

Electronic Supplementary Information

**Gold(I) catalysed sequential dehydrative cyclisation/ intermolecular [4+2] cycloaddition of
alkynyldienols onto activated alkynes/ alkenes; A facile route to substituted
norbornadienes/ norbornenes**

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1	Copies of $^1\text{H}/^{13}\text{C}$ NMR spectra of all new compounds (Figures S1-S90)	S2-S47
2	HRMS of the reaction mixture using 5bb in the absence of DMAD showing the intermediate (Figure S91)	S48
3	HPLC trace for compounds 27-29 (Figure S92-S94)	S49-S50
4	X-ray structure of compounds 5aa and 25 (Figure S95-S96)	S51

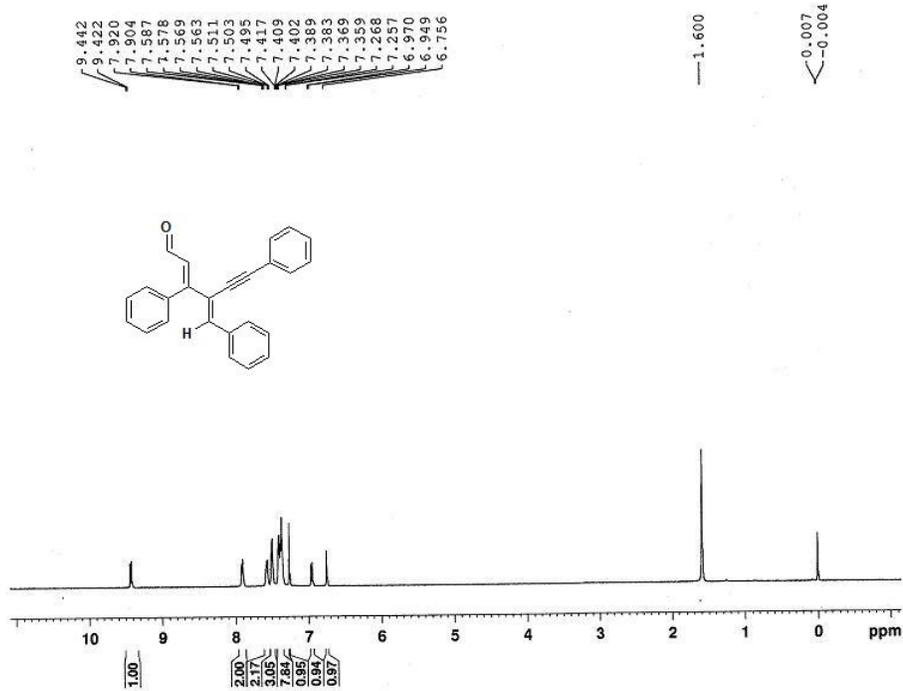


Figure S1. ¹H NMR spectrum of compound 4aa

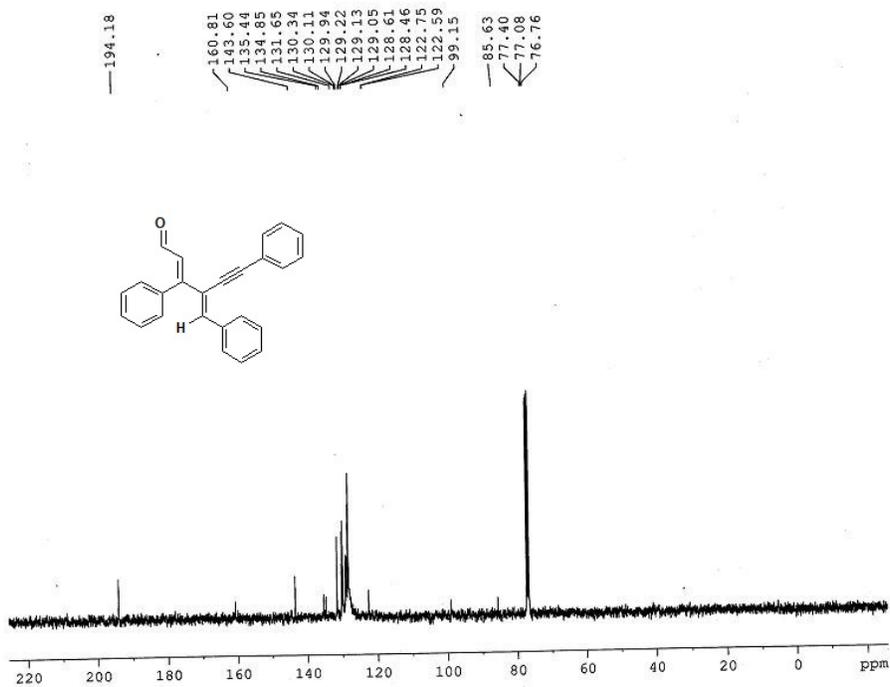


Figure S2. ¹³C NMR spectrum of compound 4aa

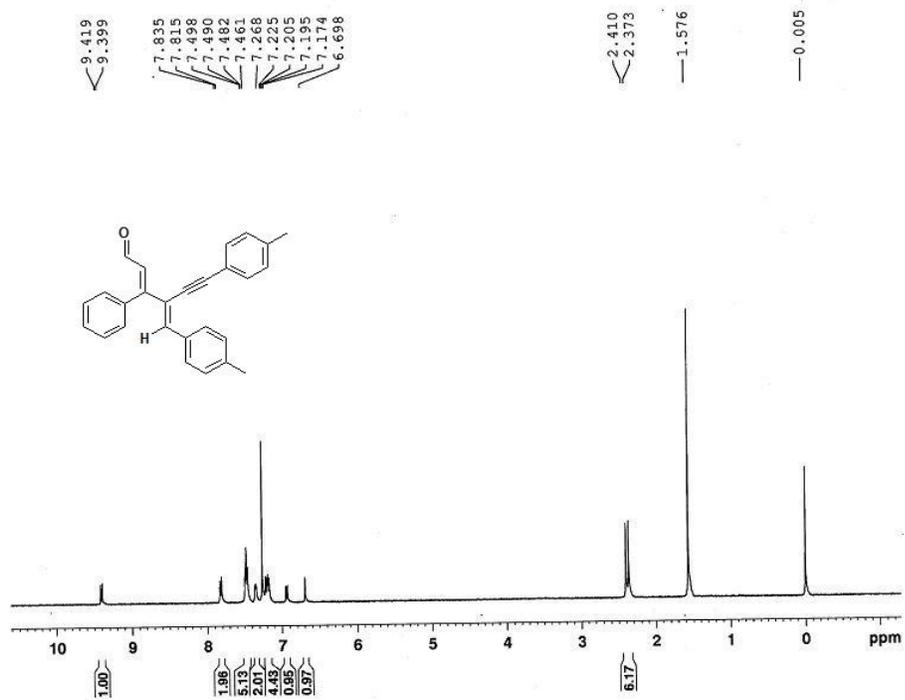


Figure S3. ¹H NMR spectrum of compound 4ab

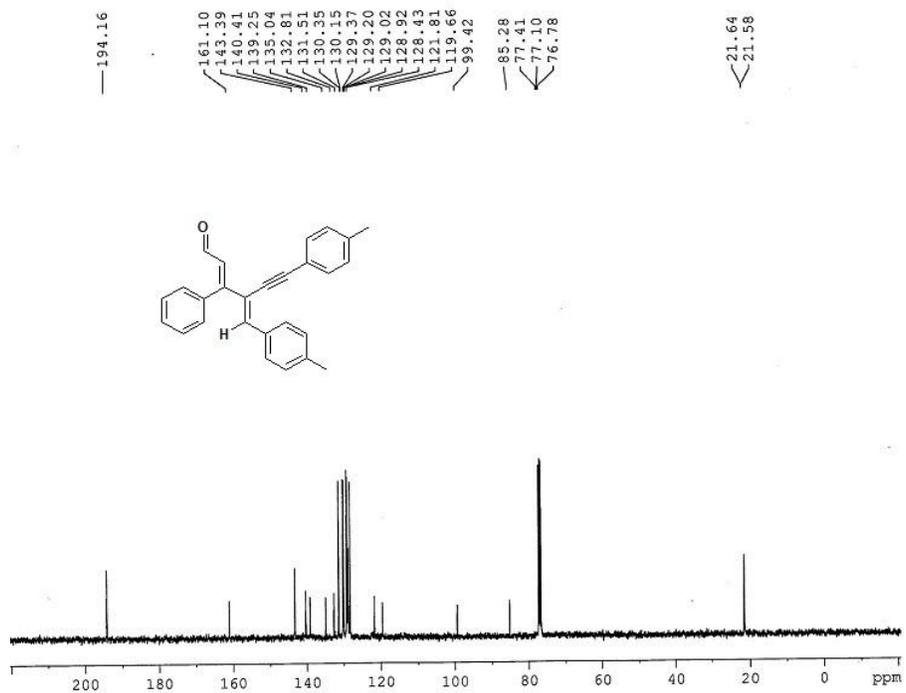


Figure S4. ¹³C NMR spectrum of compound 4ab

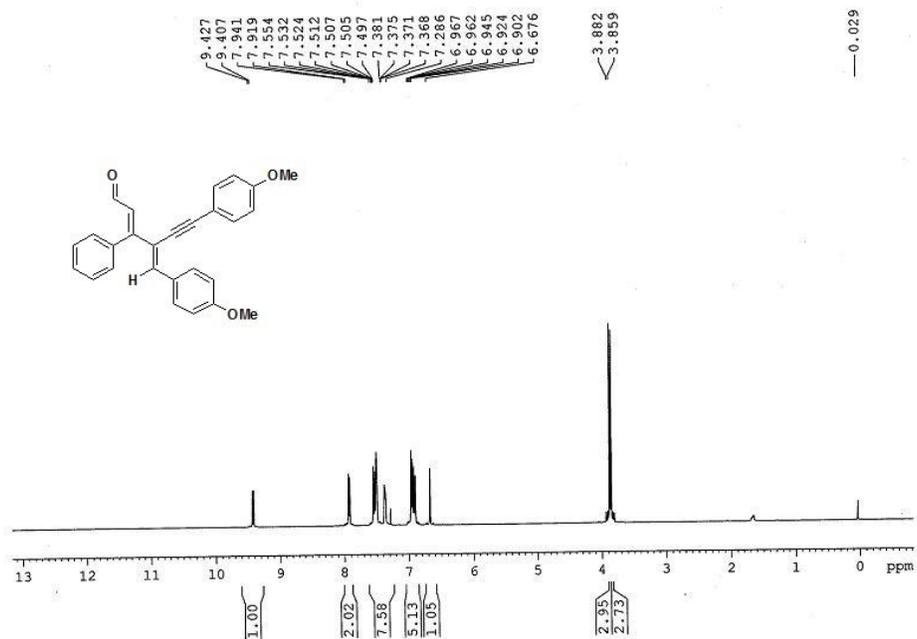


Figure S5. ¹H NMR spectrum of compound 4ac

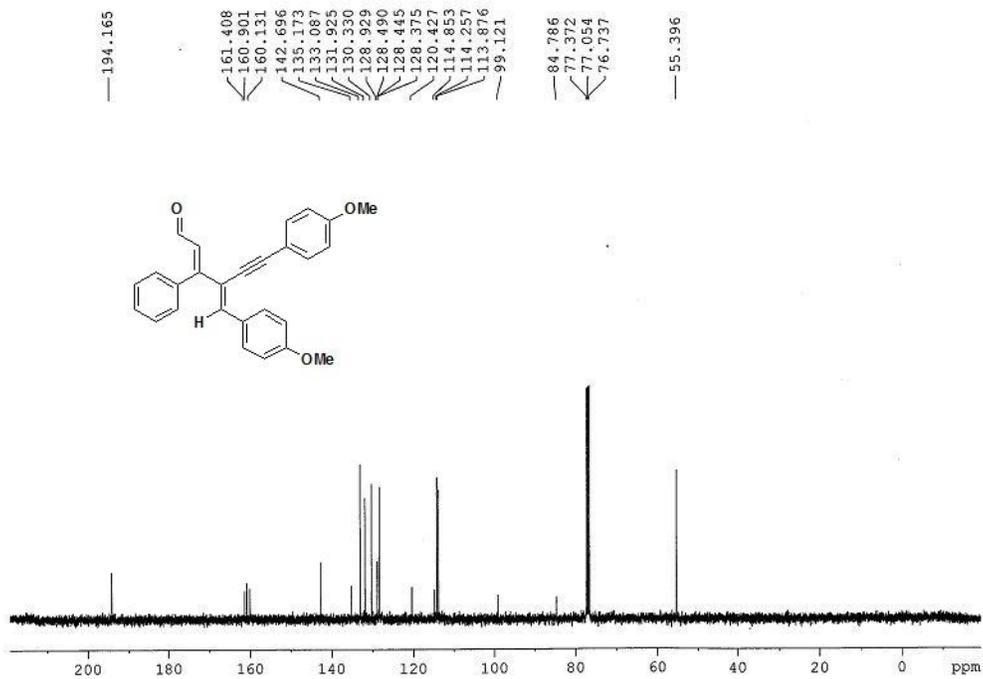


Figure S6. ¹³C NMR spectrum of compound 4ac

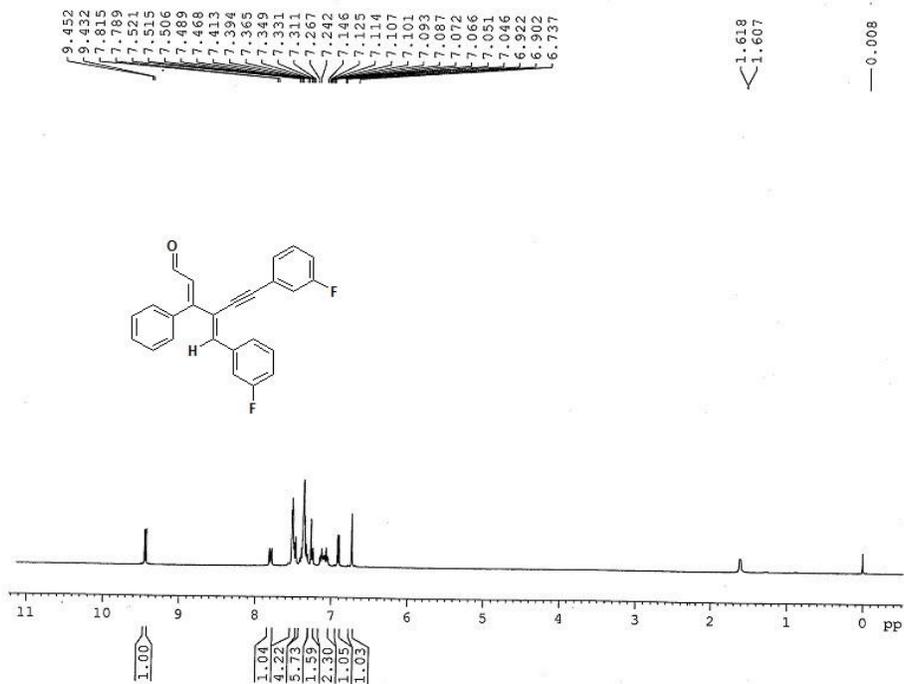


Figure S7. ¹H NMR spectrum of compound 4ad

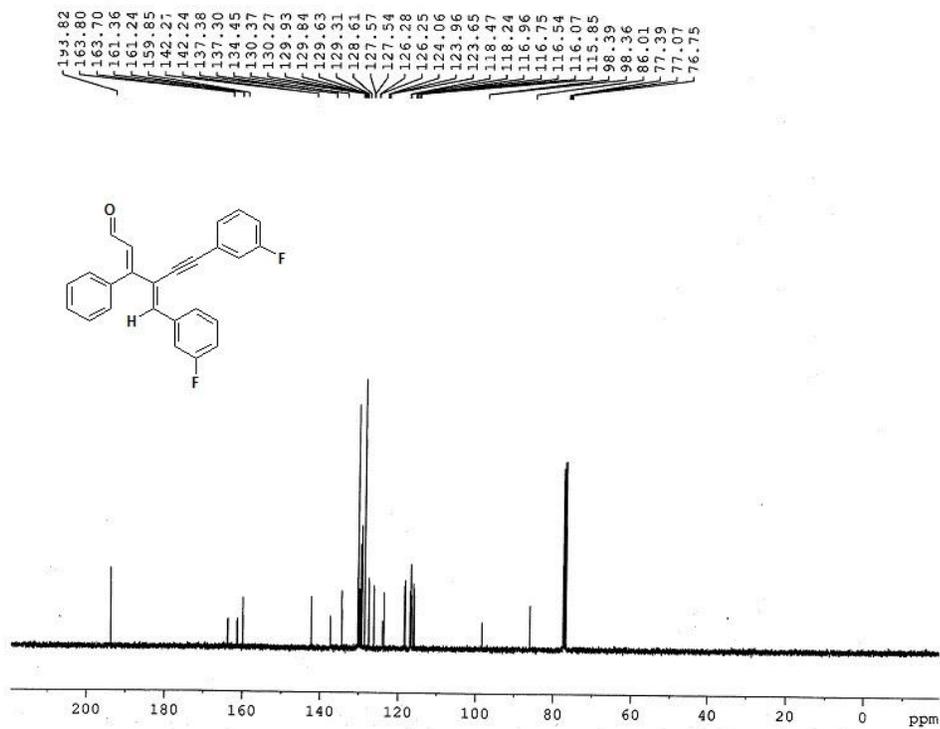


Figure S8. ¹³C NMR spectrum of compound 4ad

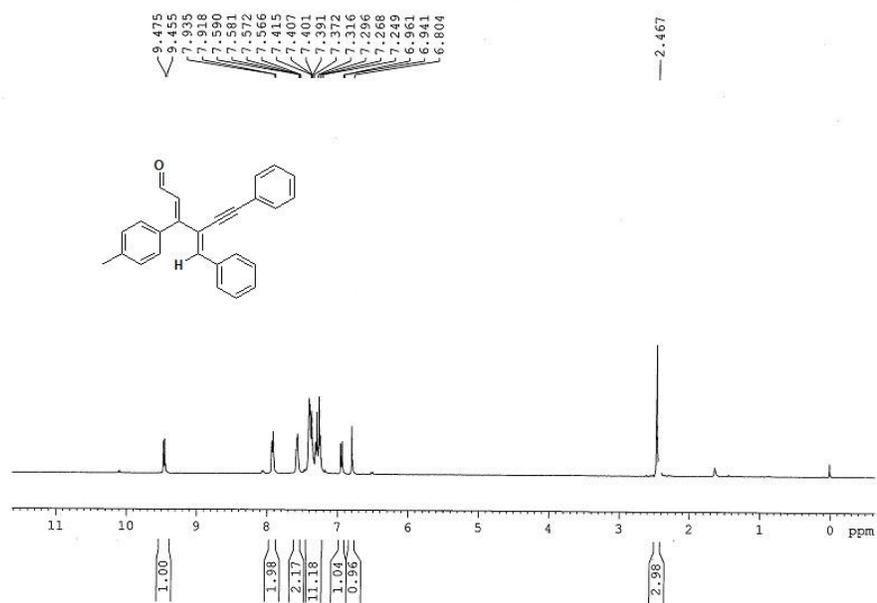


Figure S9. ¹H NMR spectrum of compound 4ba

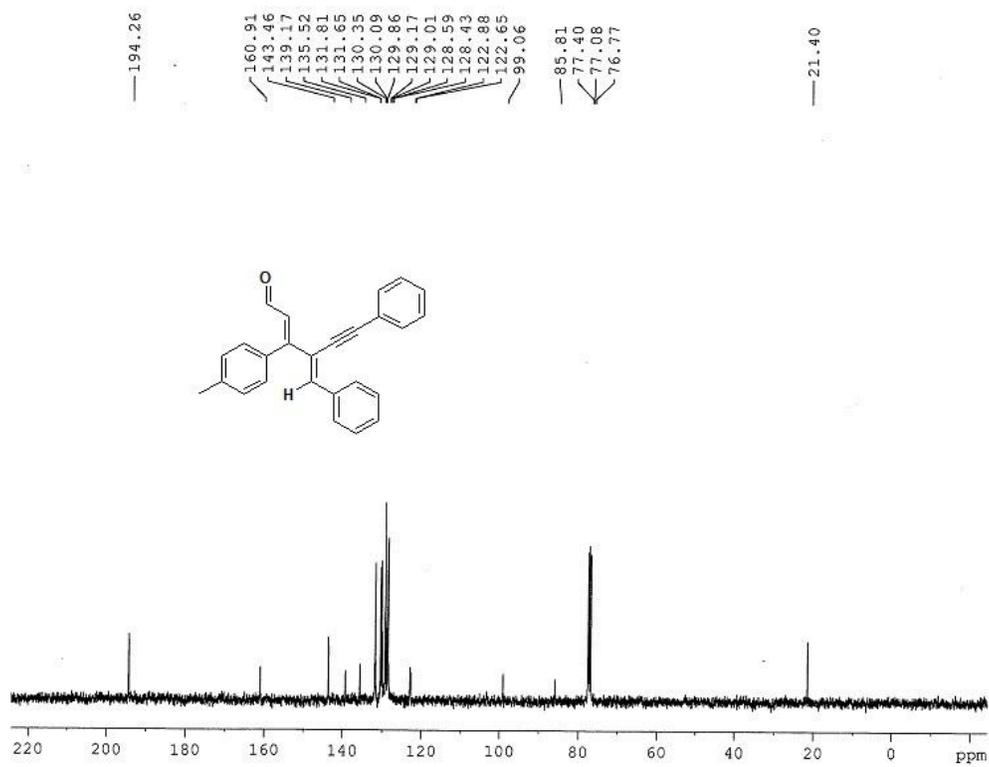


Figure S10. ¹³C NMR spectrum of compound 4ba

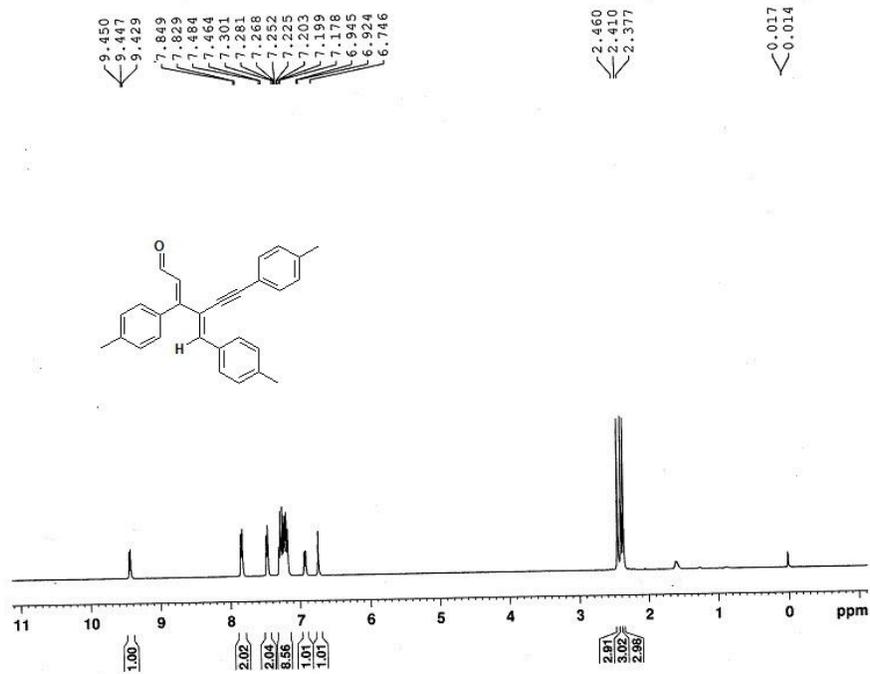


Figure S11. ¹H NMR spectrum of compound 4bb

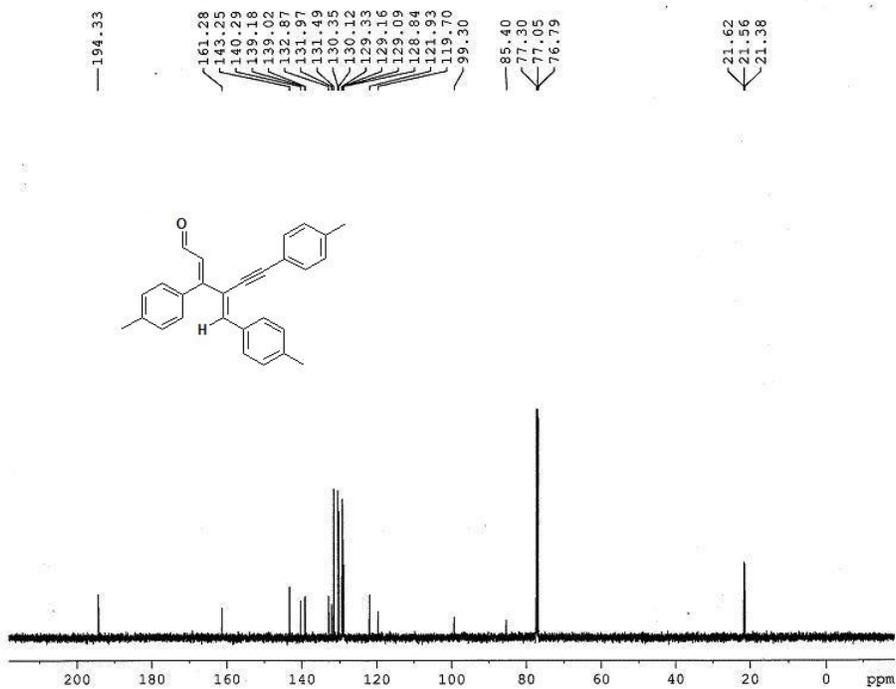


Figure S12. ¹³C NMR spectrum of compound 4bb

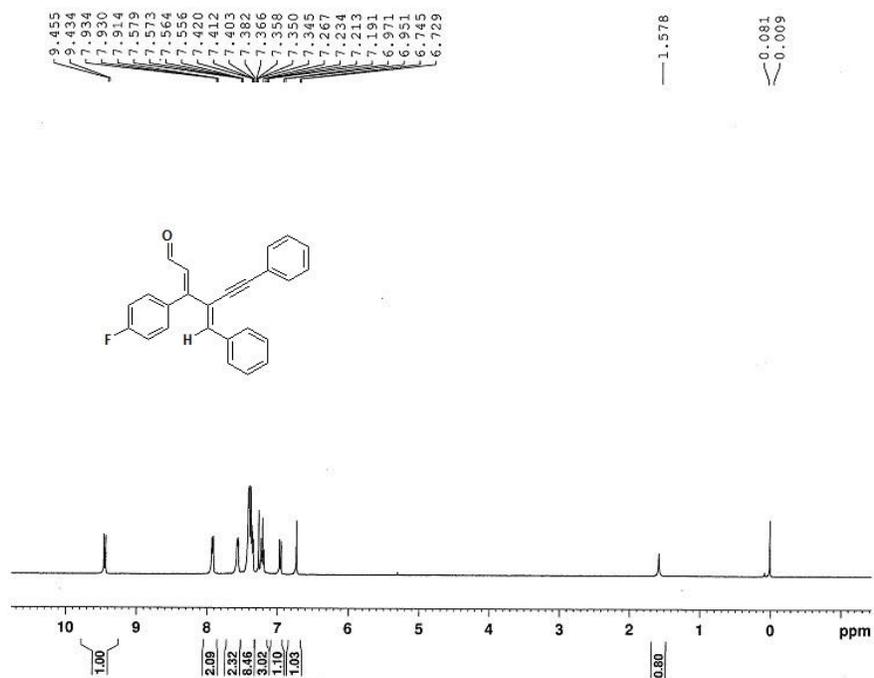


Figure S13. ¹H NMR spectrum of compound **4ca**

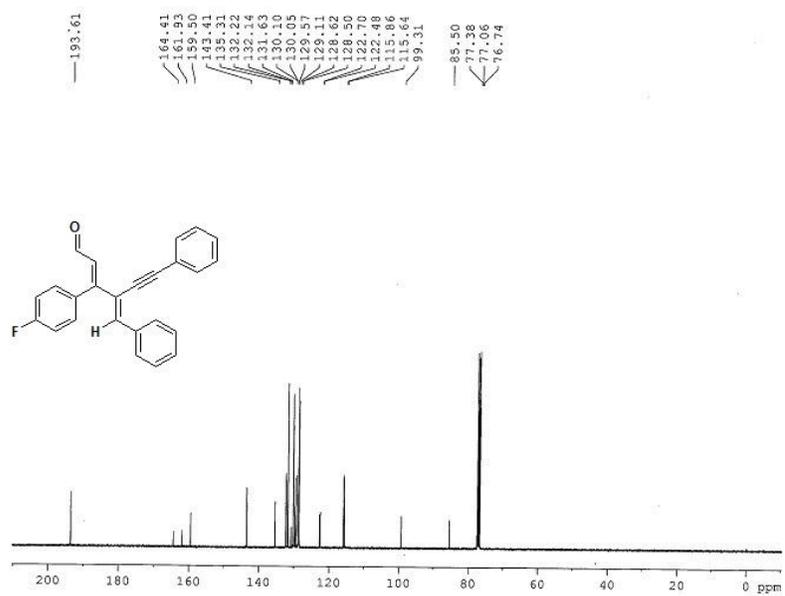


Figure S14. ¹³C NMR spectrum of compound **4ca**

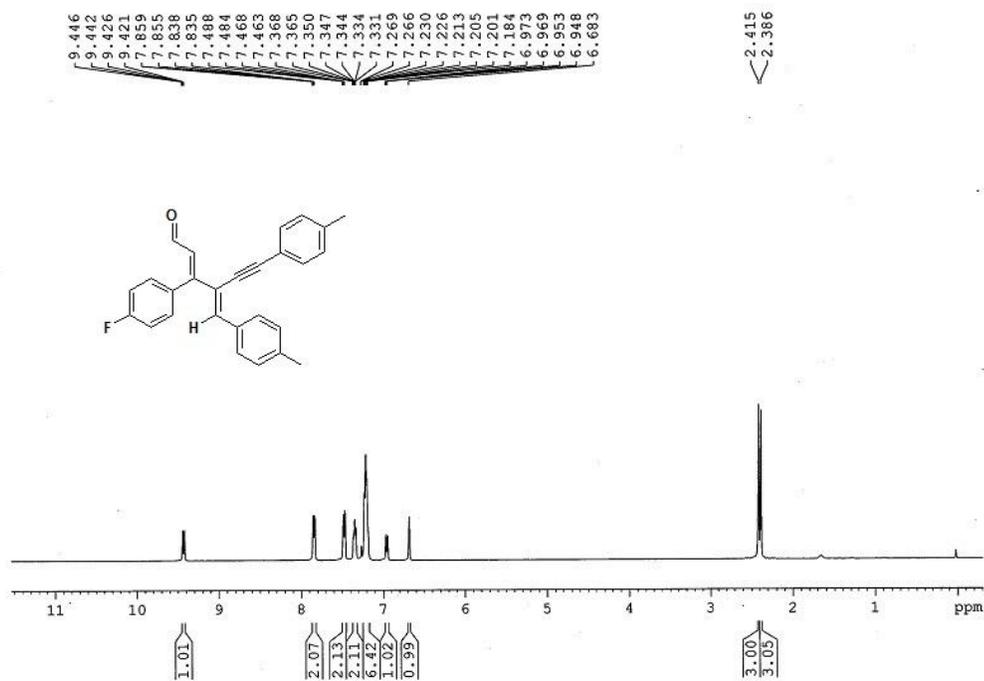


Figure S15. ¹H NMR spectrum of compound 4cb

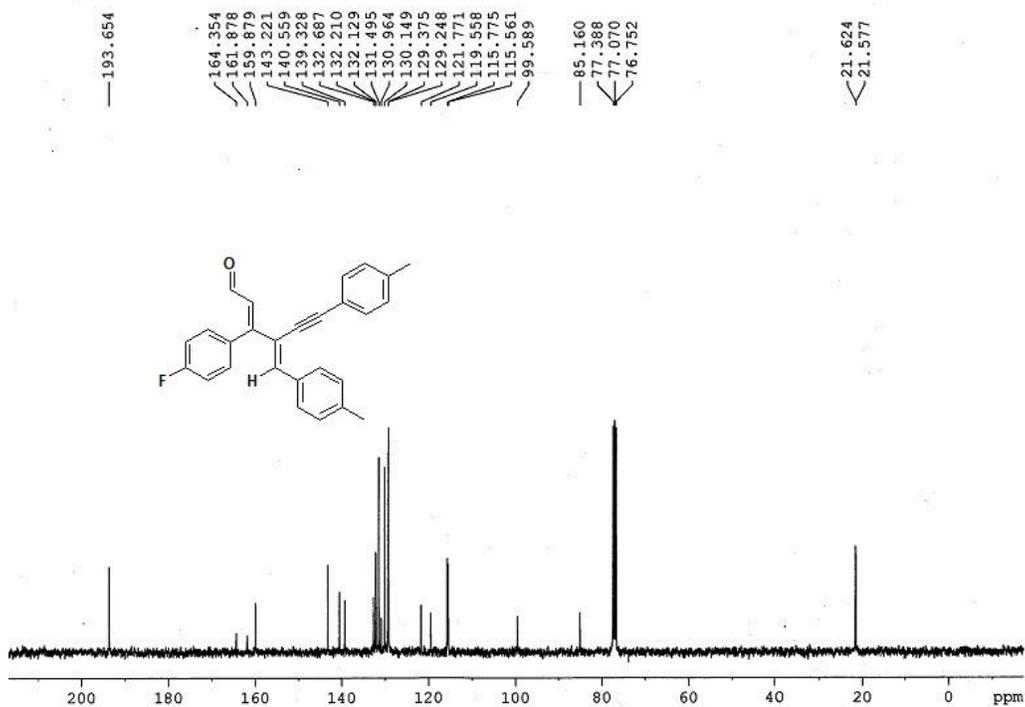


Figure S16. ¹³C NMR spectrum of compound 4cb

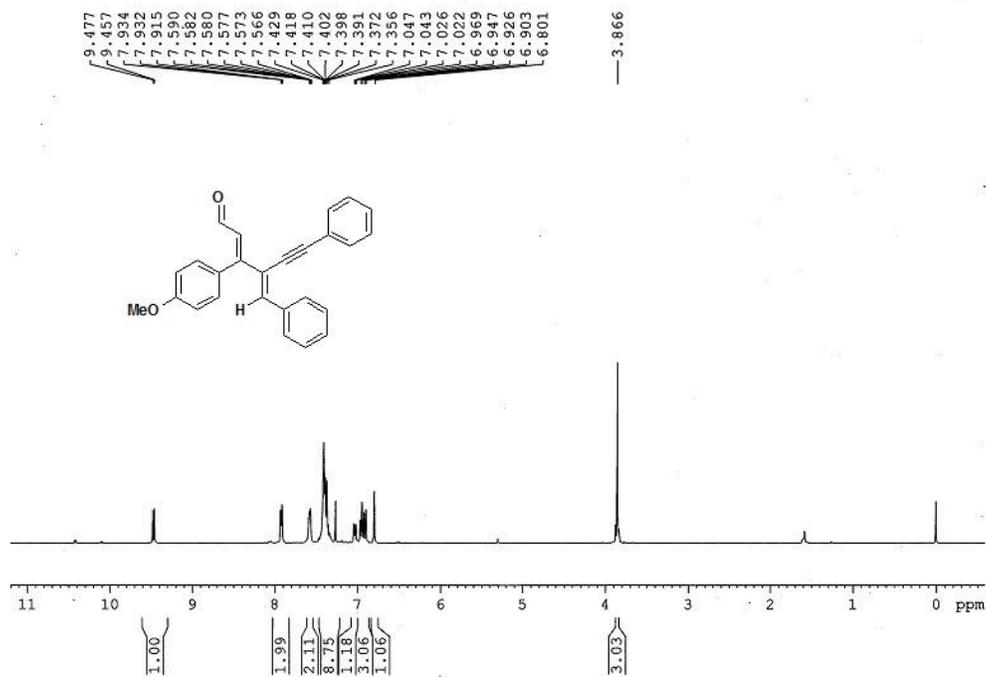


Figure S17. ¹H NMR spectrum of compound 4da

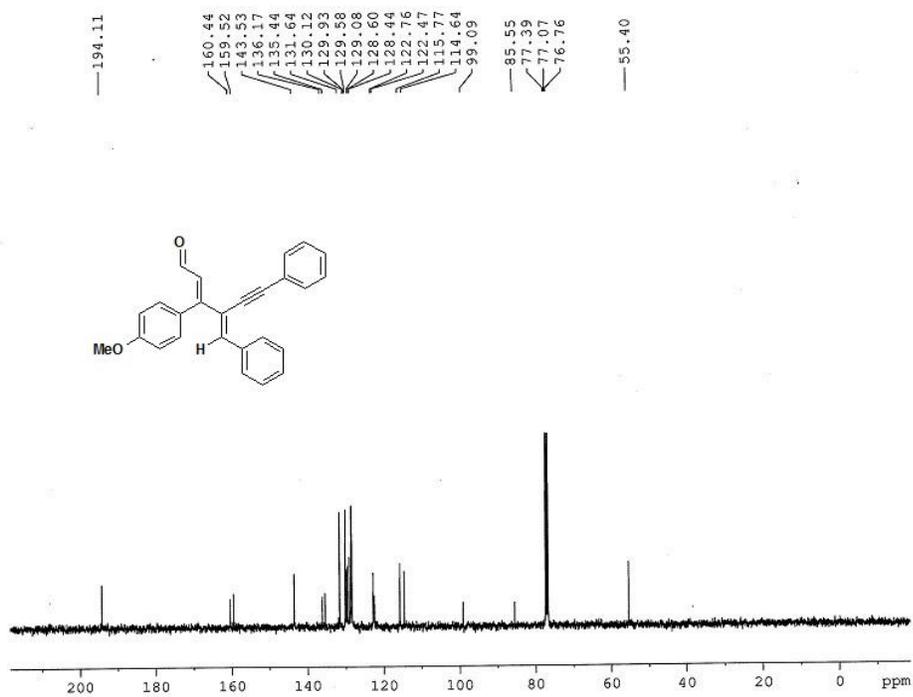


Figure S18. ¹³C NMR spectrum of compound 4da

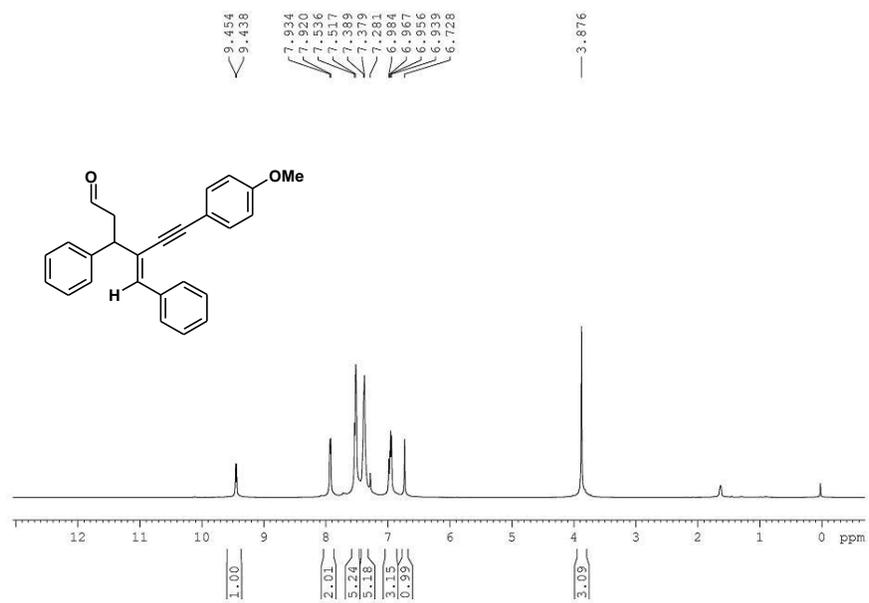


Figure S19. ¹H NMR spectrum of compound 4aac

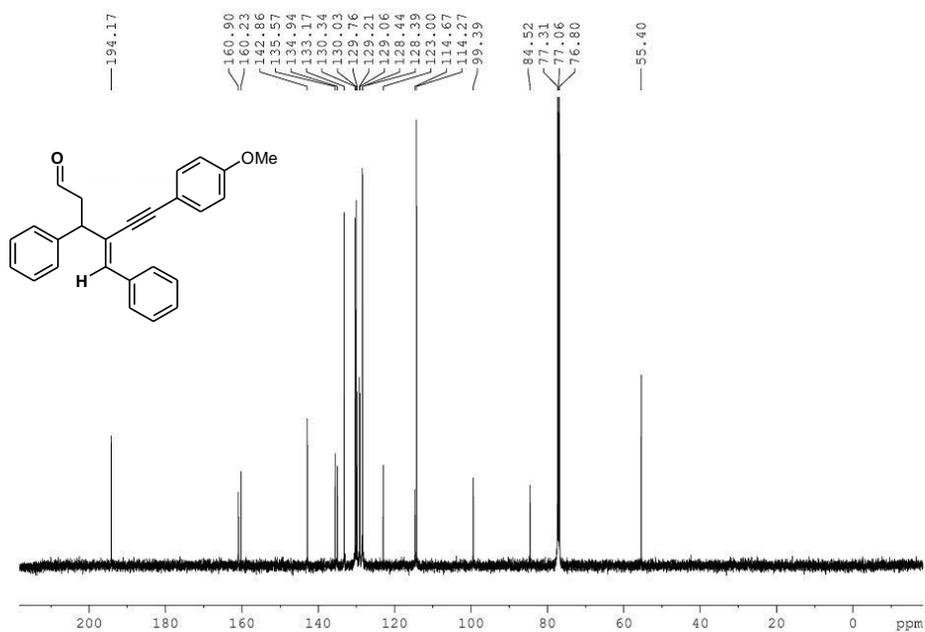


Figure S20. ¹³C NMR spectrum of compound 4aac

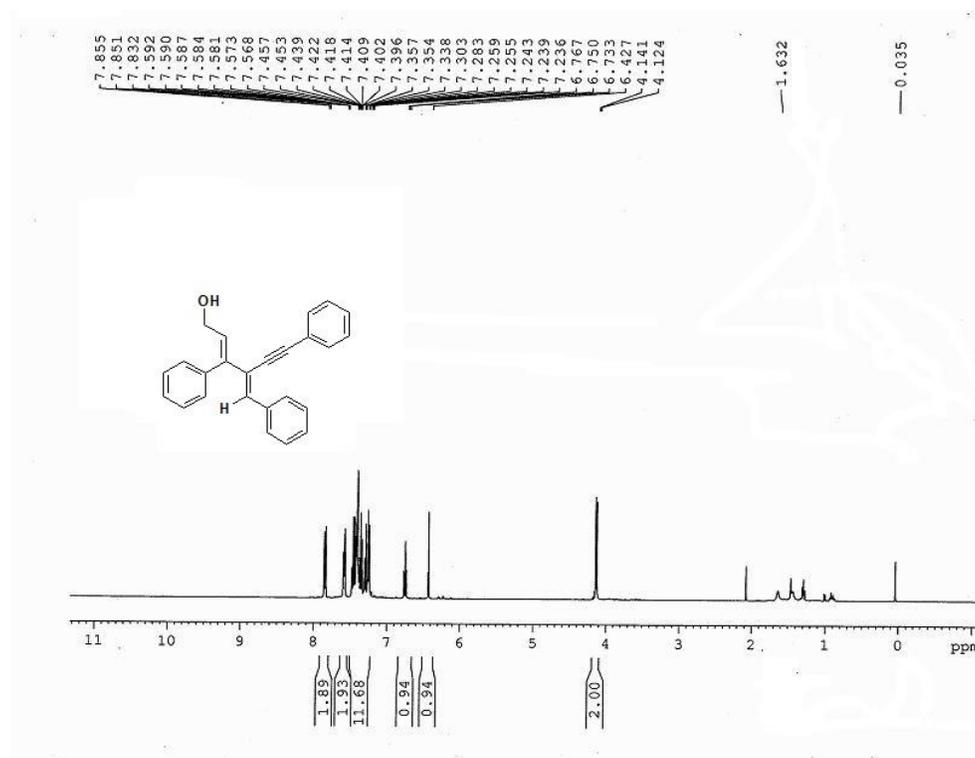


Figure S21. ¹H NMR spectrum of compound 5aa

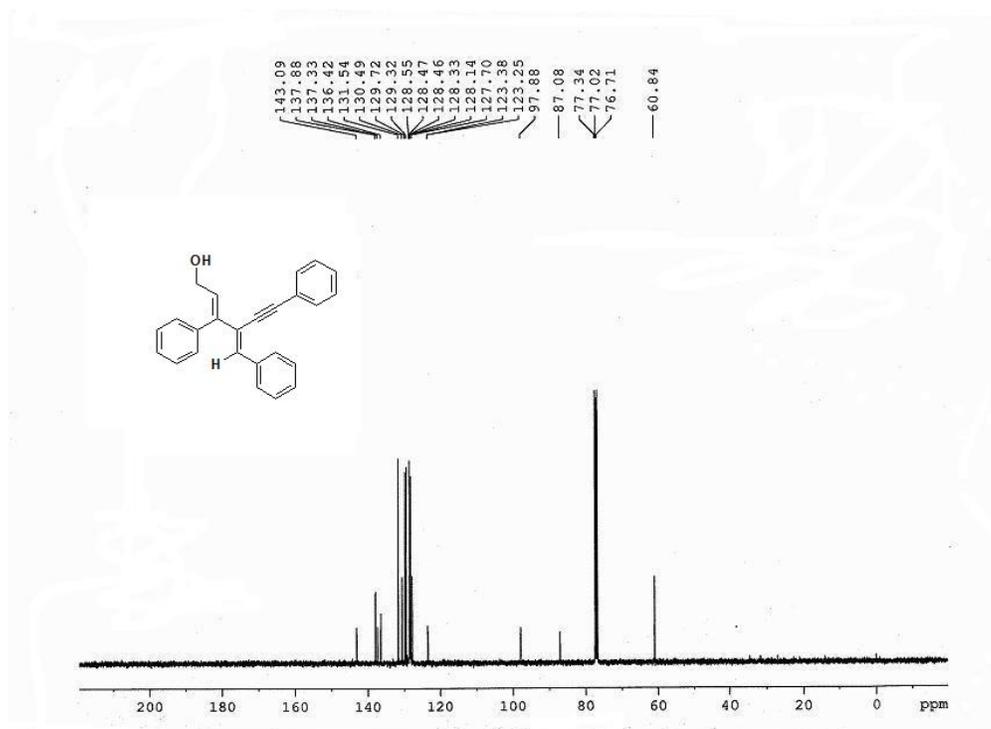


Figure S22. ¹³C NMR spectrum of compound 5aa

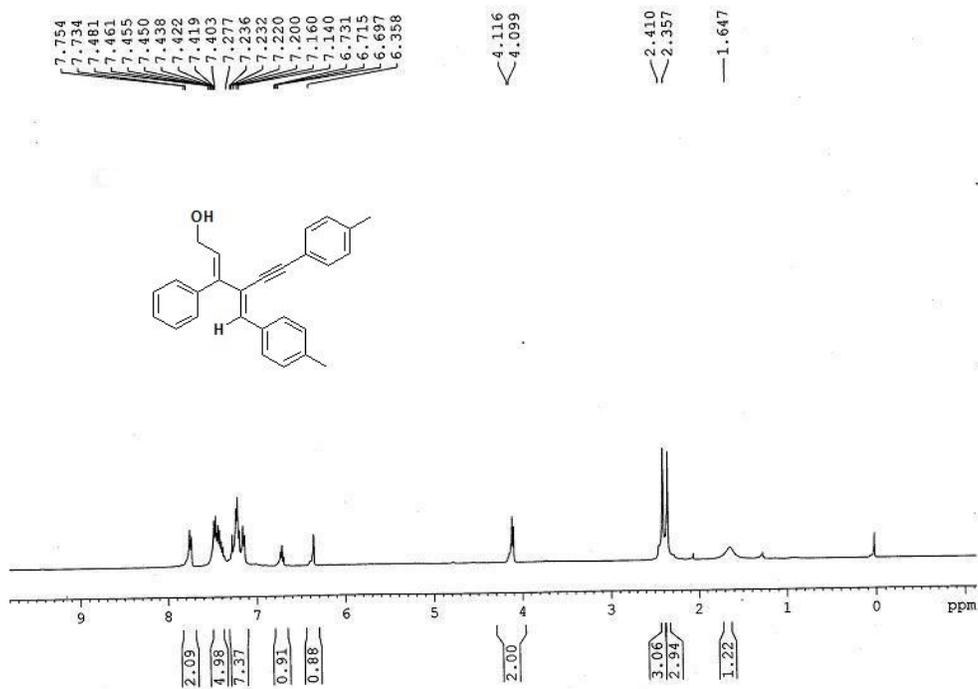


Figure S23. ¹H NMR spectrum of compound 5ab

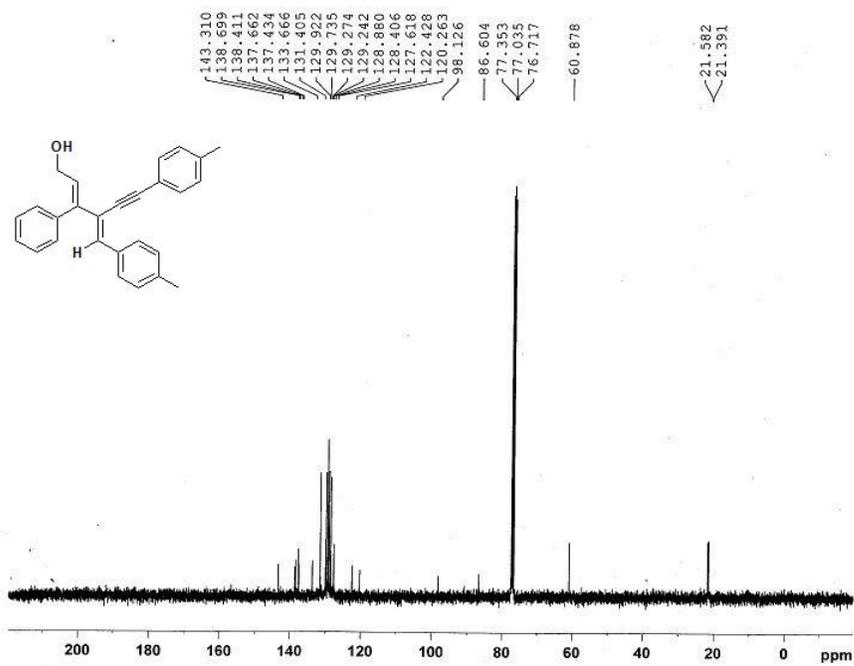


Figure S24. ¹³C NMR spectrum of compound 5ab

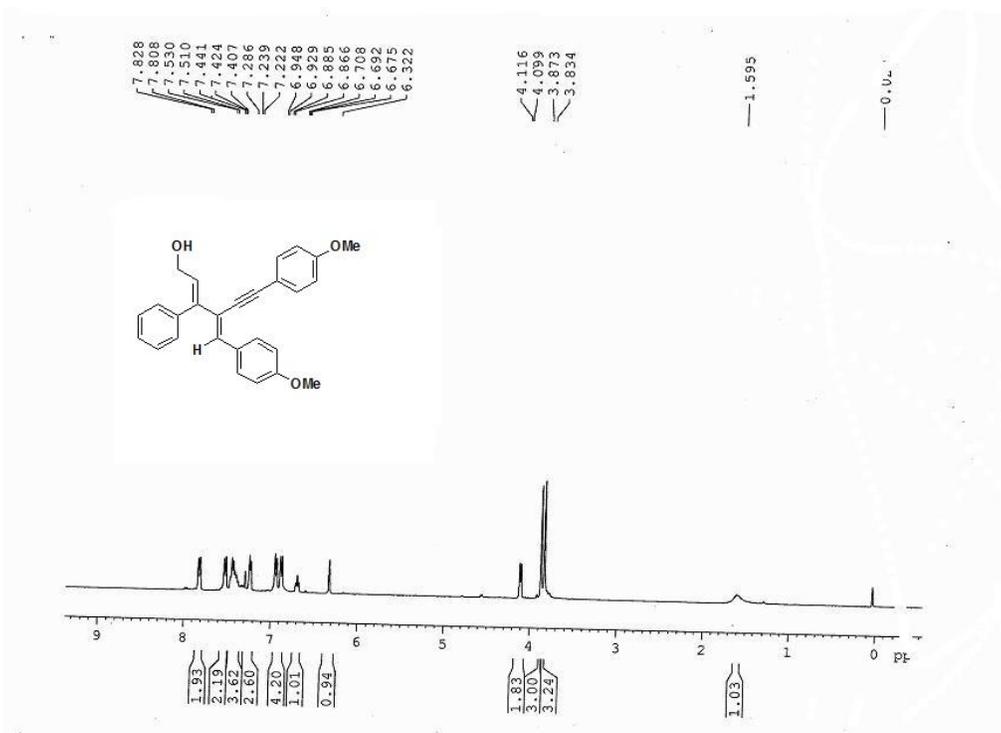


Figure S25. ¹H NMR spectrum of compound 5ac

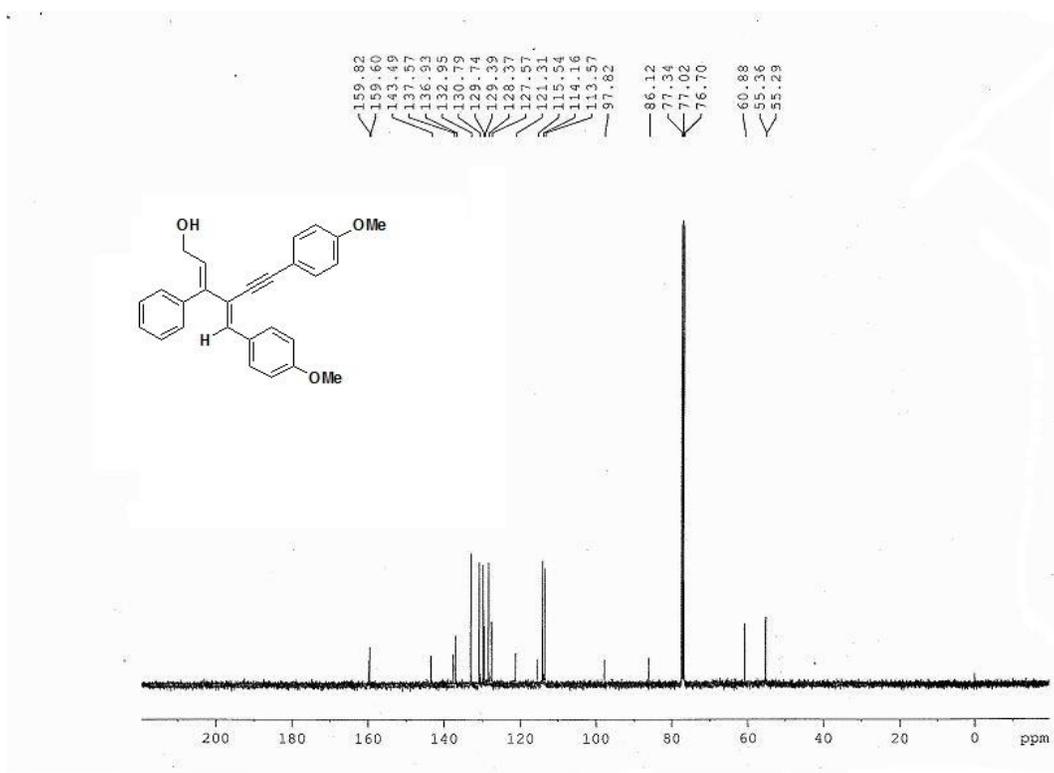


Figure S26. ¹³C NMR spectrum of compound 5ac

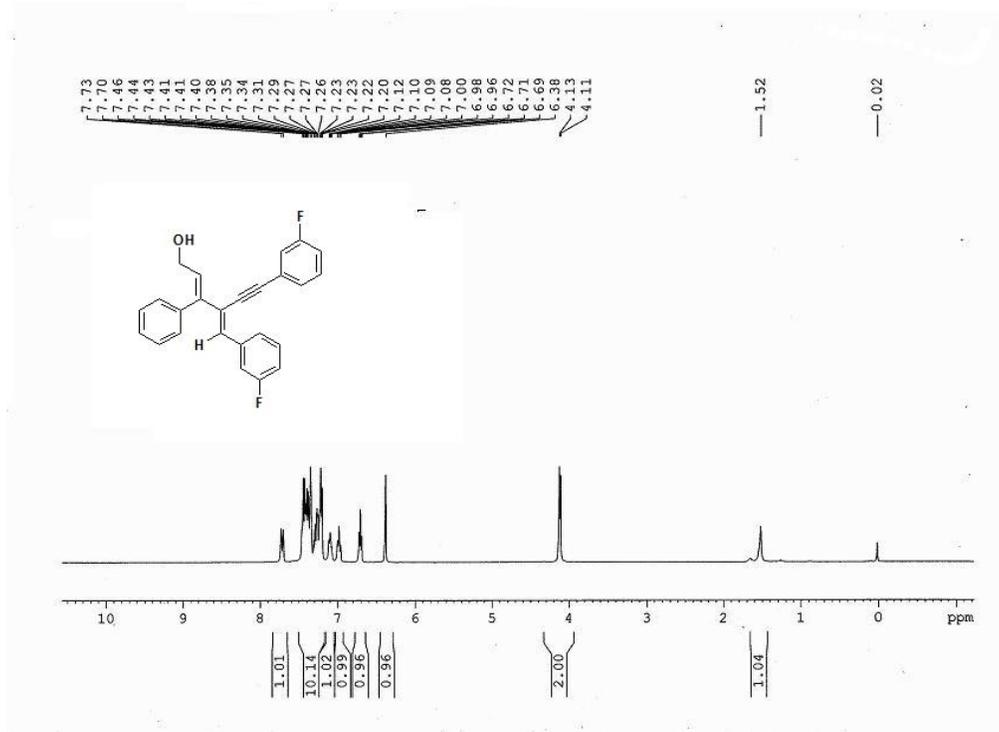


Figure S27. ¹H NMR spectrum of compound 5ad

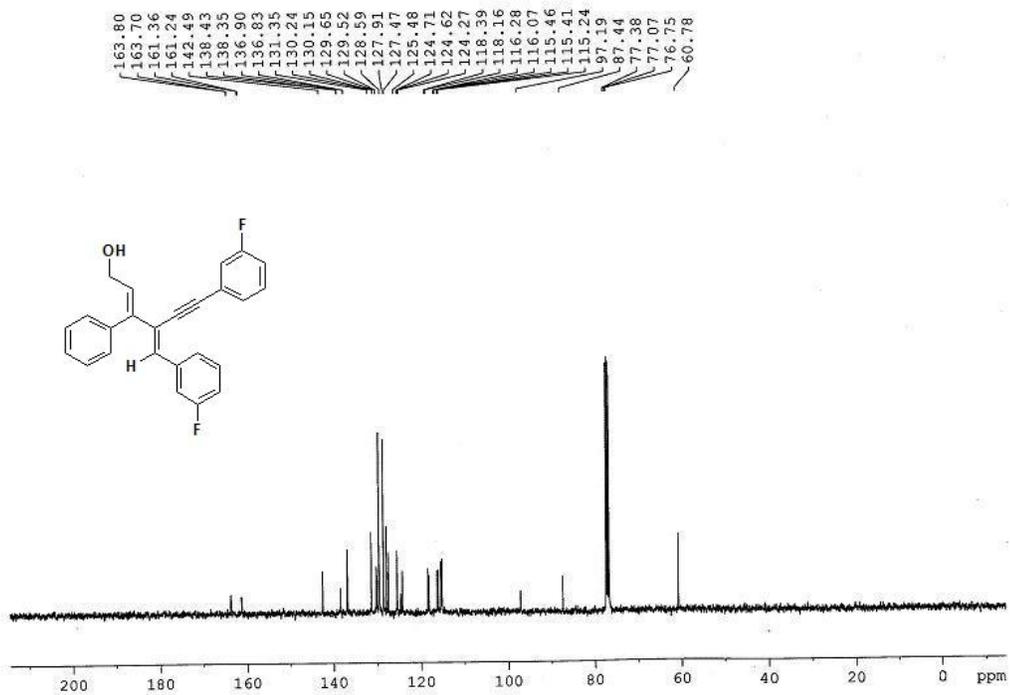


Figure S28. ¹³C NMR spectrum of compound 5ad

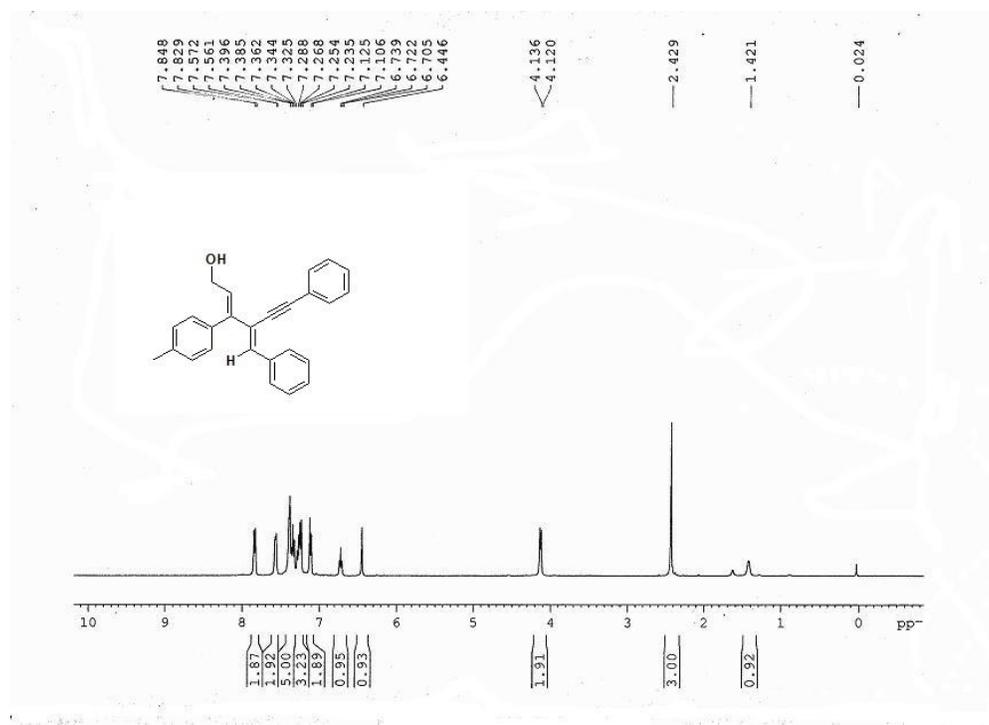


Figure S29. ¹H NMR spectrum of compound 5ba

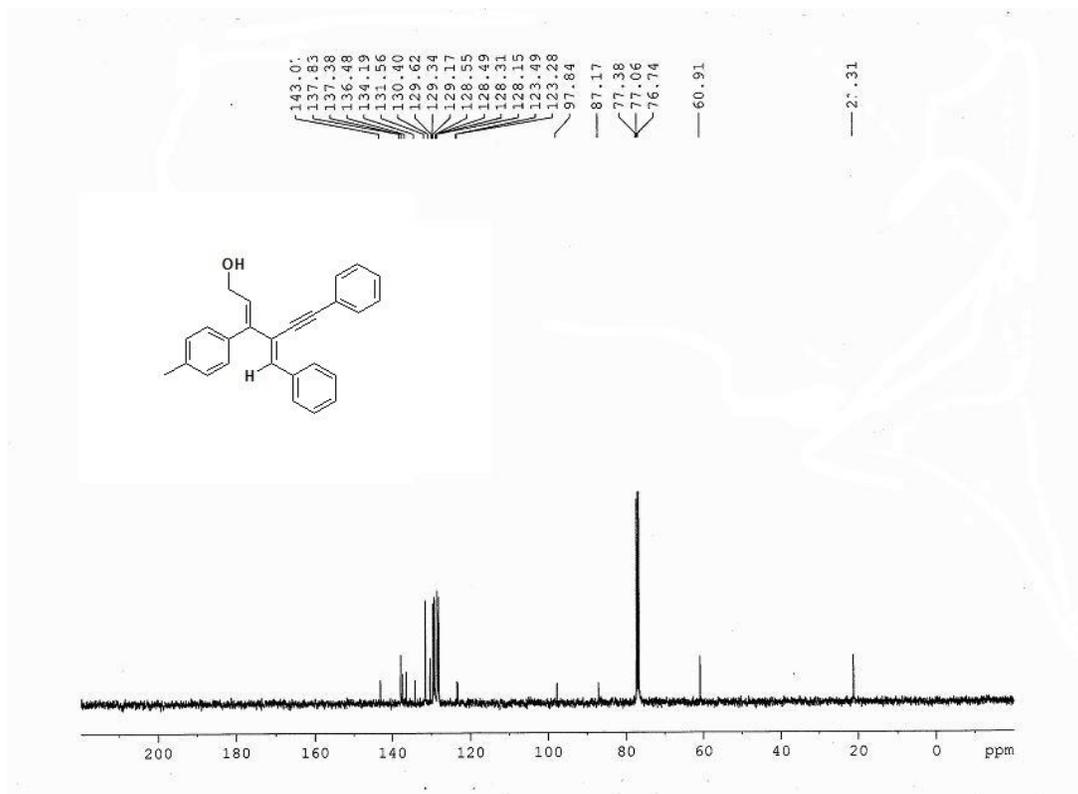


Figure S30. ¹³C NMR spectrum of compound 5ba

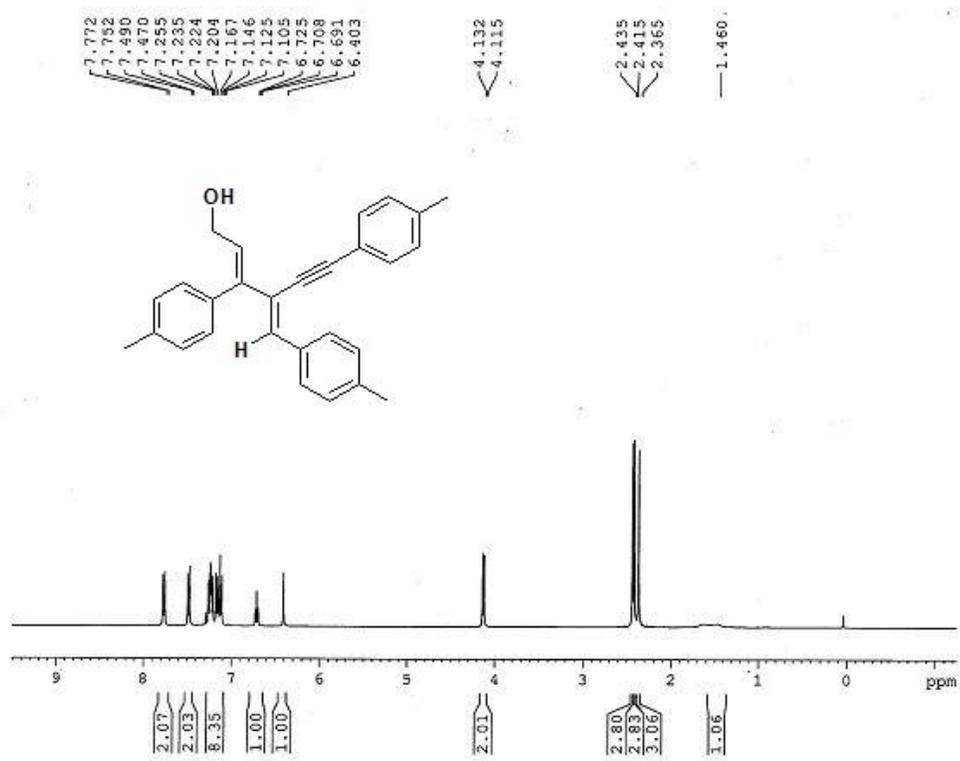


Figure S31. ^1H NMR spectrum of compound **5bb**

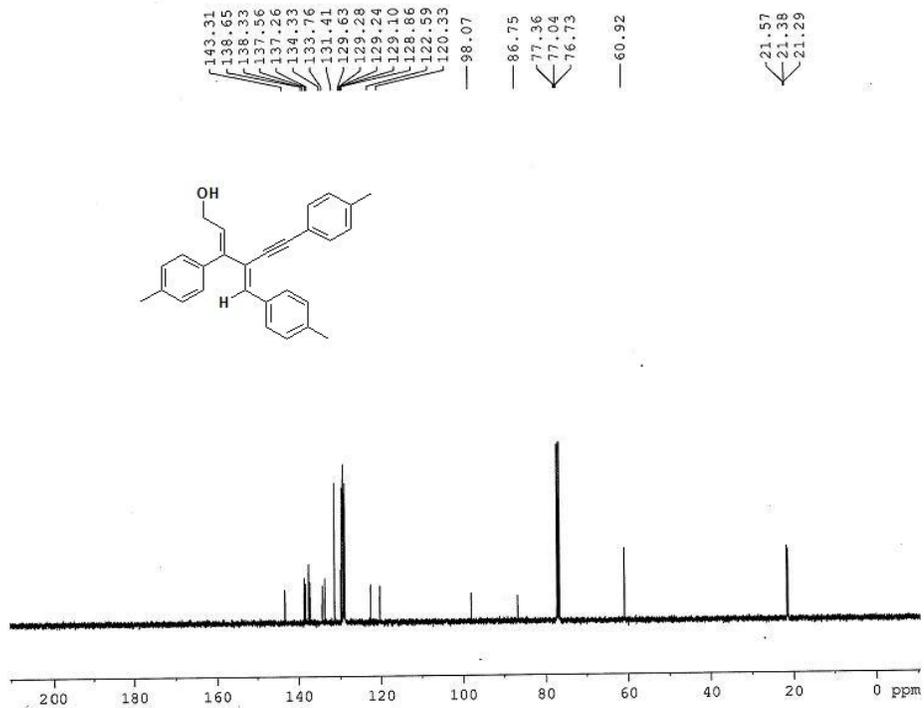


Figure S32. ^{13}C NMR spectrum of compound **5bb**

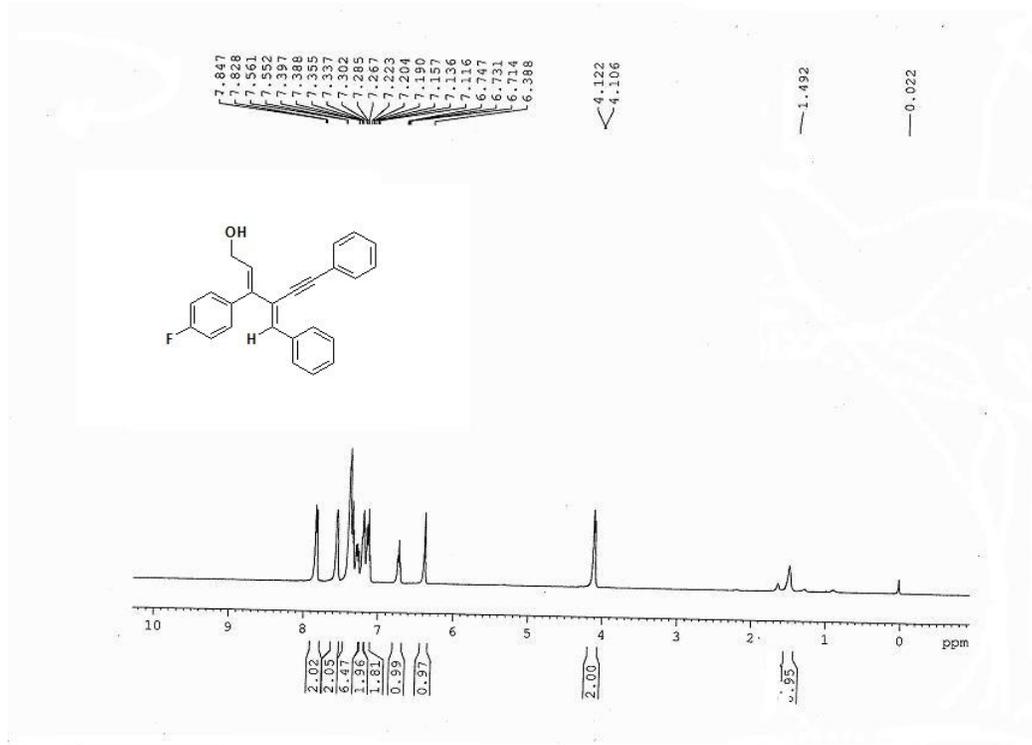


Figure S33. ¹H NMR spectrum of compound 5ca

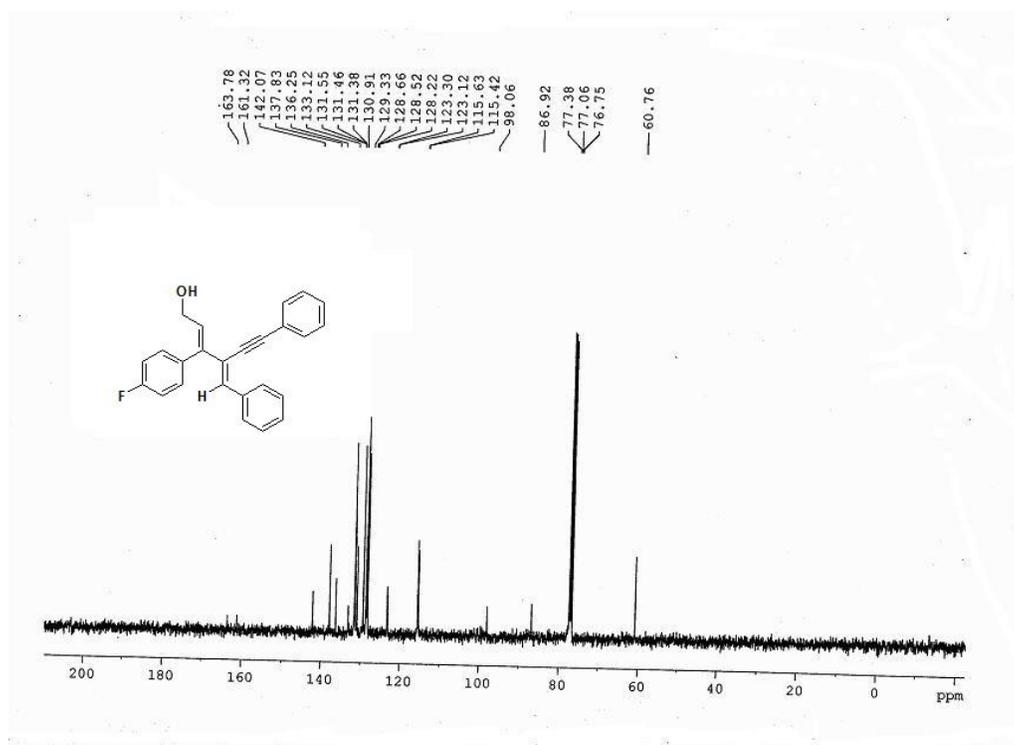


Figure S34. ¹³C NMR spectrum of compound 5ca

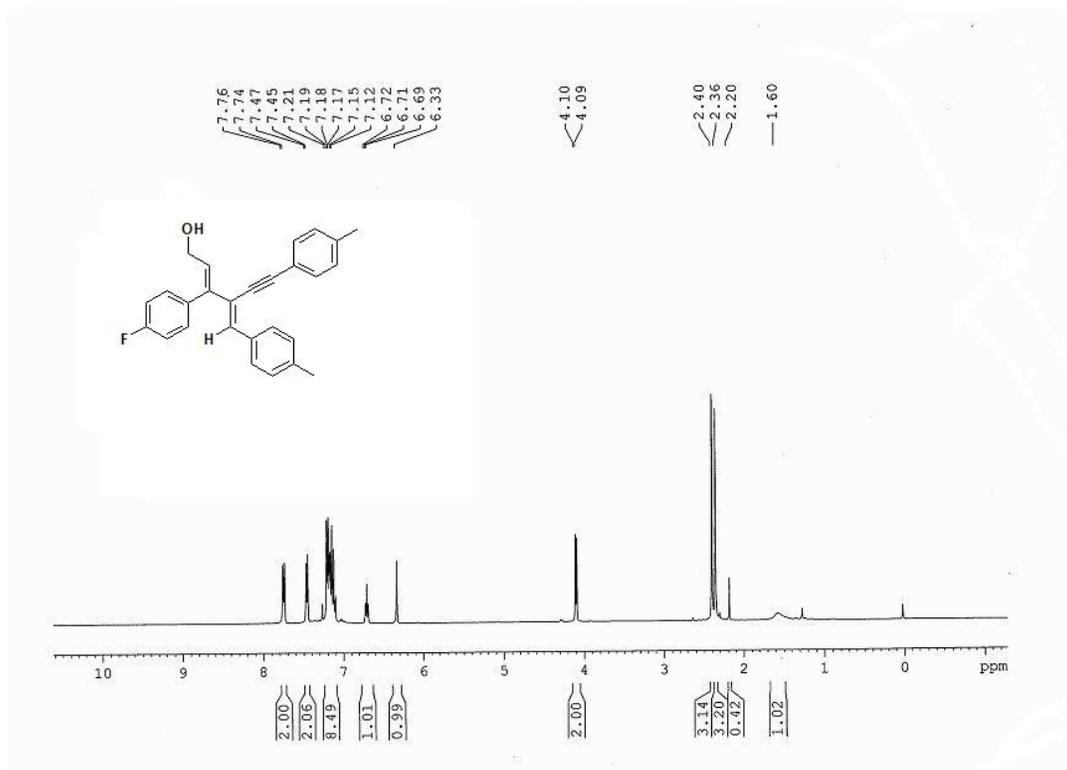


Figure S35. ¹H NMR spectrum of compound 5cb

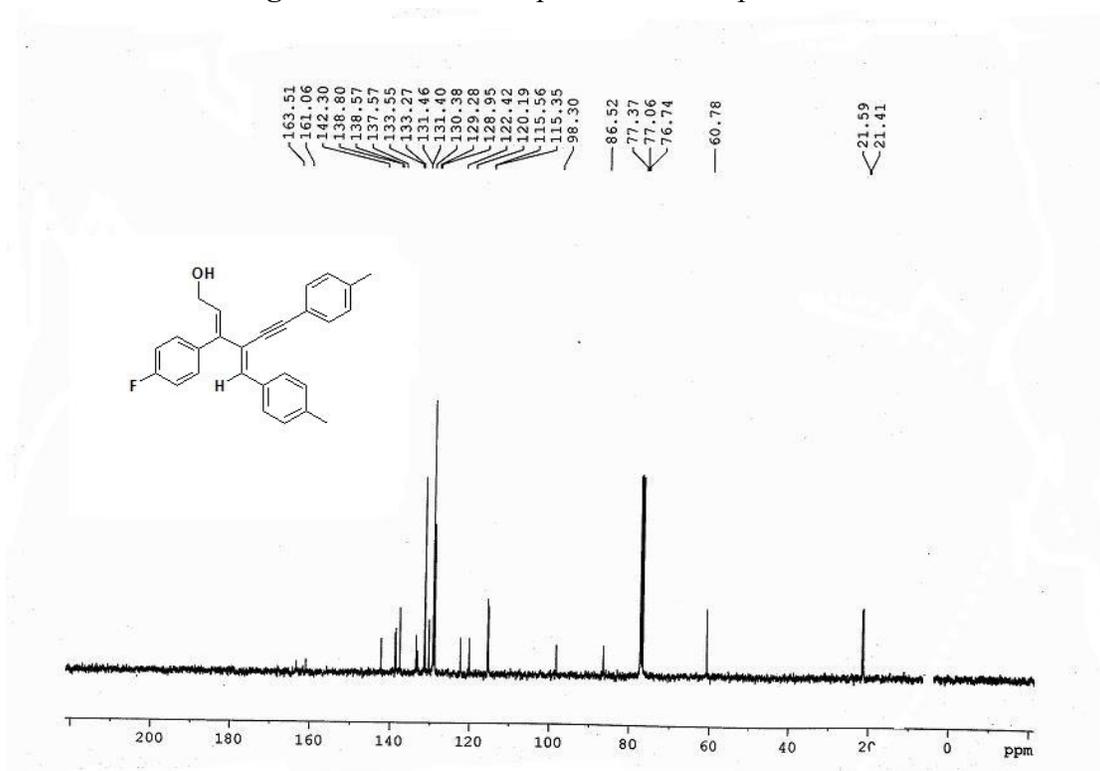
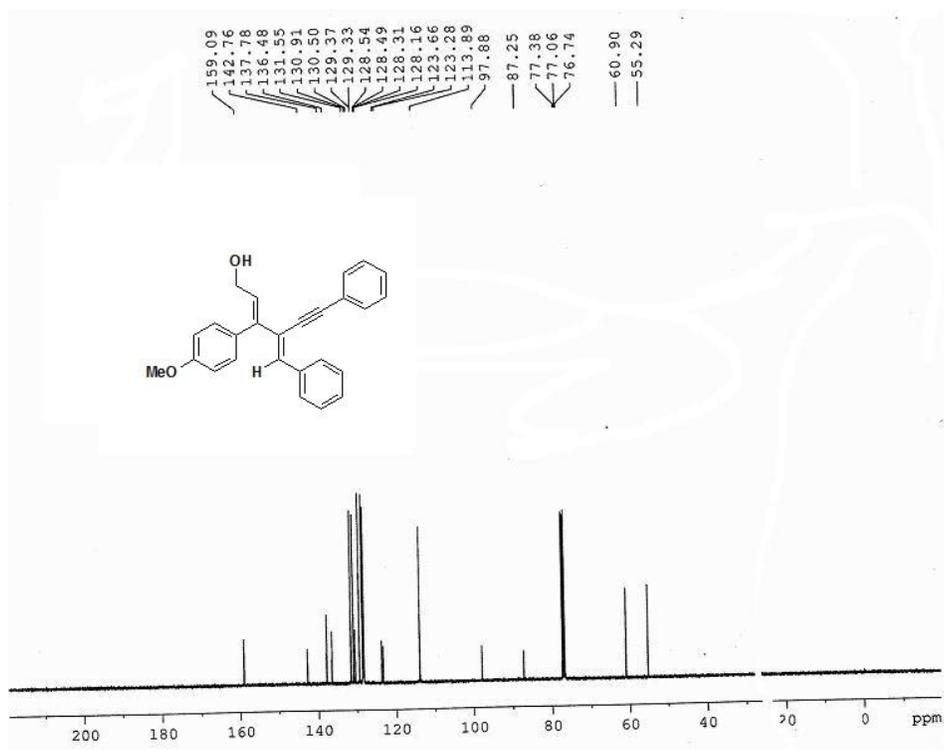
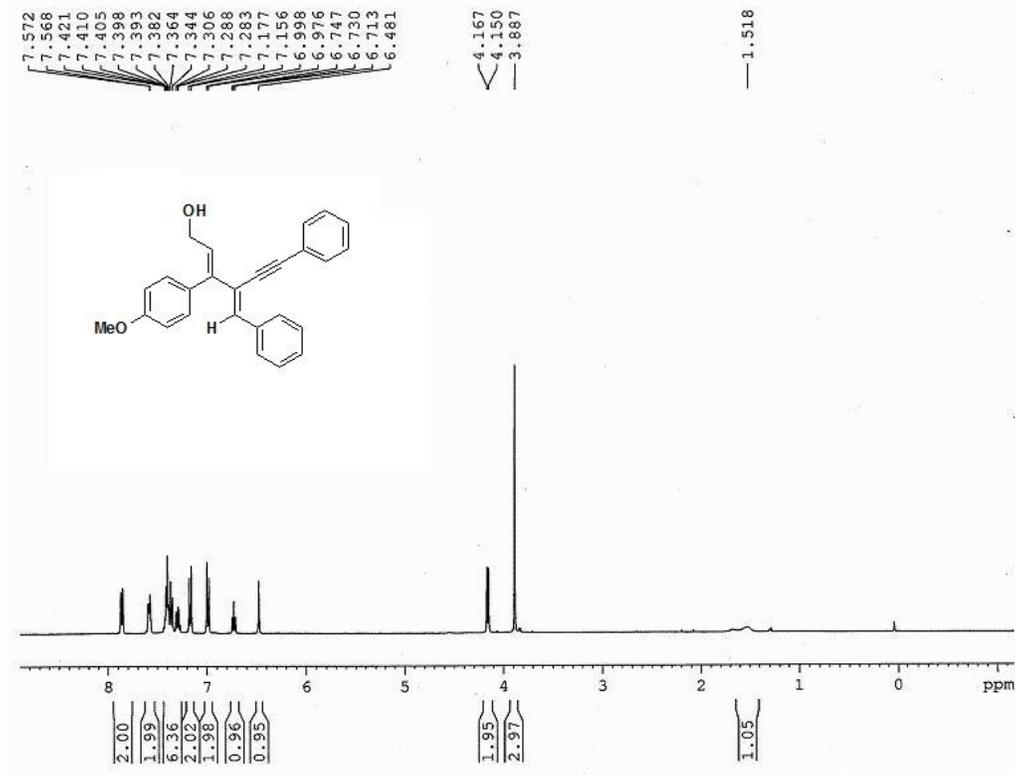


Figure S36. ¹³C NMR spectrum of compound 5cb



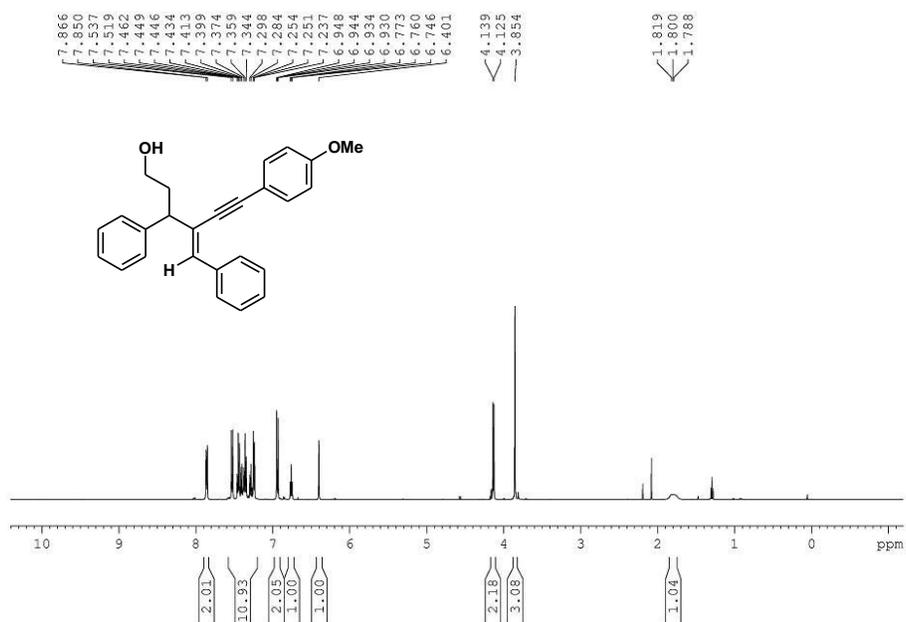


Figure S39. ¹H NMR spectrum of compound 5aac

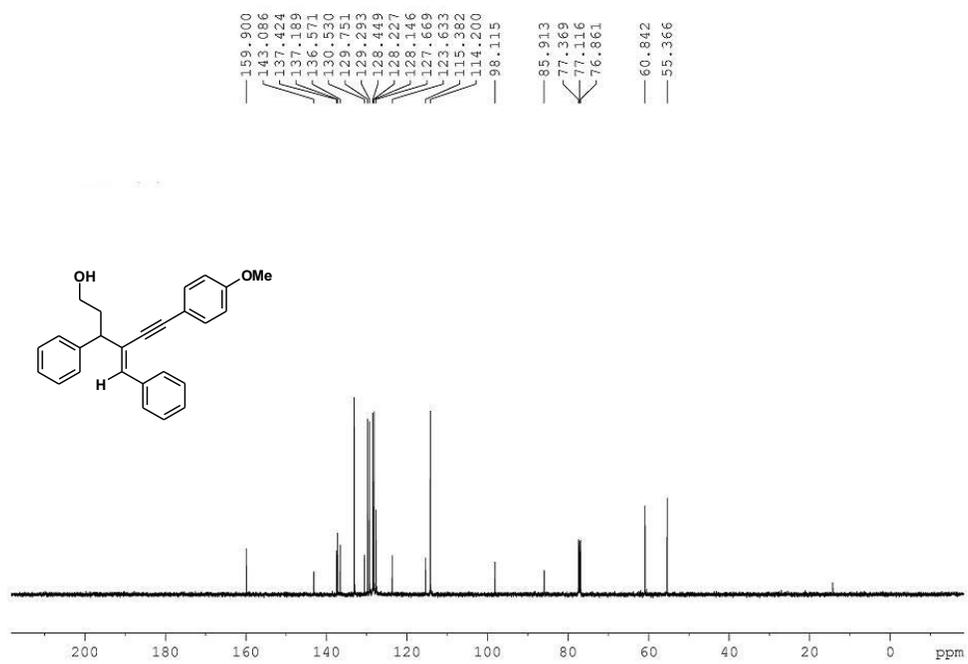


Figure S40. ¹³C NMR spectrum of compound 5aac

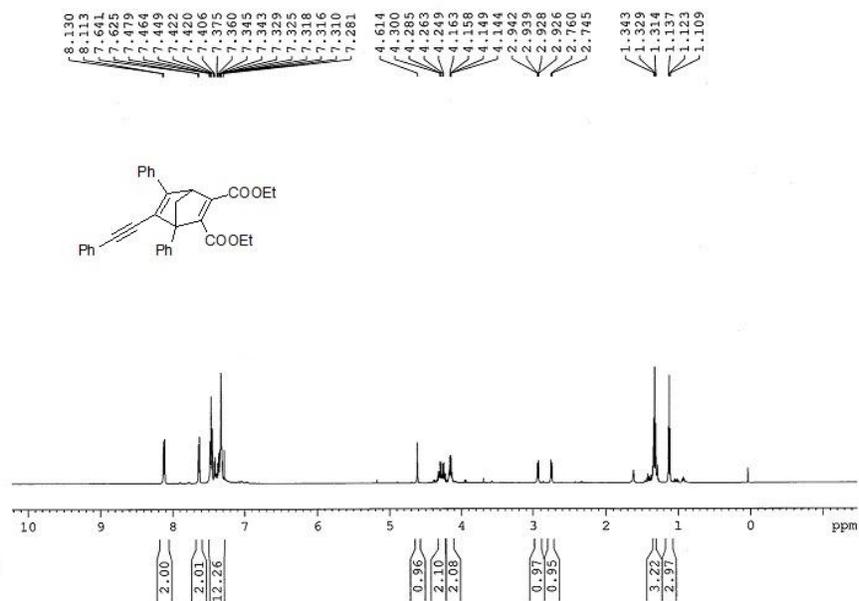


Figure S41. ¹H NMR spectrum of compound 8

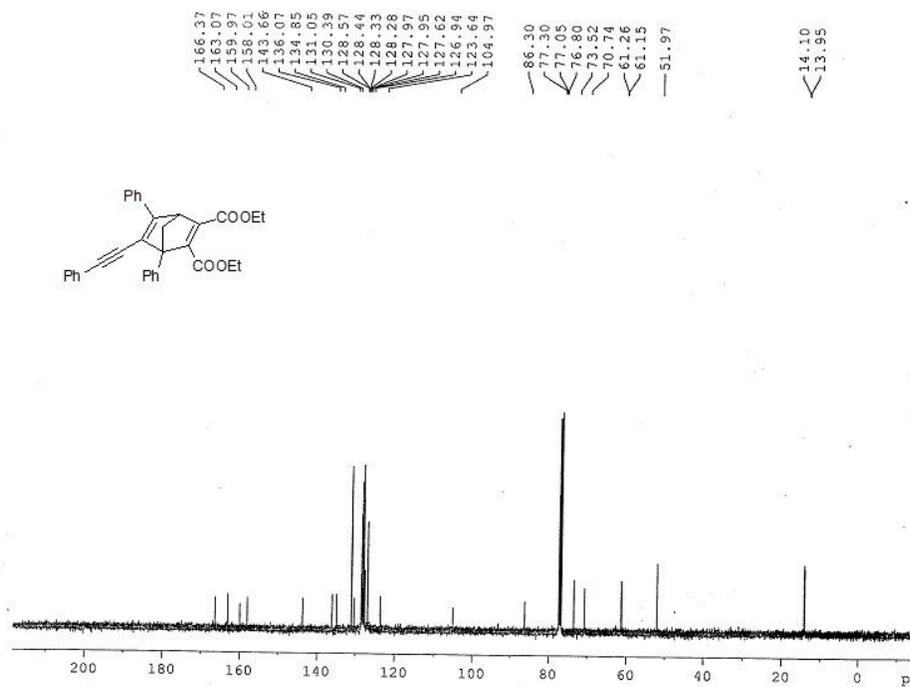


Figure S42. ¹³C NMR spectrum of compound 8

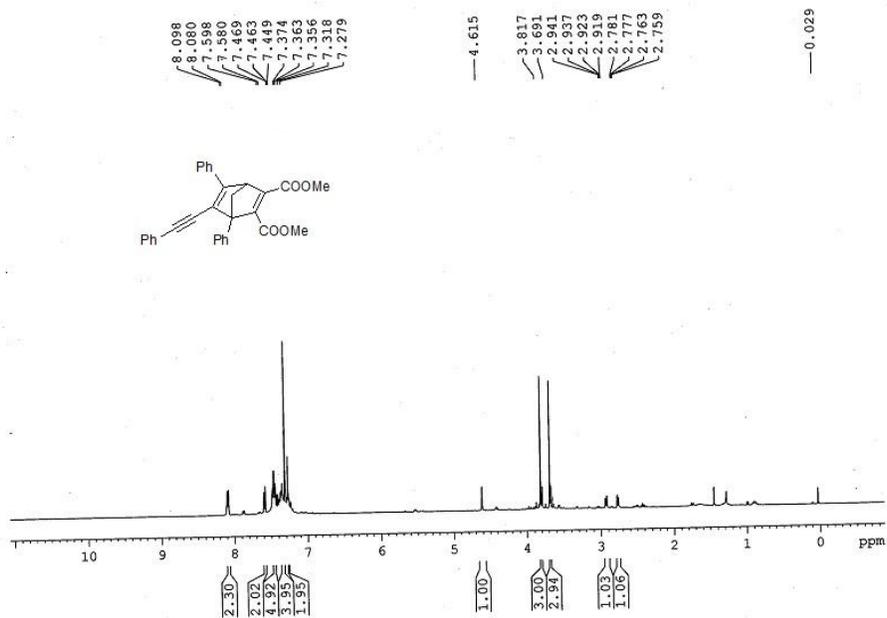


Figure S43. ¹H NMR spectrum of compound 9

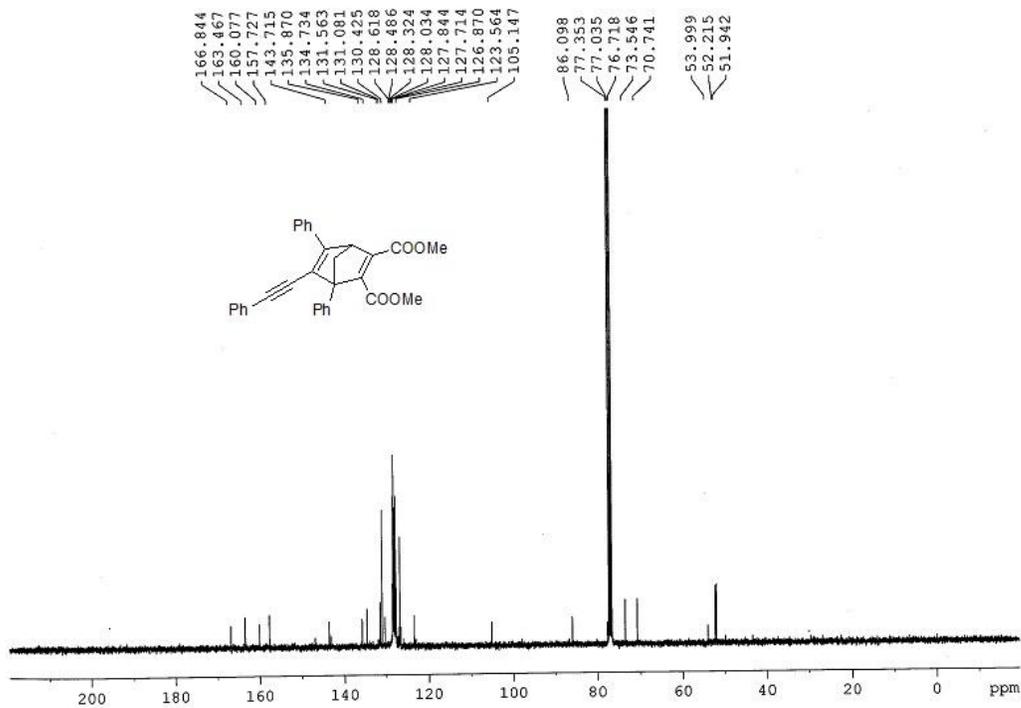


Figure S44. ¹³C NMR spectrum of compound 9

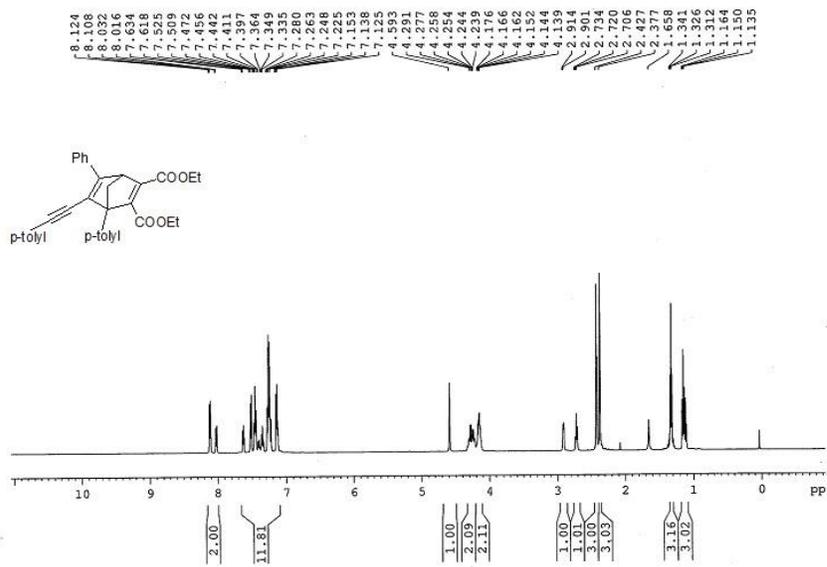


Figure S45. ¹H NMR spectrum of compound 10

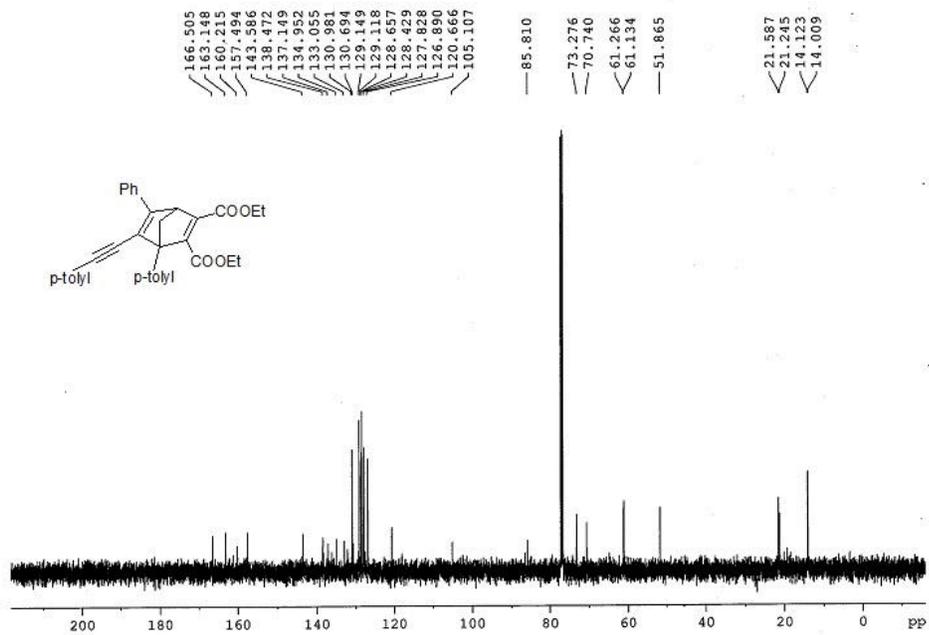


Figure S46. ¹³C NMR spectrum of compound 10

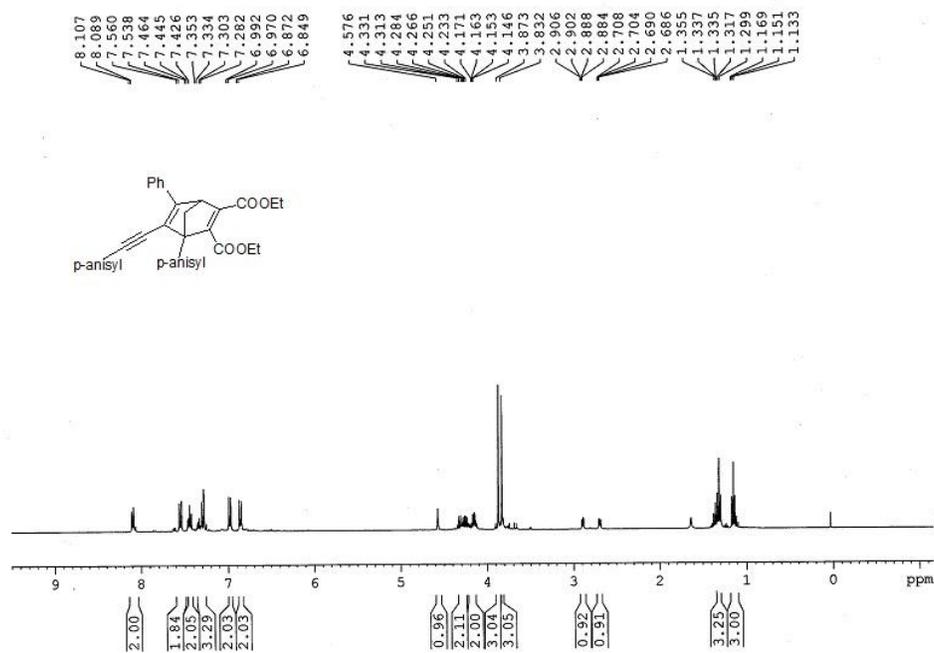


Figure S47. ¹H NMR spectrum of compound 11

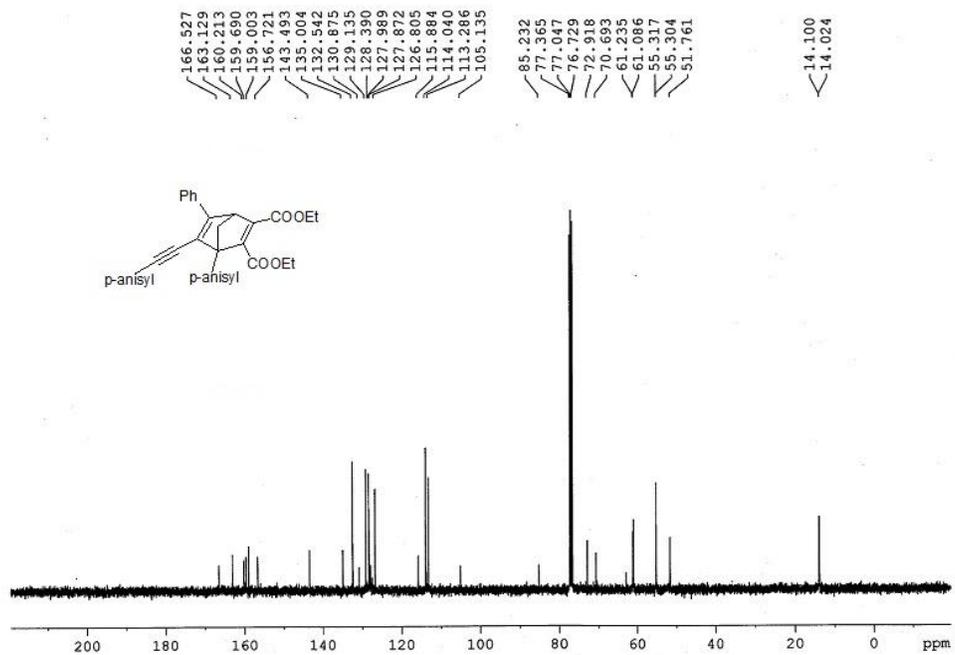


Figure S48. ¹³C NMR spectrum of compound 11

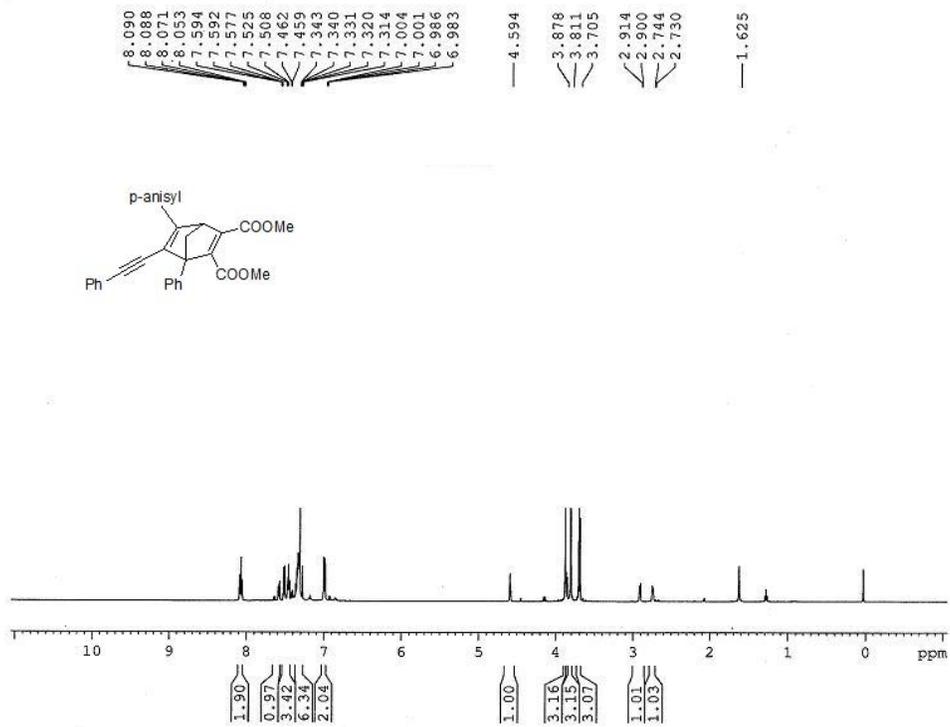


Figure S49. ¹H NMR spectrum of compound 12

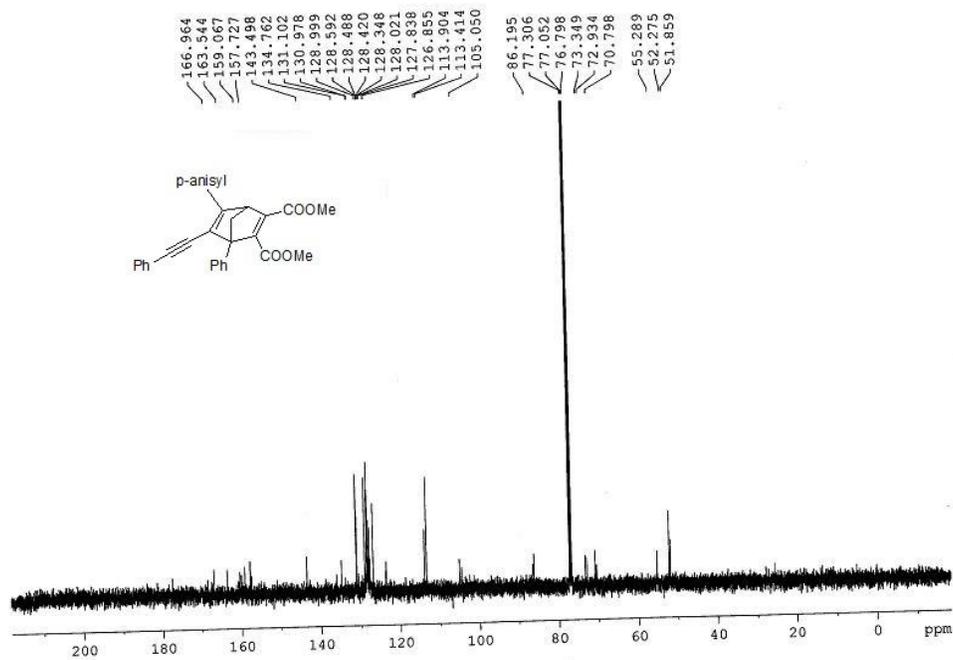


Figure S50. ¹³C NMR spectrum of compound 12

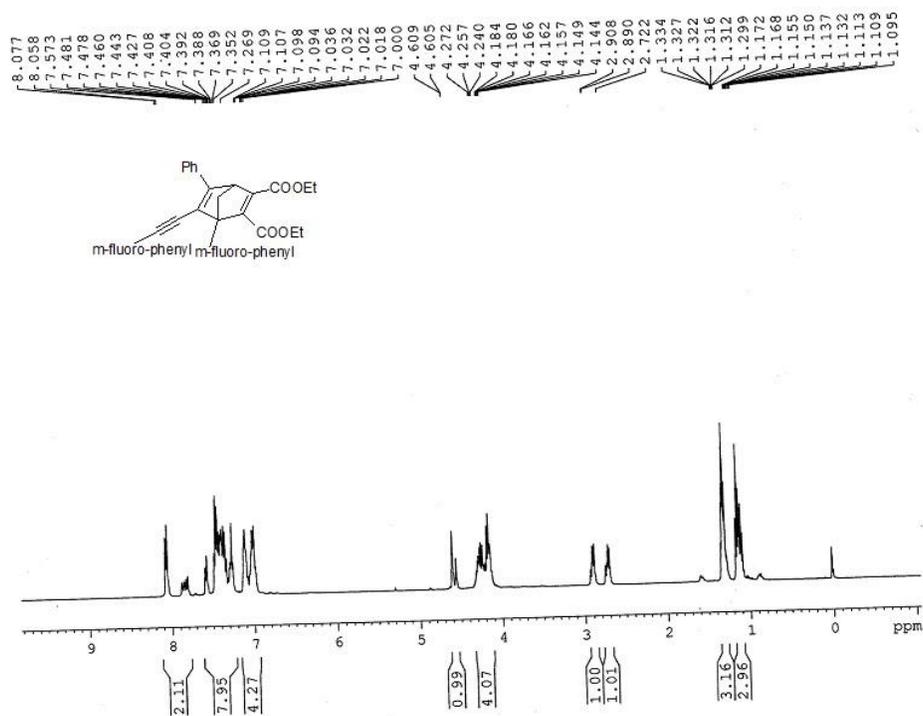


Figure S51. ¹H NMR spectrum of compound 13

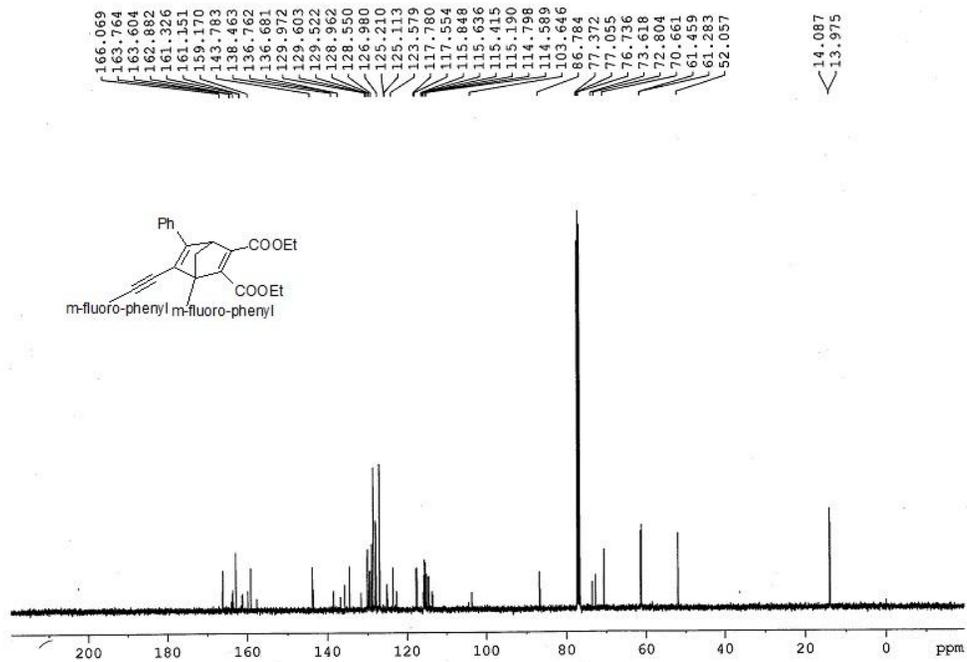


Figure S52. ¹³C NMR spectrum of compound 13

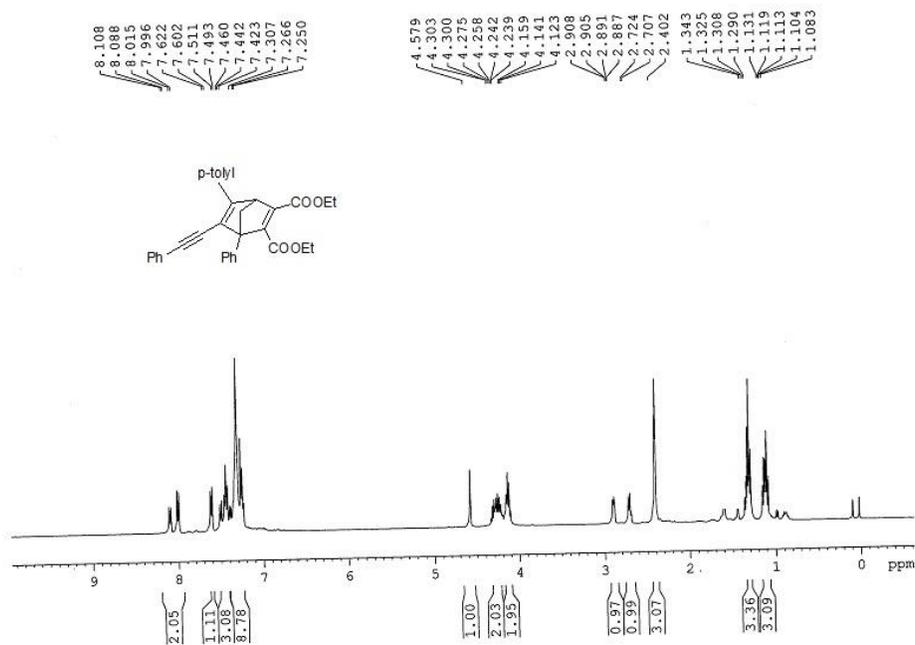


Figure S53. ¹H NMR spectrum of compound 14

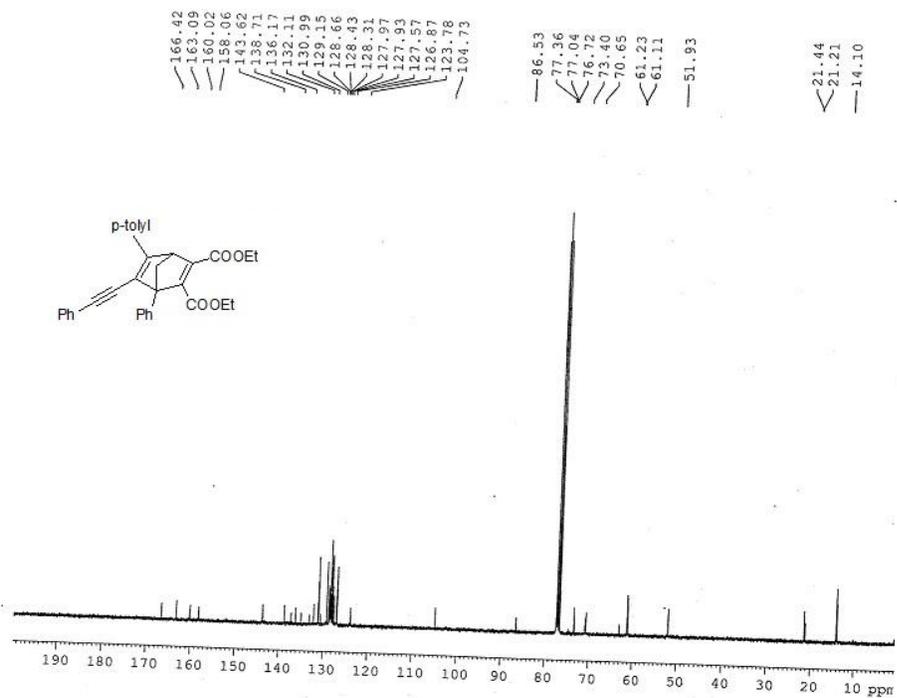


Figure S54. ¹³C NMR spectrum of compound 14

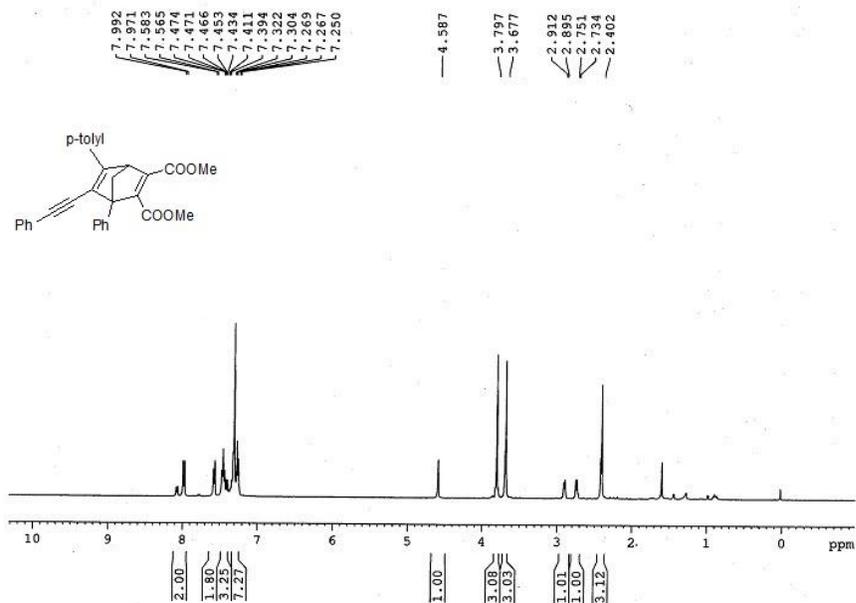


Figure S55. ¹H NMR spectrum of compound 15

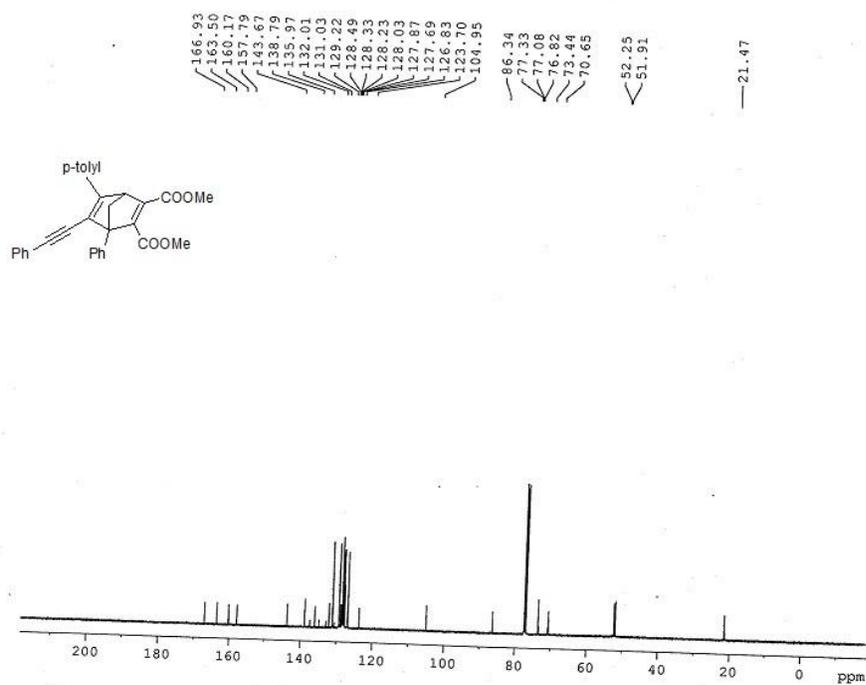


Figure S56. ¹³C NMR spectrum of compound 15

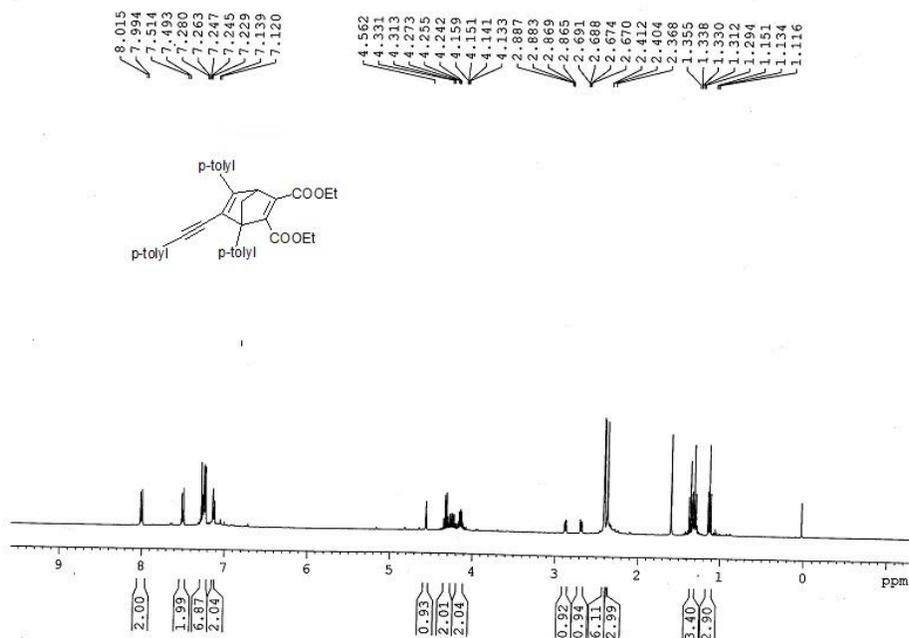


Figure S57. ¹H NMR spectrum of compound 16

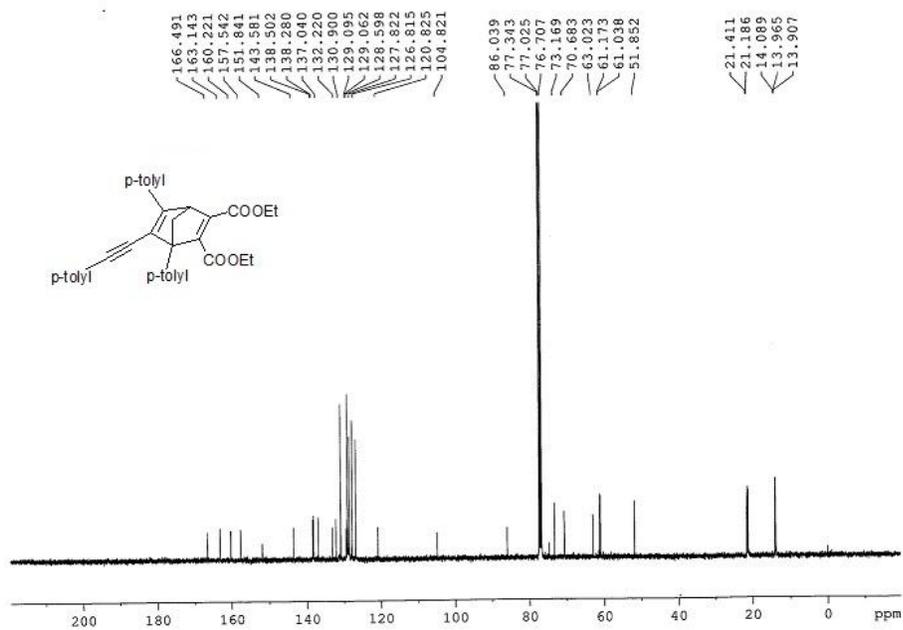


Figure S58. ¹³C NMR spectrum of compound 16

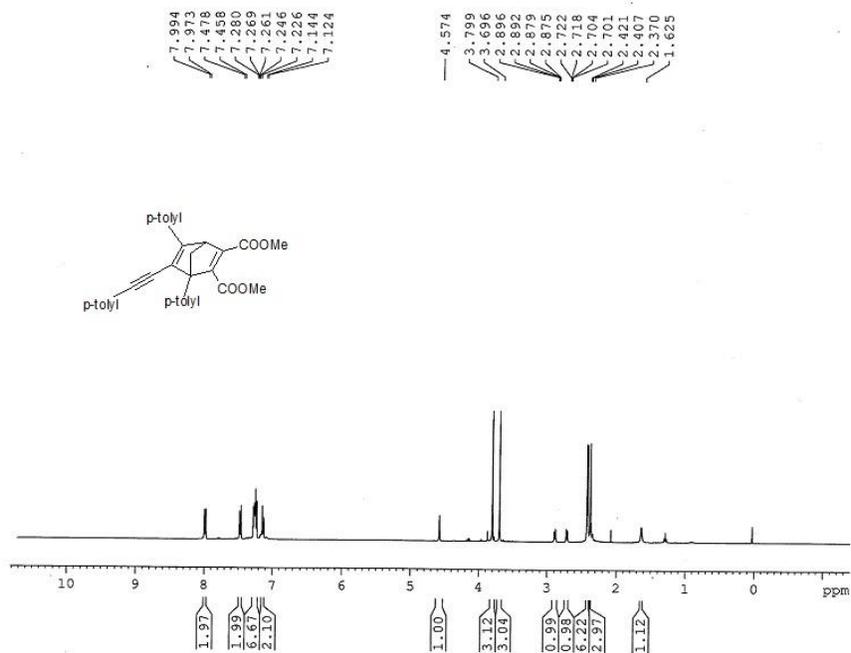


Figure S59. ¹H NMR spectrum of compound 17

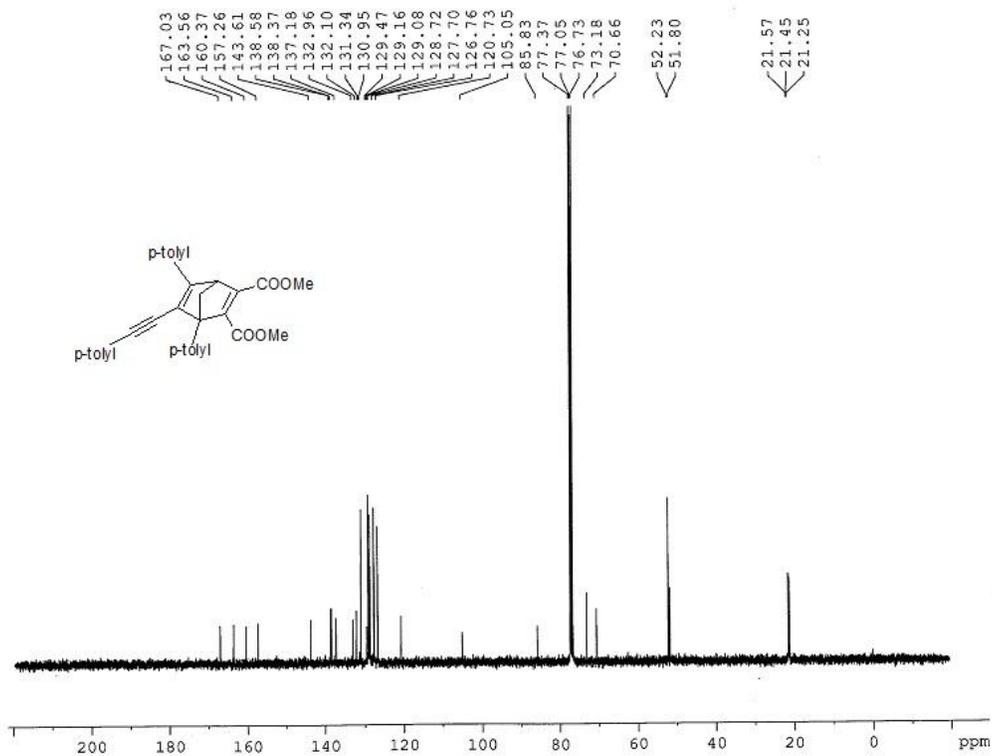


Figure S60. ¹³C NMR spectrum of compound 17

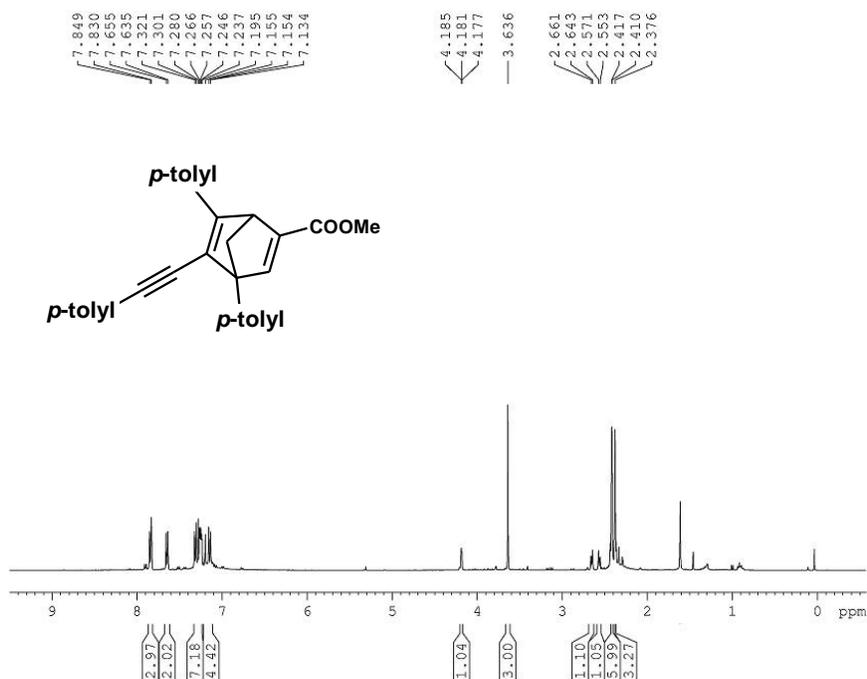


Figure S61. ¹H NMR spectrum of compound **18** (cf. main text for details)

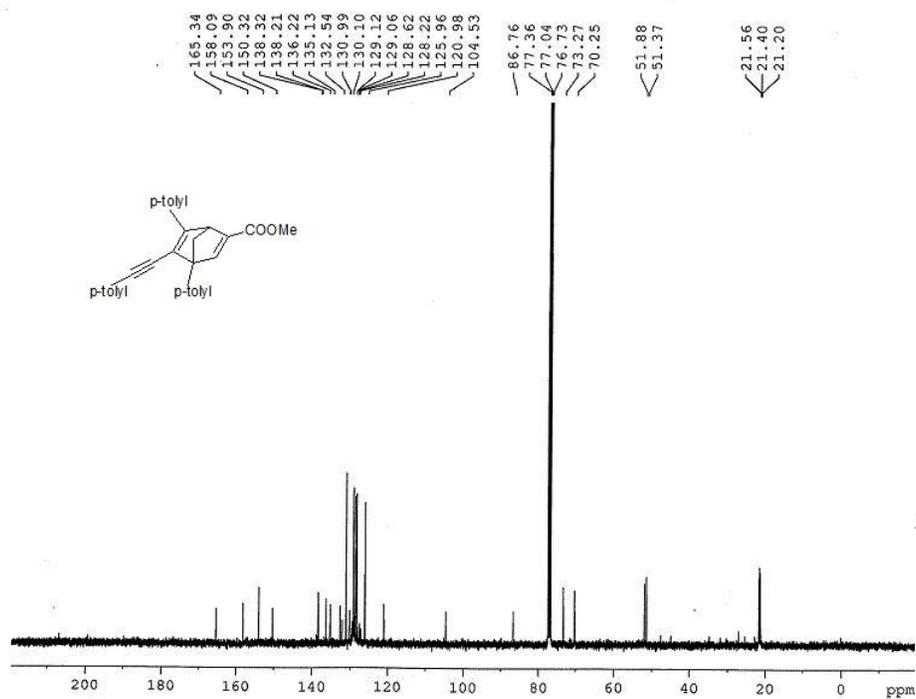


Figure S62. ¹³C NMR spectrum of compound **18** (cf. main text for details)

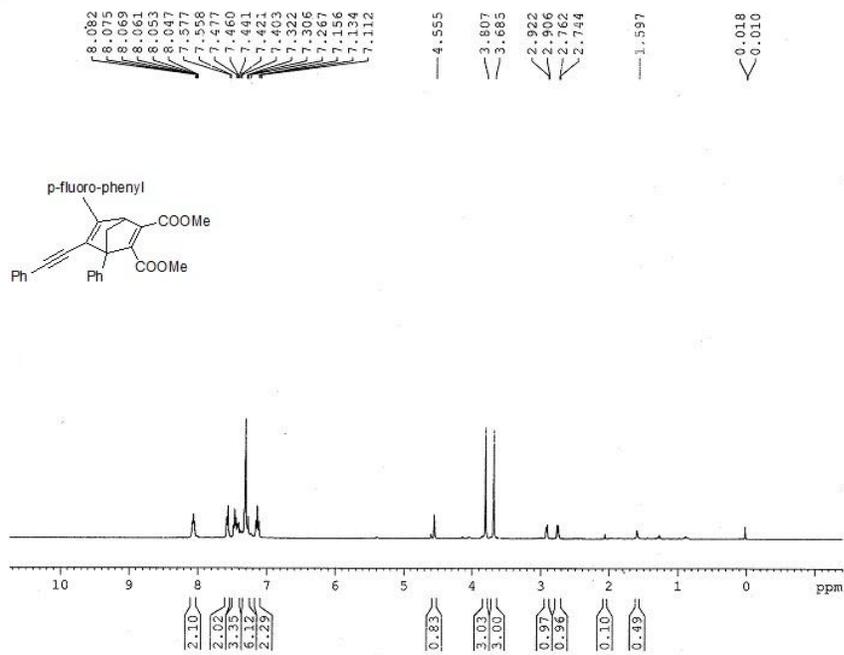


Figure S63. ¹H NMR spectrum of compound 19

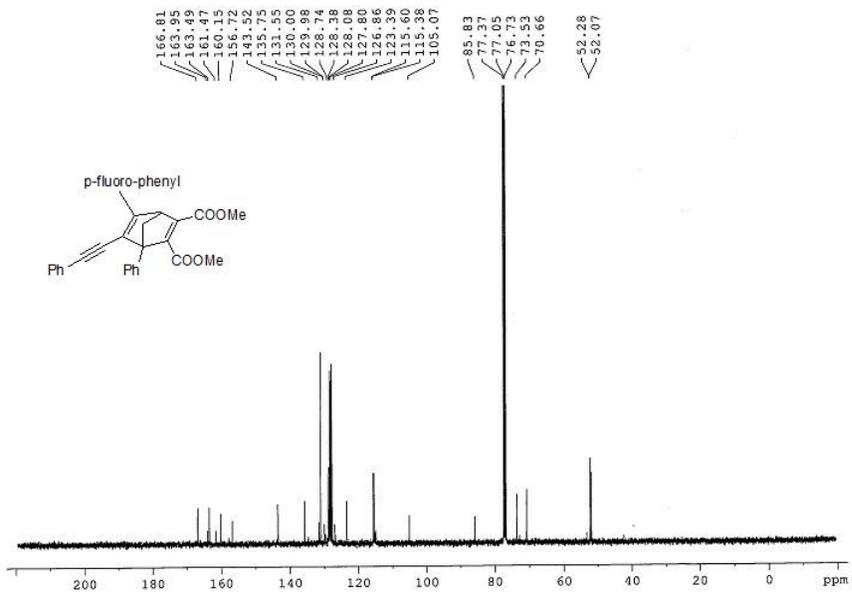


Figure S64. ¹³C NMR spectrum of compound 19

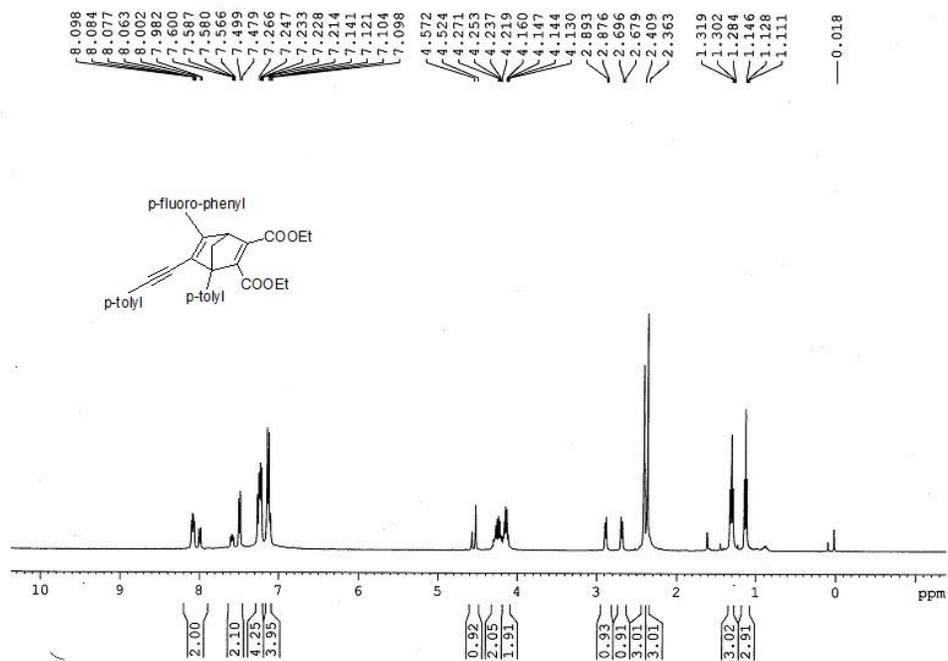


Figure S65. ¹H NMR spectrum of compound 20

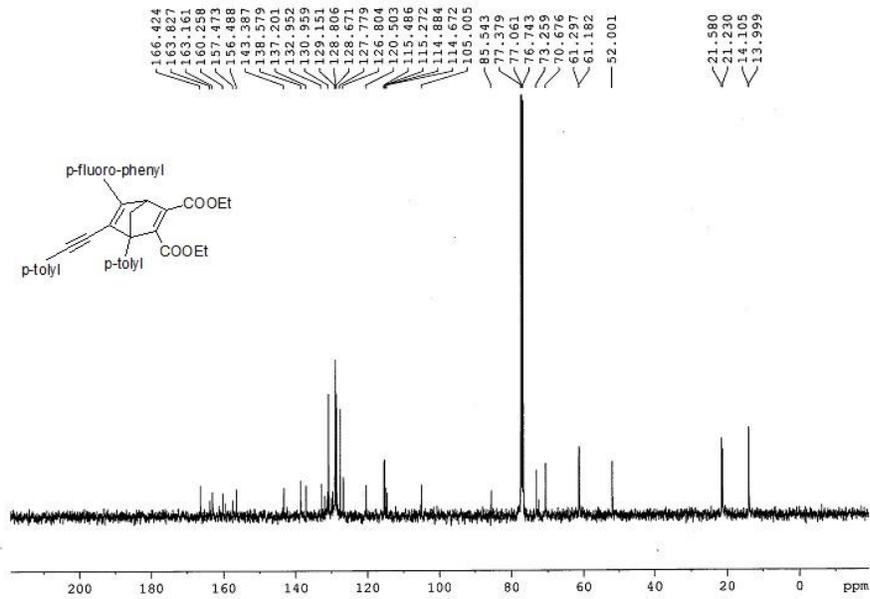


Figure S66. ¹³C NMR spectrum of compound 20

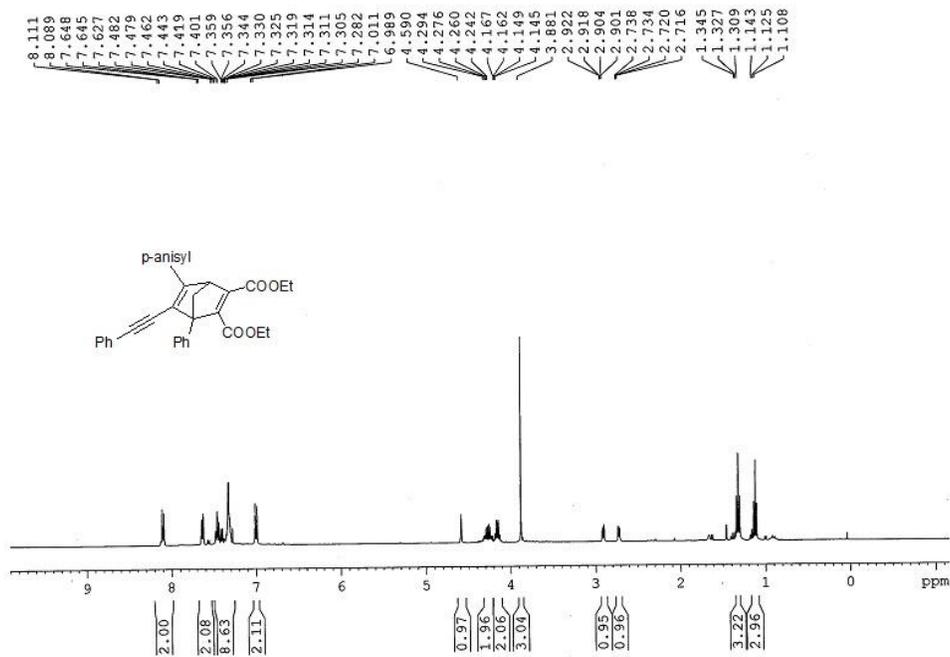


Figure S67. ¹H NMR spectrum of compound 21

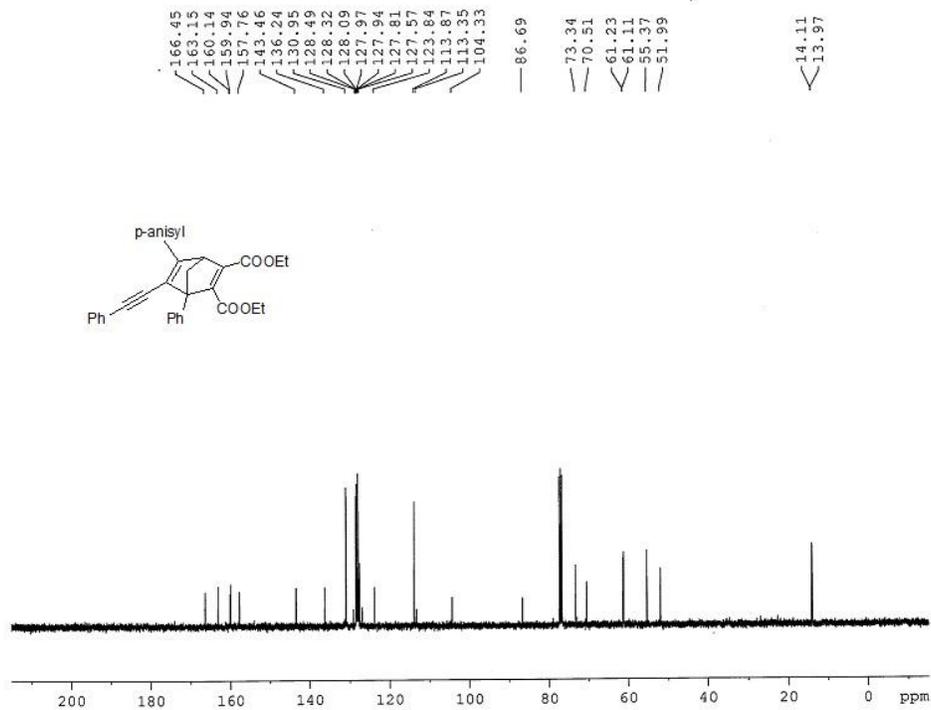


Figure S68. ¹³C NMR spectrum of compound 21

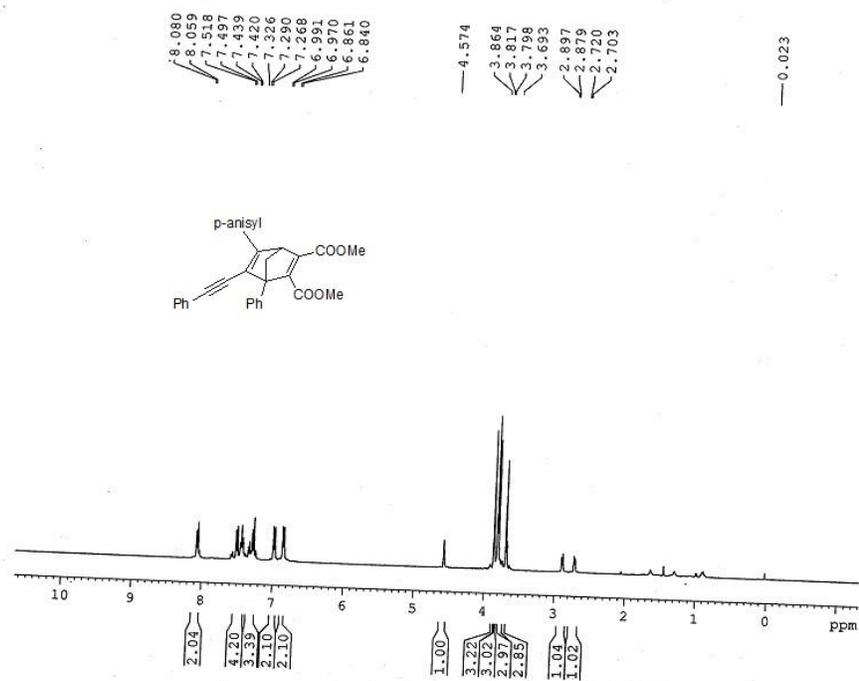


Figure S69. ^1H NMR spectrum of compound 22

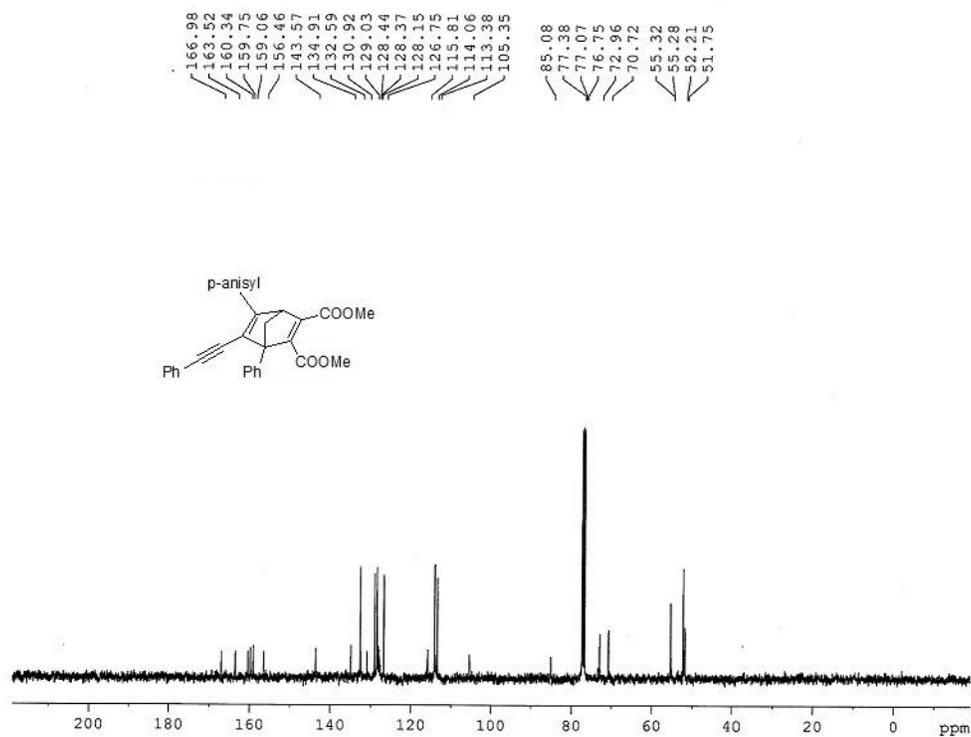


Figure S70. ^{13}C NMR spectrum of compound 22

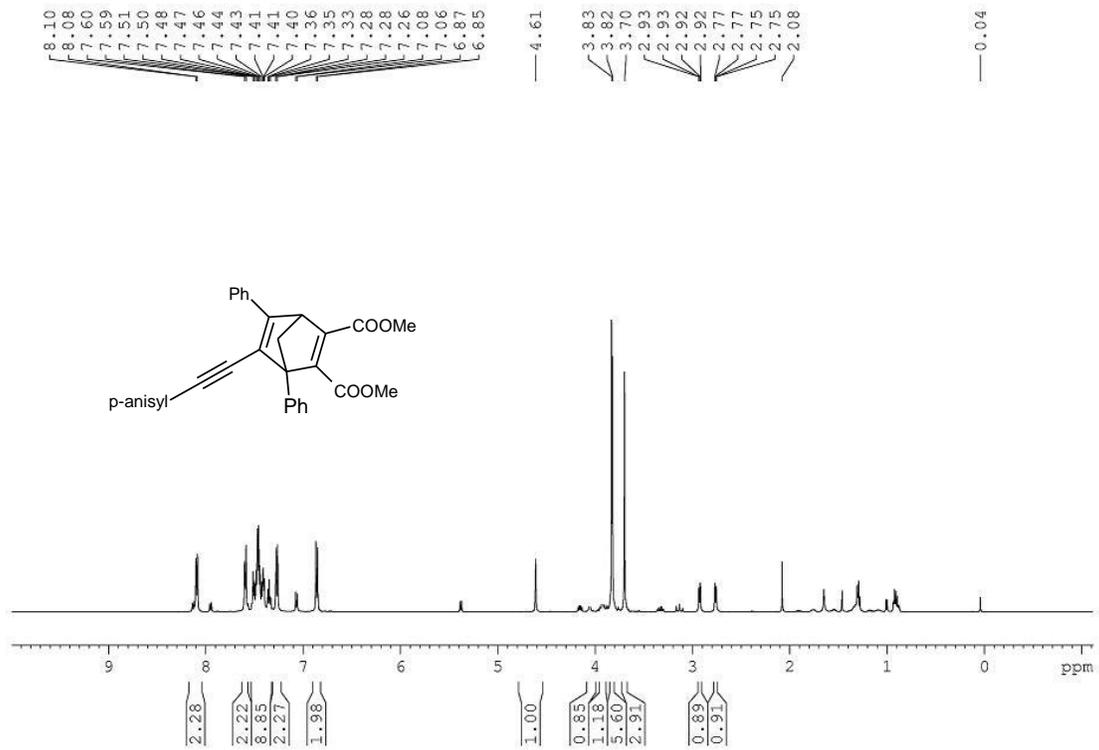


Figure S71. ¹H NMR spectrum of compound **23**

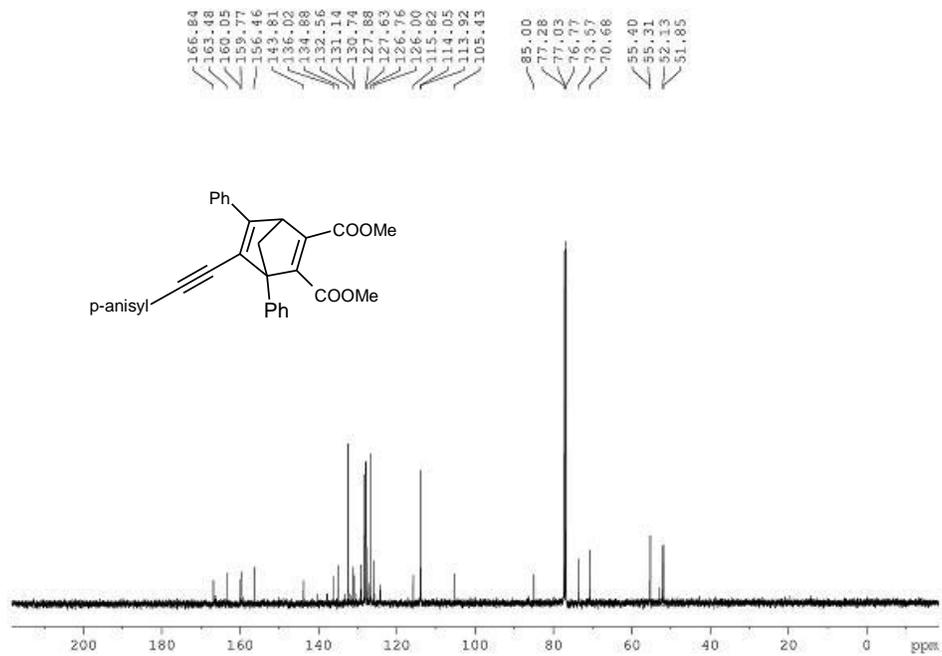


Figure S72. ¹³C NMR spectrum of compound **23**

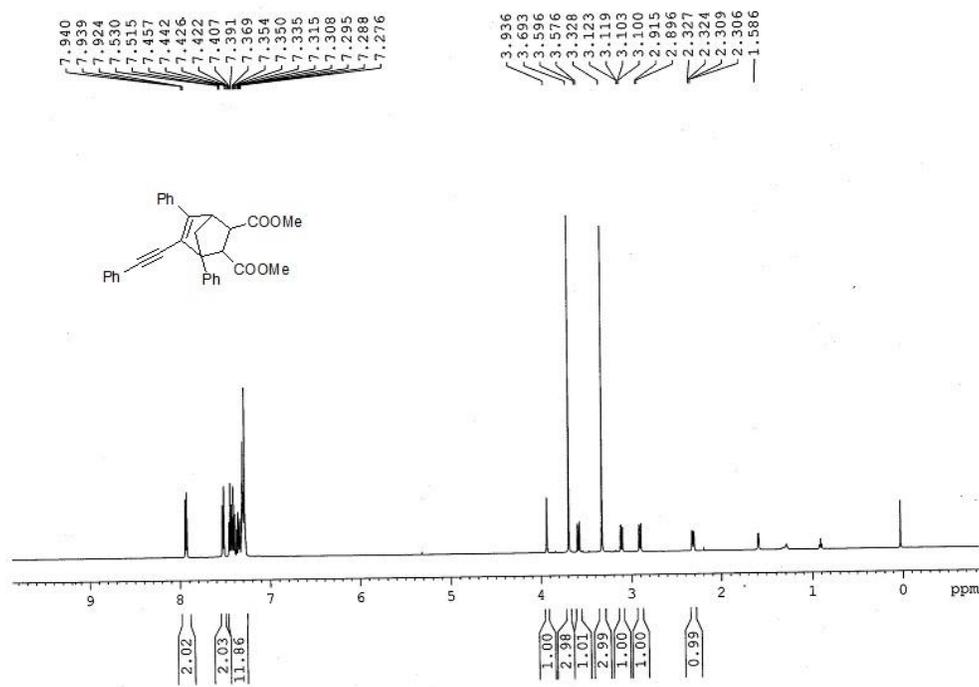


Figure S73. ¹H NMR spectrum of compound 24

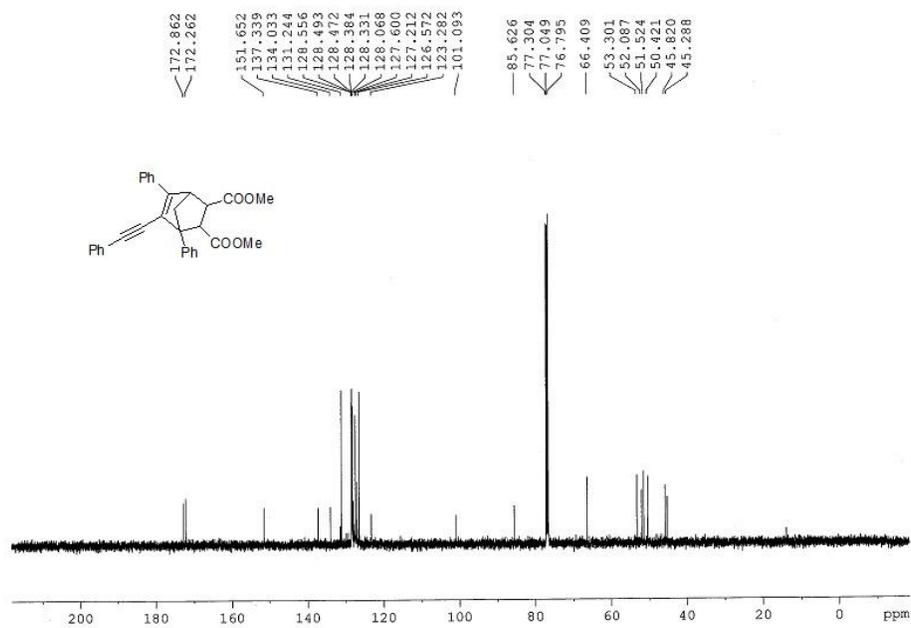


Figure S74. ¹³C NMR spectrum of compound 24

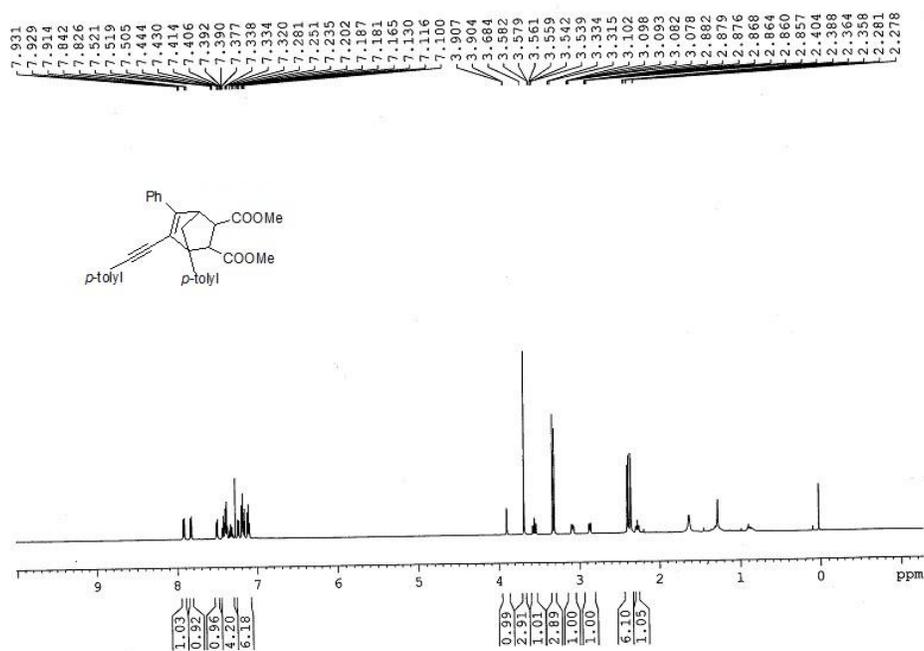


Figure S75. ¹H NMR spectrum of compound 25

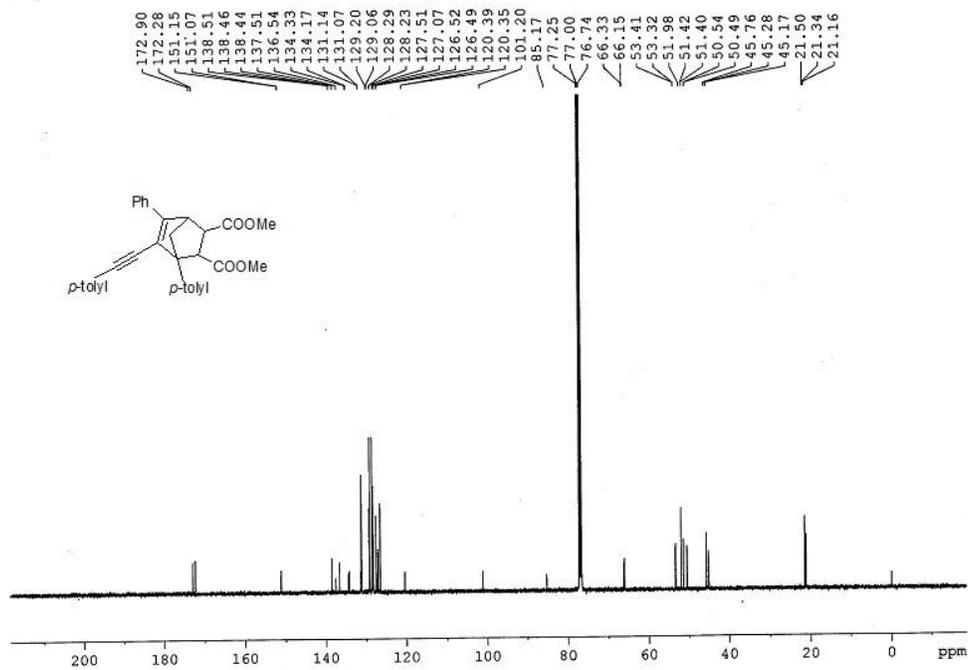


Figure S76. ¹³C NMR spectrum of compound 25

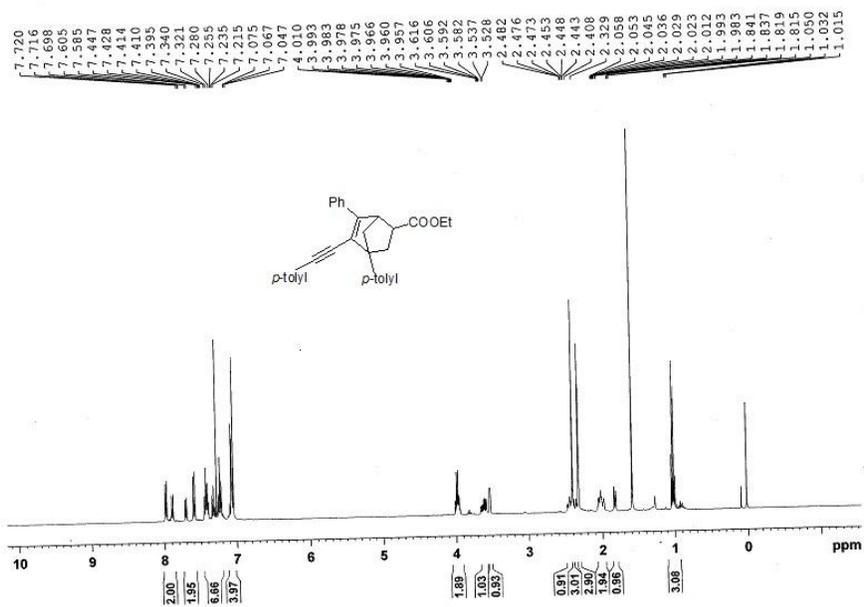


Figure S77. ¹H NMR spectrum of compound 26

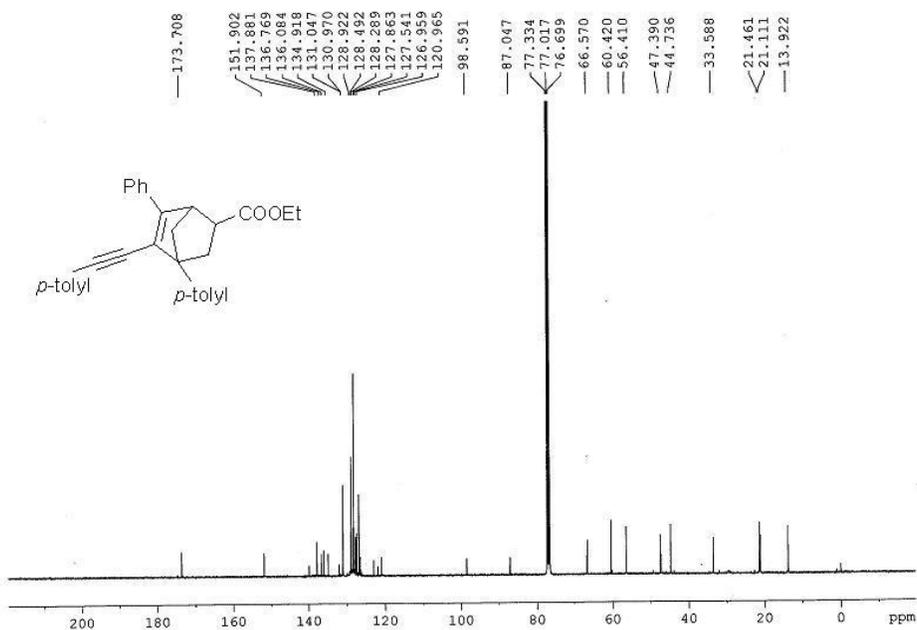


Figure S78. ¹³C NMR spectrum of compound 26

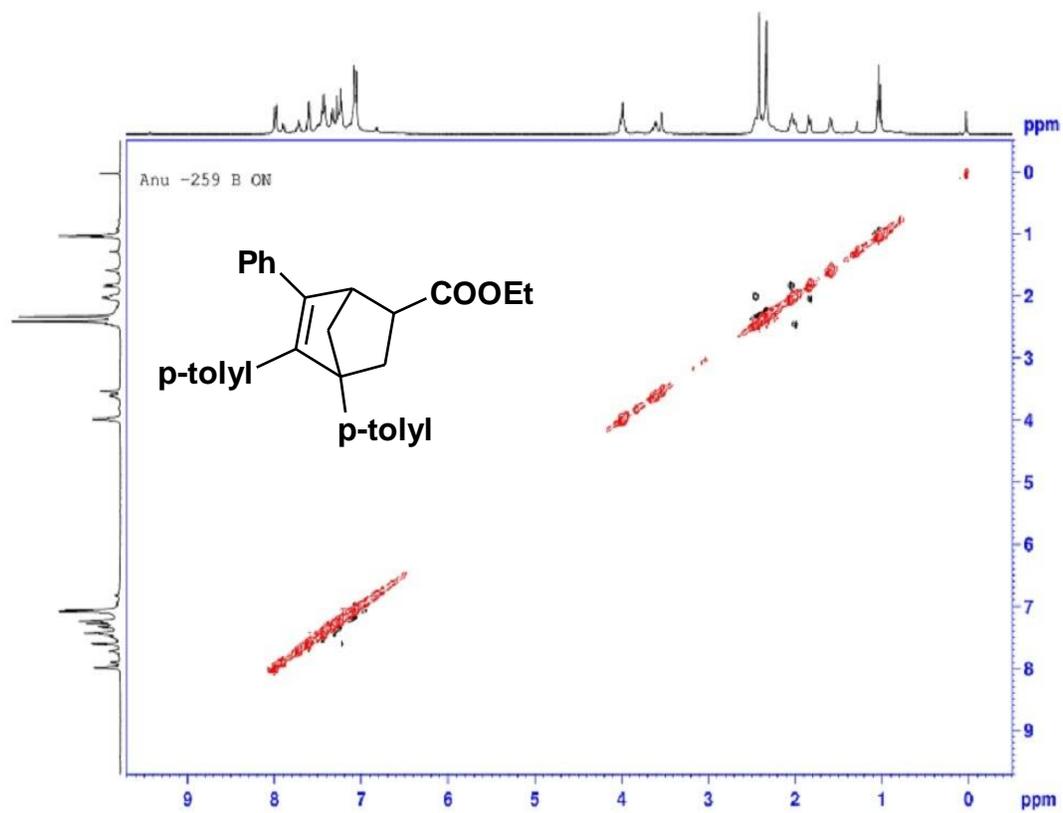


Figure S79. NOESY spectrum of compound 26

Anu -259 B ON

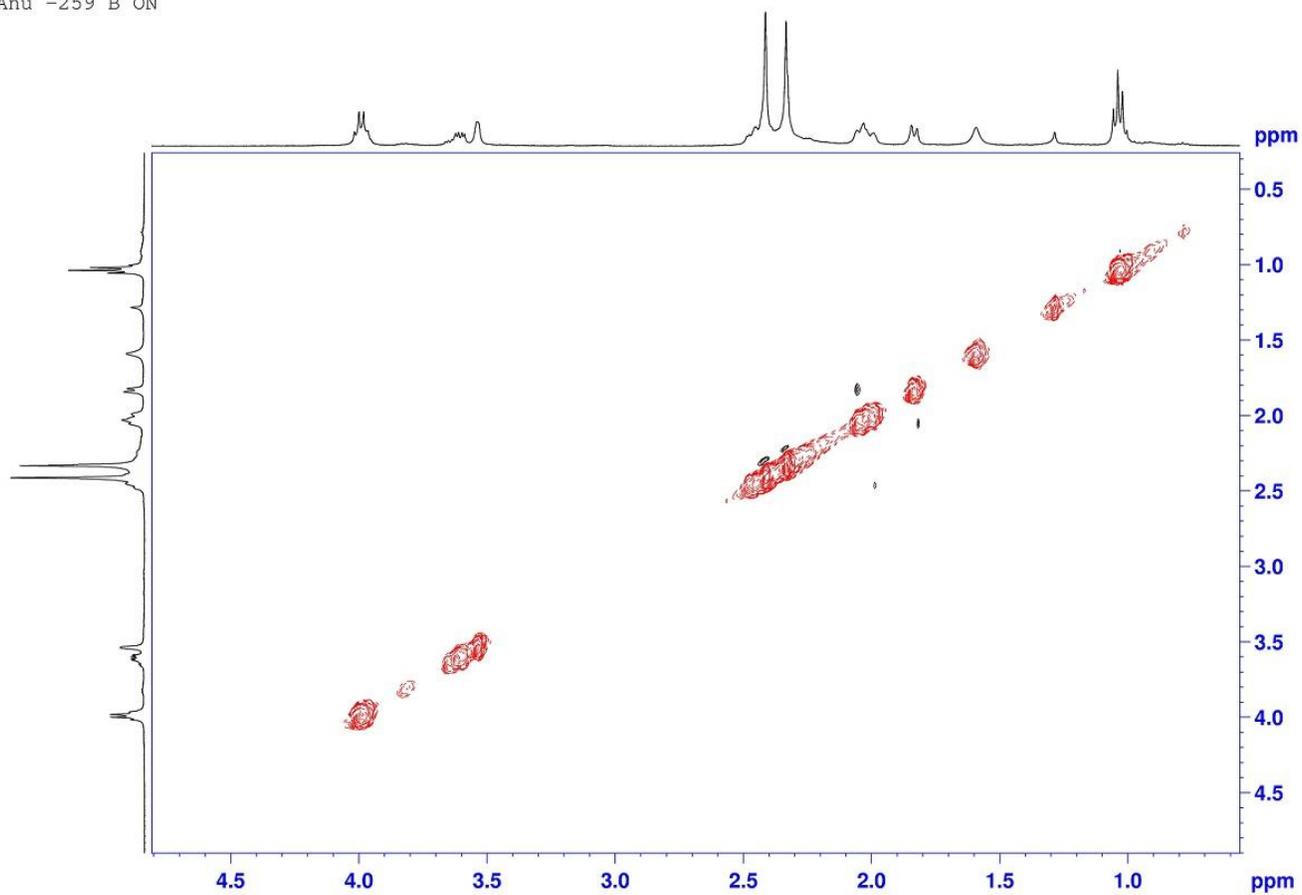


Figure S80. NOESY expansion of compound 26

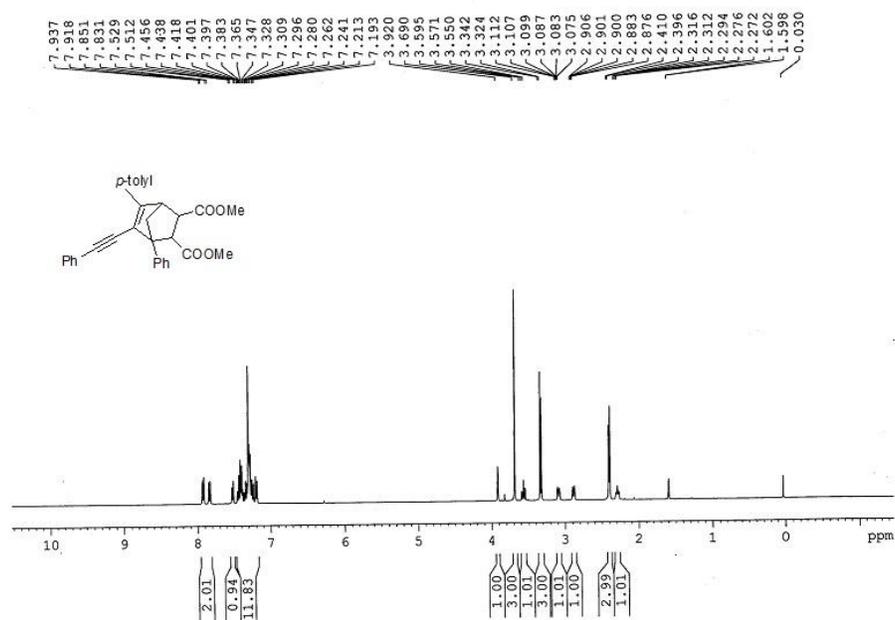


Figure S81. ¹H NMR spectrum of compound 27

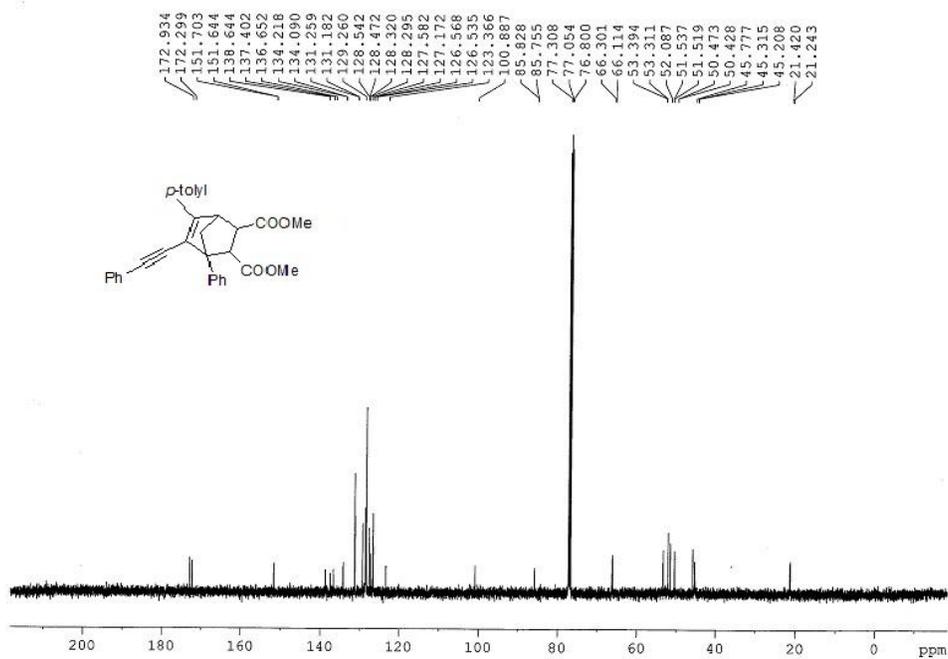


Figure S82. ¹³C NMR spectrum of compound 27

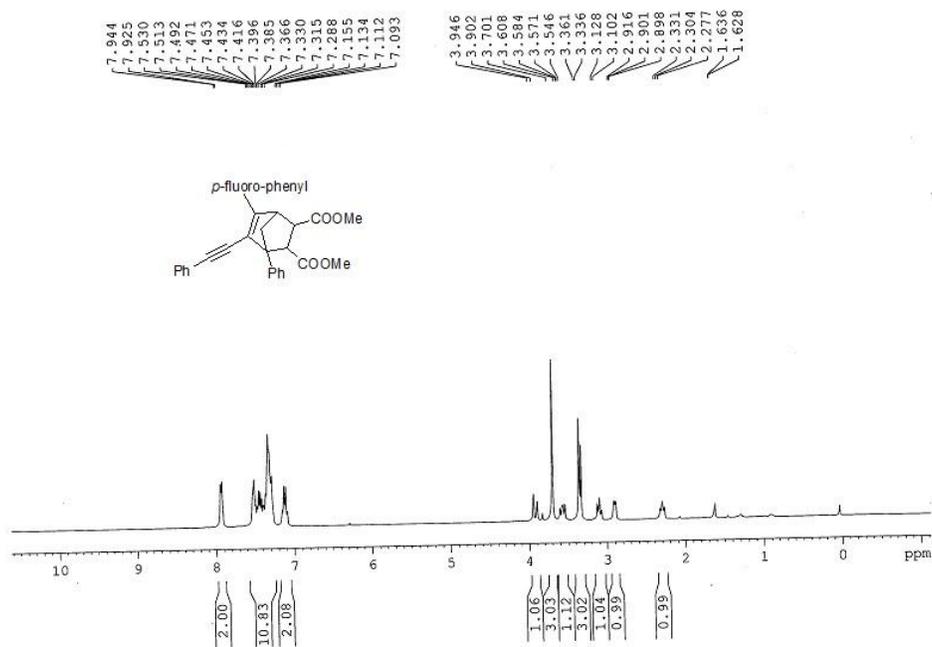


Figure S83. ¹H NMR spectrum of compound 28

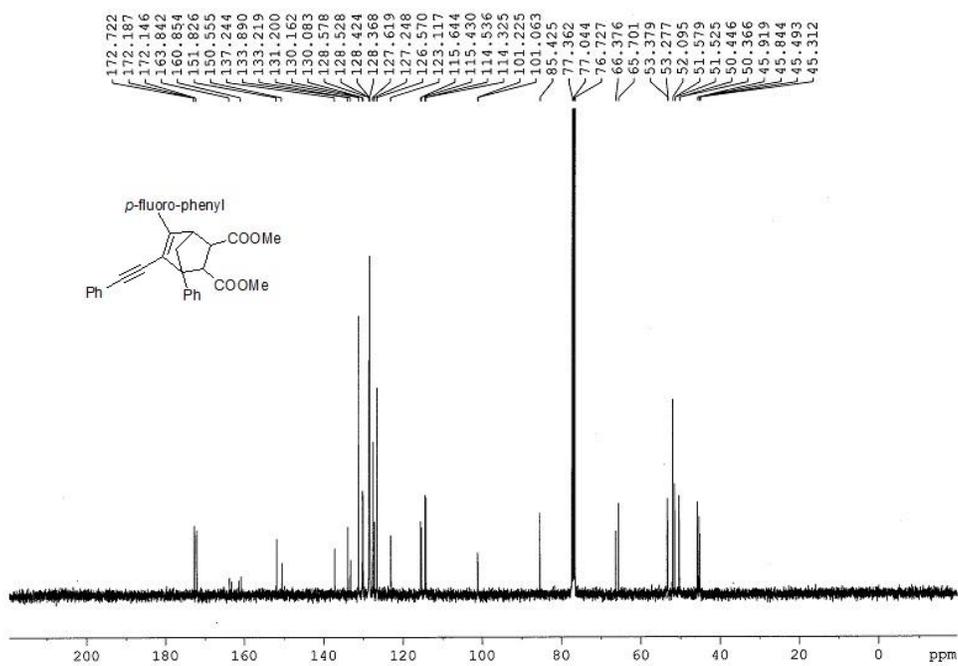


Figure S84. ¹³C NMR spectrum of compound 28

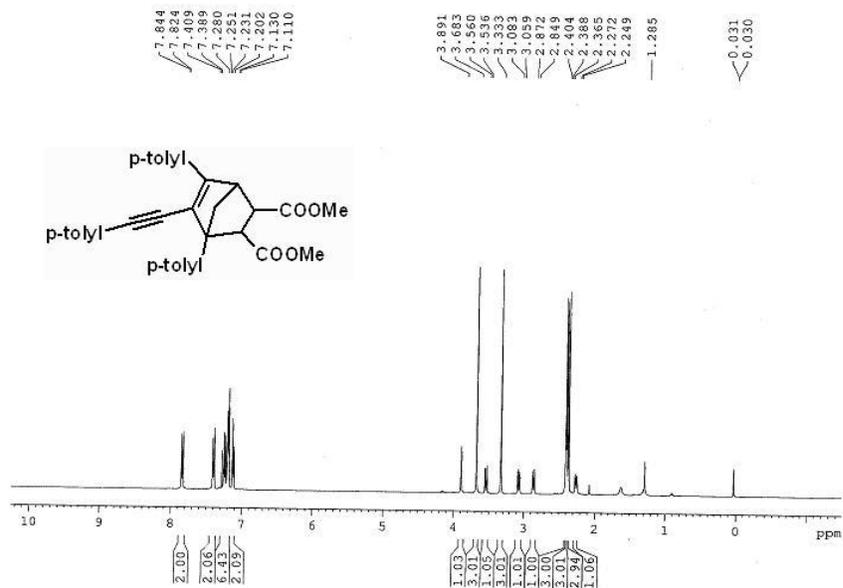


Figure S85. ¹H NMR spectrum of compound 29

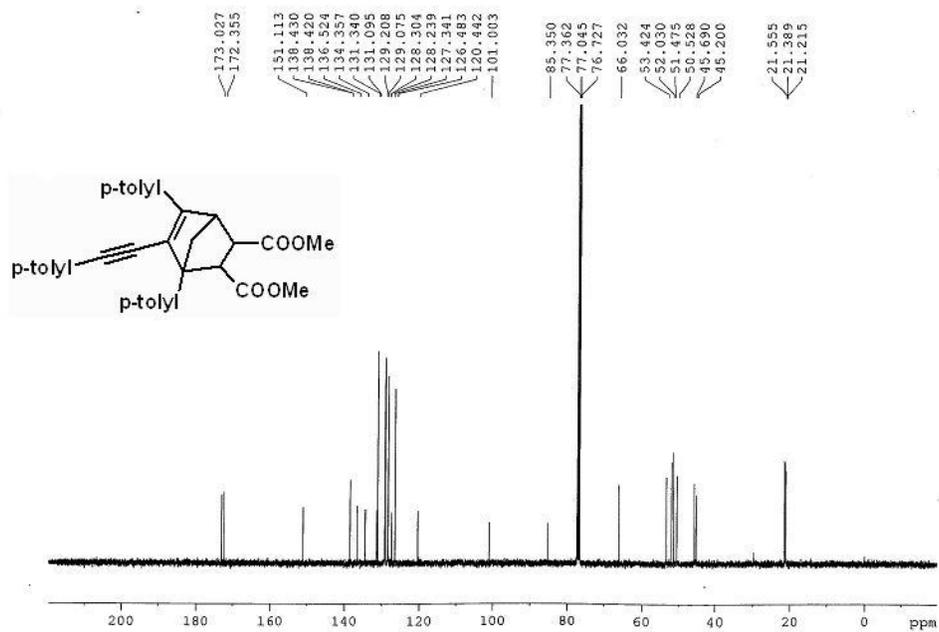


Figure S86. ¹³C NMR spectrum of compound 29

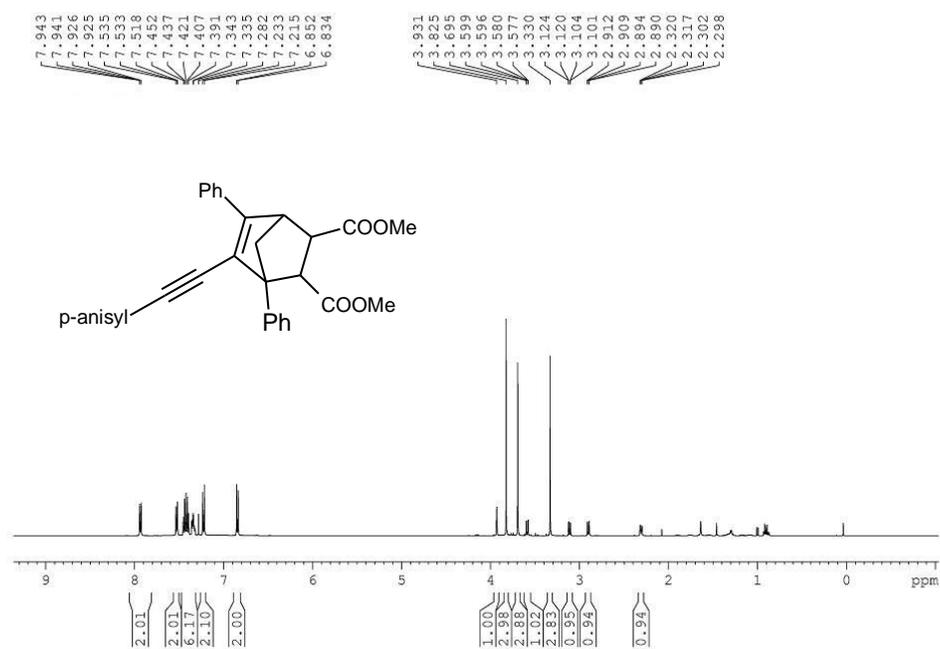


Figure S87. ¹H NMR spectrum of compound 30

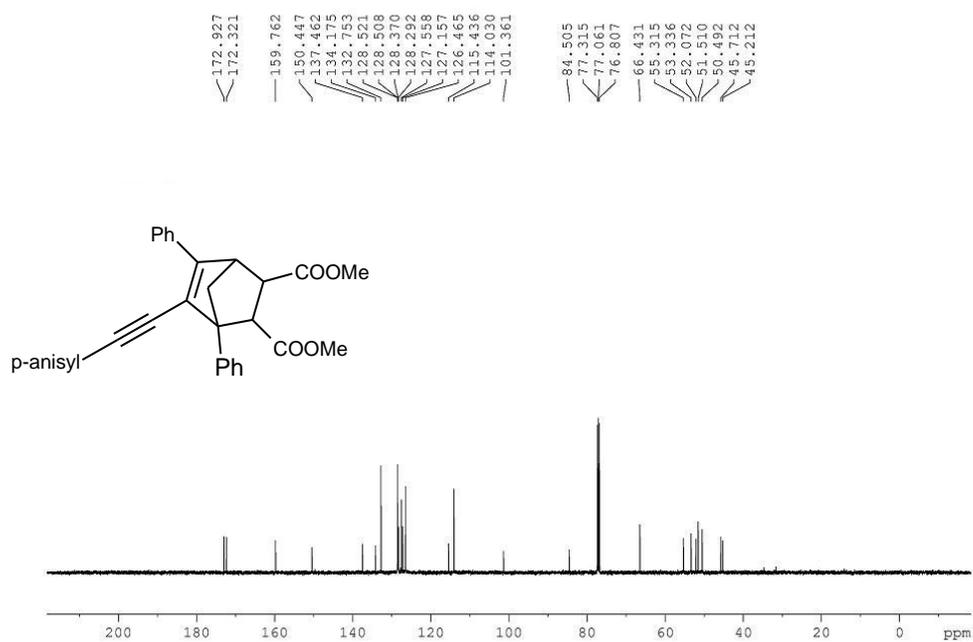


Figure S88. ¹³C NMR spectrum of compound 30

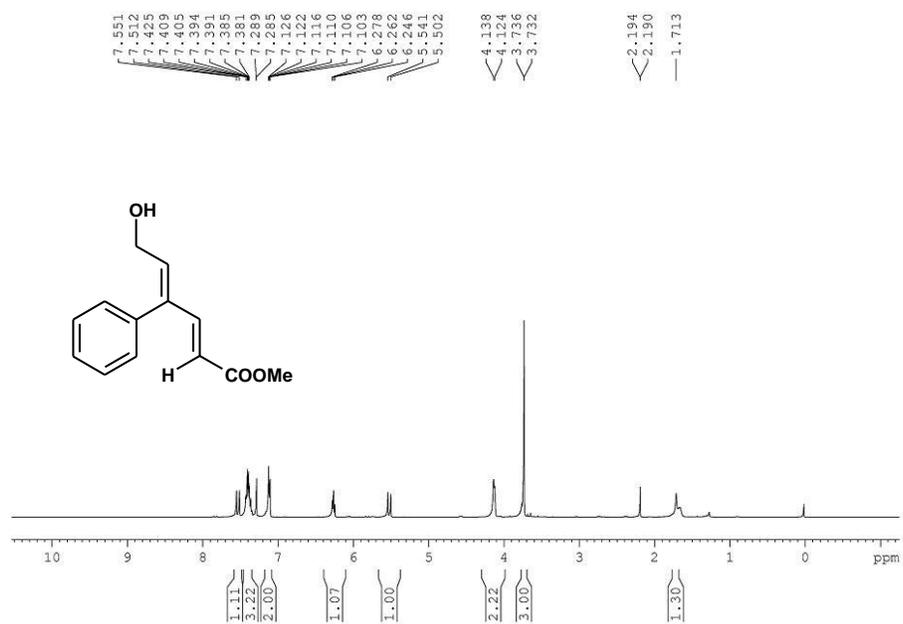


Figure S89. ¹H NMR spectrum of compound 31

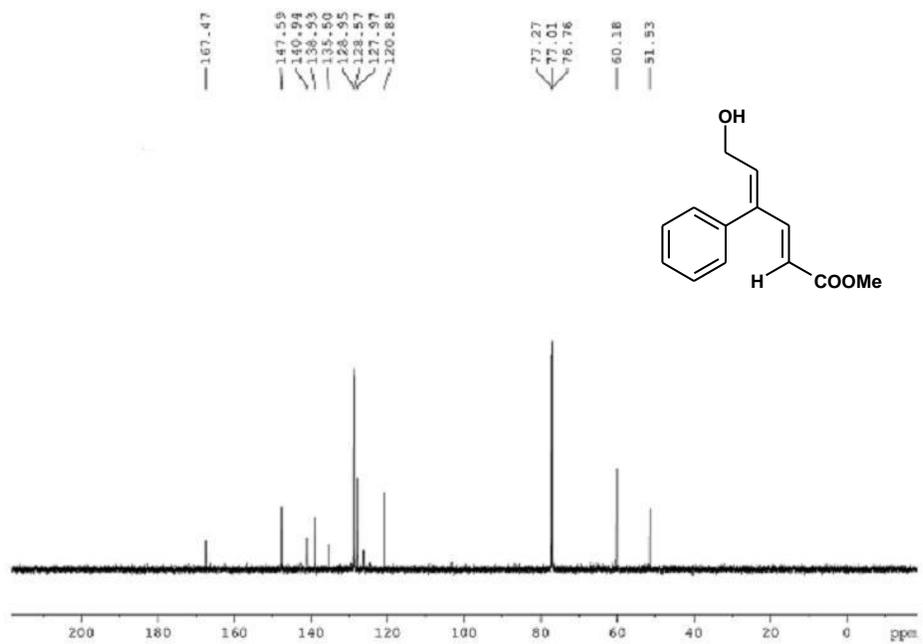


Figure S90. ¹³C NMR spectrum of compound 31

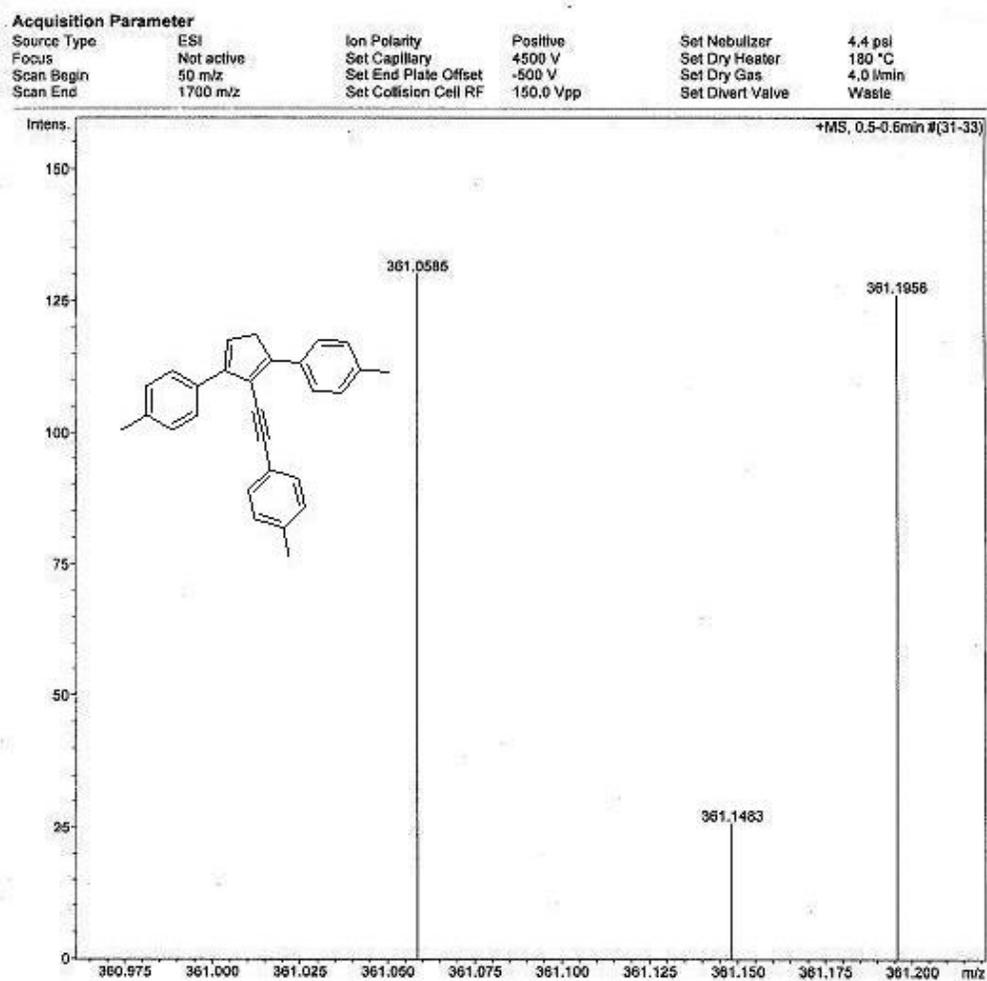
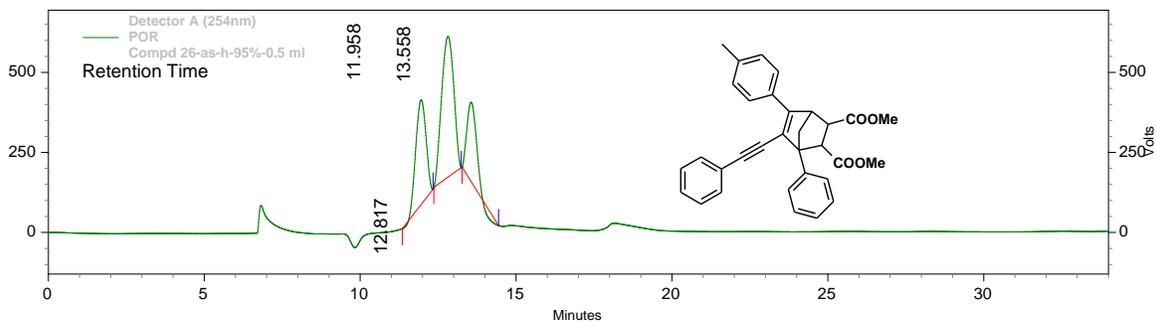


Figure S91. HRMS for the blank reaction mixture using 5bb + AuCl (i.e., without DMAD)

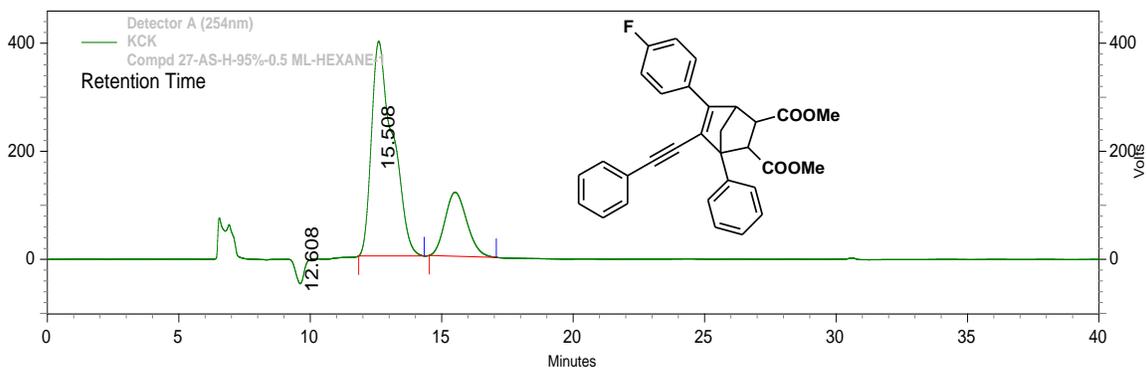


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.958	7486871	30.866	326658	32.242
2	12.817	12009002	49.509	438856	43.316
3	13.558	4760397	19.625	247632	24.442

Totals		24256270	100.000	1013146	100.000
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Figure S92. HPLC of compound 27 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~ 7 min is due to solvent)

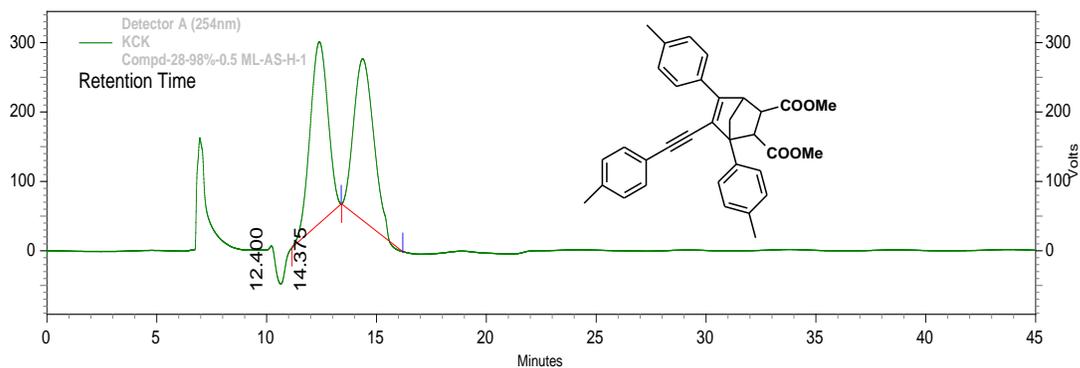


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.608	22290103	76.512	397169	77.016
2	15.508	6842829	23.488	118527	22.984

Totals		29132932	100.000	515696	100.000
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Figure S93. HPLC of compound 28 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~ 7 min is due to solvent)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.400	14737730	50.183	261739	52.935
2	14.375	14630446	49.817	232715	47.065

Totals		29368176	100.000	494454	100.000
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Figure S94. HPLC of compound 29 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~ 7 min is due to solvent)

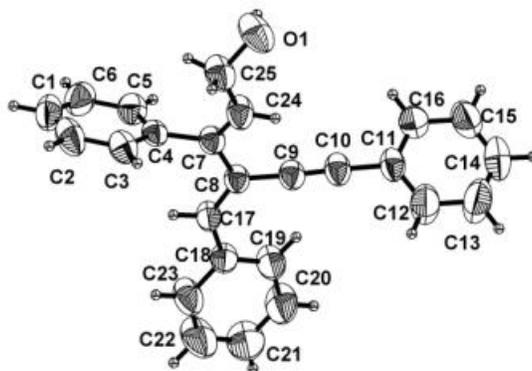


Fig. S95. ORTEP (probability level 50%) of compound **5aa**. Only one molecule (of the four) is shown. Selected bond lengths [Å] with esds in parentheses: O(1)-C(25) 1.408(3), C(7)-C(8) 1.490(2), C(8)-C(9) 1.436(3), C(9)-C(10) 1.194(3), C(10)-C(11) 1.438(3), C(8)-C(17) 1.351(2), C(24)-C(25) 1.486(3).

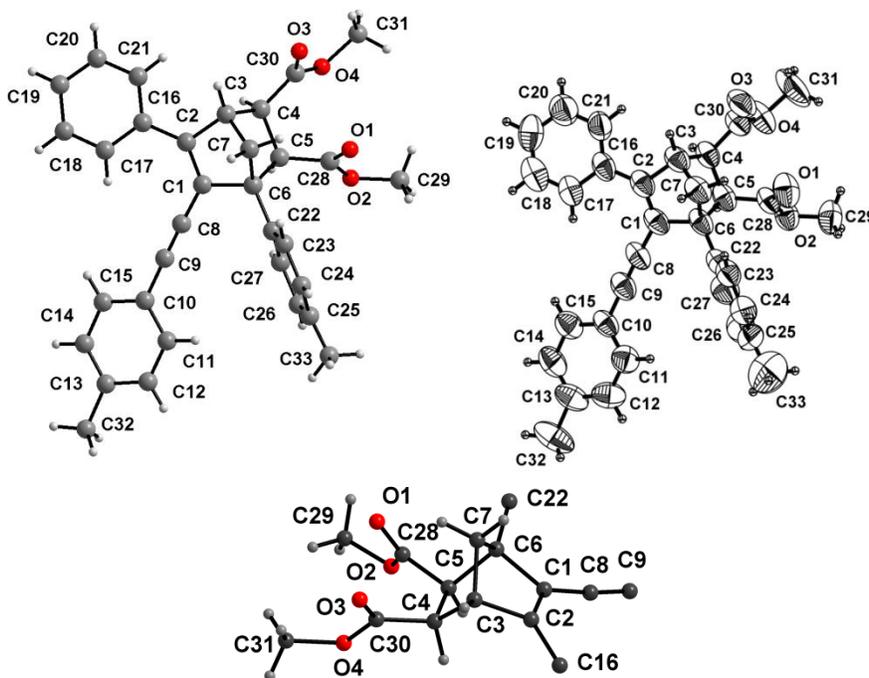


Figure S96. Molecular pictures of compound **25** (ORTEP probability level 50%). Selected bond lengths [Å] with esds in parentheses: C(1)-C(2) 1.345(6), C(1)-C(6) 1.559(6), C(1)-C(8) 1.418(6), C(2)-C(3) 1.532(5), C(3)-C(4) 1.550(6), C(3)-C(7) 1.502(6), C(4)-C(5) 1.533(6), C(5)-C(6) 1.592(5), C(8)-C(9) 1.191(5). The data quality was only moderate for this structure, and there appears to be some residual electron density close to C19. The exo-stereochemistry is clarified in the lower drawing.