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

Supplementary Information

Regioselective carboannulation of electron-deficient allenes with dialkyl (2-formylphenyl)malonates leading to multisubstituted naphthalenes

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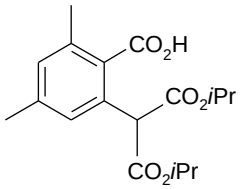
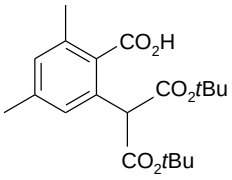
General procedure for the synthesis of carboxylic acid precursors to 1j and 1k:

Compounds 2-(1,3-diisopropoxy-1,3-dioxopropan-2-yl)benzoic acid and 2-(1,3-di-*tert*-butoxy-1,3-dioxopropan-2-yl)benzoic acid were prepared by a literature procedure.[11b]



2-(1,3-Diisopropoxy-1,3-dioxopropan-2-yl)benzoic acid (precursor to 1j). Yield 1.5 g (using 6.66 mmol of 2,4-dimethylbenzoic acid), 67% (white solid): mp 150-152 ^{0}C; IR (KBr, cm^{-1}) 2981, 1731, 1611, 1375, 1178, 1101, 1025, 833, 731; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.08 (s, 1H), 5.18-5.08 (m, 2H), 4.97 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 167.9, 140.8, 137.4, 131.9, 131.6, 129.1, 127.9, 69.6, 56.0, 21.6, 21.5, 21.3, 21.0; HRMS (ESI) Calcd. for $C_{18}H_{24}O_6Na$ [M^{+}+Na]: *m/z* 359.1471. Found: 359.1474.



2-(1,3-Di-tert-butoxy-1,3-dioxopropan-2-yl)benzoic acid (precursor to 1k). Yield 1.6 g (using 6.66 mmol of 2,4-dimethylbenzoic acid), 66% (white gummy solid): IR (neat, cm^{-1}) 2981, 1731, 1616, 1457, 1375, 1299, 1129, 1036, 855, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.06 (s, 1H), 4.87 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 1.5 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 167.8, 140.7, 137.4, 132.6, 131.4, 129.2, 127.7, 82.4, 57.6, 27.9, 21.4, 21.1; HRMS (ESI) Calcd. for $C_{20}H_{29}O_6$ [M^{+}+H]: *m/z* 365.1964. Found: 365.1959.

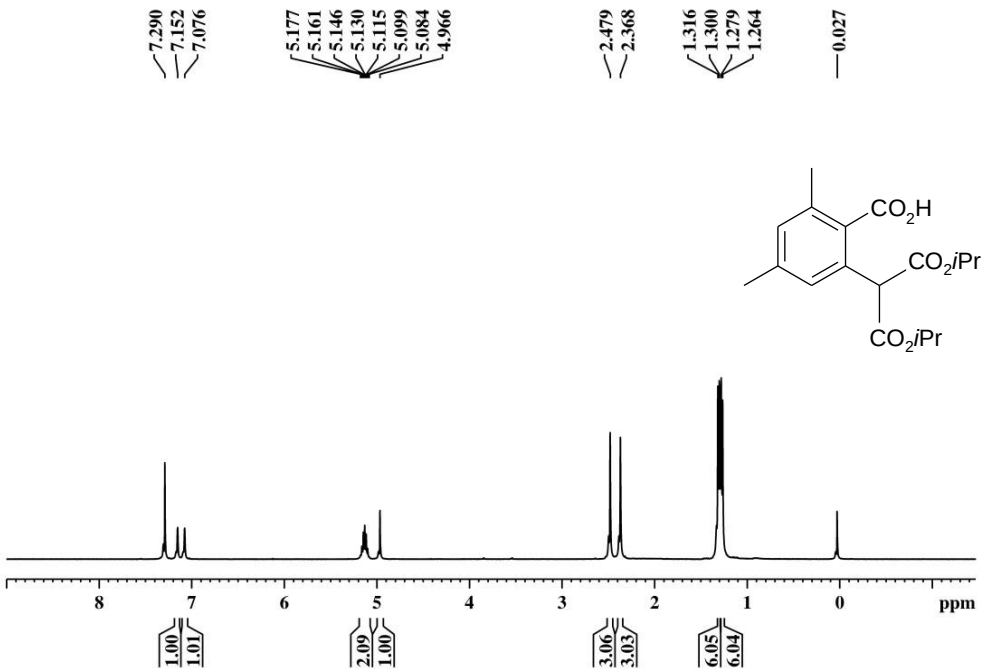


Figure S2. ^{1}H NMR spectrum of compound **163**

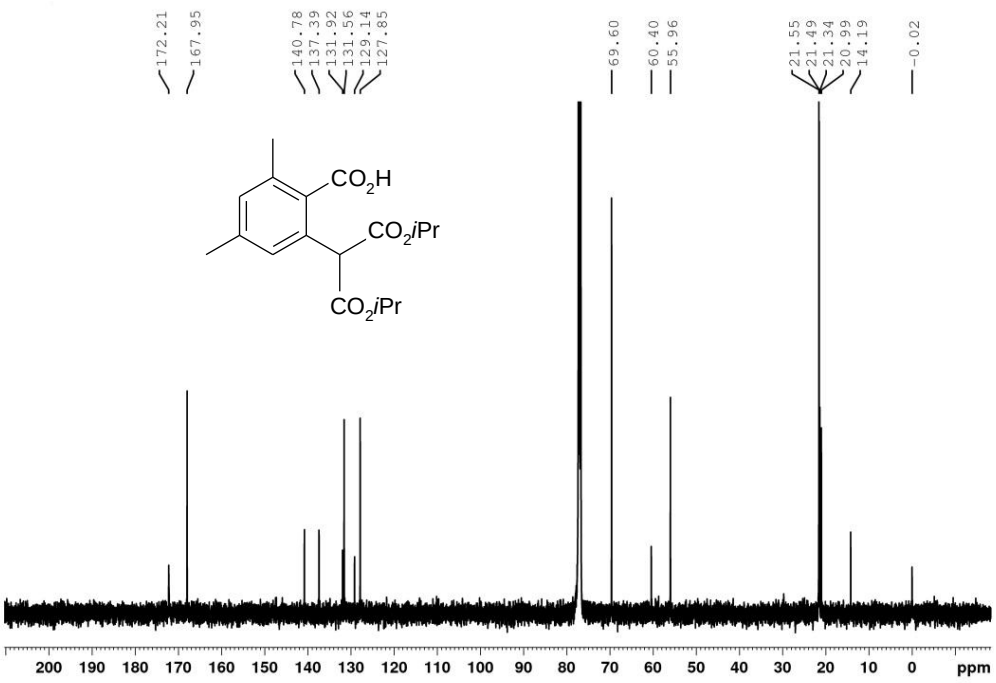


Figure S3. ^{13}C NMR spectrum of compound **163**

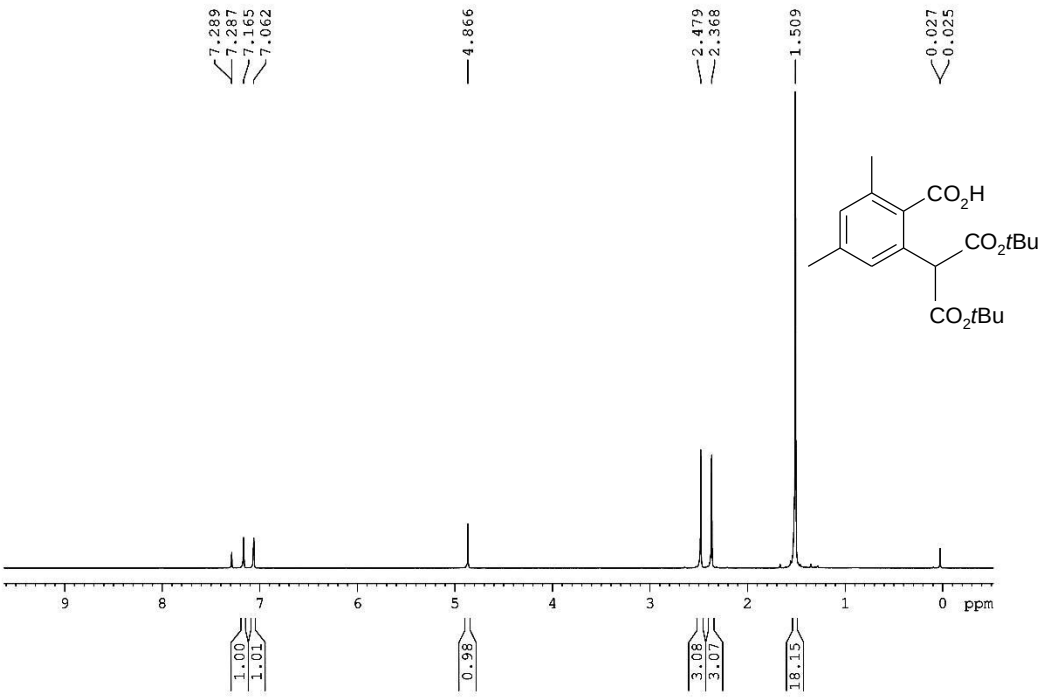


Figure S4. ^{1}H NMR spectrum of compound **164**

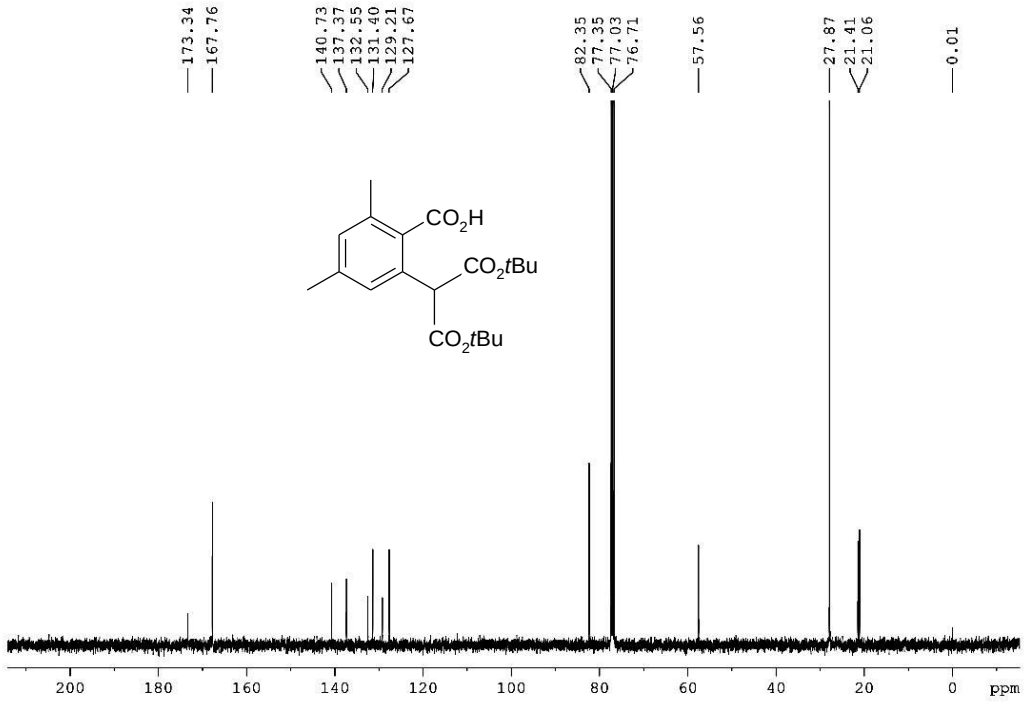


Figure S5. ^{13}C NMR spectrum of compound **164**

Figure S6. ^{1}H NMR spectrum of compound **1b**

Figure S7. ^{13}C NMR spectrum of compound **1b**

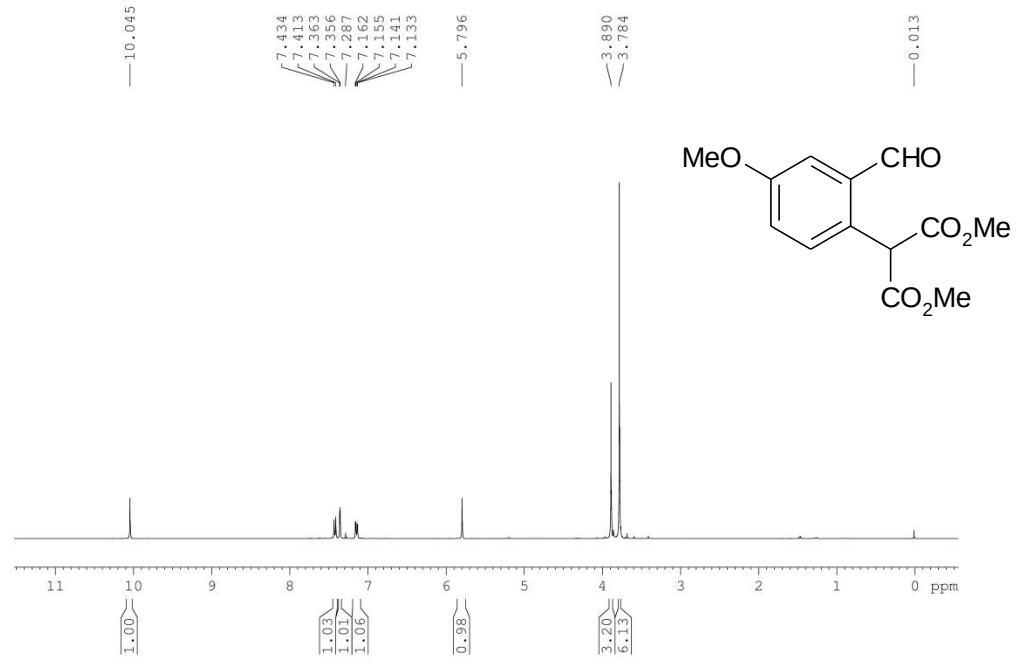


Figure S8. ^{1}H NMR spectrum of compound **1c**

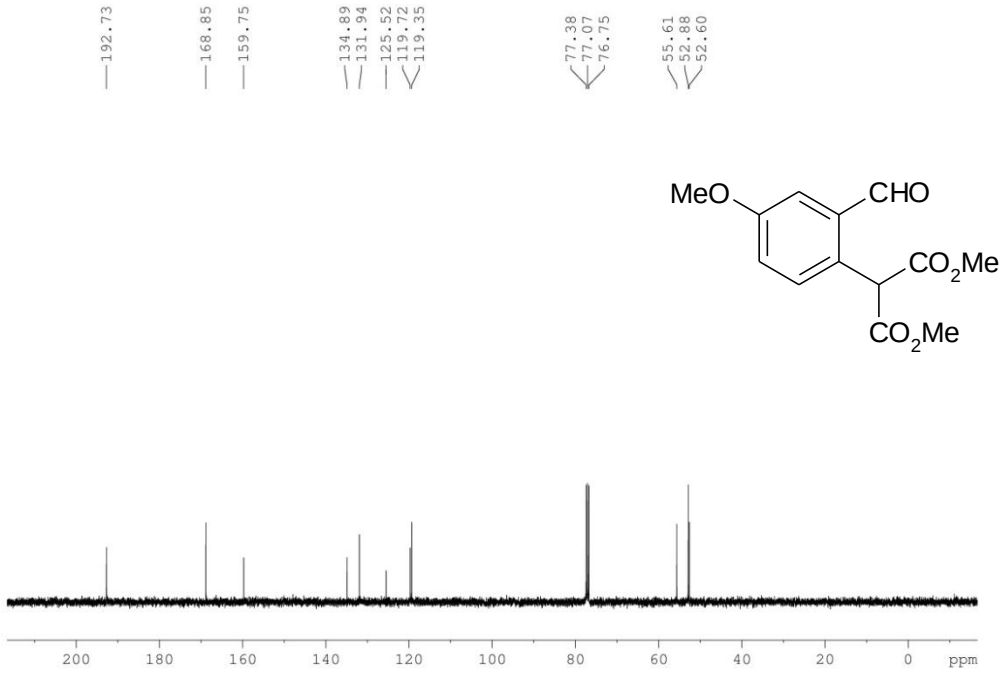


Figure S9. ^{13}C NMR spectrum of compound **1c**

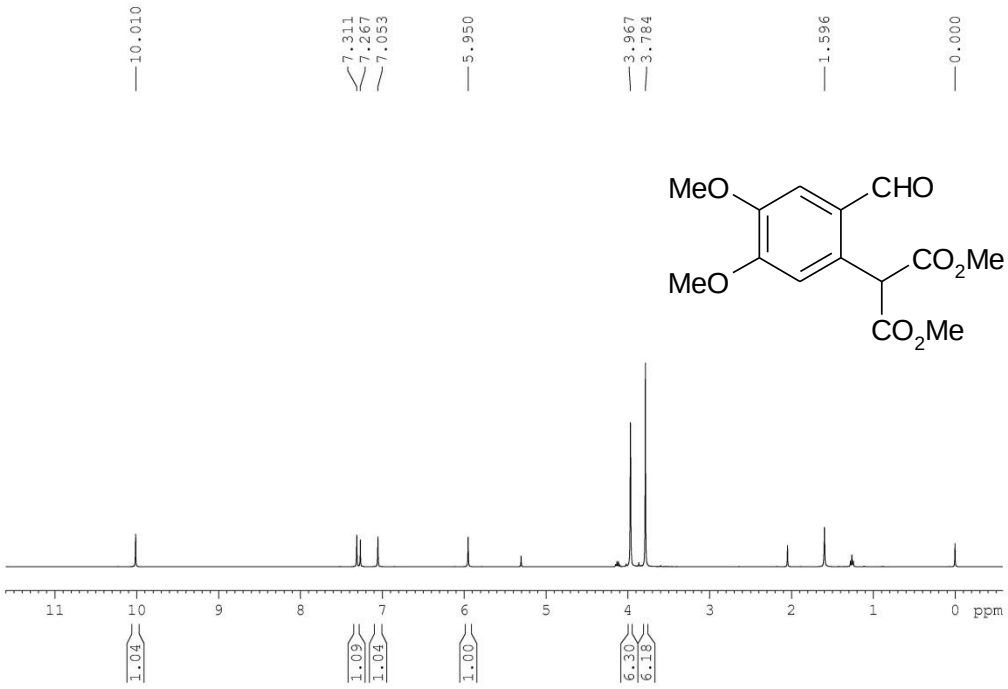


Figure S10. ^{1}H NMR spectrum of compound **1d**

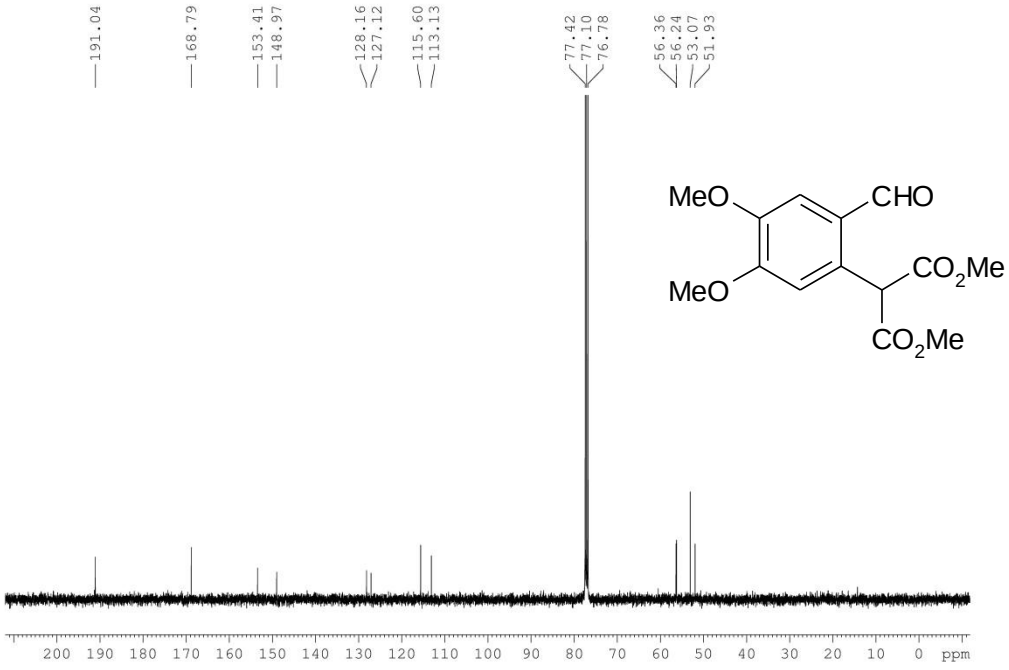


Figure S11. ^{13}C NMR spectrum of compound **1d**

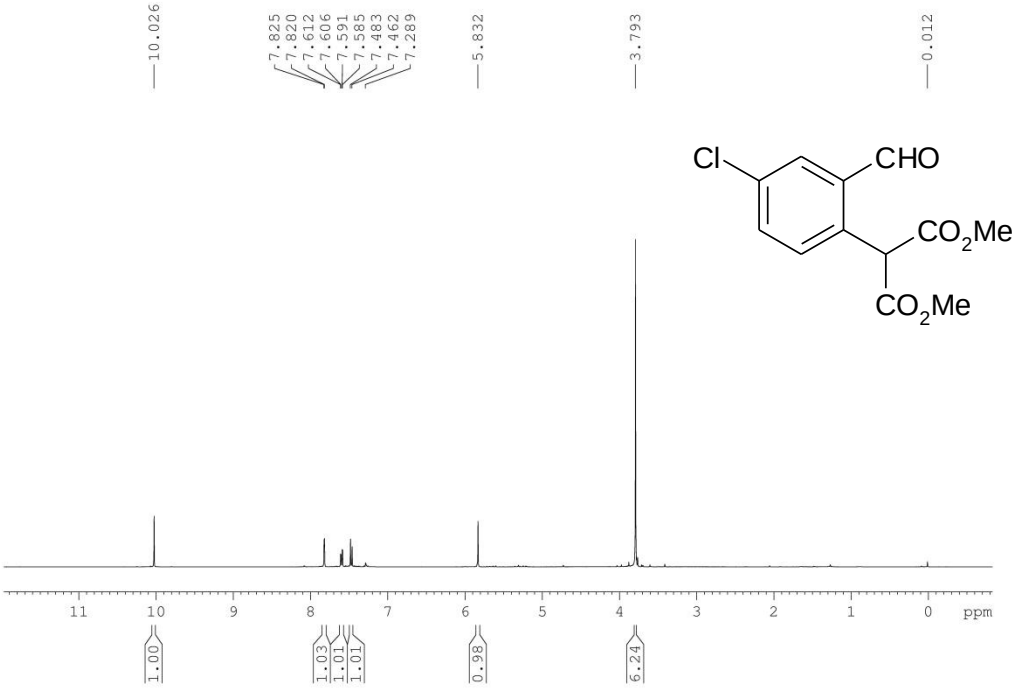


Figure S12. ^{1}H NMR spectrum of compound **1e**

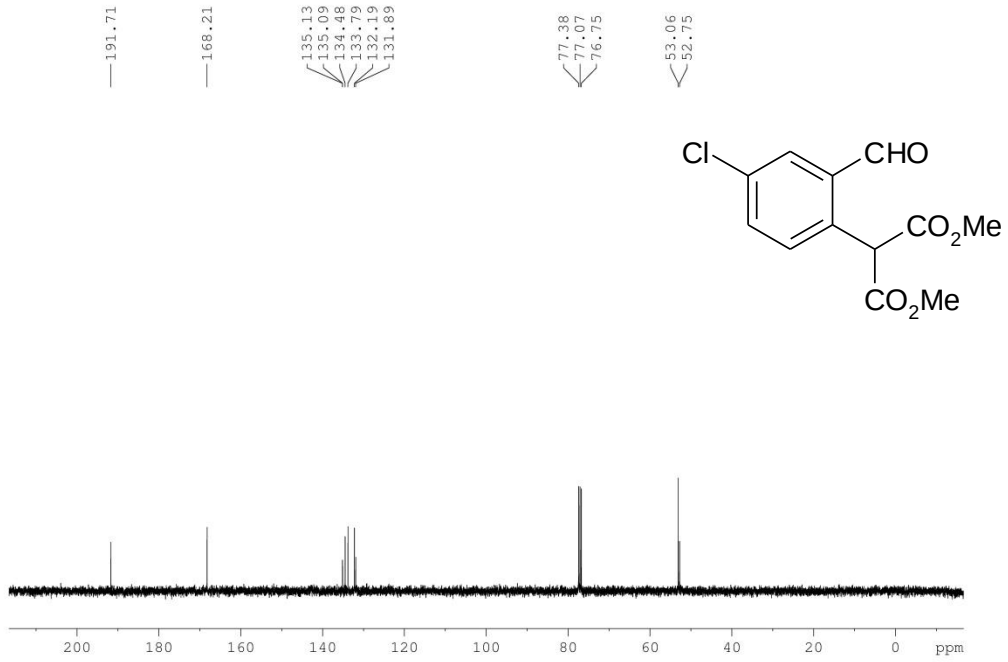


Figure S13. ^{13}C NMR spectrum of compound **1e**

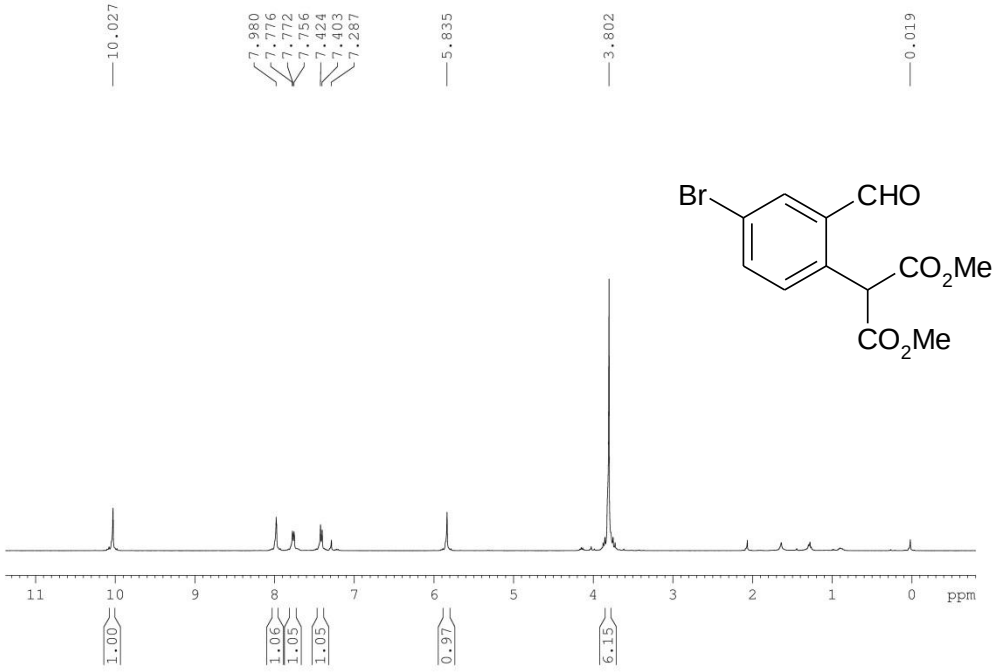


Figure S14. ^{13}C NMR spectrum of compound **1f**

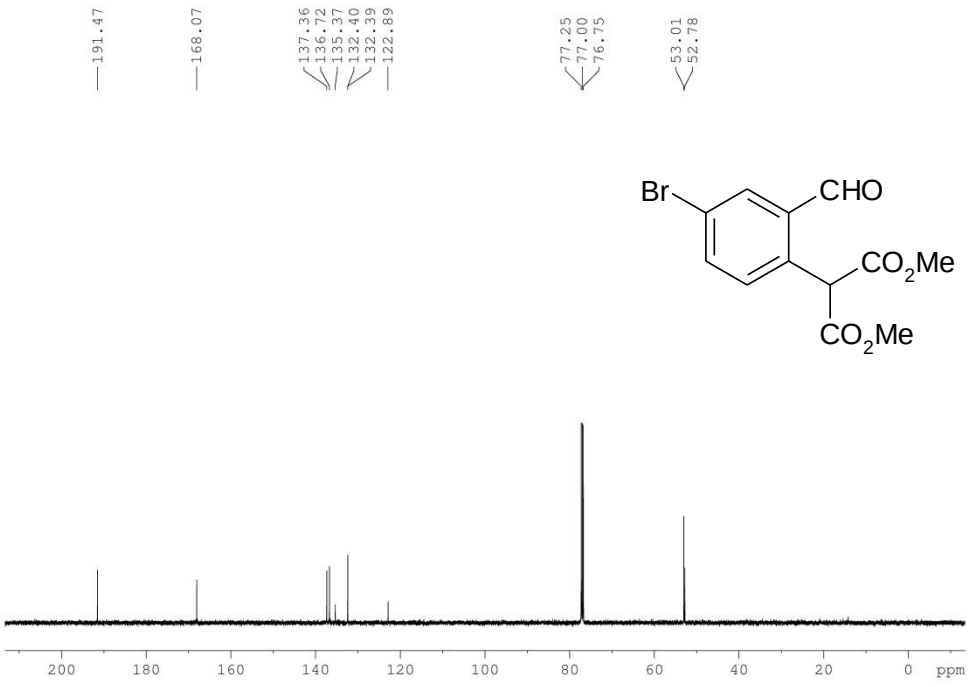


Figure S15. ^{13}C NMR spectrum of compound **1f**

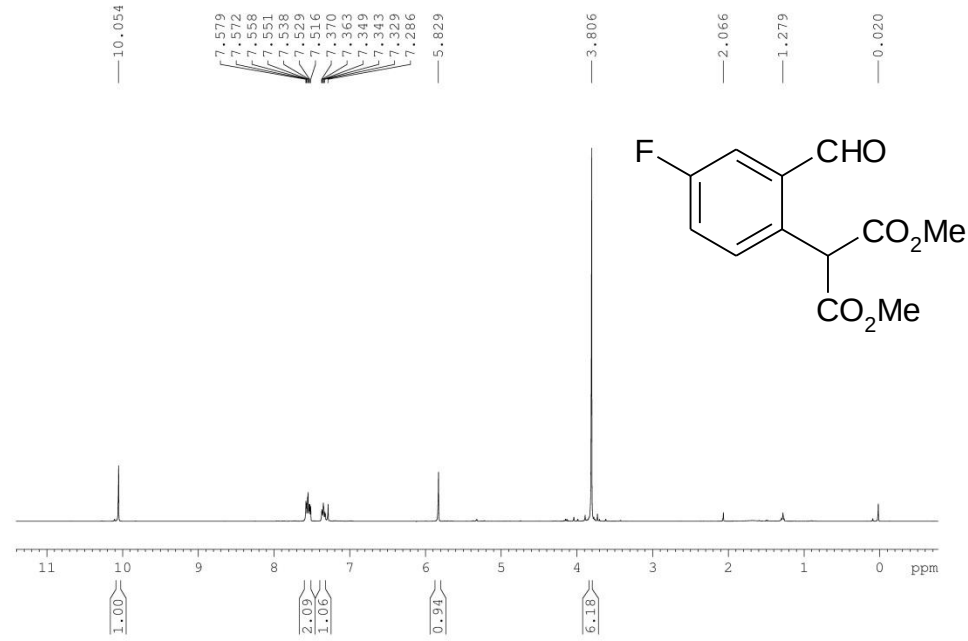


Figure S16. ^{13}C NMR spectrum of compound **1g**

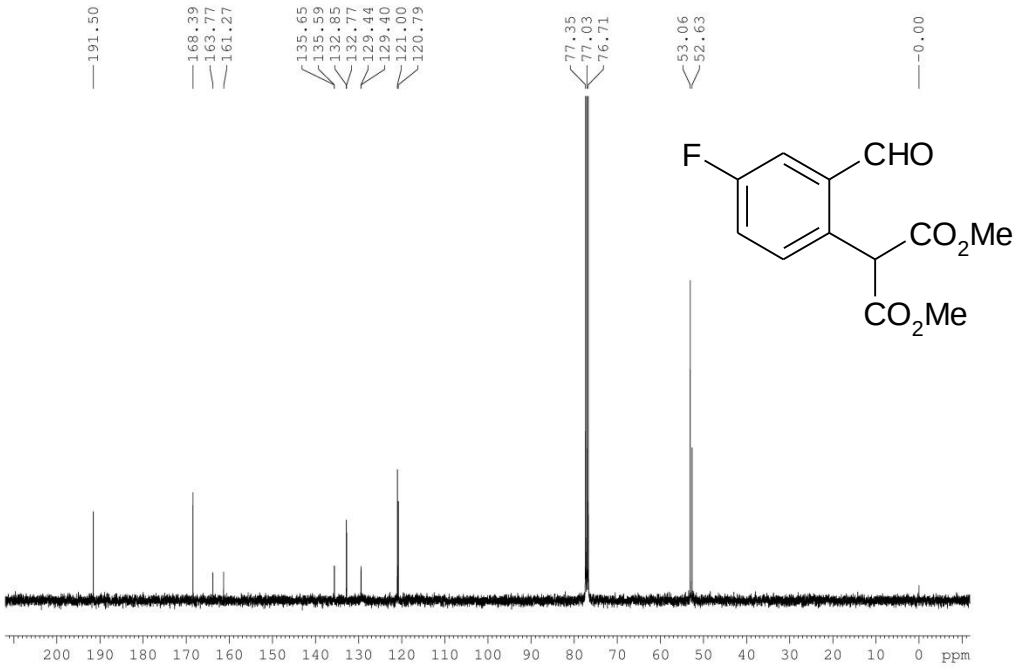


Figure S17. ^{13}C NMR spectrum of compound **1g**

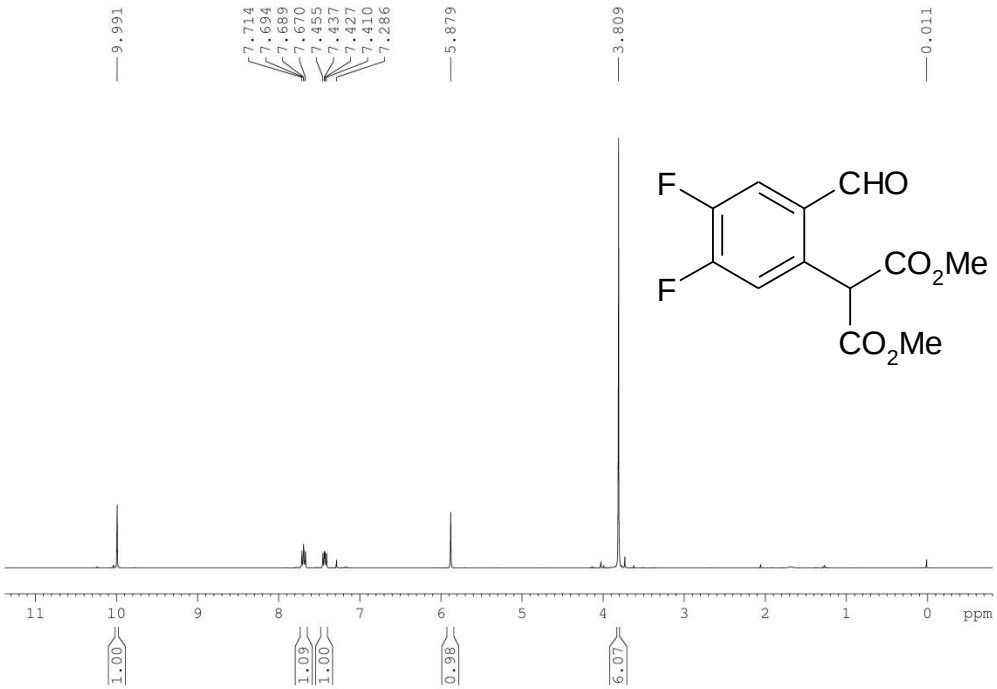


Figure S18. ^{1}HNMR spectrum of compound **1h**

Figure S19. ^{13}C NMR spectrum of compound **1h**

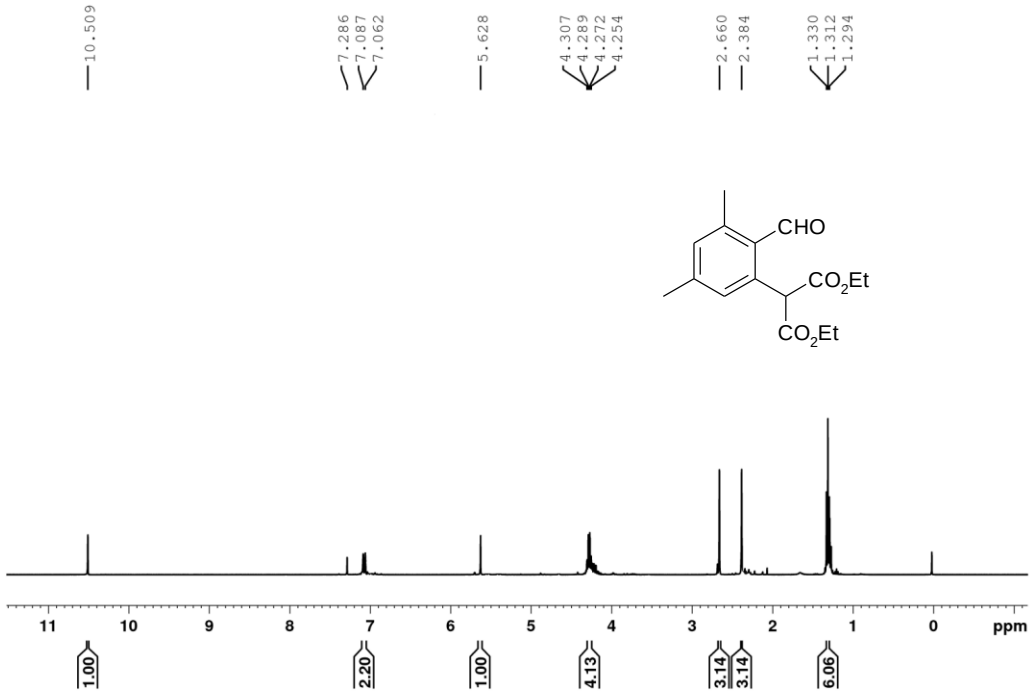


Figure S20. [1]HNMR spectrum of compound **1i**

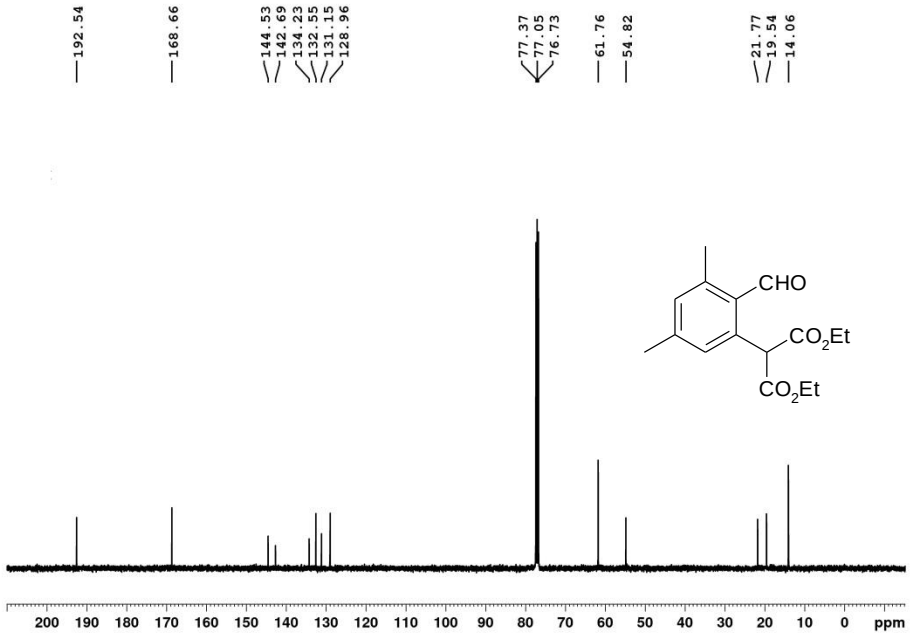


Figure S21. [13]C NMR spectrum of compound **1i**

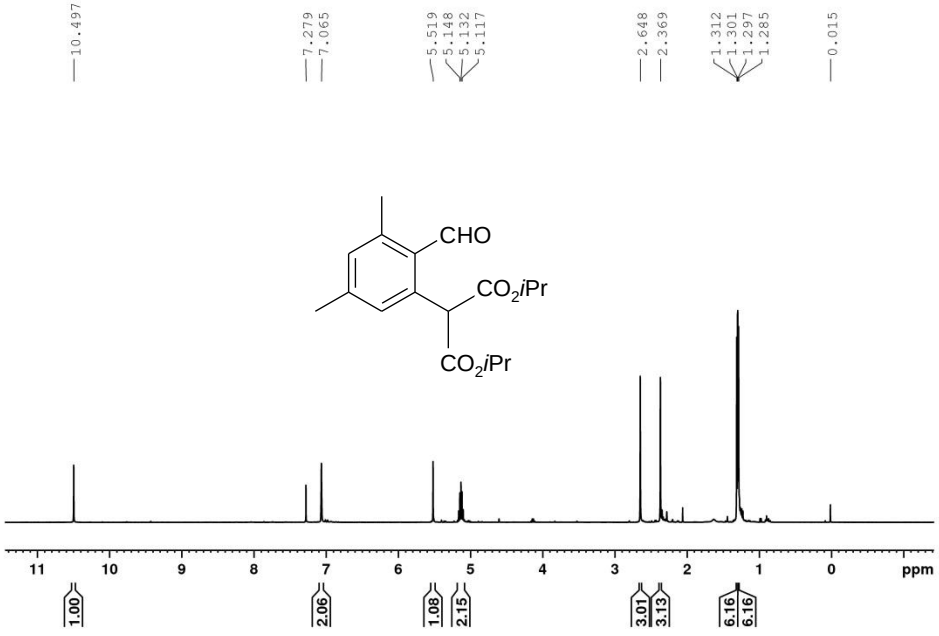


Figure S22. [1]H NMR spectrum of compound **1j**

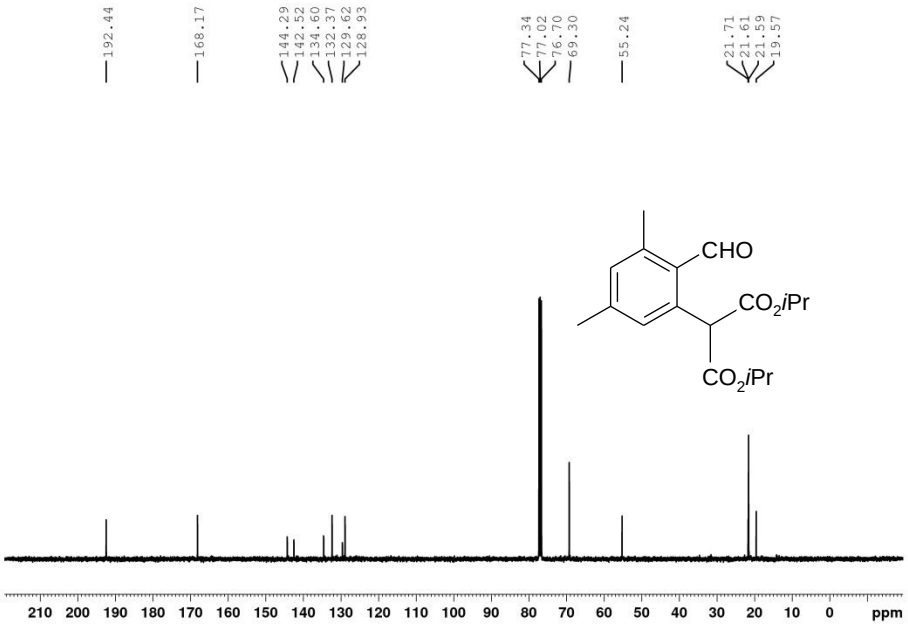


Figure S23. ^{13}C NMR spectrum of compound **1j**

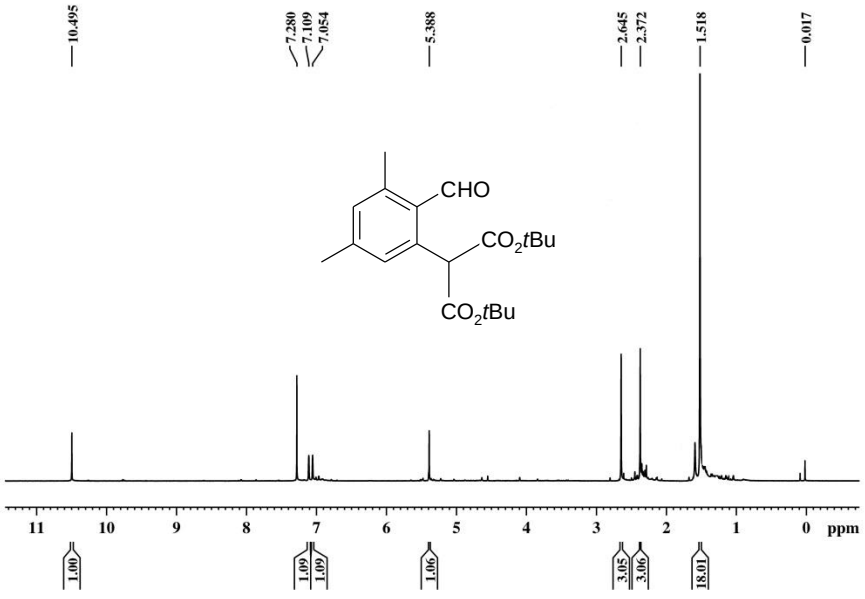


Figure S24. ^{1}H NMR spectrum of compound **1k**

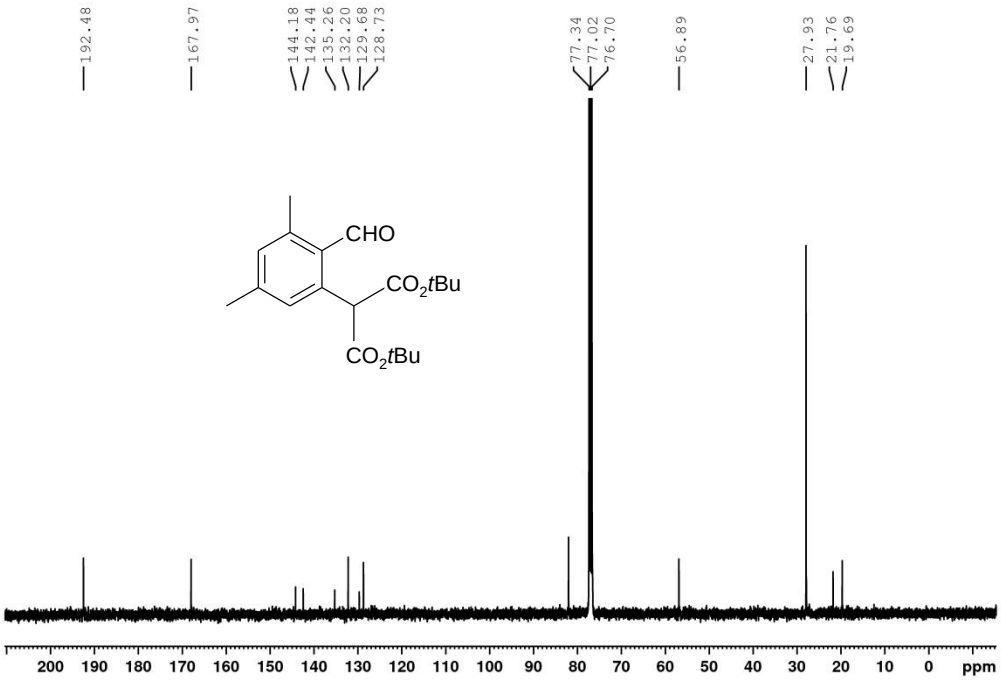


Figure S25. ^{13}C NMR spectrum of compound **1k**

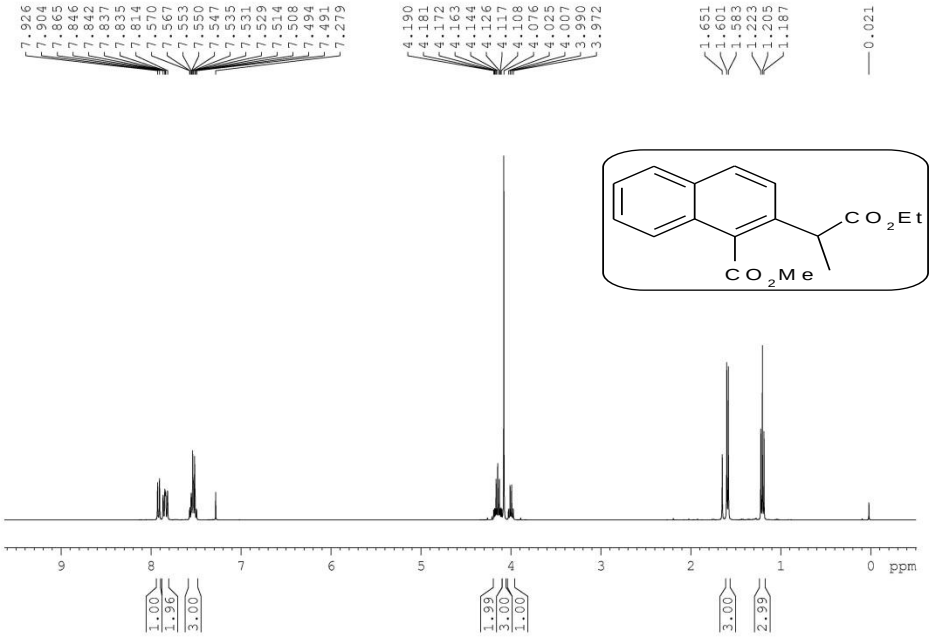


Figure S26. ^{1}H NMR spectrum of compound **3aa**

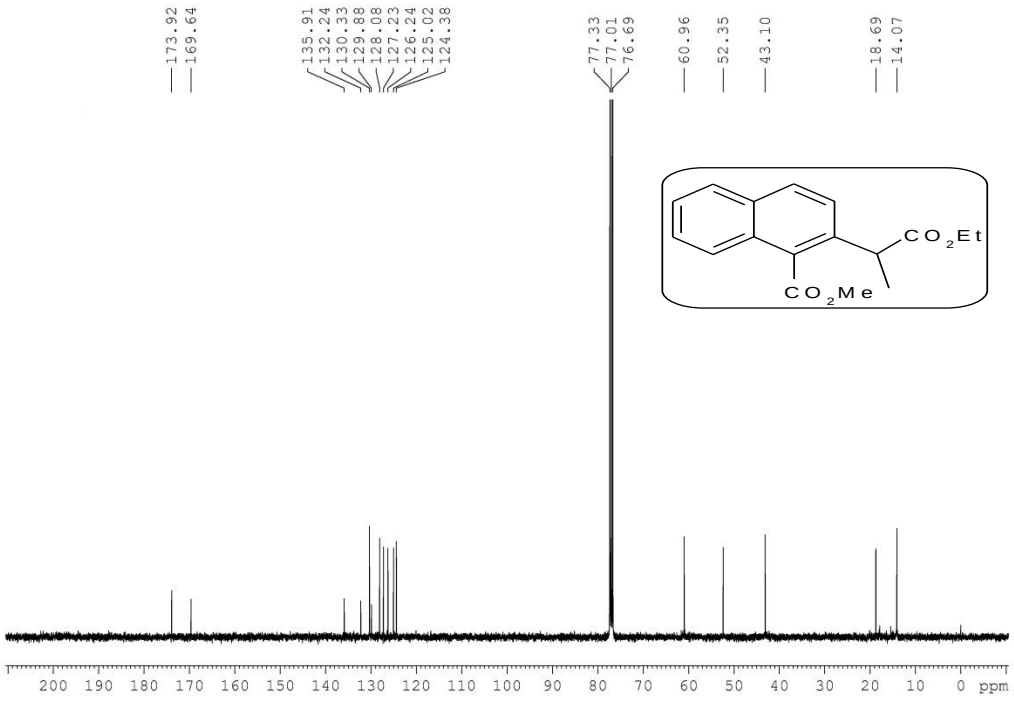


Figure S27. ^{13}C NMR spectrum of compound **3aa**

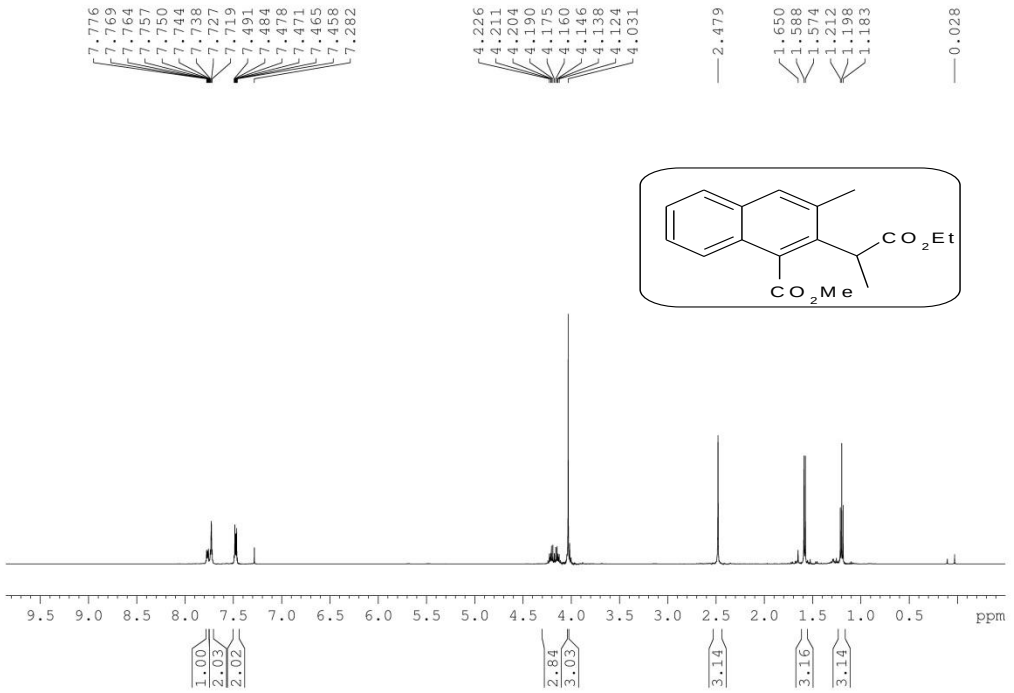


Figure S28. ^{1}H NMR spectrum of compound **3ab**

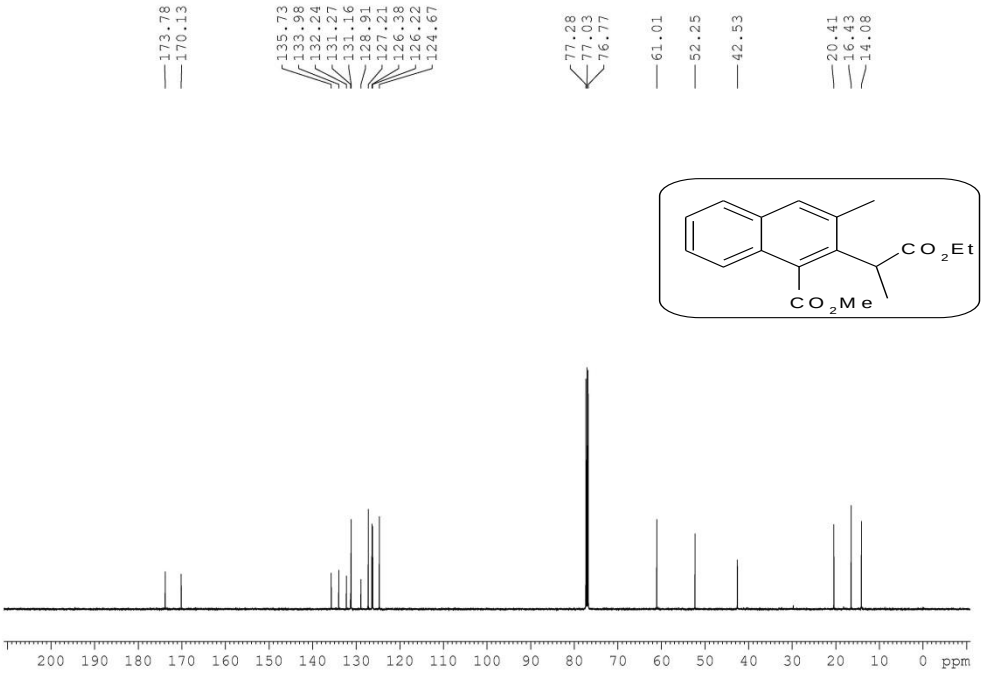


Figure S29. ^{13}C NMR spectrum of compound **3ab**

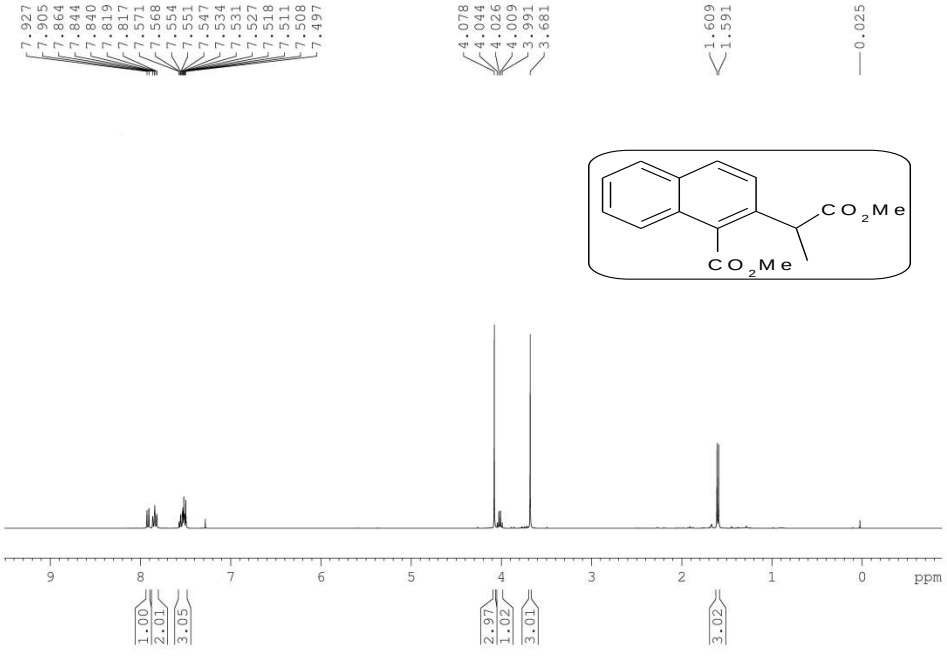


Figure S30. ^{1}H NMR spectrum of compound **3ac**

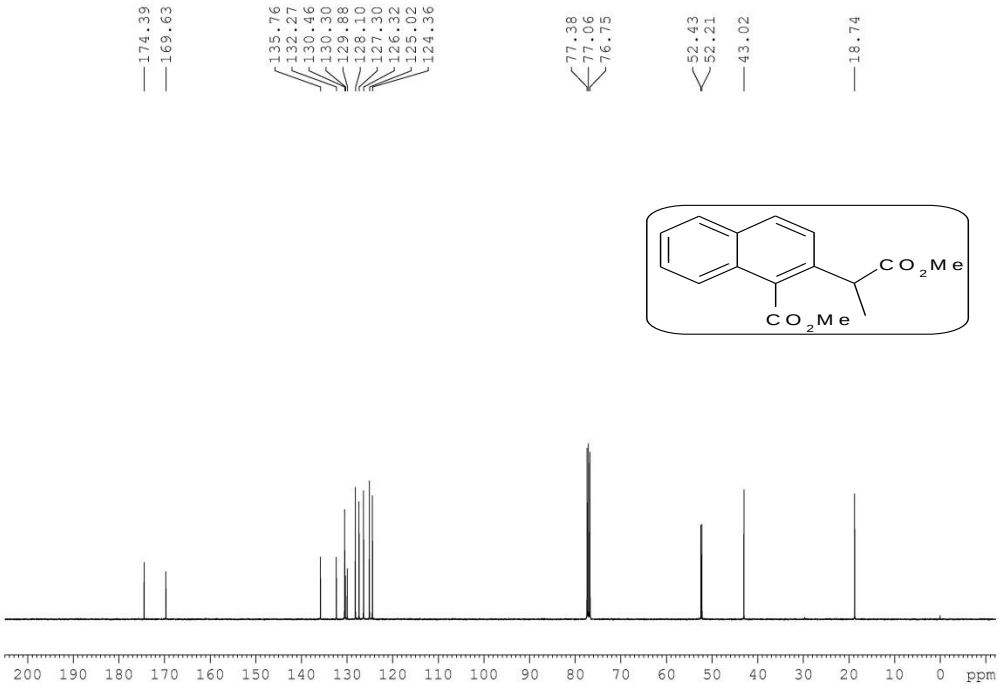


Figure S31. ^{13}C NMR spectrum of compound **3ac**

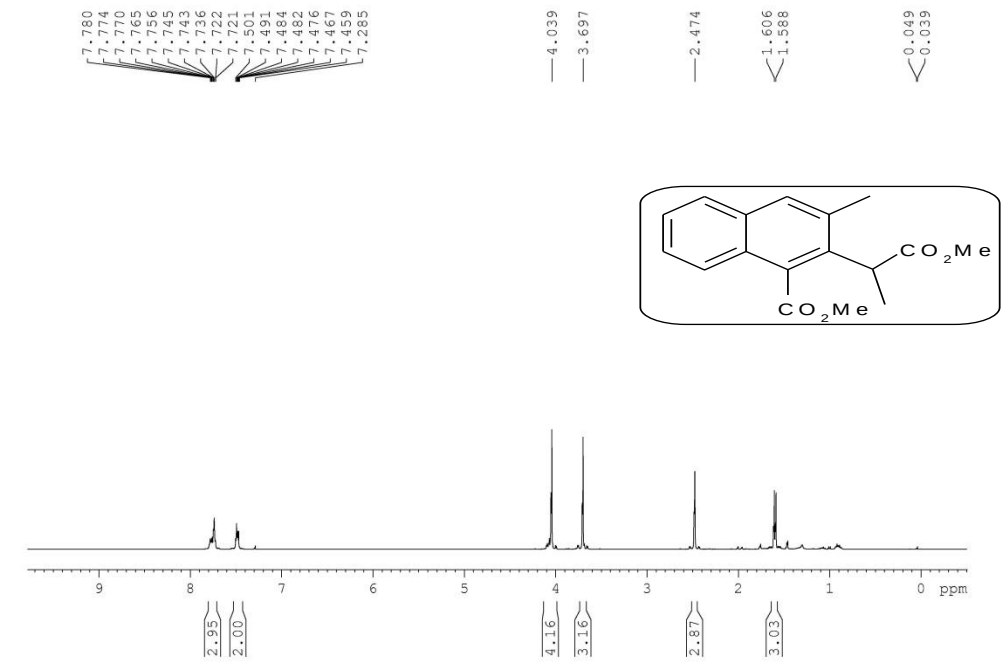


Figure S32. ^{1}H NMR spectrum of compound **3ad**

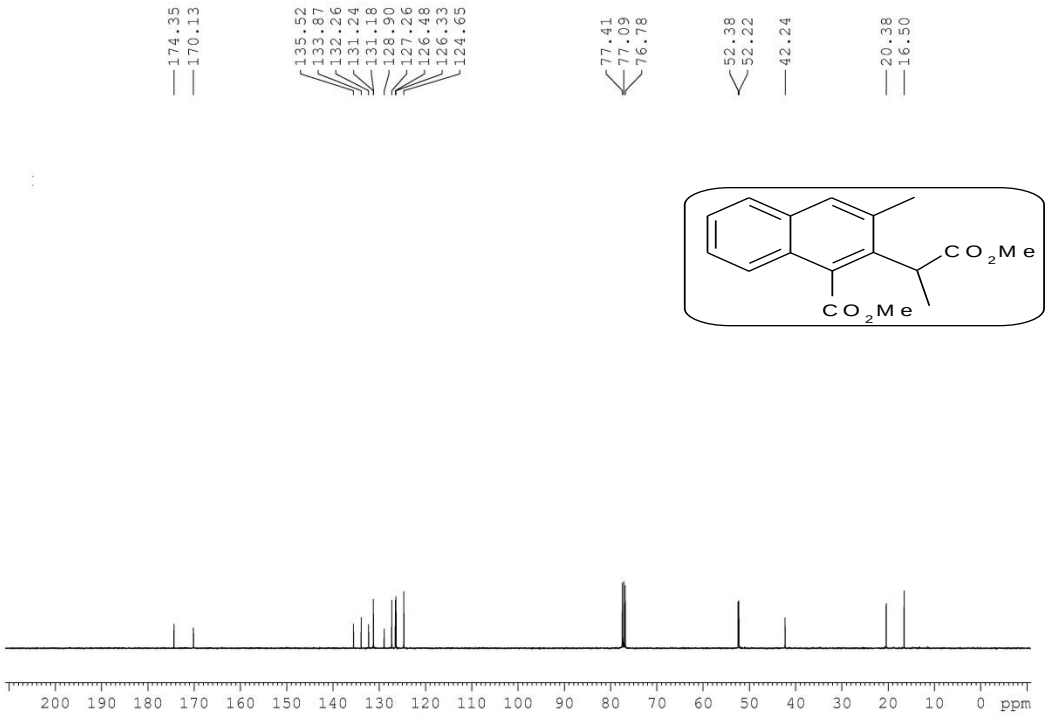


Figure S33. ^{13}C NMR spectrum of compound **3ad**

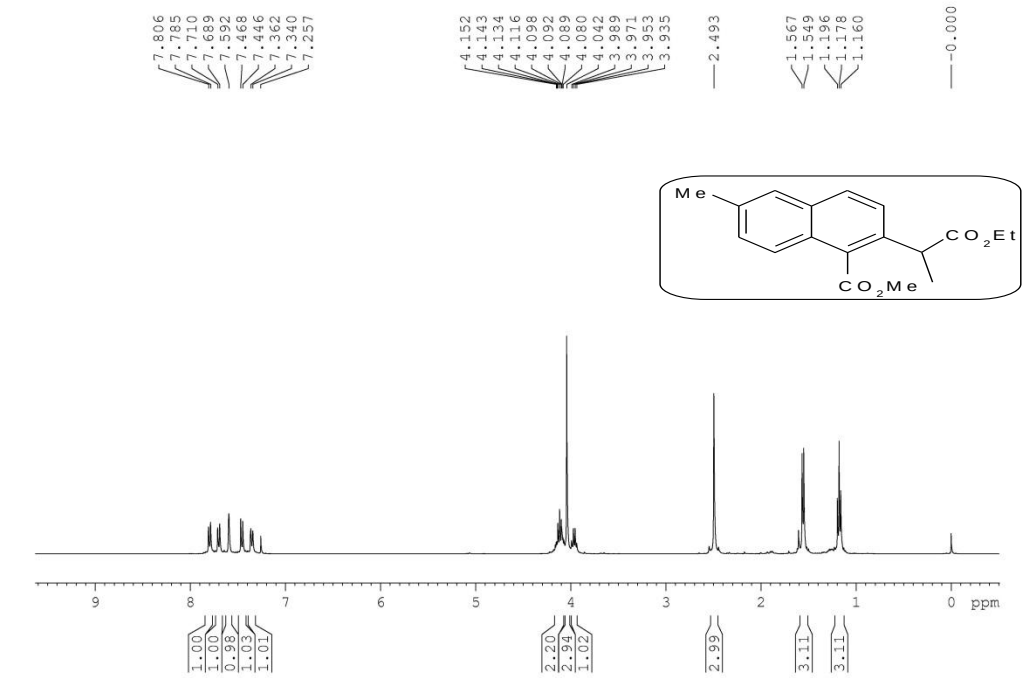


Figure S34. ^{1}H NMR spectrum of compound **3ba**

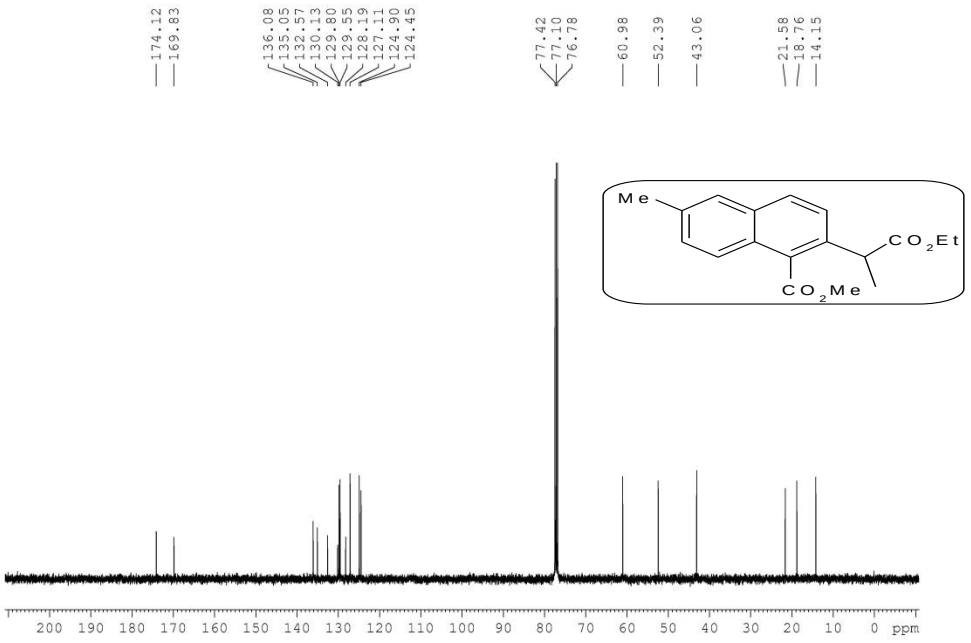


Figure S35. ^{13}C NMR spectrum of compound **3ba**

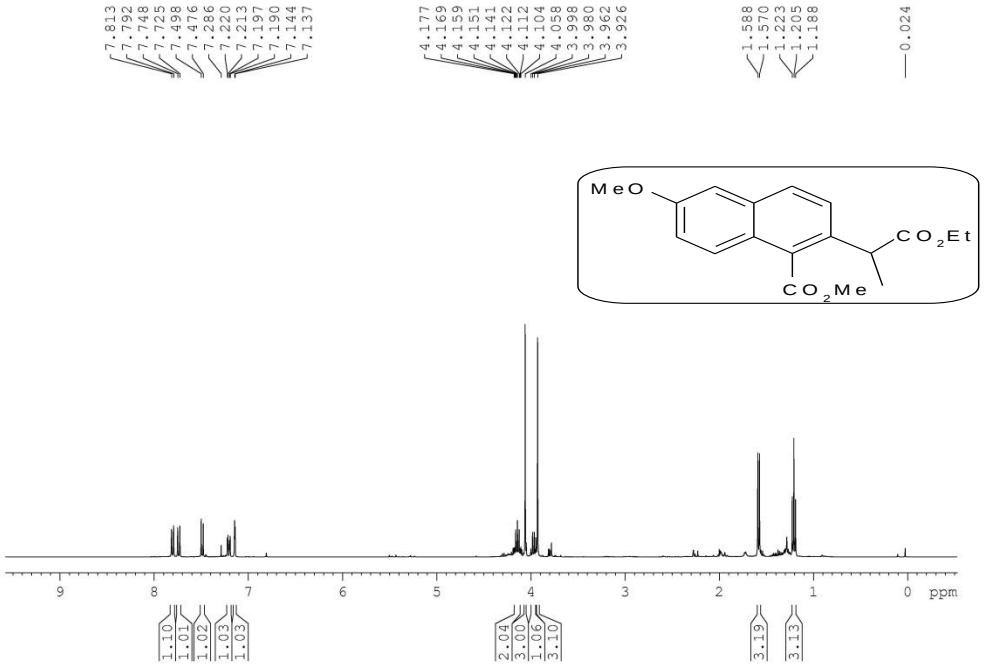


Figure S36. ^{1}H NMR spectrum of compound **3ca**

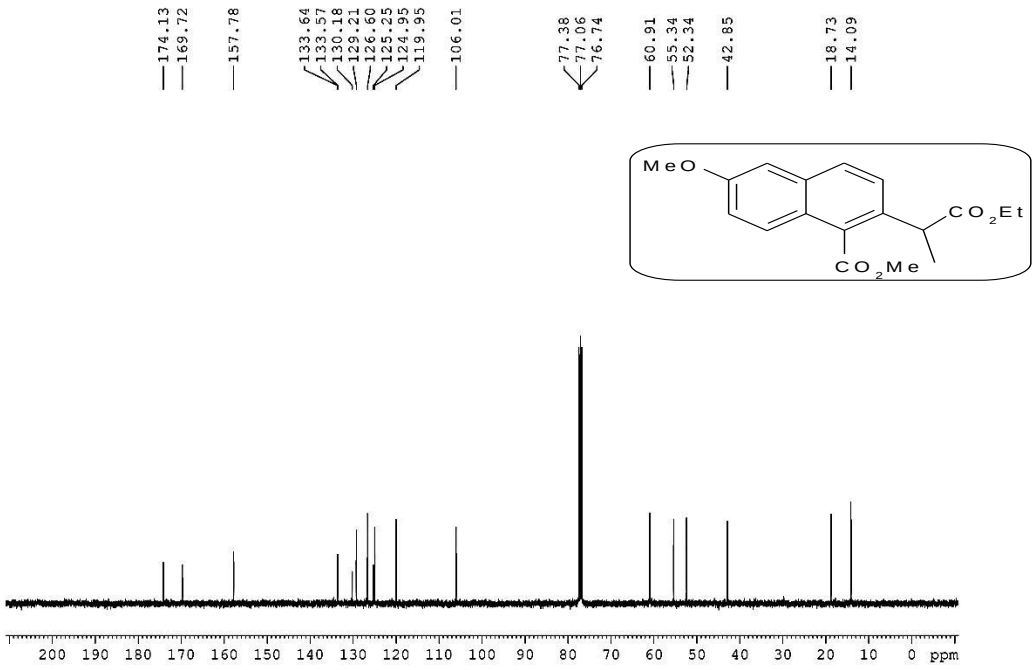


Figure S37. ^{13}C NMR spectrum of compound **3ca**

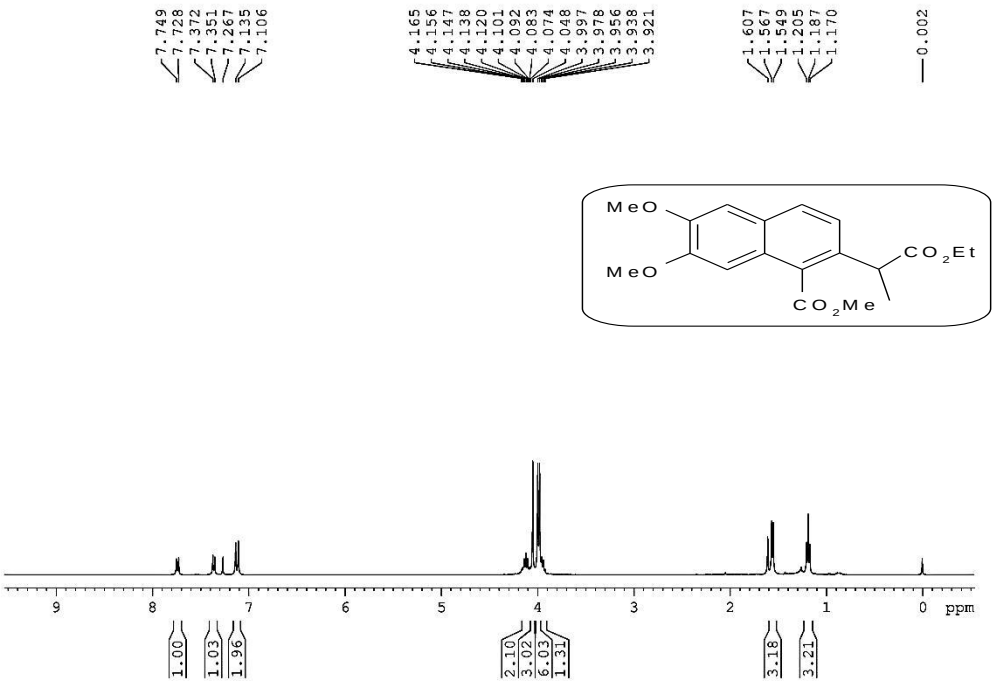


Figure S38. ^{1}H NMR spectrum of compound **3da**

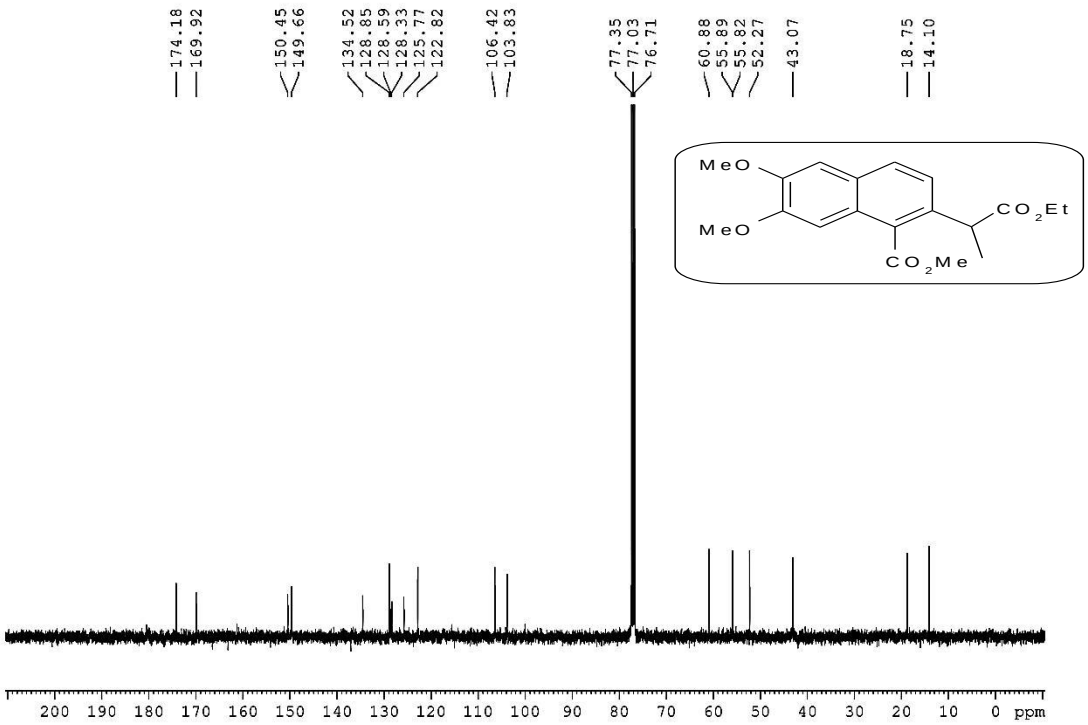


Figure S39. ^{13}C NMR spectrum of compound **3da**

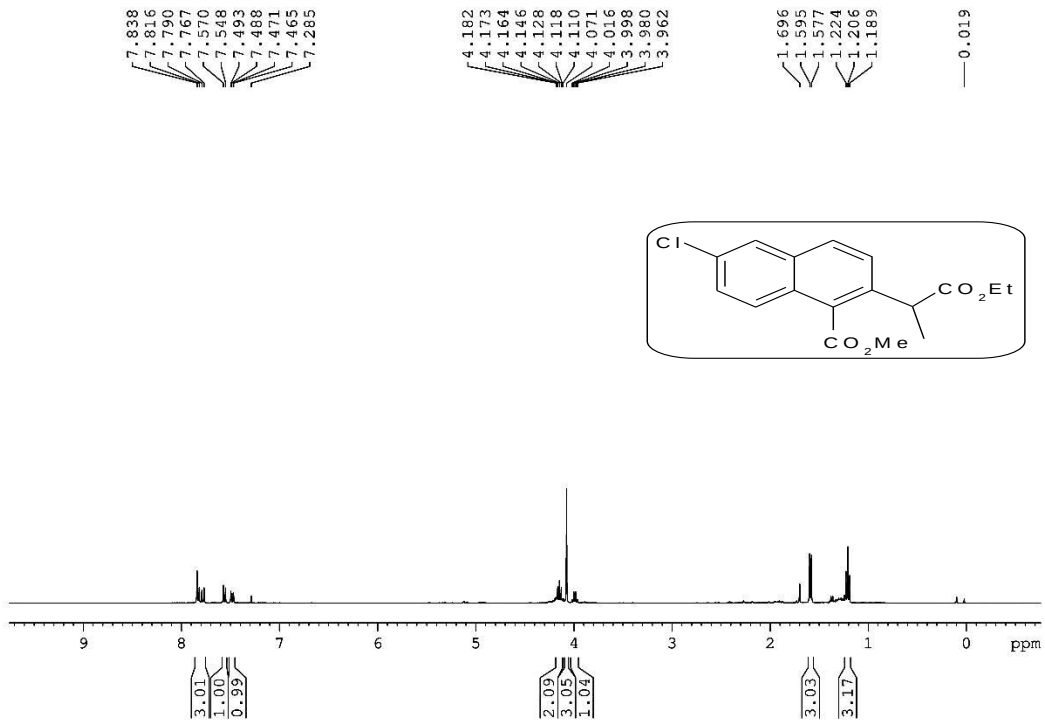


Figure S40. ^{1}H NMR spectrum of compound **3ea**

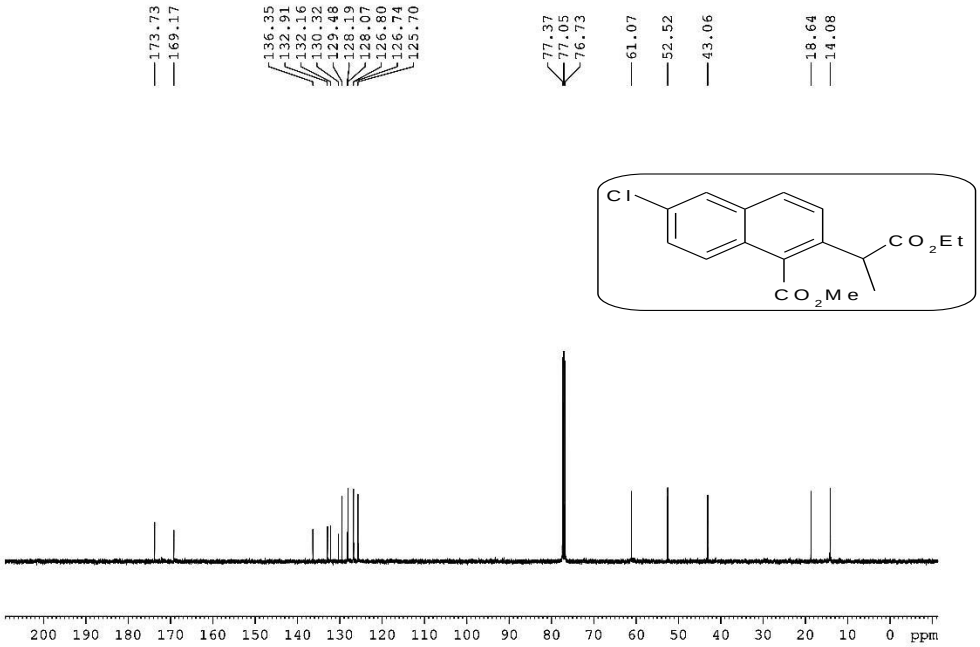


Figure S41. ^{13}C NMR spectrum of compound **3ea**

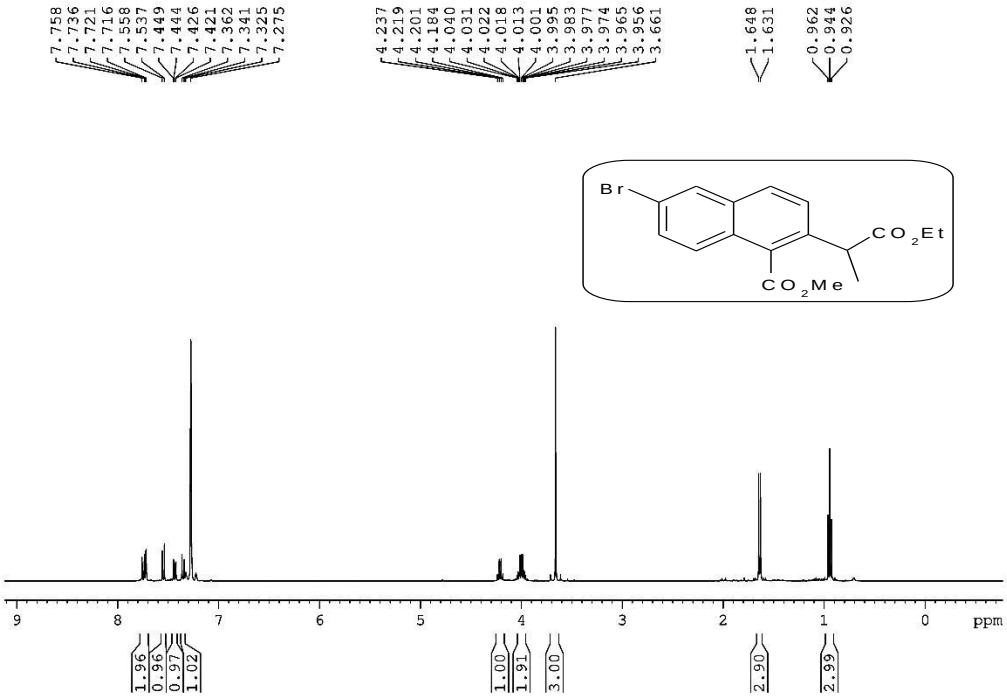


Figure S42. ^{1}H NMR spectrum of compound **3fa**

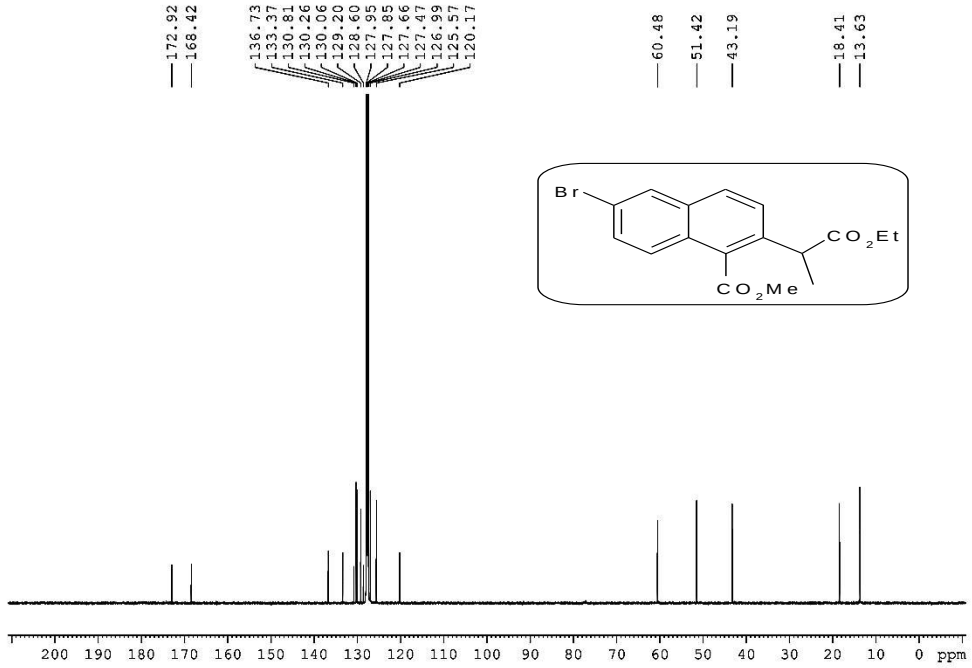


Figure S43. ^{13}C NMR spectrum of compound **3fa**

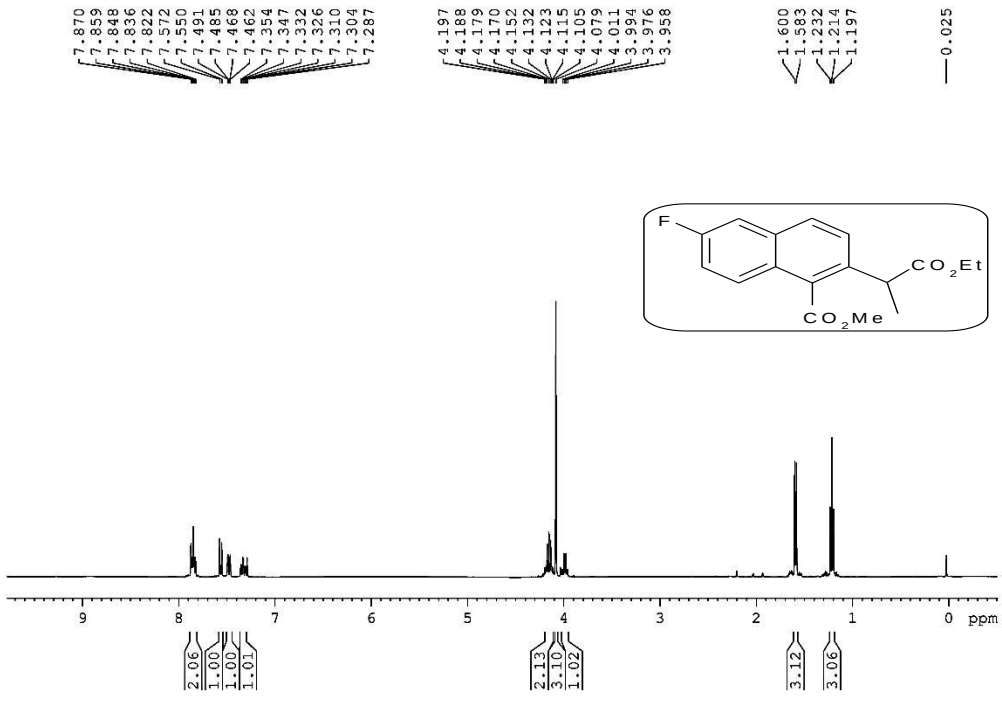


Figure S44. ^{1}H NMR spectrum of compound **3ga**

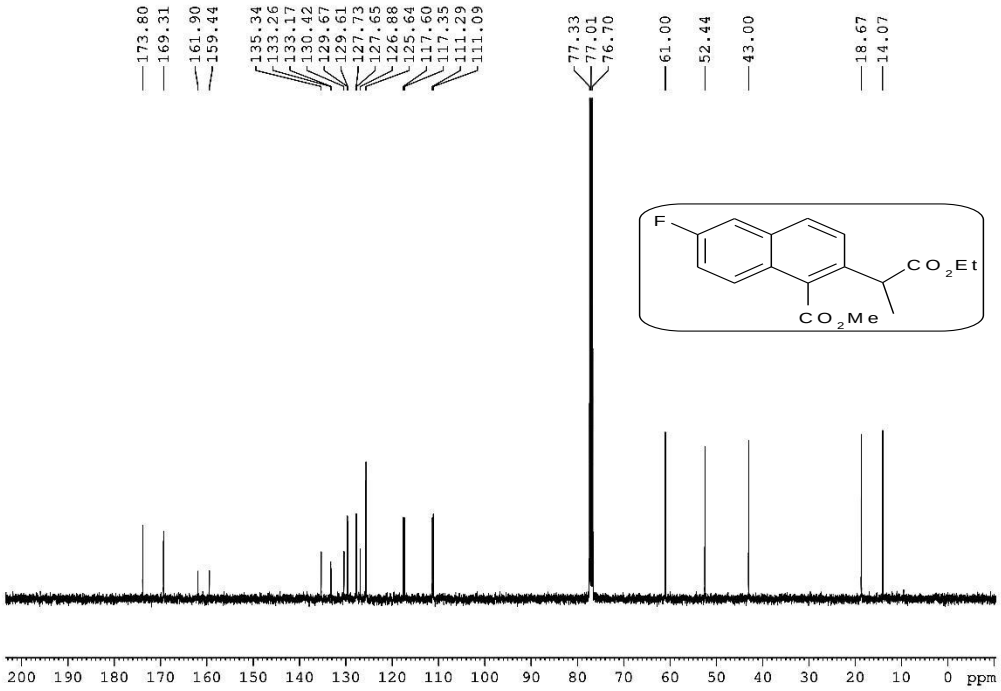


Figure S45. ^{13}C NMR spectrum of compound **3ga**

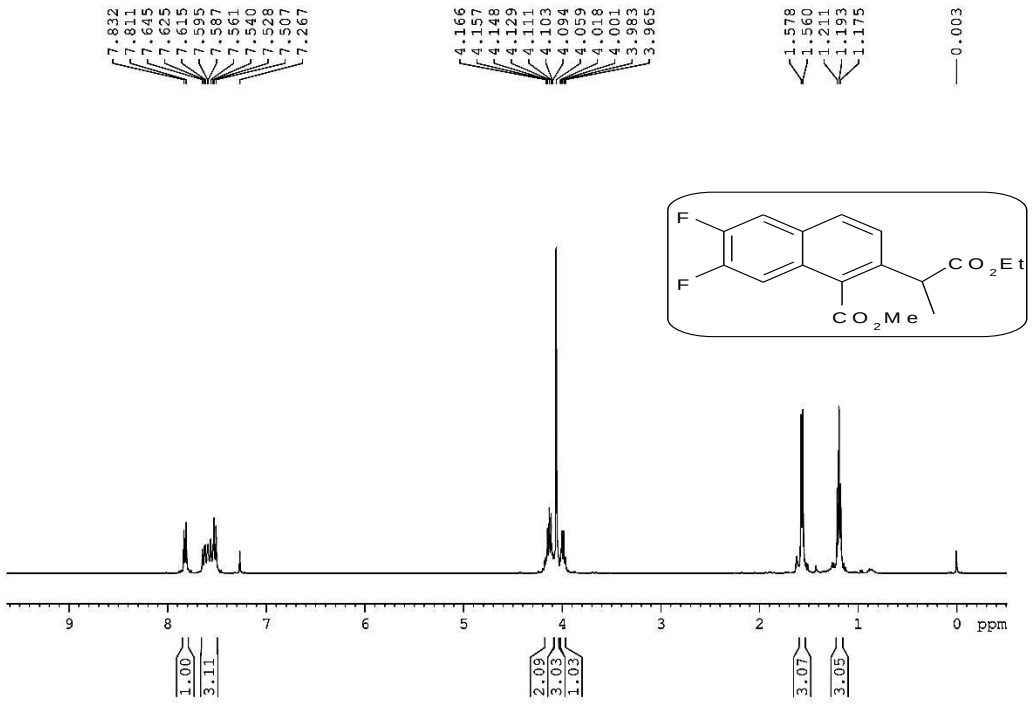


Figure S46. ^{1}H NMR spectrum of compound **3ha**

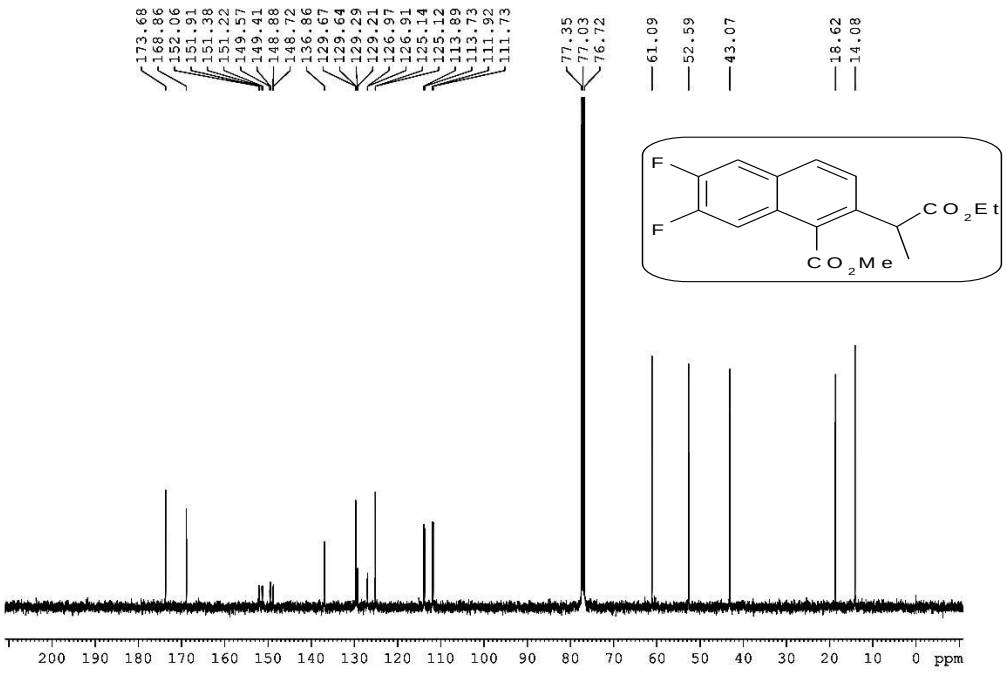


Figure S47. ^{13}C NMR spectrum of compound **3ha**

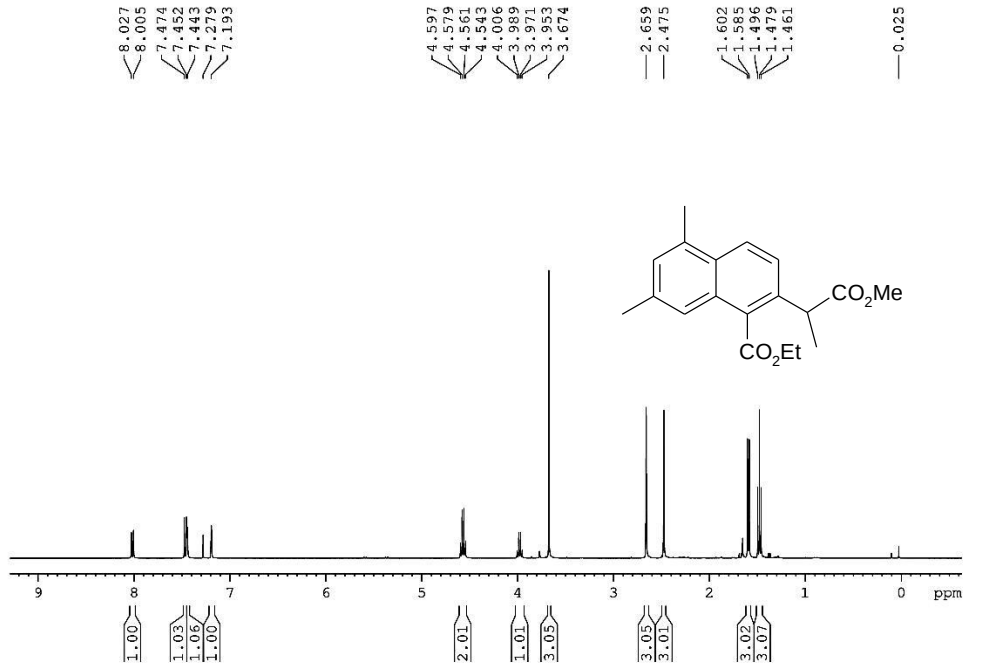


Figure S48. ^{1}H NMR spectrum of compound **3ic**

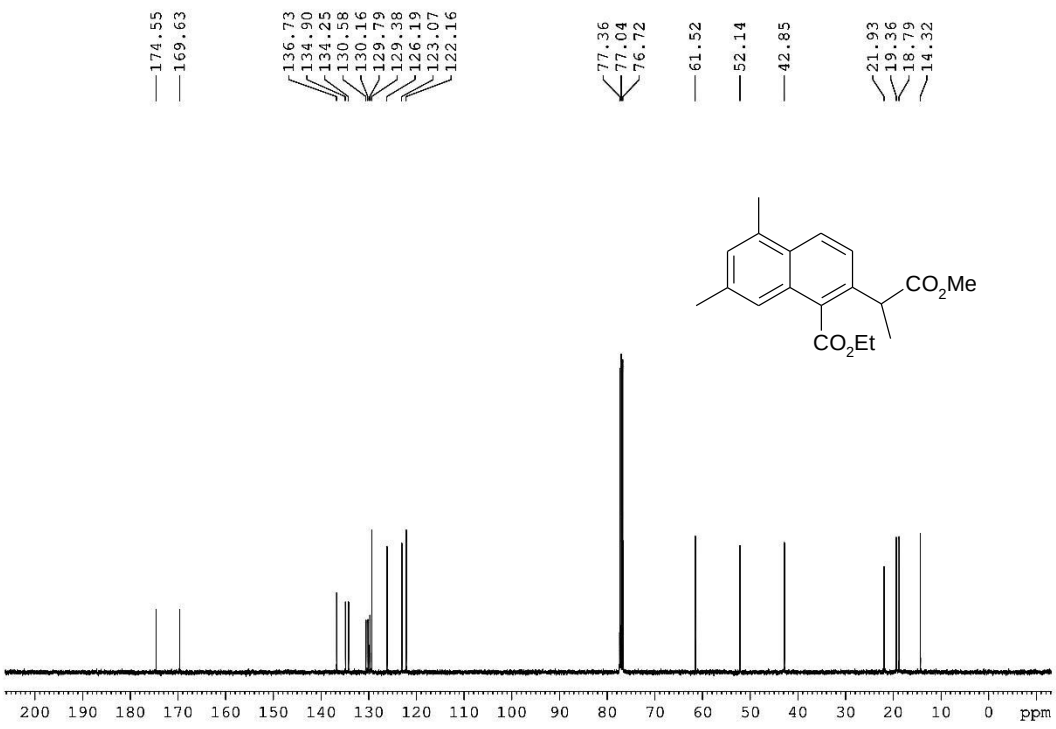


Figure S49. ^{13}C NMR spectrum of compound **3ic**

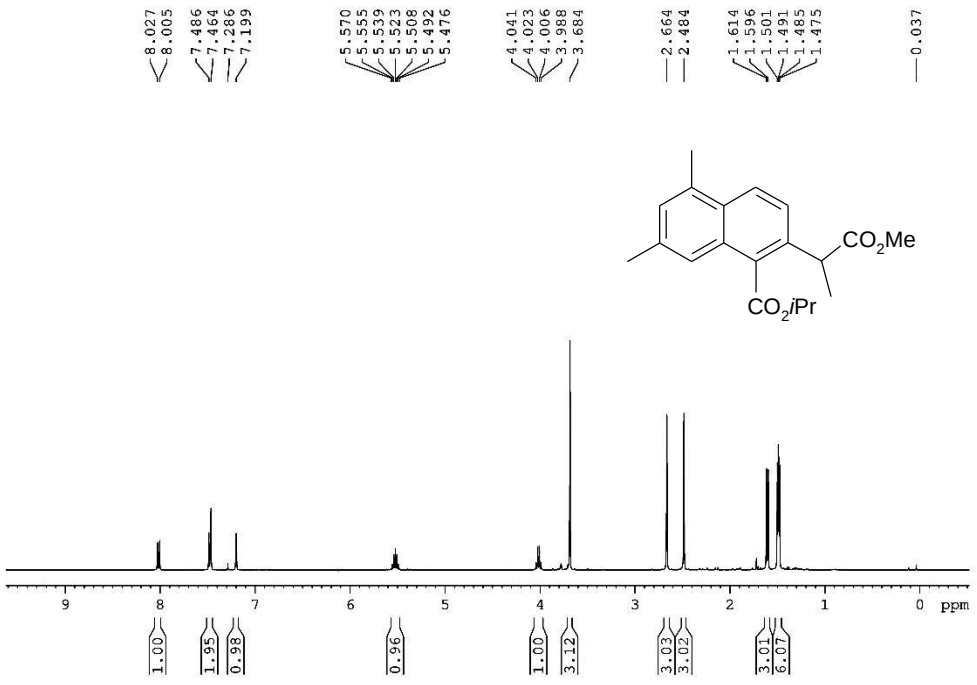


Figure S50. ^{1}H NMR spectrum of compound **3jc**

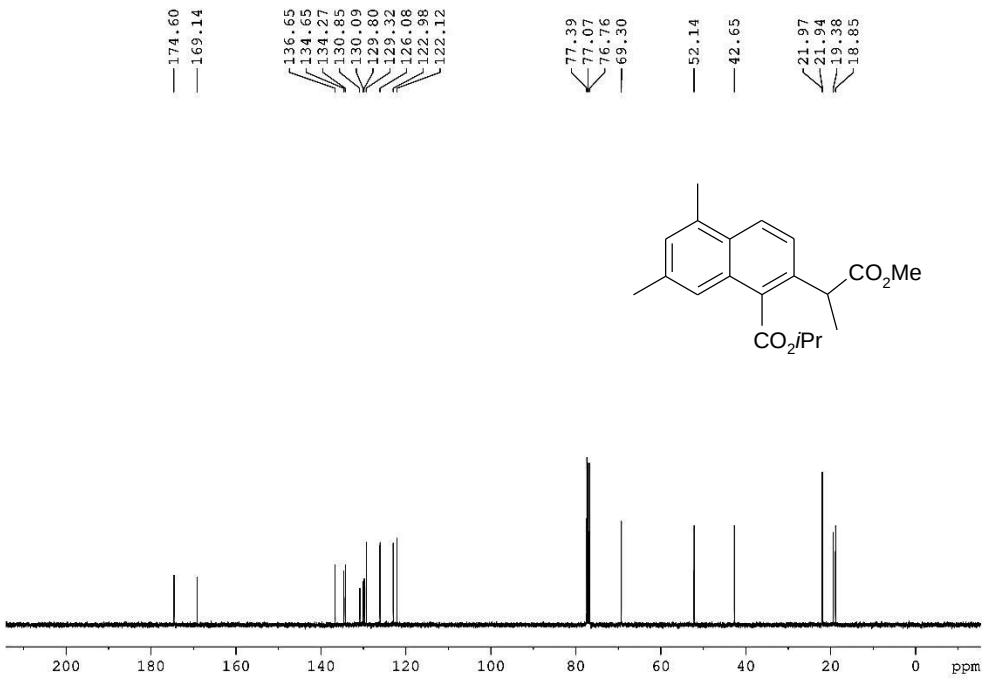


Figure S51. ^{13}C NMR spectrum of compound **3jc**

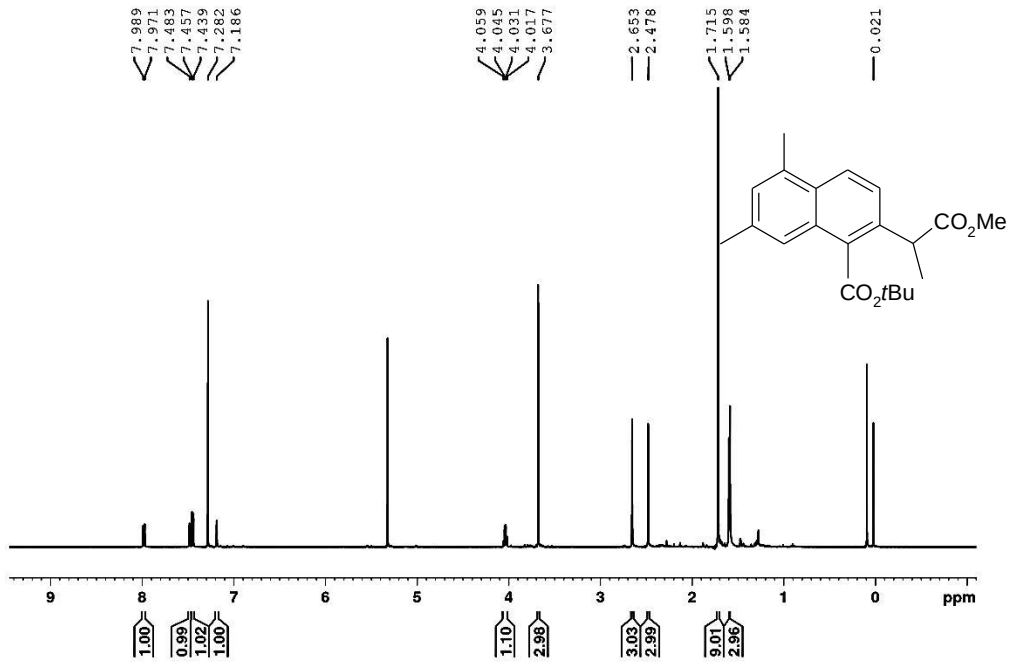


Figure S52. ^{1}H NMR spectrum of compound **3kc**

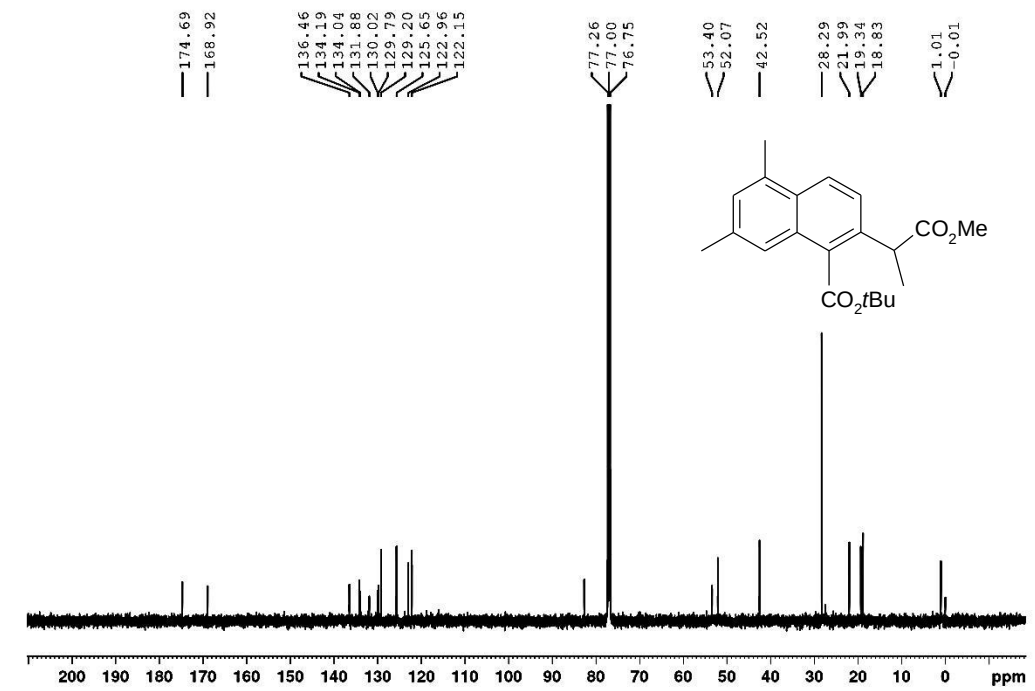


Figure S53. ^{13}C NMR spectrum of compound **3kc**

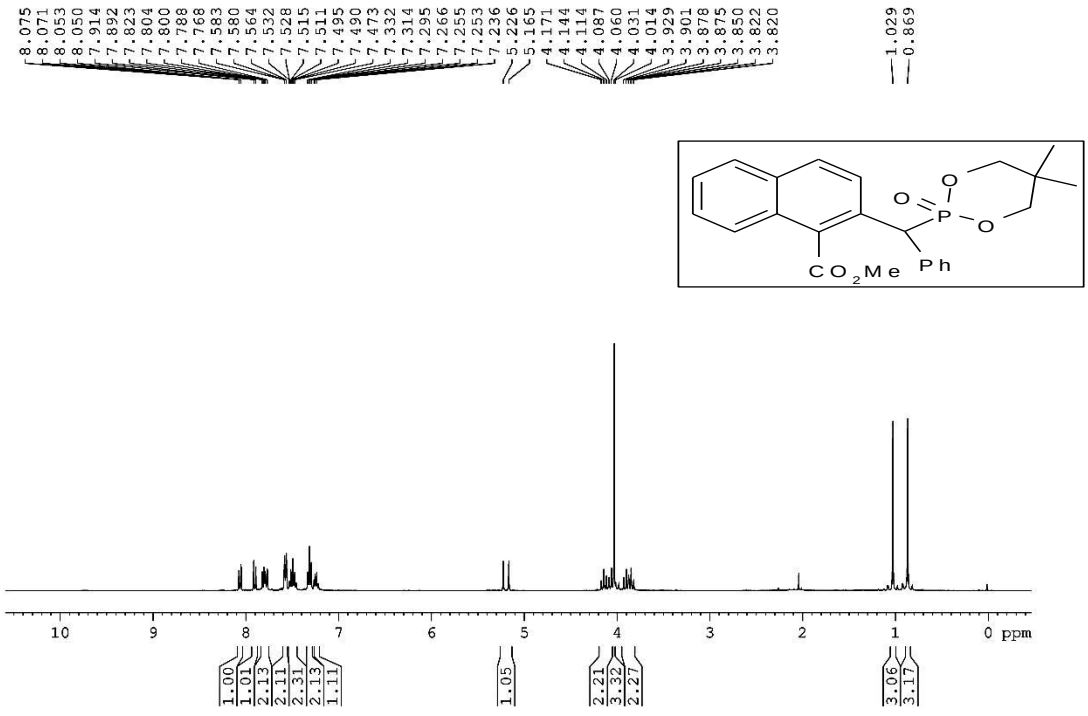


Figure S54. ^{1}H NMR spectrum of compound **3ae**

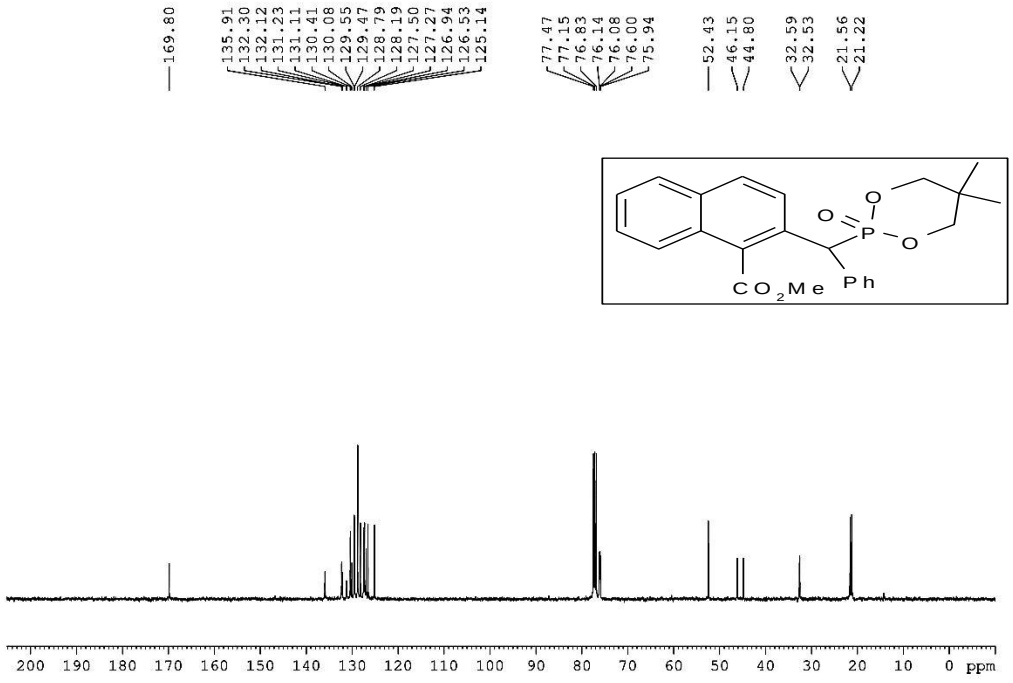


Figure S55. ^{13}C NMR spectrum of compound **3ae**

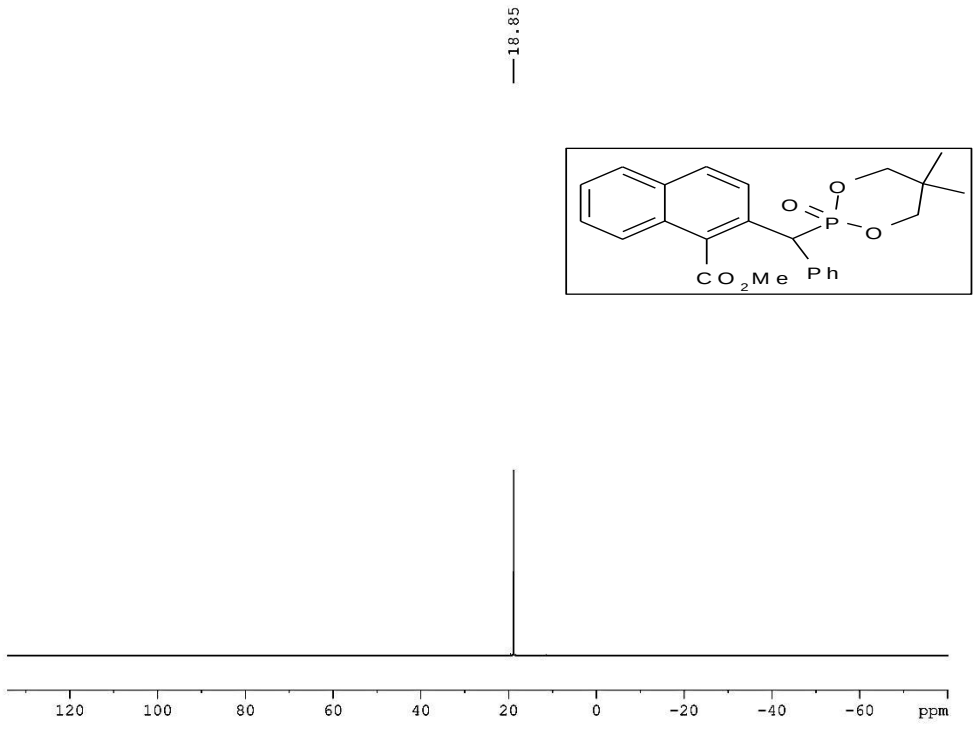


Figure S56. ^{31}P NMR spectrum of compound **3ae**

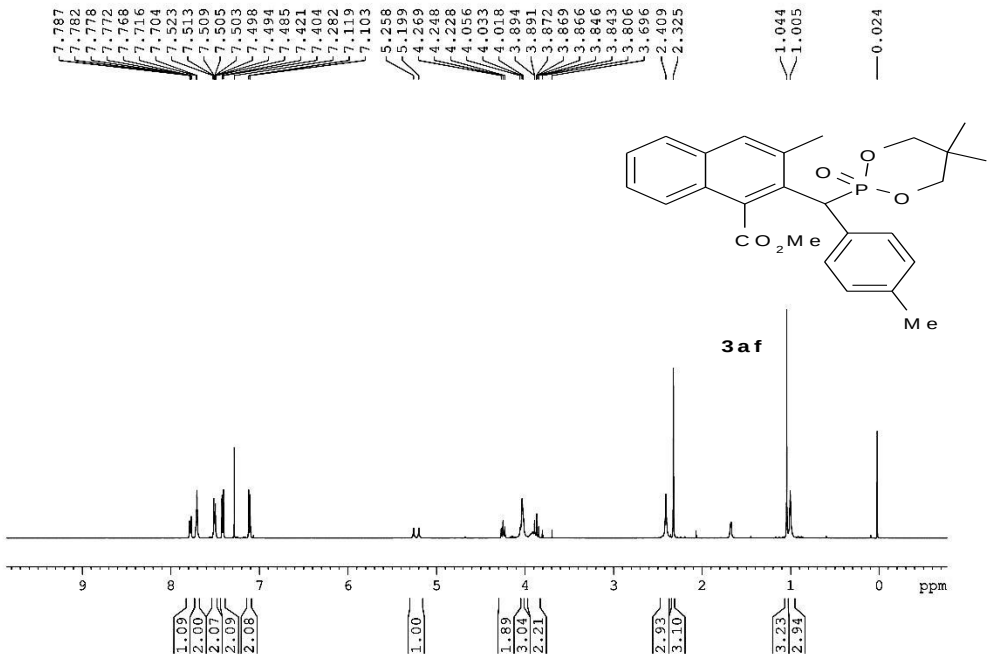


Figure S57. ^{1}H NMR spectrum of compound **3af**

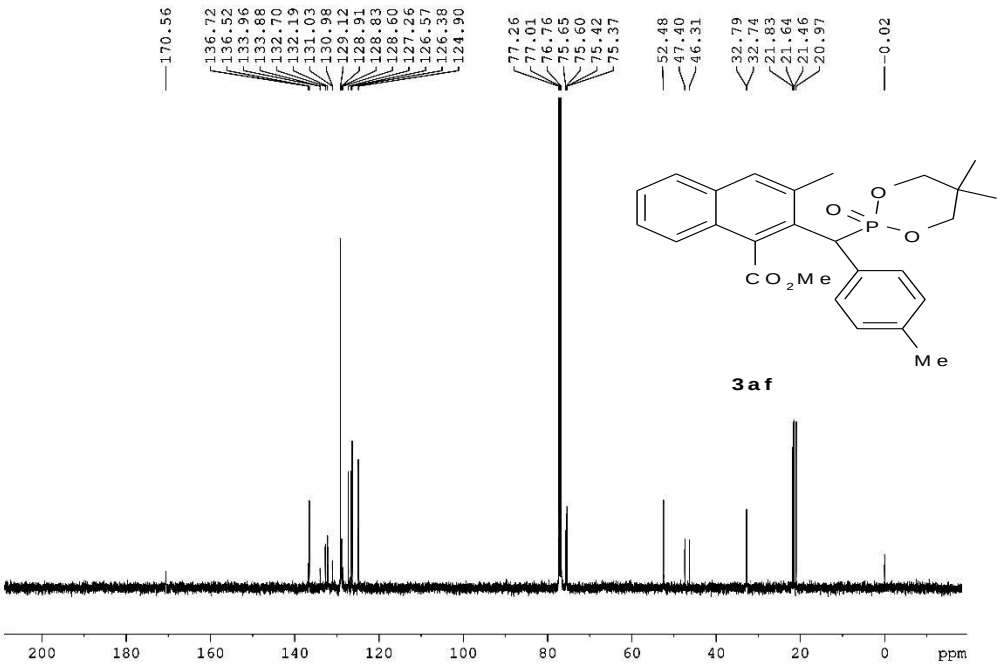


Figure S58. ^{13}C NMR spectrum of compound **3af**

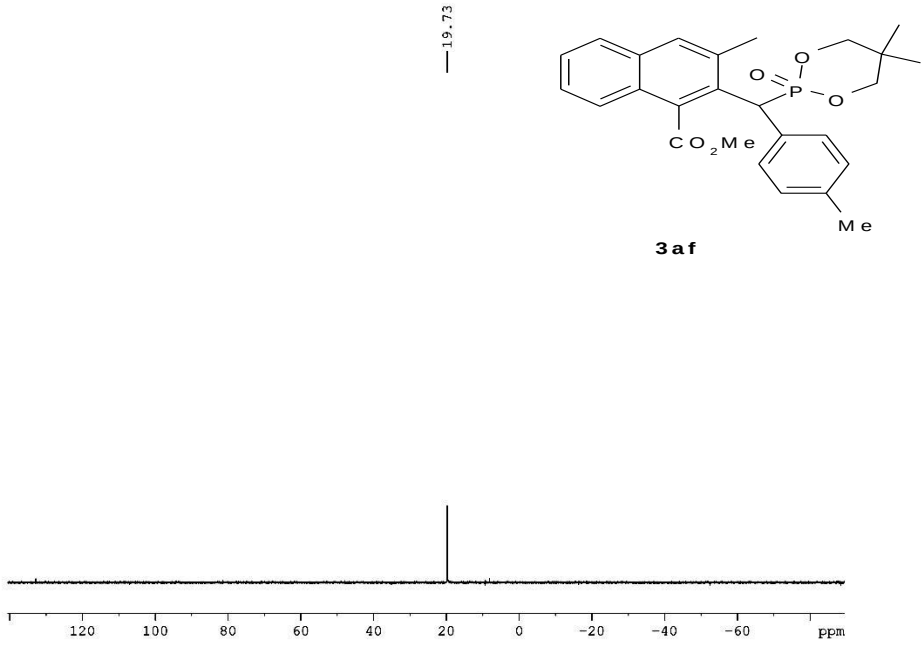


Figure S59. ^{31}P NMR spectrum of compound **3af**

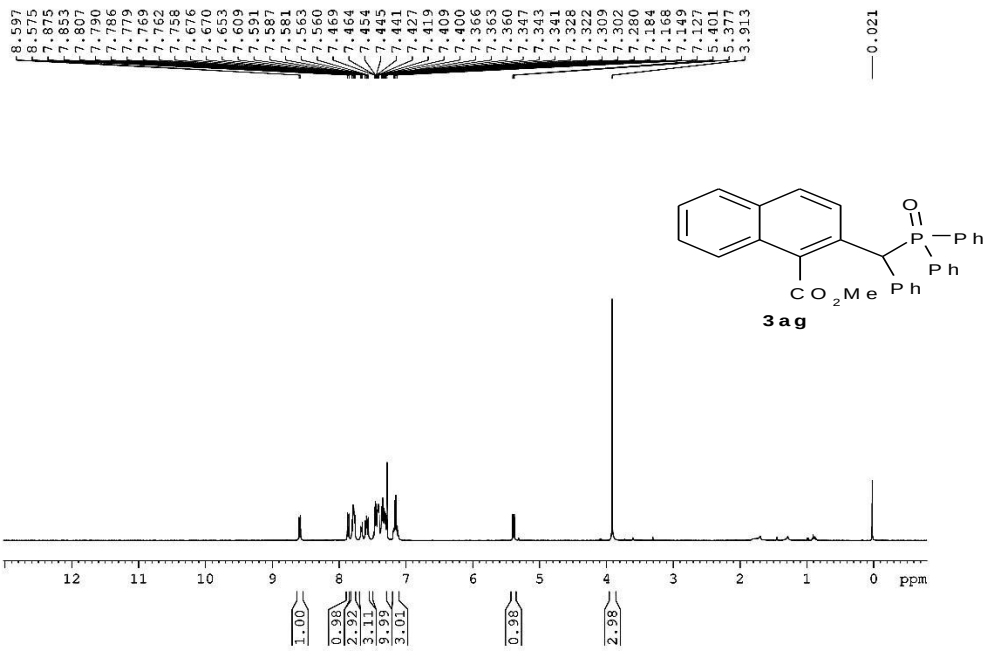


Figure S60. ^{1}H NMR spectrum of compound **3ag**

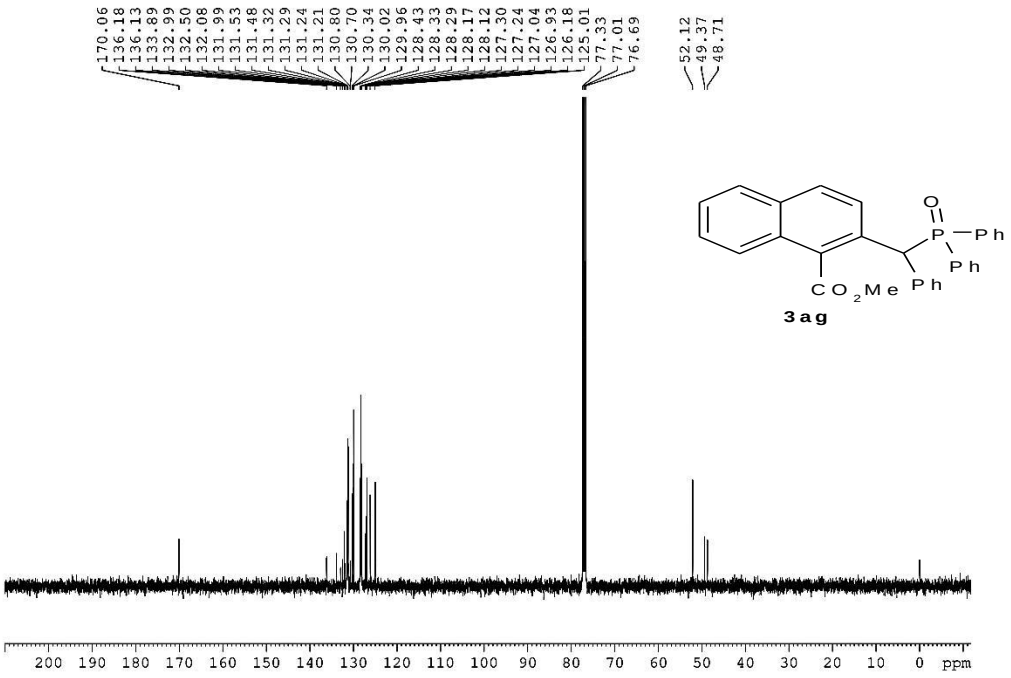


Figure S61. ^{13}C NMR spectrum of compound **3ag**

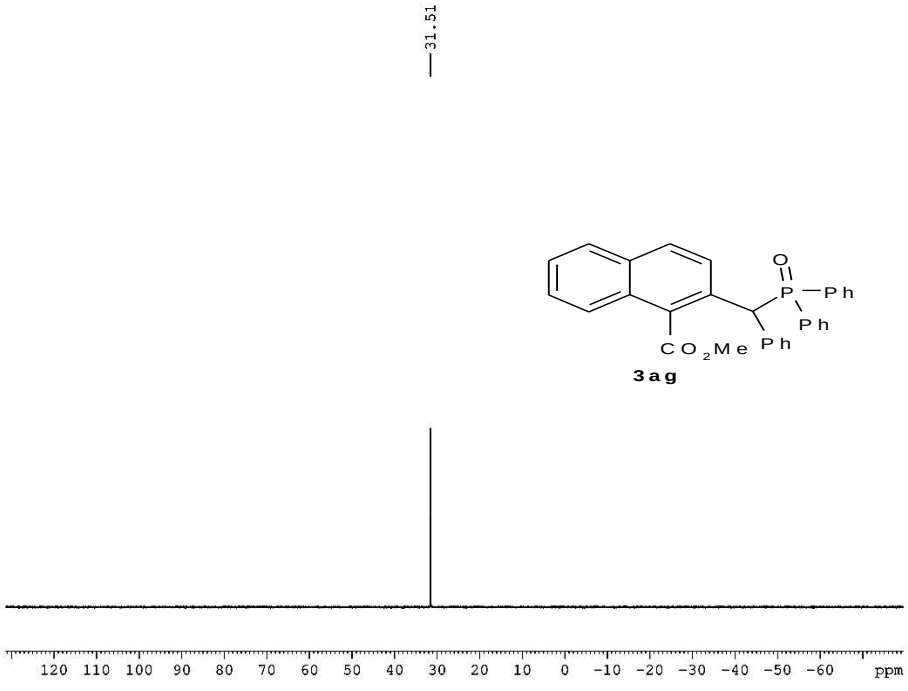


Figure S62. ^{31}P NMR spectrum of compound **3ag**

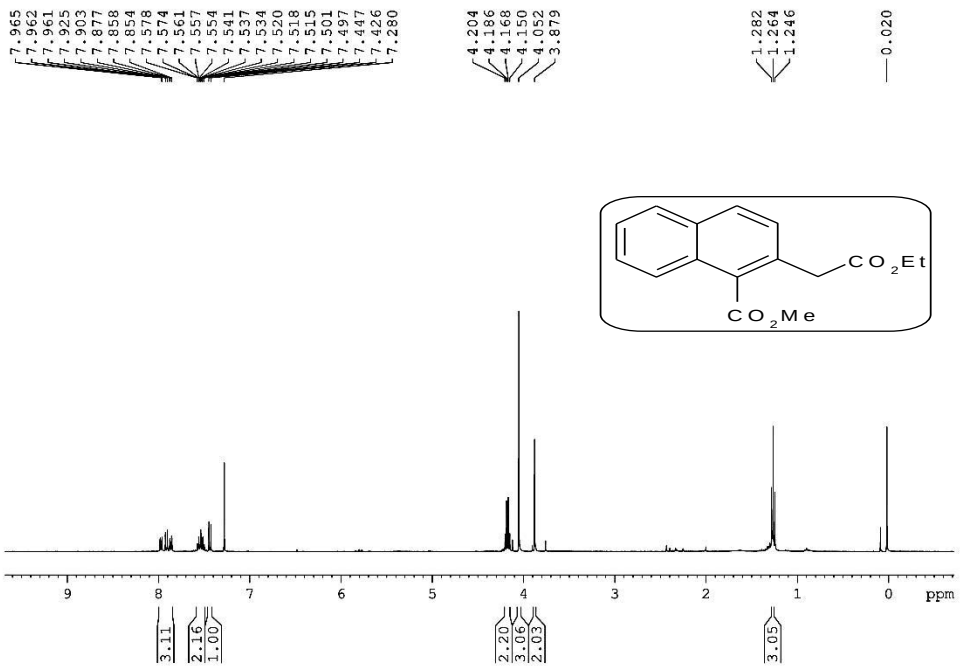


Figure S63. ^{1}H NMR spectrum of compound **3ah**

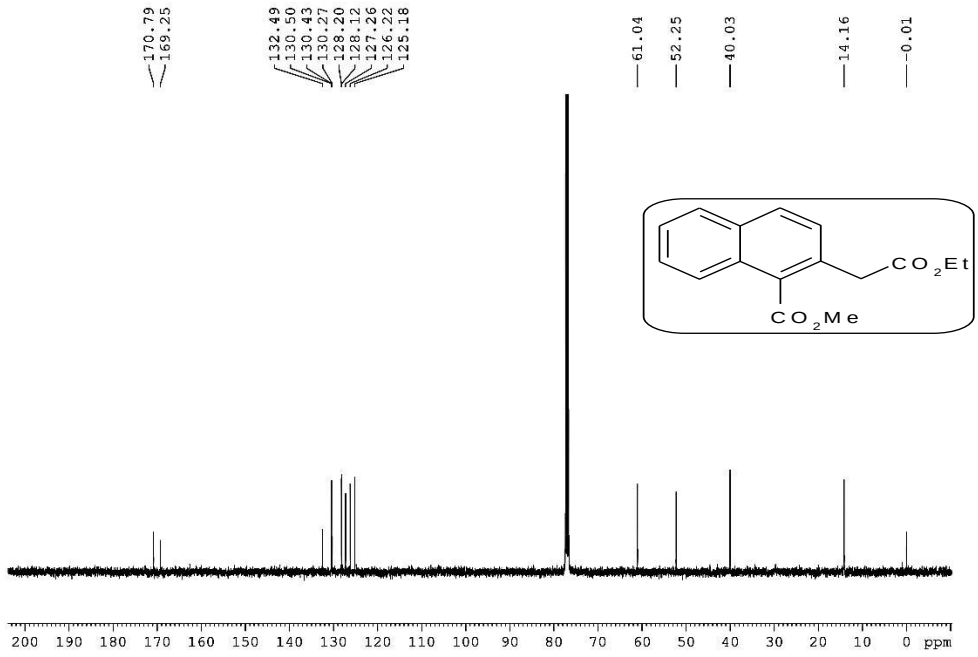


Figure S64. ^{13}C NMR spectrum of compound **3ah**

Figure S65. ^{1}H NMR spectrum of compound **4ah**

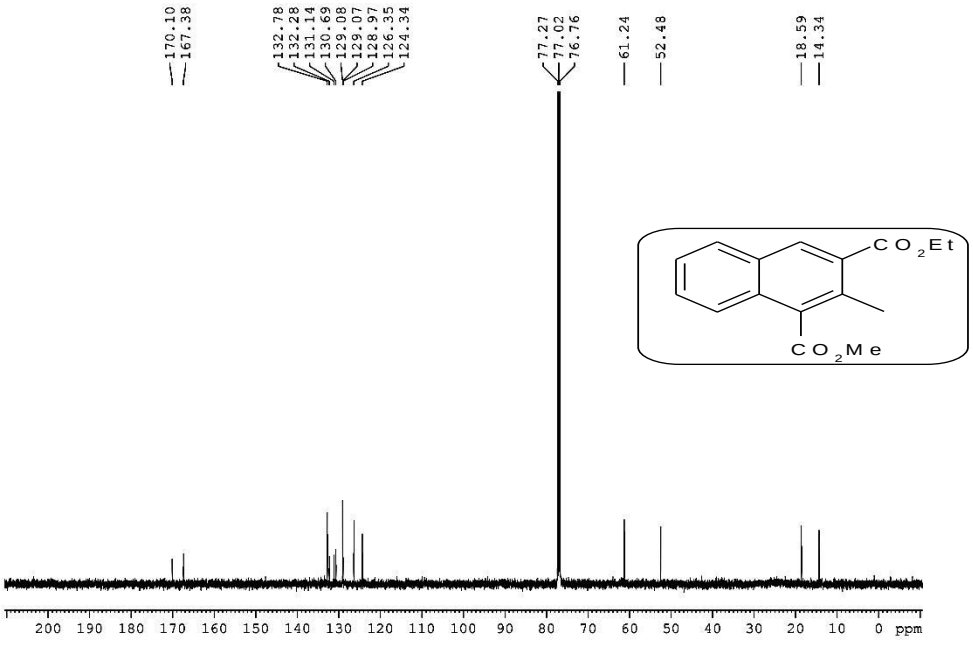


Figure S66. ^{13}C NMR spectrum of compound **4ah**

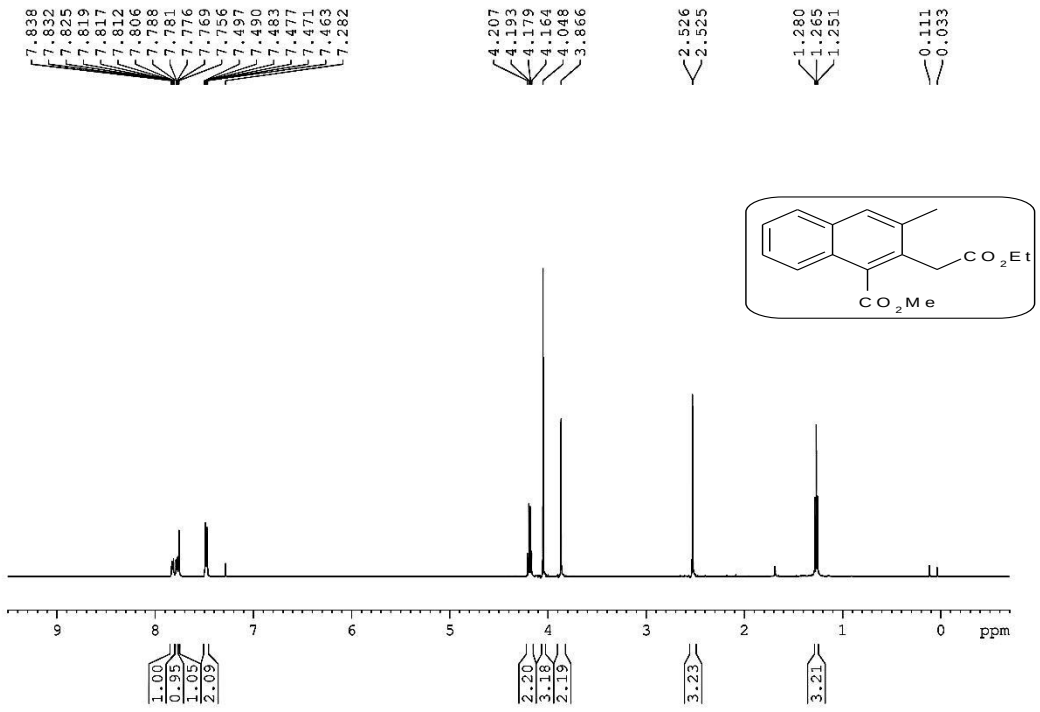


Figure S67. ^{1}H NMR spectrum of compound **3ai**

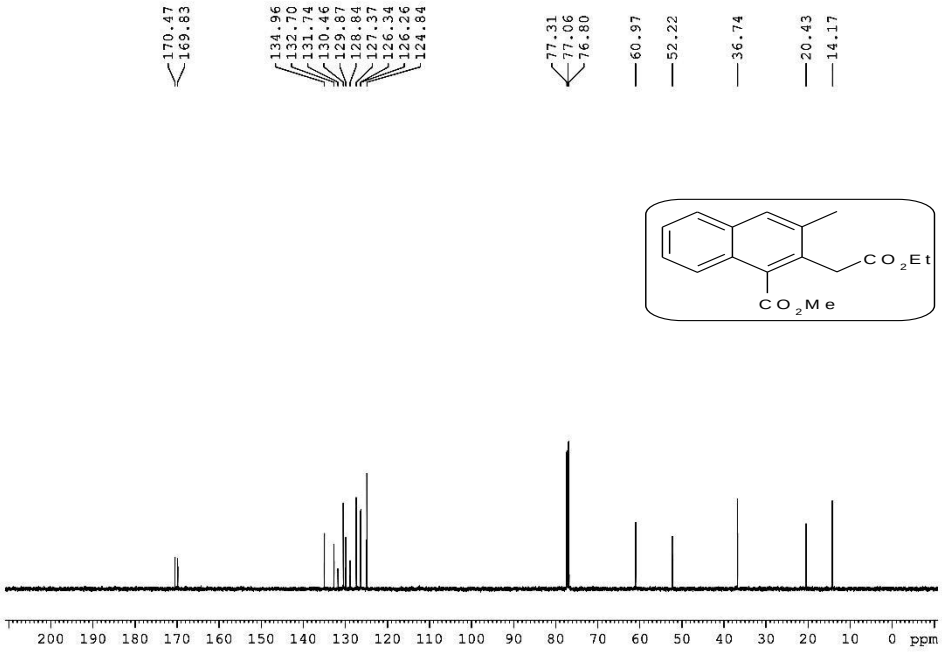


Figure S68. ^{13}C NMR spectrum of compound **3ai**

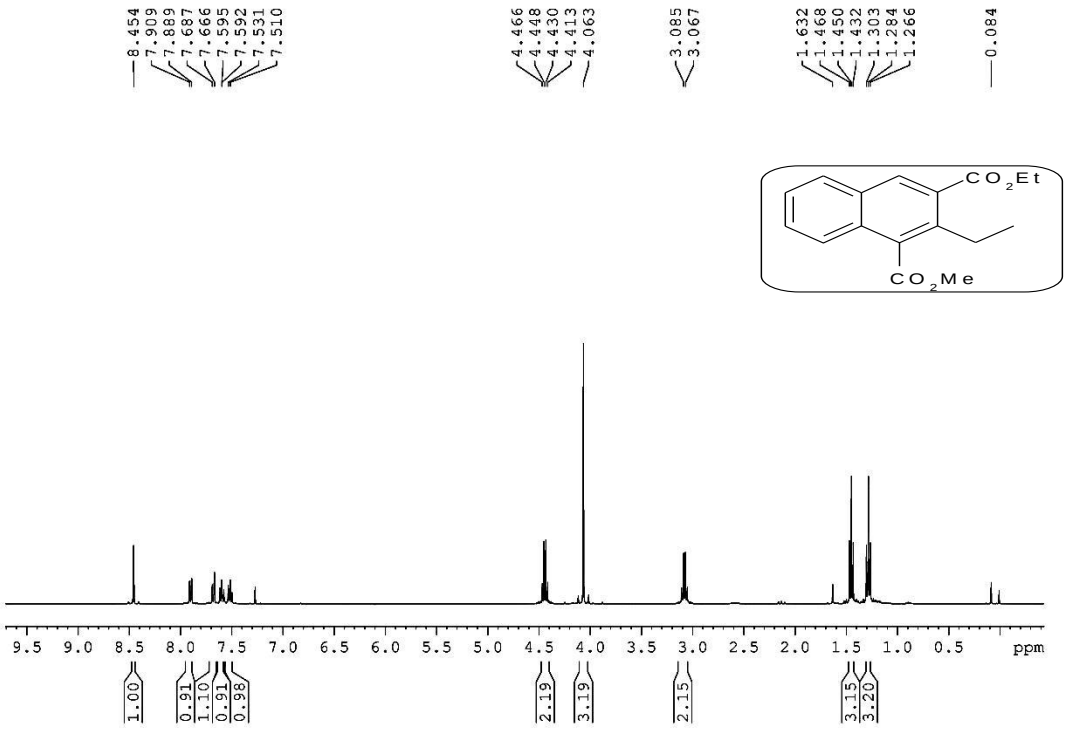


Figure S69. ^{1}H NMR spectrum of compound **4ai**

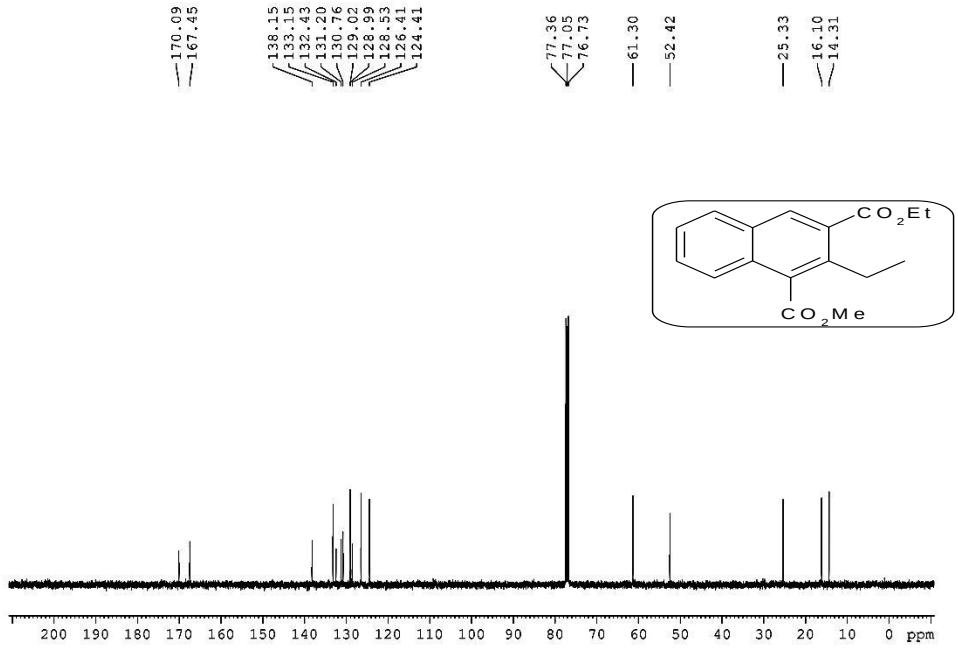


Figure S70. ^{13}C NMR spectrum of compound **4ai**

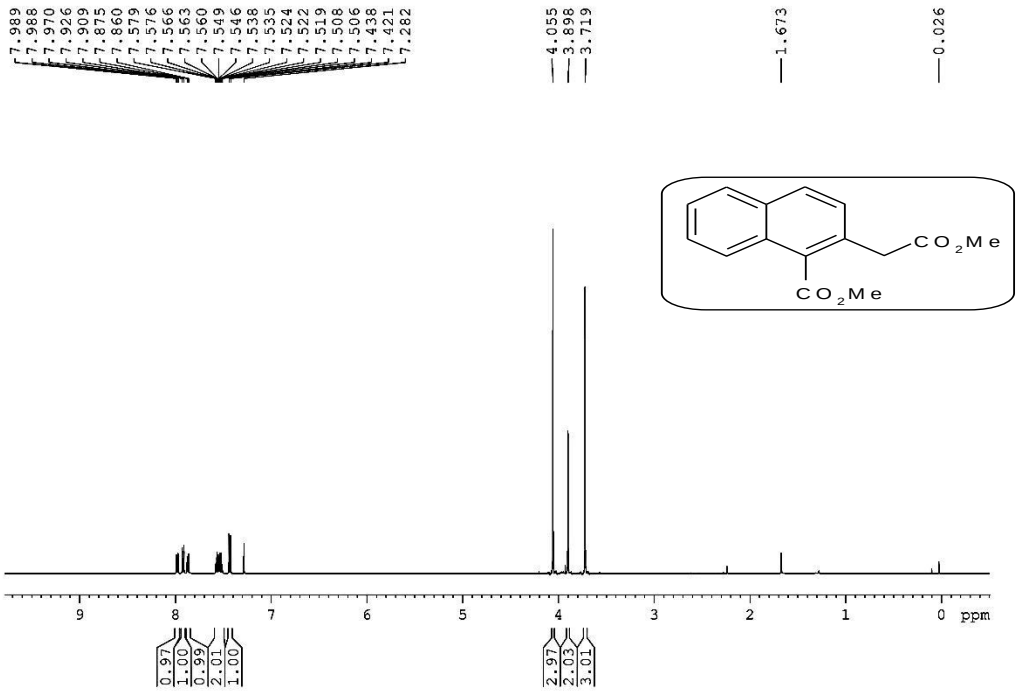


Figure S71. ^{1}H NMR spectrum of compound **3aj**

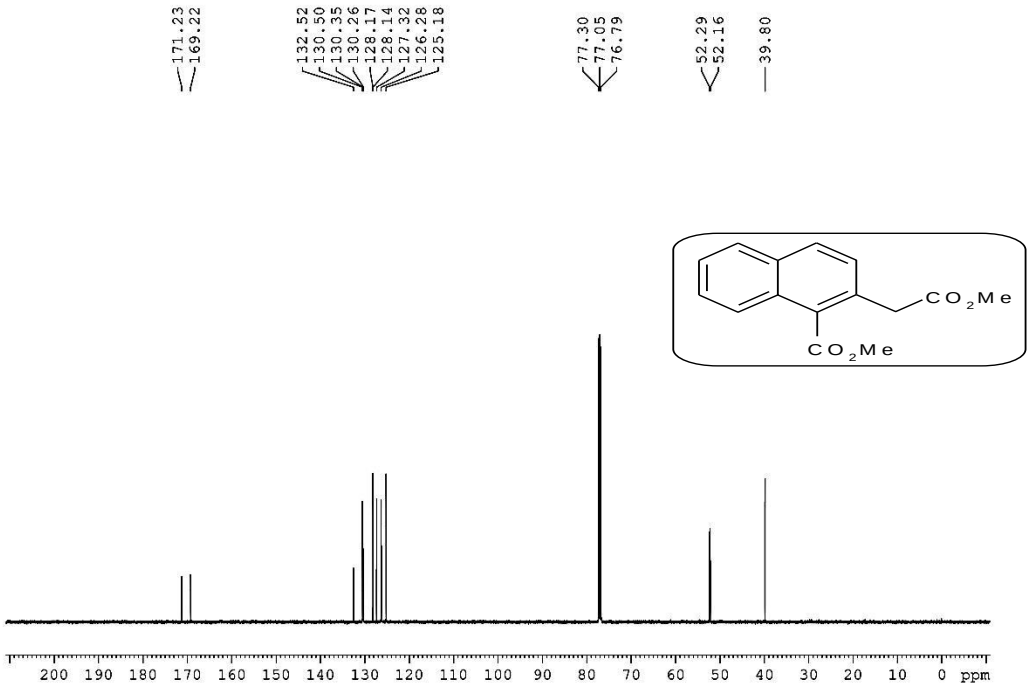


Figure S72. ^{13}C NMR spectrum of compound **3aj**

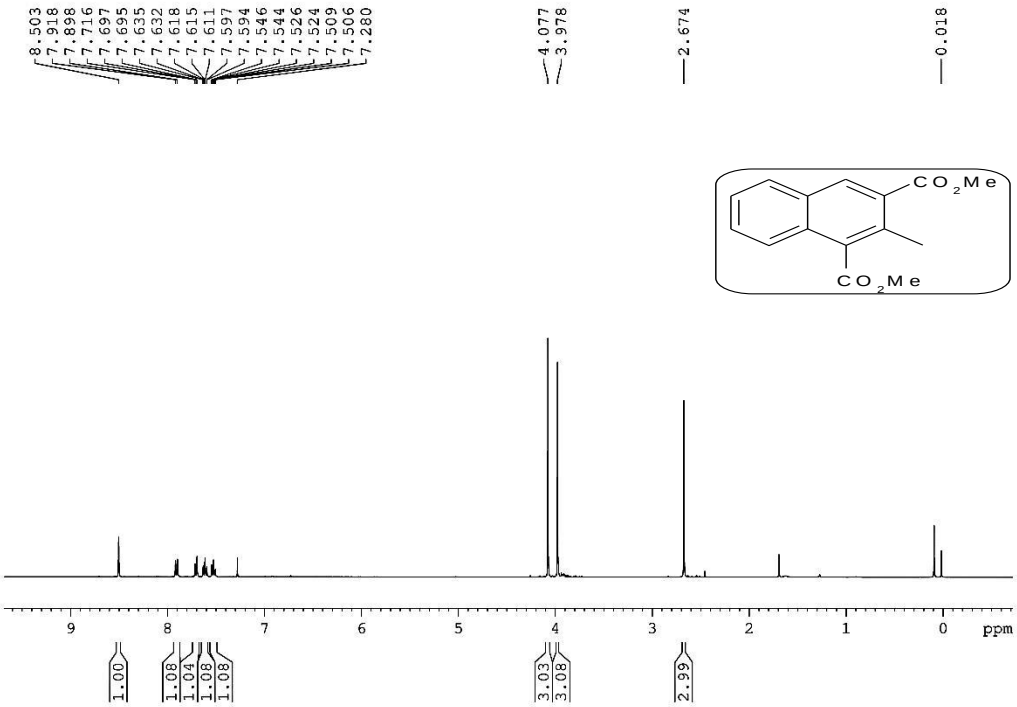


Figure S73. ^{1}H NMR spectrum of compound **4aj**

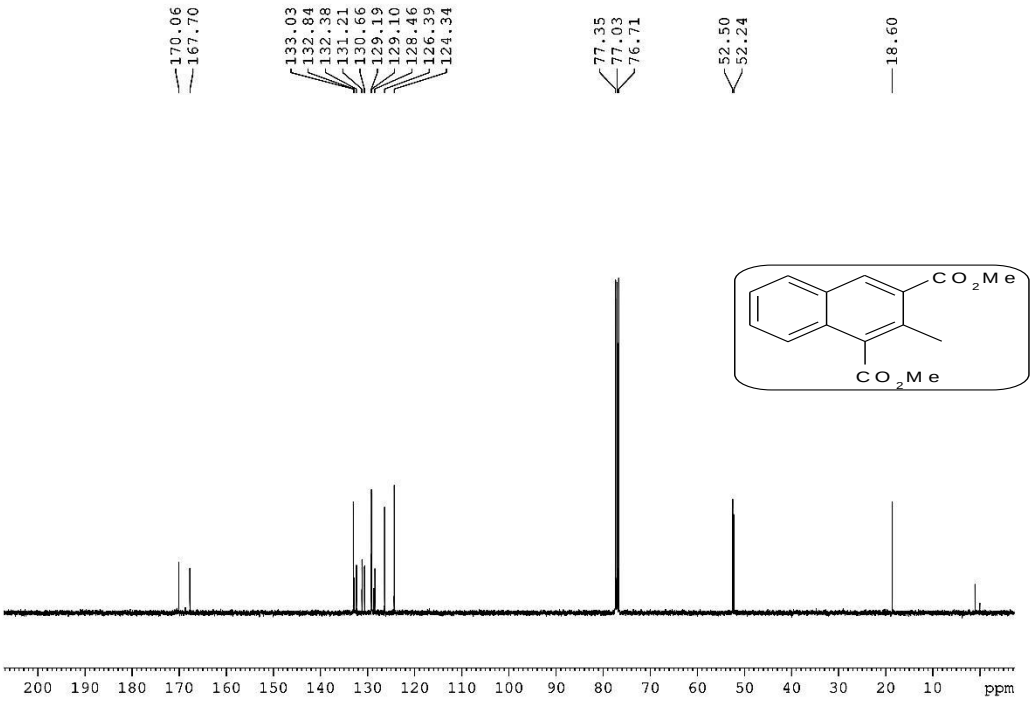


Figure S74. ^{13}C NMR spectrum of compound **4aj**

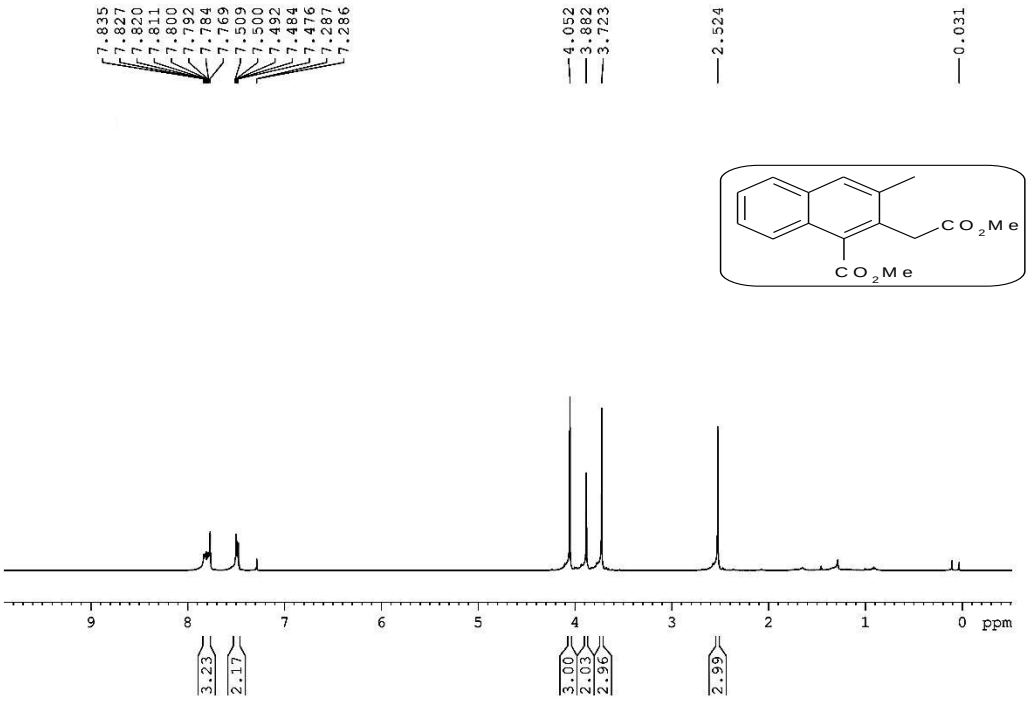


Figure S75. ^{1}H NMR spectrum of compound **3ak**

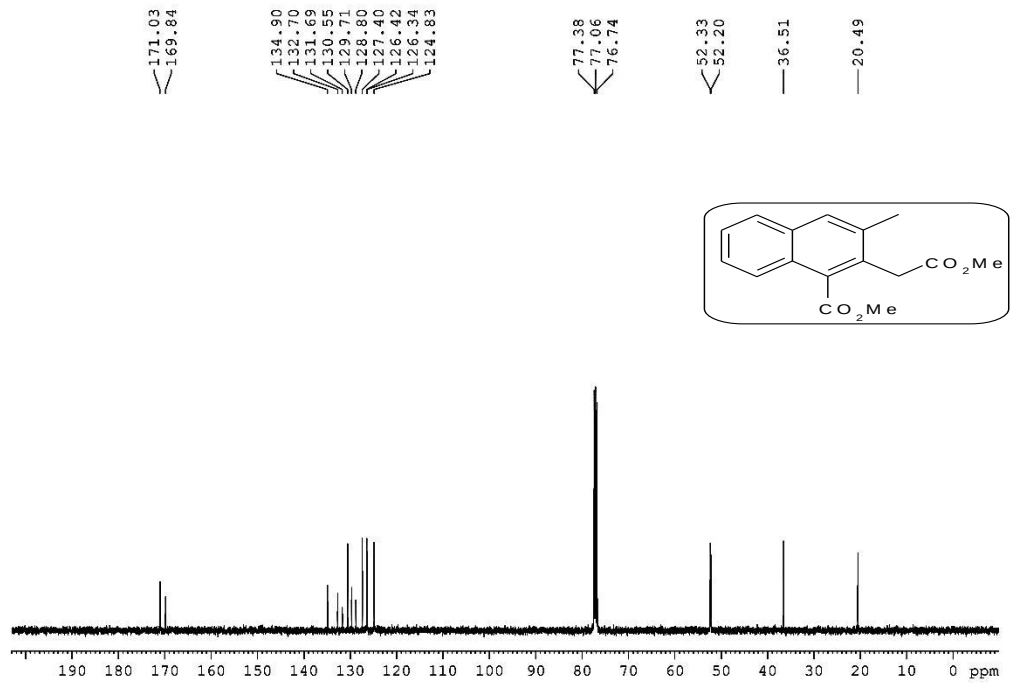


Figure S76. ^{13}C NMR spectrum of compound **3ak**

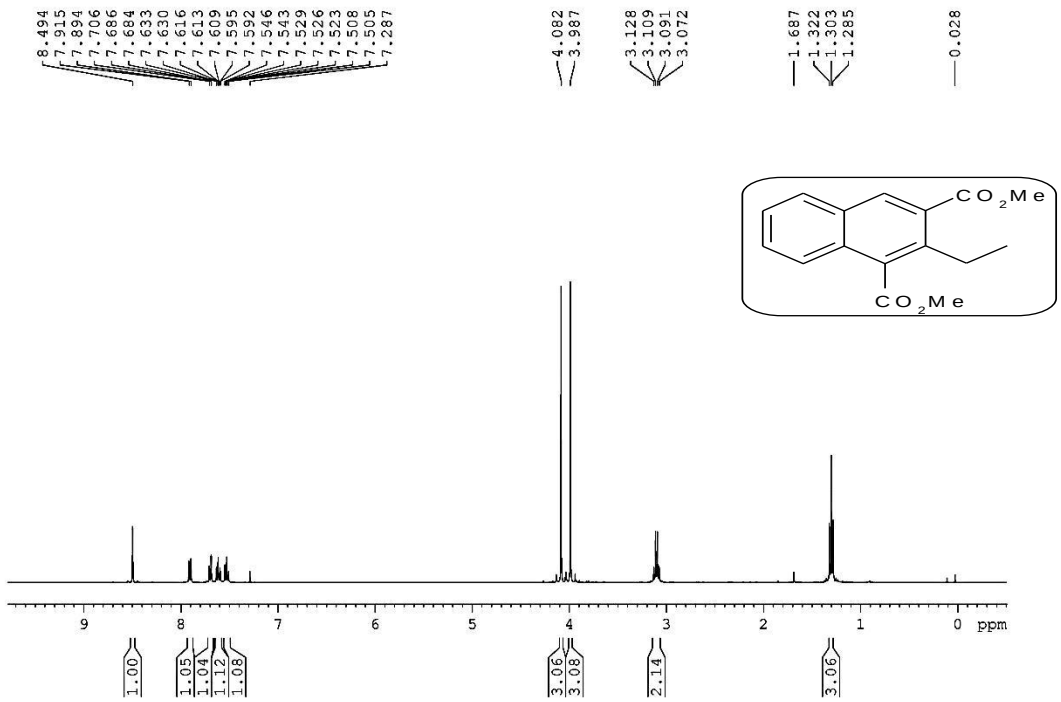


Figure S77. ^{1}H NMR spectrum of compound **4ak**

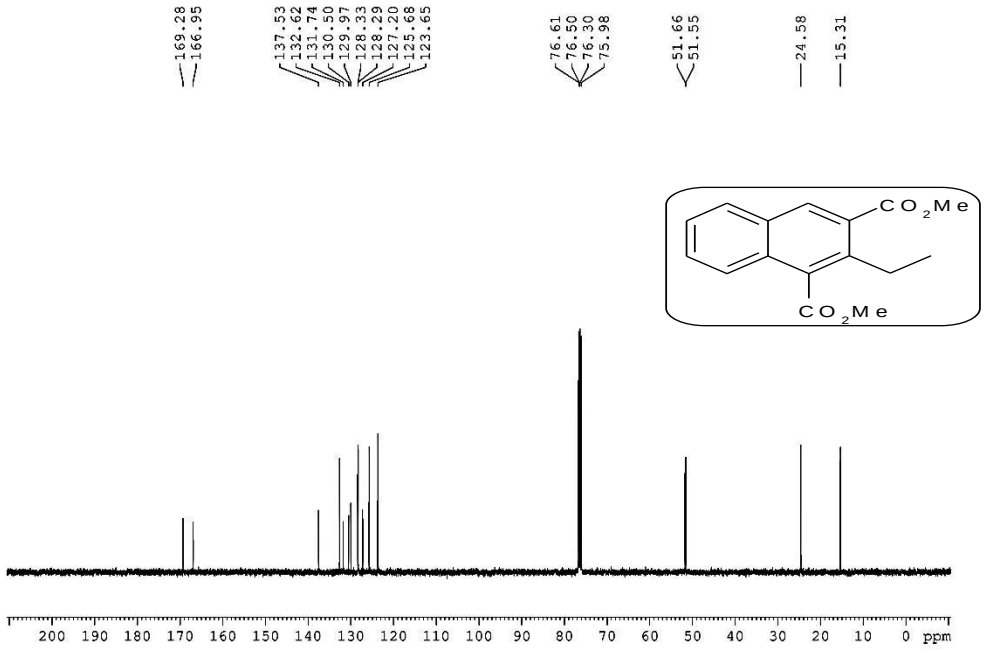


Figure S78. ^{13}C NMR spectrum of compound **4ak**

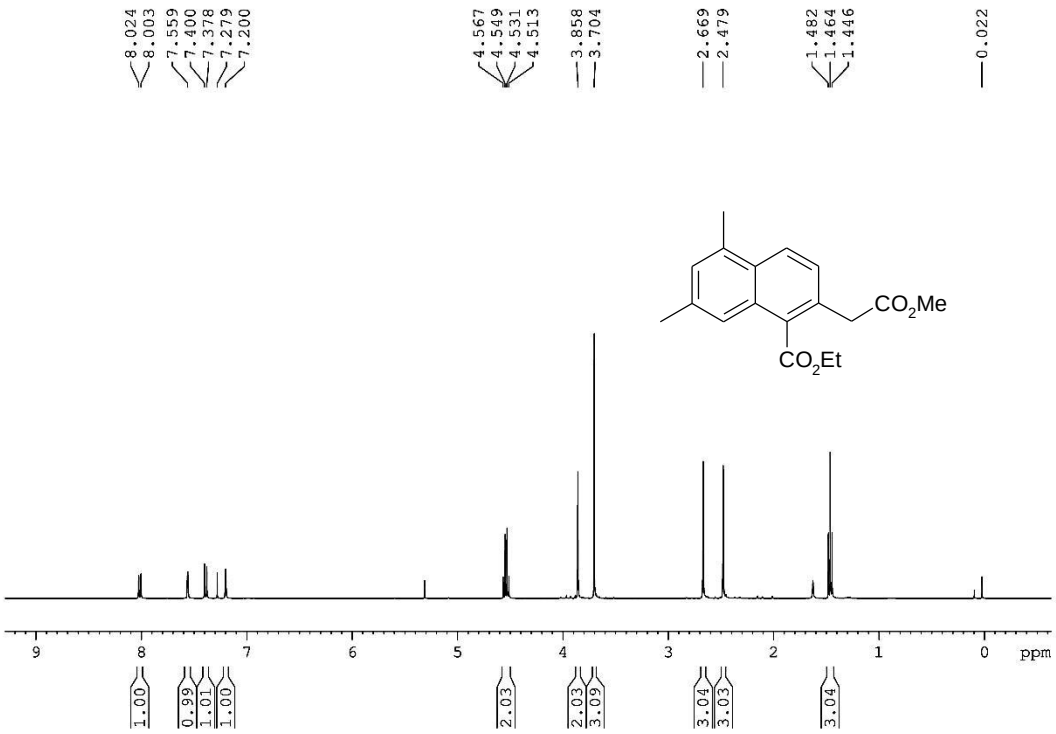


Figure S79. ^{1}H NMR spectrum of compound **3ij**

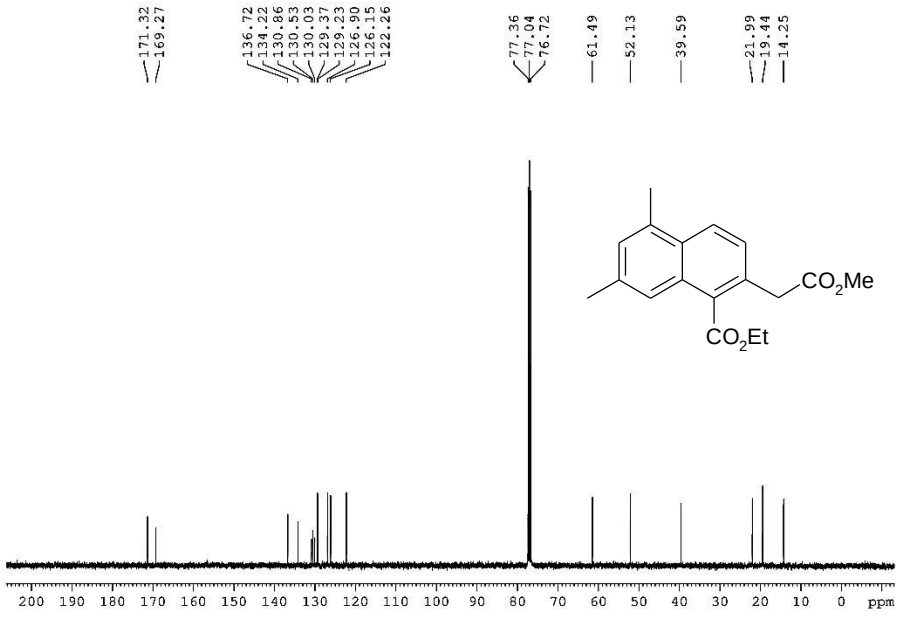


Figure S80. ^{13}C NMR spectrum of compound **3ij**

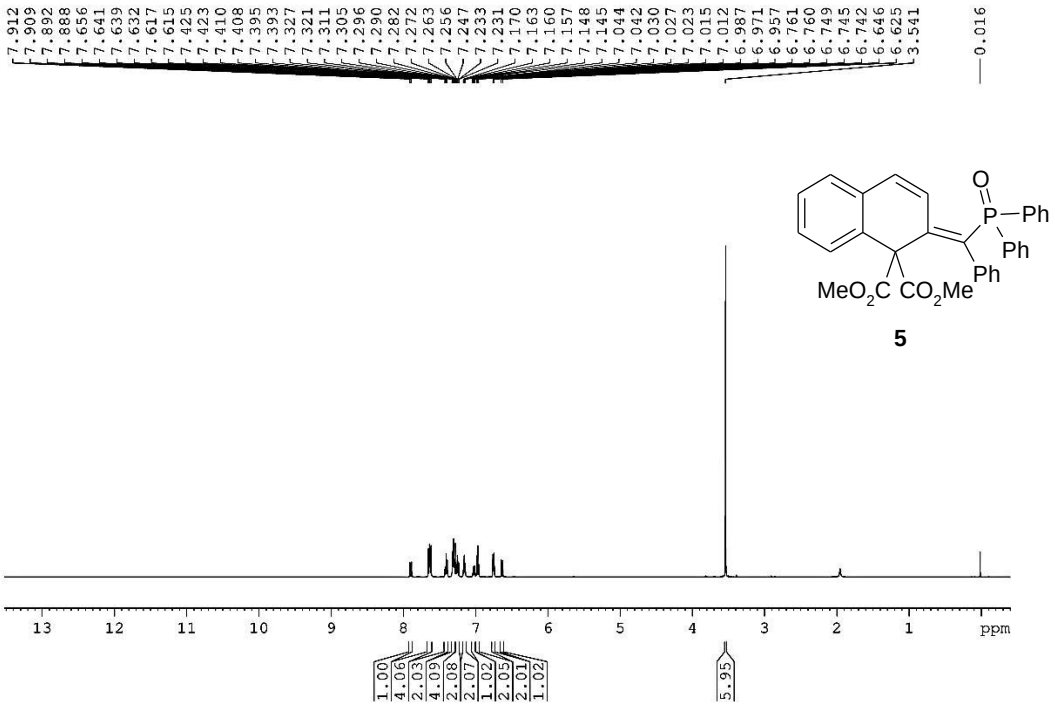


Figure S81. ^{1}H NMR spectrum of compound **5**

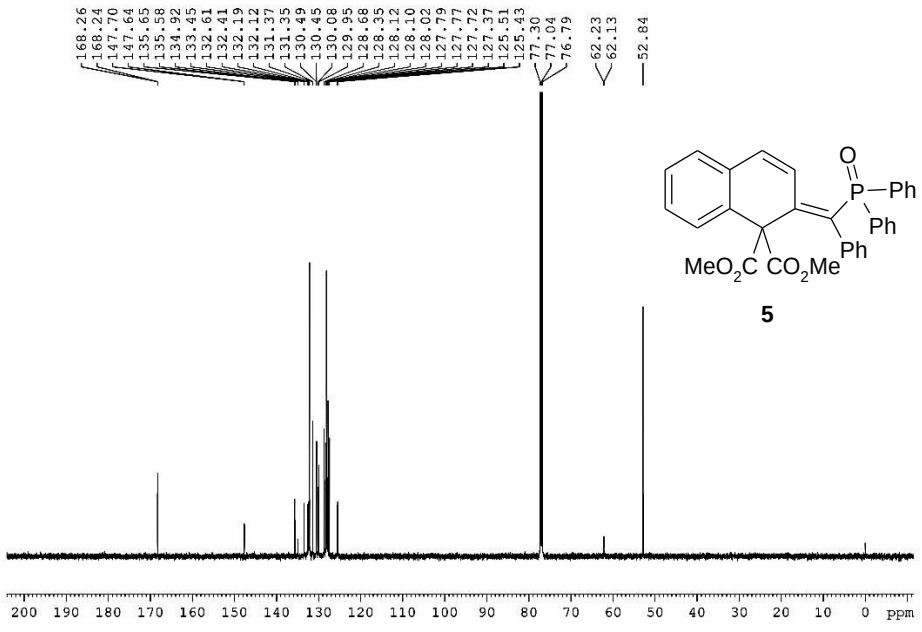


Figure S82. ^{13}C NMR spectrum of compound **5**

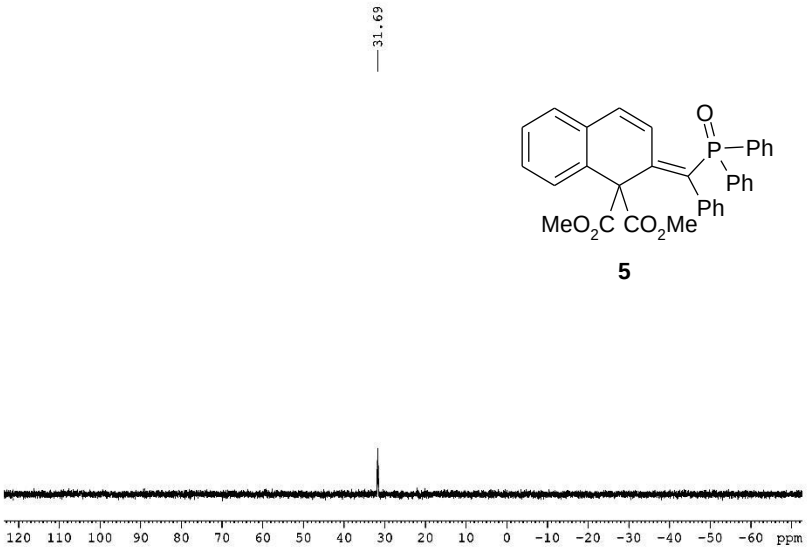


Figure S83. ^{31}P NMR spectrum of compound **5**