Supporting Information

Recyclable Cu@C_3N_4-catalyzed hydroxylation of aryl boronic acids in water under visible-light: Synthesis of phenols under ambient condition and room temperature

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1. General information

All solvents and reagents were purchased from Zhengzhou Alfa chem Co., Ltd. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods prior to use. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. The blue LEDs were provided by Beijing Roger tech Ltd.

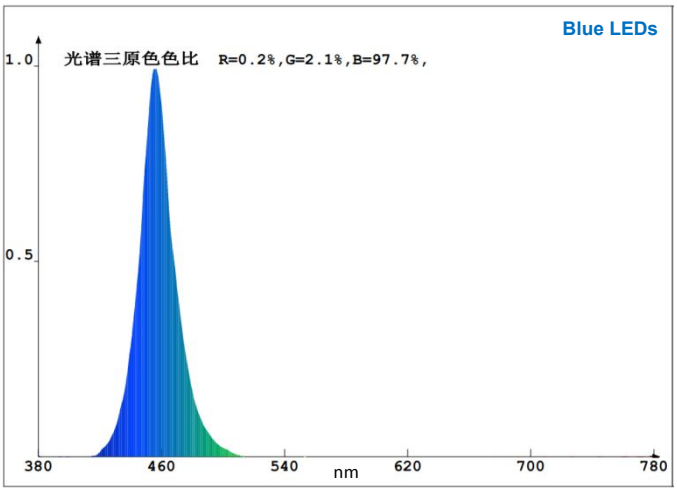
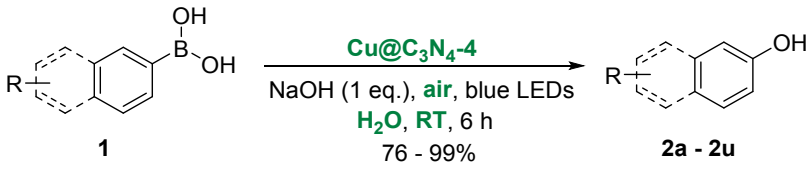


Figure S1. The spectrum of blue LEDs

2. Experimental section

2.1 General procedure for the synthesis of phenols



In a 25 mL oven dried reaction tube, photocatalyst (10 mg), arylboronic acids **1** (0.5 mmol), NaOH (1 equiv., 39.9 mg) and H_2O (1.5 mL) were added. The mixture was allowed to stir under blue light (460 nm) on room temperature for 6 h. After the reaction was completed, HCl (2 M with 15 mL water) was slowly added to the reaction.

After that, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product.

2.2 ^{18}O-Labeling Experiments

In a 25 mL oven-dried Schlenk tube, photocatalyst **Cu@C_3N_4-4** (10 mg) as catalyst, phenylboronic acids (0.5 mmol), NaOH (1 equiv., 39.9 mg) and H_2O (1.5 mL) were added. The reaction tube was evacuated and backfilled with $^{18}O_2$ three times. Then the mixture was allowed to stir under $^{18}O_2$ balloon with blue light (460 nm) irradiation on room temperature for 6 h. After the reaction was completed, HCl (2 M with 15 mL water) was slowly added to the reaction. After that, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product ^{18}O-**2a**.

The GC-MS shows a m/z peak of 96, which is in good agreement with that of ^{18}O-**2a**.

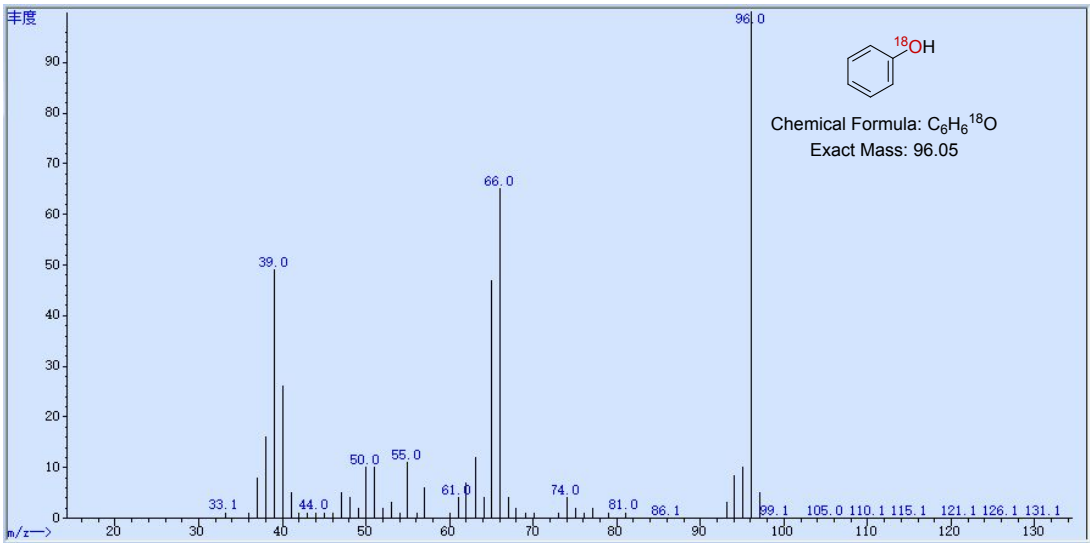
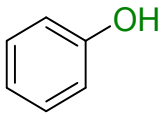


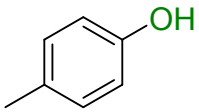
Figure S2. The GC-MS spectrum

3. Characterization data of products



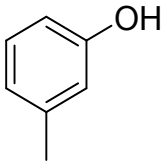
Phenol (2a)[1]

White solid (Yield 95%, 44.8 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz,) δ: 7.30 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.36 – 5.23 (m, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 155.31, 129.79, 120.96, 115.43



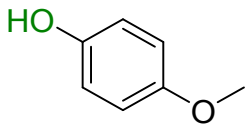
p-cresol (2b) [2]

Yellow solid (Yield 93%, 43.9 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.17 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 155.51, 130.29, 128.07, 115.67, 20.50.



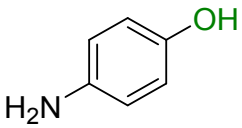
m-cresol (2c) [3]

Colorless liquid (Yield 86%, 40.5 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.41 – 7.19 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 6.3 Hz, 2H), 6.79 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 155.23, 140.27, 129.86, 122.26, 116.60, 112.86, 21.51.



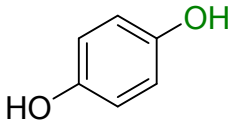
4-methoxyphenol (2d) [1]

White solid (Yield 88%, 41.5 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 6.92 – 6.74 (m, 4H), 5.93 – 5.66 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 153.49, 149.57, 116.23, 115.06, 55.98.



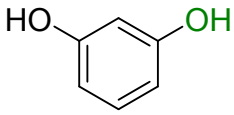
4-aminophenol (2e) [4]

Brown solid (Yield 89%, 42.0 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.33 – 8.22 (m, 1H), 7.94 – 7.84 (m, 1H), 7.63 – 7.48 (m, 3H), 7.42 – 7.27 (m, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 5.46 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 155.35, 129.77, 120.93, 115.41.



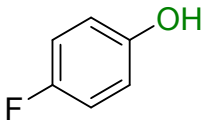
hydroquinone (2f) [5]

White solid (Yield 92%, 43.3 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.65 (s, 2H), 6.57 (s, 4H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 150.18, 116.16.



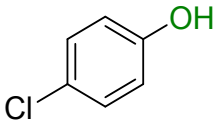
resorcinol (2g) [5]

White solid (Yield 85%, 40.2 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.17 (s, 2H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.27 – 6.16 (m, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 158.88, 130.21, 106.70, 102.94.



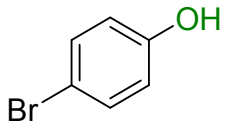
4-fluorophenol (2h) [6]

White solid (Yield 90%, 42.5 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.02 – 6.90 (m, 2H), 6.87 – 6.71 (m, 2H), 5.27 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 157.50, 157.13, 151.37, 151.35, 116.30, 116.22, 116.15, 115.91.



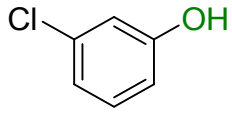
4-chlorophenol (2i) [6]

White solid (Yield 95%, 44.8 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.22 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.41 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 153.91, 129.60, 125.81, 116.71.



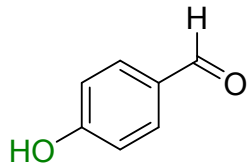
4-bromophenol (2j) [7]

White solid (Yield 92%, 43.5 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.44 – 7.31 (m, 2H), 6.81 – 6.70 (m, 2H), 5.42 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 154.46, 133.54, 117.25, 113.01.



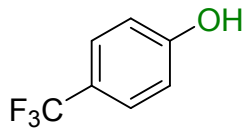
3-chlorophenol (2k) [3]

Brown liquid (Yield 82%, 38.7 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.21 (t, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.97 (t, *J* = 2.3 Hz, 1H), 6.91 – 6.74 (m, 2H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 155.58, 135.09, 130.85, 121.74, 116.10, 114.02.



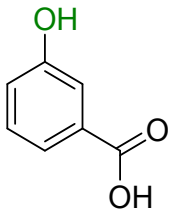
4-hydroxybenzaldehyde (2l) [2]

White solid (Yield 90%, 42.6 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 10.61 (s, 1H), 9.79 (s, 1H), 7.95 – 7.56 (m, 2H), 7.11 – 6.73 (m, 2H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 163.76, 131.55, 128.88, 116.29.



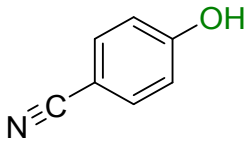
4-(trifluoromethyl)phenol (2m) [8]

White solid (Yield 95%, 44.6 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 10.29 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 161.17, 127.35, 127.32, 127.28, 127.24, 126.58, 123.89, 120.13, 119.81, 116.08.



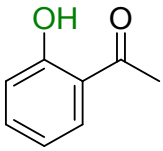
3-hydroxybenzoic acid (2n) [5]

White solid (Yield 84%, 39.7 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.78 (s, 1H), 9.79 (s, 1H), 7.58 – 7.14 (m, 3H), 7.00 (dd, *J* = 8.1, 2.3 Hz, 1H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 167.79, 156.83, 132.47, 130.03, 120.45, 120.30, 116.26.



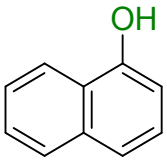
4-hydroxybenzonitrile (2o) [8]

Light brown white solid (Yield 99%, 46.7 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 7.78 – 7.38 (m, 3H), 7.02 – 6.90 (m, 2H), 6.61 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 160.15, 133.35, 119.25, 116.47, 103.13.



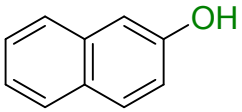
1-(2-hydroxyphenyl)ethan-1-one (2p) [5]

Colorless liquid (Yield 96%, 45.3 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.16 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.43 (m, 1H), 6.98 – 6.85 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 205.02, 162.69, 135.56, 131.63, 121.29, 118.33, 117.00, 27.29.



naphthalen-1-ol (2q) [1]

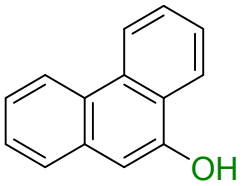
White to off white solid (Yield 95%, 44.7 mg), ^{1}H NMR (Chloroform-*d,* 400 MHz) δ: 8.31 – 8.20 (m, 1H), 7.93 – 7.83 (m, 1H), 7.62 – 7.47 (m, 3H), 7.43 – 7.33 (m, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 5.46 (s, 1H). ^{13}C NMR (Chloroform-*d,* 101 MHz) δ: 151.32, 135.81, 127.77, 126.53, 125.91, 125.38, 124.39, 121.57, 120.82, 108.75.



naphthalen-2-ol (2r) [1]

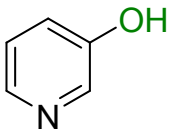
Slight brown solid (Yield 82%, 38.7 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.79 (s, 2H), 7.77 (d, *J* = 2.2 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.26

(t, *J* = 7.4 Hz, 2H), 7.23 – 7.09 (m, 4H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 155.79, 135.09, 129.77, 128.21, 128.01, 126.57, 126.46, 123.10, 119.10, 109.15.



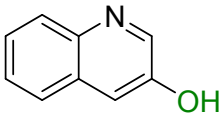
phenanthren-9-ol (2s) [9]

Brown solid (Yield 87%, 40.9 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 10.40 (s, 1H), 8.75 (d, *J* = 7.9 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.32 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.83 – 7.60 (m, 3H), 7.48 (dt, *J* = 32.4, 7.3 Hz, 2H), 7.13 (s, 1H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 151.53, 133.49, 131.47, 127.54, 127.36, 126.90, 126.72, 126.56, 125.78, 123.98, 123.29, 123.12, 123.00, 105.32.



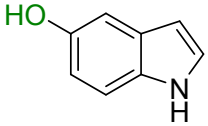
pyridin-3-ol (2t) [9]

White solid (Yield 92%, 43.3 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.98 (s, 1H), 8.17 (d, *J* = 2.6 Hz, 1H), 8.03 (dd, *J* = 4.4, 1.7 Hz, 1H), 7.37 – 7.02 (m, 2H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 154.16, 140.64, 138.43, 124.57, 122.51.



quinolin-3-ol (2u) [7]

White solid (Yield 79%, 37.2 mg), ^{1}H NMR (Chloroform-*d*, 400 MHz) δ: 8.82 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.38 (m, 2H), 7.35 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.3 Hz, 1H). ^{13}C NMR (Chloroform-*d*, 101 MHz) δ: 152.38, 147.97, 138.34, 136.20, 128.62, 127.76, 121.78, 117.95, 110.34, 26.96.



1*H*-indol-5-ol (2v) [7]

brown solid (Yield 76%, 35.8 mg), ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 10.76 (s, 1H), 8.61 (s, 1H), 7.29 – 7.13 (m, 2H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.24 (t, *J* = 2.4 Hz, 1H), 3.44 (s, 1H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 150.93, 130.89, 128.82, 125.91, 112.05, 111.73, 104.28, 100.65.

References

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4. ^{1}H NMR and ^{13}C NMR spectra

^{1}HNMR

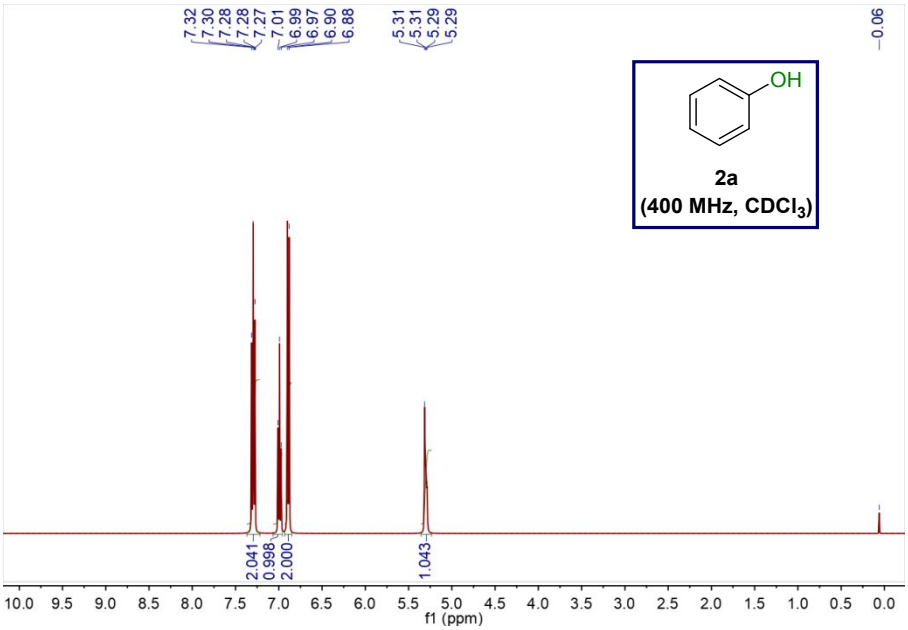

Figure S3. The ^{1}H NMR spectrum of **2a**

^{13}CNMR

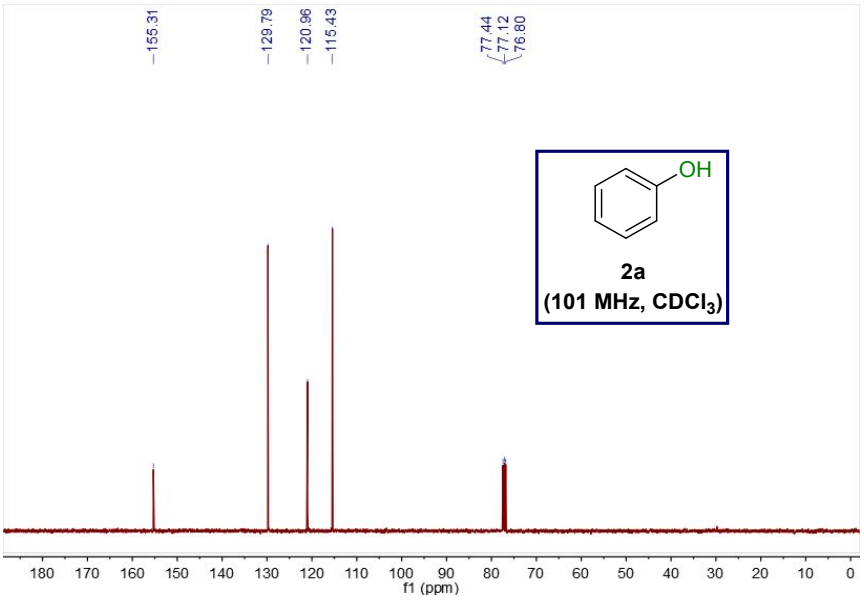

Figure S4. The ^{13}C NMR spectrum of **2a**

[1]HNMR

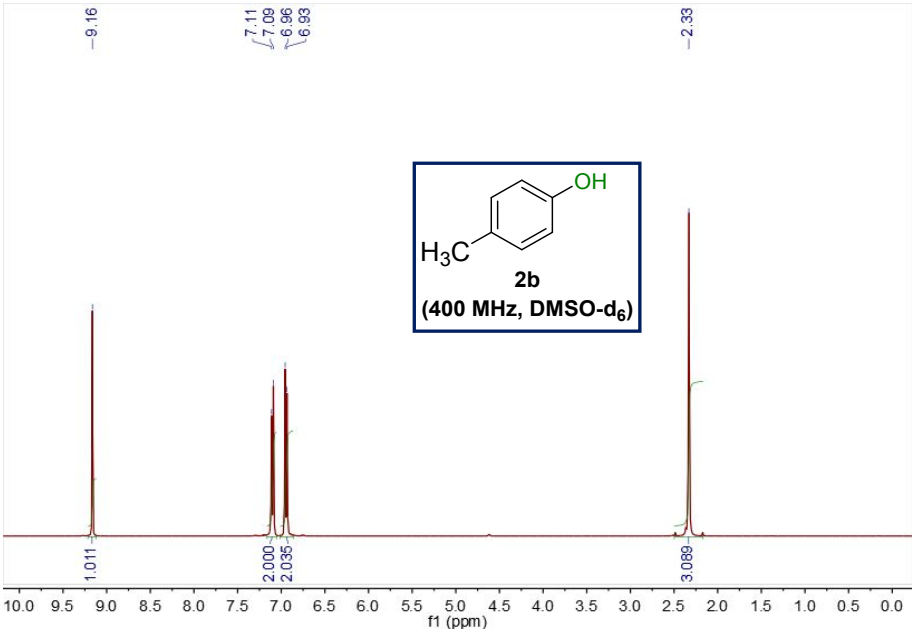

Figure S5. The [1]H NMR spectrum of **2b**

[13]CNMR

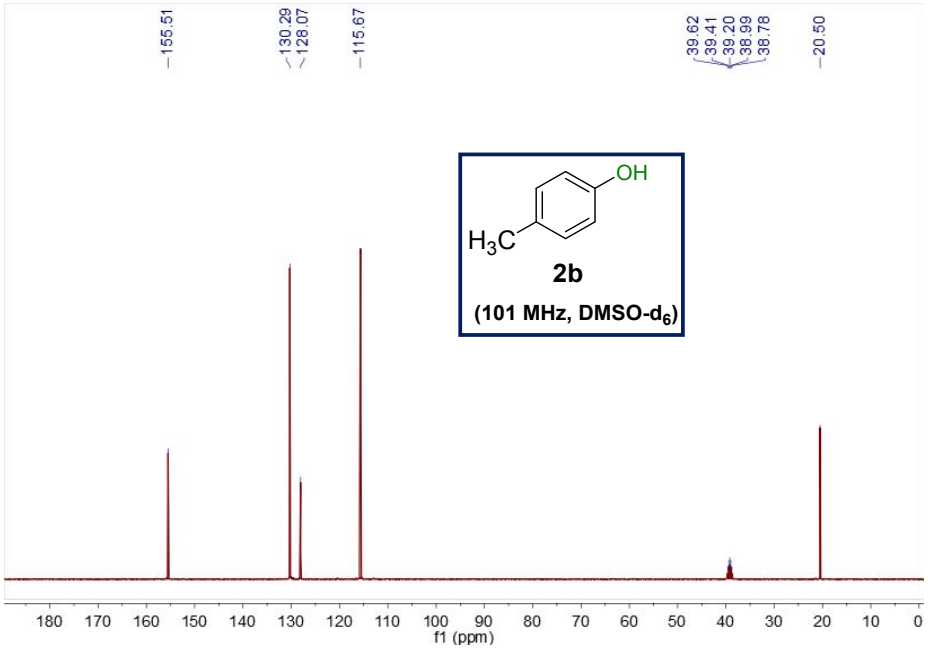

Figure S6. The [13]C NMR spectrum of **2b**

^{1}HNMR

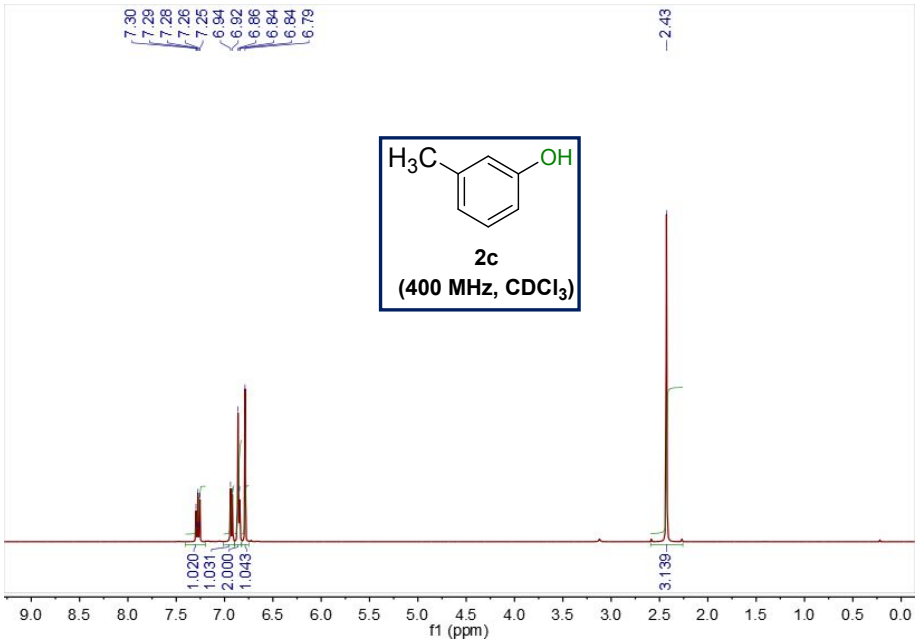

Figure S7. The ^{1}H NMR spectrum of **2c**

^{13}CNMR

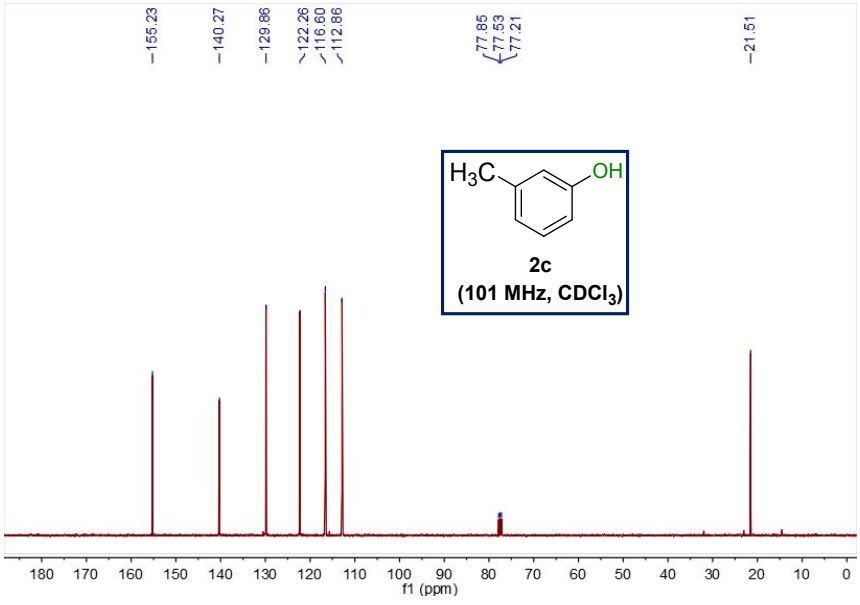

Figure S8. The ^{13}C NMR spectrum of **2c**

^{1}HNMR

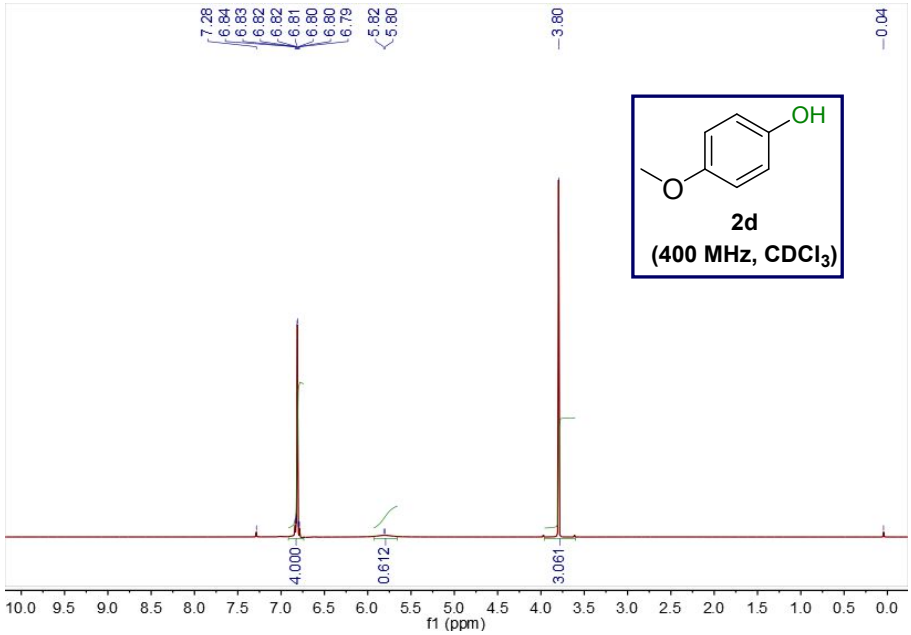

Figure S9. The ^{1}H NMR spectrum of **2d**

^{13}CNMR

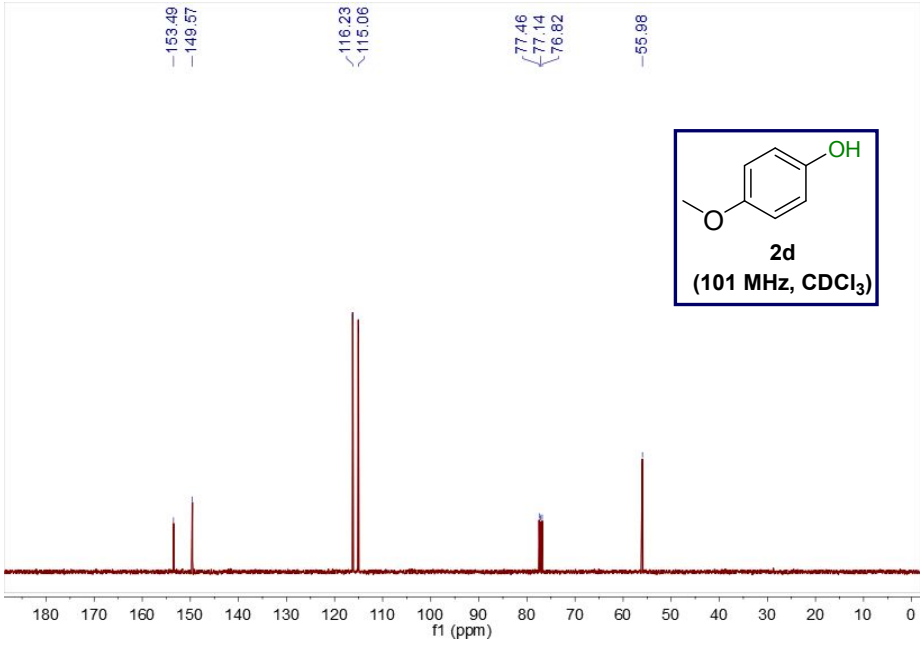

Figure S10. The ^{13}C NMR spectrum of **2d**

^{1}HNMR

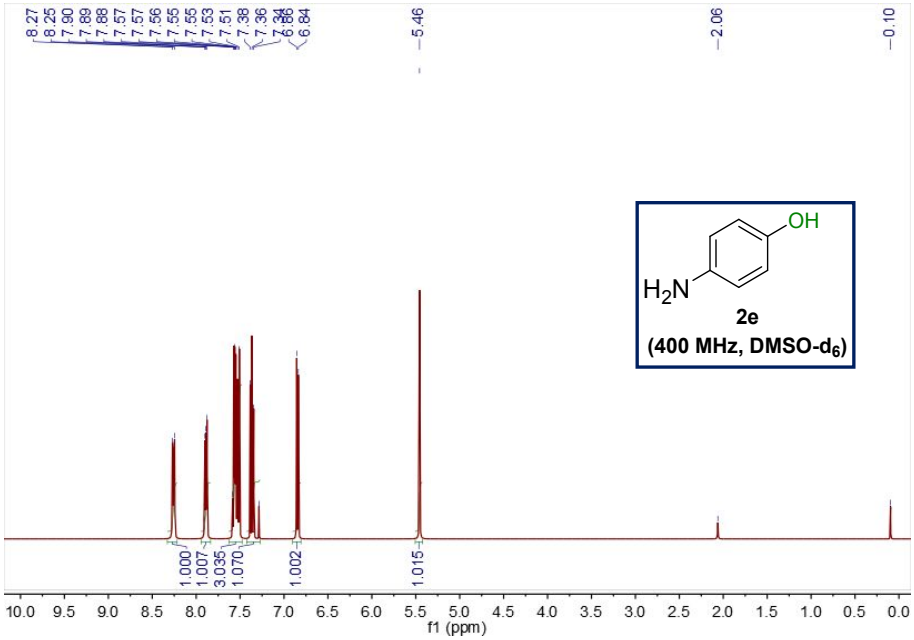

Figure S11. The ^{1}H NMR spectrum of **2e**

^{13}CNMR

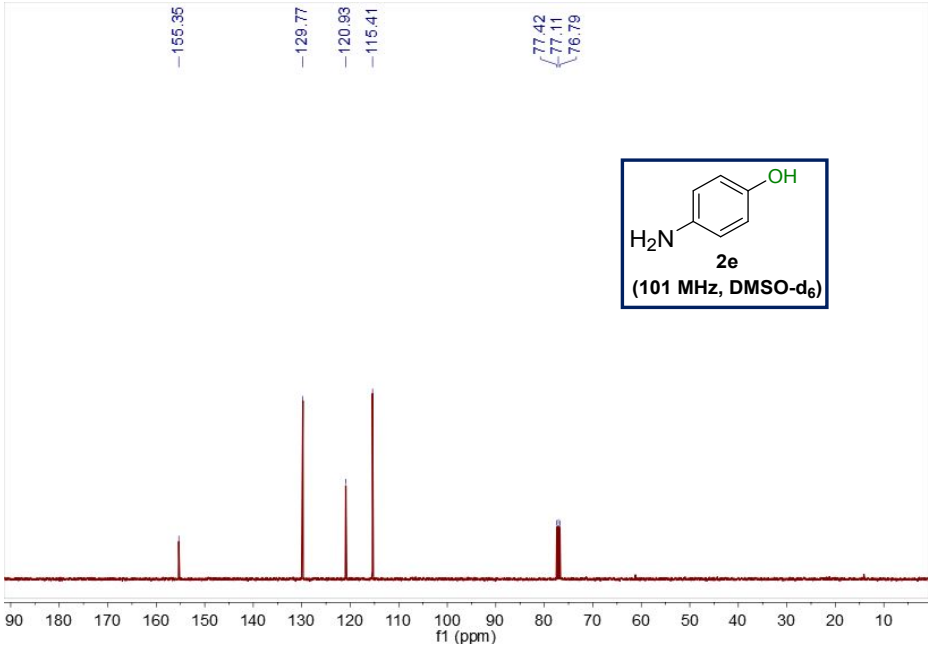

Figure S12. The ^{13}C NMR spectrum of **2e**

^{1}HNMR

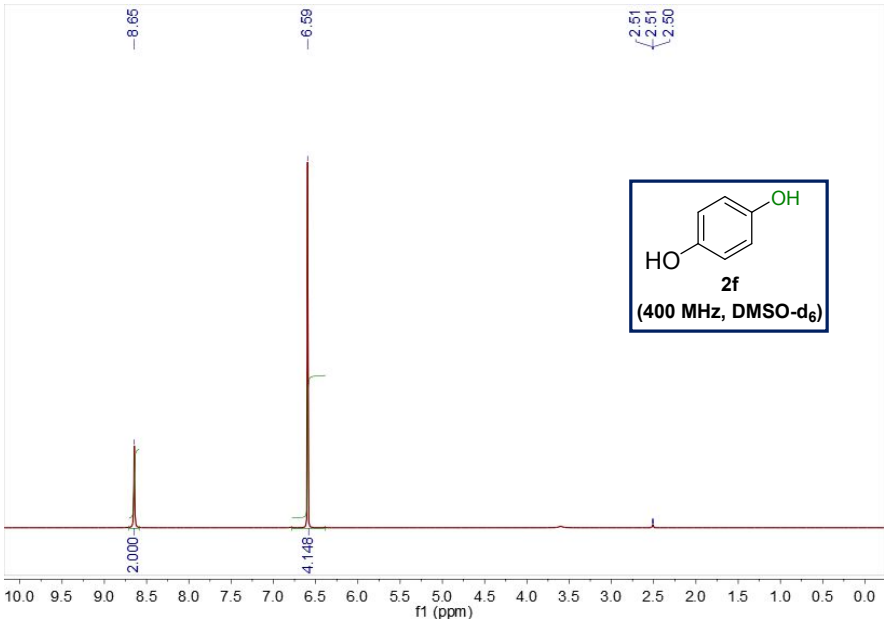

Figure S13. The ^{1}H NMR spectrum of **2f**

^{13}CNMR

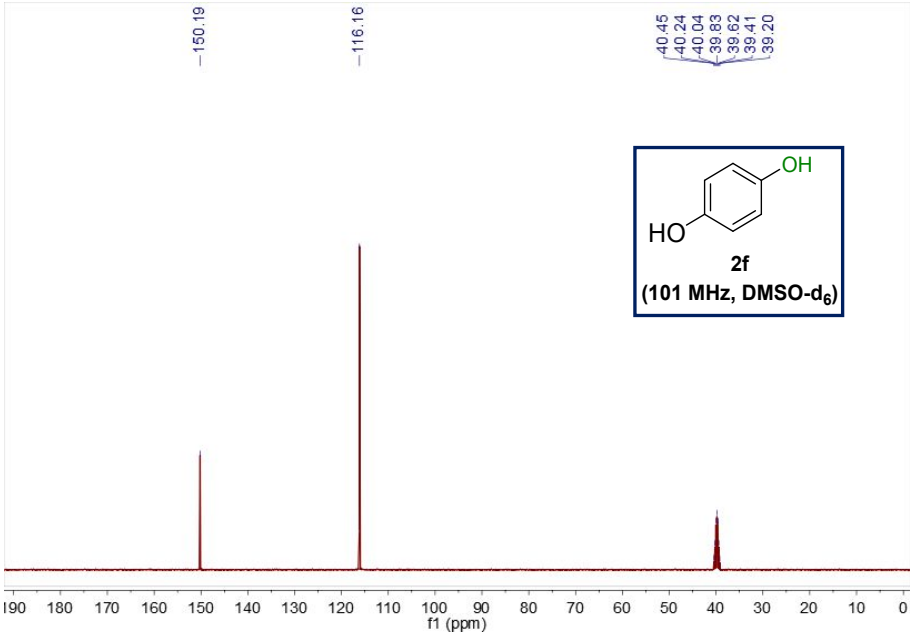

Figure S14. The ^{13}C NMR spectrum of **2f**

^{1}HNMR

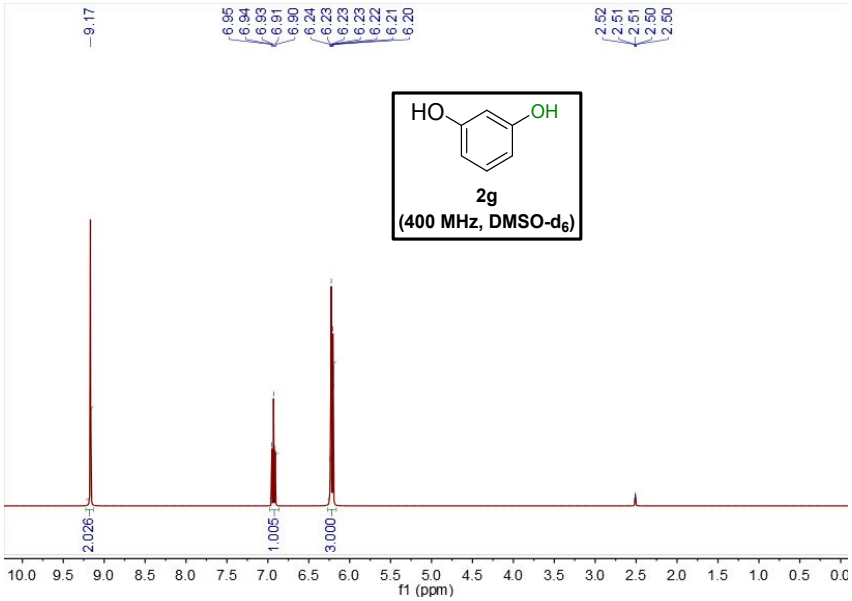

Figure S15. The ^{1}H NMR spectrum of **2g**

^{13}CNMR

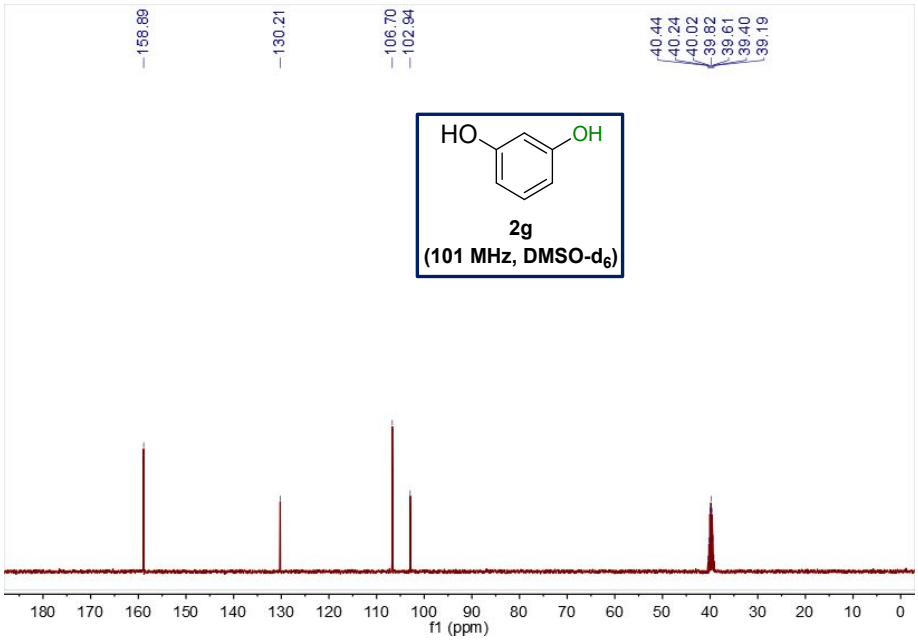

Figure S16. The ^{13}C NMR spectrum of **2g**

^{1}HNMR

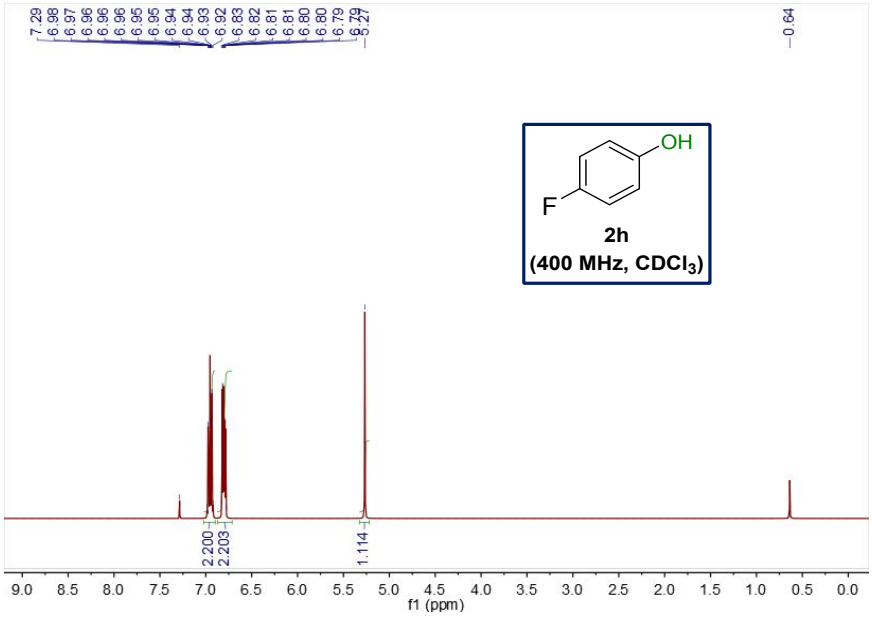

Figure S17. The ^{1}H NMR spectrum of **2h**

^{13}CNMR

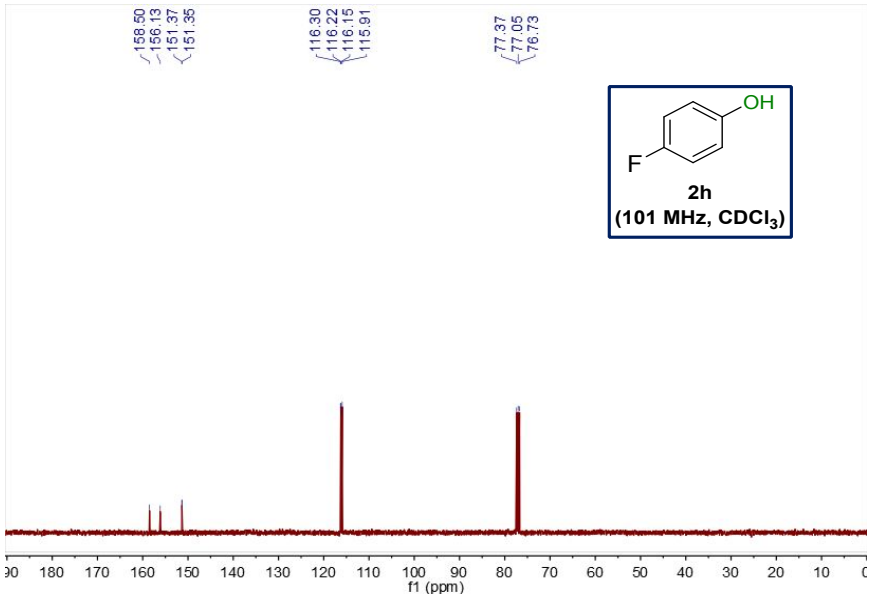

Figure S18. The ^{13}C NMR spectrum of **2h**

^{1}HNMR

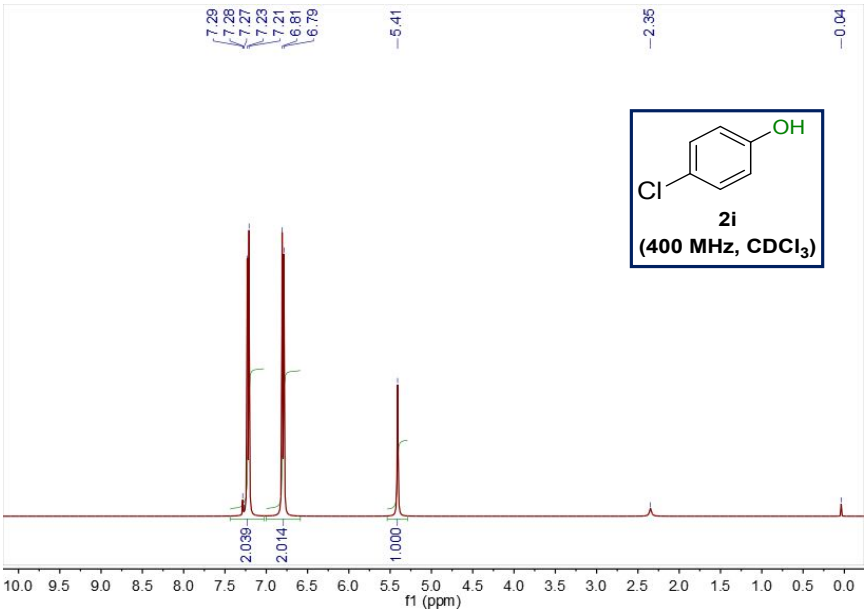

Figure S19. The ^{1}H NMR spectrum of **2i**

^{13}CNMR

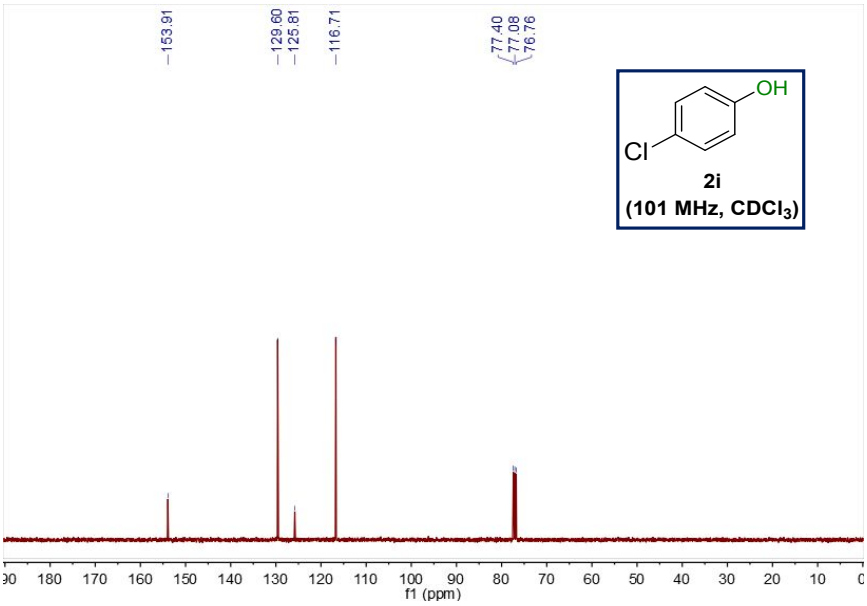

Figure S20. The ^{13}C NMR spectrum of **2i**

^{1}HNMR

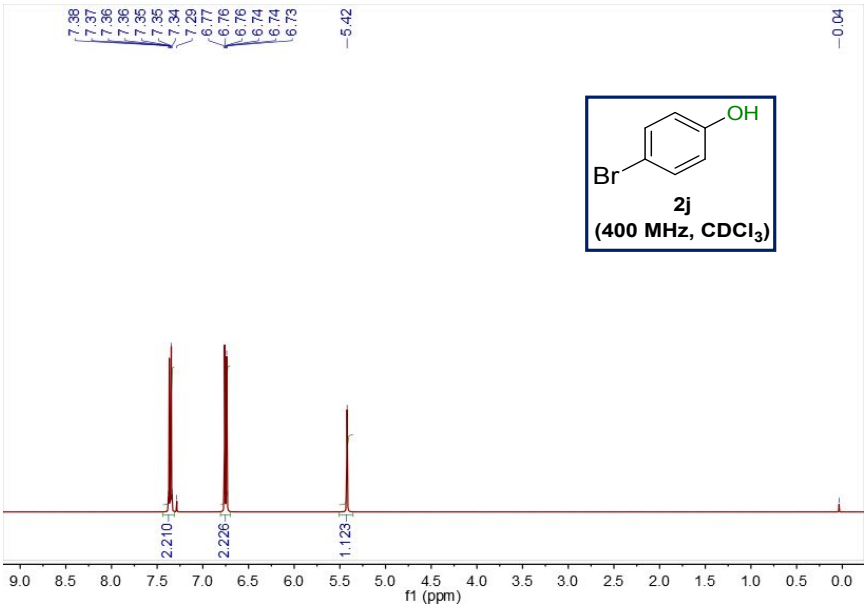

Figure S21. The ^{1}H NMR spectrum of **2j**

^{13}CNMR

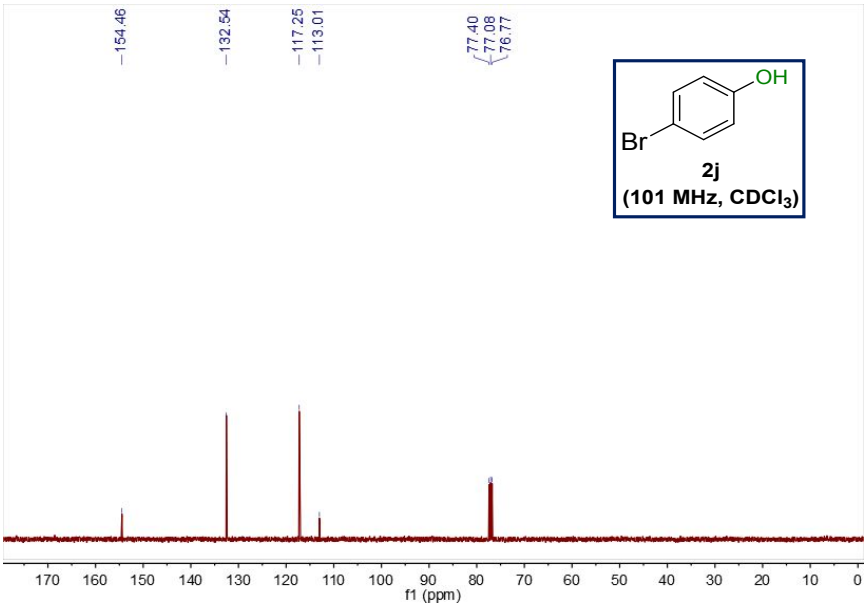

Figure S22. The ^{13}C NMR spectrum of **2j**

^{1}HNMR

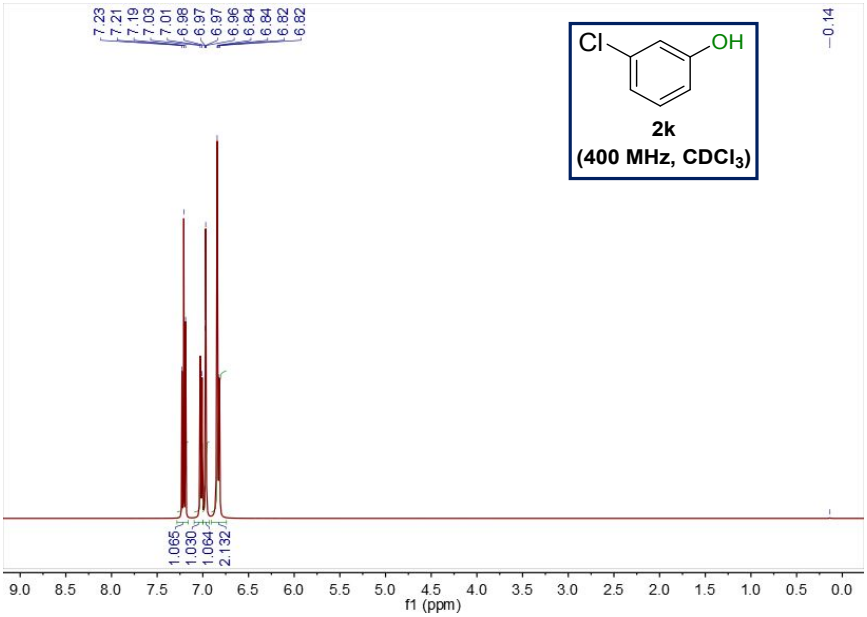

Figure S23. The ^{1}H NMR spectrum of **2k**

^{13}CNMR

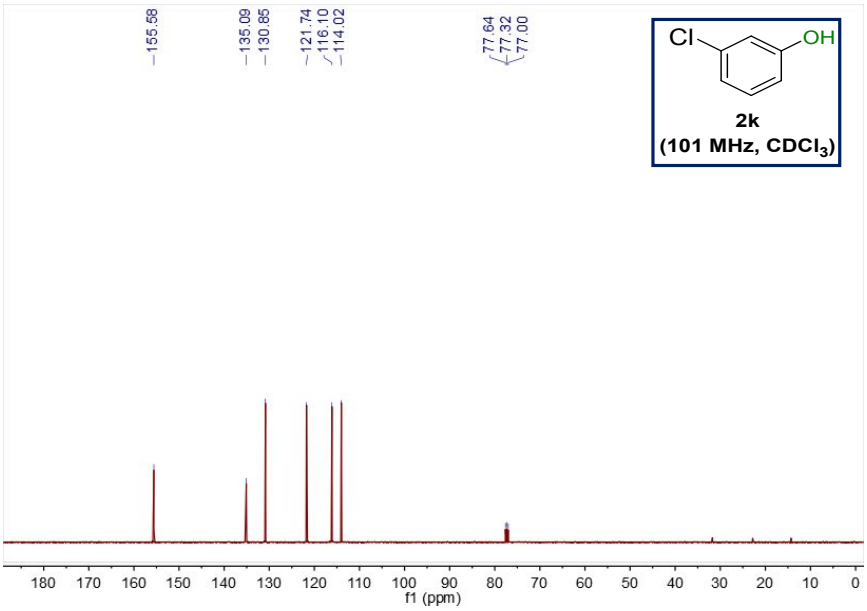

Figure S24. The ^{13}C NMR spectrum of **2k**

^{1}HNMR

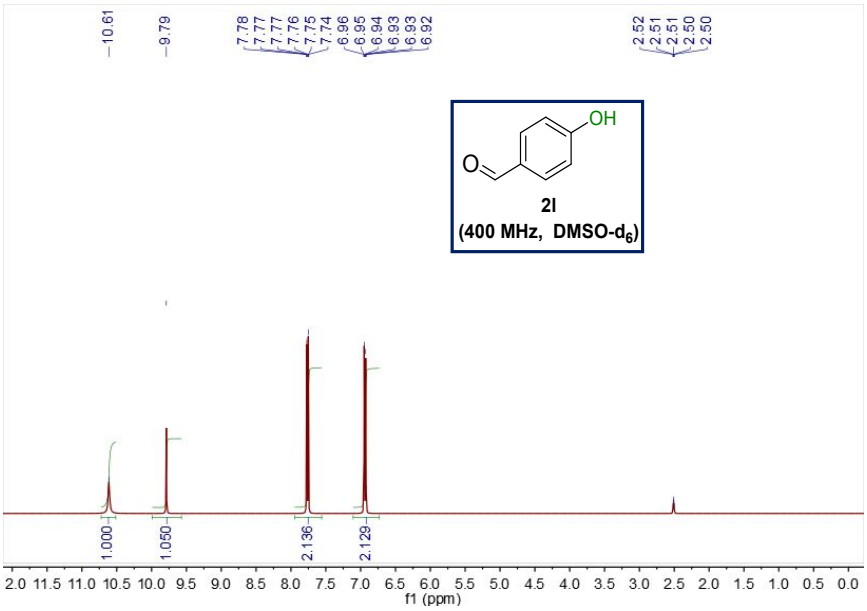

Figure S25. The ^{1}H NMR spectrum of **2l**

^{13}CNMR

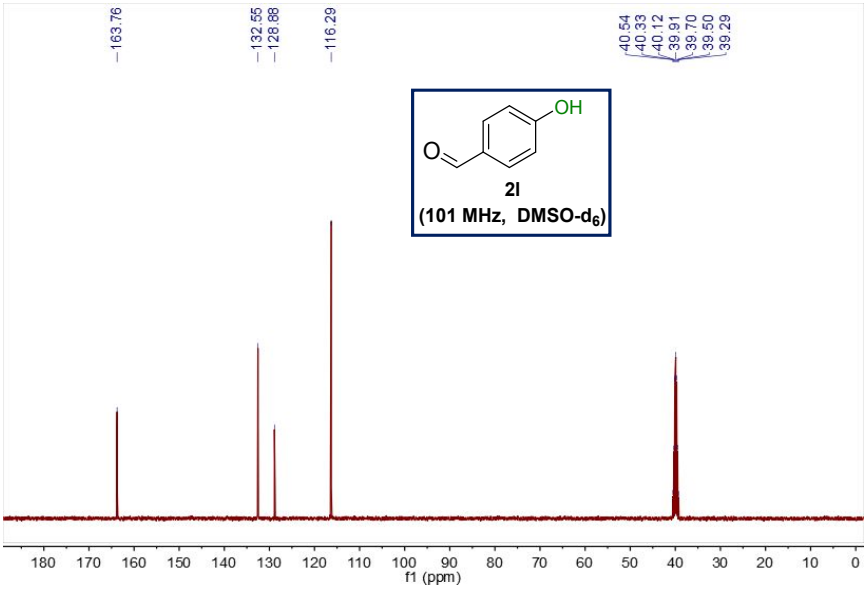

Figure S26. The ^{13}C NMR spectrum of **2l**

^{1}HNMR

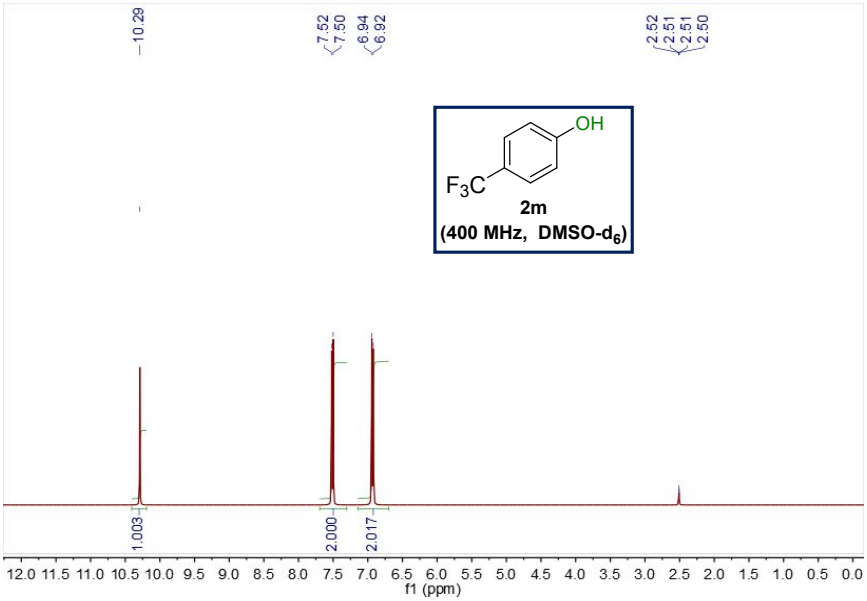

Figure S27. The ^{1}H NMR spectrum of **2m**

^{13}CNMR

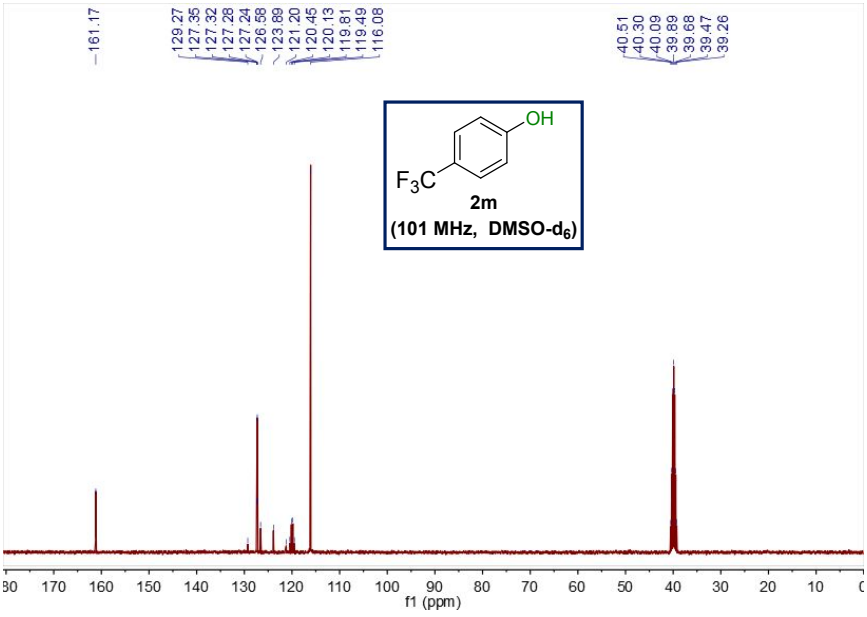

Figure S28. The ^{13}C NMR spectrum of **2m**

^{1}HNMR

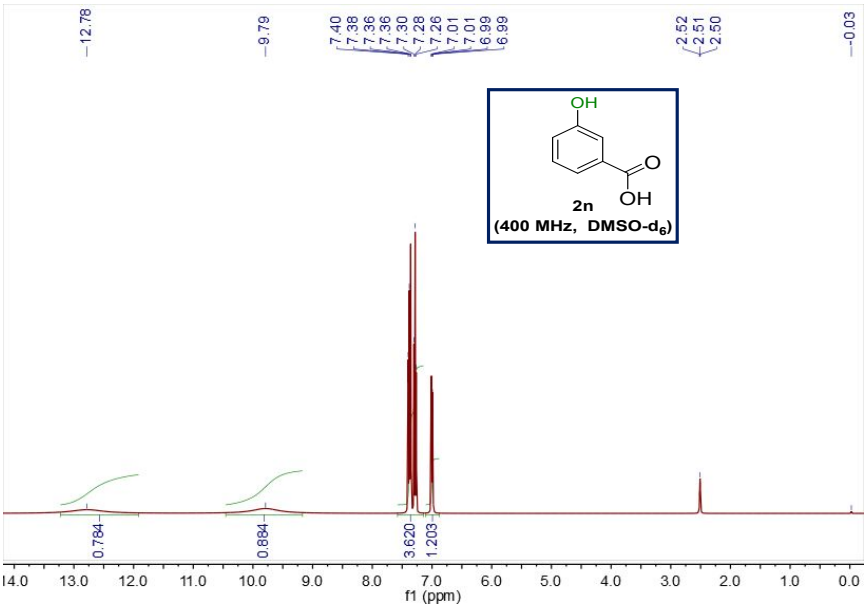

Figure S29. The ^{1}H NMR spectrum of **2n**

^{13}CNMR

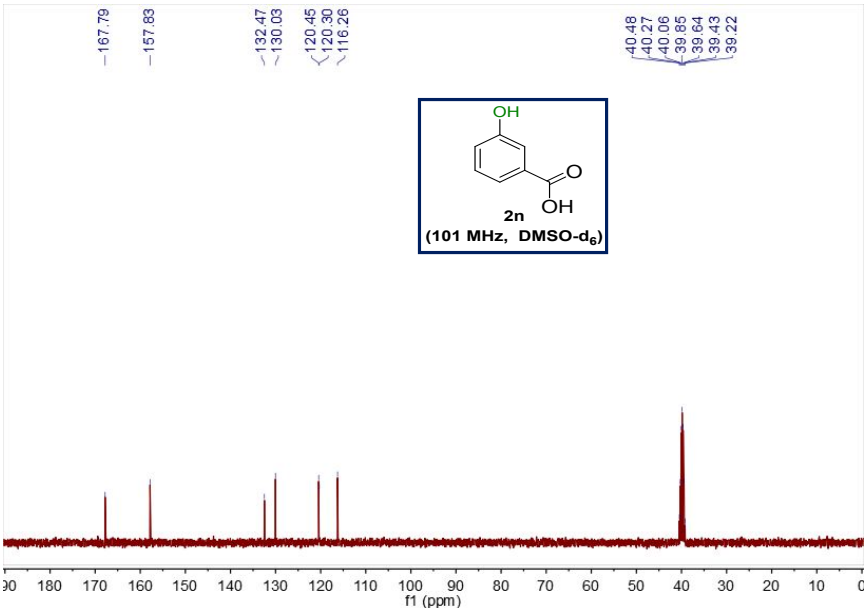

Figure S30. The ^{13}C NMR spectrum of **2n**

^{1}HNMR

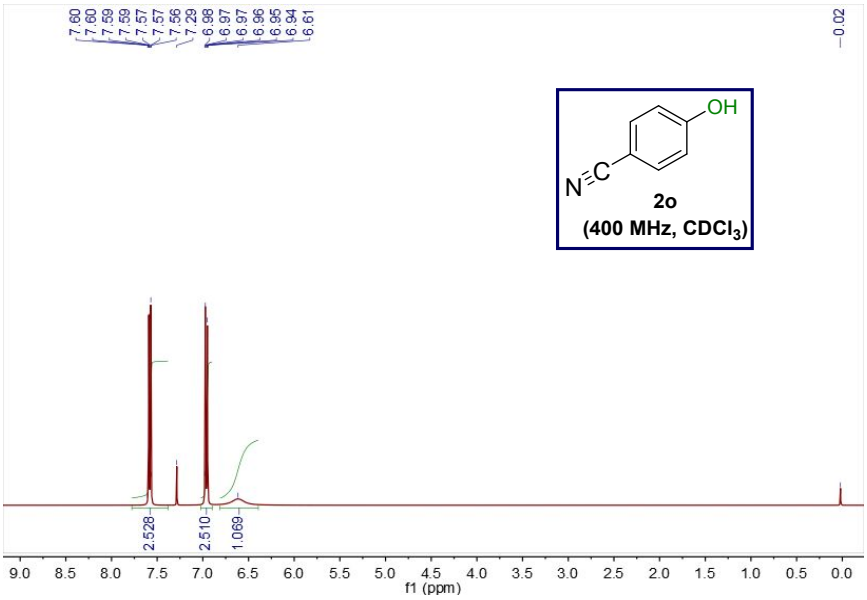

Figure S31. The ^{1}H NMR spectrum of **2o**

^{13}CNMR

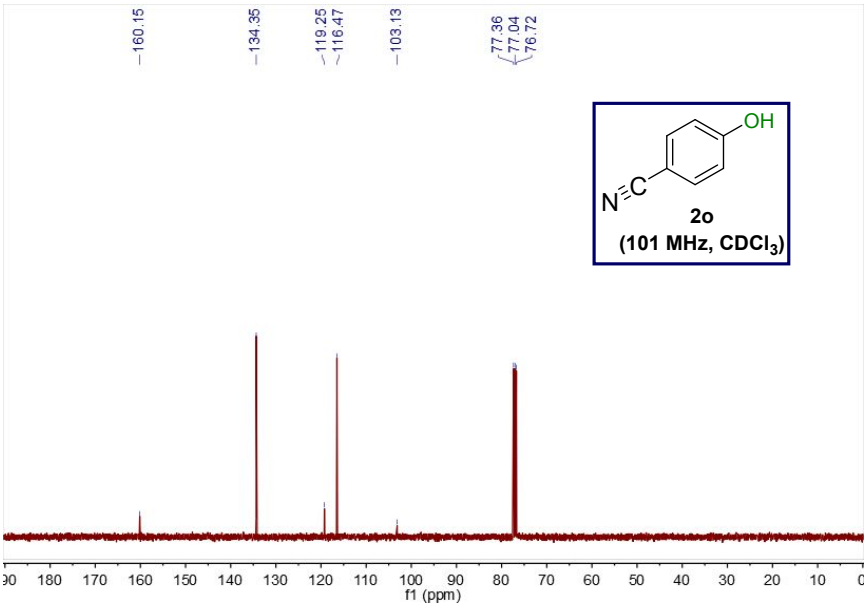

Figure S32. The ^{13}C NMR spectrum of **2o**

^{1}HNMR

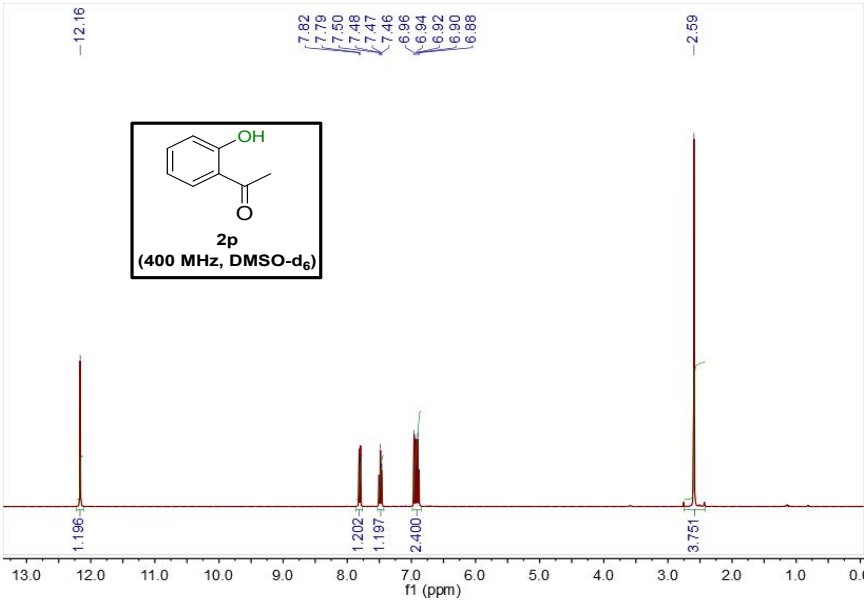

Figure S33. The ^{1}H NMR spectrum of **2p**

^{13}CNMR

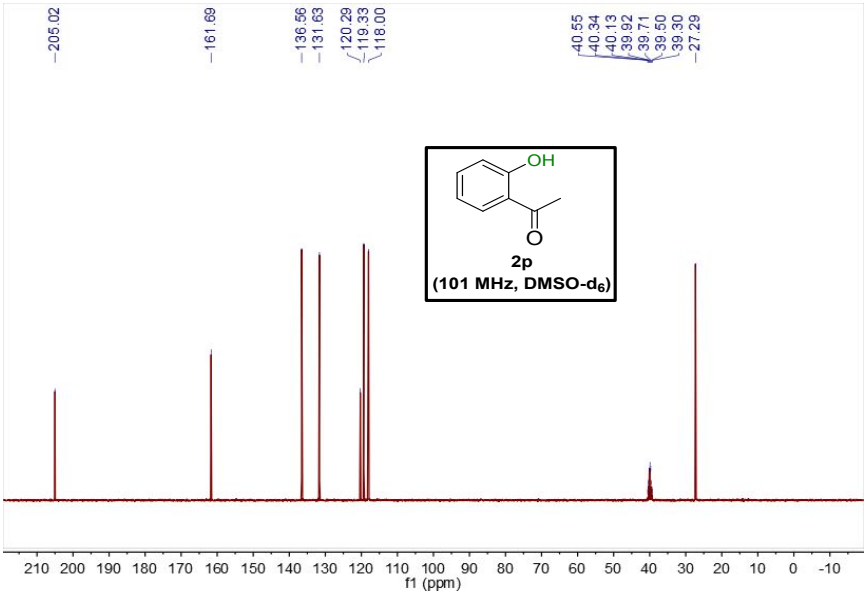

Figure S34. The ^{13}C NMR spectrum of **2p**

^{1}HNMR

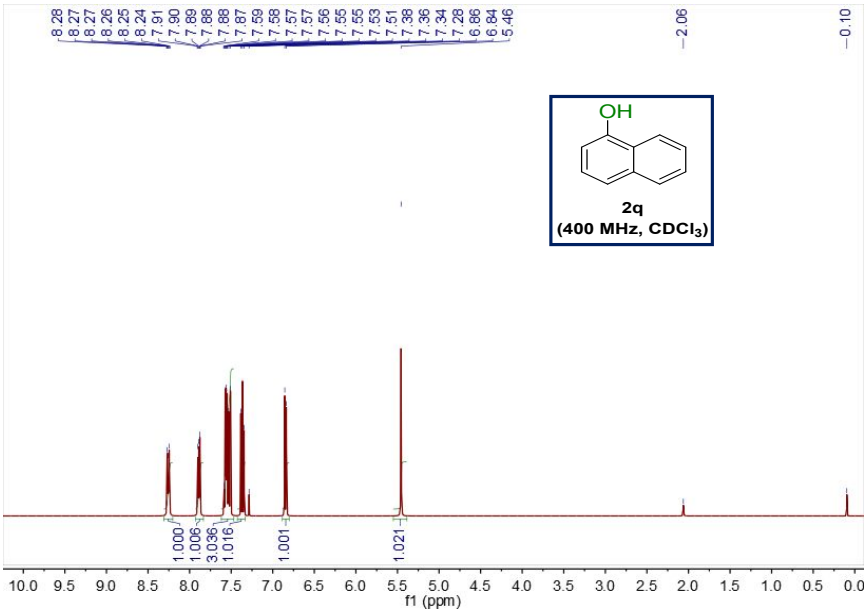

Figure S35. The ^{1}H NMR spectrum of **2q**

^{13}CNMR

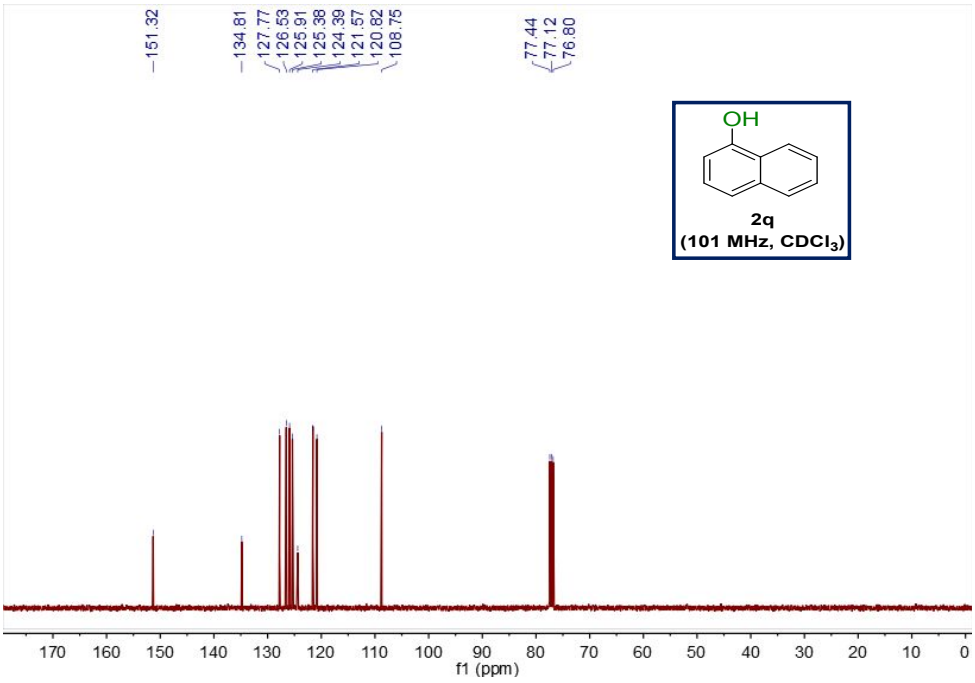

Figure S36. The ^{13}C NMR spectrum of **2q**

^{1}HNMR

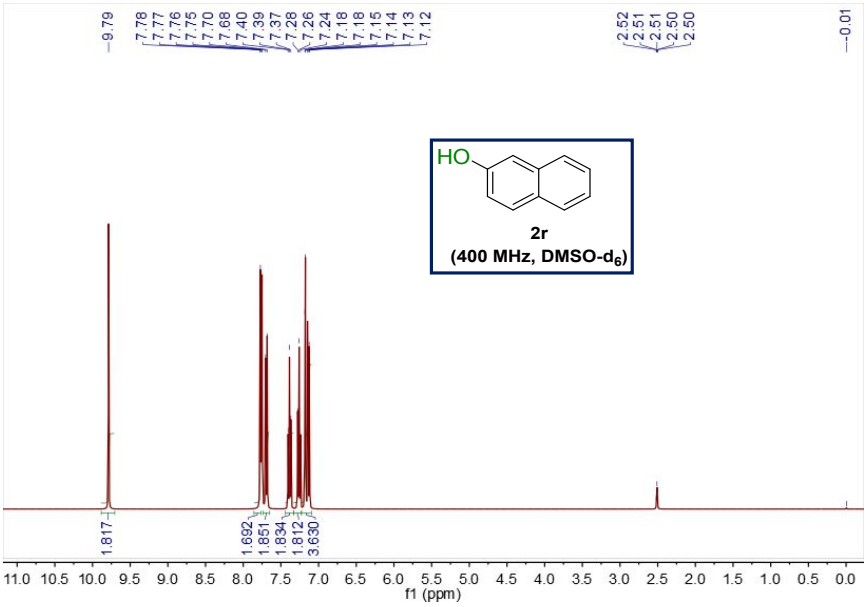

Figure S37. The ^{1}H NMR spectrum of **2r**

^{13}CNMR

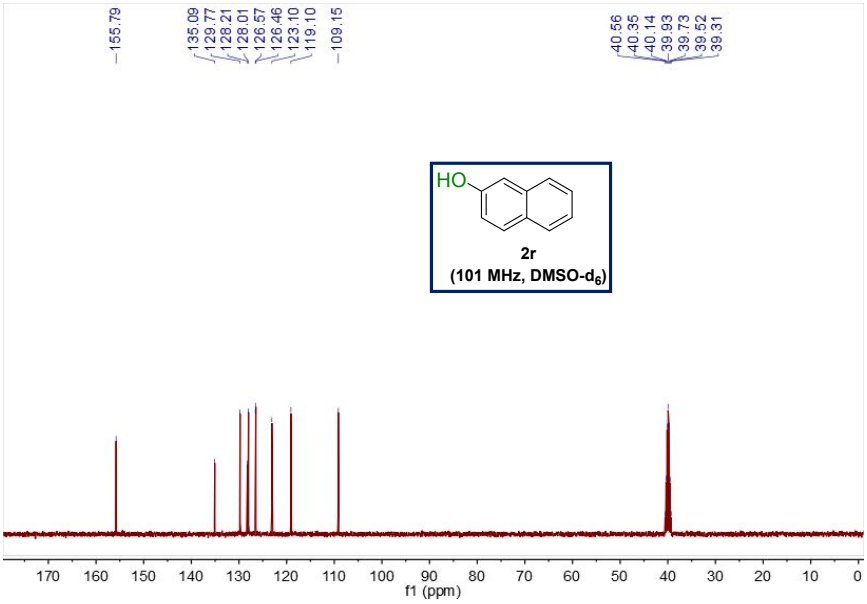

Figure S38. The ^{13}C NMR spectrum of **2r**

^{1}HNMR

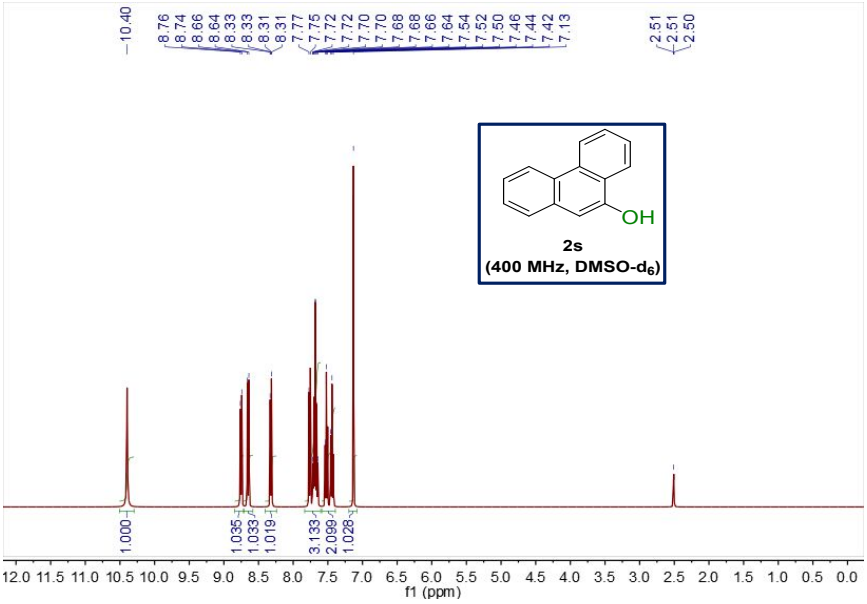

Figure S39. The ^{1}H NMR spectrum of **2s**

^{13}CNMR

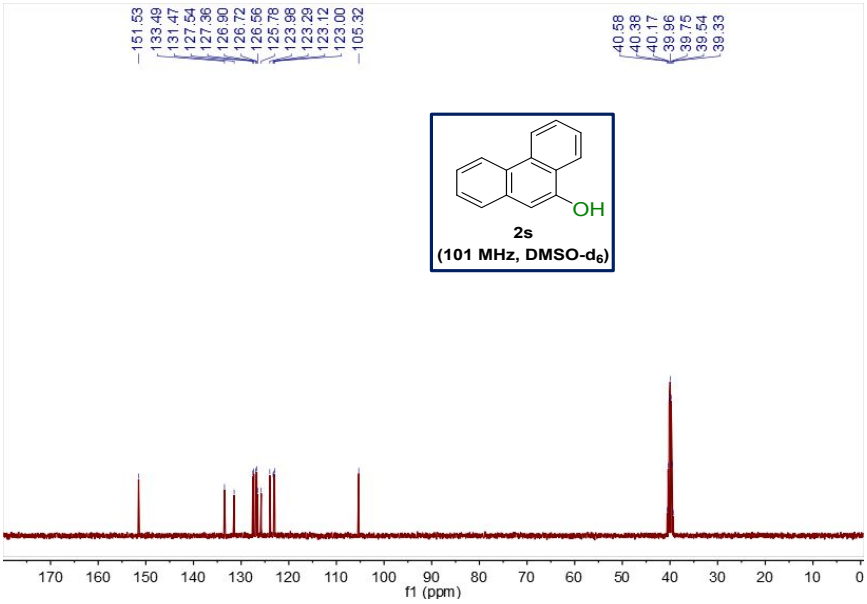

Figure S40. The ^{13}C NMR spectrum of **2s**

^{1}HNMR

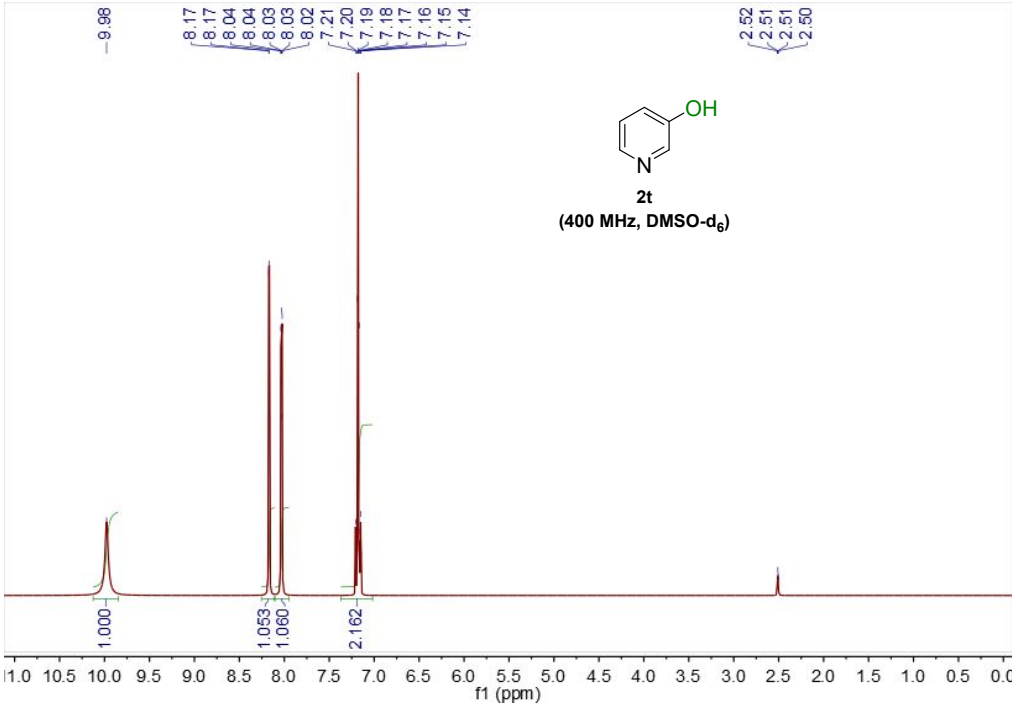

Figure S41. The ^{1}H NMR spectrum of **2t**

^{13}CNMR

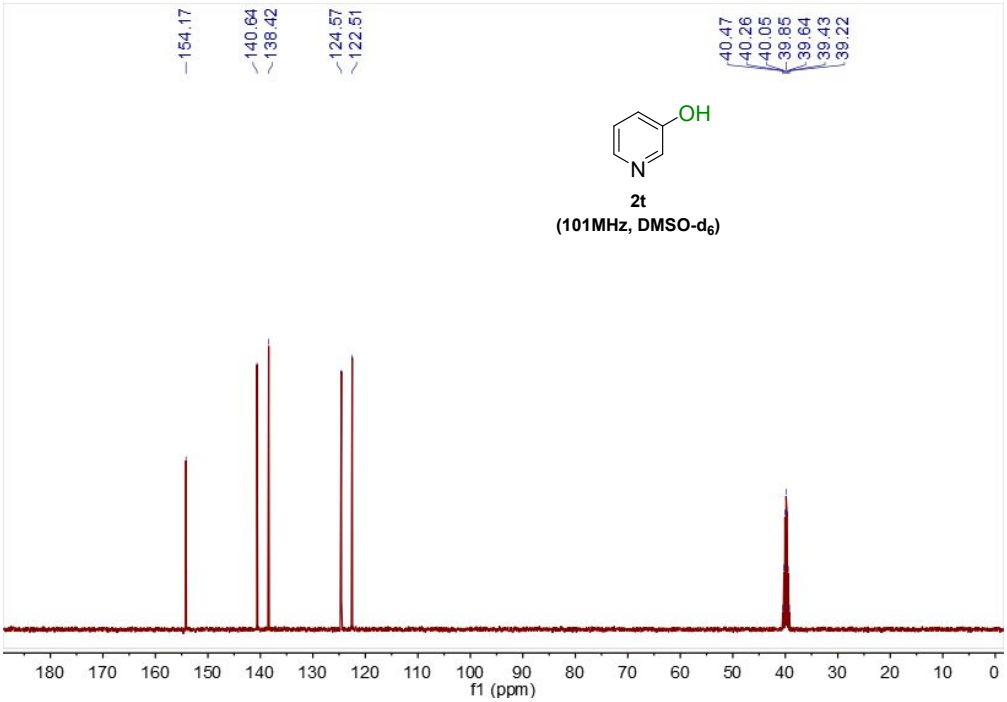

Figure S42. The ^{13}C NMR spectrum of **2t**

^{1}HNMR

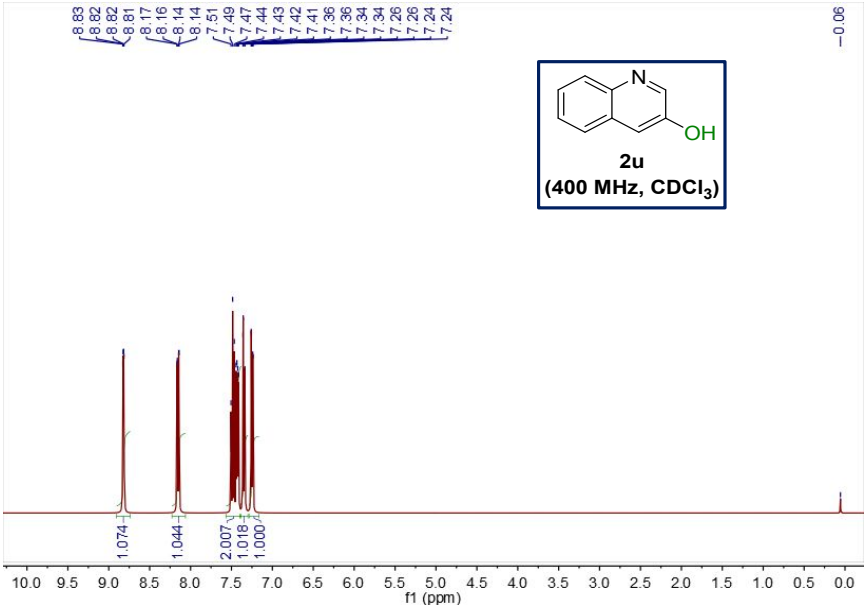

Figure S43. The ^{1}H NMR spectrum of **2u**

^{13}CNMR

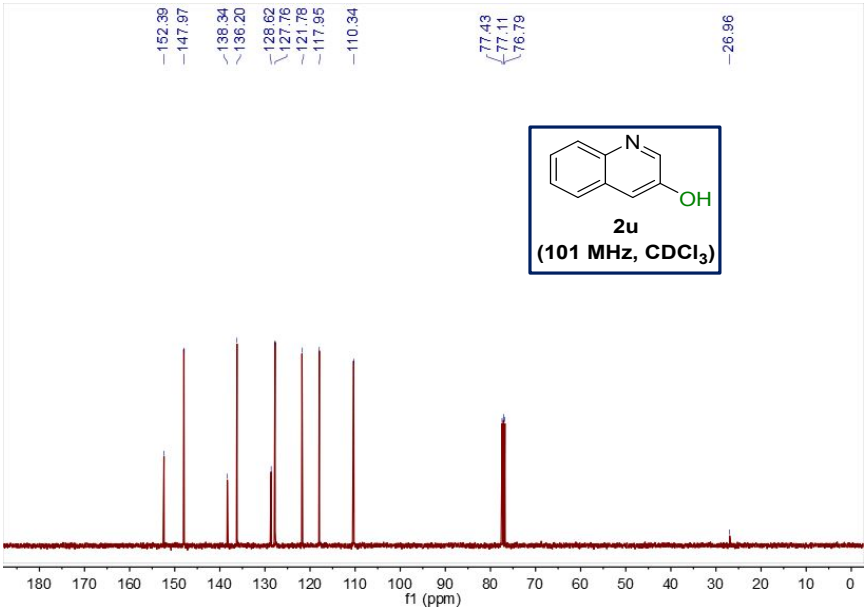

Figure S44. The ^{13}C NMR spectrum of **2u**

^{1}HNMR

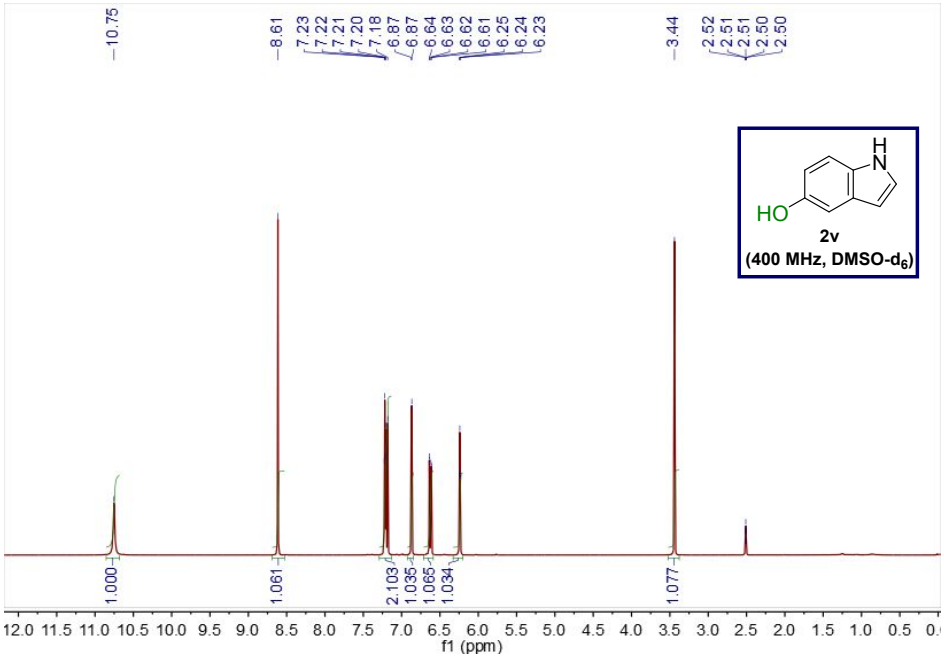

Figure S45. The ^{1}H NMR spectrum of **2v**

^{13}CNMR

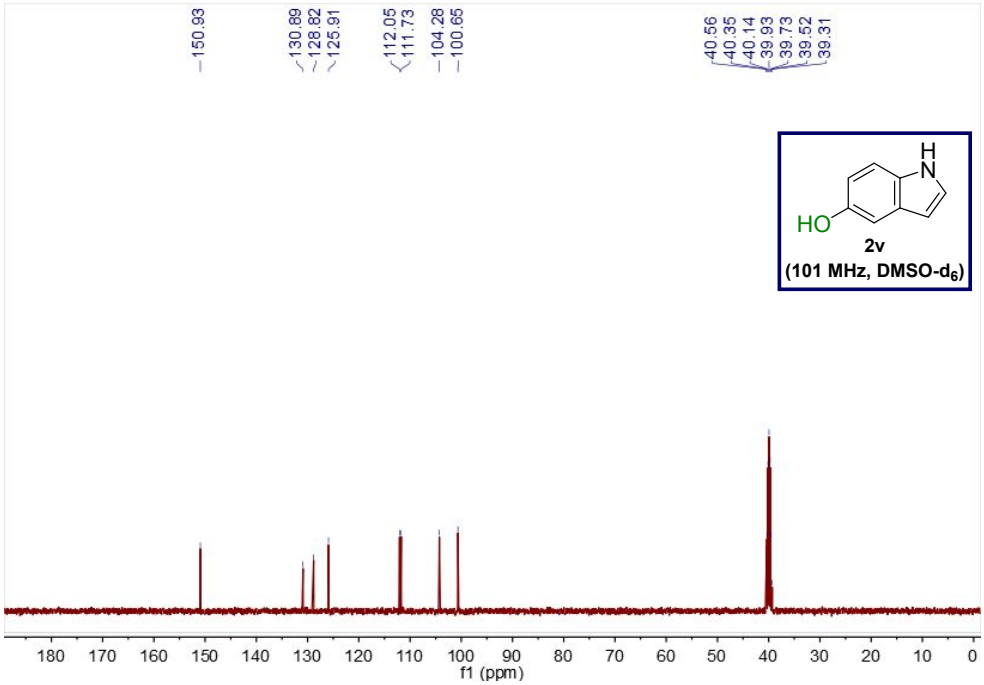

Figure S46. The ^{13}C NMR spectrum of **2v**