Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Ligand Centered Redox Enabled Sustainable Synthesis of Triazines and Pyrimidines Using A Zinc-Stabilized Azo-Anion Radical Catalyst

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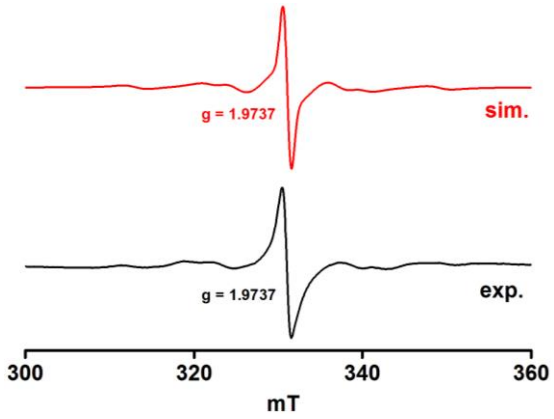


Fig S1 X-band EPR spectrum of [**1a**]$^{-}$ in dichloromethane at 77K.[1]

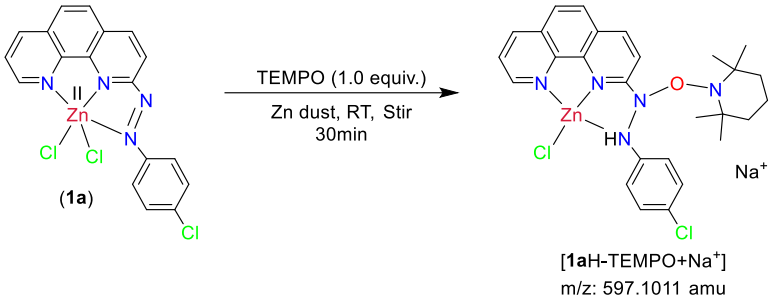
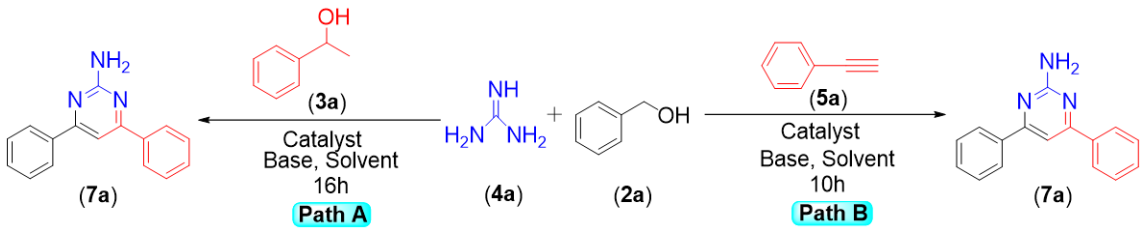


Fig S2. Trapping of TEMPO bound single electron reduced catalyst **1a**.[1]

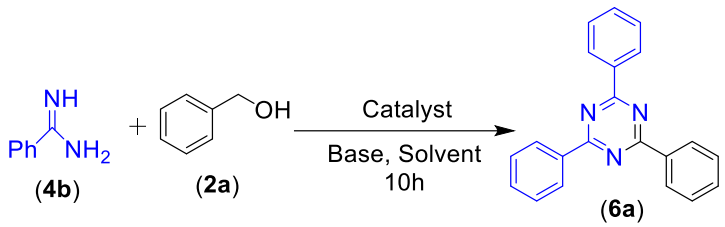
Table S1. Solvent and base screening for the optimization of the reaction conditions for 2,4,6-trisubstituted pyrimidine synthesis.[a-c]



1	**1a**(5.0 mol%)	Toluene	NaO^{t}Bu(0.7equiv.)	110	82	83
2	**1a**(5.0 mol%)	Toluene	K_3PO_4 (0.7 equiv.)	110	50	52
3	**1a**(5.0 mol%)	Toluene	KOH (0.7 equiv.)	110	77	78
4	**1a**(5.0 mol%)	Toluene	NaOH (0.7 equiv.)	110	75	77
5	**1a** (3.0mol%)	ACN	KO^{t}Bu (0.5 equiv.)	100	trace	trace
6	**1a**(3.0 mol%)	Ethanol	KO^{t}Bu (0.5 equiv.)	100	trace	trace
7	**1a**(3.0 mol%)	THF	KO^{t}Bu (0.5 equiv.)	100	69	70
8	**1a**(3.0 mol%)	Xylene	KO^{t}Bu (0.5 equiv.)	100	82	83

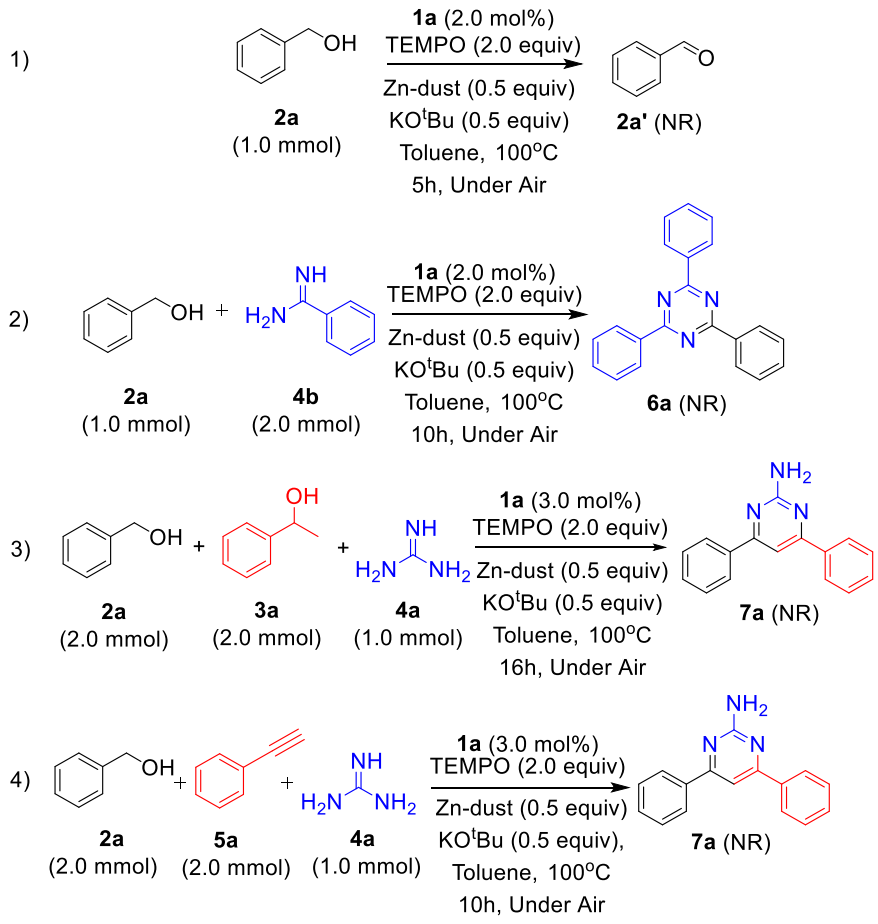
[a]Stoichiometry: For Path A: benzylalcohol (2.0 mmol), 1-phenylethanol (2.0 mmol), guanidine (1.0 mmol), Zn-dust (0.5 equiv). For Path B: benzylalcohol (2.0 mmol), phenylacetylene (2.0 mmol), guanidine (1.0 mmol), Zn-dust (0.5 equiv). [b]Isolated yields after column chromatography. [c]Under air.

Table S2. Optimization of the reaction conditions for 2,4,6-trisubstituted triazine synthesis.[a-f]



Entry	Catalyst (mol%)	Solvent	Base	Temp. (°C)	Yield (%)
1	**1a** (5.0 mol%)	Toluene	KO^{t}Bu(0.7 equiv.)	110	85
2	**1a** (5.0 mol%)	Toluene	NaO^{t}Bu(0.7 equiv.)	110	83
3	**1a** (5.0 mol%)	Toluene	K_3PO_4 (0.7 equiv.)	110	51
4	**1a** (5.0 mol%)	Toluene	KOH (0.7 equiv.)	110	78
5	**1a** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	110	79
6	**1a** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	85
7	**1a** (3.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	85
8	**1a** (2.0mol%)	ACN	KO^{t}Bu (0.5 equiv.)	100	trace
9	**1a** (2.0 mol%)	Ethanol	KO^{t}Bu (0.5 equiv.)	100	trace
10	**1a** (2.0 mol%)	THF	KO^{t}Bu (0.5 equiv.)	100	71
11	**1a** (2.0 mol%)	Xylene	KO^{t}Bu (0.5 equiv.)	100	84
12	**1a** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	90	83
13[d]	**1a** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	80
14	**1b** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	81
15	**1a** (2.0 mol%)	Toluene	-	100	trace
16	$ZnCl_2$ (5.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	NR
17	L[1a,b] (5.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	40
18	-	Toluene	KO^{t}Bu (0.5 equiv.)	100	trace
19	$ZnCl_2$+L[1a] (1:1) (5.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	46
20[e]	**1a** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	85
21[f]	**1a** (2.0 mol%)	Toluene	KO^{t}Bu (0.5 equiv.)	100	trace

[a]Stoichiometry: benzylalcohol (1.0 mmol), benzamidine (1.0 mmol), Zn-dust (0.5 equiv). [b]Isolated yields after column chromatography. [c]Under air. [d]Reaction time 8h. [e]Under pure oxygen. [f]Under argon atmosphere.



Scheme S1. Control experiments with TEMPO.

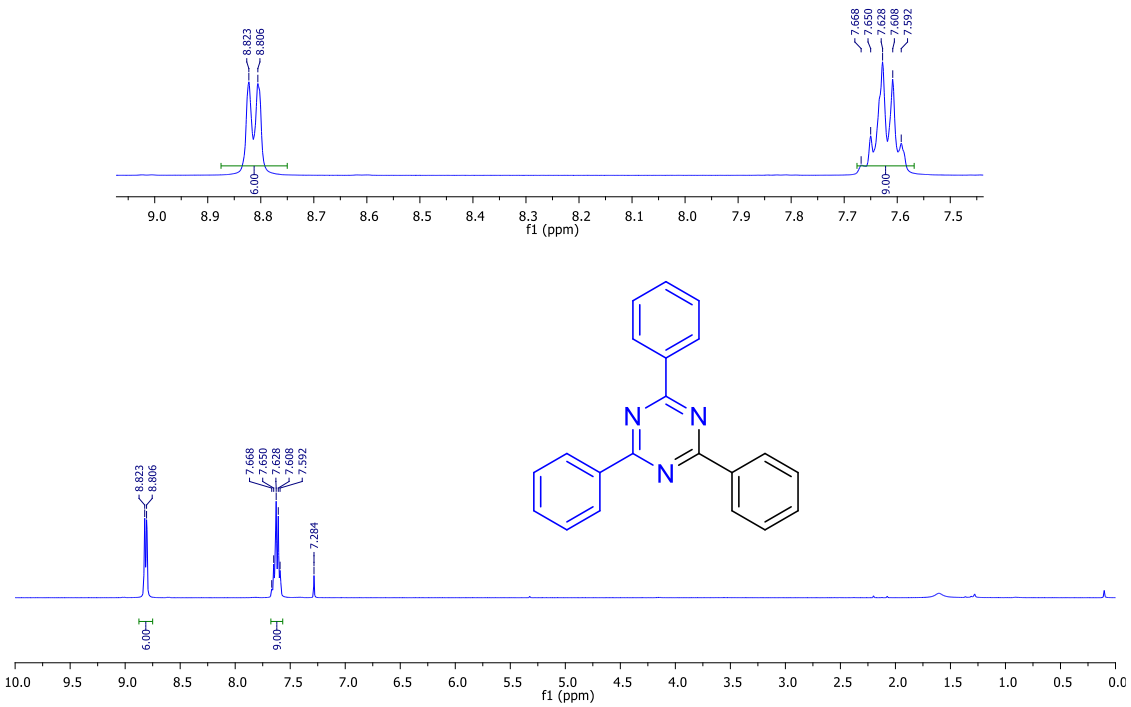


Fig S3. ^{1}H NMR spectrum of compound **6a** (400 MHz, $CDCl_3$).

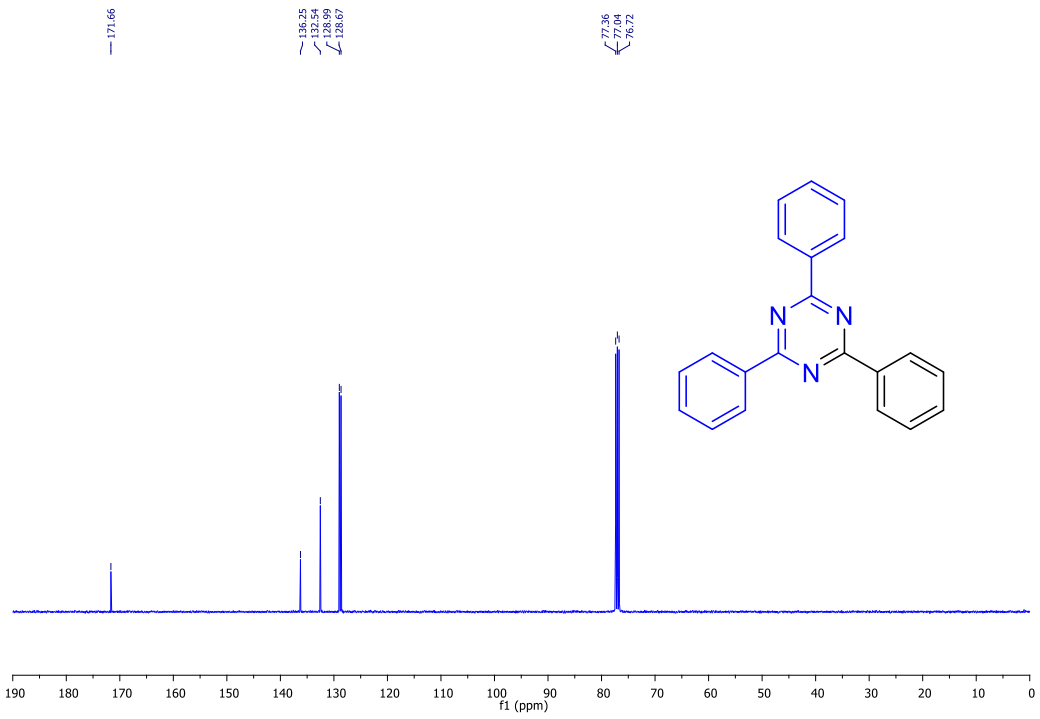


Fig S4. ^{13}C NMR spectrum of compound **6a** (100 MHz, $CDCl_3$).

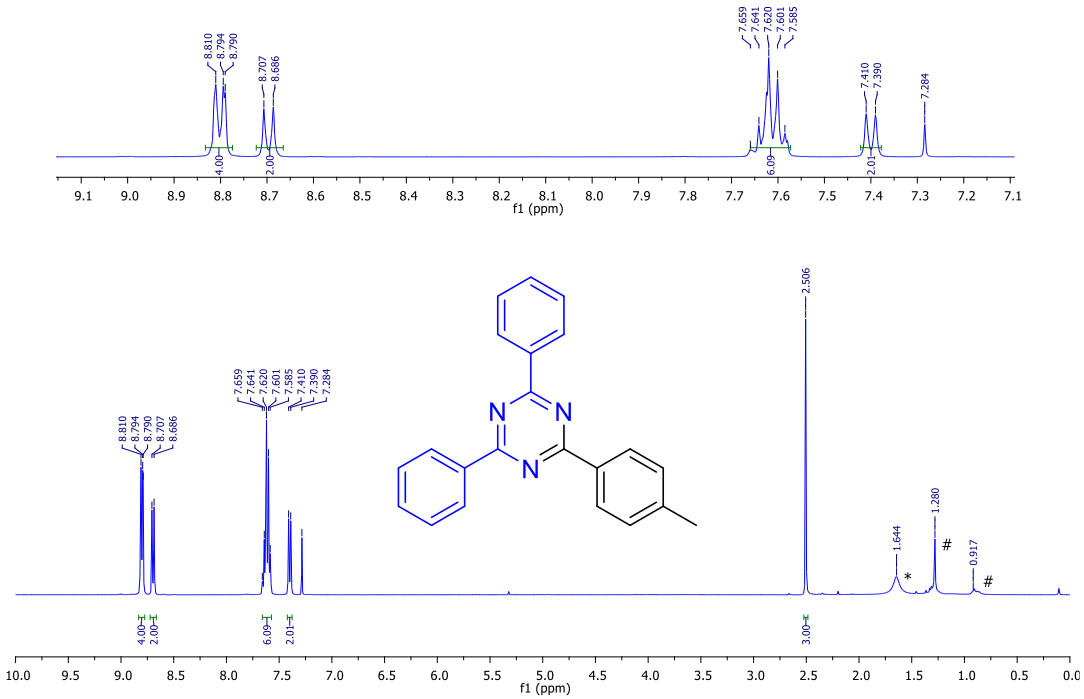


Fig S5. ^{1}H NMR spectrum of compound **6b** (100 MHz, $CDCl_3$) (*water, $^{\#}$hexane).

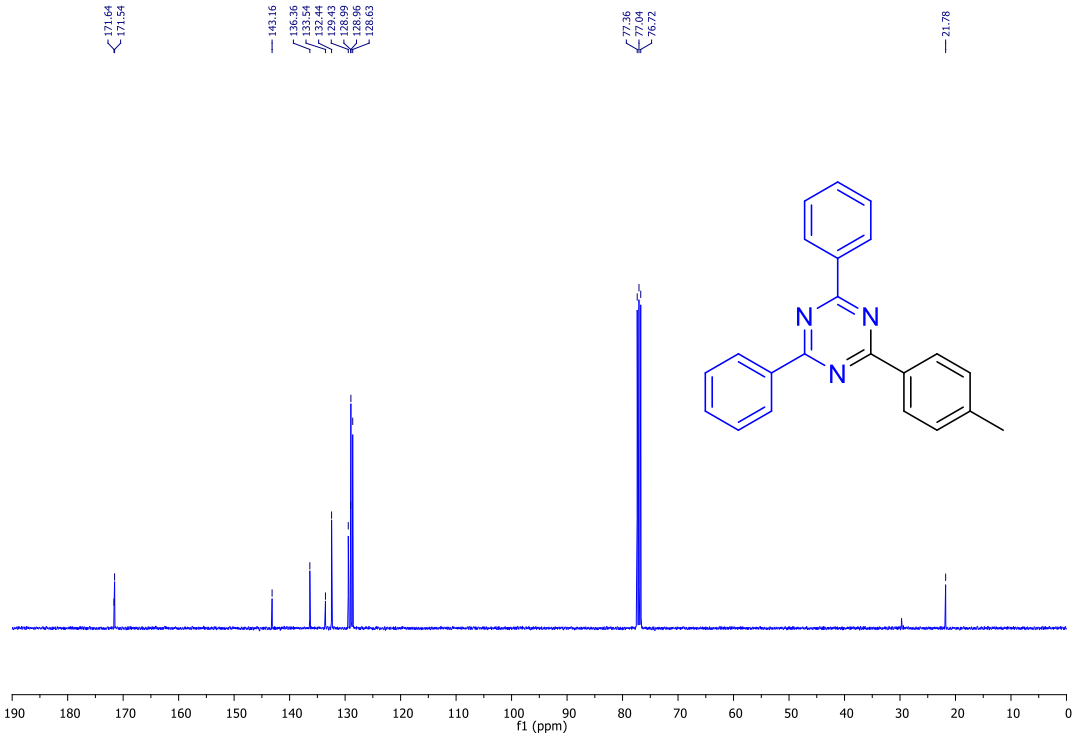


Fig S6. ^{13}C NMR spectrum of compound **6b** (100 MHz, $CDCl_3$).

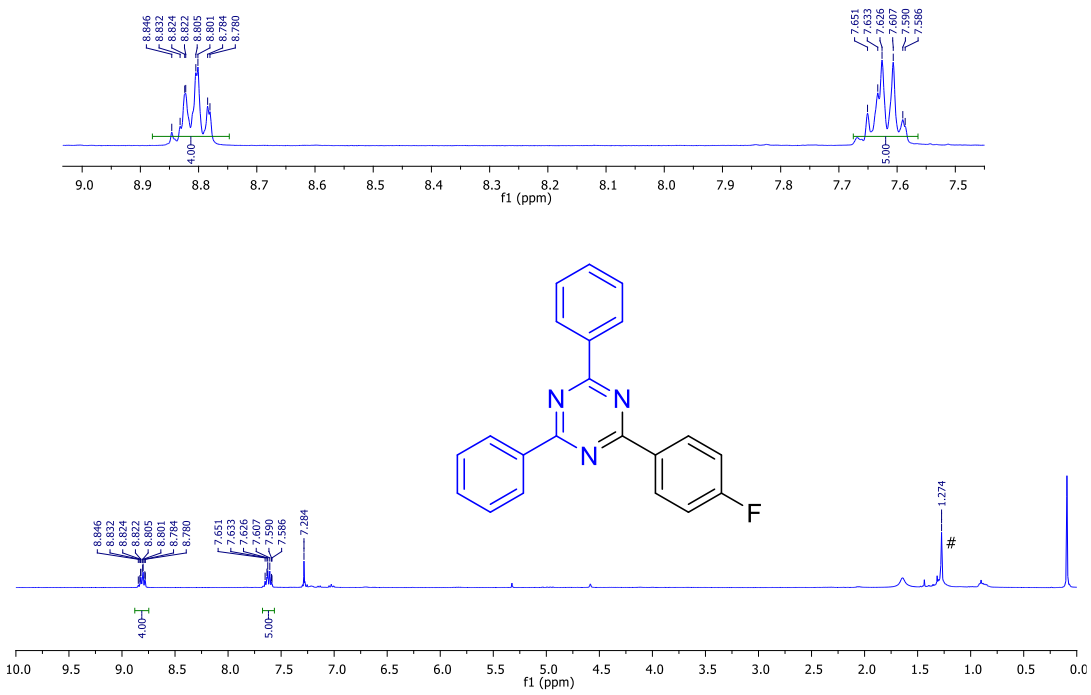


Fig S7. ^{1}H NMR spectrum of compound **6c** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

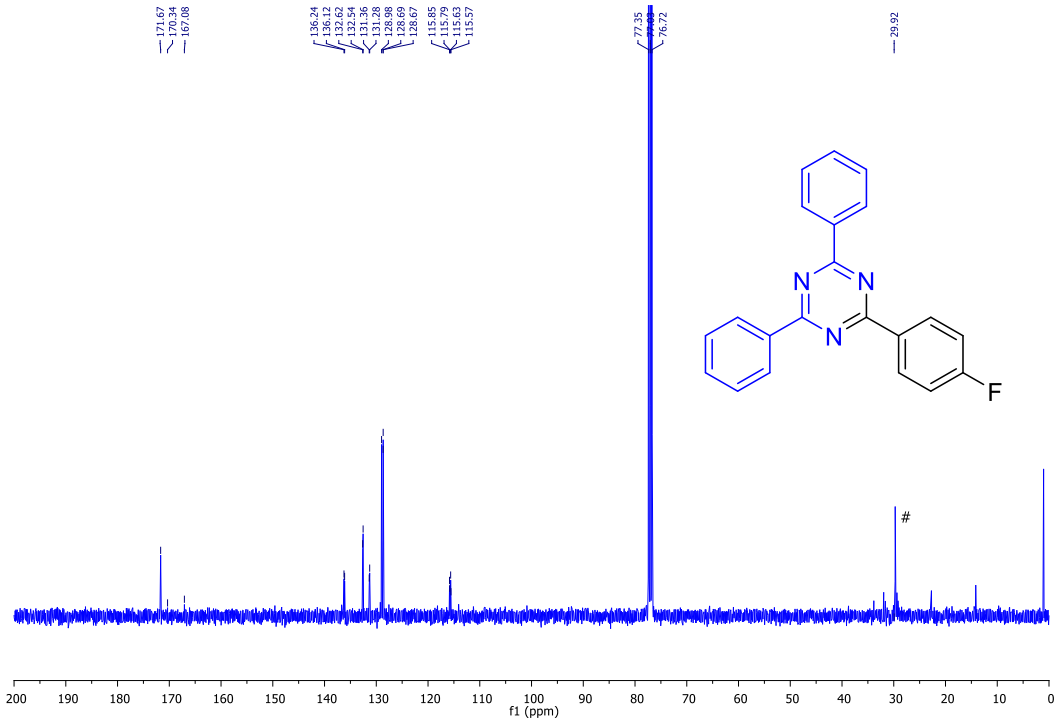


Fig S8. ^{13}C NMR spectrum of compound **6c** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

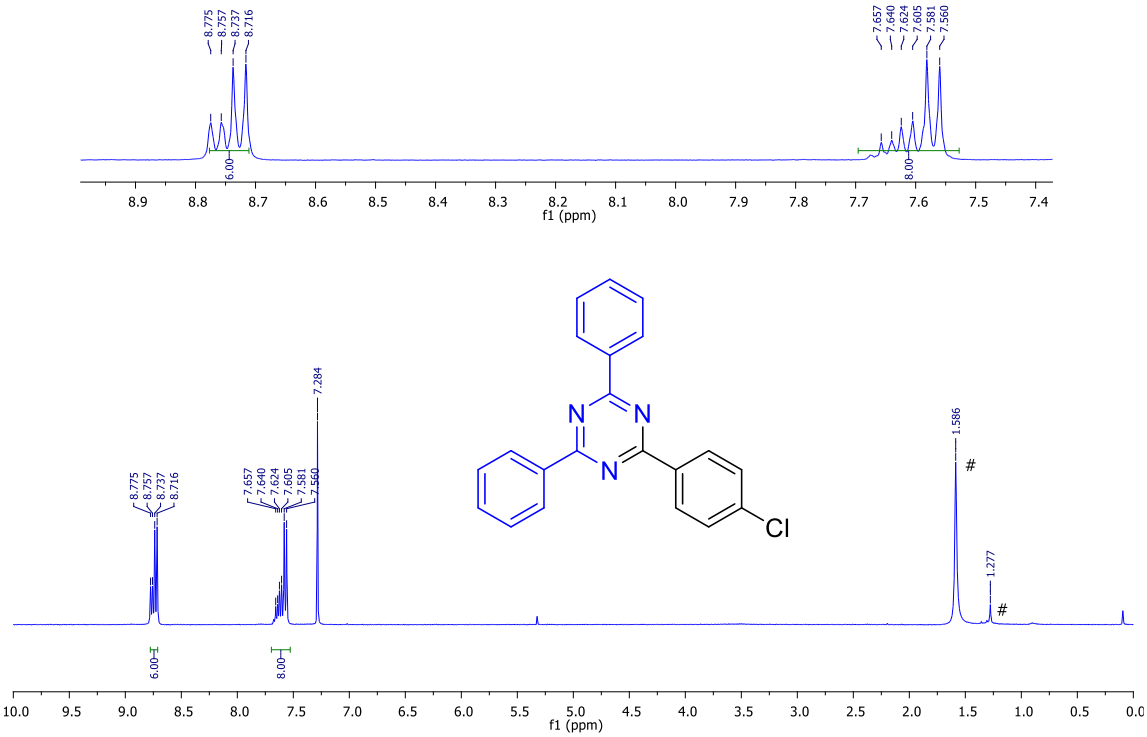


Fig S9. ^{1}H NMR spectrum of compound **6d** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

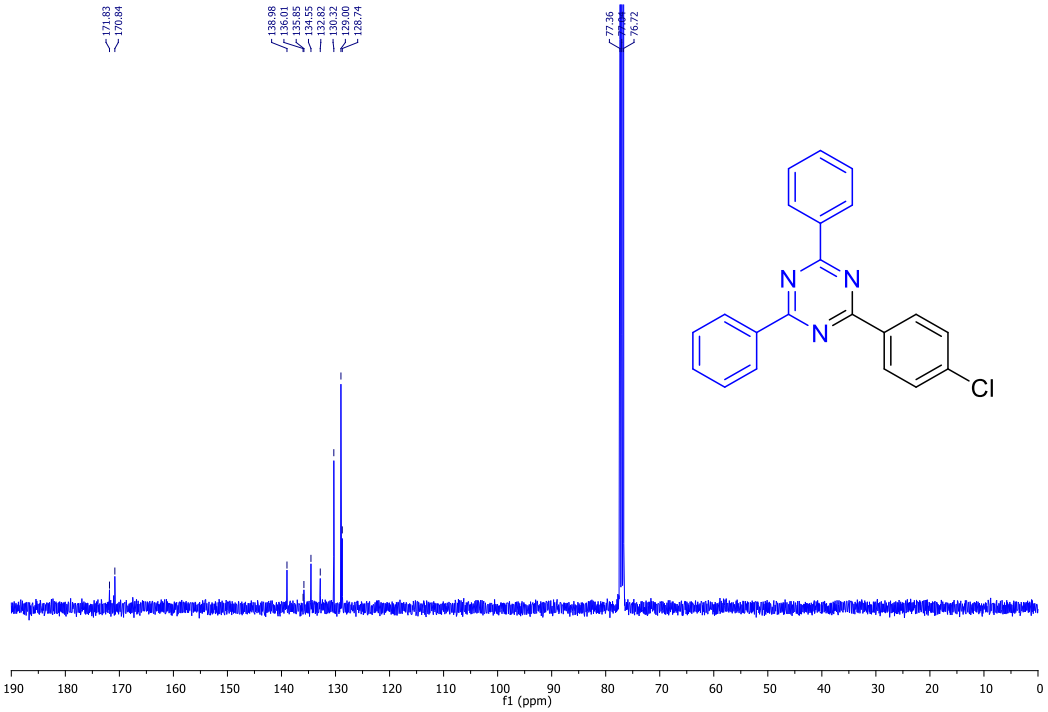


Fig S10. ^{13}C NMR spectrum of compound **6d** (100 MHz, $CDCl_3$).

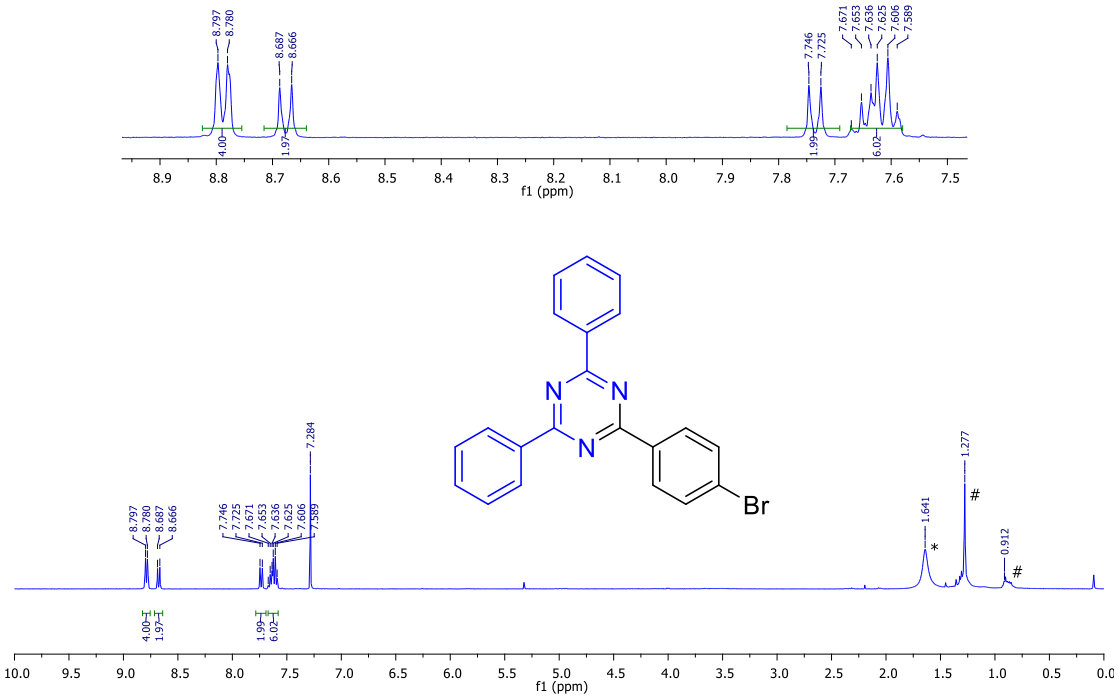


Fig S11. ^{1}H NMR spectrum of compound **6e** (400 MHz, $CDCl_3$) (*water, #hexane).

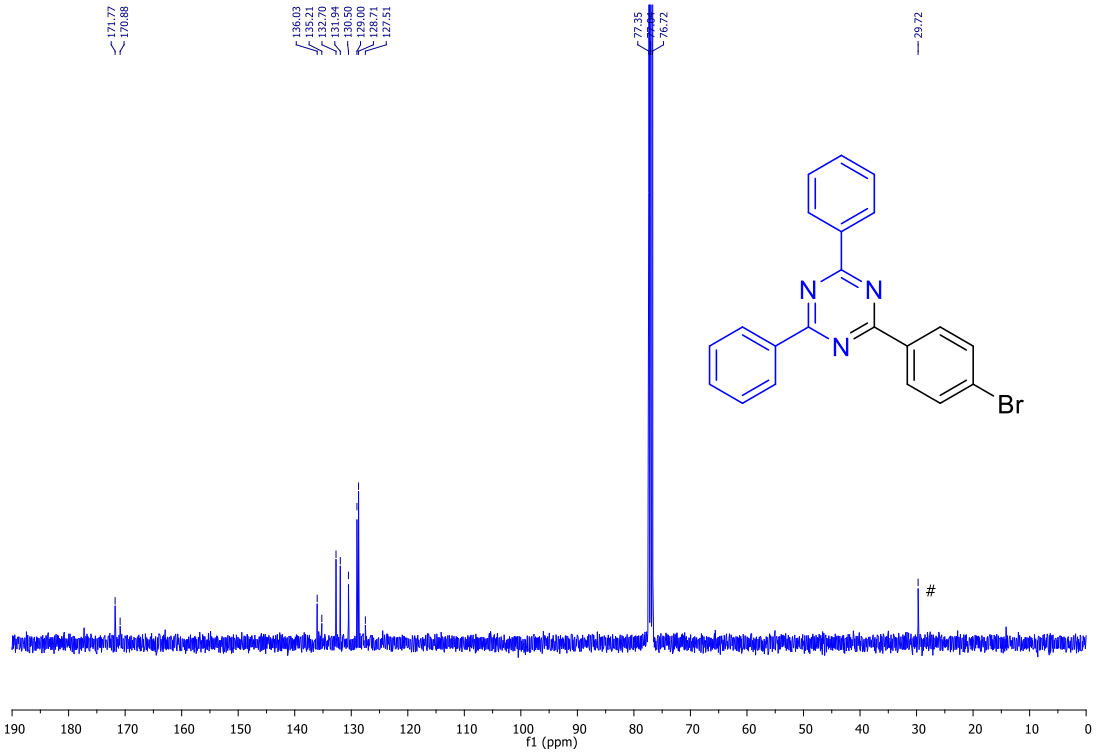


Fig S12. ^{13}C NMR spectrum of compound **6e** (100 MHz, $CDCl_3$) (#hexane).

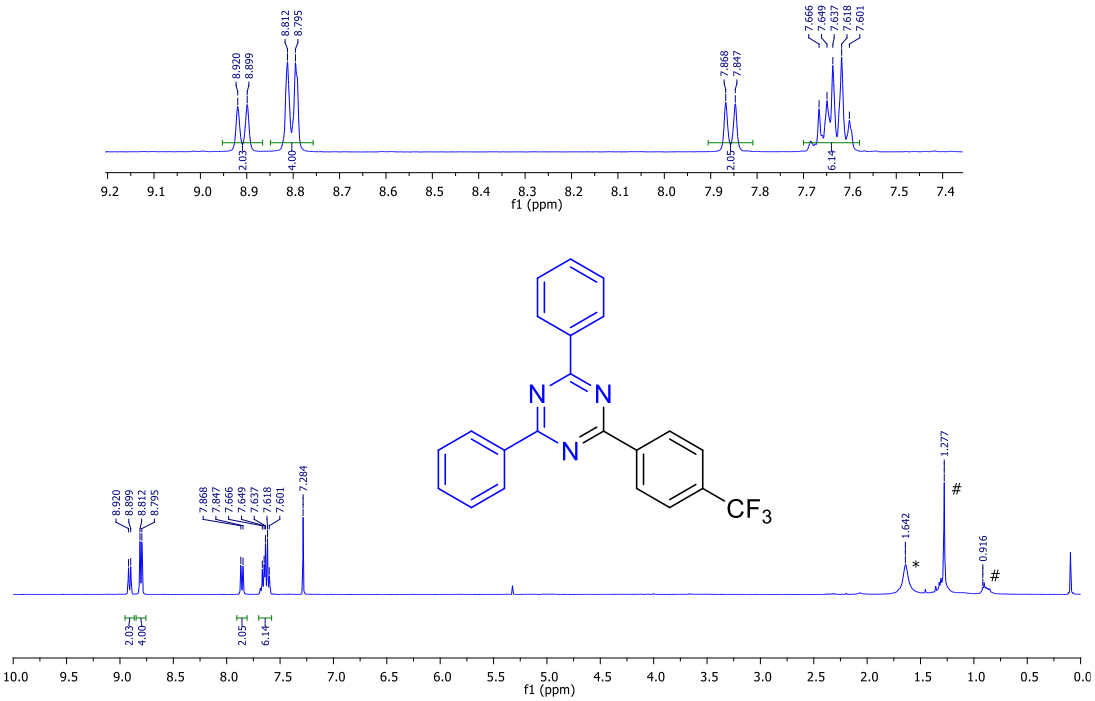


Fig S13. ^{1}H NMR spectrum of compound **6f** (400 MHz, $CDCl_3$) (*water, #hexane).

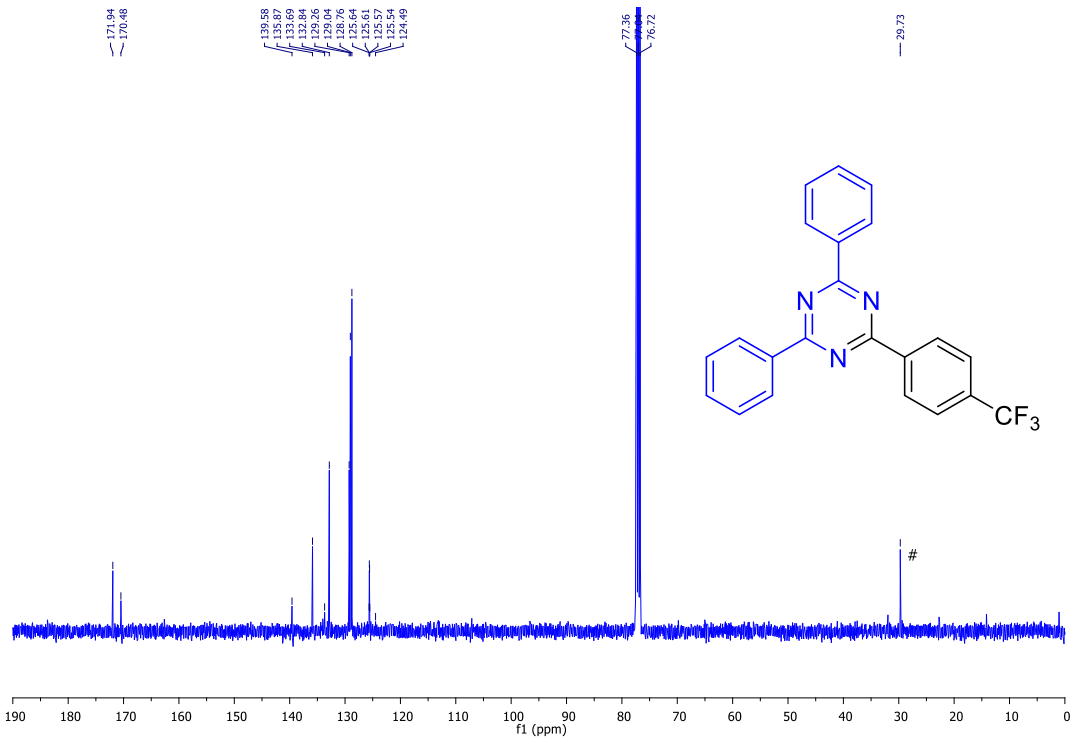


Fig S14. ^{13}C NMR spectrum of compound **6f** (100 MHz, $CDCl_3$) (#hexane).

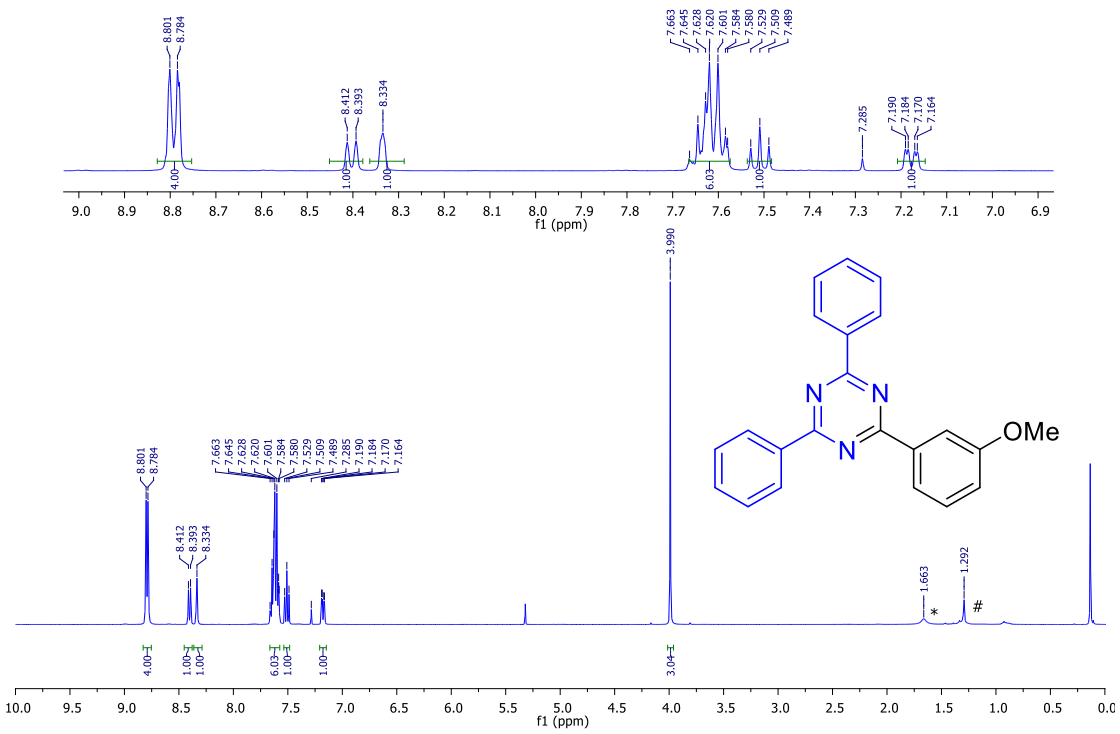


Fig S15. ^{1}H NMR spectrum of compound **6g** (400 MHz, $CDCl_3$) (*water, $^{\#}$hexane).

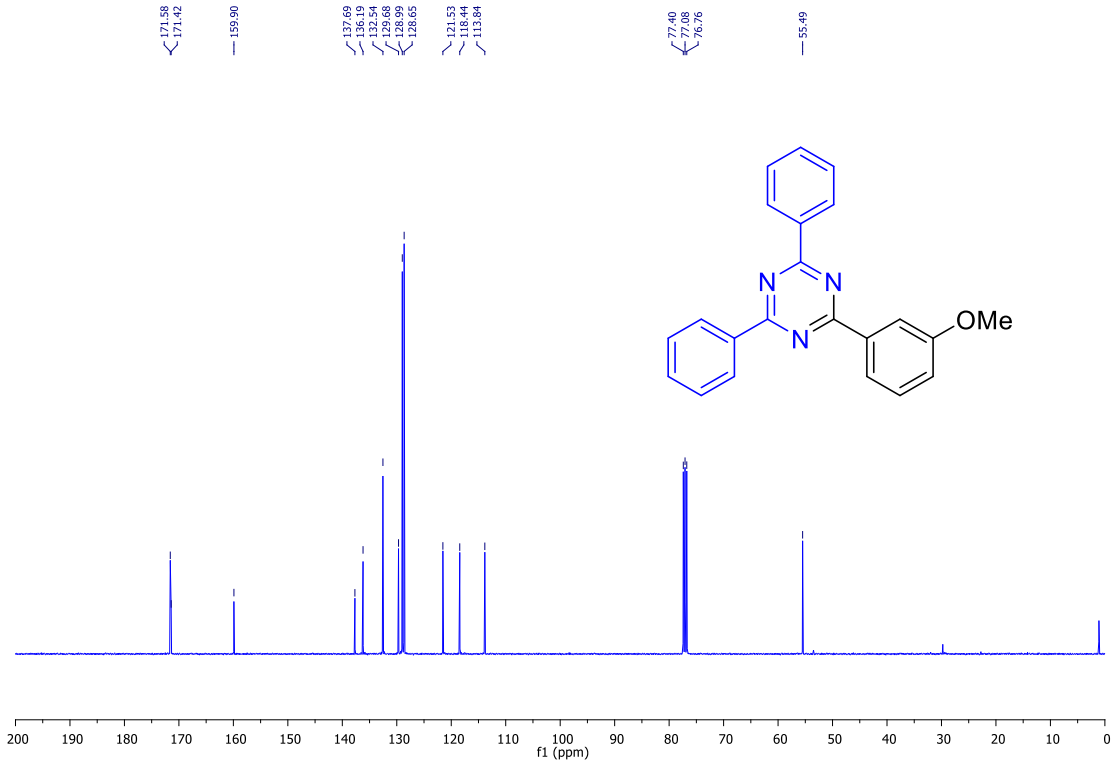


Fig S16. ^{13}C NMR spectrum of compound **6g** (100 MHz, $CDCl_3$).

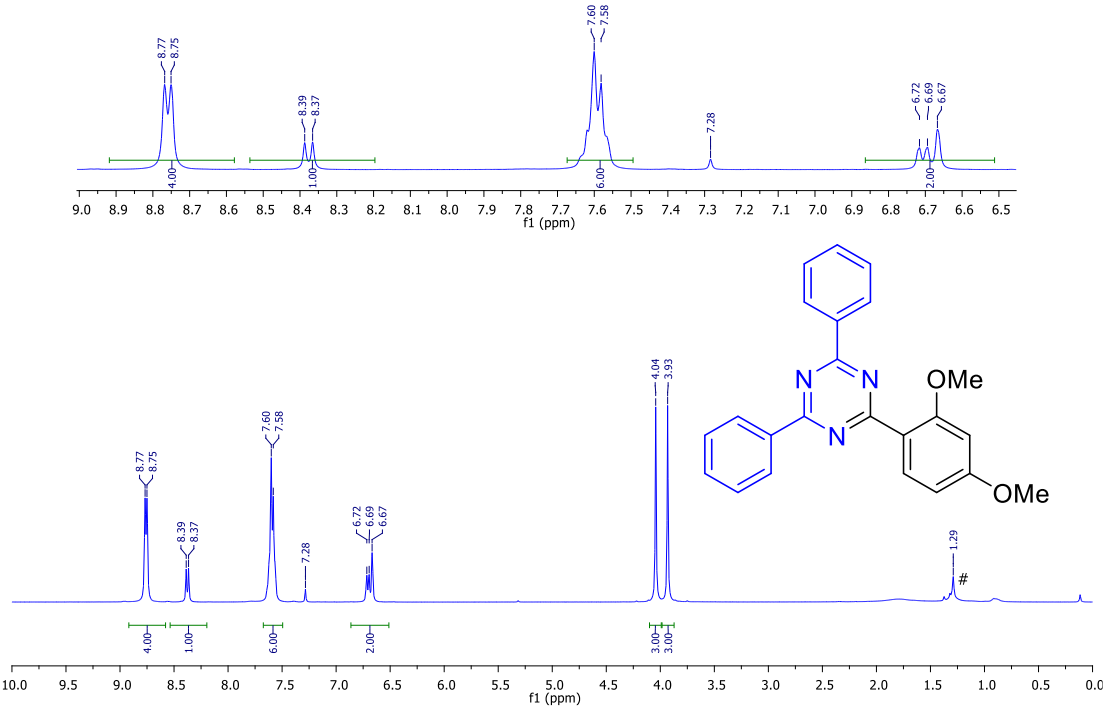


Fig S17. ^{1}H NMR spectrum of compound **6h** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

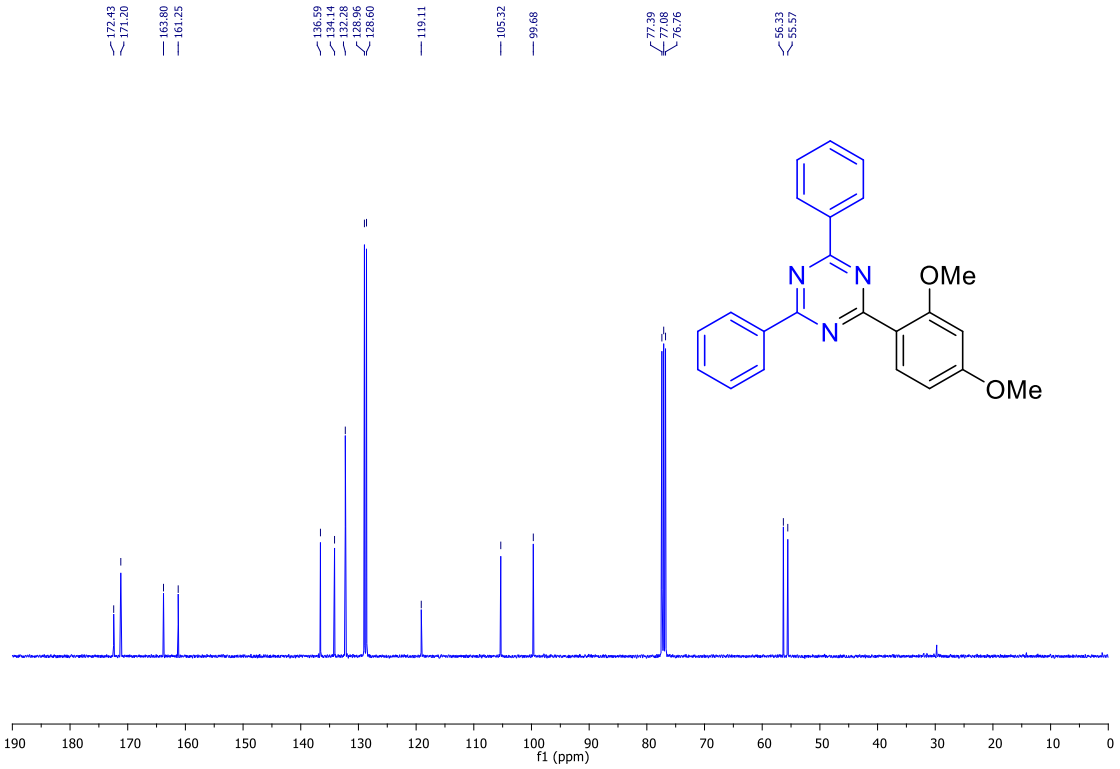


Fig S18. ^{13}C NMR spectrum of compound **6h** (100 MHz, $CDCl_3$).

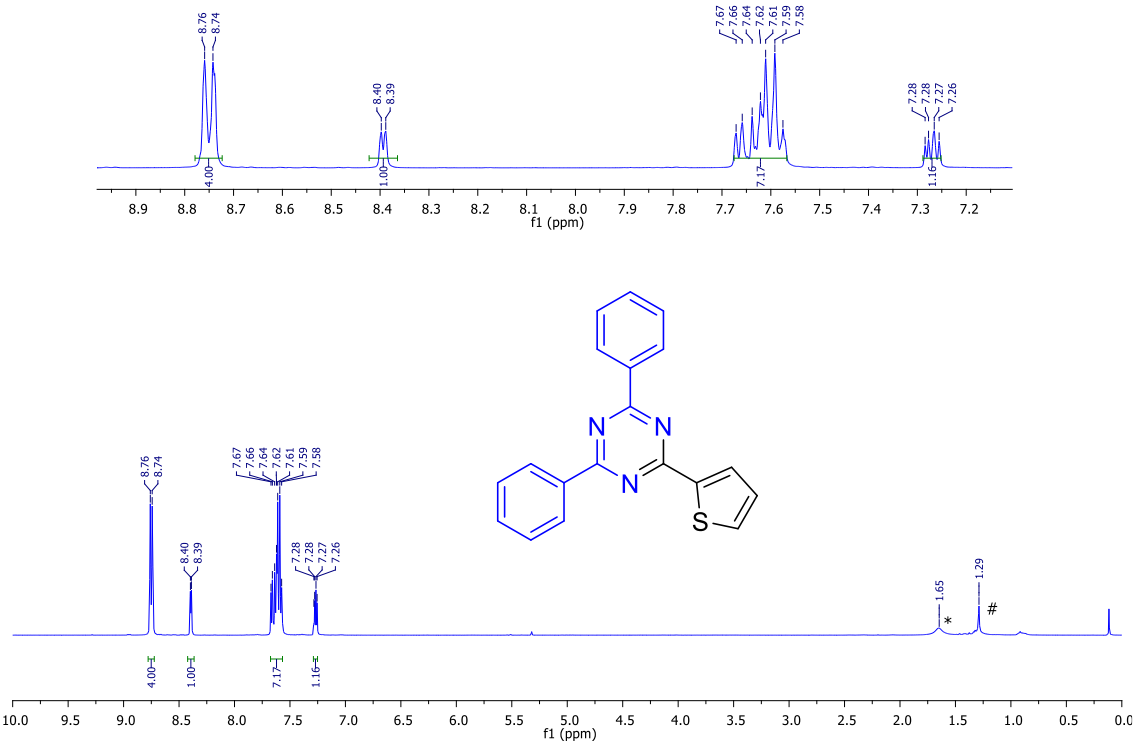


Fig S19. ^{1}H NMR spectrum of compound **6i** (400 MHz, $CDCl_3$) (*water, $^{\#}$hexane).

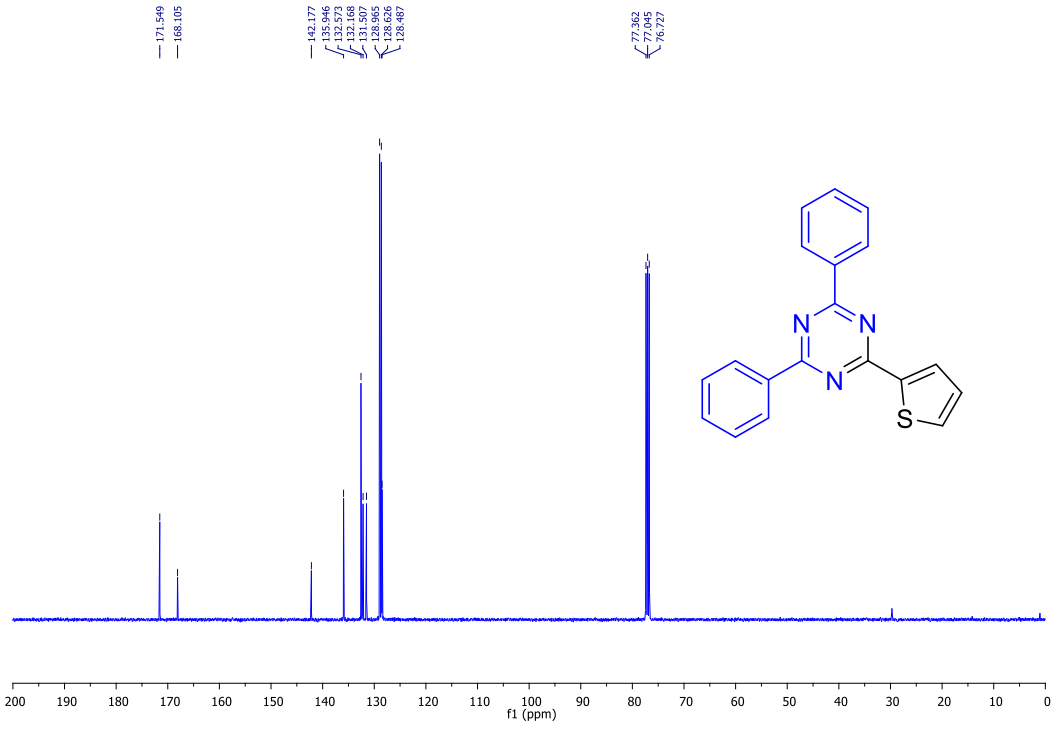


Fig S20. ^{13}C NMR spectrum of compound **6i** (100 MHz, $CDCl_3$).

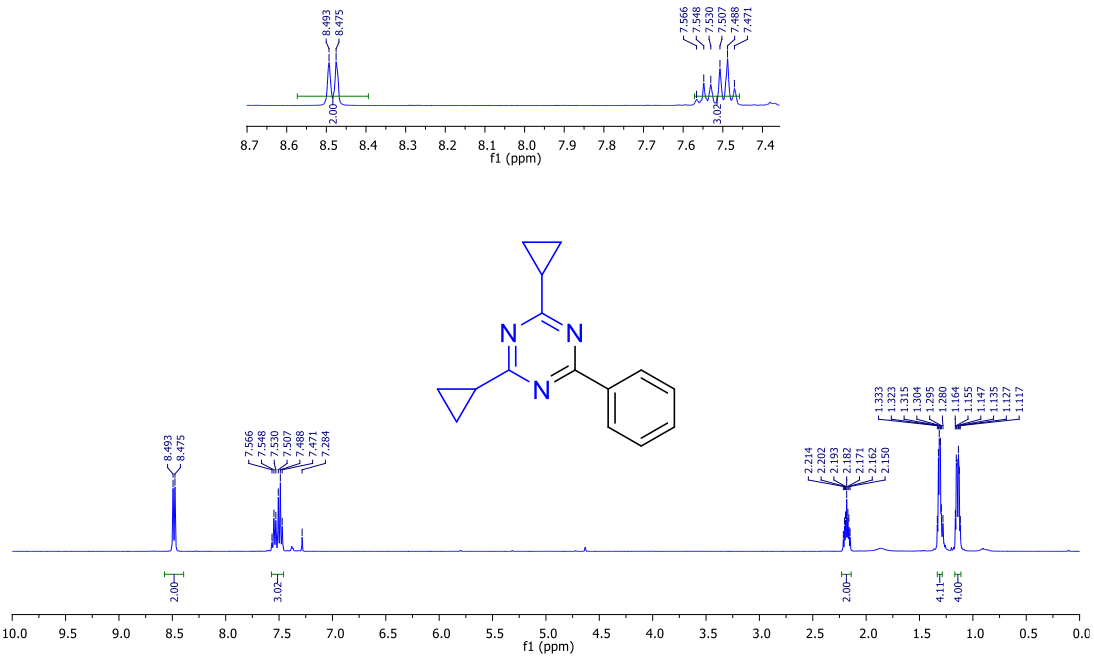


Fig S21. ^{1}H NMR spectrum of compound **6j** (400 MHz, $CDCl_3$).

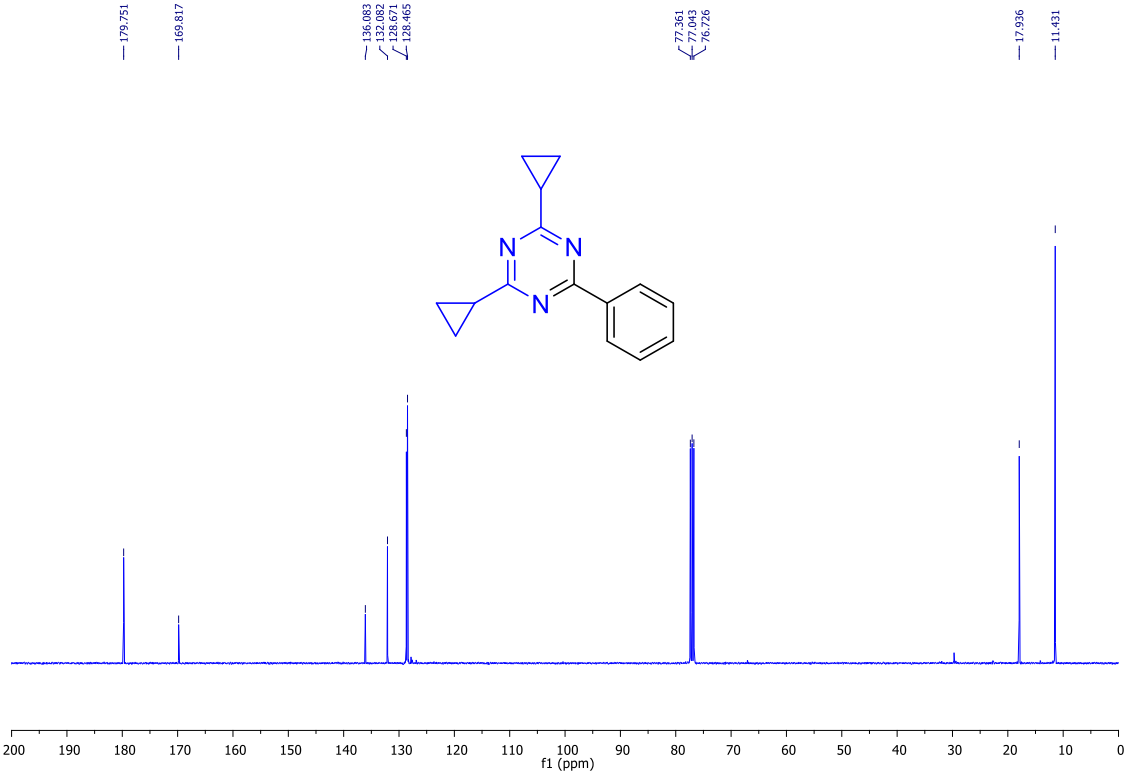


Fig S22. ^{13}C NMR spectrum of compound **6j** (100 MHz, $CDCl_3$).

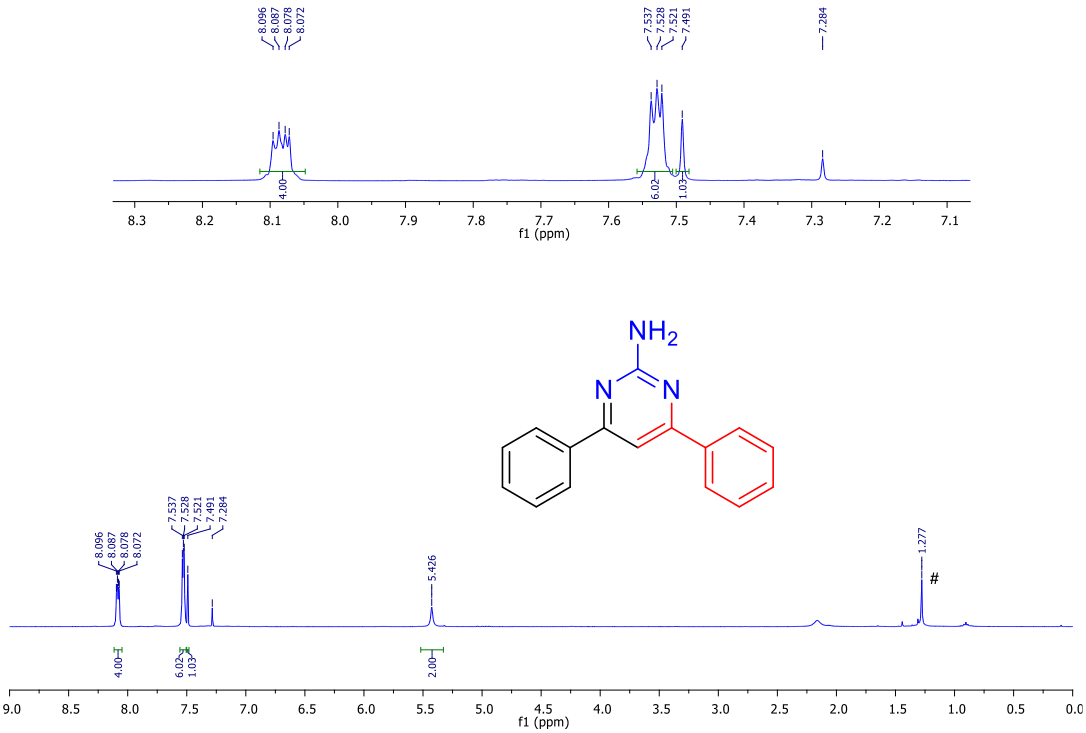


Fig S23. ^{1}H NMR spectrum of compound **7a** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

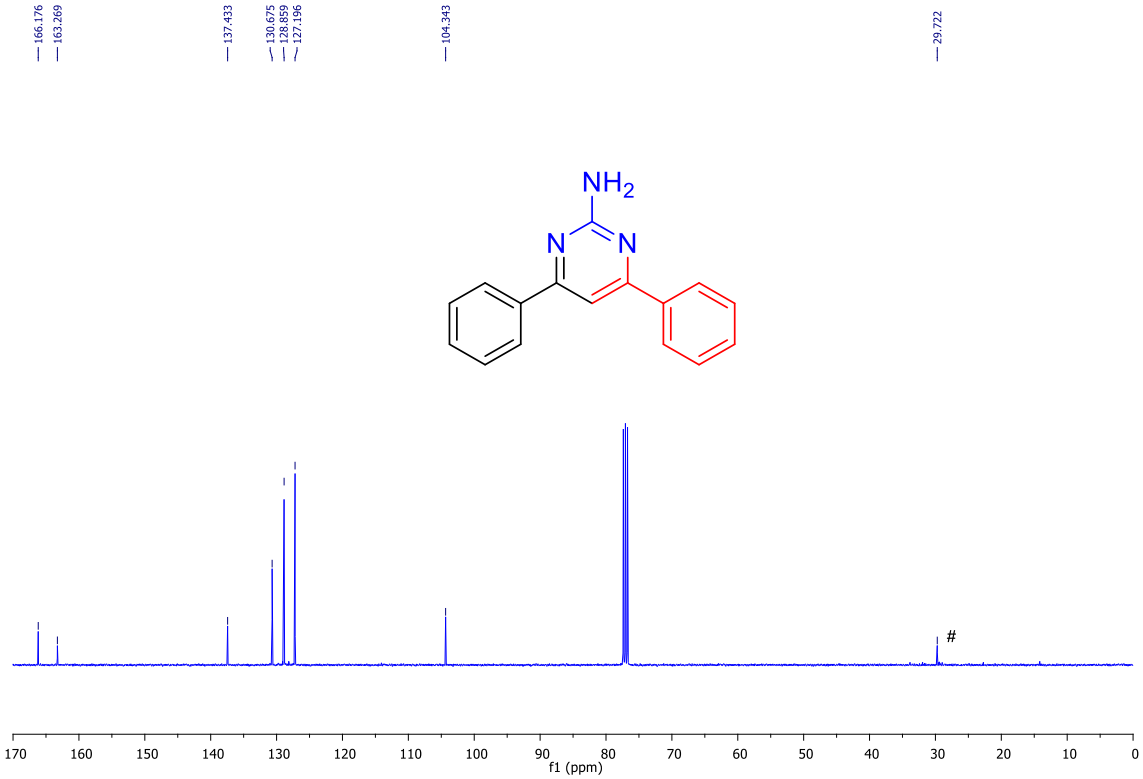


Fig S24. ^{13}C NMR spectrum of compound **7a** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

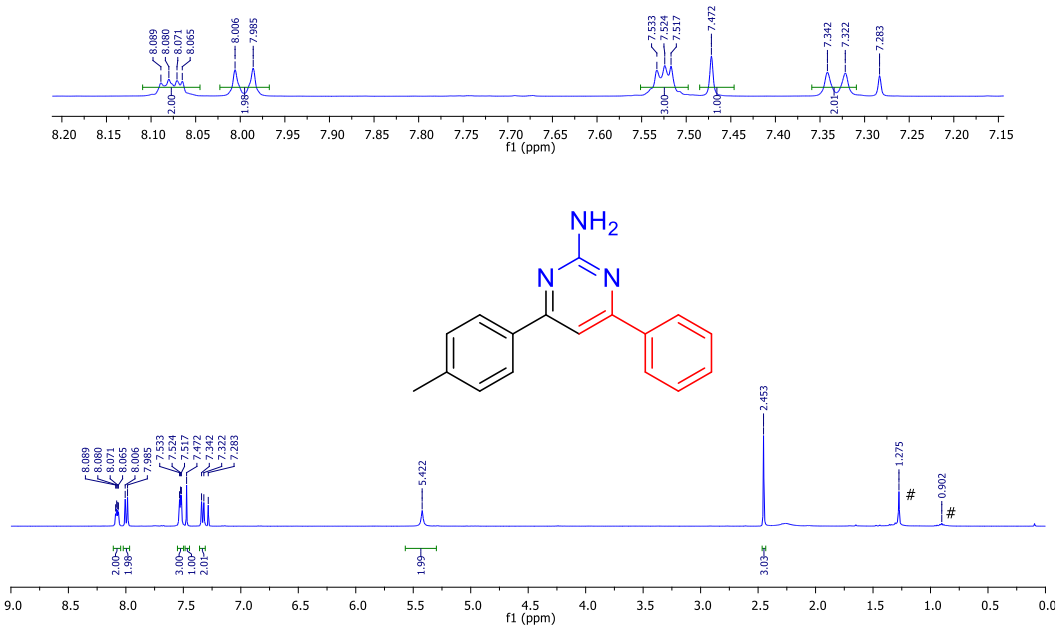


Fig S25. ^{1}H NMR spectrum of compound **7b** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

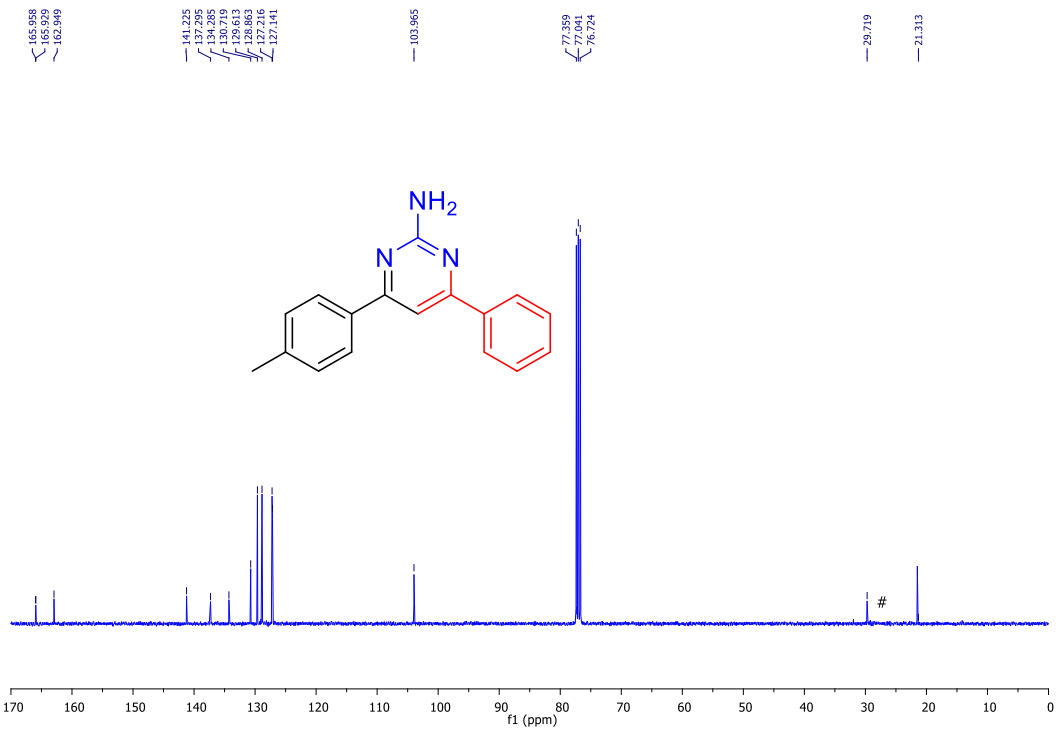


Fig S26. ^{13}C NMR spectrum of compound **7b** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

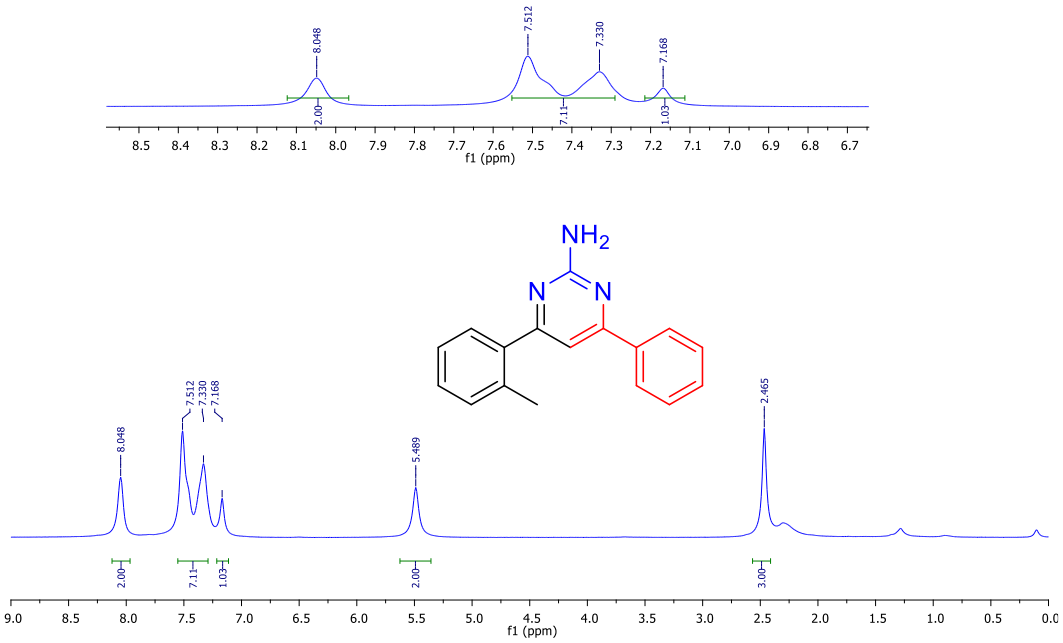


Fig S27. ^{1}H NMR spectrum of compound **7c** (400 MHz, $CDCl_3$).

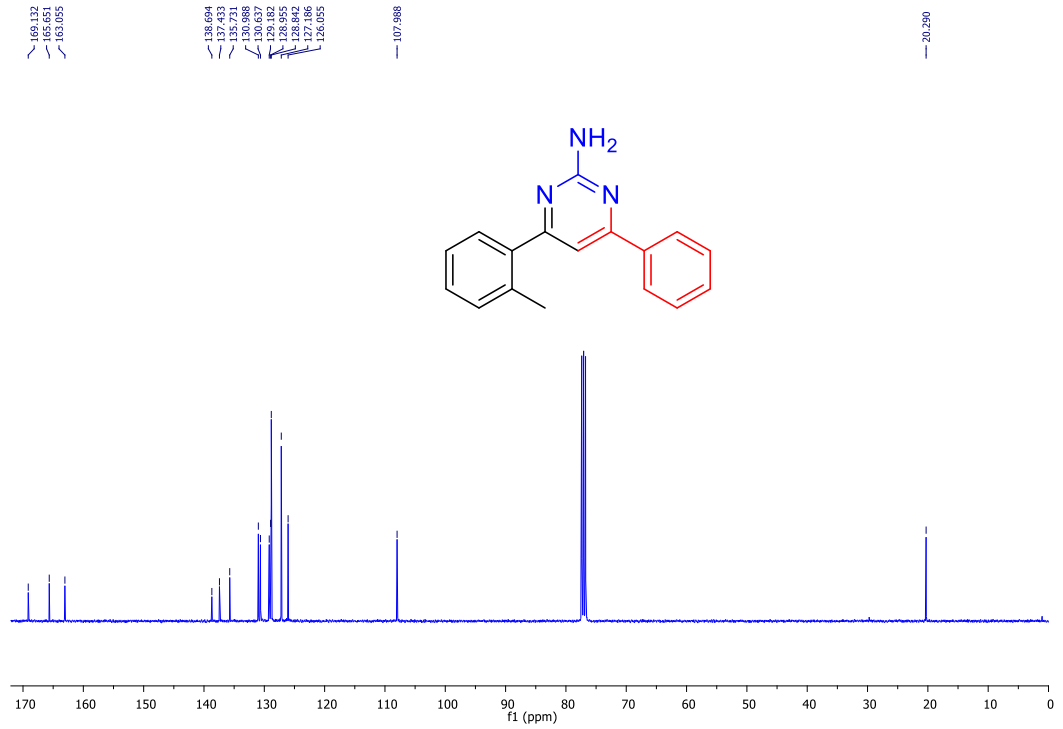


Fig S28. ^{13}C NMR spectrum of compound **7c** (100 MHz, $CDCl_3$).

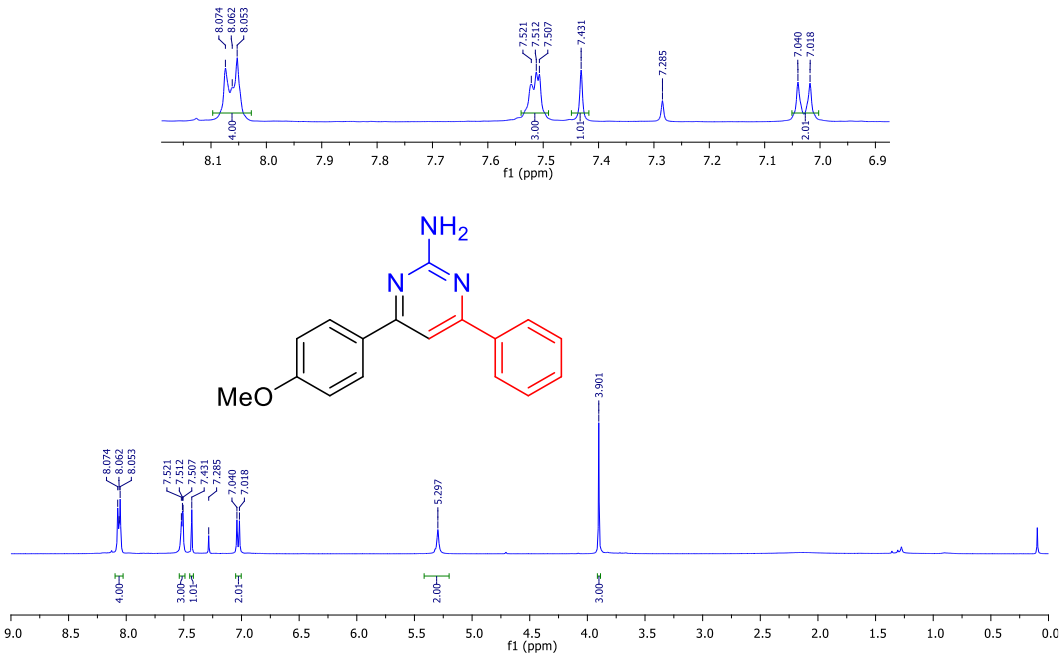


Fig S29. ^{1}H NMR spectrum of compound **7d** (400 MHz, $CDCl_3$).

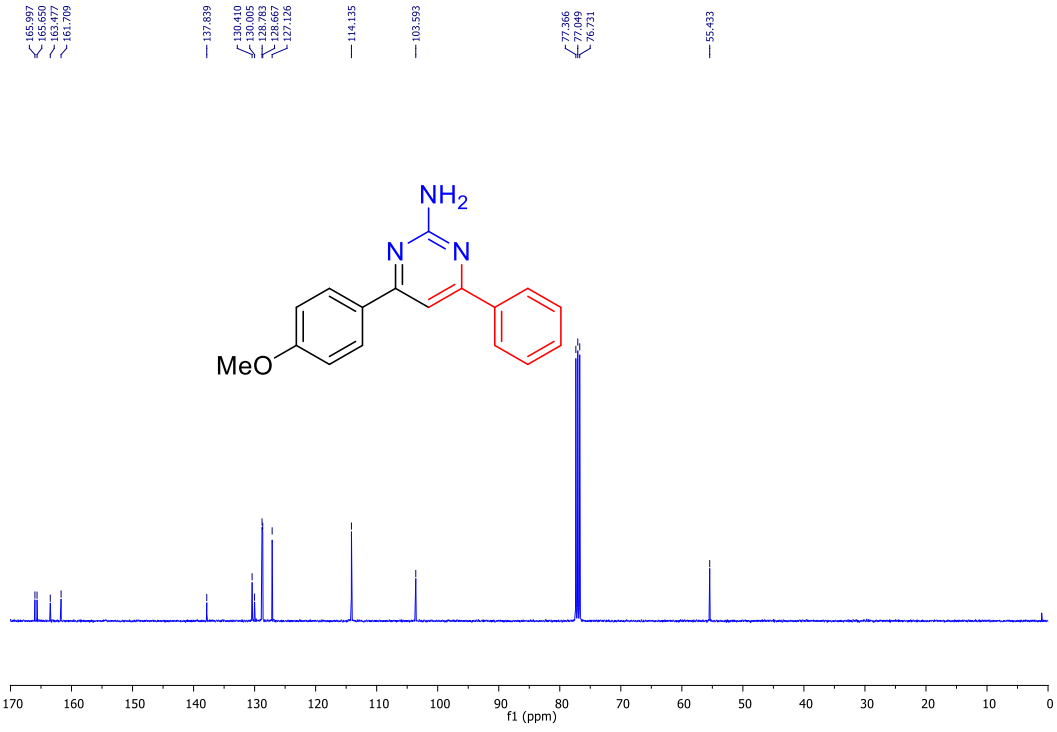


Fig 30. ^{13}C NMR spectrum of compound **7d** (100 MHz, $CDCl_3$).

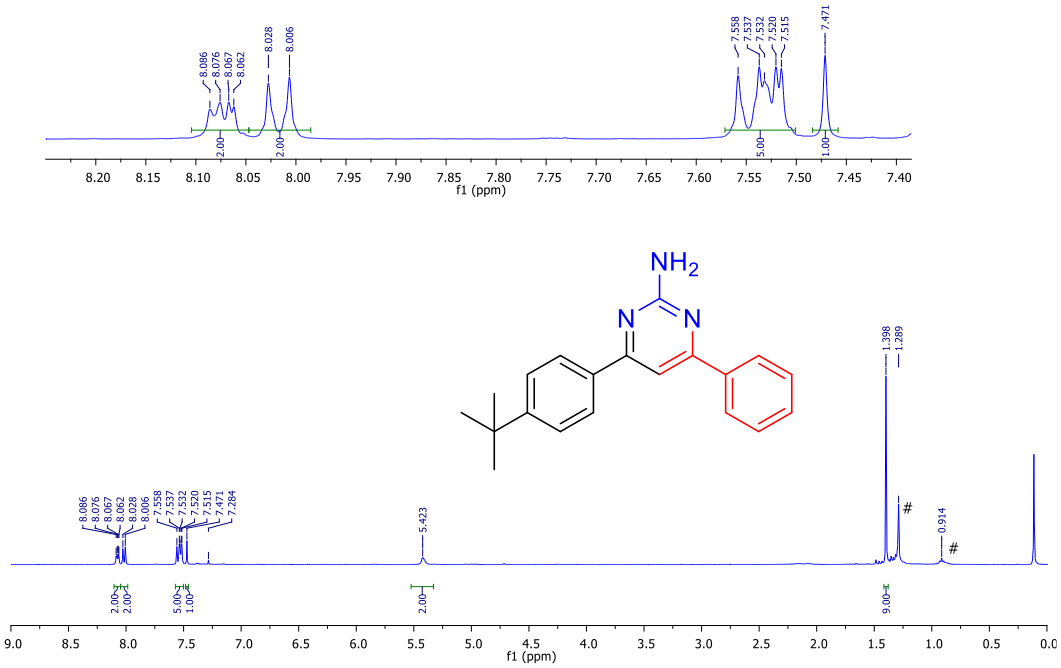


Fig S31. ^{1}H NMR spectrum of compound **7e** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

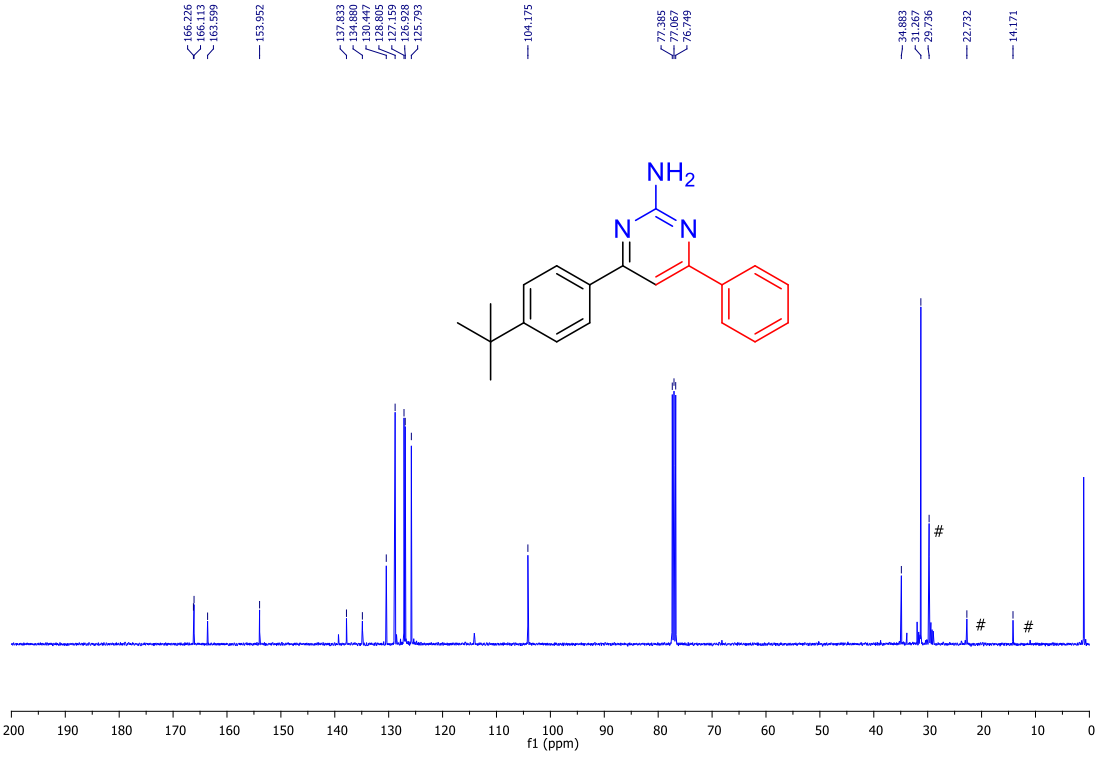


Fig S32. ^{13}C NMR spectrum of compound **7e** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

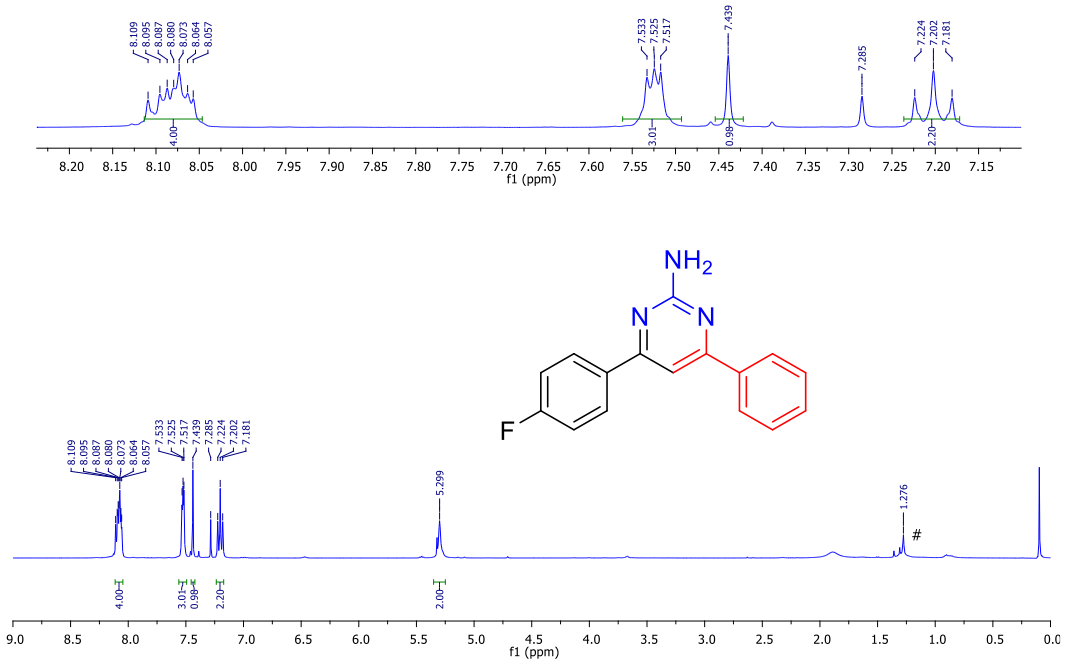


Fig S33. ^{1}H NMR spectrum of compound **7f** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

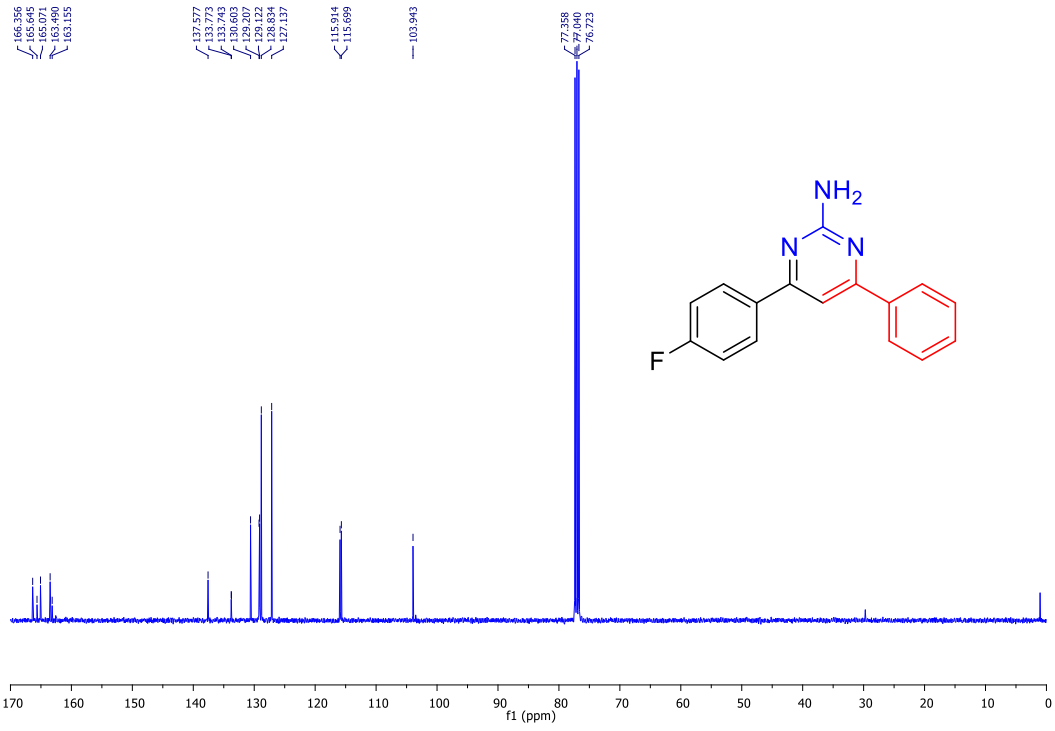


Fig S34. ^{13}C NMR spectrum of compound **7f** (100 MHz, $CDCl_3$).

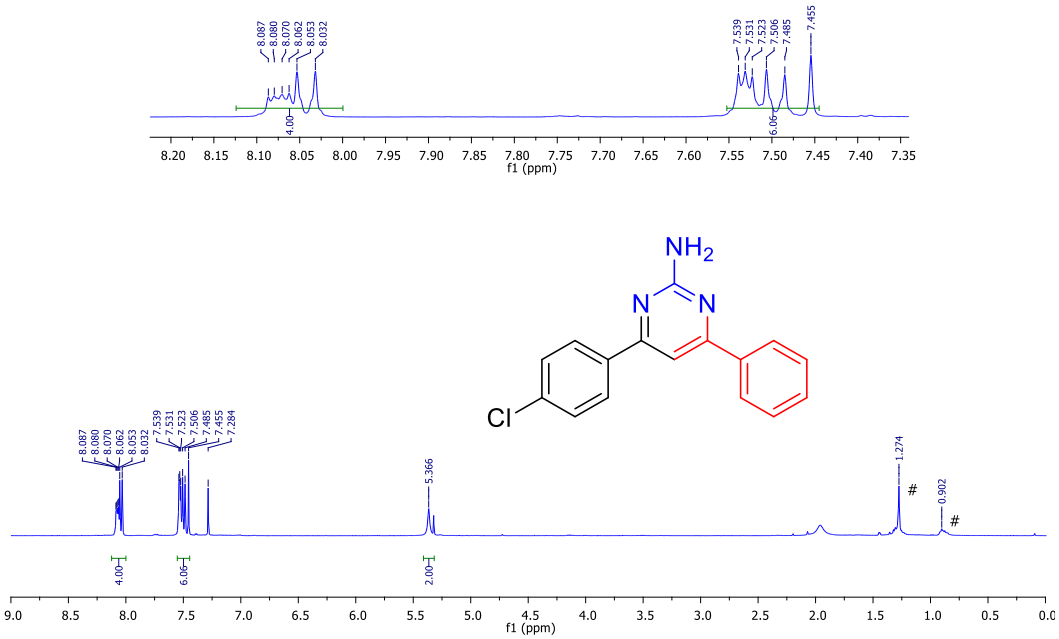


Fig S35. ^{1}H NMR spectrum of compound **7g** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

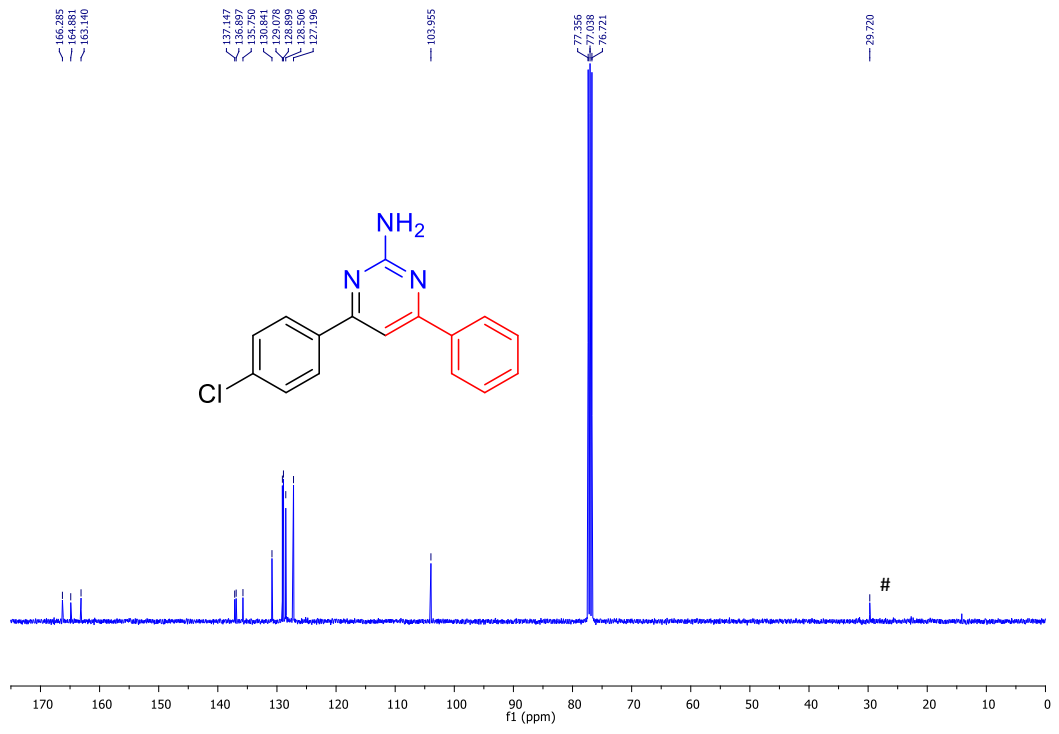


Fig S36. ^{13}C NMR spectrum of compound **7g** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

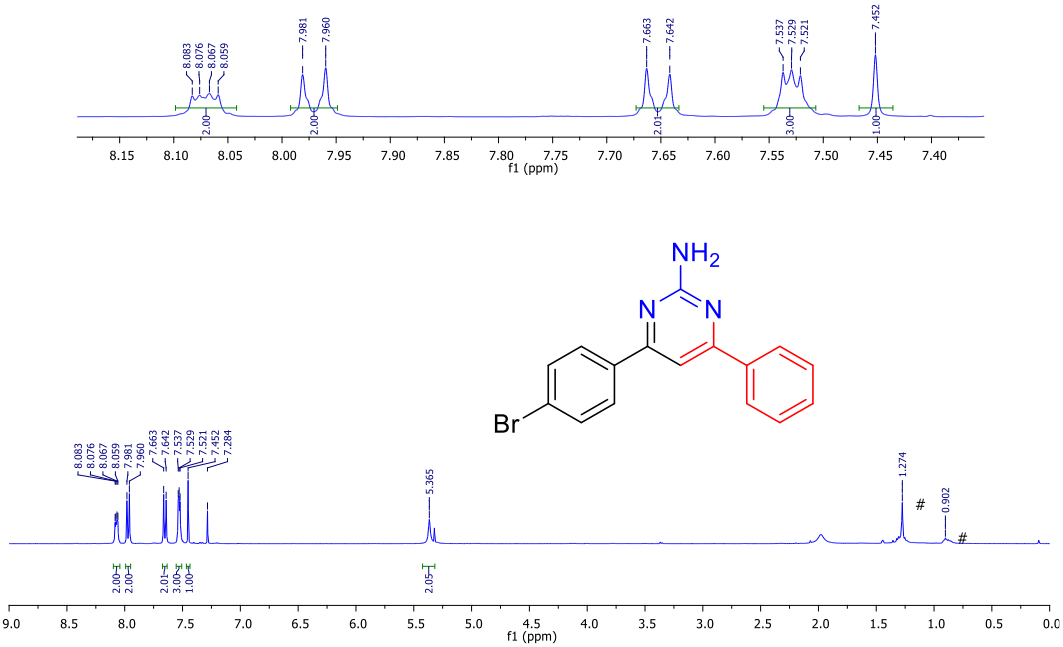


Fig S37. ^{1}H NMR spectrum of compound **7h** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

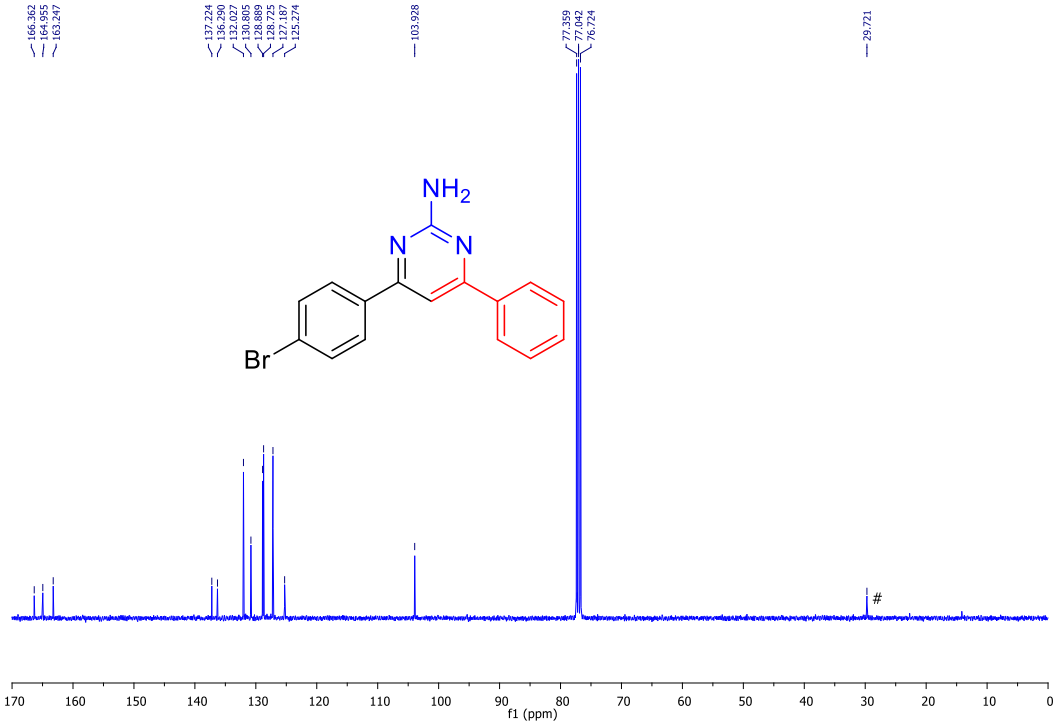


Fig S38. ^{13}C NMR spectrum of compound **7h** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

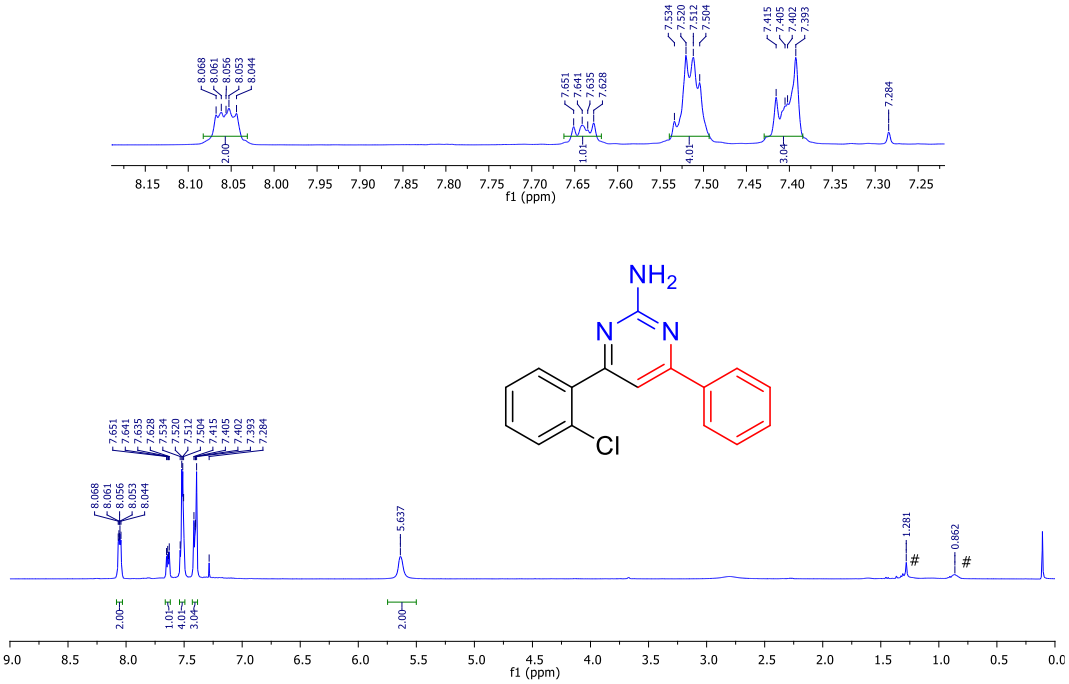


Fig S39. ^{1}H NMR spectrum of compound **7i** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

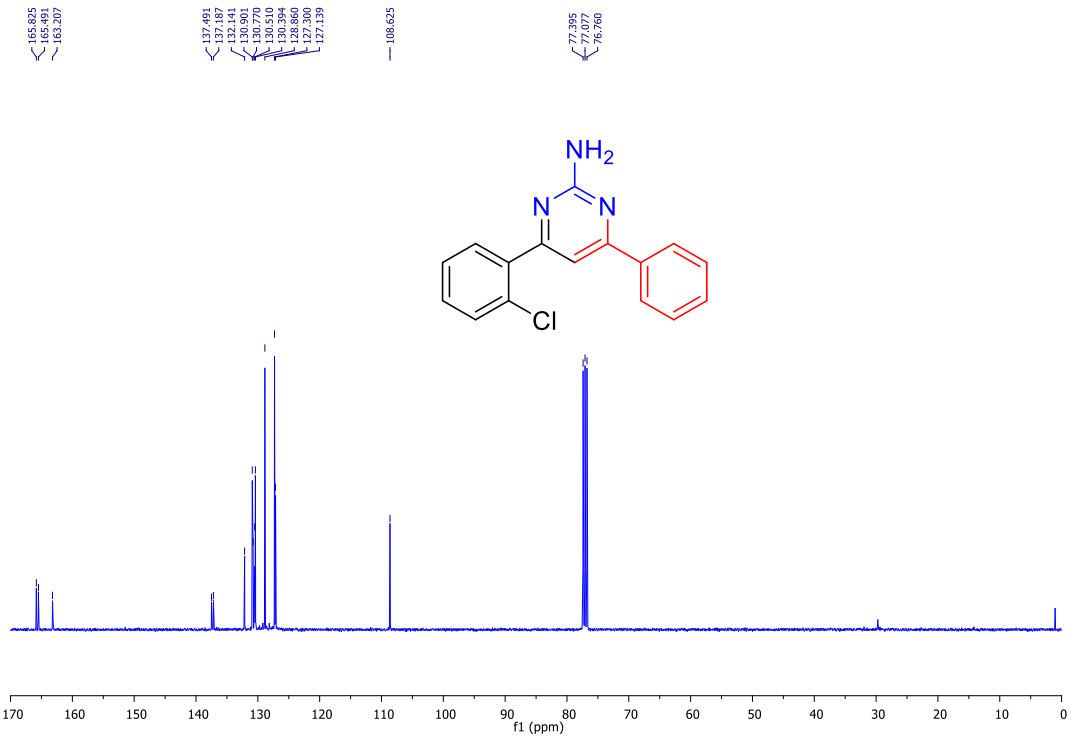


Fig S40. ^{13}C NMR spectrum of compound **7i** (100 MHz, $CDCl_3$).

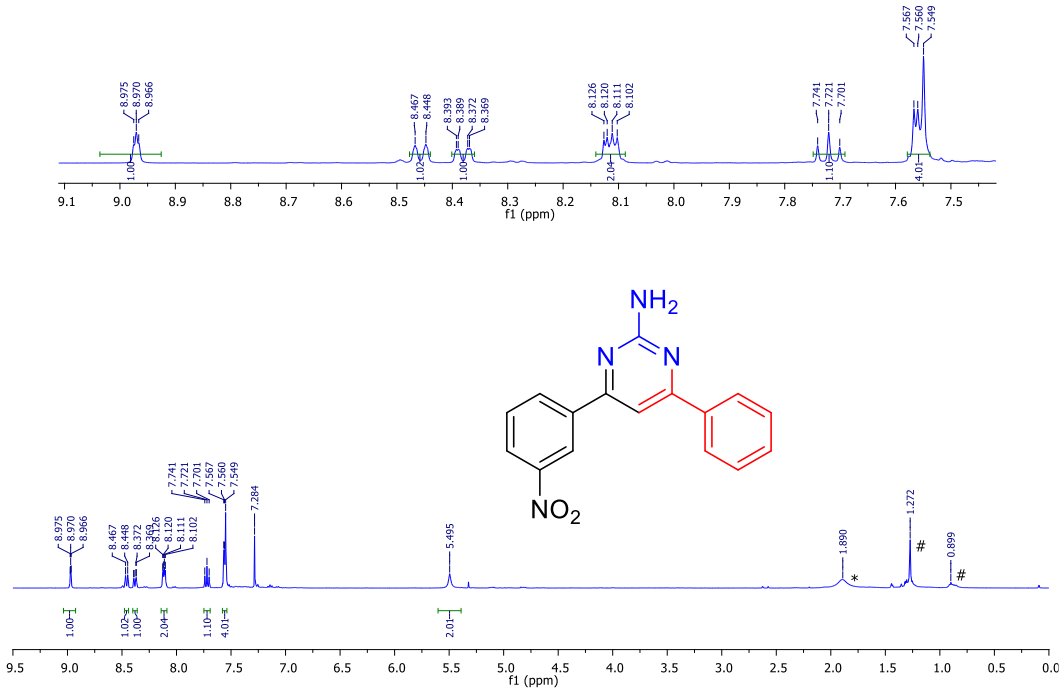


Fig S41. ^{1}H NMR spectrum of compound **7j** (400 MHz, $CDCl_3$) (*water, #hexane).

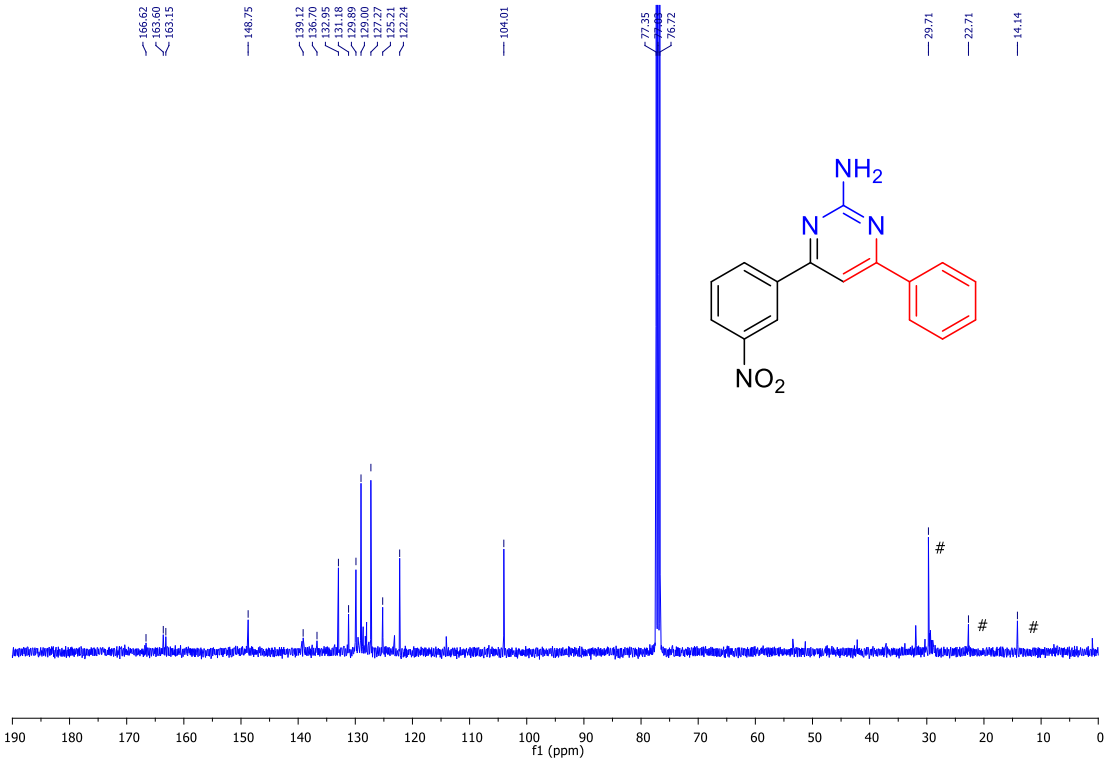


Fig S42. ^{1}H NMR spectrum of compound **7j** (100 MHz, $CDCl_3$) (#hexane).

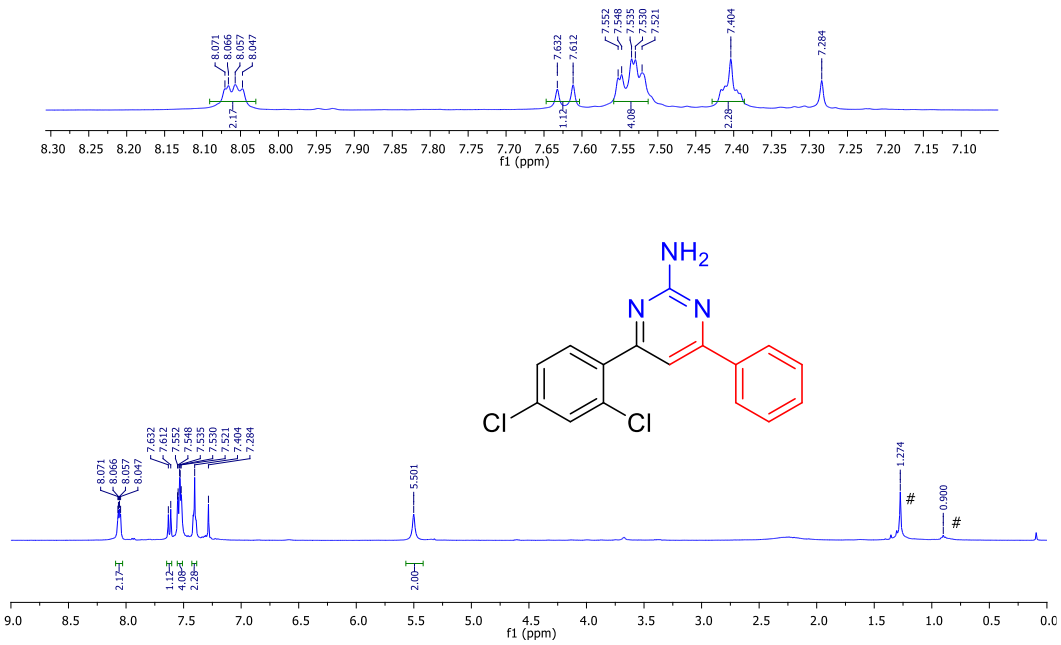


Fig S43. ^{1}H NMR spectrum of compound **7k** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

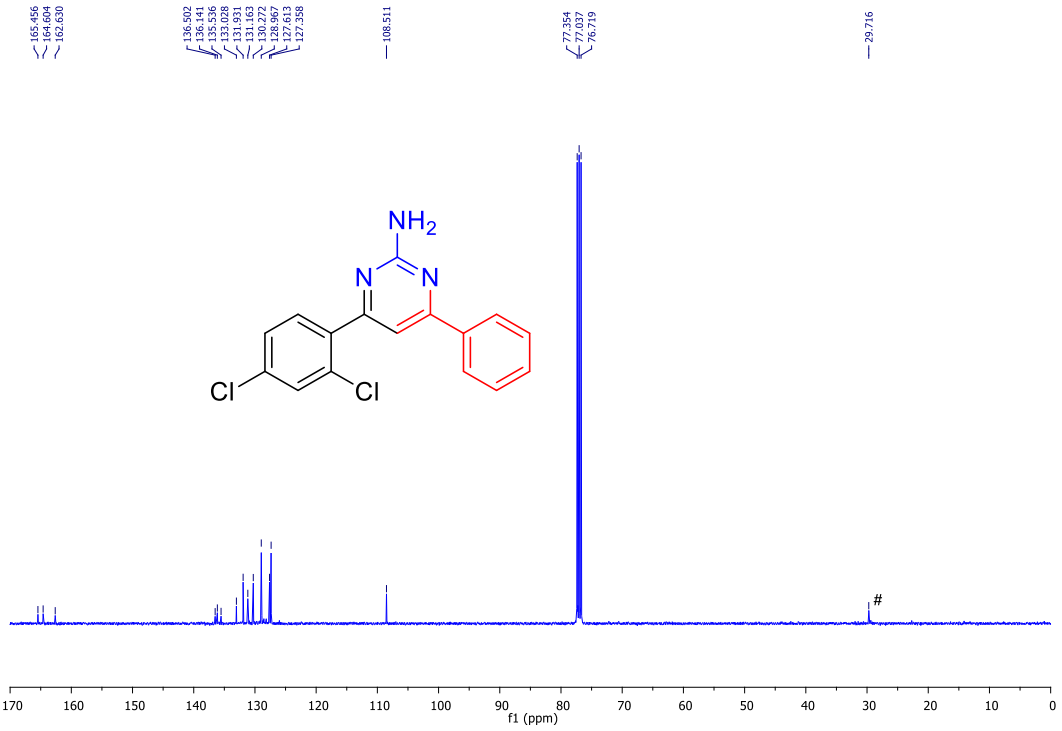


Fig S44. ^{13}C NMR spectrum of compound **7k** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

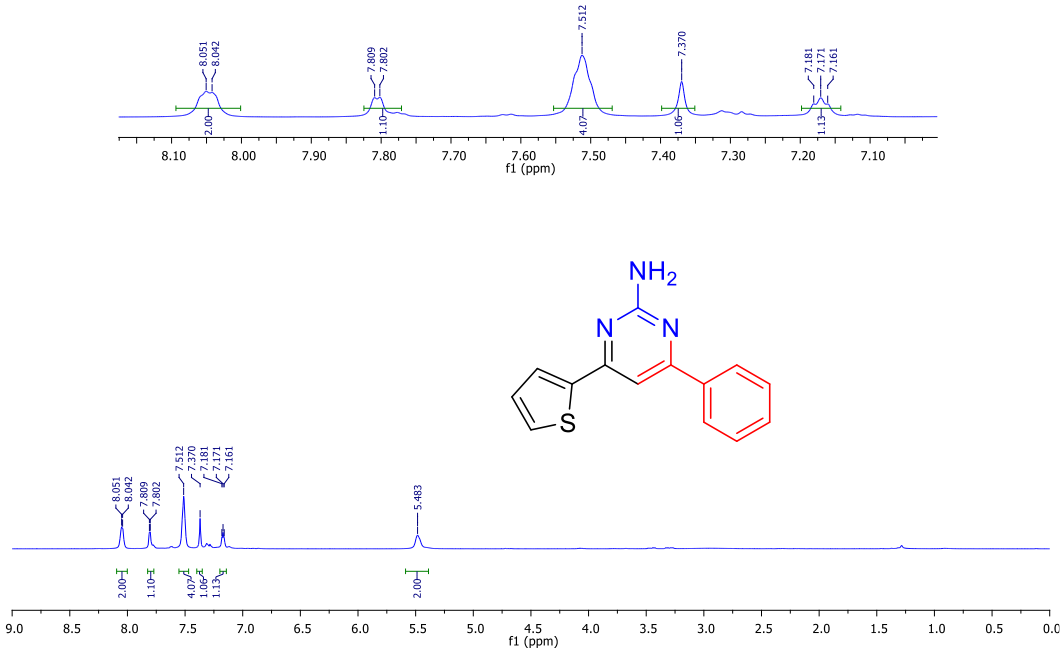


Fig S45. ^{1}H NMR spectrum of compound **7l** (400 MHz, $CDCl_3$).

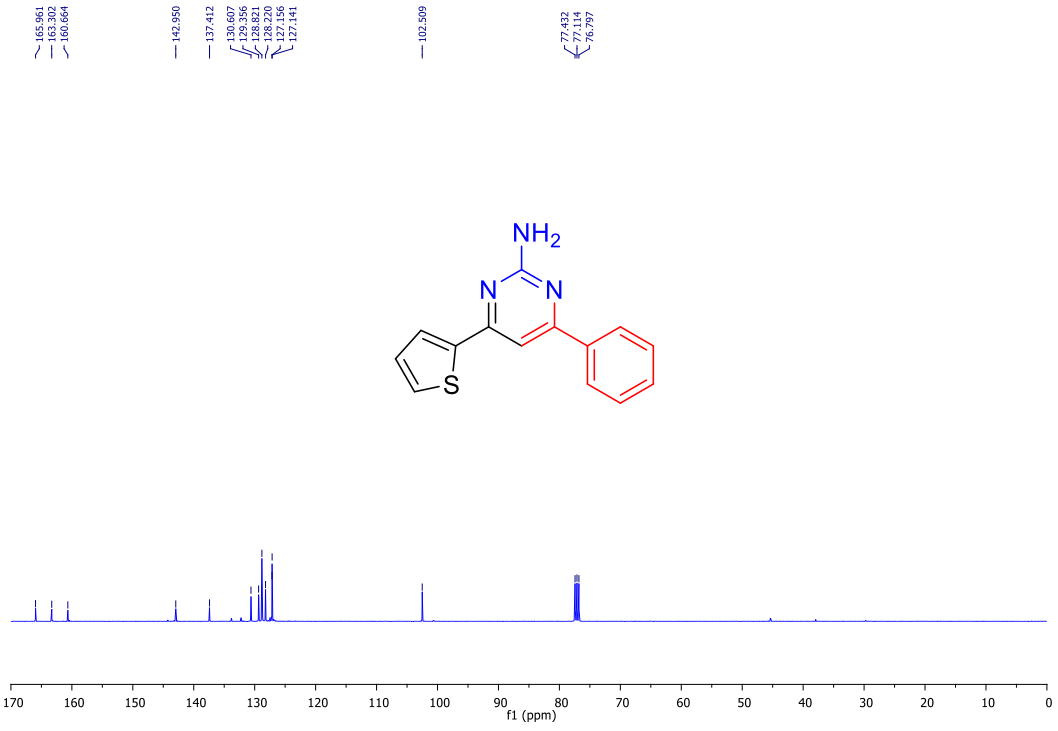


Fig S46. ^{13}C NMR spectrum of compound **7l** (100 MHz, $CDCl_3$).

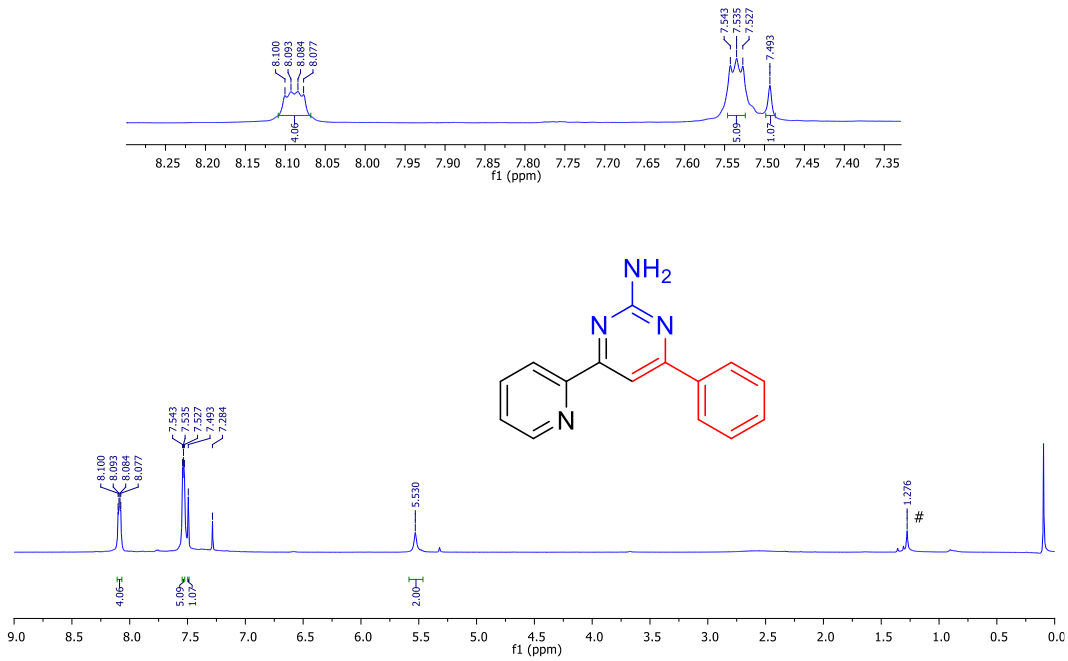


Fig S47. ^{1}H NMR spectrum of compound **7m** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

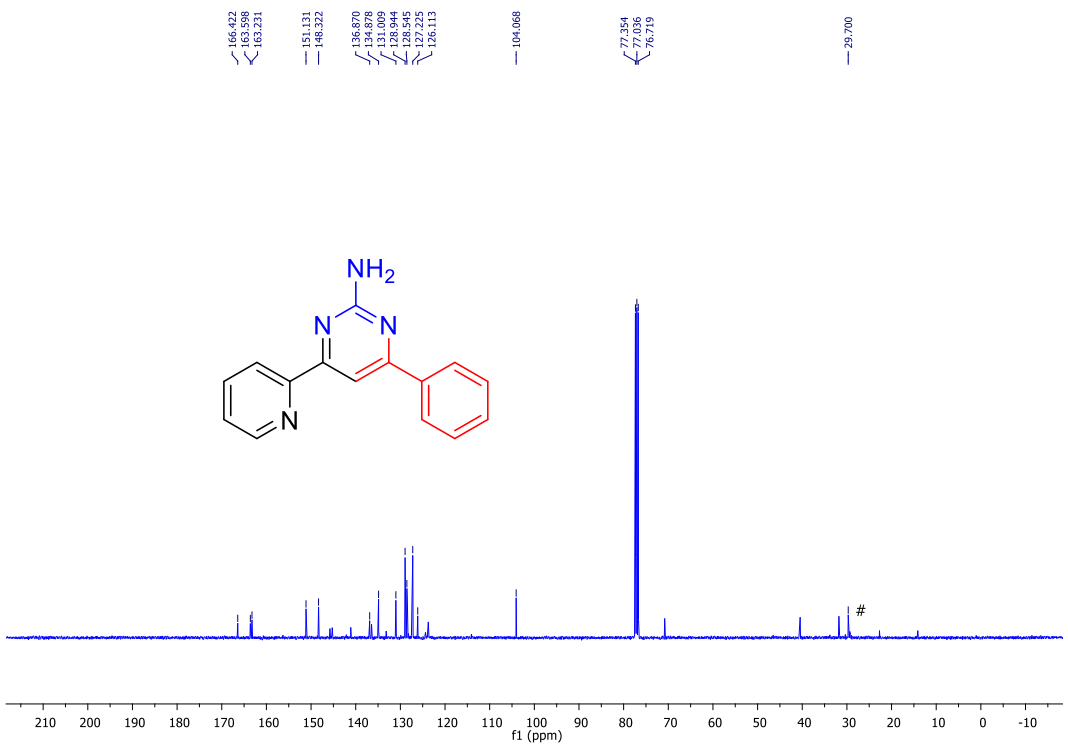


Fig S48. ^{13}C NMR spectrum of compound **7m** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

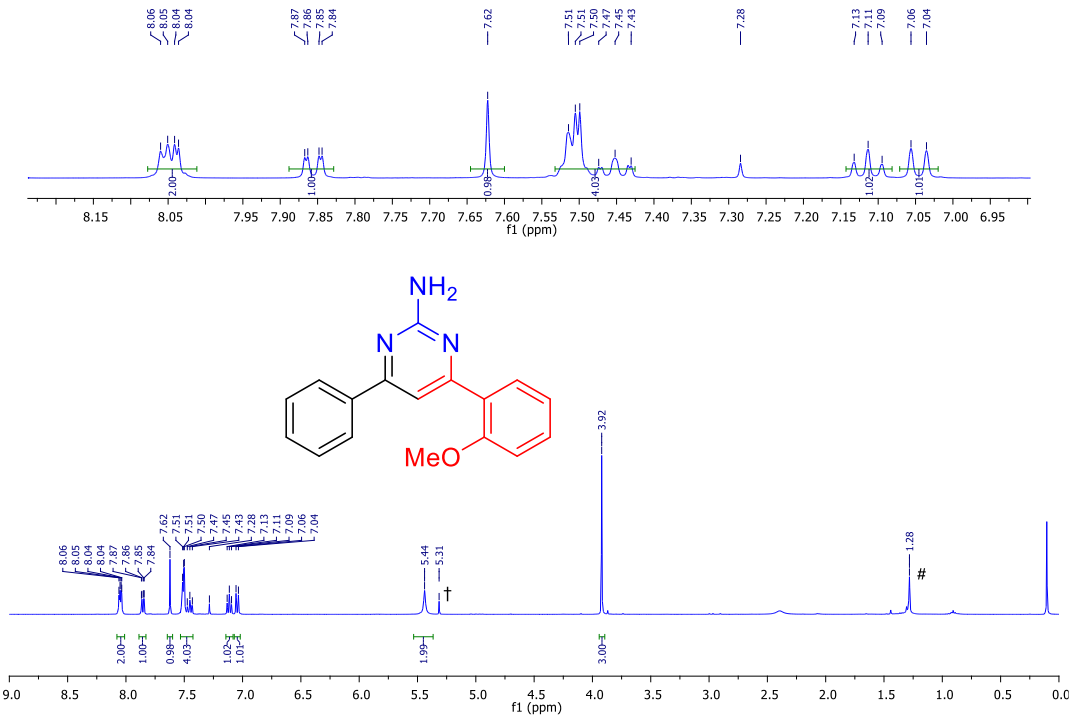


Fig S49. ^{1}H NMR spectrum of compound **7n** (400 MHz, $CDCl_3$) (†DCM, $^{\#}$hexane).

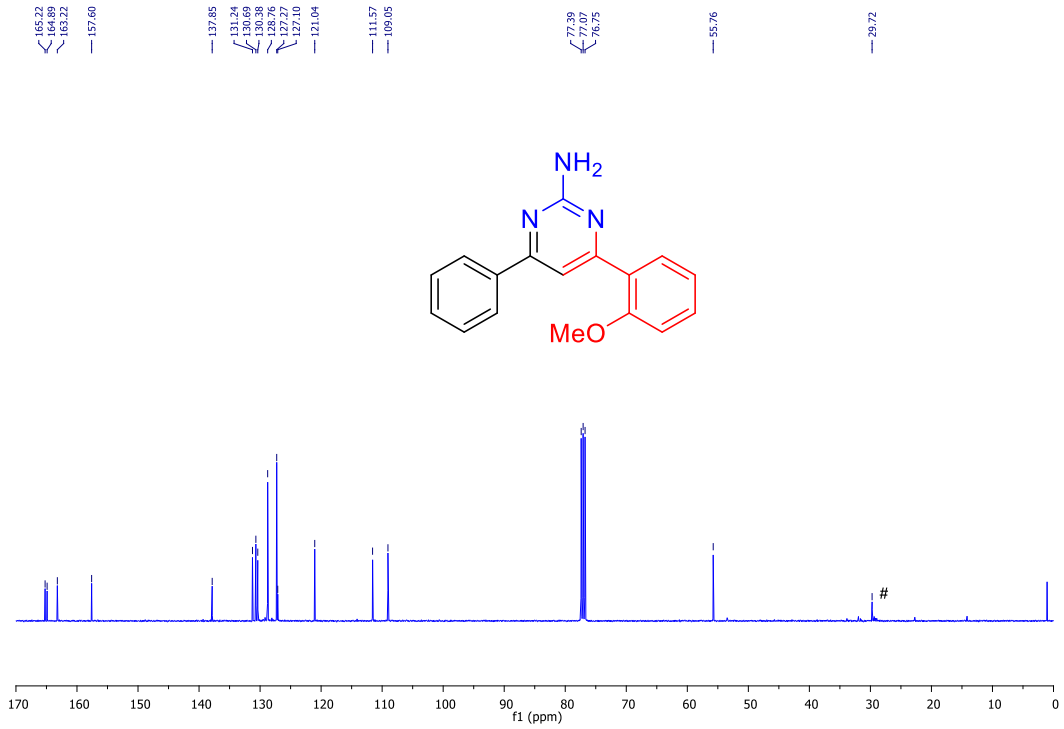


Fig S50. ^{13}C NMR spectrum of compound **7n** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

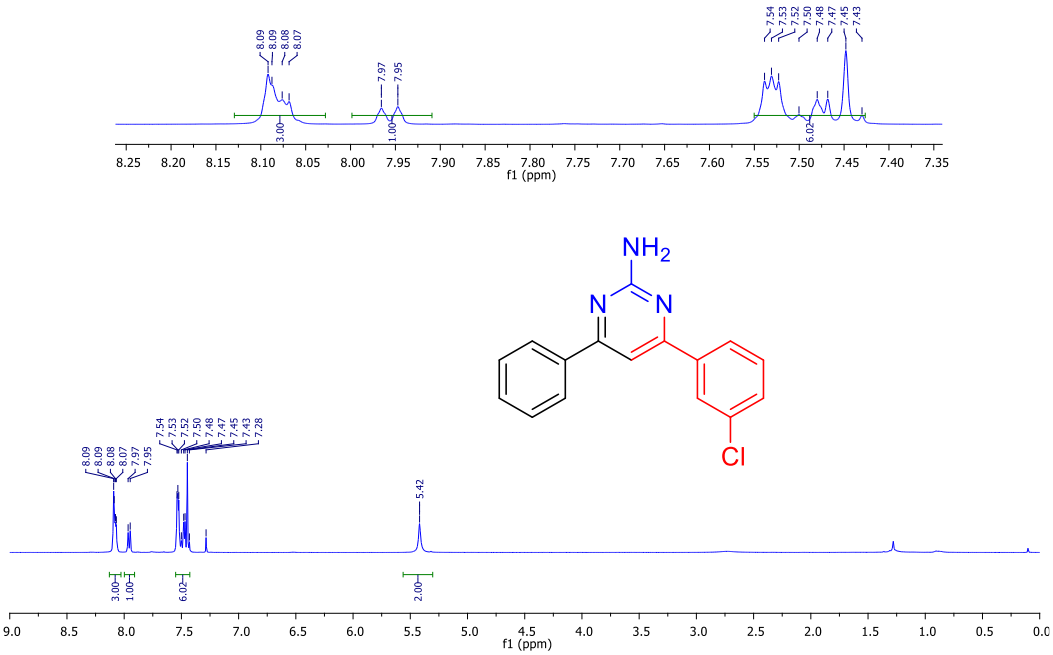


Fig S51. ^{1}H NMR spectrum of compound **7o** (400 MHz, $CDCl_3$).

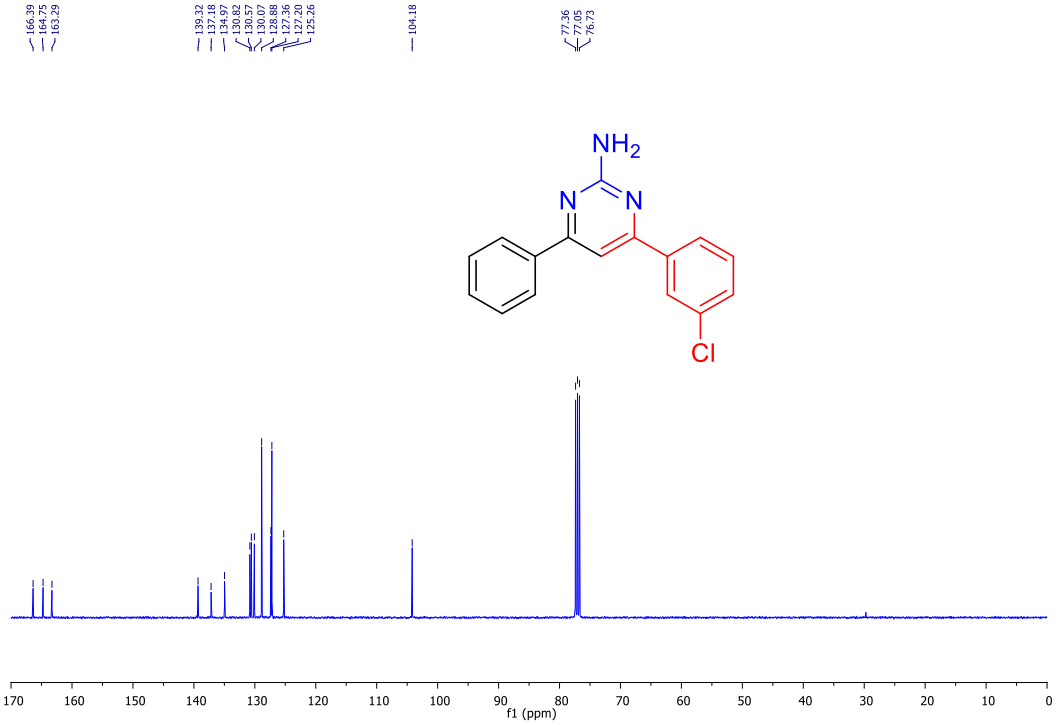


Fig S52. ^{13}C NMR spectrum of compound **7o** (100 MHz, $CDCl_3$).

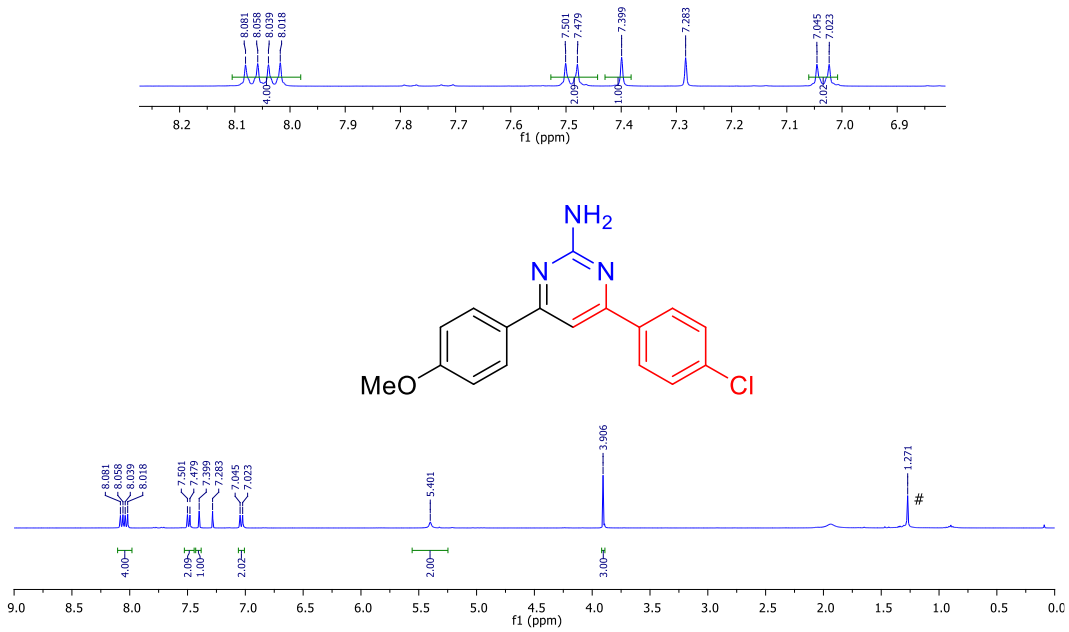


Fig S53. ^{1}H NMR spectrum of compound **7p** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

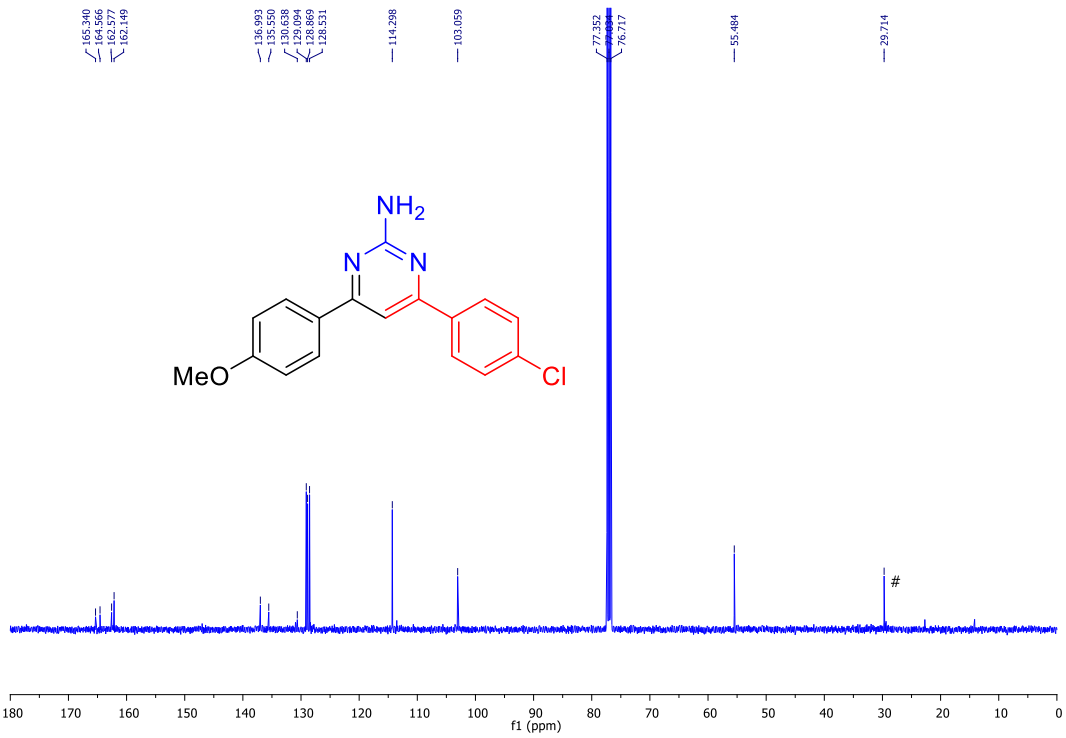


Fig S54. ^{13}C NMR spectrum of compound **7p** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

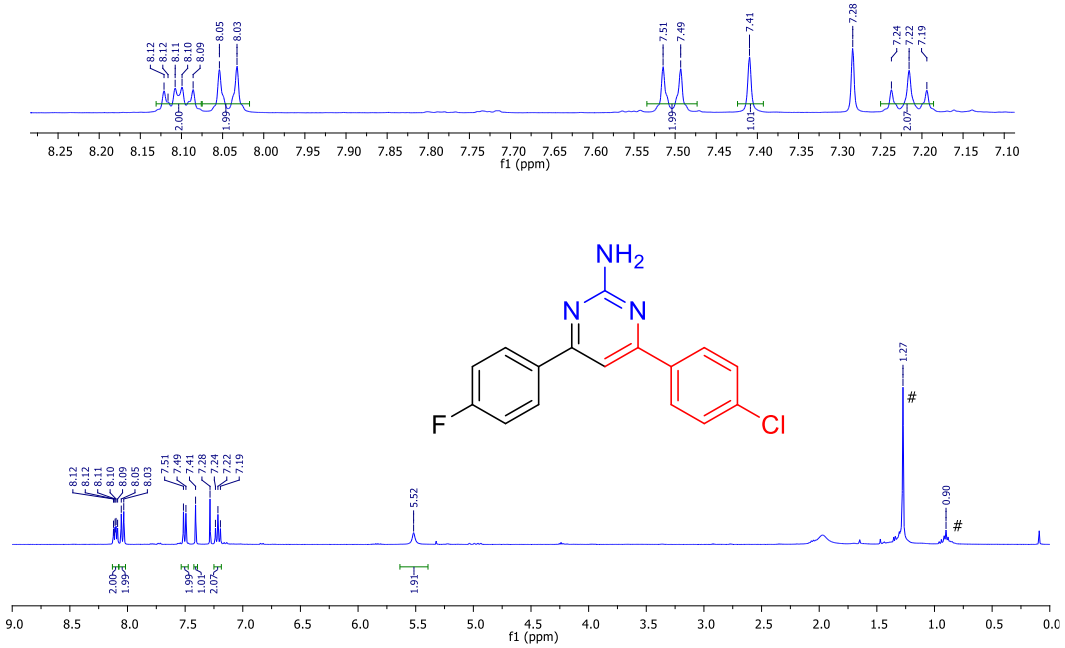


Fig S55. ^{1}H NMR spectrum of compound **7q** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

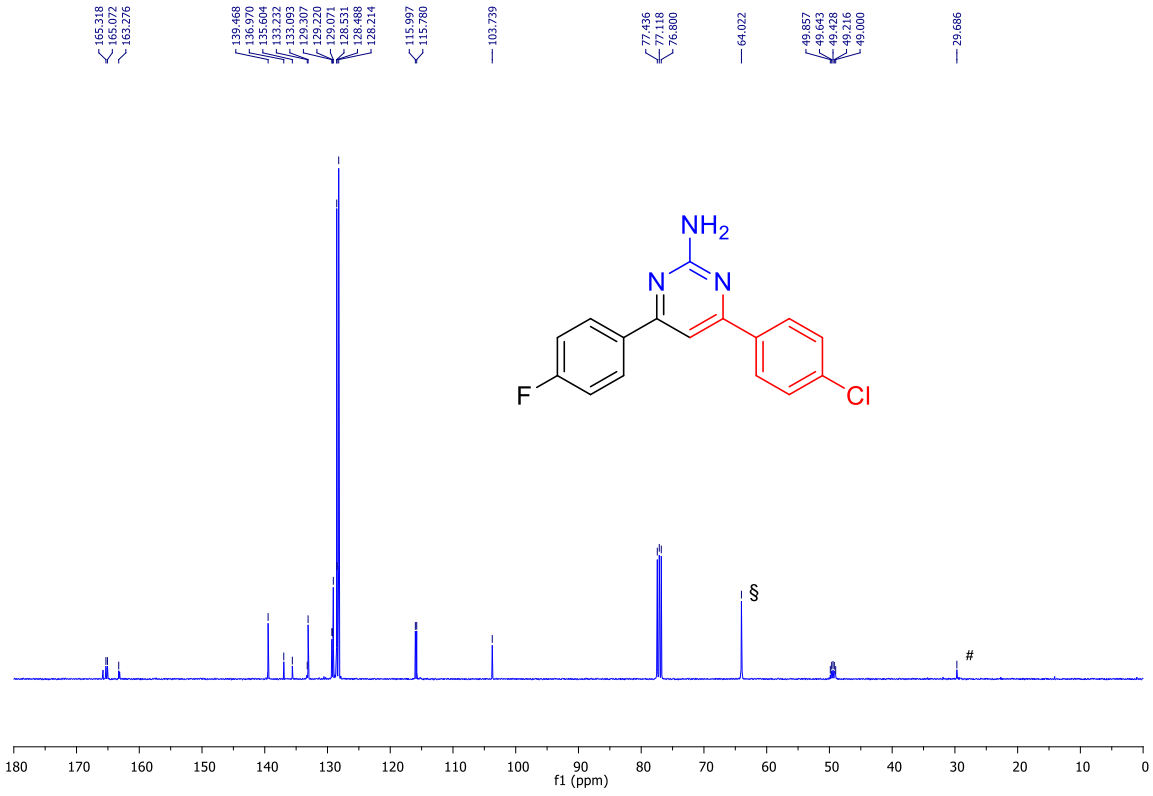


Fig S56. ^{13}C NMR spectrum of compound **7q** (100 MHz, $CDCl_3$ + 1drop CD_3OD) (§diethyl ether, $^{\#}$hexane).

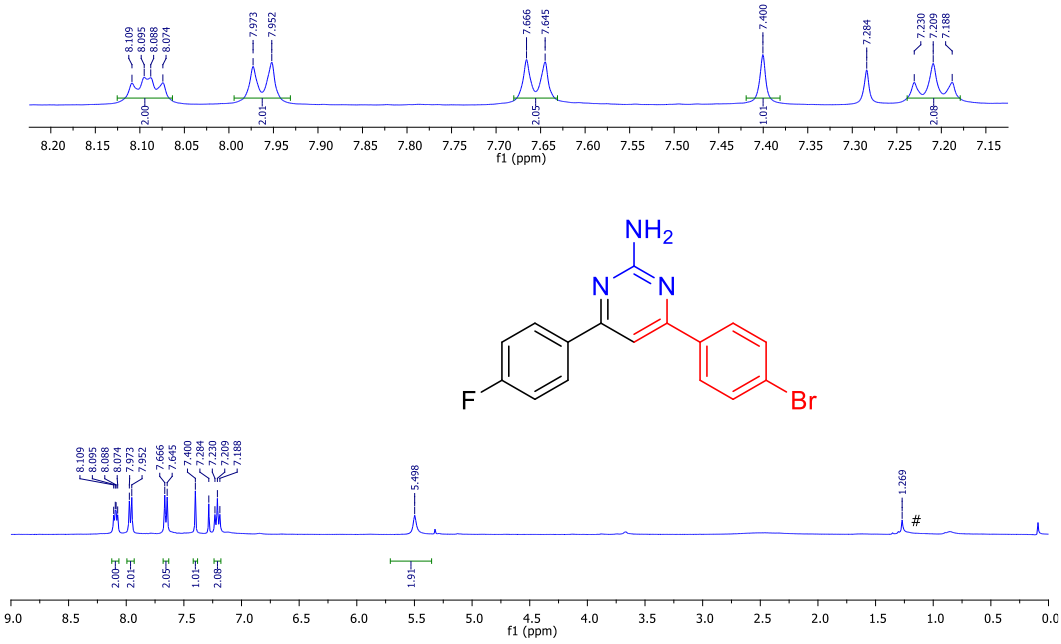


Fig S57. ^{1}H NMR spectrum of compound **7r** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

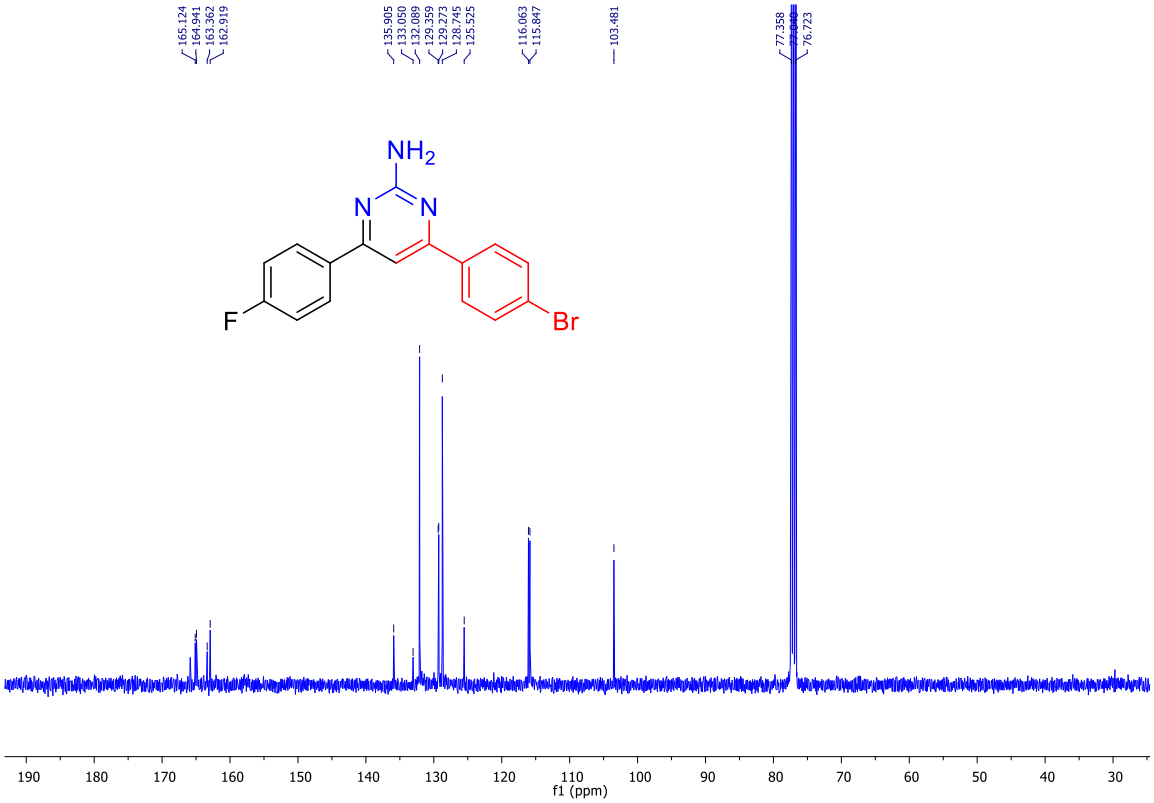


Fig S58. ^{13}C NMR spectrum of compound **7r** (100 MHz, $CDCl_3$).

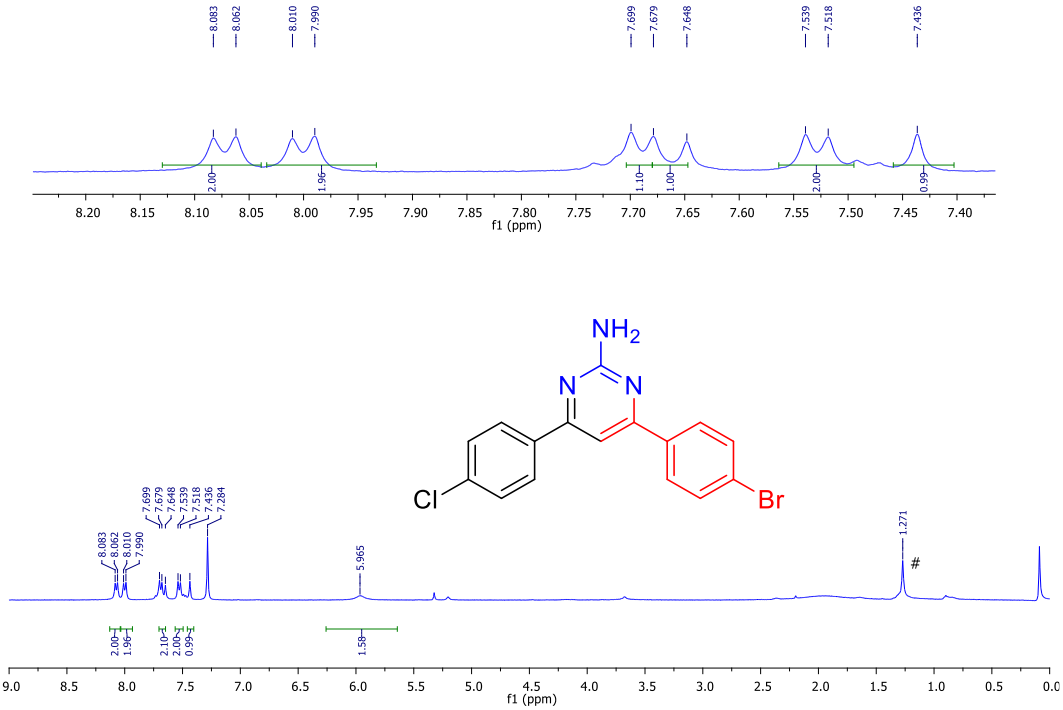


Fig 59. ^{1}H NMR spectrum of compound **7s** (400 MHz, $CDCl_3$) ($^{\#}$hexane).

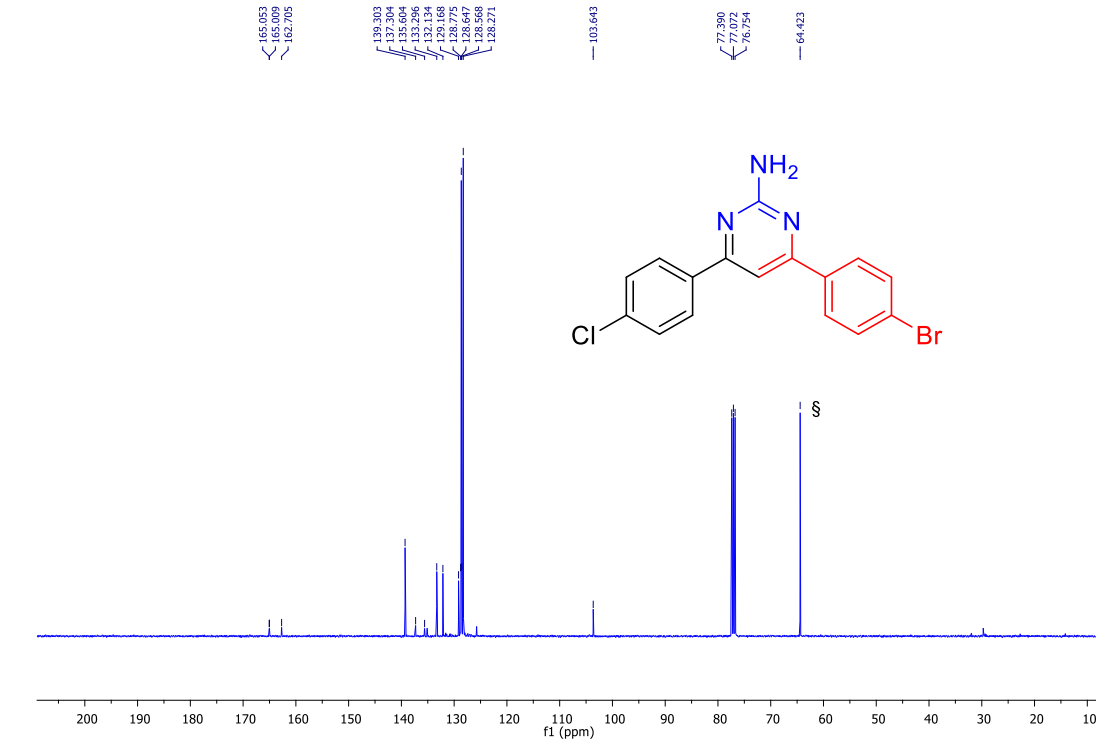


Fig 60. ^{13}C NMR spectrum of compound **7s** (100 MHz, $CDCl_3$) (§diethyl ether, $^{\#}$hexane).

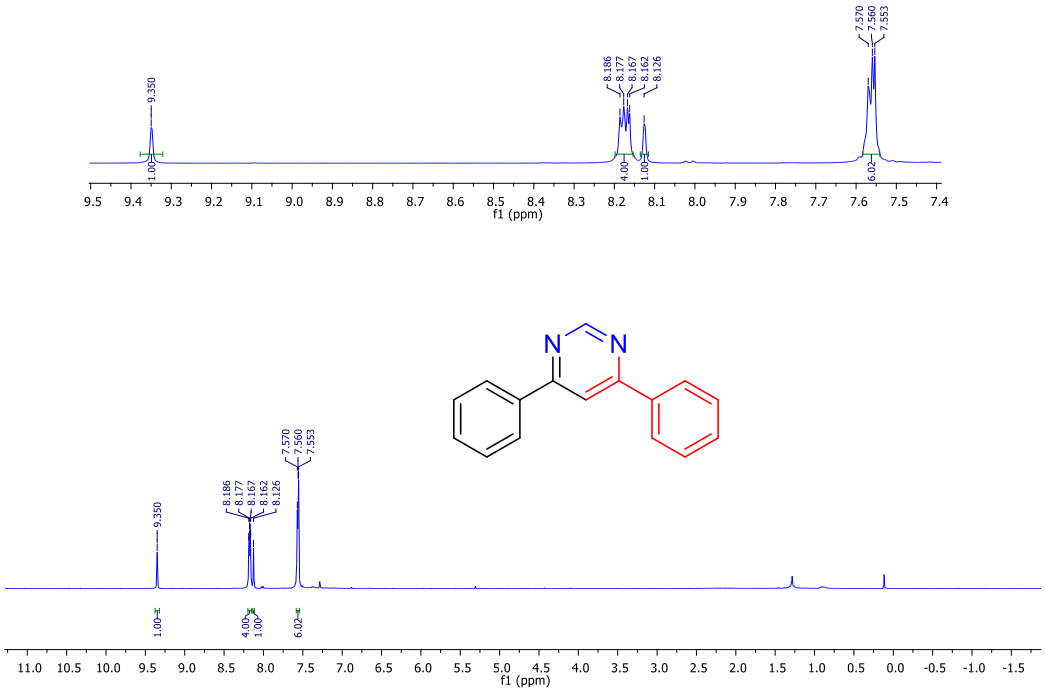


Fig S61. ^{1}H NMR spectrum of compound **7t** (400 MHz, $CDCl_3$).

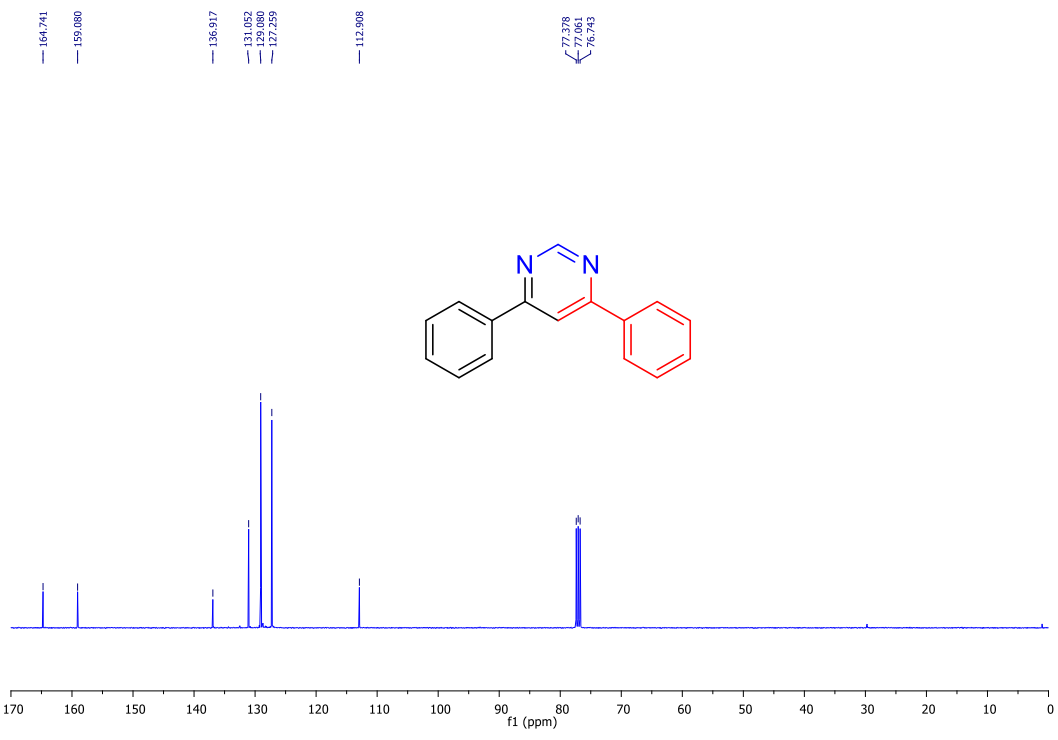


Fig S62. ^{13}C NMR spectrum of compound **7t** (100 MHz, $CDCl_3$).

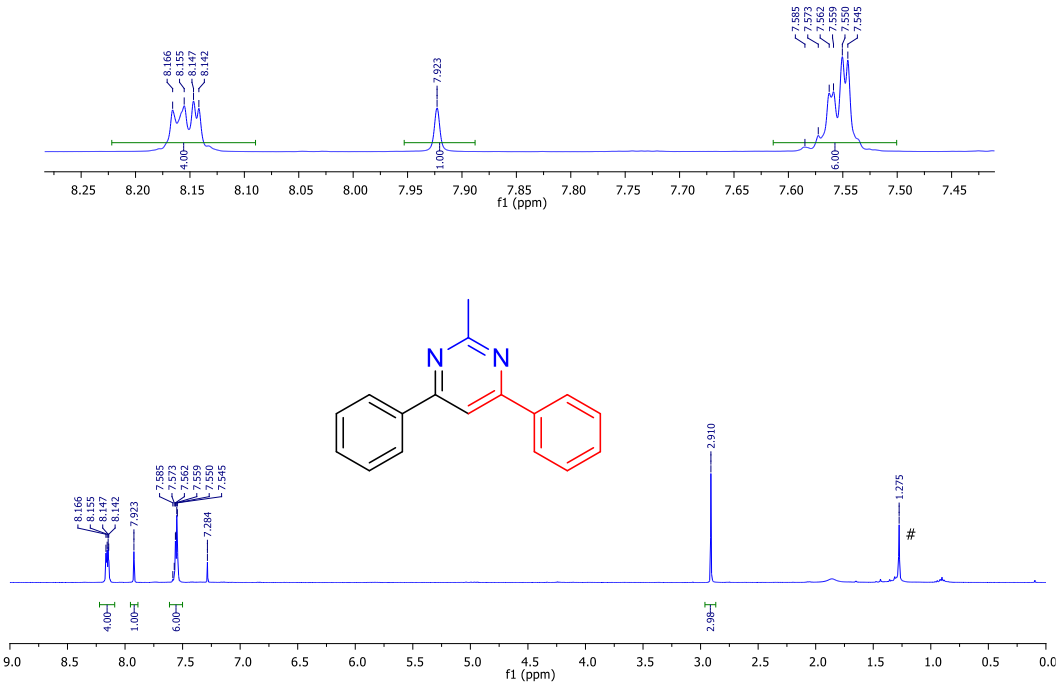


Fig S63. ^{1}H NMR spectrum of compound **7u** (400 MHz, $CDCl_3$).

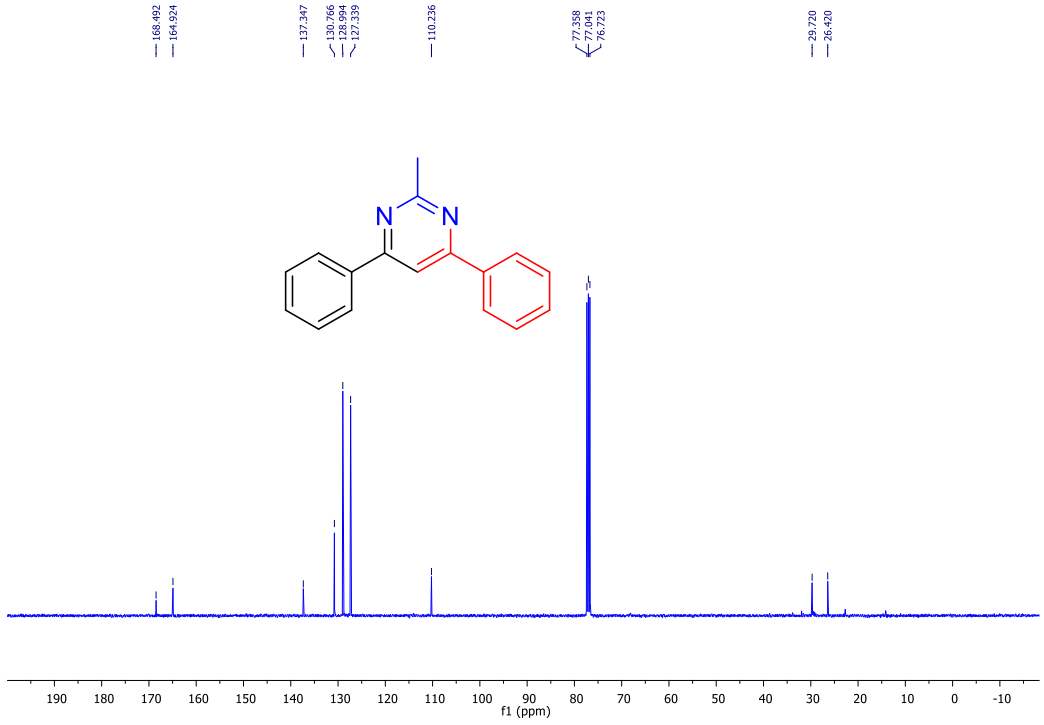


Fig S64. ^{13}C NMR spectrum of compound **7u** (100 MHz, $CDCl_3$).

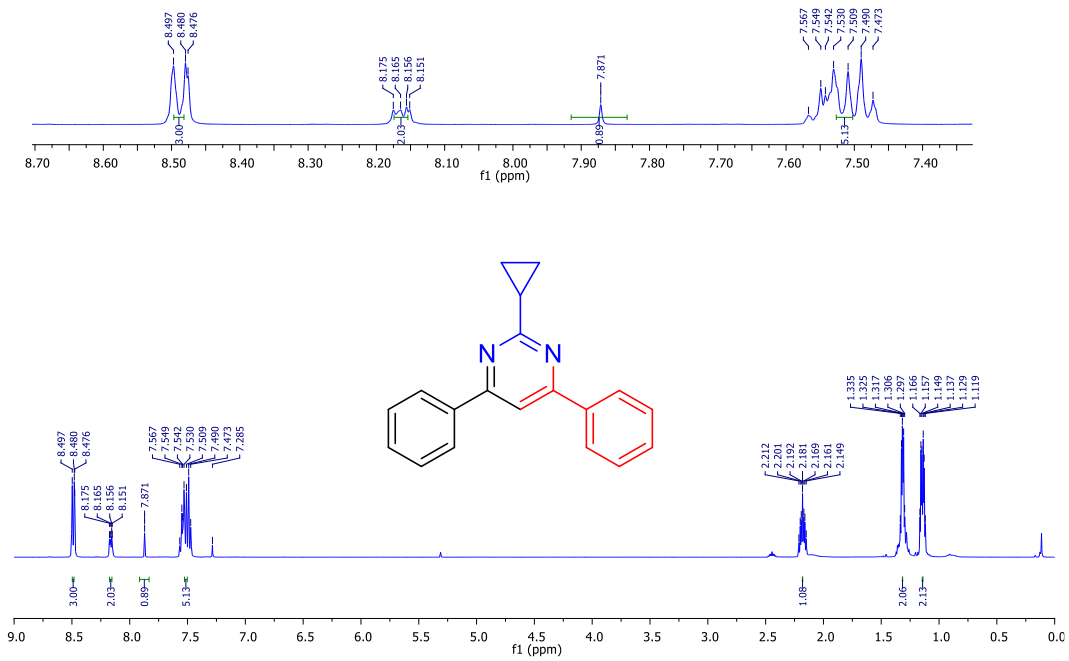


Fig S65. ^{1}H NMR spectrum of compound **7v** (400 MHz, $CDCl_3$).

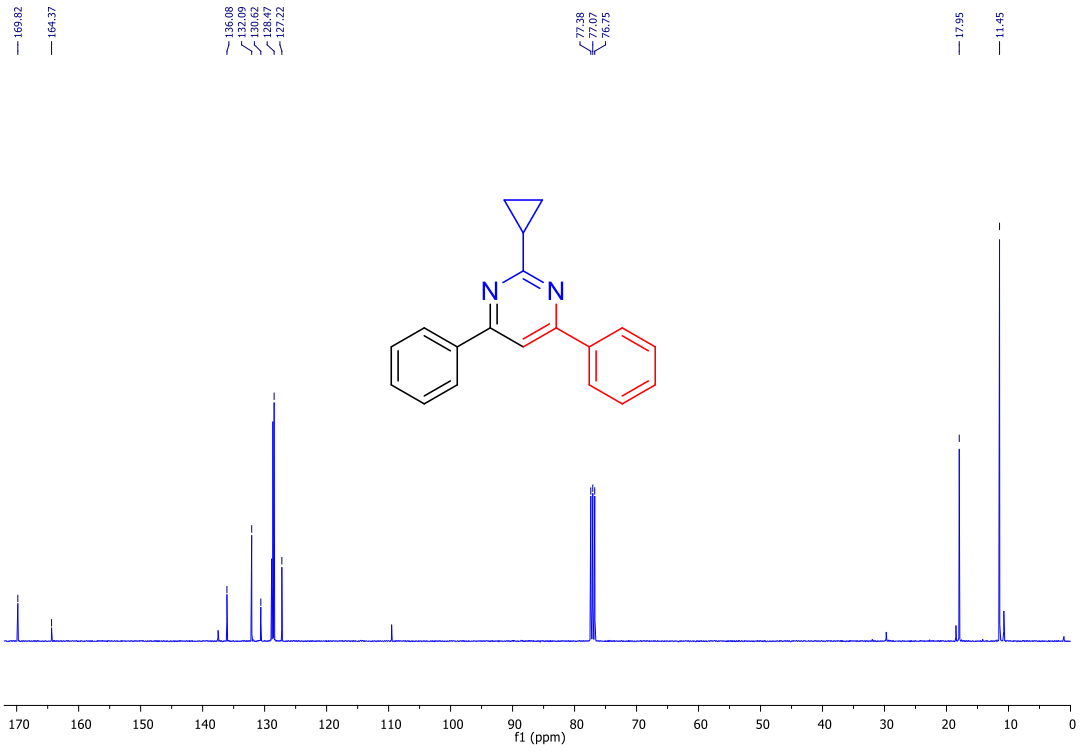


Fig S66. ^{13}C NMR spectrum of compound **7v** (100 MHz, $CDCl_3$).

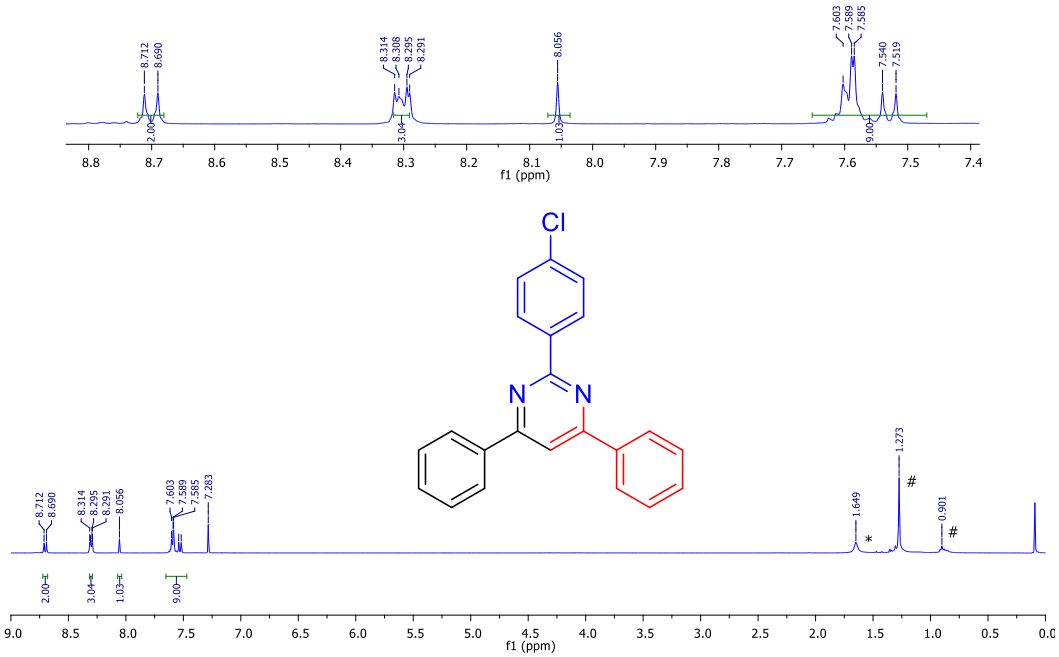


Fig S67. ^{1}H NMR spectrum of compound **7x** (400 MHz, $CDCl_3$) (*water, $^{\#}$hexane).

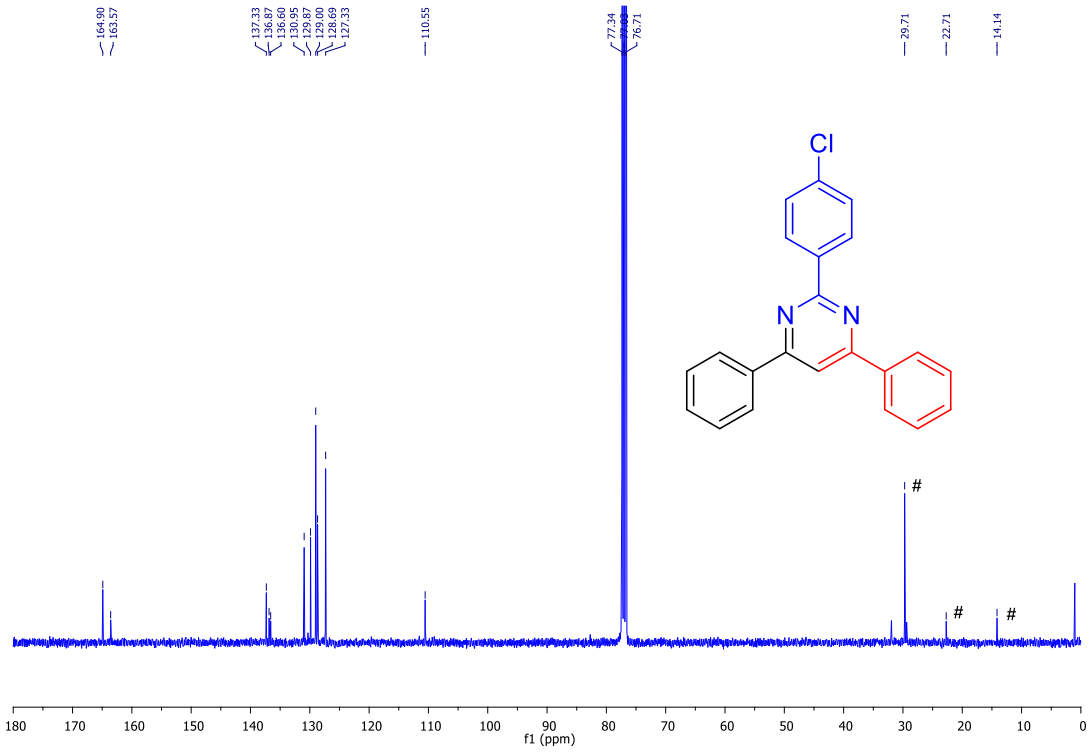


Fig S68. ^{13}C NMR spectrum of compound **7x** (100 MHz, $CDCl_3$) ($^{\#}$hexane).

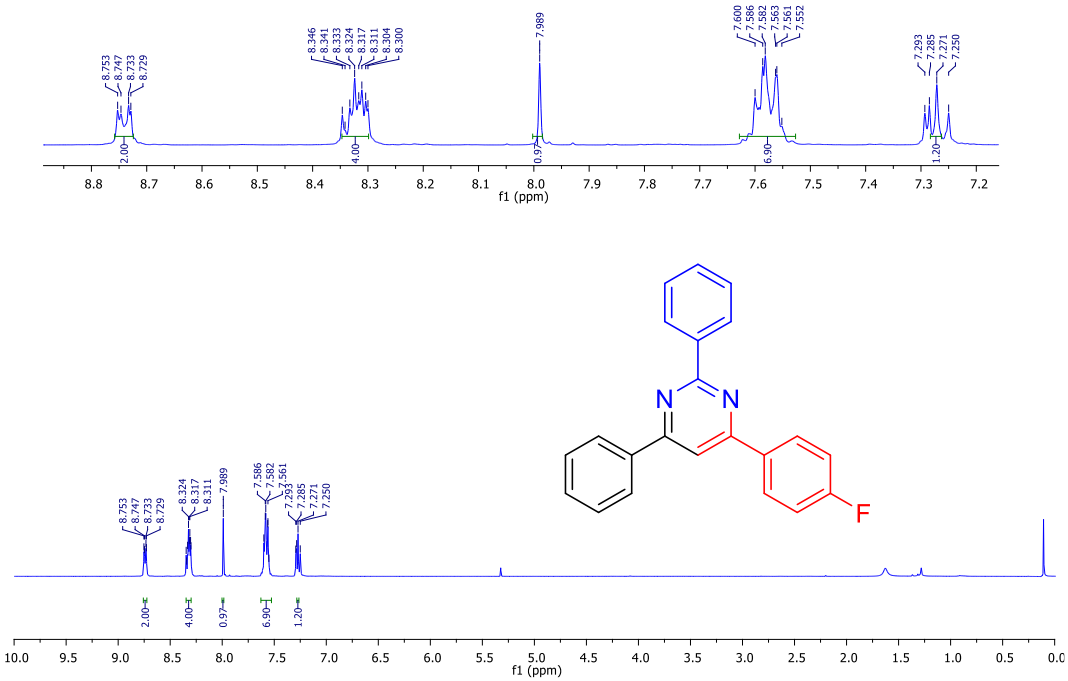


Fig S69. ^{1}H NMR spectrum of compound **7y** (400 MHz, $CDCl_3$).

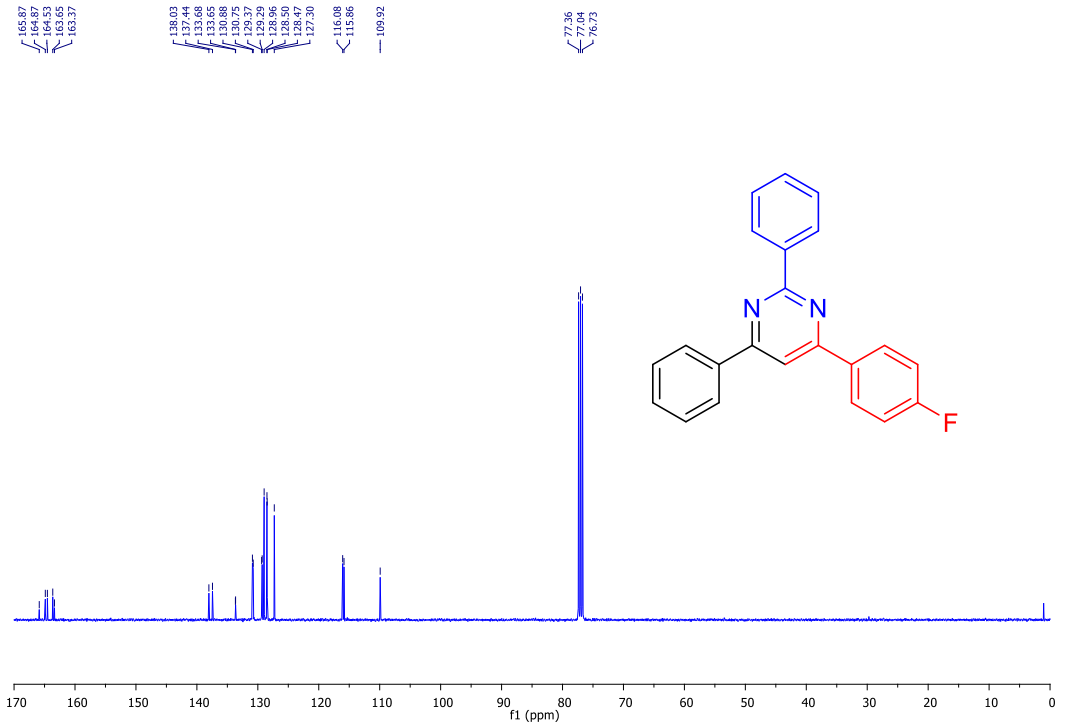


Fig S70. ^{13}C NMR spectrum of compound **7y** (100 MHz, $CDCl_3$).

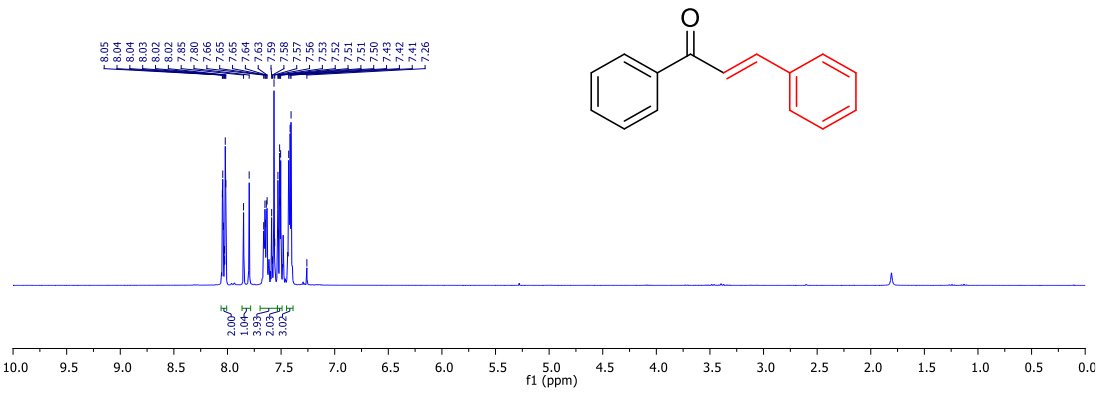


Fig S71. ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$).

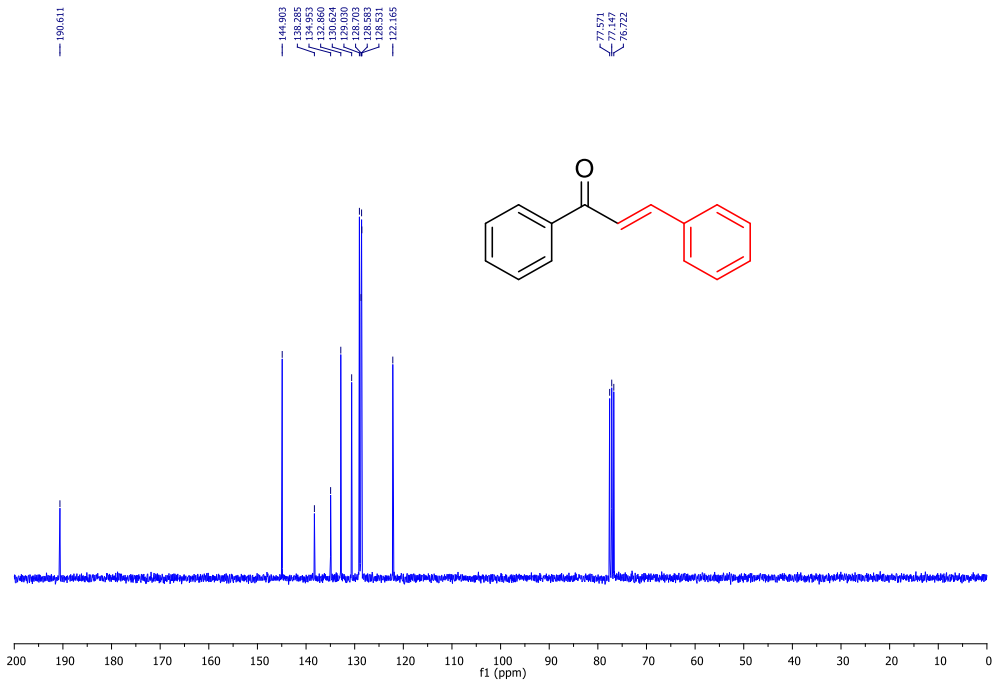


Fig S72. ^{13}C NMR spectrum of compound **8** (75 MHz, $CDCl_3$).

Reference

1. S. Das, R. Mondal, G. Chakraborty, A. K. Guin, A. Das and N. D. Paul. *ACS Catal.*, 2021, **11**, 7498−7512.