Supporting Information

A facile and highly chemoselective synthesis of 1-thia-3a,6-diaza-benzo[e]azulen-3-ones by 7-*exo-dig/trig*halocyclizations

BilashKuila[a],Dinesh Mahajan[b*], PrabhpreetSingh[c] and Gaurav Bhargava[a,*]

[a]*Departmentof Applied Sciences, Punjab Technical University, Kapurthala 144603, Punjab, India*
[b]*Drug Discovery Research Centre, Translational Health Science and Technology Institute, Faridabad-121001, 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.Thin layer chromatography (TLC) was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds visualized in ultraviolate lamp.NMR spectra were recorded on a Bruker 300 MHz spectrometeroperating 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($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR; DMSO-d_6 δ = 2.50 for ^{1}H NMR and δ = 39.9 for ^{13}C NMR). Coupling constants are given in Hz and chemical shifts are reported asδ values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, m = multiplet), coupling constants (Hz), and integration. High resolutionmass spectra were recorded on a Bruker-micrOTOF-Q II mass spectrometer.

EXPERIMENTAL PROCEDURES

General procedure for the preparation of 3-allyl/propargyl-2-(2-nitrophenyl)thiazolidin-4-one 4a-d: To a solution of compound **1a** (0.5g, 3.31 mmol, 1 *equiv*.) in DCE (20 ml) was added successively allylamine (0.62 mL, 8.27 mmol, 2.5 *equiv*.) and $MgSO_4$ (3.97g, 33.11 mmol, 10 *equiv*.). The reaction mixture was heated at 55 °C for 2 hrs. Thioglycolic acid (0.36g, 3.97 mmol, 1.2 *equiv*.) was added in the reaction mixture and reaction mixture was heated at 80 °C for another 16 hrs. The progress of the reaction was monitored by *tlc* taking **1a** as the limiting reactant.After completion of reaction, the solvent was dried under reduced pressure. The crude product was purified *via* column chromatography using 20-25 % mixture ofethyl acetate in

*Corresponding author. Tel.: +91 9478098058; fax: +91-1822255504; e-mail: gaurav@ptu.ac.in (Gaurav Bhargava)

hexane as eluent. Thecompoundwasrecrystallized using methanol as solvent to get **4a**as pure compound.

3-allyl-2-(2-nitrophenyl)thiazolidin-4-one(**4a**): Yellow solid;yield: 0.80g, 92%; mp: 69-74°C;^{1}H NMR (300 MHz, $CDCl_3$): δ 3.16 (t, J = 7.5 Hz, 1H), 3.69 (t, J = 16.8 Hz, 1H), 3.74 (t, J = 15.6 Hz, 1H), 4.55 (t, J = 15.6 Hz, 1H), 5.07 (dt, J = 24, 0.6 Hz, 2H), 5.56-5.67 (m, 1H), 6.13 (d, J = 1.2 Hz, 1H), 7.33 (dd, J = 8.4, 1.2 Hz, 1H), 7.51 (dd, J = 8.4, 1.2 Hz, 1H), 7.76 (dd, J = 8.1, 1.5 Hz, 1H), 8.08 (dd, J = 8.1, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.7, 45.7, 57.9, 119.2, 125.8, 126.2, 129.3, 130.5, 134.5, 136.2, 147.0, 172.0;LRMS: 265.1 (M+1), HRMS calcd for $C_{12}H_{13}N_2O_3S$ (MH^+): 265.0647, found: 265.0645.

2-(2-nitrophenyl)-3-(prop-2-ynyl)thiazolidin-4-one(**4b**): Pale Yellow solid; yield: 0.70g, 81%; mp:117–121°C;^{1}H NMR (300 MHz, $CDCl_3$): δ2.23 (t, J= 2.7 Hz,1H), 3.48 (dd, J = 17.7, 2.1 Hz, 1H), 3.63 (t, J = 15.9 Hz, 1H), 3.73 (dd, J = 15.9,1.2 Hz, 1H), 4.63 (dd, J = 17.7, 2.7 Hz, 1H), 6.34(d, J = 1.5 Hz, 1H), 7.33 (dd, J = 7.8, 1.2 Hz, 1H), 7.54 (dd, J = 7.5, 1.2 Hz, 1H), 7.69 (dd, J = 7.5, 1.2 Hz, 1H), 8.07 (dd, J = 8.4, 1.2 Hz, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ 31.7, 32.9, 57.8, 74.2, 75.9, 125.7, 126.4, 129.5, 134.6, 135.6,147.2, 171.6;LRMS: 263.2 (M+1), HRMS calcd for $C_{12}H_{11}N_2O_3S$ (MH^+): 263.0490, found:263.0494.

3-allyl-2-(4,5-dimethoxy-2-nitrophenyl)thiazolidin-4-one(**4c**): Brown solid; yield: 0.72g, 94%; mp: 82–89°C;^{1}H NMR (300 MHz, $CDCl_3$): δ 3.20 (q, J = 18.0 Hz, 1H), 3.81 (d, J = 6 Hz, 1H), 3.88 (d, J = 6 Hz, 1H), 3.92 (s, 3H), 3.95 (s, 3H), 4.53(dq, J = 15.3, 1.5 Hz, 1H), 5.04 (dd, J = 17.1, 0.6 Hz, 1H), 5.18 (dd, J = 9.6, 0.6 Hz, 1H), 5.64-5.69 (m, 1H), 6.26 (d, J = 1.8 Hz, 1H), 6.63 (s, 1H), 7.64 (s, 1H); ^{13}C NMR (75 MHz,$CDCl_3$): δ 31.8, 45.9, 56.5, 56.6, 58.2, 107.1, 108.5, 119.4, 130.4, 130.8, 139.7, 148.7, 154.2, 172.1;LRMS: 325.1 (M+1), HRMS calcd for $C_{14}H_{17}N_2O_5S$ (MH^+): 325.0858, found: 325.0860.

2-(4,5-dimethoxy-2-nitrophenyl)-3-(prop-2-ynyl)thiazolidin-4-one(**4d**): Light brown solid;yield: 0.63g, 83%; mp: 135–139°C;^{1}H NMR (300 MHz, $CDCl_3$): δ2.23 (t, J= 2.7 Hz, 1H), 3.59-3.81 (m, 3H), 3.95 (s, 3H), 3.98 (s, 3H), 4.58 (dd, J = 17.4, 2.4 Hz, 1H), 6.50(d,J = 1.5 Hz, 1H), 6.71 (s, 1H), 7.65 (s, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ 31.8, 33.2, 56.5, 56.6, 58.3, 74.0, 76.0, 107.4, 108.4, 129.9, 140.1,148.9, 154.1, 171.8;LRMS: 322.8 (M+1), HRMS calcd for $C_{14}H_{15}N_2O_5S$ (MH^+): 323.0702, found:323.0705.

General procedure for the preparation of 3-allyl/propargyl-2-(2-aminophenyl)thiazolidin-4-one5a-d:To a solution of compound **4a** (0.2g, 0.757mmol, 1 *equiv*.) in an ethanol and water mixture (2:1) (10 ml) were added successively ironpowder (0.17g, 3.03 mmol, 4*equiv*.) and NH_4Cl (0.162g, 3.03 mmol, 4*equiv*.). The reaction mixture was heated at 60°C for 3 hrs. The progress of the reaction was monitored by *tlc*taking **4a** as the limiting reactant.After completion of reactions, the solvent was dried under reduced pressure and reaction mixture was extracted with DCM (3 X 50ml). Combined organic layers were washed with water and brine solution, dried over Na_2SO_4 and concentrated to get crude product. The crude product was purified

*via*column chromatography using 35-40 % mixture of ethyl acetate in hexane as eluent,to get **5a** as pure compounds.

3-allyl-2-(2-aminophenyl)thiazolidin-4-one(**5a**): Yellow semisolid; yield: 0.156g, 88%; ^{1}H NMR (300 MHz, DMSO-d_6): δ3.15 (dd, J = 15.6, 6.0 Hz, 1H), 3.63 (d, J = 15.6 Hz, 1H), 3.72 (d, J = 15.6 Hz, 1H), 4.24(d, J = 12.9 Hz, 1H), 5.01-5.13 (m, 2H), 5.18 (bs, 2H), 5.64-5.72 (m, 1H), 5.90 (s, 1H), 6.57 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz,DMSO-d_6): δ31.7, 45.1, 58.3, 116.4, 116.8, 118.0, 129.4, 132.3, 146.6, 171.2; LRMS: 235.2 (M+1), HRMS calcd for $C_{12}H_{15}N_2OS$ (MH^+): 235.0905, found: 235.0903.

2-(2-aminophenyl)-3-(prop-2-ynyl)thiazolidin-4-one(**5b**): Brown stickysolid;yield: 0.16g, 90%;^{1}H NMR (300 MHz, $CDCl_3$): δ2.22 (s, 1H), 3.28 (d, J = 17.4 Hz, 1H), 3.71 (s, 2H), 3.79 (bs, 2H), 4.64 (dd, J = 17.4, 2.4 Hz, 1H), 5.95 (s, 1H), 6.66-6.77 (m, 2H), 7.06-7.18 (m, 2H); ^{13}C NMR (75 MHz,$CDCl_3$): δ31.9, 32.9, 57.8,72.8, 77.6, 117.6, 118.8, 130.6, 131.1, 145.5, 170.7; LRMS: 233.1 (M+1), HRMS calcd for $C_{12}H_{13}N_2OS$ (MH^+): 233.0749, found: 233.0752.

3-allyl-2-(2-amino-4,5-dimethoxyphenyl)thiazolidin-4-one(**5c**): Brownsemi solid; yield: 0.154g, 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ3.19 (q, J = 7.8 Hz, 1H), 3.74 (d, J = 1.5 Hz, 2H), 3.79 (s, 3H), 3.84 (s, 3H), 4.43 (dd, J = 15, 4.5 Hz, 1H), 5.02 (d, J= 16.2 Hz, 1H), 5.17 (d, J= 9.6 Hz, 1H), 5.63-5.72 (m, 1H), 5.75 (s, 1H), 6.26 (s, 1H), 6.55 (s, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ33.0, 45.1, 55.8, 56.7, 102.1, 118.9,131.2, 139.8, 142.1, 150.7, 170.7;LRMS: 295.1 (M+1), HRMS calcd for $C_{14}H_{19}N_2O_3S$ (MH^+): 295.1116, found: 295.1112.

2-(2-amino-4,5-dimethoxyphenyl)-3-(prop-2-ynyl)thiazolidin-4-one(**5d**):Light brown semi solid; yield:0.156g 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ2.23 (s, 1H), 3.32 (d, J = 17.4 Hz, 1H), 3.75 (s, 2H), 3.81 (s, 3H), 3.85 (s, 3H), 4.65 (dd, J = 17.4, 2.1 Hz, 1H), 5.95 (s, 1H), 6.26 (s, 1H), 6.67 (s, 1H); ^{13}C NMR (75 MHz,$CDCl_3$): δ31.8, 33.1, 55.8, 56.6, 72.5, 77.1, 102.1,140.0, 142.2, 151.0, 170.5; LRMS: 292.9 (M+1), HRMS calcd for $C_{14}H_{17}N_2O_3S$ (MH^+): 293.096, found: 293.0957.

General procedure for the preparation of6-(halomethyl/methylene)-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-ones 6a-c and**7a-d:**To a solution of compound **5b** (0.1 g, 0.429 mmol, 1 *equiv*.) in DCM (10 ml) was added iodine (0.120g, 0.472 mmol, 1.1 *equiv*.). The reaction was stirred for 20 minutes. This was followed by addition of K_2CO_3 (0.148 g, 1.07 mmol, 2.5 *equiv*.). The solution was stirred for 2 hrs. The progress of the reaction was monitored with the help of *tlc*taking **5b** as the limiting reactant. After completion of the reaction, reaction mixture was diluted with DCM and washed with $Na_2S_2O_3$and water solution followed by brine solution. The organic layer was dried over anhydrous Na_2SO_4 and solvent was evaporated. The crude productobtained after evaporation was purified *via*silica gel column chromatography using 25-30% mixture of ethyl acetate in hexane as eluent, to **7a** as pure compound.

6-(iodomethyl)-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**6a**): Light brownsemi solid; yield:0.130g 84%;^{1}H NMR (300 MHz,$CDCl_3$): δ2.95 (d, J= 9.6 Hz, 1H), 3.01-3.19 (m, 1H), 3.35-3.47 (m, 4H), 4.30-4.35 (t,J = 3.6 Hz, 1H), 5.66 (s, 1H), 7.01- 7.09 (m, 2H), 7.19-7.26 (m, 2H),7.80(d,J= 7.5 Hz, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ 8.7, 31.9, 48.5, 56.8, 64.0,122.4, 123.6, 128.3, 129.3, 129.6, 142.9, 171.2; LRMS: 361.0 (M+1), HRMS calcd for $C_{12}H_{14}IN_2OS$ (MH^+): 360.9872, found: 360.9869.

6-(bromomethyl)-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**6b**): Brownsticky solid; yield:0.092g 69%;^{1}H NMR (300 MHz,$CDCl_3$): δ2.94-2.99 (m, 1H), 3.63-3.74 (m, 4H), 4.05-4.09 (m, 1H), 4.56-4.61 (m, 1H), 6.10 (s, 1H), 6.70-6.80 (m, 1H), 7.15-7.17 (m, 2H), 7.26-7.29 (m, 2H);^{13}C NMR (75 MHz,$CDCl_3$): δ29.1, 33.5, 48.2, 53.5, 60.4, 110.7, 117.7, 119.1, 119.6, 133.5, 144.3, 171.6 ; LRMS: 313.0 (M+1), HRMS calcd for $C_{12}H_{14}BrN_2OS$ (MH^+): 313.0010, found: 313.0014.

6-(iodomethyl)-9,10-dimethoxy-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**6c**): Light brownsemisolid;yield:0.114g,80%;^{1}H NMR (300 MHz,$CDCl_3$): δ 3.23-3.31 (m, 2H),3.70-3.74 (m, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 4.39-4.45 (m,1H),5.08-5.18 (m, 1H), 6.22 (s, 1H), 6.56 (s, 1H), 6.81(s, 1H), 8.34 (s, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ8.9, 32.7, 49.5, 56.5, 56.8, 57.3, 63.1,103.1, 113.1, 117.3, 135.1, 142.9, 151.2, 171.1; LRMS: 421.0 (M+1), HRMS calcd for $C_{14}H_{18}IN_2O_3S$ (MH^+): 421.0083, found: 421.0079.

6-(iodomethylene)-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**7a**): Pale yellow solid; yield: 0.131g, 86%; mp: 140–144 ^{o}C;^{1}H NMR (300 MHz,$CDCl_3$): δ 3.73-3.80 (m, 2H), 3.89 (dd, J = 15.6, 1.2 Hz, 1H), 4.03 (bs, 1H), 4.67 (dd, J = 15.6, 1.2 Hz, 1H), 5.79 (s, 1H), 6.71- 6.81 (m, 2H), 7.02 (dd, J = 7.5, 1.2 Hz,1H), 7.14 (s, 1H), 7.15-7.21 (m, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ33.1, 52.8, 56.7, 83.9, 96.8, 117.9,119.3, 130.6, 142.1, 145.6, 171.1 ; LRMS: 358.8 (M+1), HRMS calcd for $C_{12}H_{12}IN_2OS$ (MH^+): 358.9715, found: 358.9715.

6-(bromomethylene)-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**7b**): Yellow solid;yield: 0.093g, 70%; mp: 159–164^{o}C;^{1}H NMR (300 MHz,$CDCl_3$): δ3.69-3.85 (m, 2H), 3.87 (d, J = 14.1 Hz, 1H),3.95 (bs, 1H), 4.69 (d,J = 15.3 Hz, 1H), 5.65 (s, 1H), 6.57-6.63(m, 2H), 7.10 (d, J = 1.8 Hz,1H), 7.22-7.26 (m, 2H); ^{13}C NMR (75 MHz,$CDCl_3$): δ32.7, 45.8, 57.4, 82.6, 92.2, 107.8, 117.7, 119.3, 119.6, 133.3, 144.8, 171.1 ; LRMS: 311.1 (M+1), HRMS calcd for $C_{12}H_{12}BrN_2OS$ (MH^+): 310.9854, found: 310.9851.

6-(iodomethylene)-9,10-dimethoxy-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**7c**): Brown sticky solid;yield:0.117g, 82%;^{1}H NMR ($CDCl_3$): δ 3.72-3.83 (m, 2H), 3.84 (s, 3H), 3.88 (s, 3H), 3.89-3.92 (m, 2H), 4.62 (dd, J = 15, 4.5 Hz, 1H), 5.72 (s, 1H), 6.27 (s, 1H), 6.52 (s, 1H), 7.14 (s, 1H);^{13}C NMR ($CDCl_3$): δ33.3, 52.7, 55.9, 56.0, 56.8, 84.1, 97.1, 102.4, 114.0, 116.3, 137.4, 142.5, 151.1, 171.0; LRMS: 419.1 (M+1), HRMS calcd for $C_{14}H_{16}IN_2O_3S$ (MH^+): 418.9926, found: 418.9929.

6-(bromomethylene)-9,10-dimethoxy-5,6,7,11b-tetrahydrobenzo[f]thiazolo[3,2-d][1,4]diazepin-3(2H)-one (**7d**): Yellow solid;yield: 0.086g, 68%; mp: 171–175°C;^{1}H NMR (300 MHz,$CDCl_3$): δ 3.70-3.78 (m, 2H), 3.85 (s, 3H), 3.89(s, 3H), 4.07-4.14 (m, 1H), 4.40 (bs, 1H), 4.85-4.99 (m, 1H), 5.75 (s, 1H), 6.26 (s, 1H), 6.56 (s, 1H), 6.96 (s, 1H);^{13}C NMR (75 MHz,$CDCl_3$): δ34.1, 53.3, 56.1, 56.3, 56.9,83.6, 89.2102.6,111.3, 117.3, 137.3, 142.5, 150.6, 170.3; LRMS: 371.0 (M+1), HRMS calcd for $C_{14}H_{16}BrN_2O_3S$ (MH^+): 371.0065, found: 371.0063.

Characterization data:

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

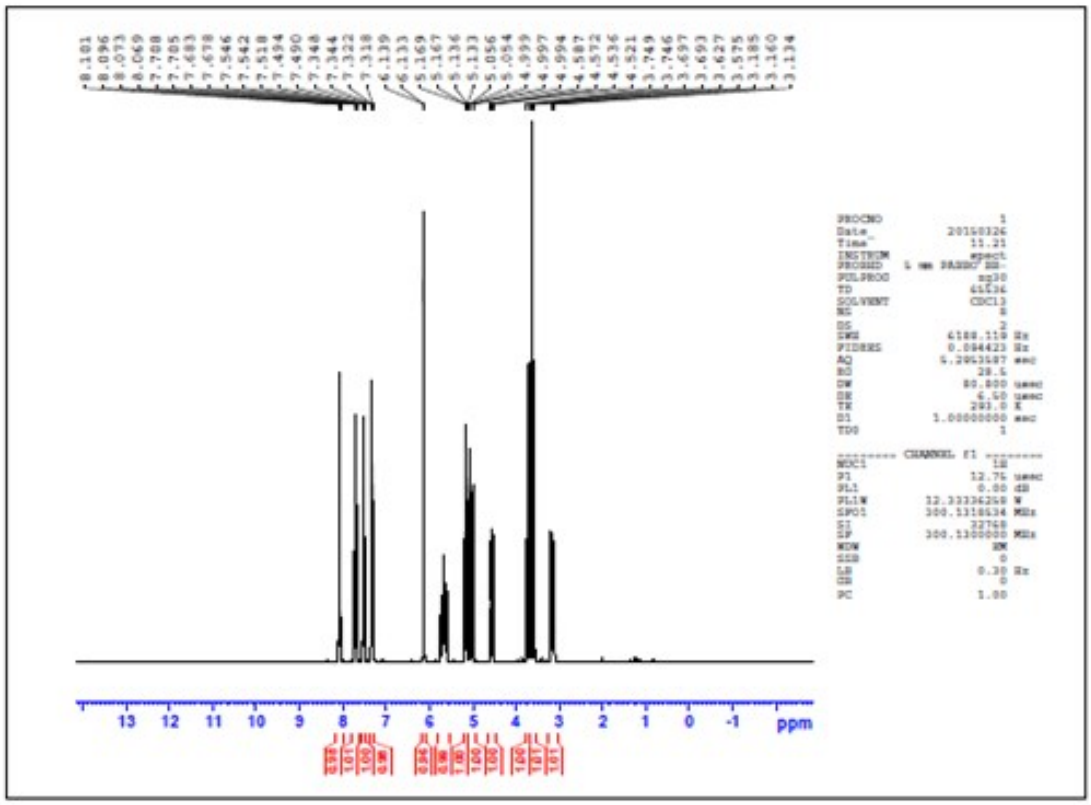

Figure S 1. ^{1}H NMR (300 MHz, $CDCl_3$) of **4a**.

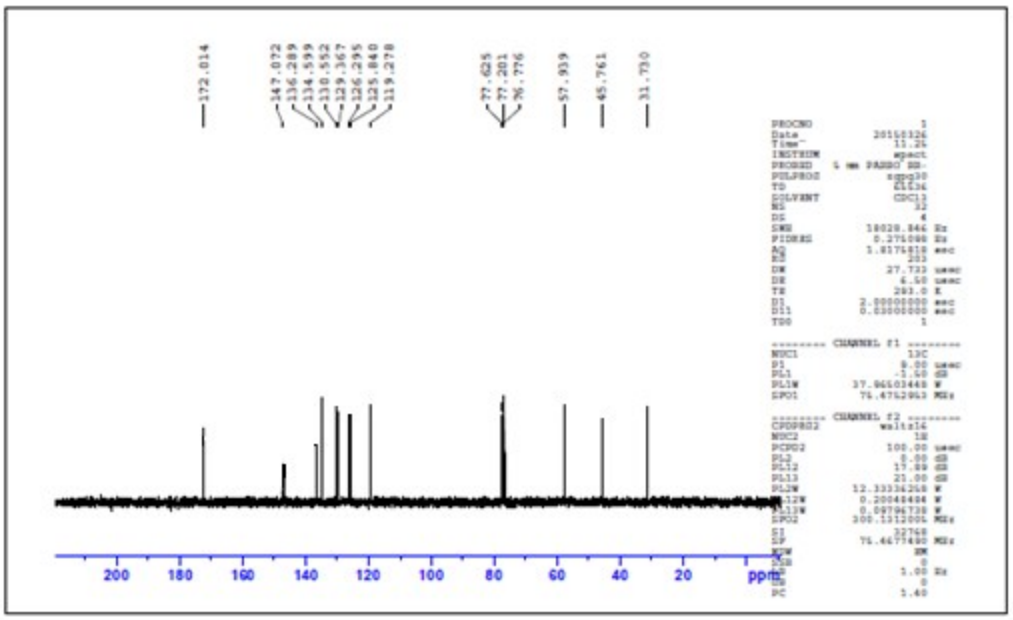

Figure S 2.[13]C NMR (75 MHz, $CDCl_3$) of **4a**.

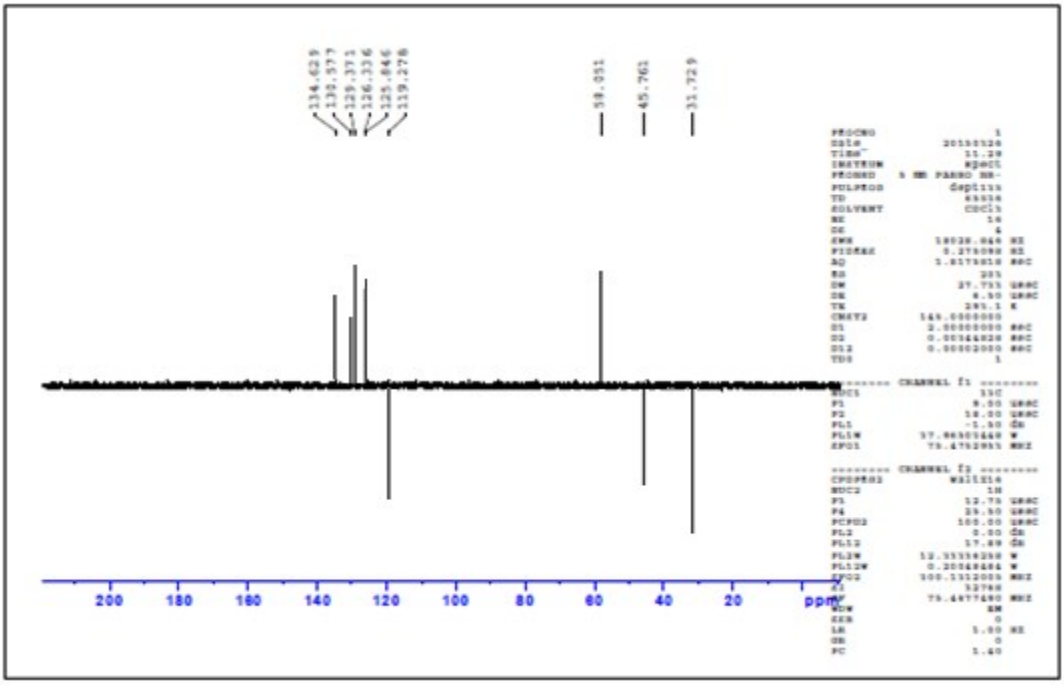

Figure S 3. DEPTNMR (75 MHz, $CDCl_3$) of **4a**.

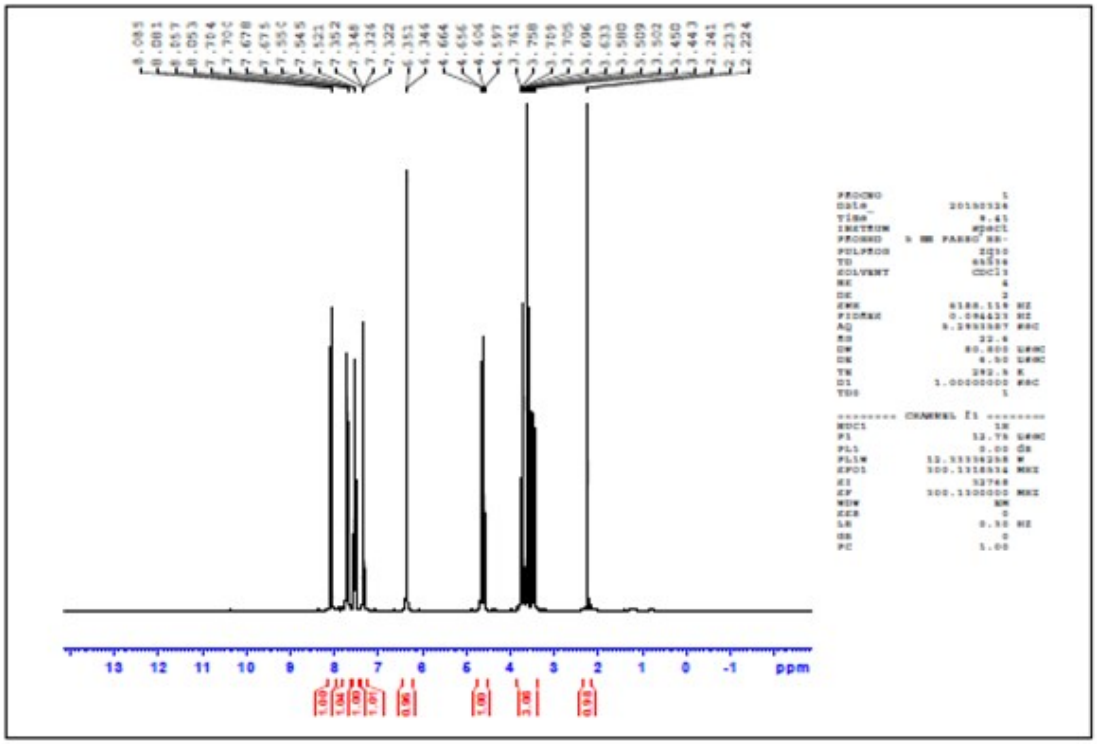

Figure S 4.[1]HNMR (300 MHz, $CDCl_3$) of **4b**.

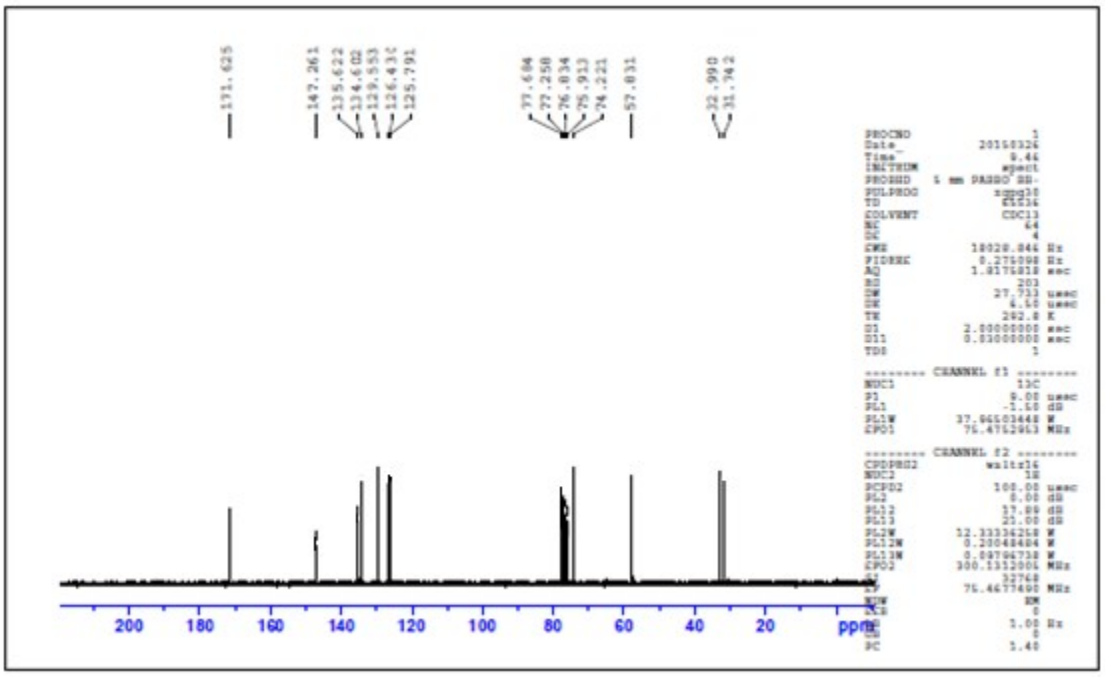

Figure S 5.[13]CNMR (75 MHz, $CDCl_3$) of **4b**.

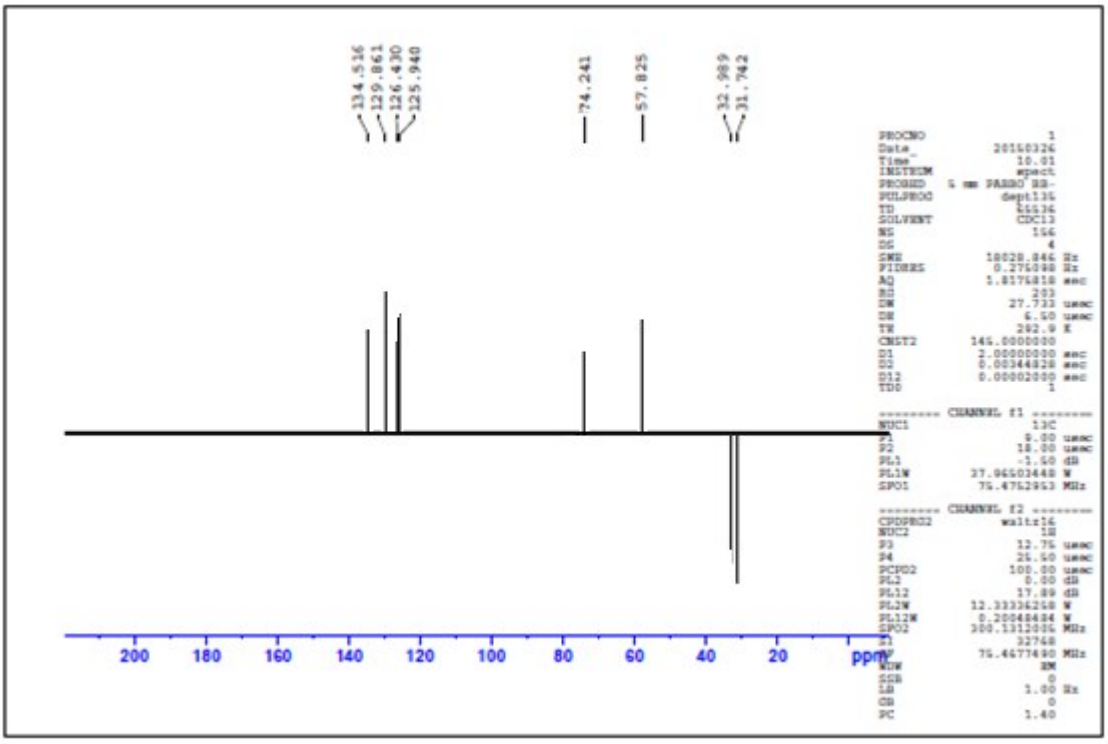

Figure S 6. DEPTNMR (75 MHz, $CDCl_3$) of **4b**.

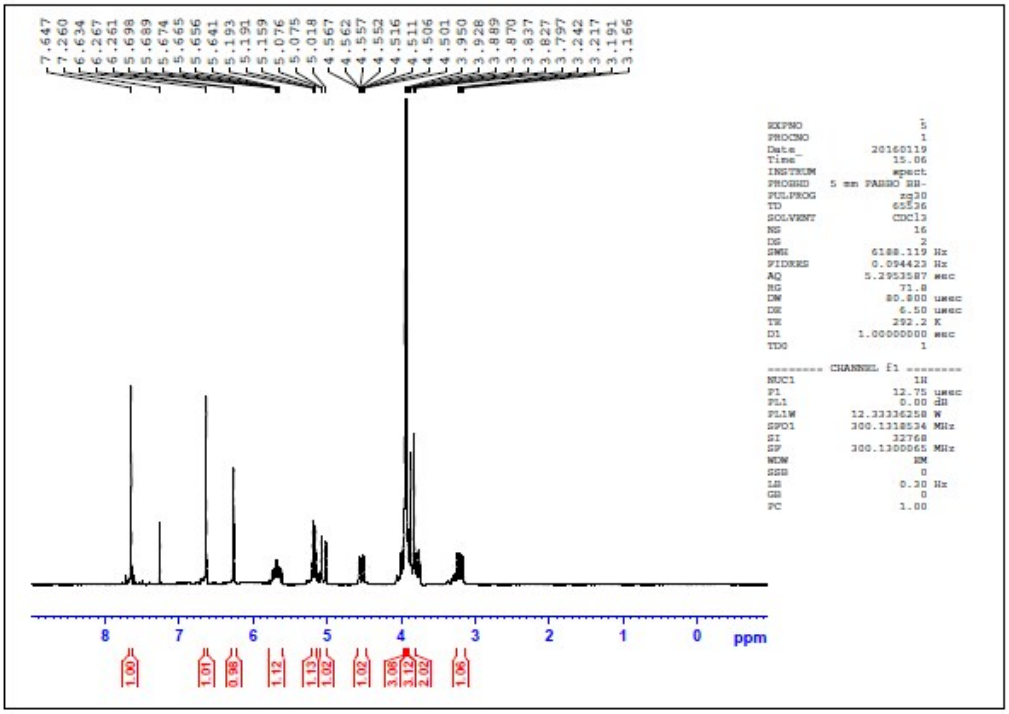

Figure S 7.[1]H NMR (300 MHz, $CDCl_3$) of **4c**.

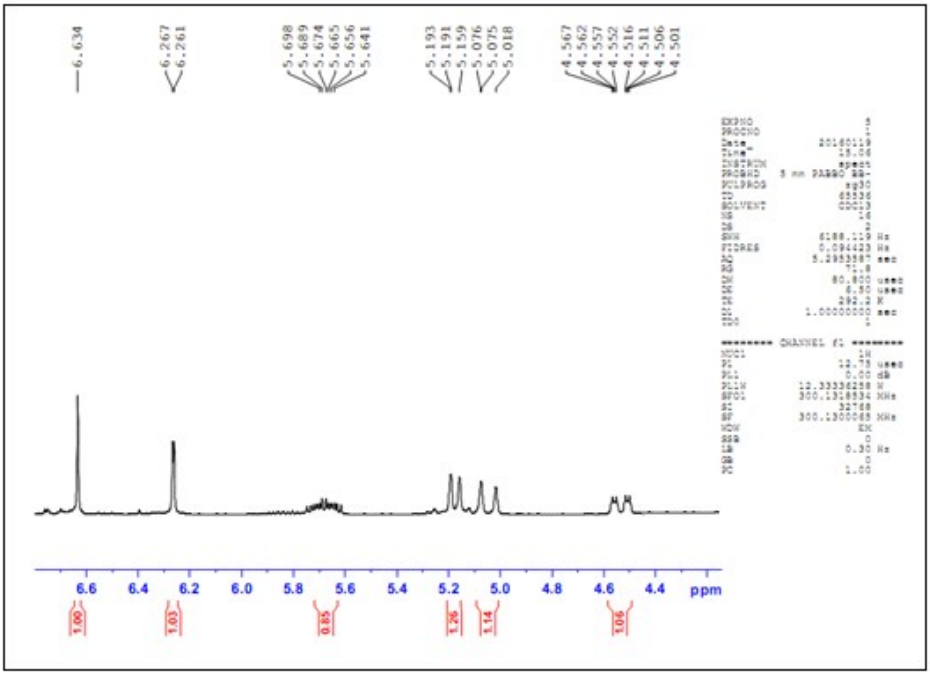

Figure S 8.[1]HNMR (300 MHz, $CDCl_3$) of **4c**expansion.

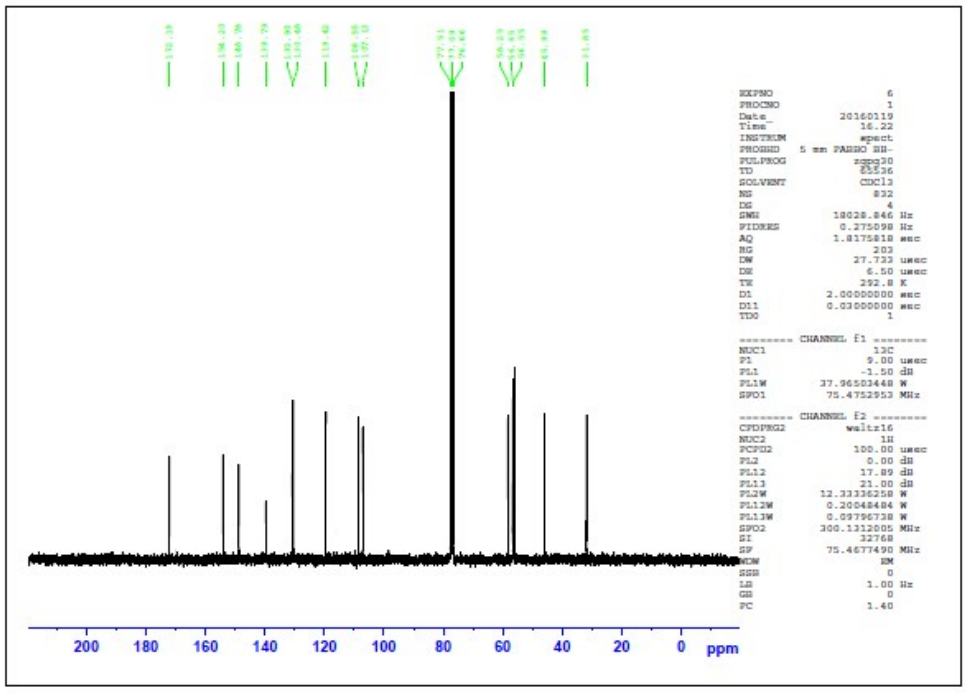

Figure S 9.[13]CNMR (75 MHz, $CDCl_3$) of **4c**.

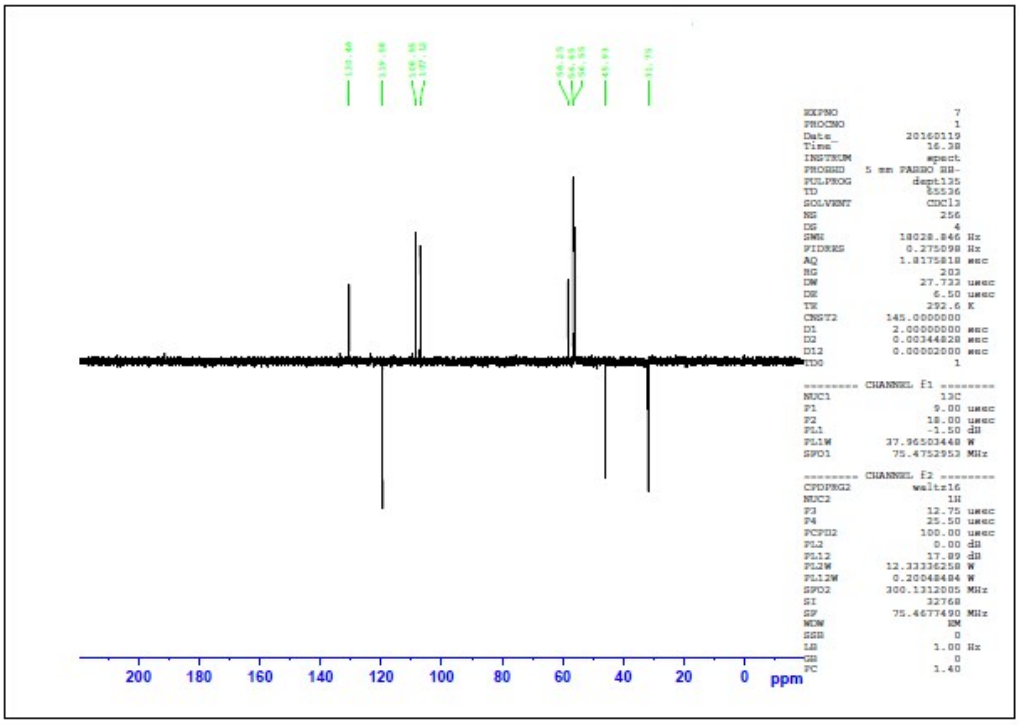

Figure S 10. DEPTNMR (75 MHz, $CDCl_3$) of **4c**.

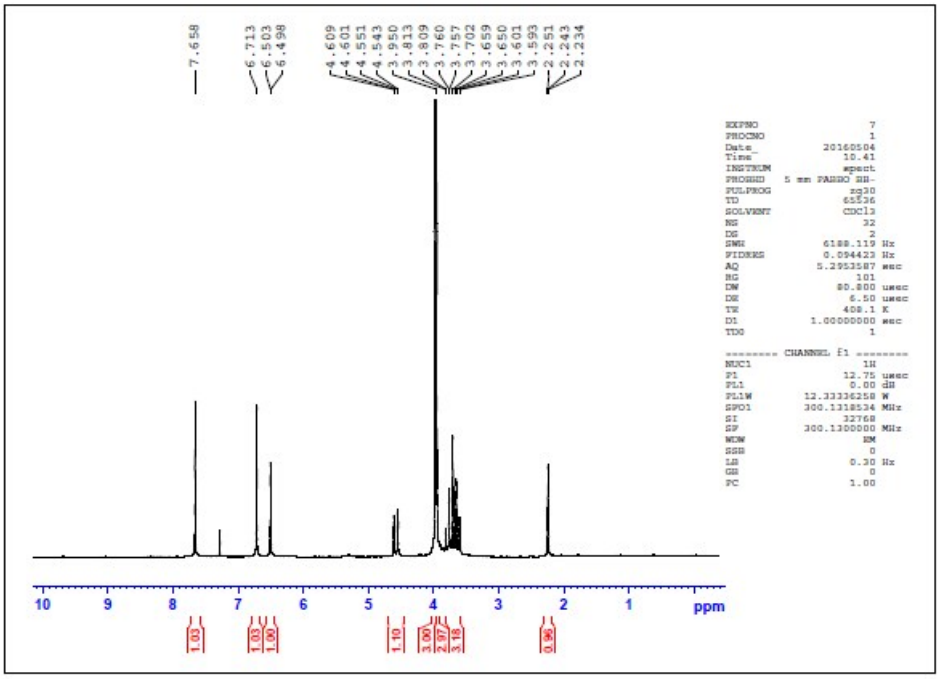

Figure S 11. ^{1}HNMR (300 MHz, $CDCl_3$) of **4d.**

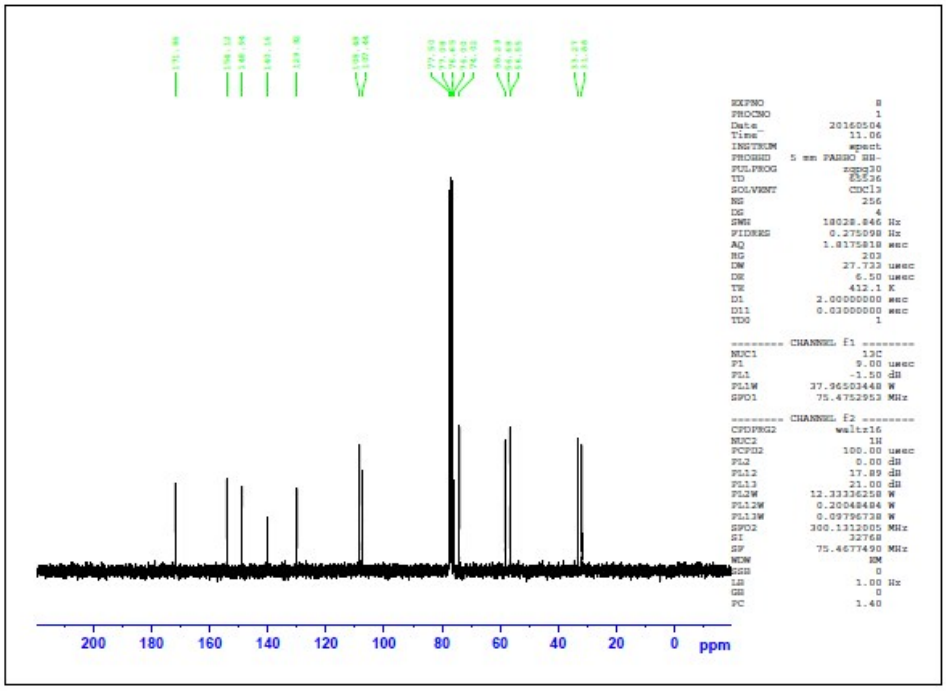

Figure S 12.[13]C NMR (75 MHz, $CDCl_3$) of **4d**.

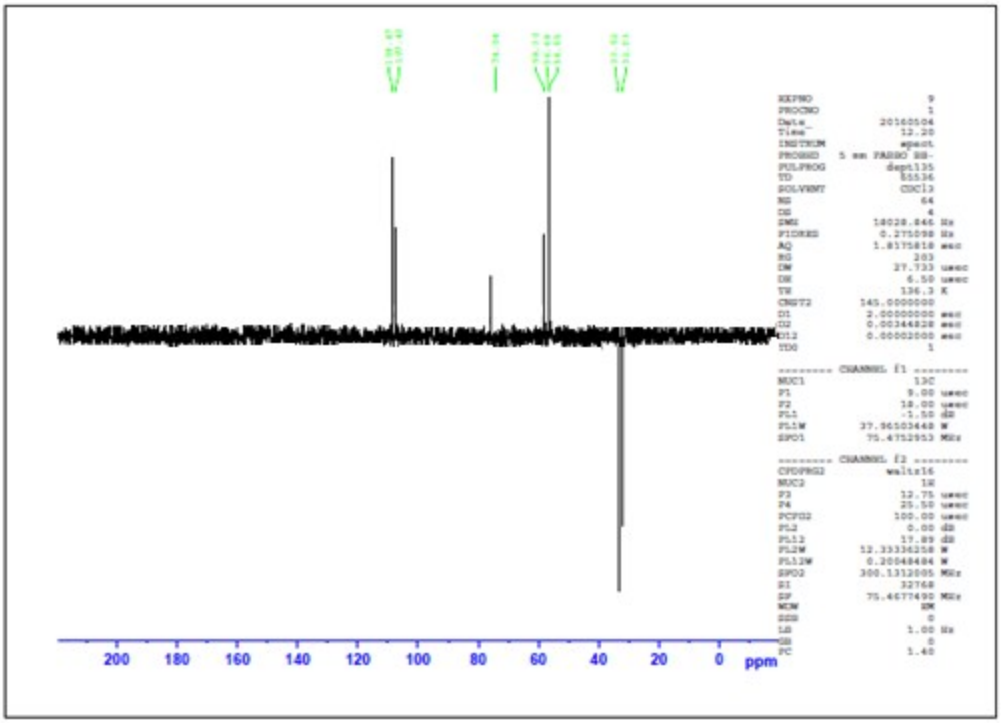

Figure S 13. DEPTNMR (75 MHz, $CDCl_3$) of **4d**.

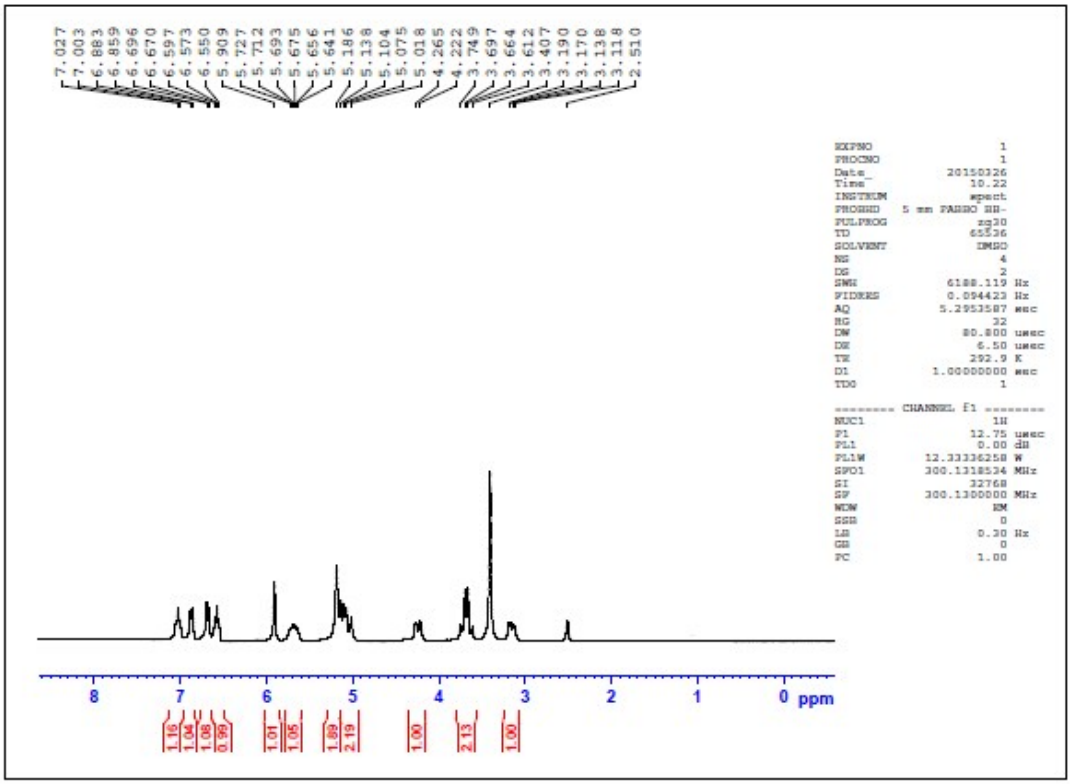

Figure S 14. ^{1}H NMR (300 MHz, $CDCl_3$) of **5a**.

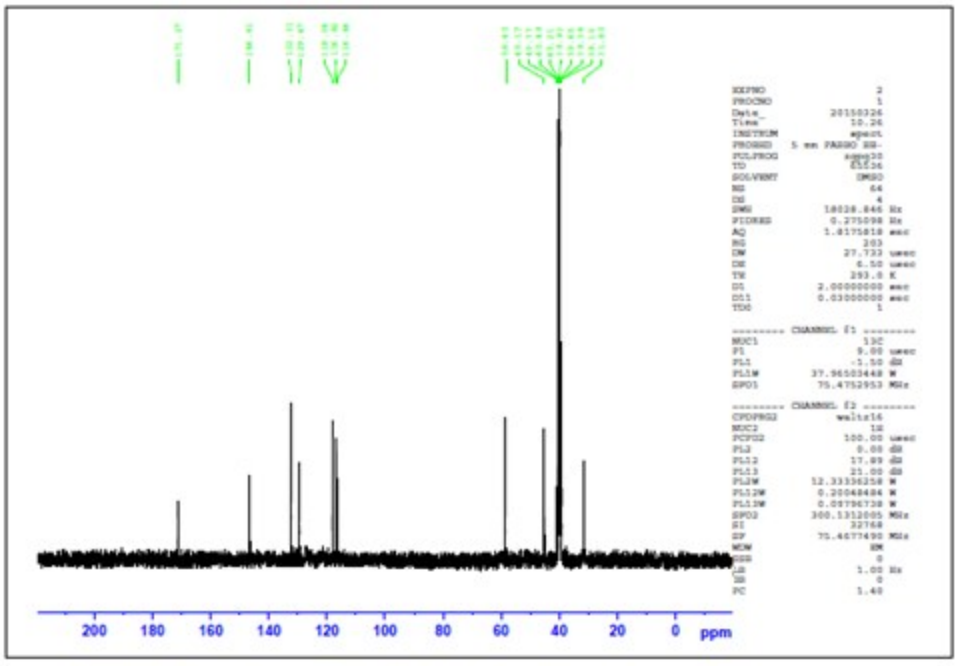

Figure S 15.^{13}C NMR (75 MHz, $CDCl_3$) of **5a**.

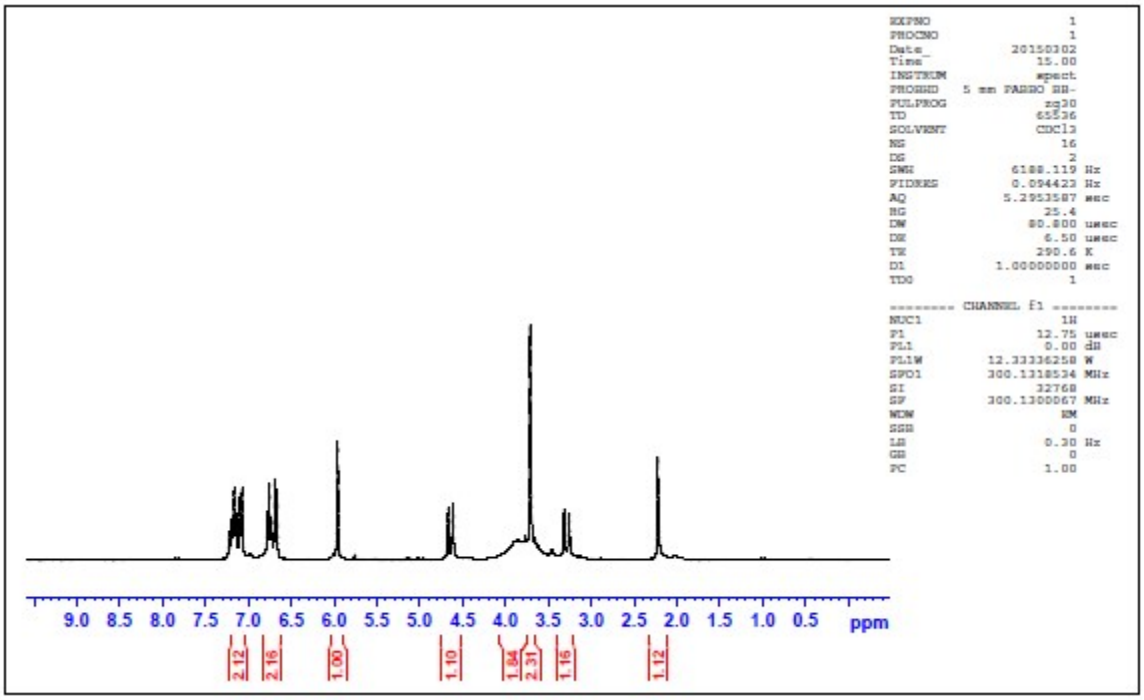

Figure S 16. ^{1}H NMR (300 MHz, $CDCl_3$) of **5b**.

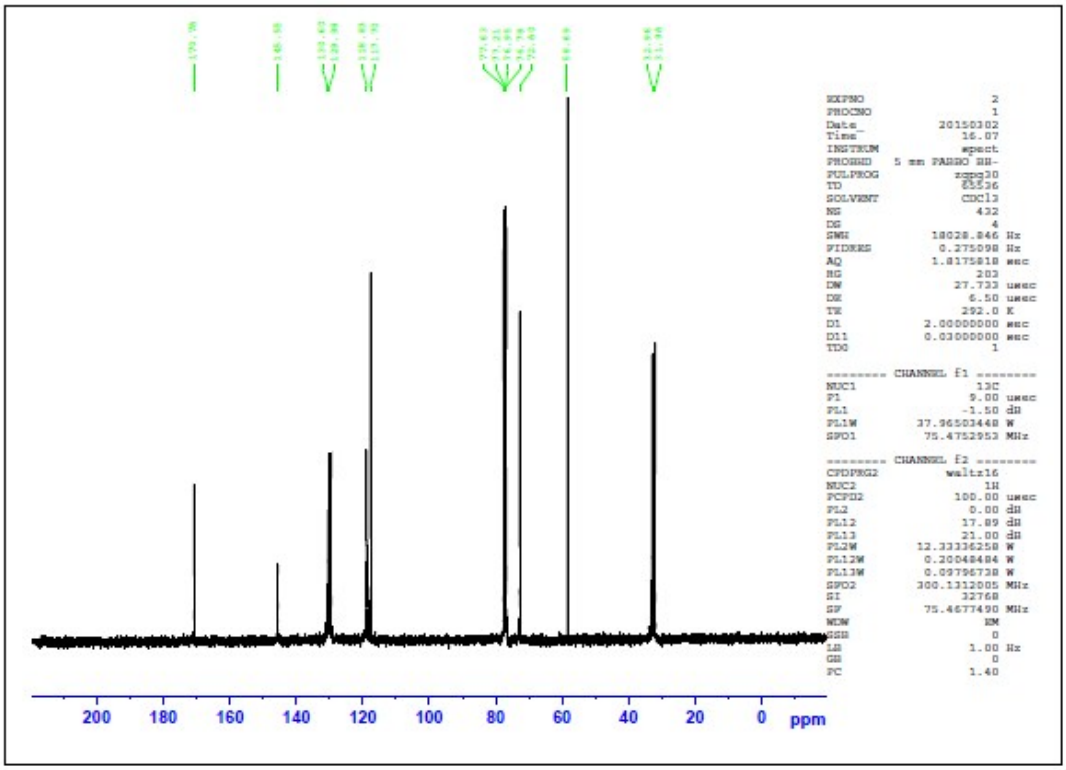

Figure S 17.^{13}C NMR (75 MHz, $CDCl_3$) of **5b**.

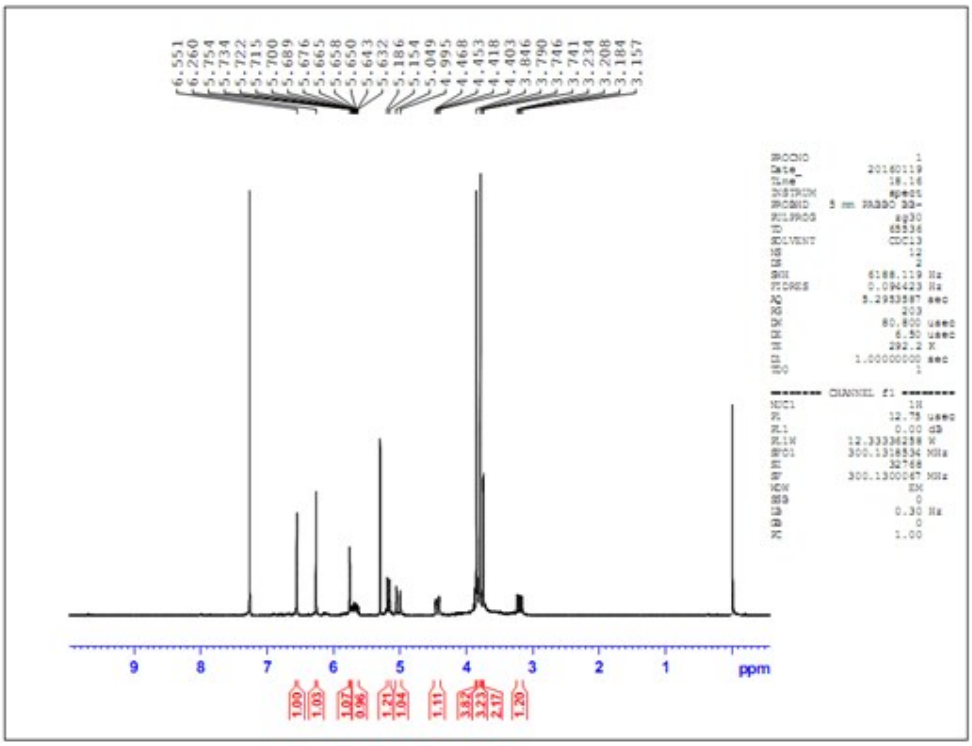

Figure S 18.[1]HNMR (300 MHz, $CDCl_3$) of **5c**.

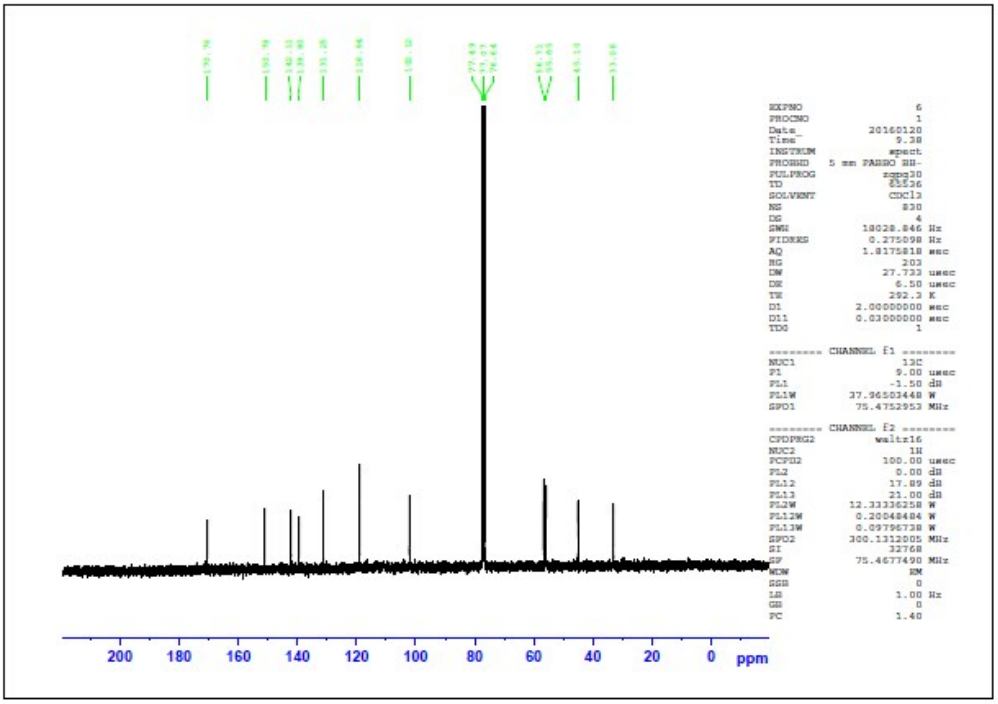

Figure S 19.[13]C NMR (75 MHz, $CDCl_3$) of **5c**.

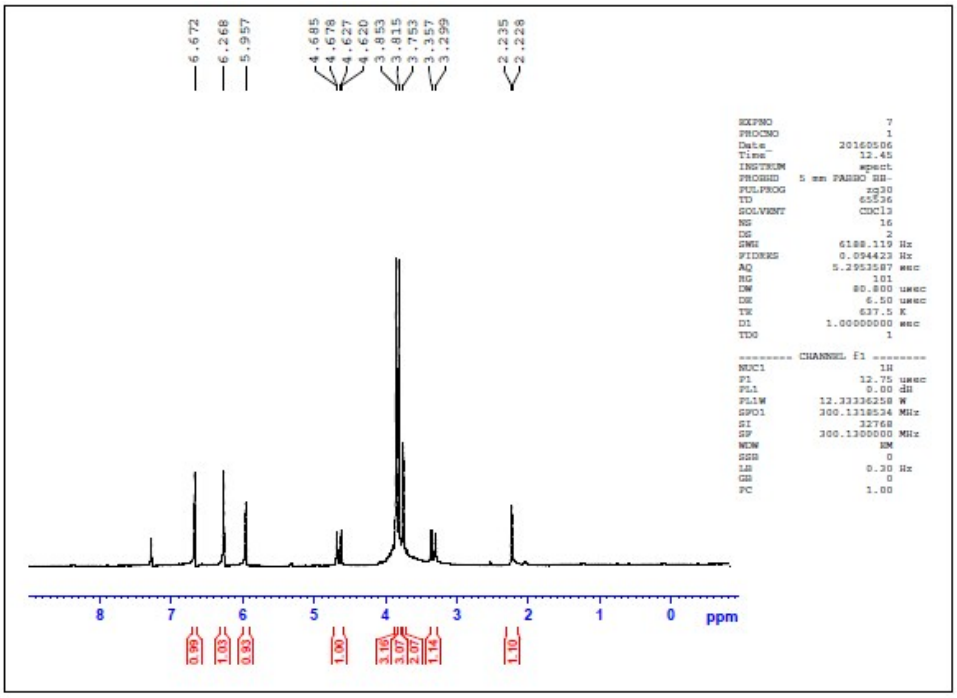

Figure S 20.[1]HNMR (300 MHz, $CDCl_3$) of **5d**.

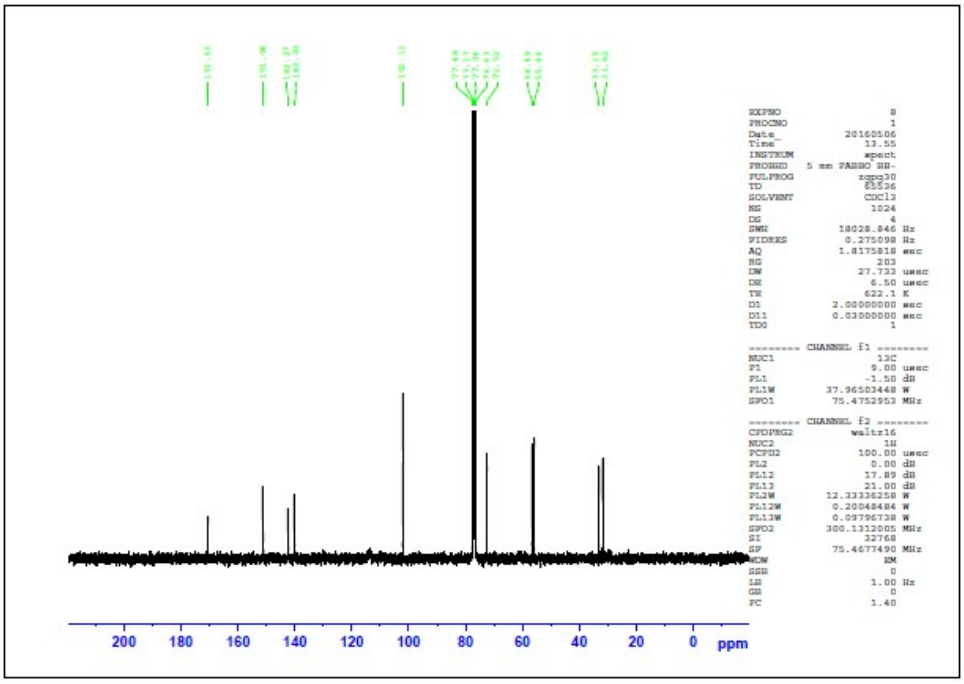

Figure S 21.[13]C NMR (75 MHz, $CDCl_3$) of **5d**.

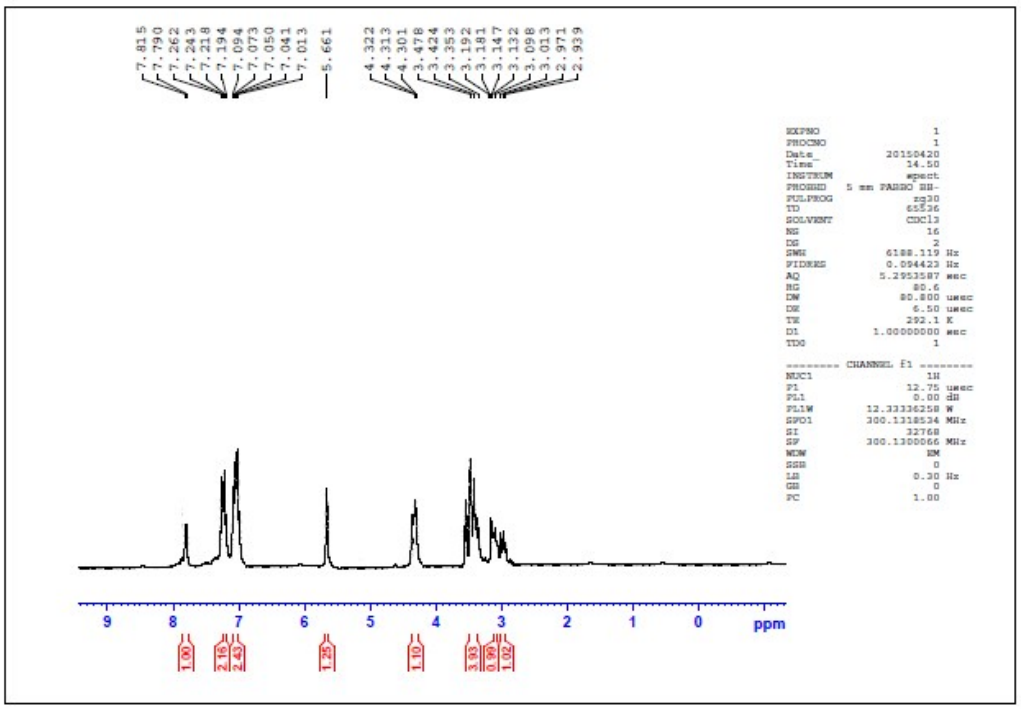

Figure S 22.[1]HNMR (300 MHz, $CDCl_3$) of **6a**.

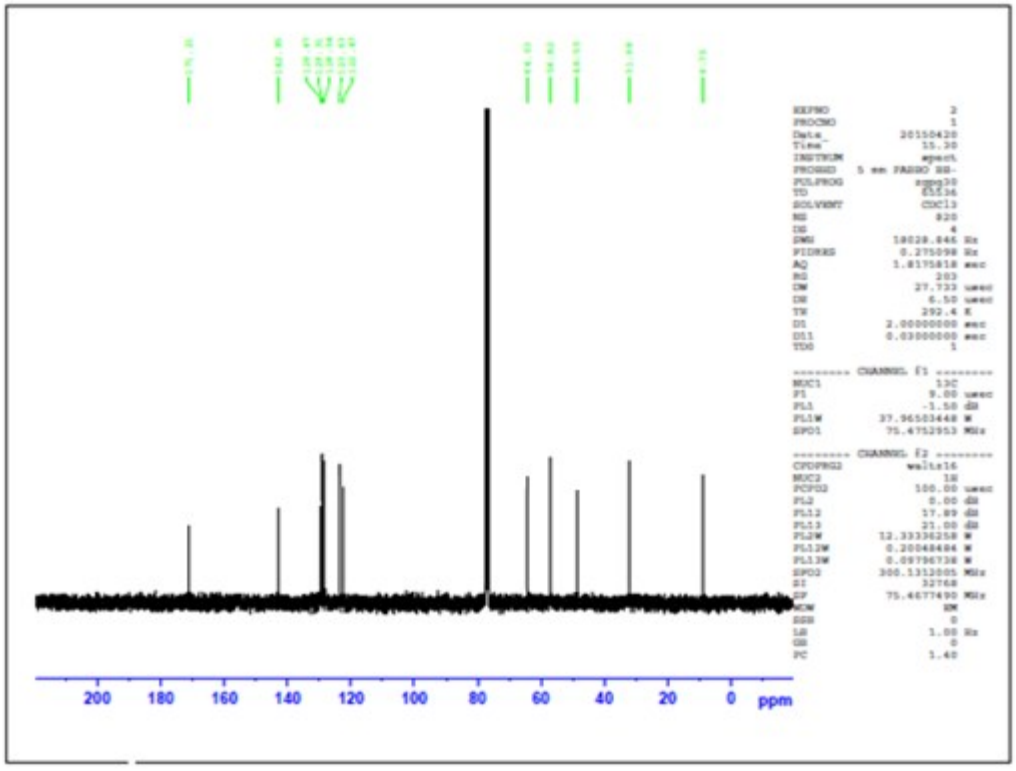

Figure S 23.[13]CNMR (75 MHz, $CDCl_3$) of **6a**.

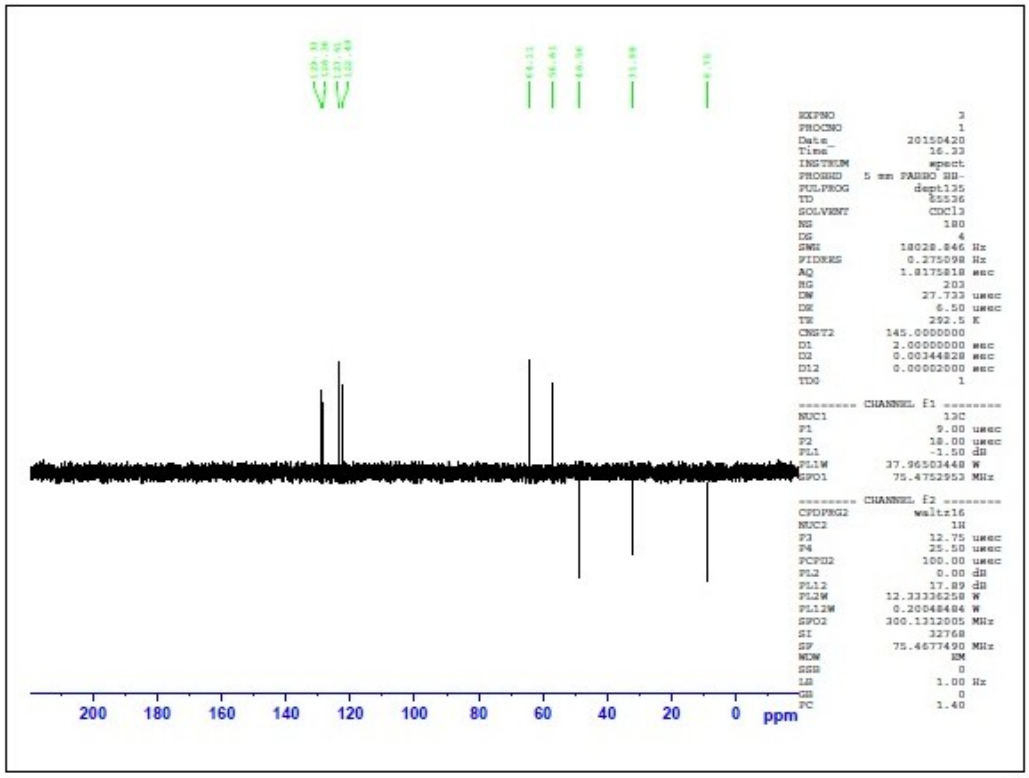

Figure S 24.DEPTNMR (75 MHz, $CDCl_3$) of **6a.**

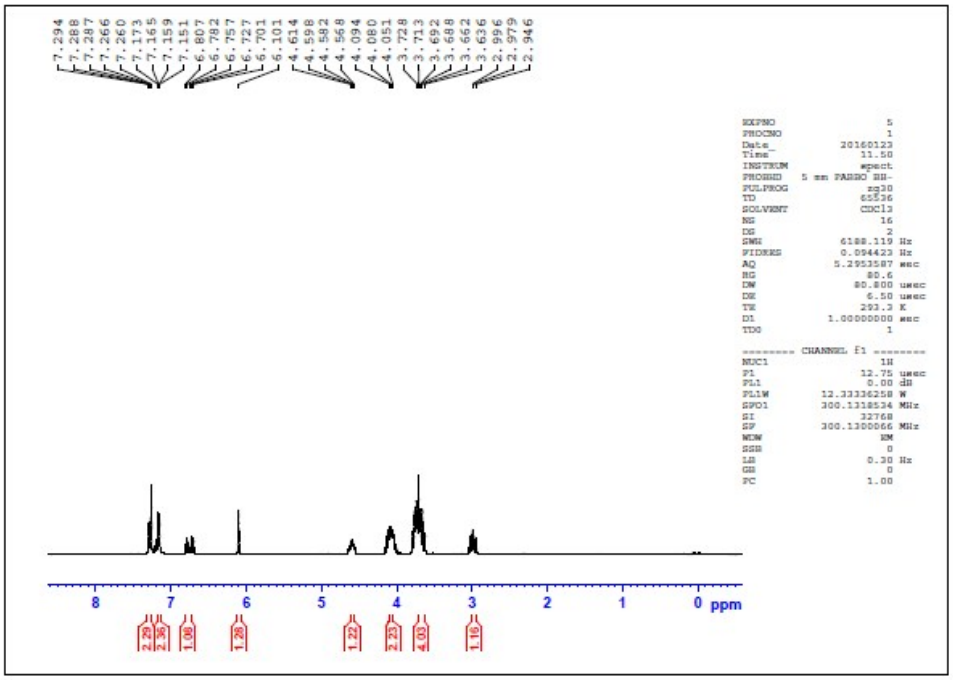

Figure S 25.[1]HNMR (300 MHz, $CDCl_3$) of **6b.**

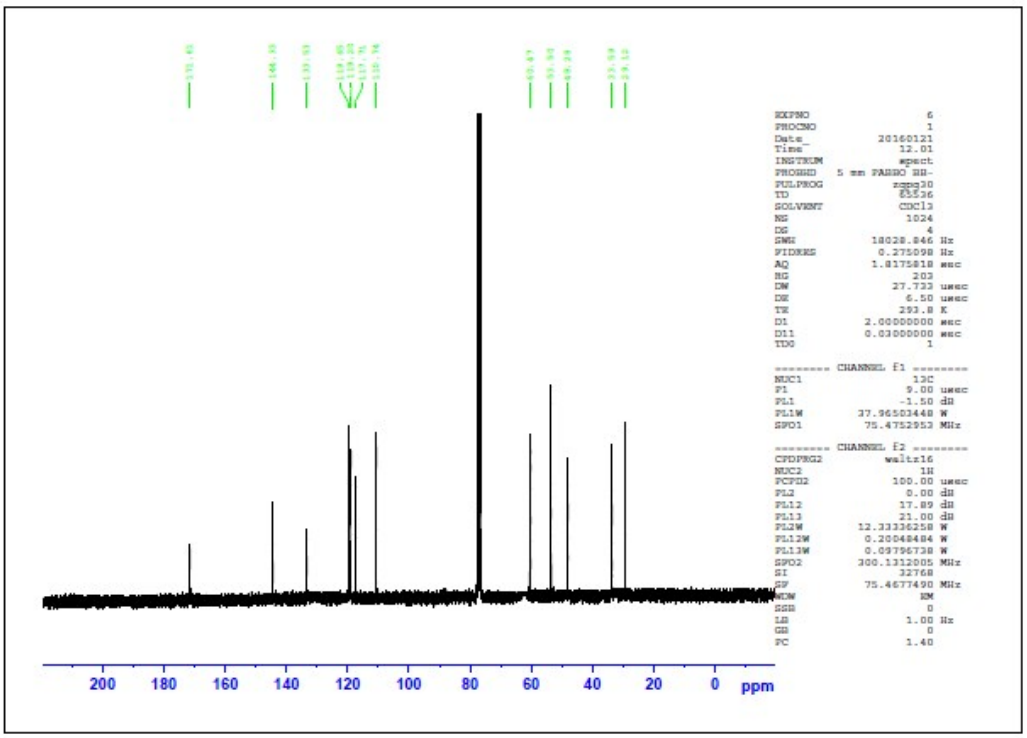

Figure S 26.[13]C NMR (75 MHz, $CDCl_3$) of **6b.**

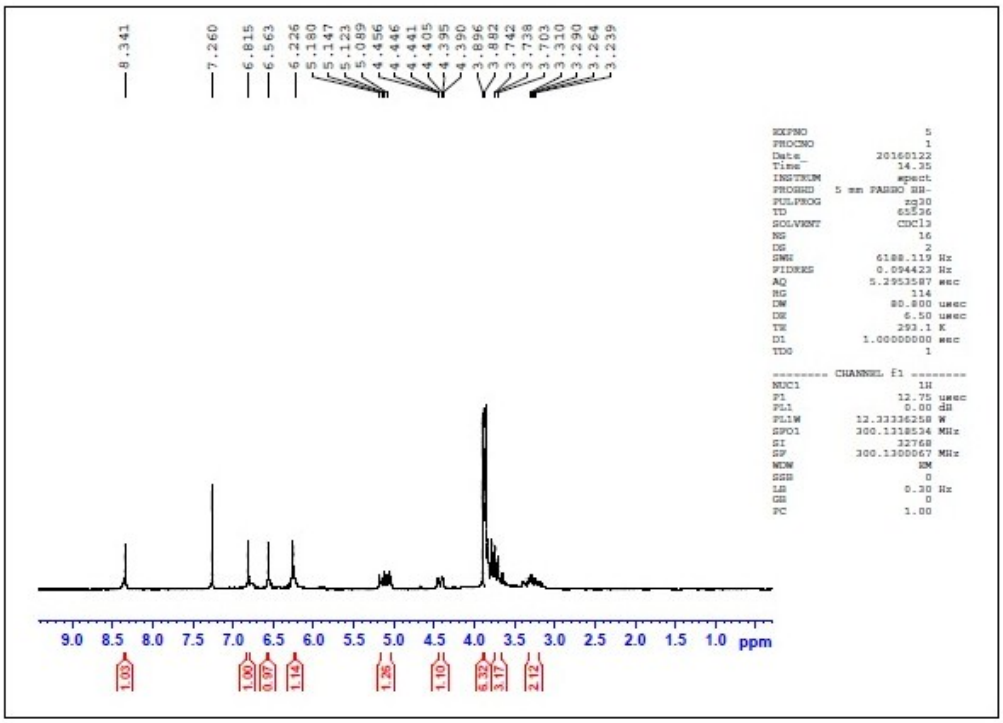

Figure S 27.[1]H NMR (300 MHz, $CDCl_3$) of **6c**.

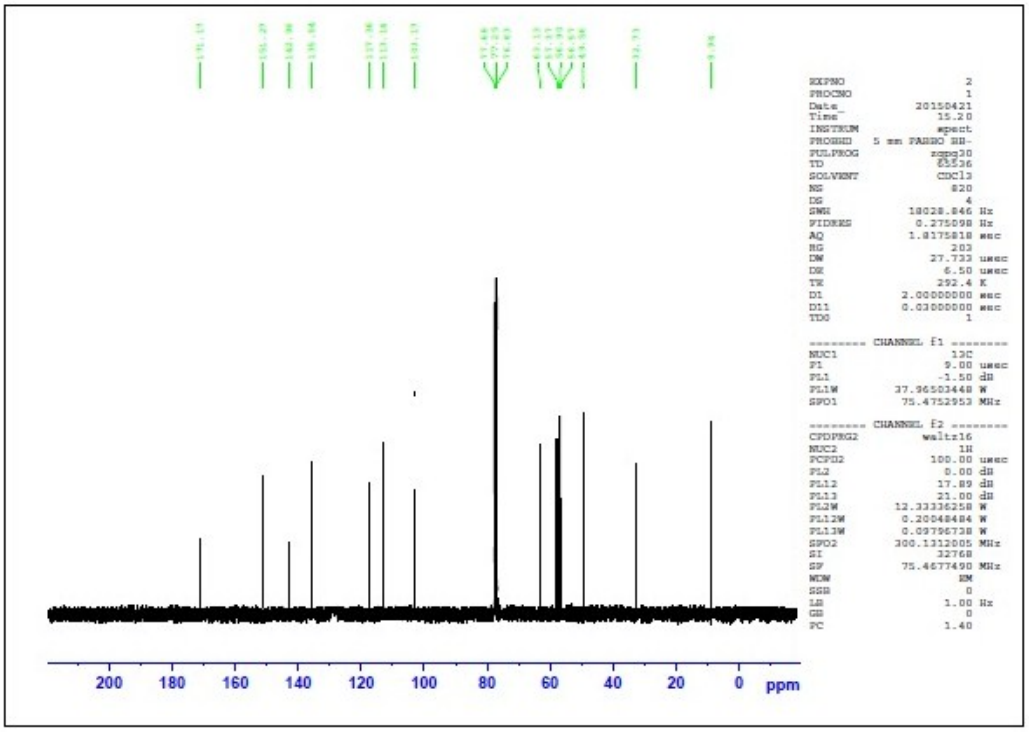

Figure S 28.[13]C NMR (75 MHz, $CDCl_3$) of **6c**.

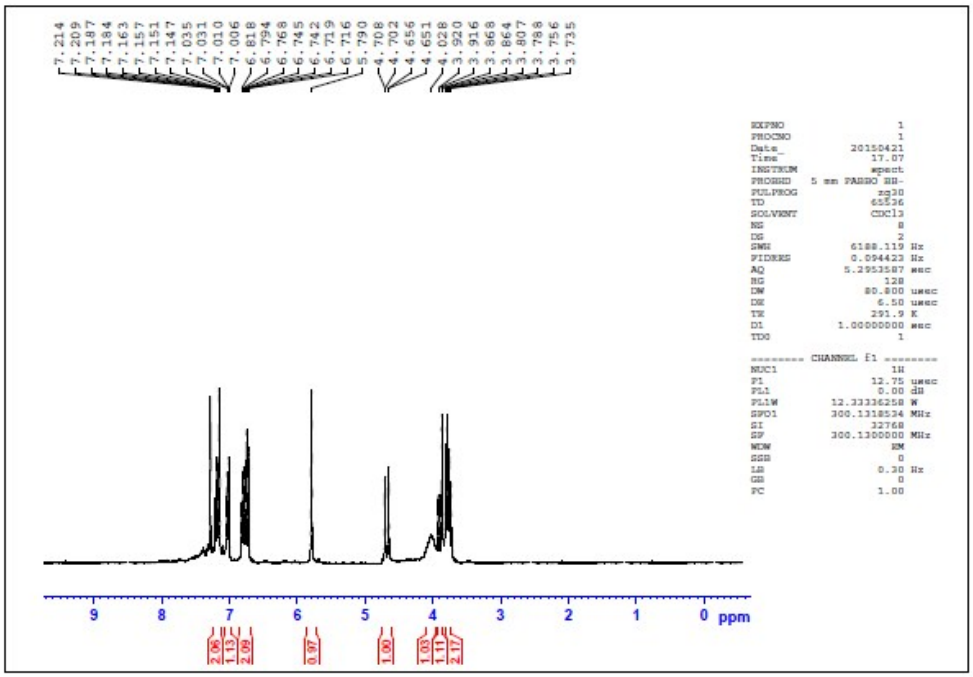

Figure S 29.[1]H NMR (300 MHz, $CDCl_3$) of **7a**.

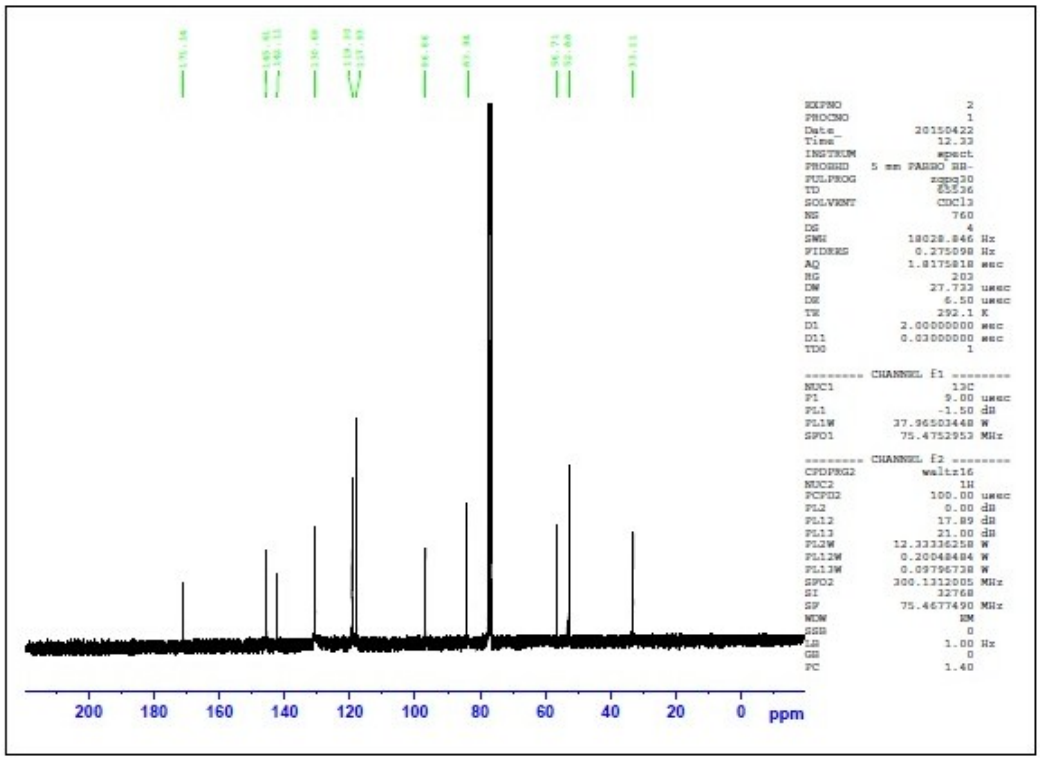

Figure S 30.^{13}C NMR (75 MHz, $CDCl_3$) of **7a**.

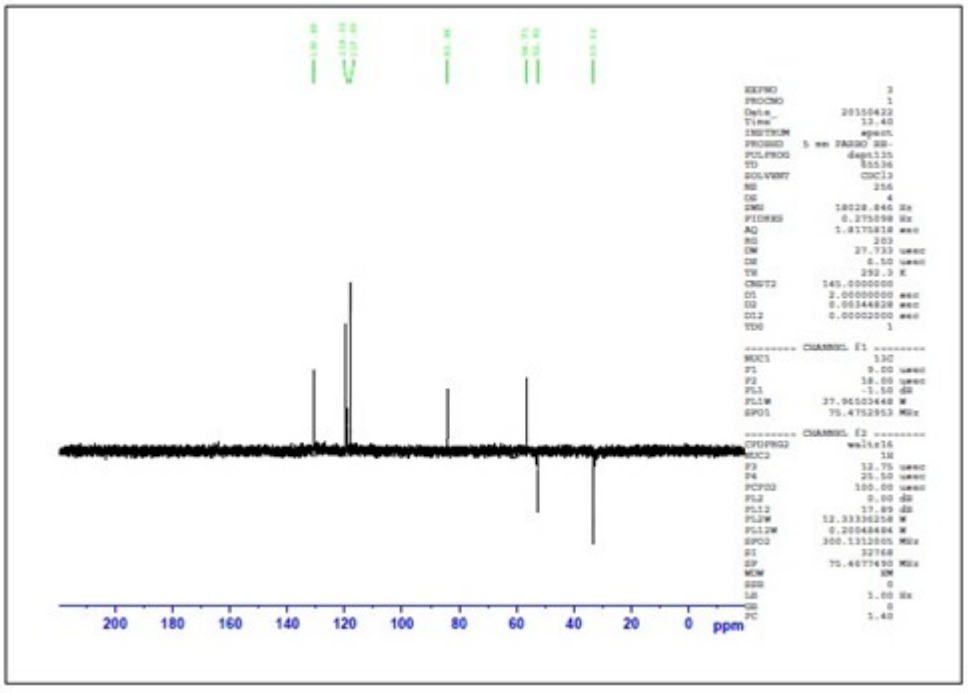

Figure S 31.DEPT NMR (75 MHz, $CDCl_3$) of **7a**.

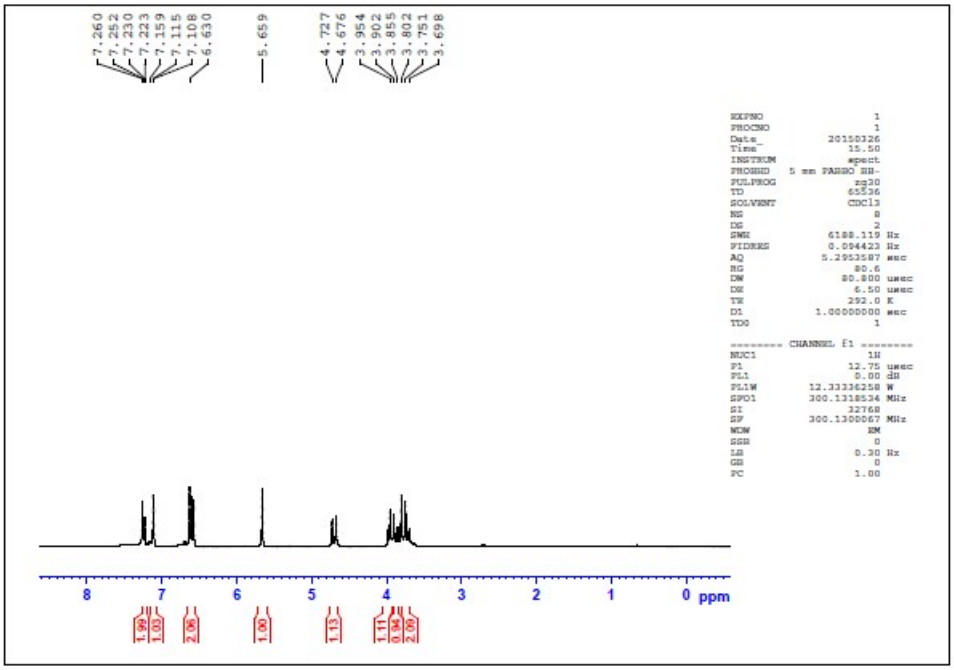

Figure S 32.[1]HNMR (300 MHz, $CDCl_3$) of **7b.**

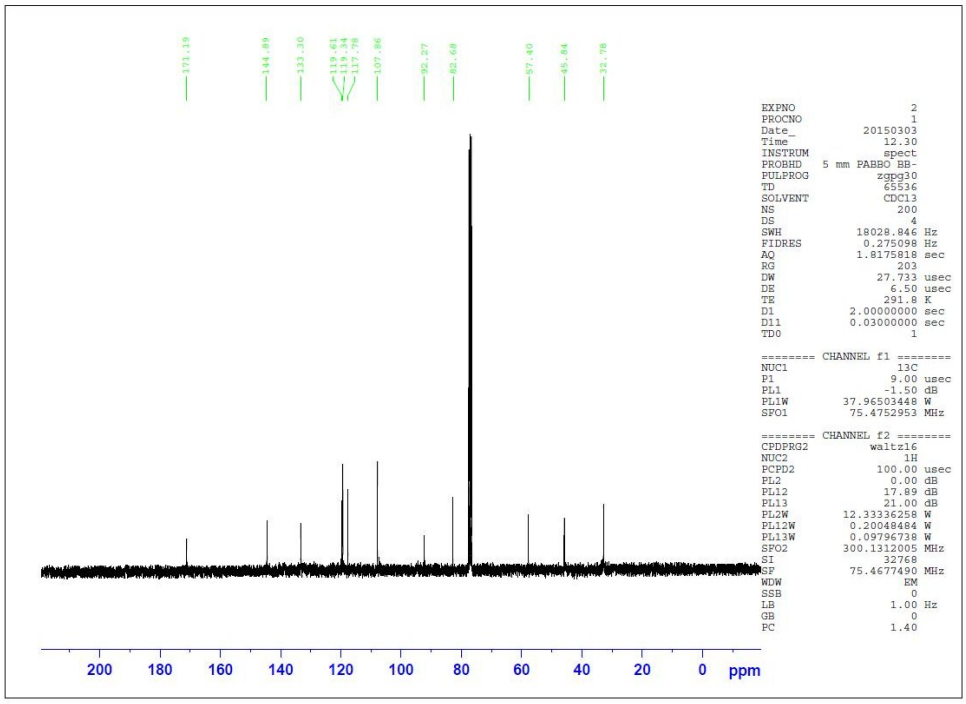

Figure S 33.[13]C NMR (75 MHz, $CDCl_3$) of **7b**.

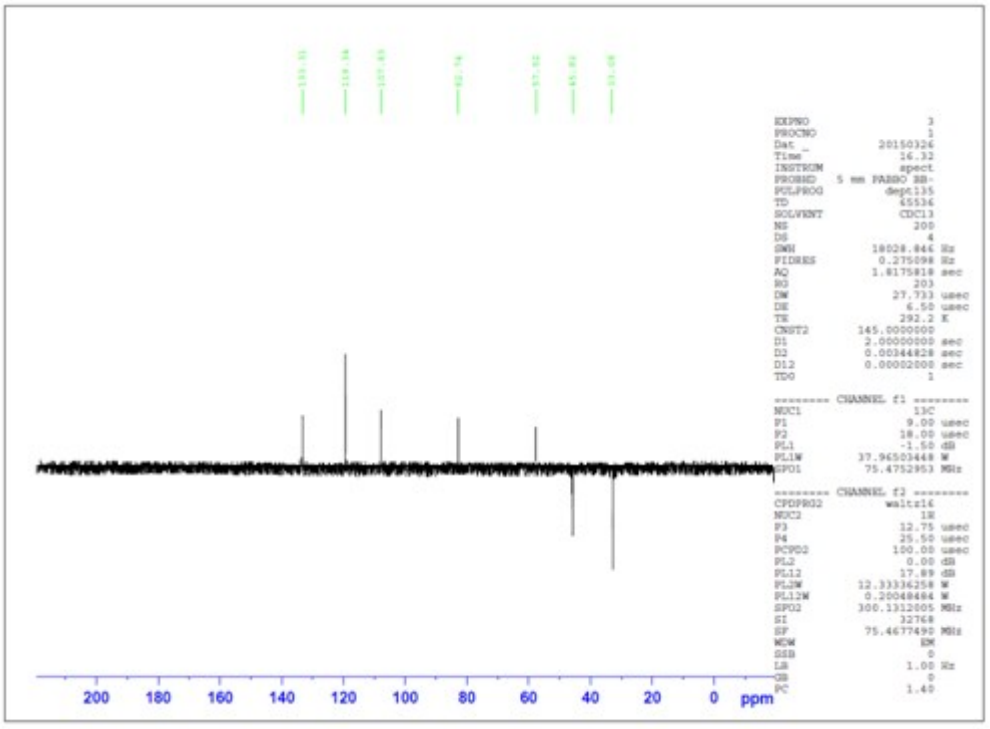

Figure S 34.DEPT NMR (75 MHz, $CDCl_3$) of **7b**.

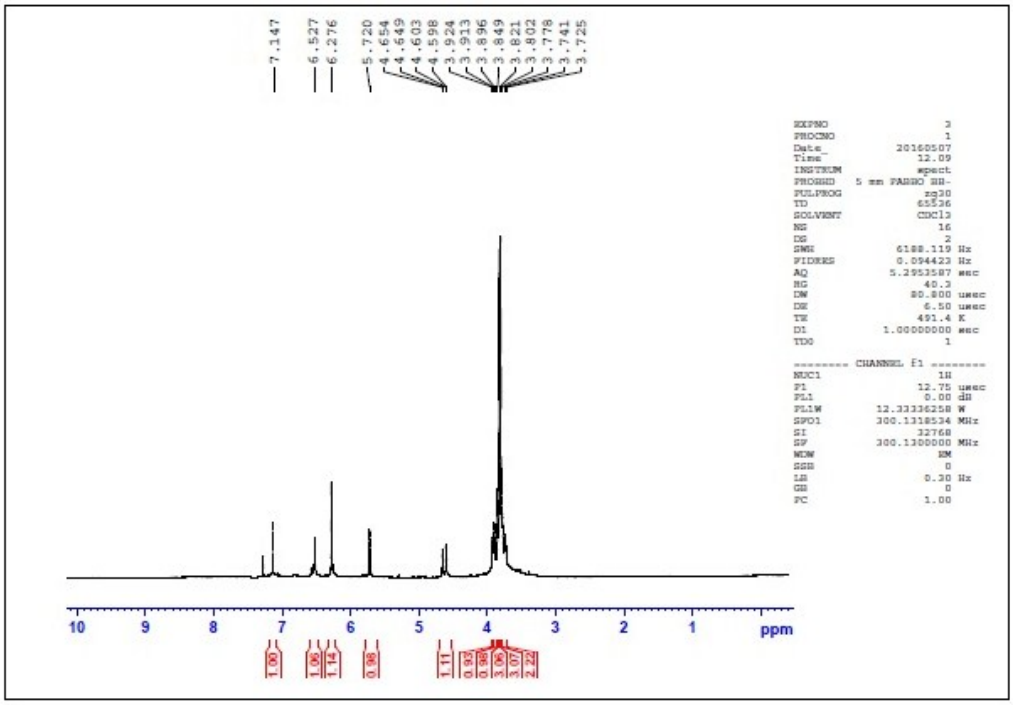

Figure S 35.^{1}H NMR (300 MHz, $CDCl_3$) of **7c**.

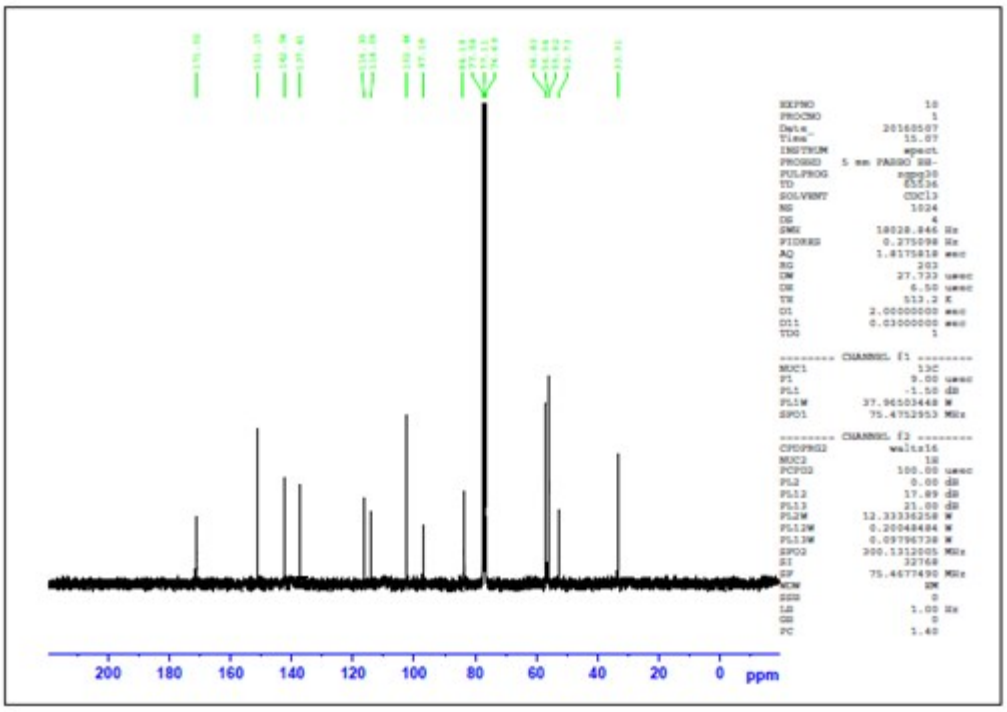

Figure S 36.[13]C NMR (75 MHz, $CDCl_3$) of **7c**.

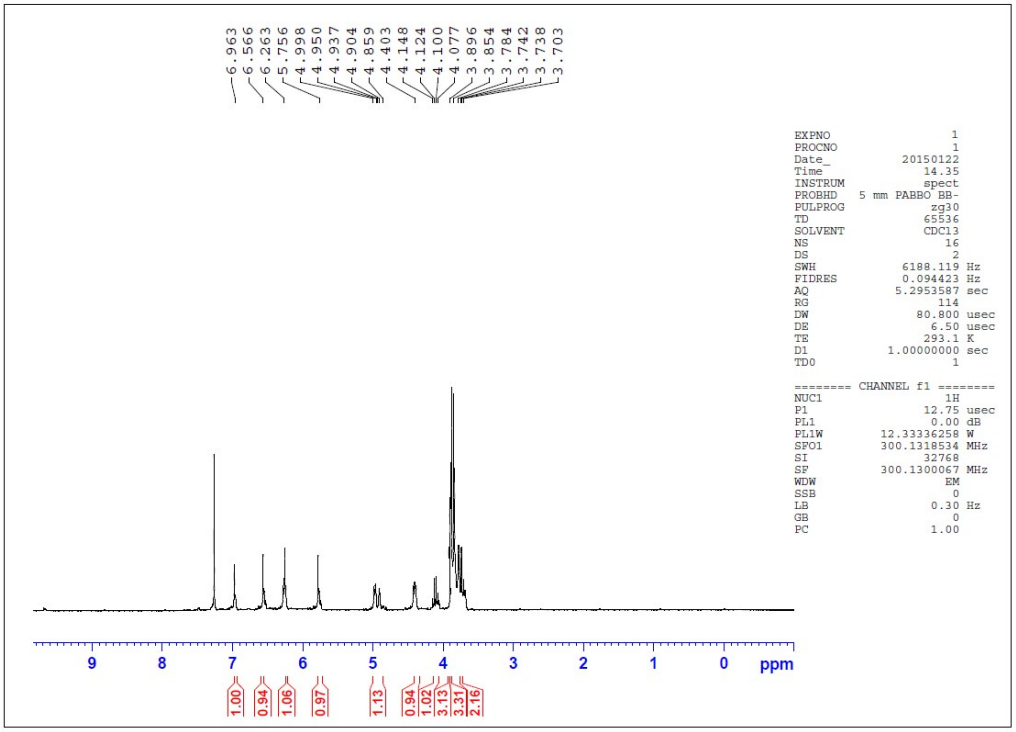

Figure S 37.[1]HNMR (300 MHz, $CDCl_3$) of **7d**.

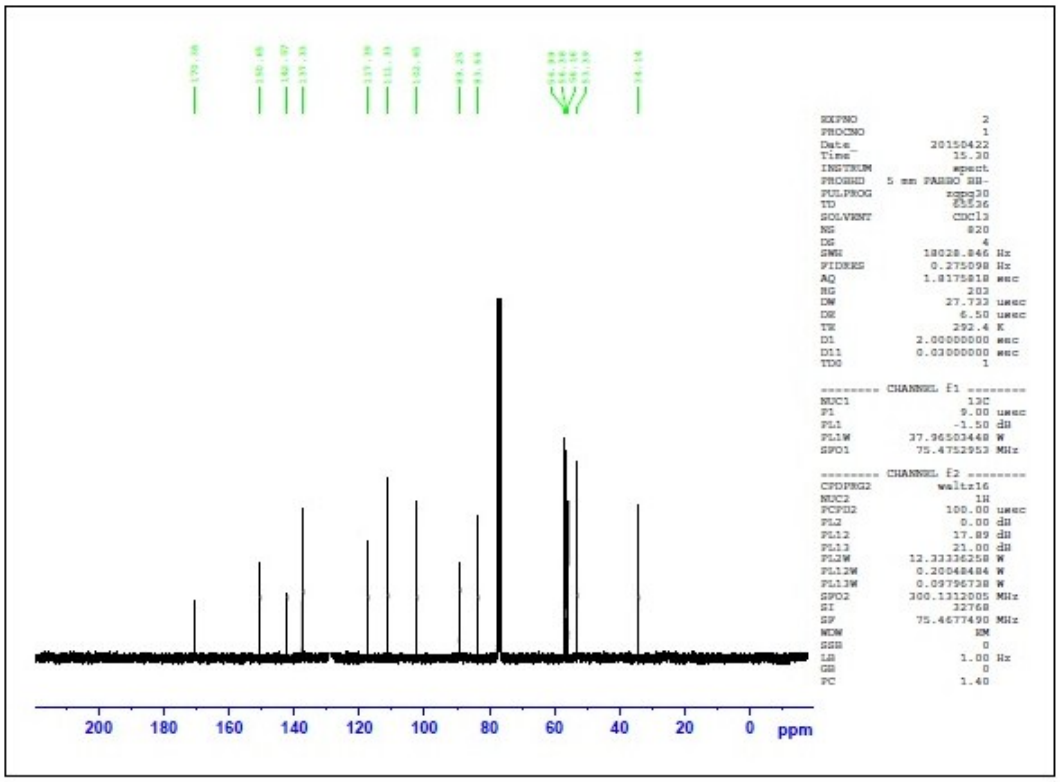

Figure S 38.^{13}C NMR (75 MHz, $CDCl_3$) of **7d**.