Room-temperature, Copper-Free Sonogashira Reactions Facilitated by Air-stable, Mono-ligated Precatalyst [DTBNpP] Pd(crotyl)Cl

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Supporting information

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1. Additional Tables

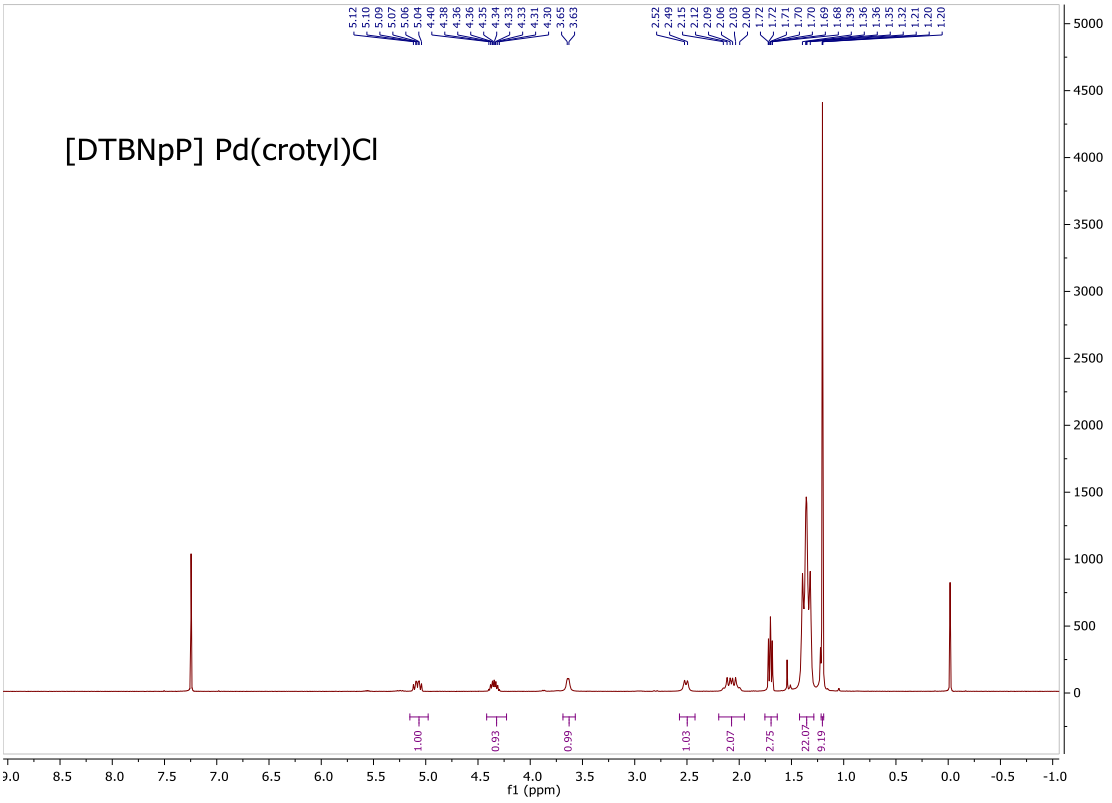
Table S1. Evaluation of Alternate and Sustainable Solvents with optimized base (TMP).[a]

entry	base	solvent	**3** (yield, %)[b]	
			t = 2 h	t = 18 h
1	TMP	THF	26	70
2	TMP	2-MeTHF	36	58
3	TMP	Sulfolane	43	70
4	TMP	EtOAc	40	62
5	TMP	ACN	77	100

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.8 mmol), **P2** (.0025 mmol, 5 mol%), TMP (1.0 mmol), solvent (2.5 mL), rt for 18 h with argon atmosphere. [b]Yield was determined by LC/MS with pyrene as internal standard.

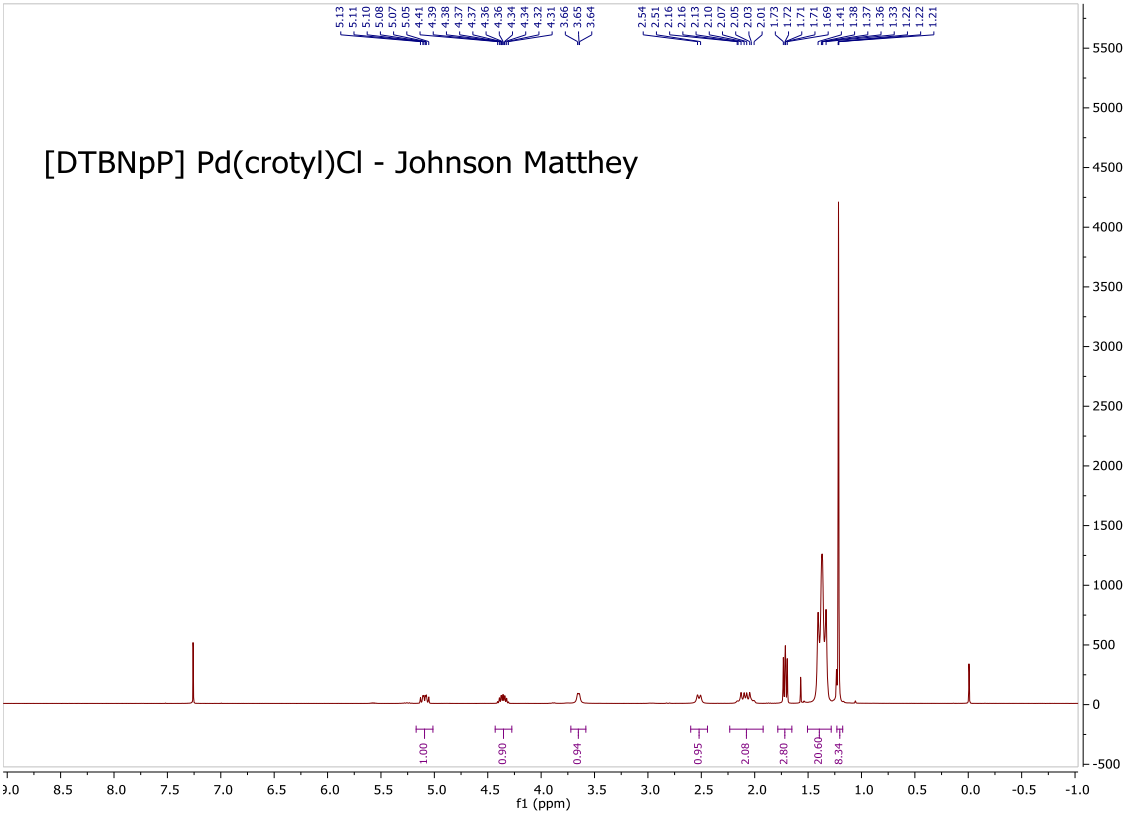
2. Catalyst Characterization Data

Figure S1: ^{1}H NMR for [DTBNpP] Pd(crotyl)Cl (**P2**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.08 (dt, *J* = 12.5, 8.9 Hz, 1H), 4.35 (ddt, *J* = 15.0, 13.2, 6.5 Hz, 1H), 3.64 (d, *J* = 6.5 Hz, 1H), 2.51 (d, *J* = 11.6 Hz, 1H), 2.06 (dt, *J* = 27.1, 13.7 Hz, 2H), 1.70 (td, *J* = 7.3, 1.2 Hz, 3H), 1.42 – 1.29 (m, 22H), 1.20 (d, *J* = 1.3 Hz, 9H).

Figure S2: ^{1}H NMR for [DTBNpP] Pd(crotyl)Cl sample from JM



^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.09 (dt, *J* = 12.7, 9.0 Hz, 1H), 4.43 – 4.27 (m, 1H), 3.72 – 3.58 (m, 1H), 2.52 (d, *J* = 11.5 Hz, 1H), 2.09 (qd, *J* = 16.4, 15.4, 6.9 Hz, 2H), 1.78 – 1.65 (m, 3H), 1.51 – 1.28 (m, 21H), 1.22 (d, *J* = 1.2 Hz, 8H).

[DTBNpP] Pd(η^3-1-*t*-Bu-indenyl)Cl (**P5**)

Synthetic procedure: Synthesis of **P5** follow a modified procedure of Hazari et. al as described in the text. To an oven-dried 100 mL round-bottom flask, di-*tert*-butylneopentylphosphine (10 wt% in hexanes) (5.08 mL, 1.60 mmol) was added into Chloro(1-t-butylindenyl)palladium(II) dimer (500 mg, 0.80 mmol, 1.00 equiv) and THF (11 mL). The flask was capped and purged with argon for 5 minutes. The solution was stirred for 2 h at room temperature. The resulting product was filtered, washed with pentane, and dried under vacuum to afford **P5** (red solid, 330 mg, 78%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 2.9 Hz, 1H), 5.74 (d, *J* = 2.9 Hz, 1H), 2.29 (dd, *J* = 14.6, 11.7 Hz, 1H), 1.81 (t, *J* = 14.6 Hz, 1H), 1.48 (s, 9H), 1.35 (d, *J* = 13.3 Hz, 9H), 1.18 (d, *J* = 13.0 Hz, 9H), 1.13 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 139.88, 138.60, 138.55, 126.25, 125.57, 125.34,

124.73, 120.26, 119.34, 108.51, 108.45, 67.34, 67.31, 37.81, 37.68, 35.09, 34.97, 34.90, 34.86, 34.04, 33.94, 33.10, 33.03, 31.05, 31.03, 30.68, 30.64, 30.35, 30.30, 29.61, 29.56, 26.98, 12.76. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 70.86. **HRMS** (ESI+): Expected 493.2210 $[M\text{-}Cl]^+$ ($C_{26}H_{44}PPd$). Observed 493.2242.

Figure S3: ^{1}H NMR

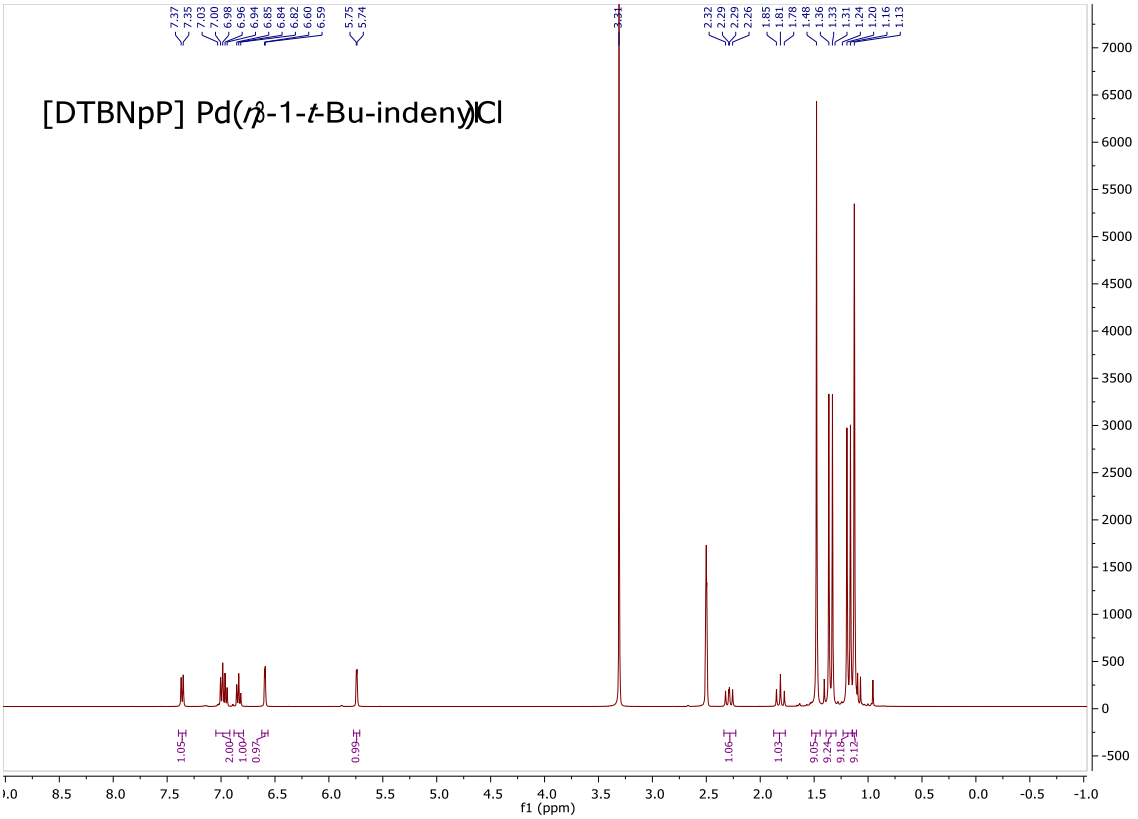


Figure S4: ^{13}C NMR

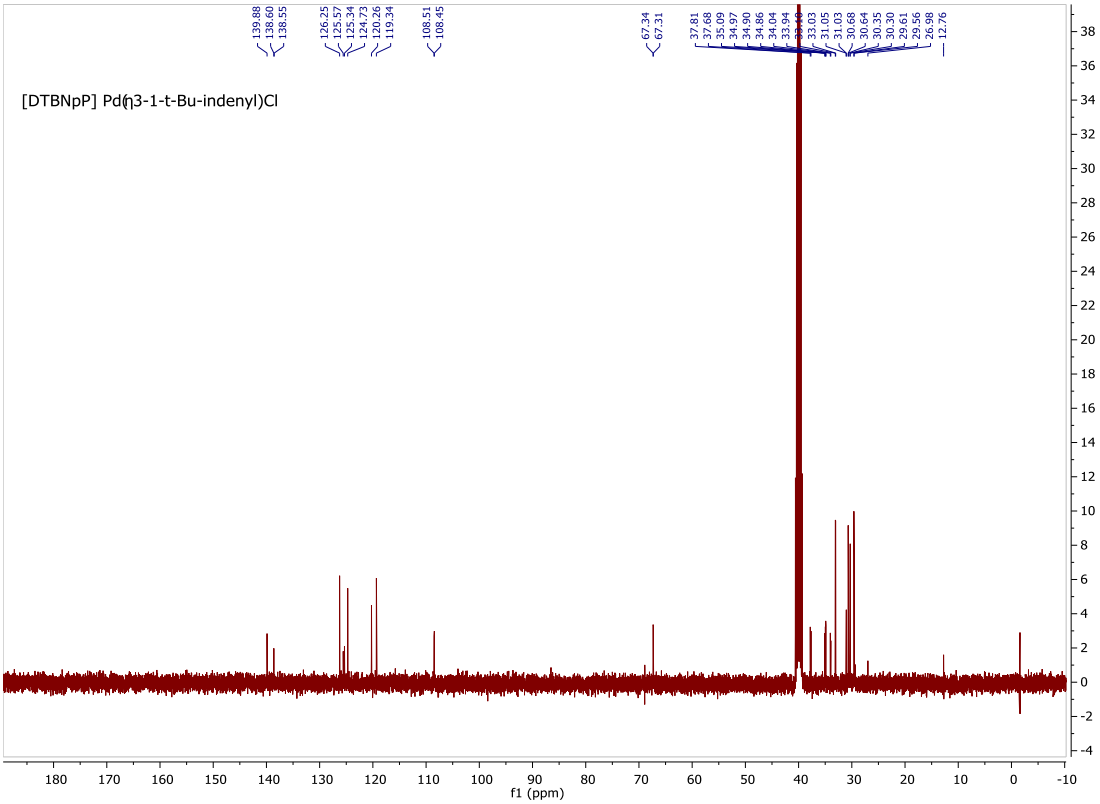
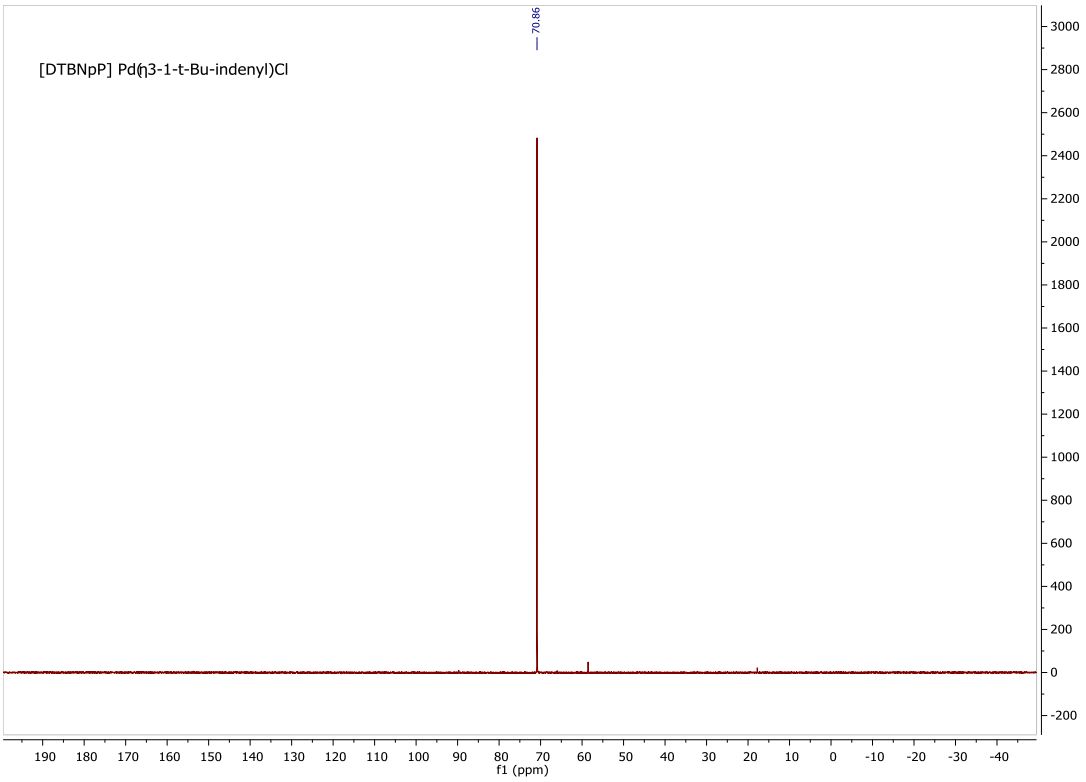


Figure S5: ^{19}F NMR



3. Compound Characterization Data

I. Spectral Data

Figure S6: ^{1}H NMR

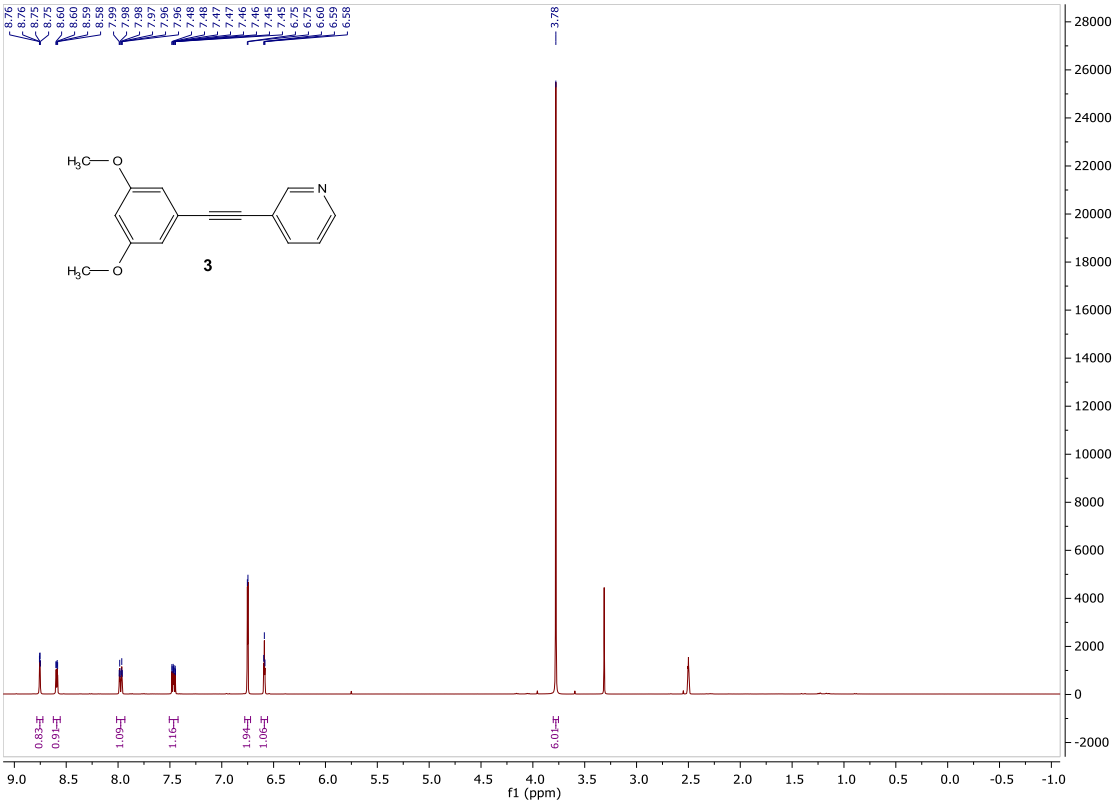


Figure S7: ^{13}C NMR

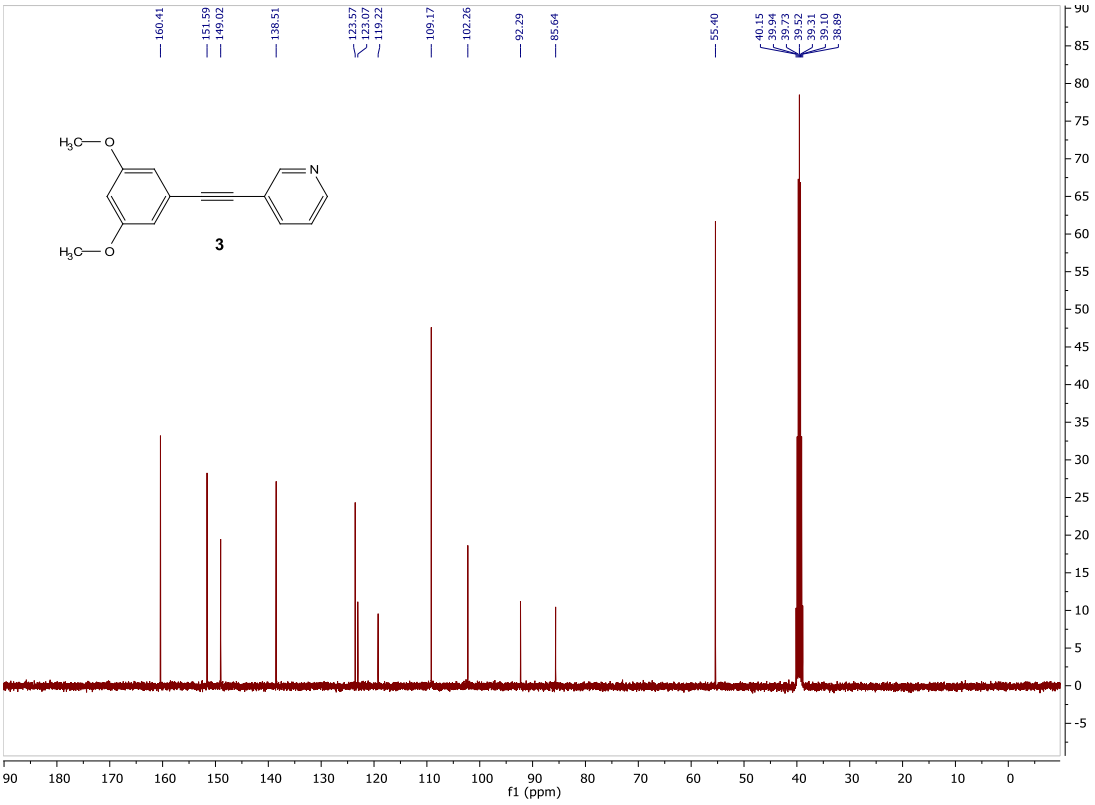


Figure S8: ^{1}H NMR

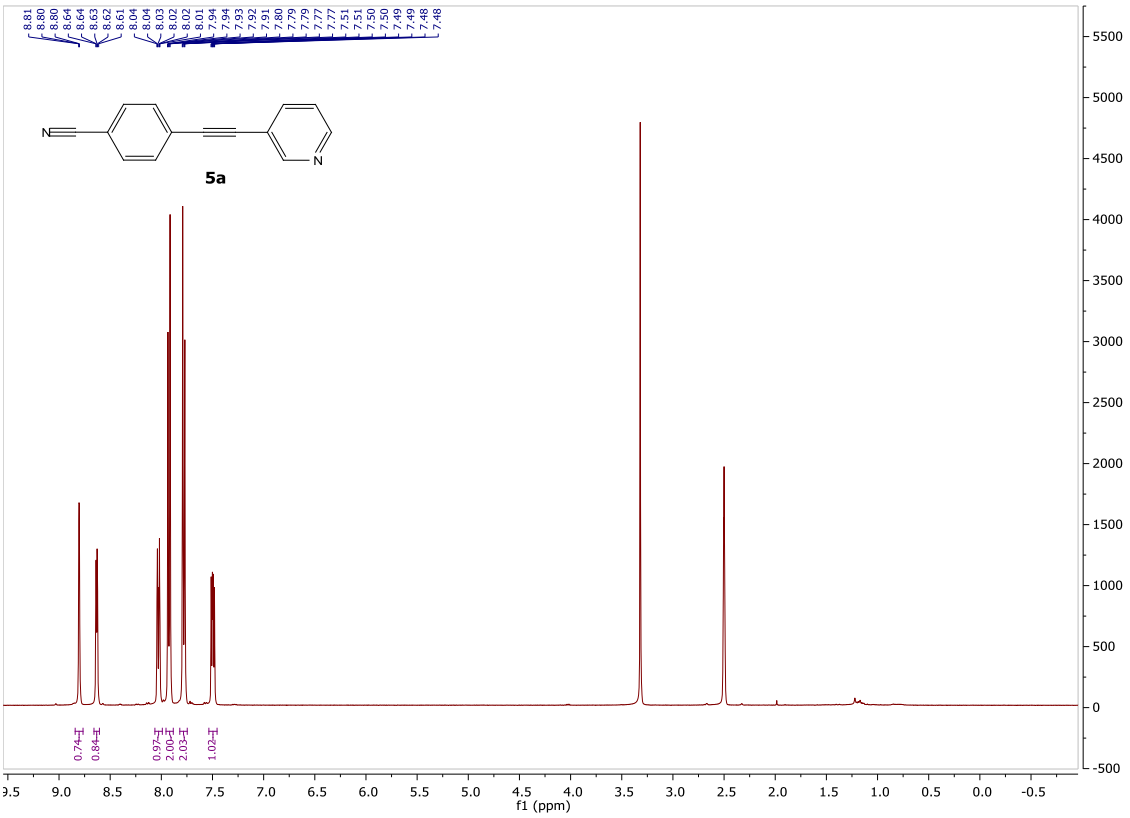


Figure S9: ^{13}**C** NMR

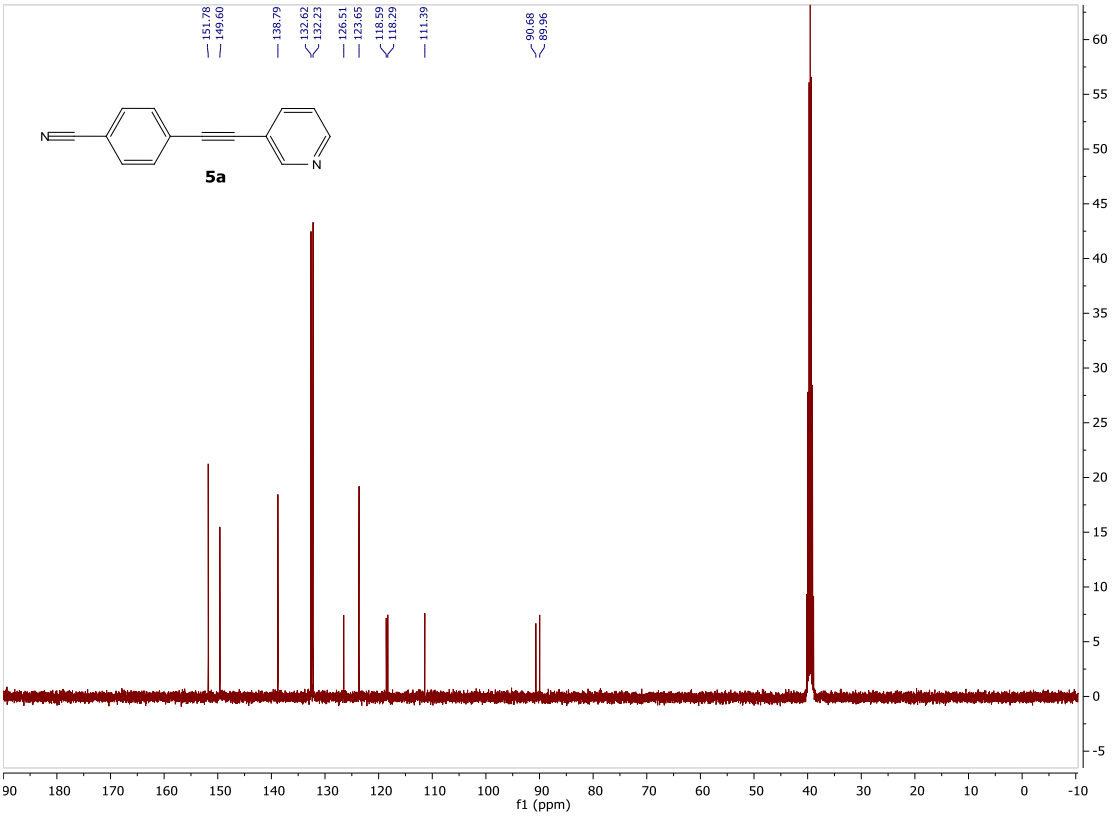


Figure S10: 1H NMR

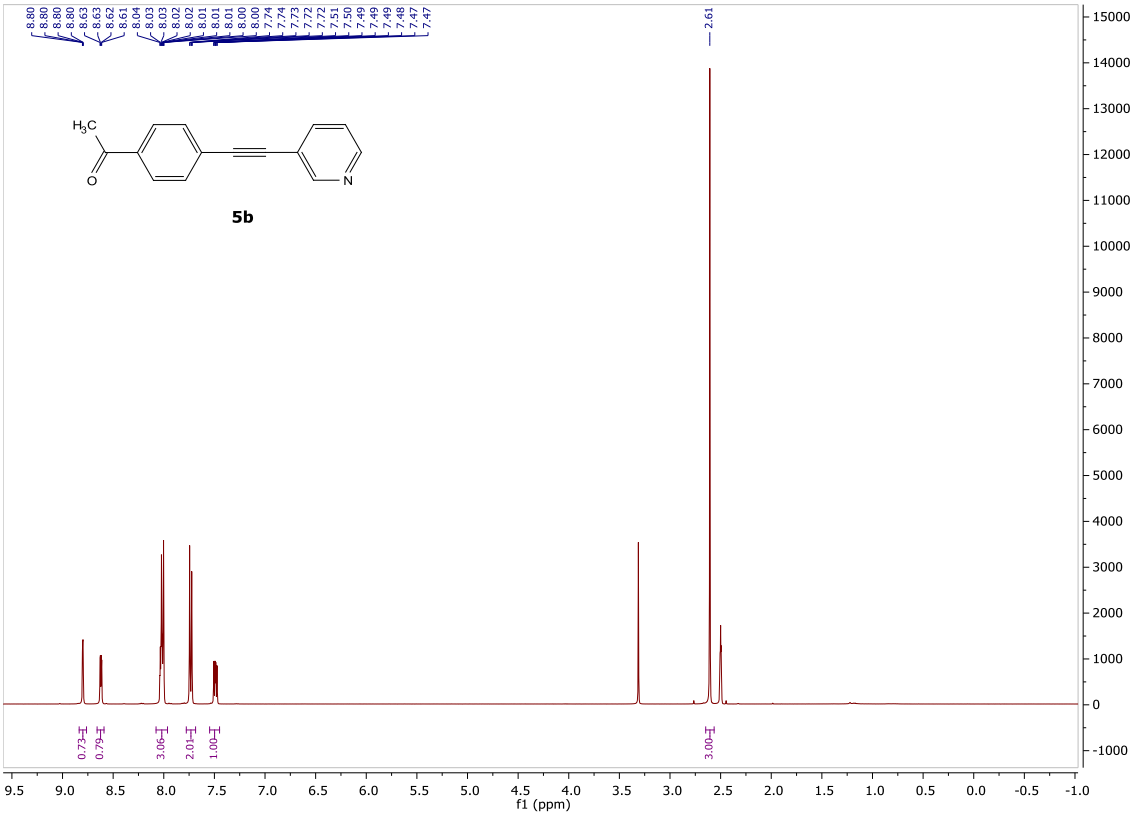


Figure S11: 13C NMR

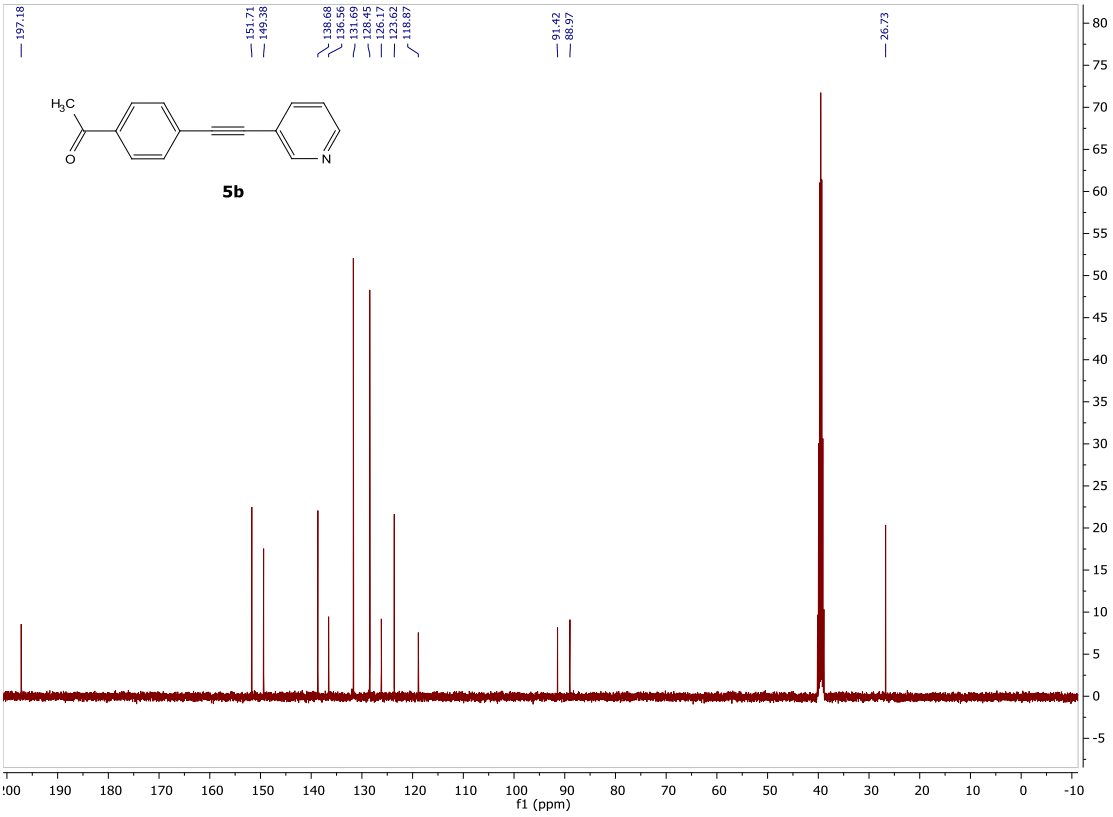


Figure S12: ^{1}H NMR

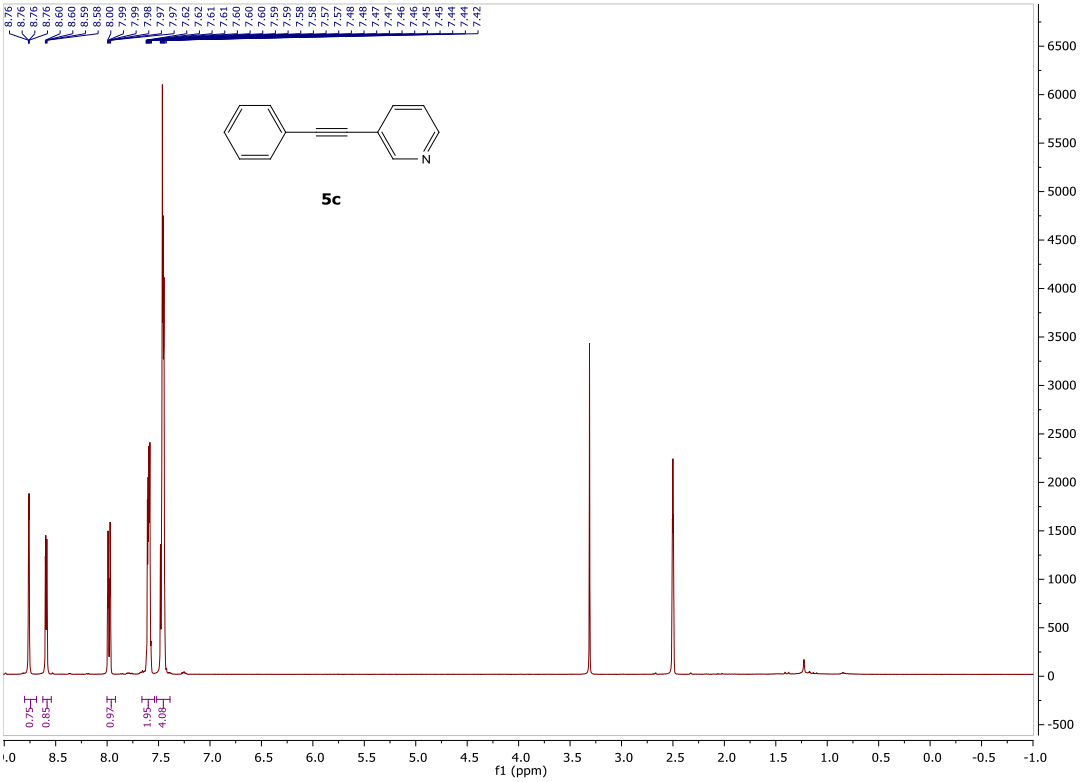


Figure S13: ^{13}C NMR

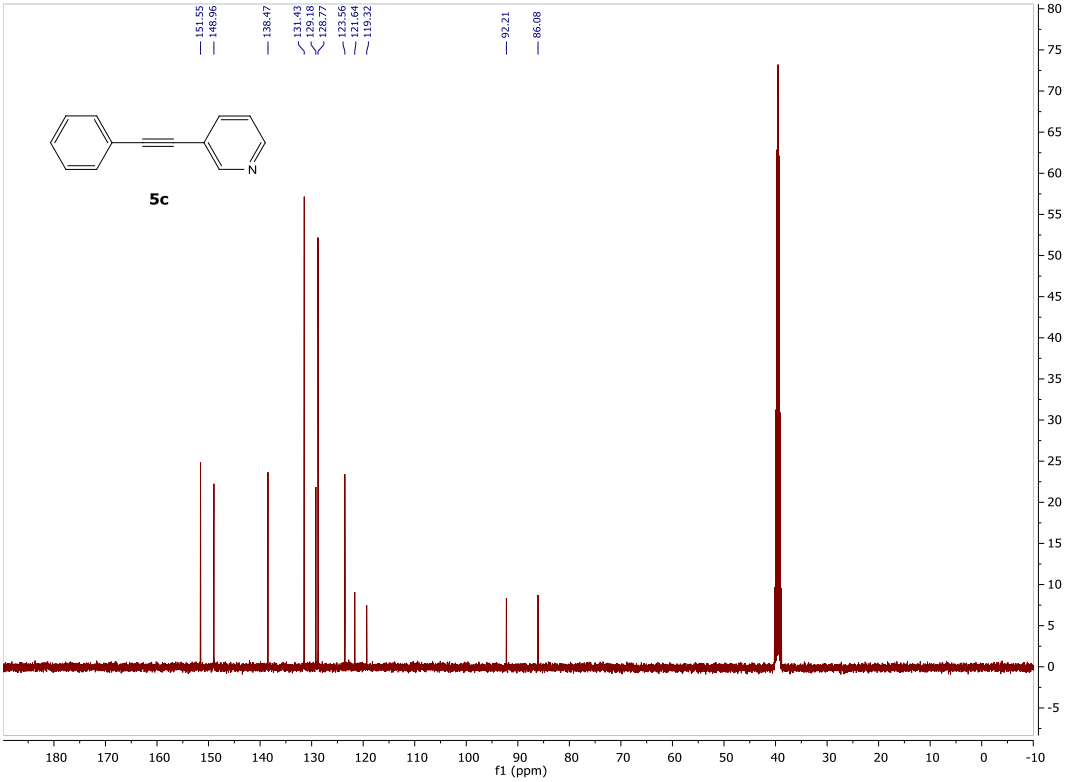


Figure S14: ^{1}H NMR

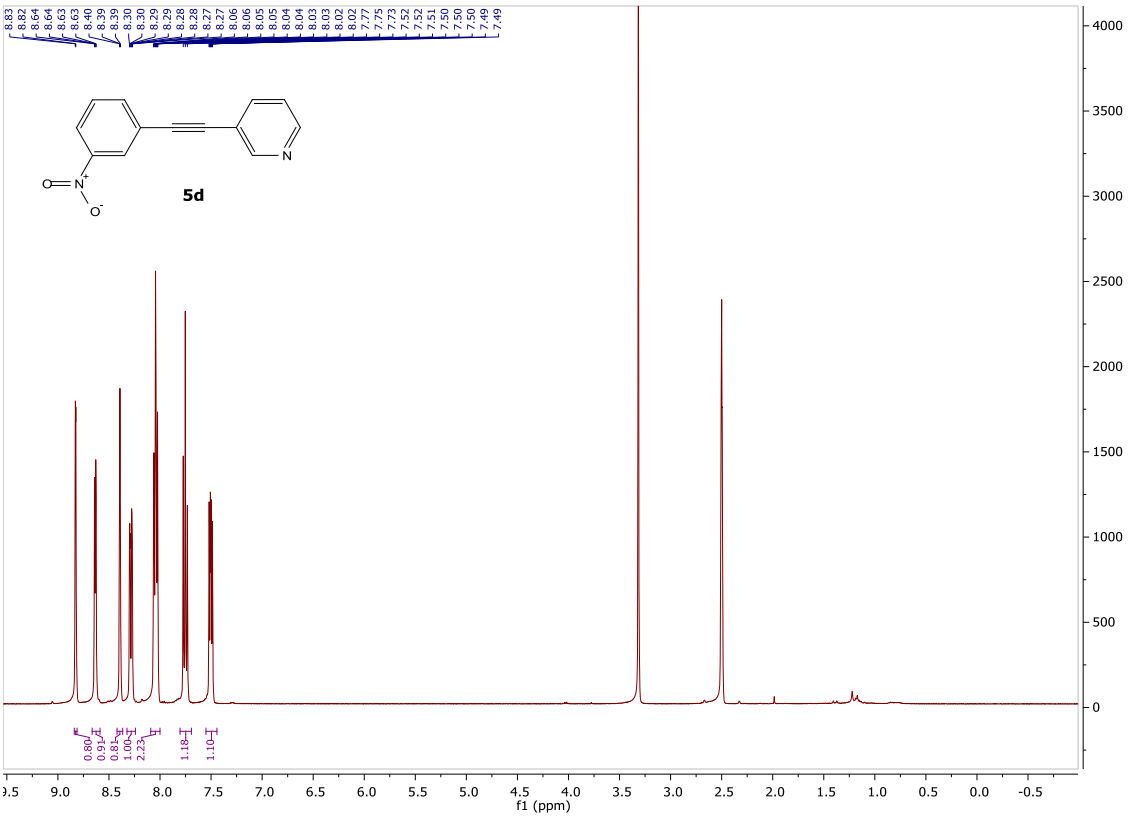


Figure S15: ^{13}C NMR

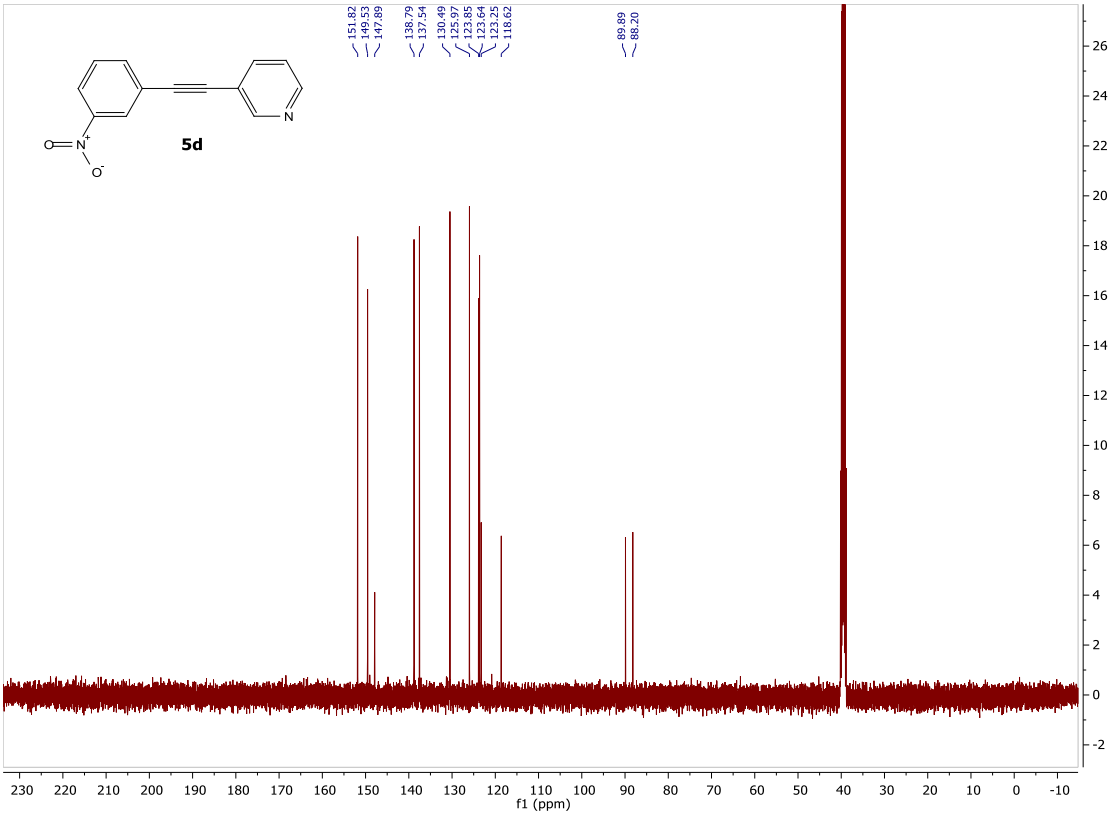


Figure S16: ^{1}H NMR

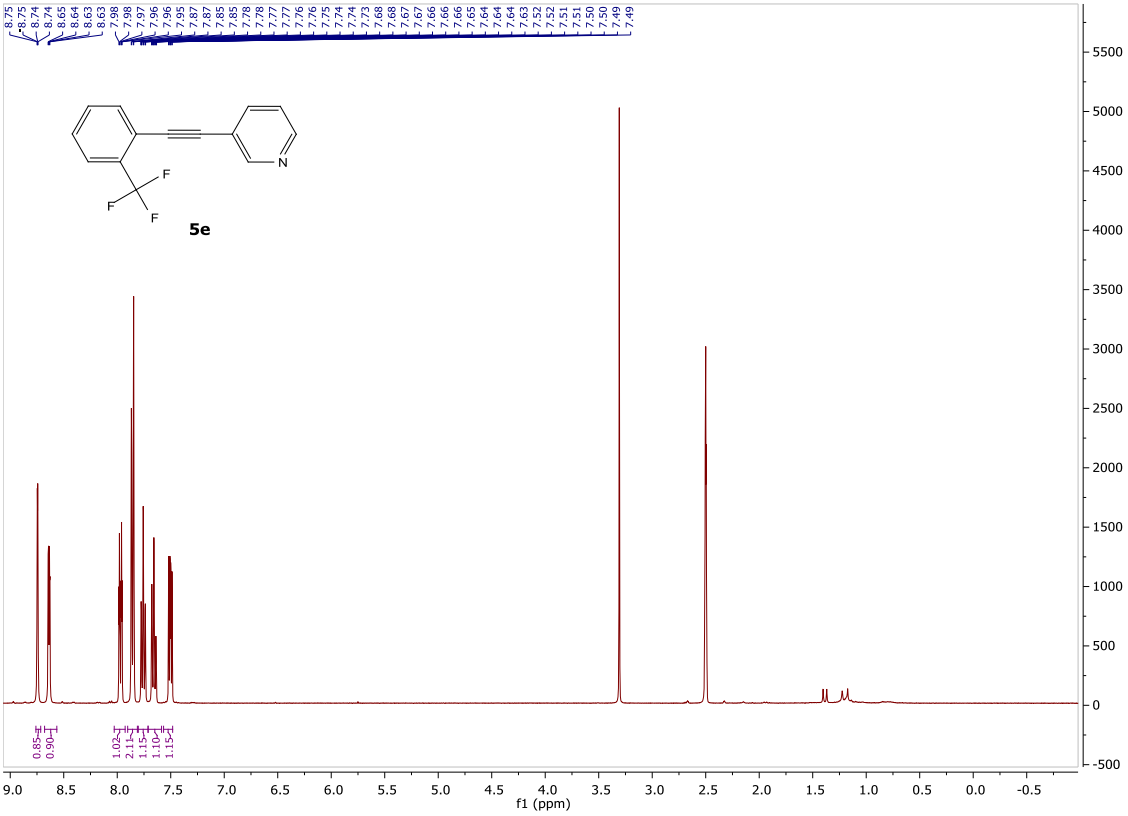


Figure S17: ^{13}C NMR

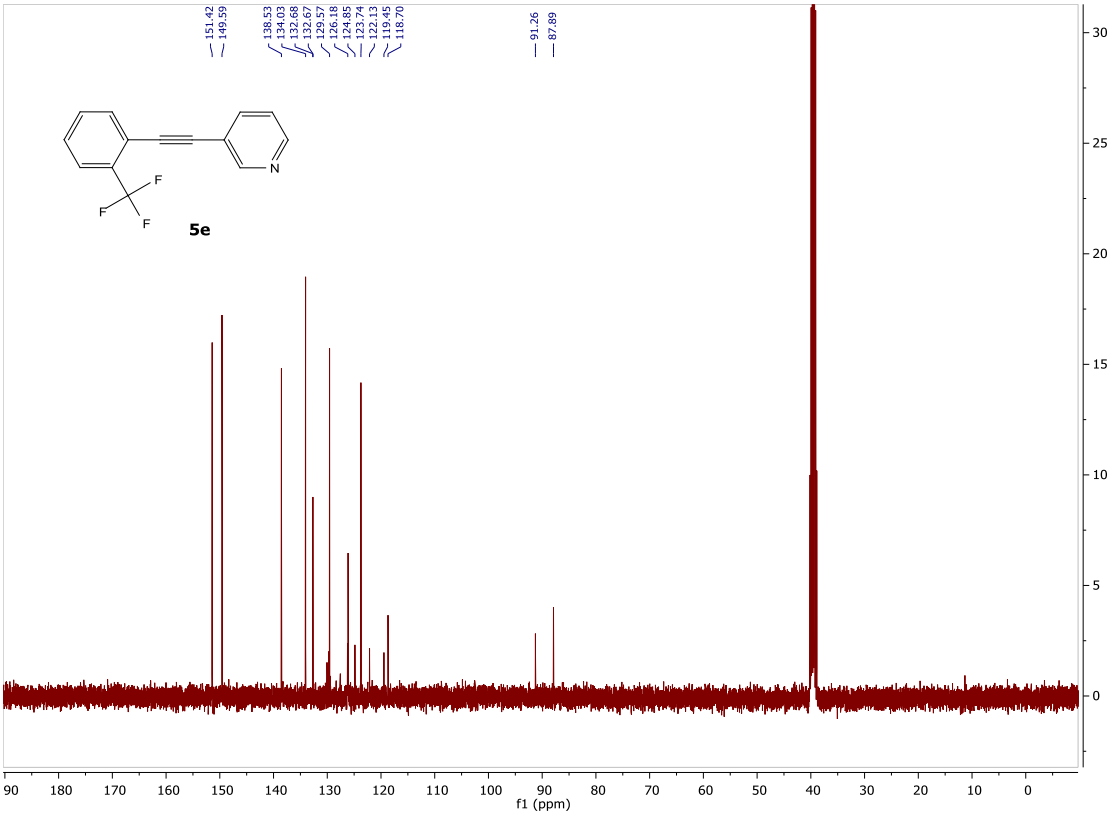


Figure S18: ^{1}H NMR

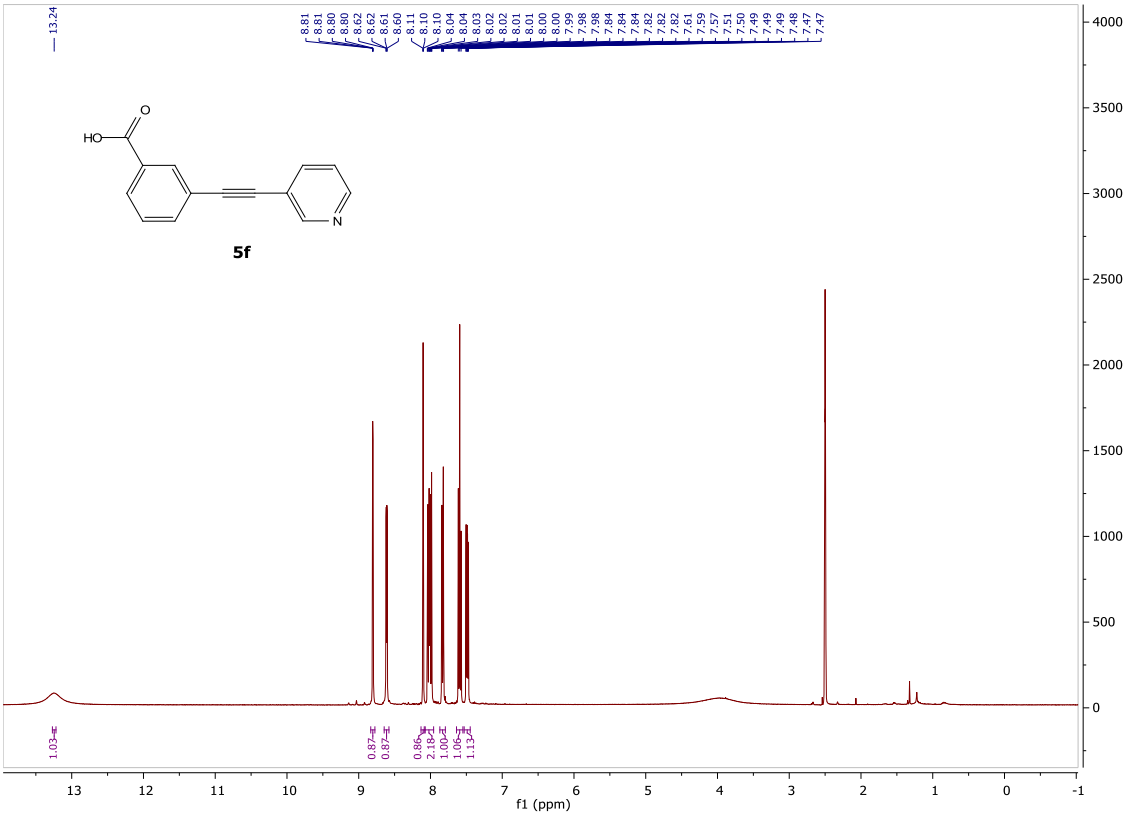


Figure S19: ^{13}C NMR

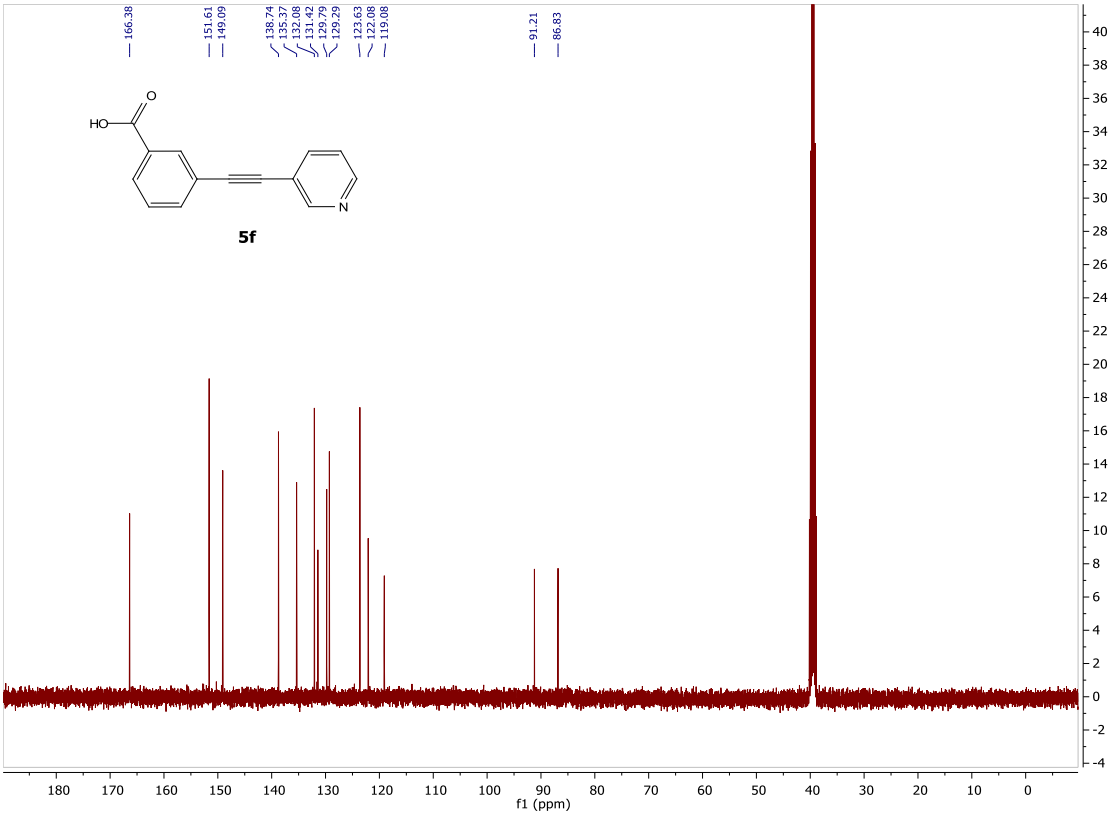


Figure S20: ^{1}H NMR

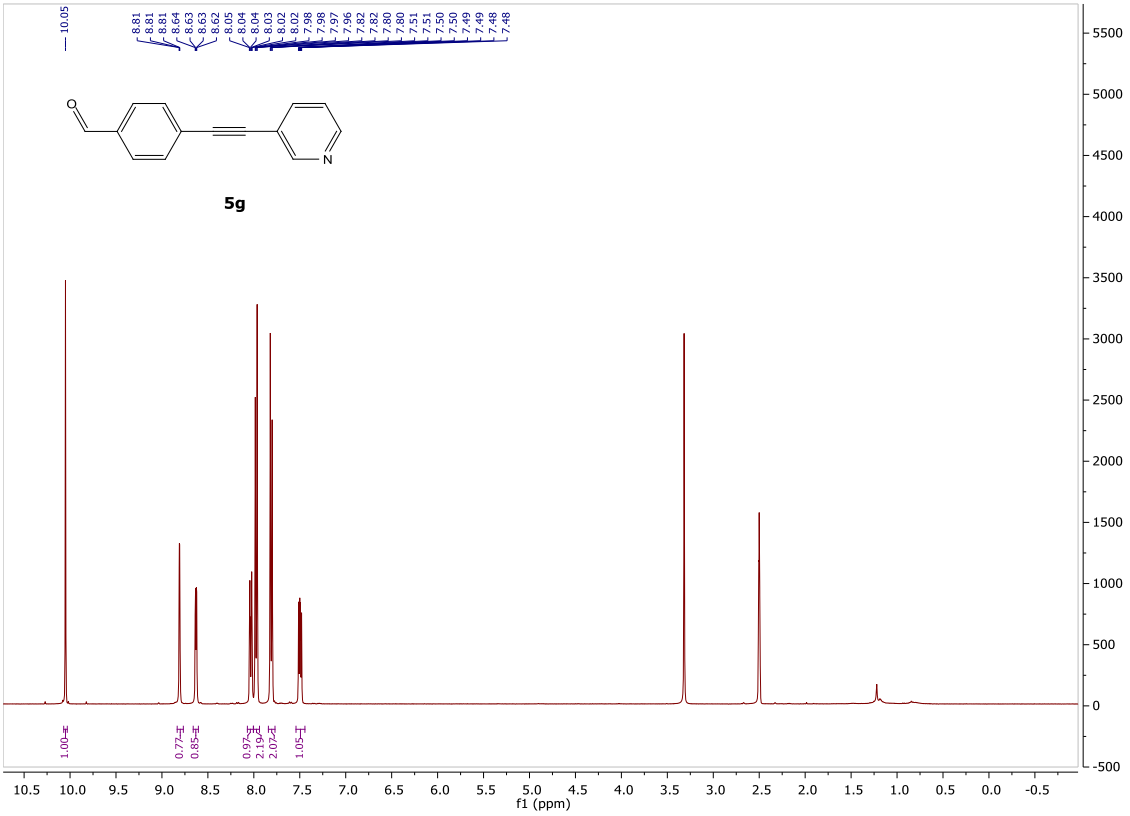


Figure S21: ^{13}C NMR

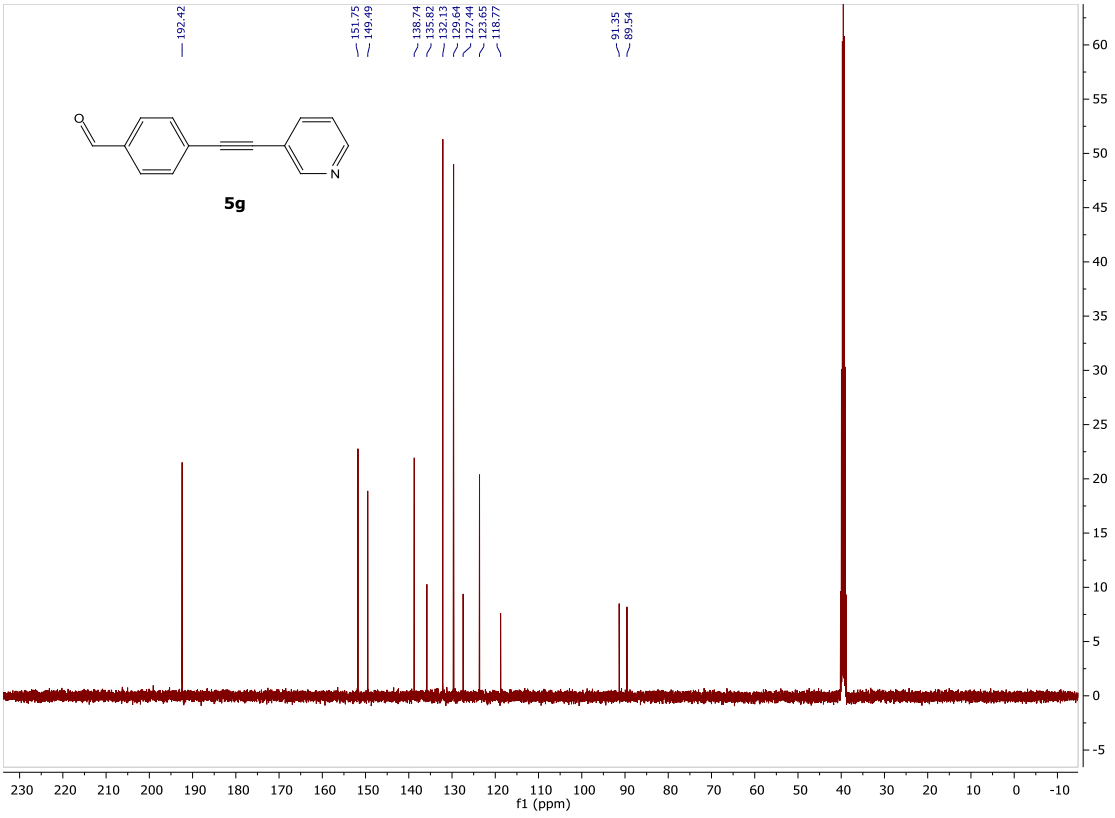


Figure S22: ^{1}H NMR

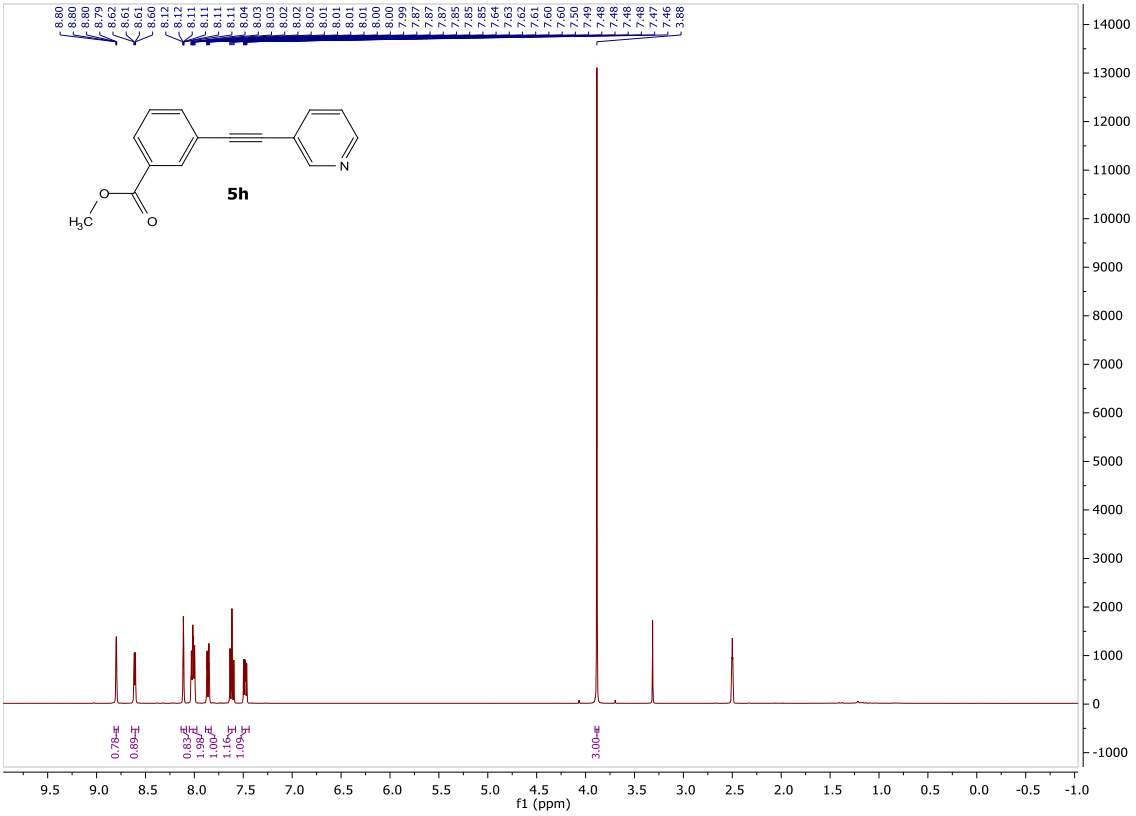


Figure S23: ^{13}C NMR

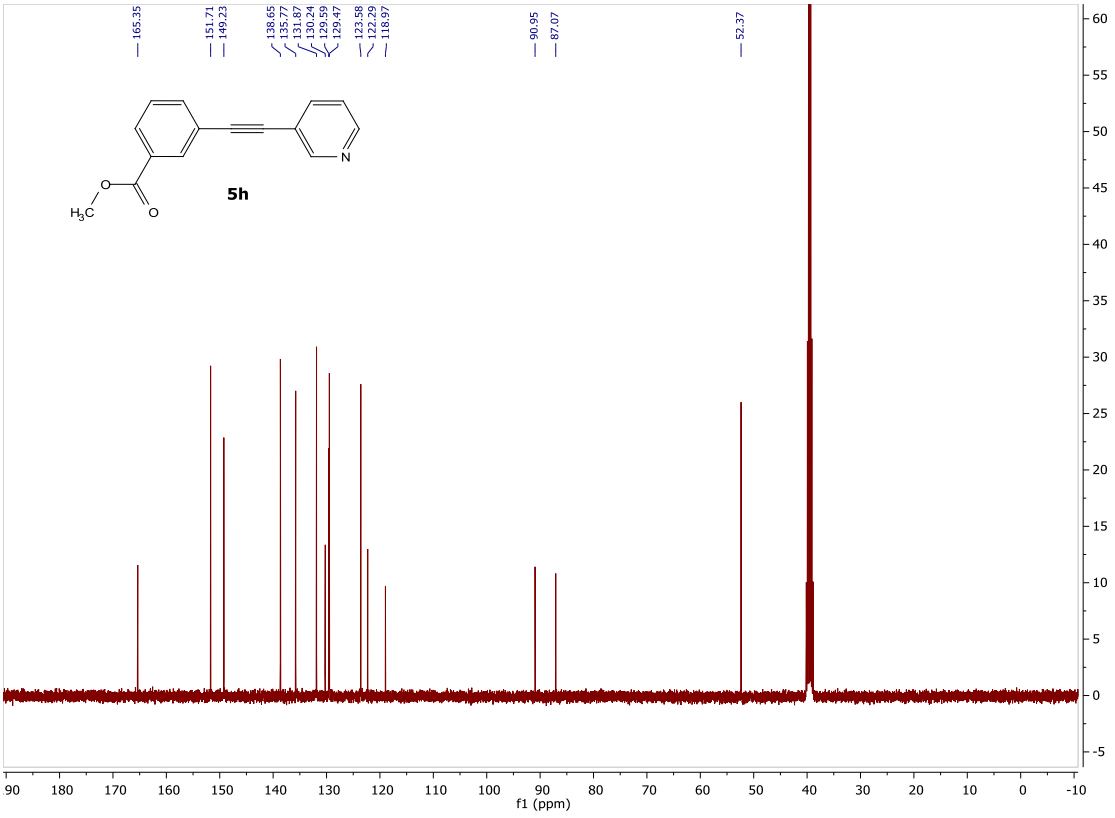


Figure S24: ^{1}H NMR

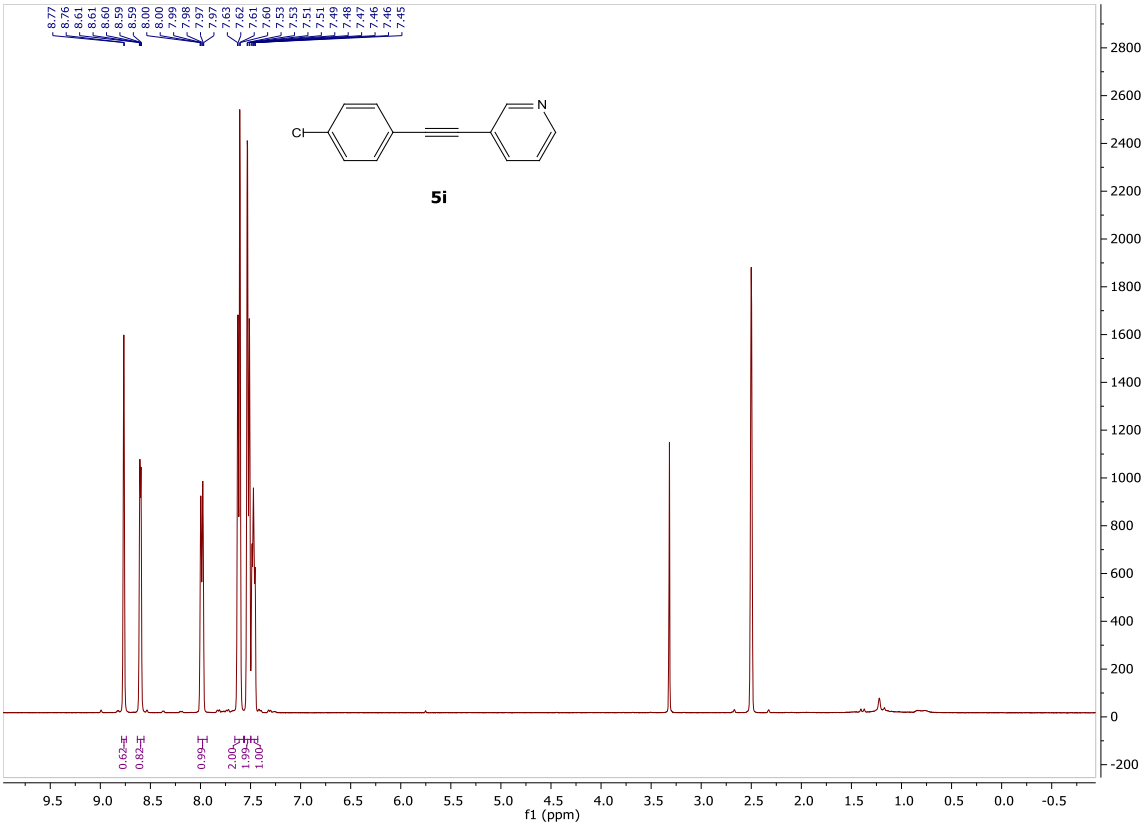


Figure S25: ^{13}C NMR

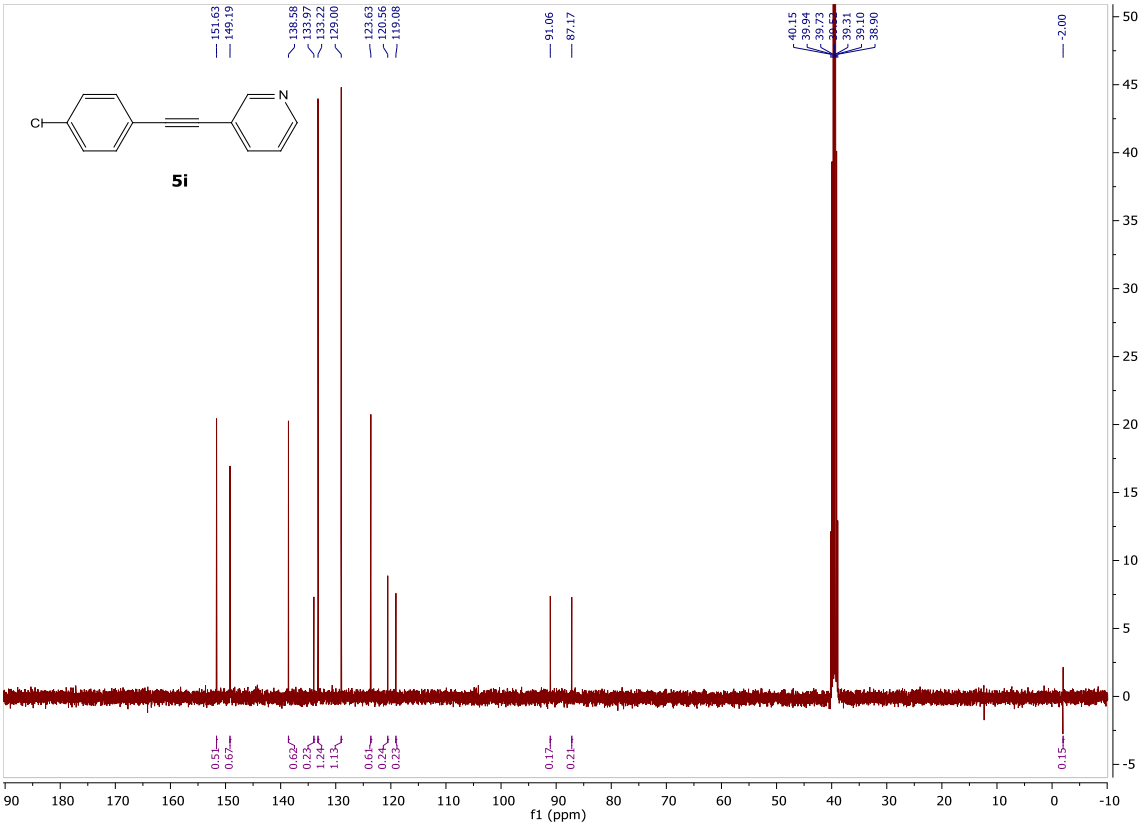


Figure S26: ^{1}H NMR

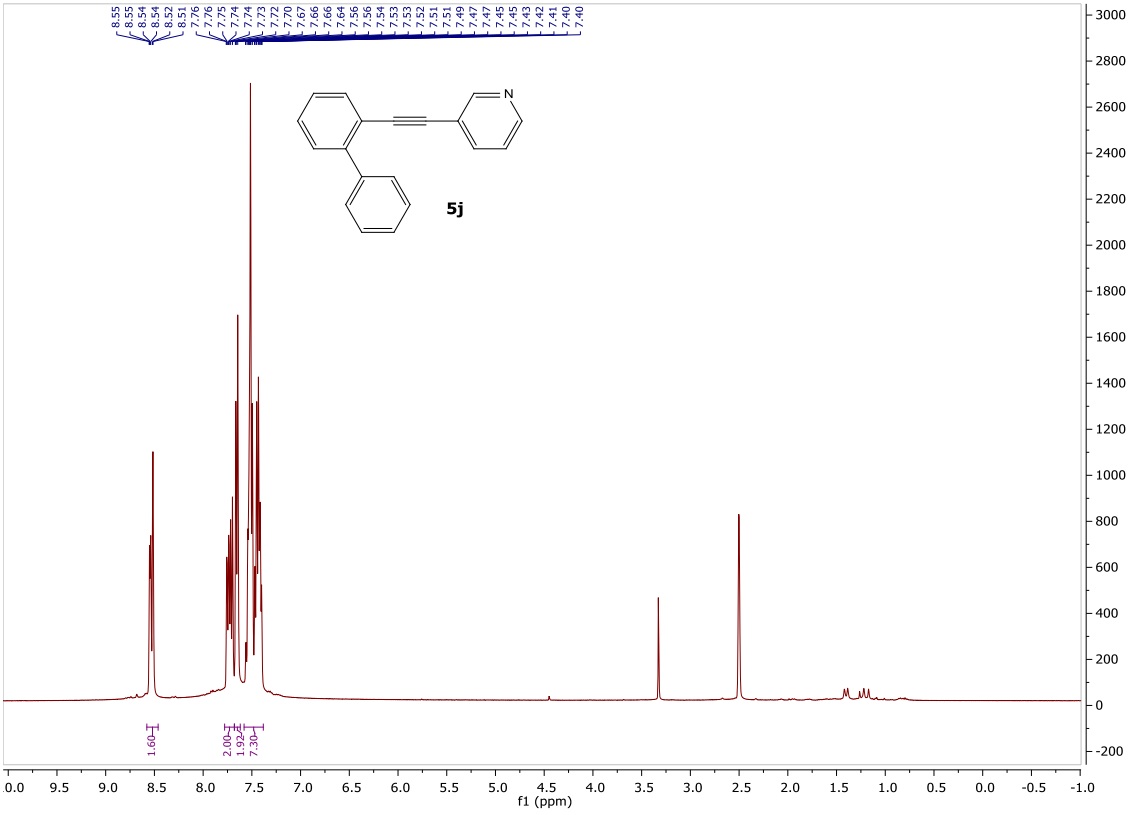


Figure S27: ^{13}C NMR

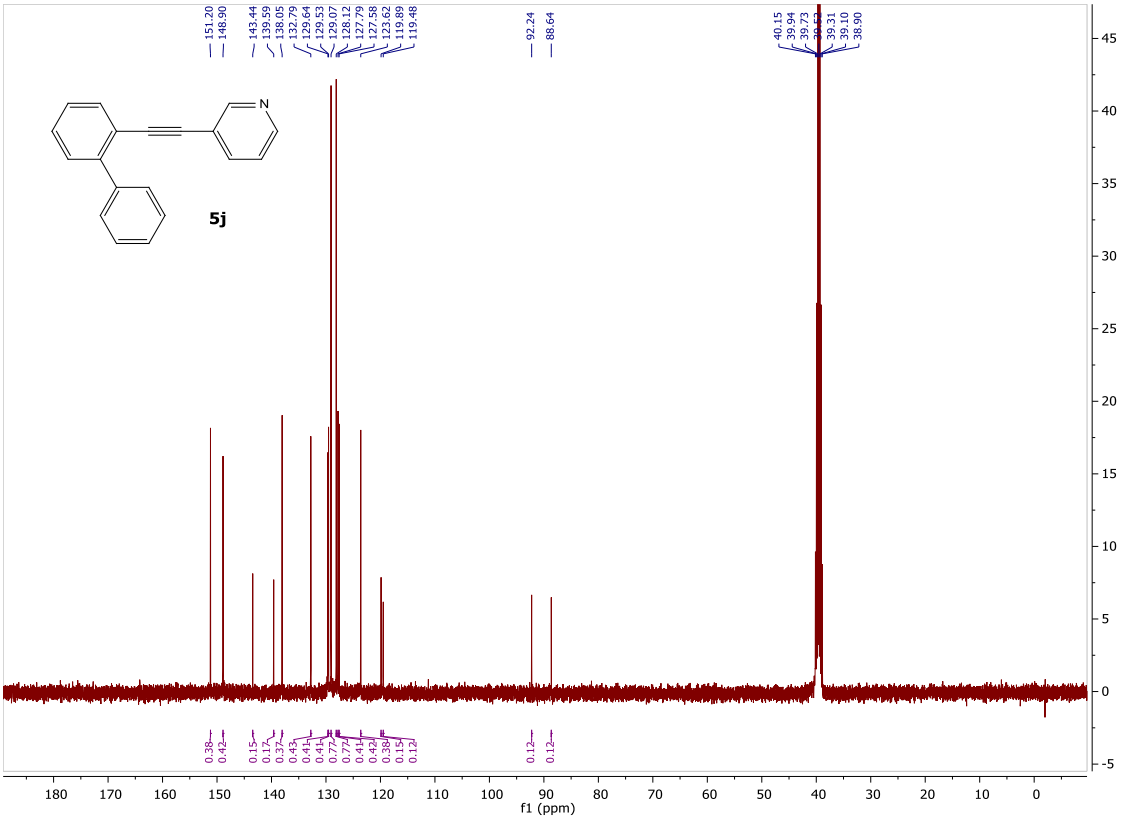


Figure S28: ^{1}H NMR

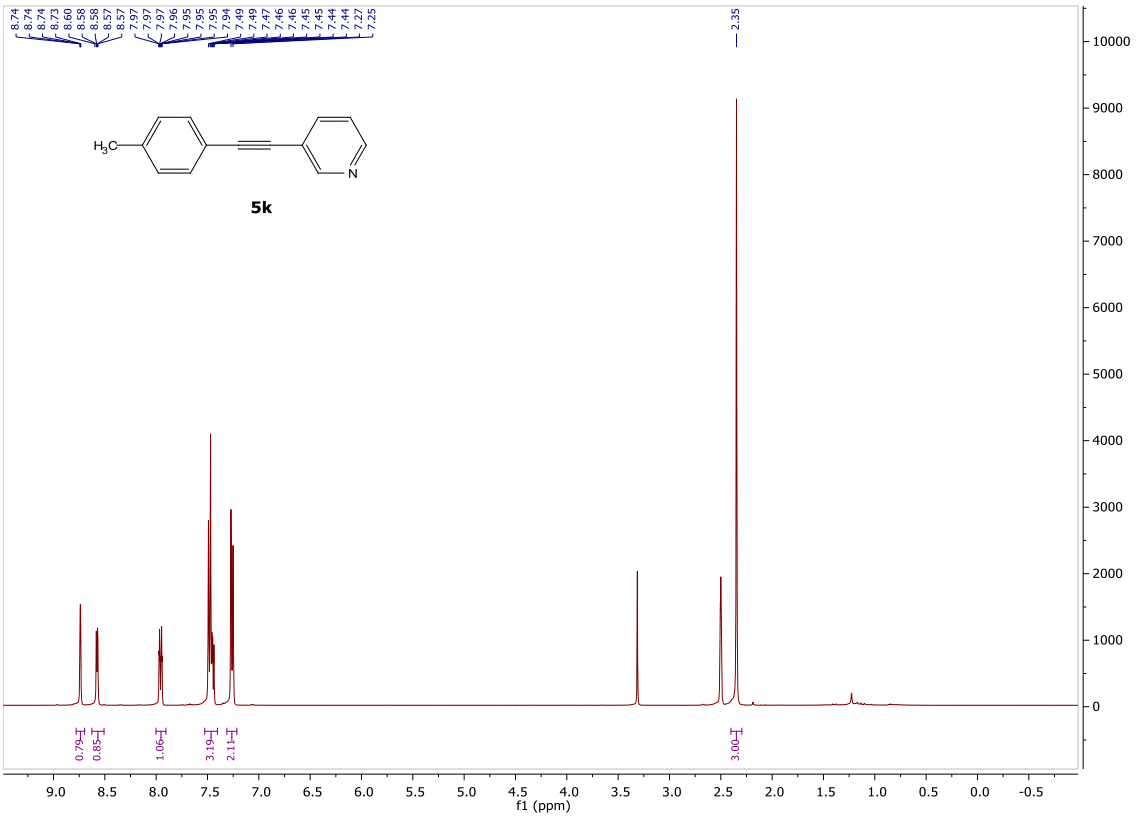


Figure S29: ^{13}C NMR

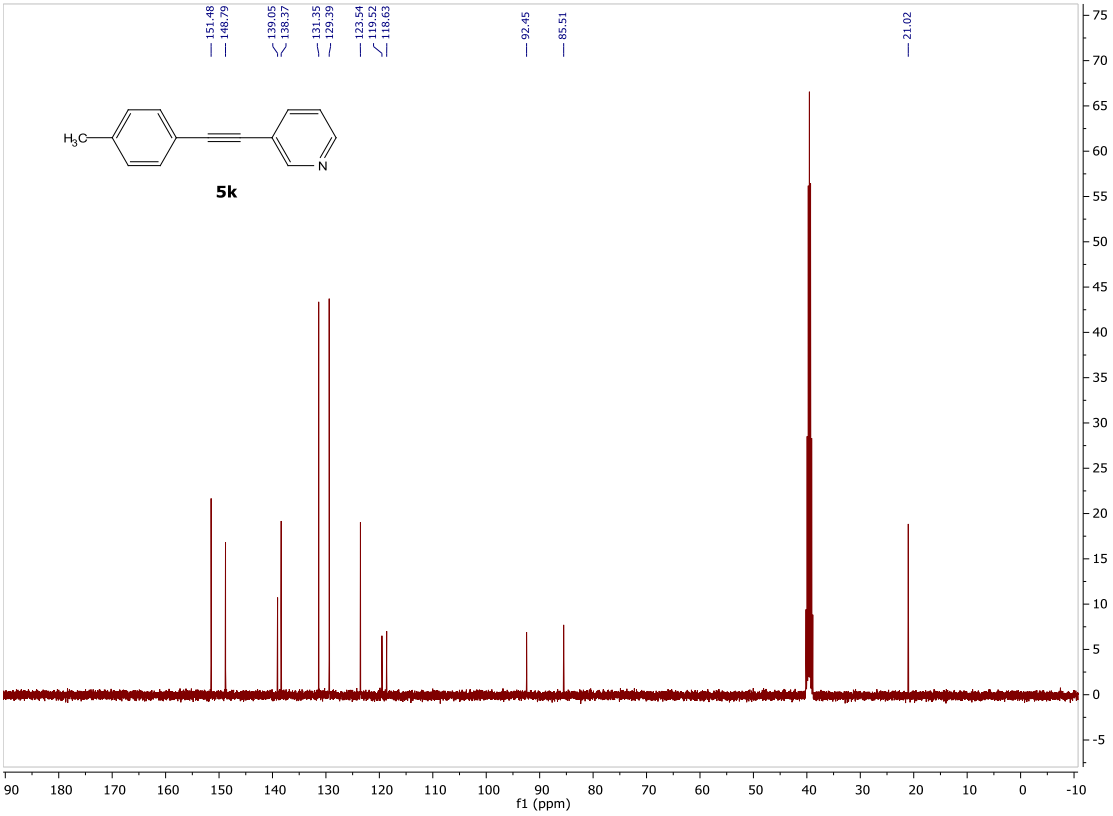


Figure S30: ^{1}H NMR

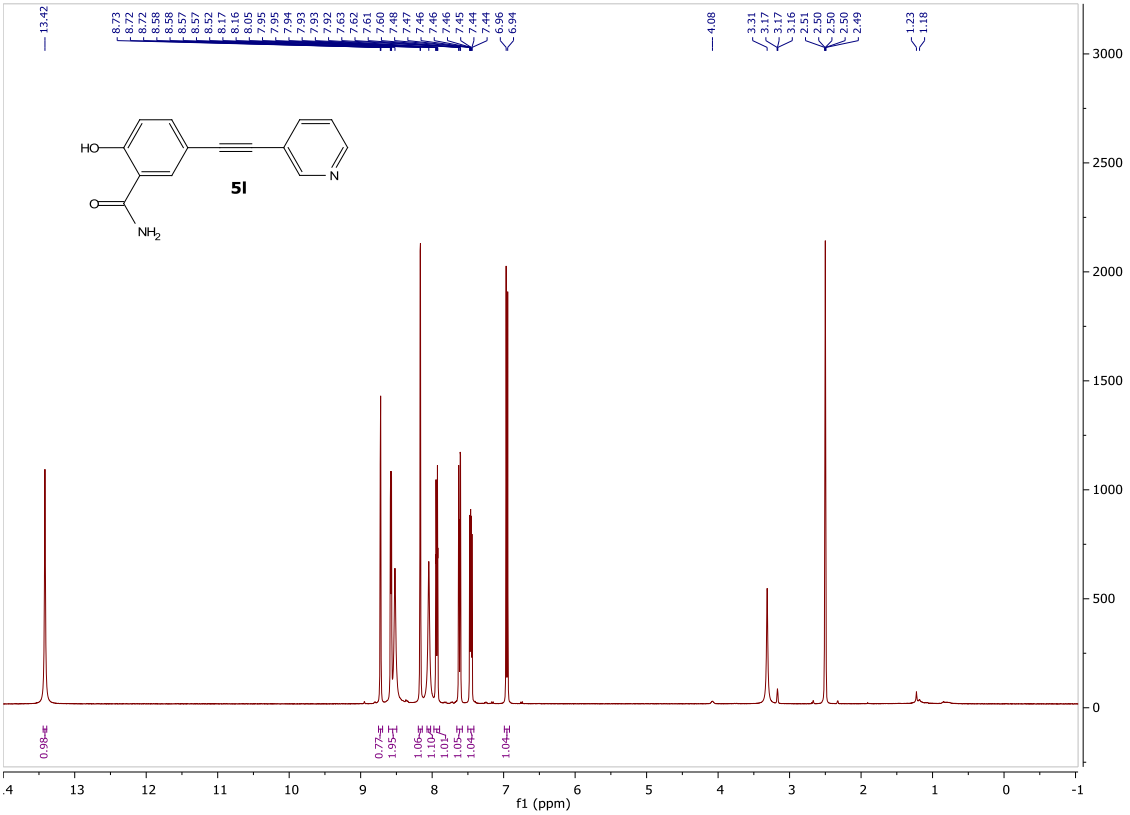


Figure S31: ^{13}C NMR

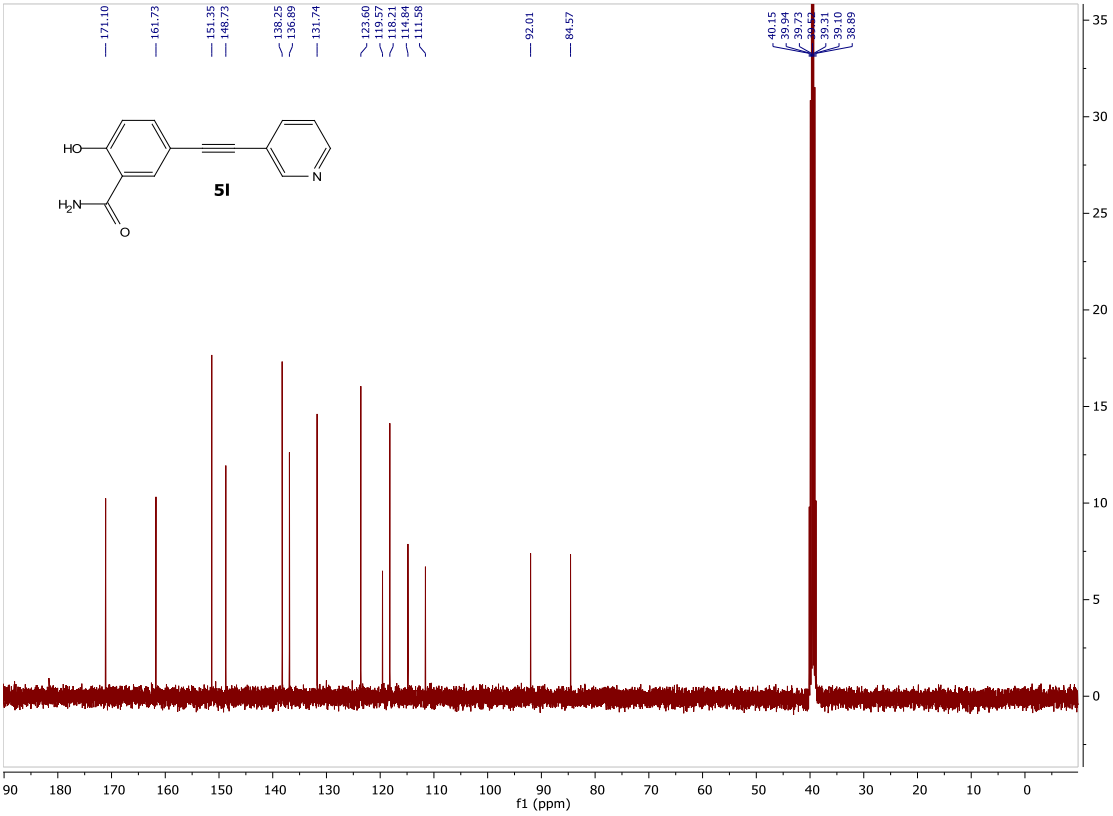


Figure S32: ^{1}H NMR

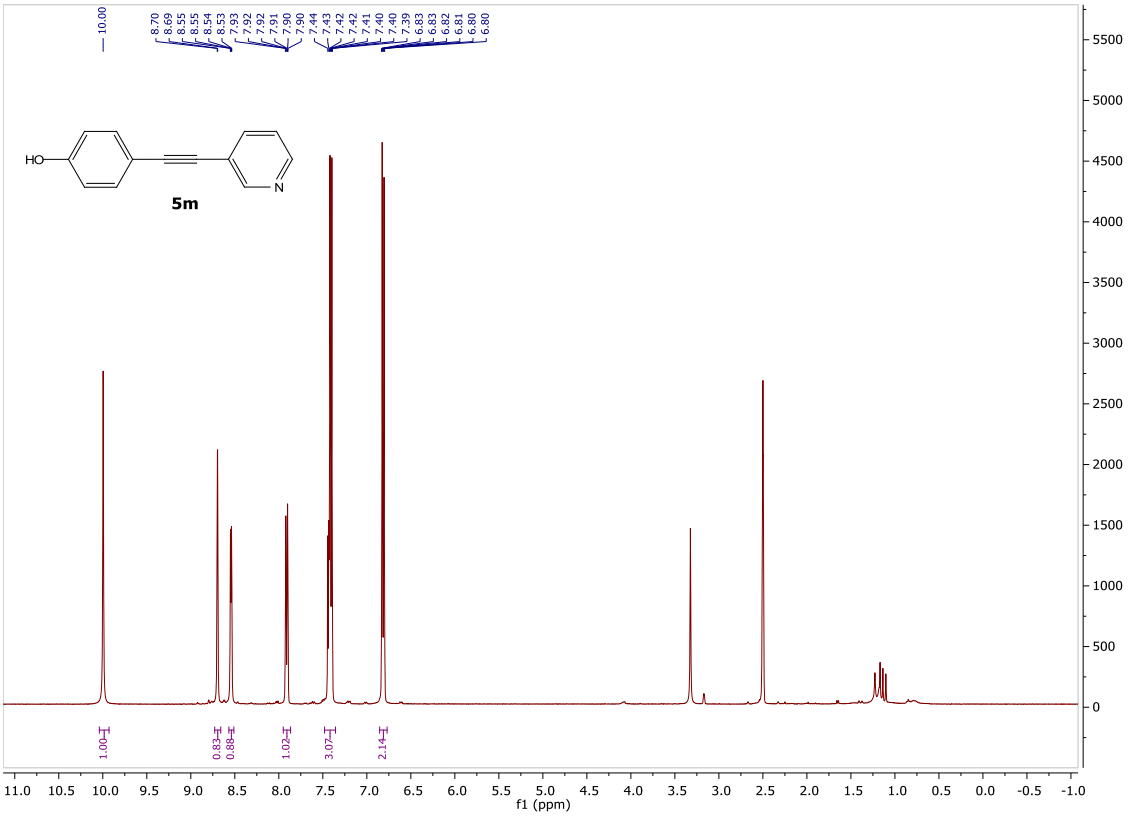


Figure S33: ^{13}C NMR

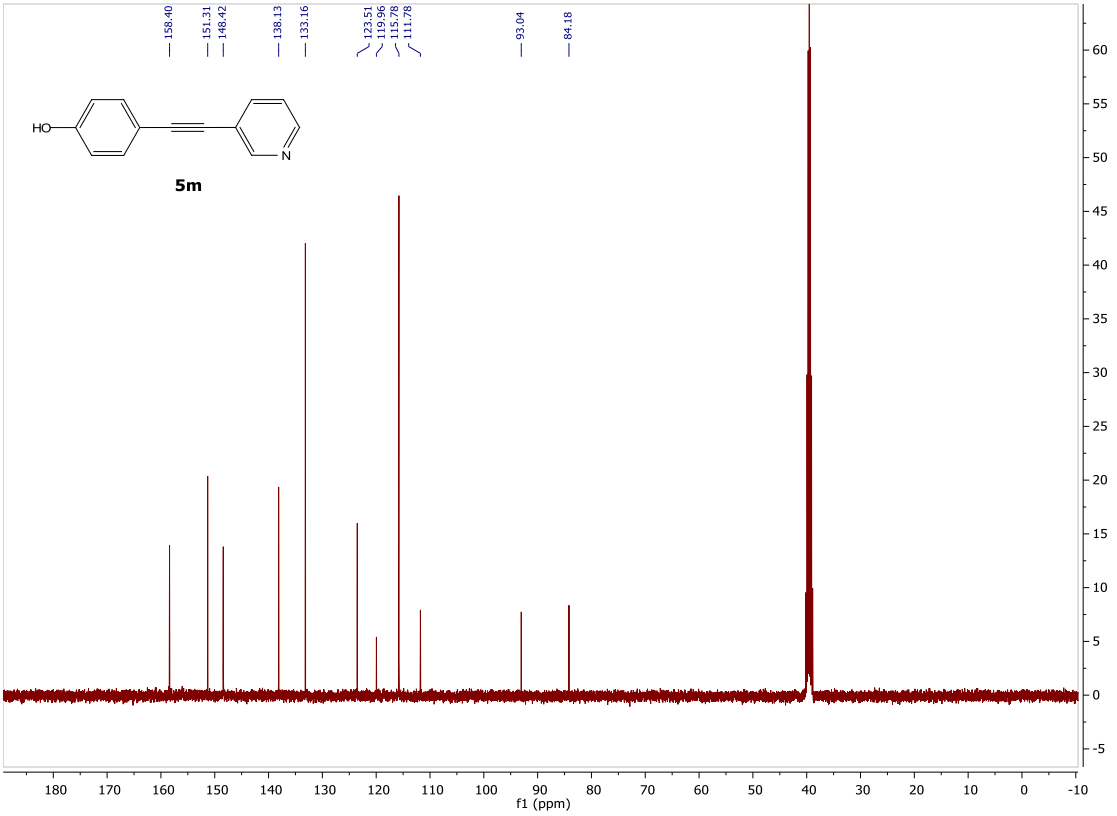


Figure S34: ^{1}H NMR

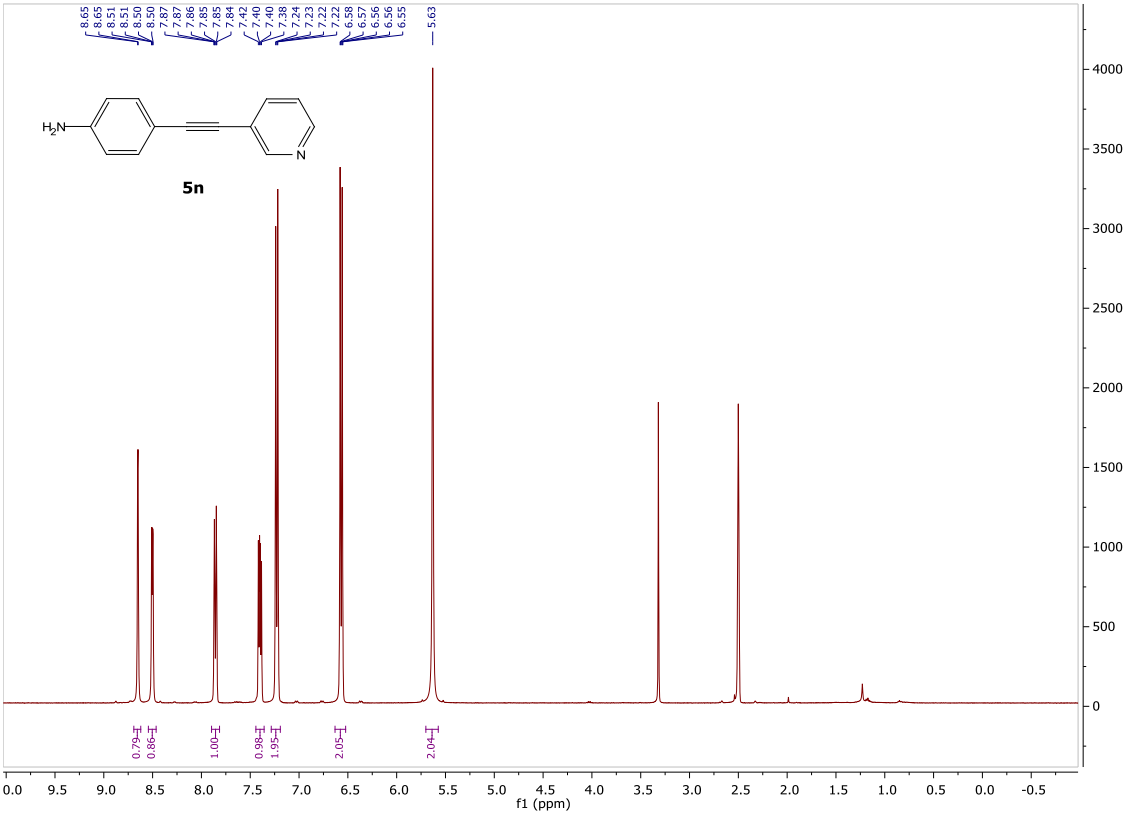


Figure S35: ^{13}C NMR

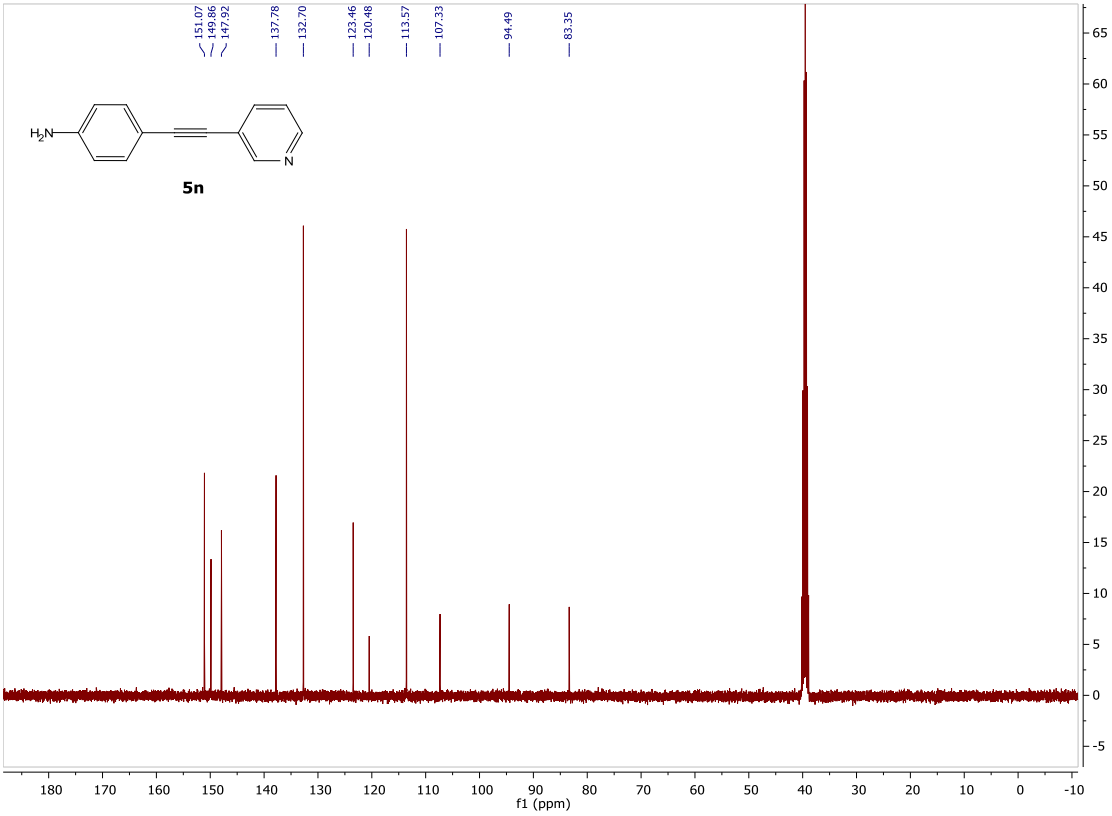


Figure S36: ^{1}H NMR

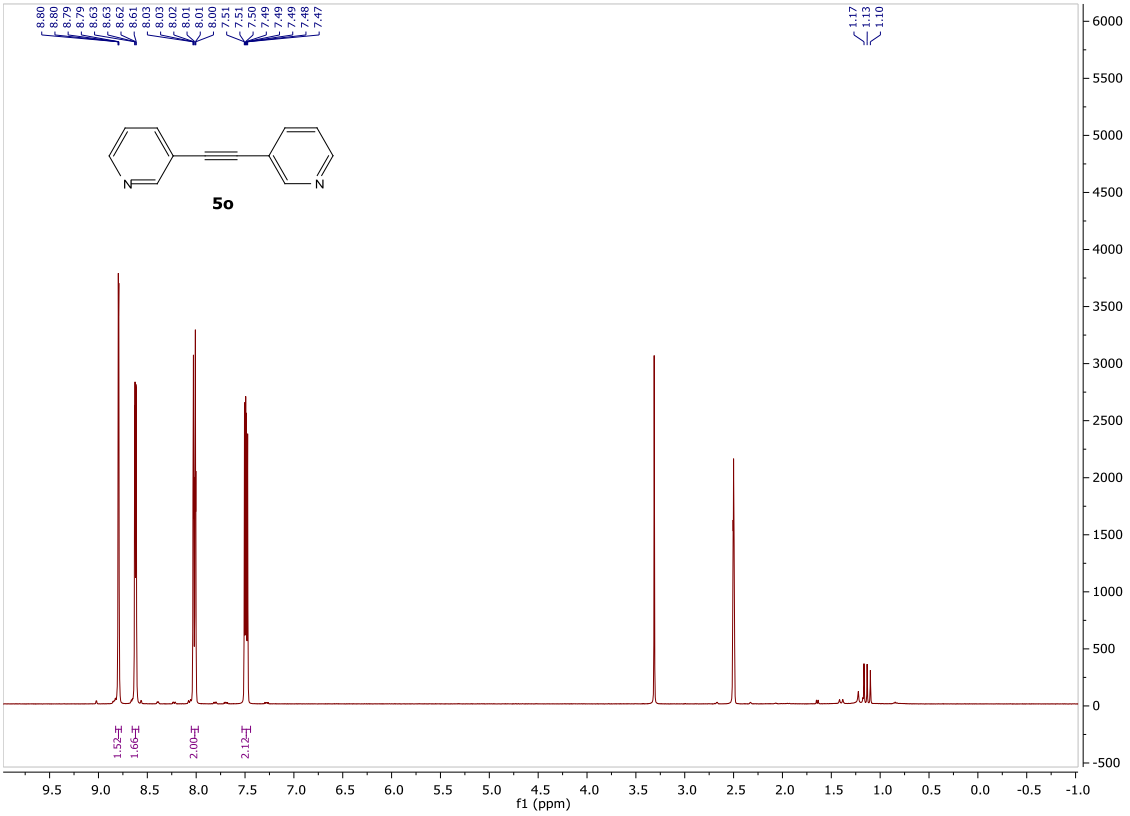


Figure S37: ^{13}C NMR

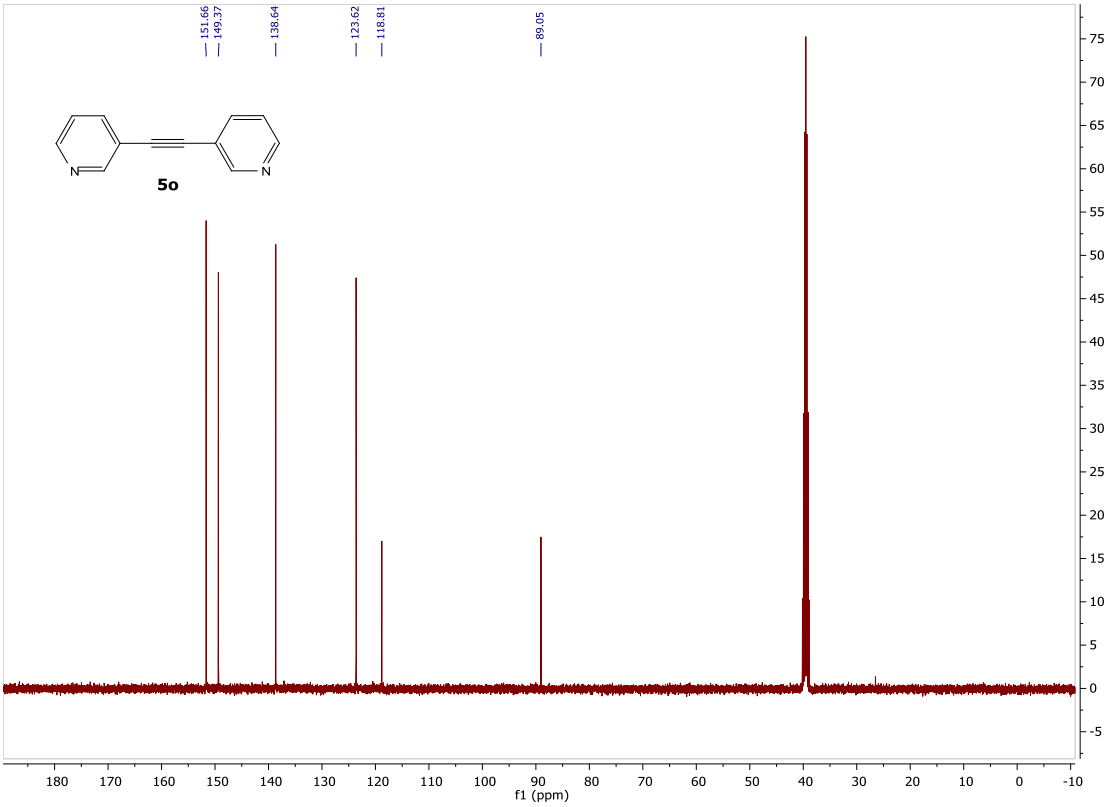


Figure S38: ^{1}H NMR

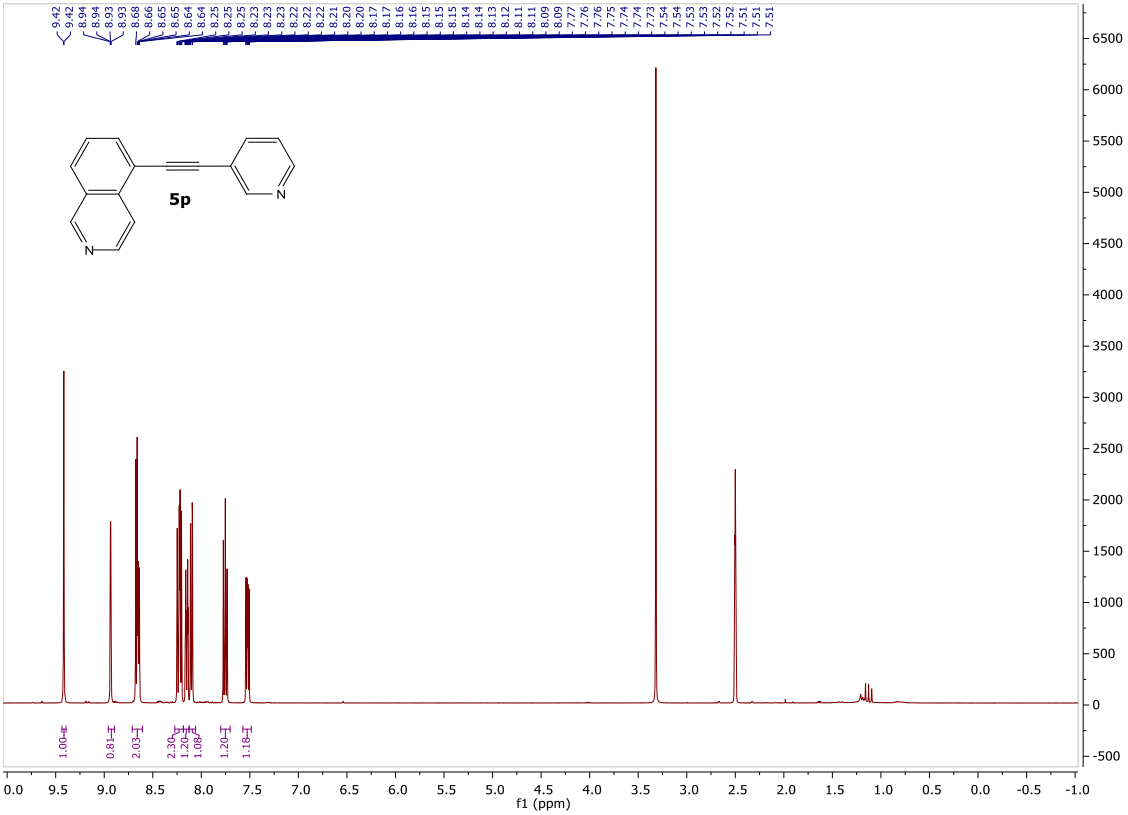


Figure S39: ^{13}C NMR

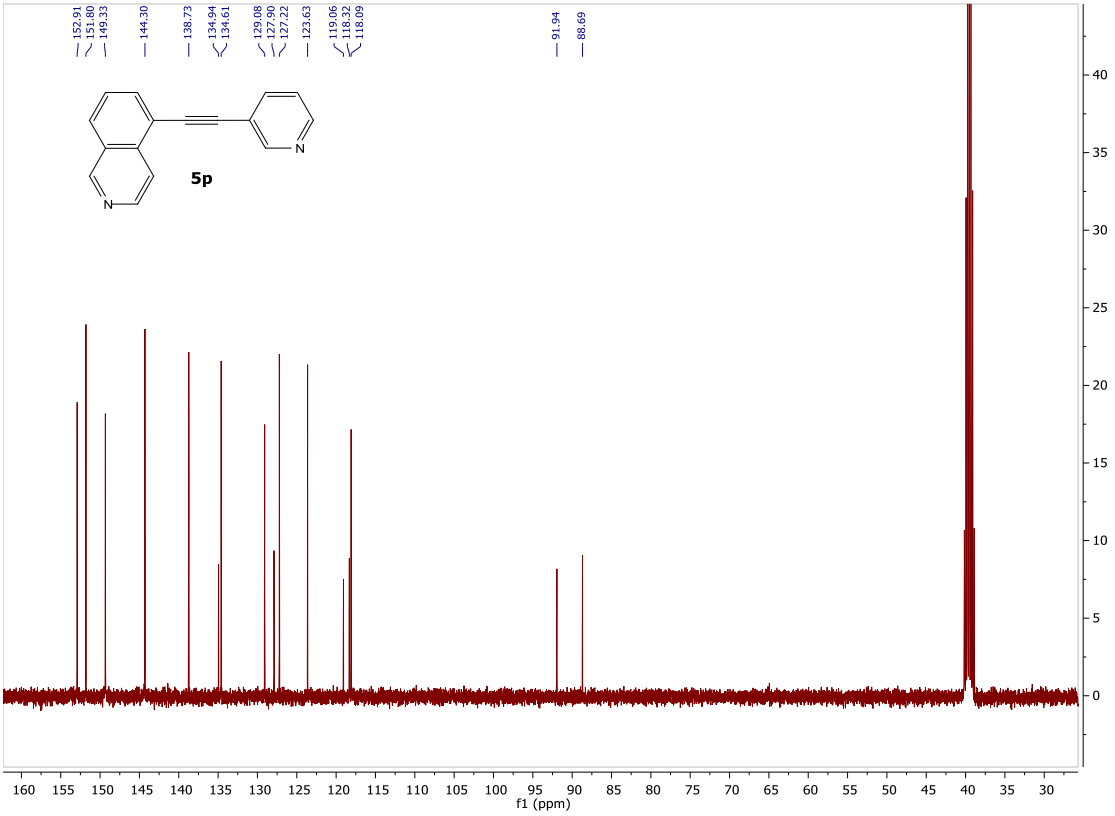


Figure S40: ^{1}H NMR

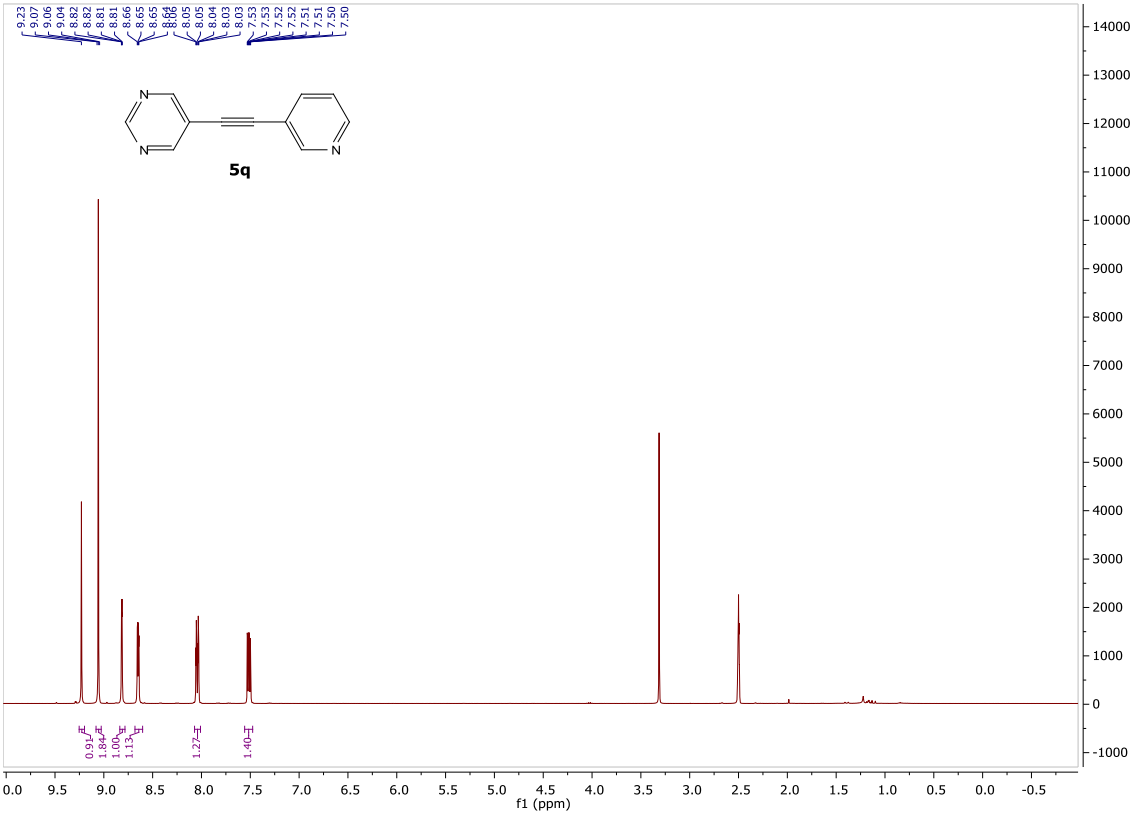


Figure S41: ^{13}C NMR

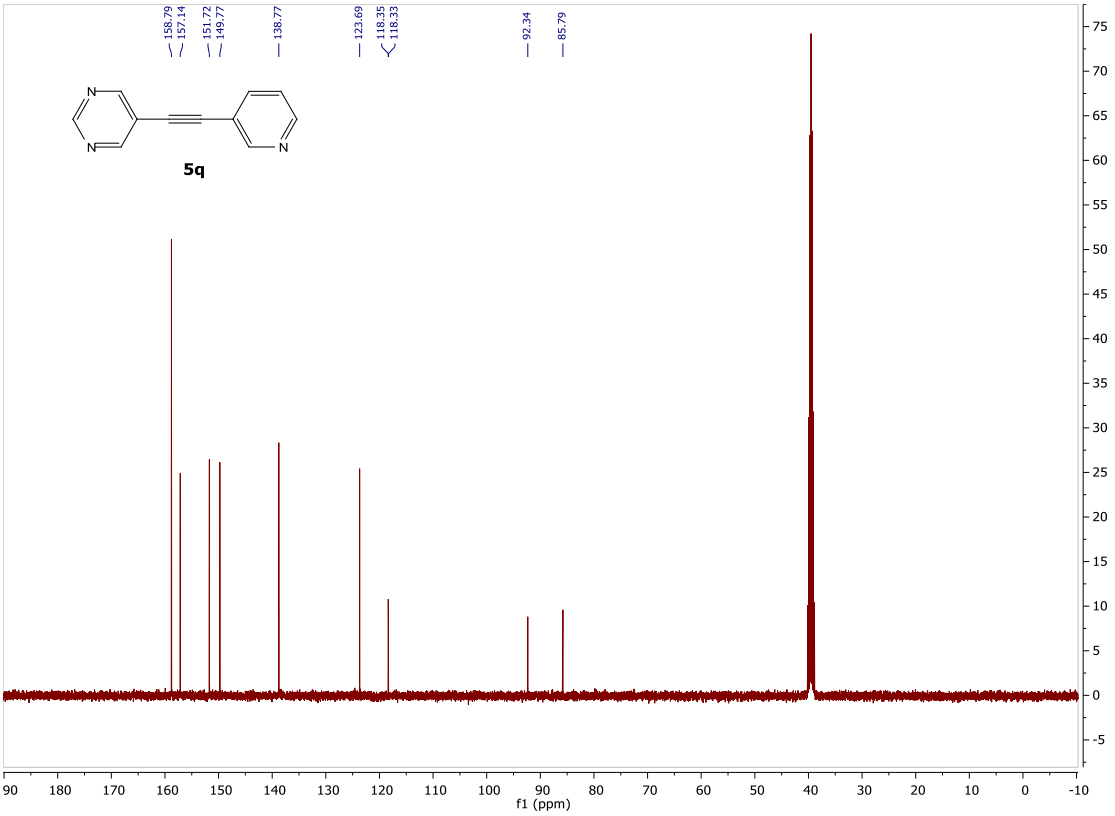


Figure S42: ^{1}H NMR

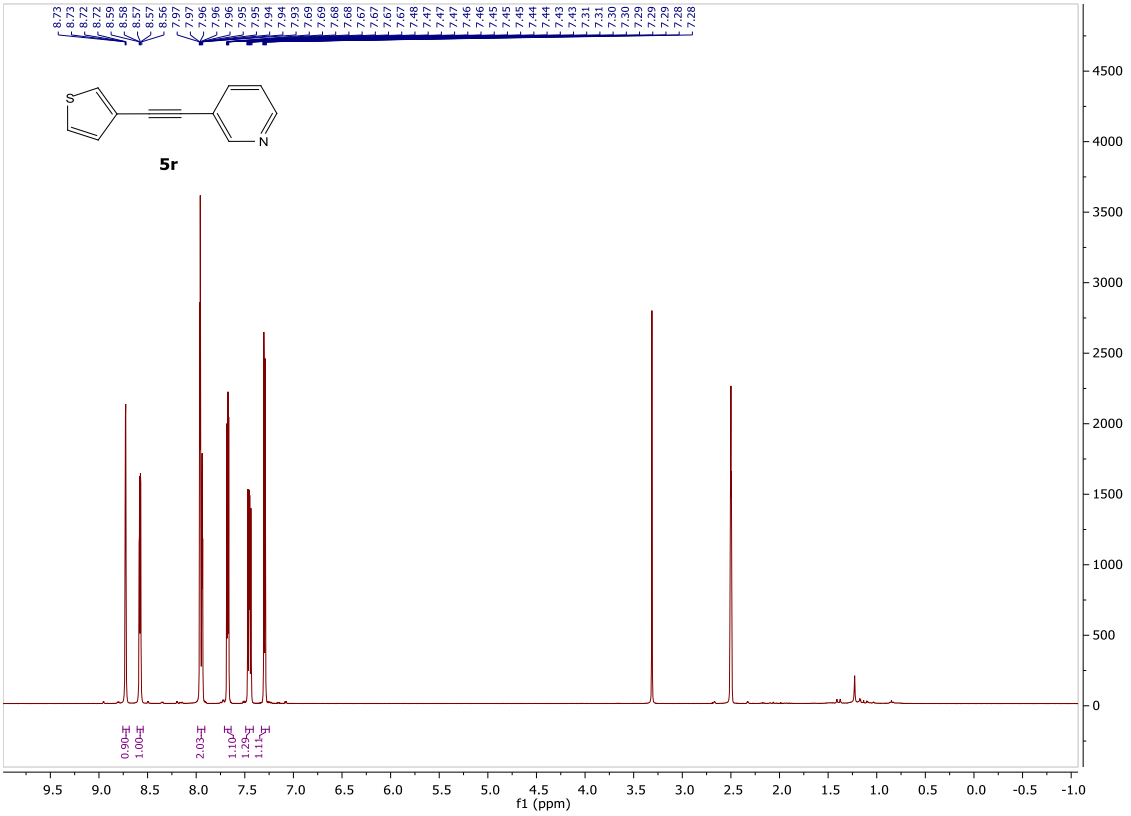


Figure S43: ^{13}C NMR

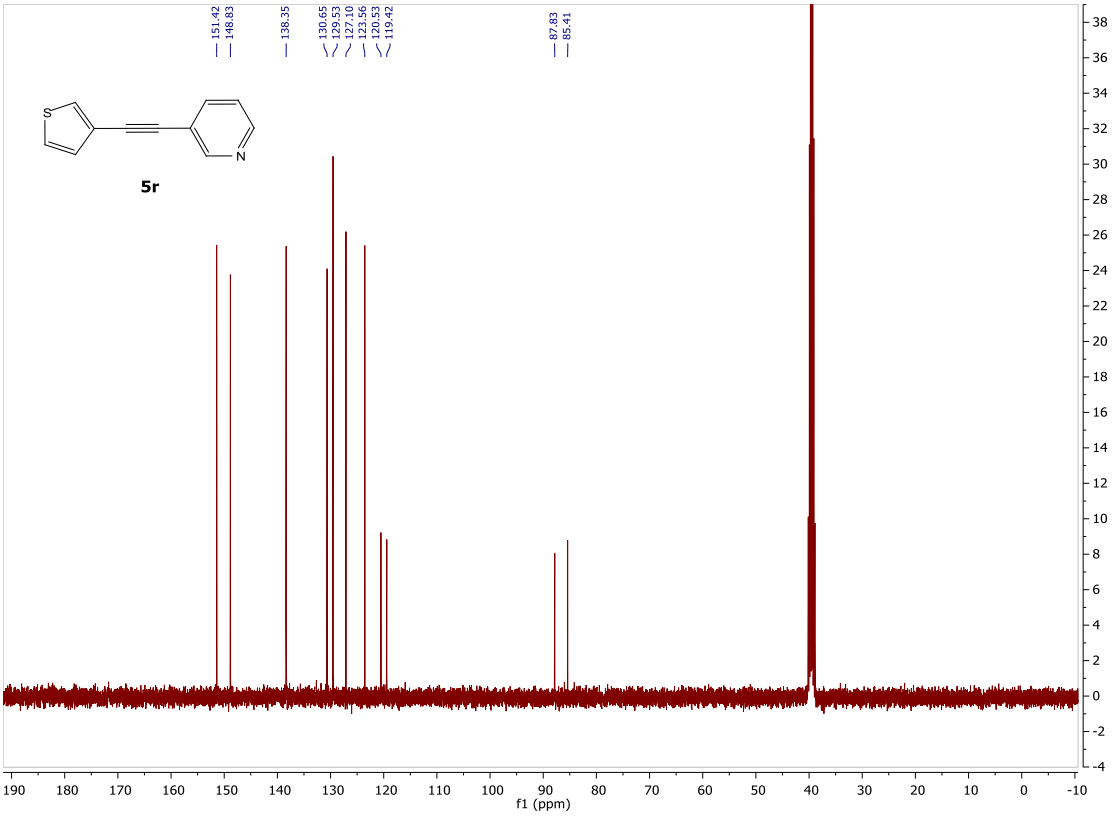


Figure S44: ^{1}H NMR

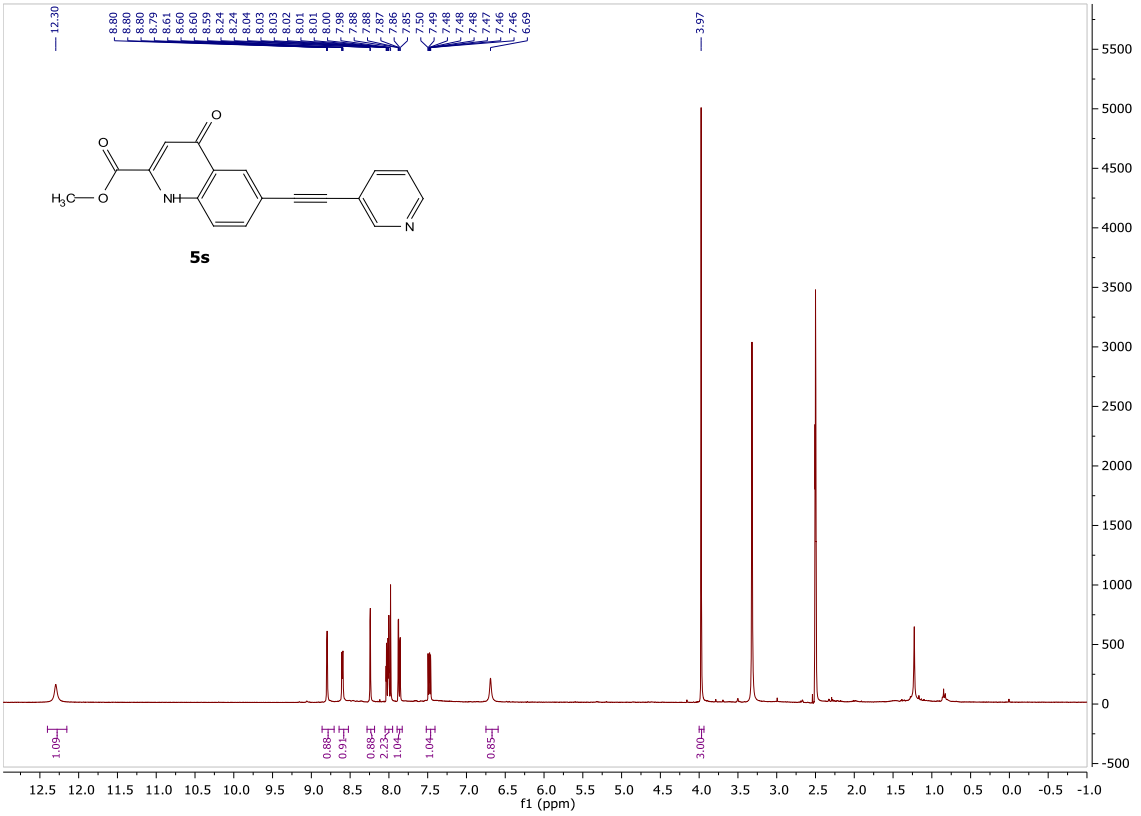
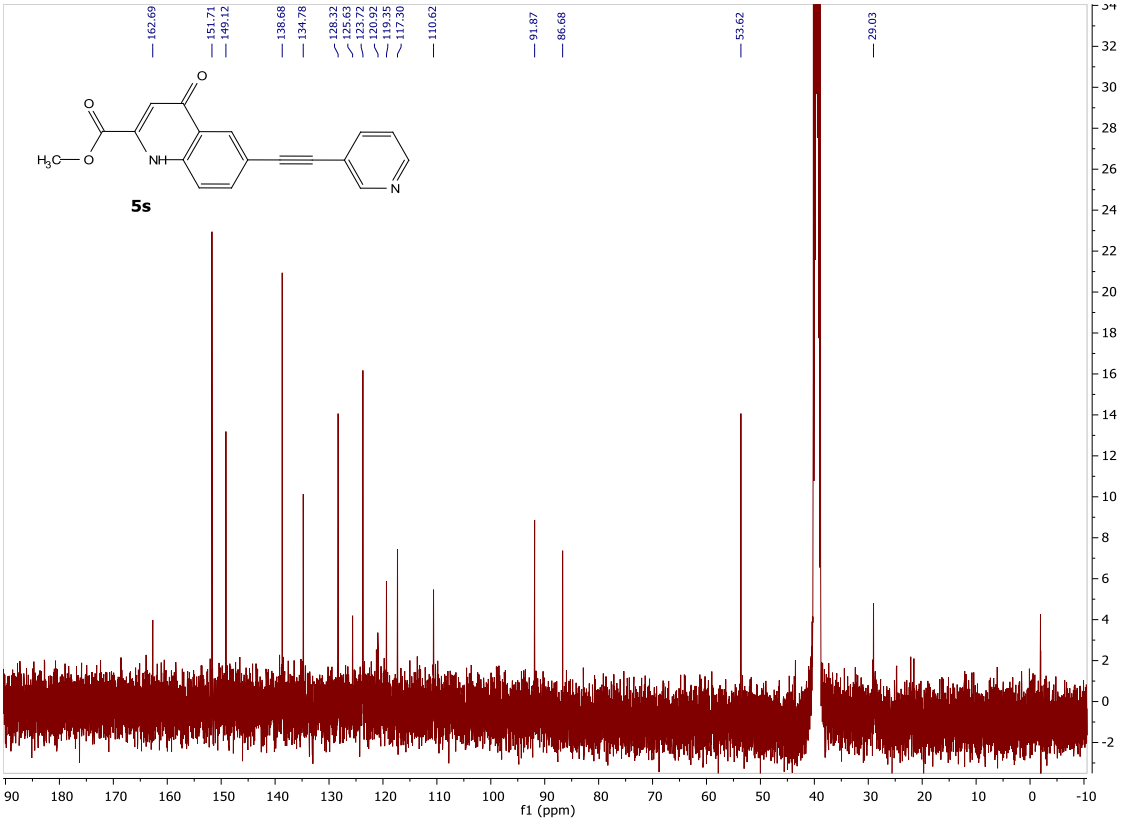


Figure S45: ^{13}C NMR



*weak intensity due to insolubility

Figure S46: ^{1}H NMR

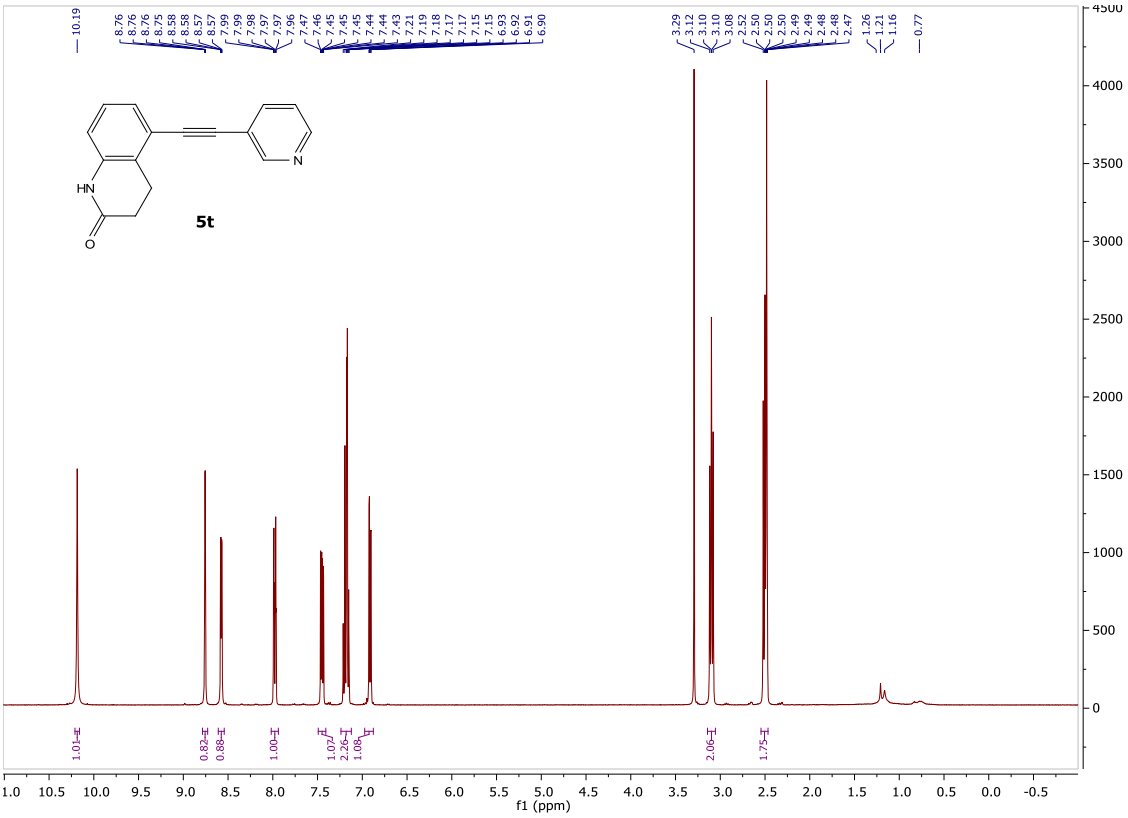


Figure S47: ^{13}C NMR

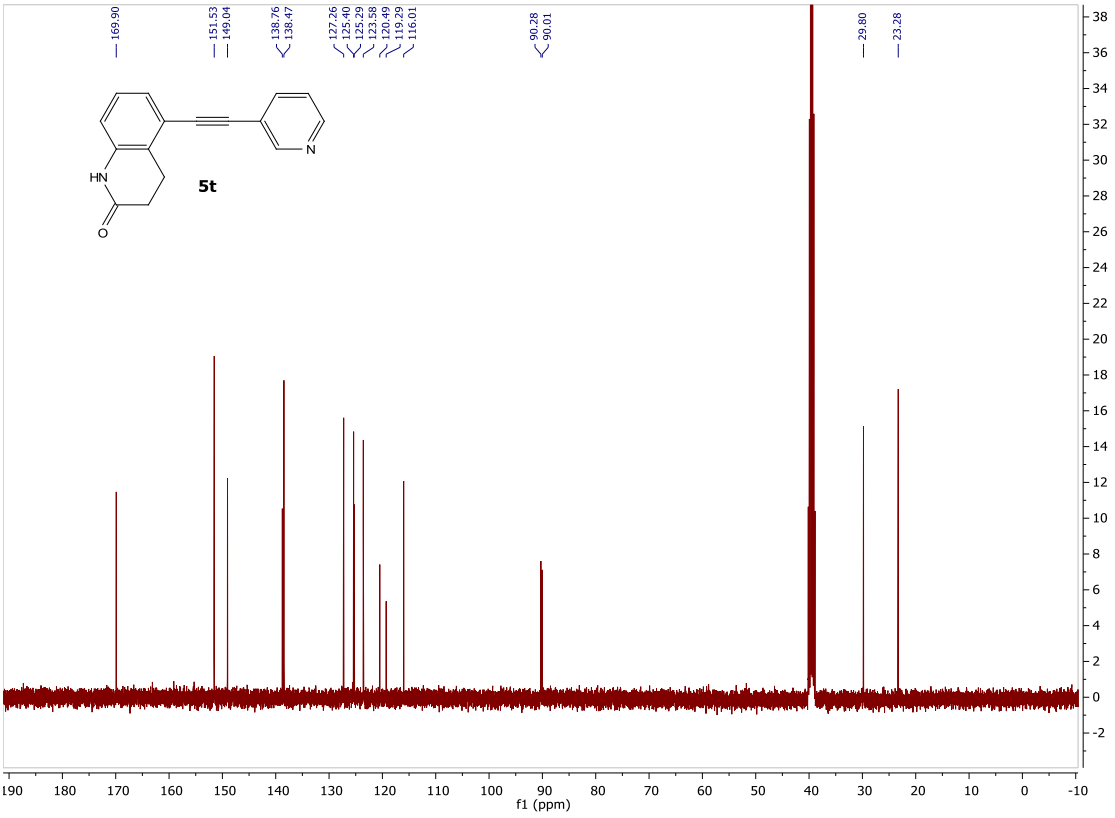


Figure S48: ^{1}H NMR

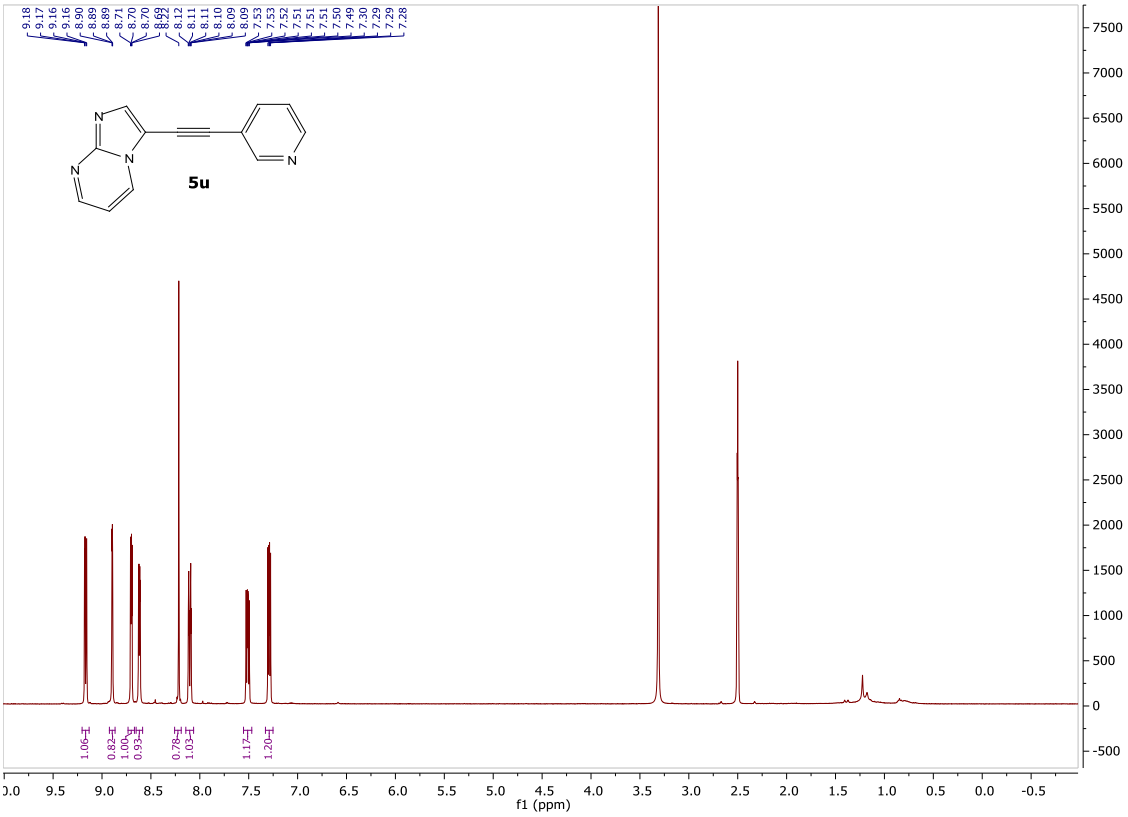


Figure S49: ^{13}C NMR

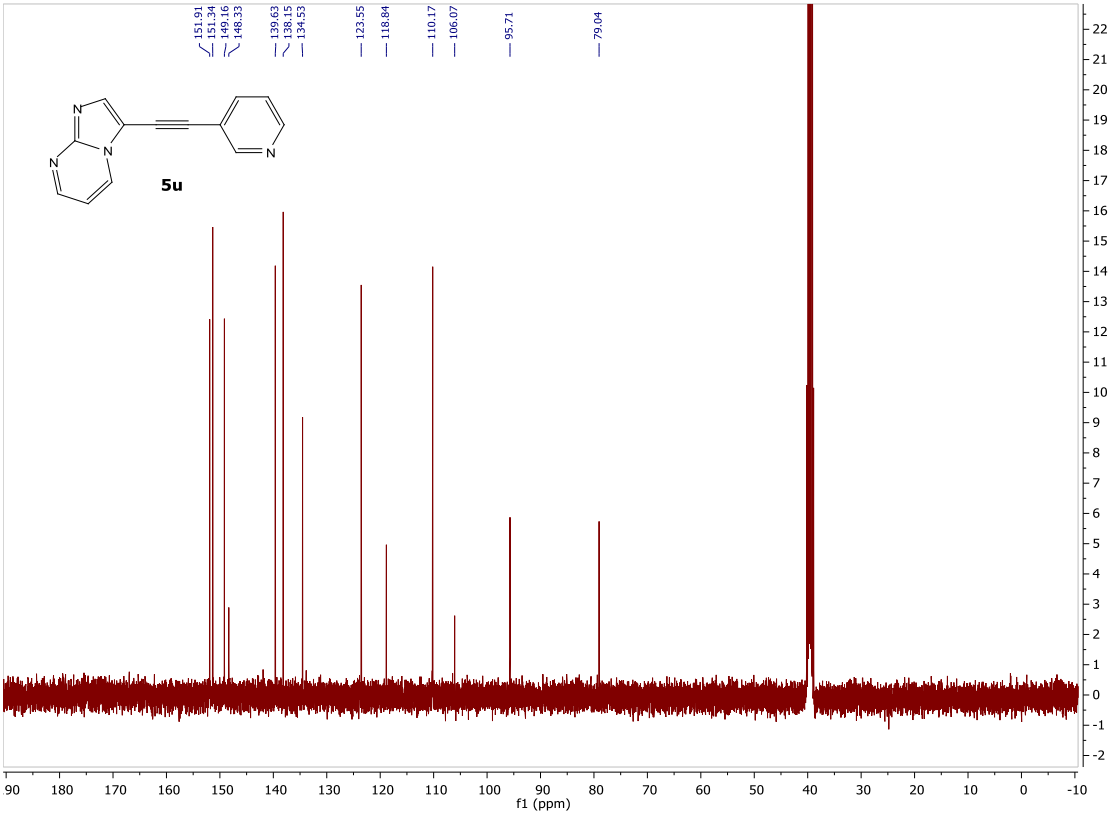


Figure S50: ^{1}H NMR

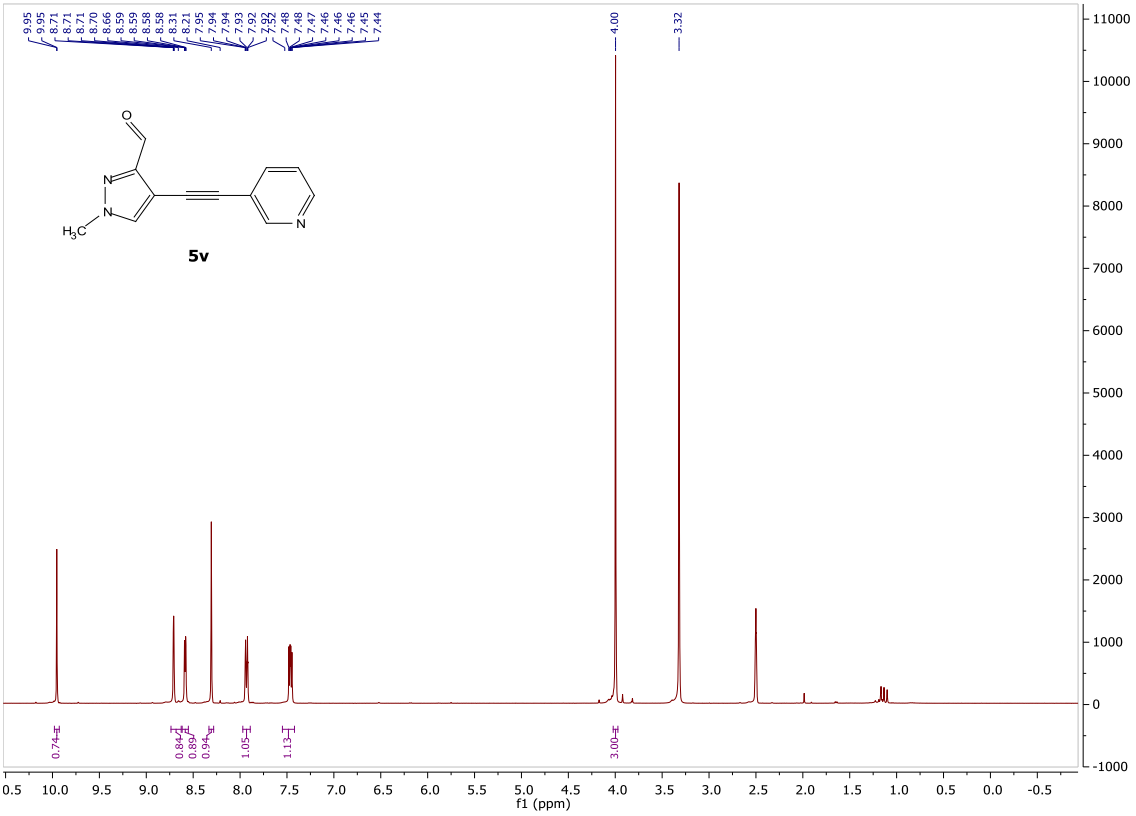


Figure S51: ^{13}C NMR

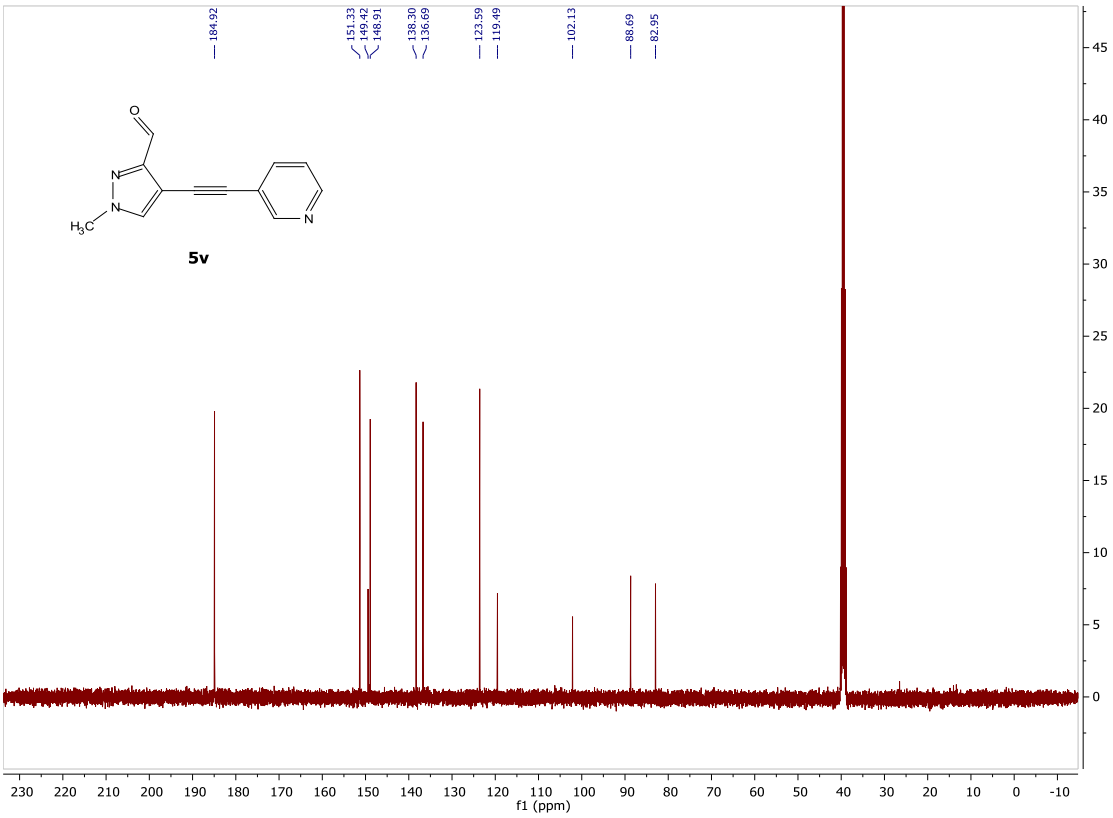


Figure S52: ^{1}H NMR

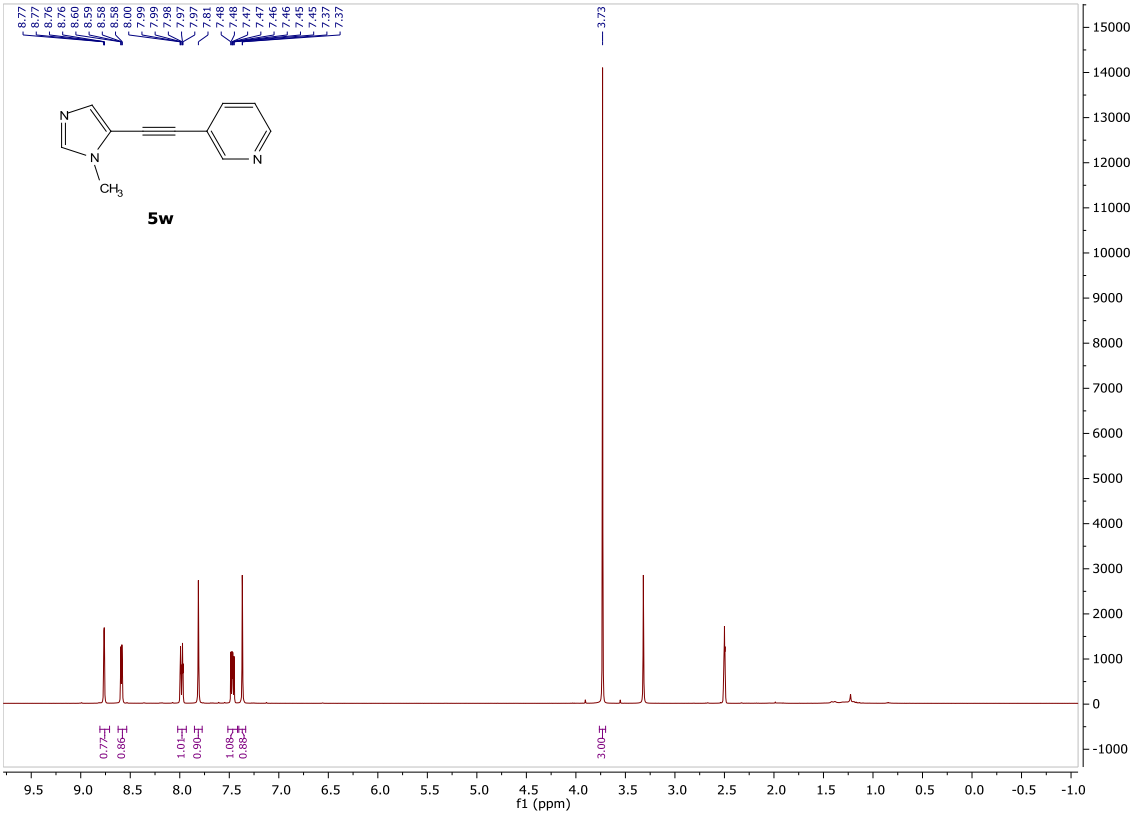


Figure S53: ^{13}C NMR

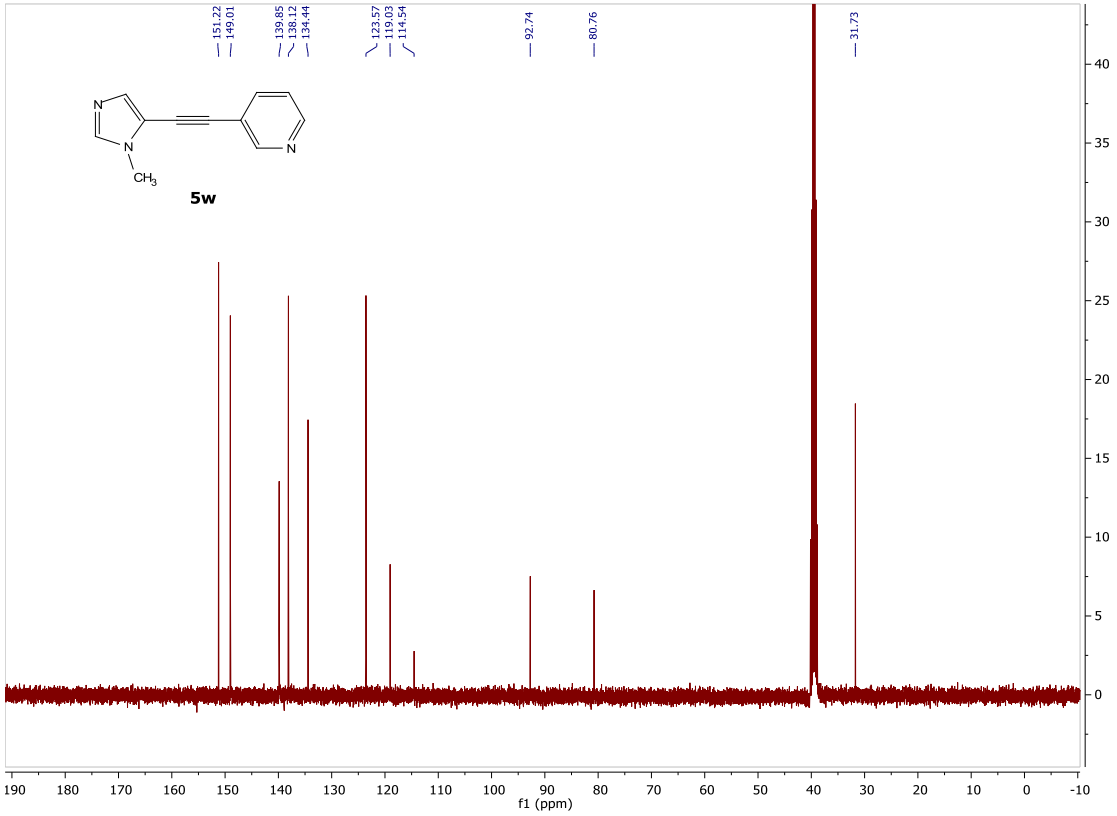


Figure S54: ^{1}H NMR

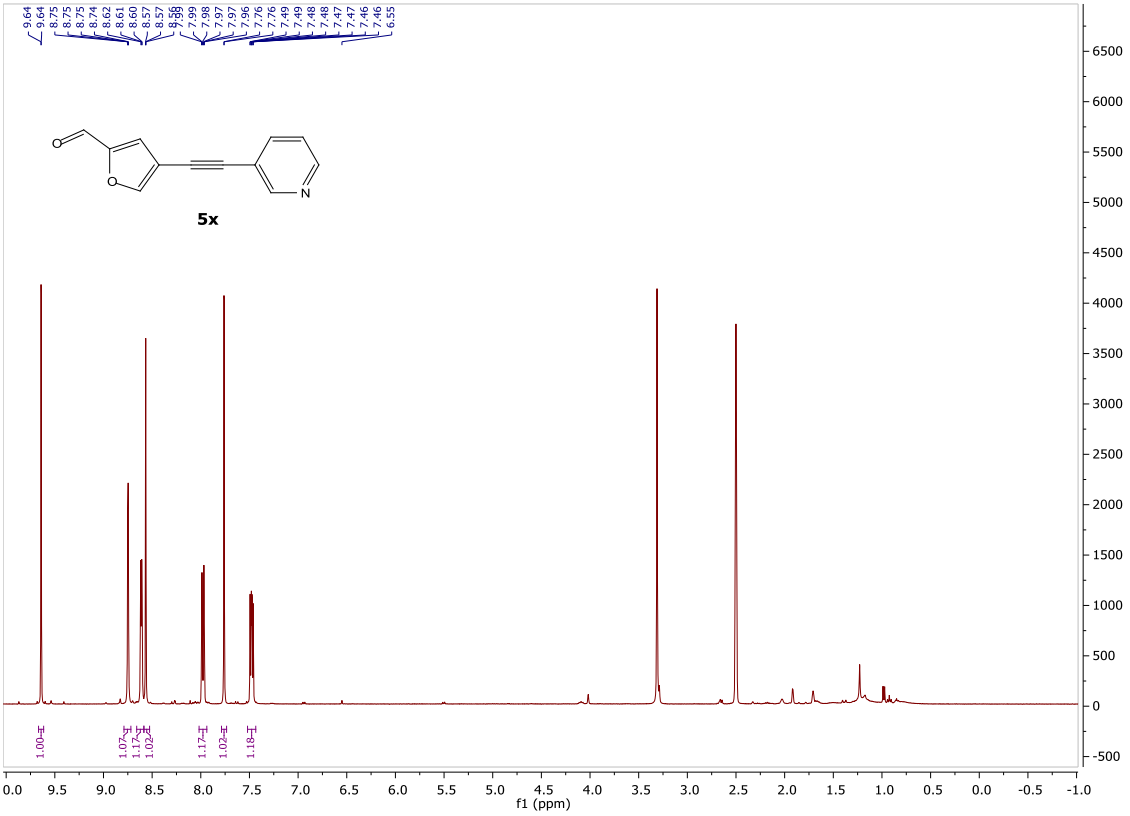


Figure S55: ^{13}C NMR

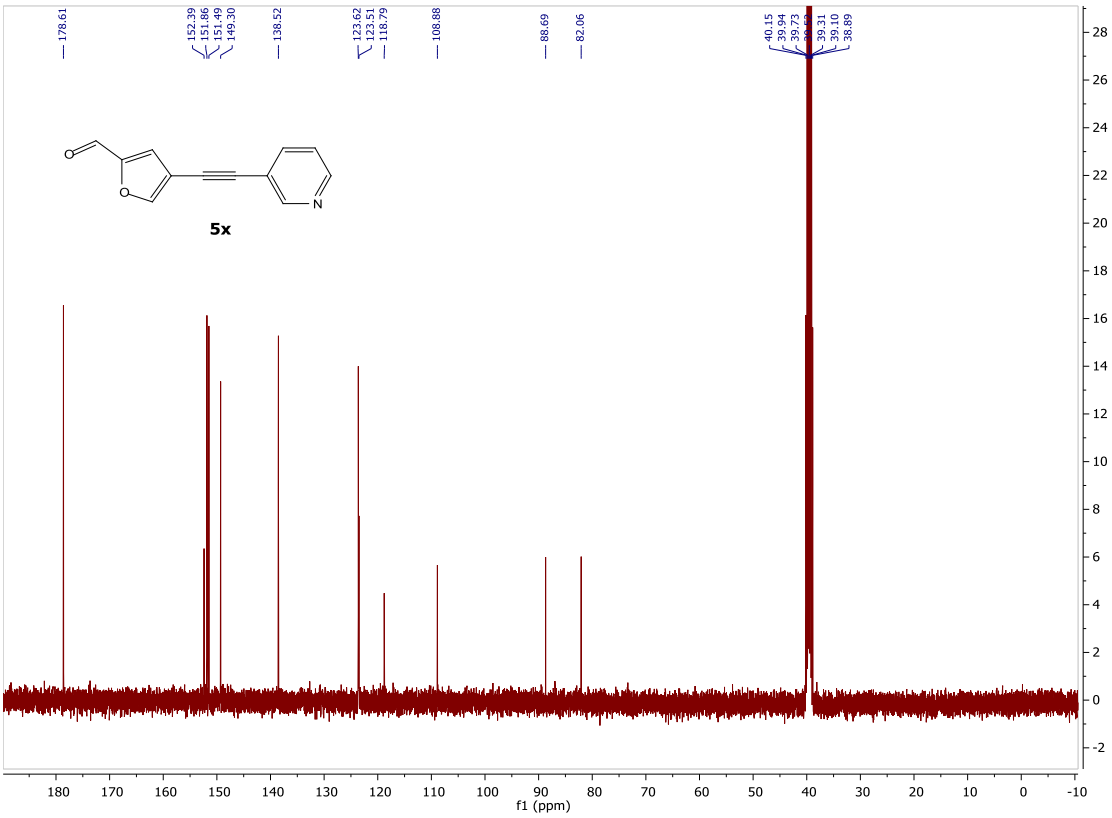


Figure S56: ^{1}H NMR

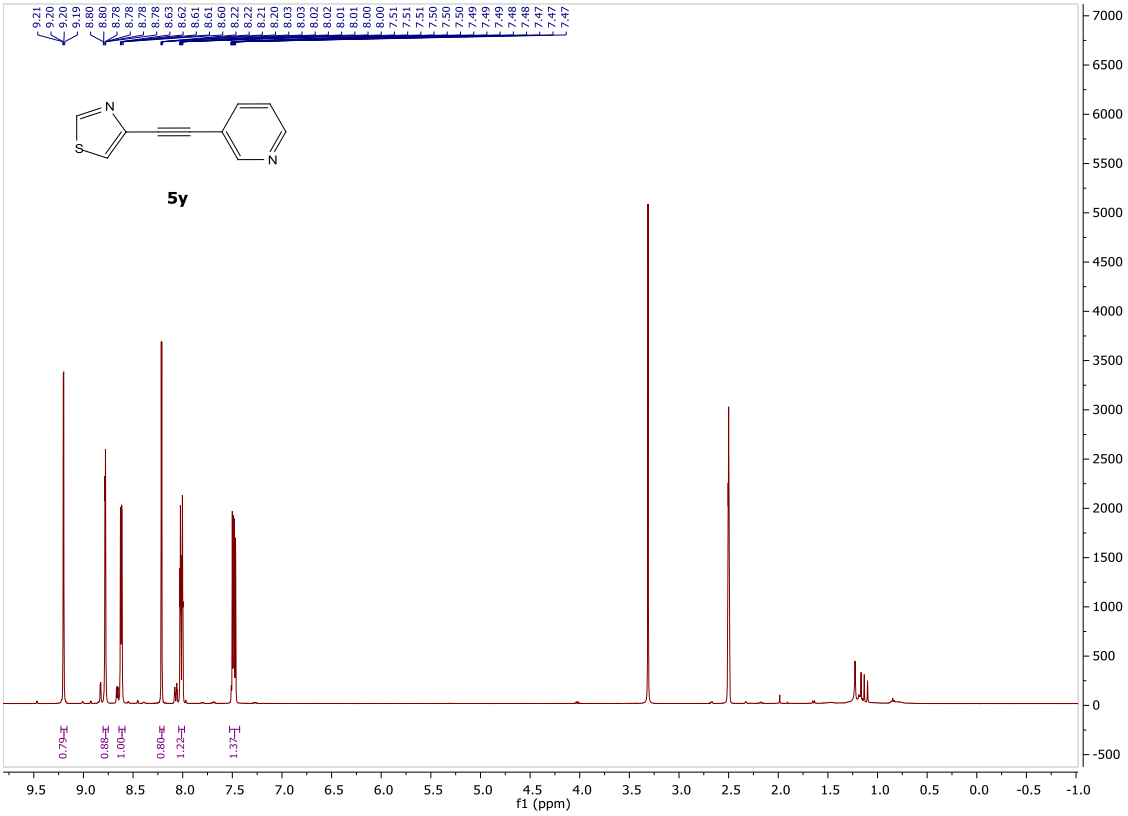


Figure S57: ^{13}C NMR

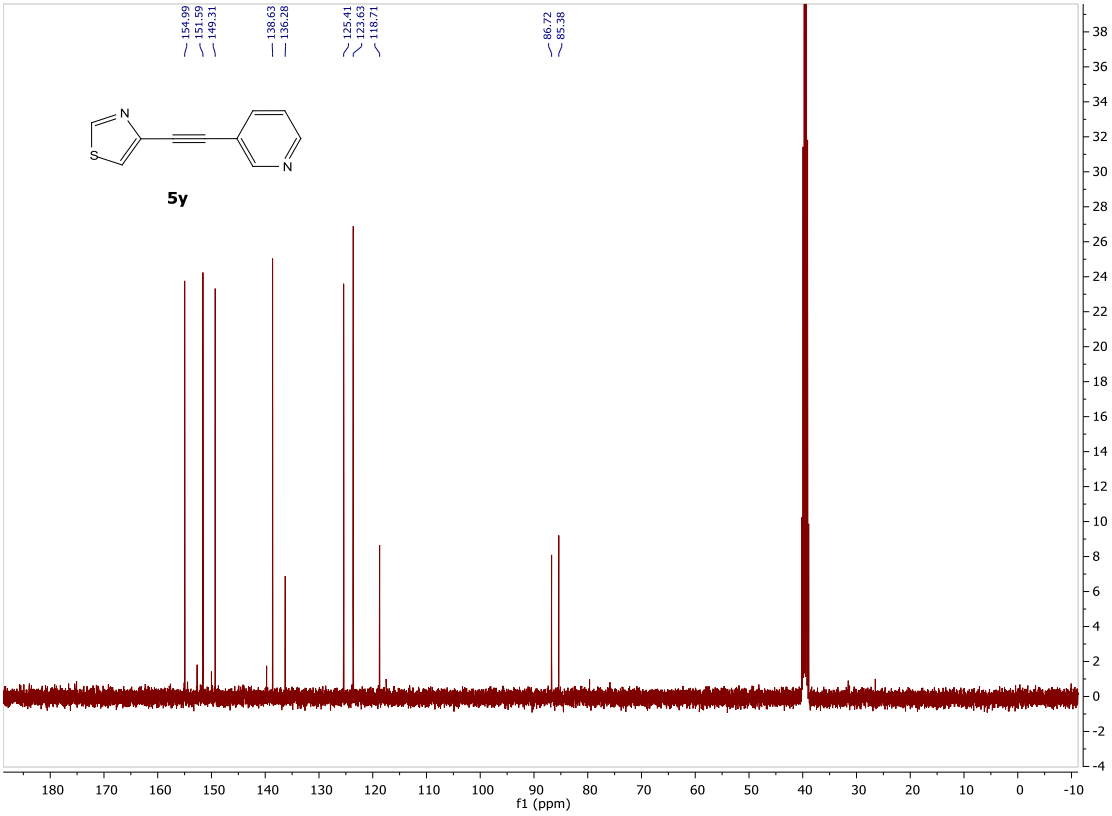


Figure S58: ^{1}H NMR

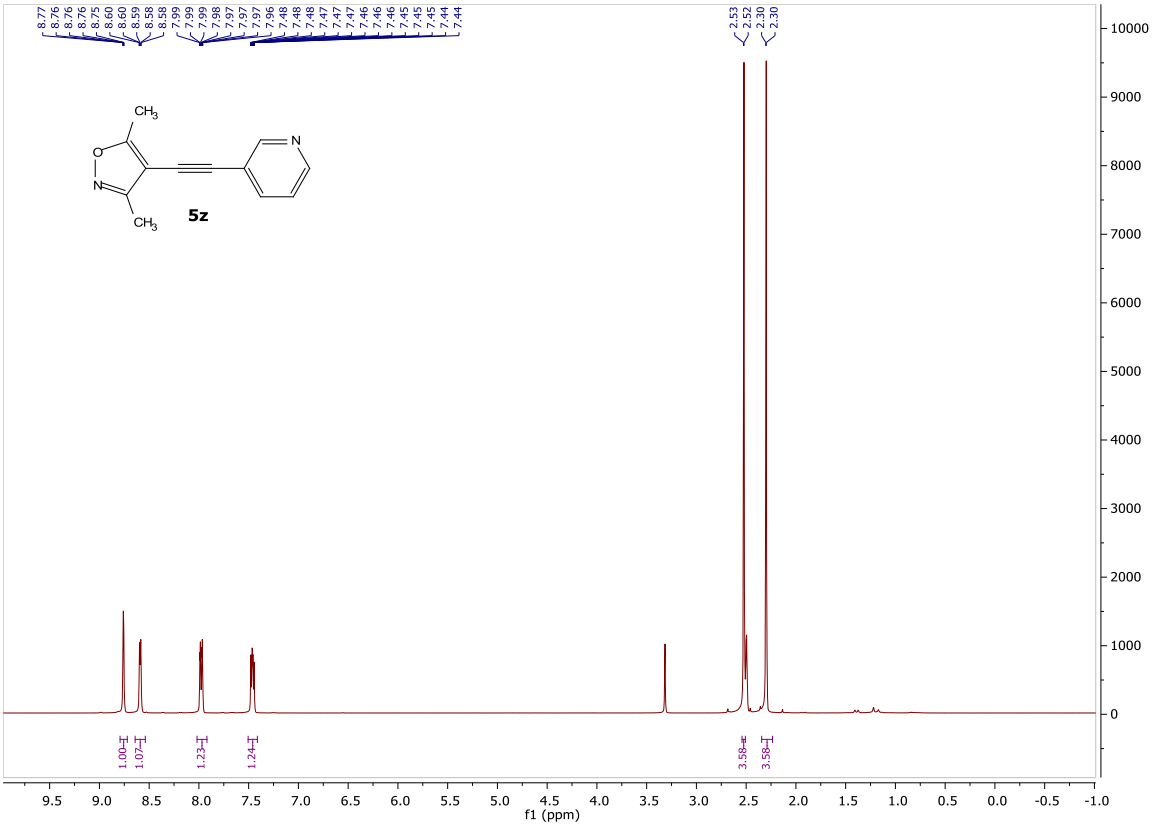


Figure S59: ^{13}C NMR

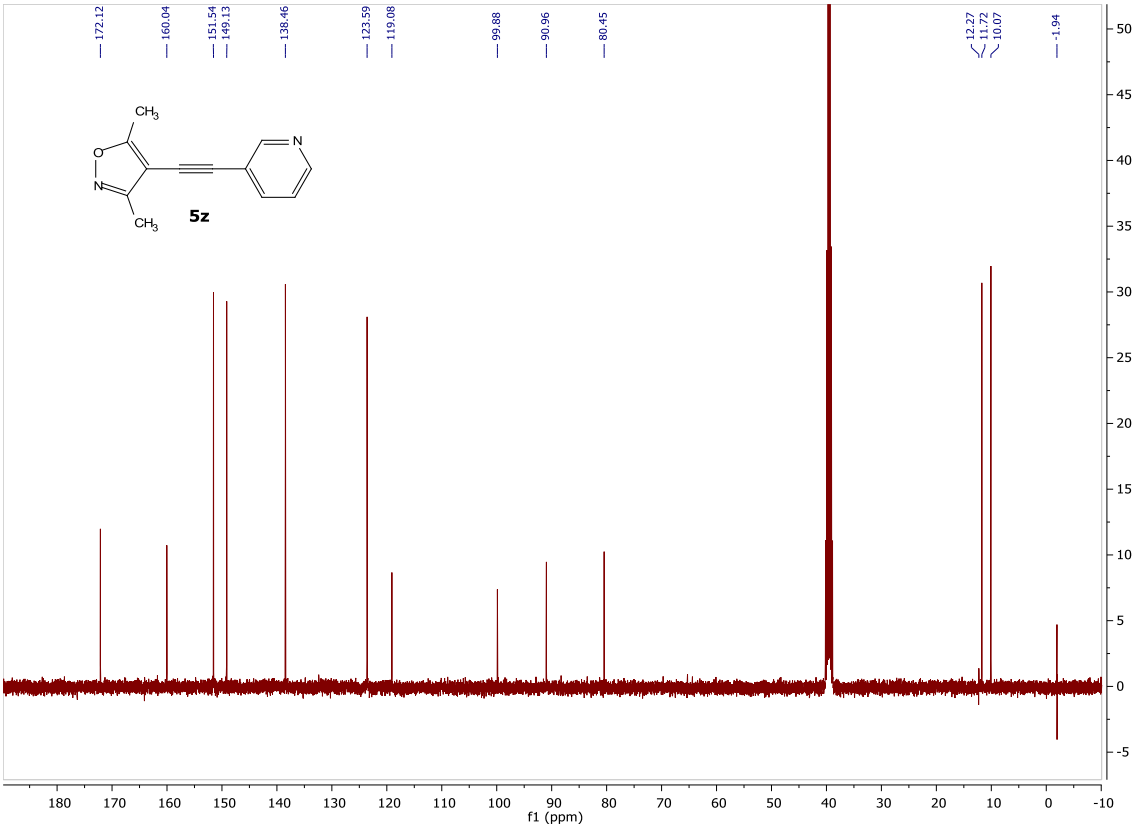


Figure S60: ^{1}H NMR

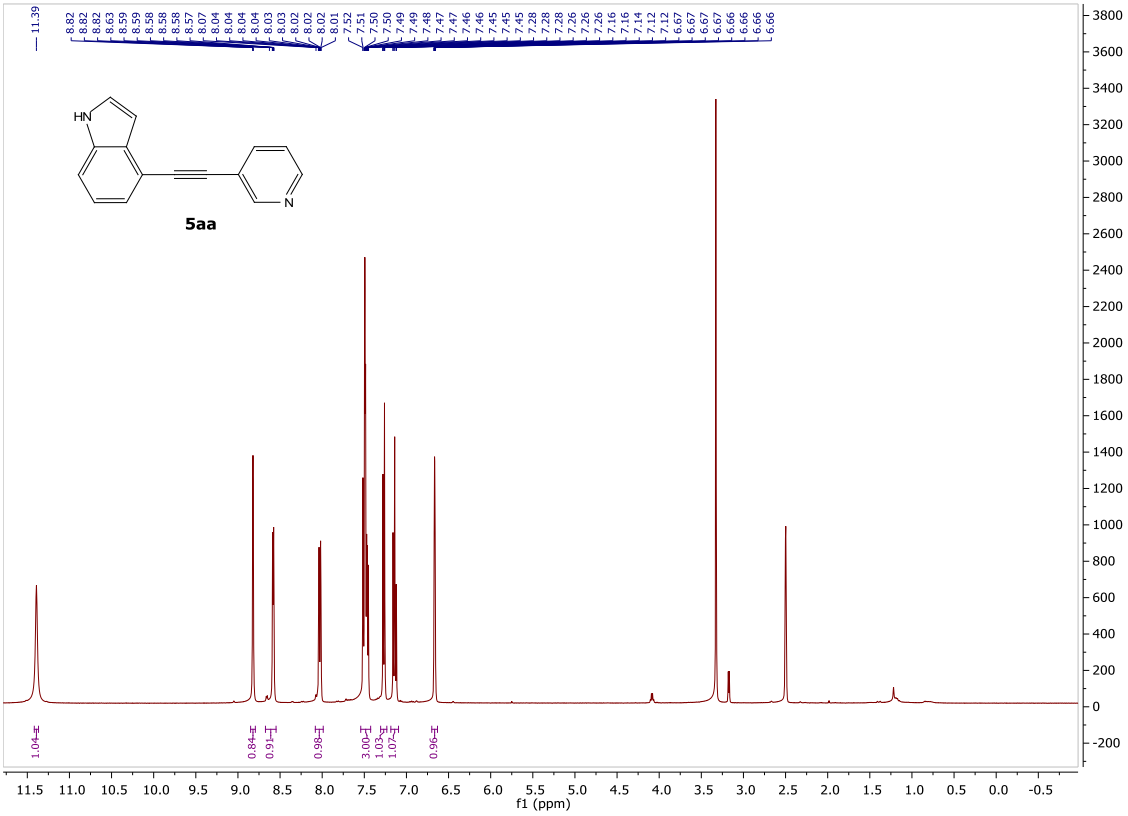


Figure S61: ^{13}C NMR

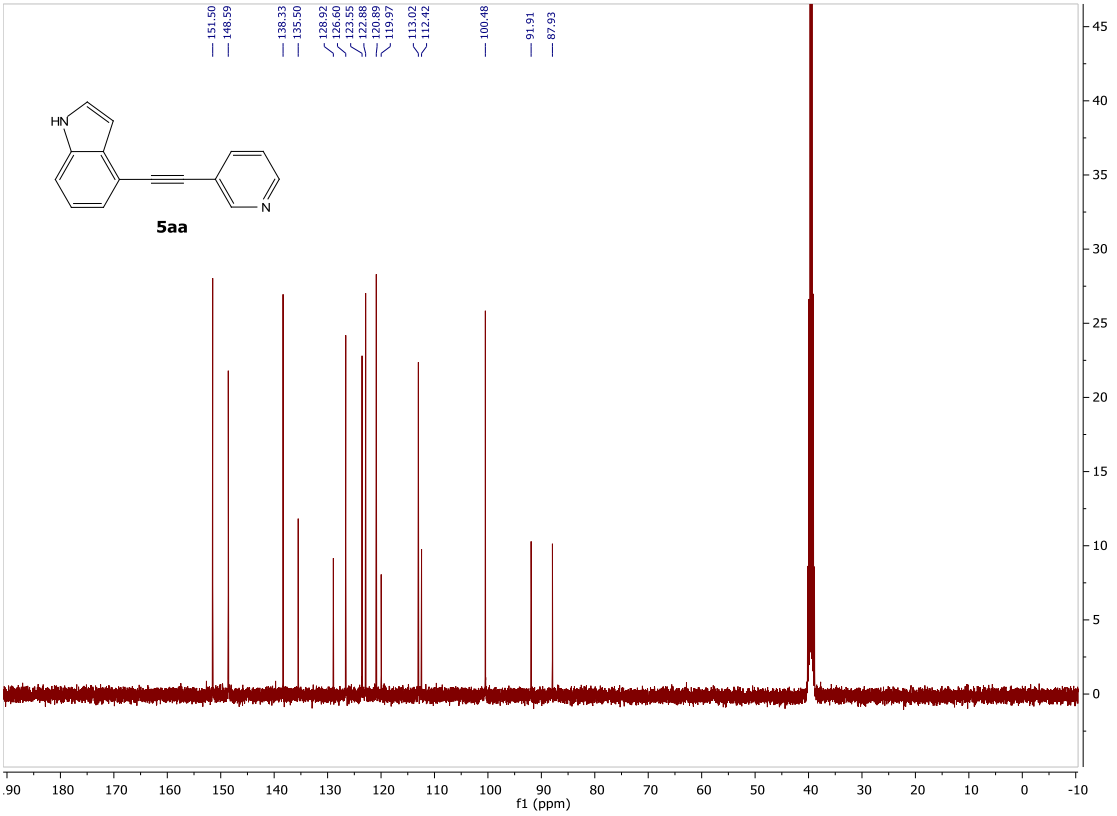


Figure S62: ^{1}H NMR

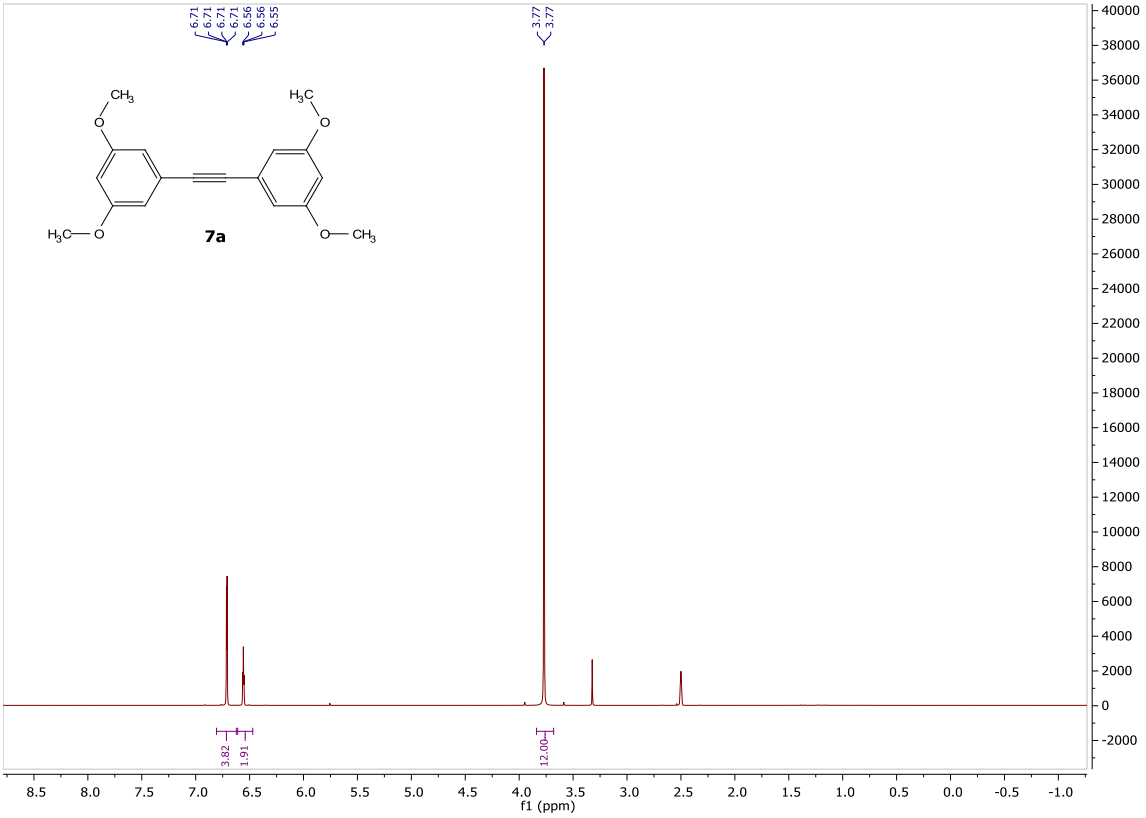


Figure S63: ^{13}C NMR

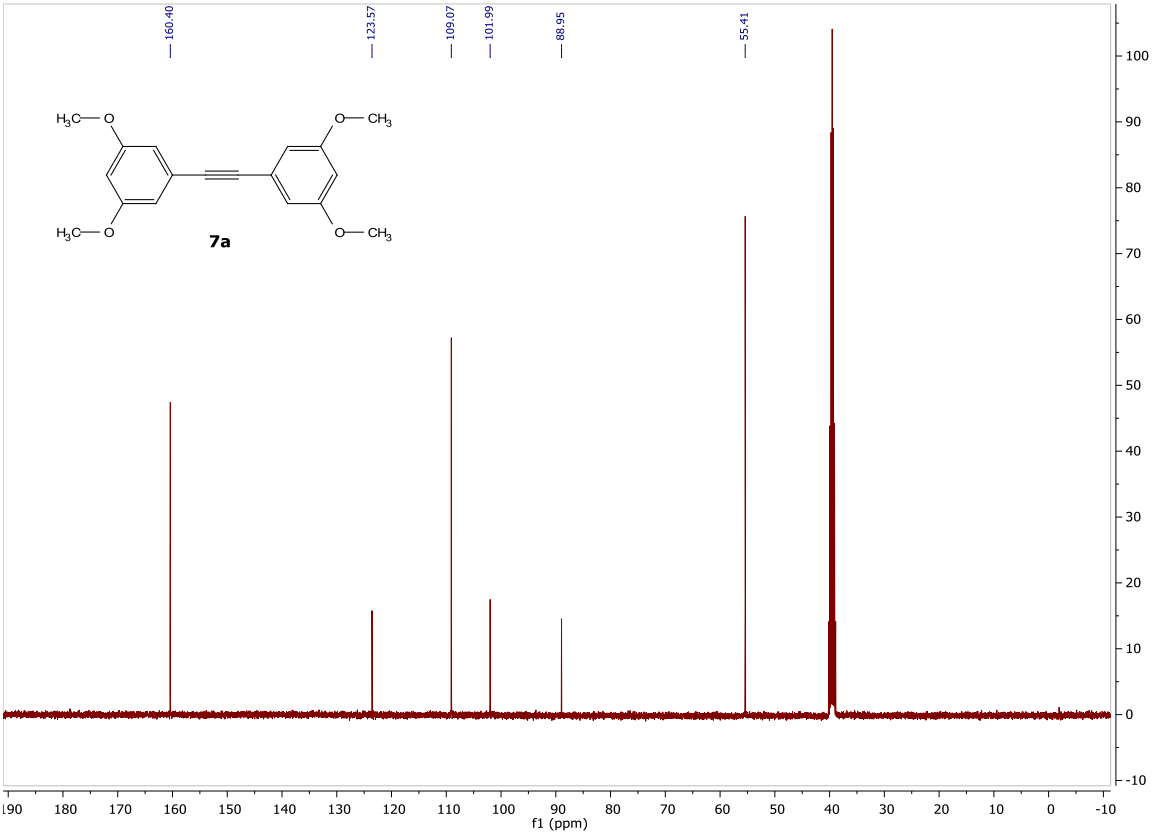


Figure S64: ^{1}H NMR

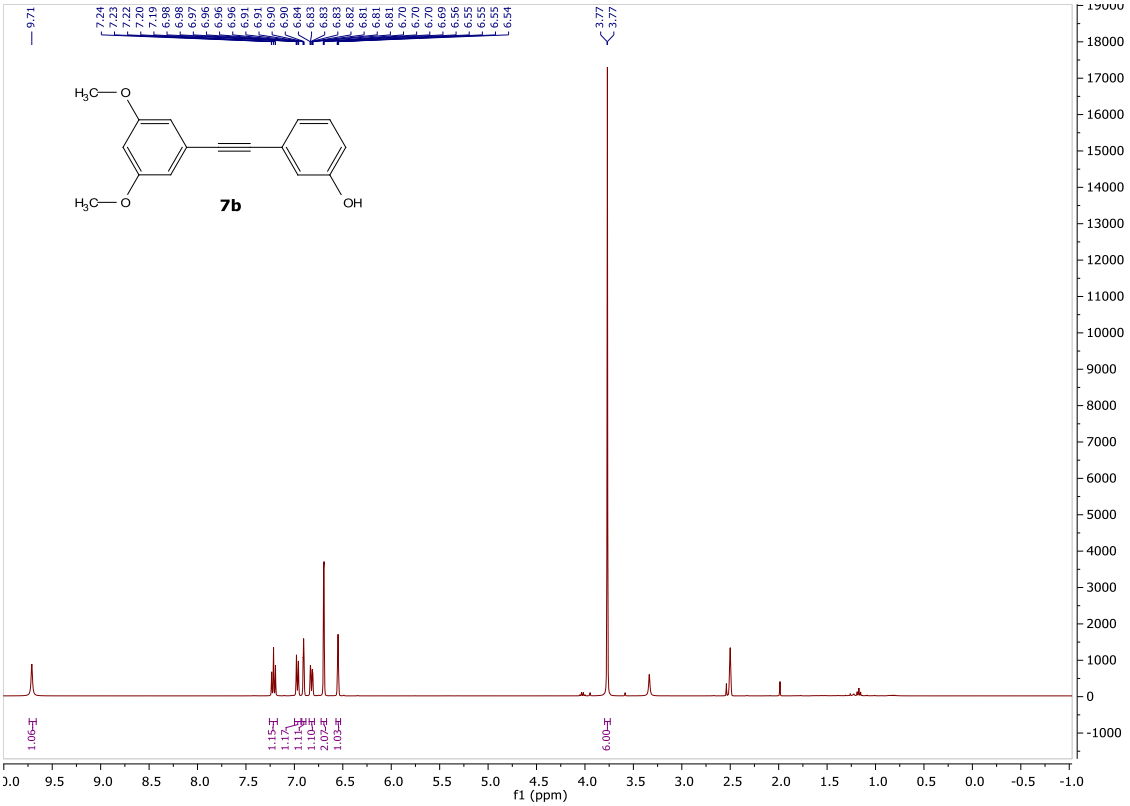


Figure S65: ^{13}C NMR

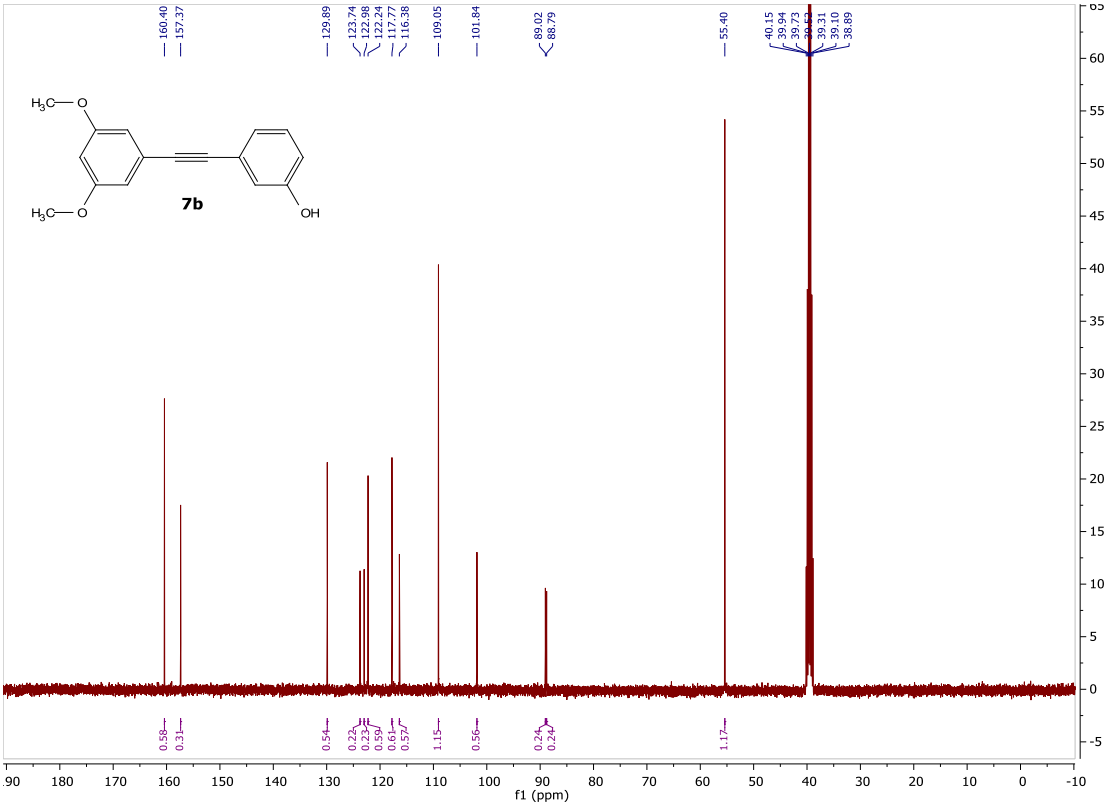


Figure S66: ^{1}H NMR

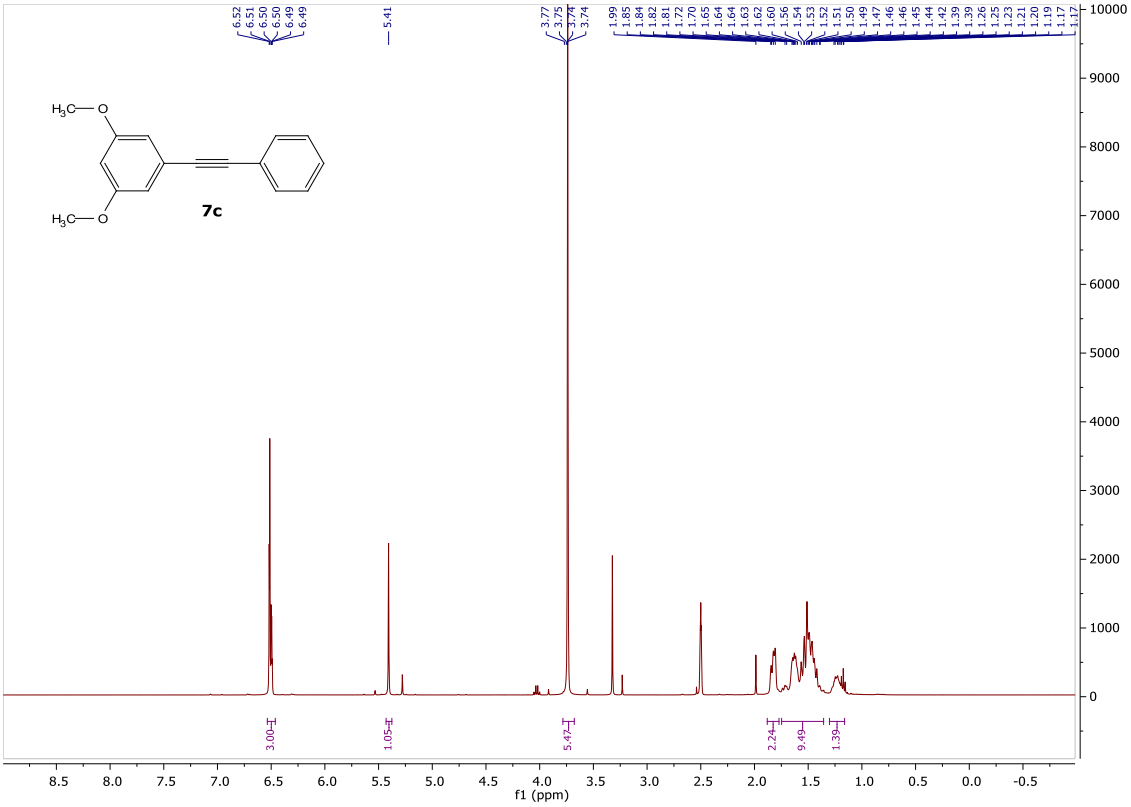


Figure S67: ^{13}C NMR

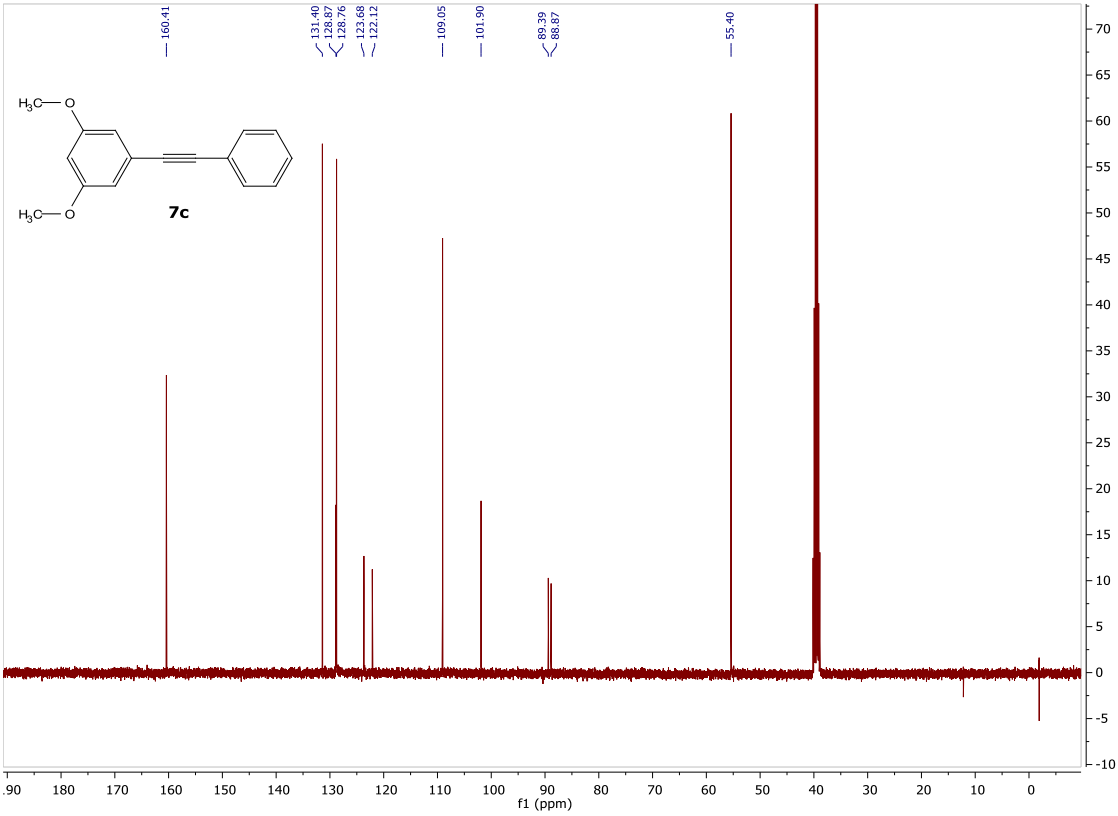


Figure S68: ^{1}H NMR

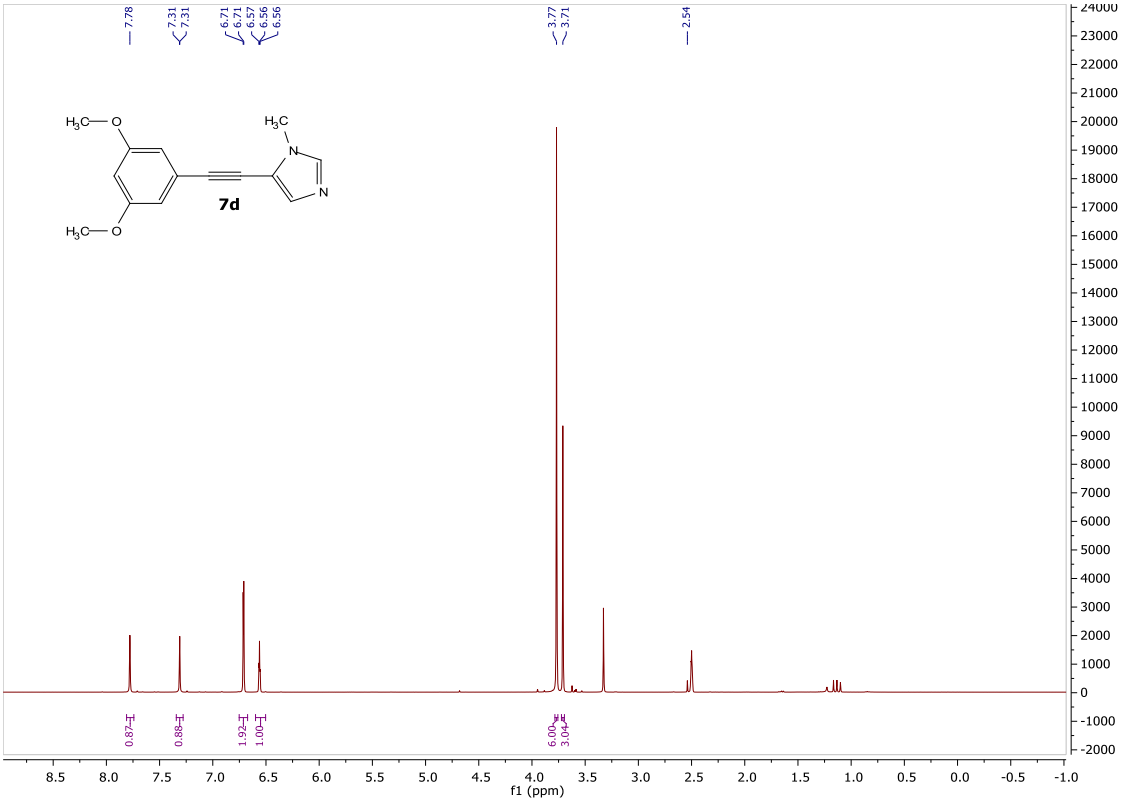


Figure S69: ^{13}C NMR

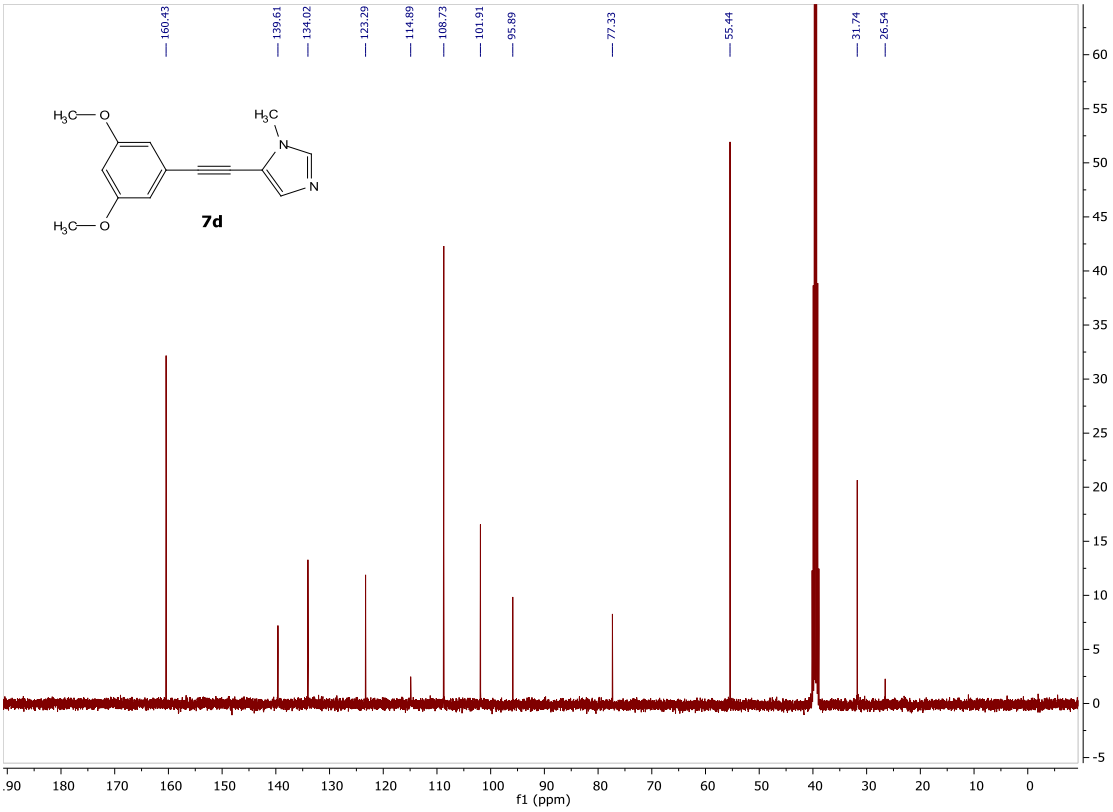


Figure S70: ^{1}H NMR

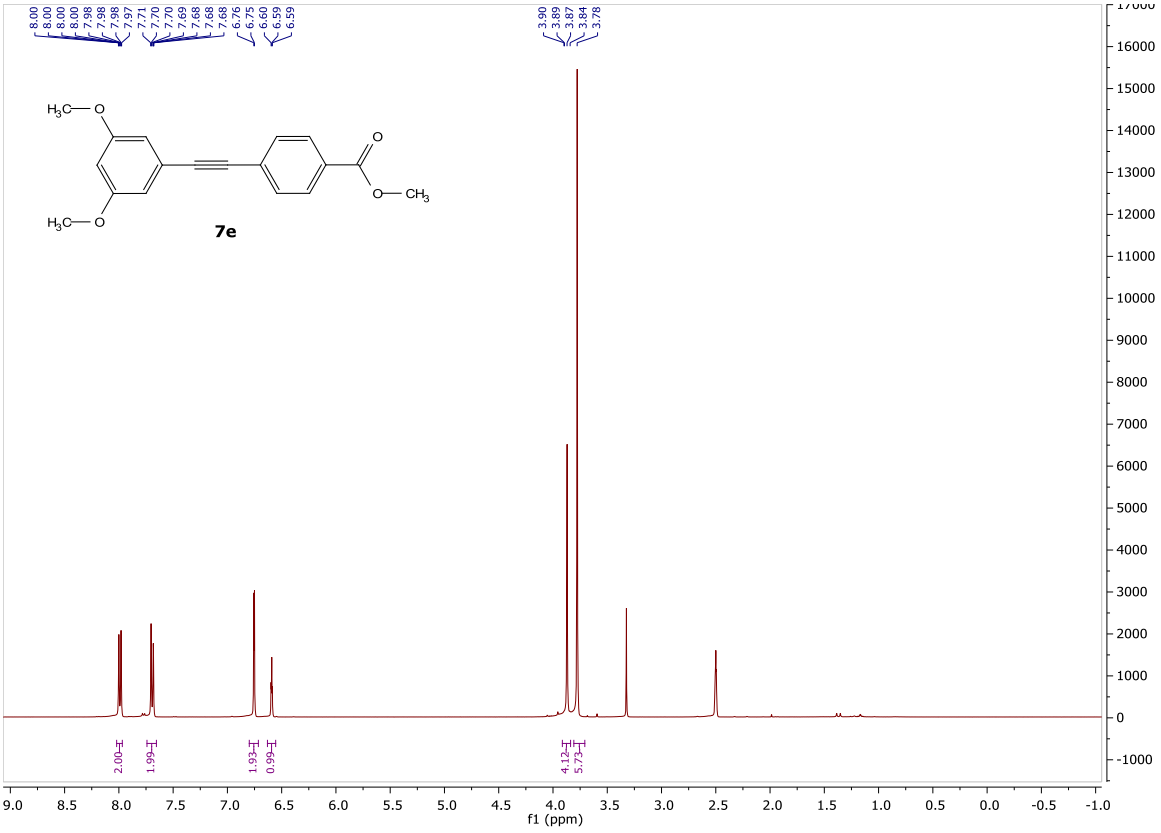


Figure S71: ^{13}C NMR

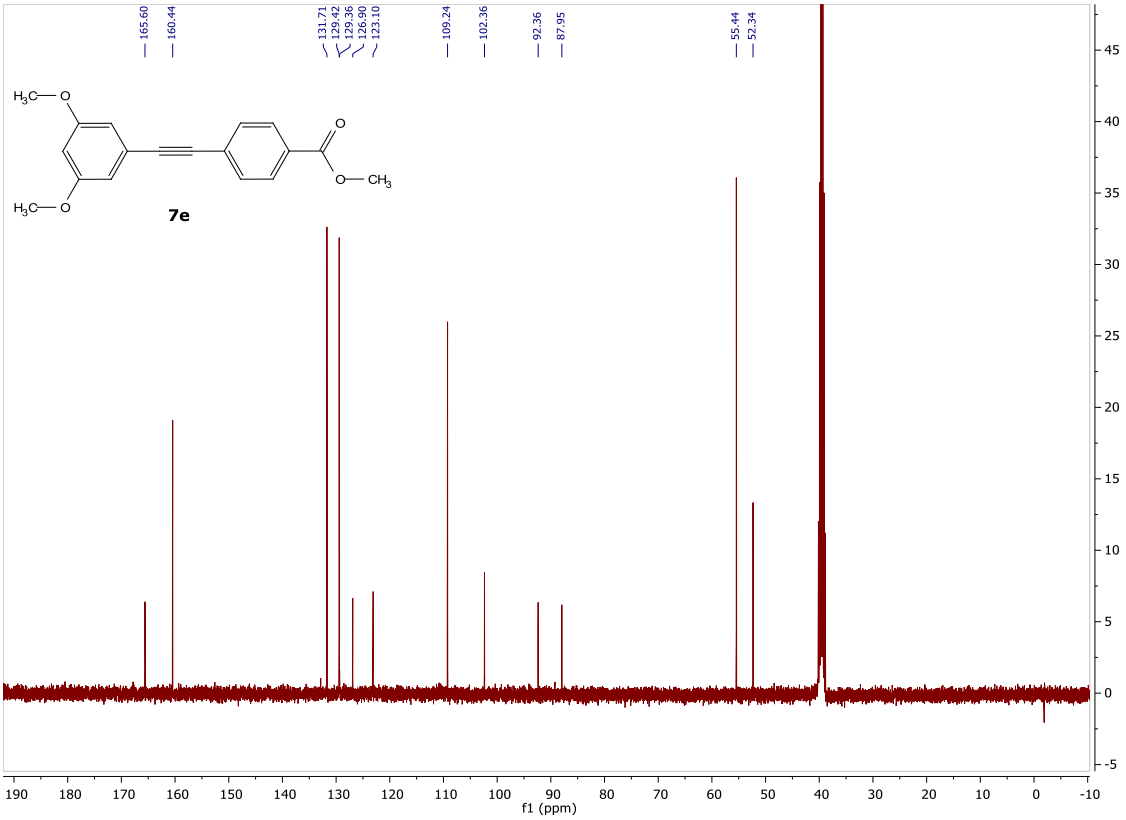


Figure S72: ^{1}H NMR

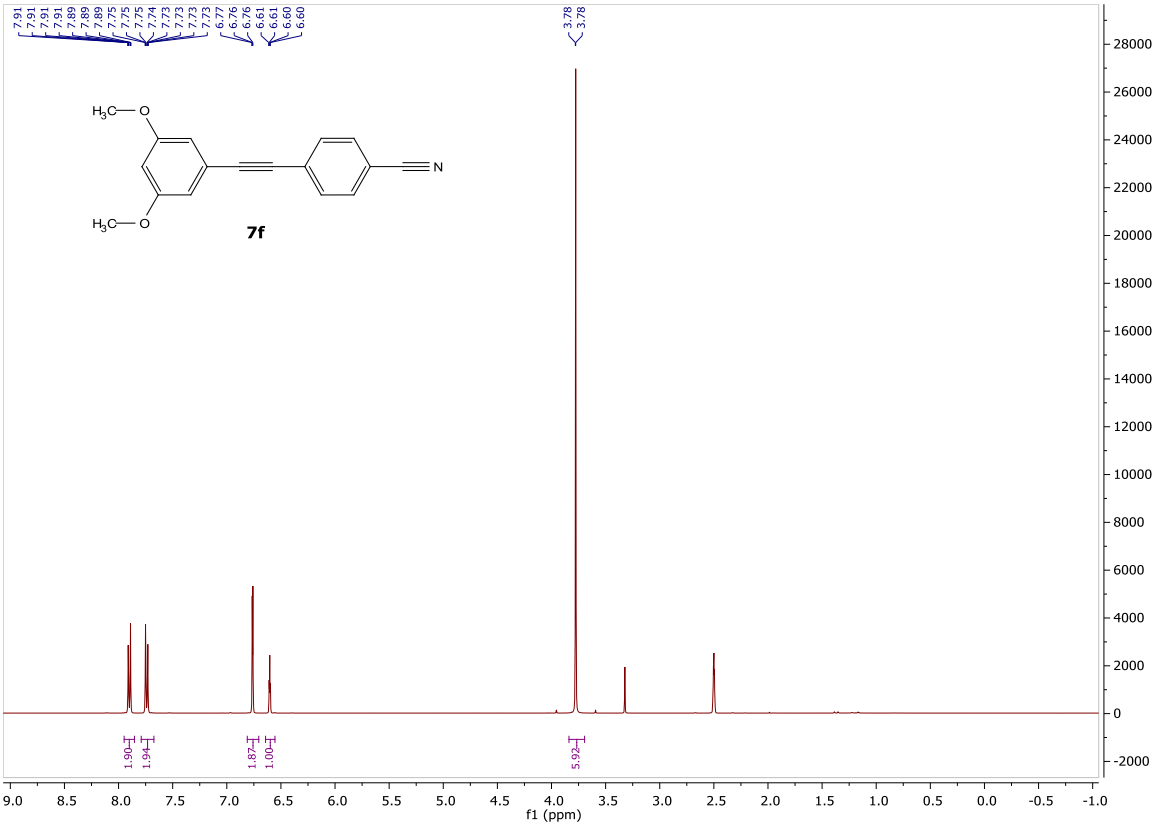


Figure S73: ^{13}C NMR

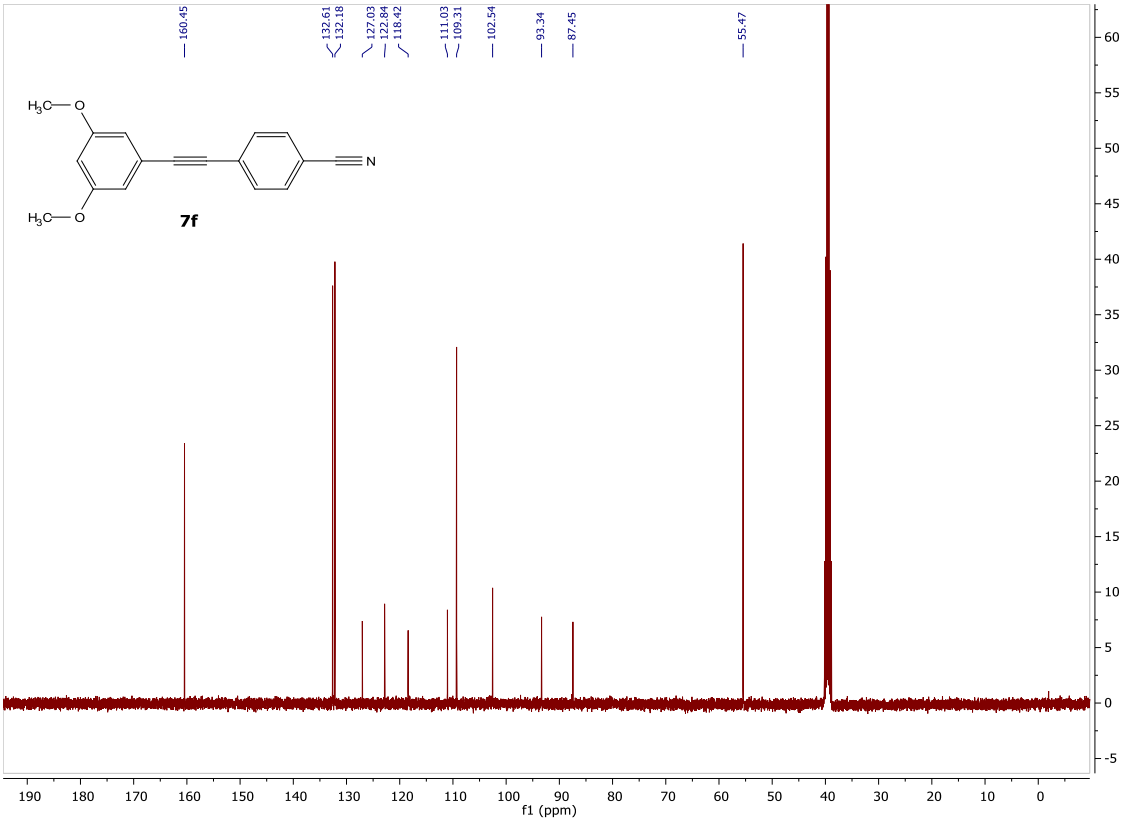


Figure S74: ^{1}H NMR

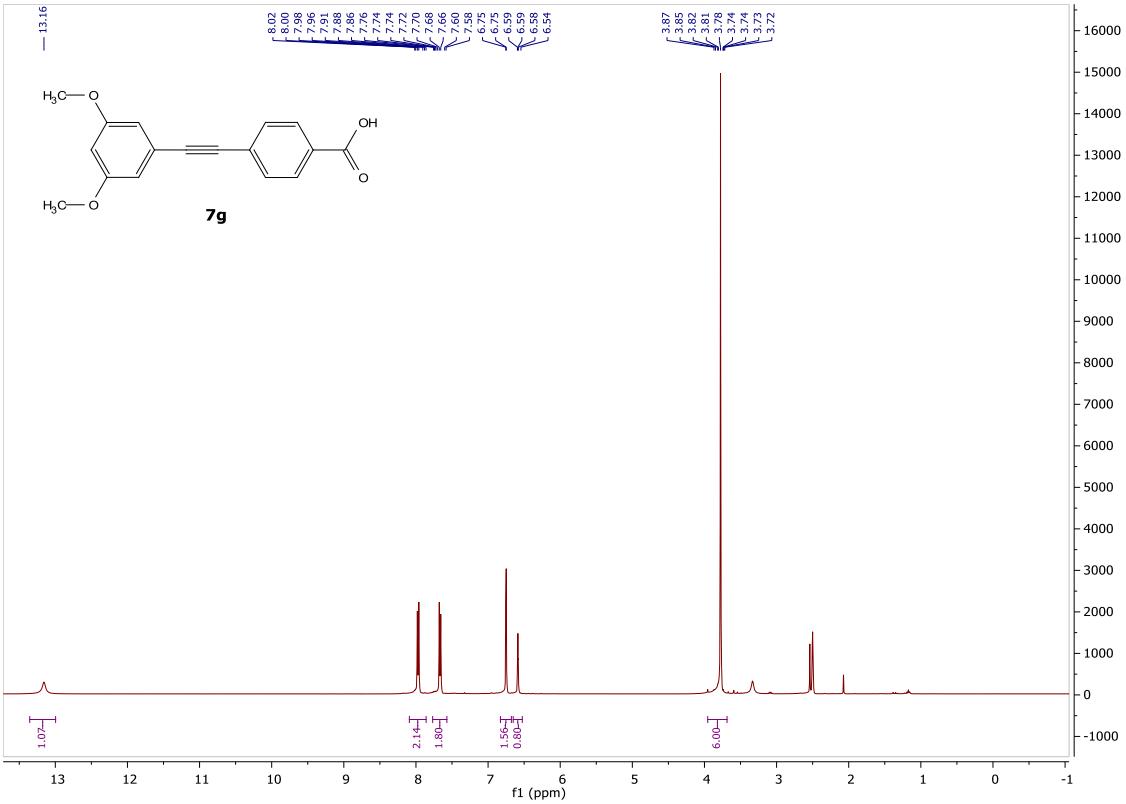


Figure S75: ^{13}C NMR

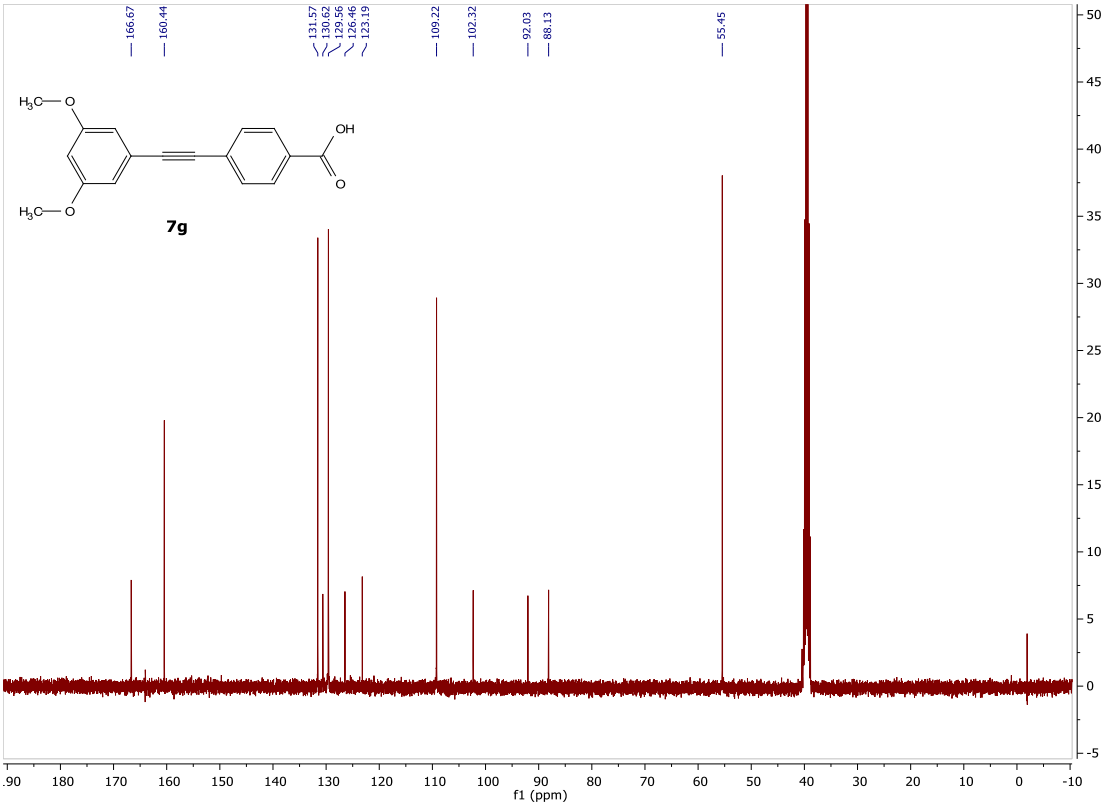


Figure S76: ^{1}H NMR

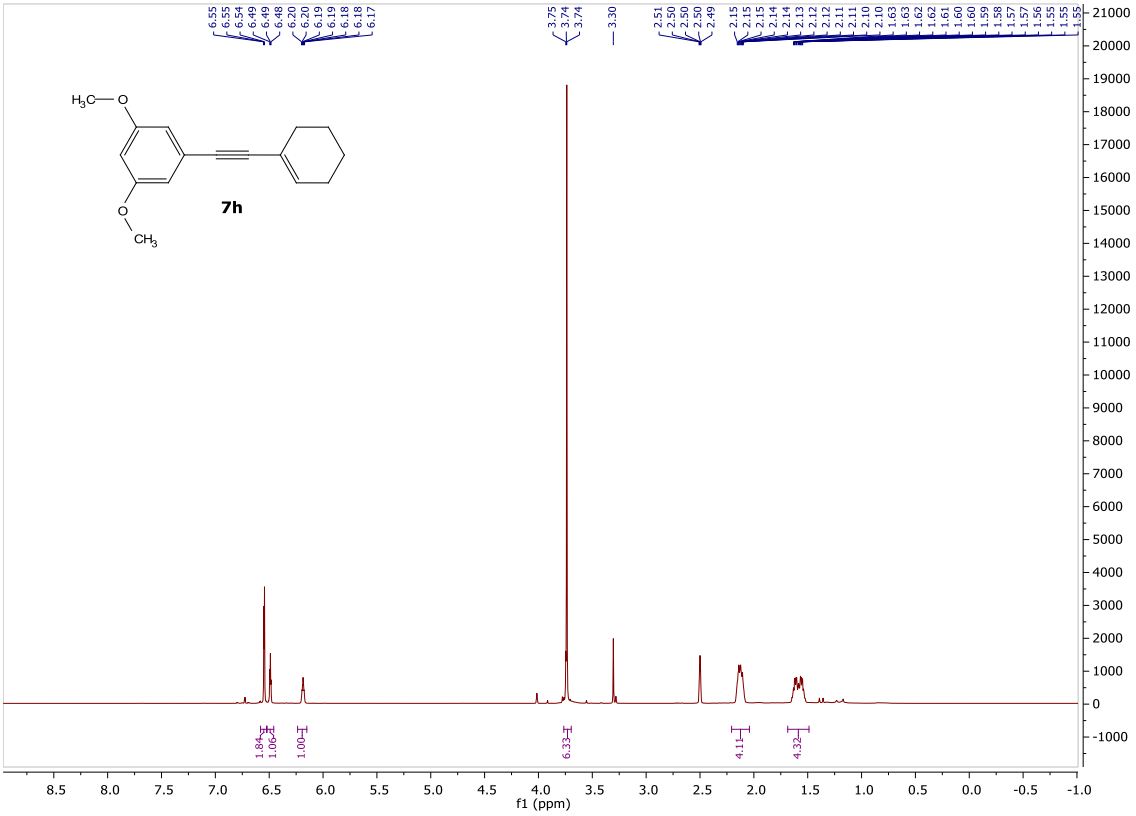


Figure S77: ^{13}C NMR

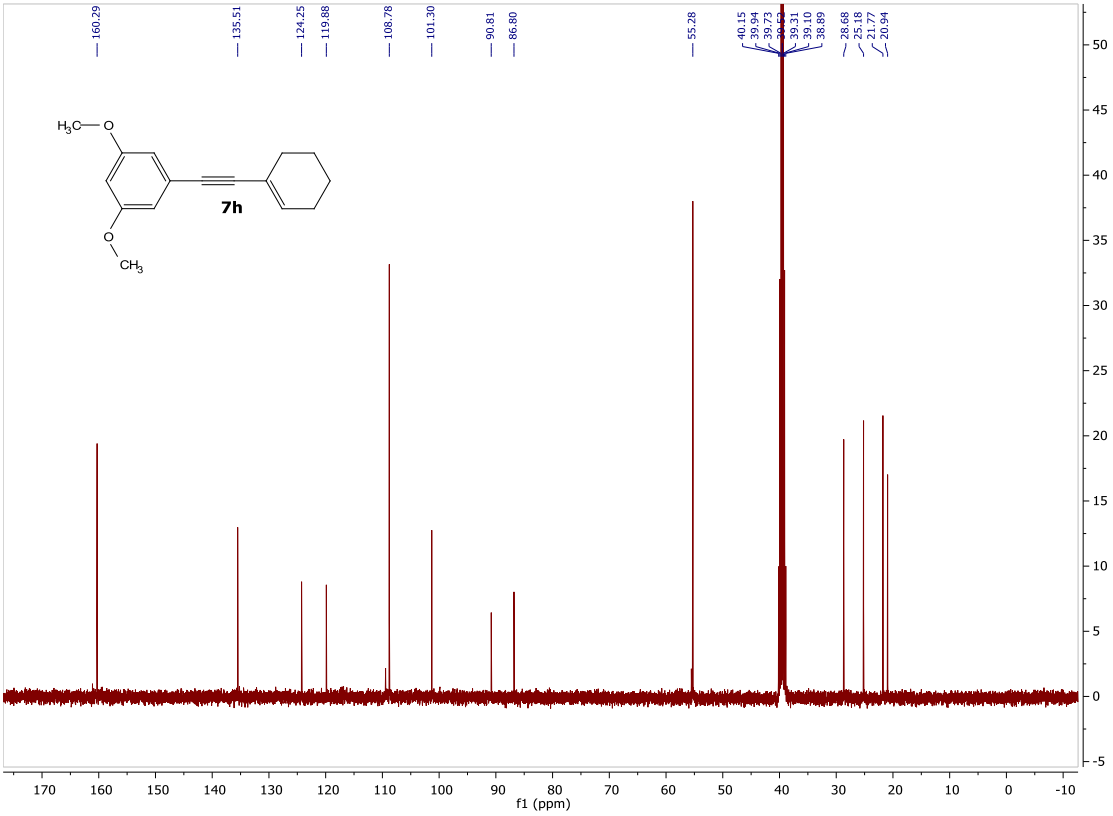


Figure S78: ^{1}H NMR

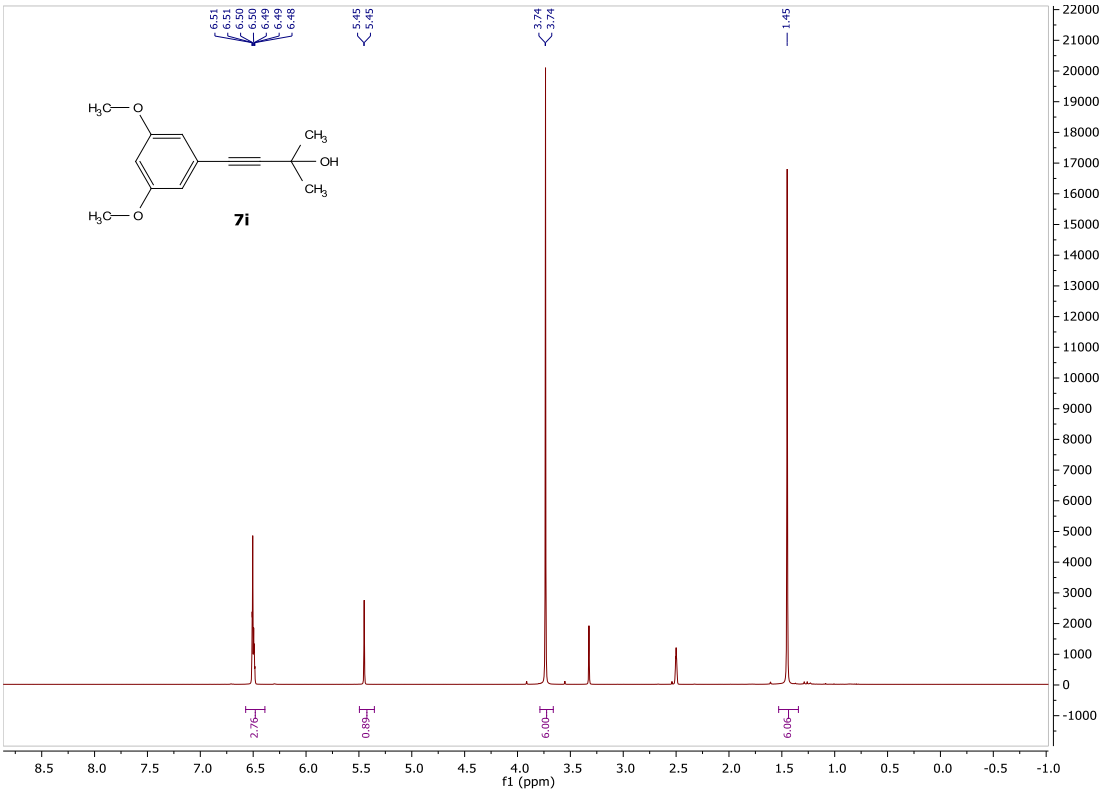


Figure S79: ^{13}C NMR

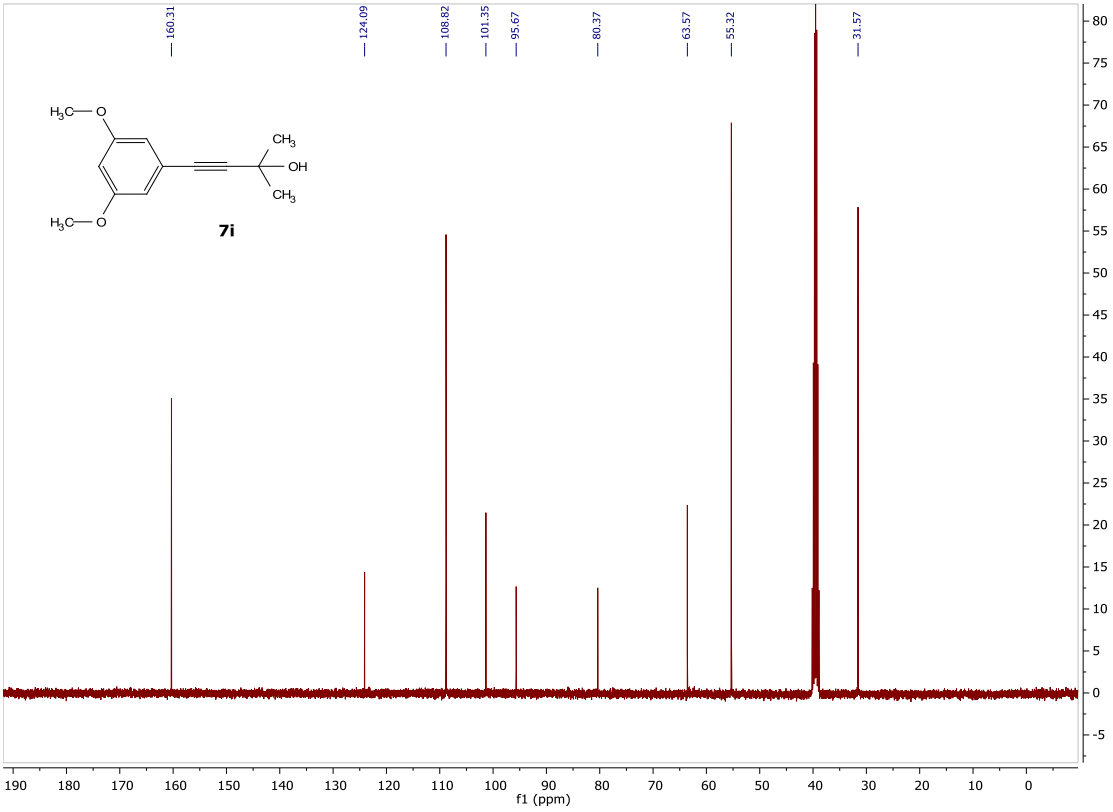


Figure S80: ^{1}H NMR

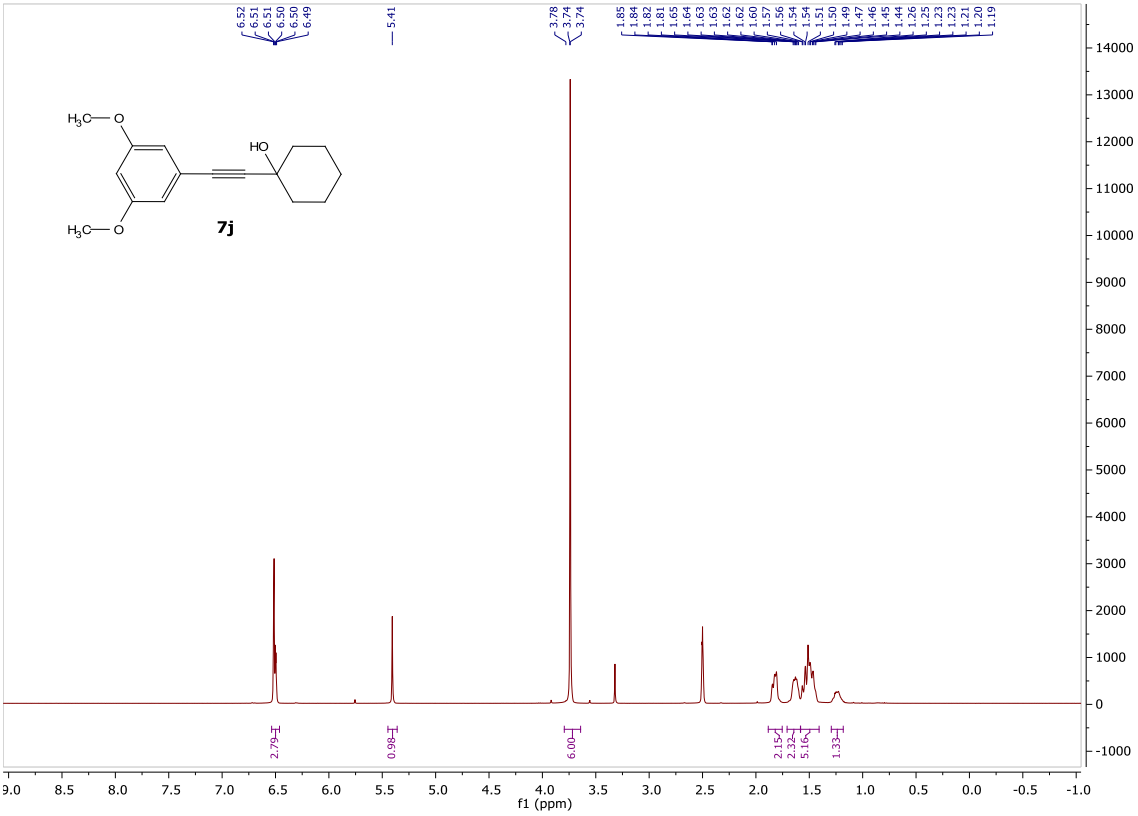


Figure S81: ^{13}C NMR

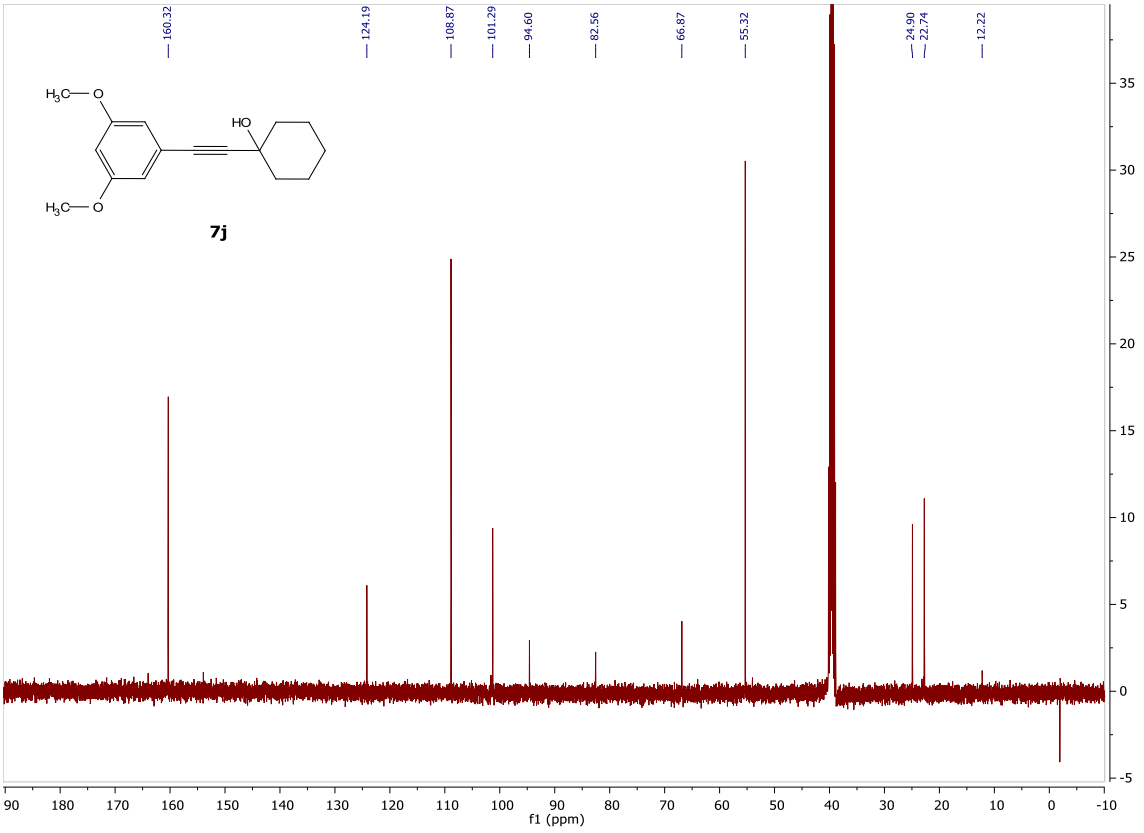


Figure S82: ^{1}H NMR

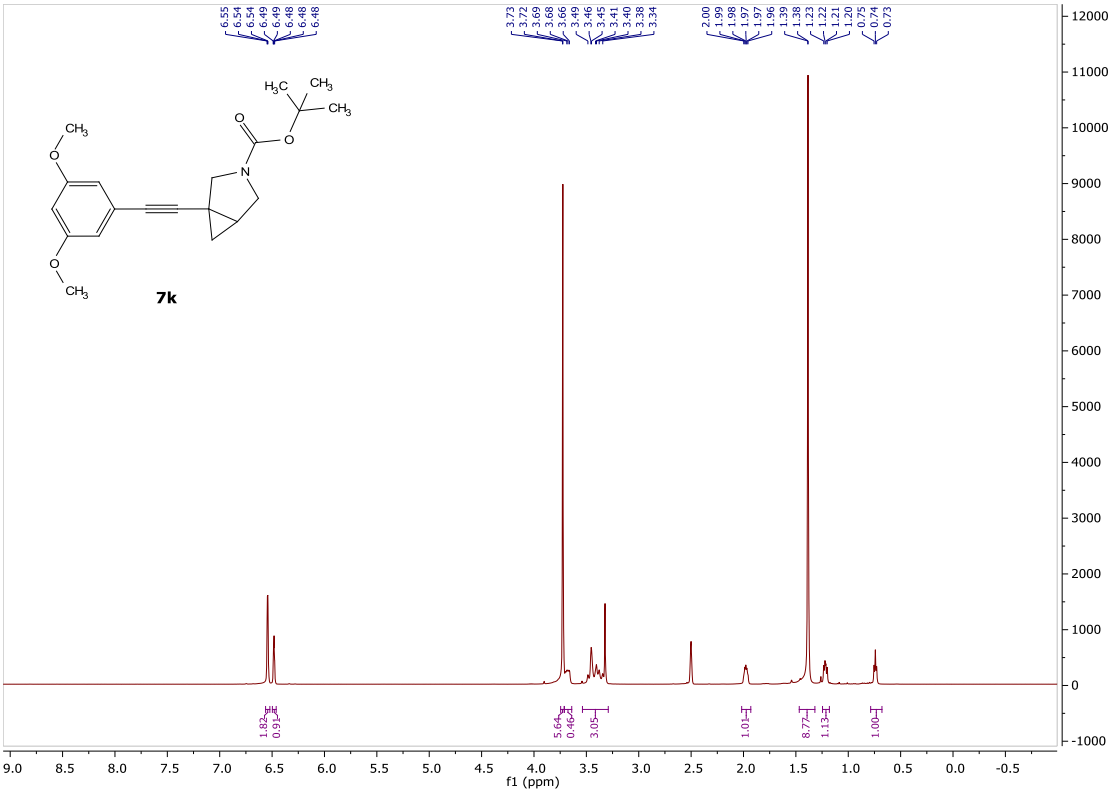


Figure S83: ^{13}C NMR

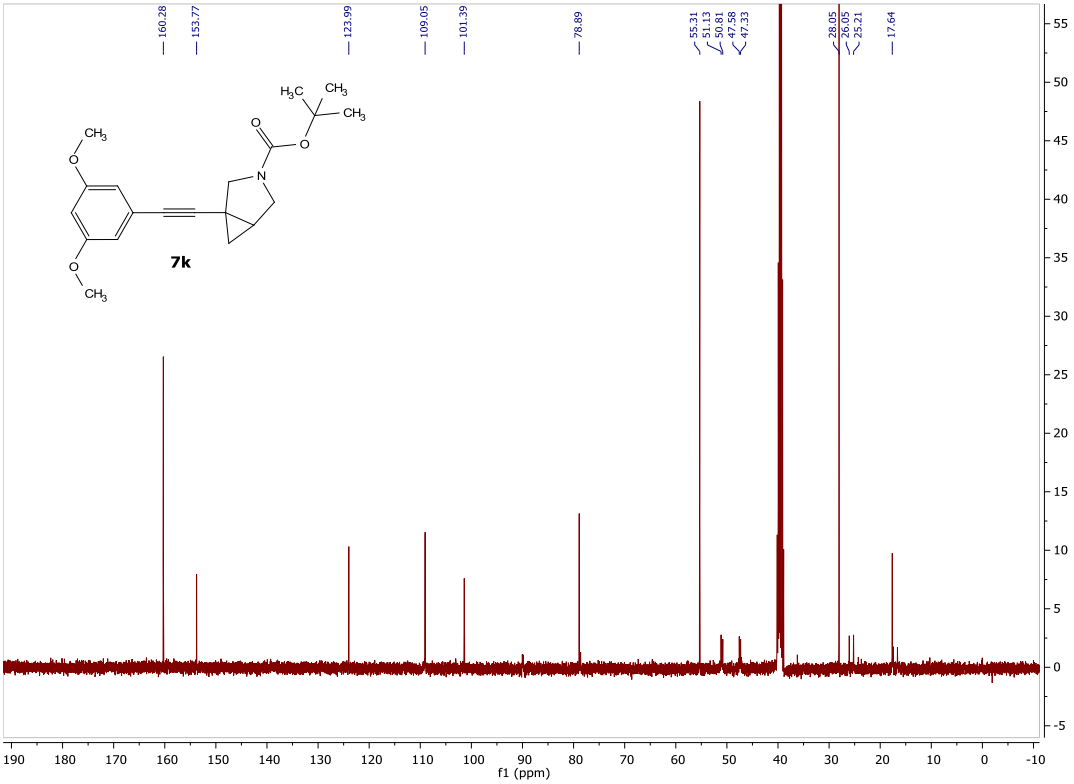


Figure S84: ^{1}H NMR

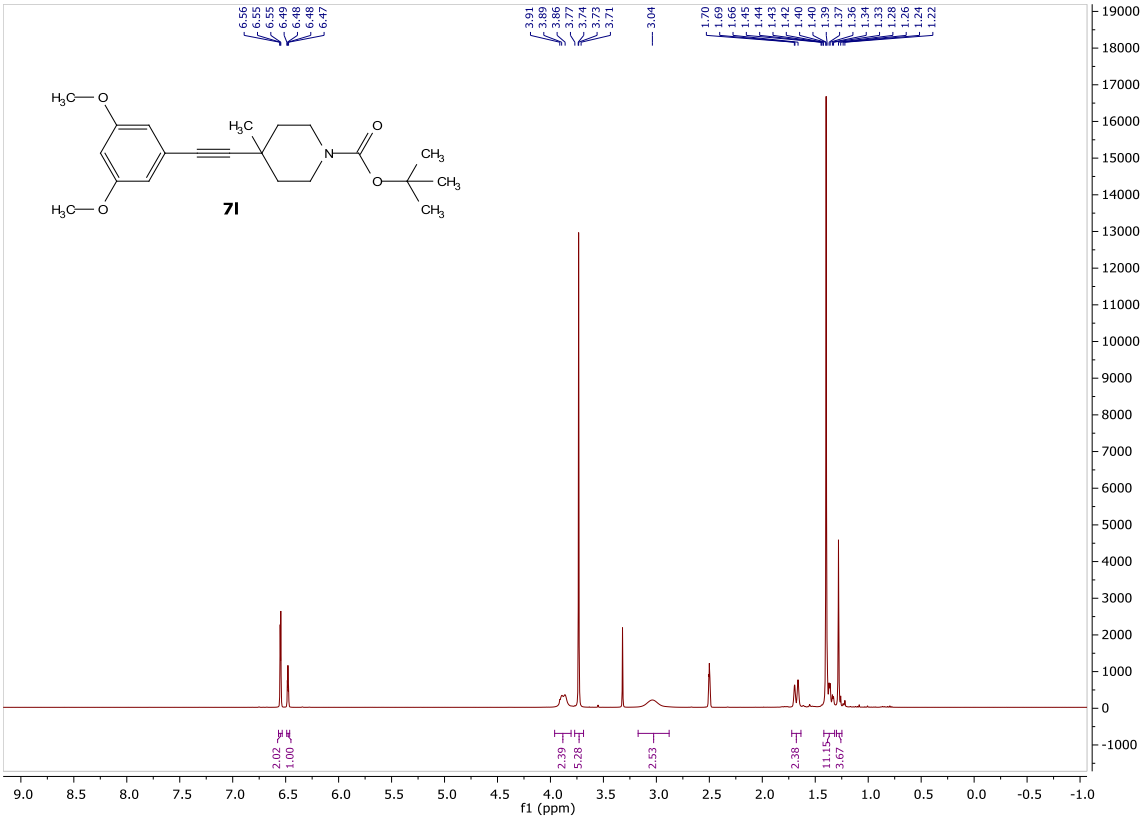


Figure S85: ^{13}C NMR

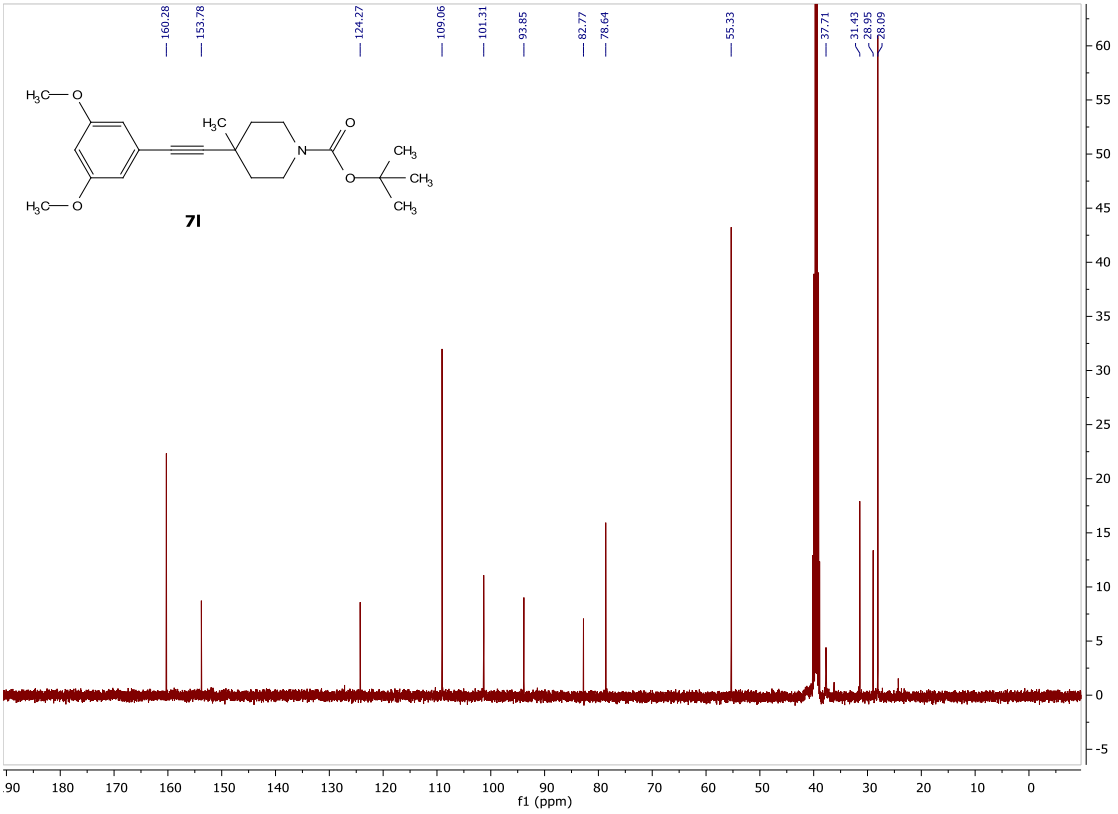


Figure S86: ^{1}H NMR

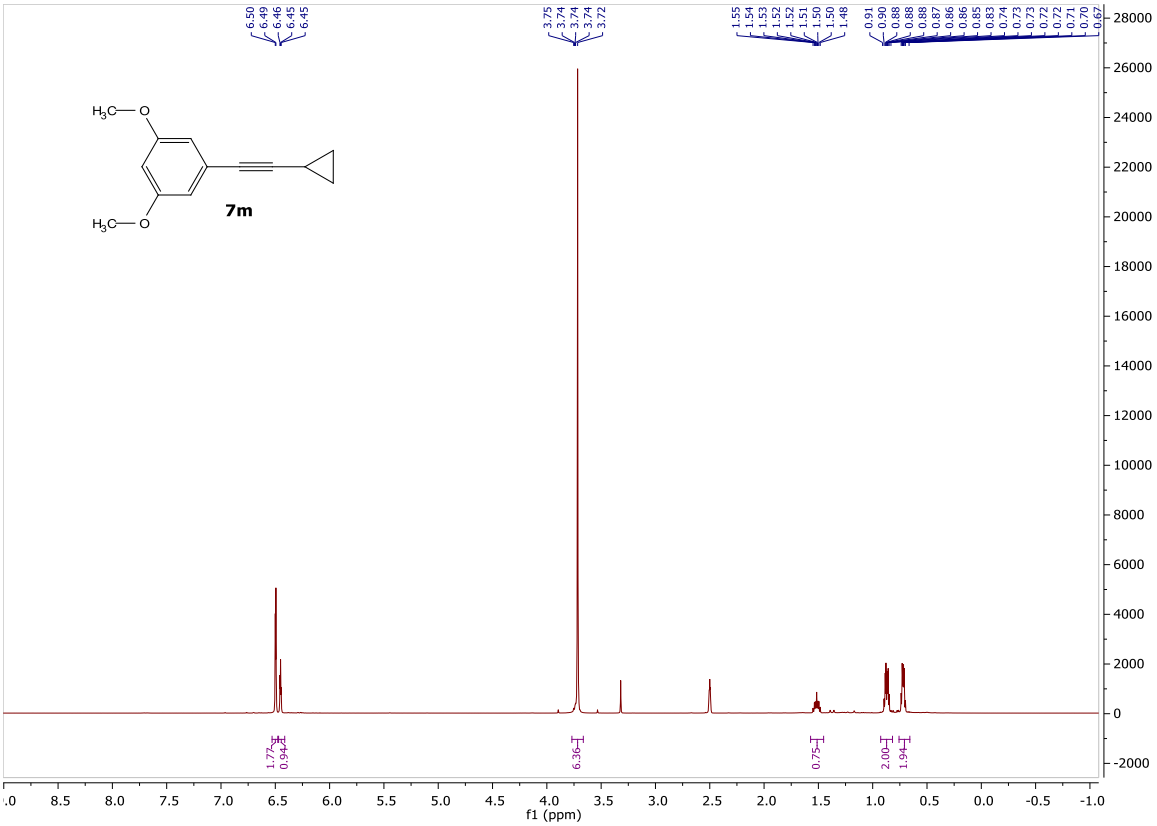


Figure S87: ^{13}C NMR

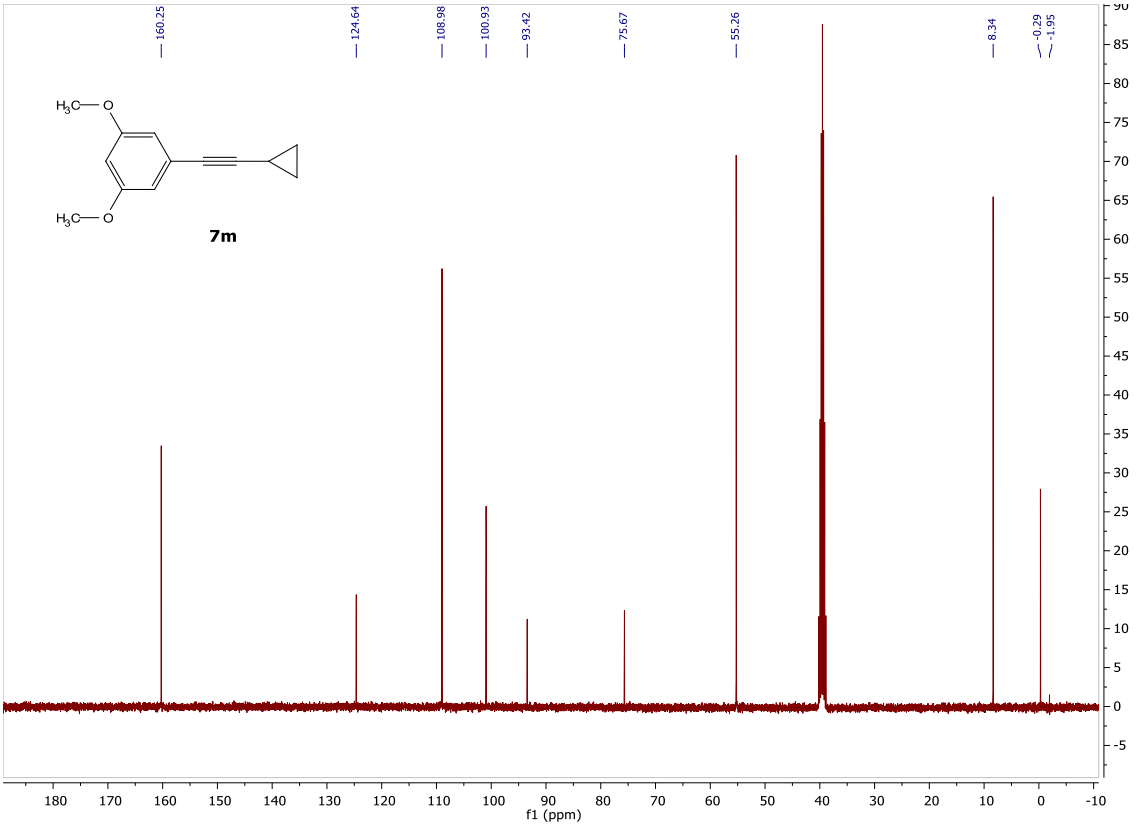


Figure S88: ^{1}H NMR

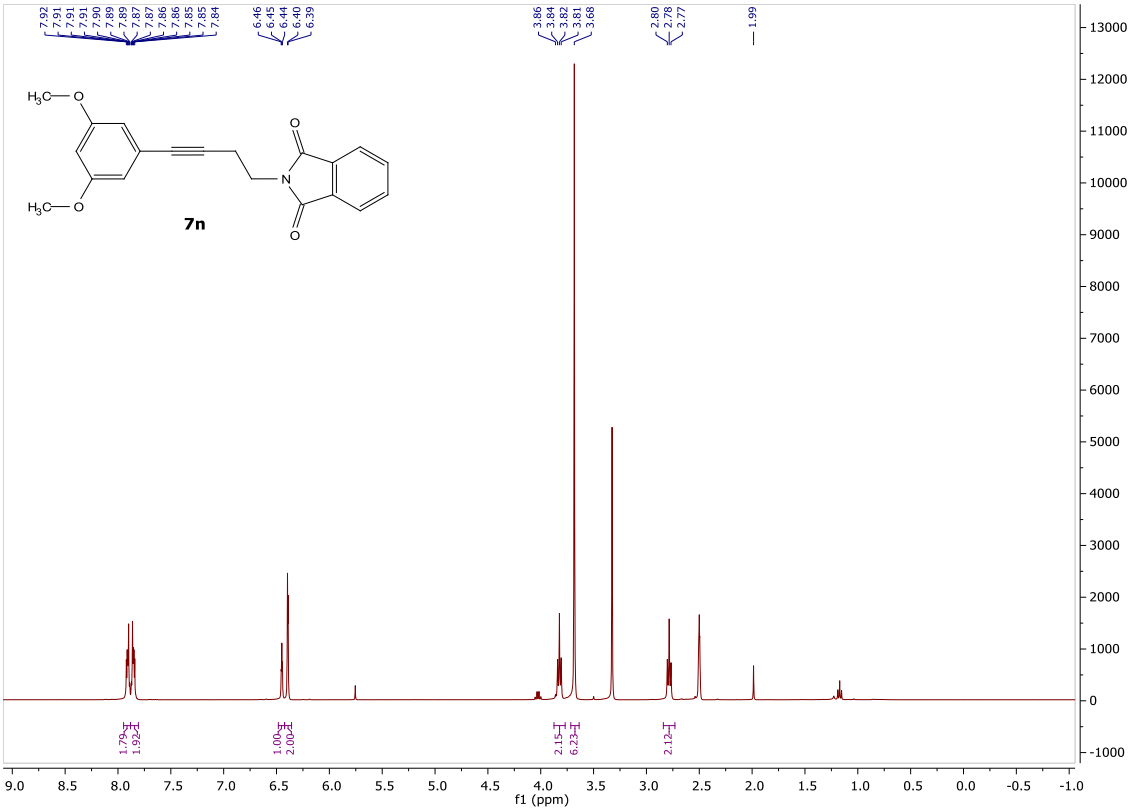


Figure S89: ^{13}C NMR

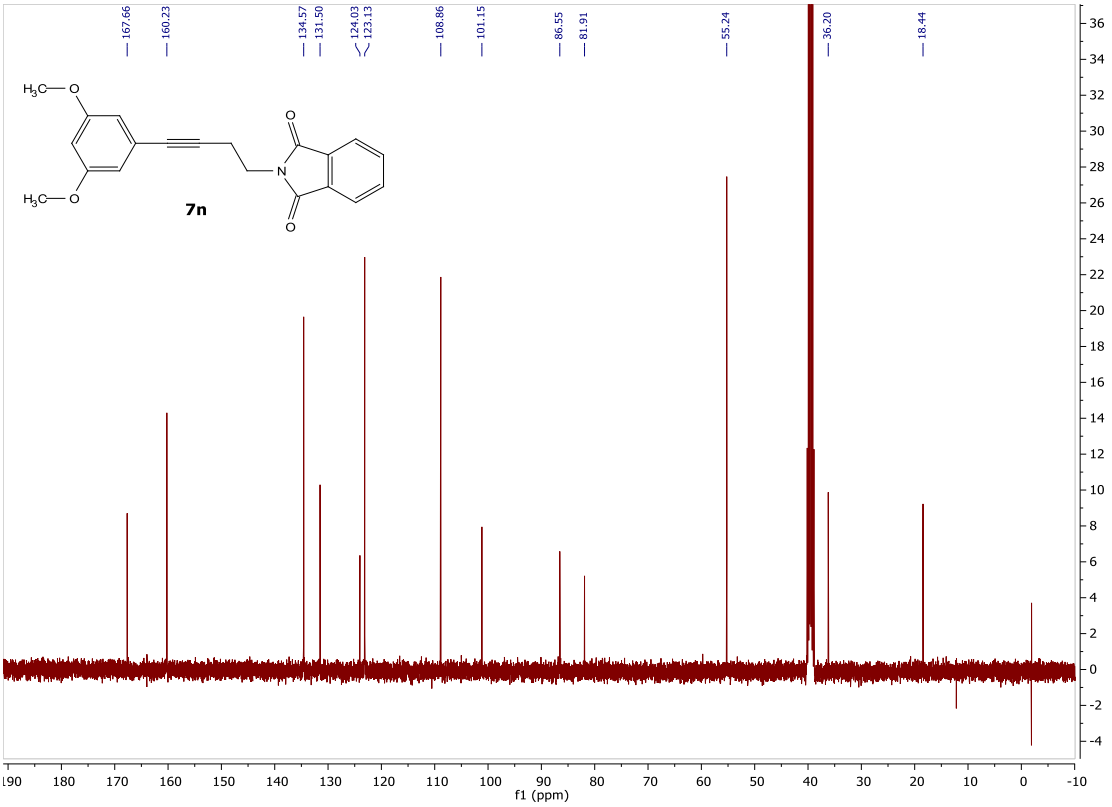


Figure S90: ^{1}H NMR

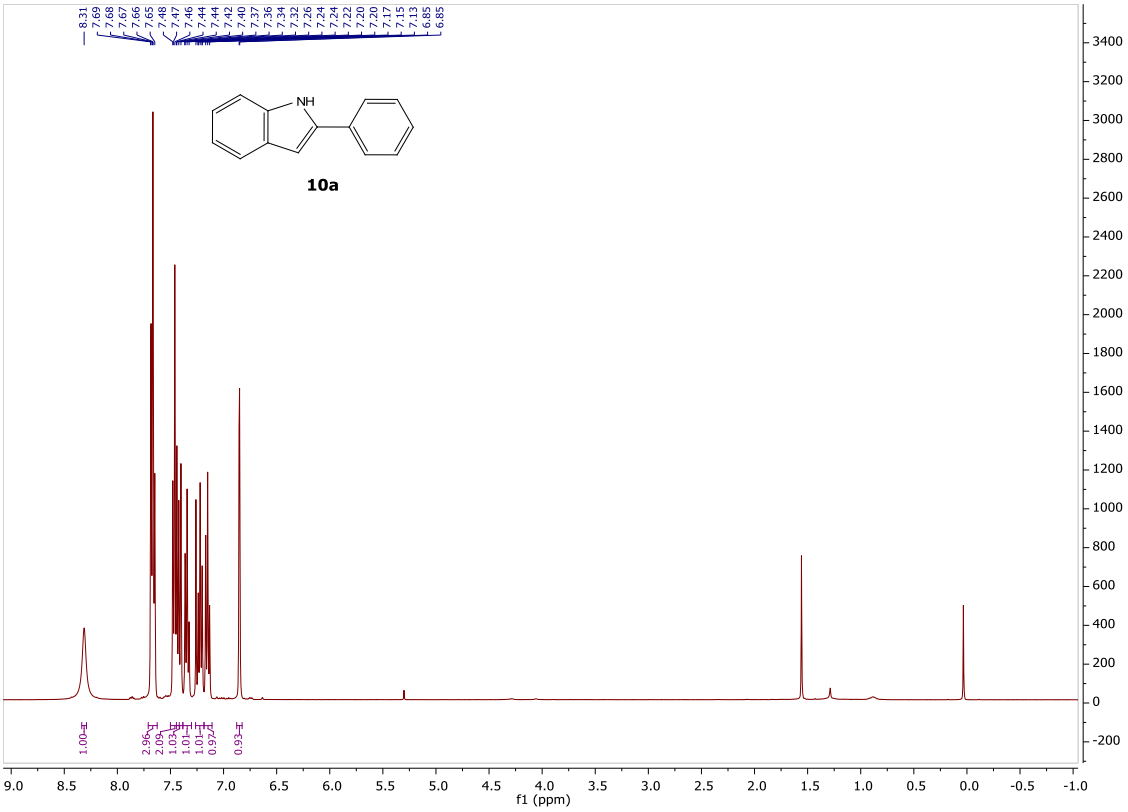


Figure S91: ^{13}C NMR

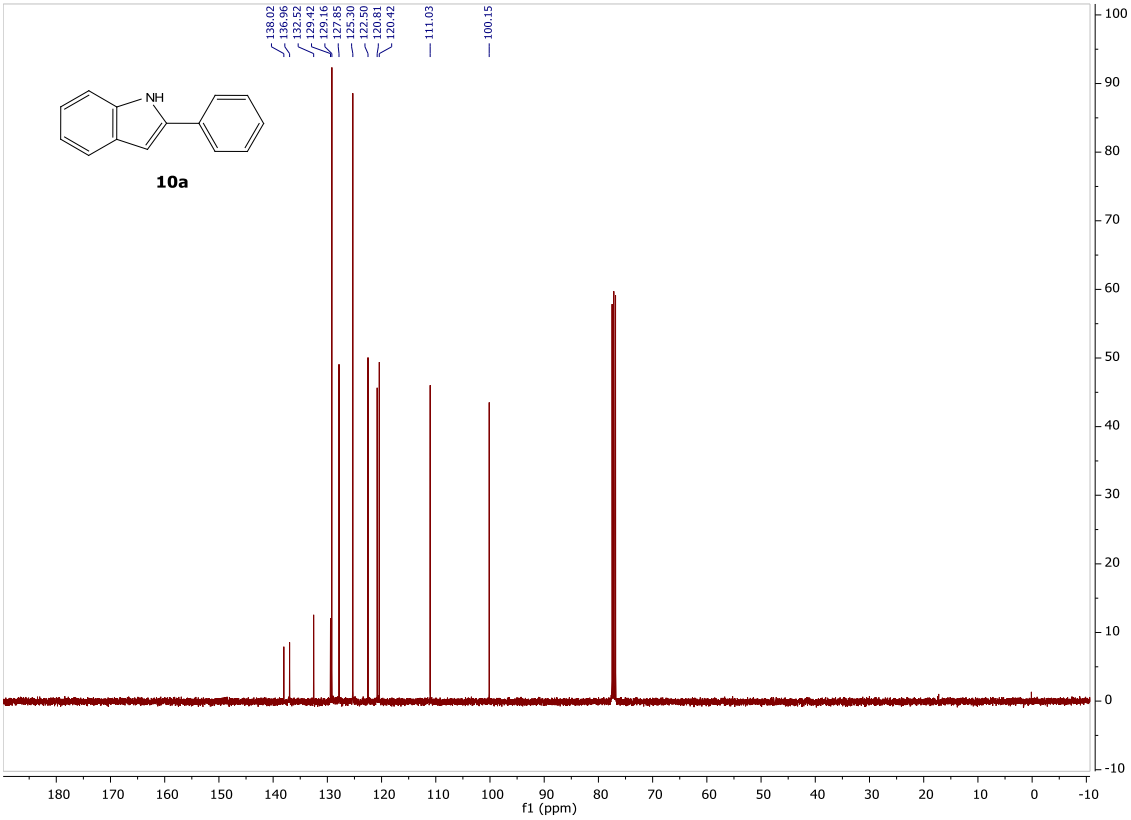


Figure S92: ^{1}H NMR

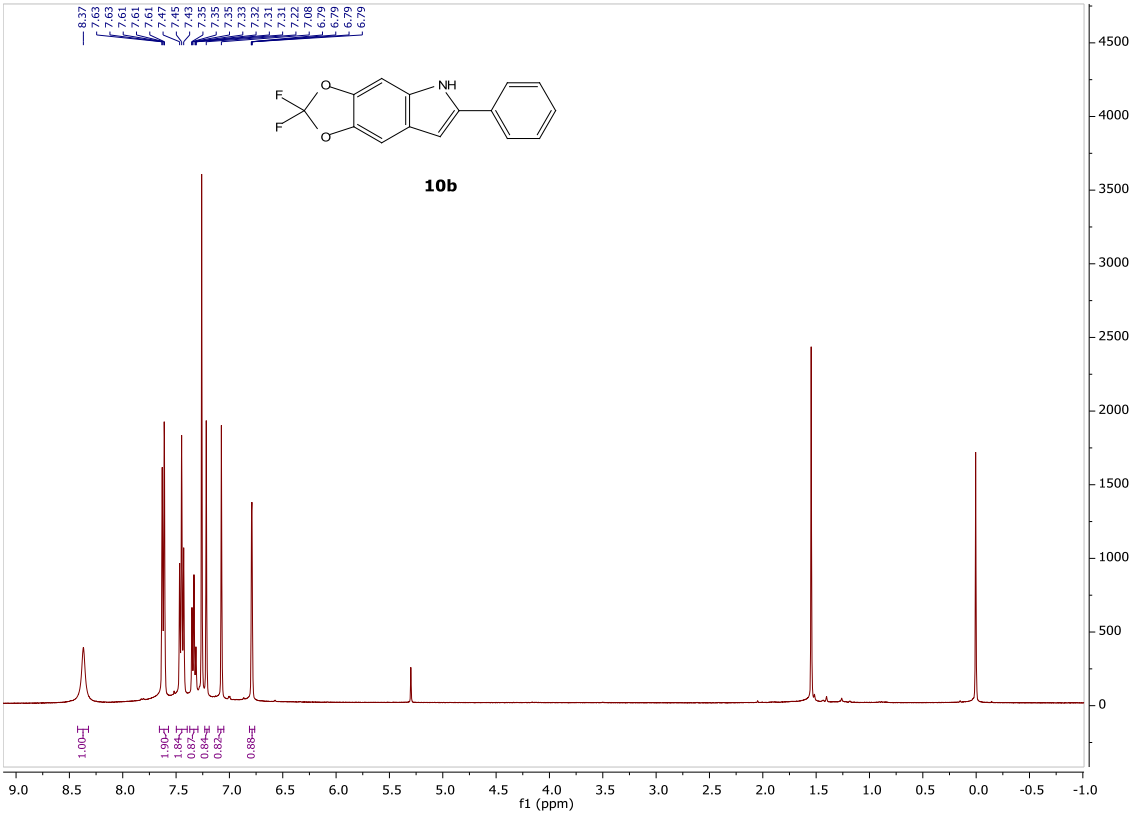


Figure S93: ^{13}C NMR

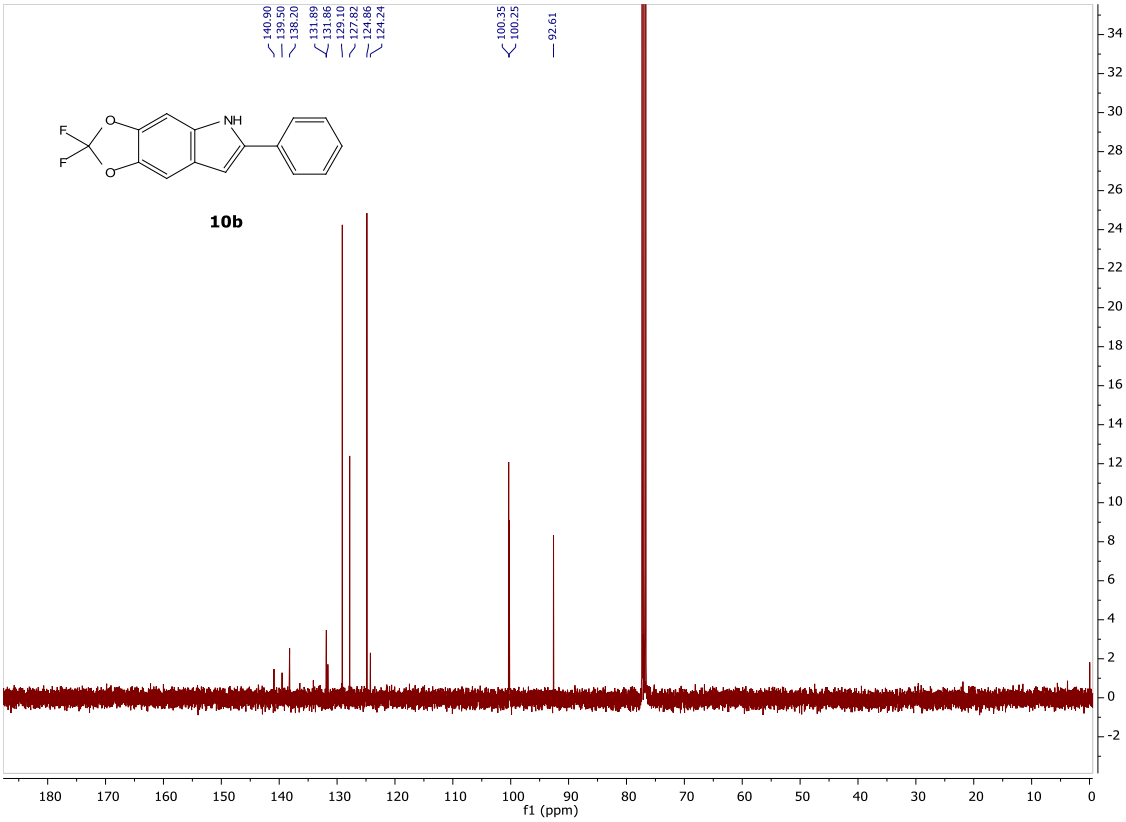


Figure S94: ^{1}H NMR

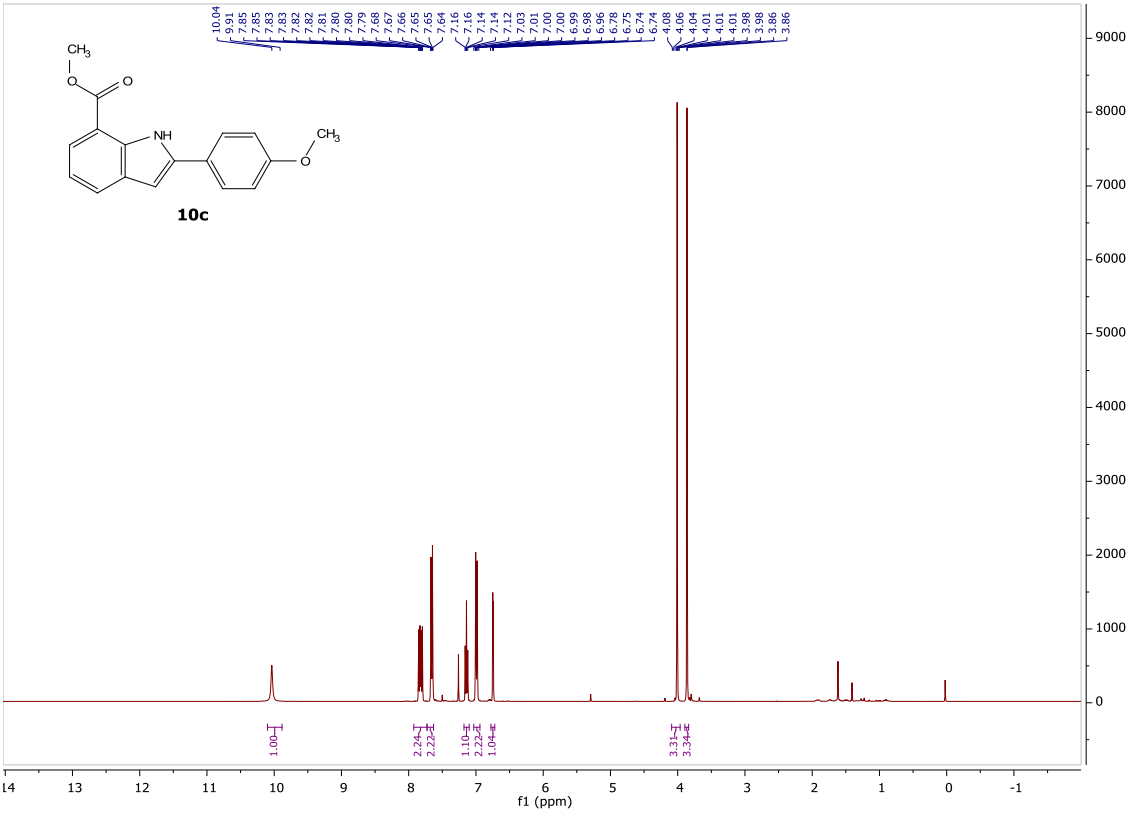


Figure S95: ^{13}C NMR

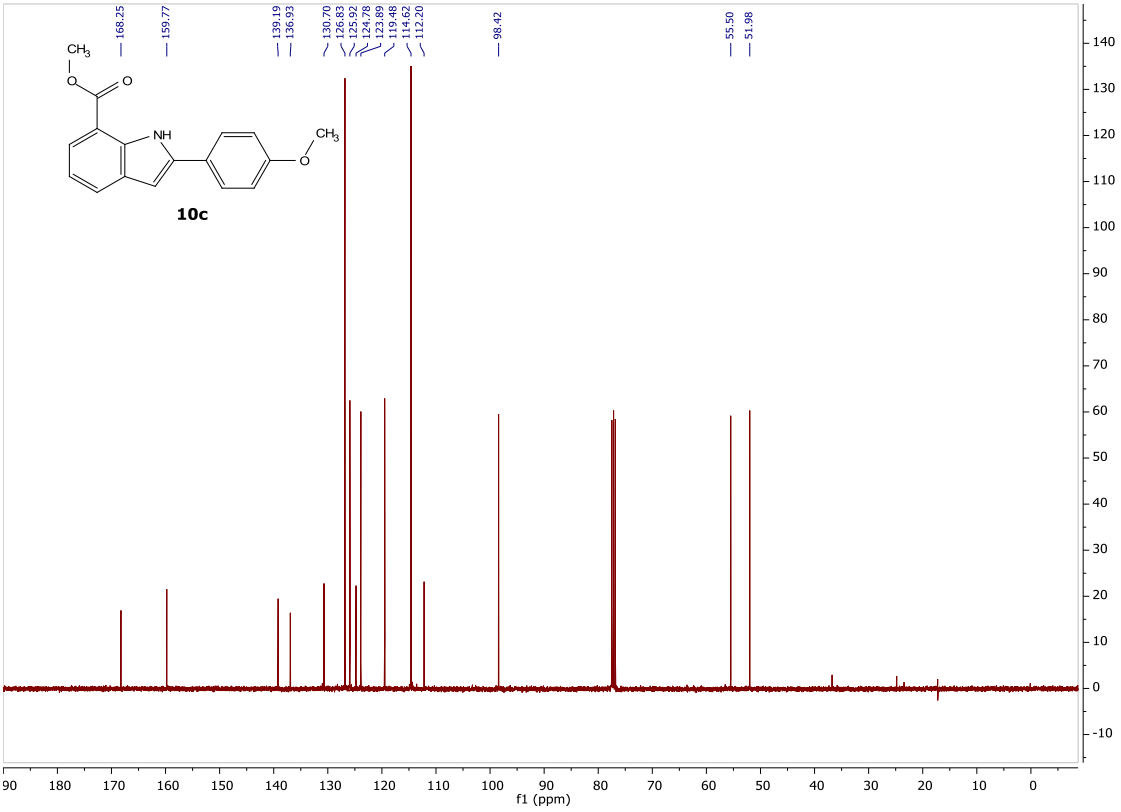


Figure S96: ^{1}H NMR

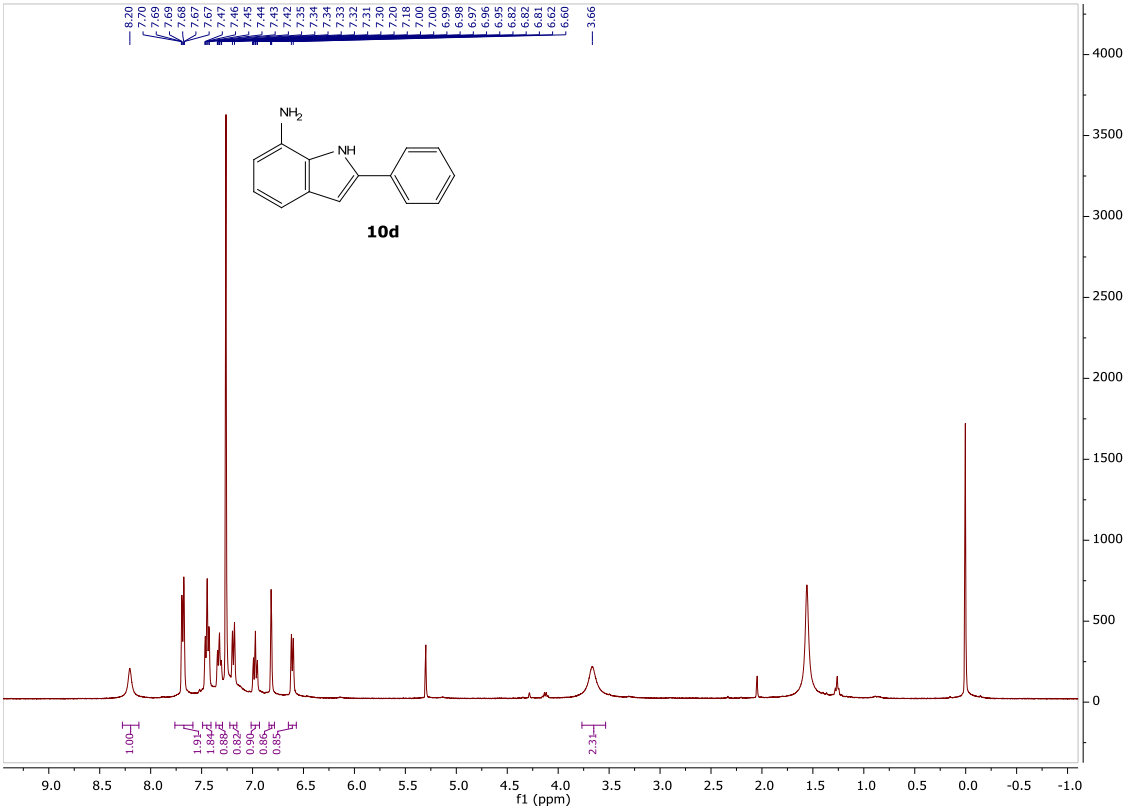


Figure S97: ^{13}C NMR

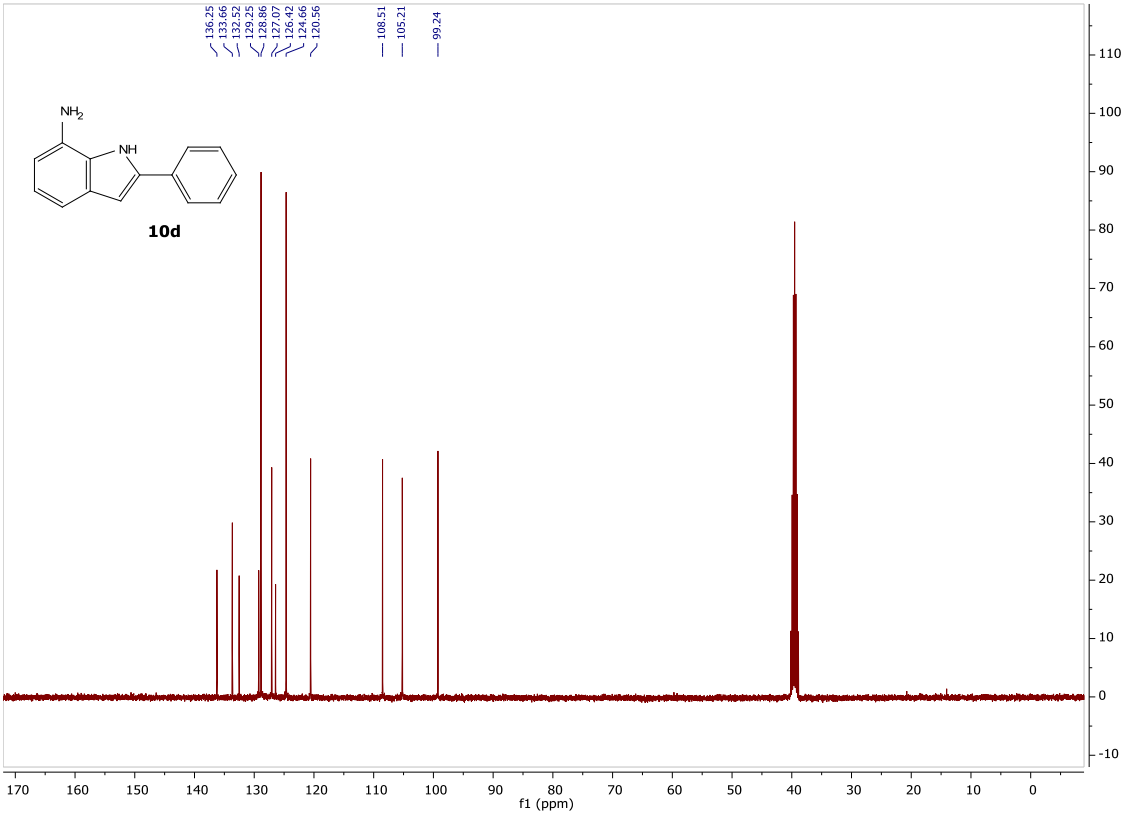


Figure S98: ^{1}H NMR

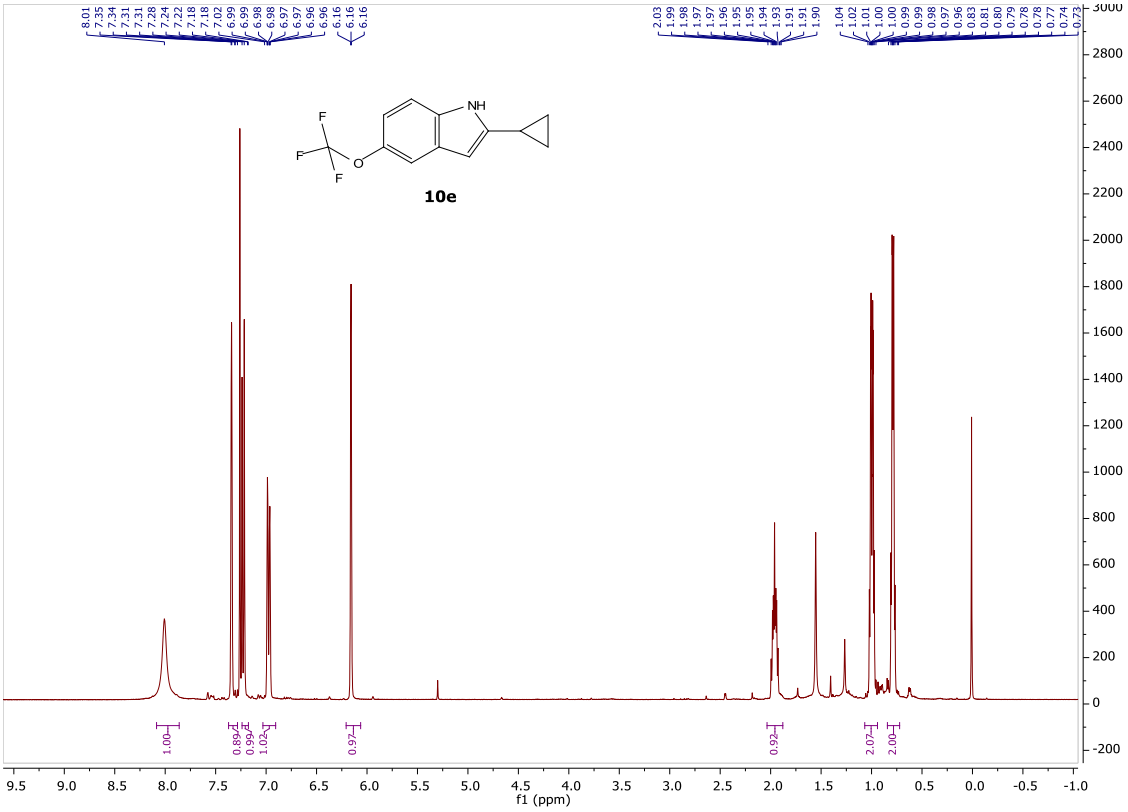


Figure S99: ^{13}C NMR

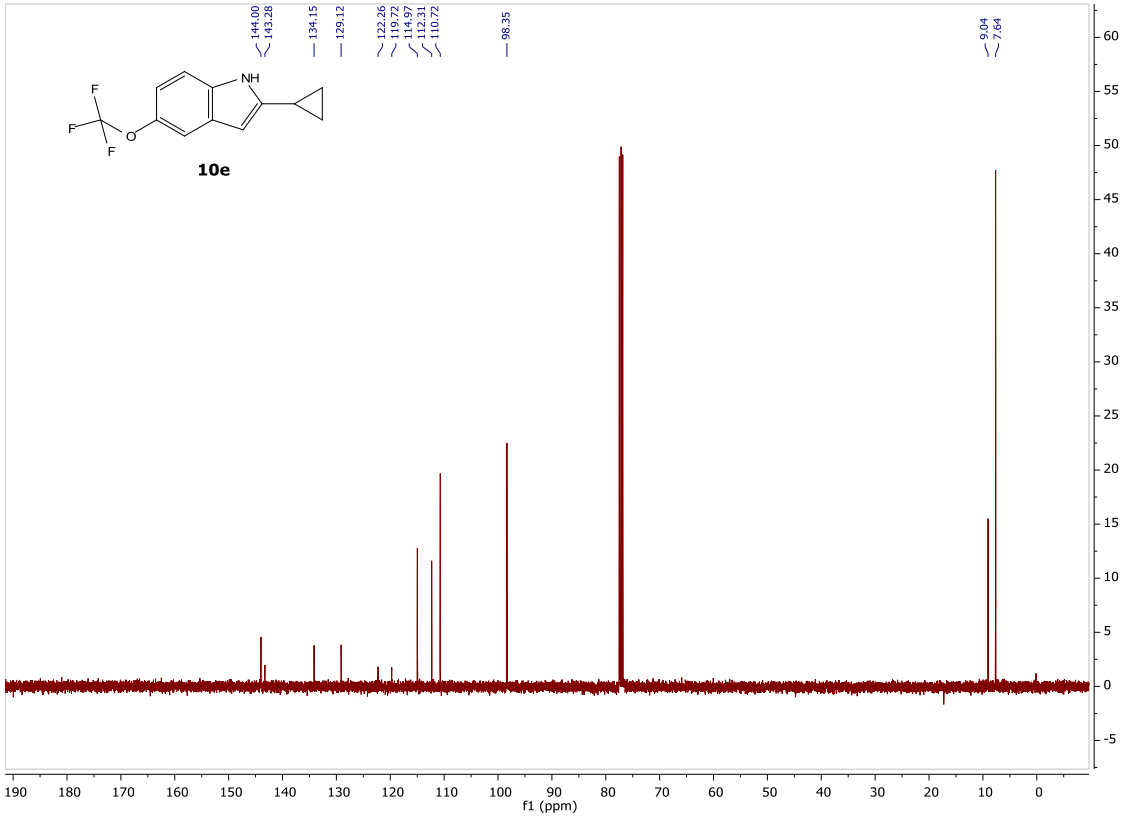


Figure S100: ^{1}H NMR

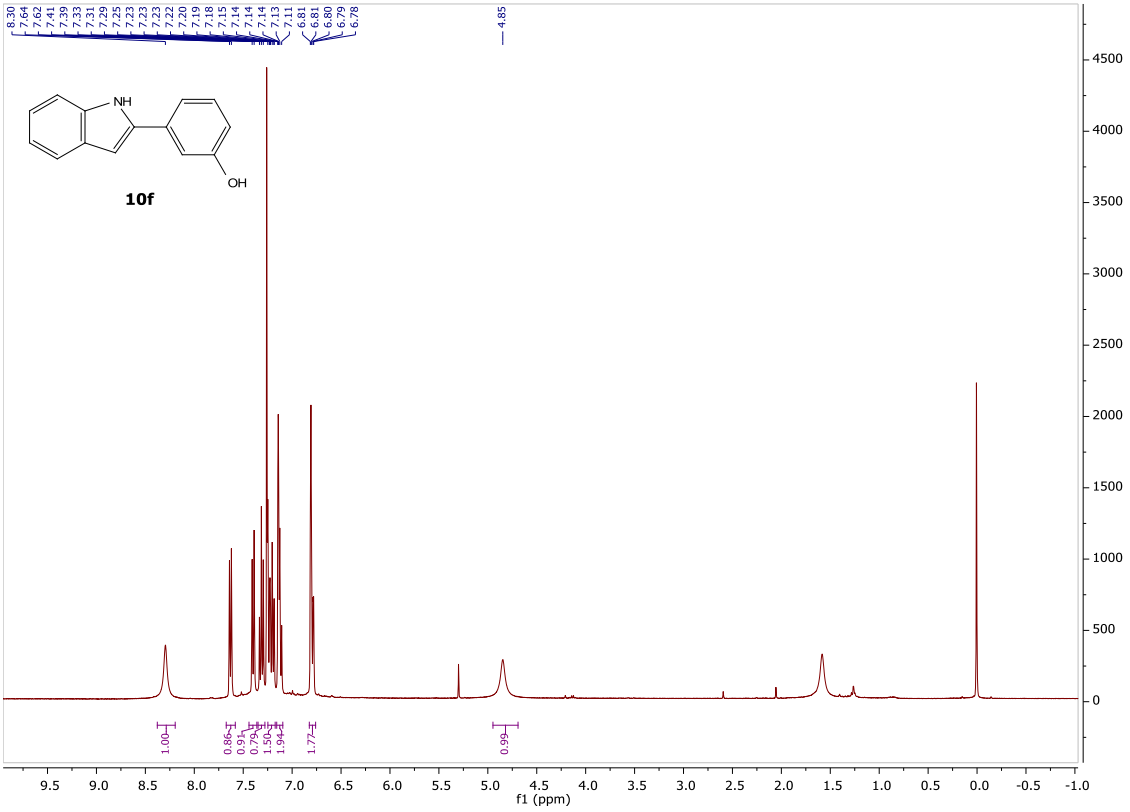


Figure S101: ^{13}C NMR