Electronic Supplementary Information

NHC-Gold(I) catalysed [4+2] cycloaddition/ acyclic addition of dialkyl substituted propargylic esters with 1,3-diphenylisobenzofuran: Synthesis of novel benzo[*c*]fluorenols and substituted dienes

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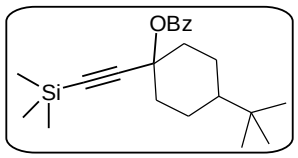
General: Solvents were dried according to known methods as appropriate.[1] ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162 MHz) were recorded using a 400 MHz spectrometer in $CDCl_3$ with shifts referenced to $SiMe_4$ (δ 0) or 85% H_3PO_4 (δ 0). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a Perkin-Elmer 240C CHN or Thermo Finnigan EA1112 CHNS analyser from School of Chemistry, University of Hyderabad, Hyderabad. Mass spectra were recorded using LC-MS and HRMS (ESI-TOF analyser) equipment.

Compounds **1a-a"**, **1c-e**, **1g** and **1k-l** are known.[2] The compound (1-ethynylcyclohexyl acetate) [cf. entry 8, Table 1] was prepared similarly.

Experimental procedures and characterisation data for compounds I-V and propargylic esters 1b, 1f, 1h-j

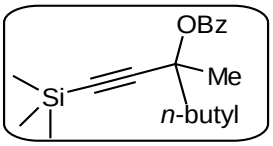
(i) Synthesis of silyl substituted propargylic esters I-V:

Compound I



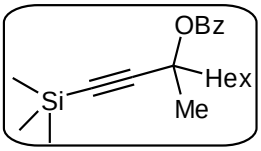
This compound was synthesised by following a literature procedure for analogous compounds.[3] Trimethylsilyl acetylene (2 mL, 14.7 mmol) was taken in dry THF (40 mL) and *n*-BuLi (9.1 mL of 1.6M solution) was added slowly at -78 ^{o}C with continuous stirring. The temperature of the reaction mixture was allowed to raise to -40 ^{o}C, maintained at this temperature for 30 min, cooled again to -78^{o}C and then and 4-*t*-butylcyclohexanone (2.23 g, 14.7 mmol) was added. After allowing the temperature to attain rt (25 ^{o}C), the mixture was stirred for 6 h and cooled to 0 ^{o}C. Benzoyl chloride (3.4 mL, 28.9 mmol) was added at 0 ^{o}C via a syringe, the mixture brought to rt and stirred for 6 h. Saturated $NaHCO_3$ solution (50 mL) was added and the solubles were extracted with ethyl acetate (2x100 mL). The organic layer was separated and washed with saturated $NaHCO_3$ solution (2x100 mL) and then by brine solution (100 mL). Solvent was removed and the crude product was purified by column chromatography by using ethyl acetate/ hexane mixture (1:50) as eluent. White solid; Yield 3.20 g (62%); %); Mp 82-84 ^{o}C; IR υ_{max} (KBr) 2959, 2865, 2169, 1715, 1599, 1452, 1369, 1276, 1112, 1024, 843, 760, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H, Si(C*H*$_3$)$_3$), 0.90 (s, 9H, (C*H*$_3$)$_3$C), 1.52-1.81 and 2.56-2.59 (m, 9H, cyclohexyl-*H*), 7.41-8.04 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1 (Si(*C*H$_3$)$_3$), 24.3, 27.6, 32.4, 37.5 and 47.1 (cyclohexyl-*C* + *C*(*C*H$_3$)$_3$), 77.4 (*C*-OBz), 92.7 and 104.6 (*C*≡*C*), 128.3, 129.7, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh); HRMS (ESI): Calcd. for $C_{22}H_{32}NaO_2Si$ [M^++Na]: *m/z* 379.2070. Found: 279.2067.

Compound II



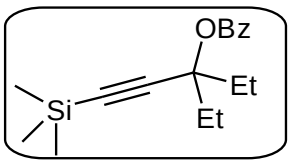
This compound was prepared by following a procedure similar to that for **I** using trimethylsilyl acetylene (2.07 g, 14.7 mmol) and 2-hexanone (1.77 g, 14.7 mmol). Colourless oil; Yield 2.63 g (60%,); IR υ_{max} (neat) 2964, 2865, 2169, 1726, 1605, 1452, 1282, 1254, 1112, 1024, 893, 843, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H, $Si(CH_3)_3$), 0.97 (t, ^{3}J(H-H) = 7.4 Hz, 3H, CH_3CH_2), 1.34-1.56 (m, 4H, butyl-*H*), 1.81 (s, 3H, CH_3), 1.95-2.11 (m, 2H, butyl-*H*), 7.41-8.04 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1 ($Si(CH_3)_3$), 14.1, 22.7, 26.5, 26.7 and 41.4 (alkyl-*C*), 76.2 (*C*-OBz), 89.6 and 105.7 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh); HRMS (ESI): Calcd. for $C_{18}H_{26}NaO_2Si$ $[M^{+}+Na]$: *m/z* 325.1600. Found: 325.1599.

Compound III



This compound was prepared by following a procedure similar to that for **I** using trimethylsilyl acetylene (1.38 g, 14.7 mmol), 2-octanone (2.1 ml, 14.7 mmol). Colourless oil; Yield 2.47 g (54%,); IR υ_{max} (Neat): 29540, 2928, 2861, 2172, 1727, 1447, 1276, 1116, 1069, 1027, 847, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H, $Si(CH_3)_3$), 0.92 (t, ^{3}J(H-H) = 6.6 Hz, 3H, CH_3CH_2), 1.33-1.61 and 1.80-2.11 (m, 13H, Hexyl-*H* + CH_3), 7.41-8.03 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0 ($Si(CH_3)_3$), 14.2, 22.6, 24.2, 26.7, 29.3, 31.7, 41.7 (Hexyl-*C* + CH_3), 76.2 (*C*-OBz), 89.7 and 105.7 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh); HRMS (ESI) :Calcd. for $C_{20}H_{30}SiO_2$ $[M^{+}+Na]$: *m/z* 353.1913. Found: 353.1913.

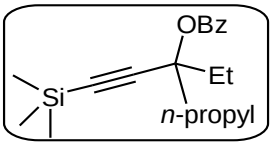
Compound IV



This compound was prepared by following a procedure similar to that for **I** using trimethylsilyl acetylene (1.38 g, 14.7 mmol), 3-pentanone (1.5 mL, 14.7 mmol). Colourless oil; Yield 2.35 g

(56%,); IR υ_{max} (Neat) 2970, 2934, 2882, 2158, 1723, 1454, 1273, 1102, 1071, 1024, 843, 766, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.01 (s, 9H, $Si(CH_3)_3$), 1.05 (t, ^3J(H-H) = 7.4 Hz, 3H, CH_3CH_2), 2.00-2.23 (m, 4H, CH_3CH_2), 7.42-8.04 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0 ($Si(CH_3)_3$), 8.6 (CH_3CH_2), 31.1 (CH_3CH_2), 80.8 (CEt_2), 90.8, 104.6 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh); HRMS (ESI): Calcd. for $C_{17}H_{24}NaO_2Si$ [M^++Na]: *m/z* 311.1444. Found: 311.1446.

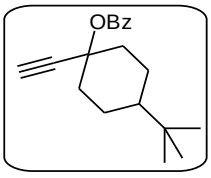
Compound V



This compound was prepared by following a procedure similar to that for **I** using trimethylsilyl acetylene (1.38 g, 14.7 mmol), 3-hexanone (1.77 g, 14.7 mmol). Colourless oil; Yield 2.37 g (54%); IR υ_{max} (neat): 2961, 2937, 2877, 2164, 1728, 1606, 1451, 1274, 1107, 1069, 1026, 845, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):δ 0.19 (s, 9H, $Si(CH_3)_3$), 0.97 and 1.05 (2 t, ^3J(H-H) = 7.4 Hz each, 6H, CH_3CH_2), 1.51-1.55 and 1.20-2.20 (m, 6H, alkyl-*H*), 7.41-8.03 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0 ($Si(CH_3)_3$), 8.6, 14.3, 17.5, 31.6 and 40.3 (alkyl-*C*), 80.3 (*C*-OBz), 90.7 and 104.8 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh); HRMS (ESI): Calcd. for $C_{18}H_{26}NaO_2Si$ [M^++Na]: *m/z* 325.1600. Found: 325.1596.

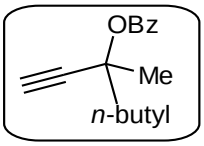
(ii) Synthesis of propargylic esters:

Compound 1b



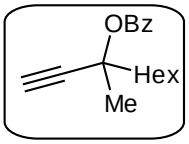
This compound[4] was obtained by desilylation[5] of the silyl substituted propargylic ester **I** (1.00 g, 2.8 mmol) in dry THF (15 ml) by adding TBAF (0.74 g, 2.8 mmol) at 0 ^oC. The reaction mixture was stirred for 1 h at rt. Solvent was removed under vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane mixtue (1:20) as the eluent. Yield 0.700 g (88%).

Compound 1f



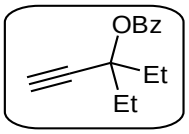
This compound was prepared by following a route similar to that for **1b** using **II** (2.00 g, 6.6 mmol). Colourless oil; Yield 1.36 g (89%); IR υ_{max} (neat): 3310, 3063, 2953, 2932, 2866, 2115, 1721, 1458, 1375, 1277, 1112, 1069, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$):δ 0.96 (t, ^{3}J(H-H) = 7.4 Hz, 3H, CH_3CH$_2$), 1.33-1.44 and 1.55-1.99 (m, 9H, butyl-*H* + CH_3), 2.61 (s, 1H, ≡C*H*), 7.42-8.04 (m, 5H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.7, 26.3, 26.6 and 41.4 (butyl-*C* + *C*H$_3$), 73.5 (*C*-OBz), 75.5 and 83.9 (*C*≡*C*), 128.3, 129.6, 131.0, 132.8 (Ar-*C*), 164.7 (O*C*OPh). HRMS (ESI): Calcd. for $C_{15}H_{18}NaO_2$ [M^++Na]: *m/z* 253.1203. Found: 253.1205.

Compound 1h



This compound was prepared by following a route similar to that for **1b** using **III** (0.75 g, 2.4 mmol). Colourless oil; Yield 0.540 g (87%); IR υ_{max} (Neat): 3304, 2959, 2926, 2867, 2115, 1721, 1600, 1452, 1375, 1271, 1107, 1025, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, ^{3}J(H-H) = 6.6 Hz, 3H, CH_3CH$_2$), 1.33-1.62 and 1.82-2.11 (m, 13H, Hexyl-*H* + CH_3), 2.61 (s, 1H, ≡C*H*), 7.41-8.03 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 24.1, 26.6, 29.3, 31.7 and 41.7 (Hexyl-*C* + *C*H$_3$), 73.5 (*C*-OBz), 75.5 and 84.0 (*C*≡*C*), 128.3, 129.6, 130.9, 132.9 (Ar-*C*), 164.8 (O*C*OPh); HRMS (ESI): Calcd. for $C_{17}H_{22}NaO_2$ [M^++Na]: *m/z* 281.1518. Found: 281.1531.

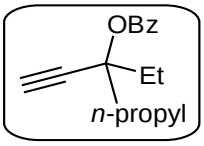
Compound 1i



This compound was prepared by following a route similar to that for **1b** using **IV** (0.85 g, 3.0 mmol). Colourless oil; Yield 0.55 g (84%); IR υ_{max} (Neat): 3301, 3265, 2975, 2934, 2877, 2111, 1723, 1599, 1449, 1268, 1107, 1071, 1030, 916, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07

(t, ^{3}J(H-H) = 7.4 Hz, 3H, CH_3CH$_2$), 2.05-2.24 (m, 4H, CH$_3$CH_2), 2.62 (s, 1H, ≡C*H*), 7.41-8.04 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.3 (*C*H$_3$CH$_2$), 30.9 (CH$_3$*C*H$_2$), 74.3 (*C*Et$_2$), 79.8, 82.9 (*C*≡*C*), 128.3, 129.5, 130.9, 132.8 (Ar-*C*), 164.7 (O*C*OPh); HRMS (ESI): Calcd. for $C_{14}H_{16}NaO_2$ [M^++Na]: *m/z* 239.1048. Found: 239.1048.

Compound 1j



This compound was prepared by following a route similar to that for **1b** using **V** (2.00 g, 6.6 mmol). Colourless oil; Yield 1.40 g (92%); IR υ_{max} (neat): 3304, 3260, 3063, 2959, 2931, 2871, 2121, 1726, 1605, 1452, 1271, 1177, 1101, 1030, 931 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 and 1.08 (2 t, ^{3}J(H-H) = 7.4 Hz each, 6H, CH_3CH$_2$), 1.51-1.60 and 1.96-2.24 (m, 6H, alkyl-*H*), 2.62 (s, 1H, ≡C*H*), 7.42-8.04 (m, 5H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.4, 14.2, 17.4, 31.5 and 40.2 (alkyl-*C*), 74.3 (*C*-OBz), 79.5 and 83.2 (*C*≡*C*), 128.3, 129.6, 131.0, 132.9 (Ar-*C*), 164.7 (O*C*OPh); HRMS (ESI): Calcd. for $C_{15}H_{18}NaO_2$ [M^++Na]: *m/z* 253.1203. Found: 253.1203.

(iii) **NMR spectra for the all new compounds**

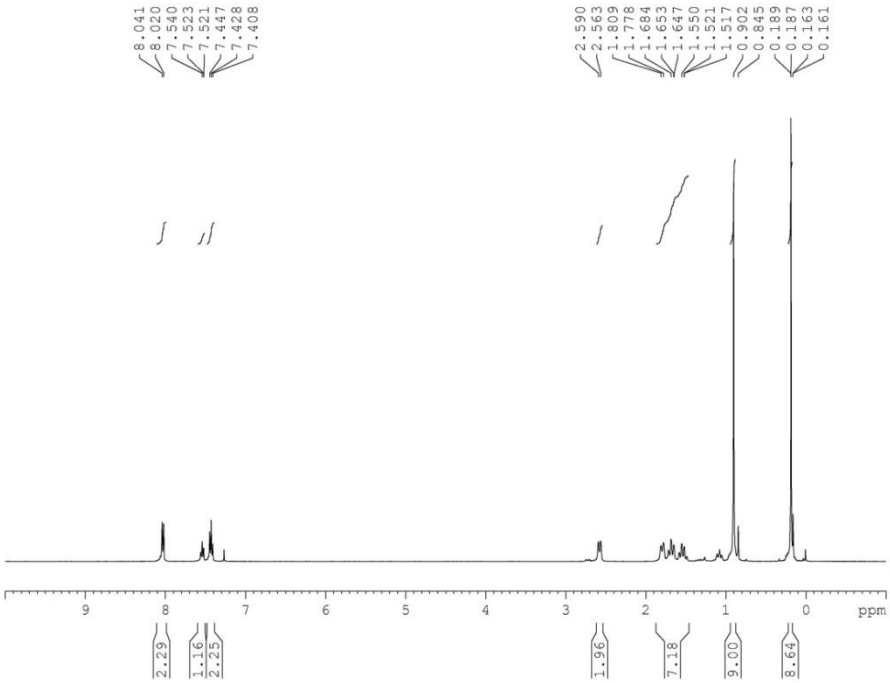


Figure S1. ^{1}H NMR spectrum of compound **I**

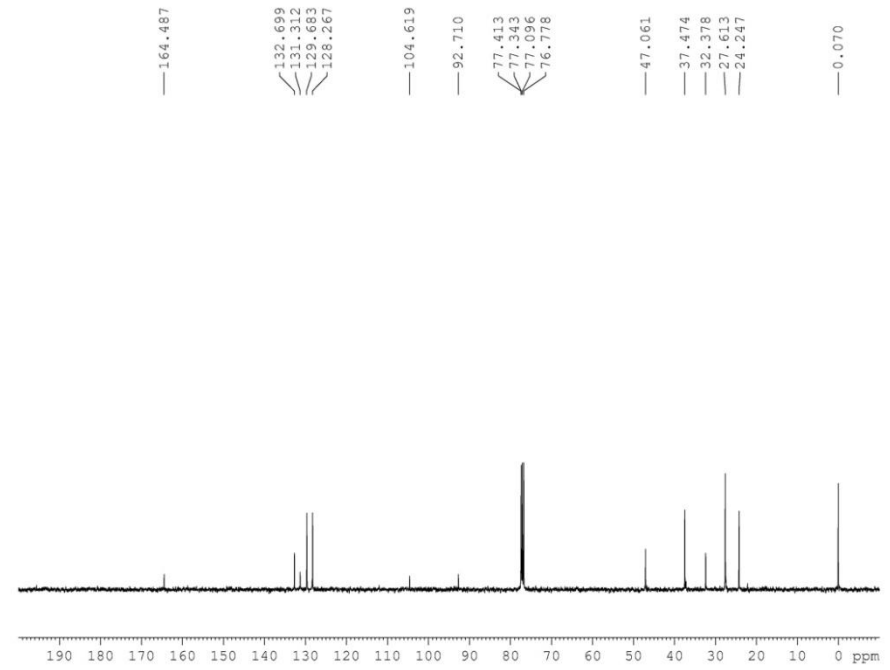


Figure S2. ^{13}C NMR spectrum of compound **I**

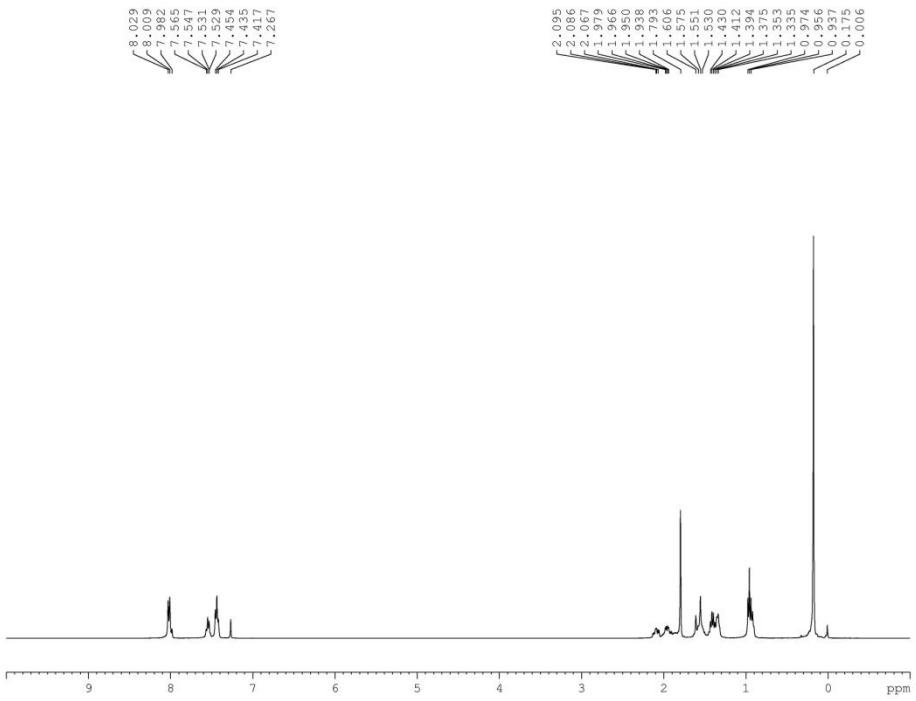


Figure S3. ^{1}H NMR spectrum of compound **II**

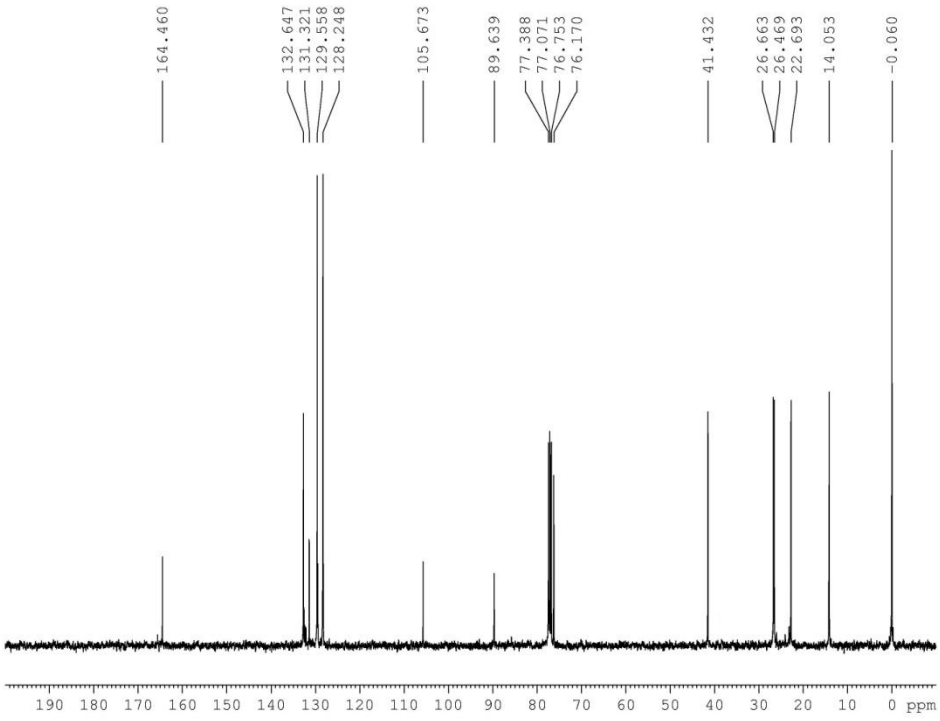


Figure S4. ^{13}C NMR spectrum of compound **II**

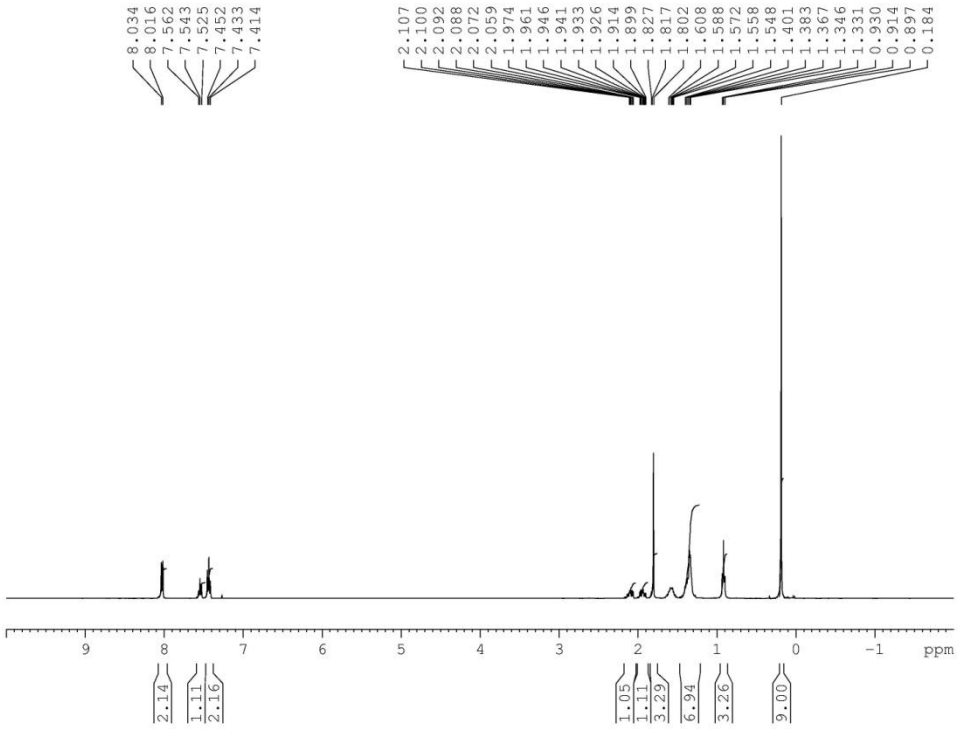


Figure S5. ^{1}H NMR spectrum of compound **III**

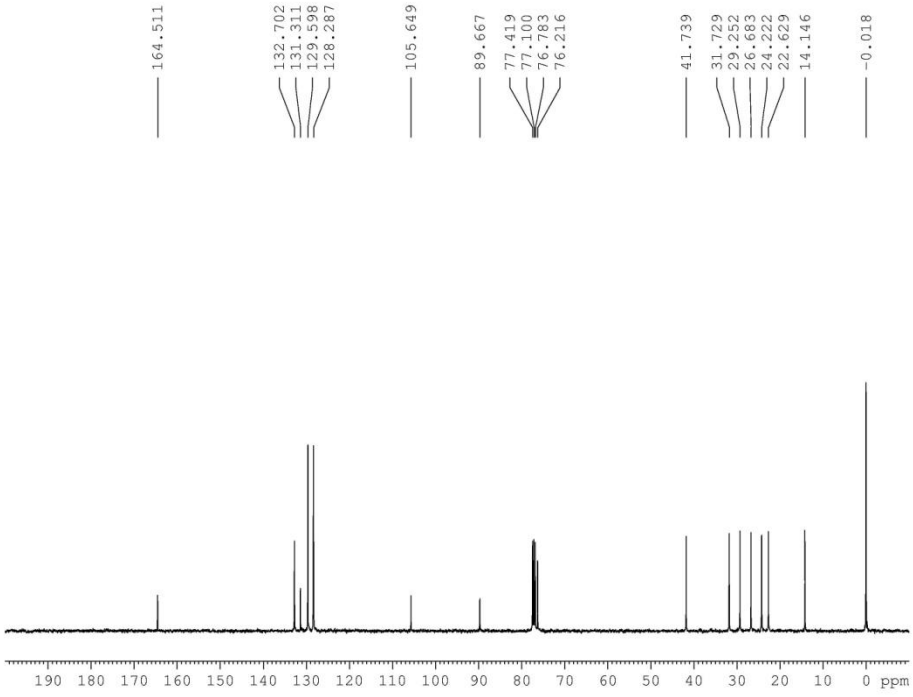


Figure S6. ^{13}C NMR spectrum of compound **III**

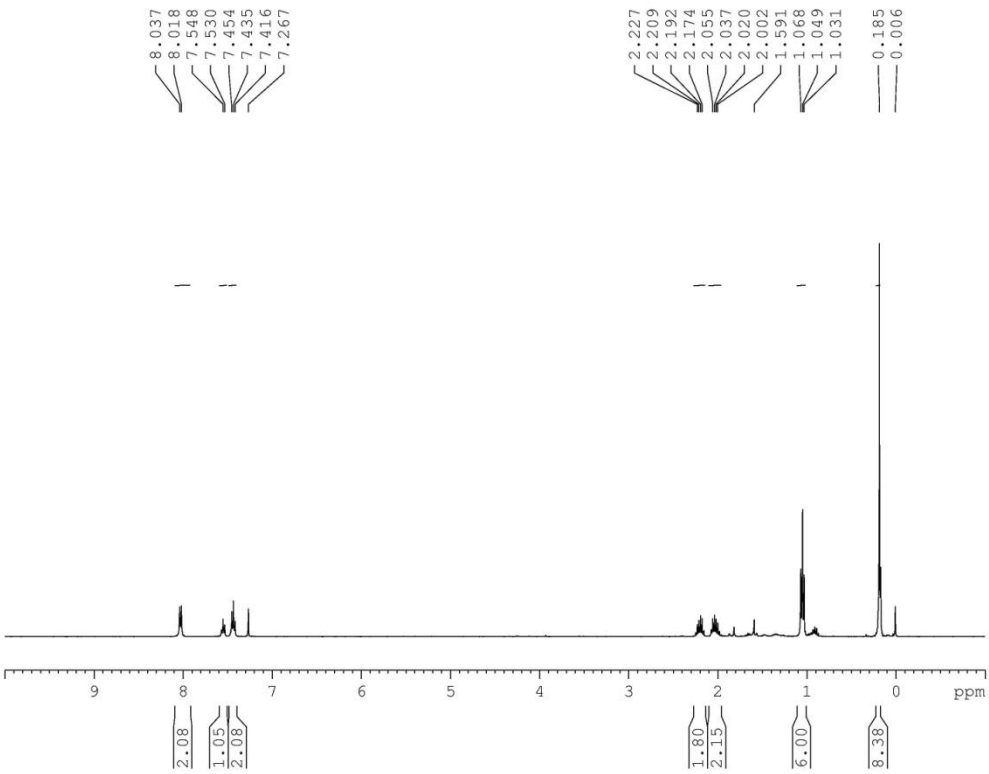


Figure S7. ^{1}H NMR spectrum of compound **IV**

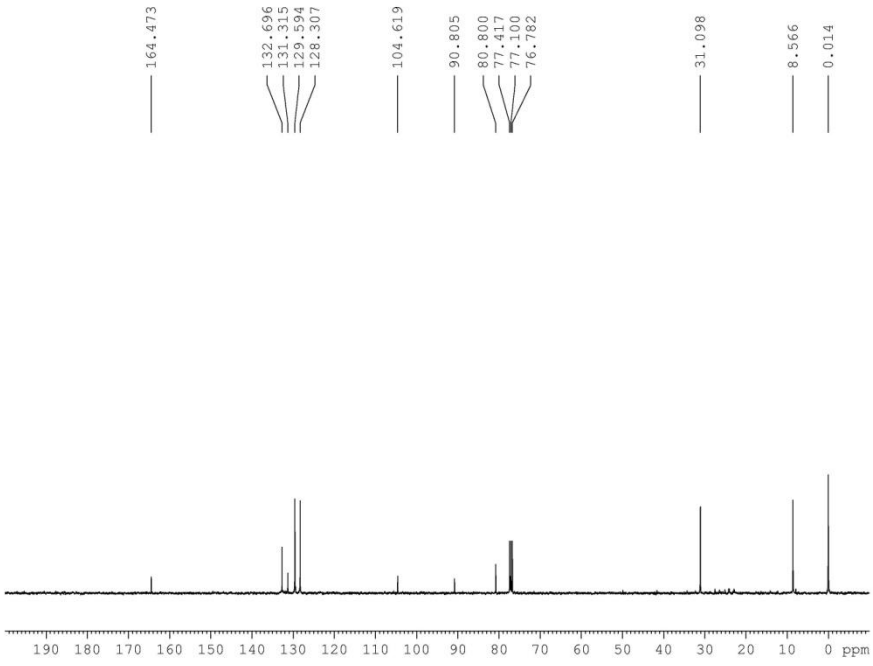


Figure S8. ^{13}C NMR spectrum of compound **IV**

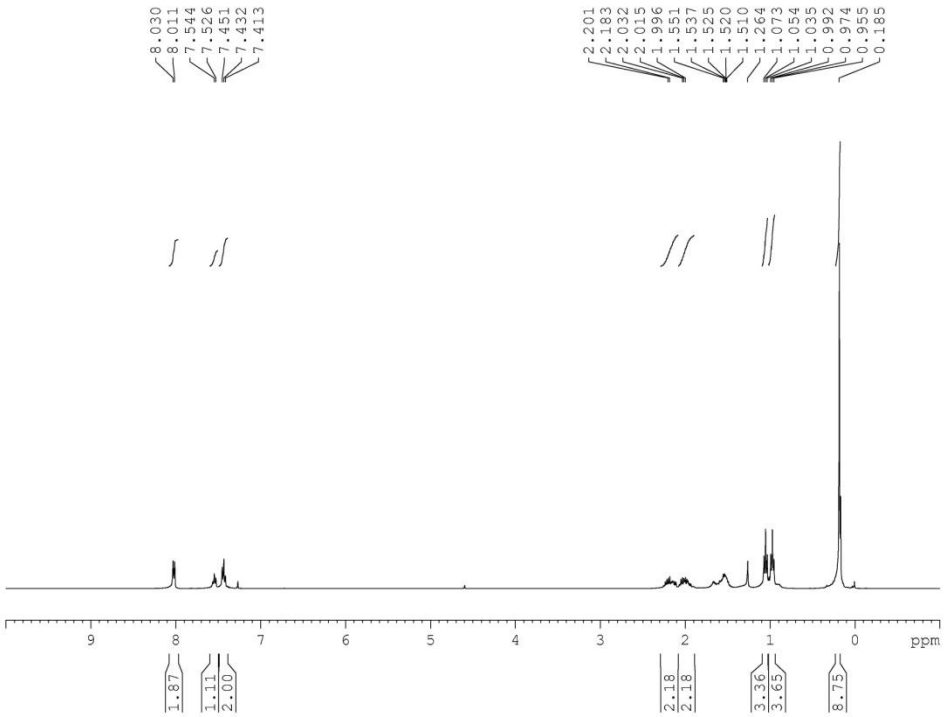


Figure S9. ^{1}H NMR spectrum of compound **V**

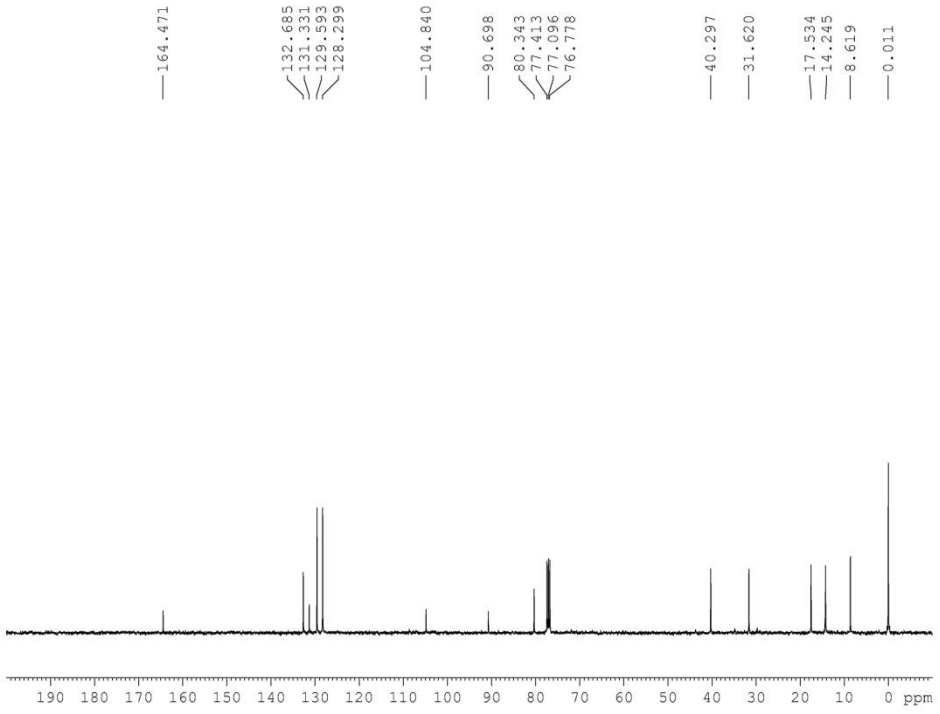


Figure S10. ^{13}C NMR spectrum of compound **V**

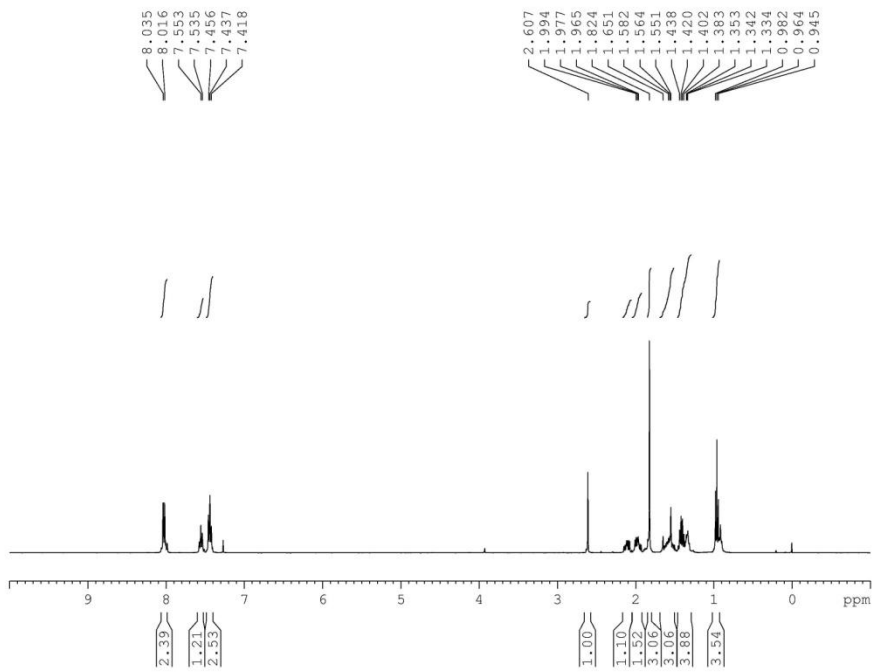


Figure S11. ^{1}H NMR spectrum of compound **1f**

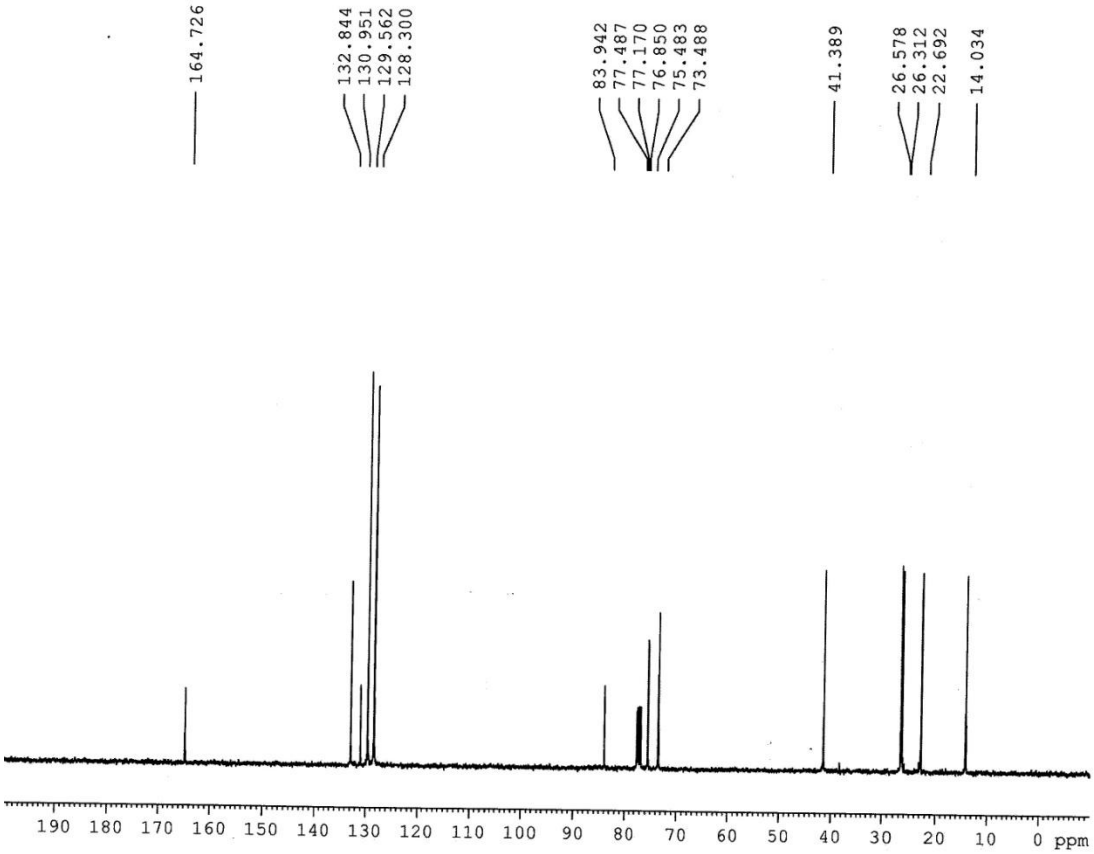


Figure S12. ^{13}C NMR spectrum of compound **1f**

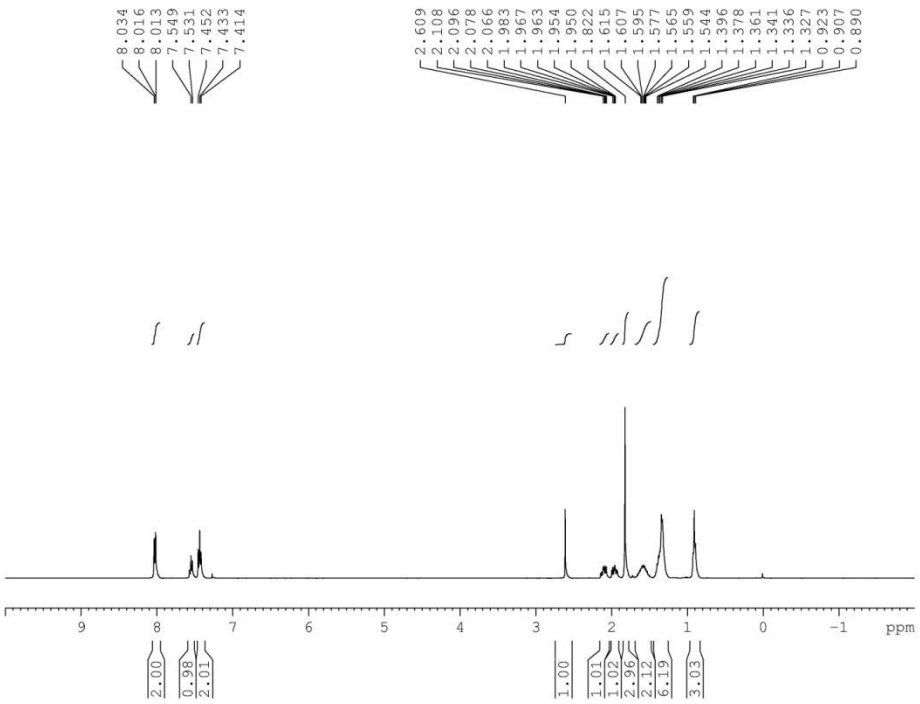


Figure S13. ^{1}H NMR spectrum of compound **1h**

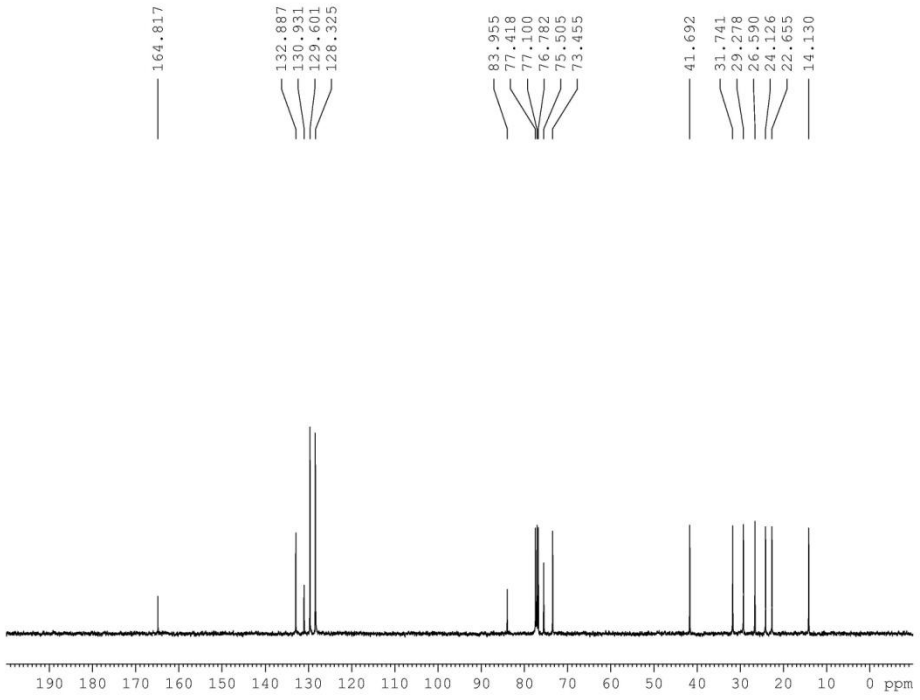


Figure S14. ^{13}C NMR spectrum of compound **1h**

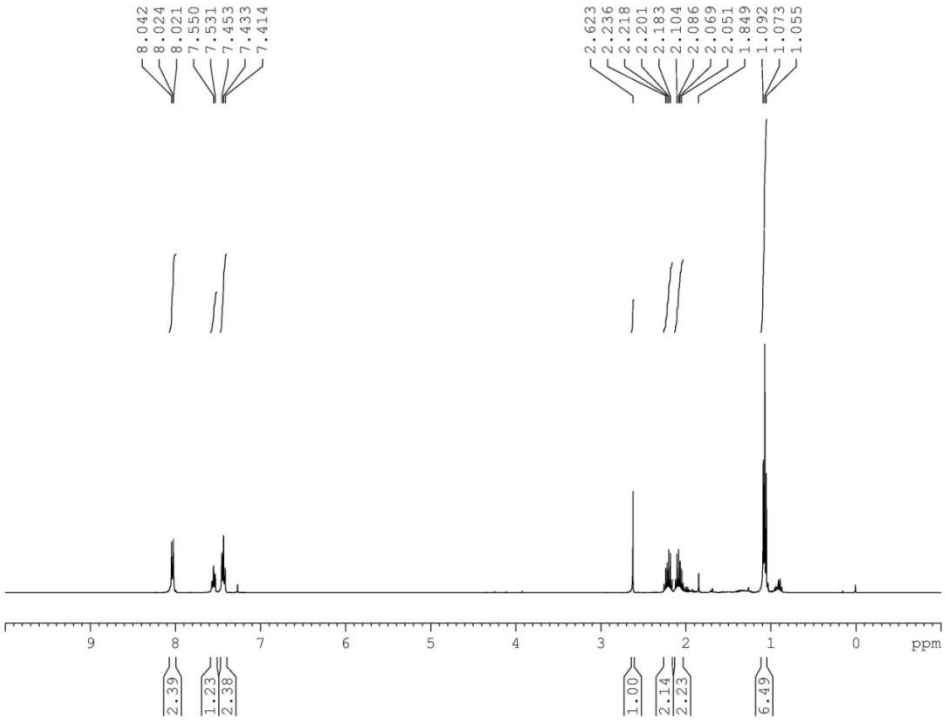


Figure S15. ^{1}H NMR spectrum of compound **1i**

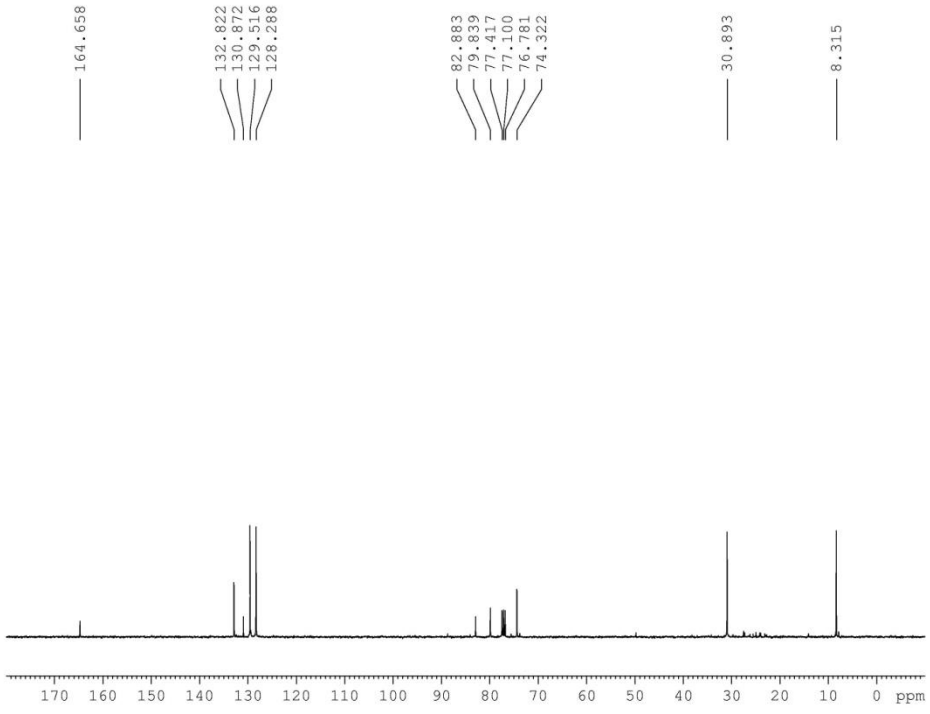


Figure S16. ^{13}C NMR spectrum of compound **1i**

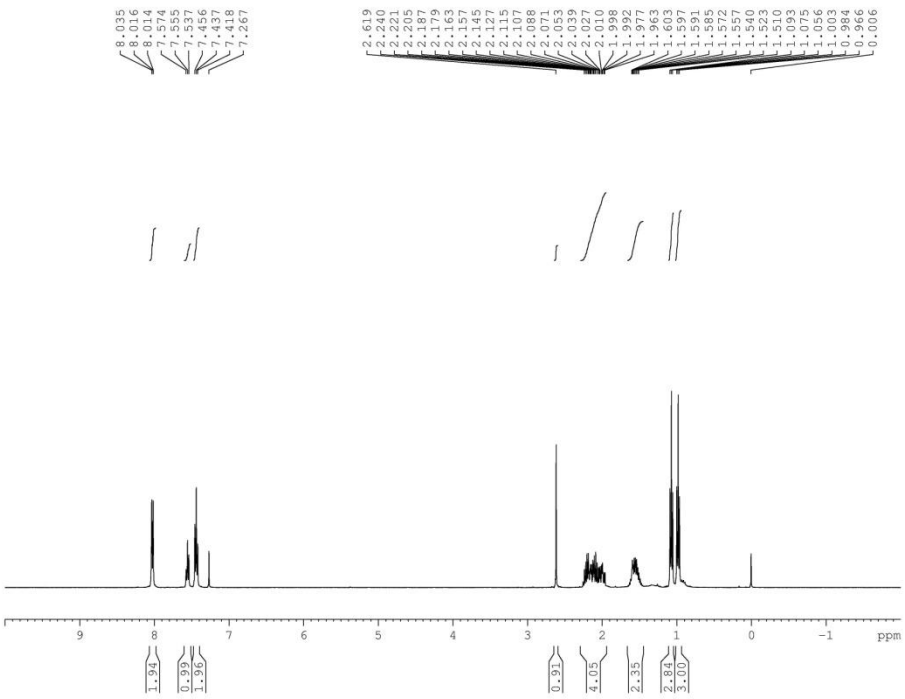


Figure S17. ^{1}H NMR spectrum of compound **1j**

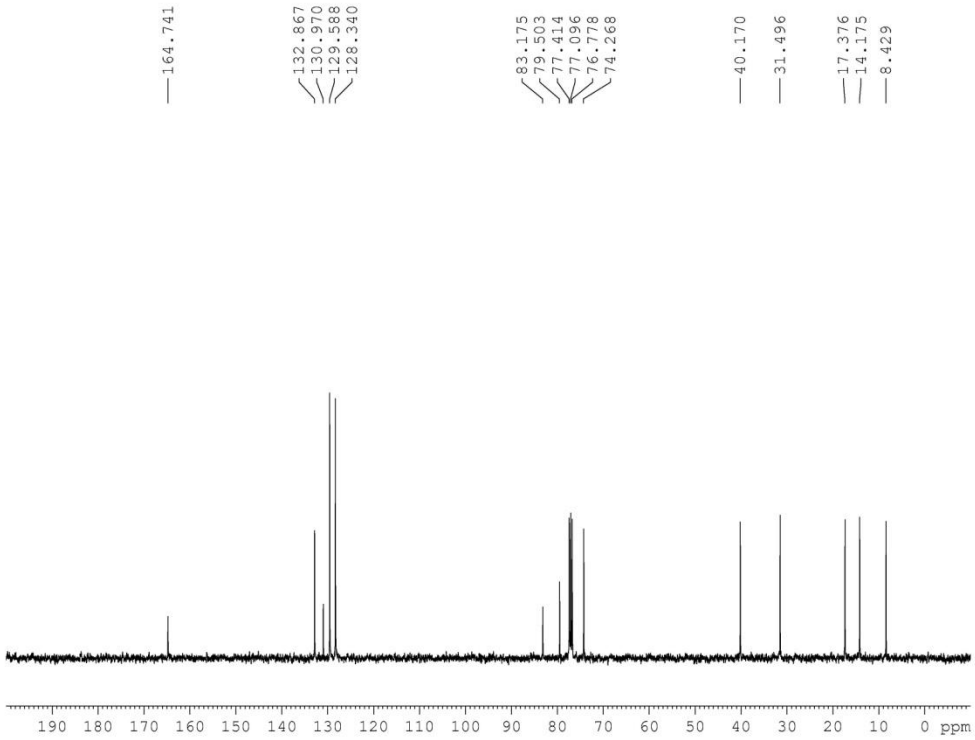


Figure S18. ^{13}C NMR spectrum of compound **1j**

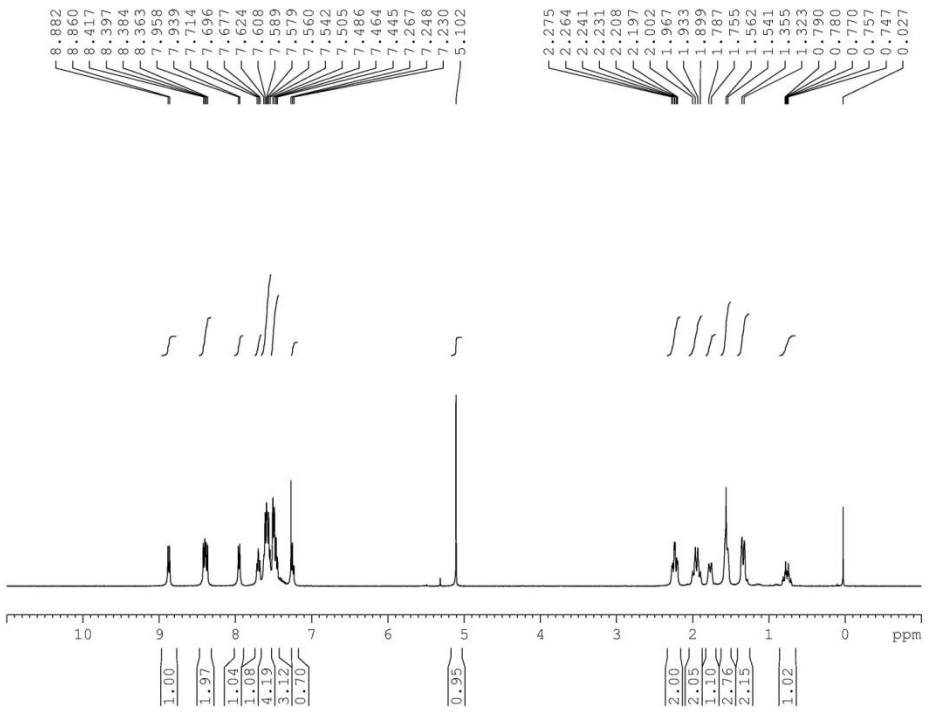


Figure S19. ^{1}H NMR spectrum of compound **3a**

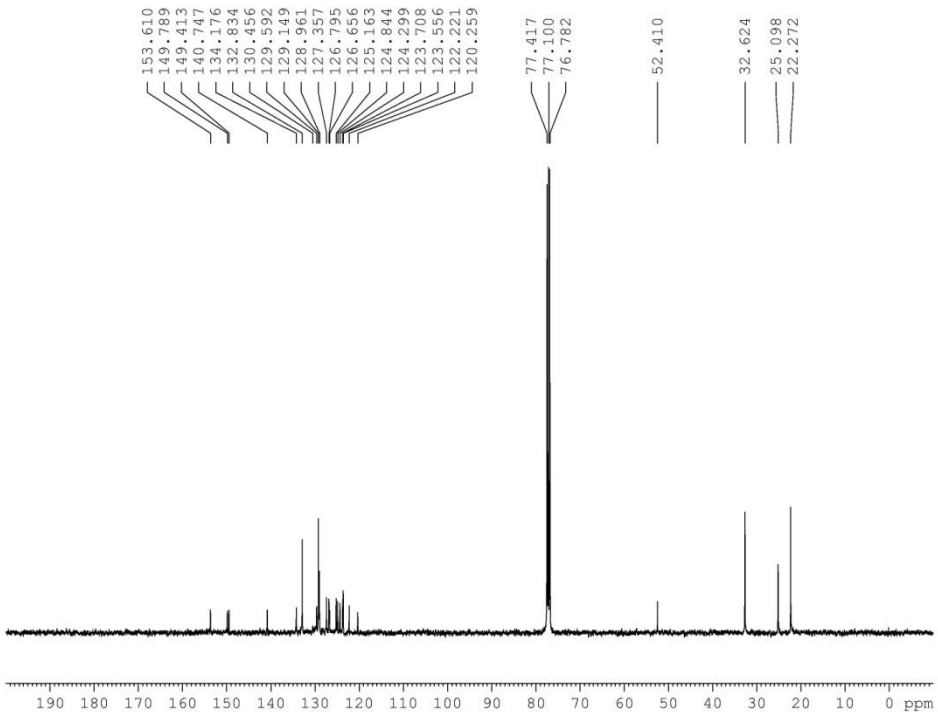


Figure S20. ^{13}C NMR spectrum of compound **3a**

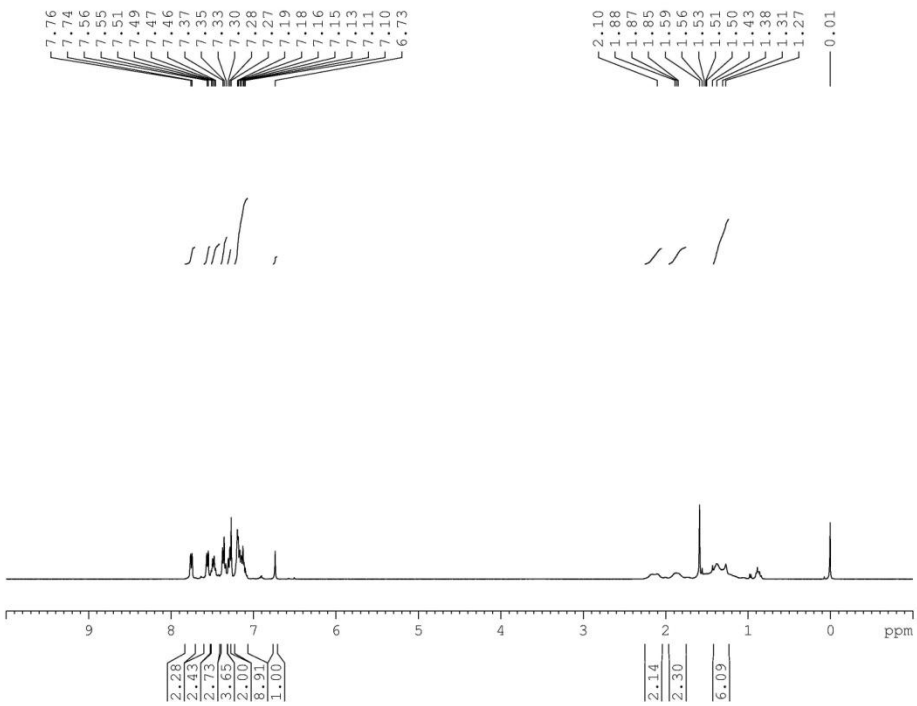


Figure S21. ^{1}H NMR spectrum of compound **4a**

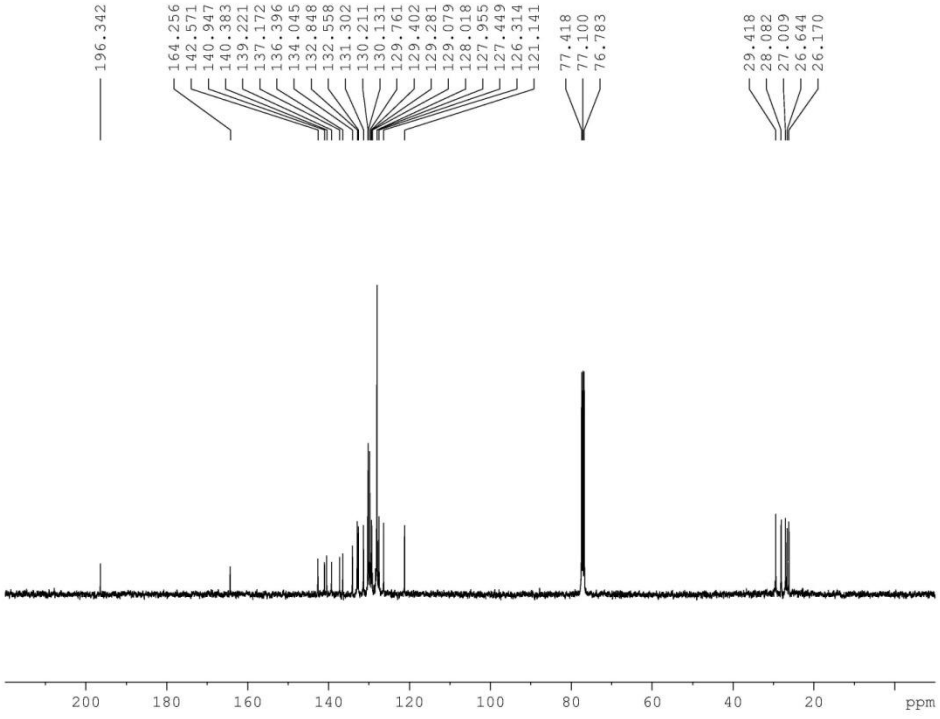


Figure S22. ^{13}C NMR spectrum of compound **4a**

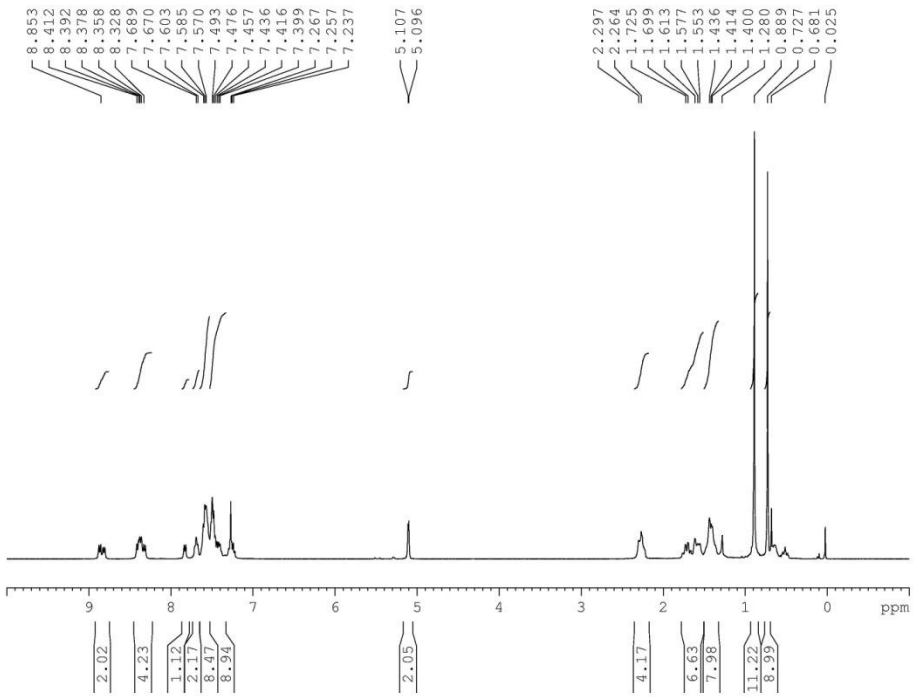


Figure S23. ^{1}H NMR spectrum of compound **3b**

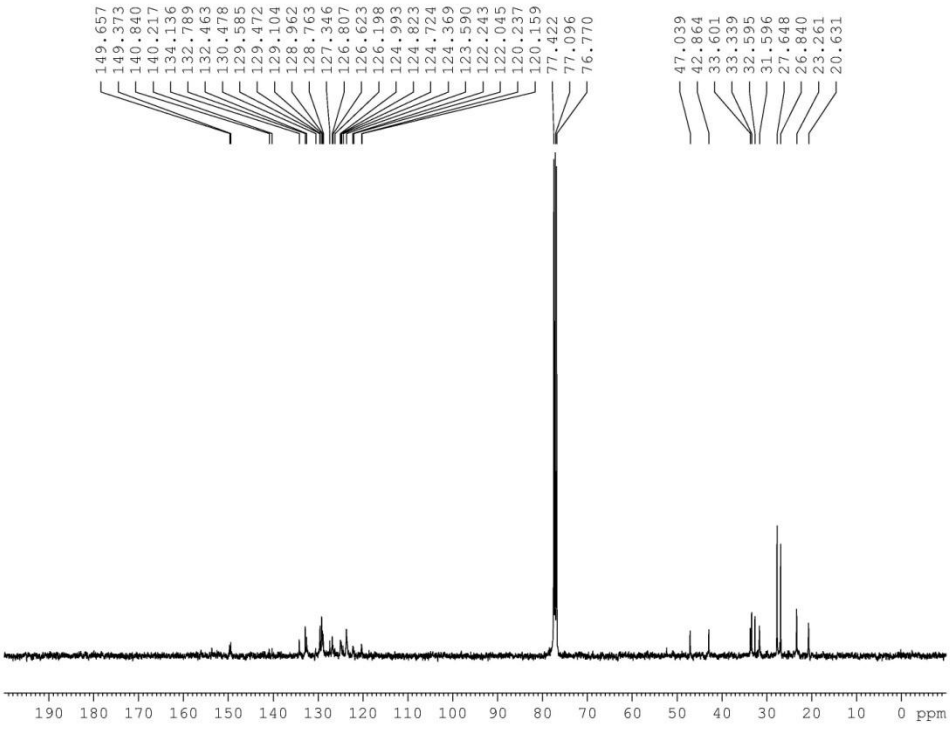


Figure S24. ^{13}C NMR spectrum of compound **3b**

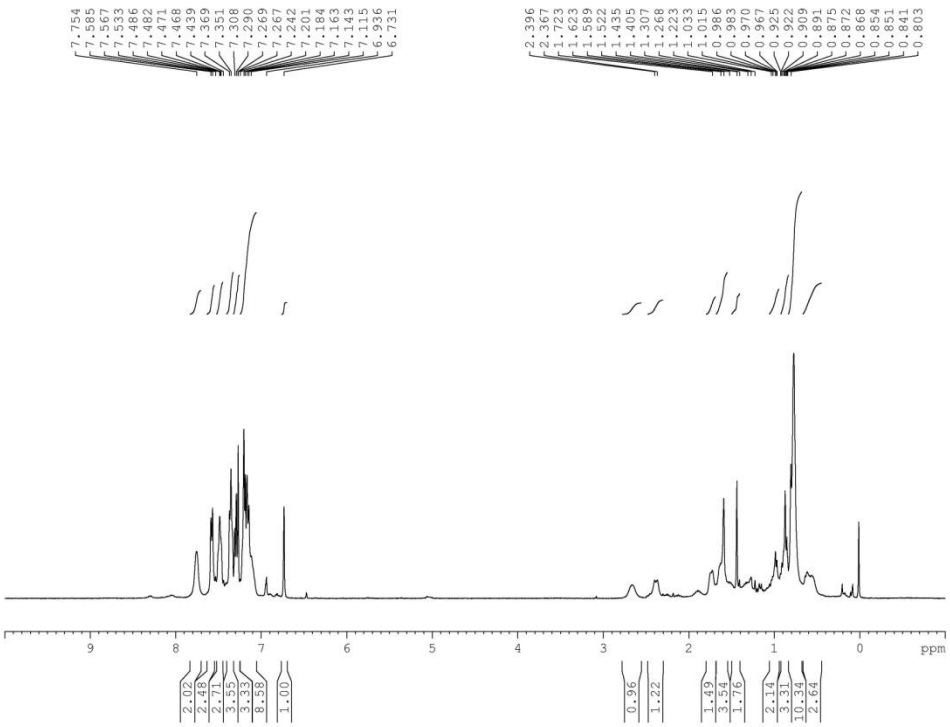


Figure S25. ^{1}H NMR spectrum of compound **4b**

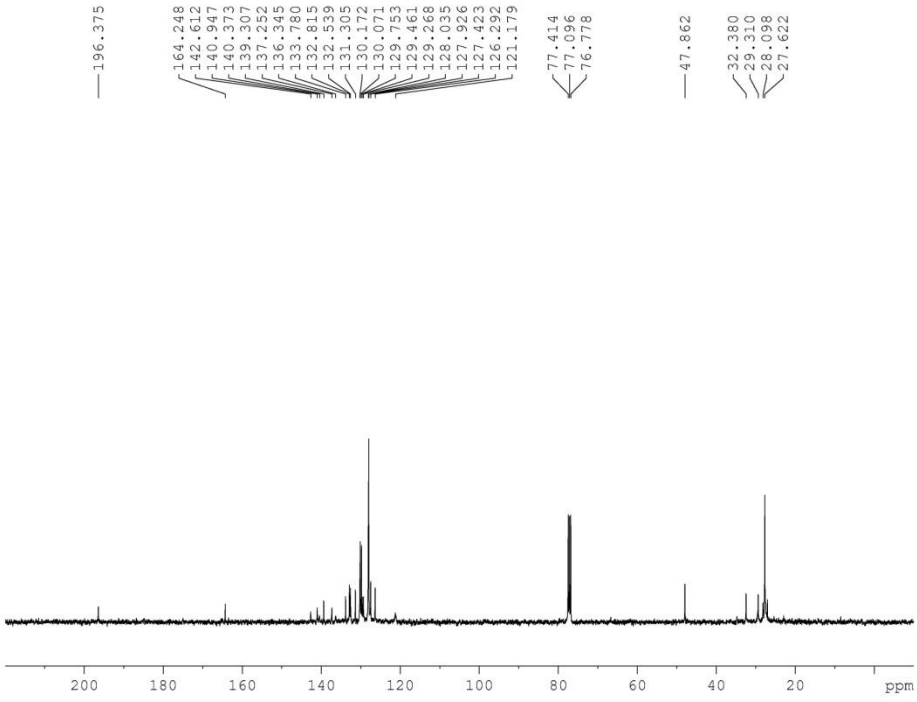


Figure S26. ^{13}C NMR spectrum of compound **4b**

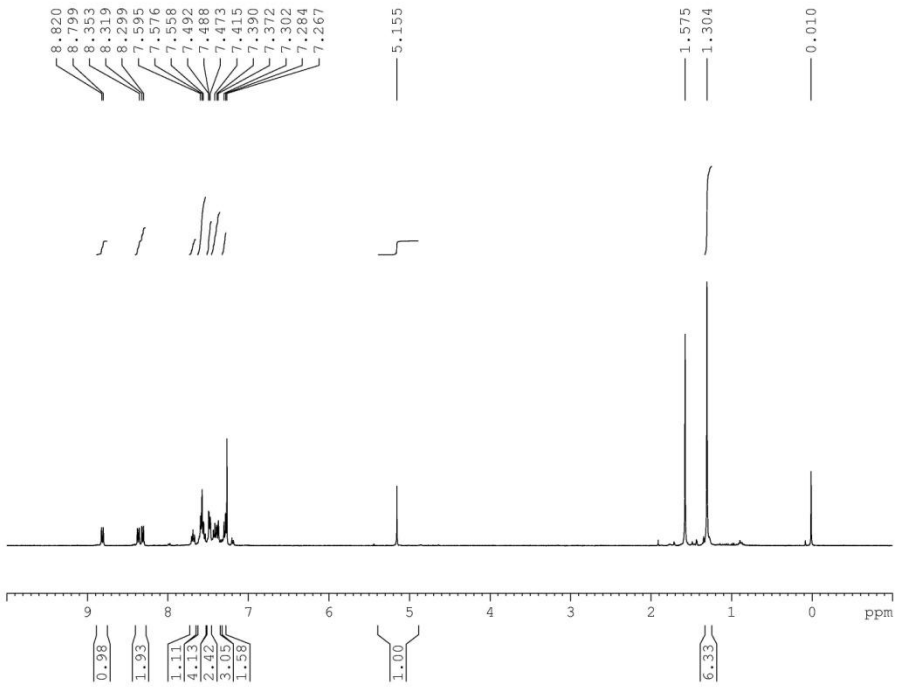


Figure S27. ^{1}H NMR spectrum of compound **3c**

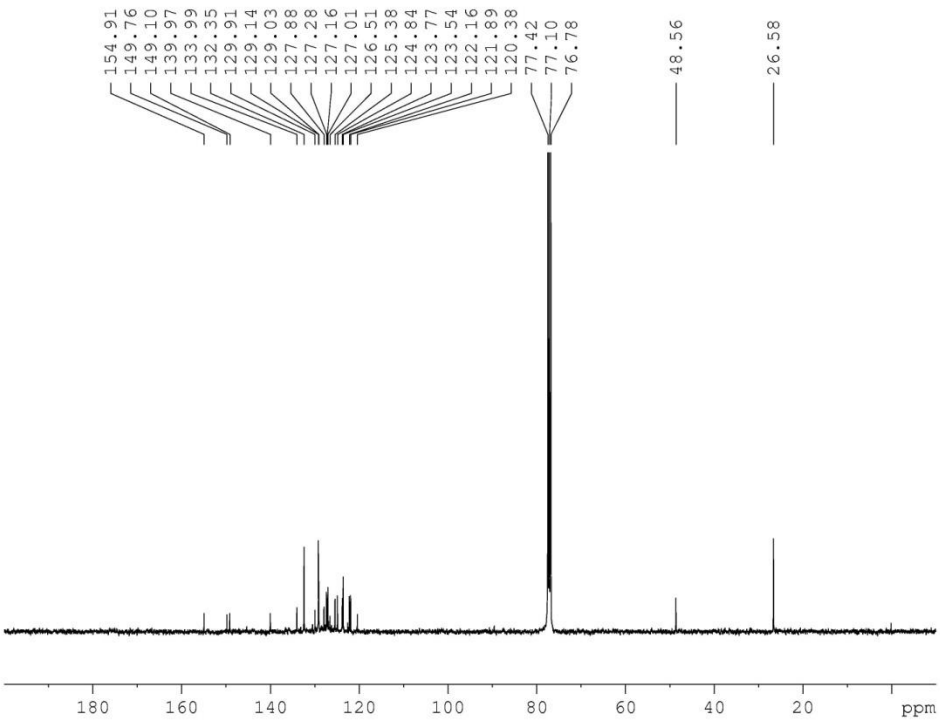


Figure S28. ^{13}C NMR spectrum of compound **3c**

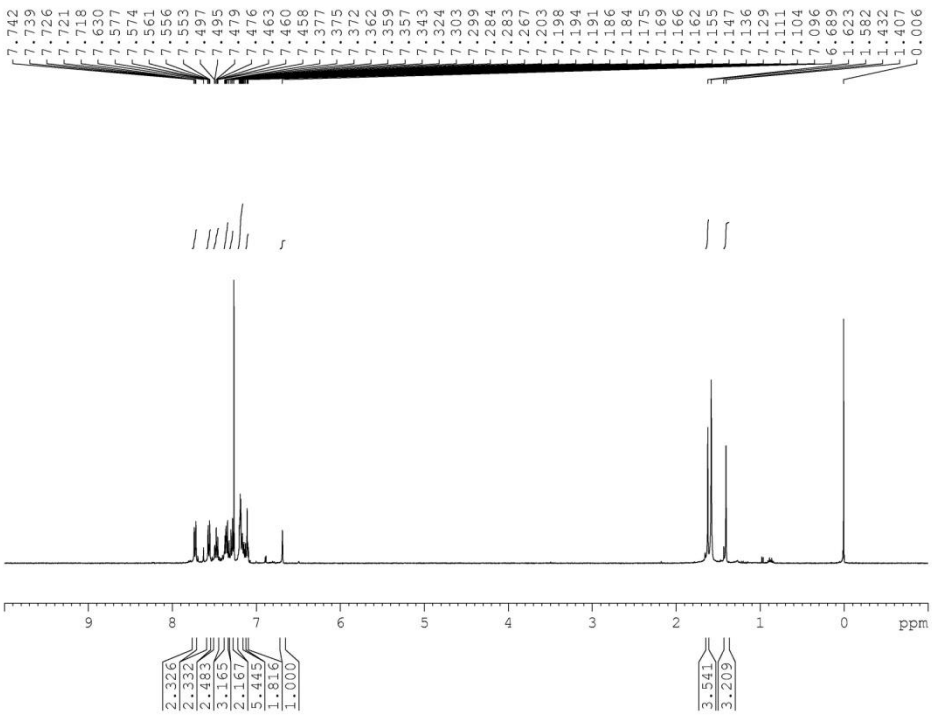


Figure S29. ^{1}H NMR spectrum of compound **4c**

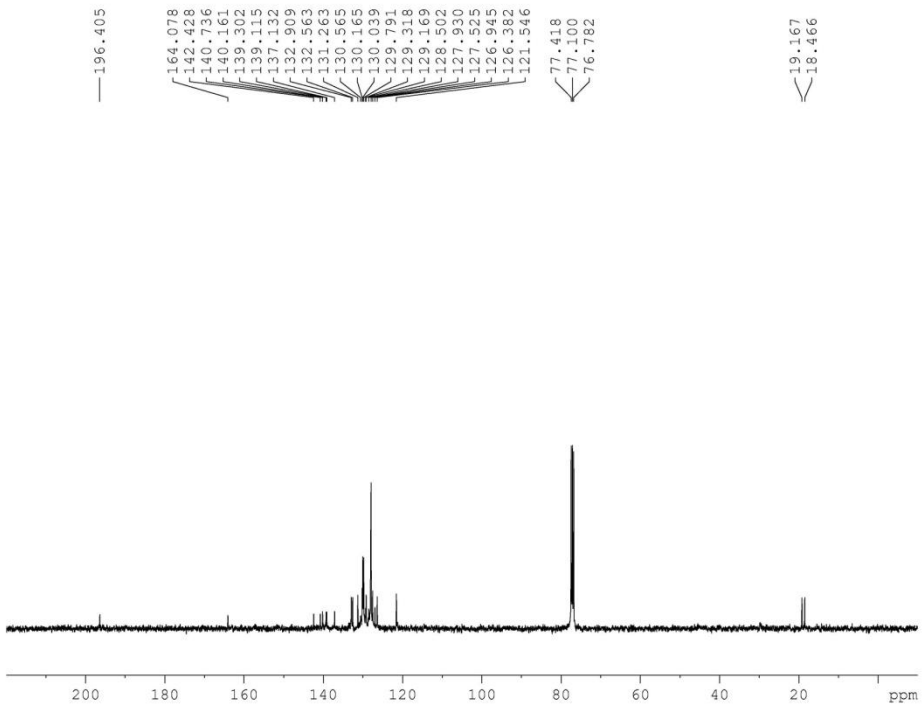


Figure S30. ^{13}C NMR spectrum of compound **4c**

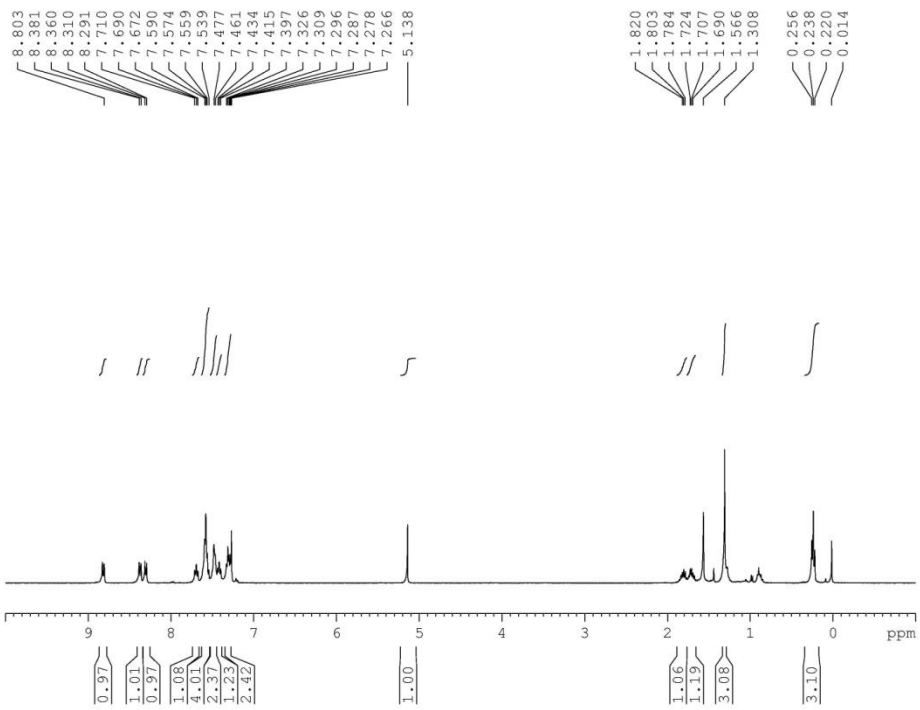


Figure S31. ^{1}H NMR spectrum of compound **3d**

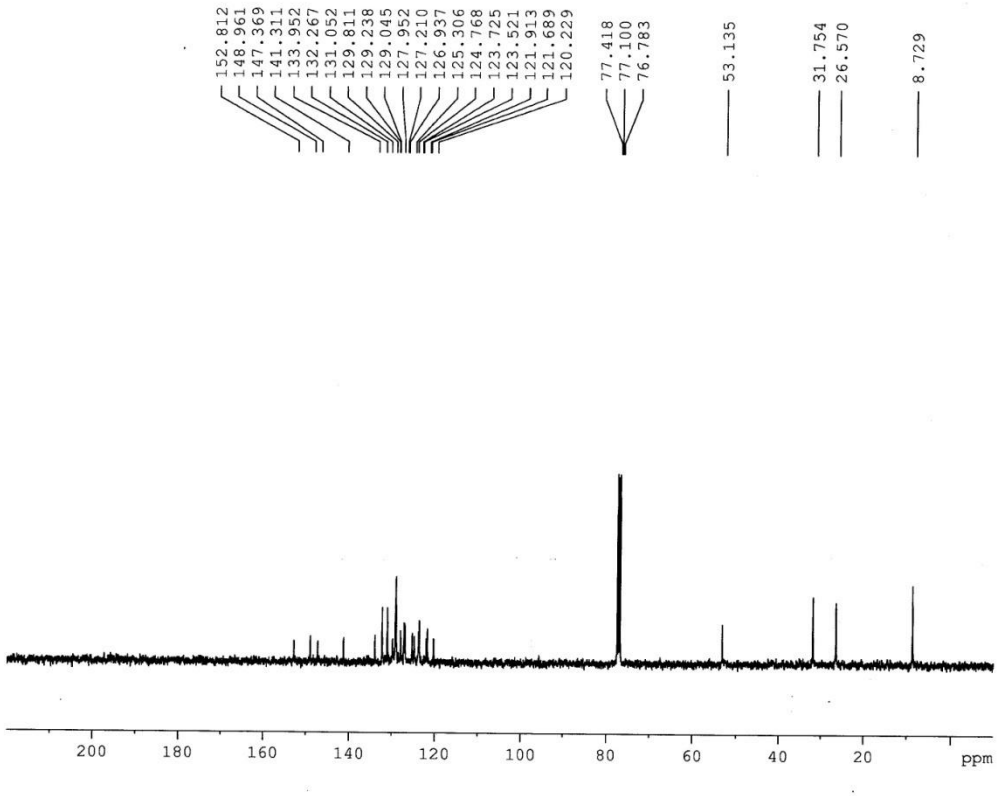


Figure S32. ^{13}C NMR spectrum of compound **3d**

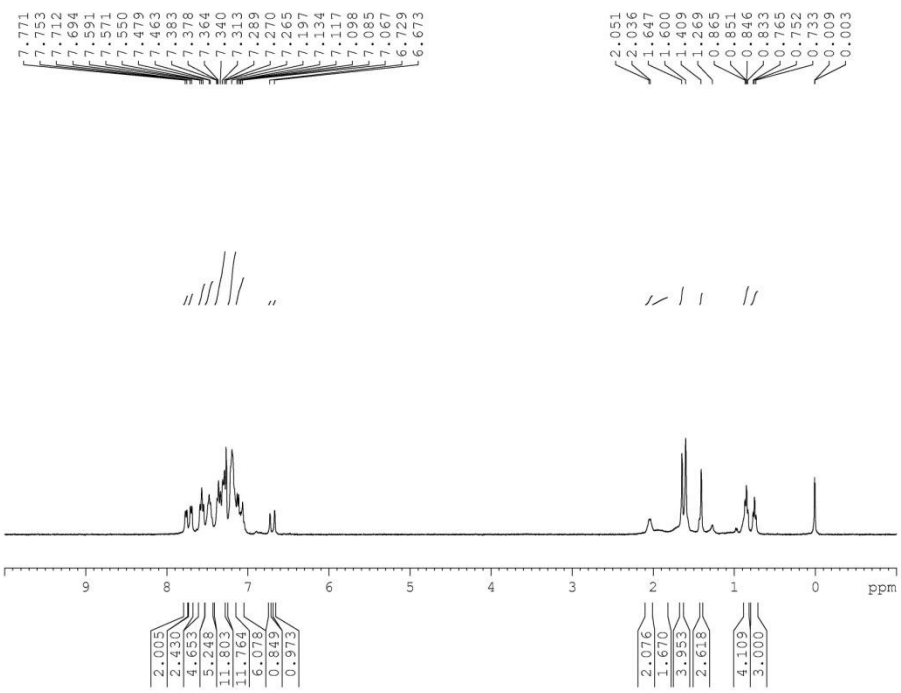


Figure S33. ^{1}H NMR spectrum of compound **4d**

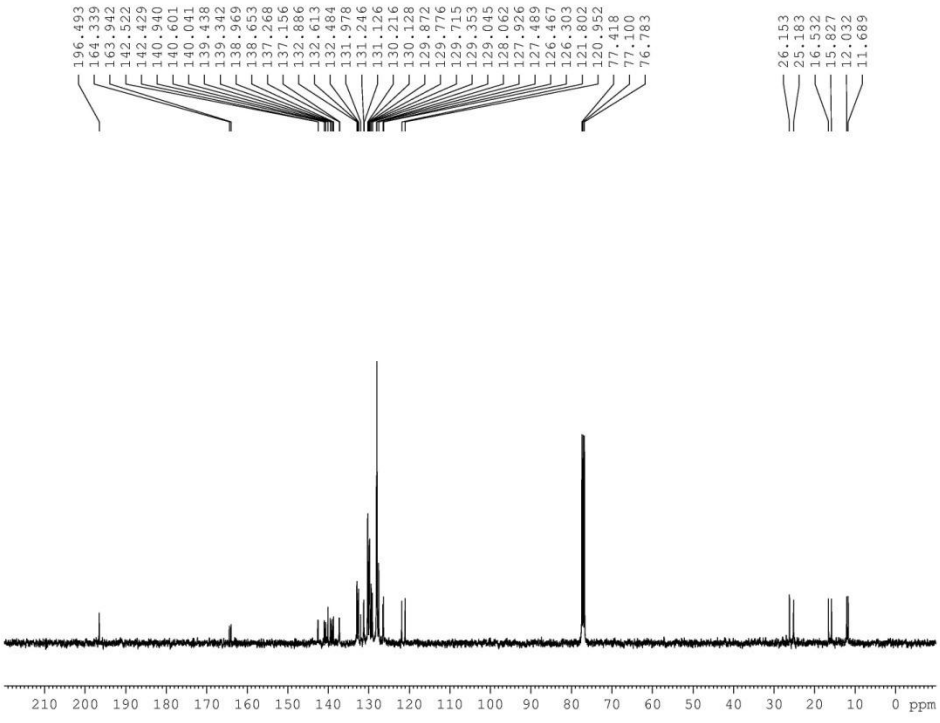


Figure S34. ^{13}C NMR spectrum of compound **4d**

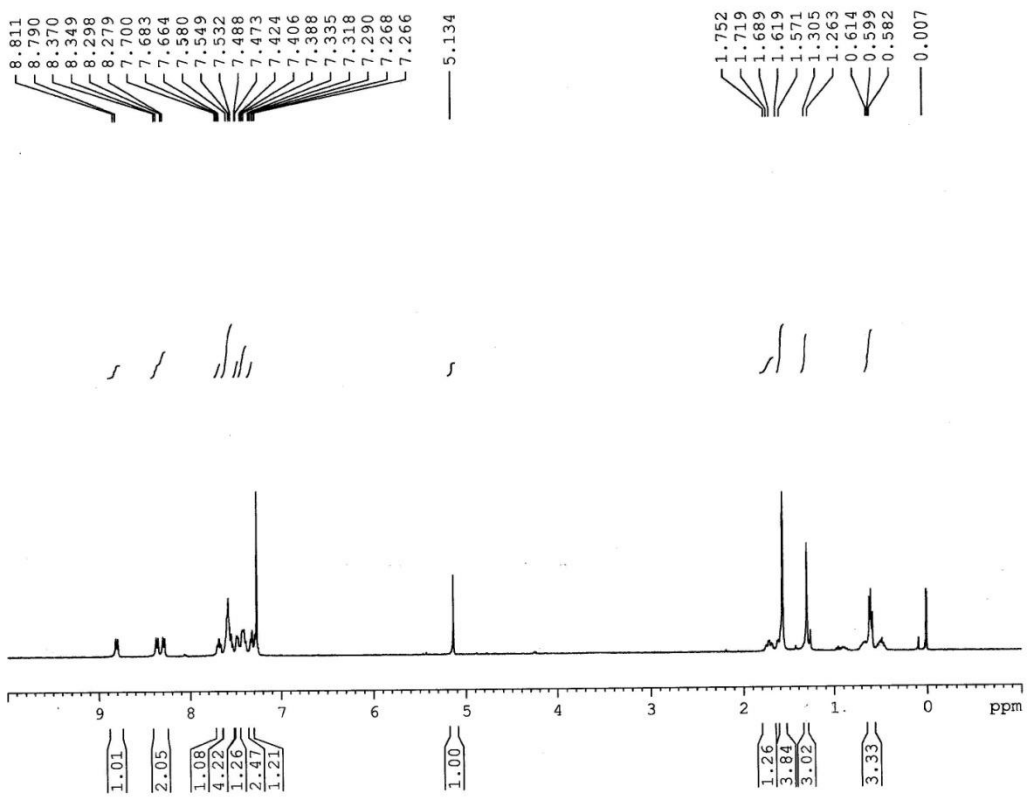


Figure S35. ^{1}H NMR spectrum of compound **3e**

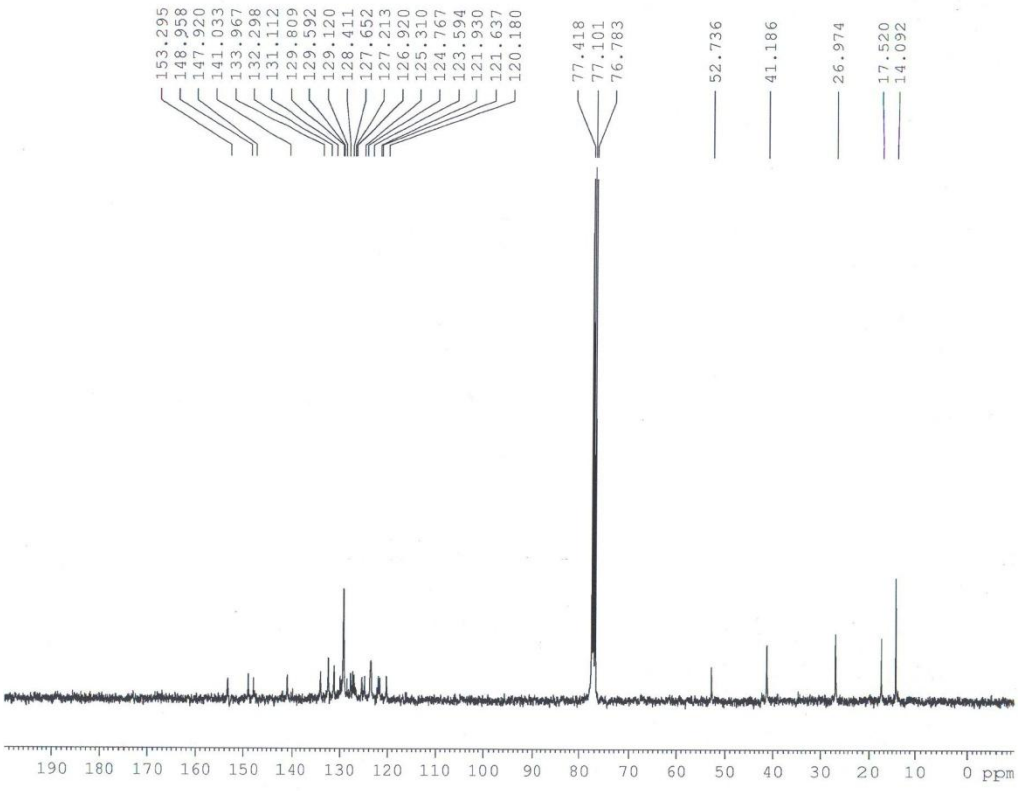


Figure S36. ^{13}C NMR spectrum of compound **3e**

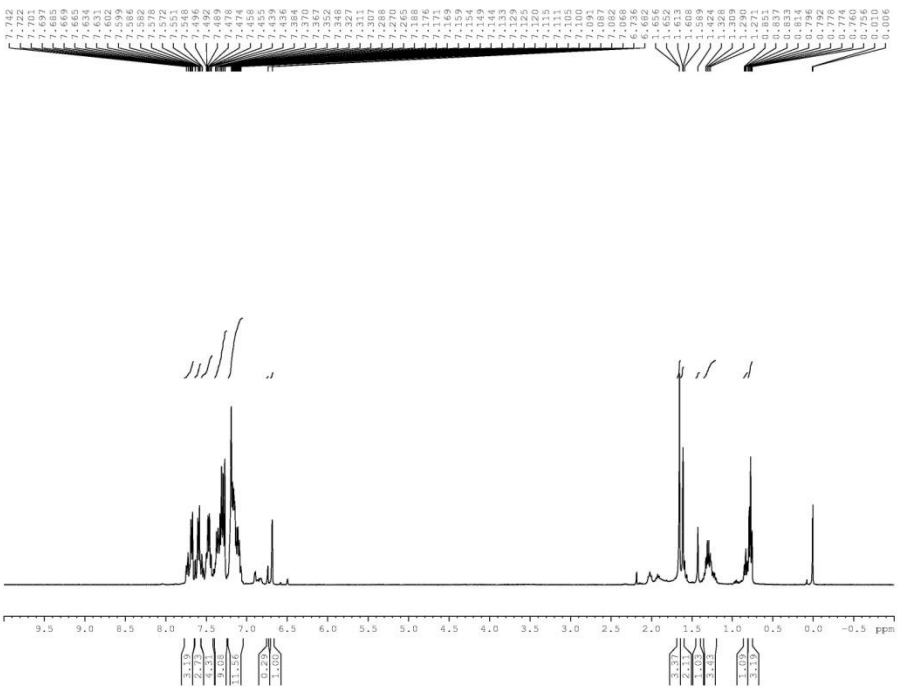


Figure S37. ^{1}H NMR spectrum of compound **4e**

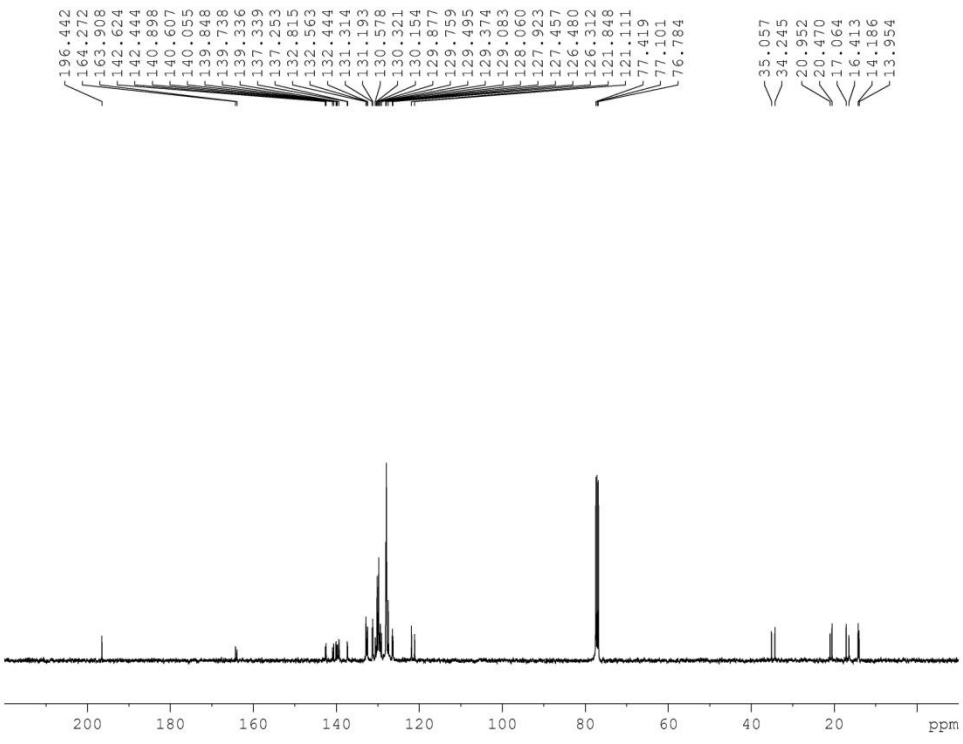


Figure S38. ^{13}C NMR spectrum of compound **4e**

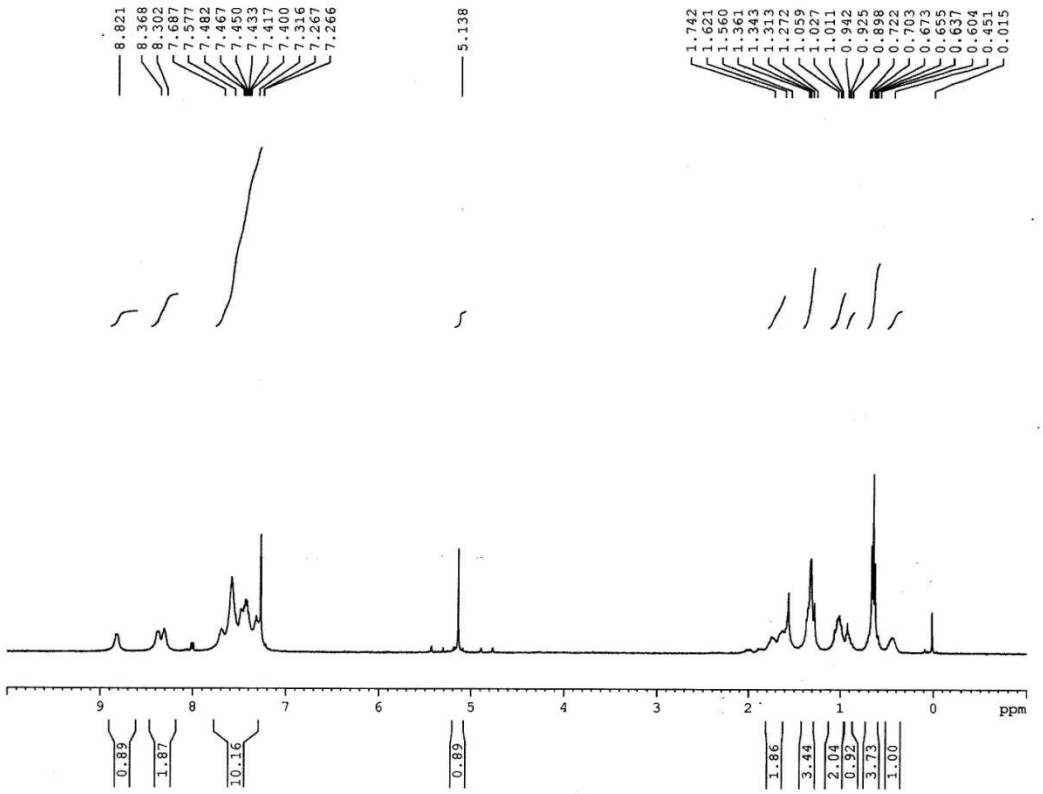


Figure S39. ^{1}H NMR spectrum of compound **3f**

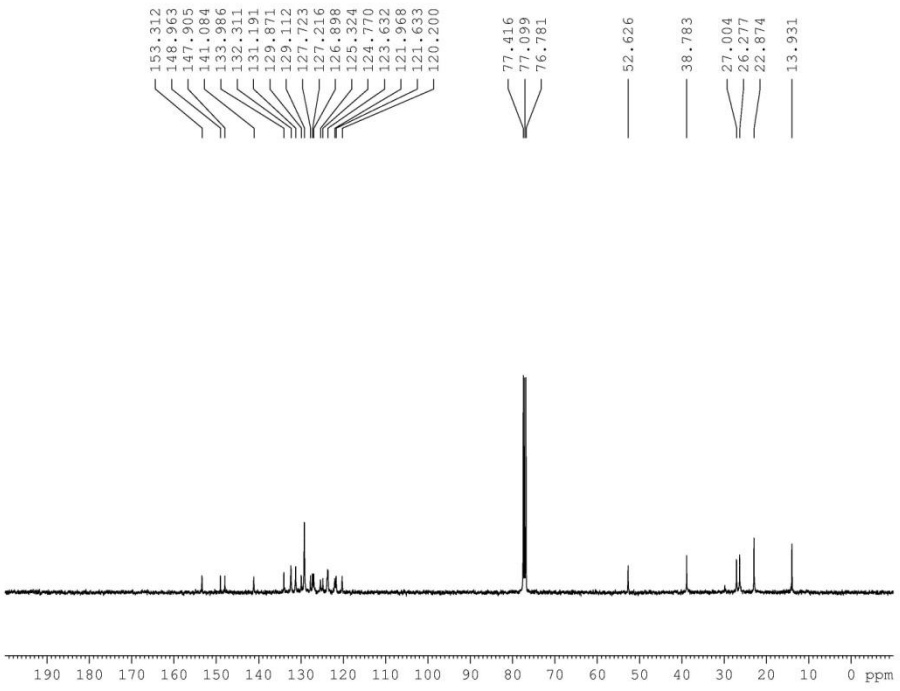


Figure S40. ^{13}C NMR spectrum of compound **3f**

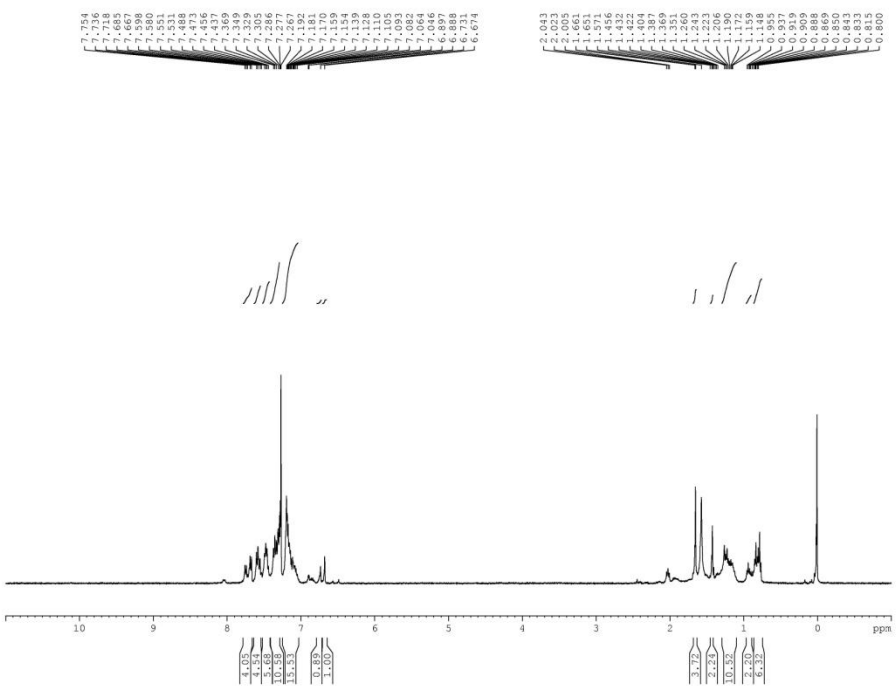


Figure S41. ^{1}H NMR spectrum of compound **4f**

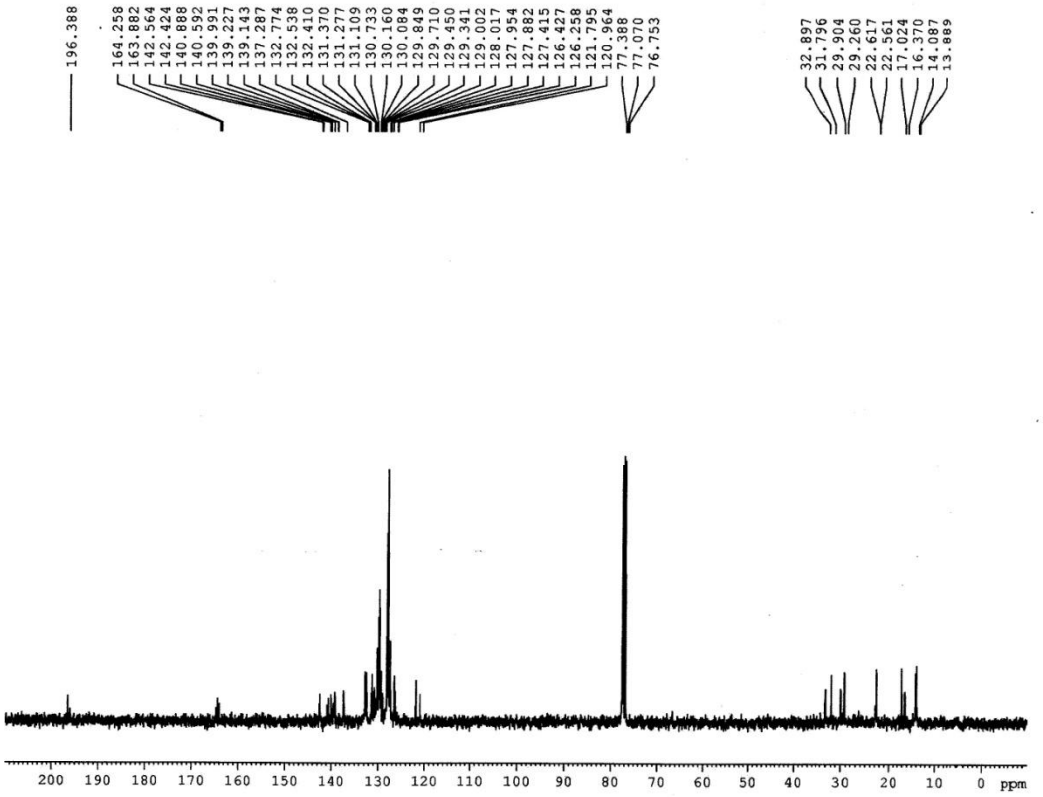


Figure S42. ^{13}C NMR spectrum of compound **4f**

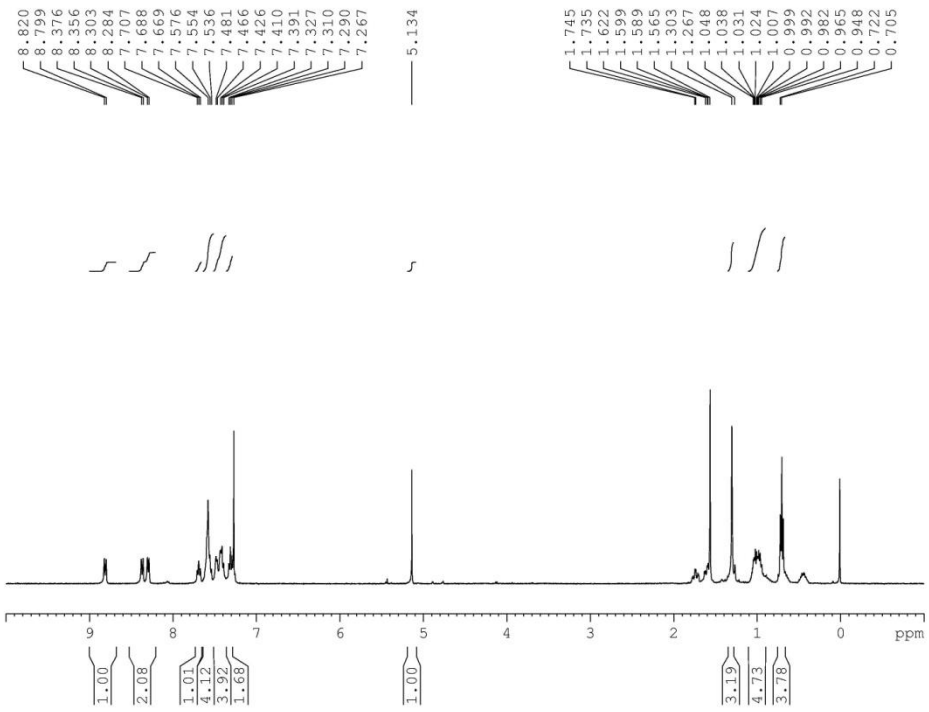


Figure S43. ^{1}H NMR spectrum of compound **3g**

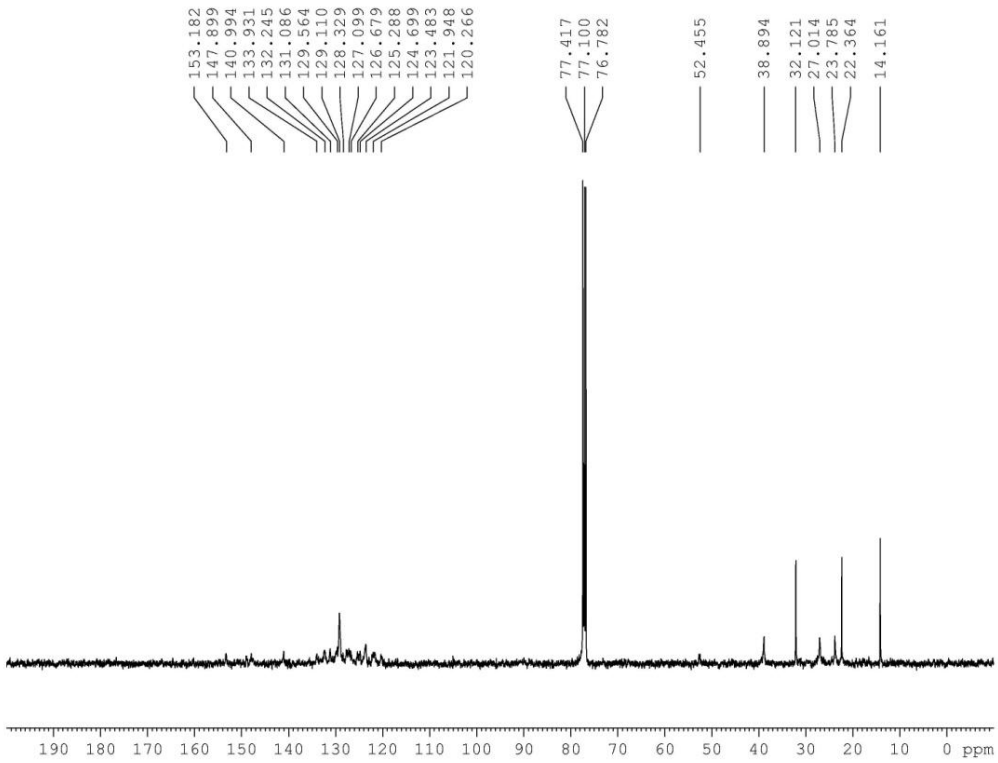


Figure S44. ^{13}C NMR spectrum of compound **3g**

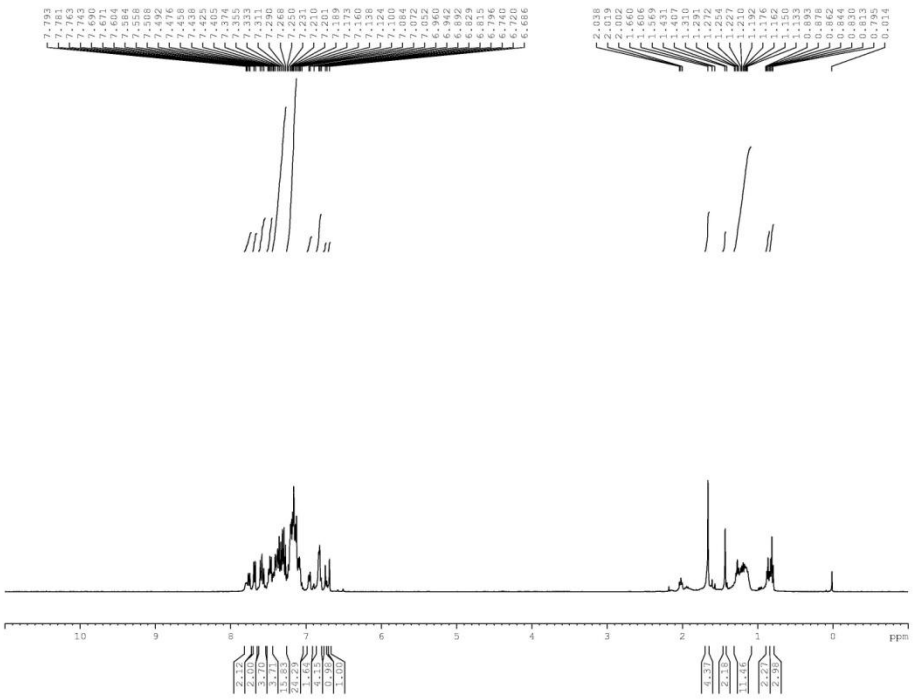


Figure S45. ^{1}H NMR spectrum of compound **4g**

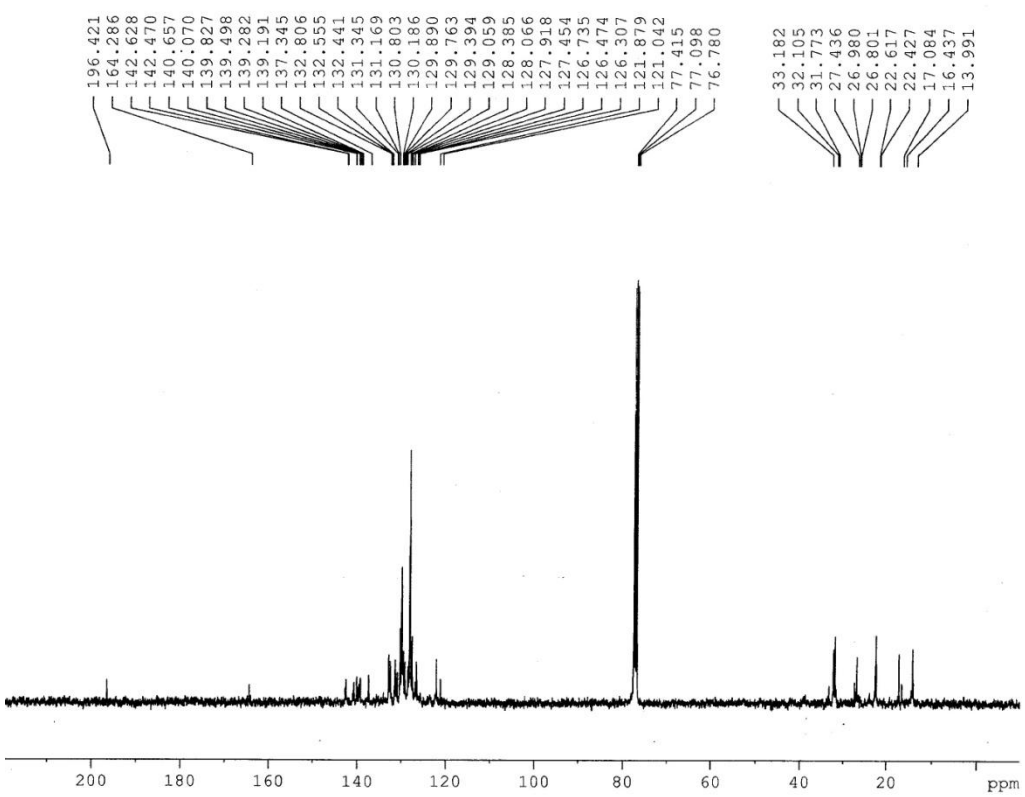


Figure S46. ^{13}C NMR spectrum of compound **4g**

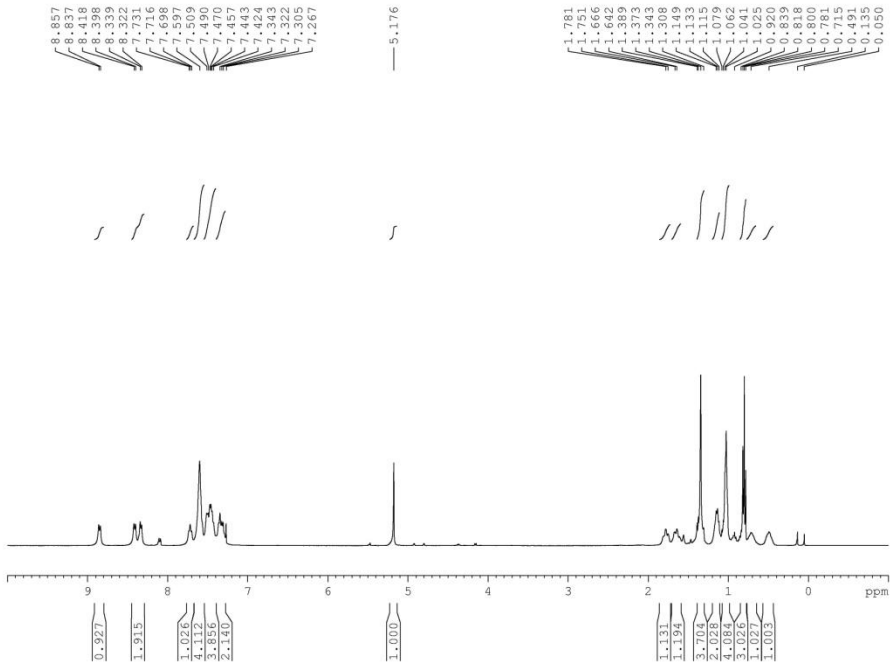


Figure S47. ^{1}H NMR spectrum of compound **3h**

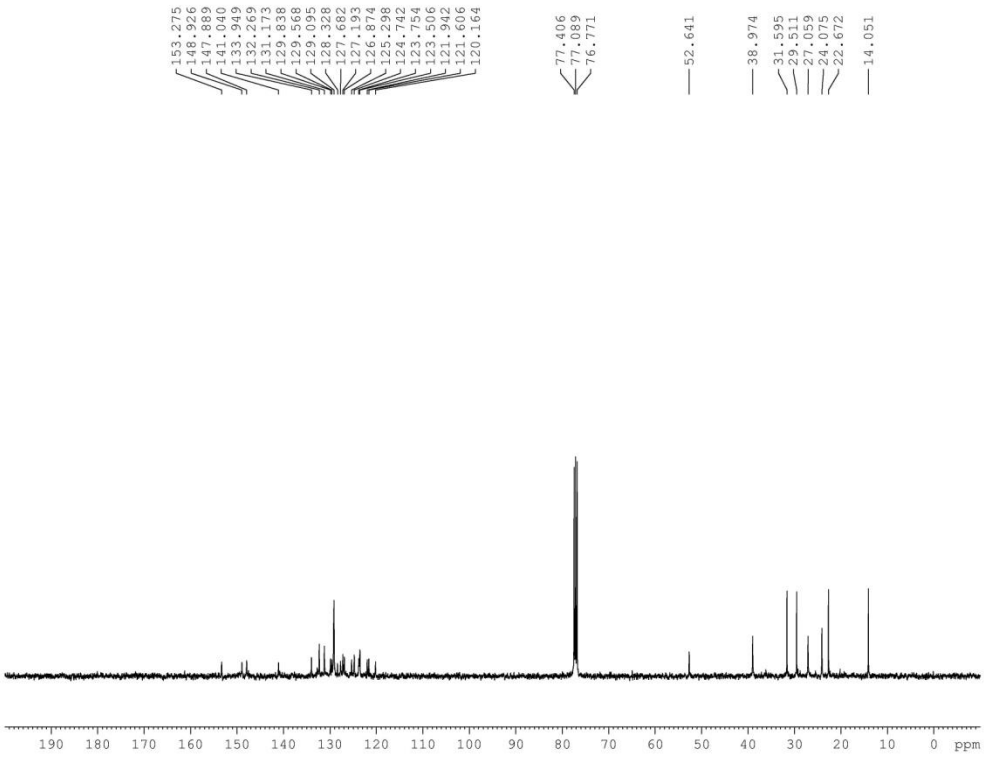


Figure S48. ^{13}C NMR spectrum of compound **3h**

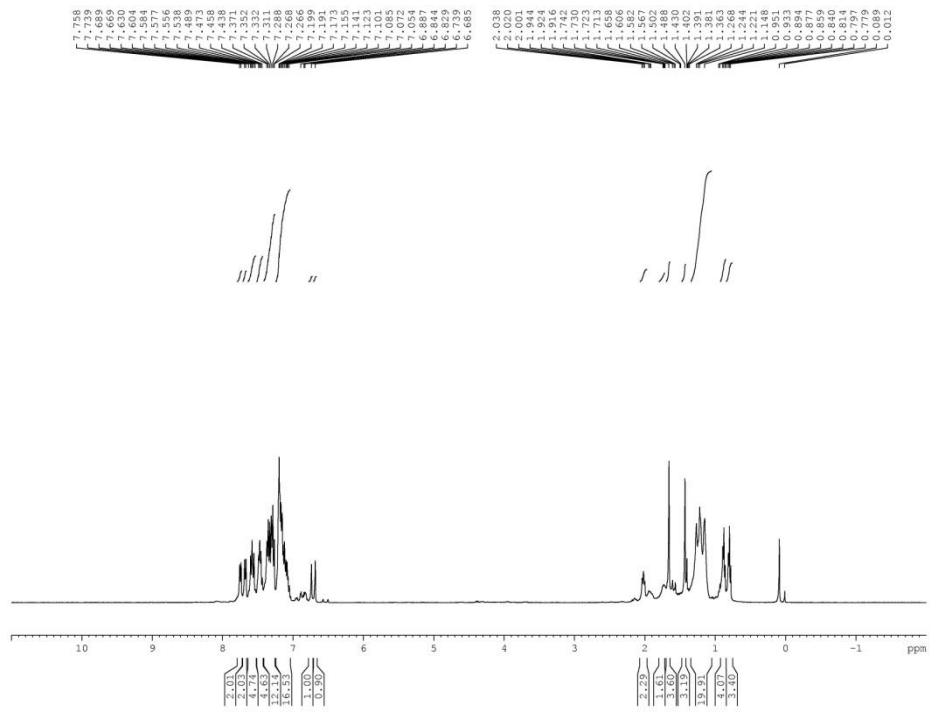


Figure S49. ^{1}H NMR spectrum of compound **4h**

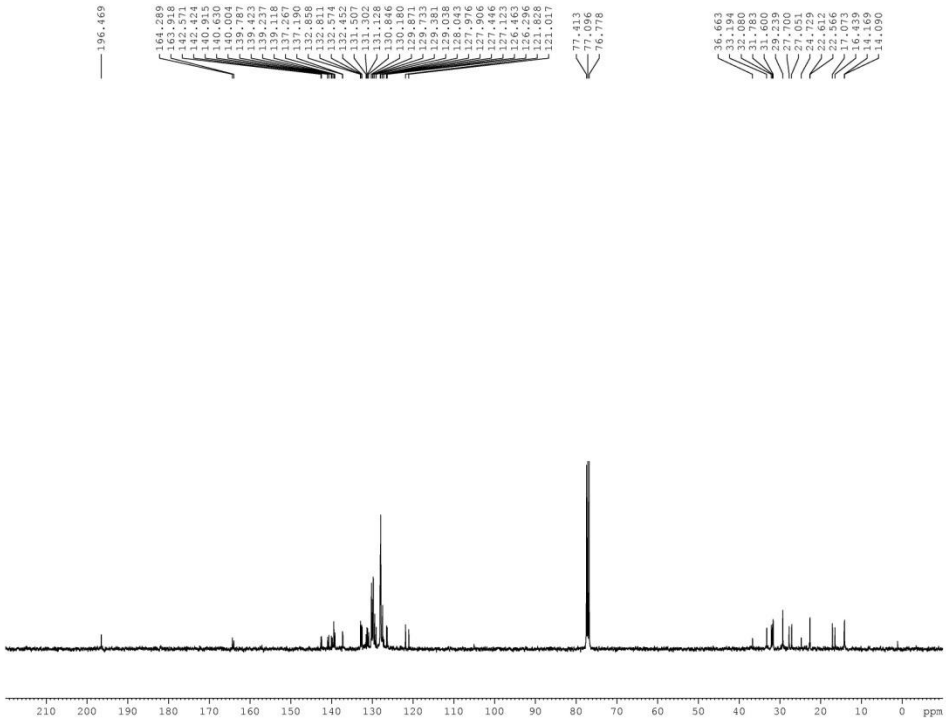


Figure S50. ^{13}C NMR spectrum of compound **4h**

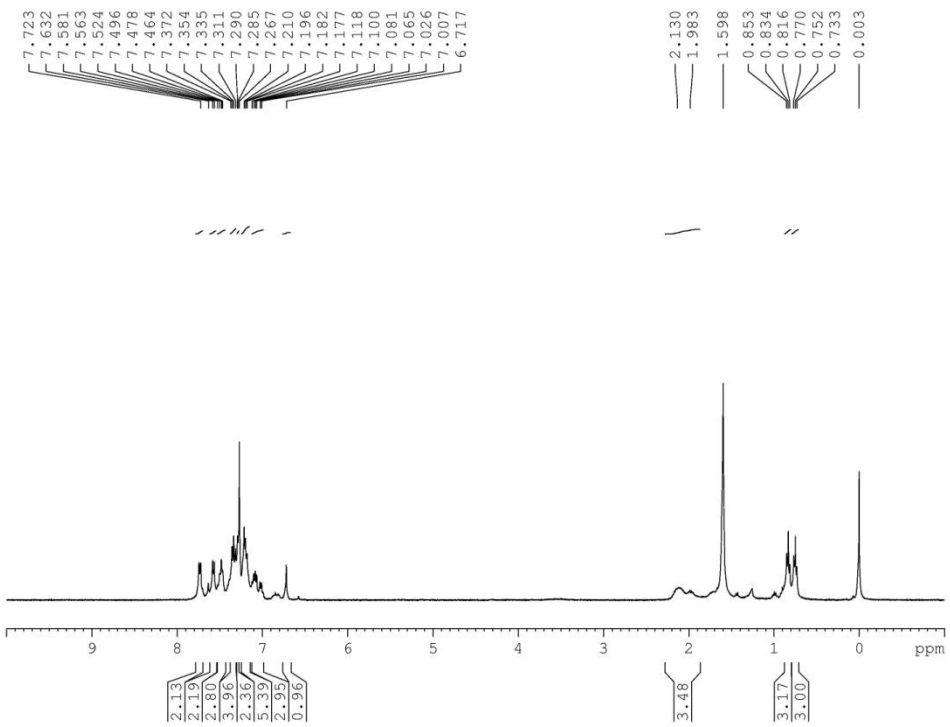


Figure S51. ^{1}H NMR spectrum of compound **3i**

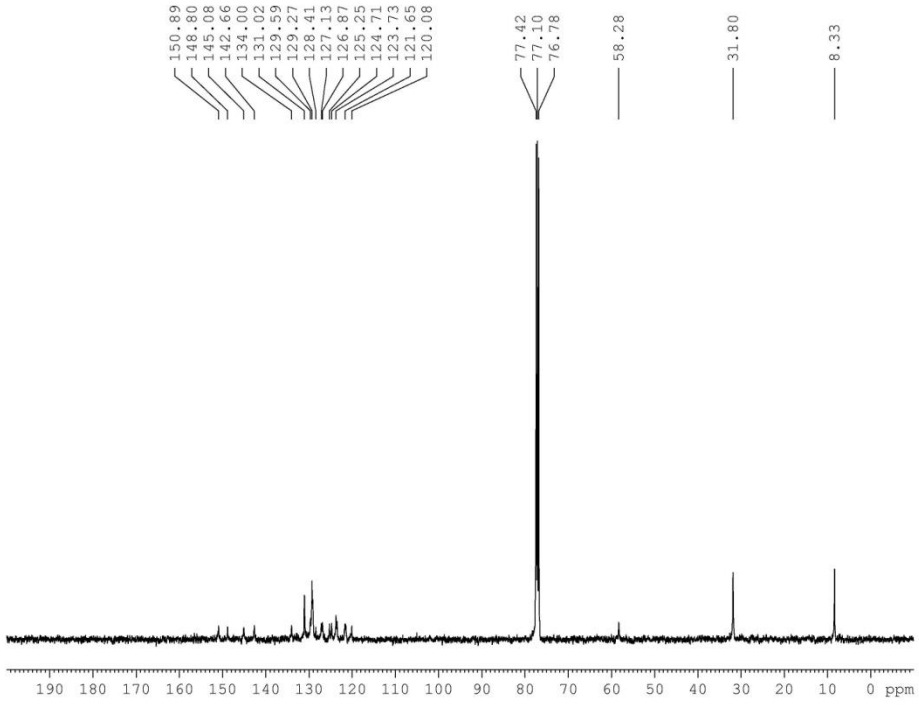


Figure S52. ^{13}C NMR spectrum of compound **3i**

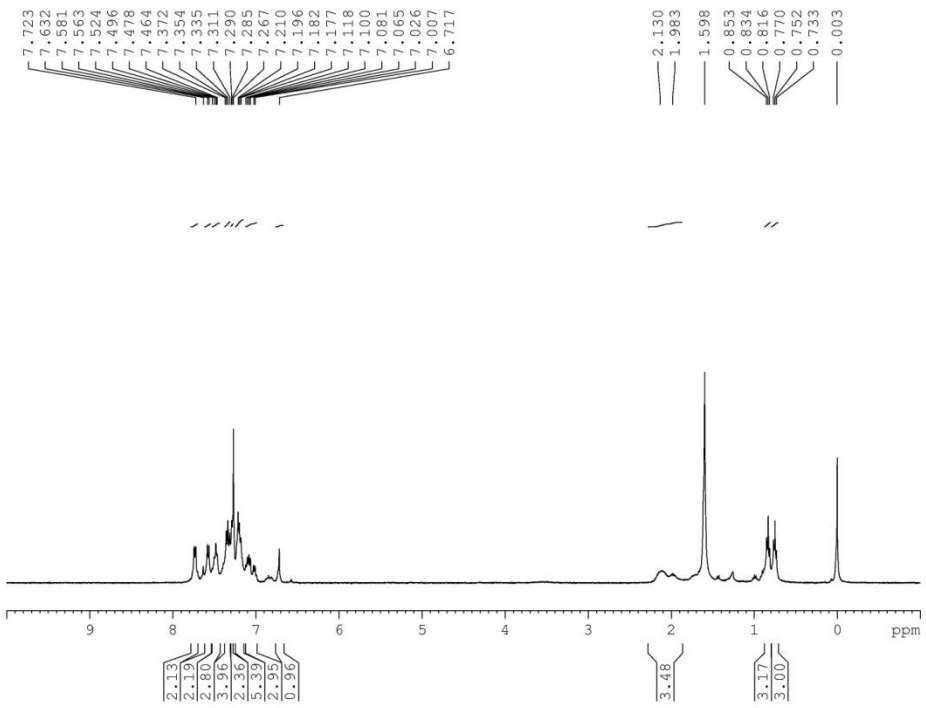


Figure S53. ^{1}H NMR spectrum of compound **4i**

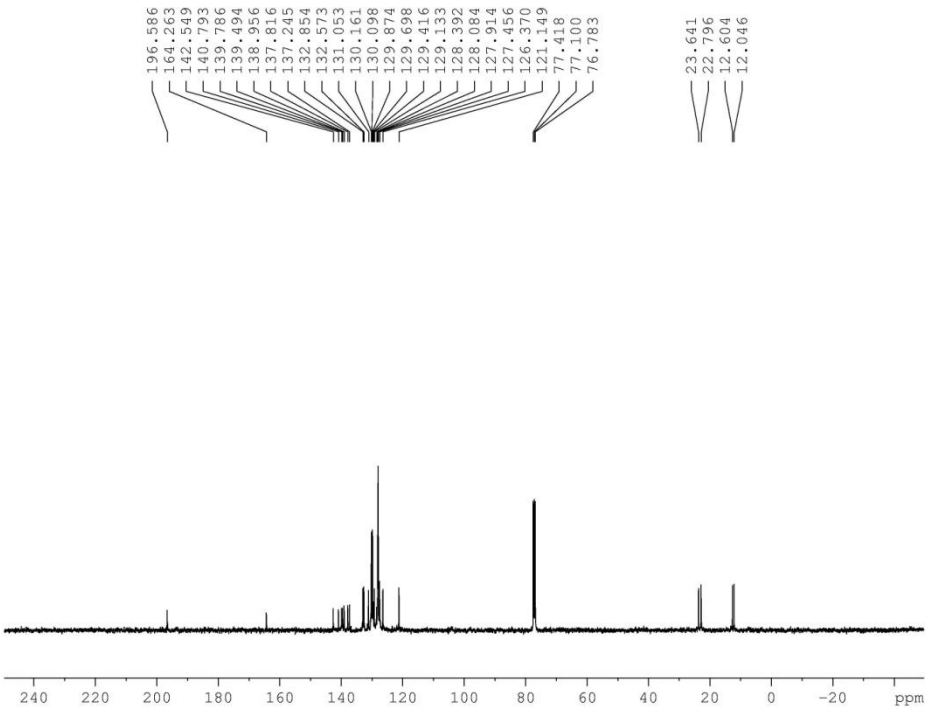


Figure S54. ^{13}C NMR spectrum of compound **4i**

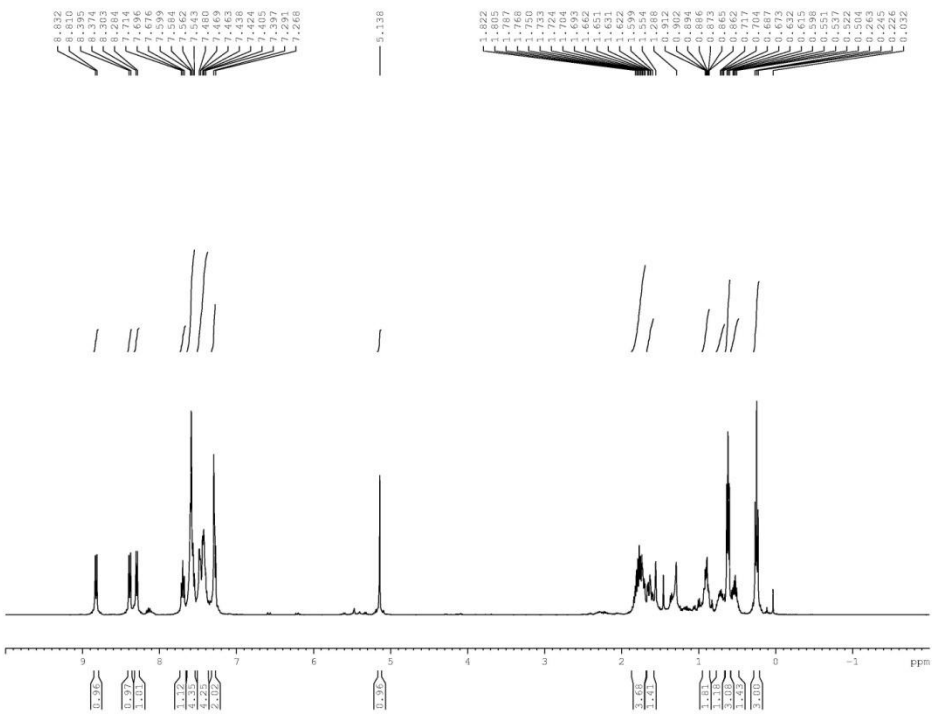


Figure S55. ^{1}H NMR spectrum of compound **3j**

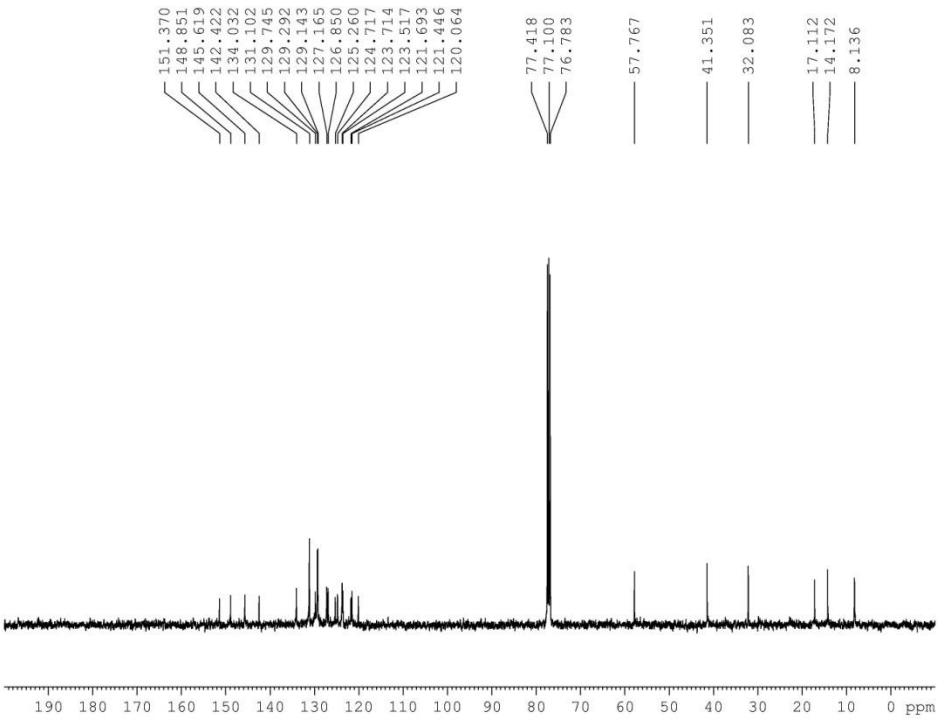


Figure S56. ^{13}C NMR spectrum of compound **3j**

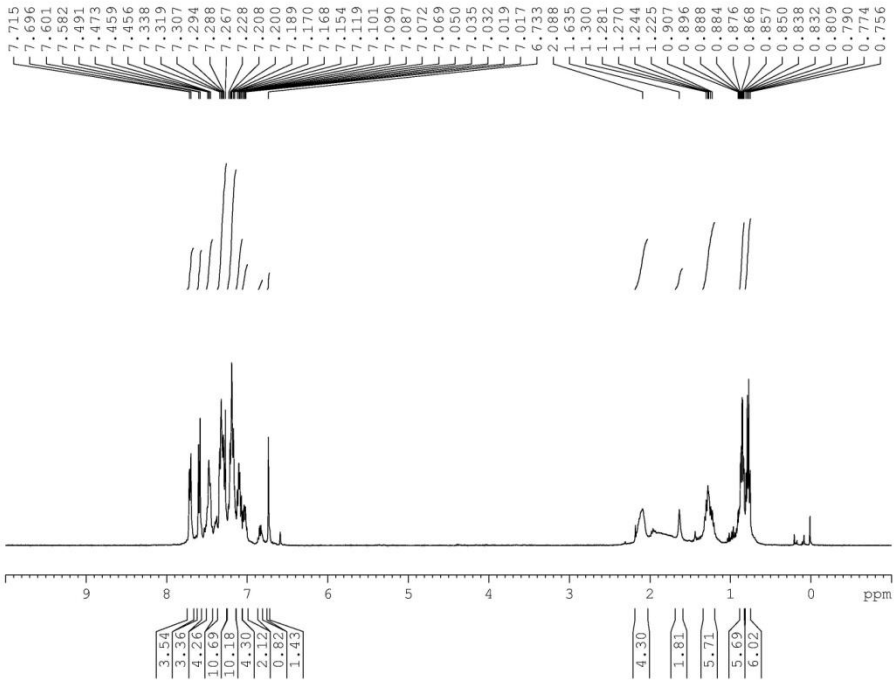


Figure S57. ^{1}H NMR spectrum of compound **4j**

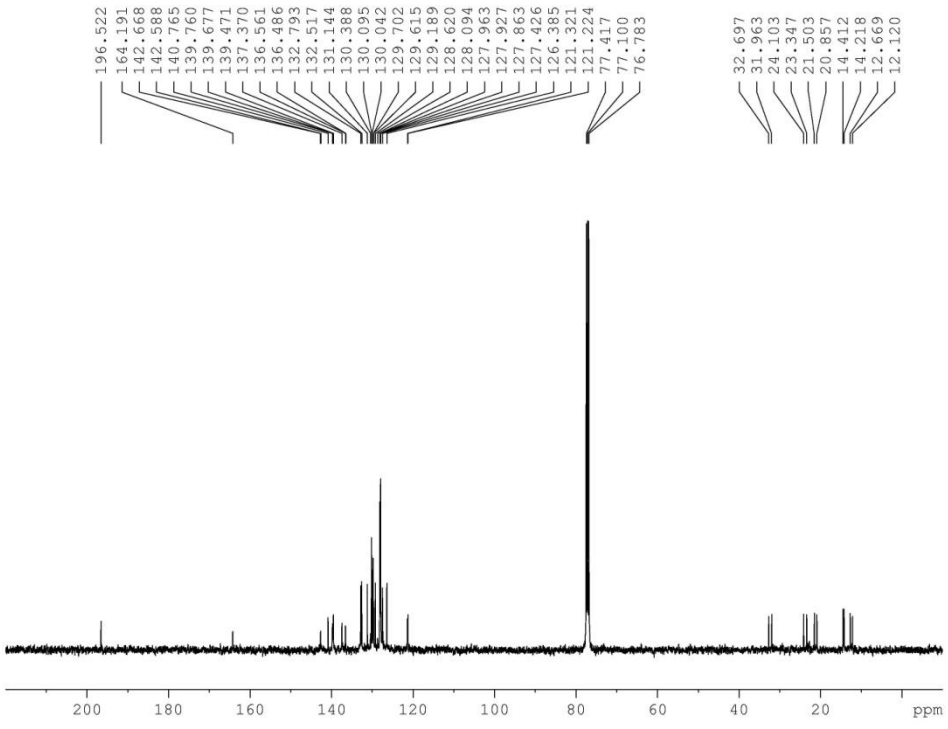


Figure S58. ^{13}C NMR spectrum of compound **4j**

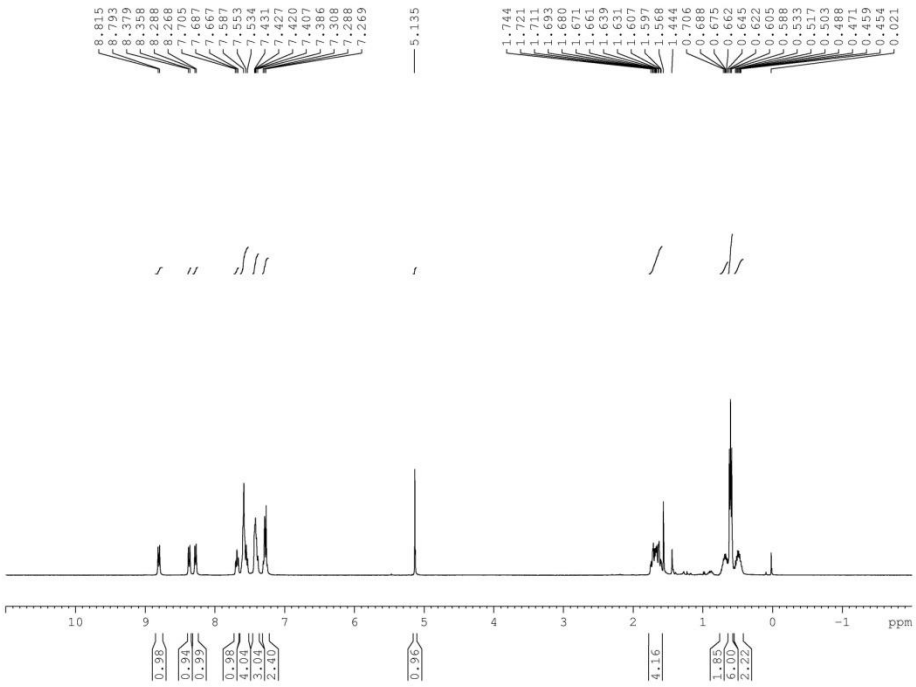


Figure S59. ^{1}H NMR spectrum of compound **3k**

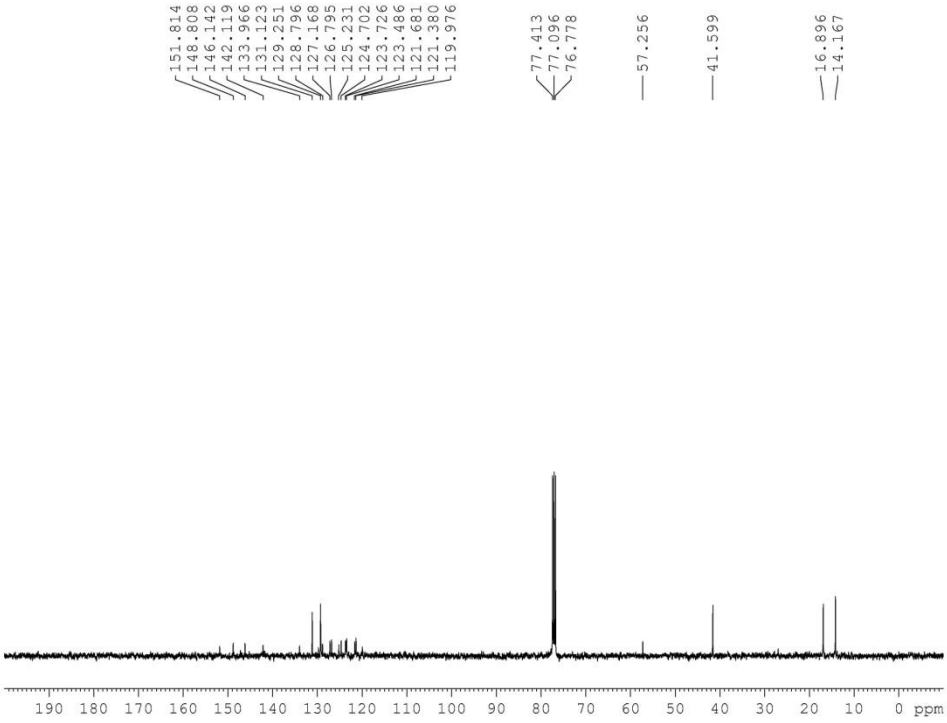


Figure S60. ^{13}C NMR spectrum of compound **3k**

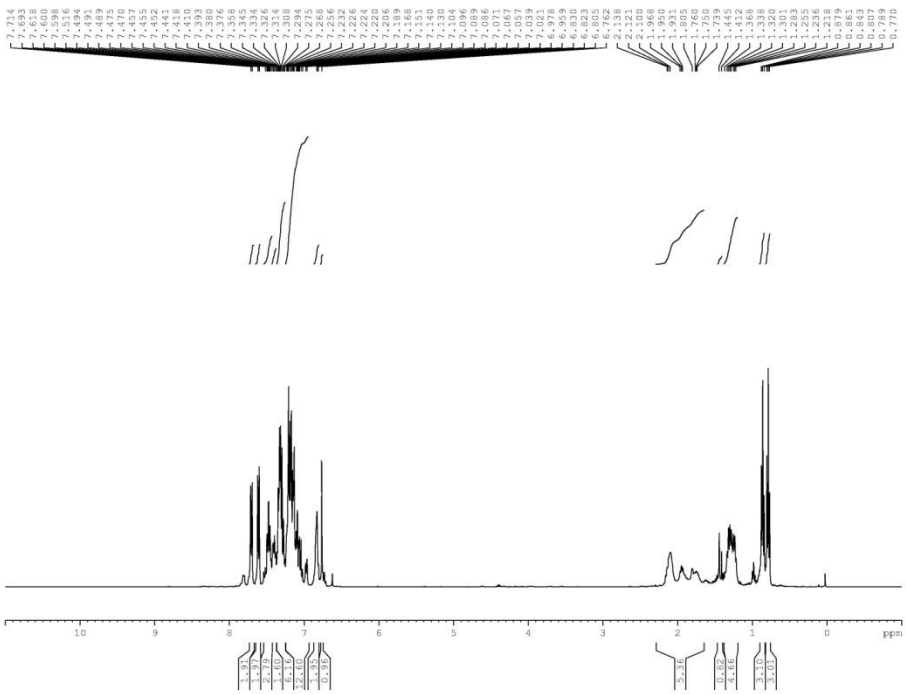


Figure S61. ^{1}H NMR spectrum of compound **4k**

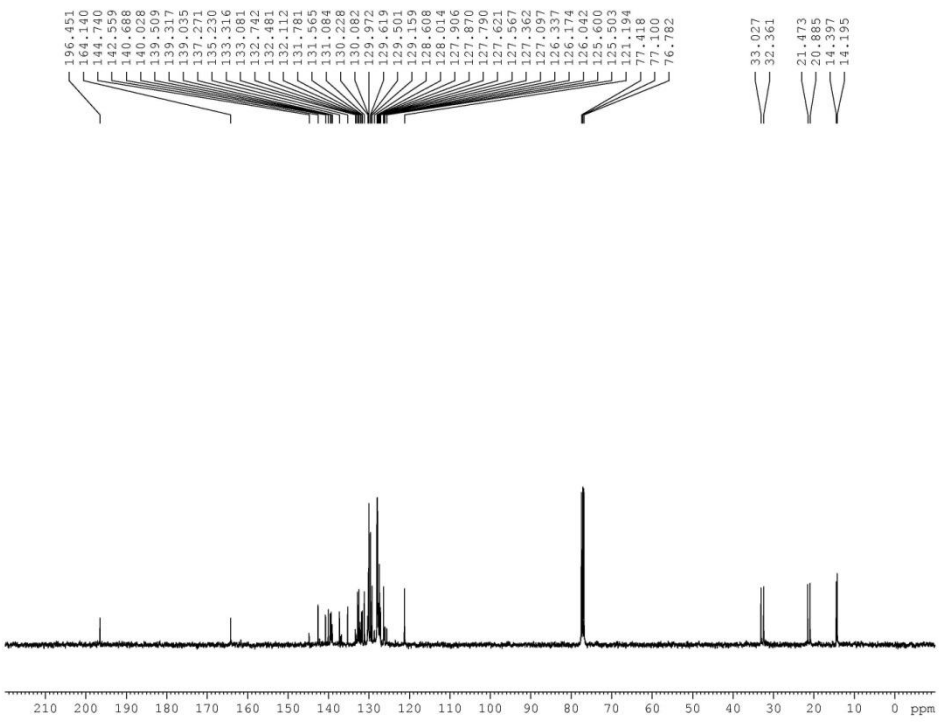


Figure S62. ^{13}C NMR spectrum of compound **4k**

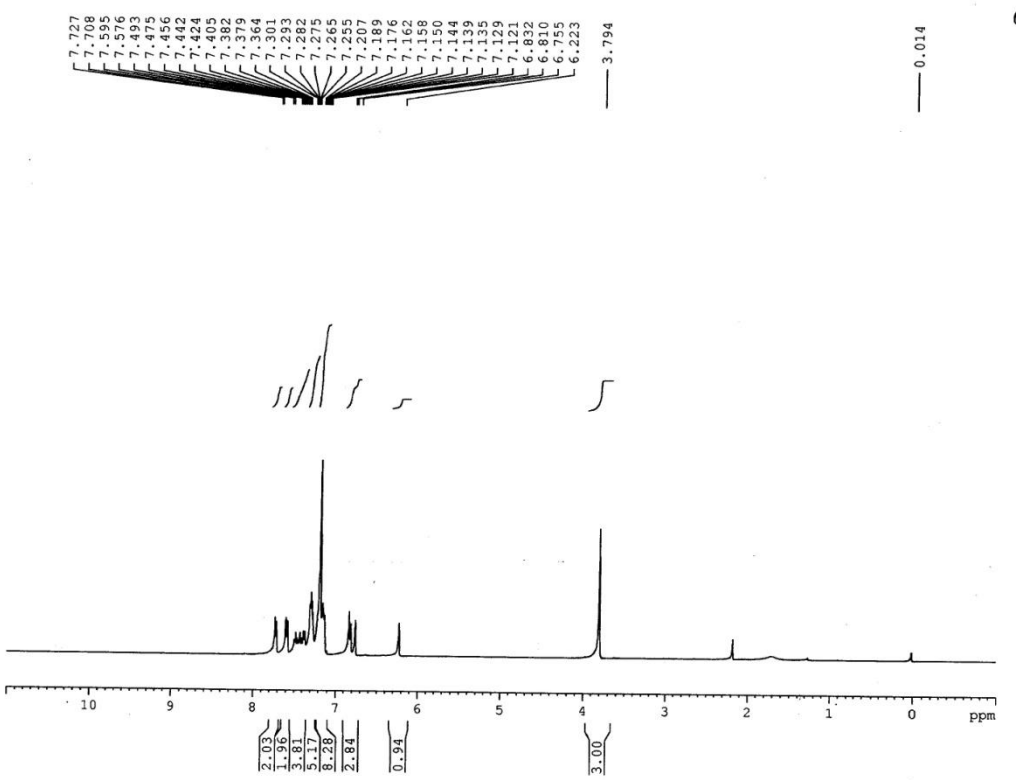


Figure S63. ^{1}H NMR spectrum of compound **4l**

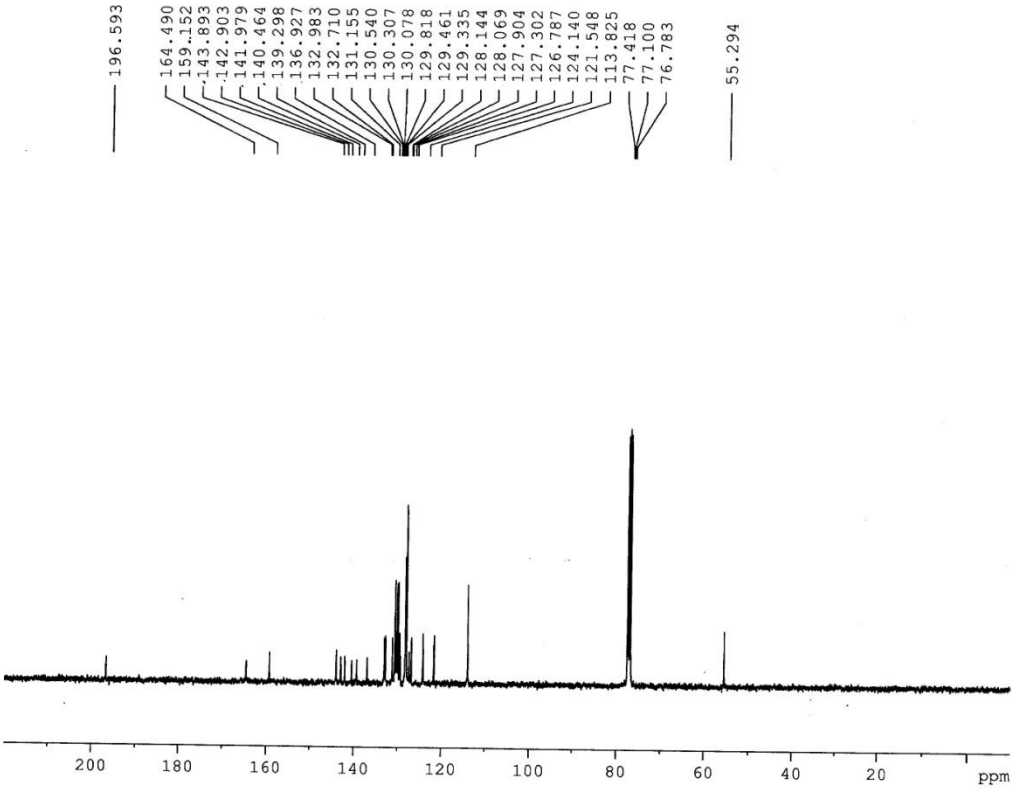


Figure S64. ^{13}C NMR spectrum of compound **4l**

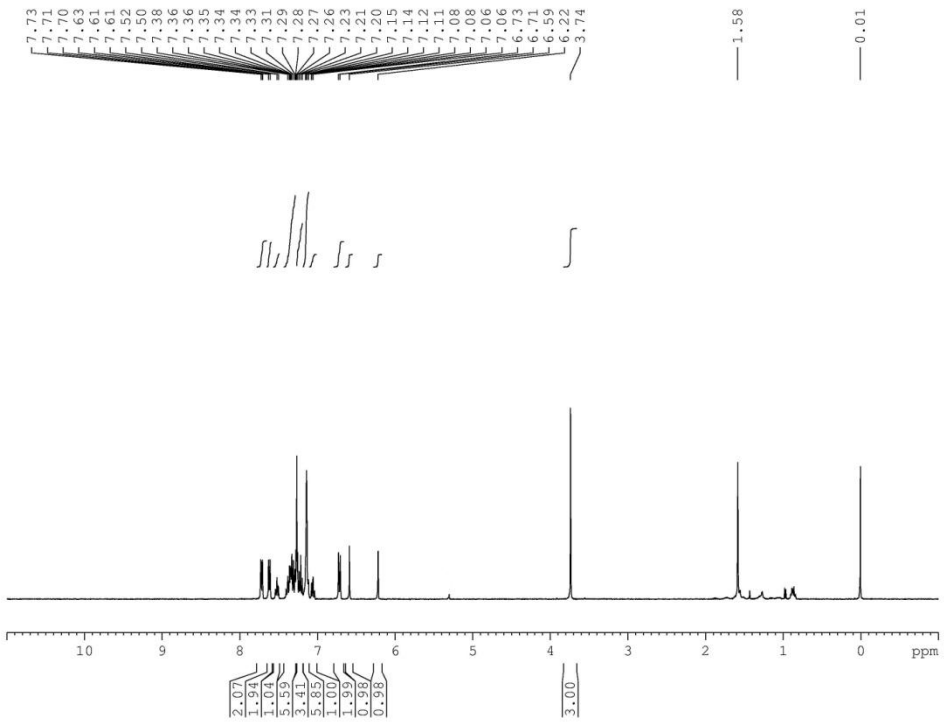


Figure S65. ^{1}H NMR spectrum of compound **4l'**

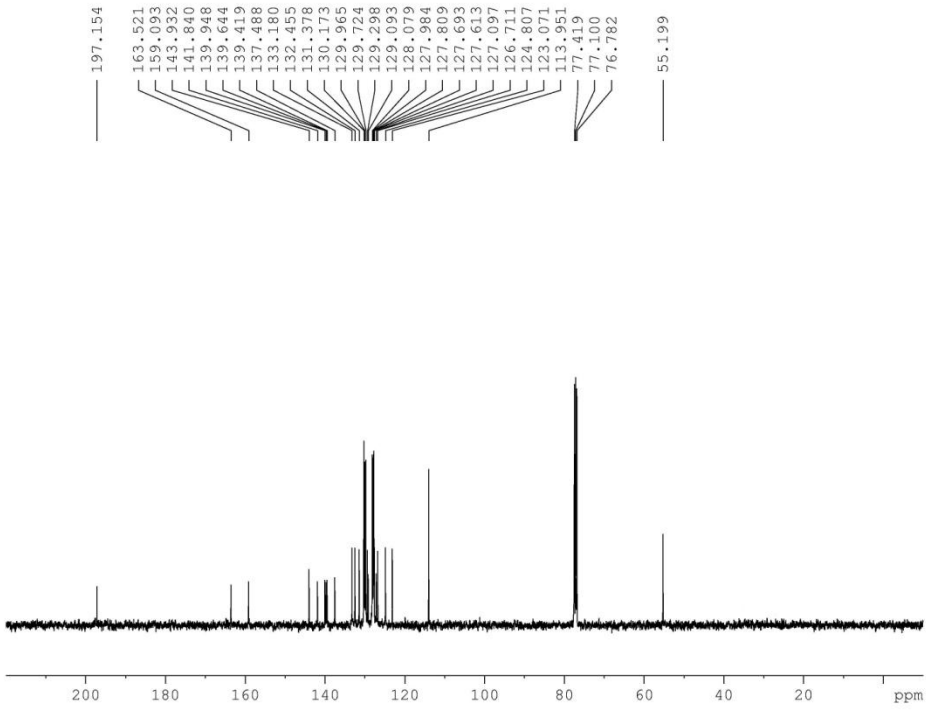


Figure S66. ^{13}C NMR spectrum of compound **4l'**

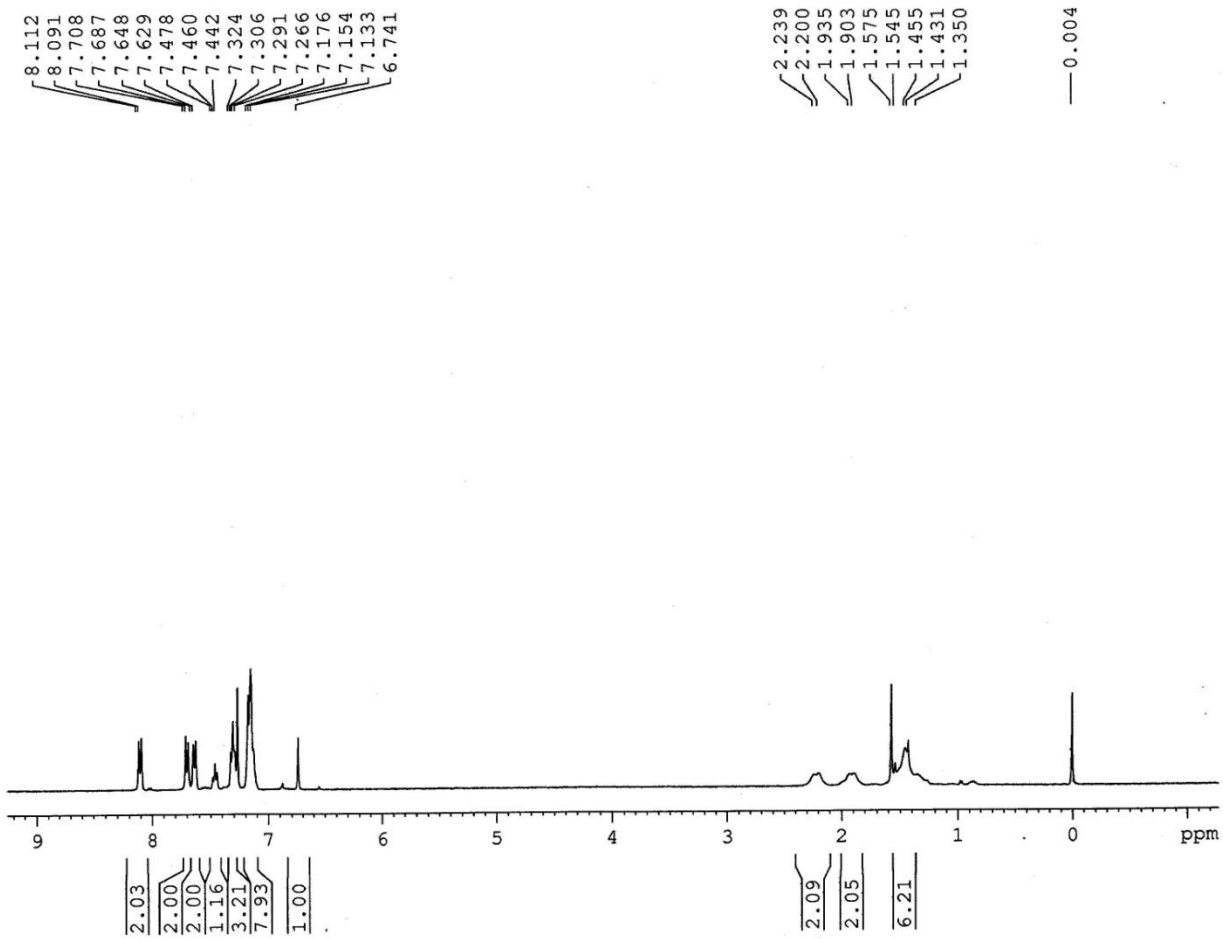


Figure S67. ^{1}H NMR spectrum of compound **5**

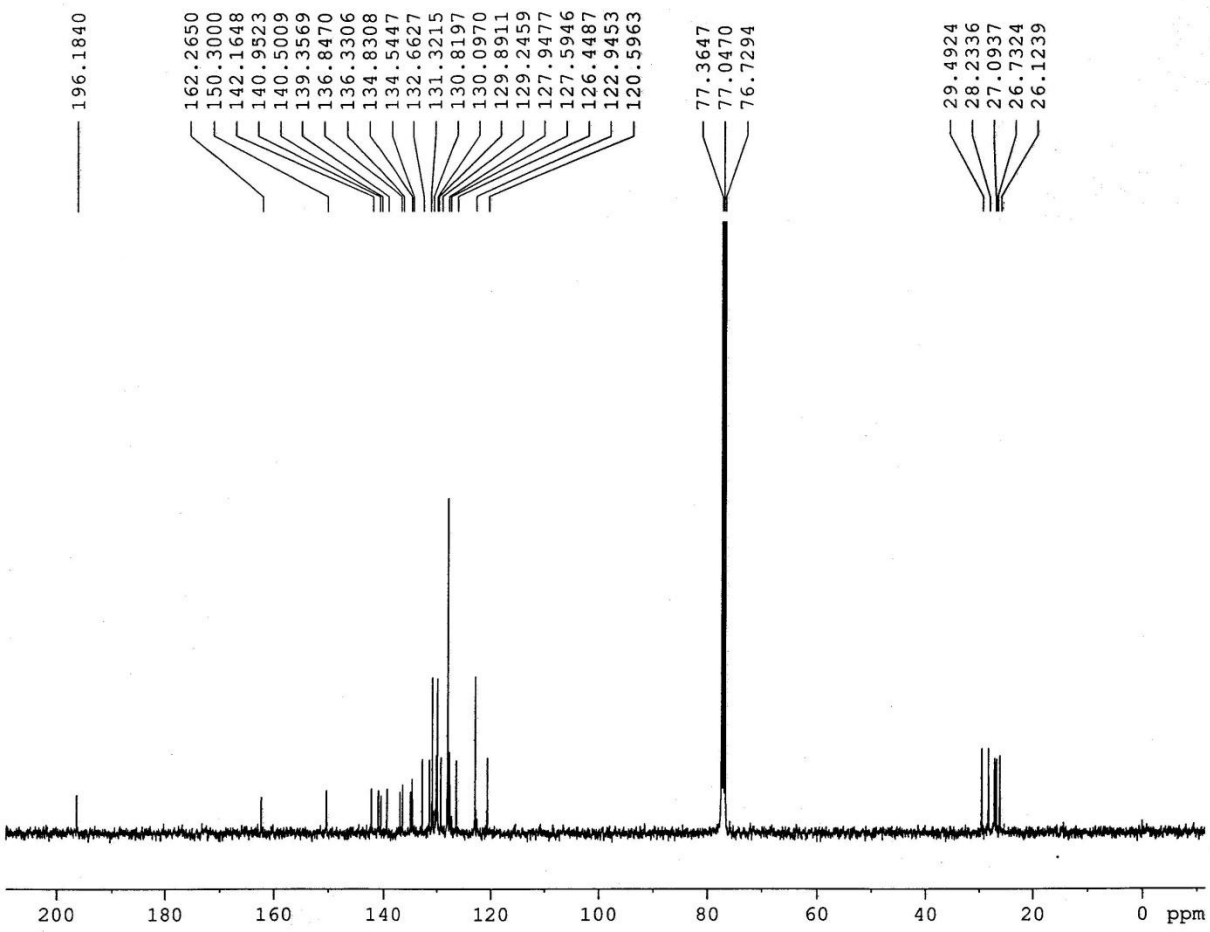


Figure S68. ^{13}C NMR spectrum of compound **5**

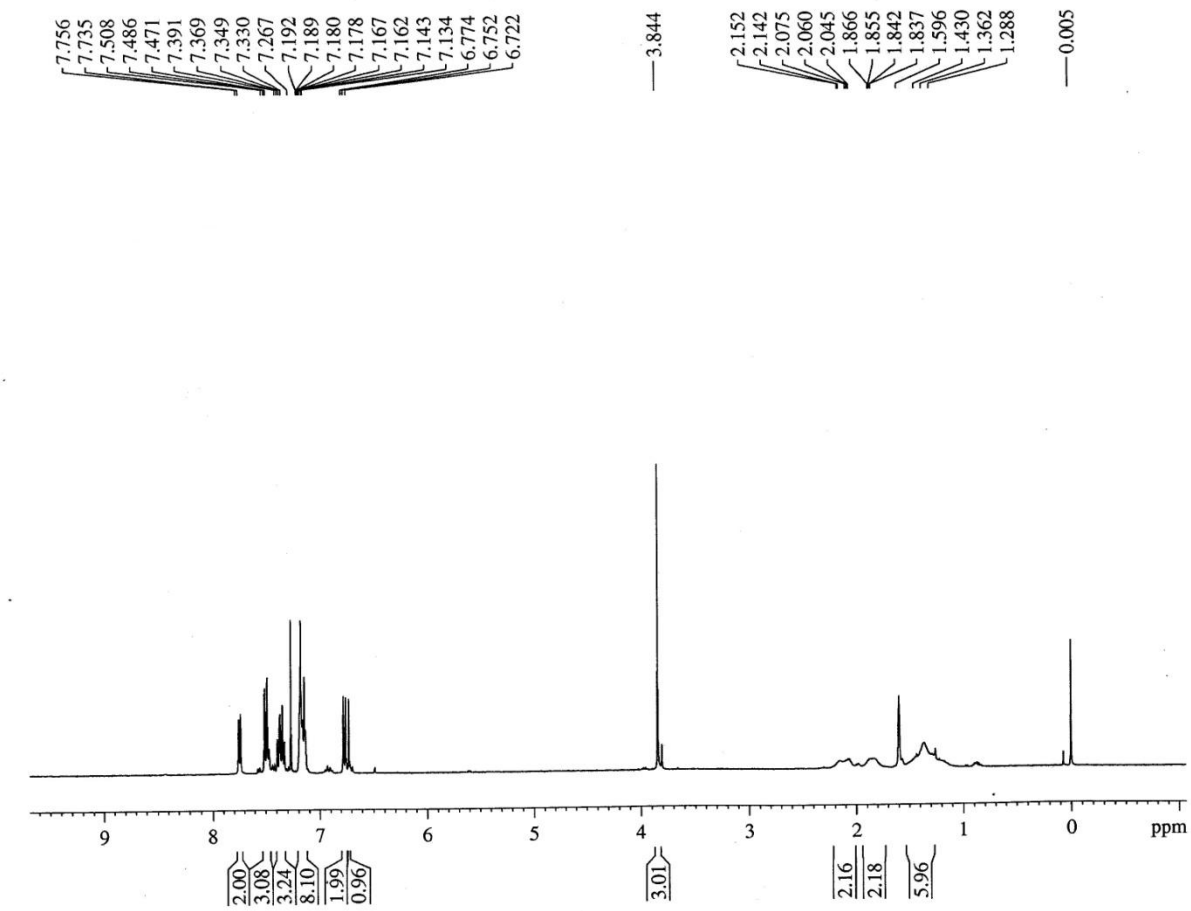


Figure S69. ^{1}H NMR spectrum of compound **6**

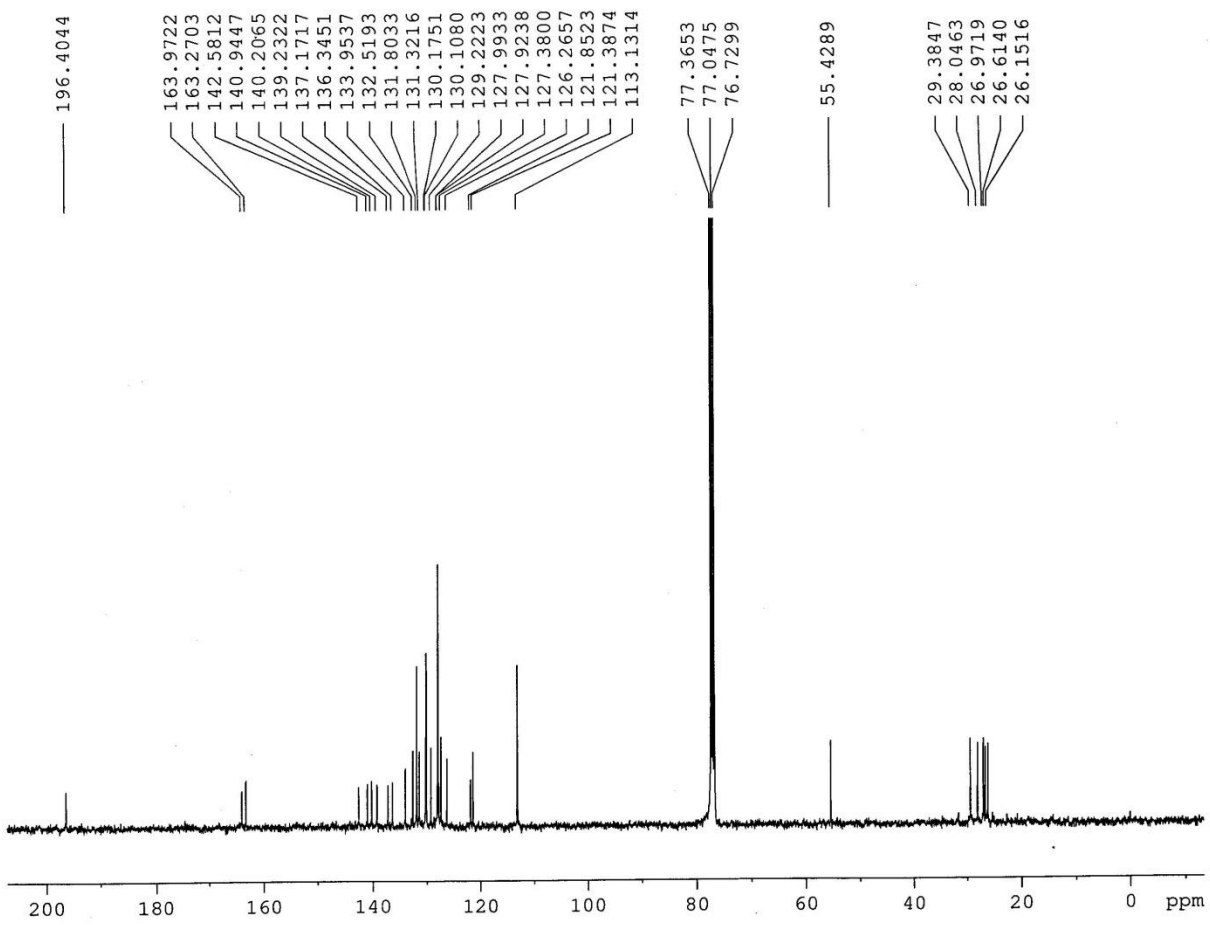


Figure S70. ^{13}C NMR spectrum of compound **6**

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