

SUPPORTING INFORMATION

Cobalt-Catalyzed Cross-Coupling Reactions of Arylboronic Esters and Aryl Halides

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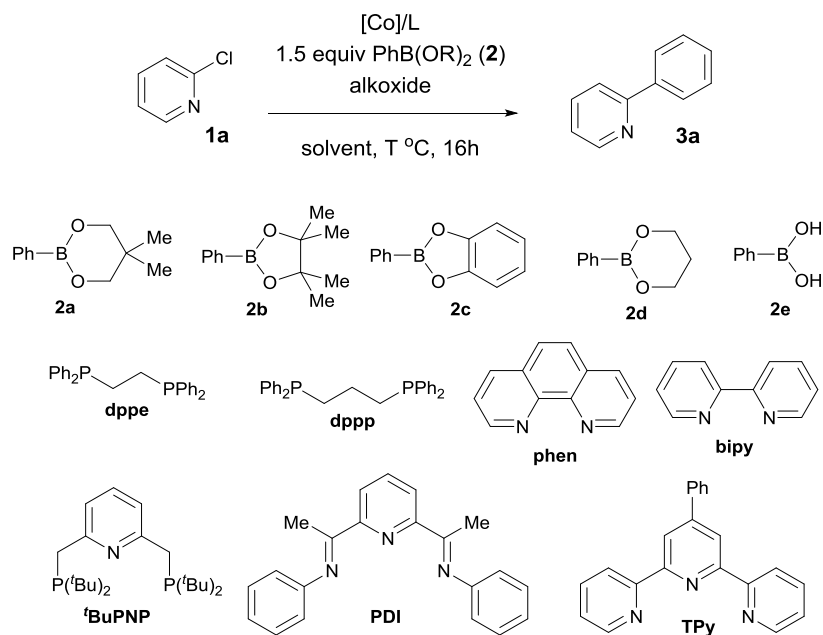
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General information. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF and DMF were dried over alumina under N₂ using a Grubbs-type solvent purification system. Cobalt(II) chloride (97%, Alfa Aesar), cobalt(II) chloride (99.998%, Strem), cobalt(II) acetate (Alfa Aesar), cobalt(II) bromide (99%, Alfa Aesar), cobalt(II) iodide (Alfa Aesar), cobalt(II) acetylacetonate (Sigma Aldrich), cobalt(III) acetylacetonate (Sigma Aldrich), potassium methoxide (Fluka and Sigma Aldrich), aryl bromides and aryl chlorides were purchased from commercial sources and used as received. Terpyridine and arylboronic esters were synthesized according to literature procedures.¹ Reactions were monitored by thin-layer chromatography (TLC), which was performed on 0.25 mm silica gel plates visualized using UV radiation (254 nm). Column chromatography was performed on silica gel (200-300 mesh) by elution with appropriate solvent. GC–MS analysis was performed by using an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5MS capillary column by using helium as the carrier gas. NMR spectra were recorded with a 400 or 600 MHz instrument and were calibrated by using residual nondeuterated solvent (CDCl₃: δ_{H} = 7.26 ppm; δ_{C} = 77.10 ppm; (CD₃)₂CO: δ_{H} = 2.05 ppm; δ_{C} = 29.84 ppm) as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad.

(1) (a) Wang, J.; Hanan, G. S. *Synlett* **2005**, 8, 1251. (b) Duong, H. A.; Nguyen, T. M.; Rosman, N. Z.; Tan, L. J. L. *Synthesis* **2014**, 46, 1881.

Optimizations of the Co-catalyzed of cross-coupling of 1a and 2a:



Entry	2	[Co]	L	Alkoxide	Solvent	T (°C)	% conv. ^a	% yield ^a
1	2a	12 mol% CoCl ₂	none	1.5 equiv KOMe	THF	60	61	38
2	2b	12 mol% CoCl ₂	none	1.5 equiv KOMe	THF	60	11	0
3	2c	12 mol% CoCl ₂	none	1.5 equiv KOMe	THF	60	27	15
4	2d	12 mol% CoCl ₂	none	1.5 equiv KOMe	THF	60	45	29
5	2e	12 mol% CoCl ₂	none	1.5 equiv KOMe	THF	60	0	0
6	2a	12 mol% CoCl ₂	none	1.5 equiv KOEt	THF	60	45	31
7	2a	12 mol% CoCl ₂	none	1.5 equiv KO ^t Bu	THF	60	60	10
8	2a	12 mol% CoCl ₂	none	1.5 equiv NaOMe	THF	60	60	7
9	2a	12 mol% CoCl ₂	none	1.5 equiv NaO ^t Bu	THF	60	57	13
10	2a	12 mol% CoCl ₂	none	1.5 equiv LiOMe	THF	60	34	9
11	2a	12 mol% CoCl ₂	none	1.5 equiv LiO ⁱ Pr	THF	60	38	18
12	2a	12 mol% CoCl ₂	12 mol% dppp	1.5 equiv KOMe	THF	60	52	31
13	2a	12 mol% CoCl ₂	12 mol% dppe	1.5 equiv KOMe	THF	60	45	22
14	2a	12 mol% CoCl ₂	12 mol% phen	1.5 equiv KOMe	THF	60	83	14
15	2a	12 mol% CoCl ₂	12 mol% bipy	1.5 equiv KOMe	THF	60	87	41
16	2a	12 mol% CoCl ₂	12 mol% ^t BuPNP	1.5 equiv KOMe	THF	60	51	31
17	2a	12 mol% CoCl ₂	12 mol% PDI	1.5 equiv KOMe	THF	60	16	2
18	2a	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	THF	60	100	90
19	2a	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	Toluene	60	34	11
20	2a	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	Dioxane	60	11	0
21	2a	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	100	94
22	2a	5 mol% CoCl ₂	5 mol% TPy	1.5 equiv KOMe	THF	60	50	42
23	2a	5 mol% CoCl ₂	5 mol% TPy	1.5 equiv KOMe	DMF	60	43	38
24	2a	5 mol% CoCl ₂	5 mol% TPy	1.5 equiv KOMe	DMF	80	100	93
25	2a	12 mol% CoCl ₂	12 mol% TPy	0.5 equiv KOMe	DMF	60	47	46
26	2a	12 mol% Co(OAc) ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	64	62
27	2a	12 mol% CoI ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	65	59

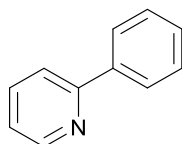
28	2a	12 mol% CoBr ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	100	92
29	2a	12 mol% Co(acac) ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	47	38
30	2a	12 mol% Co(acac) ₃	12 mol% TPy	1.5 equiv KOMe	DMF	60	3	0
31 ^b	2a	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	100	94
32	2a	none	12 mol% TPy	1.5 equiv KOMe	DMF	60	16	0
33	2a	12 mol% PdCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	80	12
34	2a	12 mol% NiCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	15	8
35	2a	12 mol% CuCl	12 mol% TPy	1.5 equiv KOMe	DMF	60	9	0
36	2a	12 mol% FeCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	0	0
37	2b	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	52	40
38	2e	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOMe	DMF	60	85	75
39	2e	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOtBu	DMF	60	8	7
40	2e	12 mol% CoCl ₂	12 mol% TPy	1.5 equiv KOEt	DMF	60	100	92

^a Determined by GC using dodecane as an internal standard. ^b CoCl₂ (99.998%) was employed.

General Procedure for Cobalt-catalyzed Suzuki Cross-coupling Reaction of Aryl Chlorides and Bromides:

In a glovebox, CoCl₂ (3.2mg, 0.025 mmol, 5 mol%), TP (7.7mg, 0.025 mmol, 5 mol%), KOMe (52.6mg, 0.75 mmol, 1.5 eq) were charged to a dried reaction tube. 0.5ml DMF was added. The mixture was allowed to stir at rt for 5 min before a solution of aryl halide (0.5 mmol, 1.0 eq) and arylboronic ester (0.75 mmol, 1.5 eq) in 0.5 ml DMF was added. The tube was sealed, taken out of the glovebox and stirred at 80 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once the reaction was completed, the reaction mixture was quenched with water and extracted with ethyl acetate several times. The combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

2-Phenylpyridine (**3a**)²



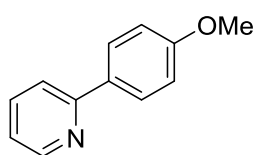
3a was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (1-10% of Et₂O /petroleum ether) to afford the desired product as a colourless oil (71 mg, 91%).

(2) Liu, K. M.; Liao, L. Y.; Duan, X. F. *Chem. Comm.* **2015**, 51, 1124.

3a was prepared from 2-bromopyridine (79 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (1-10% of Et₂O /petroleum ether) to afford the desired product as a colourless oil (67 mg, 86%).

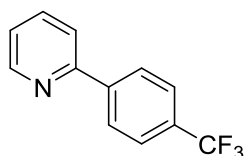
¹H NMR (400 MHz, CDCl₃) δ 8.70 (dt, *J* = 4.9, 1.4 Hz, 1H), 8.08 – 7.97 (m, 2H), 7.76 – 7.69 (m, 2H), 7.53 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 7.21 (td, *J* = 5.2, 3.0 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 157.4, 149.6, 139.3, 136.8, 129.0, 128.7, 126.9, 122.1, 120.6.

2-(4-Methoxyphenyl)pyridine (**3b**)²



3b was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (165 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5-10% of Et₂O /petroleum ether) to afford the desired product as a white solid (78 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.70 – 7.59 (m, 2H), 7.12 (ddd, *J* = 6.7, 4.8, 1.9 Hz, 1H), 7.01 – 6.94 (m, 2H), 3.81 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.4, 157.0, 149.4, 136.6, 131.9, 128.1, 121.3, 119.7, 114.0, 55.2.

2-(4-(Trifluoromethyl)phenyl)pyridine (**3c**)³

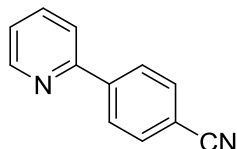


3c was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and 5,5-dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (194 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (3-5% Et₂O with 1% TEA/pentane) to afford the desired product as a colourless oil (101 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 8.73 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.15 – 8.09 (m, 2H), 7.84 – 7.75 (m, 2H), 7.75 – 7.71 (m, 2H),

(3) Martinez-Solorio, D.; Melillo, B.; Sanchez, L.; Liang, Y.; Lam, E.; Smith, A. B. *J. Am. Chem. Soc.* **2016**, *138*, 1836.

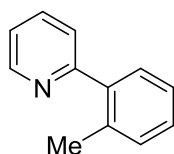
7.30 (ddd, $J = 7.0, 4.8, 1.6$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.8, 149.9, 142.7, 137.0, 130.8 (q, $J = 33.3$ Hz), 127.2, 125.7 (q, $J = 4.0$ Hz), 124.3 (q, $J = 273.7$ Hz), 123.0, 120.9.

4-(Pyridin-2-yl)benzonitrile (**3d**)⁴



3d was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (161 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (3-30% Et_2O with 1% TEA/pentane) to afford the desired product as a white solid (57 mg, 63%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 8.76 – 8.70 (m, 1H), 8.38 – 8.30 (m, 2H), 8.06 (dd, $J = 8.0, 1.1$ Hz, 1H), 8.00 – 7.85 (m, 3H), 7.43 (dd, $J = 7.6, 4.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) δ 155.5, 150.8, 144.2, 138.1, 133.4, 128.3, 124.4, 121.7, 119.3, 113.2.

2-(*o*-Tolyl)pyridine (**3e**)⁵



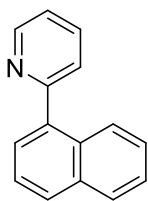
3e was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and 5,5-dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborinane (153 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (3% Et_2O with 1% TEA/pentane) to afford the desired product as a colourless oil (66 mg, 78%). ^1H NMR (400 MHz, CDCl_3) δ 8.70 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 7.75 (td, $J = 7.7, 1.9$ Hz, 1H), 7.40 (ddd, $J = 7.9, 2.2, 1.3$ Hz, 2H), 7.33 – 7.22 (m, 4H), 2.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.0, 149.1, 140.4, 136.2, 135.7, 130.7, 129.6, 128.3, 125.9, 124.1, 121.6, 20.3.

2-(Naphthalen-1-yl)pyridine (**3f**)⁶

(4) Kan, J.; Huang, S.; Lin, J.; Zhang, M.; Su, W.; *Angew. Chem. Int. Ed.* **2015**, 54, 2199.

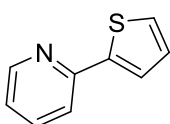
(5) Laha, J. K.; Jethava, K. P.; Patel, S.; Patel, K. V. *J. Org. Chem.* **2017**, 82, 76.

(6) Zhu, F.; Wang, Z-X. *J. Org. Chem.* **2014**, 79, 4285.



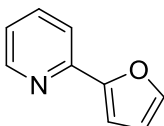
3f was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and 5,5-dimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane (180 mg, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et₂O with 1% TEA/pentane) to afford the desired product as a yellow oil (98 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 8.82 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.79 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.67 – 7.44 (m, 5H), 7.32 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.1, 149.3, 138.3, 136.3, 133.8, 131.0, 128.8, 128.2, 127.4, 126.4, 125.7, 125.5, 125.2, 124.9, 121.9.

2-(Thiophen-2-yl)pyridine (**3g**)⁷



3g was prepared from 2-chloropyridine (28 mg, 0.25 mmol) and 5,5-dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane (74 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15% Et₂O with 1% TEA/petroleum ether) to afford the desired product as yellow oil (30 mg, 75%). 0.25 mmol scale 0.25 mmol ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.55 – 8.47 (m, 1H), 7.88 – 7.76 (m, 2H), 7.73 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.54 (dt, *J* = 5.1, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1H), 7.14 (ddd, *J* = 4.8, 3.6, 0.9 Hz, 1H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 153.4, 150.3, 146.0, 137.6, 128.9, 128.6, 125.5, 122.9, 119.3.

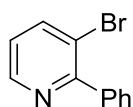
2-(furan-2-yl)pyridine (**3h**)⁶



(7) Luzung, M. R.; Patel, J. S.; Yin, J. *J. Org. Chem.* **2010**, 75, 8330.

3h was prepared from 2-chloropyridine (28 mg, 0.25 mmol) and 2-(furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (68 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15-20% of Et₂O with 1% TEA /petroleum ether) to afford the desired product as a colourless oil (33mg, 46%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.56 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.83 (td, *J* = 7.8, 1.8 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.24 (ddt, *J* = 6.9, 4.7, 1.0 Hz, 1H), 7.08 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.60 (dd, *J* = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 154.9, 150.5, 150.2, 144.4, 137.6, 122.9, 118.8, 112.9, 109.3.

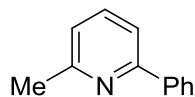
3-Bromo-2-phenylpyridine (**3i**)⁸



3i was prepared from 3-bromo-2-chloropyridine (96 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (2% acetone /petroleum ether) to afford the desired product as a colourless oil (74 mg, 63%) together with an impure mixture of 2-phenylpyridine **3a** (11 mg, ca. 14%).

¹H NMR (400 MHz, CDCl₃) δ 8.63 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.52 – 7.38 (m, 3H), 7.15 (dd, *J* = 8.0, 4.6 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 158.2, 148.0, 141.3, 139.5, 129.3, 128.8, 128.0, 123.2, 119.8.

2-Methyl-6-phenylpyridine (**3j**)⁹



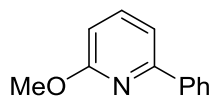
3j was prepared from 2-chloro-6-methylpyridine (64 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et₂O with 1% TEA/petroleum ether) to afford the desired product as a colourless oil (65 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.52 (dt, *J*

(8) Zhou, Q.; Zhang, B.; Su, L.; Jiang, T.; Chen, R.; Du, T.; Ye, Y.; Shen, J.; Dai, G.; Han, D.; Jiang, H. *Tetrahedron* **2013**, 69, 10996.

(9) Yuen, O. Y.; So, C. M.; Man, H. W.; Kwong, F. Y., *Chem. Eur. J.* **2016**, 22, 6471.

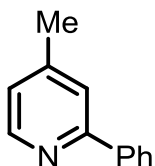
= 7.8, 0.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.10 (d, J = 7.6 Hz, 1H), 2.64 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 158.4, 157.0, 139.8, 136.9, 128.7, 128.7, 127.0, 121.6, 117.6, 24.8.

2-Methoxy-6-phenylpyridine (**3k**)¹⁰



3k was prepared from 2-bromo-6-methoxypyridine (94 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et_2O with 0.5% TEA/petroleum ether) to afford the desired product as a colourless oil (75 mg, 81%). ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 1.6 Hz, 1H), 8.05 (t, J = 1.4 Hz, 1H), 7.64 (dd, J = 8.2, 7.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 7.35 (dd, J = 7.5, 0.7 Hz, 1H), 6.70 (dd, J = 8.2, 0.7 Hz, 1H), 4.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.8, 154.7, 139.2, 139.1, 128.9, 128.6, 126.7, 112.8, 109.3, 53.2.

4-Methyl-2-phenylpyridine (**3l**)¹¹

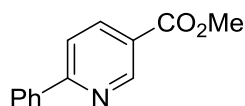


3l was prepared from 2-bromo-4-methylpyridine (86 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et_2O with 1% TEA/pentane) to afford the desired product as a white solid (72 mg, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.55 (dd, J = 5.0, 0.8 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.54 (dq, J = 1.6, 0.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 7.04 (ddt, J = 5.0, 1.4, 0.7 Hz, 1H), 2.40 (d, J = 0.8 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 157.3, 149.4, 147.8, 139.5, 128.8, 128.7, 126.9, 123.1, 121.6, 21.2.

Methyl 6-phenylnicotinate (**3m**)³

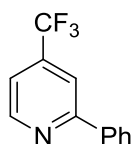
(10) Wang, X.; He, Y.; Ren, M.; Liu, S.; Liu, H.; Huang, G. *J. Org. Chem.* **2016**, *81*, 7958.

(11) Chen, M.; Micalizio, G. C.; *J. Am. Chem. Soc.* **2012**, *134*, 1352.



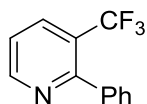
3m was prepared from methyl 6-chloronicotinate (86 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15% Et₂O with 1% TEA/petroleum ether) to afford the desired product as white solid (71 mg, 67%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 9.20 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.38 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.25 – 8.18 (m, 2H), 8.09 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.59 – 7.46 (m, 3H), 3.95 (s, 3H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 166.1, 161.2, 151.3, 139.0, 138.6, 130.8, 129.7, 128.1, 125.3, 120.6, 52.6.

2-Phenyl-4-(trifluoromethyl)pyridine (**3n**)¹²



3n was prepared from 2-bromo-4-(trifluoromethyl)pyridine (113 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et₂O with 1% TEA/petroleum ether) to afford the desired product as a colorless oil (86 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.87 (dt, *J* = 5.0, 0.8 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.93 (dq, *J* = 1.6, 0.8 Hz, 1H), 7.56 – 7.41 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 150.7, 139.2 (q, *J* = 33.1 Hz), 138.1, 129.9, 129.0, 127.1, 123.0 (q, *J* = 273.7 Hz), 117.6 (q, *J* = 3.0 Hz), 116.1 (q, *J* = 4.0 Hz).

2-Phenyl-3-(trifluoromethyl)pyridine (**3o**)¹³



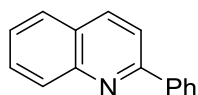
3o was prepared from 2-bromo-3-(trifluoromethyl)pyridine (113 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et₂O with 0.5% TEA/petroleum ether) to afford the desired product as a colourless oil (67 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 8.85 (ddd, *J* = 4.7, 1.7, 0.8 Hz,

(12) Rosner, S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2016**, 55, 10463.

(13) Lin, X.; Hou, C.; Li, H.; Weng, Z. *Chem. Eur. J.* **2016**, 22, 2075.

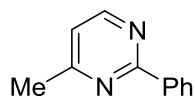
1H), 8.09 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.58 – 7.36 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 158.5, 151.8, 139.1, 135.0 (q, $J = 5.1$ Hz), 128.9, 128.7 (q, $J = 1.0$ Hz), 128.1, 125.1 (q, $J = 18.2$ Hz), 122.3 (q, $J = 274.7$ Hz), 121.8.

2-Phenylquinoline (**3p**)⁹



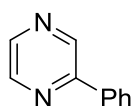
3p was prepared from 2-chloroquinoline (82 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (2-10% Et_2O /pentane) to afford the desired product as a colorless oil (83 mg, 81%) ^1H NMR (400 MHz, CDCl_3) δ 8.25 – 8.15 (m, 4H), 7.92 – 7.79 (m, 2H), 7.74 (s, 1H), 7.60 – 7.44 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 157.4, 148.3, 139.7, 136.8, 129.7, 129.7, 129.4, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0.

4-Methyl-2-phenylpyrimidine (**3q**)¹⁴



3q was prepared from 2-chloro-4-methylpyrimidine (64 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et_2O with 0.5% TEA/petroleum ether) to afford the desired product as a colourless oil (60 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 8.65 (d, $J = 5.1$ Hz, 1H), 8.48 – 8.40 (m, 2H), 7.52 – 7.44 (m, 3H), 7.05 (d, $J = 5.0$ Hz, 1H), 2.59 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.3, 164.3, 156.7, 137.8, 130.6, 128.5, 128.2, 118.6, 24.4.

2-Phenylpyrazine (**3r**)¹⁵



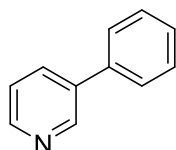
(14) Zhao, D.; Wang, T.; Shen, Q.; Li, J. *Chem. Comm.* **2014**, 50, 4302.

(15) Thapa, S.; Basnet, P.; Gurung, S. K.; Giri, R. *Chem. Comm.* **2015**, 51, 4009.

3r was prepared from 2-chloropyrazine (29 mg, 0.25 mmol) and PhB(neo) (72 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (10% Et₂O with 1% TEA/petroleum ether) to afford the desired product as white solid (27.7 mg, 71%).

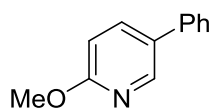
¹H NMR (400 MHz, CDCl₃) δ 9.04 (d, *J* = 1.6 Hz, 1H), 8.64 (dd, *J* = 2.5, 1.6 Hz, 1H), 8.52 (d, *J* = 2.5 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.57 – 7.44 (m, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 153.1, 144.4, 142.5, 141.9, 136.2, 130.2, 129.2, 127.1.

3-Phenylpyridine (**3s**)⁹



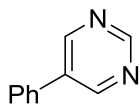
3s was prepared from 3-bromopyridine (40 mg, 0.25 mmol) and PhB(neo) (71 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (10% Et₂O with 1% TEA/pentane) to afford the desired product as a colourless oil (21 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ 8.85 (dd, *J* = 2.4, 0.9 Hz, 1H), 8.59 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.89 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.34 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.1, 148.0, 137.7, 136.8, 134.7, 129.1, 128.2, 127.2, 123.7.

2-Methoxy-5-phenylpyridine (**3t**)¹⁰



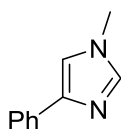
3t was prepared from 5-bromo-2-methoxypyridine (94 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5% Et₂O with 1% TEA/pentane) to afford the desired product as a colourless oil (61 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 8.39 (dd, *J* = 2.6, 0.8 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.49 – 7.41 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 6.82 (dd, *J* = 8.6, 0.8 Hz, 1H), 3.99 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 163.6, 145.0, 137.9, 137.6, 130.2, 129.0, 127.4, 126.7, 110.9, 53.6.

5-Phenylpyrimidine (**3u**)¹⁰



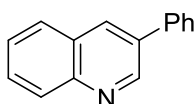
3u was prepared from 5-bromopyrimidine (80 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (30% DCM with 1% TEA/ pentane) to afford the desired product as a yellow oil (68mg, 87%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 9.14 (s, 1H), 9.05 (d, *J* = 1.6 Hz, 2H), 7.82 – 7.71 (m, 2H), 7.61 – 7.45 (m, 3H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 158.3, 155.6, 135.4, 134.9, 130.2, 129.7, 127.9.

1-Methyl-4-phenyl-1*H*-imidazole (**3v**)¹⁶



3v was prepared from 4-bromo-1-methyl-1*H*-imidazole (81 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (20% acetone / dichloromethane) to afford the desired product as a colourless oil (61 mg, 77%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.81 (dd, *J* = 2.0, 1.4 Hz, 1H), 7.79 (t, *J* = 1.0 Hz, 1H), 7.51 (d, *J* = 1.3 Hz, 1H), 7.45 (d, *J* = 1.3 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.19 – 7.13 (m, 1H), 3.76 (s, 3H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 142.5, 139.1, 136.1, 129.2, 126.9, 125.3, 117.2, 33.4.

3-Phenylquinoline (**3w**)¹⁷



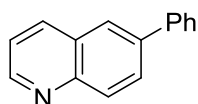
3w was prepared from 3-bromoquinoline (104 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5-30%

(16) Kuma, S.; Jaller, D.; Patel, B.; LaLonde, J. M.; DuHadaway, J. B.; Malachowski, W. P.; Prendergast, G. C.; Muller, A. J. *J. Med. Chem.* **2008**, *51*, 4968.

(17) Qiu, D.; Jin, L.; Zheng, Z.; Meng, H.; Mo, F.; Wang, X.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 1923.

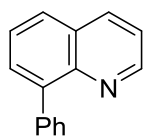
Et₂O with 1% TEA/pentane) to afford the desired product as a colourless oil (80 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 9.19 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.34 – 8.28 (m, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.89 (dq, *J* = 8.2, 1.4 Hz, 1H), 7.78 – 7.68 (m, 3H), 7.56 (dddd, *J* = 22.7, 8.0, 6.6, 1.4 Hz, 3H), 7.44 (td, *J* = 7.4, 1.4 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.8, 147.3, 137.8, 133.8, 133.3, 129.4, 129.2, 129.2, 128.1, 128.0, 127.4, 127.0.

6-Phenylquinoline (**3x**)⁹



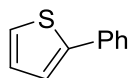
3x was prepared from 6-bromoquinoline (104 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (30% Et₂O with 1% TEA/pentane) to afford the desired product as a white solid (65 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.92 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.8, 6.0 Hz, 2H), 7.99 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.50 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.46 – 7.38 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.2, 147.5, 140.3, 139.5, 136.5, 129.8, 129.4, 129.0, 128.5, 127.8, 127.5, 125.5, 121.5.

8-Phenylquinoline (**3y**)¹⁰



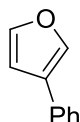
3y was prepared from 8-bromoquinoline (104 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (10% Et₂O with 1% TEA/pentane) to afford the desired product as a yellow oil (76 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.62 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.50 – 7.38 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.2, 146.0, 140.9, 139.6, 136.3, 130.6, 130.3, 128.7, 128.0, 127.5, 127.4, 126.3, 121.0.

2-Phenylthiophene (**3z**)³



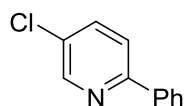
3z was prepared from 2-bromothiophene (82 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (petroleum ether) to afford the desired product as a yellow solid (59mg, 75%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.71 – 7.63 (m, 2H), 7.48 – 7.37 (m, 4H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.7 Hz, 1H). ¹³C NMR (101 MHz, (CD₃)₂CO) δ 144.9, 135.2, 129.9, 129.1, 128.3, 126.5, 125.9, 124.2.

3-Phenylfuran (**3aa**)¹⁸



3aa was prepared from 3-bromofuran (74 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (petroleum ether) to afford the desired product as a white solid (44mg, 61%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.01 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.66 – 7.58 (m, 3H), 7.42 – 7.34 (m, 2H), 7.30 – 7.23 (m, 1H), 6.88 (dd, *J* = 1.9, 0.9 Hz, 1H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 144.9, 139.8, 133.4, 129.6, 127.7, 127.3, 126.5, 109.5.

5-Chloro-2-phenylpyridine (**3ab**)¹⁹

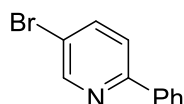


(18) Heijne, D.; Tosi, F.; Vila, C.; Stuart, M.C.A.; Elsinga, P. H.; Szymanski, W.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2017**, *56*, 3354.

(19) Liu, K. M.; Liao, L. Y.; Duan, X. F. *Chem. Comm.* **2015**, *51*, 1124.

3ab was prepared from 2,5-dichloropyridine (74 mg, 0.5 mmol) and PhB(neo) (114 mg, 0.6 mmol, 1.2 eq). The crude mixture was purified by flash column chromatography (1-5% Et₂O /petroleum ether) to afford the desired product as a white solid (89 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ 8.64 (dd, *J* = 2.5, 0.8 Hz, 1H), 8.03 – 7.91 (m, 2H), 7.78 – 7.63 (m, 2H), 7.54 – 7.37 (m, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 155.6, 148.4, 138.1, 136.7, 130.7, 129.4, 128.9, 126.9, 121.3.

5-Bromo-2-phenylpyridine (**3ac**)

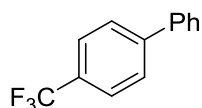


3ac was prepared from 5-bromo-2-chloropyridine (96 mg, 0.5 mmol) and PhB(neo) (114 mg, 0.6 mmol, 1.2 eq). The crude mixture was purified by flash column chromatography (1-5% Et₂O /petroleum ether) to afford the desired product as a white solid (87 mg, 74%) together with 2-Chloro-5-phenylpyridine (**3ac'**) (8 mg, 8%).

3ac:²⁰ ¹H NMR (400 MHz, CDCl₃) δ 8.74 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.02 – 7.92 (m, 2H), 7.87 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.63 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.54 – 7.38 (m, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 156.0, 150.7, 139.5, 138.2, 129.5, 129.0, 126.9, 121.8, 119.4.

3ac':²¹ ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 2.5 Hz, 1H), 7.84 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 (ddd, *J* = 7.6, 6.7, 1.4 Hz, 2H), 7.42 (dd, *J* = 12.6, 7.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 148.1, 137.3, 136.6, 135.8, 129.3, 128.6, 127.1, 124.3.

4-(Trifluoromethyl)-1,1'-biphenyl (**3ae**)⁹



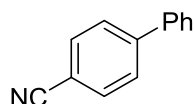
3ae was prepared from 1-bromo-4-(trifluoromethyl)benzene (56 mg, 0.25 mmol) and PhB(neo) (71 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (petroleum ether) to afford the desired product as a white solid (43 mg 77%).

(20) Wang, J.; Wang, S.; Wang, G.; Zhang, J.; Yu, X. *Chem. Comm.* **2012**, 48, 11769.

(21) Zhang, E.; Tang, J.; Li, S.; Wu, P.; Moses, J. E.; Sharpless, K. B. *Chem. A Eur. J.* **2016**, 22, 5692

^1H NMR (400 MHz, CDCl_3) δ 7.70 (s, 4H), 7.63 – 7.58 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 144.8 (q, 2.0 Hz), 139.9, 129.3 (d, $^2J = 32.3$ Hz), 129.1, 128.8, 128.3, 127.4, 127.3, 125.8 (q, $^3J = 3.0$ Hz), 121.7 (q, $J = 272.7$ Hz).

[1,1'-Biphenyl]-4-carbonitrile (**3af**)⁹

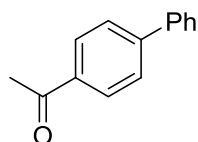


3af was prepared from 4-bromobenzonitrile (46 mg, 0.25 mmol) and PhB(neo) (71 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15% DCM with 1% TEA/ petroleum ether) to afford the desired product as a white solid (33 mg, 74%).

3af was prepared from 4-chlorobenzonitrile (34 mg, 0.25 mmol) and PhB(neo) (71 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15% DCM with 1% TEA/ petroleum ether) to afford the desired product as a white solid (27 mg, 60%).

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.88 (m, $J = 2.0$ Hz, 4H), 7.77 – 7.71 (m, 2H), 7.57 – 7.49 (m, 2H), 7.46 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) δ 146.2, 139.9, 133.5, 130.0, 129.5, 128.6, 128.0, 119.4, 111.8.

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (**3ag**)²²

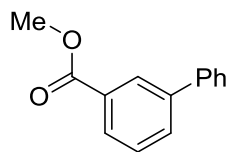


3ag was prepared from 5-bromo-2-chloropyridine (99 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (10-20% Et_2O with 1% TEA/petroleum ether) to afford the desired product as a white solid (51 mg, 52%). ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.01 (m, 2H), 7.71 – 7.67 (m, 2H), 7.66 – 7.61

(22) Penafiel, I., Pastor, I. M., Yus, M., *Eur. J. Org. Chem.* **2013**, 1479.

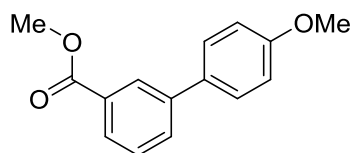
(m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 2.65 (s, 3H). ^{13}C { ^1H } NMR (101 MHz, CDCl_3) δ 197.8, 145.9, 140.0, 135.9, 129.0, 129.0, 128.3, 127.4, 127.3, 26.8.

Methyl [1,1'-biphenyl]-3-carboxylate (**3ah**)⁹



3ah was prepared from methyl 3-bromobenzoate (108 mg, 0.5 mmol) and PhB(neo) (143 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (5-20% DCM with 1% TEA/ petroleum ether) to afford the desired product as a colourless oil (69mg, 65%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 8.26 (t, J = 1.8 Hz, 1H), 8.00 (dt, J = 7.7, 1.4 Hz, 1H), 7.92 (ddd, J = 7.8, 2.0, 1.2 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.61 (td, J = 7.8, 0.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.46 – 7.38 (m, 1H), 3.92 (s, 3H). ^{13}C { ^1H } NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) δ 167.1, 142.2, 140.7, 132.2, 131.8, 130.0, 129.8, 129.0, 128.7, 128.5, 127.8, 52.4.

Methyl 4'-methoxy-[1,1'-biphenyl]-3-carboxylate (**3ak**)²³

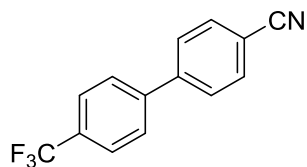


3ak was prepared from methyl 3-bromobenzoate (108 mg, 0.5 mmol) and 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (165 mg, 0.75 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (20% DCM with 1% TEA/ petroleum ether) to afford the desired product as a white solid (88 mg, 73%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 8.24 – 8.19 (m, 1H), 7.95 (ddd, J = 7.7, 1.7, 1.2 Hz, 1H), 7.88 (ddd, J = 7.8, 2.0, 1.1 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.57 (td, J = 7.8, 0.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C { ^1H } NMR (101 MHz, $(\text{CD}_3)_2\text{CO}$) δ 160.7, 141.8, 133.0, 131.7, 129.9, 128.8, 128.3, 127.9, 115.2, 55.6, 52.4.

4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (**3al**)²⁴

(23) Leowanawat, P.; Zhang, N.; Resmerita, A-M.; Rosen, B. M.; Percec, V. *J. Org. Chem.* **2011**, 76, 9946.

(24) Hua, X.; Masson-Makdissi, J.; Sullivan, R. J.; Newman, S. G. *Org. Lett.* **2016**, 18, 5312.



3al was prepared from 4-chlorobenzonitrile (34 mg, 0.25 mmol) and PhB(neo) (72 mg, 0.375 mmol, 1.5 eq). The crude mixture was purified by flash column chromatography (15% Et₂O /petroleum ether) to afford the desired product as a white solid (58 mg, 93%). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.01 – 7.91 (m, 6H), 7.89 – 7.84 (m, 2H). ¹³C{¹H} NMR (101 MHz, (CD₃)₂CO) δ 144.6, 143.8, 133.7, 130.8 (q, *J* = 32.3 Hz), 129.0, 128.9, 126.8 (q, *J* = 4.0 Hz), 125.3 (q, *J* = 271.7 Hz), 119.1, 112.8.

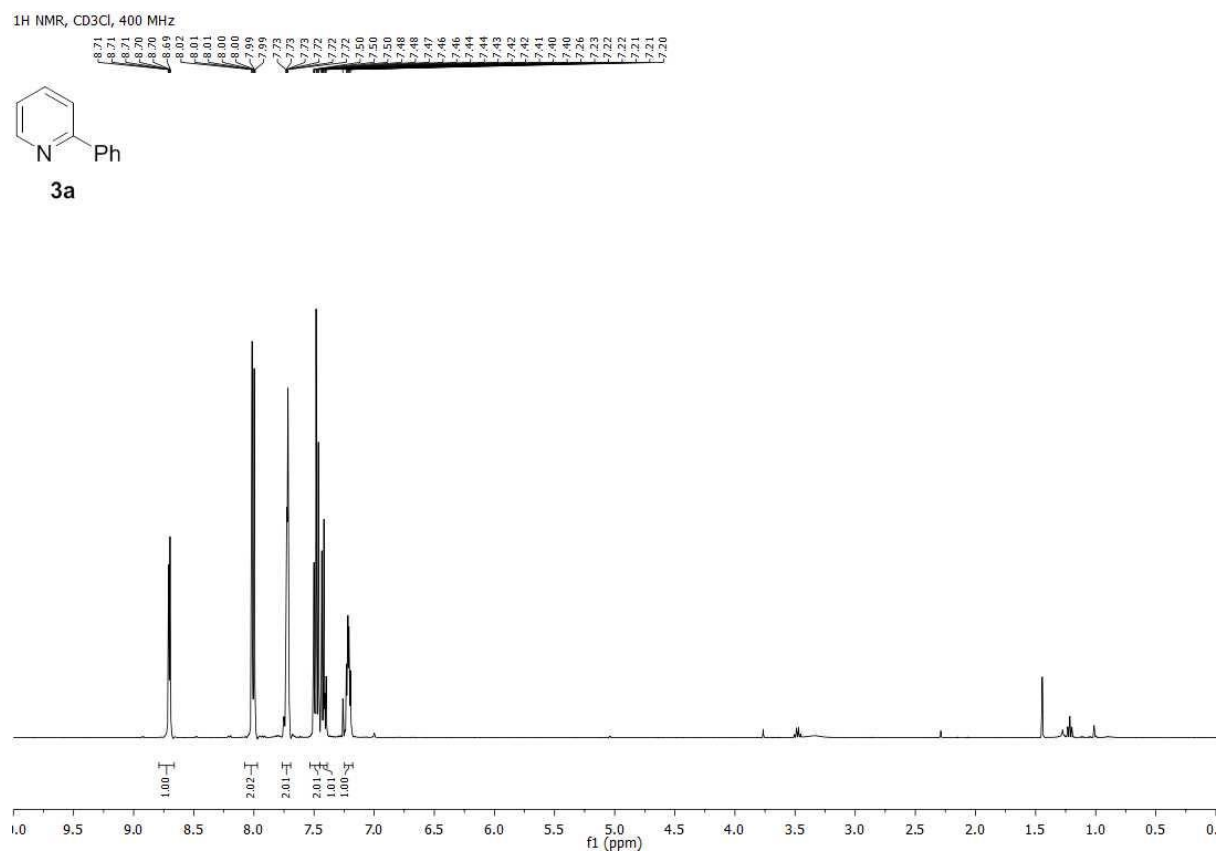


Figure S1. ¹H Spectra of **3a**

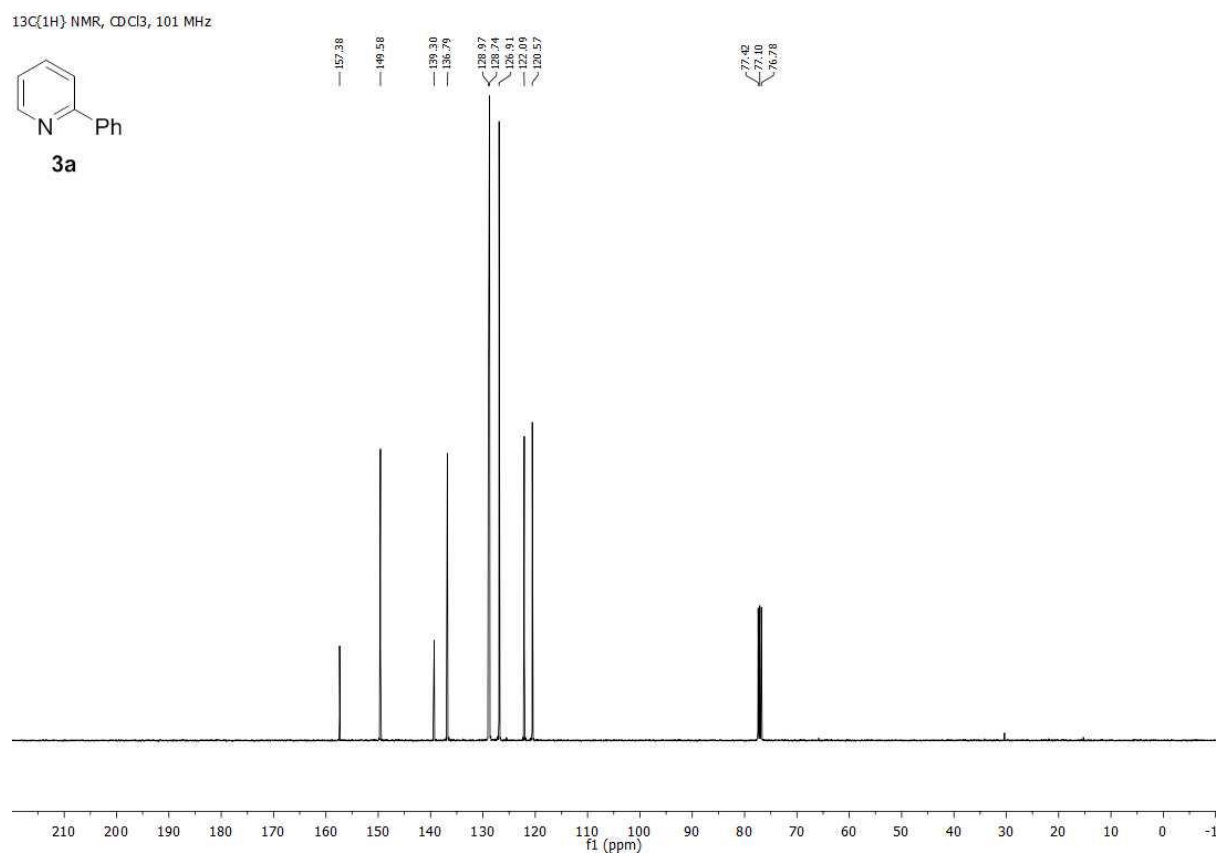


Figure S2. ¹³C Spectra of **3a**

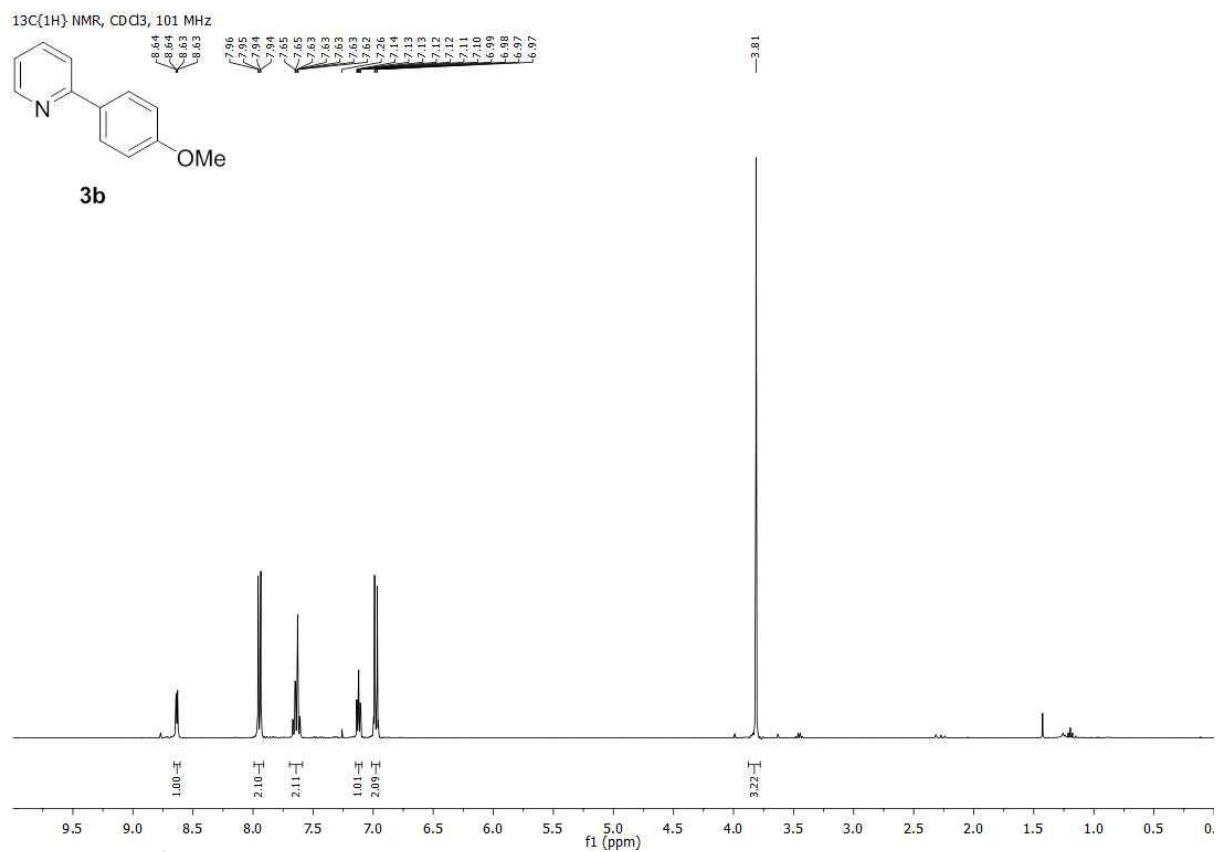


Figure S3. ¹H Spectra of **3b**

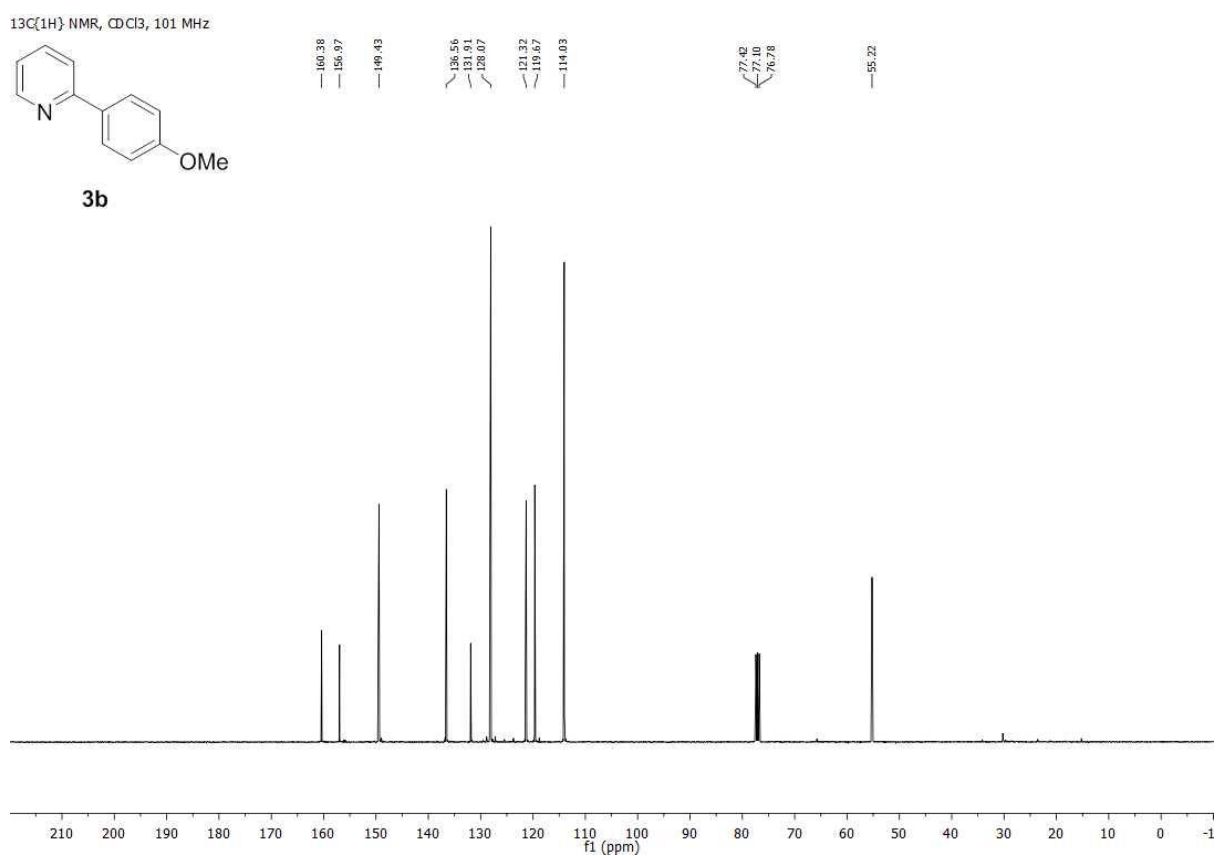


Figure S4. ¹³C Spectra of **3b**

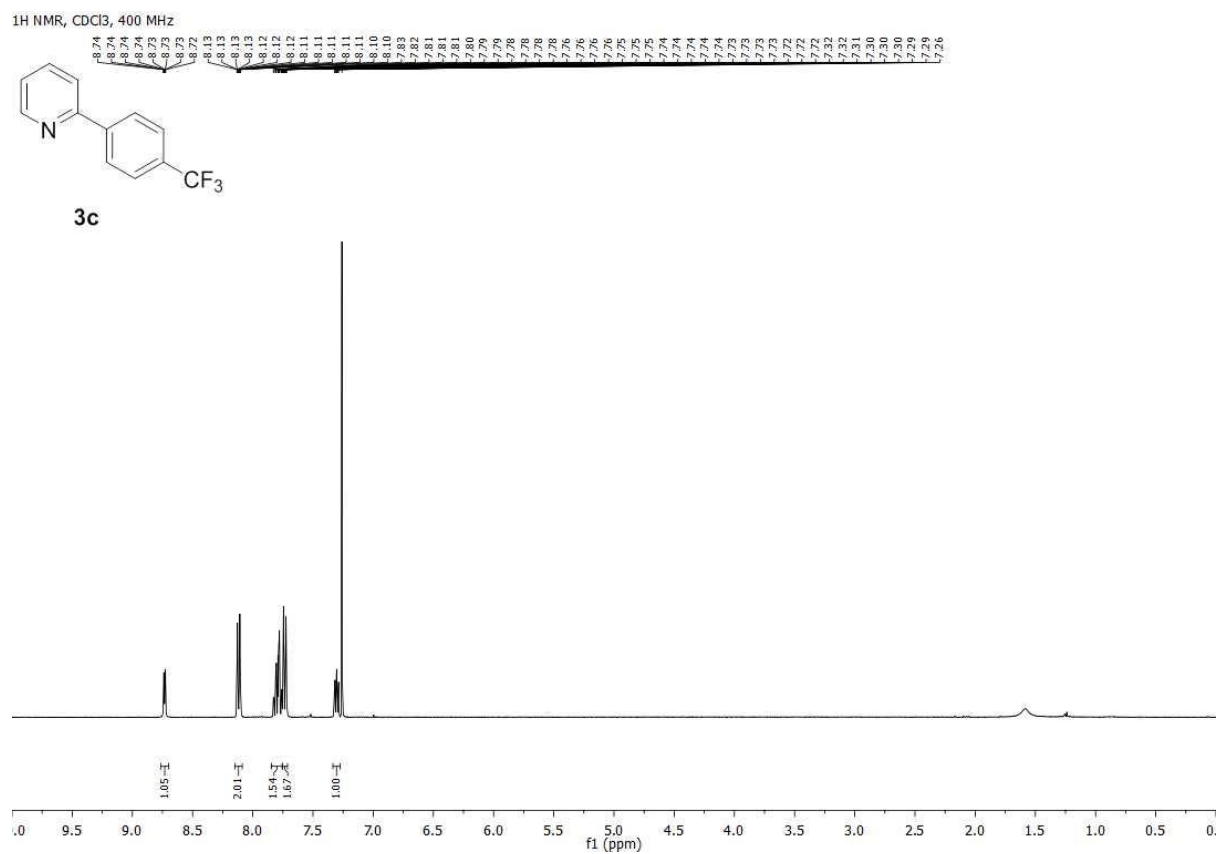


Figure S5. ¹H Spectra of **3c**

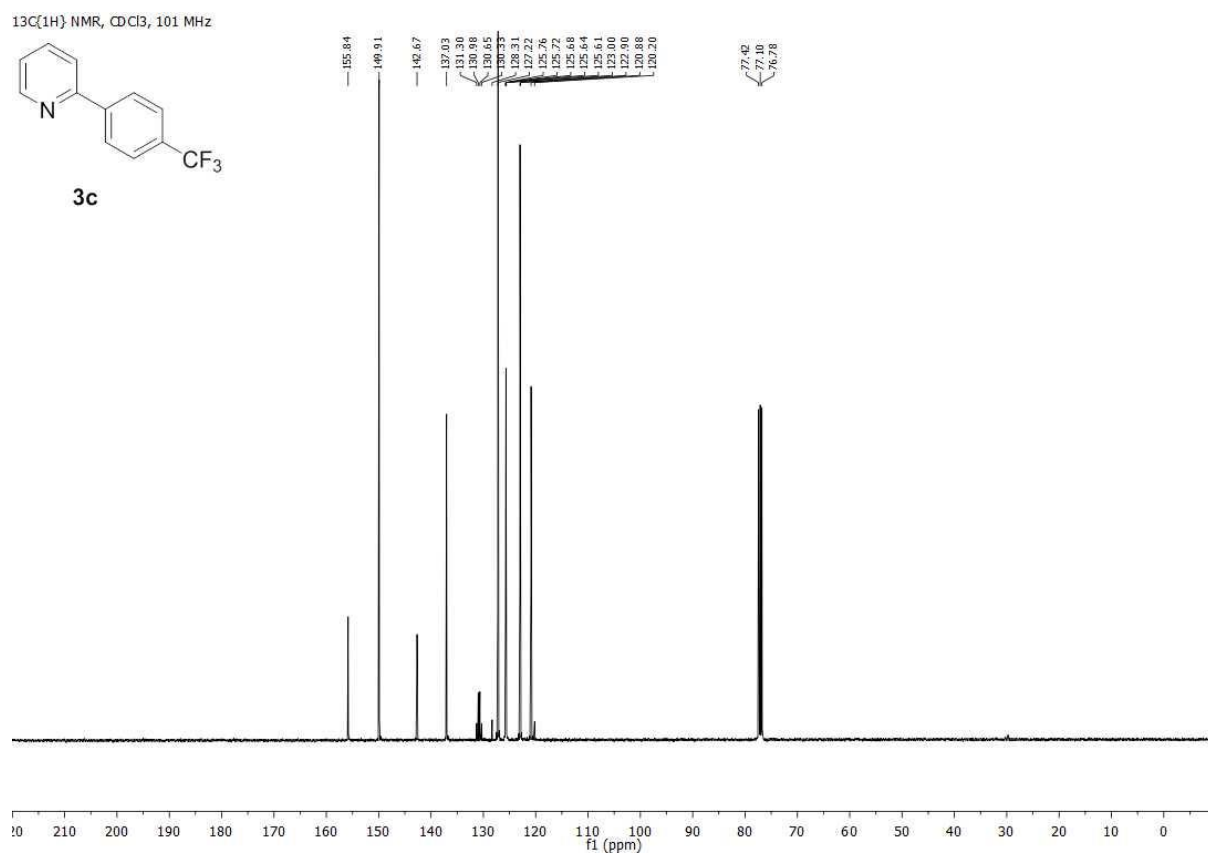


Figure S6. ¹³C Spectra of **3c**

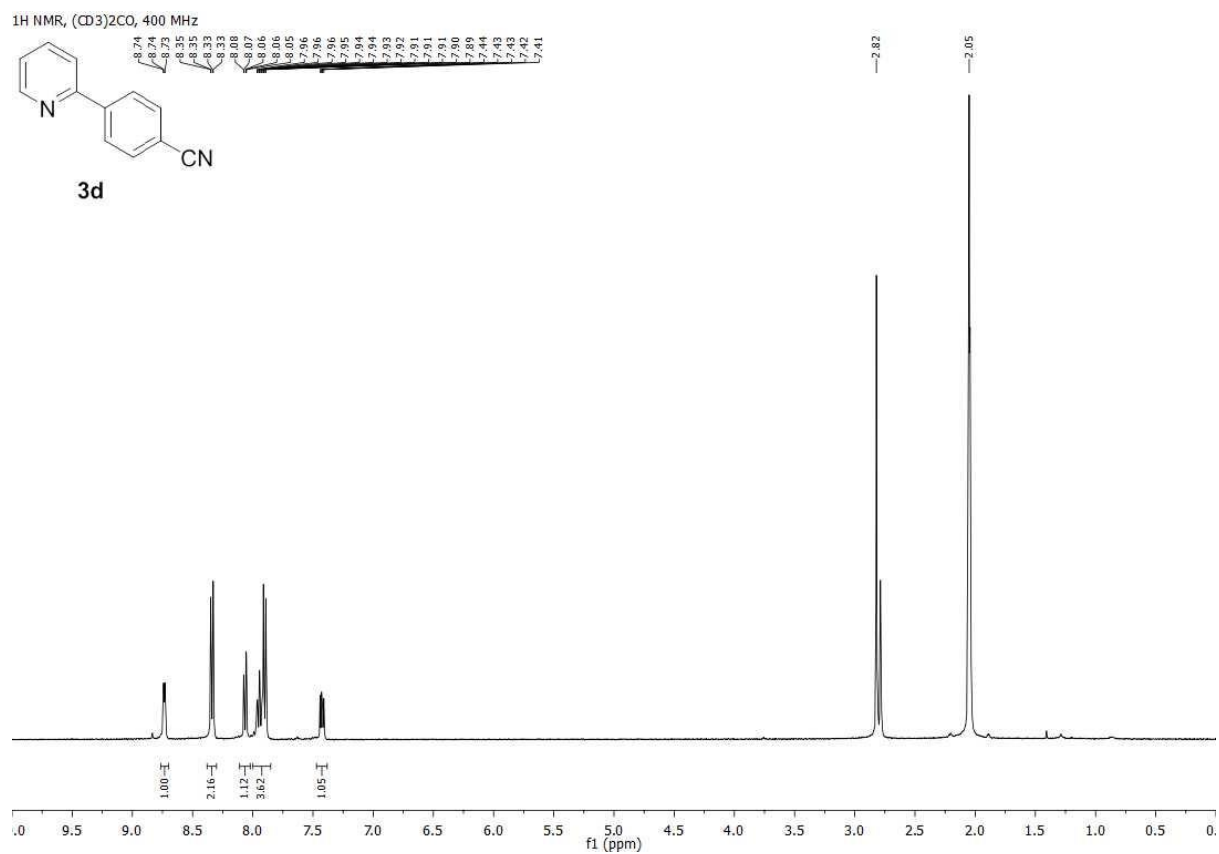


Figure S7. ¹H Spectra of **3d**

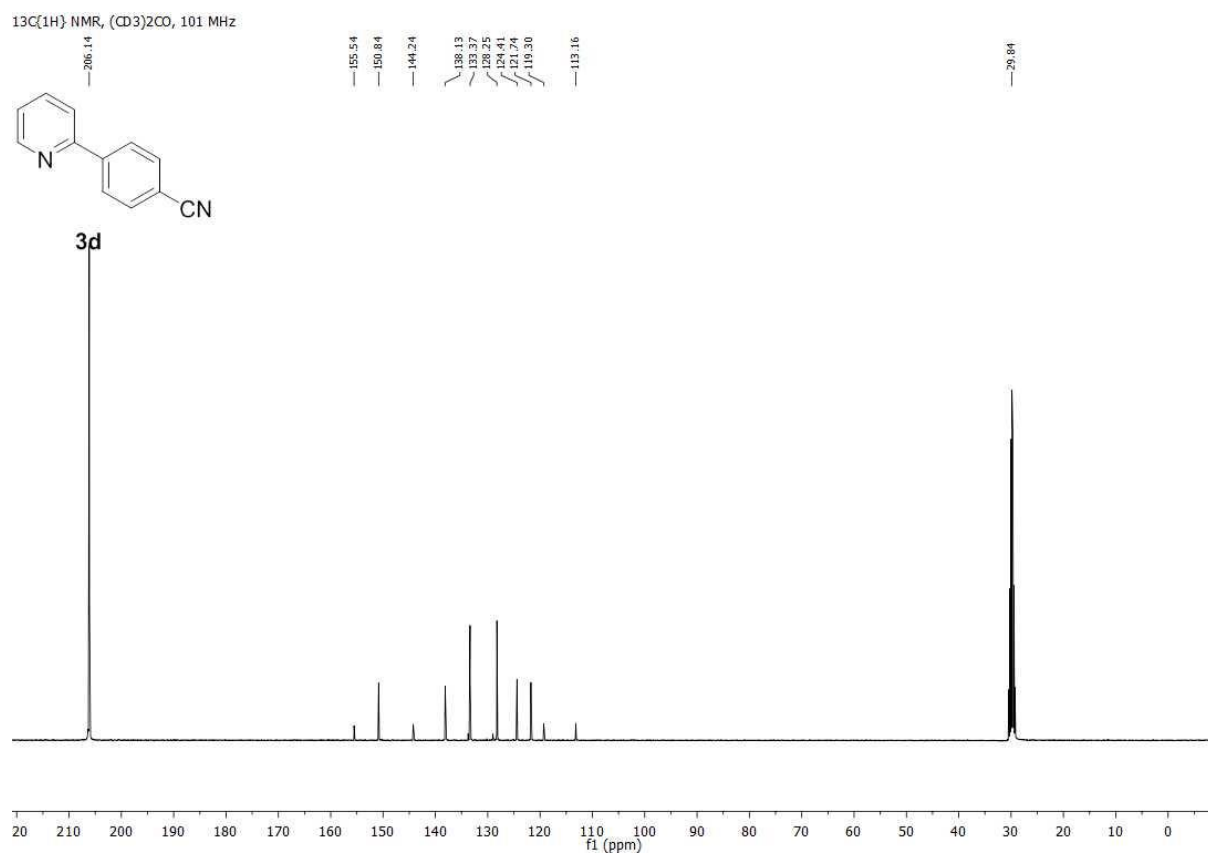


Figure S8. ¹³C Spectra of **3d**

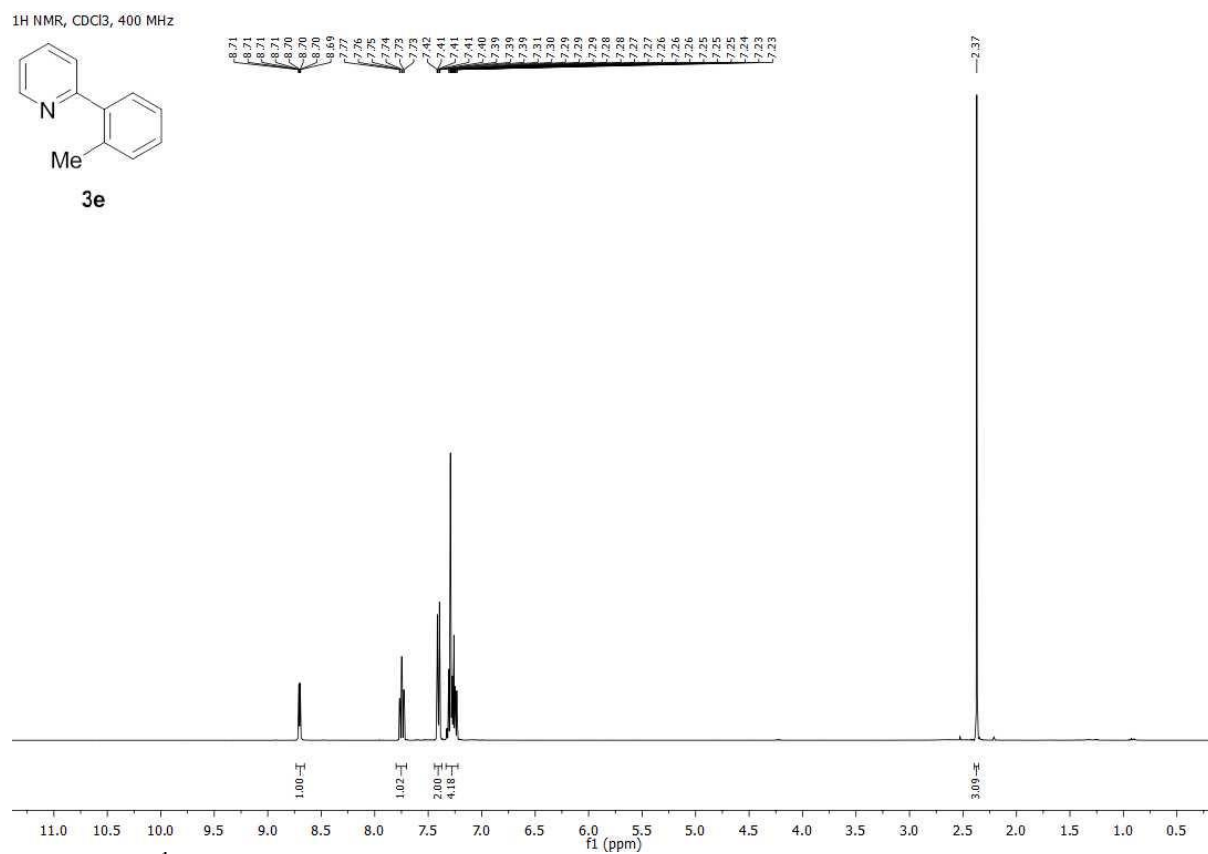


Figure S9. ¹H Spectra of **3e**

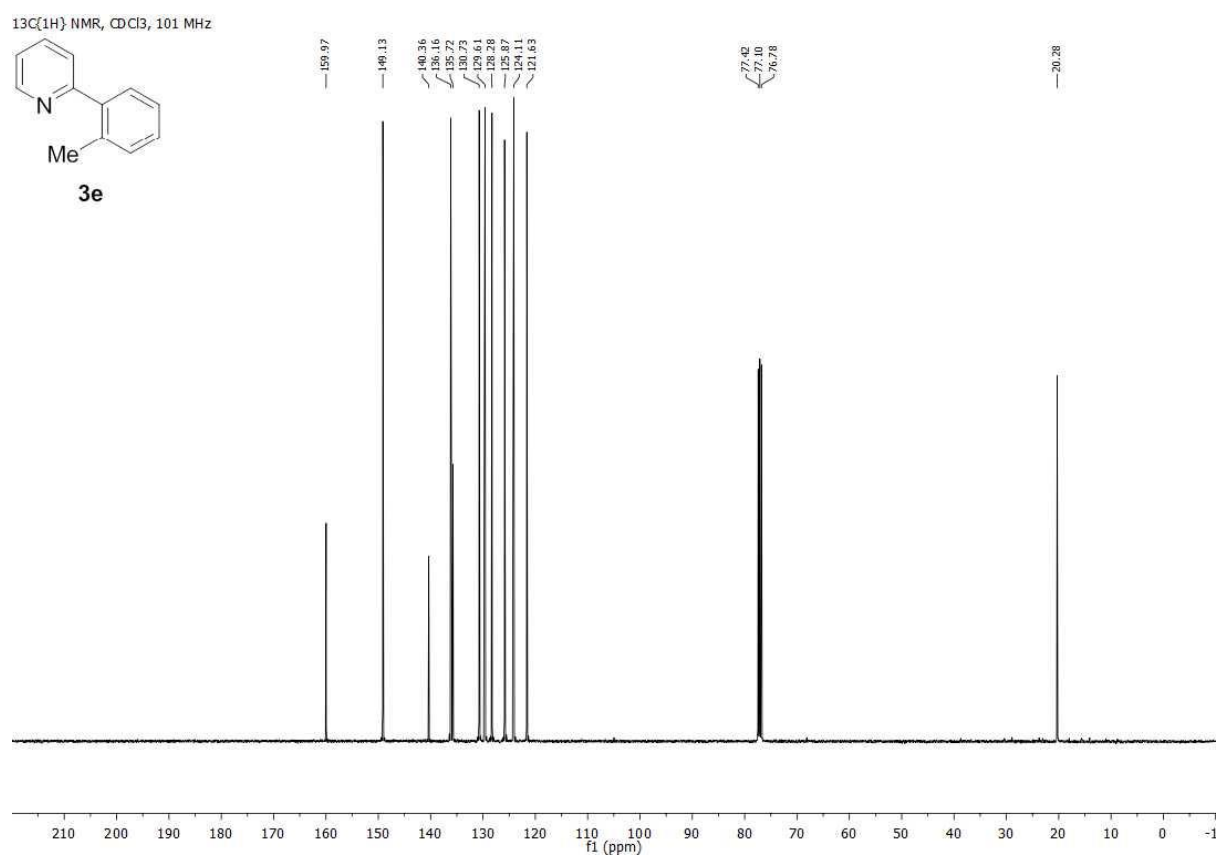


Figure S10. ¹³C Spectra of **3e**

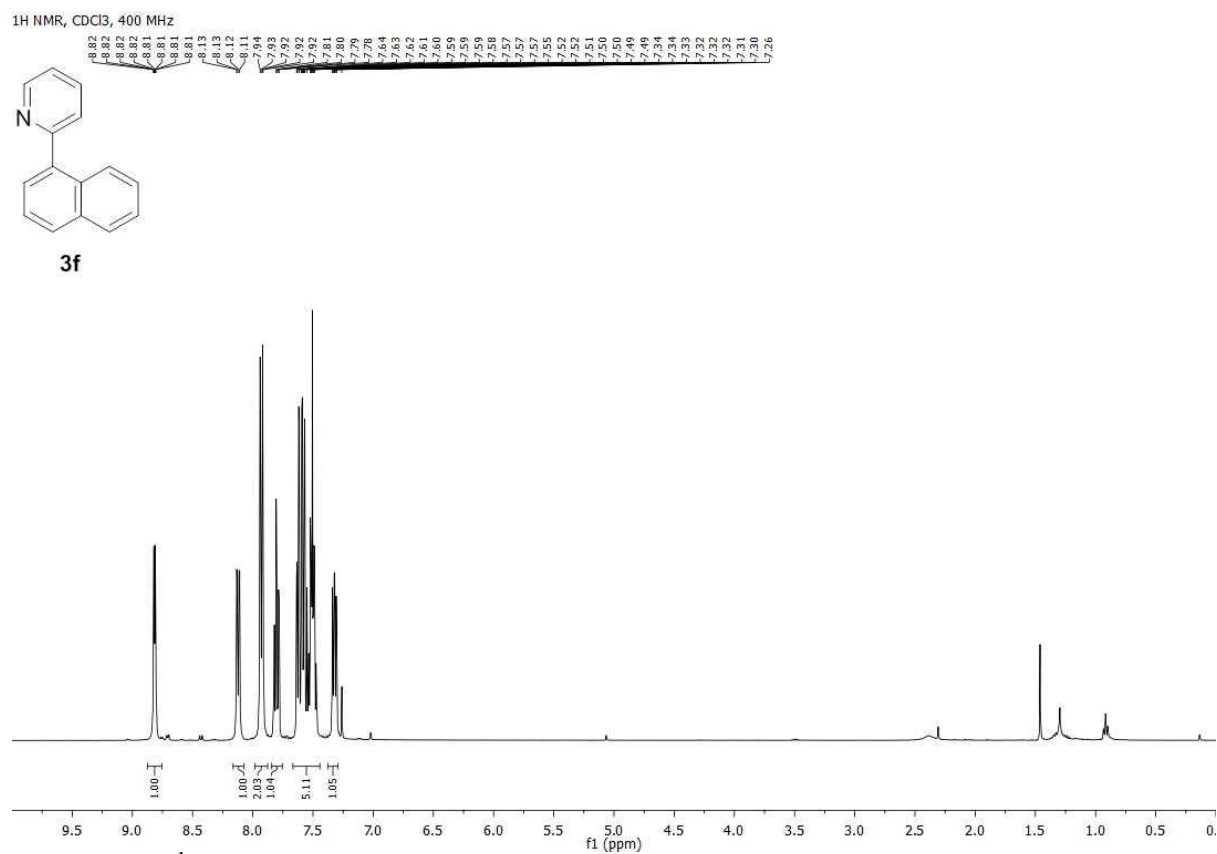


Figure S11. ¹H Spectra of **3f**

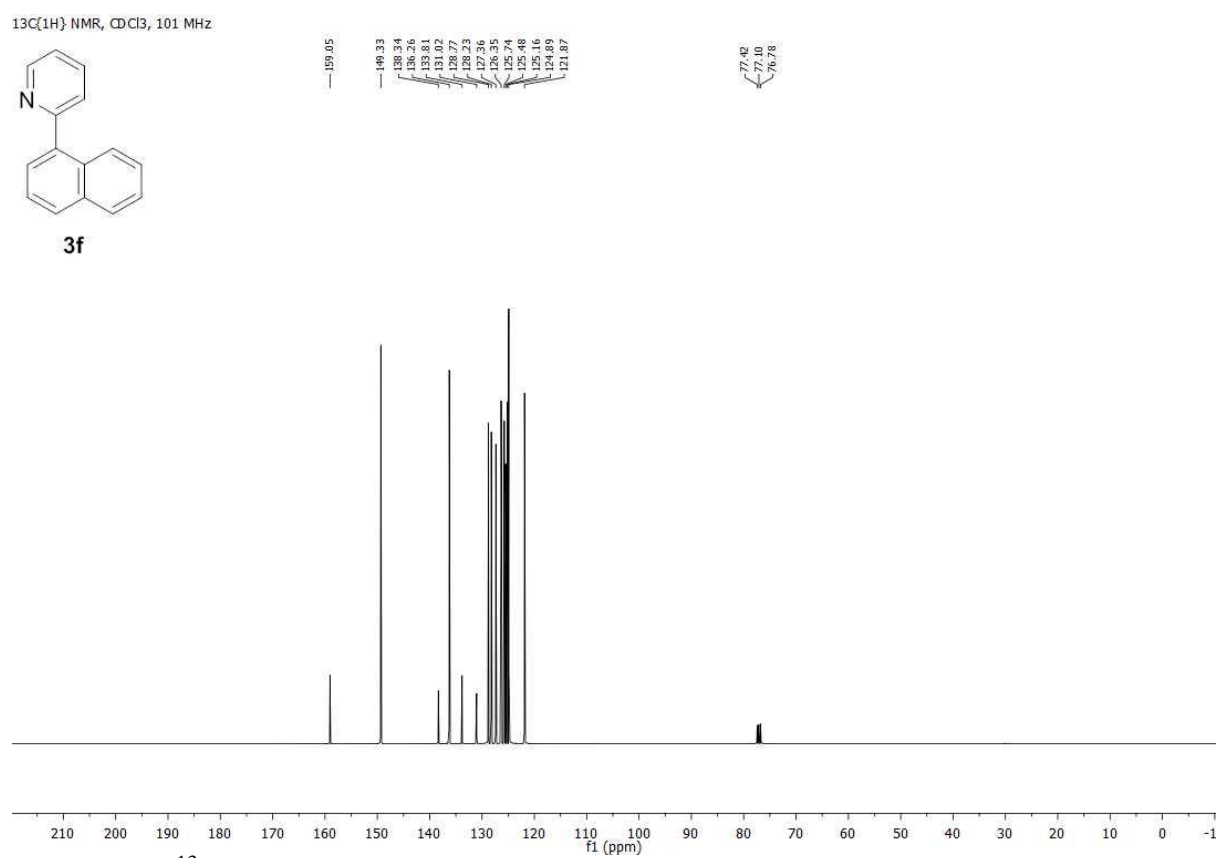


Figure S12. ¹³C Spectra of **3f**

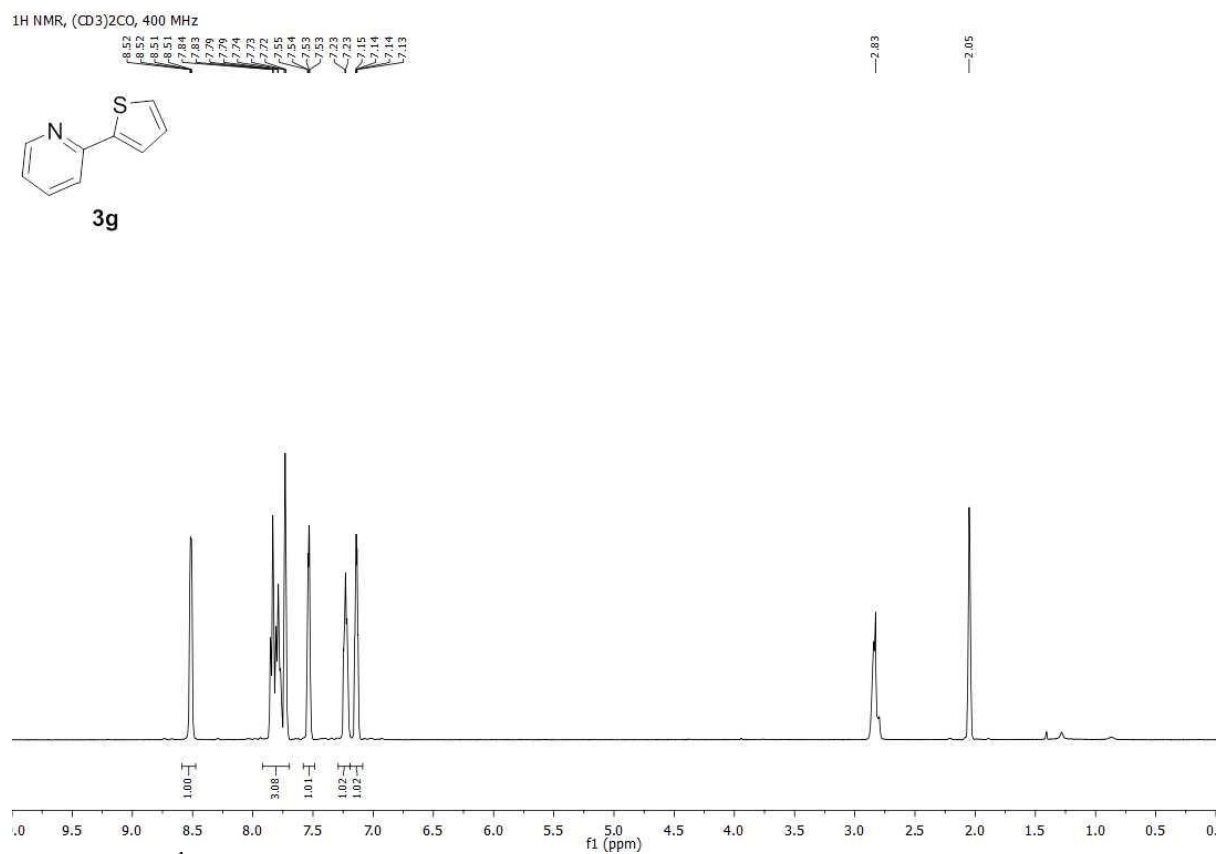


Figure S13. ¹H Spectra of **3g**

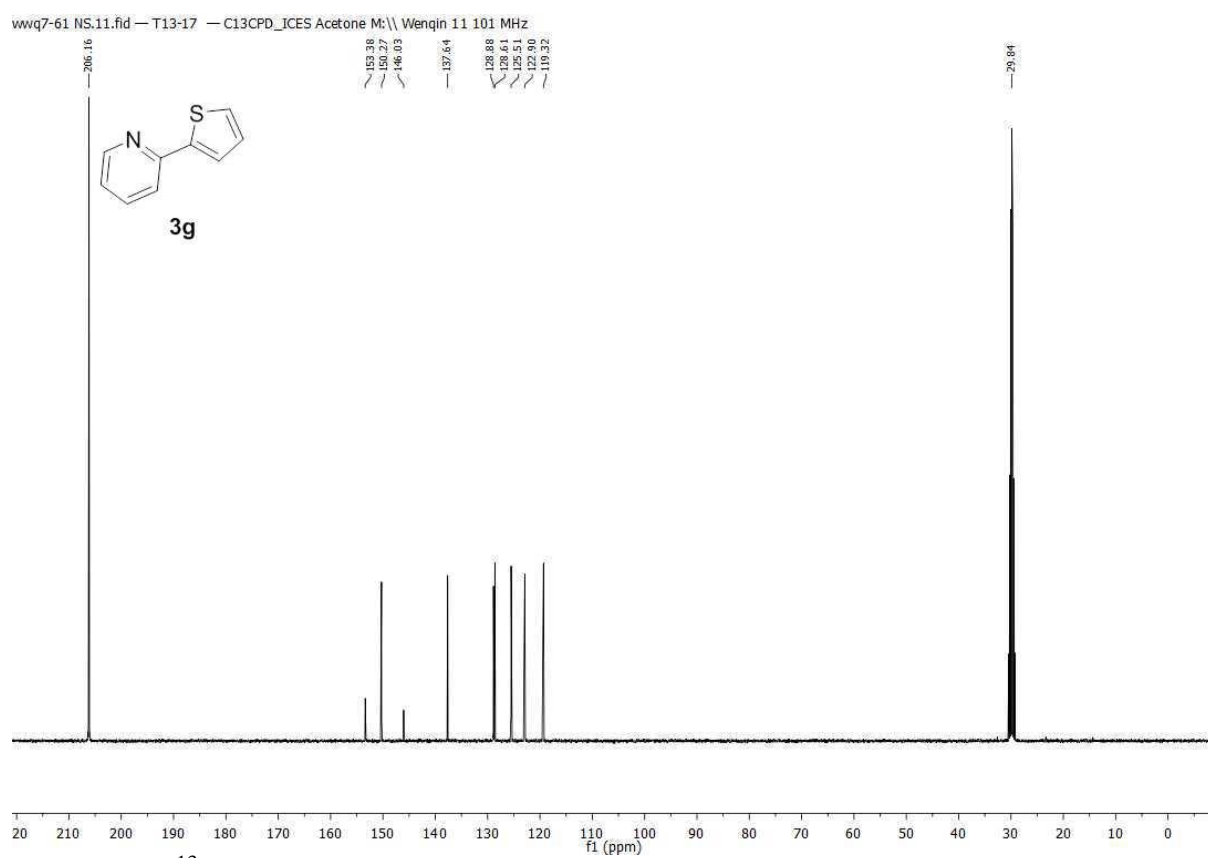


Figure S14. ¹³C Spectra of **3g**

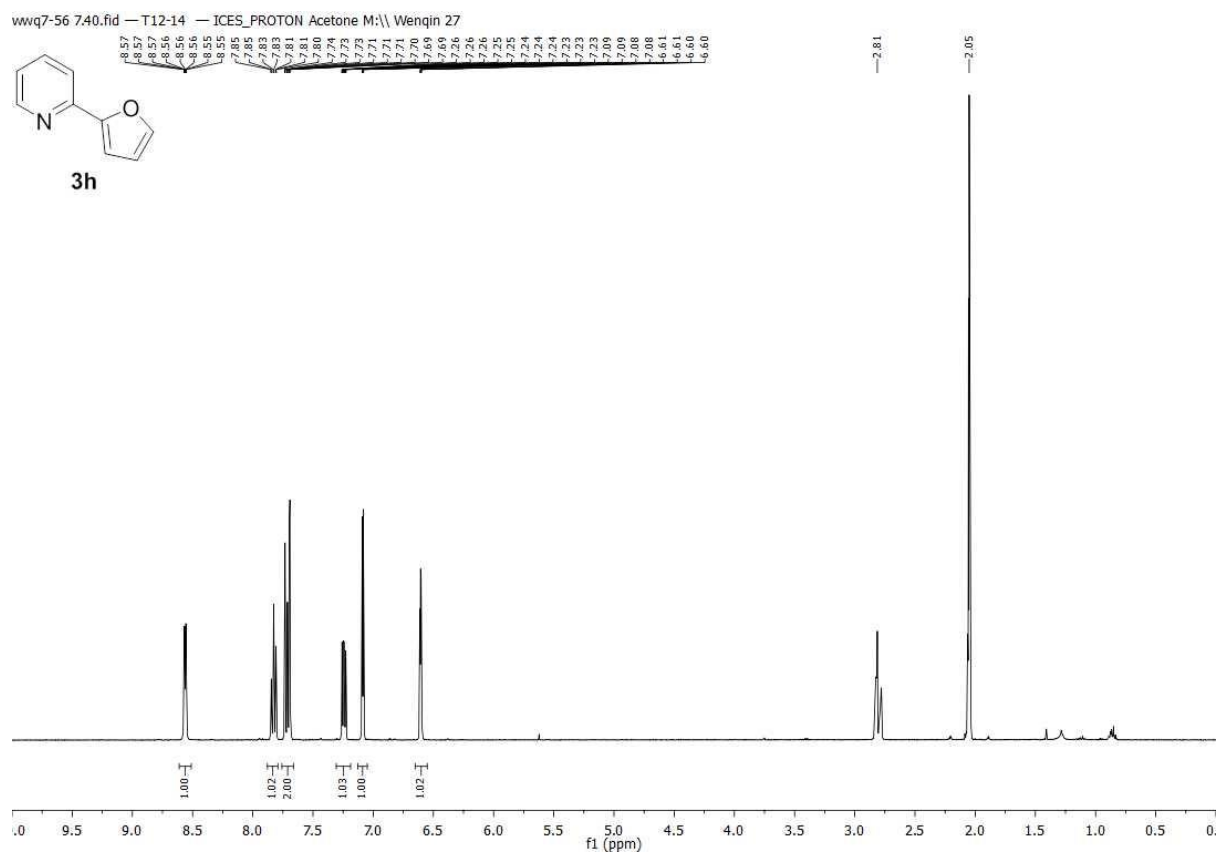


Figure S15. ^1H Spectra of **3h**

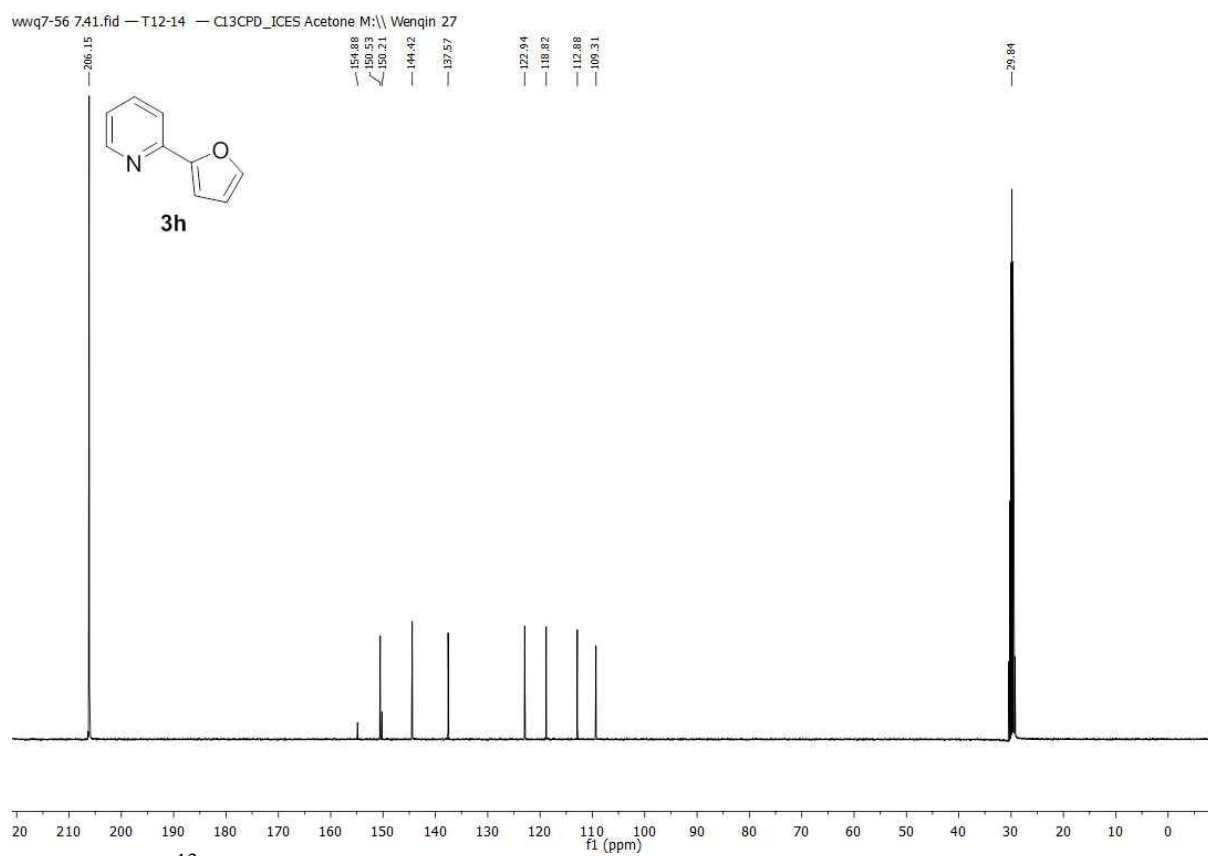


Figure S16. ^{13}C Spectra of **3h**

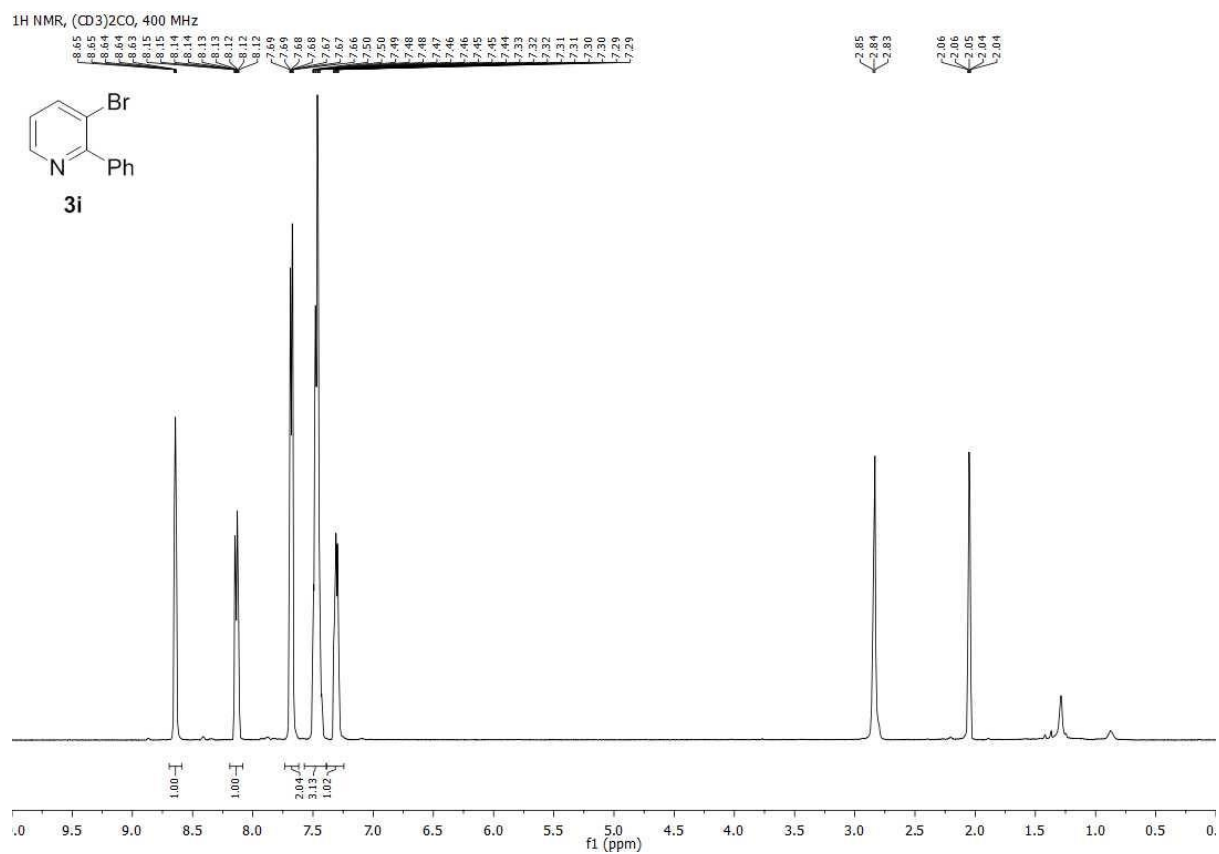


Figure S17. ¹H Spectra of **3i**

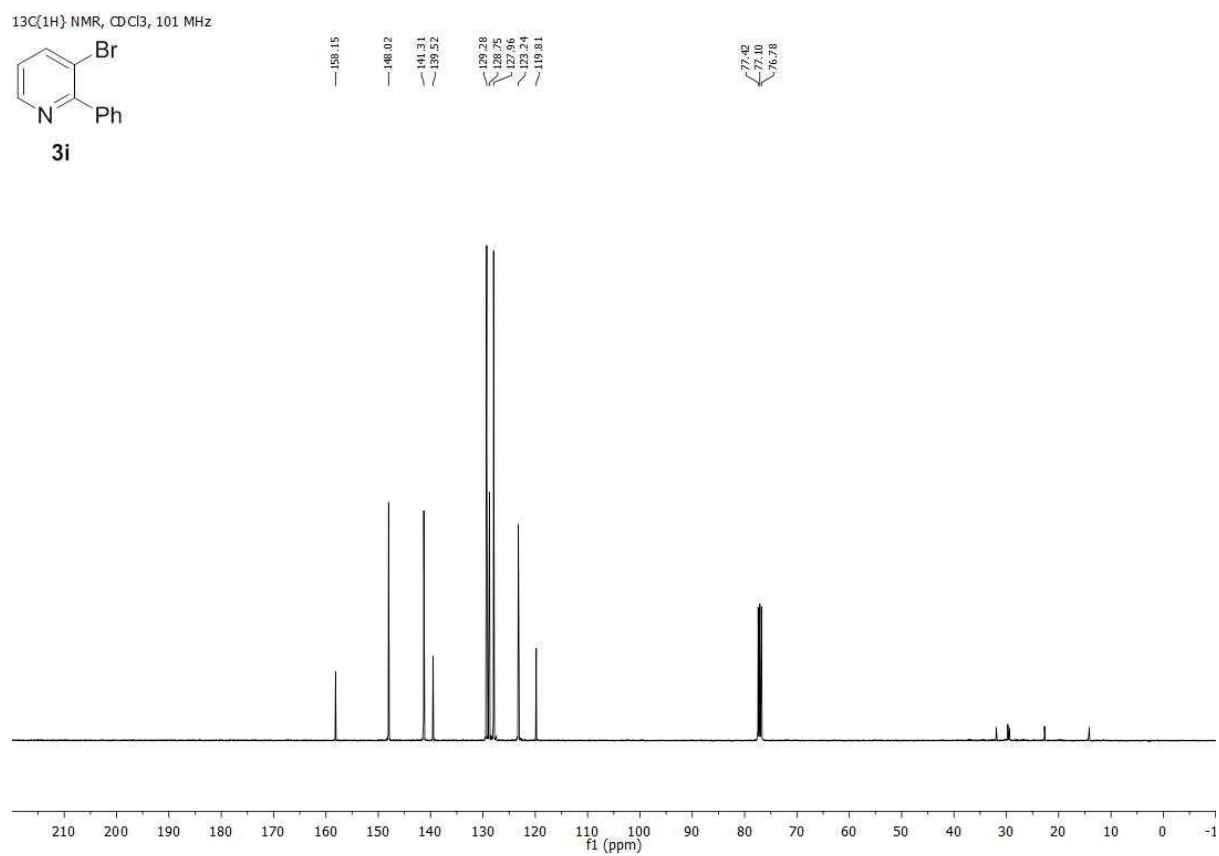


Figure S18. ¹³C Spectra of **3i**

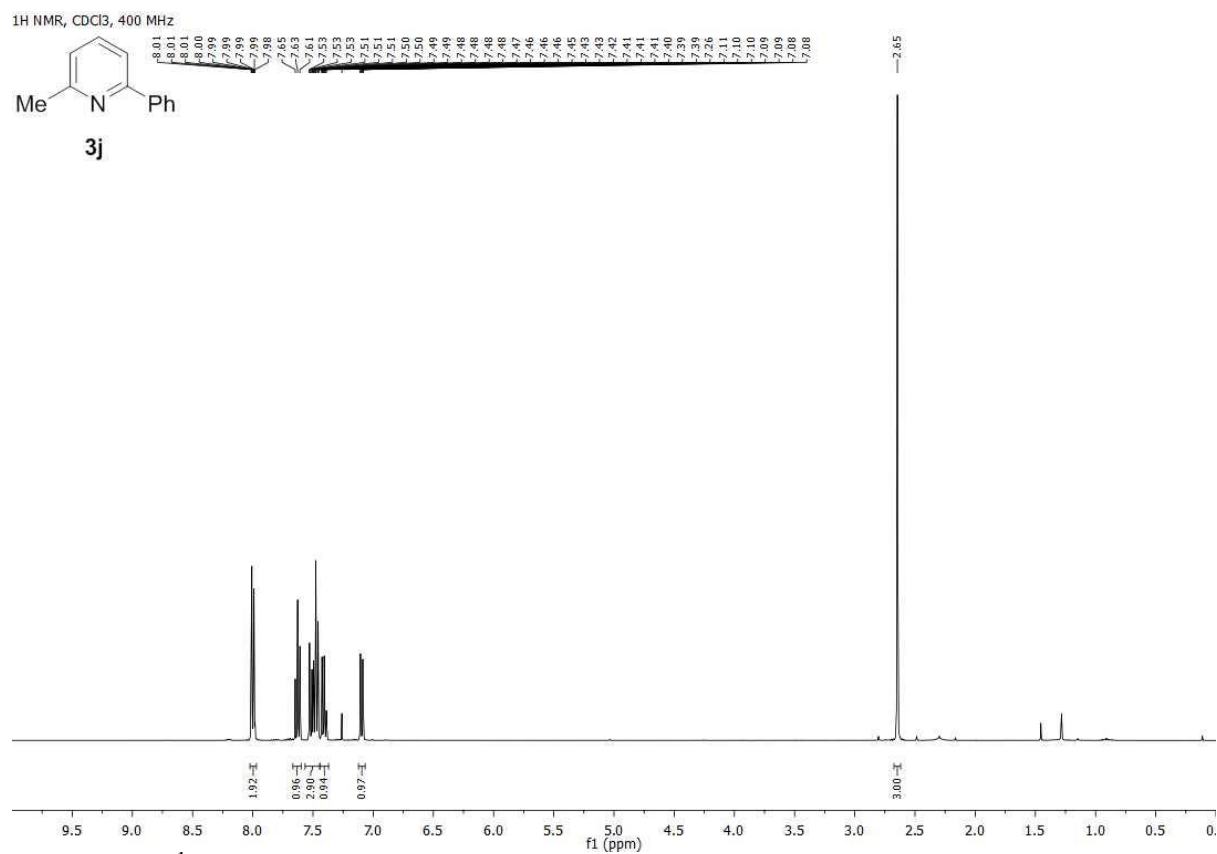


Figure S19. ¹H Spectra of **3j**

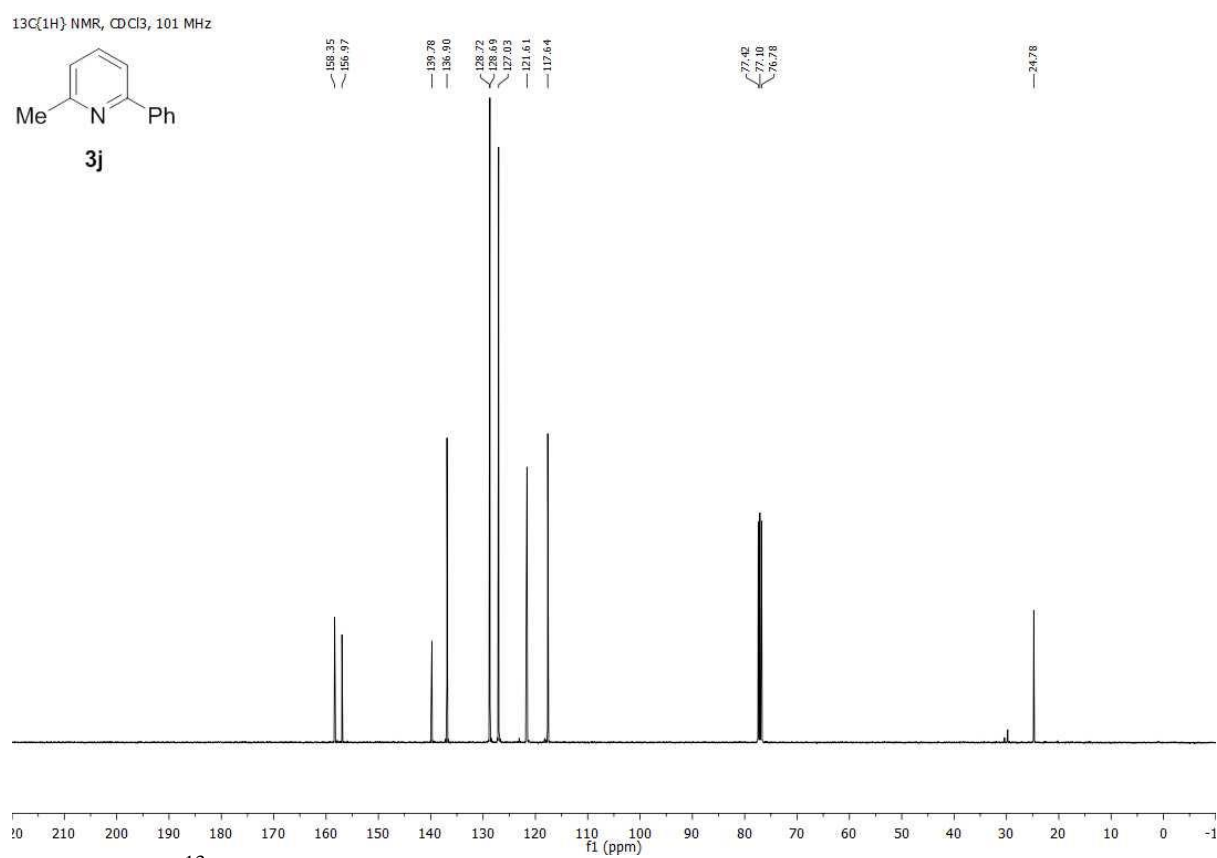


Figure S20. ¹³C Spectra of **3j**

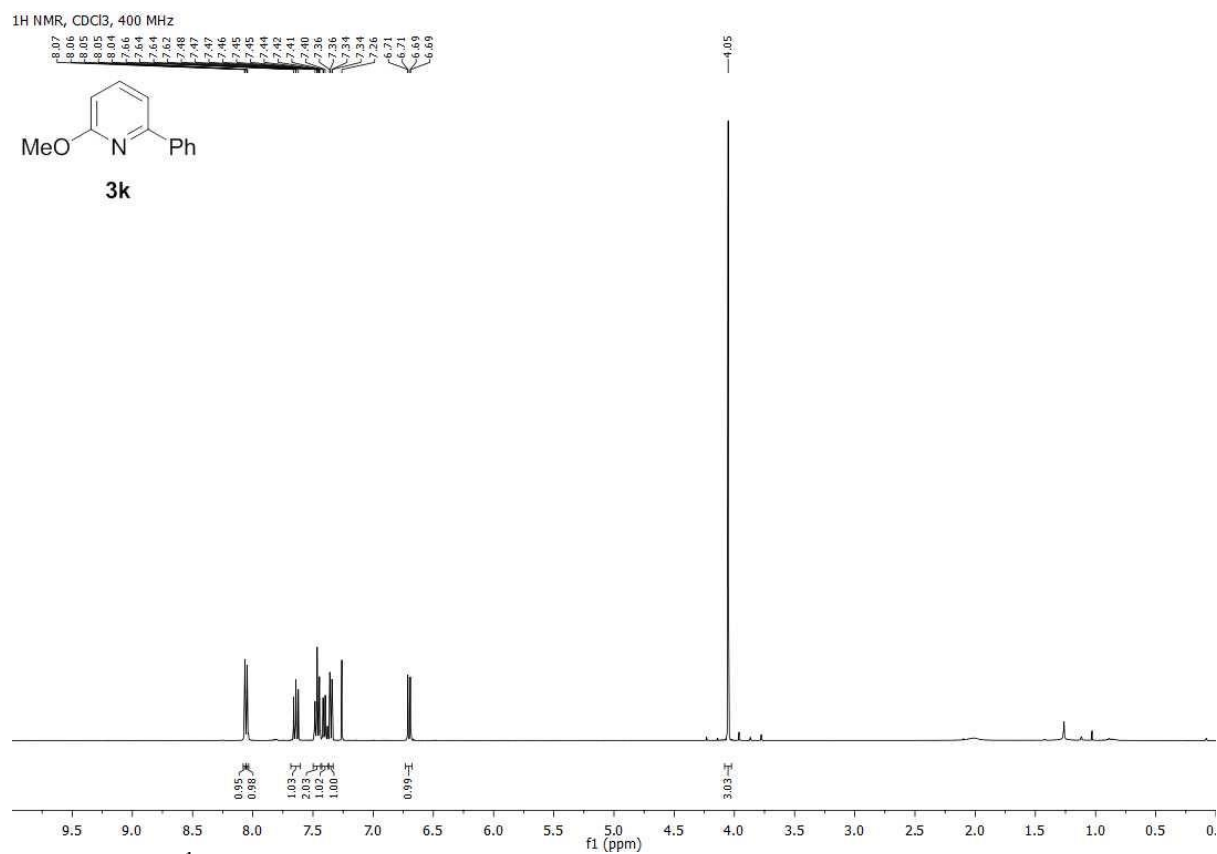


Figure S21. ¹H Spectra of **3k**

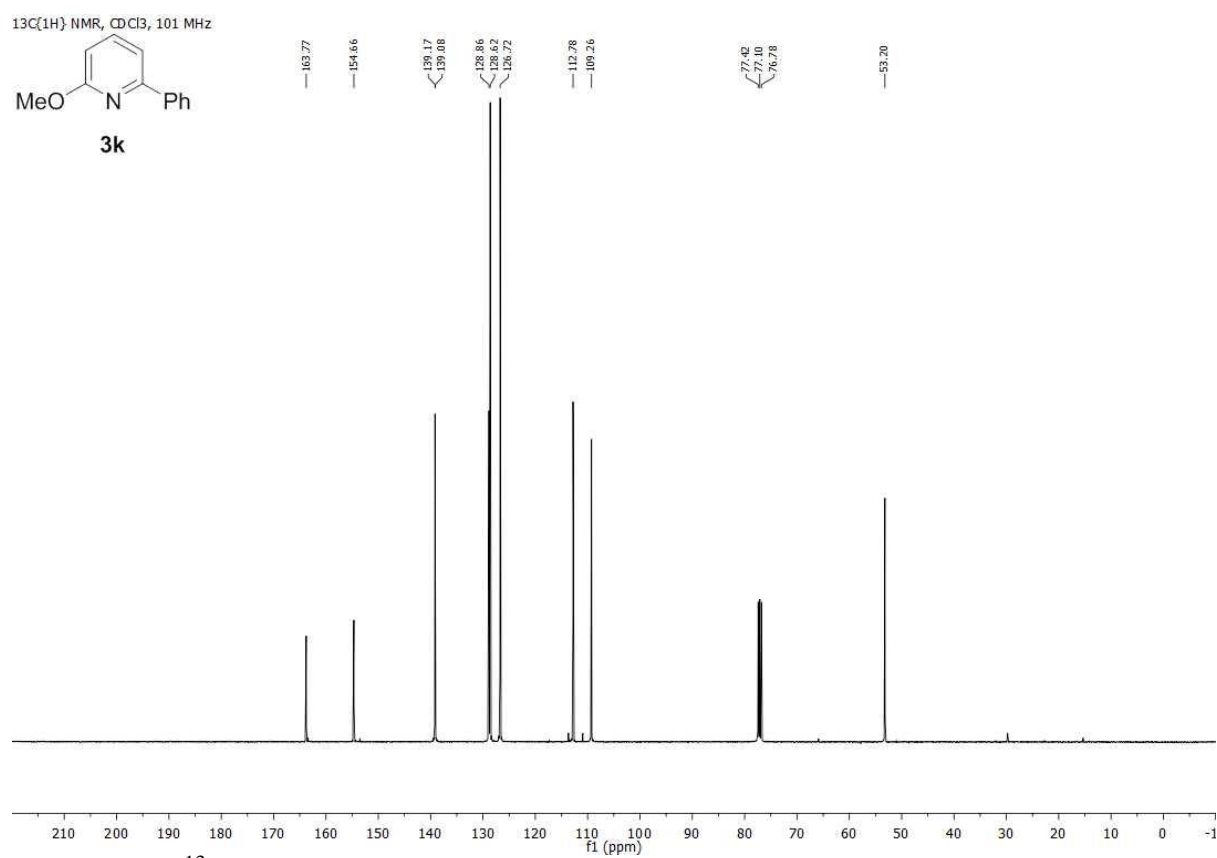


Figure S22. ¹³C Spectra of **3k**

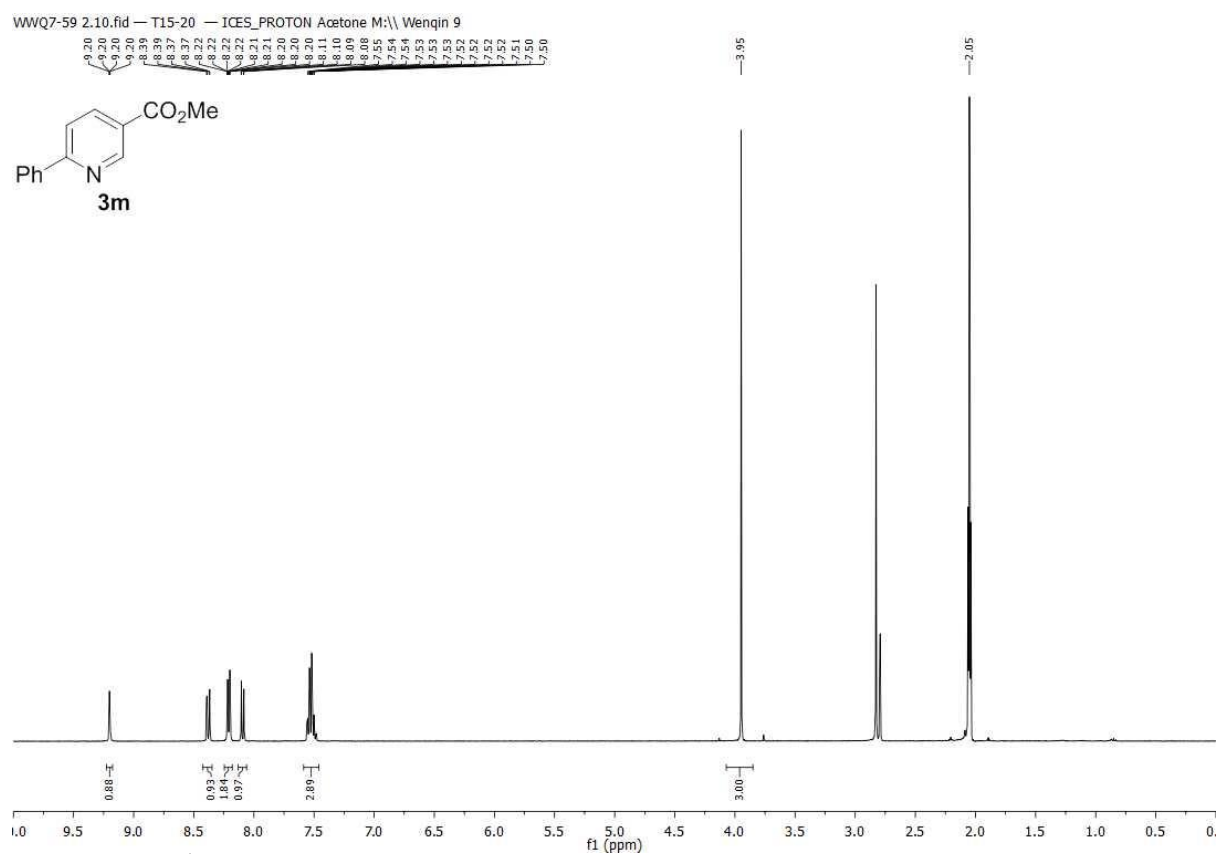


Figure S25. ^1H Spectra of **3m**

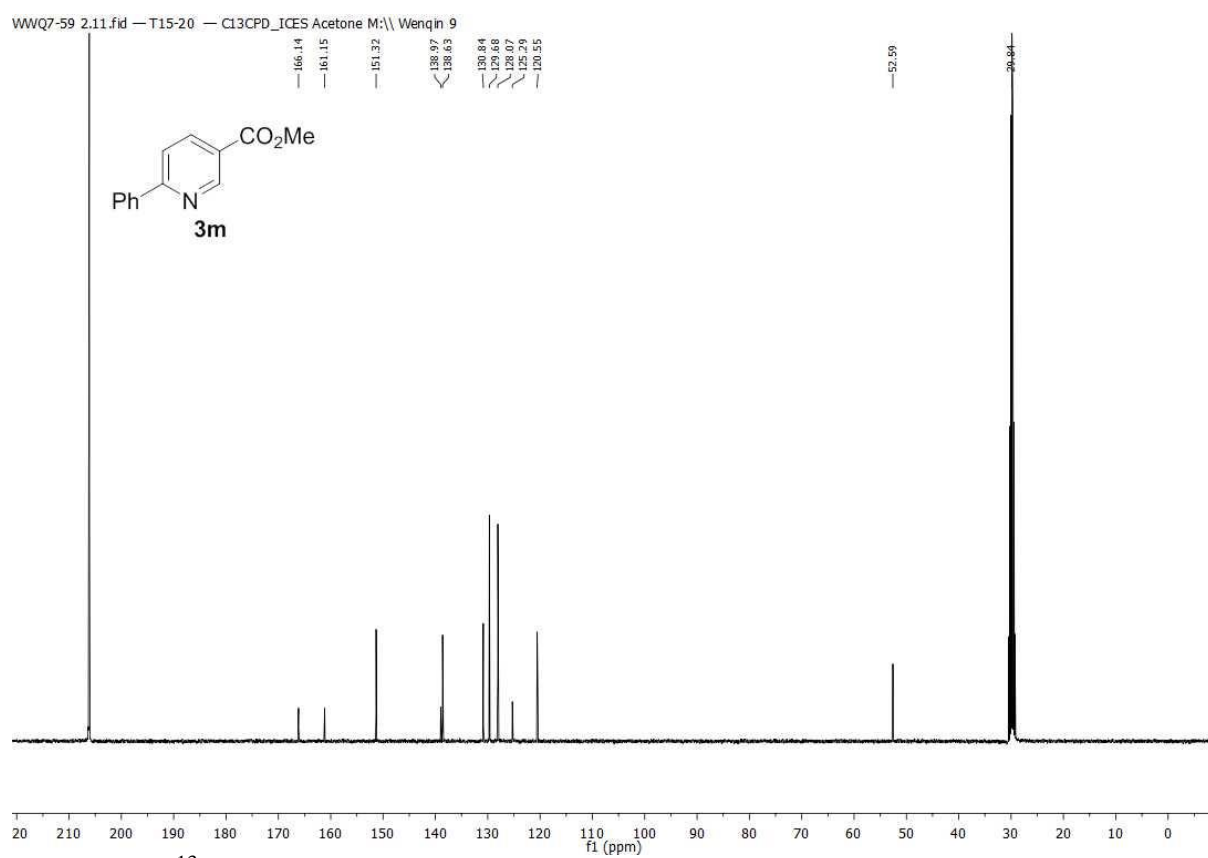


Figure S26. ^{13}C Spectra of **3m**

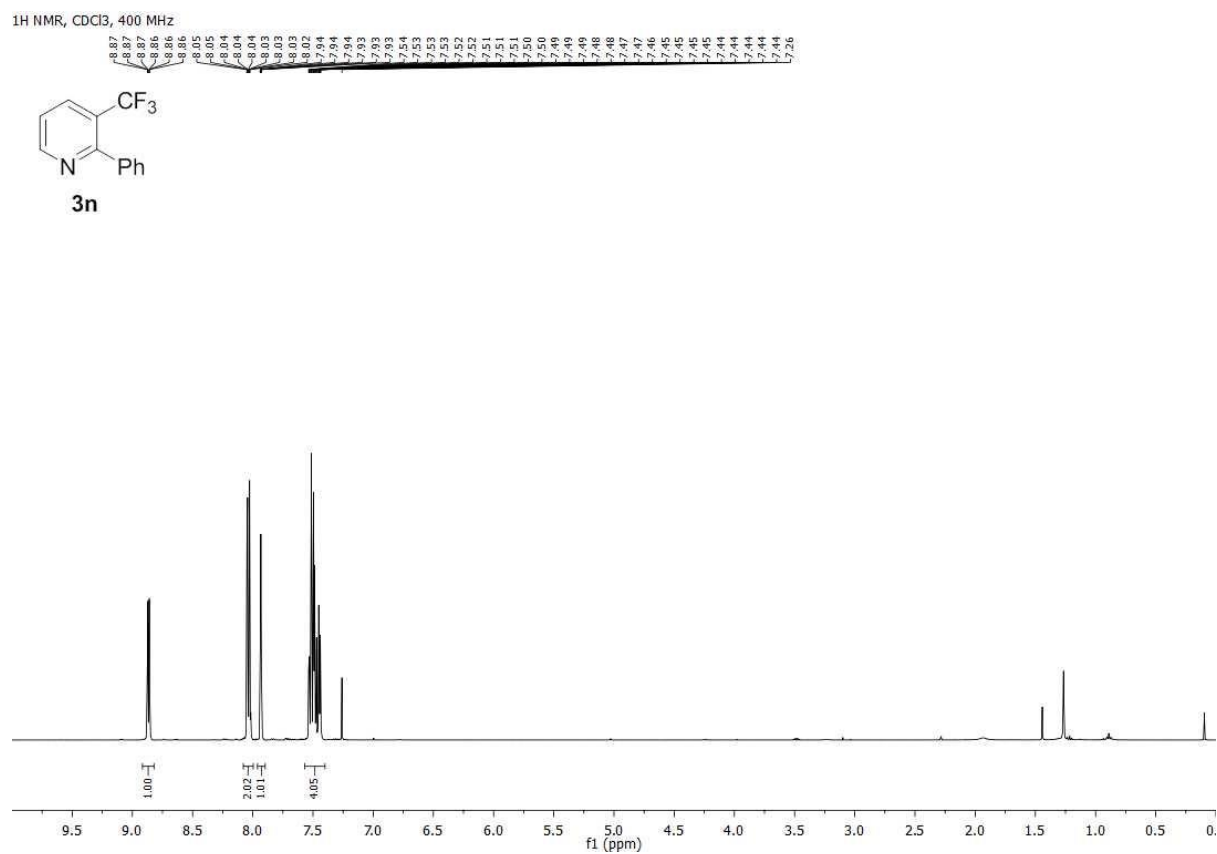


Figure S27. ¹H Spectra of **3n**

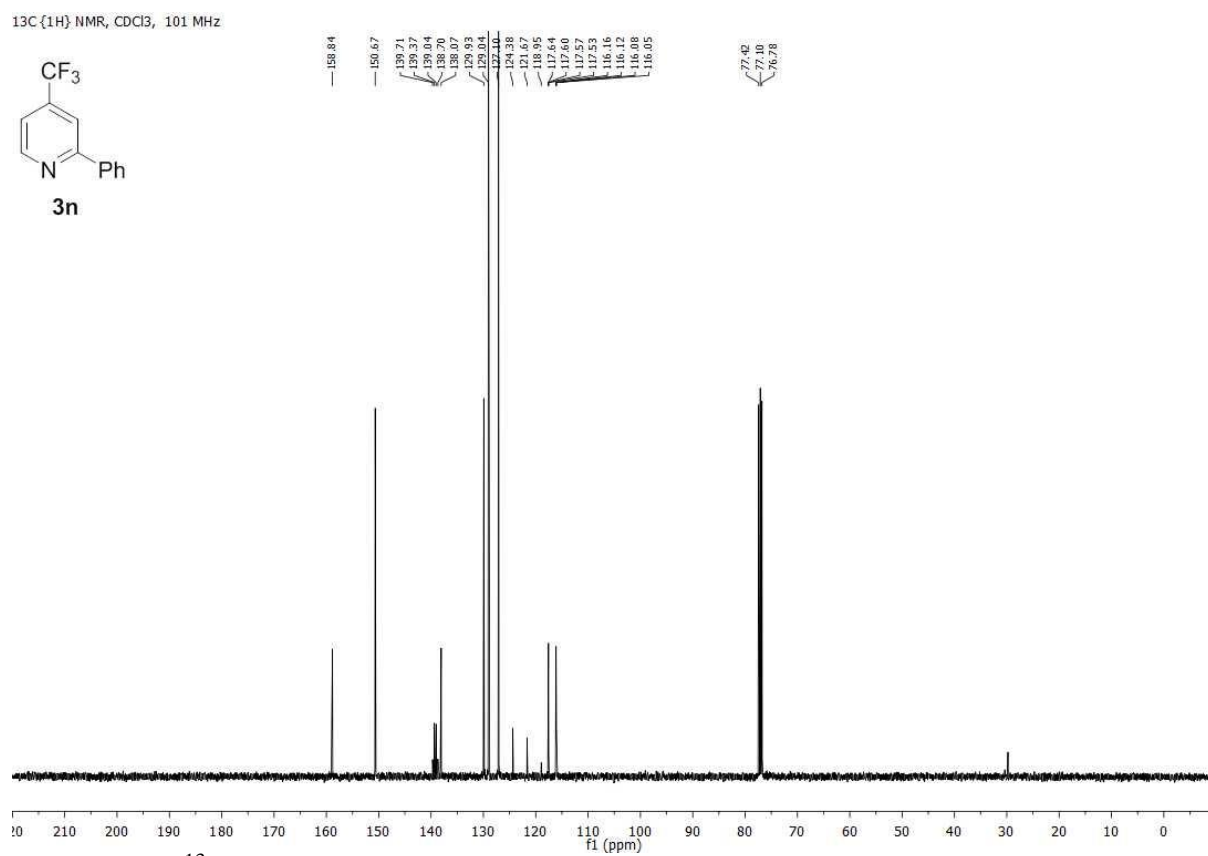


Figure S28. ¹³C Spectra of **3n**

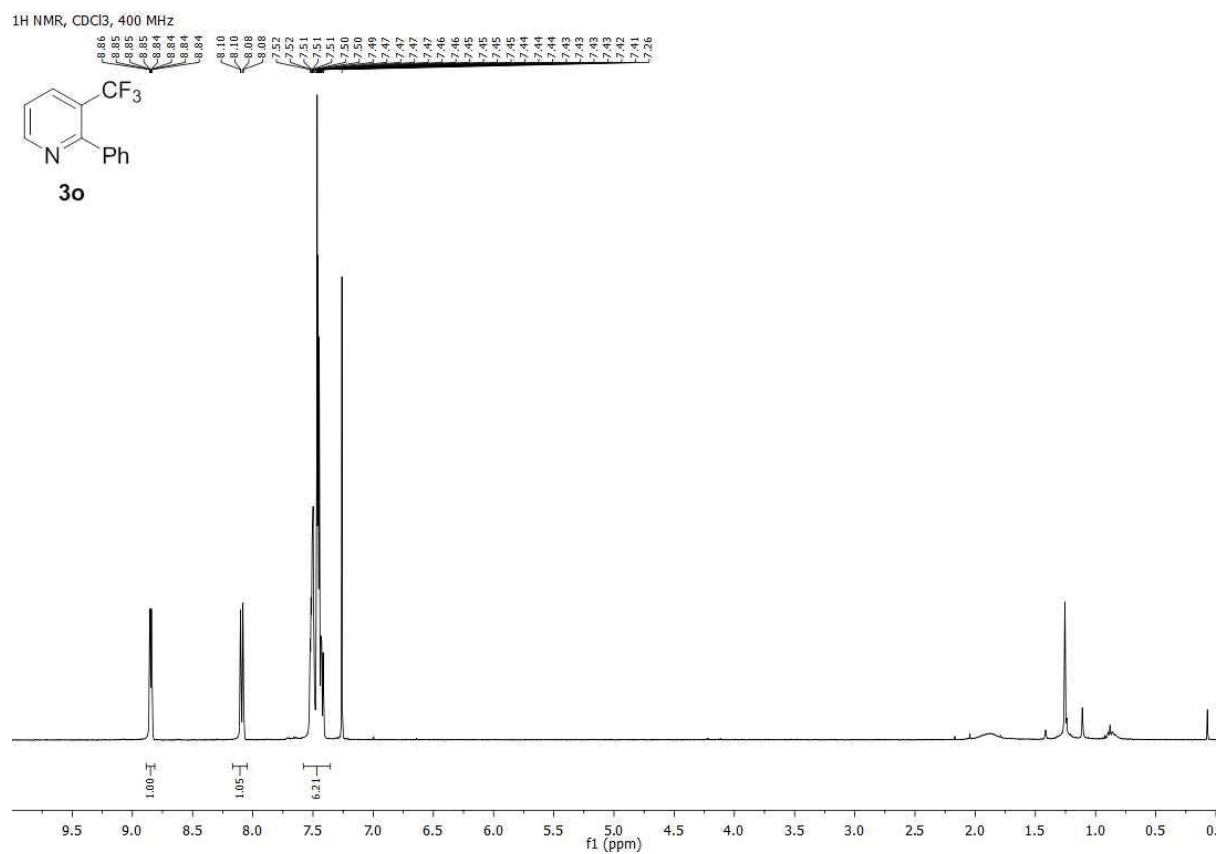


Figure S29. ¹H Spectra of **3o**

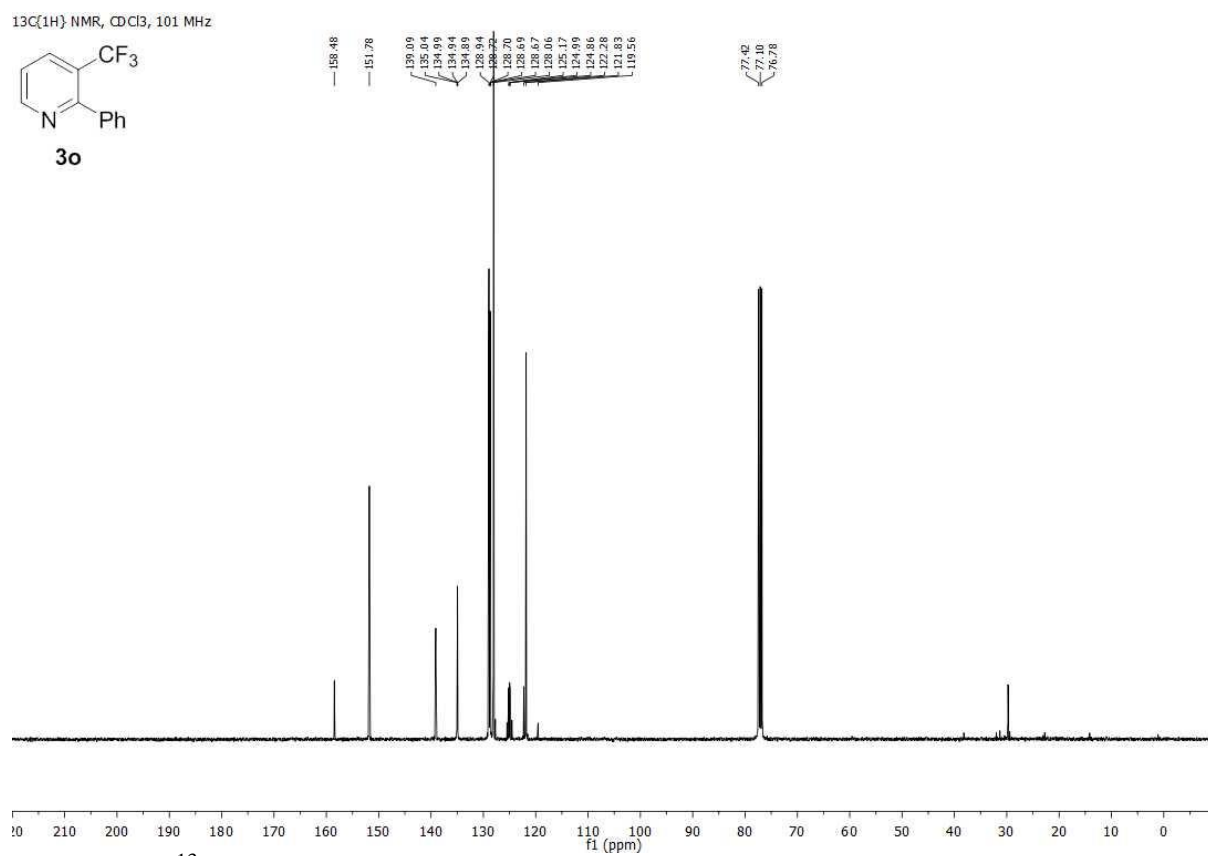


Figure S30. ¹³C Spectra of **3o**

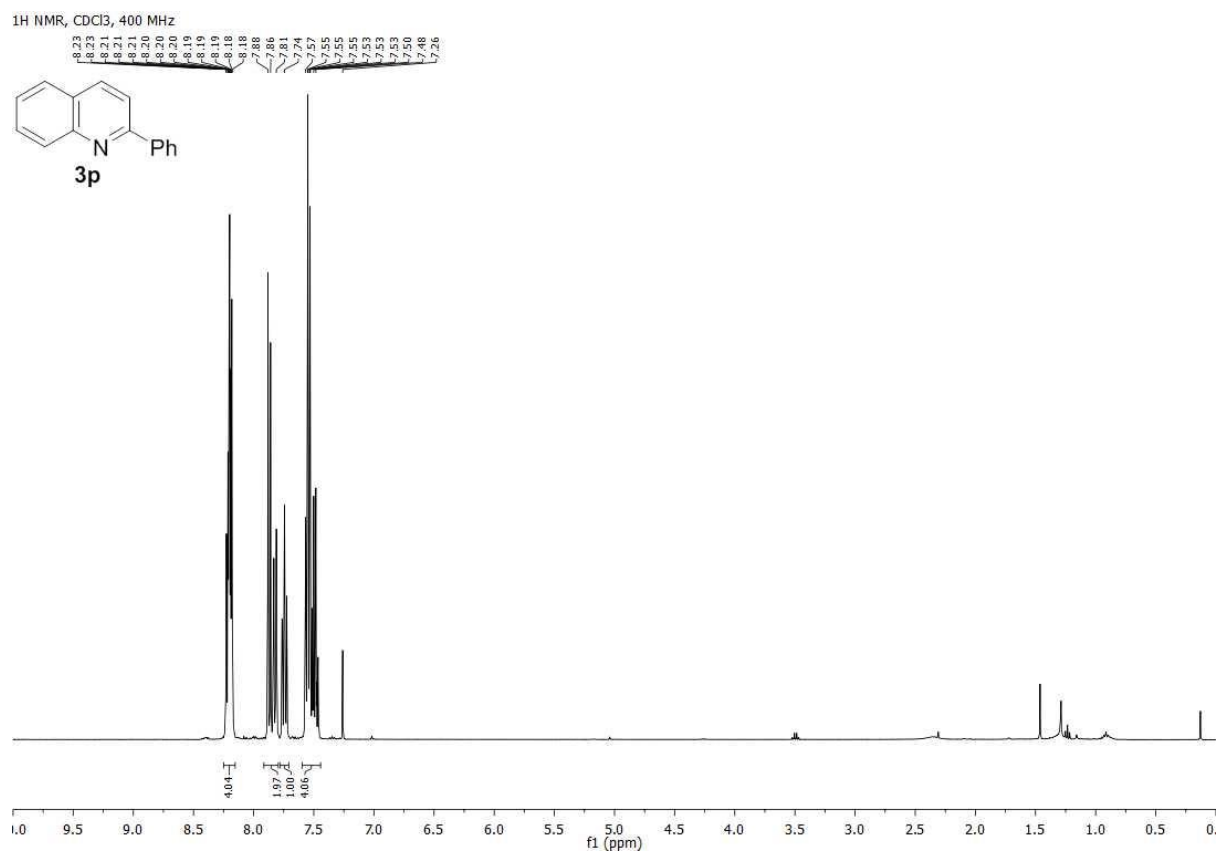


Figure S31. ¹H Spectra of **3p**

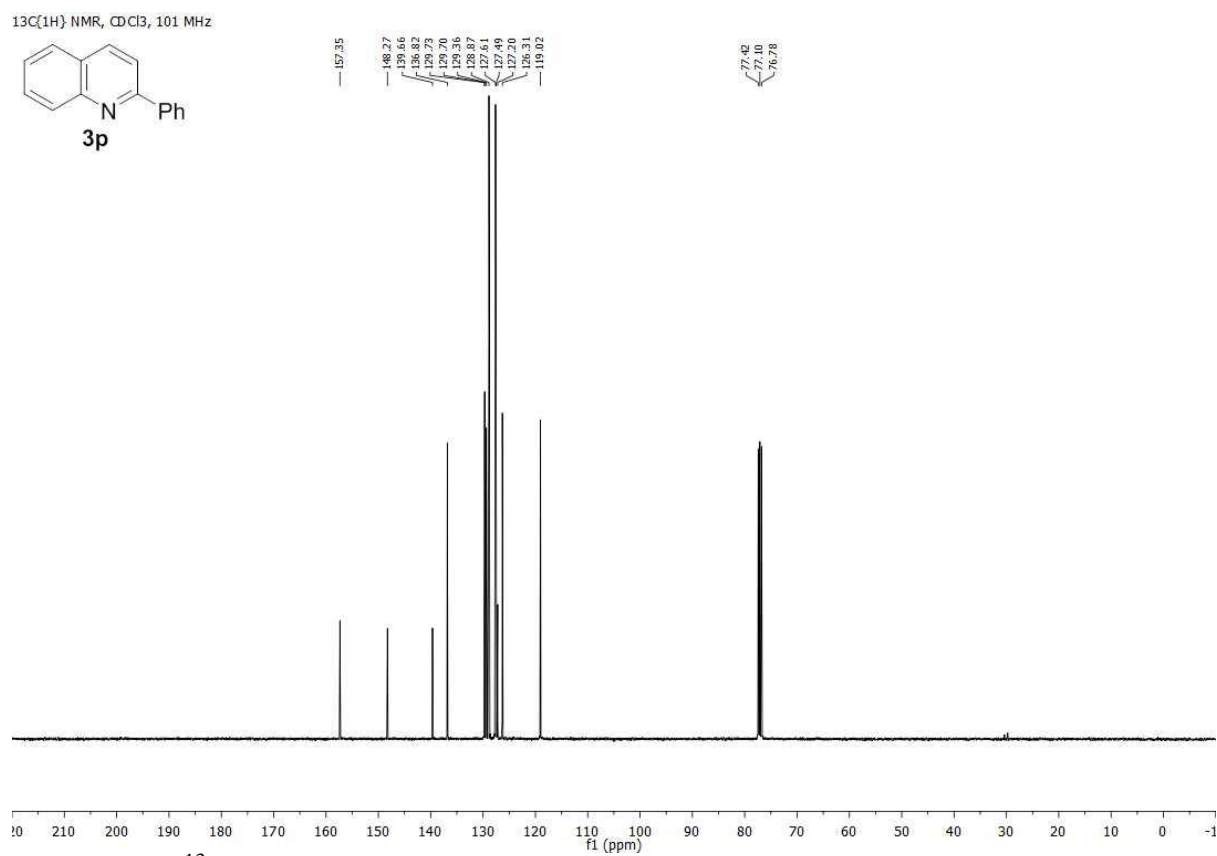


Figure S32. ¹³C Spectra of **3p**

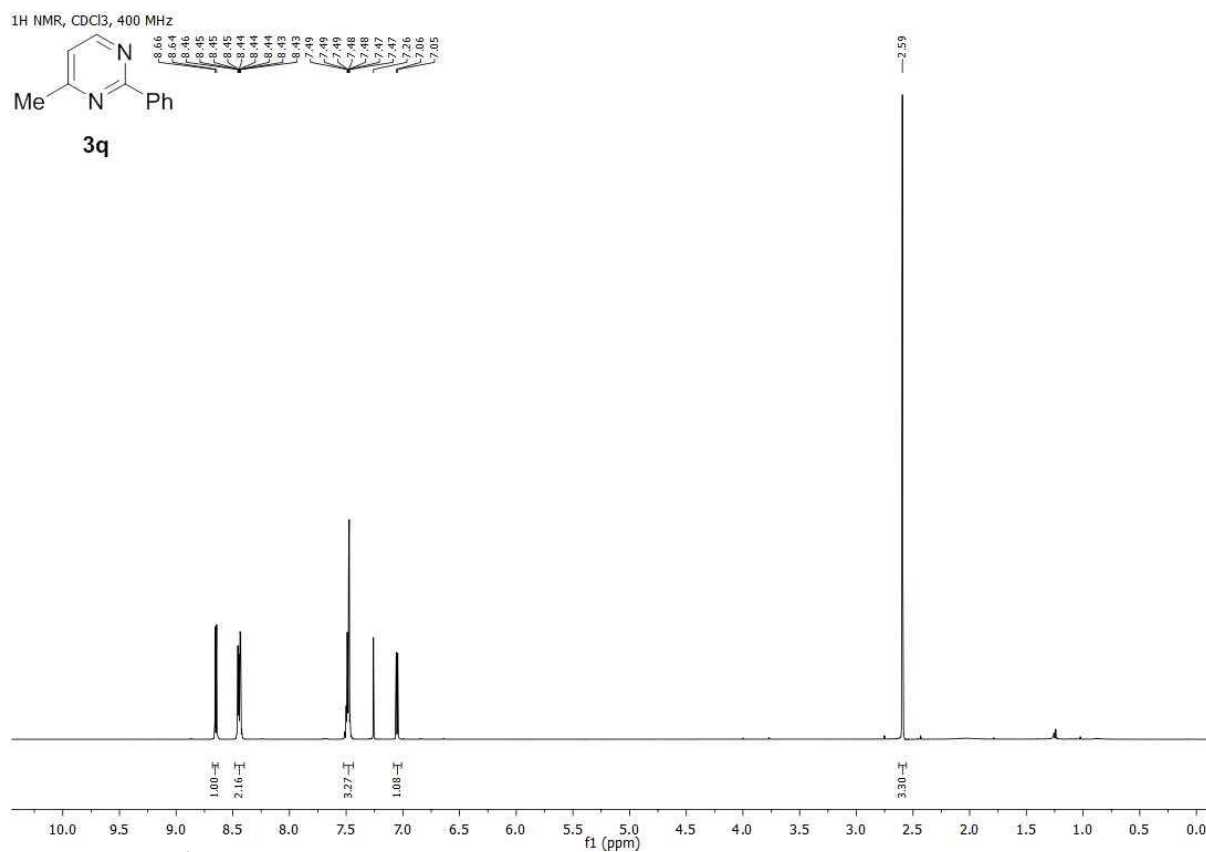


Figure S33. ¹H Spectra of **3q**

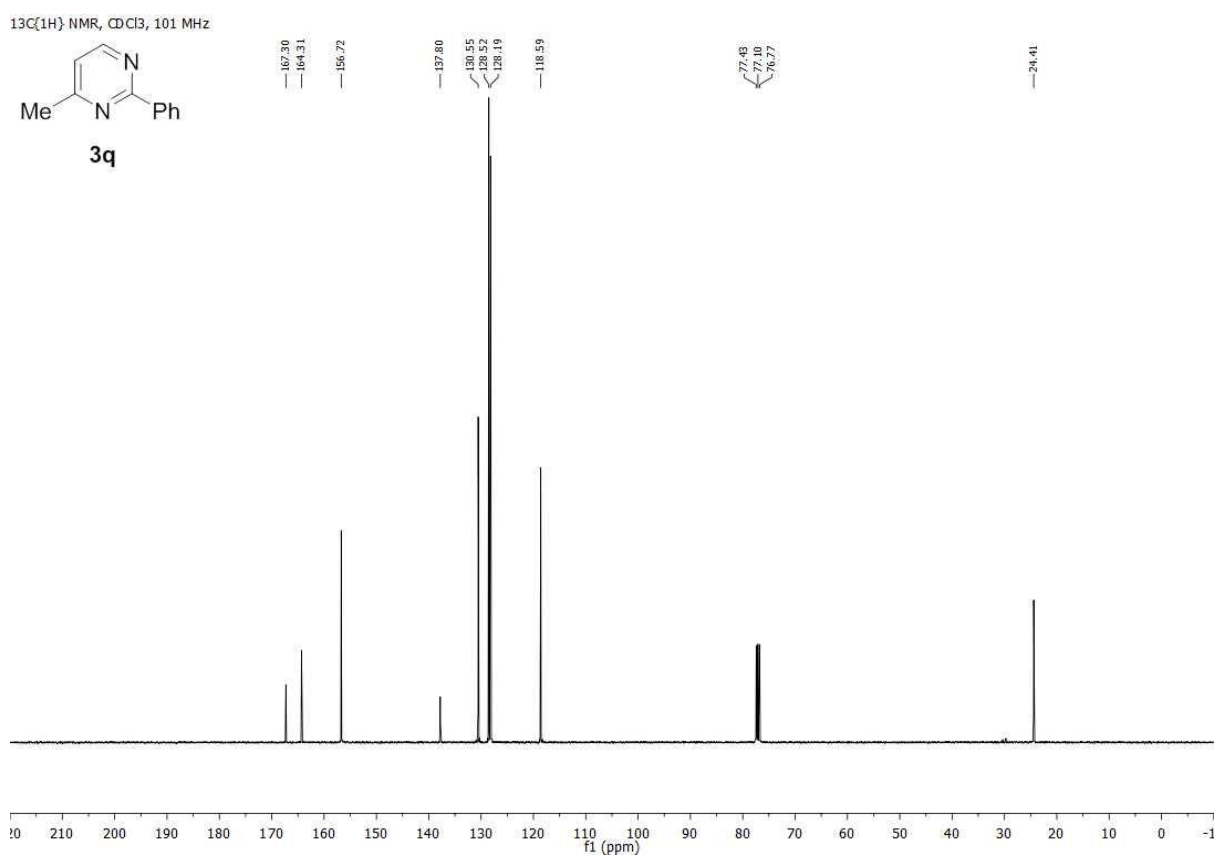


Figure S34. ¹³C Spectra of **3q**

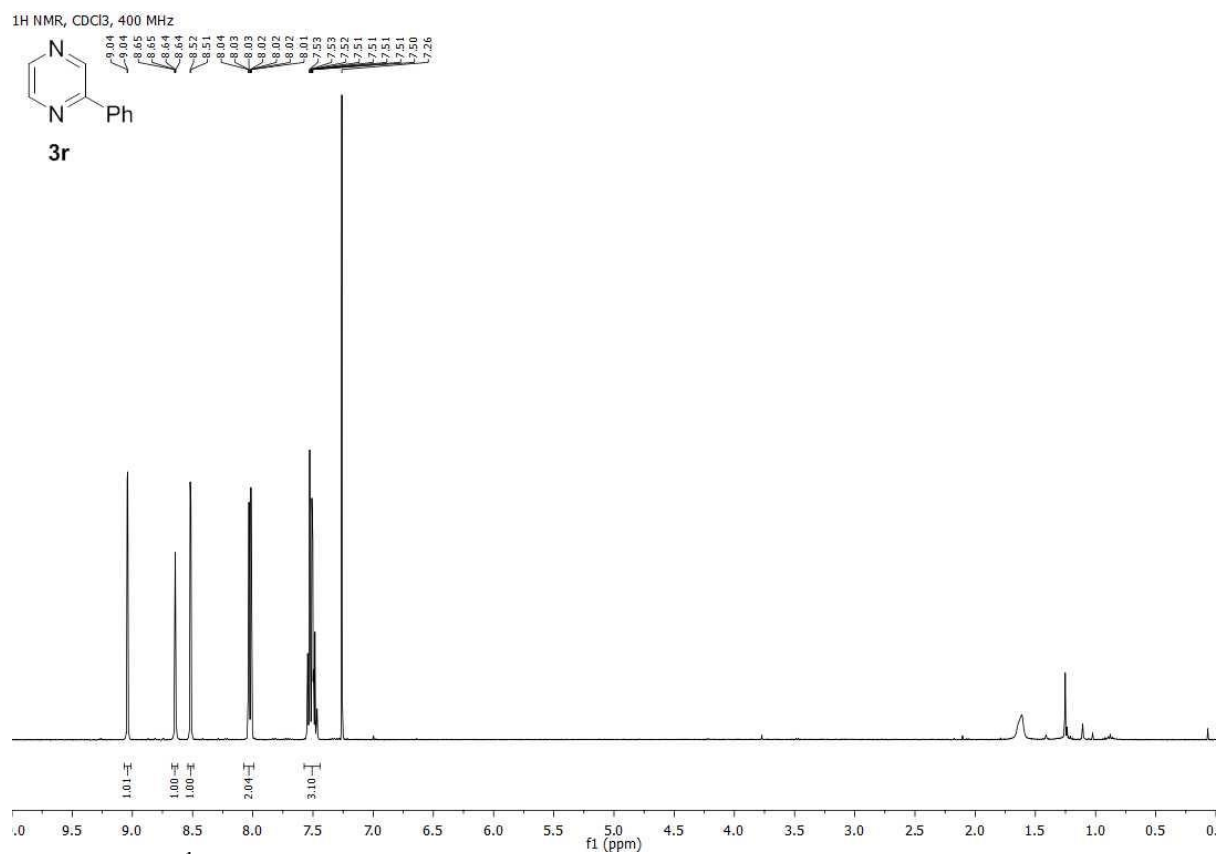


Figure S35. ¹H Spectra of **3r**

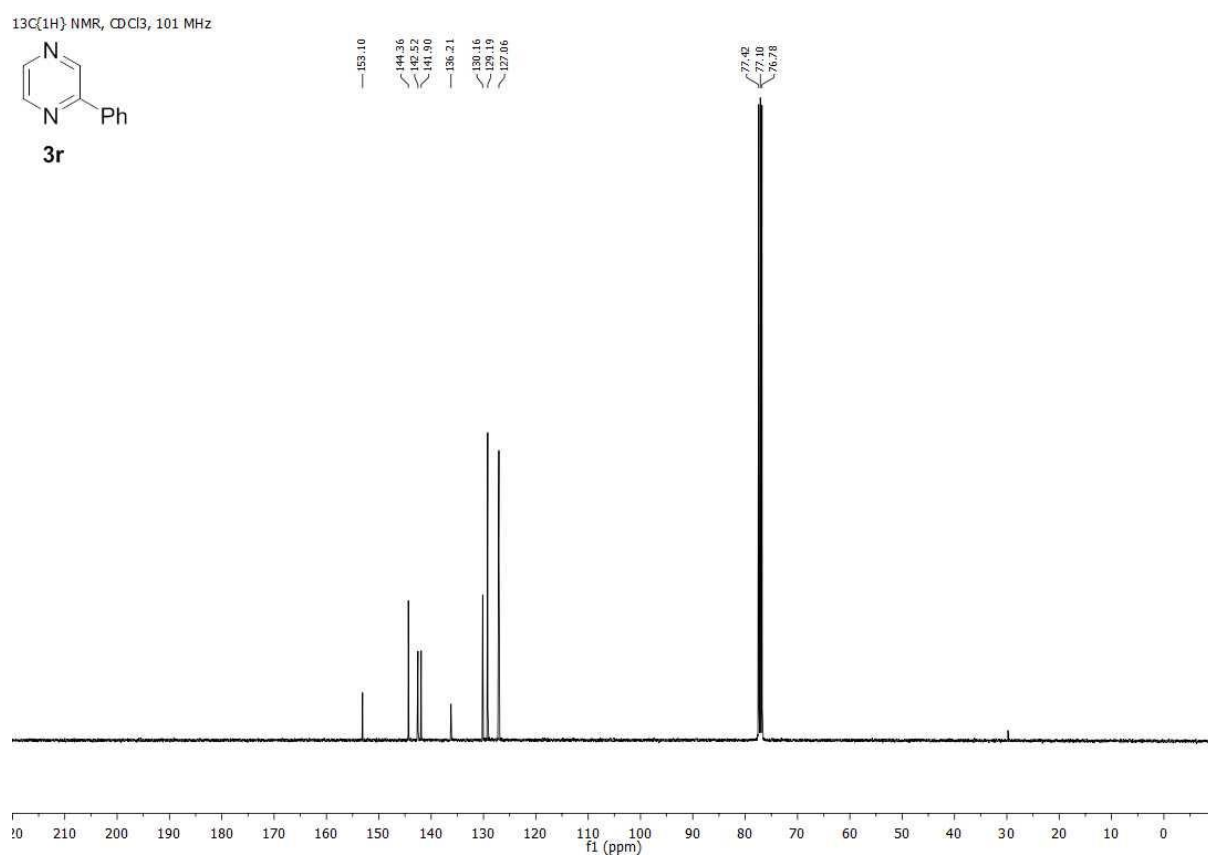


Figure S36. ¹³C Spectra of **3r**

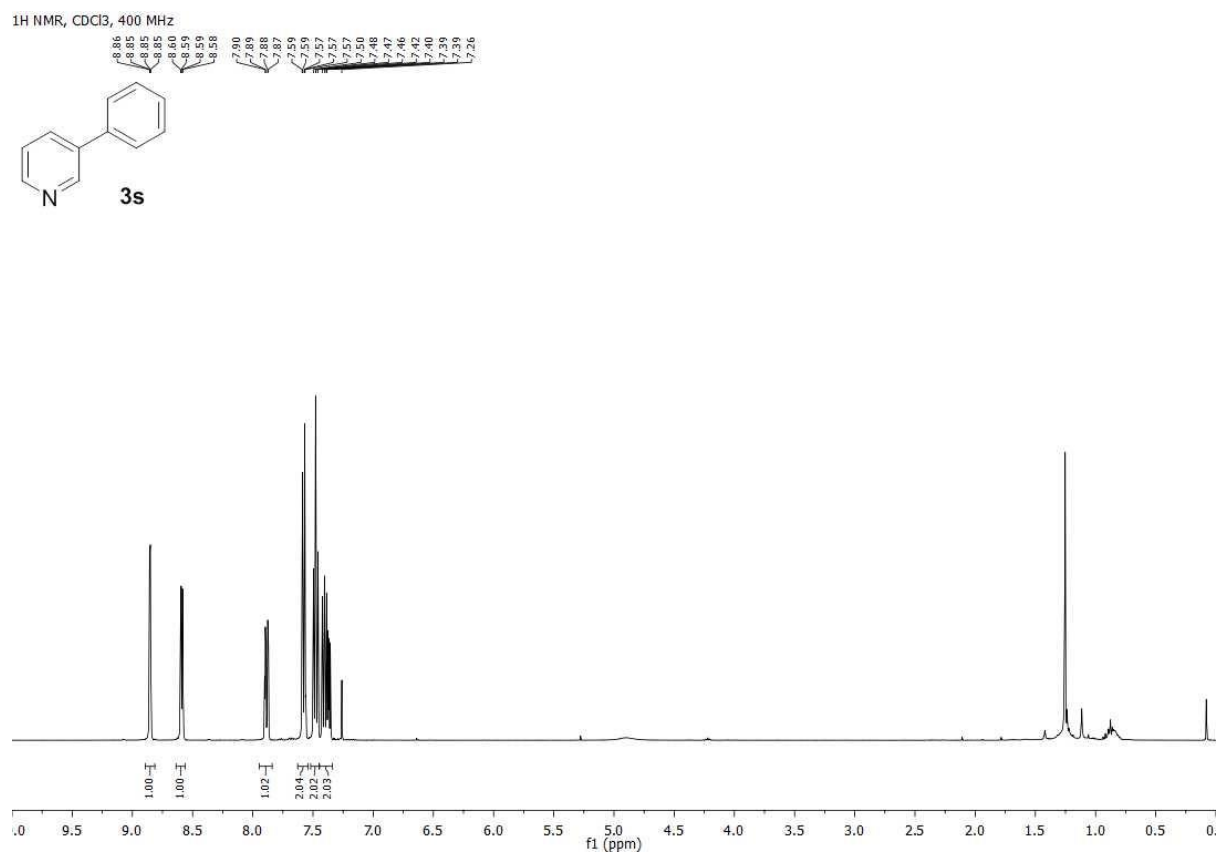


Figure S37. ¹H Spectra of **3s**

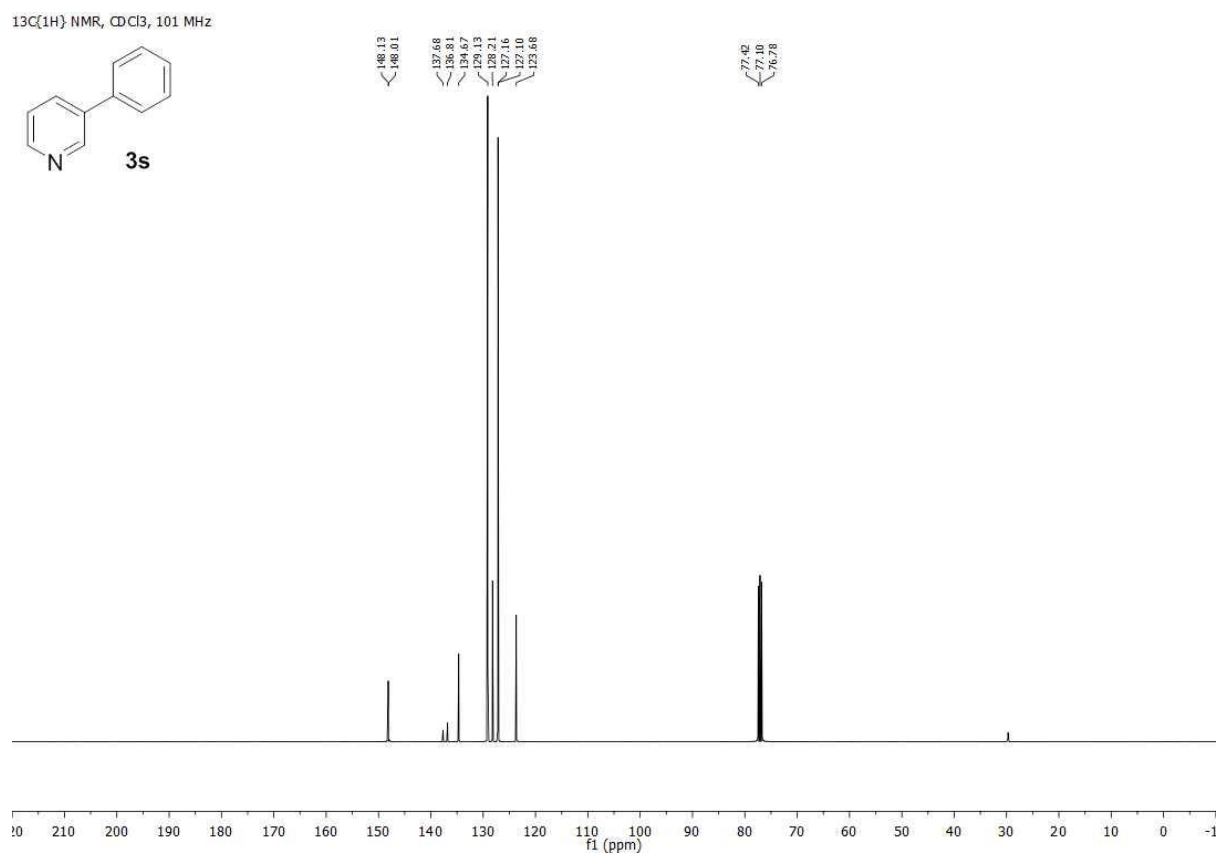


Figure S38. ¹³C Spectra of **3s**

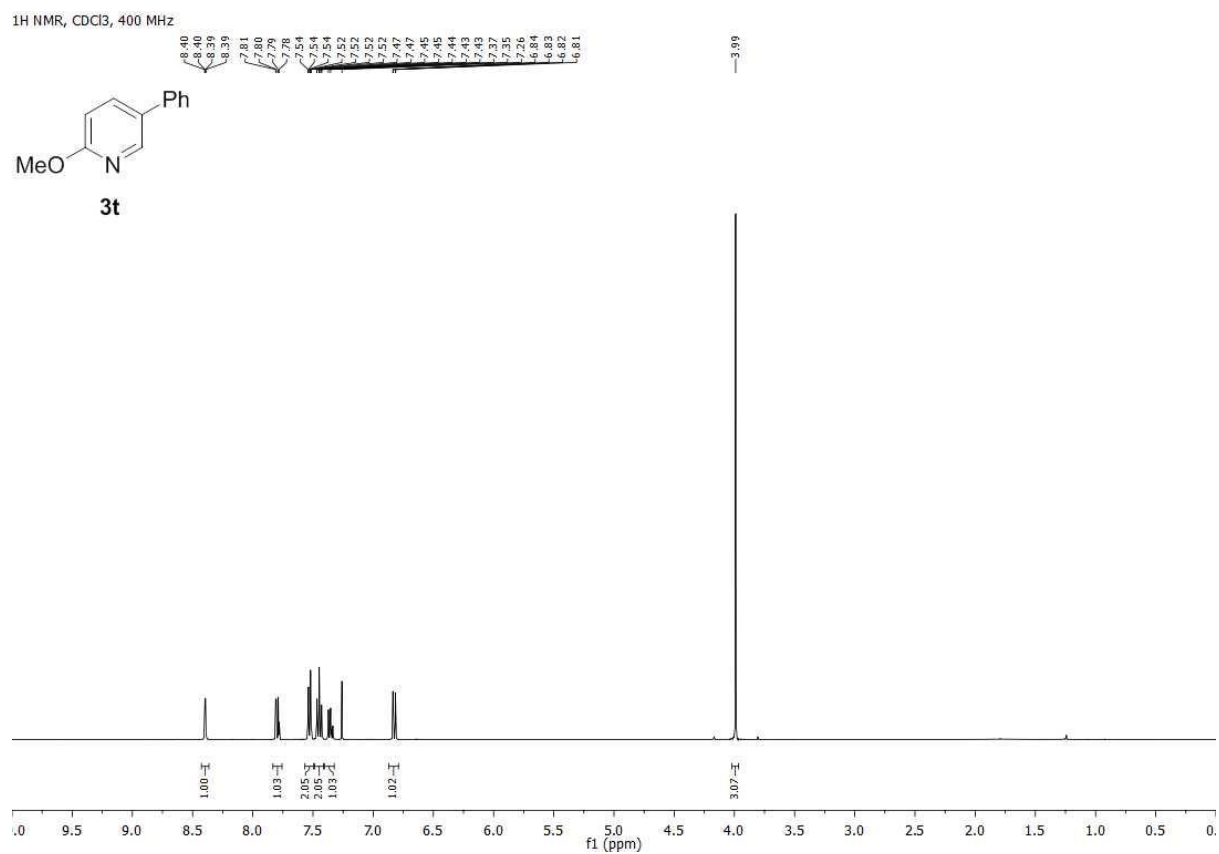


Figure S39. ¹H Spectra of **3t**

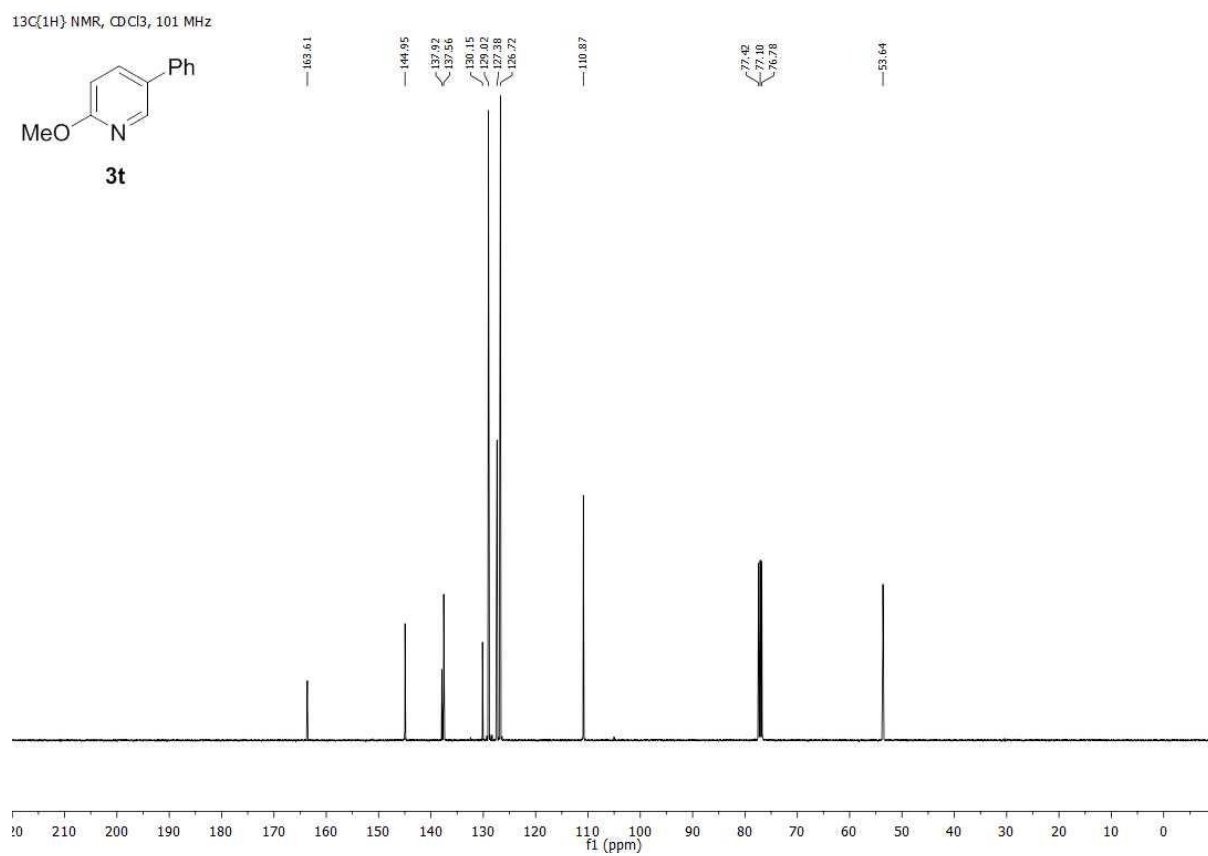


Figure S40. ¹³C Spectra of **3t**

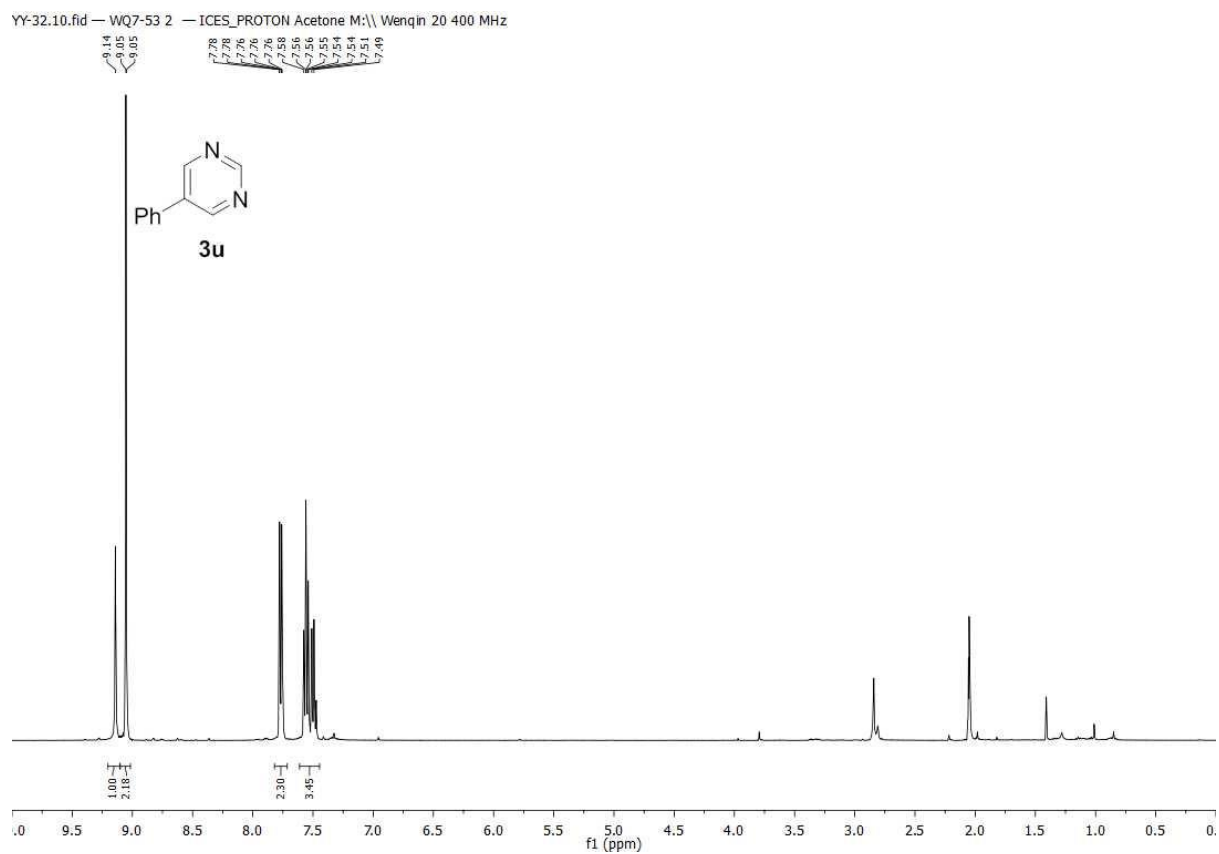


Figure S41. ^1H Spectra of **3u**

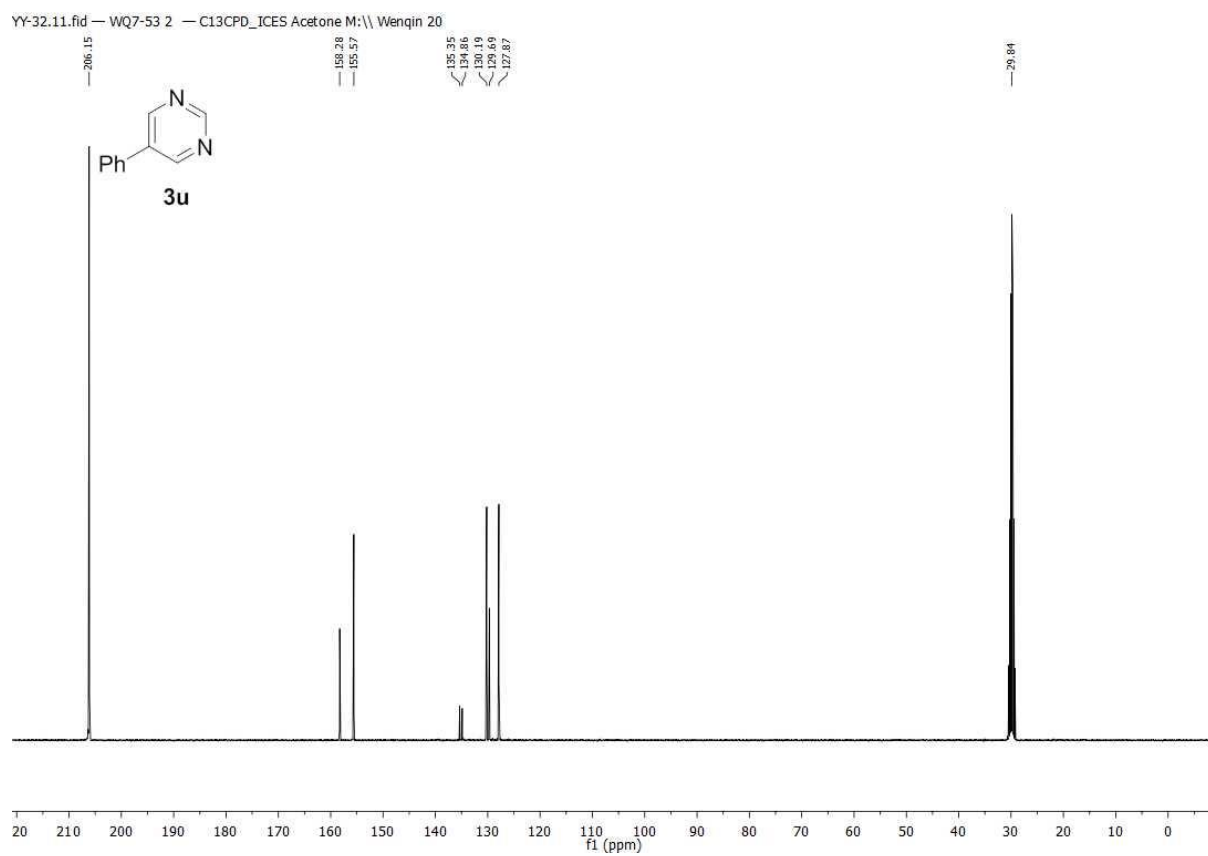


Figure S42. ^{13}C Spectra of **3u**

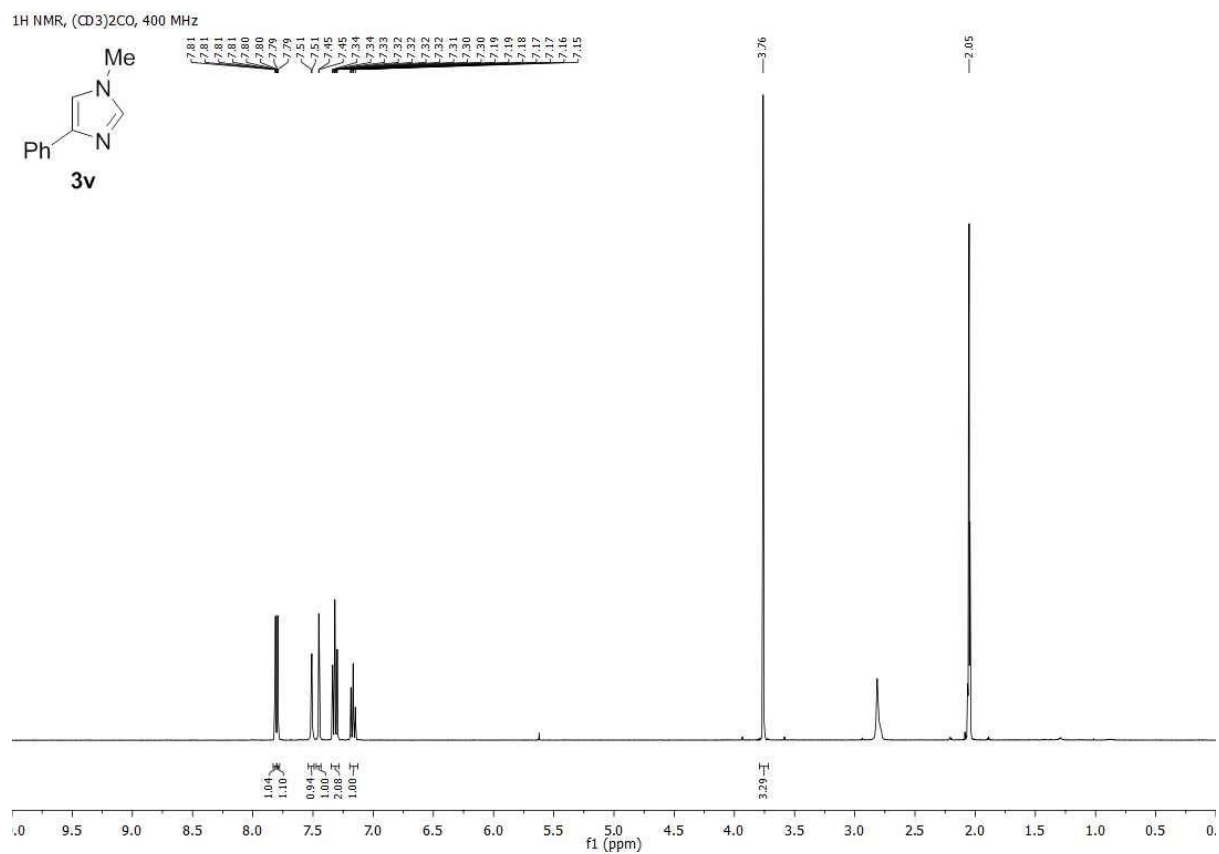


Figure S43. ¹H Spectra of **3v**

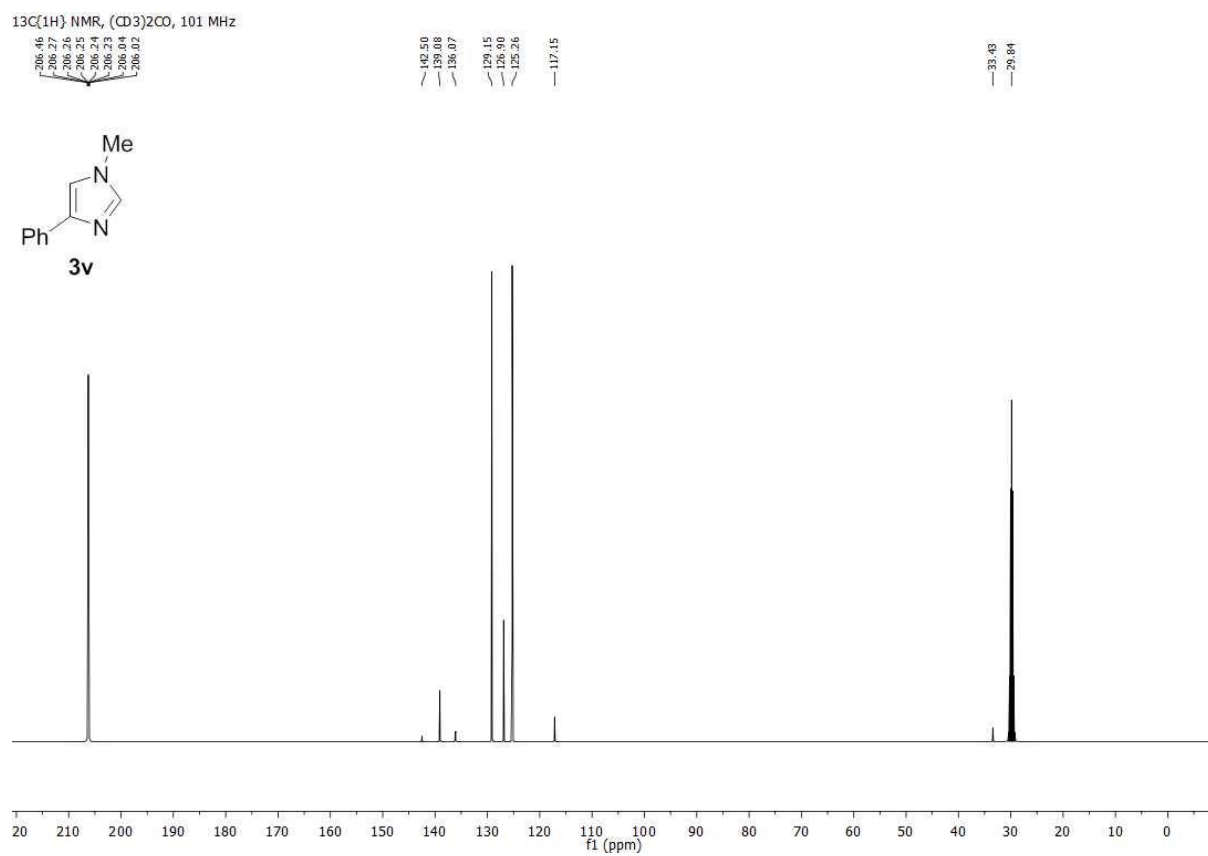


Figure S44. ¹³C Spectra of **3v**

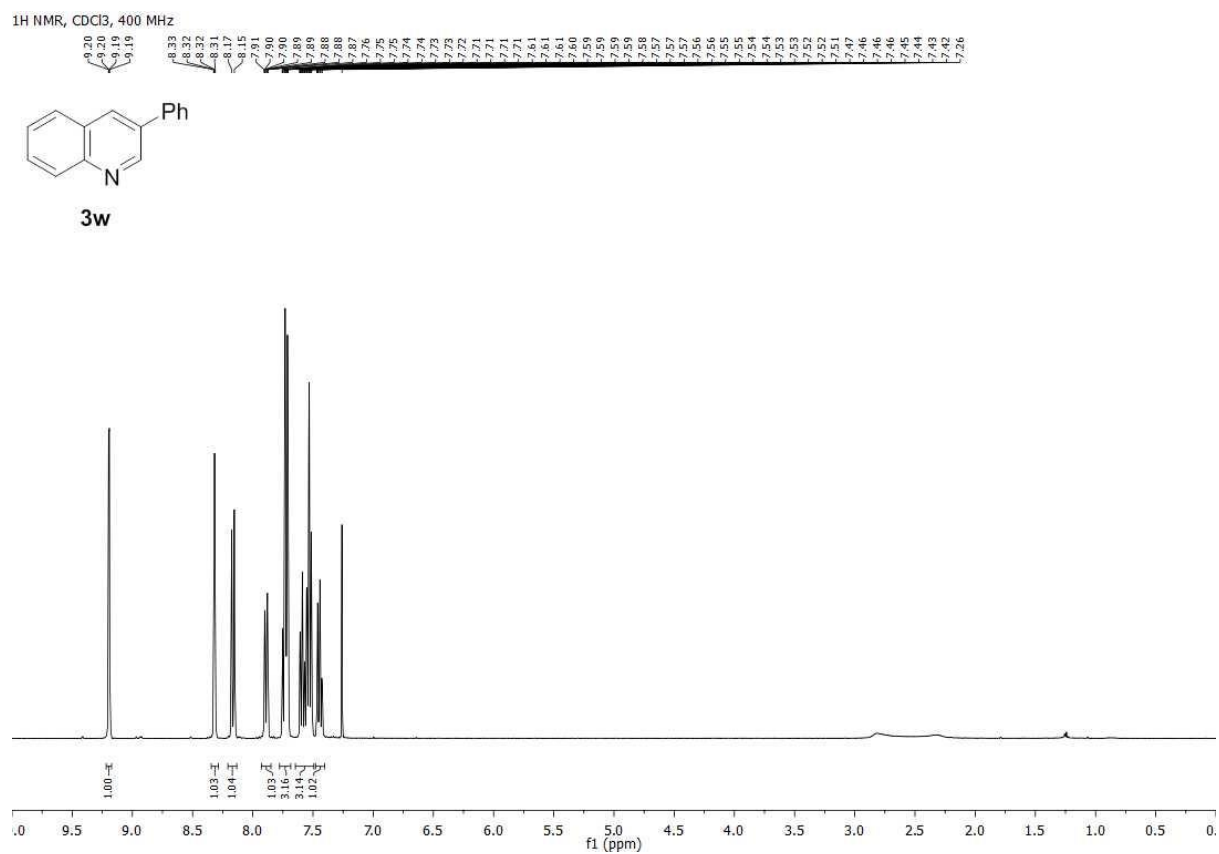


Figure S45. ¹H Spectra of **3w**

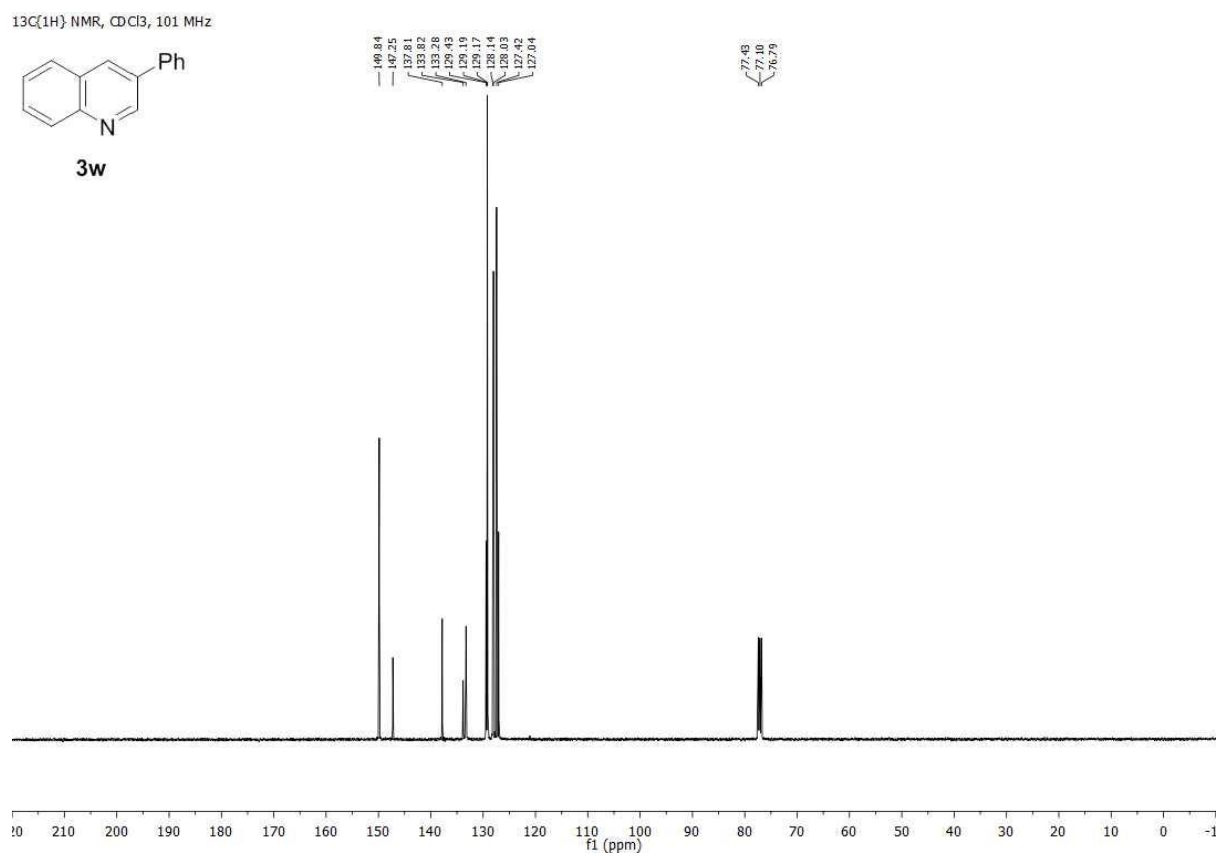


Figure S46. ¹³C Spectra of **3w**

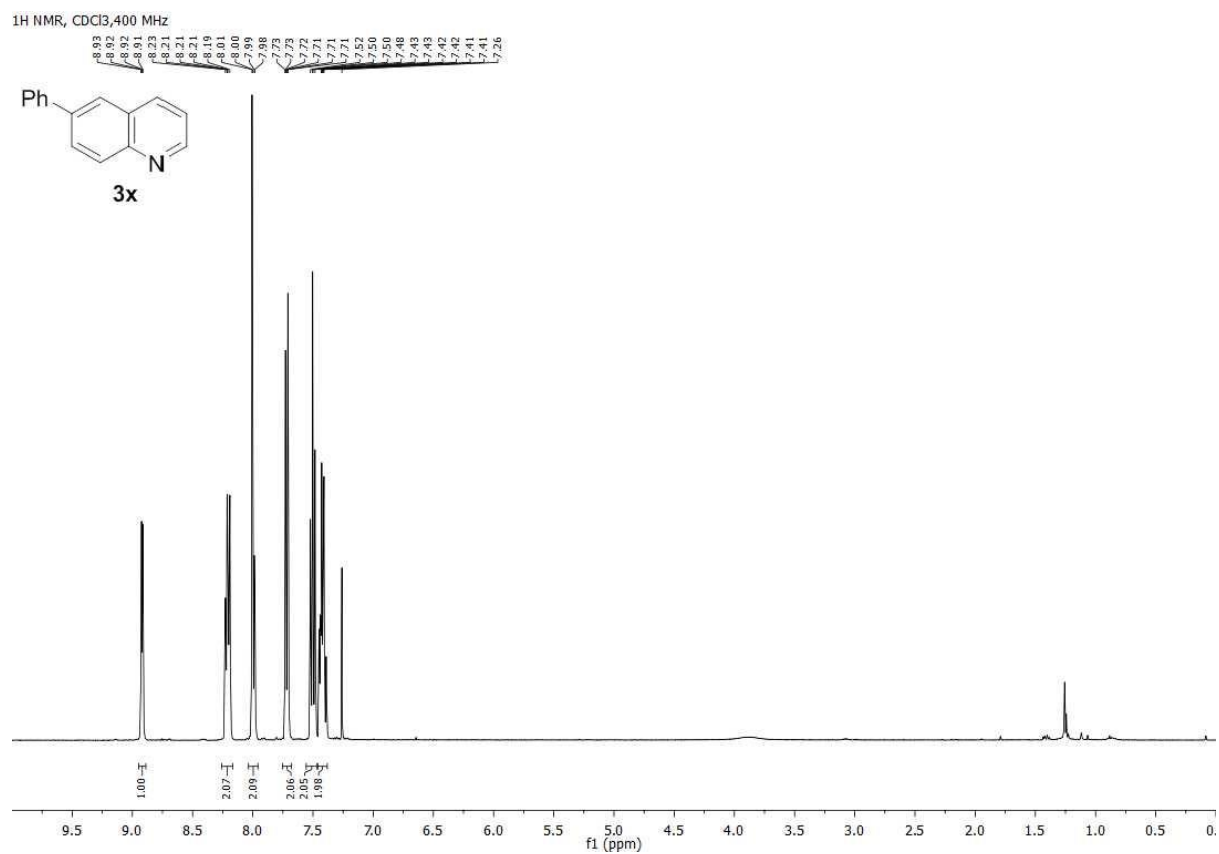


Figure S47. ¹H Spectra of **3x**

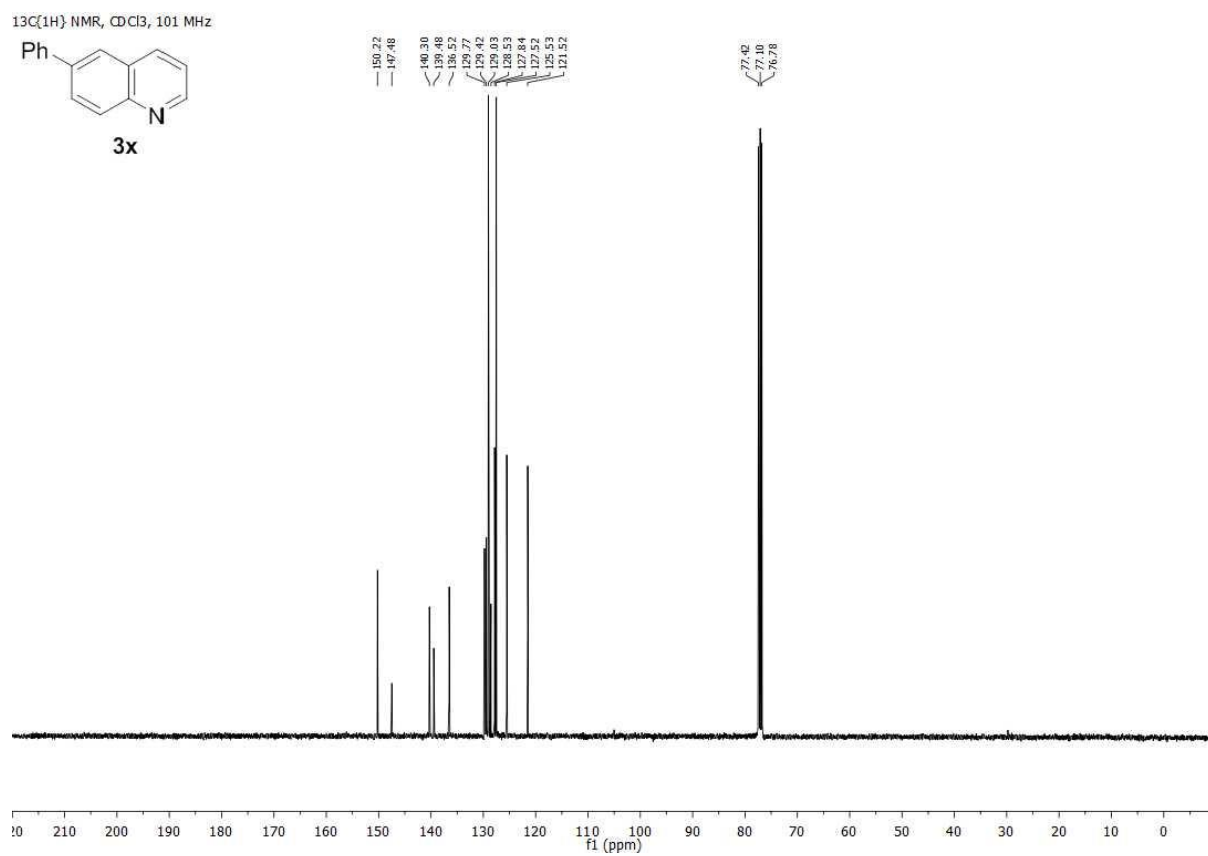


Figure S48. ¹³C Spectra of **3x**

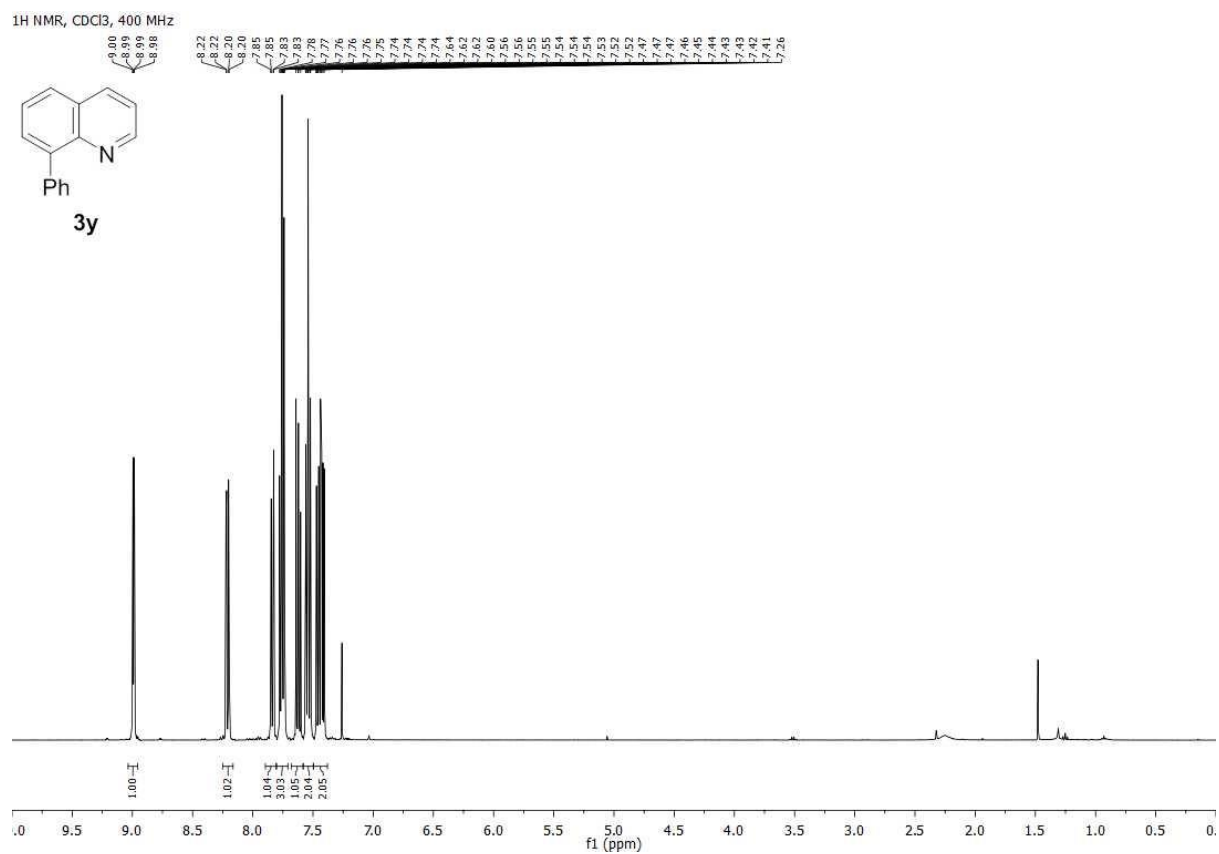


Figure S49. ¹H Spectra of **3y**

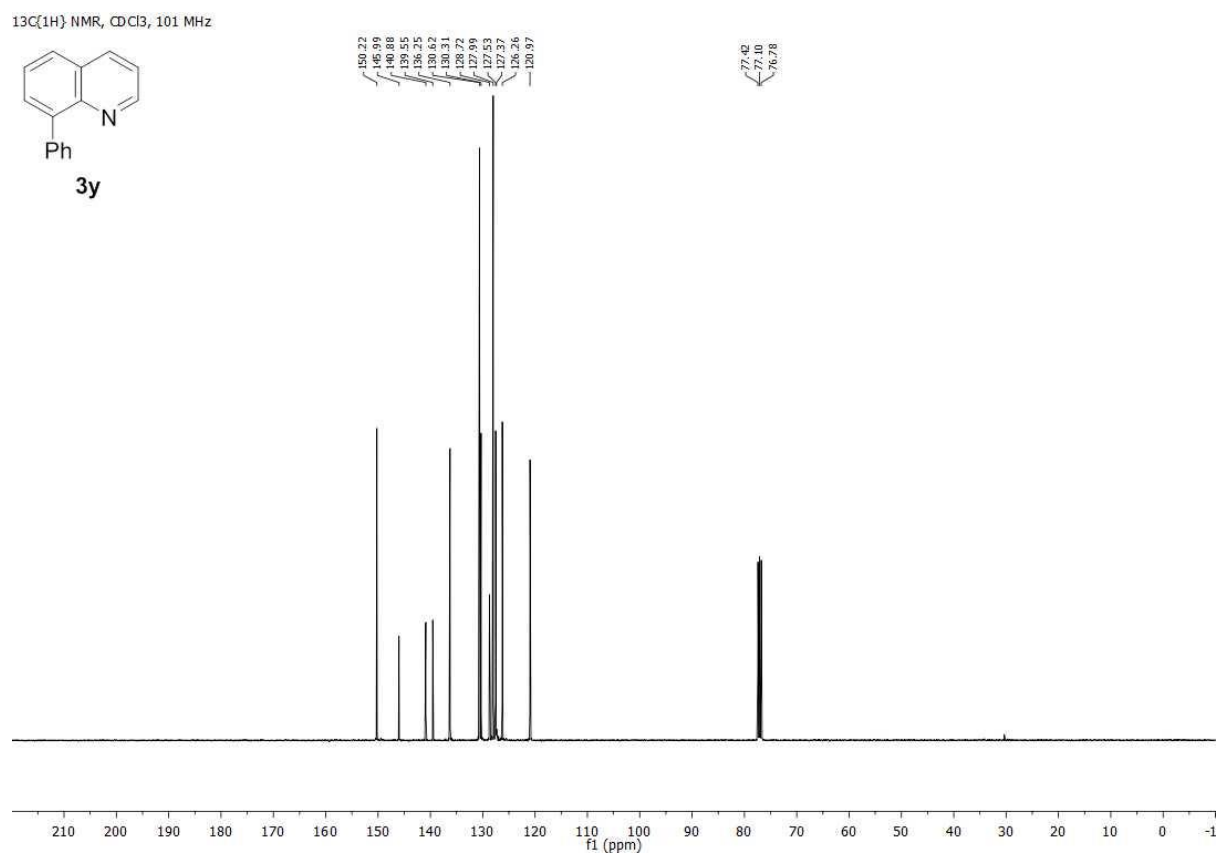


Figure S50. ¹³C Spectra of **3y**

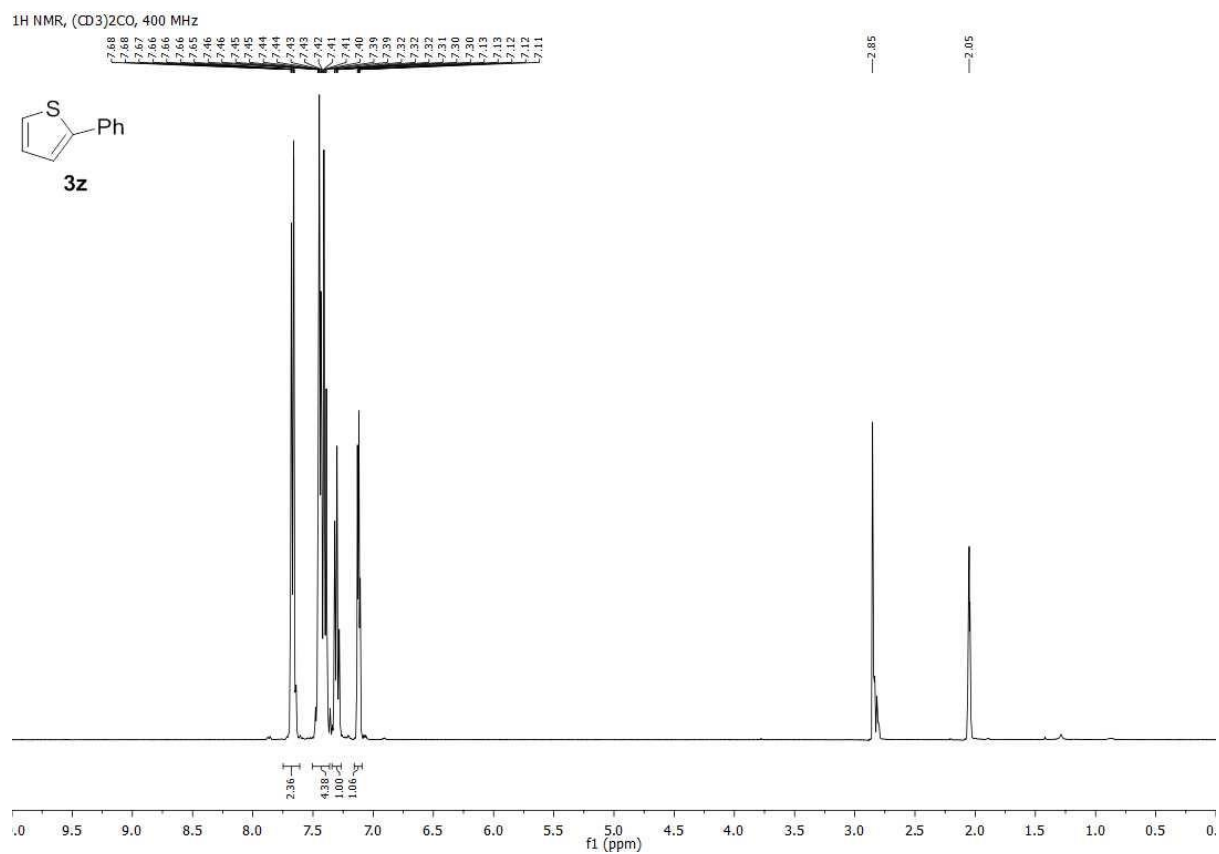


Figure S51. ¹H Spectra of **3z**

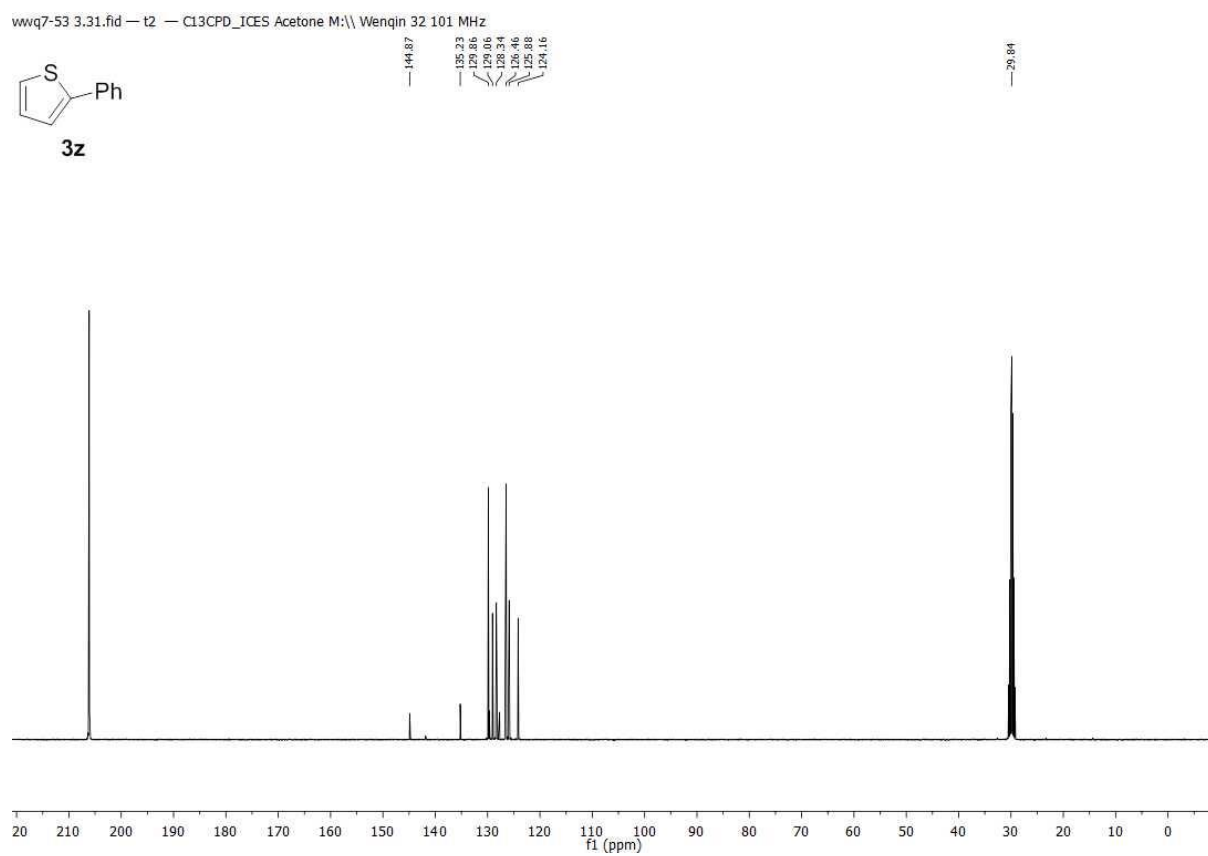


Figure S52. ¹³C Spectra of **3z**

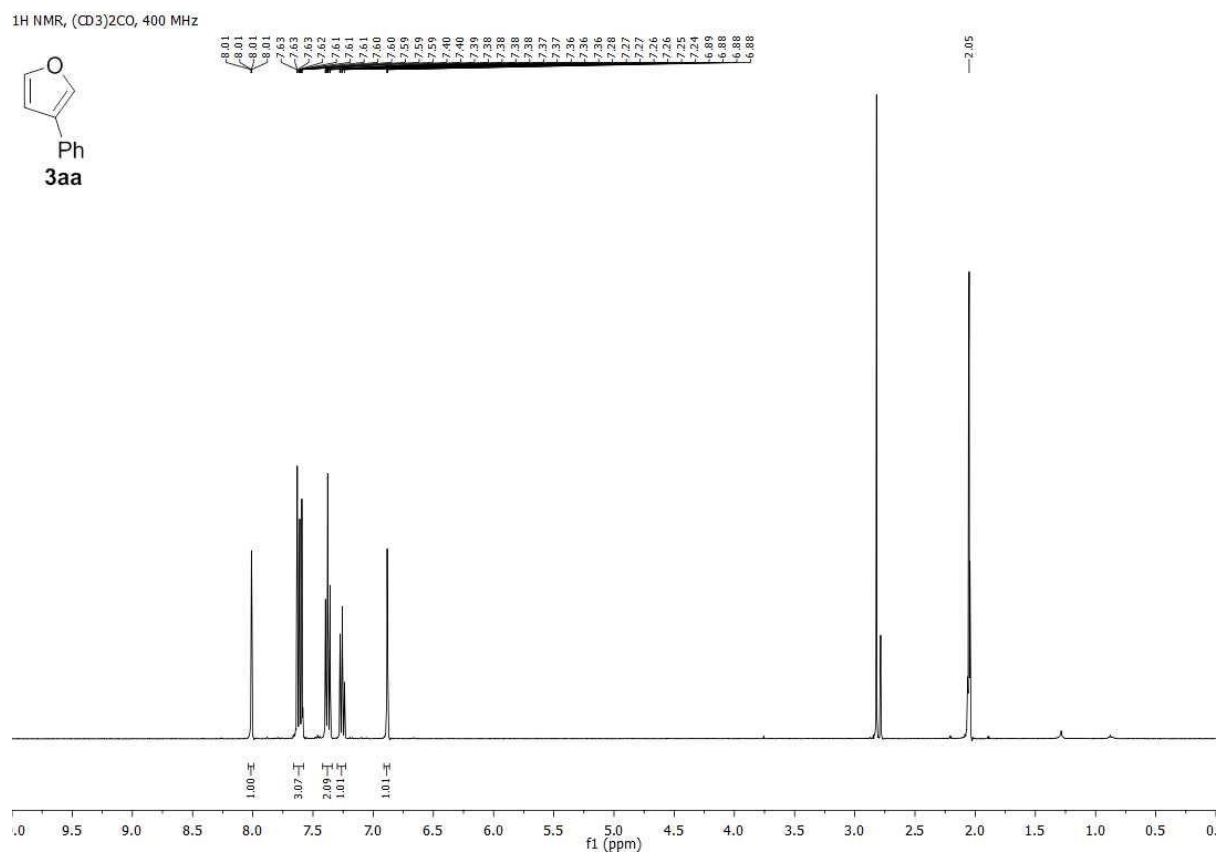


Figure S53. ¹H Spectra of 3aa

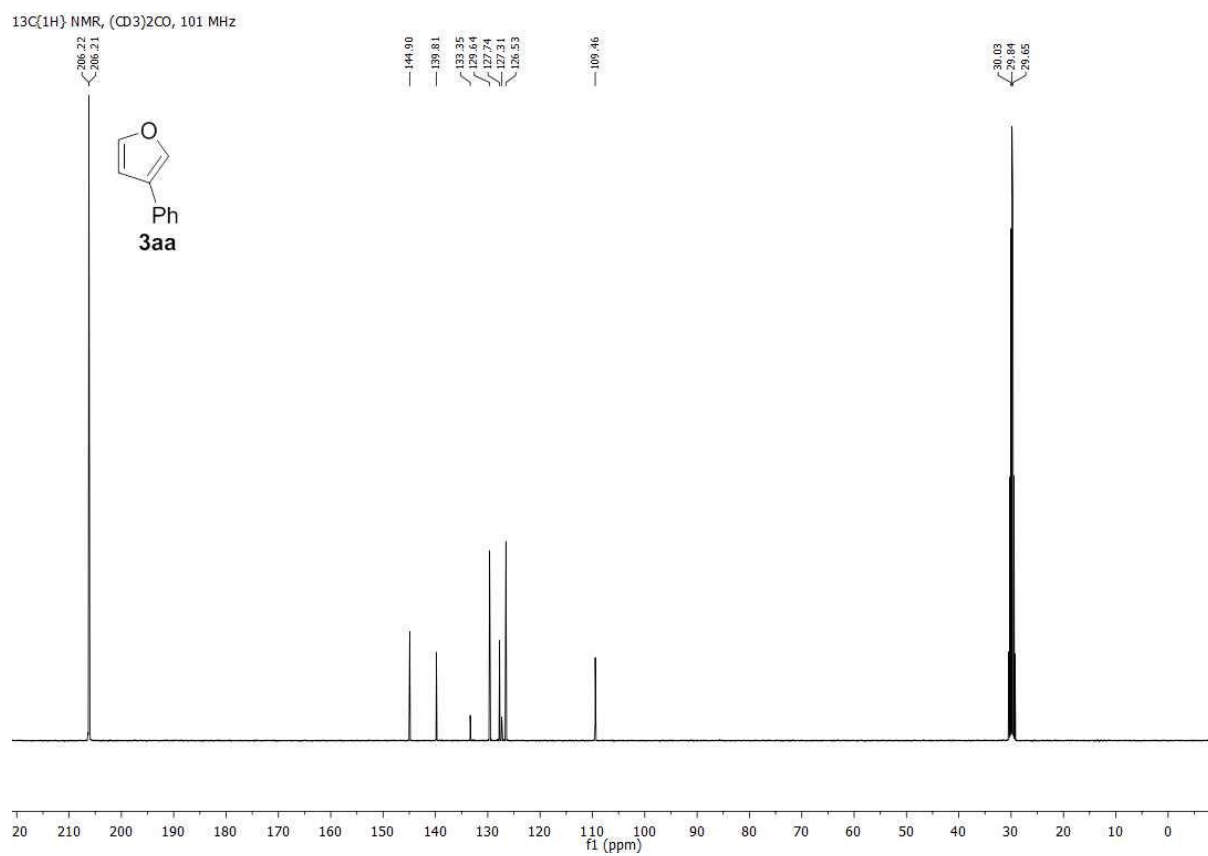


Figure S54. ¹³C Spectra of 3aa

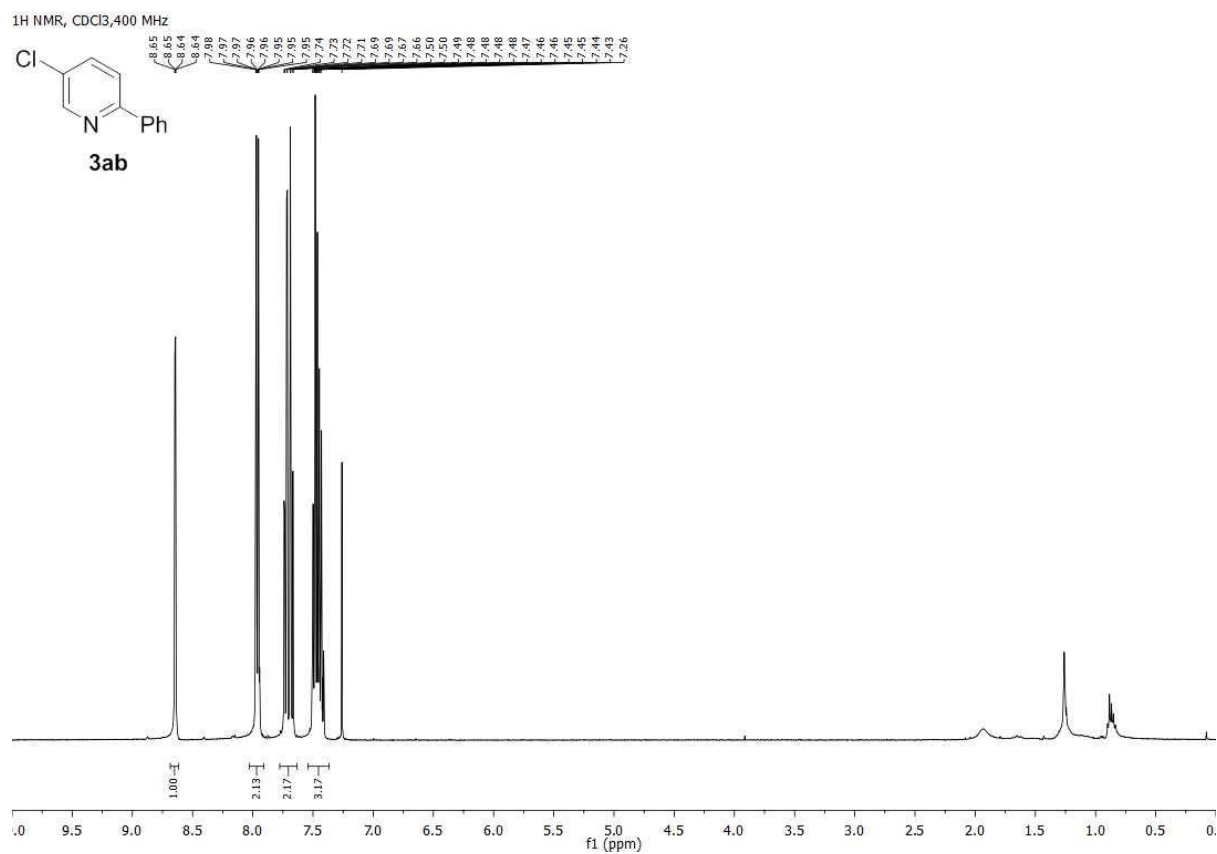


Figure S55. ¹H Spectra of **3ab**

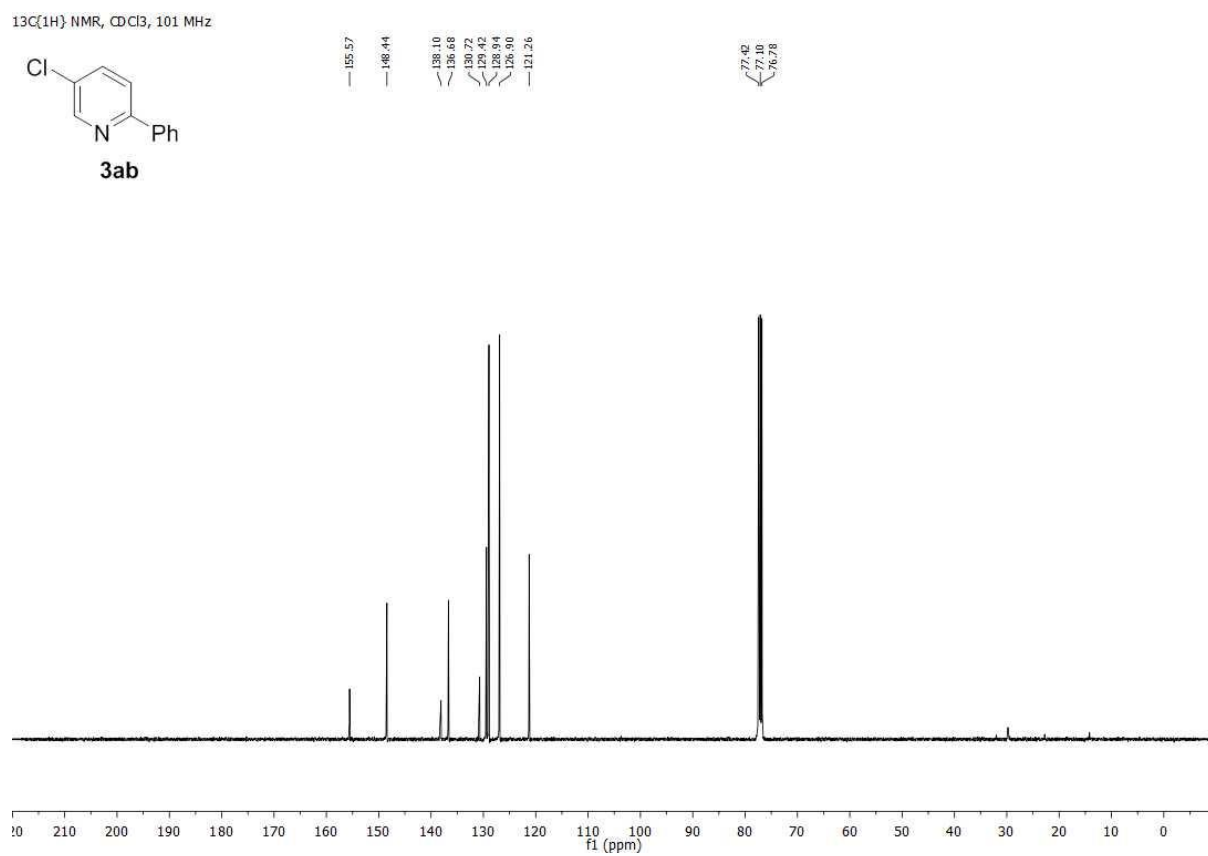


Figure S56. ¹³C Spectra of **3ab**

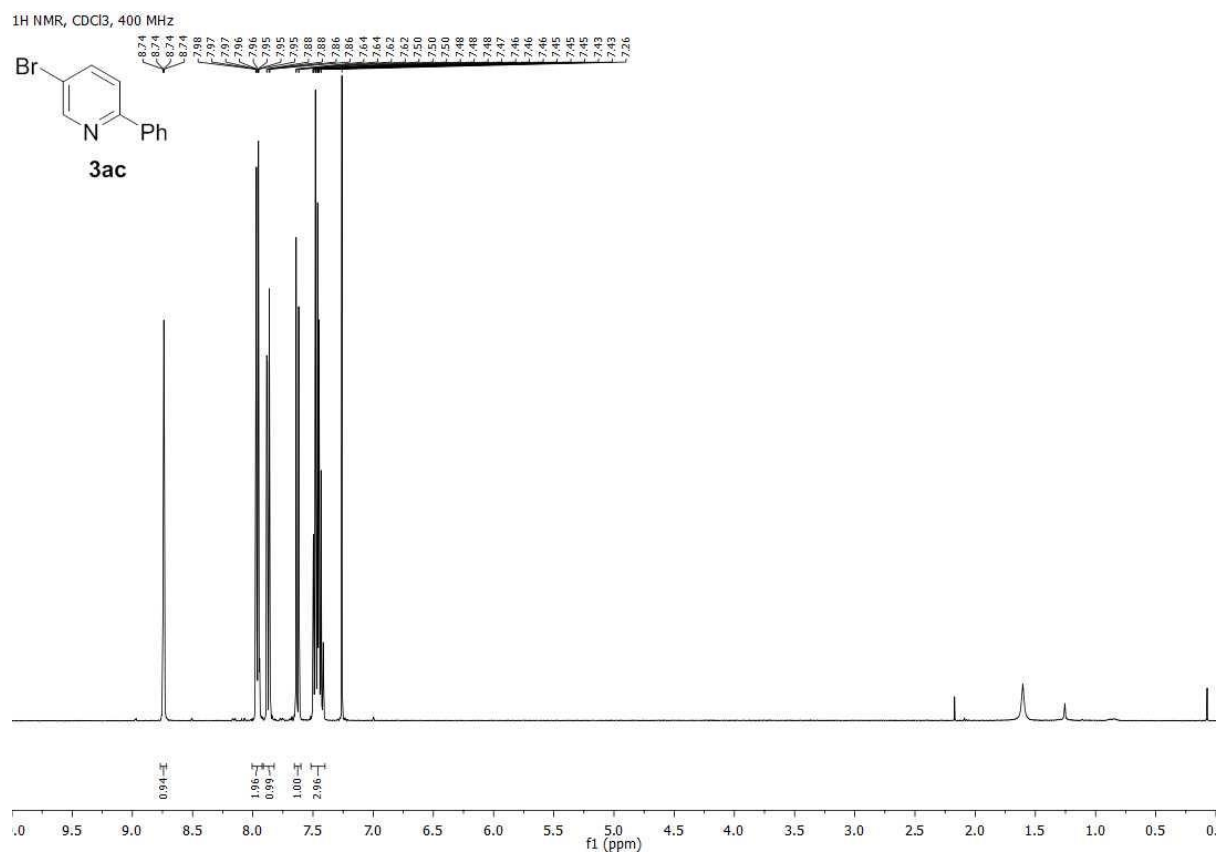


Figure S57. ¹H Spectra of **3ac**

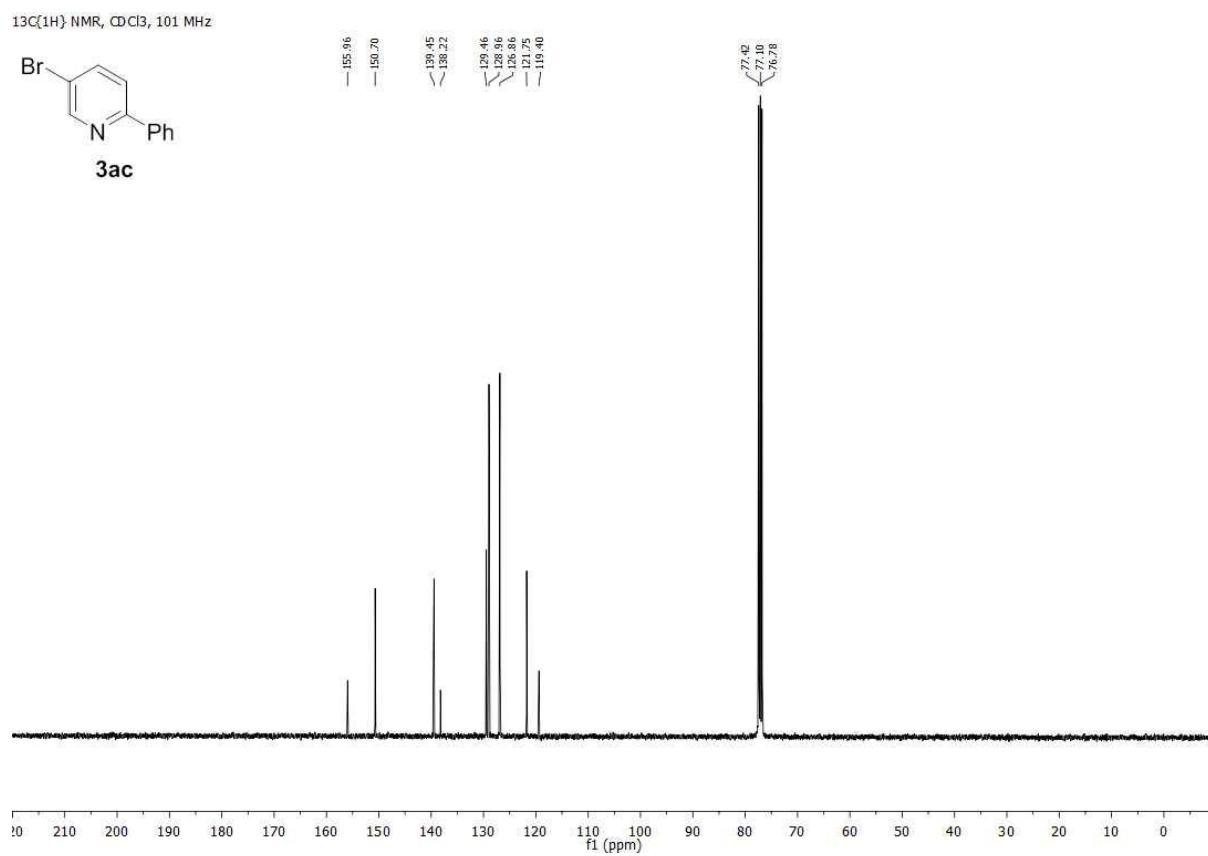
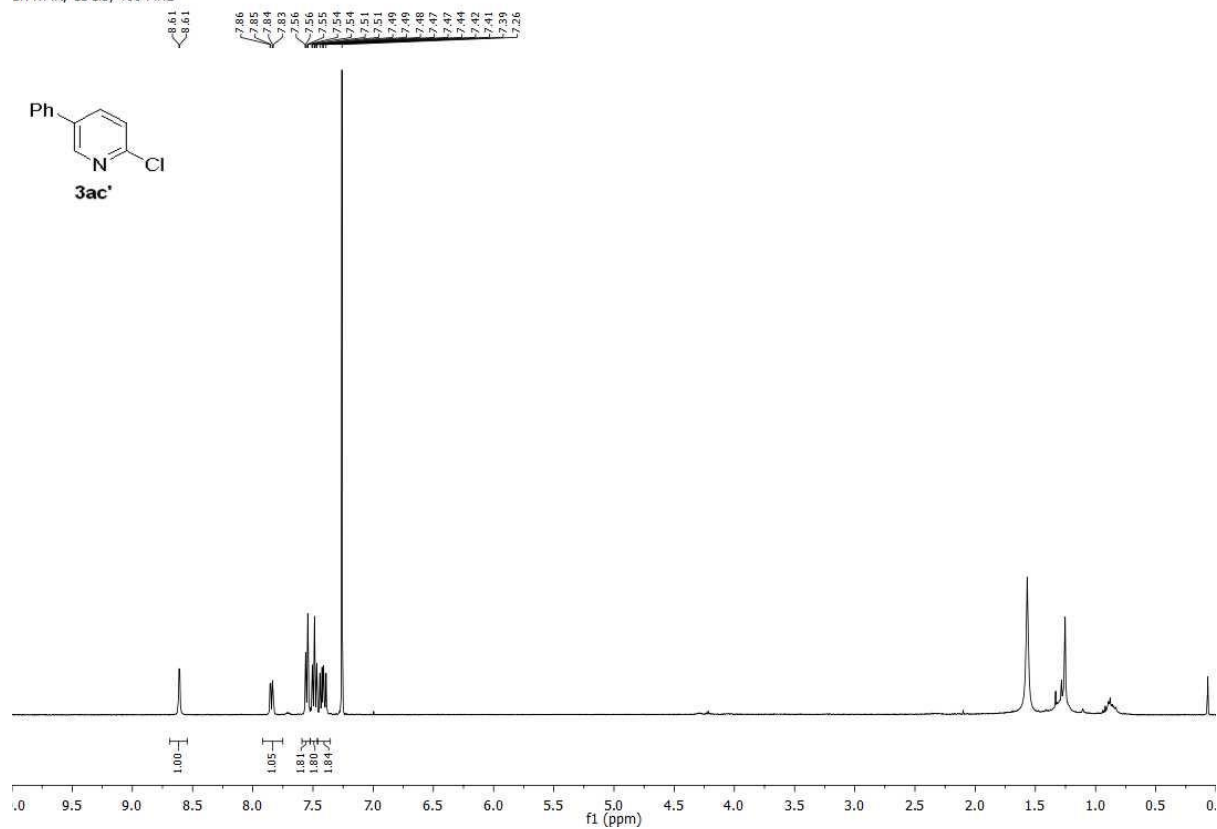
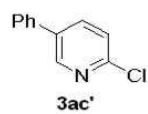
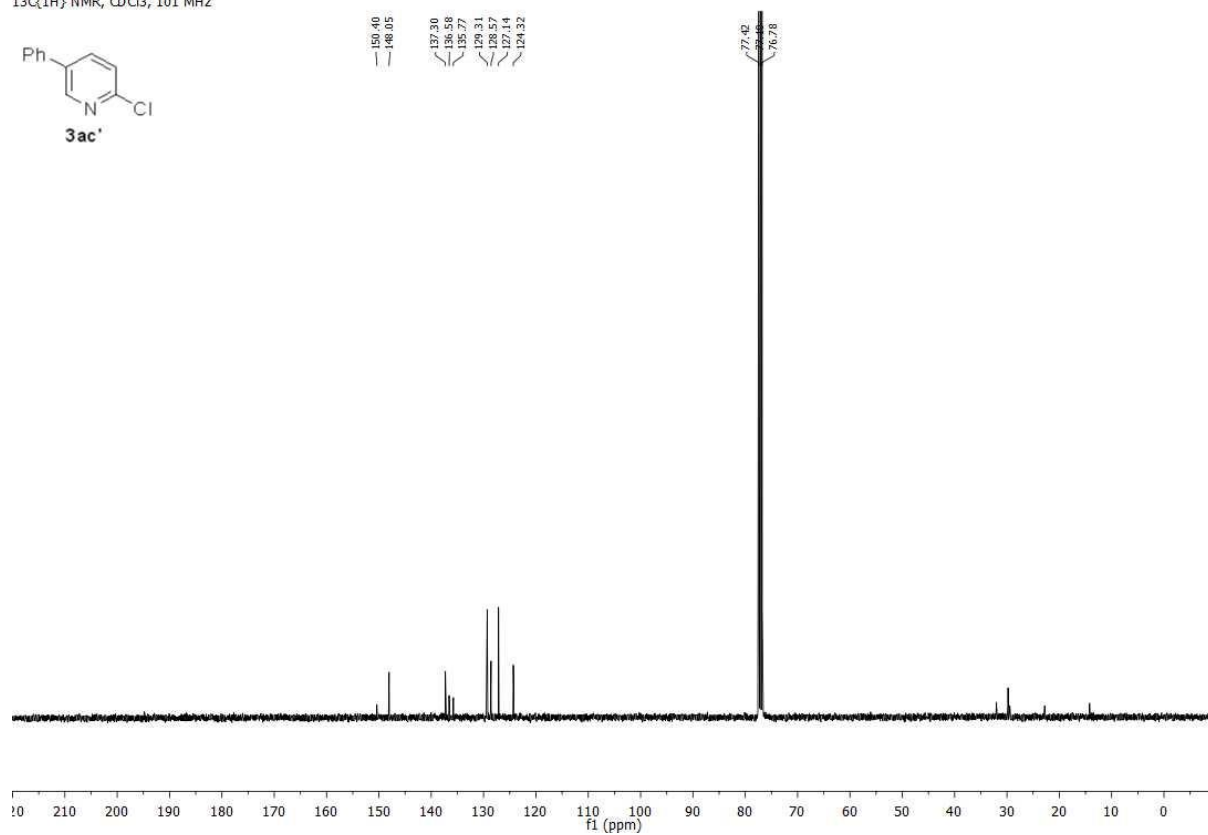
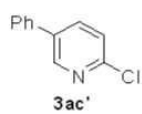


Figure S58. ¹³C Spectra of **3ac**

¹H NMR, CDCl₃, 400 MHz



¹³C{¹H} NMR, CDCl₃, 101 MHz



¹H NMR, CDCl₃, 400 MHz

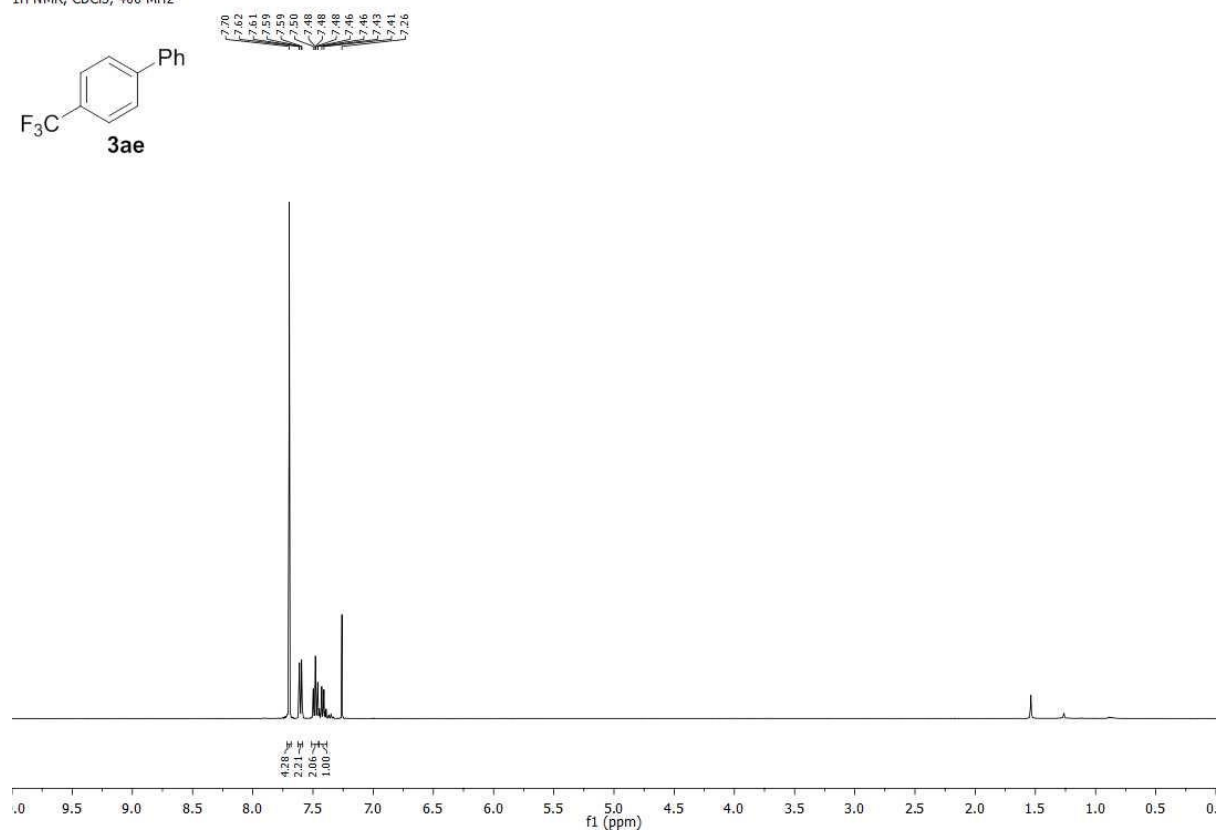
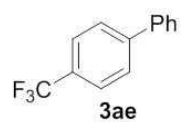


Figure S59. ¹H Spectra of **3ae**

wwq7-54 CF3.11.fid — T7-10 — C13CPD_ICES CDCl₃ M:\ Wenqin 57 101 MHz

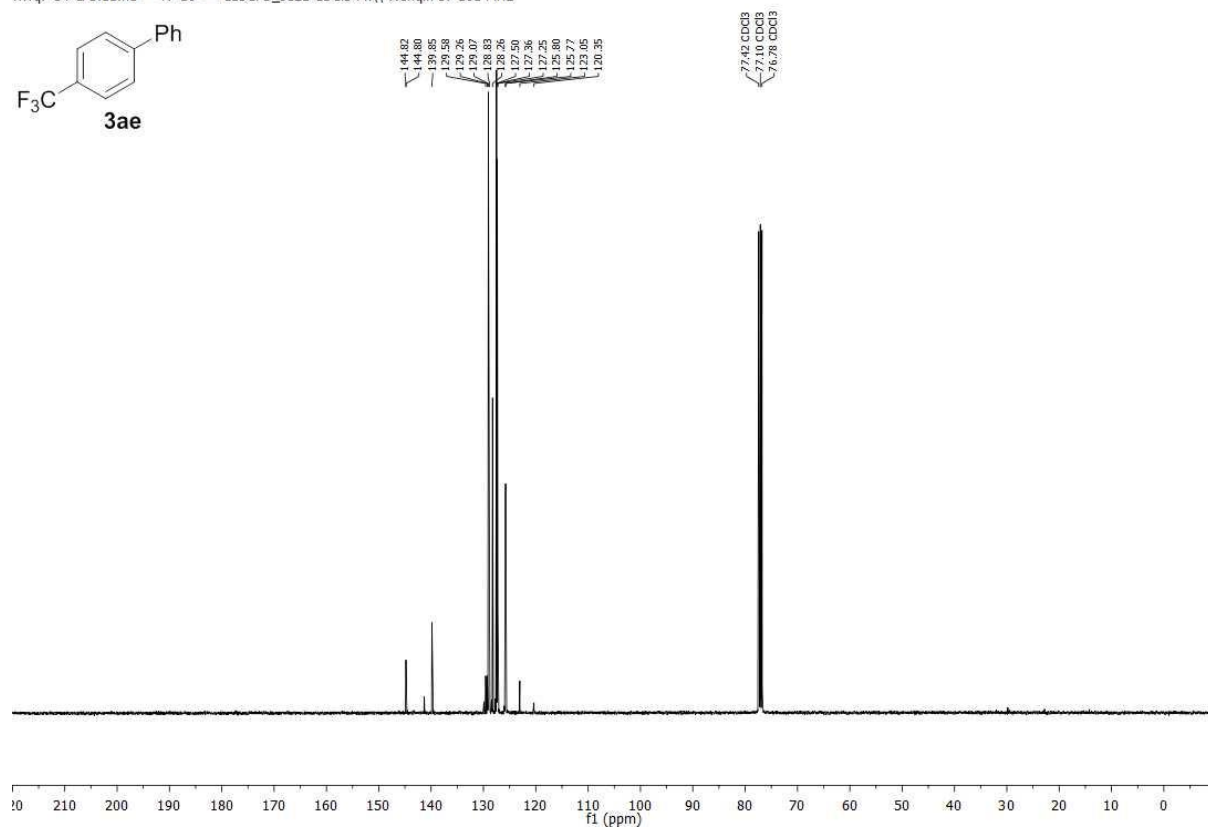
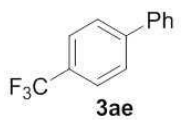


Figure S60. ¹³C Spectra of **3ae**

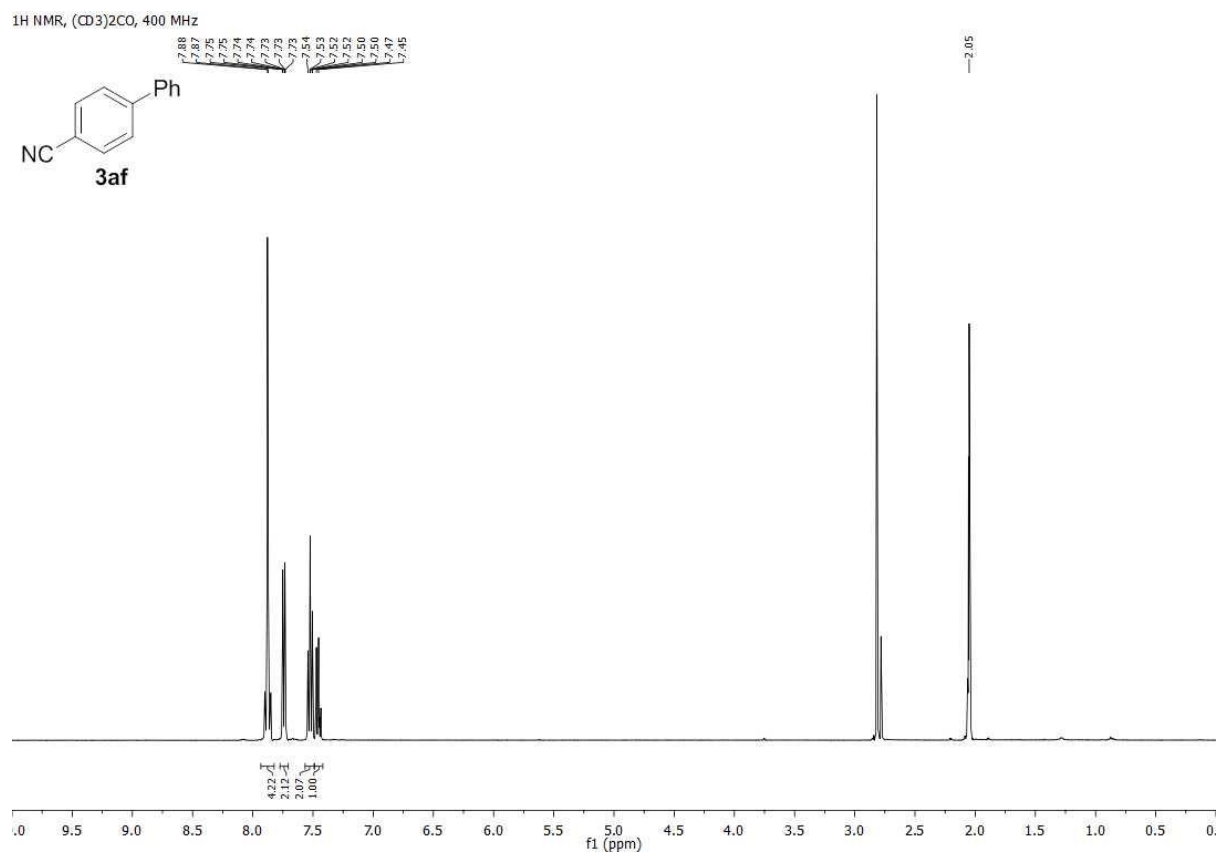


Figure S61. ¹H Spectra of **3af**

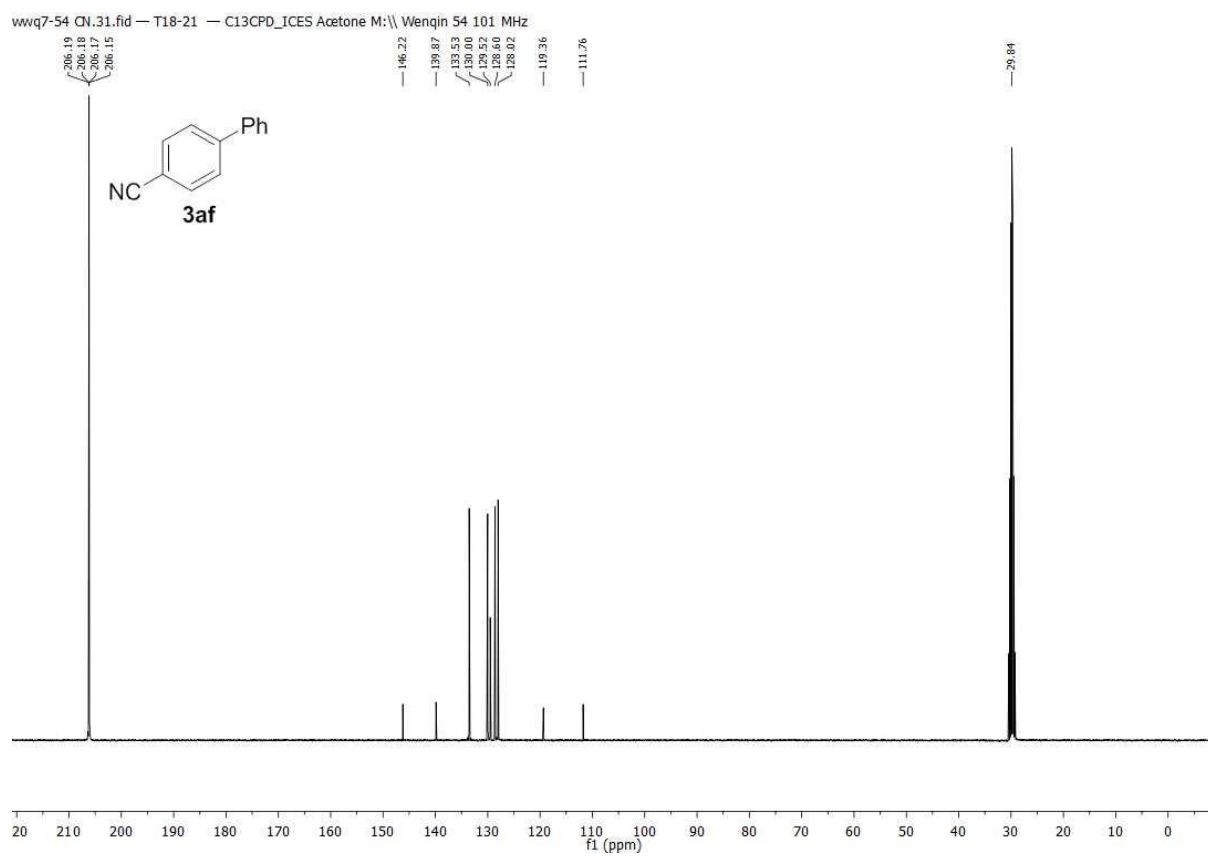


Figure S62. ¹³C Spectra of **3af**

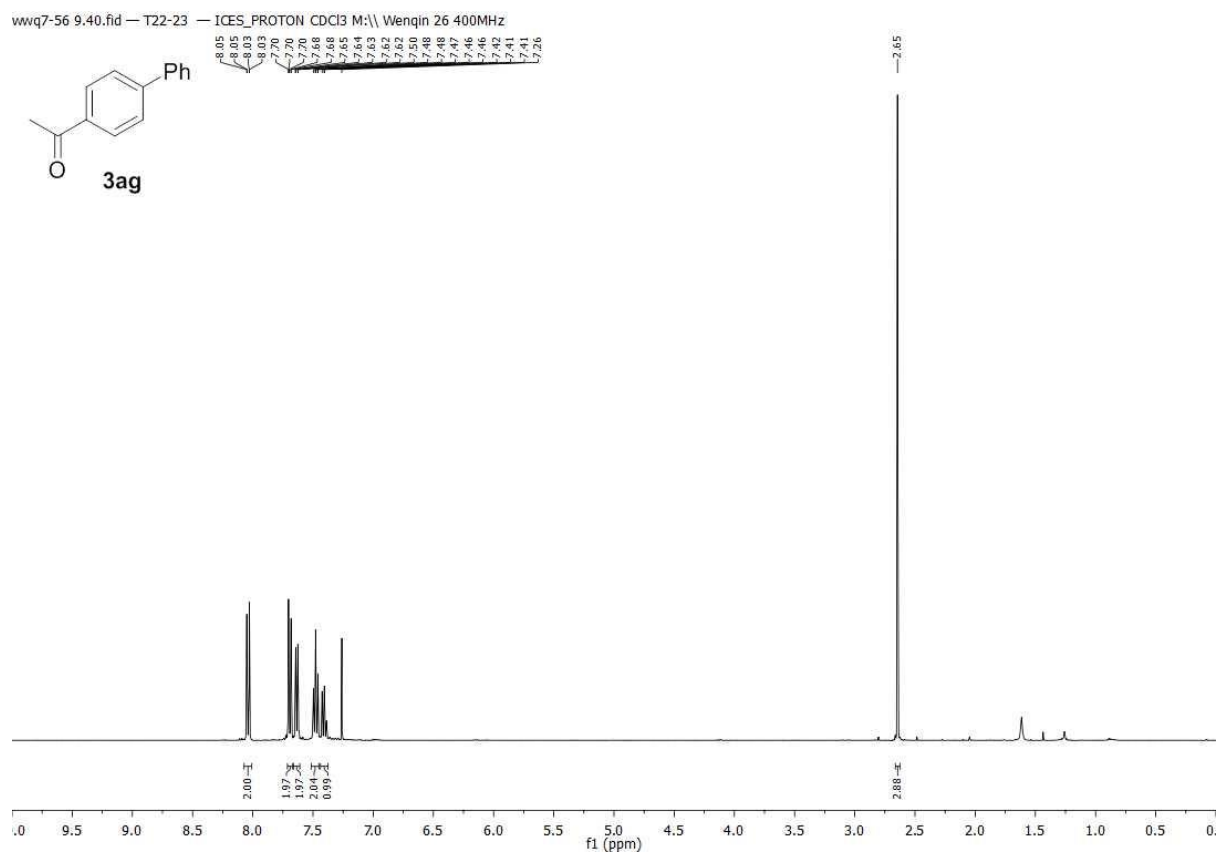


Figure S63. ¹H Spectra of **3ag**

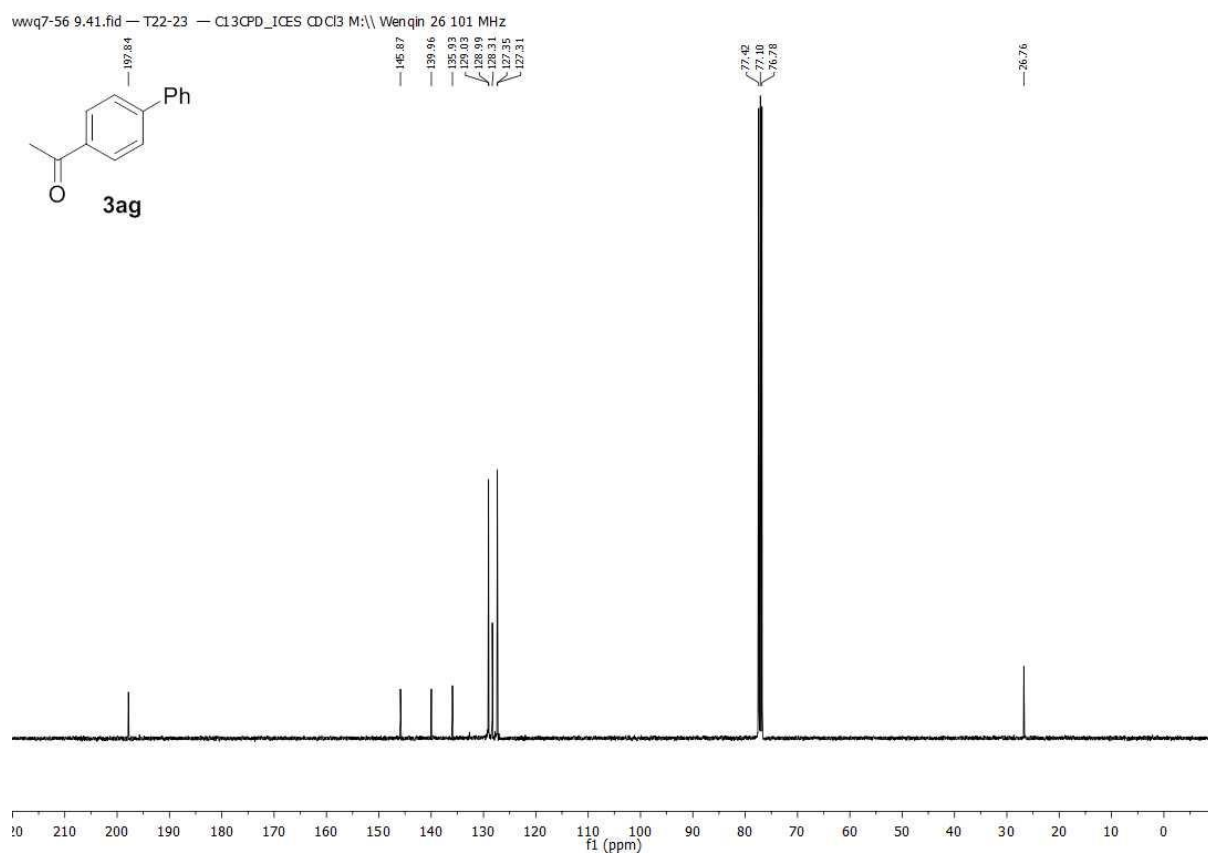


Figure S64. ¹³C Spectra of **3ag**

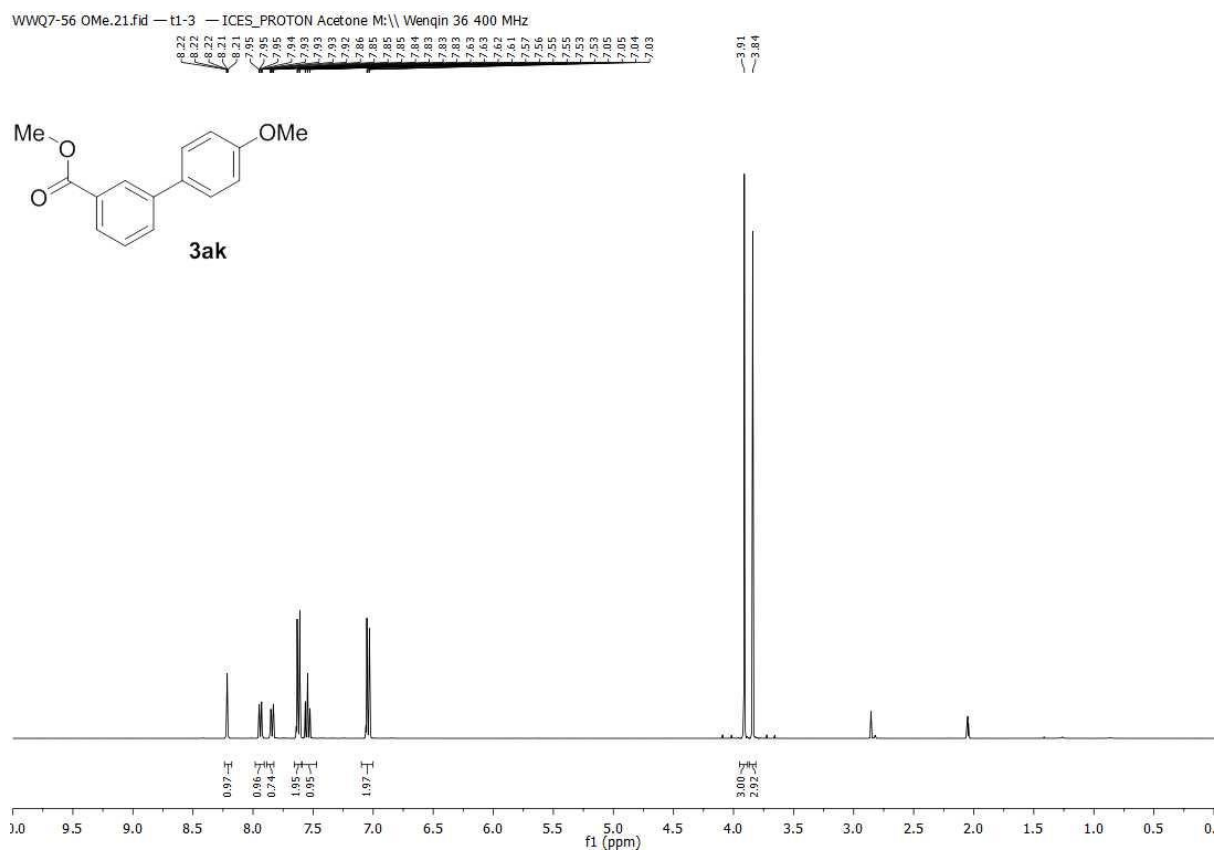


Figure S67. ^1H Spectra of **3ak**

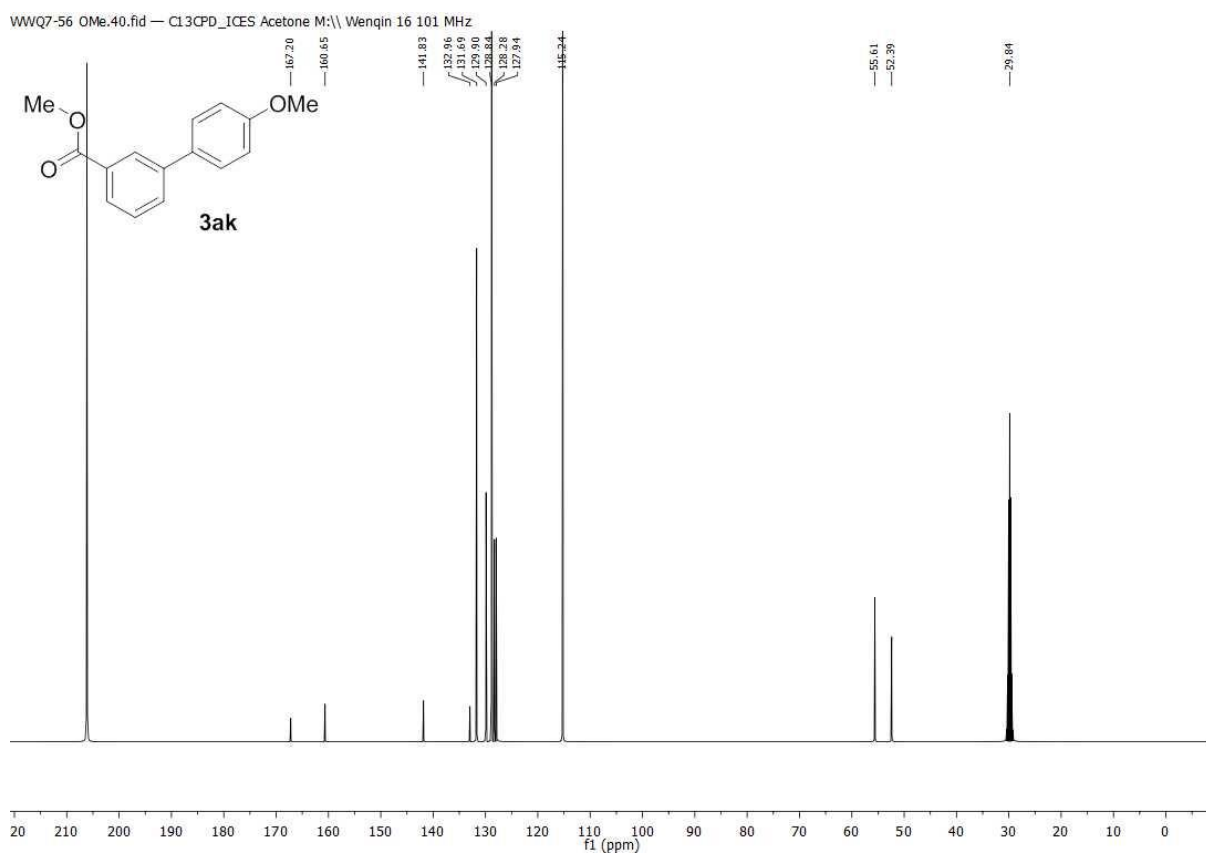


Figure S68. ^{13}C Spectra of **3ak**

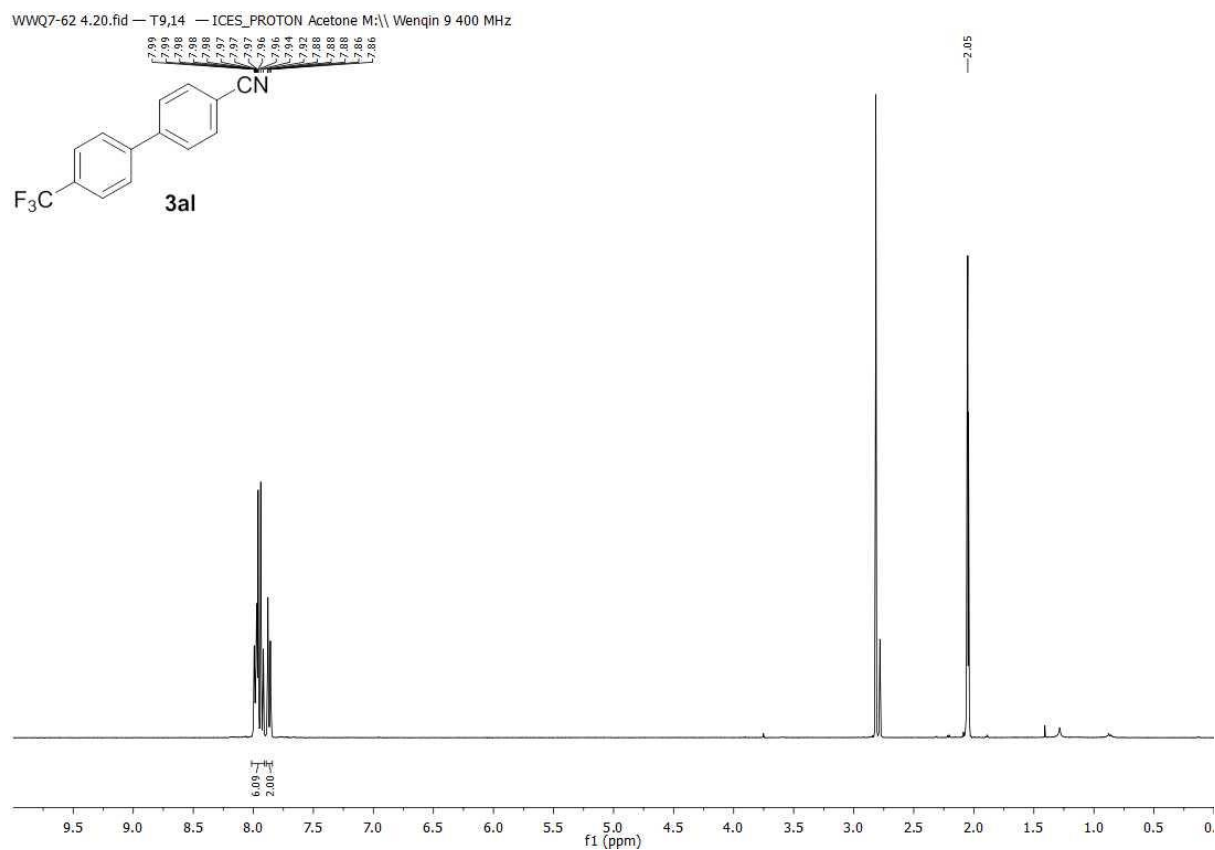


Figure S69. ^1H Spectra of **3al**

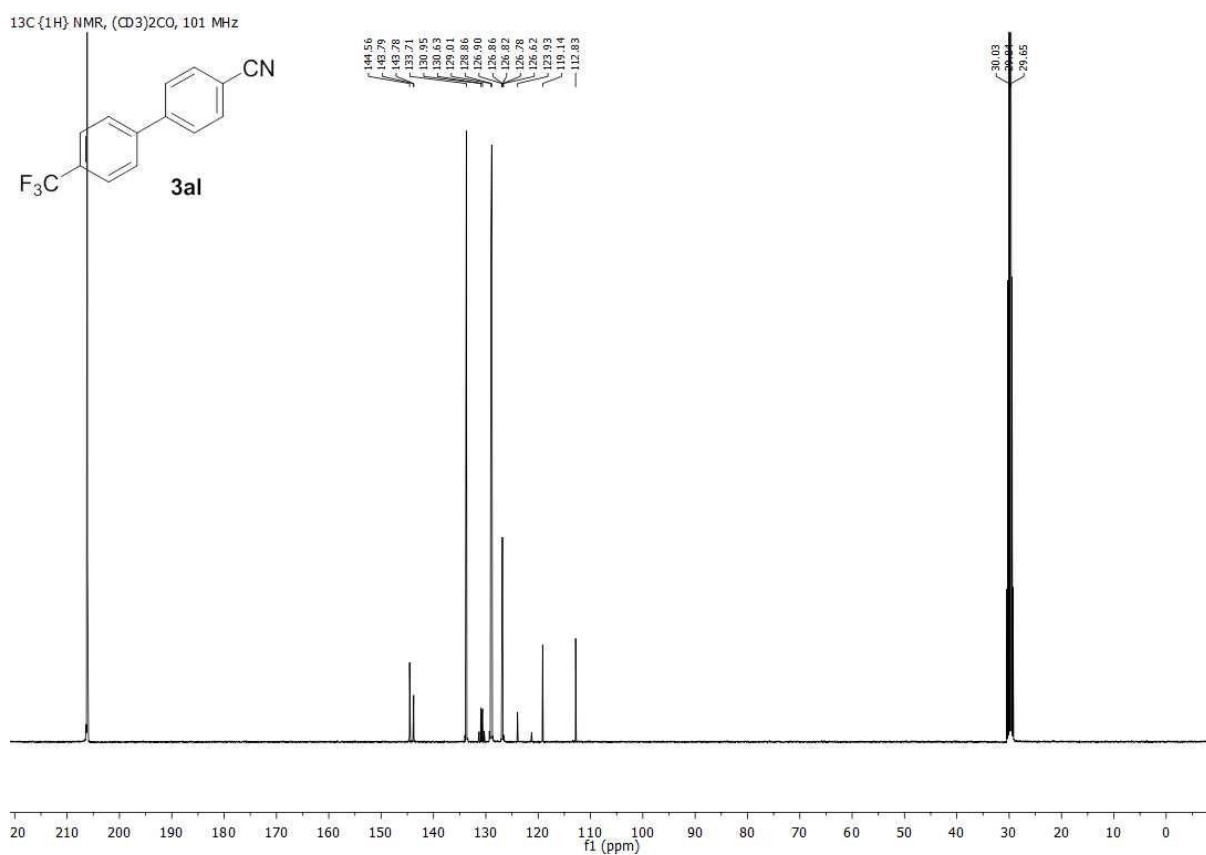


Figure S70. ^{13}C Spectra of **3al**