Supporting Information

Oxidant-free Synthesis of Benzimidazoles from Alcohols and Aromatic Diamines Catalysed by New Ru(II)-PNS(O) Pincer Complexes

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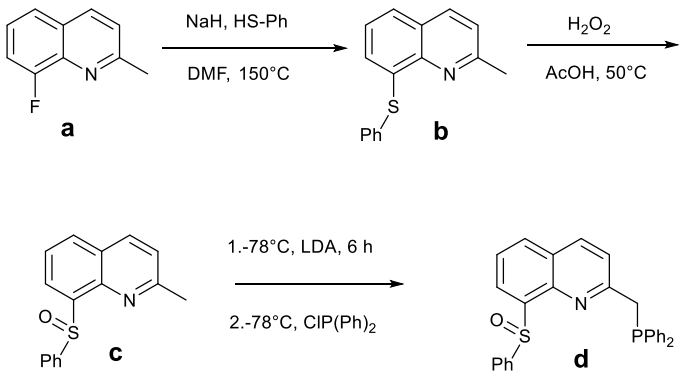
1. General Information

All experiments with metal complexes were carried out under purified argon atmosphere using standard schlenk techniques. 1-hexanol, cyclohexylmethanol and benzyl alcohol were purified according to standard procedures under argon atmosphere. Other reagents were used as received. Solvents were distilled and degassed with argon and kept in the spherical reservoir bottle with 4 Å molecular sieve. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz/75 MHz Varian Gemini 300 spectrometer. The ^{1}H NMR chemical shifts are referenced to the residual hydrogen signals of the deuterated solvents or TMS, and the ^{13}C NMR chemical shifts are referenced to the ^{13}C signals of the deuterated solvents.

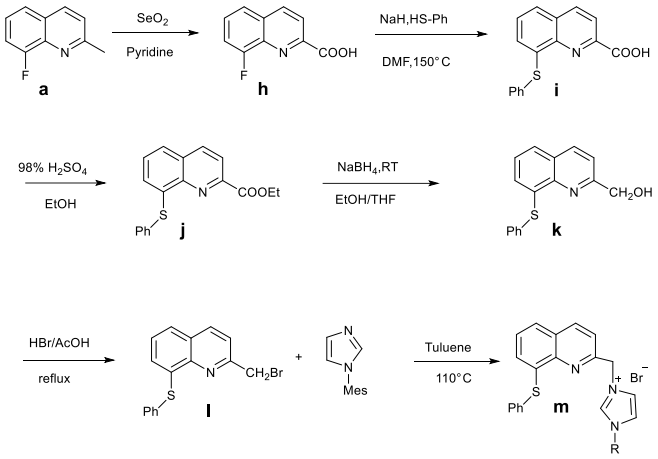
2. Experimental Procedures

2.1 Schemes for the syntheses of ligands L1 and L2

Scheme 1S. The synthesis of 2-(diphenylphosphinomethyl)-8- (phenyl-sulfinyl)-quinoline (PNS(O), L1)

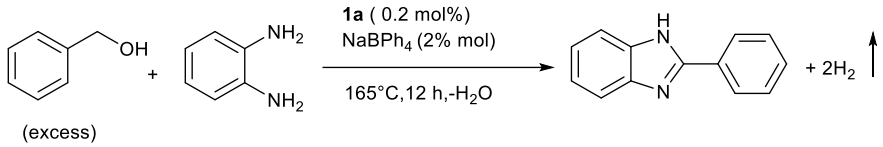


Scheme 2S. The synthesis of 1-mesityl-3-(8-phenylthioquinolyl-2- methyl)imidazolium bromide (HL2Br)



2.2 The production of H_2 catalyzed by complex 1a

Table 1S. Condensation of benzyl alcohol and benzene-1,2-diamine: [a]

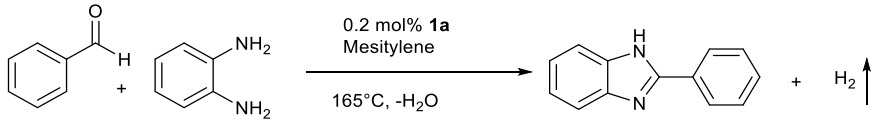


Reaction Time	Total Volume of H_2 [b]	Mole number of H_2 [c]
1h	38 mL	1.43 mol
2h	62 mL	2.33 mol
4h	97 mL	3.64 mol
6h	107 mL	4.02 mol
12h	109 mL	4.10 mol

[a] Reaction conditions: benzene-1,2-diamine (2.5 mmol), benzyl alcohol (7.5 mmol), $NaBPh_4$ (0.05 mmol), **1a** (0.005 mmol), 165 ℃, 12 h. [b] The volume of H_2 was collected through gravity drainage method, and the blank experimental volume was removed. [c] The standard atmospheric pressure P = 101.325 KPa; room temperature T = 305.15 K, the corresponding vapor pressure P_0 = 4.758 KPa; The approximate amount of H_2 was calculated by Van der Waals equation: $(P-P_0)V = nRT$ (R = 8.314 KPa L mol^{-1} K^{-1}).

After the reaction was complete, the 2-phenyl-benzimidazole was isolated through the column chromatography, yield 0.412 g (85%). The yield of H_2 was 82%.

Table 2S. Condensation of benzaldehyde and benzene-1,2-diamine: [a]



Reaction Time	Total Volume of H_2 [b]	Mole number of H_2 [c]
5 mim	23 mL	0.86 mmol
10 min	57 mL	2.14 mmol
15 min	87 mL	3.26 mmol
20 min	104 mL	3.90 mmol
25 min	112 mL	4.20 mmol
30 min	115 mL	4.32 mmol
60 min	115 mL	4.32 mmol

[a] Reaction condition: benzene-1,2-diamine (6 mmol), benzaldehyde (5 mmol), **1a** (0.01 mmol), mesitylene (2 mL)165 ℃, 1 h. [b] The volume of H_2 was collected through gravity drainage method, and the blank experimental volume was removed. [c] The standard atmospheric pressure P = 101.325 KPa; room temperature T = 305.15 K, the corresponding vapor pressure P_0 = 4.758 KPa; The approximate amount of H_2 was calculated by Van der Waals equation: $(P-P_0)V = nRT$ ($R = 8.314$ KPa L mol^{-1} K^{-1}).

After the reaction was complete, the 2-phenyl-benzimidazole was isolated through the column chromatography, yield 0.874 g (90%). The yield of H_2 was 86%.

2.3 Characterization of *in situ* generated dearomatic Ru(II) species by the reaction of 1a and KOBu^t.

1a (12.3 mg, 0.02 mmol), KOBu^t (2.2mg, 0.02 mmol) and 0.6 mL DMSO-D_6 were added into a NMR tube under N_2 atmosphere. After the solution was stirred at room temperature (20℃) for 2 h, the ^{1}H NMR spectrum was recorded, which shows **1a** is remaining as the dominant Ru(II) complex. Upon the solution was heated at 80℃ for 2 h, the ^{1}H NMR spectrum shows a singlet at 4.47 ppm and a doublet at -14.21 ppm, indicating the corresponding dearomatic Ru(II) hydride species formed in about 30% yield.[1, 2] Only one singlet with the integration of nine protons appears at 3.37 ppm assigned to the *tert*-butyl of free $^-$OBu^t and *tert*-butanol, indicating the $^-$OBu^t is not coordinated to the Ru(II) center.

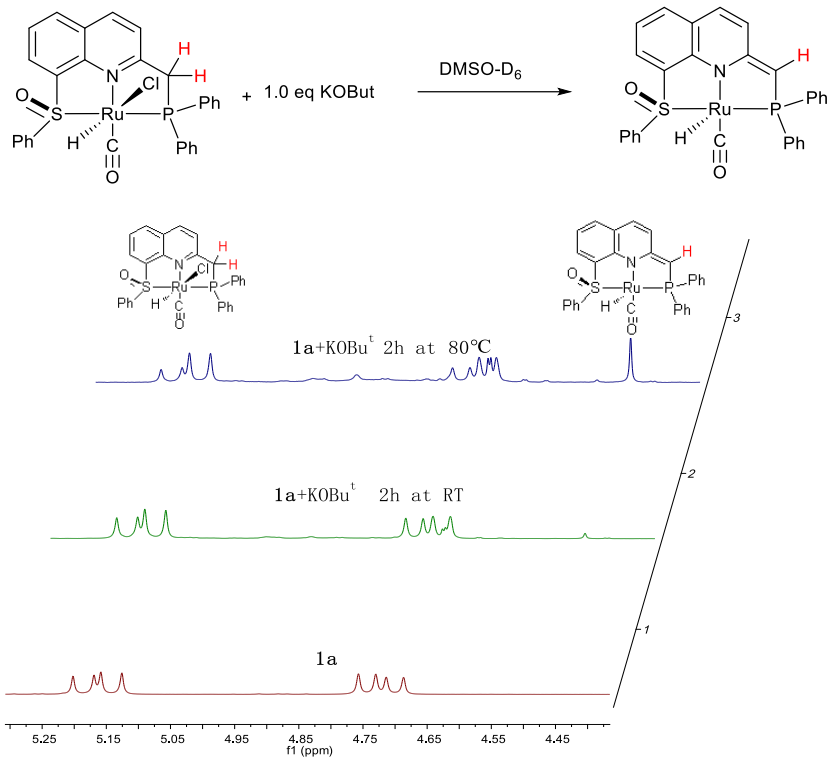


Figure 1S. ^{1}H NMR spectrum of the '=CHP' of the dearomatic Ru(II) hydride species.

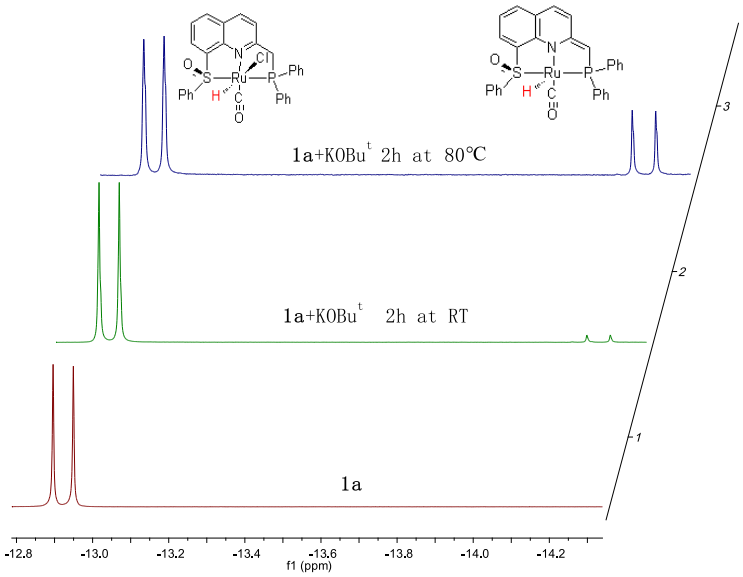


Figure 2S. ^{1}H NMR spectrum of the 'Ru-H' of the Ru(II) hydride species: A new signal appears at -14.21 ppm as a doublet.

2.3 NMR Spectra for all the intermediates and compounds

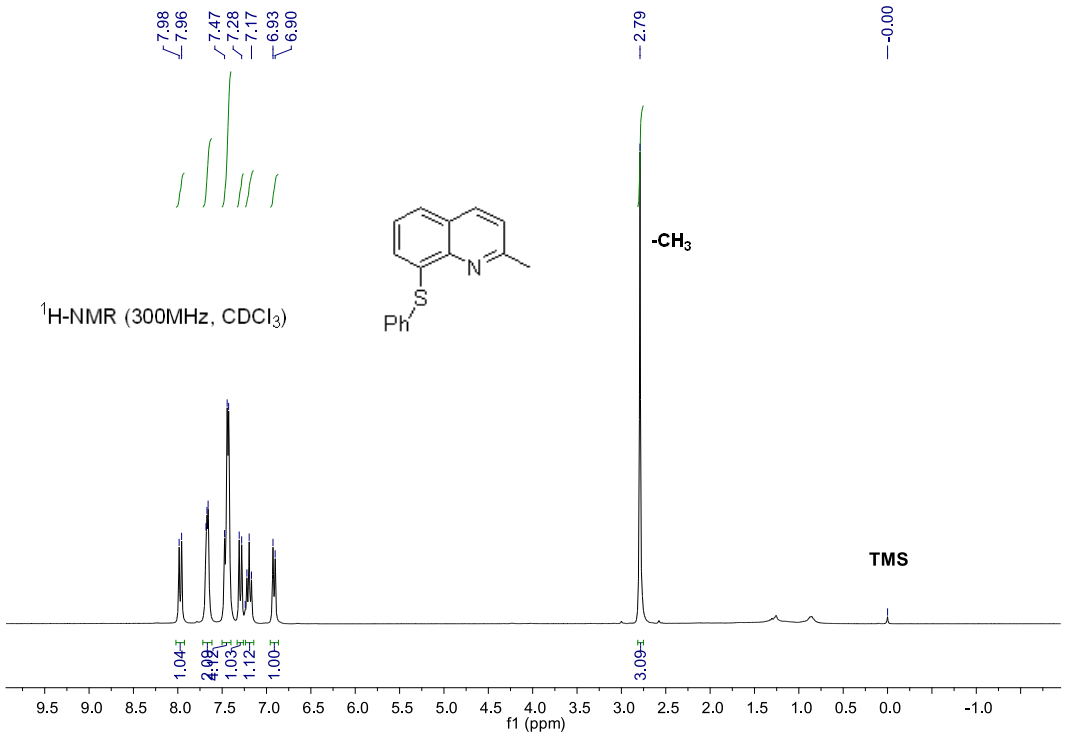


Figure 3S. ^{1}H NMR spectrum of compound **b**.

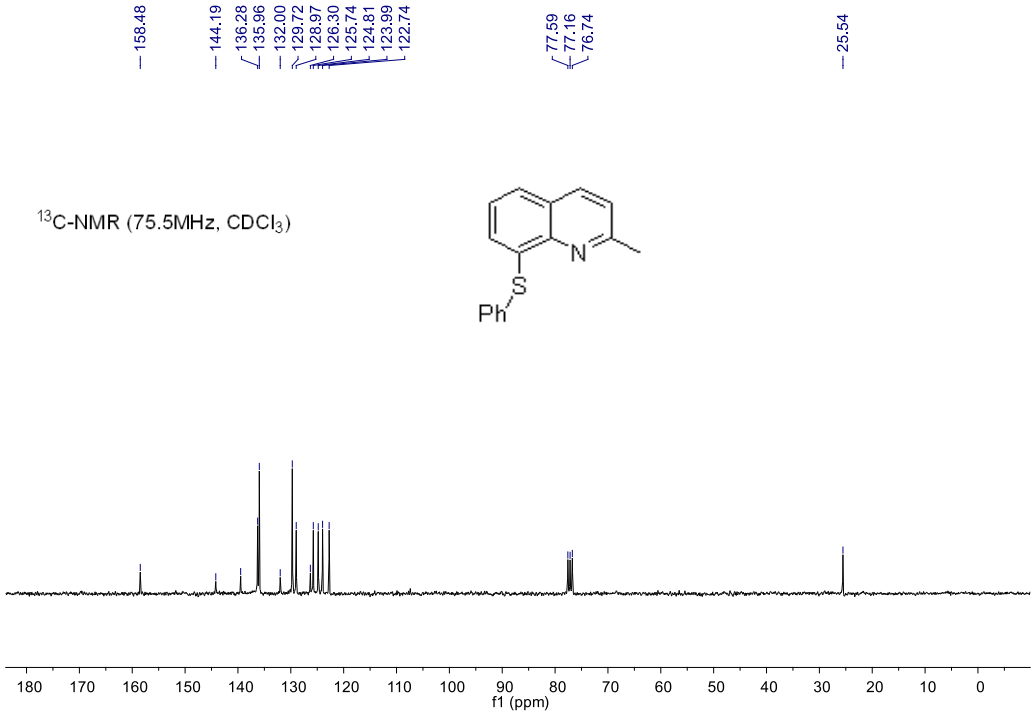


Figure 4S. ^{13}C{^{1}H} NMR spectrum of compound **b.**

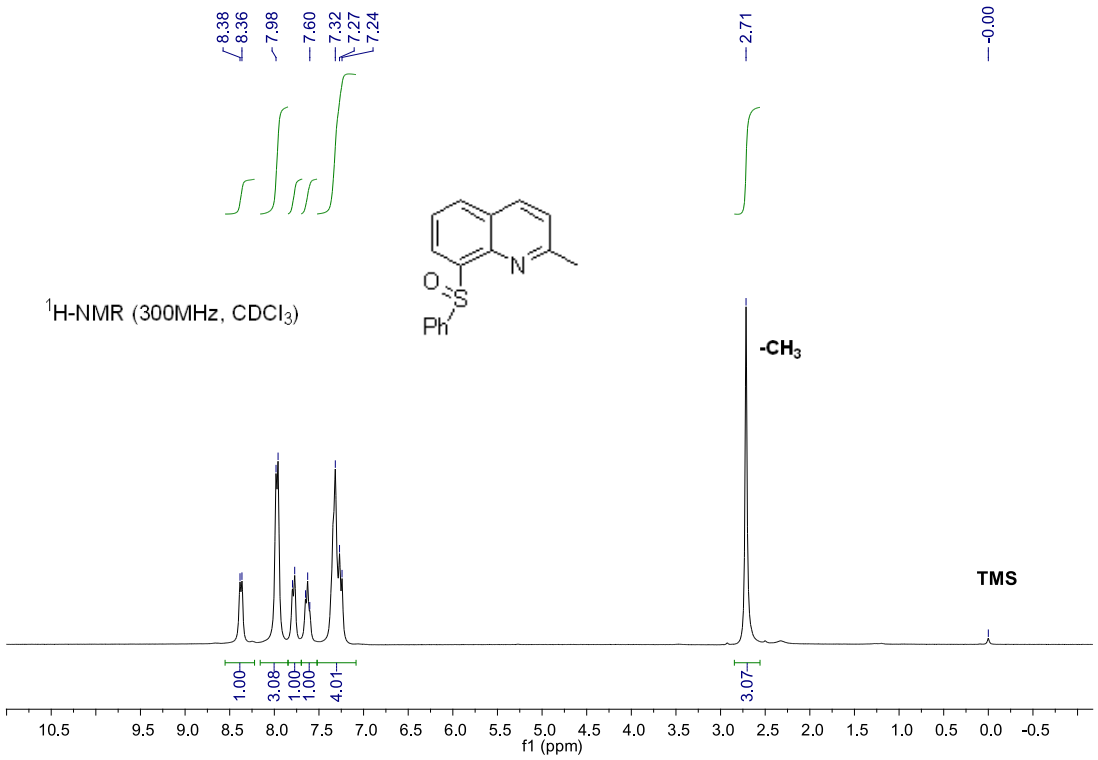


Figure 5S.[1]H NMR spectrum of **c**.

Figure 6S. [13]C{[1]H} NMR spectrum of **c**.

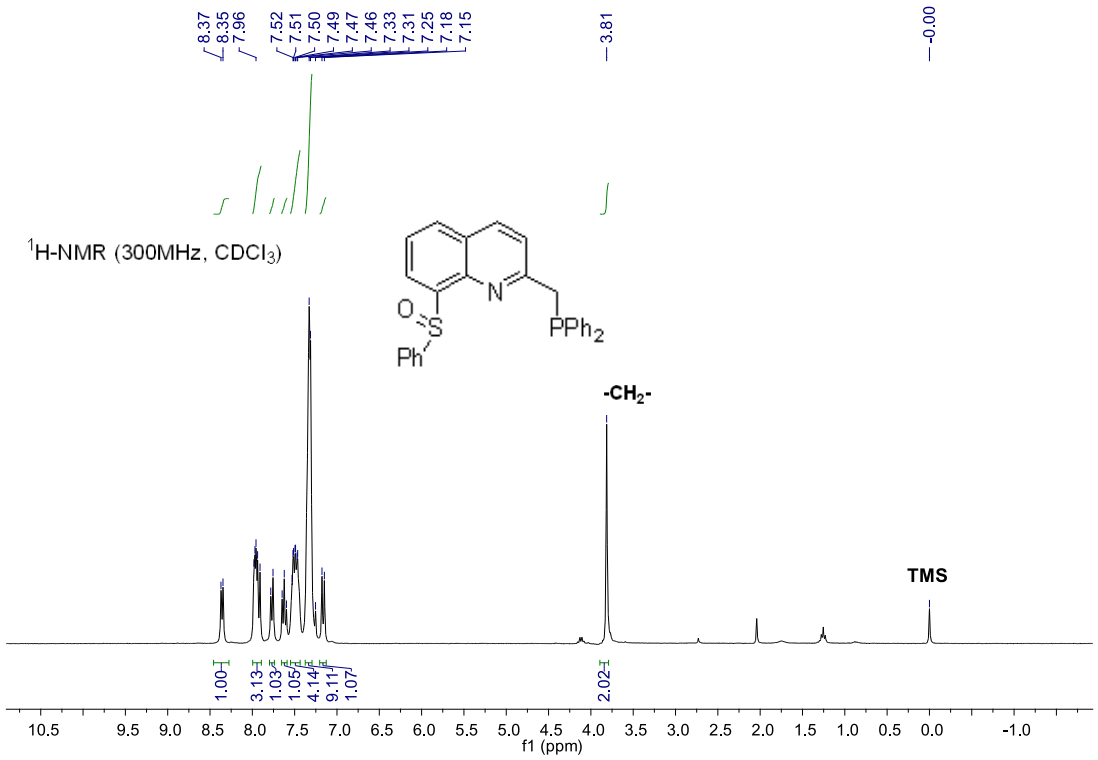


Figure 7S.^{1}H NMR spectrum of **d**.

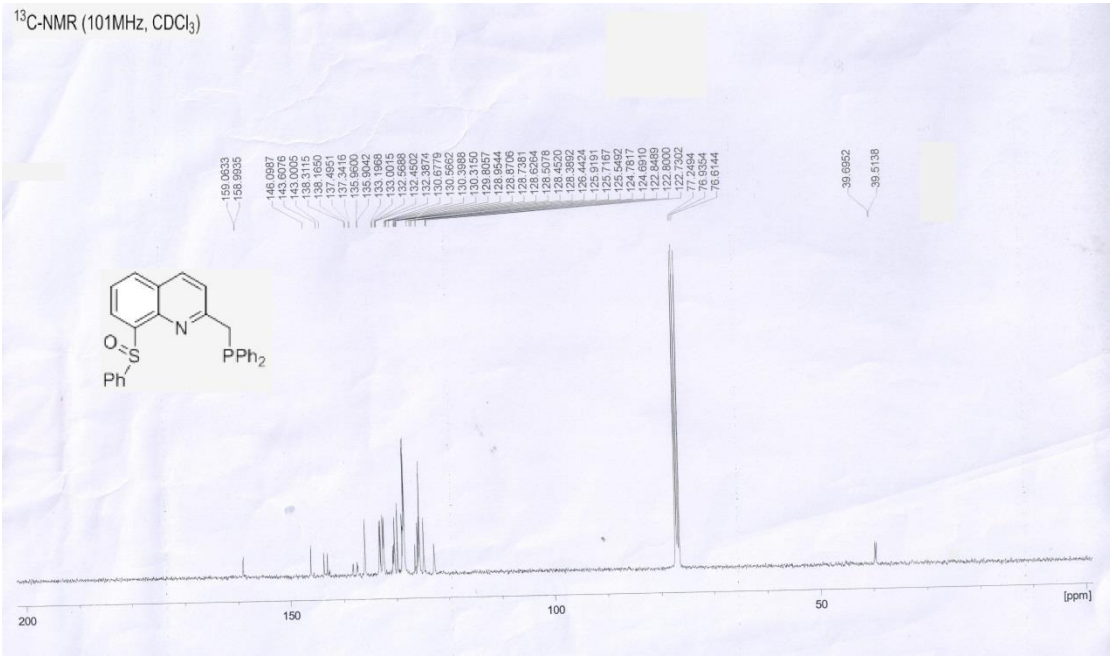


Figure 8S. ^{13}C{^{1}H} NMR spectrum of **d**.

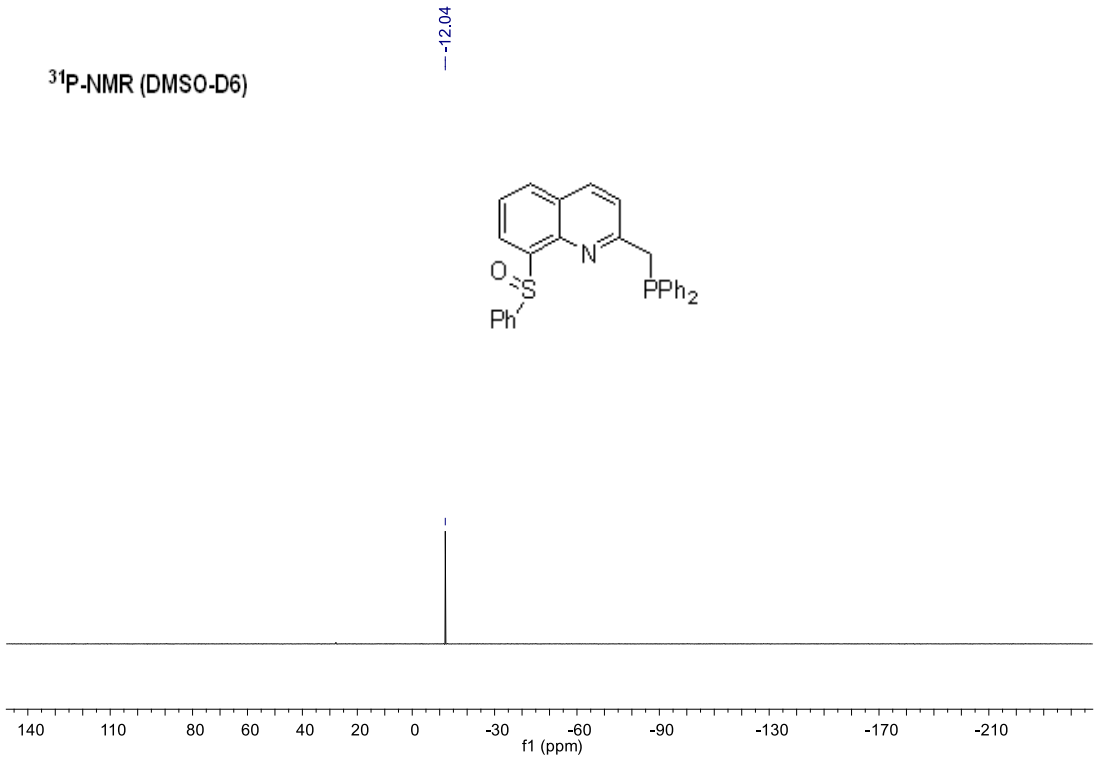


Figure 9S. $^{31}P\{^{1}H\}$ NMR spectrum of **d**.

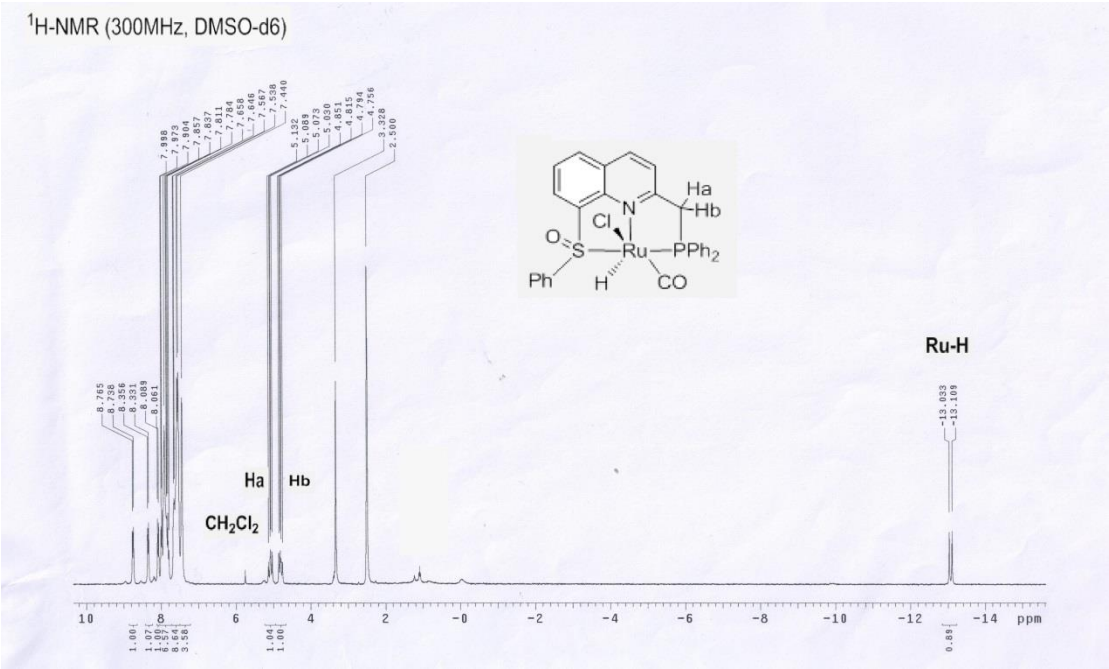


Figure 10S.^{1}H NMR spectrum of **1a**.

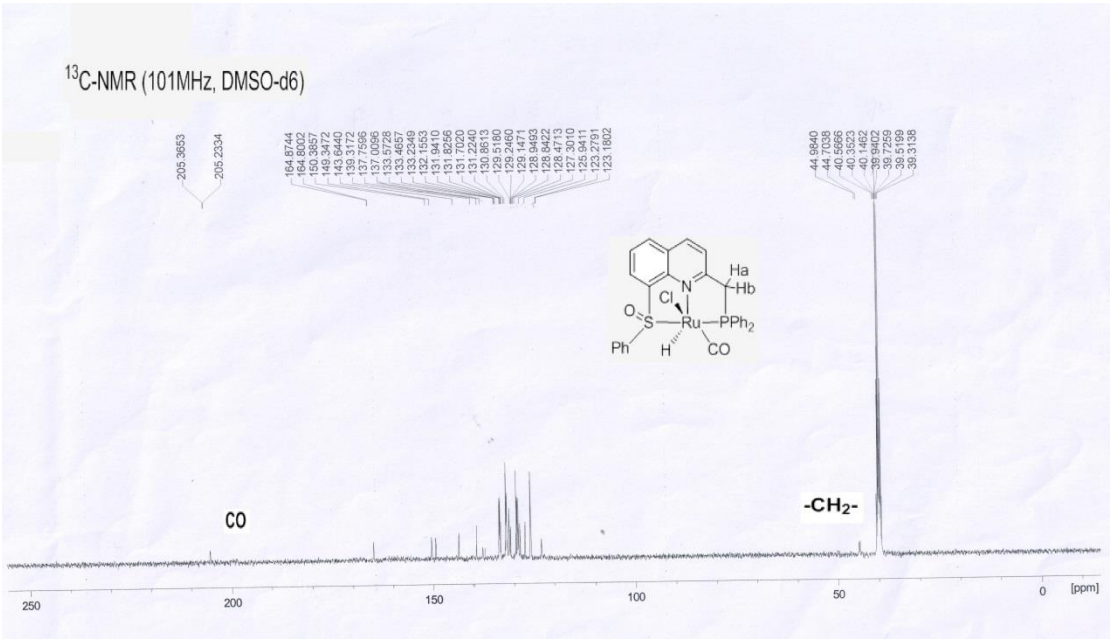


Figure 11S. $^{13}C\{^{1}H\}$ NMR spectrum of **1a**.

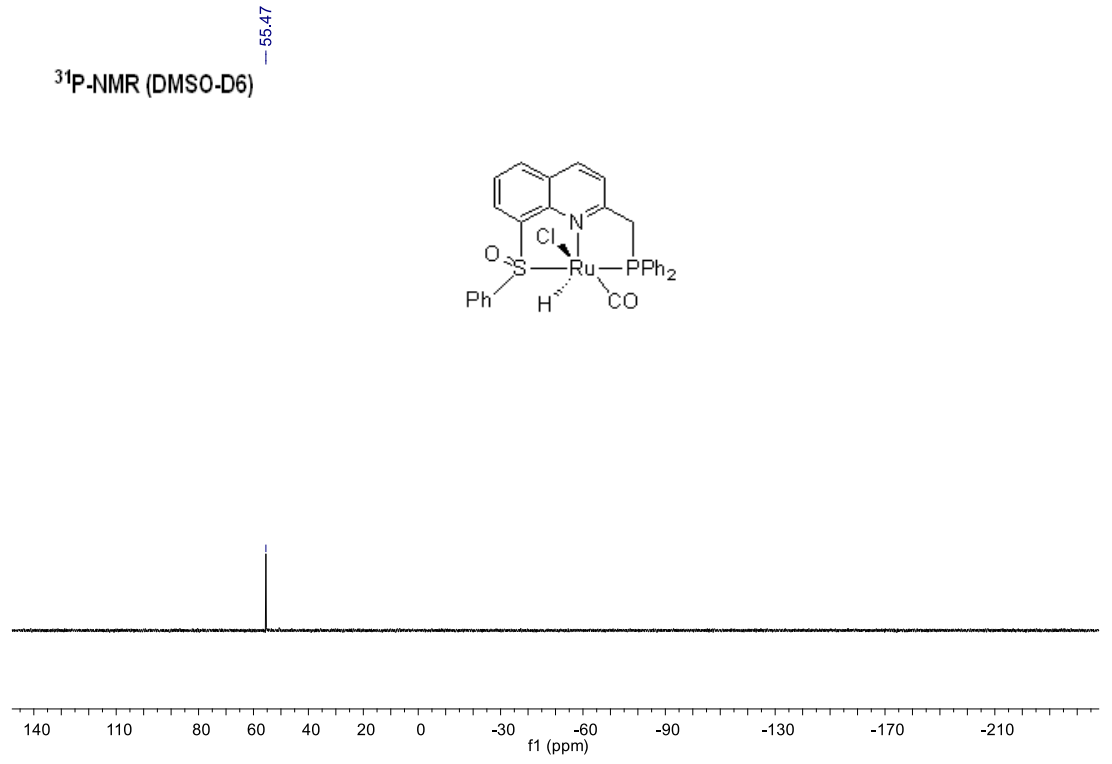


Figure 12S. $^{31}P\{^{1}H\}$ NMR spectrum of **1a**.

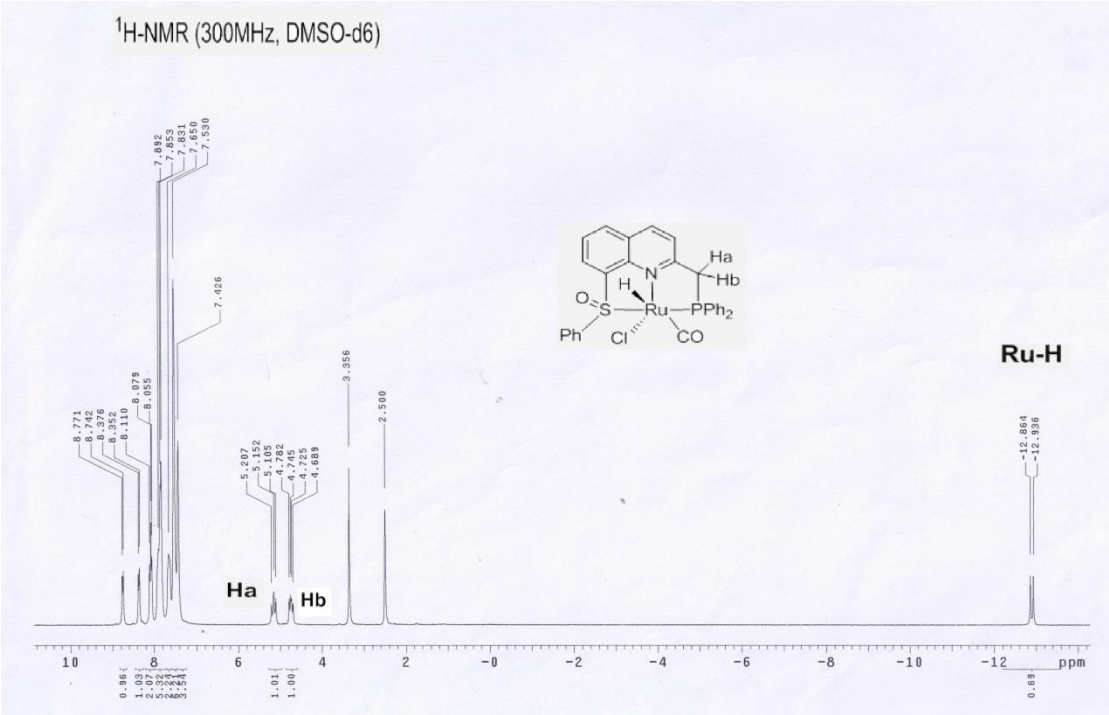


Figure 13S.[1]H NMR spectrum of **1b**.

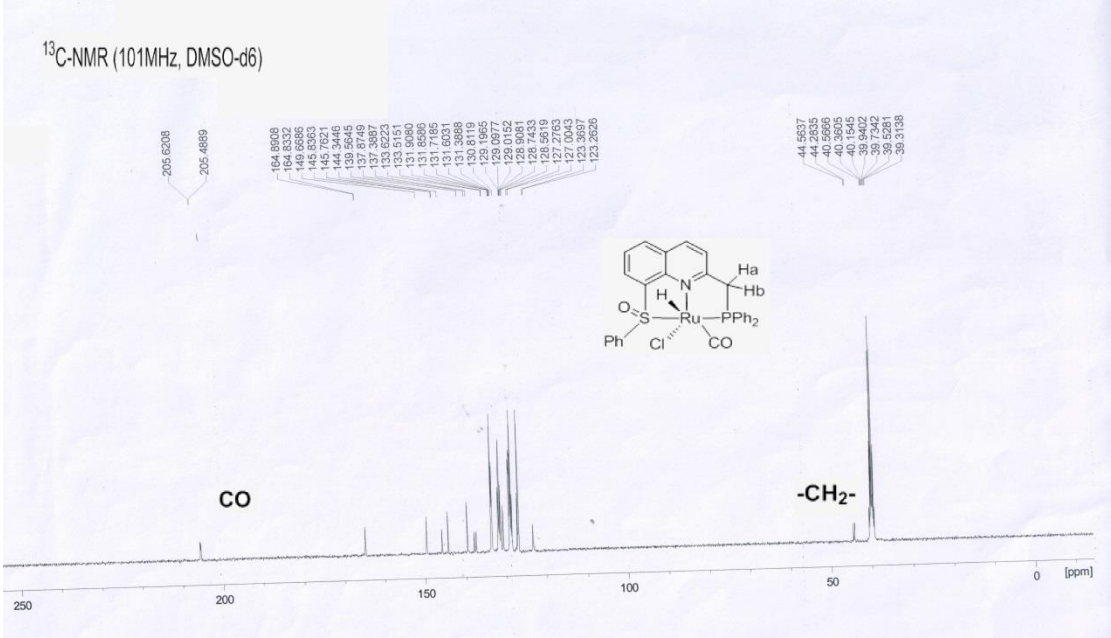


Figure 14S. [13]C{[1]H} NMR spectrum of **1b**.

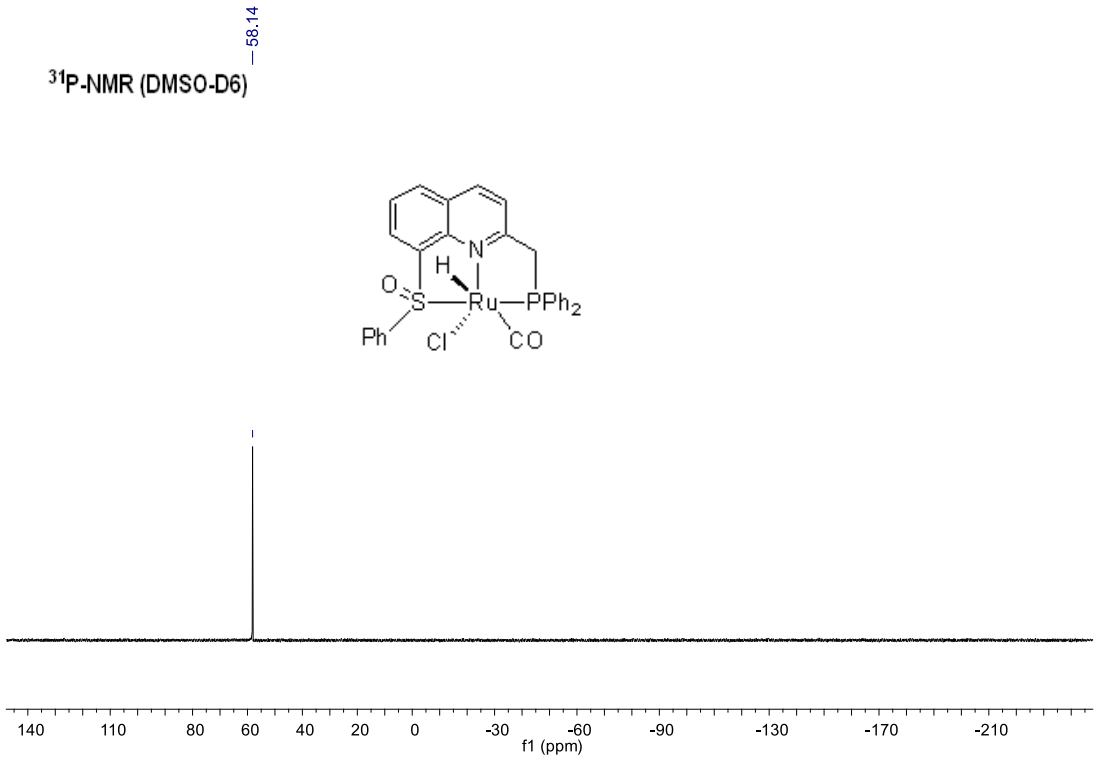


Figure 15S. $^{31}P\{^{1}H\}$ NMR spectrum of **1b**.

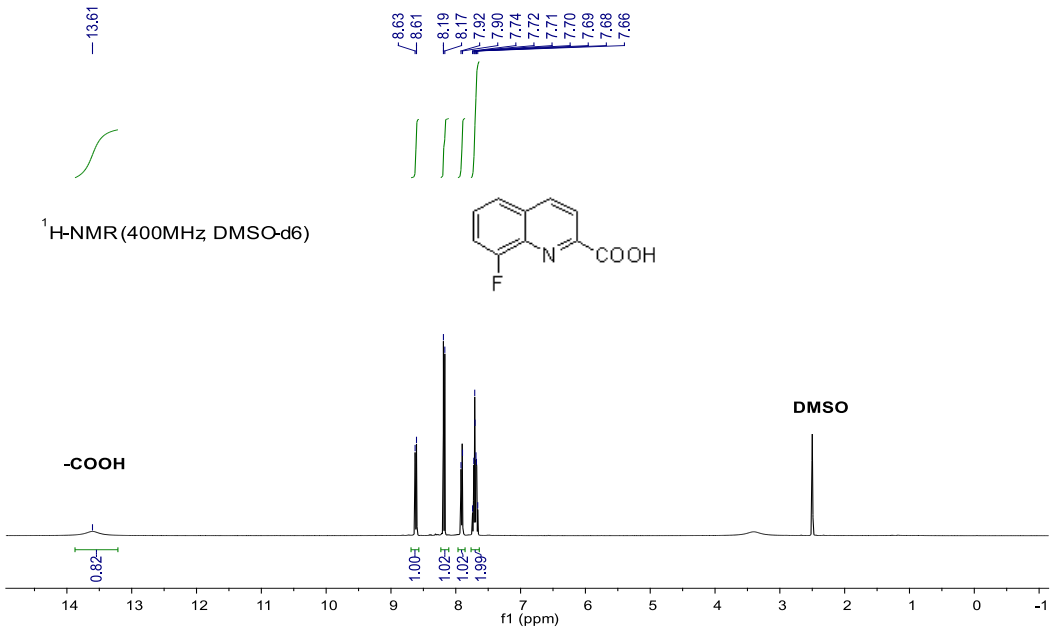


Figure 16S.^{1}H NMR spectrum of **h**.

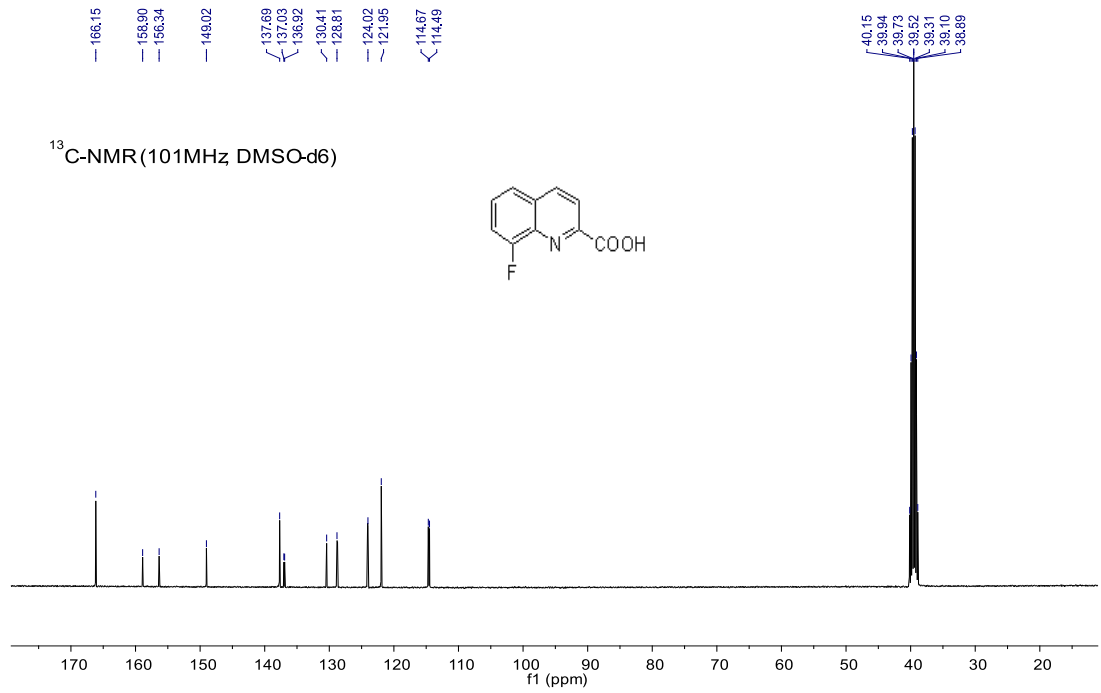


Figure 17S. $^{13}C\{^{1}H\}$ NMR spectrum of **h**.

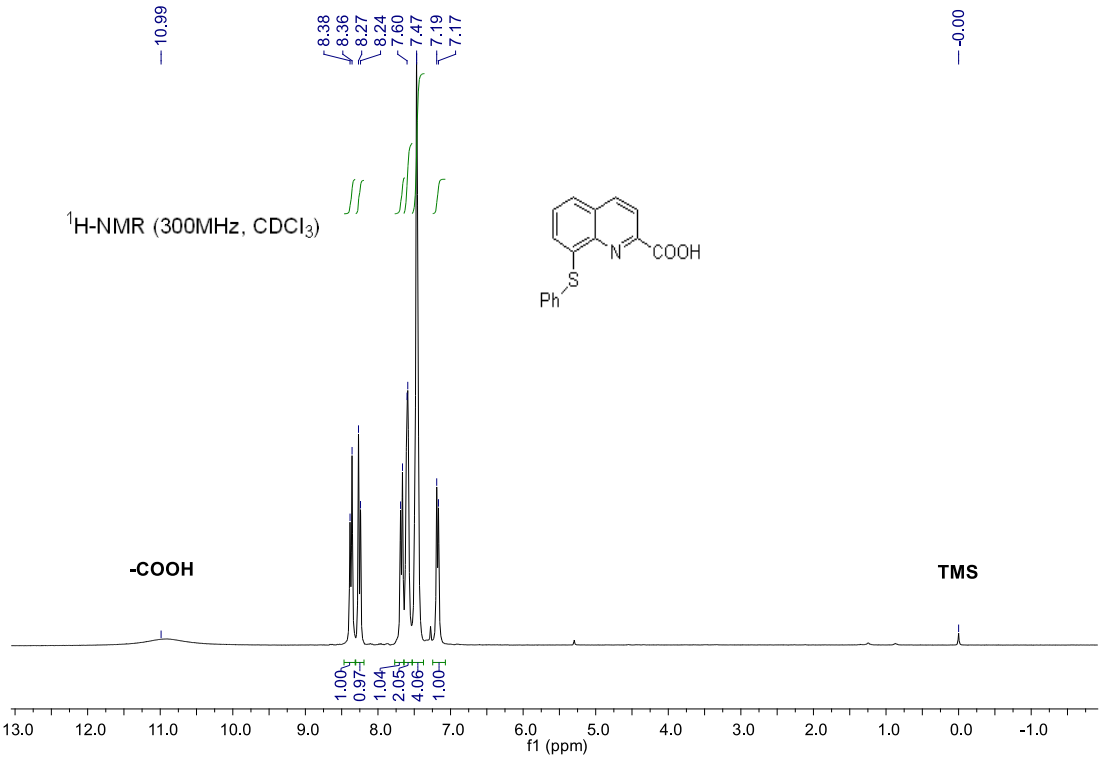


Figure 18S.^{1}H NMR spectrum of **i**.

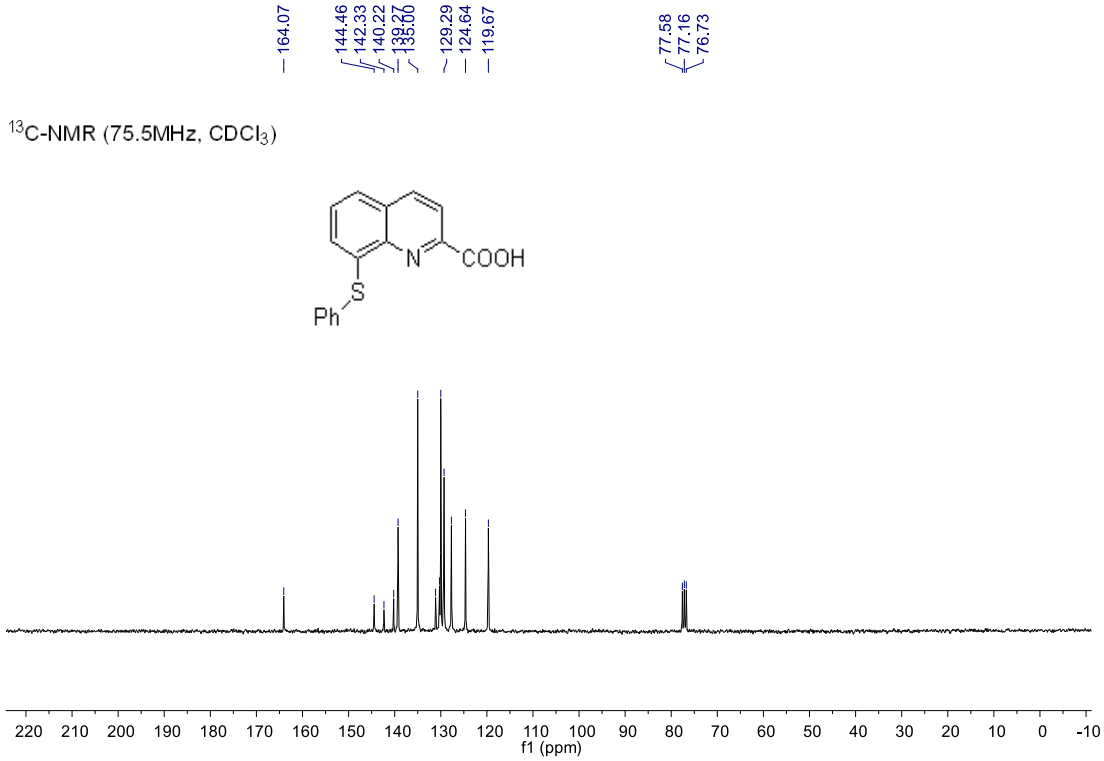


Figure 19S. $^{13}C\{^{1}H\}$ NMR spectrum of **i**.

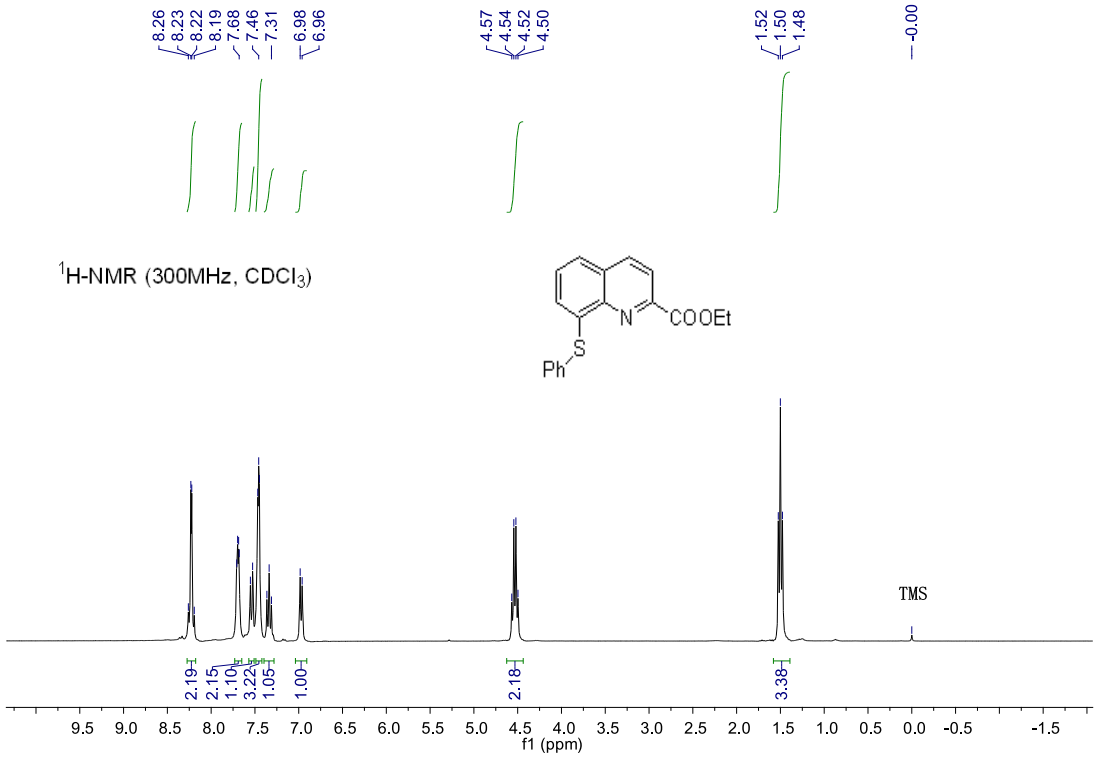


Figure 20S.^{1}H NMR spectrum of **j**.

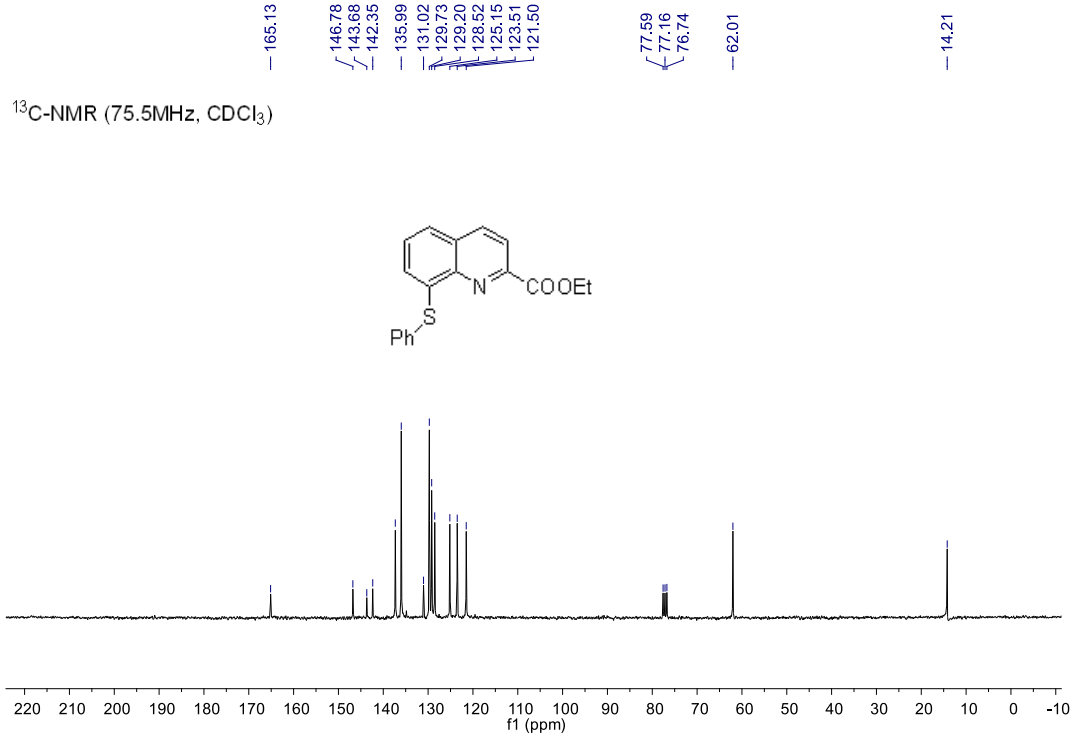


Figure 21S. $^{13}C\{^{1}H\}$ NMR spectrum of **j**.

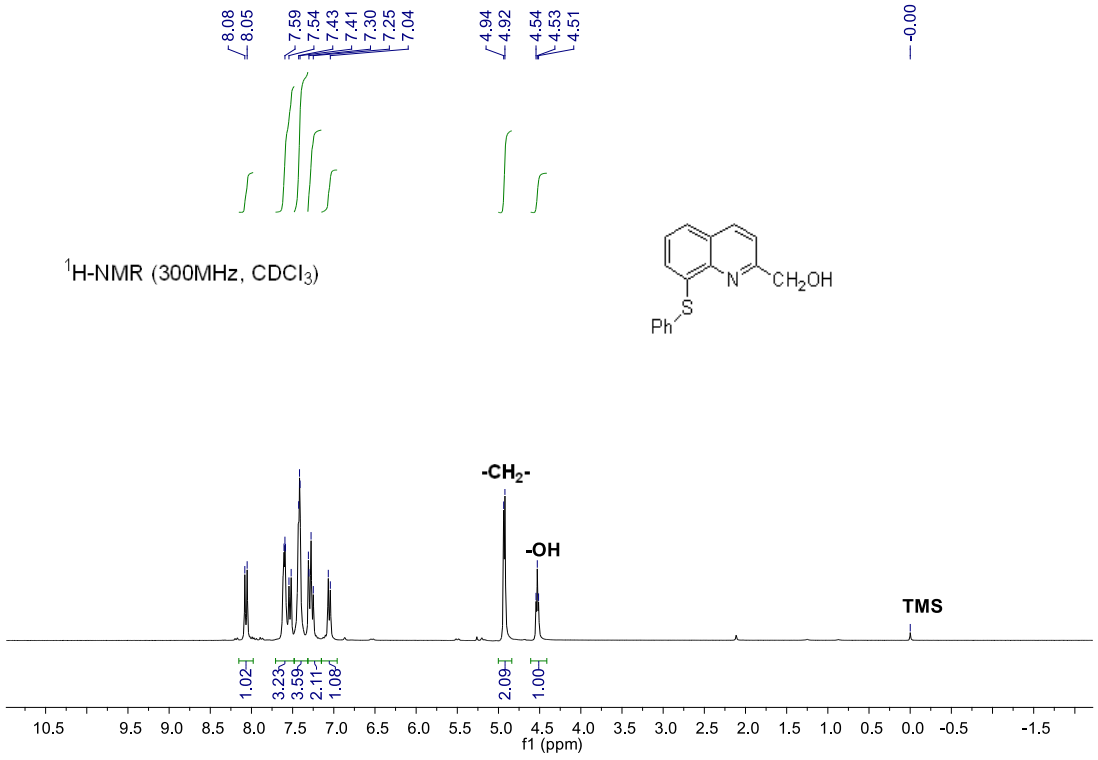


Figure 22S.^{1}H NMR spectrum of **k**.

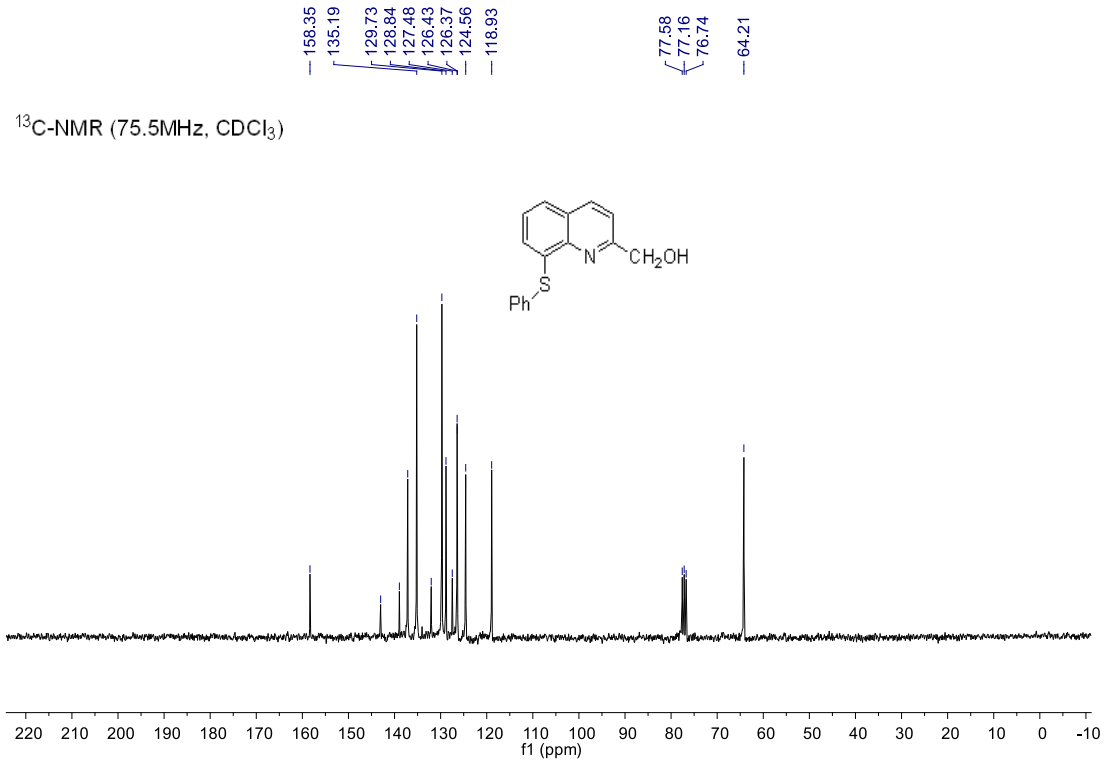


Figure 23S. $^{13}C\{^{1}H\}$ NMR spectrum of **k**.

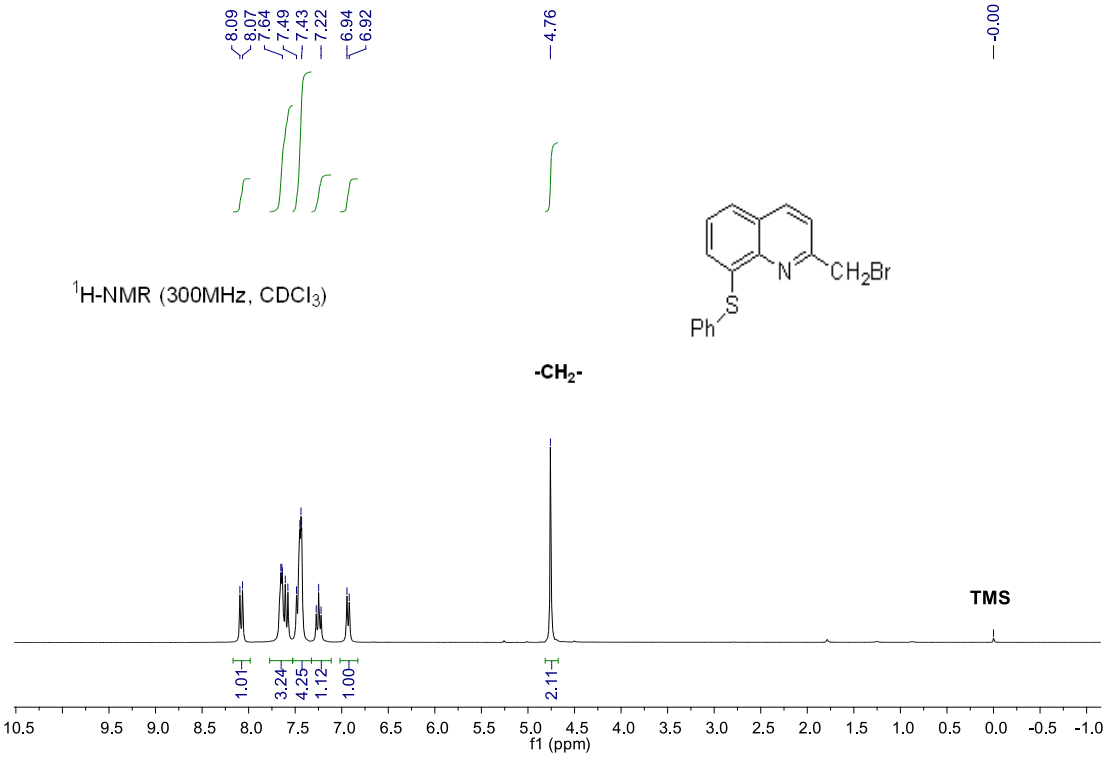


Figure 24S.^{1}H NMR spectrum of **l**.

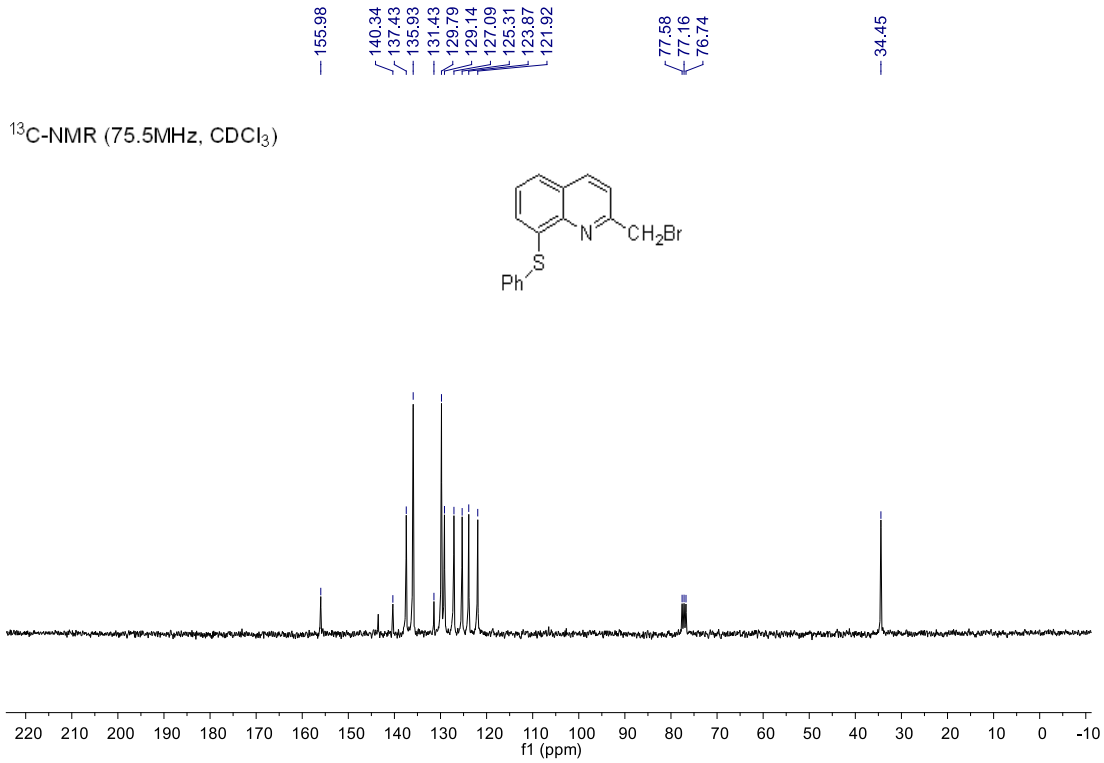


Figure 25S. $^{13}C\{^{1}H\}$ NMR spectrum of **l**.

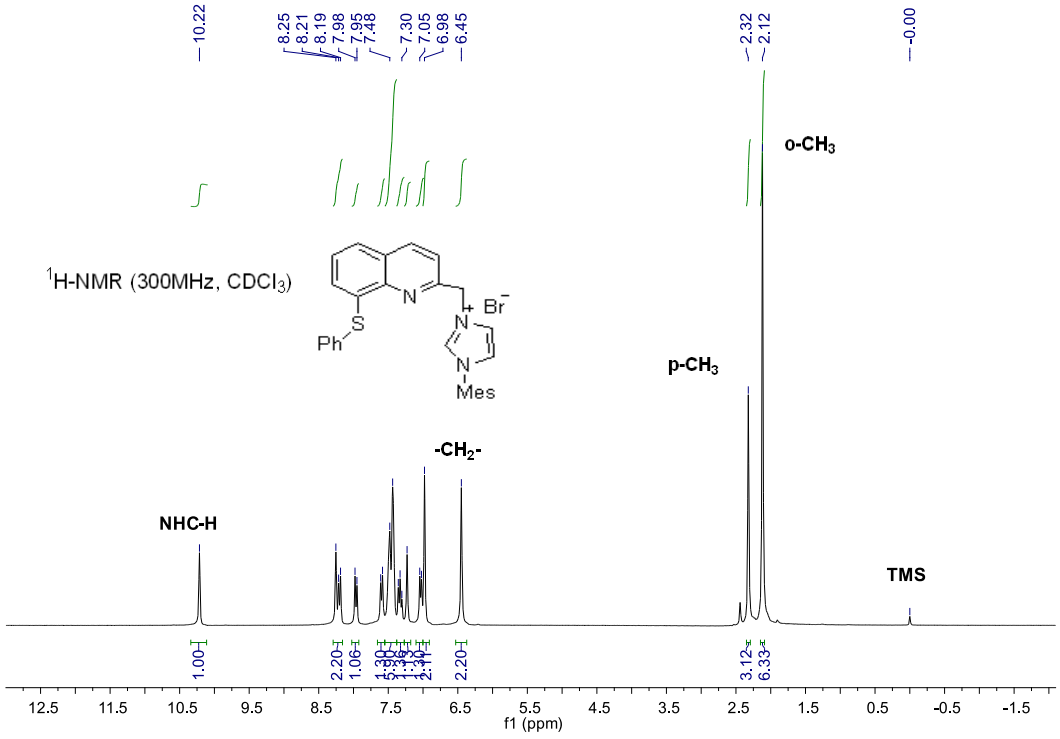


Figure 26S.^{1}H NMR spectrum of **m**.

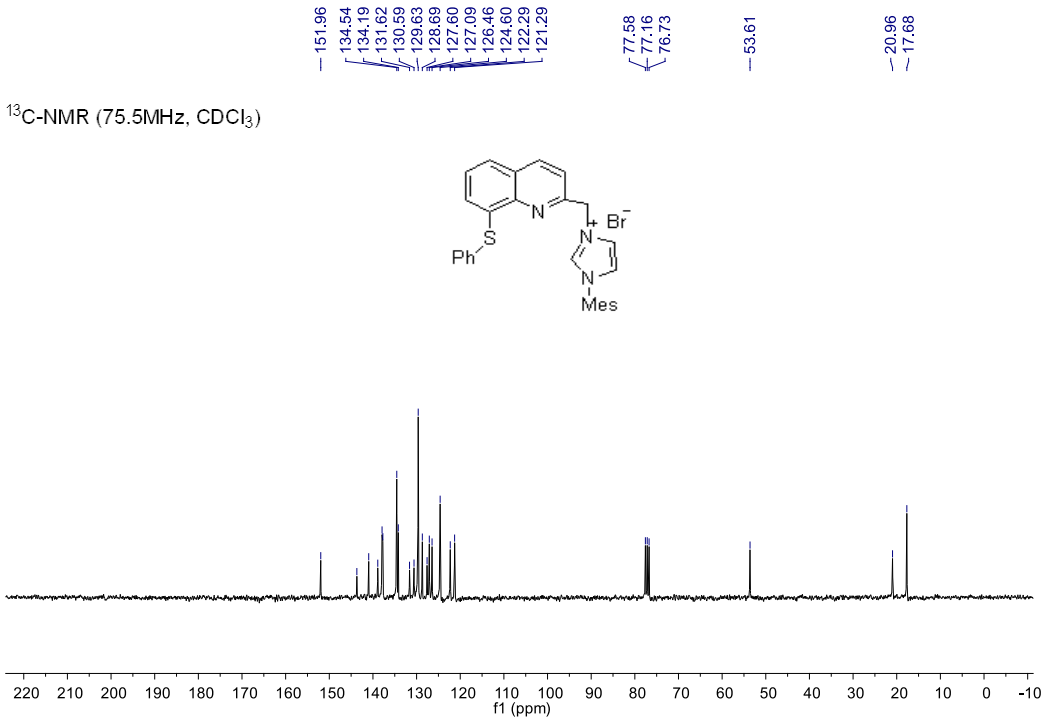


Figure 27S. $^{13}C\{^{1}H\}$ NMR spectrum of **m**.

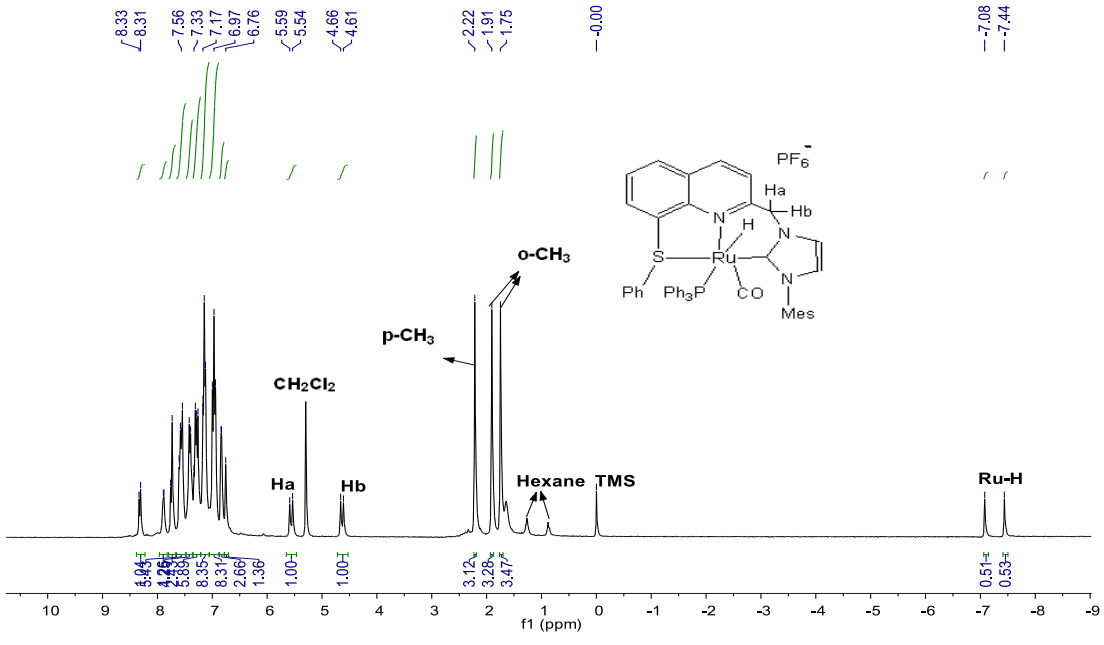


Figure 28S.^{1}H NMR spectrum of **2**.

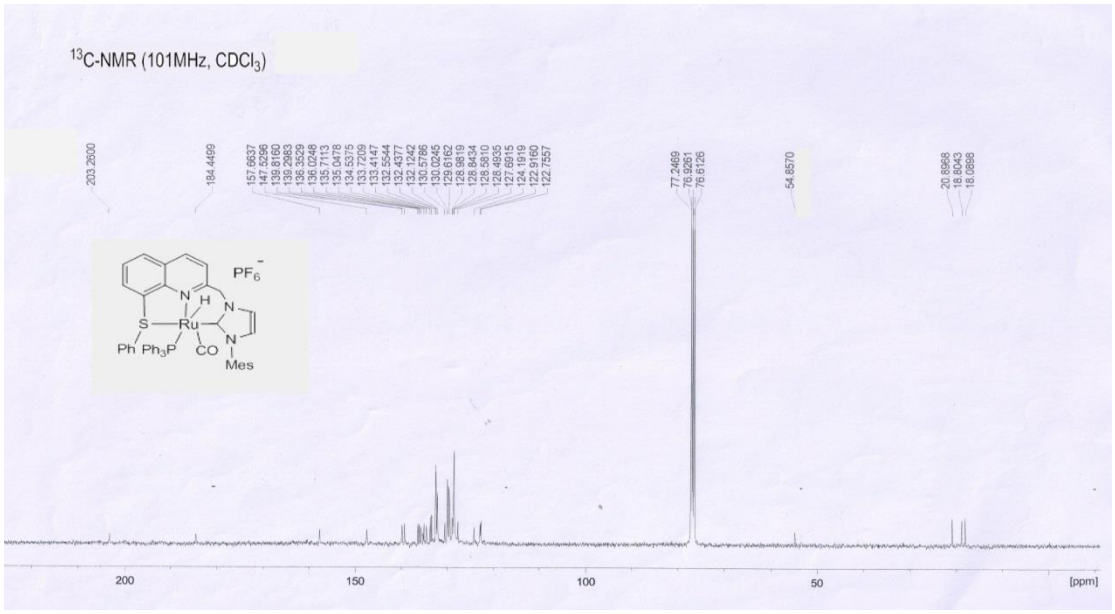


Figure 29S. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

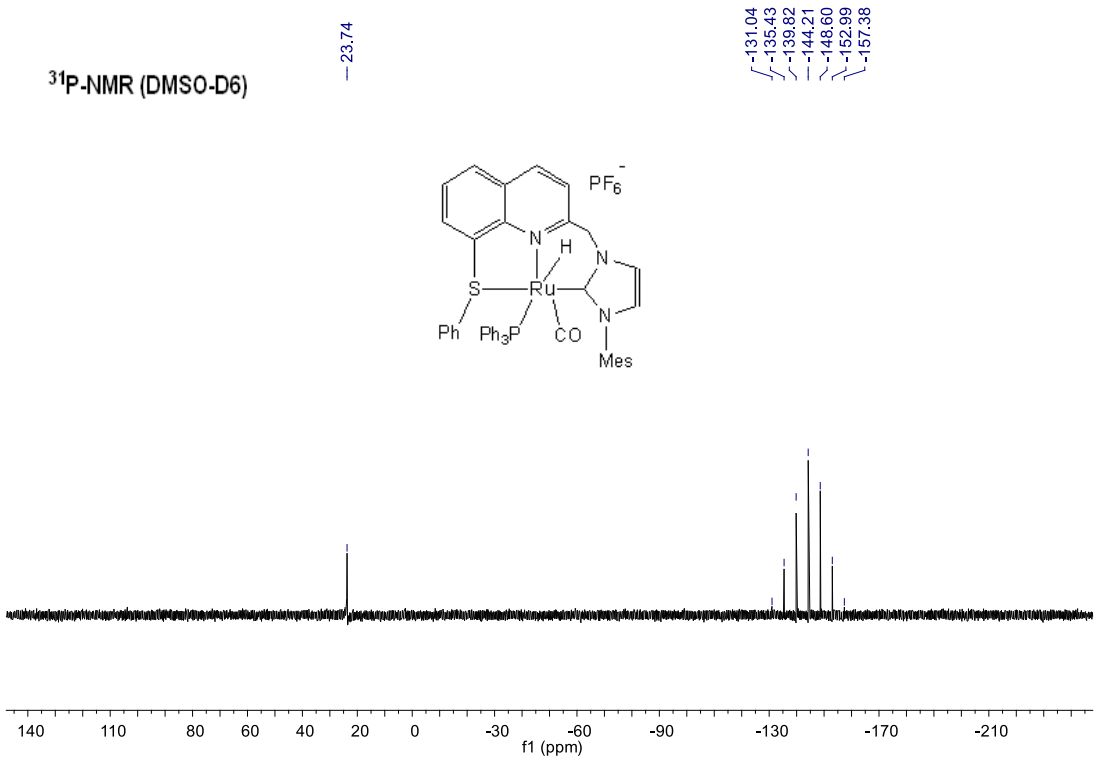
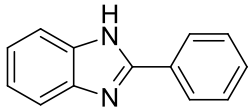


Figure 30S. $^{31}P\{^{1}H\}$ NMR spectrum of **2**.

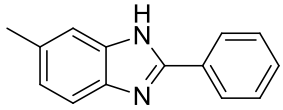
2.4 Characterization of benzimidazole derivatives:



2-phenyl-1*H*-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 11.68 (brs, 1H), 8.11 - 8.26 (m, 2H), 7.31 - 7.48 (m, 3H), 7.23 - 7.38 (m, 2H), 7.04 - 7.22 (m, 2H).

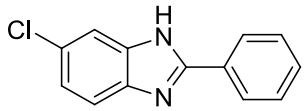
^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 155.9, 132.4, 130.2, 127.6, 124.0, 122.6, 118.0, 109.1, 104.1.



5-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 12.78 (brs, 1H), 8.15 (d, 2H, *J* = 6.9 Hz), 7.50 - 7.35 (m, 5H), 7.07-6.99 (m, 1H), 2.44 (s, 3H).

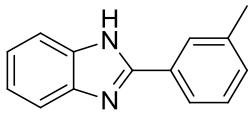
^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 152.03, 137.80, 132.80, 130.30, 130.03, 129.07, 128.98, 127.80, 127.05, 127.03, 124.30, 112.06, 112.00, 23.50.



5-Chloro-2-phenyl-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 13.10 (brs, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.60-7.50 (m, 5H), 7.26-7.21 (m, 1H).

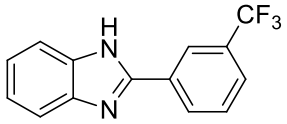
^{13}C NMR (75.5MHz, DMSO-D_6, 296 K): δ (ppm): 153.10, 137.90, 130.31, 130.30, 129.70, 129.65, 129.18, 129.01, 126.20, 126.00, 122.52, 118.00, 112.5.



2-(3-Methylphenyl)-1*H*-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 12.87 (brs, 1H), 8.03 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.13-7.25 (m, 2H),2.41 (s, 3H).

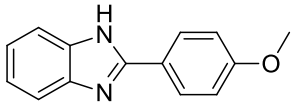
^{13}C NMR(75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 20.9, 111.1, 118.7, 121.5, 122.3, 123.4, 126.9, 128.7, 129.9, 130.3, 134.8, 138.0, 143.7, 151.2.



2-(3-(Trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm):13.12 (brs, 1H), 8.51 (s, 1H), 8.46 (d, *J*= 7.6 Hz, 1H), 7.77 - 7.85 (m, 2H), 7.69 (d, *J*= 7.2 Hz, 1H), 7.56 (d, *J*= 7.6 Hz, 1H), 7.19 - 7.26 (m, 2H).

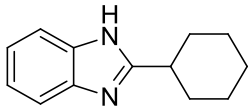
^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 111.4, 119.3, 122.2, 123.1, 123.6, 126.0, 129.4, 130.0, 130.7, 131.1, 131.4, 135.2, 150.3.



2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole:

^{1}HNMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 11.73 (brs, 1H), 8.05 - 8.13 (m, 2H), 7.57 - 7.65 (m, 1H), 7.33 - 7.42 (m, 1H), 7.07 - 7.14 (m, 2H), 6.98 - 7.05 (m, 2H), 3.83 (s, 3H).

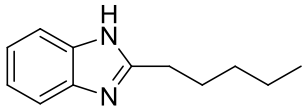
^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 161.3, 151.8, 128.0, 123.7, 121.9, 121.4, 119.2, 114.1, 110.4, 54.8, 29.6.



2-Cyclohexyl-1H-benzo[*d*]imidazole

^{1}HNMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 12.08 (brs, 1H), 7.46–7.48 (m, 2H), 7.09 - 7.11 (m, 2H), 2.84 (t, *J* = 10.8 Hz, 1H), 2.01-2.05 (m, 2H), 1.56– 1.81 (m, 5H), 1.23–1.44 (m, 3H).

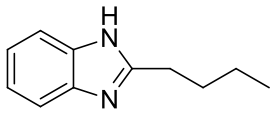
^{13}C NMR (75.5 MHz, DMSO-D_6, 296K): δ (ppm): 25.7, 25.8, 31.7, 38.1, 111.2, 118.6, 121.2, 121.8, 134.6, 143.5, 159.3.



2-pentyl-1*H*-benzo[*d*]imidazole:

^{1}H NMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 10.62 (brs, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.22-7.19 (m, 2H), 2.93 (t, 2H),1.89-1.82 (m, 2H, CH2), 1.37-1.28 (m, 4H), 0.85 (t, 3H).

^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm): 155.32, 140.68, 140.68, 122.21, 122.20, 119.68, 119.65, 31.50, 29.37, 28.00, 22.36, 13.90.



2-butyl-1H-benzo[*d*]imidazole

^{1}HNMR (300 MHz, DMSO-D_6, 296 K): δ (ppm): 11.73 (brs, 1H), 7.45–7.48 (m, 2H), 7.09 - 7.11 (m, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 1.70–1.71 (m, 2H), 1.30– 1.39 (m, 2H), 0.87 - 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75.5 MHz, DMSO-D_6, 296 K): δ (ppm):155.62, 138.59, 122.07, 114.58, 30.43, 29.06, 22.41, 13.67.

References:

1. Montag, M.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2012**, *134*, 10325-10328.
2. Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840-10841.