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Supporting Information

Nickel (0) Catalyzed (3+2) Cycloadditions of Bis(alkylidenecyclopropanes) with Diazenes: A Facile Synthesis of Functionalized Pyrazolidine-1,2-dicarboxylates

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General information:

Methods and Materials:

Unless otherwise noted, commercially available materials were used without further purification. Air sensitive reactions were carried out under argon atmosphere. Anhydrous solvents were obtained from Merck. Analytical thin layer chromatography (TLC) was conducted on Merck Kieselgel 60 F254 and compounds visualized in para-anisaldehyde strain. ^{1}H NMR spectra were obtained with $CDCl_3$ at 300 MHz, using Bruker spectrometers (residual chloroform referenced to 7.26 ppm). Chemical shift values are expressed as parts per million downfield from TMS and *J* values are in hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, dd: double doublet, and br: broad peak. ^{13}C NMR spectra were recorded with $CDCl_3$ at 75 MHz, using Bruker spectrometers (residual chloroform referenced to 77.0 ppm). HRMS were recorded on Bruker high resolution spectrometer (BrukermicrOTOF QII).

General procedure for synthesis of nickel catalyst [3+2] cycloadducts (3a–f): To a solution of bis(methylenecyclopropane) (**1**) (0.2 mmol, 1 *equiv.*) in toluene (4 ml), dialkyl azodicarboxylate **2** (2 mmol, 10 *equiv.*) was added and reaction mixture was degassed for 10 minutes under argon atmosphere. This is followed by the addition of 5 mole % $Ni(COD)_2$. The reaction was heated at 90^{o}C for 16 hrs. After completion of reaction, the reaction mixture was cooled to room

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temperature and directly loaded into the silica column without evaporation and purified by flash chromatography (silica gel 100-200, eluting with ethylacetate/hexanes) to get compound (**3a-f**).

***diethyl (E)-3-(5-cyclopropylidene-3,3-bis(methoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3a*:** Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.71 (m, 1H), 5.48 (m, 1H), 4.13-4.20 (m, 4H), 3.71 (s, 6H), 3.65 (m, 2H), 2.75 (d, J = 9, Hz, 2H), 2.49 (bs, 2H), 2.01 (m, 2H), 1.22-1.27 (m, 6H), 0.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 156.3, 137.7, 126.9, 116.0, 112.3, 61.5, 57.7, 52.1, 46.7, 37.0, 35.5, 29.3, 14.6, 2.6, 2.0; LRMS 439.2 (M+1), HRMS calcd for $C_{21}H_{31}N_2O_8$ (M+1): 439.2080, found: 439.2067.

***diethyl (E)-3-(5-cyclopropylidene-3,3-bis(ethoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3b*:** Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.69 (m, 1H), 5.58 (m, 1H), 4.17-4.30 (m, 8H), 3.68 (m,2H), 2.89 (d, J = 7.2 Hz, 2H), 2.55 (bs, 2H), 1.97 (m, 2H), 1.22-1.31 (m, 12H), 1.03 (m, 2H), 0.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 155.9, 137.2, 127.1, 115.2, 112.5, 61.5, 61.1, 57.5, 47.2, 37.2, 35.1, 29.2, 14.6, 14.1, 2.4, 1.9; LRMS 467.2 (M+1), HRMS calcd for $C_{23}H_{35}N_2O_8$ (MH^+): 467.2393, found: 467.2383.

diethyl (E)-3-(5-cyclopropylidene-3,3-bis(isopropoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3c: Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.61 (m, 1H), 5.57 (m, 1H), 5.03 (m, 2H), 4.19 (m , 4H), 3.70 (m, 2H), 2.76 (d, J = 7.2 Hz, 2H), 2.66 (bs, 2H), 1.78 (m, 2H), 1.20-1.32 (m, 18H), 1.05 (t, J = 4.5 Hz, 2H), 1.02 (t, J = 4.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 155.6, 137.7, 126.2, 115.5, 112.1, 69.0, 62.4, 57.0, 46.1, 37.8, 35.8, 29.6, 21.5, 14.5, 2.8, 2.0 ; LRMS 495.3 (M+1), HRMS calcd for $C_{25}H_{39}N_2O_8$ (MH^+): 495.2706, found: 495.2718.

diisopropyl (E)-3-(5-cyclopropylidene-3,3-bis(methoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3d: Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (m, 1H), 5.45 (m, 1H), 5.02 (m, 2H), 3.75 (s, 6H), 3.64 (m, 2H), 2.78 (d, J = 7.8 Hz, 2H), 2.58 (bs, 2H), 1.99 (m, 2H), 1.23-1.30 (m, 12H), 0.93-0.96 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 156.5, 138.2, 127.3, 116.2, 112.8, 69.3, 58.0, 50.1, 46.7, 36.2, 35.8, 29.3, 21.5, 2.3, 2.1; LRMS 467.3 (M+1). HRMS calcd for $C_{23}H_{35}N_2O_8$: 467.2393, found: 467.2401

***diisopropyl (E)-3-(5-cyclopropylidene-3,3-bis(ethoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3e*:** Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.73 (m, 1H), 5.30

(m, 1H), 4.99 (m, 2H), 4.11-4.18 (m, 4H), 3.67 (m, 2H), 2.88 (d, *J* = 7.5 Hz, 2H), 2.60 (bs, 2H), 1.85 (bs, 2H), 1.18-1.31 (m, 18H), 0.95-1.05 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 155.2, 137.2, 126.7, 115.7, 112.3, 68.8, 61.3, 57.7, 49.2, 36.9, 35.1, 29.7, 21.1, 14.3, 2.6, 1.9; LRMS 495.2 (M+1), HRMS calcd for $C_{25}H_{39}N_2O_8$: 495.2706, found: 495.2711.

***diisopropyl (E)-3-(5-cyclopropylidene-3,3-bis(isopropoxycarbonyl)pentylidene)pyrazolidine-1,2-dicarboxylate 3f*:** Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.63 (m, 1H), 5.55 (m, 1H), 5.02 (m, 4H), 3.66 (m, 2H), 2.88 (d, *J* = 8.1 Hz, 2H), 2.59 (bs, 2H), 1.86 (m, 2H), 1.24-1.33 (m, 24H), 0.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 156.6, 137.2, 126.2, 115.1, 111.9, 69.1, 57.5, 46.1, 38.1, 35.1, 29.3, 21.1, 20.9, 2.6, 2.1; LRMS 523.2 (M+1), HRMS calcd for $C_{27}H_{43}N_2O_8$: 523.3019, found: 523.3026.

Characterization data:

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

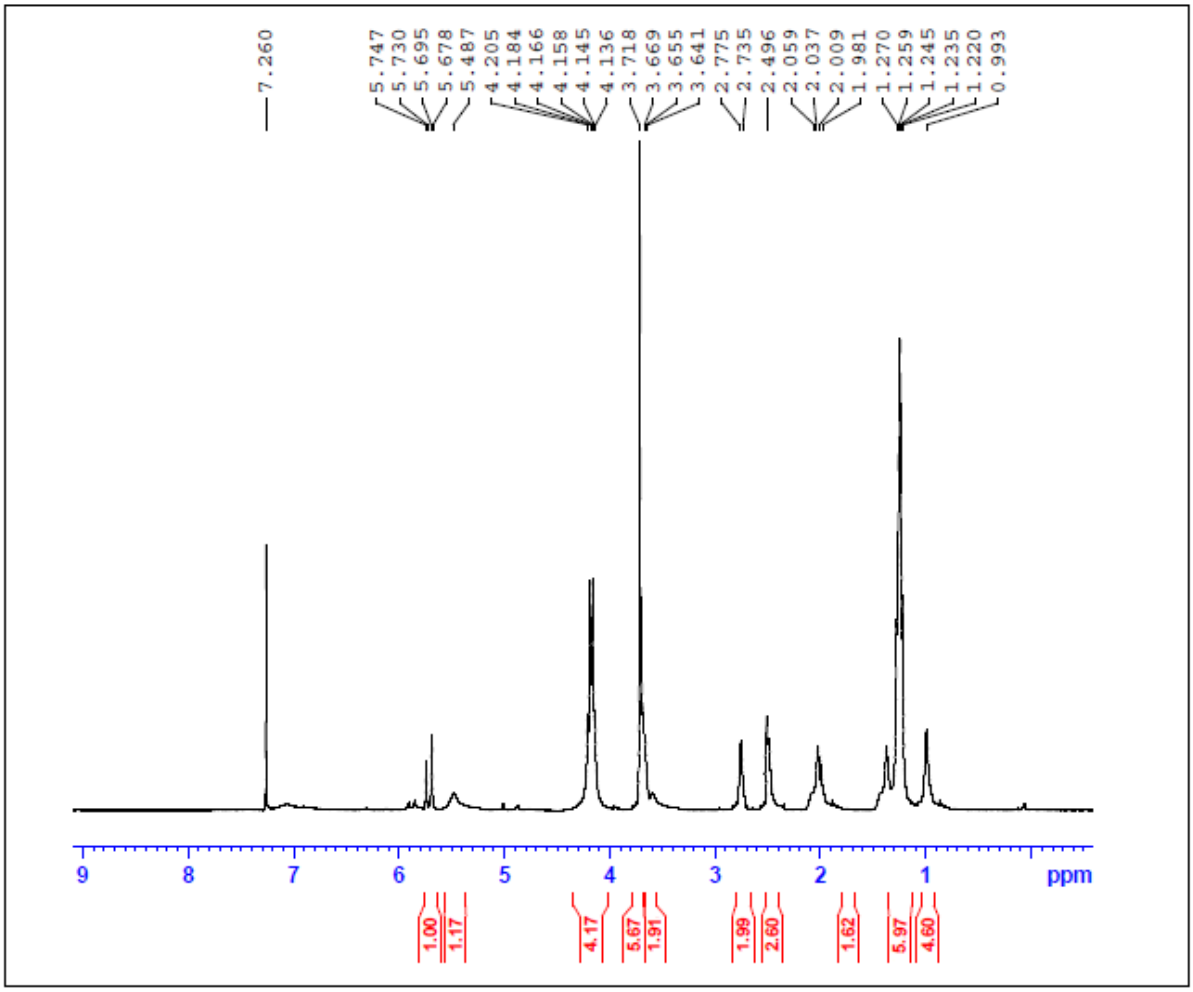

Figure S 1. ^{1}H NMR (300 MHz, $CDCl_3$) of **3a**

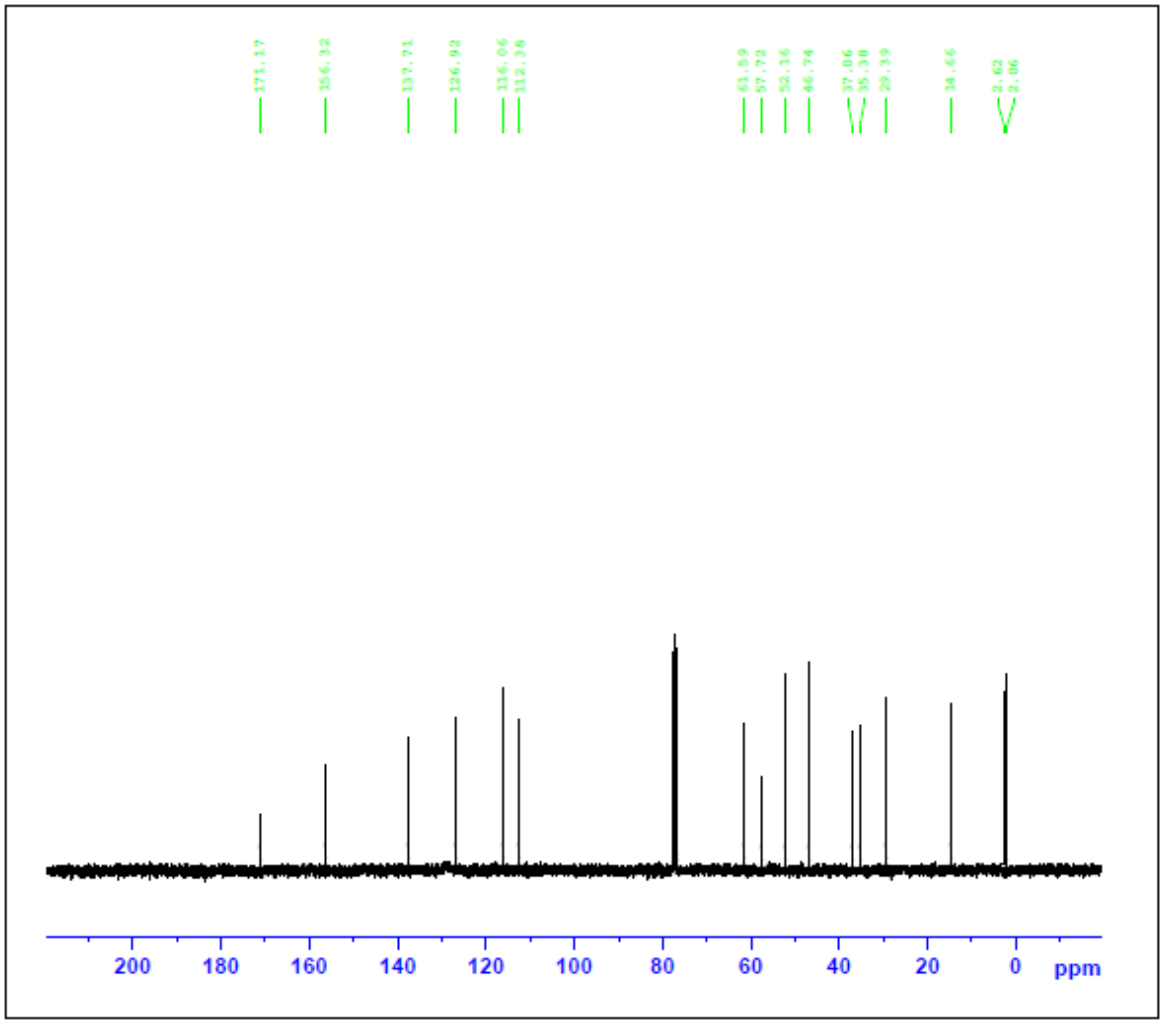

Figure S 2. ^{13}C NMR (75 MHz, $CDCl_3$) of **3a**

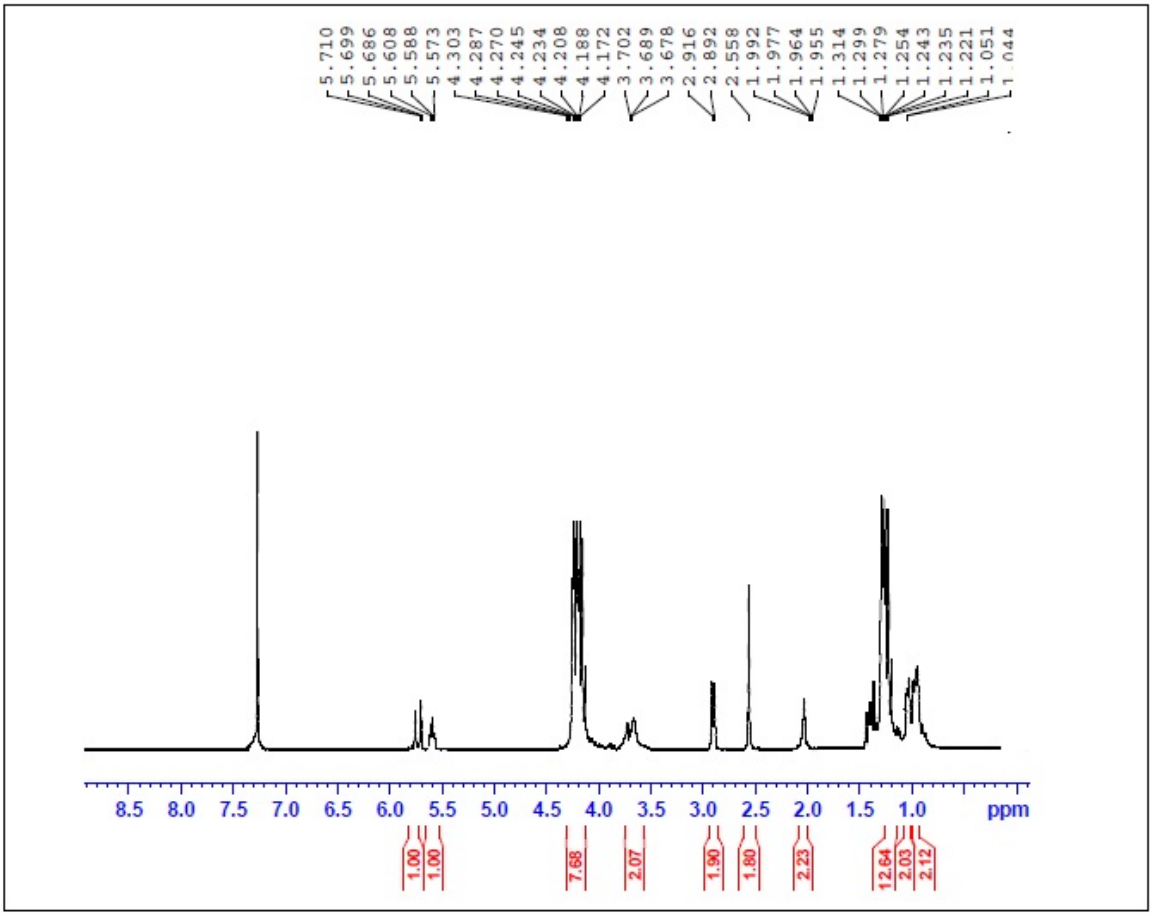

Figure S 3. ^{1}H NMR (300 MHz, $CDCl_3$) of **3b**

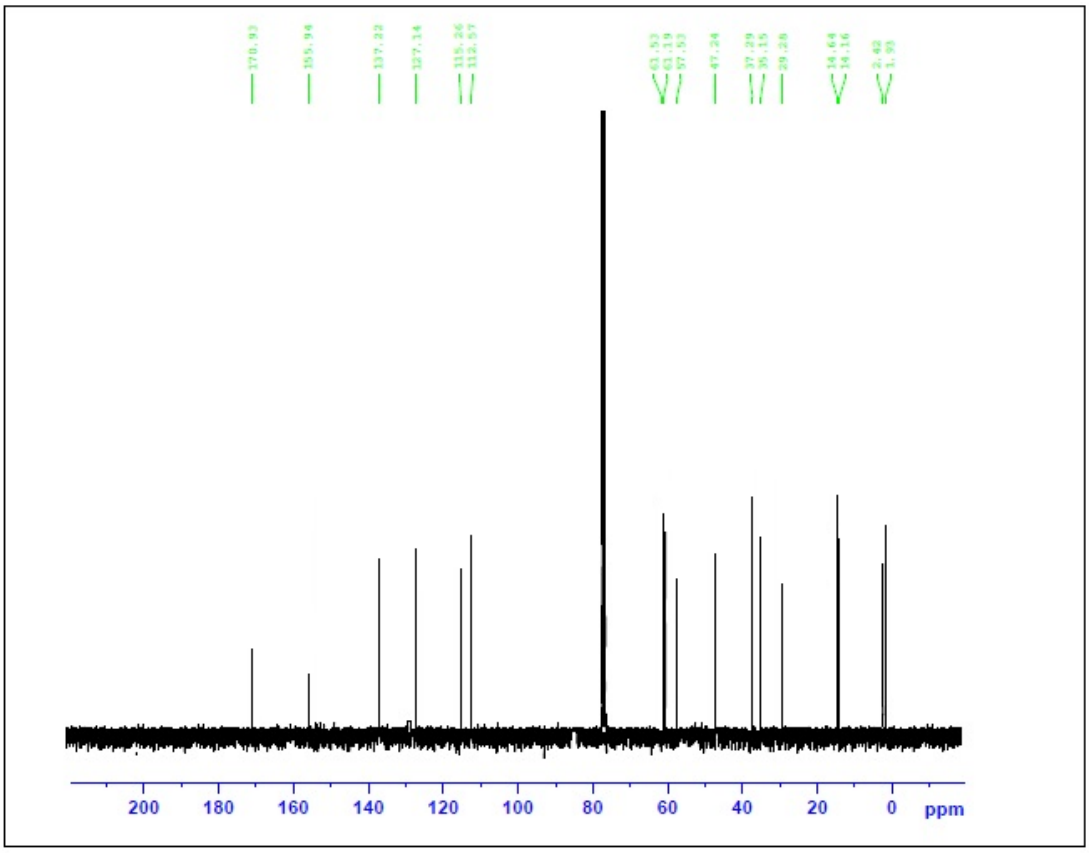

Figure S 4. ^{13}C NMR (75 MHz, $CDCl_3$) of **3b**

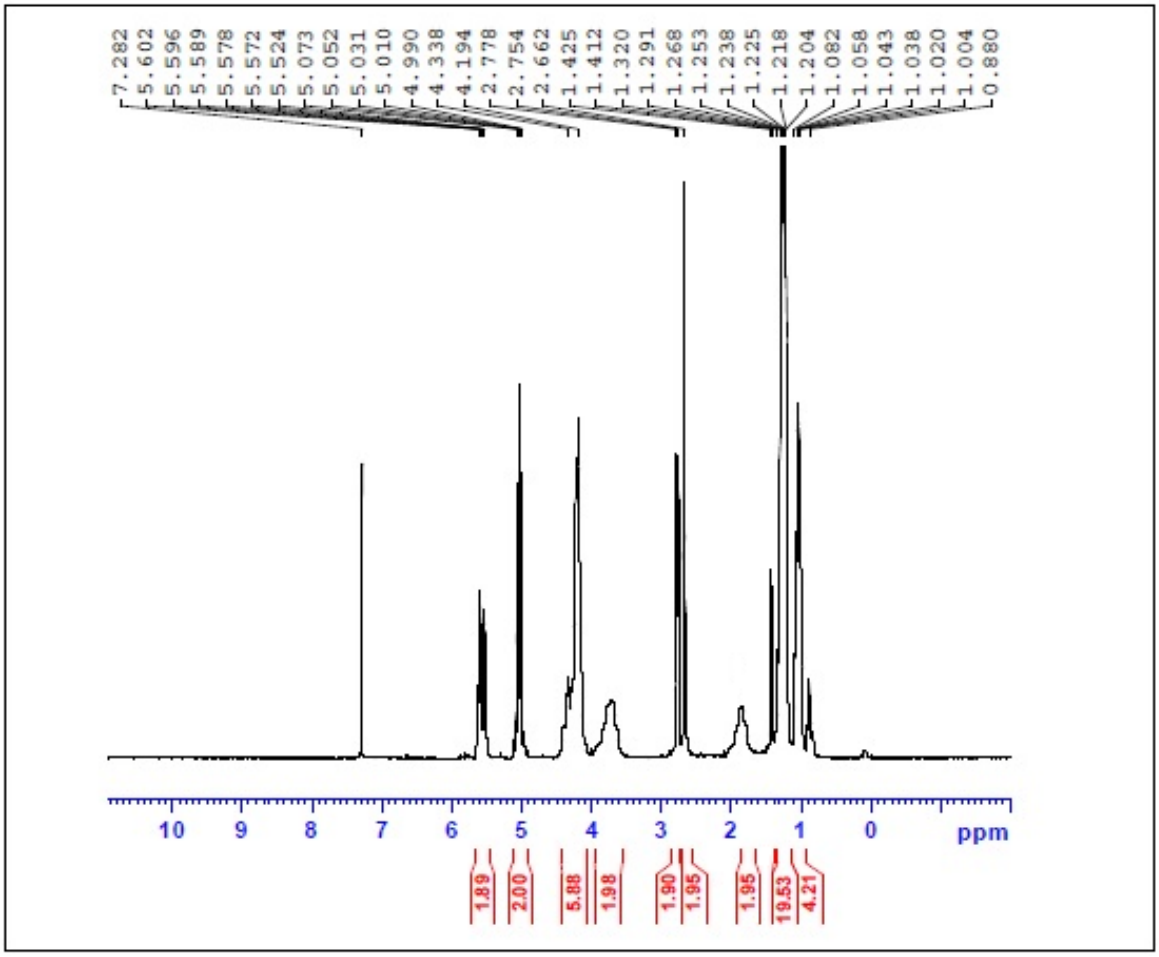

Figure S 5. ^{1}H NMR (300 MHz, $CDCl_3$) of **3c**

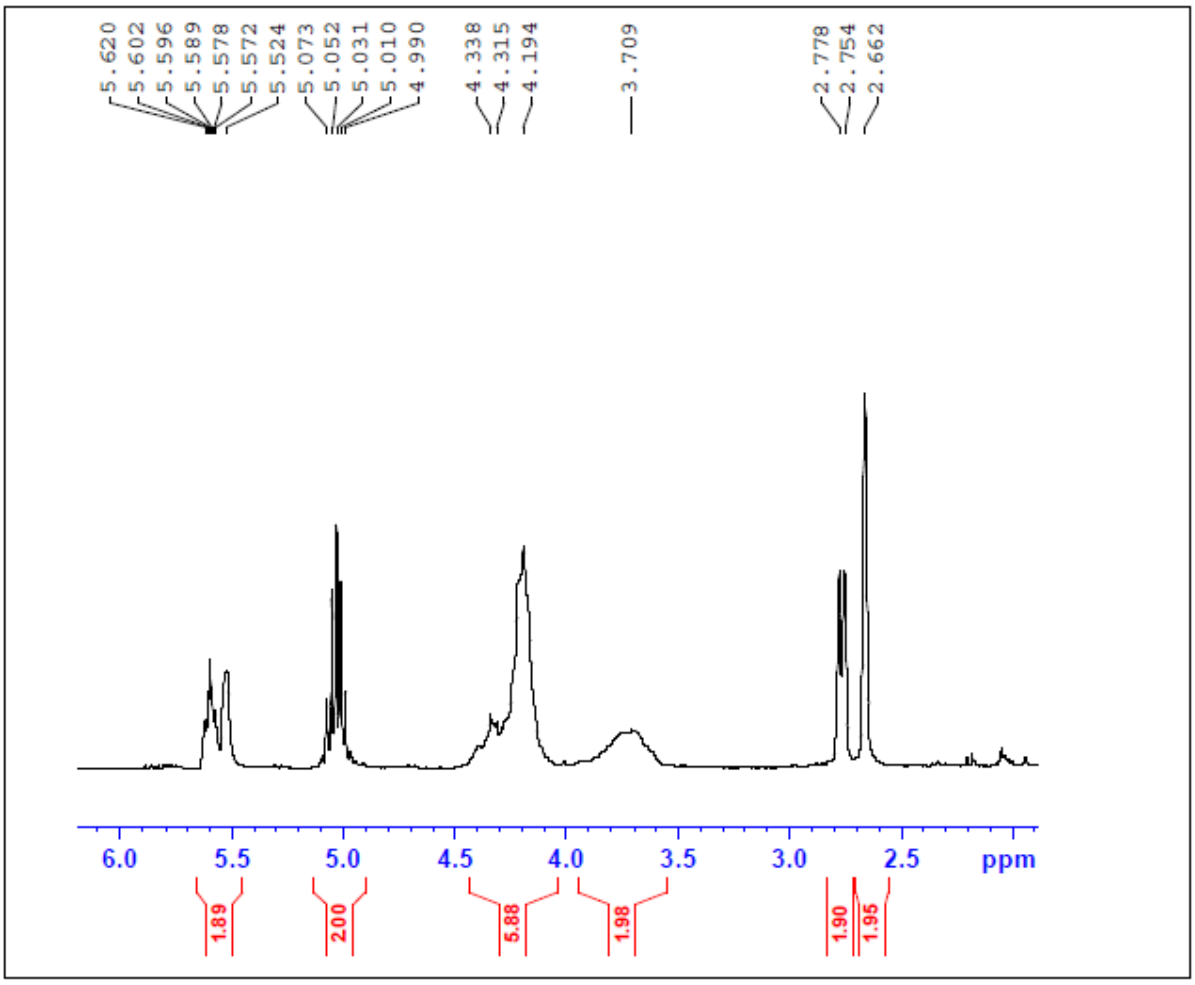

Figure S 6. ^{1}H NMR (300 MHz, $CDCl_3$) of **3c-expansion1**

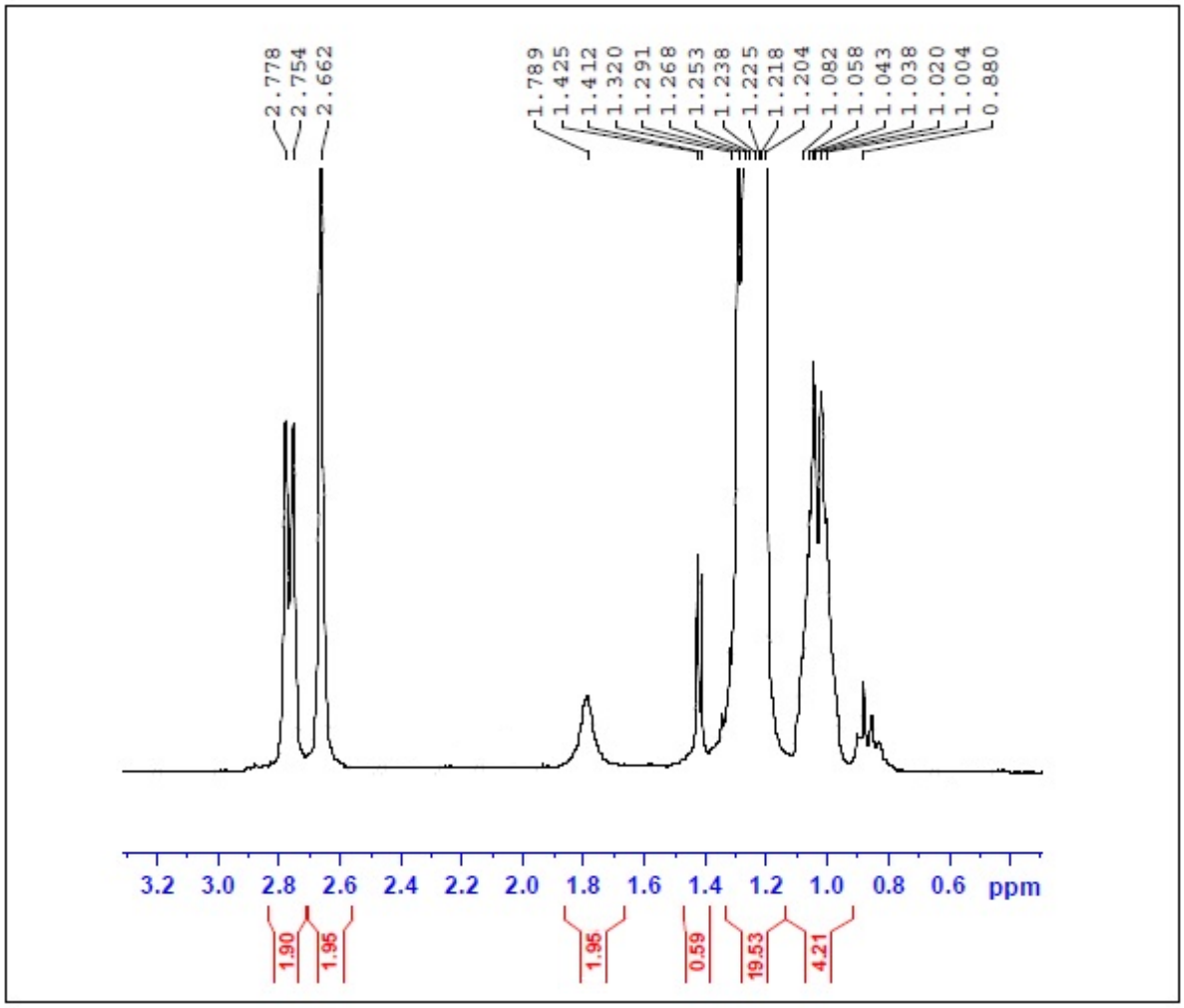

Figure S 7. ^{1}H NMR (300 MHz, $CDCl_3$) of **3c-expansion2**

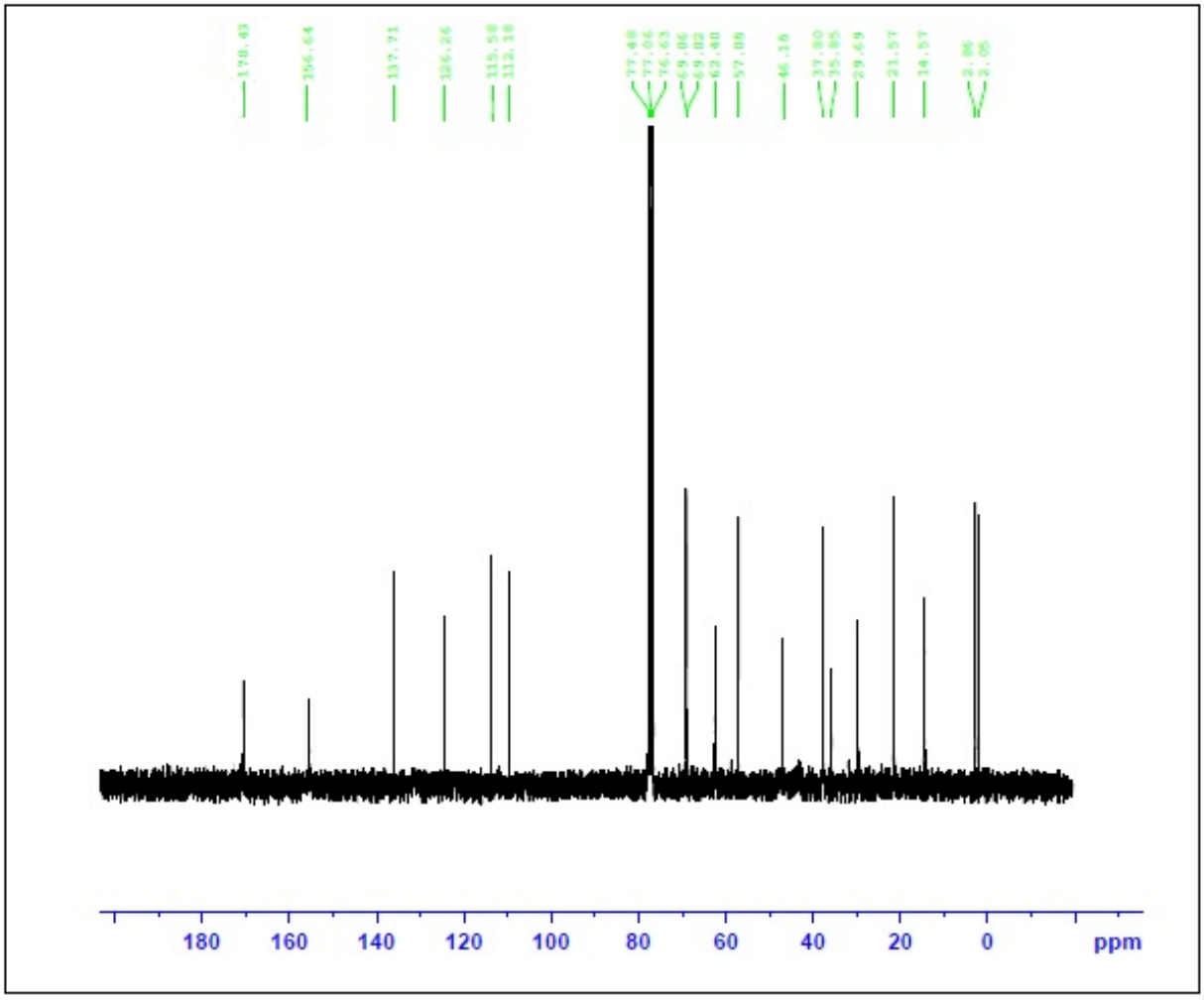

Figure S 8. ^{13}C NMR (75 MHz, $CDCl_3$) of **3c**

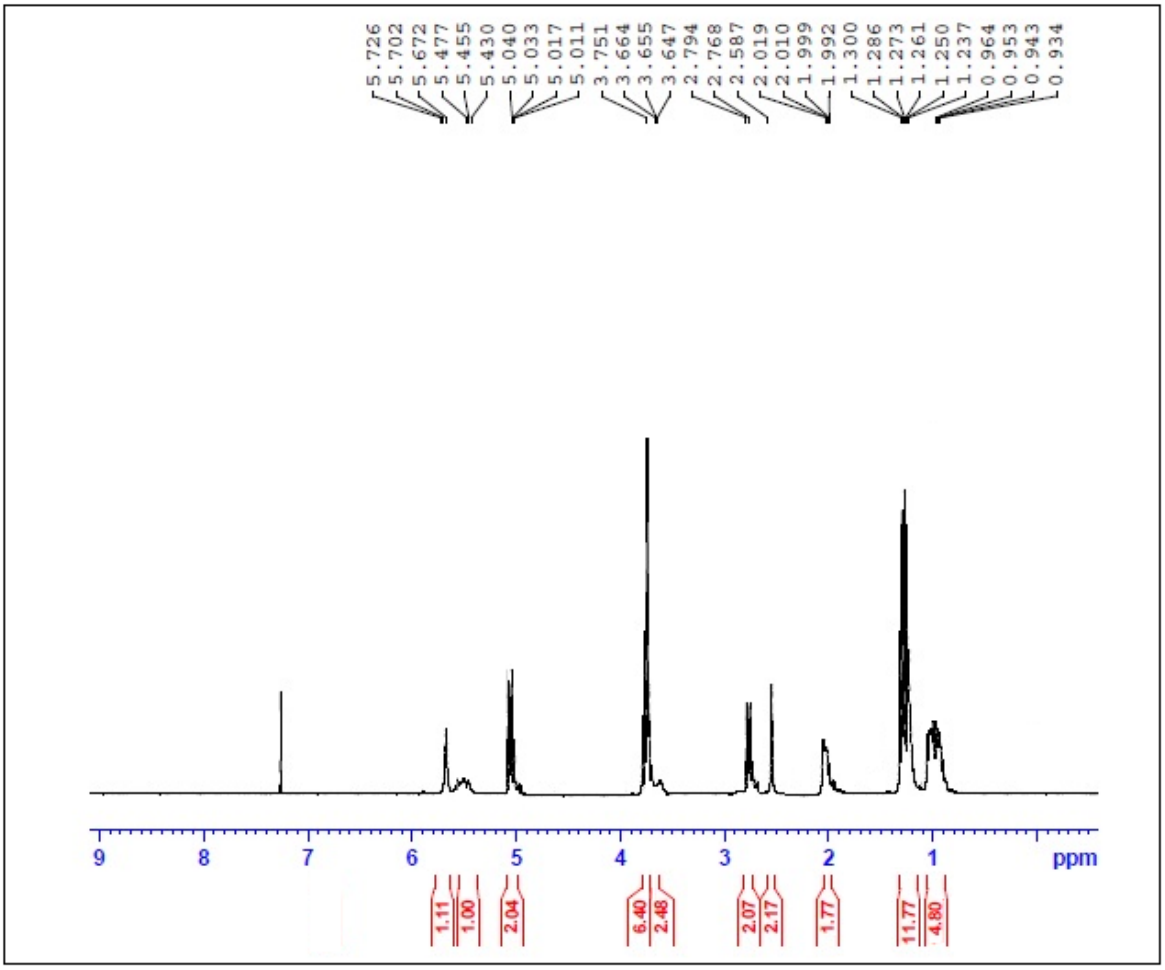

Figure S 9. ^{1}H NMR (300 MHz, $CDCl_3$) of **3d**

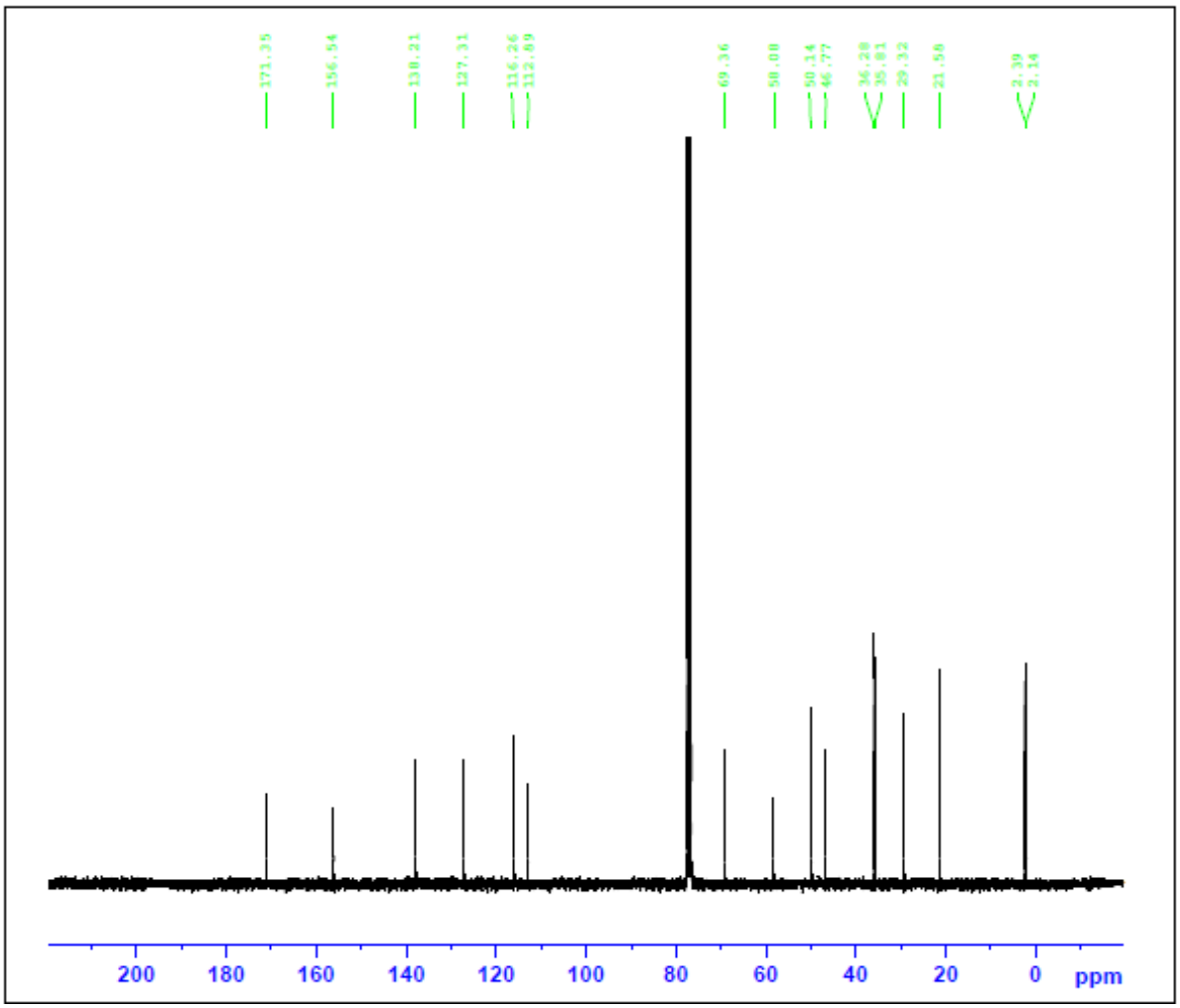

Figure S 10. ^{13}C NMR (75 MHz, $CDCl_3$) of **3d**

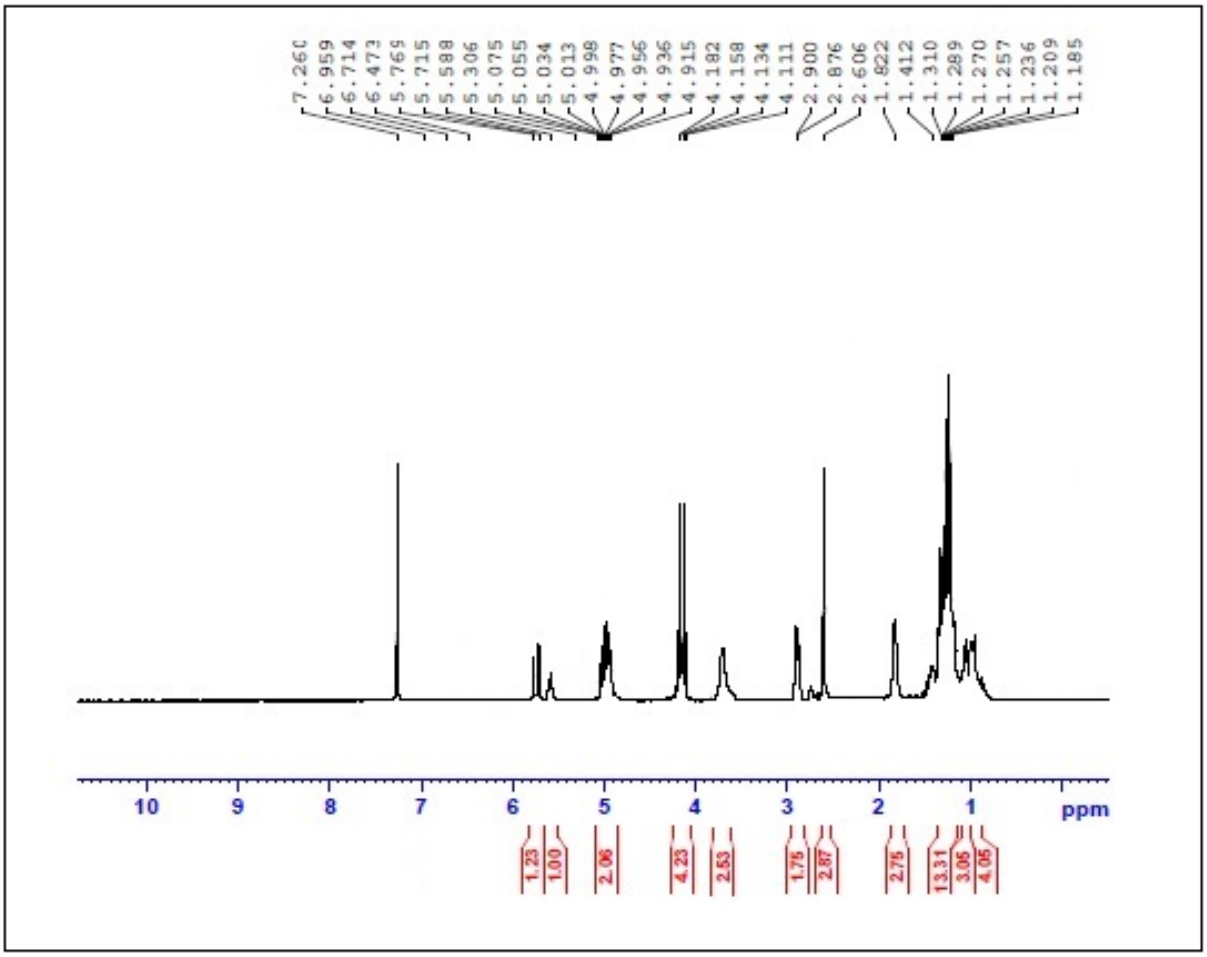

Figure S 11. ^{1}H NMR (300 MHz, $CDCl_3$) of **3e**

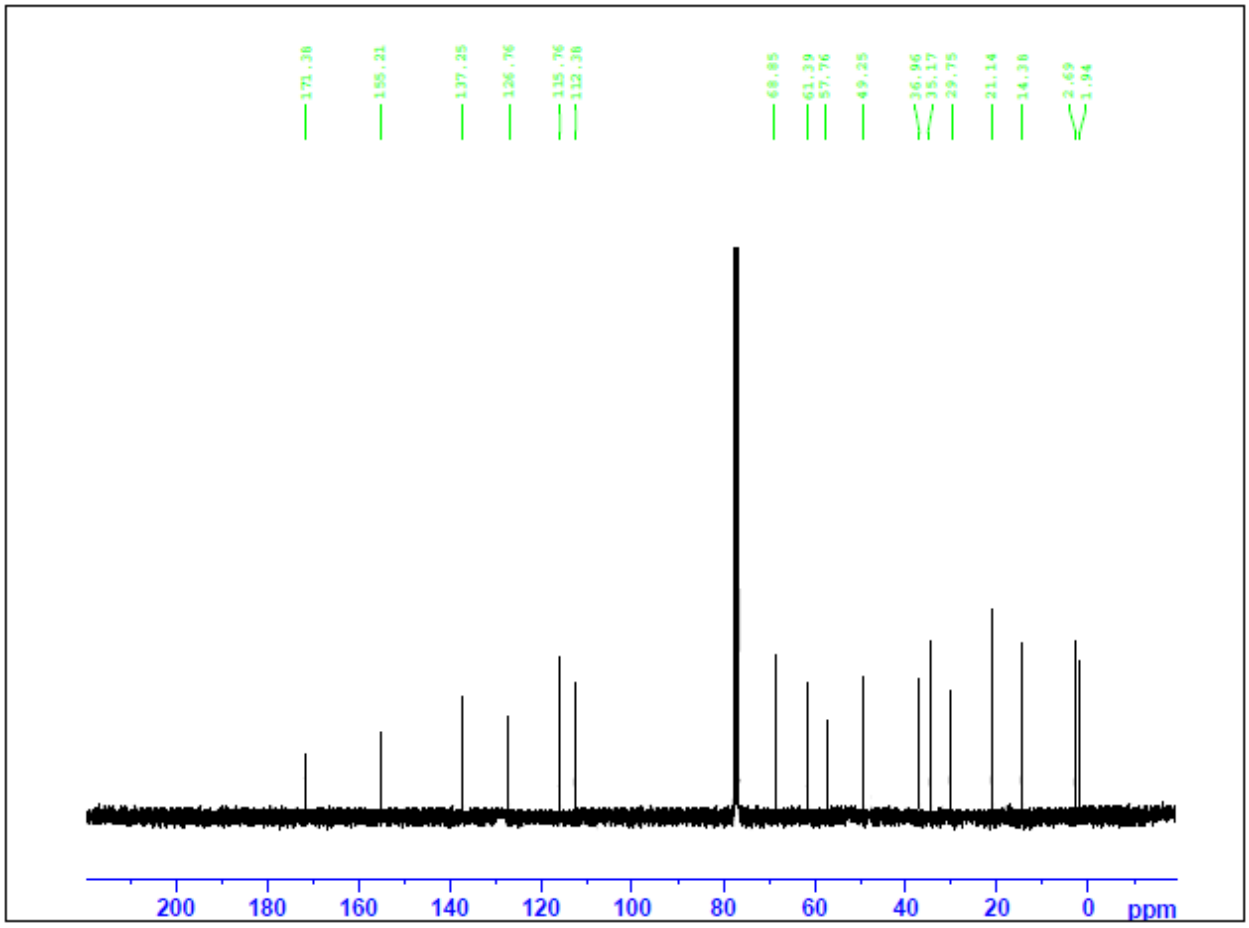

Figure S 12. ^{13}C NMR (75 MHz, $CDCl_3$) of **3e**