Supporting Information

A Facile and Chemoselective Synthesis of 1,4-Benzodiazepin-2-ones and Dienyl Thiazolidin-4-ones

Bilash Kuila[a], Yogesh Kumar[a], Dinesh Mahajan[b], Kapil Kumar[c], Prabhpreet Singh[c], Gaurav Bhargava[a]*

[a]*Departmentof Applied Sciences, I. K. Gujral PunjabTechnical University, Kapurthala 144603, Punjab, India*
[b]*SphaeraPharma Pvt. Ltd, Plot 32, Sec-5, IMT Manesar, Gurgaon, Haryana, India*
[c]*Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, Punjab, India*

General information:

METHODS AND MATERIALS:

Unless otherwise noted, commercial available materials were used without further purification. Air sensitive reactions were carried out under argon atmosphere. Anhydrous solvents were obtained from Sigma Aldrich, Merck.Thin layer chromatography (tlc) was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds viewed under an ultraviolet lamp. NMR spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts (δ) are quoted in parts per million (ppm) relative to internal solvent reference ($CDCl_3$ $\delta = 7.26$ for ^{1}H NMR and $\delta = 77.0$ for ^{13}C NMR and DMSO-d_6 $\delta = 2.50$ for ^{1}H NMR and $\delta = 39.9$ for ^{13}C NMR). Coupling constants are given in Hz. Data is reported as followed: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were recorded on a Bruker-micrOTOF-Q II mass spectrometer.

EXPERIMENTAL PROCEDURES:

General procedure for the preparation of 2-(aryl)-3-(2-oxo-4-styryl-1-arylazetidin-3-yl)thiazolidin-4-one 4a-i and 6a-g: To a solution of compound **1** (0.5 g, 1 *equiv.*) in toluene (10 mL) was added successively aldehyde (1.2 *equiv.*) and $MgSO_4$ (10 *equiv.*). The reaction mixture was heated at 80 ˚C for 4 hrs. Thioglycolic acid (1.3 *eq.*) was added in the reaction mixture and reaction mixture was heated at 80 ˚C for additional 12 hrs. The progress of the reaction was monitored by *tlc* considering 3-amino-2-azetidinone as the limiting reactant. After completion of

reaction, excess of solvent was evaporated under reduced pressure. The crude product was purified *via* column chromatography using 20-35% mixture of ethyl acetate in hexane as eluent to get **4** and **6** as pure compounds.

2-(4-methoxyphenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**4a**): White solid; yield 90%; mp: 125-129 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.74 (d, J = 1.8 Hz, 1H), 3.76 (d, J = 1.2 Hz, 1H), 3.83 (s, 3H), 4.44 (t, J = 6 Hz, 1H), 4.51 (d, J = 5.4 Hz, 1H), 5.68 (s, 1H), 6.44 (d, J = 7.2 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 7.27-7.37 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 20.9, 32.7, 55.4, 61.6, 63.9, 65.3, 114.0, 117.0, 124.1, 126.8, 128.5, 128.8, 129.5, 129.7, 130.0, 133.8, 135.2, 135.7, 137.5, 160.6, 161.6, 171.8; LRMS: 471.2 (M+1), HRMS calcd for $C_{28}H_{27}N_2O_3S$ (MH^+): 471.1742, found: 471.1739.

3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)-2-phenylthiazolidin-4-one (**4b**): White solid; yield 82%; mp: 140-143 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.76 (d, J = 1.8 Hz, 1H), 3.77 (d, J = 1.2 Hz, 1H), 4.44 (dt, J = 5.7, 1.2 Hz, 1H), 4.54 (d, J = 5.7 Hz, 1H), 5.71 (s, 1H), 6.43 (d, J = 6.6 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 7.28-7.43 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 20.9, 32.6, 61.6, 64.1, 65.7, 117.0, 124.1, 126.8, 128.5, 128.5, 128.7, 128.8, 129.5, 129.8, 133.8, 135.2, 135.7, 137.5, 138.2, 161.4, 171.8; LRMS: 441.1 (M+1), HRMS calcd for $C_{27}H_{25}N_2O_2S$ (MH^+): 441.1637, found: 441.1640.

2-(2,5-dimethylphenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**4c**): Pale yellow solid; yield 86%; mp: 145-150 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.26 (s, 3H), 2.32 (s, 3H), 3.74 (d, J = 1.5 Hz, 1H), 3.76 (d, J = 0.6 Hz, 1H), 4.51 (d, J = 5.4 Hz, 1H), 4.63-4.67 (m, 1H), 6.09 (s, 1H), 6.56-6.64 (m, 1H), 6.76 (d, J = 16.2 Hz, 1H), 7.05 (d, J = 8.1 Hz, 4H), 7.15 (s, 1H), 7.27-7.40 (m, 5H), 7.47 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 18.6, 20.9, 21.0, 32.5, 60.0, 61.9, 64.2, 117.1, 124.5, 126.9, 128.6, 128.8, 129.5, 129.9, 130.9, 133.8, 135.2, 135.6, 136.3, 137.6, 161.6, 172.7; LRMS: 469.2 (M+1), HRMS calcd for $C_{29}H_{29}N_2O_2S$ (MH^+): 469.1950, found: 469.1954.

2-(furan-2-yl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**4d**): White solid; yield 83%; mp: 178-182 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.65 (d, J = 15.6 Hz, 1H), 3.84 (d, J = 15.6 Hz, 1H), 4.63 (t, J = 5.4 Hz, 1H), 4.84 (d, J = 5.4 Hz, 1H), 5.65 (s, 1H), 6.17-

6.25 (m, 1H), 6.32-6.41 (m, 3H), 7.07 (d, J = 8.1 Hz, 2H), 7.22-7.31 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 20.9, 32.1, 57.8, 61.1, 64.3, 109.6, 110.7, 117.0, 123.0, 126.7, 128.3, 128.7, 129.5, 133.9, 135.2, 135.8, 136.2, 143.7, 151.0, 160.8, 171.1; LRMS: 431.1 (M+1), HRMS calcd for $C_{25}H_{23}N_2O_3S$ (MH^+): 431.1429, found: 431.1432.

3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)-2-(pyridin-2-yl)thiazolidin-4-one (**4e**): White solid; yield 59%; mp: 215-218 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.53 (d, J = 15.6 Hz, 1H), 3.90 (dd, J = 15.6, 1.5 Hz, 1H), 4.67 (d, J = 5.4 Hz, 1H), 4.88 (dd, J = 8.1, 5.4 Hz, 1H), 5.76 (s, 1H), 6.18 (dd, J = 16.2, 8.1 Hz, 1H), 6.74 (d, J = 16.2 Hz, 1H), 7.07 (dd, J = 8.1, 4.5 Hz, 2H), 7.21-7.39 (m, 8H), 7.57 (d, J = 8.1 Hz, 1H), 7.73 (dd, J = 8.1, 1.8 Hz, 1H), 8.51 (t, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.9, 31.8, 60.6, 63.5, 64.2, 117.0, 121.1, 123.4, 123.9, 126.8, 128.7, 129.5, 134.0, 135.1, 135.6, 136.4, 137, 149.4, 159.0, 160.5, 172.7; LRMS: 442.2 (M+1), HRMS calcd for $C_{26}H_{24}N_3O_2S$ (MH^+): 442.1589, found: 442.1587.

3-(1-(4-chlorophenyl)-2-oxo-4-styrylazetidin-3-yl)-2-phenylthiazolidin-4-one (**4f**): White solid; yield 85%; mp: 214-220 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (d, J = 6 Hz, 2H), 4.43 (t, J = 5.4 Hz, 1H), 4.55 (d, J = 5.4 Hz, 1H), 5.71 (s, 1H), 6.34-6.49 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.25-7.41 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 32.6, 61.8, 64.2, 65.7, 118.2, 123.4, 126.8, 128.5, 128.7, 128.8, 128.9, 129.1, 129.2, 129.9, 135.5, 136.1, 137.9, 138.0, 161.7, 171.9; LRMS: 461.2 (M+1), HRMS calcd for $C_{26}H_{22}ClN_2O_2S$ (MH^+): 461.1091, found: 461.1087.

3-(1-(4-chlorophenyl)-2-oxo-4-styrylazetidin-3-yl)-2-(2,5-dimethylphenyl)thiazolidin-4-one (**4g**): Yellow solid; yield 84%; mp:150-155 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.20 (s, 3H), 2.32 (s, 3H), 3.69-3.83 (m, 2H), 4.49 (d, J = 5.7 Hz, 1H), 4.64 (dd, J = 8.7, 5.7 Hz, 1H), 6.09 (s, 1H), 6.55-6.63 (m, 1H), 6.86 (d, J = 15.6 Hz, 1H), 7.05 (d, J = 0.9 Hz, 2H), 7.15-7.35 (m, 8H), 7.37 (d, J = 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 18.6, 21.0, 32.5, 62.2, 64.4, 68.0, 118.3, 123.9, 126, 128.8, 128.9, 129.1, 129.2, 130.0, 131.8, 133.5, 135.4, 136.1, 136.4, 138.1, 161.9, 172.7; LRMS: 489.0 (M+1), HRMS calcd for $C_{28}H_{26}ClN_2O_2S$ (MH^+): 489.1404, found: 489.1400.

3-(1-(4-chlorophenyl)-2-oxo-4-styrylazetidin-3-yl)-2-(furan-2-yl)thiazolidin-4-one (**4h**): White solid; yield 82%; mp: 216-222 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (d, J = 15.6 Hz, 1H), 3.84 (dd, J = 15.6, 1.5 Hz, 1H), 4.63 (t, J = 5.1 Hz, 1H), 4.83 (d, J = 5.1 Hz, 1H), 5.64 (d, J = 1.2 Hz, 1H), 6.14-6.23 (m, 1H), 6.31-6.41 (m, 3H), 7.21-7.31 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 32.1, 57.8,

61.1, 64.5, 109.7, 110.7, 118.3, 122.4, 126.7, 128.5, 128.7, 129.1, 129.3, 135.6, 136.1, 136.7, 143.7, 150.9, 161, 171.1; LRMS: 451.0 (M+1), HRMS calcd for $C_{24}H_{20}ClN_2O_3S$ (MH^+): 451.0883, found: 451.0885.

3-(1-(4-chlorophenyl)-2-oxo-4-styrylazetidin-3-yl)-2-(pyridin-2-yl)thiazolidin-4-one (**4i**): Brown solid; yield 57%; mp: 190-198 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (d, J = 15.6 Hz, 1H), 3.87 (dd, J = 15.6, 1.8 Hz, 1H), 4.60 (bs, 1H), 5.07 (d, J = 5.1 Hz, 1H), 5.74 (d, J = 1.2 Hz, 1H), 6.20-6.32 (m, 2H), 7.20-7.35 (m, 10H), 7.39 (d, J = 7.8 Hz, 1H), 7.56 (dt, J = 7.8, 1.2 Hz, 1H), 8.50 (dd, J = 3.9, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 31.9, 61, 64.5, 65.7, 118.3, 121.6, 122.7, 123.8, 126.7, 128.6, 128.8, 129.1, 135.4, 136, 136.8, 137.2, 149.3, 158.7, 160.9, 172.2; LRMS: 462.1 (M+1), HRMS calcd for $C_{25}H_{21}ClN_3O_2S$ (MH^+): 462.1043, found: 462.1045.

2-(2-nitrophenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**6a**): Yellow solid; yield 86%; mp: 191-195 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 3.49 (d, J = 15.9 Hz, 1H), 3.68 (dd, J = 15.9, 1.2 Hz, 1H), 4.89 (dd, J = 5.4, 2.1 Hz, 1H), 5.28 (d, J = 4.8 Hz, 1H), 6.38 (dd, J = 15.9, 8.1 Hz, 1H), 6.47 (s, 1H), 6.79 (d, J = 15.1 Hz, 1H), 7.08 (d, J = 8.1 Hz, 2H), 7.26-7.53 (m, 9H), 7.63 (dd, J = 7.5, 0.9 Hz, 1H), 8.17 (dd, J = 7.5, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.9, 30.9, 59.8, 60.0, 64.1, 117.1, 122.4, 125.8, 126.8, 128.7, 128.8, 129.3, 129.6, 134.1, 134.5, 134.8, 135.5, 137.3, 137.4, 146.3, 159.7, 173.1; LRMS: 486.2 (M+1), HRMS calcd for $C_{27}H_{24}N_3O_4S$ (MH^+): 486.1488, found: 486.1479.

3-(1-(4-fluorophenyl)-2-oxo-4-styrylazetidin-3-yl)-2-(2-nitrophenyl)thiazolidin-4-one (**6b**): white solid; yield 90%; mp: 136-140 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (d, J = 1.2 Hz, 1H), 3.74 (d, J = 1.2 Hz, 1H), 4.87 (dd, J = 7.8, 5.1 Hz, 1H), 5.25 (d, J = 5.1 Hz, 1H), 6.31-6.44 (m, 1H), 6.45 (s, 1H), 6.77 (d, J = 16.2 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.00-7.61 (m, 10H), 8.14 (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 31.0, 50.8, 59.9, 64.4, 115.8, 116.1, 118.6, 118.7, 121.8, 125.7, 126.8, 127.1, 128.8, 128.9, 129.4, 133.5, 134.1, 135.3, 137.8, 159.9, 173.1; LRMS: 490.1 (M+1), HRMS calcd for $C_{26}H_{21}FN_3O_4S$ (MH^+): 490.1237, found: 490.1241.

2-(2-nitrophenyl)-3-(2-oxo-1-phenyl-4-styrylazetidin-3-yl)thiazolidin-4-one (**6c**): Yellow solid; yield 82%; mp: 85-88 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.52 (d, J = 15.9 Hz, 1H), 3.70 (dd, J = 15.9, 1.2 Hz, 1H), 4.92 (dd, J = 7.8, 5.4 Hz, 1H), 5.30 (d, J = 4.8 Hz, 1H), 6.39 (dd, J = 15.9, 4.8 Hz, 1H), 6.48 (s, 1H), 6.81 (d, J = 15.9 Hz, 1H), 7.11 (t, J = 7.2 Hz, 2H), 7.27-7.64 (m, 11H),

8.18 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 30.9, 59.9, 60.1, 64.2, 117.1, 122.1, 124.8, 125.8, 126.9, 128.8, 128.9, 129.2, 129.3, 134.1, 135.4, 137.2, 137.5, 160.0, 173.1; LRMS: 472.0 (M+1), HRMS calcd for $C_{26}H_{22}N_3O_4S$ (MH^+): 472.1331, found: 472.1333.

3-(2-(4-methoxystyryl)-4-oxo-1-phenylazetidin-3-yl)-2-(2-nitrophenyl)thiazolidin-4-one (**6d**): Yellow solid; yield 79%; mp: 154-158 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.54 (d, J = 15.9 Hz, 1H), 3.67-3.72 (dd, J = 15.9, 1.2 Hz, 1H), 3.94 (s, 3H), 4.89 (dd, J =8.1, 4.8 Hz, 1H), 5.22 (d, J = 4.8 Hz, 1H), 6.42-6.50 (m, 2H), 6.99 (t, J = 7.5 Hz, 2H), 7.11 (d, J = 6 Hz, 2H), 7.28-7.32 (m, 3H), 7.41 (dd, J = 9, 1.2 Hz, 2H), 7.52-7.63 (m, 3H), 7.65 (d, J = 6.6 Hz, 1H), 8.17 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 31.0, 55.4, 60.0, 60.9, 64.2, 110.0, 117.2, 120.8, 123.1, 124.6, 125.7, 127.2, 127.7, 129.1, 129.3, 129.8, 132.9, 134.1, 137.4, 146.4, 157.0, 160.2, 173.0; LRMS: 502.1 (M+1), HRMS calcd for $C_{27}H_{24}N_3O_5S$ (MH^+): 502.1437, found: 502.1434.

2-(4,5-dimethoxy-2-nitrophenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**6e**): White solid; yield 80%; mp: 186-190 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.48 (dd, J = 16.2, 6 Hz, 1H), 3.67 (dd, J = 16.2, 5.4 Hz, 1H), 3.85 (s, 3H), 3.97 (s, 3H), 4.90 (t, J = 5.4 Hz, 1H), 5.40 (d, J = 5.1 Hz, 1H), 6.28 (dd, J = 16.2, 7.5 Hz, 1H), 6.62 (d, J = 5.7 Hz, 1H), 6.74-6.83 (m, 2H), 7.08 (t, J = 5.1 Hz, 2H), 7.24-7.45 (m, 7H), 7.74 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.9, 30.9, 56.4, 56.5, 59.8, 61.9, 63.9, 108.0, 108.6, 117.1, 122.0, 126.9, 128.7, 128.8, 129.6, 132.0, 134.6, 134.7, 135.4, 137.3, 138.8, 148.7, 153.9, 159.6, 173.3; LRMS: 546.2 (M+1), HRMS calcd for $C_{29}H_{28}N_3O_6S$ (MH^+): 546.1699, found: 546.1697.

3-(2-(4-methoxystyryl)-4-oxo-1-phenylazetidin-3-yl)-2-(4,5-dimethoxy-2-nitrophenyl)thiazolidin-4-one (**6f**): Pale yellow solid; yield 84%; mp: 139-142 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.47-3.53 (m, 1H), 3.68 (dd, J = 15.9, 0.9 Hz, 1H), 3.84 (s, 3H), 3.89 (s, 3H), 3.98 (s, 3H), 4.91 (dd, J = 7.8, 5.4 Hz, 1H), 5.41 (d, J = 5.4 Hz, 1H), 6.39 (dd, J = 16.2, 8.4 Hz, 1H), 6.60 (d, J = 0.9 Hz, 1H), 6.82 (s, 1H), 6.93 (dd, J = 16.2, 8.4 Hz, 2H), 7.08 (t, J = 6.3 Hz, 1H), 7.24-7.31 (m, 4H), 7.39 (dd, J = 8.4, 0.9 Hz, 2H), 7.51 (dd, J = 7.5, 1.5 Hz, 1H) 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 31.0, 55.4, 56.4, 56.5, 59.9, 60.7, 64.0, 108.3, 108.5, 110.9, 117.2, 120.7, 122.6, 124.6, 127.7, 129.1, 129.8, 131.8, 132.8, 137.3, 137.3, 139.0, 148.7, 153.9, 157.1, 160.2, 173.2; LRMS: 562.2 (M+1), HRMS calcd for $C_{29}H_{28}N_3O_7S$ (MH^+): 562.1648, found: 562.1650.

2-(4,5-dimethoxy-2-nitrophenyl)-3-(2-oxo-1-phenyl-4-((E)-1-phenylprop-1-en-2-yl)azetidin-3-yl)thiazolidin-4-one (**6g**): White solid; yield 82%; mp: 155-160 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 3H), 3.74 (s, 3H), 3.78 (d, *J* = 16.4 Hz, 1H), 3.87 (dd, *J* = 16.4, 1.5 Hz, 1H), 4.01 (s, 3H), 4.81 (d, *J* = 2.4 Hz, 1H), 4.87 (bs, 1H), 6.49 (s, 1H), 6.59 (bs, 1H), 7.01 (d, *J* = 5.1 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.25-7.39 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 12.2, 32.0, 56.2, 56.6, 58.9, 64.4, 64.6, 108.0, 109.7, 116.9, 124.6, 127.4, 128.3, 128.9, 129.1, 129.4, 130.7, 132.1, 135.9, 137.5, 140.4, 149.1, 153.6, 161.2, 172.1; LRMS: 546.2 (M+1), HRMS calcd for $C_{29}H_{28}N_3O_6S$ (MH^+): 546.1699, found: 546.1694.

General procedure for the preparation of 2-(4,5-disubstituted-2-aminophenyl)-3-(2-oxo-4-styryl-1-arylazetidin-3-yl)thiazolidin-4-one 7a-g: To a solution of compound **6** (0.2 g, 1 *equiv.*) in a mixture of ethanol and water (ratio 2:1; 6 mL) were added successively iron powder (4 *equiv.*) and NH_4Cl (4 *equiv.*). The reaction mixture was heated at 60 ˚C for 4 hrs. The progress of the reaction was monitored by *tlc* considering **6** as a limiting reactant. After completion of reaction, excess of solvent was evaporated under reduced pressure and reaction mixture was extracted with DCM (3 X 50 mL). Combined organic layers were washed with water (50 mL) followed by brine solution (50 mL). The organic layer thus obtained was dried over anhyNa_2SO_4 and concentrated to get crude product. The crude product was purified *via* column chromatography using 30-50% mixture of ethyl acetate in hexane as eluent to obtain **7** as pure compound.

2-(2-aminophenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**7a**): White solid; yield 96%; mp: 155-159 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 3.69-3.89 (m, 2H), 4.55-4.63 (m, 2H), 5.94 (s, 1H), 6.44-6.62 (m, 3H), 6.76 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.28-7.45 (m, 7H); ^{13}C NMR ($CDCl_3$): δ 20.9, 32.4, 59.3, 61.7, 64.0, 117.0, 117.7, 118.8, 124.1, 126.8, 128.4, 128.7, 129.5, 130.5, 133.8, 135.8, 135.9, 137.2, 145.1, 161.6, 171.8; LRMS: 456.2 (M+1), HRMS calcd for $C_{27}H_{26}N_3O_2S$ (MH^+): 456.1746, found: 456.1743.

2-(2-aminophenyl)-3-(1-(4-fluorophenyl)-2-oxo-4-styrylazetidin-3-yl)thiazolidin-4-one (**7b**): White solid; yield 95%; mp: 203-207 ˚C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.67 (d, *J* = 15.9 Hz, 1H), 3.78 (d, *J* = 15.9 Hz, 1H), 4.76 (d, *J* = 5.4 Hz, 1H), 4.79 (d, *J* = 5.4 Hz, 1H), 6.22 (s, 1H), 6.30 (dd, *J* = 15.9, 6.6 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 7.01 (d, *J* =

7.8 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.20-7.44 (m, 7H); ^{13}C NMR (DMSO-d_6): δ 32.0, 59.6, 61.6, 64.5, 116.2, 116.5 118.6, 118.7, 121.8, 124.1, 127.0, 128.8, 129.3, 129.6, 134.7, 136.3, 138.1, 146.4, 157.0, 162.1, 172.5; LRMS: 460.2 (M+1), HRMS calcd for $C_{26}H_{23}FN_3O_2S$ (MH^+): 460.1495, found: 460.1491

2-(2-aminophenyl)-3-(2-oxo-1-phenyl-4-styrylazetidin-3-yl)thiazolidin-4-one (**7c**): White solid; yield 91%; mp: 158-162 ˚C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.68 (d, *J* = 15.9 Hz, 1H), 3.73 (d, *J* = 15.9 Hz, 1H), 4.78 (dd, *J* = 9, 5.7 Hz, 1H), 4.90 (bs, 1H), 5.32 (bs, 2H), 6.23 (s, 1H), 6.30-6.42 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.96-7.07 (m, 3H), 7.31-7.46 (m, 9H); ^{13}C NMR (DMSO-d_6): δ 31.8, 59.7, 61.4, 64.3, 116.2, 116.9, 121.8, 124.1, 124.7, 126.9, 128.7, 129.3, 129.6, 133, 136.3, 137.8, 138.2, 146.4, 162.3, 172.5; LRMS: 442.2 (M+1), HRMS calcd for $C_{26}H_{24}N_3O_2S$ (MH^+): 442.1589, found: 442.1591.

3-(2-(4-methoxystyryl)-4-oxo-1-phenylazetidin-3-yl)-2-(2-aminophenyl)thiazolidin-4-one (**7d**): White solid; yield 83%; mp: 138-142 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63-3.83 (m, 2H), 3.95 (s, 3H), 4.55-4.65 (m, 2H), 5.98 (s, 1H), 6.49 (dd, *J* = 16.2, 9 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 2H), 7.18-7.33 (m, 5H), 7.42- 7.49 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 32.5, 55.5, 59.6, 62.3, 63.9, 110.9, 117.1, 117.5, 120.9, 124.1, 124.6, 124.9, 127.4, 129.0, 129.6, 130.6, 132.5, 138.3, 156.4, 162.3, 172.1; LRMS: 472.2 (M+1), HRMS calcd for $C_{27}H_{26}N_3O_3S$ (MH^+): 472.1695, found: 472.1699.

2-(2-amino-4,5-dimethoxyphenyl)-3-(2-oxo-4-styryl-1-p-tolylazetidin-3-yl)thiazolidin-4-one (**7e**): Pale yellow solid; yield 85%; mp: 98–102 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 3.70-3.79 (m, 2H), 3.93 (s, 3H), 4.00 (s, 3H), 4.45 (d, *J* = 5.7 Hz, 1H), 5.00 (dd, *J* = 9, 5.7 Hz, 1H), 6.28 (s, 1H), 6.45-6.53 (m, 1H), 6.92-6.97 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.20-7.48 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 20.7, 31.8, 53.5, 53.9, 59.4, 60.9, 63.9, 102.3, 110.1, 116.9, 122.4, 127.3, 128.7, 129.1, 129.6, 131.8, 134.5, 134.8, 135.8, 137.3, 138.3, 148.8, 154.2, 160.9, 172.1; LRMS: 516.2 ; LRMS: 516.2 (M+1), HRMS calcd for $C_{29}H_{30}N_3O_4S$ (MH^+): 516.1957, found: 516.1960.

3-(2-(4-methoxystyryl)-4-oxo-1-phenylazetidin-3-yl)-2-(2-amino-4,5-dimethoxyphenyl) thiazolidin-4-one (**7f**): Pale yellow solid; yield 87%; mp: 137–142 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.55 (s, 3H), 3.63-3.71 (m, 2H), 3.82 (s, 3H), 3.85 (s, 3H), 4.52-4.59 (m, 2H), 5.98 (bs, 1H), 6.21 (s, 1H), 6.50 (dd, *J* = 16.2, 8.7 Hz, 1H), 6.69 (s, 1H), 6.85-6.93 (m, 3H), 7.01 (t, *J*

= 6.9 Hz, 1H), 7.20-7.27 (m, 4H), 7.38-7.44 (m, 4H) ; ^{13}C NMR ($CDCl_3$): δ 32.7, 55.4, 55.8, 56.4, 60.8, 62.3, 63.6, 101.9, 110.8, 117.1, 117.3, 120.8, 124.0, 124.5, 124.7, 127.3, 128.1, 129.01, 129.07, 129.6, 132.0, 137.8, 151.0, 156.5, 162.5, 170.0; LRMS: 532.2 ; LRMS: 532.2 (M+1), HRMS calcd for $C_{29}H_{30}N_3O_5S$ (MH^+): 532.1906, found: 532.1904.

2-(2-amino-4,5-dimethoxyphenyl)-3-(2-oxo-1-phenyl-4-((E)-1-phenylprop-1-en-2-yl)azetidin-3-yl)thiazolidin-4-one (**7g**): Yellow semi-solid; yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (s, 3H), 3.41 (s, 3H), 3.80 (s, 3H), 3.83-3.89 (m, 2H), 4.18 (bs, 1H), 5.02 (d, J = 2.7 Hz, 1H), 5.80 (bs, 2H), 6.64 (bs, 1H), 6.71 (s, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.21-7.43 (m, 11H); ^{13}C NMR (DMSO-d_6): δ 11.4, 32.5, 53.4, 55.3, 56.6, 63.3, 64.9, 102.6, 117.0, 124.2, 127.2, 128.2, 128.3, 128.9, 129.0, 129.1, 131.1, 132.1, 136.6, 141.8, 151.1, 162.9, 170.7; LRMS: 516.2 ;LRMS: 516.2 (M+1), HRMS calcd for $C_{29}H_{30}N_3O_4S$ (MH^+): 516.1957, found: 516.1955.

General procedure for the preparation of (3E,4Z)-3-((E)-3-arylallylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one 8a-e: To a solution of compound **7** (0.2 g, 1 *equiv.*) in methanol (5 mL) was added successively sodium methoxide (5 *equiv.*). The reaction mixture was stirred at room temperature for 60 hrs. The progress of the reaction was monitored by *tlc* considering **7** as a limiting reactant. After completion of reaction, the excess of solvent was evaporated under reduced pressure. The crude product thus obtained, was purified *via* column chromatography using 20-25% mixture of ethyl acetate in hexane as eluent to obtain **8** as pure compound.

(3E,4Z)-3-((E)-3-phenylallylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one (**8a**): Yellow solid; yield 86%; mp:78-83 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (t, J = 8.1 Hz, 2H), 6.96 (d, J = 11.4 Hz, 1H), 7.16 (t, J = 8.1 Hz, 1H), 7.29-7.52 (m, 8H), 7.70 (bs, 1H), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 119.8, 123.1, 123.8, 125.1, 127.2, 128.5, 128.7, 131.7, 131.8, 132.8, 136.7, 136.8, 138.1, 138.3, 156.9, 169.1; LRMS: 275.1 (M+1), HRMS calcd for $C_{18}H_{15}N_2O$ (MH^+): 275.1184, found: 275.1179.

(3E,4Z)-7,8-dimethoxy-3-((E)-3-phenylallylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one (**8b**): Yellow solid; yield 82%; mp: 140-144 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 4.03 (s, 3H), 6.62 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 6 Hz, 2H), 7.24-7.38 (m, 6H), 7.75 (bs, 1H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 52.6, 52.7, 109.3, 109.8, 119.9, 123.8, 125.8, 127.2, 128.5, 128.7,

131.1, 131.7, 132.1, 136.7, 136.8, 138.3, 138.7, 156.9, 169.2; LRMS: 335.2 (M+1), HRMS calcd for $C_{20}H_{19}N_2O_3$ (MH^+): 335.1396, found: 335.1393.

(3E,4Z)-3-((E)-3-(4-methoxyphenyl)allylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one (**8c**): Yellow solid; yield 85%; mp: 120-123 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.85-6.98 (m, 3H), 7.14 (t, J = 7.2 Hz, 1H), 7.22-7.28 (m, 2H), 7.36-7.46 (m, 3H), 7.51-7.64 (m, 2H), 7.81 (bs, 1H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 55.5, 110.6, 118.8, 121.2, 123.1, 124.1, 125.1, 127.2, 129.2, 129.7, 131.7, 132.8, 136.7, 138.1, 144.2, 157.2, 170.0; LRMS: 305.1 (M+1), HRMS calcd for $C_{19}H_{17}N_2O_2$ (MH^+): 305.1290, found: 305.1293.

(3E,4Z)-7,8-dimethoxy-3-((E)-3-(4-methoxyphenyl)allylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one (**8d**): Yellow solid; yield 88%; mp: 166-169 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.89 (s, 3H), 3.93 (s, 3H), 6.50 (s, 1H), 6.81 (s, 1H), 6.88-6.95 (m, 3H), 7.17-7.25 (m, 2H), 7.52 (dd, J = 15.9, 11.4 Hz, 1H), 7.62 (d, J = 7.2 Hz, 1H), 8.15 (s, 1H), 8.75 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 55.5, 56.2, 102.9, 110.9, 112.7, 117.7, 120.6, 123.4, 125.4, 126.8, 129.6, 131.4, 131.6, 132.5, 137.8, 145.2, 152.7, 156.2, 157.1, 169.1; LRMS: 365.2 (M+1), HRMS calcd for $C_{21}H_{21}N_2O_4$ (MH^+): 365.1501, found: 365.1504.

(3E,4Z)-7,8-dimethoxy-3-((E)-4-phenylbut-3-en-2-ylidene)-1H-benzo[e][1,4]diazepin-2(3H)-one (**8e**): Yellow solid; yield 73%; mp: 140-144 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 6.58 (s, 1H), 6.74 (s, 1H), 6.85 (s, 1H), 7.24-7.36 (m, 6H), 8.24 (s, 1H), 8.41 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 56.2, 56.3, 103.1, 107.6, 112.0, 118.7, 121.2, 125.0, 126.8, 128.1, 129.2, 129.3, 131.4, 136.5, 145.4, 152.5, 156.6, 169.7; LRMS: 349.1 (M+1), HRMS calcd for $C_{21}H_{21}N_2O_3$ (MH^+): 349.1552, found: 349.1550.

General procedure for the preparation of methyl 2-(4-oxo-2-arylthiazolidin-3-yl)-5-phenylpenta-2,4-dienoate 9a-g: To a solution of compound **4** (0.2 g, 1 *equiv.*) in methanol (5 mL) was added sodium methoxide (3 *equiv.*). The reaction mixture was stirred at room temperature for 36 hrs. The progress of the reaction was monitored by *tlc* considering **4** as a limiting reactant. After completion of reaction, the excess of solvent was evaporated under reduced pressure to obtain crude product. The crude product was purified *via* column chromatography using 20-25% mixture of ethyl acetate in hexane as eluent to obtain **9** as pure compound.

(2Z,4E)-methyl-2-(2-(4-methoxyphenyl)-4-oxothiazolidin-3-yl)-5-phenylpenta-2,4-dienoate (**9a**): Pale yellow solid; yield 91%; mp: 149-154 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H), 3.76 (s, 3H), 3.90 (d, J = 1.5 Hz, 1H), 3.91 (d, J = 1.2 Hz, 1H), 6.05 (s, 1H), 6.63 (d, J = 11.1 Hz, 1H), 6.76 (dd, J = 15.6, 1.8 Hz, 2H), 6.82 (d, J = 15.6 Hz, 1H), 7.33-7.43 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 33.5, 52.4, 55.2, 64.4, 113.8, 121.8, 124.1, 127.6, 128.5, 128.8, 129.6, 130.1, 135.7, 142.1, 142.8, 160.4, 163.9, 171.5; LRMS: 396.2 (M+1); HRMS calcd for $C_{22}H_{22}NO_4S$ (MH^+): 396.1270 found 396.1275.

(2Z,4E)-methyl 2-(4-oxo-2-phenylthiazolidin-3-yl)-5-phenylpenta-2,4-dienoate (**9b**): white solid; yield 88%; mp: 121-124 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.94 (s, 2H), 6.09 (s, 1H), 6.64 (dd, J = 15.6, 11.1 Hz, 1H), 6.82 (d, J = 15.6 Hz, 1H), 7.24-7.47 (m, 11H); ^{I3}C NMR ($CDCl_3$): δ 33.4, 52.3, 64.7, 121.8, 124, 127.6, 128.2, 128.5, 128.7, 128.8, 129.6, 135.7, 136.9, 142.2, 142.9, 163.9, 171.5; LRMS: 366.1 (M+1); HRMS calcd for $C_{21}H_{20}NO_3S$ (MH^+) 366.1164 found 366.1170.

(2Z,4E)-methyl 2-(2-(2,5-dimethylphenyl)-4-oxothiazolidin-3-yl)-5-phenylpenta-2,4-dienoate (**9c**): yellow solid; yield 84%; mp: 170-174 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H), 2.26 (s, 3H), 3.76 (s, 3H), 3.92 (d, J = 1.2 Hz, 1H), 3.93 (d, J = 1.2 Hz, 1H), 6.48 (s, 1H), 6.72-6.94 (m, 4H), 7.35-7.45 (m, 7H); ^{I3}C NMR ($CDCl_3$): δ 18.4, 20.9, 33.5, 52.4, 64.7, 115.2, 122.0, 124.0, 127.6, 128.8, 129.2, 129.6, 129.7, 129.8, 130.4, 133.4, 134.6, 135.7, 136.0, 142.1, 142.9, 164.0, 171.8; LRMS: 394.1 (M+1); HRMS calcd for $C_{23}H_{24}NO_3S$ (MH^+): 394.1477 found 394.1475.

X-Ray crystal data and structure refinement for **9c**. CCDC 1429502 contains the supplementary crystallographic data for this Note. $C_{23}H_{23}NO_3S$, V = 1959.1(2) Å^3 Mr = 393.48, Z = 4, orthorhombic, a = 7.2967(5) Å, b = 18.0150(13) Å, T = 100(2) K, c = 15.0313(11) Å, alpha = 90, beta = 97.477(2), gamma = 90; T_{min} = 0.959, T_{max} = 0.963, R_{int} = 0.0277(3403) measured reflections, wR(F2) = 0.0704 (3540), S = 1.053.

(2Z,4E)-methyl 2-(2-(furan-2-yl)-4-oxothiazolidin-3-yl)-5-phenylpenta-2,4-dienoate (**9d**): Orange solid; yield 85%; mp: 156-160 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.87 (d, J = 9 Hz, 1H), 4.01 (dd, J = 15.6, 1.5 Hz, 1H), 5.95 (s, 1H), 6.21 (dd, J = 3.3, 1.5 Hz, 1H), 6.37 (d, J = 3.3 Hz, 1H), 6.67 (dd, J = 15.6, 11.1 Hz, 1H), 6.87 (d, J = 15.6 Hz, 1H), 7.30-7.43 (m, 7H);

^{13}C NMR ($CDCl_3$): δ 33.1, 52.1, 59.1, 108.1, 110.7, 113.6, 122.1, 123.6, 127.7, 128.8, 129.2, 130.2, 135.7, 142.5, 151.1, 164.2, 170.2; LRMS: 356.1 (M+1); HRMS calcd for $C_{19}H_{18}NO_4S$ (MH^+): 356.0957 found 356.0960.

(2Z,4E)-methyl 5-(4-methoxyphenyl)-2-(2-(2-nitrophenyl)-4-oxothiazolidin-3-yl)penta-2,4-dienoate (**9e**): Yellow solid; yield 81%; mp: 133-136 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.80-3.86 (m, 1H), 3.90 (s, 3H), 3.96 (dd, J = 15.9, 1.2 Hz, 1H), 6.67 (t, J = 9.3 Hz, 2H), 6.73 (d, J = 7.5 Hz, 1H), 6.89-6.98 (m, 2H), 7.15 (dd, J = 8.1, 7.5 Hz, 2H), 7.41-7.49 (m, 2H), 7.61 (t, J = 9.3 Hz, 1H), 7.84 (dd, J = 8.1, 1.2 Hz, 1H), 8.1 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 32.5, 52.4, 55.5, 59.0, 111.1, 115.3, 118.5, 120.9, 124.4, 124.7, 127.1, 129.2, 129.7, 129.9, 131.1, 133.3, 139.6, 142.7, 146.3, 158.0, 163.7, 171.7; LRMS: 441.1 (M+1); HRMS calcd for $C_{22}H_{21}N_2O_6S$ (MH^+) 441.1120 found 441.1125.

(2Z,4E)-methyl 2-(2-(4,5-dimethoxy-2-nitrophenyl)-4-oxothiazolidin-3-yl)-5-(4-methoxyphenyl)penta-2,4-dienoate (**9f**): yellow semi-solid; yield 84 %: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.83 (s, 3H), 3.87-3.91 (m, 2H), 3.92 (s, 3H), 3.94 (s, 3H), 6.44 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.85-6.92 (m, 2H), 7.05-7.46 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 32.9, 53.1, 54.5, 54.8, 56.1, 61.0, 108.1, 109.0, 110.8, 118.1, 121.0, 124.2, 127.1, 128.0, 129.7, 130.3, 132.6, 139.6, 146.3, 151.9, 157.2, 162.8, 170.2; LRMS: 501.1 (M+1); HRMS calcd for $C_{24}H_{25}N_2O_8S$ (MH^+) 501.1332 found 501.1328.

(2Z,4E)-methyl 2-(2-(2-amino-4,5-dimethoxyphenyl)-4-oxothiazolidin-3-yl)-5-(4-methoxyphenyl)penta-2,4-dienoate (**9g**): pale yellow solid; yield 48 %; mp: 143-146 ˚C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 3.81 (m, 1H), 3.86 (s, 3H), 3.99 (m, 1H), 6.11 (s, 1H), 6.39 (bs, 1H), 6.73 (bs, 1H), 6.87-7.05 (m, 3H), 7.22 (s, 1H), 7.31-7.34 (m, 1H), 7.49 (d, J = 11.1 Hz, 1H), 7.55 (dd, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 33.5, 52.3, 55.5, 55.6, 56.2, 61.1, 101.7, 110.3, 111.0, 120.6, 122.9, 123.2, 124.9, 127.6, 130.7, 137.8, 140.2, 142.0, 143.1, 150.6, 157.6, 164.5, 171.1; LRMS: 471.2 (M+1); HRMS calcd for $C_{24}H_{27}N_2O_6S$ (MH^+) 471.1590 found 471.1593.

Characterization data:

^{1}H NMR AND ^{13}C NMR SPECTRA

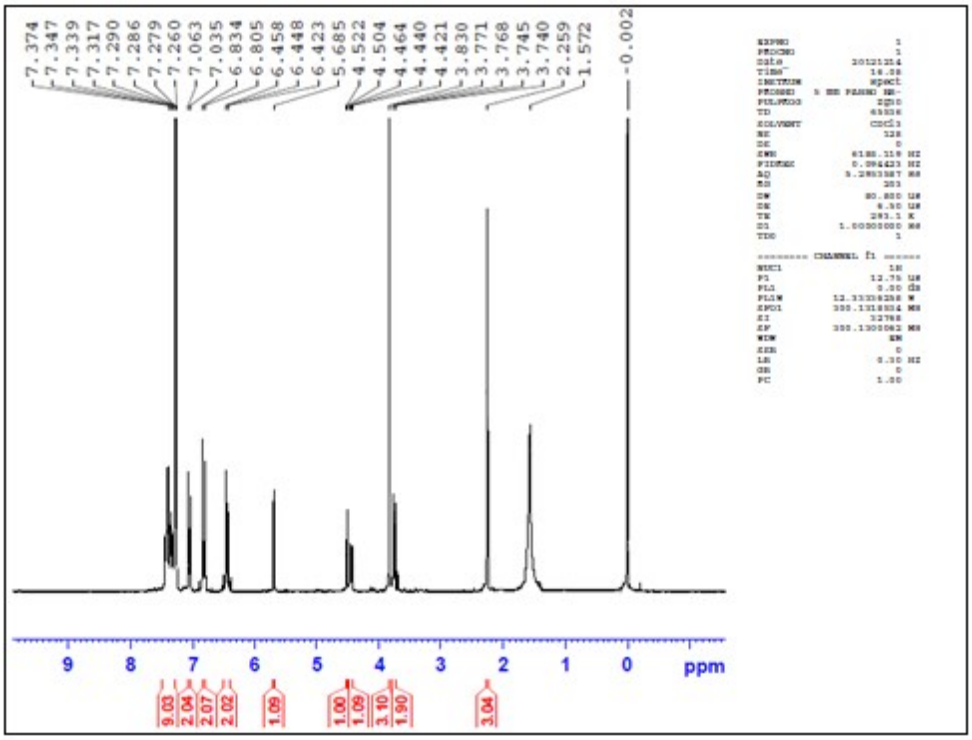


Figure S 1. ^{1}H NMR (300 MHz, $CDCl_3$) of **4a**.

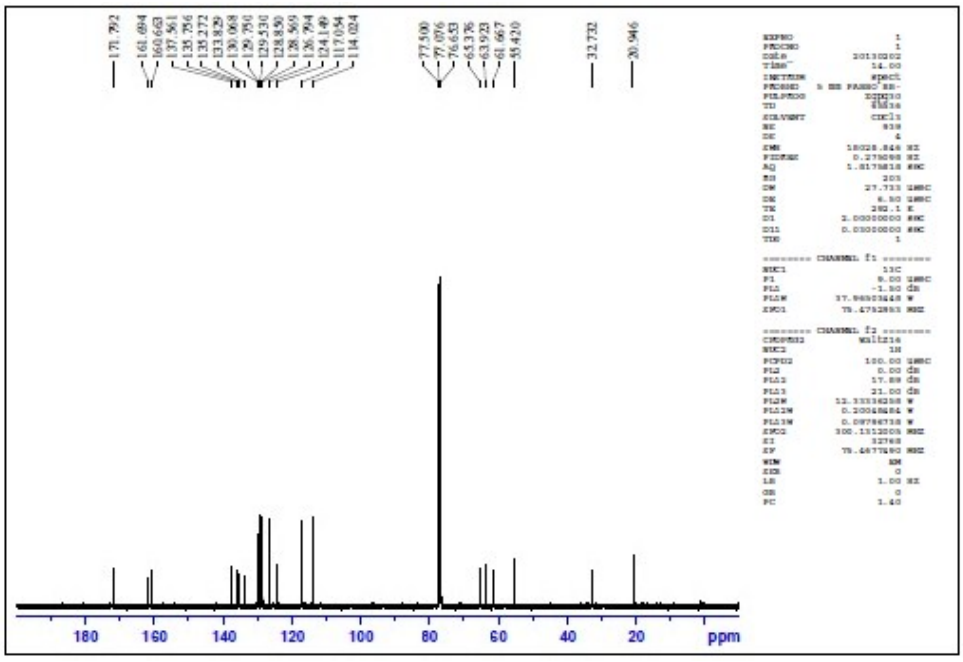


Figure S 2. ^{13}C NMR (75 MHz, $CDCl_3$) of **4a**.

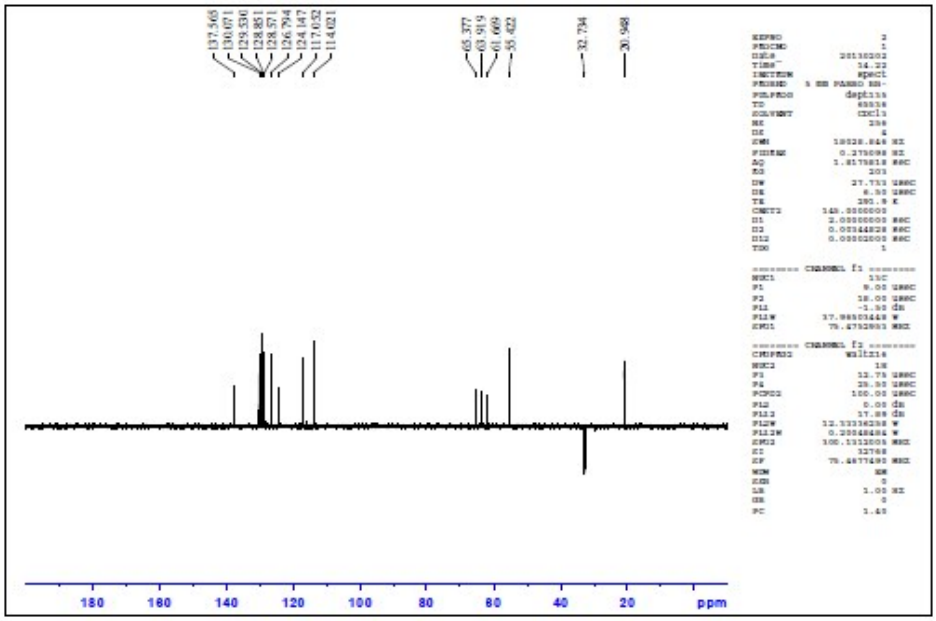


Figure S 3. DEPT NMR (75 MHz, $CDCl_3$) of **4a**.

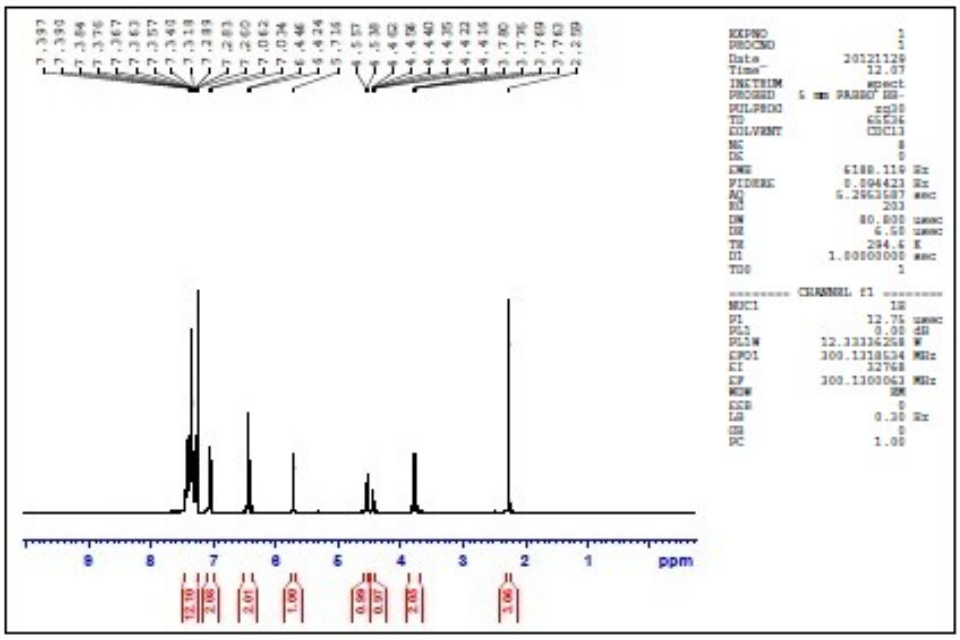


Figure S 4. ^1H NMR (300 MHz, $CDCl_3$) of **4b**.

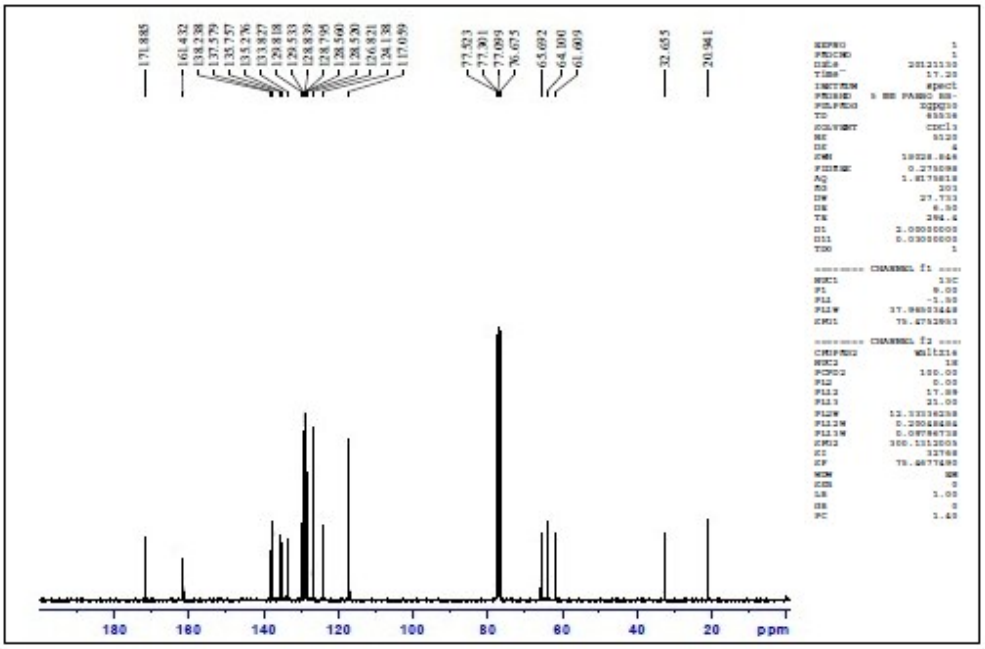


Figure S 5. ^{13}C NMR (75 MHz, $CDCl_3$) of **4b**.

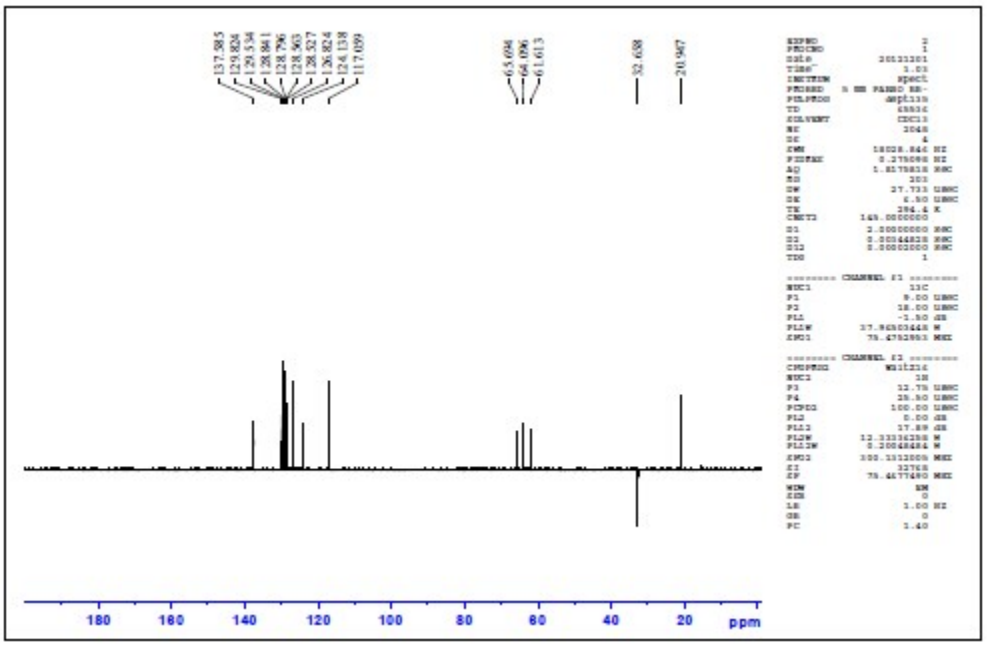


Figure S 6. DEPT NMR (75 MHz, $CDCl_3$) of **4b**.

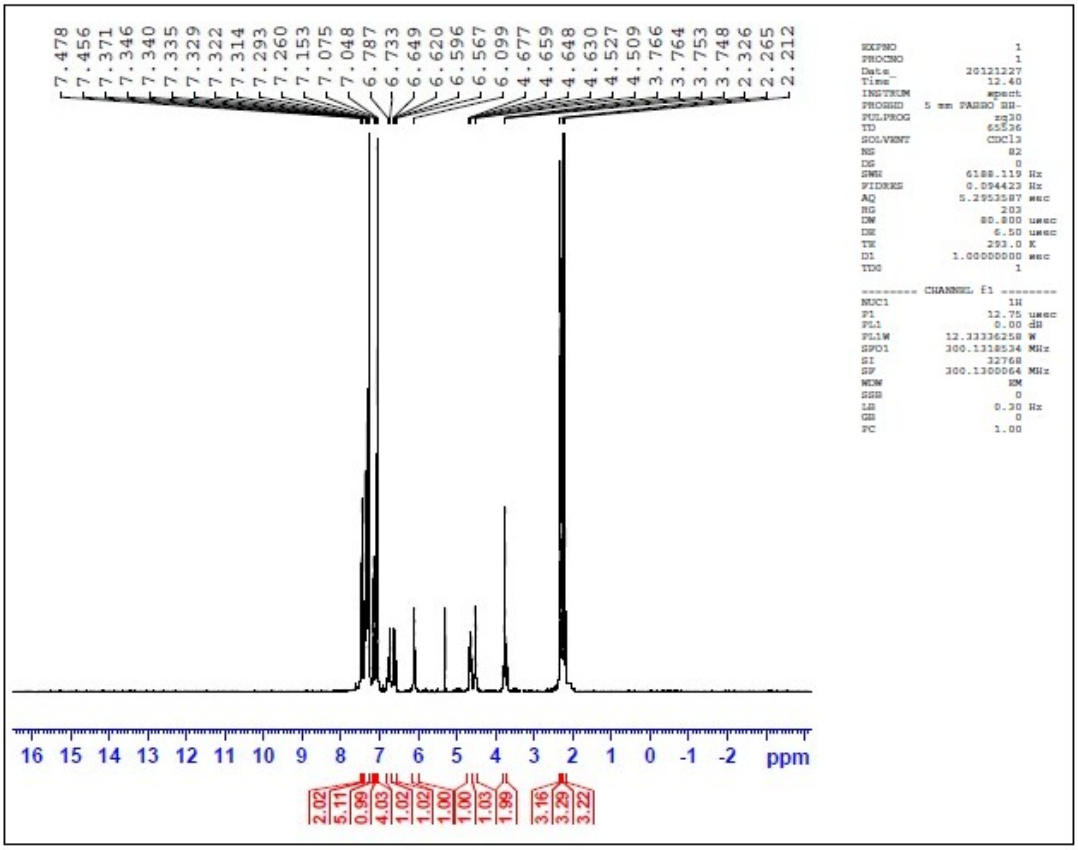


Figure S 7. ^{1}H NMR (300 MHz, $CDCl_3$) of **4c**.

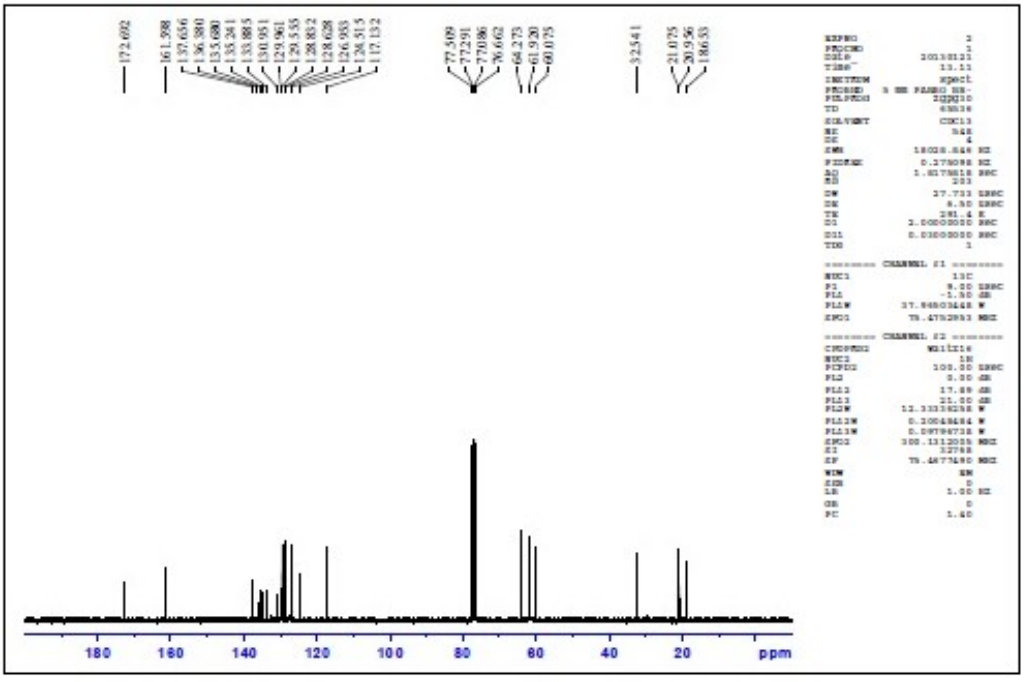


Figure S 8. ^{13}C NMR (75 MHz,$CDCl_3$) of **4c**.

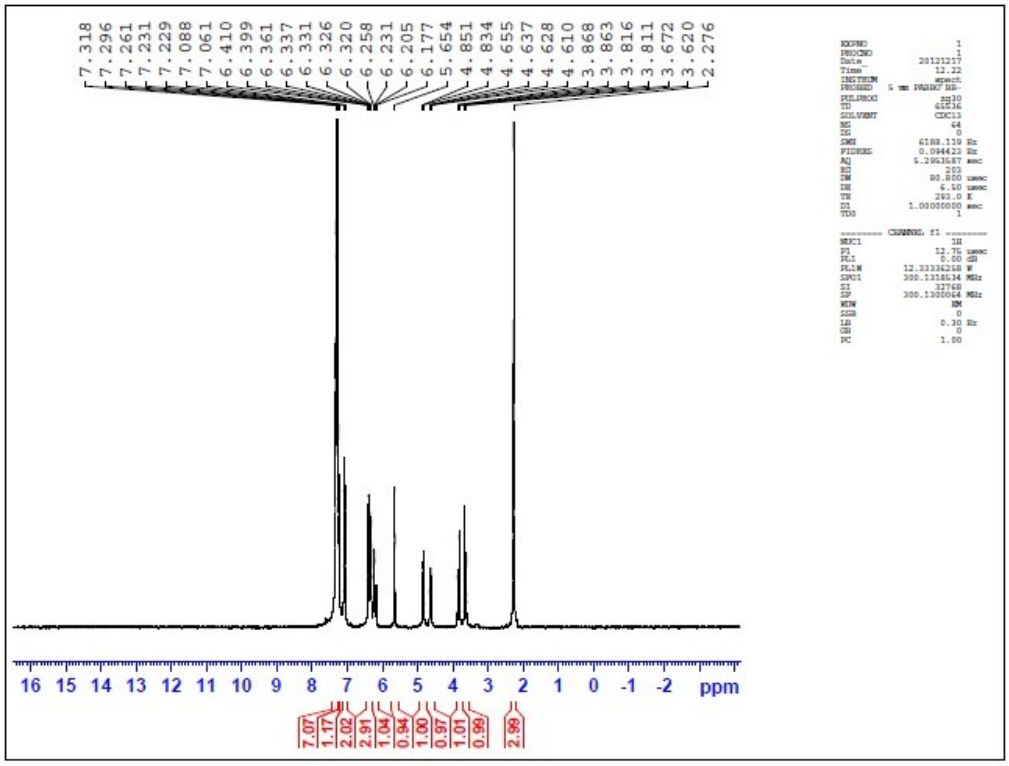


Figure S 9. ^{1}H NMR (300 MHz, $CDCl_3$) of **4d**.

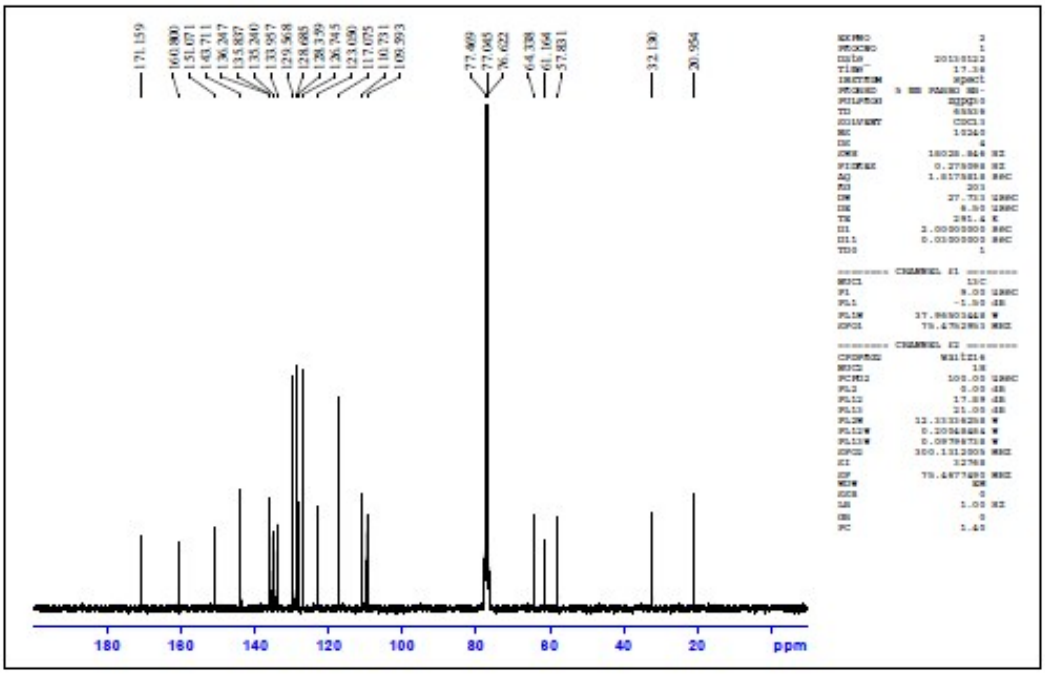


Figure S 10. ^{13}C NMR (75 MHz, $CDCl_3$) of **4d**.

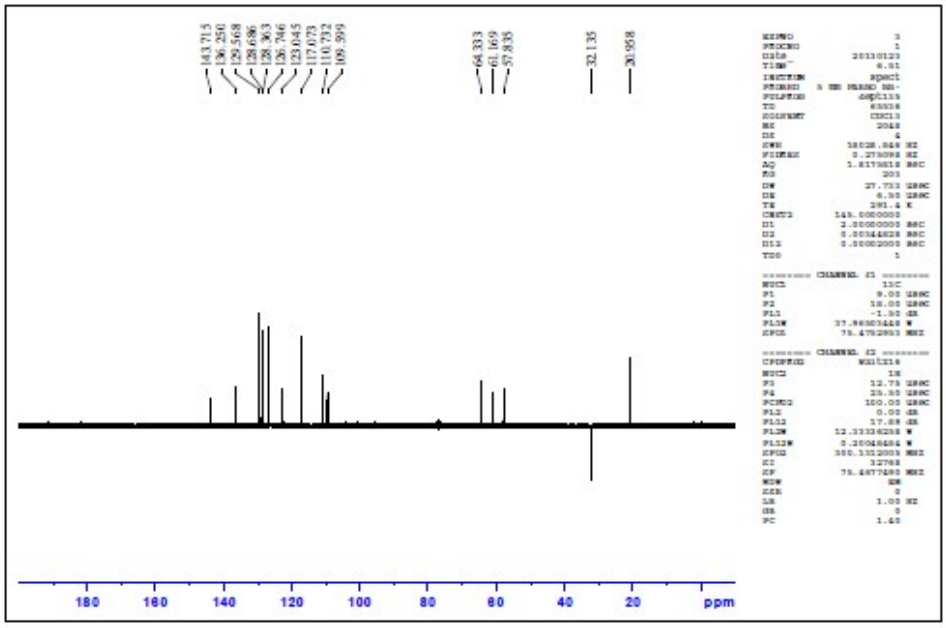


Figure S 11. DEPT NMR (75 MHz, $CDCl_3$) of **4d**.

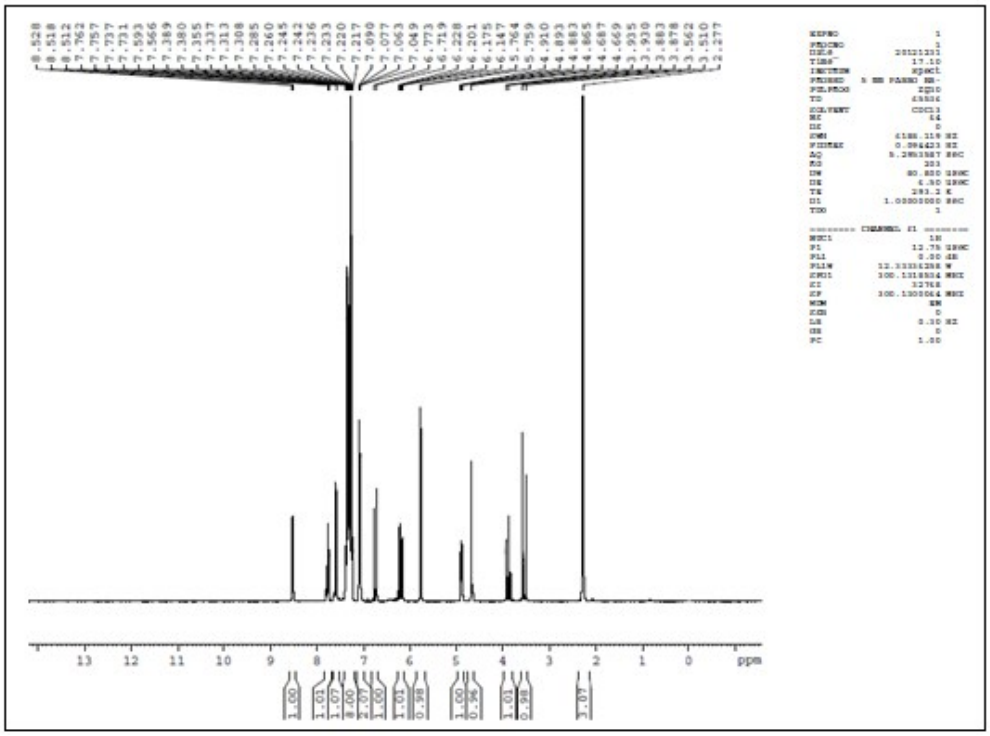


Figure S 12. ^1H NMR (300 MHz, $CDCl_3$) of **4e**.

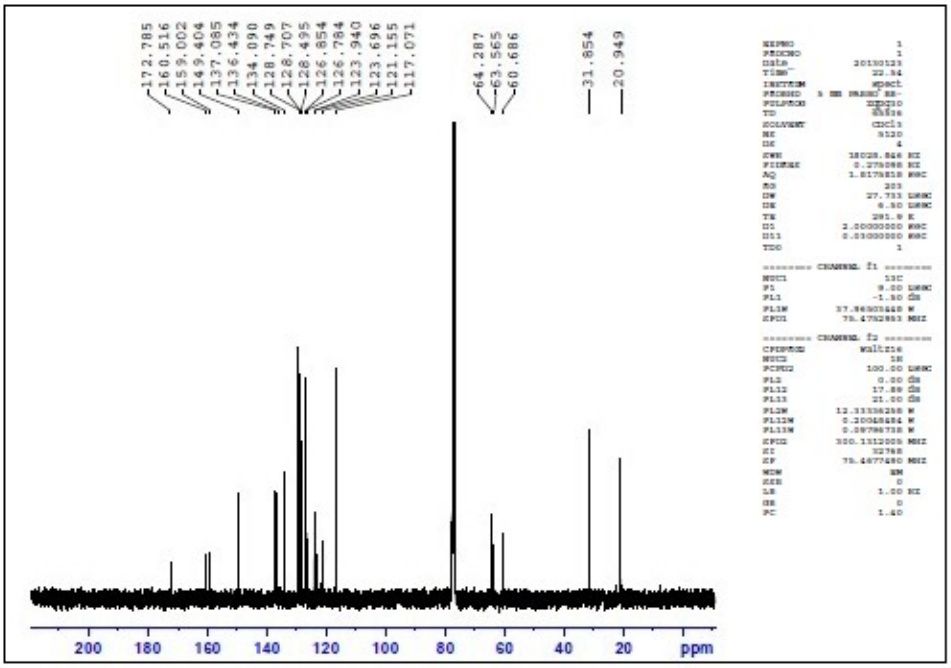


Figure S 13. ^{13}C NMR (75 MHz,$CDCl_3$) of **4e**.

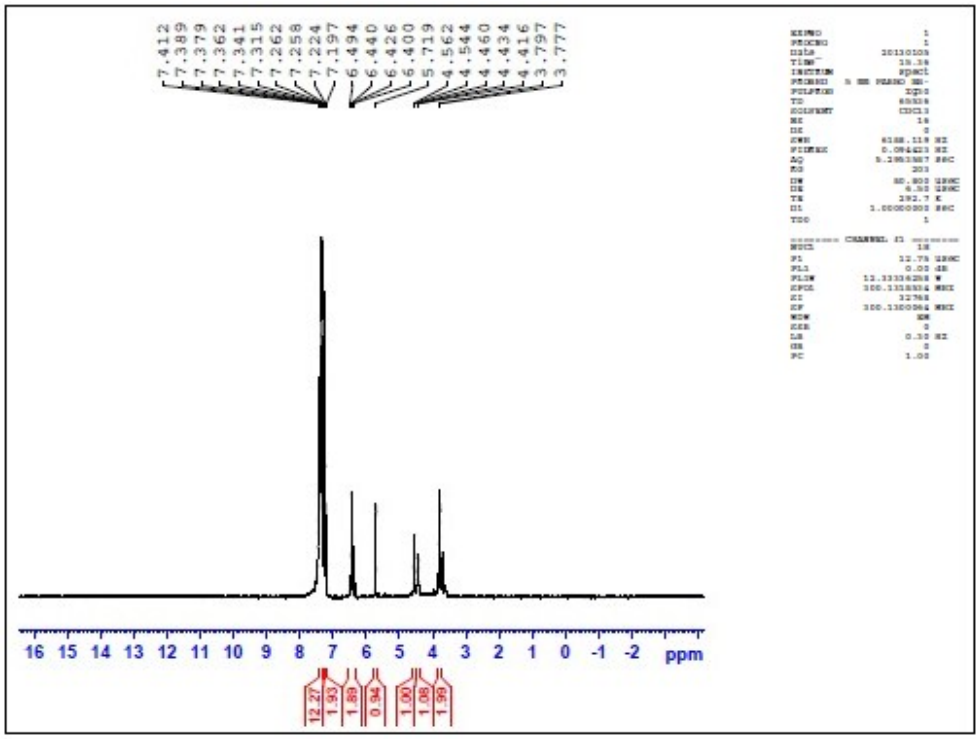


Figure S 14. ^{1}H NMR (300 MHz, $CDCl_3$) of **4f**.

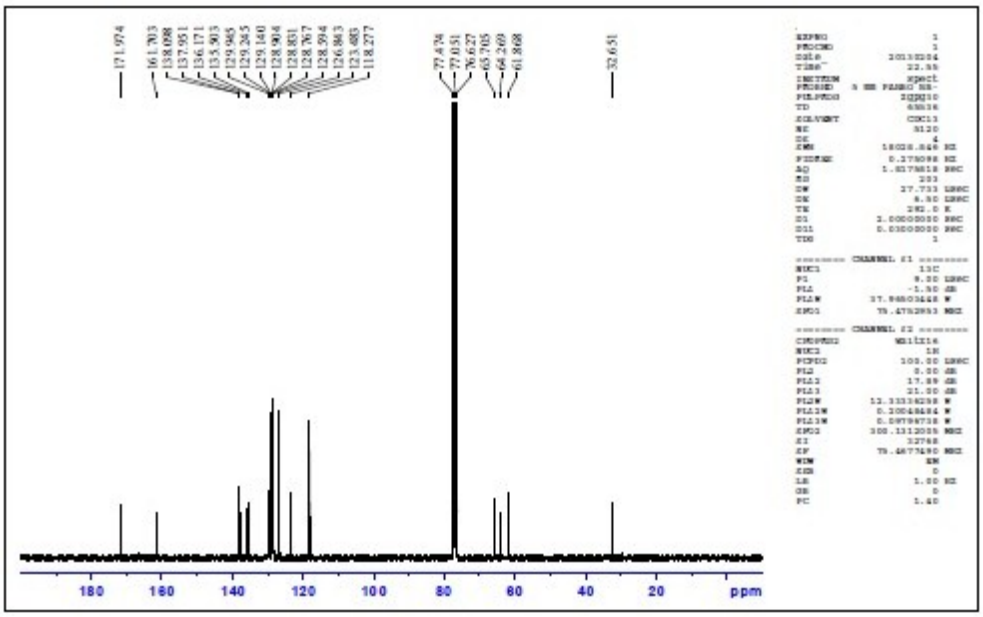


Figure S 15. ^{13}C NMR (75 MHz, $CDCl_3$) of **4f**.

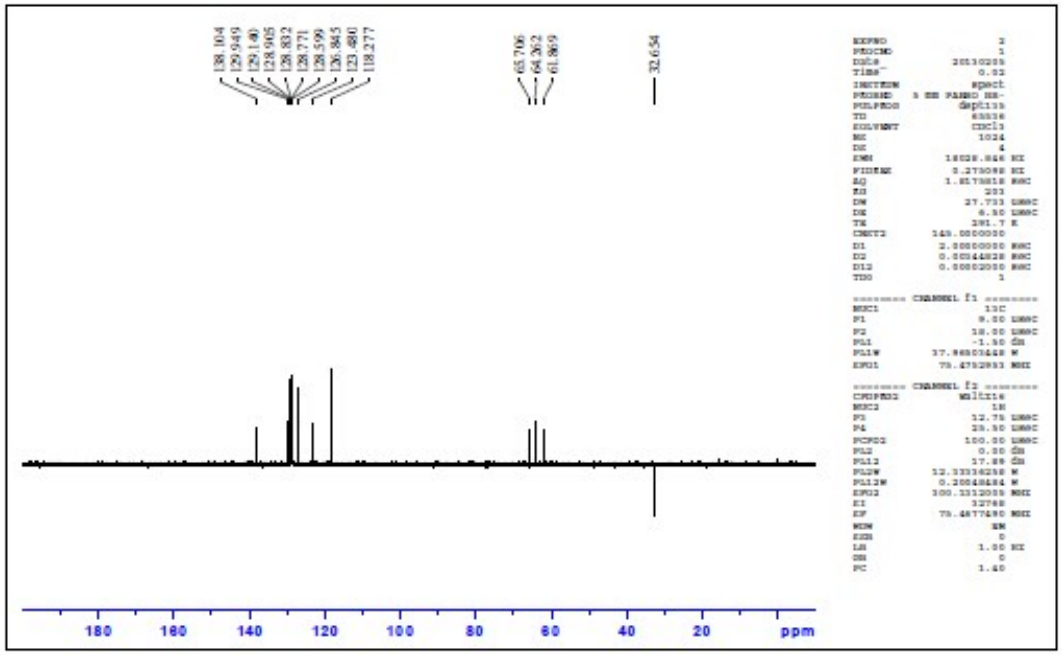


Figure S 16. DEPT NMR (75 MHz, $CDCl_3$) of **4f**.

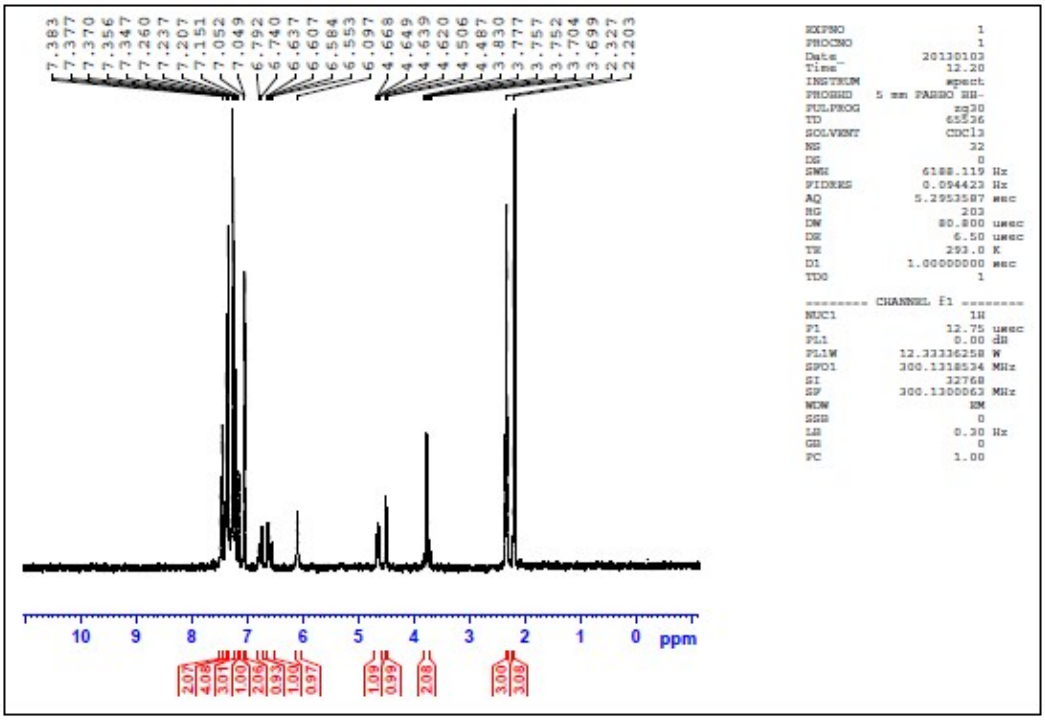


Figure S 17. ^{1}H NMR (300 MHz, $CDCl_3$) of **4g**.

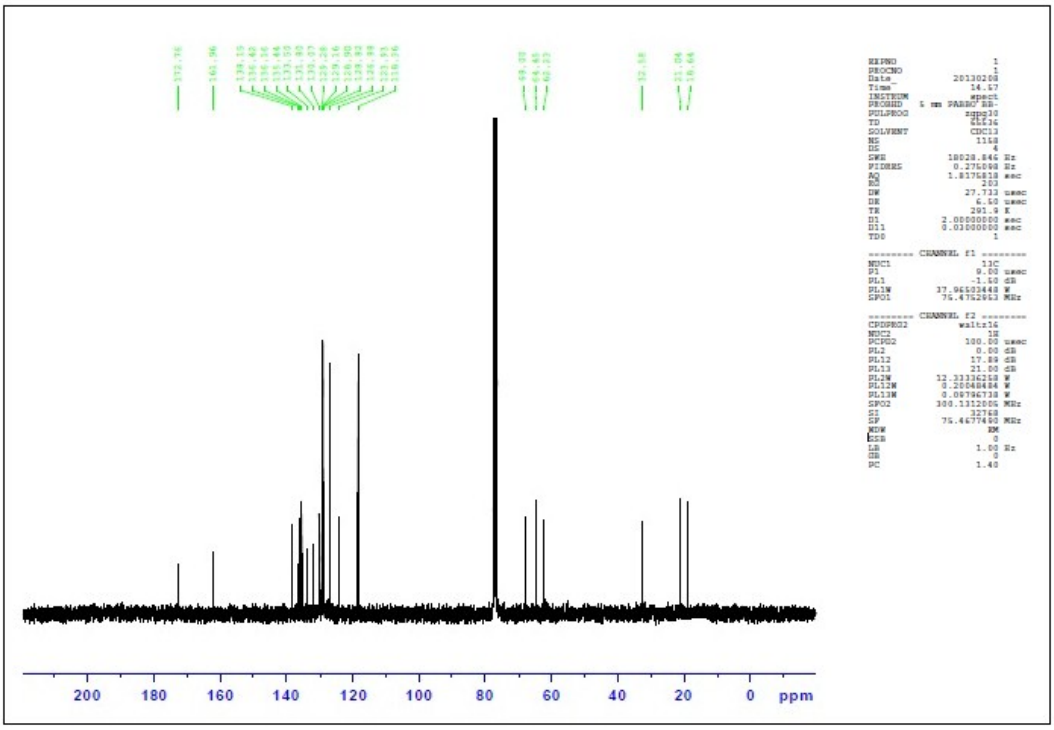


Figure S 18. ^{13}C NMR (75 MHz, $CDCl_3$) of **4g**.

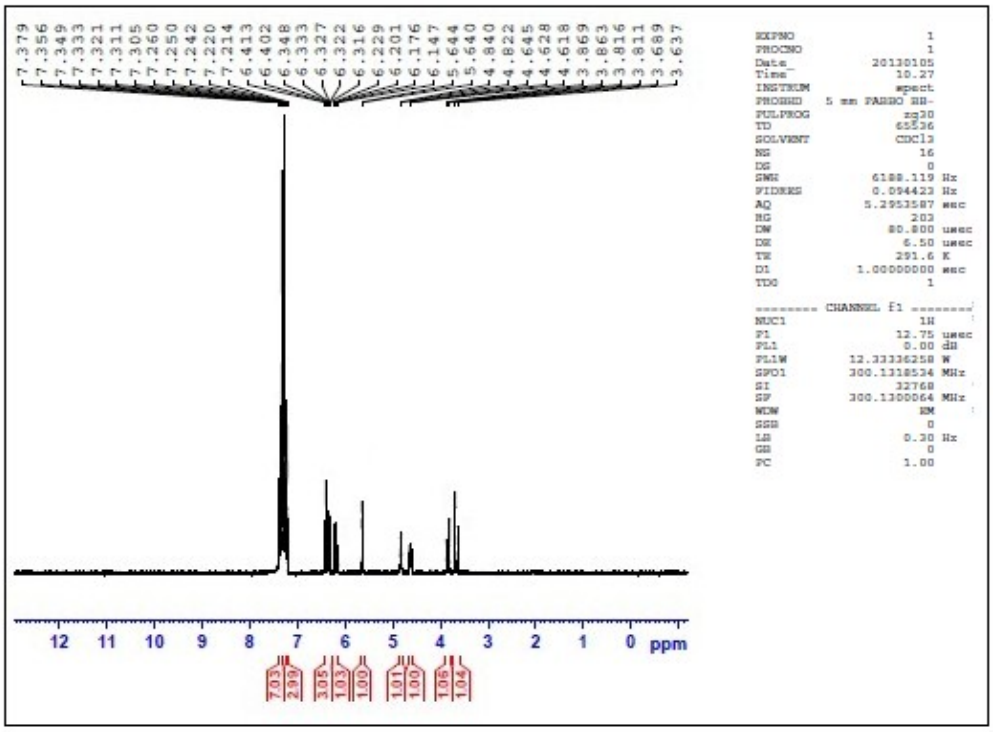


Figure S 19. ^{1}H NMR (300 MHz, $CDCl_3$) of **4h**.

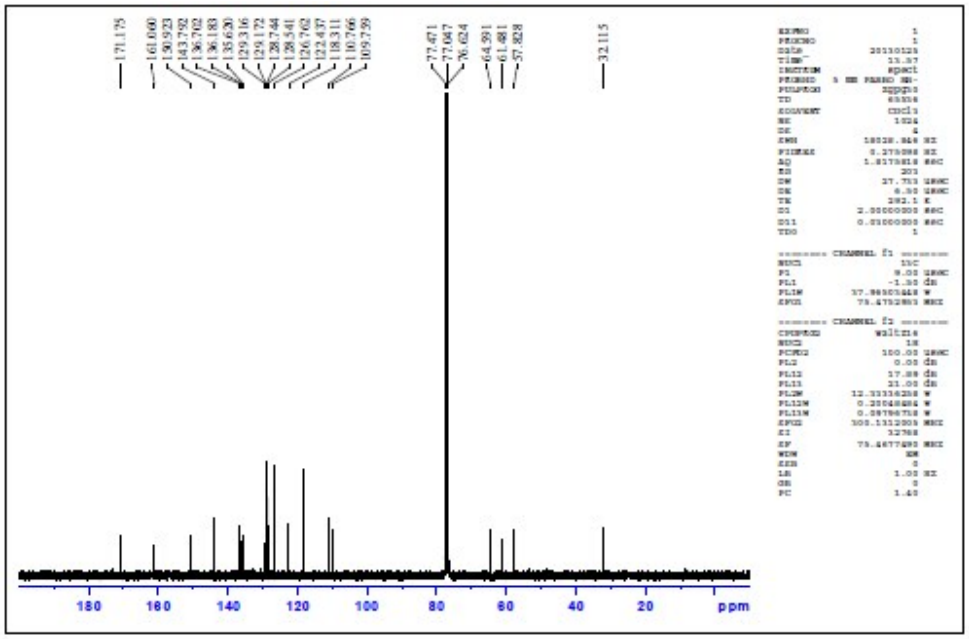


Figure S 20. ^{13}C NMR (75 MHz, $CDCl_3$) of **4h**.

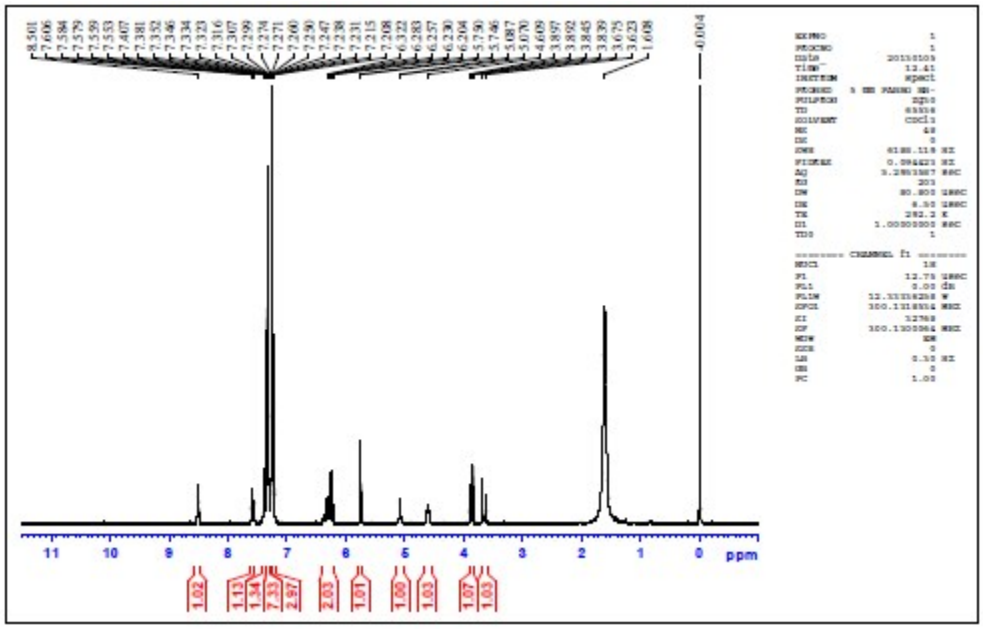


Figure S 21. ^{1}H NMR (300 MHz, $CDCl_3$) of **4i**.

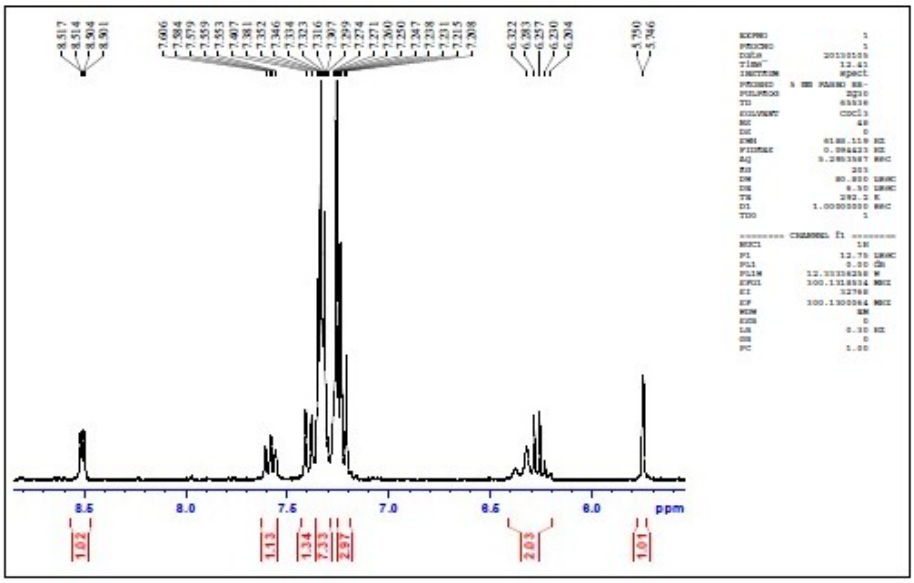


Figure S 22. ^{1}H NMR (300 MHz, $CDCl_3$) of **4i** expansion.

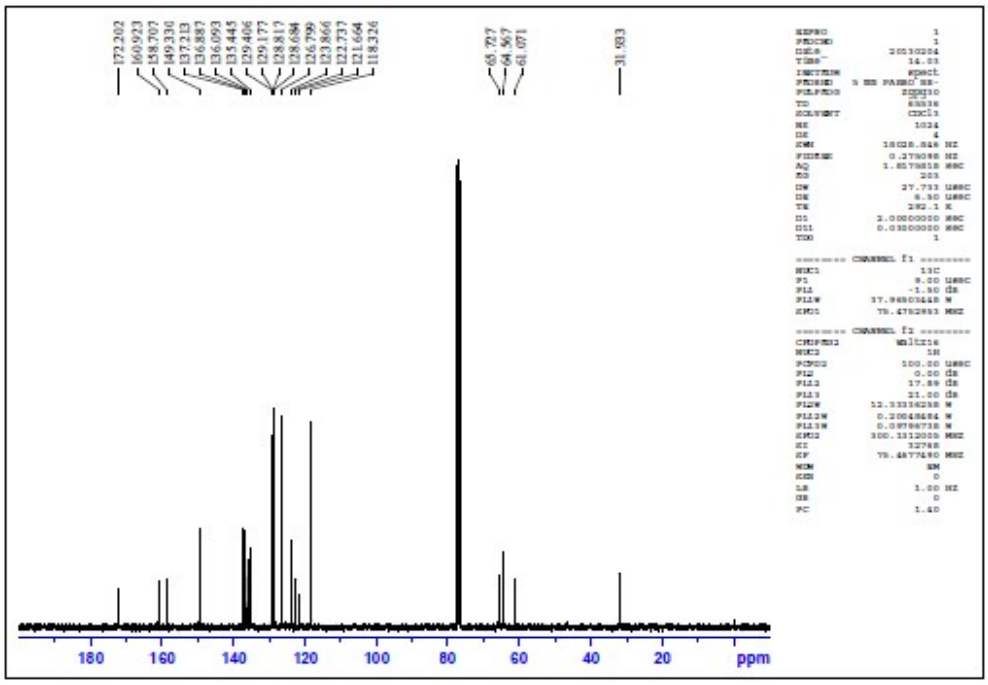
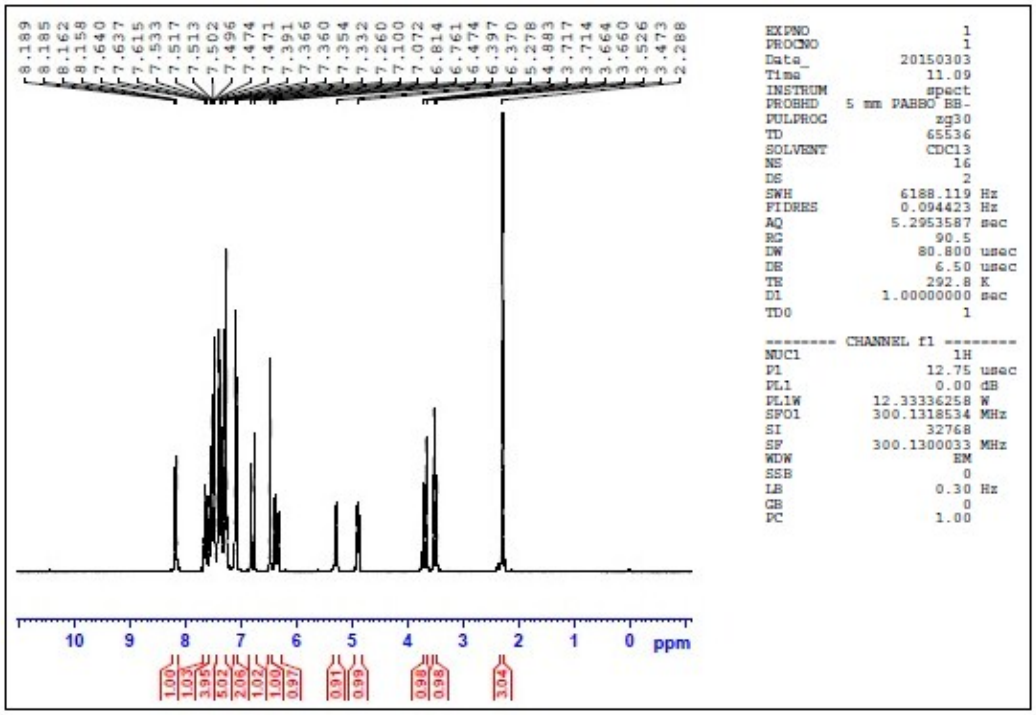


Figure S 23. ^{13}C NMR (75 MHz, $CDCl_3$) of **4i**.



EXPNO	1
PROCNO	1
Data_	20150303
Time	11.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	90.5
DW	80.800 usec
DE	6.50 usec
TE	292.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.75 usec
PL1	0.00 dB
PL1W	12.33336258 W
SFO1	300.1318534 MHz
SI	32768
SF	300.1300033 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Figure S 24. ^{1}H NMR (300 MHz, $CDCl_3$) of **6a**.

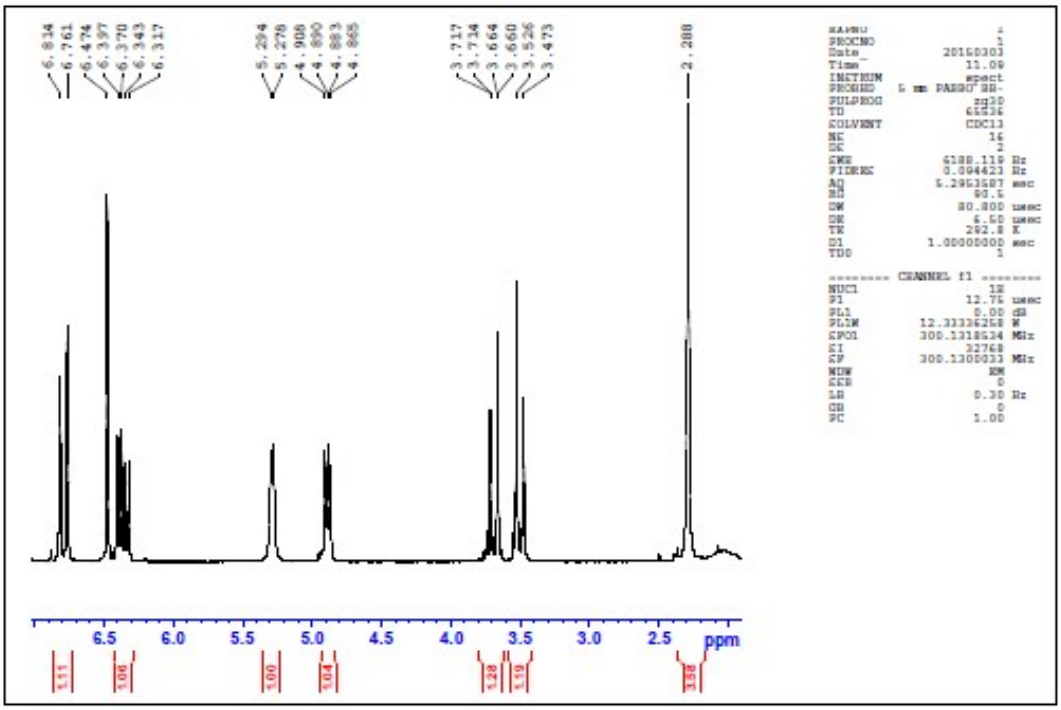


Figure S 25. ^{1}H NMR (300 MHz, $CDCl_3$) of **6a** expansion.

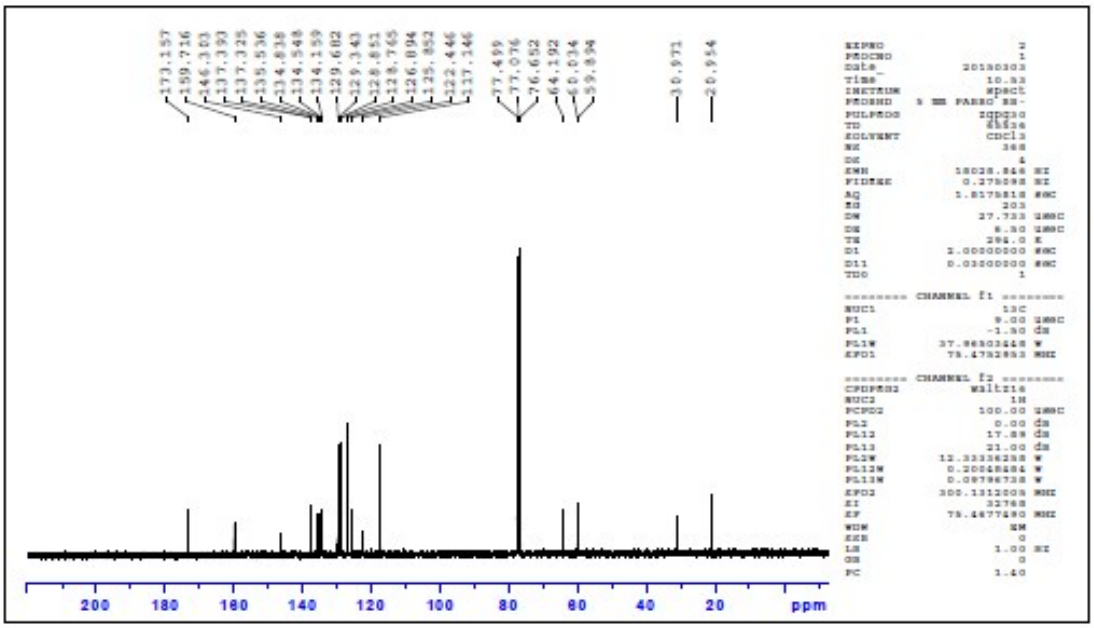


Figure S 26. ^{13}C NMR (75 MHz, $CDCl_3$) of **6a**.

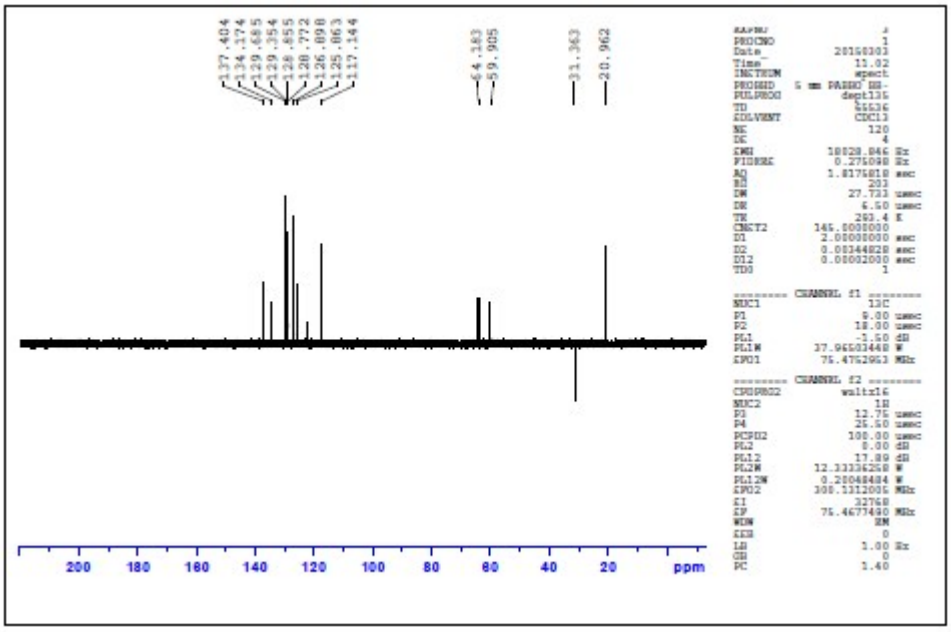


Figure S 27. DEPT NMR (75 MHz, $CDCl_3$) of **6a**.

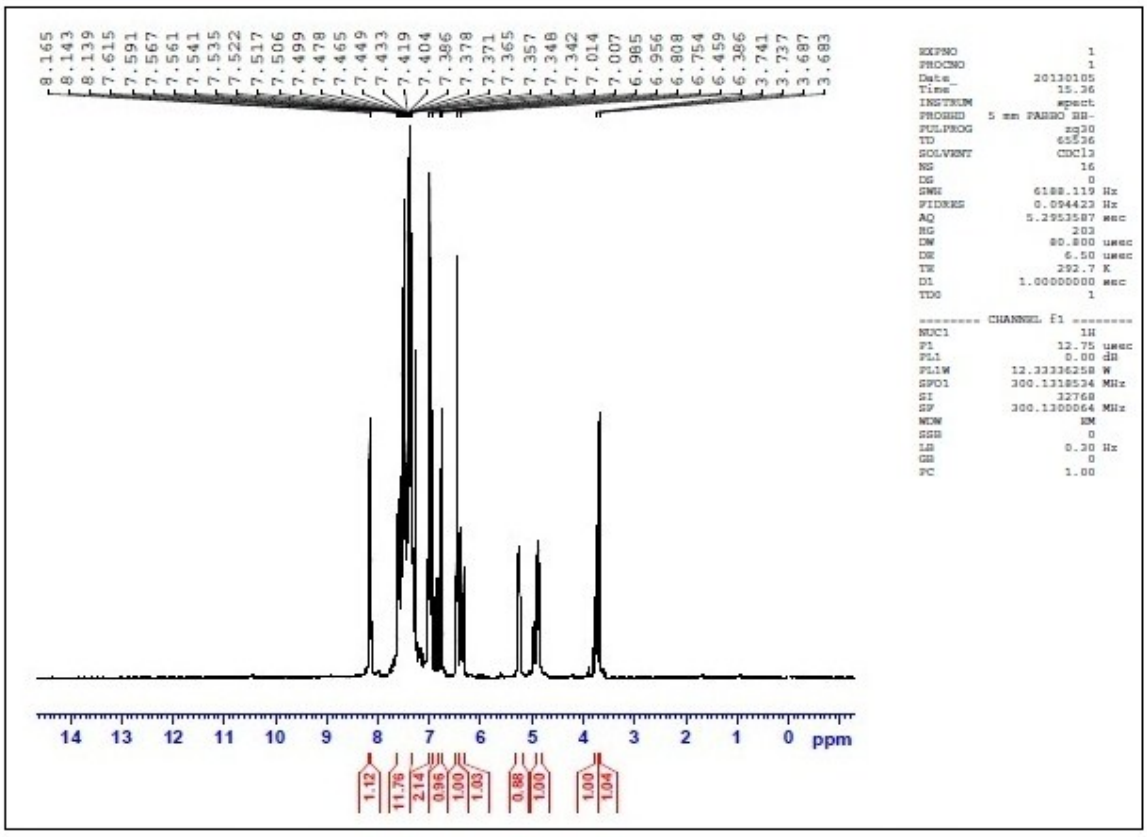


Figure S 28. ^1H NMR (300 MHz, $CDCl_3$) of **6b**.

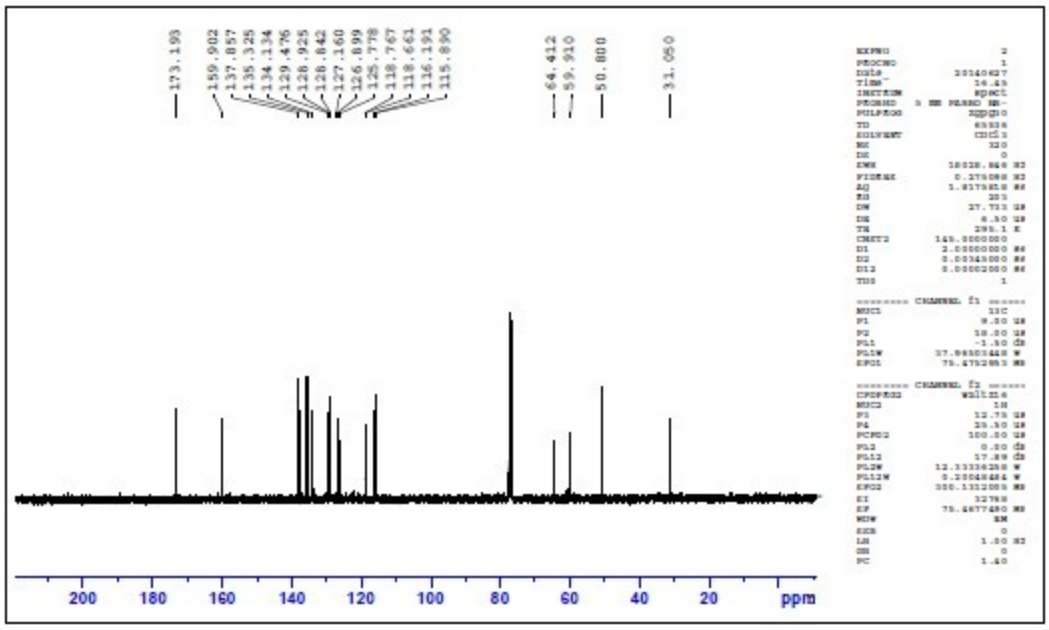


Figure S 29. ^{13}C NMR (75 MHz, $CDCl_3$) of **6b**.

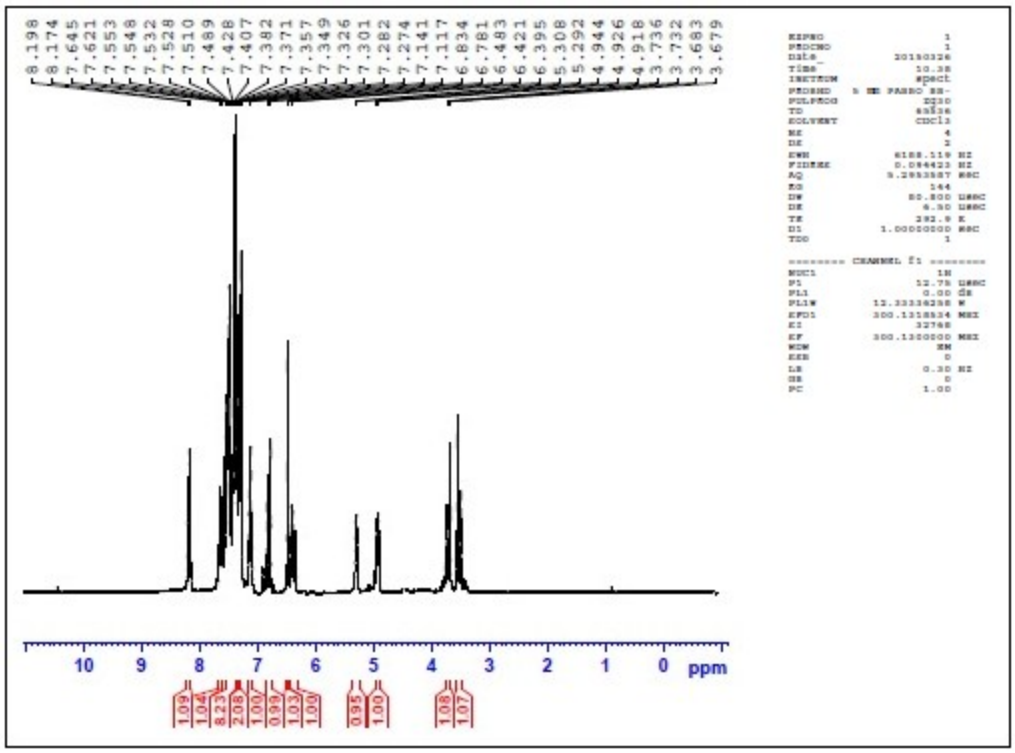


Figure S 30. ^{1}H NMR (300 MHz, $CDCl_3$) of **6c**.

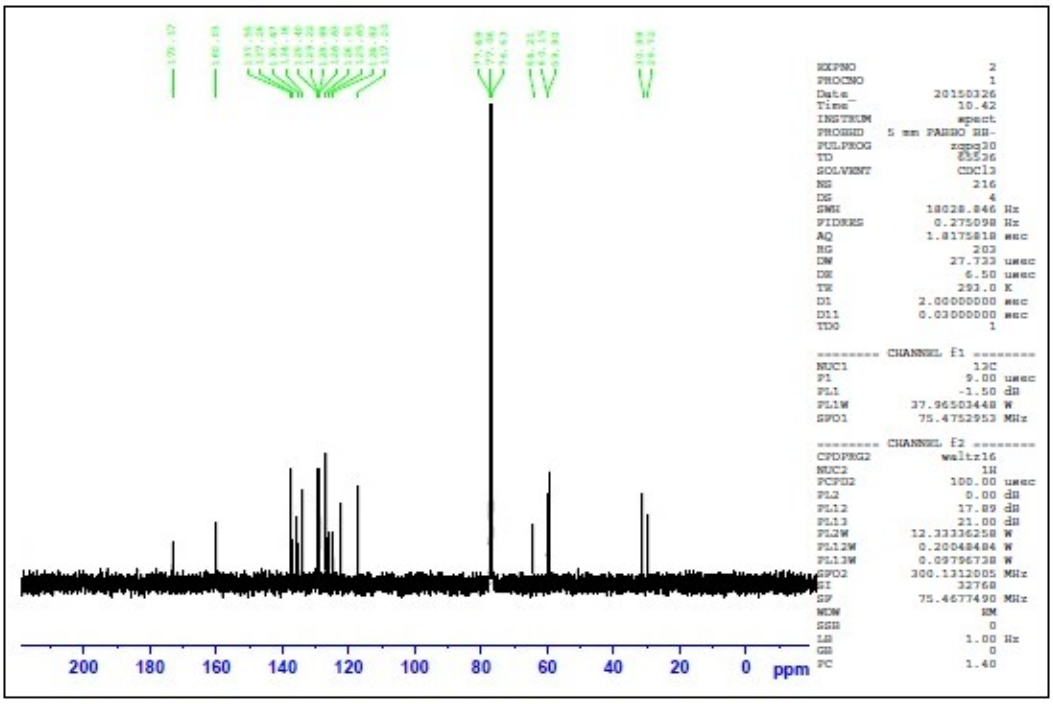


Figure S 31. ^{13}C NMR (75 MHz, $CDCl_3$) of **6c**.

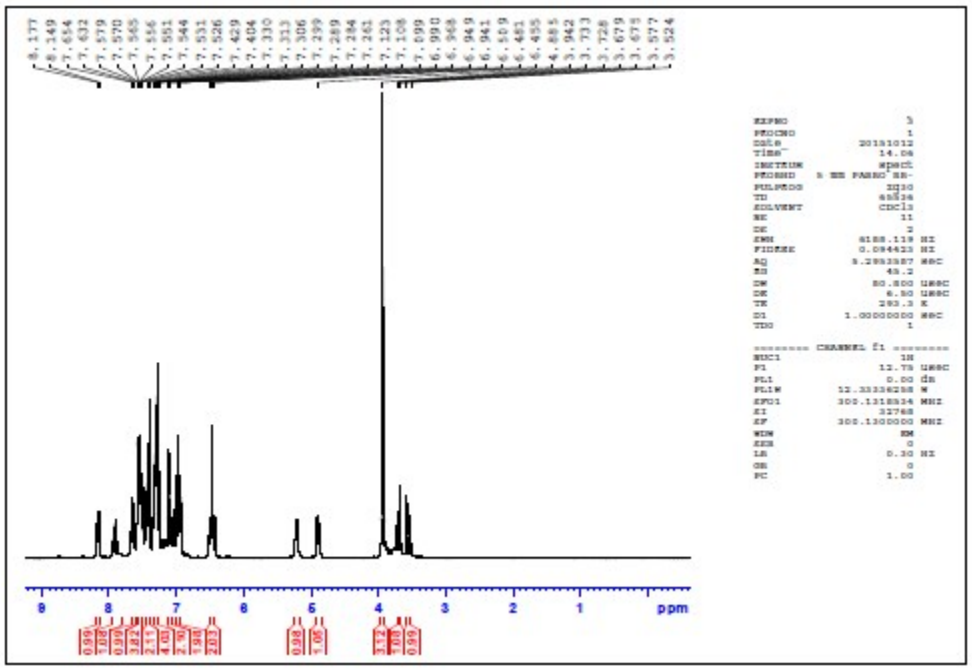


Figure S 32. ^{1}H NMR (300 MHz, $CDCl_3$) of **6d**.

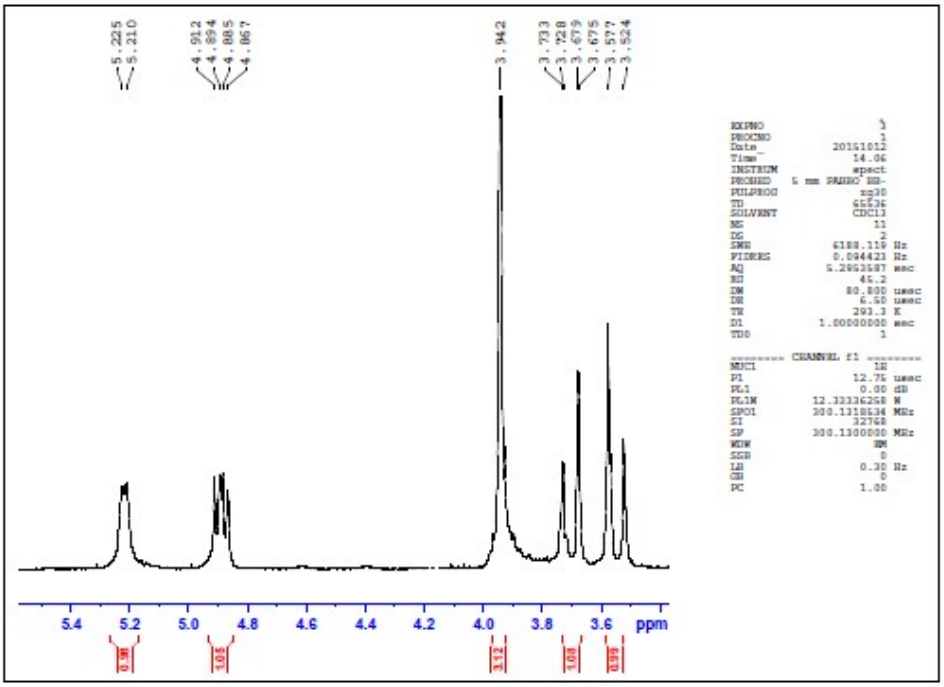


Figure S 33. ^{1}H NMR (300 MHz, $CDCl_3$) of **6d** expansion.

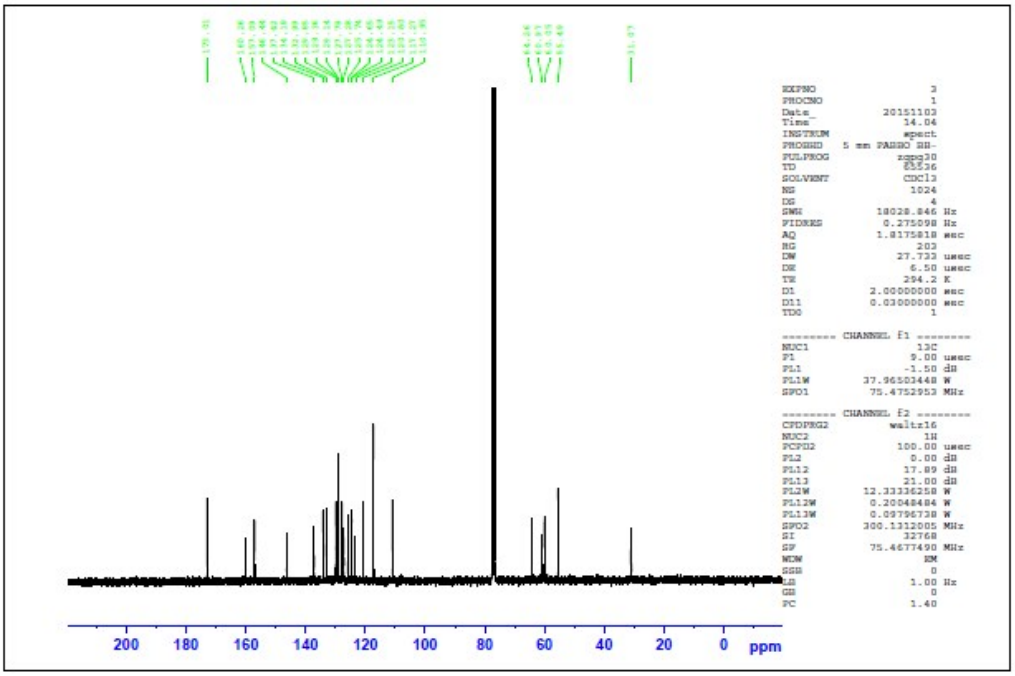


Figure S 34. ^{13}C NMR (75 MHz, $CDCl_3$) of **6d**.

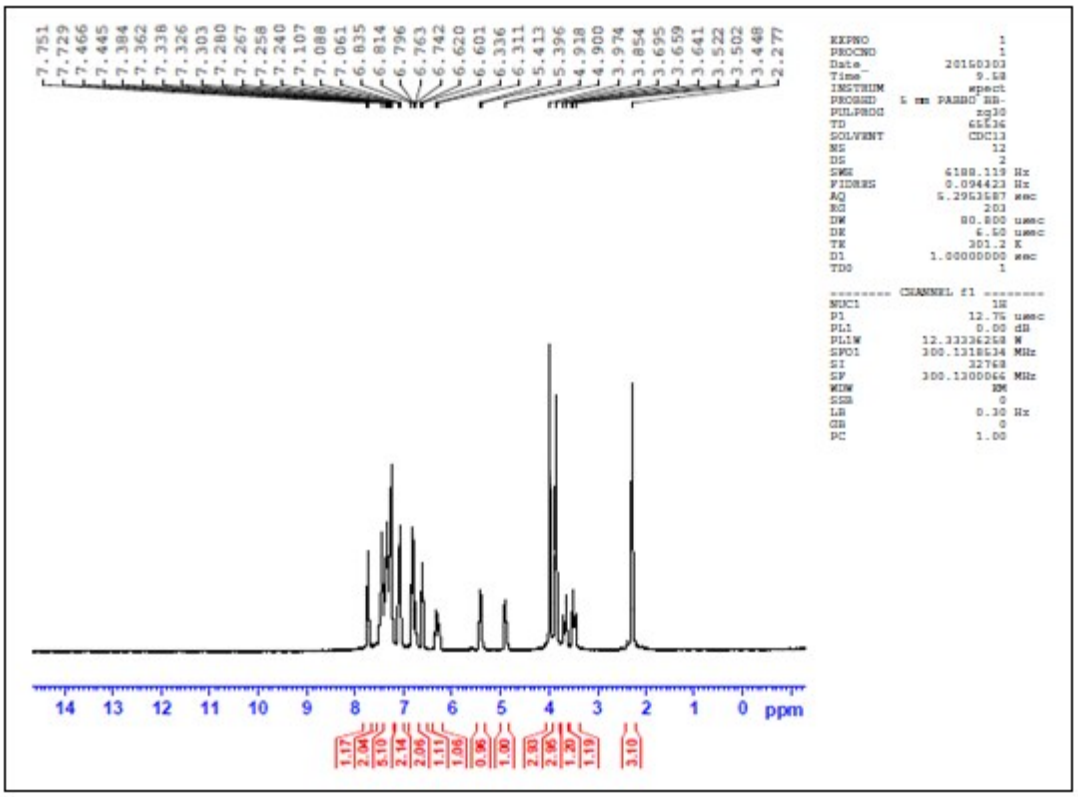


Figure S 35. ^{1}H NMR (300 MHz, $CDCl_3$) of **6e**.

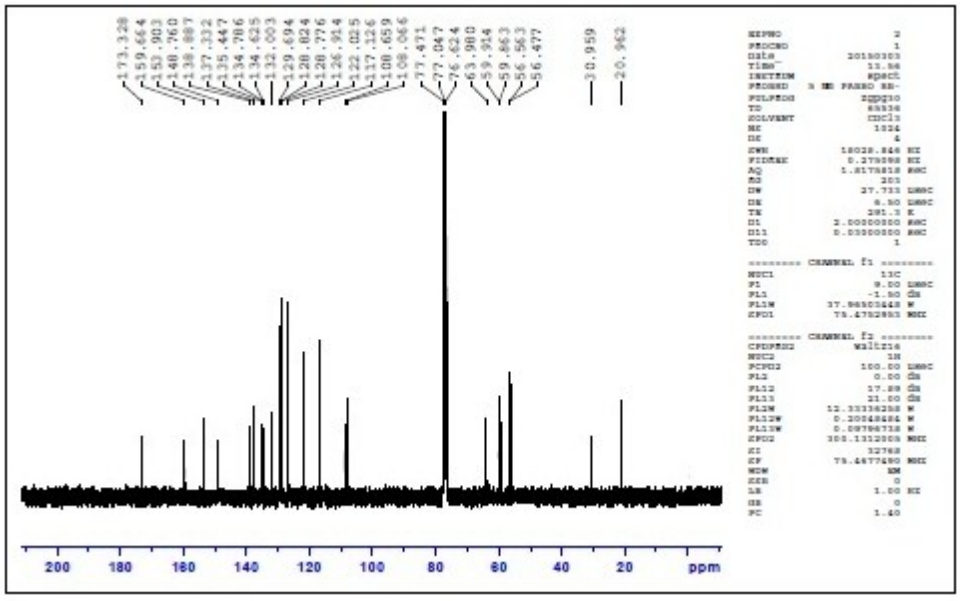


Figure S 36. ^{13}C NMR (75 MHz, $CDCl_3$) of **6e**.

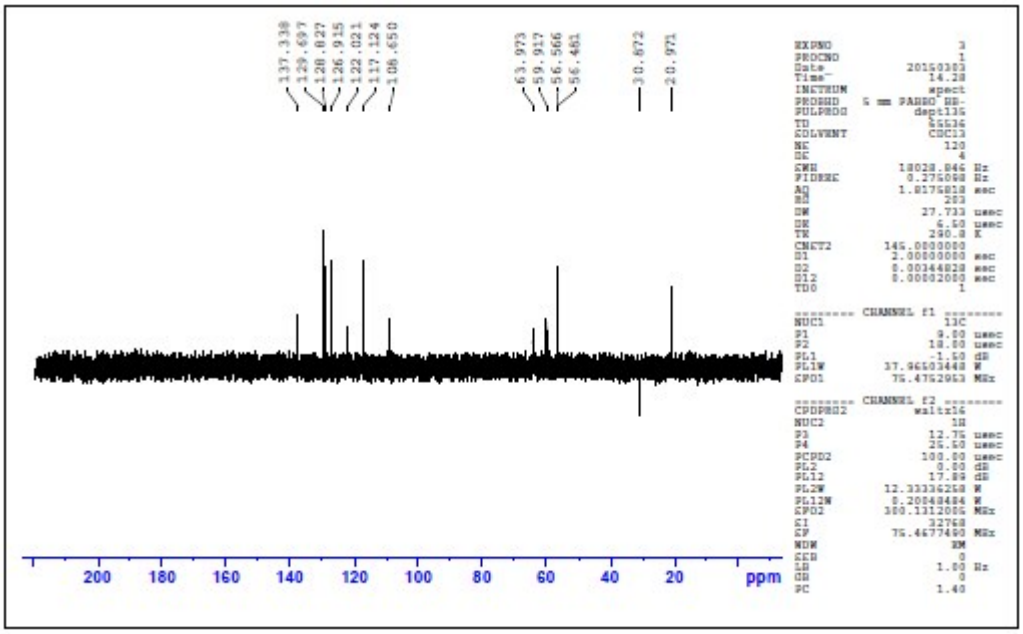


Figure S 37. DEPT NMR (75 MHz, $CDCl_3$) of **6e**.

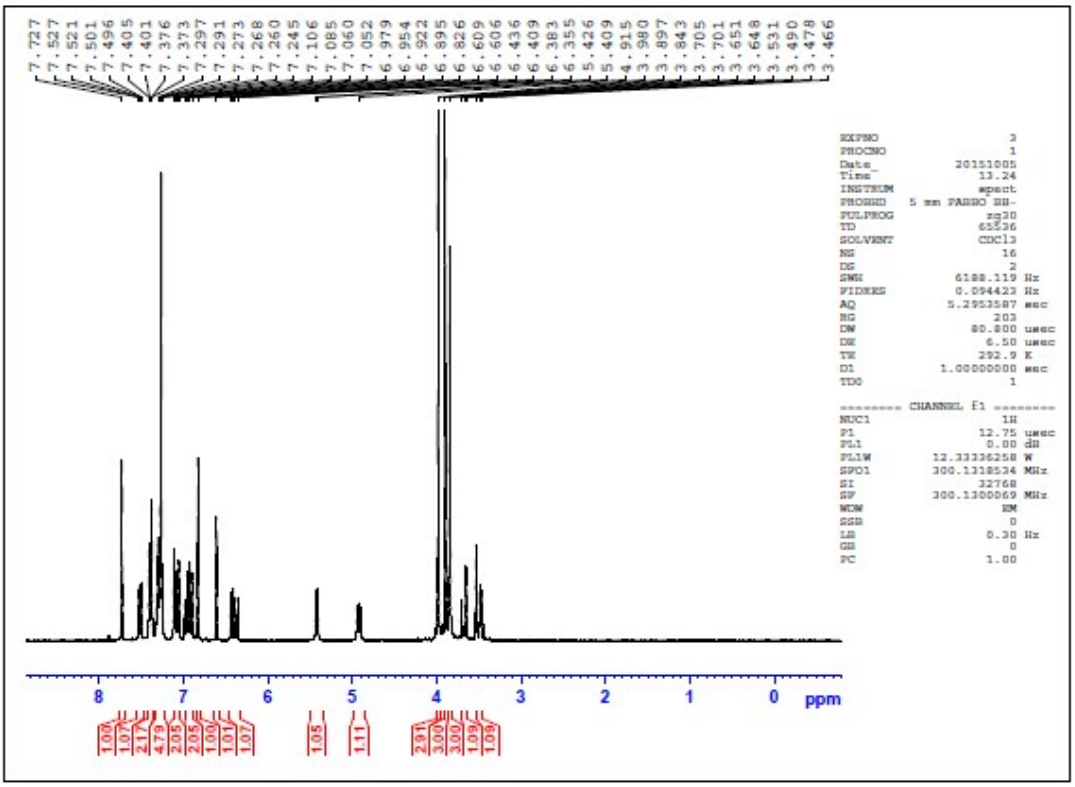


Figure S 38. ^1H NMR (300 MHz, $CDCl_3$) of **6f**.

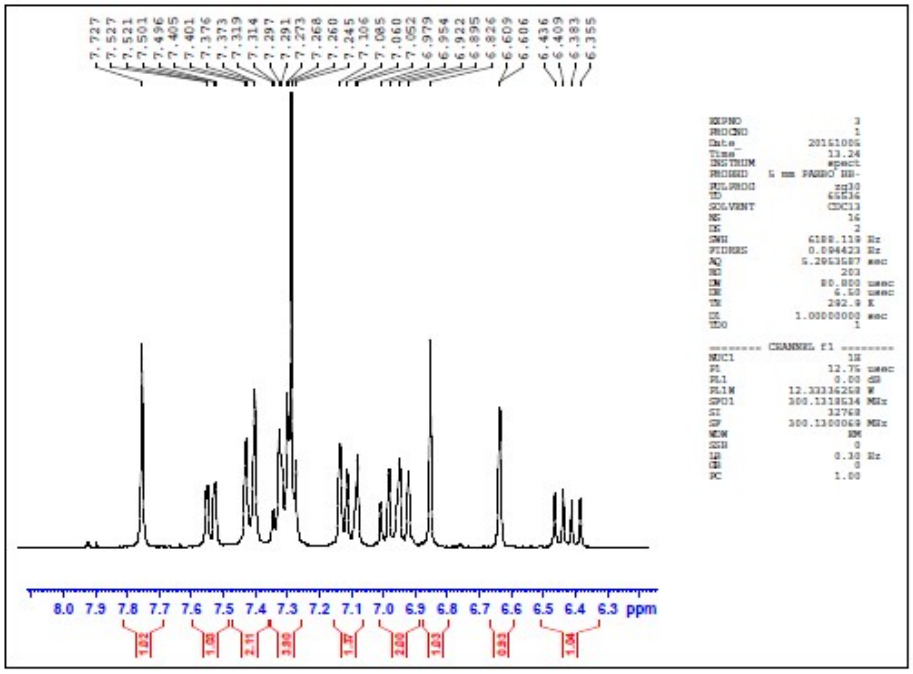


Figure S 39. ^{1}H NMR (300 MHz, $CDCl_3$) of **6f** expansion.

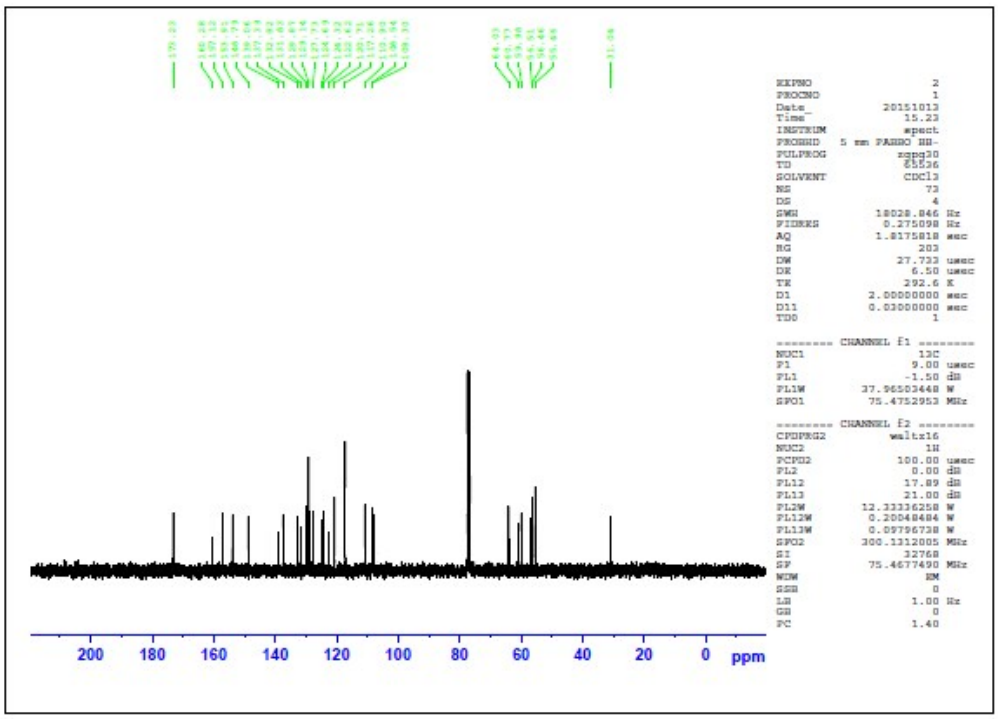


Figure S40. ^{13}C NMR (75 MHz, $CDCl_3$) of **6f**.

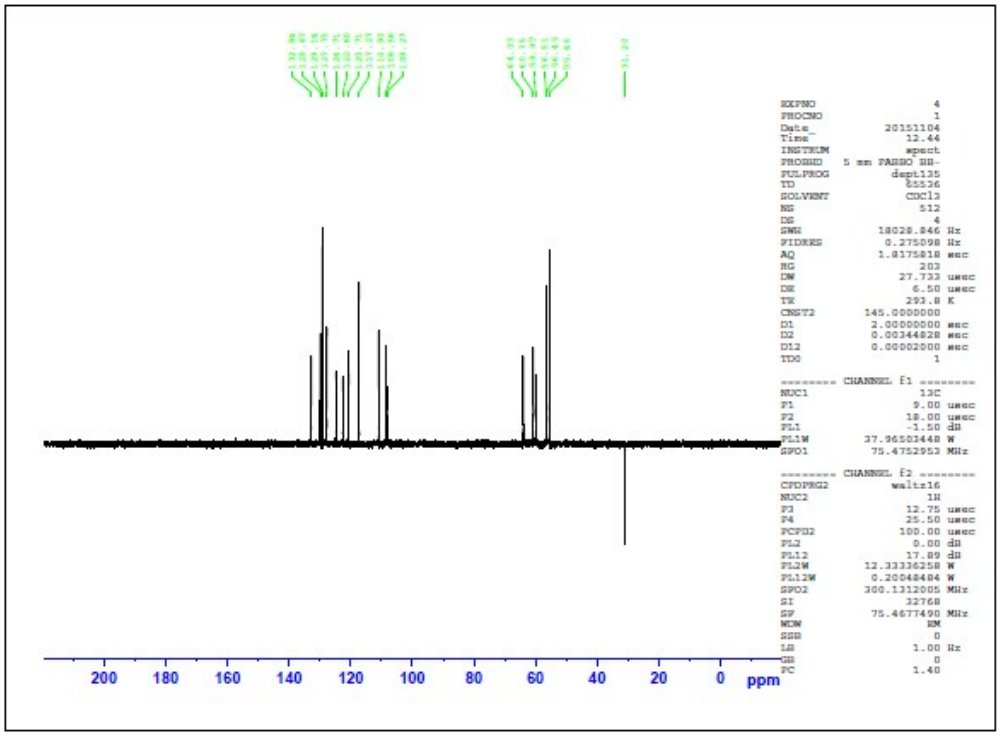


Figure S 41. DEPT NMR (75 MHz, $CDCl_3$) of **6f**.

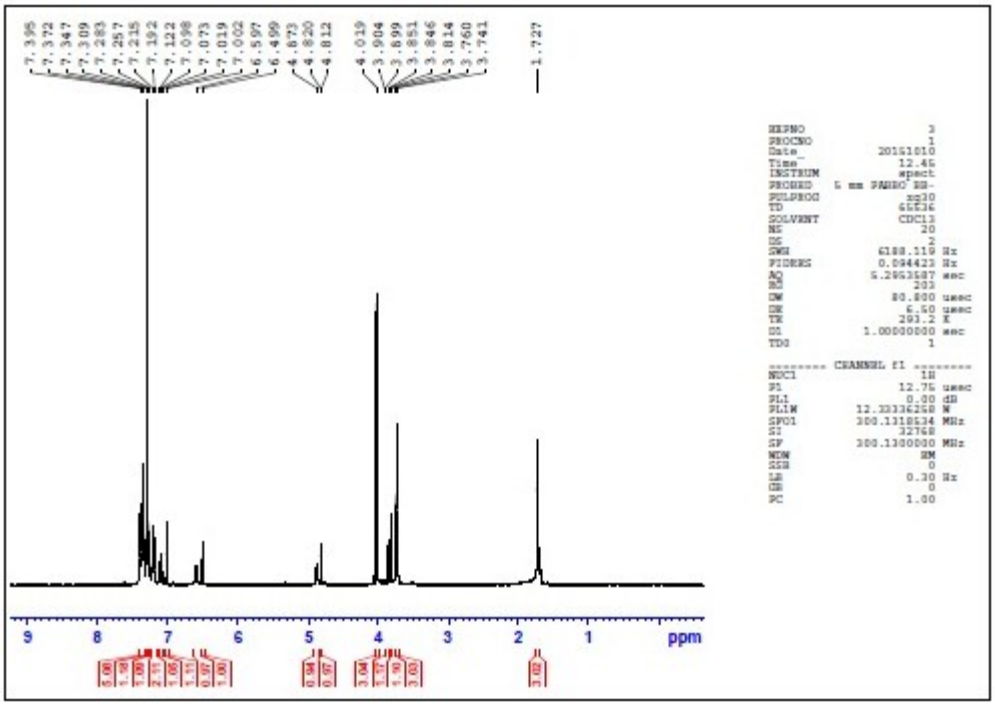


Figure S 42. ^1H NMR (300 MHz, $CDCl_3$) of **6g**.

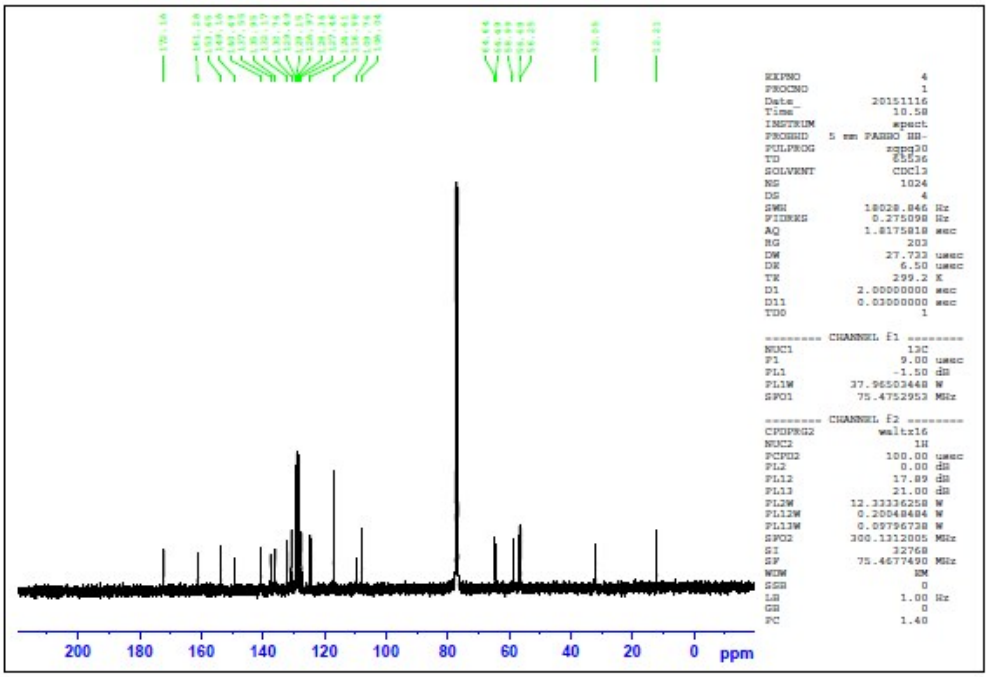


Figure S 43. ^{13}C NMR (75 MHz, $CDCl_3$) of **6g**.

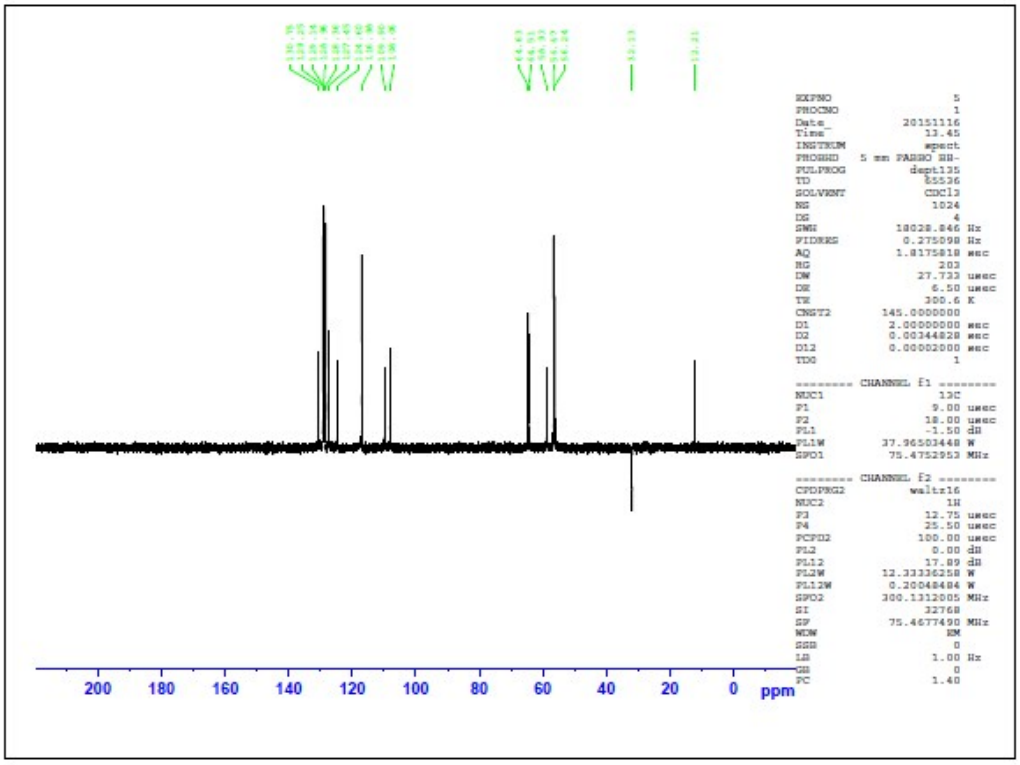


Figure S 44. DEPT NMR (75 MHz, $CDCl_3$) of **6g**.

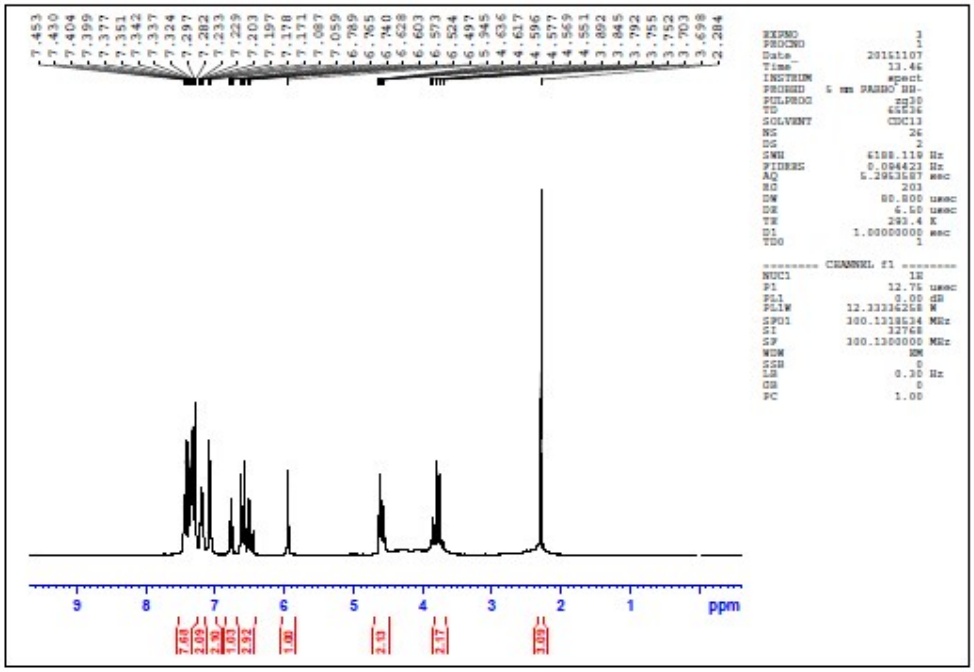


Figure S 45. ^{1}H NMR (300 MHz, $CDCl_3$) of **7a**.

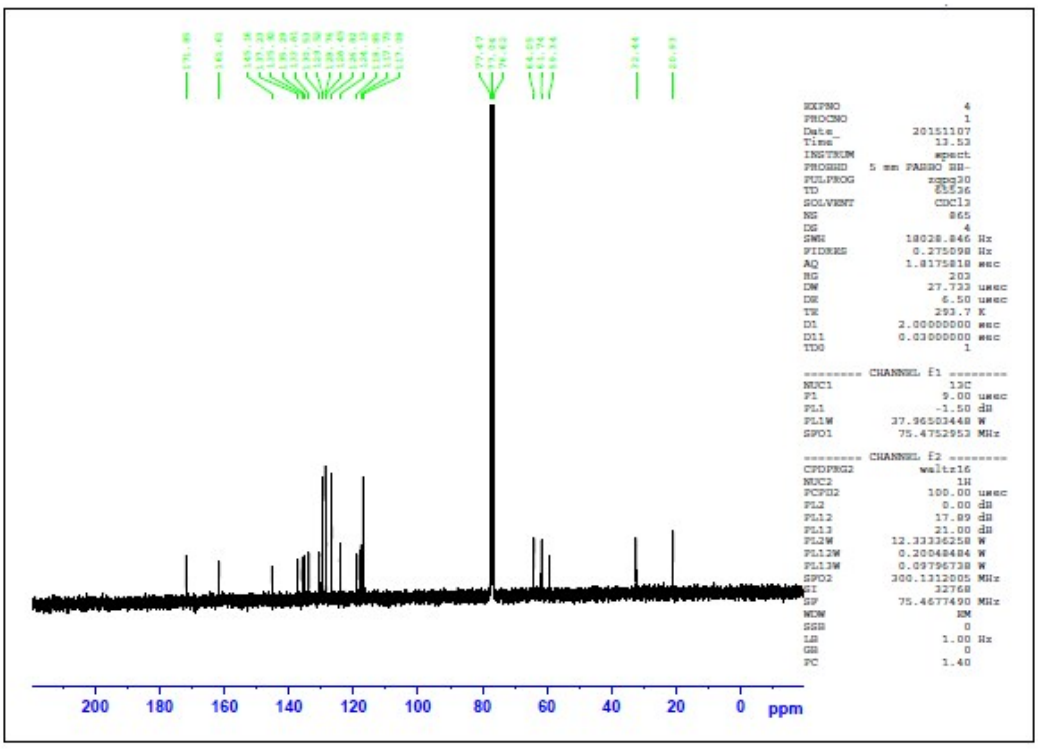


Figure S 46. ^{13}C NMR (75 MHz, $CDCl_3$) of **7a**.

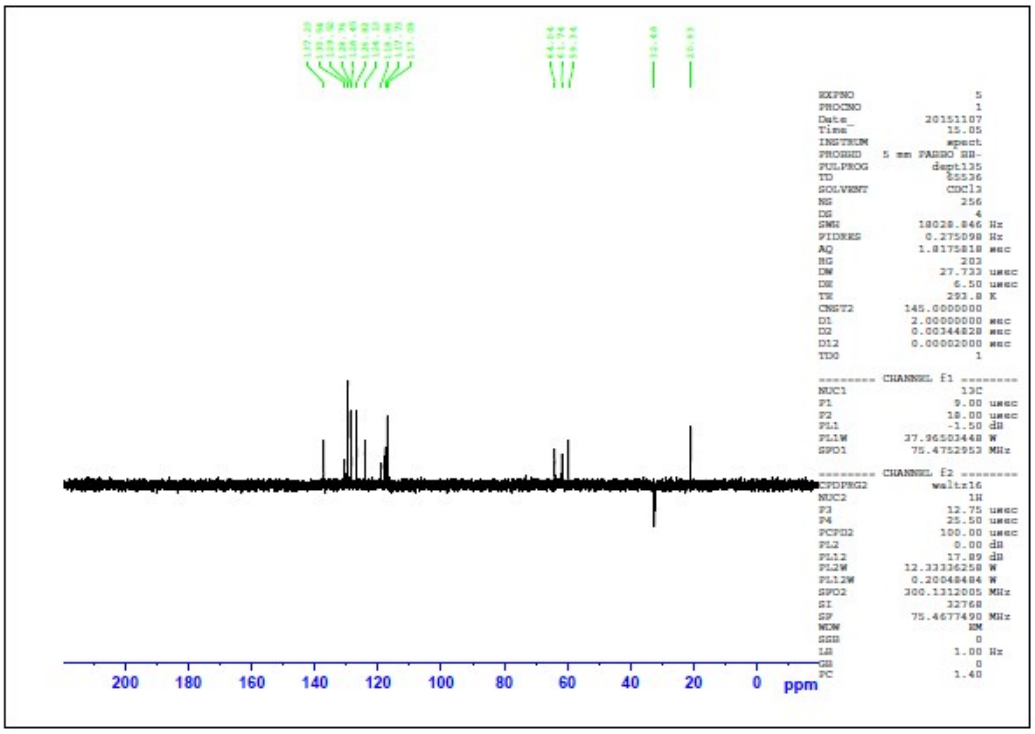


Figure S 47. DEPT NMR (75 MHz, $CDCl_3$) of **7a**.

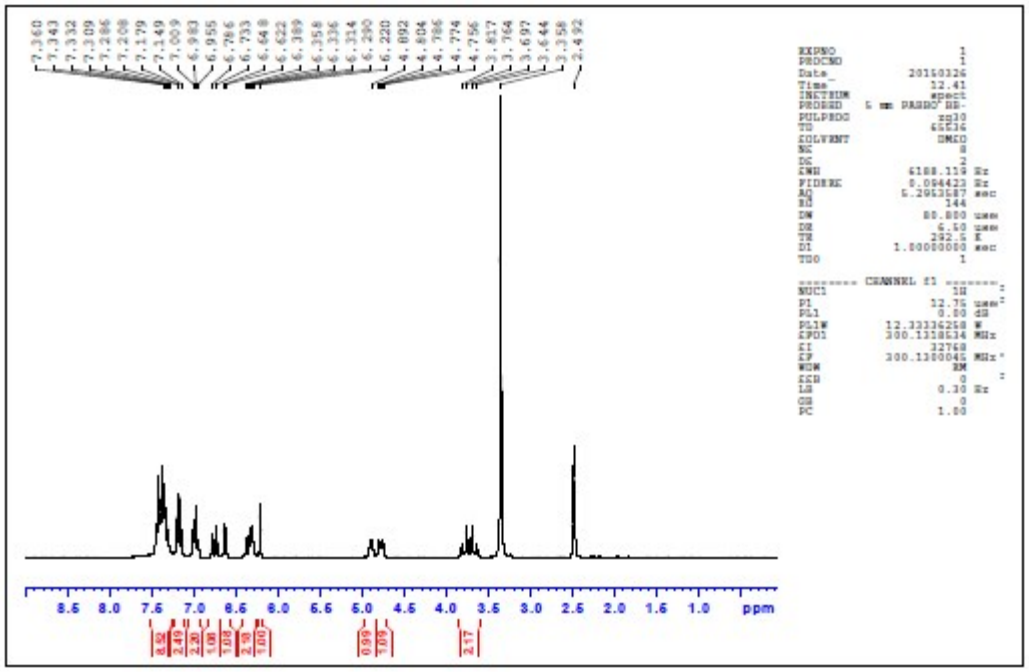


Figure S 48. ^1H NMR (300 MHz, DMSO-d_6) of **7b**.

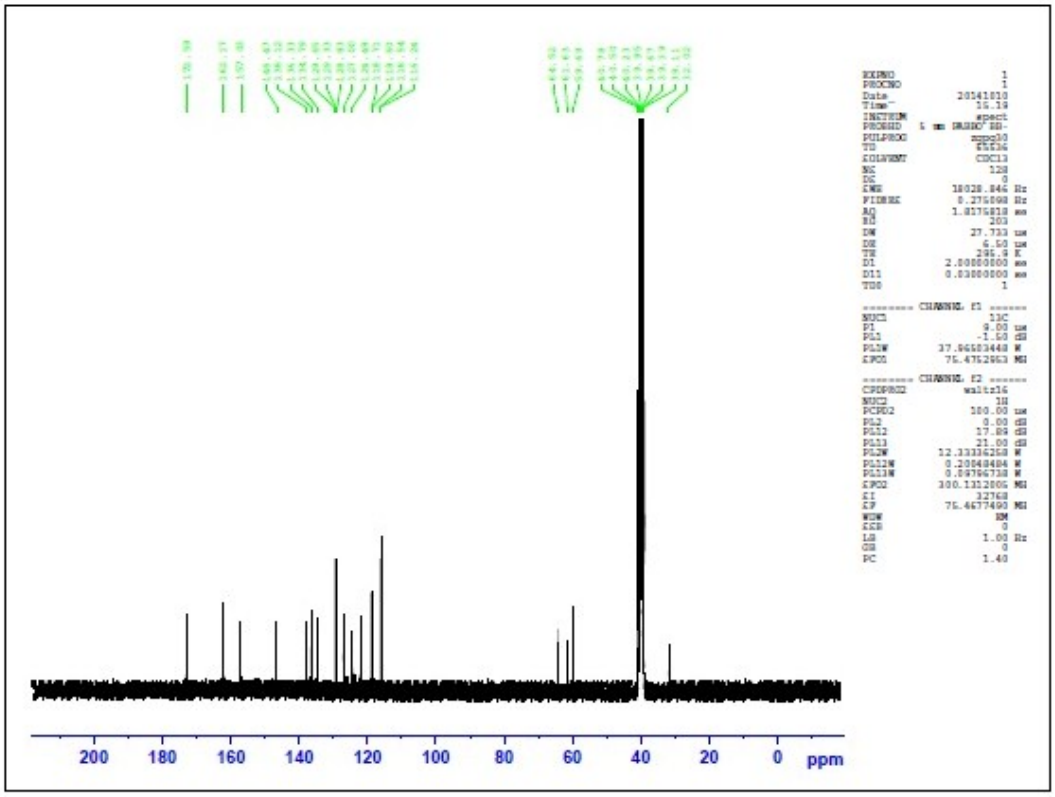


Figure S 49. ^{13}C NMR (75 MHz, DMSO-d_6) of **7b**.

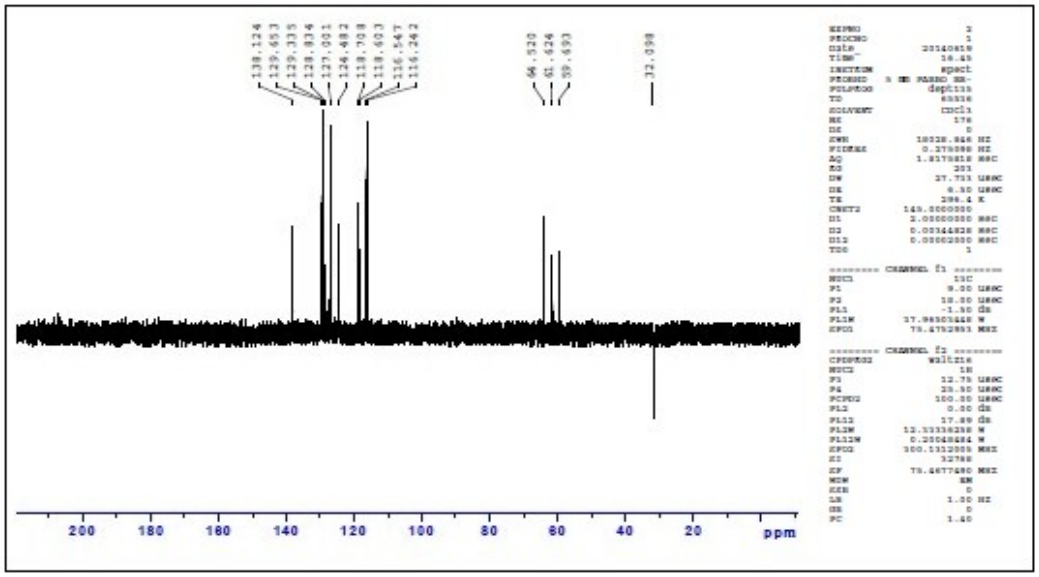


Figure S 50. ^{13}C NMR (75 MHz, DMSO) of **7b**.

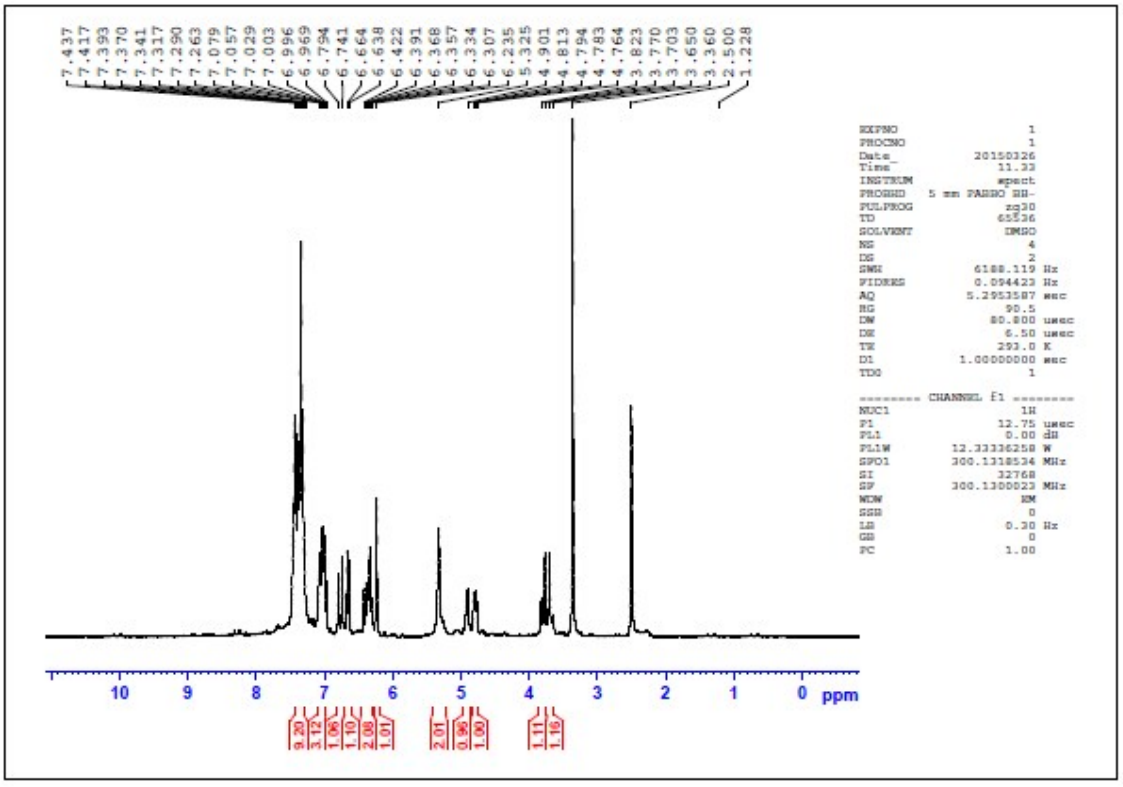


Figure S 51. ^{1}H NMR (300 MHz, DMSO-d_6) of **7c**.

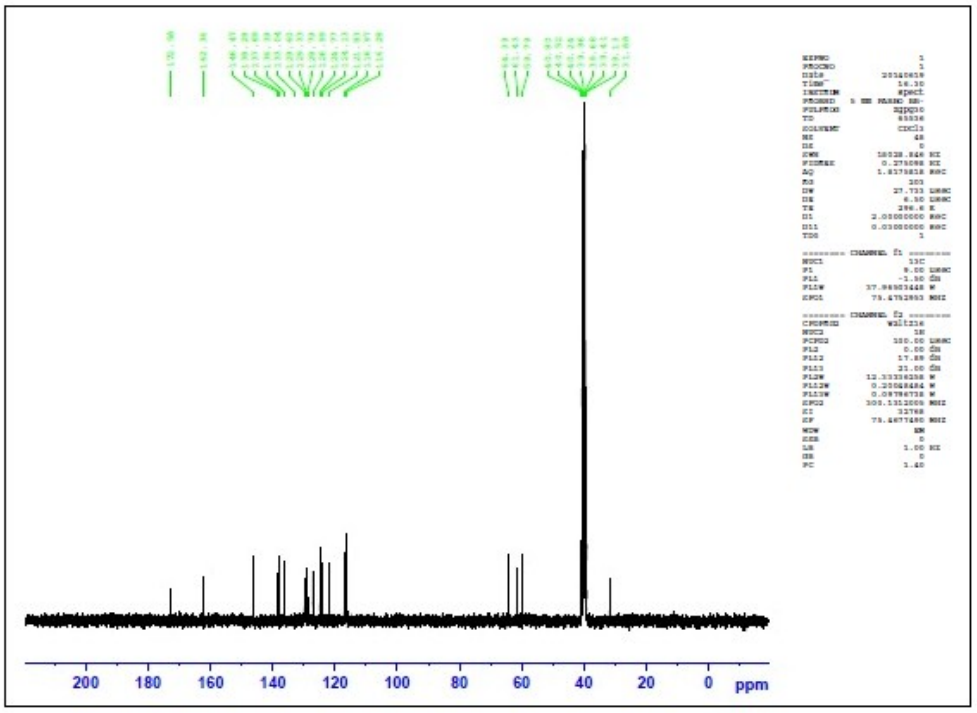


Figure S 52. ^{13}C NMR (75 MHz, DMSO-d_6) of **7c**.

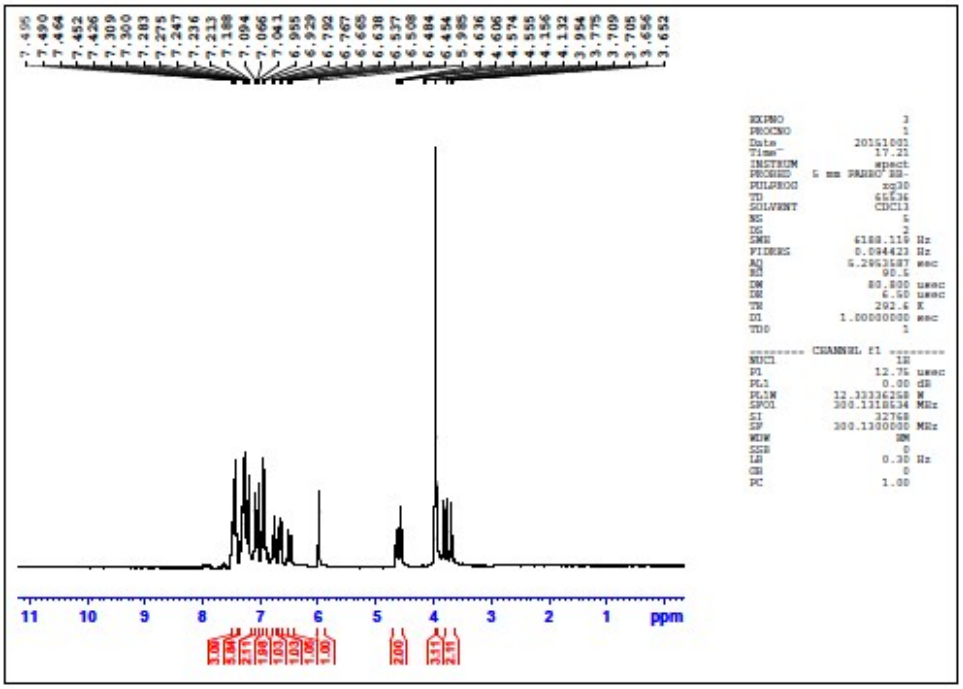


Figure S 53. ^{1}H NMR (300 MHz, $CDCl_3$) of **7d**.

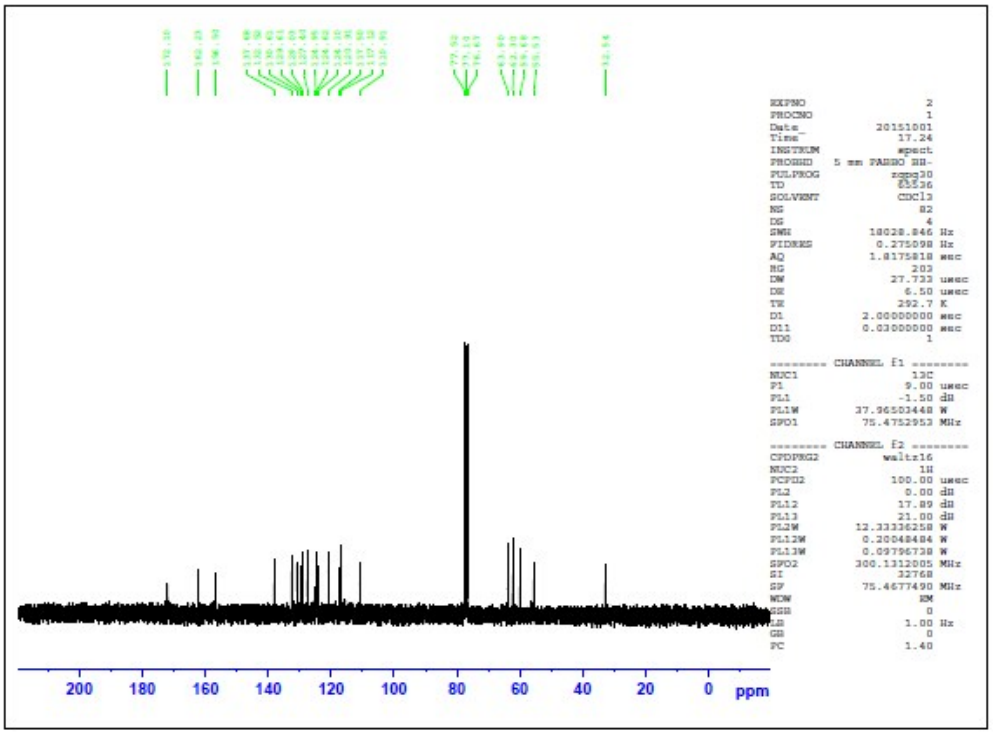


Figure S 54. ^{13}C NMR (75 MHz, $CDCl_3$) of **7d**.

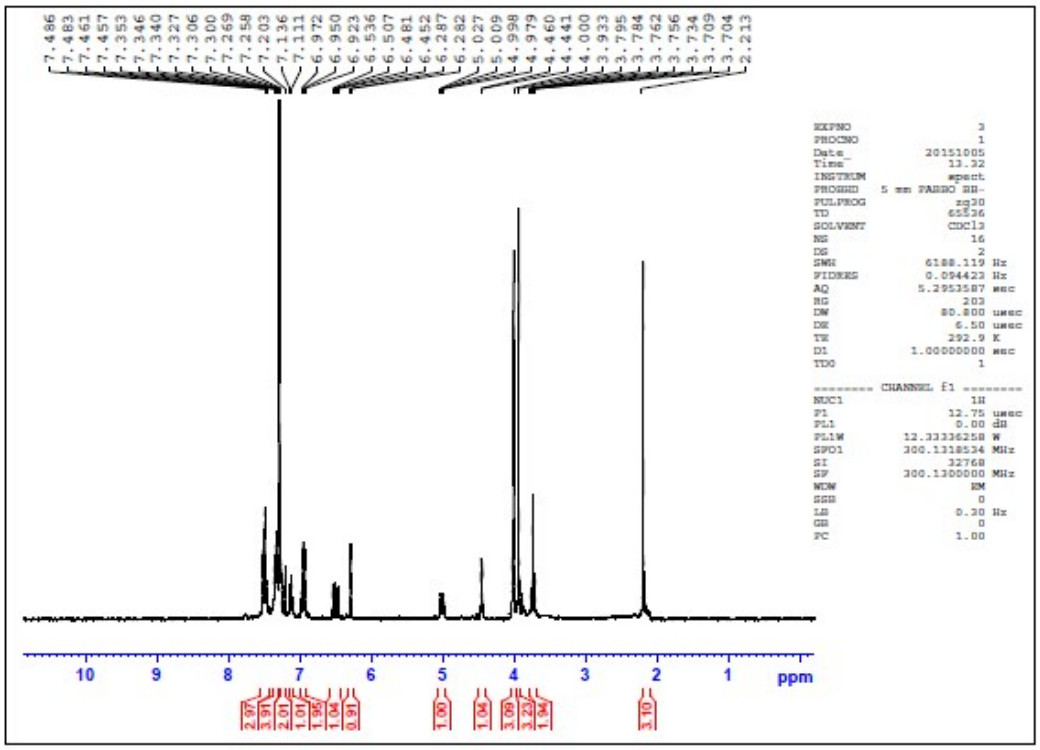


Figure S 55. ^{1}H NMR (300 MHz, $CDCl_3$) of **7e**.

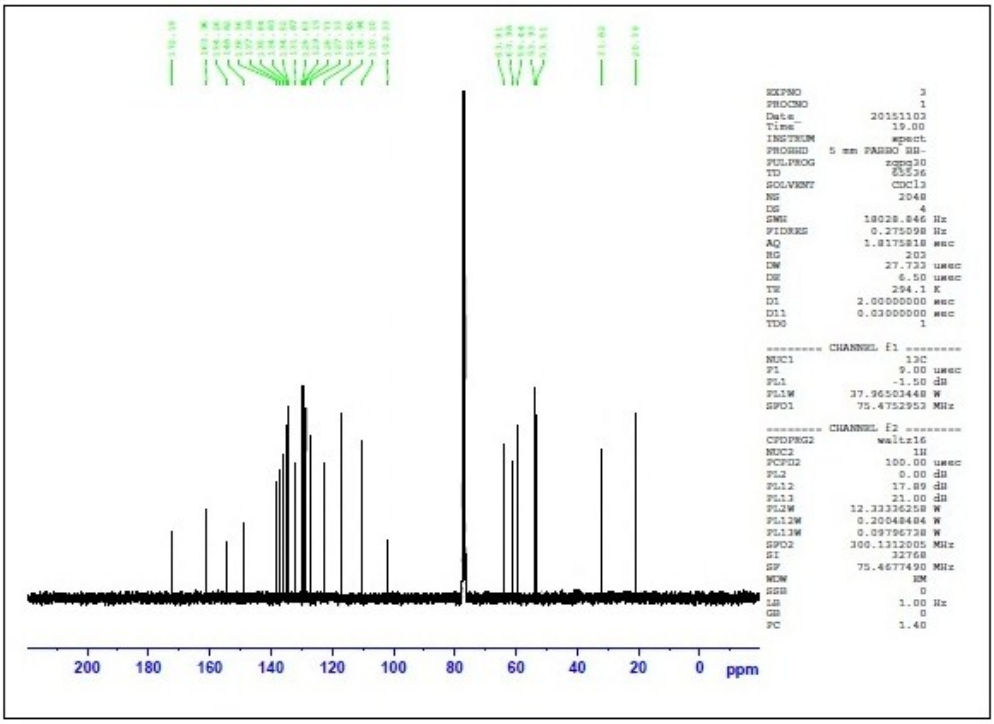


Figure S 56. ^{13}C NMR (75 MHz, $CDCl_3$) of **7e**.

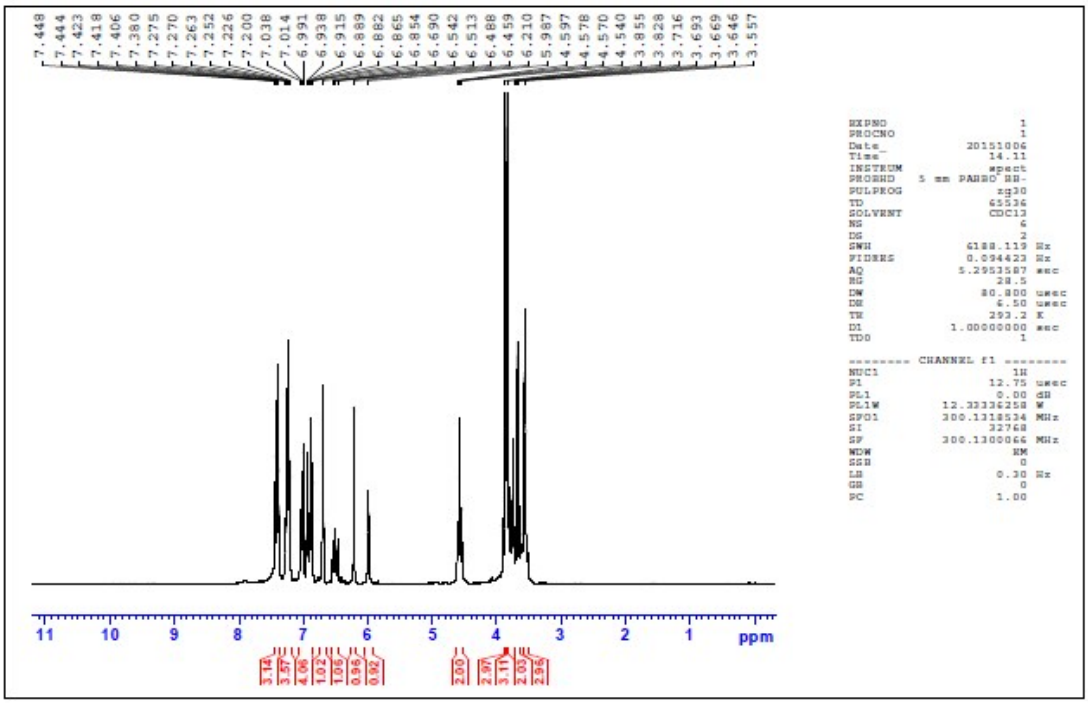


Figure S 57. ^{1}H NMR (300 MHz, $CDCl_3$) of **7f**.

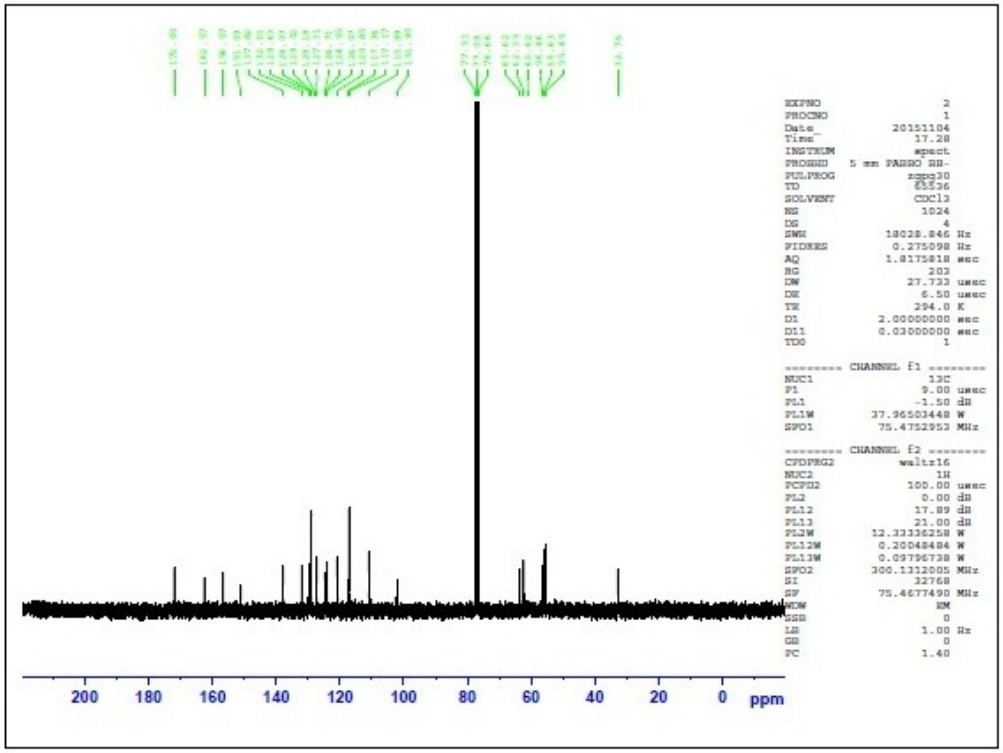


Figure S 58. ^{13}C NMR (75 MHz, $CDCl_3$) of **7f**.

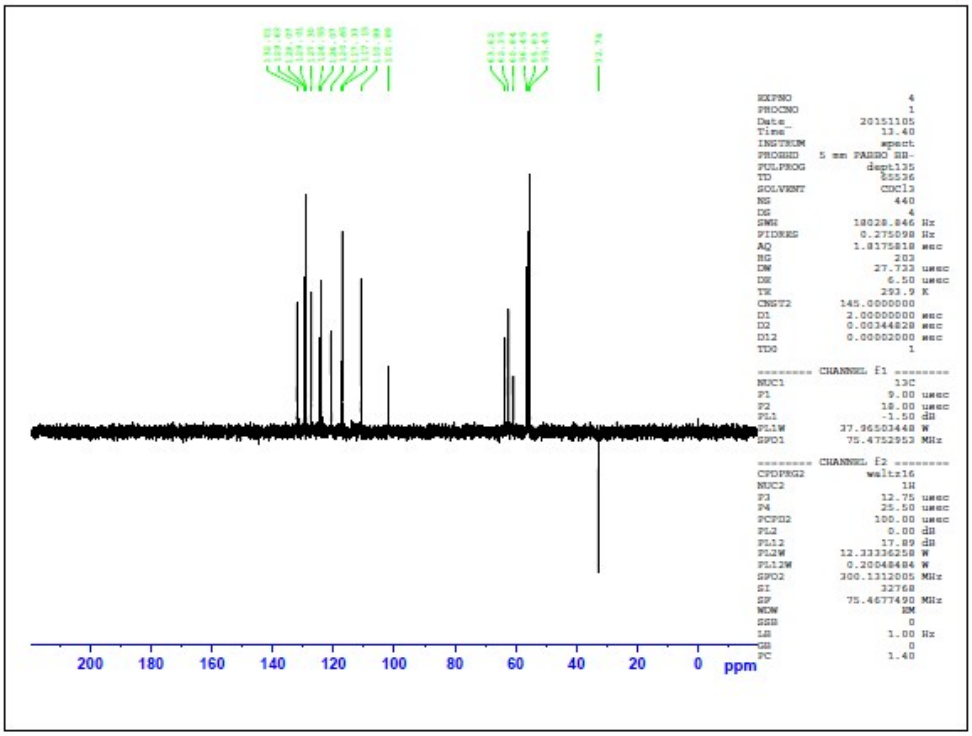


Figure S 59. DEPT NMR (75 MHz, $CDCl_3$) of **7f**.

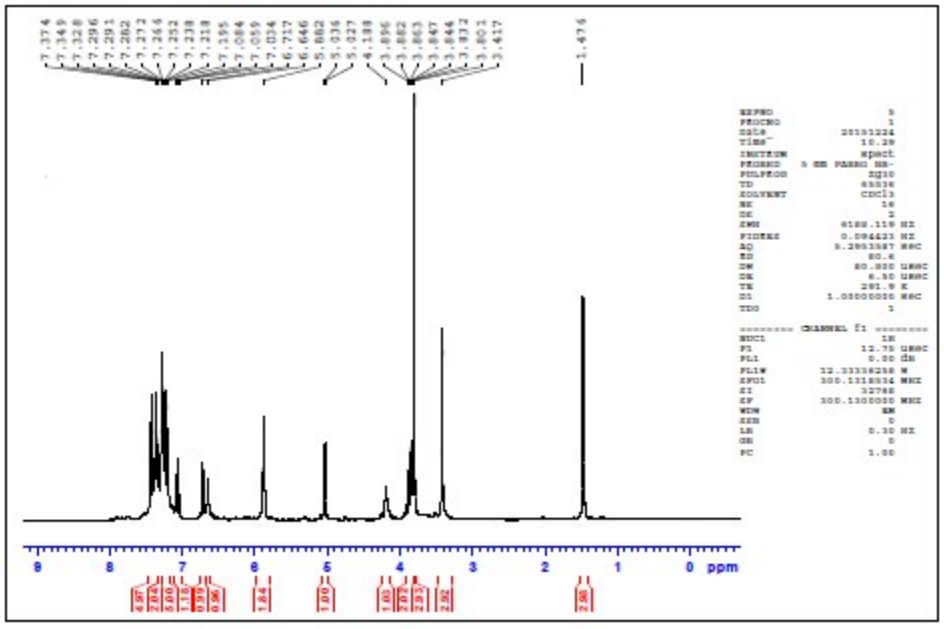


Figure S 60. ^1H NMR (300 MHz, $CDCl_3$) of **7g**.

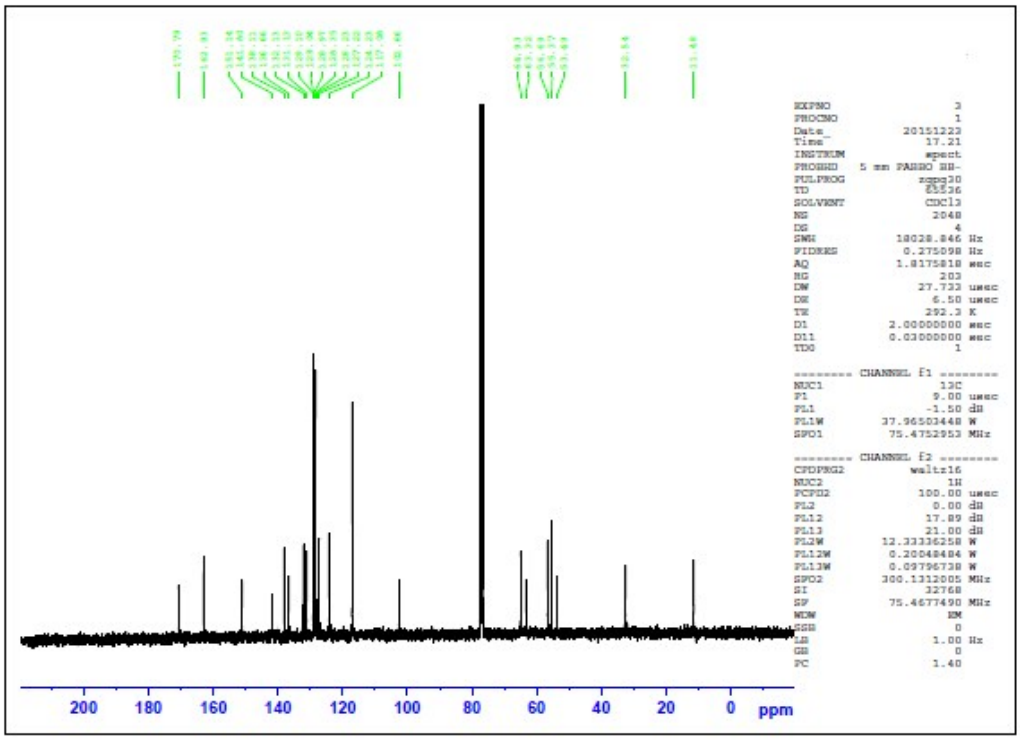


Figure S 61. ^{13}C NMR (75 MHz, $CDCl_3$) of **7g**.

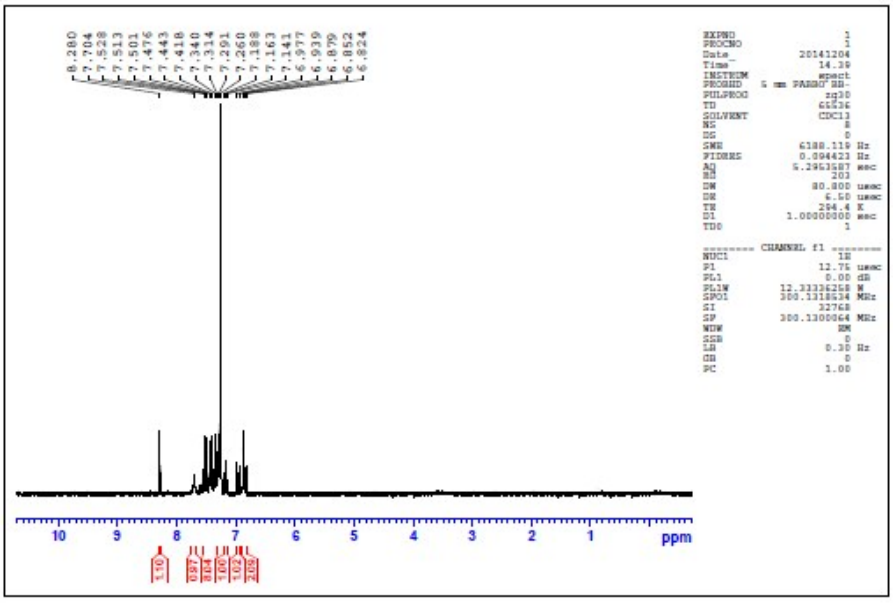


Figure S 62. ^{1}H NMR (300 MHz, $CDCl_3$) of **8a**.

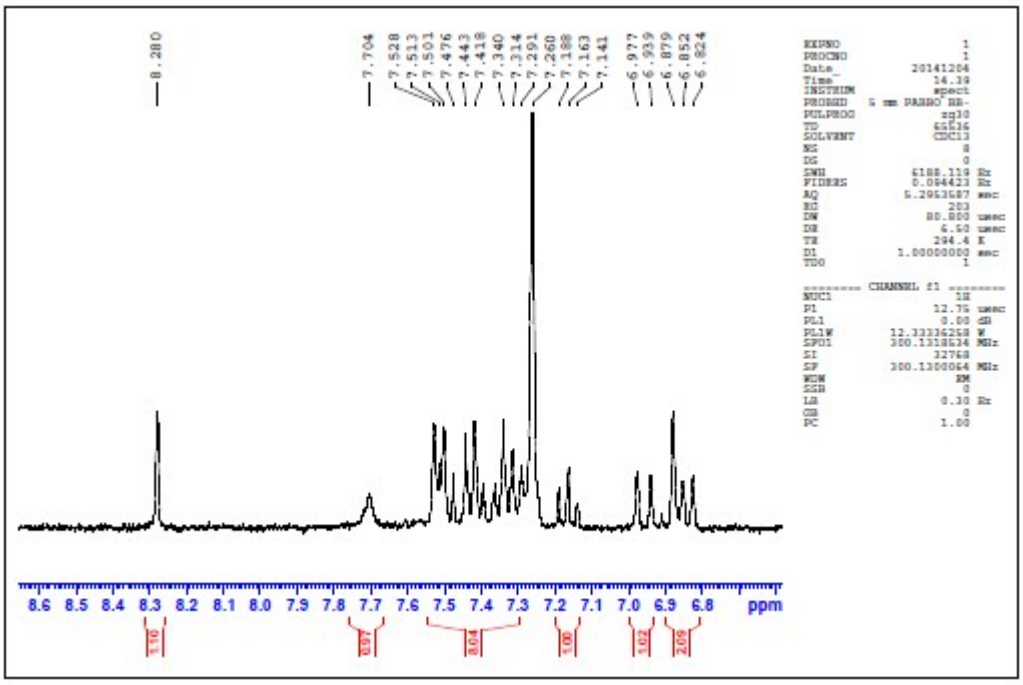


Figure S 63. ^{1}H NMR (300 MHz, $CDCl_3$) of **8a** extension.

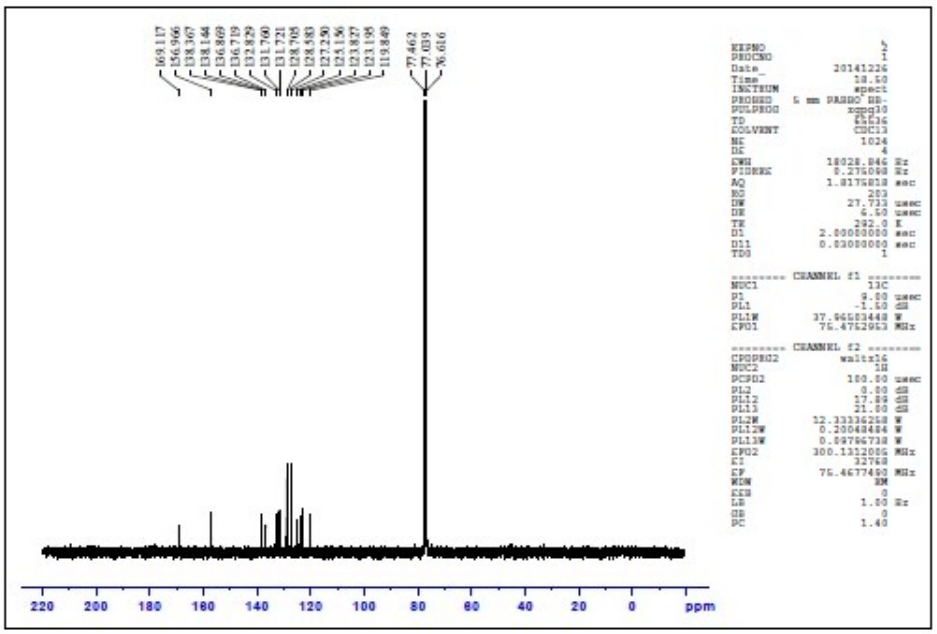


Figure S 64. ^{13}C NMR (75 MHz, $CDCl_3$) of **8a**.

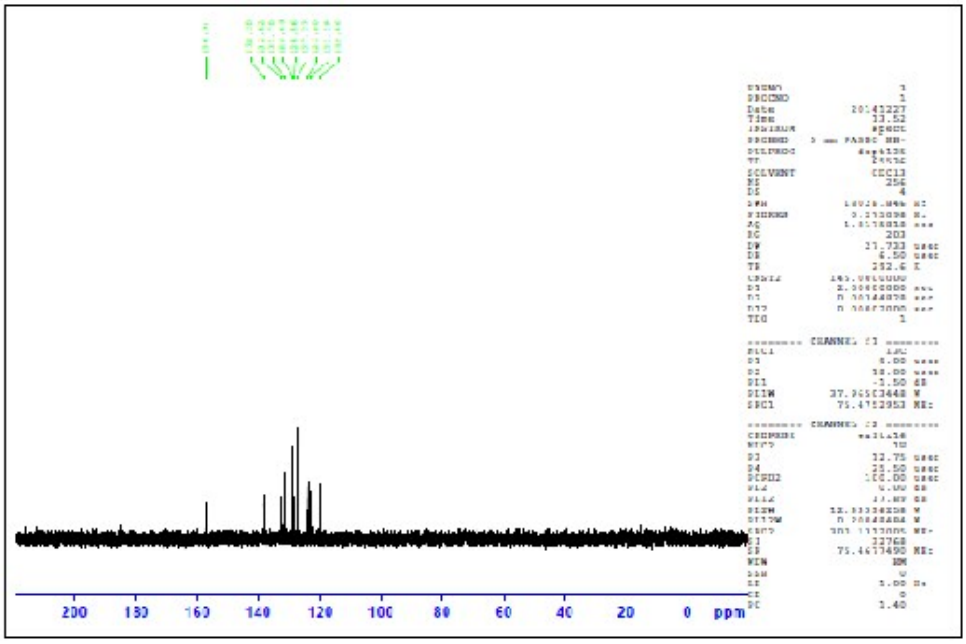


Figure S 65. DEPT NMR (75 MHz, $CDCl_3$) of **8a**.

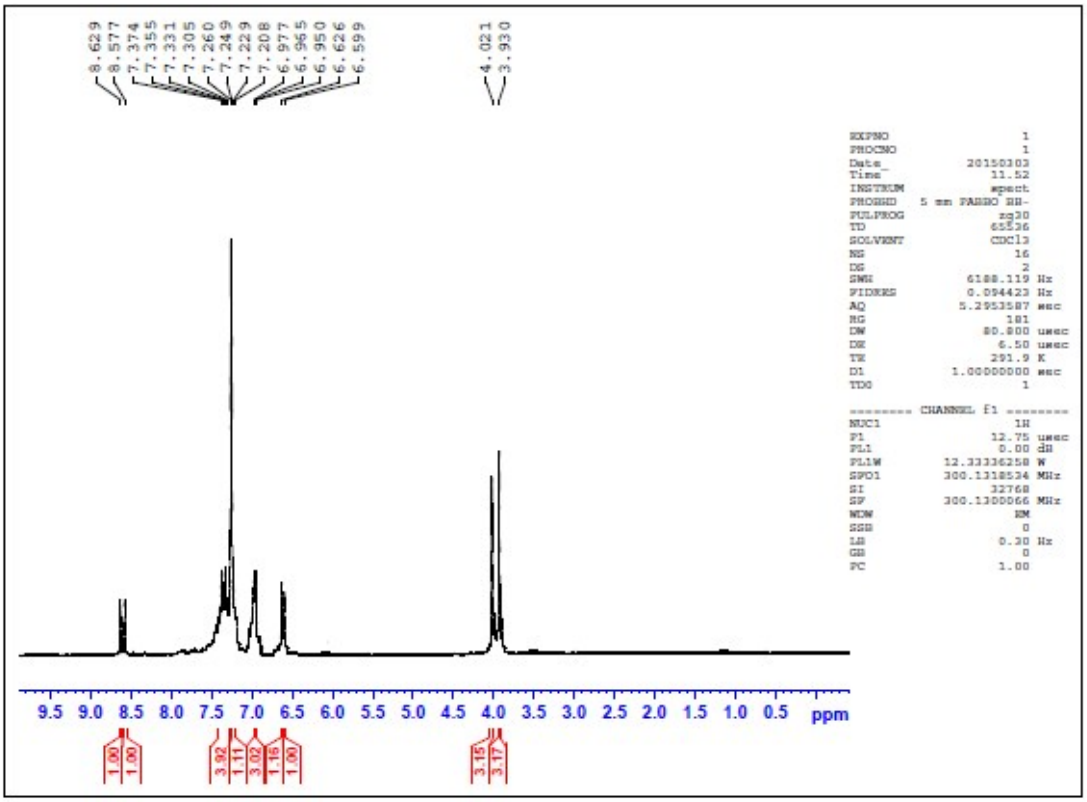


Figure S 66. ^1H NMR (300 MHz, $CDCl_3$) of **8b**.

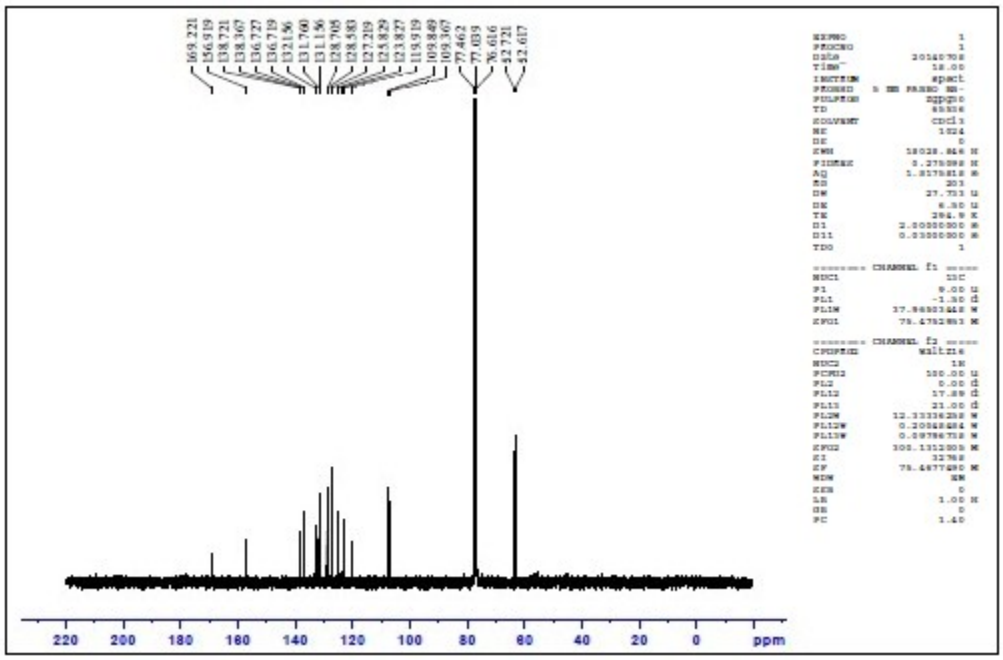


Figure S 67. ^{13}C NMR (75 MHz, $CDCl_3$) of **8b**.

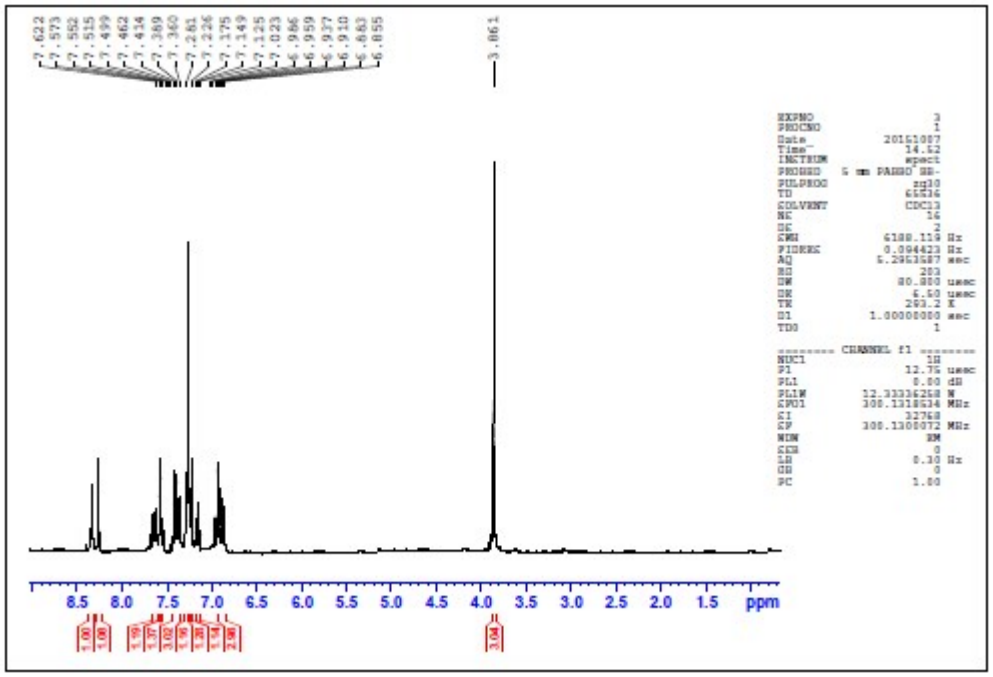


Figure S 68. ^{1}H NMR (300 MHz, $CDCl_3$) of **8c**.

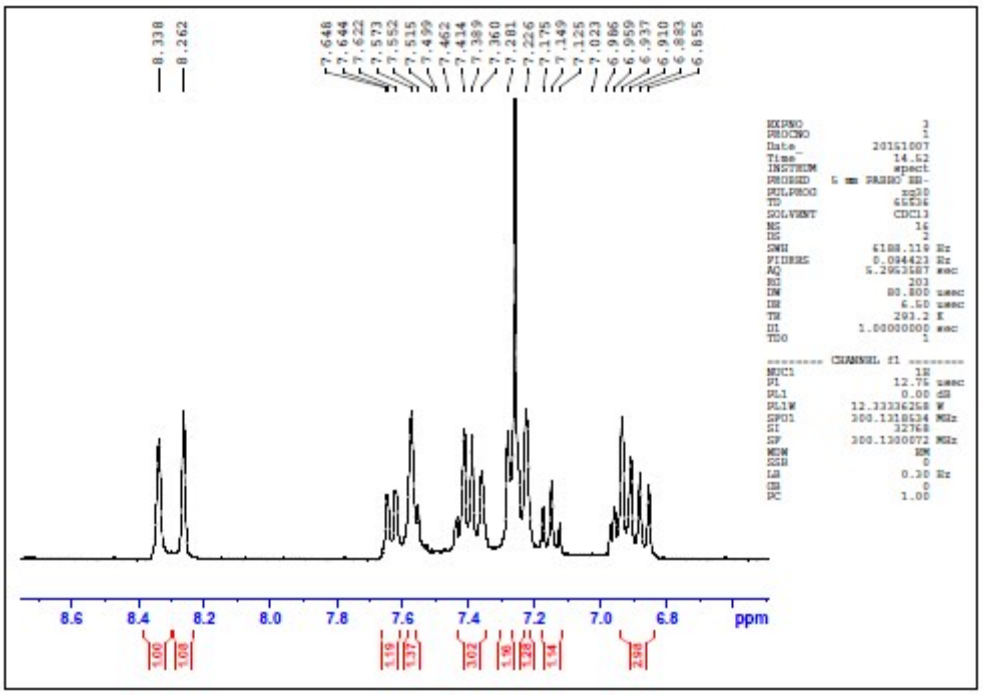


Figure S 69. ^{1}H NMR (300 MHz, $CDCl_3$) of **8c** expansion.

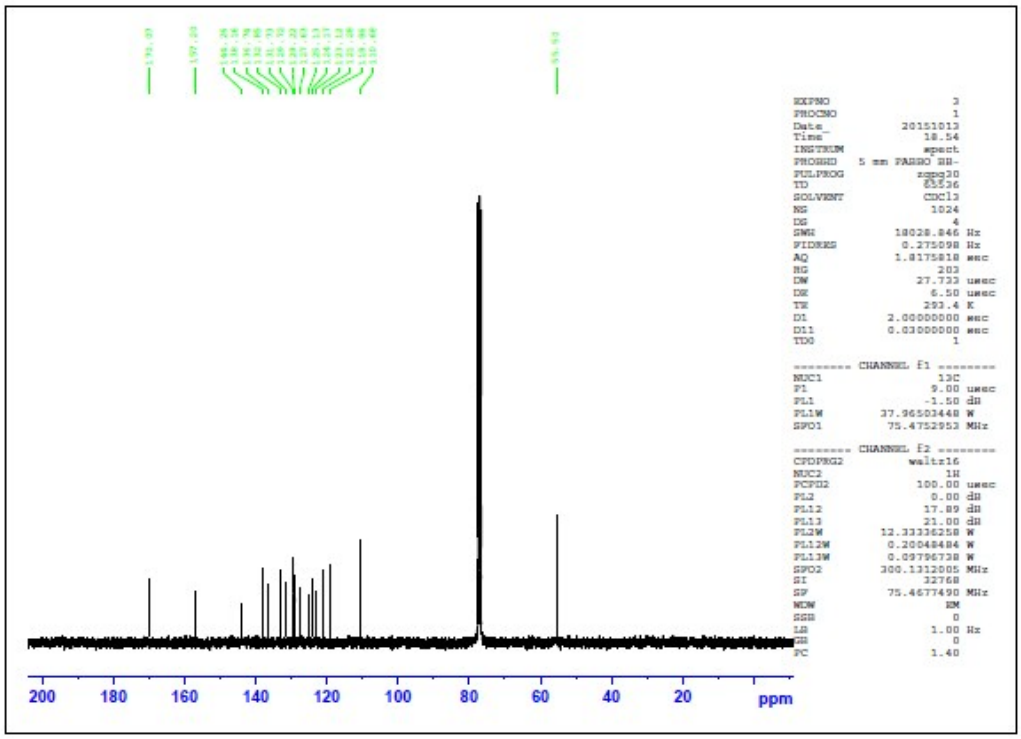


Figure S 70. ^{13}C NMR (75 MHz, $CDCl_3$) of **8c**.

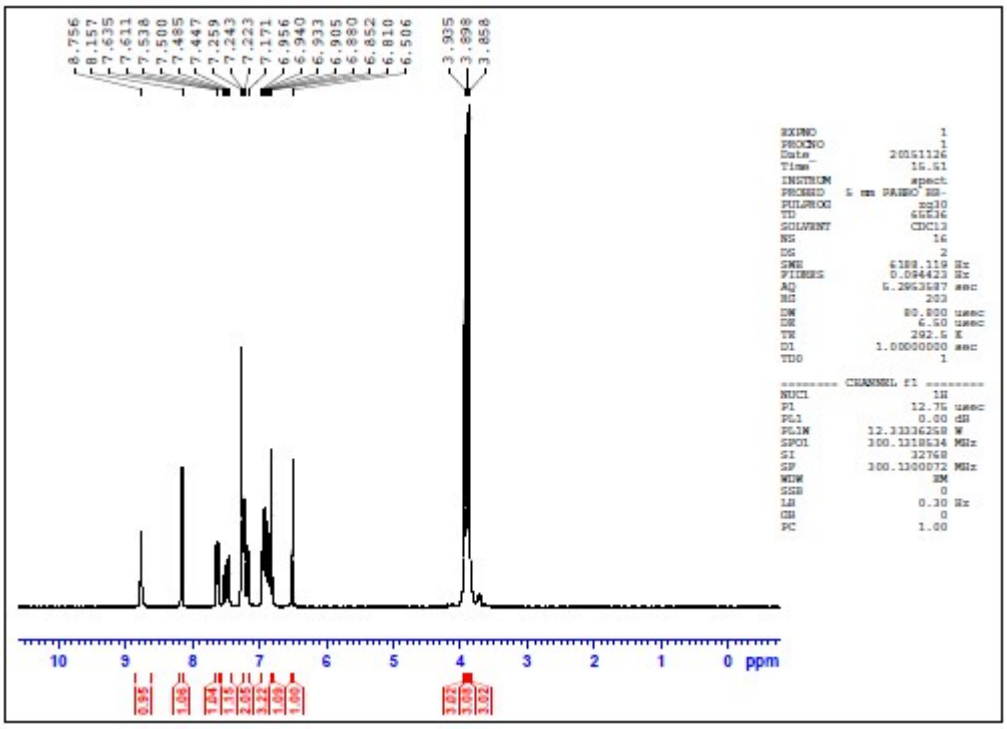


Figure S 71. ^{1}H NMR (300 MHz, $CDCl_3$) of **8d**.

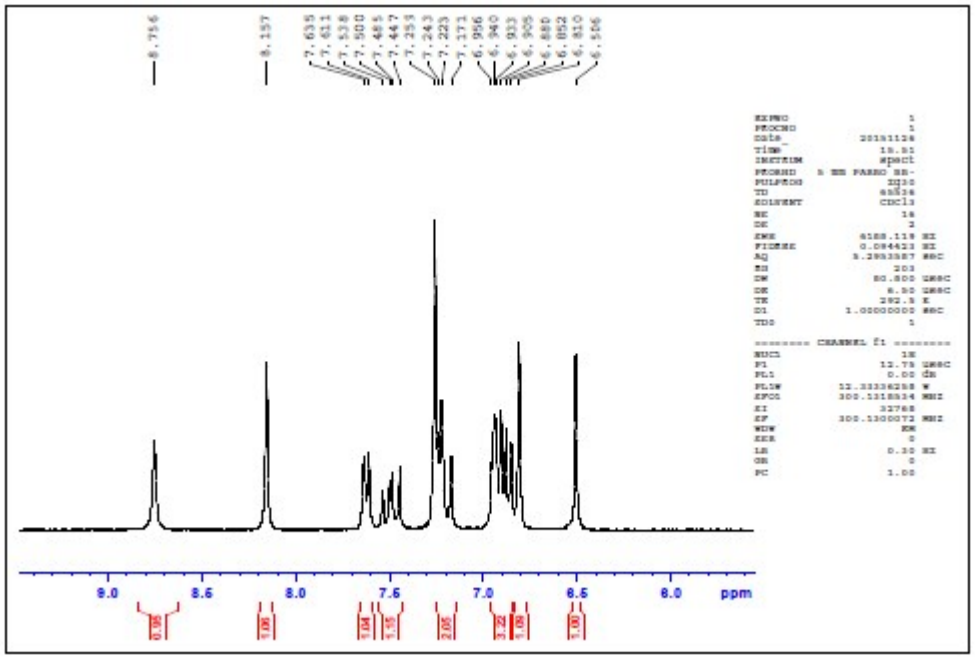


Figure S 72. ^{1}H NMR (300 MHz, $CDCl_3$) of **8d** expansion.

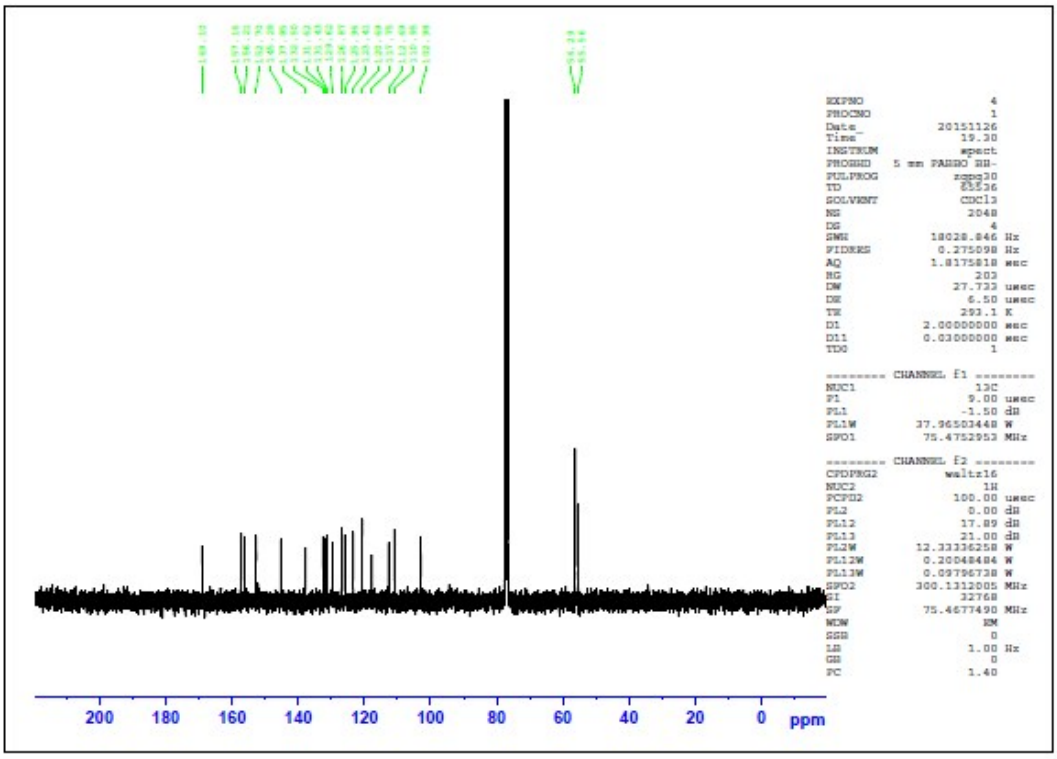


Figure S 73. ^{13}C NMR (75 MHz, $CDCl_3$) of **8d**.

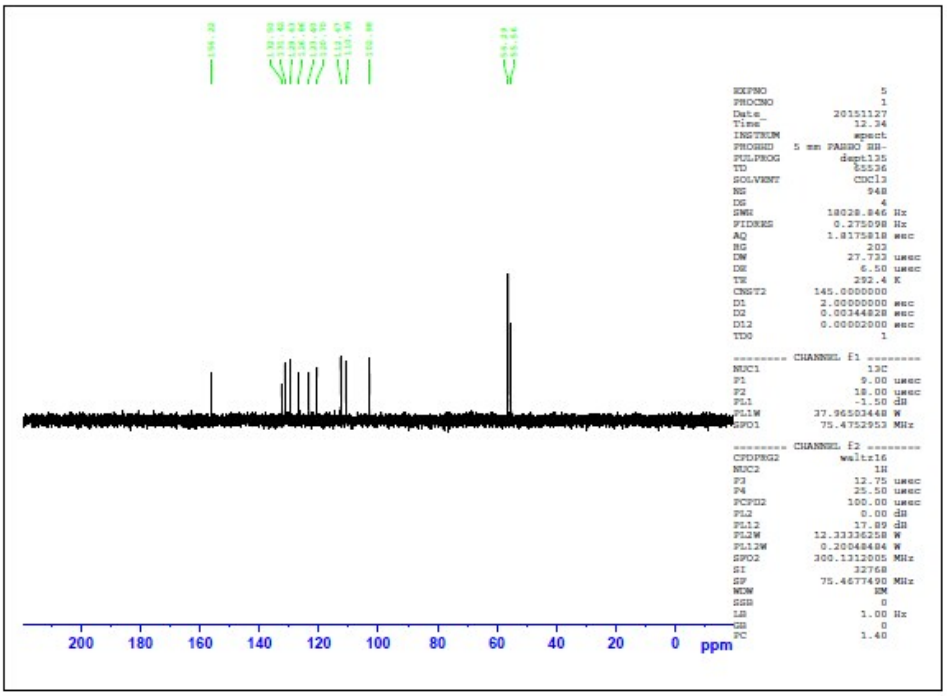


Figure S 74. DEPT NMR (75 MHz, $CDCl_3$) of **8d**.

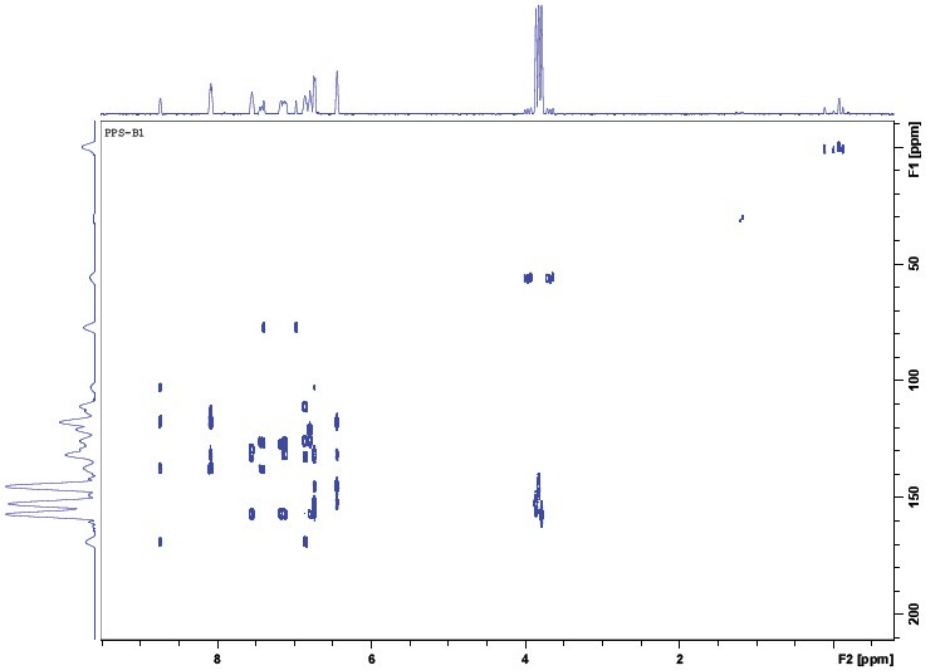


Figure S 75. HMBC NMR (75 MHz, $CDCl_3$) of **8d**.

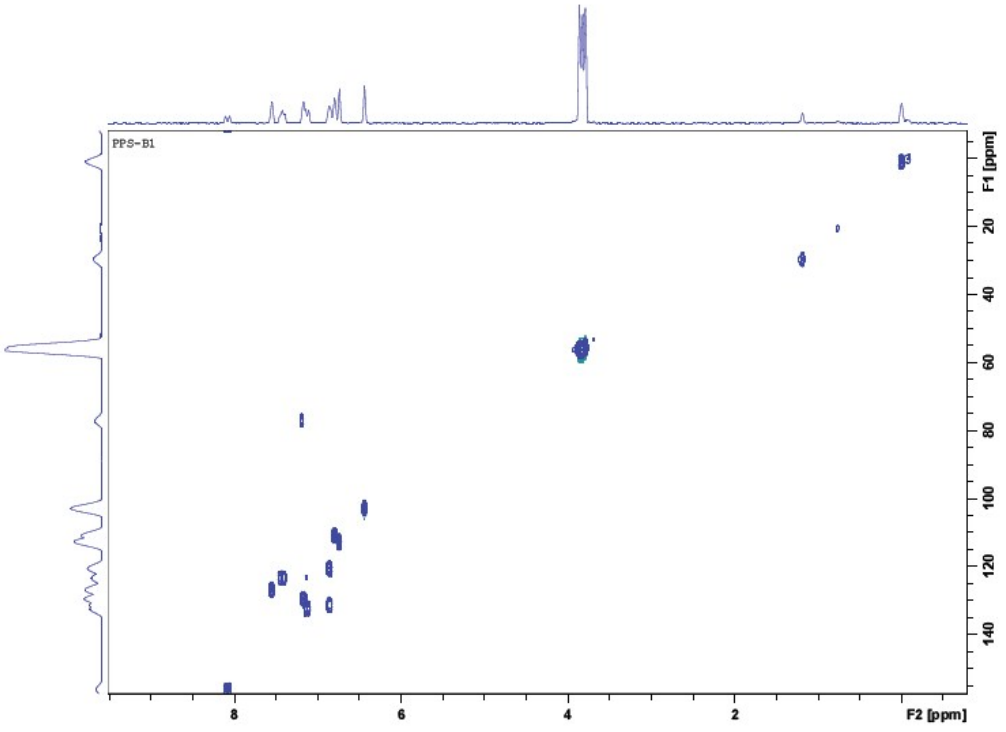


Figure S 76. HSQC NMR (75 MHz, $CDCl_3$) of **8d**.

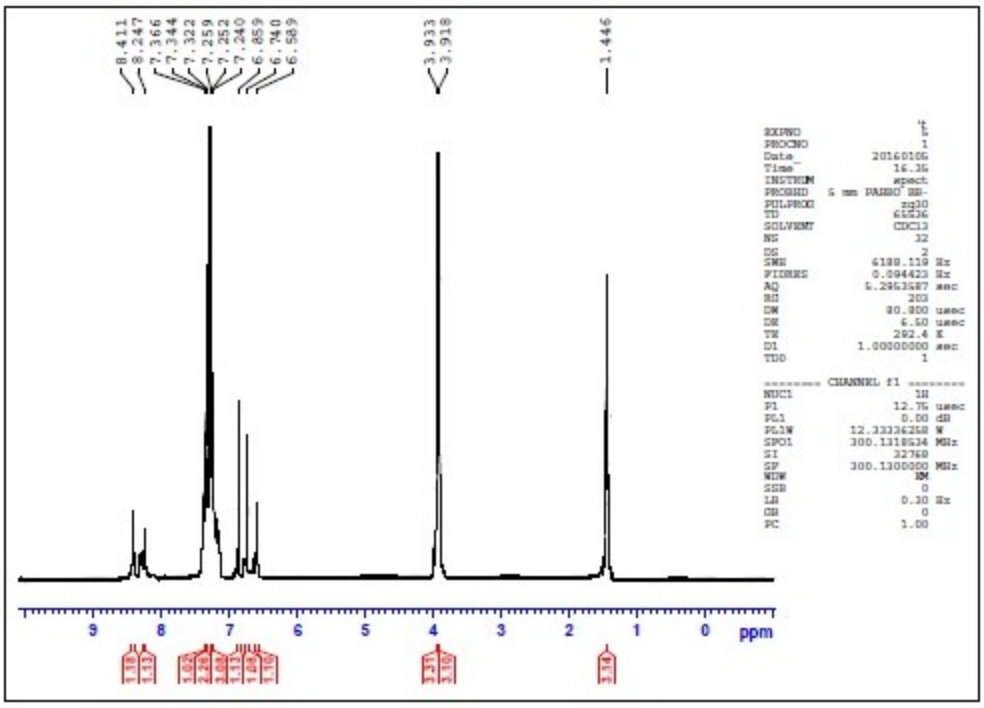


Figure S 77. ^{1}H NMR (300 MHz, $CDCl_3$) of **8e**.

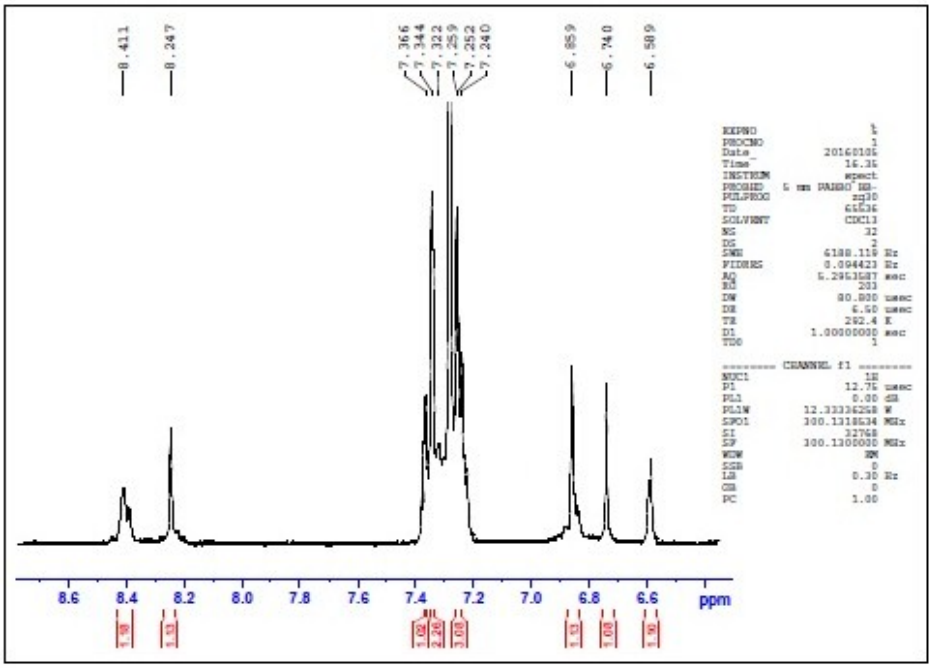


Figure S 78. ^{1}H NMR (300 MHz, $CDCl_3$) of **8e** expansion.

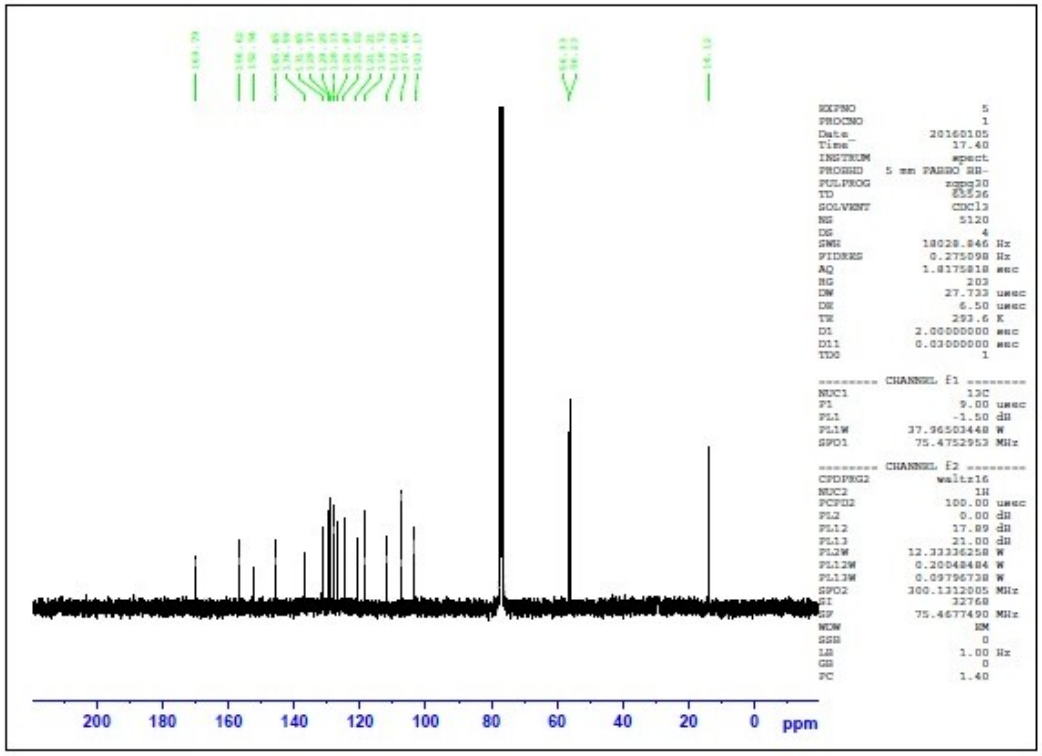


Figure S 79. ^{13}C NMR (75 MHz, $CDCl_3$) of **8e**.

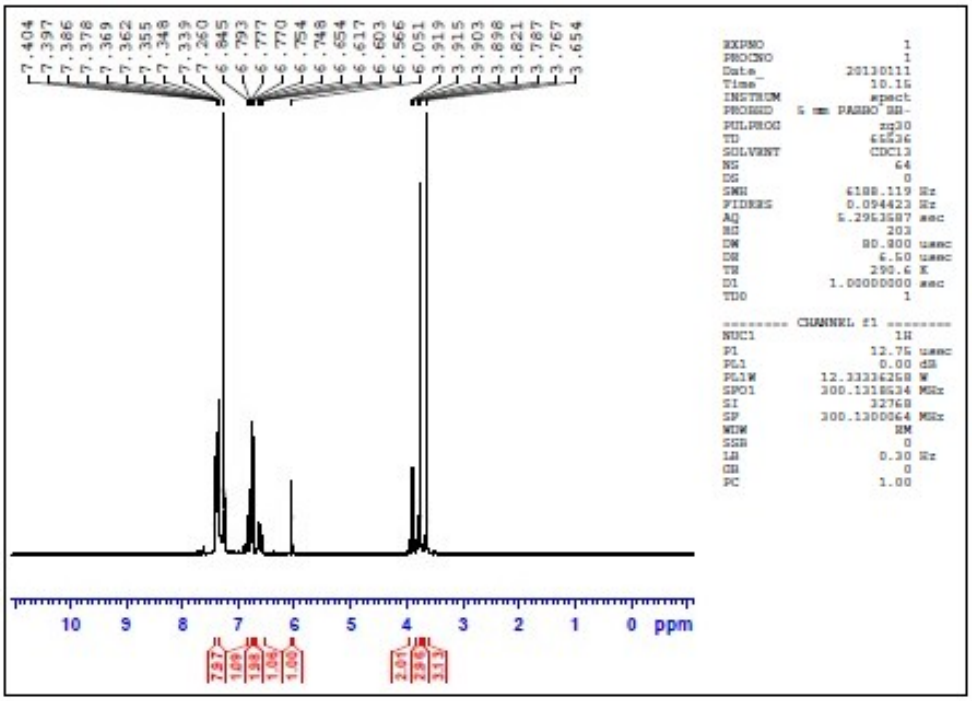


Figure S 80. ^{1}H NMR (300 MHz, $CDCl_3$) of **9a**.

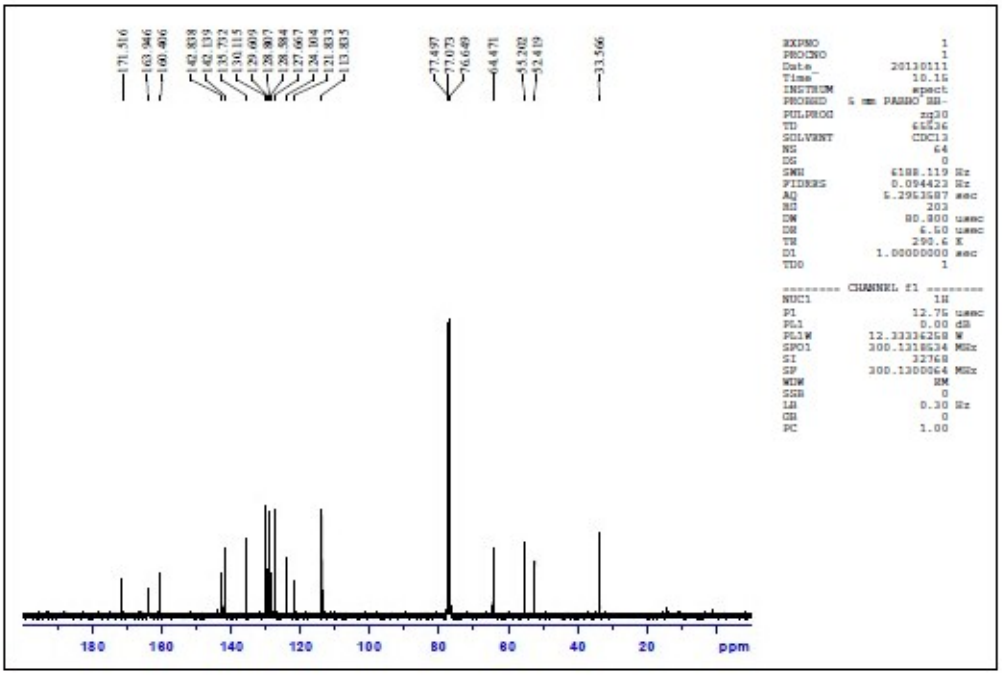


Figure S 81. ^{13}C NMR (75 MHz, $CDCl_3$) of **9a**.

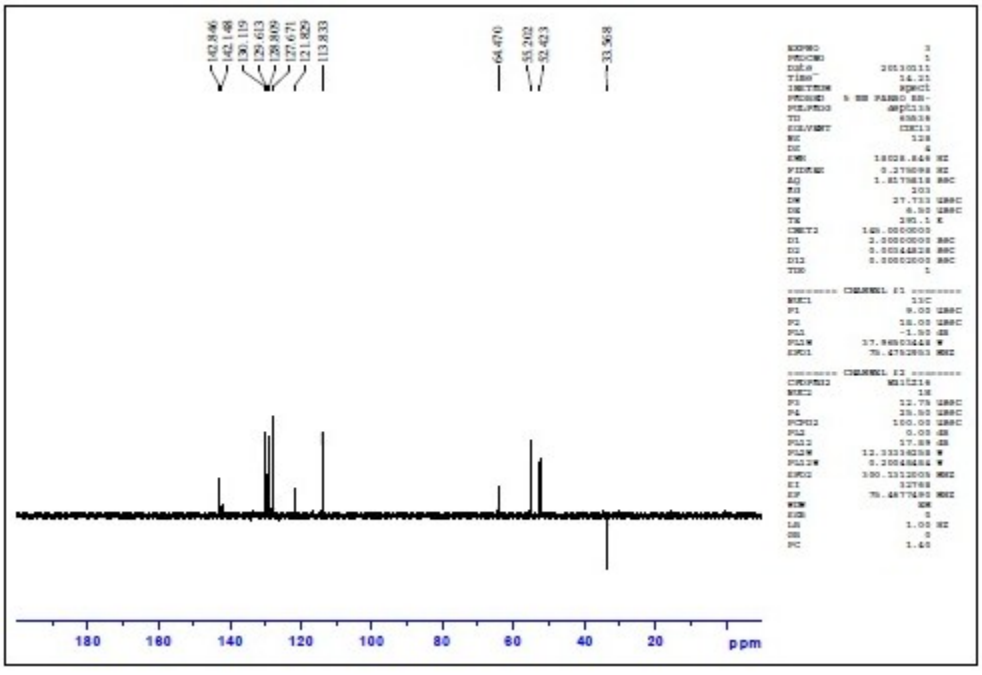


Figure S 82. DEPT NMR (75 MHz, $CDCl_3$) of **9a**.

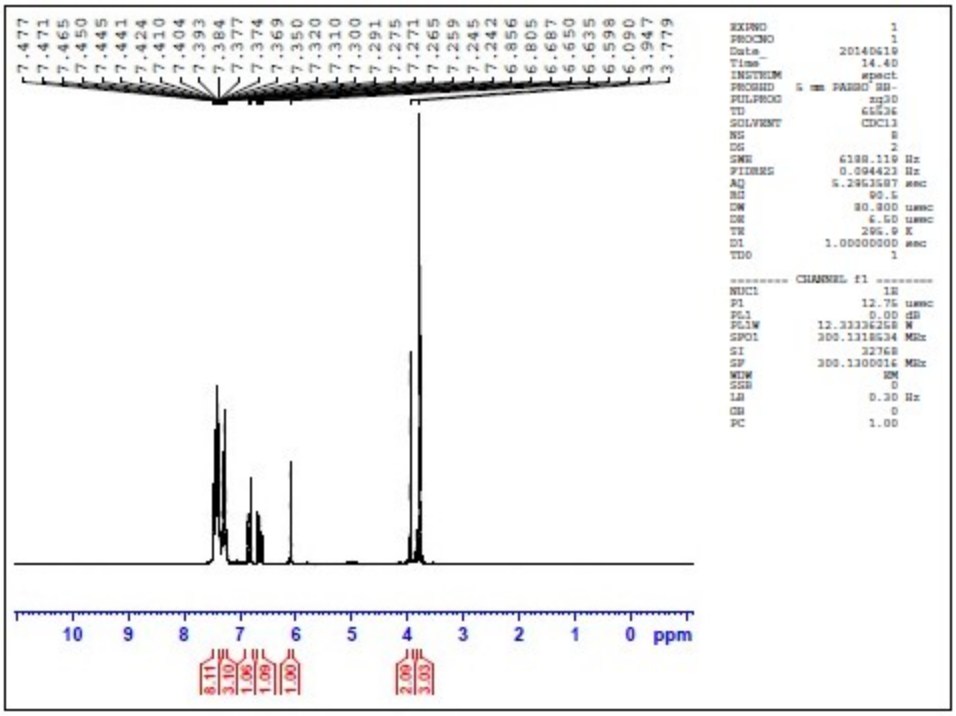


Figure S 83. ^{1}H NMR (300 MHz, $CDCl_3$) of **9b**.

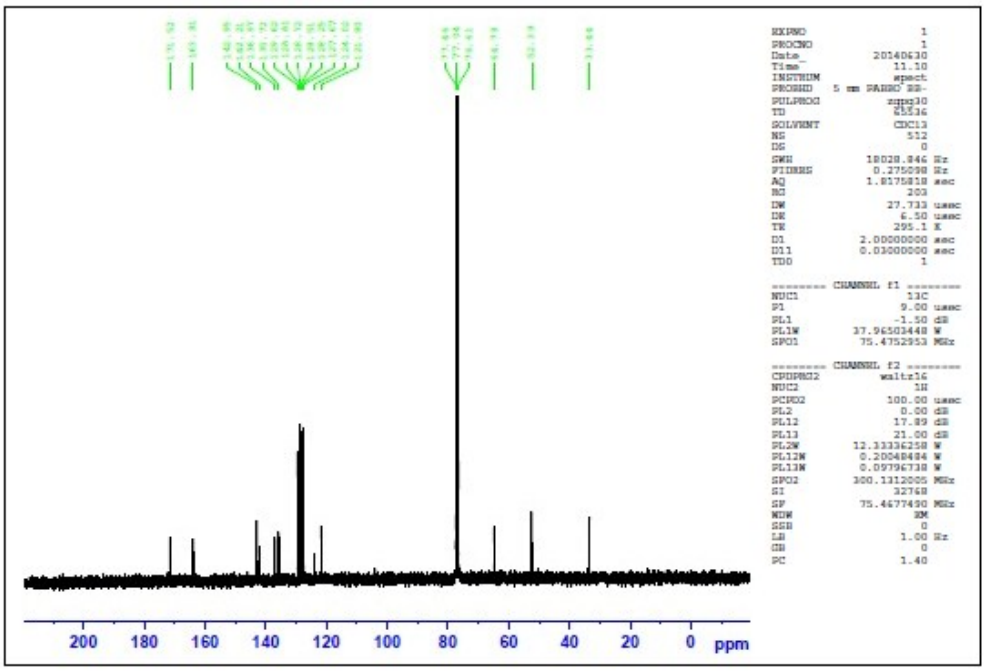


Figure S 84. ^{13}C NMR (75 MHz, $CDCl_3$) of **9b**.

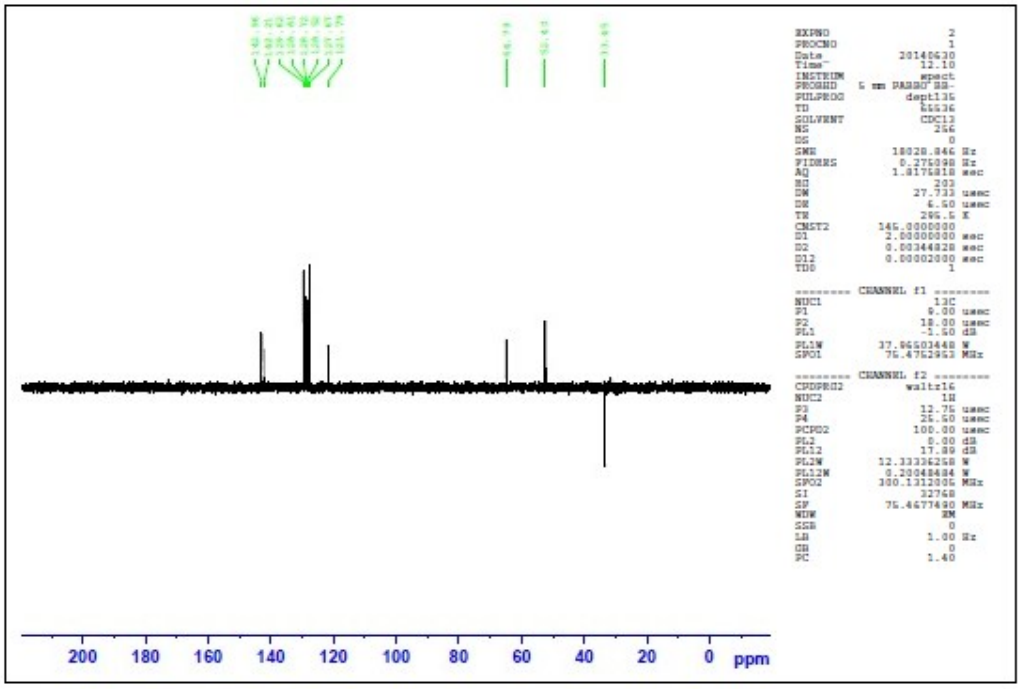


Figure S 85. DEPT NMR (75 MHz, $CDCl_3$) of **9b**.

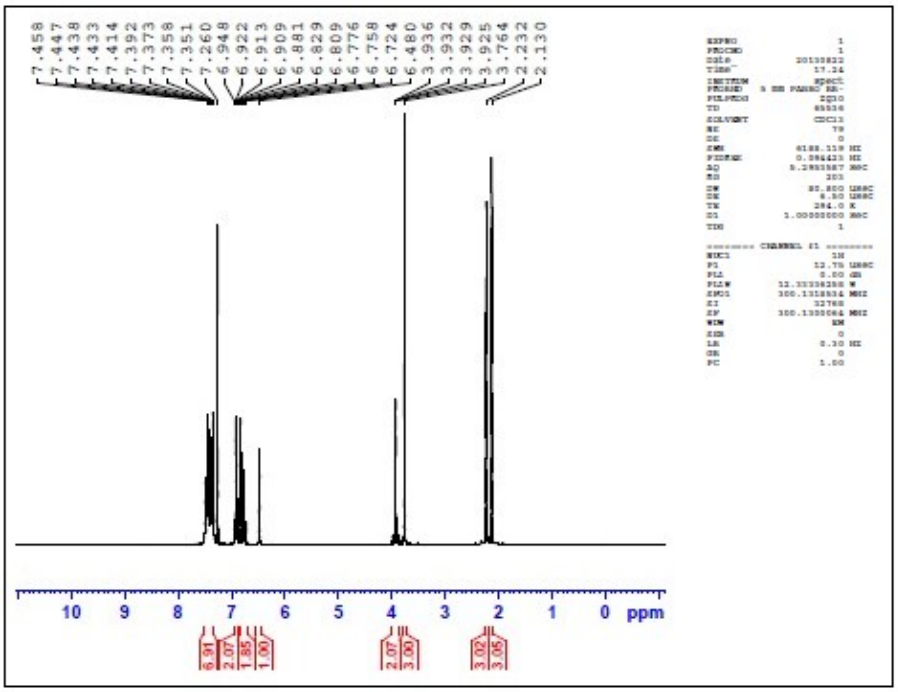


Figure S 86. ^1H NMR (300 MHz, $CDCl_3$) of **9c**.

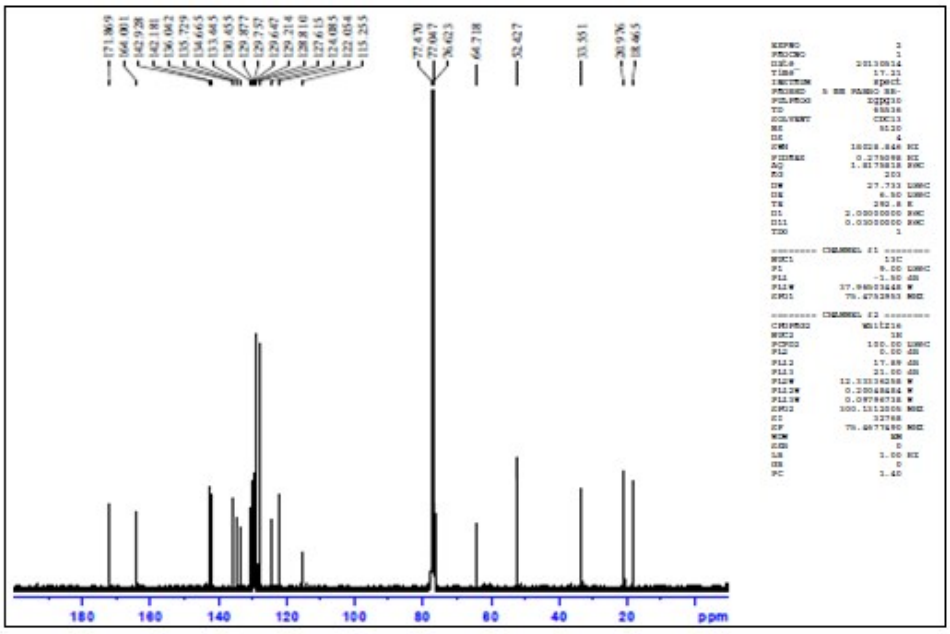


Figure S 87. ^{13}C NMR (75 MHz, $CDCl_3$) of **9c**.

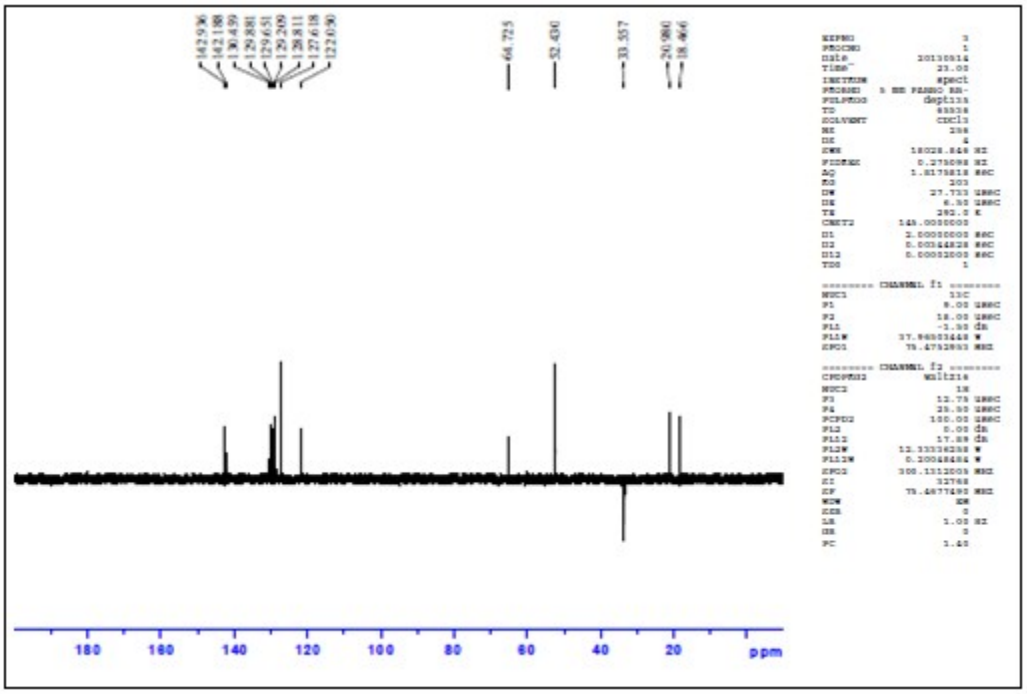


Figure S 88. DEPT NMR (75 MHz, $CDCl_3$) of **9c**.

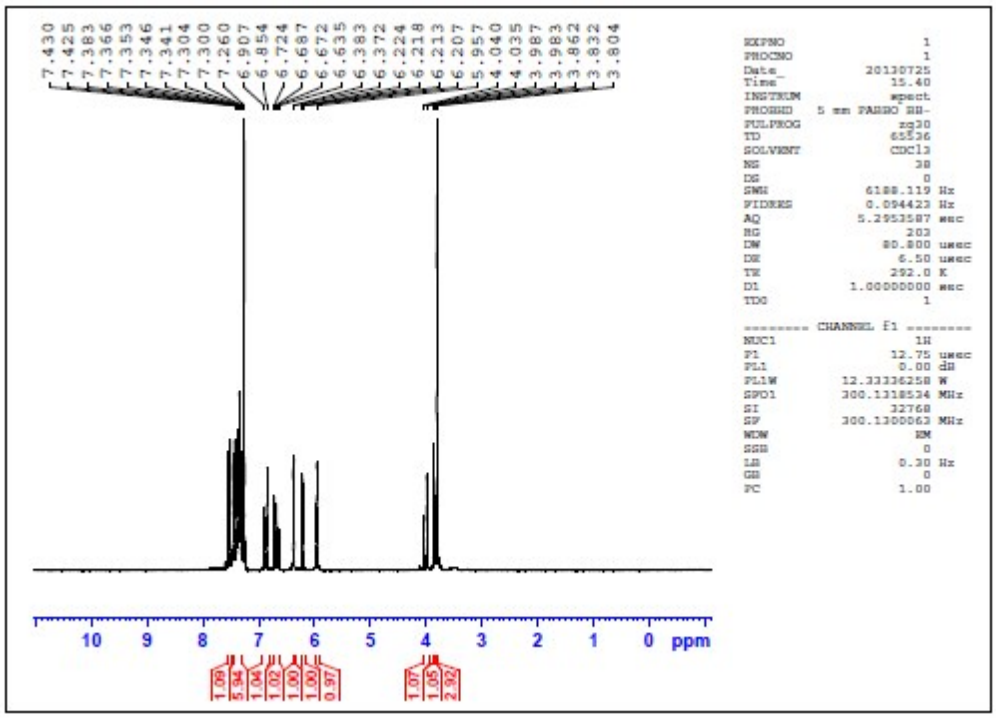


Figure S 89. ^{1}H NMR (300 MHz, $CDCl_3$) of **9d**.

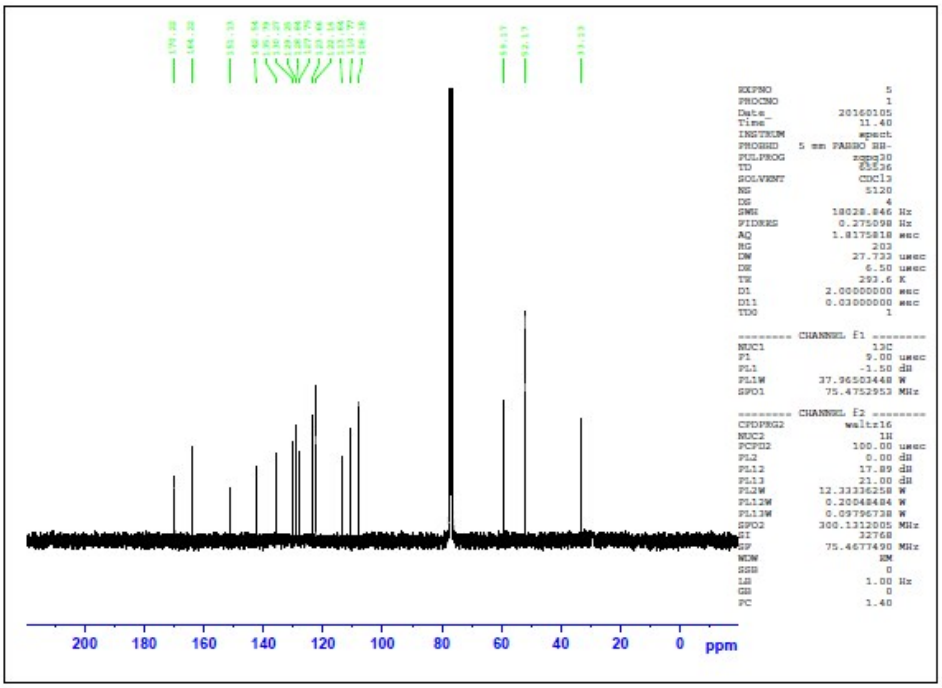


Figure S 90. ^{13}C NMR (75 MHz, $CDCl_3$) of **9d**.

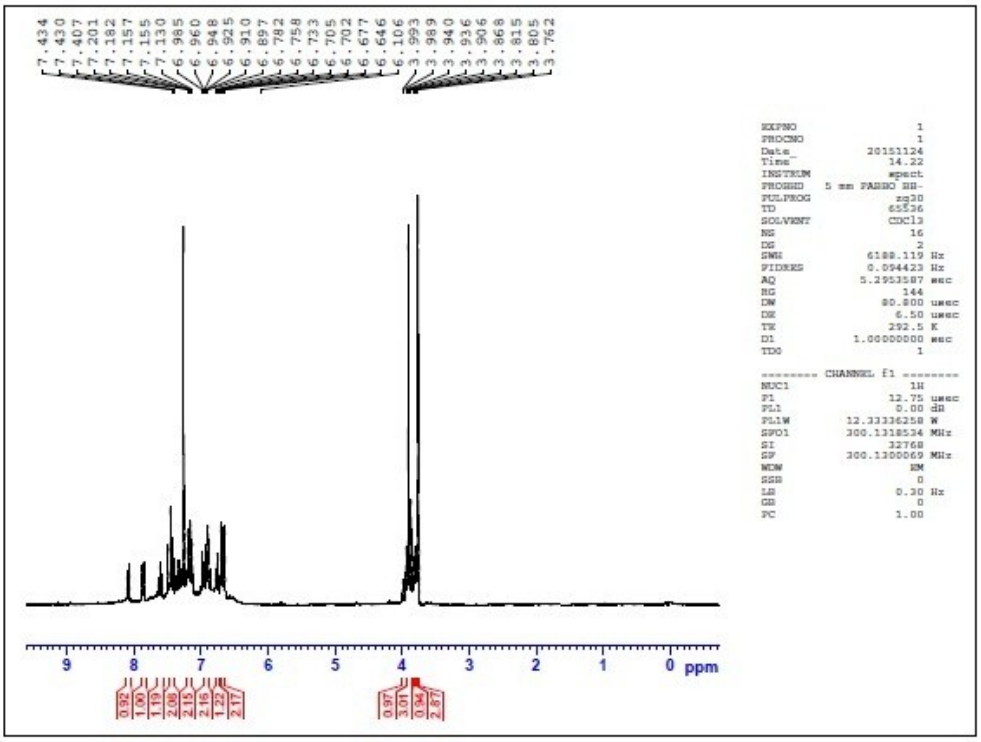


Figure S 91. ^{1}H NMR (300 MHz, $CDCl_3$) of **9e**.

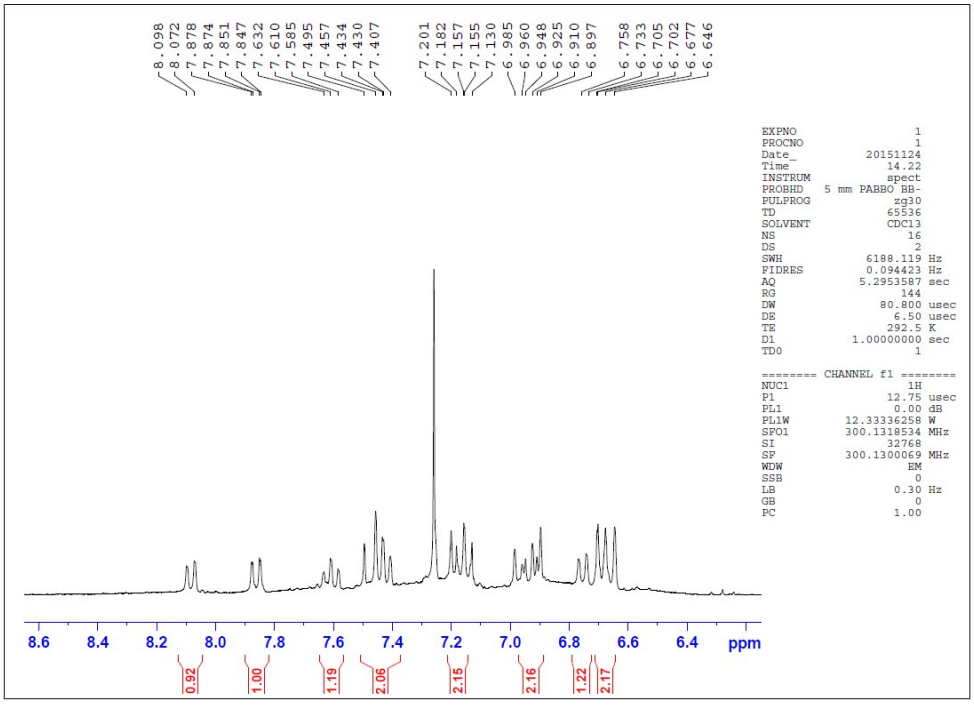


Figure S 91A. ^{1}H NMR (300 MHz, $CDCl_3$) of **9e** expansion.

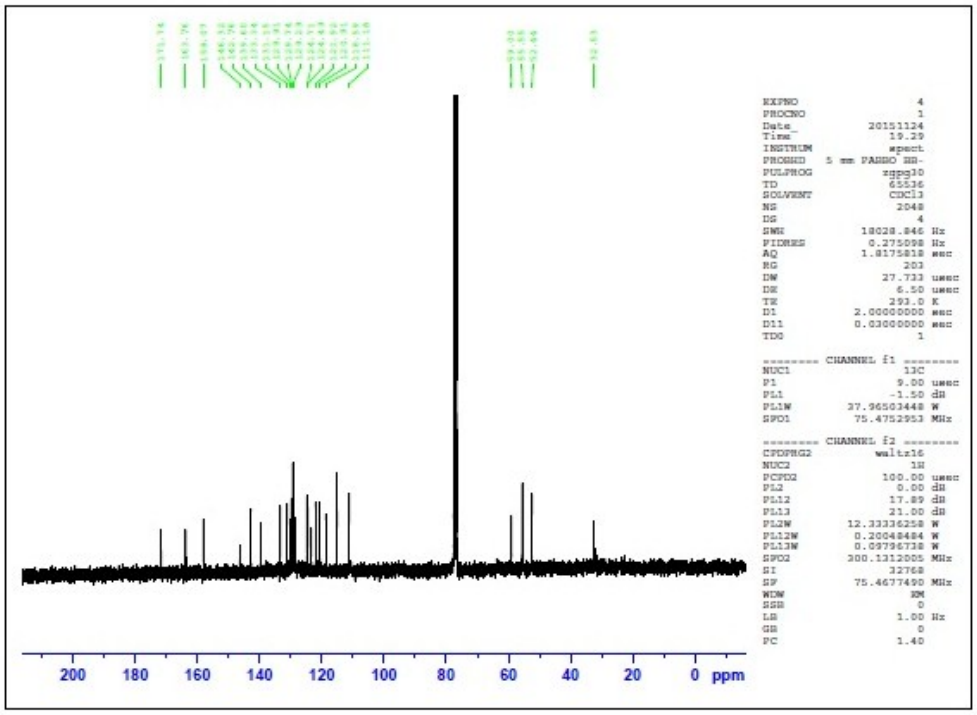


Figure S 92. ^{13}C NMR (75 MHz, $CDCl_3$) of **9e**.

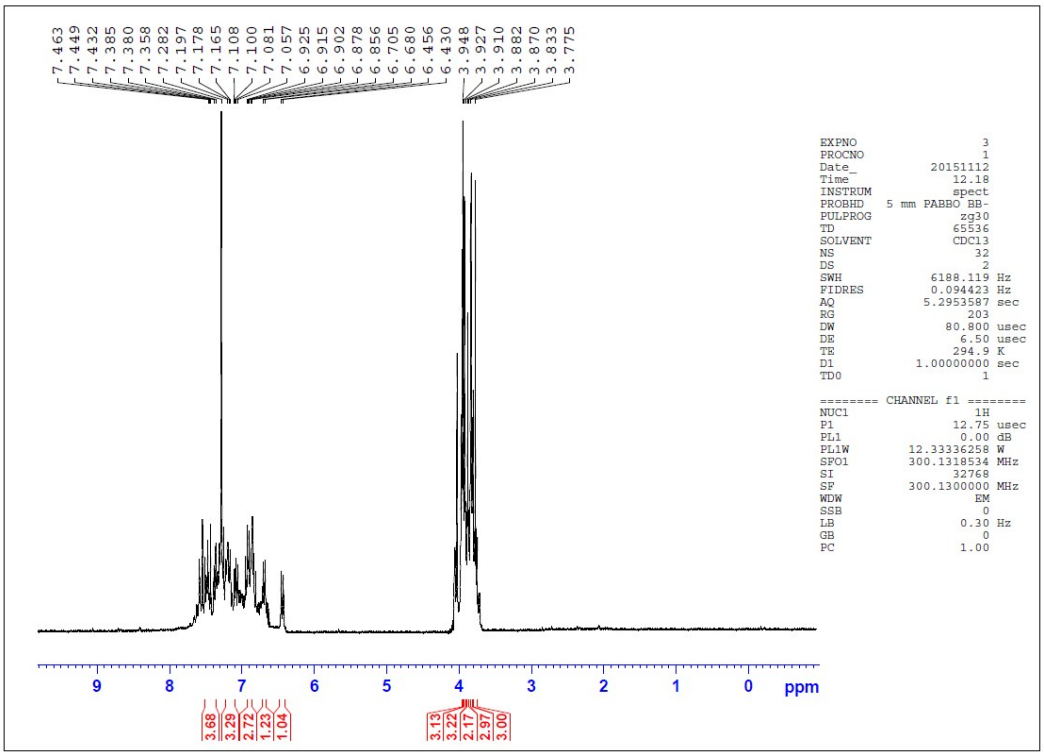


Figure S 93. ^{1}H NMR (300 MHz, $CDCl_3$) of **9f**.

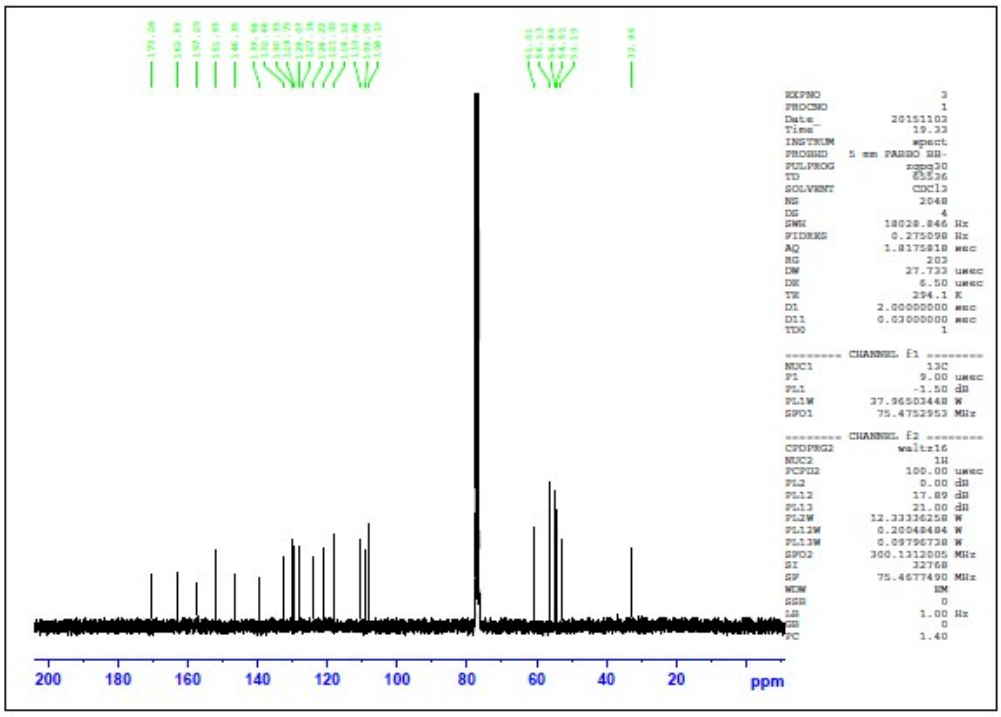


Figure S 94. ^{13}C NMR (75 MHz, $CDCl_3$) of **9f**.

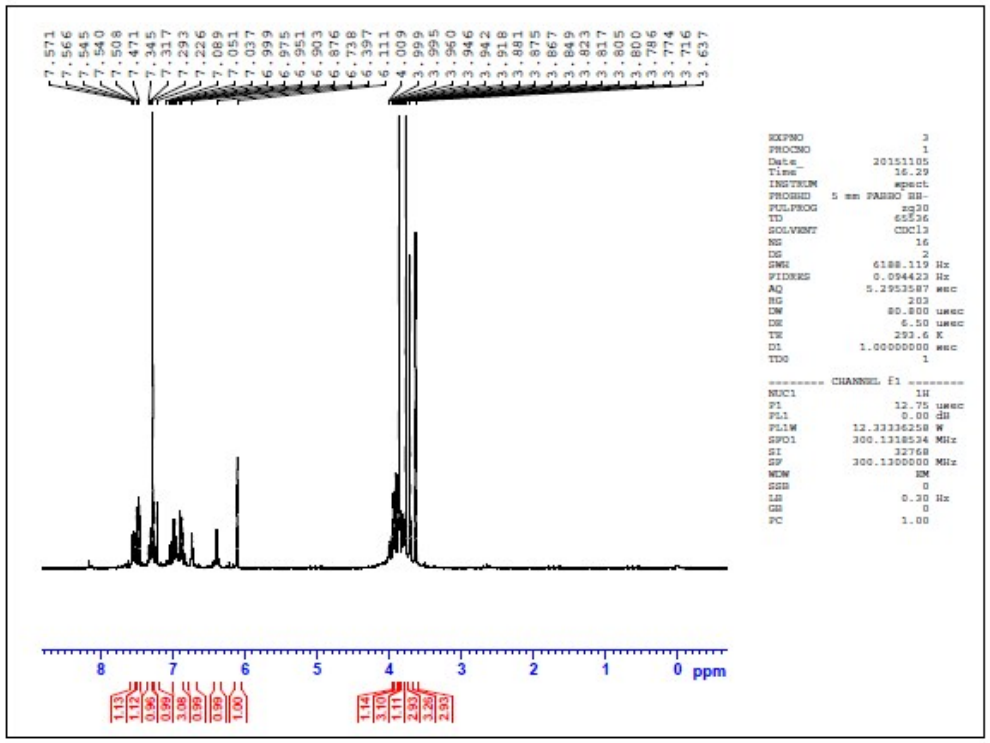


Figure S 95. ^{1}H NMR (300 MHz, $CDCl_3$) of **9g**.

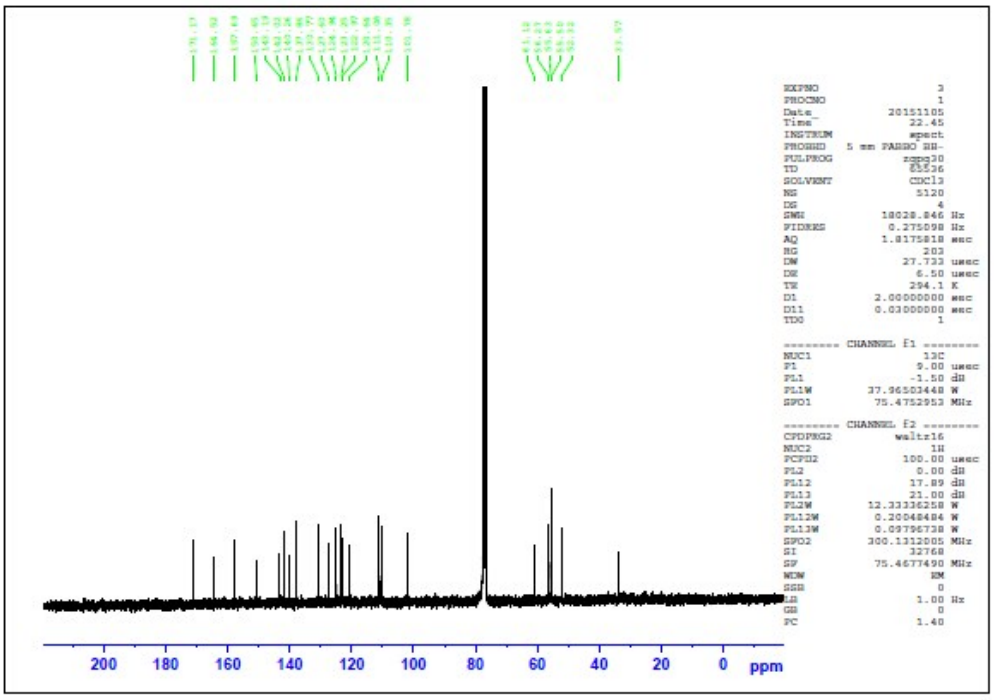


Figure S 96. ^{13}C NMR (75 MHz, $CDCl_3$) of **9g**.

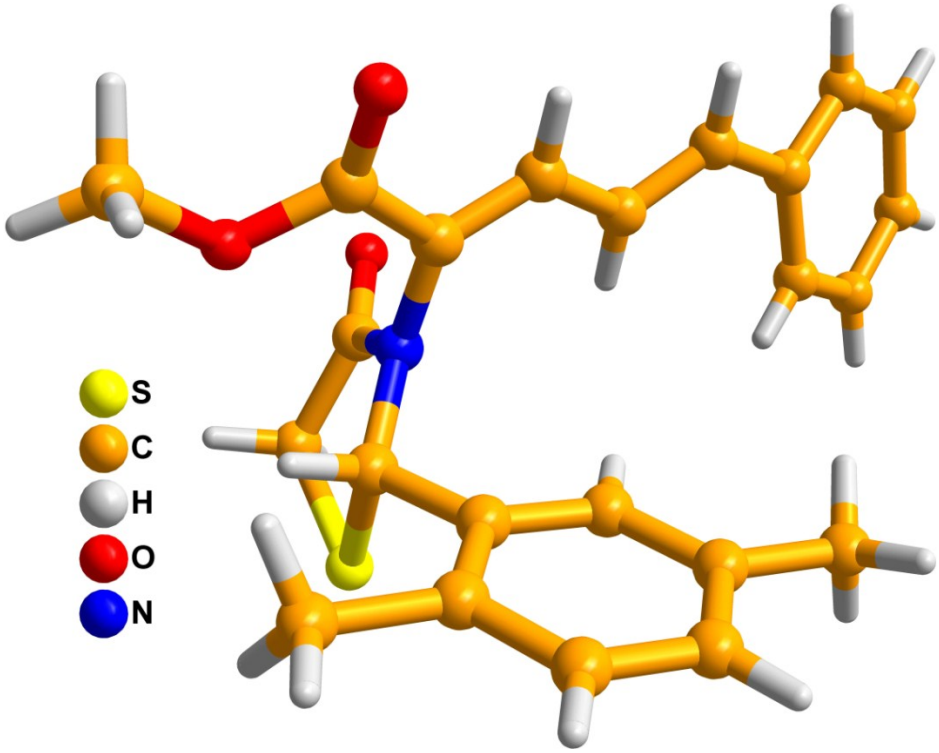


Figure S 97. Crystral structure of **9c**.

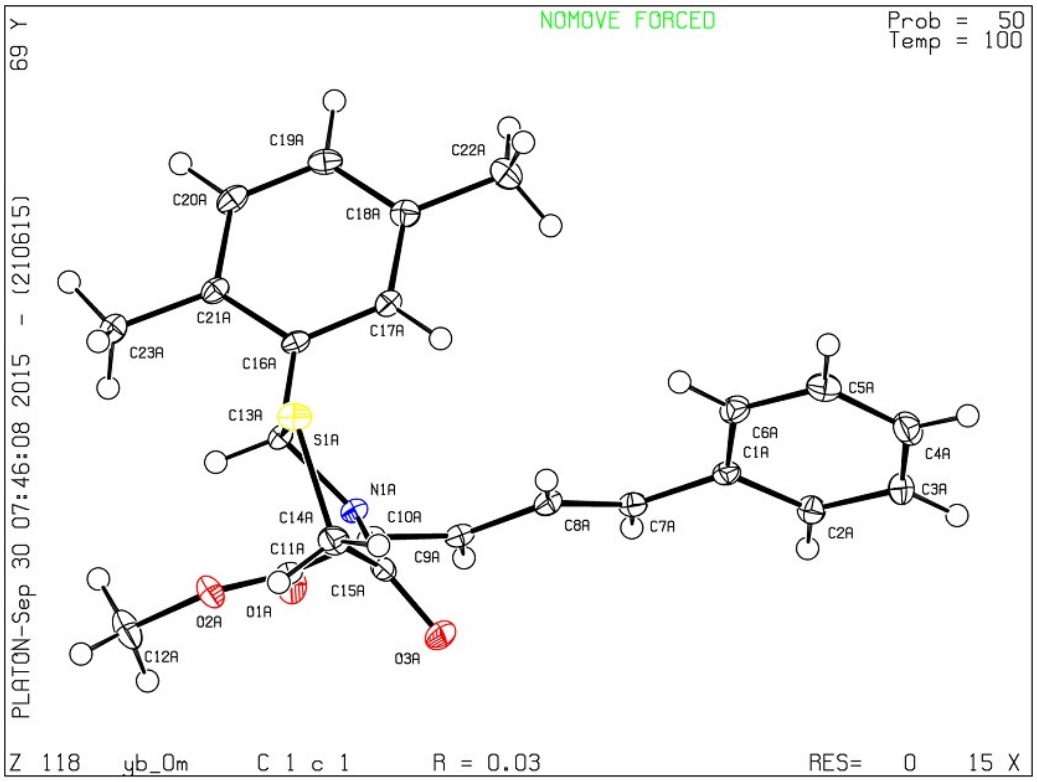


Figure S 98. X-ray crystal structure of **9c** with atom numbers **(**Ellipsoid plot).

Table S1. Crystal data and structure refinement for **9c**.

Identification code	yb_0m
Empirical formula	$C_{23}H_{23}NO_3S$
Mr	393.48
Temperature	100 K
Wavelength	0.71073 Å
Space group	C1(1)
Unit cell dimensions	a = 7.2967(5) Å alpha= 90°
	b = 18.0150(13) Å beta= 97.477()°
	c = 15.0313(11) Å gamma= 90°
Bond precision:	C-C = 0.0021 A
Volume	1959.1 (2) Å3
Dx,g cm-3	1.334
Z	4
Mu (mm-1)	0.189
F000	832.0
h, k, l max	9, 24, 20
Nref	3540
Npar	256
Tmin, Tmax	0.959 and 0.963
Absorption correction	PSI-SCAN
Data completeness	1.45/0.73

Theta(max)	28.310
R(reflections)	0.0277(3403)
wR2(reflections)	0.0704(3540)
S	1.053