Supporting Information

Designed pincer ligands supported Co(II)-based catalysts for dehydrogenative activation of alcohols: Studies on *N*-alkylation of amines, α-alkylation of ketones and synthesis of quinolines

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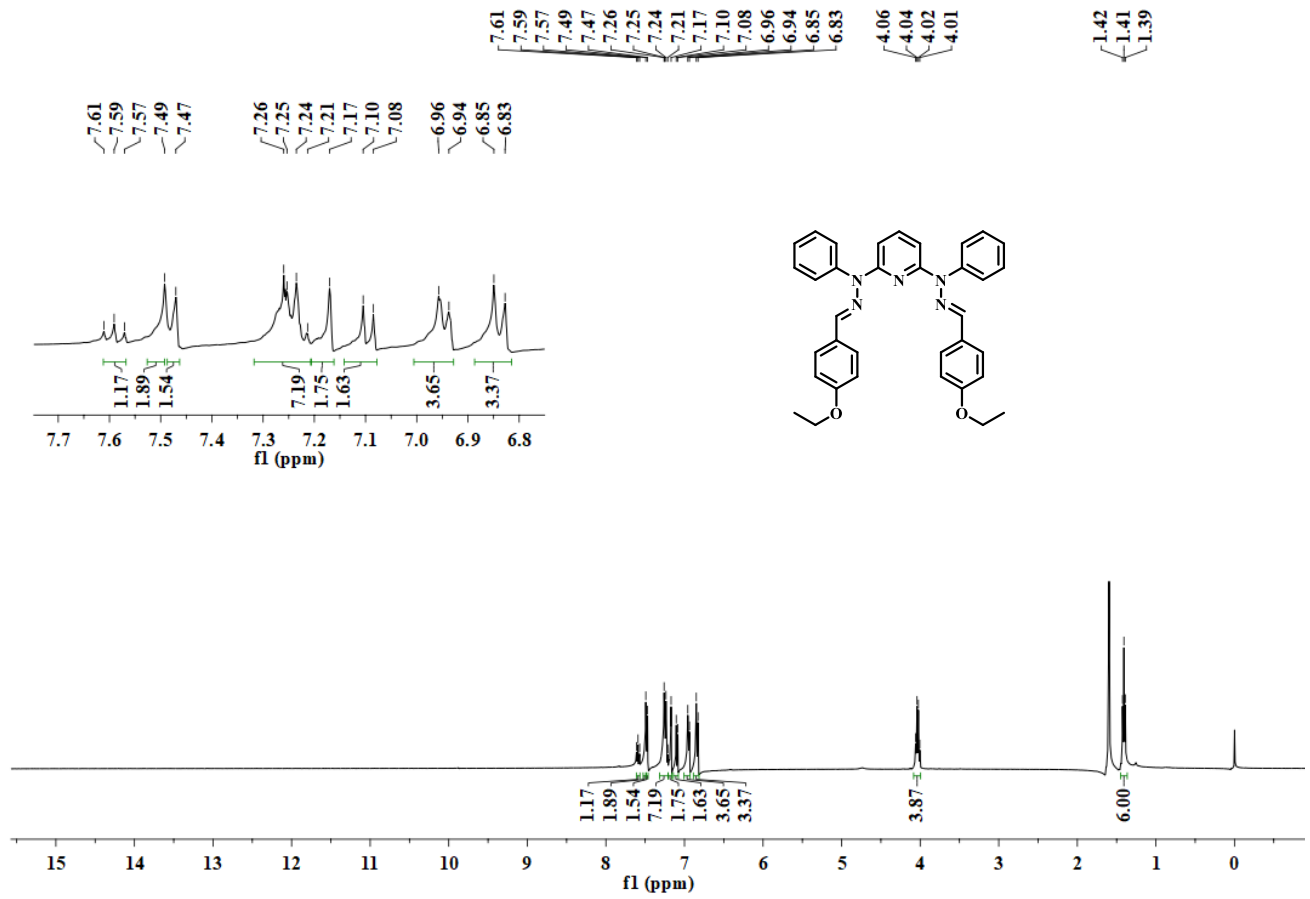

Figure S1. ^{1}H NMR spectrum of L^{1} taking $CDCl_3$ as solvent.

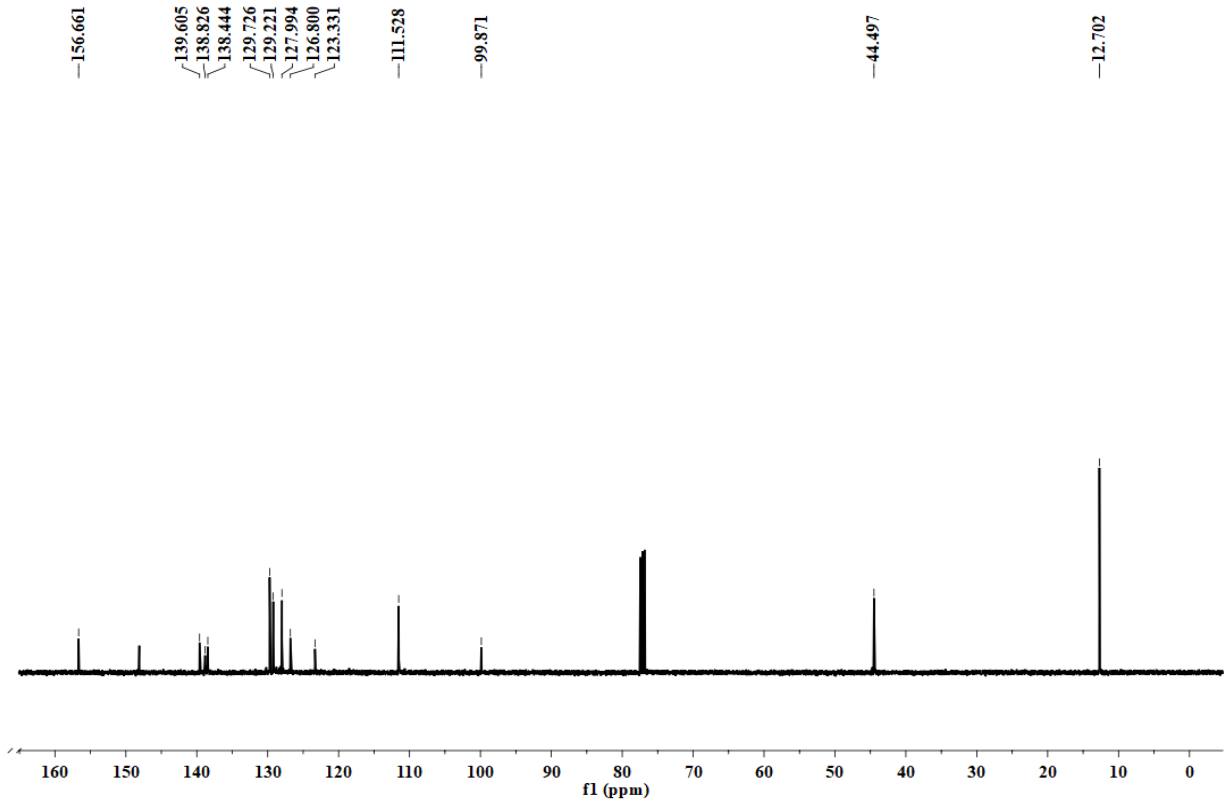

Figure S2. ^{13}C NMR spectrum of L^{1} taking $CDCl_3$ as solvent.

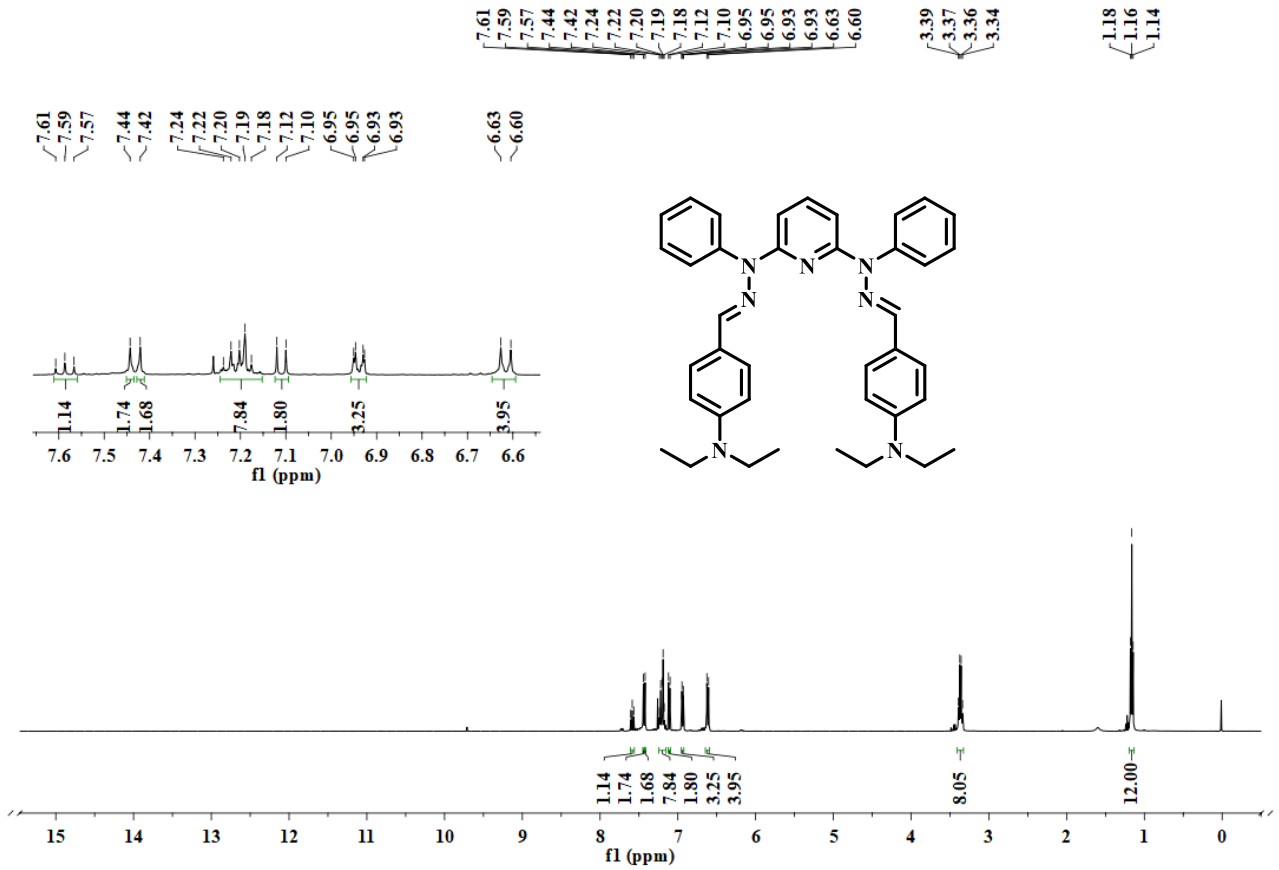

Figure S3. ^{1}H NMR spectrum of L^{2} taking $CDCl_3$ as solvent.

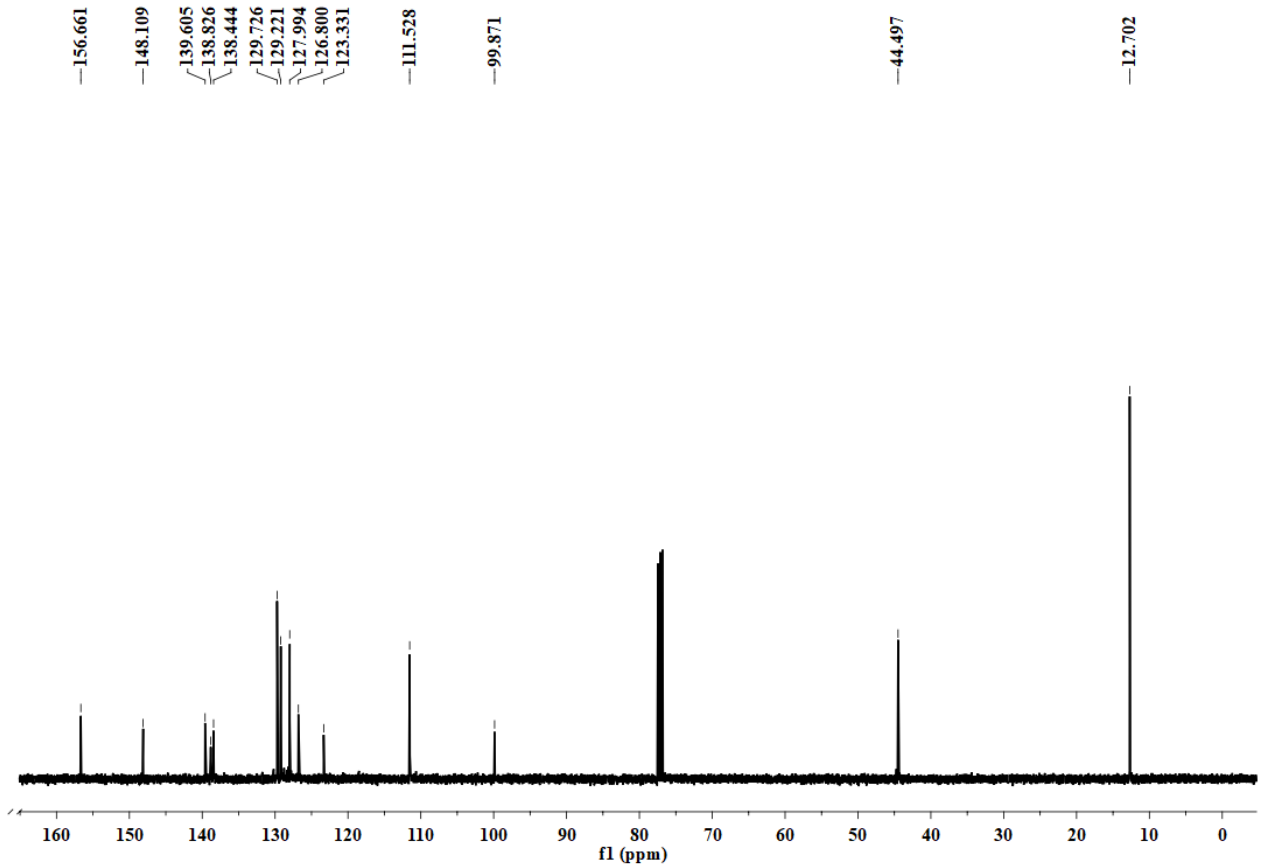

Figure S4. ^{13}C NMR spectrum of L^{2} taking $CDCl_3$ as solvent.

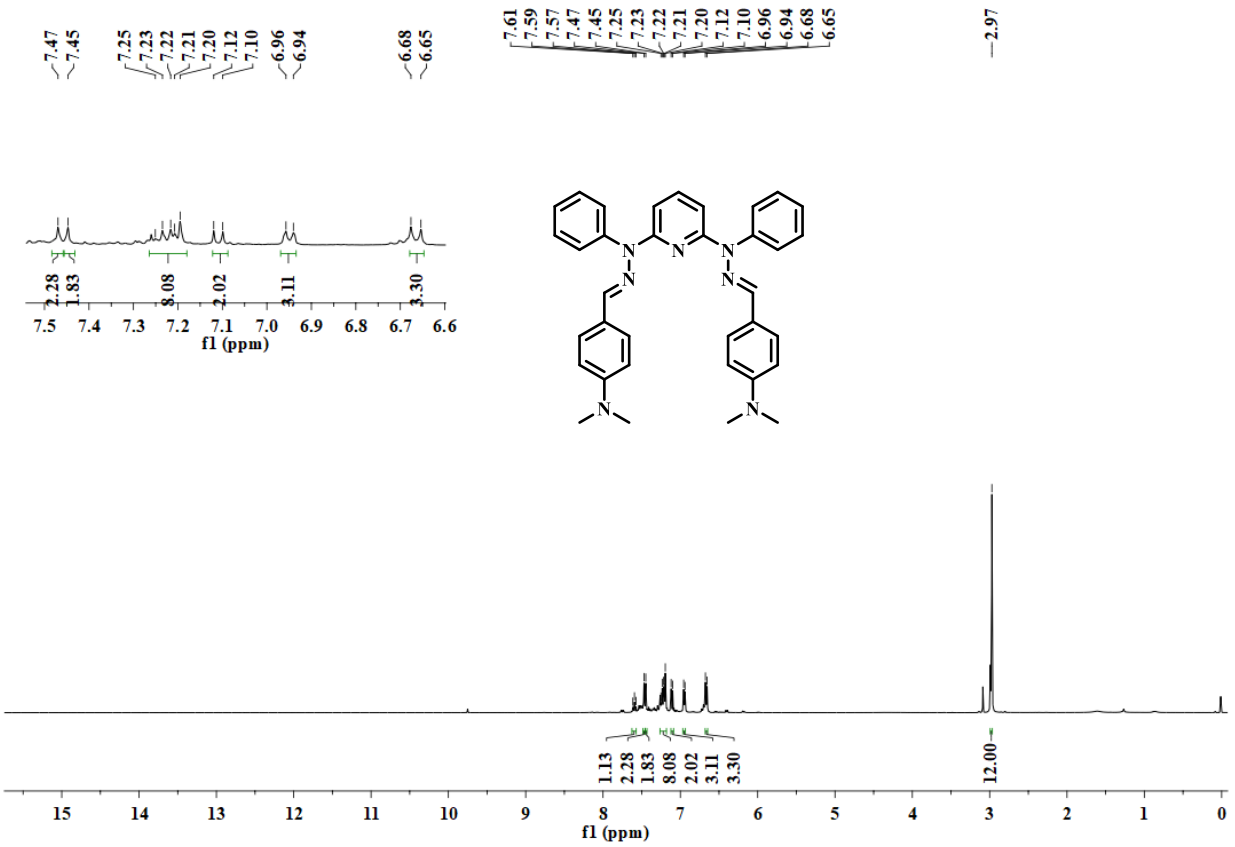

Figure S5. ^{1}H NMR spectrum of L^{3} taking $CDCl_3$ as solvent.

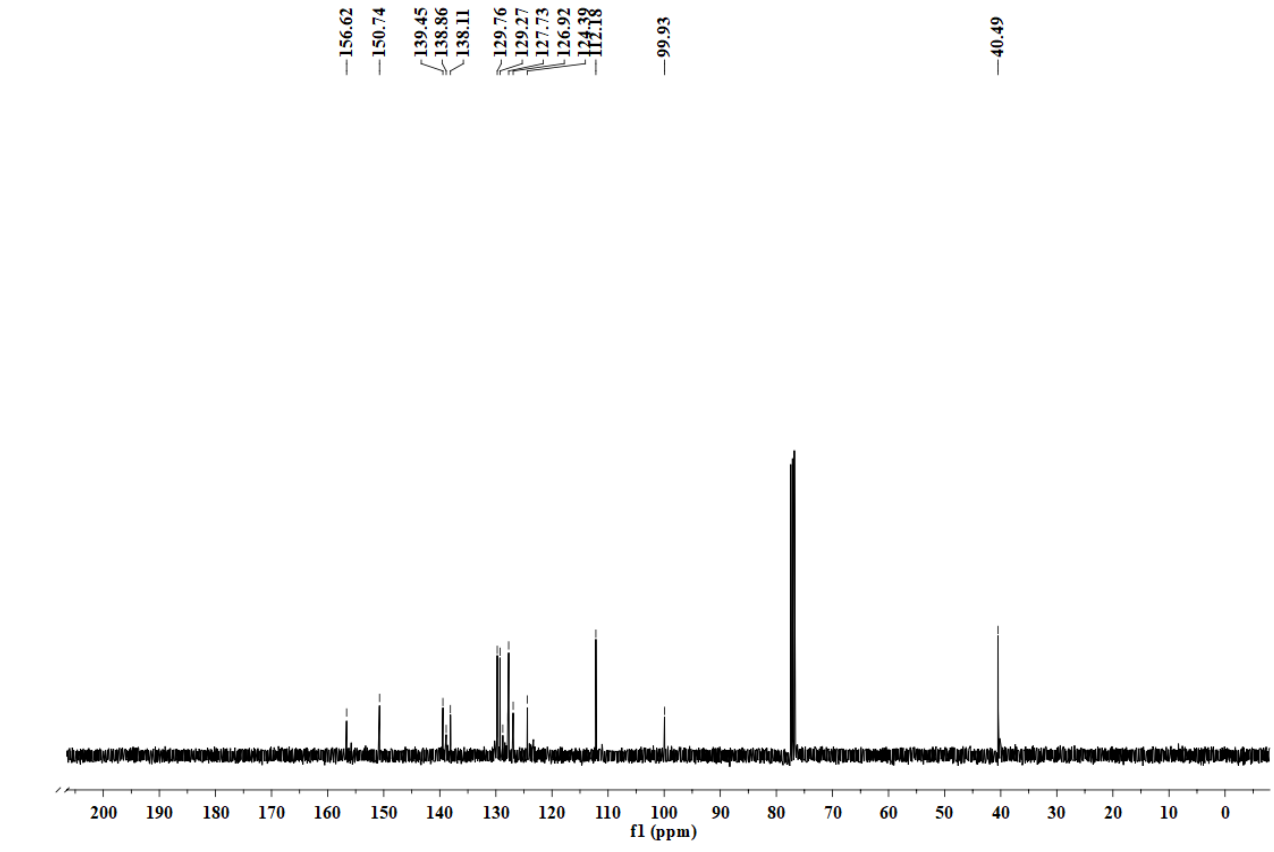

Figure S6. ^{13}C NMR spectrum of L^{3} taking $CDCl_3$ as solvent.

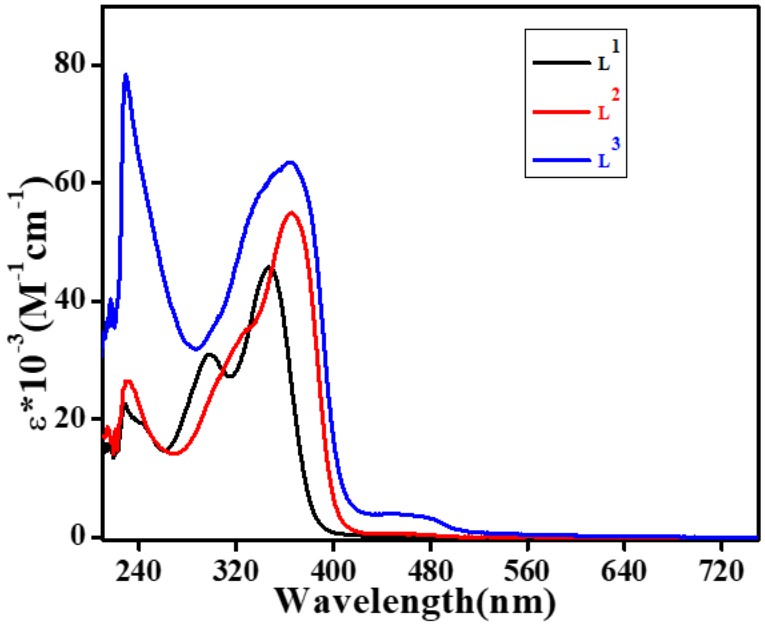

Figure S7. Electronic absorption spectra of ligands L^1-L^3 in dichloromethane solution.

Molecule	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)
L^1	364, 473	64100, 3680
L^2	326, 366	35040, 55430
L^3	365, 471	63510, 3990

Table S1. Spectral data of ligands L^1-L^3 in dichloromethane solution.

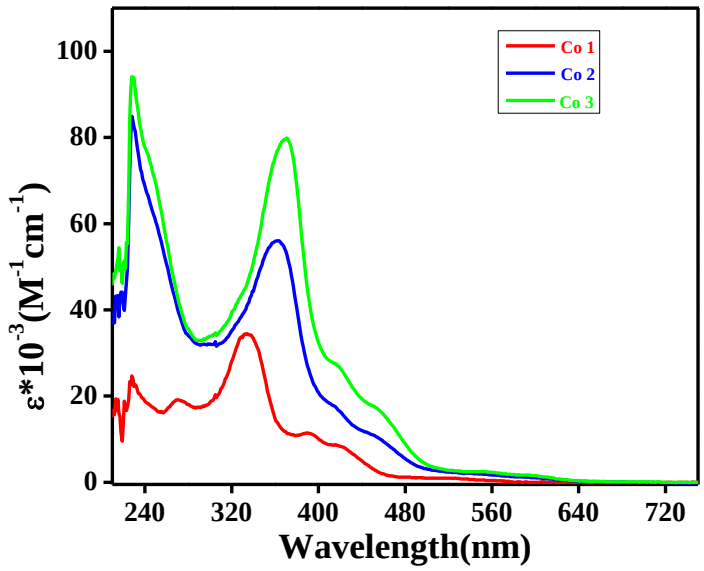

Figure S8. Electronic absorption spectra of complexes **Co1-Co3** in dichloromethane solution.

Molecule	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)
Co1	334, 390, 420	35020, 11960, 9220
Co2	356, 418, 454	56300, 17060, 10790
Co3	369, 419, 456	80400, 27440, 17240

Table S2. Spectral data of complexes **Co1-Co3** in dichloromethane solution.

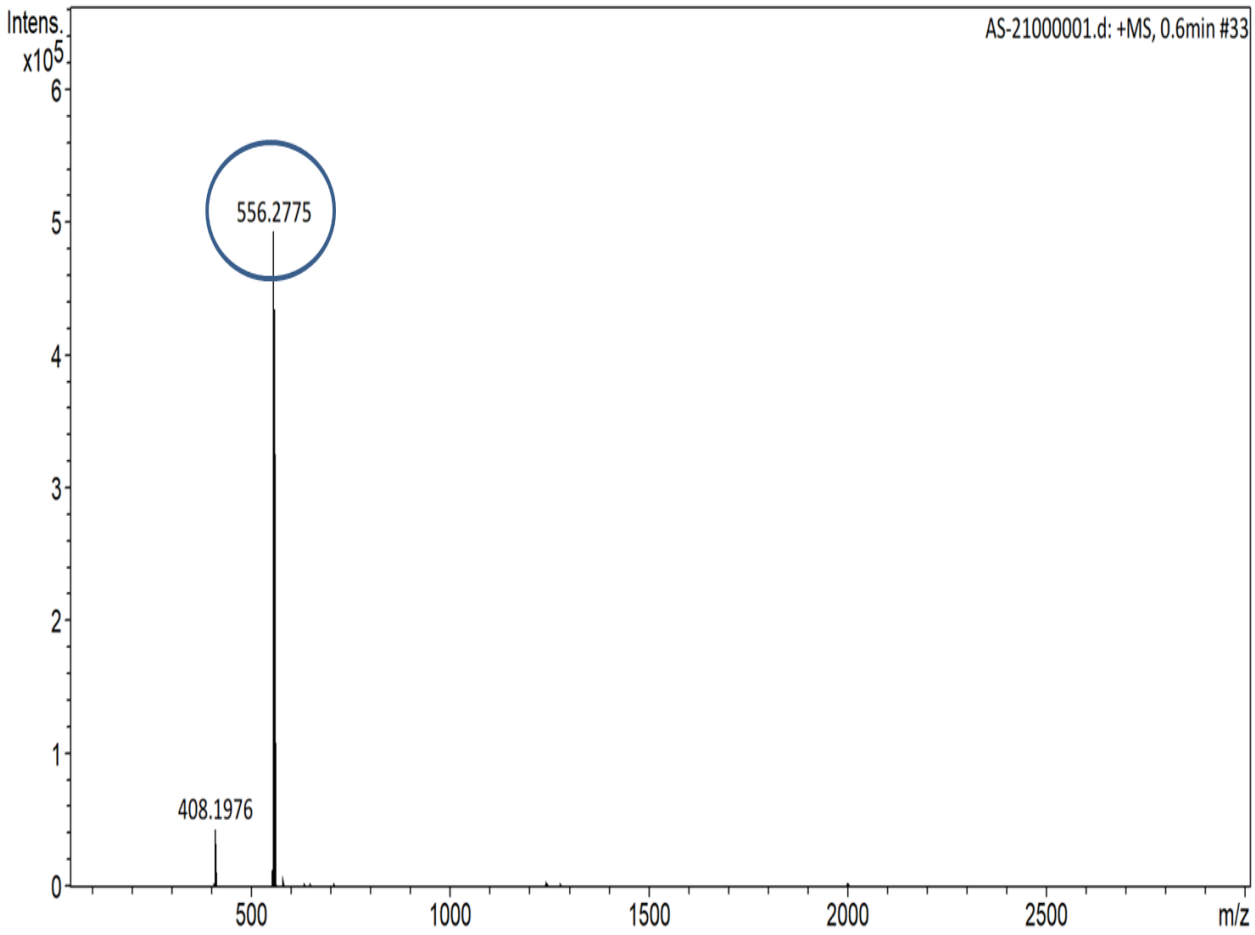

Figure S9. ESI-MS of ligand L^1 in acetonitrile solution.

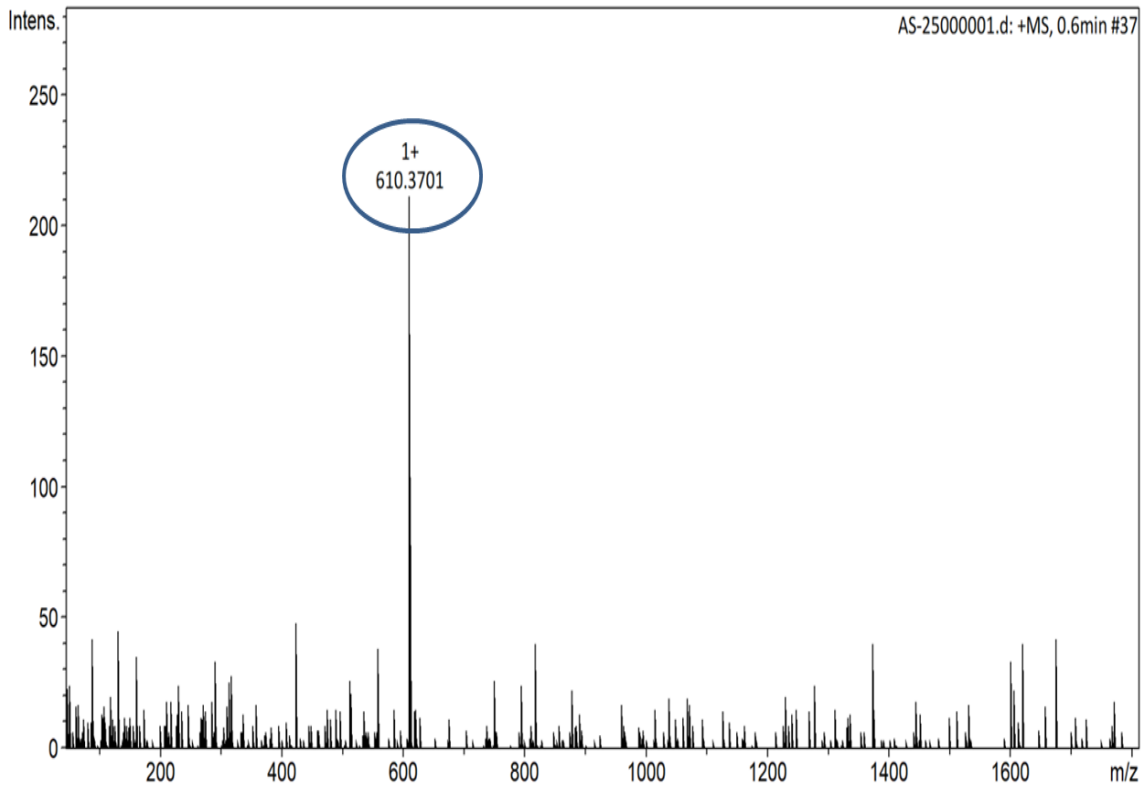

Figure S10. ESI-MS of ligand L^2 in acetonitrile solution.

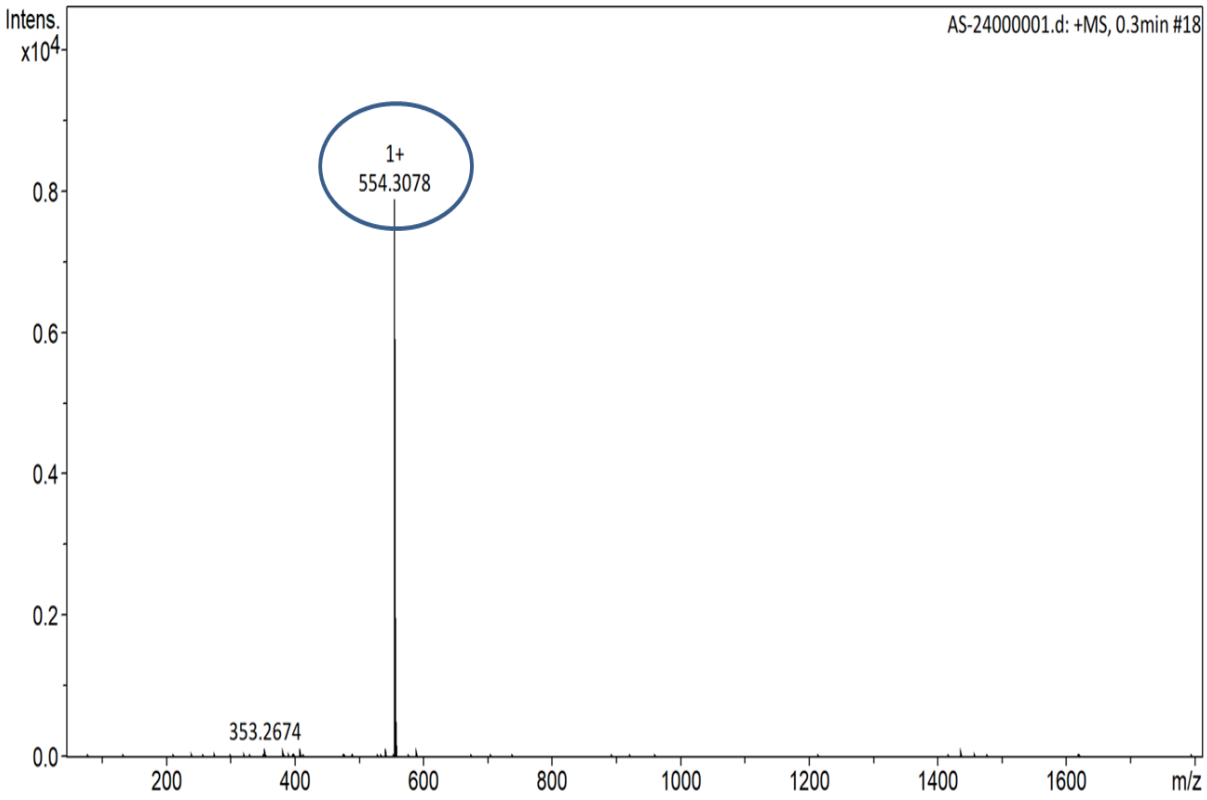

Figure S11. ESI-MS of ligand L^3 in acetonitrile solution.

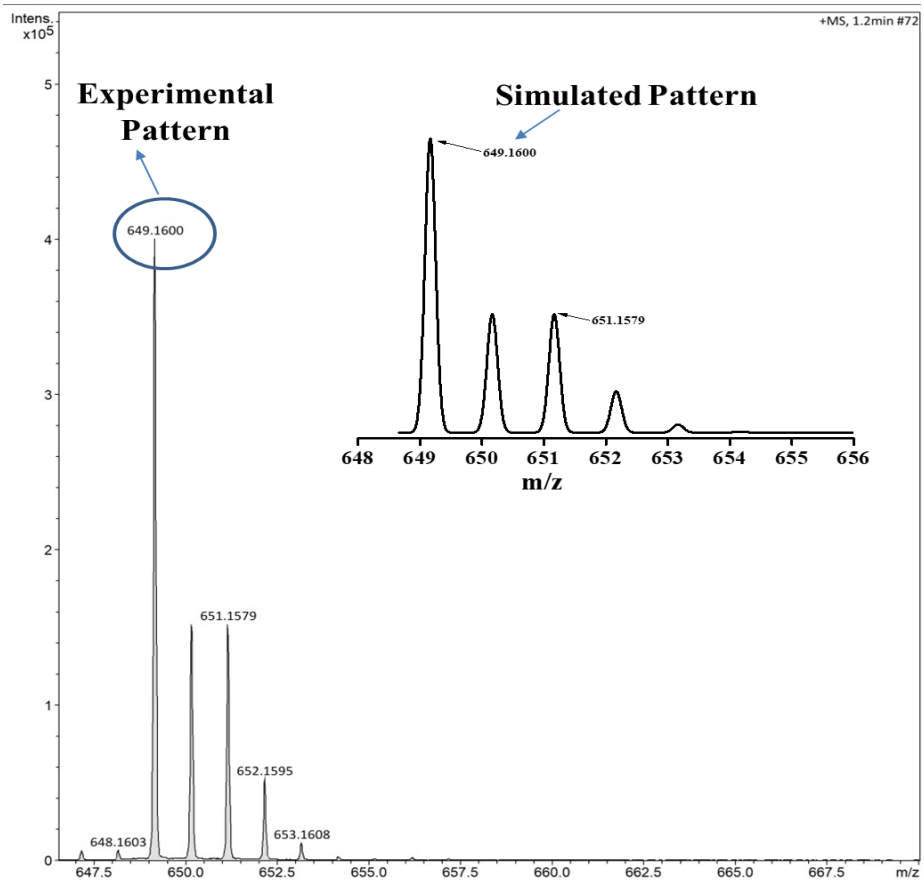

Figure S12. ESI-MS of **Co1** in acetonitrile solution.

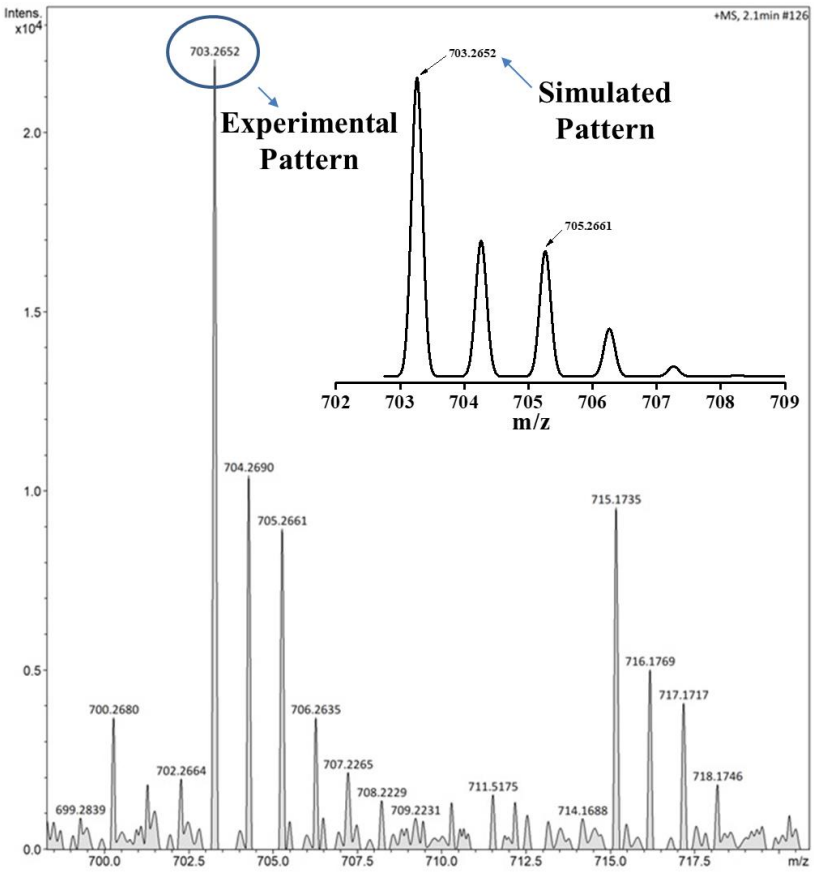

Figure S13. ESI-MS of **Co2** in acetonitrile solution.

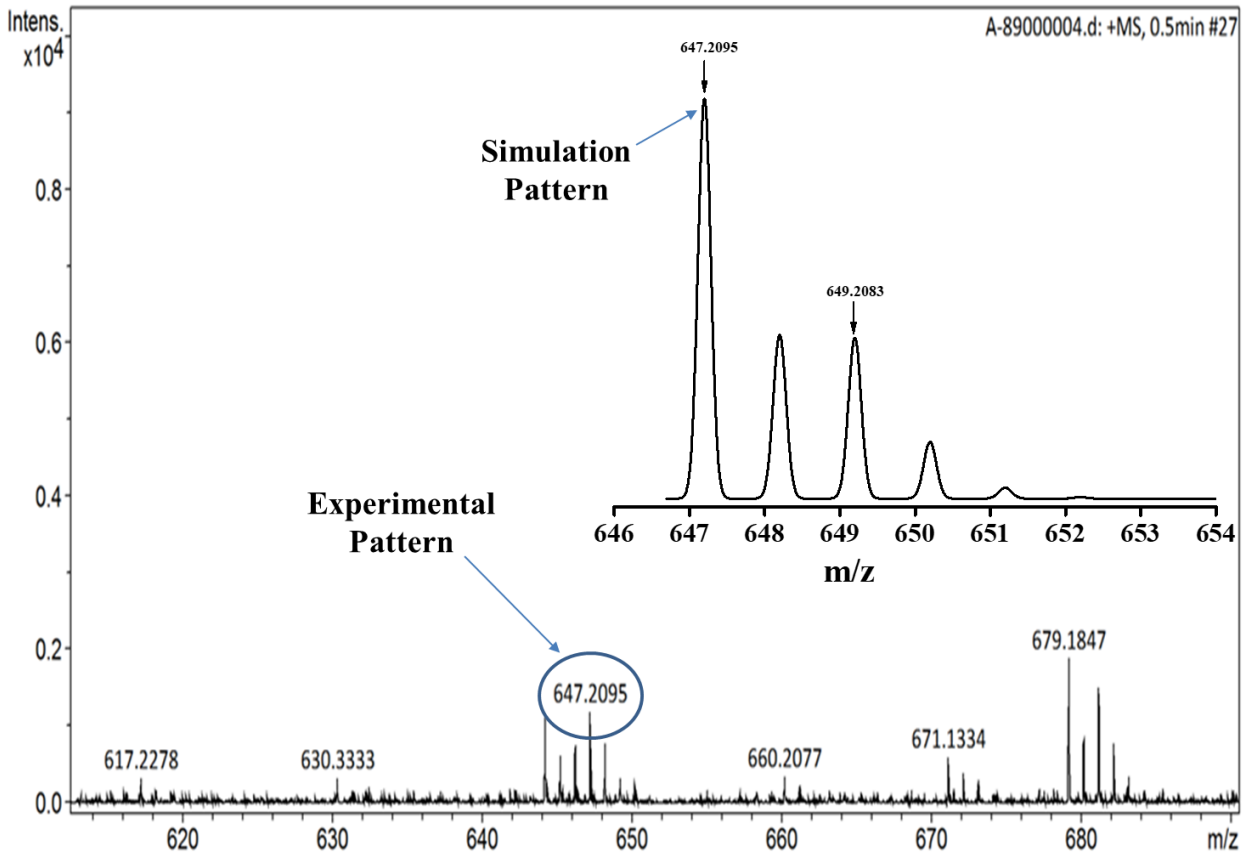

Figure S14. ESI-MS of **Co3** in acetonitrile solution.

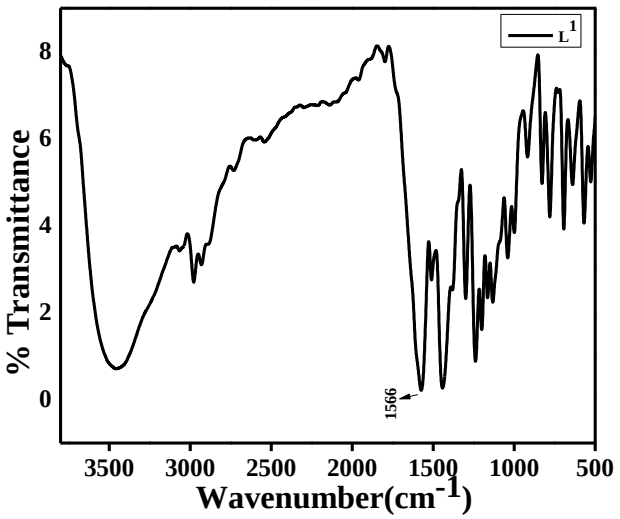

Figure S15. FT-IR spectrum of free ligand L^1.

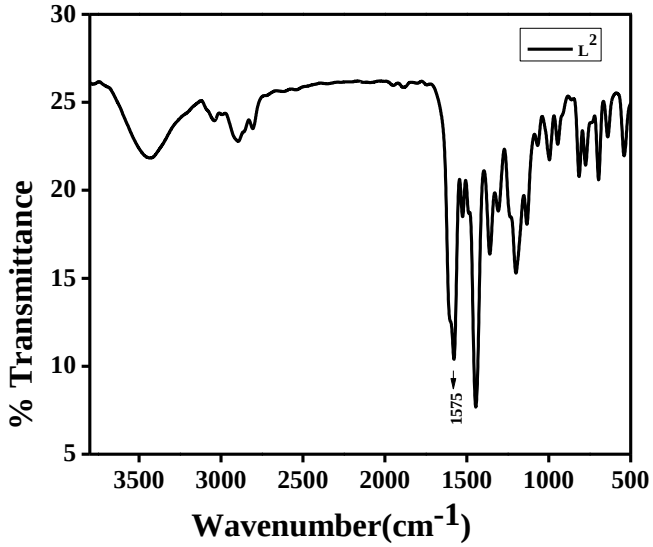

Figure S16. FT-IR spectrum of free ligand L^2.

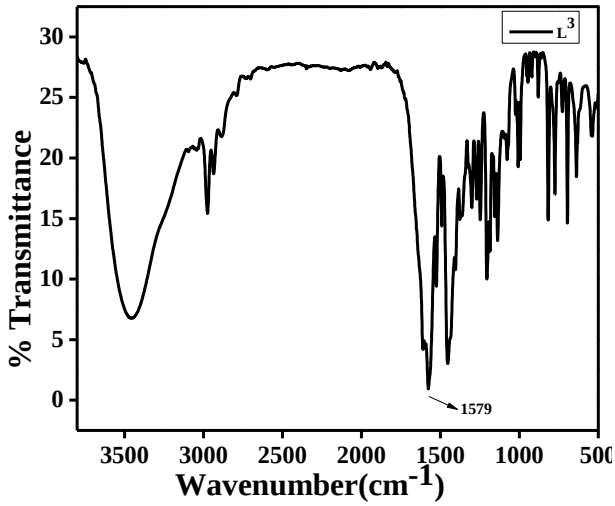

Figure S17. FT-IR spectrum of free ligand L^3.

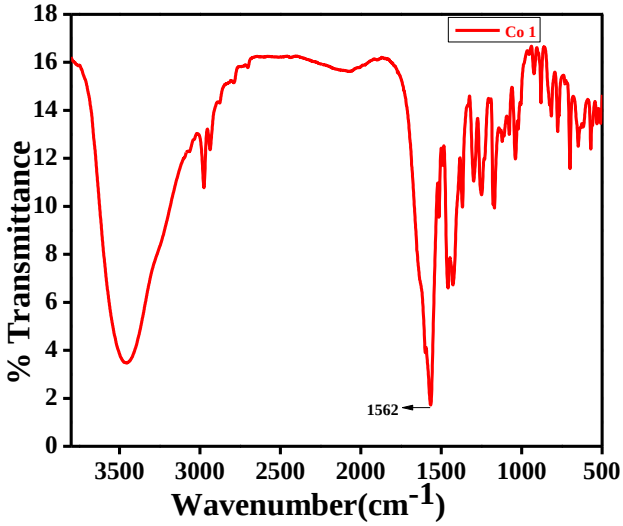

Figure S18. FT-IR spectrum of complex **Co1**.

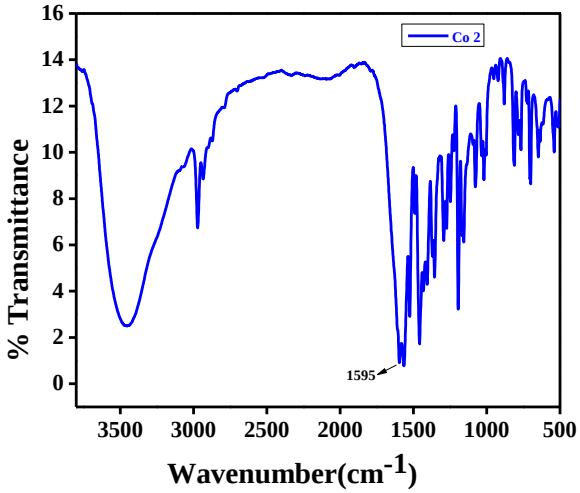

Figure S19. FT-IR spectrum of complex **Co2**.

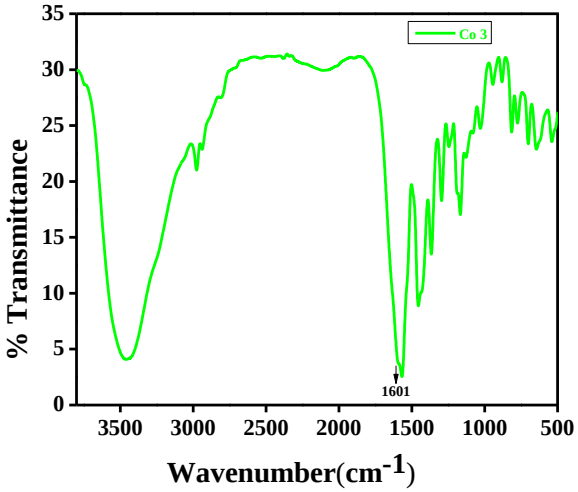

Figure S20. FT-IR spectrum of complex **Co3**.

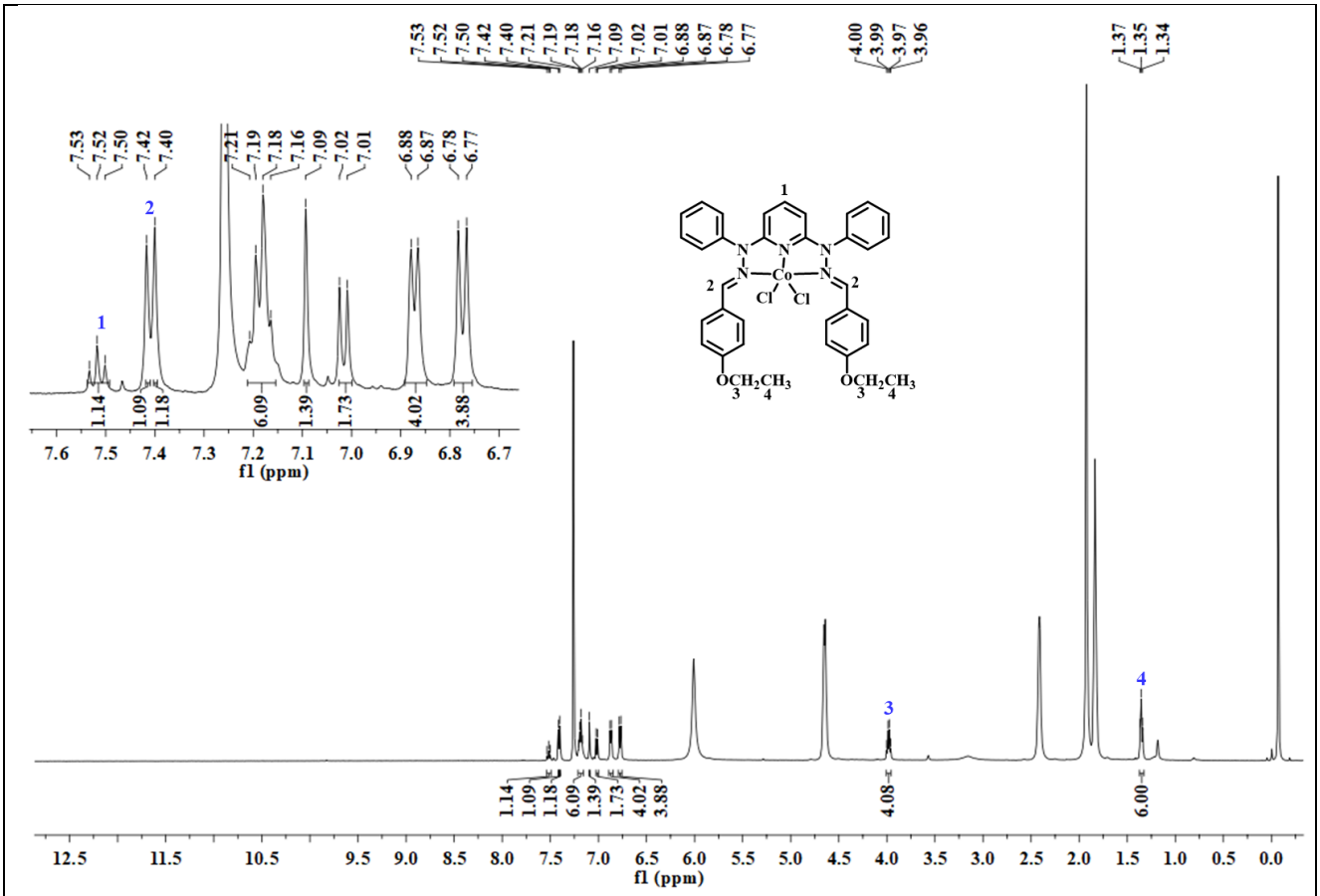

Figure S21. ^{1}H NMR spectrum of **Co1** taking $CDCl_3$ as solvent.

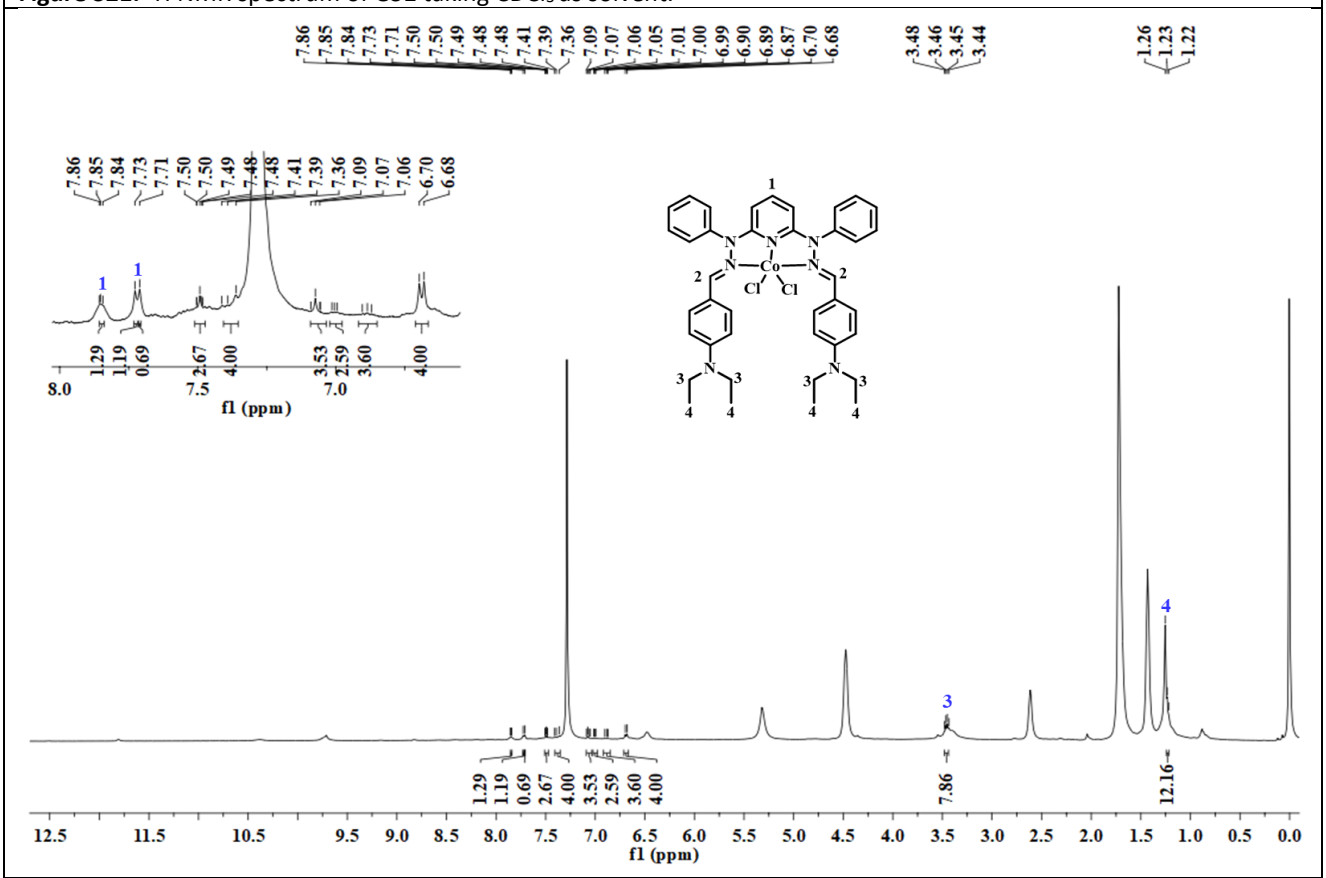

Figure S22. ^{1}H NMR spectrum of **Co2** taking $CDCl_3$ as solvent.

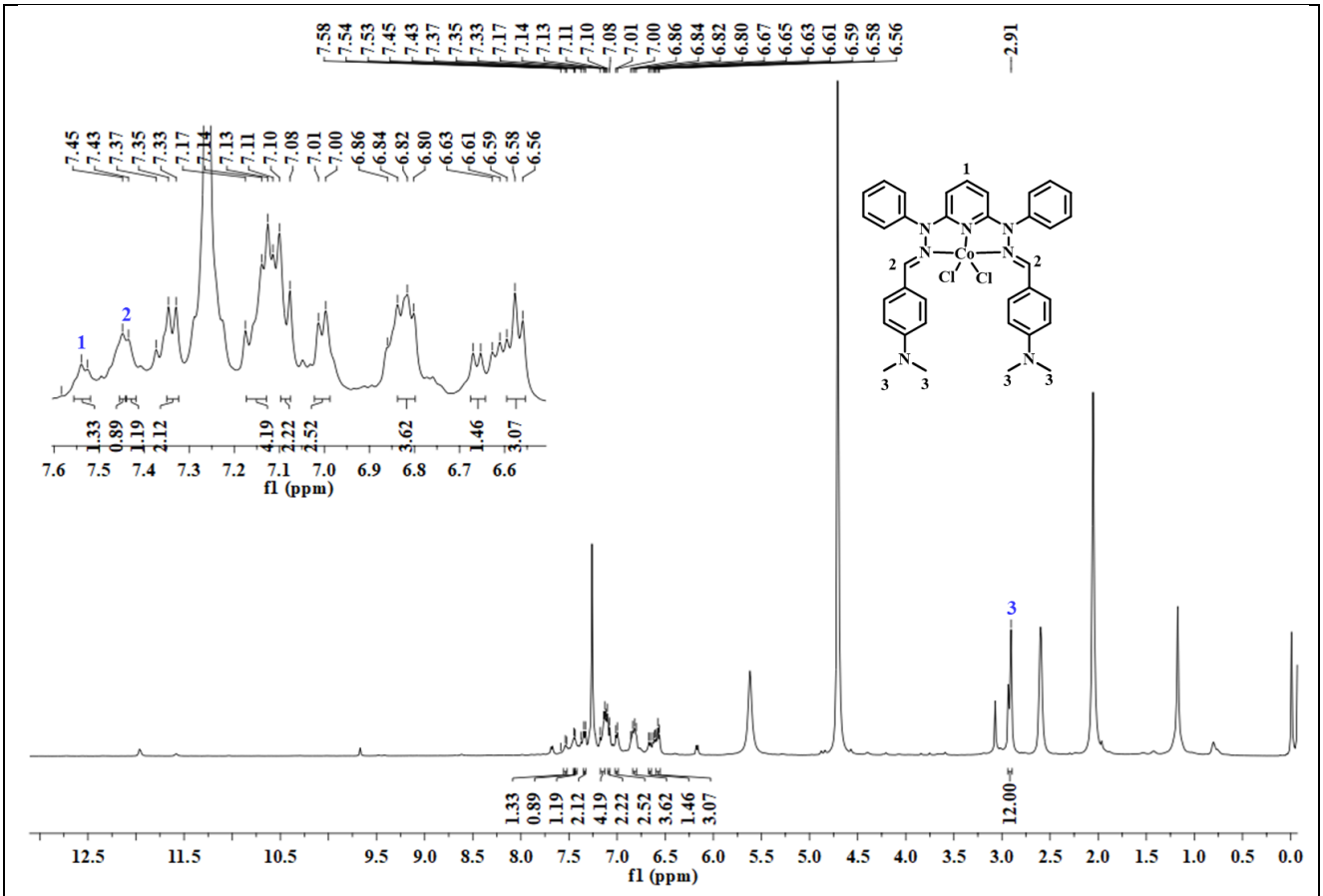

Figure S23. ^{1}H NMR spectrum of **Co3** taking $CDCl_3$ as solvent.

Table S3. Crystal data and structural refinement parameters for complexes **Co1** and **Co3**.		
Empirical formula	**C35 H33 Cl2 Co N5 O2 [+ solvent]**	**C35 H35 Cl2 Co N7**
Color	Clear light red	Red
Formula weight	685.49	683.53
Temperature (K)	150	293(2)
λ (Å) (Mo-Kα)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*C 1 2/c 1*	*P 1 21/n 1*
a(Å)	38.476(2)	10.1685(6)
b(Å)	16.3803(10)	35.634(2)
c(Å)	11.5978(7)	10.5820(7)
α(°)	90	90
β(°)	93.820(5)	114.904(4)
γ(°)	90	90
Z	8	4
ρ_{calc}(gcm^{-3})	1.249	1.306
F(000)	2840.0	1420.0
θ range for data collection	2.608-32.812	2.198-28.416
Index ranges	-42<h<56, -24<k<21 -16<l<16	-13<h<11, -47<k<40 -14<l<13
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data/restraint/parameters	12566/0/408	8596/0/410
GOF[a] on F^2	0.961	1.076
R_1[b] [I > 2σ(I)]	0.0887	0.0994
R_1 (all data)	0.2089	0.1612
wR_2[c] (I > 2σ(I))	0.1893	0.2439
wR_2 (all data)	0.2606	0.2703

[a]GOF = $[\Sigma[w(Fo^2-Fc^2)^2] /M-N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R1= \Sigma \| |Fo| - |Fc| \| / \Sigma |Fo|$, [c] $wR_2 = [\Sigma[w(Fo^2-Fc^2)_2]/\Sigma [w(Fo_2)_2]]^{1/2}$

Table S4. Selected bond lengths and bond angles of complex **Co1**.			
Bond Lengths (Å)		**Bond Angles(°)**	
Co1—N1	2.233(4)	**N3—Co1—N1**	76.42(13)
Co1—N3	1.988(3)	**N3—Co1— N5**	77.53(13)
Co1—N5	2.236(4)	**N1— Co1—N5**	153.49(12)
Co1—Cl1	2.2952(12)	**N3—Co1—Cl2**	120.09(10)
Co1—Cl2	2.2499(12)	**N3— Co1— Cl1**	107.97(10)
		N1— Co1— Cl2	96.39(10)
		N1— Co1—Cl1	91.37(10)
		N5— Co1— Cl2	92.38(10)
		N5— Co1— Cl1	101.26(9)
		Cl2— Co1— Cl1	131.83(5)

Table S5. Selected bond lengths and bond angles of complex **Co3**.			
Bond Lengths (Å)		**Bond Angles(°)**	
Co1—N1	2.192(5)	**N3—Co1—N1**	77.5(2)
Co1—N3	1.980(5)	**N3—Co1— N5**	77.9(2)
Co1—N5	2.169(5)	**N1— Co1—N5**	155.3(2)
Co1—Cl1	2.255(2)	**N3—Co1—Cl2**	105.07(16)
Co1—Cl2	2.297(2)	**N3— Co1— Cl1**	112.28(17)
		N1— Co1— Cl2	94.85(15)
		N1— Co1—Cl1	93.55(15)
		N5— Co1— Cl2	93.78(17)
		N5— Co1— Cl1	93.51(16)
		Cl2— Co1— Cl1	142.64(8)

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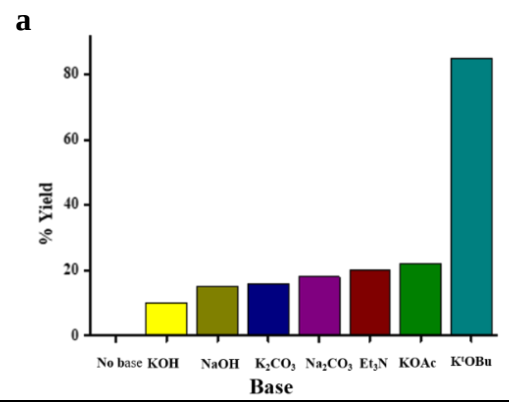
<td> 
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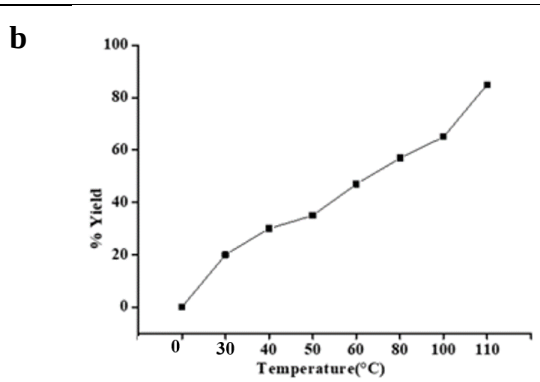
<td> 
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<td>General reaction conditions: Aniline (1 mmol), Benzyl alcohol (1 mmol), Co1 (4 mol%), bases (0.5 mmol), Toluene 2 ml, Temperature 110 °C for 24 h.</td>
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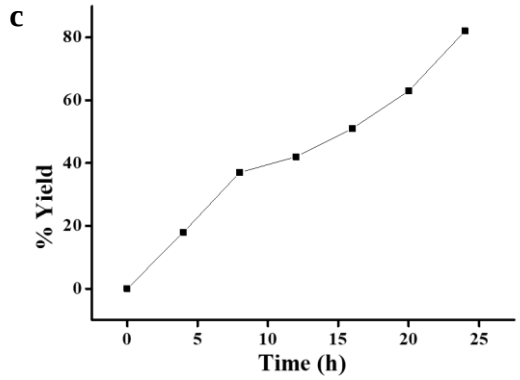
<td> 
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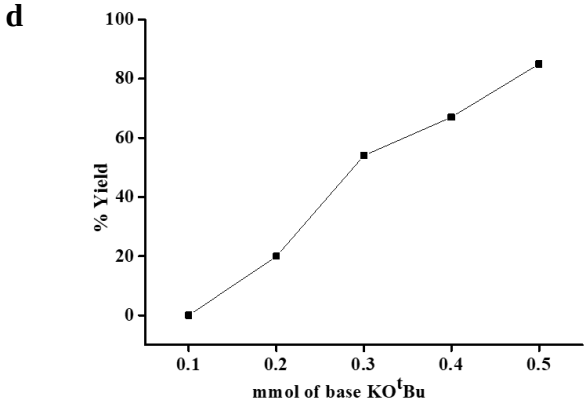
<td> 
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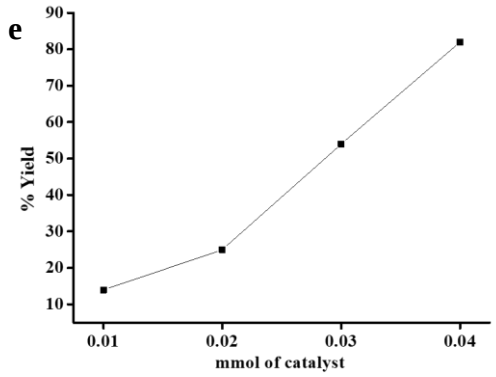
<td> 
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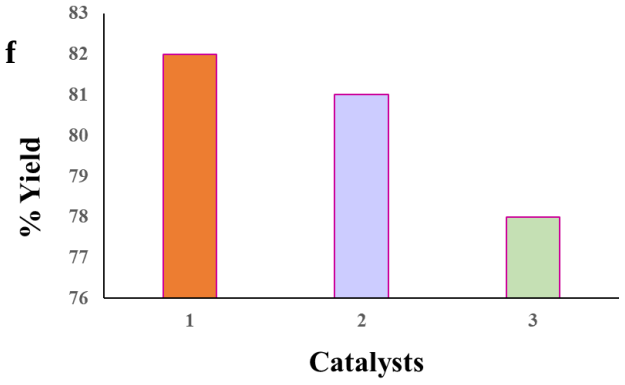
<td> 
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<td>General reaction conditions: Aniline (1 mmol), Benzyl alcohol (1 mmol), catalysts (Co1-Co3) (4 mol%), KO^tBu (0.5 mmol), Toluene 2 ml, Temperature (110 °C) for 24 h.</td>
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<td colspan="2">Figure S24. The reaction profile of cobalt catalyzed N-alkylation of anilines with benzyl alcohols (a) Effect of bases (5 mol%) (b) Effect of temperature (c) Effect of time (d) Loading of base KO^tBu (e) Loading of catalysts (f) Effect of catalysts.</td>
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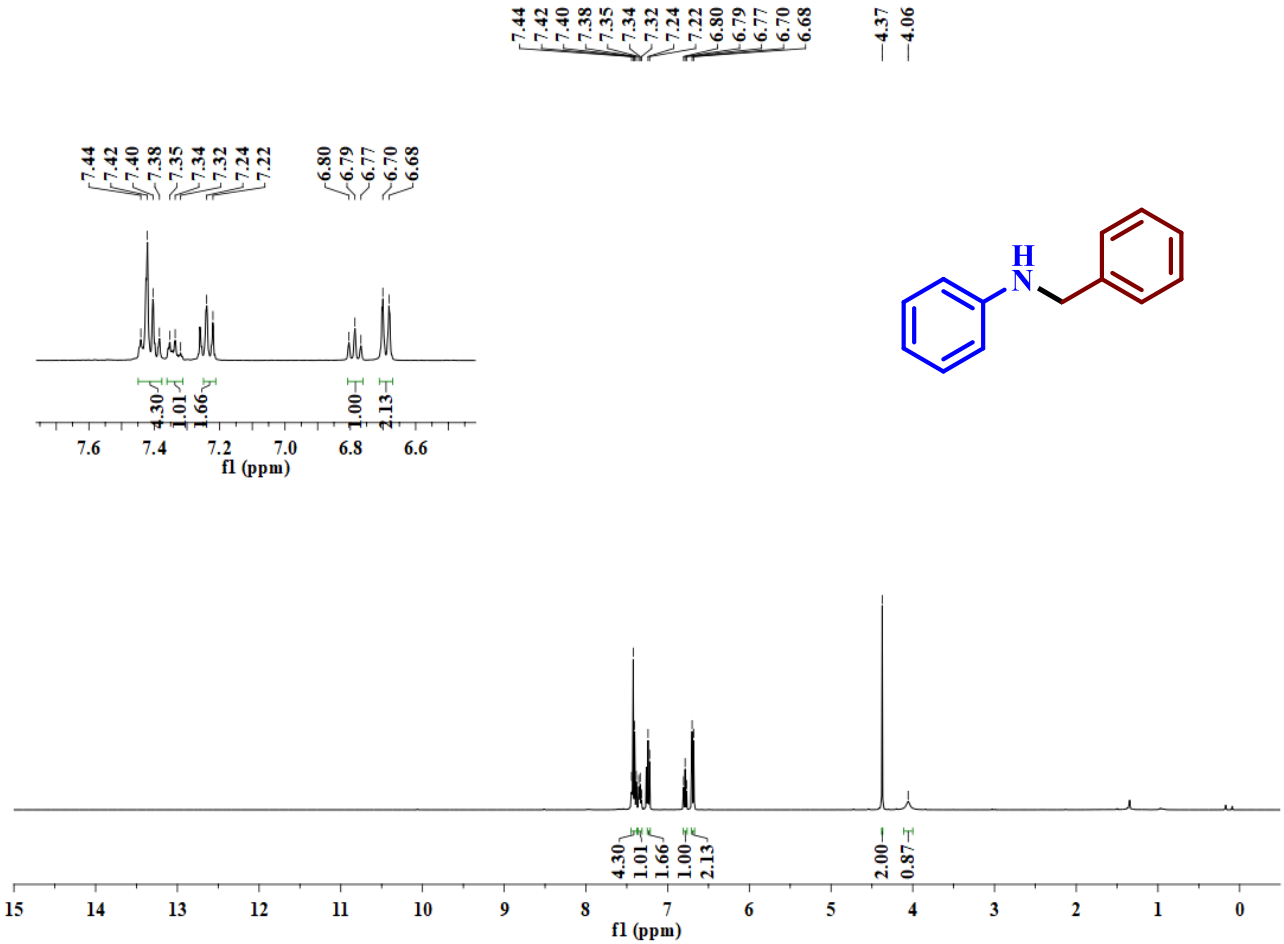


Figure S25. ^{1}H NMR spectrum of **3aa** taking $CDCl_3$ as solvent.

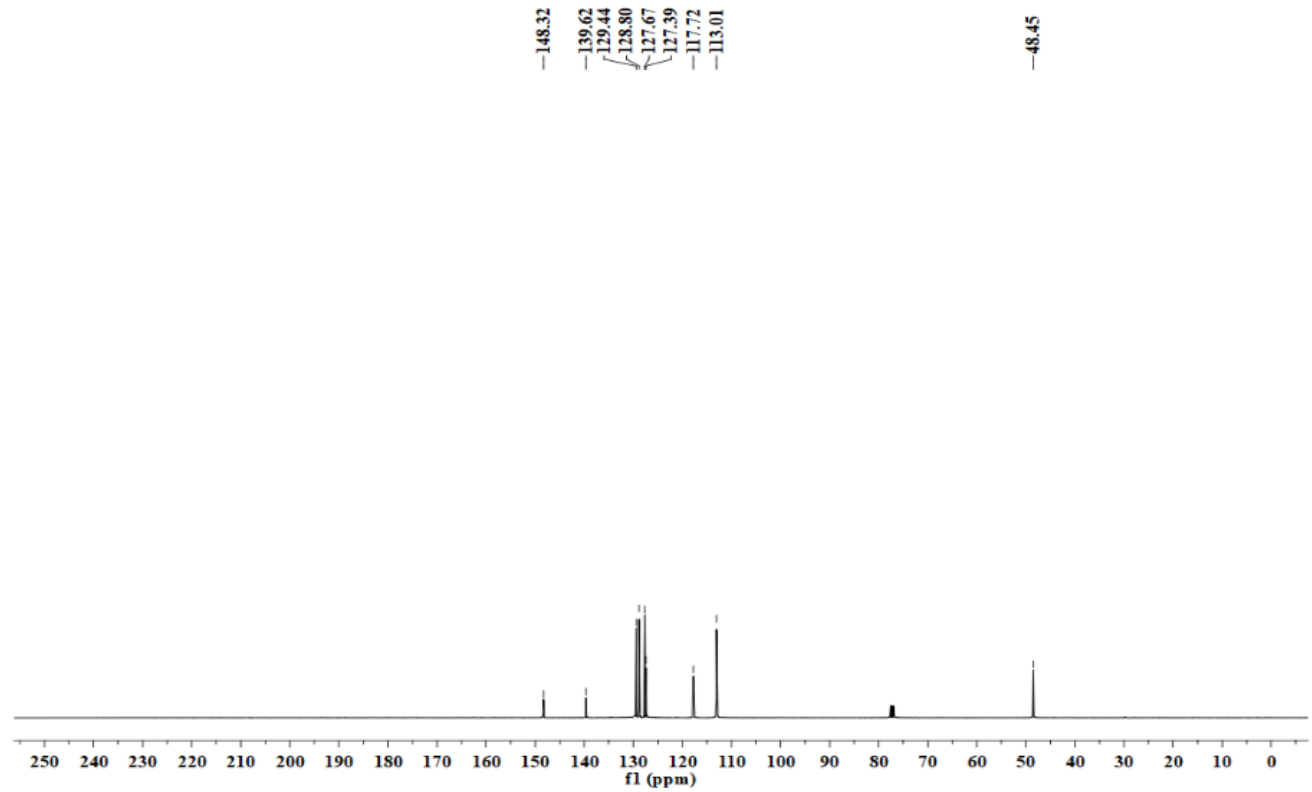


Figure S26. ^{13}C NMR spectrum of **3aa** taking $CDCl_3$ as solvent.

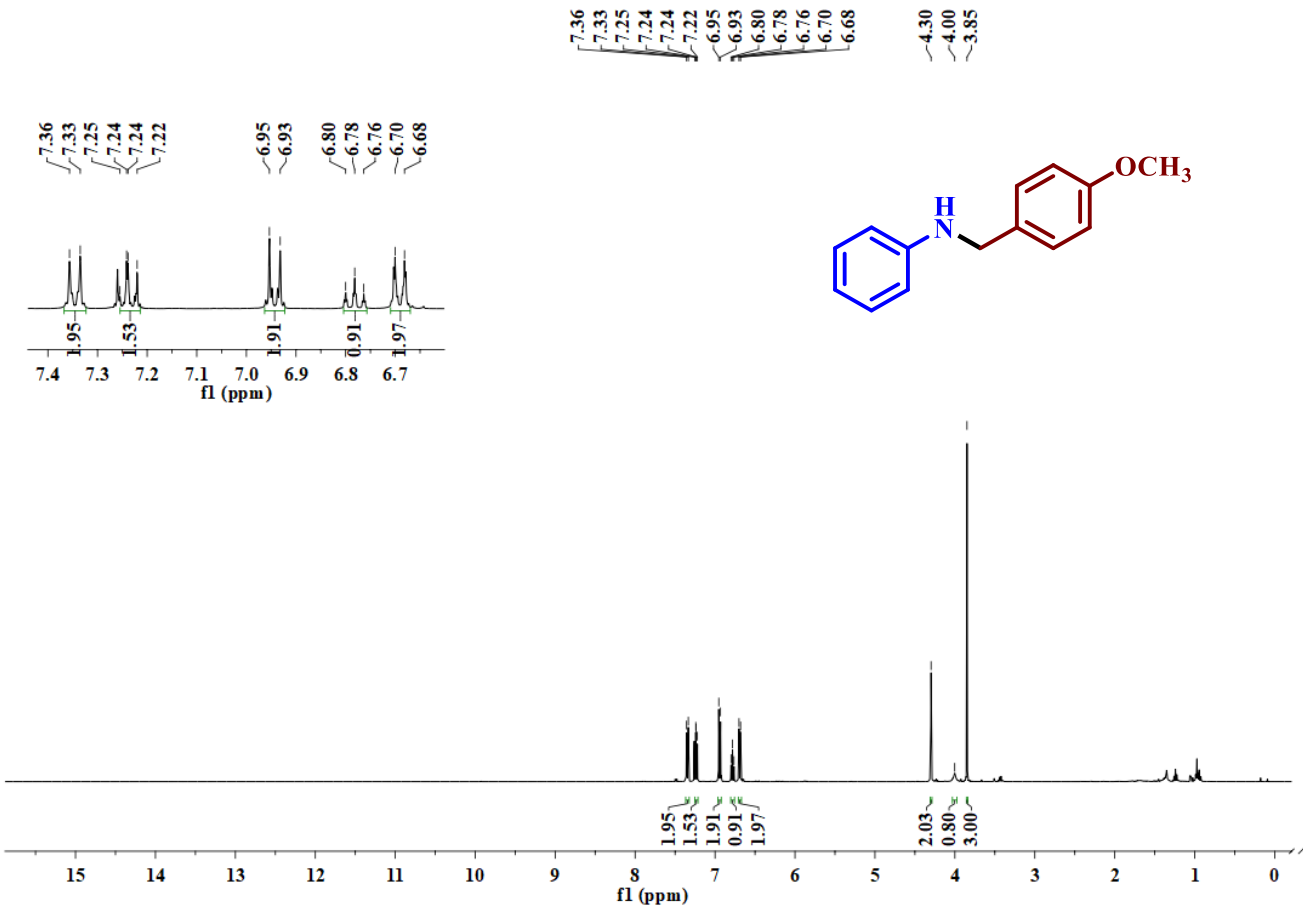


Figure S27. ^{1}H NMR spectrum of **3ab** taking $CDCl_3$ as solvent.

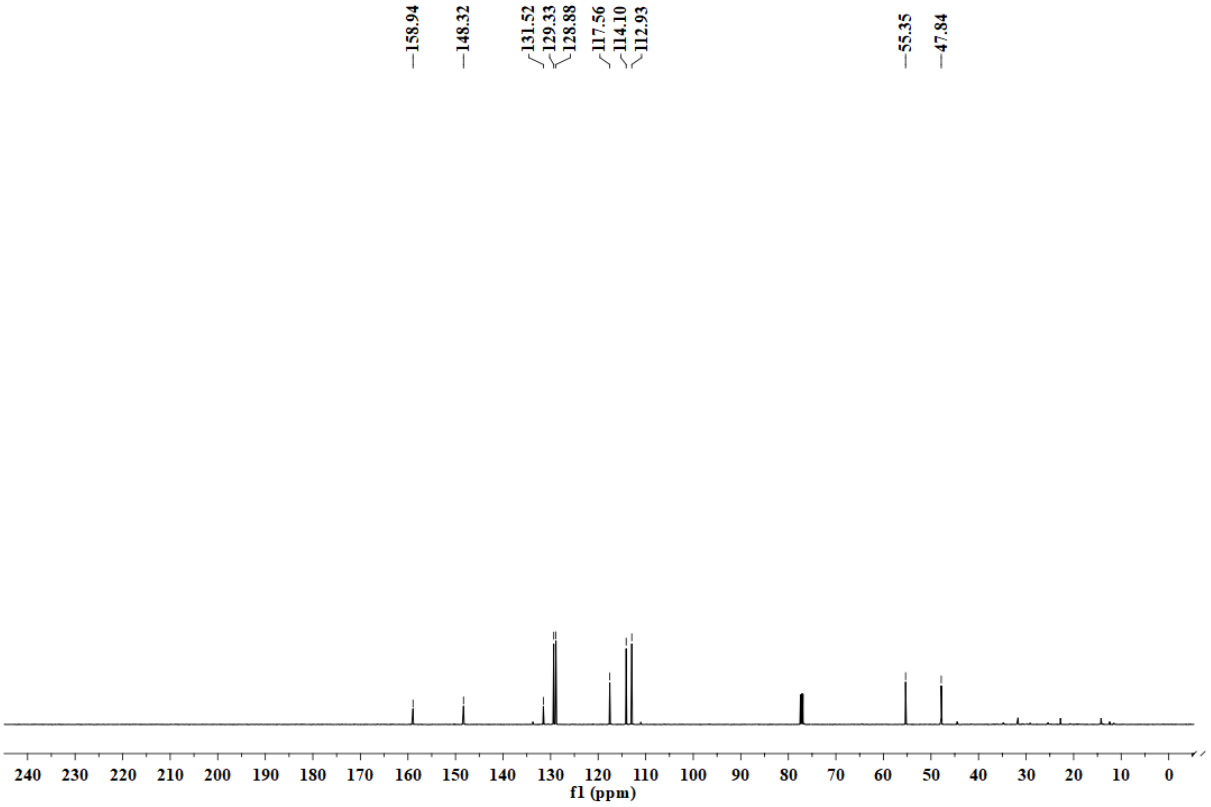


Figure S28. ^{13}C NMR spectrum of **3ab** taking $CDCl_3$ as solvent.

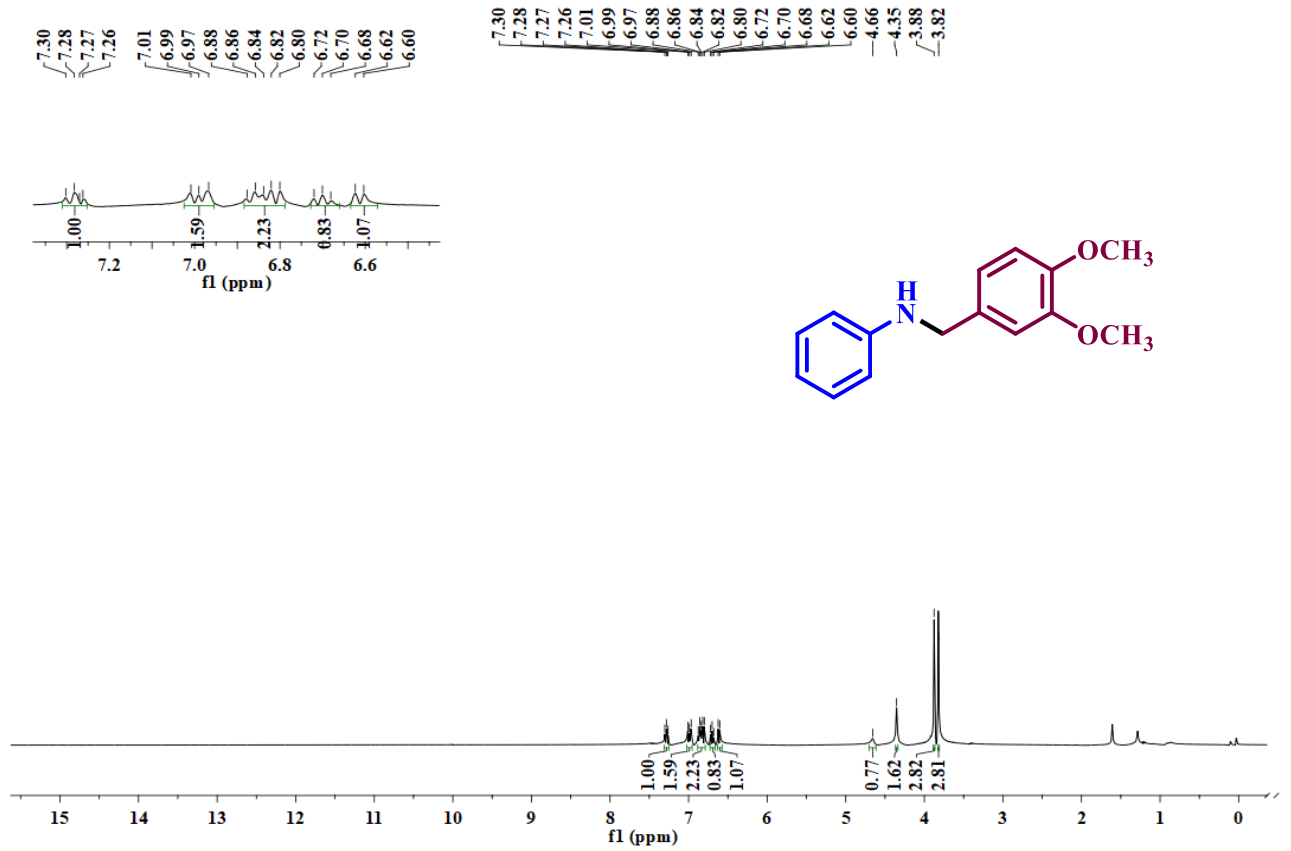


Figure S29. ^{1}H NMR spectrum of **3ac** taking $CDCl_3$ as solvent.

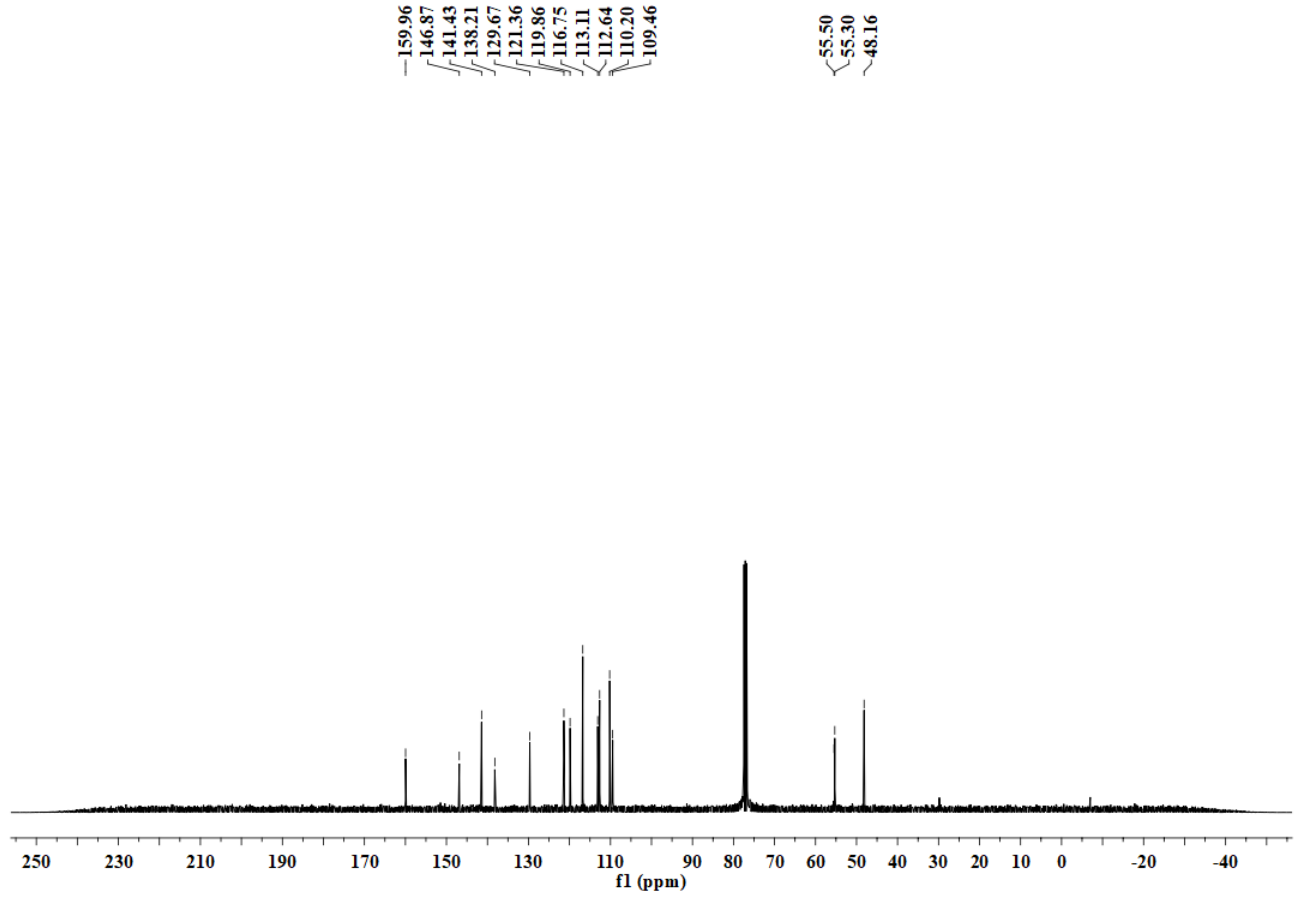


Figure S30. ^{13}C NMR spectrum of **3ac** taking $CDCl_3$ as solvent.

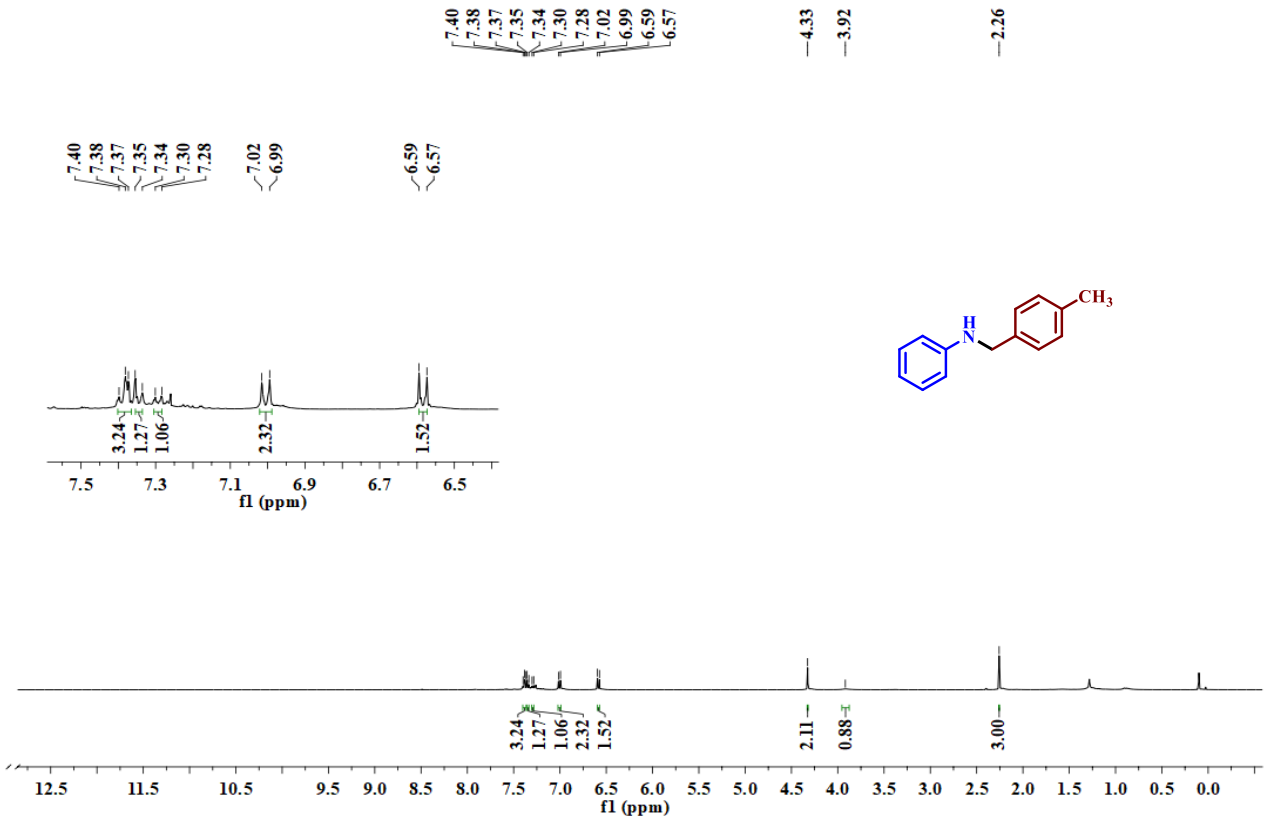


Figure S31. ^{1}H NMR spectrum of **3ad** taking $CDCl_3$ as solvent.

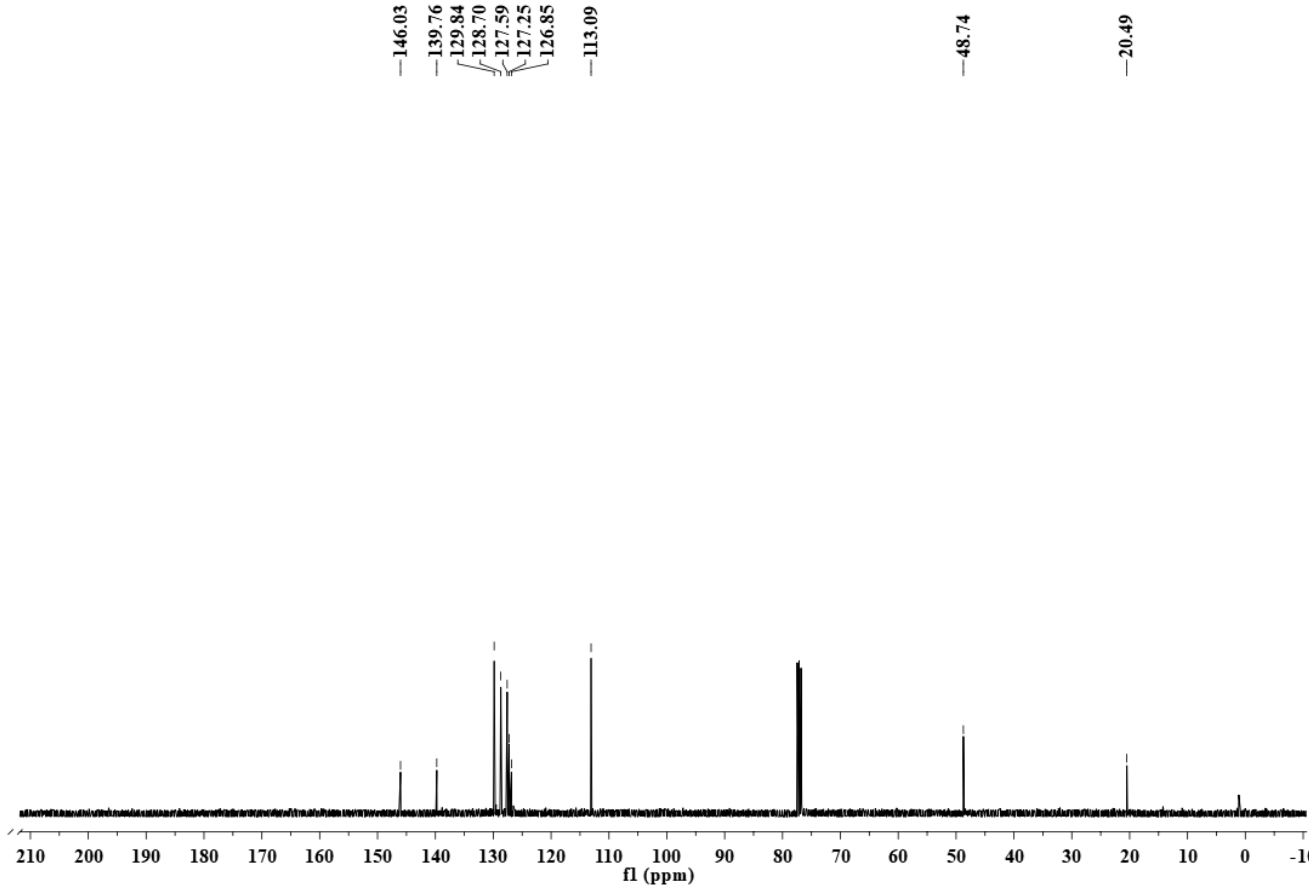


Figure S32. ^{13}C NMR spectrum of **3ad** taking $CDCl_3$ as solvent.

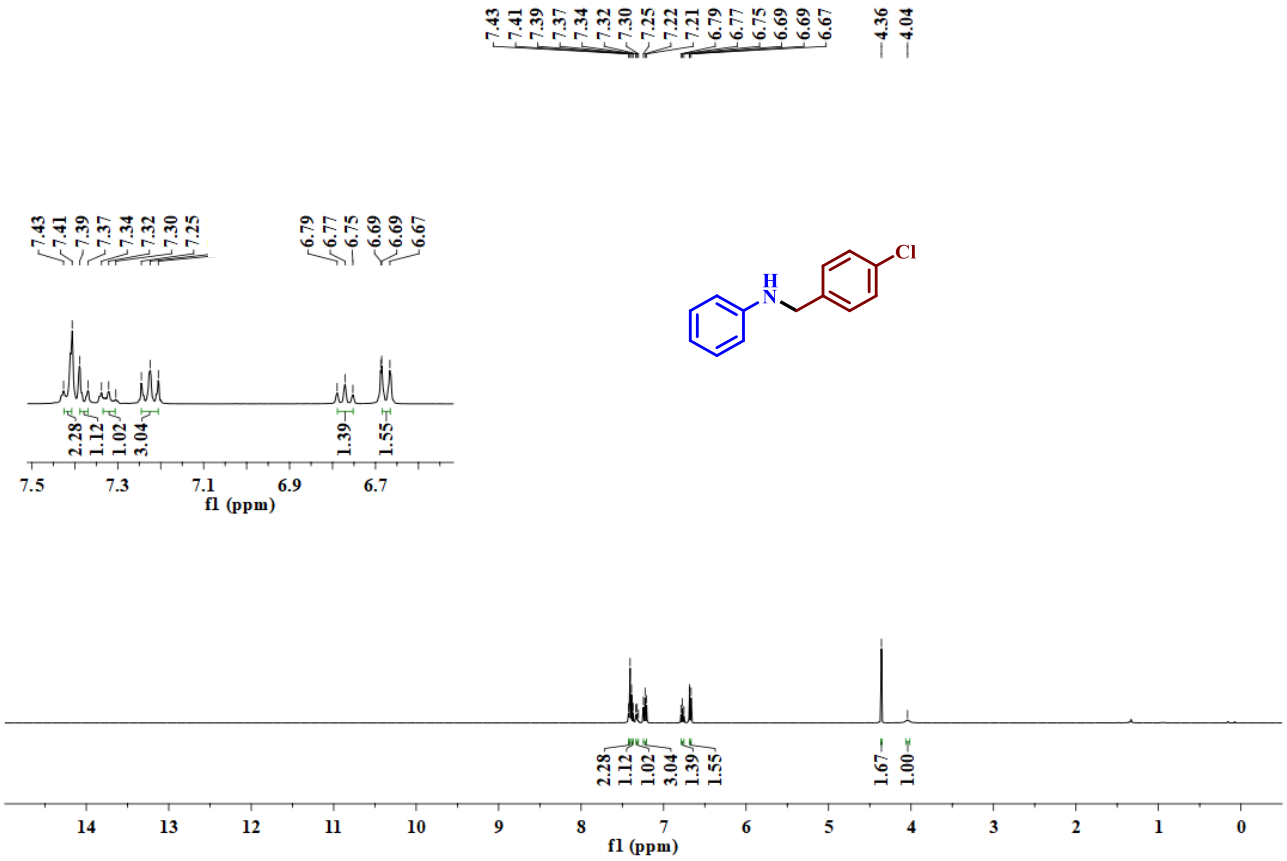


Figure S33. ^{1}H NMR spectrum of **3ae** taking $CDCl_3$ as solvent.

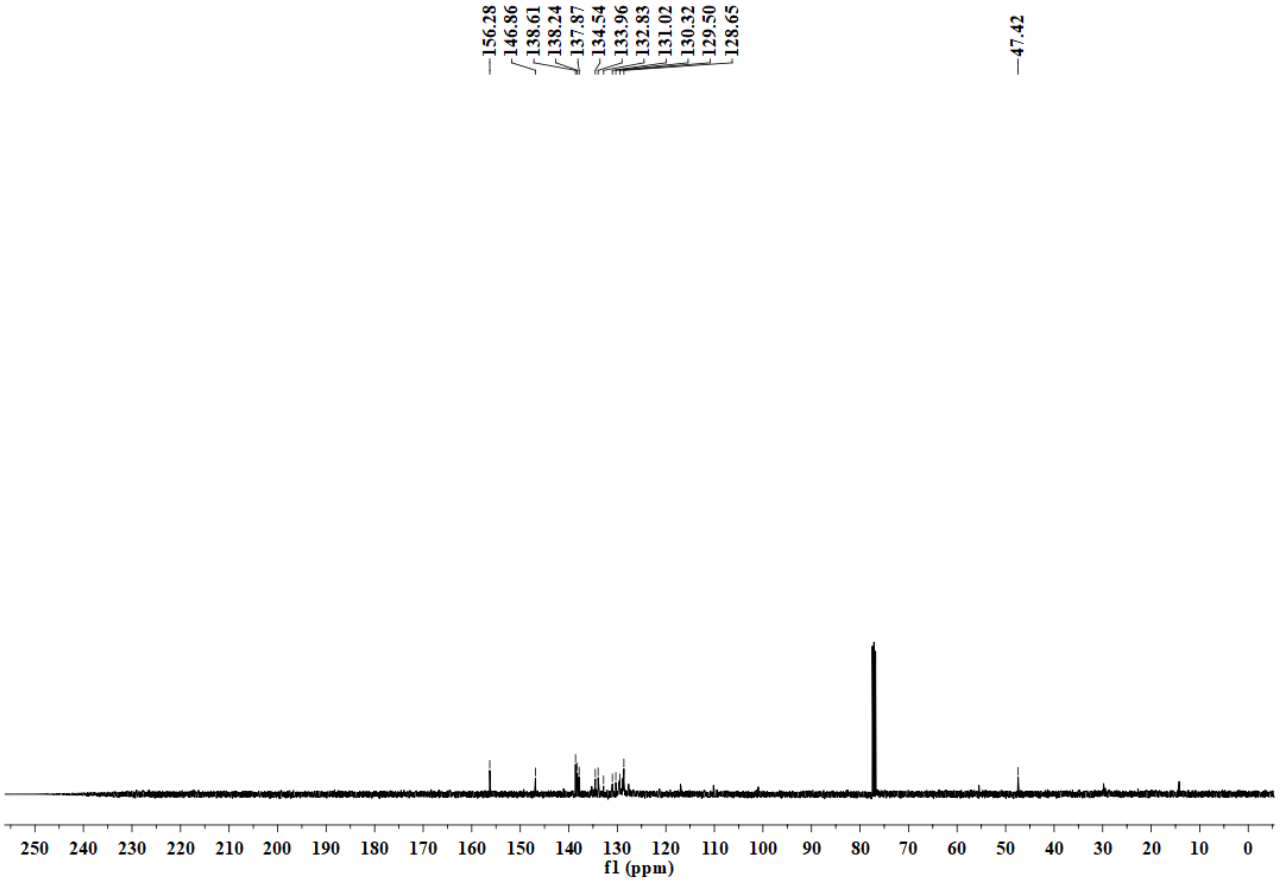


Figure. S34 ^{13}C NMR spectrum of **3ae** taking $CDCl_3$ as solvent.

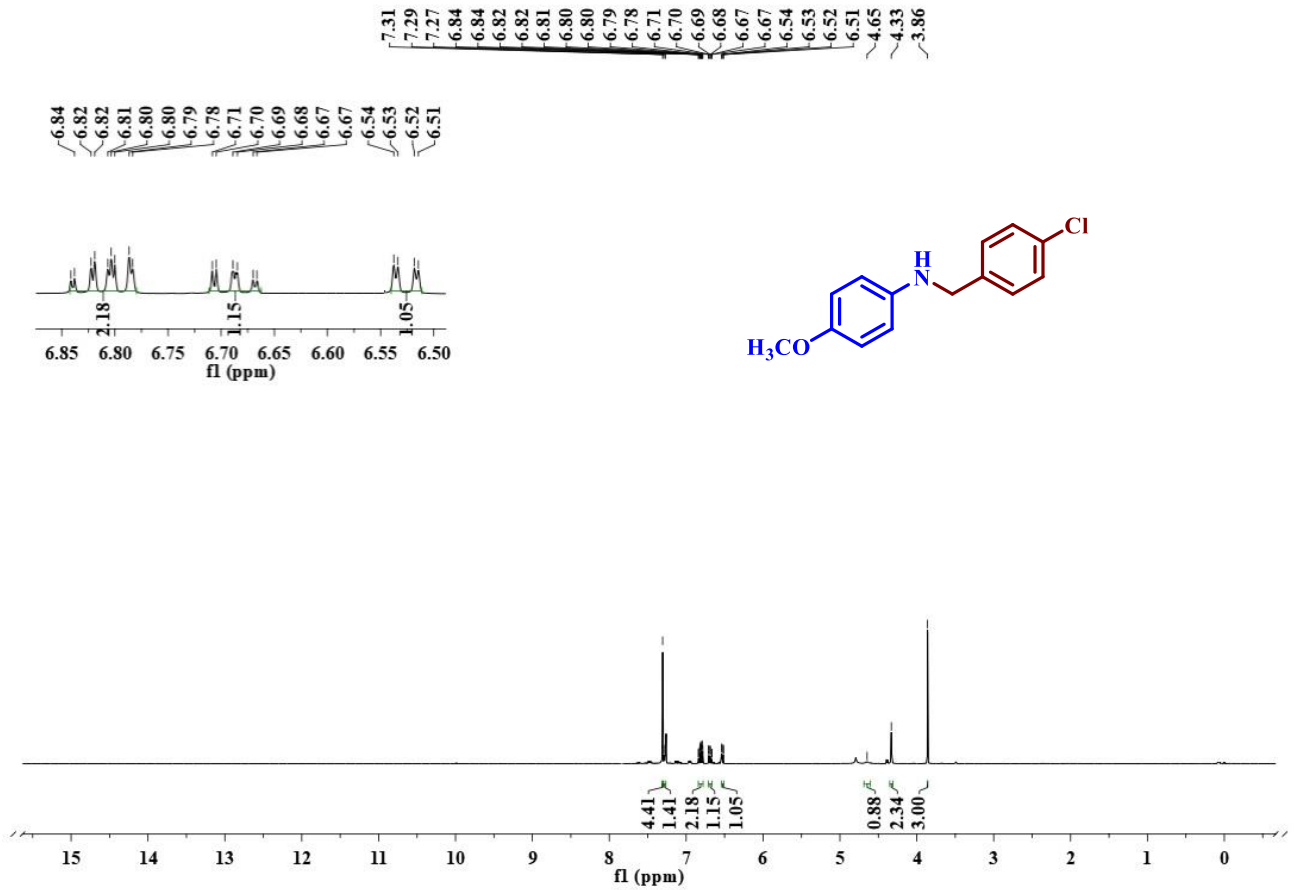


Figure S35. ^{1}H NMR spectrum of **3ba** taking $CDCl_3$ as solvent.

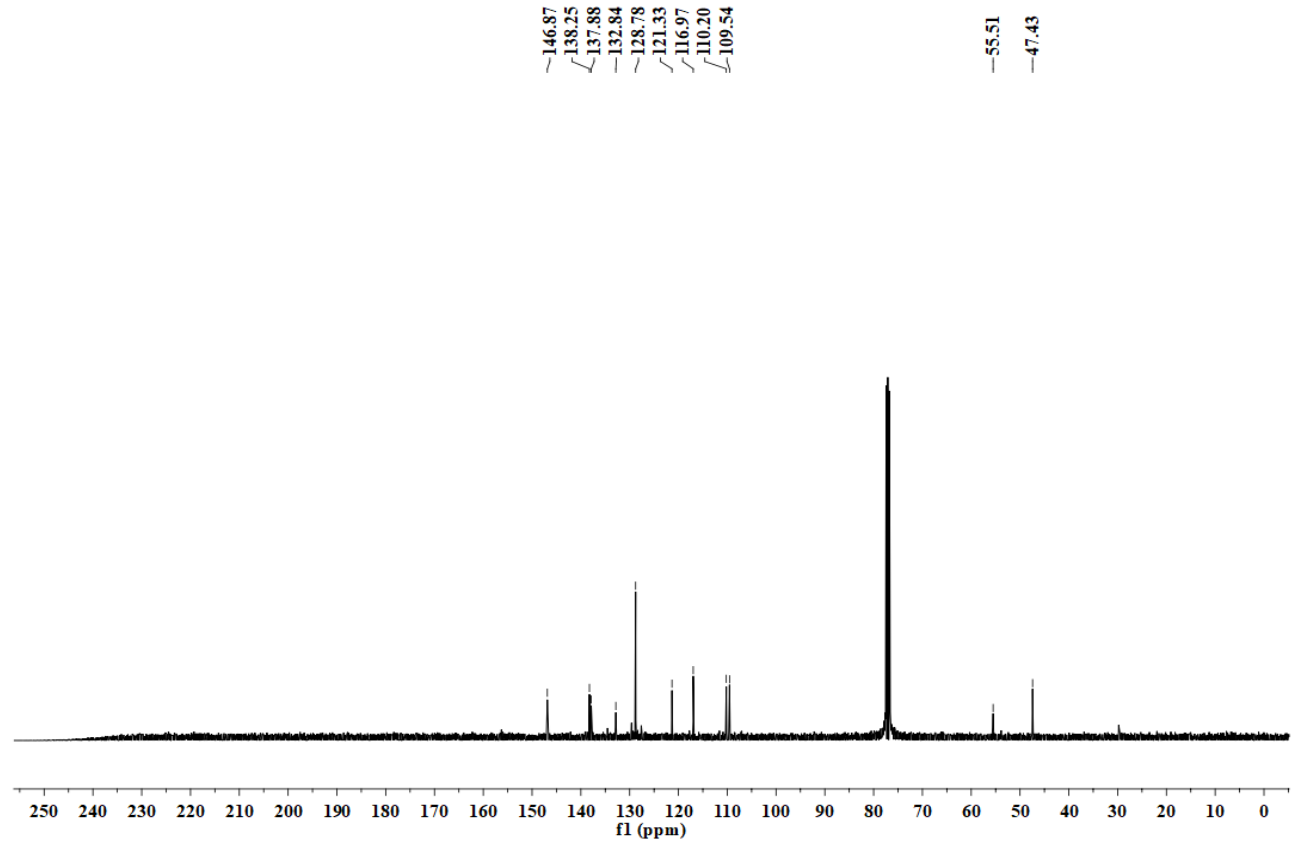


Figure S36. ^{13}C NMR spectrum of **3ba** taking $CDCl_3$ as solvent.

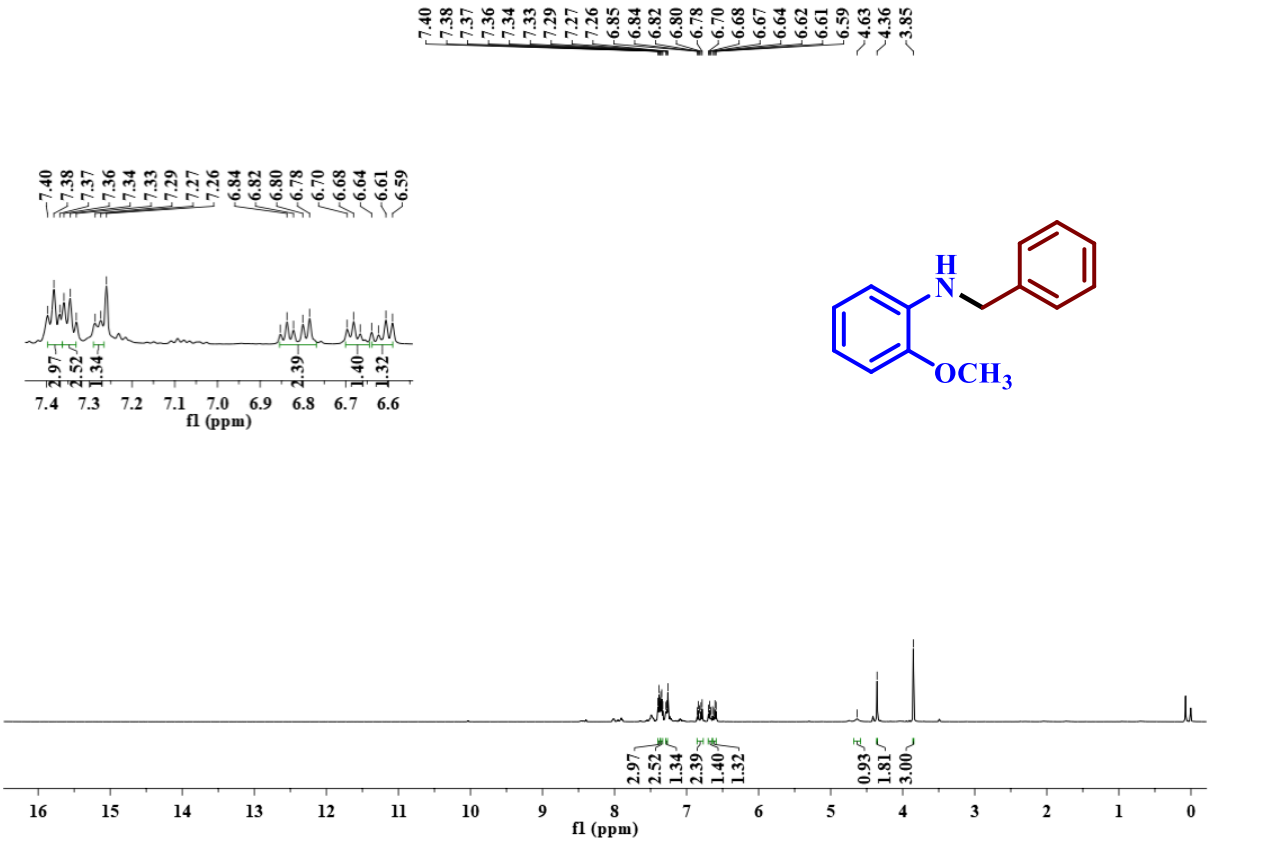


Figure S37. ^{1}H NMR spectrum of **3ca** taking $CDCl_3$ as solvent.

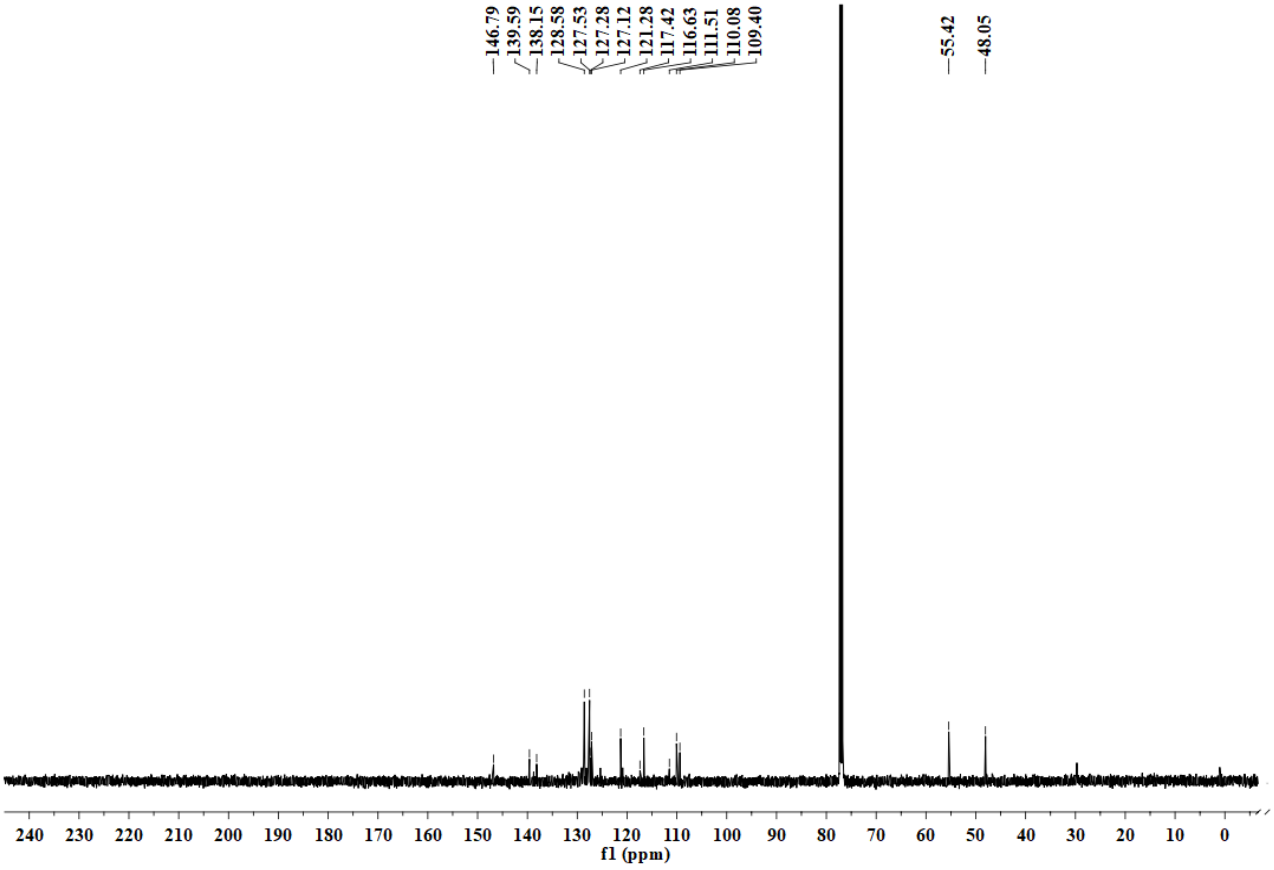


Figure S38. ^{13}C NMR spectrum of **3ca** taking $CDCl_3$ as solvent.

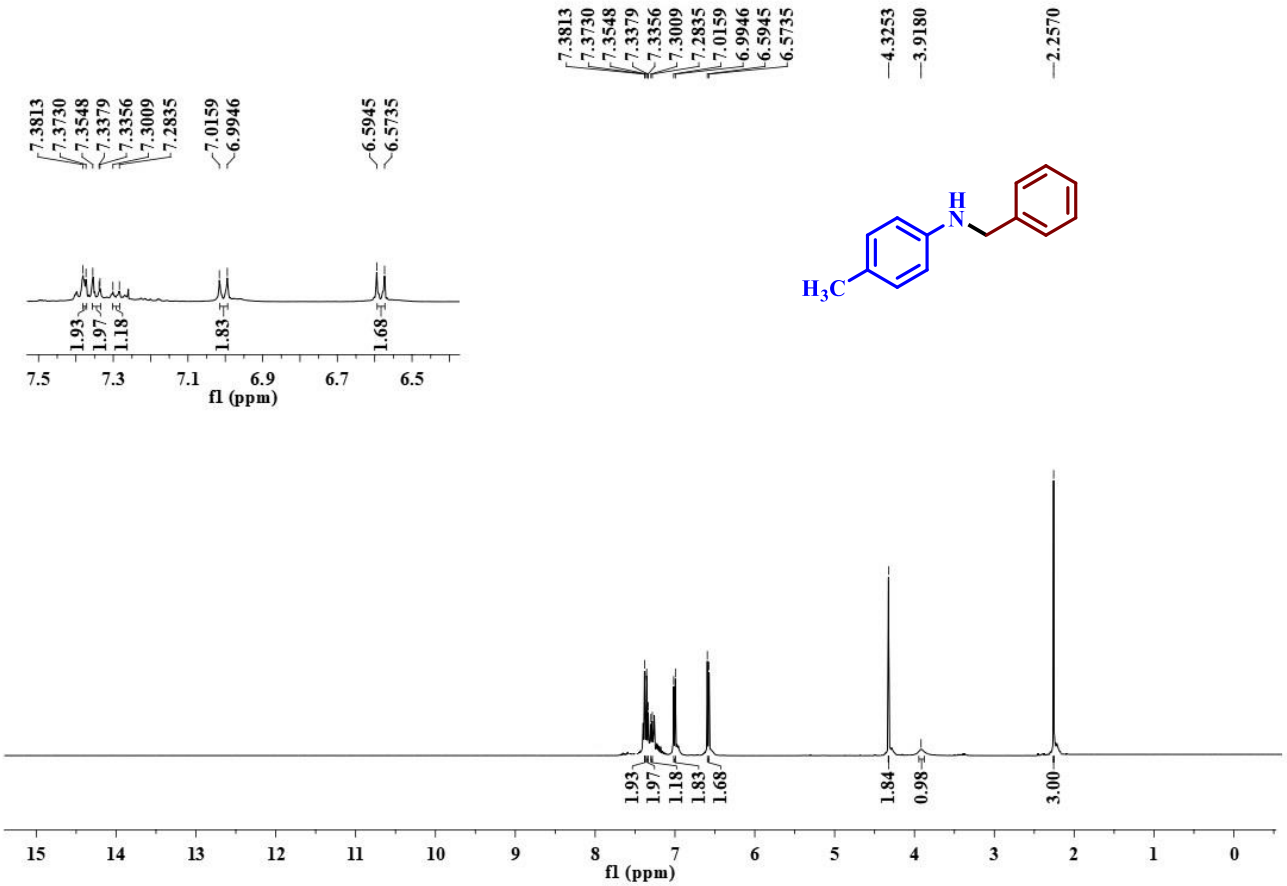


Figure S39. ^{1}H NMR spectrum of **3da** taking $CDCl_3$ as solvent.

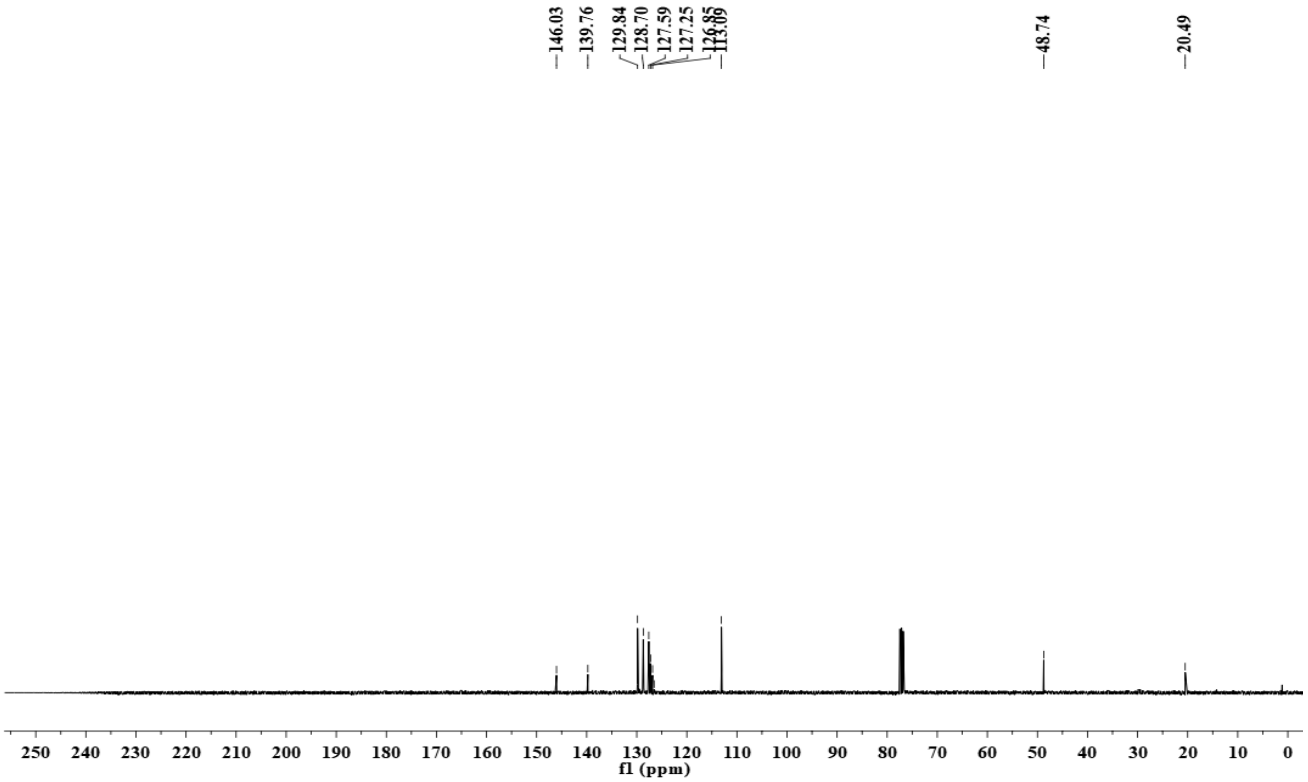


Figure S40. ^{13}C NMR spectrum of **3da** taking $CDCl_3$ as solvent.

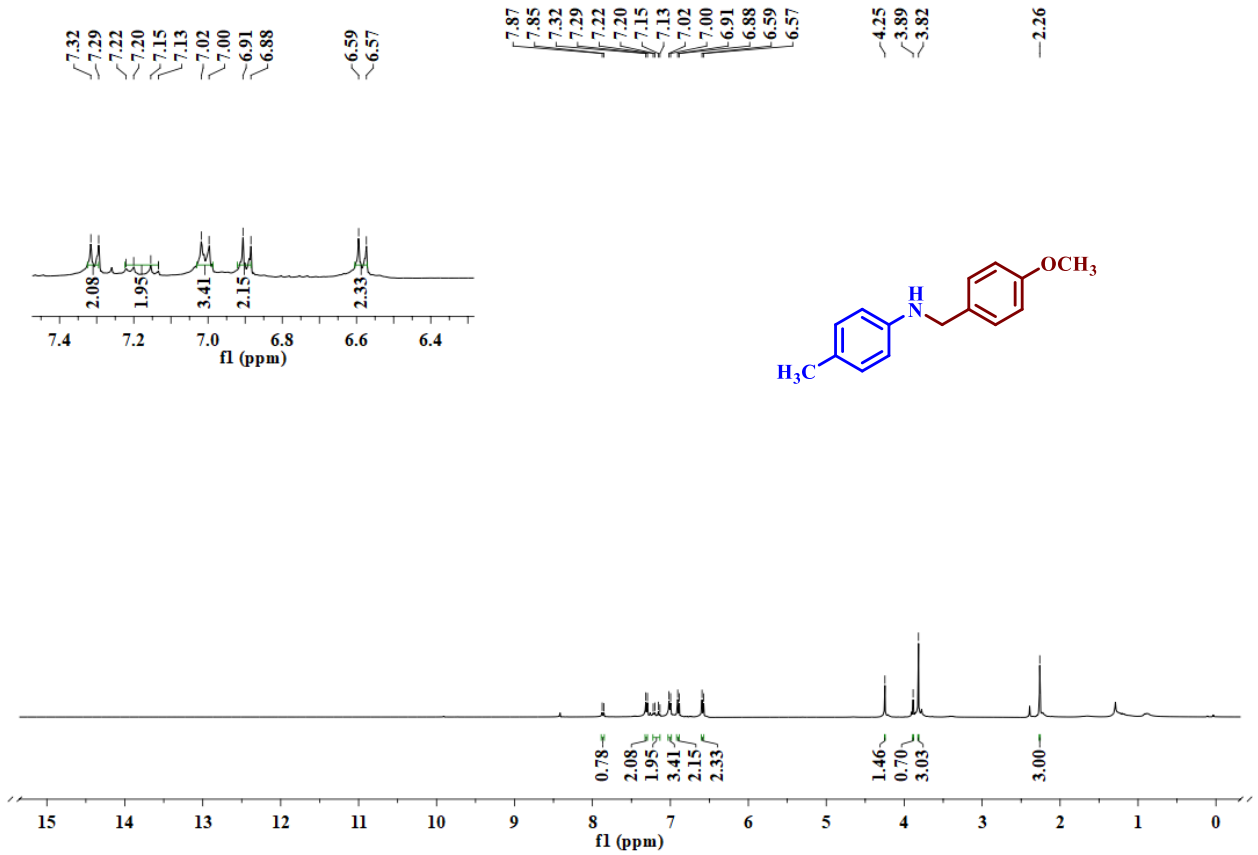


Figure S41. ^{1}H NMR spectrum of **3db** taking $CDCl_3$ as solvent.

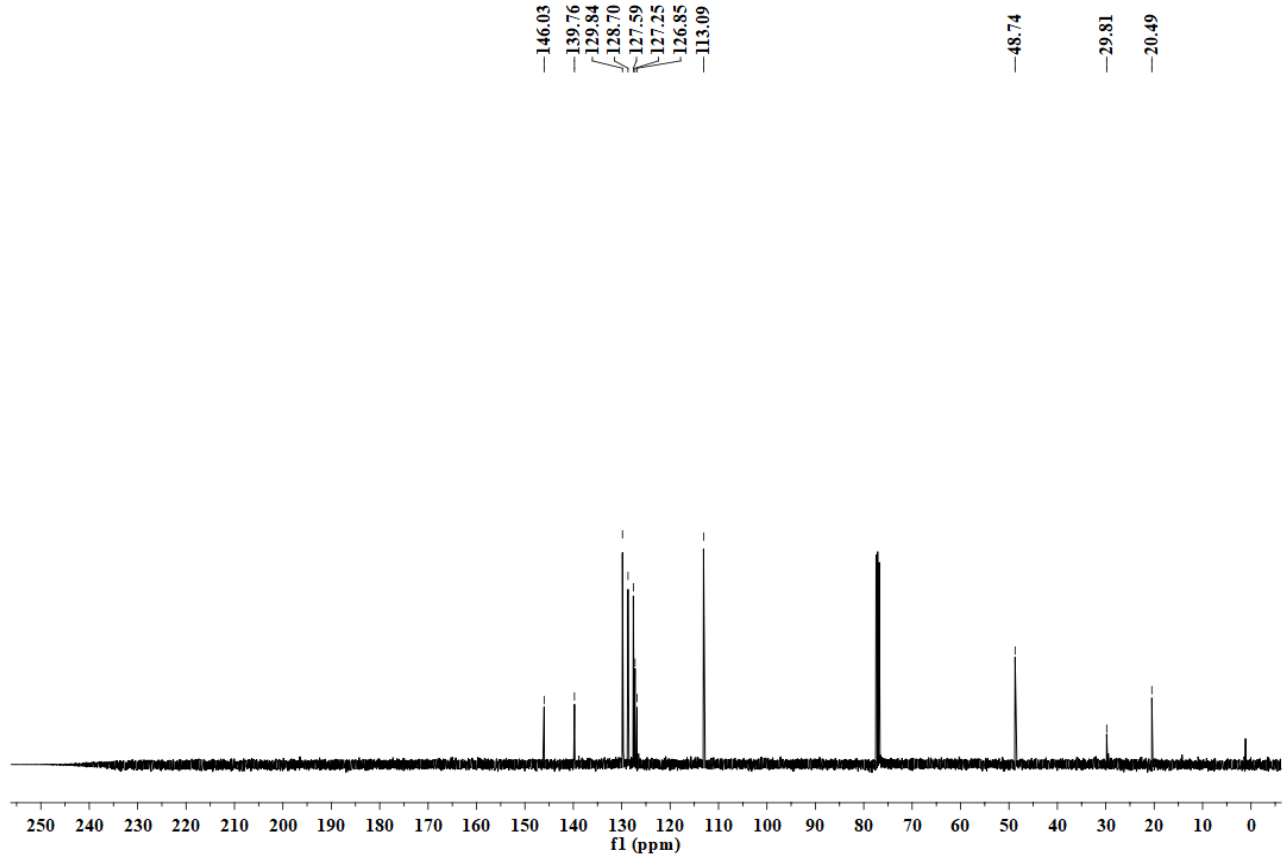


Figure S42. ^{1}H NMR spectrum of **3db** taking $CDCl_3$ as solvent.

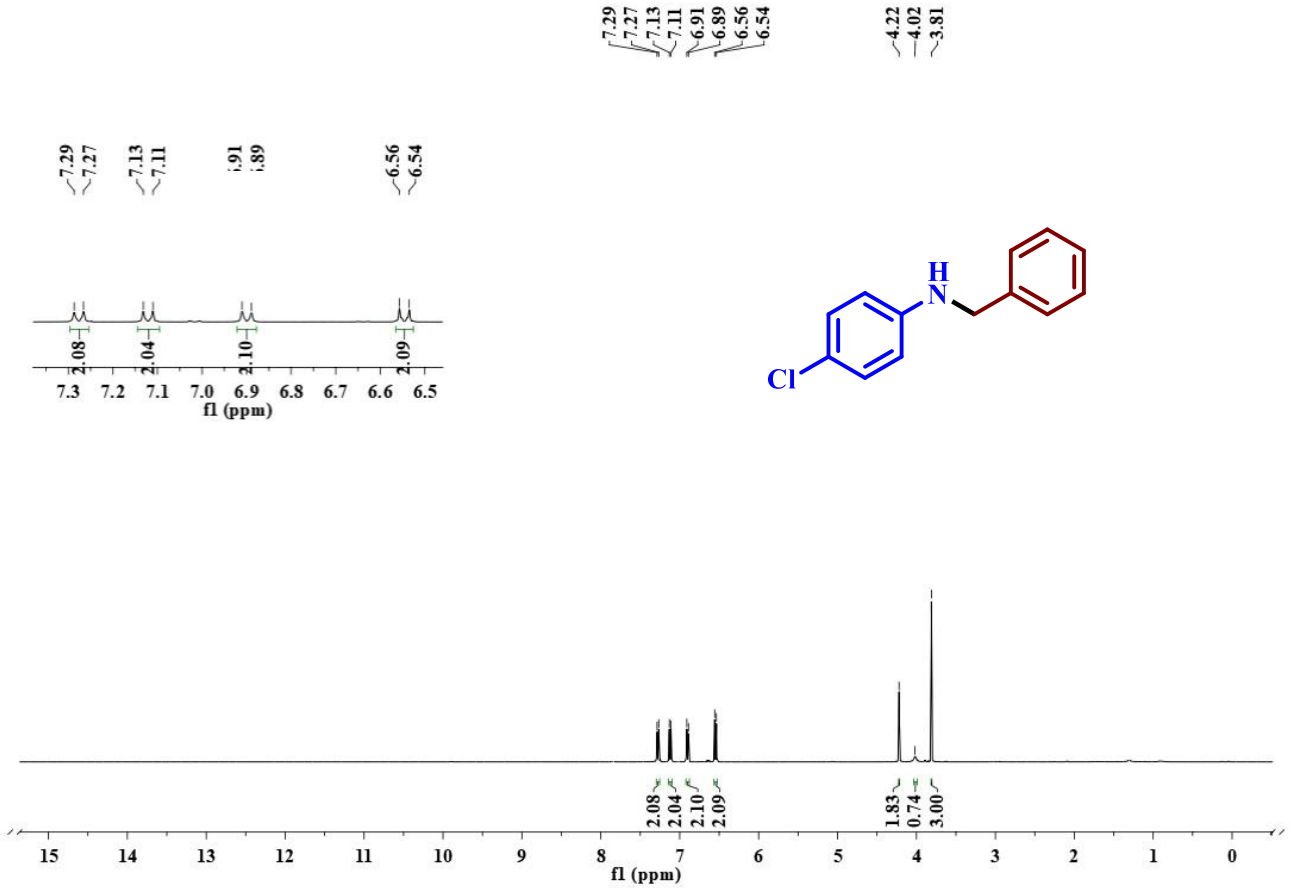


Figure S43. ^{1}H NMR spectrum of **3ea** taking $CDCl_3$ as solvent.

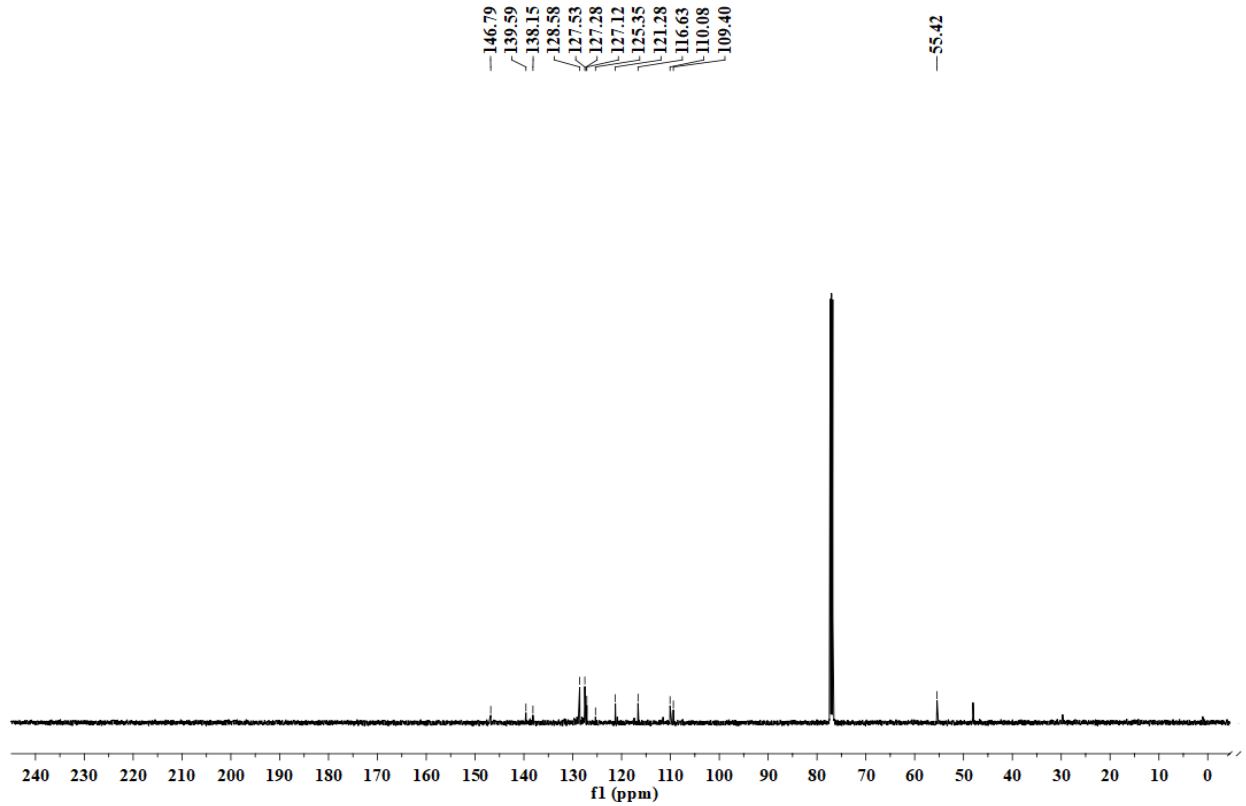


Figure S44. ^{1}H NMR spectrum of **3ea** taking $CDCl_3$ as solvent.

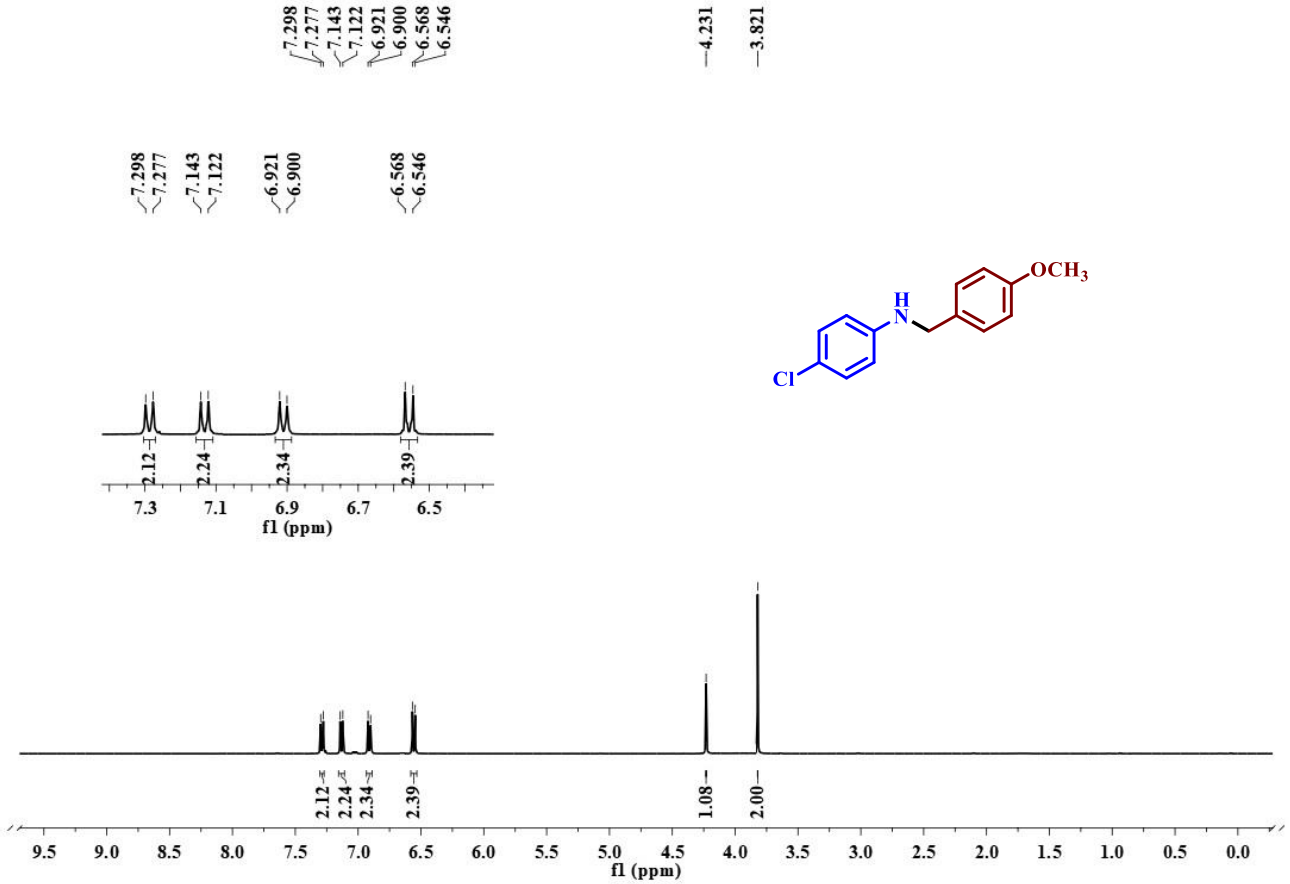


Figure S45. ^{1}H NMR spectrum of **3eb** taking $CDCl_3$ as solvent.

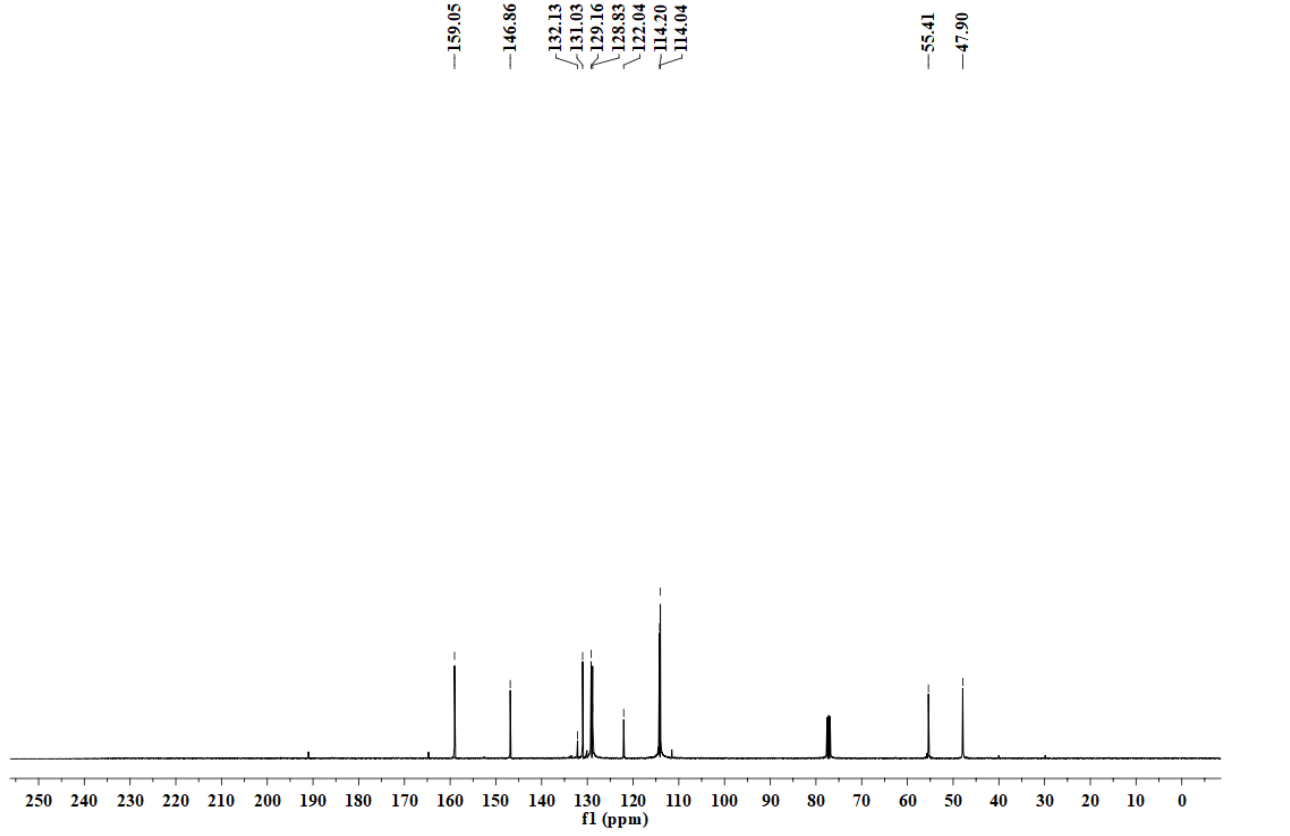


Figure S46. ^{1}H NMR spectrum of **3eb** taking $CDCl_3$ as solvent.

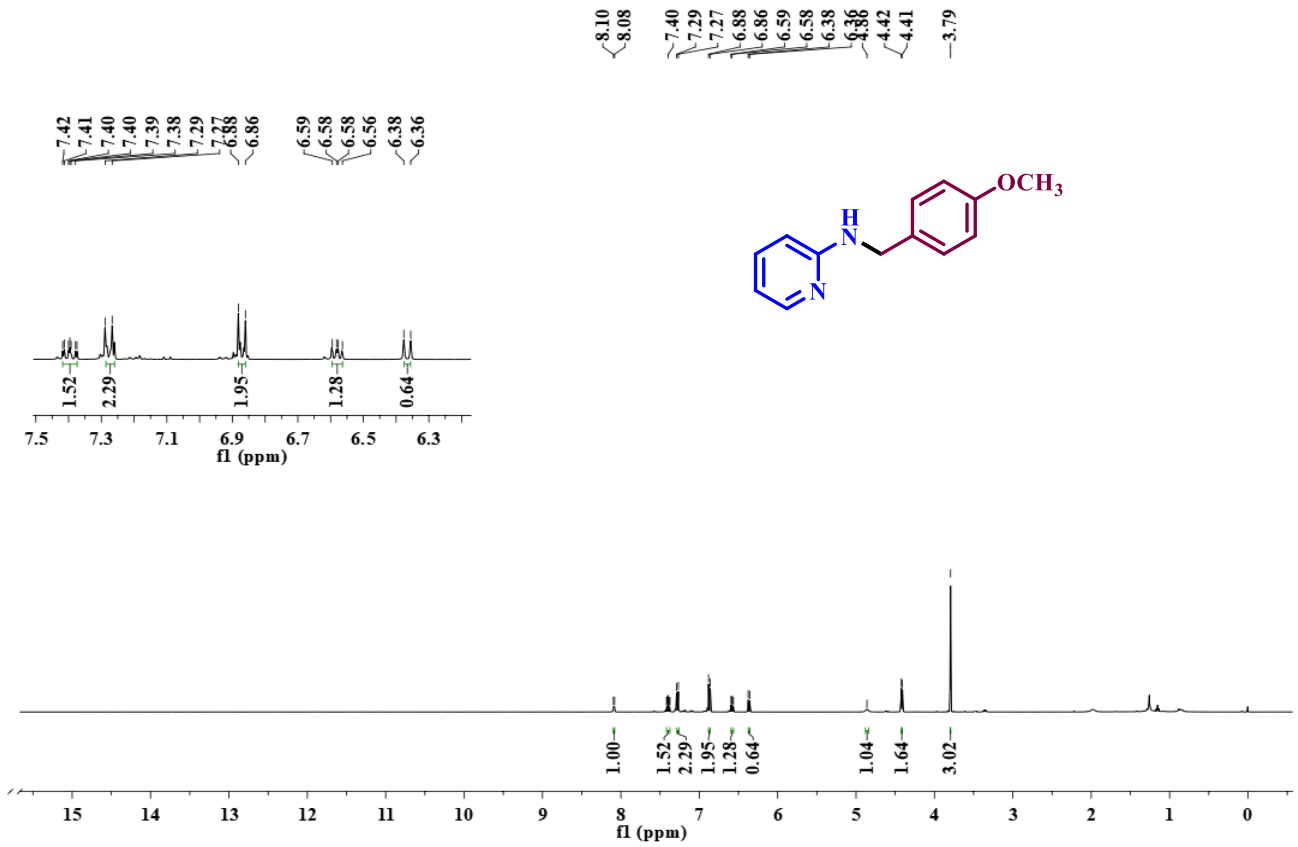


Figure S47. ^{1}H NMR spectrum of **3fa** taking $CDCl_3$ as solvent.

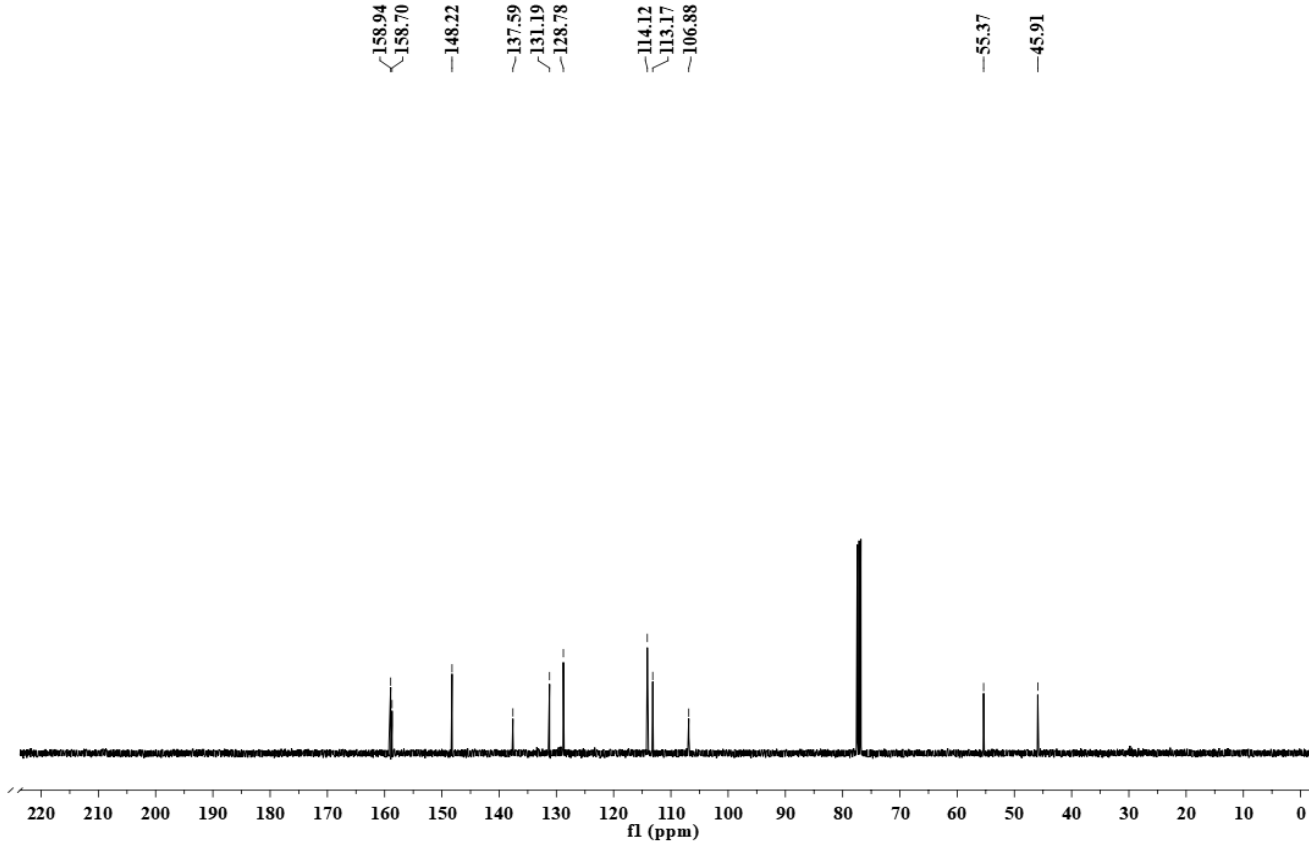
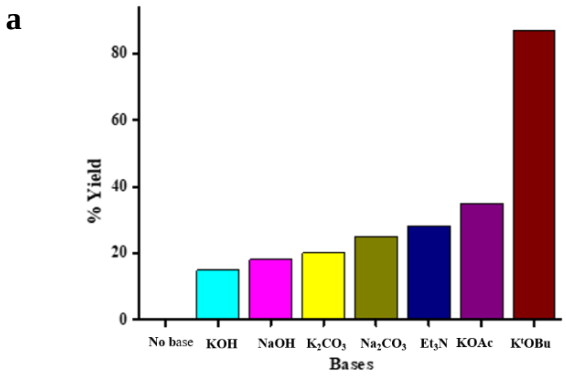
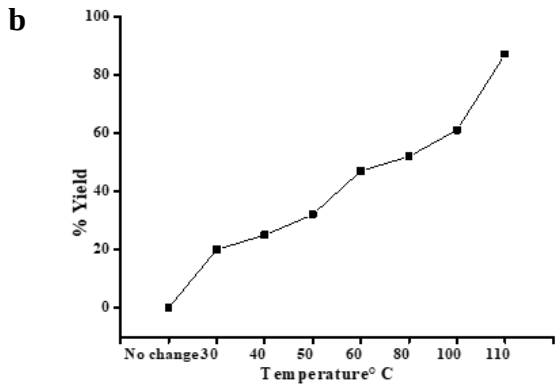


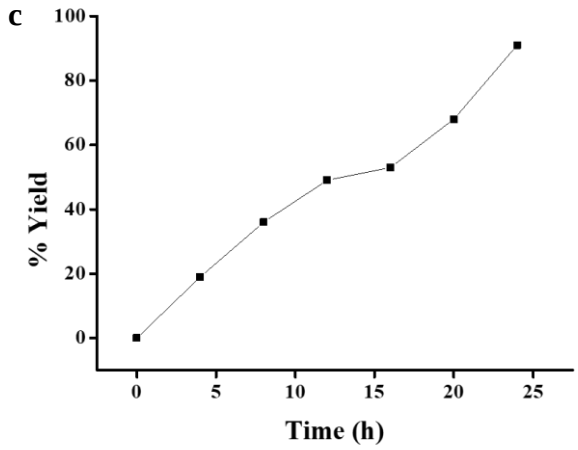
Figure S48. ^{1}H NMR spectrum of **3fa** taking $CDCl_3$ as solvent.



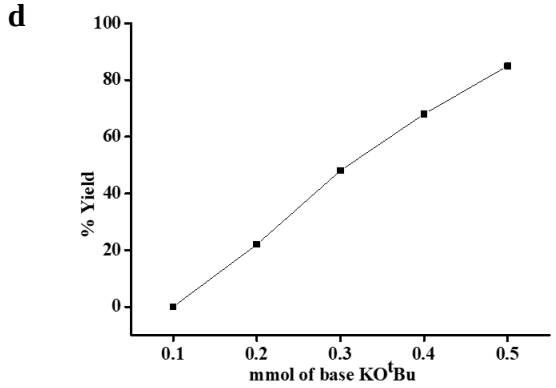
Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (2 mol%), bases (0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h.



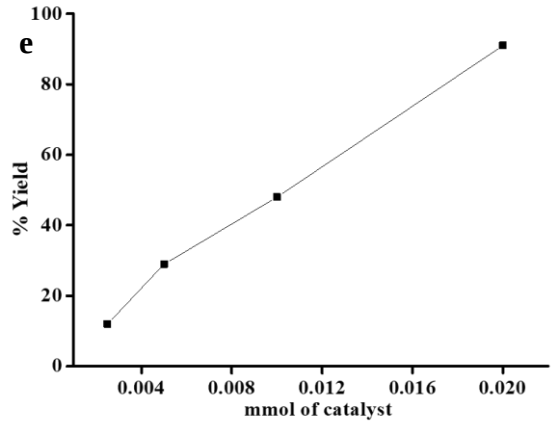
Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature (30°C -110 °C) for 24 h.



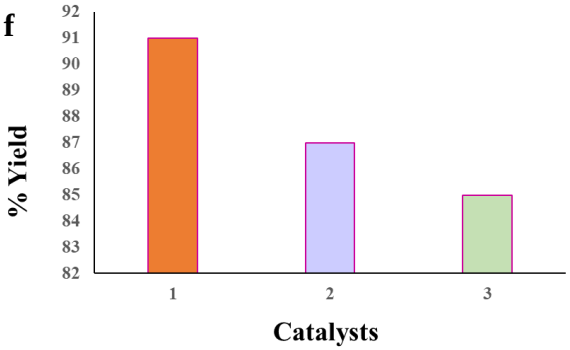
Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature 110 °C for (0-24 h).



Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.1-0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h.



Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalyst (0.4 mol%-2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h.



Reaction Condition: Acetophenone (1 mmol), Benzyl alcohol (1 mmol), catalysts (**Co1-Co3**) (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml Temperature 110 °C for 24 h.

Figure S49. The reaction profile of cobalt catalyzed α-alkylation of acetophenone with benzyl alcohol (**a**) Effect of bases (**b**) Effect of temperature (**c**) Effect of time (**d**) Loading of base KO^{t}Bu (**e**) Loading of catalysts (**f**) Effect of catalysts.

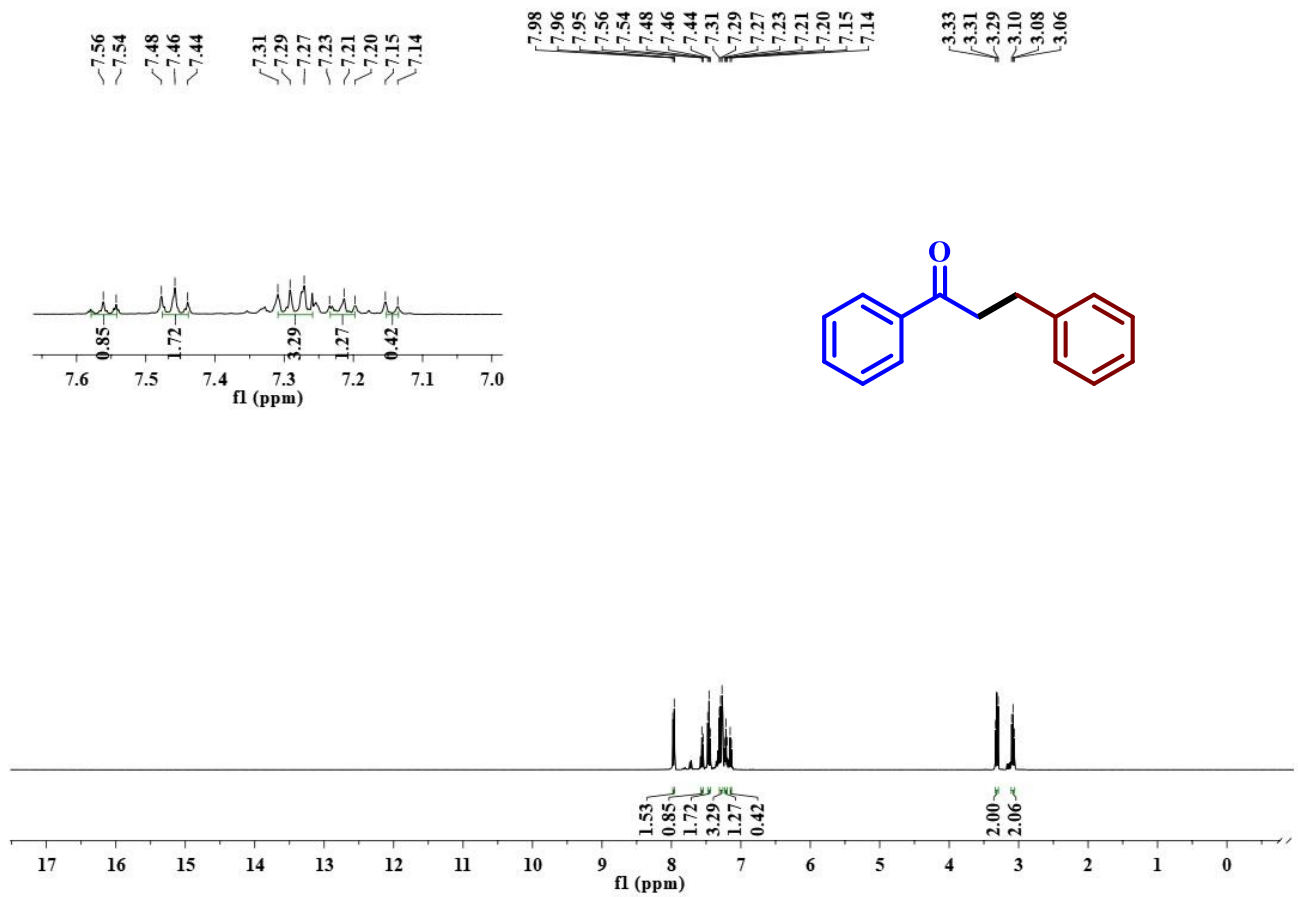


Figure S50. ^{1}H NMR spectrum of **5aa** taking $CDCl_3$ as solvent.

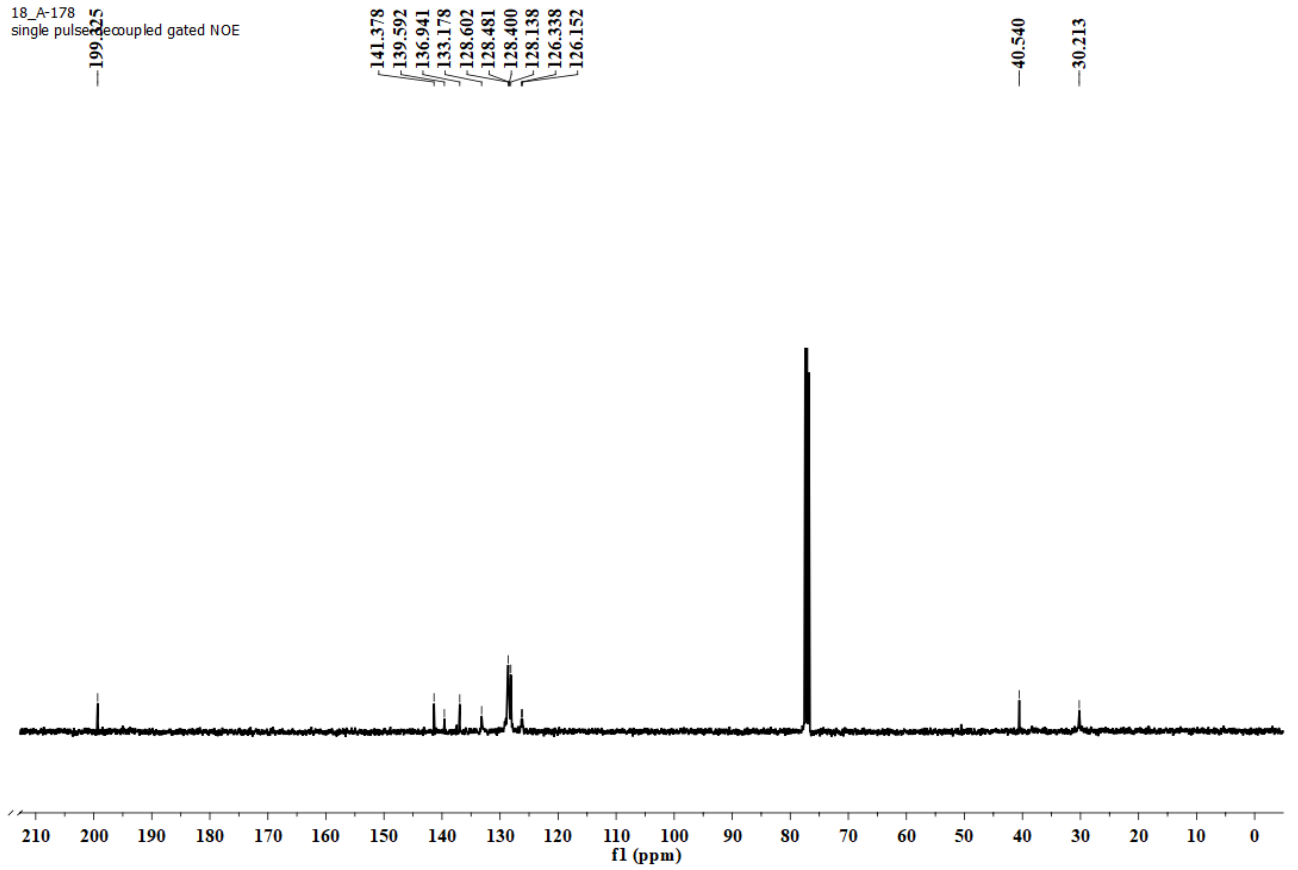


Figure S51. ^{13}C NMR spectrum of **5aa** taking $CDCl_3$ as solvent.

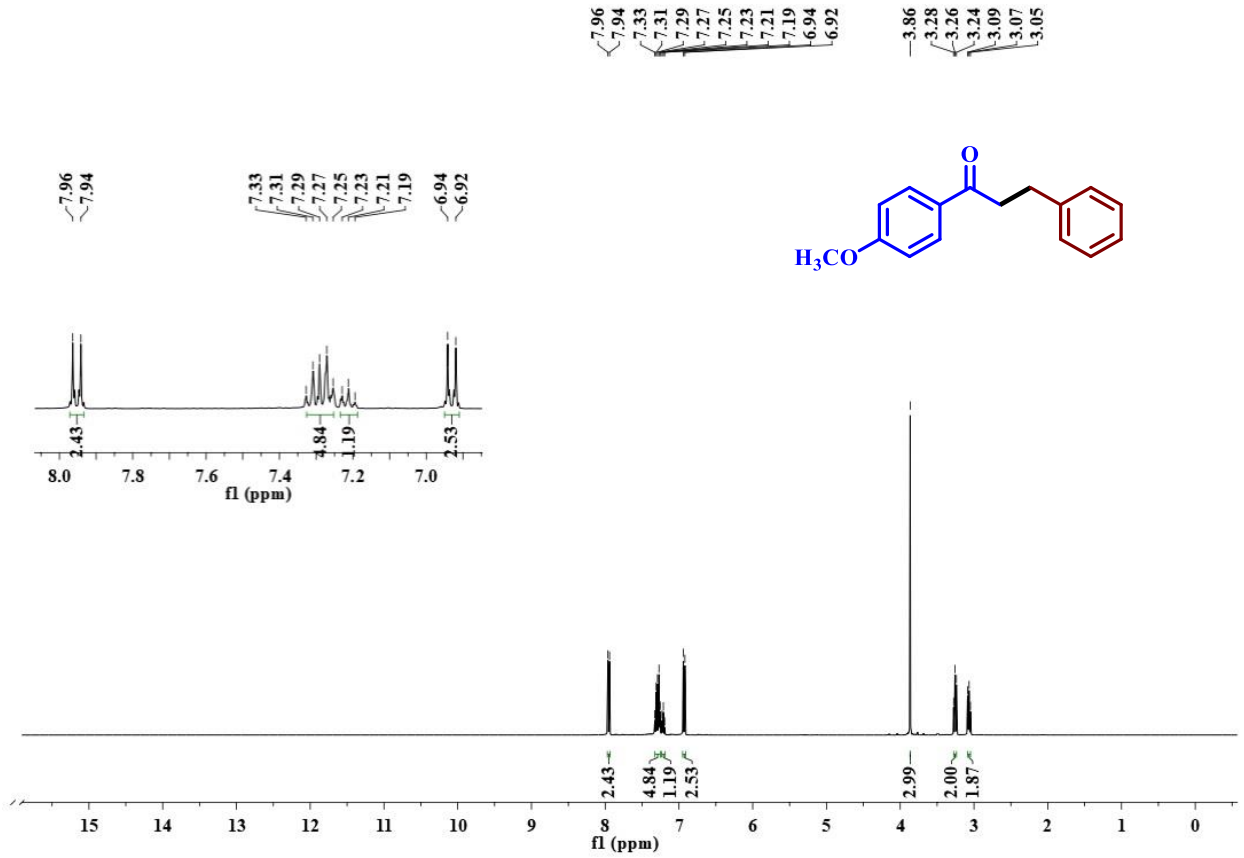


Figure S52. ^{1}H NMR spectrum of **5ab** taking $CDCl_3$ as solvent.

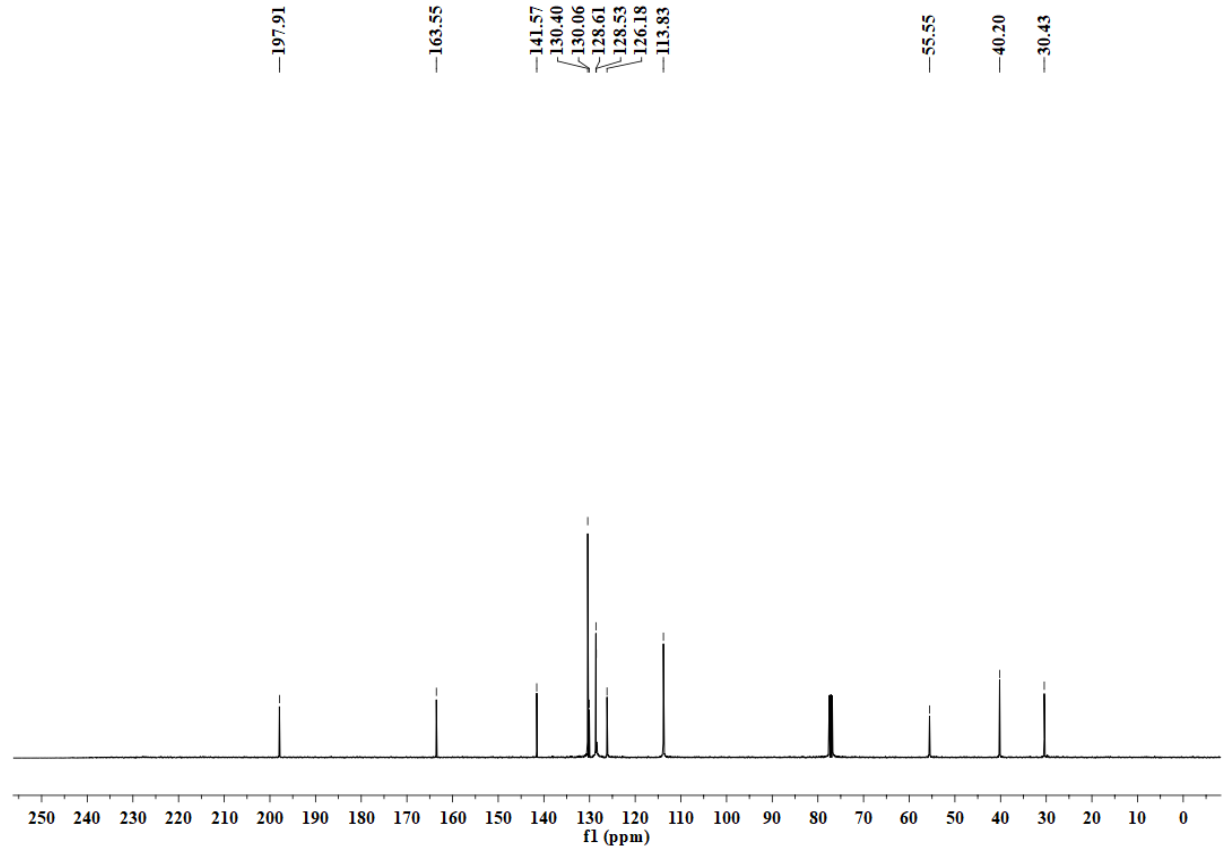


Figure S53. ^{13}C NMR spectrum of **5ab** taking $CDCl_3$ as solvent.

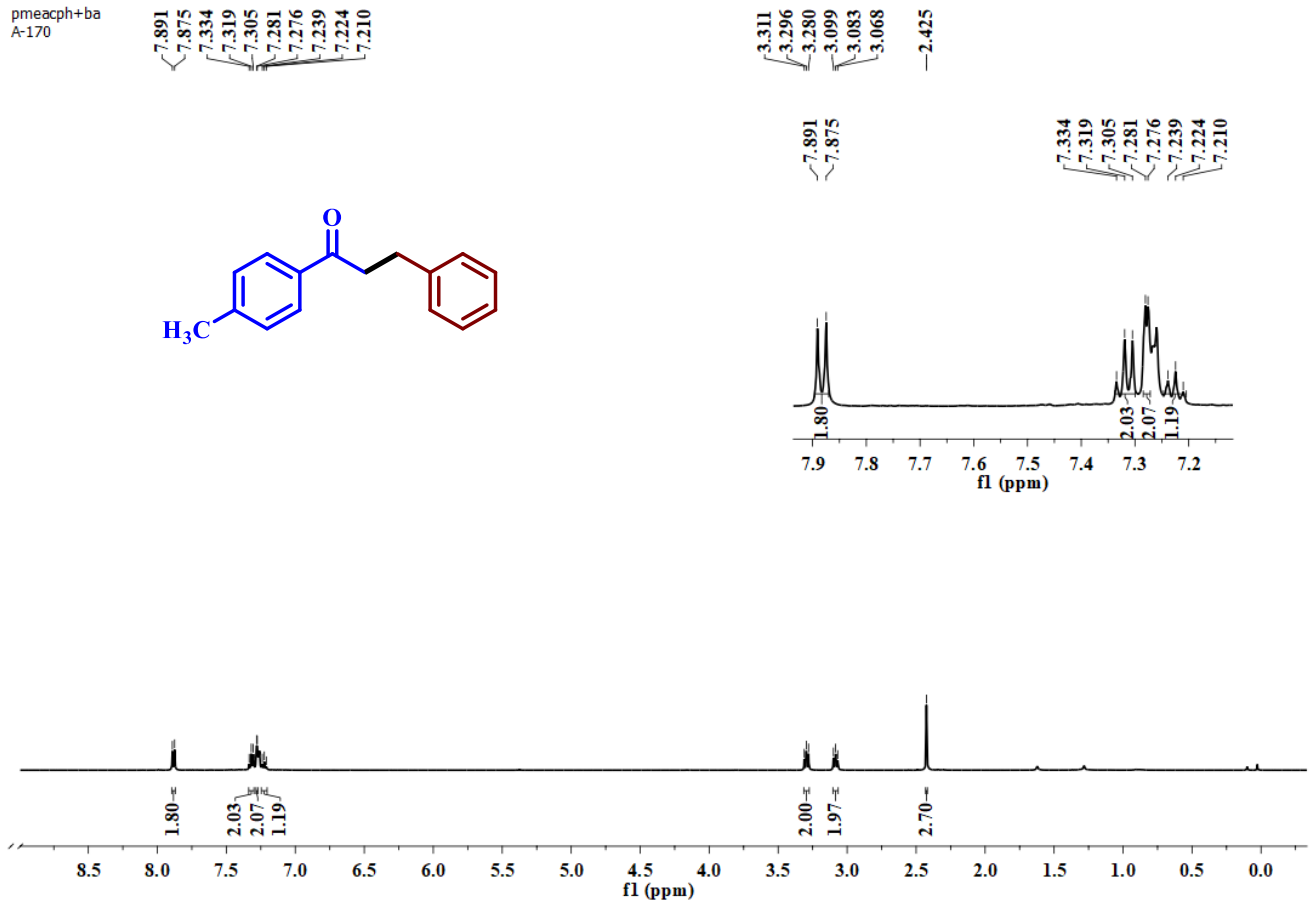


Figure S54. ^{1}H NMR spectrum of **5ac** taking $CDCl_3$ as solvent.

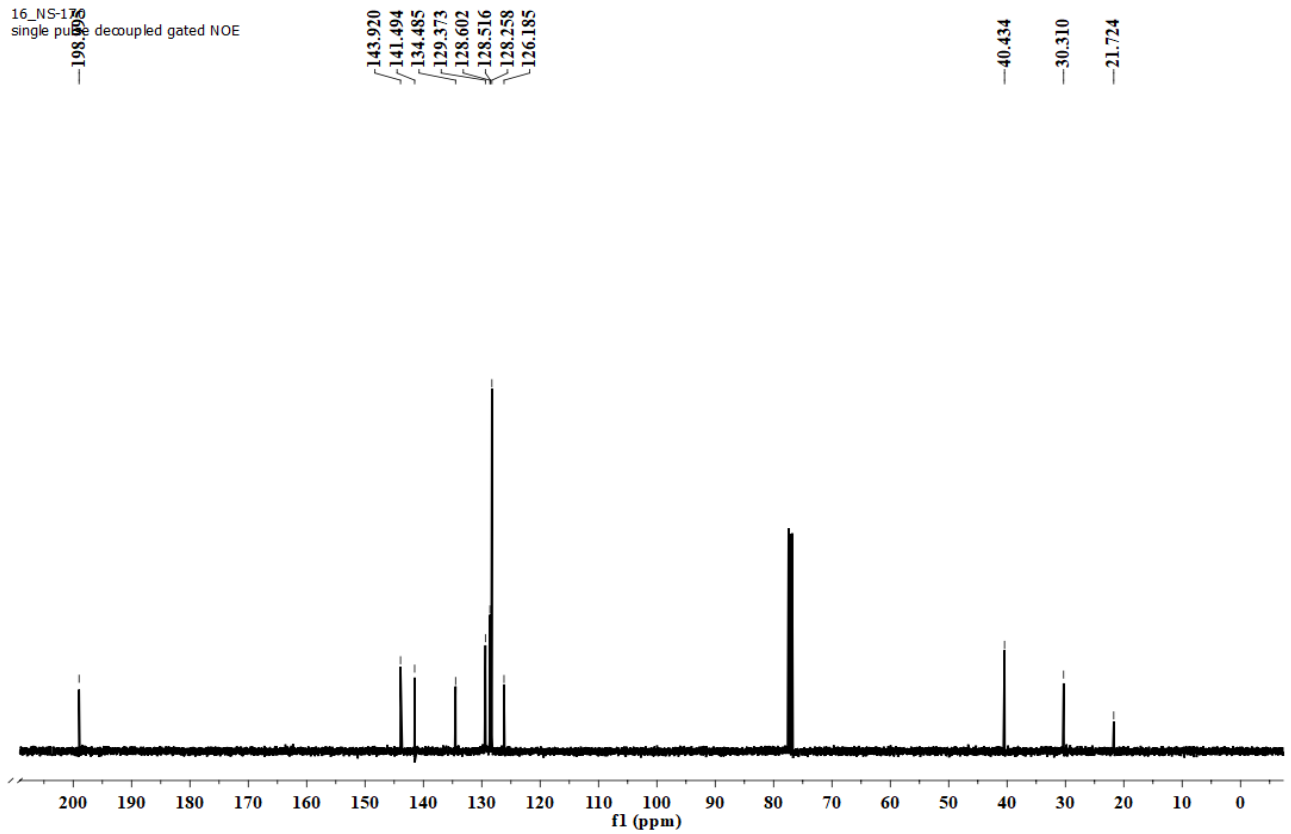


Figure S55. ^{13}C NMR spectrum of **5ac** taking $CDCl_3$ as solvent.

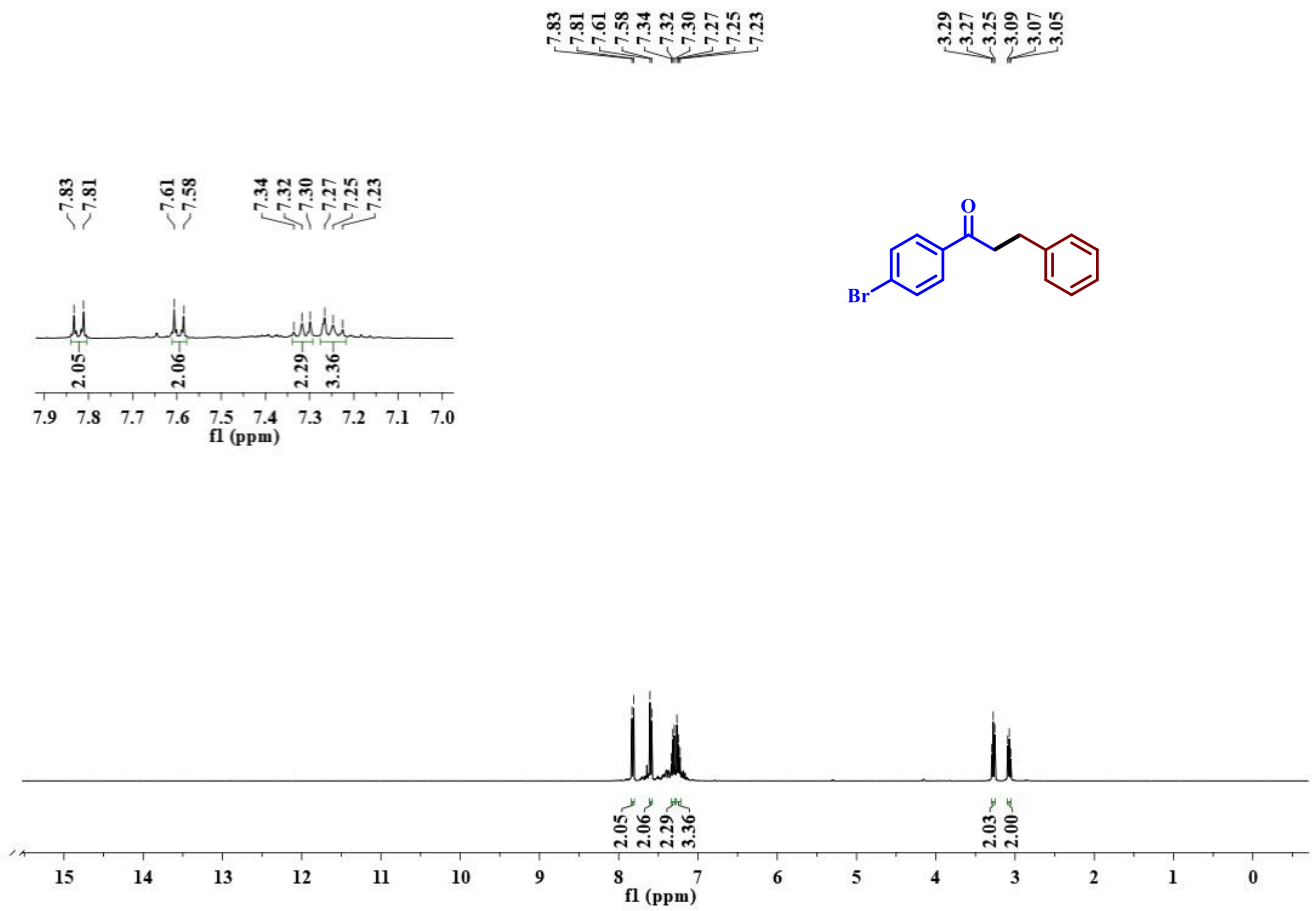


Figure S56. ^{1}H NMR spectrum of **5ad** taking $CDCl_3$ as solvent.

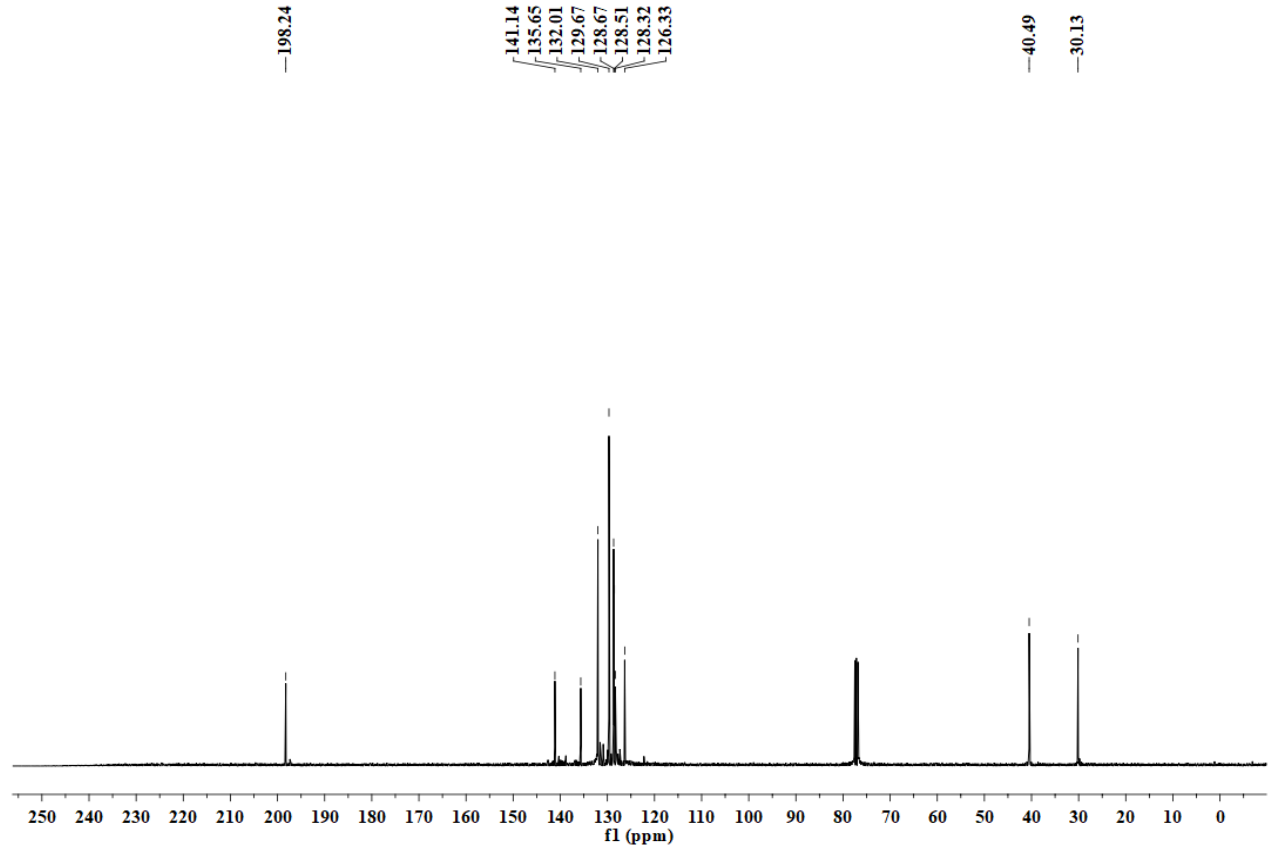


Figure S57. ^{13}C NMR spectrum of **5ad** taking $CDCl_3$ as solvent.

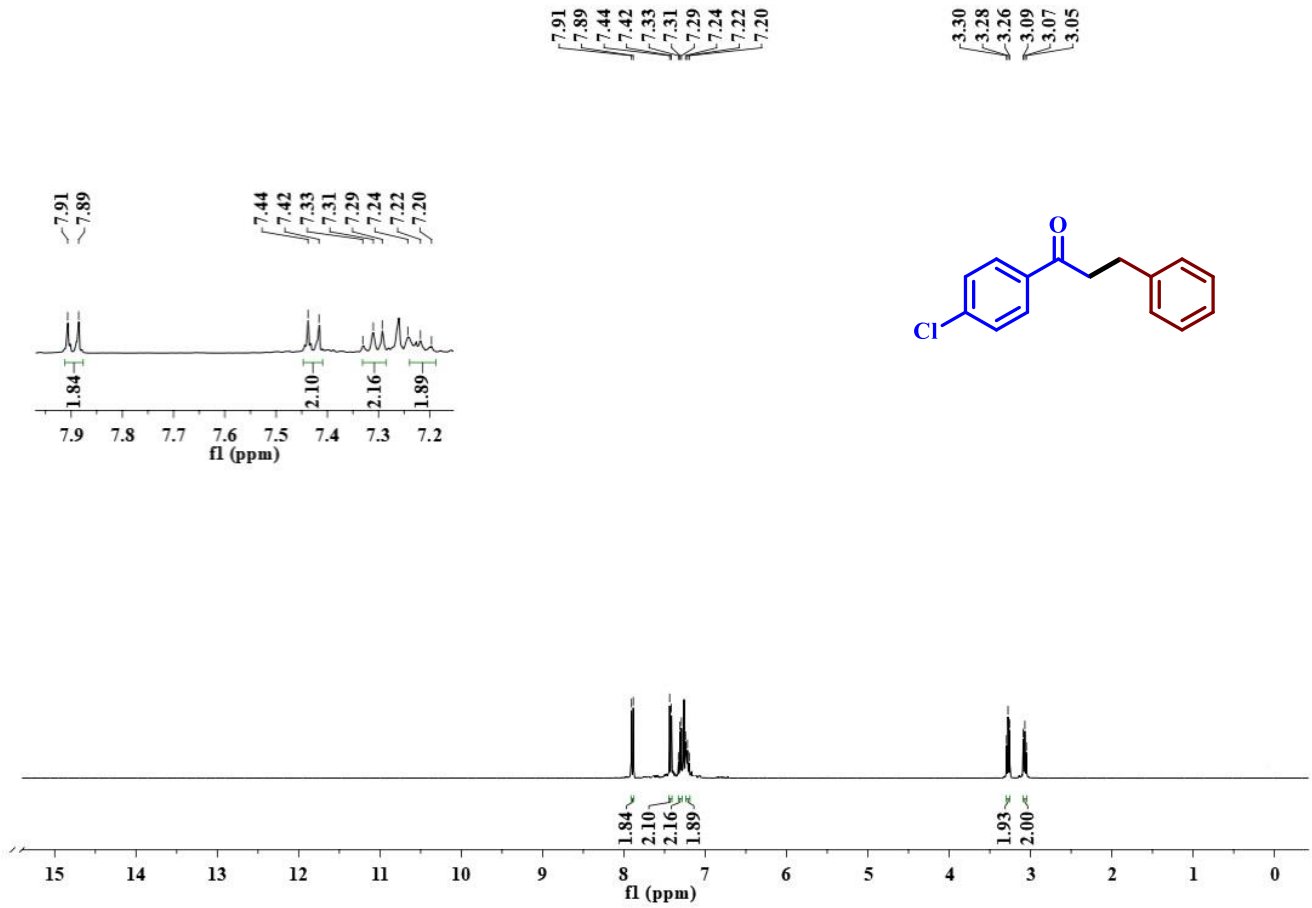


Figure S58. ^{1}H NMR spectrum of **5ae** taking $CDCl_3$ as solvent.

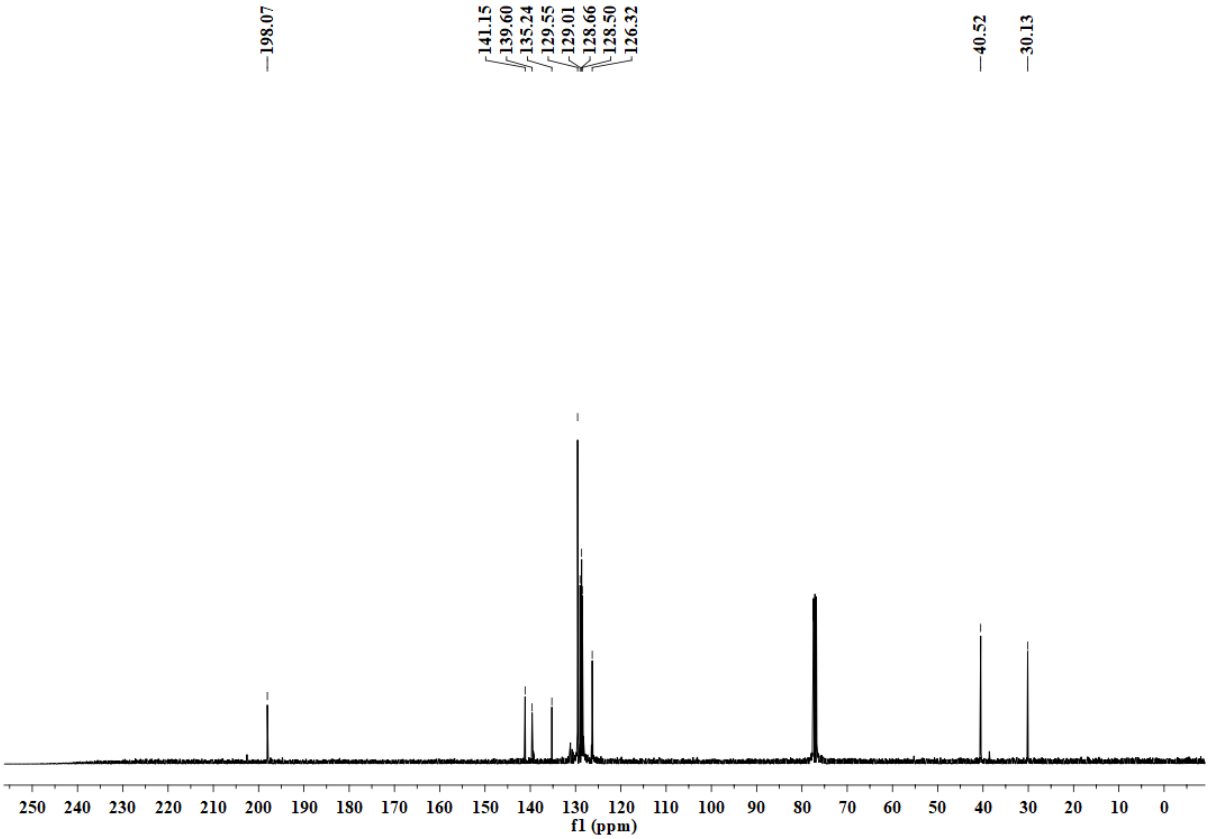


Figure S59. ^{13}C NMR spectrum of **5ae** taking $CDCl_3$ as solvent.

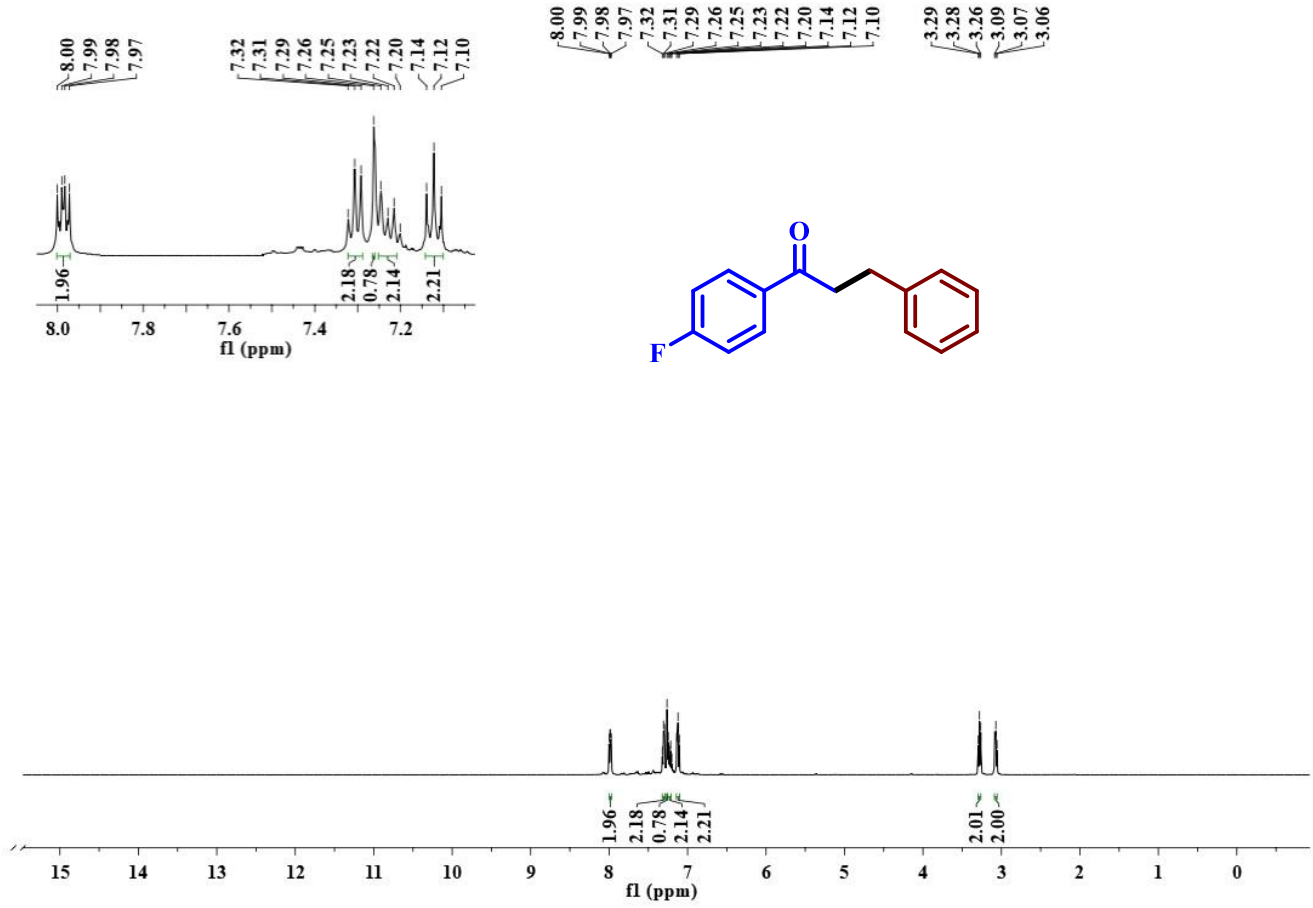


Figure S60. ^{1}H NMR spectrum of **5af** taking $CDCl_3$ as solvent.

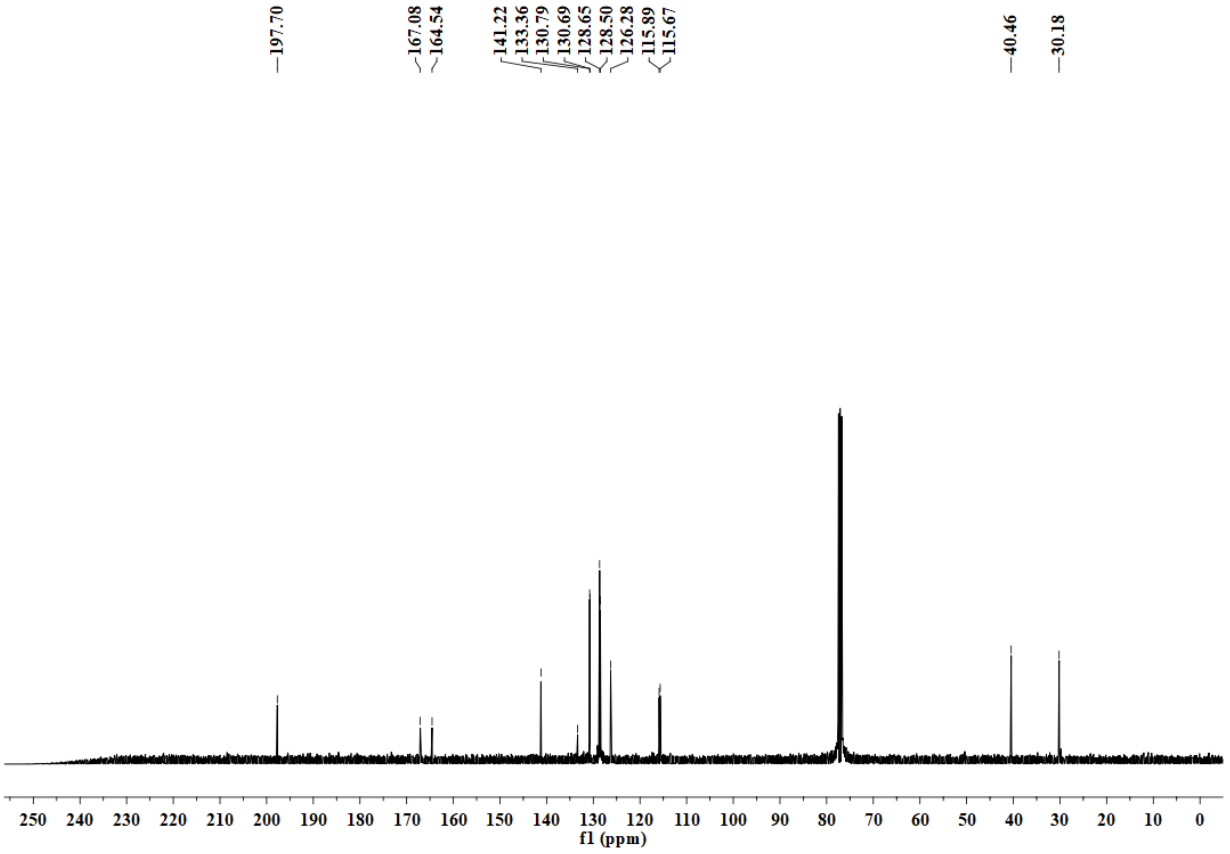


Figure S61. ^{13}C NMR spectrum of **5af** taking $CDCl_3$ as solvent.

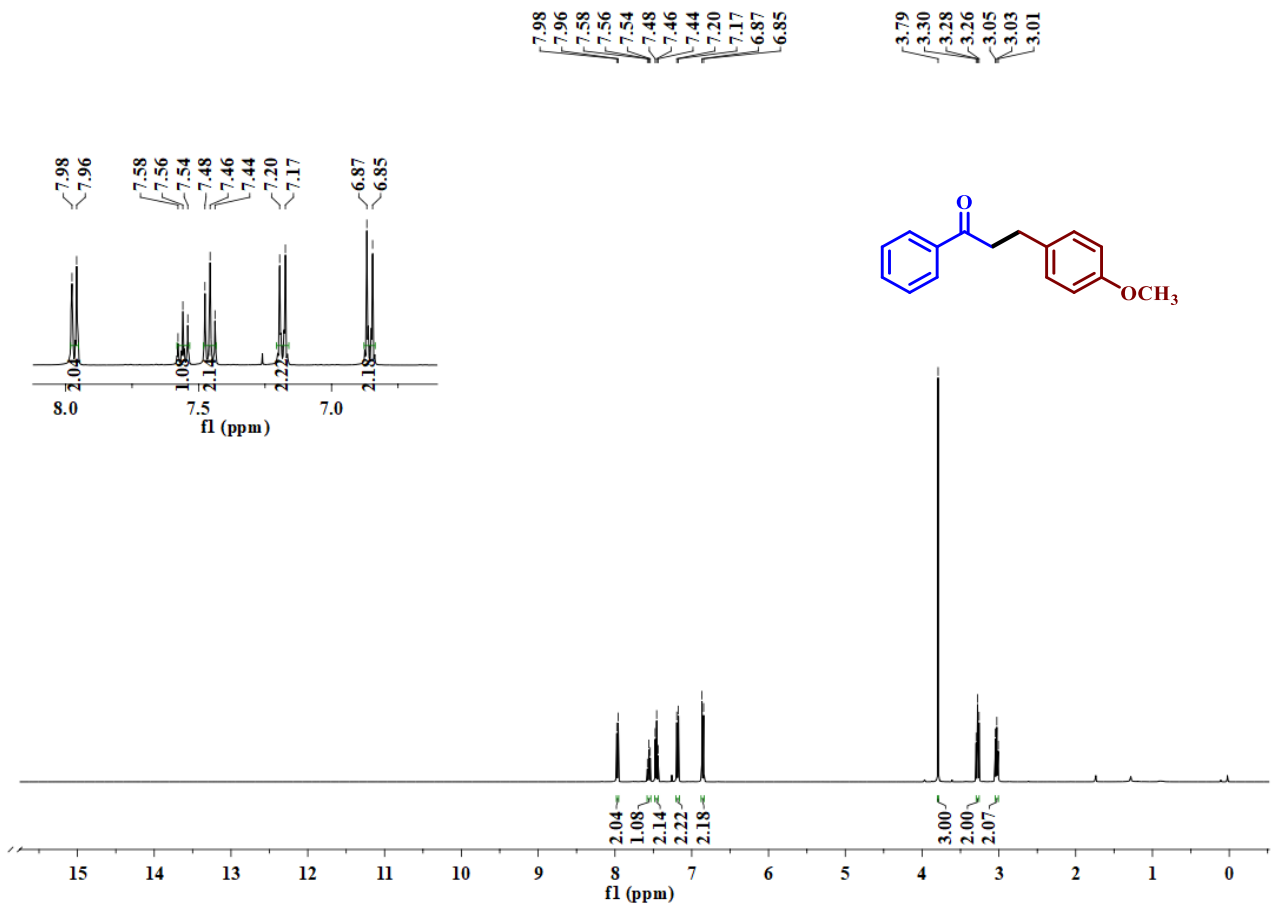


Figure S62. ^{1}H NMR spectrum of **5ba** taking $CDCl_3$ as solvent.

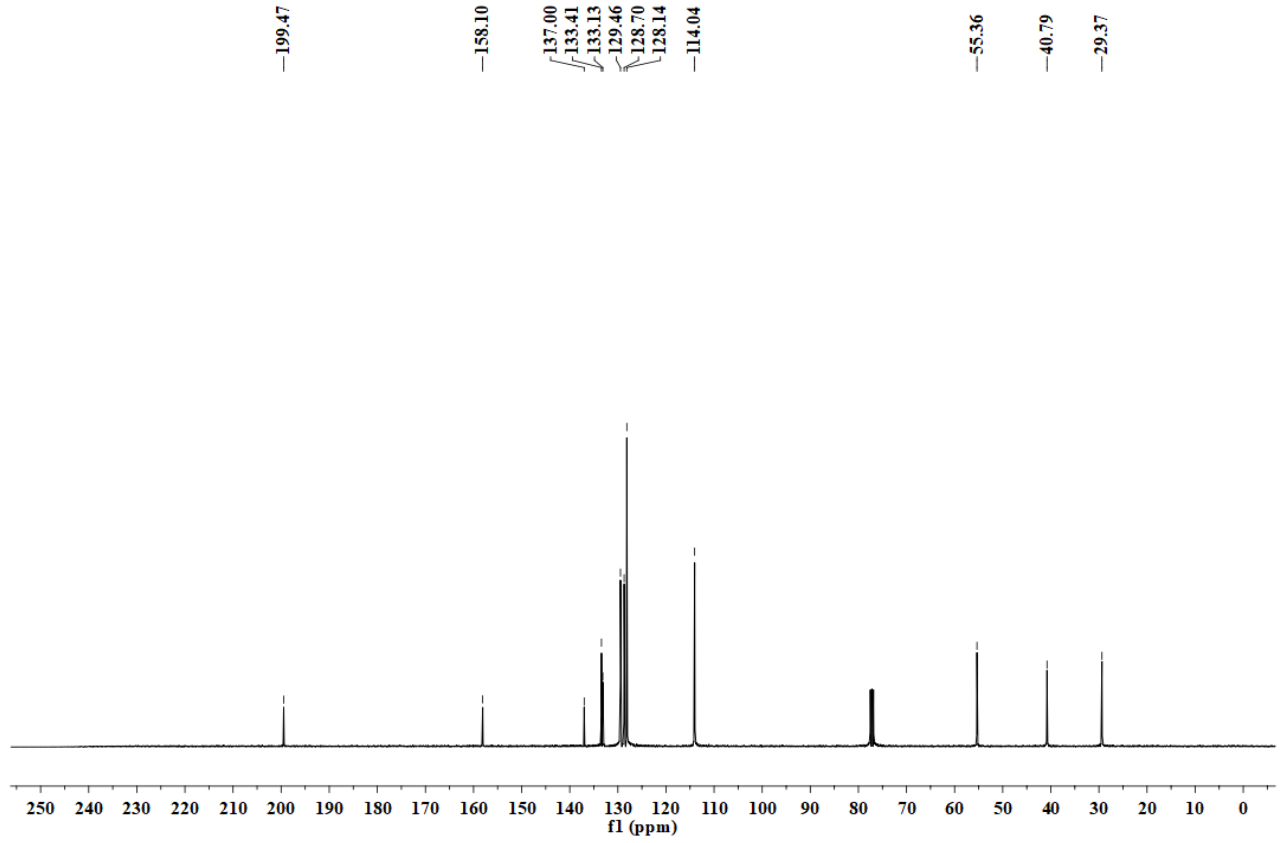


Figure S63. ^{13}CNMR spectrum of **5ba** taking $CDCl_3$ as solvent.

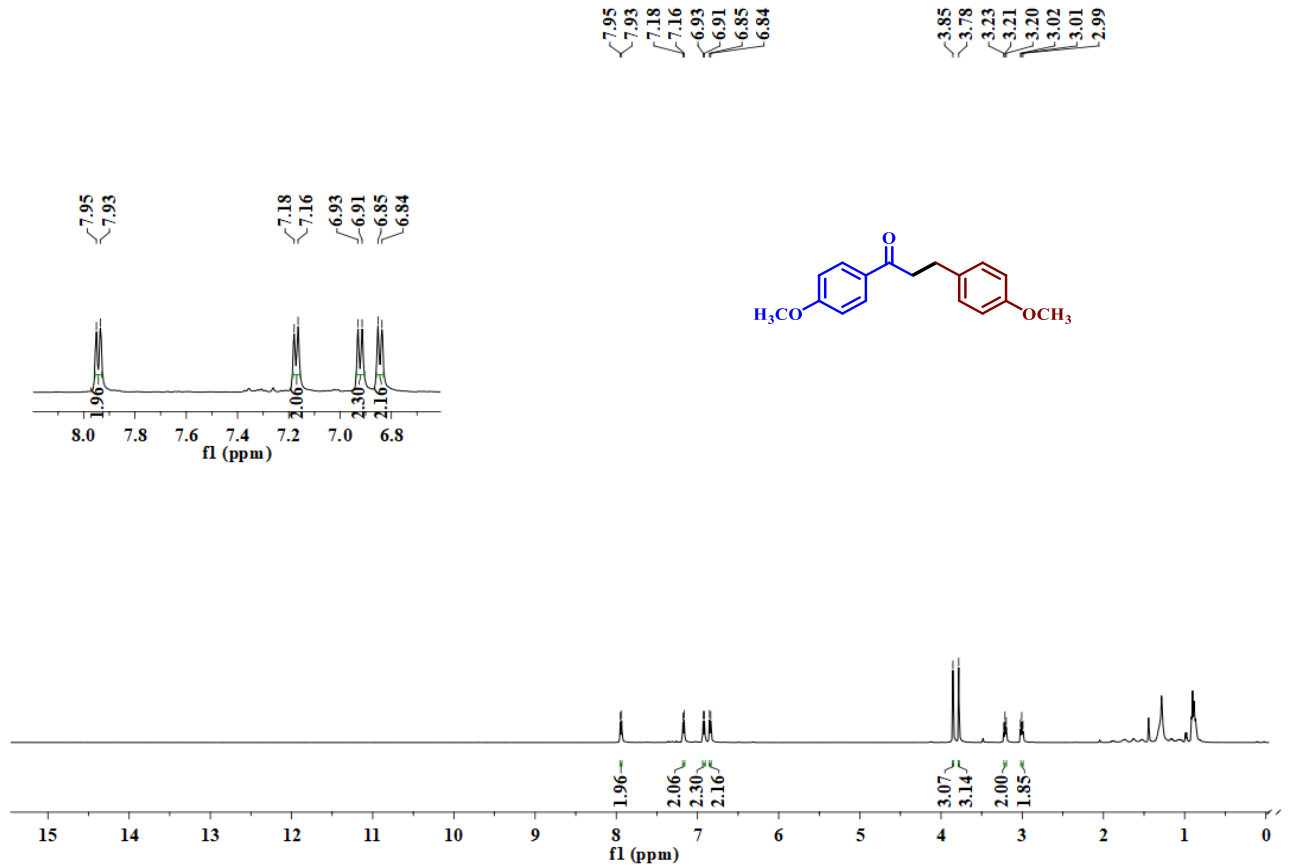


Figure S64. ^{1}H NMR spectrum of **5bb** taking $CDCl_3$ as solvent.

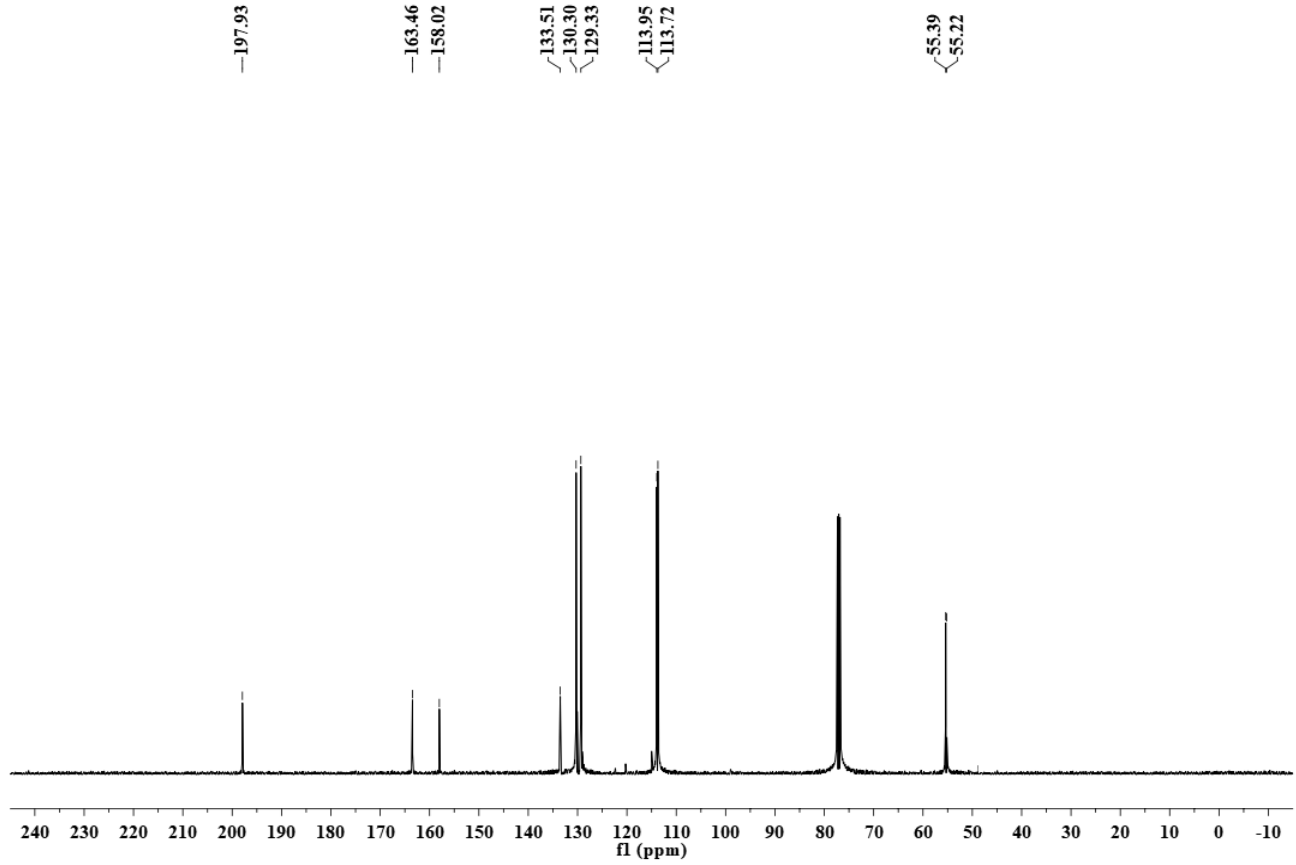


Figure S65. ^{13}CNMR spectrum of **5bb** taking $CDCl_3$ as solvent.

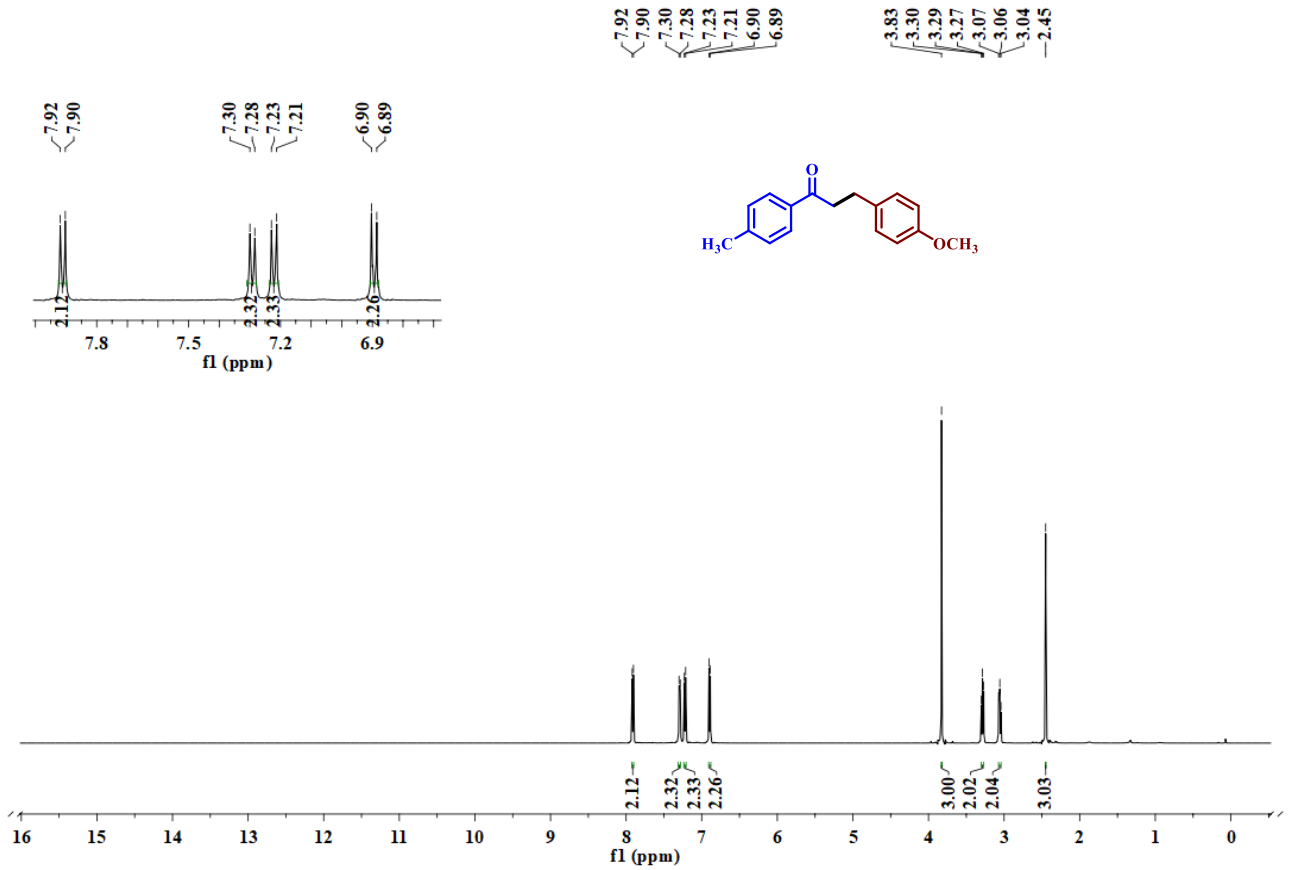


Figure S66. ^{1}H NMR spectrum of **5bc** taking $CDCl_3$ as solvent.

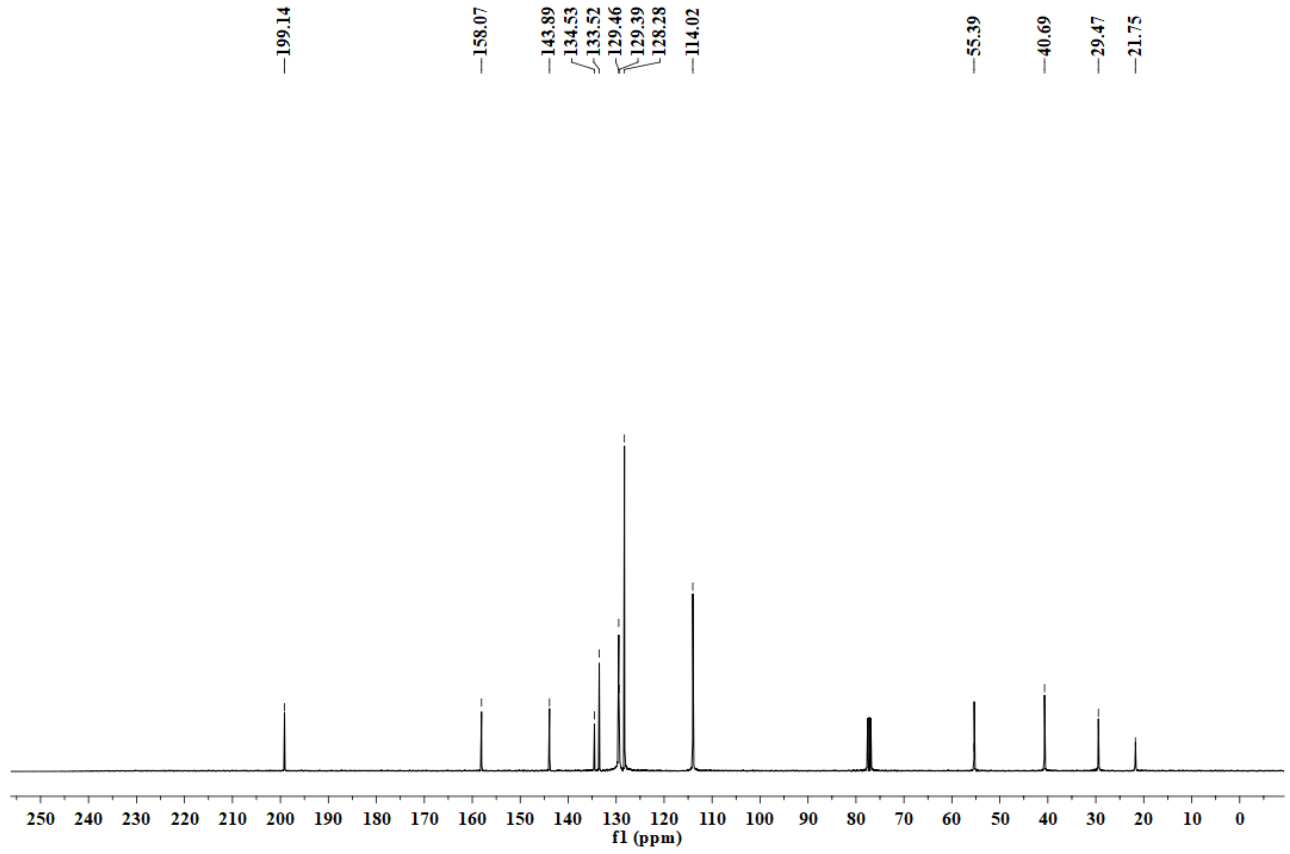


Figure S67. ^{13}CNMR spectrum of **5bc** taking $CDCl_3$ as solvent.

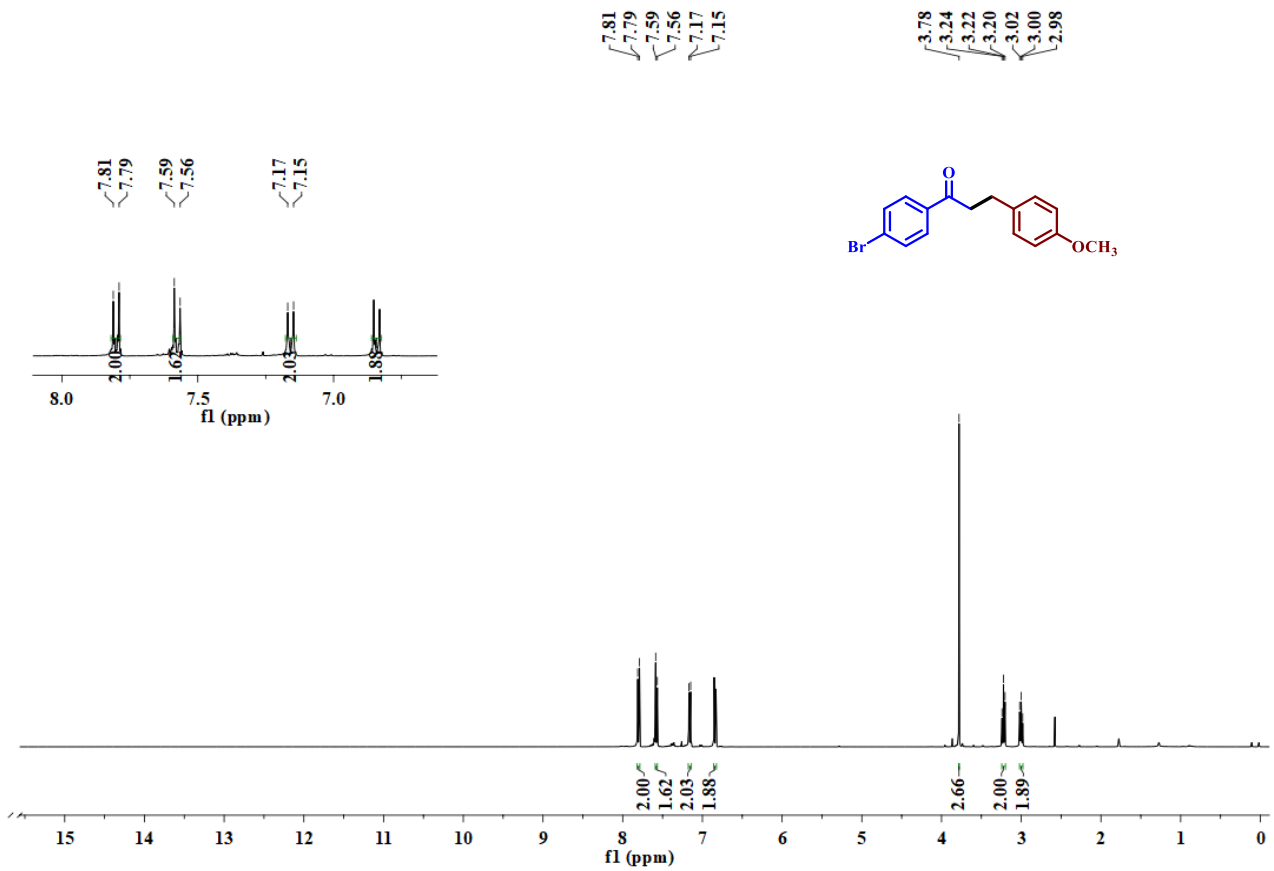


Figure S68. ^{1}H NMR spectrum of **5bd** taking $CDCl_3$ as solvent.

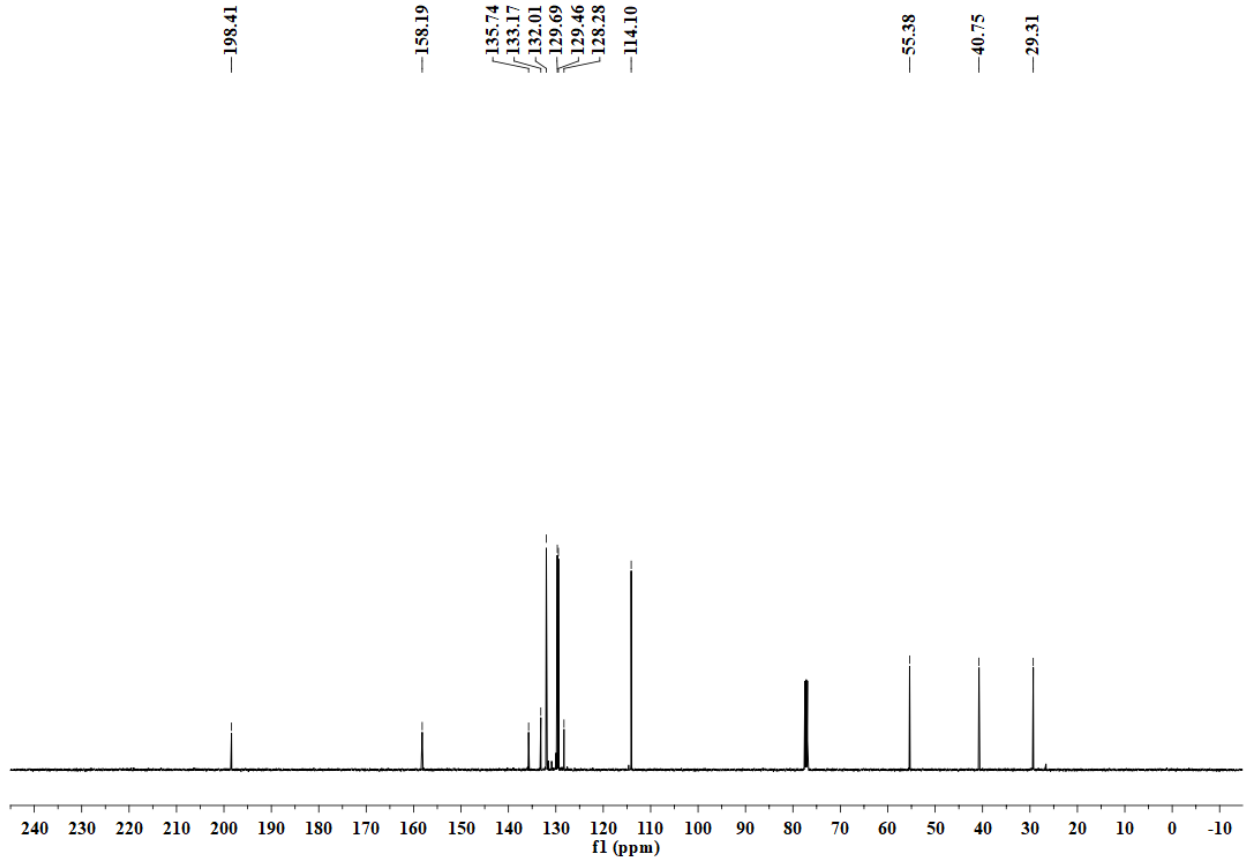


Figure S69. ^{13}CNMR spectrum of **5bd** taking $CDCl_3$ as solvent.

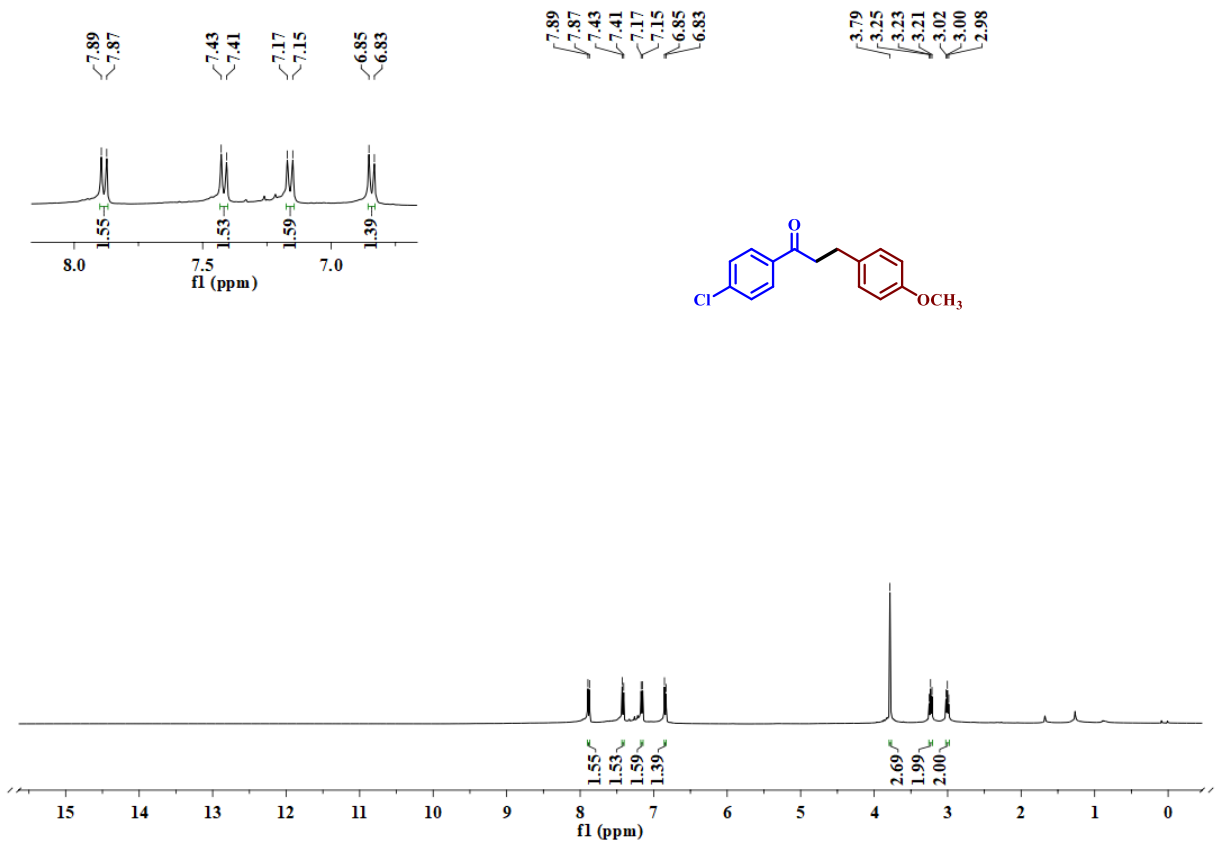


Figure S70. ^{1}H NMR spectrum of **5be** taking $CDCl_3$ as solvent.

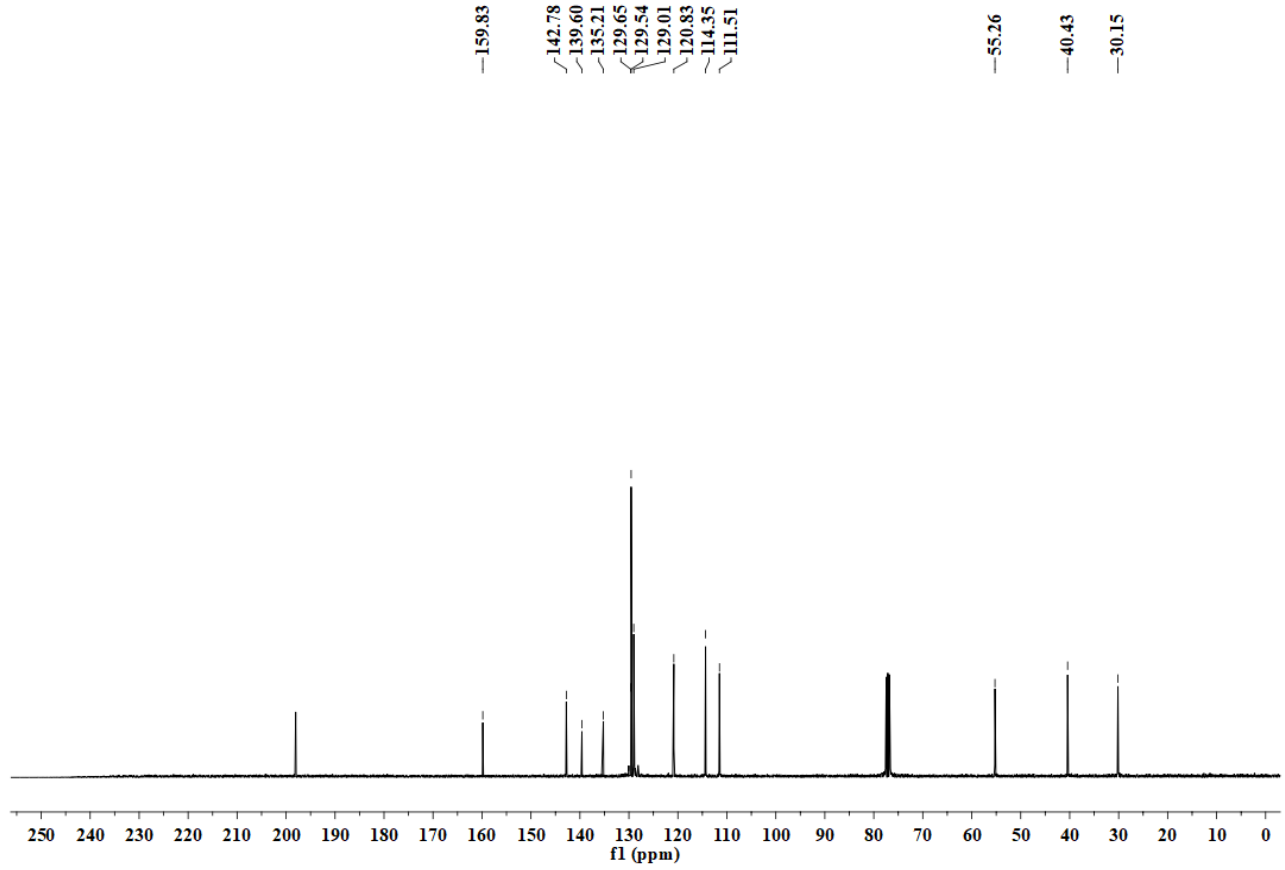


Figure S71. ^{13}CNMR spectrum of **5be** taking $CDCl_3$ as solvent.

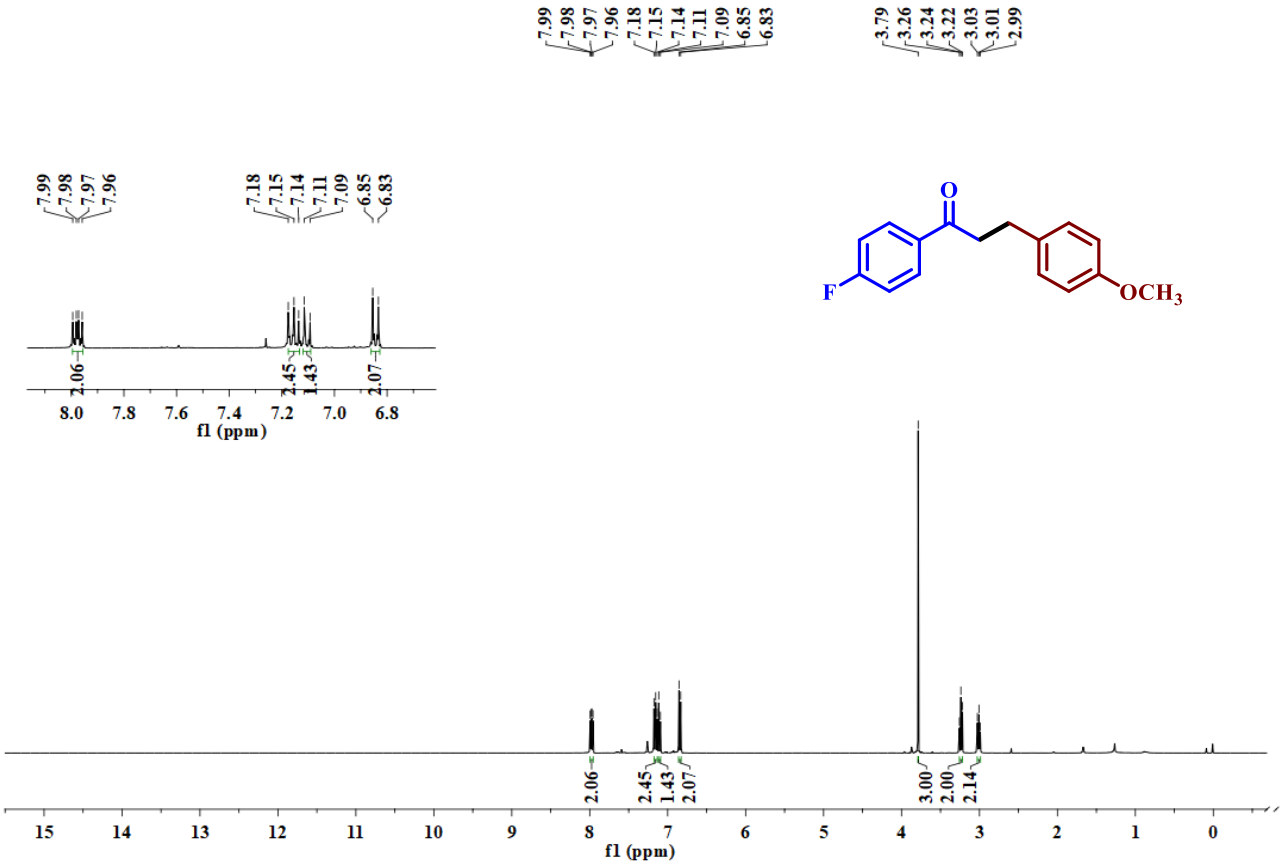


Figure S72. ^{1}H NMR spectrum of **5bf** taking $CDCl_3$ as solvent.

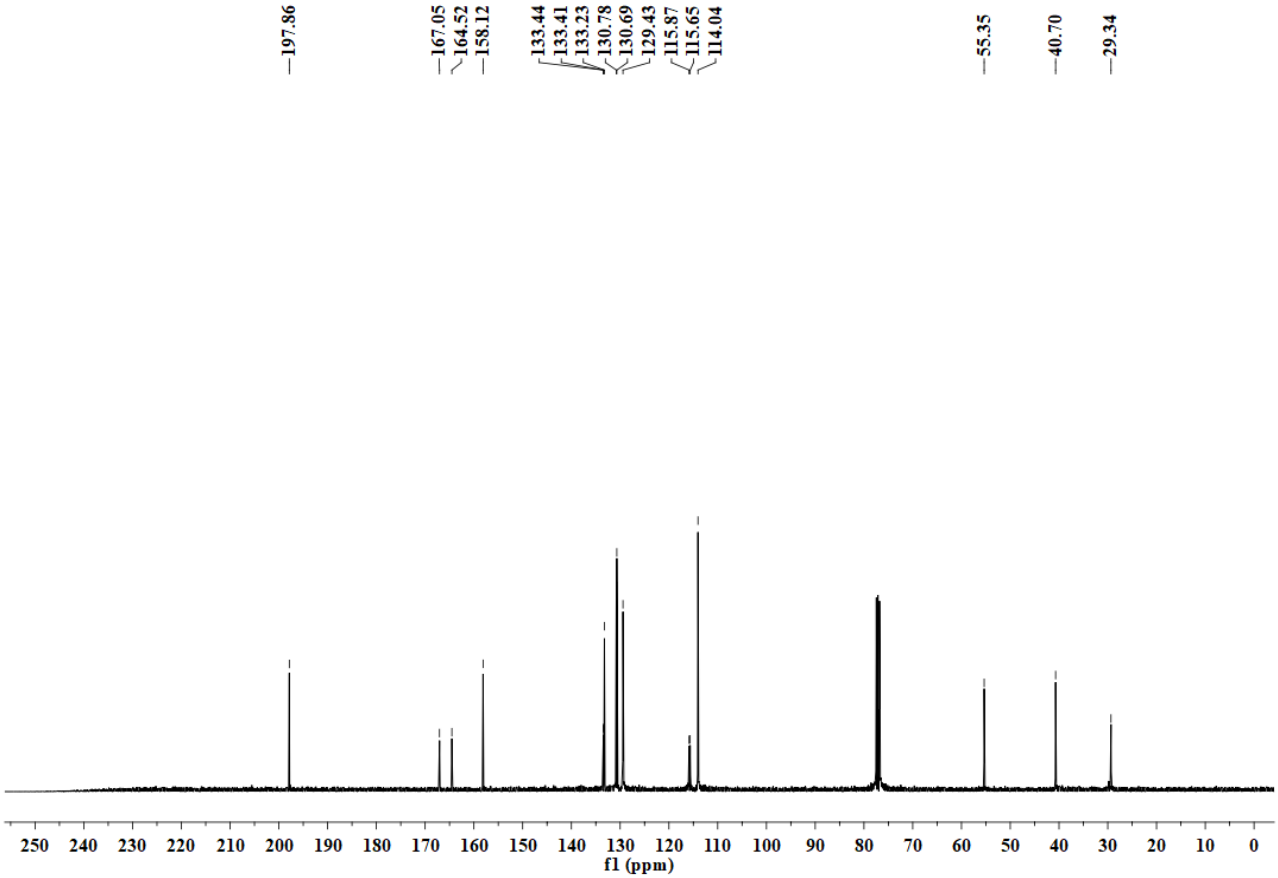


Figure S73. ^{13}CNMR spectrum of **5bf** taking $CDCl_3$ as solvent.

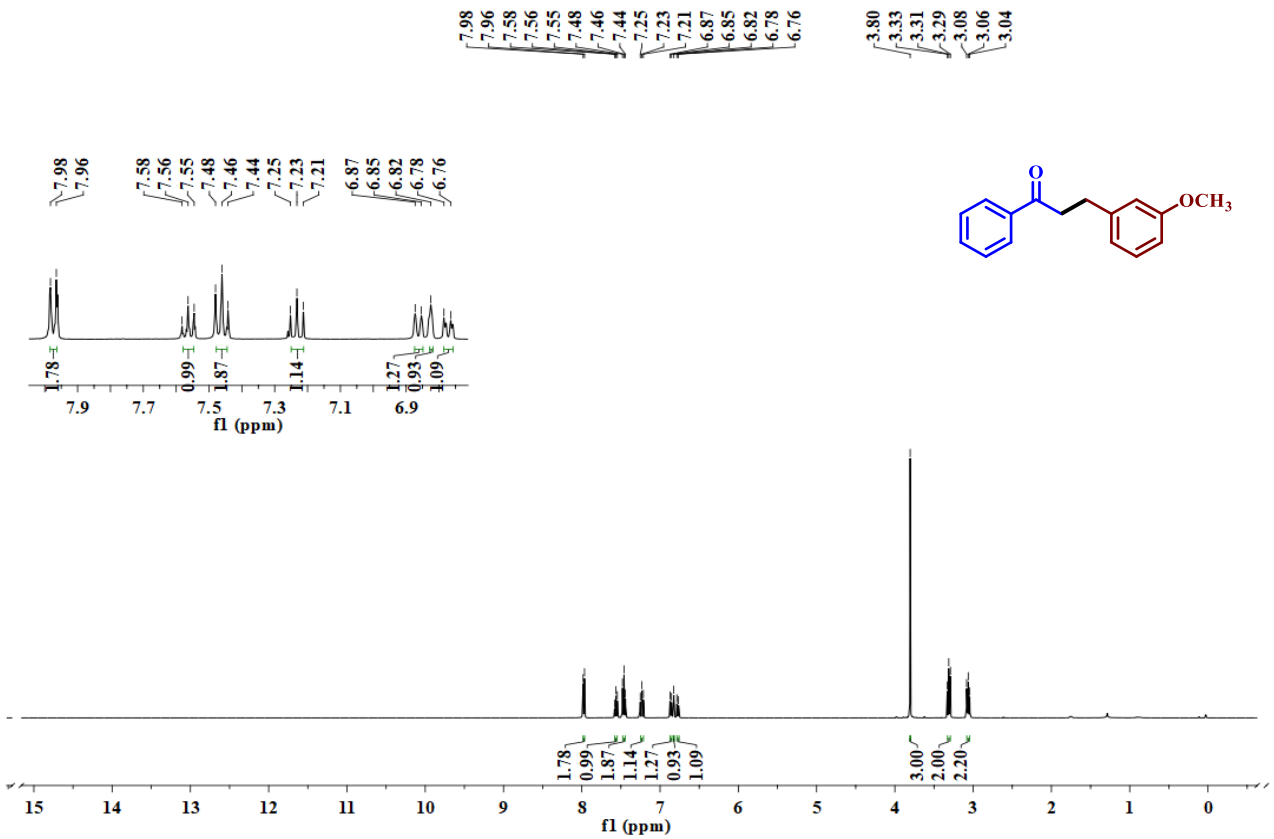


Figure S74. ^{1}H NMR spectrum of **5ca** taking $CDCl_3$ as solvent.

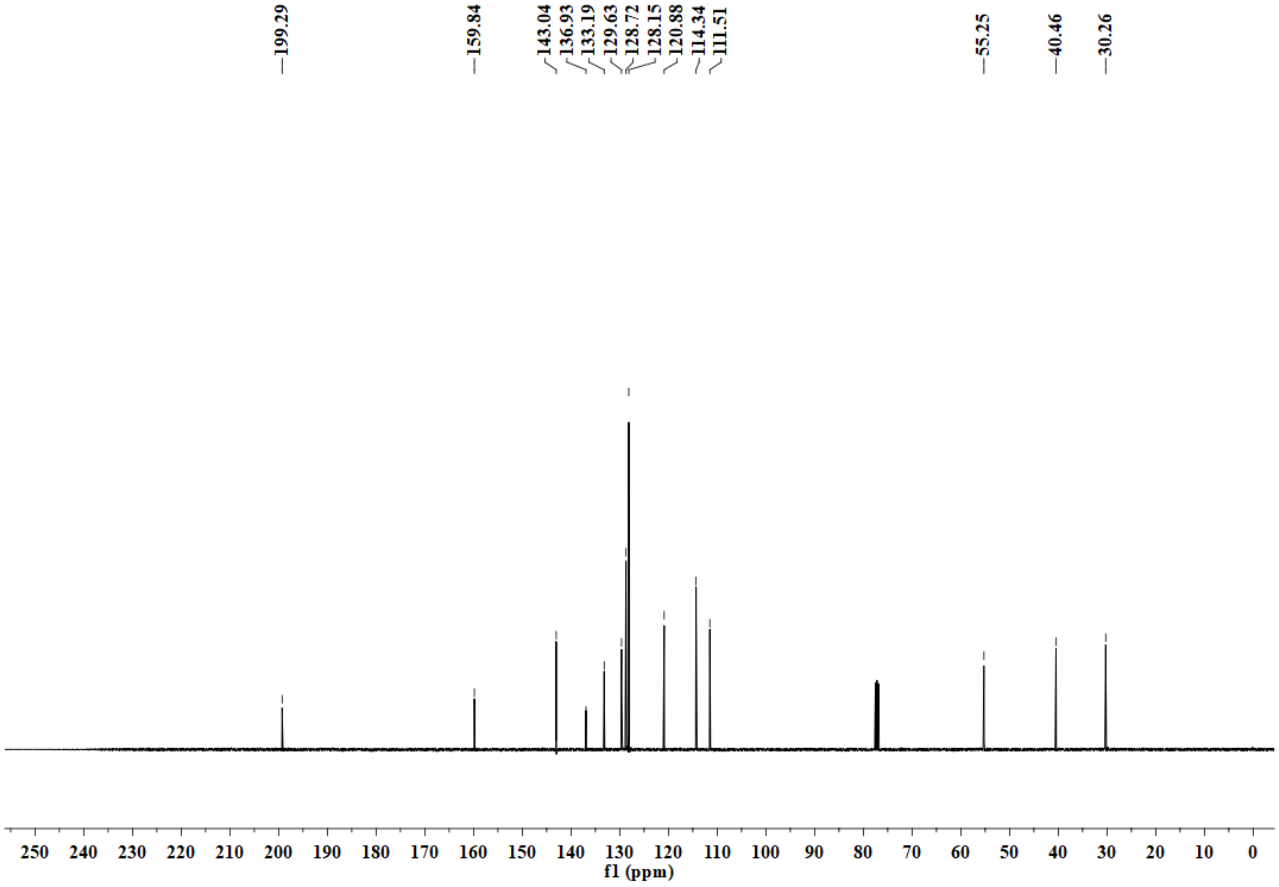


Figure S75. ^{13}CNMR spectrum of **5ca** taking $CDCl_3$ as solvent.

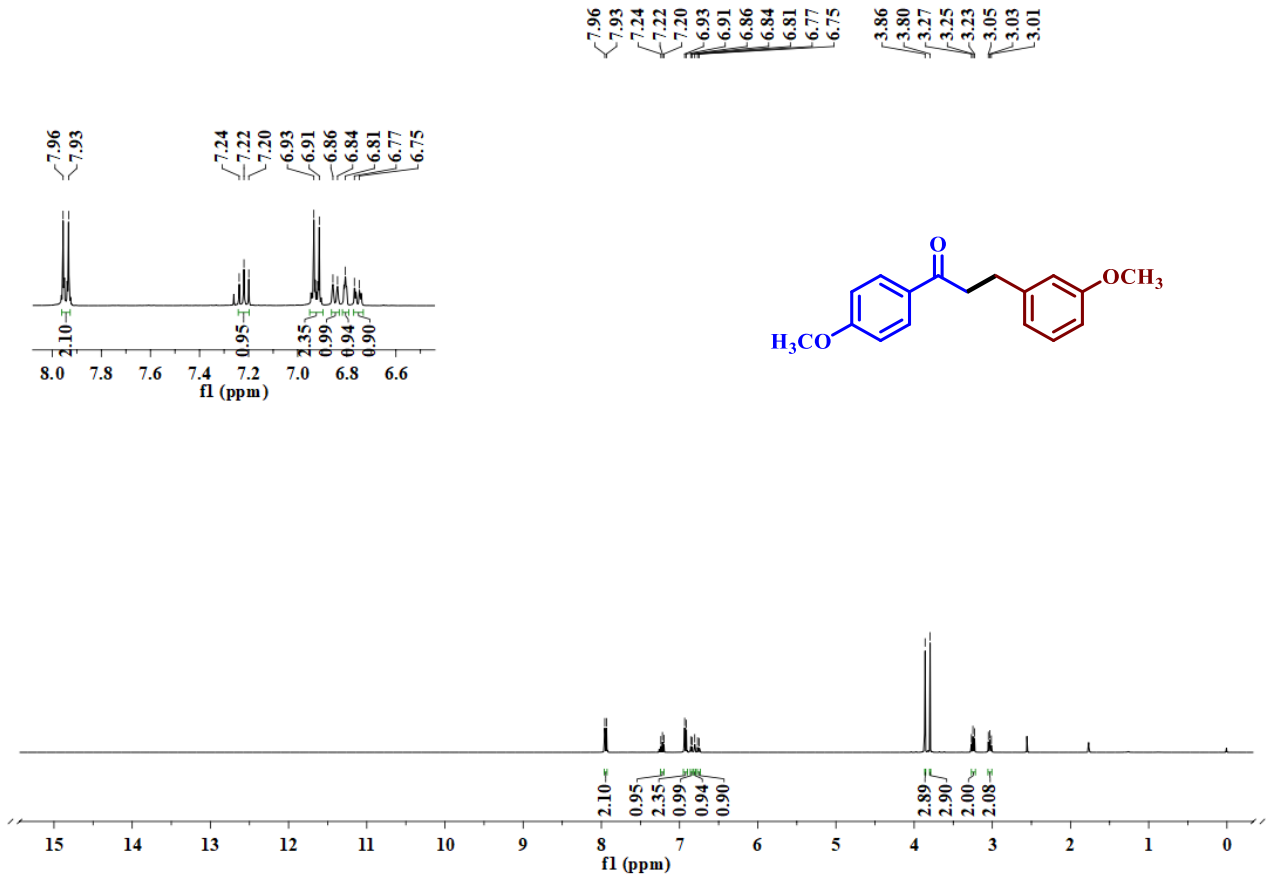


Figure S76. ^{1}H NMR spectrum of **5cb** taking $CDCl_3$ as solvent.

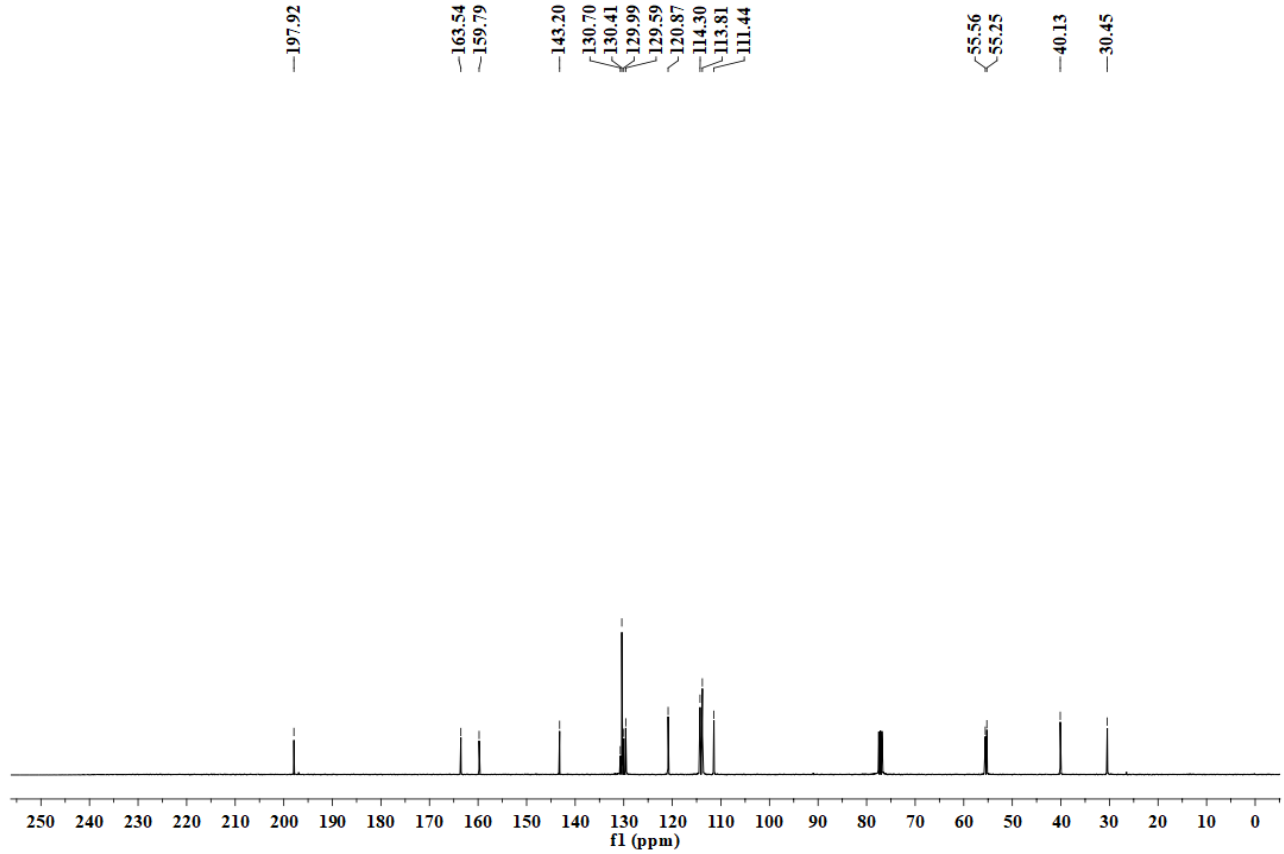


Figure S77. ^{13}CNMR spectrum of **5cb** taking $CDCl_3$ as solvent.

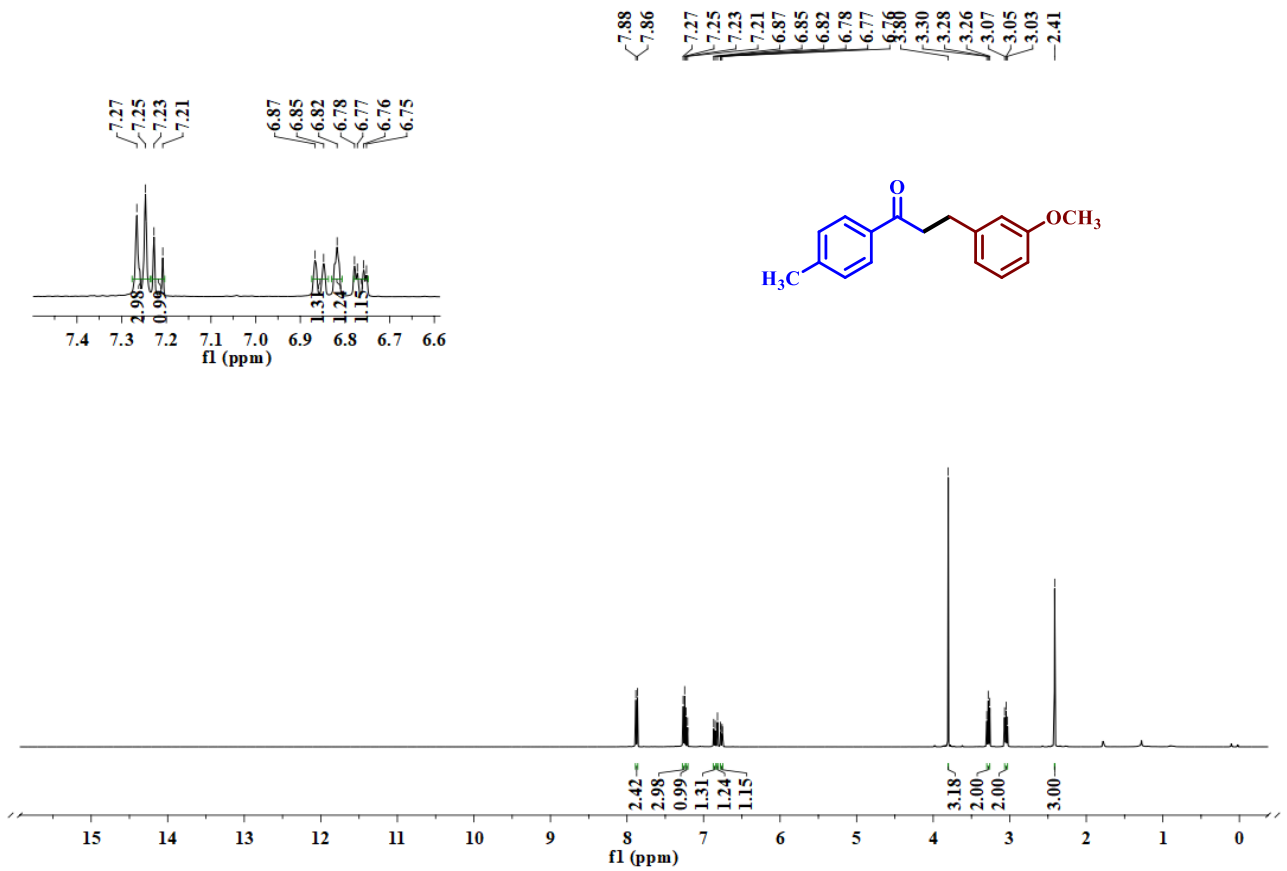


Figure S78. ^{1}H NMR spectrum of **5cc** taking $CDCl_3$ as solvent.

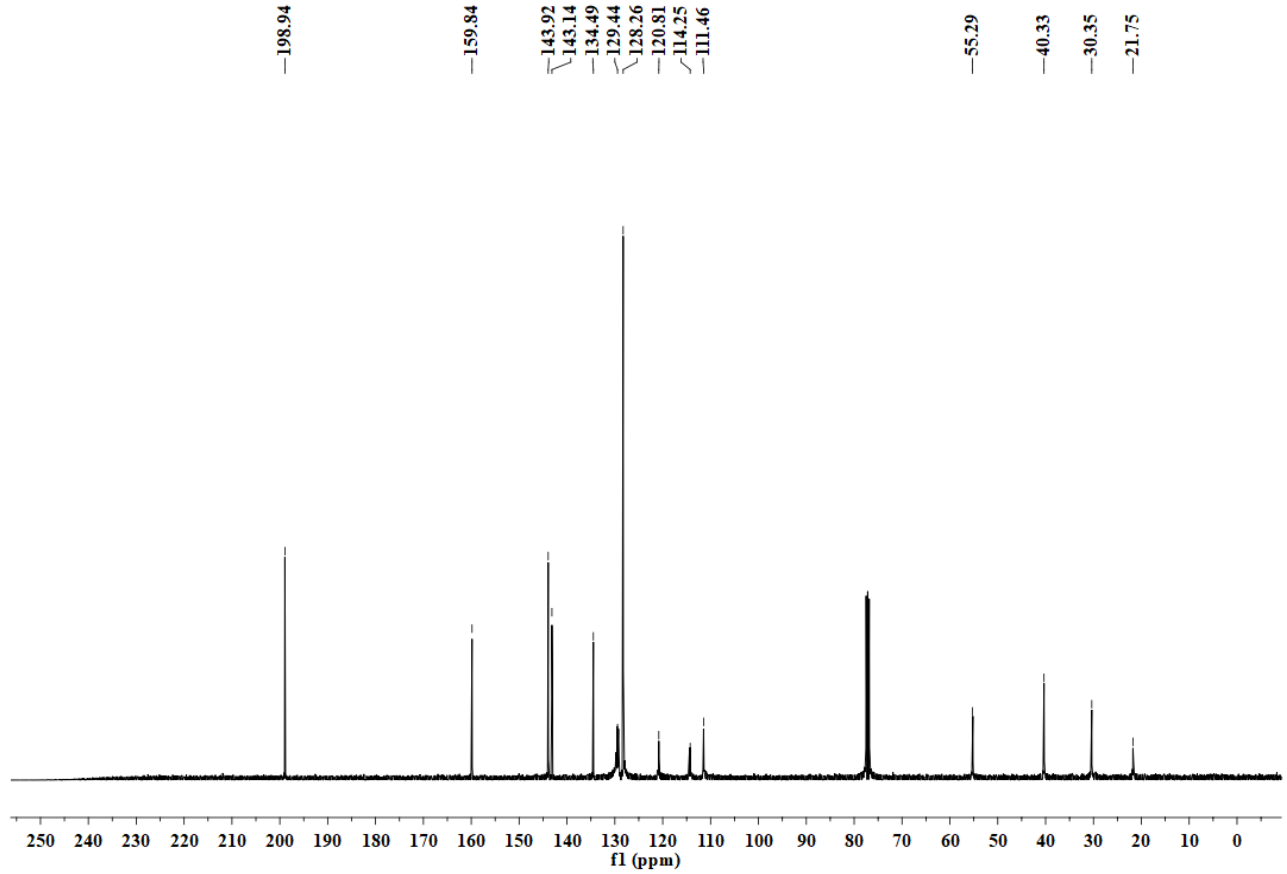


Figure S79. ^{13}CNMR spectrum of **5cc** taking $CDCl_3$ as solvent.

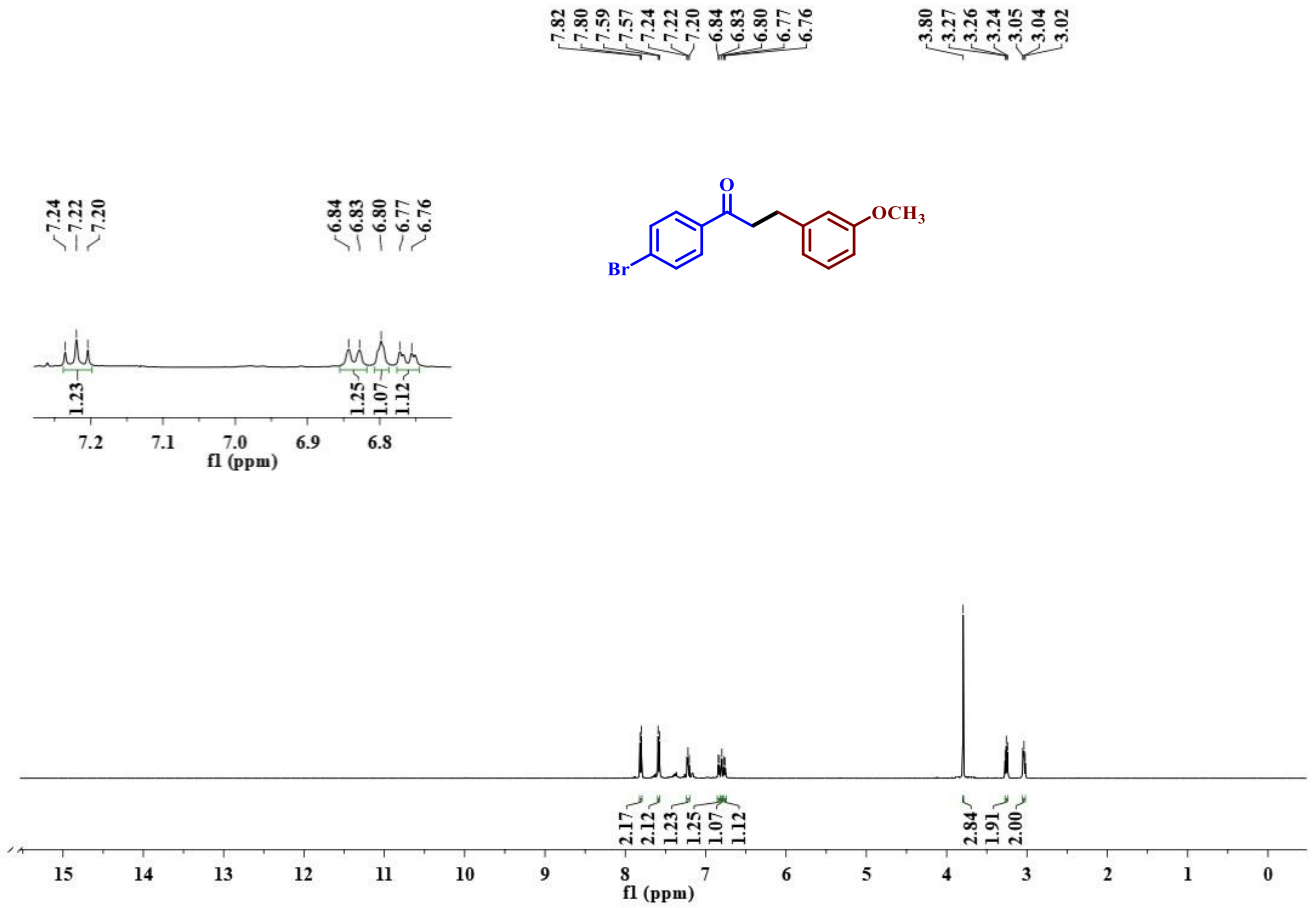


Figure S80. ^{1}H NMR spectrum of **5cd** taking $CDCl_3$ as solvent.

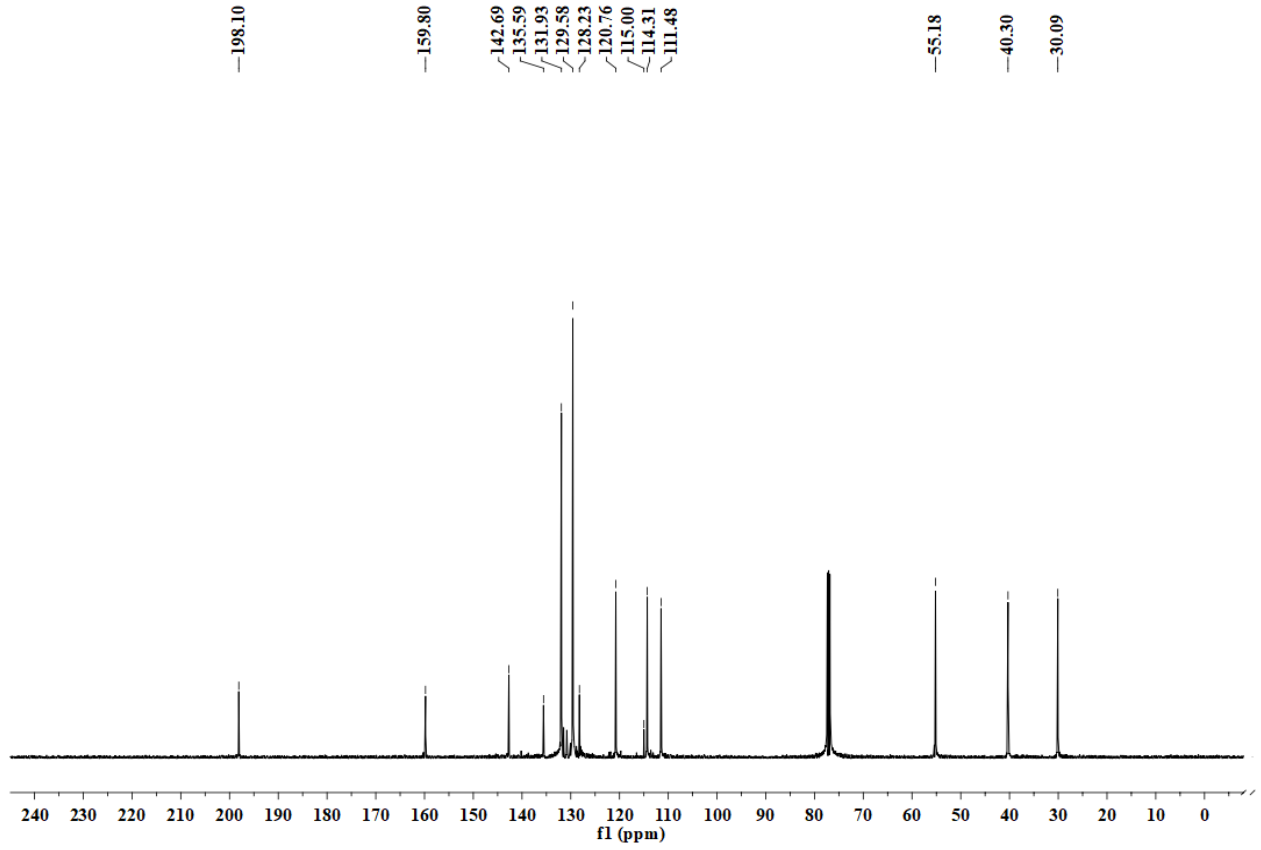


Figure S81. ^{13}CNMR spectrum of **5cd** taking $CDCl_3$ as solvent.

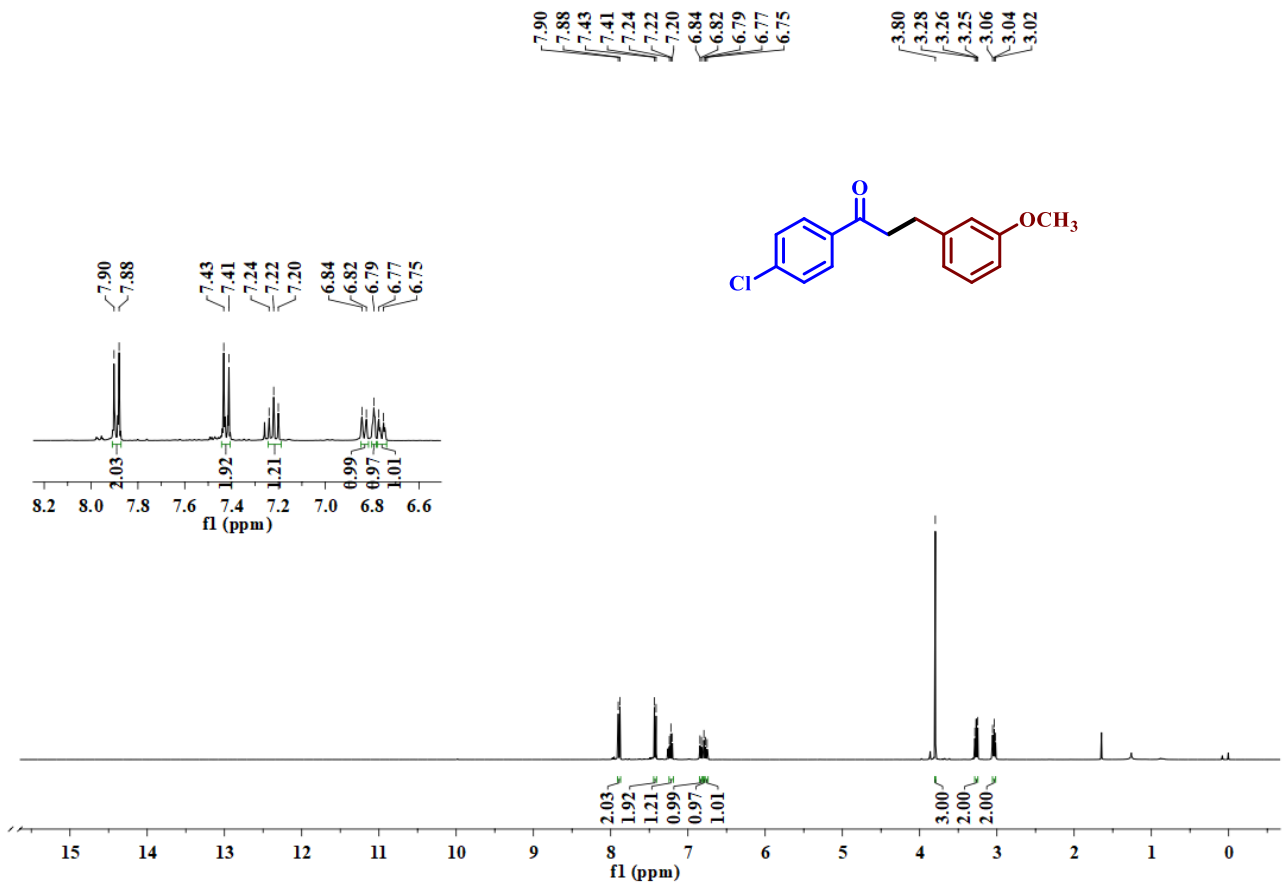


Figure S82. ^{1}H NMR spectrum of **5ce** taking $CDCl_3$ as solvent.

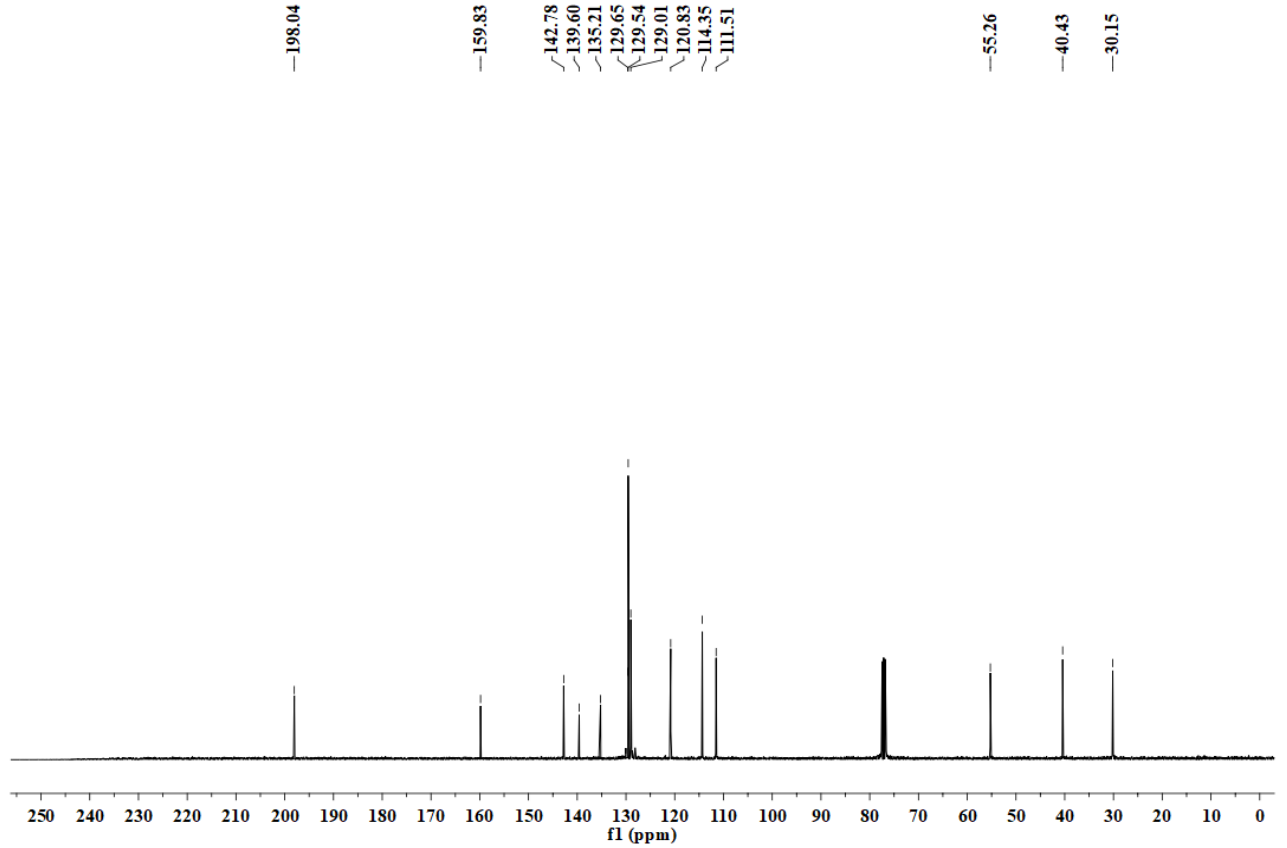


Figure S83. ^{13}CNMR spectrum of **5ce** taking $CDCl_3$ as solvent.

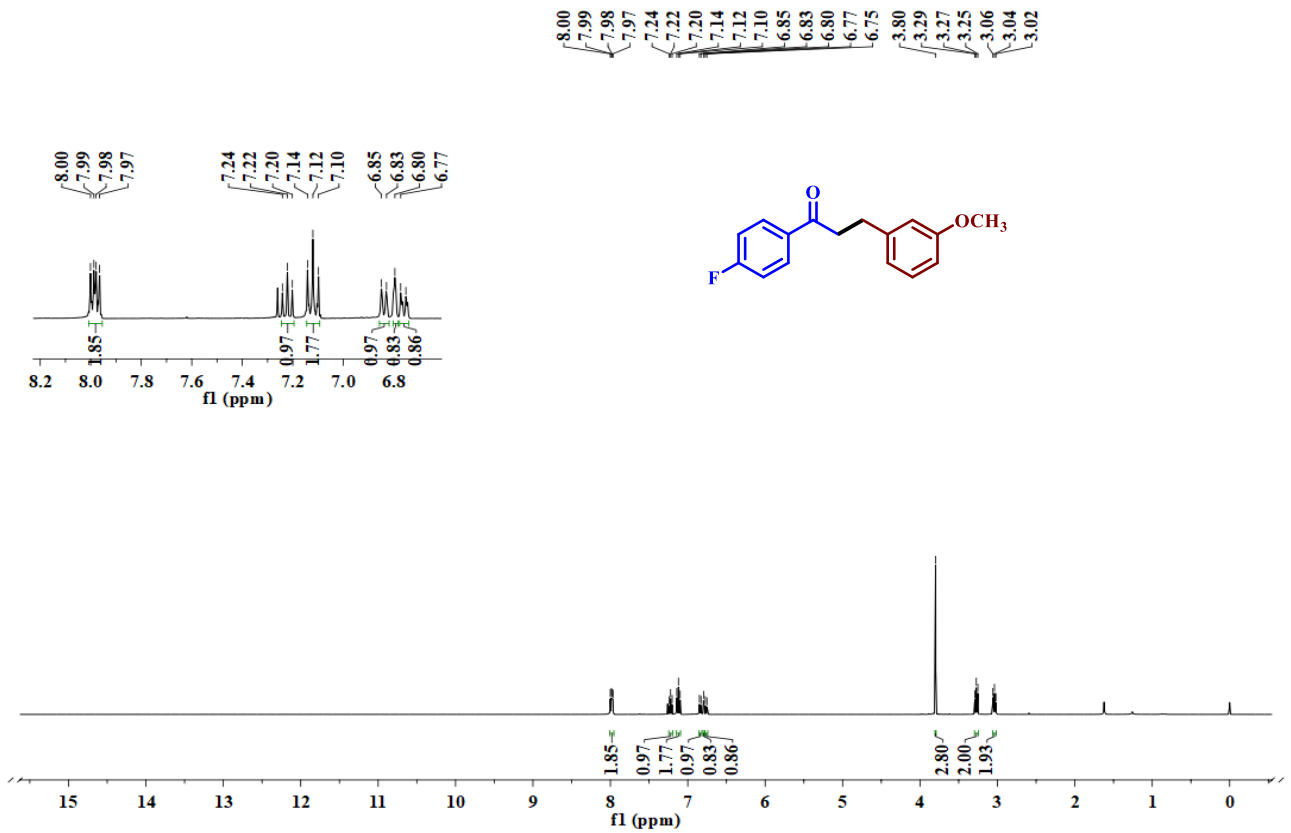


Figure S84. ^{1}H NMR spectrum of **5cf** taking $CDCl_3$ as solvent.

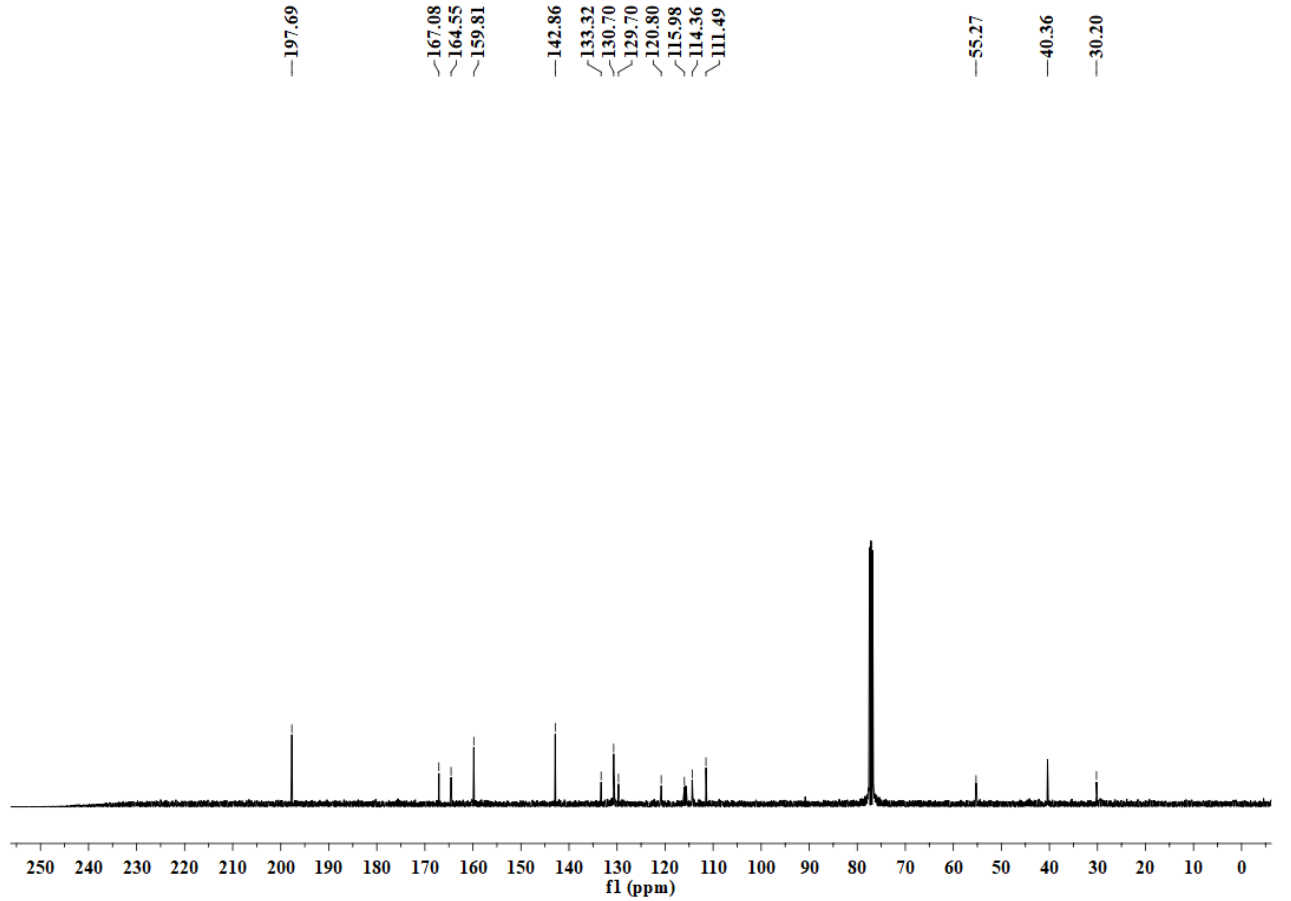


Figure S85. ^{13}CNMR spectrum of **5cf** taking $CDCl_3$ as solvent.

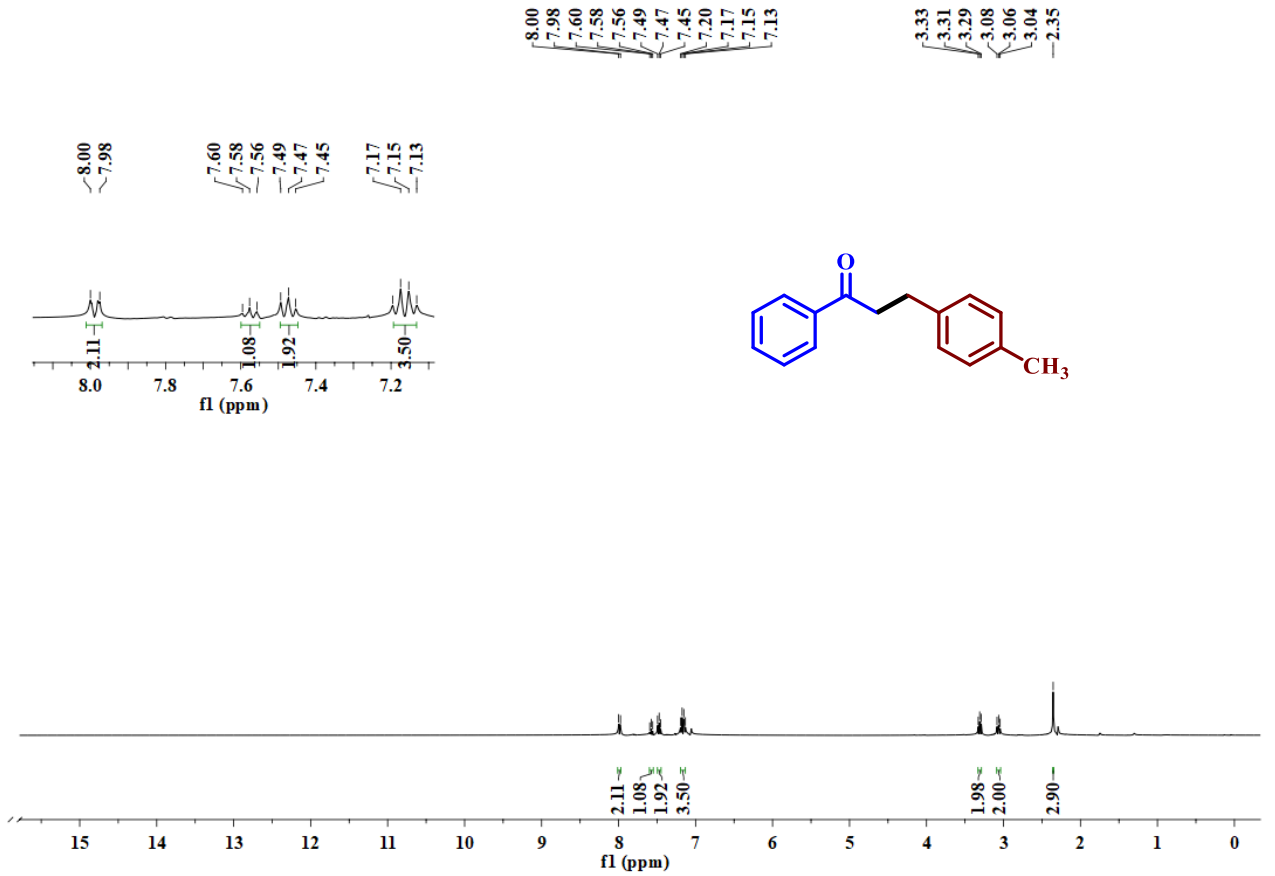


Figure S86. ^{1}H NMR spectrum of **5da** taking $CDCl_3$ as solvent.

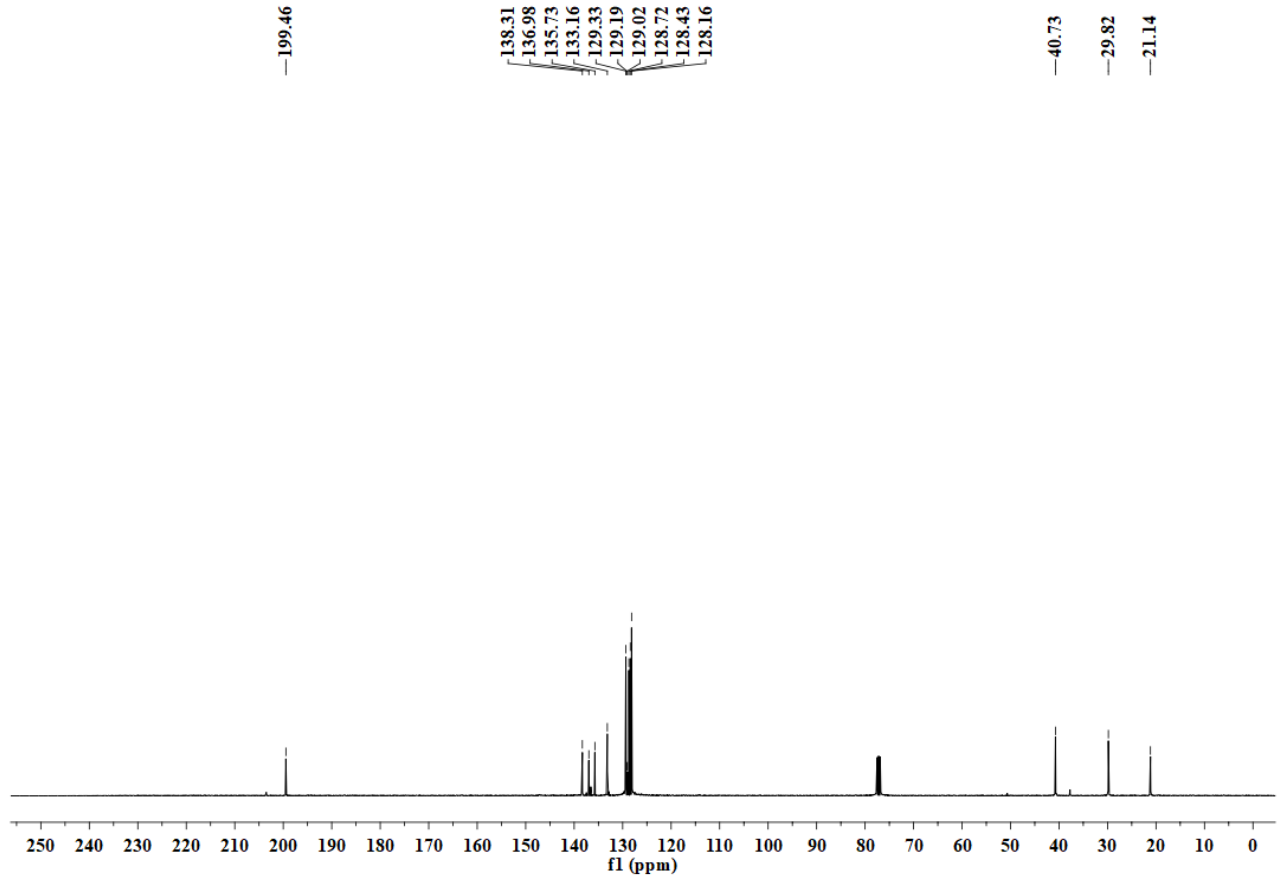


Figure S87. ^{13}CNMR spectrum of **5da** taking $CDCl_3$ as solvent.

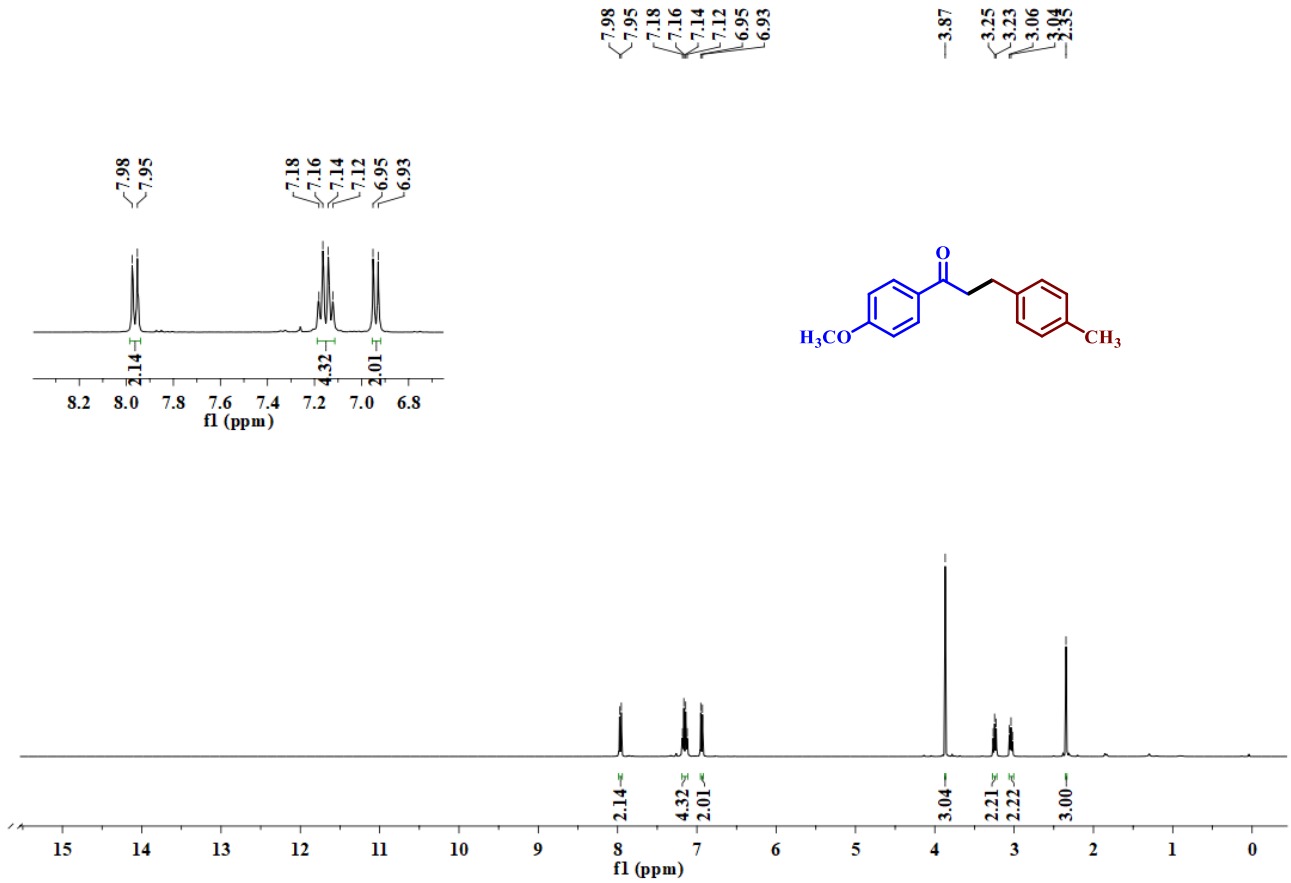


Figure S88. ^{1}H NMR spectrum of **5db** taking $CDCl_3$ as solvent.

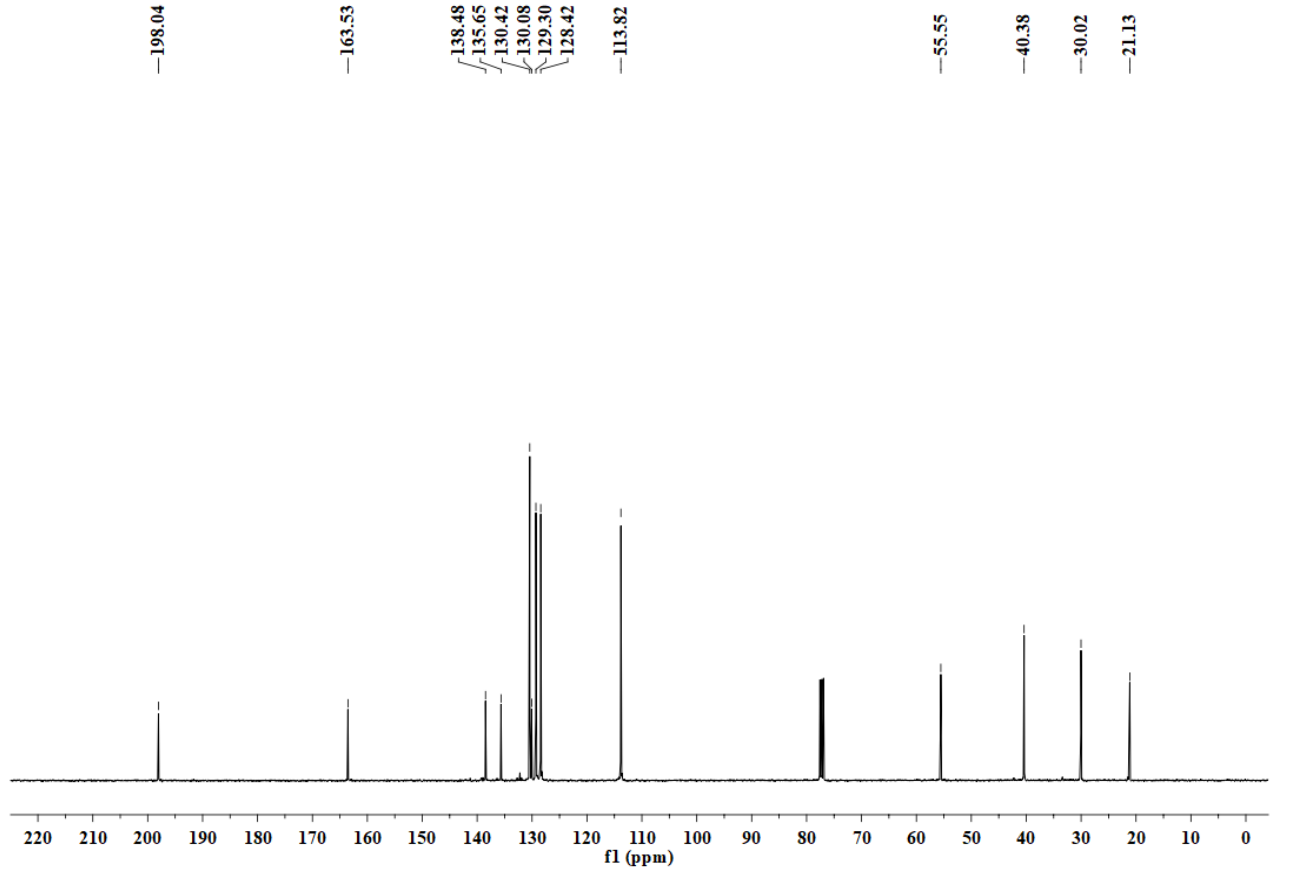


Figure S89. ^{13}CNMR spectrum of **5db** taking $CDCl_3$ as solvent.

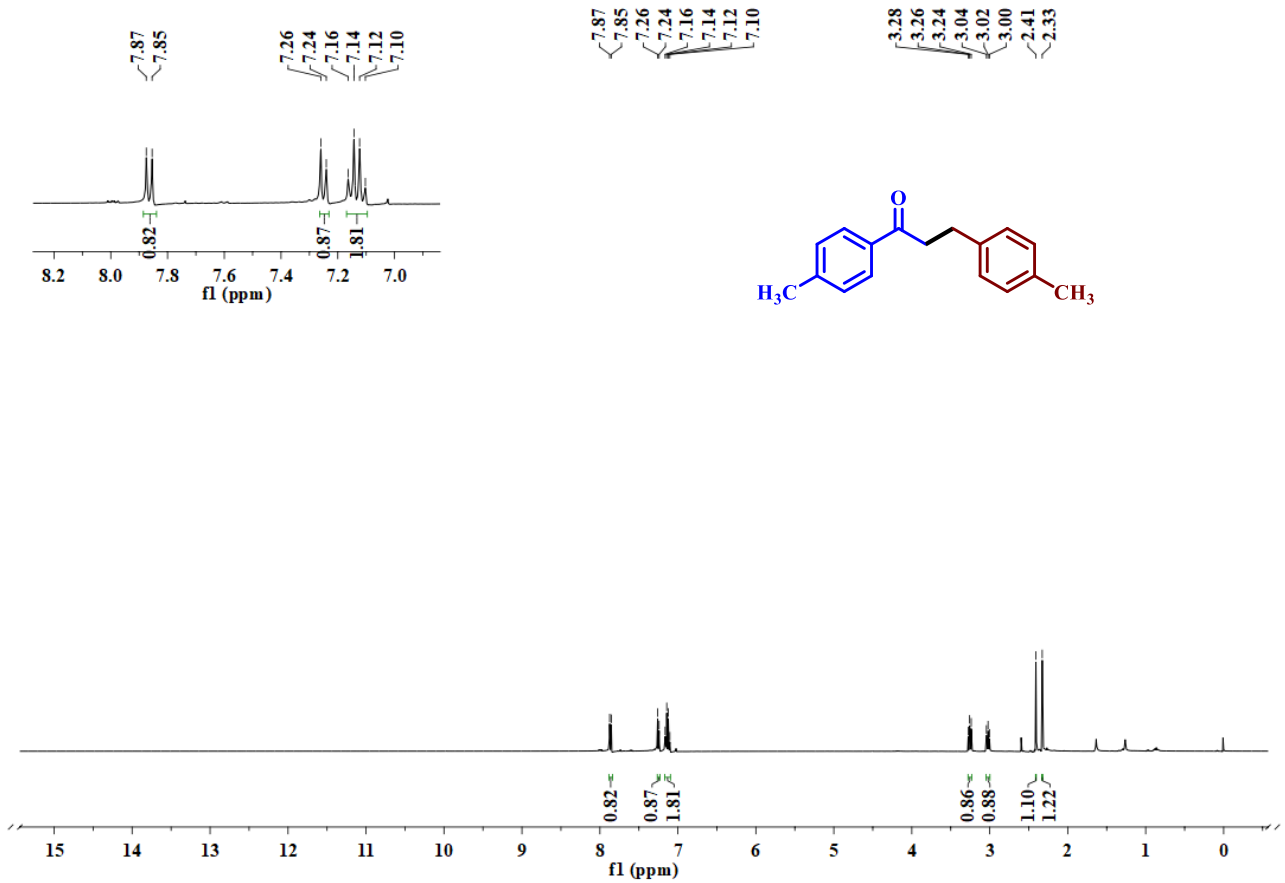


Figure S90. ^{1}H NMR spectrum of **5dc** taking $CDCl_3$ as solvent.

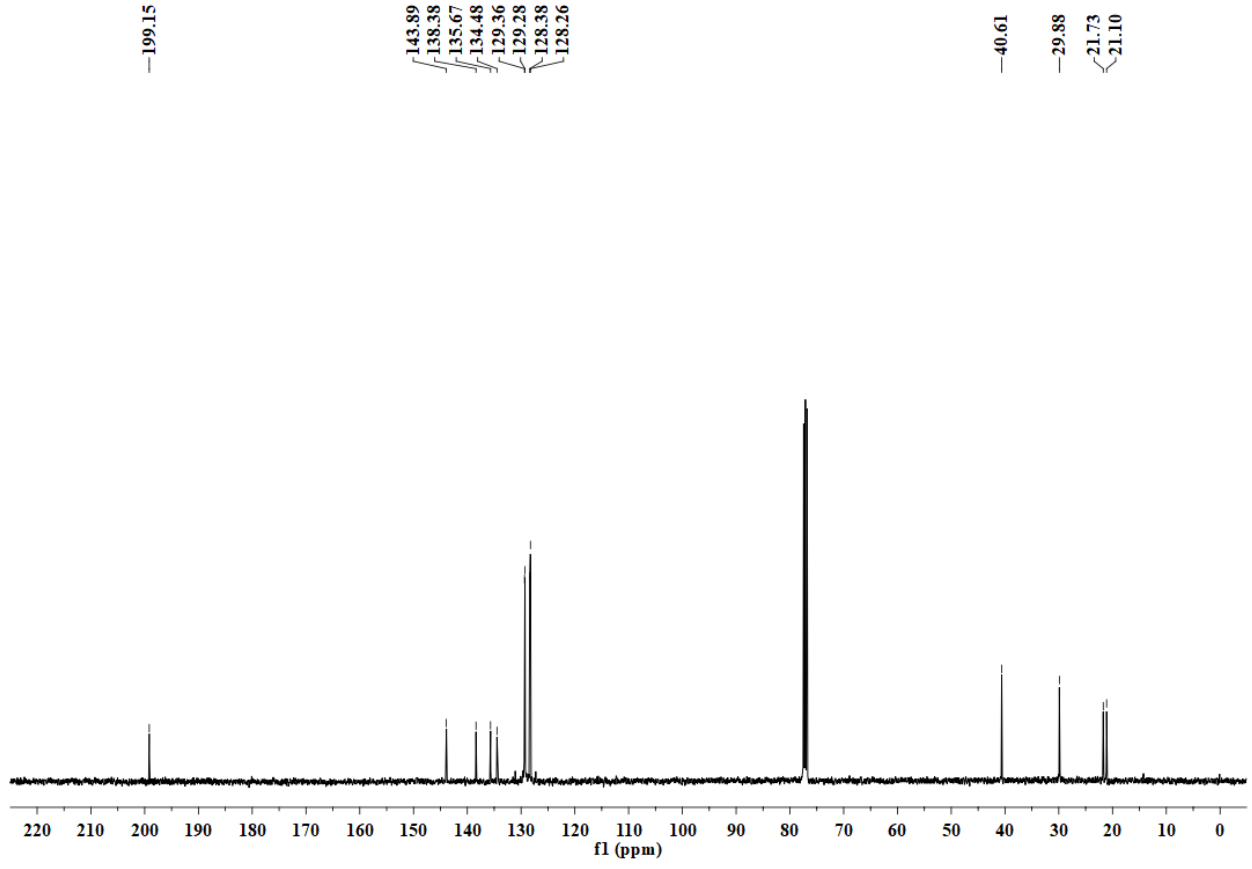


Figure S91. ^{13}CNMR spectrum of **5dc** taking $CDCl_3$ as solvent.

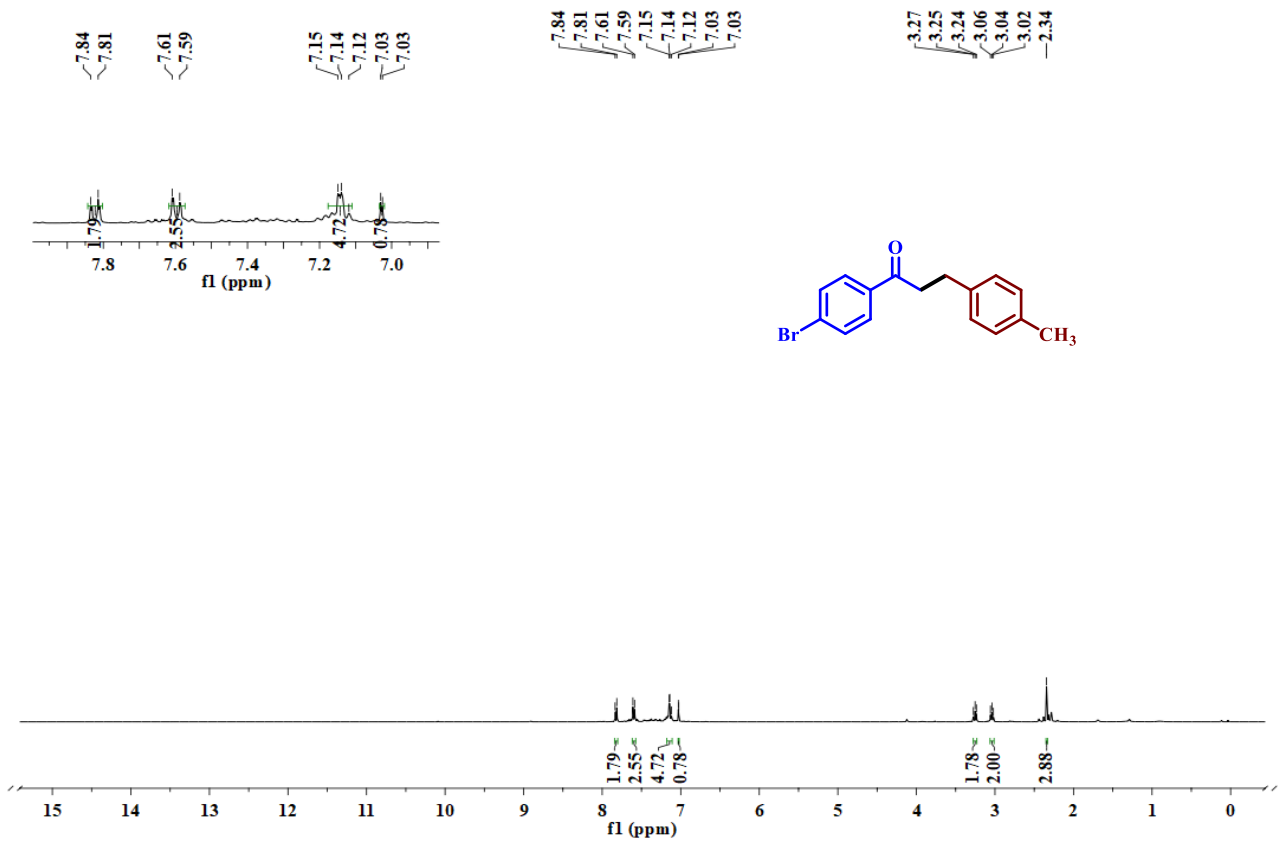


Figure S92. ^{1}H NMR spectrum of **5dd** taking $CDCl_3$ as solvent.

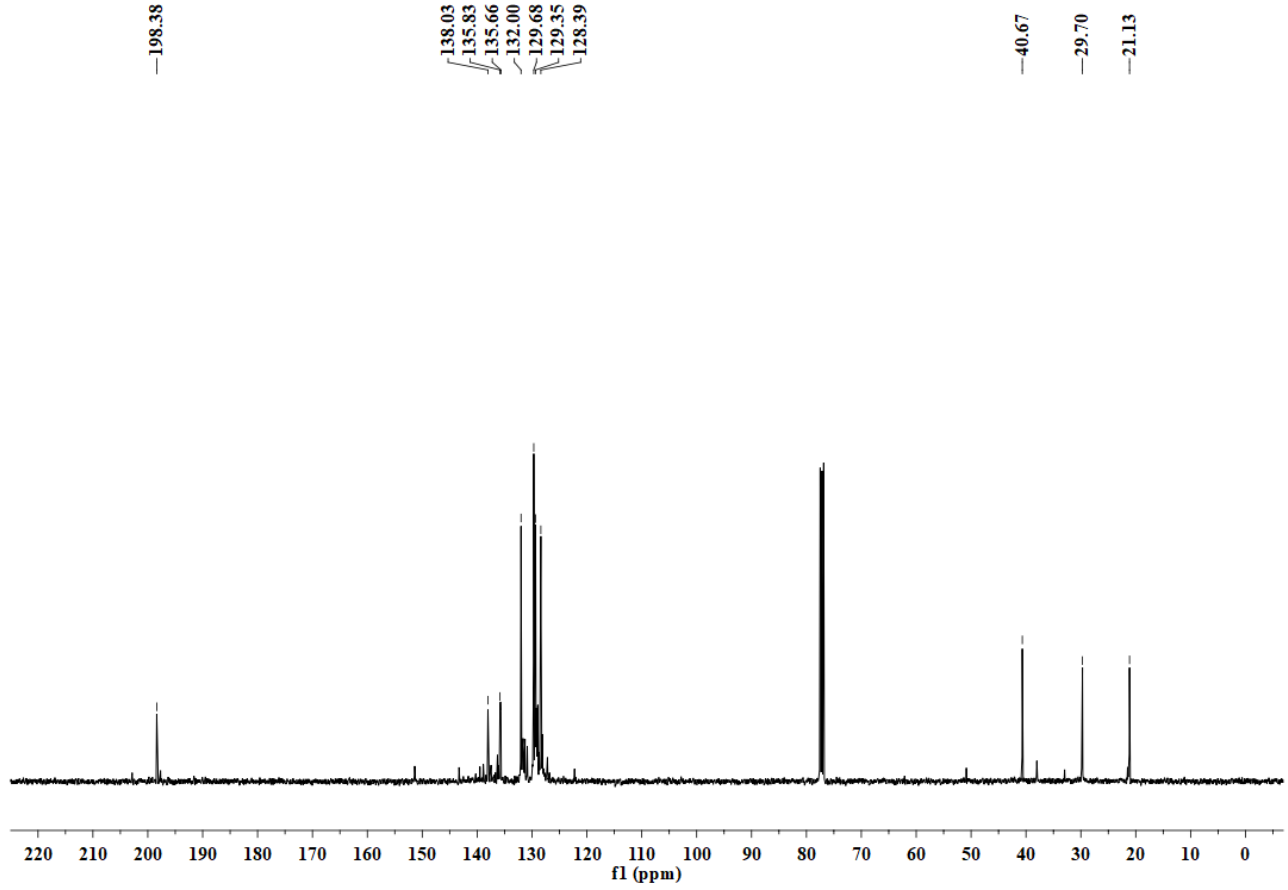


Figure S93. ^{13}CNMR spectrum of **5dd** taking $CDCl_3$ as solvent.

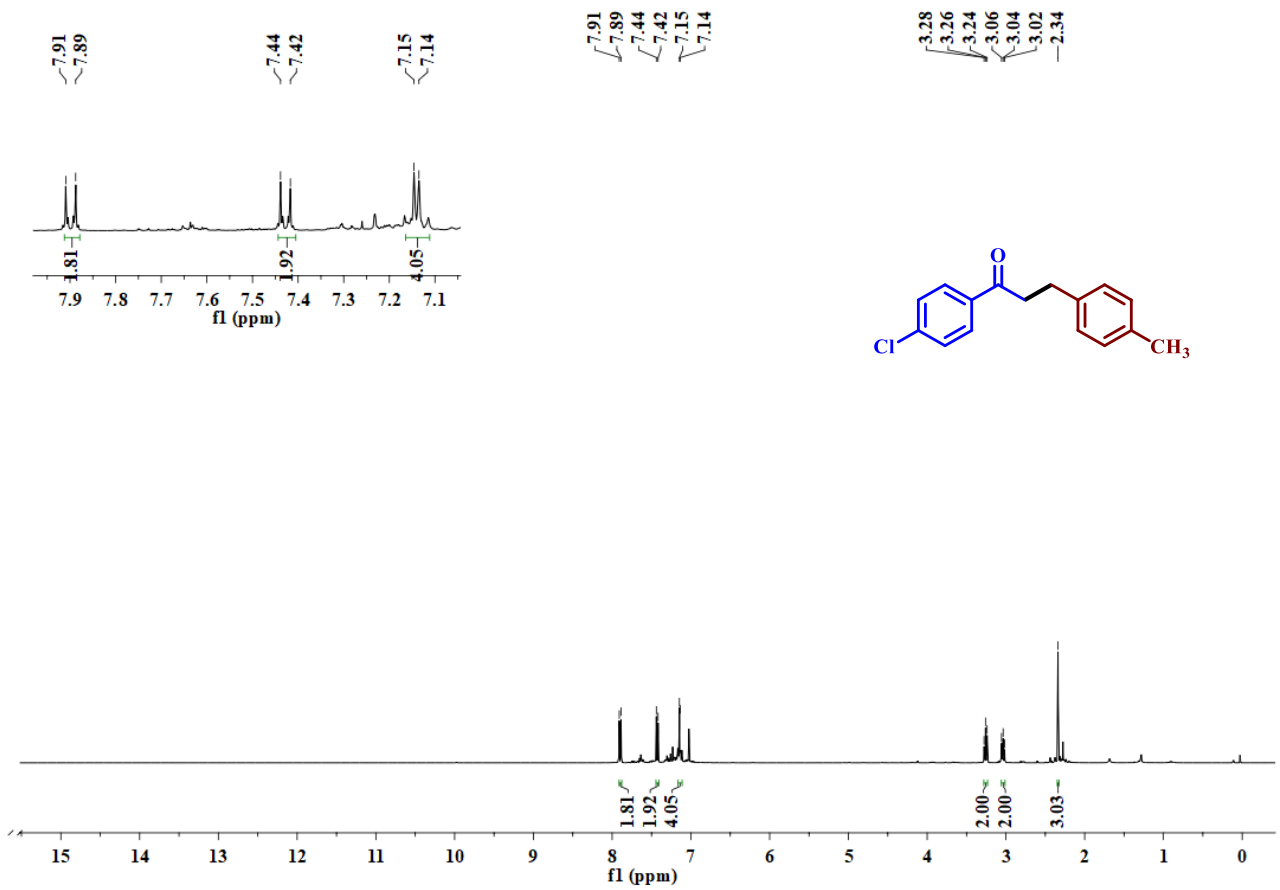


Figure S94. ^{1}H NMR spectrum of **5de** taking $CDCl_3$ as solvent.

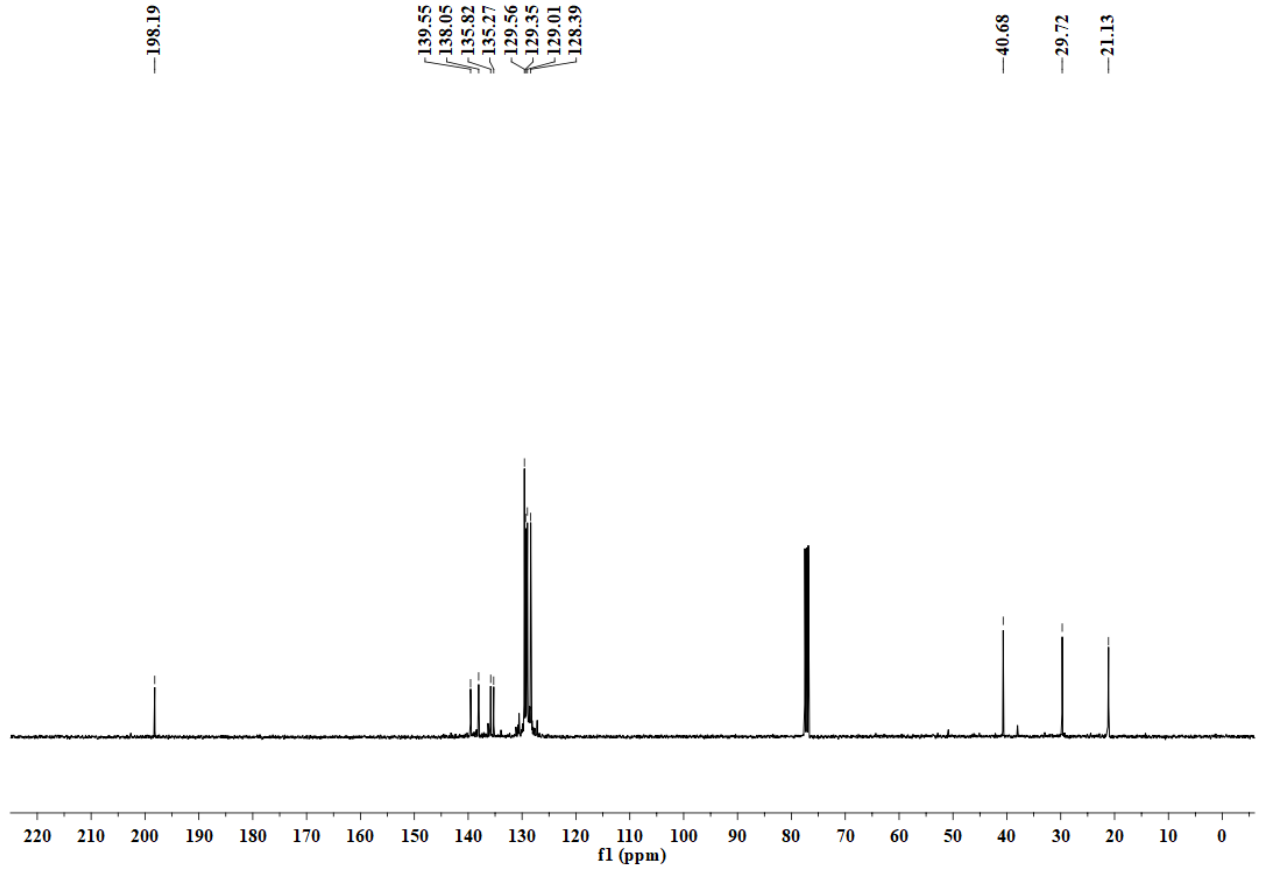


Figure S95. ^{13}CNMR spectrum of **5de** taking $CDCl_3$ as solvent.

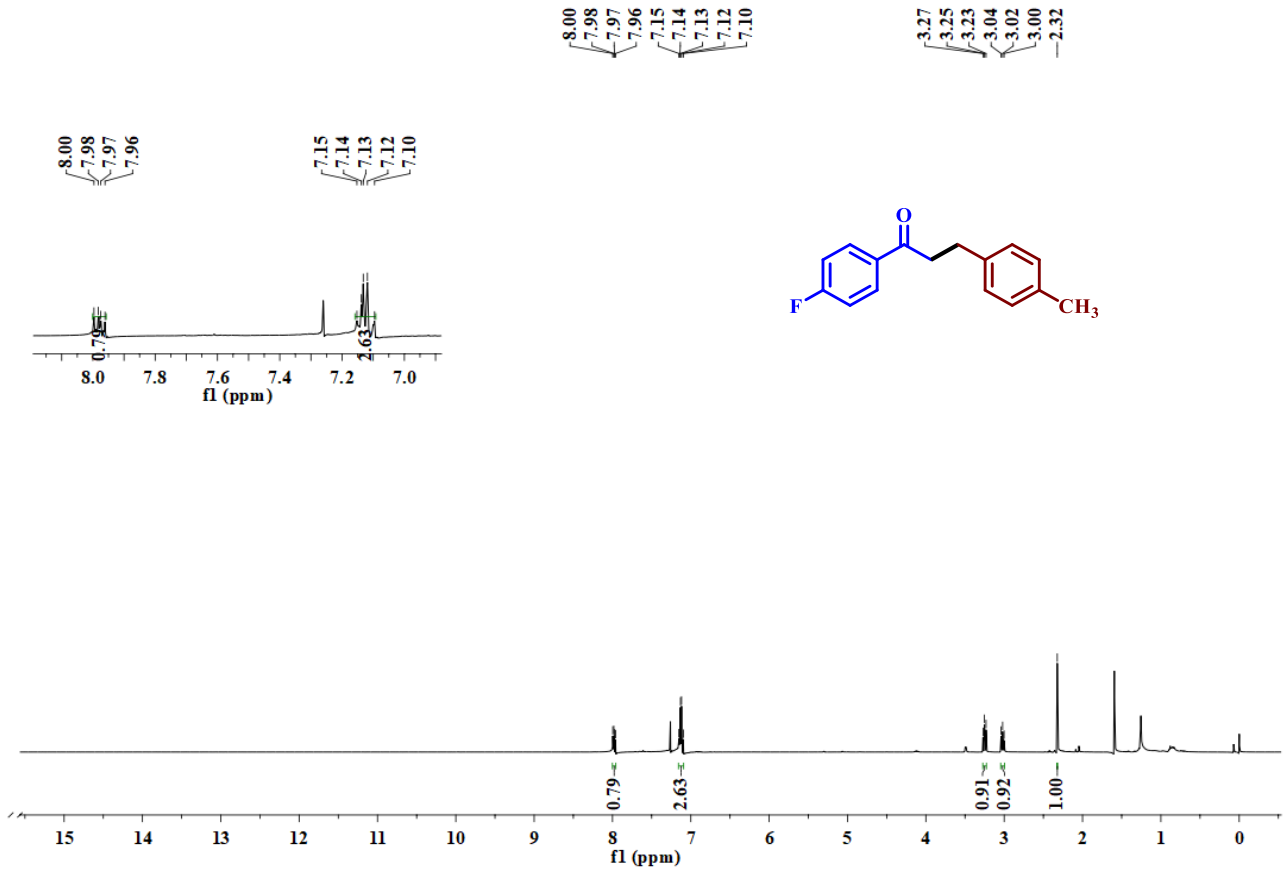


Figure S96. ^{1}H NMR spectrum of **5df** taking $CDCl_3$ as solvent.

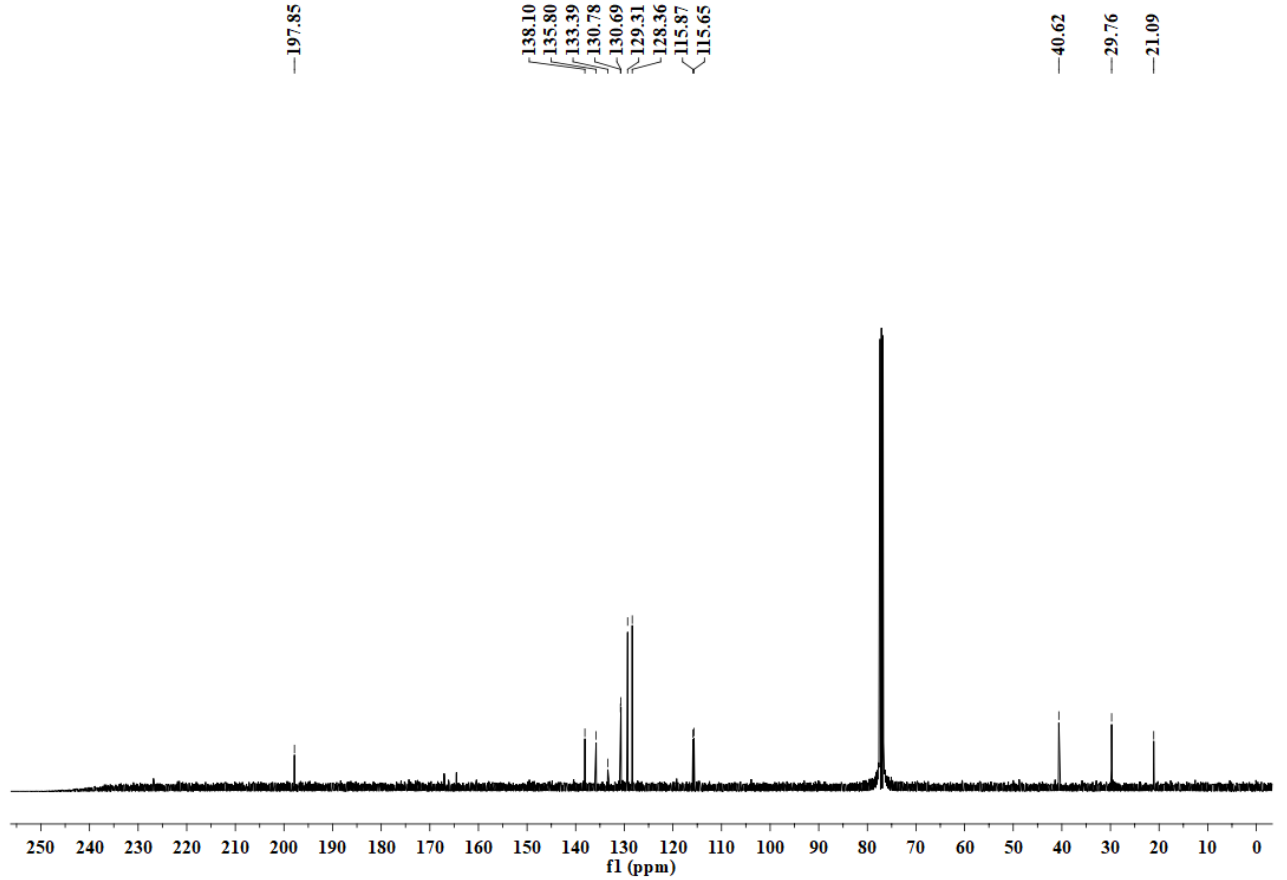


Figure S97. ^{13}CNMR spectrum of **5df** taking $CDCl_3$ as solvent.

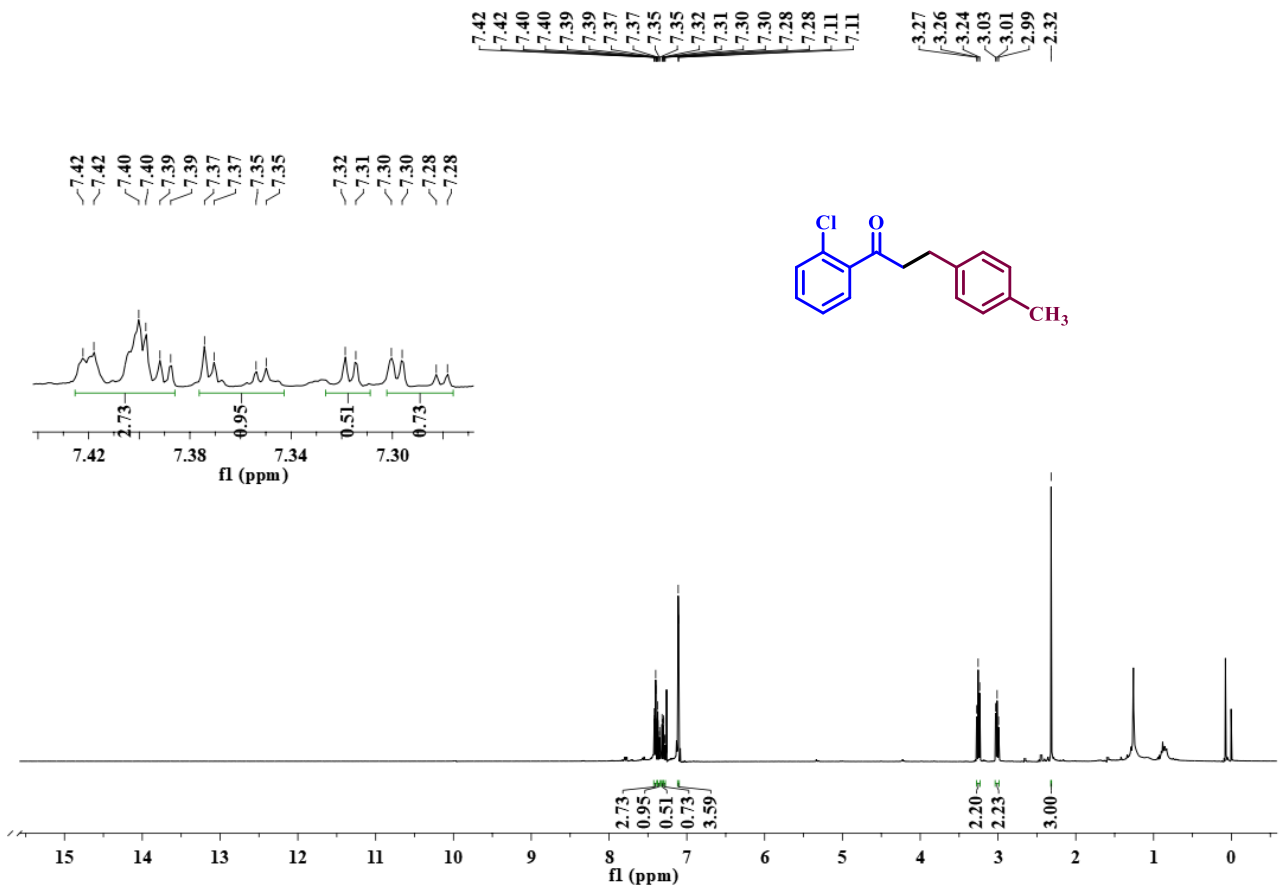


Figure S98. ^{1}H NMR spectrum of **5dg** taking $CDCl_3$ as solvent.

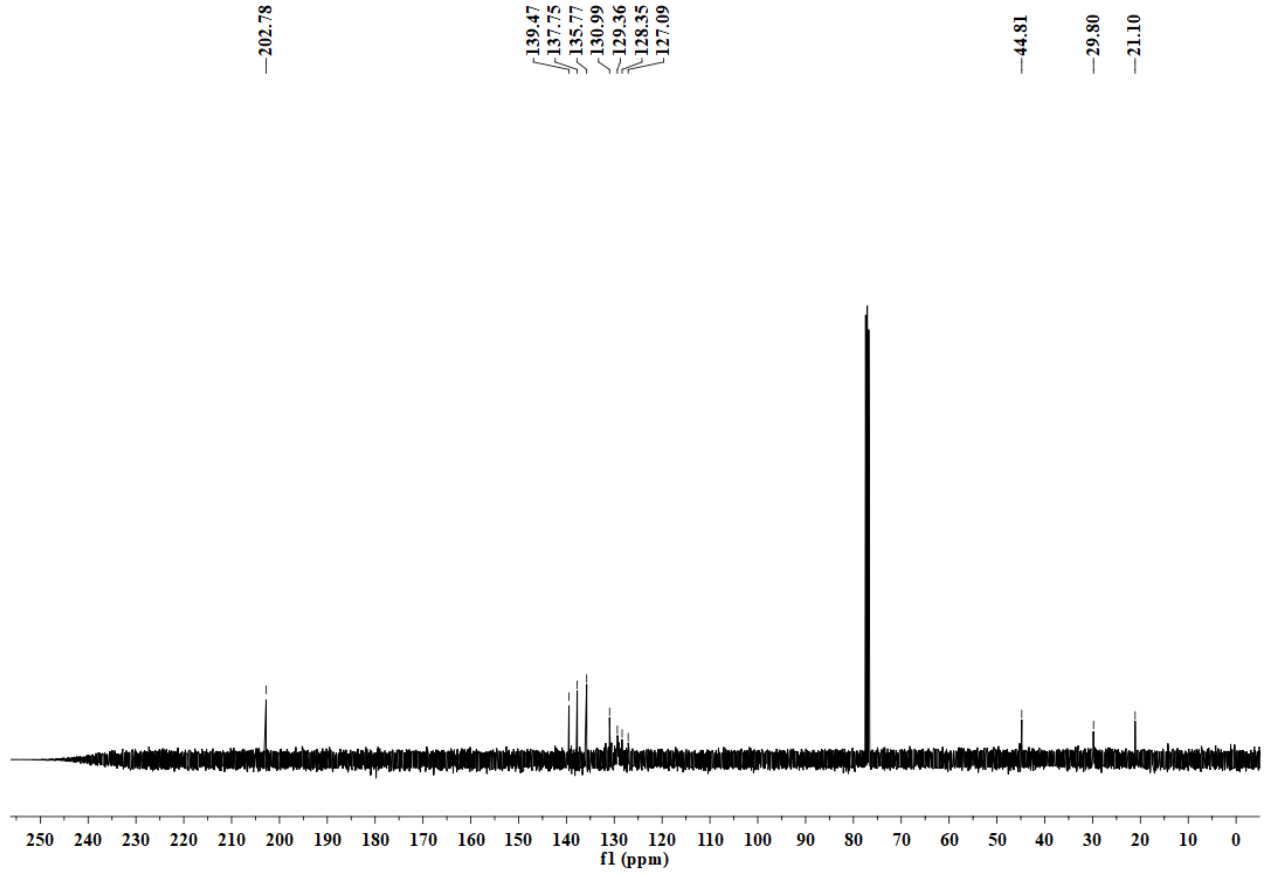


Figure S99. ^{13}CNMR spectrum of **5dg** taking $CDCl_3$ as solvent.

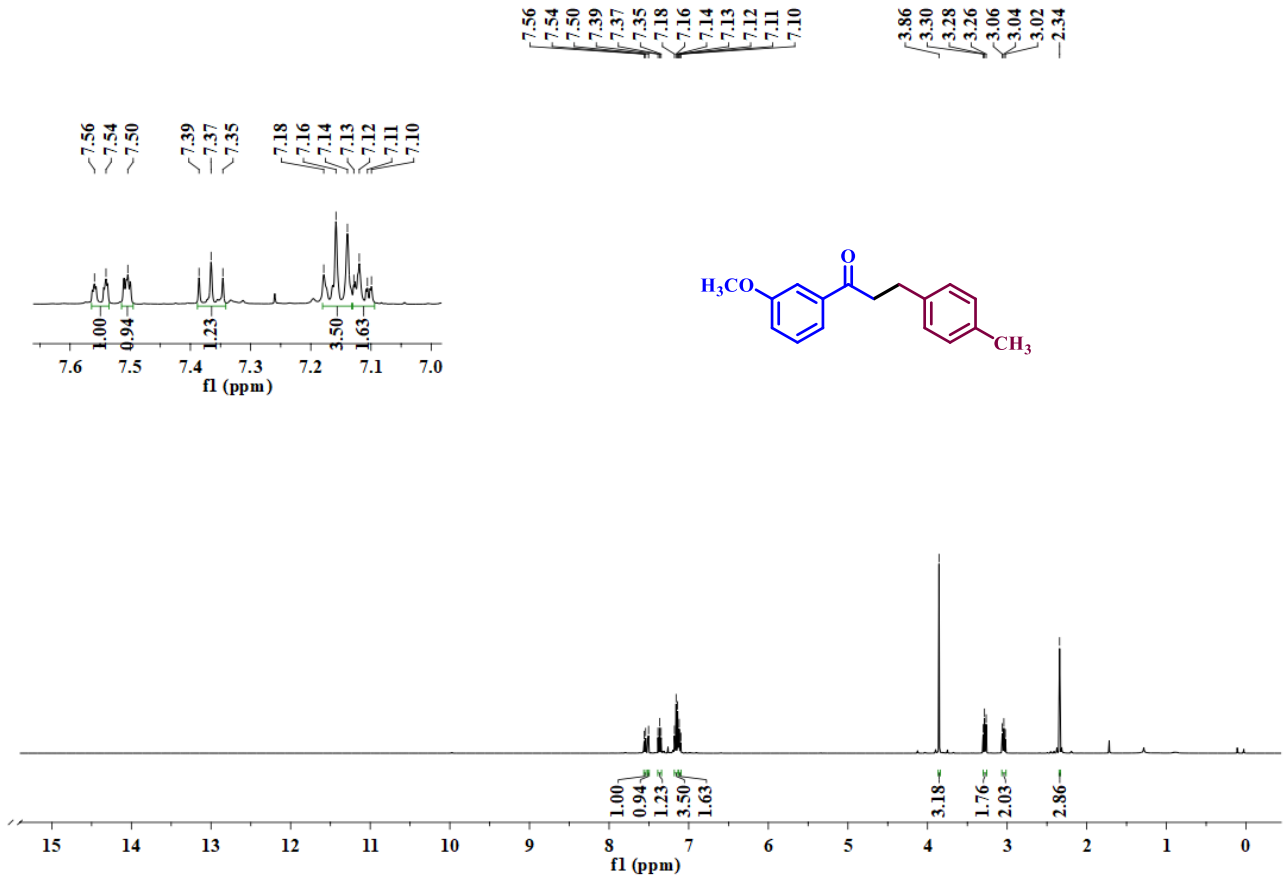


Figure S100. ^{1}H NMR spectrum of **5dh** taking $CDCl_3$ as solvent.

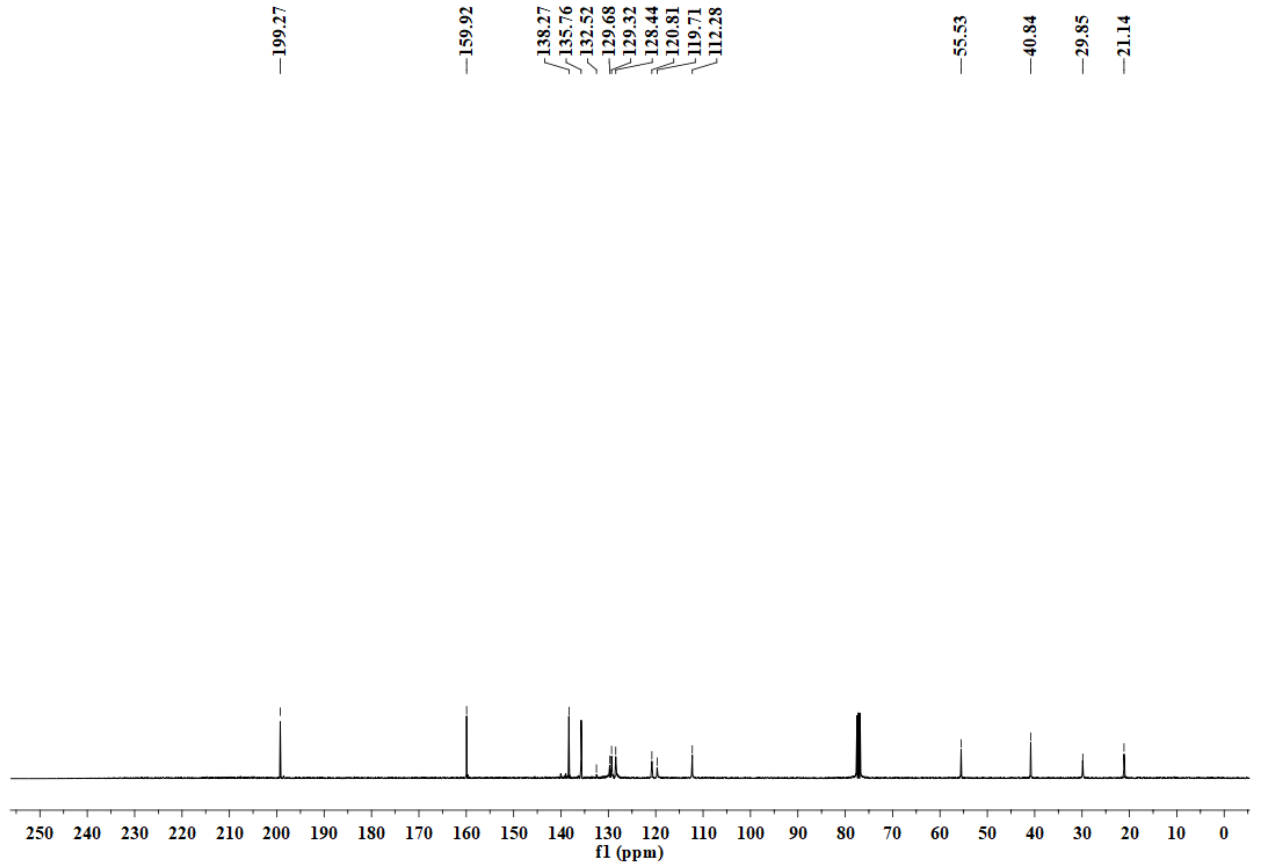


Figure S101. ^{13}CNMR spectrum of **5dh** taking $CDCl_3$ as solvent.

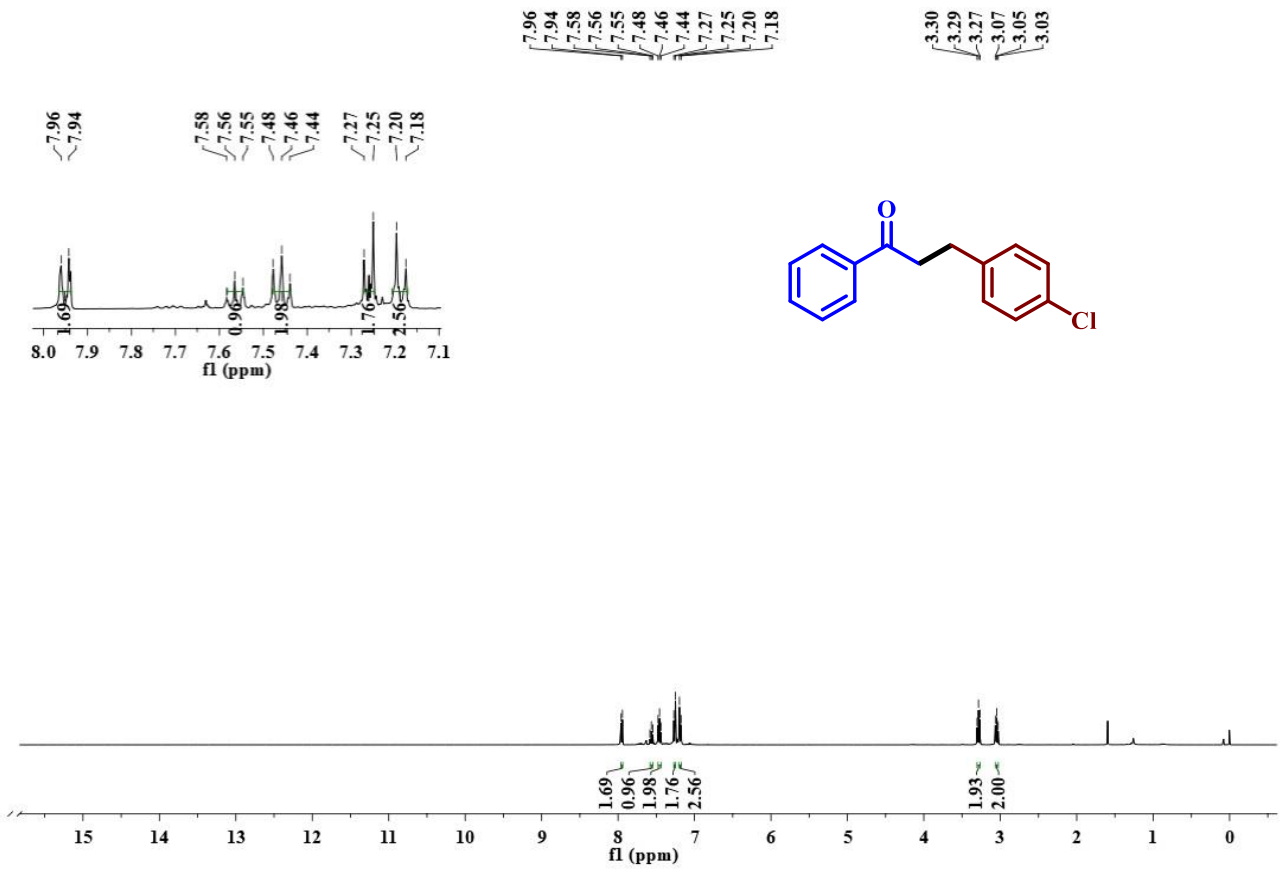


Figure S102. ^{1}H NMR spectrum of **5ea** taking $CDCl_3$ as solvent.

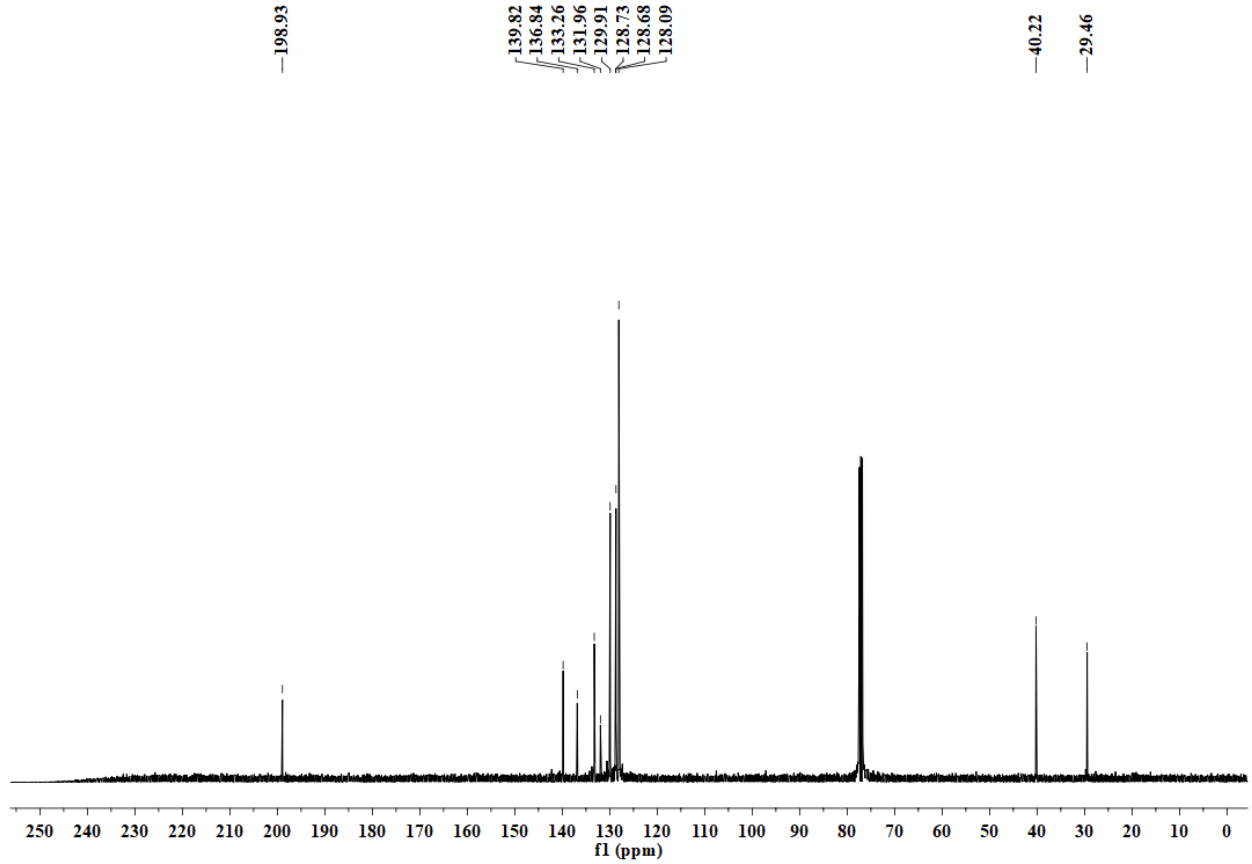


Figure S103. ^{13}CNMR spectrum of **5ea** taking $CDCl_3$ as solvent.

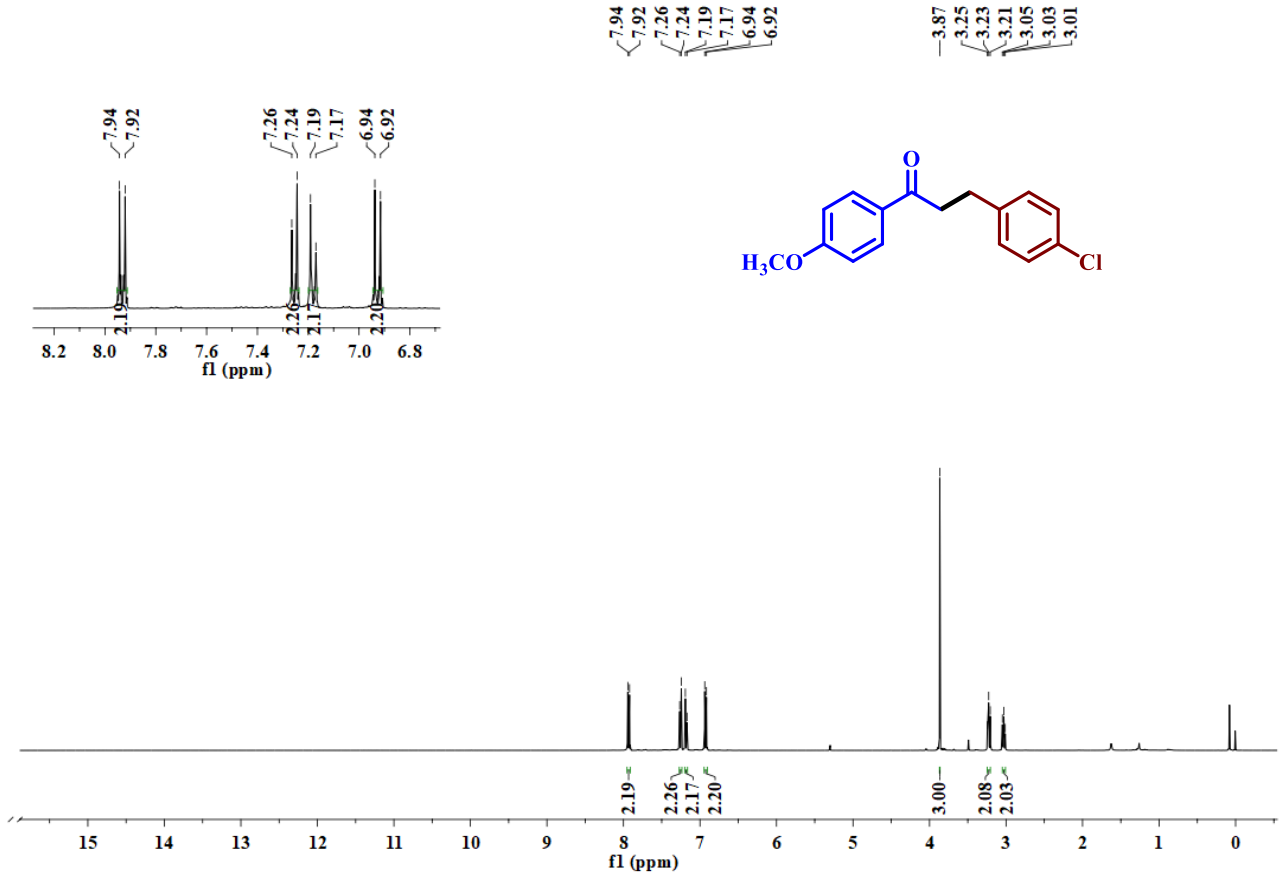


Figure S104. ^{1}H NMR spectrum of **5eb** taking $CDCl_3$ as solvent.

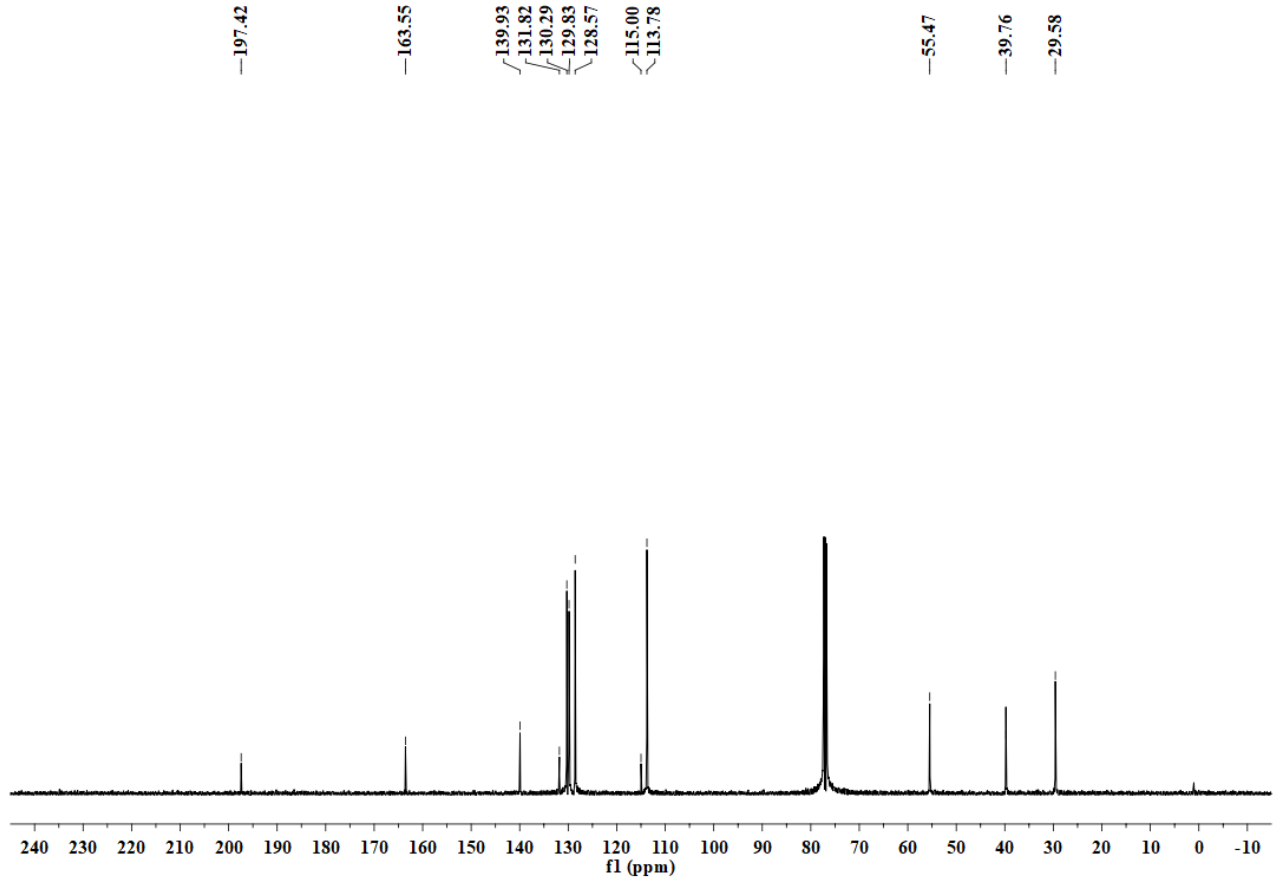


Figure S105. ^{13}CNMR spectrum of **5eb** taking $CDCl_3$ as solvent.

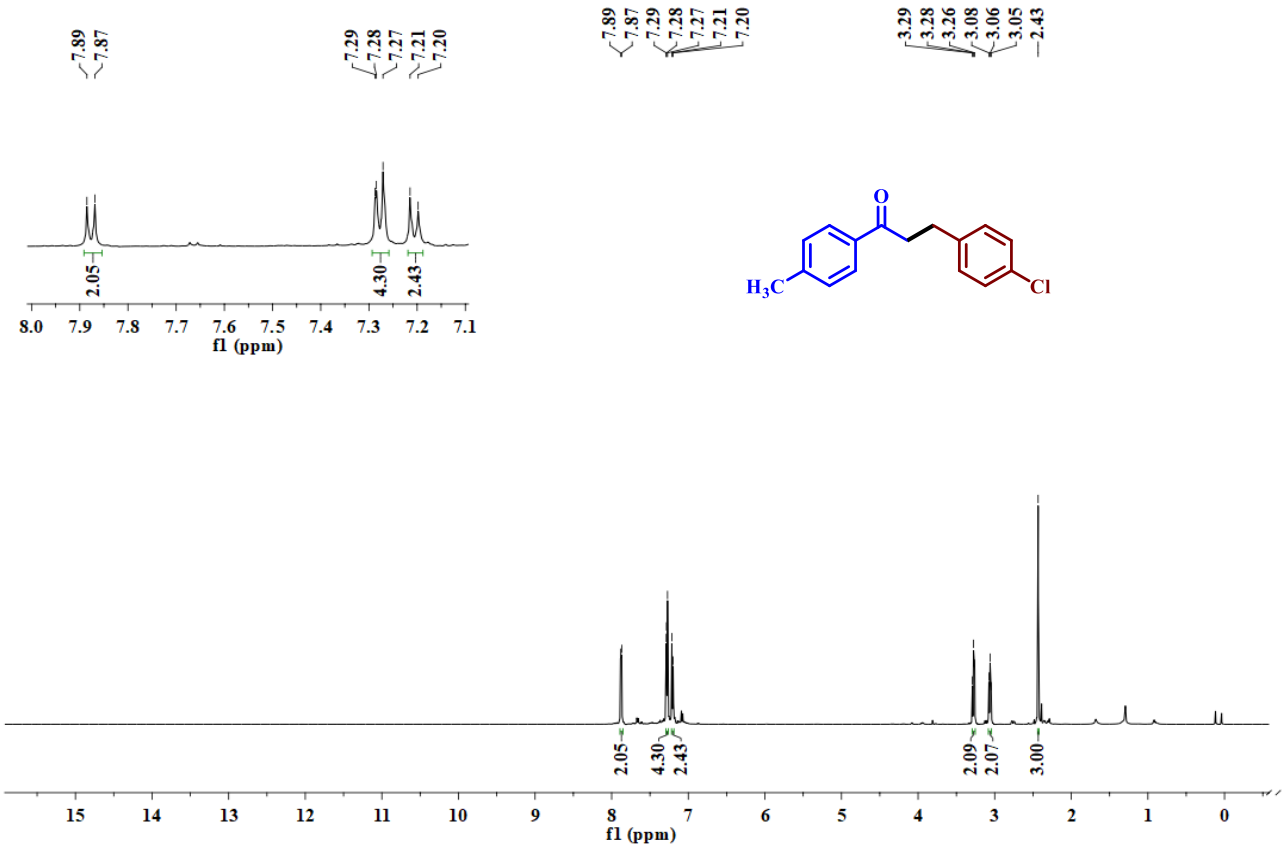


Figure S106. ^{1}H NMR spectrum of **5ec** taking $CDCl_3$ as solvent.

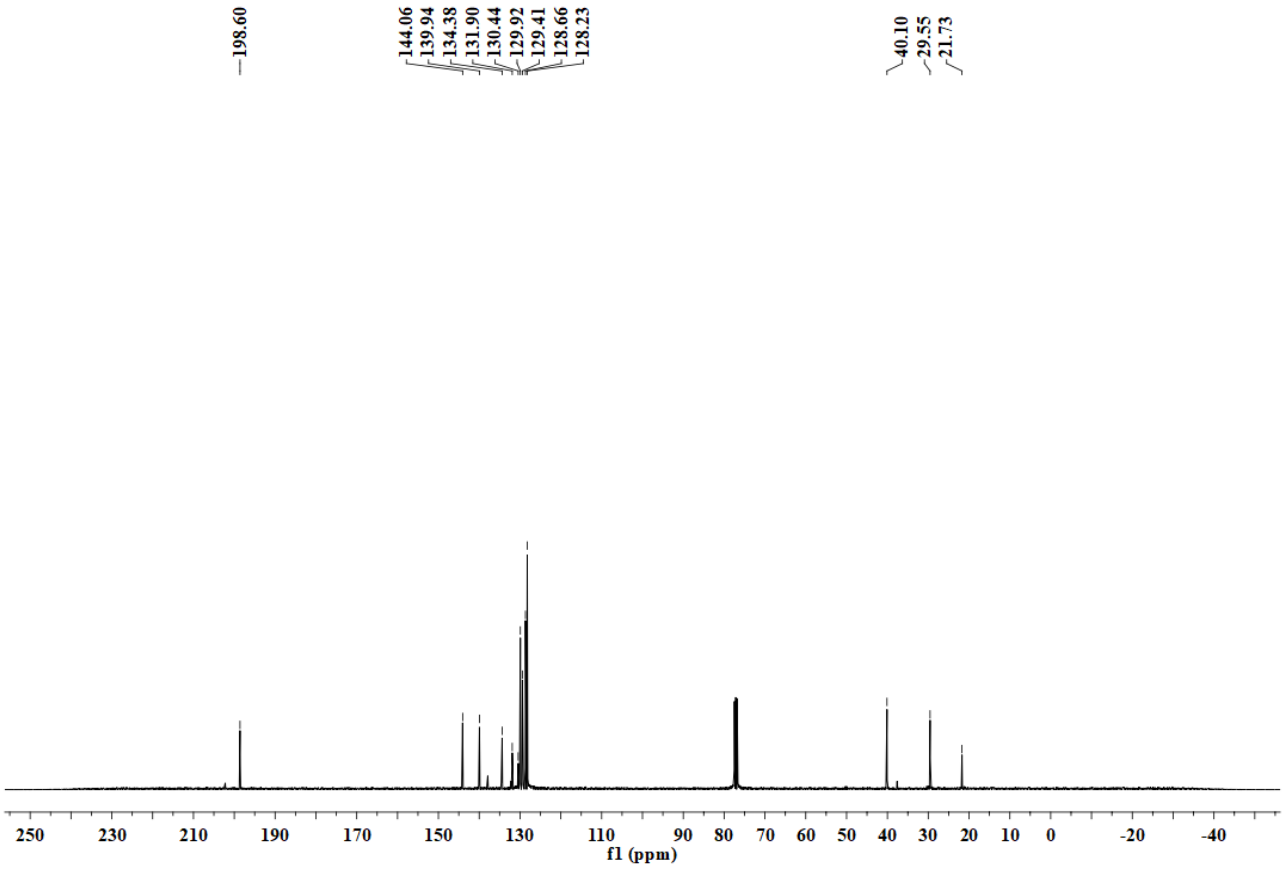


Figure S107. ^{13}CNMR spectrum of **5ec** taking $CDCl_3$ as solvent.

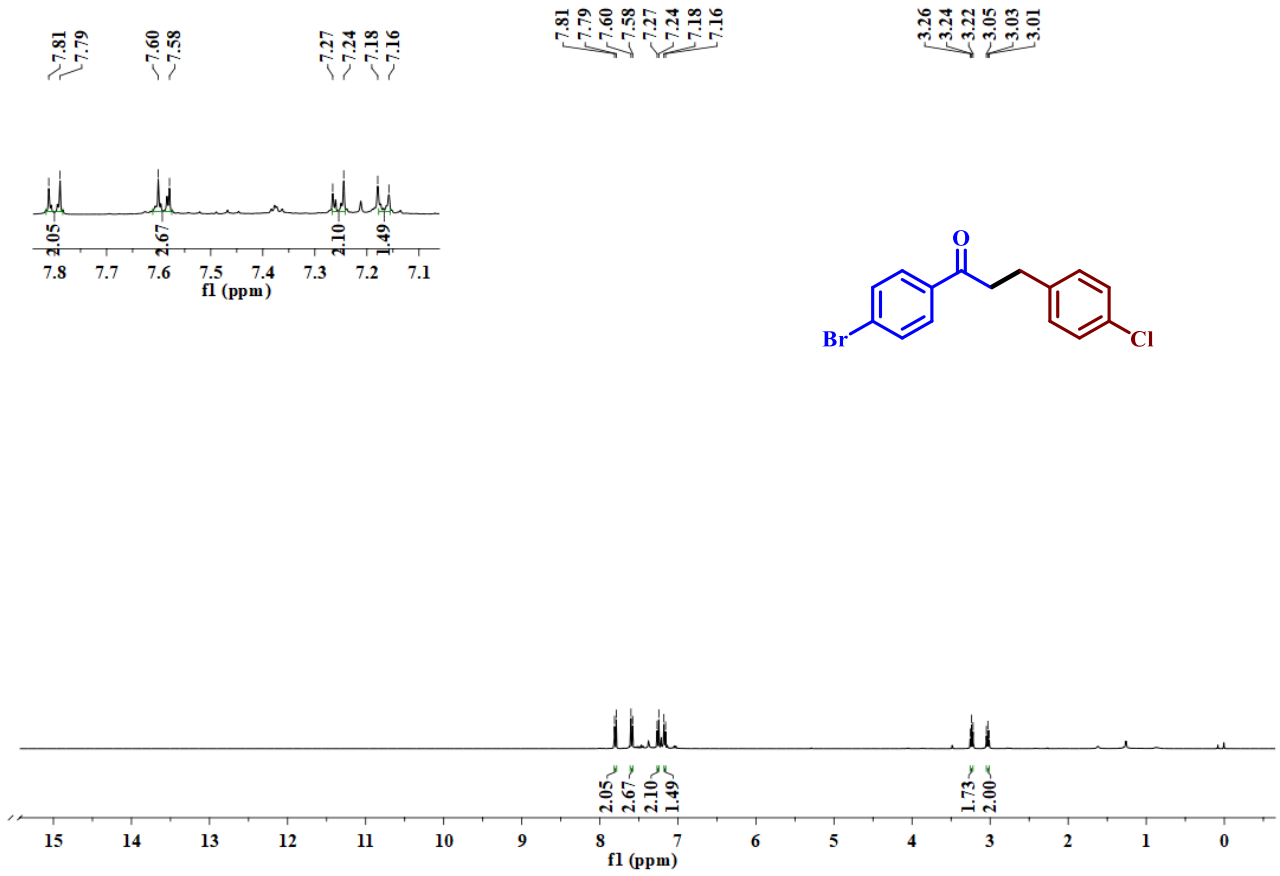


Figure S108. ^{1}H NMR spectrum of **5ed** taking $CDCl_3$ as solvent.

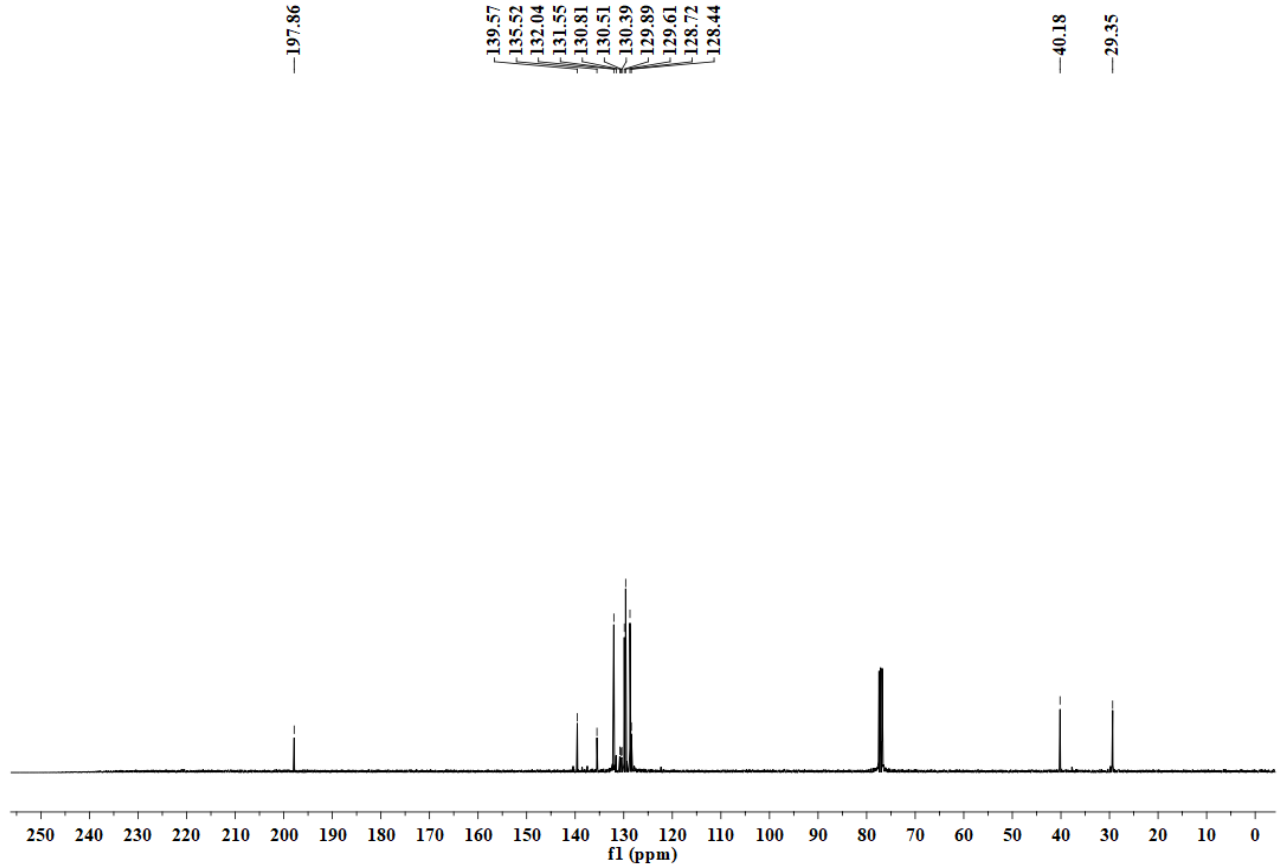


Figure S109. ^{13}CNMR spectrum of **5ed** taking $CDCl_3$ as solvent.

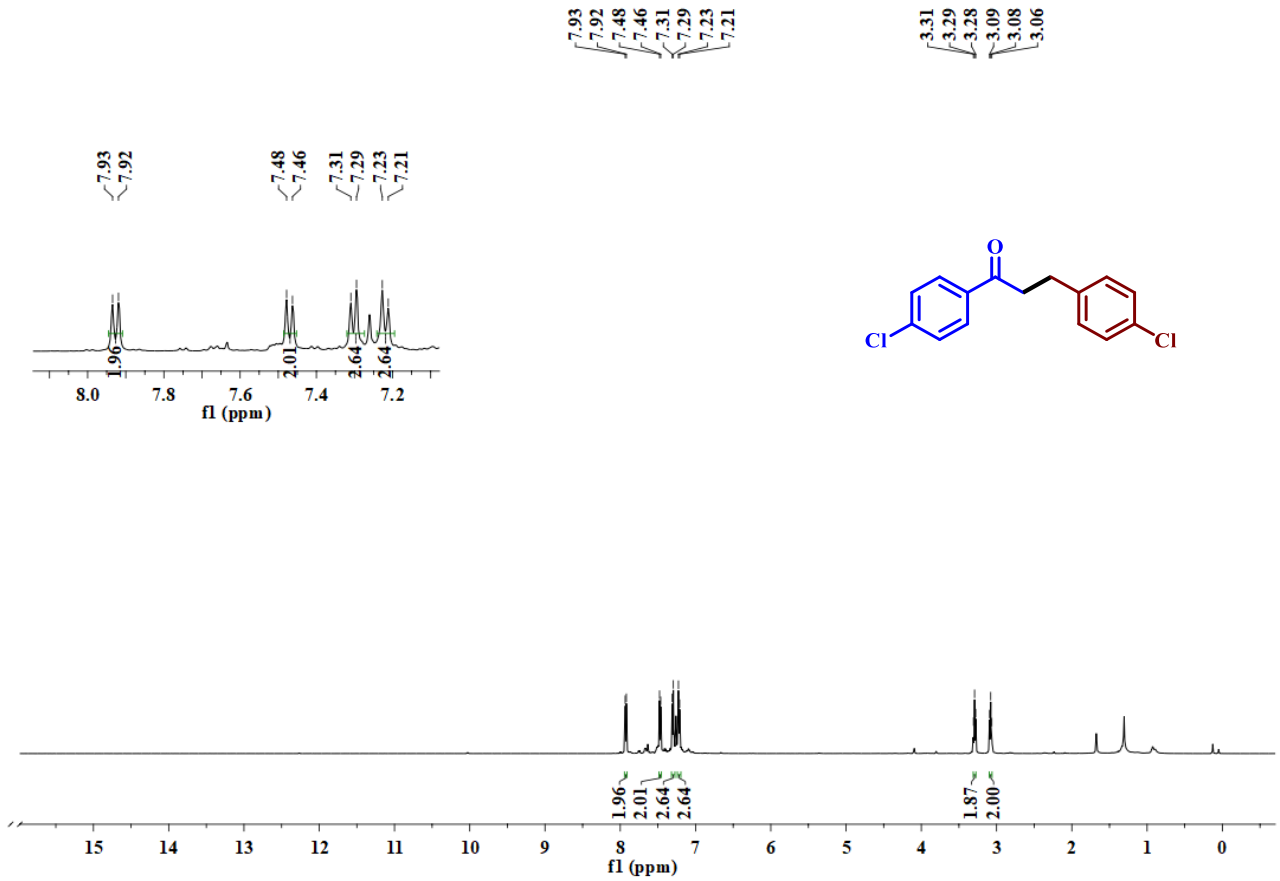


Figure S110. ^{1}H NMR spectrum of **5ee** taking $CDCl_3$ as solvent.

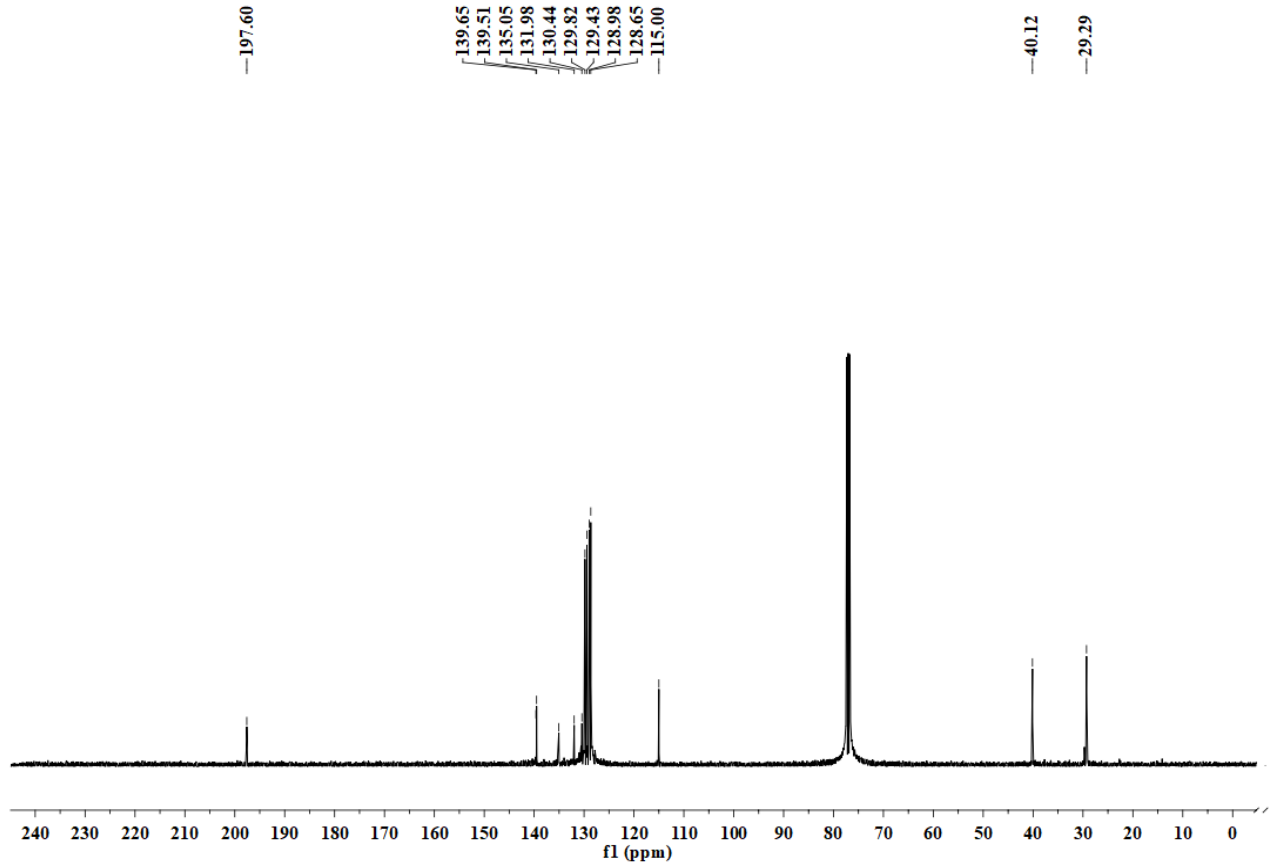


Figure S111. ^{13}CNMR spectrum of **5ee** taking $CDCl_3$ as solvent.

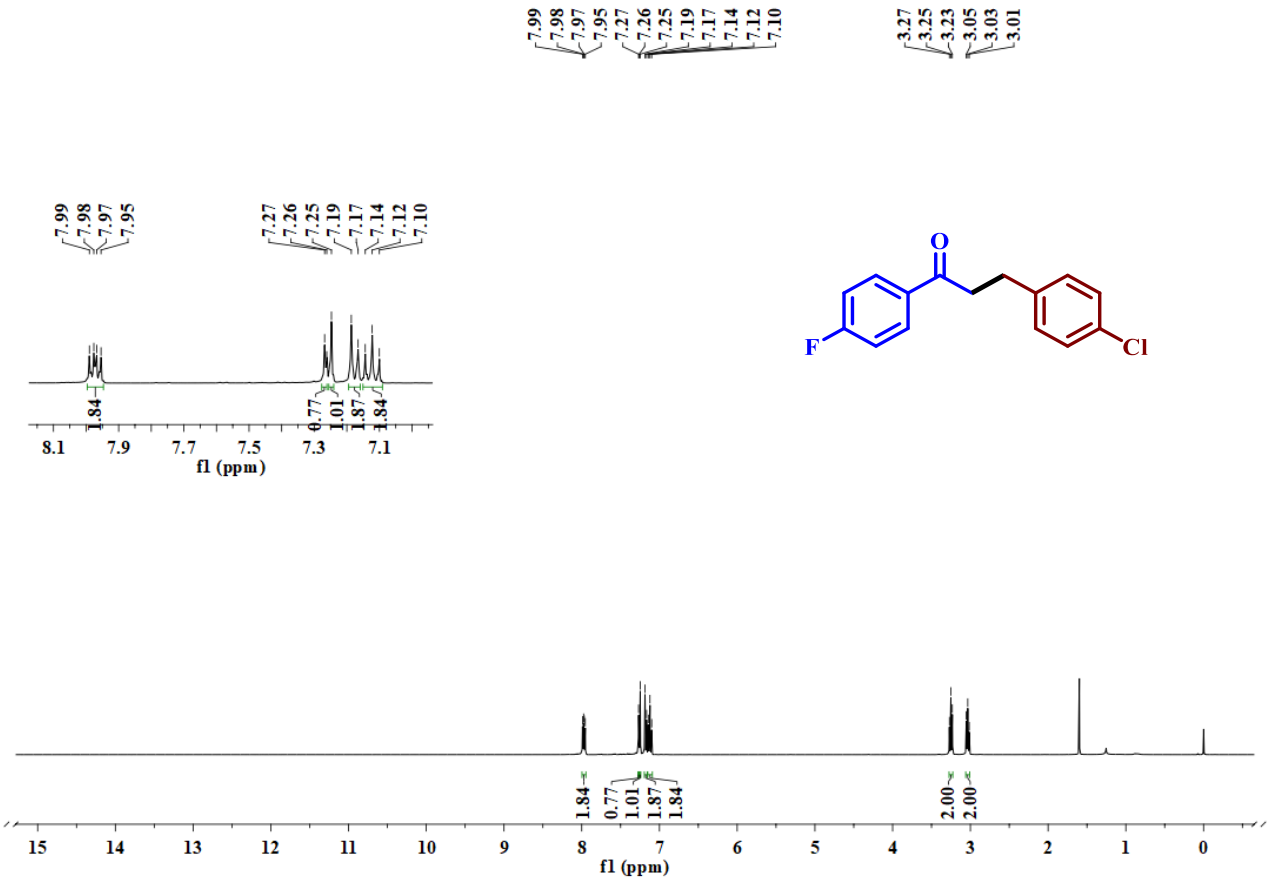


Figure S112. ^{1}H NMR spectrum of **5ef** taking $CDCl_3$ as solvent.

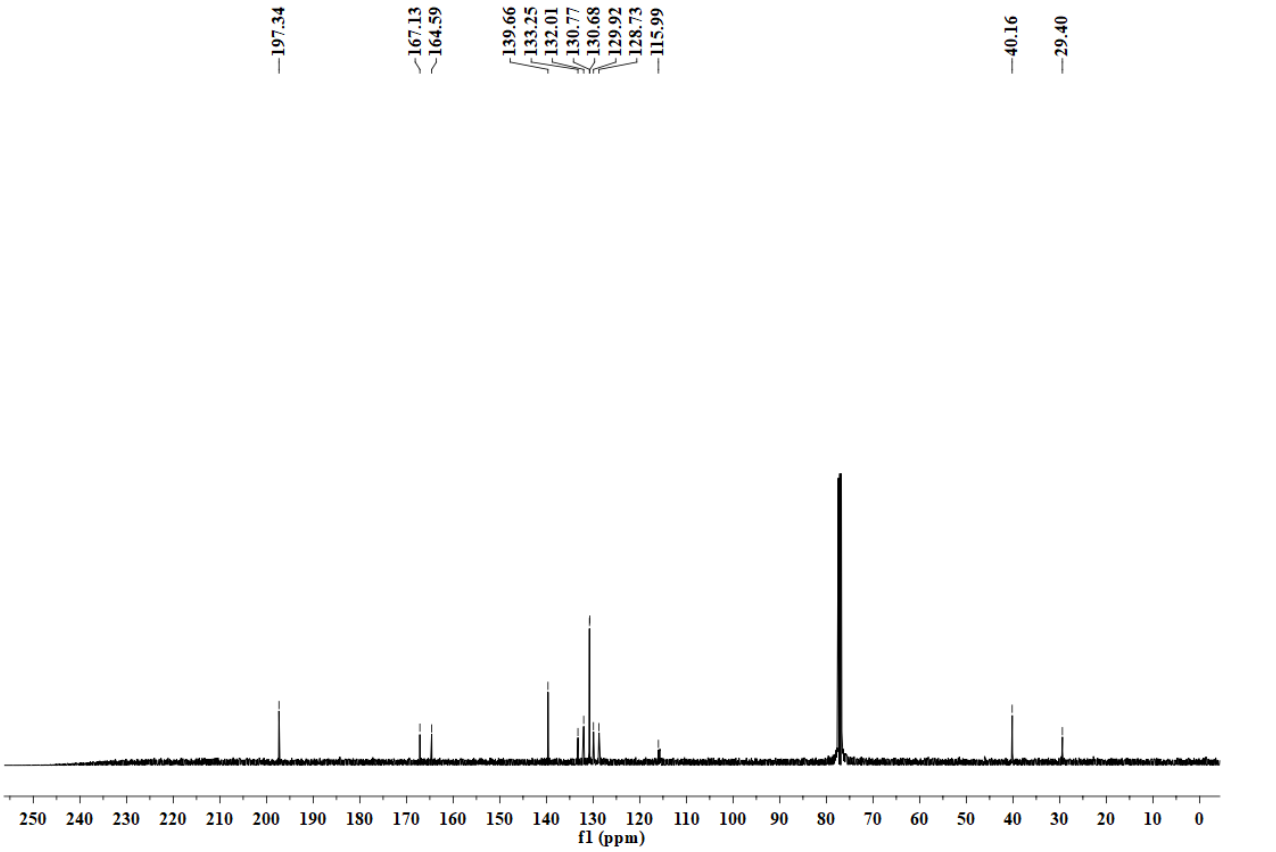


Figure S113. ^{13}CNMR spectrum of **5ef** taking $CDCl_3$ as solvent.

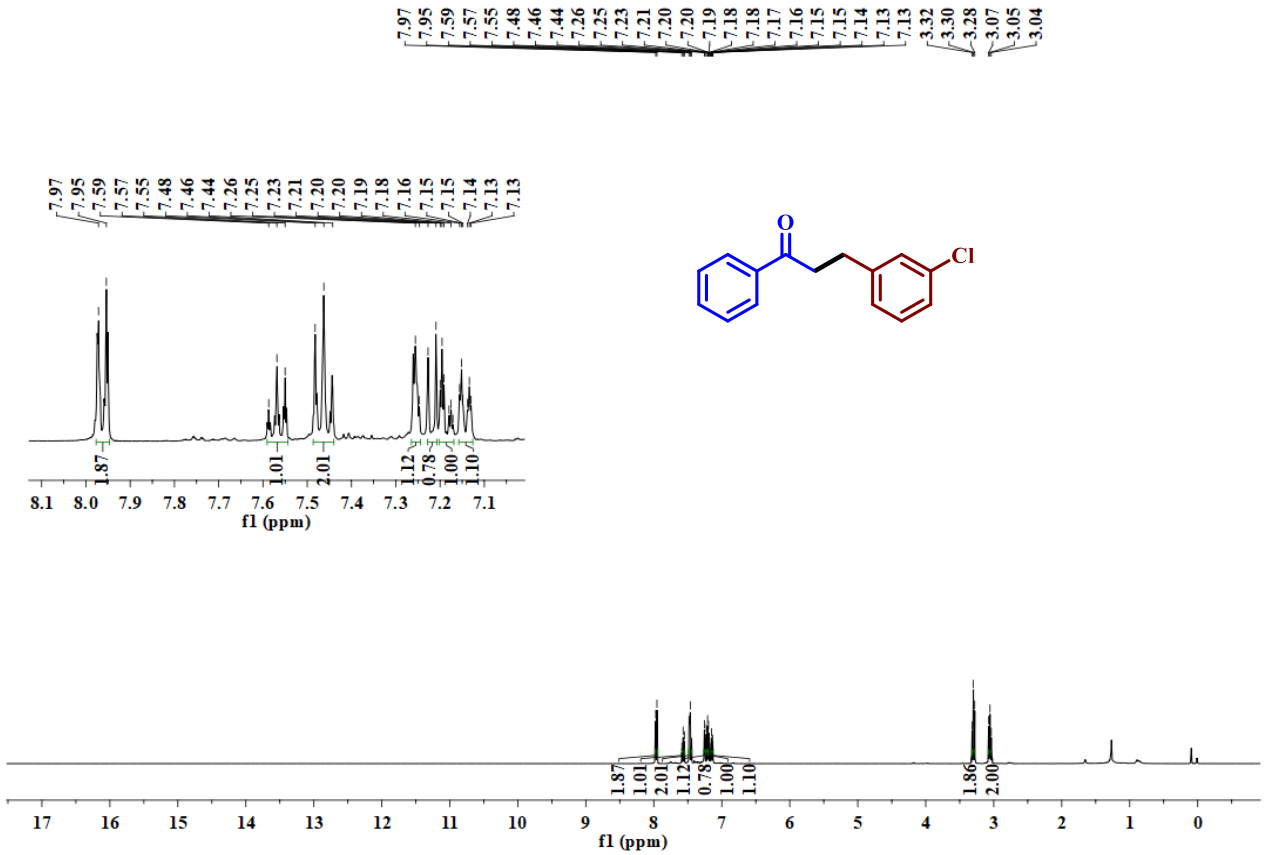


Figure S114. ^{1}H NMR spectrum of **5fa** taking $CDCl_3$ as solvent.

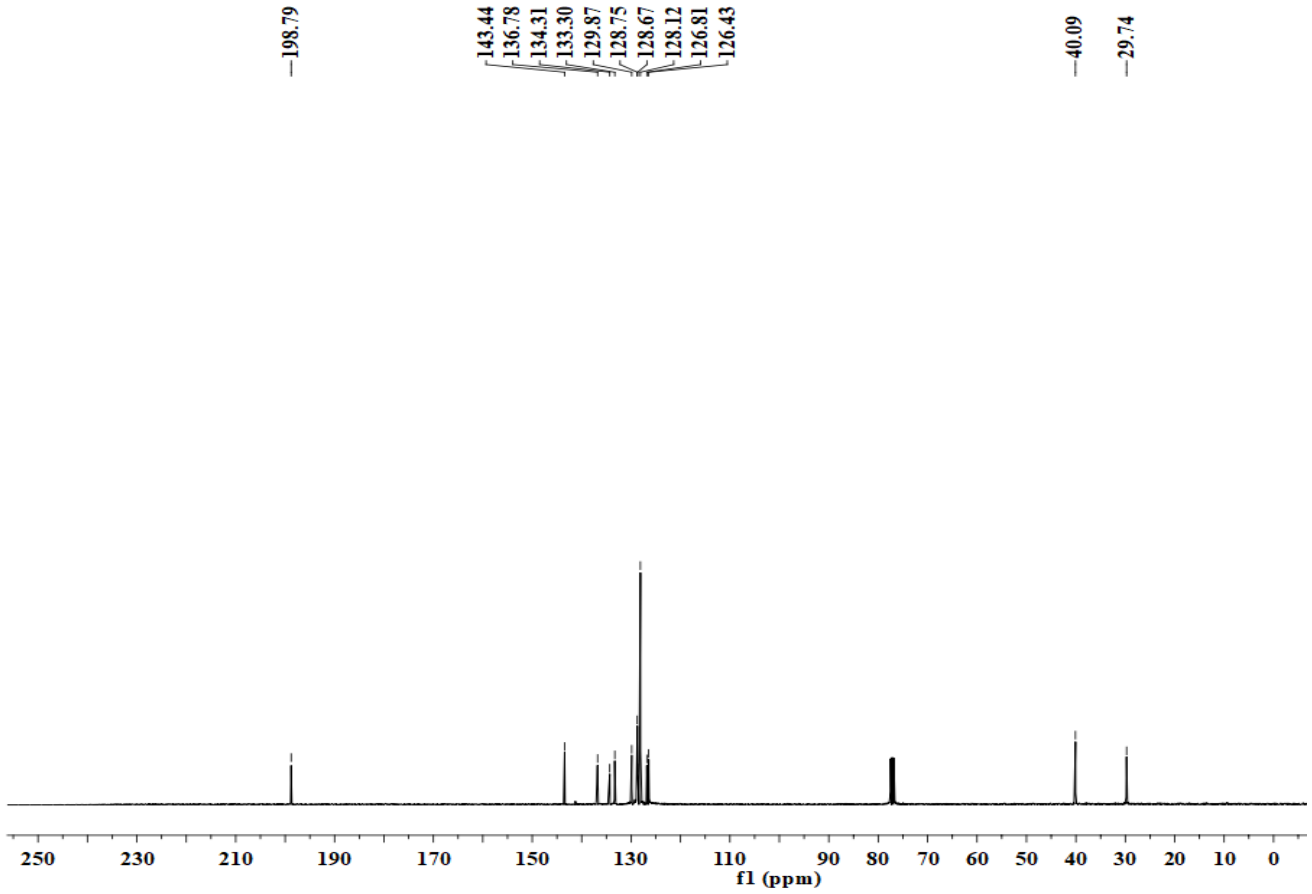


Figure S115. ^{13}CNMR spectrum of **5fa** taking $CDCl_3$ as solvent.

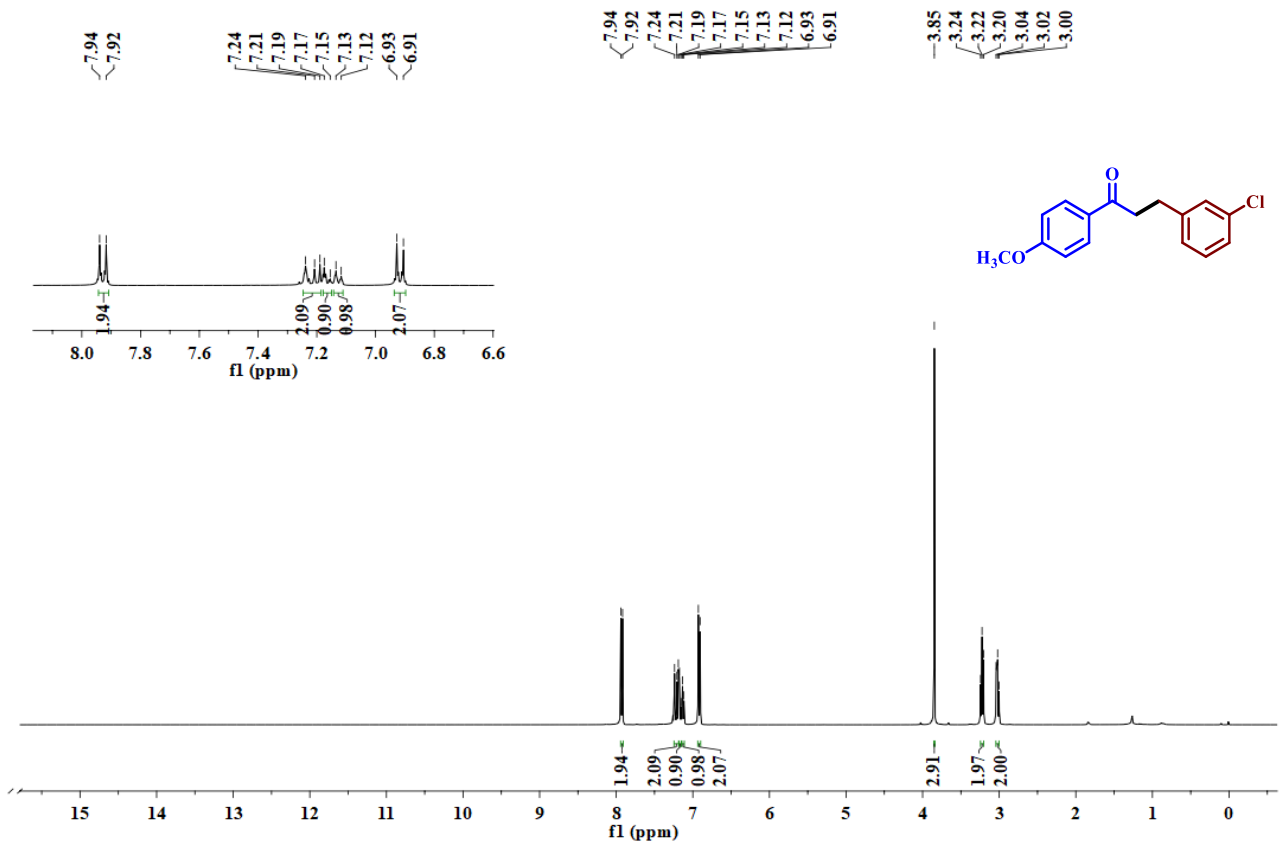


Figure S116. ^{1}H NMR spectrum of **5fb** taking $CDCl_3$ as solvent.

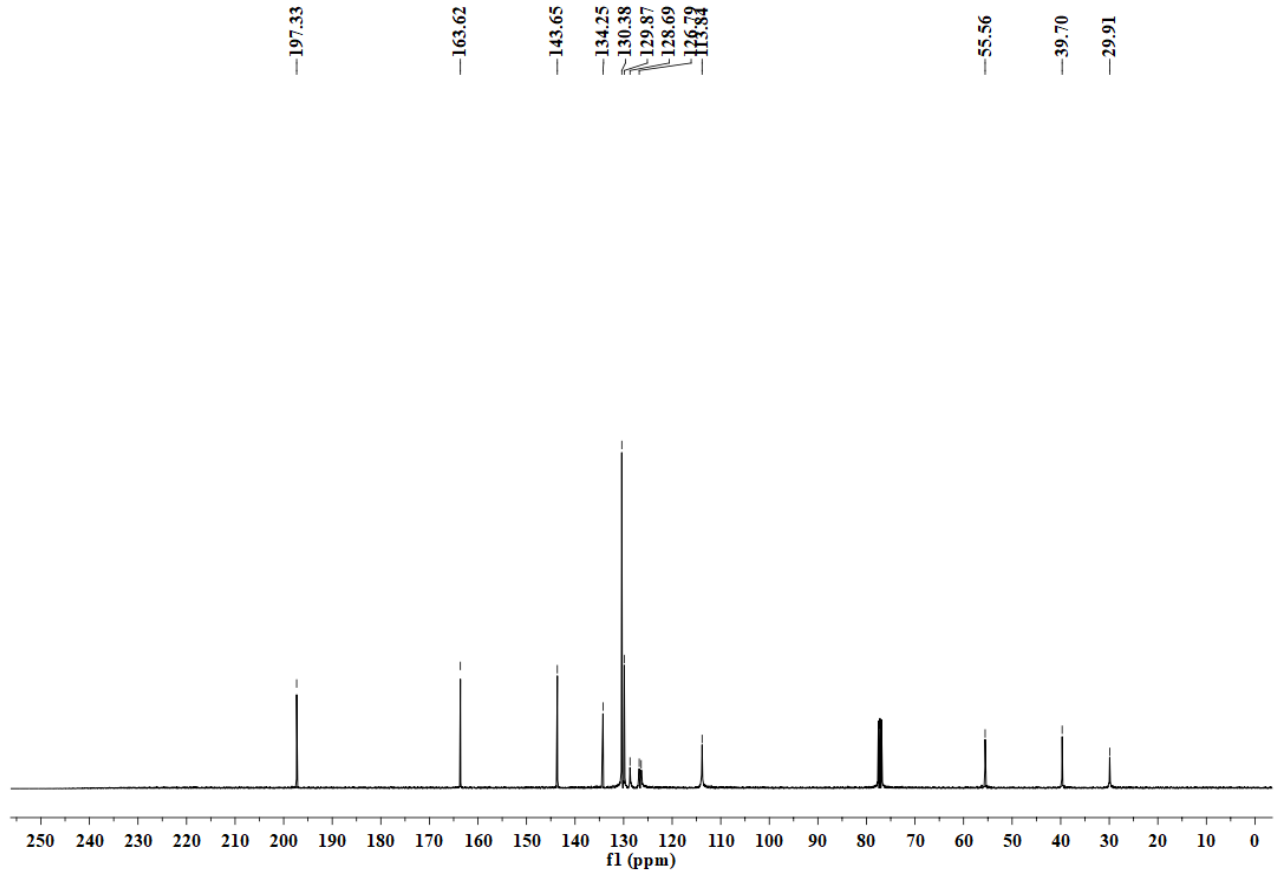


Figure S117. ^{13}CNMR spectrum of **5fb** taking $CDCl_3$ as solvent.

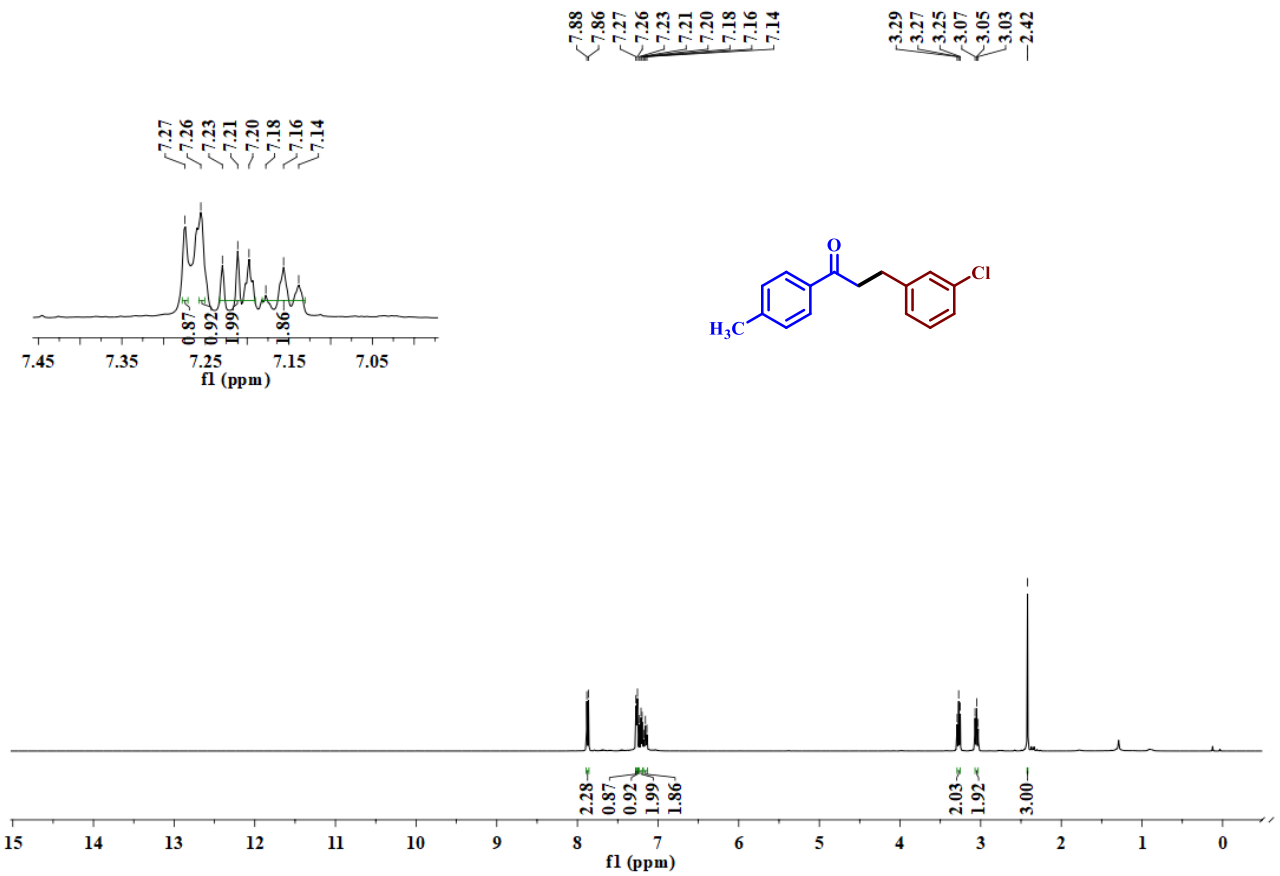


Figure S118. ^{1}H NMR spectrum of **5fc** taking $CDCl_3$ as solvent.

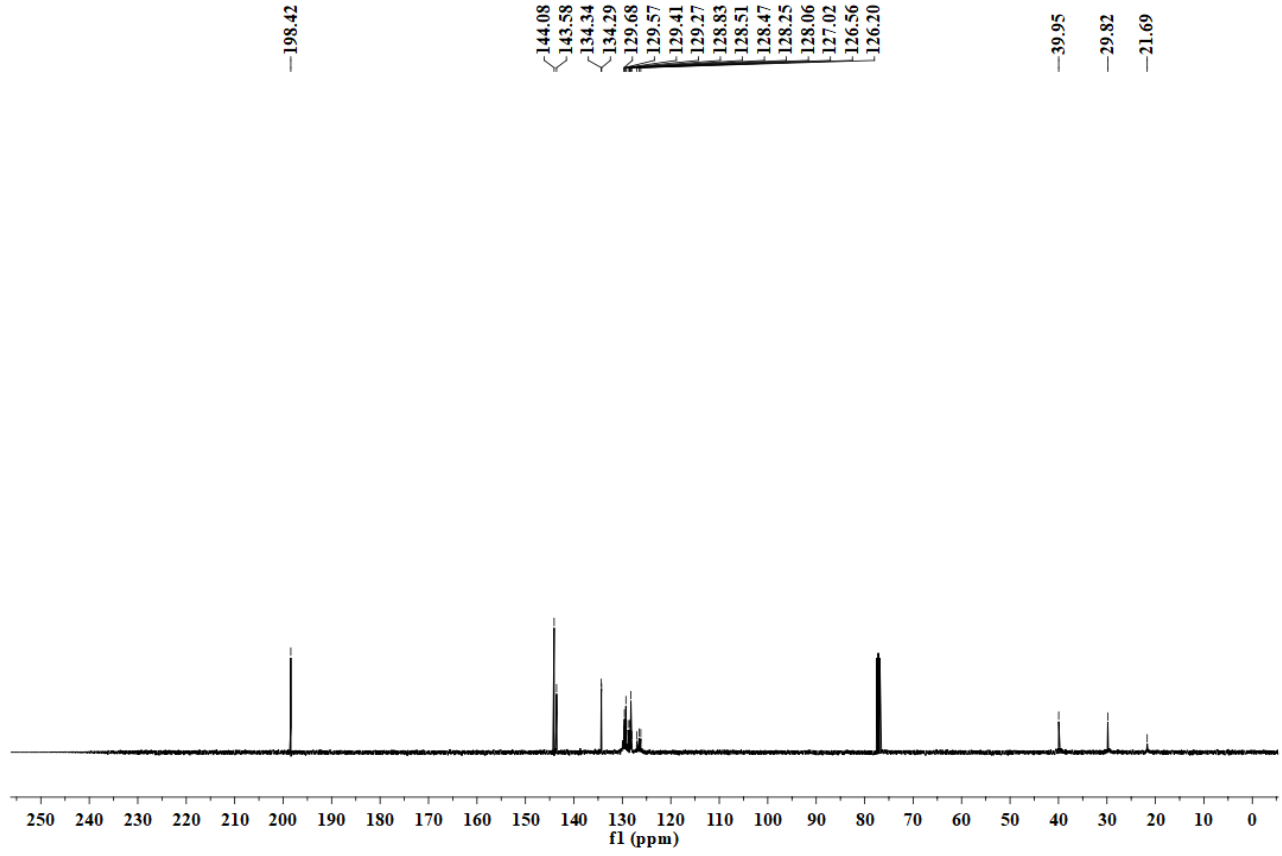


Figure S119. ^{13}CNMR spectrum of **5fc** taking $CDCl_3$ as solvent.

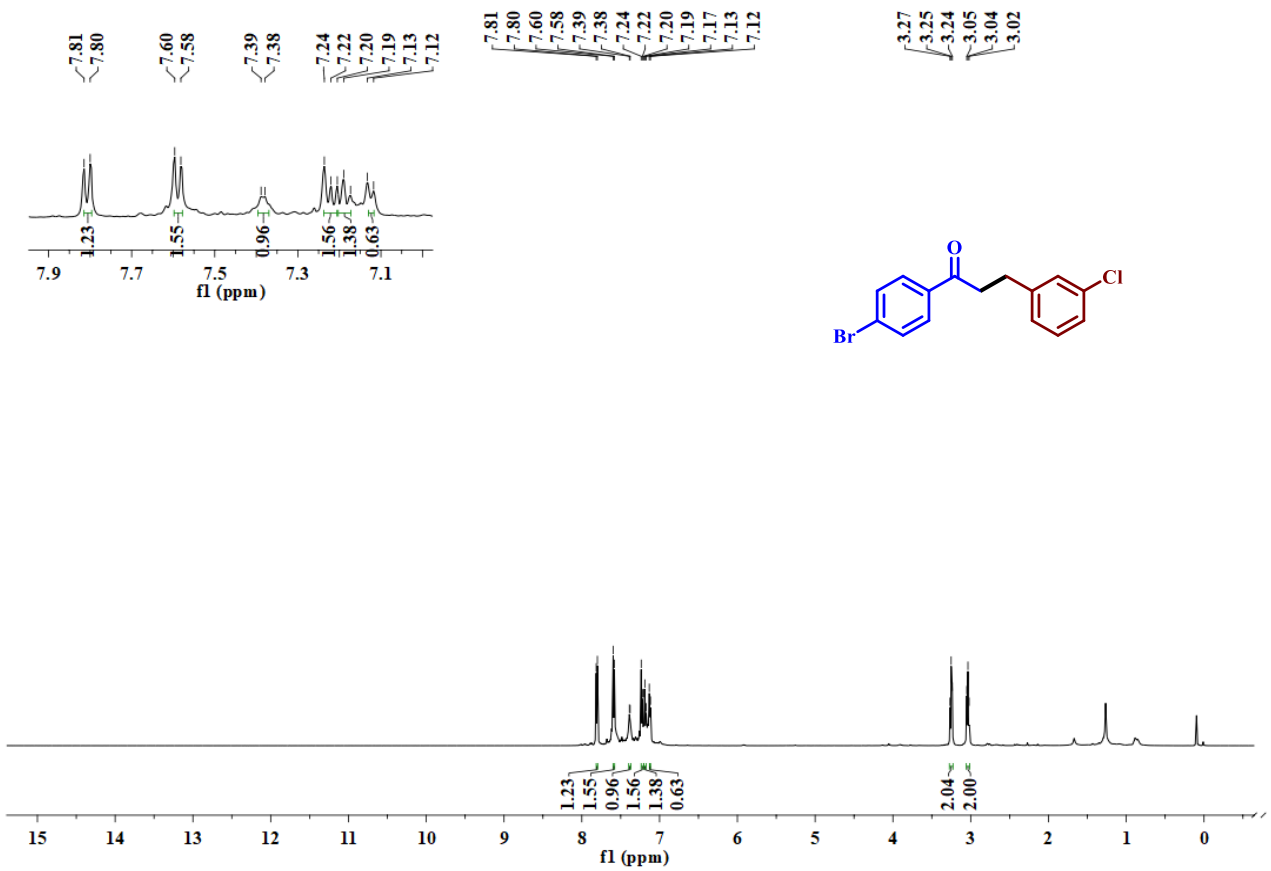


Figure S120. ^{1}H NMR spectrum of **5fd** taking $CDCl_3$ as solvent.

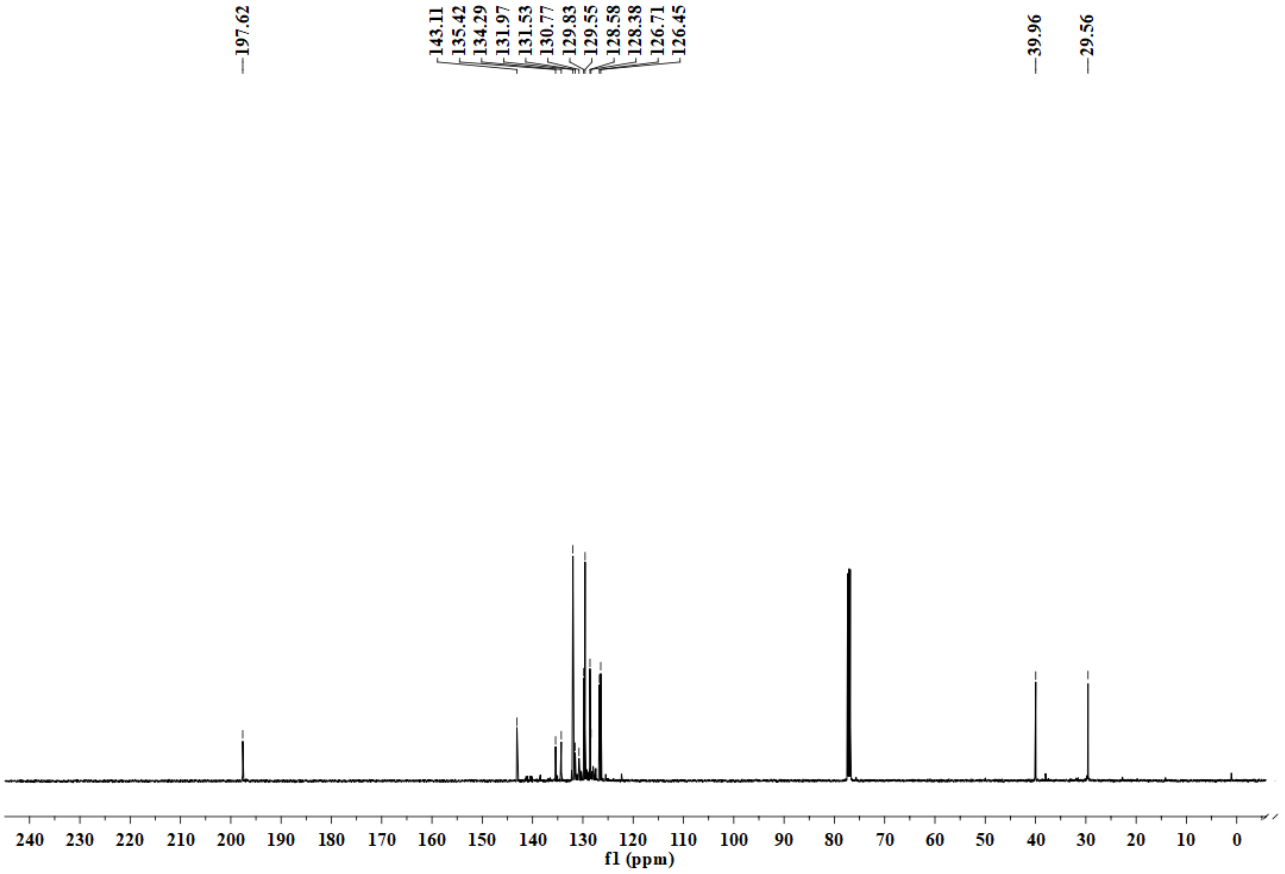


Figure S121. ^{13}CNMR spectrum of **5fd** taking $CDCl_3$ as solvent.

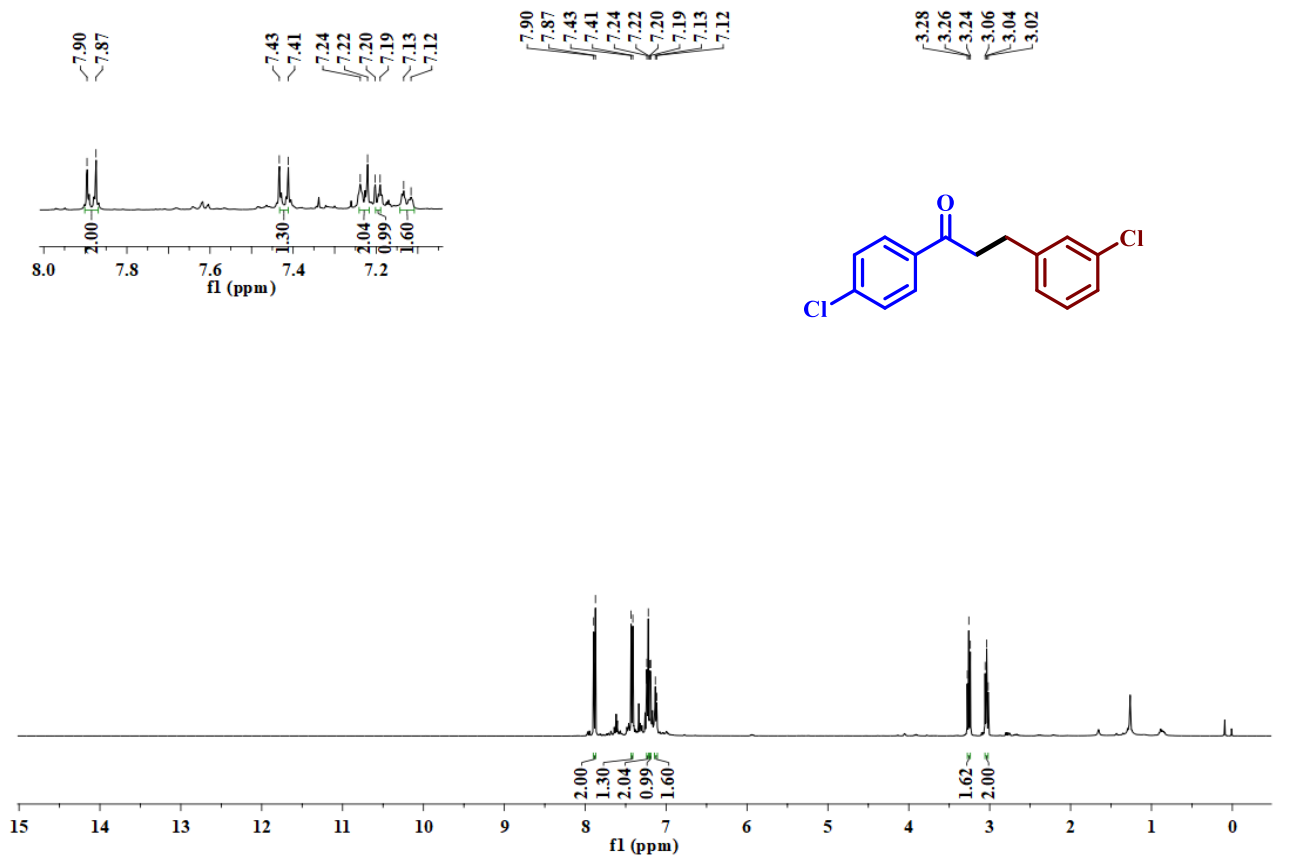


Figure S122. ^{1}H NMR spectrum of **5fe** taking $CDCl_3$ as solvent.

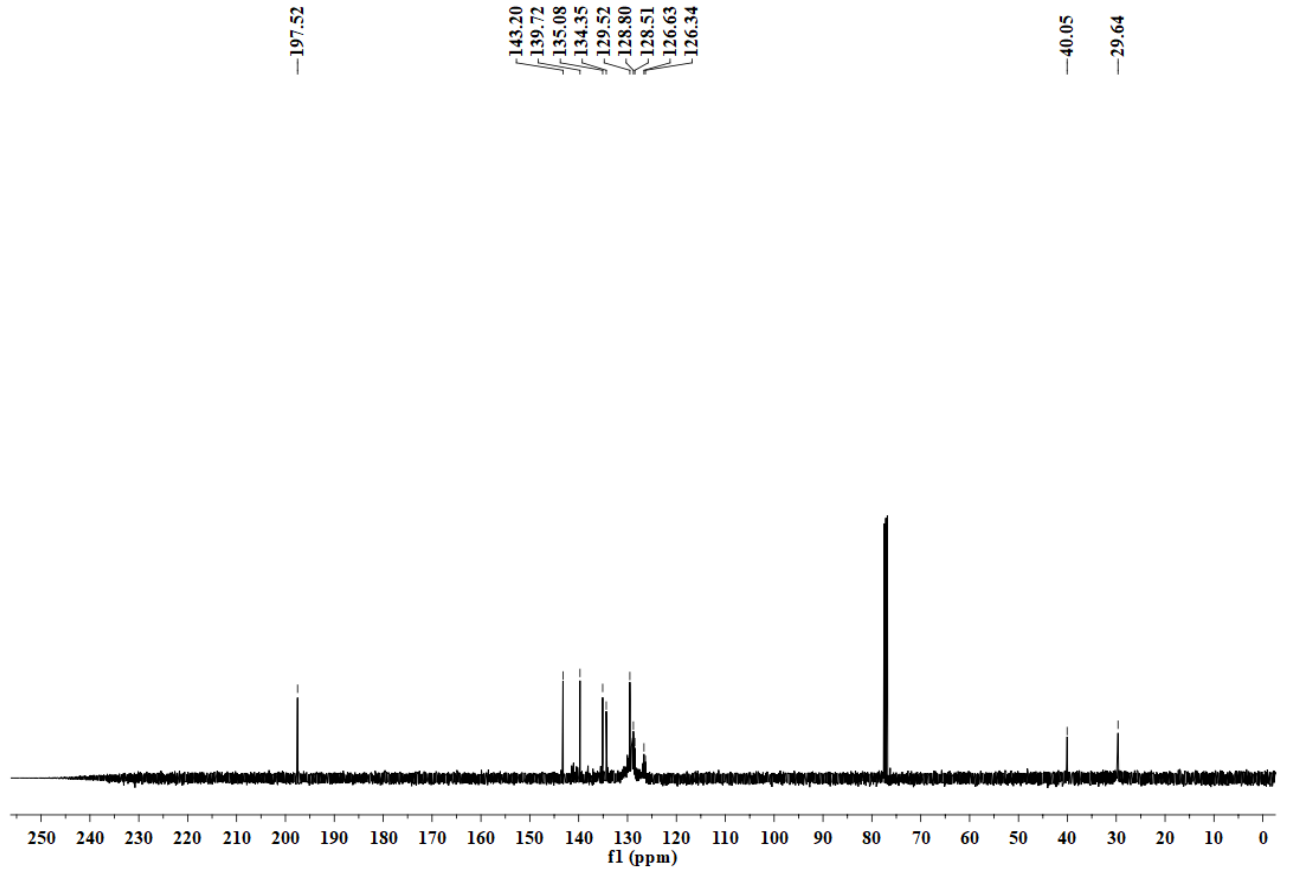


Figure S123. ^{13}CNMR spectrum of **5fe** taking $CDCl_3$ as solvent.

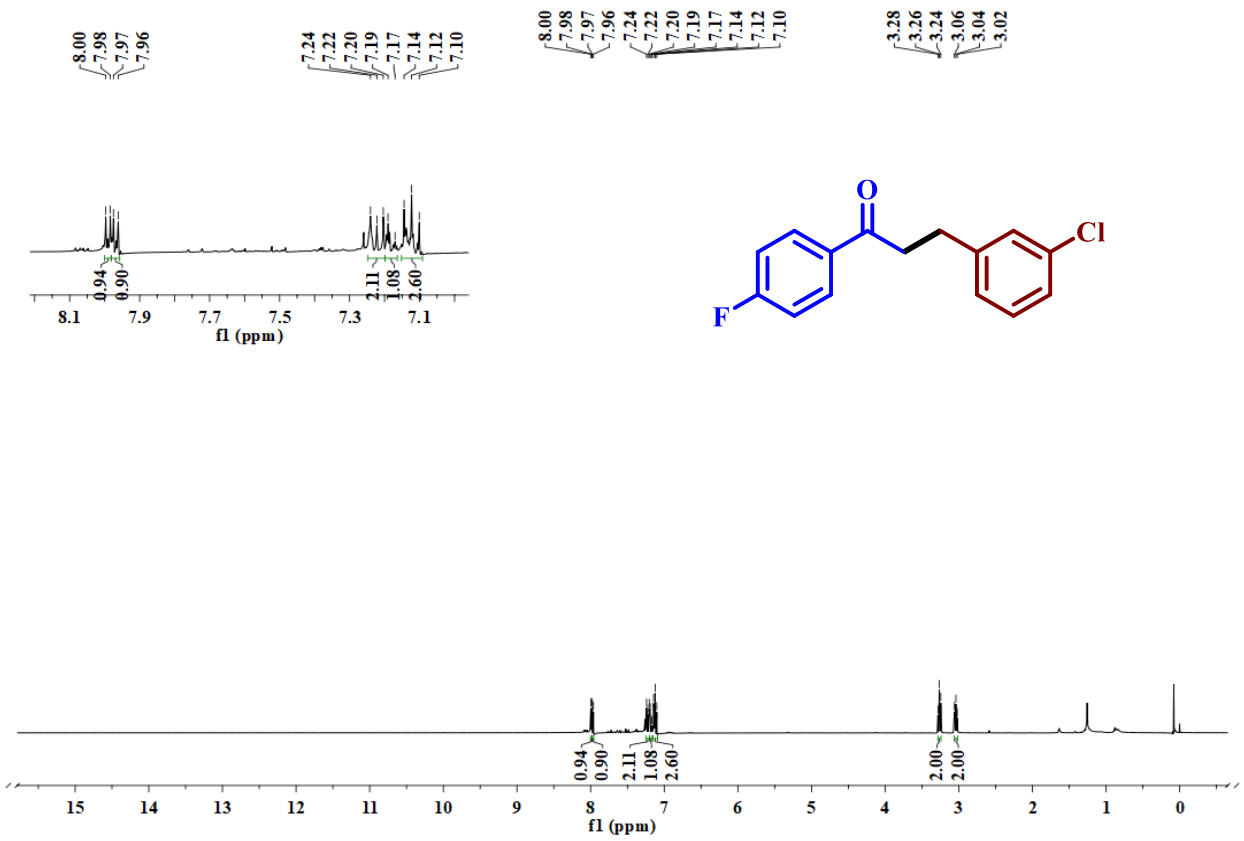


Figure S124. ^{1}H NMR spectrum of **5ff** taking $CDCl_3$ as solvent.

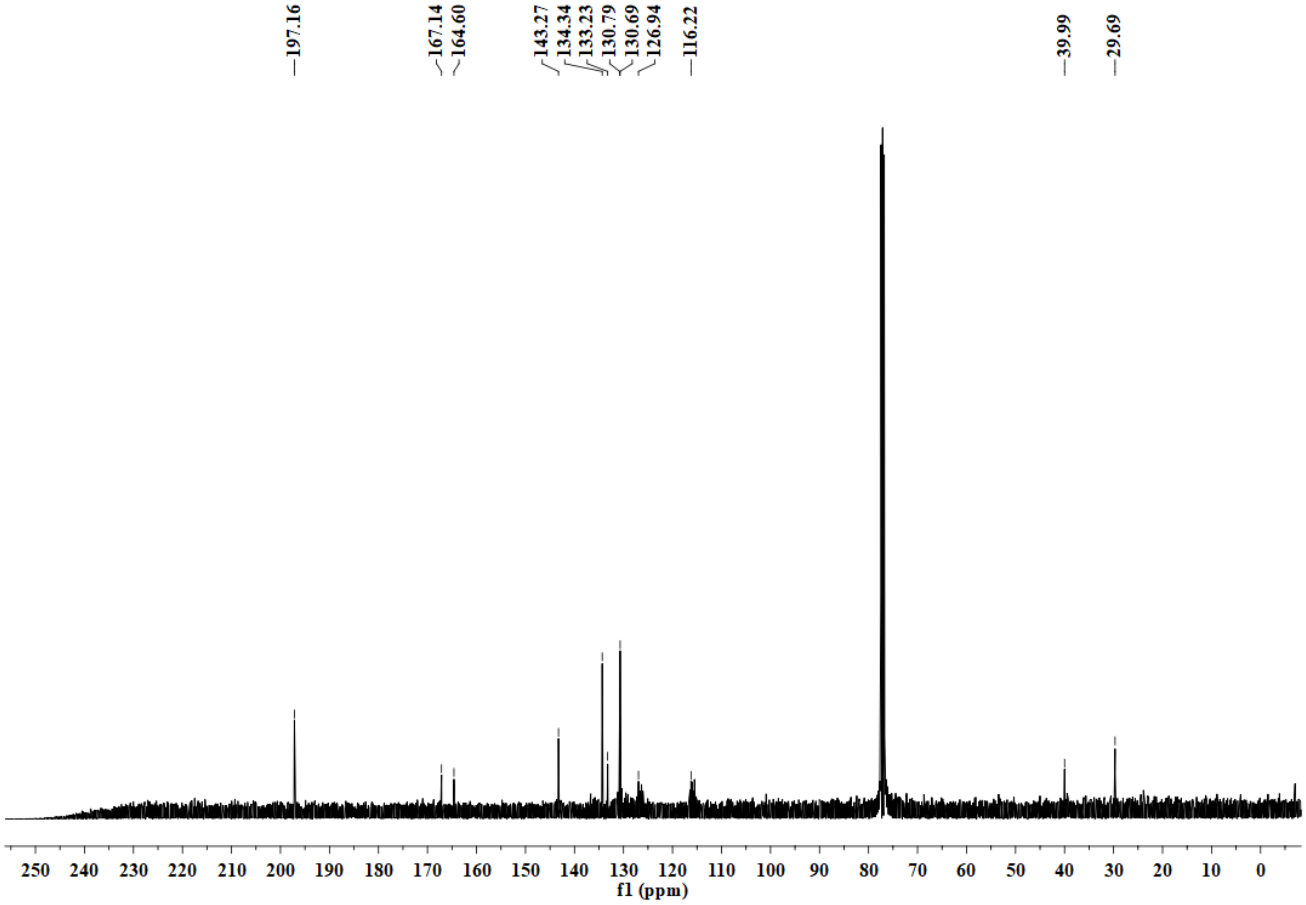


Figure S125. ^{13}CNMR spectrum of **5ff** taking $CDCl_3$ as solvent.

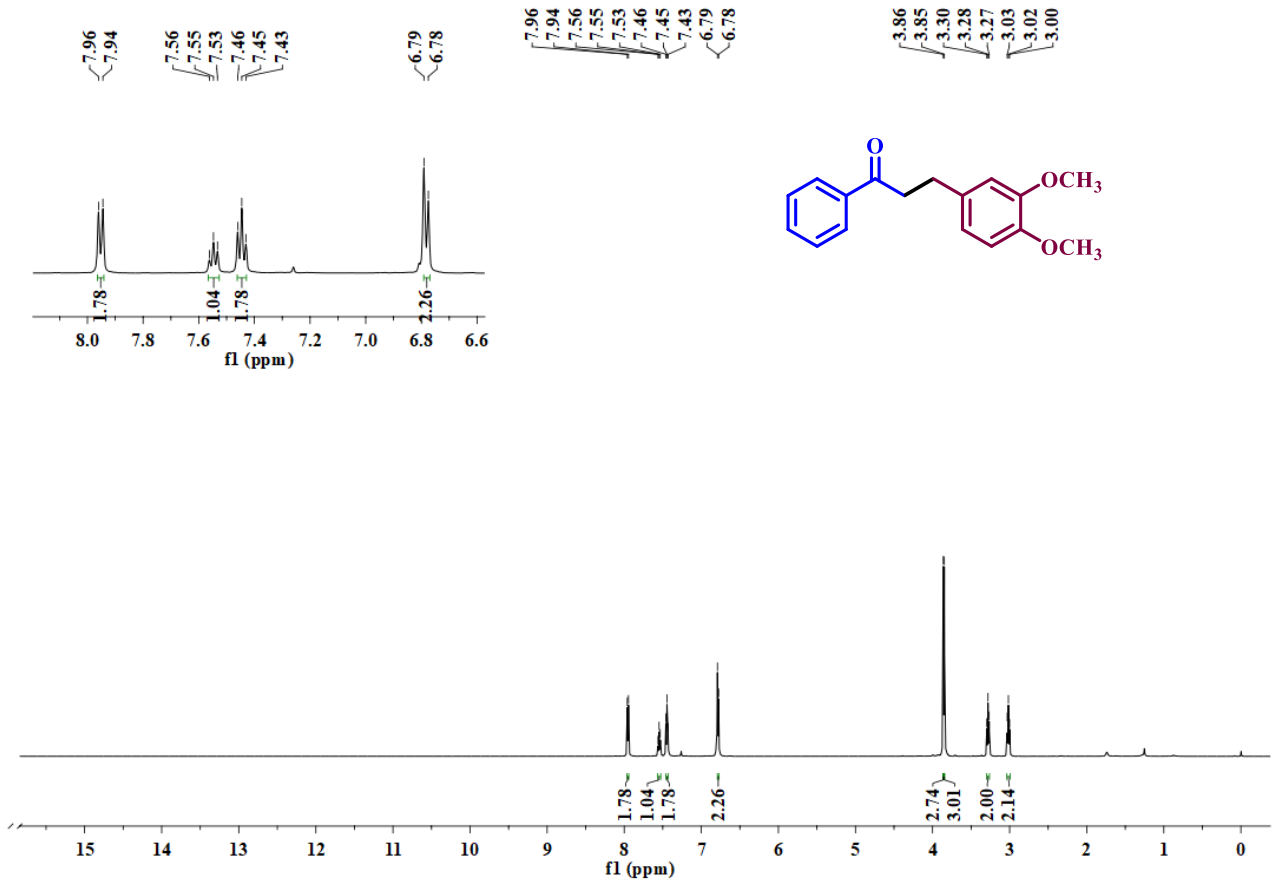


Figure S126. ^{1}H NMR spectrum of **5ga** taking $CDCl_3$ as solvent.

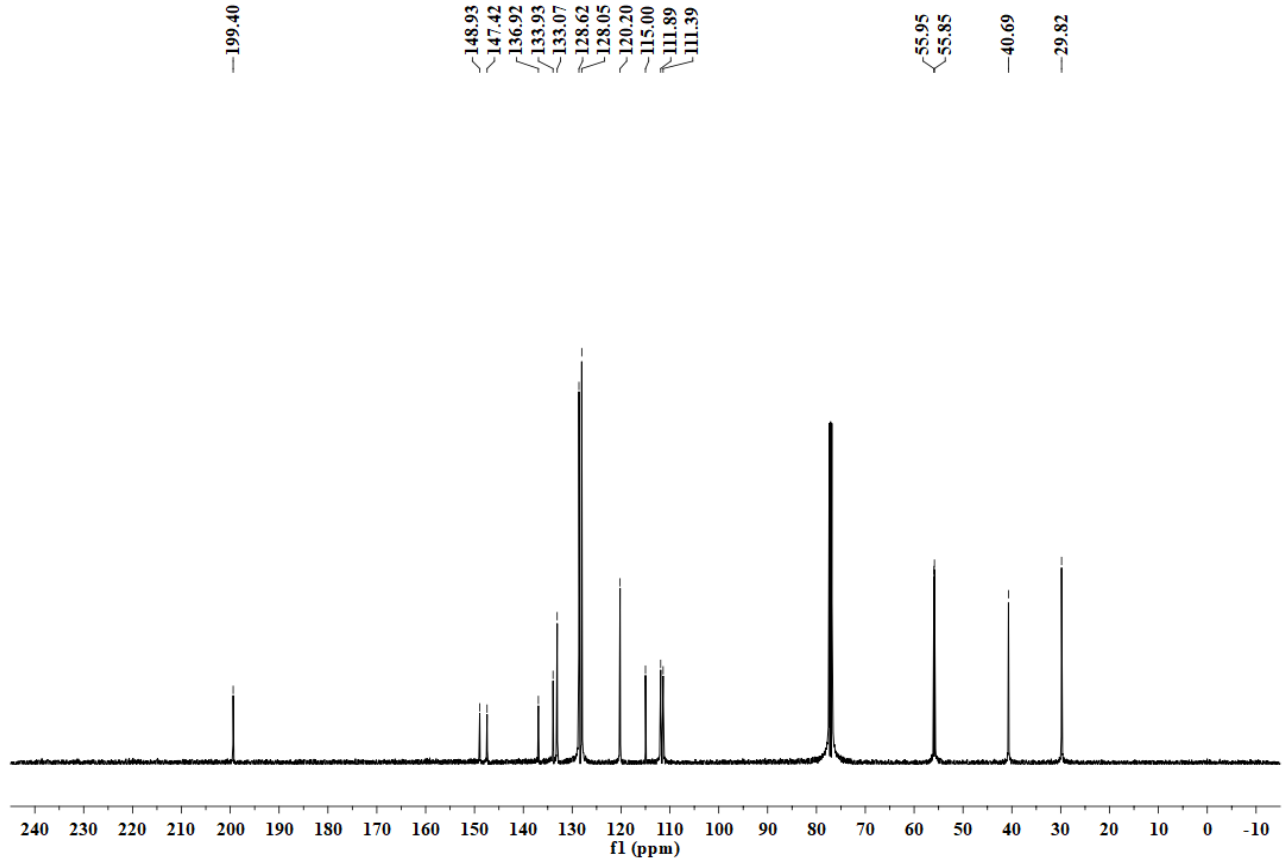


Figure S127. ^{13}CNMR spectrum of **5ga** taking $CDCl_3$ as solvent.

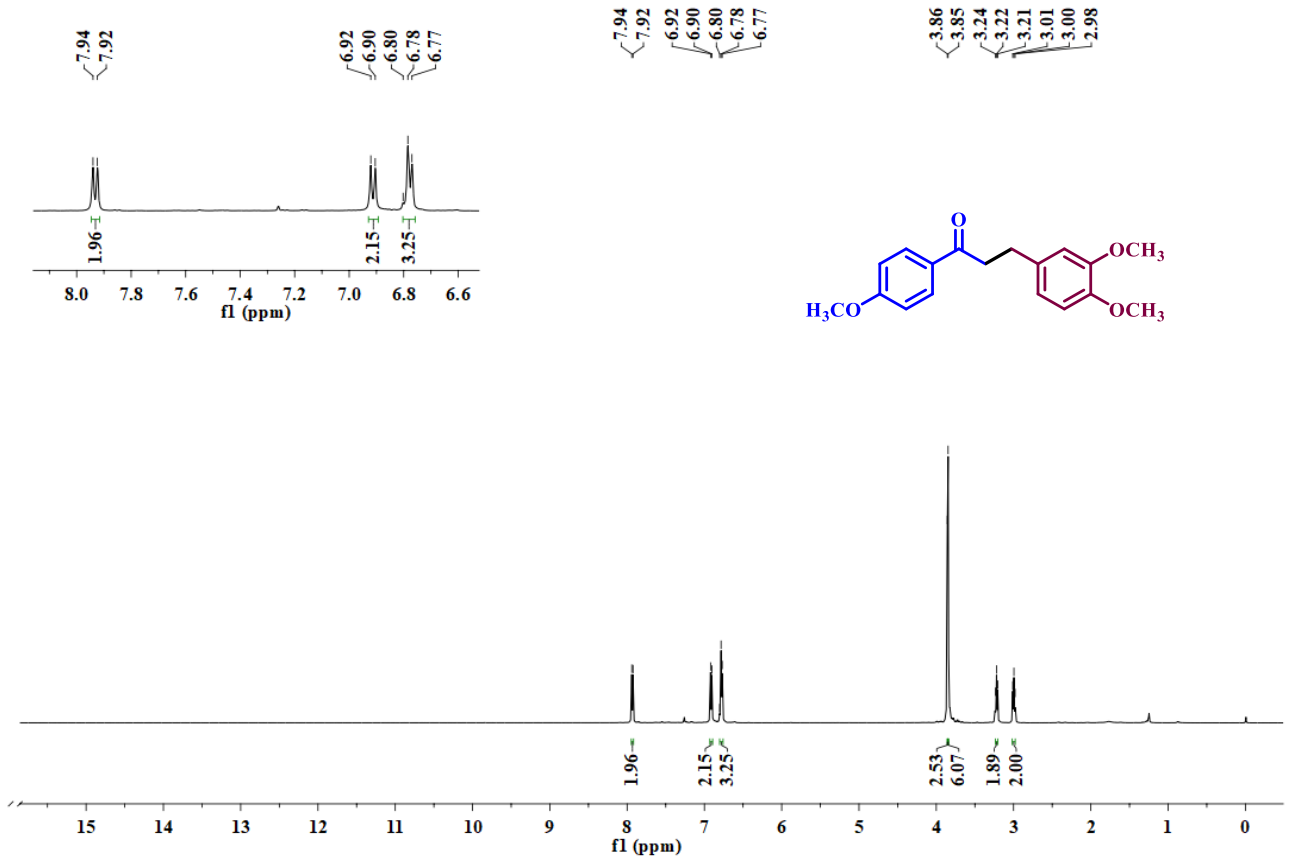


Figure S128. ^{1}H NMR spectrum of **5gb** taking $CDCl_3$ as solvent.

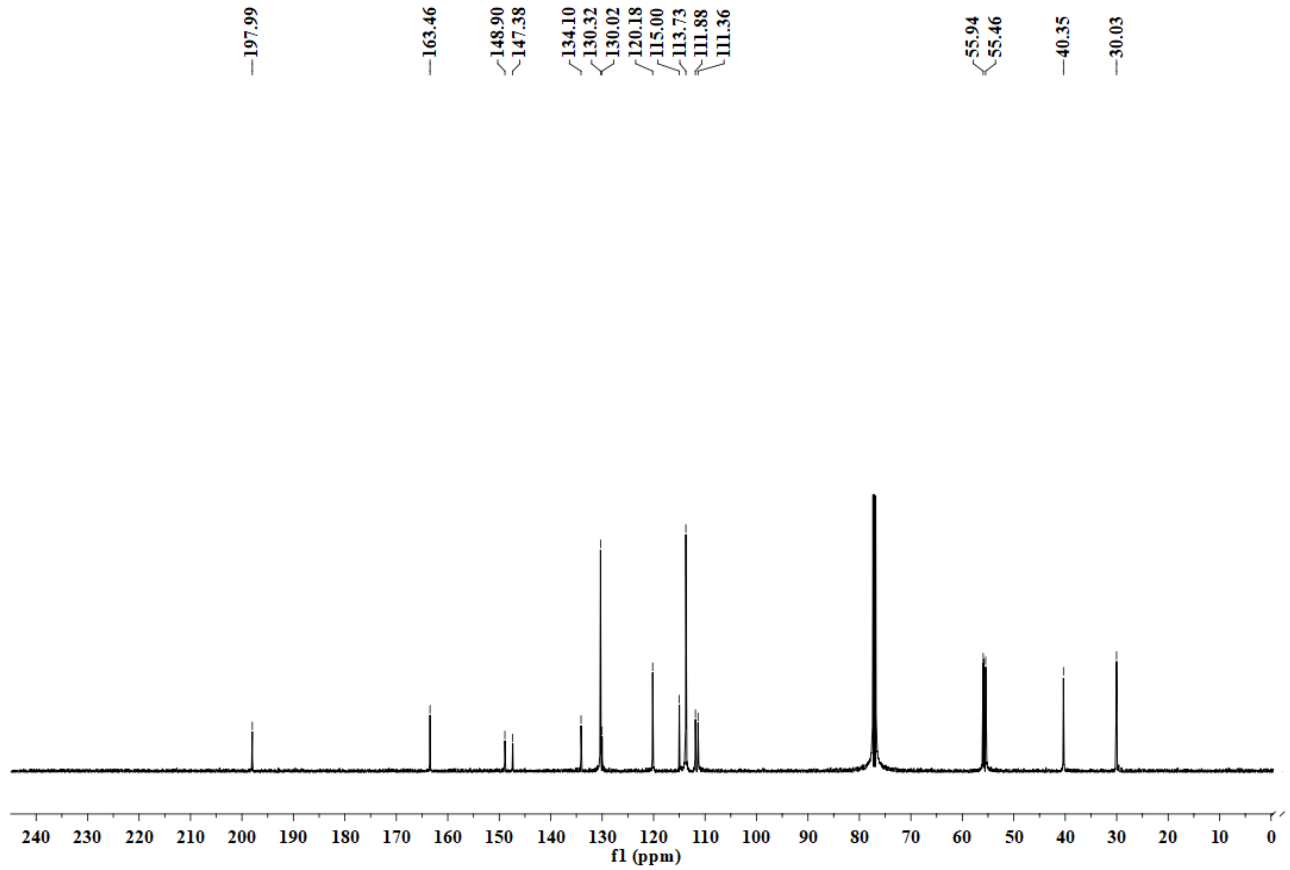


Figure S129. ^{13}CNMR spectrum of **5gb** taking $CDCl_3$ as solvent.

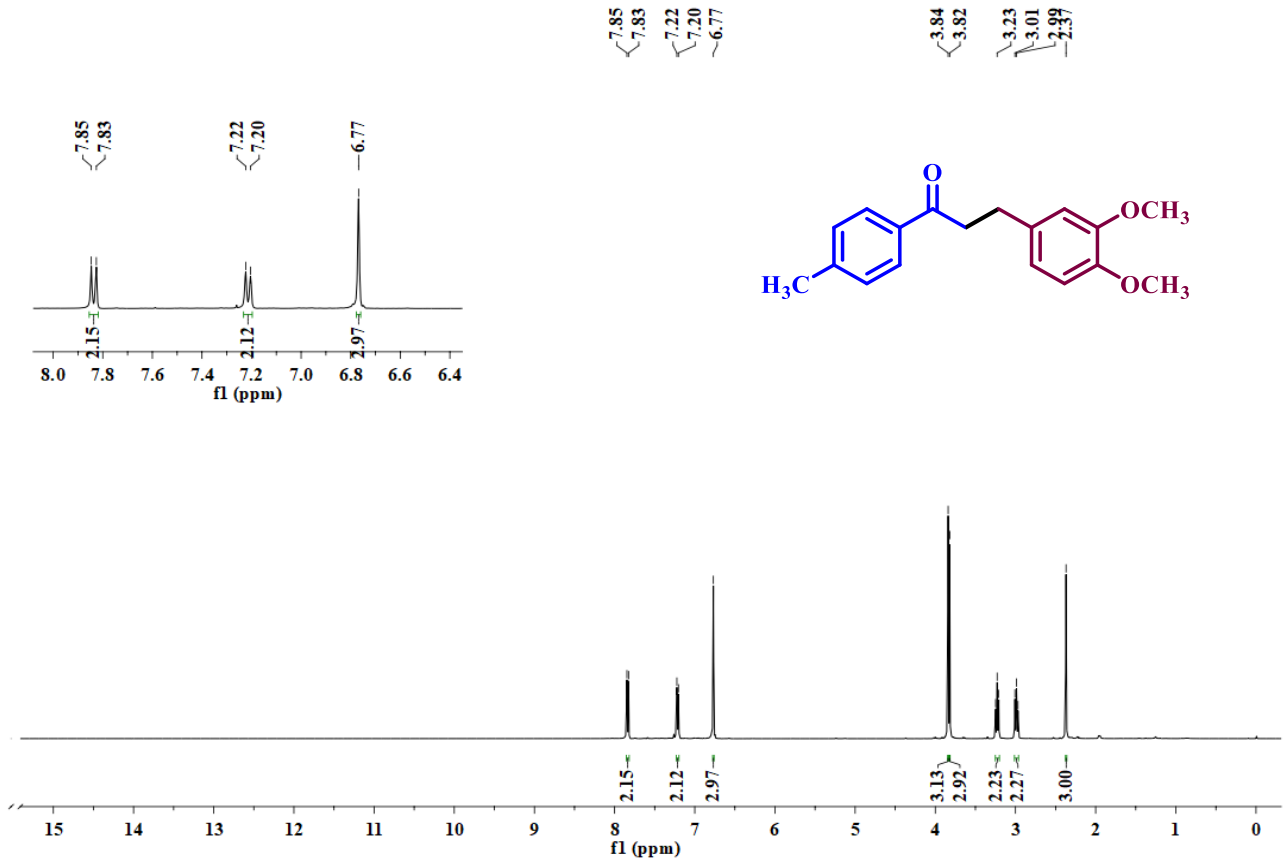


Figure S130. ^{1}H NMR spectrum of **5gc** taking $CDCl_3$ as solvent.

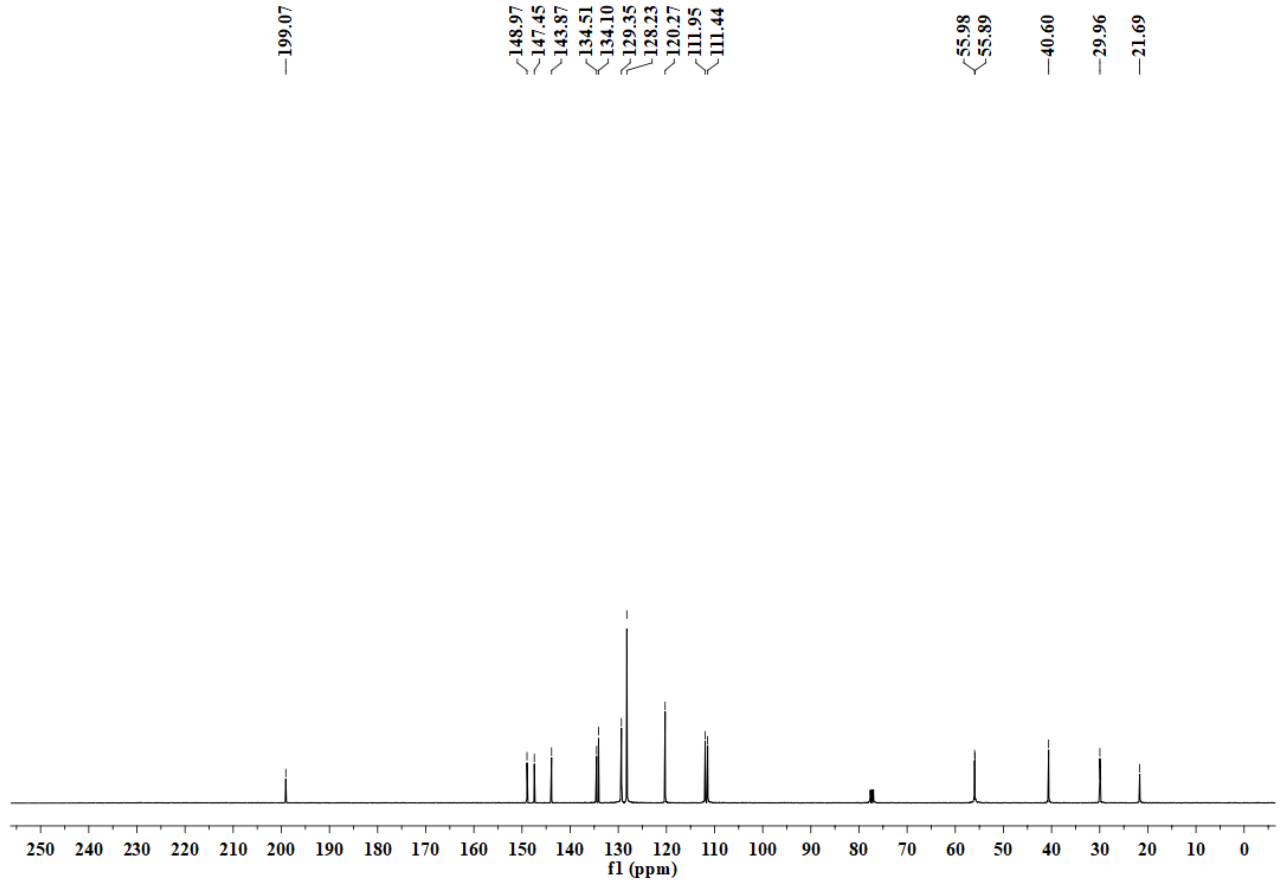


Figure S131. ^{13}CNMR spectrum of **5gc** taking $CDCl_3$ as solvent.

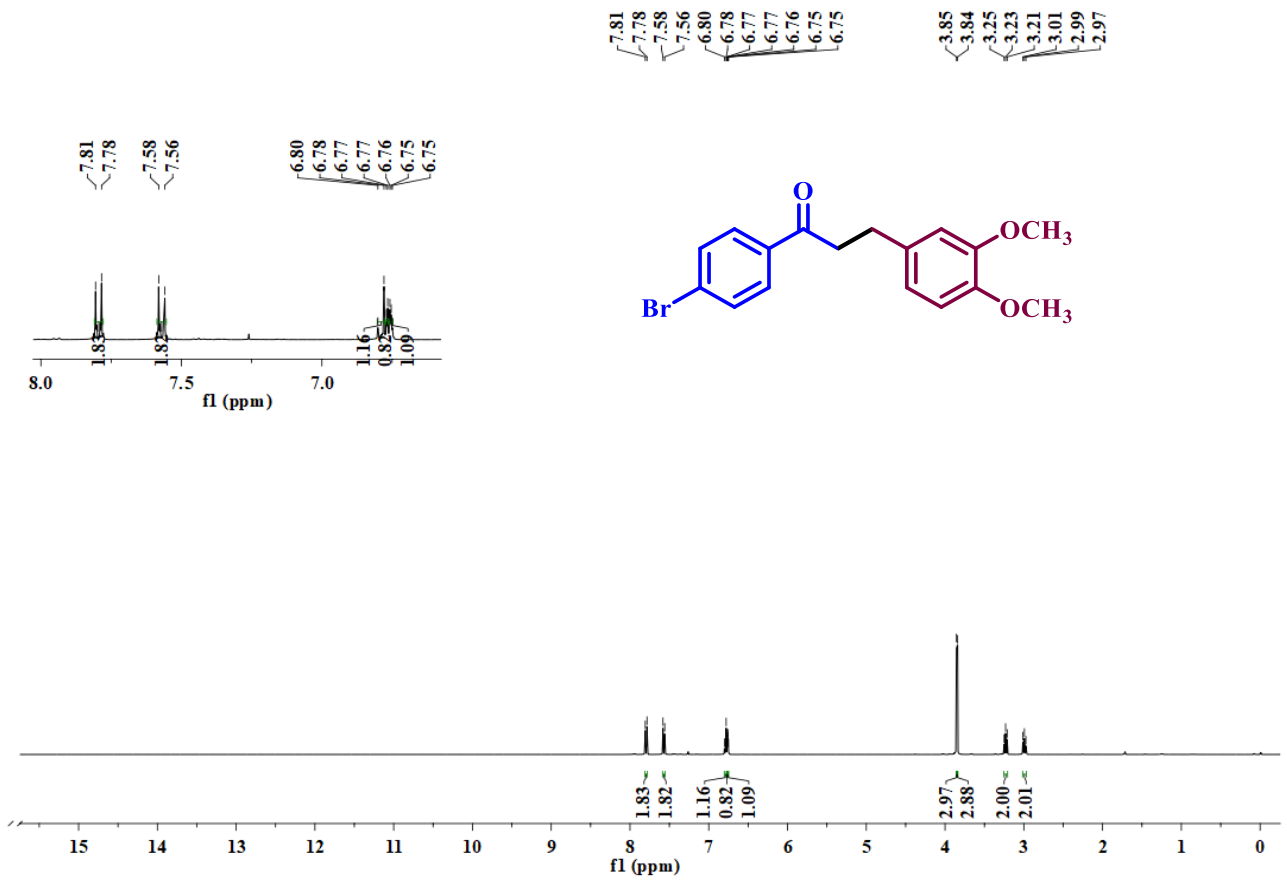


Figure S132. ^{1}H NMR spectrum of **5gd** taking $CDCl_3$ as solvent.

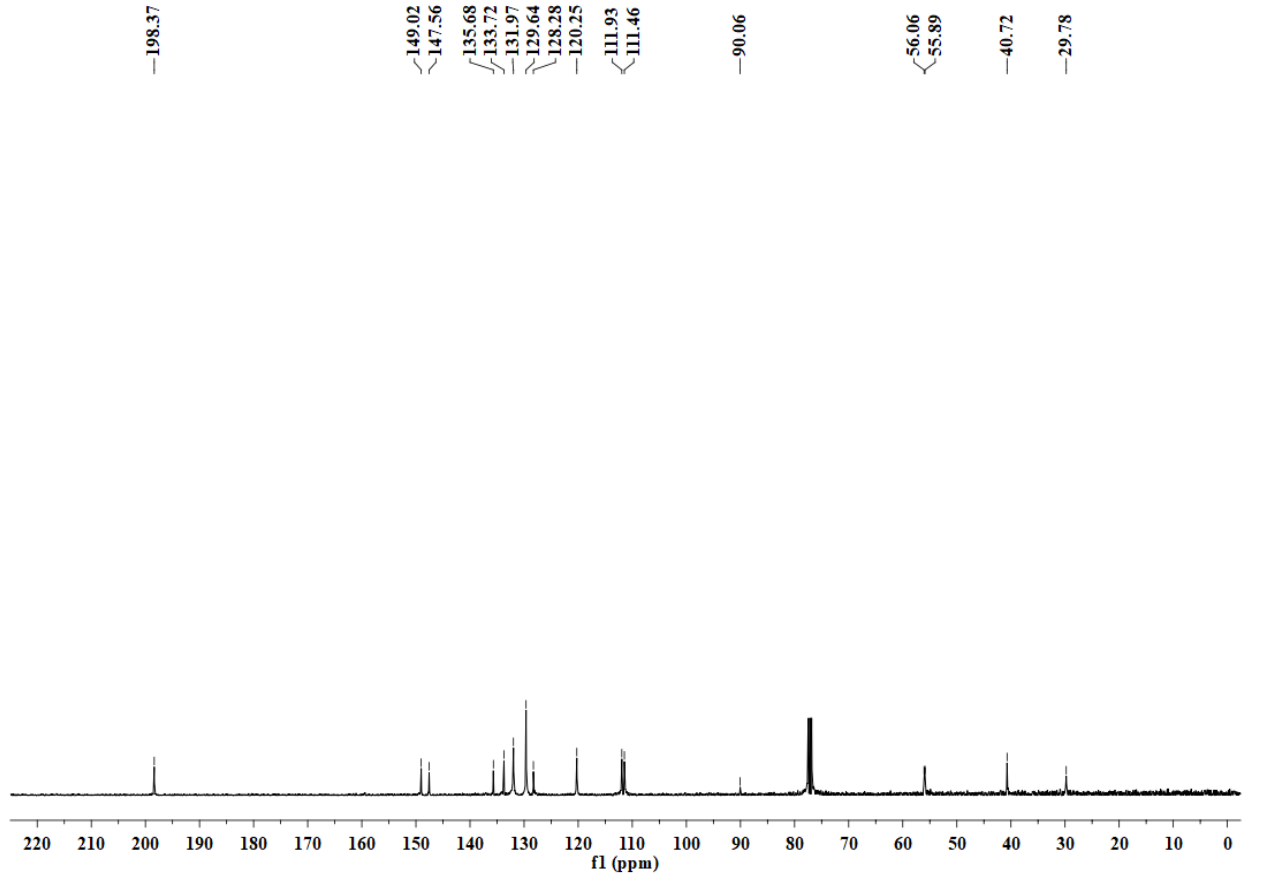


Figure S133. ^{13}CNMR spectrum of **5gd** taking $CDCl_3$ as solvent.

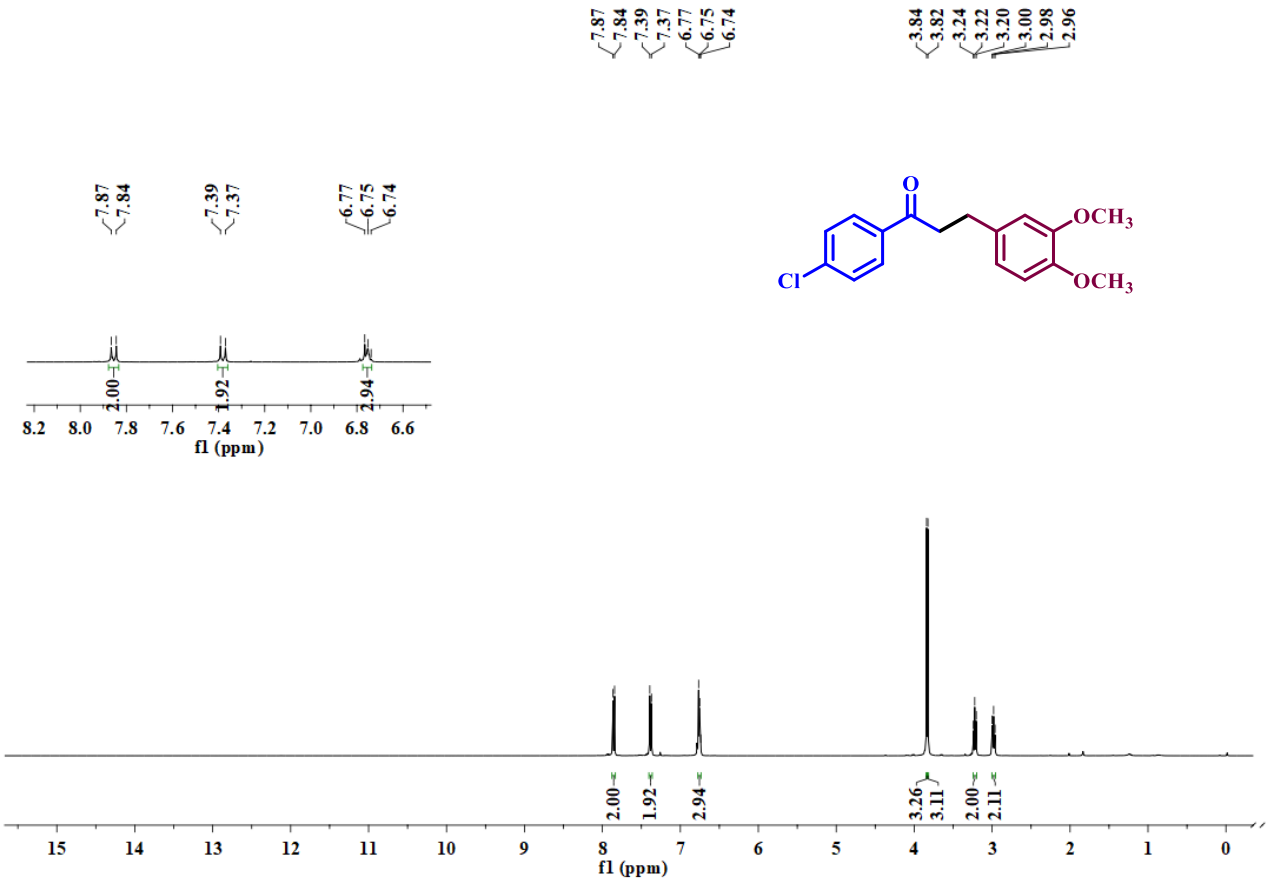


Figure S134. ^{1}H NMR spectrum of **5ge** taking $CDCl_3$ as solvent.

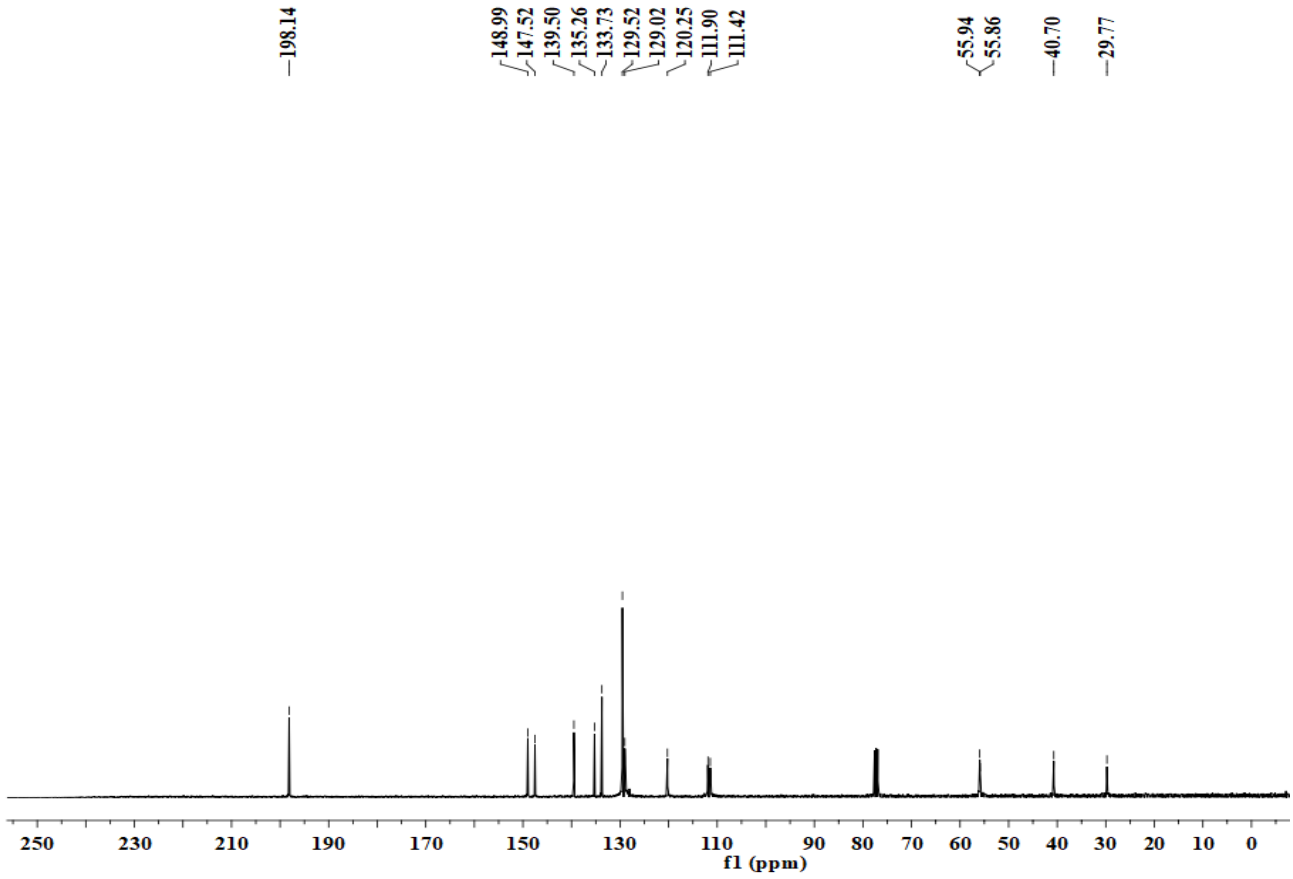


Figure S135. ^{13}CNMR spectrum of **5ge** taking $CDCl_3$ as solvent.

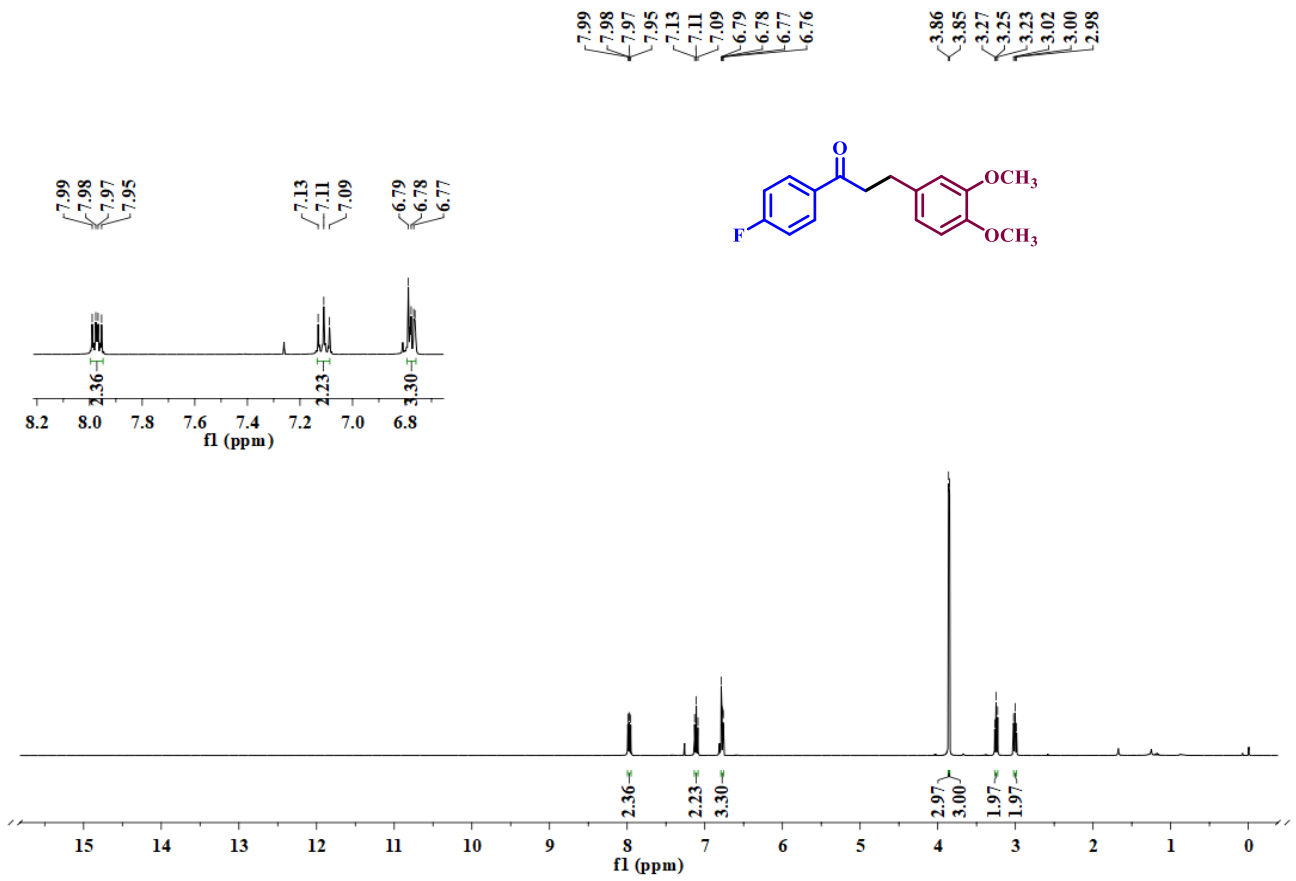


Figure S136. ^{1}H NMR spectrum of **5gf** taking $CDCl_3$ as solvent.

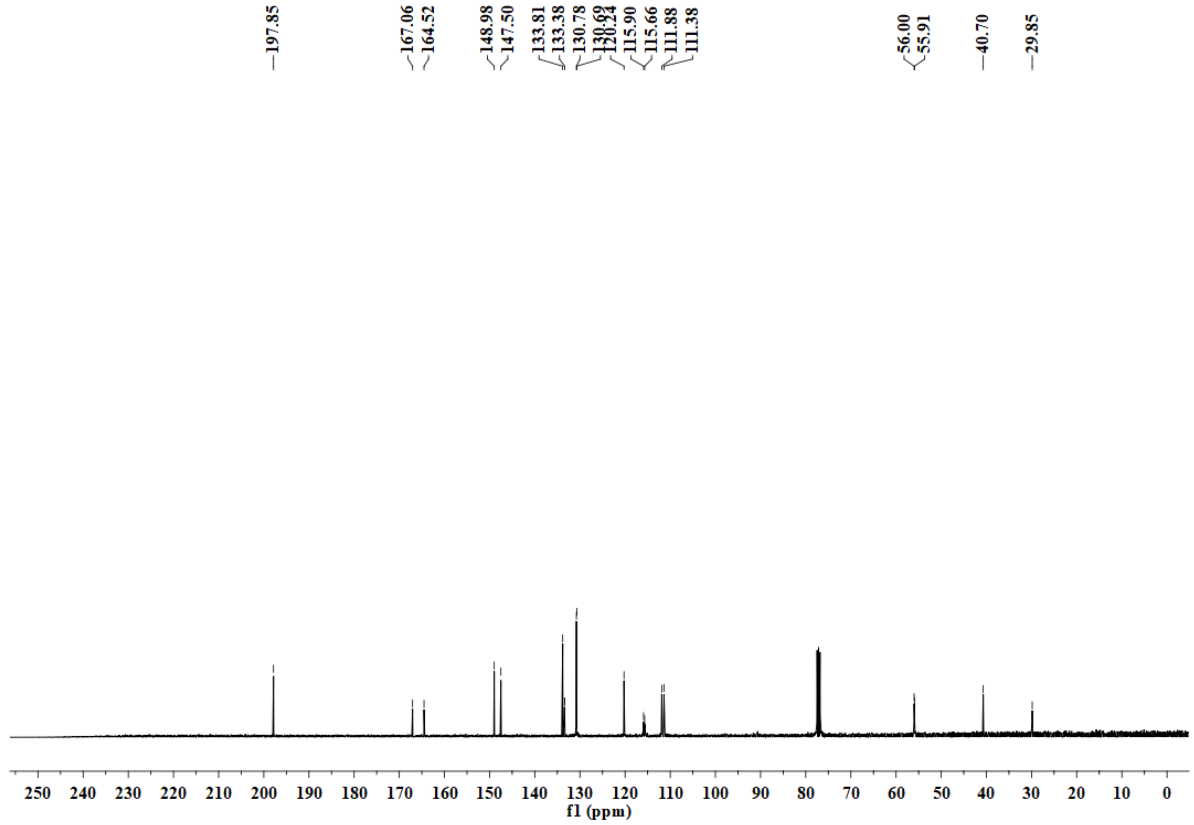
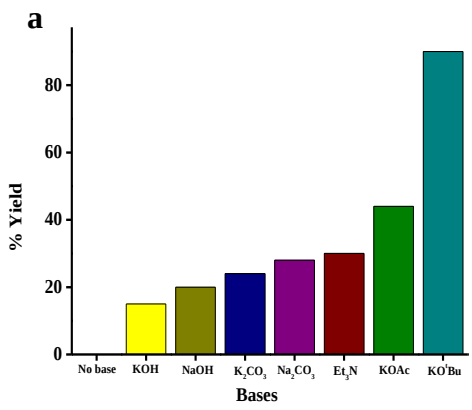
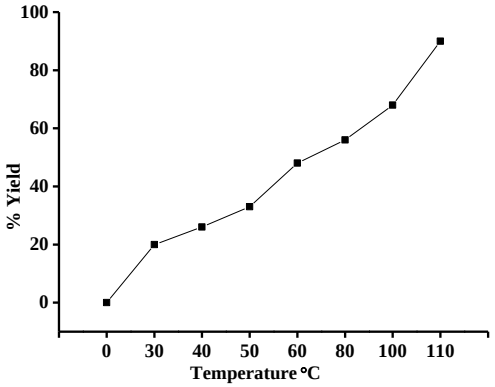


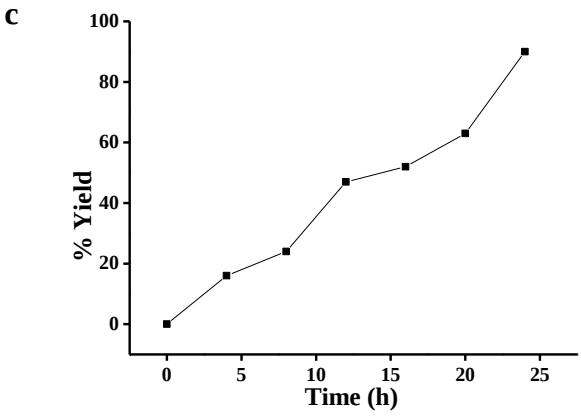
Figure S137. ^{13}CNMR spectrum of **5gf** taking $CDCl_3$ as solvent.



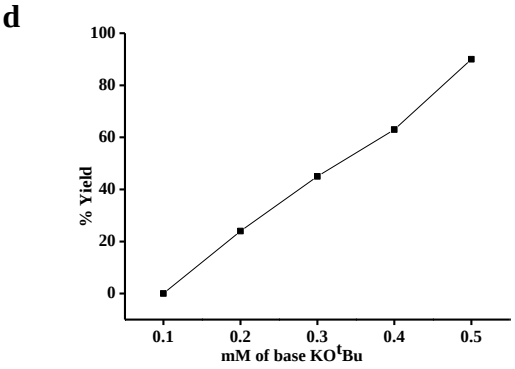
Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (2 mol%), bases (0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h.



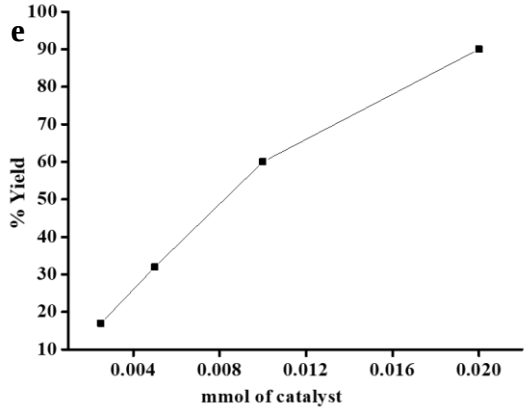
Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 0°C -110 °C for 24 h.



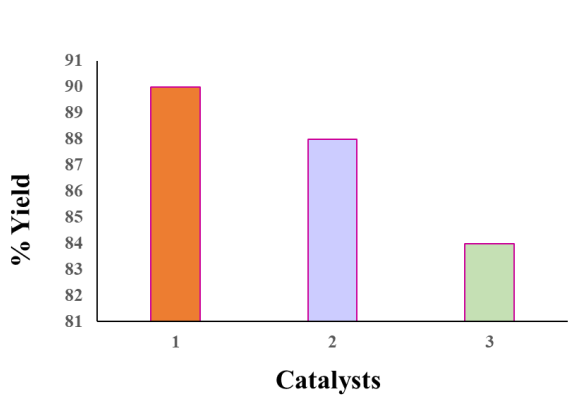
Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 110 °C for 0 h-24 h.



Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (2 mol%), KO^{t}Bu (0.1 mmol-0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h.



Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalyst (0.4 mol%-2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h.



Reaction Condition: 2-amino benzyl alcohol (1 mmol), Acetophenone derivatives (1 mmol), catalysts (**Co1**-**Co3**) (2 mol%), KO^{t}Bu (0.5 mmol) Toluene 2 ml heated at 110 °C for 24 h. Isolated yields.

Figure S138. The reaction profile of cobalt catalyzed dehydrogenative cyclization of 2-amino benzyl alcohol (**a**) Effect of bases (**b**) Effect of temperature (**c**) Effect of time (**d**) Loading of base KO^{t}Bu (**e**) Loading of catalysts (**f**) Effect of catalysts.

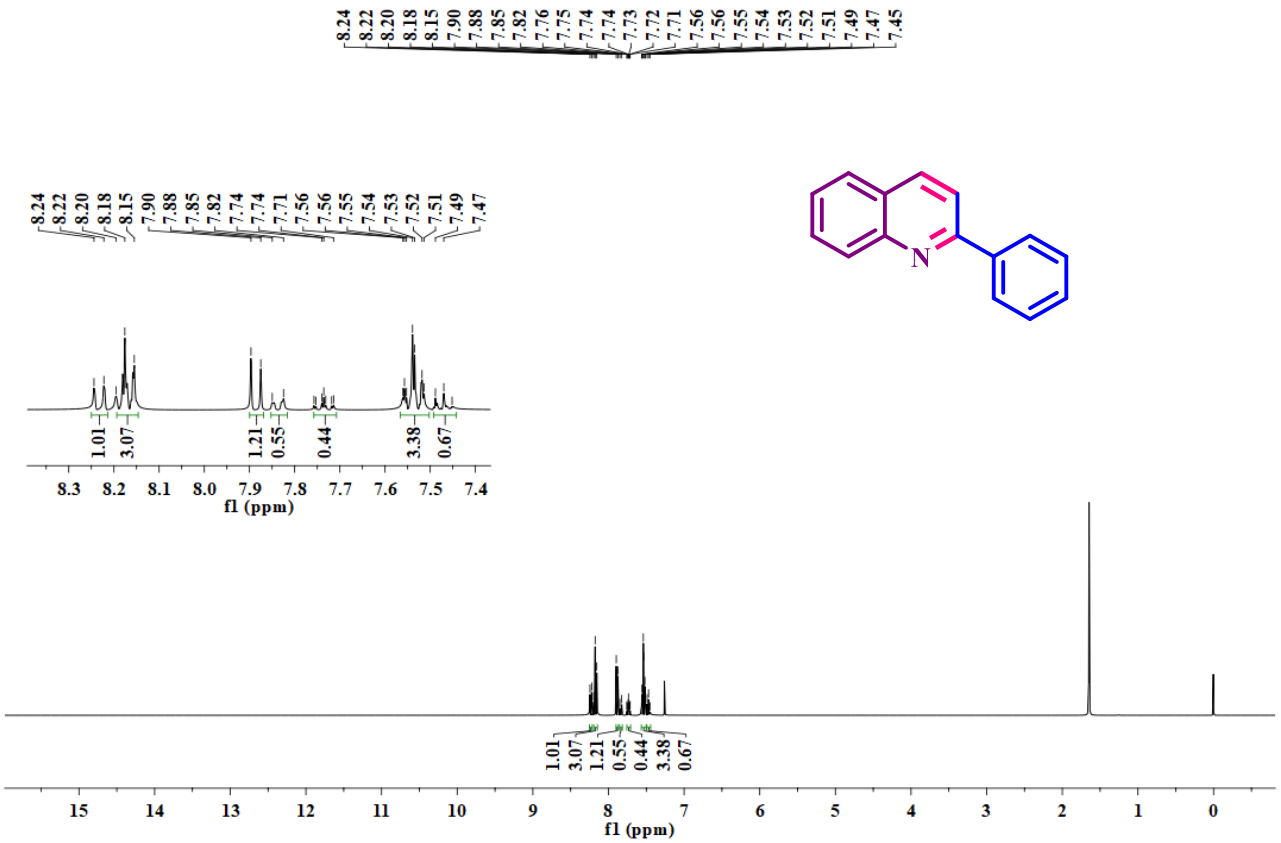


Figure S139. ^{1}H NMR spectrum of **7aa** taking $CDCl_3$ as solvent.

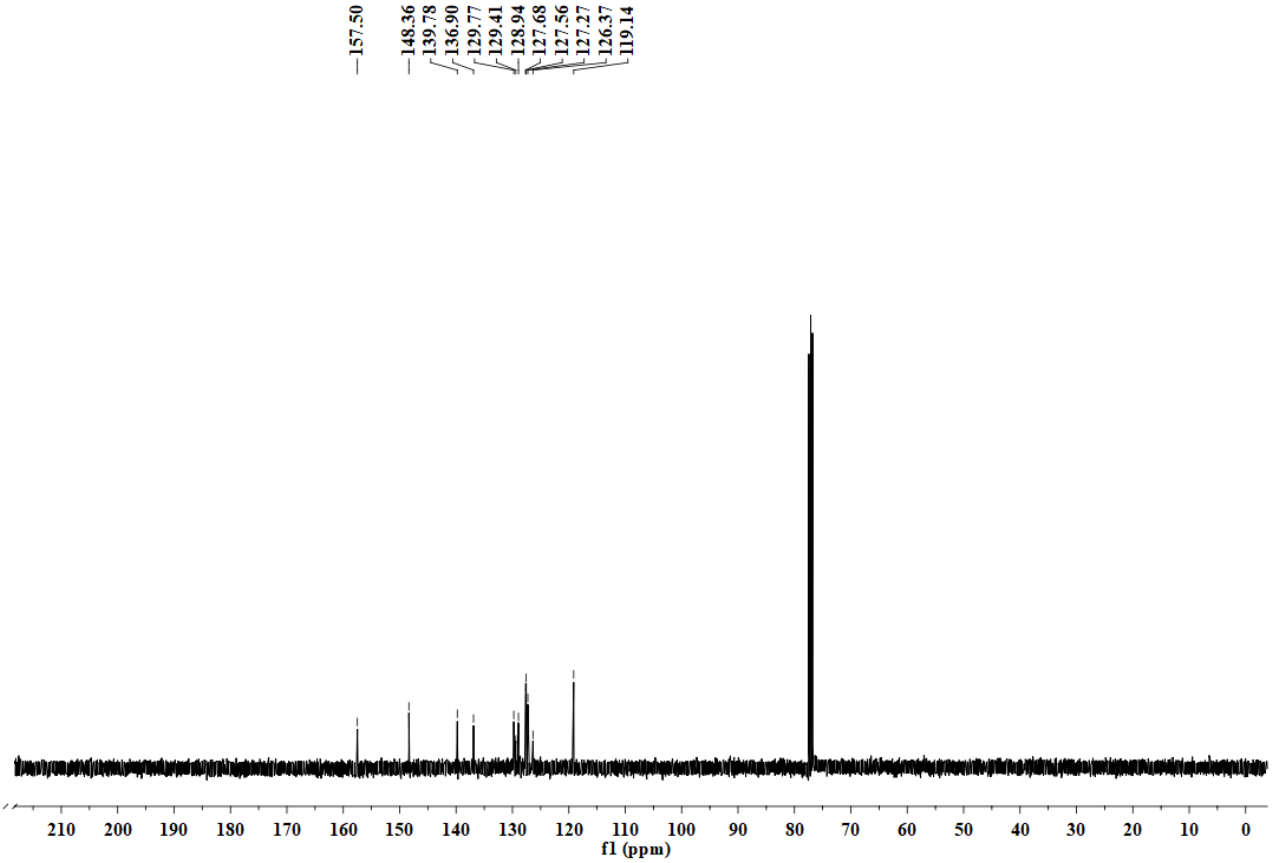


Figure S140. ^{13}CNMR spectrum of **7aa** taking $CDCl_3$ as solvent.

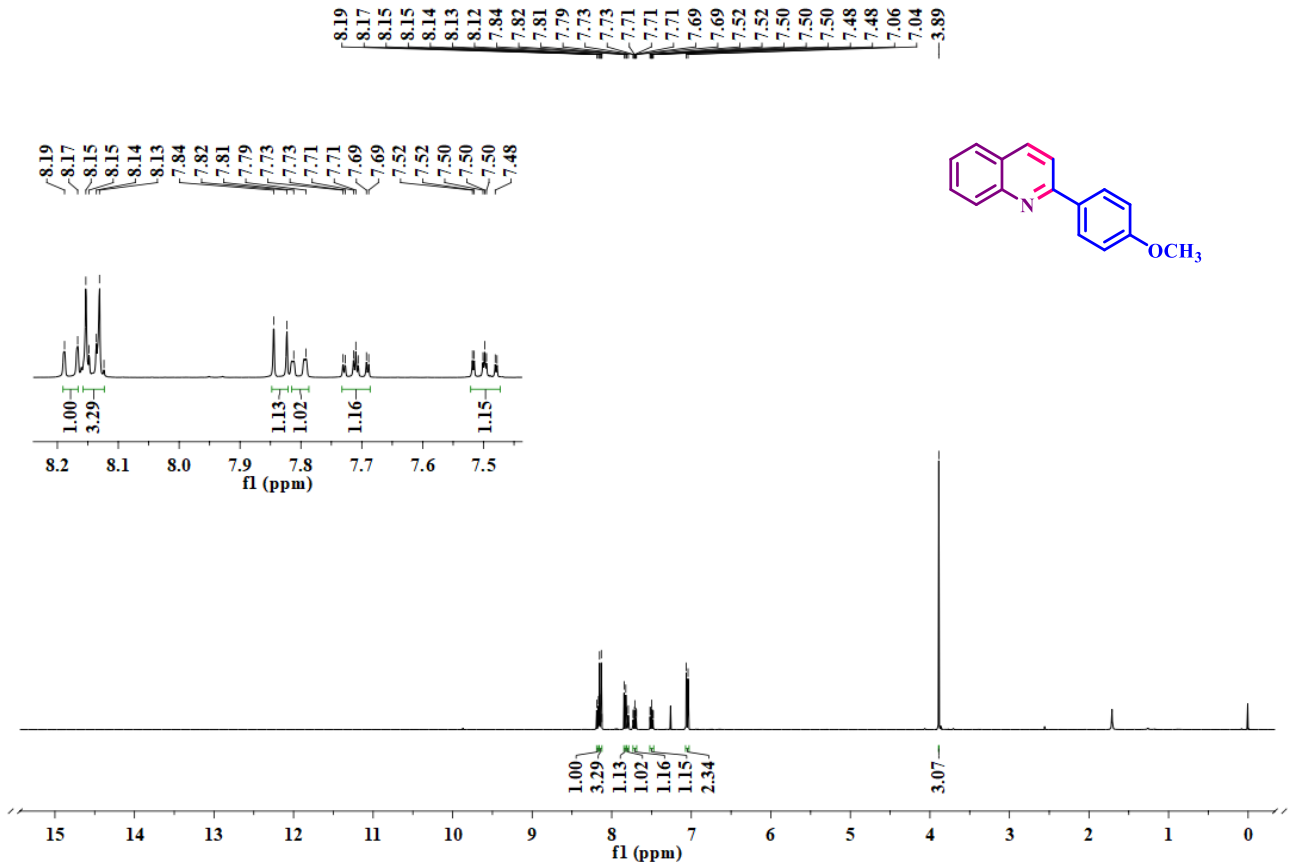


Figure S141. ^{1}H NMR spectrum of **7ab** taking $CDCl_3$ as solvent.

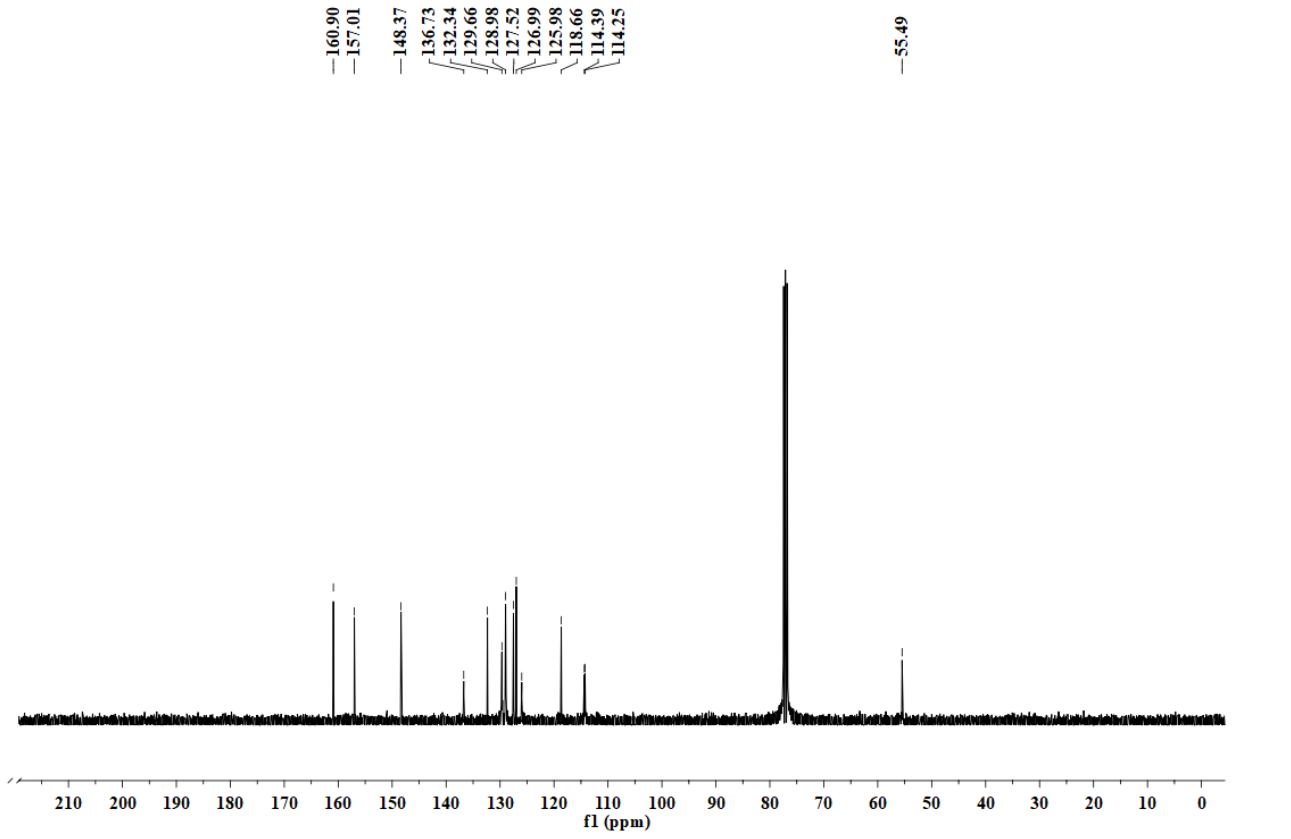


Figure S142. ^{13}CNMR spectrum of **7ab** taking $CDCl_3$ as solvent.

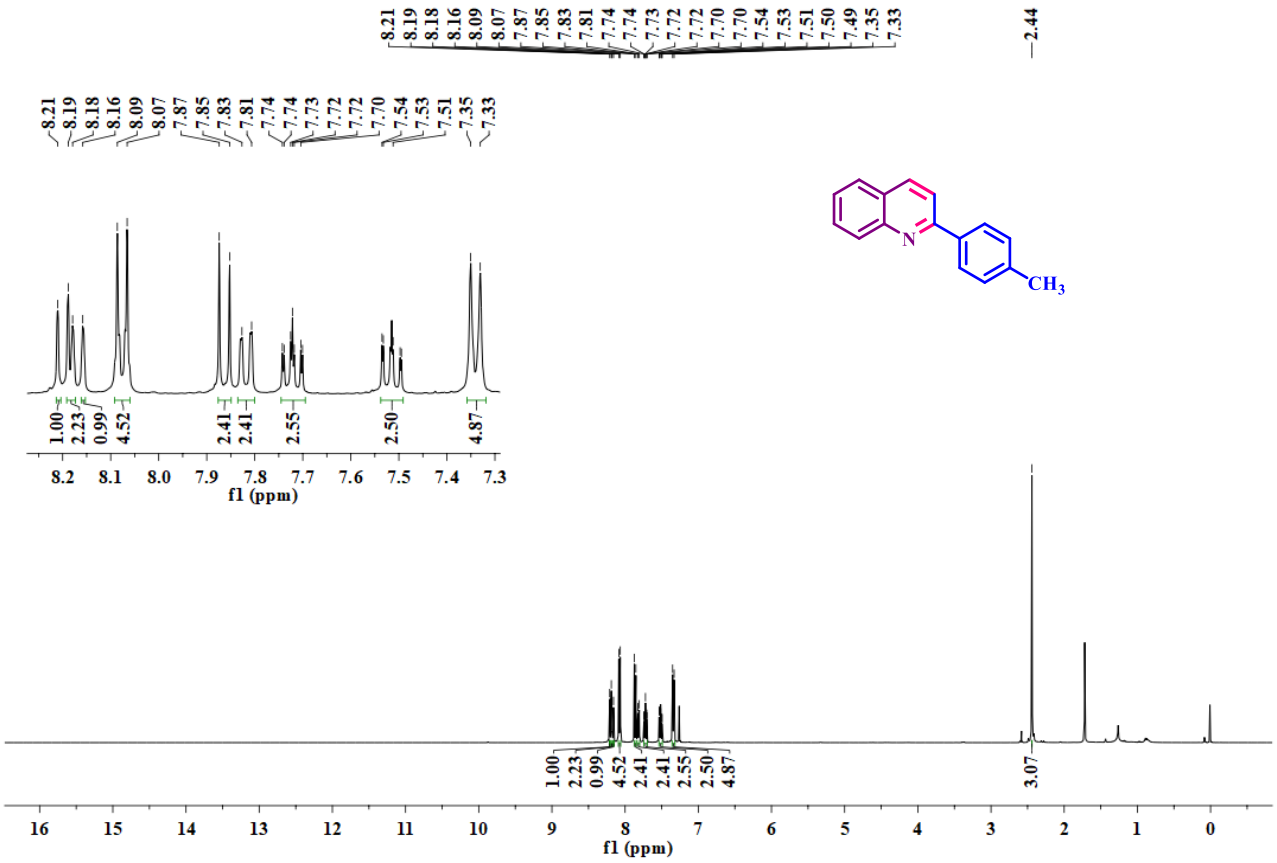


Figure S143. ^{1}H NMR spectrum of **7ac** taking $CDCl_3$ as solvent.

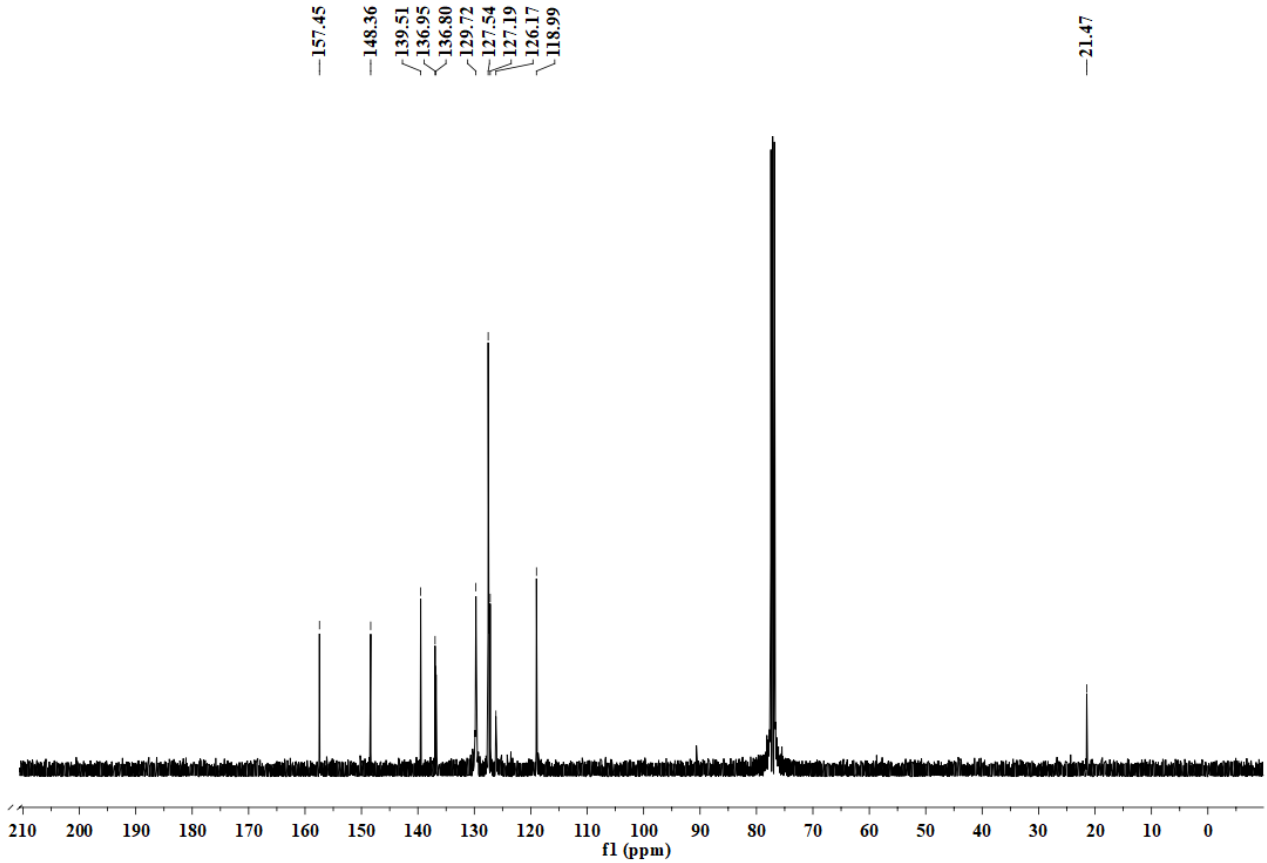


Figure S144. ^{13}CNMR spectrum of **7ac** taking $CDCl_3$ as solvent.

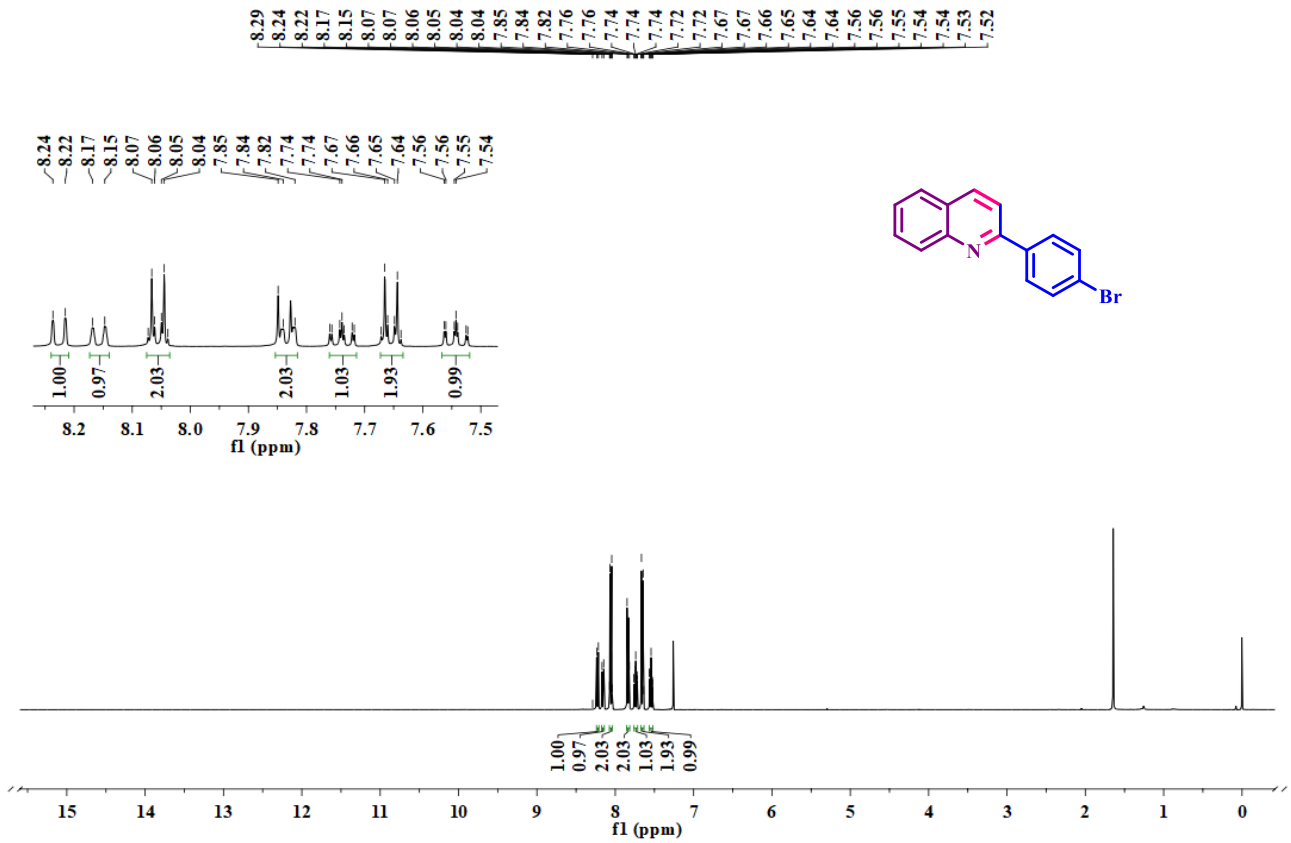


Figure S145. ^{1}H NMR spectrum of **7ad** taking $CDCl_3$ as solvent.

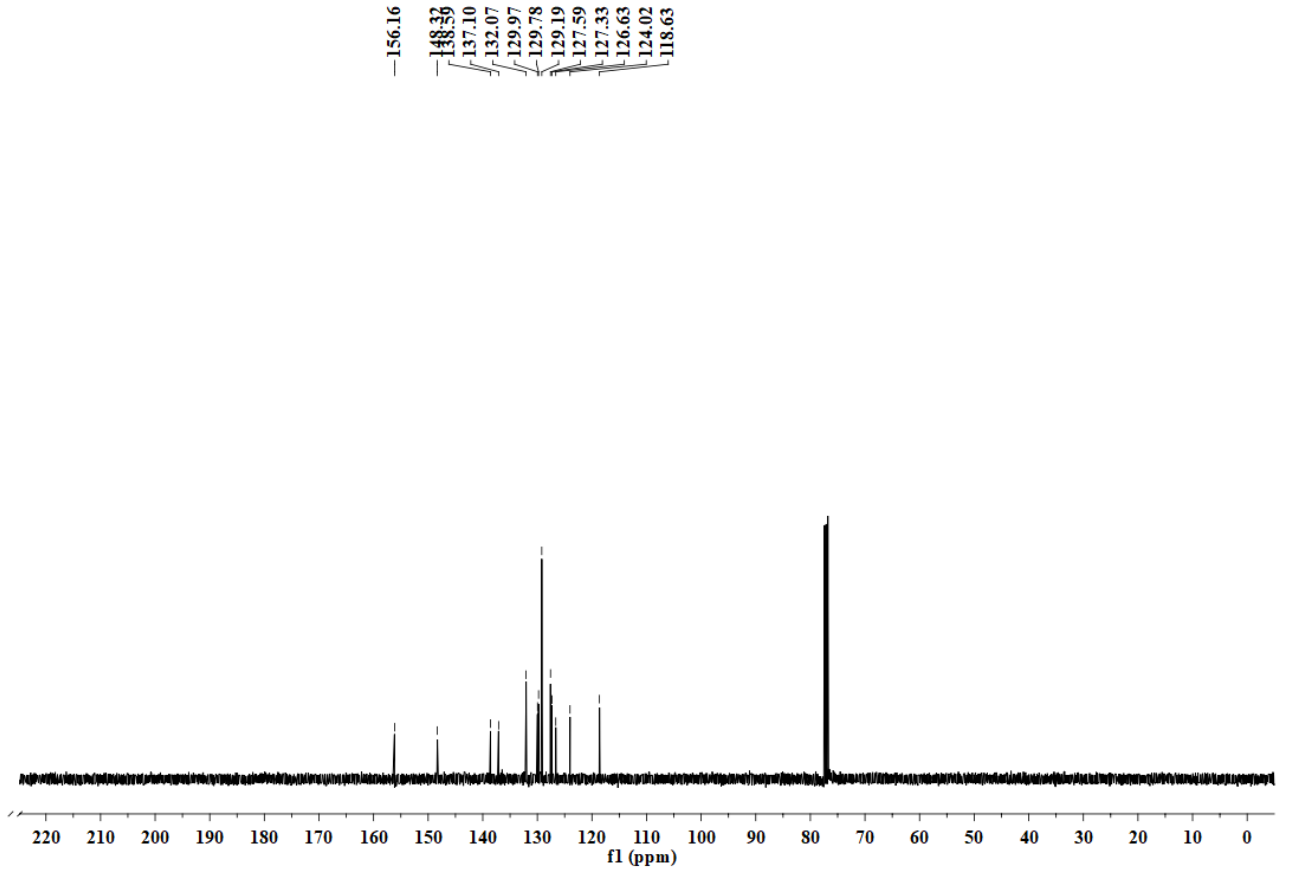


Figure S146. ^{13}CNMR spectrum of **7ad** taking $CDCl_3$ as solvent.

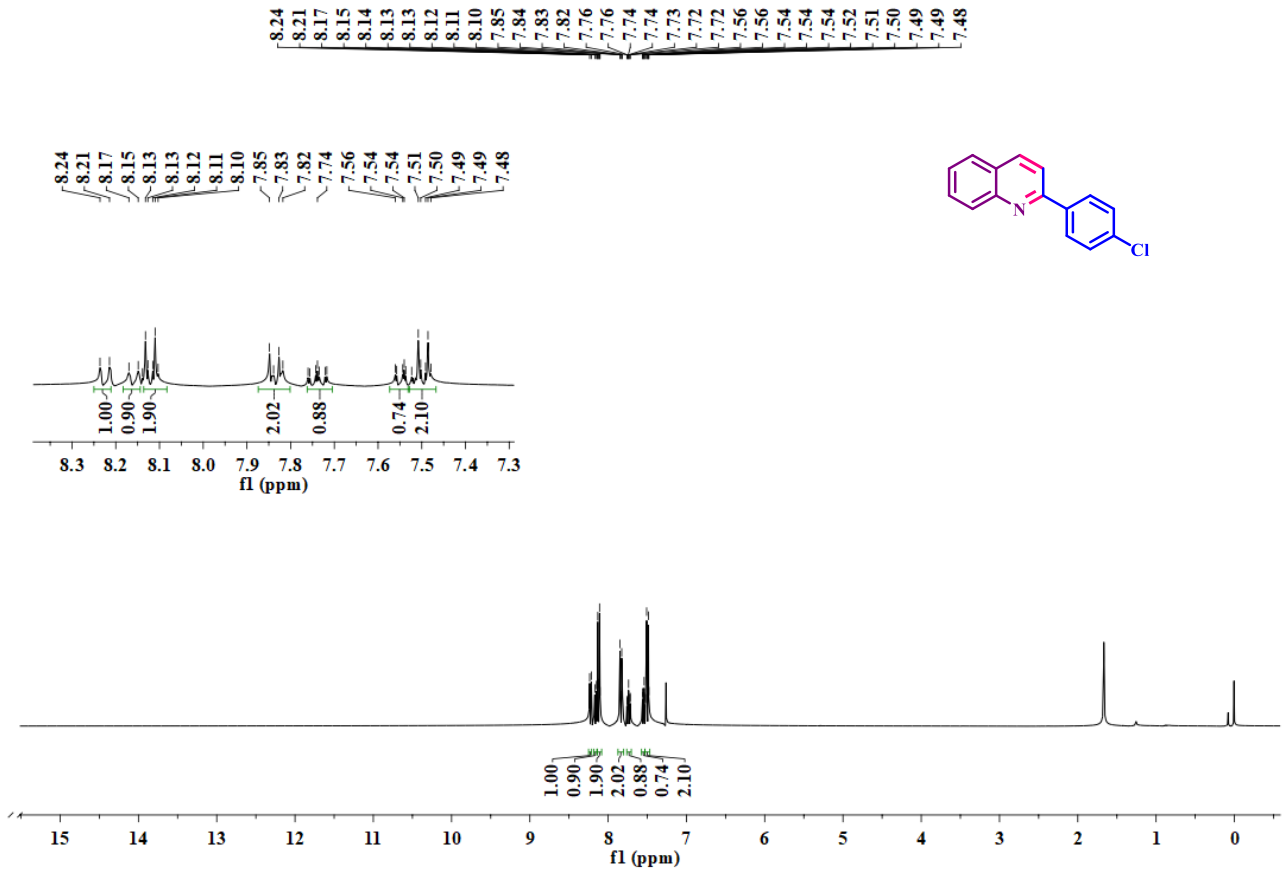


Figure S147. ^{1}H NMR spectrum of **7ae** taking $CDCl_3$ as solvent.

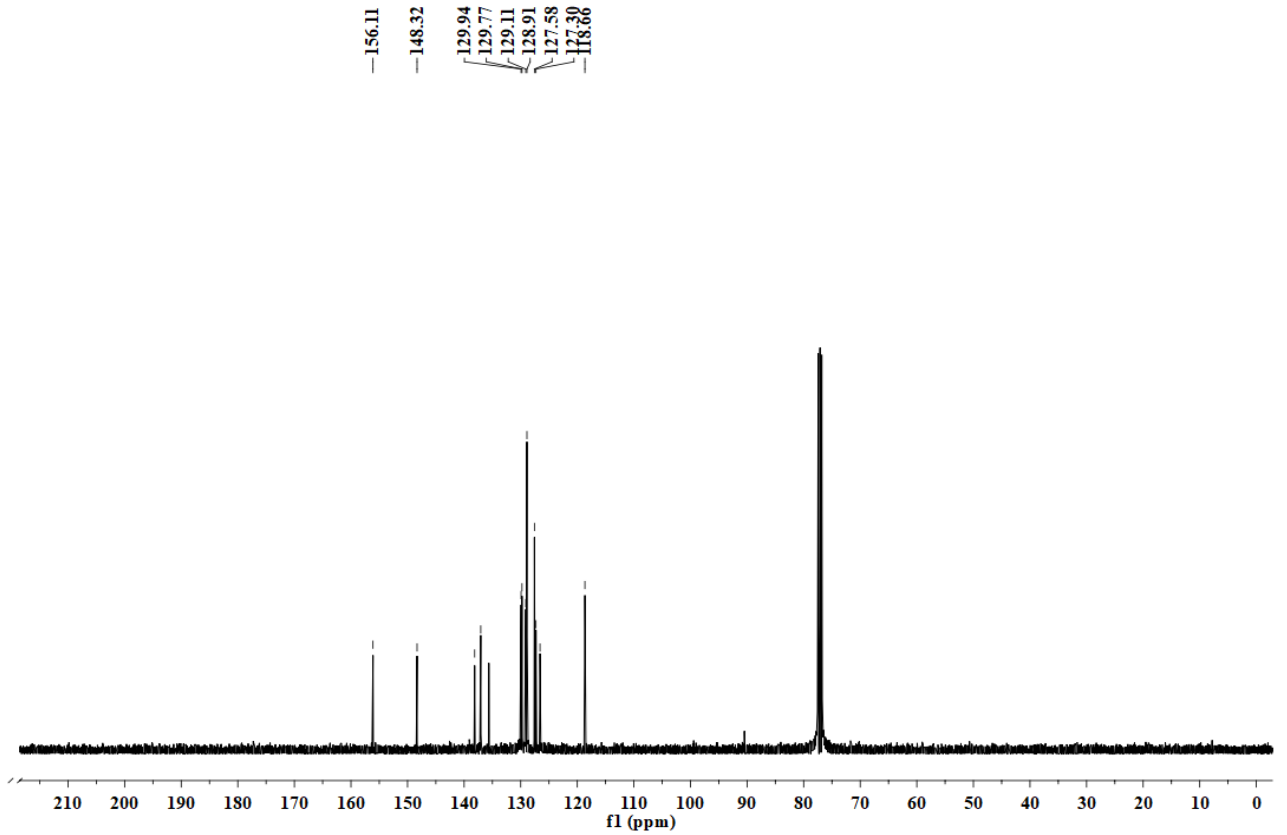


Figure S148. ^{13}CNMR spectrum of **7ae** taking $CDCl_3$ as solvent.

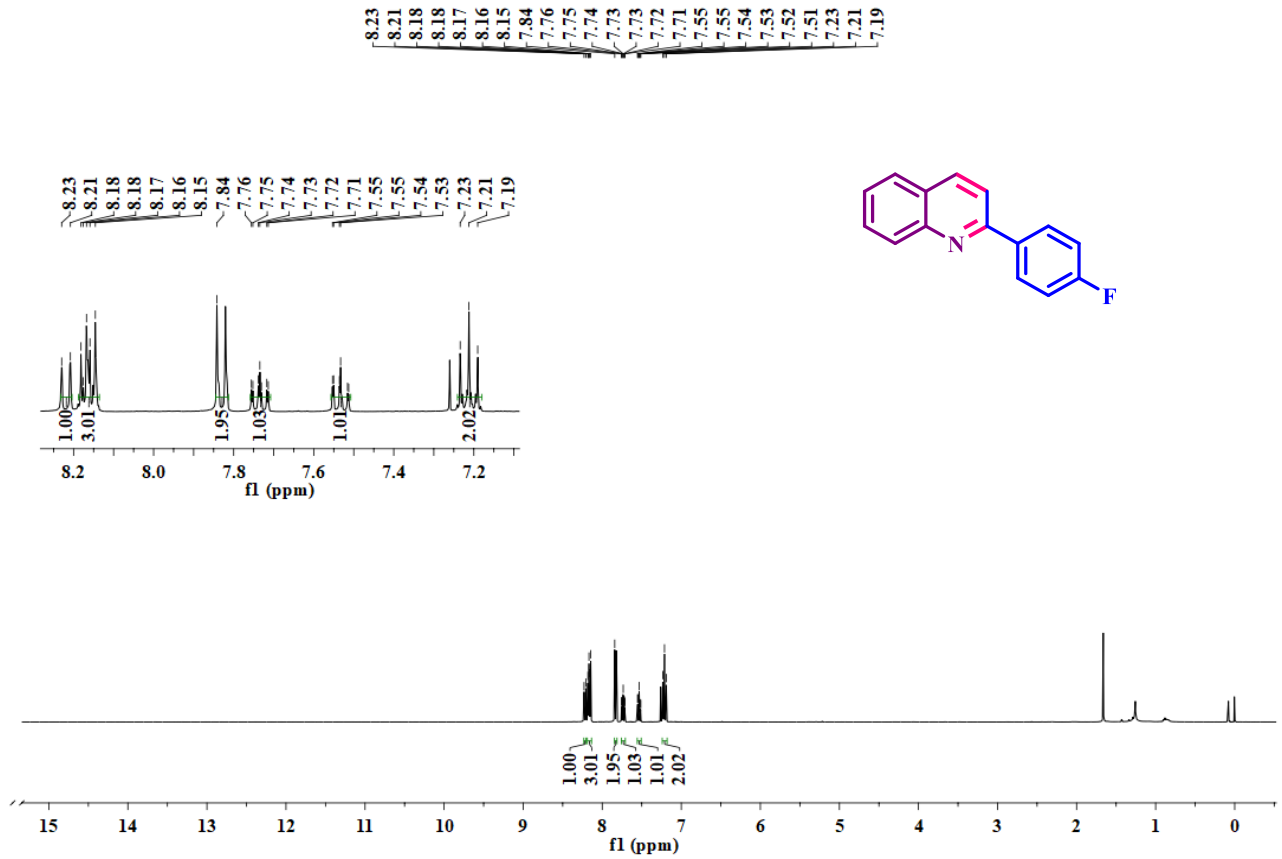


Figure S149. ^{1}H NMR spectrum of **7af** taking $CDCl_3$ as solvent.

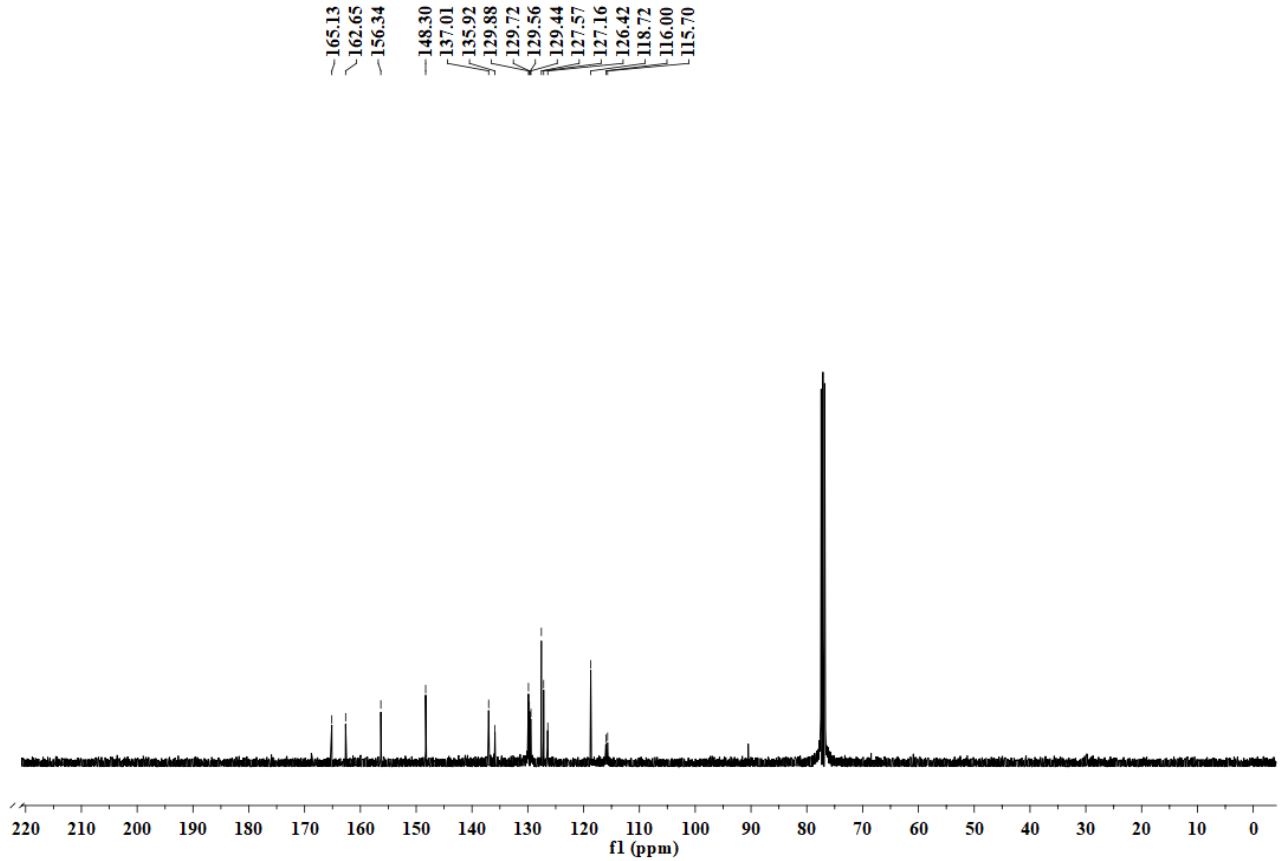


Figure S150. ^{13}CNMR spectrum of **7af** taking $CDCl_3$ as solvent.

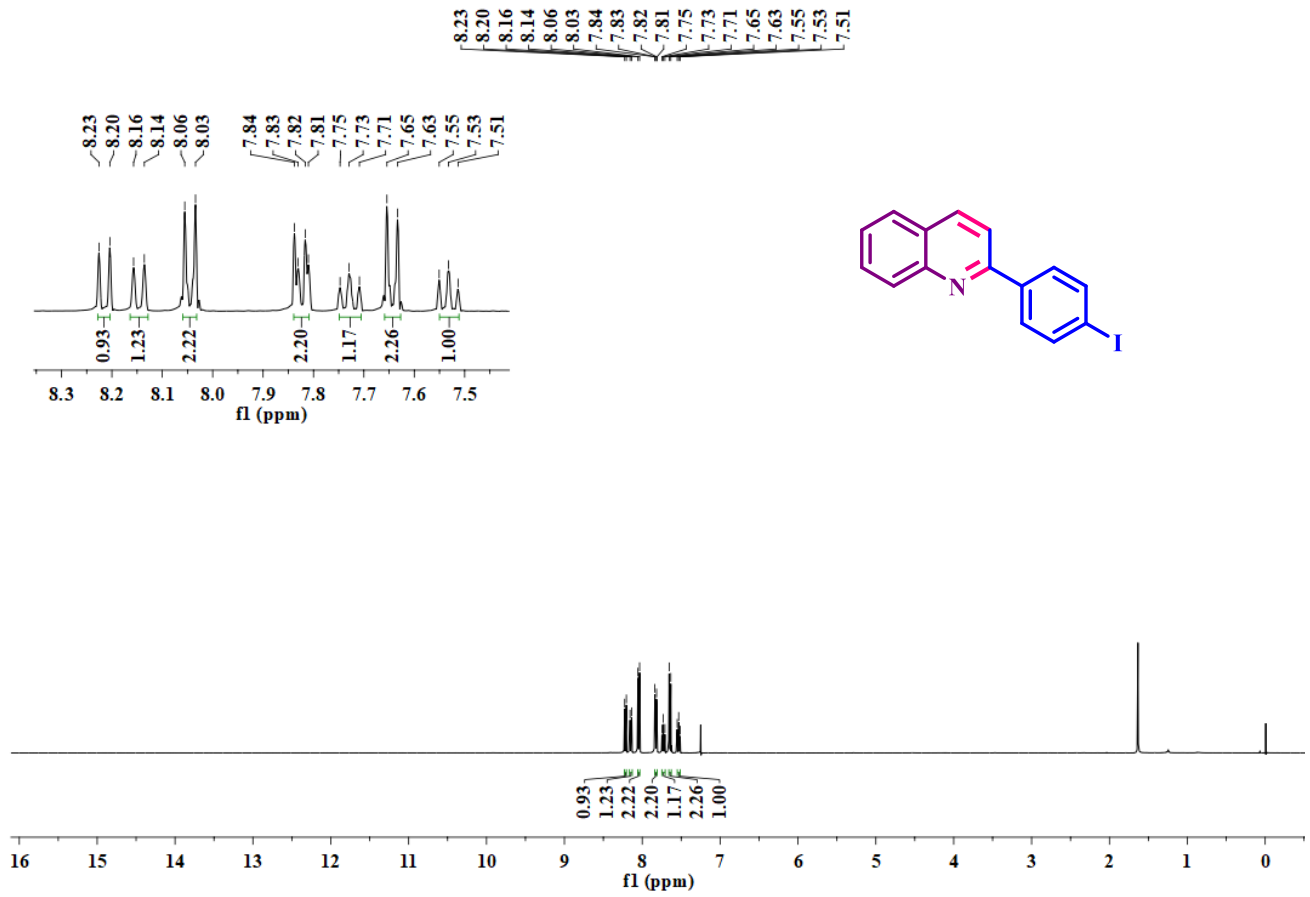


Figure S151. ^{1}H NMR spectrum of **7ag** taking $CDCl_3$ as solvent.

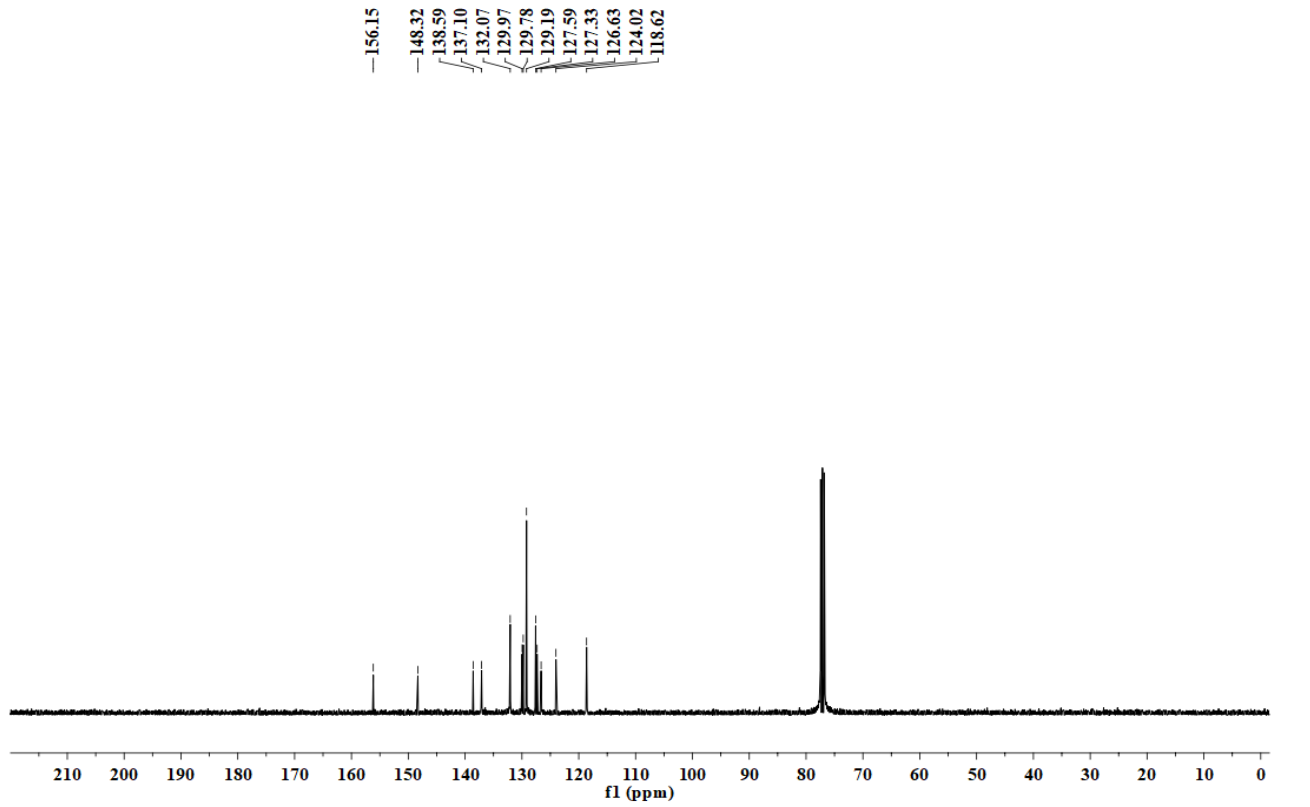


Figure S152. ^{13}CNMR spectrum of **7ag** taking $CDCl_3$ as solvent.

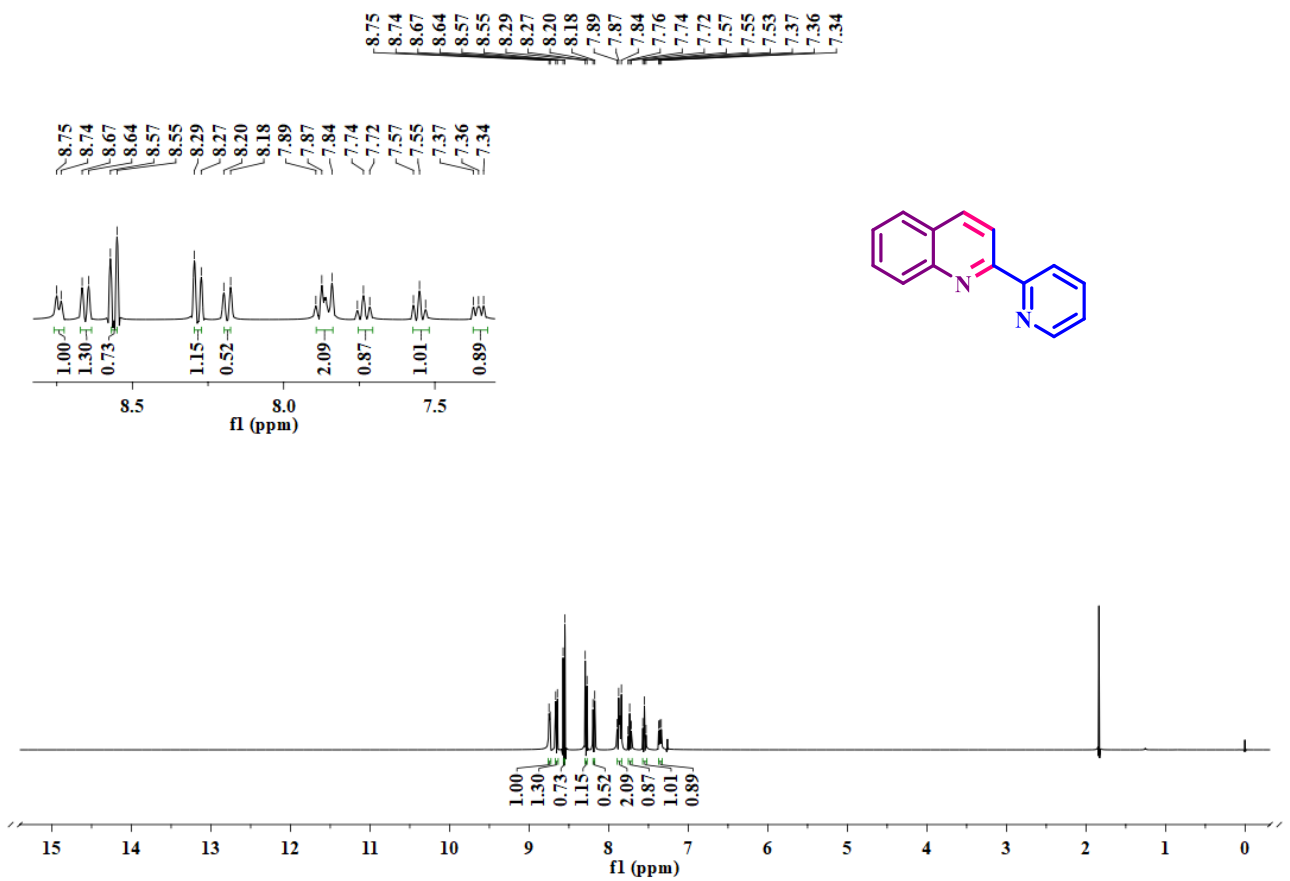


Figure S153. ^{1}H NMR spectrum of **7ah** taking $CDCl_3$ as solvent.

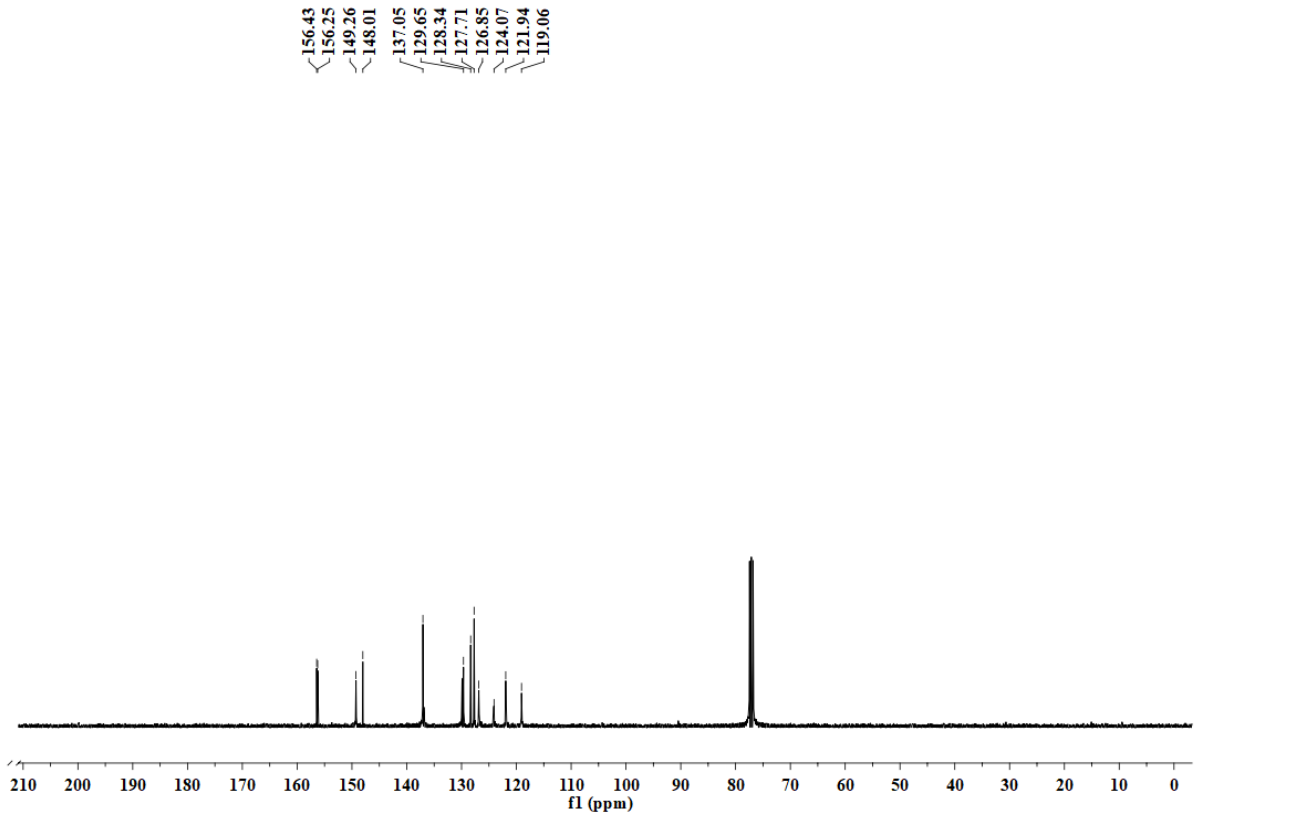


Figure S154. ^{13}CNMR spectrum of **7ah** taking $CDCl_3$ as solvent.

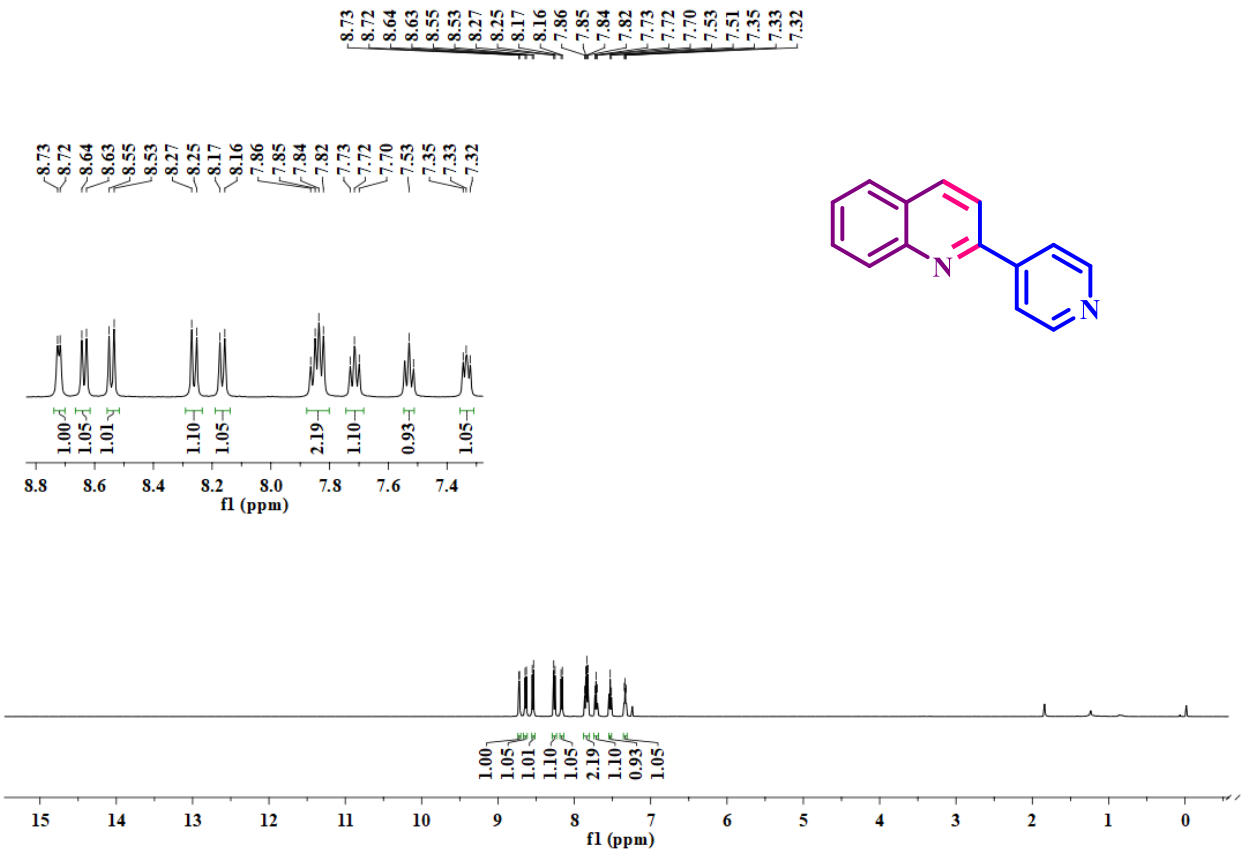


Figure S155. ^{1}H NMR spectrum of **7ai** taking $CDCl_3$ as solvent.

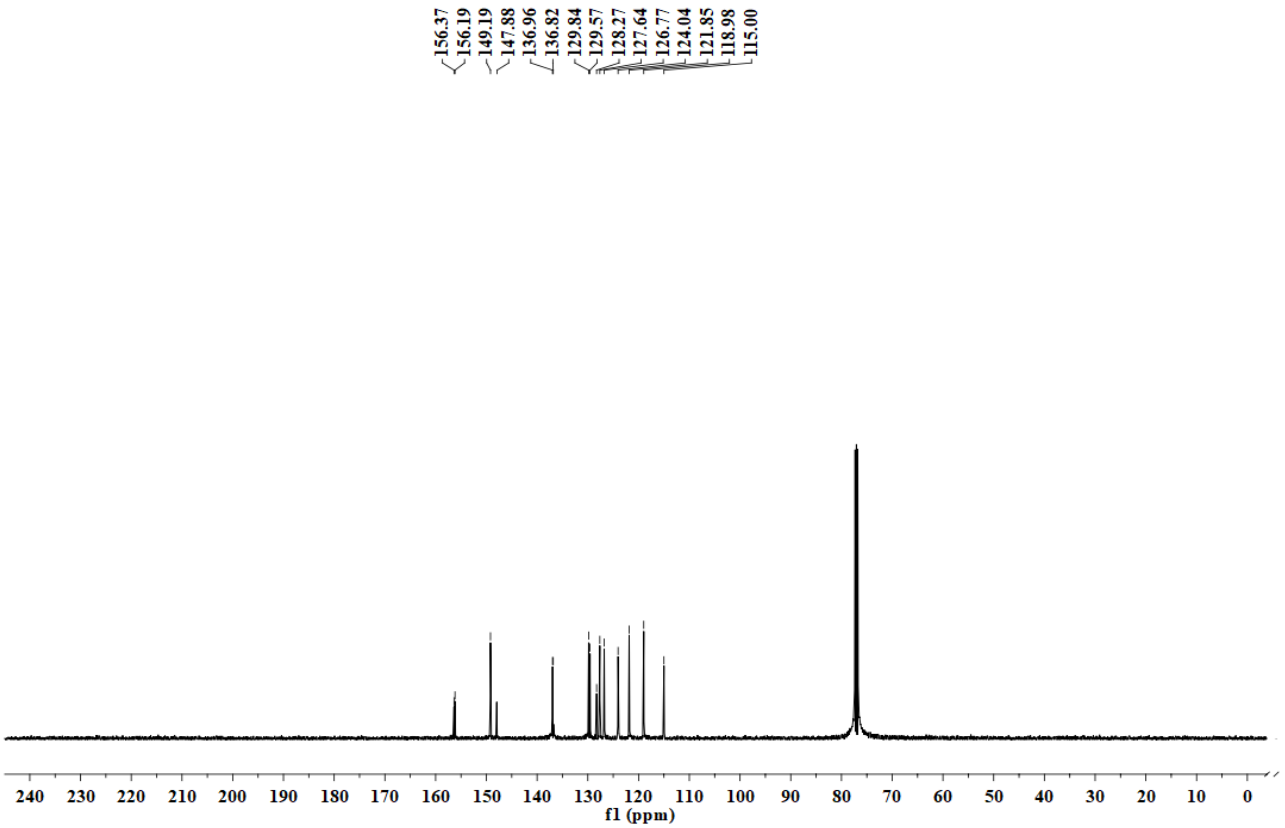


Figure S156. ^{13}CNMR spectrum of **7ai** taking $CDCl_3$ as solvent.

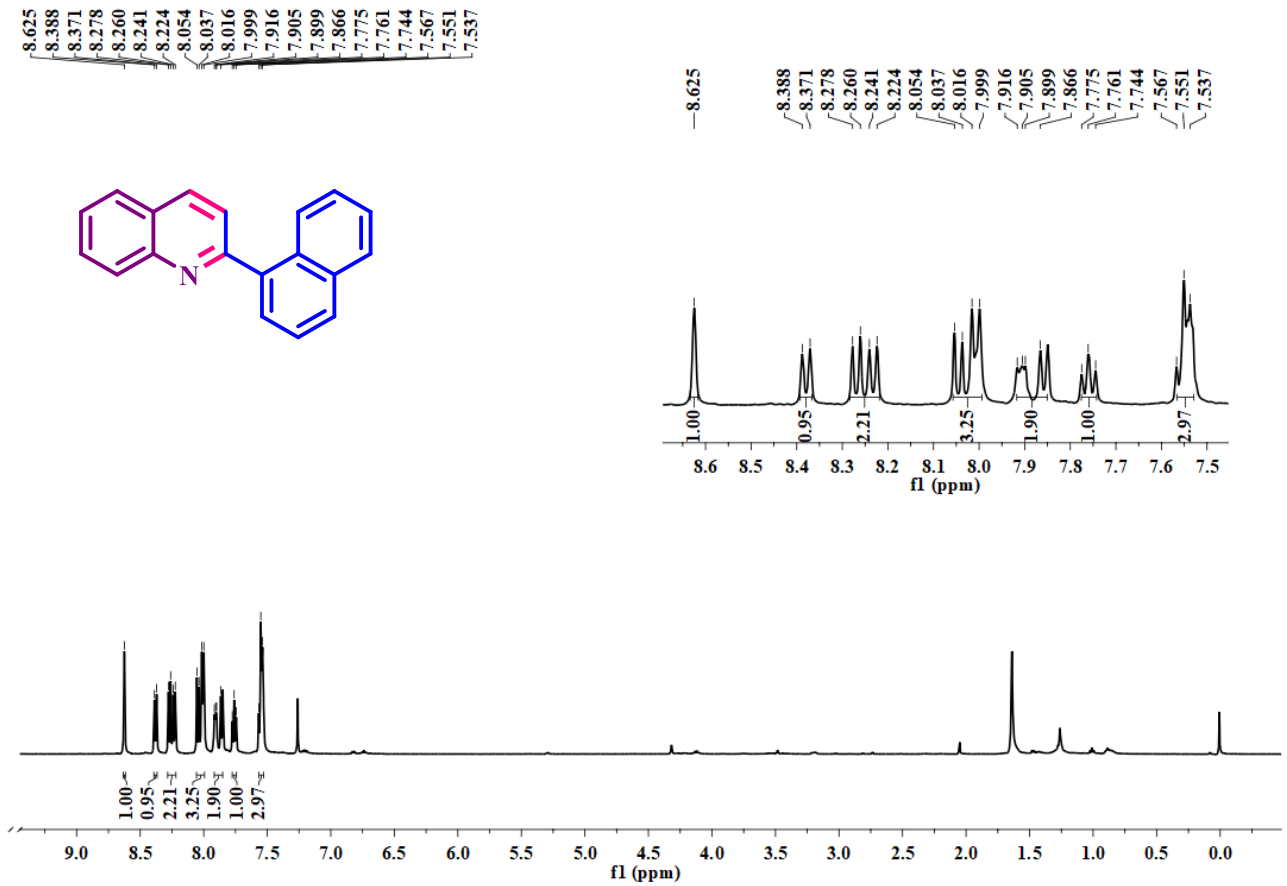


Figure S157. ^{1}H NMR spectrum of **7aj** taking $CDCl_3$ as solvent.

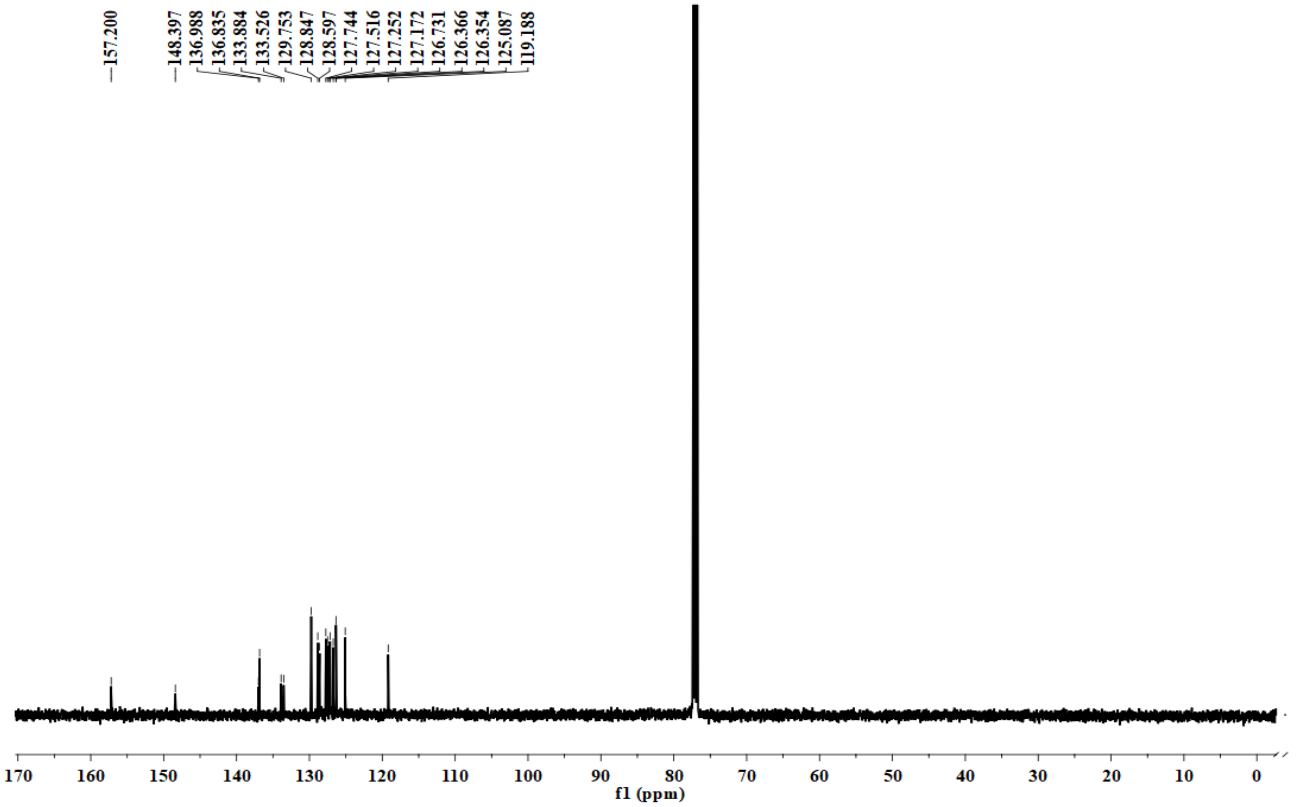


Figure S158. ^{13}CNMR spectrum of **7aj** taking $CDCl_3$ as solvent.

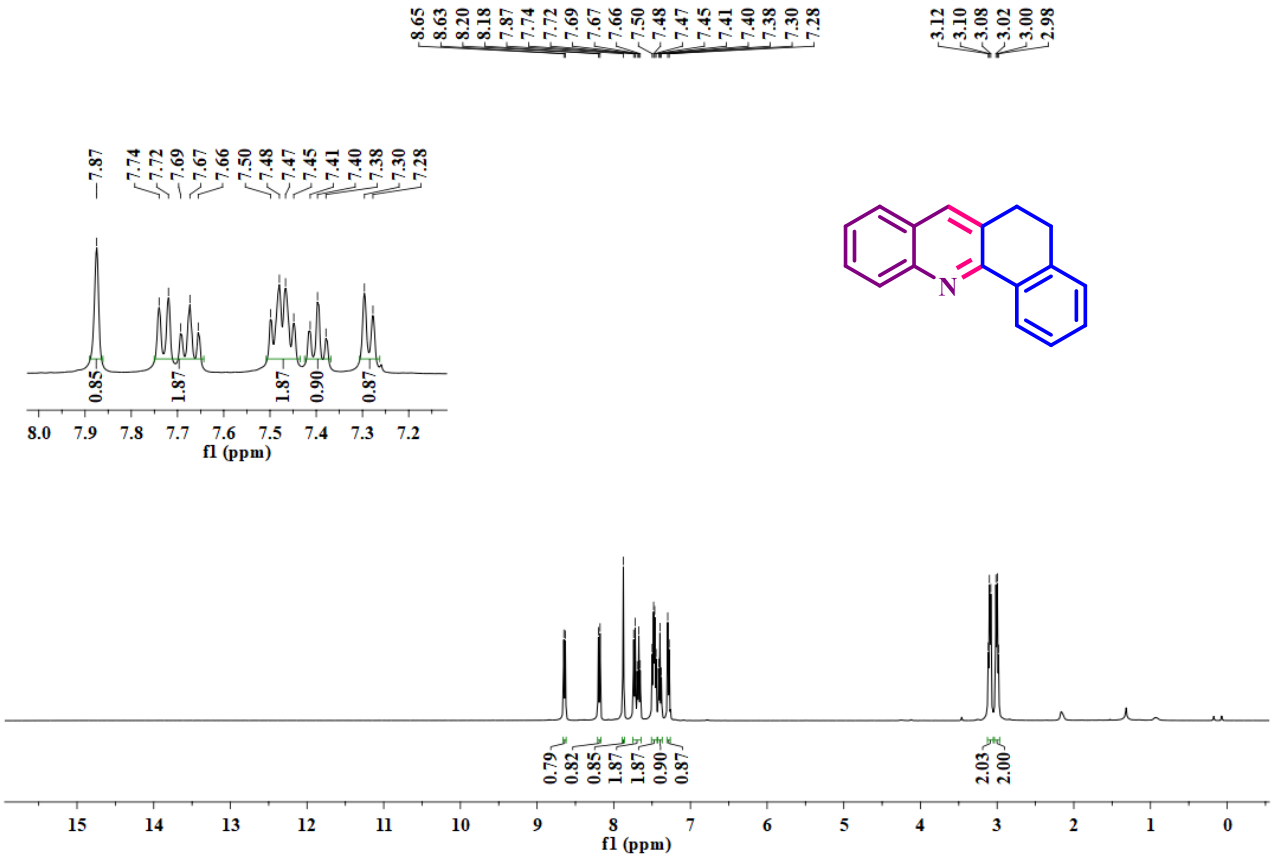


Figure S159. ^{1}H NMR spectrum of **7ak** taking $CDCl_3$ as solvent.

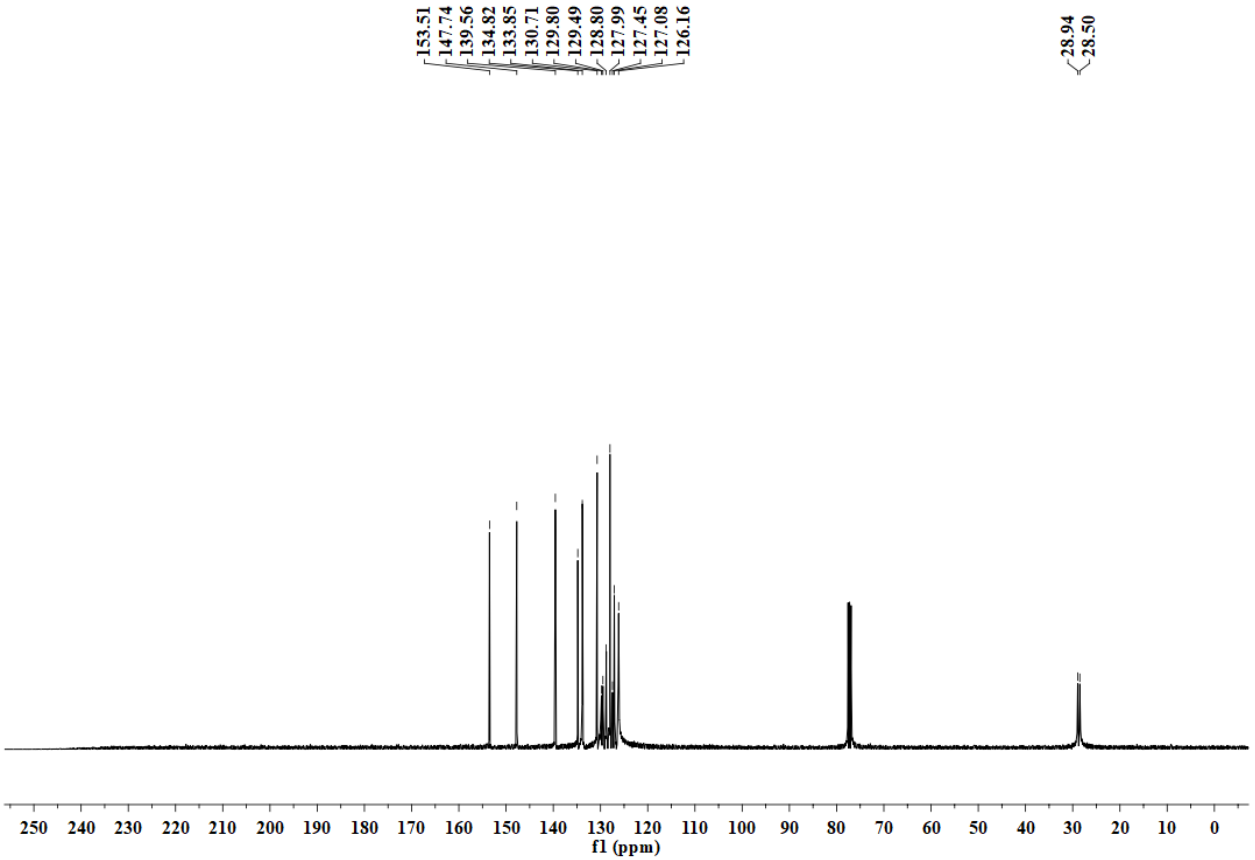


Figure S160. ^{13}CNMR spectrum of **7ak** taking $CDCl_3$ as solvent.

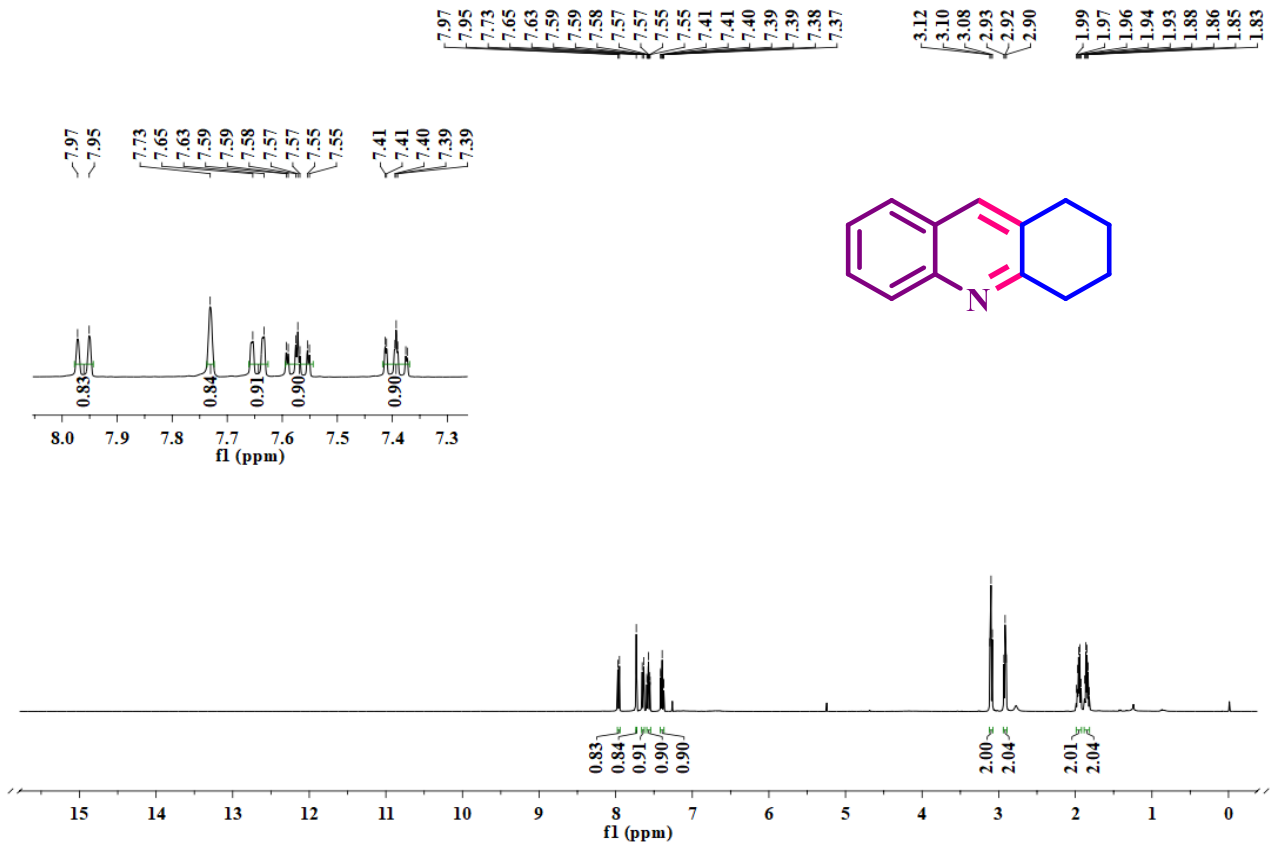


Figure S161. ^{1}H NMR spectrum of **7al** taking $CDCl_3$ as solvent.

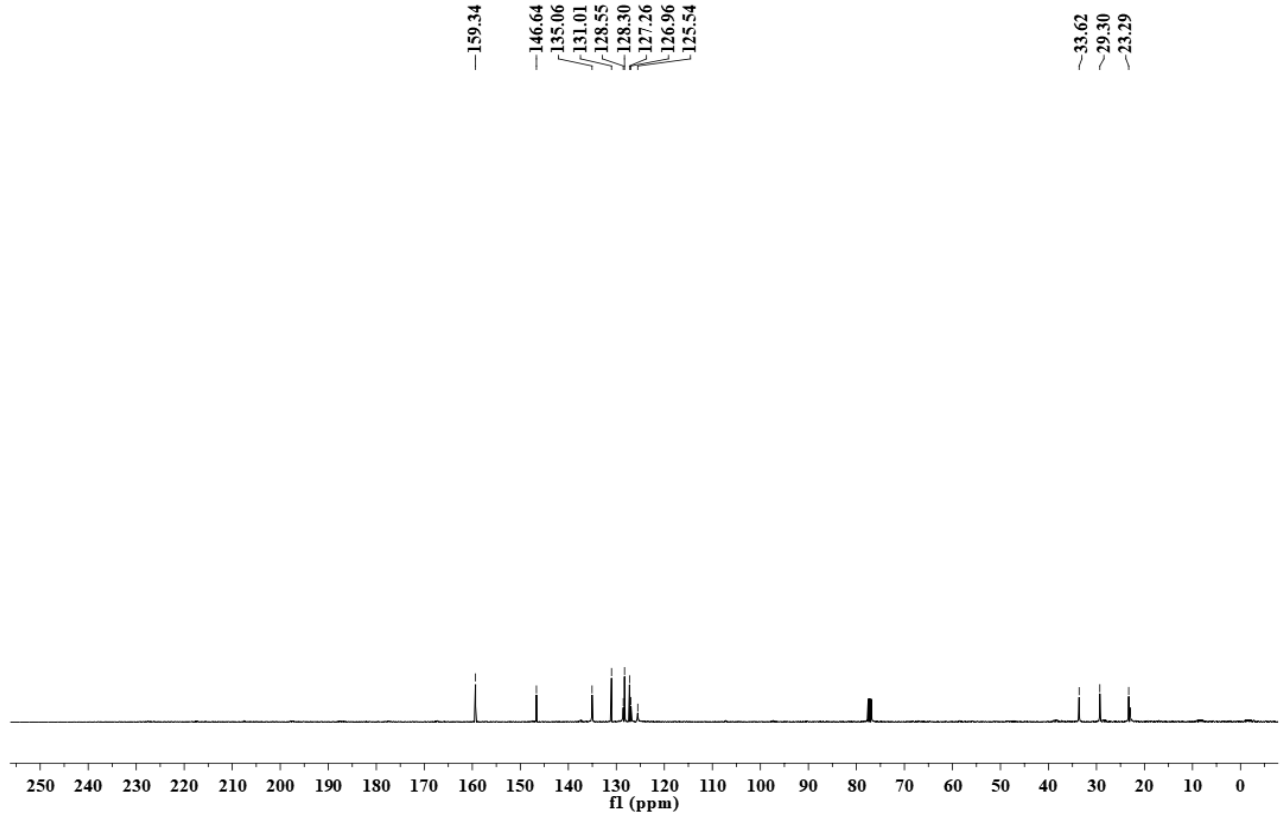
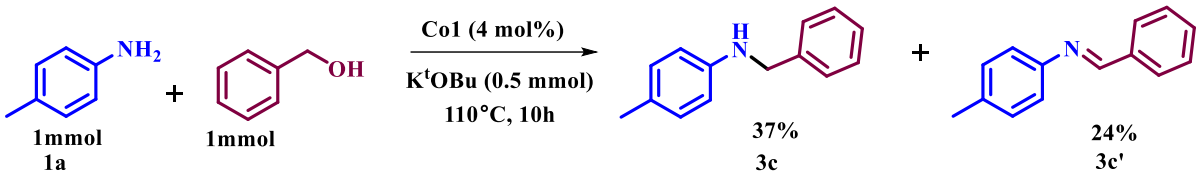


Figure S162. ^{13}CNMR spectrum of **7al** taking $CDCl_3$ as solvent.



Scheme S1. Control experiment scheme 3B.

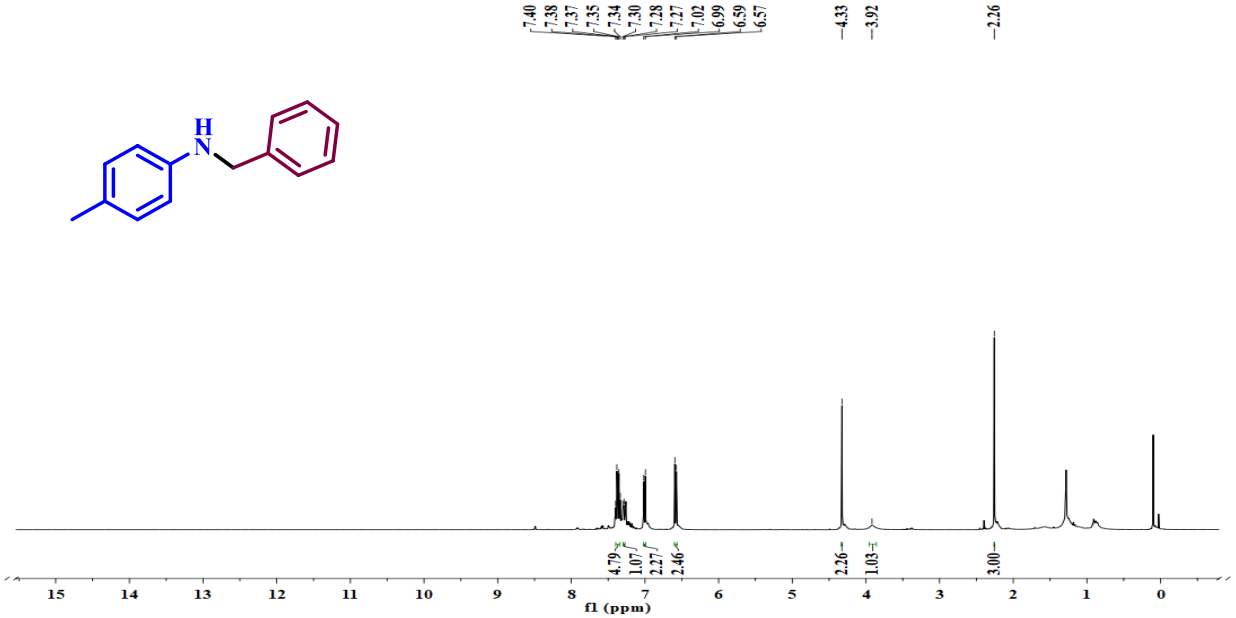


Figure S163. ^{1}H NMR spectrum of 3c taking $CDCl_3$ as solvent.

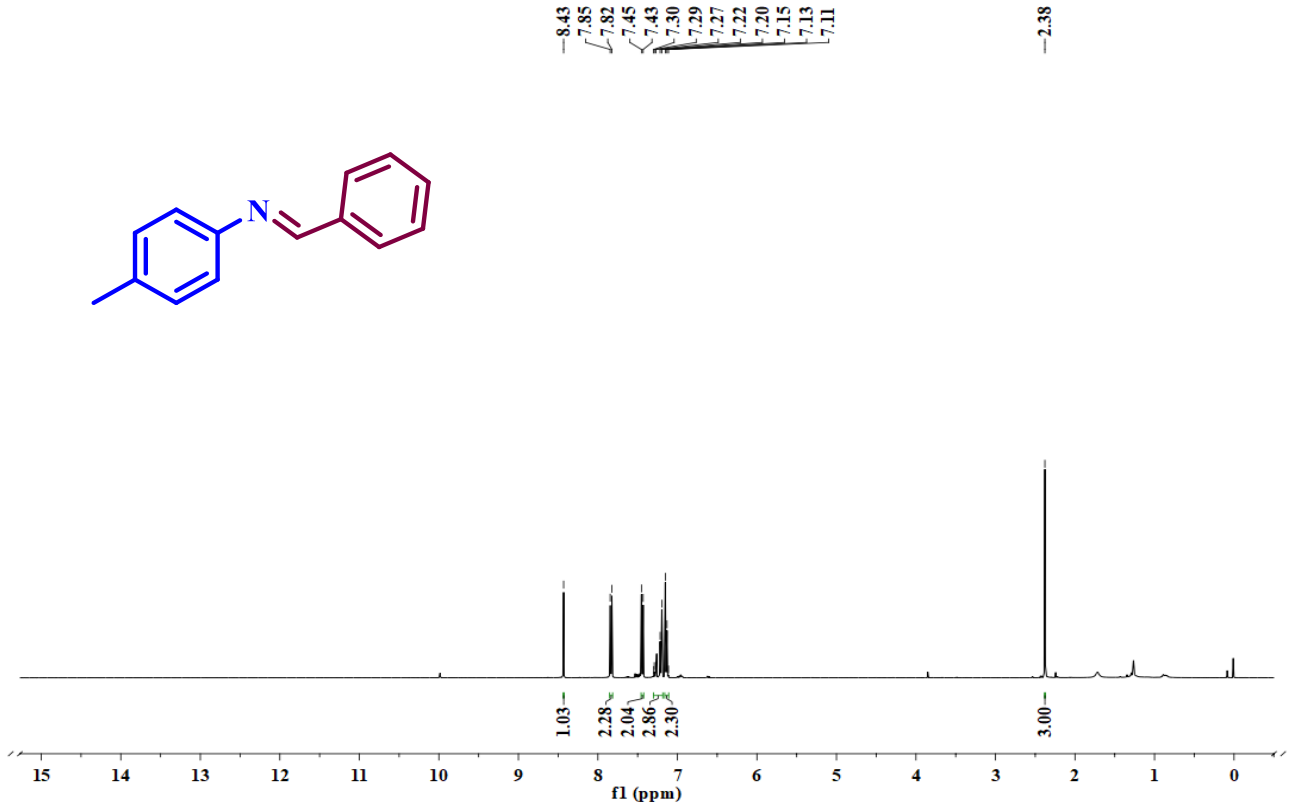
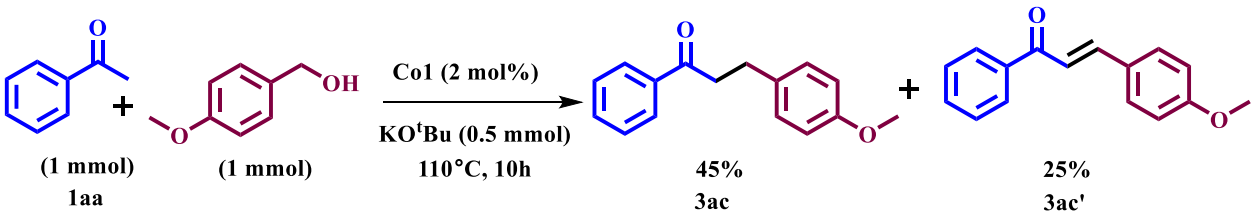


Figure S164. ^{1}H NMR spectrum of 3c′ taking $CDCl_3$ as solvent.



Scheme S2. Control experiment scheme 5B.

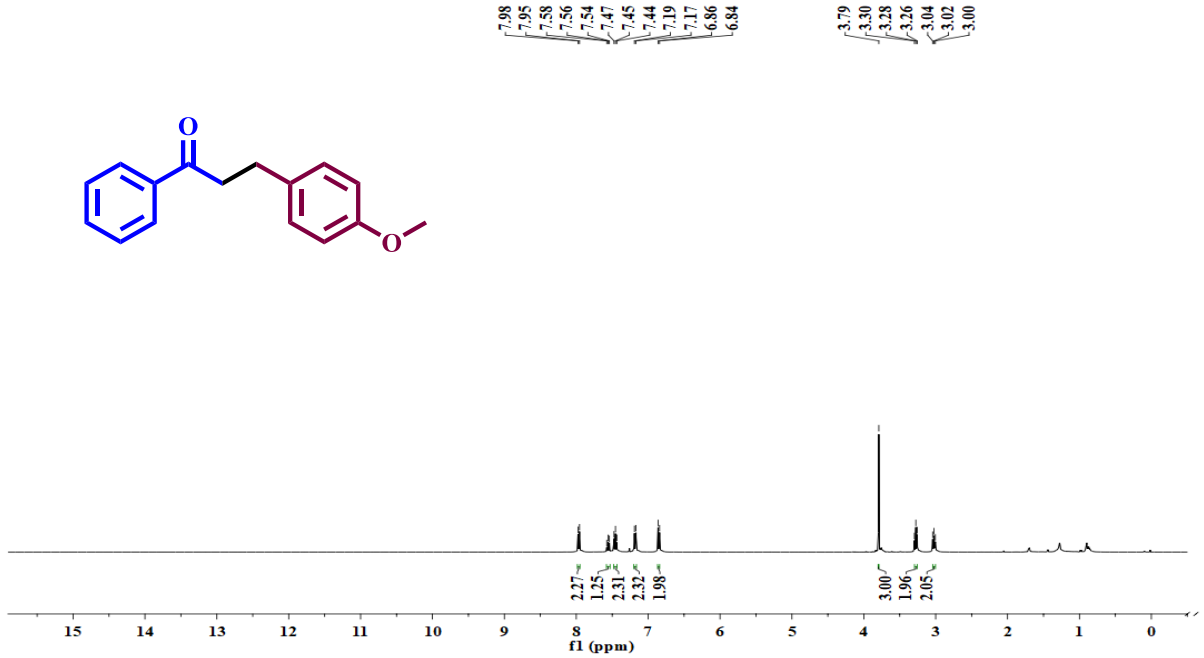


Figure S165. ^{1}H NMR spectrum of 3ac taking $CDCl_3$ as solvent.

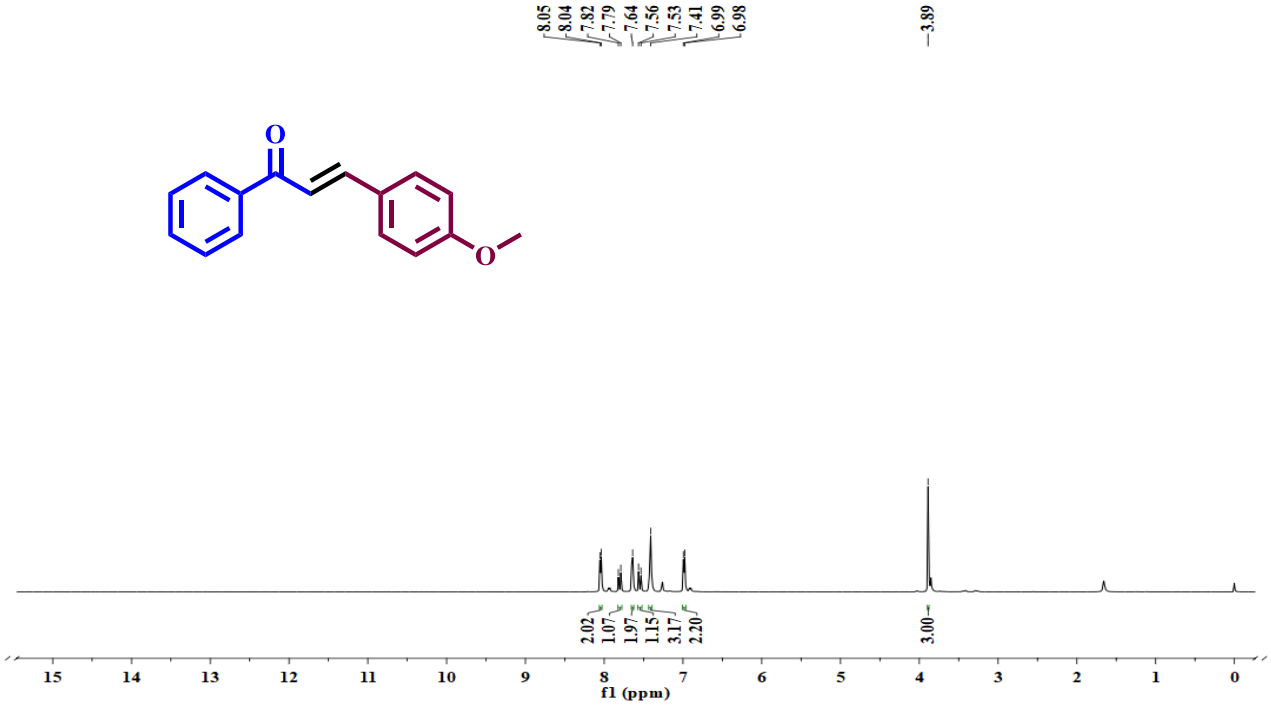


Figure S166. ^{1}H NMR spectrum of 3ac′ taking $CDCl_3$ as solvent.

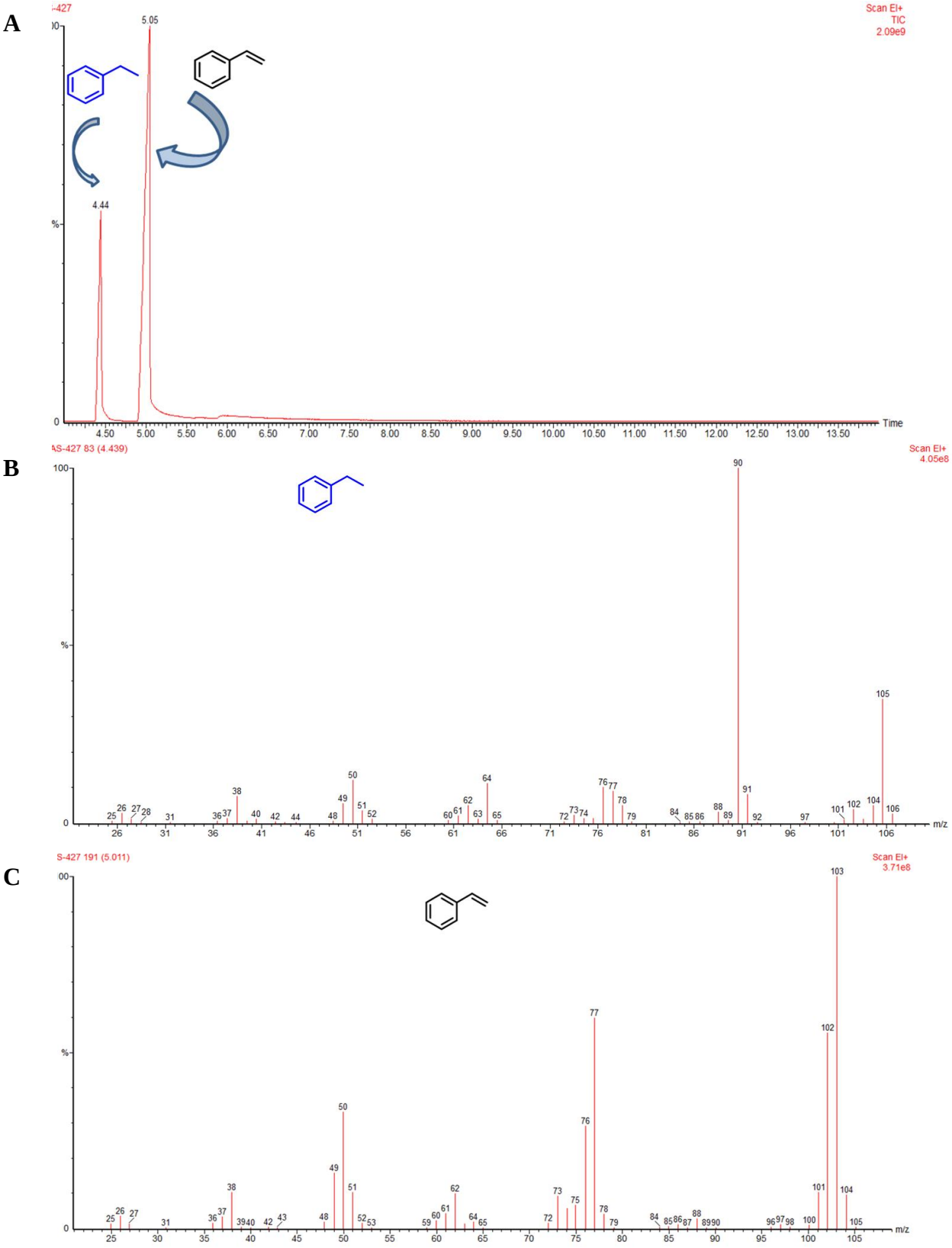


Figure S167. (A) GC-MS spectrum of the reaction mixture of scheme 3D. (**B**) GC-MS mass distribution for ethylbenzene (**C**) GC-MS mass distribution for styrene.

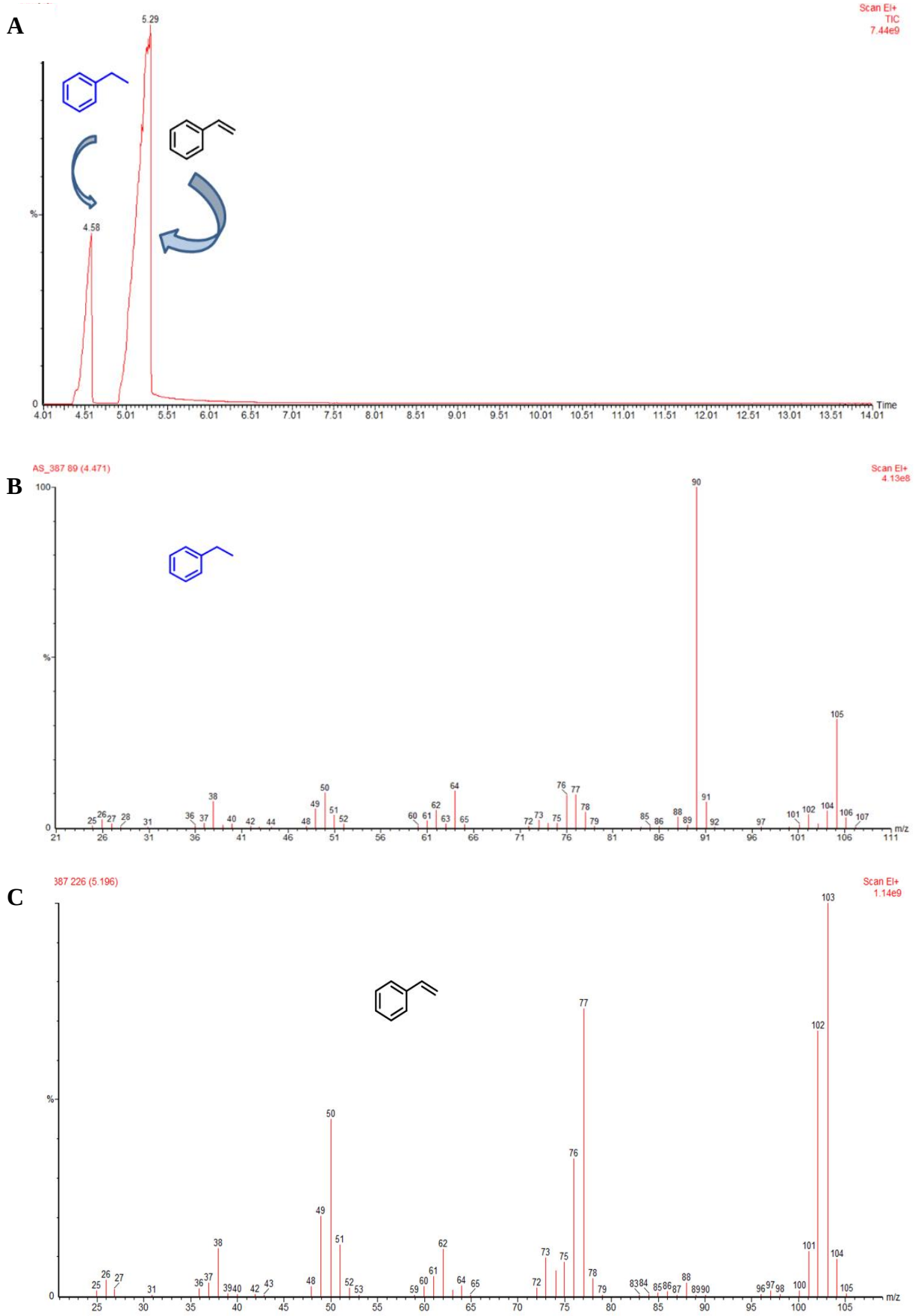


Figure S168. (A) GC-MS spectrum of the reaction mixture of scheme 5D. (**B**) GC-MS mass distribution for ethylbenzene (**C**) GC-MS mass distribution for styrene.

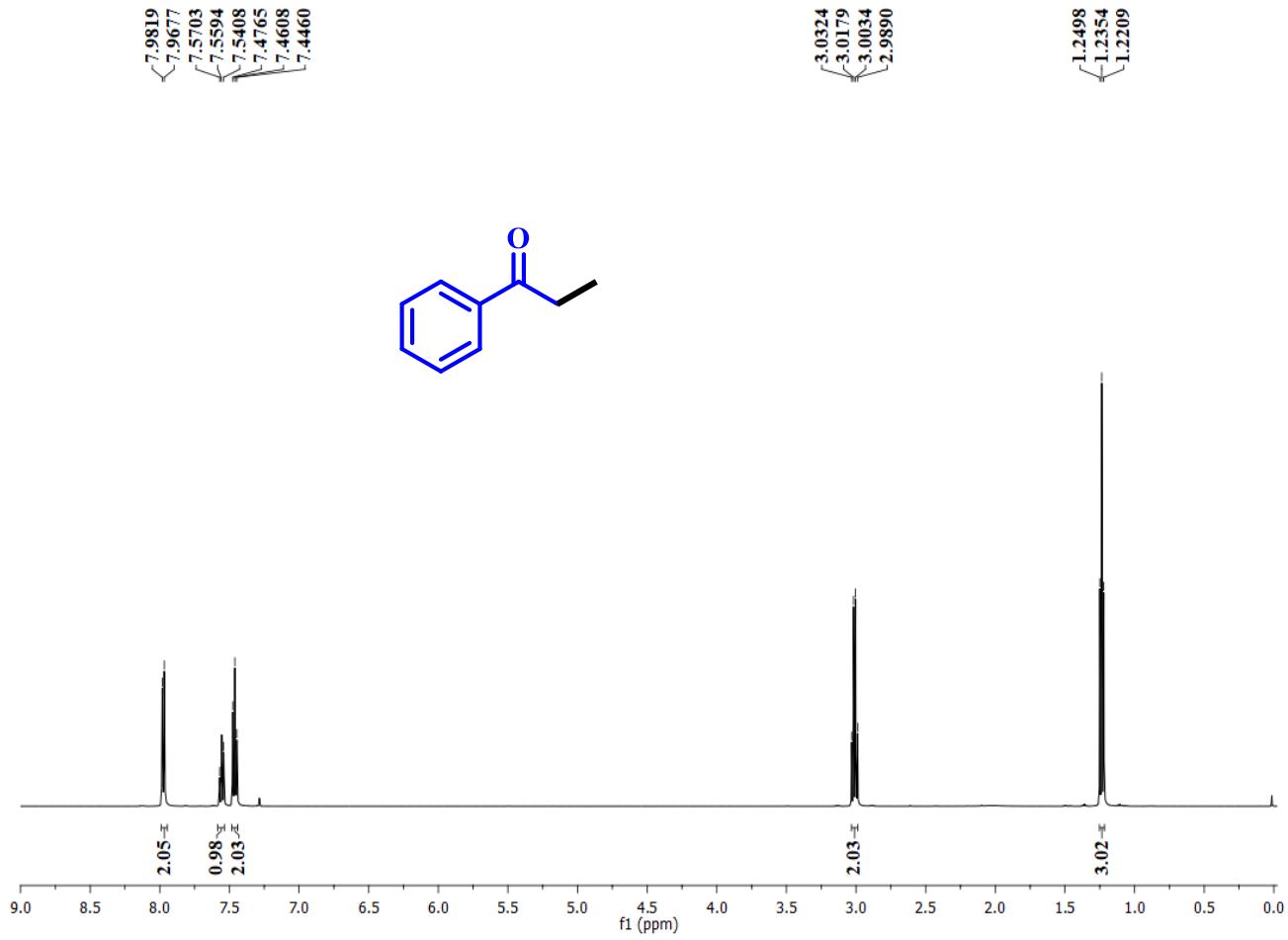


Figure S169. ^{1}H NMR spectrum of 5ha taking $CDCl_3$ as solvent.

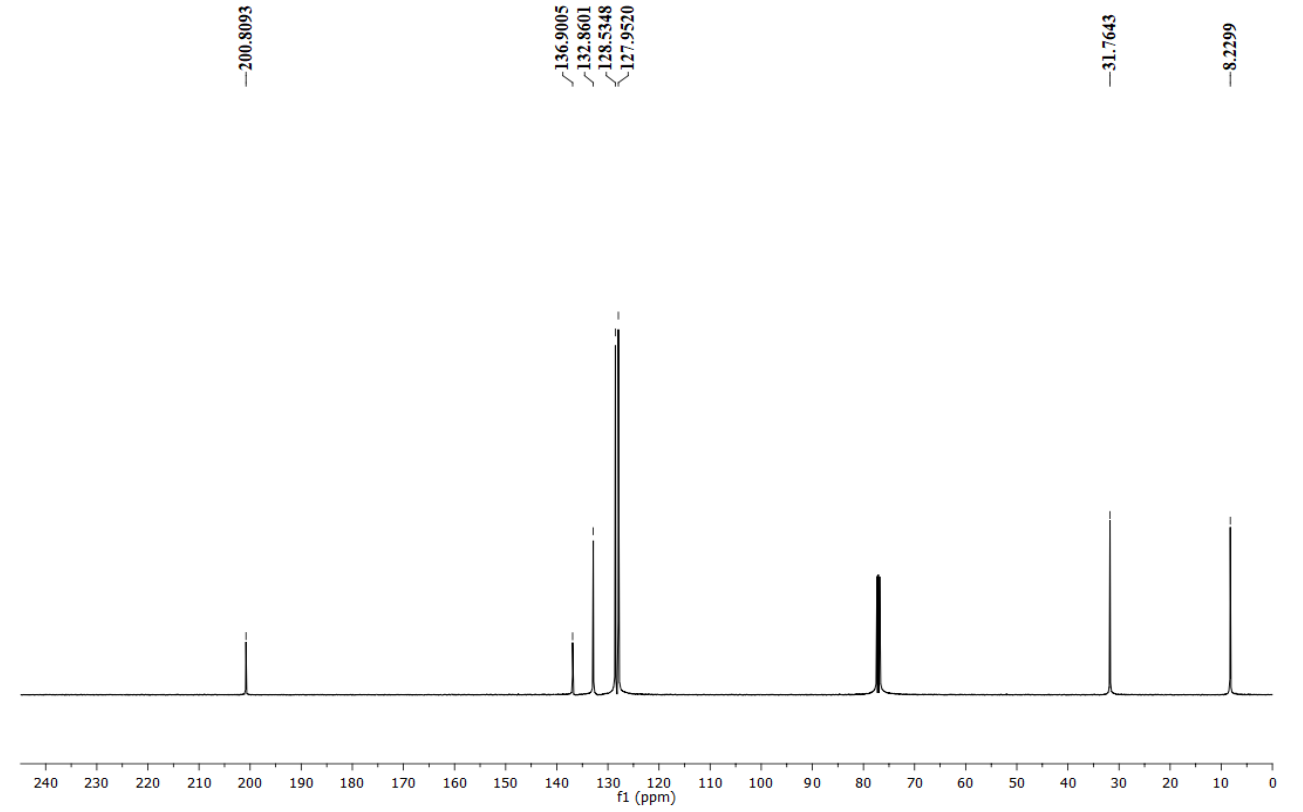


Figure S170. ^{13}C NMR spectrum of 5ha taking $CDCl_3$ as solvent.

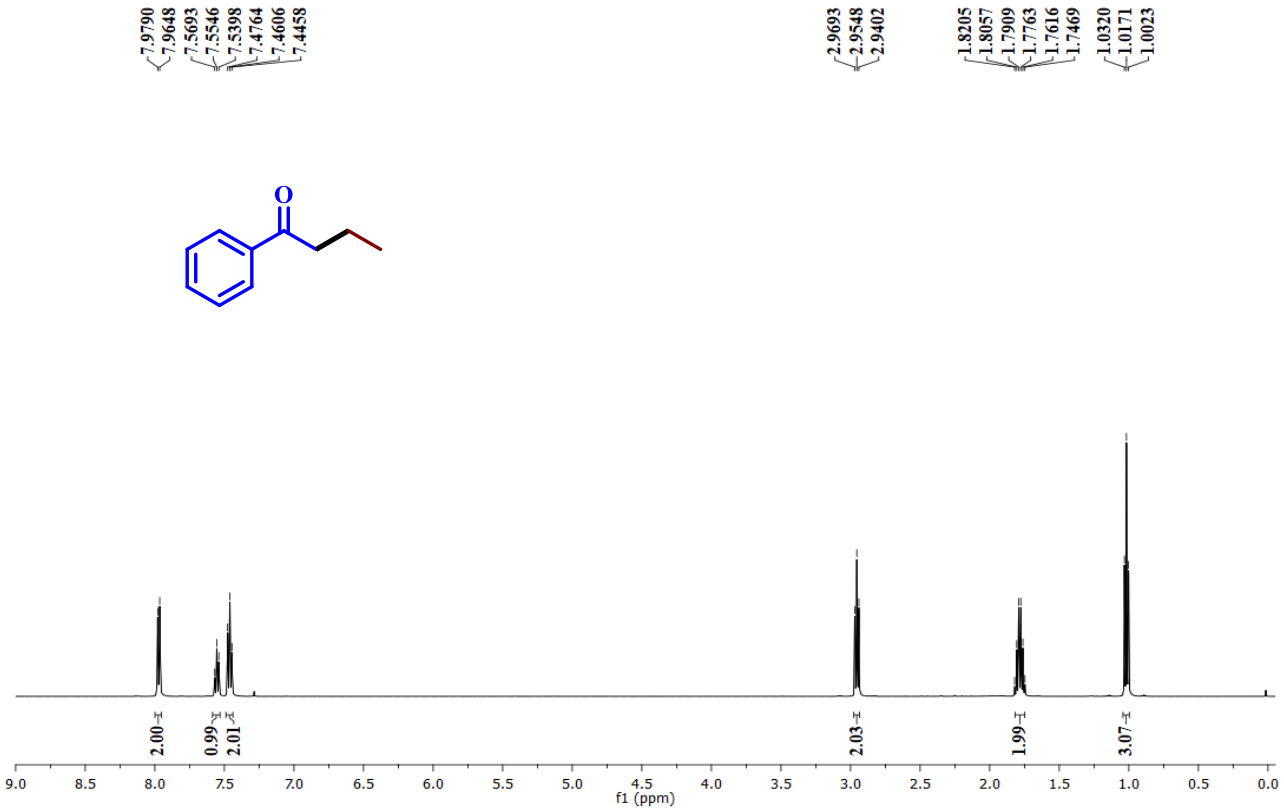


Figure S171. ^{1}H NMR spectrum of 5hb taking $CDCl_3$ as solvent.

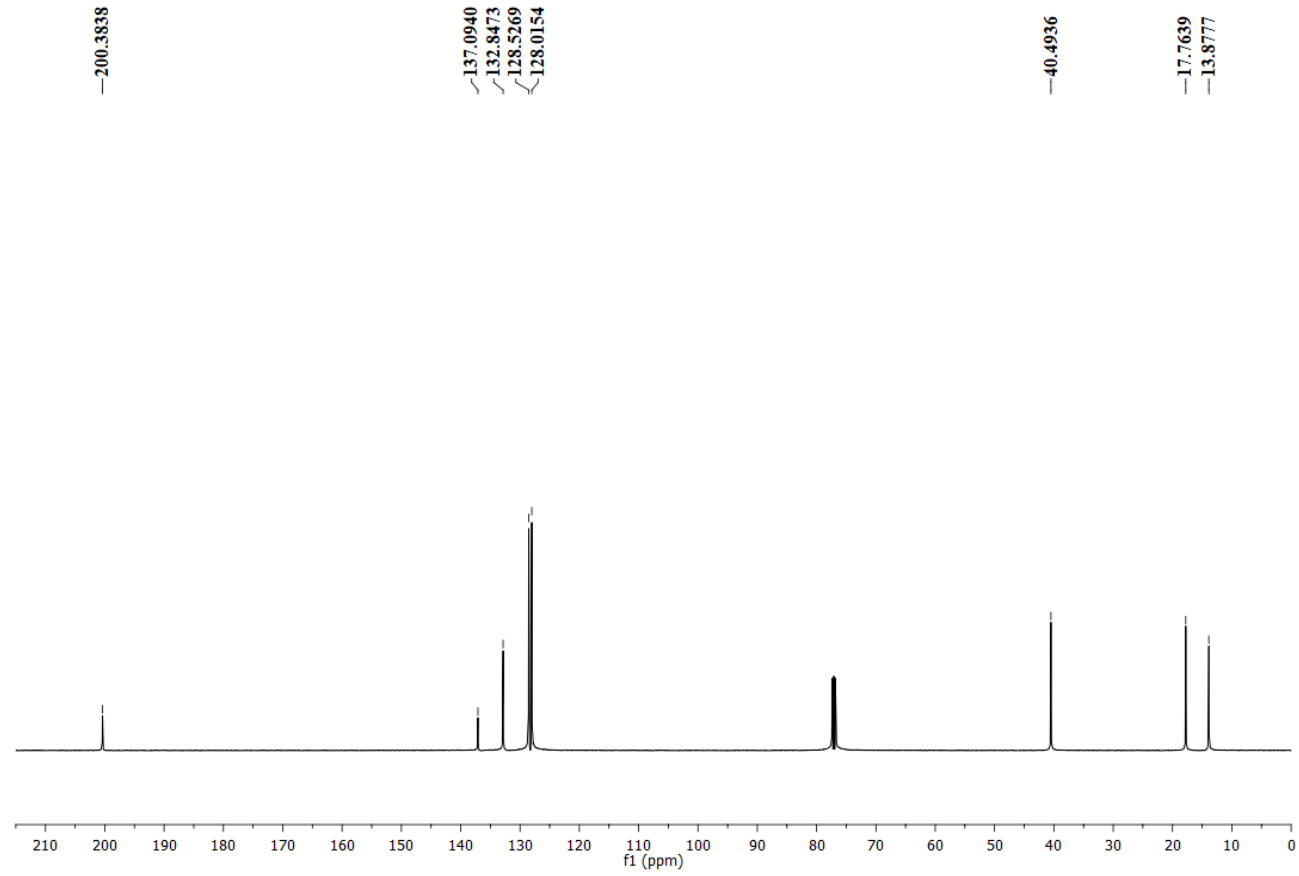


Figure S172. ^{13}C NMR spectrum of 5hb taking $CDCl_3$ as solvent.

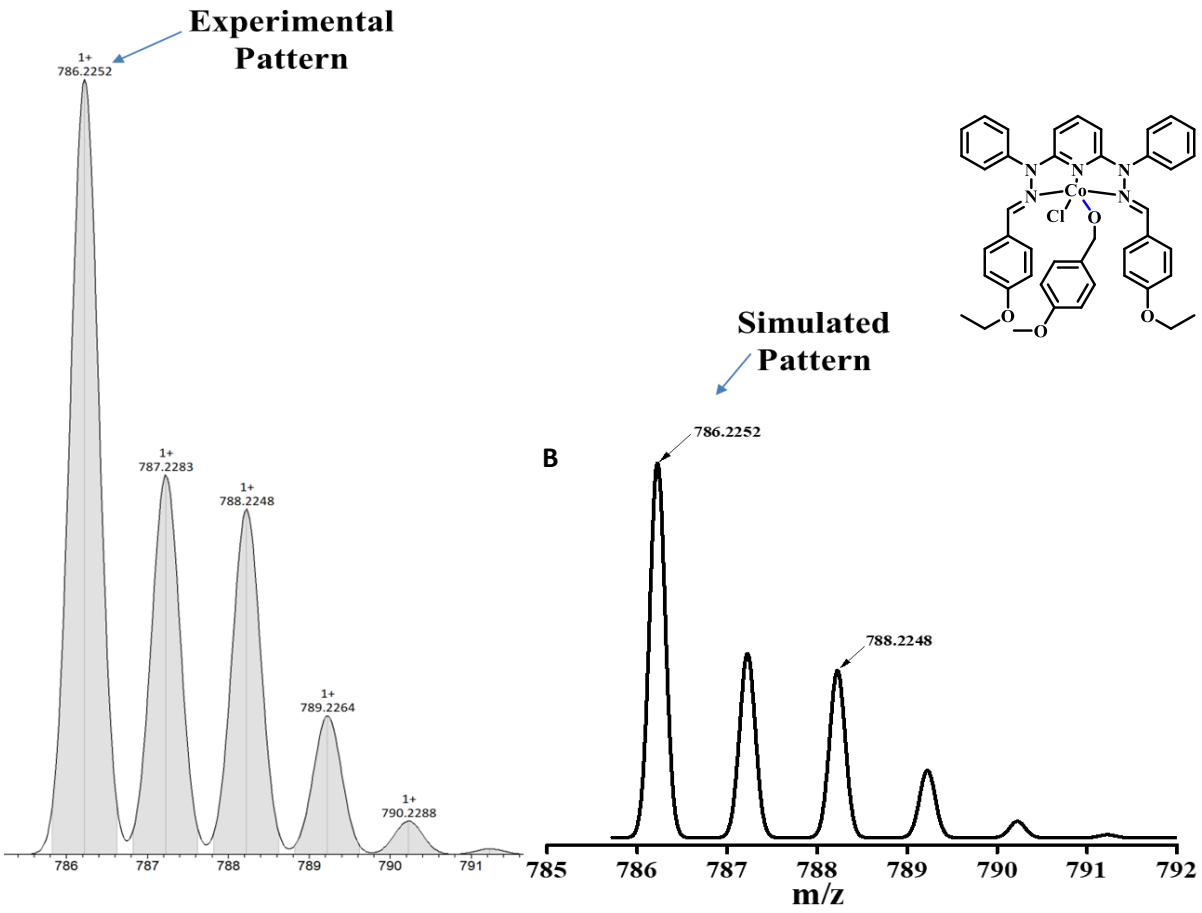


Figure S173. The ESI-MS spectrum of Co-alkoxide species (A) Experimental Pattern (B) Simulated Pattern.

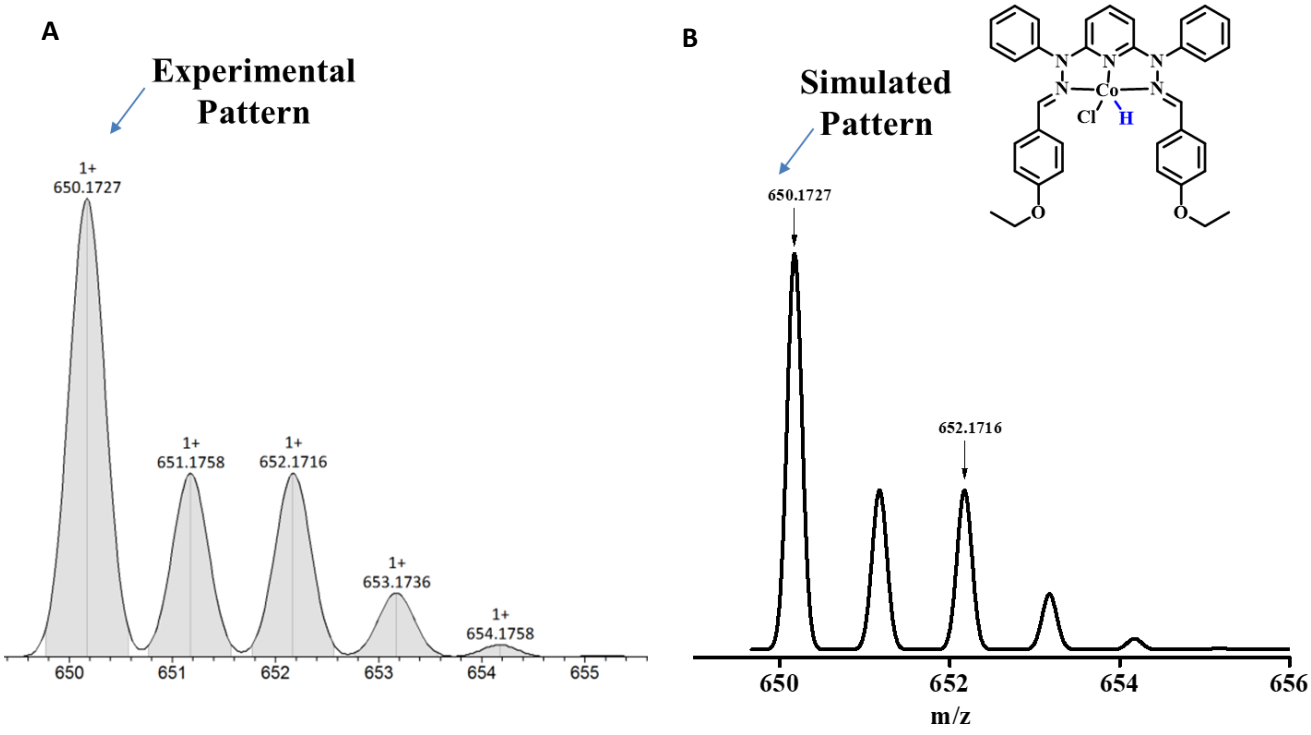


Figure S174. The ESI-MS spectrum of Co–H species (A) Experimental Pattern (B) Simulated Pattern.

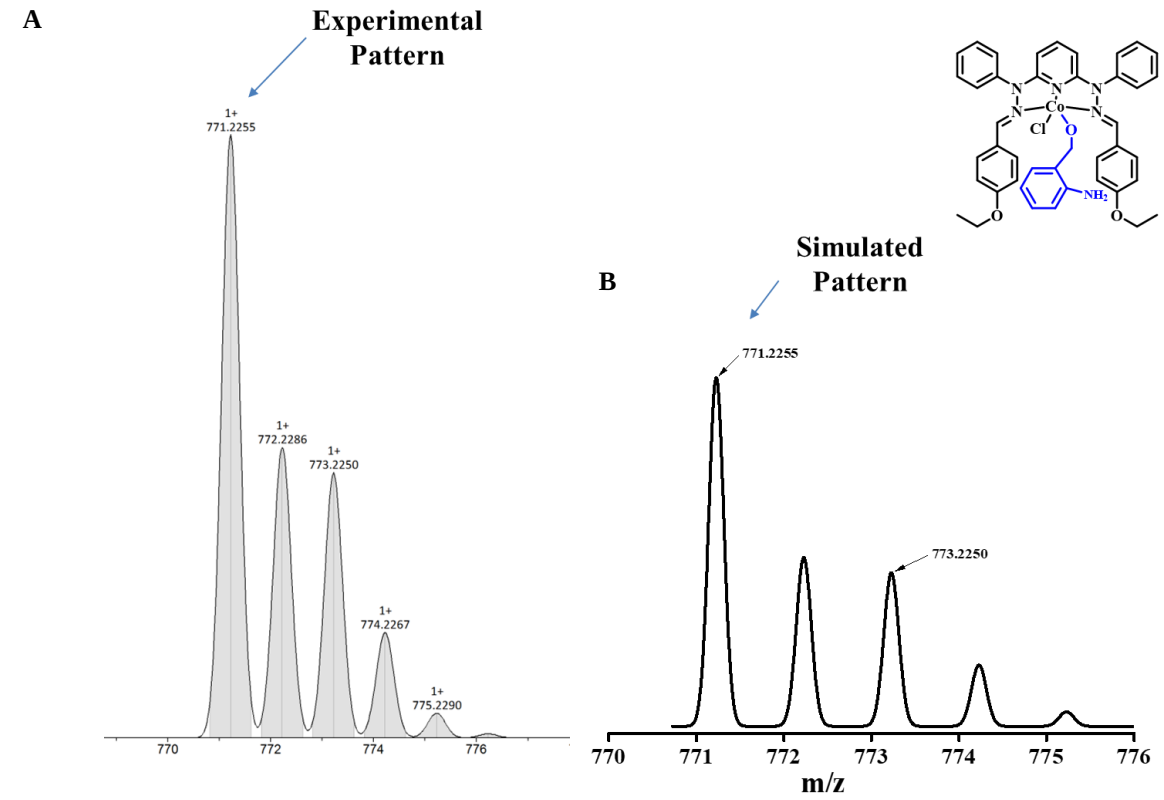


Figure S175. The ESI-MS spectrum of Co-alkoxide species (A) Experimental Pattern (B) Simulated Pattern.

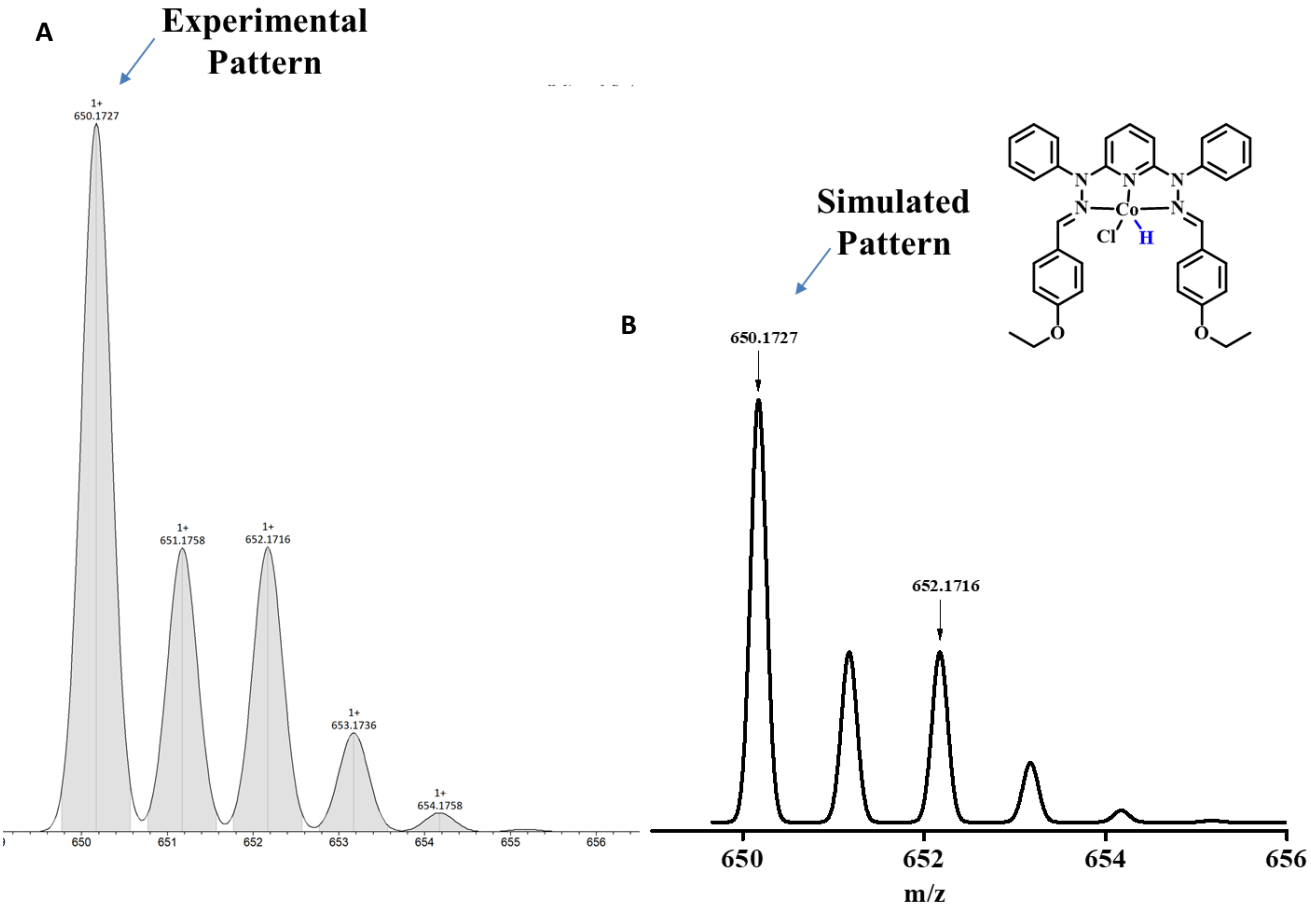


Figure S176. The ESI-MS spectrum of Co–H species (A) Experimental Pattern (B) Simulated Pattern.

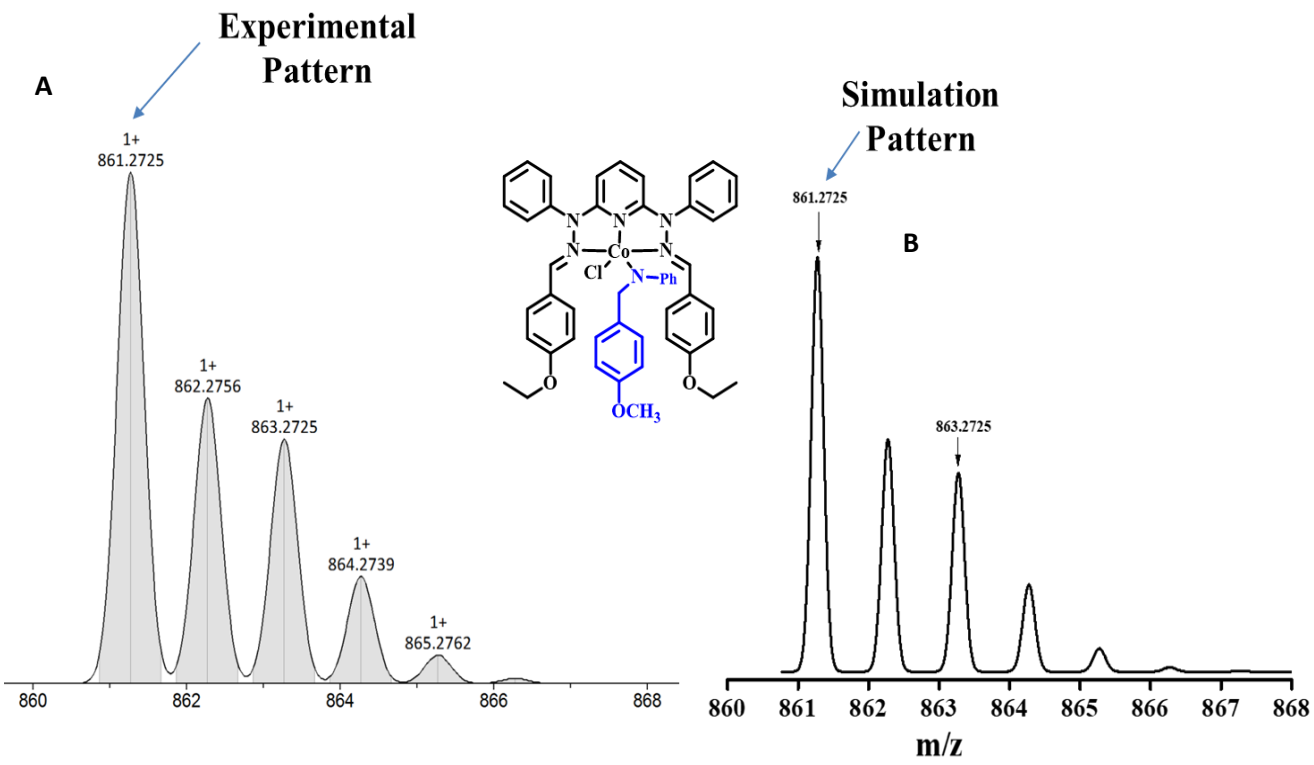
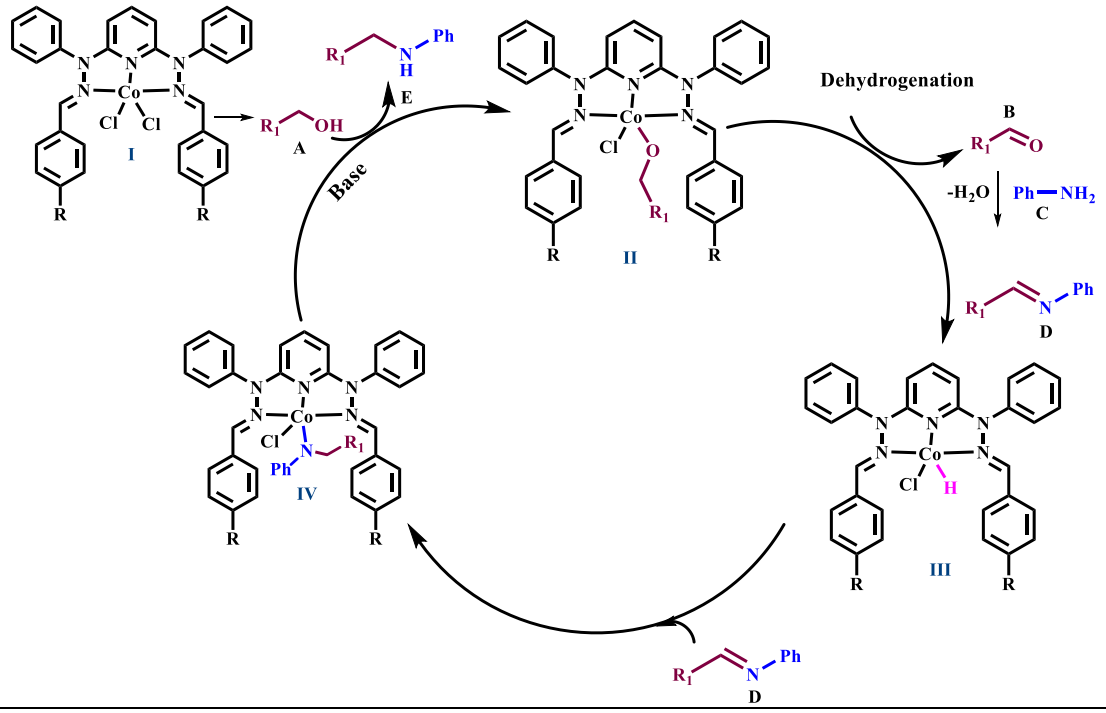
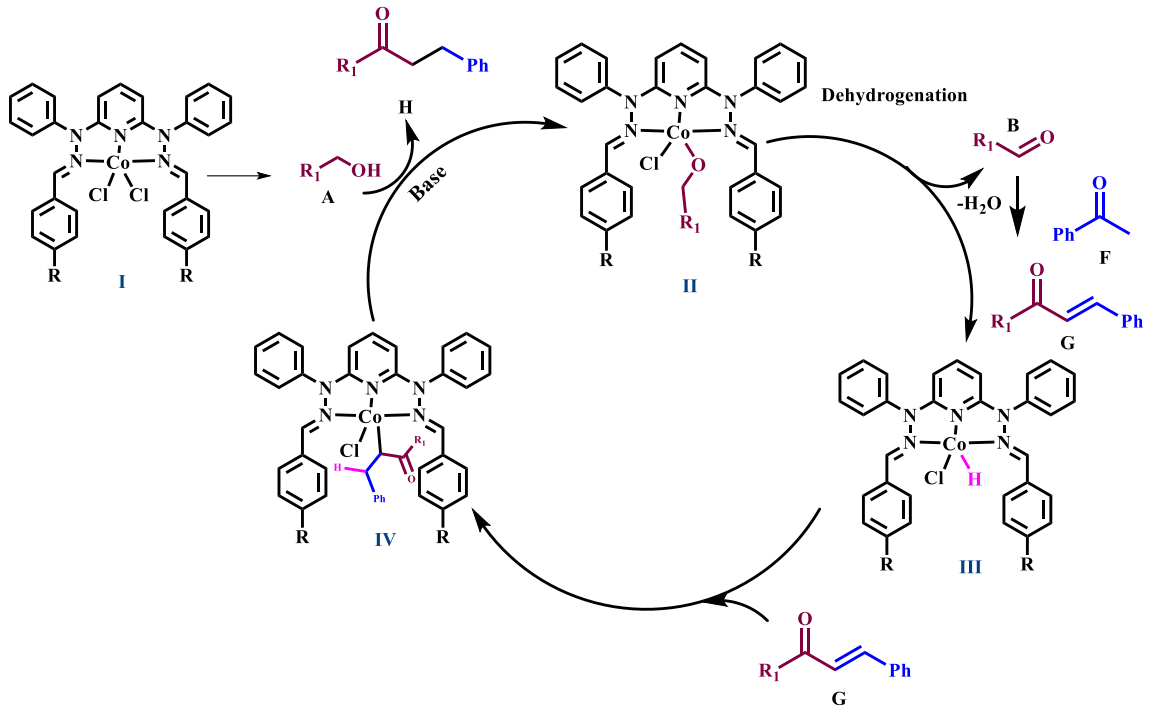


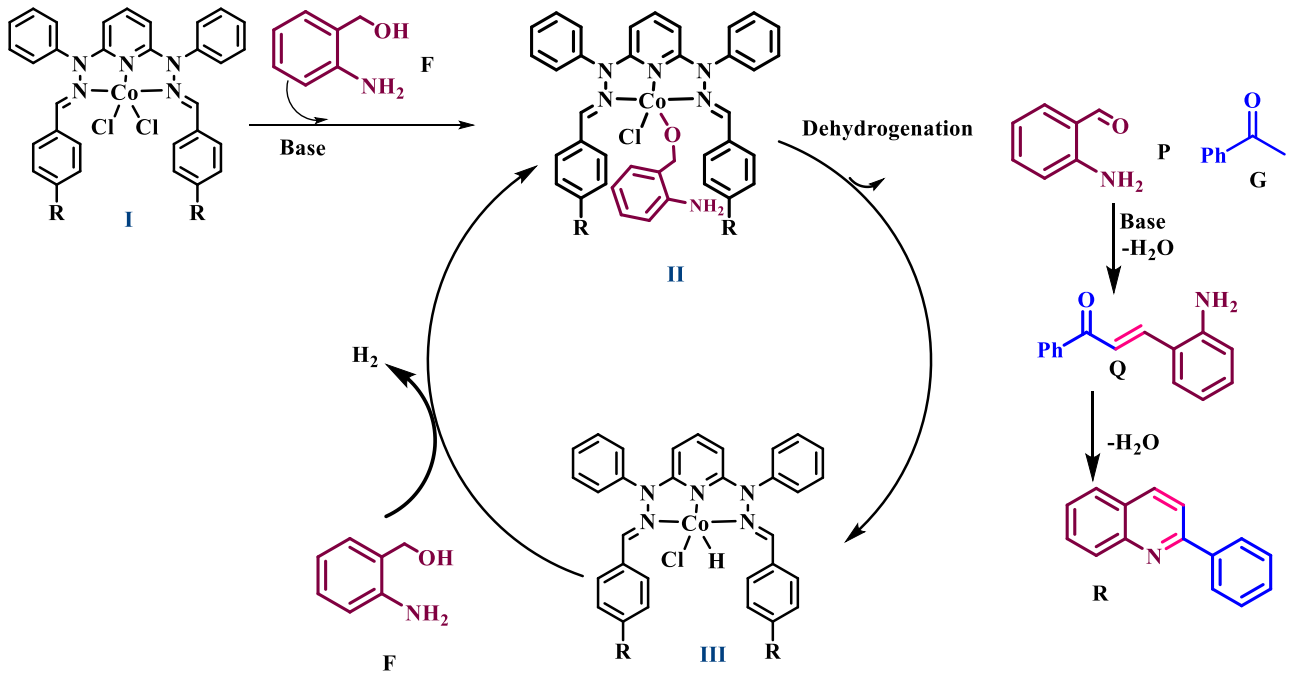
Figure S177. The ESI-MS spectrum of intermediate **IV** of *N*-alkylation of anilines (A) Experimental Pattern (B) Simulated Pattern.



Scheme S3. Probable mechanism of *N*-alkylation of anilines.



Scheme S4. Probable mechanism of α-alkylation of ketones.



Scheme S5. Probable mechanism of dehydrogenative cyclization.