SUPPLEMENTARY INFORMATION

for

Facile synthesis of heavily-substituted alkynylpyridines via Sonogashira approach

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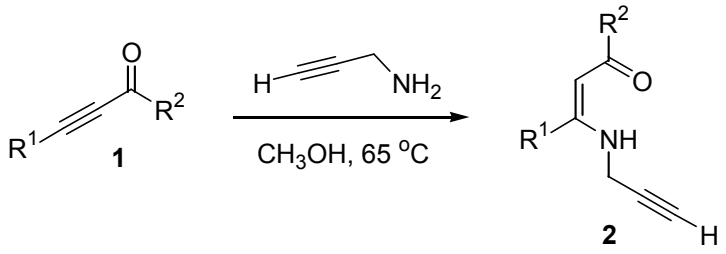
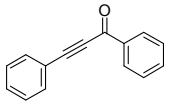
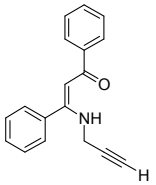
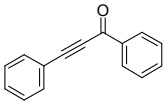
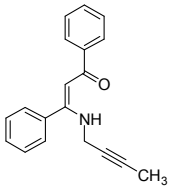
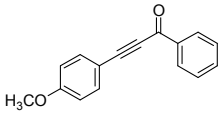
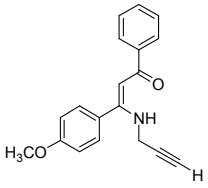
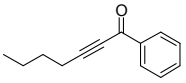
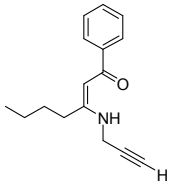
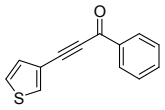
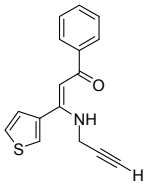
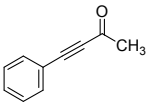
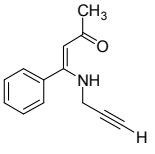
Synthesis of 5-iodopyridines 4.

5-Iodopyridines **4** used in this study were synthesized starting from α,β-alkynic ketones **1** as shown in Tables S1, S2 and S3, according to our recent report.[1] For spectral data and ^{1}H and ^{13}C NMR spectra of the synthesized *N*-propargylic β-enaminones **2** (Table S1), *N*-propargylic β-enaminones **3** (Table S2) and 5-iodopyridines **4** (Table S3), see reference 1 and its Supplementary Material. 3-Iodo-2-methoxypyridine (**8a**) and 2,3-diiodopyridine (**8b**) were commercially available.

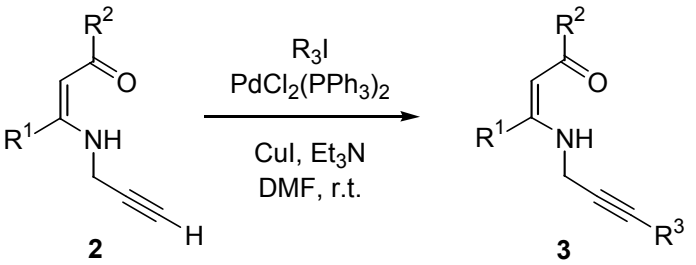
Table S1. Synthesis of *N*-propargylic β-enaminones **2** from α,β-alkynic ketones **1** via conjugate addition of propargylamine.



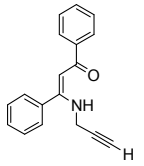
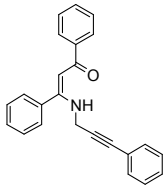
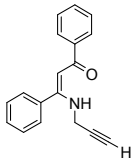
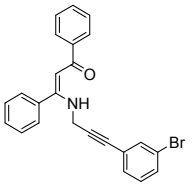
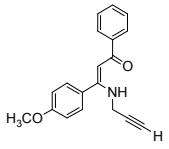
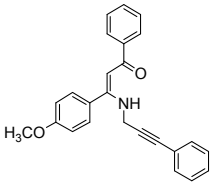
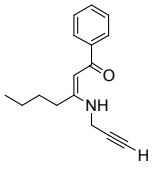
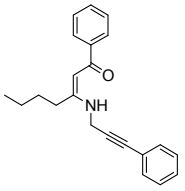
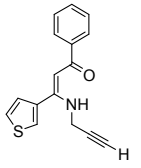
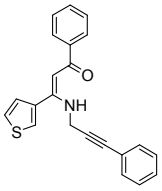
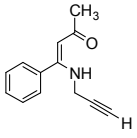
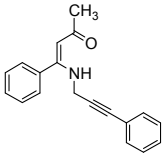
Entry	Alkynone **1**	β-Enaminone **2**	%Yield[a]	Entry	Alkynone **1**	β-Enaminone **2** (or **3**)	%Yield[a]
1	 **1a**	 **2a**	98	4[b]	 **1a**	 **3e**	93
2	 **1b**	 **2b**	98	5	 **1d**	 **2d**	92
3	 **1c**	 **2c**	94	6	 **1e**	 **2e**	85

[a]Isolated yield. [b]In this reaction, 2-butynylamine[2] (CH_3-C≡C-CH_2-NH_2) was used instead of propargylamine, which afforded β-enaminone **3e**.

Table S2. Synthesis of *N*-propargylic β-enaminones **3** from β-enaminones **2** via Sonogashira reaction.

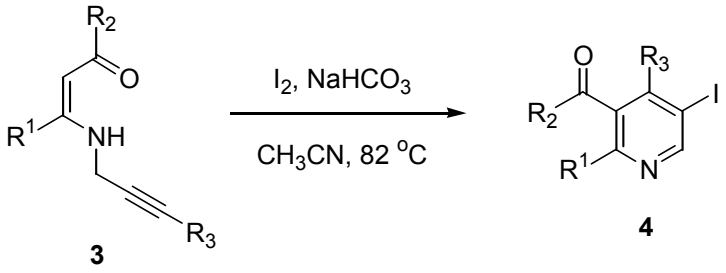


2 **3**

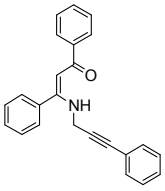
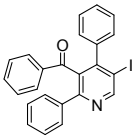
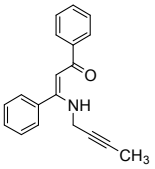
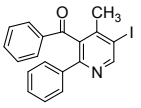
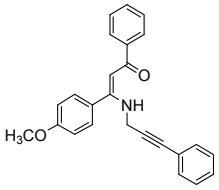
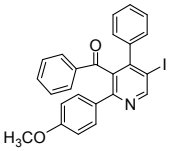
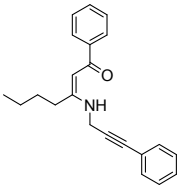
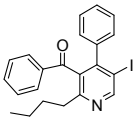
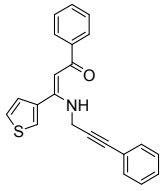
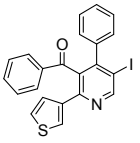
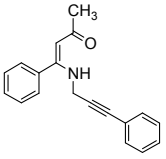
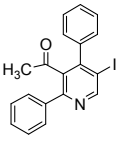
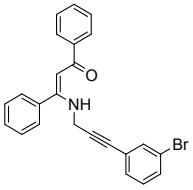
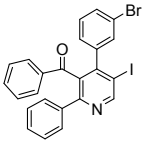
Entry	β-Enaminone **2**	Aryl iodide	β-enaminone **3**	%Yield[a]	Entry	β-Enaminone **2**	Aryl iodide	β-Enaminone **3**	%Yield[a]
1	 **2a**		 **3a**	88	4	 **2a**		 **3d**	88
2	 **2b**		 **3b**	84	5	 **2d**		 **3f**	90
3	 **2c**		 **3c**	83	6	 **2e**		 **3g**	69

[a]Isolated yield.

Table S3. Synthesis of 5-iodopyridines **4** from *N*-propargylic β-enaminones **3** via electrophilic cyclization.



3 **4**

Entry	*N*-propargylic β-enaminone **3**	5-Iodopyridine **4**	% Yield[a]	Entry	*N*-propargylic β-enaminone **3**	5-Iodopyridine **4**	% Yield[a]
1	 **3a**	 **4a**	80	5	 **3e**	 **4e**	51
2	 **3b**	 **4b**	62	6	 **3f**	 **4f**	65
3	 **3c**	 **4c**	75	7	 **3g**	 **4g**	47
4	 **3d**	 **4d**	57				

[a]Isolated yield.

Copies of ^{1}H and ^{13}C NMR spectra

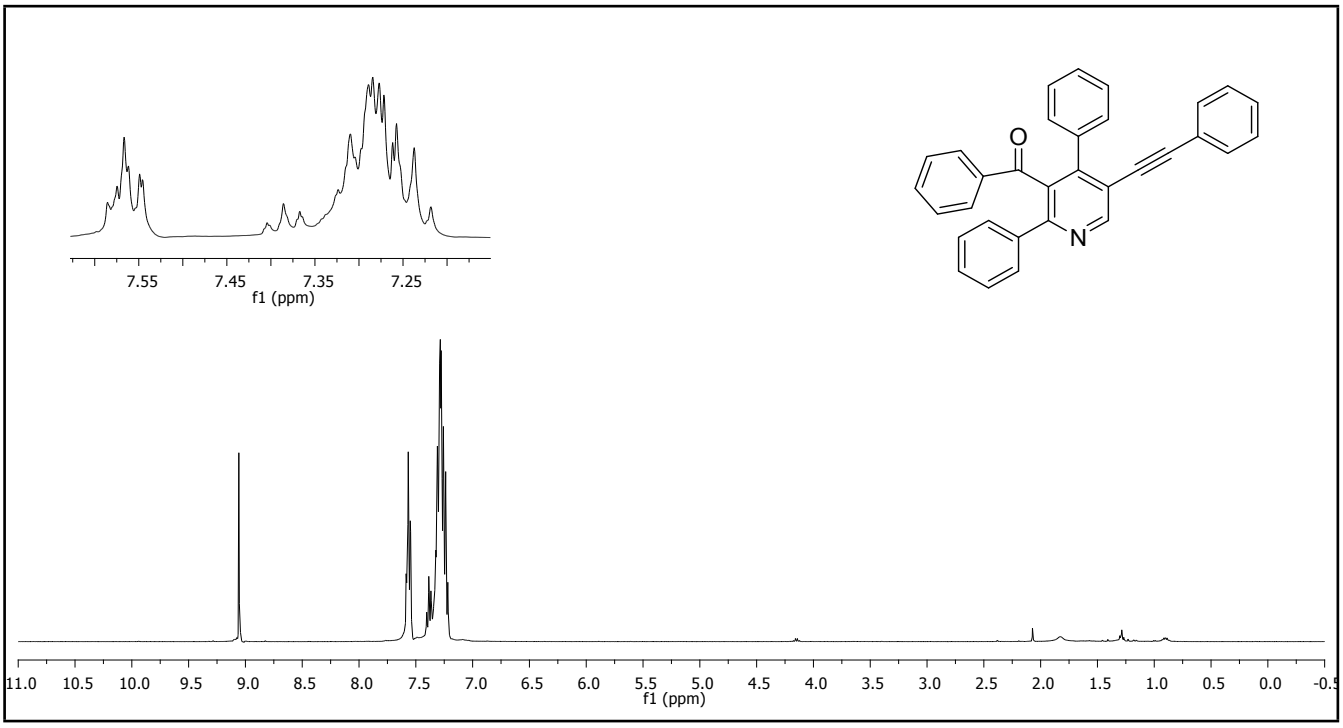


Figure S1. ^{1}H NMR spectrum of compound **7a**.

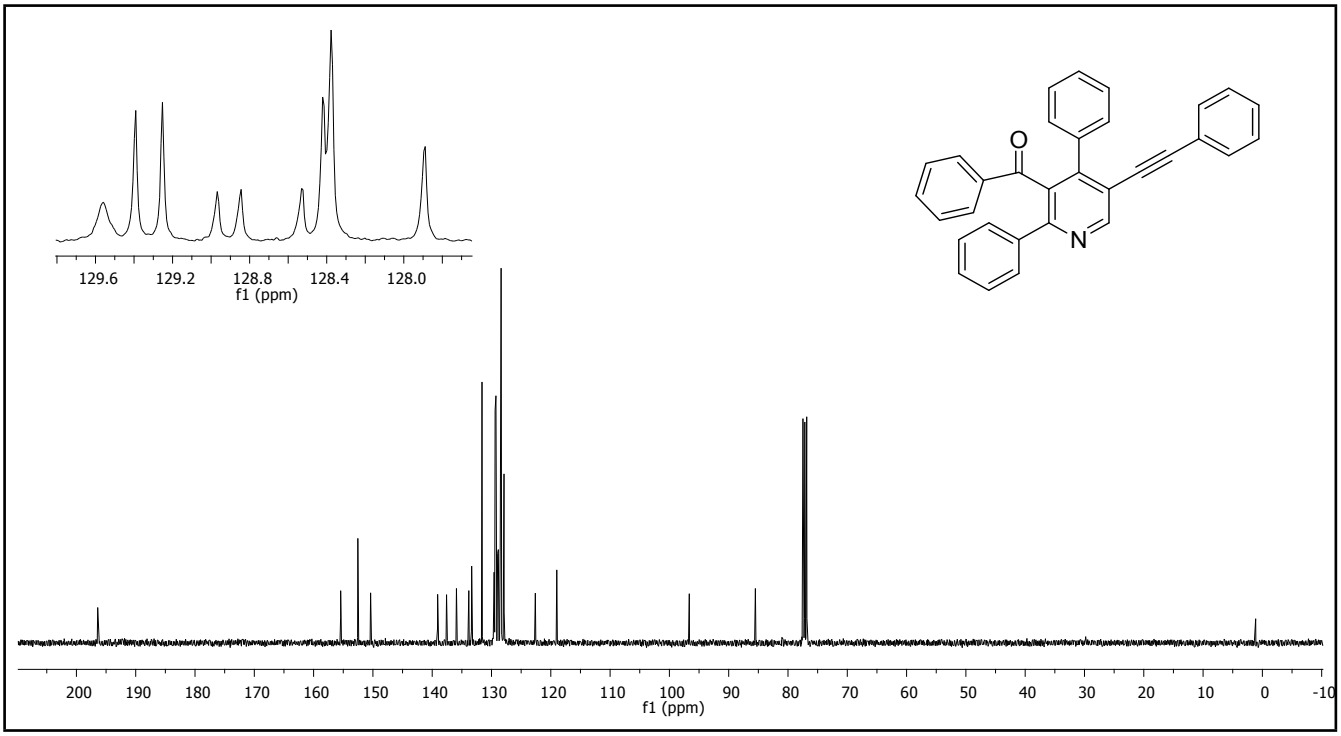


Figure S2. ^{13}C NMR spectrum of compound **7a**.

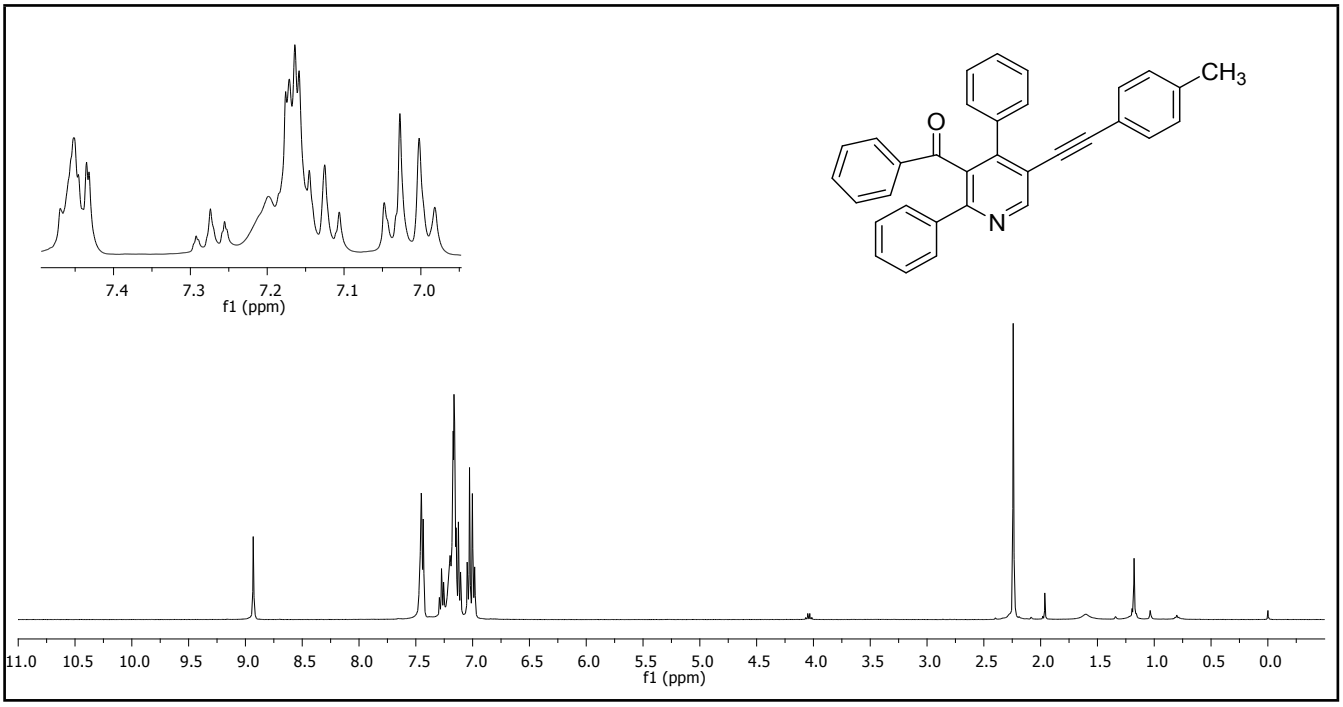


Figure S3. ^{1}H NMR spectrum of compound **7b**.

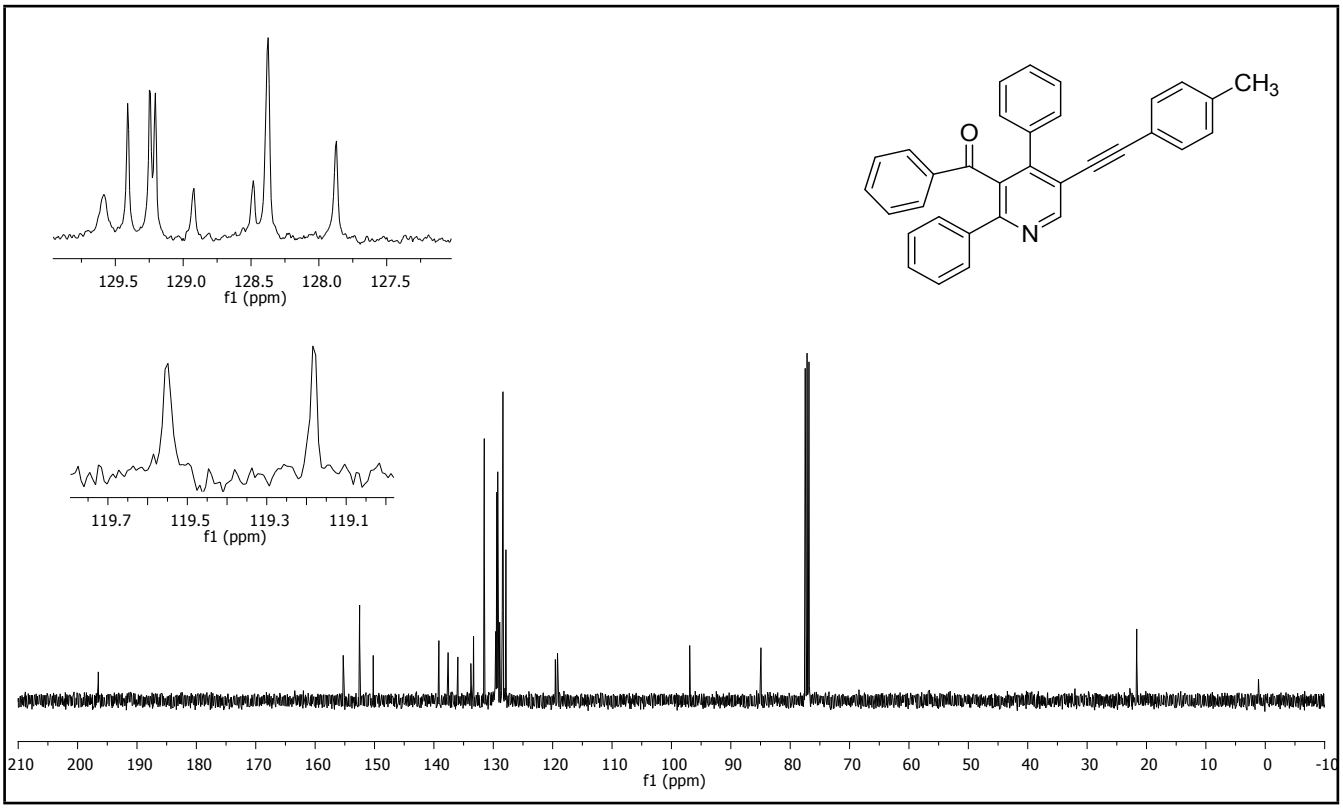


Figure S4. ^{13}C NMR spectrum of compound **7b**.

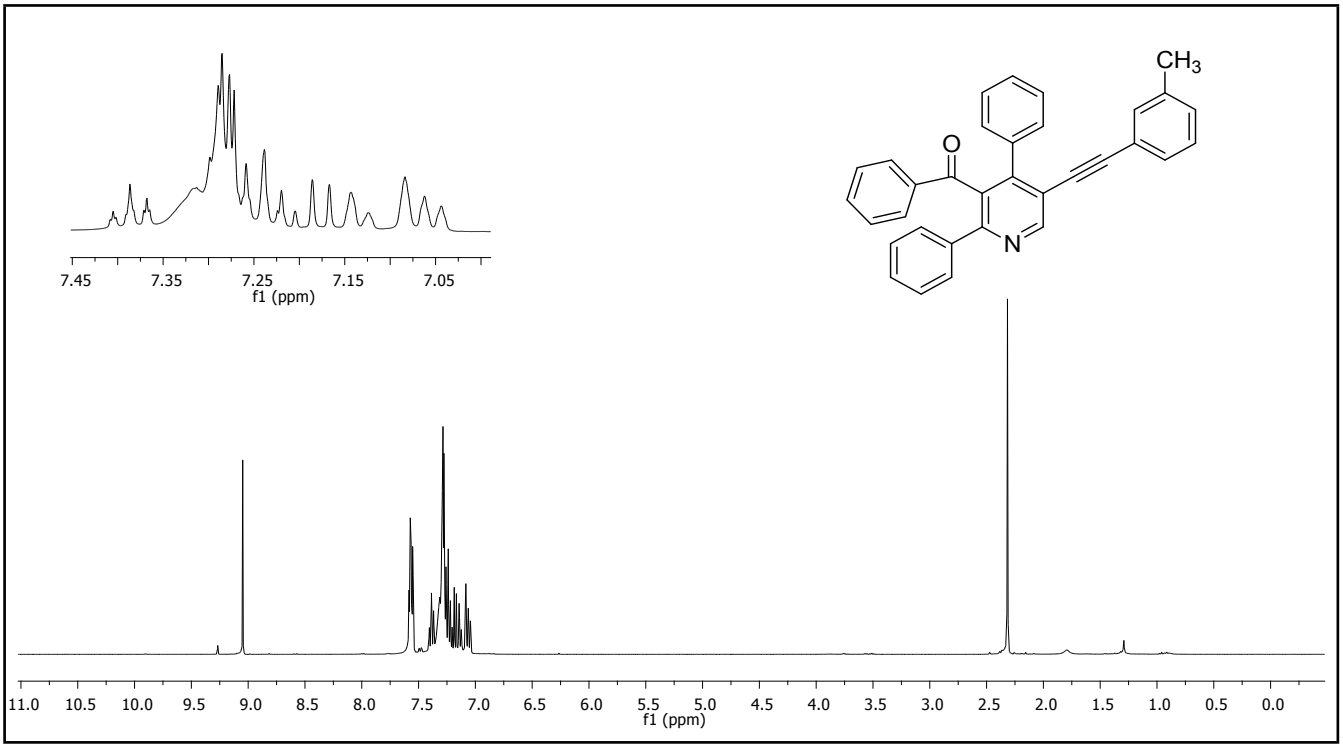


Figure S5. ^{1}H NMR spectrum of compound **7c**.

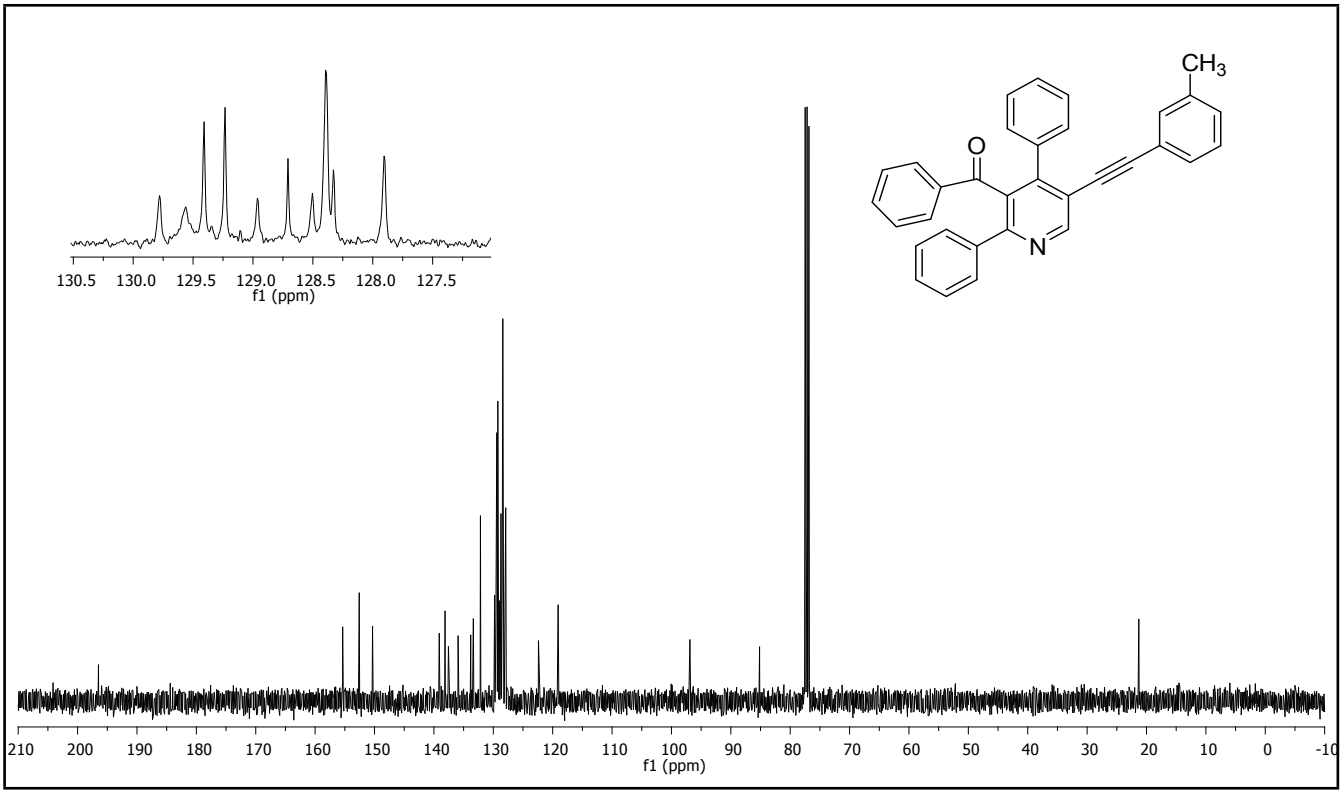


Figure S6. ^{13}C NMR spectrum of compound **7c**.

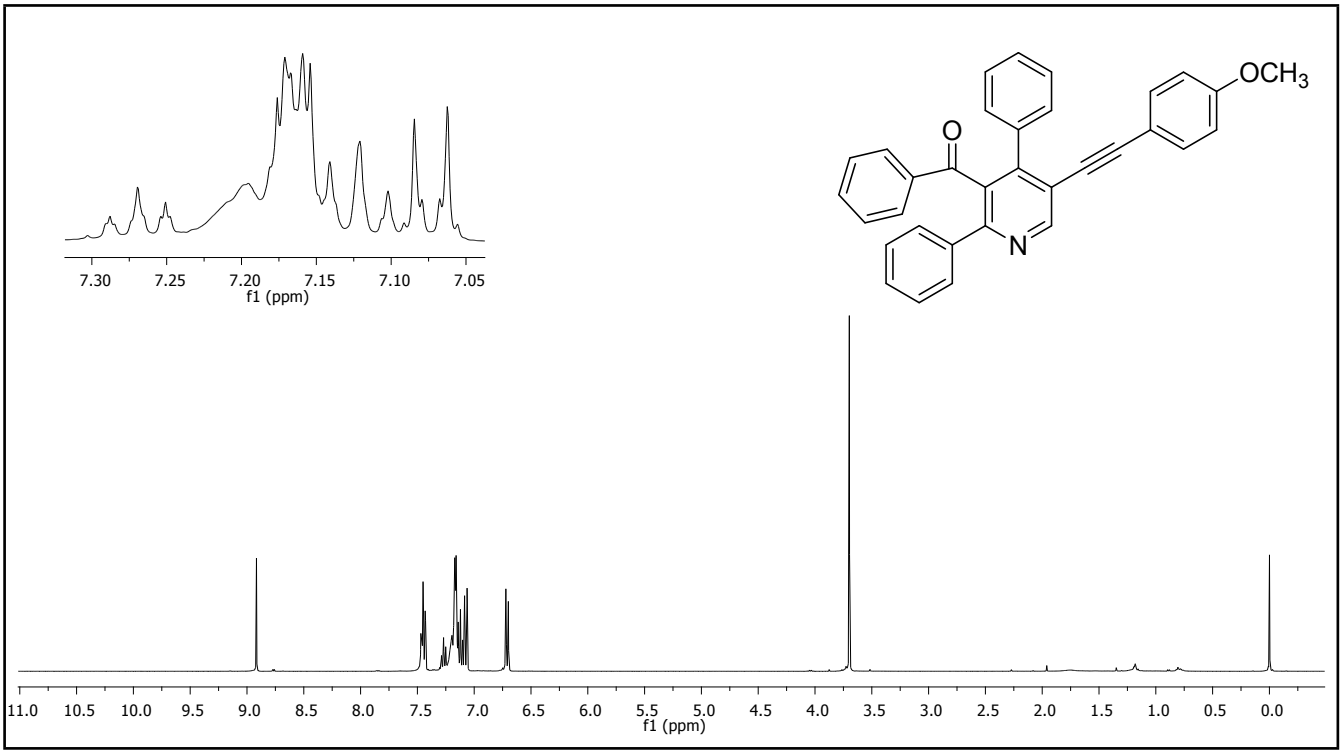


Figure S7. ^{1}H NMR spectrum of compound **7d**.

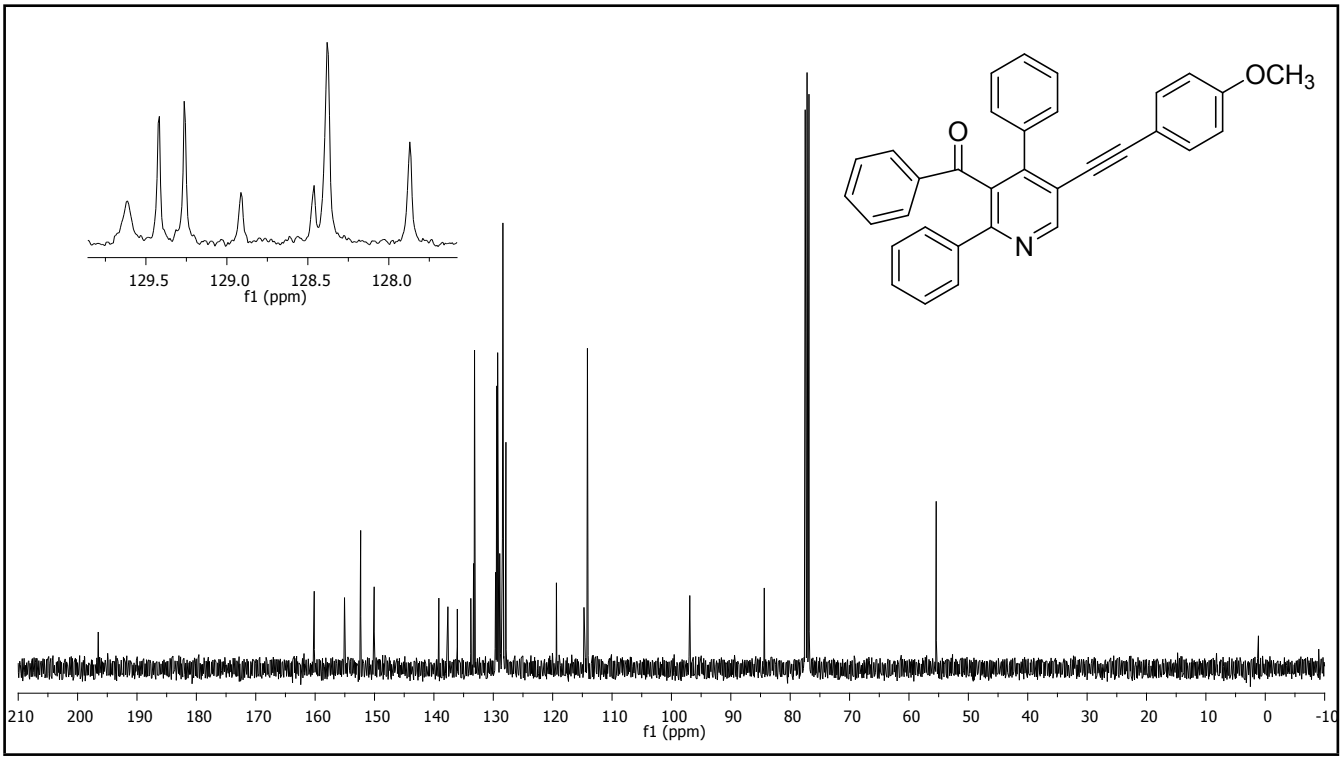


Figure S8. ^{13}C NMR spectrum of compound **7d**.

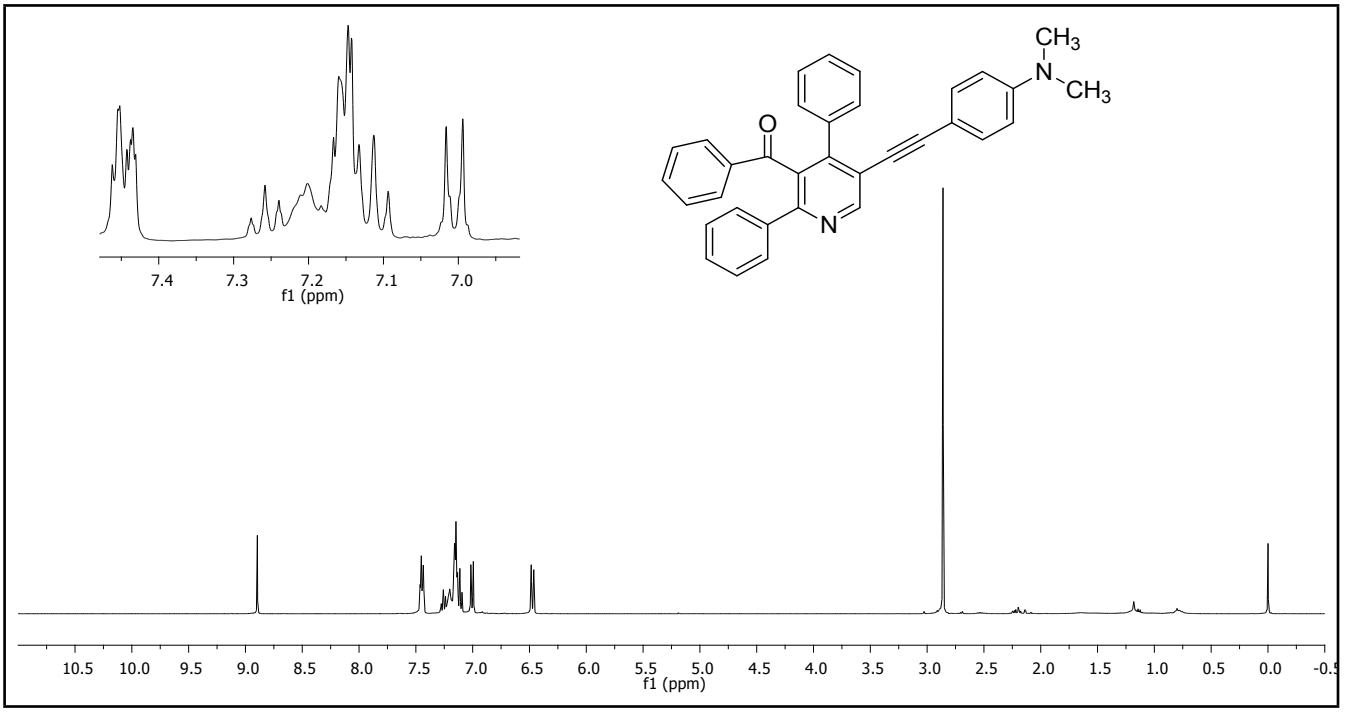


Figure S9. ^{1}H NMR spectrum of compound **7e**.

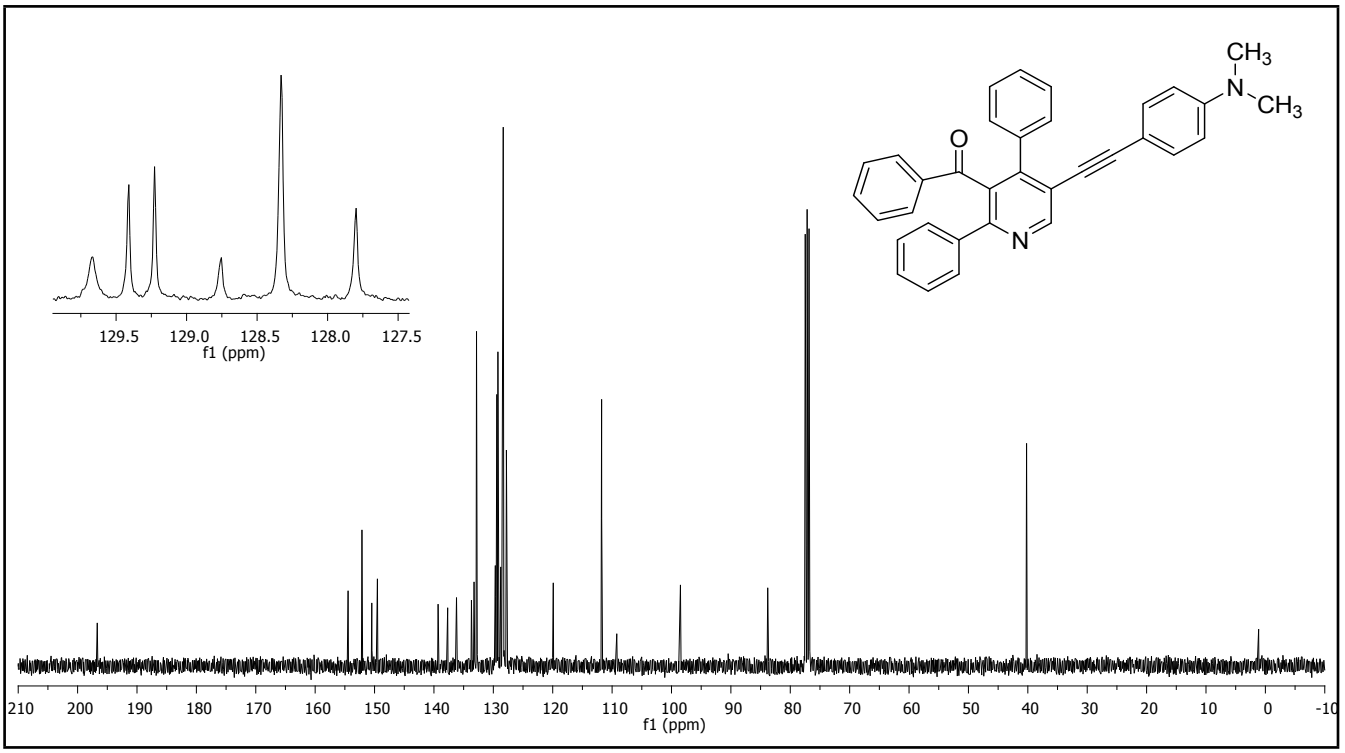


Figure S10. ^{13}C NMR spectrum of compound **7e**.

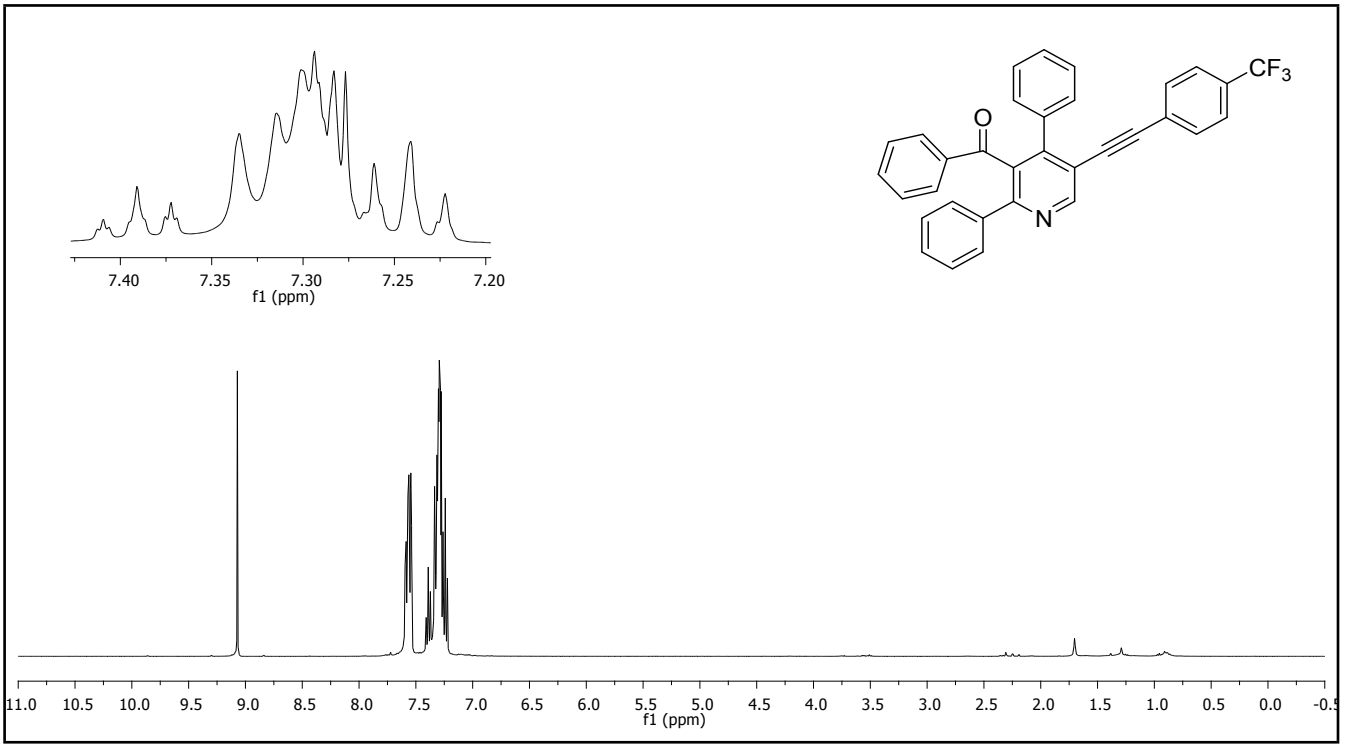


Figure S11. ^{1}H NMR spectrum of compound **7f**.

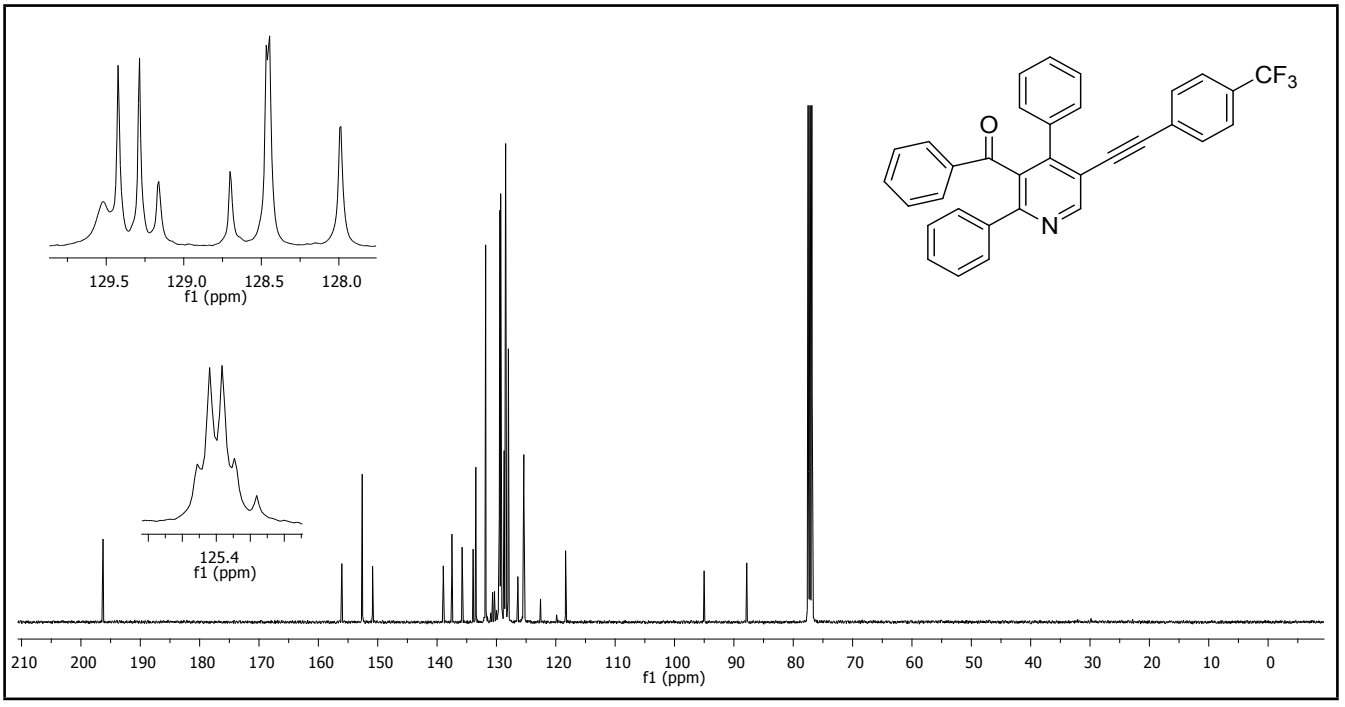


Figure S12. ^{13}C NMR spectrum of compound **7f**.

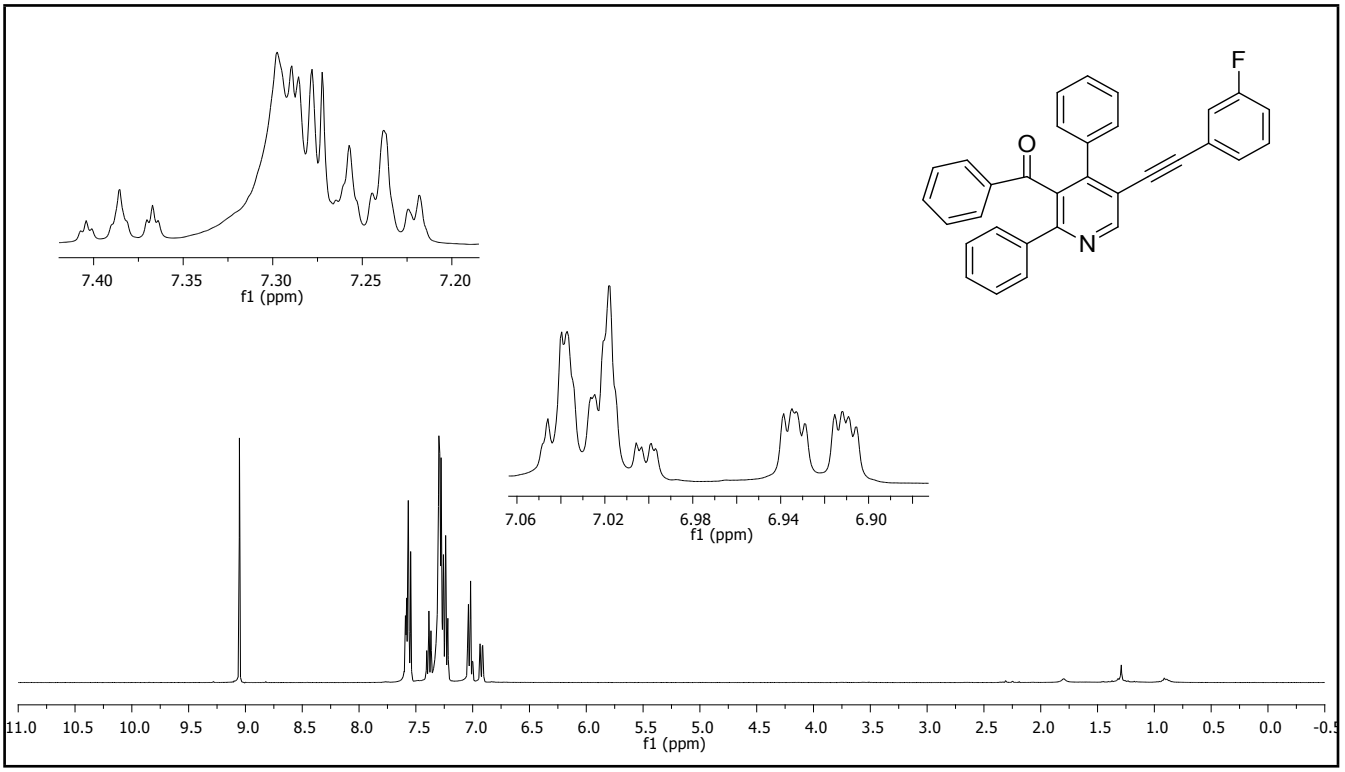


Figure S13. ^{1}H NMR spectrum of compound **7g**.

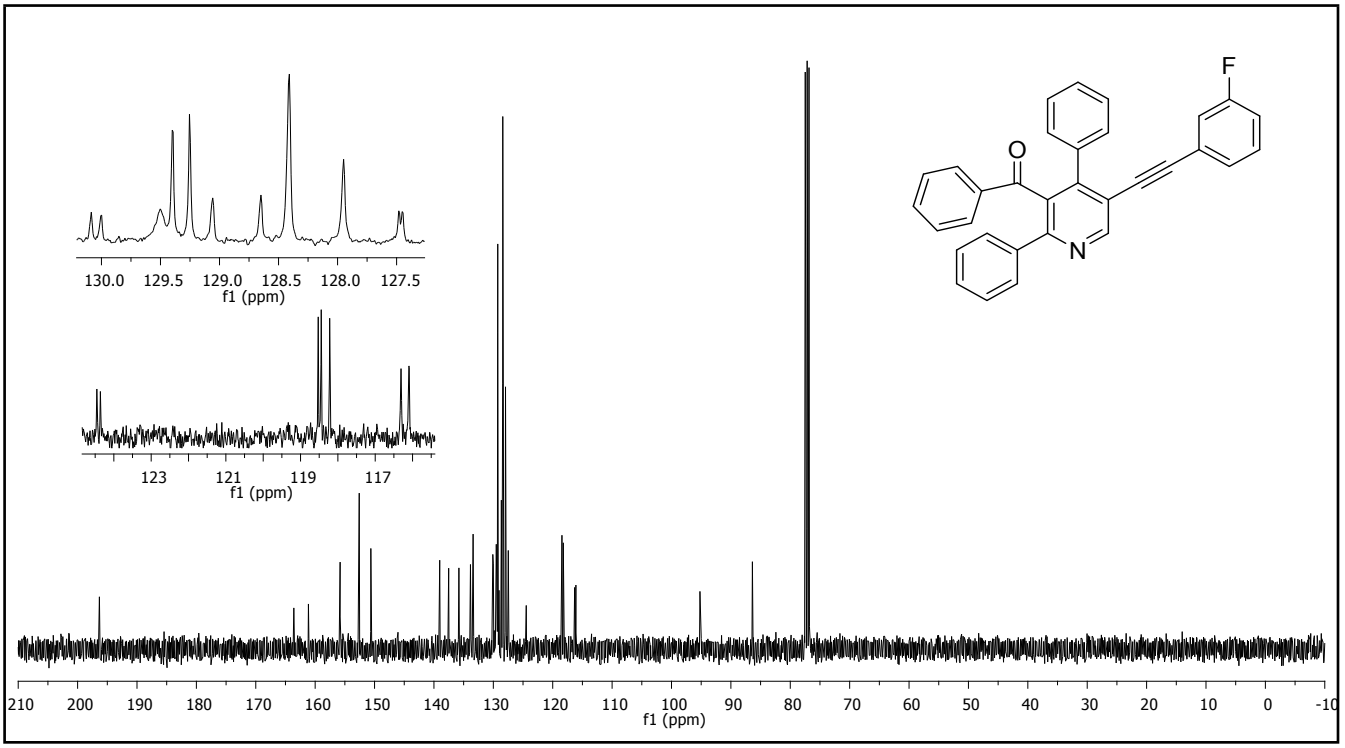


Figure S14. ^{13}C NMR spectrum of compound **7g**.

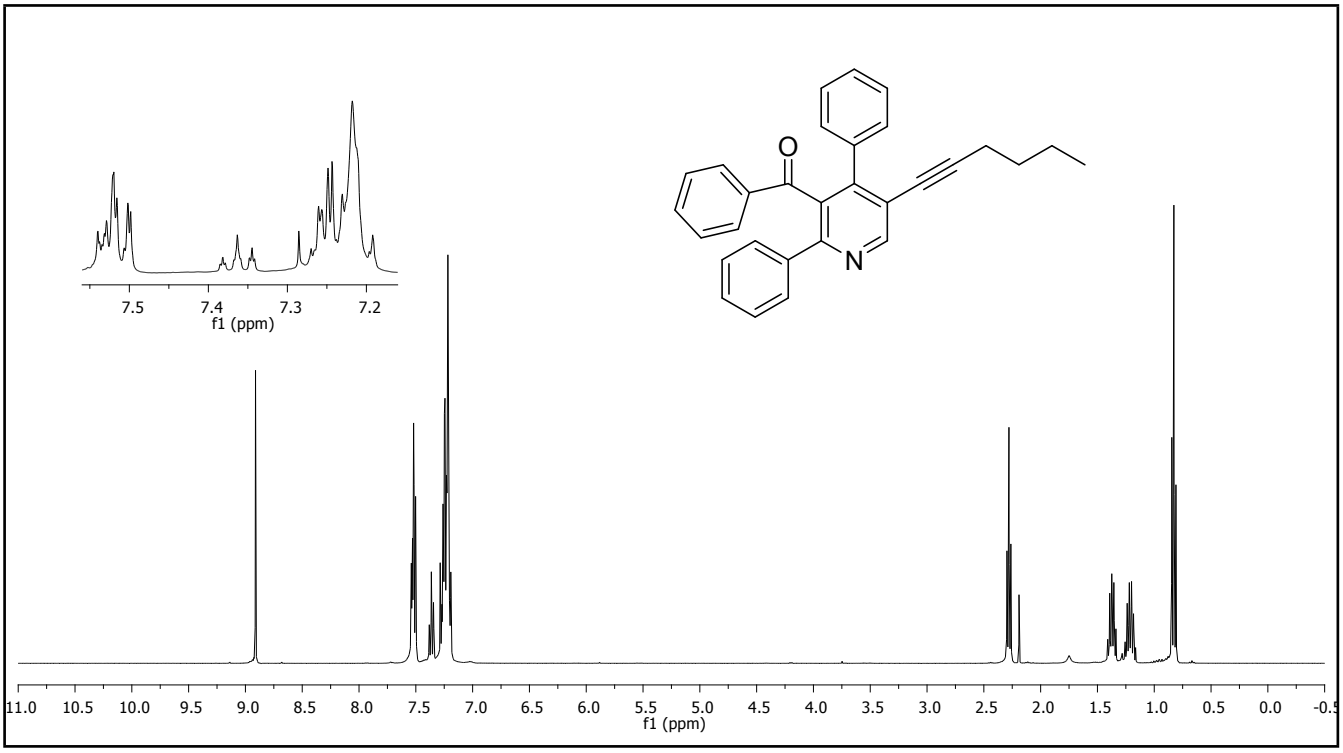


Figure S15. ^{1}H NMR spectrum of compound **7h.**

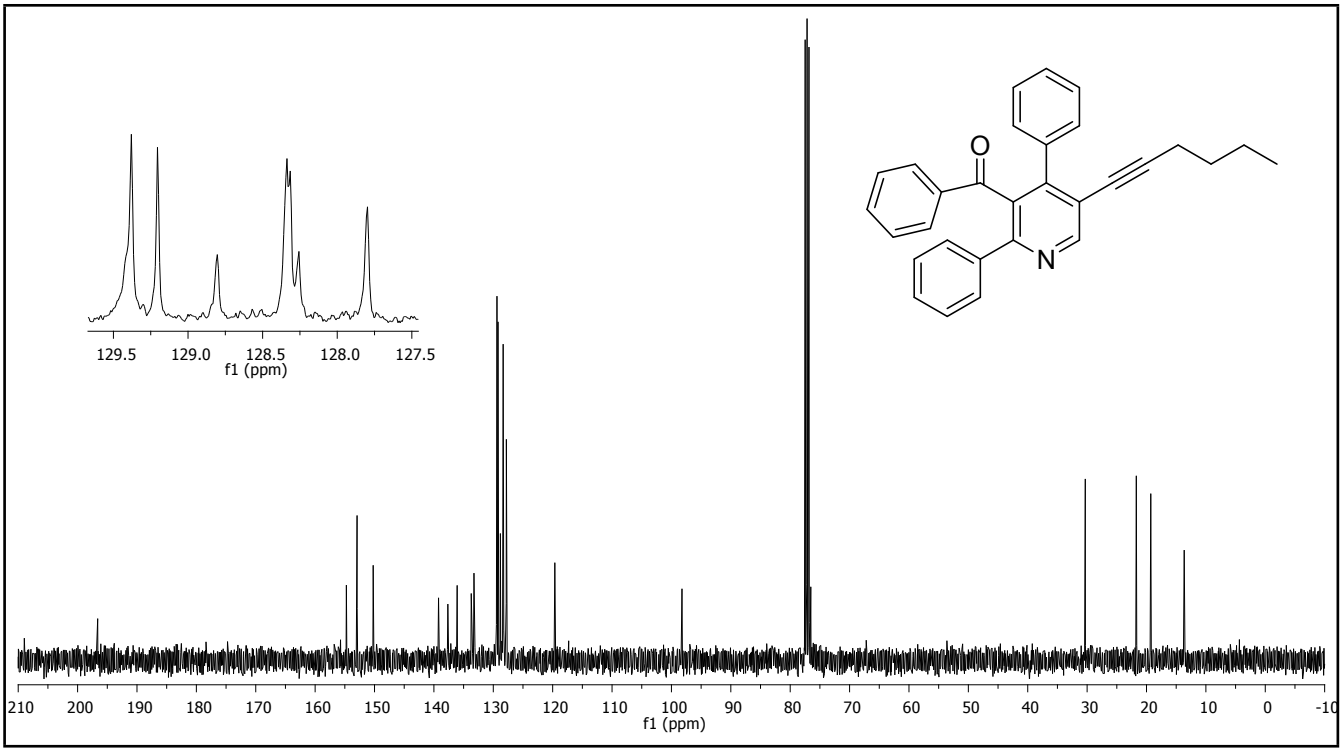


Figure S16. ^{13}C NMR spectrum of compound **7h**.

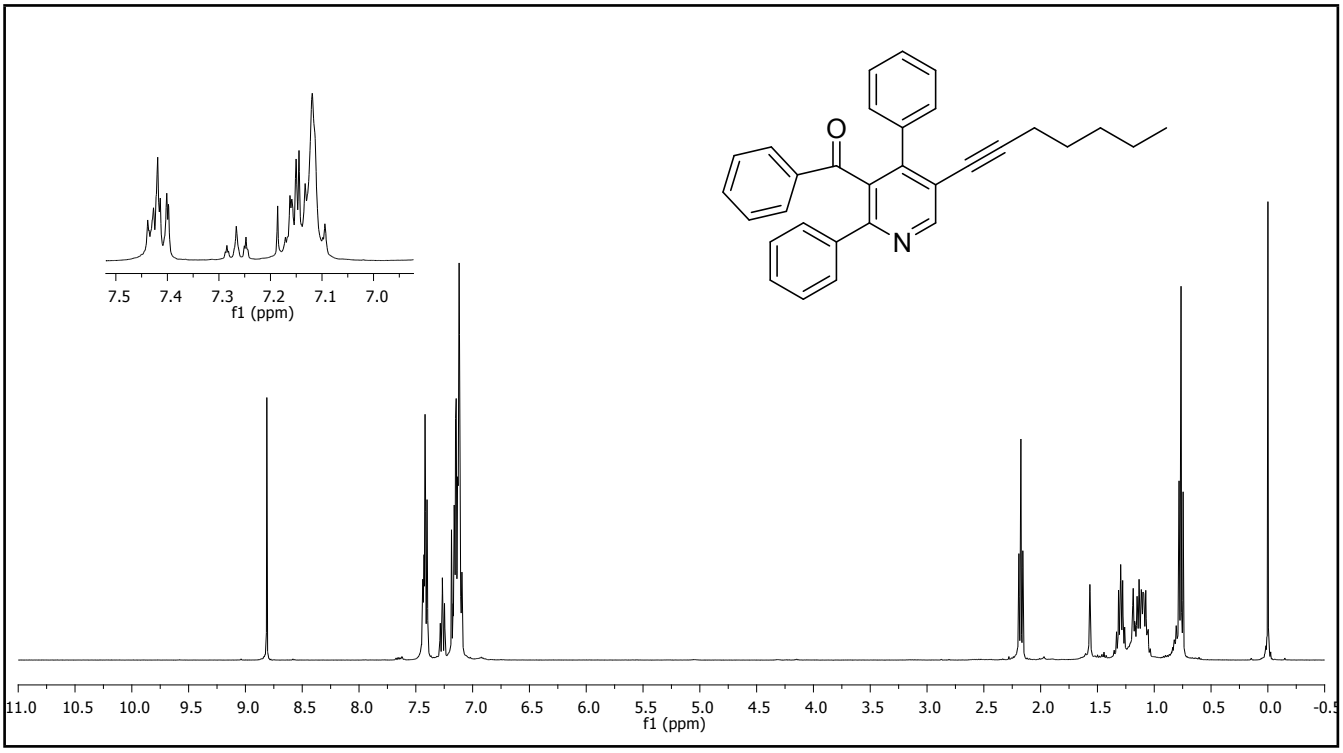


Figure S17. ^{1}H NMR spectrum of compound **7i**.

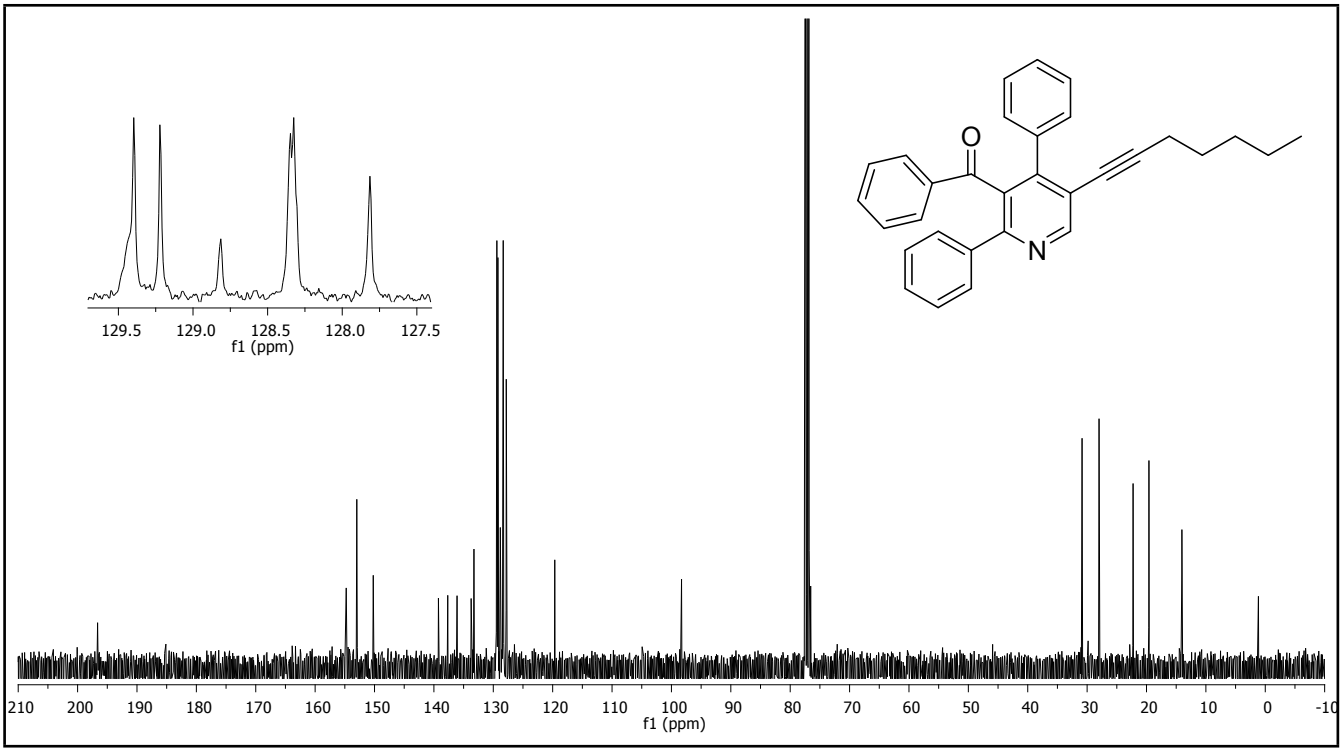


Figure S18. ^{13}C NMR spectrum of compound **7i**.

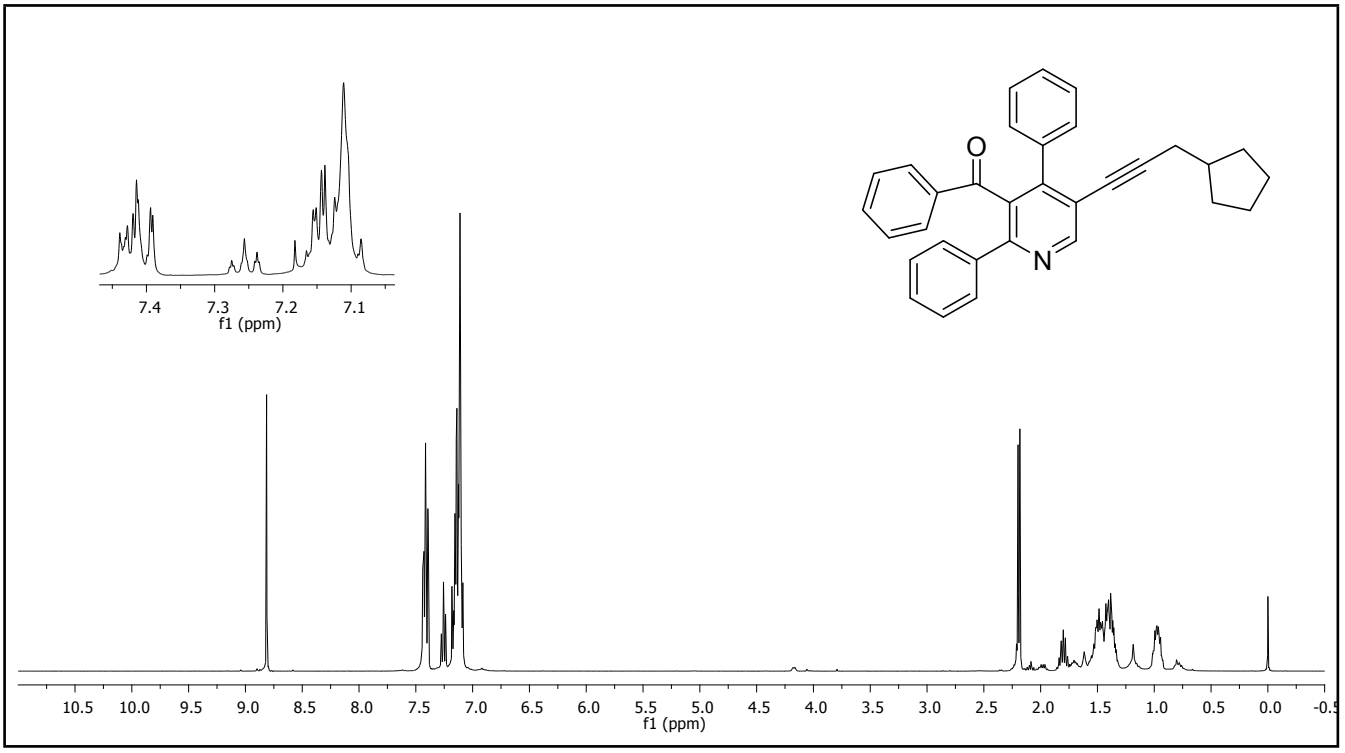


Figure S19. ^{1}H NMR spectrum of compound **7j**.

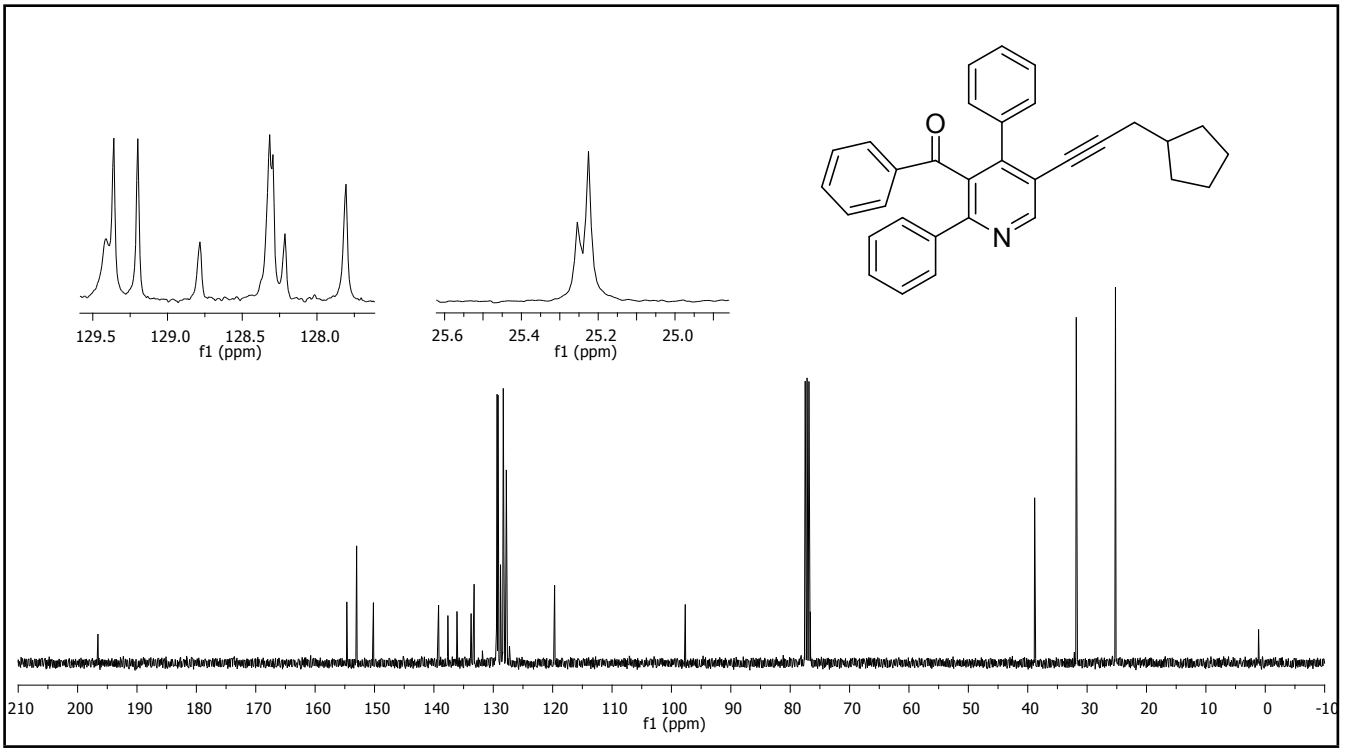


Figure S20. ^{13}C NMR spectrum of compound **7j**.

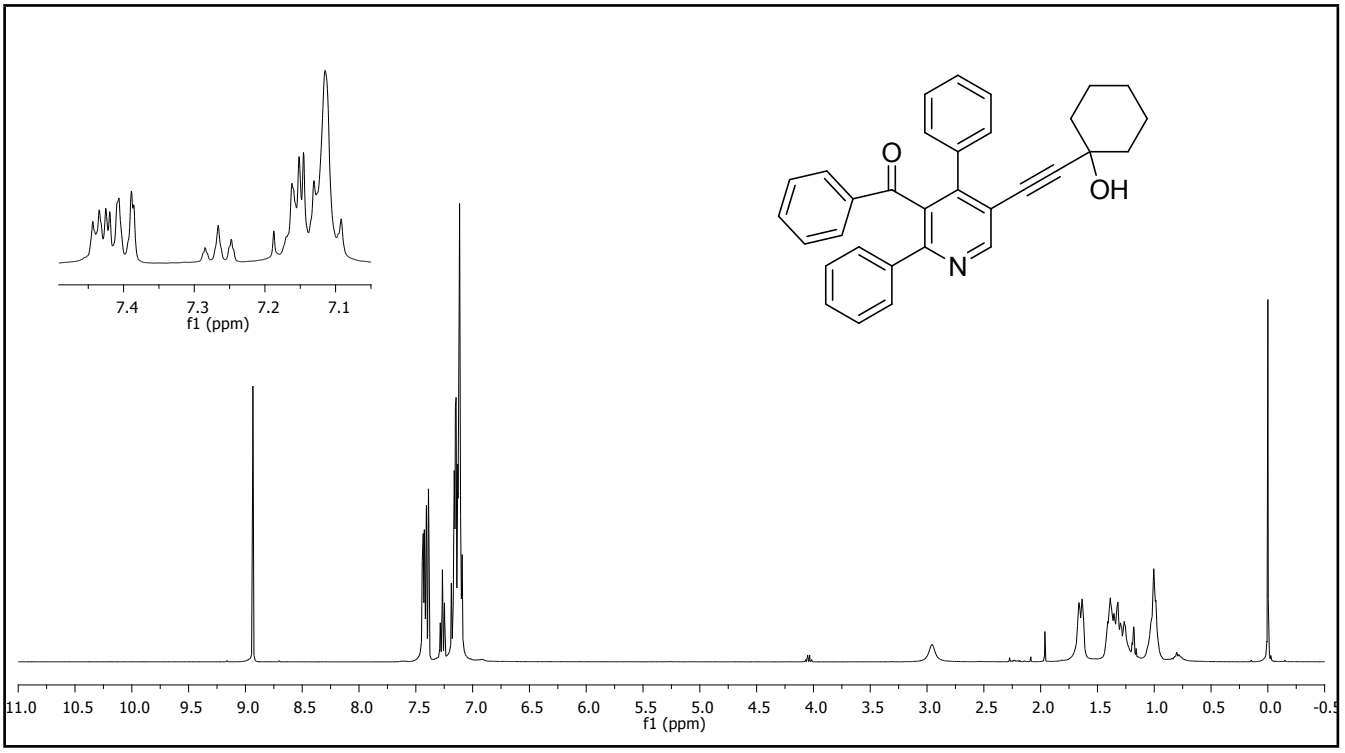


Figure S21. ^{1}H NMR spectrum of compound **7k**.

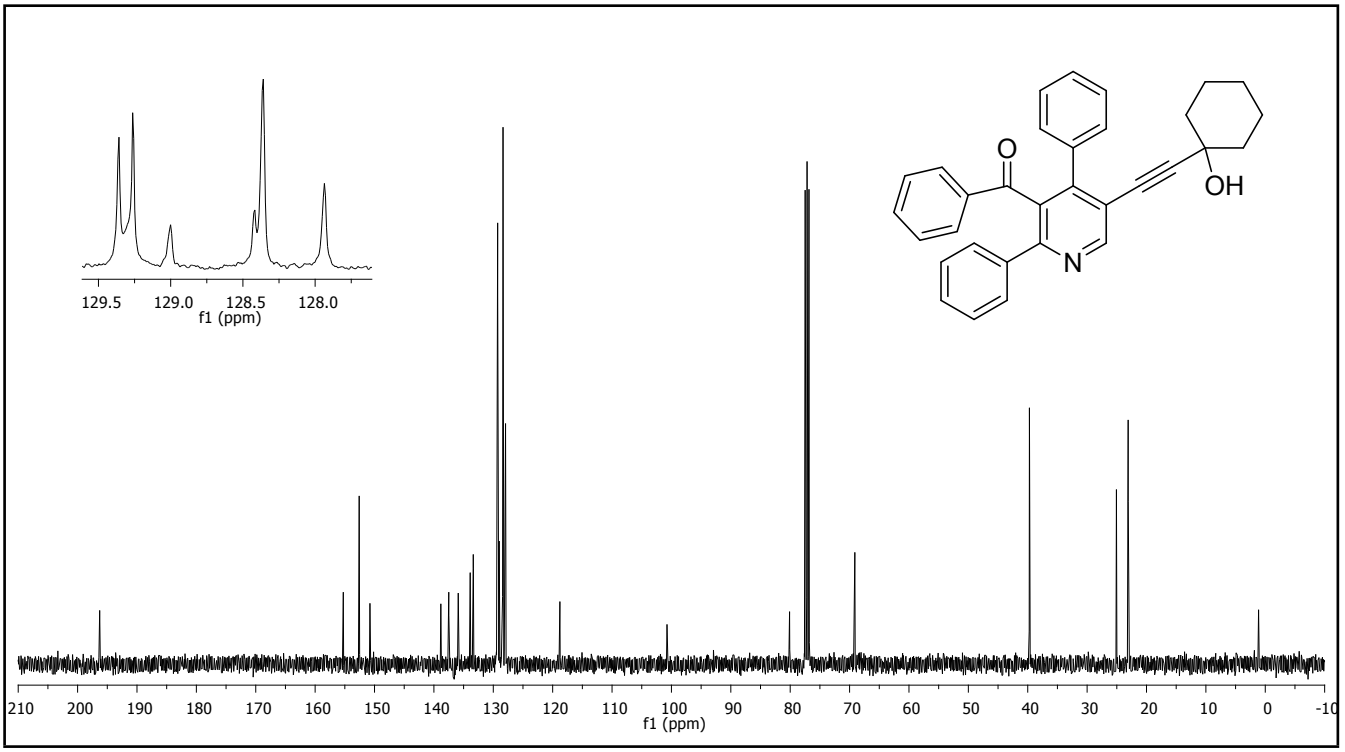


Figure S22. ^{13}C NMR spectrum of compound **7k**.

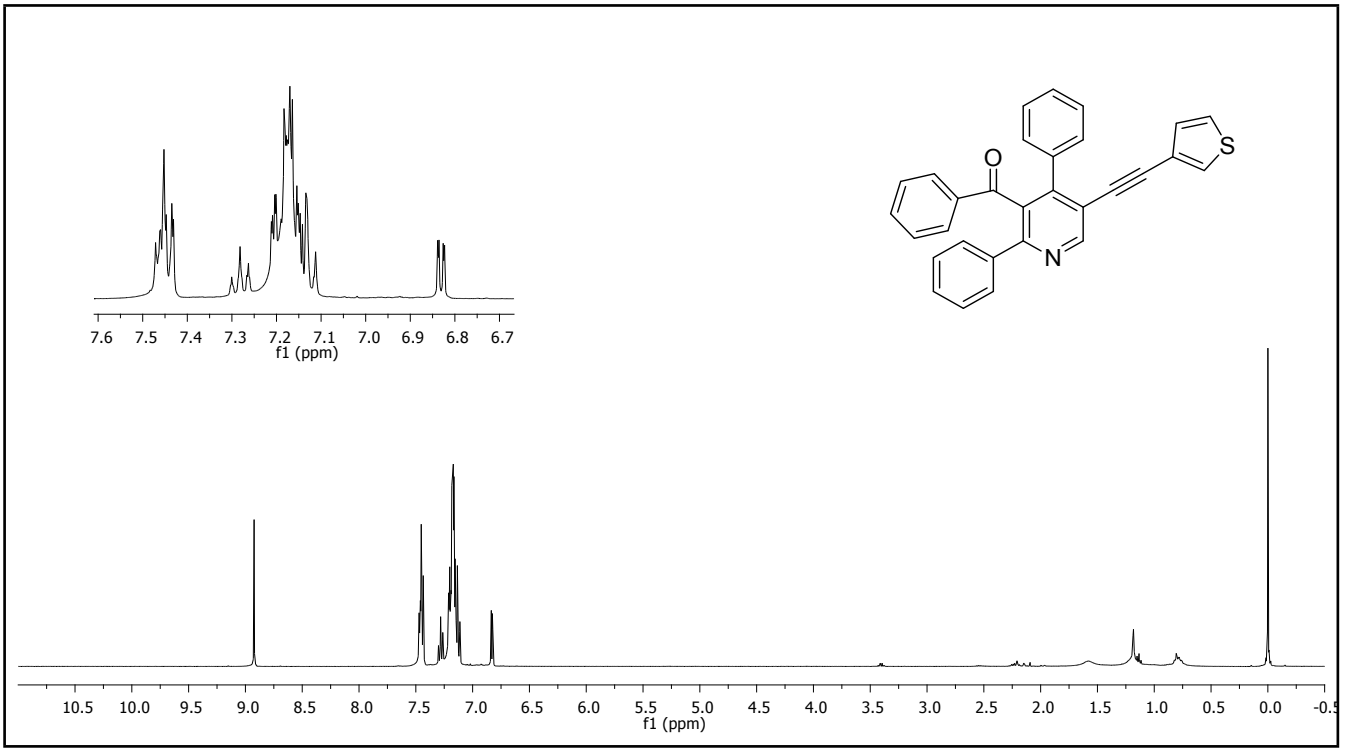


Figure S23. ^{1}H NMR spectrum of compound **7l**.

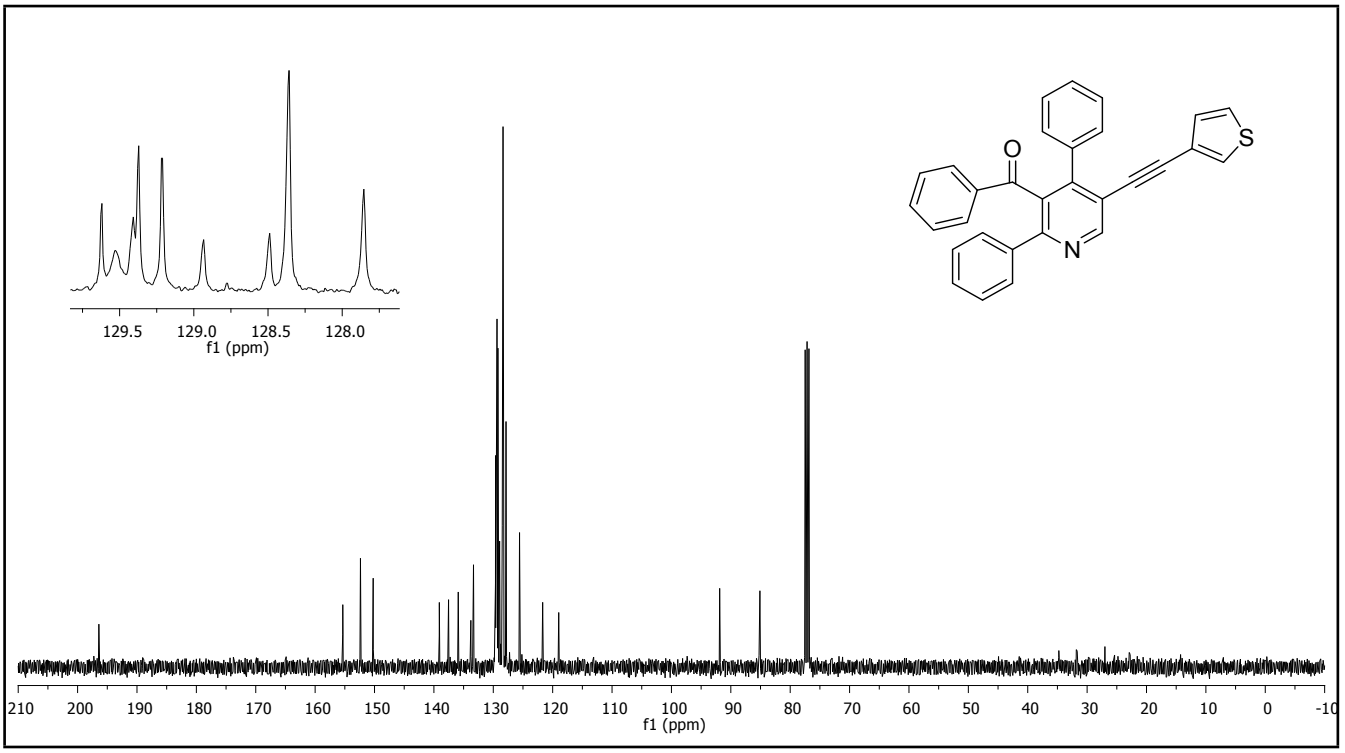


Figure S24. ^{13}C NMR spectrum of compound **7l**.

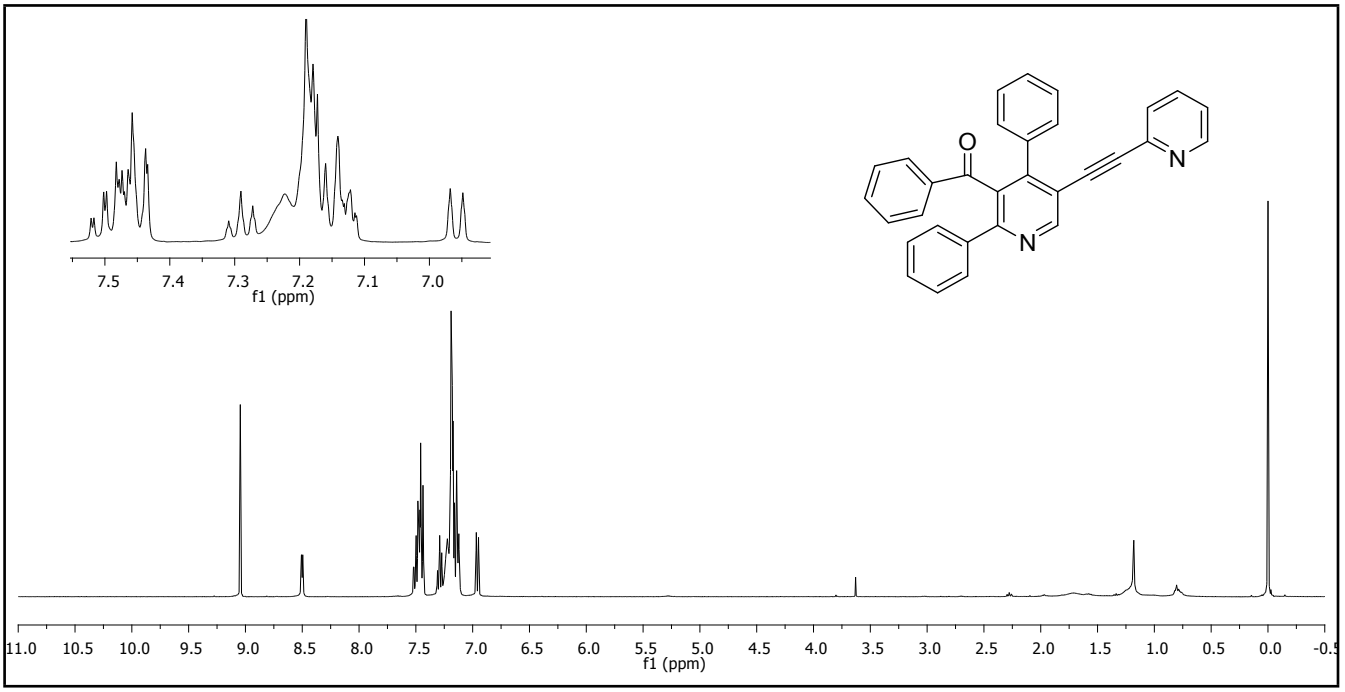


Figure S25. ^{1}H NMR spectrum of compound **7m**.

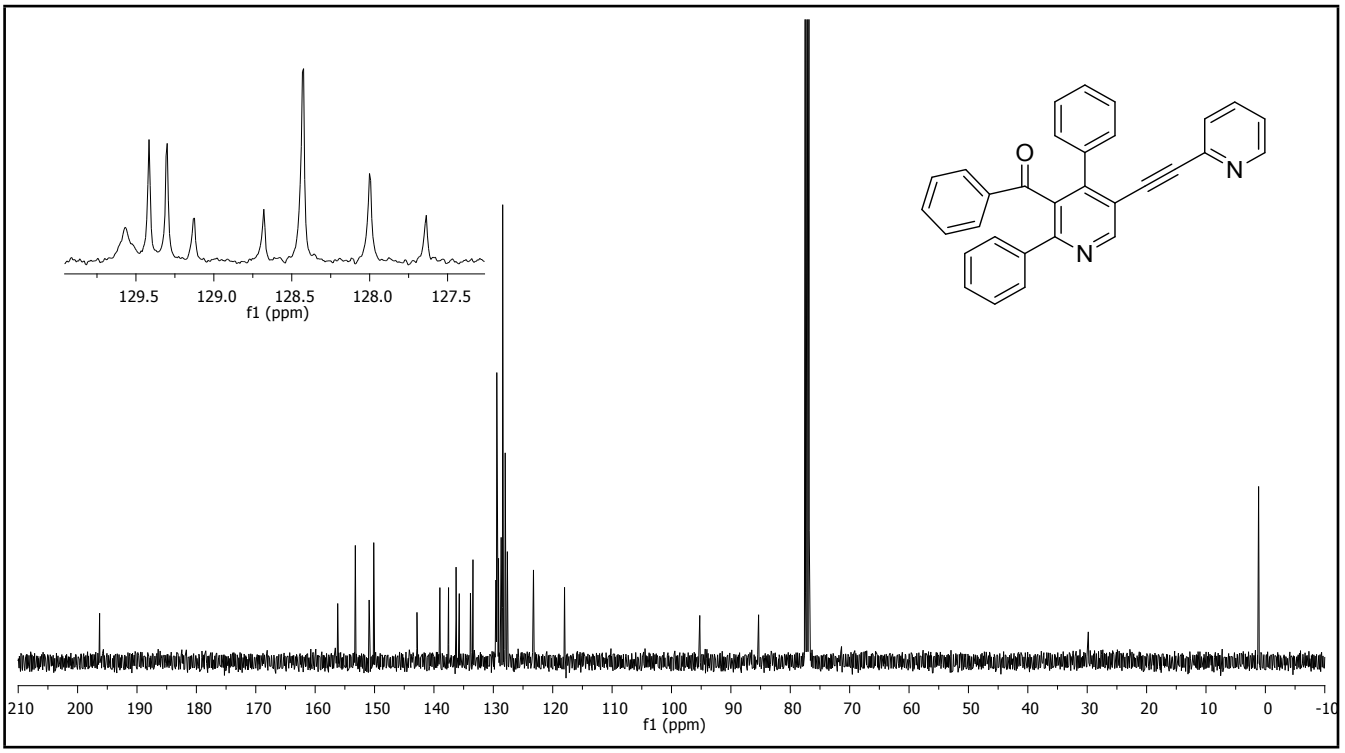


Figure S26. ^{13}C NMR spectrum of compound **7m**.

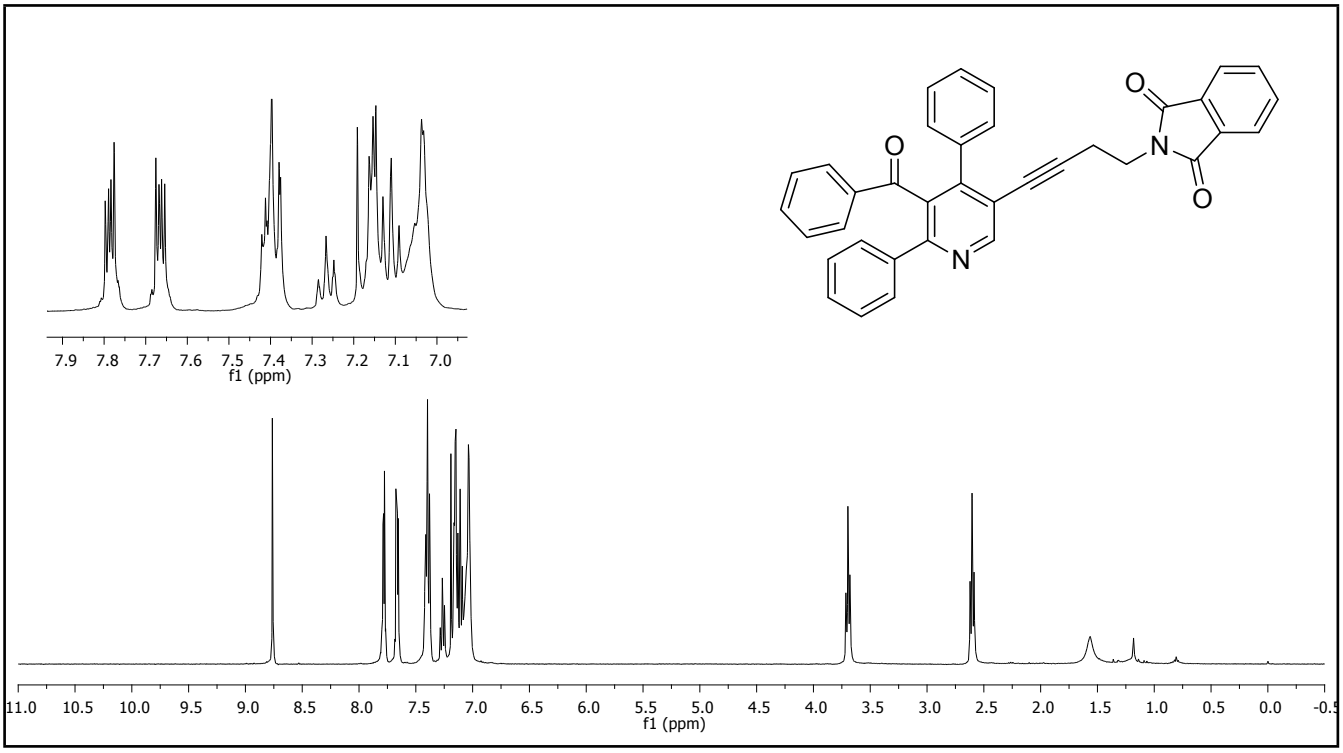


Figure S27. ^{1}H NMR spectrum of compound **7n**.

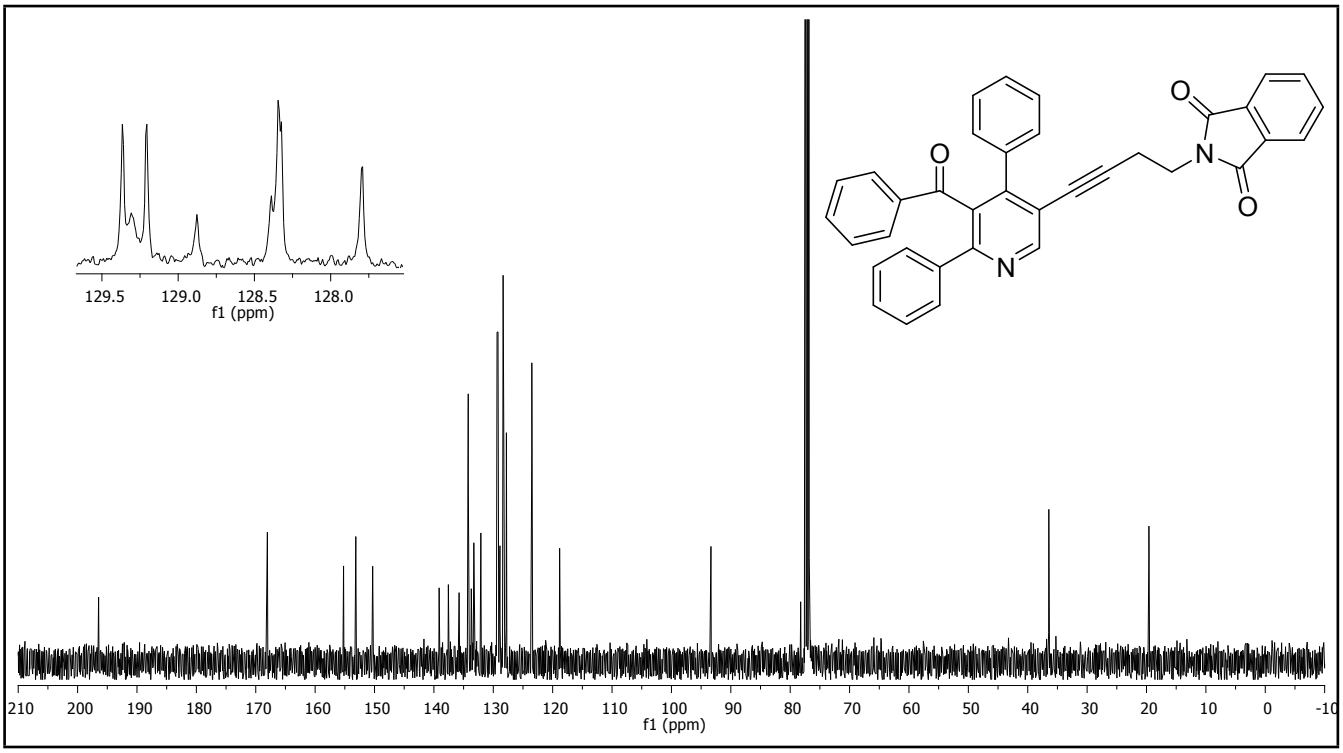


Figure S28. ^{13}C NMR spectrum of compound **7n**.

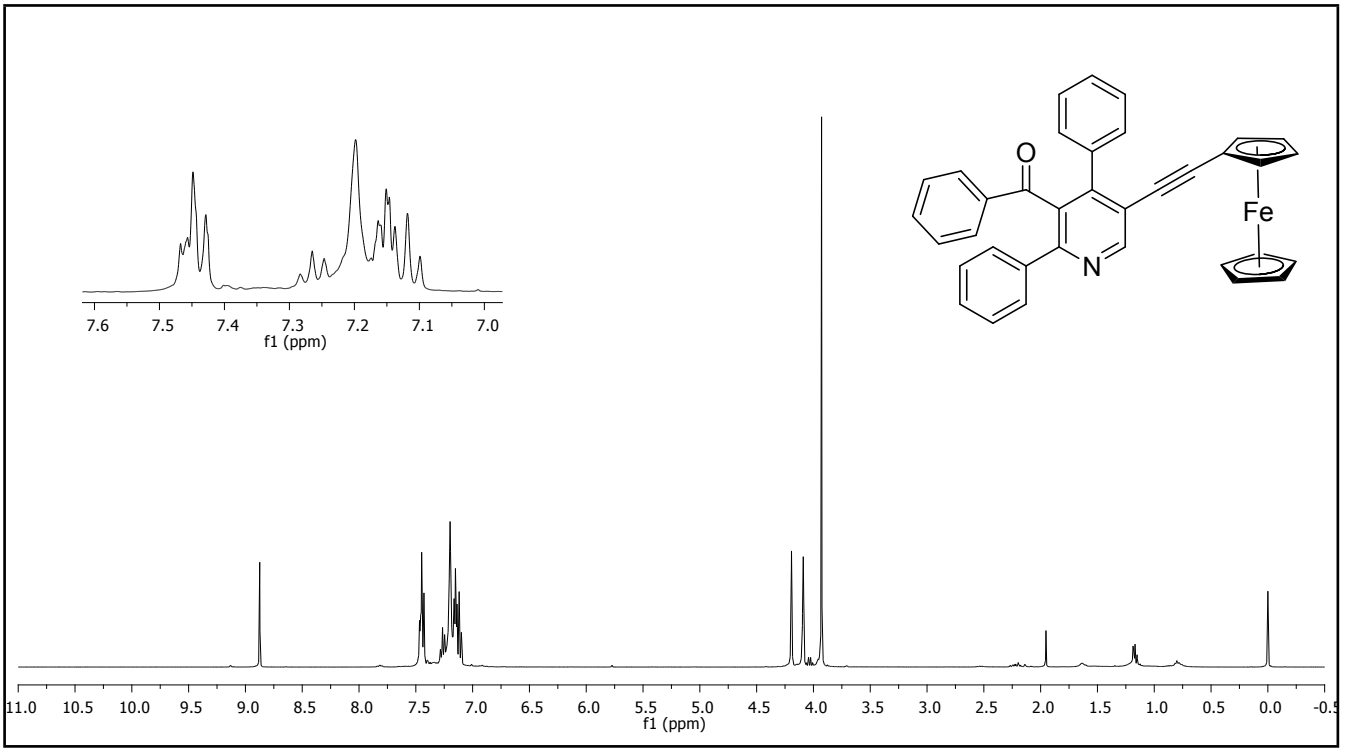


Figure S29. ^{1}H NMR spectrum of compound **7o**.

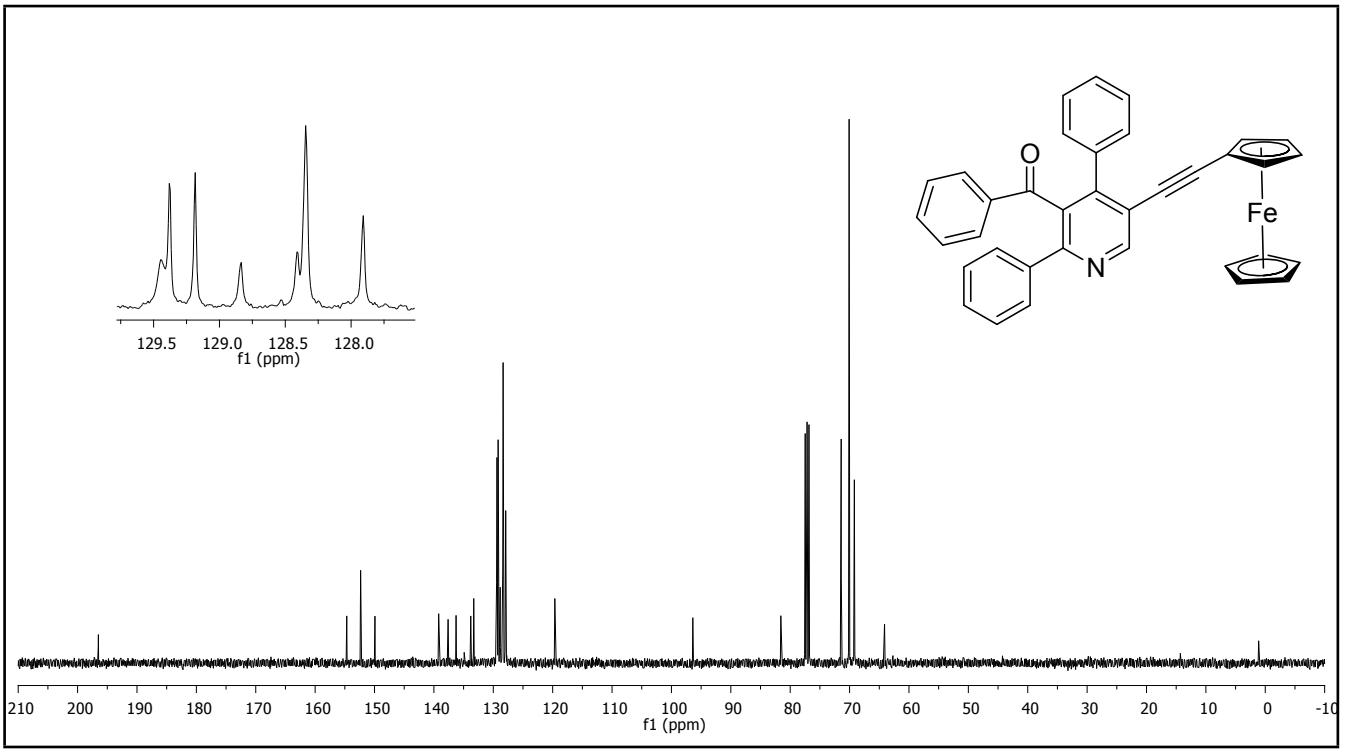


Figure S30. ^{13}C NMR spectrum of compound **7o**.

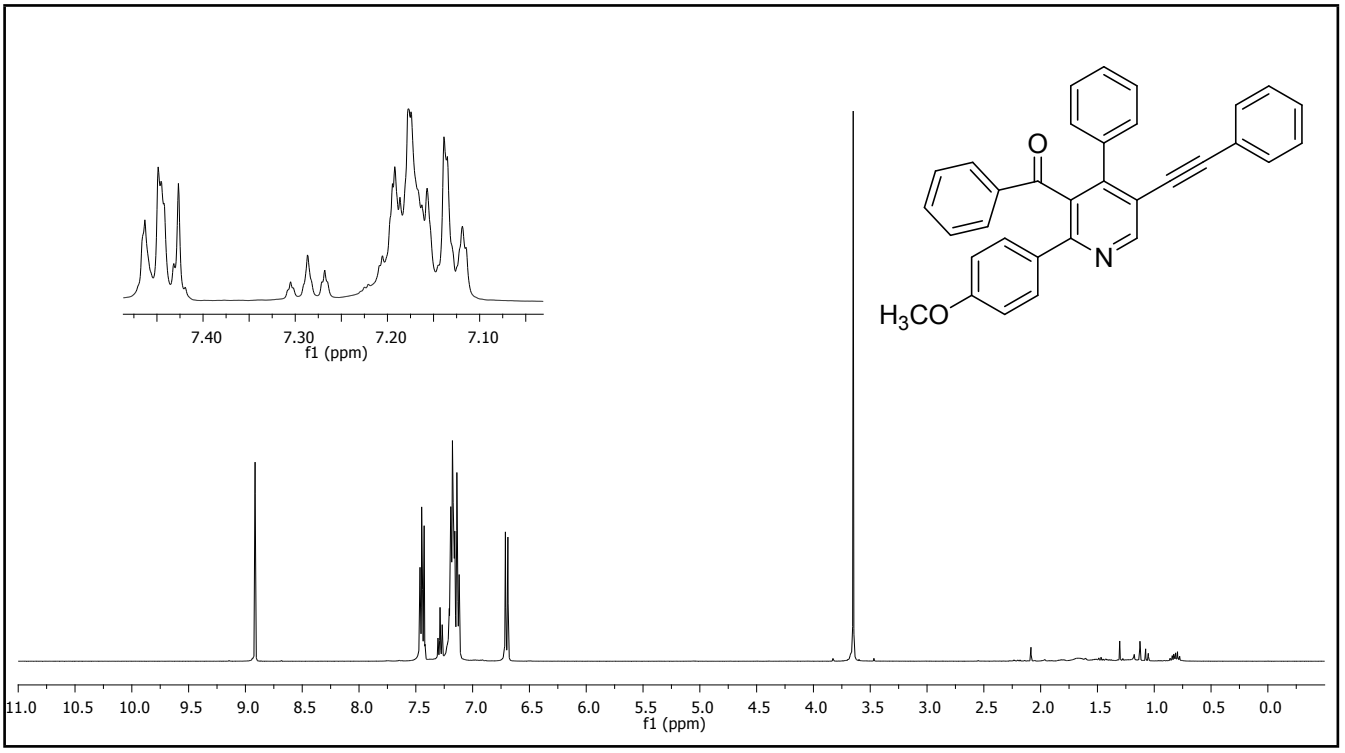


Figure S31. ^{1}H NMR spectrum of compound **7p**.

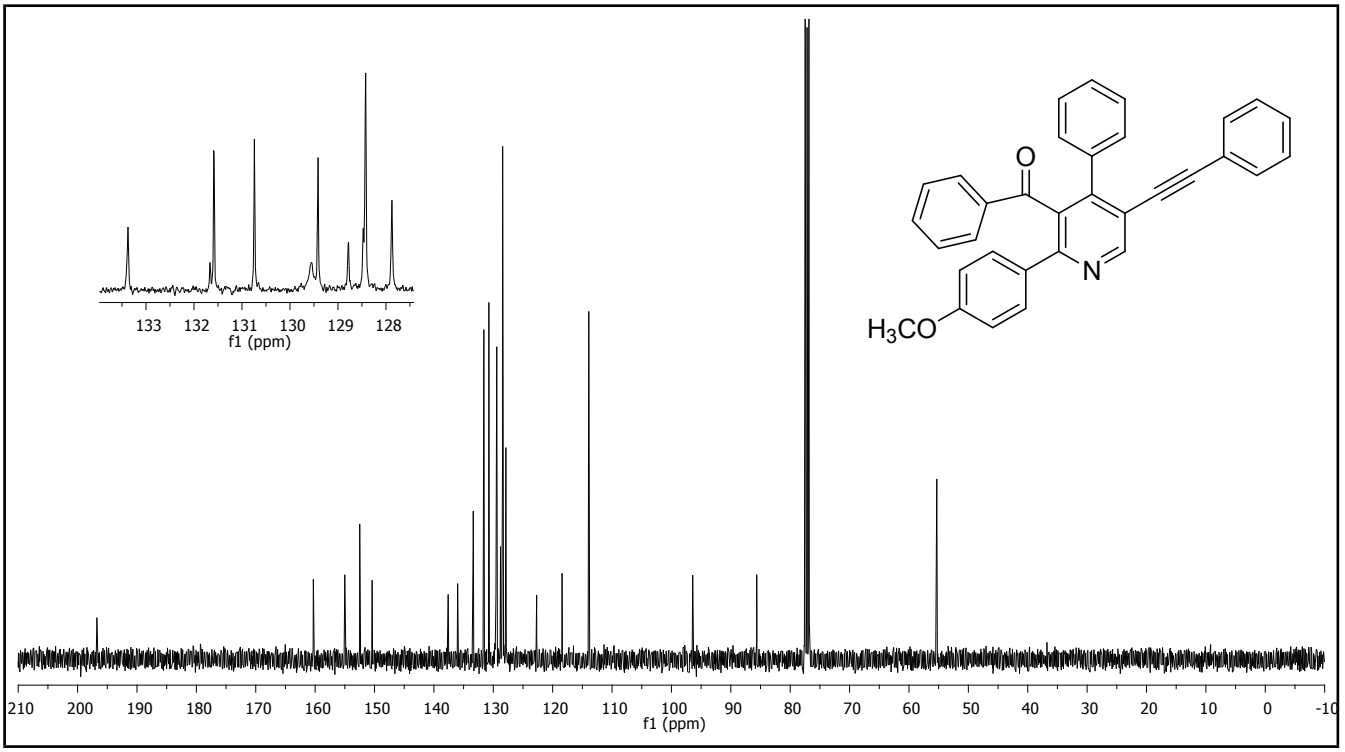


Figure S32. ^{13}C NMR spectrum of compound **7p**.

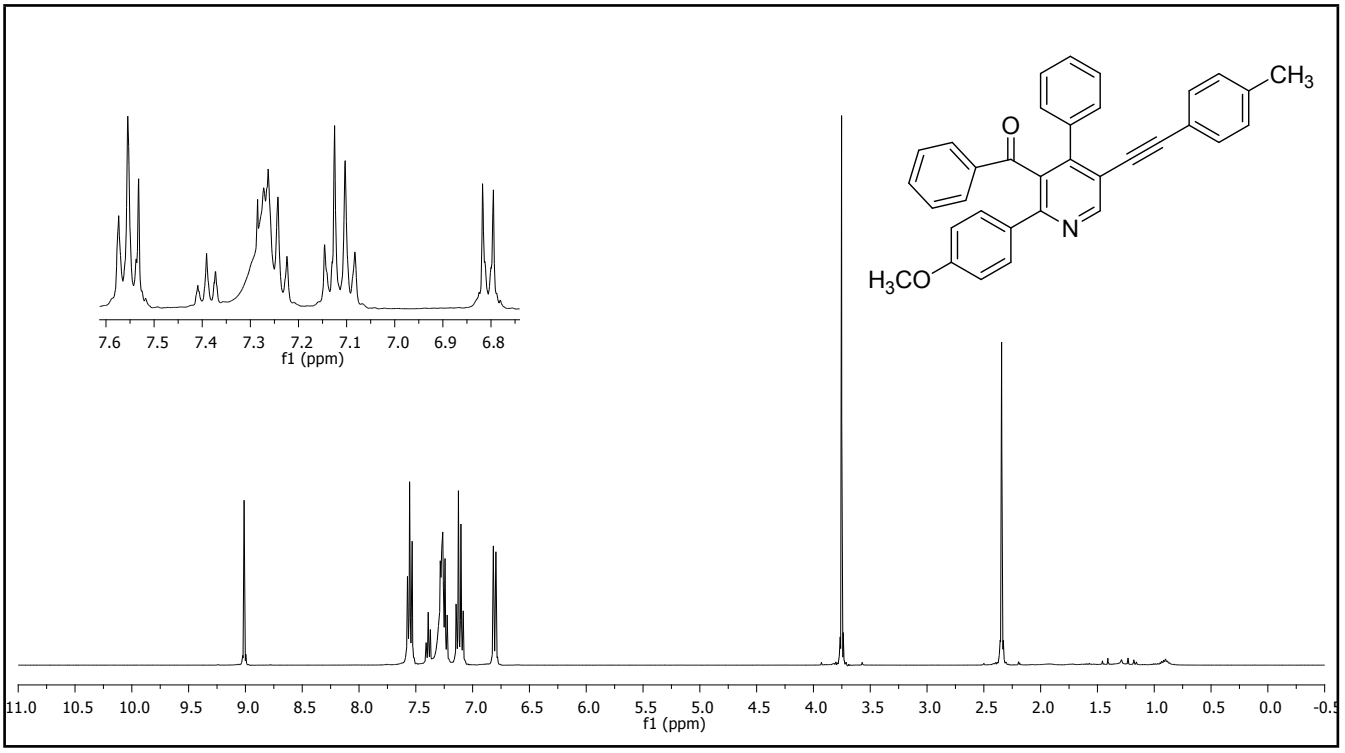


Figure S33. ^{1}H NMR spectrum of compound **7q**.

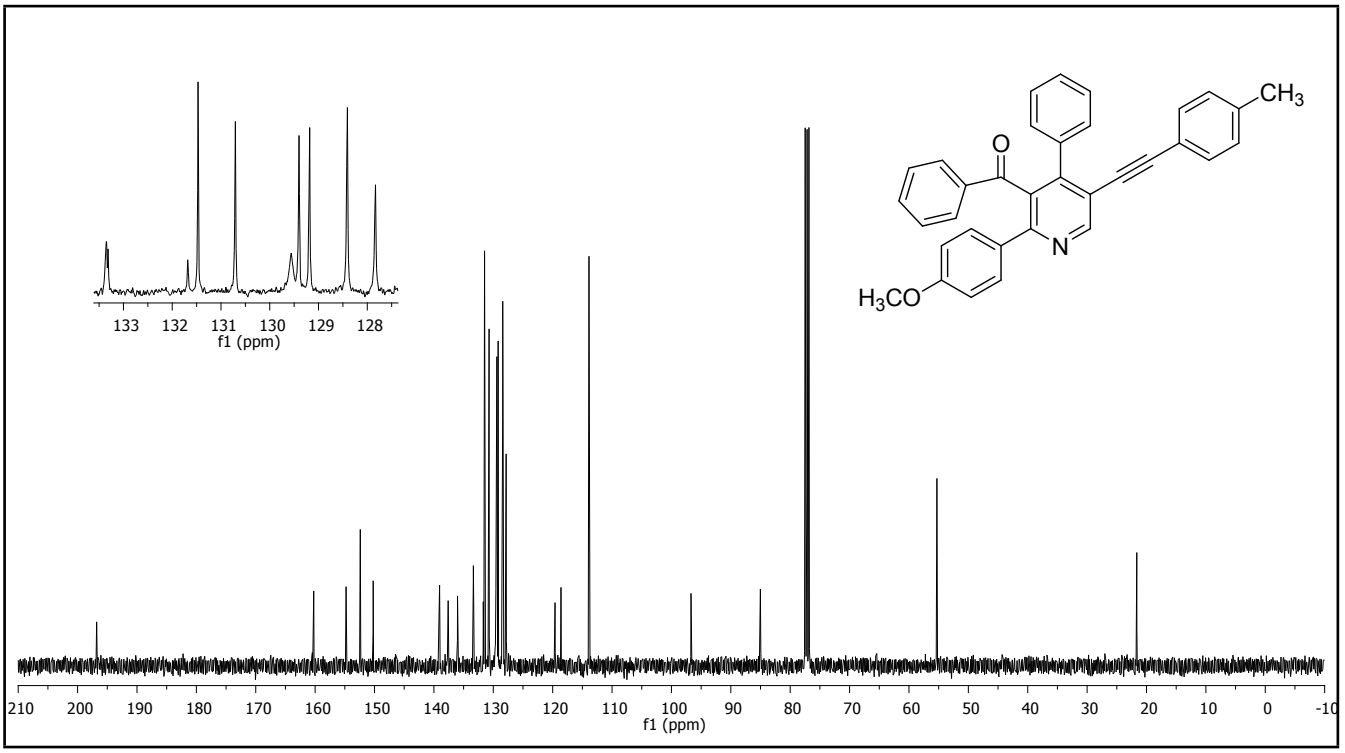


Figure S34. ^{13}C NMR spectrum of compound **7q**.

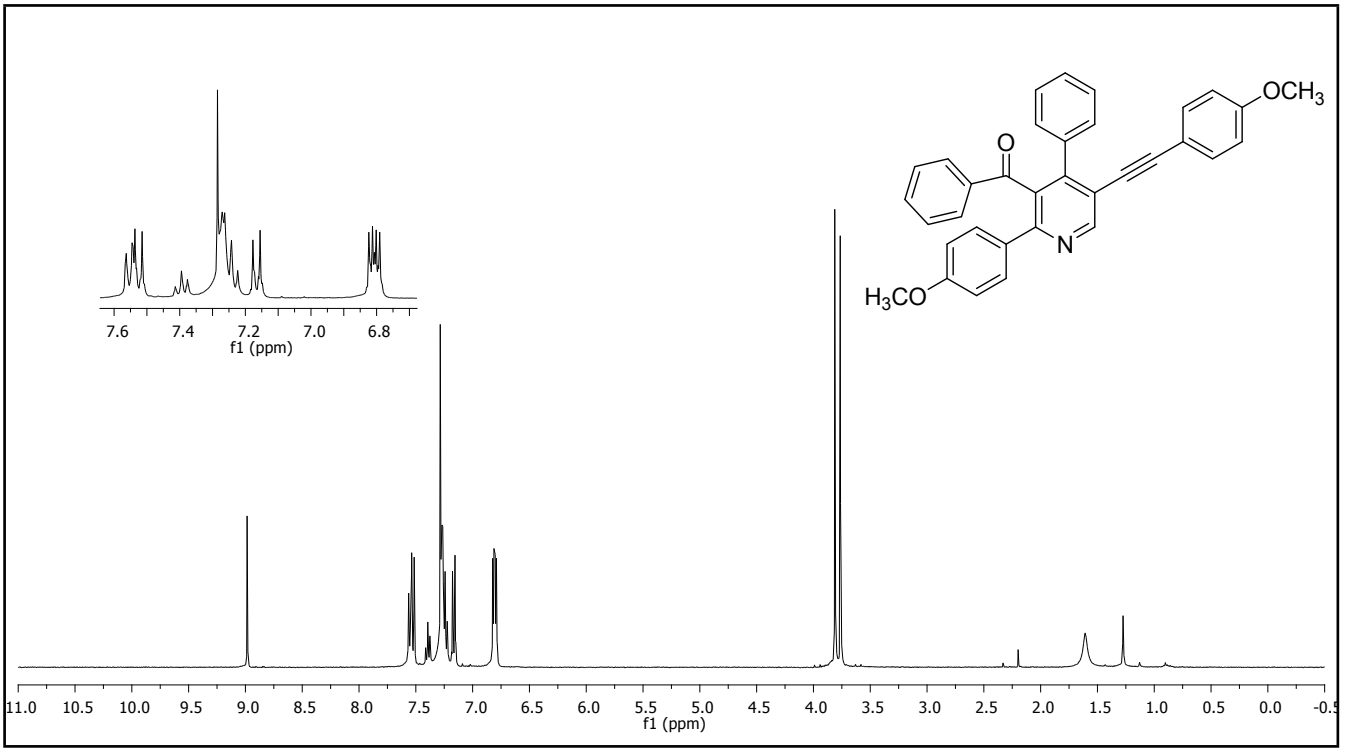


Figure S35. ^{1}H NMR spectrum of compound **7r**.

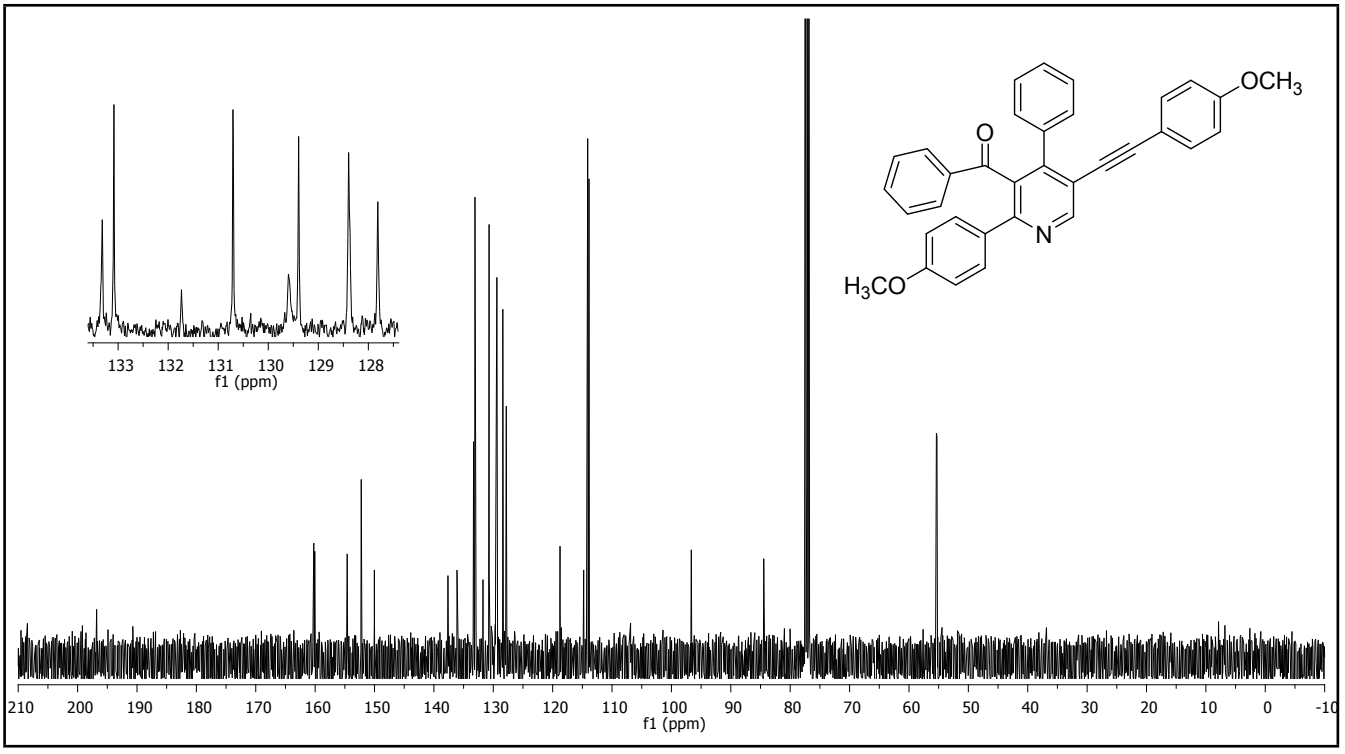


Figure S36. ^{13}C NMR spectrum of compound **7r**.

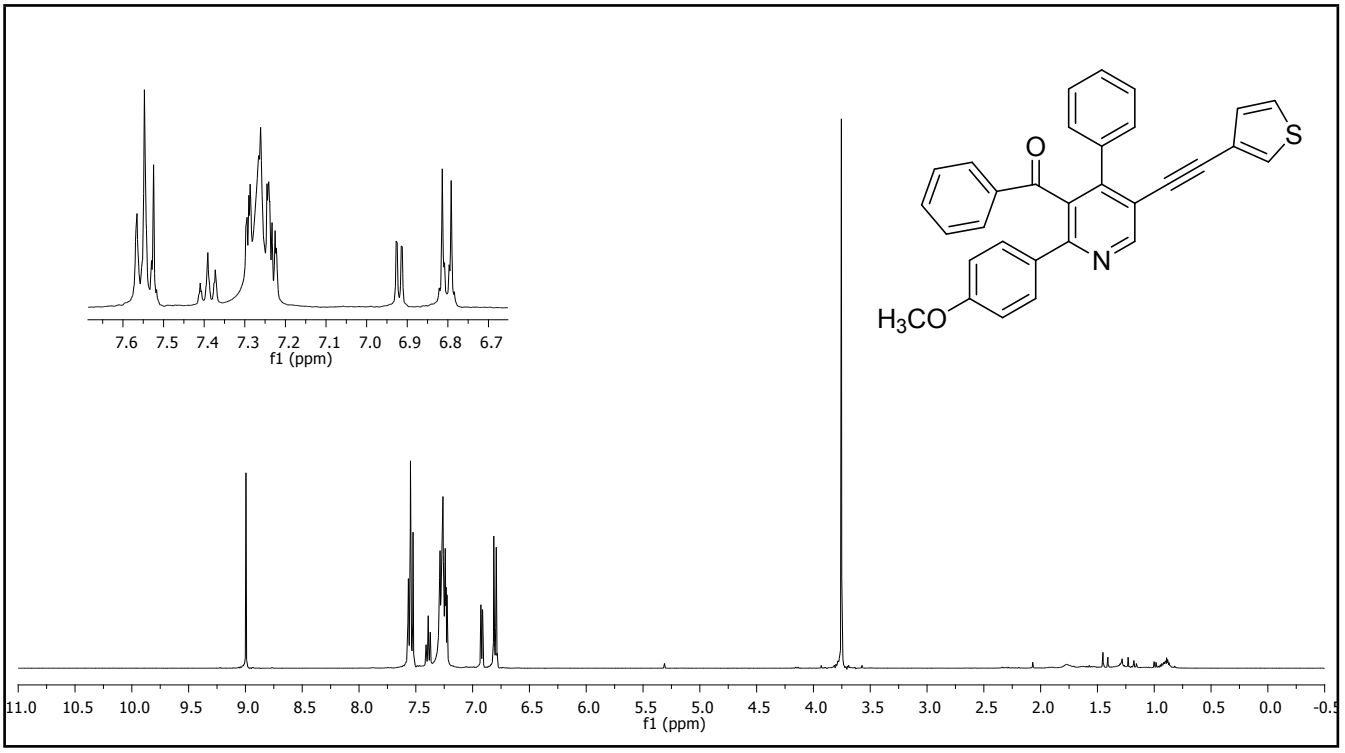


Figure S37. ^{1}H NMR spectrum of compound **7s**.

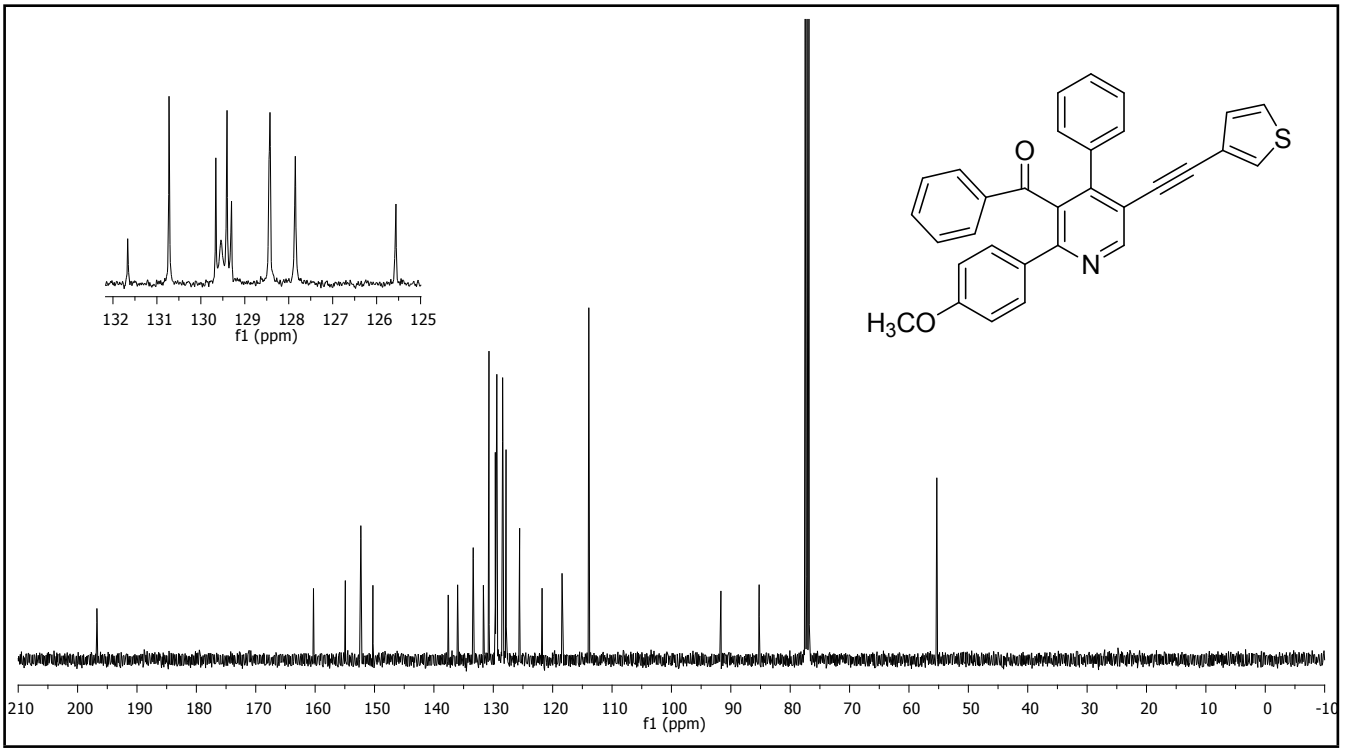


Figure S38. ^{13}C NMR spectrum of compound **7s**.

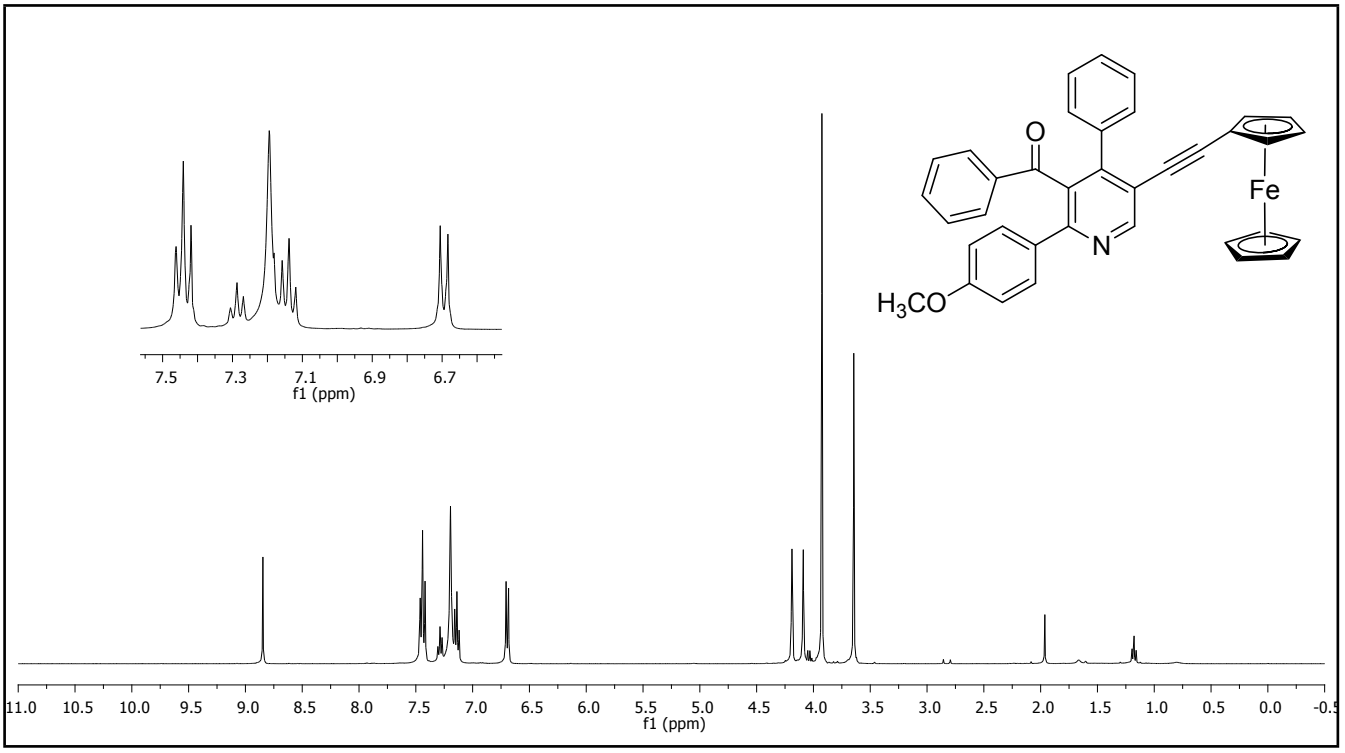


Figure S39. ^{1}H NMR spectrum of compound **7t**.

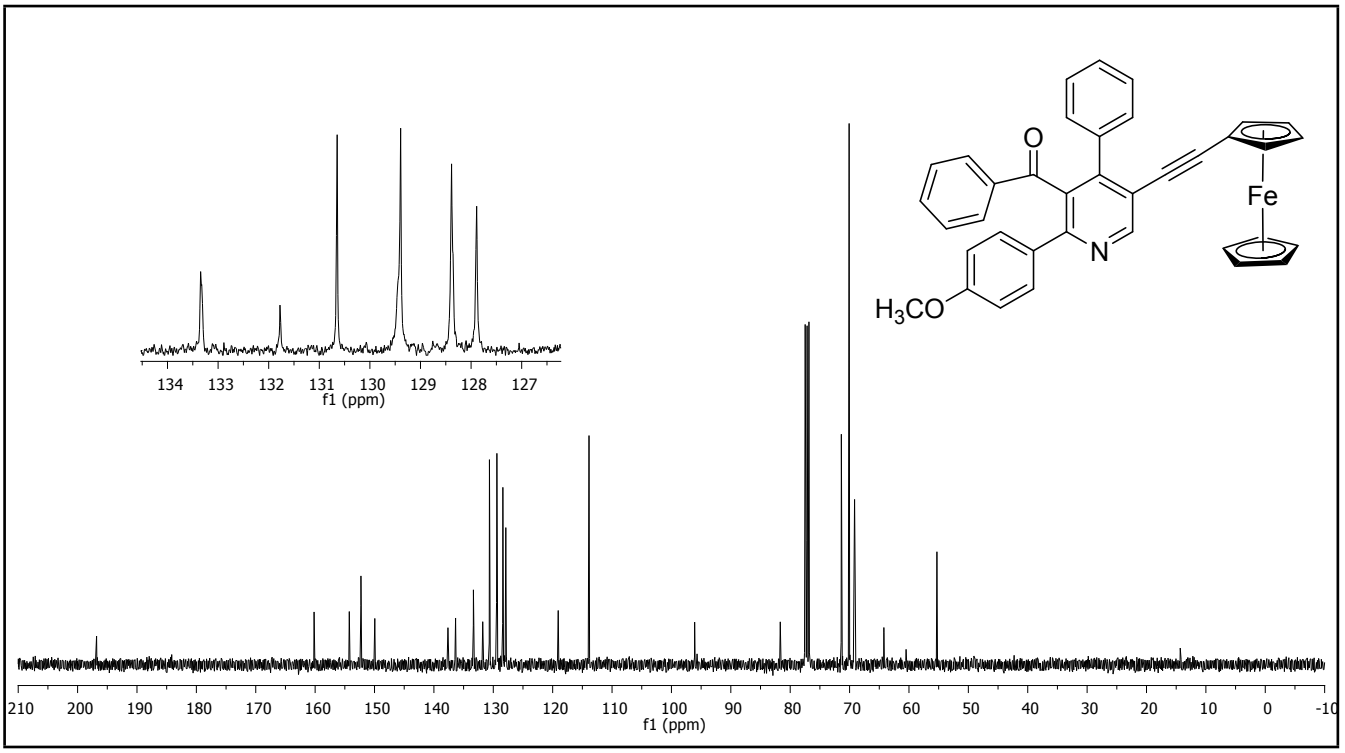


Figure S40. ^{13}C NMR spectrum of compound **7t**.

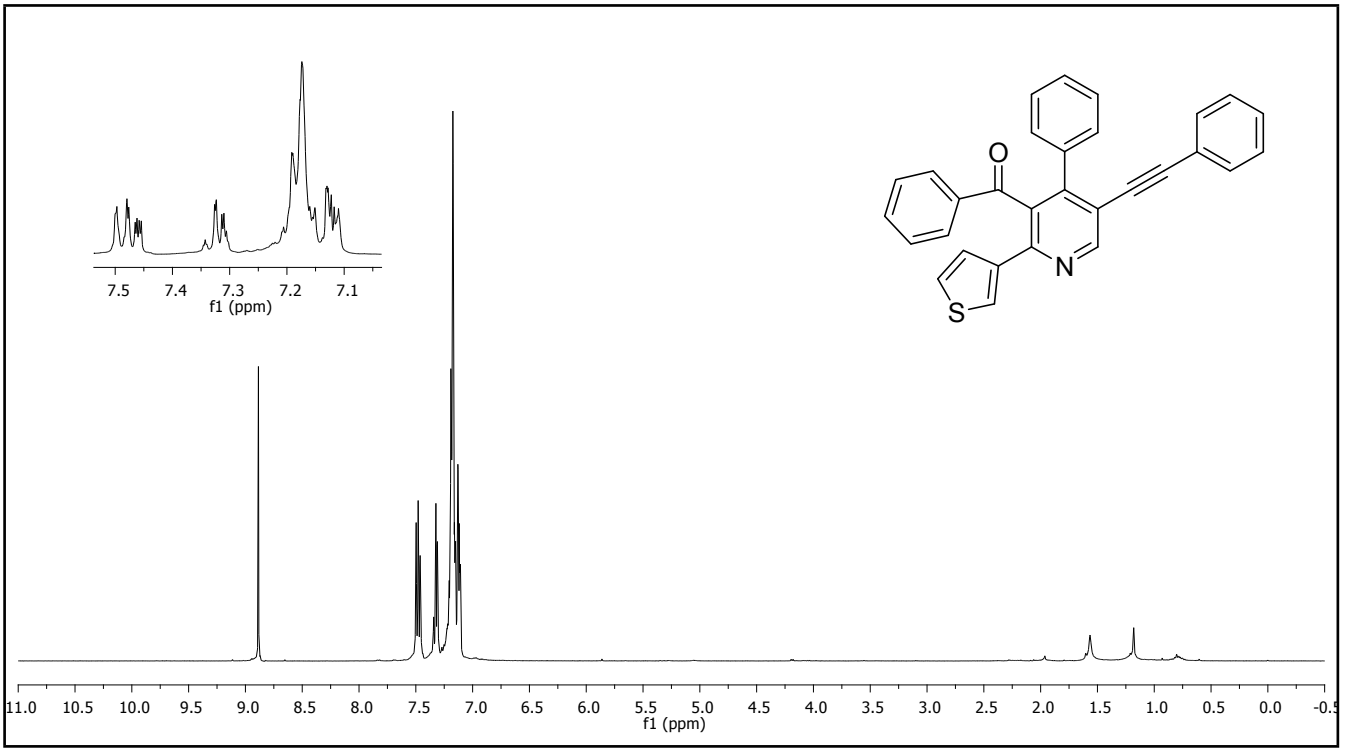


Figure S41. ^{1}H NMR spectrum of compound **7u.**

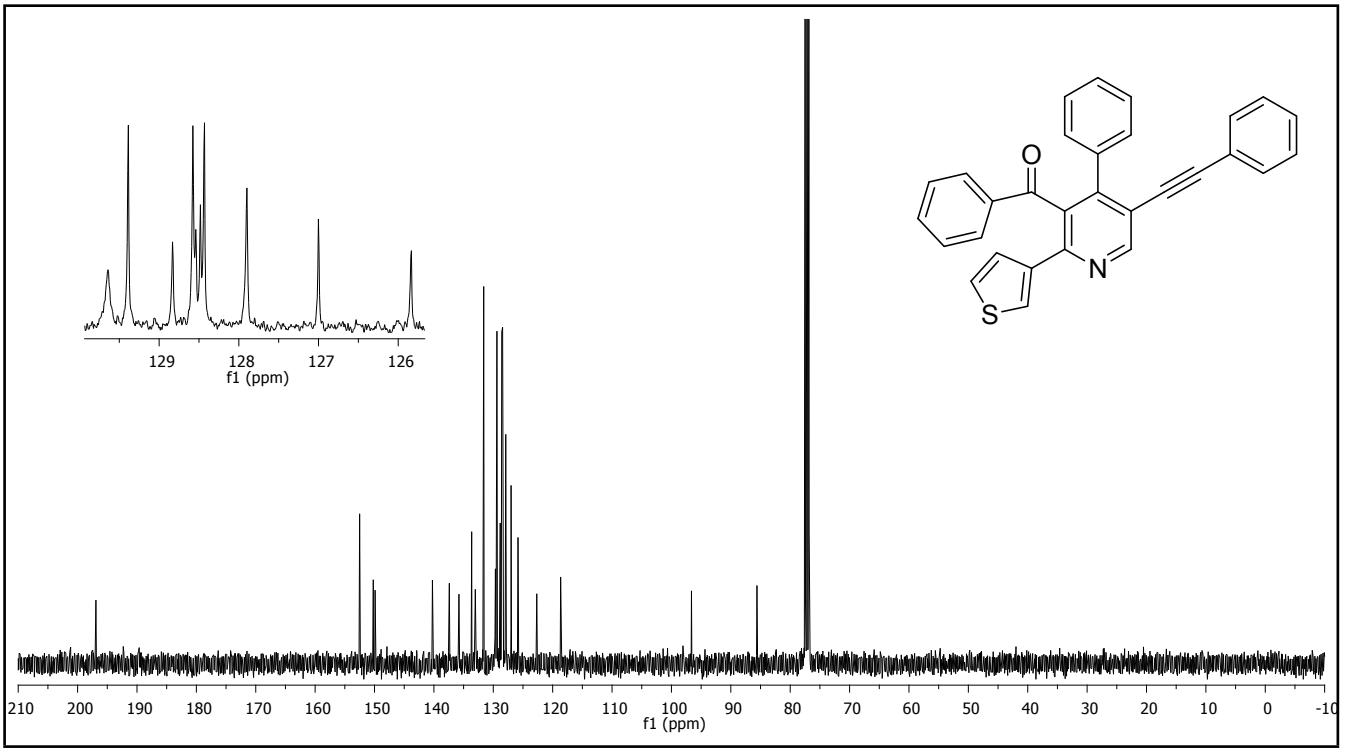


Figure S42. ^{13}C NMR spectrum of compound **7u**.

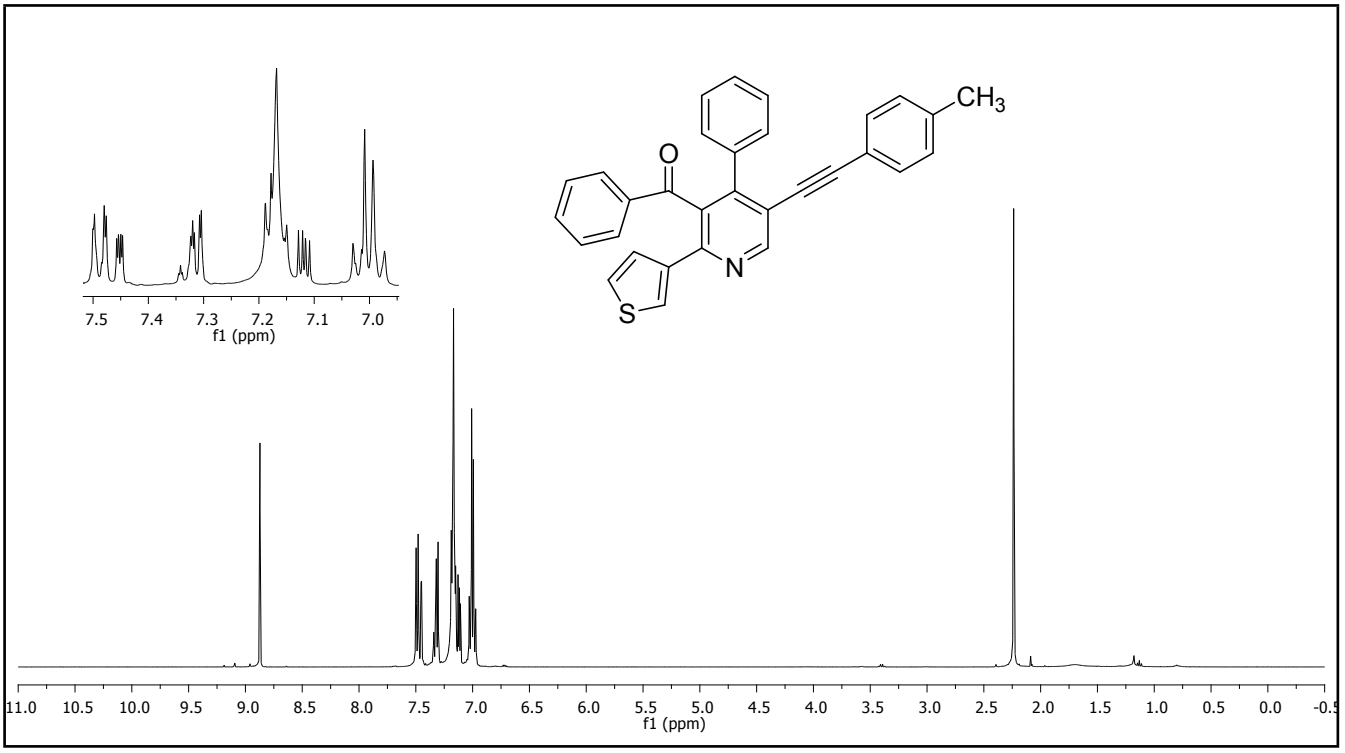


Figure S43. ^{1}H NMR spectrum of compound **7v**.

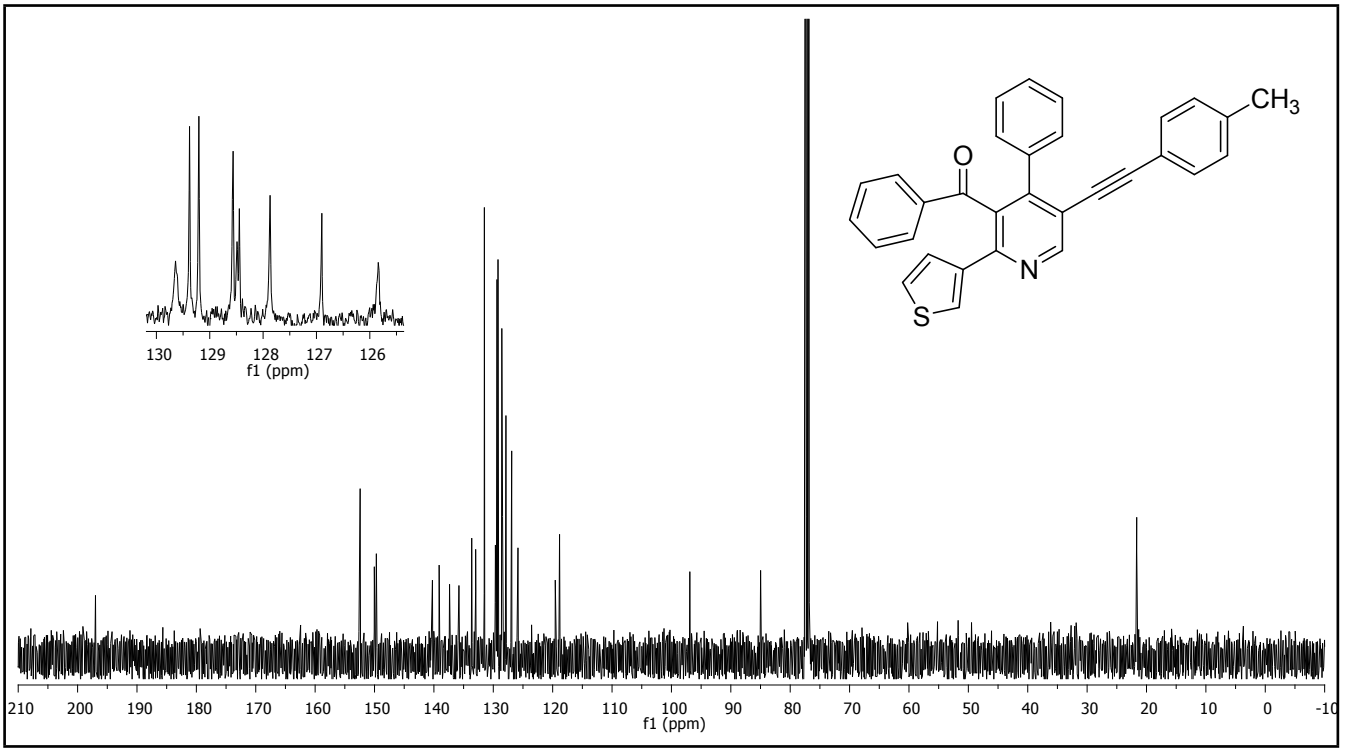


Figure S44. ^{13}C NMR spectrum of compound **7v**.

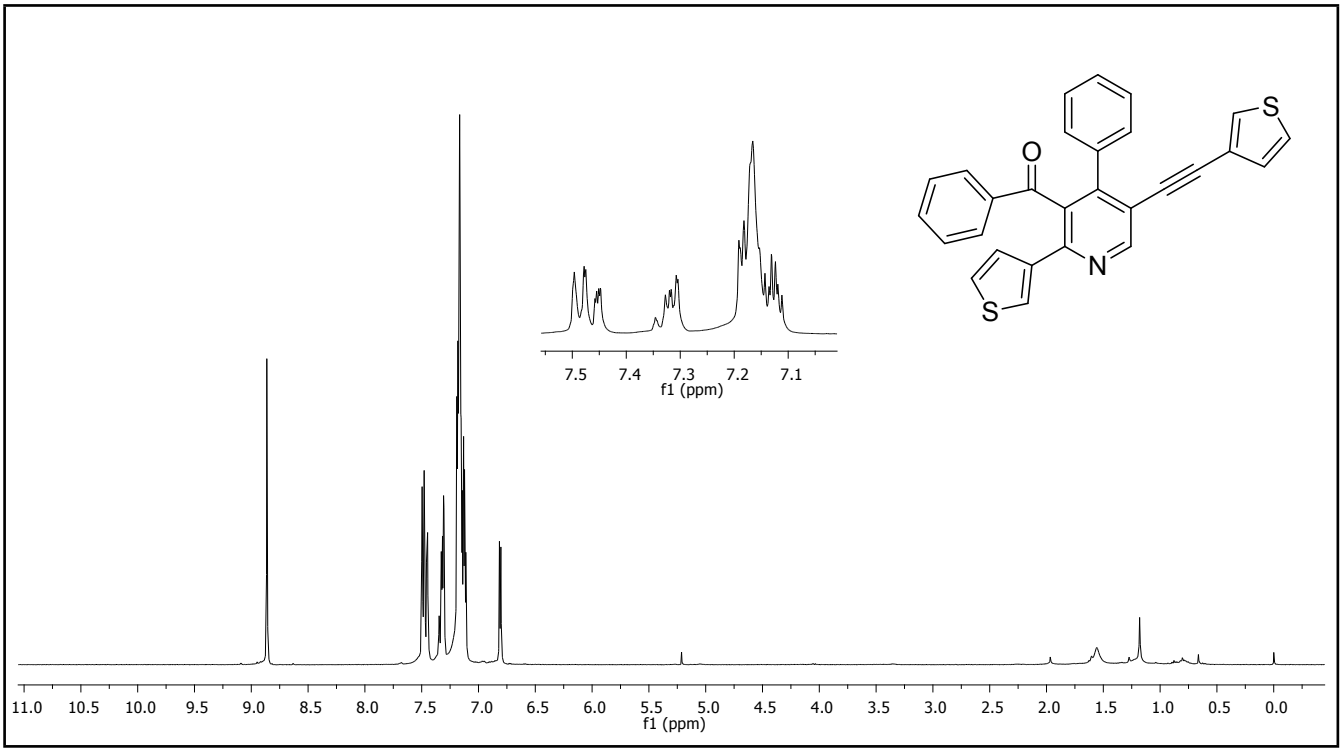


Figure S45. ^{1}H NMR spectrum of compound **7w**.

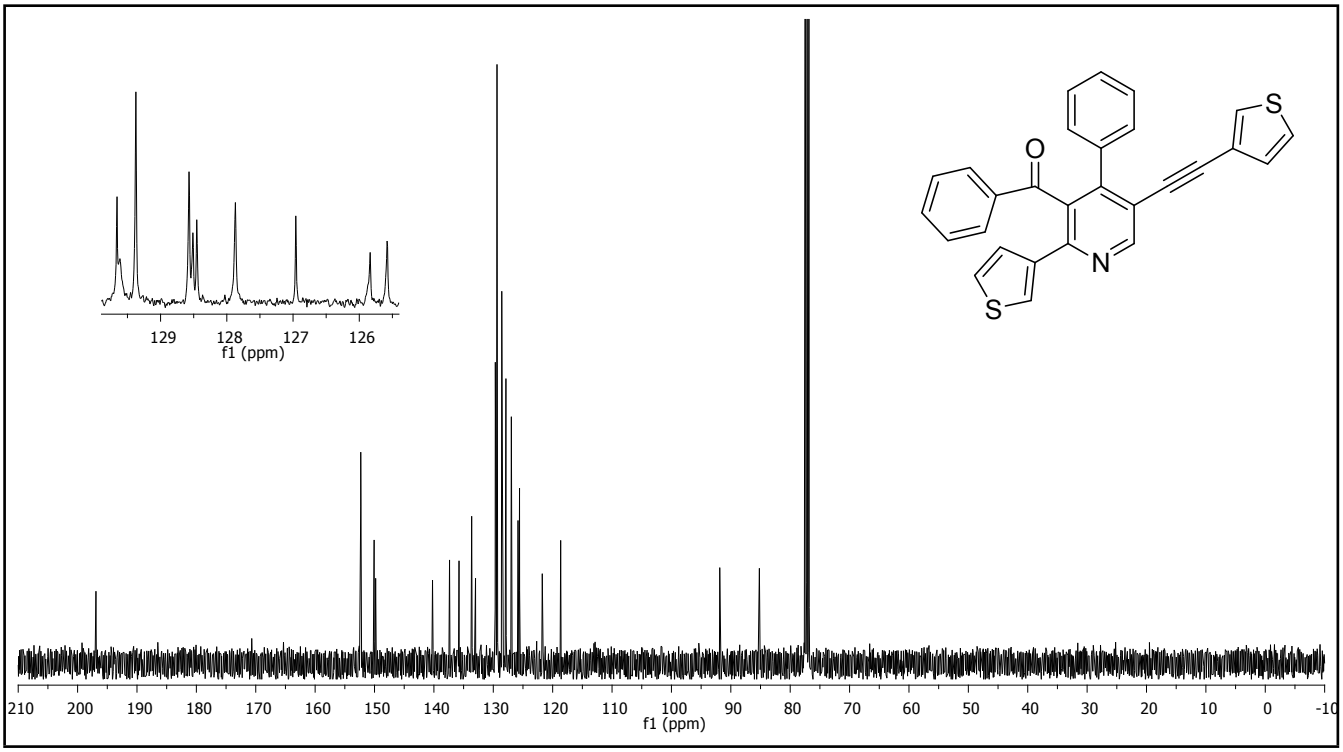


Figure S46. ^{13}C NMR spectrum of compound **7w**.

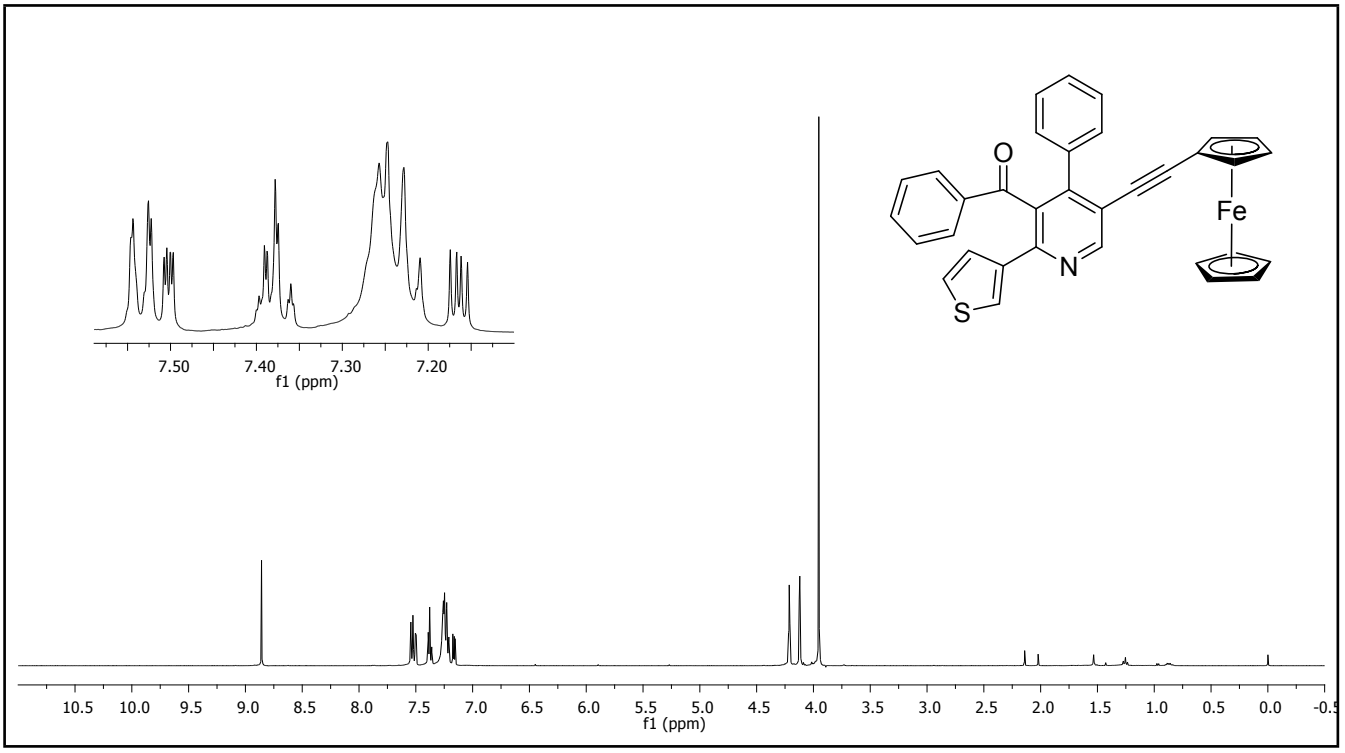


Figure S47. ^{1}H NMR spectrum of compound **7x**.

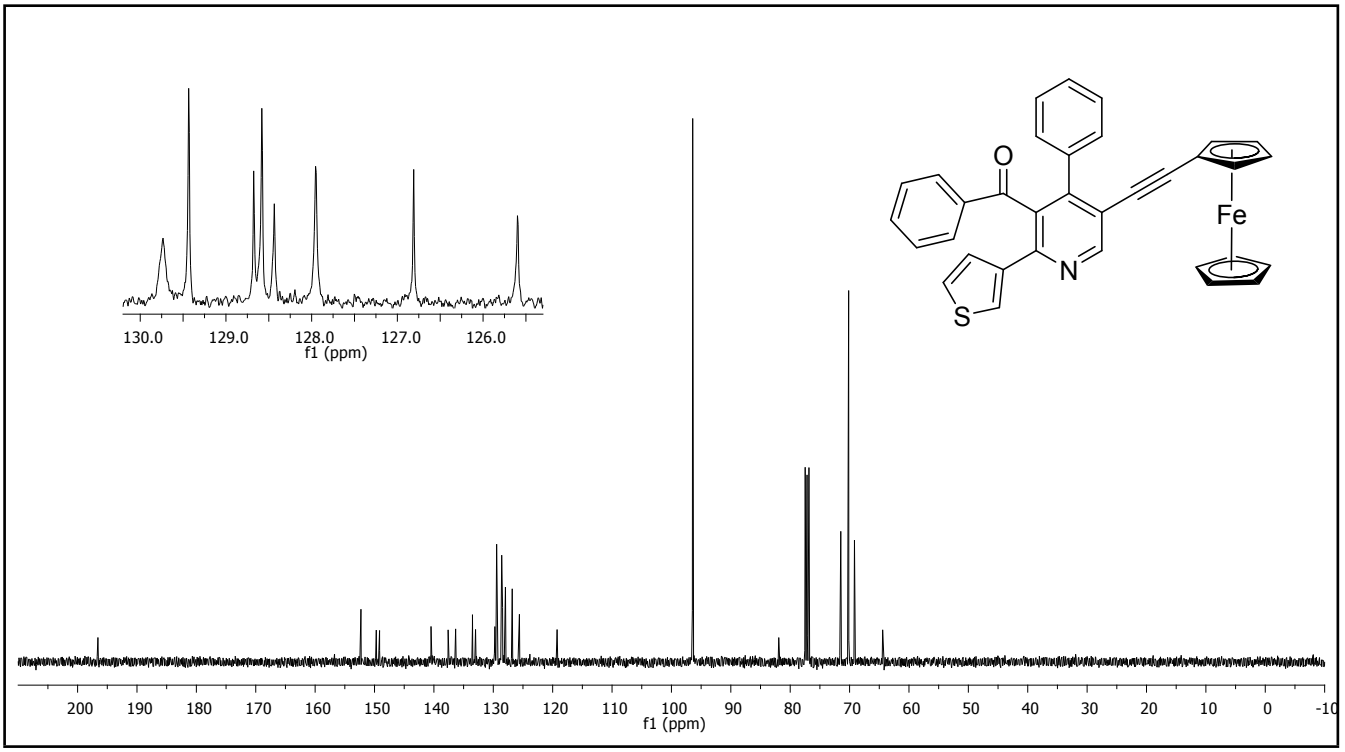


Figure S48. ^{13}C NMR spectrum of compound **7x**.

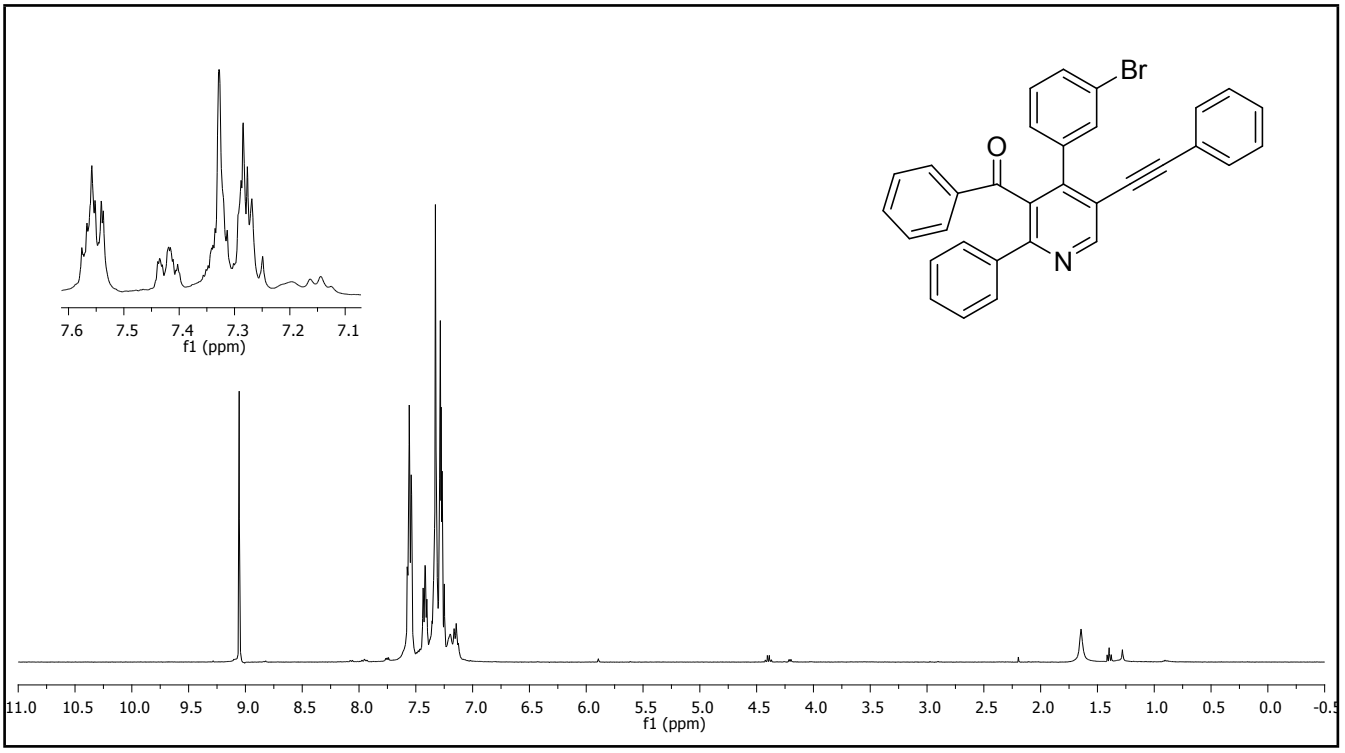


Figure S49. ^{1}H NMR spectrum of compound **7y**.

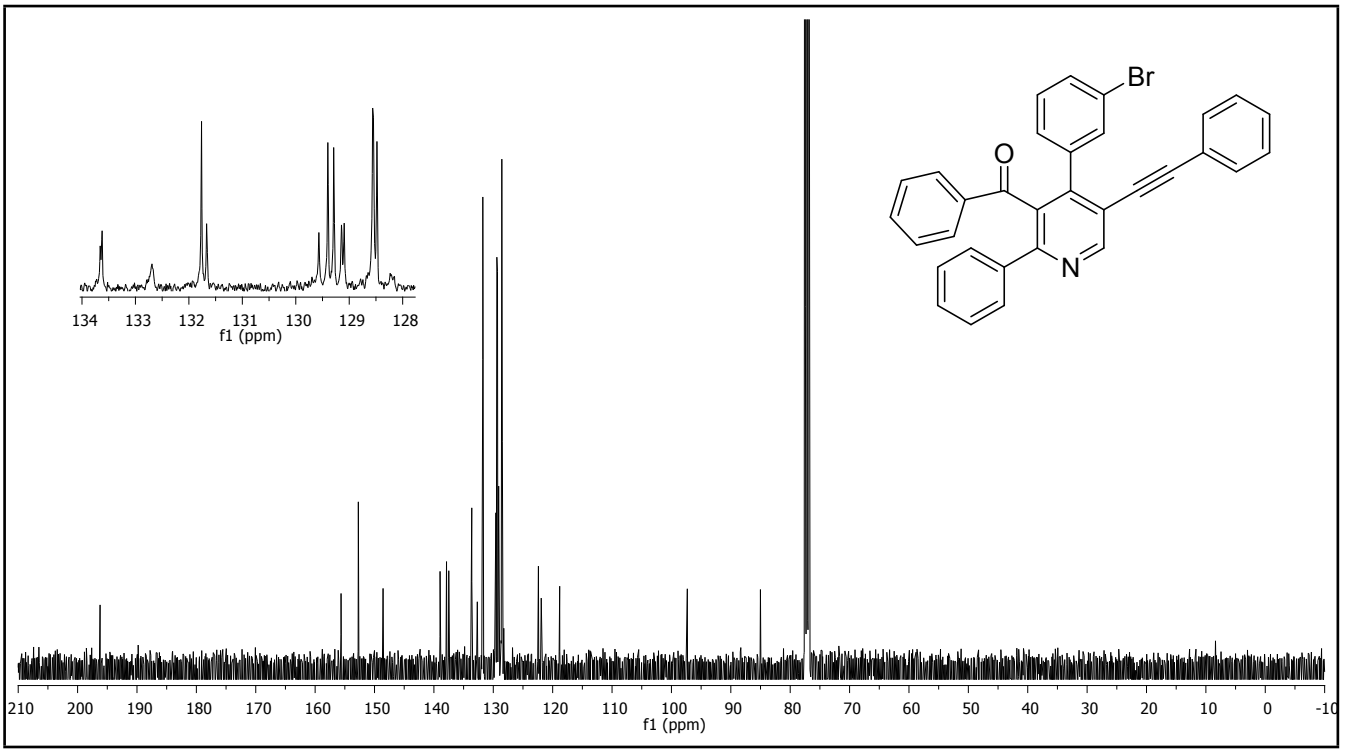


Figure S50. ^{13}C NMR spectrum of compound **7y**.

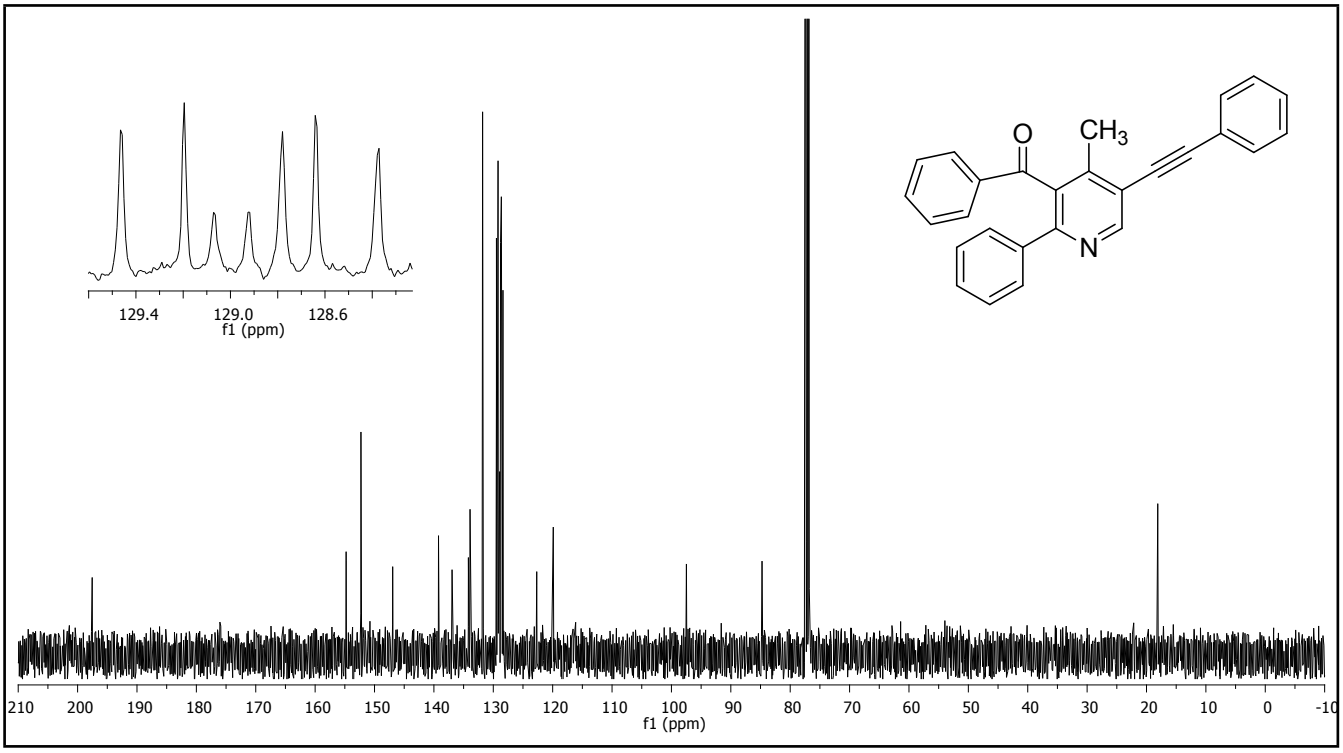


Figure S51. ^{1}H NMR spectrum of compound **7z**.

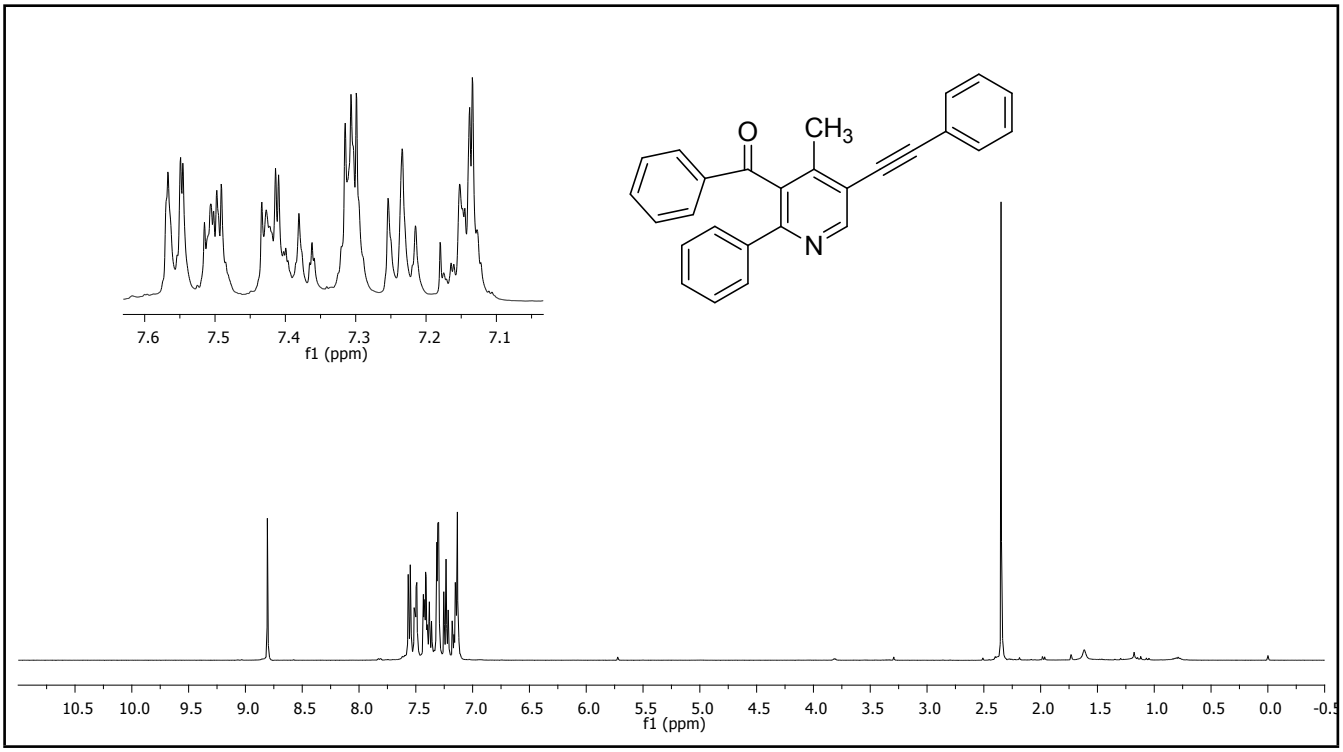


Figure S52. ^{13}C NMR spectrum of compound **7z**.

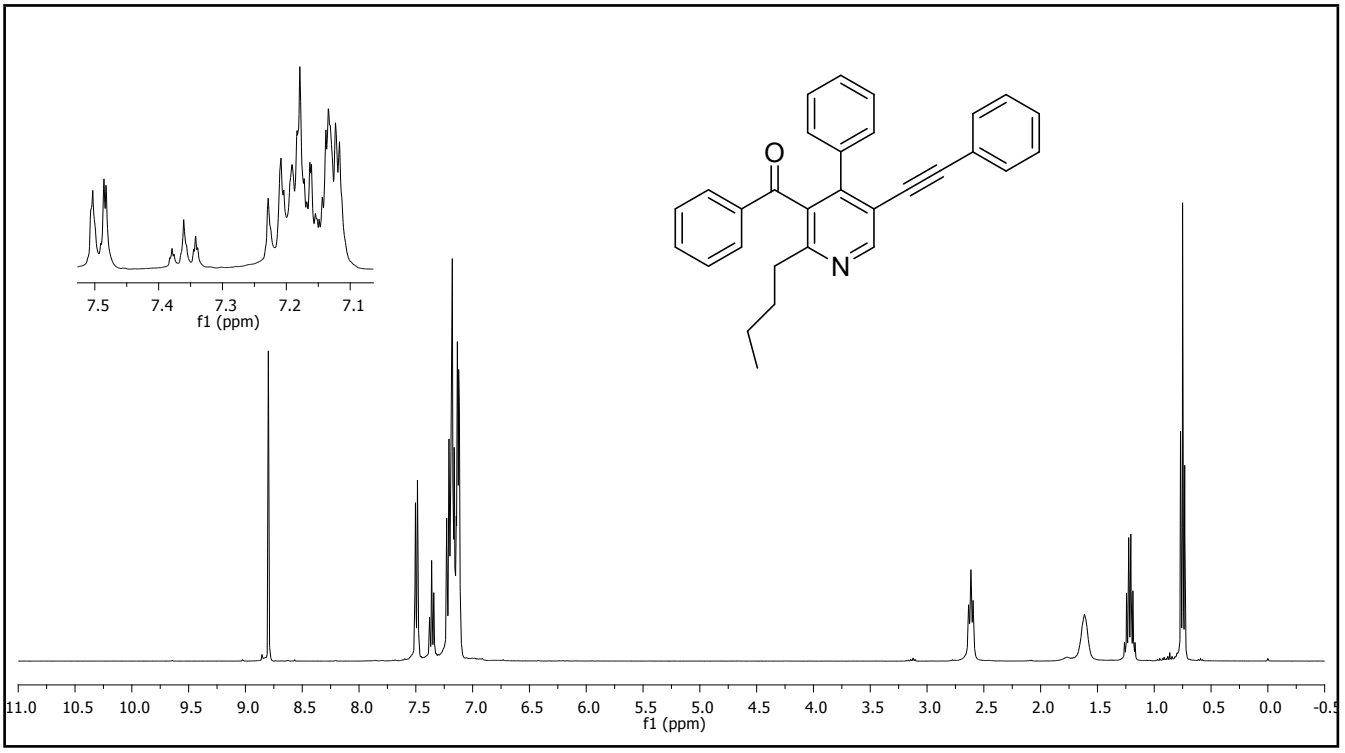


Figure S53. ^{1}H NMR spectrum of compound **7aa**.

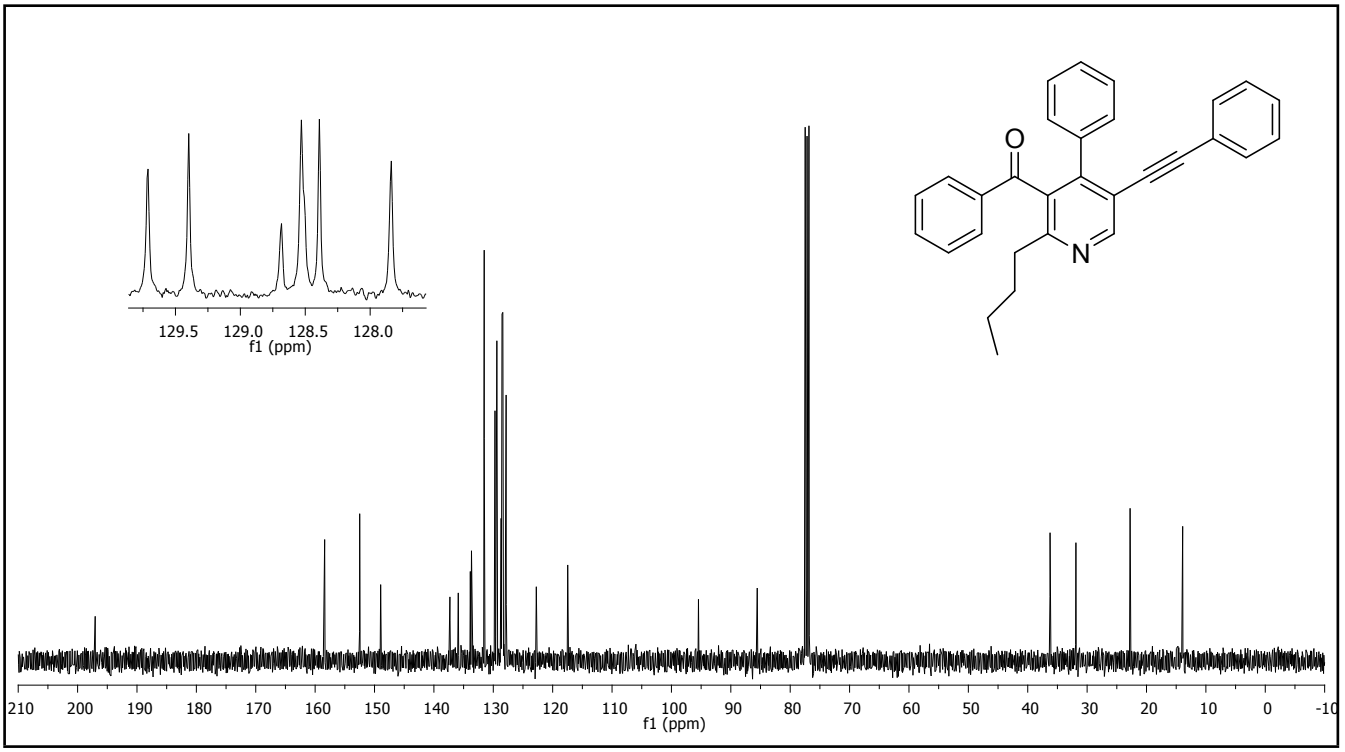


Figure S54. ^{13}C NMR spectrum of compound **7aa**.

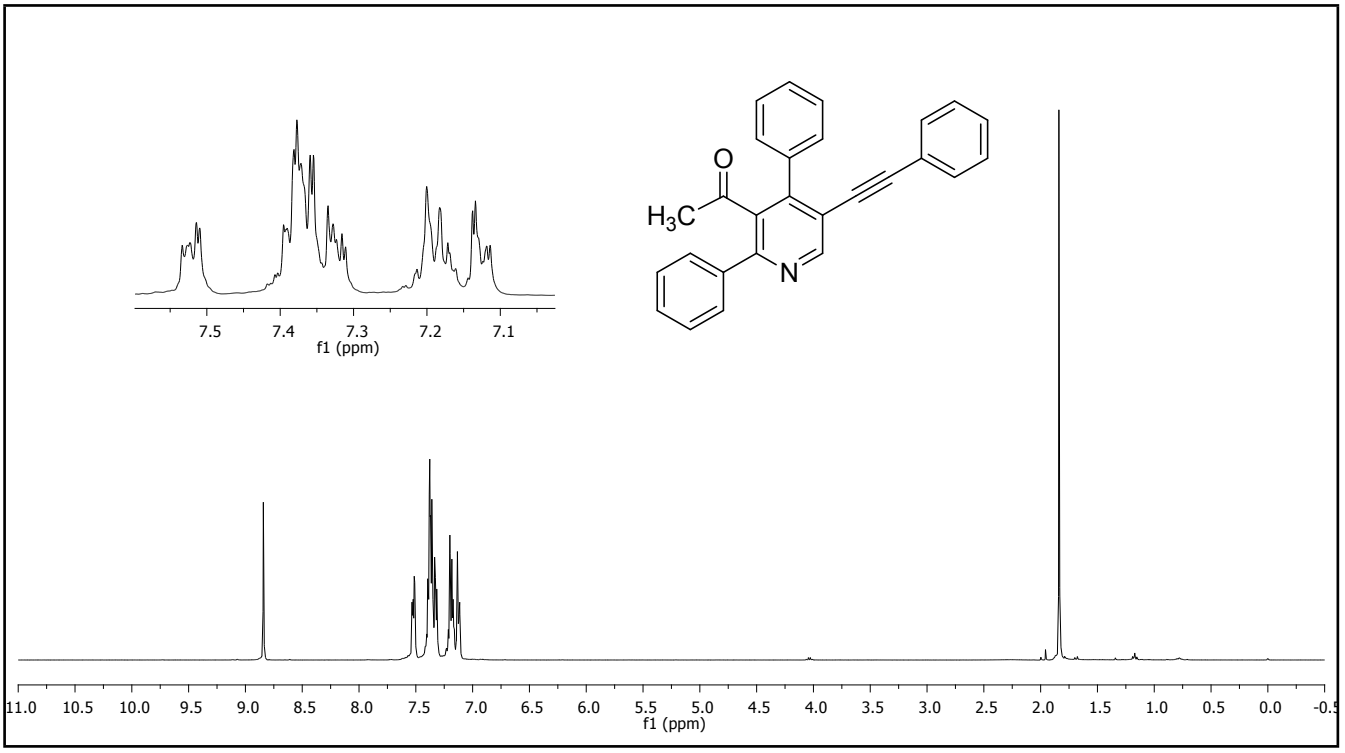


Figure S55. ^{1}H NMR spectrum of compound **7ab**.

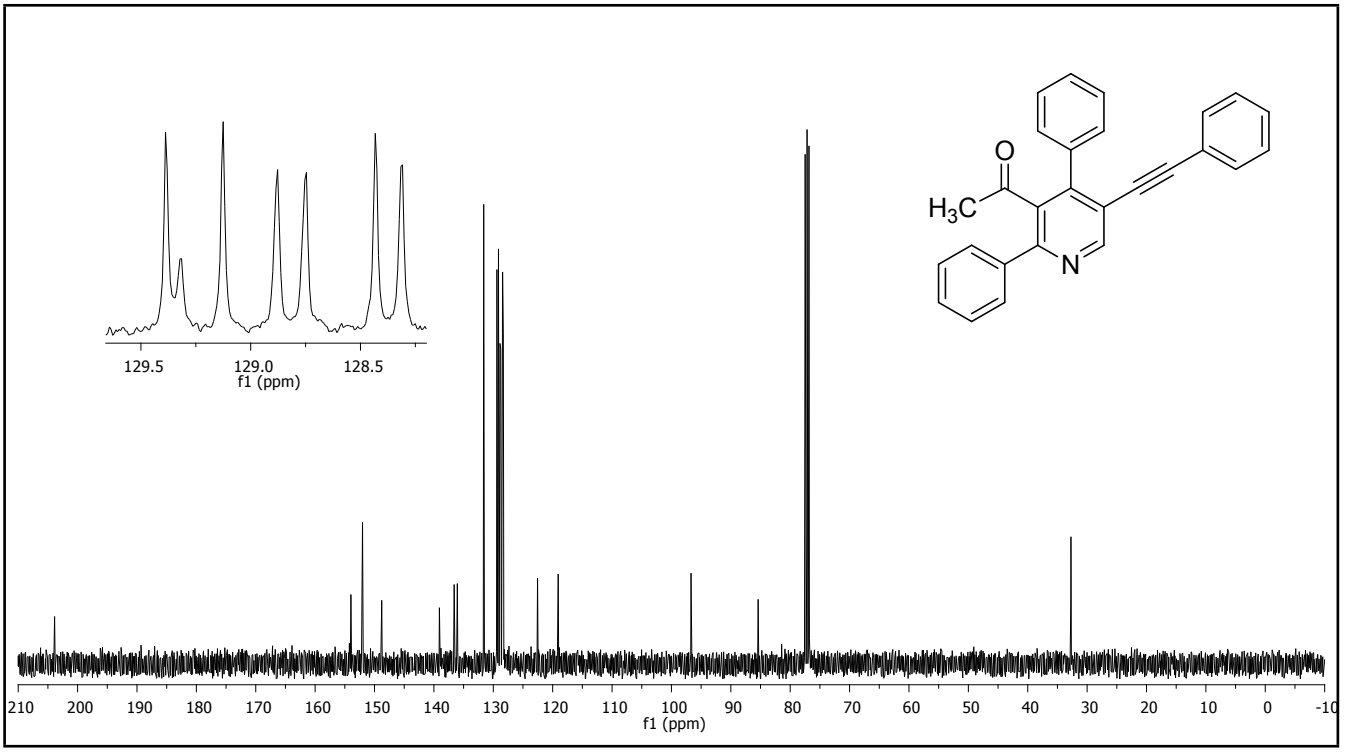


Figure S56. ^{13}C NMR spectrum of compound **7ab**.

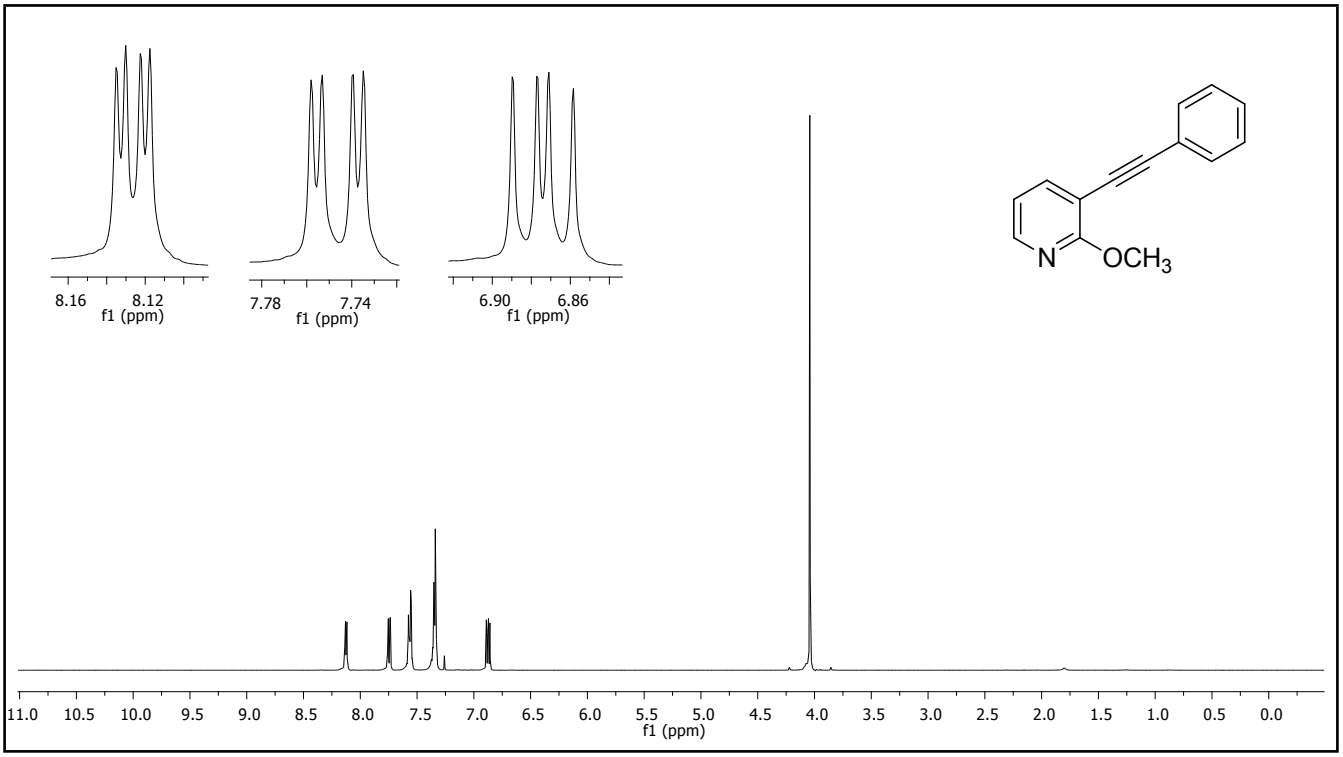


Figure S57. ^{1}H NMR spectrum of compound **9**.

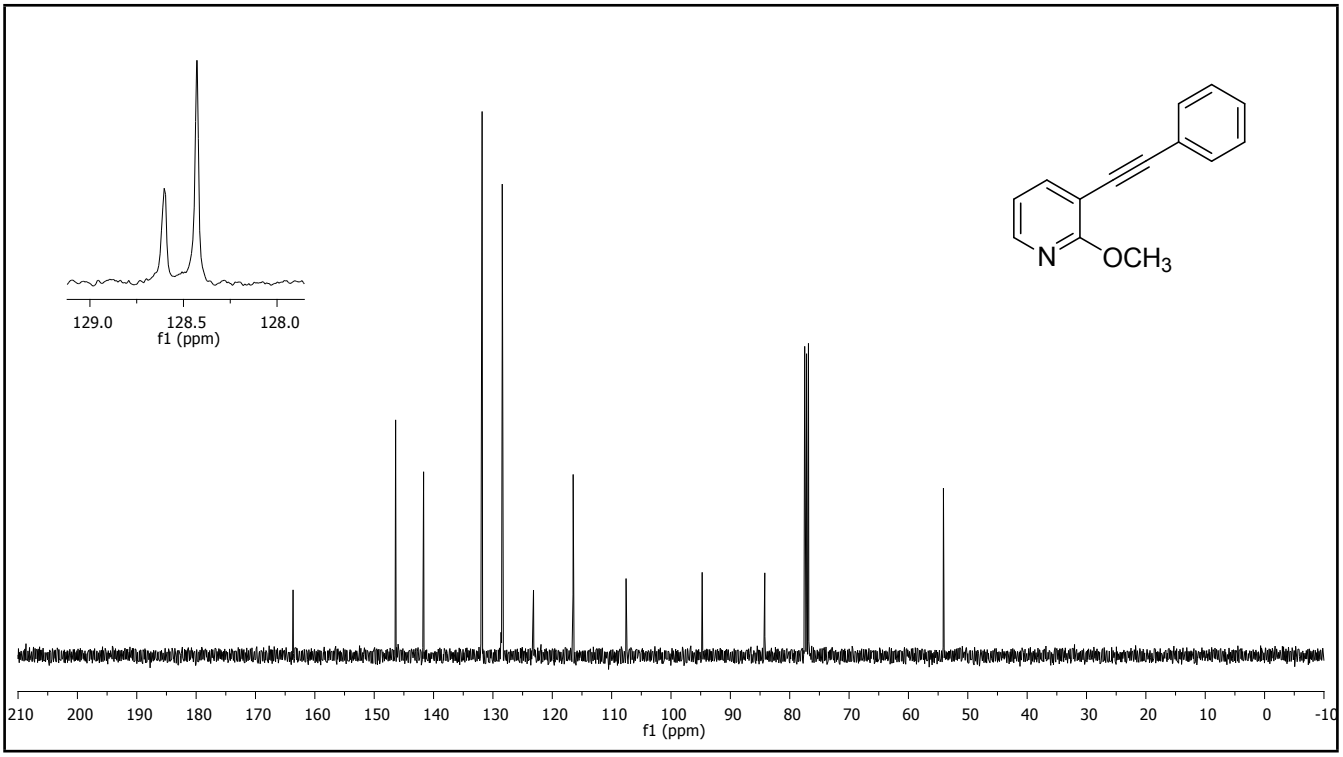


Figure S58. ^{13}C NMR spectrum of compound **9**.

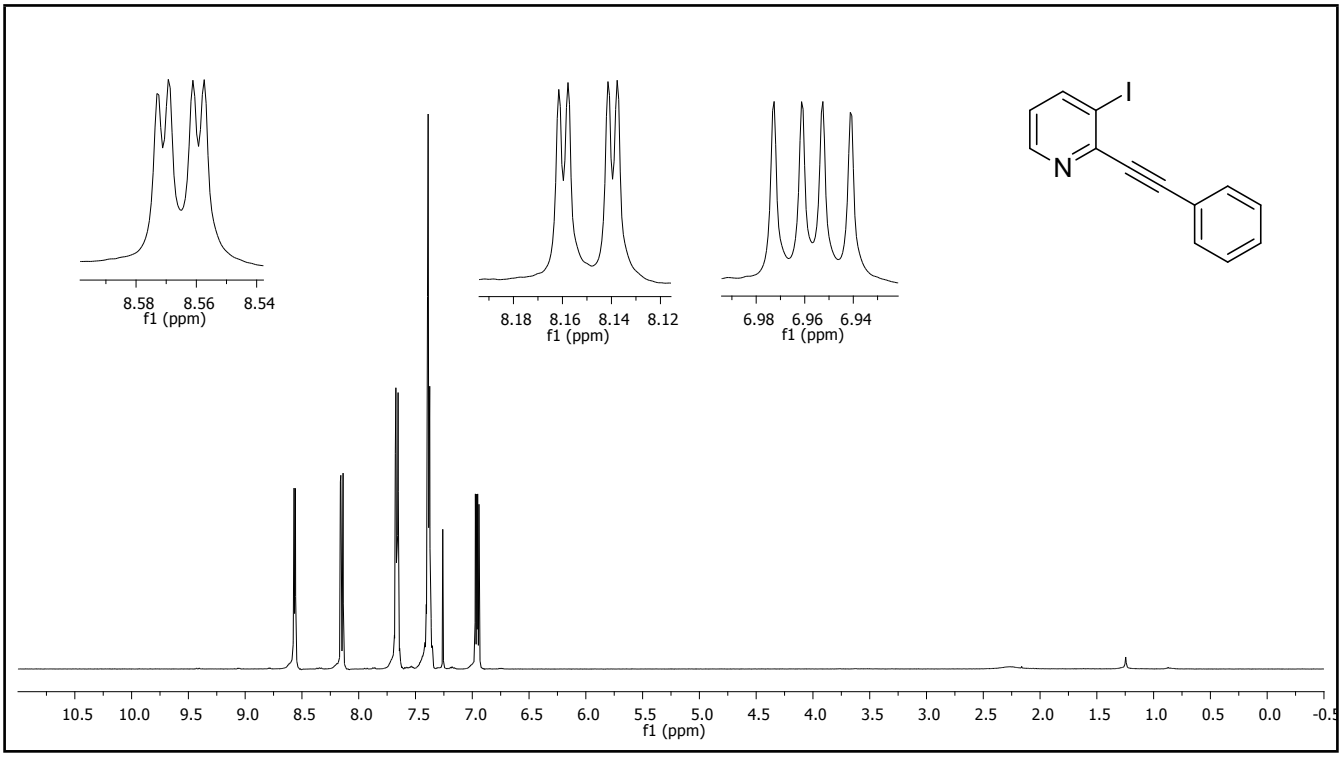


Figure S59. ^{1}H NMR spectrum of compound **10**.

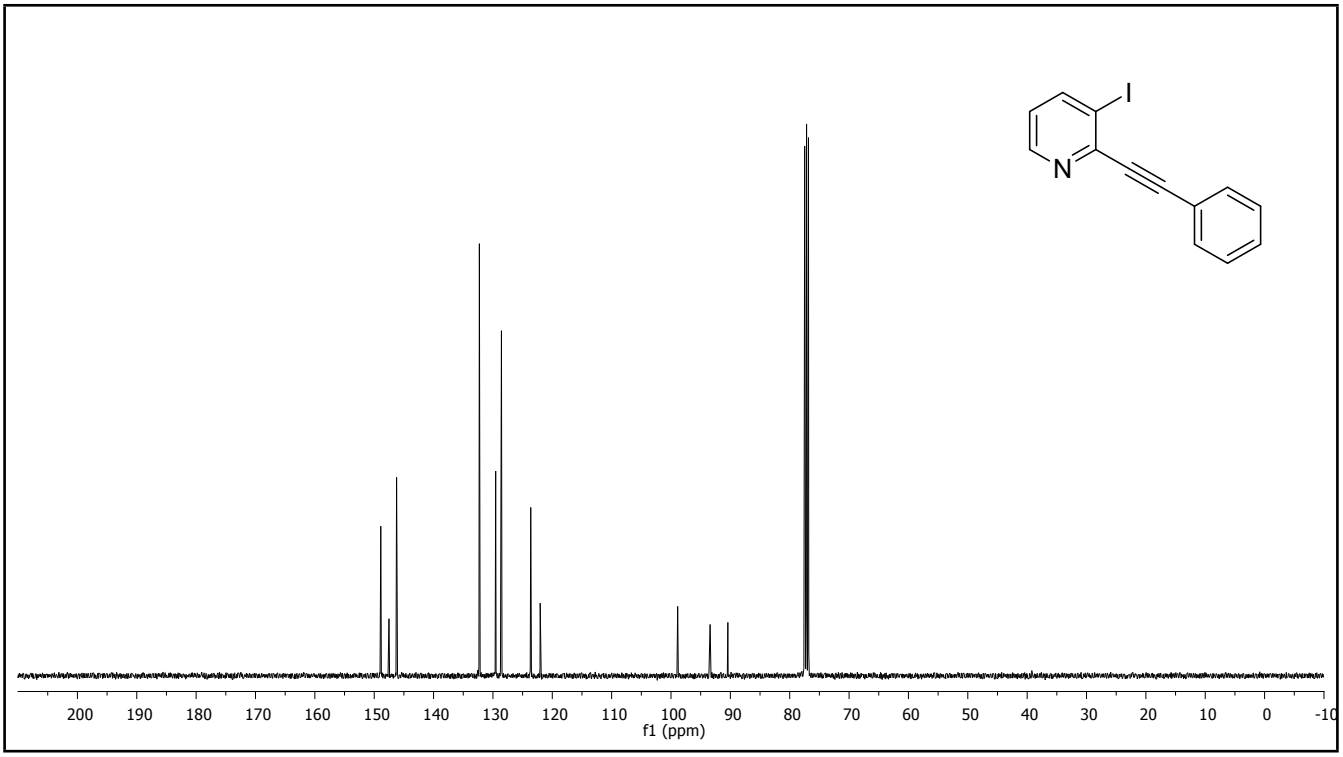


Figure S60. ^{13}C NMR spectrum of compound **10**.

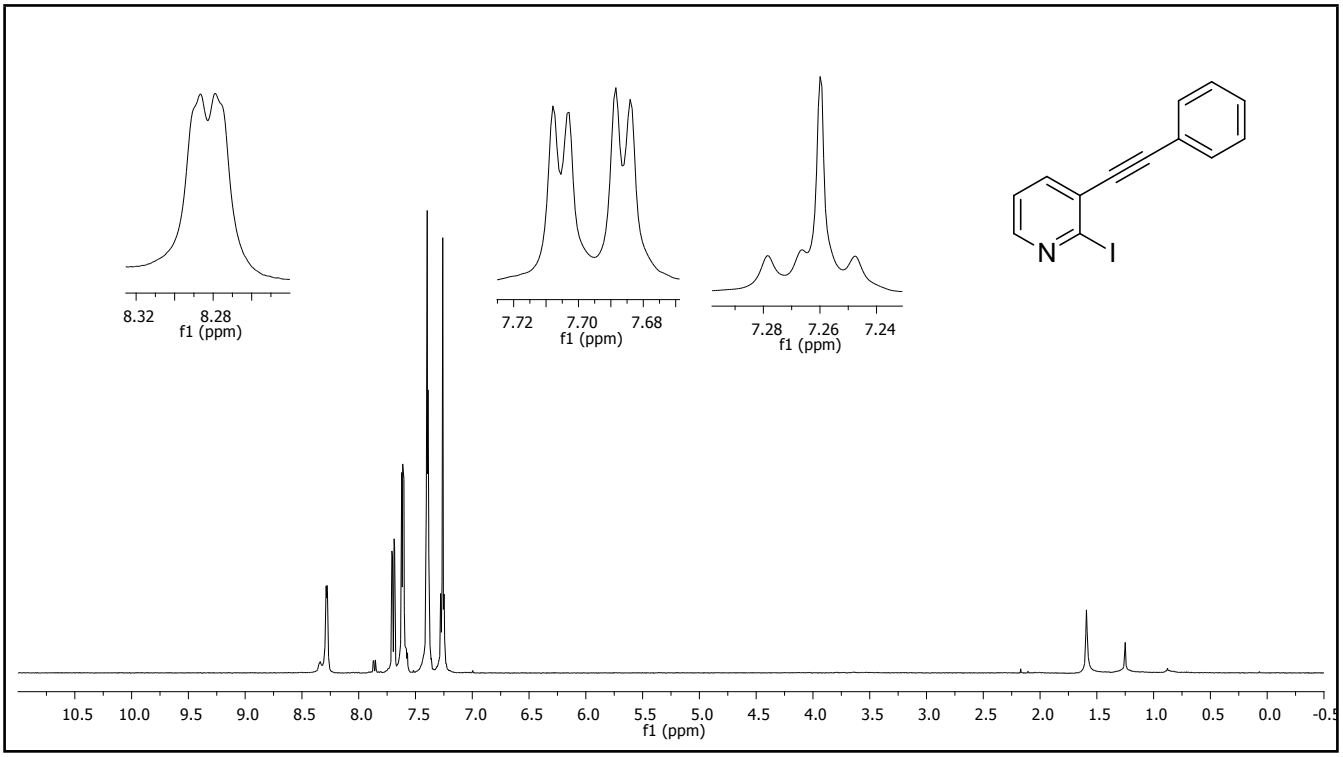


Figure S61. ^{1}H NMR spectrum of compound **11**.

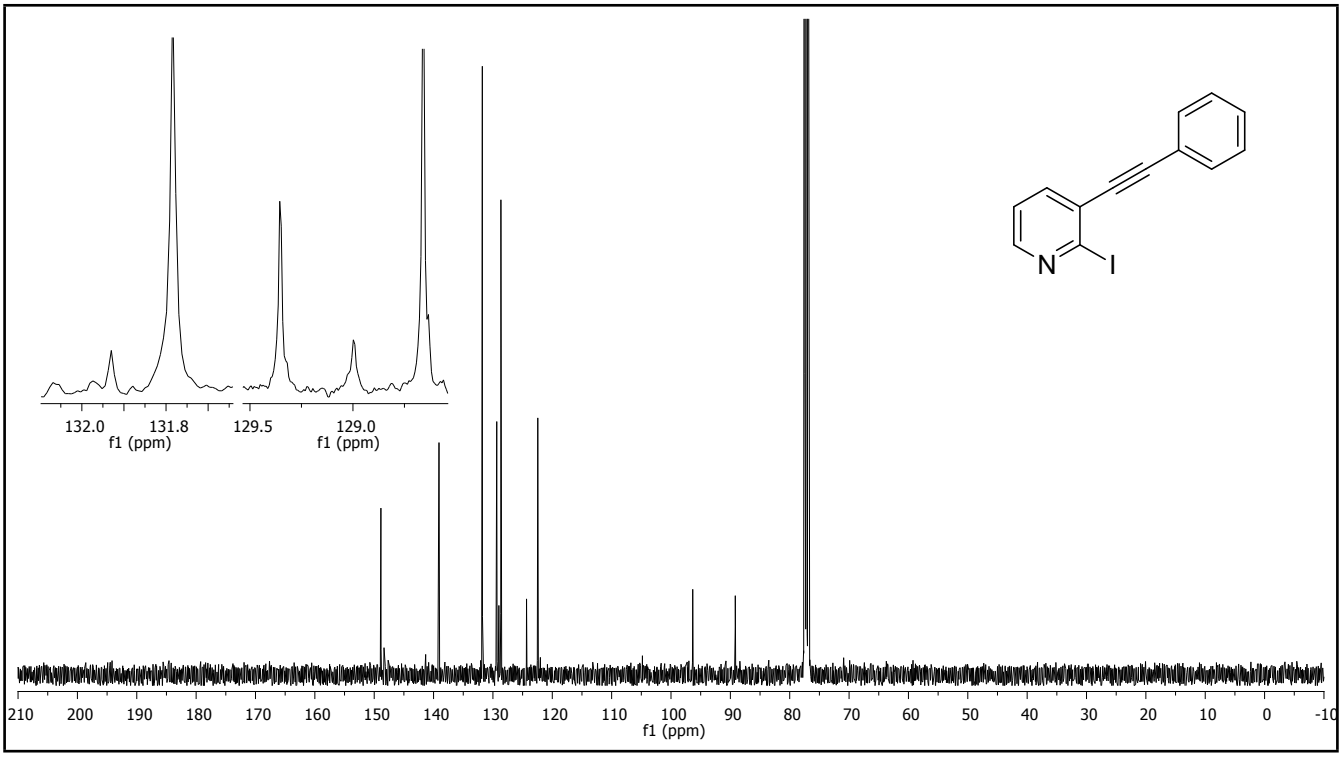


Figure S62. ^{13}C NMR spectrum of compound **11**.

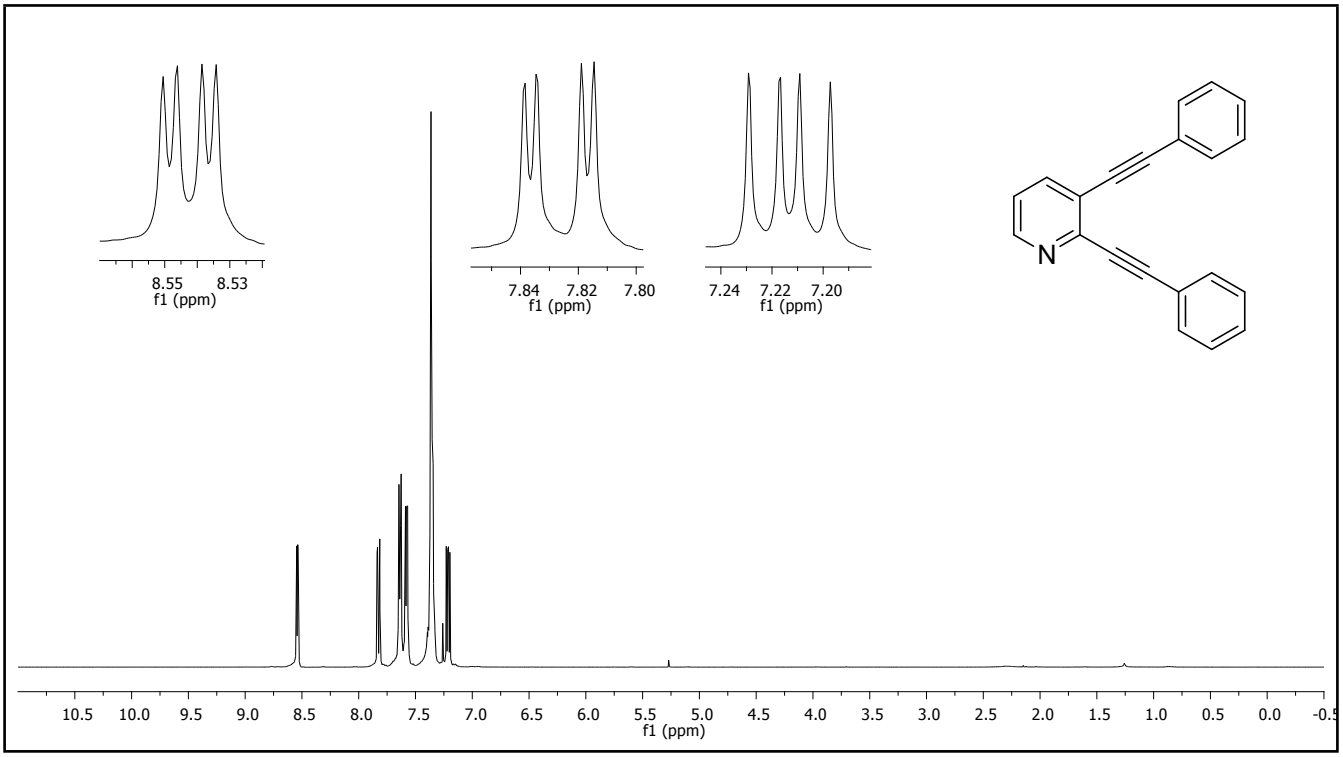


Figure S63. ^{1}H NMR spectrum of compound **12**.

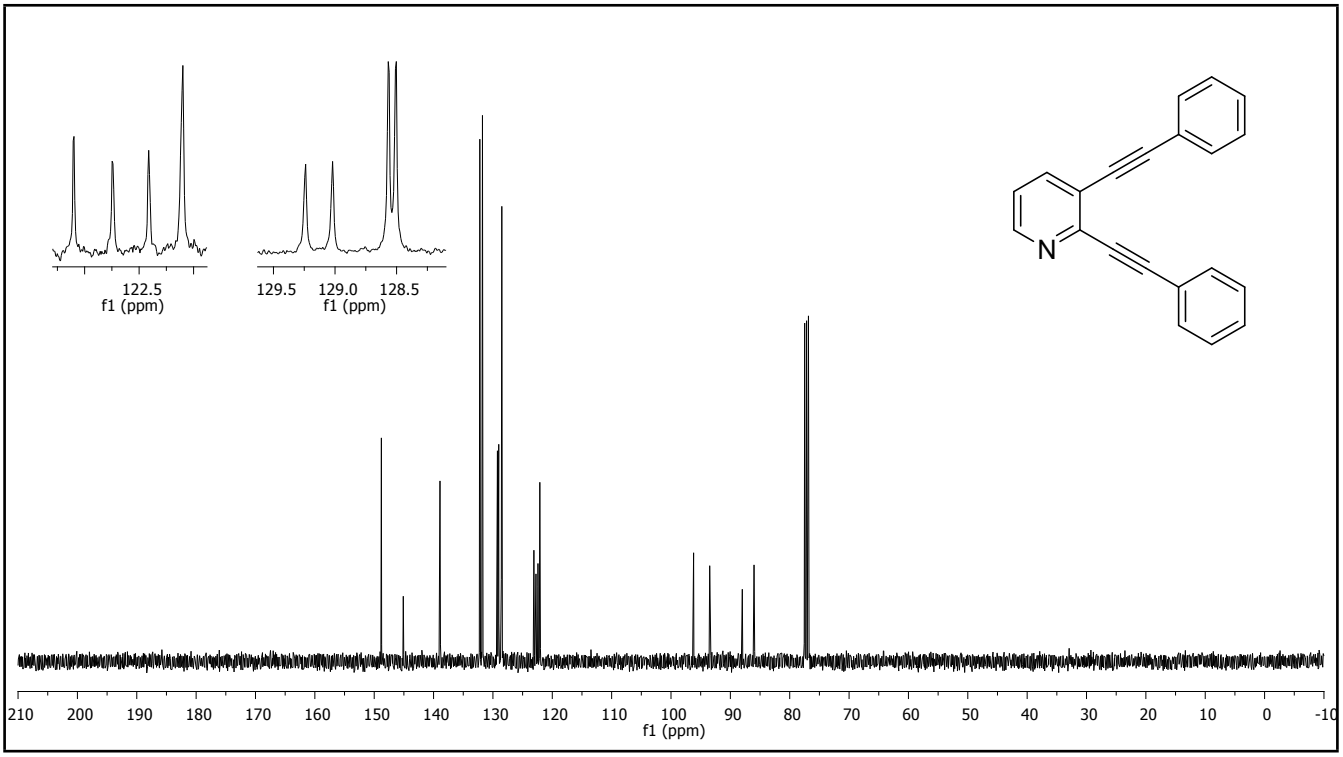


Figure S64. ^{13}C NMR spectrum of compound **12**.

References

1 Karabiyikoglu, S.; Kelgokmen, Y.; Zora, M. *Tetrahedron* **2015**, *71*, 4324.

2 2-Butynylamine was prepared from 1-bromo-2-butyne according to recent literature procedures. See: (a) Trost, B. M.; Rudd, M. T. *Org. Lett.* **2013**, *5*, 1467. (b) Roy, S.; Anoop, A.; Biradha, K.; Basak, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 8316.