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1,2,3-Triazole ferrocenyldendrimers through click chemistry approach and their optical and electrochemical properties

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Supplementary Material

EXPERIMENTAL

Materials method

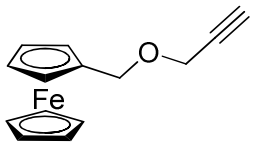
All the reagents and solvents employed were of the best grade available and were used without further purification. The melting points were determined using a Toshniwal melting point apparatus by open capillary tube method and were uncorrected. 1H NMR and 13C NMR spectra were recorded on BRUKER 300 MHz instruments. Tetramethylsilane (TMS) was used as the internal standard. MS: EI-MS spectra on Jeol DX-303 mass spectrometer. The elemental analyses for the compounds were carried out using the Perkin-Elmer 240B elemental analyzer. Column chromatography was performed on silica gel (ACME, 100–200 mesh). Routine monitoring of the reaction was made using thin layer chromatography developed on glass plates coated with silica gel-G (ACME) of 25 mm thickness and visualized with iodine. The UV-Vis spectra were recorded on a Shimadzu 260 spectrophotometer.

General procedure for electrochemical studies

Cyclic voltammetric measurements were performed in a conventional three electrode system on CHI model 1100A series electrochemical analyzer (CH Instrument, Tennison Hill Drive, Austin, USA). Glassy carbon electrode (GCE) was used as working electrode with Pt foil (large surface area) and a silver-silver chloride (Ag/AgCl) as counter and reference electrodes, respectively. Prior to each electrochemical experiment, this GCE was mechanically polished with 0.05 micron alumina powder and cleaned in a 1 : 1 acetone/ethanol mixture in an ultrasonic bath to remove impurities, rinsed with water and then dried in air. Then the electrode was cleaned by cycling between the potentials of -1.5 to 1.2 V versus AgCl in 1 X 10^{-3} M of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in DMSO at a scan rate of 50 mV s^{-1} for approximately 30 min until reproducible scans were

recorded. All the electrochemical experiments were performed in a quiescent solution at room temperature (25 ± 1 ºC).

Ferrocenyl alkyne 7:

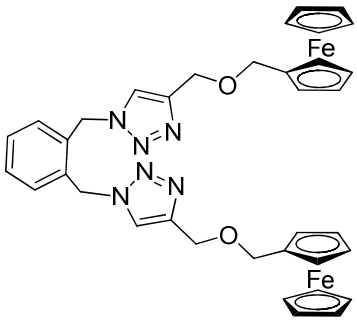


A mixture of the corresponding ferrocenyl alcohol **6** (2.0 g, 9.30 mmol), propargyl bromide (1.4 mL, 11.0 mmol) and NaH (0.45 g, 18.6 mmol) in mixture of DMF-toluene (1:4) was stirred at rt for 4 h. The mixture was poured into H_2O (100 mL) and extracted with EtOAc (2 X 100 mL). The organic layer was washed with saturated NaCl (100 mL), dried over Na_2SO_4, and the Pale yellow solid residue obtained was purified by column chromatography using chloroform: hexane (1:1) as eluting solvent. Yield: 83%; mp.: 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.38 (t, J = 1.8 Hz, 1H), 4.05, 4.08, 4.09 (m, 9H; Cp), 4.18 (s, 2H), 4.32 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, (67.5, 67.6, Cp), 68.5, 73.3, 78.9 ppm. MS (EI): *m/z* 254 (M^+). Elemental Anal.Calcd for $C_{14}H_{14}FeO$: C, 66.17; H, 5.55 %. Found: C, 66.00; H, 5.51 %.

General procedure for the Cu-Catalyzed Huisgen 'Click reaction'

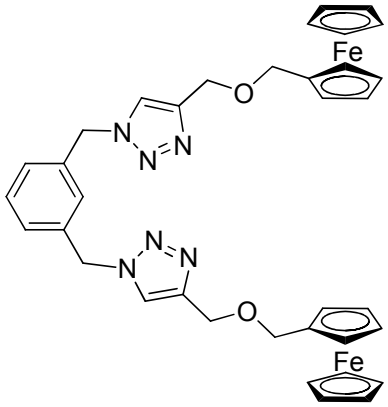
A mixture of azide, alkyne and $CuSO_4.5H_2O$ (5 mol %) /NaAsc (10 mol %) mixture in THF/H_2O (1:1, 20 mL) was stirred for 12 h at room temperature. The residue obtained after evaporation of the solvent was dissolved in $CHCl_3$ (150 mL) and washed with brine (150 mL), water (100 mL), dried over Na_2SO_4 and evaporated to give the crude triazole, which was purified by column chromatography (SiO_2).

Ferrocenyldendrimer 1a:



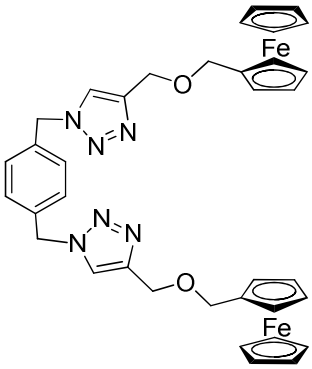
Pale yellow solid; yield: 86%; mp.: 111-113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.12, 4.22 (m, 18H; Cp), 4.36 (s, 4H), 4.58 (s, 4H), 5.57 (s, 4H), 7.22-7.26 (m, 4H), 7.41 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.6, 63.3, (68.6, 69.0, 69.6, Cp), 82.7, 122.4, 128.8, 130.2, 135.3, 146.1 ppm. MS (EI): *m/z* 696 (M^+). Elemental Anal.Calcd for $C_{36}H_{36}Fe_2N_6O_2$: C, 62.09; H, 5.21; N, 12.07 %. Found: C, 61.93; H, 5.20; N, 11.98 %.

Ferrocenyldendrimer 1b:



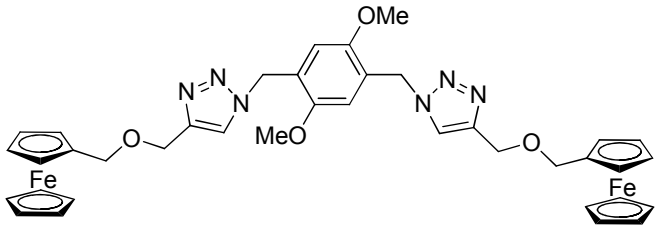
Pale yellow solid; yield: 88%; mp.: 111-113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.11, 4.14, 4.23 (m, 18H; Cp), 4.31 (s, 4H), 4.59 (s, 4H), 5.47 (s, 4H), 7.20-7.27 (m, 4H), 7.47 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.5, 63.3, (68.6, 69.0, 69.7, Cp), 82.6, 122.4, 128.3, 128.9, 135.3, 146.4 ppm. MS (EI): *m/z* 696 (M^+). Elemental Anal.Calcd for $C_{36}H_{36}Fe_2N_6O_2$: C, 62.09; H, 5.21; N, 12.07 %. Found: C, 62.01; H, 5.25; N, 11.92 %.

Ferrocenyldendrimer 1c:



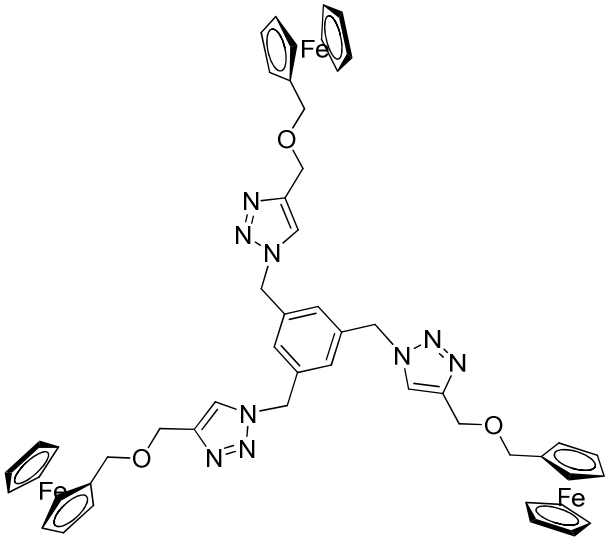
Pale yellow solid; yield: 92%; mp.: 128-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.11, 4.14, 4.22 (m, 18H; Cp), 4.36 (s, 4H), 4.59 (s, 4H), 5.48 (s, 4H), 7.18-7.24 (m, 4H), 7.40 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.6, 63.3, (68.6, 69.0, 69.6, Cp), 82.8, 122.4, 128.8, 135.3, 146.1 ppm. MS (EI): *m/z* 696 (M^+). Elemental Anal.Calcd for $C_{36}H_{36}Fe_2N_6O_2$: C, 62.09; H, 5.21; N, 12.07 %. Found: C, 61.90; H, 5.11; N, 11.96 %.

Ferrocenyldendrimer 2:



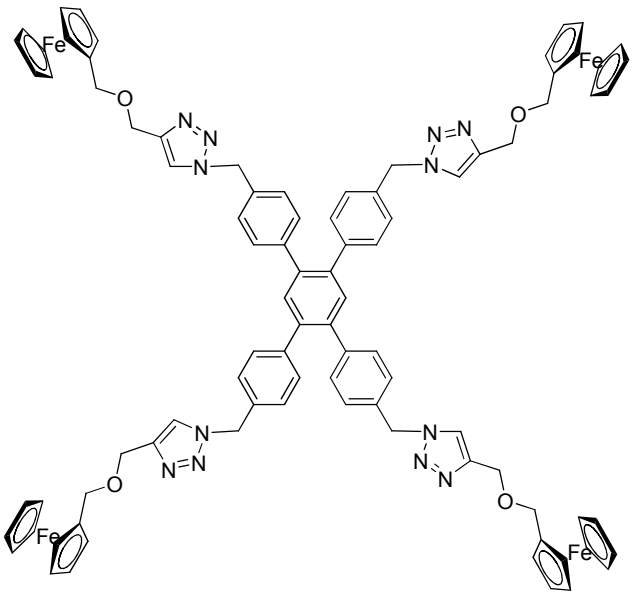
Pale yellow solid; yield: 77%; mp.: 78-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.78 (s, 6H), 4.11, 4.14, 4.22 (m, 18H; Cp), 4.35 (s, 4H), 4.58 (s, 4H), 5.48 (s, 4H), 6.89 (s, 2H), 7.50 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.7, 56.1, 63.3, (68.4, 68.6, 68.8, 69.5, Cp), 82.8, 113.3, 122.8, 124.3, 129.2, 146.8, 151.1 ppm. MS (EI): *m/z* 756 (M^+). Elemental Anal.Calcd for $C_{38}H_{40}Fe_2N_6O_4$: C, 60.34; H, 5.33; N, 11.11 %. Found: C, 60.23; H, 5.19; N, 11.02 %.

Ferrocenyldendrimer 3:



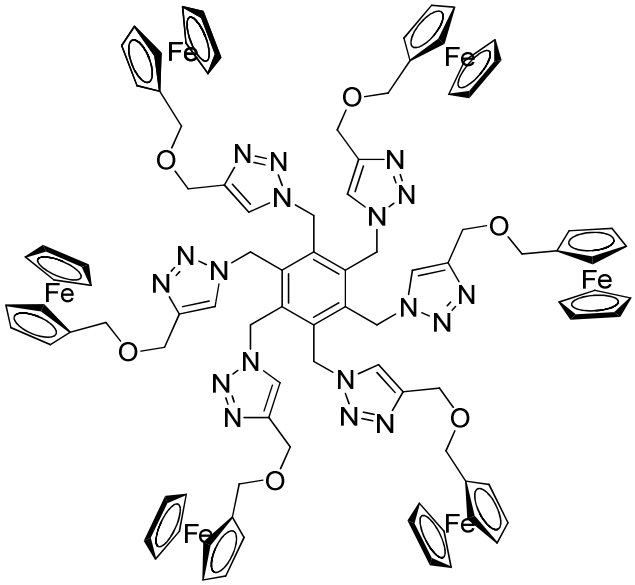
Pale yellow solid; yield: 90%; mp.: 81-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.12, 4.15, 4.23 (m, 27H; Cp), 4.38 (s, 6H), 4.59 (s, 6H), 5.40 (s, 6H), 7.08 (s, 3H), 7.41 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.3, 63.2, (68.5, 68.7, 69.1, 69.6, Cp), 82.8, 122.6, 127.6, 136.8, 146.2 ppm. MS (EI): *m/z* 1005 (M^+). Elemental Anal.Calcd for $C_{51}H_{51}Fe_3N_9O_3$: C, 60.92; H, 5.11; N, 12.54 %. Found: C, 60.80; H, 5.07; N, 12.41 %.

Ferrocenyldendrimer 4:



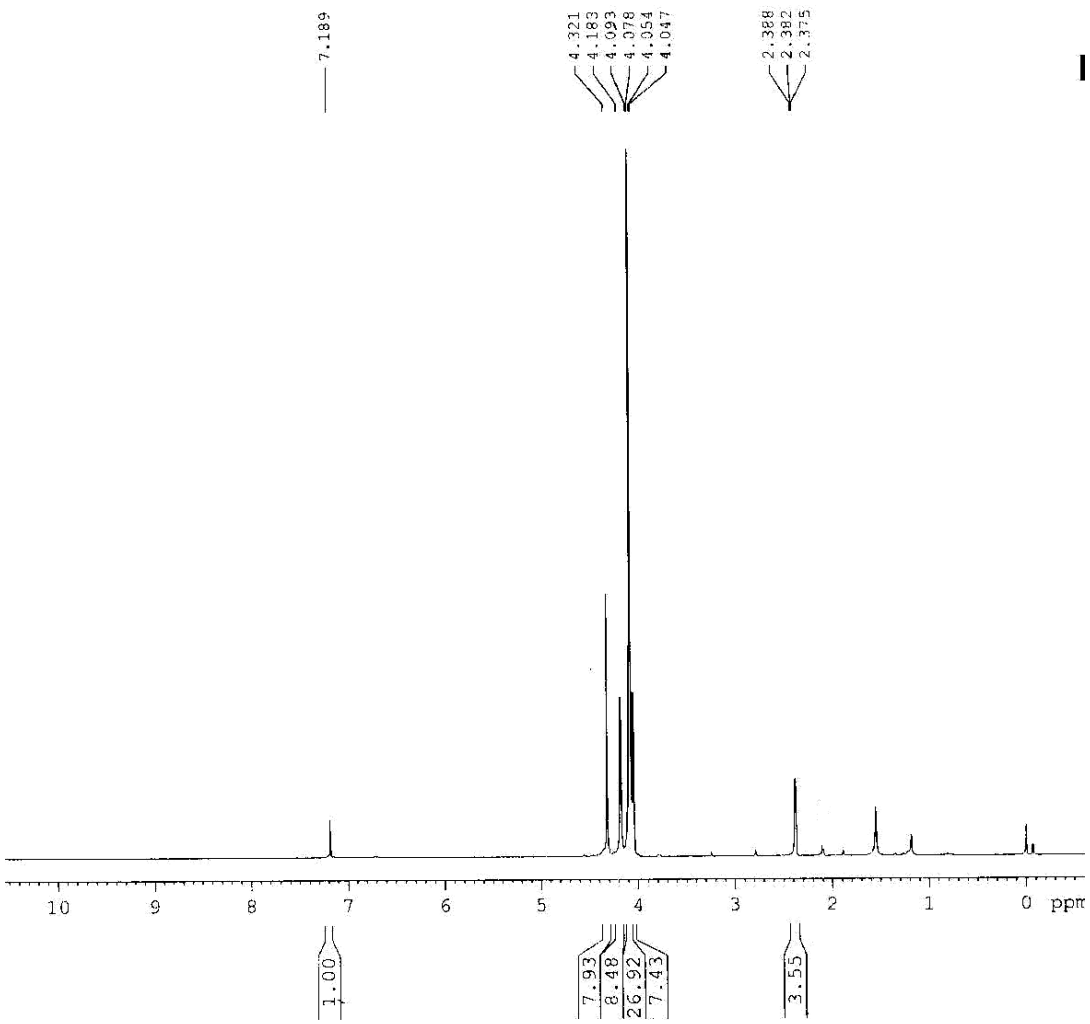
Pale yellow solid; yield: 81%; mp.: 98-100 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.11, 4.22 (m, 36H; Cp), 4.38 (s, 8H), 4.61 (s, 8H), 5.45 (s, 8H), 6.96-7.13 (m, 16H), 7.40 (s, 2H), 7.56 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.7, 63.1, (68.5, 68.7, 69.6, Cp), 82.8, 122.5, 122.8, 126.6, 127.9, 129.6, 130.4, 145.9 ppm. MS (EI): *m/z* 1667 (M^+). Elemental Anal.Calcd for $C_{93}H_{94}Fe_4N_{12}O_4$: C, 67.00; H, 5.68; N, 10.08 %. Found: C, 66.90; H, 5.57; N, 9.99 %.

Ferrocenyldendrimer 5:

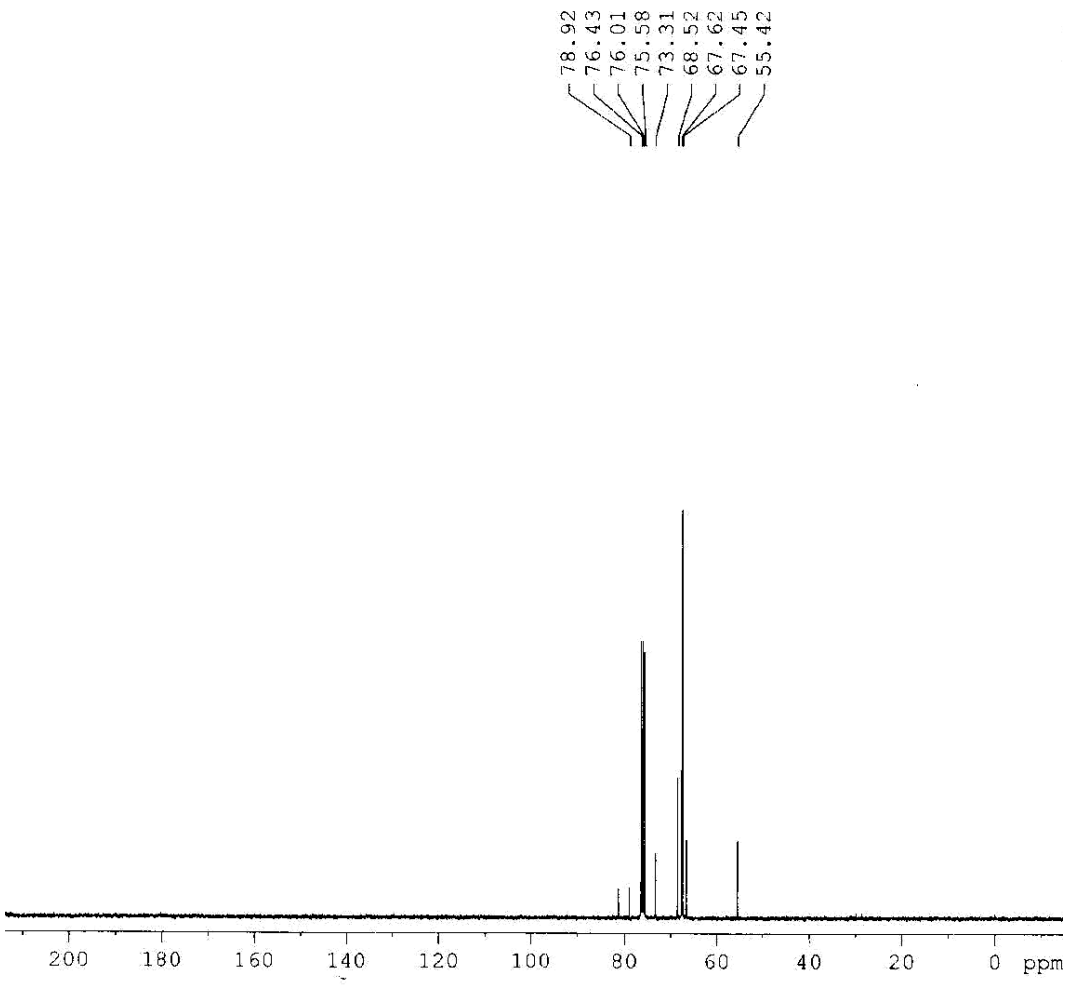


Pale yellow solid; yield: 81%; mp.: 98-100 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 3.92, 4.02 (m, 54H; Cp), 4.18 (s, 12H), 4.22 (s, 12H), 5.60 (s, 12H), 7.14 (s, 6H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 42.5, 57.5, (63.2, 63.2, 63.6, 64.3, Cp), 77.5, 117.9, 132.4, 140.5 ppm. MS (EI): *m/z* 2063 (M^+). Elemental Anal.Calcd for $C_{106}H_{106}Fe_6N_{18}O_6$: C, 61.71; H, 5.18; N, 12.22 %. Found: C, 61.60; H, 5.04; N, 12.23 %.

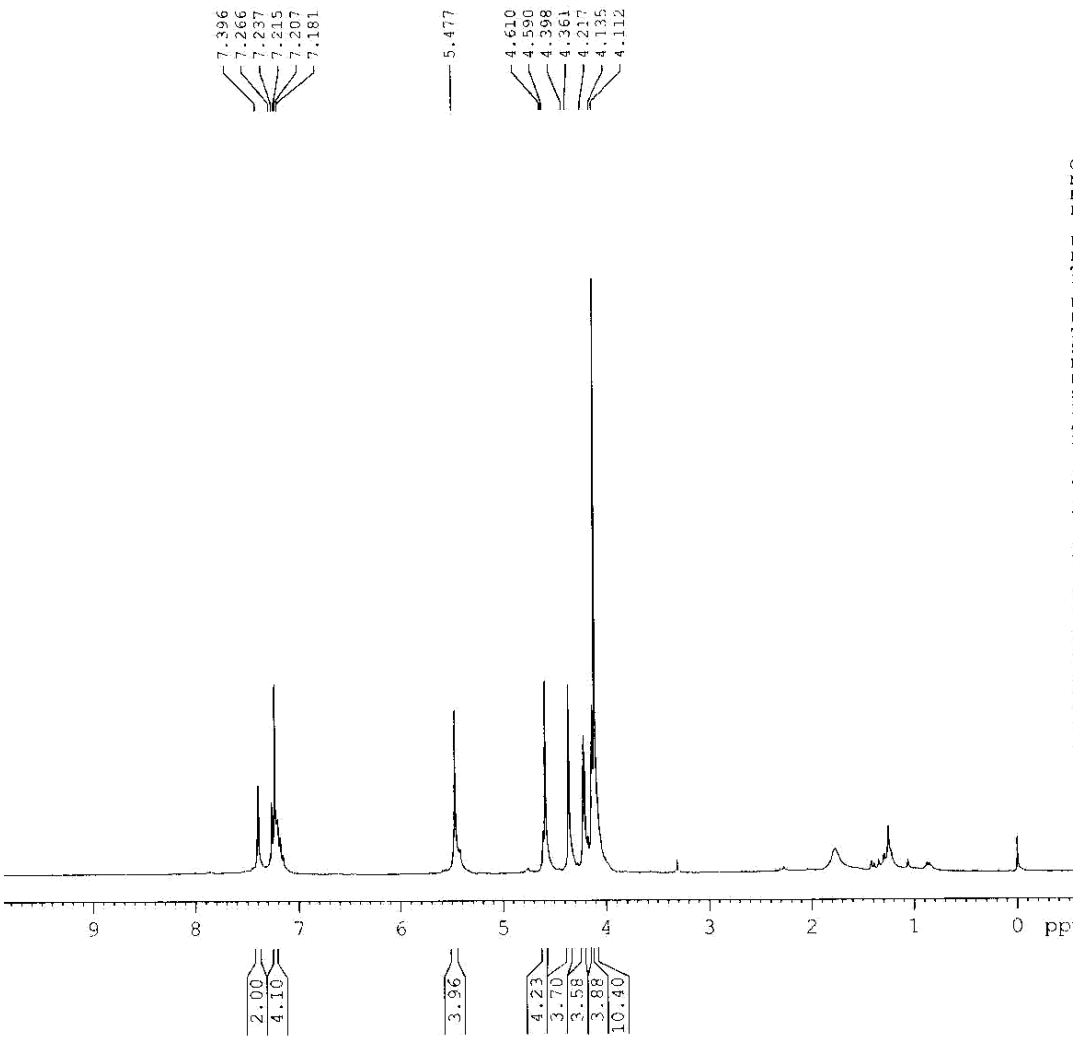
^{1}H and ^{13}C NMR Spectra of Synthesized Compounds



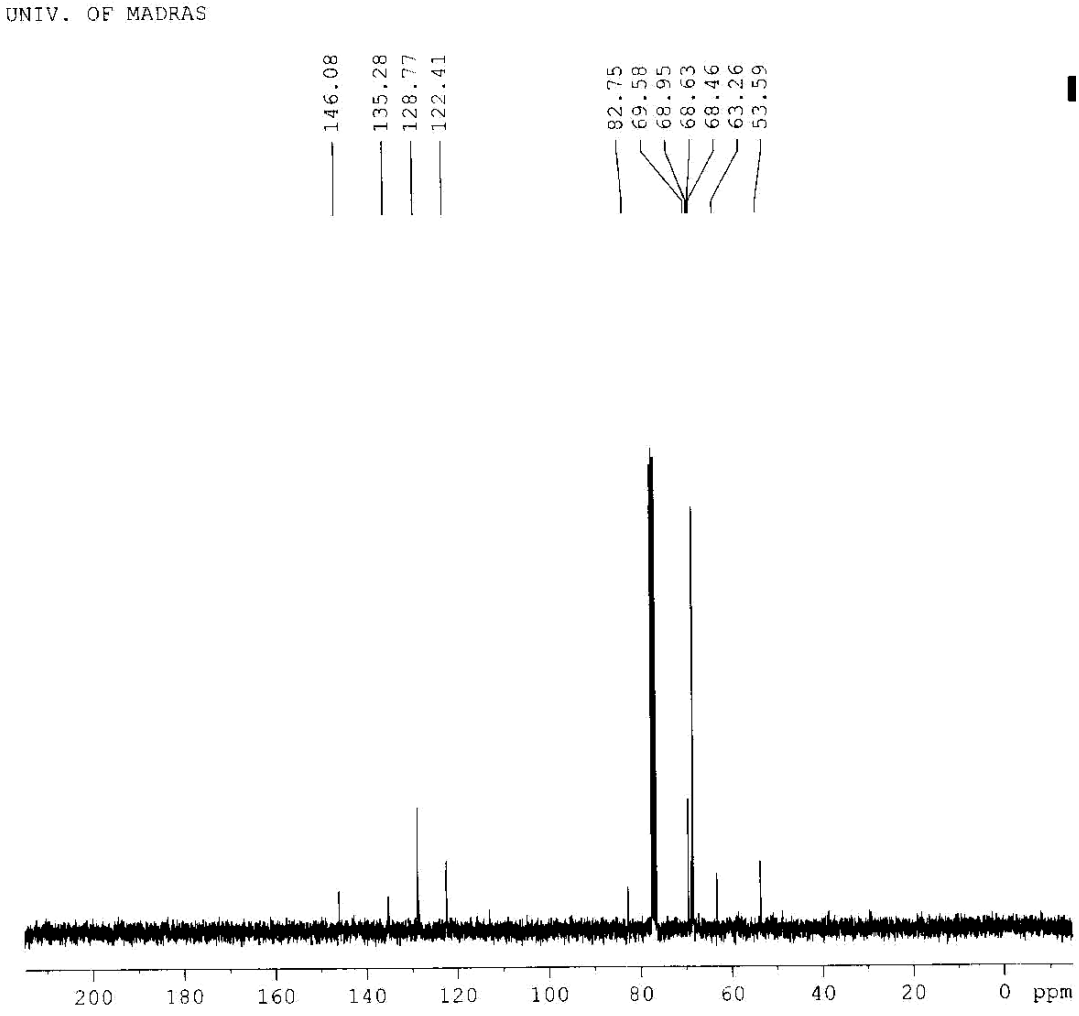
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ferrocenyl alkyne 7



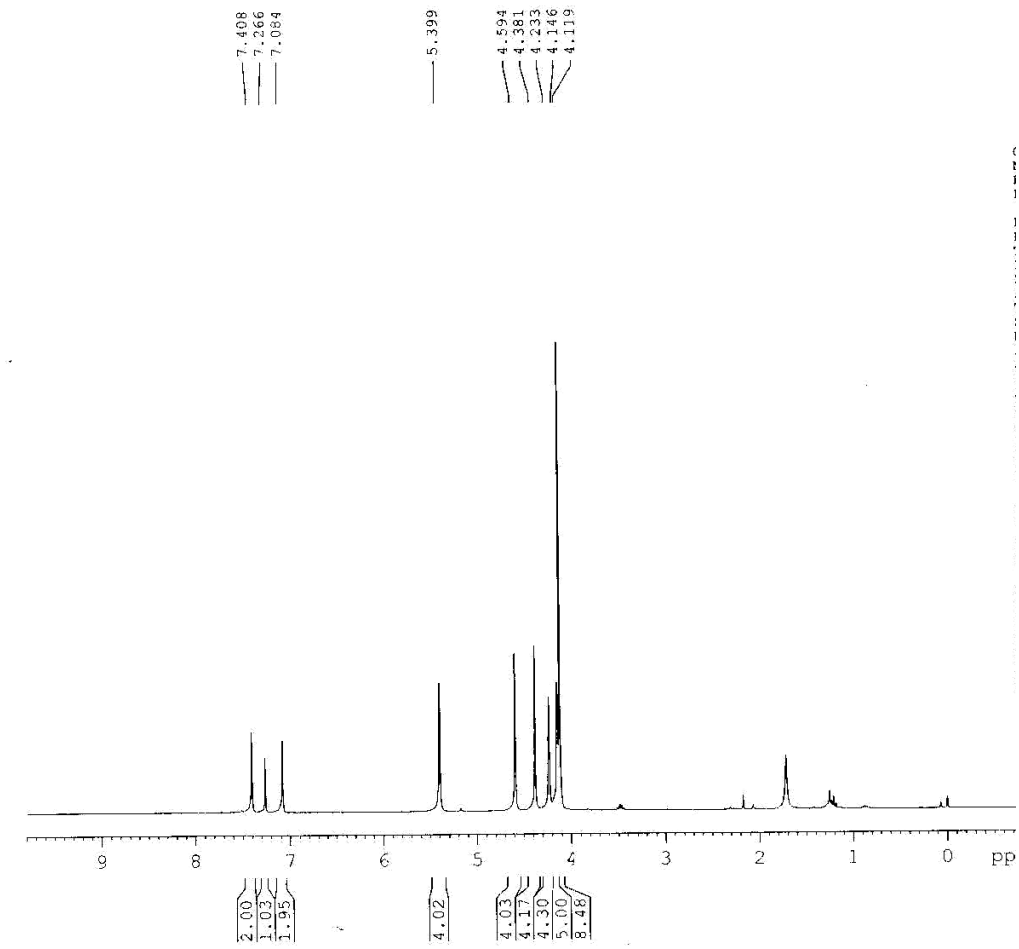
^{13}C NMR (300 MHz, $CDCl_3$) spectrum of ferrocenyl alkyne 7



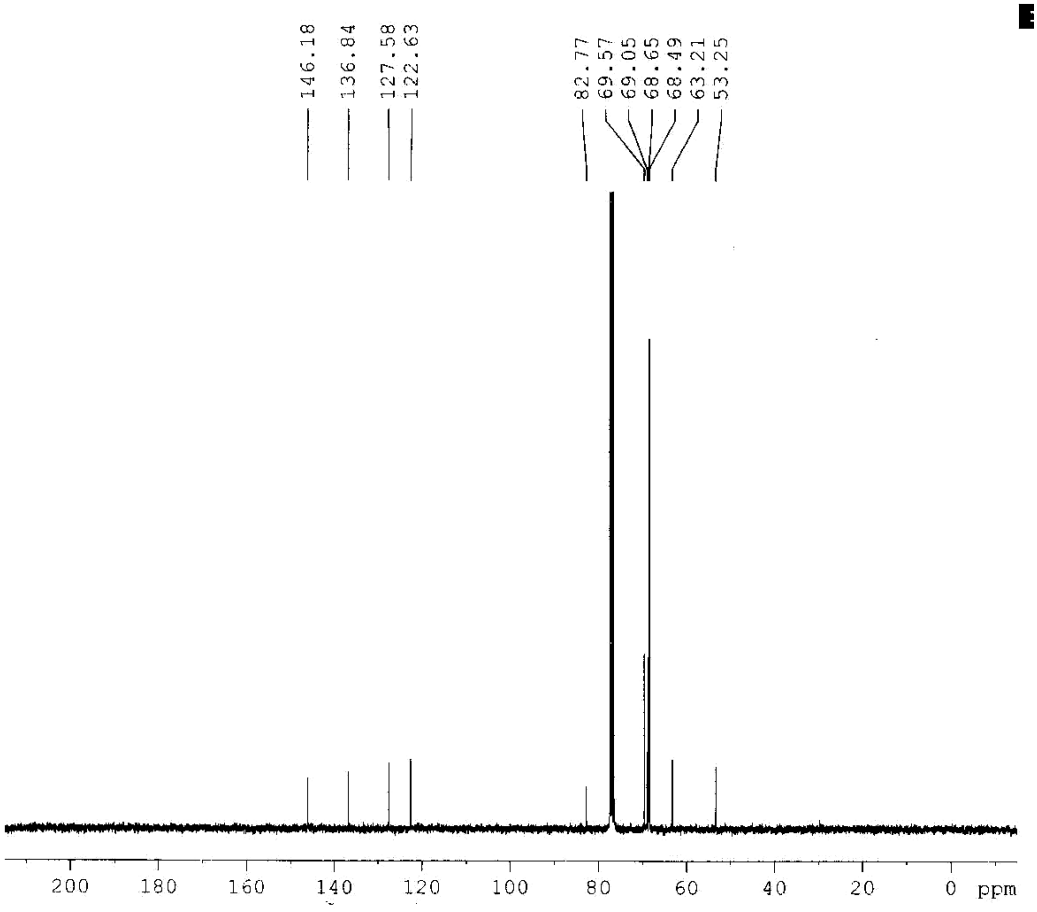
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ferrocenyldendrimer 1c



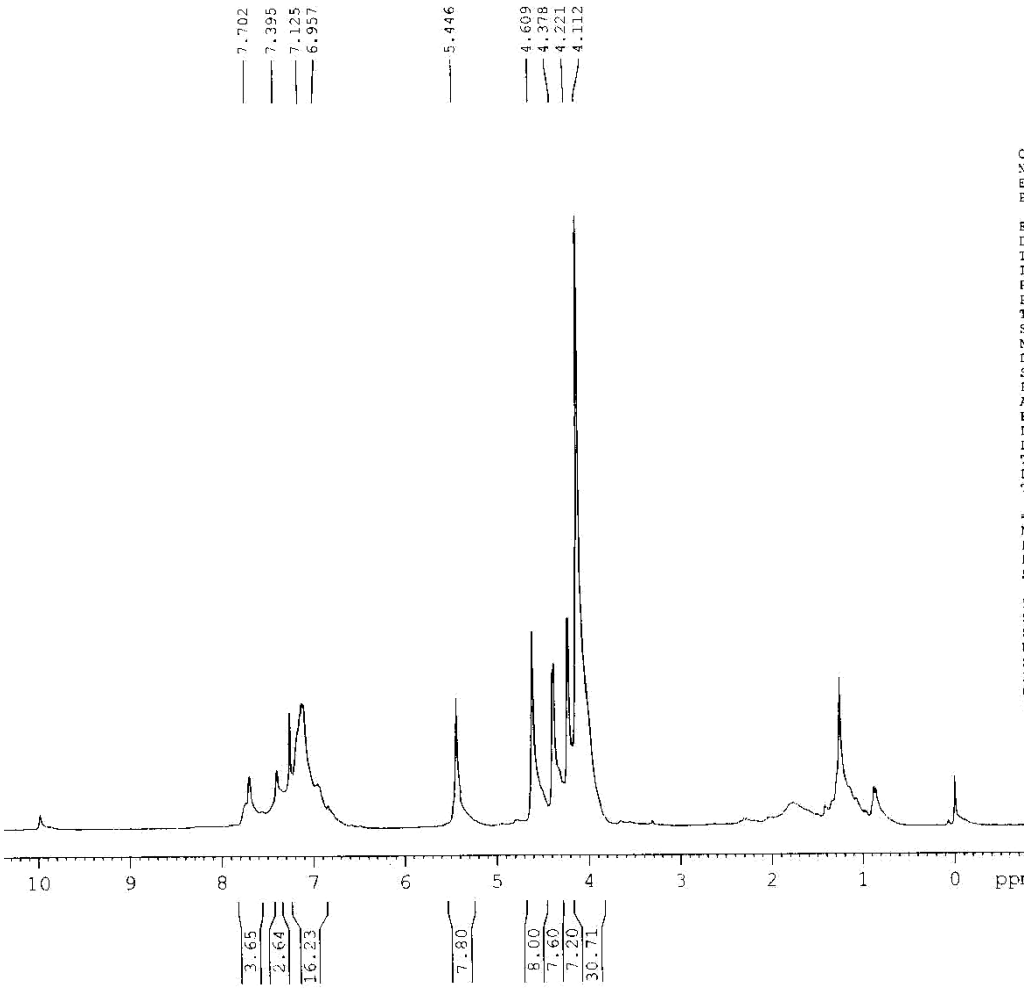
^{13}CH NMR (75 MHz, $CDCl_3$) spectrum of co ferrocenyldendrimer 1c



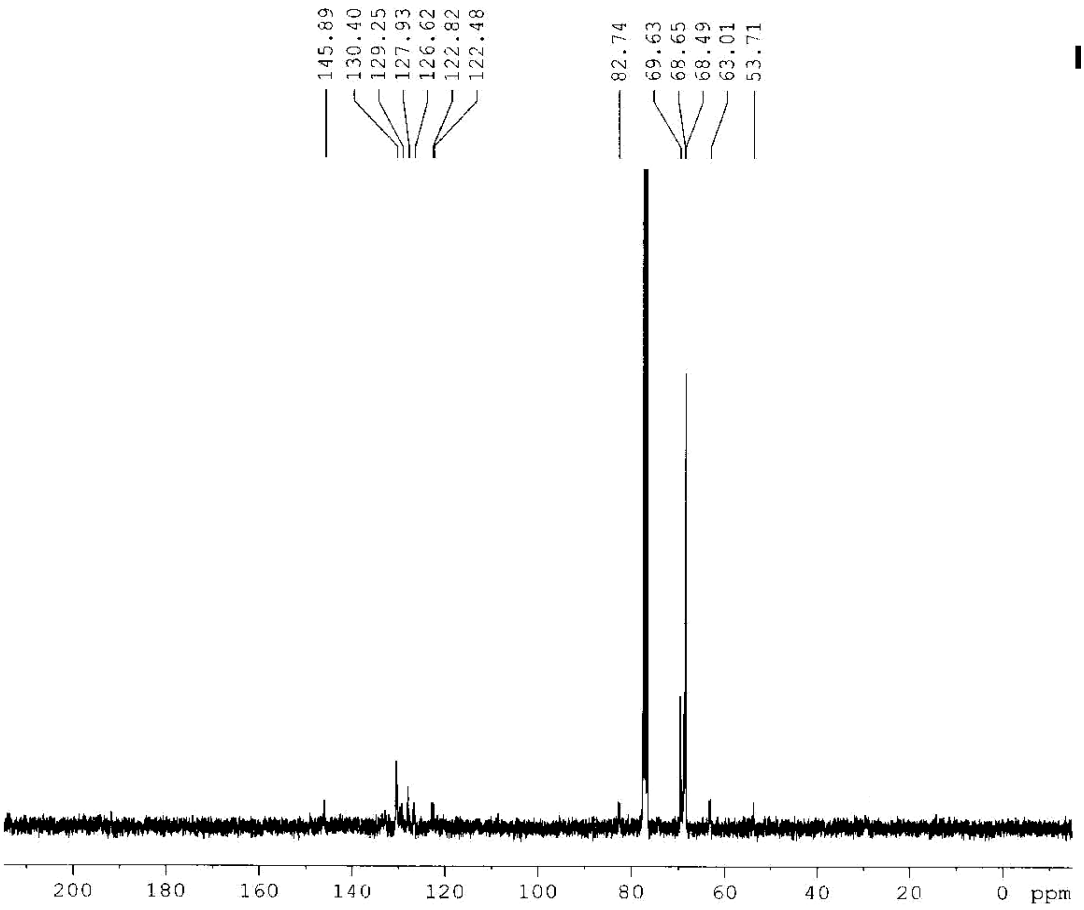
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ferrocenyldendrimer 3



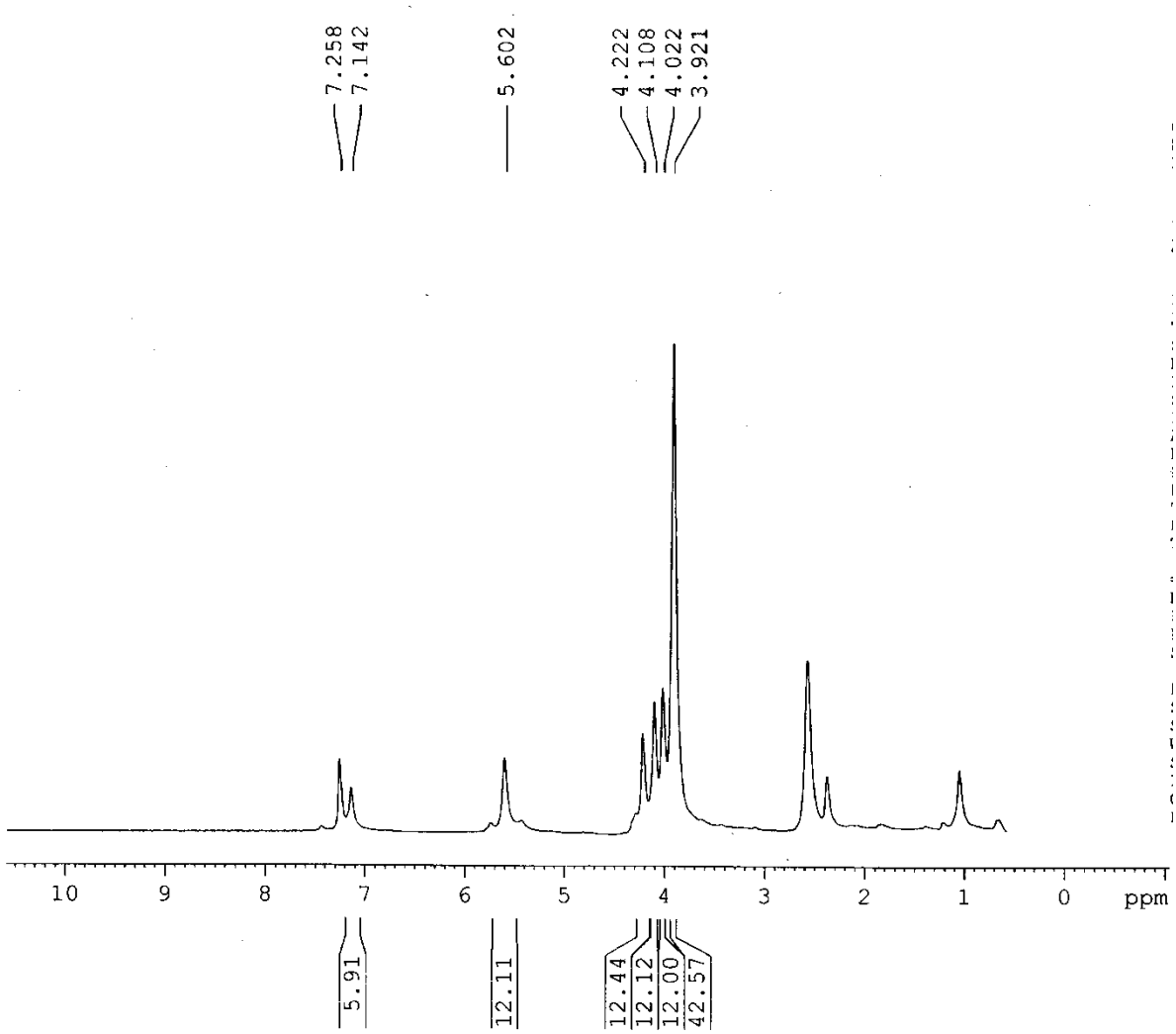
^{13}CH NMR (75 MHz, $CDCl_3$) spectrum of ferrocenyldendrimer 3



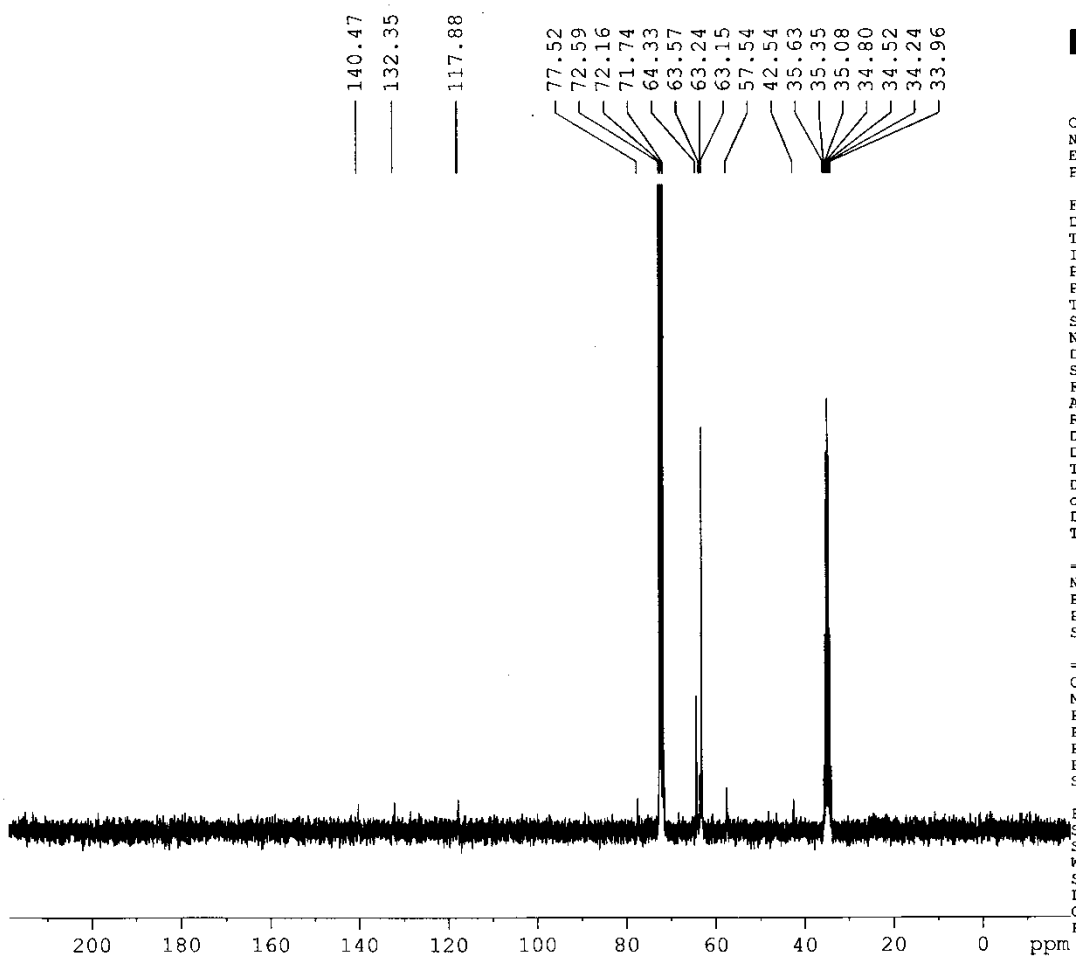
^{1}H NMR ($CDCl_3$) spectrum of ferrocenyldendrimer 4



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ferrocenyldendrimer 4



^{1}H NMR (300 MHz, DMSO-d_6) spectrum of ferrocenyldendrimer 5



^{13}C NMR (75 MHz, DMSO-d_6) spectrum of ferrocenyldendrimer 5