Supporting Information

Ruthenium Metathesis Catalysts with Imidazole Ligands

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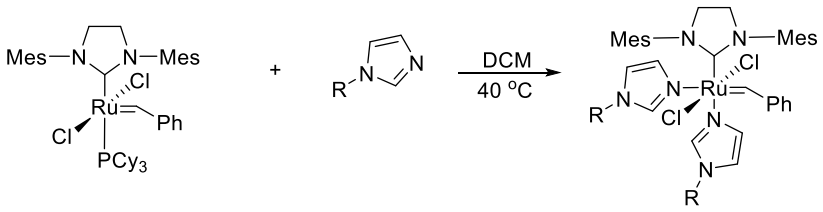
1. General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a N_2 atmosphere. All solvents were purchased from J&K. Chem Co., Ltd. Commercial materials were obtained from Adamas-beta, TCI shanghai, Alfa Aesar and Bidepharmatech. 1-mesityl-1H-imidazole 5b were synthesized according to published procedures.[1]

Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using commercially precoated silica gel plates produced from Yantai Xinnuo Silica Gel development Co., Ltd, and visualized by UV light 254 nm or potassium permanganate solution. Organic solutions were concentrated under reduced pressure on XY-2000 rotary evaporator. Flash column chromatography was performed on Silica Gel (200-300 mesh) purchased from Yantai Xinnuo Silica Gel development Co., Ltd.

^{1}H and ^{13}C NMR spectra were recorded on Bruker instruments (400 MHz and 101 MHz, manual and auto simpler respectively) and internally referenced to tetramethylsilane (TMS) signal or residual protic solvent signals. ^{19}F NMR spectra were recorded on a Bruker instrument (376 MHz) referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Melting points were determined on a SGWX-4B melting point apparatus. High resolution mass spectrum (HRMS) was performed on a Bruker mior OTOF-QII instrument.

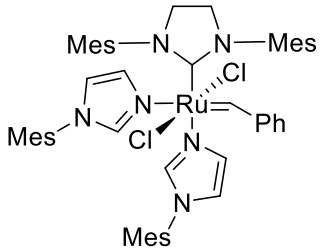
2. General Procedure for Synthesis of Ru Complexes



2 **5** **6a**, R = Mes
6b, R = Bn

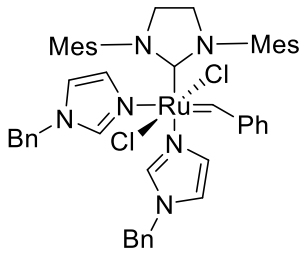
In a glovebox a 20 mL vial was charged with corresponding ruthenium complex (1 equiv.) dissolved in anhydrous DCM followed by imidazole (2.0 equiv.). The resulting mixture was stirred for 0.5 h at 40 °C. After the reaction time was completed, DCM was evaporated, the brown residue was dissolved in DCM (0.5 mL), and the obtained solution was added hexane (2.5 mL). Then, the obtained green solid was filtered through a funnel, and crystalized from DCM/hexane, the precipitate was filtered, and dried in vacuum.

[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)bis(N-(2,4,6-trimethylphenyl)imidazole)ruthenium (6a)



Green solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 19.08 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.61 (s, 1H), 7.47 (s, 1H), 7.41 (s, 1H), 7.23 (s, 1H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.96 (s, 4H), 6.83 (s, 6H), 6.46 (s, 1H), 4.06 (s, 4H), 2.43 (d, *J* = 21.8 Hz, 6H), 2.29 (d, *J* = 29.6 Hz, 18H), 1.98 (s, 6H), 1.70 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.5, 152.3, 139.0, 138.8, 138.6, 138.3, 138.2, 138.0, 137.9, 137.6, 137.1, 135.0, 134.9, 133.4, 130.3, 130.1, 129.8, 129.4, 129.3, 129.0, 128.8, 127.5, 119.2, 118.8, 51.5, 21.0, 19.3, 17.7, 17.0. HRMS (ESI) m/z: $[M + K]^+$ Calcd for $C_{52}H_{61}Cl_2N_6Ru$ 981.1703; found 980.3008.

[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)bis(N-benzylimidazole)ruthenium (6b)

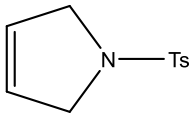


Green solid in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 19.15 (s, 1H), 7.67 (d, *J* = 30.7 Hz, 3H), 7.49 – 7.27 (m, 6H), 7.22 – 6.98 (m, 8H), 6.94 (s, 1H), 6.76 (d, *J* = 51.4 Hz, 6H), 6.38 (s, 1H), 5.02 (s, 2H), 4.75 (s, 2H), 4.00 (s, 4H), 2.72 – 2.16 (m, 18H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 219.5, 152.5, 138.7, 138.3, 137.9, 137.6, 137.4, 135.6, 130.4, 130.0, 129.7, 129.7, 129.5, 129.3, 129.2, 129.0, 129.0, 128.8, 128.7, 128.6, 128.1, 127.9, 127.5, 127.3, 126.7, 117.6, 51.5, 50.8, 21.1, 19.4, 19.1, 18.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{48}H_{53}Cl_2N_6Ru$ 886.9720; found 886.2831.

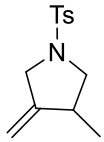
3. Characterization data

1-tosyl-2,5-dihydro-1H-pyrrole (8)



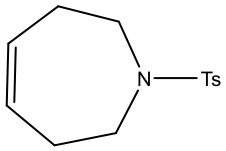
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.65 (s, 2H), 4.12 (s, 4H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 129.8, 127.4, 125.5, 54.9, 21.6.

3-methyl-4-methylene-1-tosylpyrrolidine (9)



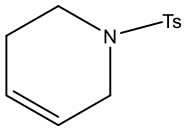
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.90 – 4.85 (m, 2H), 3.95 (d, *J* = 14.1 Hz, 1H), 3.73 (d, *J* = 14.1 Hz, 1H), 3.57 (s, 1H), 2.71 – 2.67 (m, 2H), 2.44 (s, 3H), 1.04 (d, *J* = 6.3, 2.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) *δ* 149.29, 143.63, 132.78, 129.70, 127.81, 106.04, 55.10, 52.19, 37.46, 21.58, 16.07.

1-tosyl-2,3,6,7-tetrahydro-1H-azepine (10)



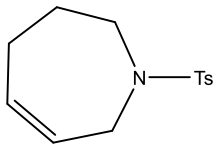
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.67 (t, *J* = 3.5 Hz, 2H), 3.20 (t, J = 5.4 Hz, 4H), 2.34 (s, 3H), 2.24 (q, *J* = 4.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 136.2, 130.2, 129.7, 127.1, 48.3, 29.9, 21.5.

1-tosyl-1,2,3,6-tetrahydropyridine (12)



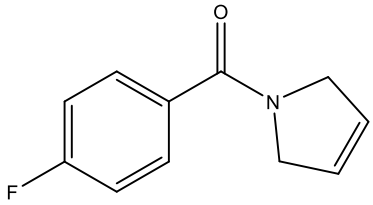
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.67 – 5.63 (m, 1H), 5.54 – 5.50 (m, 1H), 3.48 (t, *J* = 2.8 Hz, 2H), 3.08 (t, *J* = 5.7 Hz, 2H), 2.33 (s, 3H), 2.14 – 2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.3, 129.6, 127.6, 125.0, 122.7, 44.8, 42.7, 25.2, 21.5.

1-tosyl-2,3,4,7-tetrahydro-1H-azepine (14)



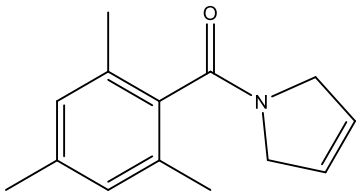
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.79 – 5.73 (m, 1H), 5.67 – 5.62 (m, 1H), 3.82 (d, *J* = 5.8 Hz, 2H), 3.38 (t, *J* = 6.1 Hz, 2H), 2.41 (s, 3H), 2.17 (q, *J* = 5.6 Hz, 2H), 1.80 (q, *J* = 6.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 136.2, 132.9, 129.6, 127.2, 126.6, 49.6, 46.4, 26.8, 26.8, 21.5.

(2,5-dihydro-1H-pyrrol-1-yl)(4-fluorophenyl)methanone (18)



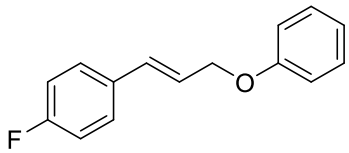
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.04 – 6.99 (m, 2H), 5.85 – 5.83 (m, 1H), 5.69 – 5.67 (m, 1H), 4.37 (s, 2H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 163.4 (d, *J* = 251.5 Hz), 132.8 (d, *J* = 3.0 Hz), 129.1 (d, *J* = 8.1 Hz), 126.0, 125.1, 115.4 (d, *J* = 22.2 Hz), 55.8, 53.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.1.

7-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)quinazoline (20)



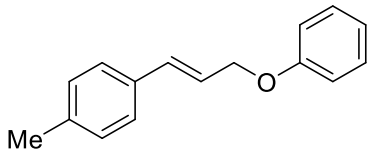
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.91 – 5.89 (m, 1H), 5.74 –5.71 (m, 1H), 4.45 – 4.42 (m, 2H), 3.82 – 3.79 (m, 2H), 2.26 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 138.0, 134.5, 132.8, 128.3, 125.9, 125.3, 54.1, 52.2, 21.1, 18.8.

(E)-1-fluoro-4-(3-phenoxyprop-1-en-1-yl)benzene (23)



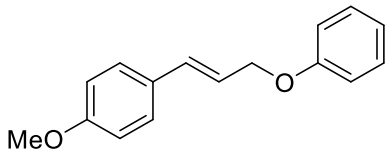
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.02 – 6.94 (m, 5H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.36 – 6.69 (m, 1H), 4.70 – 4.63 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.5 Hz), 158.6, 132.6 (d, *J* = 3.0 Hz), 131.8, 129.6, 128.1 (d, *J* = 7.1Hz), 124.3 (d, *J* = 2.0 Hz), 121.0, 115.6 (d, *J* = 21.2 Hz), 114.8, 68.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9.

(E)-1-methyl-4-(3-phenoxyprop-1-en-1-yl)benzene (24)



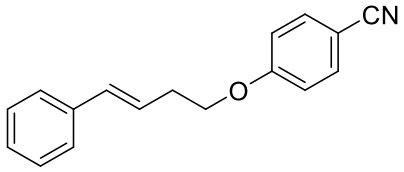
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.93 (m, 3H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.40 – 6.34 (m, 1H), 4.67 (d, *J* = 5.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 137.8, 133.7, 133.1, 129.5, 129.3, 126.5, 123.4, 120.9, 114.8, 77.4, 77.1, 76.8, 68.7, 21.3.

(E)-1-methoxy-4-(3-phenoxyprop-1-en-1-yl)benzene (25)



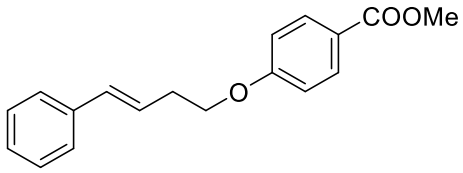
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 2.8 Hz, 1H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.86 – 6.82 (m, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 5.8 Hz, 2H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 152.8, 136.5, 132.8, 128.6, 127.9, 126.6, 124.8, 115.8, 114.7, 69.4, 55.7.

(E)-4-((4-phenylbut-3-en-1-yl)oxy)benzonitrile (26)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.22 (t, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.30 – 6.23 (m, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 2.72 (q, *J* = 6.4 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 137.1, 134.0, 132.7, 128.6, 127.5, 126.1, 125.3, 119.3, 115.3, 103.9, 67.8, 32.7.

methyl (E)-4-((4-phenylbut-3-en-1-yl)oxy)benzoatea (27)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.31 – 6.24 (m, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 2.72 – 2.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.7, 137.3, 132.5, 131.7, 131.6, 128.6, 127.4, 126.1, 125.7, 122.6, 114.2, 67.6, 51.9, 32.8.

4. References

(1) Penn, K. R.; Anders, E. J.; Lindsay, V. N. G. Expedient Synthesis of Bis(imidazolium) Dichloride Salts and Bis(NHC) Complexes from Imidazoles Using DMSO as a Key Polar Additive. *Organometallics*, **2021**, *40*, 3871-3875.

5. NMR Spectra of the described compounds

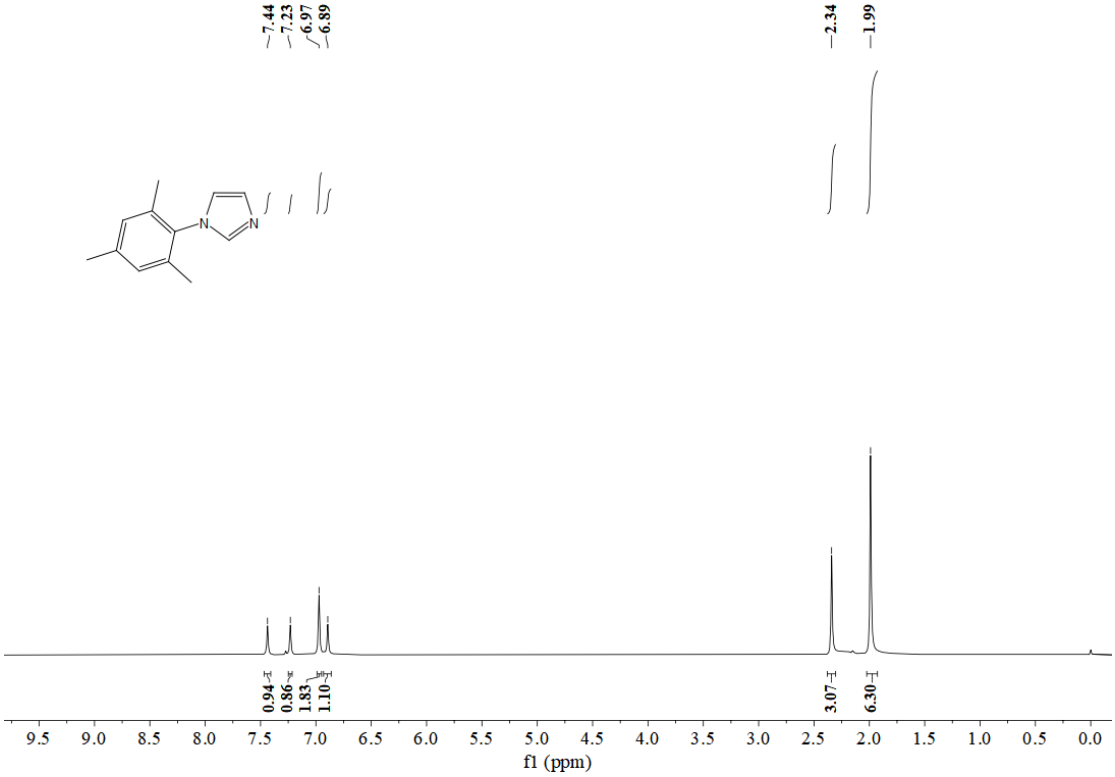


Figure S1. ^{1}H NMR Spectrum of **5a**

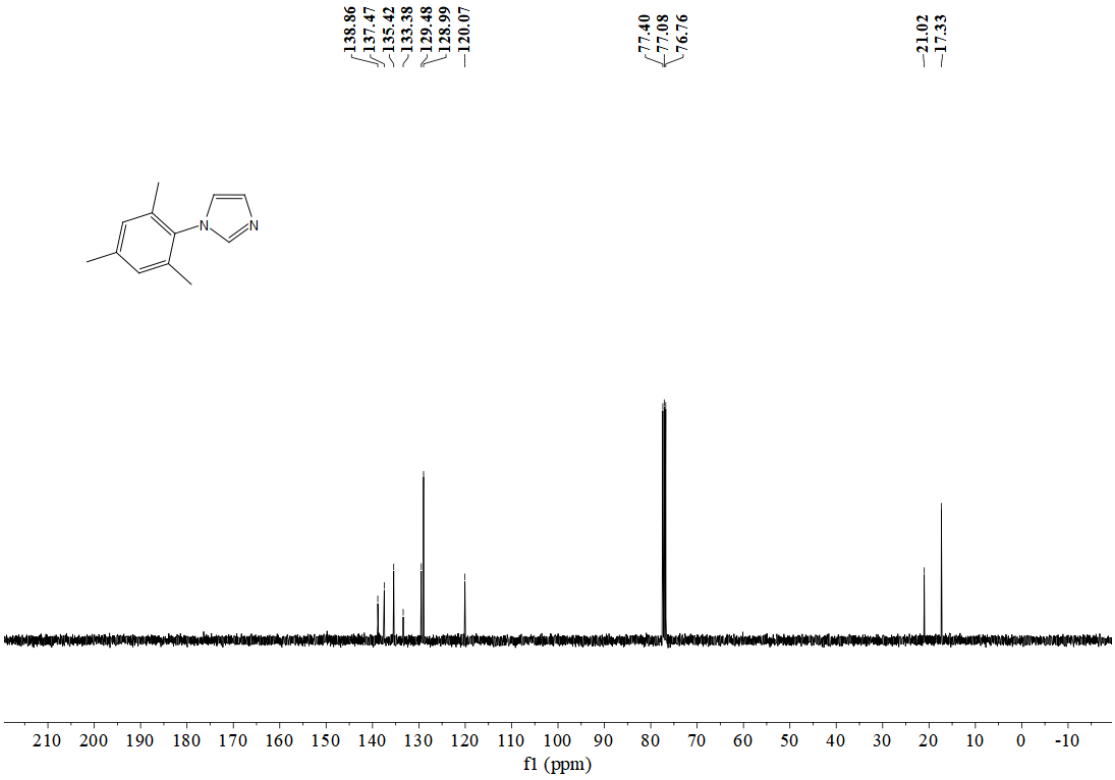


Figure S2. ^{13}C NMR Spectrum of **5a**

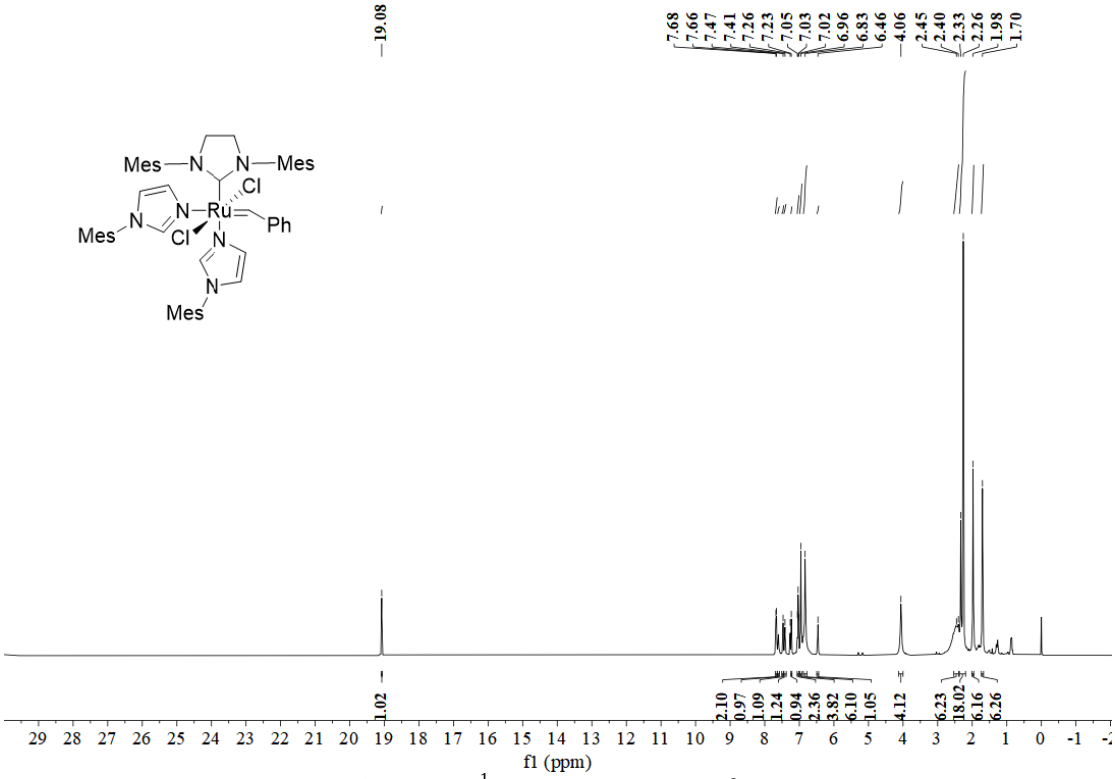


Figure S3. ^{1}H NMR Spectrum of **6a**

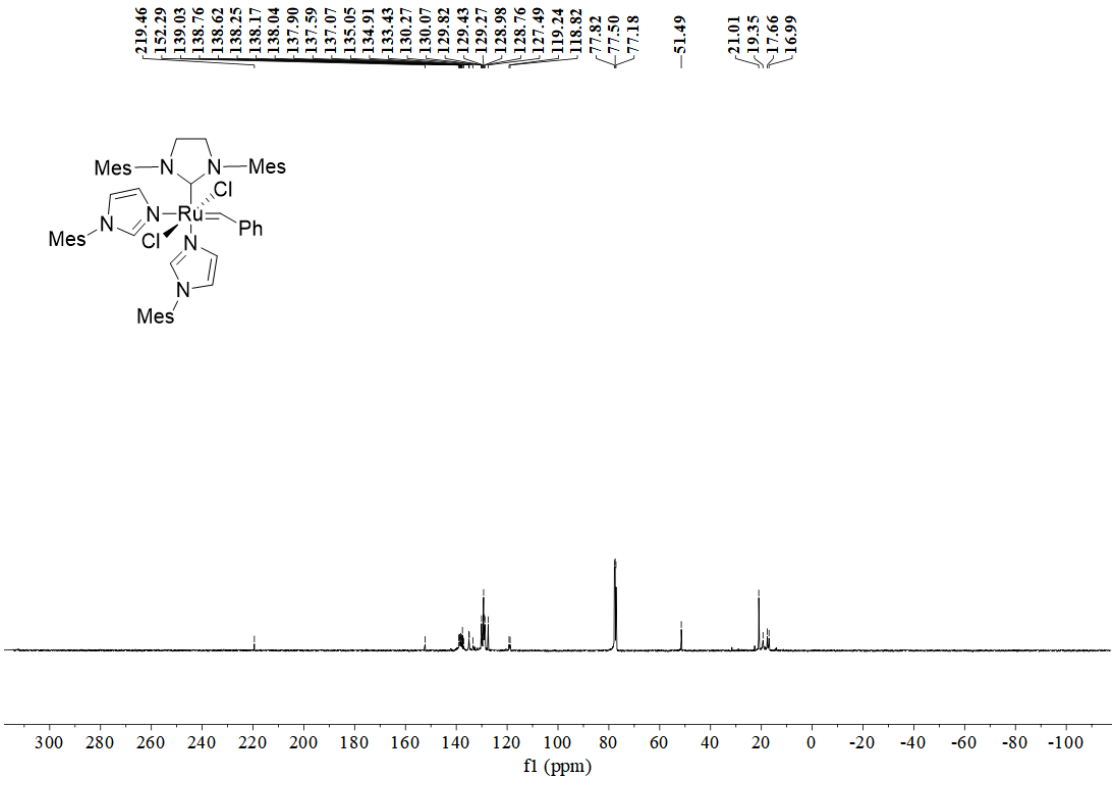


Figure S4. ^{13}C NMR Spectrum of **6a**

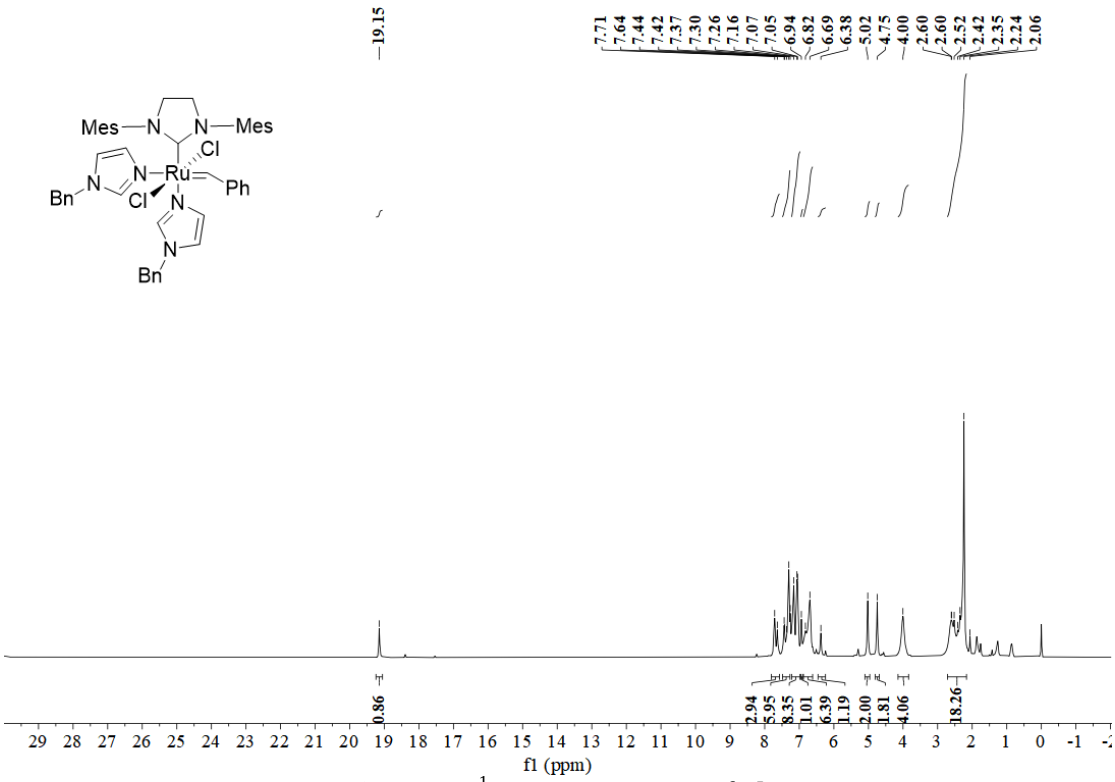


Figure S5. ^{1}H NMR Spectrum of **6b**

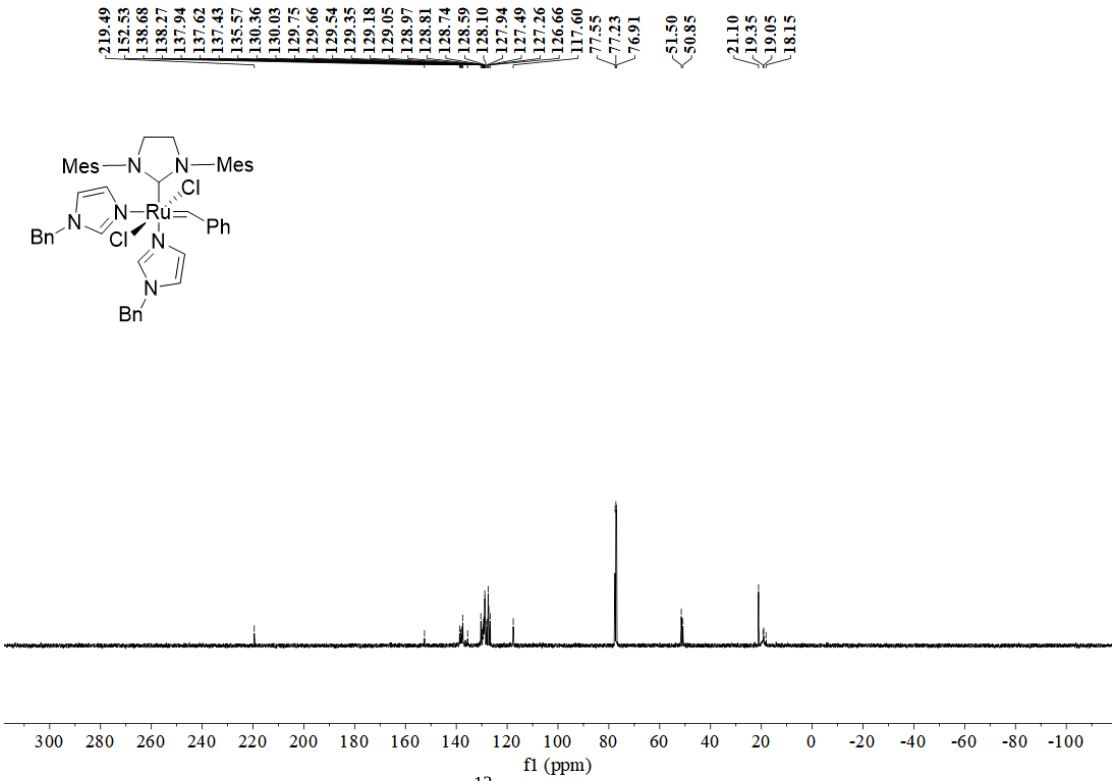


Figure S6. ^{13}C NMR Spectrum of **6b**

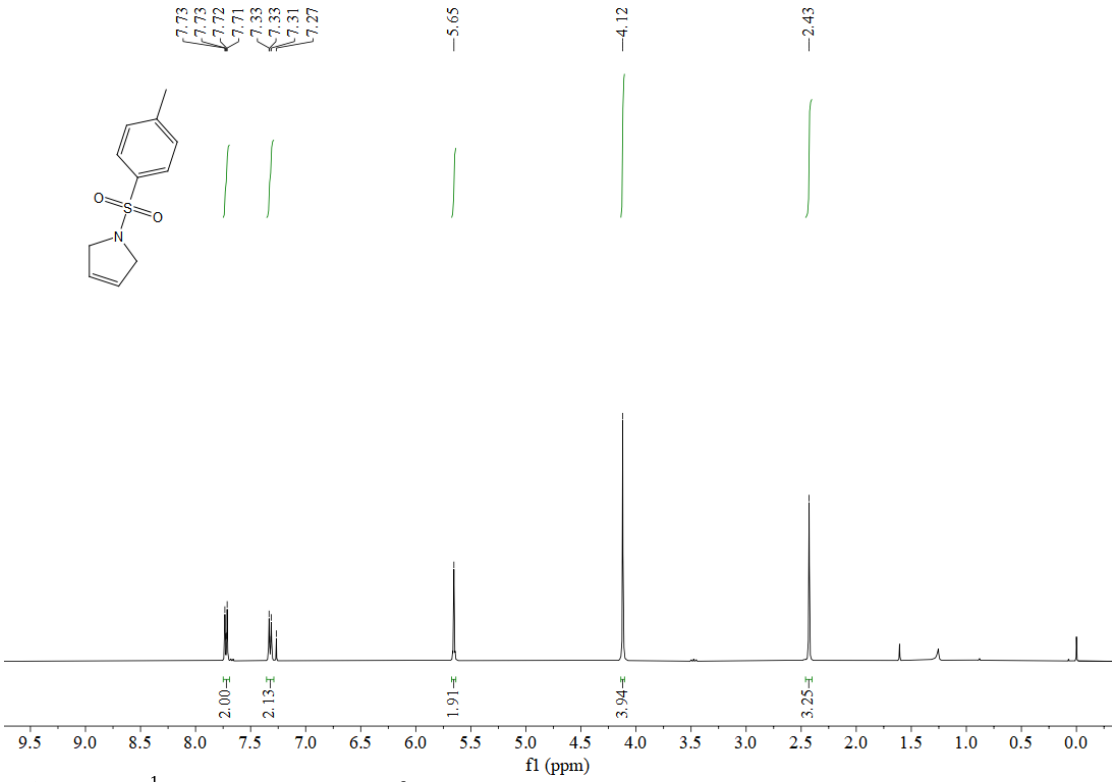


Figure S7. ^{1}H NMR Spectrum of **8**

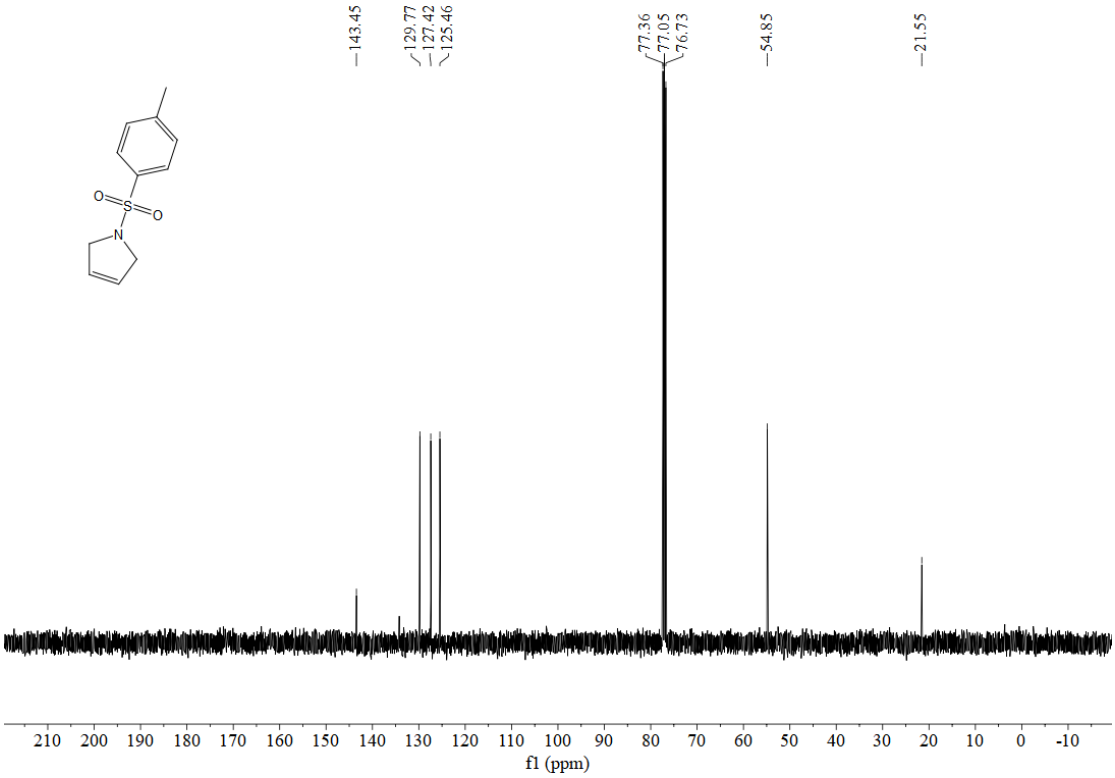


Figure S8. ^{13}C NMR Spectrum of **8**

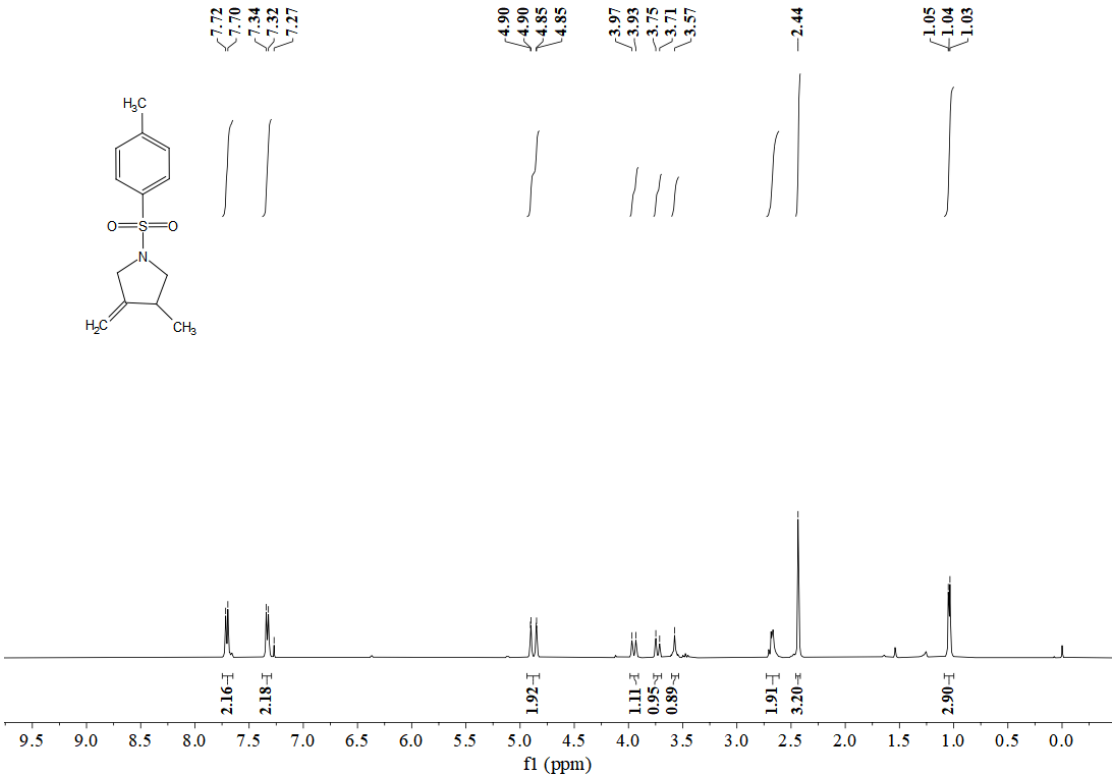


Figure S9. ^{1}H NMR Spectrum of **9**

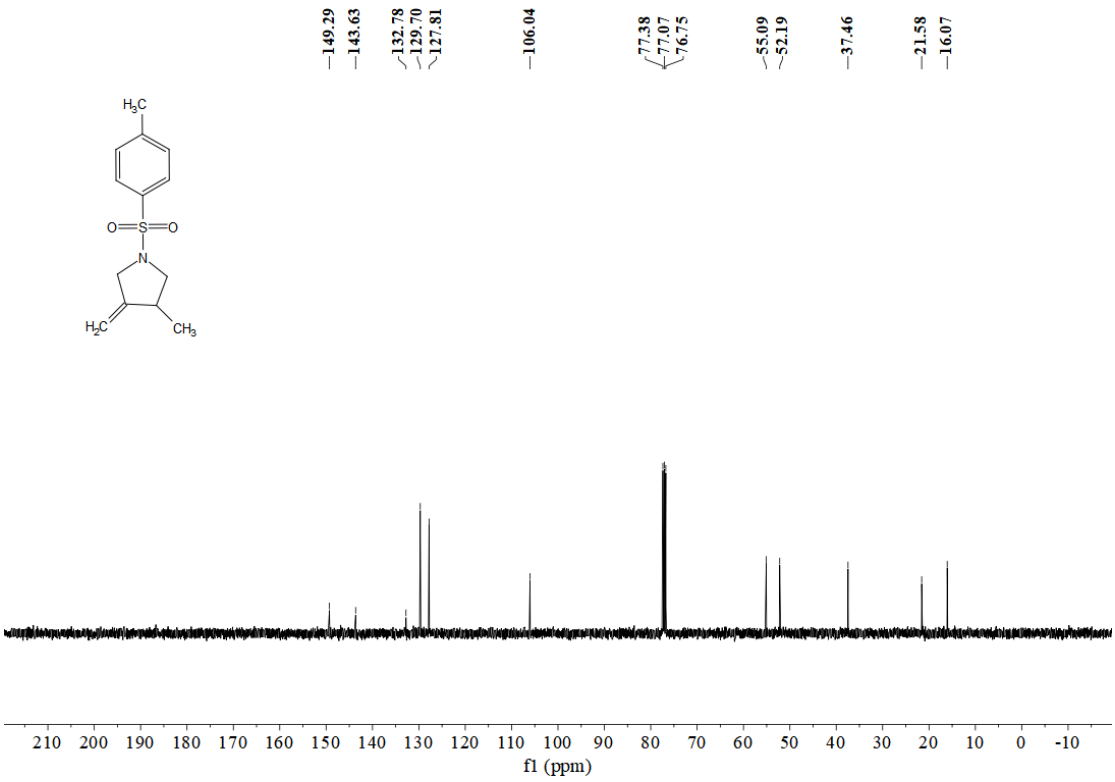


Figure S10. ^{13}C NMR Spectrum of **9**

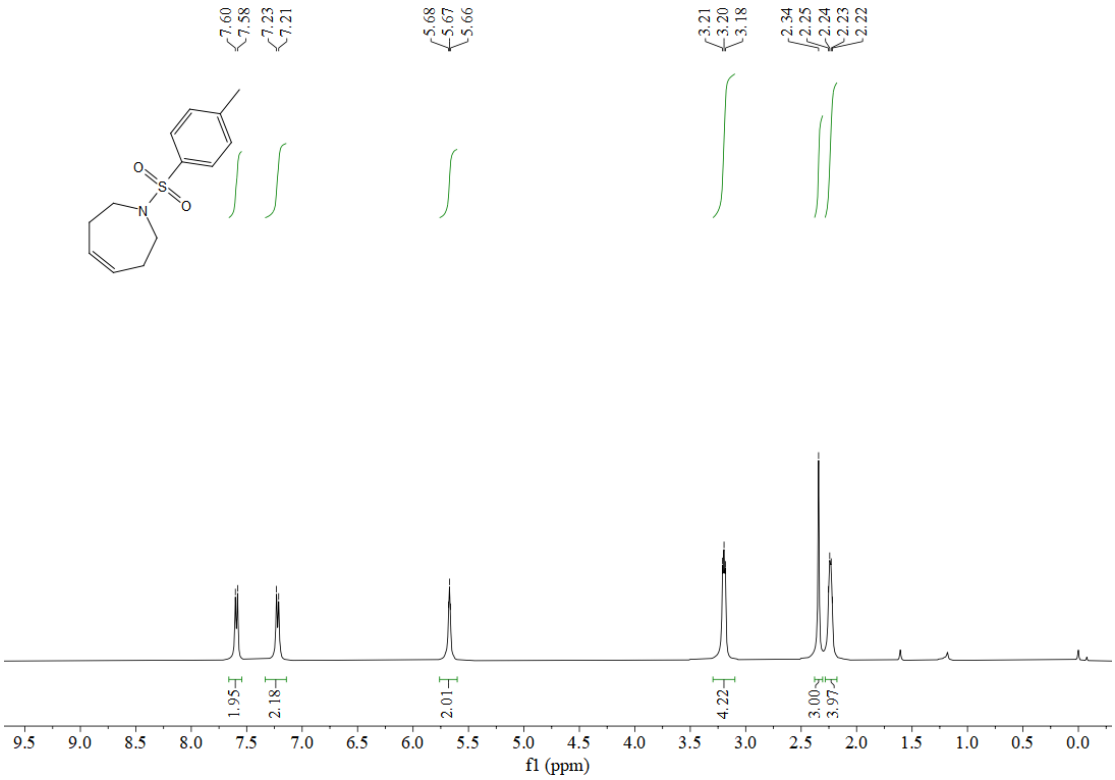


Figure S11. ^{1}H NMR Spectrum of **10**

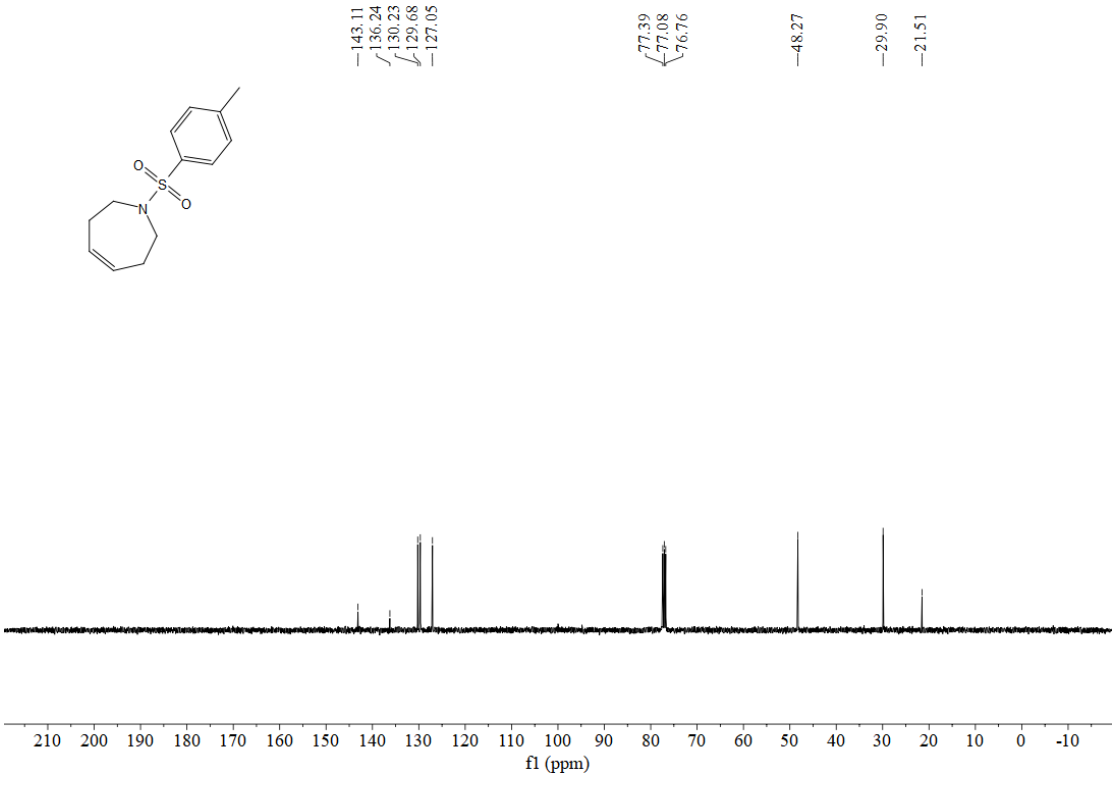


Figure S12. ^{13}C NMR Spectrum of **10**

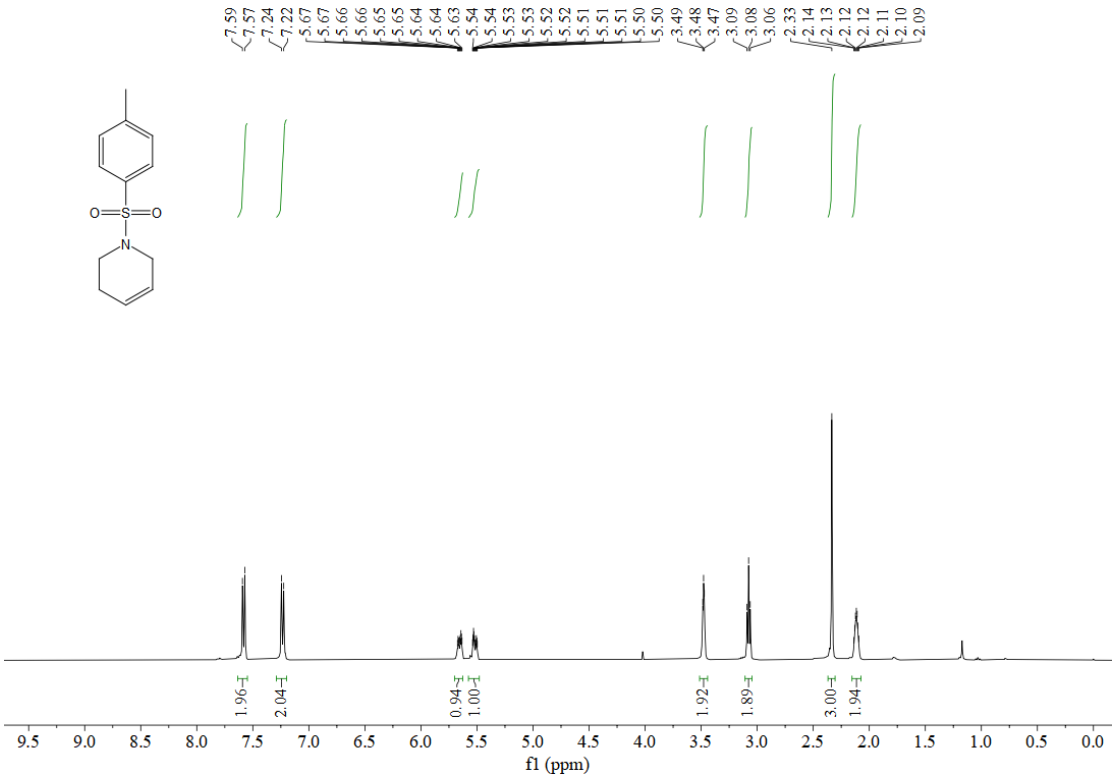


Figure S13. ^{1}H NMR Spectrum of **12**

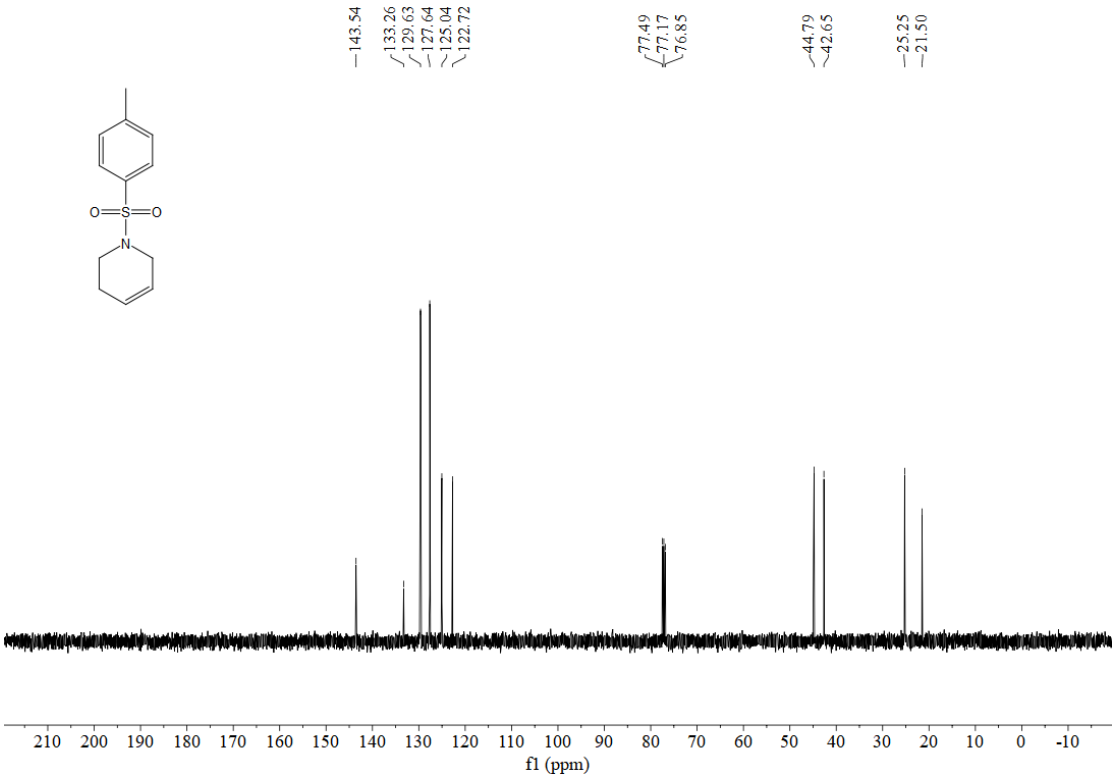


Figure S14. ^{13}C NMR Spectrum of **12**

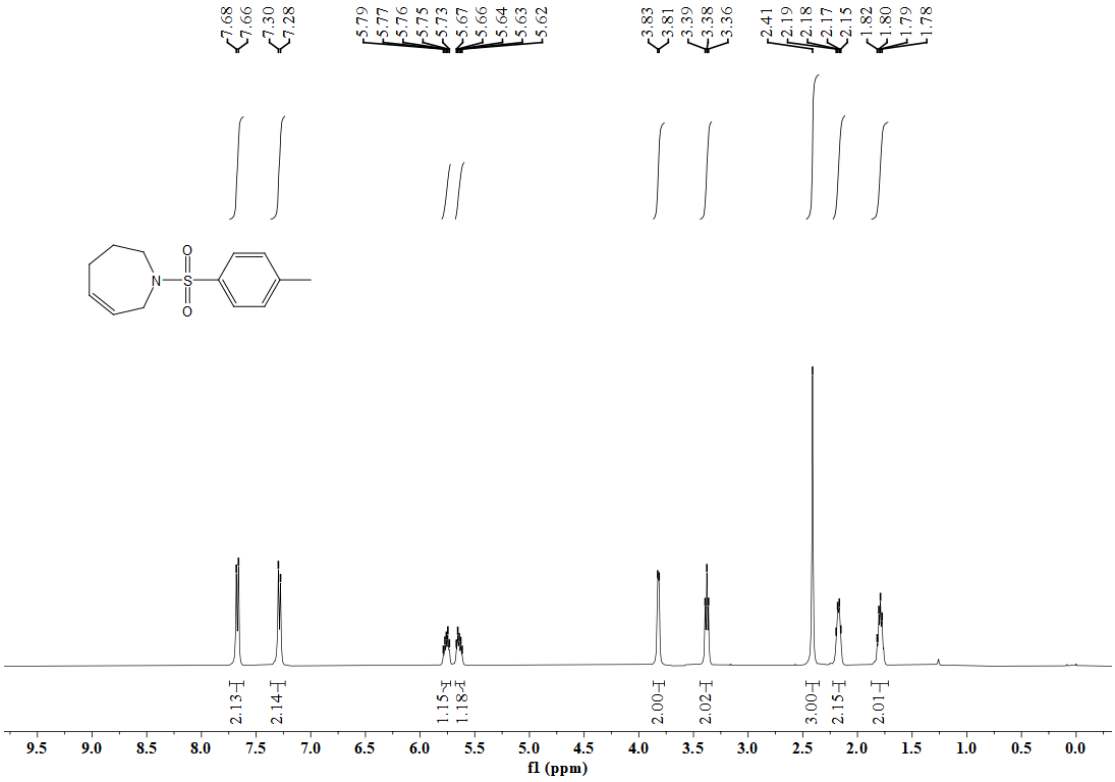


Figure S15. ^{1}H NMR Spectrum of **14**

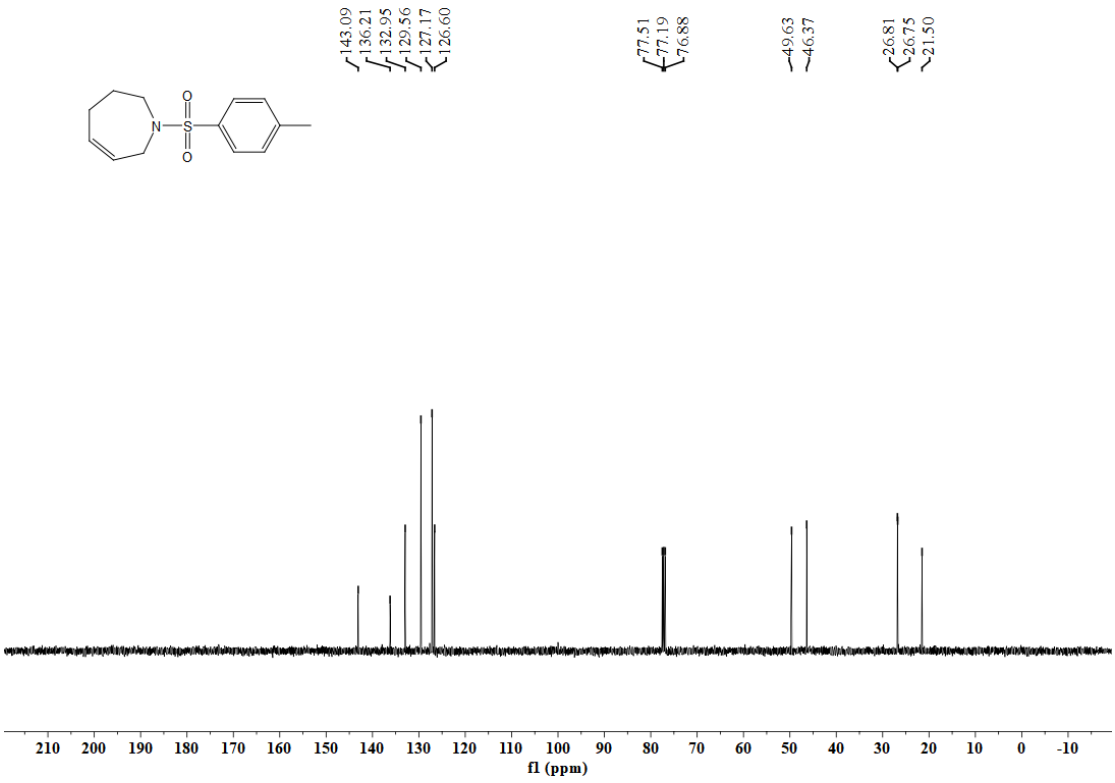


Figure S16. ^{13}C NMR Spectrum of **14**

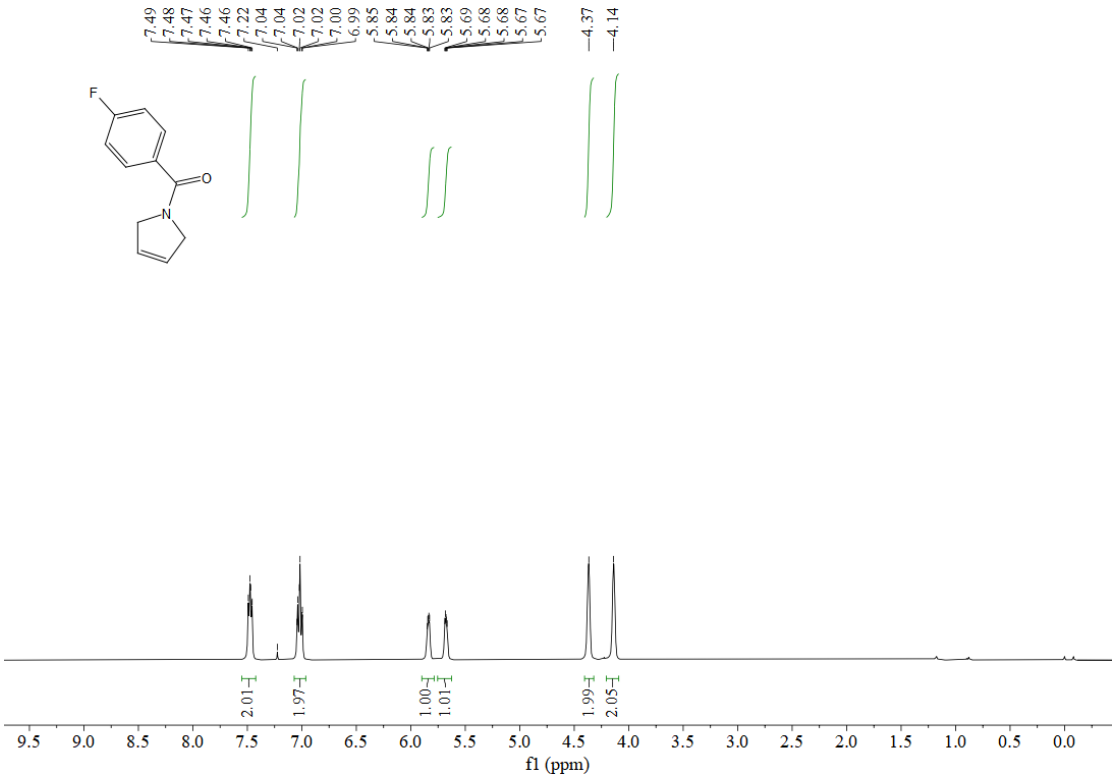


Figure S17. ^{1}H NMR Spectrum of **18**

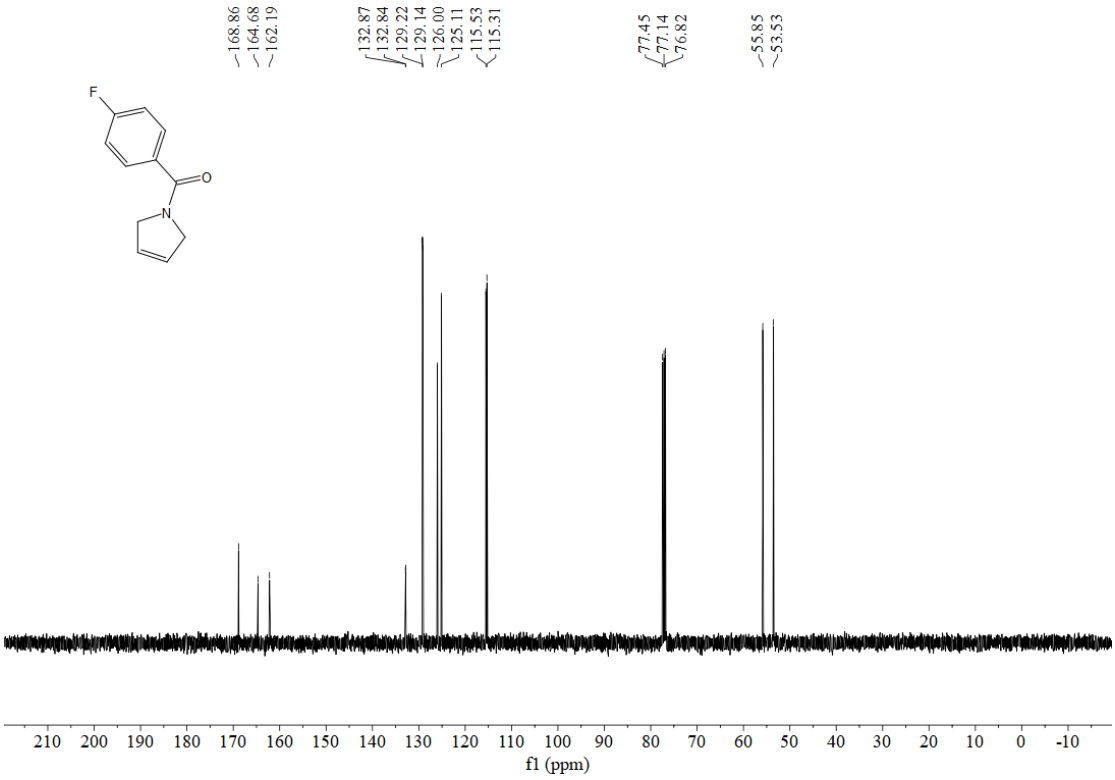


Figure S18. ^{13}C NMR Spectrum of **18**

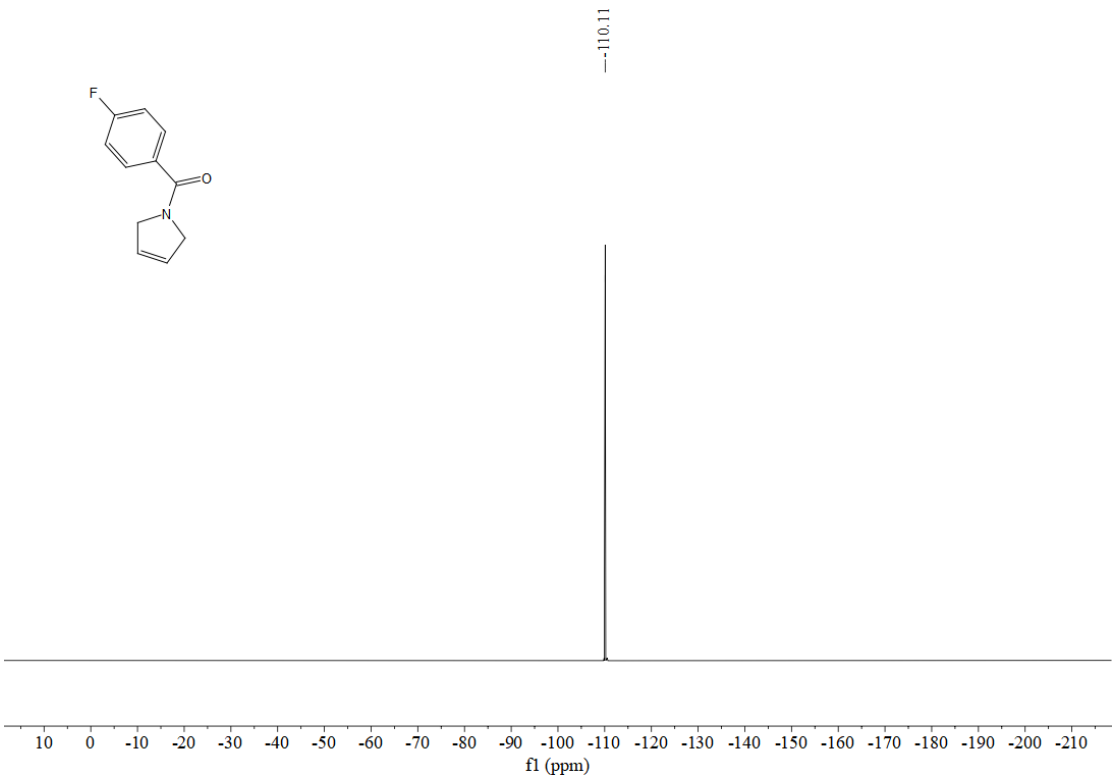


Figure S19. ^{19}F NMR Spectrum of **18**

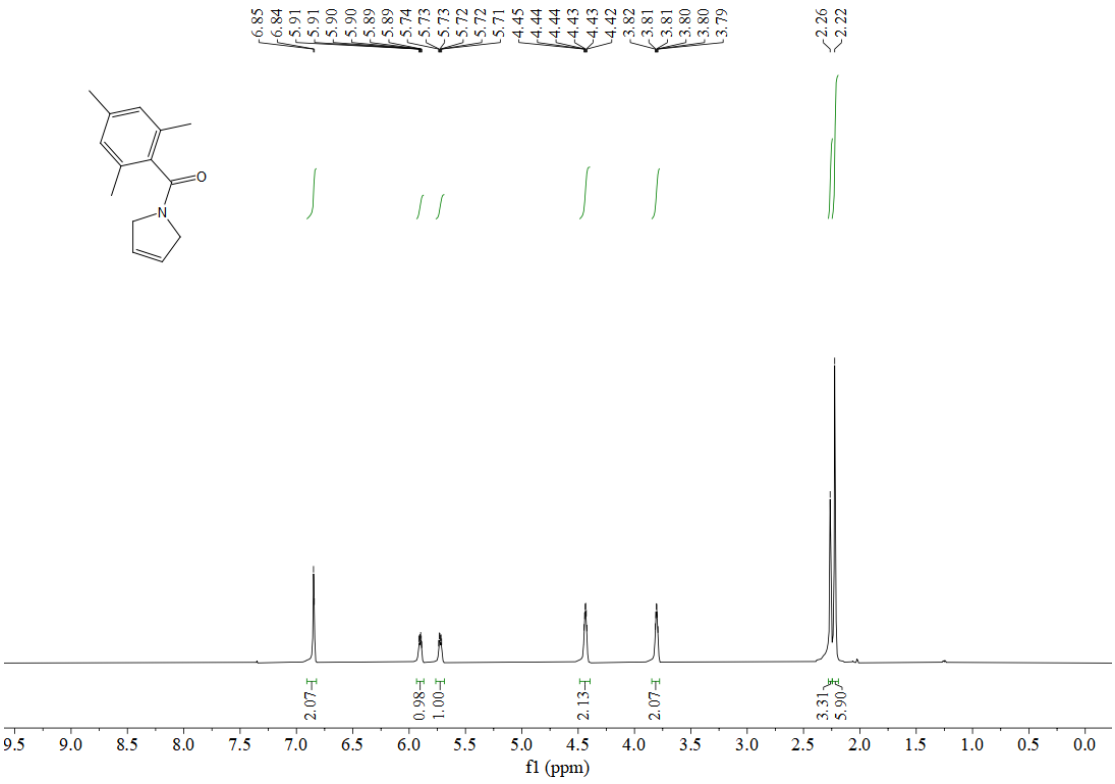


Figure S20. ^{1}H NMR Spectrum of **20**

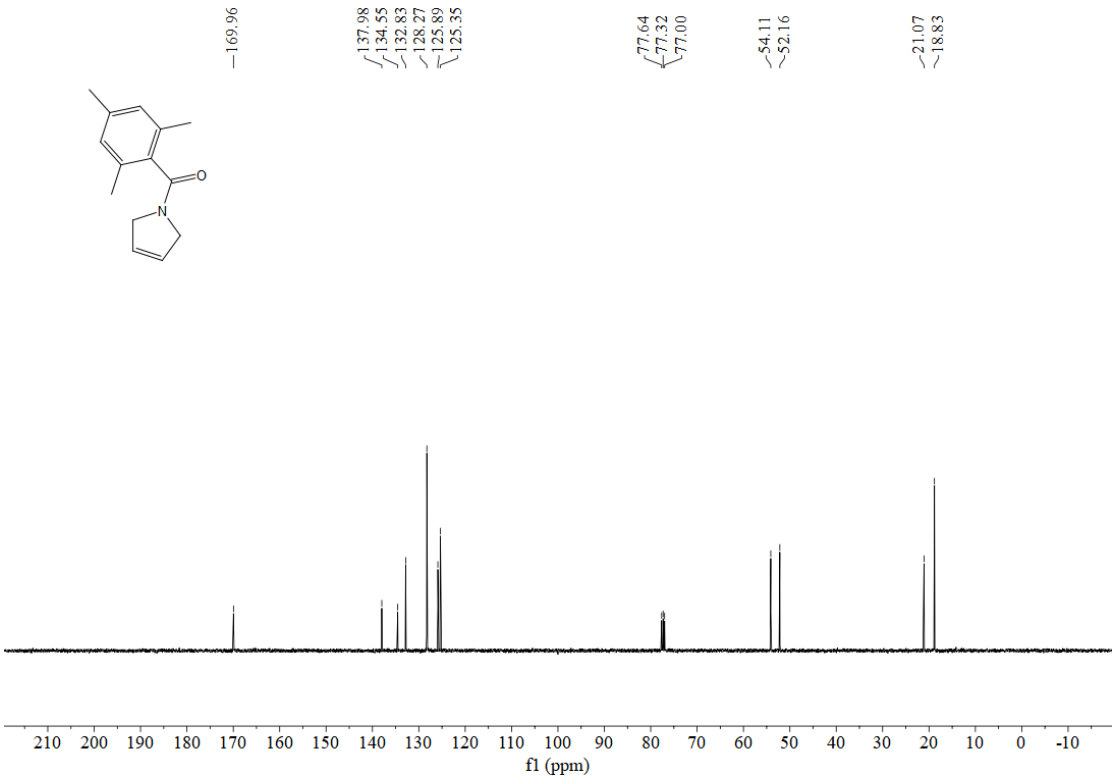


Figure S21. ^{13}C NMR Spectrum of **20**

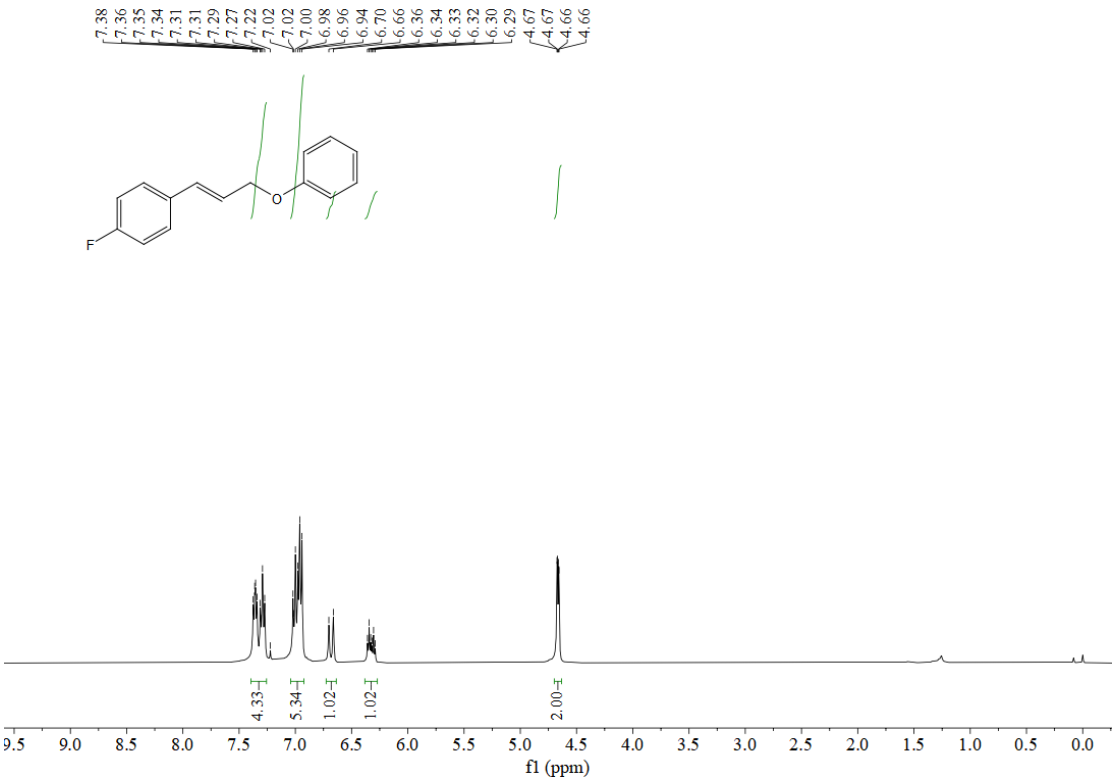


Figure S22. ^{1}H NMR Spectrum of **23**

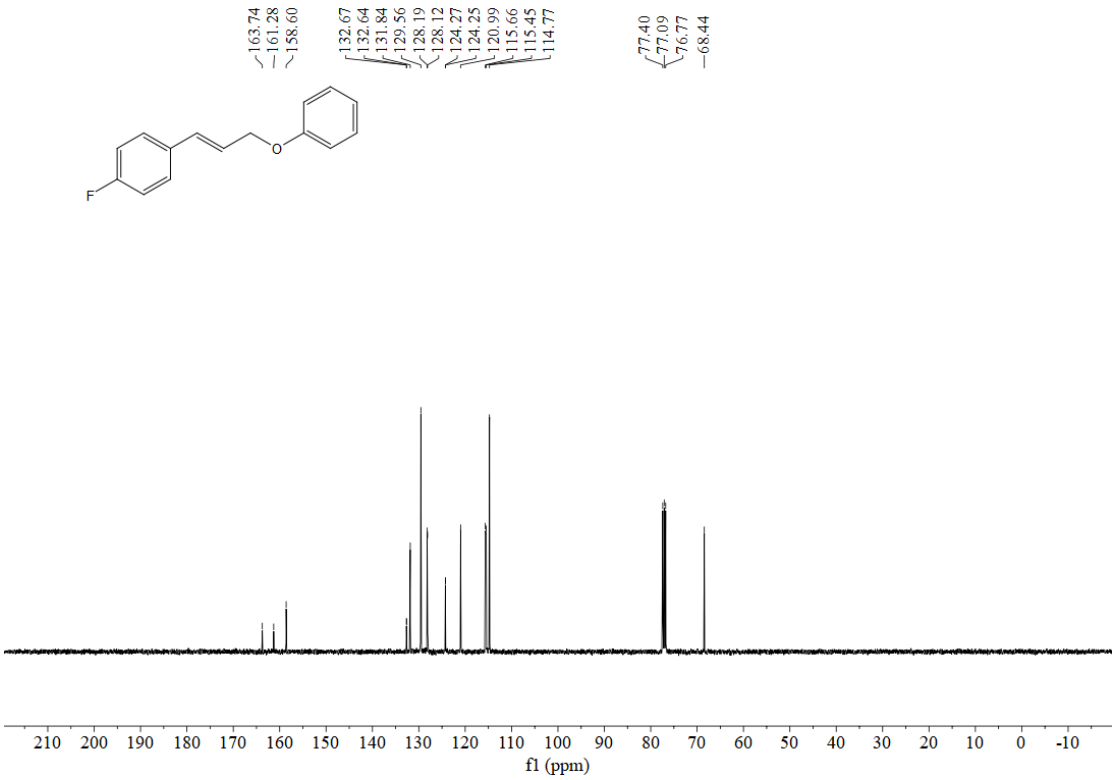


Figure S23. ^{13}C NMR Spectrum of **23**

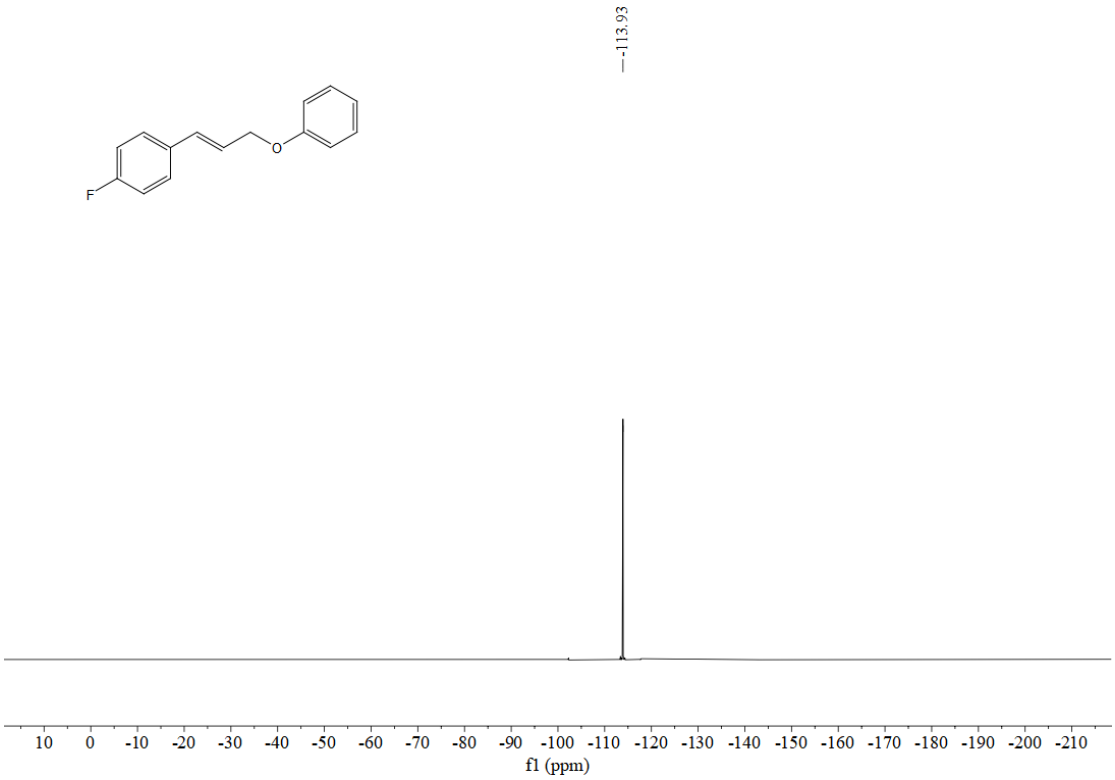


Figure S24. ^{19}F NMR Spectrum of **23**

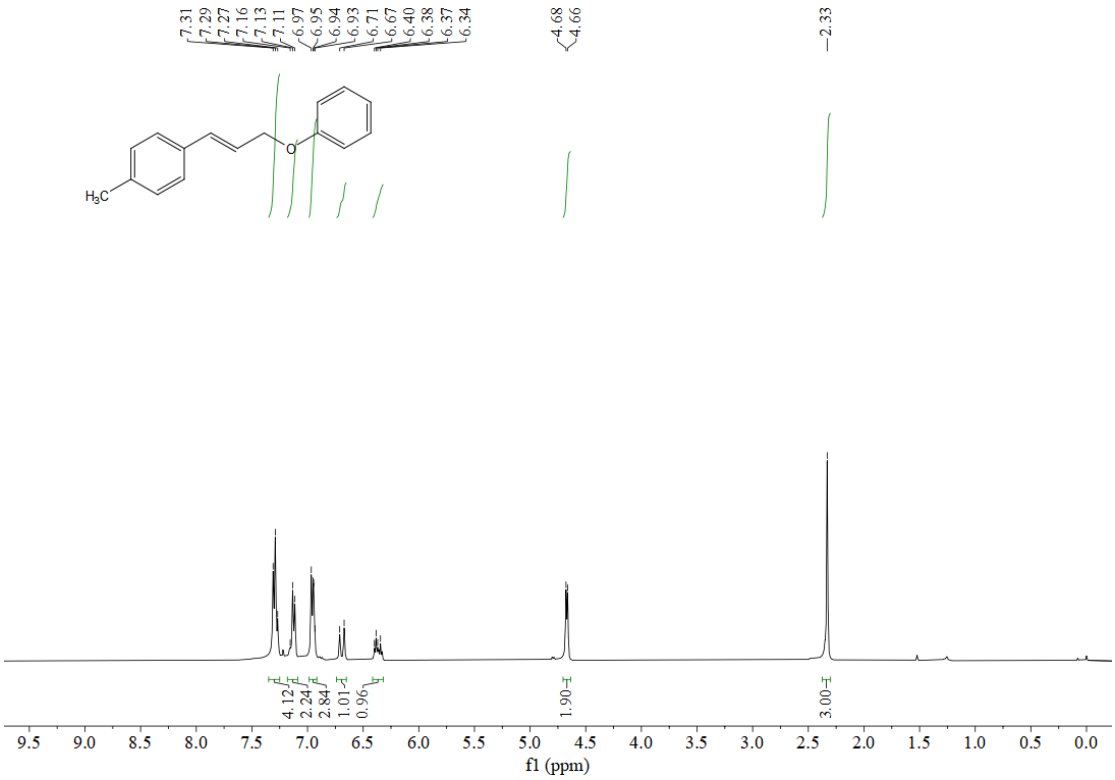


Figure S25. ^{1}H NMR Spectrum of **24**

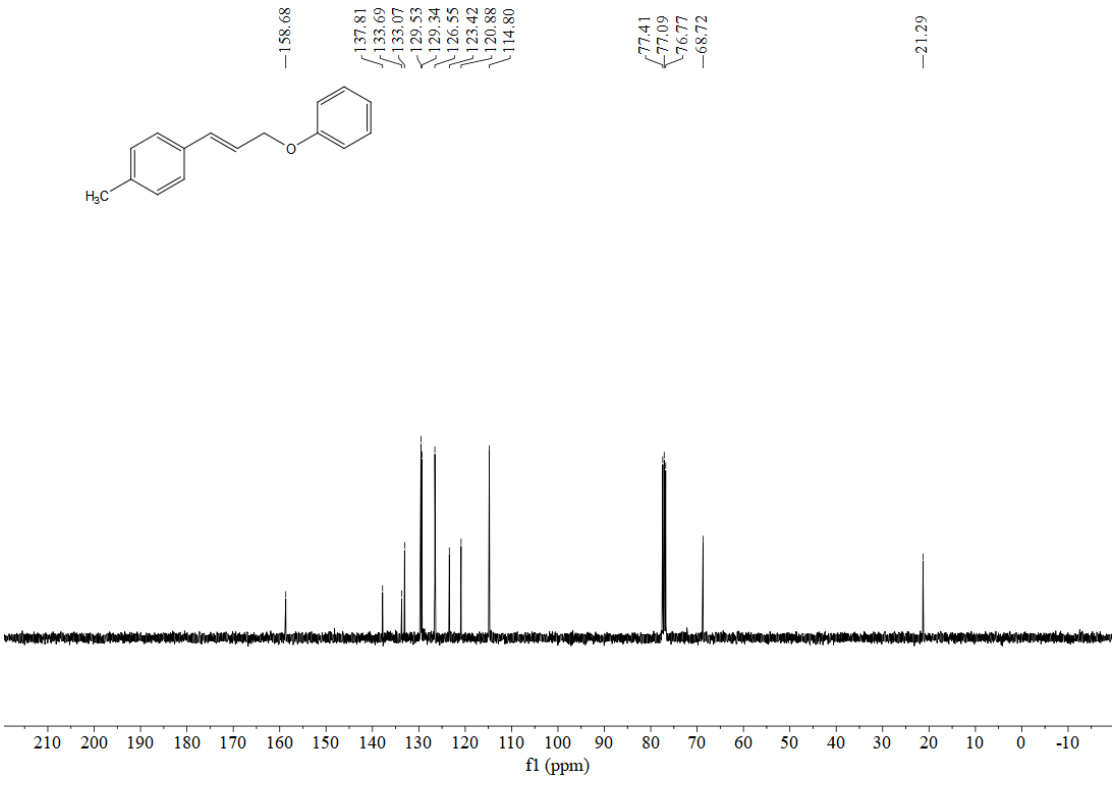


Figure S26. ^{13}C NMR Spectrum of **24**

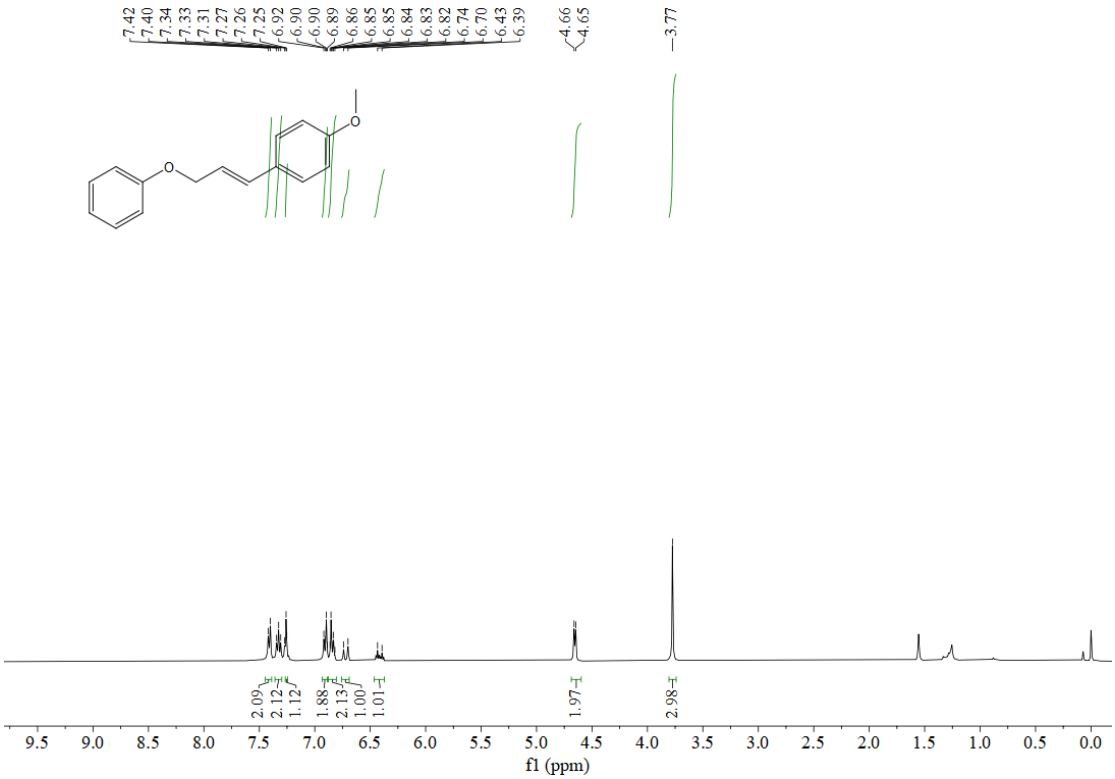


Figure S27. ^{1}H NMR Spectrum of **25**

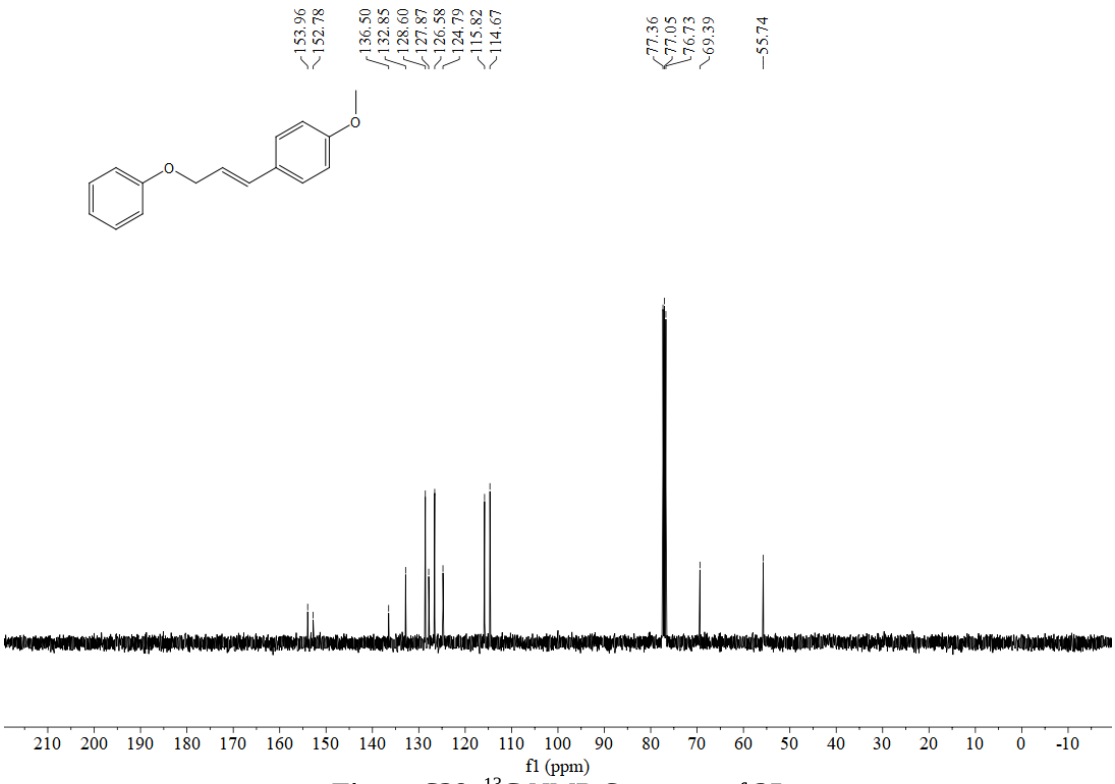


Figure S28. ^{13}C NMR Spectrum of **25**

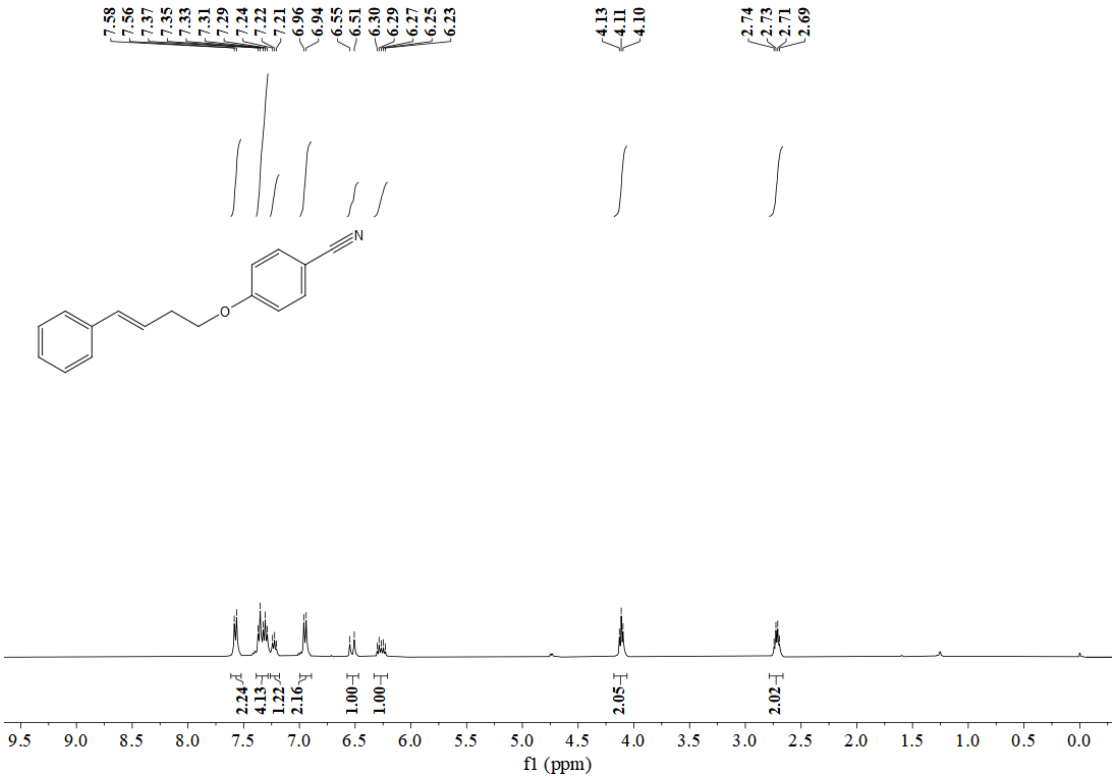


Figure S29. ^{1}H NMR Spectrum of **26**

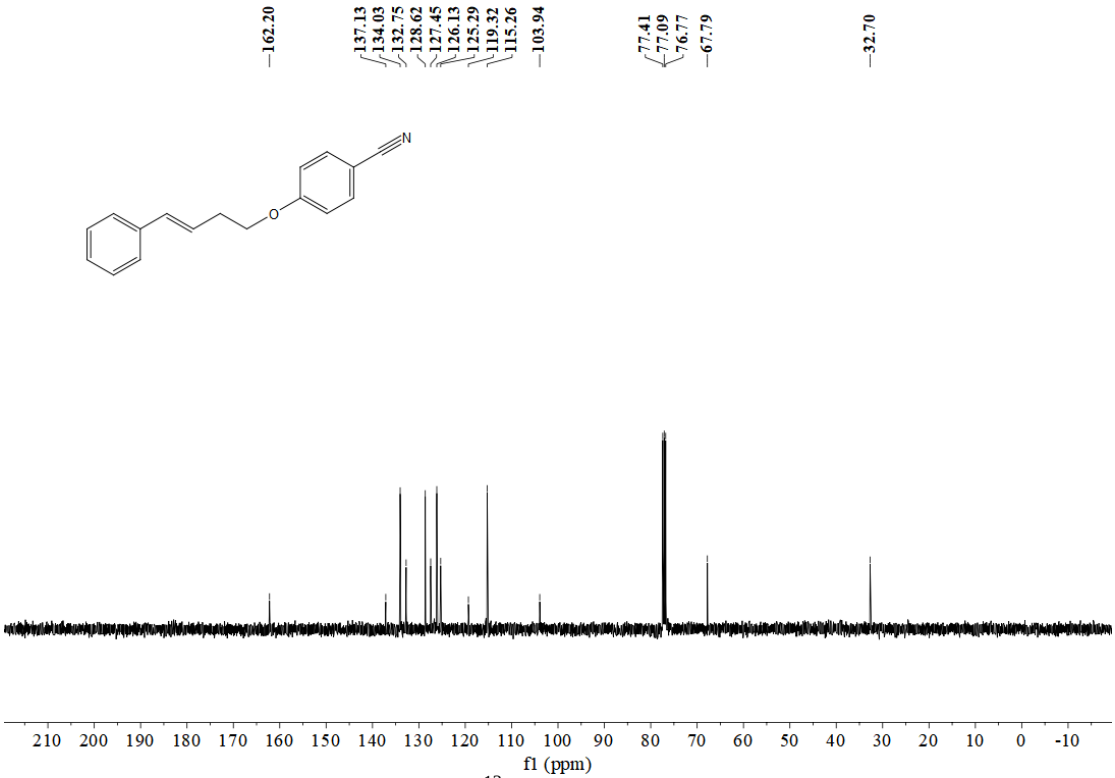


Figure S30. ^{13}C NMR Spectrum of **26**

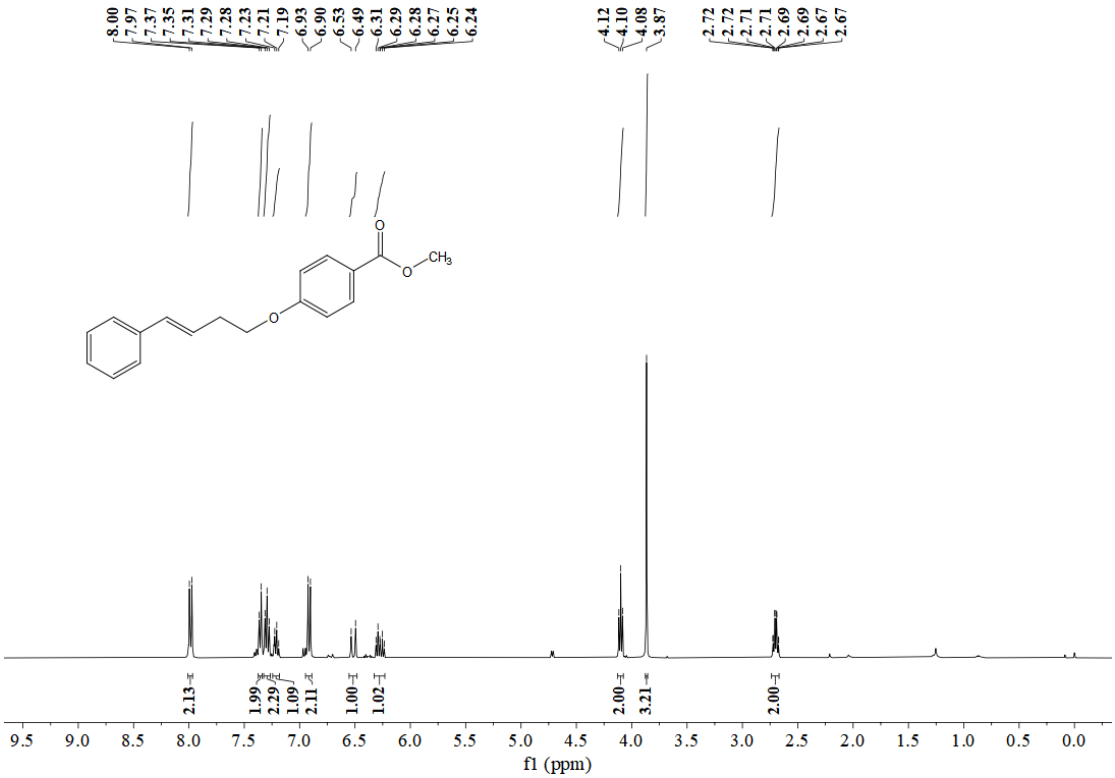


Figure S31. ^{1}H NMR Spectrum of **27**

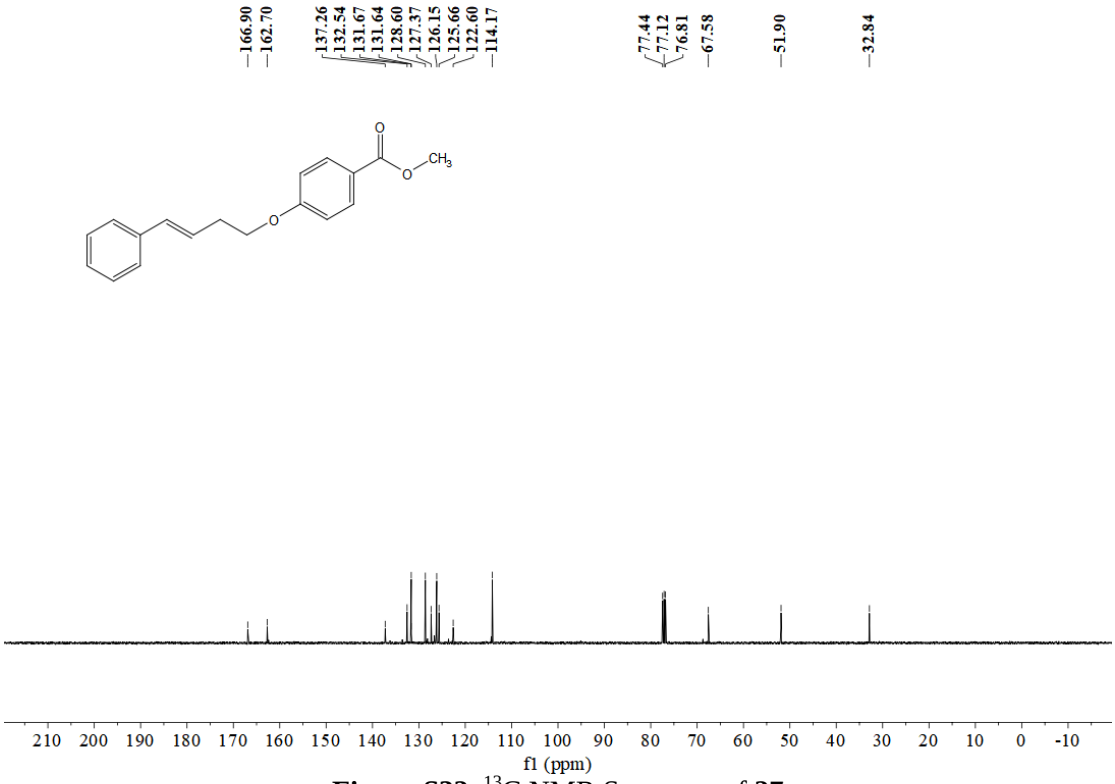


Figure S32. ^{13}C NMR Spectrum of **27**

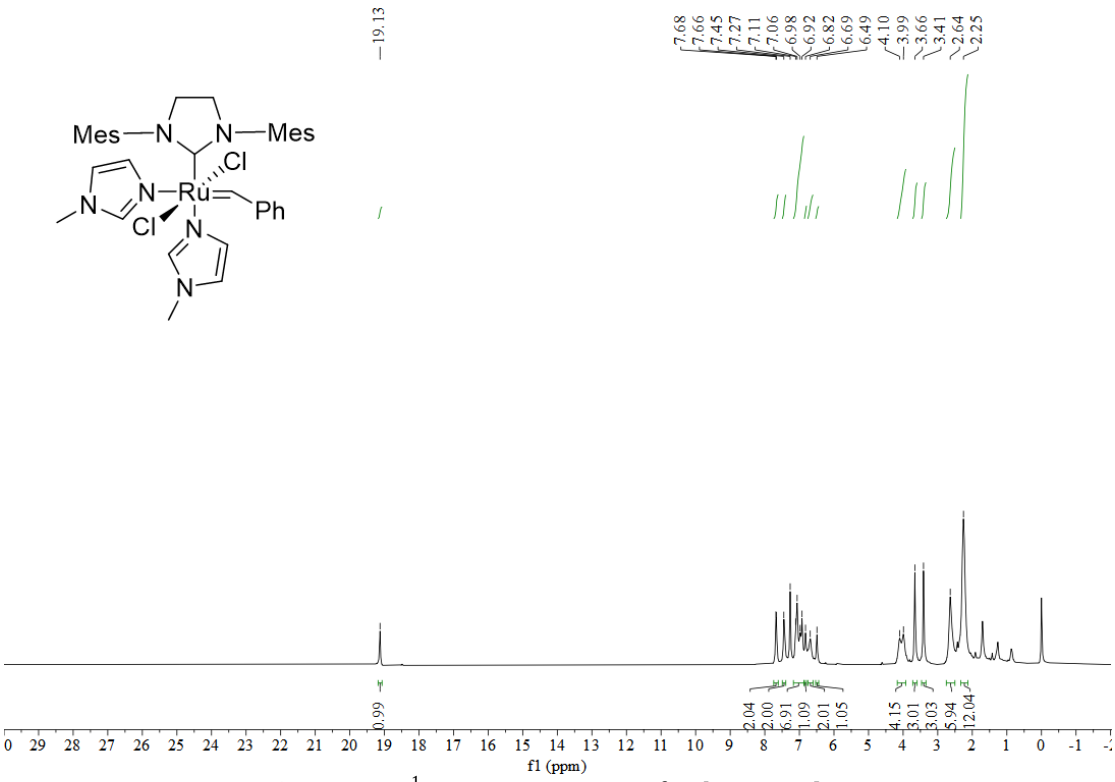


Figure S33. ^{1}H NMR Spectrum of Schanz catalyst

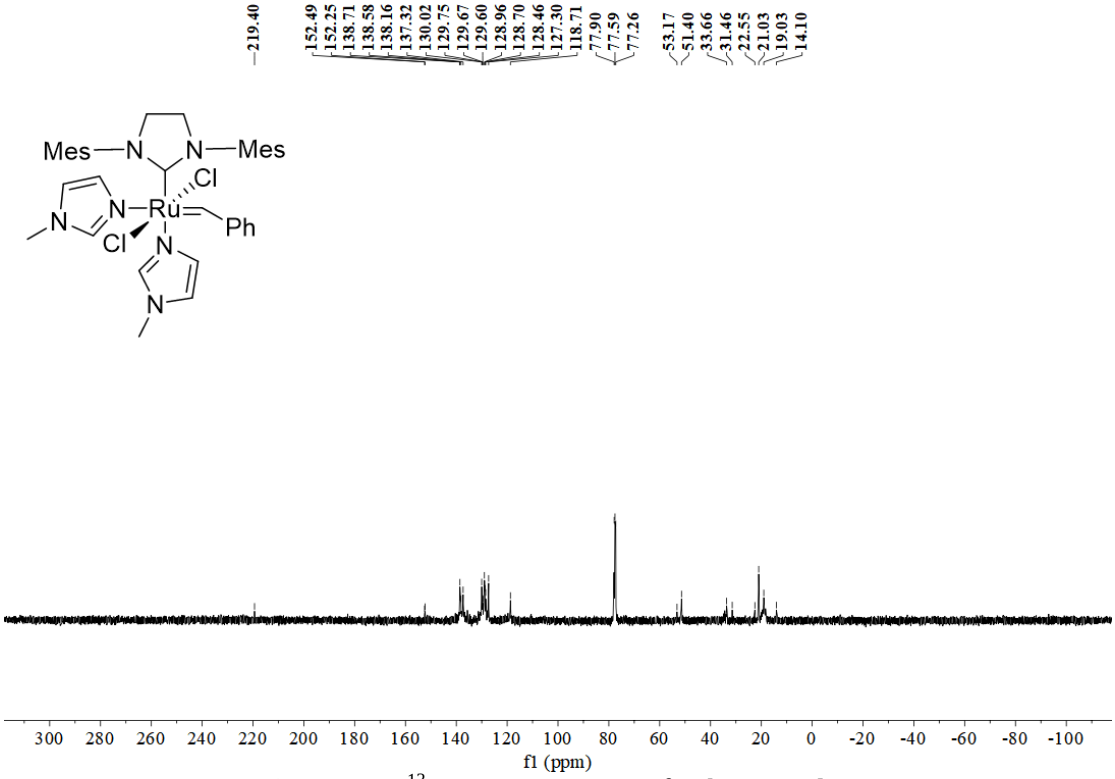


Figure S34. ^{13}C NMR Spectrum of Schanz catalyst