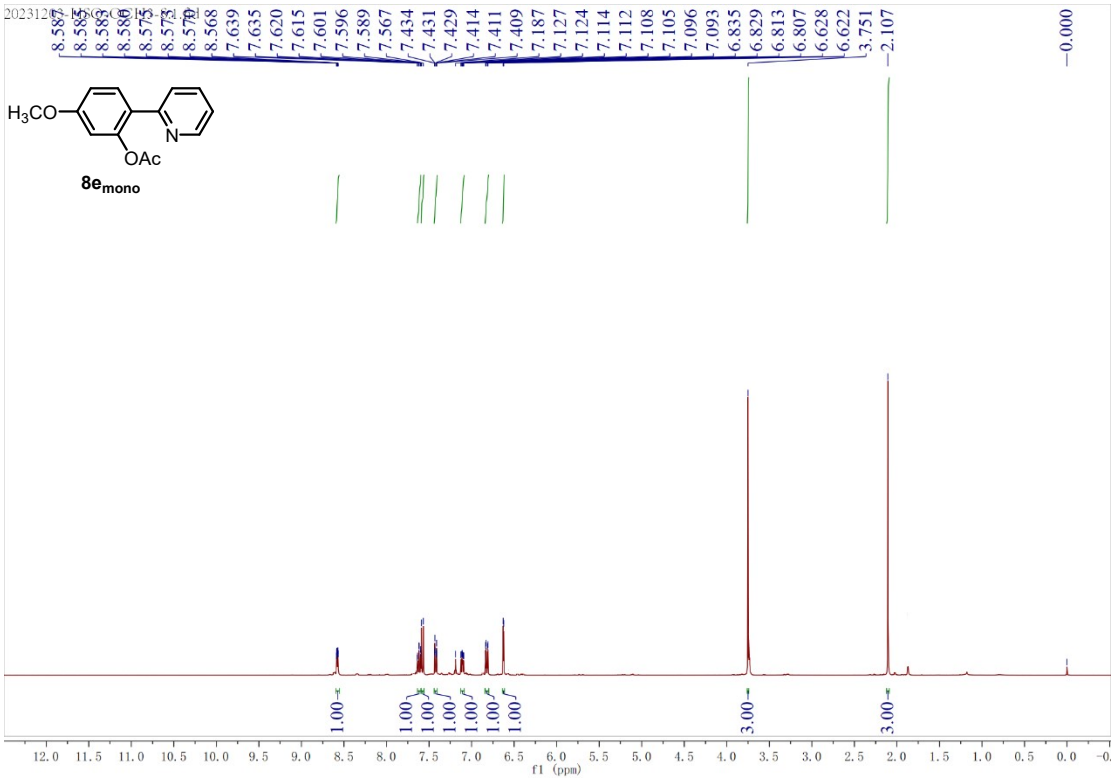


^{13}C NMR (100 MHz, $CDCl_3$)

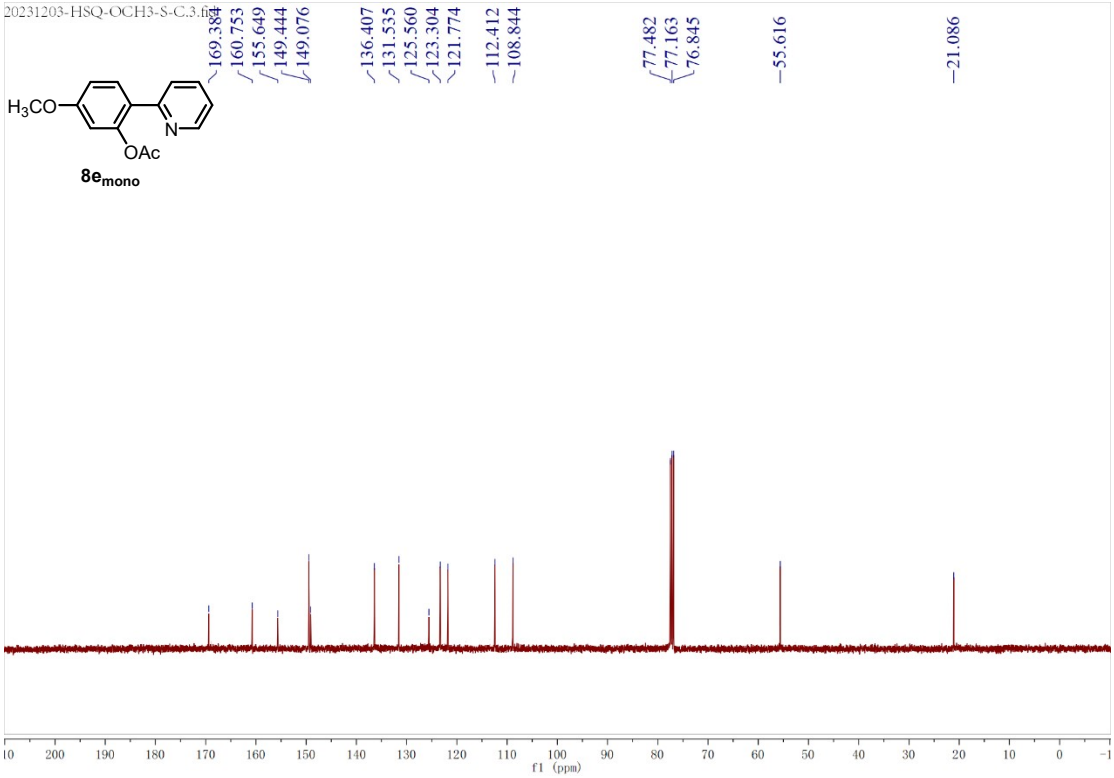


5-methoxy-2-(pyridin-2-yl)phenyl acetate (**8e$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

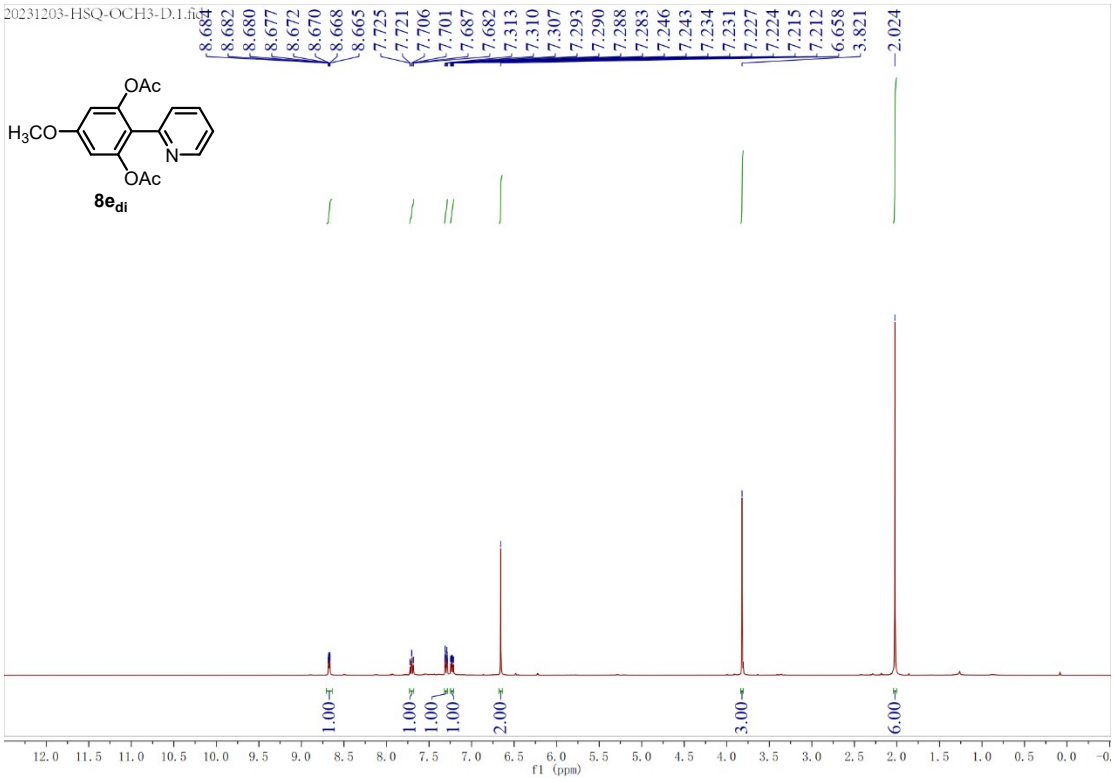


^{13}C NMR (100 MHz, $CDCl_3$)

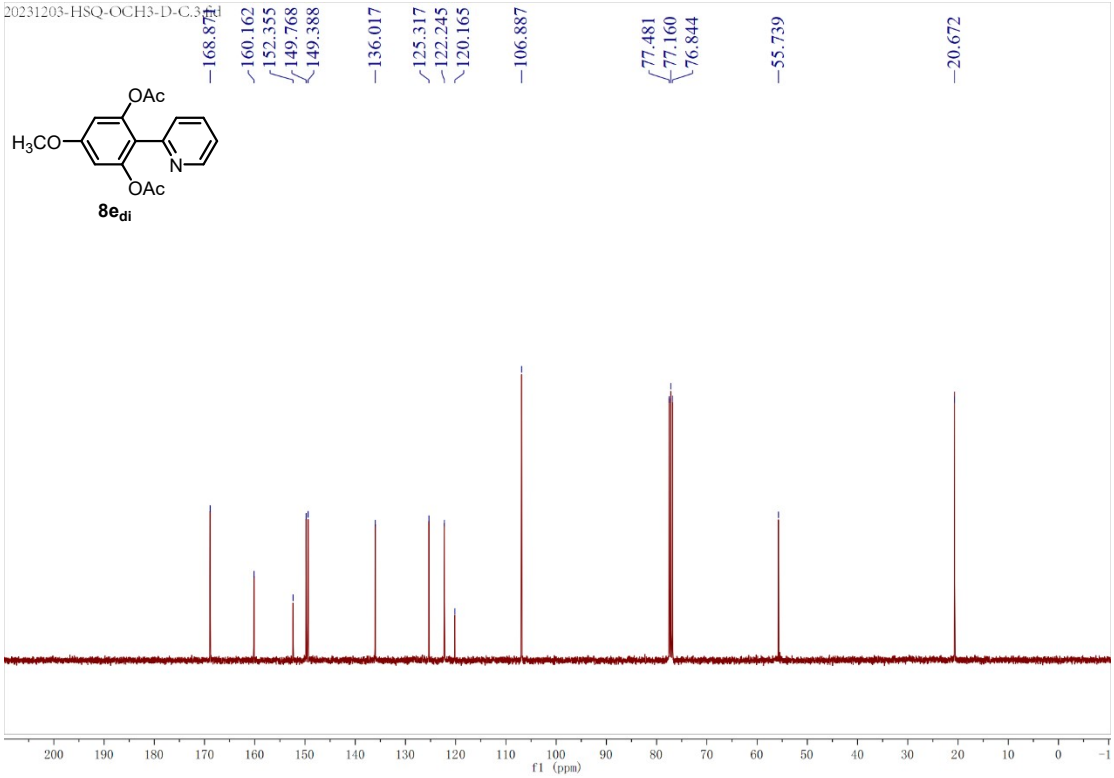


5-methoxy-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8e$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

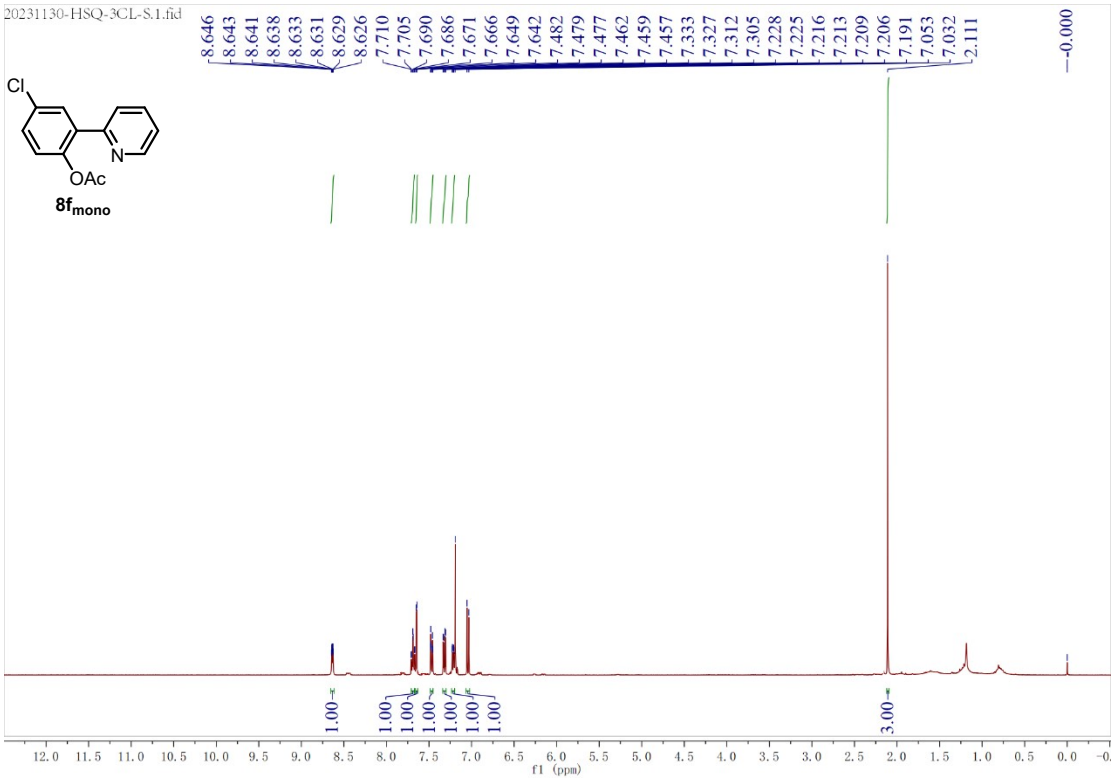


^{13}C NMR (100 MHz, $CDCl_3$)

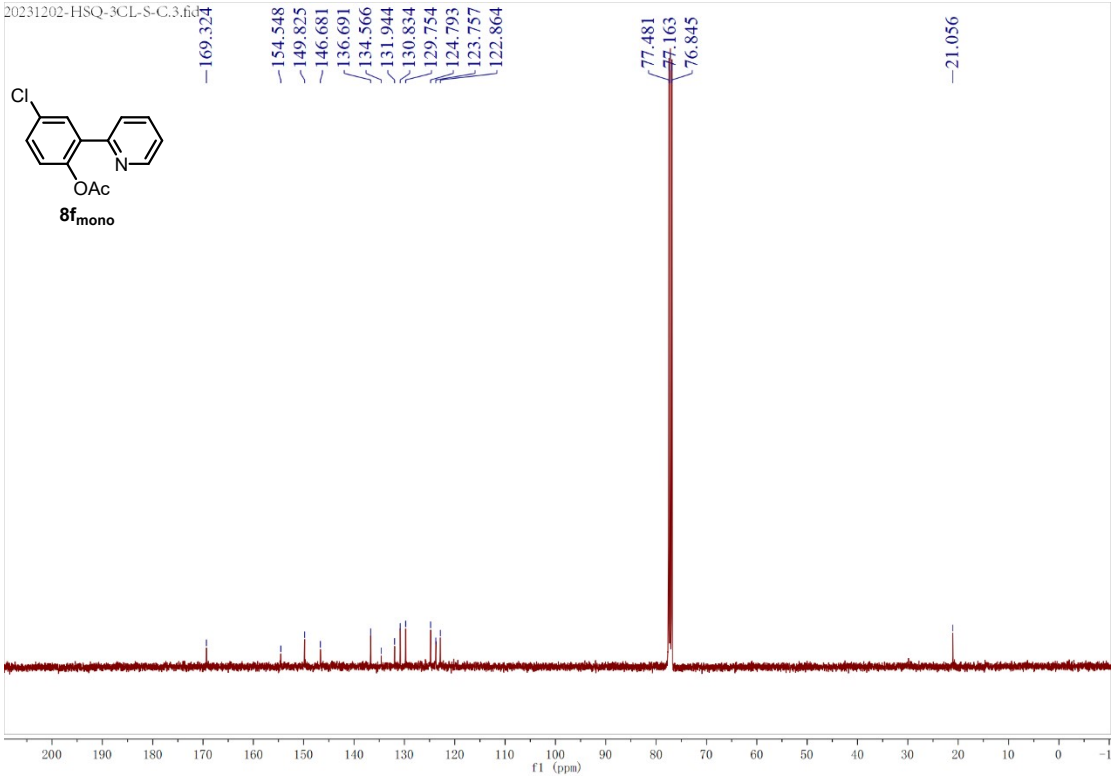


4-chloro-2-(pyridin-2-yl)phenyl acetate (**8f$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

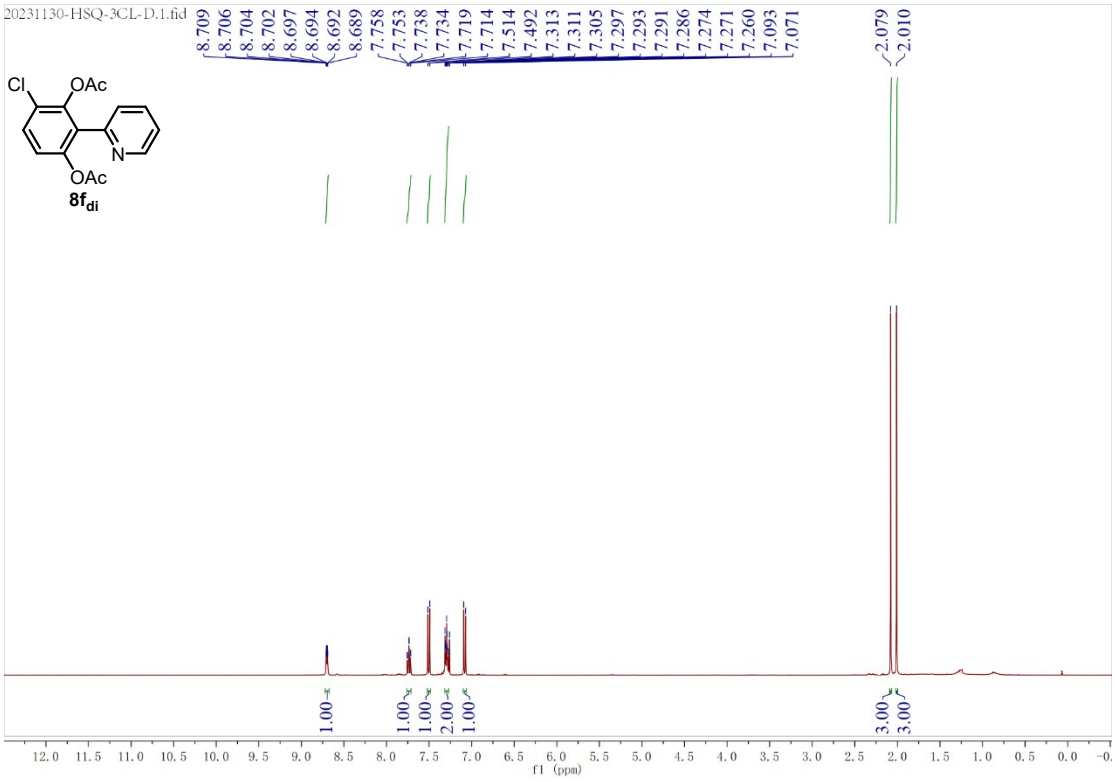


^{13}C NMR (100 MHz, $CDCl_3$)

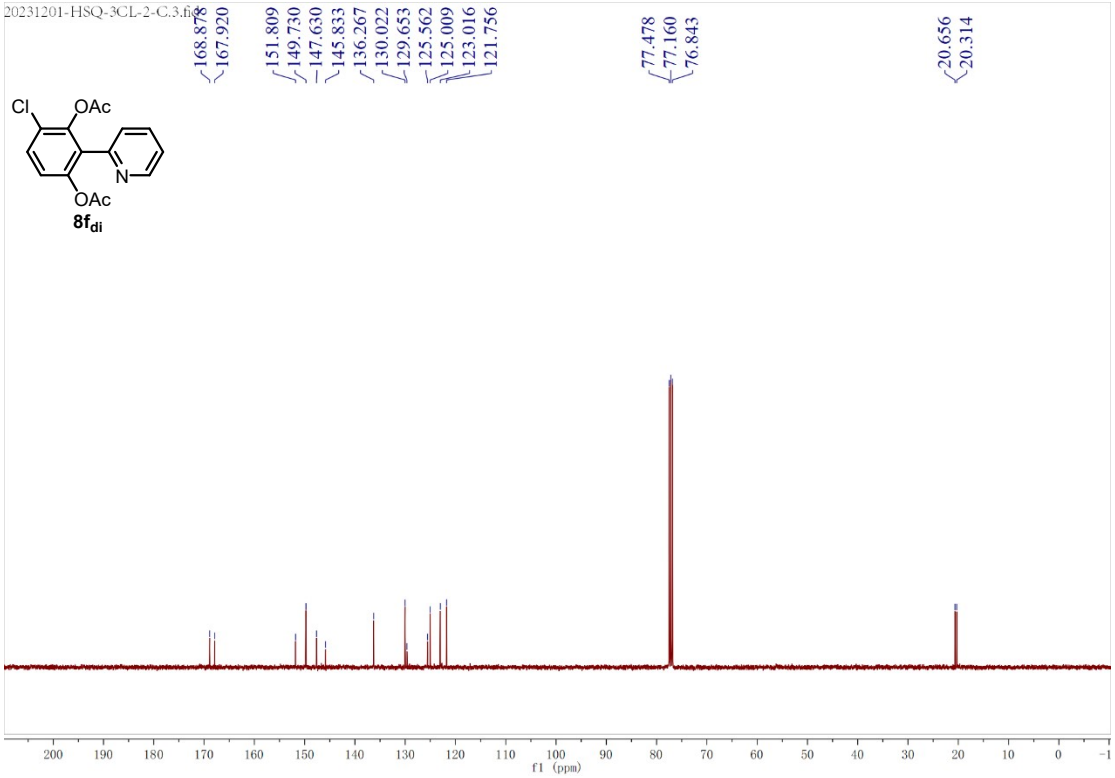


4-chloro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8f$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

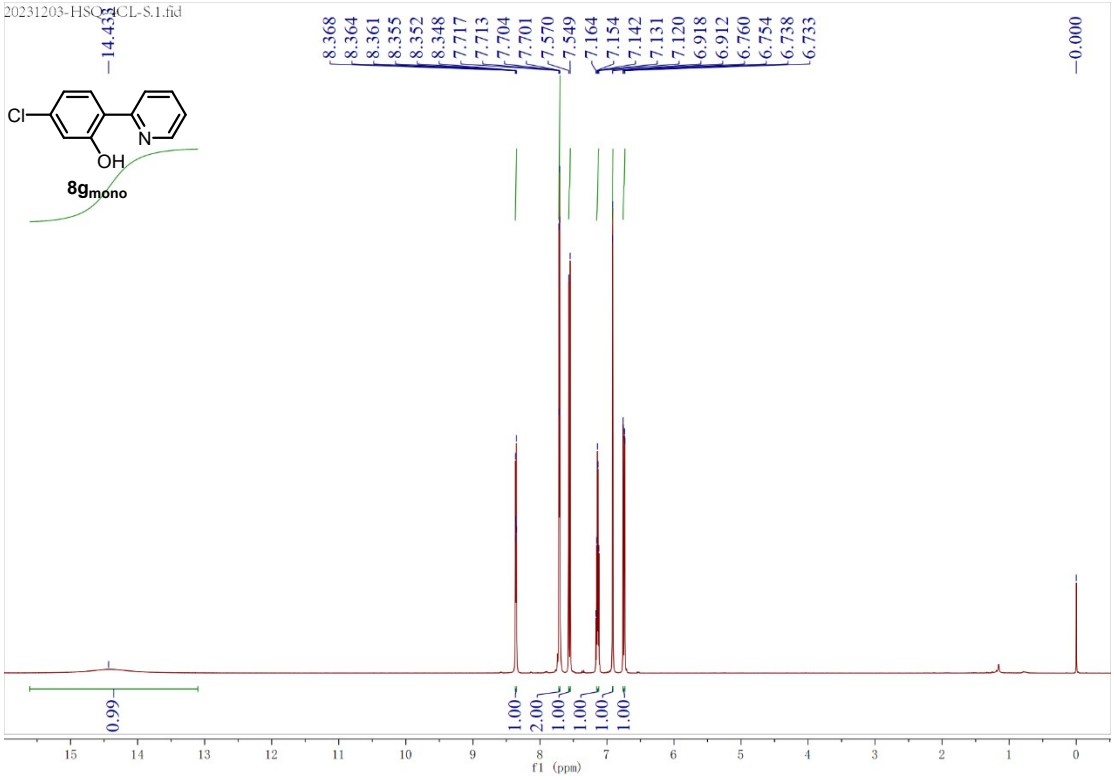


^{13}C NMR (100 MHz, $CDCl_3$)

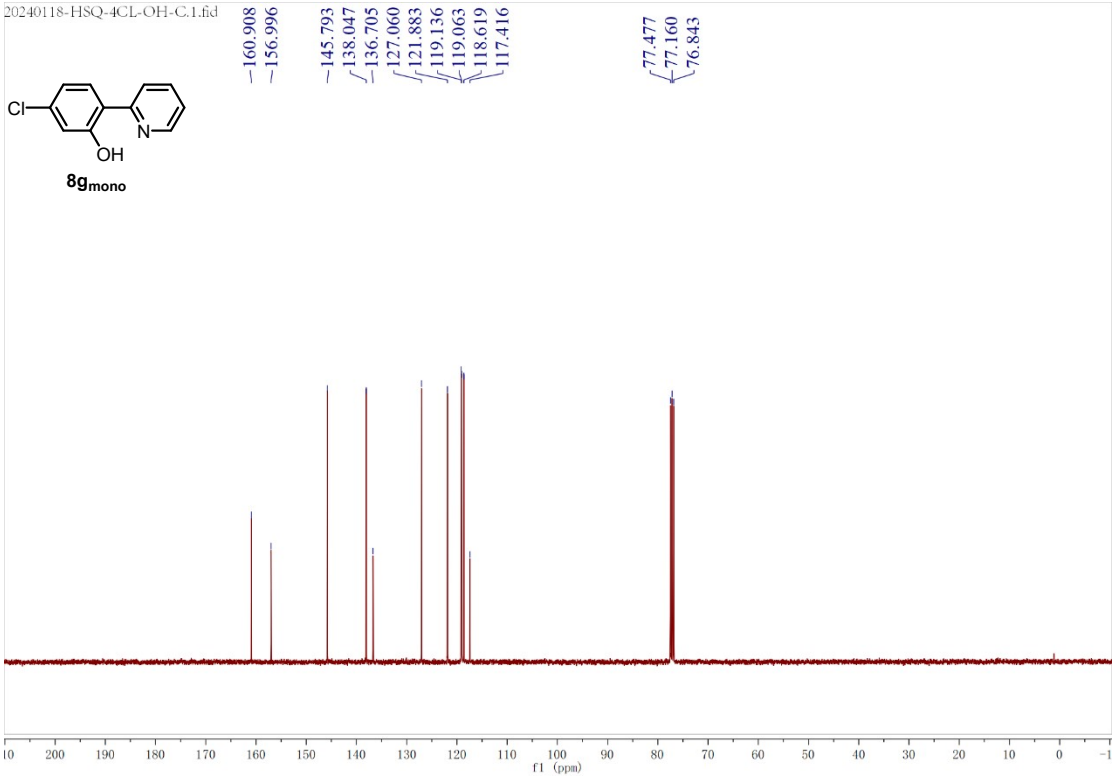


5-chloro-2-(pyridin-2-yl)phenol (**8g$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

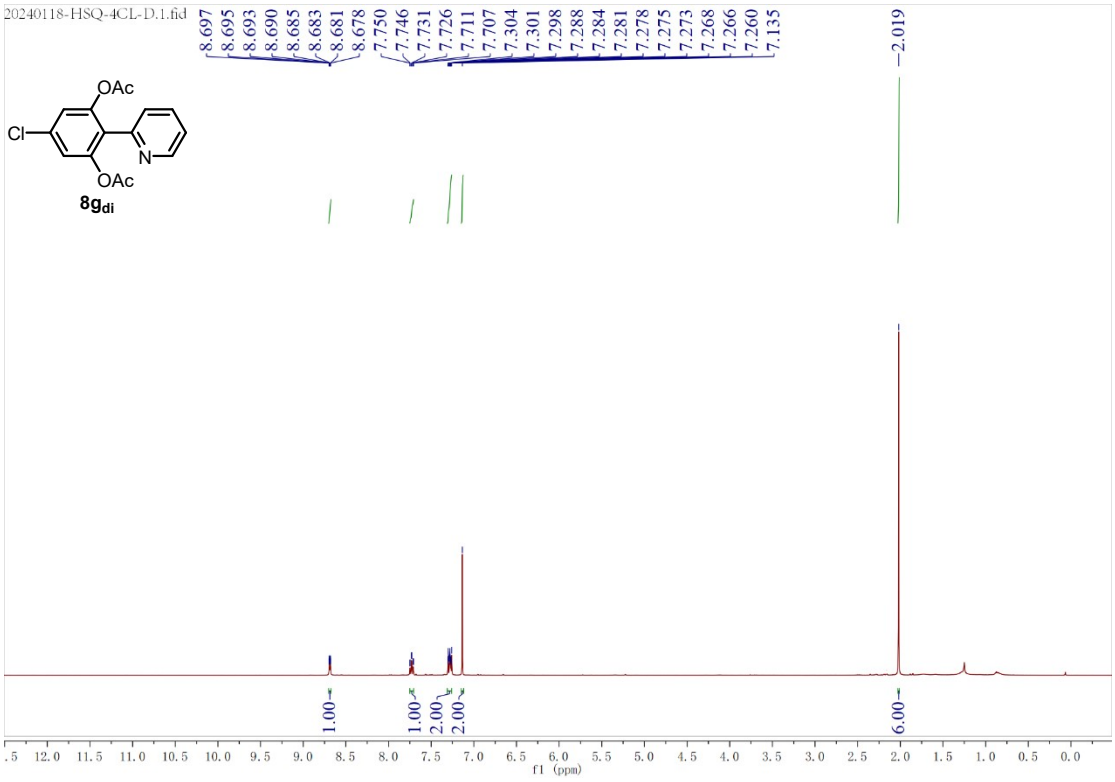


^{13}C NMR (100 MHz, $CDCl_3$)

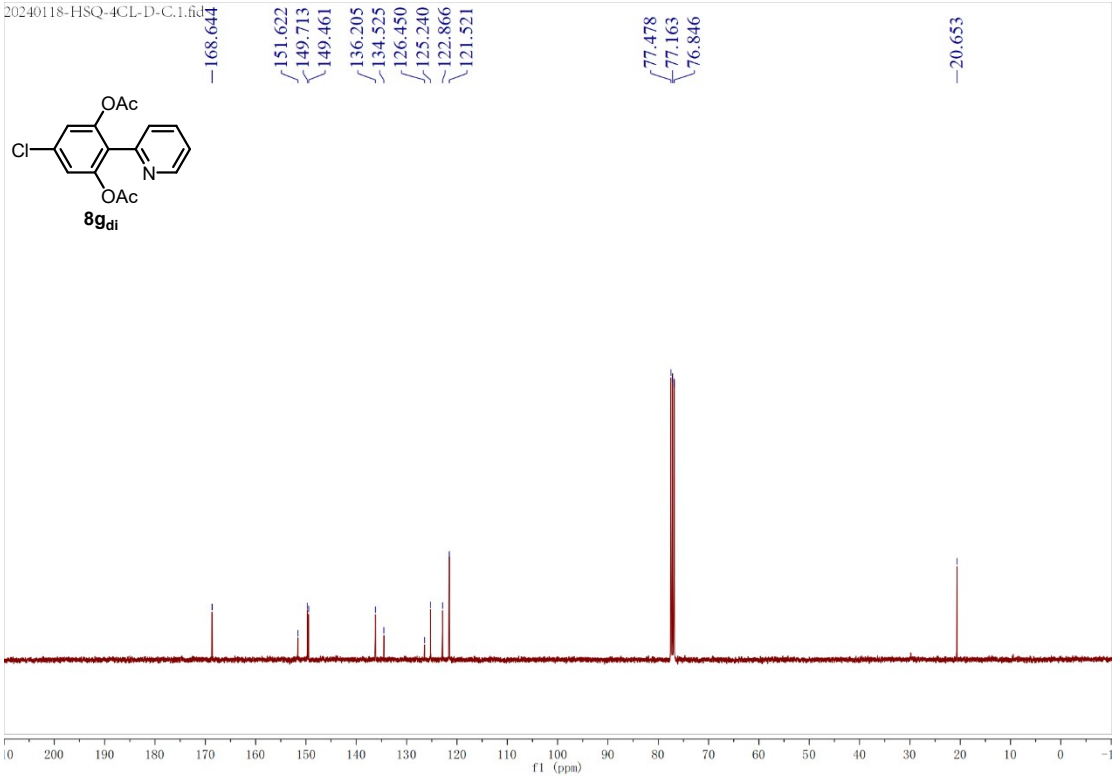


5-chloro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8g$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

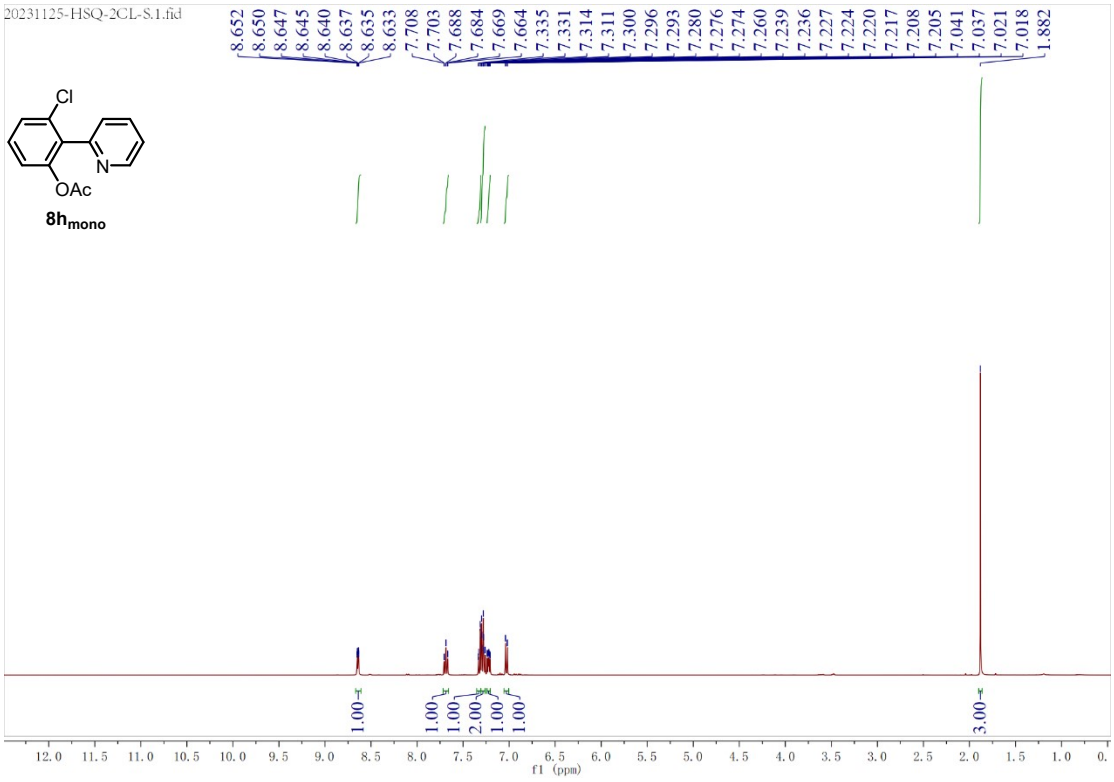


^{13}C NMR (100 MHz, $CDCl_3$)

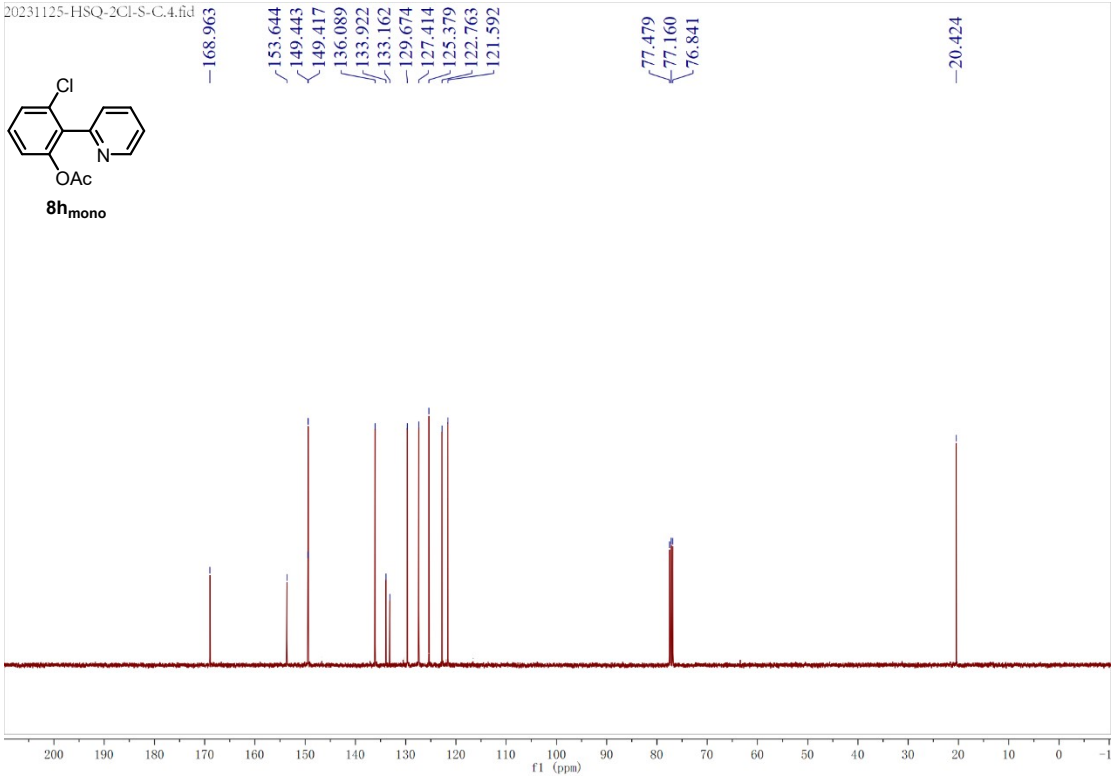


3-chloro-2-(pyridin-2-yl)phenyl acetate (**8h$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

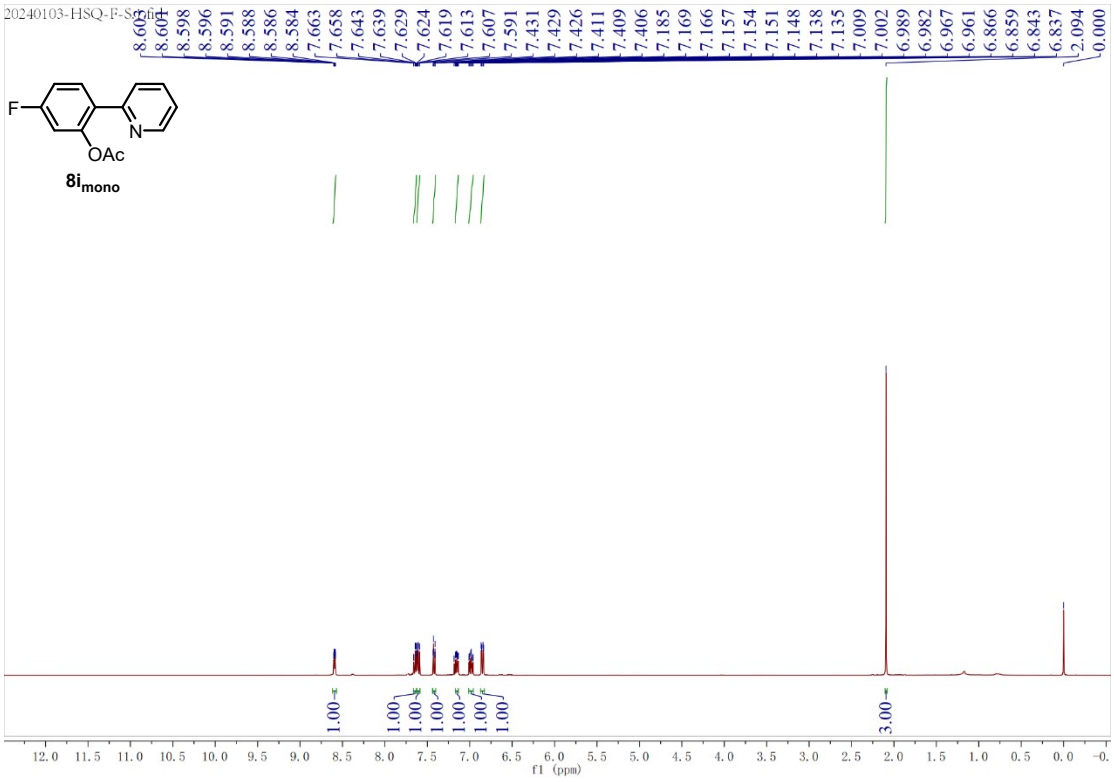


^{13}C NMR (100 MHz, $CDCl_3$)

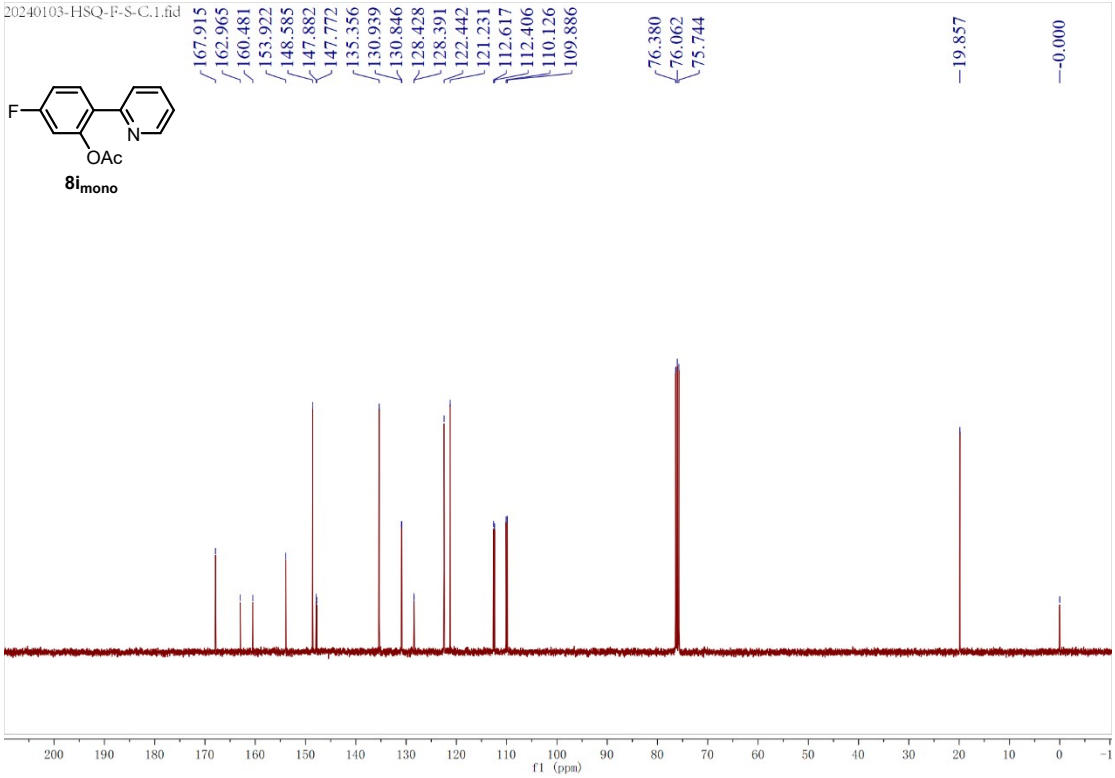


5-fluoro-2-(pyridin-2-yl)phenyl acetate (**8i$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

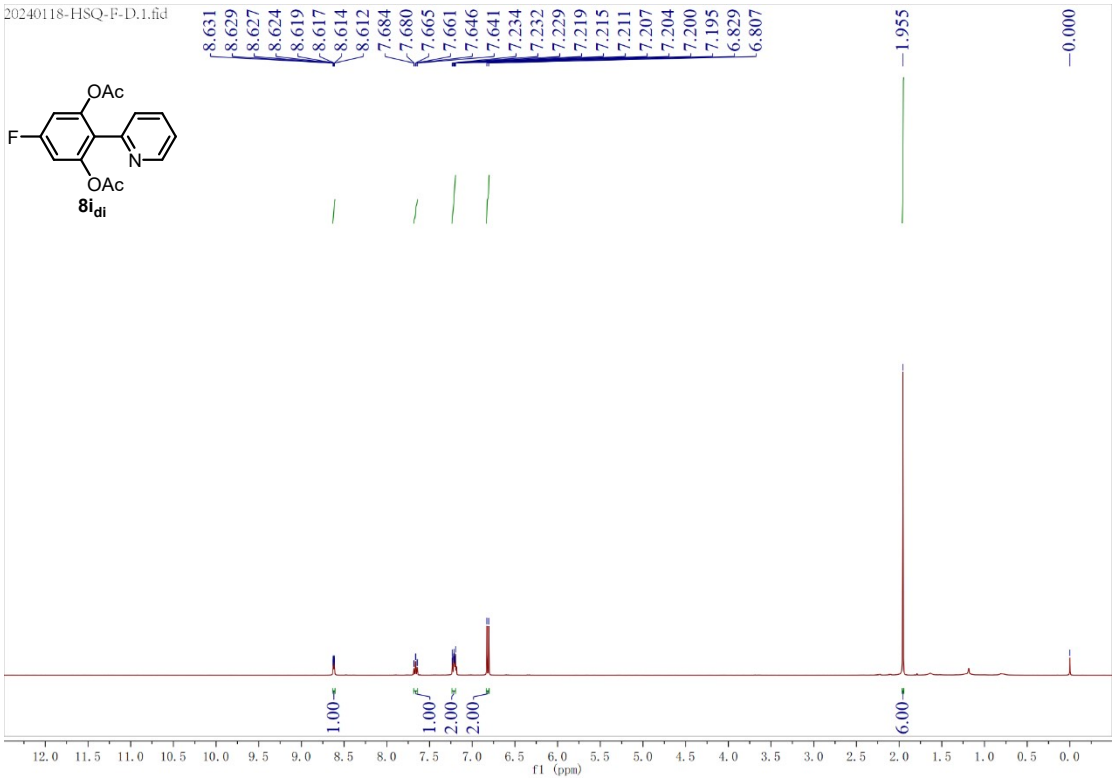


^{13}C NMR (100 MHz, $CDCl_3$)

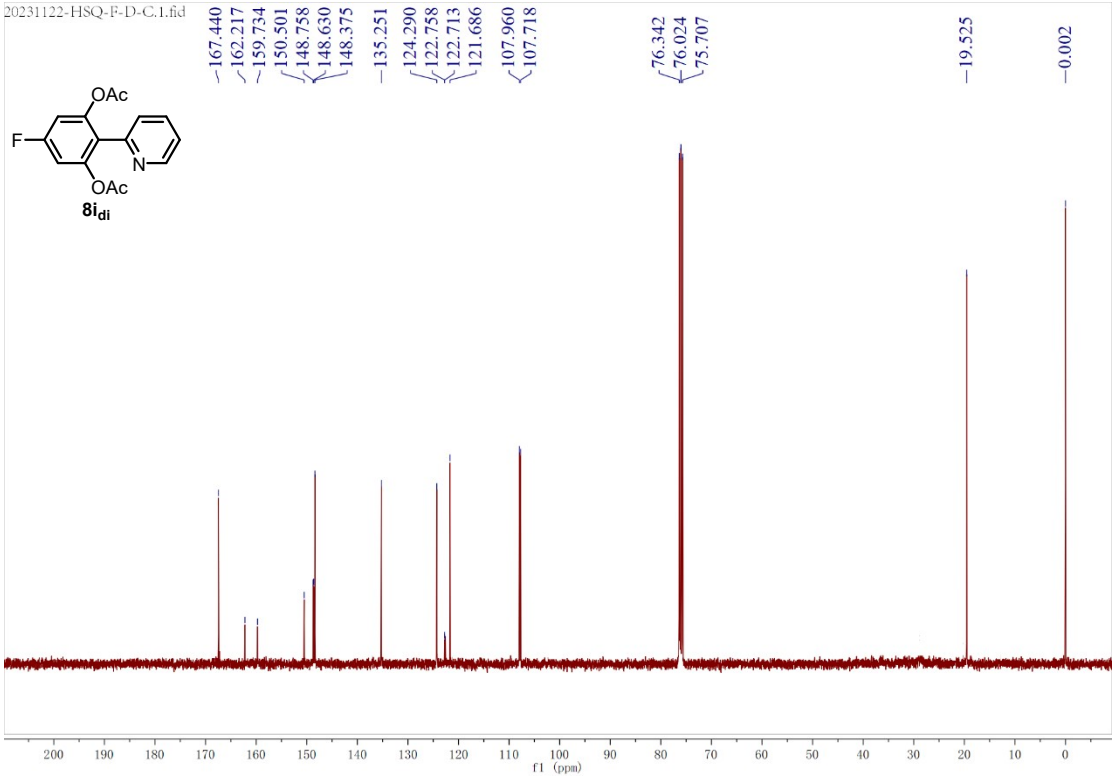


5-fluoro-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8i$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

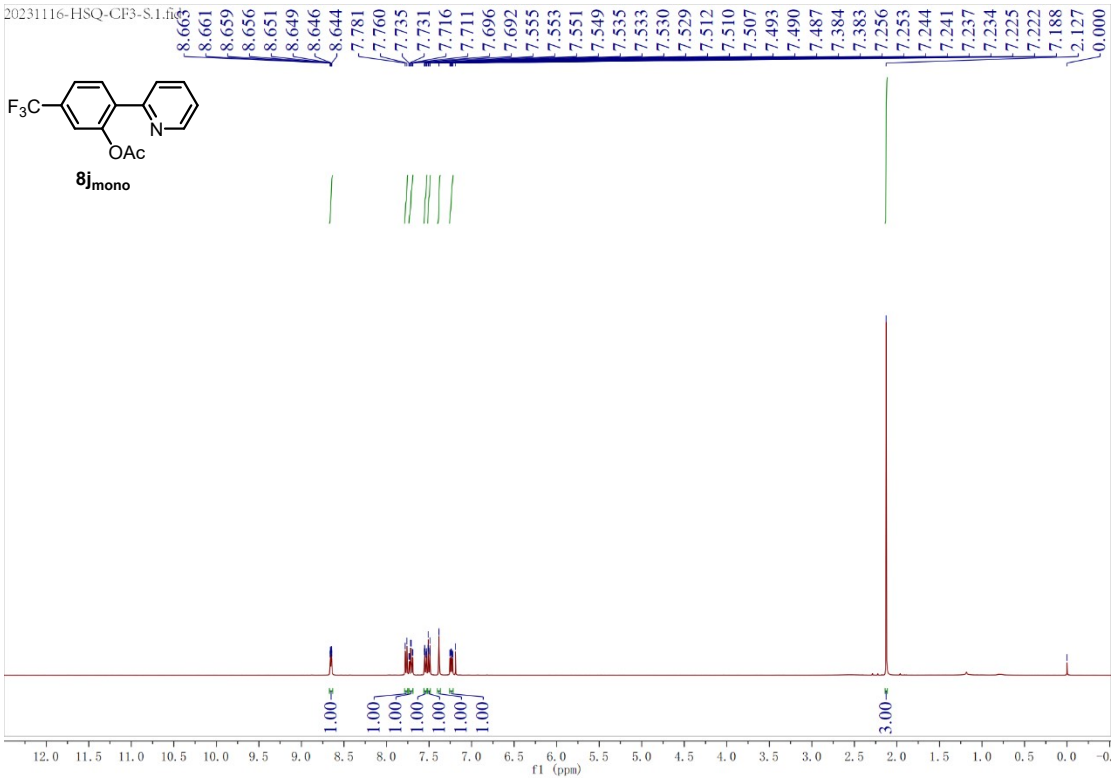


^{13}C NMR (100 MHz, $CDCl_3$)

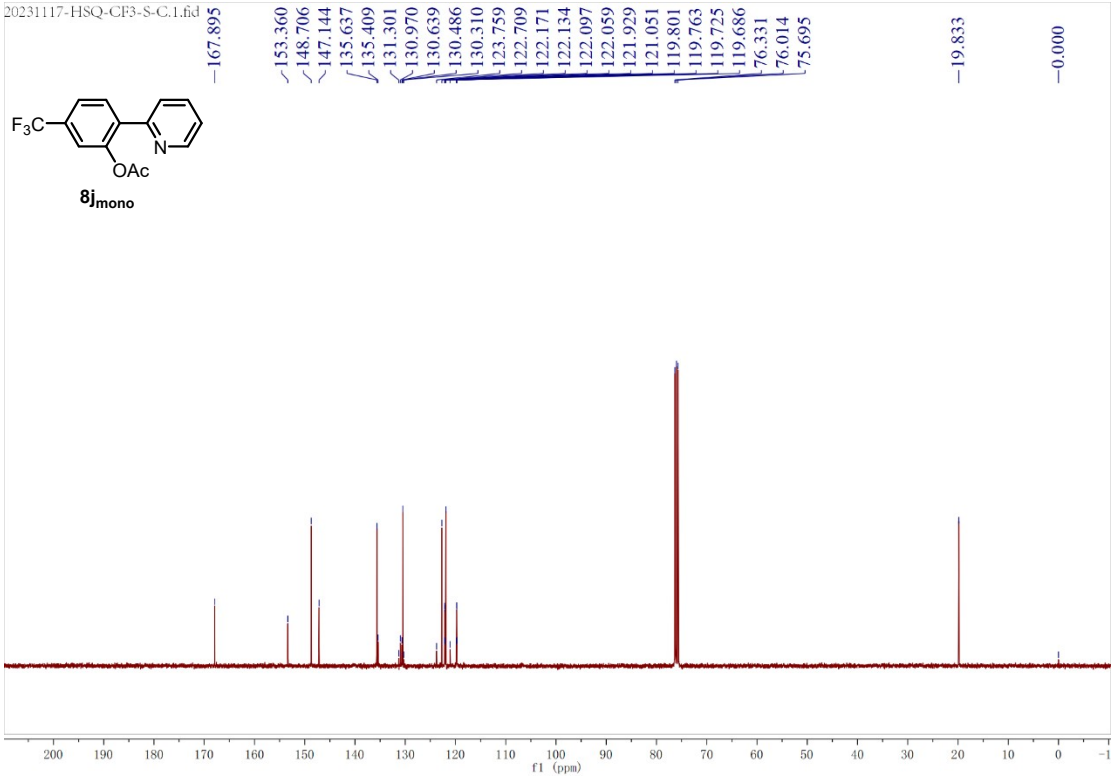


2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl acetate (**8j$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

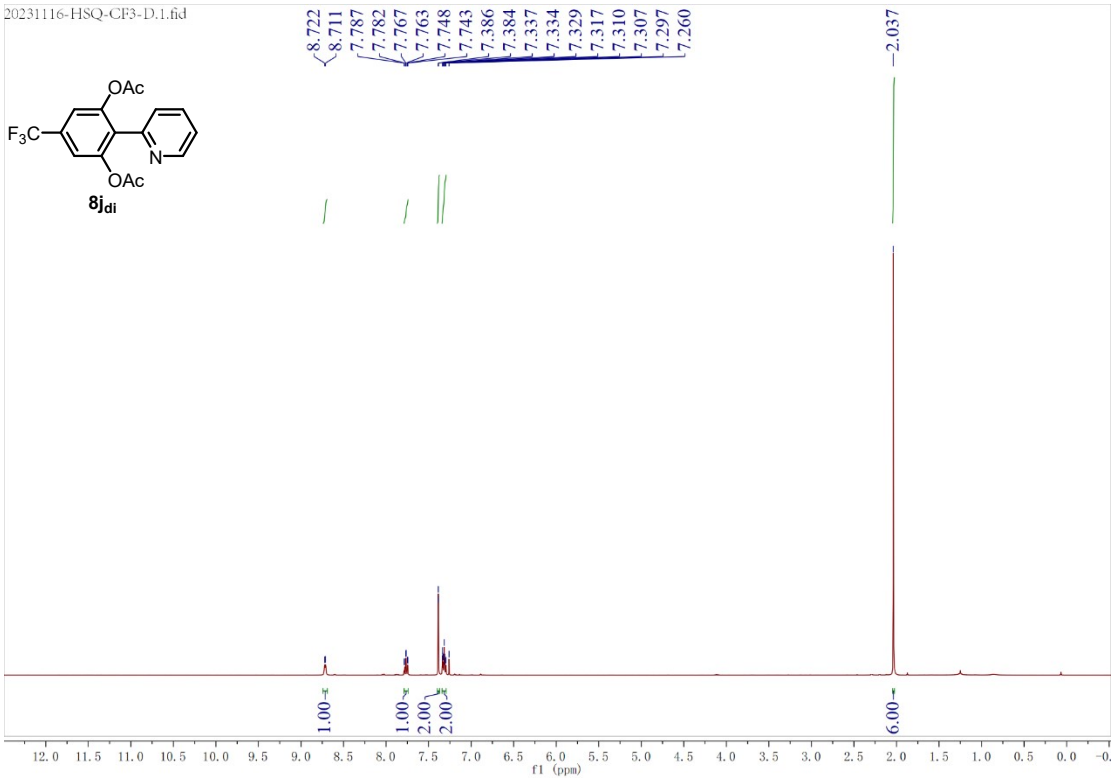


^{13}C NMR (100 MHz, $CDCl_3$)

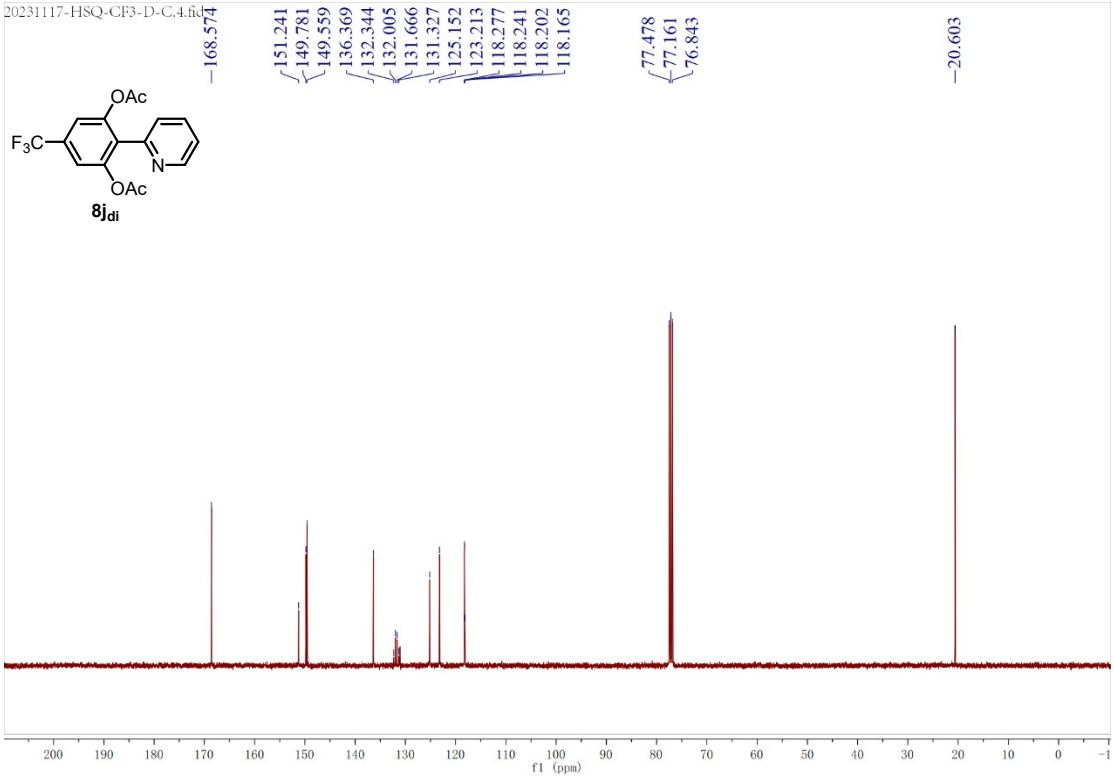


2-(pyridin-2-yl)-5-(trifluoromethyl)-1,3-phenylene diacetate (**8j$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

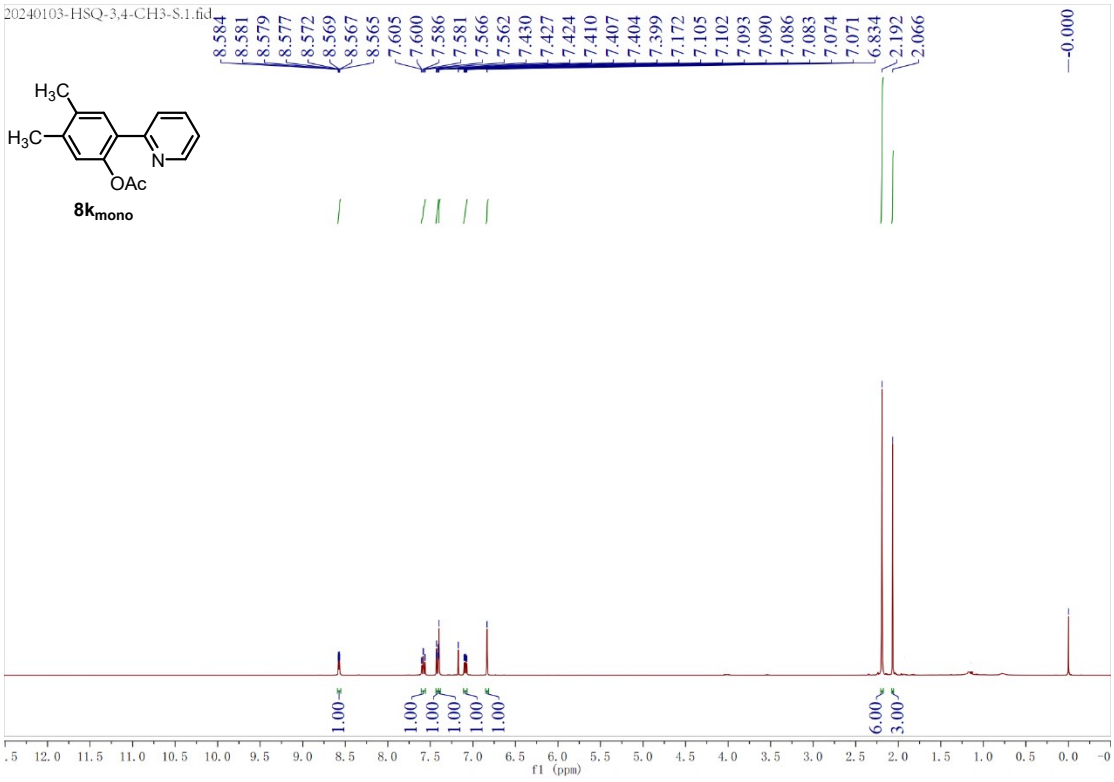


^{13}C NMR (100 MHz, $CDCl_3$)

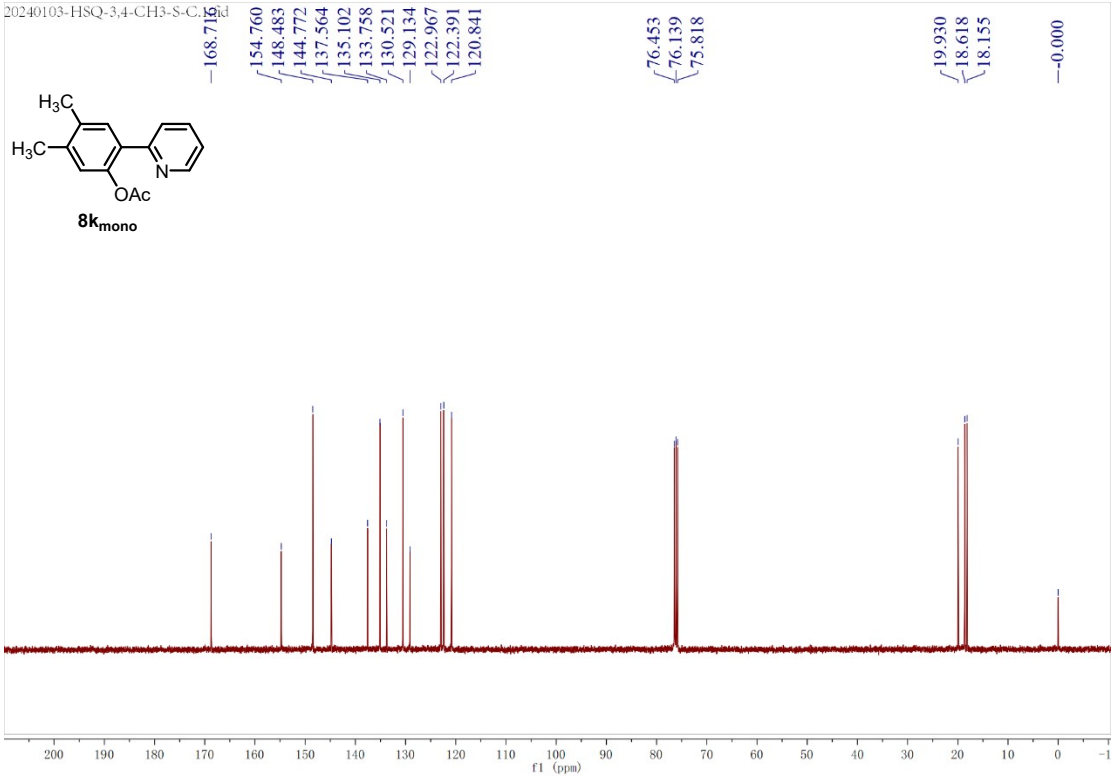


4,5-dimethyl-2-(pyridin-2-yl)phenyl acetate (**8k$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

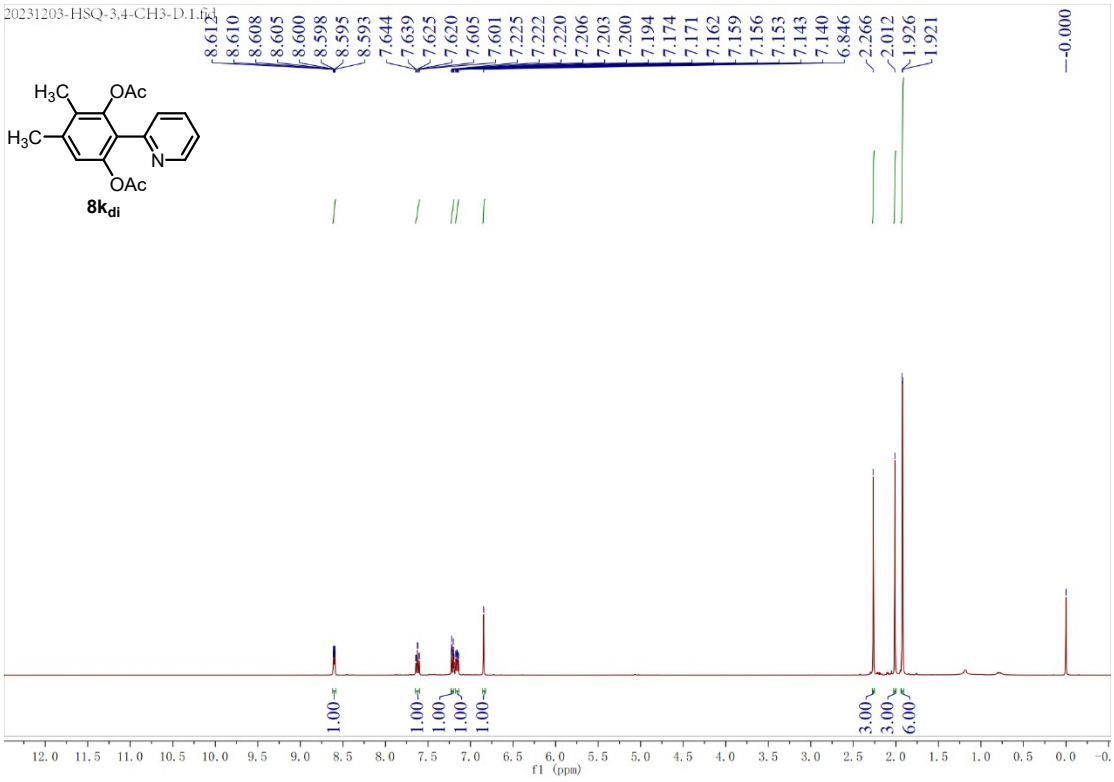


^{13}C NMR (100 MHz, $CDCl_3$)

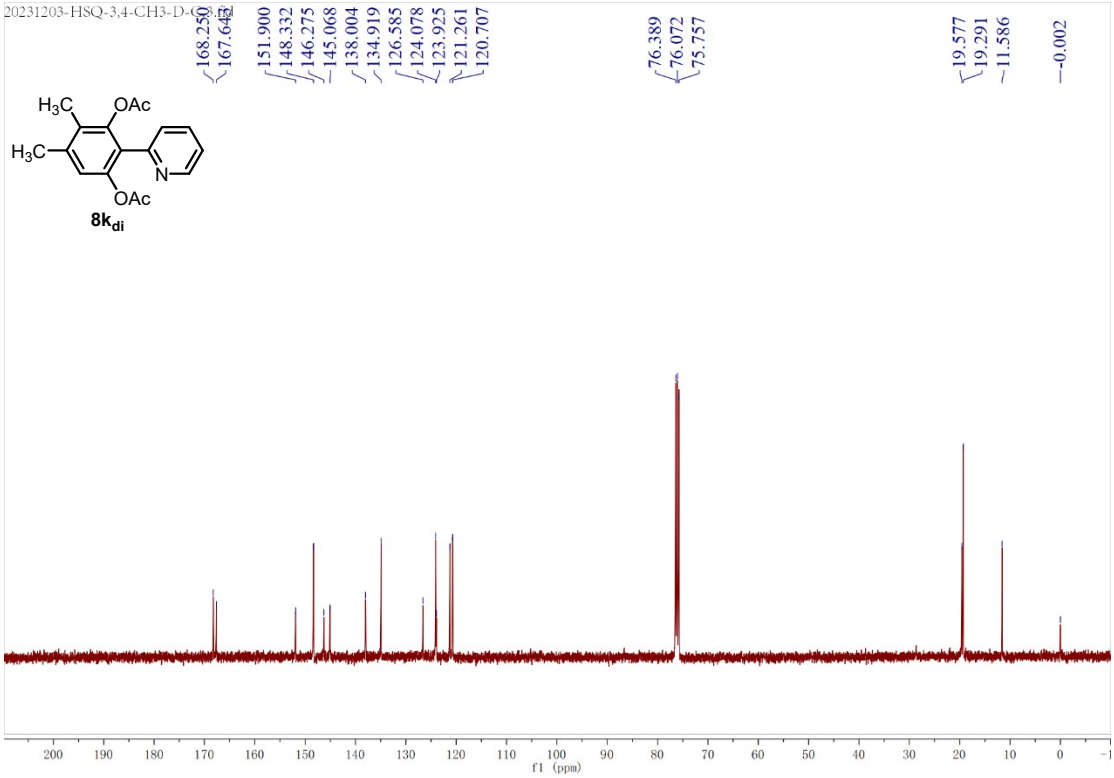


4,5-dimethyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8k$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

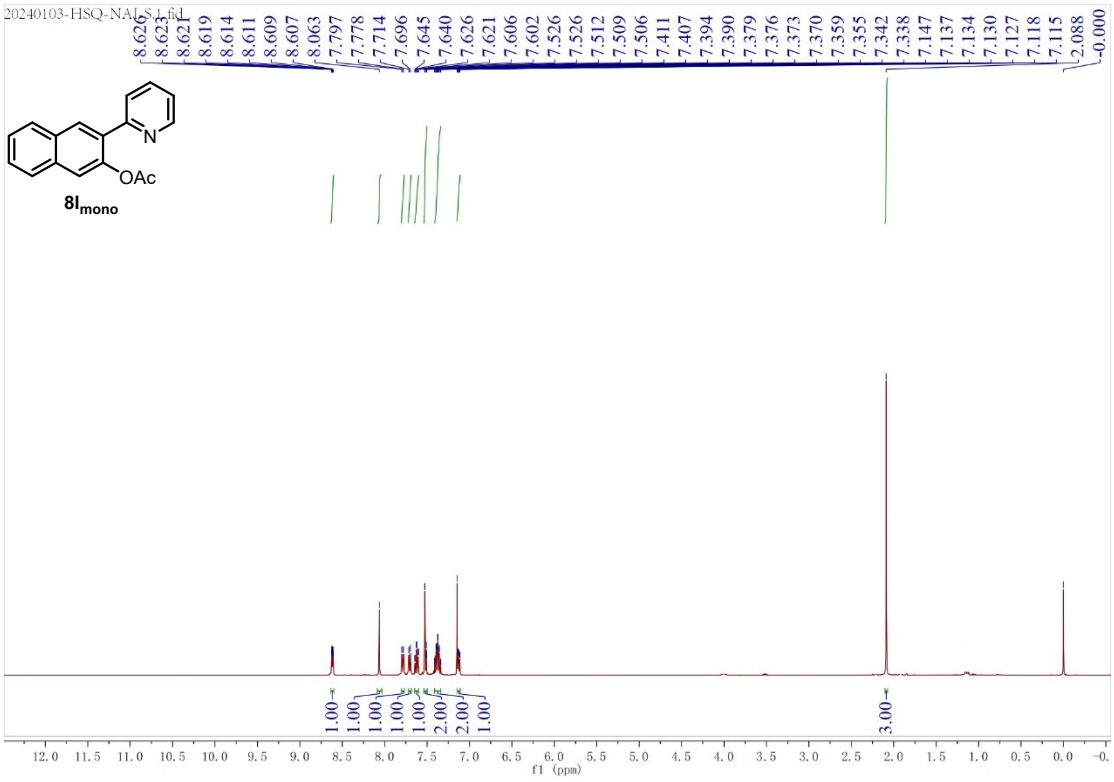


^{13}C NMR (100 MHz, $CDCl_3$)

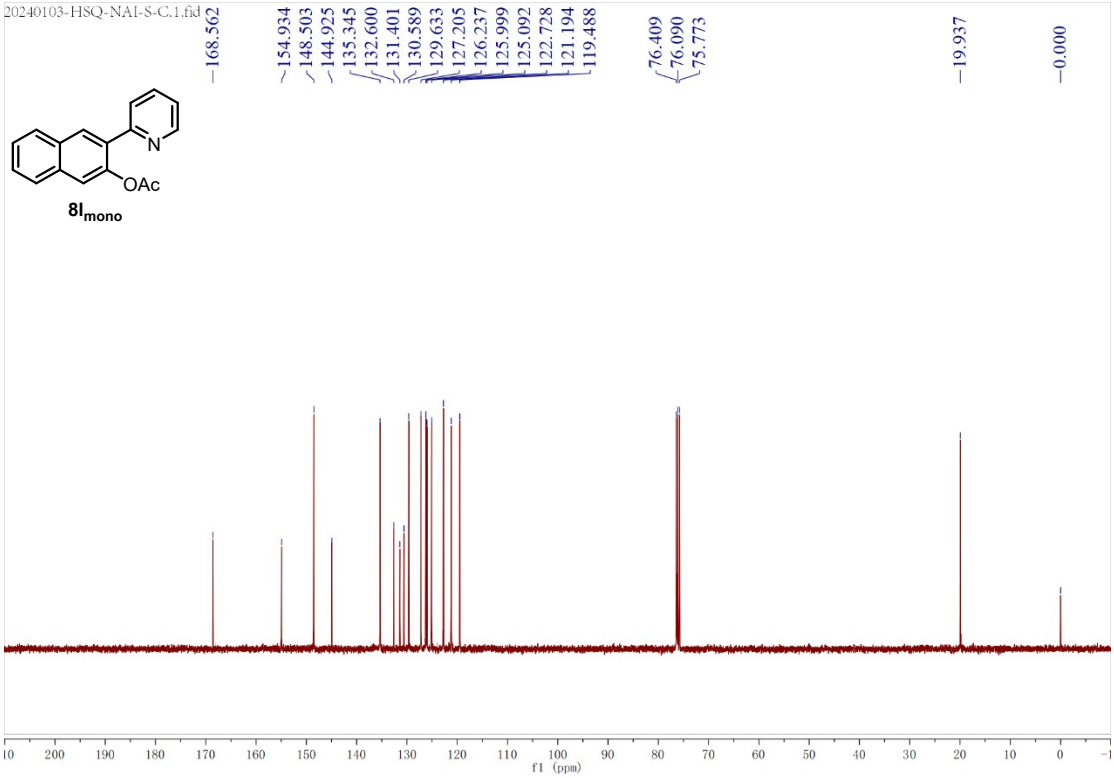


3-(pyridin-2-yl)naphthalen-2-yl acetate (**8l$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

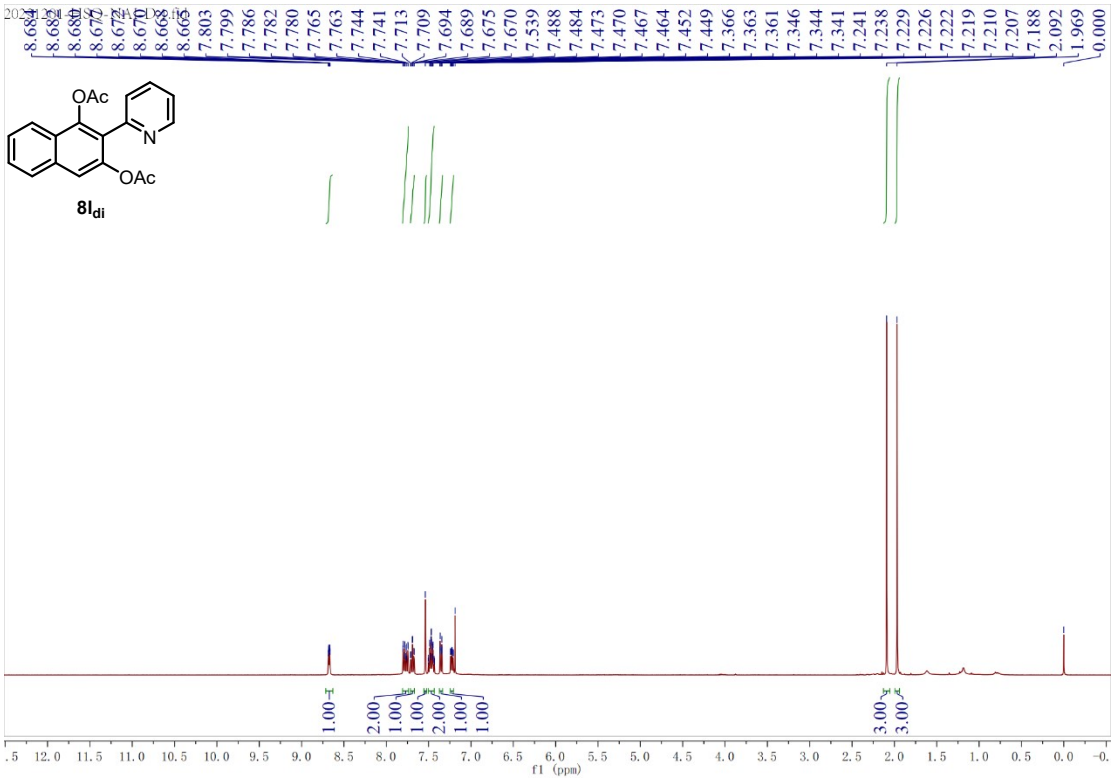


^{13}C NMR (100 MHz, $CDCl_3$)

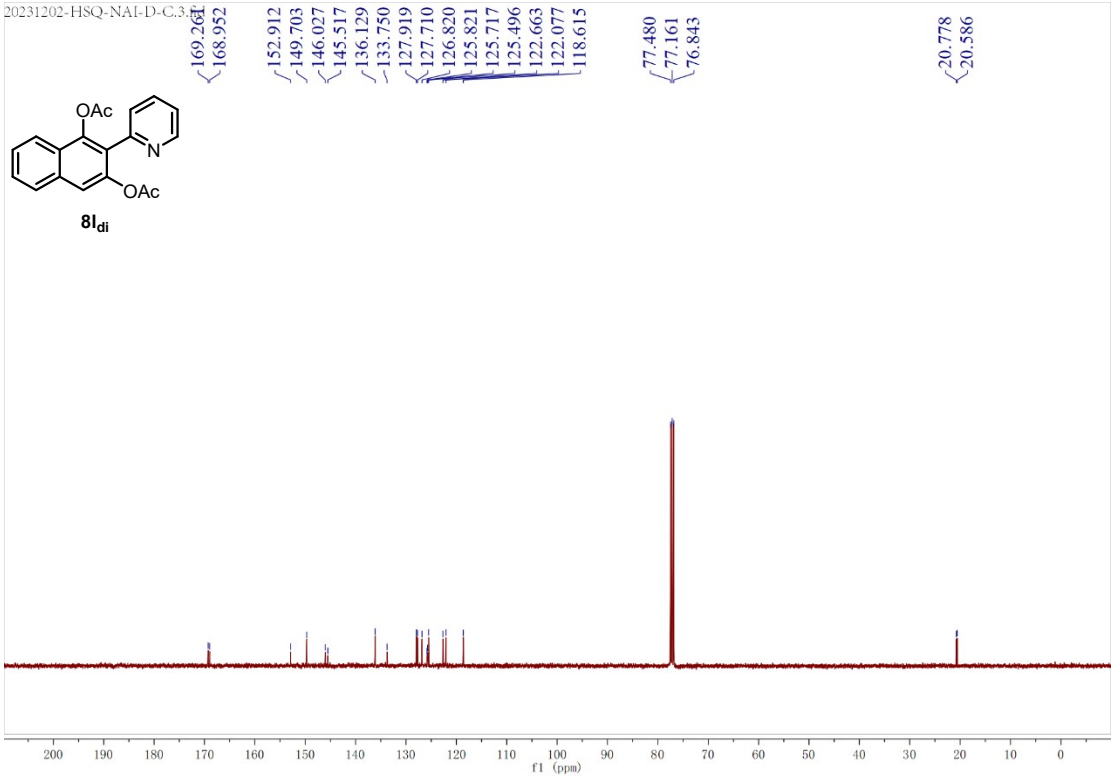


2-(pyridin-2-yl)naphthalene-1,3-diyl diacetate (**8l$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

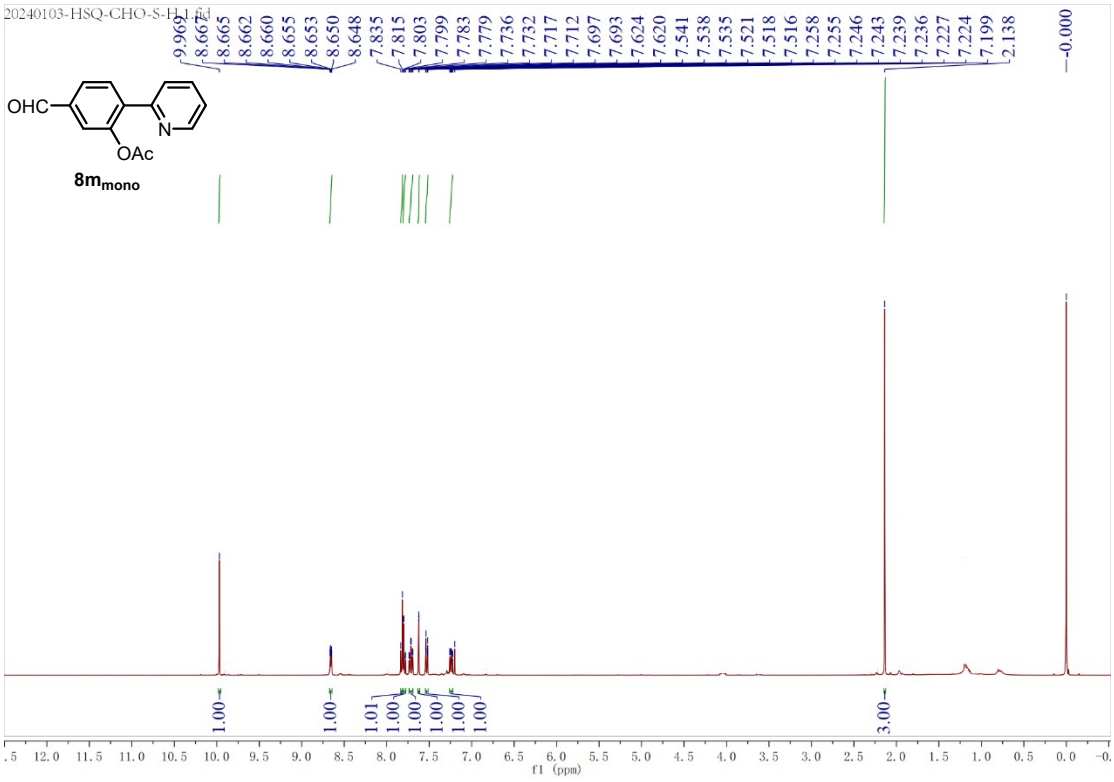


^{13}C NMR (100 MHz, $CDCl_3$)

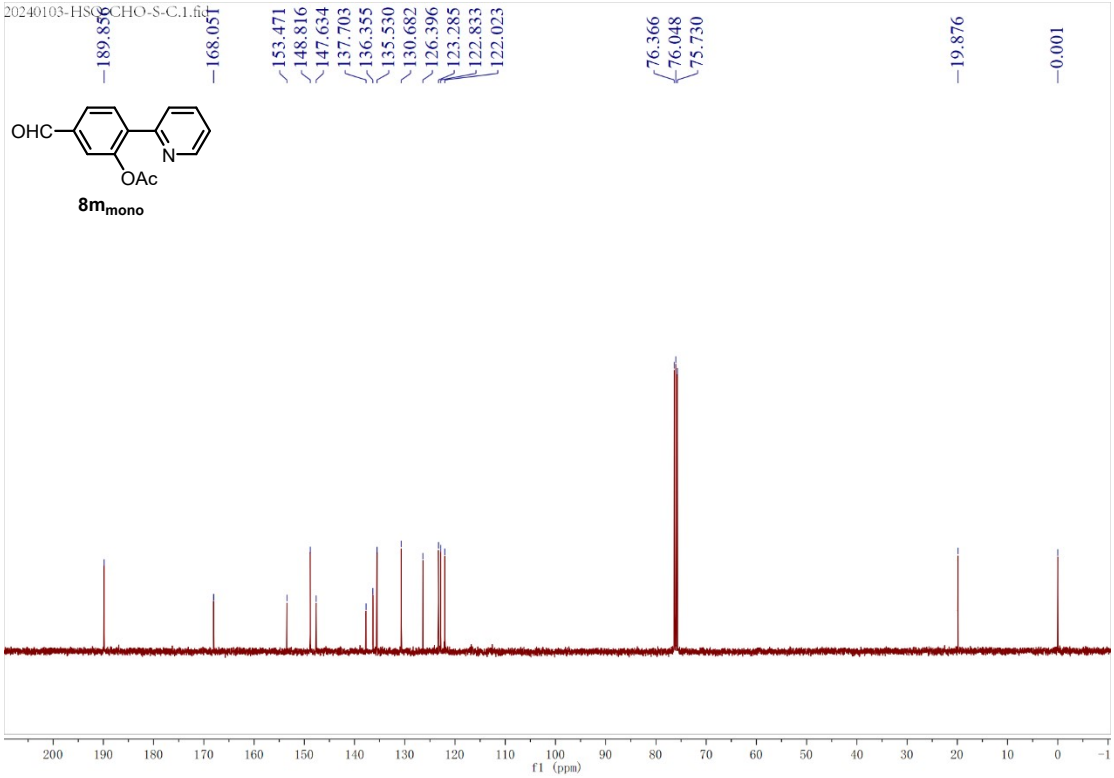


5-formyl-2-(pyridin-2-yl)phenyl acetate (**8m$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

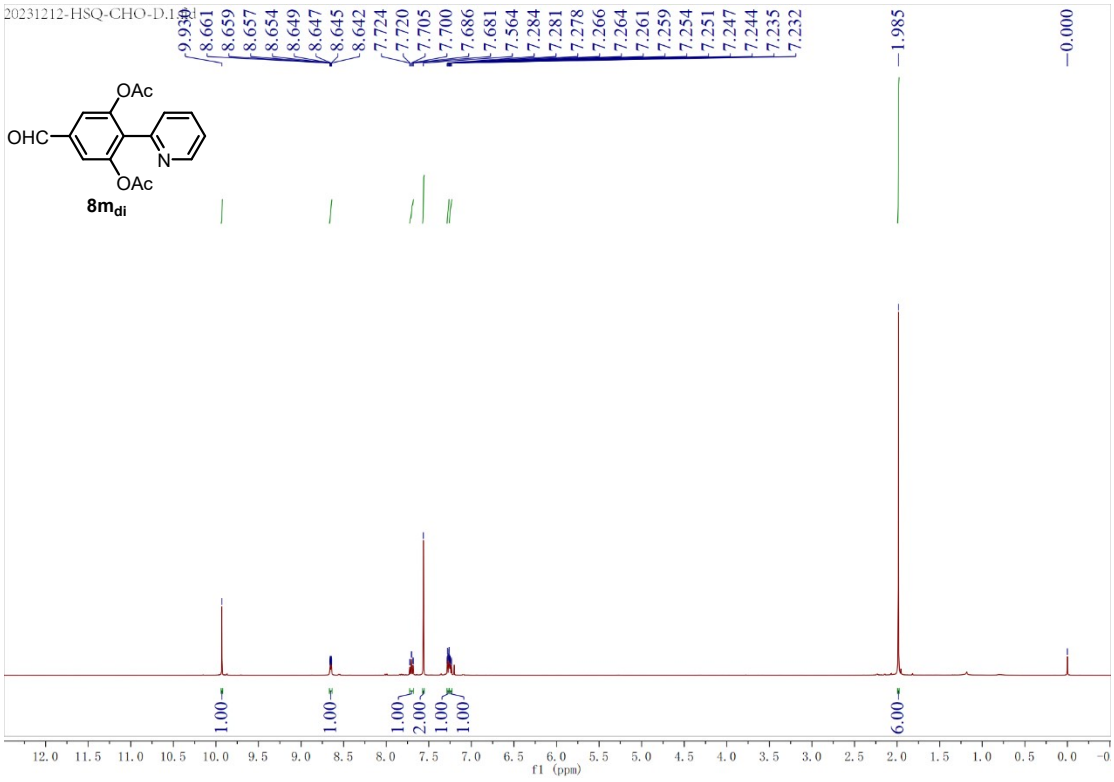


^{13}C NMR (100 MHz, $CDCl_3$)

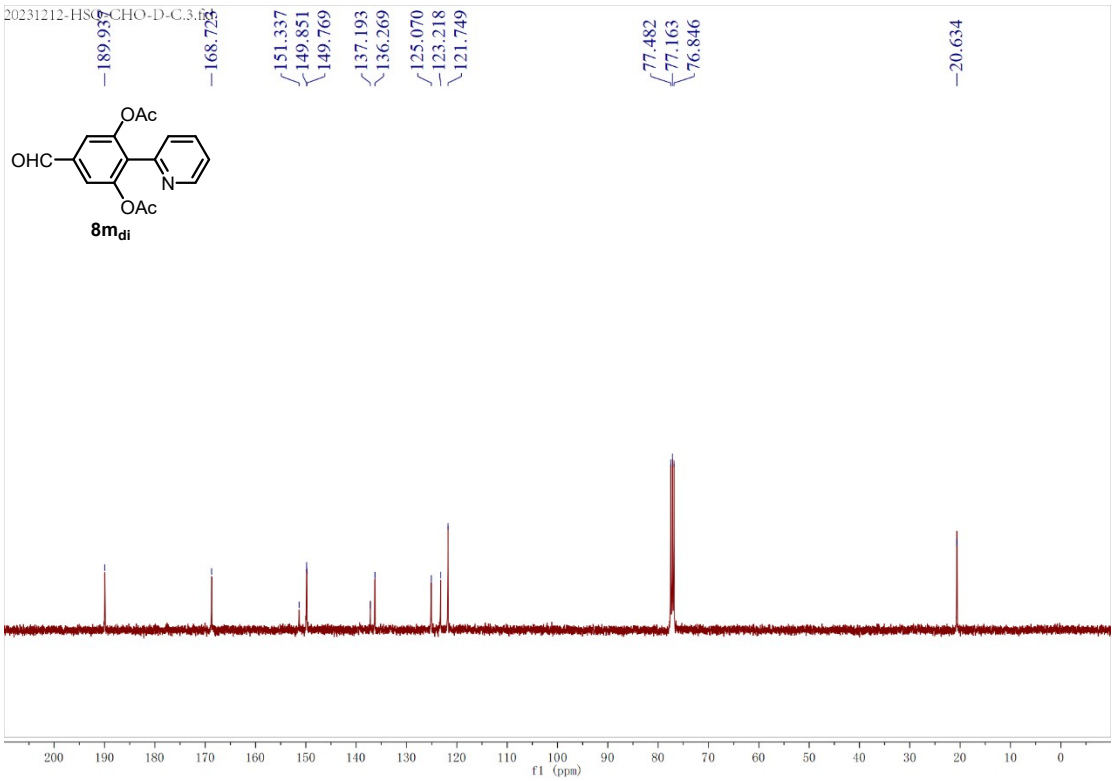


5-formyl-2-(pyridin-2-yl)-1,3-phenylene diacetate (**8m$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

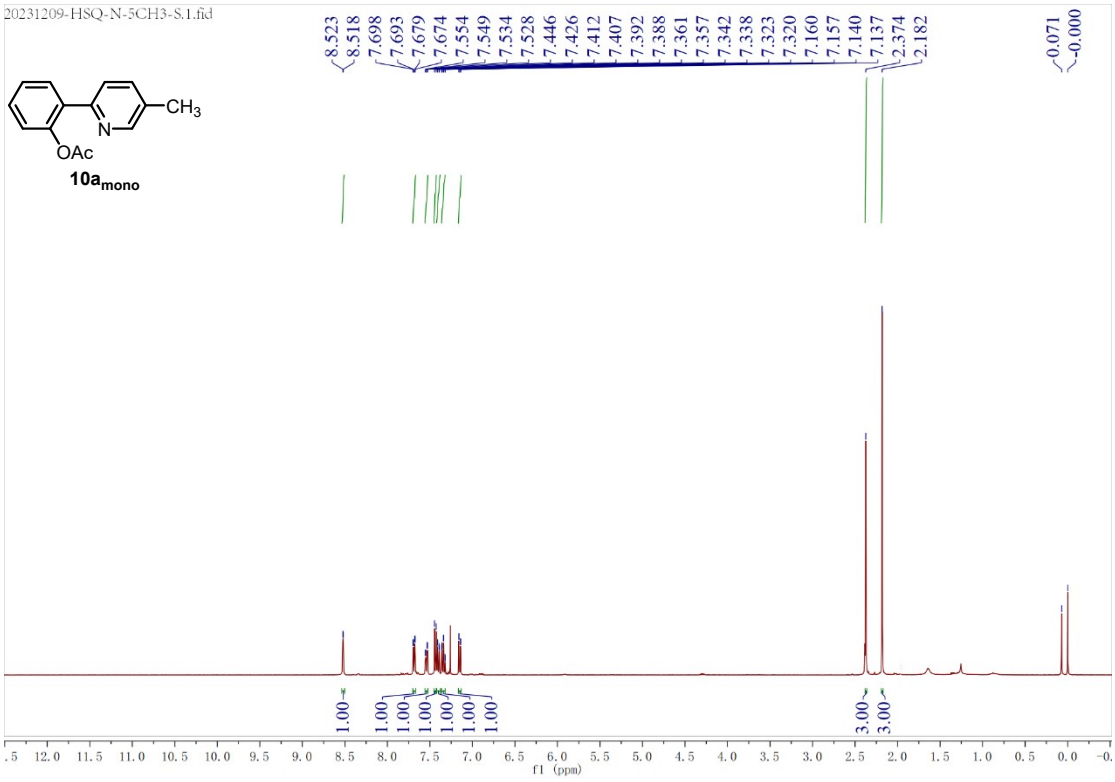


^{13}C NMR (100 MHz, $CDCl_3$)

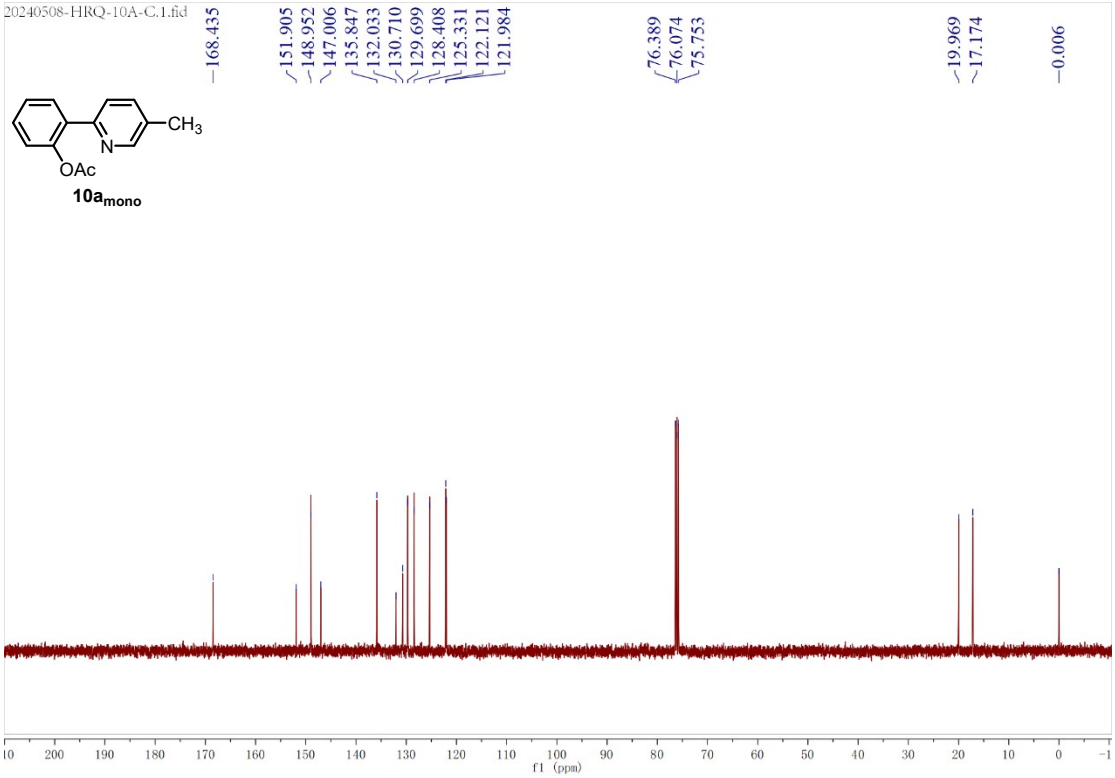


2-(5-methylpyridin-2-yl)phenyl acetate (**10a$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

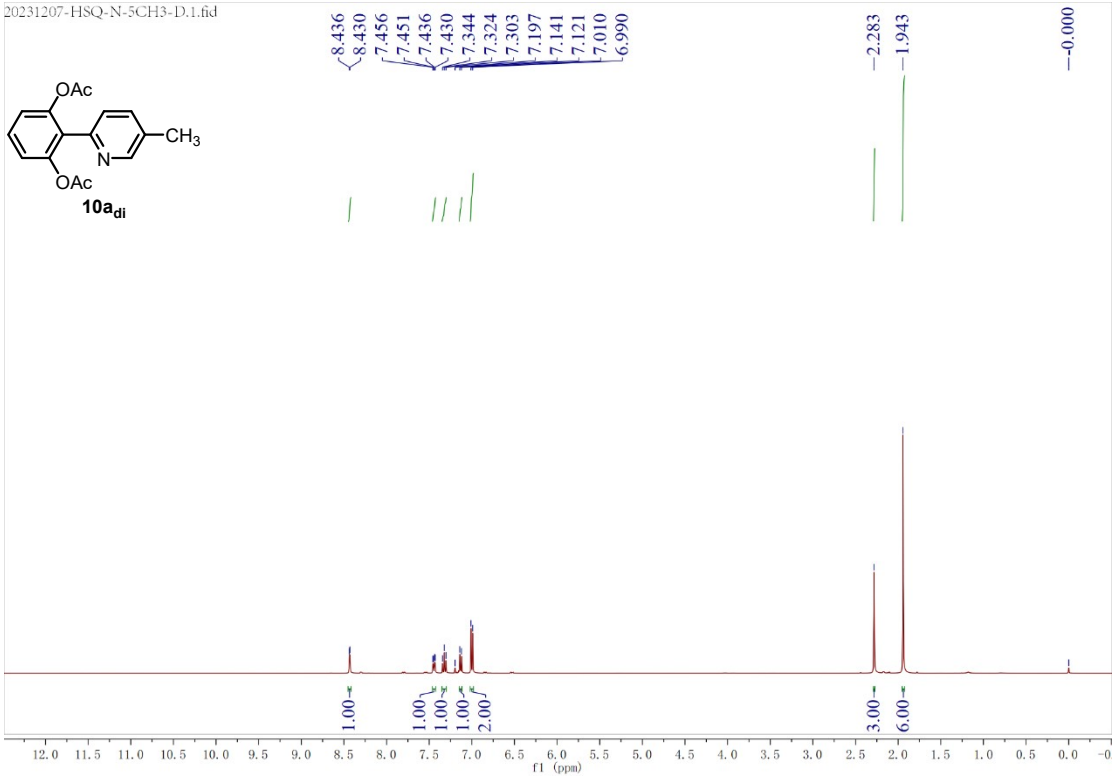


^{13}C NMR (100 MHz, $CDCl_3$)

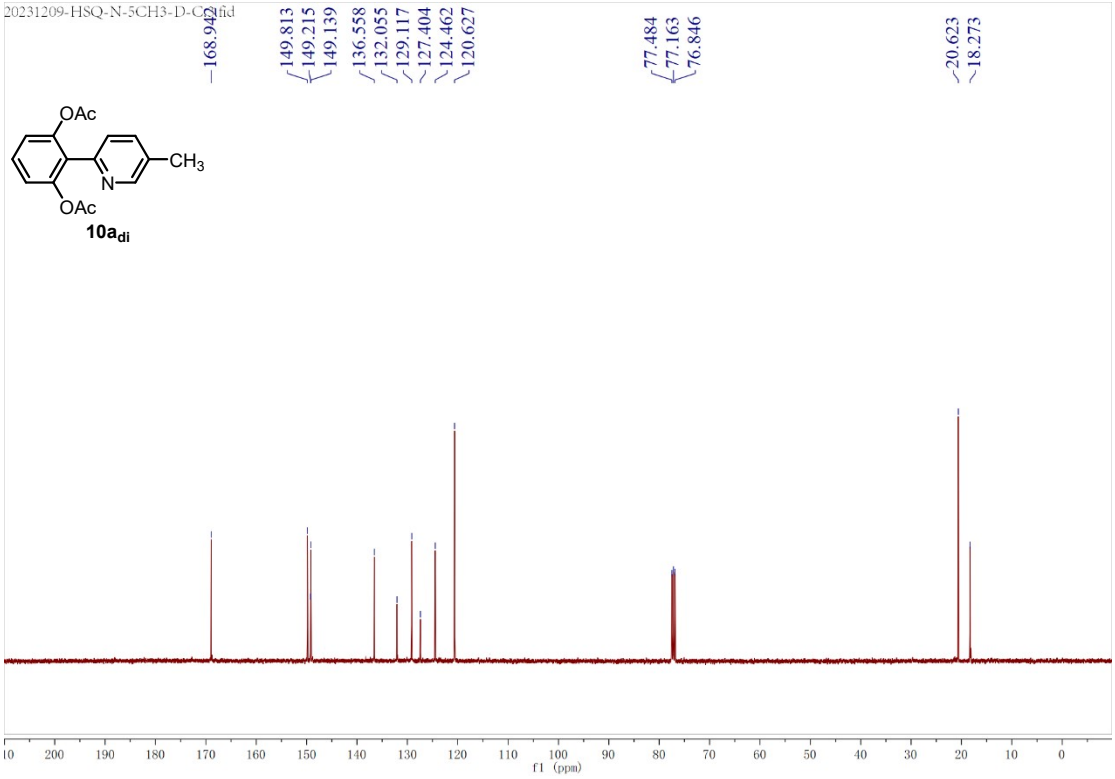


2-(5-methylpyridin-2-yl)-1,3-phenylene diacetate (**10a$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

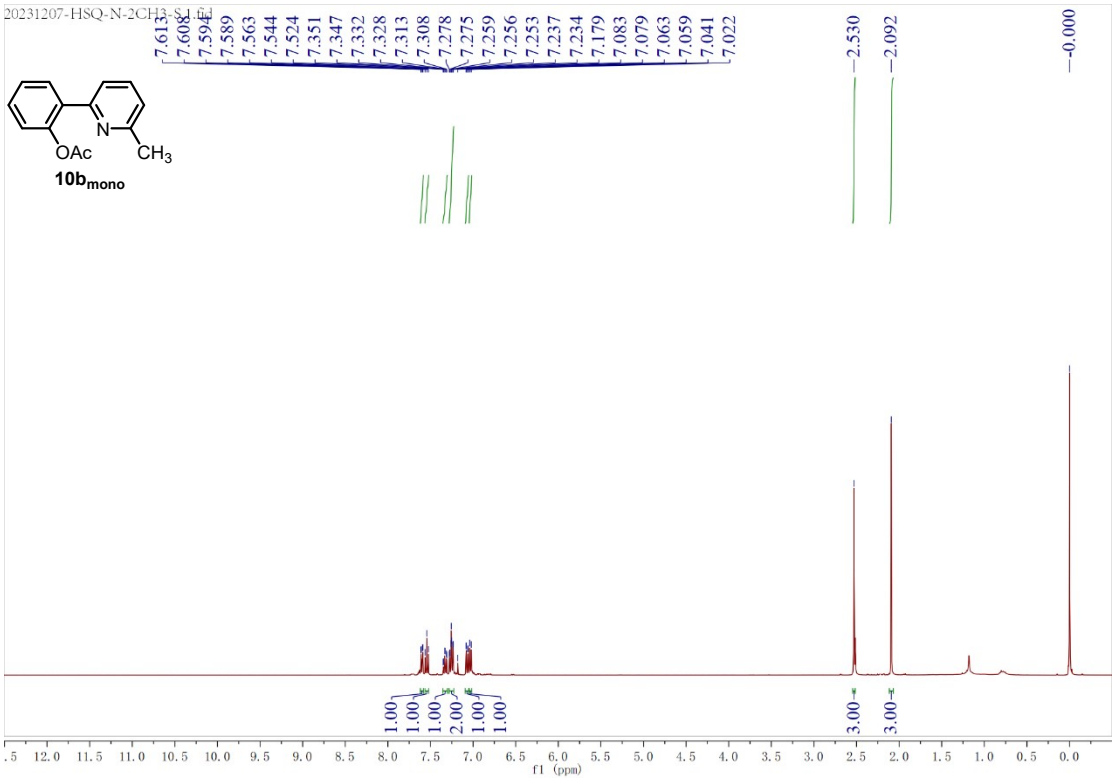


^{13}C NMR (100 MHz, $CDCl_3$)

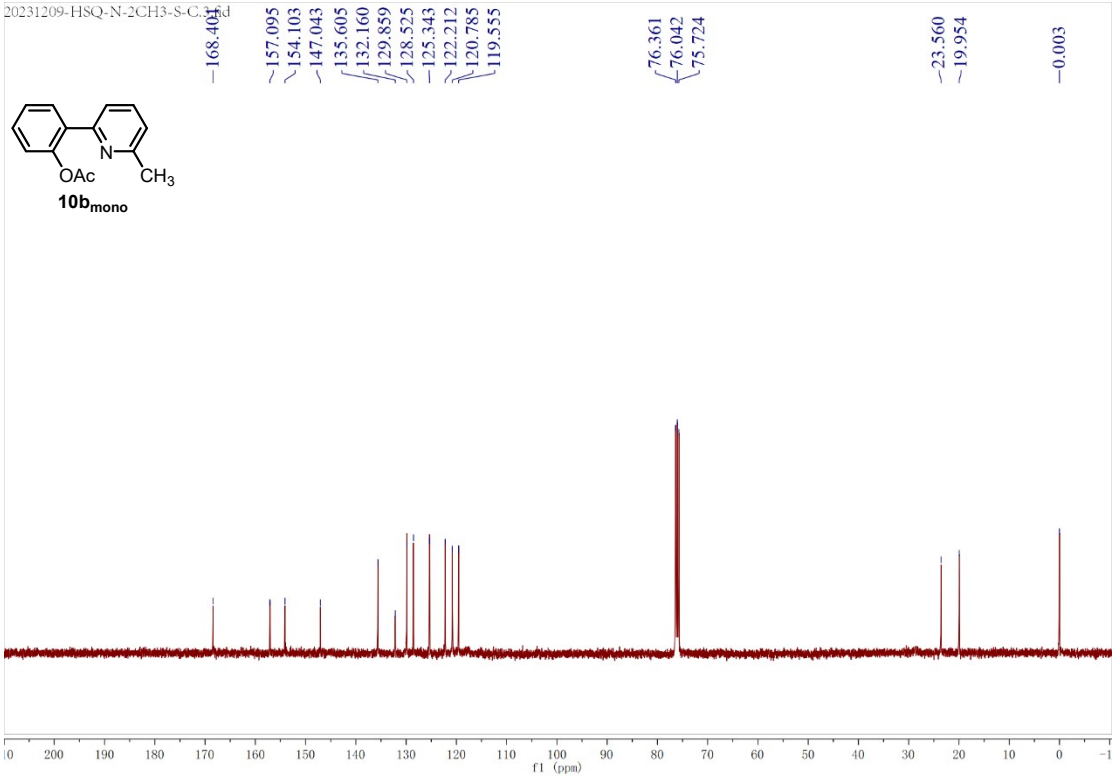


2-(6-methylpyridin-2-yl)phenyl acetate (**10b$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

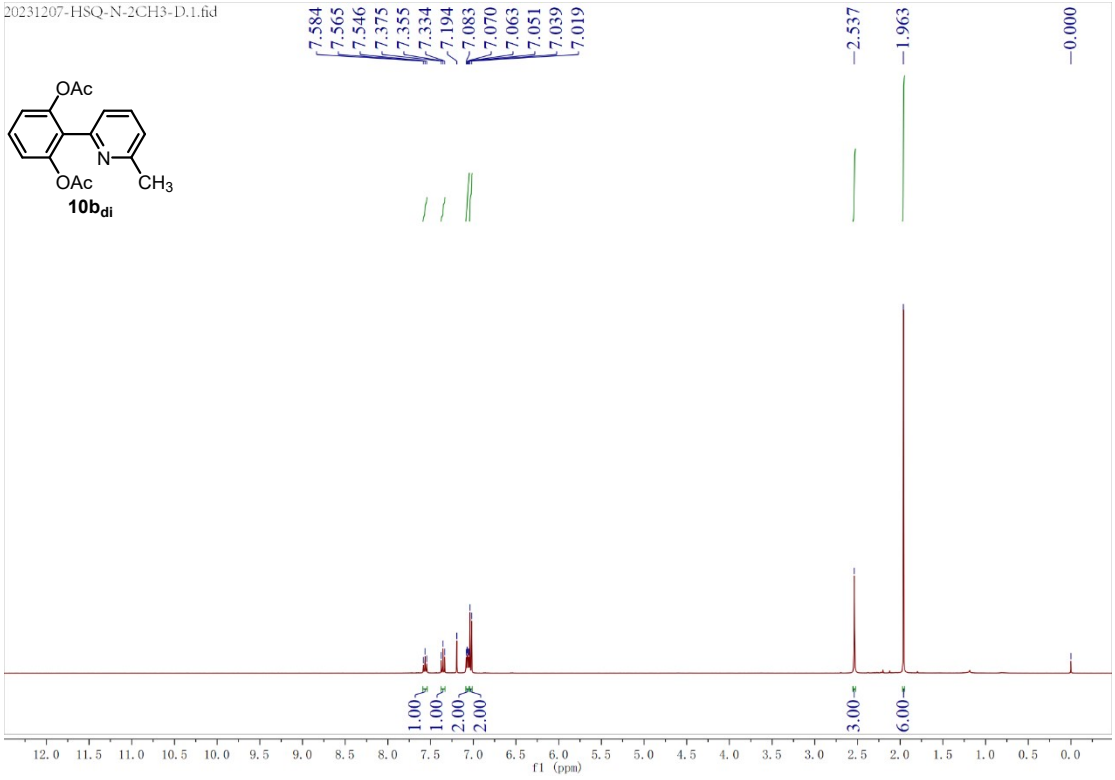


^{13}C NMR (100 MHz, $CDCl_3$)

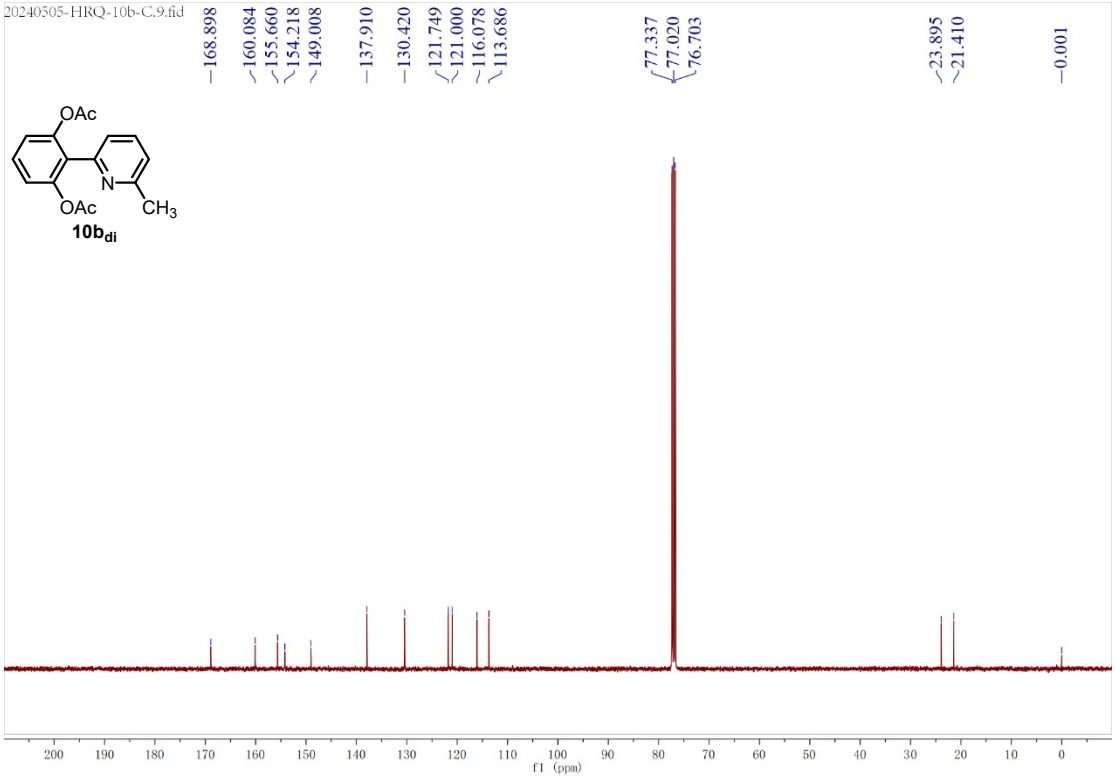


2-(6-methylpyridin-2-yl)-1,3-phenylene diacetate (**10b$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

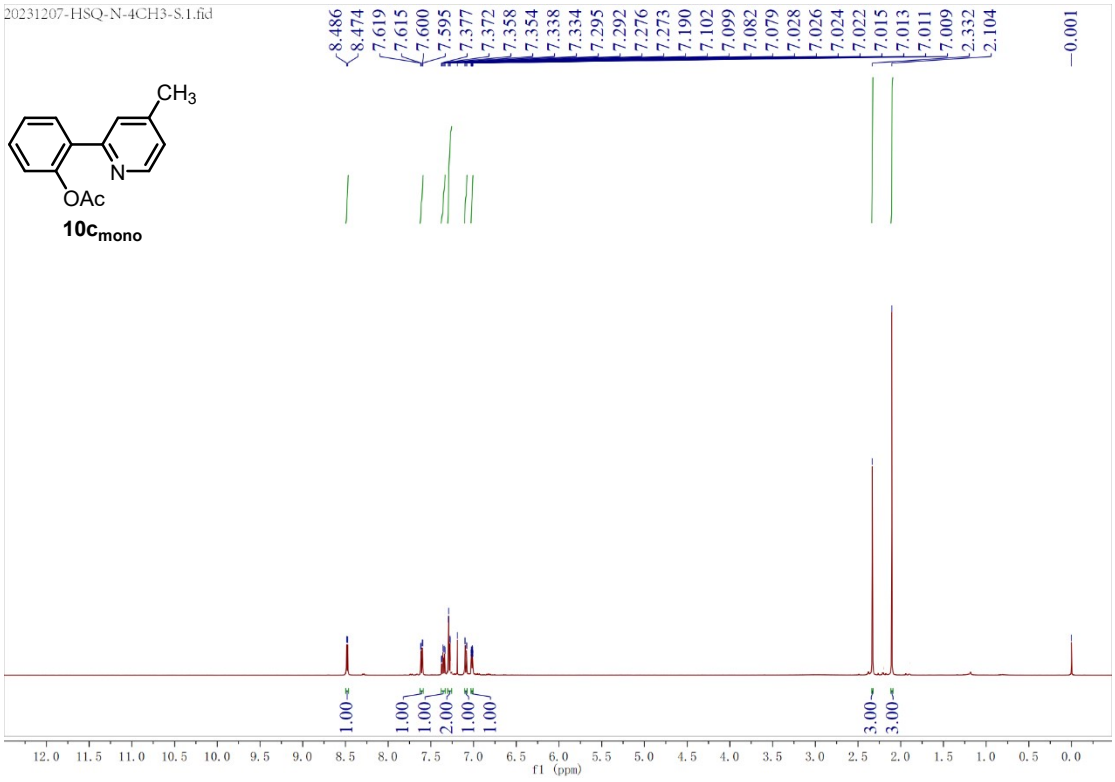


^{13}C NMR (100 MHz, $CDCl_3$)

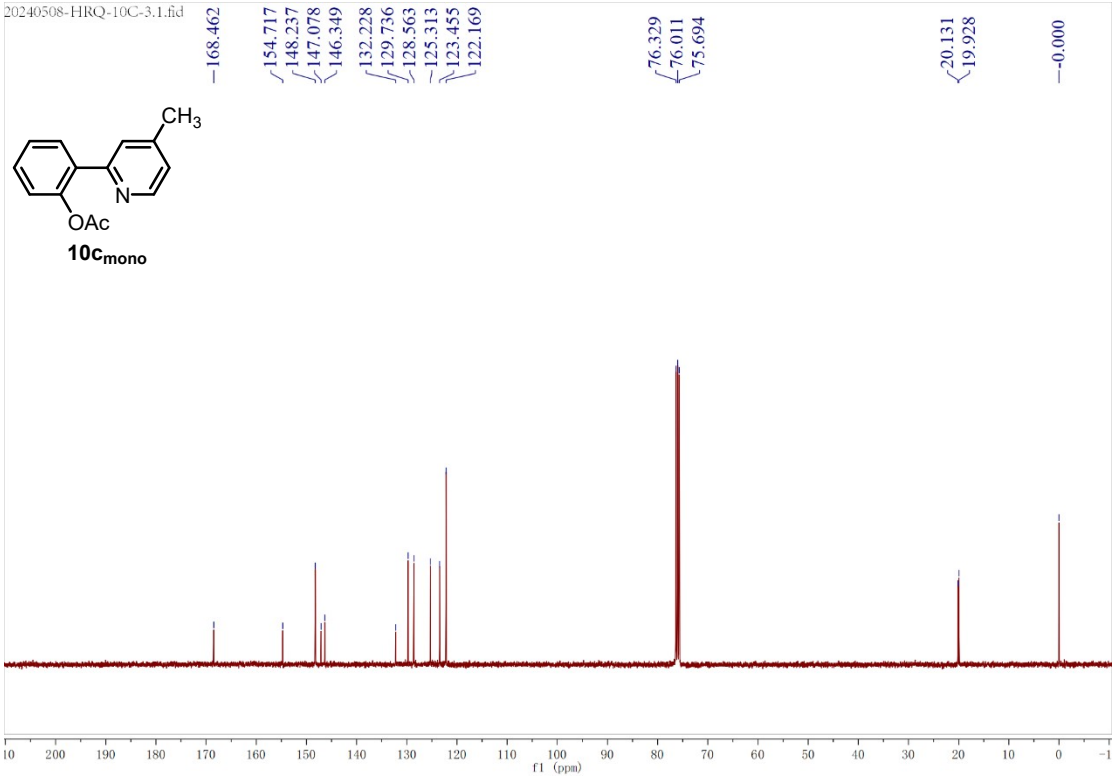


2-(4-methylpyridin-2-yl)phenyl acetate (**10c$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

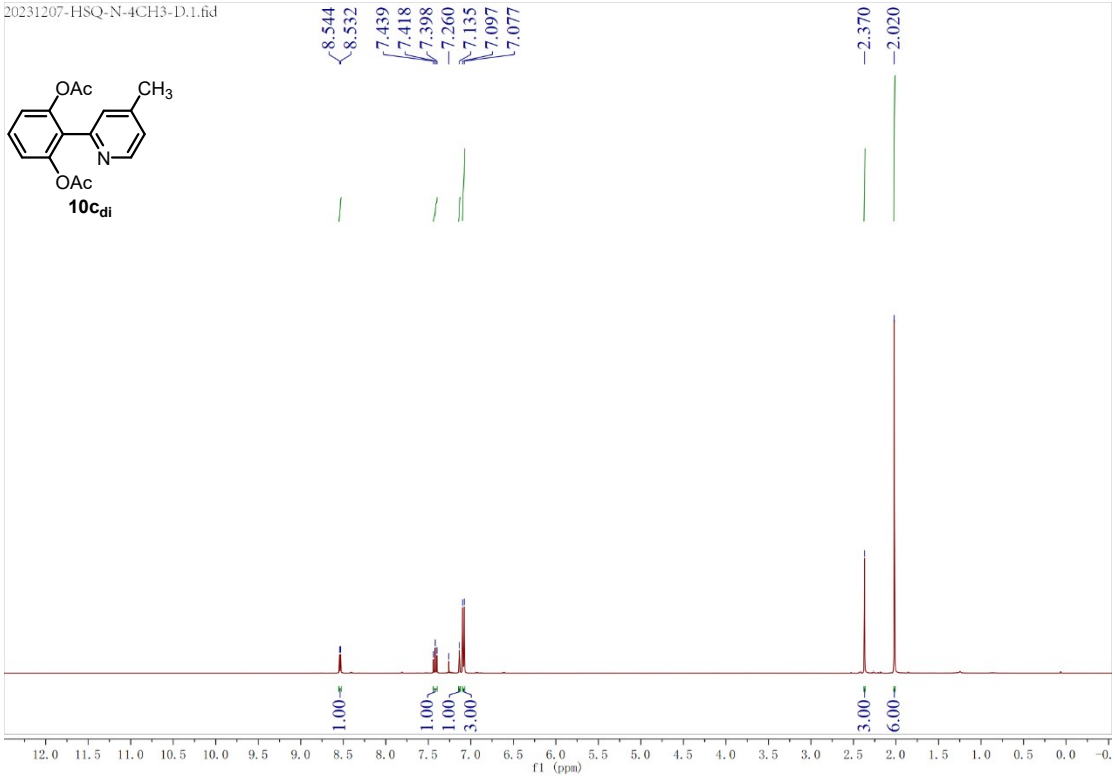


^{13}C NMR (100 MHz, $CDCl_3$)

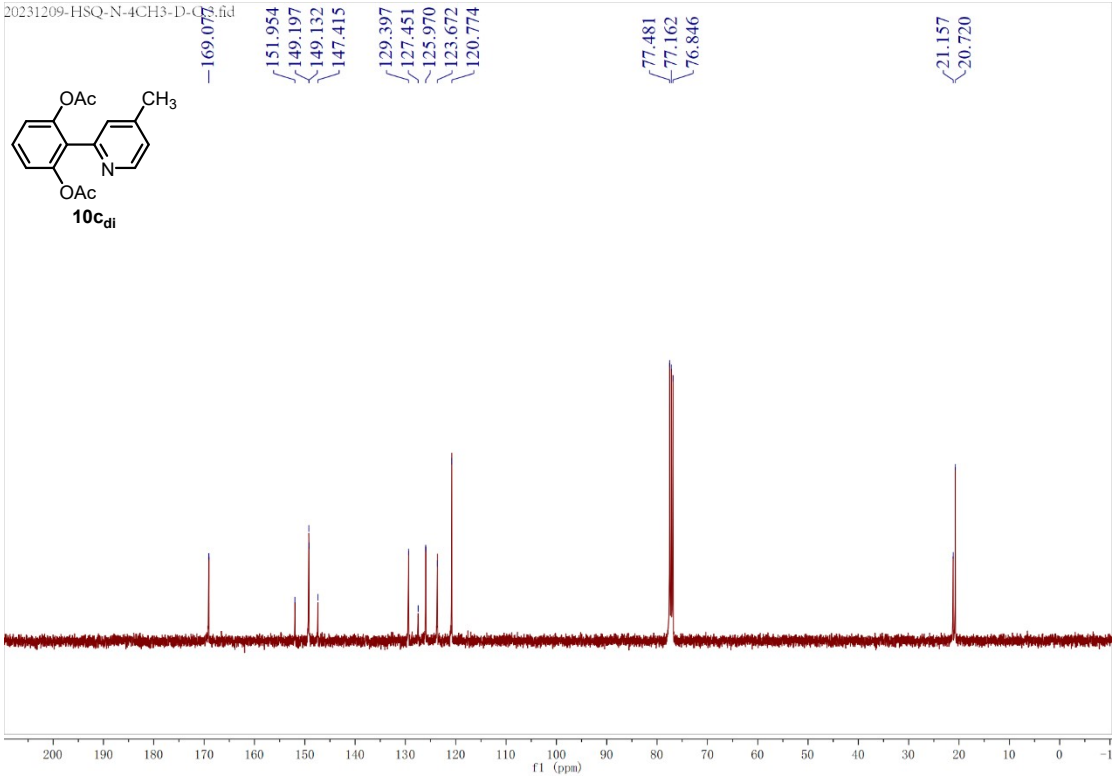


2-(4-methylpyridin-2-yl)-1,3-phenylene diacetate (**10c$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

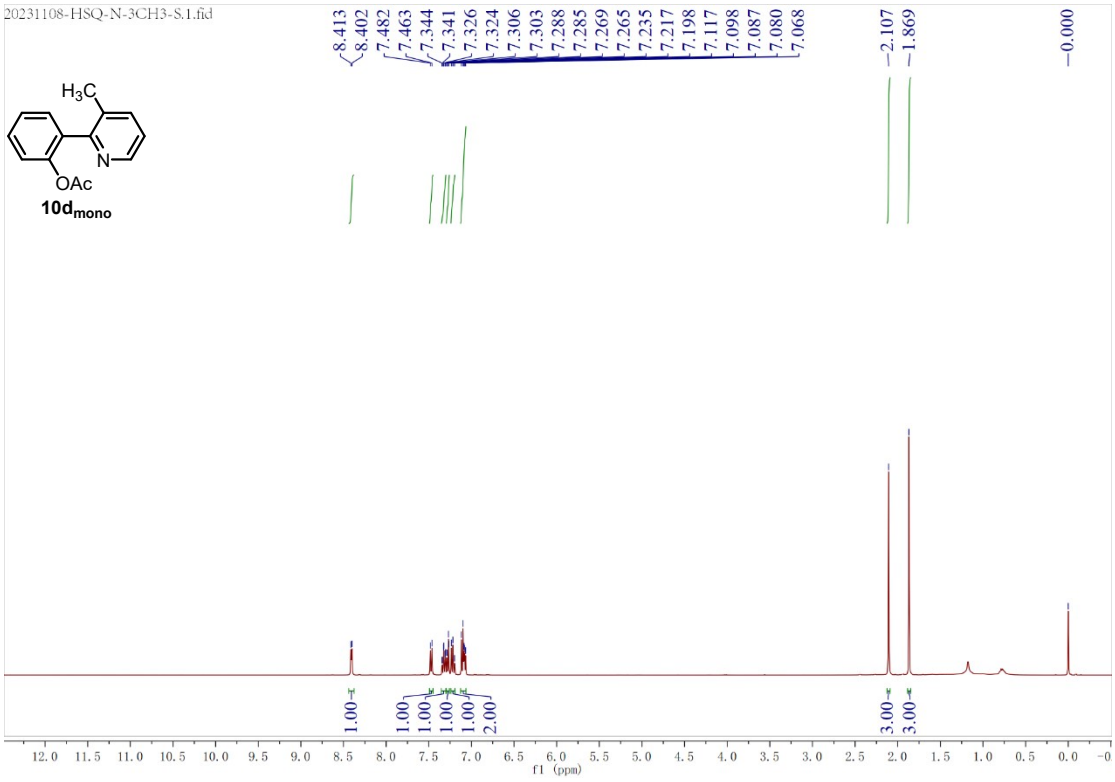


^{13}C NMR (100 MHz, $CDCl_3$)

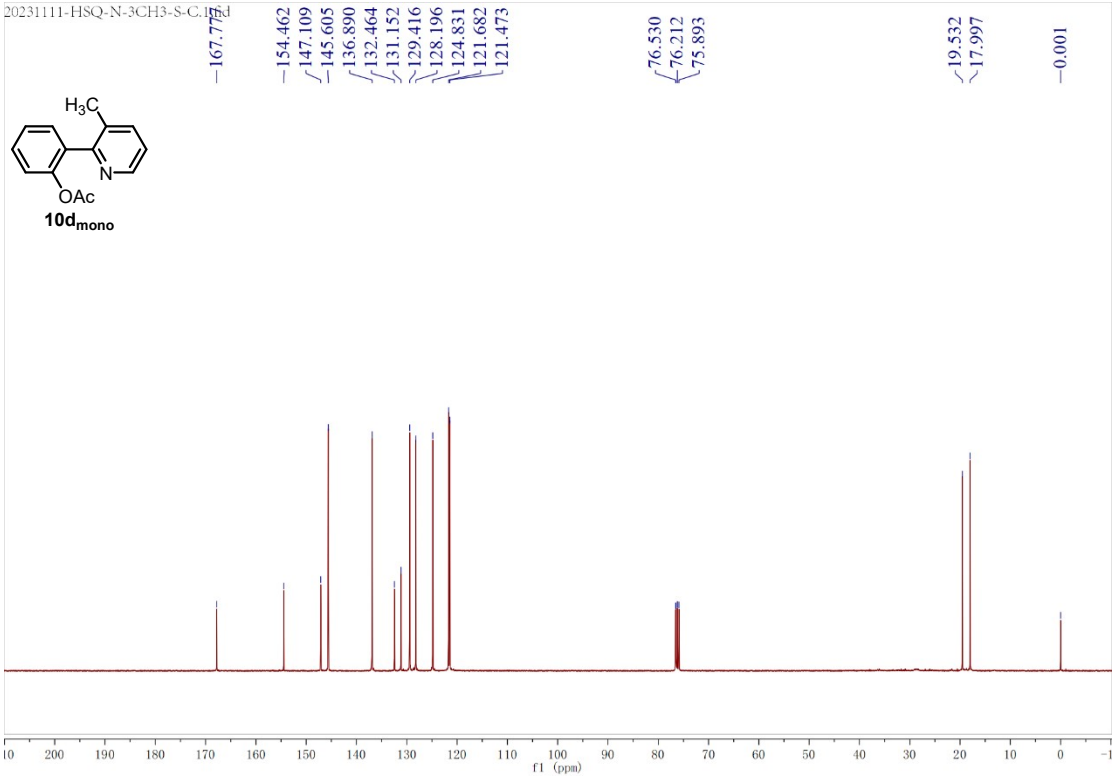


2-(3-methylpyridin-2-yl)phenyl acetate (**10d$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

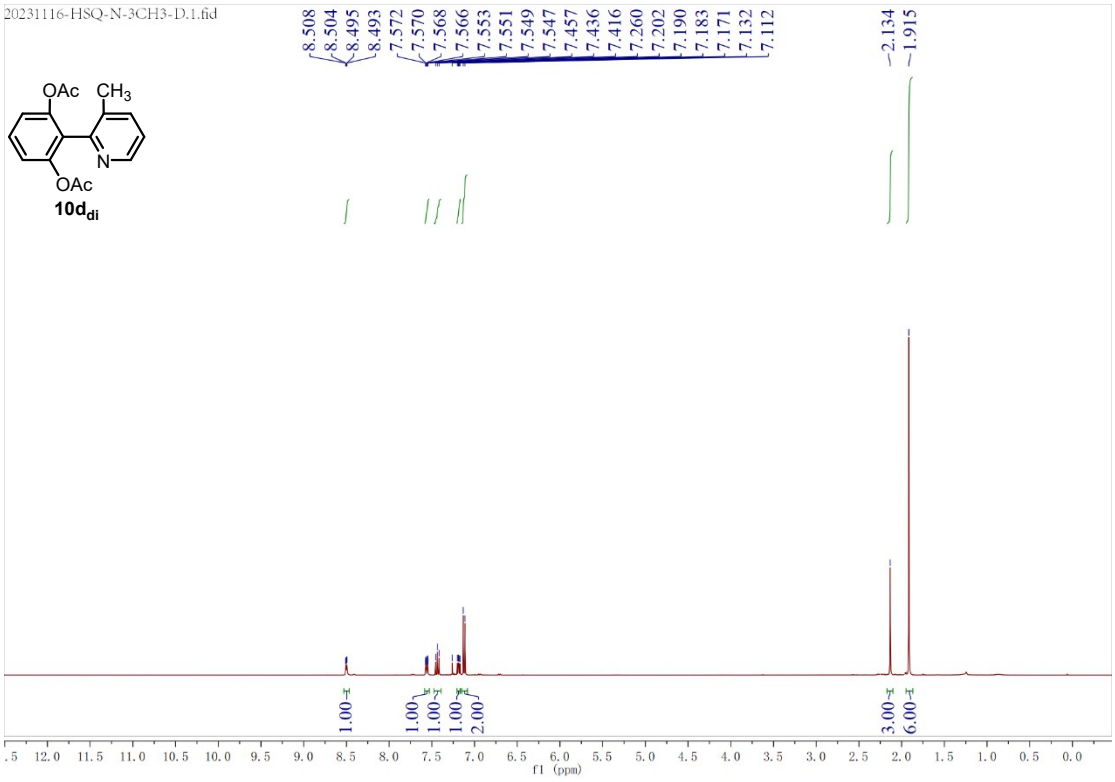


^{13}C NMR (100 MHz, $CDCl_3$)

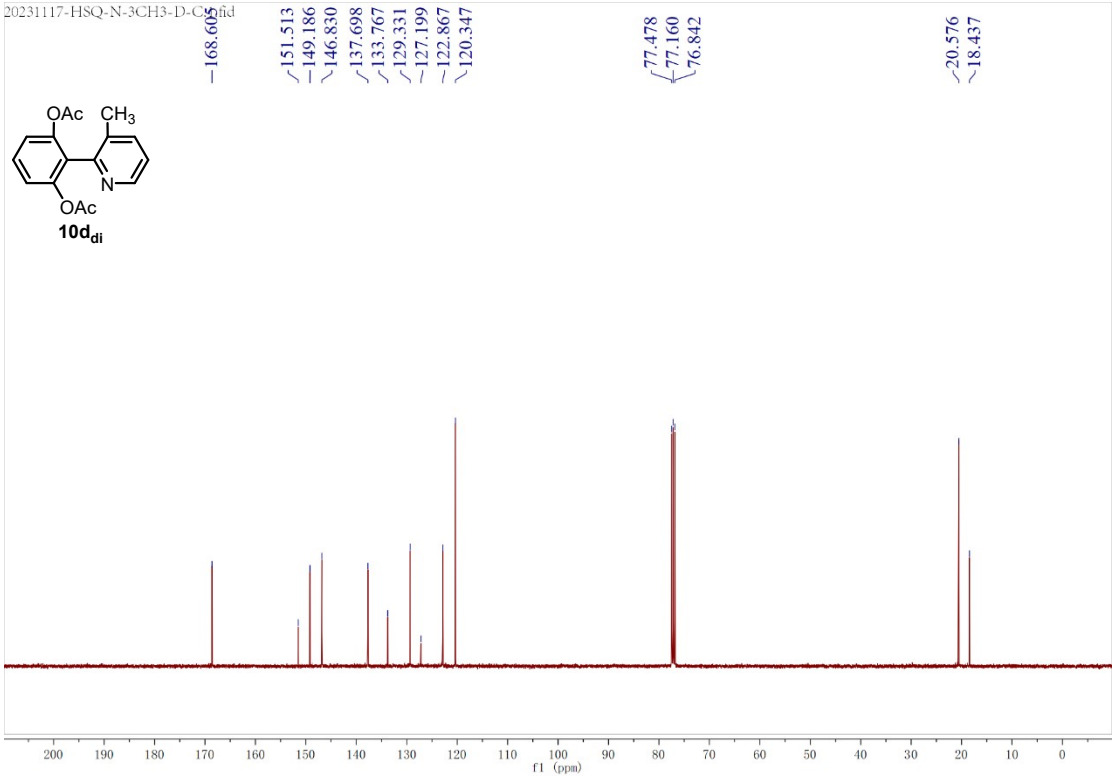


2-(3-methylpyridin-2-yl)-1,3-phenylene diacetate (**10d$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

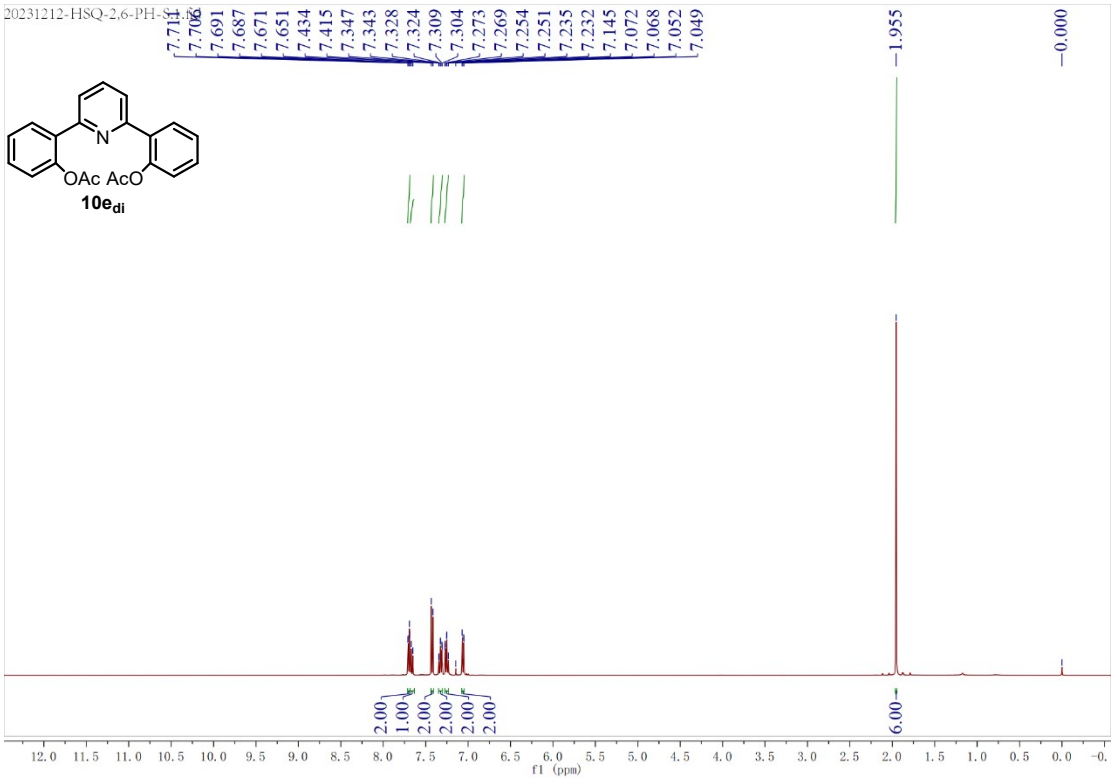


^{13}C NMR (100 MHz, $CDCl_3$)

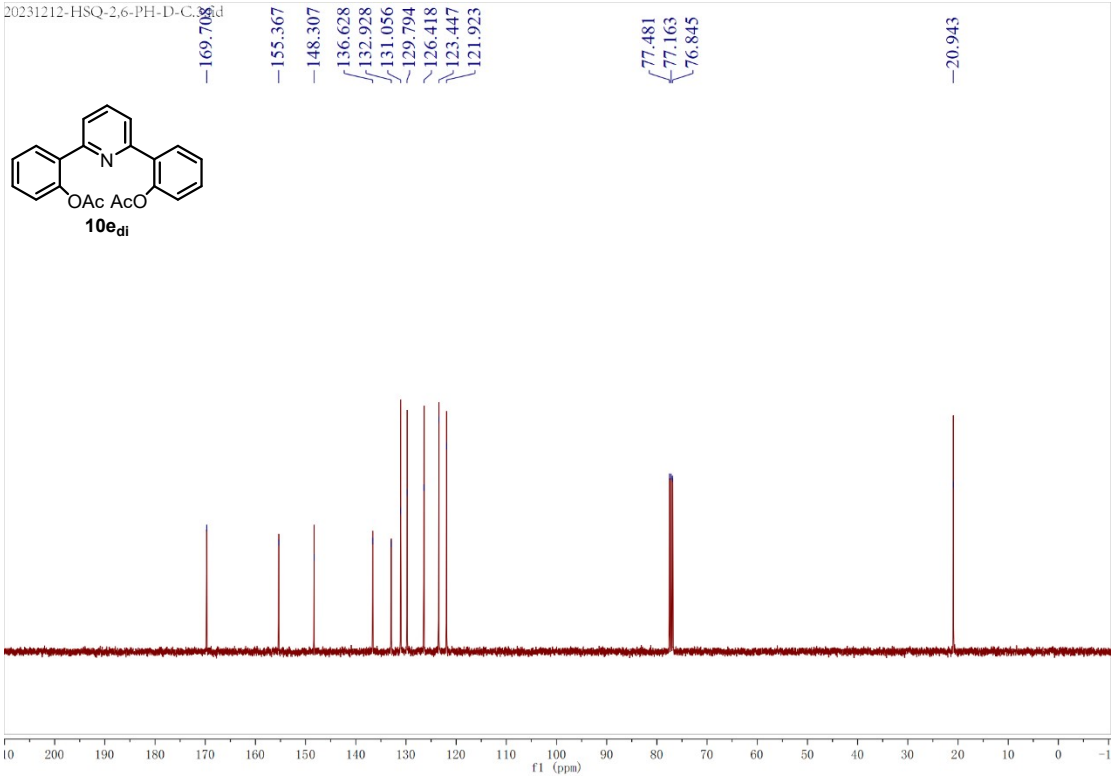


pyridine-2,6-diylbis(2,1-phenylene) diacetate (**10e$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

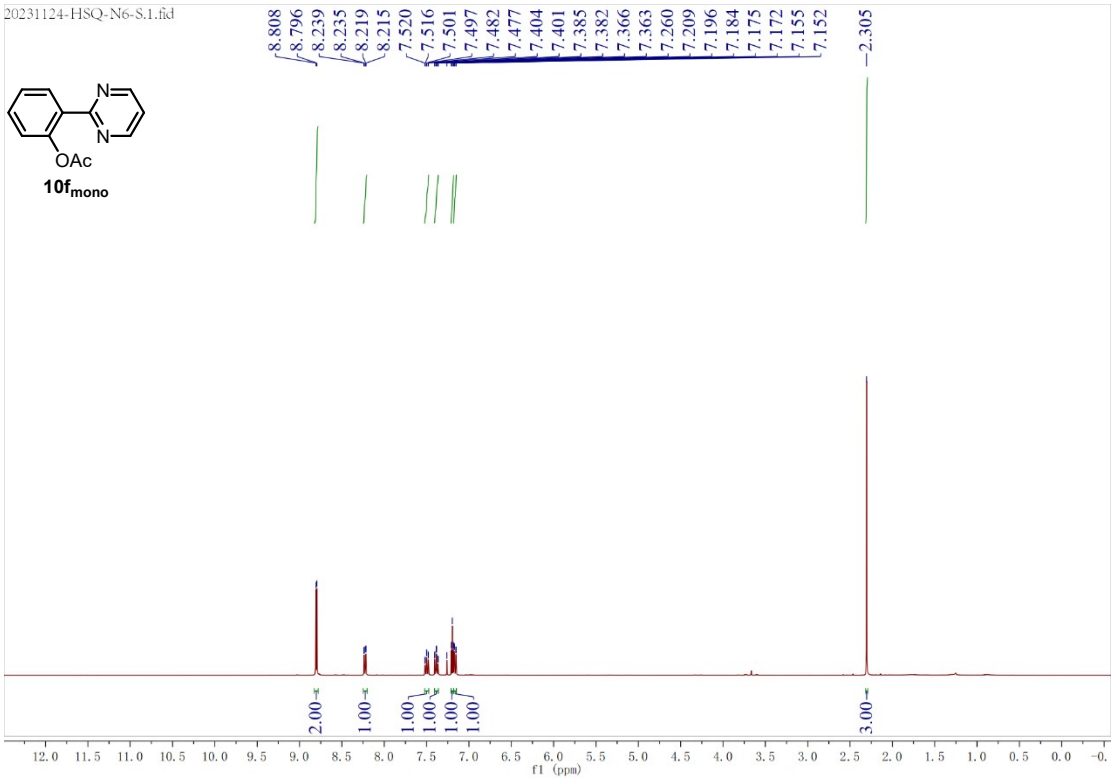


^{13}C NMR (100 MHz, $CDCl_3$)

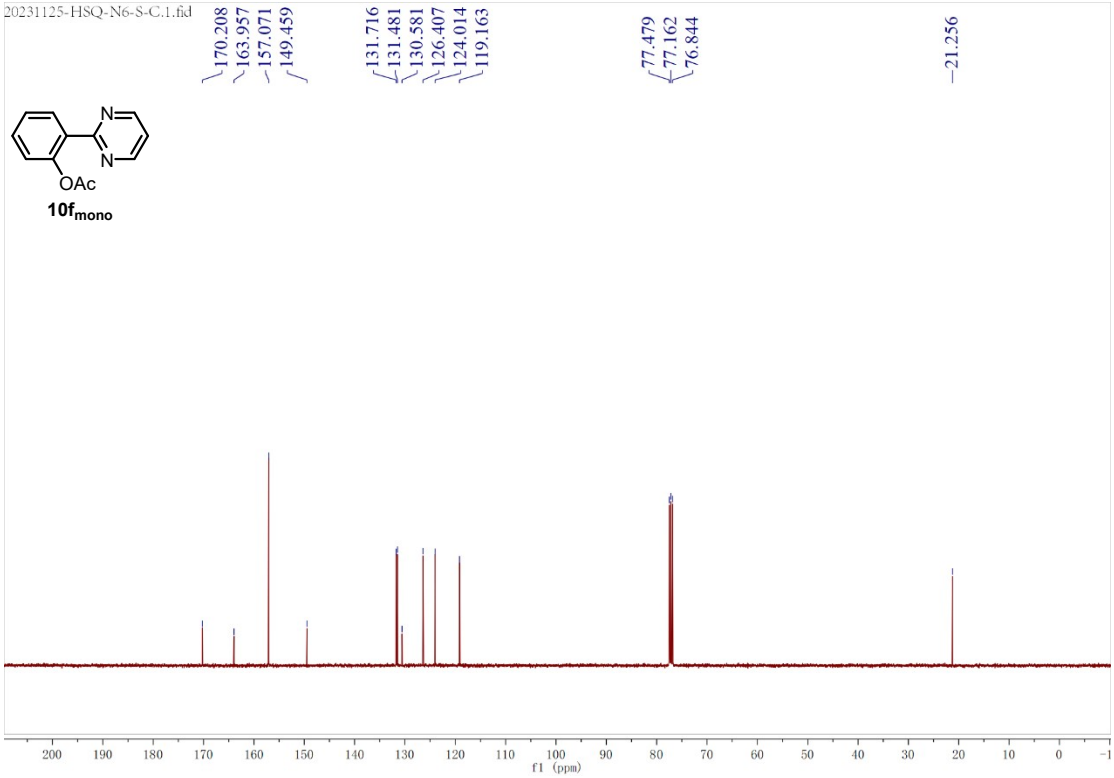


2-(pyrimidin-2-yl)phenyl acetate (**10f$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

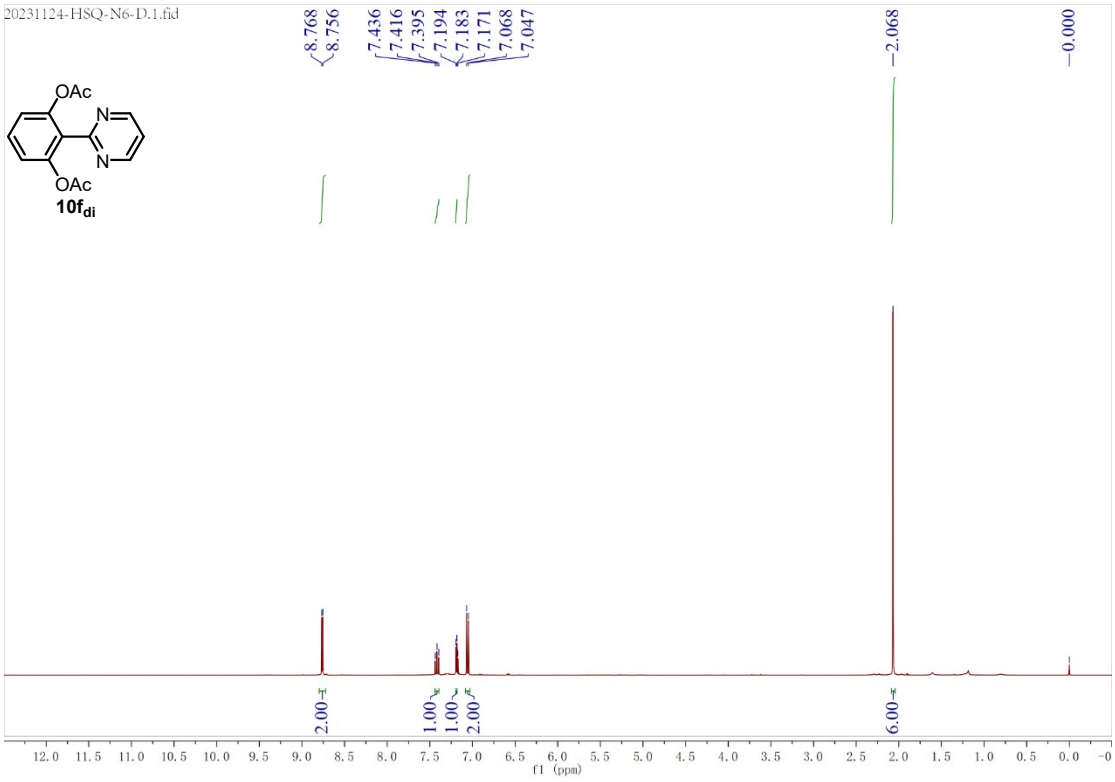


^{13}C NMR (100 MHz, $CDCl_3$)

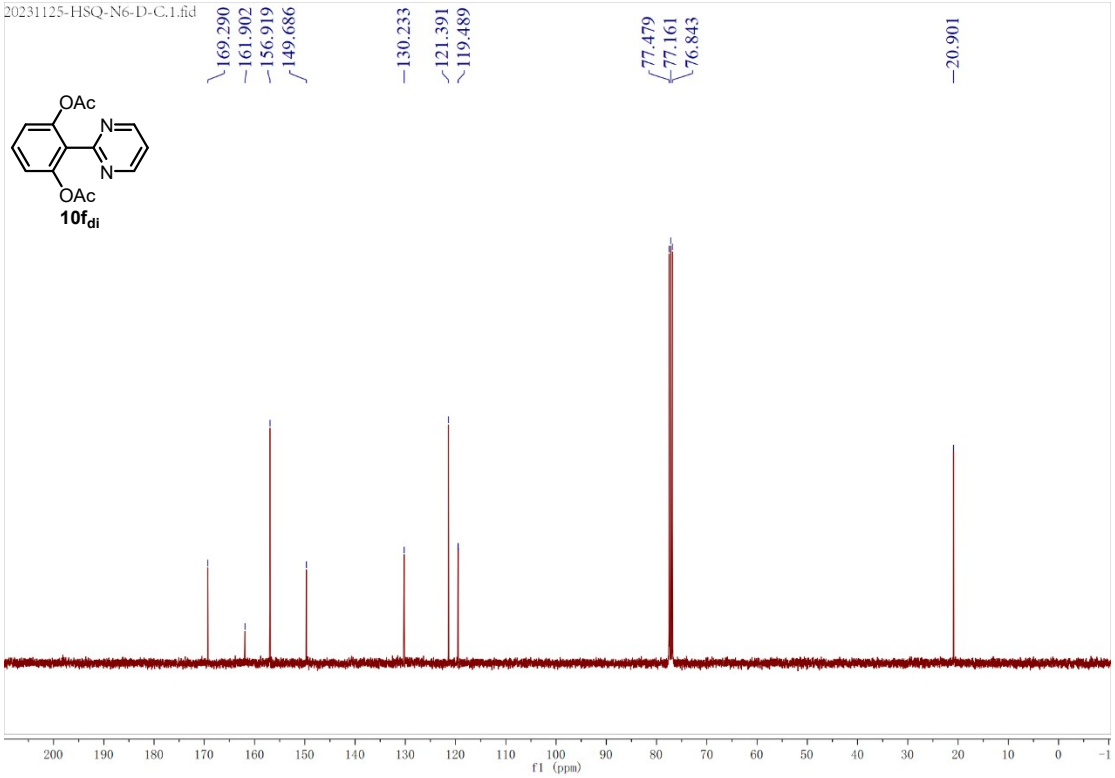


2-(pyrimidin-2-yl)-1,3-phenylene diacetate (**10f$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

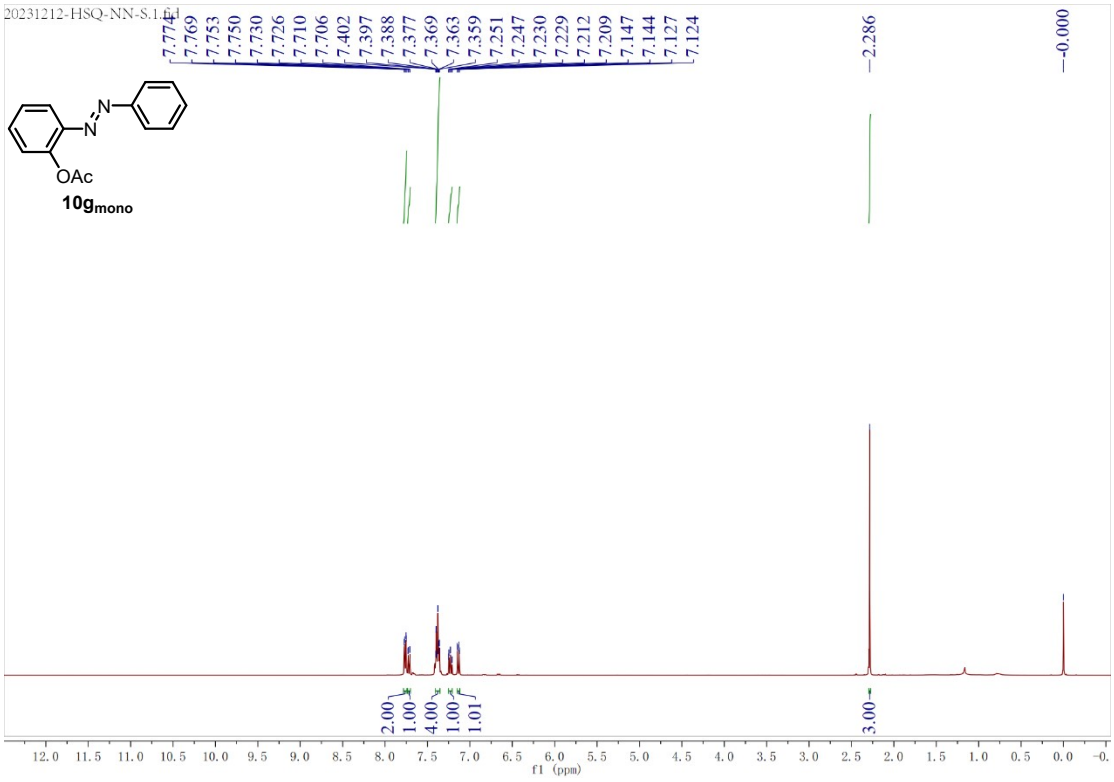


^{13}C NMR (100 MHz, $CDCl_3$)

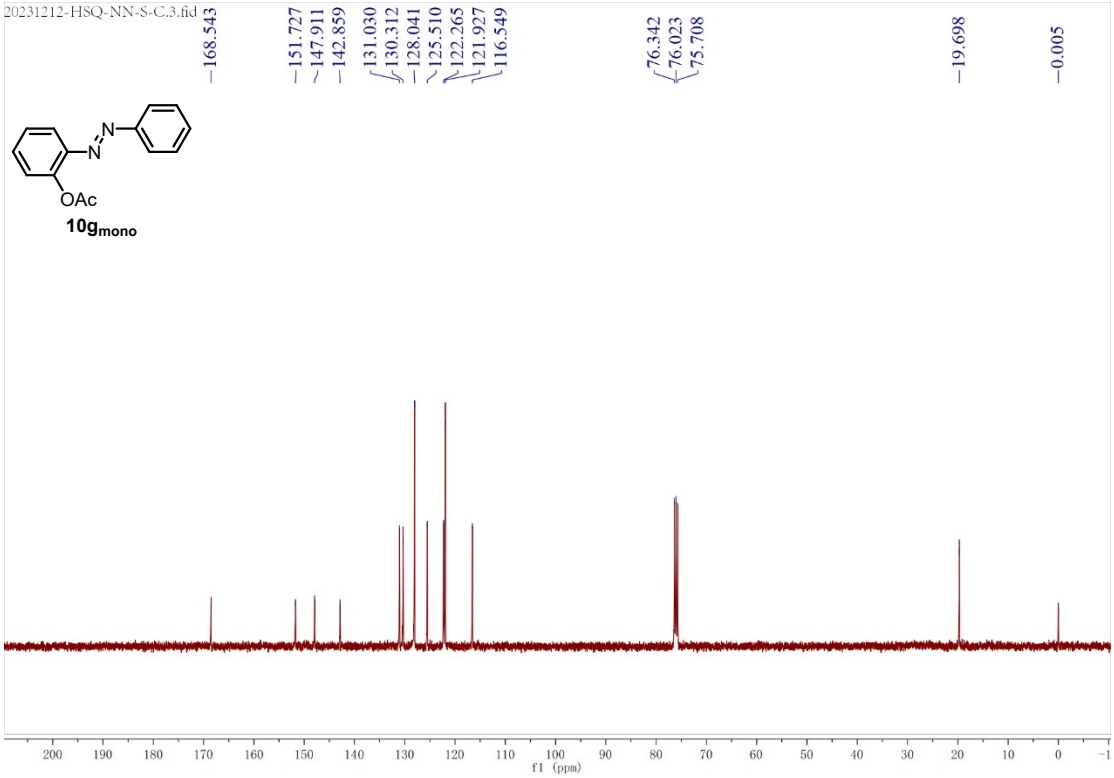


(E)-2-(phenyldiazenyl)phenyl acetate (**10g$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

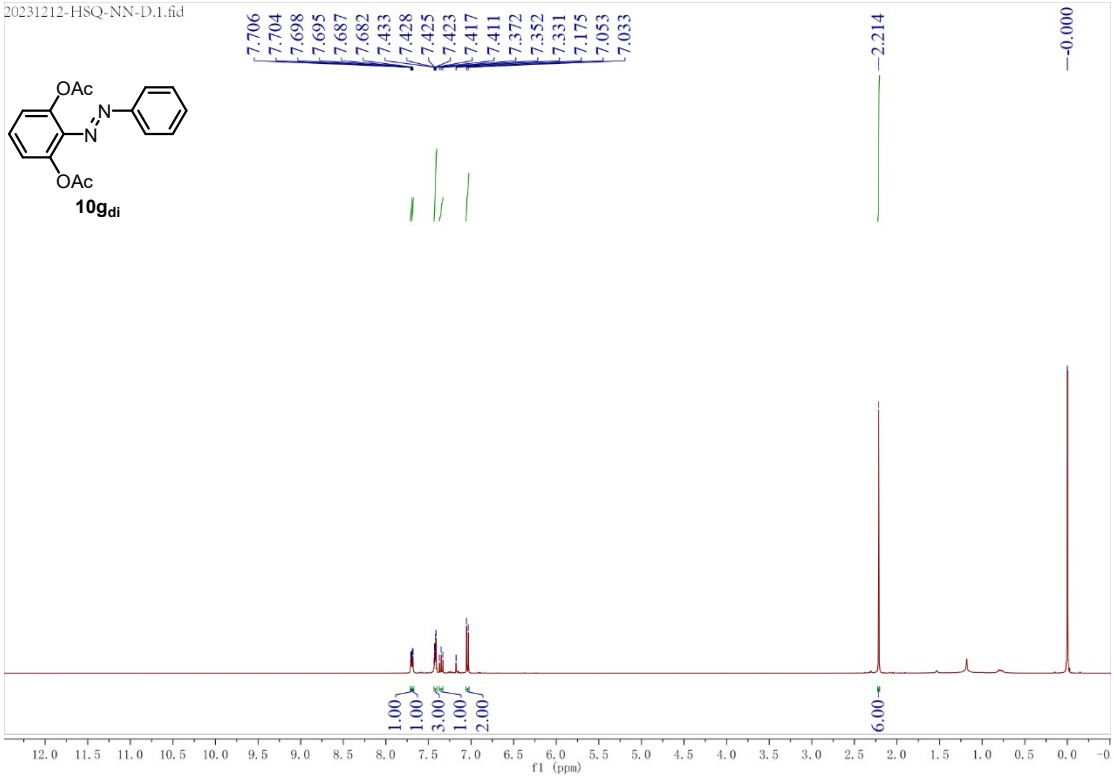


^{13}C NMR (100 MHz, $CDCl_3$)

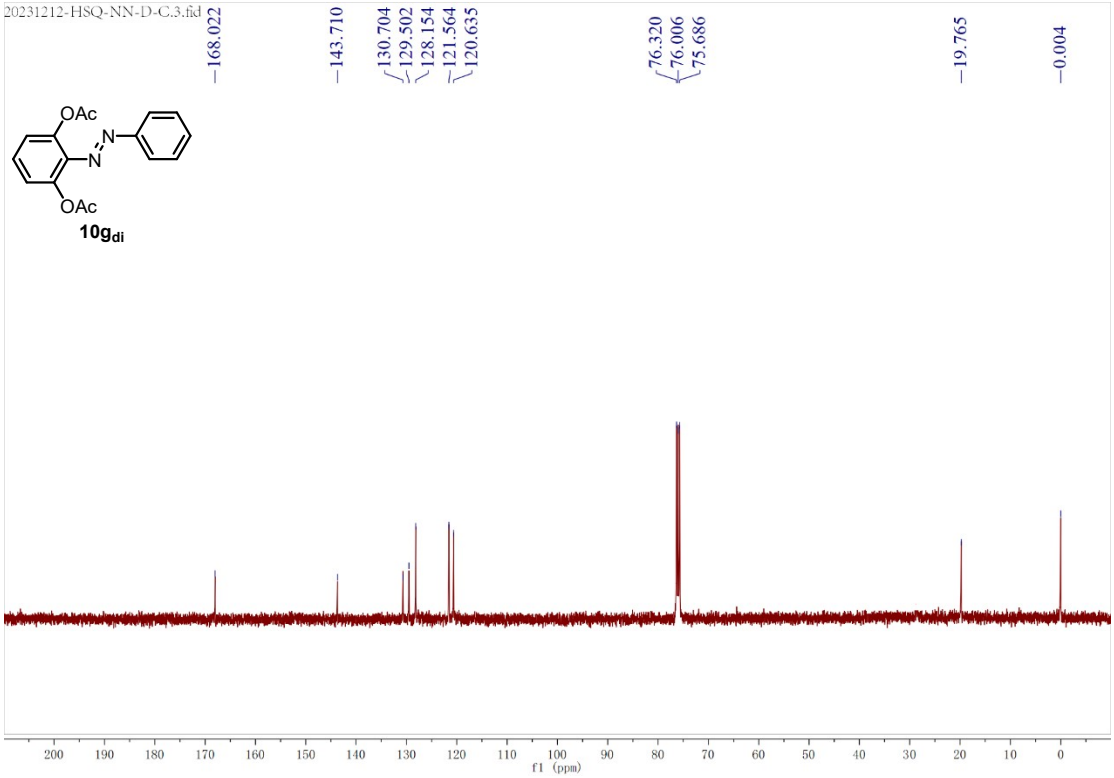


(E)-diazene-1,2-diylbis(2,1-phenylene) diacetate (**10g$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

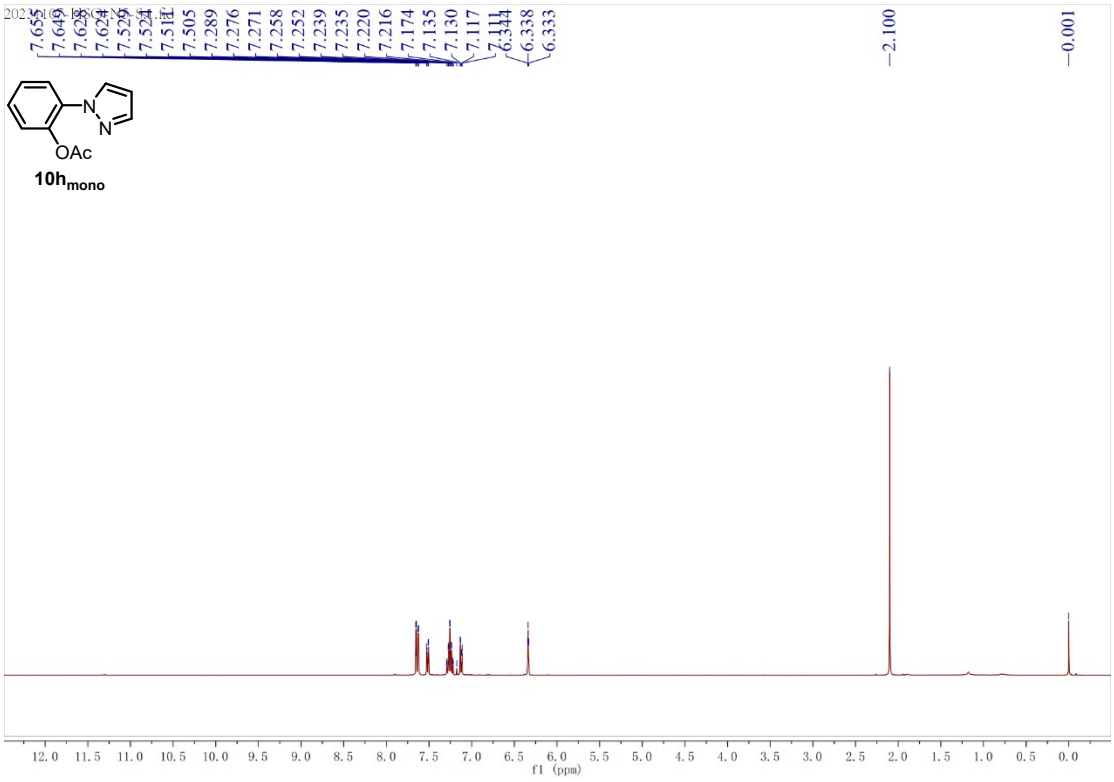


^{13}C NMR (100 MHz, $CDCl_3$)

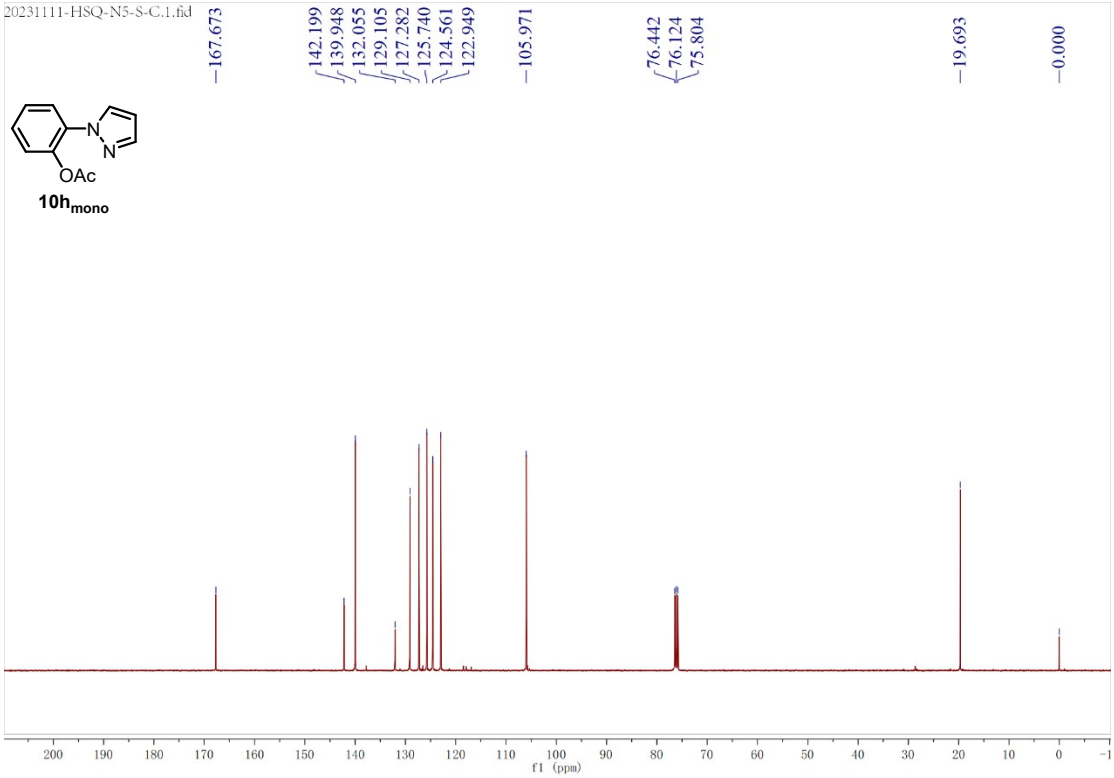


2-(2H-imidazol-2-yl)phenyl acetate (**10h$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

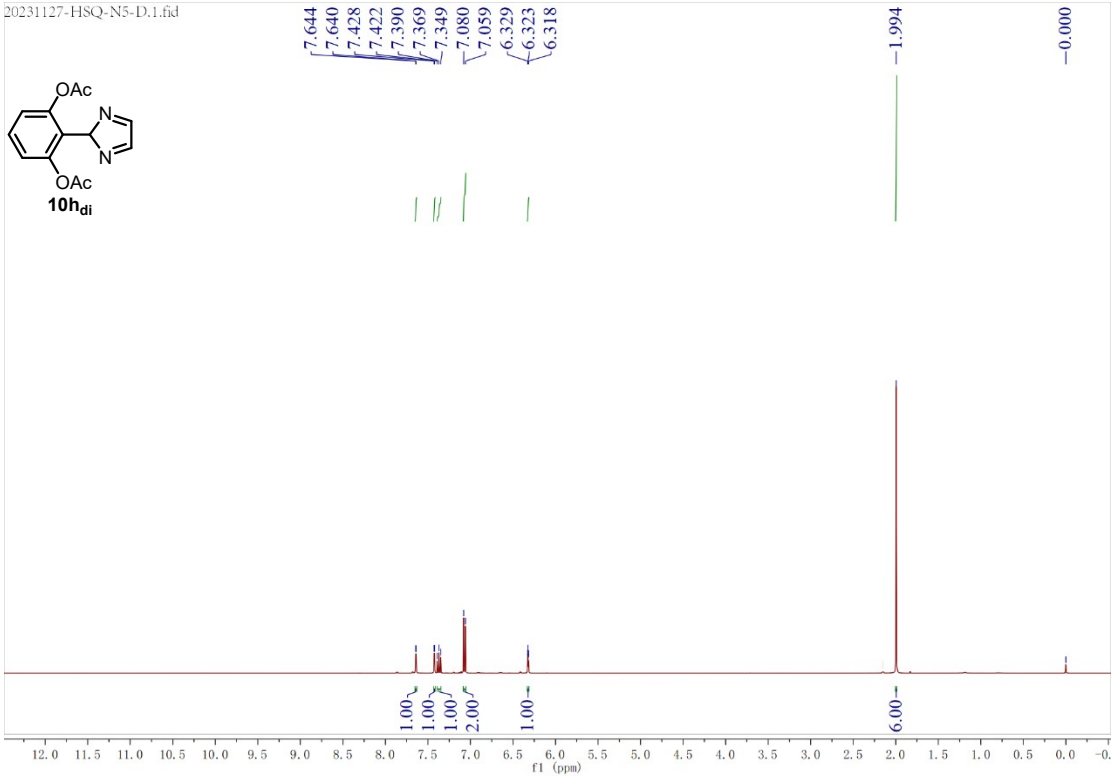


^{13}C NMR (100 MHz, $CDCl_3$)

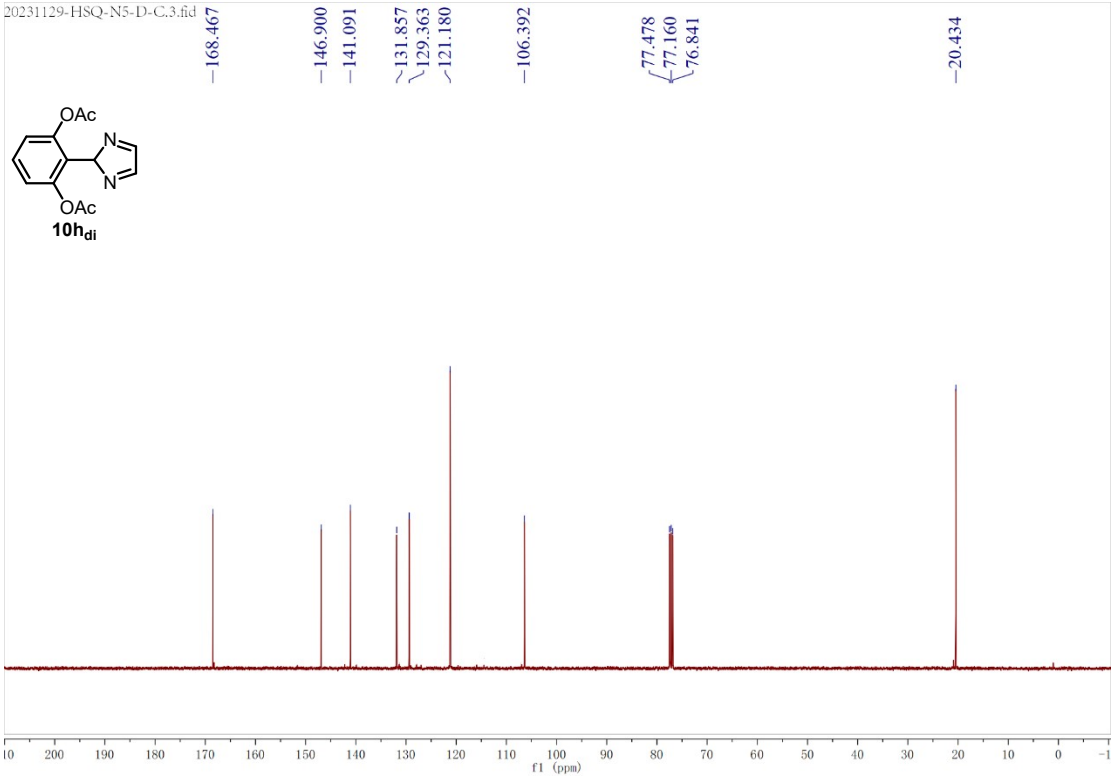


2-(2H-imidazol-2-yl)-1,3-phenylene diacetate (**10h$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

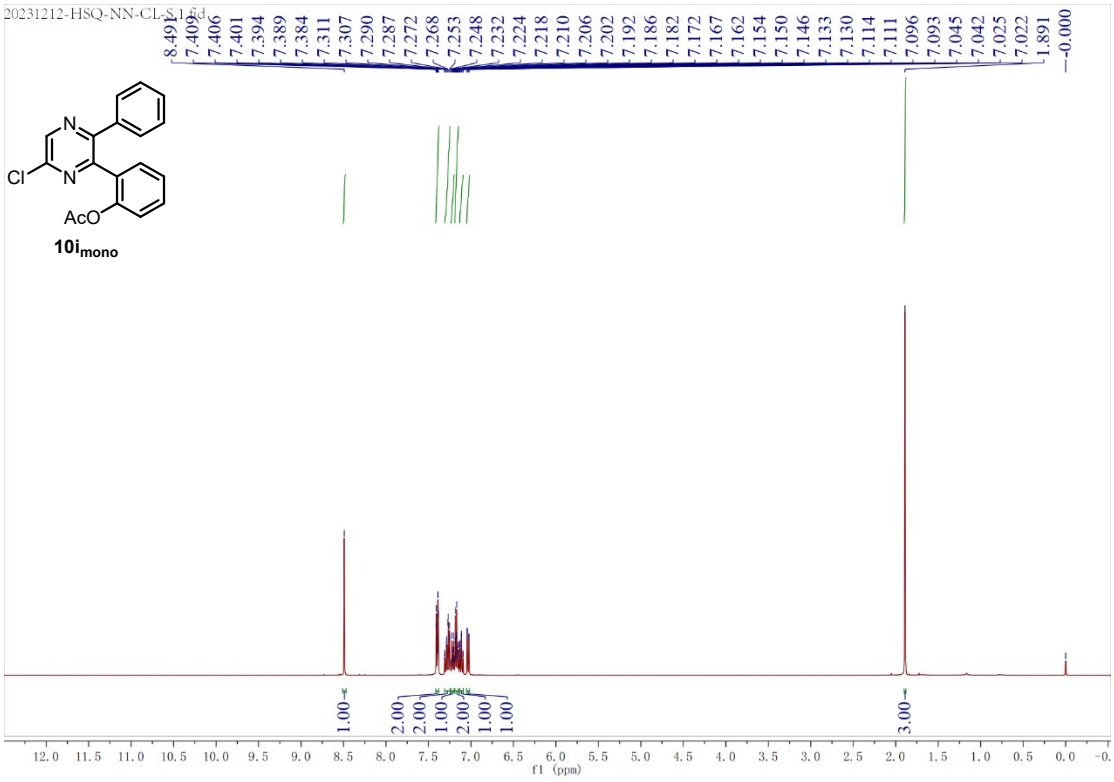


^{13}C NMR (100 MHz, $CDCl_3$)

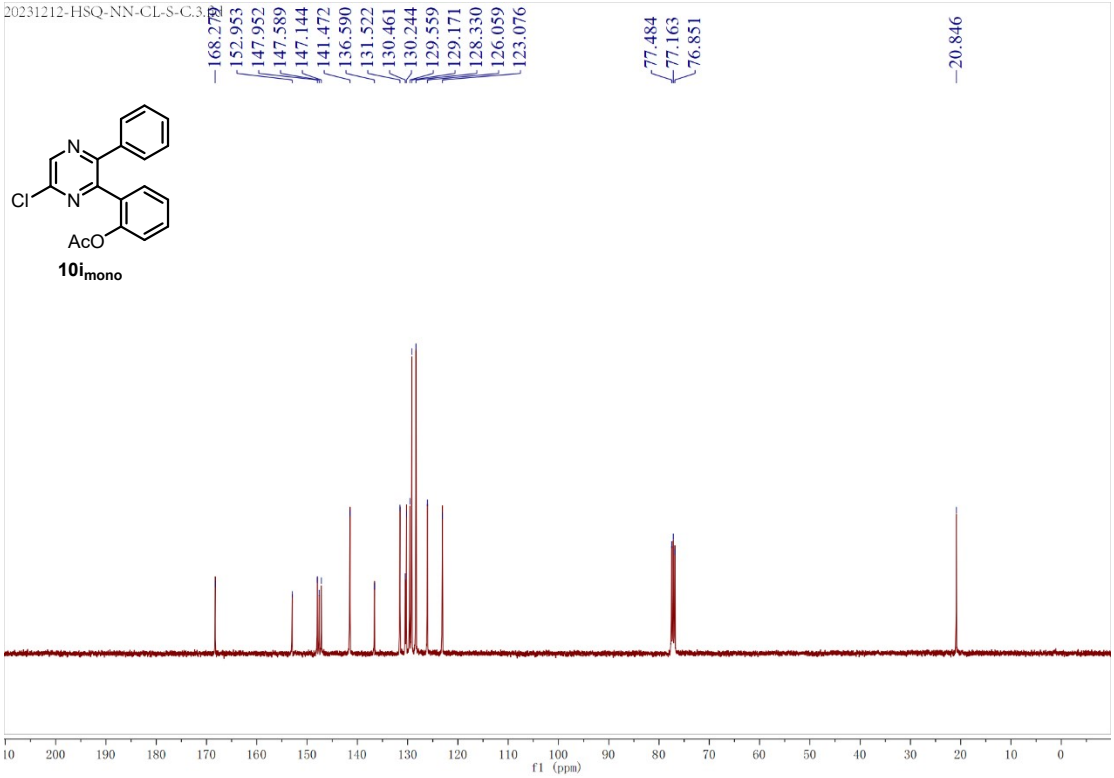


2-(6-chloro-3-phenylpyrazin-2-yl)phenyl acetate (**10i$_{mono}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

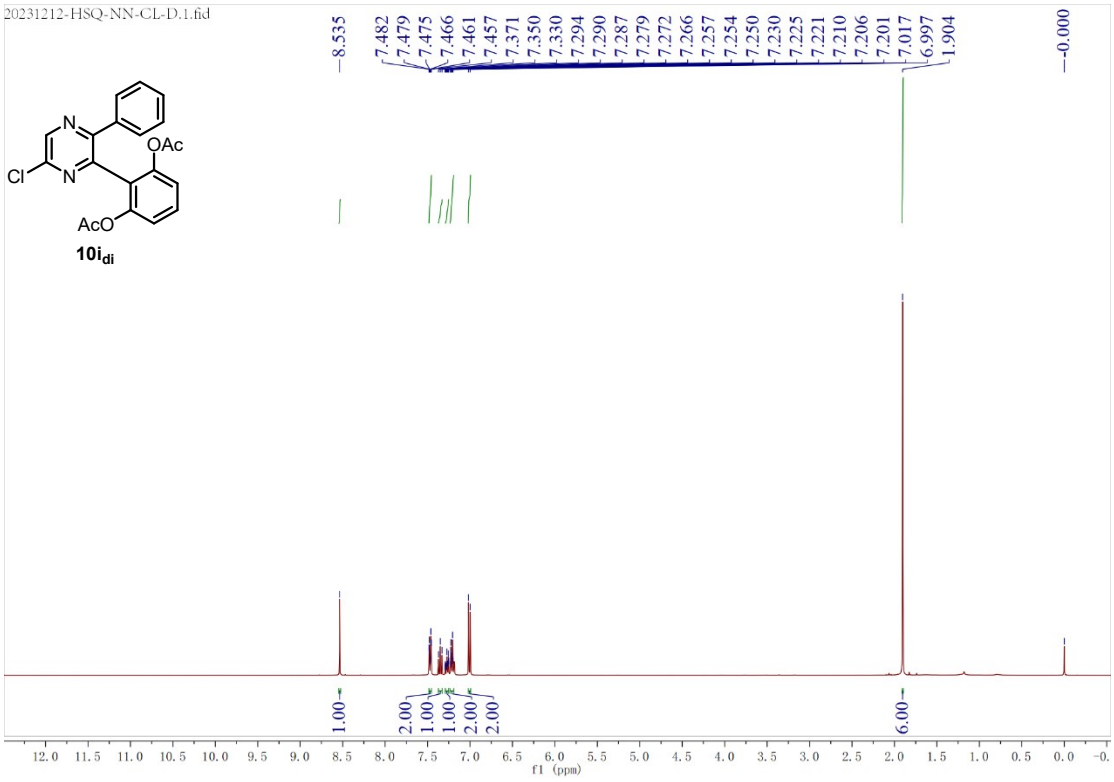


^{13}C NMR (100 MHz, $CDCl_3$)

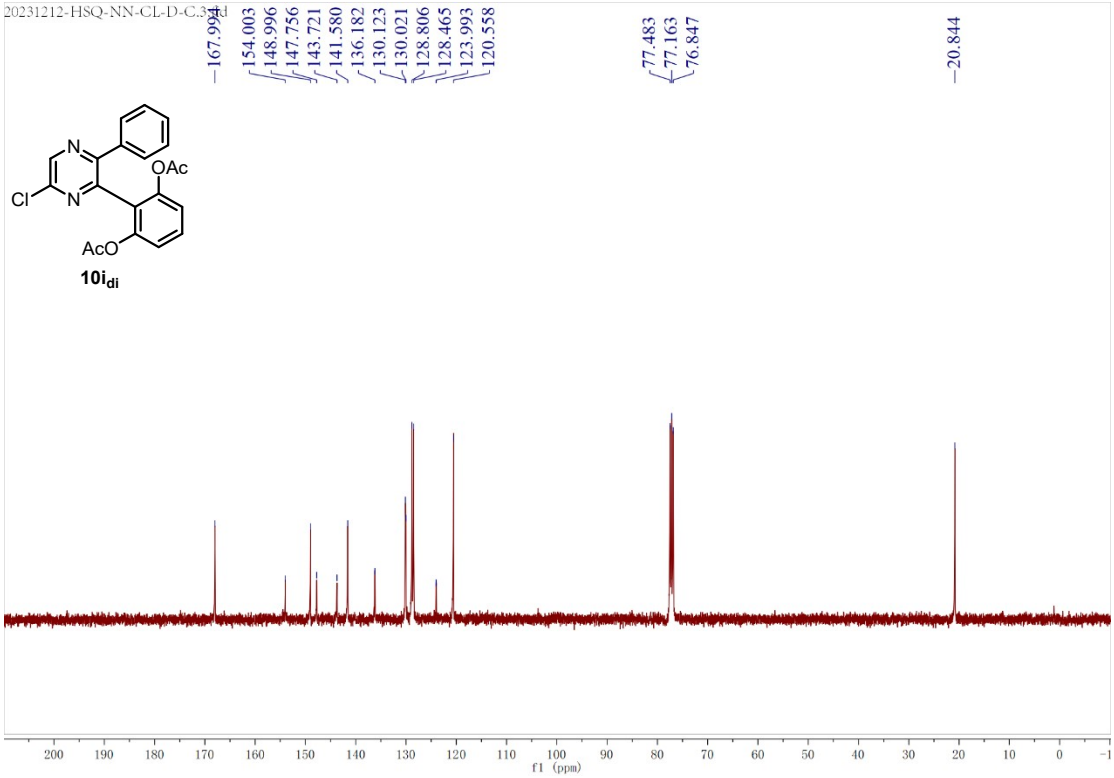


2-(6-chloro-3-phenylpyrazin-2-yl)-1,3-phenylene diacetate (**10i$_{di}$**)

^{1}H NMR (400 MHz, $CDCl_3$)

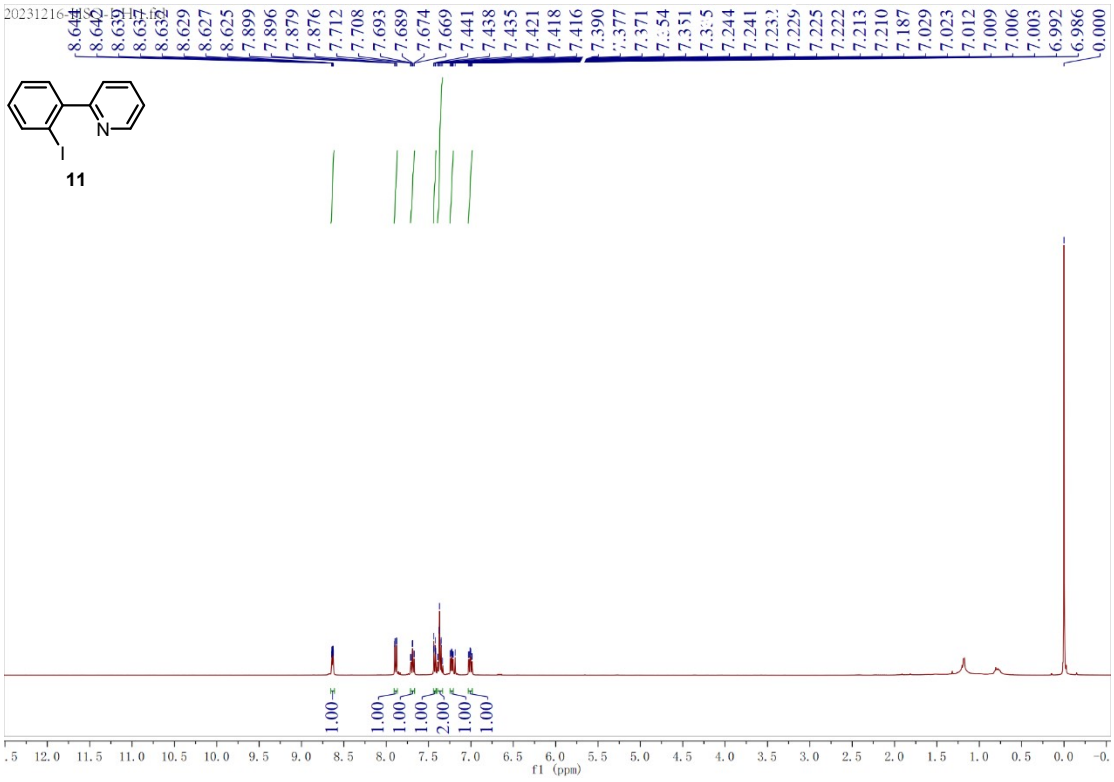


^{13}C NMR (100 MHz, $CDCl_3$)

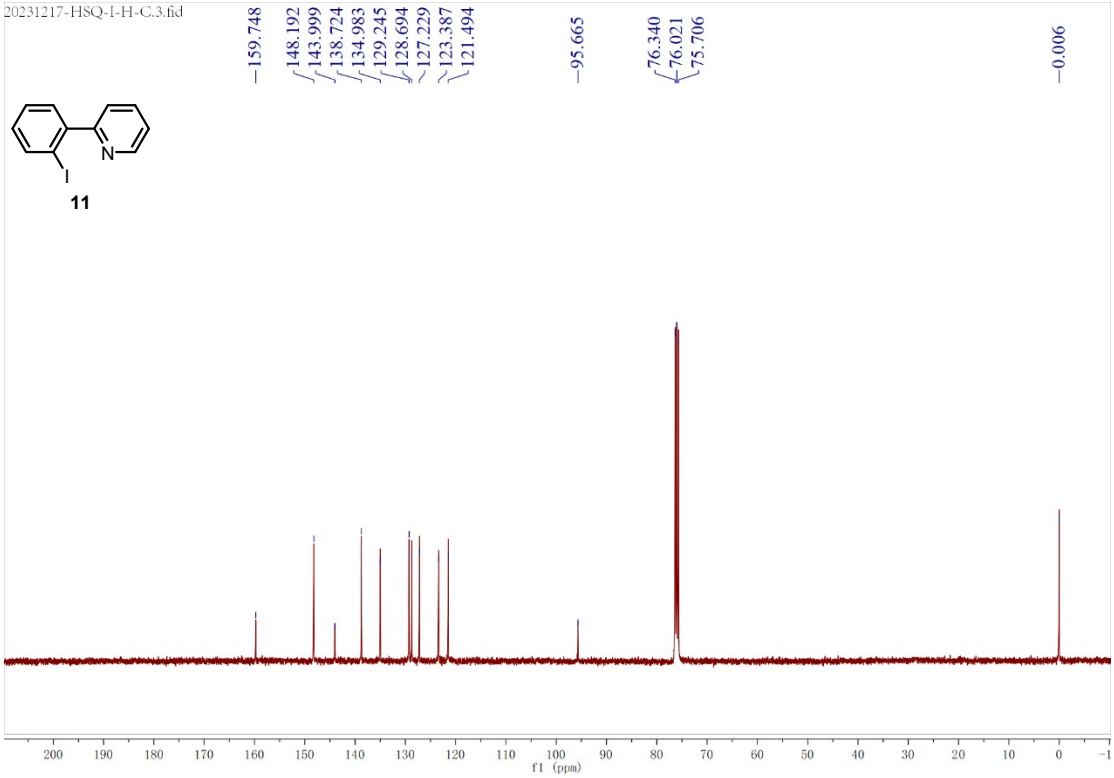


2-(2-iodophenyl)pyridine (**11**)

^{1}H NMR (400 MHz, $CDCl_3$)

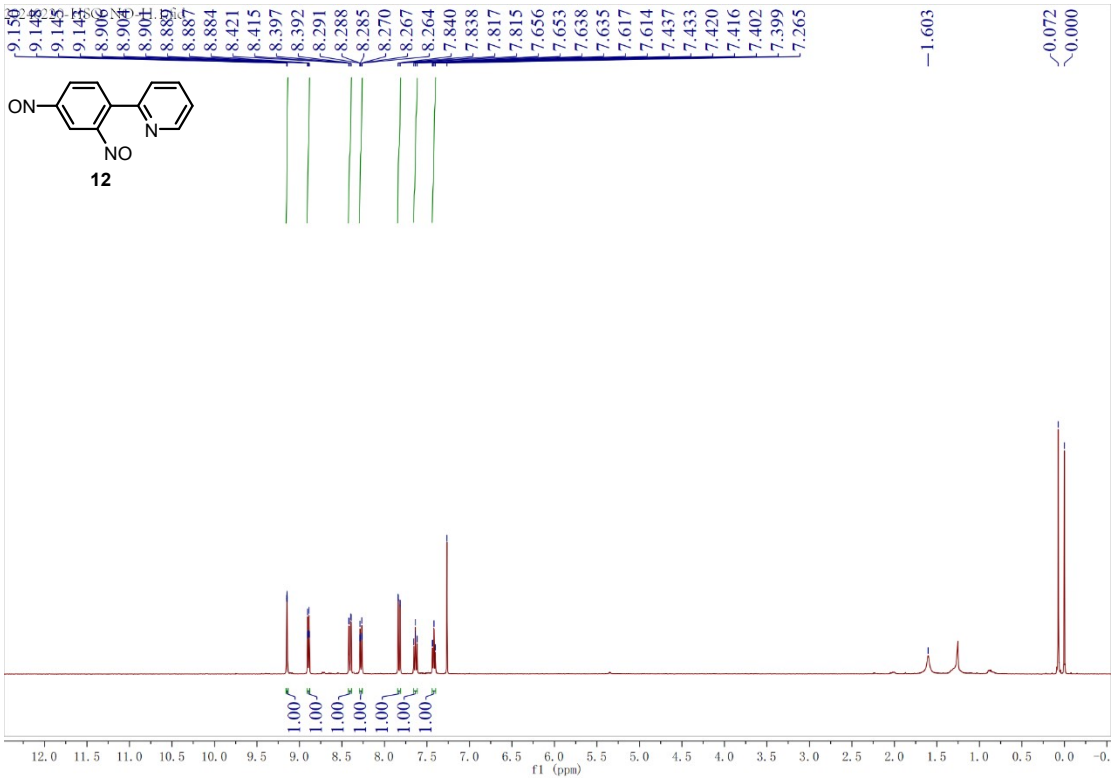


^{13}C NMR (100 MHz, $CDCl_3$)



2-(2,4-dinitrosophenyl)pyridine (**12**)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)