Supporting Information

Cobalt-catalyzed carboxylation reaction of pyridylphosphonium salts with CO_2

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Table of Contents

Experimental Section:

General Considerations:

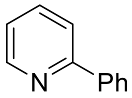
All products were prepared under CO_2 atmosphere using standard Schlenk technique. All substrates were prepared under Ar atmosphere using standard Schlenk technique. ^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{19}F (376 M Hz) were recorded on Bruker AV400 (600) NMR spectrometer with DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-d_6: δ H = 2.50 ppm, δ C = 39.43 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. High-resolution mass spectrometry (HRMS) was done on Agilent 6520 Q-TOF LC/MS mass spectrometer. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Energy Chemical without any further purification.

General Procedure for the Preparation of Starting Materials.

Preparation of substituted pyridines

The studied pyridines were shown in **Table S1**. Pyridines **B-G**, **I-M**, and **O-W** were synthesized via Suzuki coupling reaction.[1-3] All other compounds were purchased from commercial sources.

Table S1 Starting pyridines



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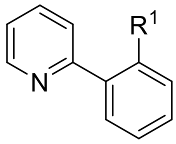
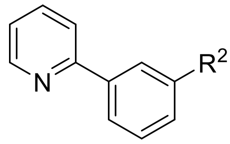
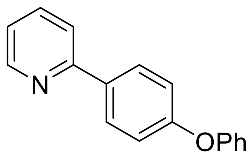


R^1 = Me, **B**
R^1 = OMe, **C**



R^2 = Me, **D**
R^2 = OMe, **E**
R^2 = CF_3, **F**
R^2 = CO_2Me, **G**



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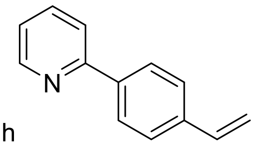

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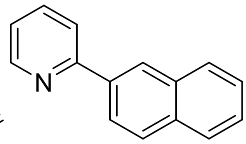

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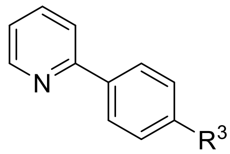
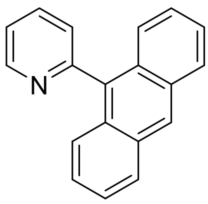


R^3 = Me, **H**
R^3 = Et, **I**
R^3 = ^{i}Pr, **J**
R^3 = ^{t}Bu, **K**
R^3 = CO_2Me, **L**
R^3 = F, **M**,
R^3 = Cl, **N**
R^3 = OMe, **O**
R^3 = CO_2Et, **P**



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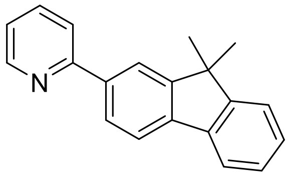

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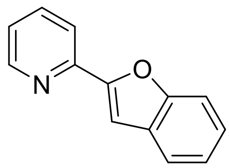

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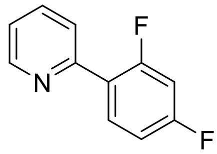

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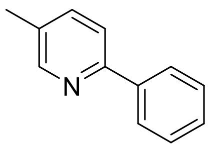

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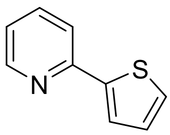

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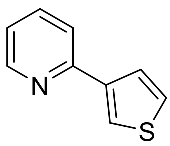

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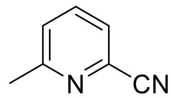
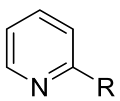
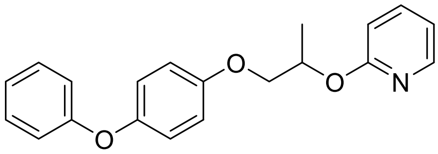


AA



R = CO_2Me, **AB**
Me, **AE**
Cl, **AF**



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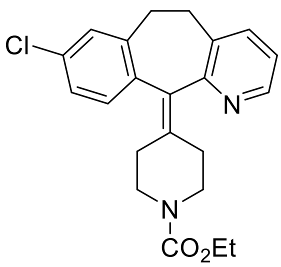
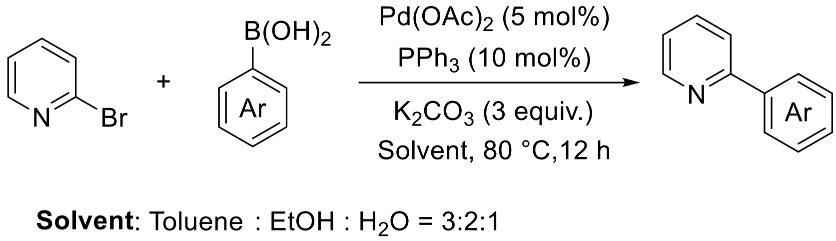


AD

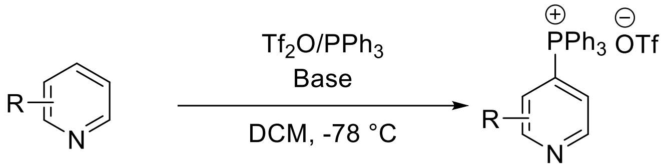
Synthesis of B-G, I-M and O-W[1-3]

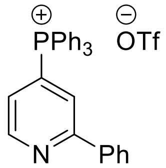


To a 500 mL round-bottom flask containing a stirring bar were added 2-bromopyridine (20 mmol, 1.0 equiv), aryl boronic acid (40 mmol, 2.0 equiv), $Pd(OAc)_2$ (1 mmol, 0.05 equiv), PPh_3 (2 mmol, 0.1 equiv), K_2CO_3 (60 mmol, 3.0 equiv.), toluene (60 mL), EtOH (40 mL), and H_2O (20 mL). The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was transferred to a separatory funnel and extracted with EA. The organic layer was dried (Na_2SO_4), then filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA = 200:1-5:1) as the eluent to give desired pyridine products.

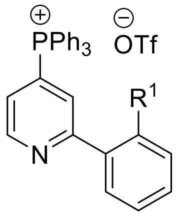
General procedure for the synthesis of pyridylphosphonium salts.[4-8]

To an oven dried 250 mL Schlenk flask containing a stir bar were added pyridines (10 mmol, 1.0 equiv) and DCM (100 mL) under argon. The reaction vessel was cooled to –78 ºC and Tf_2O (10 mmol, 1.0 equiv) was added dropwise. The reaction was stirred for 30 min before PPh_3 (11 mmol, 1.1 equiv, crushed to a powder before use) was added under argon flow. The stated organic base (NEt_3 (**1a-1w**, **1y-1z**, **1ae**, and **1af**) or DBU (**1x**, **1aa**, and **1ac-1ad**), 1.0 equiv) was added dropwise via syringe, then the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 min). The reaction mixture was quenched with H_2O (100 mL) and the mixture was transferred to a separatory funnel. The mixture was diluted with DCM and the resulting organic layer was washed three times with H_2O (3 × 50 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated under reduced pressure to approximately 10 mL. An excess of PE was added to the concentrated solution and continue to concentrate the solution under reduced pressure until the crude product precipitated. The resulting crude product was filtered on a frit, and the solid was washed with Et_2O and EA (100 mL, 5:1). The obtained product was dried in vacuo to provide the pure phosphonium salt.

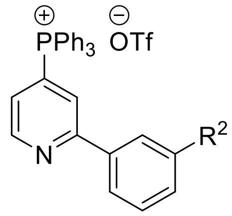




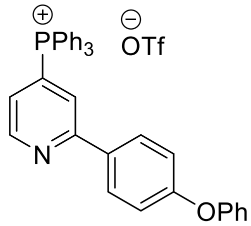
1a



R^1 = Me, **1b**
R^1 = OMe, **1c**



R^2 = Me, **1d**
R^2 = OMe, **1e**
R^2 = CF_3, **1f**
R^2 =CO_2Me, **1g**



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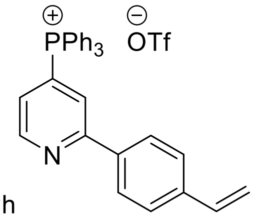
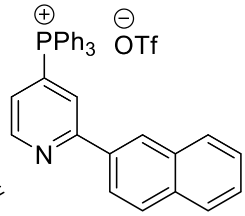
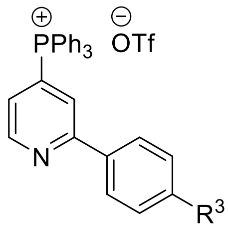


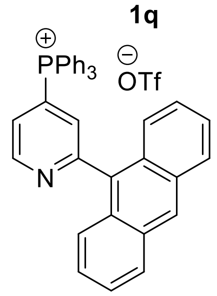
1r



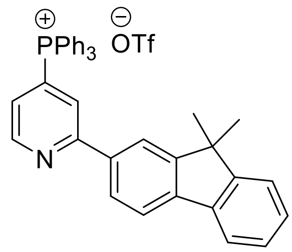
1s



R^3 = Me, **1h**
R^3 = Et, **1i**
R^3 = ^{i}Pr, **1j**
R^3 = ^{t}Bu, **1k**
R^3 = CO_2Me, **1l**
R^3 = F, **1m**
R^3 = Cl, **1n**
R^3 =OMe, **1o**
R^3 =CO_2Et, **1p**



1t



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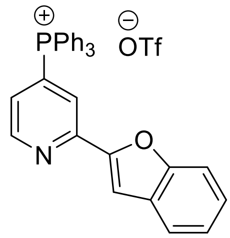
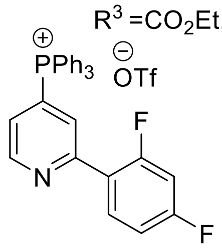
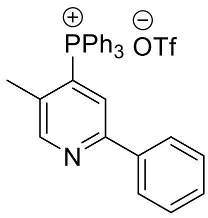


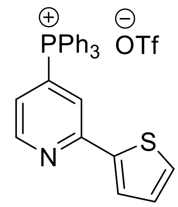
1v



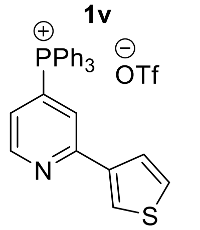
1w



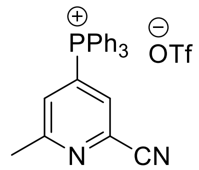
1x



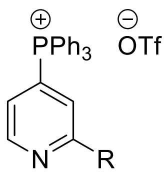
1y



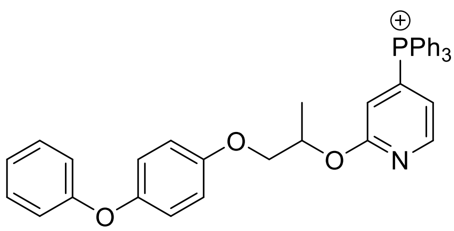
1z



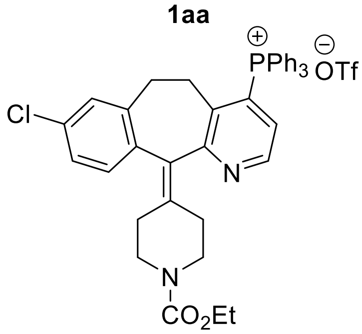
1aa



R = CO_2Me, **1ab**
Me, **1ae**
Cl, **1af**

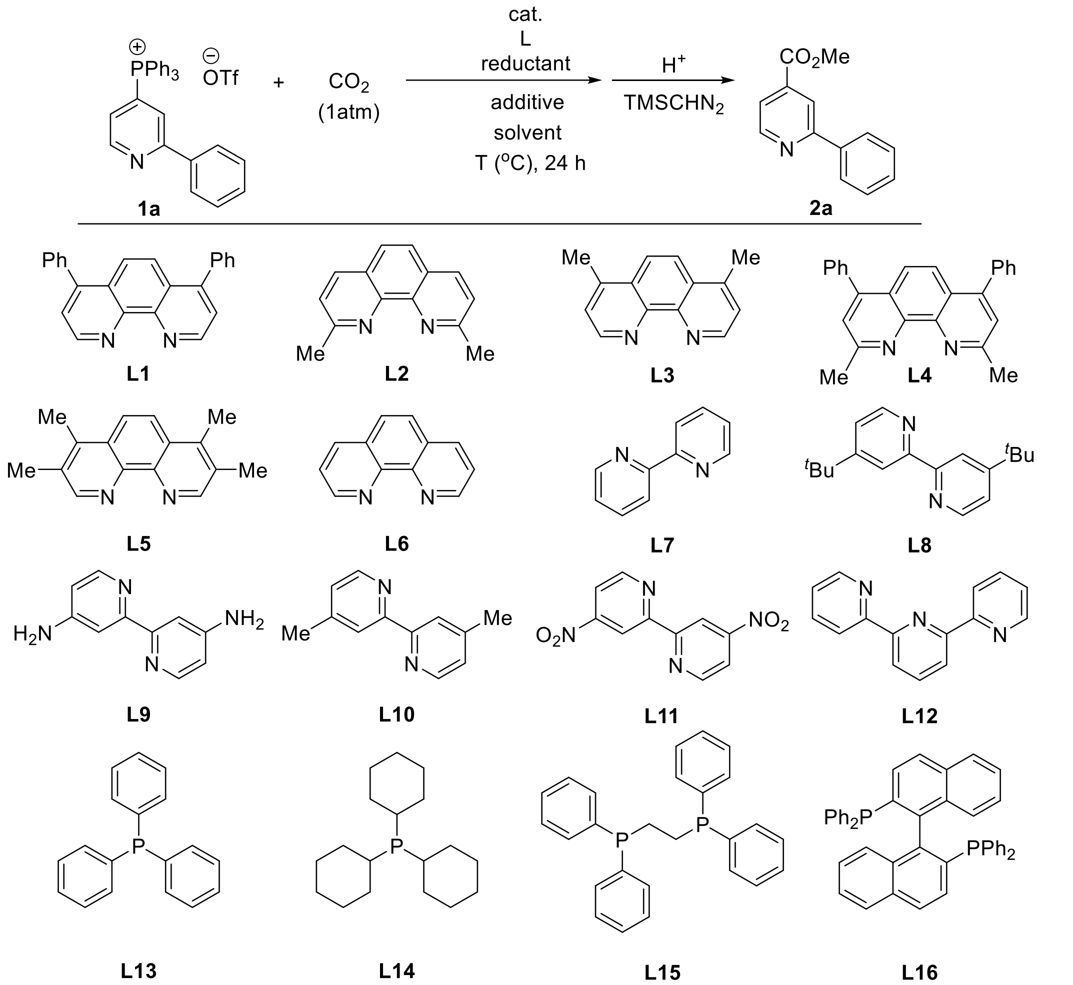


1ac



1ad

Optimization of Reaction Conditions.



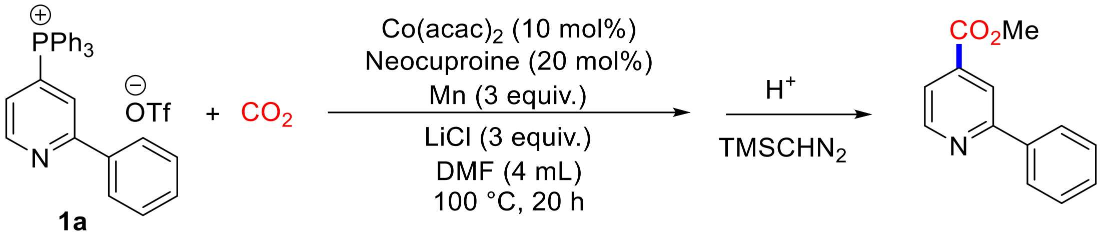
Entry[a]	Catalyst	Ligand	Reductant	Additive	Solvent	T	Yield[b] (%)
1	$Co(acac)_2$	**L1**	Mn	LiCl	DMF	100	54
2	$NiCl_2 \cdot DME_2$	**L1**	Mn	LiCl	DMF	100	N.D.
3	$CoCl_2$	**L1**	Mn	LiCl	DMF	100	35
4	$Pd(OAc)_2$	**L1**	Mn	LiCl	DMF	100	N.D.
5	$Co(acac)_2$	**L1**	Sm	LiCl	DMF	100	36
6	$Co(acac)_2$	**L1**	Zn	LiCl	DMF	100	53
7	$Co(acac)_2$	**L1**	Mg	LiCl	DMF	100	trace
8	$Co(acac)_2$	**L1**	$ZnEt_2$	LiCl	DMF	100	N.D.
9	$Co(acac)_2$	**L1**	$ZnMe_2$	LiCl	DMF	100	N.D.
10	$Co(acac)_2$	**L1**	$AlMe_3$	LiCl	DMF	100	N.D.
11	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	57
12	$Co(acac)_2$	**L3**	Mn	LiCl	DMF	100	37
13	$Co(acac)_2$	**L4**	Mn	LiCl	DMF	100	33

14	$Co(acac)_2$	**L5**	Mn	LiCl	DMF	100	35
15	$Co(acac)_2$	**L6**	Mn	LiCl	DMF	100	40
16	$Co(acac)_2$	**L7**	Mn	LiCl	DMF	100	33
17	$Co(acac)_2$	**L8**	Mn	LiCl	DMF	100	24
18	$Co(acac)_2$	**L9**	Mn	LiCl	DMF	100	34
19	$Co(acac)_2$	**L10**	Mn	LiCl	DMF	100	32
20	$Co(acac)_2$	**L11**	Mn	LiCl	DMF	100	26
20	$Co(acac)_2$	**L12**	Mn	LiCl	DMF	100	N.D.
21	$Co(acac)_2$	**L13**	Mn	LiCl	DMF	100	36
22	$Co(acac)_2$	**L14**	Mn	LiCl	DMF	100	N.D.
23	$Co(acac)_2$	**L15**	Mn	LiCl	DMF	100	34
24	$Co(acac)_2$	**L16**	Mn	LiCl	DMF	100	N.D.
25	$Co(acac)_2$	**L2**	Mn	LiCl	DMA	100	43
26	$Co(acac)_2$	**L2**	Mn	LiCl	DMSO	100	38
27	$Co(acac)_2$	**L2**	Mn	LiCl	NMP	100	36
28	$Co(acac)_2$	**L2**	Mn	LiCl	THF	100	N.D.
29	$Co(acac)_2$	**L2**	Mn	LiCl	MeCN	100	N.D.
30	$Co(acac)_2$	**L2**	Mn	LiCl	1,4-dioxane	100	N.D.
31	$Co(acac)_2$	**L2**	Mn	LiCl	MTBE	100	N.D.
32	$Co(acac)_2$	**L2**	Mn	LiCl	EtOAc	100	N.D.
33	$Co(acac)_2$	**L2**	Mn	LiBr	DMF	100	33
34	$Co(acac)_2$	**L2**	Mn	LiI	DMF	100	trace
35	$Co(acac)_2$	**L2**	Mn	LiF	DMF	100	N.D.
36	$Co(acac)_2$	**L2**	Mn	LiOAc	DMF	100	N.D.
37	$Co(acac)_2$	**L2**	Mn	LiOtBu	DMF	100	N.D.
38	$Co(acac)_2$	**L2**	Mn	$MgCl_2$	DMF	100	N.D.
39	$Co(acac)_2$	**L2**	Mn	$MgBr_2$	DMF	100	N.D.
40	$Co(acac)_2$	**L2**	Mn	$ZnCl_2$	DMF	100	N.D.
41	$Co(acac)_2$	**L2**	Mn	$ZnBr_2$	DMF	100	N.D.
42	$Co(acac)_2$	**L2**	Mn	NaI	DMF	100	N.D.
43	$Co(acac)_2$	**L2**	Mn	CsF	DMF	100	N.D.
44[c]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	43
45[d]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	53
46[e]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	22
47[f]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	31
48[g]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	55
49[h]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	59
50[i]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	65
51[j]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	72

52[k]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	100	70
53[j]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	80	49
54[j]	$Co(acac)_2$	**L2**	Mn	LiCl	DMF	120	68
55	-	**L2**	Mn	LiCl	DMF	100	N.D.
56	$Co(acac)_2$	**-**	Mn	LiCl	DMF	100	33
57	$Co(acac)_2$	**L2**	-	LiCl	DMF	100	N.D.
58	$Co(acac)_2$	**L2**	Mn	-	DMF	100	N.D.

[a]Reaction conditions: **1a** (0.2 mmol), catalyst (10 mmol%), ligand (20 mmol%), reductant (3 equiv.), additive (3 equiv.), solvent (2 mL), T (°C), 20 h. [b]Isolated yield. [c]2 equiv. LiCl. [d]4 equiv. LiCl. [e]0.4 mmol **2a**. [f]1.5 mL DMF. [g]2.5 mL DMF. [h]3 mL DMF. [i]3.5 mL DMF. [j]4 mL DMF. [k]4.5 mL DMF.

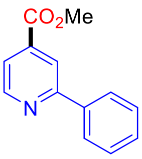
General Procedure and Characterization of Products 2.



Substrate **1a** (113.0 mg, 0.2 mmol, 1 equiv), $Co(acac)_2$ (7.1 mg, 0.02 mmol, 10 mol %), Neocuproine (8.3 mg, 0.04 mmol, 20 mol %), Mn powder (33.0 mg, 0.6 mmol, 3 equiv), and LiCl (25.4 mg, 0.6 mmol, 3.0 equiv) were added into a Schlenk tube equipped with a stir bar. The tube was then vacuumized and back-filled with CO_2 for three times. Dry DMF (4.0 mL) was added. The Schlenk tube was sealed at 1 atmospheric pressure of CO_2 and the mixture was stirred at 100 °C (oil bath) for 24 h. Afterwards, the mixture was cooled to room temperature. Then the mixture was carefully quenched with HCl solution (4 M in 1,4-dioxane) and stirred for 5 min. The mixture was diluted H_2O (40 mL) and the aqueous phase was extracted with EA (3 × 50 mL). The organic layer was dried (Na_2SO_4). After removal of solvents under reduced pressure the residue was dissolved in Et_2O/MeOH = 4:1 (ca. 2 mL) followed by treatment with $TMSCHN_2$ (2 M in hexane, 0.5 mL, 1 mmol, 5.0 equiv). After 10 min, the mixture was directly concentrated under reduced pressure to afford the crude product. The crude products were purified by flash chromatography (eluent: PE/EA = 20:1-5:1).

Characterization of products:

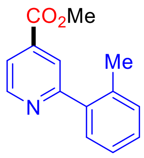
Methyl 2-phenylisonicotinate (2a) [9]



2a

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless liquid in 72% yield (30.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$). δ 8.83 (d, J = 5.0 Hz, 1H), 8.30 (s, 1H), 8.06 (d, J = 7.4 Hz, 2H), 7.77 (d, J = 4.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.5, 150.5, 138.5, 138.3, 129.6, 129.0, 127.1, 121.3, 119.9, 52.9.

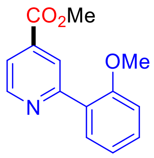
Methyl 2-(o-tolyl)isonicotinate (2b) [10]



2b

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless liquid in 60% yield (31.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.0 Hz, 1H), 7.98 (s, 1H), 7.80 (d, *J* = 4.9 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.31 – 7.27 (m, 2H), 3.97 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 161.2, 150.1, 139.7, 137.7, 136.0, 131.0, 129.8, 128.8, 126.1, 123.4, 120.9, 52.9, 20.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO_2$: 228.1020, found: 228.1022

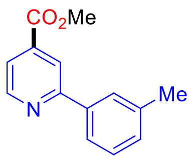
Methyl 2-(2-methoxyphenyl)isonicotinate (2c)



2c

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 44% yield (21.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.0 Hz, 1H), 8.38 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 5.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 157.3, 157.1, 150.1, 137.2, 131.2, 130.6, 128.4, 124.6, 121.2, 120.8, 111.5, 55.8, 52.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO_3$: 244.0969, found: 244.0970.

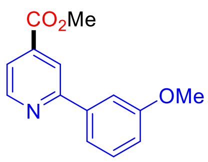
Methyl 2-(m-tolyl)isonicotinate (2d) [(10)]



2d

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 51% yield (23.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 1H), 8.28 (s, 1H), 7.89 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.18 (m, 1H), 3.97 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 158.6, 150.4, 138.6, 138.5, 138.1, 130.3, 128.8, 127.7, 124.2, 121.1, 119.8, 52.8, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO_2$: 228.1020, found: 228.1020.

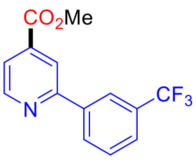
Methyl 2-(3-methoxyphenyl)isonicotinate (2e) [(10)]



2e

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 66% yield (32.1 mg). m.p. 54 – 57 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 4.6, 2.5 Hz, 1H), 8.26 (s, 1H), 7.85 – 7.69 (m, 1H), 7.63 (d, *J* = 1.1 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 (td, *J* = 7.9, 2.5 Hz, 1H), 6.98 (dd, *J* = 5.9, 2.1 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 160.2, 158.2, 150.4, 140.0, 138.2, 129.9, 121.3, 119.9, 119.4, 115.7, 112.1, 55.4, 52.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO_3$: 244.0969, found: 244.0970.

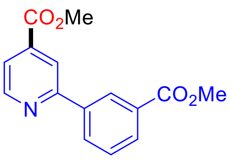
Methyl 2-(3-(trifluoromethyl)phenyl)isonicotinate (2f) (9)



2f

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 69% yield (38.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (d, J = 5.0 Hz, 1H), 8.34 (s, 1H), 8.31 (s, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 156.9, 150.8, 139.3, 138.6, δ 131.49 (q, *J* = 32.5 Hz), 130.27, 129.50, 126.20 (q, *J* = 3.8 Hz), 124.20 (q, *J* = 272.5 Hz), 124.02 (q, *J* = 3.9 Hz), 122.05, 119.87, 52.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59.

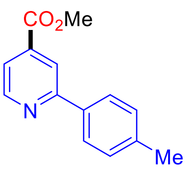
Methyl 2-(3-(methoxycarbonyl)phenyl)isonicotinate (2g)



2g

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 42% yield (22.8 mg). m.p. 71 – 73 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 1H), 8.66 (s, 1H), 8.30 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.76 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.6, 157.3, 150.6, 138.8, 138.4, 131.4, 130.9, 130.5, 129.1, 128.0, 121.7, 119.7, 52.8, 52.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}NO_4$: 272.0918, found: 272.0969.

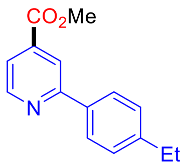
Methyl 2-(p-tolyl)isonicotinate (2h) (9)



2h

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 73% yield (33.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 1H), 8.26 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.73 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.5, 150.4, 139.7, 138.2, 135.8, 129.7, 126.9, 120.9, 119.5, 52.8, 21.4.

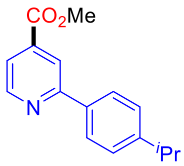
Methyl 2-(4-ethylphenyl)isonicotinate (2i)



2i

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 58% yield (28.0 mg). [1]H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 1H), 8.27 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.72 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.96 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). [13]C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.5, 150.4, 145.9, 138.1, 136.0, 128.4, 127.0, 120.8, 119.4, 52.7, 28.7, 15.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO_2$: 242.1176, found: 242.1179.

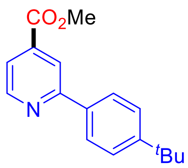
Methyl 2-(4-isopropylphenyl)isonicotinate (2j)



2j

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 53% yield (27.0 mg). [1]H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 1H), 8.27 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.72 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.96 (s, 3H), 2.97 (hept, *J* = 13.8, 6.7 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 6H). [13]C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.5, 150.5, 150.4, 138.1, 136.1, 129.2, 127.0, 120.8, 119.4, 52.7, 34.0, 23.9. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}NO_2$: 256.1333, found: 256.1336.

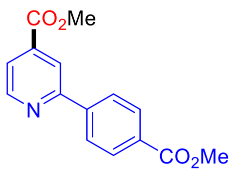
Methyl 2-(4-(tert-butyl)phenyl)isonicotinate (2k)



2k

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 43% yield (23.1 mg). [1]H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, J = 4.9 Hz, 1H), 8.28 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 3.97 (s, 3H), 1.37 (s, 9H). [13]C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.5, 152.8, 150.5, 138.1, 135.8, 126.8, 125.9, 120.9, 119.5, 52.8, 34.8, 31.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}NO_2$: 270.1489, found: 270.1493.

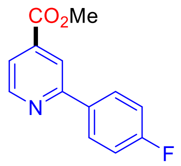
Methyl 2-(4-(methoxycarbonyl)phenyl)isonicotinate (2l) [(9)]



2l

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 60% yield (32.5 mg). [1]H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.9 Hz, 1H), 8.31 (s, 1H), 8.12 (q, *J* = 8.4 Hz, 4H), 7.80 (d, *J* = 4.9 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H). [13]C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.6, 157.3, 150.7, 142.6, 138.4, 130.9, 130.2, 127.0, 122.0, 120.2, 52.9, 52.3.

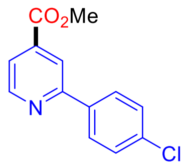
Methyl 2-(4-fluorophenyl)isonicotinate (2m)



2m

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 54% yield (25.0 mg). m.p. 41 – 43 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 1H), 8.24 (s, 1H), 8.04 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.76 (d, *J* = 4.8 Hz, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 164.0 (d, *J* = 249.5 Hz), 157.5, 150.5, 138.4, 134.7 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 8.4 Hz), 121.2, 119.5, 116.0 (d, *J* = 21.6 Hz), 52.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.73. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}FNO_2$: 232.0769, found: 232.0769.

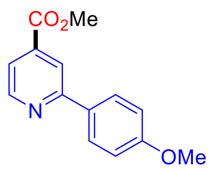
Methyl 2-(4-chlorophenyl)isonicotinate (2n) [(9)]



2n

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 65% yield (32.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.9 Hz, 1H), 8.25 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 4.9 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 157.1, 150.5, 138.3, 136.9, 135.7, 129.1, 128.3, 121.4, 119.4, 52.8.

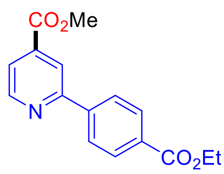
Methyl 2-(4-methoxyphenyl)isonicotinate (2o)



2o

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 74% yield (36.0 mg). m.p. 59 – 61 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.0 Hz, 1H), 8.22 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 4.9 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.97 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 161.0, 158.2, 150.4, 138.1, 131.2, 128.4, 120.5, 119.0, 114.3, 55.5, 52.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO_3$: 244.0969, found: 244.0971.

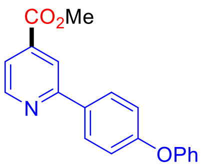
Methyl 2-(4-(ethoxycarbonyl)phenyl)isonicotinate (2p)



2p

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 74% yield (33.6 mg). m.p. 74 – 76 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.9 Hz, 1H), 8.30 (s, 1H), 8.11 (dd, *J* = 20.2, 8.5 Hz, 4H), 7.78 (d, *J* = 4.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 165.6, 157.3, 150.7, 142.5, 138.4, 131.2, 130.1, 126.9, 121.9, 1202, 61.2, 52.9, 14.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}NO_4$: 286.1074, found: 286.1077.

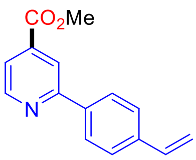
Methyl 2-(4-phenoxyphenyl)isonicotinate (2q) (10)



2q

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 43% yield (26.2 mg). m.p. 57 – 59 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, J = 4.9 Hz, 1H), 8.25 (s, 1H), 8.03 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 4.8 Hz, 1H), 7.36 (t, J = 7.9 Hz, 2H), 7.22 – 6.94 (m, 5H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 158.9, 157.8, 156.7, 150.4, 138.3, 133.4, 129.9, 128.6, 123.8, 120.8, 119.4, 119.3, 118.8, 52.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}NO_3$: 306.1125, found: 306.1128.

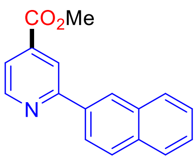
Methyl 2-(4-vinylphenyl)isonicotinate (2r) (9)



2r

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 68% yield (32.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, J = 4.8 Hz, 1H), 8.27 (s, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.80 – 7.67 (m, 1H), 7.51 (d, J = 8.2 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.83 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 158.0, 150.5, 138.7, 138.2, 137.8, 136.3, 127.2, 126.8, 121.1, 119.5, 114.9, 52.8.

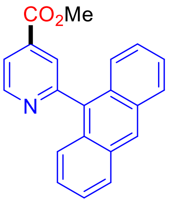
Methyl 2-(naphthalen-2-yl)isonicotinate (2s) (9)



2s

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 62% yield (32.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (d, J = 4.9 Hz, 1H), 8.55 (d, J = 0.6 Hz, 1H), 8.44 (s, 1H), 8.20 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 (dd, J = 9.0, 3.7 Hz, 2H), 7.88 (dd, J = 6.0, 3.4 Hz, 1H), 7.79 (dd, J = 4.9, 1.3 Hz, 1H), 7.56 – 7.48 (m, 2H), 4.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.4, 150.6, 138.3, 135.8, 134.0, 133.6, 128.9, 128.7, 127.8, 126.9, 126.8, 126.6, 124.5, 121.3, 120.1, 52.9.

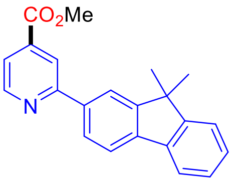
Methyl 2-(anthracen-9-yl)isonicotinate (2t) (9)



2t

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green solid in 64% yield (40.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (d, J = 5.1 Hz, 1H), 8.57 (s, 1H), 8.11 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 8.03 (dd, J = 5.1, 1.4 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.47 (dd, J = 7.8, 7.0 Hz, 2H), 7.43 – 7.35 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 159.6, 151.1, 137.9, 134.2, 131.4, 130.1, 128.7, 128.1, 126.3, 126.1, 125.7, 125.3, 121.6, 52.9.

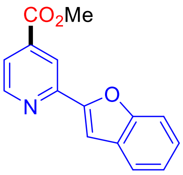
Methyl 2-(9,9-dimethyl-9H-fluoren-2-yl)isonicotinate (2u) [9]



2u

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 81% yield (53.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (d, J = 4.9 Hz, 1H), 8.37 (s, 1H), 8.19 (s, 1H), 8.05 (dd, J = 7.9, 1.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.78 (dd, J = 8.4, 2.7 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.42 – 7.32 (m, 2H), 4.01 (s, 3H), 1.58 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 157.8, 153.5, 153.4, 149.5, 139.8, 137.6, 137.3, 136.5, 126.8, 126.2, 125.3, 121.8, 120.4, 120.0, 119.5, 119.4, 118.8, 51.9, 46.2, 26.3.

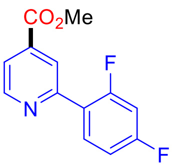
Methyl 2-(benzofuran-2-yl)isonicotinate (2v) [9]



2v

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 51% yield (25.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, J = 4.6 Hz, 1H), 8.41 (s, 1H), 7.76 (d, J = 4.6 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.48 (s, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 155.5, 154.4, 150.8, 150.3, 138.3, 128.8, 125.7, 123.4, 122.0, 121.9, 119.1, 111.7, 105.9, 52.9.

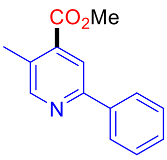
Methyl 2-(2,4-difluorophenyl)isonicotinate (2w) [9]



2w

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 51% yield (28.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, J = 5.0 Hz, 1H), 8.29 (s, 1H), 8.01 (dd, J = 15.5, 8.8 Hz, 1H), 7.80 (d, J = 5.0 Hz, 1H), 7.01 (td, J = 8.7, 2.4 Hz, 1H), 6.93 (ddd, J = 11.2, 8.8, 2.4 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 163.5 (dd, J_1 = 251.9, J_2 = 12.1 Hz) , 160.7 (dd, J_1 = 253.3, J_2 = 12.0 Hz), 153.6 (d, J = 2.5 Hz), 150.5, 138.0, 132.2 (dd, J_1 = 9.8, J_2 = 4.2 Hz), 123.4 (d, J = 9.8 Hz), 123.1 (dd, J_1 = 11.5, J_2 = 3.9 Hz), 121.6, 112.0 (dd, J_1 = 21.1, J_2 = 3.6 Hz), 104.5 (t, J = 26,1 Hz), 52.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.88, -112.30.

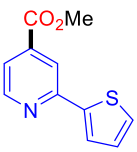
Methyl 5-methyl-2-phenylisonicotinate (2x) (9)



2x

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a green liquid in 51% yield (19.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.16 (s, 1H), 8.02 (dd, J = 5.2, 3.4 Hz, 2H), 7.49 (dd, J = 10.3, 4.7 Hz, 2H), 7.43 (t, J = 6.8 Hz, 1H), 3.97 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 155.9, 152.8, 138.5, 137.5, 132.0, 129.3, 129.0, 126.9, 120.3, 52.6, 18.1.

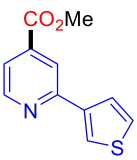
Methyl 2-(thiophen-2-yl)isonicotinate (2y) (9)



2y

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as a white solid in 63% yield (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, J = 4.8 Hz, 1H), 8.16 (s, 1H), 7.74 – 7.57 (m, 2H), 7.41 (d, J = 4.7 Hz, 1H), 7.18 – 7.03 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 153.7, 150.4, 144.0, 138.1, 128.4, 128.3, 125.5, 120.9, 118.1, 52.9.

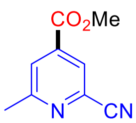
Methyl 2-(thiophen-3-yl)isonicotinate (2z) (9)



2z

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as a yellow solid in 66% yield (28.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (t, J = 5.1 Hz, 1H), 8.14 (d, J = 5.3 Hz, 1H), 7.97 (dd, J = 2.8, 1.1 Hz, 1H), 7.85 – 7.62 (m, 2H), 7.52 – 7.30 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 154.5, 150.5, 141.5, 138.1, 126.7, 126.2, 124.4, 120.8, 119.5, 52.8.

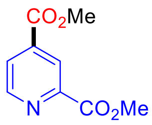
Methyl 2-cyano-6-methylisonicotinate (2aa) (9)



2aa

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/15) as a green liquid in 40% yield (14.1 mg). ^{1} HNMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 4.9 Hz, 1H), 7.87 (d, J = 4.9 Hz, 1H), 3.96 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 149.0, 138.6, 138.3, 136.5, 126.6, 116.2, 53.1, 17.4.

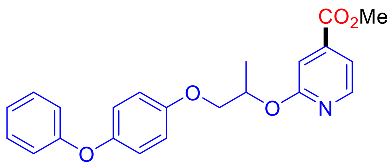
Dimethyl pyridine-2,4-dicarboxylate (2ab) (10)



2ab

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/15) as a yellow solid in 38% yield (14.8 mg). m.p. 48 – 50 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.9 Hz, 1H), 8.66 (s, 1H), 8.04 (d, *J* = 4.8 Hz, 1H), 4.05 (s, 3H), 4.00 (s,3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 164.9, 150.9, 149.1, 139.0, 126.3, 124.6, 53.3, 53.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9NO_4$: 196.0605, found: 196.0605.

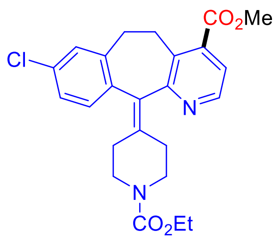
Methyl 2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)isonicotinate (2ac)



2ac

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid in 31% yield (23.5 mg). m.p. 60 – 63 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 5.1 Hz, 1H), 7.41 (d, *J* = 5.1 Hz, 1H), 7.34 (s, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.95 (dt, *J* = 15.9, 8.4 Hz, 6H), 5.91 – 5.38 (m, 1H), 4.20 (dd, *J* = 9.8, 5.5 Hz, 1H), 4.08 (dd, *J* = 9.8, 4.5 Hz, 1H), 3.93 (s, 3H), 1.50 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 163.9, 158.5, 155.2, 150.4, 147.6, 140.4, 129.7, 122.5, 120.8, 117.7, 115.9, 115.8, 112.0, 71.0, 70.2, 52.7, 17.0. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}NO_5$: 380.1493, found: 380.1492.

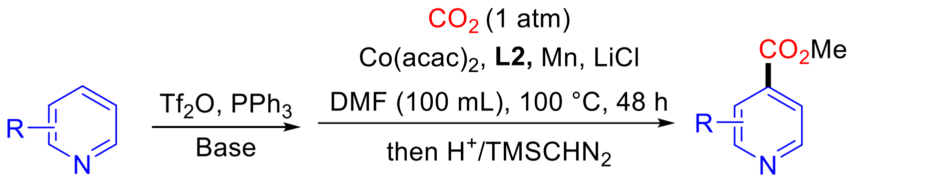
Methyl 8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine-4-carboxylate (2ad) [9]

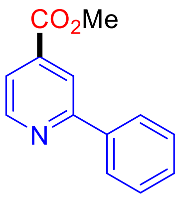


2ad

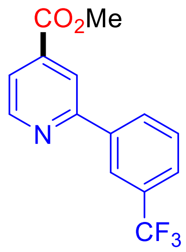
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a colorless liquid in 53% yield (46.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.9 Hz, 1H), 7.50 (d, *J* = 4.7 Hz, 1H), 7.10 (s, 3H), 4.24 – 4.04 (m, 2H), 3.94 (s, 3H), 3.81 (s, 2H), 3.48 (dt, *J* = 9.6, 4.5 Hz, 1H), 3.41 – 3.27 (m, 2H), 3.20 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.12 (ddd, *J* = 12.9, 9.6, 3.5 Hz, 1H), 2.99 (ddd, *J* = 15.9, 11.6, 4.0 Hz, 1H), 2.44 (s, 2H), 2.41 – 2.34 (m, 1H), 2.15 (d, *J* = 13.7 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 161.5, 155.6, 146.9, 139.0, 137.9, 137.6, 135.2, 133.3 (2C), 131.7, 130.1, 126.1, 122.1, 61.5, 52.8, 44.9, 44.7, 31.9, ,30.9, 30.7, 27.1, 14.8.

Gram Scale Late-Stage One-pot Two-step Method

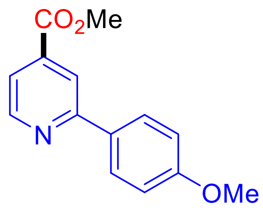




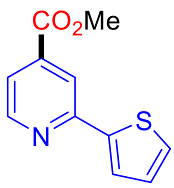
2a
1.64 g, 77%



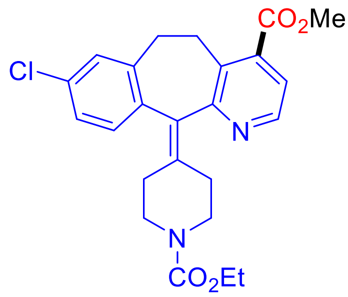
2f
1.86 g, 66%



2o
1.82 g, 75%



2y
1.07 g, 49%



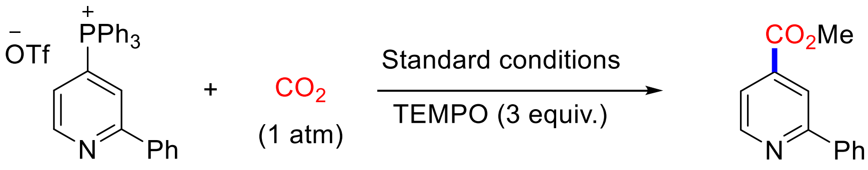
2ad
1.94 g, 44%

An oven-dried 200 mL Schlenk flask containing a stirring bar was charged with pyridines (10 mmol, 1.0 equiv) and DCM (100 mL) under an argon atmosphere. The reaction vessel was cooled to –78 ºC and Tf_2O (10 mmol, 1.0 equiv) was added dropwise. The reaction was stirred for 30 min before PPh_3 (11 mmol, 1.1 equiv, crushed to a powder before use) was added under argon flow. The stated organic base (NEt_3 (**2a**, **2f**, **2o**, and **2y**) or DBU (**2ad**), 1.0 equiv) was added dropwise via syringe, then the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 minutes). The reaction mixture was quenched with H_2O (100 mL) and the mixture was transferred to a separatory funnel. The mixture was diluted with DCM and the resulting organic layer was washed threetimes with H_2O (3 × 50 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated under reduced pressure to approximately 10 mL. An excess of PE was added to the concentrated solution and continue concentration until the formation of crude products precipitates.

An oven-dried 500 mL Schlenk flask containing a stirring bar was charged with above crude pyridylphosphonium salts $Co(acac)_2$ (10 mol %), Neocuproine (20 mol %), Mn powder (3 equiv) and LiCl (3.0 equiv). The Schlenk flask was evacuated and back-filled under CO_2 flow for three times. Then, DMF (100 mL) was added under CO_2 flow. The resulting mixture was stirred at room temperature for 12 h. The mixture was then carefully quenched with HCl solution (4 M in 1,4-dioxane) and stirred for 5 minutes. The mixture was diluted with H_2O (500 mL) and the aqueous phase was extracted with EA (4 × 500 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. After removal of solvents under reduced pressure the residue was dissolved in Et_2O/MeOH = 4:1 (ca. 20 mL) followed by treatment with $TMSCHN_2$ (2 M in hexane, 15 mL, 1 mmol, 3.0 equiv, small quantity multiple times). After 10 min, the mixture was directly concentrated under reduced pressure to afford the crude product. The crude products were purified by flash chromatography (eluent: PE/EA = 20:1-5:1) to supply the products **2a**, **2f**, **2o**, **2y**, and **2ad**.

Mechanistic Experiments

TEMPO trapping experiment



Substrate **1a** (113.0 mg, 0.2 mmol, 1 equiv), $Co(acac)_2$ (7.1 mg, 0.02 mmol, 10 mol %), 2 Neocuproine (8.3 mg, 0.04 mmol, 20 mol %), Mn powder (33.0 mg, 0.6 mmol, 3 equiv), LiCl (25.4 mg, 0.6 mmol, 3.0 equiv) and TEMPO (0.6 mmol, 3 equiv.) were added into a Schlenk tube equipped with a stir bar. The tube was then vacuumized and back-filled with CO_2 for three times. dry DMF (4.0 mL) was added. The Schlenk tube was sealed at 1 atmospheric pressure of CO_2 and the mixture was stirred at 100 °C (oil bath) for 24 h. Afterwards, the mixture was cooled to room temperature. Then the mixture was carefully quenched with HCl solution (4 M in 1,4-dioxane) and stirred for 5 minutes. The mixture was diluted H_2O (40 mL) and the aqueous phase was extracted with EA (3 × 50 mL). The organic layer was dried (Na_2SO_4). After removal of solvents under reduced pressure the residue was dissolved in Et_2O/MeOH = 4:1 (ca. 2 mL) followed by treatment with $TMSCHN_2$ (2 M in hexane, 0.5 mL, 1 mmol, 5.0 equiv). After 10 min, the mixture was directly concentrated under reduced pressure to afford the crude product. The crude products were purified by flash chromatography (eluent: PE/EA = 20:1-5:1).

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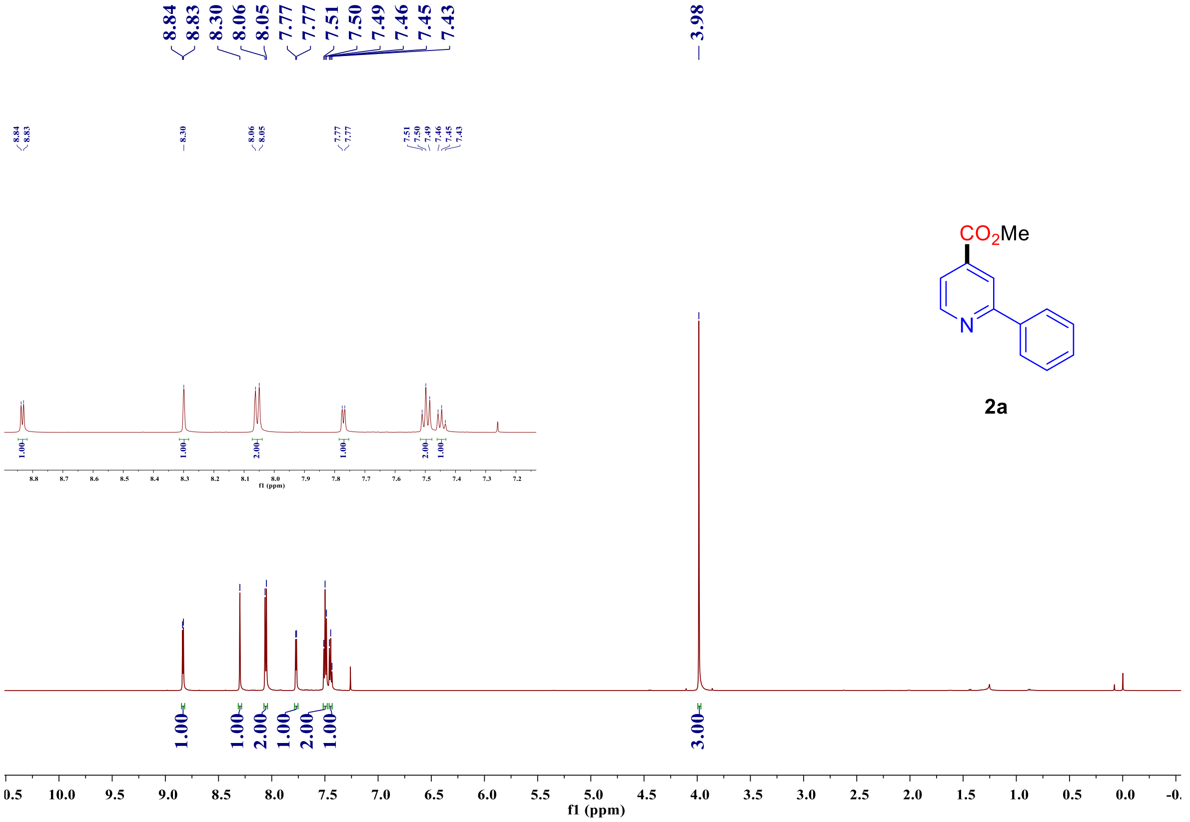
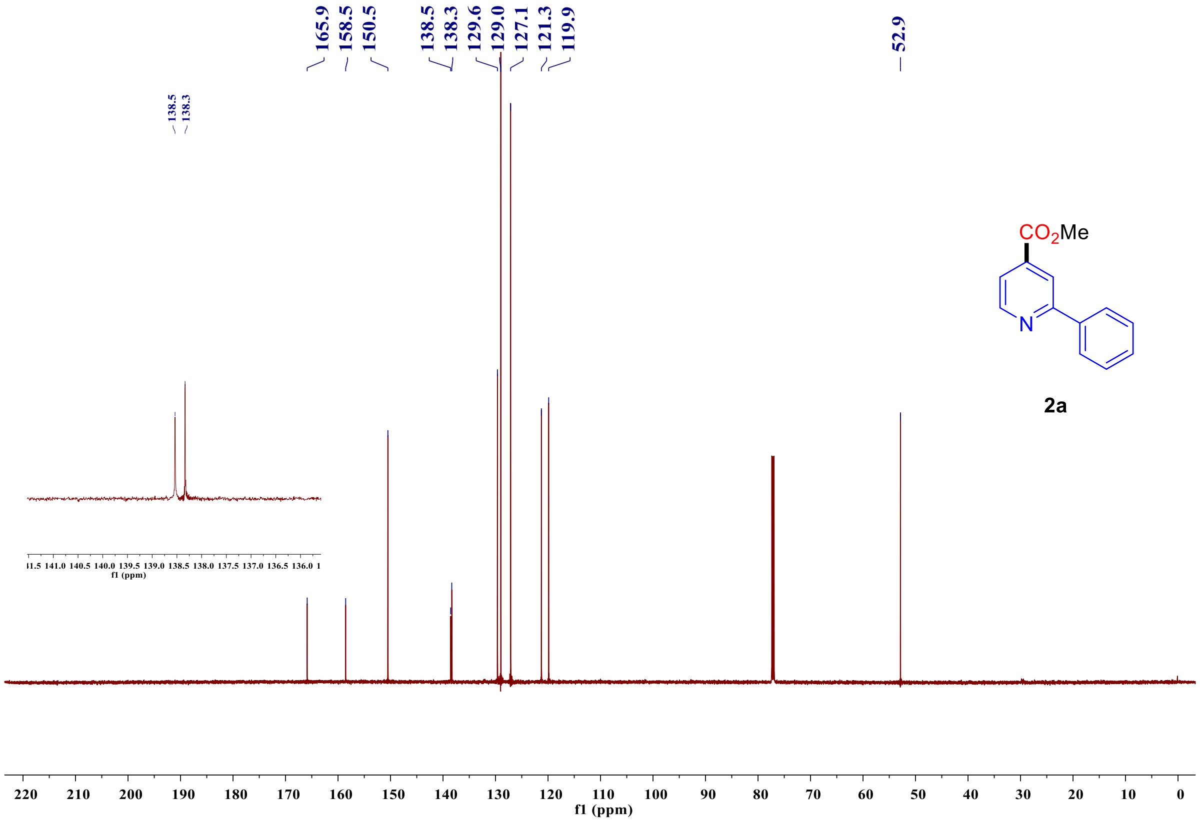
Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra for Compounds

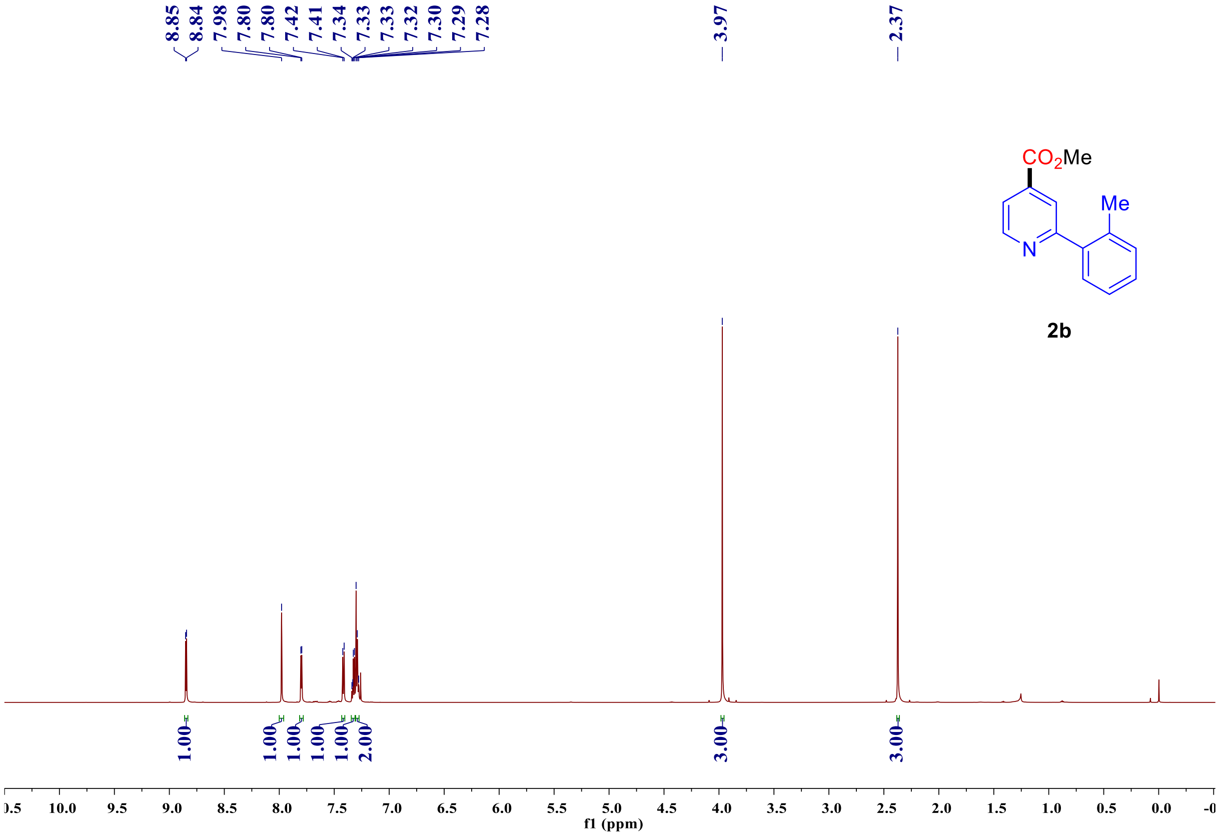
^{1}H NMR of 2a (600 MHz, $CDCl_3$)



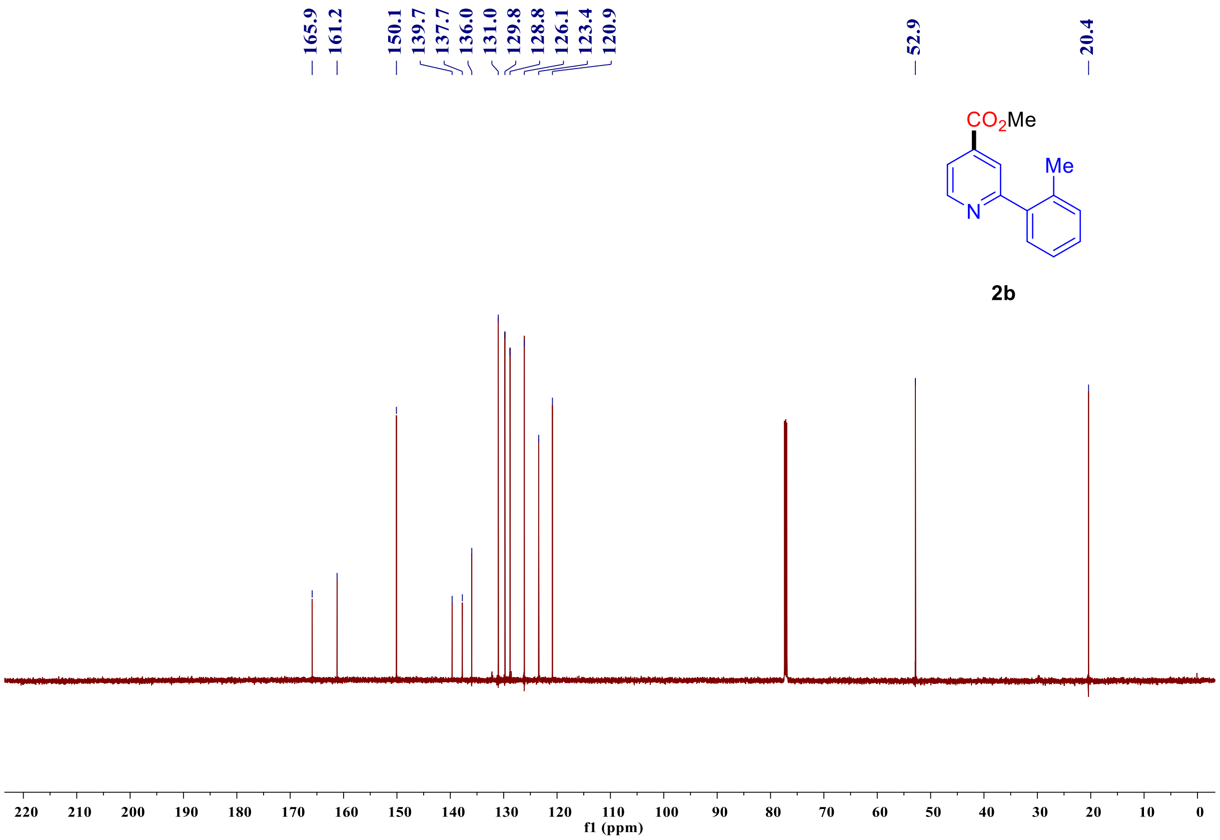
^{13}C NMR of 2a (151 MHz, $CDCl_3$)



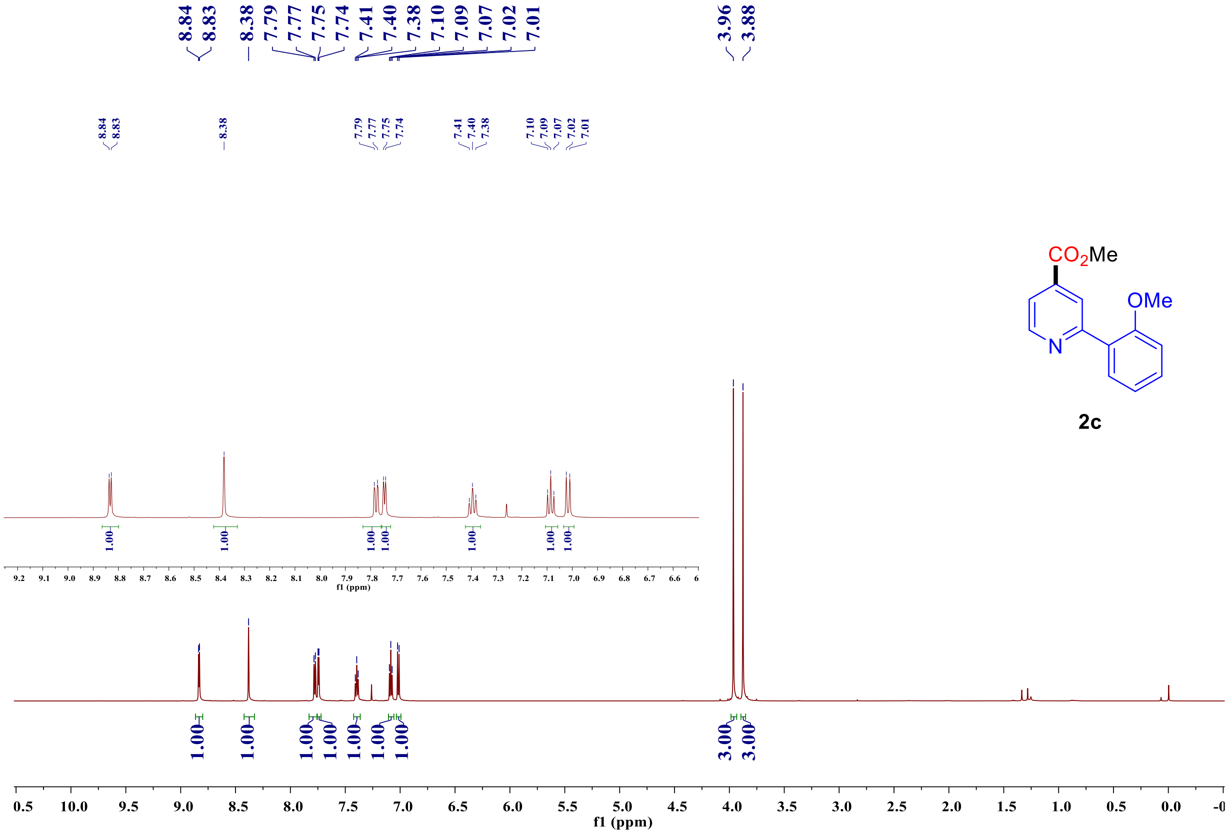
^{1}H NMR of 2b (600 MHz, $CDCl_3$)



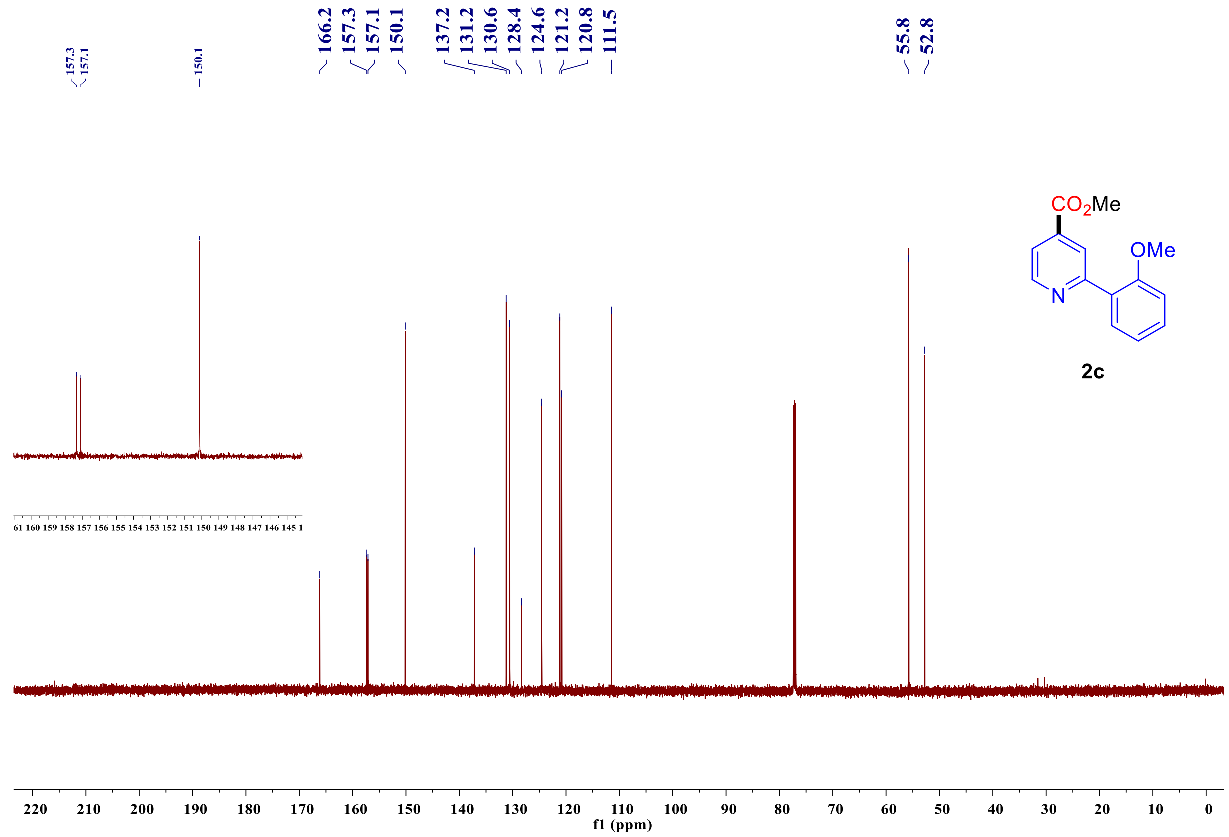
^{13}C NMR of 2b (151 MHz, $CDCl_3$)



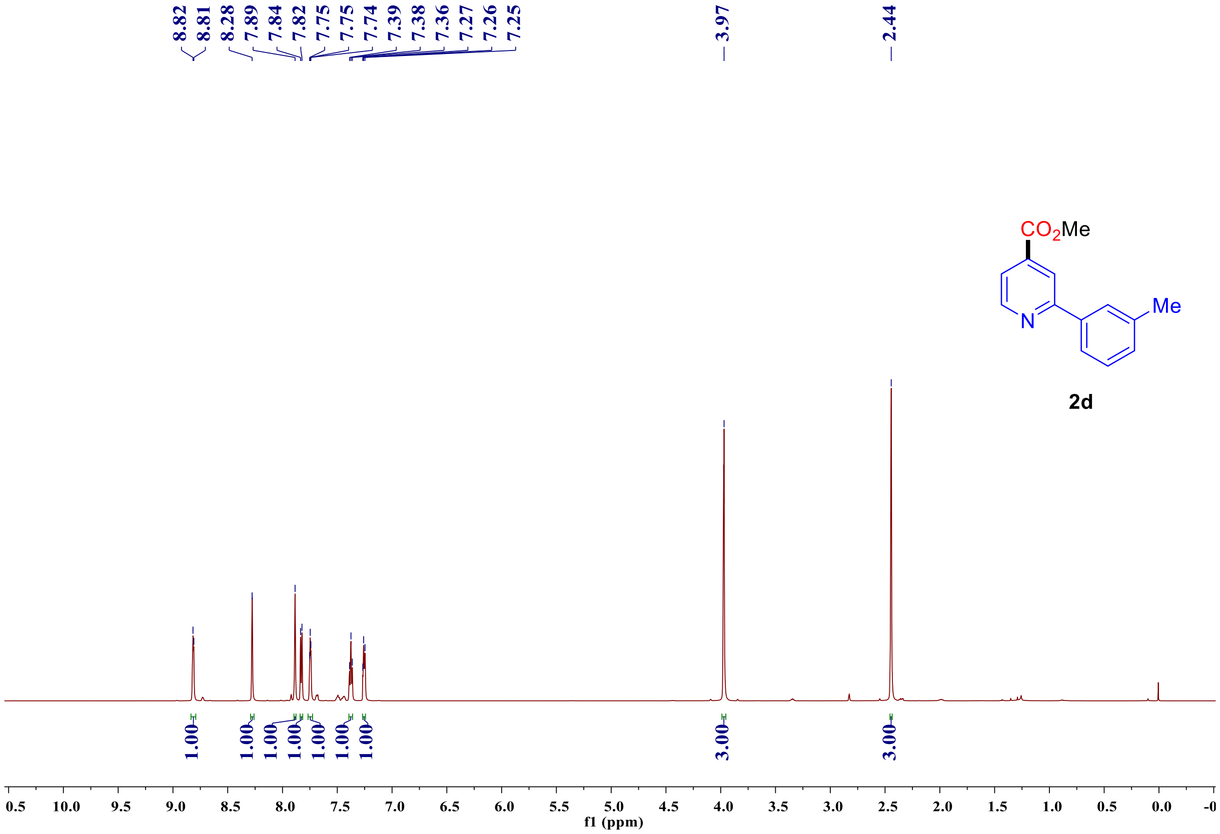
^{1}H NMR of 2c (600 MHz, $CDCl_3$)



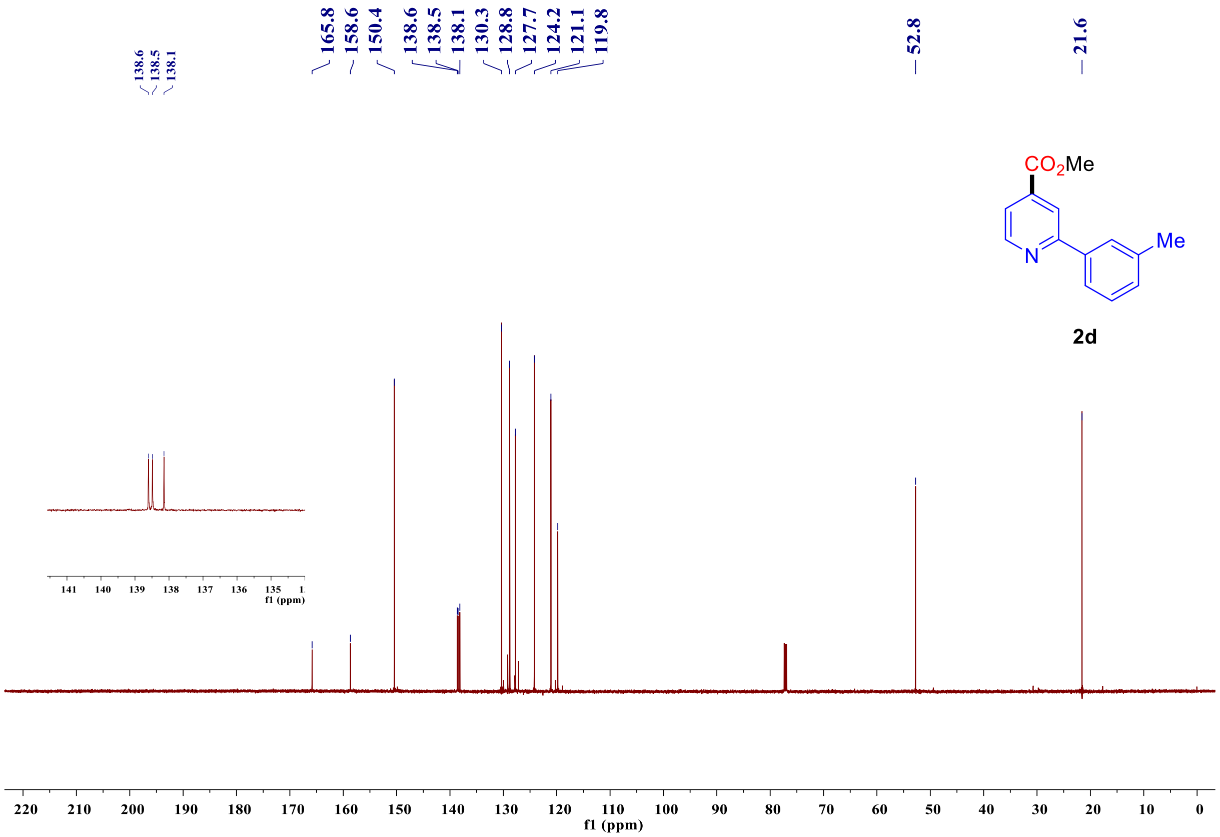
^{13}C NMR of 2c (151 MHz, $CDCl_3$)



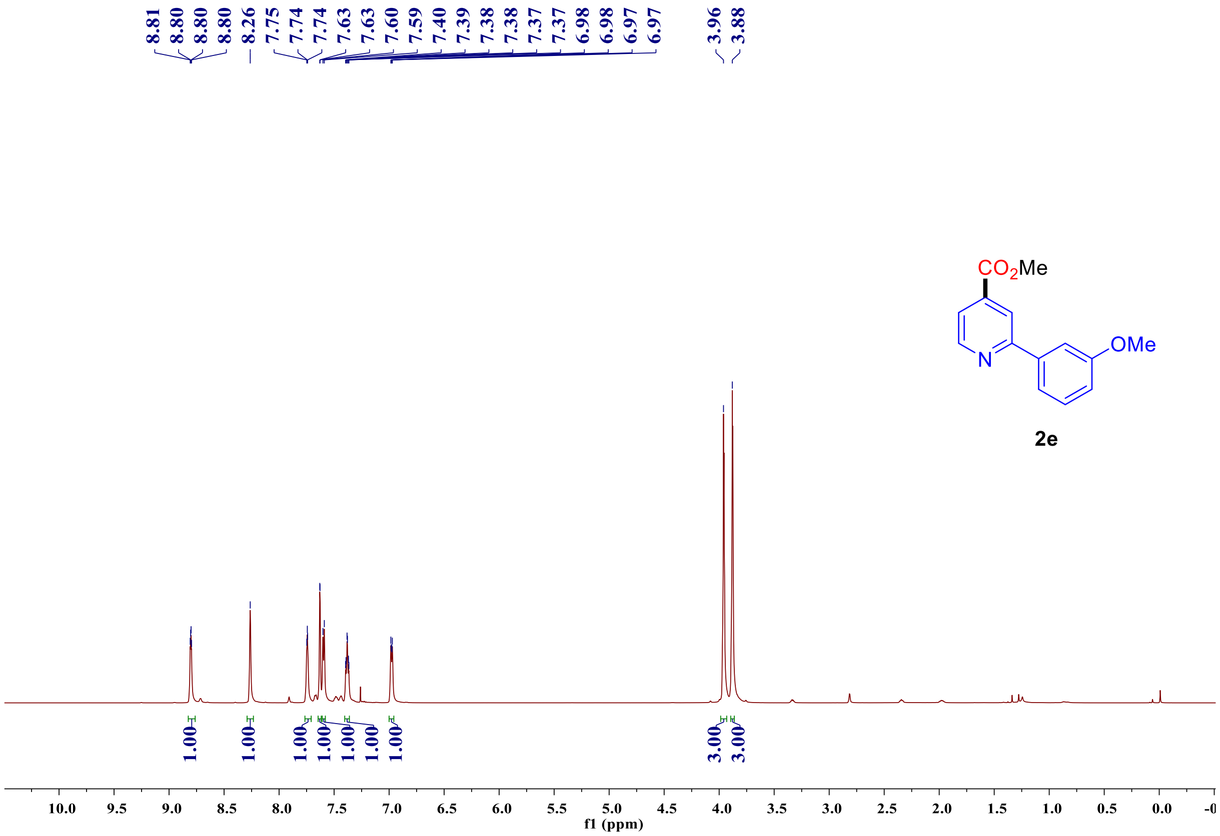
^1H NMR of 2d (600 MHz, $CDCl_3$)



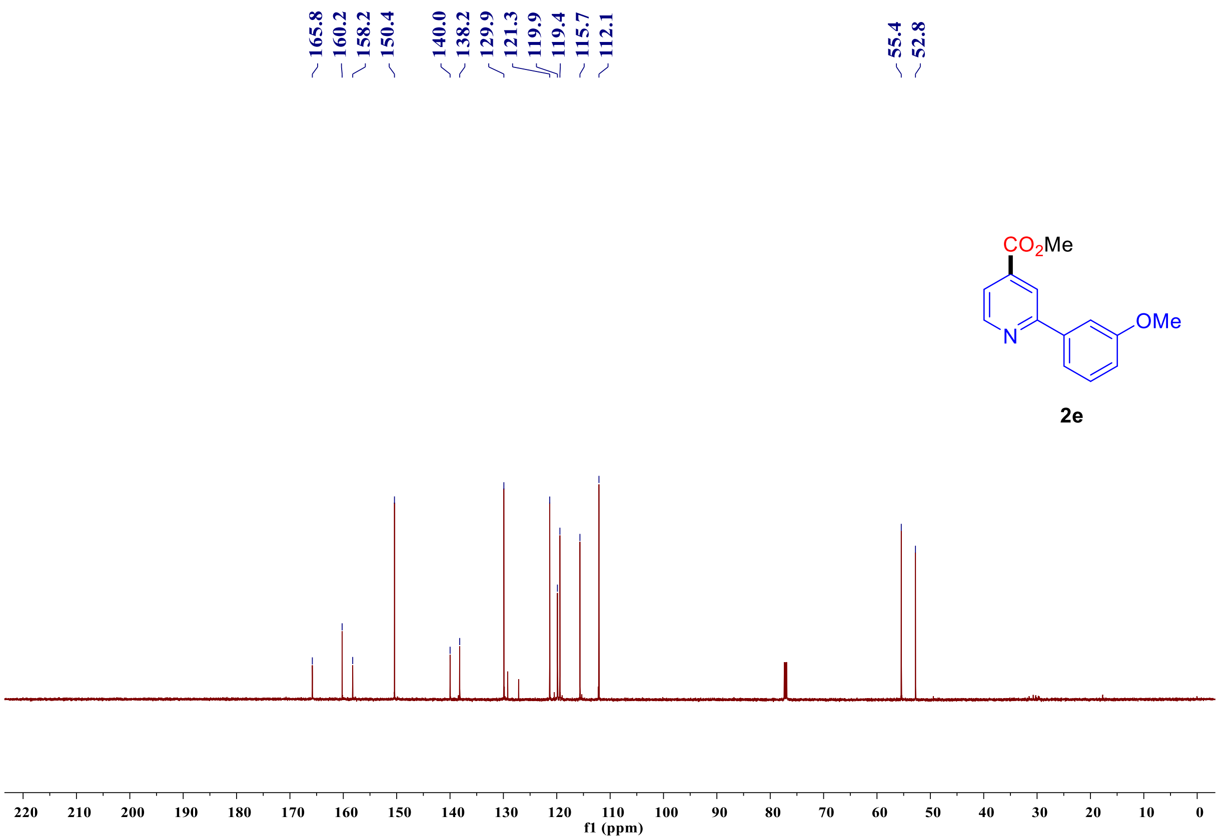
^{13}C NMR of 2d (151 MHz, $CDCl_3$)



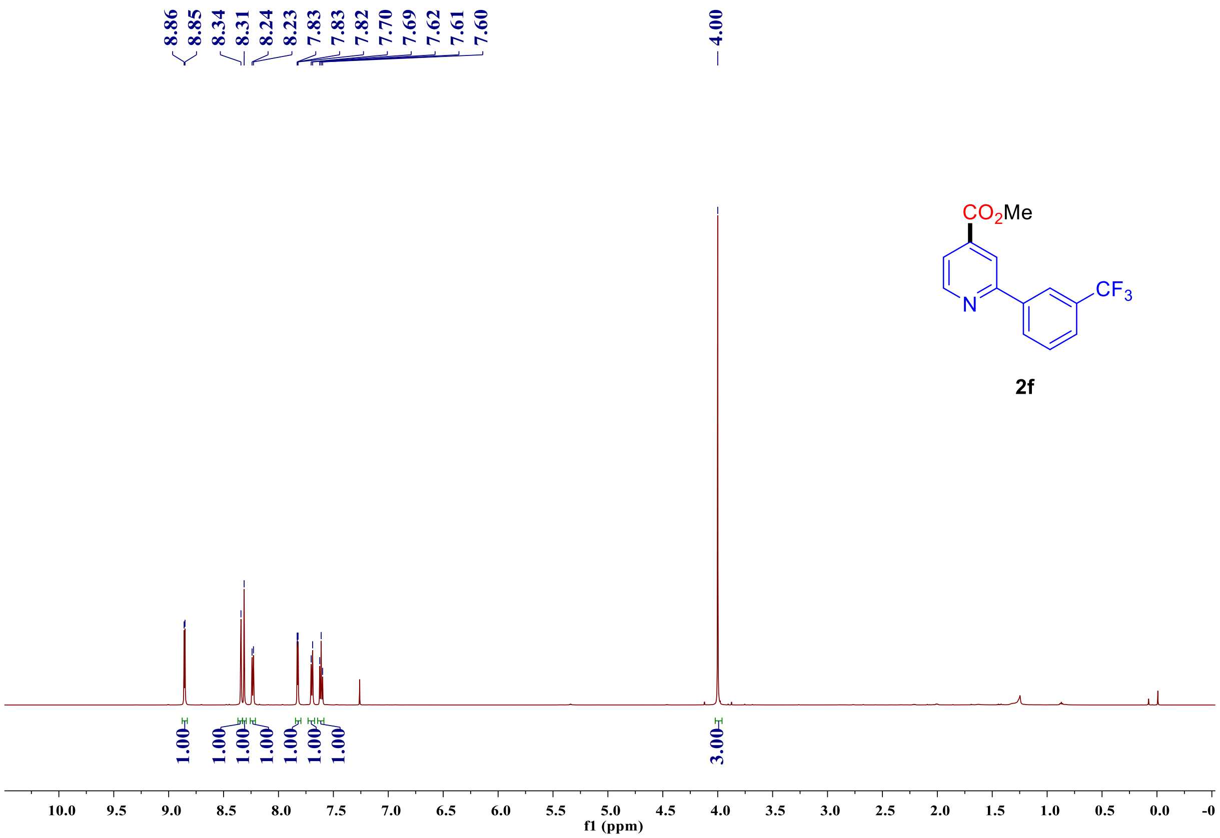
[1]H NMR of 2e (600 MHz, $CDCl_3$)



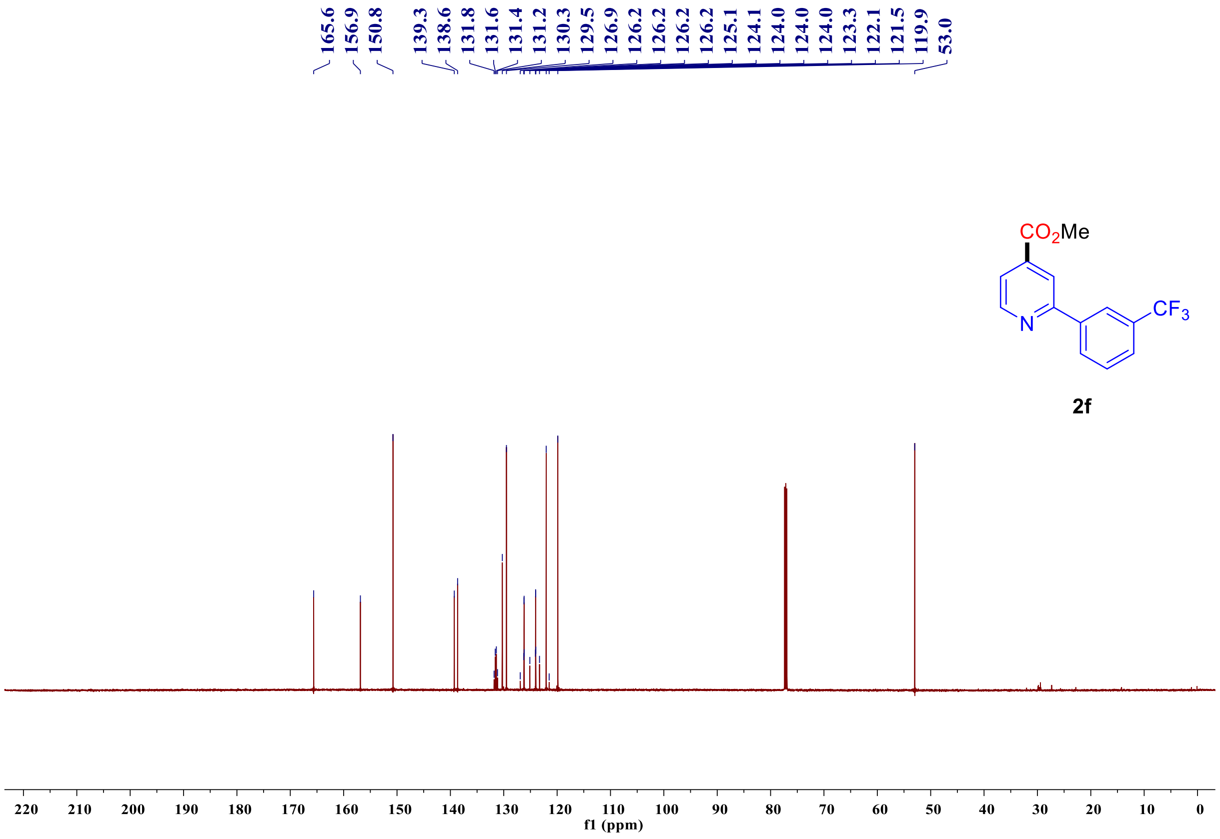
[13]C NMR of 2e (151 MHz, $CDCl_3$)



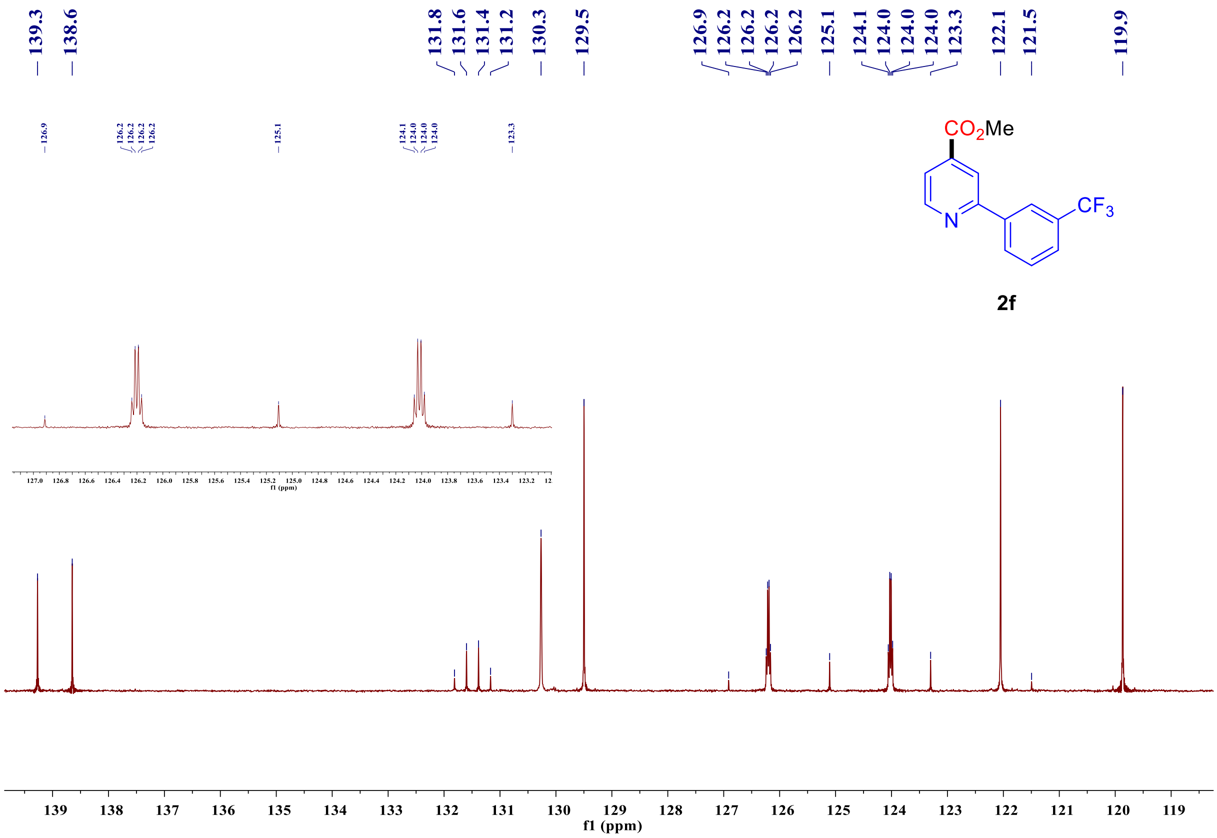
^{1}H NMR of 2f (600 MHz, $CDCl_3$)



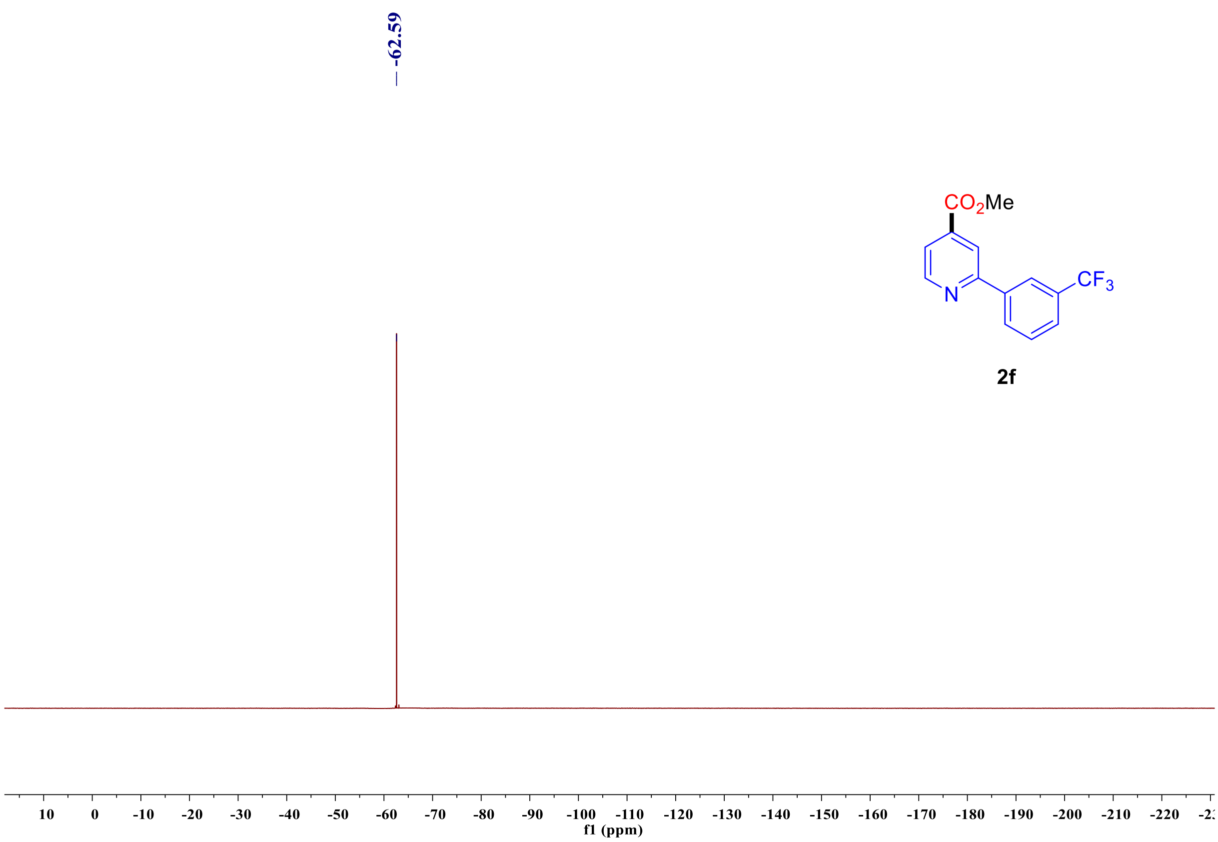
^{13}C NMR of 2f (151 MHz, $CDCl_3$)



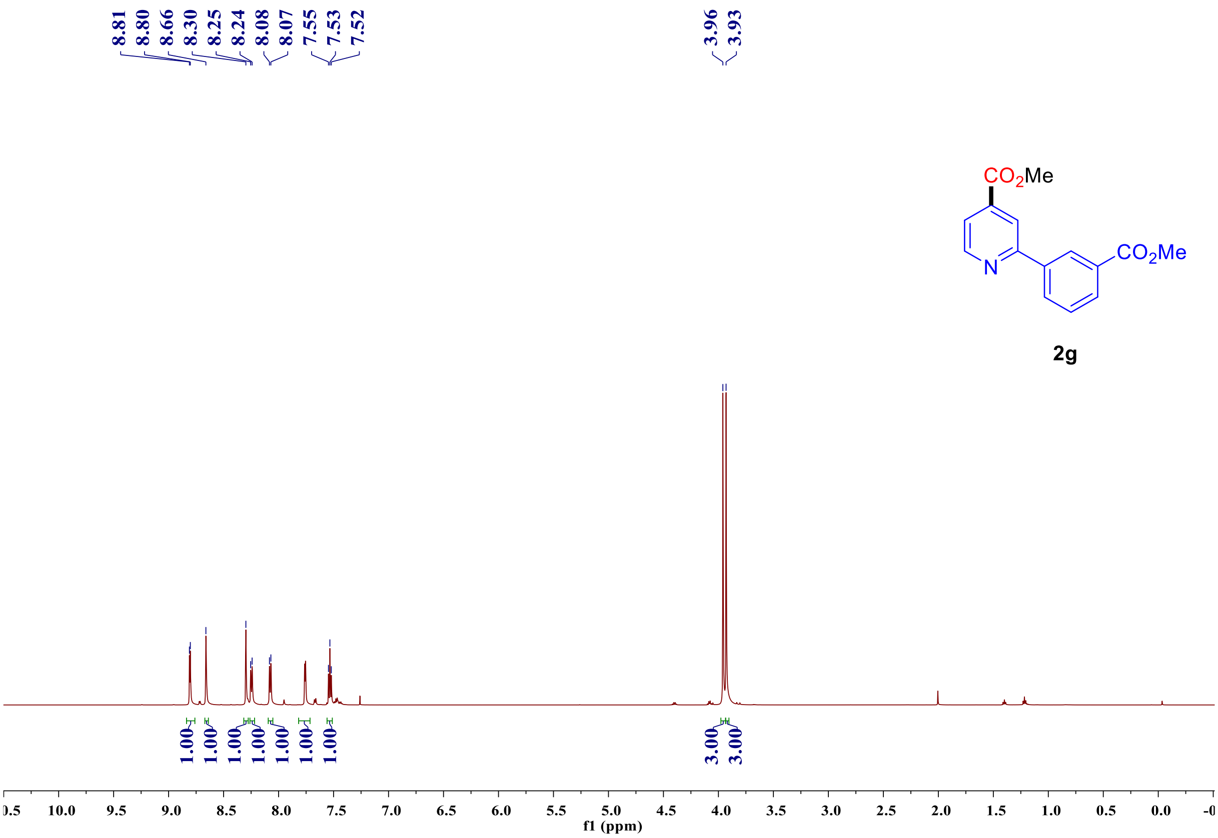
^{13}C NMR of 2f (151 MHz, $CDCl_3$)



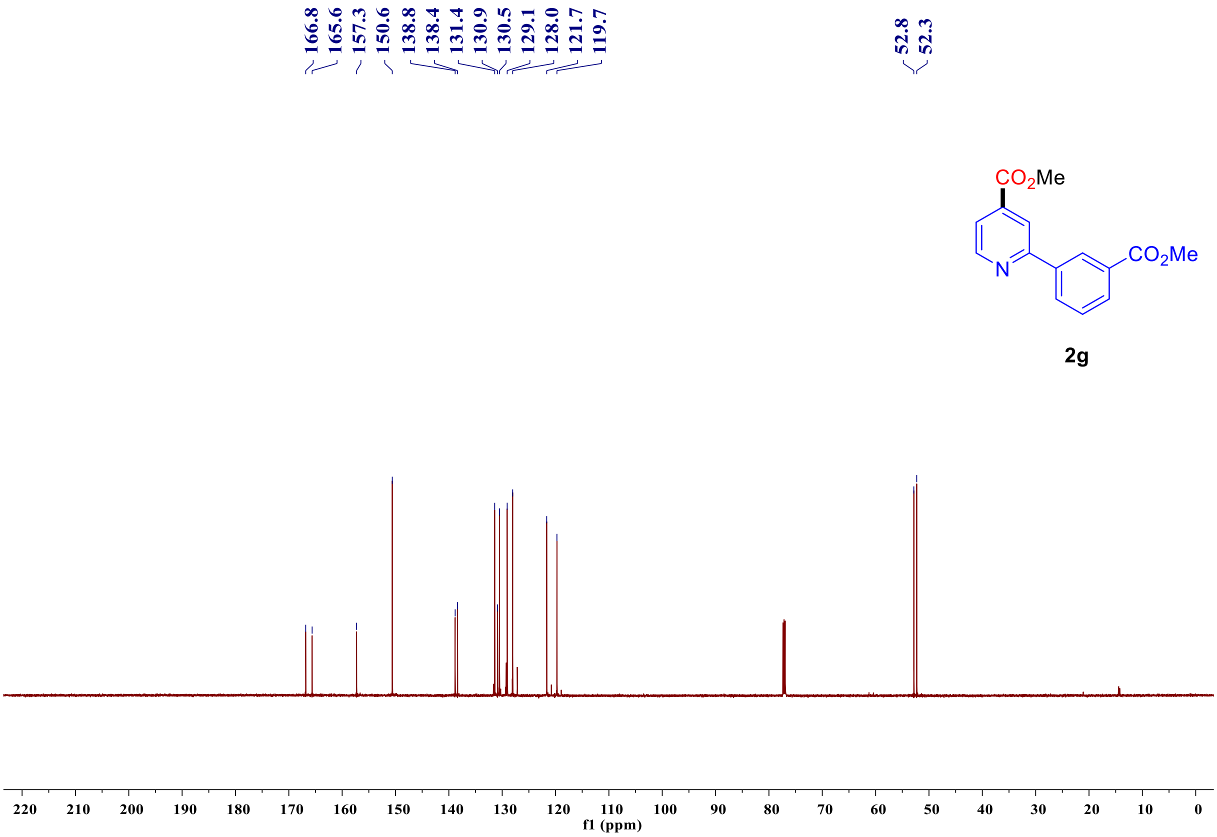
^{19}F NMR of 2f (376 MHz, $CDCl_3$)



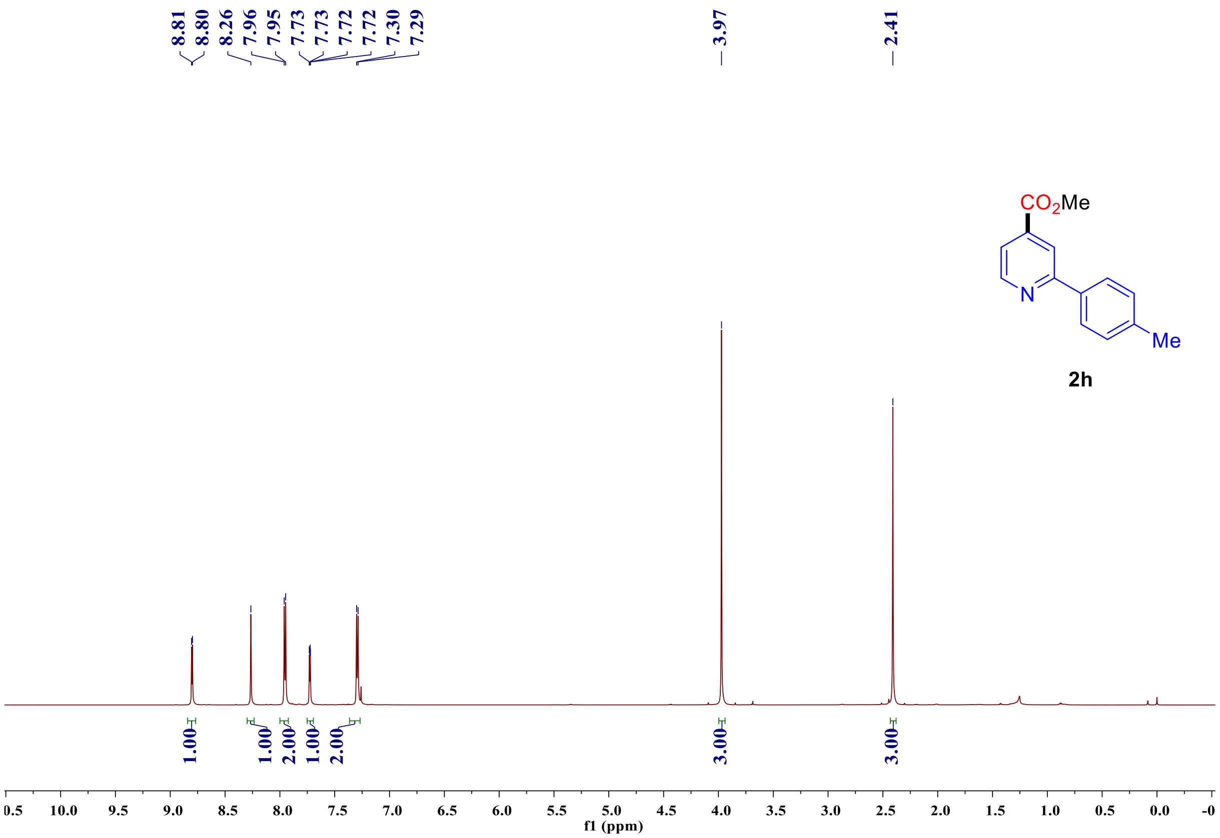
[1]H NMR of 2g (600 MHz, CDCl3)



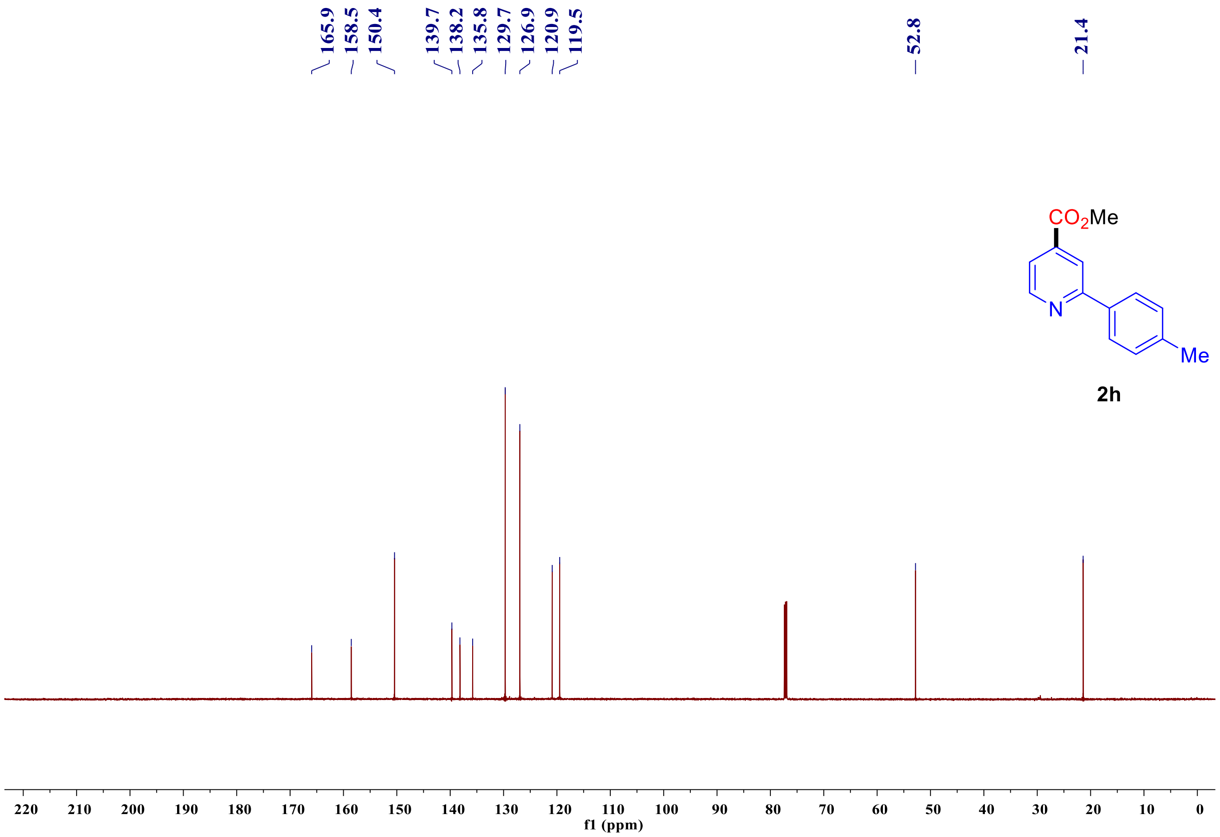
[13]C NMR of 2g (151 MHz, CDCl3)



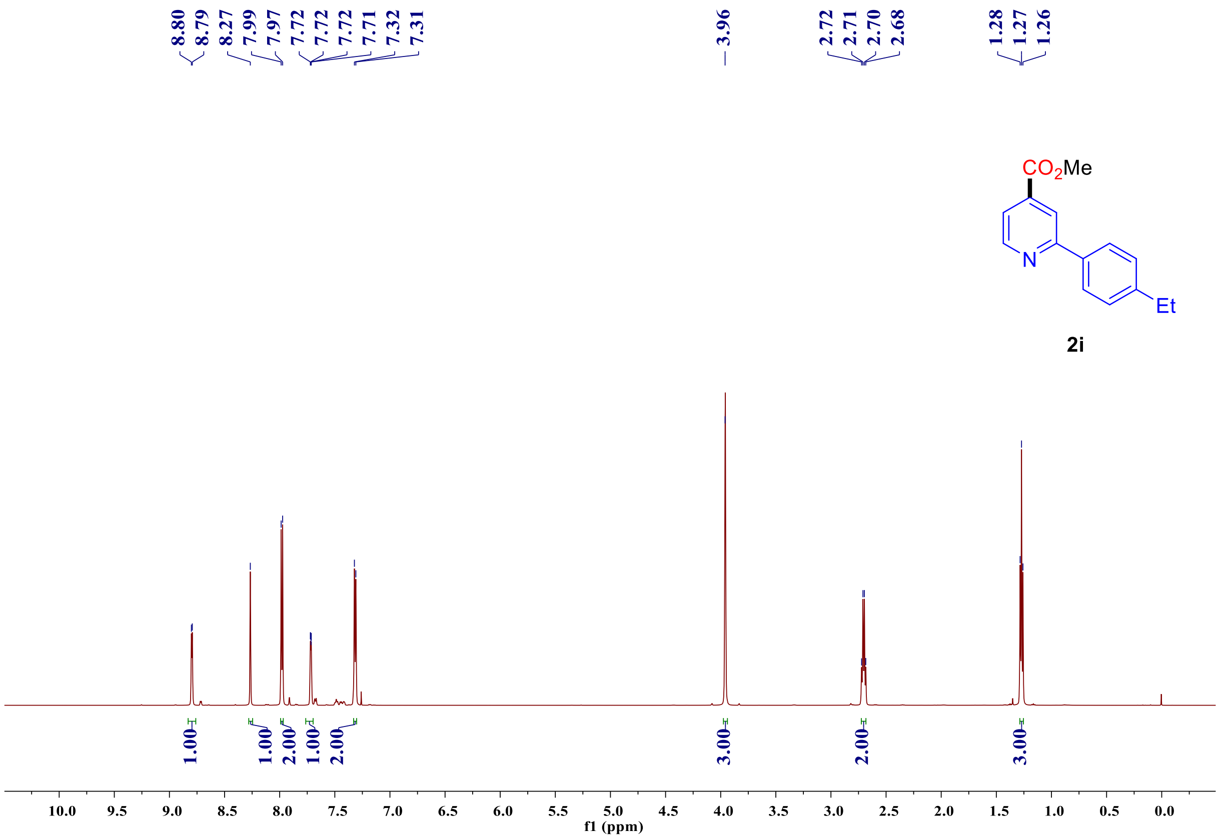
¹H NMR of 2h (600 MHz, $CDCl_3$)



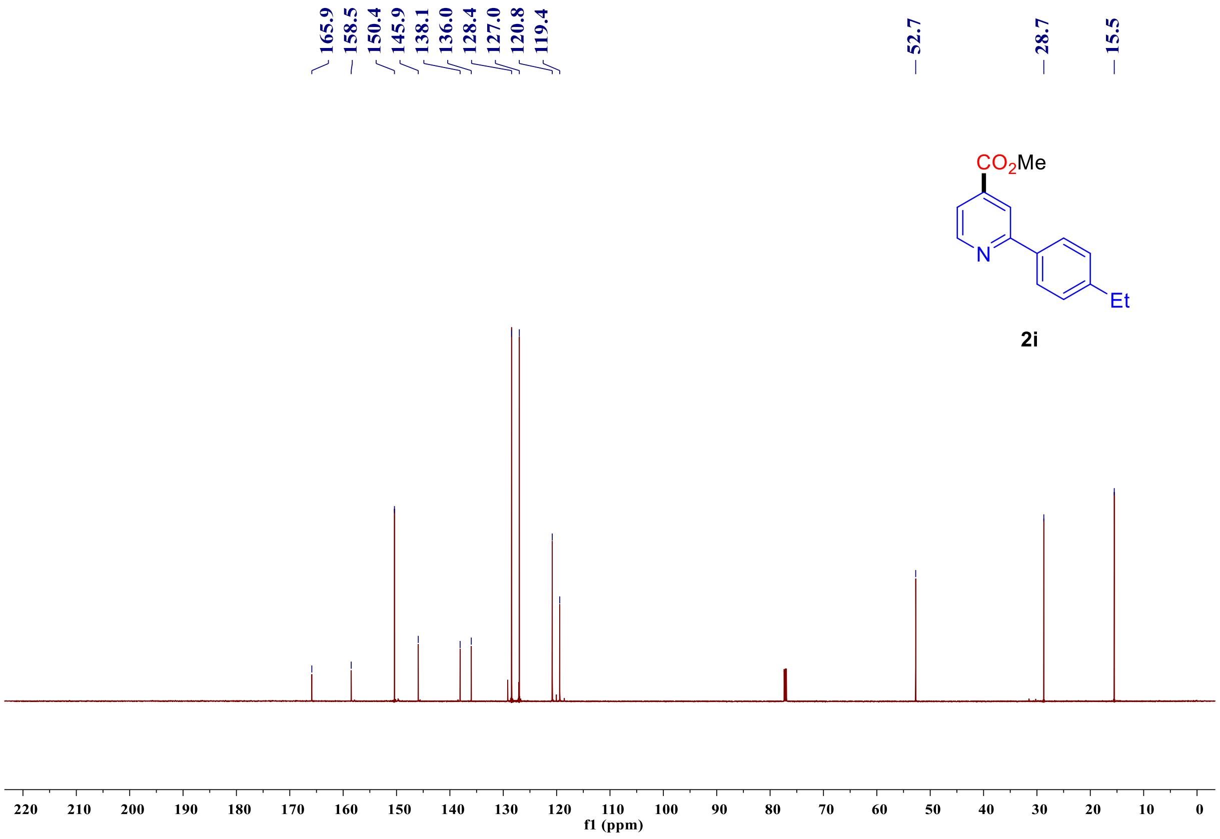
¹³C NMR of 2h (151 MHz, $CDCl_3$)



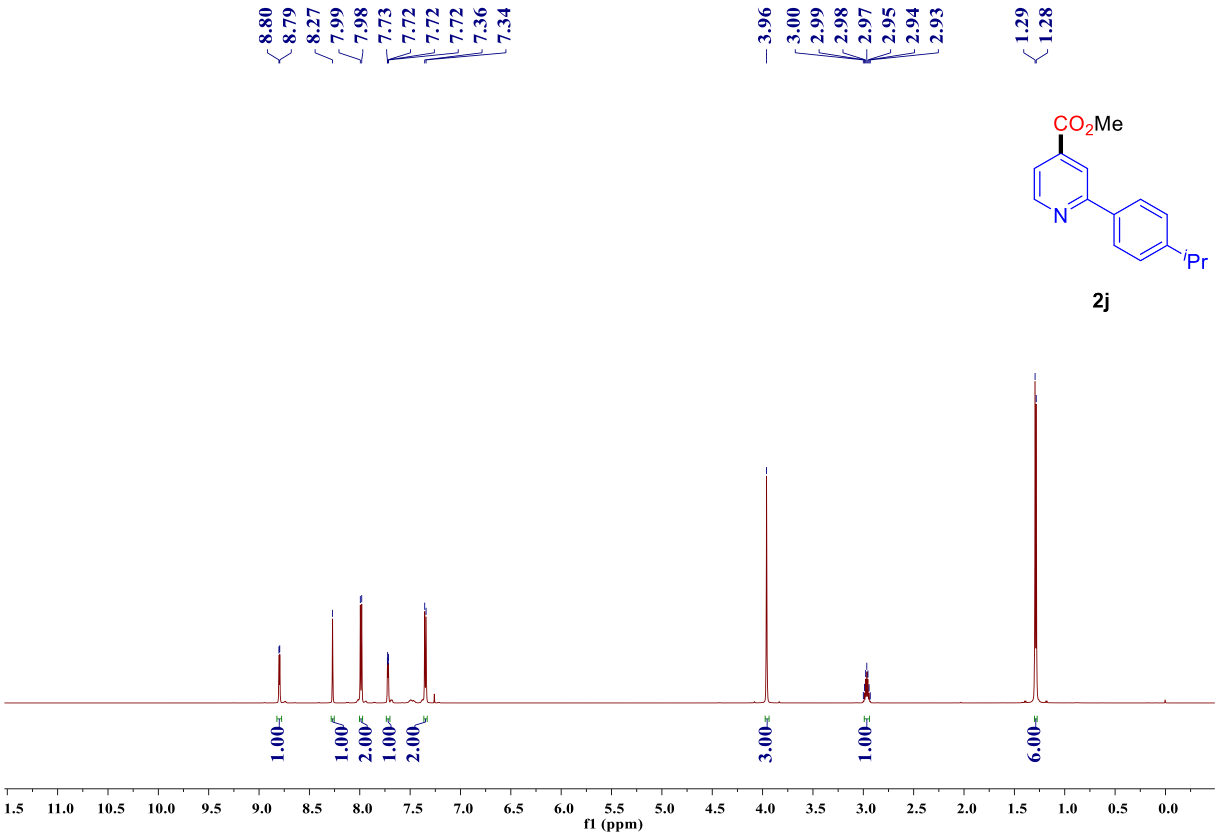
^{1}H NMR of 2i (600 MHz, $CDCl_3$)



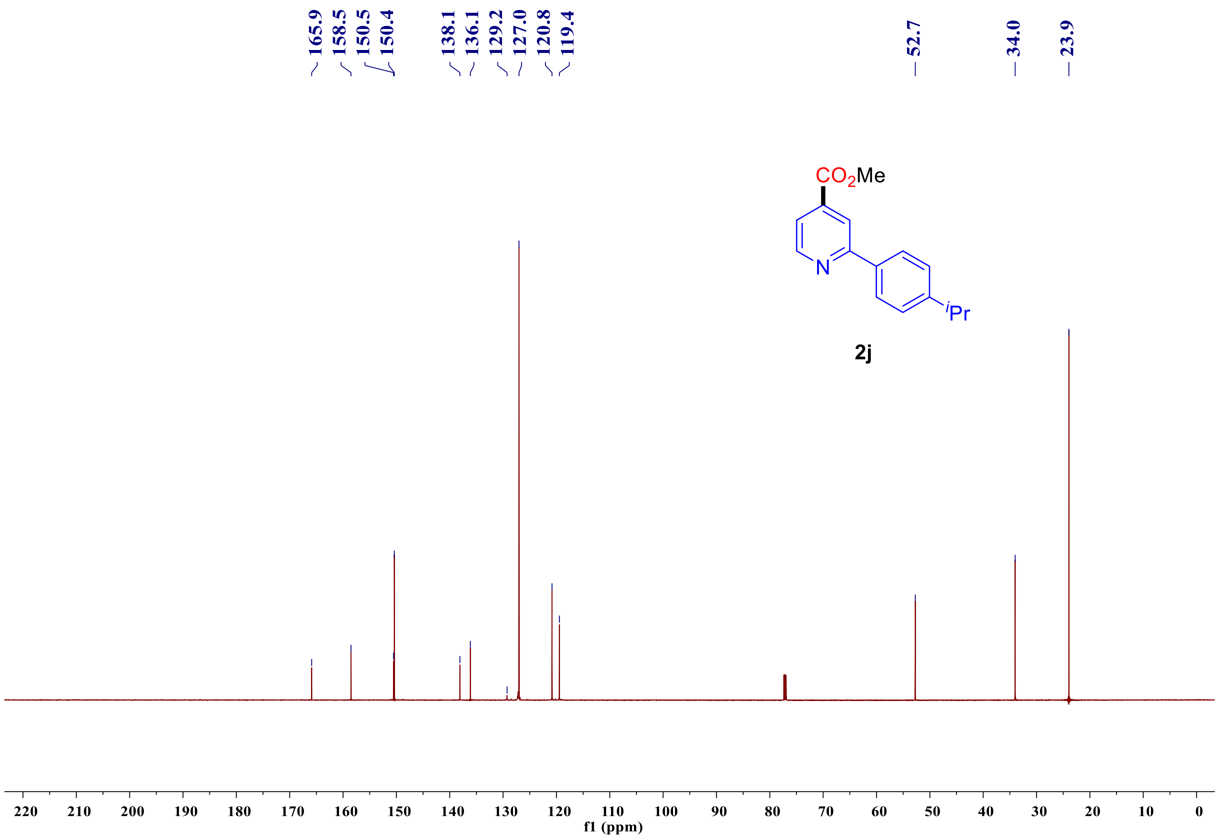
^{13}C NMR of 2i (151 MHz, $CDCl_3$)



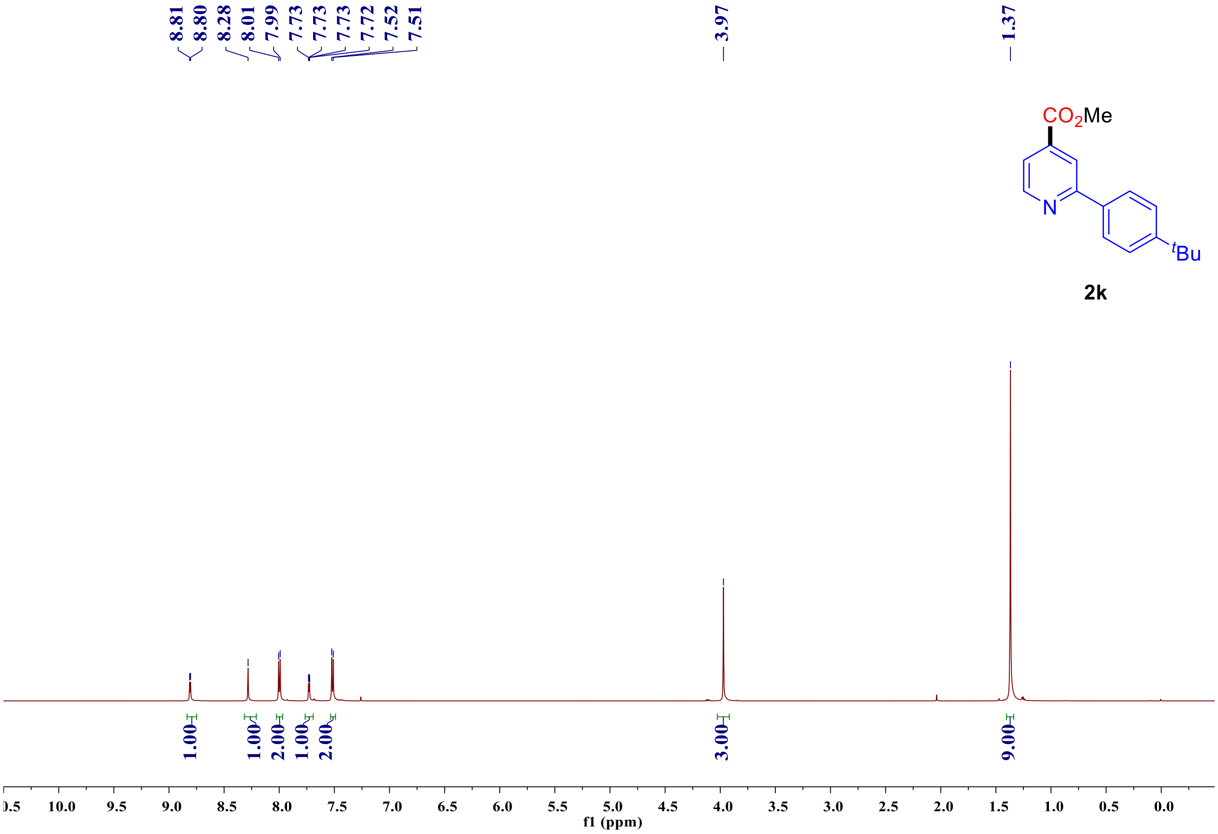
^{1}H NMR of 2j (600 MHz, $CDCl_3$)



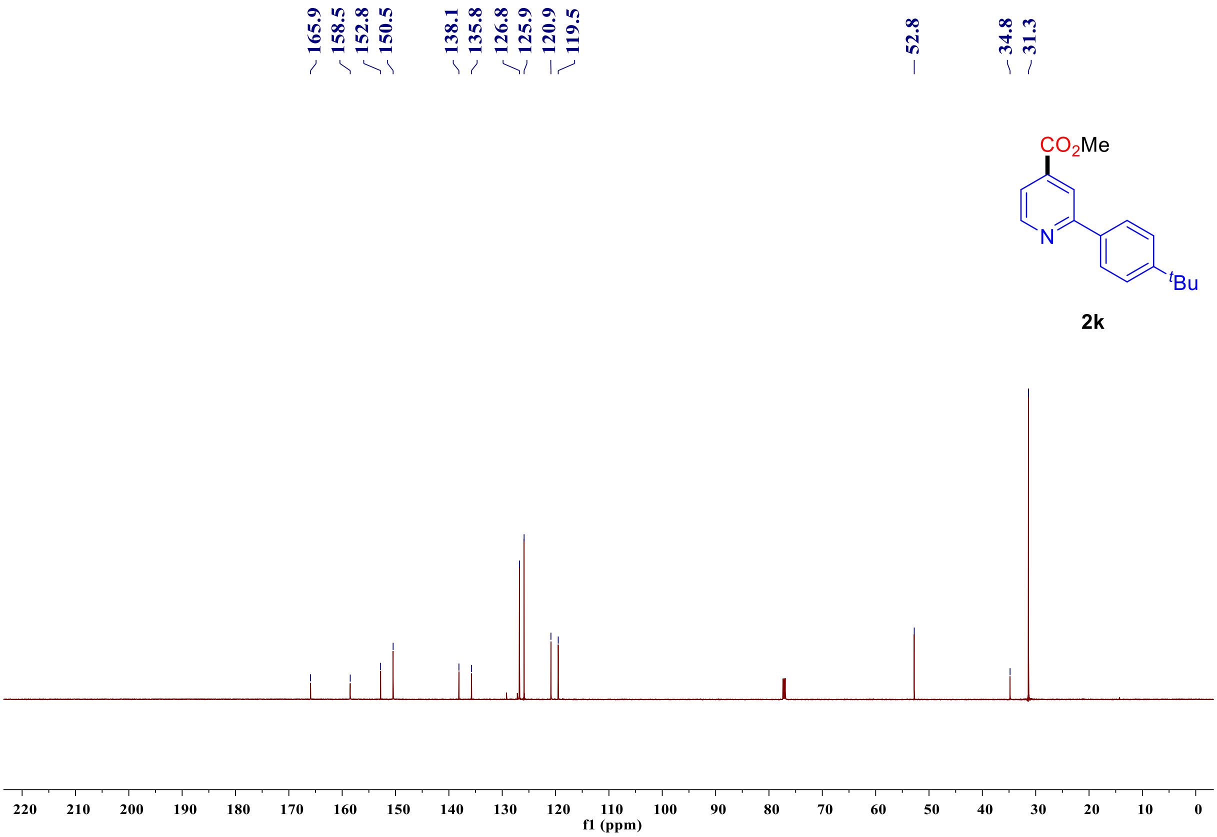
^{13}C NMR of 2j (151 MHz, $CDCl_3$)



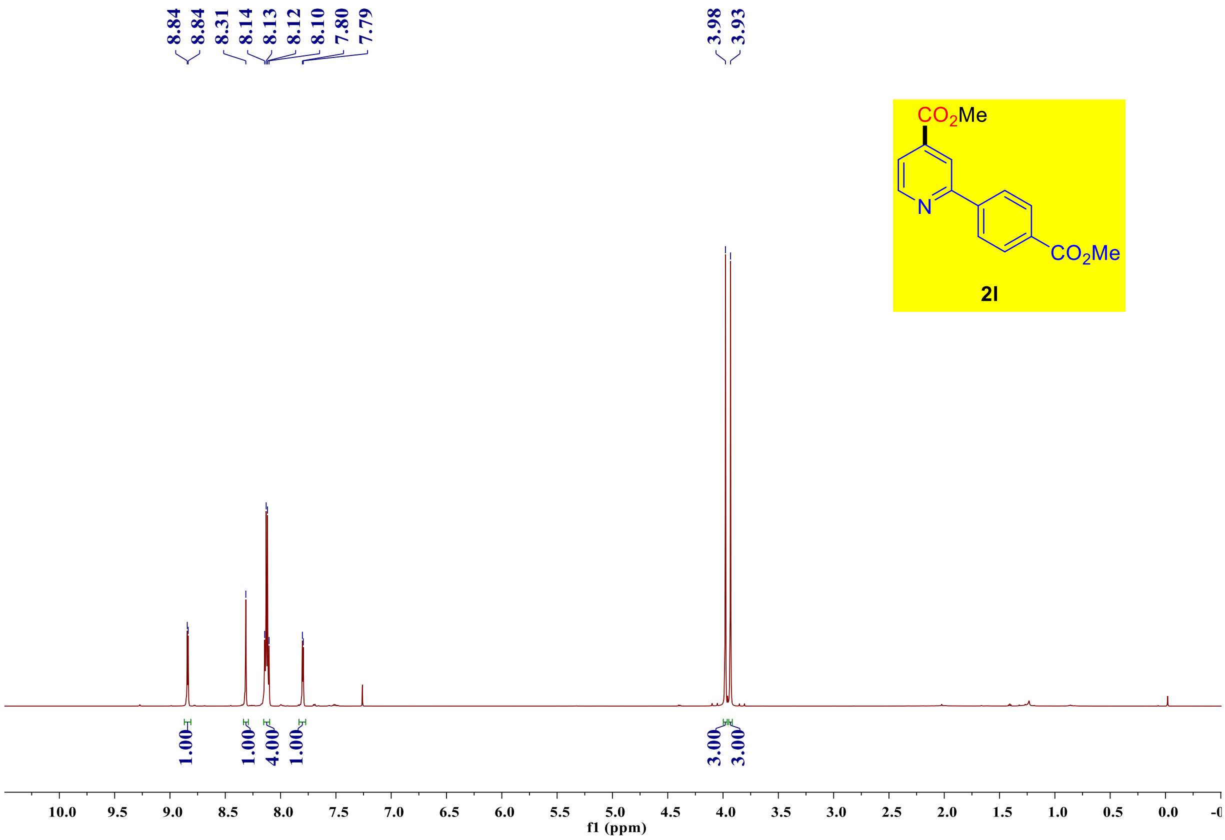
^1H NMR of 2k (600 MHz, $CDCl_3$)



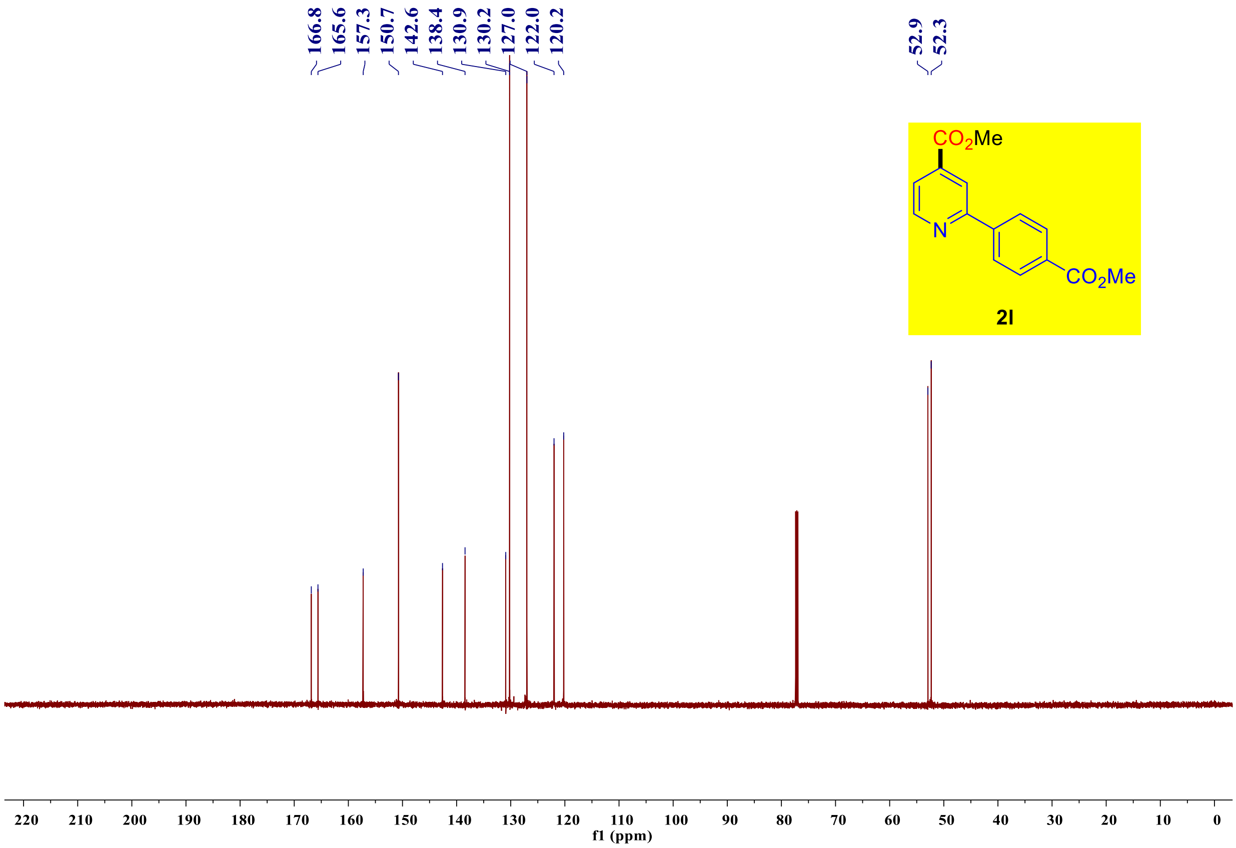
^{13}C NMR of 2k (151 MHz, $CDCl_3$)



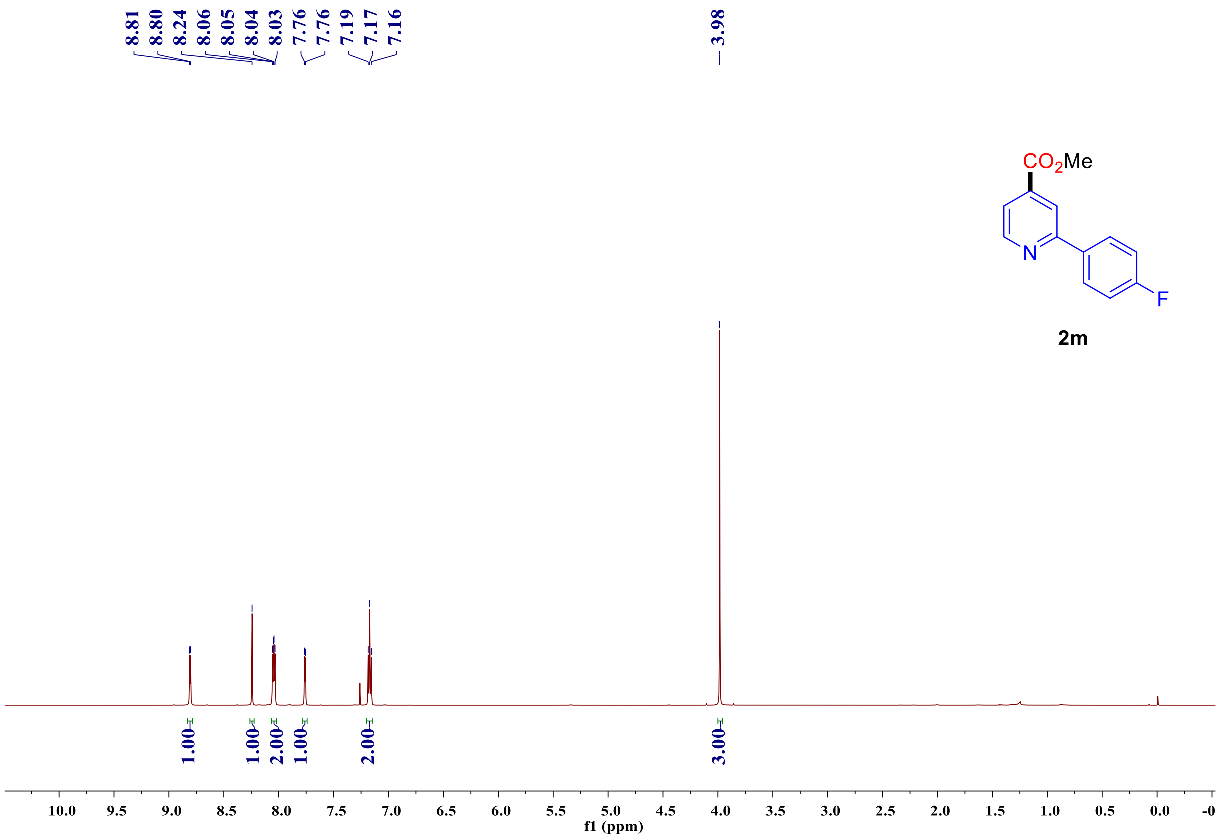
^{1}H NMR of 2l (600 MHz, $CDCl_3$)



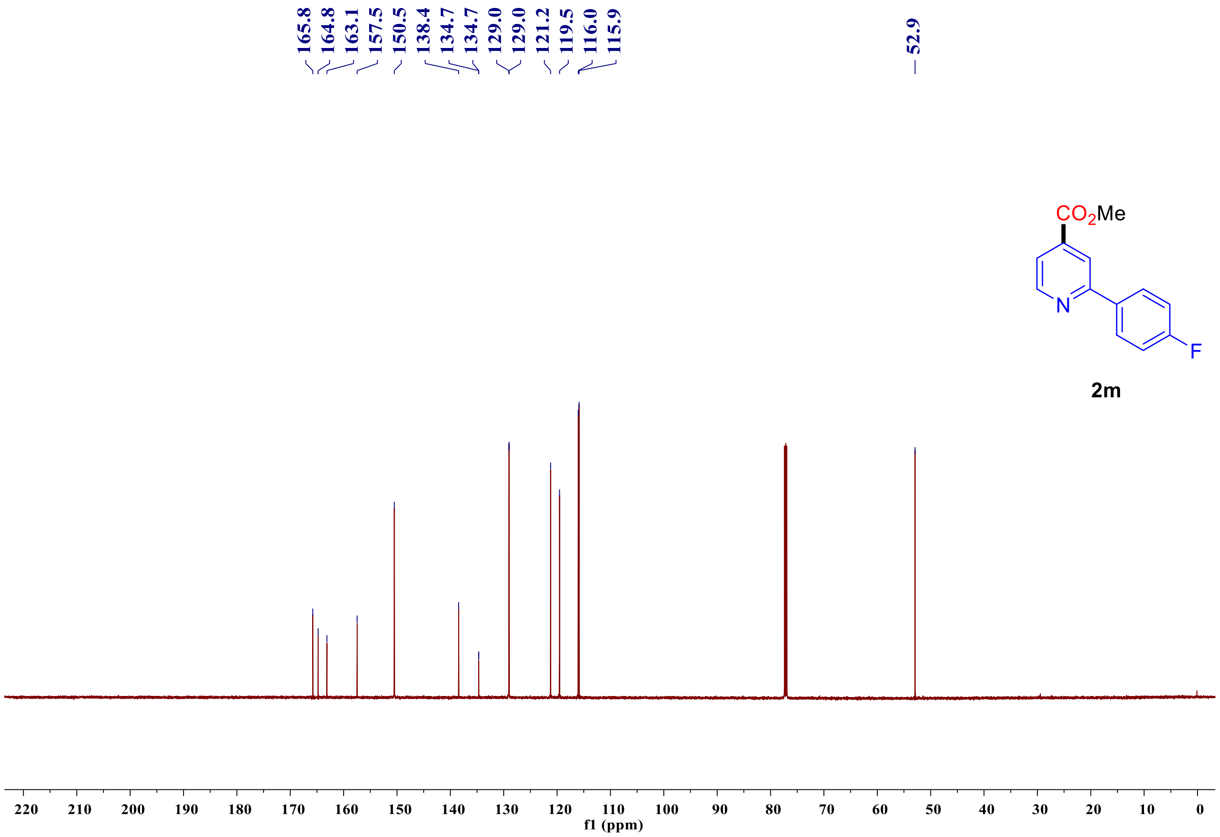
^{13}C NMR of 2l (151 MHz, $CDCl_3$)



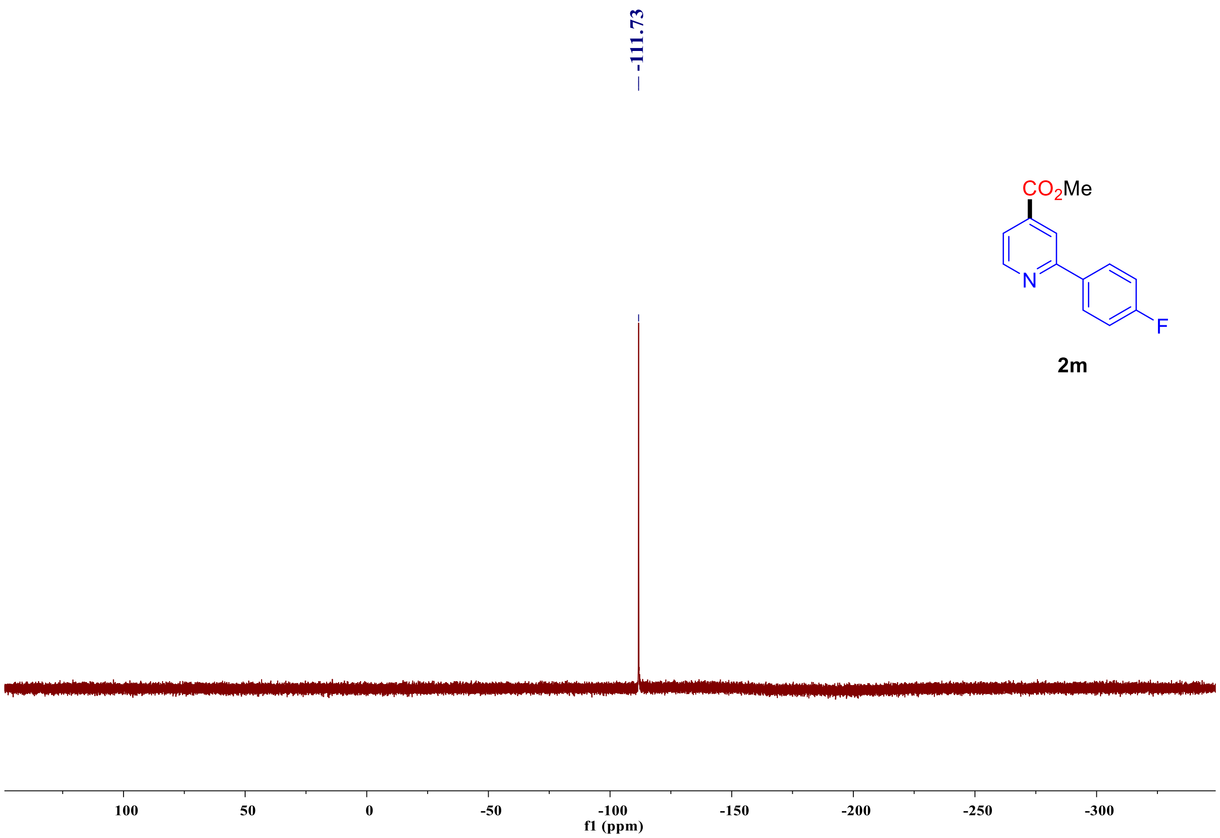
^{1}H NMR of 2m (600 MHz, $CDCl_3$)



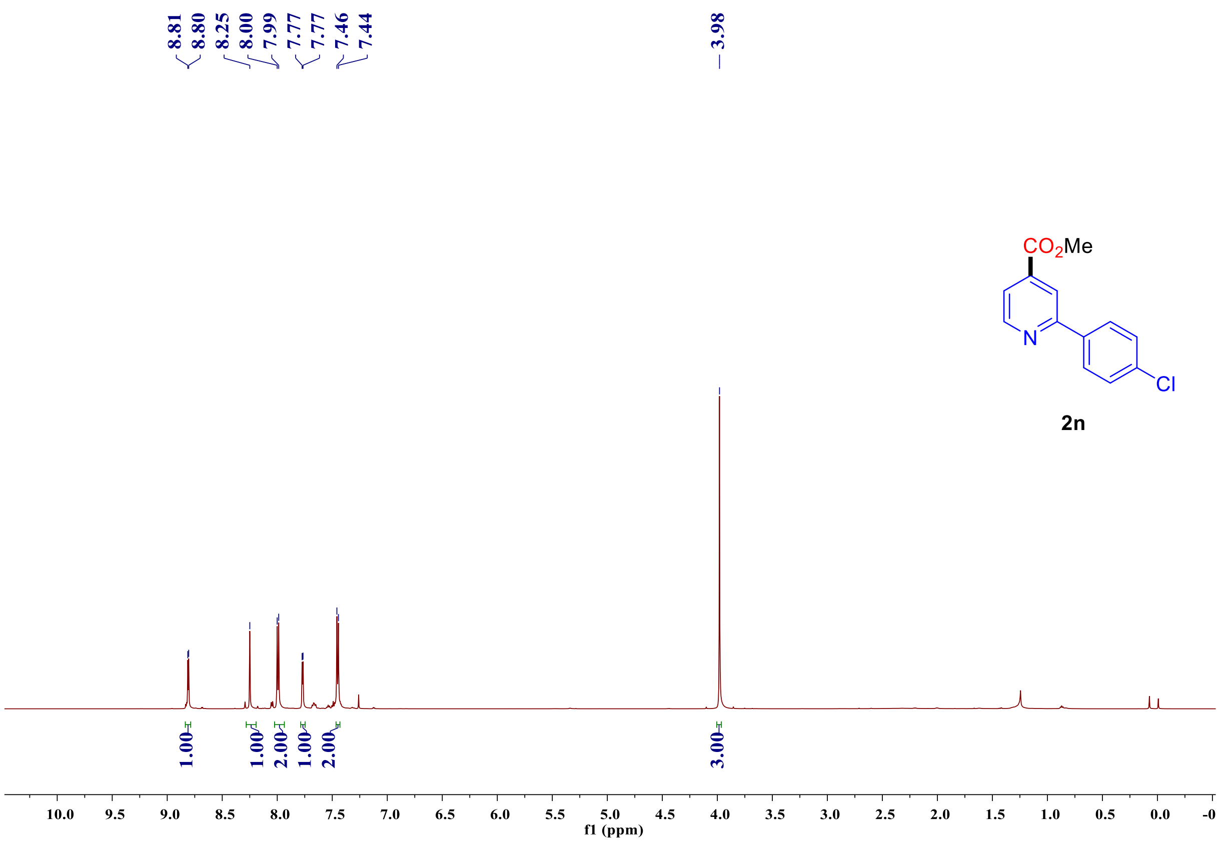
^{13}C NMR of 2m (151 MHz, $CDCl_3$)



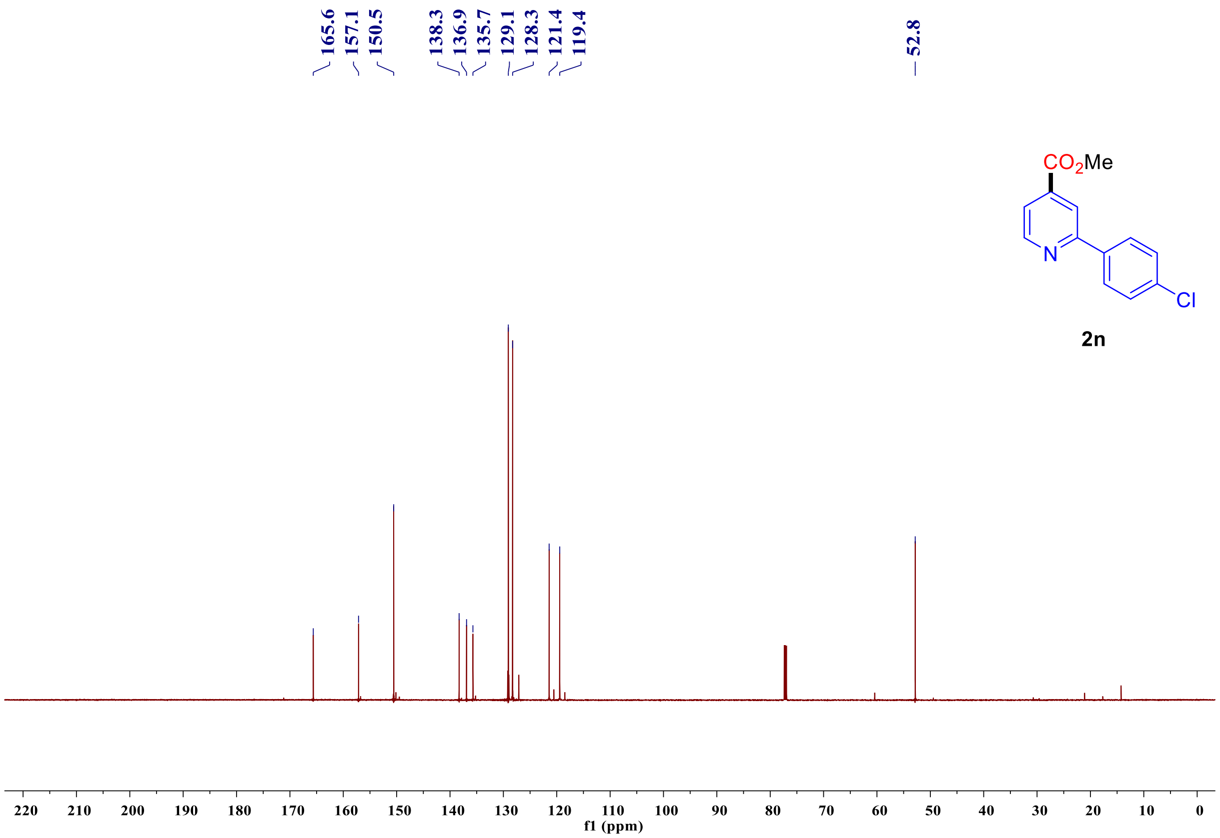
^{19}F NMR of 2m (376 MHz, $CDCl_3$)



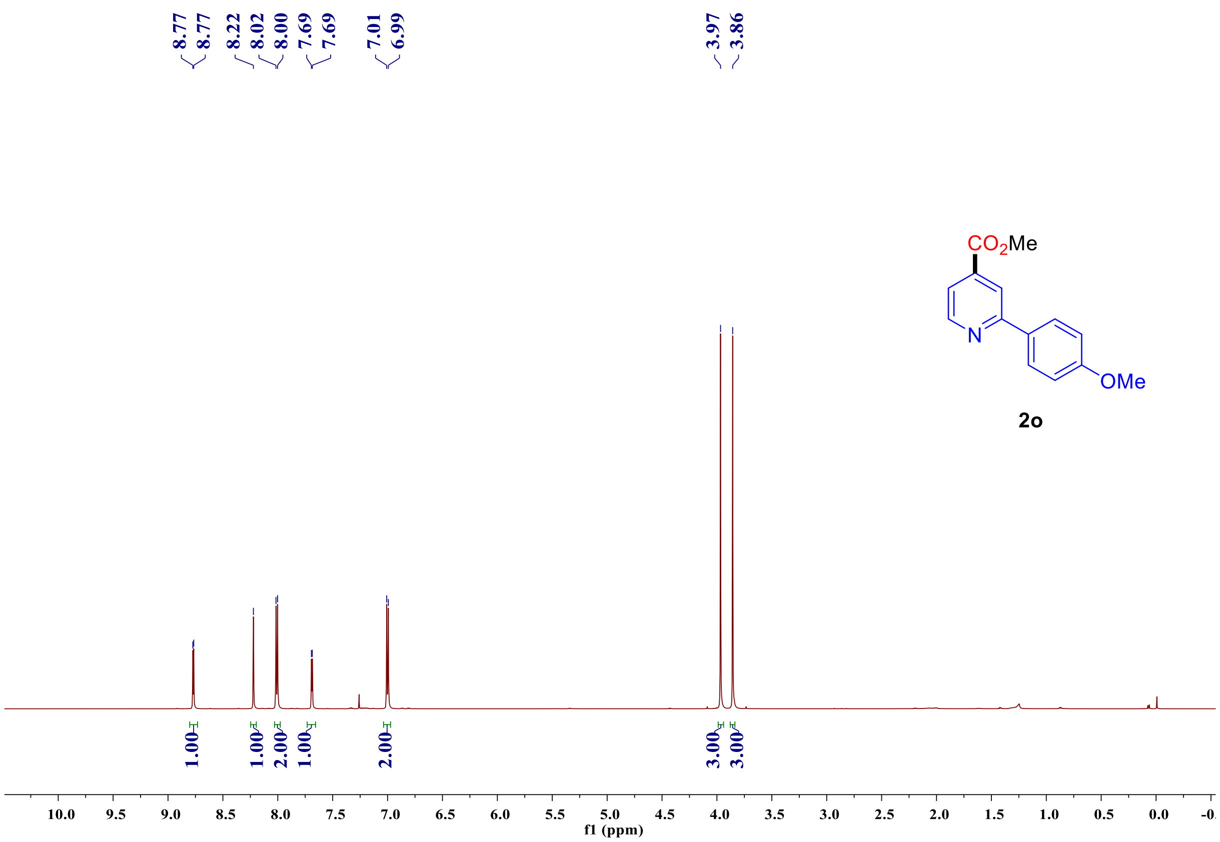
^{1}H NMR of 2n (600 MHz, $CDCl_3$)



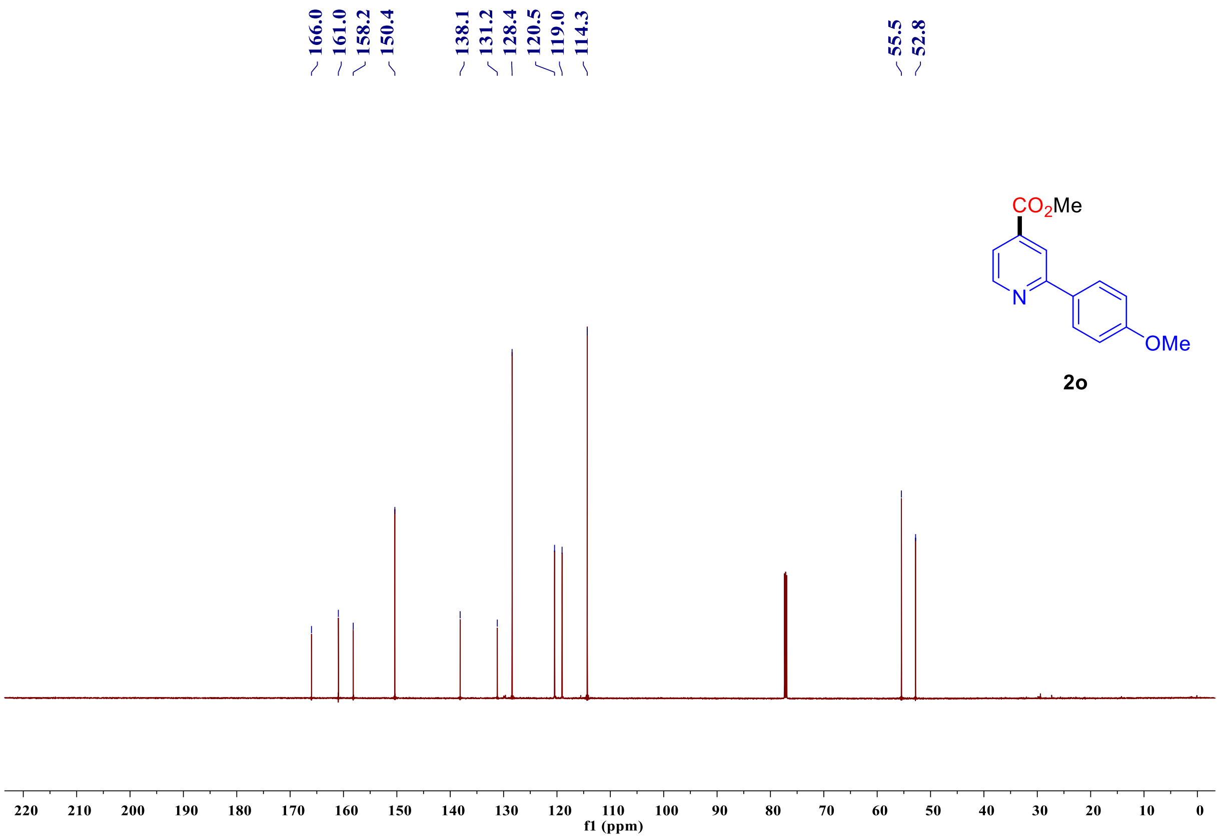
^{13}C NMR of 2n (151 MHz, $CDCl_3$)



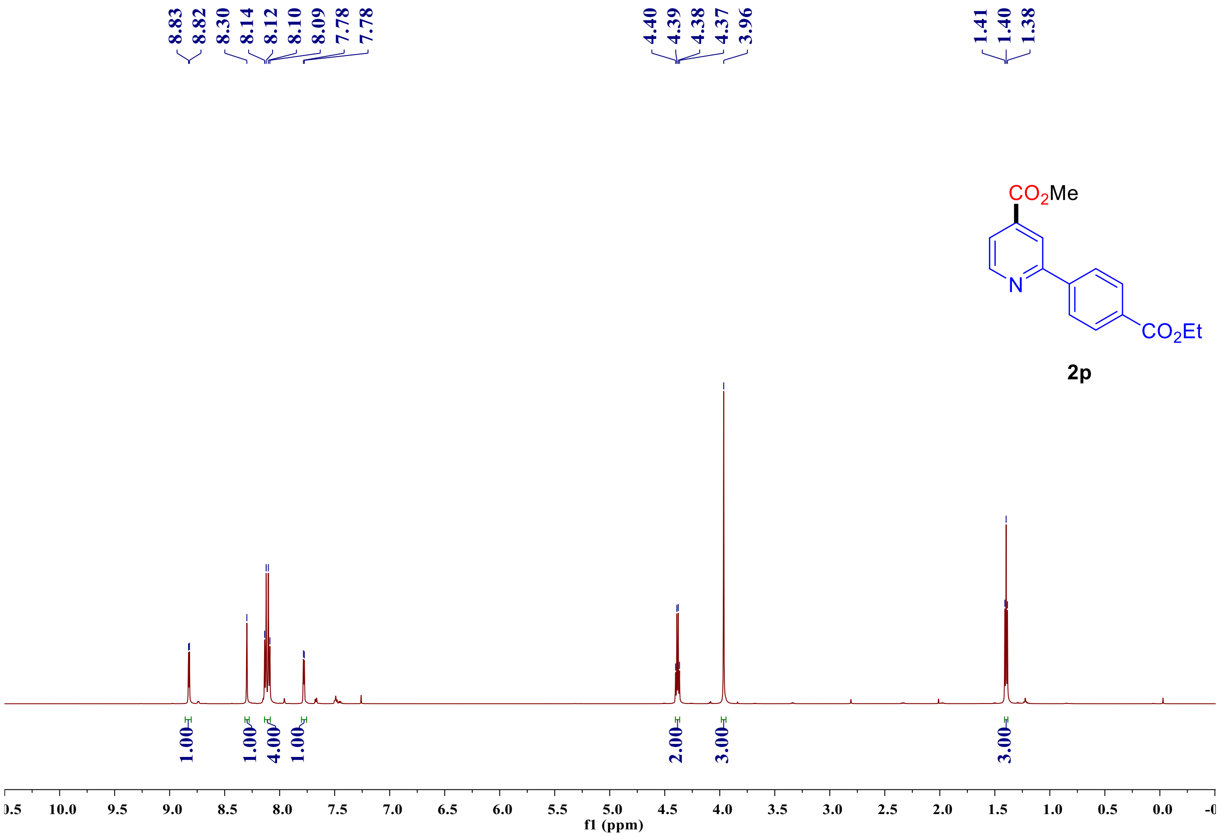
^{1}H NMR of 2o (600 MHz, $CDCl_3$)



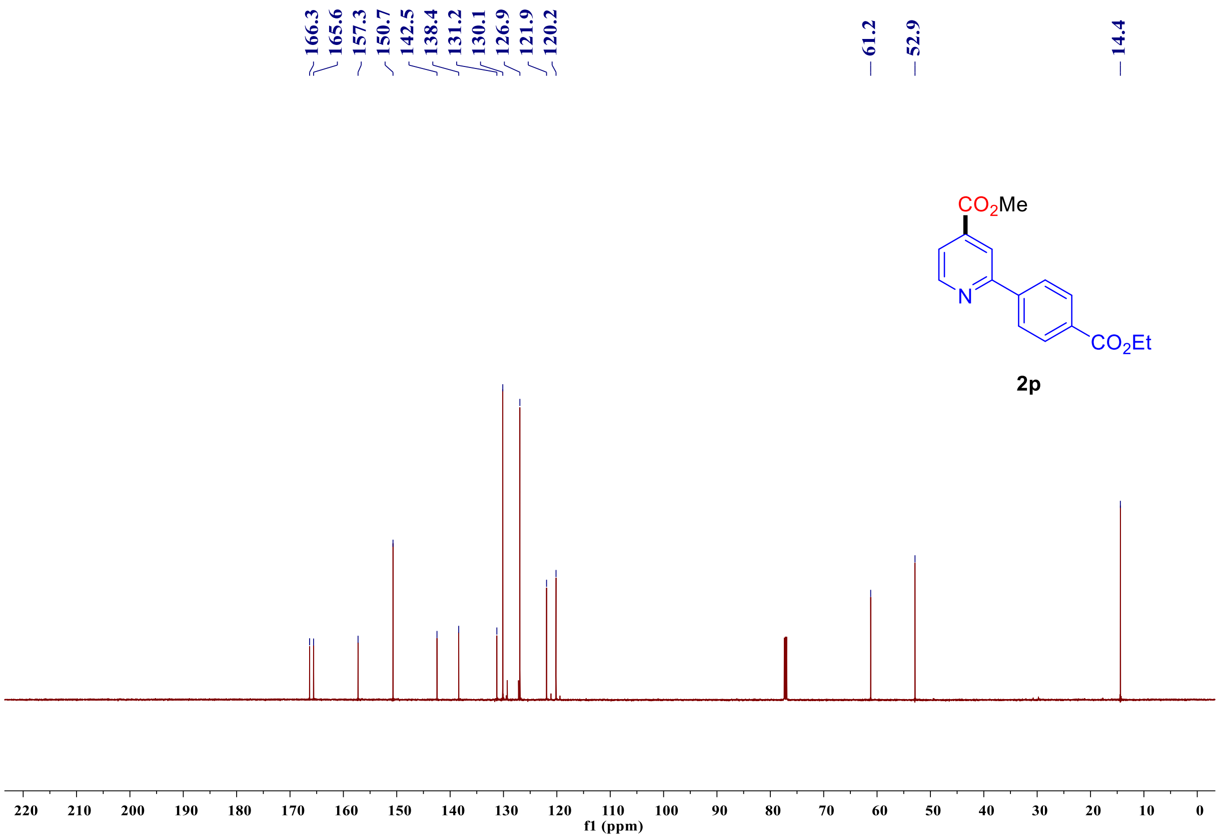
^{13}C NMR of 2o (151 MHz, $CDCl_3$)



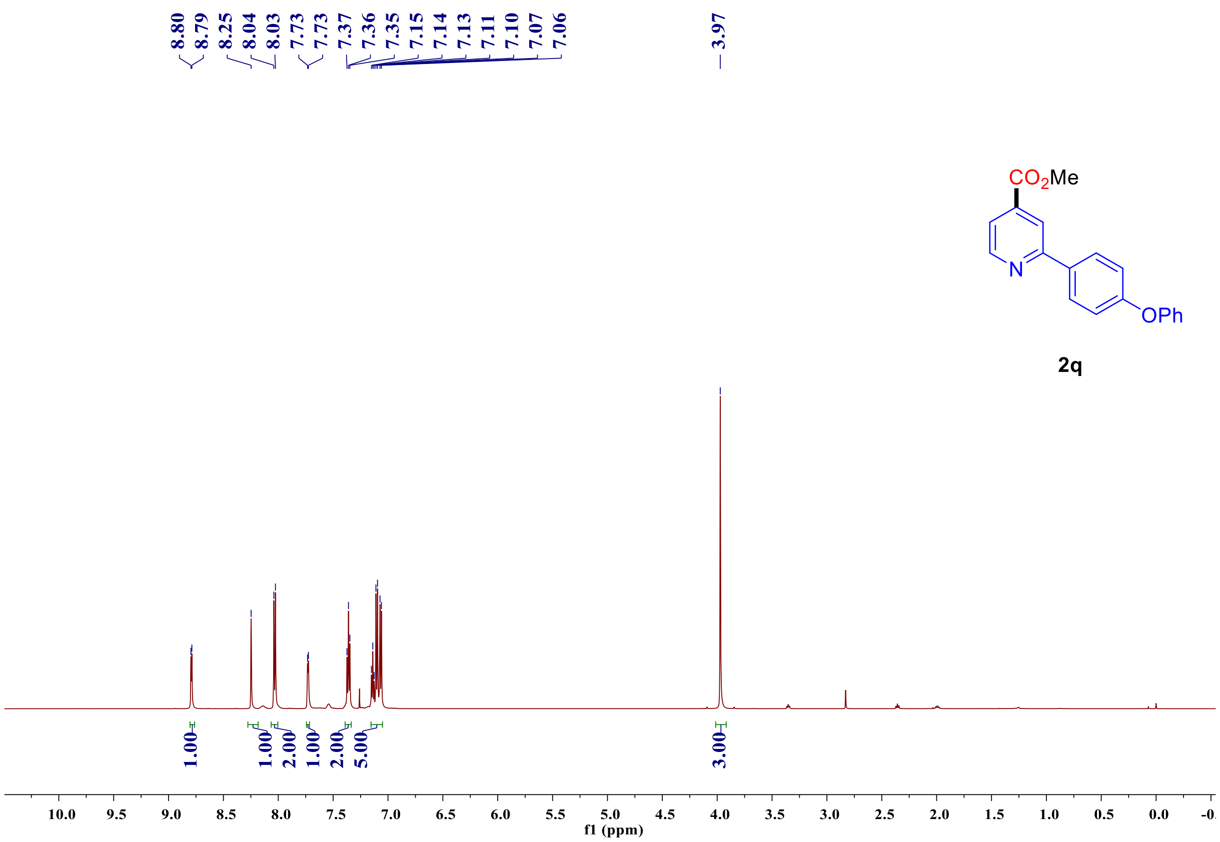
^{1}H NMR of 2p (600 MHz, $CDCl_3$)



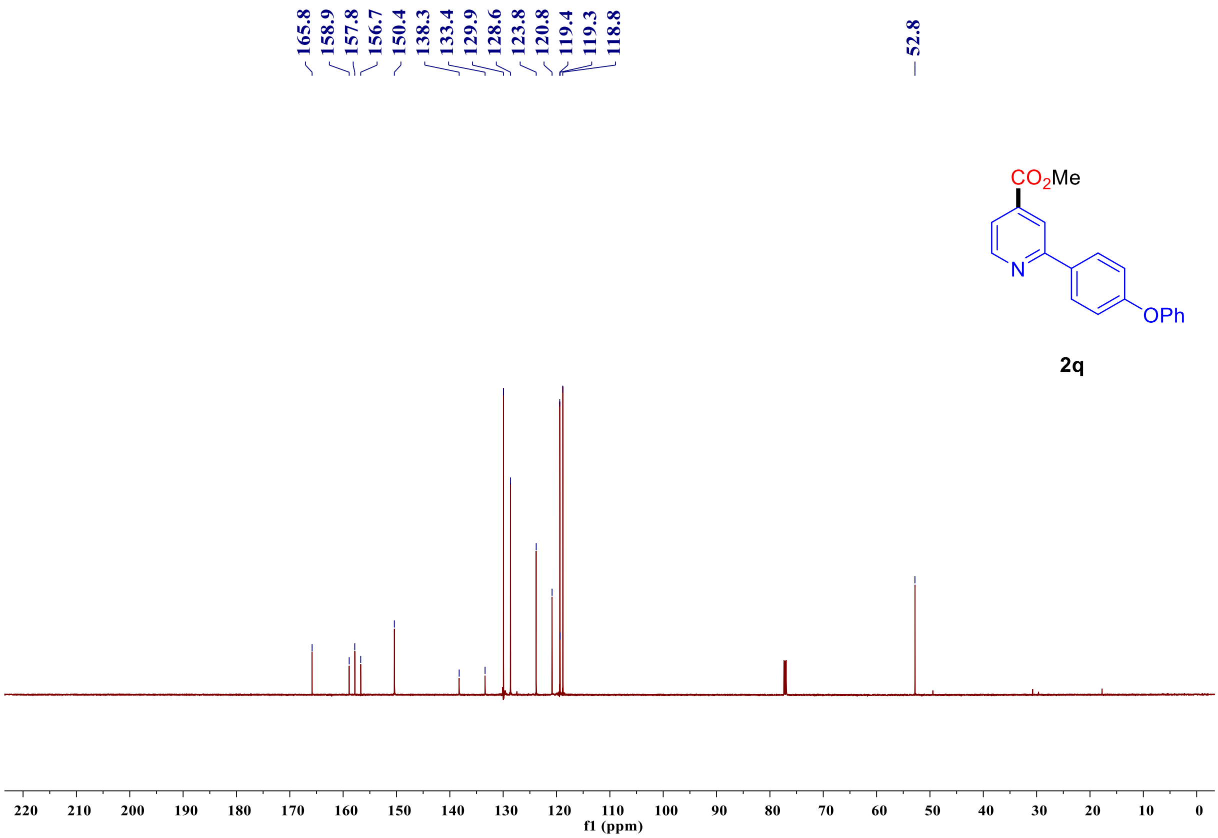
^{13}C NMR of 2p (151 MHz, $CDCl_3$)



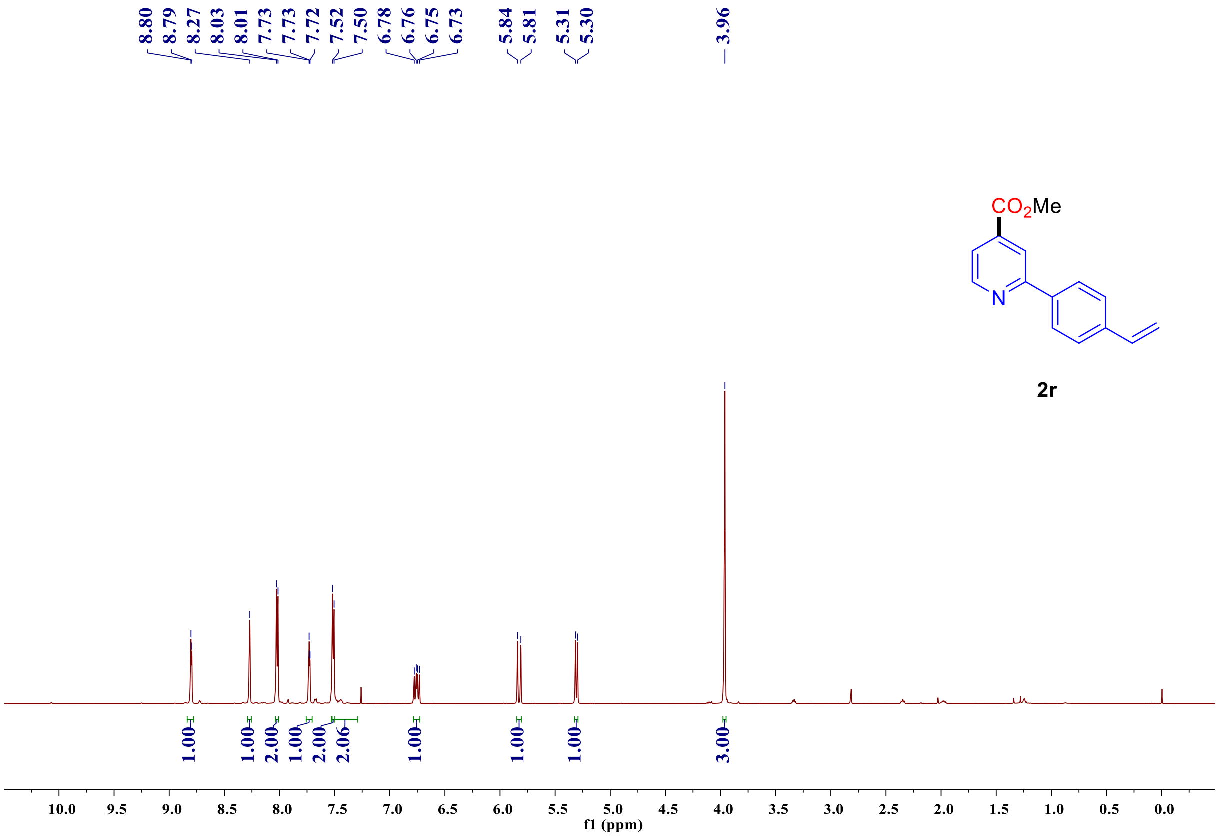
^{1}H NMR of 2q (600 MHz, $CDCl_3$)



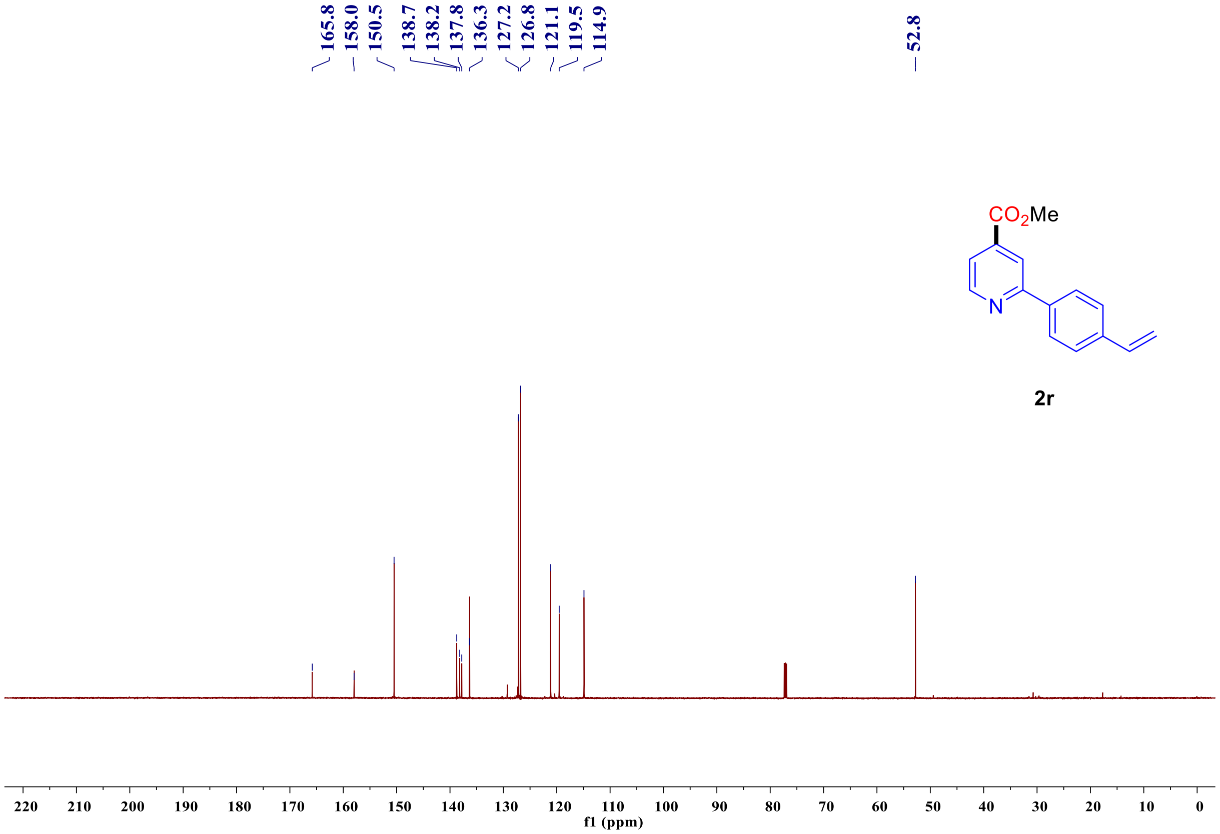
^{13}C NMR of 2q (151 MHz, CDCl$_3$)



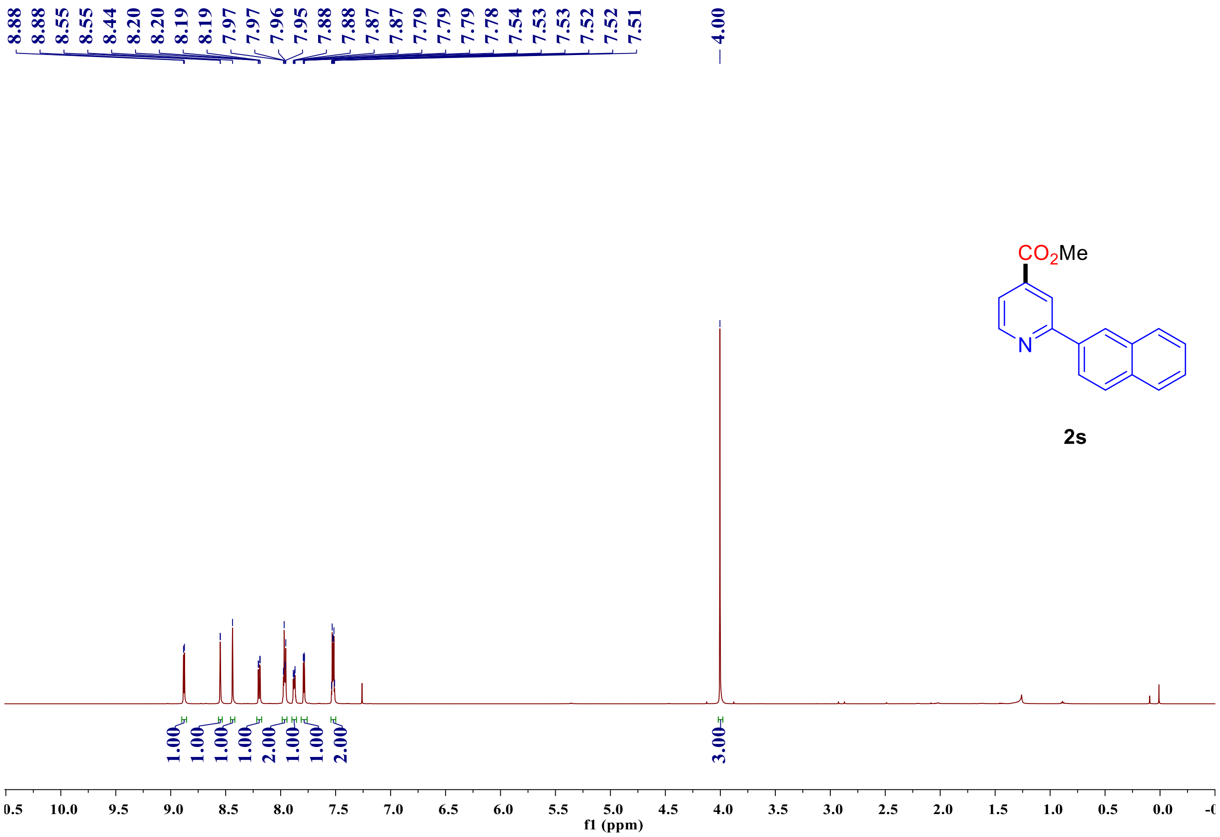
^{1}H NMR of 2r (600 MHz, CDCl$_3$)



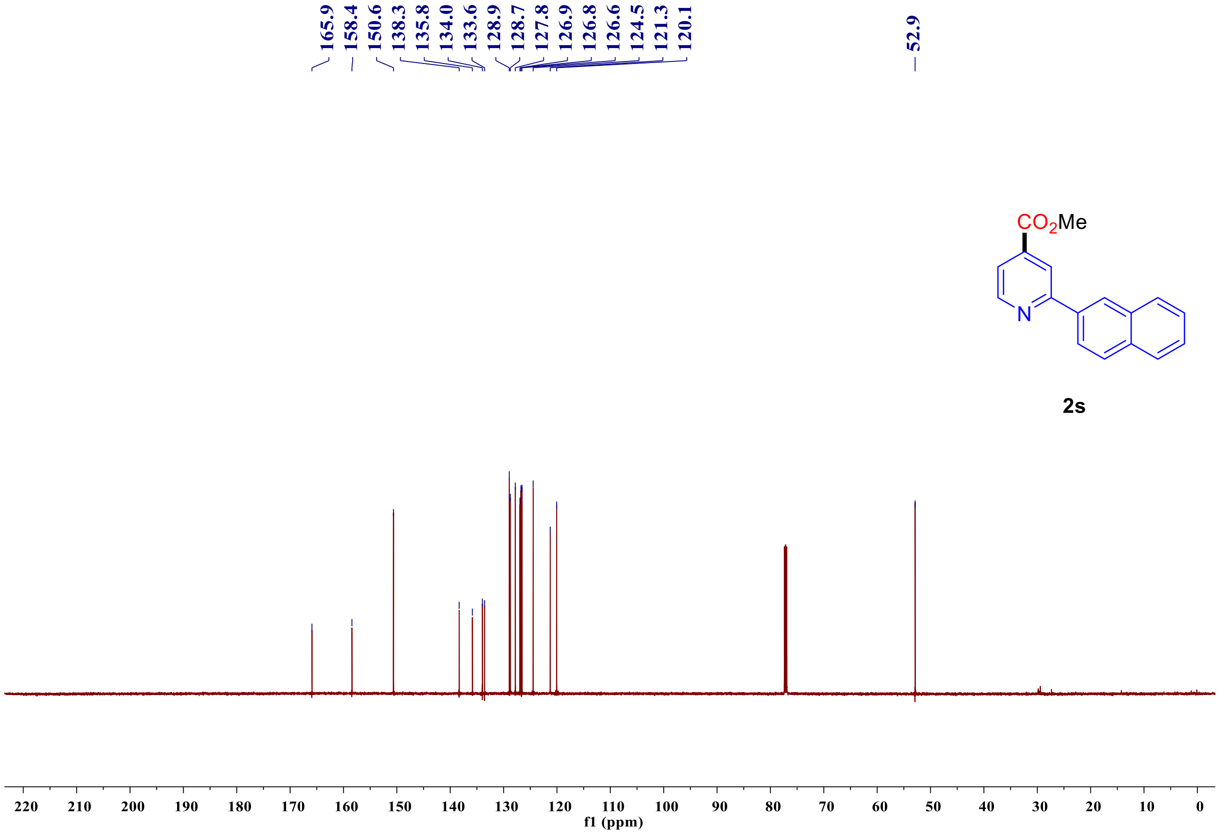
[13]C NMR of 2r (151 MHz, $CDCl_3$)



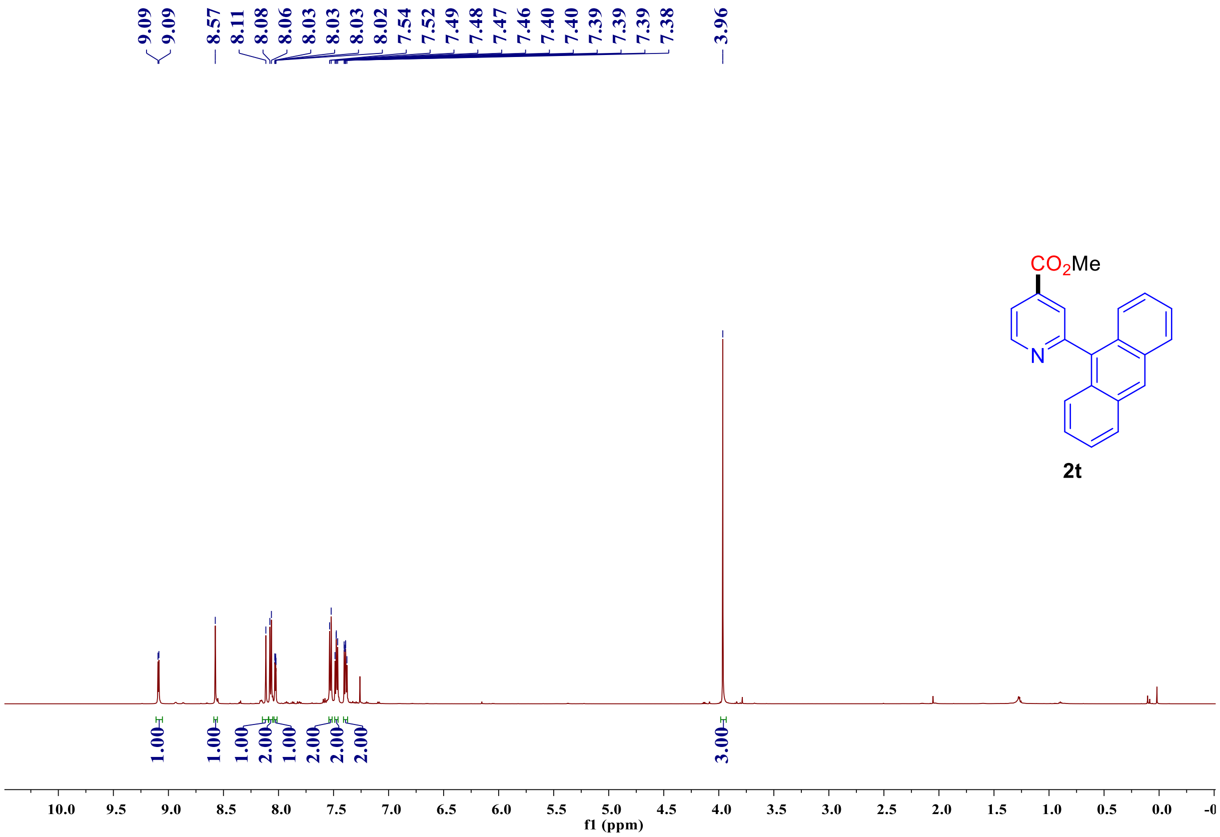
[1]H NMR of 2s (600 MHz, $CDCl_3$)



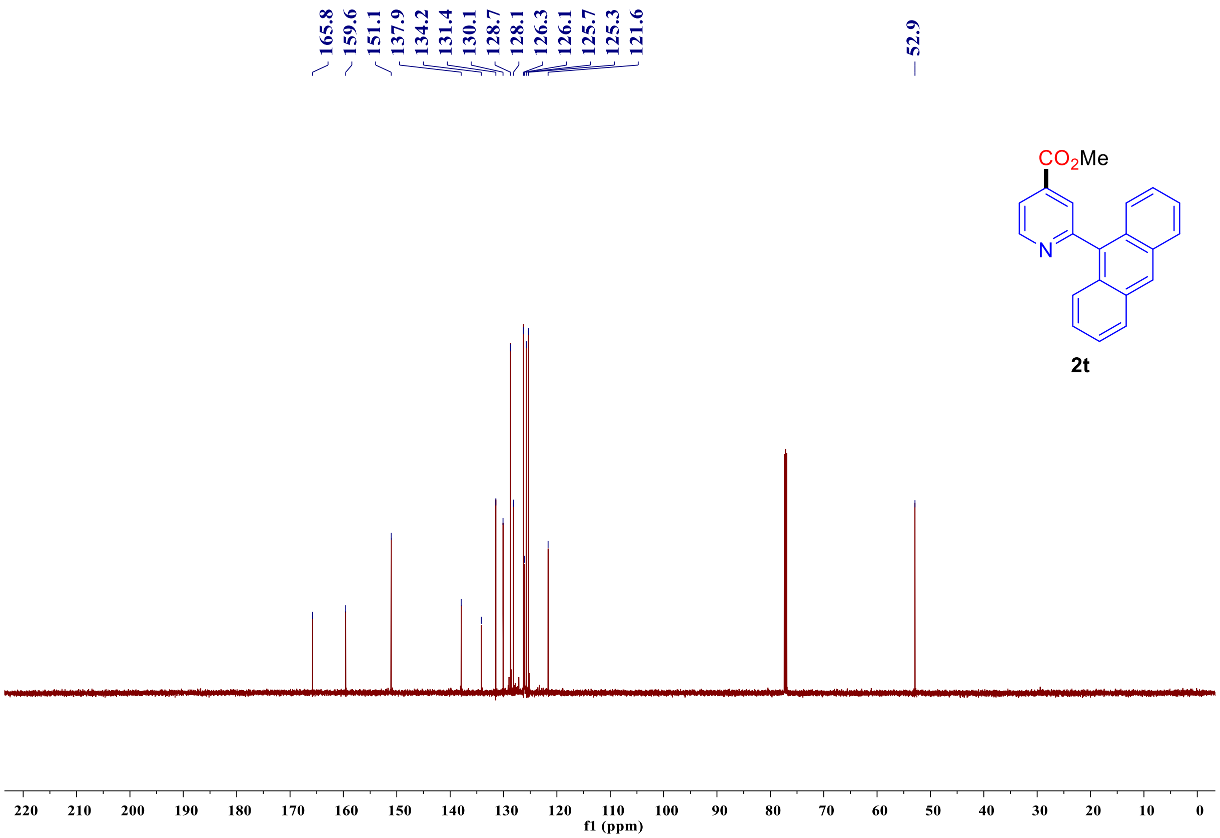
^{13}C NMR of 2s (151 MHz, $CDCl_3$)



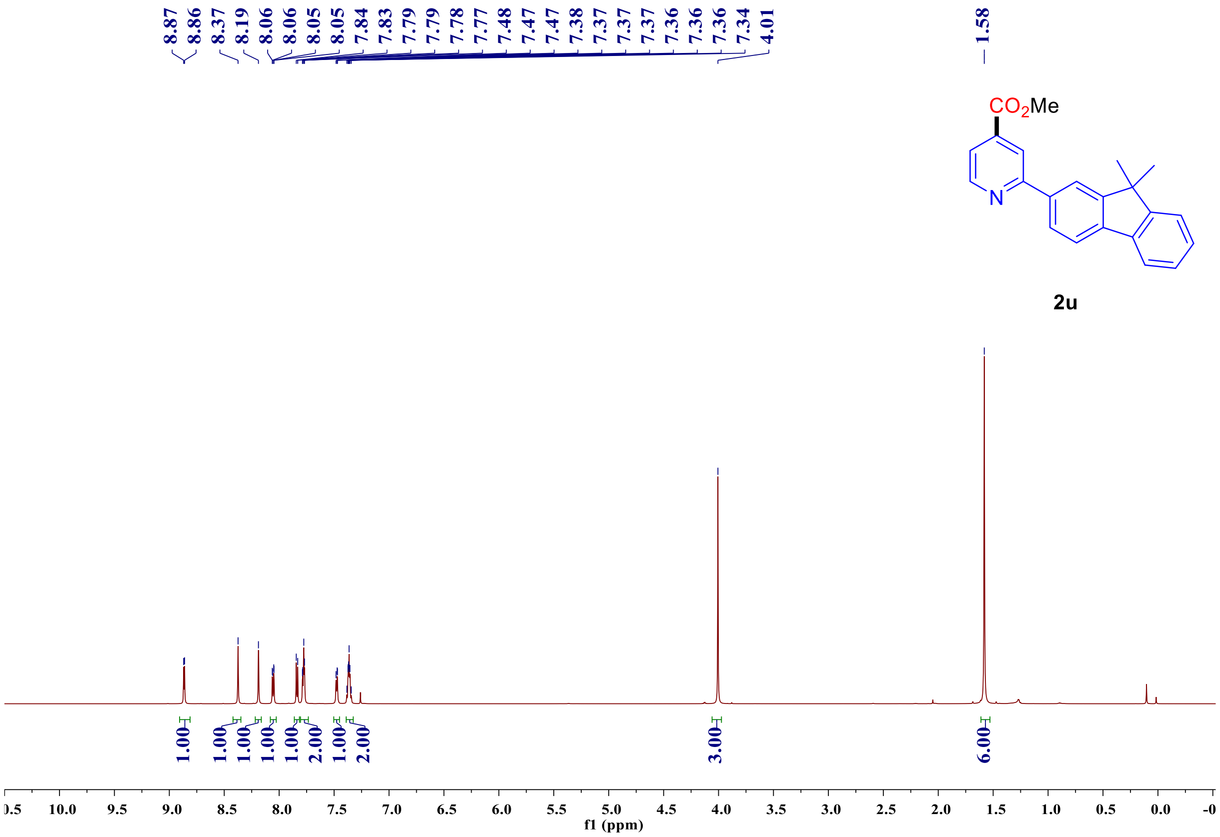
^{1}H NMR of 2t (600 MHz, $CDCl_3$)



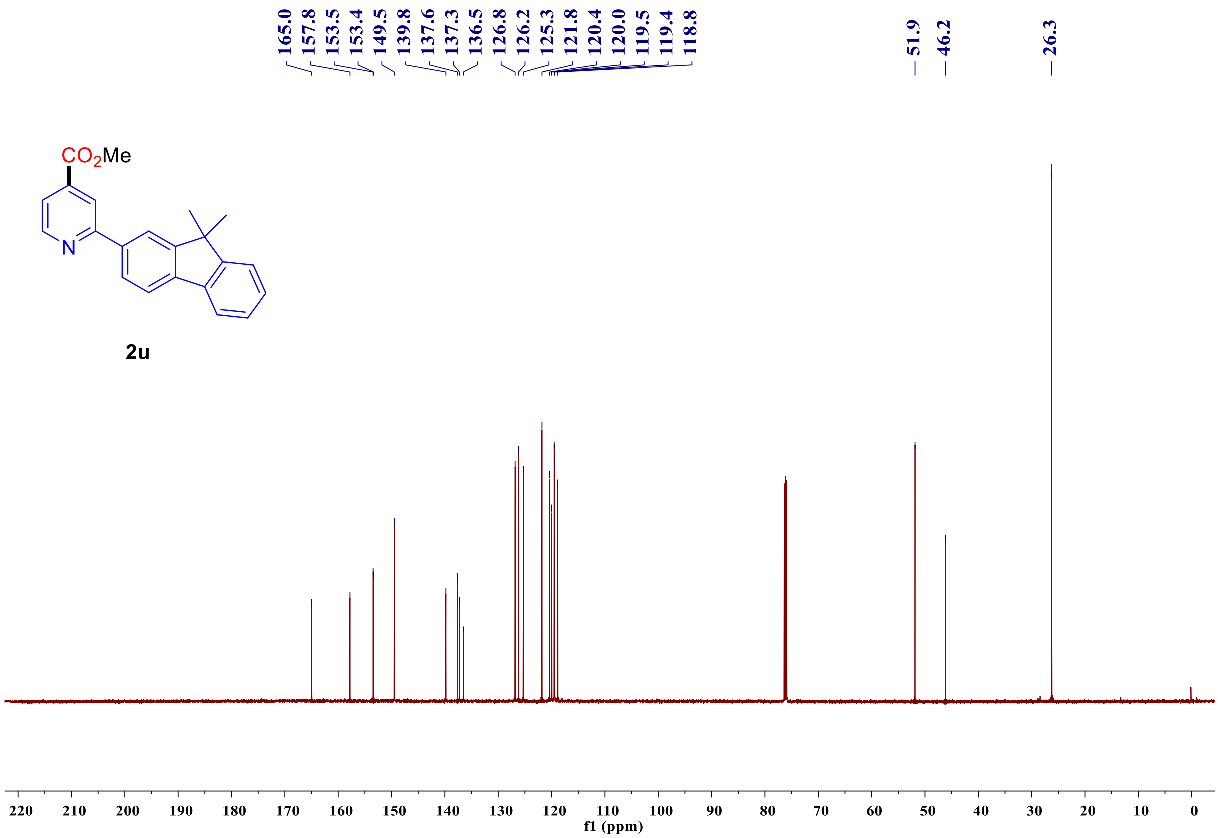
^{13}C NMR of 2t (151 MHz, $CDCl_3$)



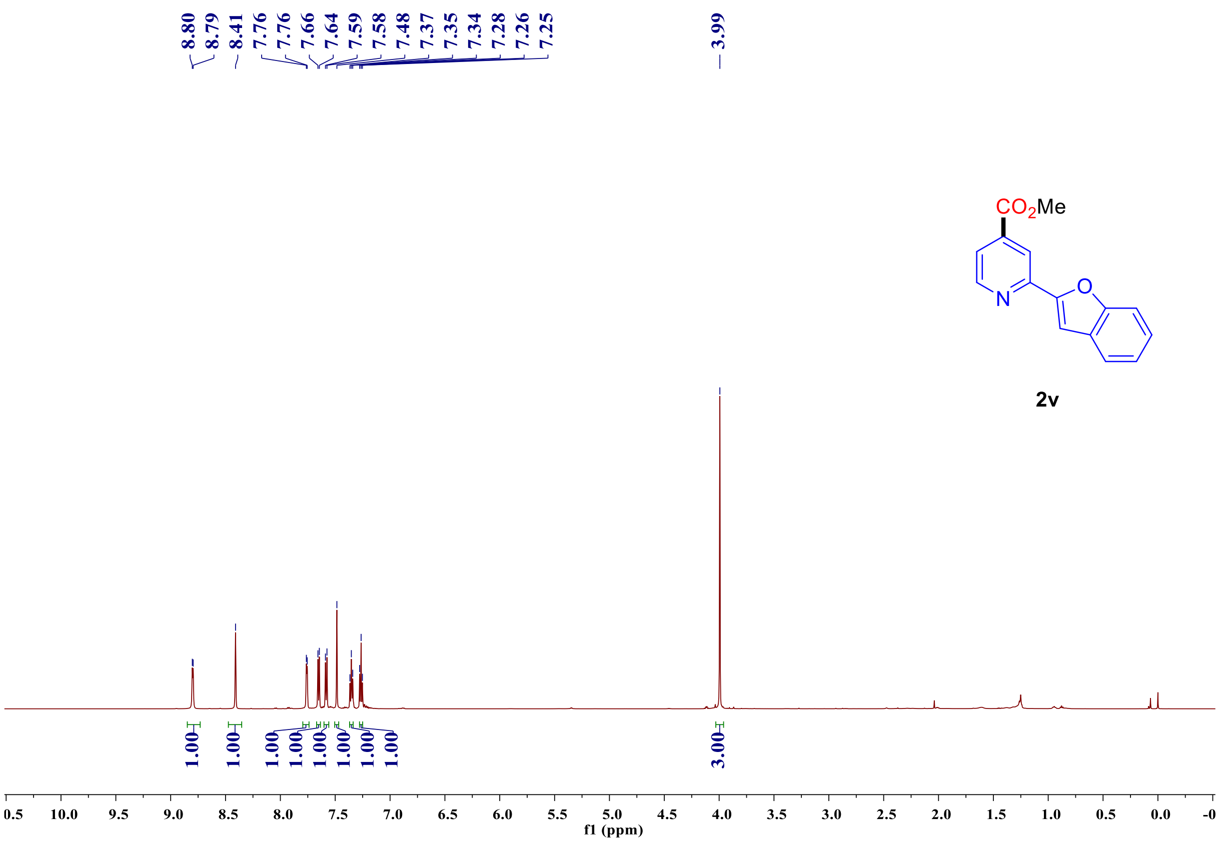
^{1}H NMR of 2u (600 MHz, $CDCl_3$)



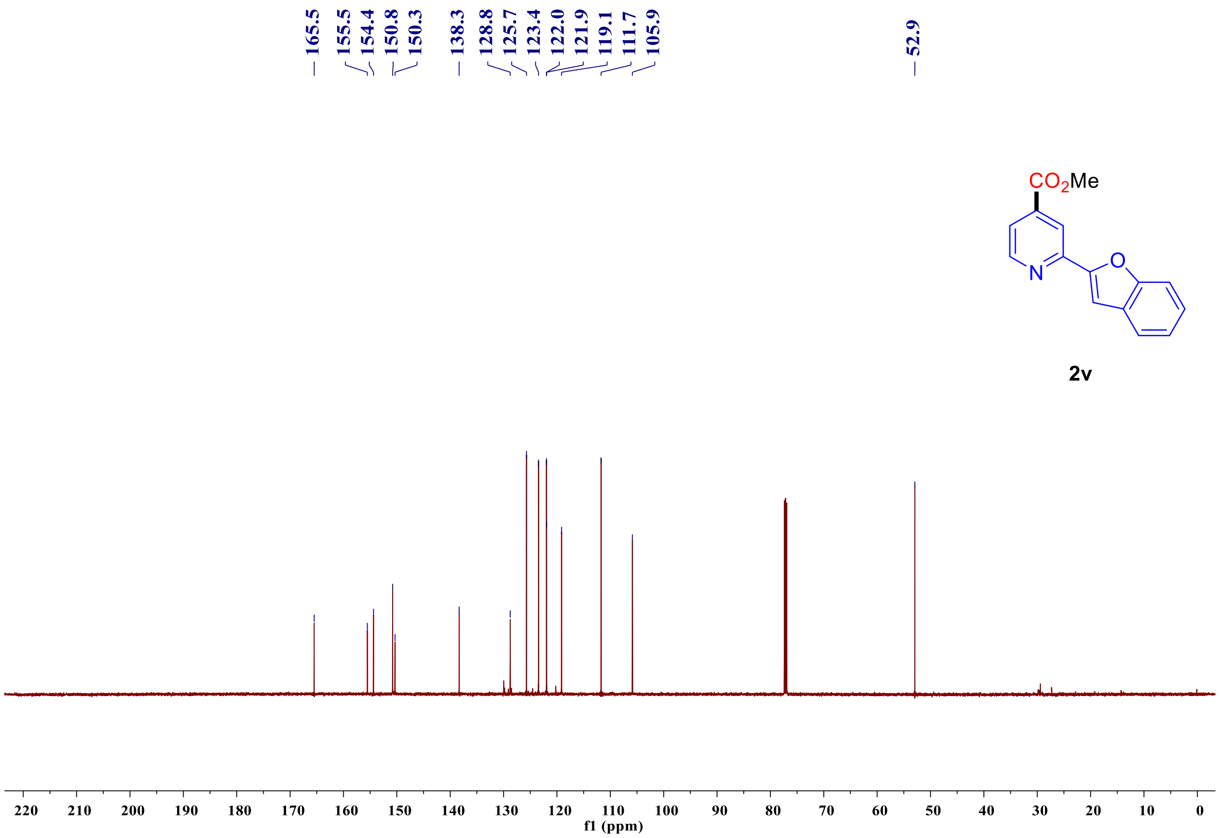
^{13}C NMR of 2u (151 MHz, $CDCl_3$)



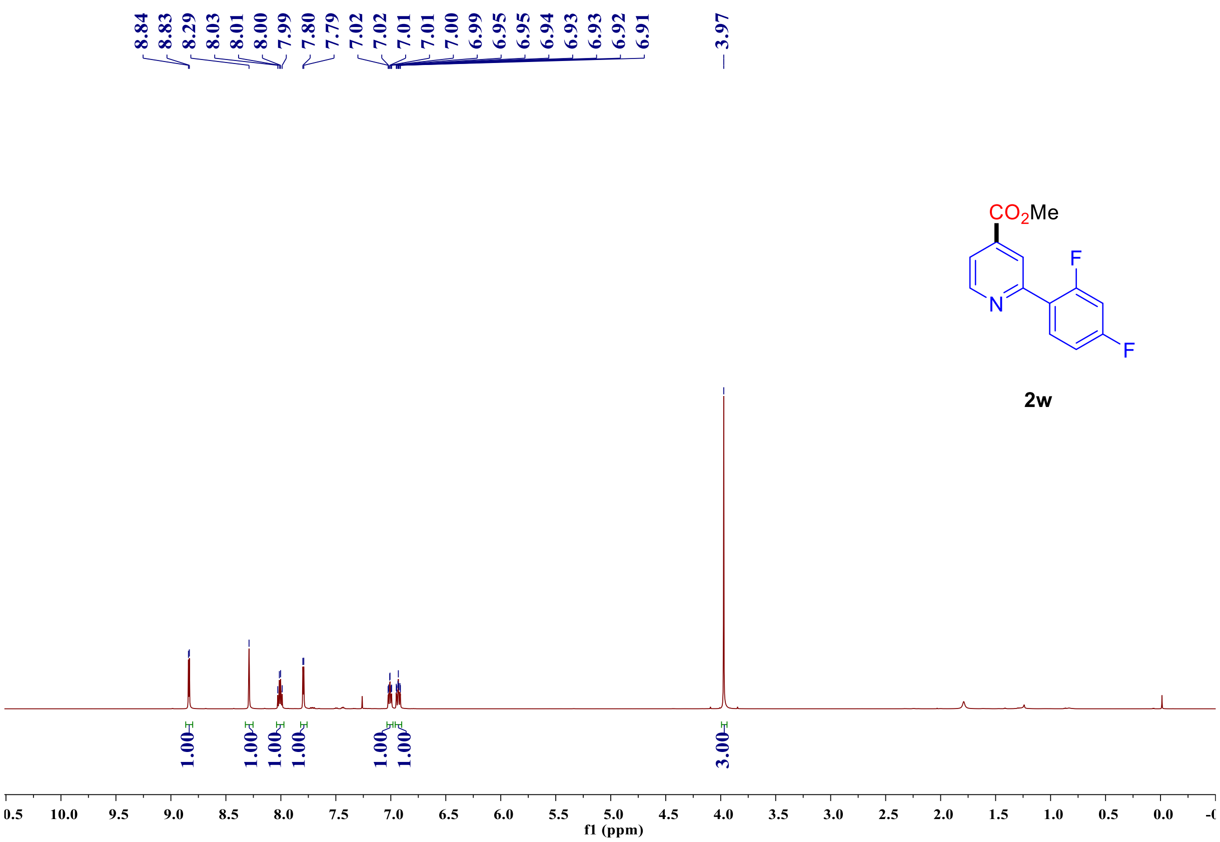
^{1}H NMR of 2v (600 MHz, $CDCl_3$)



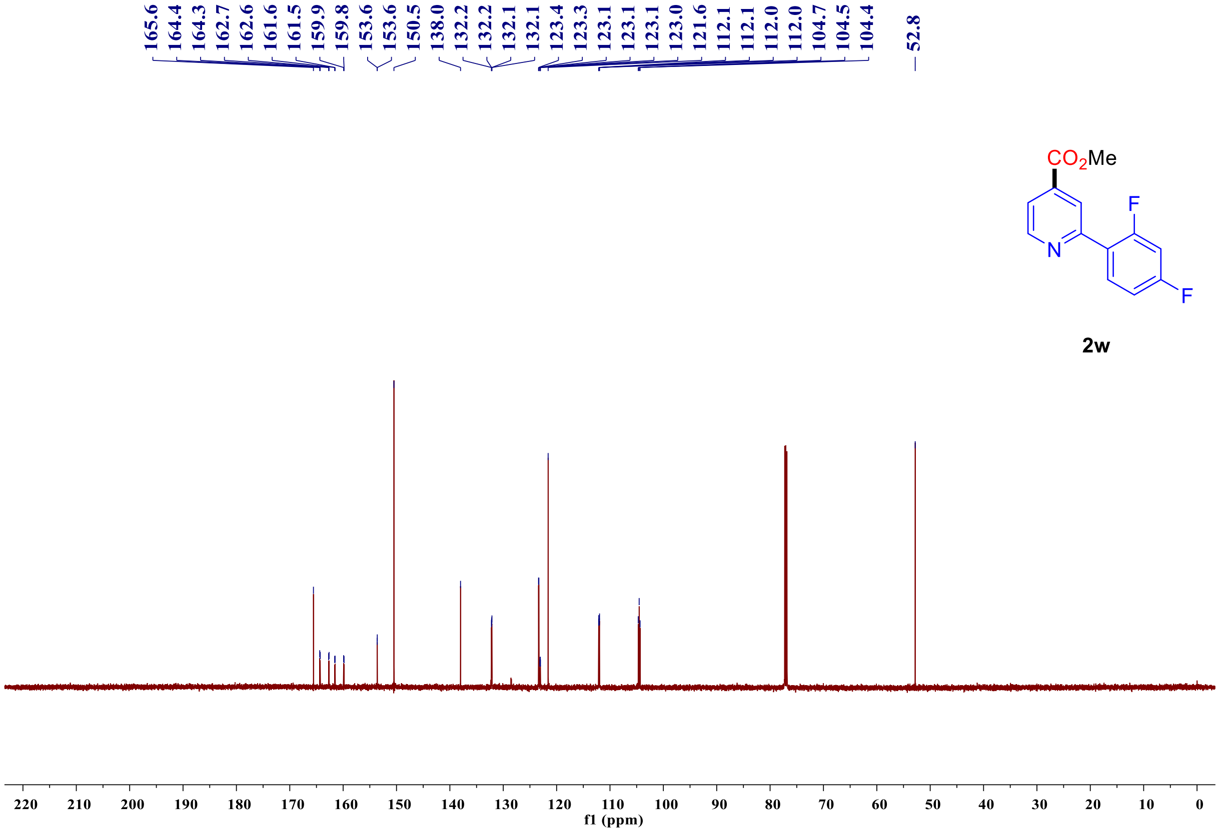
^{13}C NMR of 2v (151 MHz, $CDCl_3$)

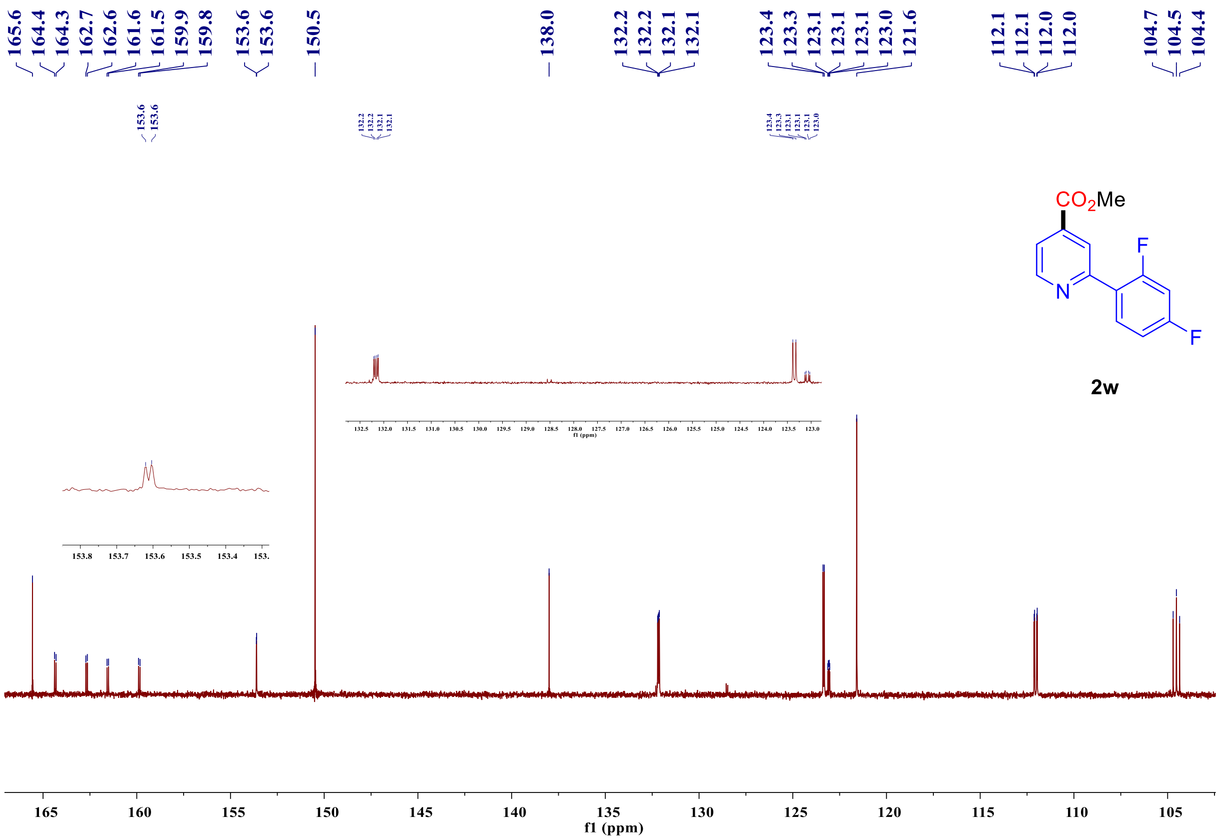


^{1}H NMR of 2w (600 MHz, $CDCl_3$)

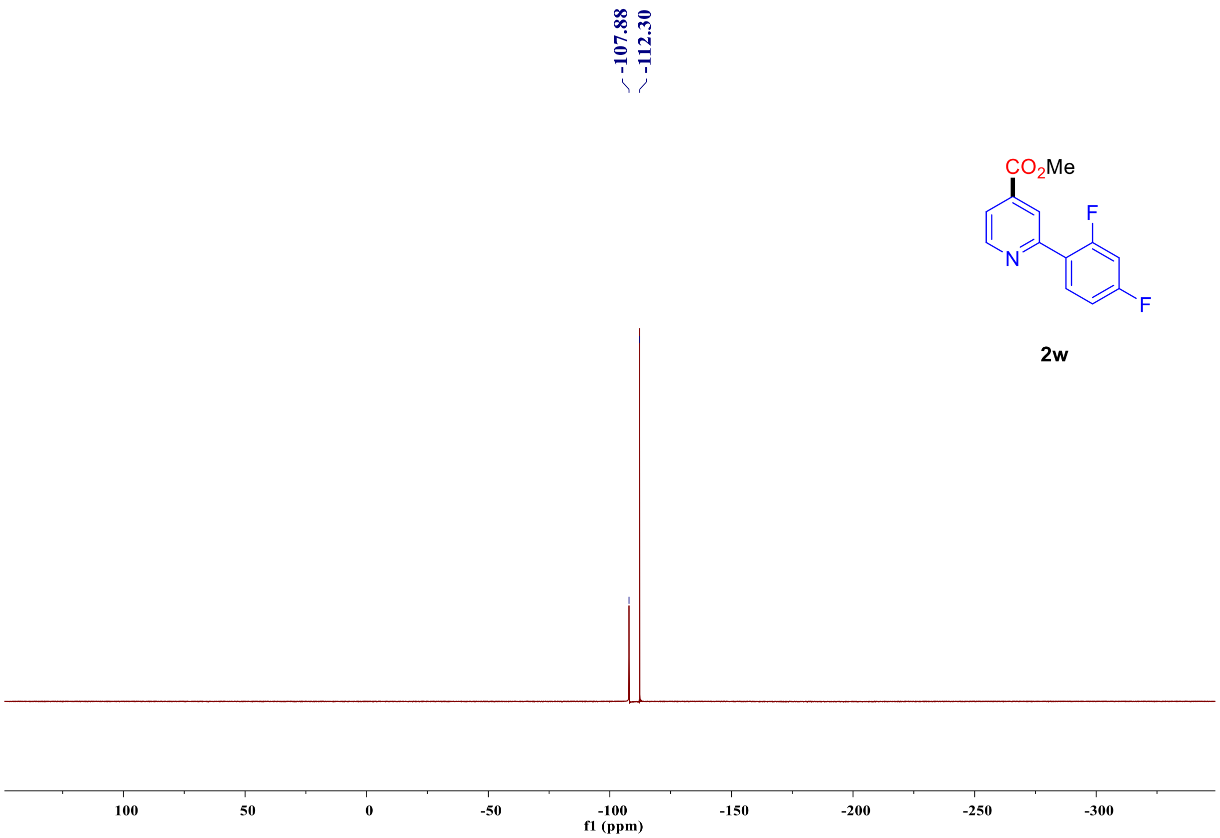


^{13}C NMR of 2w (151 MHz, $CDCl_3$)

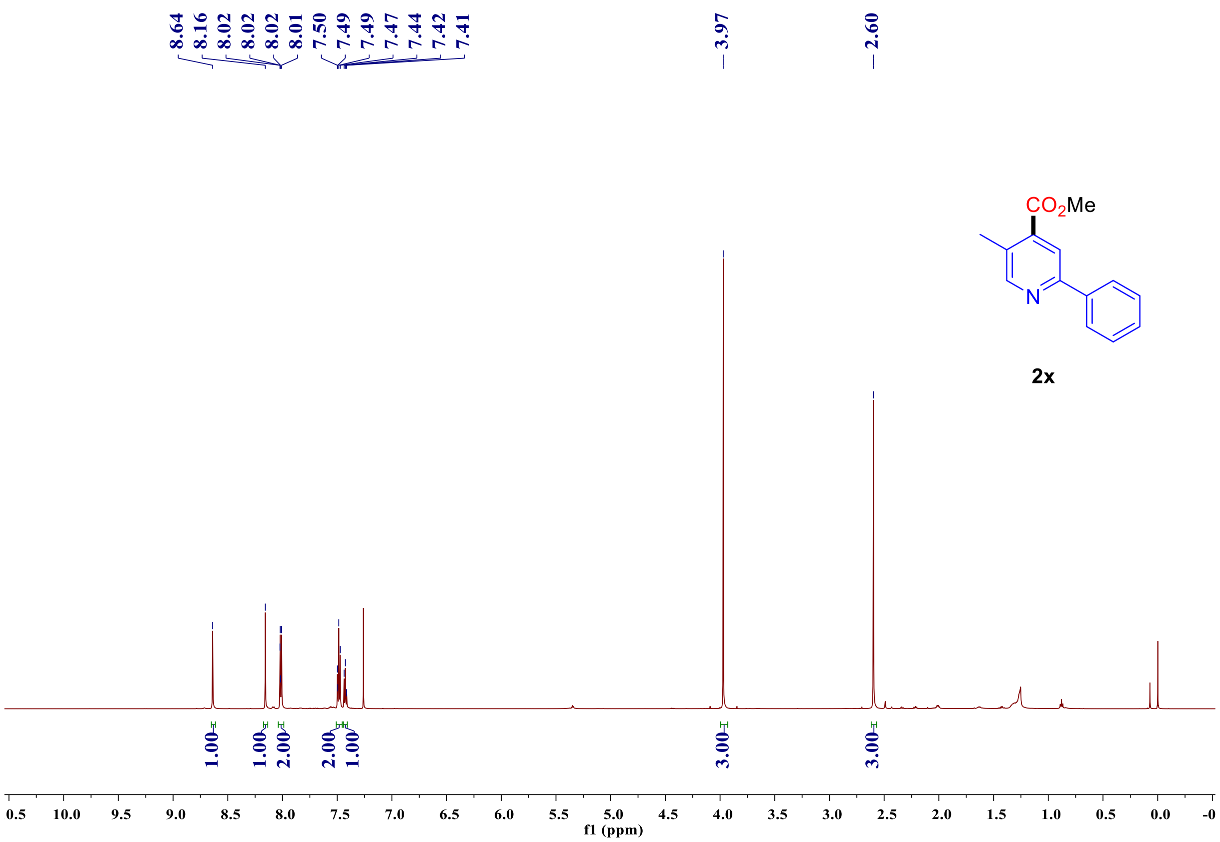




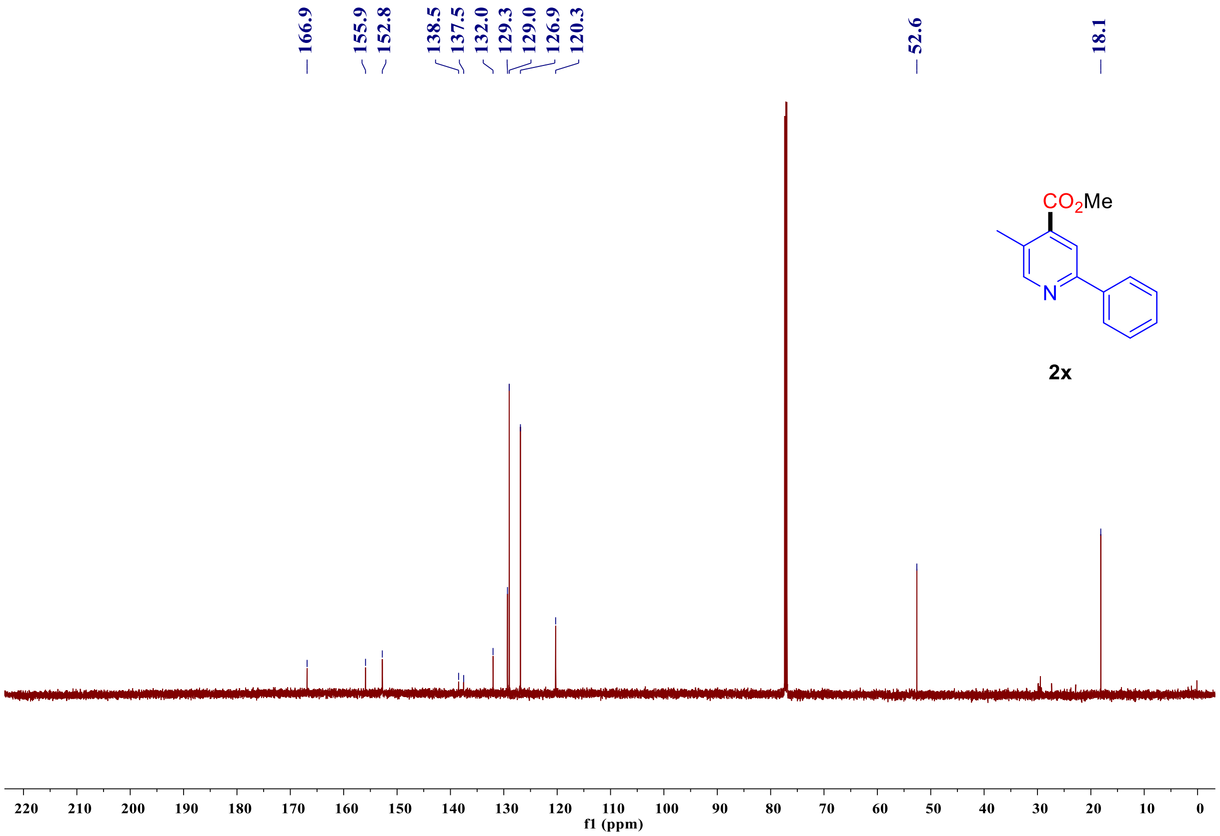
[19]F NMR of 2w (376 MHz, $CDCl_3$)



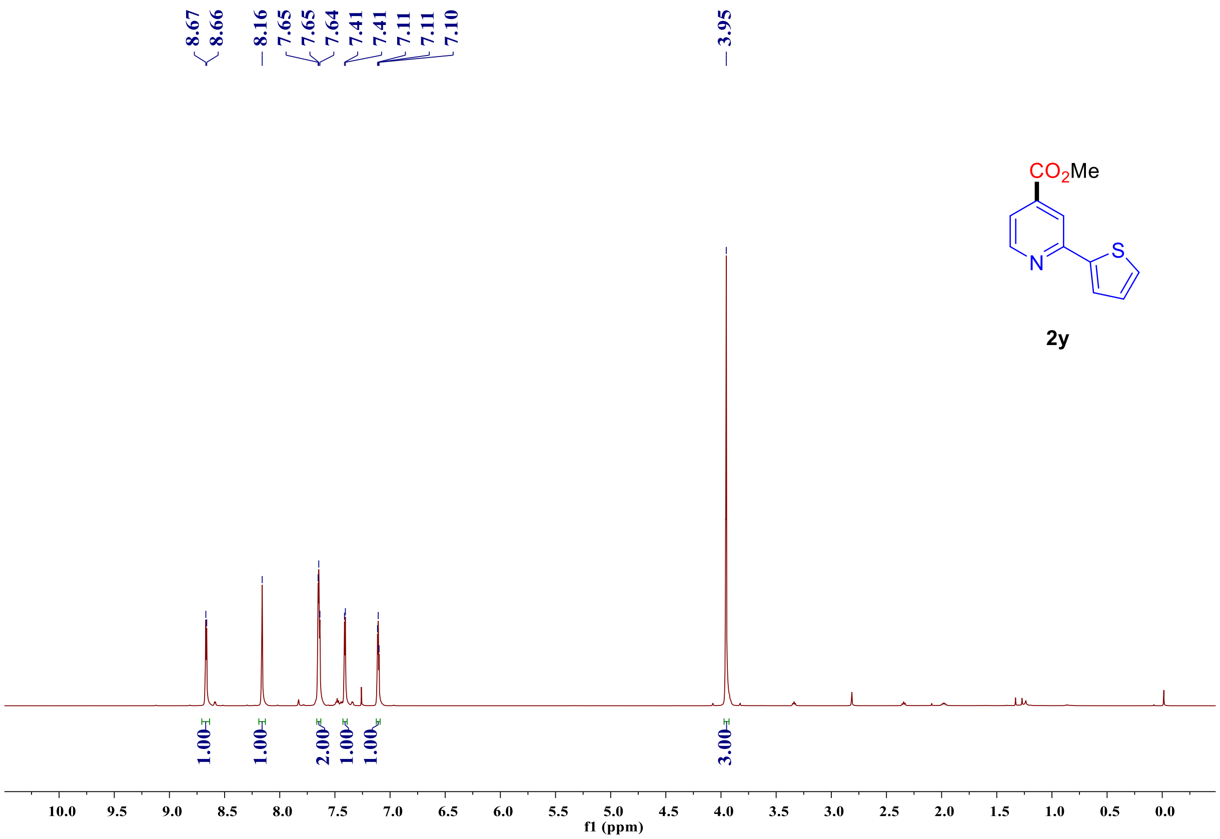
[1]H NMR of 2x (600 MHz, $CDCl_3$)



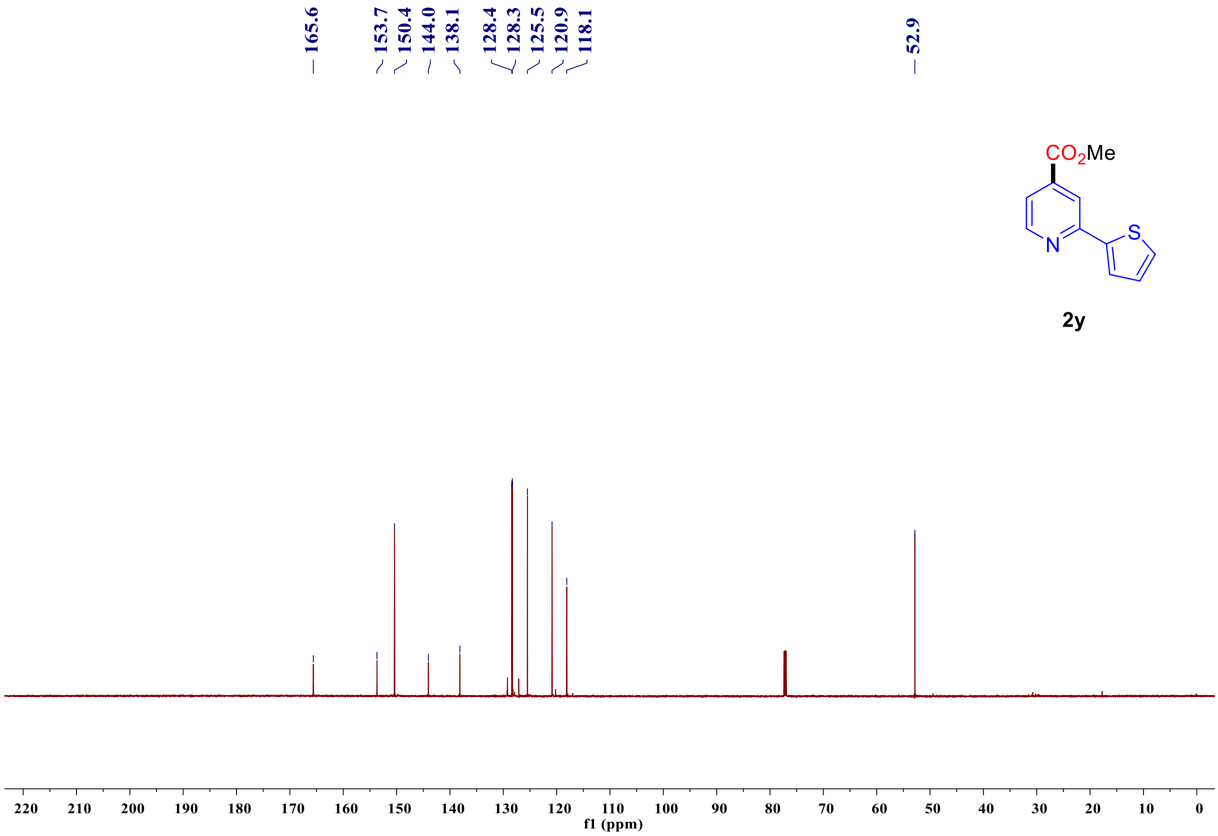
^{13}C NMR of 2x (151 MHz, $CDCl_3$)



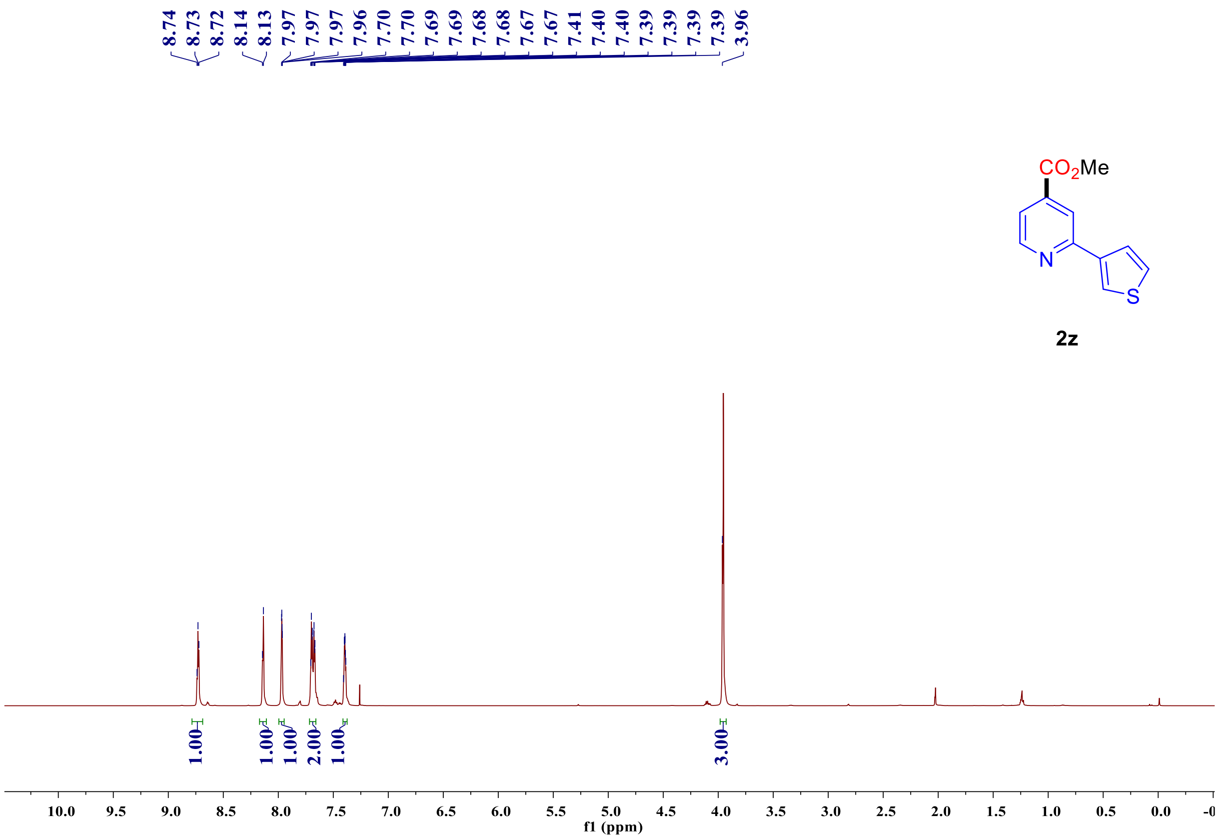
^{1}H NMR of 2y (600 MHz, $CDCl_3$)



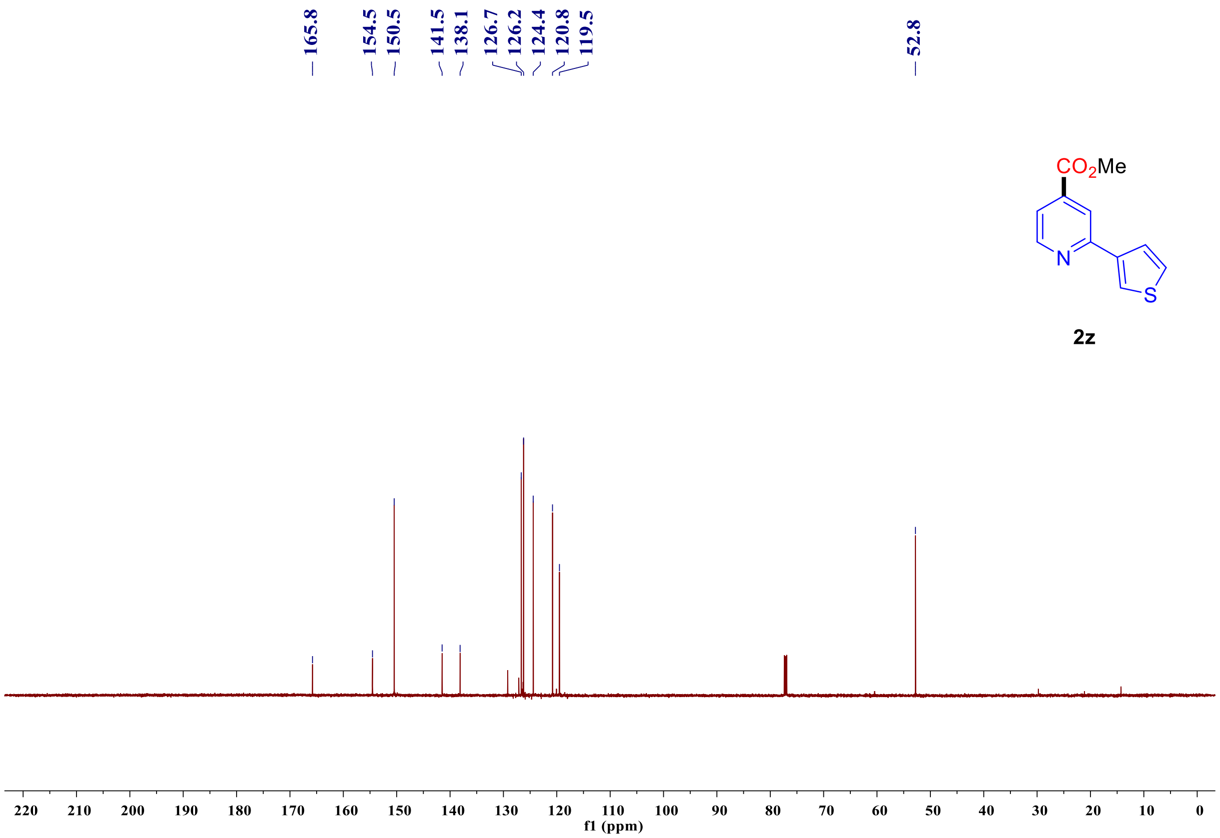
^{13}C NMR of 2y (151 MHz, $CDCl_3$)



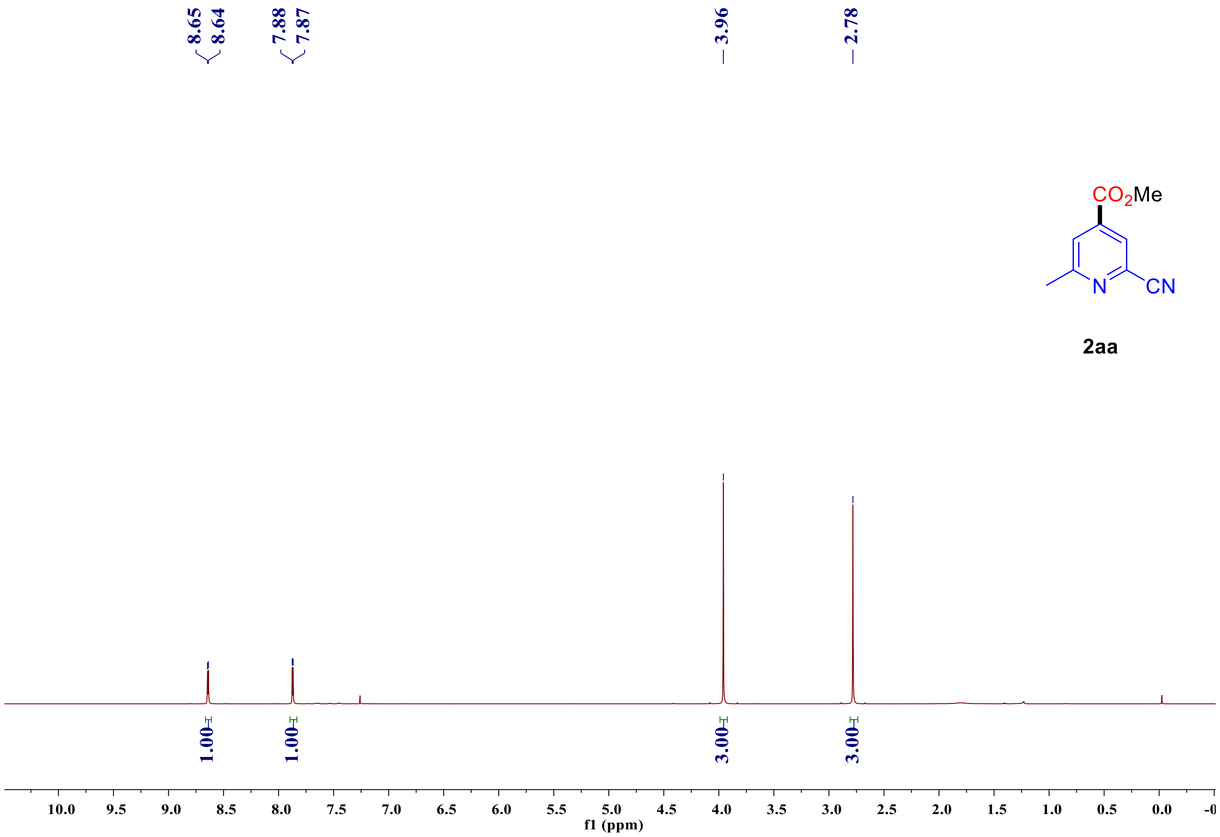
^{1}H NMR of 2z (600 MHz, $CDCl_3$)



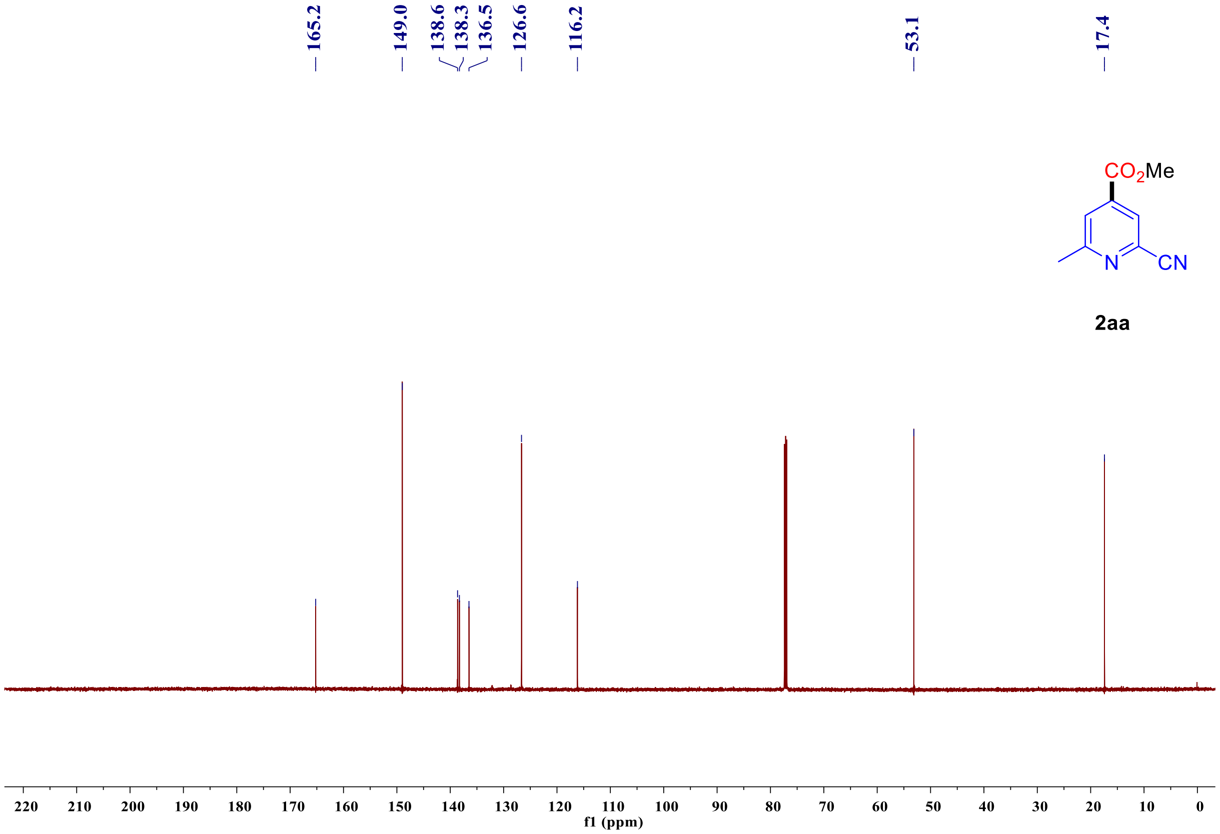
^{13}C NMR of 2z (151 MHz, $CDCl_3$)



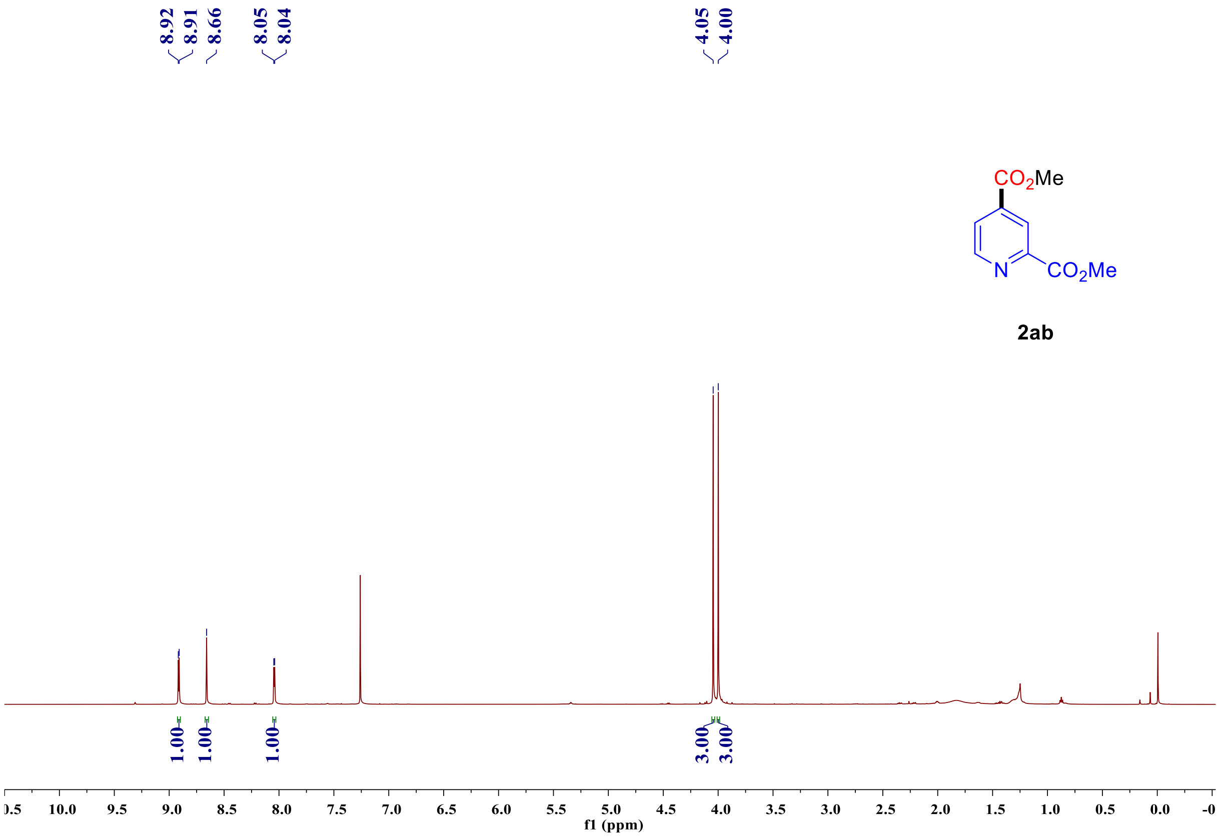
^{1}H NMR of 2aa (600 MHz, $CDCl_3$)



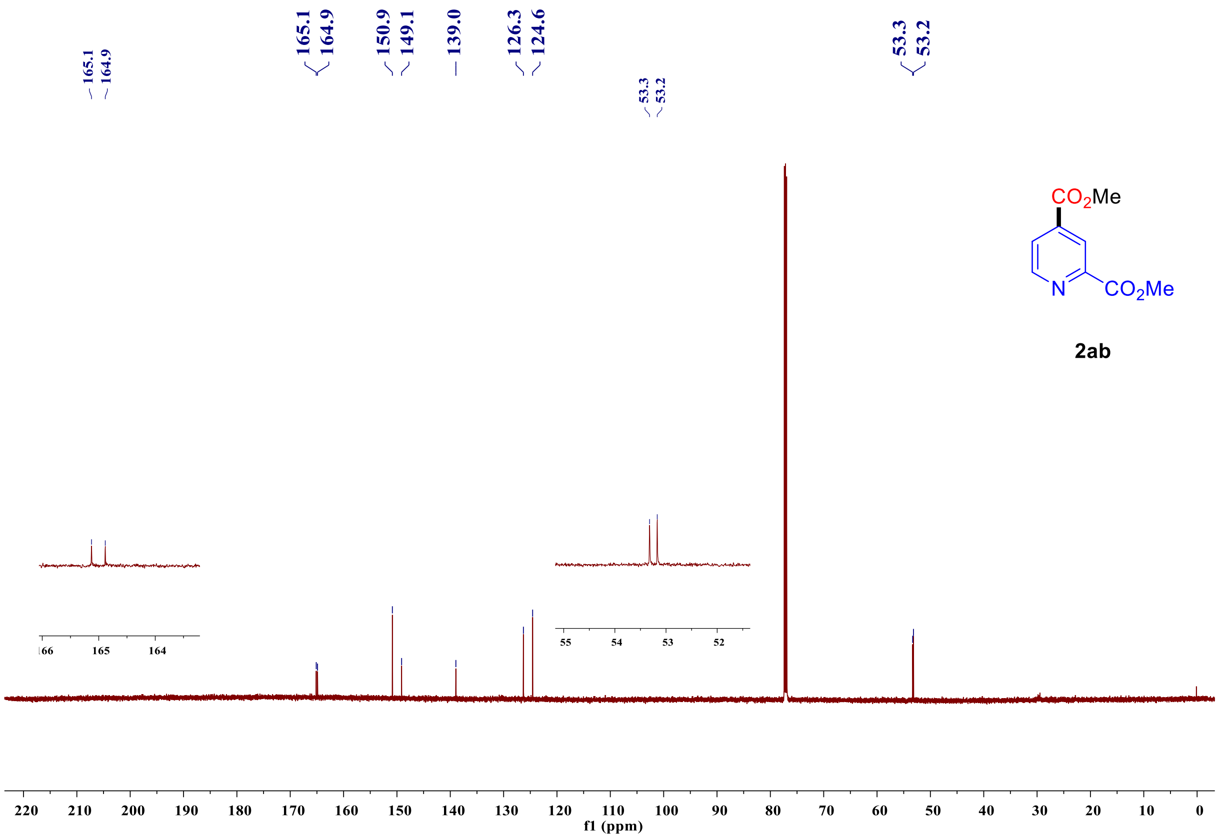
^{13}C NMR of 2aa (151 MHz, $CDCl_3$)



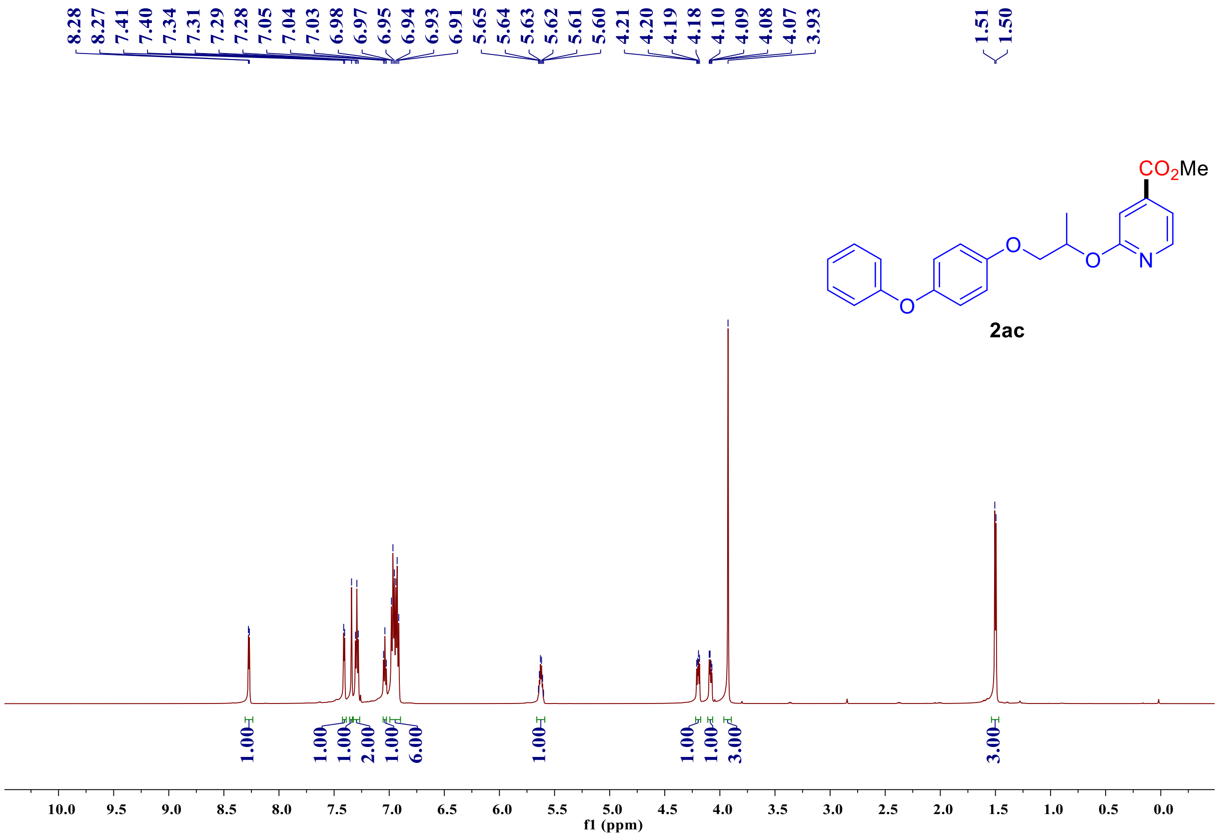
^{1}H NMR of 2ab (600 MHz, $CDCl_3$)



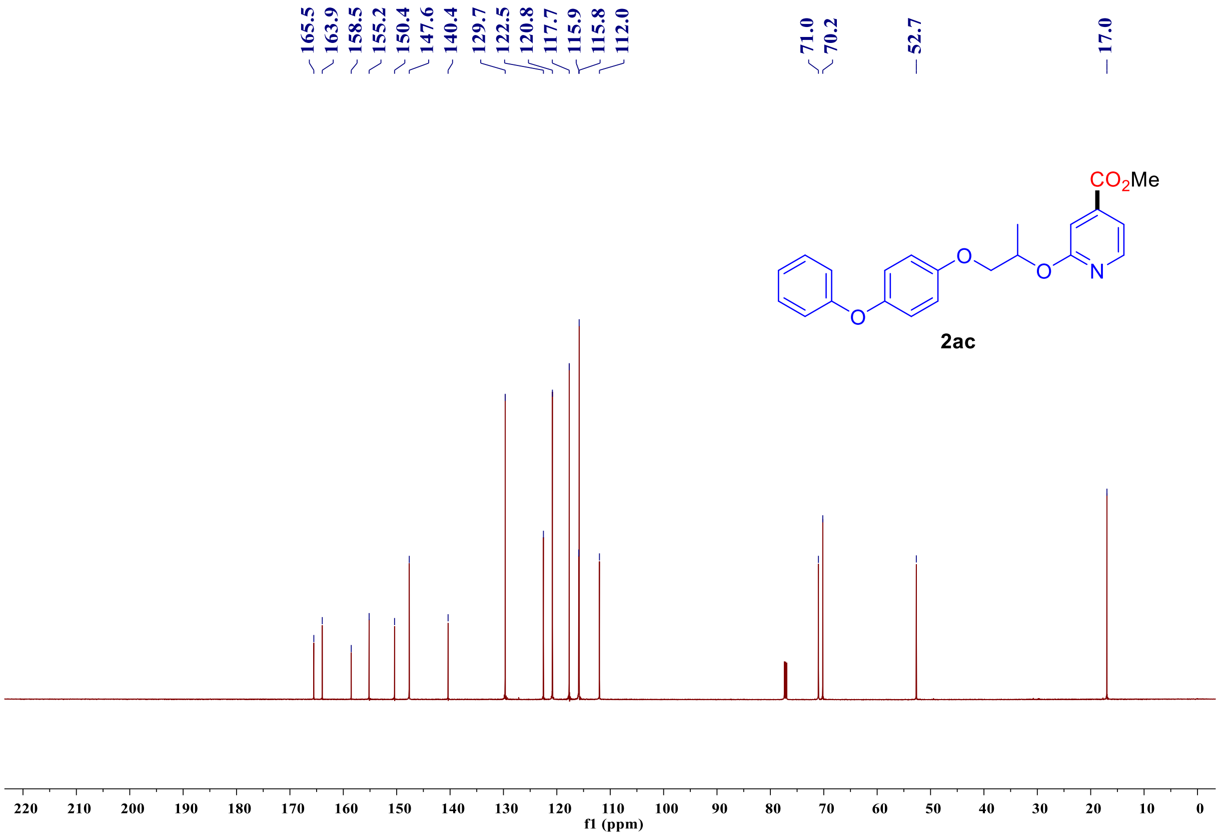
^{13}C NMR of 2ab (151 MHz, CDCl$_3$)



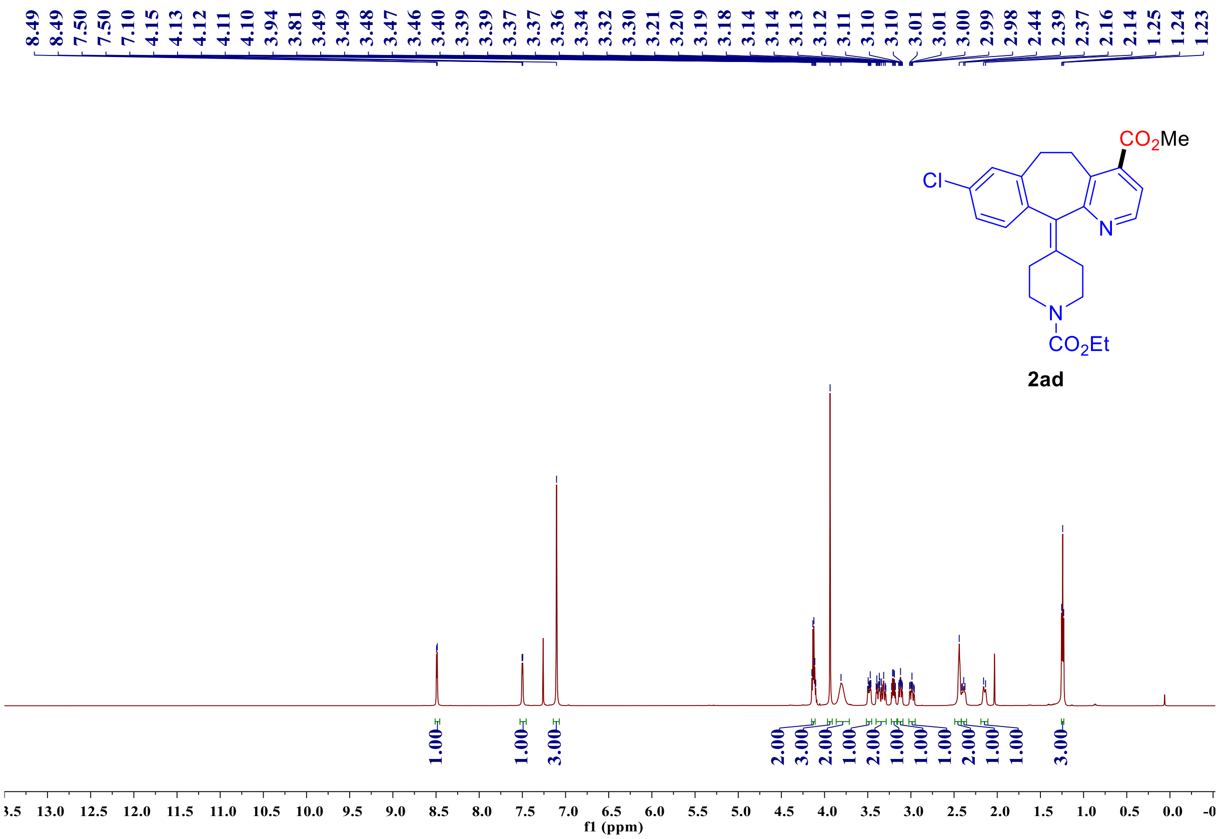
^{1}H NMR of 2ac (600 MHz, CDCl$_3$)



^{13}C NMR of 2ac (151 MHz, $CDCl_3$)



^{1}H NMR of 2ad (600 MHz, $CDCl_3$)



^{13}C NMR of 2ad (151 MHz, $CDCl_3$)