Electronic Supplementary Information

A Catalytic Hydroesterification Process Using HCO_2Na, $Ru_3(CO)_{12}$ and Alcohols for Preparing Ester Modified Polybutadienes

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1. General

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Advance II/DPX 400(400 MHz ^{1}H, 100 MHz ^{13}C) spectrometers and chemical shifts are reported relative to residual deuterated solvent peaks. ^{1}H NMR spectra were referenced to CD_2Cl_2 (for ^{1}H, δ = 5.32 ppm) as an internal standard and are reported as chemical shift multiplicity: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (for ^{13}C, δ = 77.26 ppm) as internal standard. Infrared spectra were obtained on a Bruker Vertex70 spectrometer. Fluorescence spectra were obtained on a Perkin Elmer LS 55. Thermo Gravimetric Analysis (TGA) was carried out using a Perkin Elmer STA8000, with heating from 30 to 600 ℃ at a heating rate of 20 ℃/min. Differential Scanning Calorimetry (DSC) was carried out using a Perkin Elmer DSC 8000, with heating from -80 to 100 ^{o}C, in N_2 atmosphere, at a flow rate of 20 mL/min. Analytical GPC was performed on a JASCO HPLC equipped with HF-404HQ columns (ID. 4.6 X L. 250 mm, Shodex, Tokyo, Japan) using THF as the eluent at a flow rate of 1.0 ml/min.

2. Materials

Polybutadiene (**1**) which contains 45% vinyl, 5% *cis*-1,4 internal olefin, 10% *trans*-1,4 internal olefin and 40% saturated part was purchased from Aldrich and its average molecular weight is 1800. Most reagent grade chemicals [1,4-dioxane, acetonitrile, dichloromethane, **1**, **2a-c**, **3a**, **3b**, **3d-g**, **3i-k**, **4a**, **5a**, pyrene, ferrocene carboxaldehyde, cyclobutanecarboxylic acid, copper(II) perchlorate hexahydrate, zinc(II) perchlorate hexahydrate, calcium(II) perchlorate tetrahydrate, cadmium(II) perchlorate hydrate, magnesium(II) perchlorate, nickel(II) perchlorate hexahydrate and cobalt(II) perchlorate hexahydrate] were purchased from Aldrich, Acros Organics and TCI Chemical Company and used as received unless otherwise stated. Cyclobutylmethanol (**3c**) was prepared by reduction of cyclobutanecarboxylic acid using lithium aluminum hydride. Ferrocenylmethanol (**3h**) was prepared by reduction of ferrocene carboxaldehyde using lithium aluminum hydride. Pyrenylmethyl alcohol (**3l**) was prepared by Rieche formylation of pyrene followed by reduction of the resulting aldehyde using lithium aluminum hydride.

3. Experimental

- A typical procedure for synthesis of modified polybutadiene (Table 1, entry 1)

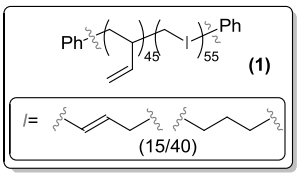
A 5 mL pressure vial was charged with polybutadiene (**1**, 50 mg, (0.416 mmol of vinyl group)), sodium formate (**2a**, 56.6 mg, (0.832 mmol)), 2-phenylethyl alcohol (**3a**, 61.0 mg, (0.499 mmol)), $Ru_3(CO)_{12}$ (**4a**, 13.4 mg, (0.02095 mmol)), 2-pyridinemethanol (**5a**, 9.1 mg, (0.0832 mmol)) and 1,4-dioxane (1 mL). The mixture was stirred at 150 ^oC for 6 h. After cooling to room temperature, the mixture was concentrated in vacuo, and the residue was washed thoroughly with methanol and dried to give the 2-phenylethyl ester containing modified polybutadiene (**6a**).

- A typical procedure for synthesis of modified polybutadiene with 1:1 ratio of mixed esters (Table 3, entry 1)

A 5 mL pressure vial was charged with polybutadiene (**1**, 50 mg, (0.416 mmol of vinyl group)), sodium formate (**2a**, 56.6 mg (0.832 mmol)), 2-phenylethyl alcohol (**3a**, 50.8 mg (0.416 mmol)), heptanol (**3b**, 48.3 mg (0.416 mmol)), $Ru_3(CO)_{12}$ (**4a**, 13.4 mg, (0.02095 mmol)), 2-pyridinemethanol (**5a**, 9.1 mg, (0.0832 mmol)) and 1,4-dioxane (1 mL). The mixture was stirred at 150 ^oC for 6 h. After cooling to room temperature, the mixture was concentrated in vacuo, and the residue was washed thoroughly with methanol and dried to give the 1:1 ratio of 2-phenylethyl and heptyl ester containing modified polybutadiene (**7a**).

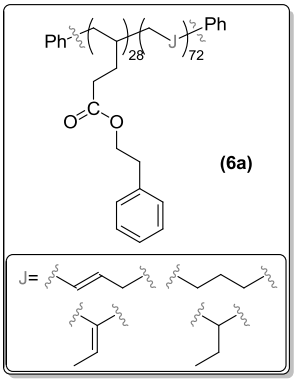
- Measurements of fluorescence spectra of 7l in the presence of various metal(II) cations

The fluorescence spectra were recorded following addition of various concentrations (0-40 x 10^{-6} M) of copper(II) perchlorate hexahydrate in acetonitrile (1 mL) into polybutadiene modified with pyrenylmethyl ester (**7l**) in 1 mL of dichloromethane (Figure 2a). Solutions of **7l** (5 x 10^{-6} M, based on pyrenylmethyl ester group in modified polybutadiene) in 1 mL of dichloromethane were independently treated with 40 x 10^{-6} M of metal(II) perchlorates (Zn^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+}) in 1 mL of acetonitrile. Fluorescence spectra of the mixtures were then recorded.

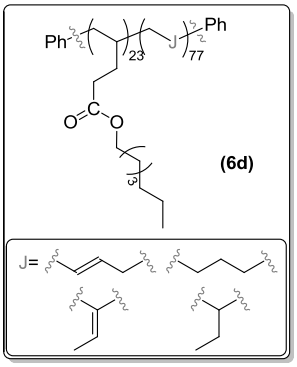


Polybutadiene (1): 45% of vinyl and 55% of internal olefins and saturated hydrocarbons based on terminal phenyl; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.24 (br m), 7.18 (br m), 5.86-5.77 (br m), 5.60-5.58 (br m), 5.39-5.31 (br m), 4.97 (br m), 2.66-2.64 (br m), 2.53 (br m), 2.38 (br s), 2.04 (br m), 1.54 (br m), 1.45 (br m), 1.43 (br m), 1.29 (br m), 0.91 (br m), 0.68 (br m), 0.66 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.4, 143.8, 143.4, 143.2, 142.9, 131.9, 130.8, 130.3, 130.2, 129.8, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 125.9, 125.8, 114.5, 114.4, 114.1, 113.1, 112.2, 111.9, 45.5, 44.0, 43.8, 12.6, 41.8, 41.3, 41.0, 40.5, 39.8, 39.5, 39.3, 39.1, 38.9, 38.4, 37.7, 36.2, 36.1, 35.8, 34.5, 34.4, 34.2, 33.7, 33.0, 32.5, 32.2, 31.6, 30.6, 30.4, 27.8, 27.6, 25.8, 25.2; IR spectrum ($CDCl_3$) 3076, 2999, 2974, 2918, 2854,

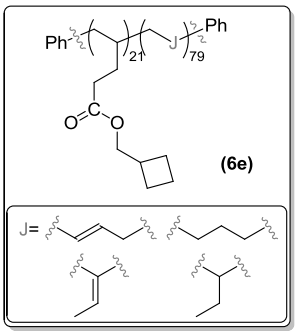
1825, 1639, 1605, 1496, 1453, 1417, 1379, 1348, 1294, 1265, 1077, 995, 968, 909, 741, 698, 679 cm^{-1}; T_d = 454 ^oC; T_g = -30.2 ^oC; M_n = 2702, M_w = 5843, PDI = 2.16.



2-Phenylethyl ester-containing modified polybutadiene (6a): 28% of 2-phenylethyl ester and the rest (72%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (72% yield, 73.9 mg); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.28-7.24 (br m), 5.18-5.10 (br m, internal -CH=CH-), 4.26 (br s), 2.93 (br s), 2.58 (br s), 2.26 (br s), 1.99 (br s), 1.68 (br s), 1.58(br s), 1.28 (br m), 0.98 (br s), 0.85 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2 (CO), 138.0, 130.5, 129.8, 129.0, 128.6, 127.7, 126.7, 64.9, 37.1, 36.7, 35.3, 33.1, 32.8, 32.4, 32.0, 29.89, 28.4, 27.8, 27.4, 13.7, 13.4, 12.9, 11.9; IR spectrum ($CDCl_3$) 2926, 2855, 2097, 1977, 1945, 1735, 1670, 1497, 1455, 1378, 1260, 1164, 747, 699 cm^{-1}; T_d = 306 ^oC, 415 ^oC; T_g = -11.2 ^oC; M_n = 4716, M_w = 10868, PDI = 2.30.

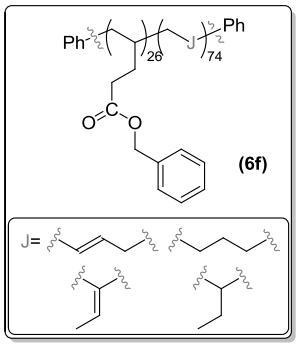


Heptyl ester-containing modified polybutadiene (6d): 23% of heptyl ester and the rest (77%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (88% yield, 90.1 mg); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 (br s), 7.16 (br s), 5.38-5.09 (br m, internal -CH=CH-), 4.02 (br s), 2.57 (br s), 2.27 (br s), 1.98 (br s), 1.58 (br s), 1.28 (br m), 0.96 (br s), 0.89 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4 (CO), 128.5, 64.6, 32.8, 32.6, 31.9, 29.9, 29.1, 28.8, 28.4, 26.1, 22.8, 14.3, 13.5, 13.1, 12.9; IR spectrum ($CDCl_3$) 2959, 2926, 2856, 2047, 1978, 1947, 1737, 1456, 1378, 1254, 1167, 1066, 968, 874, 758, 699 cm^{-1}; T_d = 254 ^oC, 396 ^oC; T_g = -23.4 ^oC; M_n = 4778, M_w = 11869, PDI = 2.48.

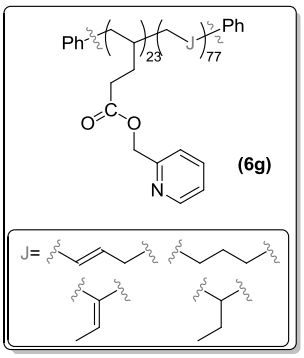


Methylcyclobutyl ester-containing modified polybutadiene (6e): 21% of methylcyclobutyl ester and the rest (79%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (84% yield, 82.0 mg); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 (br s), 7.17 (br s), 5.32-5.10 (br m, internal -CH=CH-), 4.01 (br s), 2.60 (br s), 2.29 (br s), 1.99 (br m), 1.77 (br m), 1.57 (br s), 1.27 (br m), 0.96 (br s), 0.85 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4 (CO), 13.05, 128.4, 125.7, 68.3, 38.9, 37.2, 35.4, 34.3, 33.2, 32.8, 32.1, 31.7, 30.4, 29.9, 28.4, 27.8, 26.9, 26.0, 24.9, 23.2, 18.6, 14.3; IR spectrum ($CDCl_3$) 2926, 2856, 2061, 2028, 1990, 1946, 1737, 1670, 1457, 1378, 1290, 1251, 1217, 1168, 1100, 969, 910, 807, 758, 699, 667 cm^{-1}; T_d = 257 ^oC, 406 ^oC; T_g = -16.5 ^oC; M_n = 4062, M_w = 8184, PDI = 2.01.

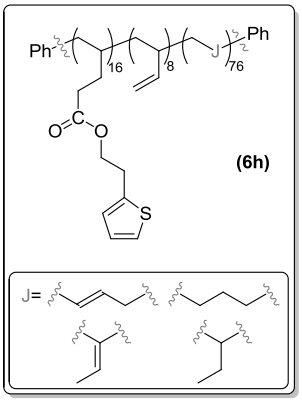
Benzyl ester-containing modified polybutadiene (6f): 26% of benzyl ester and the rest (74%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (86% yield, 84.9 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 (br s), 7.19 (br m), 5.41-5.11 (br m, internal -CH=CH-), 2.60 (br s), 2.36 (br s), 2.01 (br s), 1.59 (br s), 1.30 (br s), 0.99 (br m) 0.87 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8 (CO), 136.2, 128.6, 128.3, 66.2, 38.2, 37.1, 36.7, 35.9, 33.2, 32.8, 32.4, 30.3, 29.8, 28.7, 28.3, 27.7, 27.4, 13.4, 13.1, 12.9; IR spectrum ($CDCl_3$) 3032, 2959, 2925, 2855, 2047, 1976, 1738, 1493, 1453, 1379, 1258, 1156, 968, 882, 750, 697 cm^{-1}; T_d = 308 ^{o}C, 405 ^{o}C; T_g = -13.1 ^{o}C; M_n = 4447, M_w = 10372, PDI = 2.33.



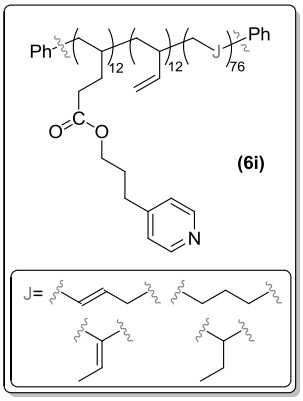
2-Pyridylmethyl ester-containing modified polybutadiene (6g): 23% of 2-pyridylmethyl ester and the rest (77%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (80% yield, 80.1 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (br s), 7.70 (br s), 7.34 (br s), 7.22 (br s), 5.32-5.19 (br m, internal -CH=CH-), 2.60 (br m), 2.42 (br m), 1.99 (br m), 1.58 (br s), 1.28 (br m), 0.97 (br s), 0.86 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (CO), 156.1, 149.5, 141.0, 136.7, 130.4, 128.4, 125.9, 125.6, 123.6, 122.8, 121.8, 66.7, 38.8, 38.3, 37.1, 36.7, 36.1, 32.3, 32.7, 32.3, 31.9, 30.2, 29.8, 29.6, 28.6, 28.3, 27.8, 26.8, 25.9, 13.6; IR spectrum ($CDCl_3$) 2925, 2855, 2046, 2026, 1974, 1943, 1740, 1666, 1633, 1594, 1573, 1454, 1378, 1265, 1240 1156, 1048, 969, 881, 755, 700 cm^{-1}; T_d = 296 ^{o}C, 415 ^{o}C; T_g = -10.0 ^{o}C; M_n = 5059, M_w = 11142, PDI = 2.20.



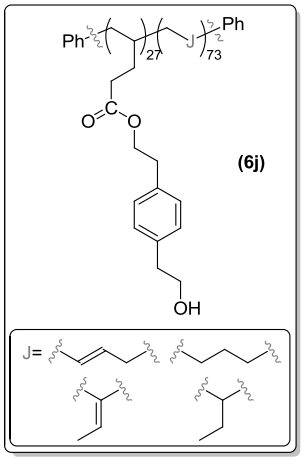
2-Thiopheneethyl ester-containing modified polybutadiene (6h): 16% of 2-thiopheneethyl ester, 8% of vinyl and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (73% yield, 78.6 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.25 (br s), 7.16 (br s), 6.94 (br s), 6.87 (br s), 5.39-5.20 (br m, internal -CH=CH-), 4.95 (br m, vinyl -CH=CH_2), 4.26 (br s), 3.14 (br s), 2.70 (br m), 2.63 (br s), 2.30 (br m), 1.98 (br s), 1.56 (br s), 1.27 (br m), 0.95 (br s), 0.85 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8 (CO), 140.0, 128.4, 126.9, 125.5, 124.0, 64.5, 44.6, 41.0, 38.9, 37.1, 36.7, 32.7, 32.3, 31.9, 30.7, 29.8, 29.4, 28.6, 28.3, 27.8, 26.8, 25.9, 23.1, 14.3; IR spectrum ($CDCl_3$) 2925, 2855, 2073, 2047, 1997, 1975, 1921, 1738, 1454, 1379, 1244, 1217, 1164, 1079, 1039, 969, 851, 823, 759, 695, 560, 504 cm^{-1}; T_d = 391 ^{o}C; T_g = 18.0 ^{o}C; M_n = 4254, M_w = 8926, PDI = 2.10.



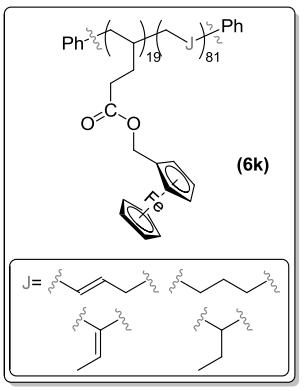
4-Pyridylpropyl ester-containing modified polybutadiene (6i): 12% of 4-pyridylpropyl ester, 12% of vinyl and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (71% yield, 80.4 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.45 (br s), 7.23 (br s), 7.17 (br s), 7.12 (br s), 5.39-5.18 (br m, internal -CH=CH-), 4.95 (br m, vinyl -CH=CH_2) 4.06 (br s), 2.68 (br s), 2.30 (br s), 1.97 (br s), 1.78 (br m), 1.56 (br s), 0.85 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2 (CO), 150.3, 140.9, 130.5, 129.9, 128.5, 124.0, 63.4, 32.8, 31.7, 29.8, 29.3, 28.3, 27.8, 27.4, 26.8, 13.4, 12.8, 12.0, 11.7; IR spectrum ($CDCl_3$) 2921, 2855, 2041, 2022, 1999, 1971, 1938, 1732, 1604, 1573, 1462, 1378, 1218, 1167, 1069, 1028, 995, 969, 880, 838, 798, 769, 700, 666 cm^{-1}; T_d = 318 °C, 415 °C; The polymer showed no obvious glass transition between -80 and 100 °C; M_n = 4071, M_w = 7526, PDI = 1.85.



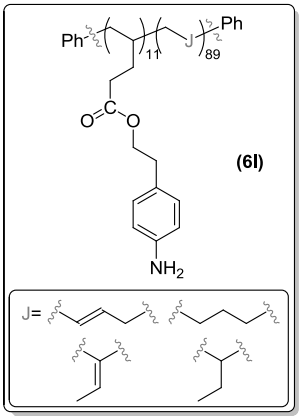
4-(2-Hydroxyethyl)phenethyl ester-containing modified polybutadiene (6j): 27% of 4-(2-hydroxyethyl)phenethyl ester and the rest (73%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (70% yield, 77.9 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.16 (br m), 5.32-5.10 (br m, internal -CH=CH-), 4.23 (br s), 3.79 (br s), 2.89-2.81 (br m), 2.59 (br s), 2.27 (br s), 1.99 (br s), 1.57 (br s), 1.27 (br s), 0.97 (br s), 0.85 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (CO), 136.9, 135.9, 129.2, 129.1, 128.4, 64.9, 63.6, 38.9, 34.8, 32.7, 32.4, 32.0, 29.8, 28.6, 28.3, 13.4, 13.1, 12.8, 12.0, 11.6; IR spectrum ($CDCl_3$) 2925, 2855, 2047, 2020, 1997, 1973, 1934, 1736, 1604, 1515, 1456, 1377, 1264, 1162, 1114, 1048, 1022, 968, 811, 761, 738, 699 cm^{-1}; T_d = 304 °C, 412 °C; T_g = 4.3 °C; M_n = 4881, M_w = 12821, PDI = 2.63.



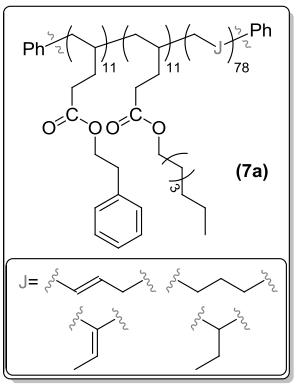
Ferrocenylmethyl ester-containing modified polybutadiene (6k): 19% of ferrocenylmethyl ester and the rest (81%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (83% yield, 97.2 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.29 (br m) 7.21 (br m), 5.32-5.13 (br m, internal -CH=CH-), 4.92 (br s), 4.29 (br s), 4.19 (br m), 2.65 (br s), 2.31 (br s), 2.00 (br s), 1.60 (br s), 1.29 (br m), 0.99 (br s), 0.87 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9 (CO), 139.9, 138.8, 131.7, 130.4, 128.4, 81.4, 69.6, 68.8, 68.6, 62.7, 39.0, 37.0, 32.7, 29.7, 28.2, 13.3, 12.8, 12.0; IR spectrum ($CDCl_3$) 2960, 2925, 2855, 2047, 2024, 1973, 1941, 1737, 1603, 1567, 1455, 1377, 1288, 1217, 1155, 1107, 1041, 1001, 968, 874, 818, 758, 698, 637 cm^{-1}; T_d = 223 °C, 409 °C; The polymer showed no obvious glass transition between -80 and 100 °C; M_n = 4453, M_w = 9396, PDI = 2.11.



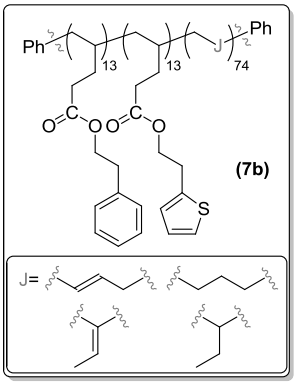
4-Amino-2-phenylethyl ester-containing modified polybutadiene (6l): 11% of 4-amino-2-phenylethyl ester and the rest (89%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (64% yield, 74.6 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26 (br s), 7.17 (br s), 6.98 (br s), 6.60 (br s), 5.39-5.10 (br m, internal -CH=CH-), 4.17 (br s), 3.64 (br s), 2.79 (br s), 2.60 (br m), 2.27 (br m), 1.98 (br m), 1.74 (br s), 1.67 (br s), 1.57 (br s), 1.27 (br s), 0.97-0.84 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2 (CO), 145.1, 129.9, 128.5, 127.7, 120.3, 115.4, 65.3, 38.8, 37.2, 34.4, 32.8, 32.1, 29.8, 28.4, 13.5, 12.9, 12.0; IR spectrum ($CDCl_3$) 3464, 3375, 3286, 2925, 2856, 2023, 2002, 1974, 1937, 1733, 1625, 1518, 1455, 1379, 1265, 1165, 1049, 968, 909, 822, 767, 700 cm^{-1}; T_d = 308 ^{o}C, 418 ^{o}C; T_g = 18.0 ^{o}C; M_n = 4056, M_w = 8470, PDI = 2.09.



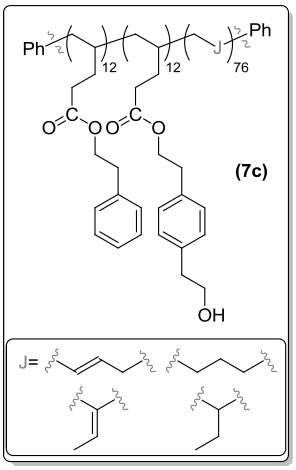
2-Phenylethyl ester and heptyl ester-containing modified polybutadiene (7a): 11% of 2-phenylethyl ester, 11% of heptyl ester and the rest (78%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (83% yield, 82.9 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27 – 7.23 (br m), 5.32-5.09 (br m, internal -CH=CH-), 4.25 (br s), 4.02 (br s), 2.92 (br s), 2.57 (br s), 2.26 (br s), 1.98 (br s), 1.58 (br s), 1.27 (br s), 0.97 (br s), 0.89-0.84 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (CO), 137.9, 129.0, 128.6, 126.6, 64.8, 64.5, 38.7, 36.7, 35.3, 33.3, 32.8, 31.9, 30.7, 30.3, 29.9, 29.1, 28.8, 28.3, 27.8, 26.9, 26.0, 22.7, 14.2; IR spectrum ($CDCl_3$) 3027, 2959, 2926, 2855, 2073, 2047, 1997, 1977, 1922, 1737, 1662, 1605, 1455, 1378, 1250, 1166, 1049, 1032, 969, 881, 758, 699, 667, 644, 560 cm^{-1}; M_n = 4736, M_w = 10811, PDI = 2.28.



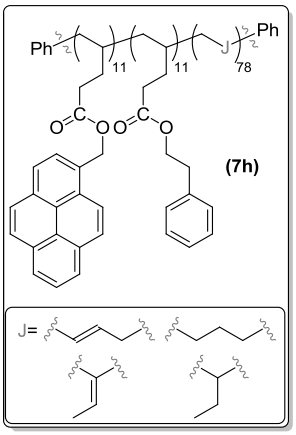
2-Phenylethyl ester and 2-thiopheneethyl ester containing modified polybutadiene (7b): 13% of 2-phenylethyl ester, 13% of 2-thiopheneethyl ester and the rest (74%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (54% yield, 55.2 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27-7.16 (br m), 6.93 (br s), 6.86 (br s), 5.38-5.10 (br m, internal -CH=CH-), 4.25 (br s), 3.13 (br s), 2.91 (br s), 2.59 (br s), 2.29 (br s), 1.97 (br s), 1.56 (br s), 1.27 (br s), 0.97 (br m), 0.83 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0 (CO), 140.1, 137.9, 129.0, 128.6, 128.5, 126.9, 126.6, 125.6, 124.1, 64.9, 64.6, 35.3, 33.3, 32.8, 32.4, 32.0, 30.3, 29.9, 29.5, 28.3, 27.8, 26.9, 25.9, 13.5, 13.1, 12.9; IR spectrum ($CDCl_3$) 3027, 2958, 2925, 2855, 2046, 2027, 1995, 1977, 1941, 1737, 1666, 1605, 1564, 1455, 1379, 1246, 1217, 1162, 969, 851, 824, 758, 698 cm^{-1}; M_n = 4642, M_w = 9841, PDI = 2.12.



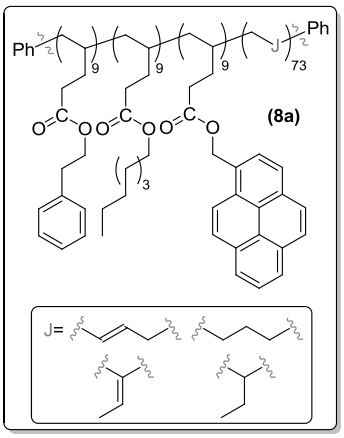
2-Phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (7c): 12% of 2-phenylethyl ester, 12% of 4-(2-hydroxyethyl)phenethyl ester and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (88% yield, 95.0 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30-7.17 (br m), 5.39-5.10 (br m, internal -CH=CH-), 4.24 (br s), 3.80 (br s), 2.90 (br s), 2.83-2.80 (br m), 2.27 (br m), 1.98 (br s), 1.68 (br s), 1.58 (br s), 1.27 (br s), 0.98 (br m), 0.85-0.84 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (CO), 141.1, 138.0, 136.9, 136.0, 129.3, 129.2, 129.0, 128.6, 126.7, 64.9, 63.7, 38.9, 37.1, 36.7, 35.3, 34.9, 33.3, 32.8, 32.5, 32.1, 30.3, 29.9, 28.4, 27.8, 26.9, 26.0, 13.5, 13.2; IR spectrum ($CDCl_3$) 3418, 2927, 2856, 2049, 1980, 1940, 1734, 1666, 1565, 1515, 1498, 1454, 1383, 1251, 1170, 1032, 969, 757, 699, 645 cm^{-1}; M_n = 3943, M_w =9017, PDI = 2.29.



2-Phenylethyl ester and pyrenyl methyl ester-containing modified polybutadiene (7h): 11% of 2-phenylethyl ester, 11% of pyrenyl methyl ester and the rest (78%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (84% yield, 91.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (br s), 8.18-8.16 (br m), 8.07 (br m), 7.22 (br s), 5.83 (br s), 5.43-5.08 (br m, internal -CH=CH-), 4.27 (br s), 2.93 (br s), 2.58 (br s), 2.31 (br m), 1.96 (br s), 1.68 (br s), 1.57 (br s), 1.25 (br s), 0.97 (br m), 0.83 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (CO), 138.0, 131.8, 131.3, 130.8, 130.5, 129.6, 129.0, 128.6, 128.4, 128.2, 127.9, 127.5, 126.7, 126.2, 125.6, 125.5, 124.9, 124.7, 123.0, 64.9, 64.7, 36.7, 35.3, 32.8, 32.5, 32.1, 29.9, 28.3, 27.8, 23.1, 13.5, 13.1, 12.9, 12.0, 11.7; IR spectrum ($CDCl_3$) 2927, 2856, 2063, 1991, 1732, 1669, 1605, 1497, 1456, 1378, 1250, 1171, 1031, 969, 847, 768, 700, 667, 643, 623, 579, 520 cm^{-1}; M_n = 4041, M_w = 8372, PDI = 2.07.



2-Phenylethyl ester, heptyl ester and pyrenyl methyl ester-containing modified polybutadiene (8a): 9% of 2-phenylethyl ester, 9% of heptyl ester, 9% of pyrenyl methyl ester and the rest (73%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (95% yield, 101.3 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.29-8.22 (br m), 8.17-8.07 (br m), 7.29-7.24 (br m), 5.83 (br s), 5.39-5.11 (br m, internal -CH=CH-), 4.27 (br s), 4.04 (br s), 2.93 (br s), 2.59 (br s), 2.30 (br m), 2.00 (br s), 1.59 (br s), 1.29



(br s), 0.99 (br m), 0.90 (br m), 0.86 (br m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (CO), 137.9, 131.7, 131.2, 130.7, 129.5, 128.9, 128.5, 127.8, 127.3, 126.6, 126.1, 125.5, 124.9, 124.6, 122.9, 64.8, 64.6, 64.5, 38.9, 37.1, 35.2, 33.2, 32.7, 32.4, 31.8, 29.8, 29.0, 28.7, 28.3, 27.7, 26.7, 26.0, 23.0, 22.7, 14.2; IR spectrum ($CDCl_3$) 3029, 2923, 2855, 2073, 2046, 2017, 1997, 1969, 1935, 1734, 1604, 1553, 1496, 1455, 1379, 1264, 1247, 1165, 1064, 1031, 1004, 969, 846, 739, 701, 682 cm^{-1}; M_n = 4521, M_w = 10637, PDI = 2.35.

- Calculation of isolated yield of ester-containing modified polybutadiene

Weight of product polymer — *Weight ratio can be calculated by ^{1}H NMR spectroscopy.*

$$\textit{mole of modified polybutadiene (mmol)} = \frac{A\ mg \times (\textit{weight ratio of ester in modified polybutadiene})}{(1800\ mg/mmol \times 0.45) + (15 \times (\textit{incorporation rate}) \times B)\ mg/mmol}$$

*Average molecular weight of polybutadiene (**1**) is 1800. Polybutadiene (**1**) contains 45% vinyl. Molecular weight of vinyl groups is 810 (= 1800 × 0.45).*

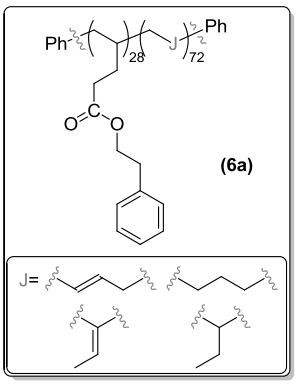
Number of vinyl group. There are fifteen vinyl groups. (= 810 / 54.09)

Increased molecular weight when one vinyl converts to one ester

Incorporation rate of ester group was calculated based on terminal phenyl in modified polybutadiene and calculated as:

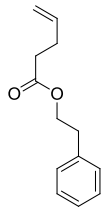
$$\frac{(\textit{ratio of ester group in modified polybutadiene})}{(45, \textit{vinyl}\%)}$$

<Calculation of isolated yield of 2-phenylethyl ester-containing modified polybutadiene (**6a**)>



Weight ratio can be calculated by ^{1}H NMR spectroscopy.

For example, 2-phenylethyl ester-containing modified polybutadiene (**6a**) contains 28% of 2-phenylethyl ester and 72% of reduced or isomerized or internal olefin part. Molecular weight of ester monomer is 204.26 g/mol and the remaining part monomer is 54.09 g/mol.



2-phenylethyl ester monomer
Molecular Weight: 204.26
28%

remaining part monomer
Molecular Weight: 54.09
72%

$$\textit{weight ratio of ester in modified polybutadiene} = \frac{204.26\ g/mol \times 0.28}{(204.26\ g/mol\ \times 0.28) + (54.09\ g/mol\ \times 0.72)}$$

$$= \ 0.595$$

The mole of 2-phenylethyl ester-containing modified polybutadiene (**6a**) :

$$\textit{mole of 2-phenylethyl ester-containing modified polybutadiene (6a) (mmol)} = \frac{73.9\ mg\ \times 0.595}{(1800\ mg/mmol\ \times 0.45)\ + (15\ \times 0.62 \times 149.16)\ mg/mmol}$$

$$= \frac{43.9705\ mg}{810\ mg/mmol + 1387.188\ mg/mmol}$$

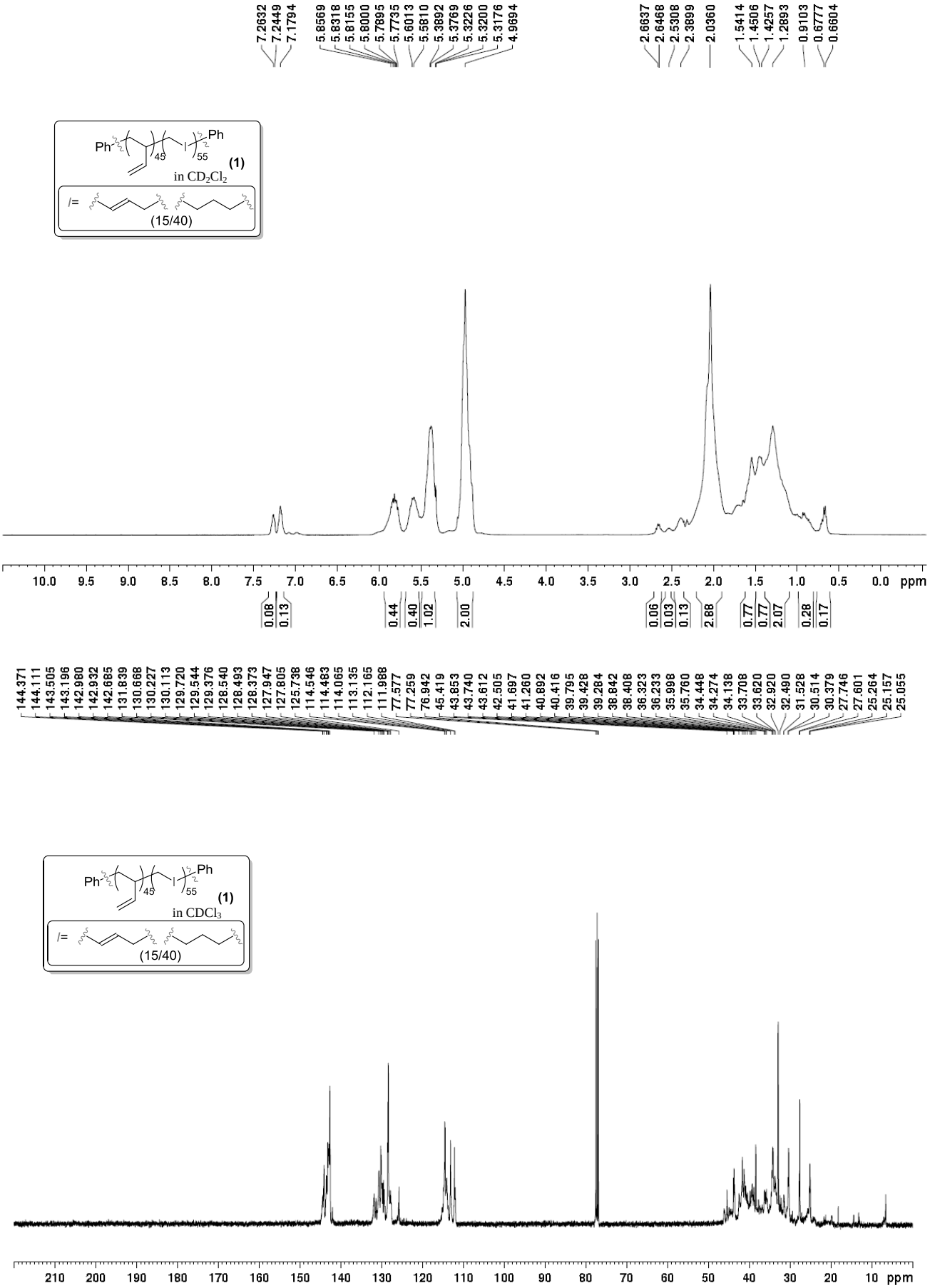
$$= \frac{43.9705\ mg}{2197.19\ mg/mmol} \ = 0.02001\ mmol$$

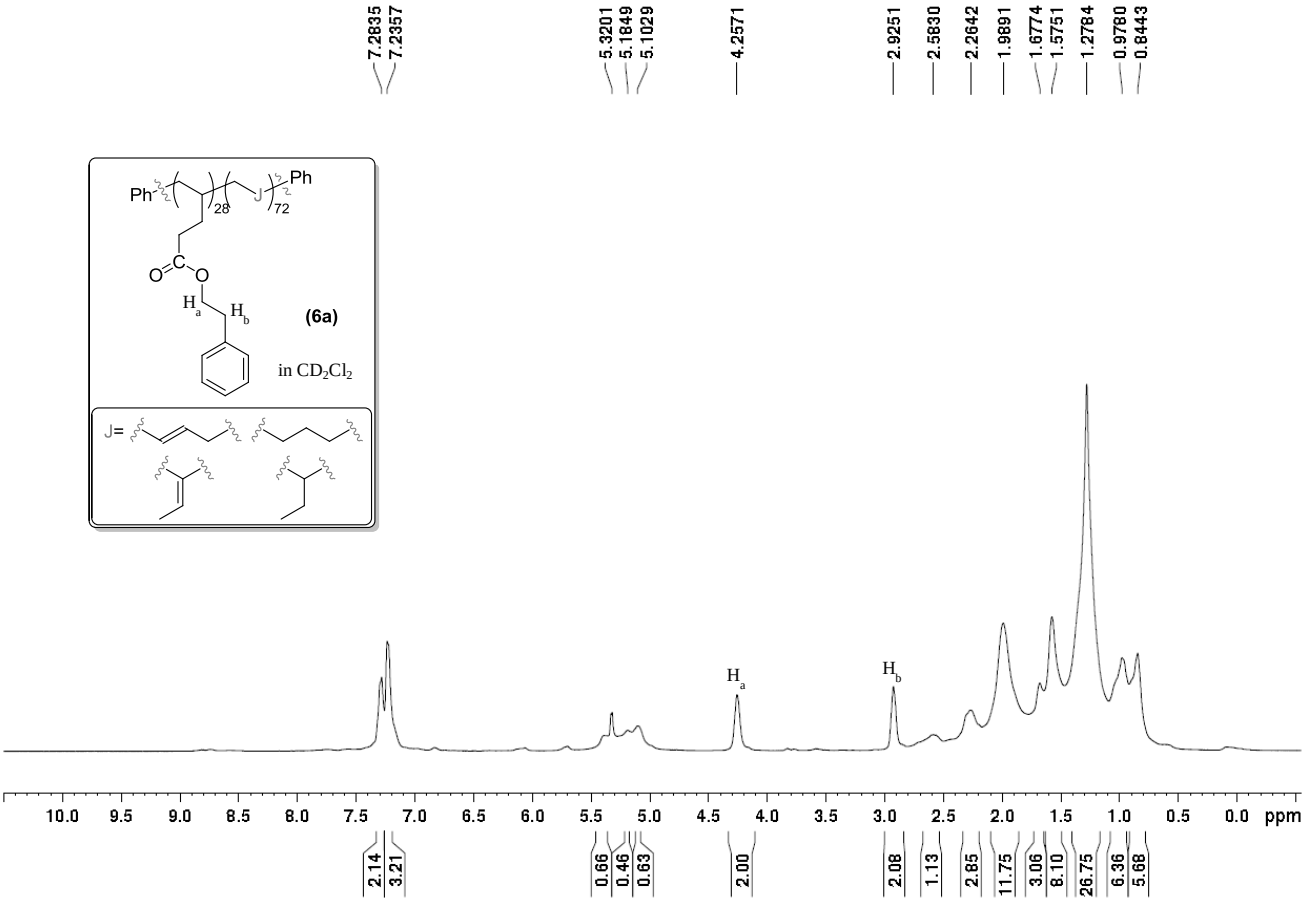
$$\textit{mole of starting Polybutadiene (1) (mmol)} = \frac{50\ mg}{1800\ mg/mmol} = \ 0.02778\ mmol$$

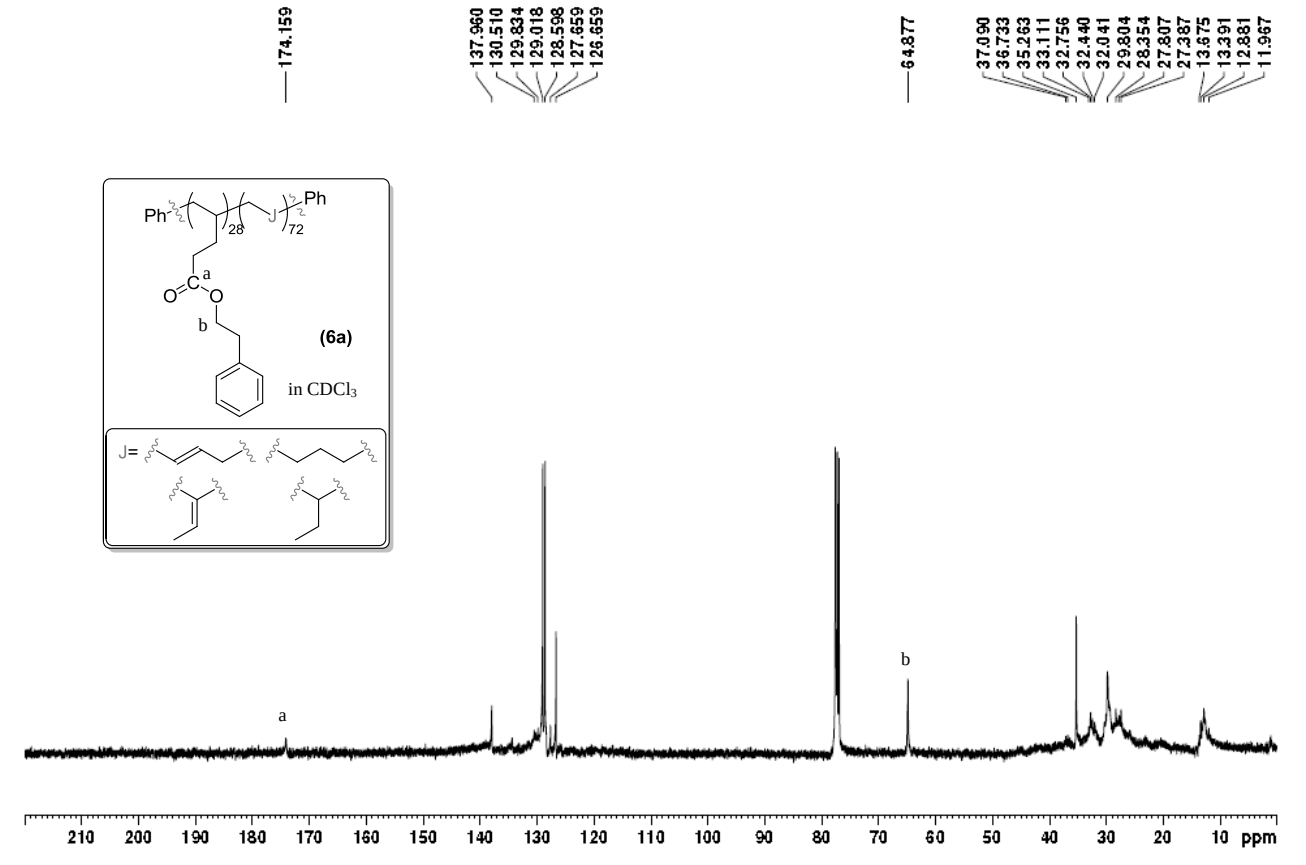
The yield of 2-phenylethyl ester-containing modified polybutadiene (**6a**) :

$$\textit{yield of 2-phenylethyl ester-containing modified polybutadiene (6a) (\%)} = \frac{0.02001\ mmol}{0.02778\ mmol} \times 100 \ = \ 72.03 \ \simeq 72\ \%$$

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




7.2635
7.2357
5.3201
5.1849
5.1029
4.2571
2.9251
2.5830
2.2642
1.9891
1.6774
1.5751
1.2784
0.9780
0.8443
Ph
28
J
72
Ph
O
C
O
Ha
Hb
(6a)
in CD2Cl2
J=
Ha
Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.14
3.21
0.66
0.46
0.63
2.00
2.08
1.13
2.85
11.75
3.06
8.10
26.75
6.36
5.68


174.159
137.960
130.510
129.834
129.018
128.598
127.659
126.659
64.877
37.090
36.733
35.263
33.111
32.756
32.440
32.041
29.804
28.354
27.807
27.387
13.675
13.391
12.881
11.967
Ph
28
J
72
Ph
a
O
C
O
b
(6a)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

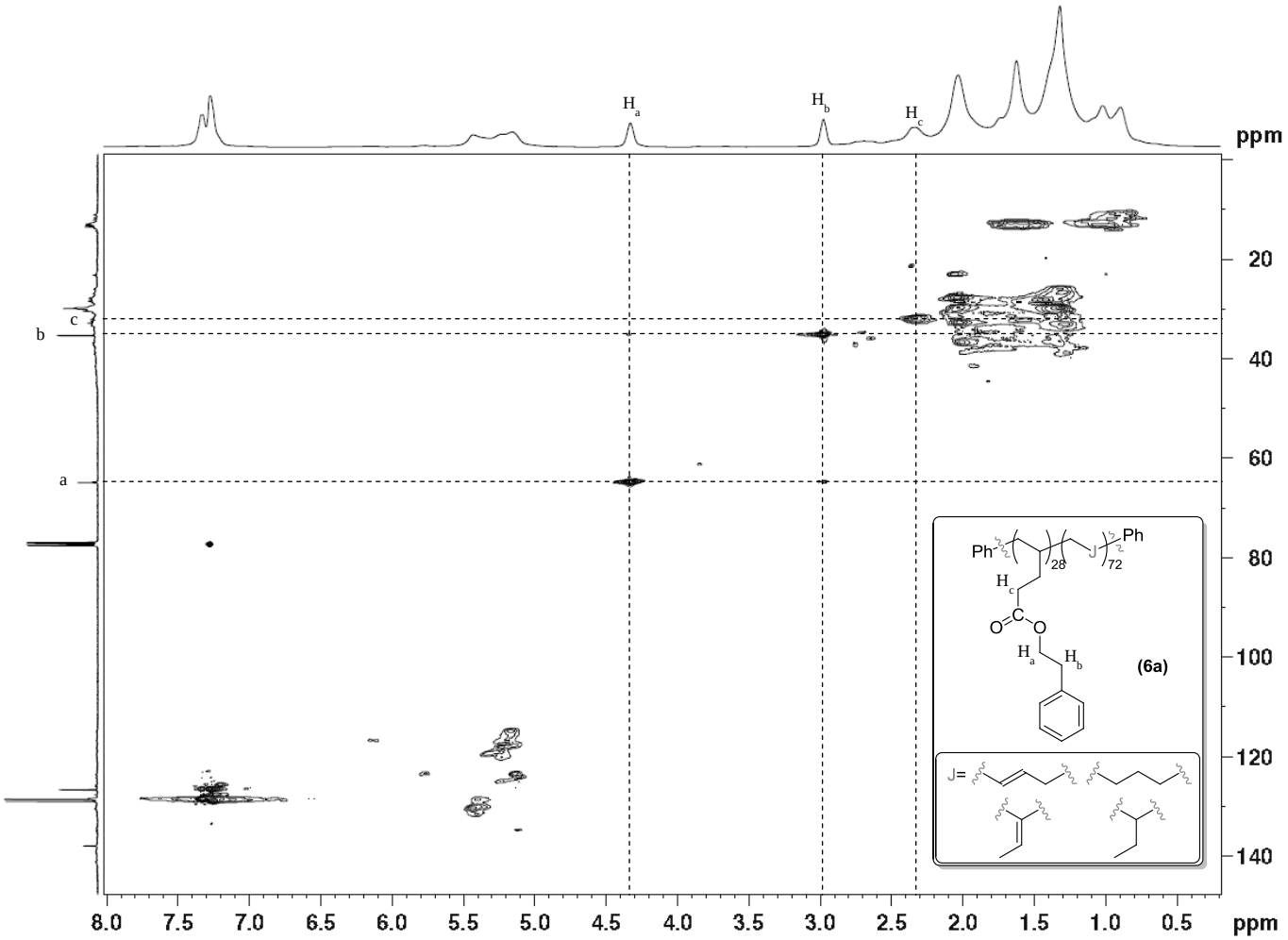
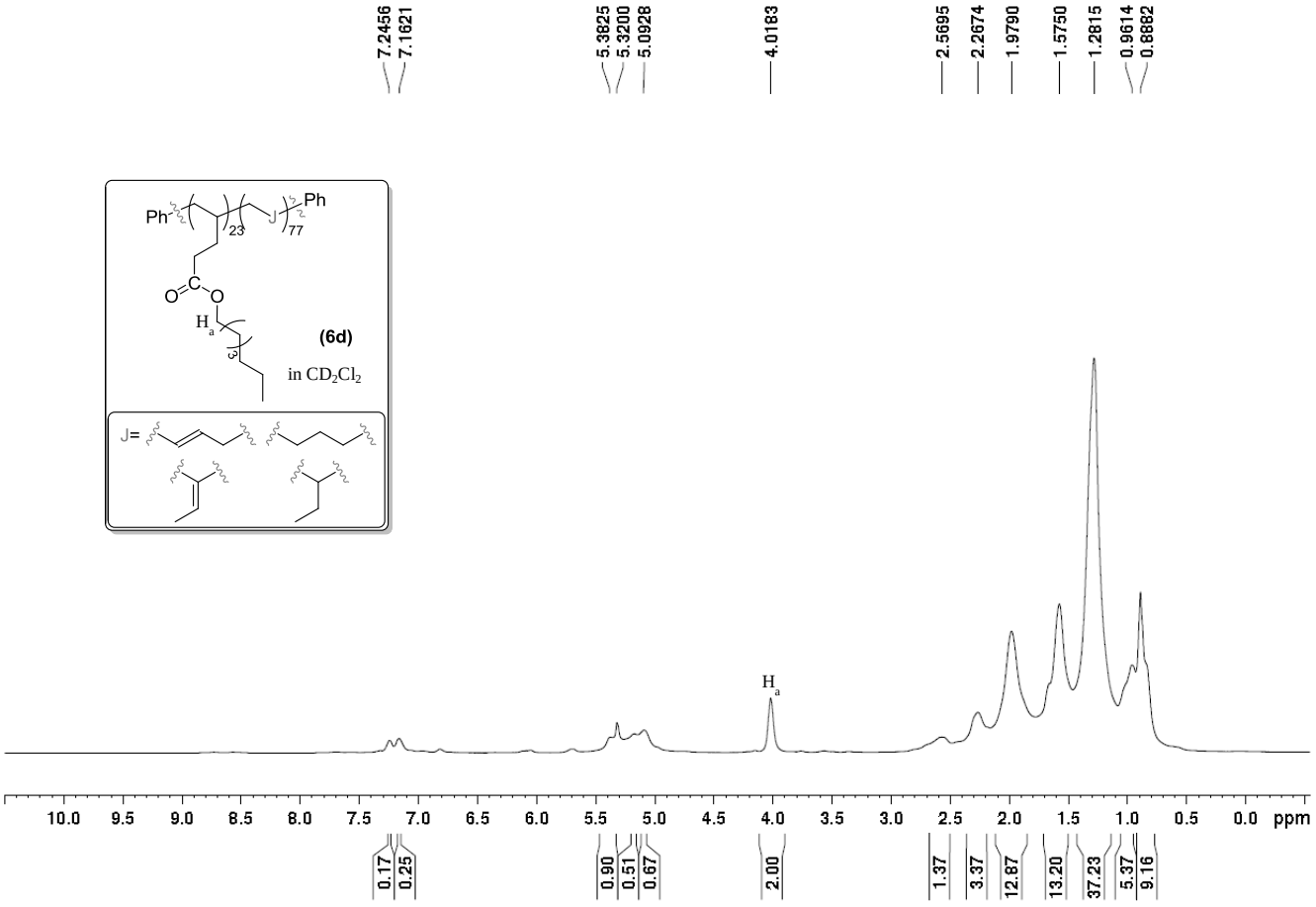
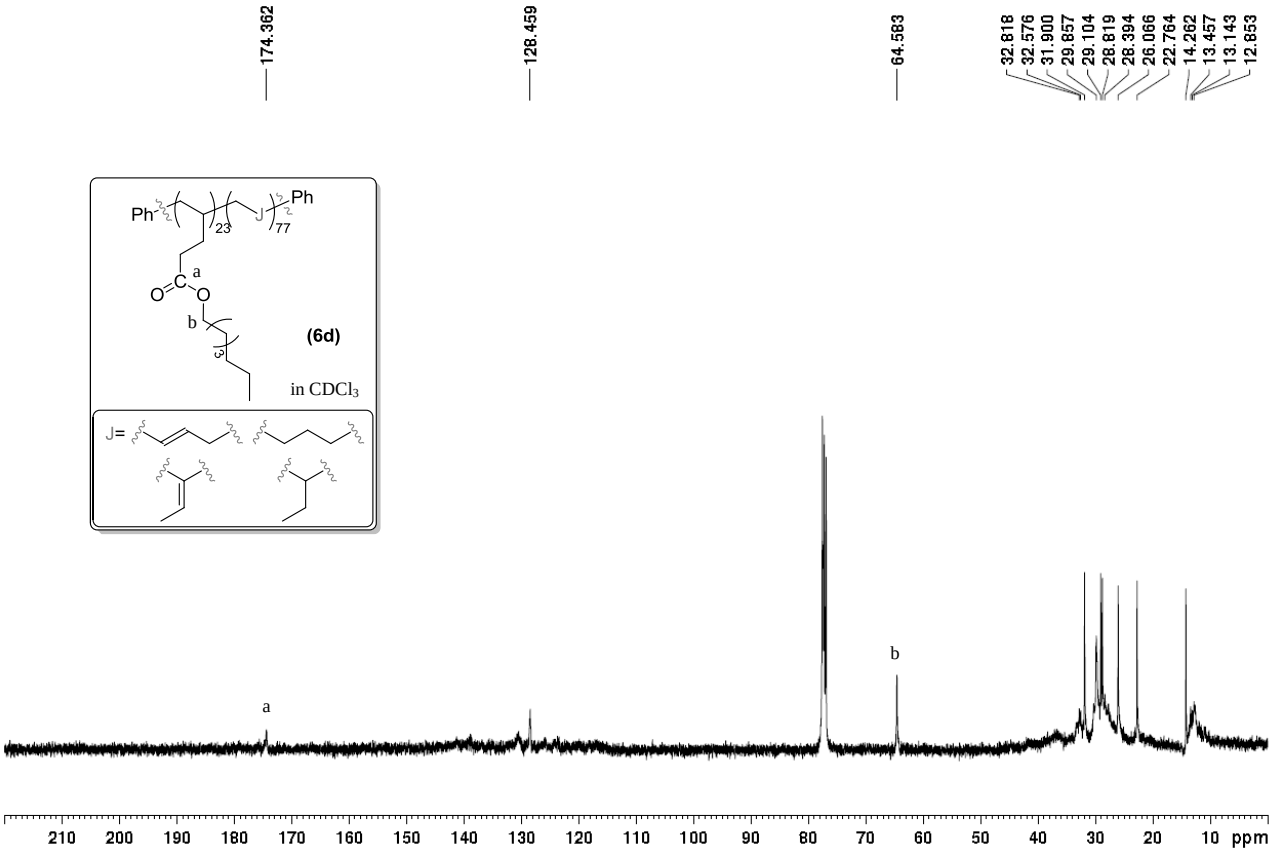
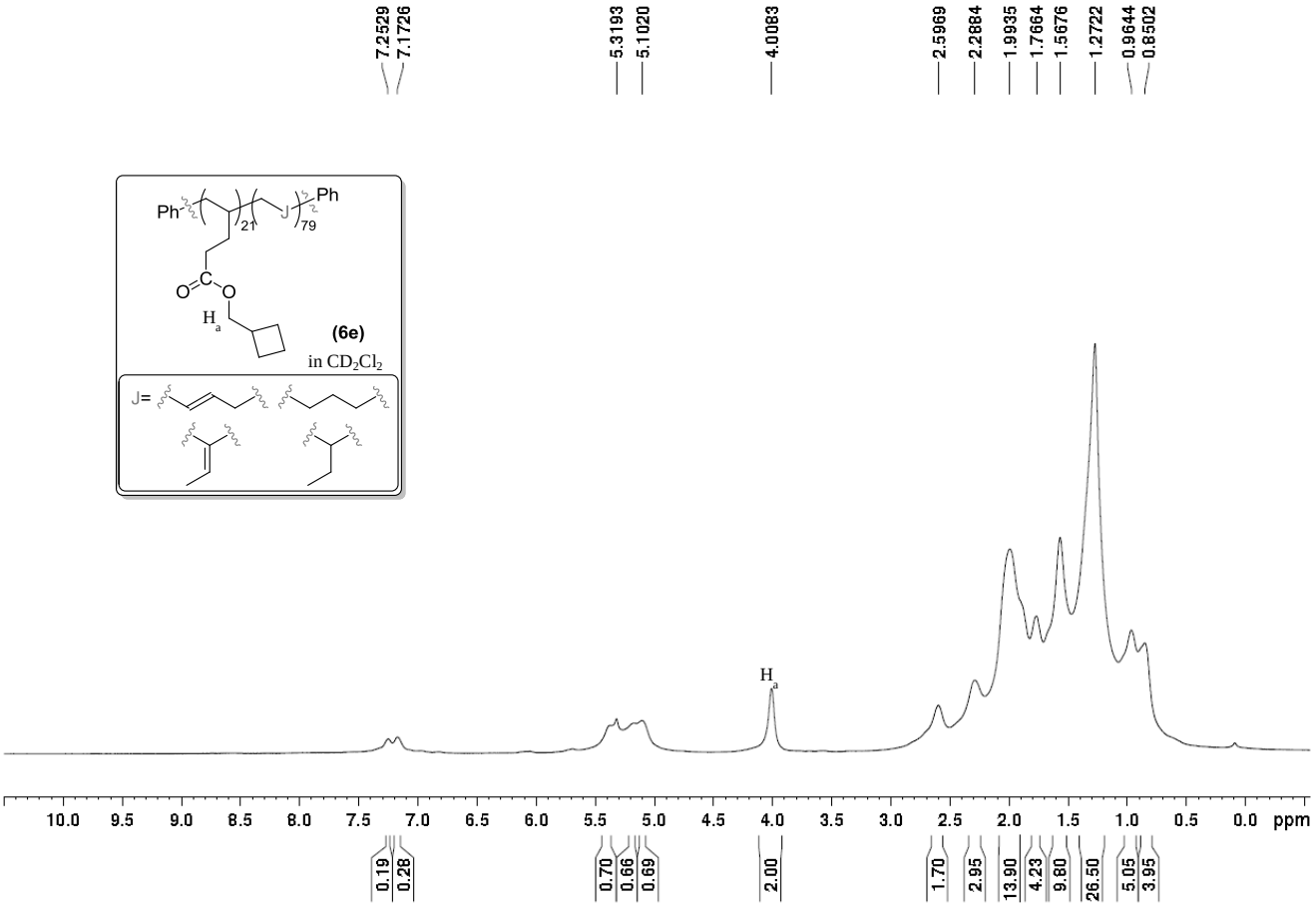
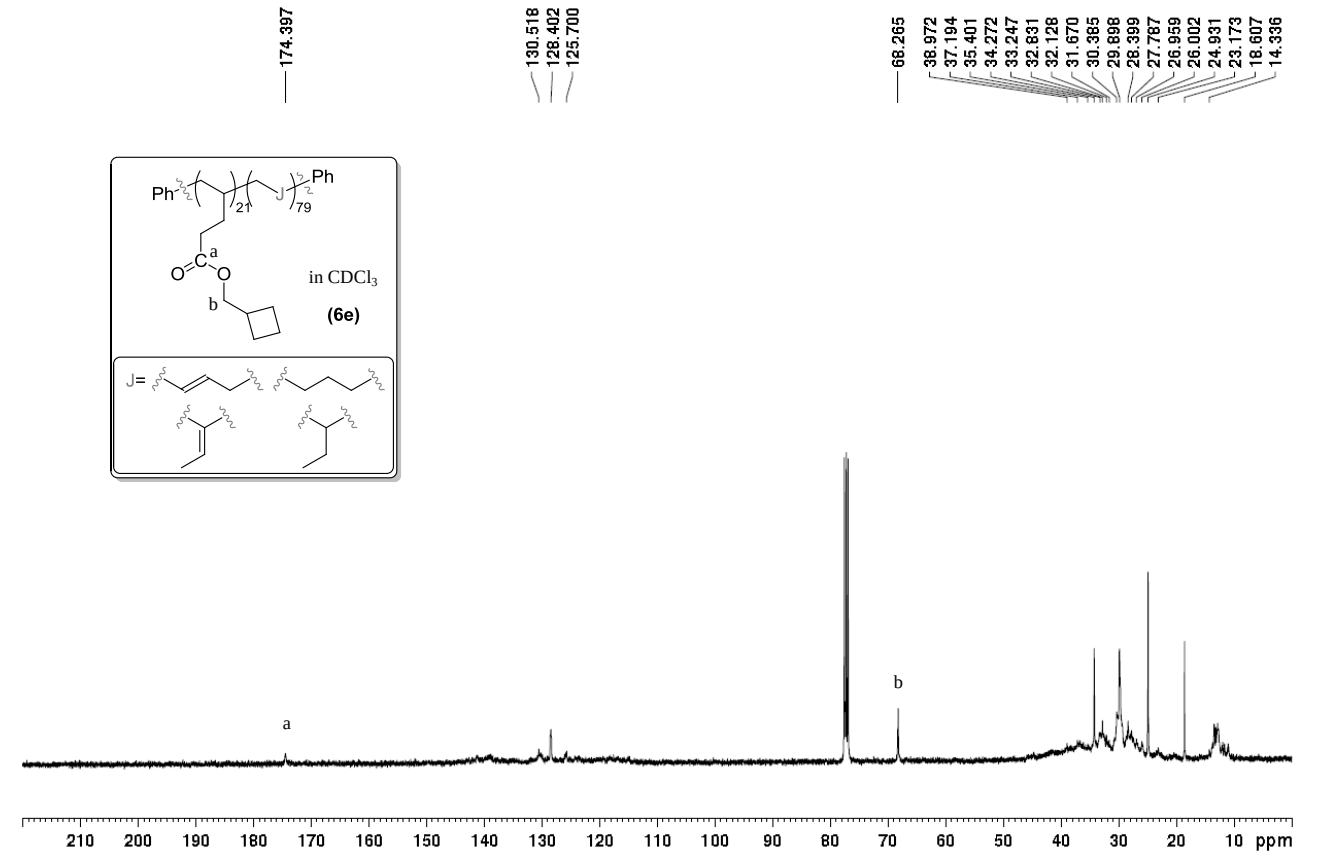


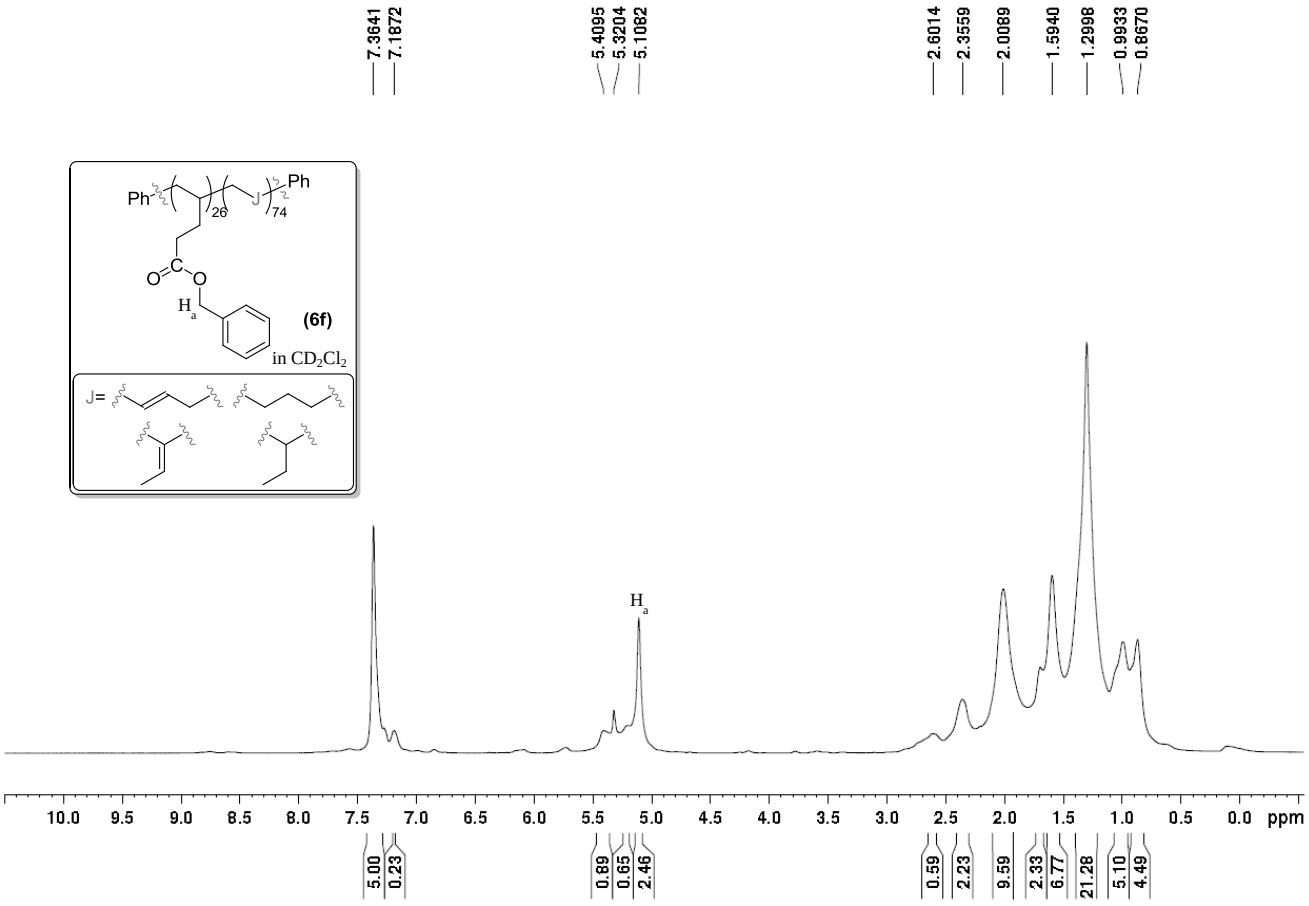
Fig S1. HSQC spectrum of **6a** in $CDCl_3$ was acquired on Bruker Advance II/DPX 400.

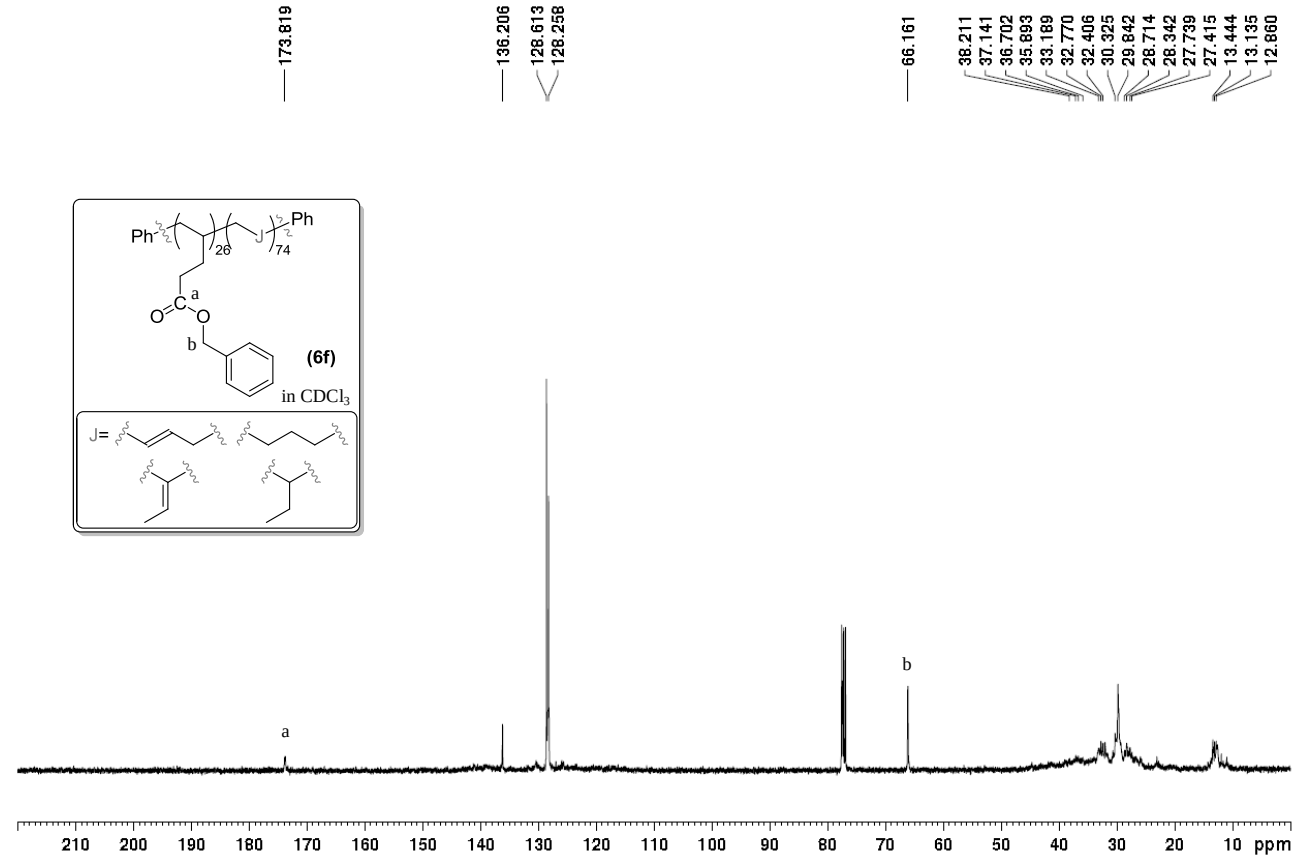

7.2456
7.1621
5.3825
5.3200
5.0928
4.0183
2.5695
2.2674
1.9790
1.5750
1.2815
0.9614
0.8882
Ph
Ph
23
J
77
O
C
O
H a
3
(6d)
in CD2Cl2
J=
Ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.17
0.25
0.90
0.51
0.67
2.00
1.37
3.37
12.87
13.20
37.23
5.37
9.16

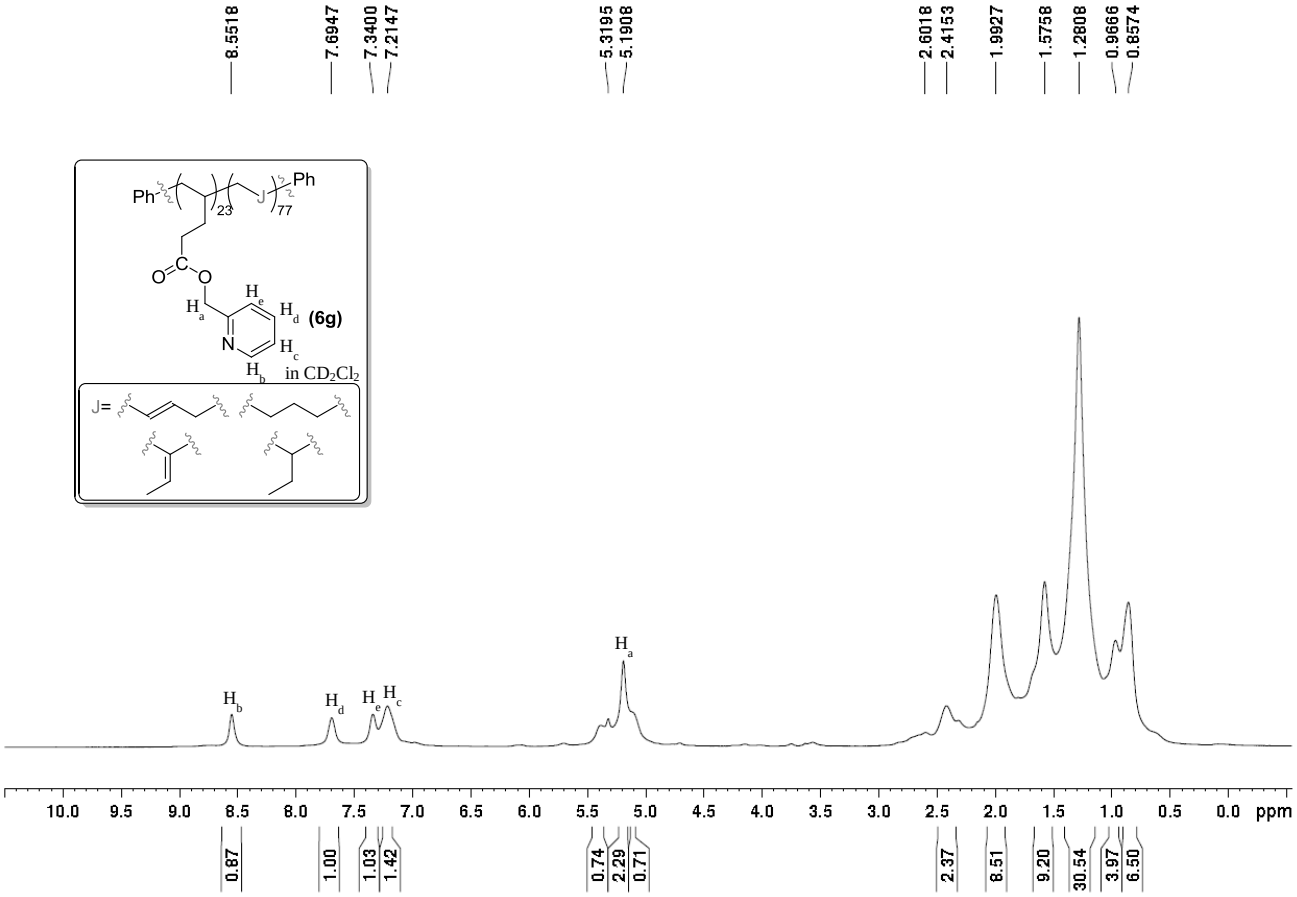

174.362
128.459
64.563
32.818
32.576
31.900
29.857
29.104
28.819
28.394
26.066
22.764
14.262
13.457
13.143
12.853
Ph
Ph
23
J
77
O
C
a
O
b
3
(6d)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

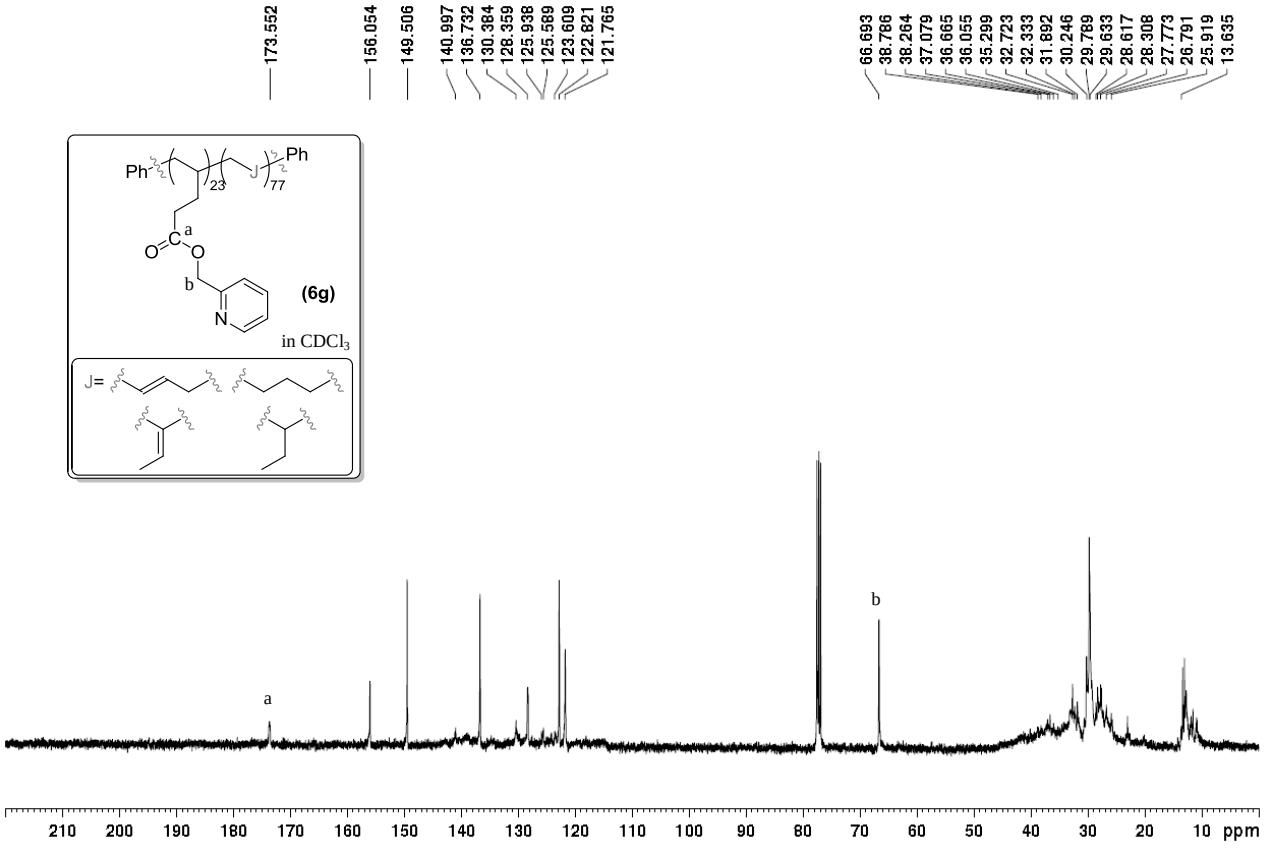

7.2529
7.1726
5.3193
5.1020
4.0083
2.5969
2.2884
1.9935
1.7664
1.5676
1.2722
0.9644
0.8502
Ph
21
J
79
Ph
O
C
O
Ha
(6e)
in CD2Cl2
J=
Ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.19
0.28
0.70
0.66
0.69
2.00
1.70
2.95
13.90
4.23
9.80
26.50
5.05
3.95

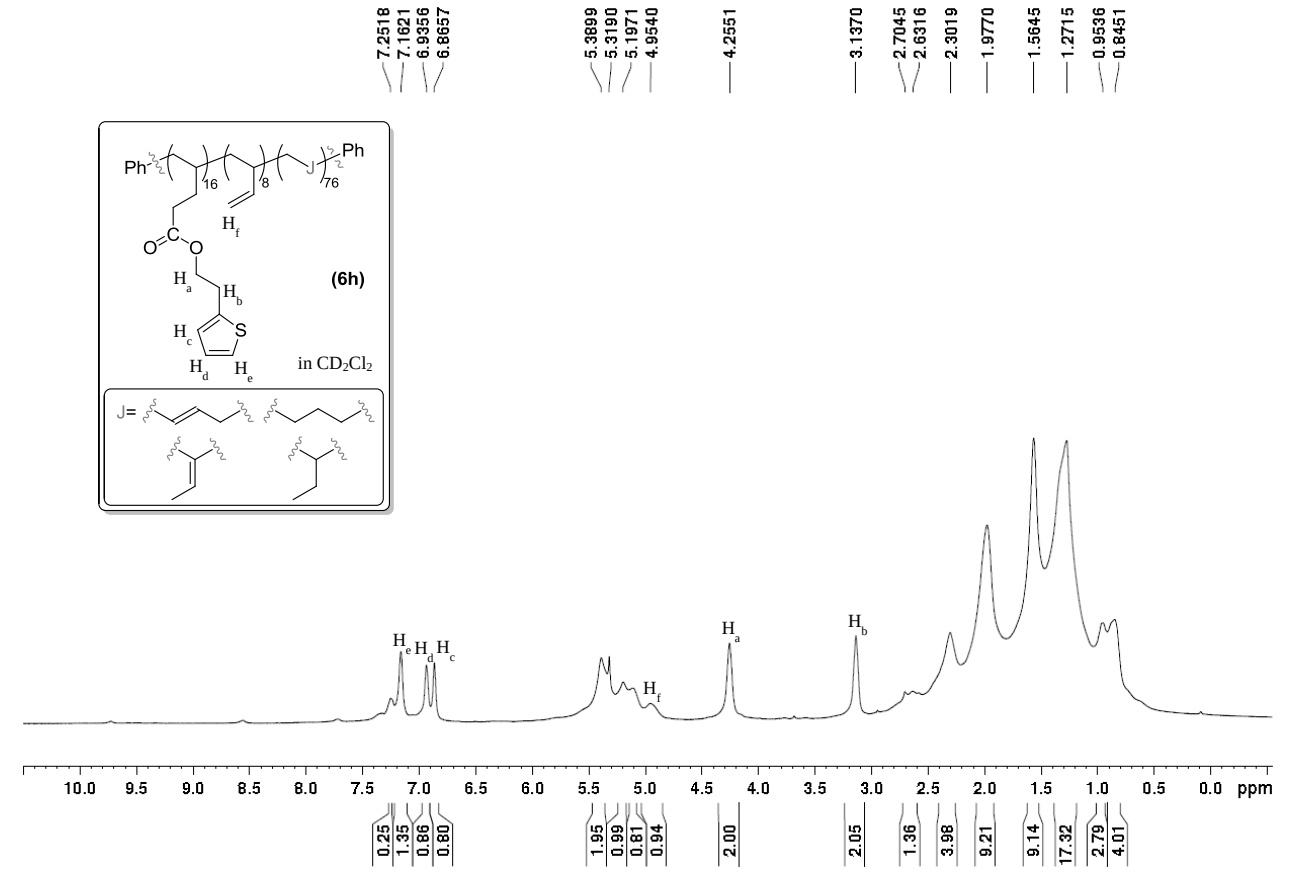

174.397
130.518
128.402
125.700
68.265
38.972
37.194
35.401
34.272
33.247
32.831
32.128
31.670
30.385
29.898
28.399
27.767
26.959
26.002
24.931
23.173
18.607
14.336
Ph
21
J
79
Ph
a
O
C
O
b
in CDCl3
(6e)
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

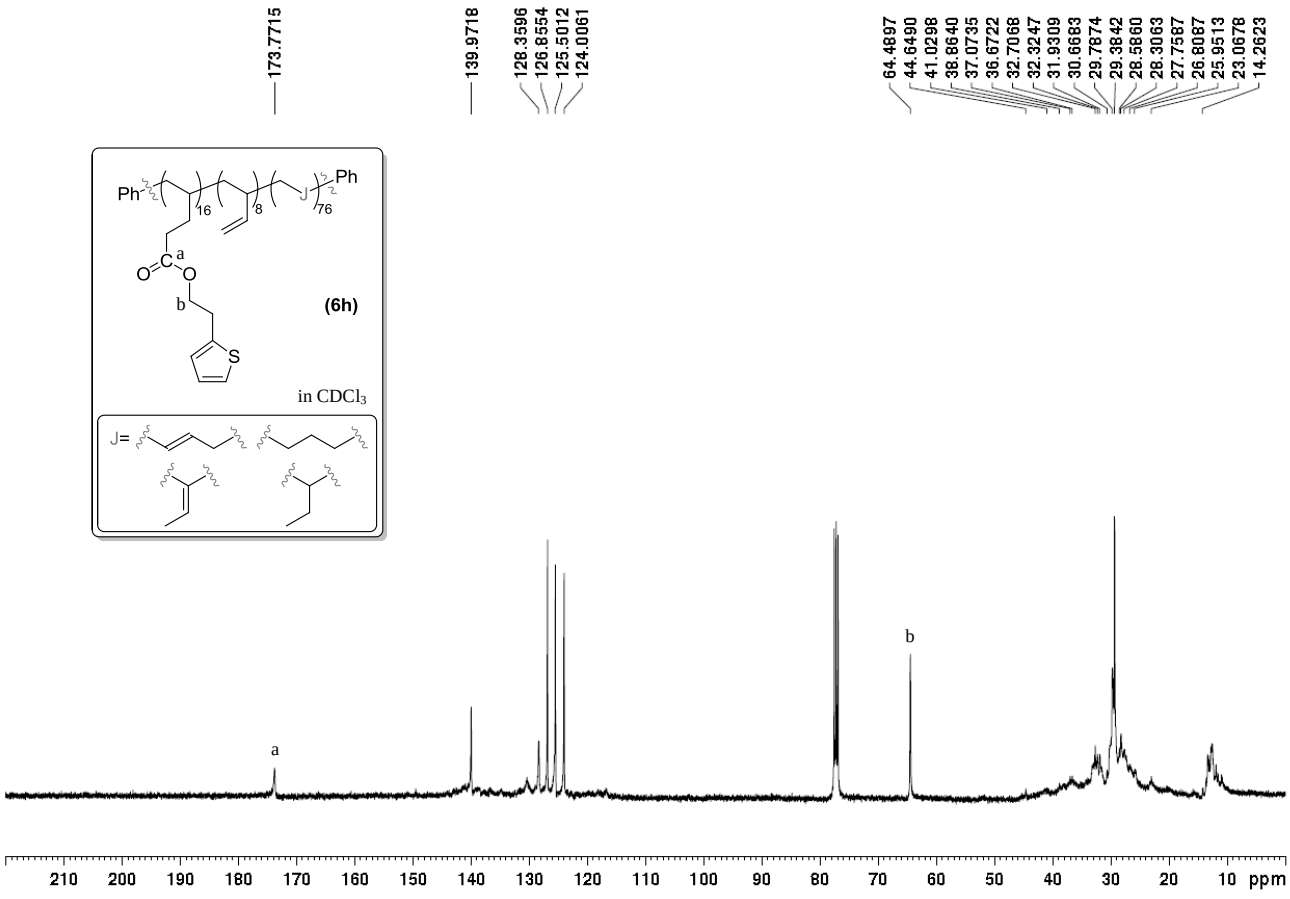

7.3641
7.1672
5.4095
5.3204
5.1082
2.6014
2.3559
2.0089
1.5940
1.2998
0.9933
0.8670
Ph
26
74
Ph
(6f)
in CD2Cl2
J=
Ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.00
0.23
0.89
0.65
2.46
0.59
2.23
9.59
2.33
6.77
21.28
5.10
4.49

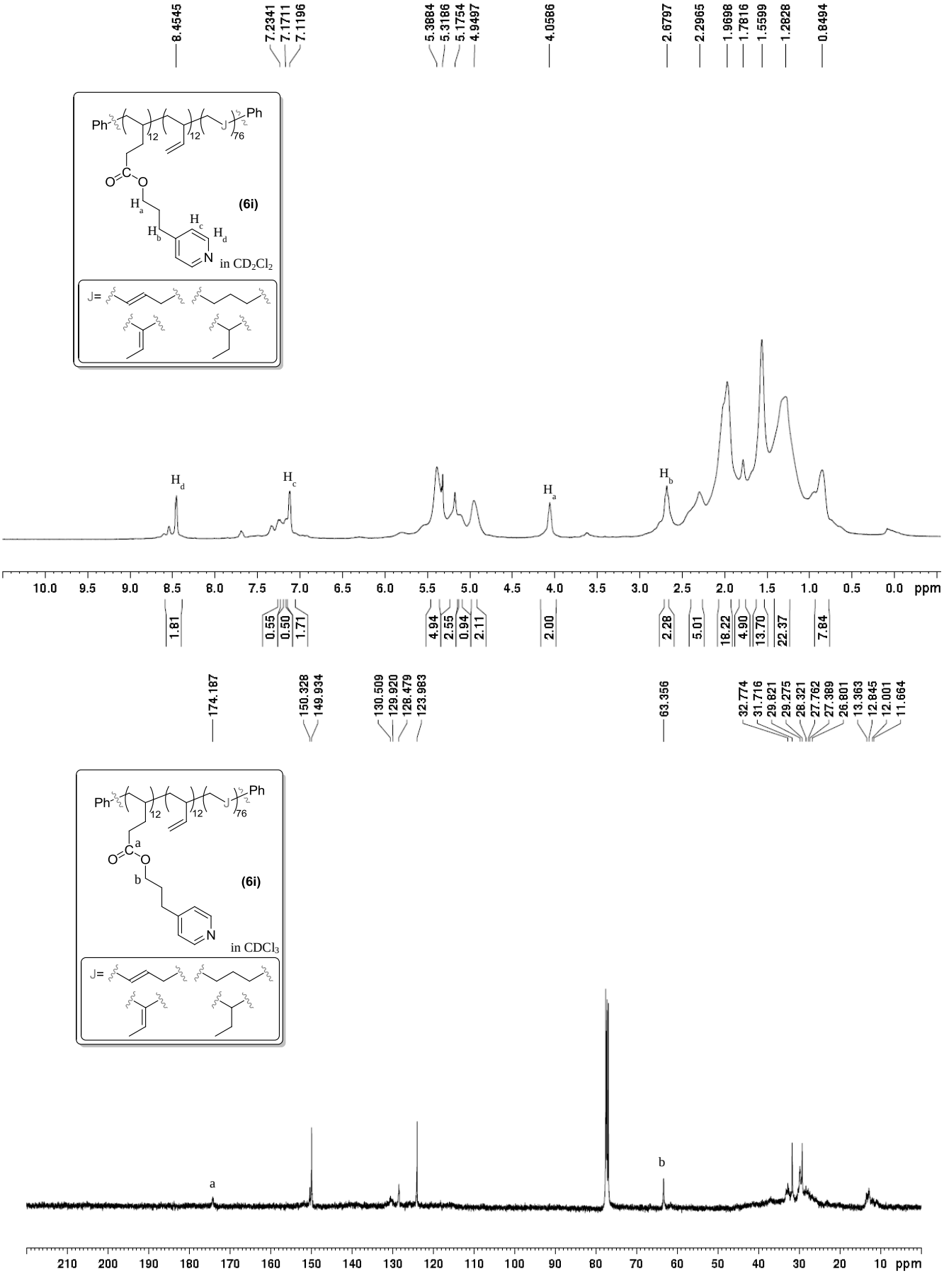

173.819
136.206
128.613
128.258
66.161
38.211
37.141
36.702
35.893
33.189
32.770
32.406
30.325
29.842
28.714
28.342
27.739
27.415
13.444
13.135
12.860
Ph
26
74
Ph
a
b
(6f)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

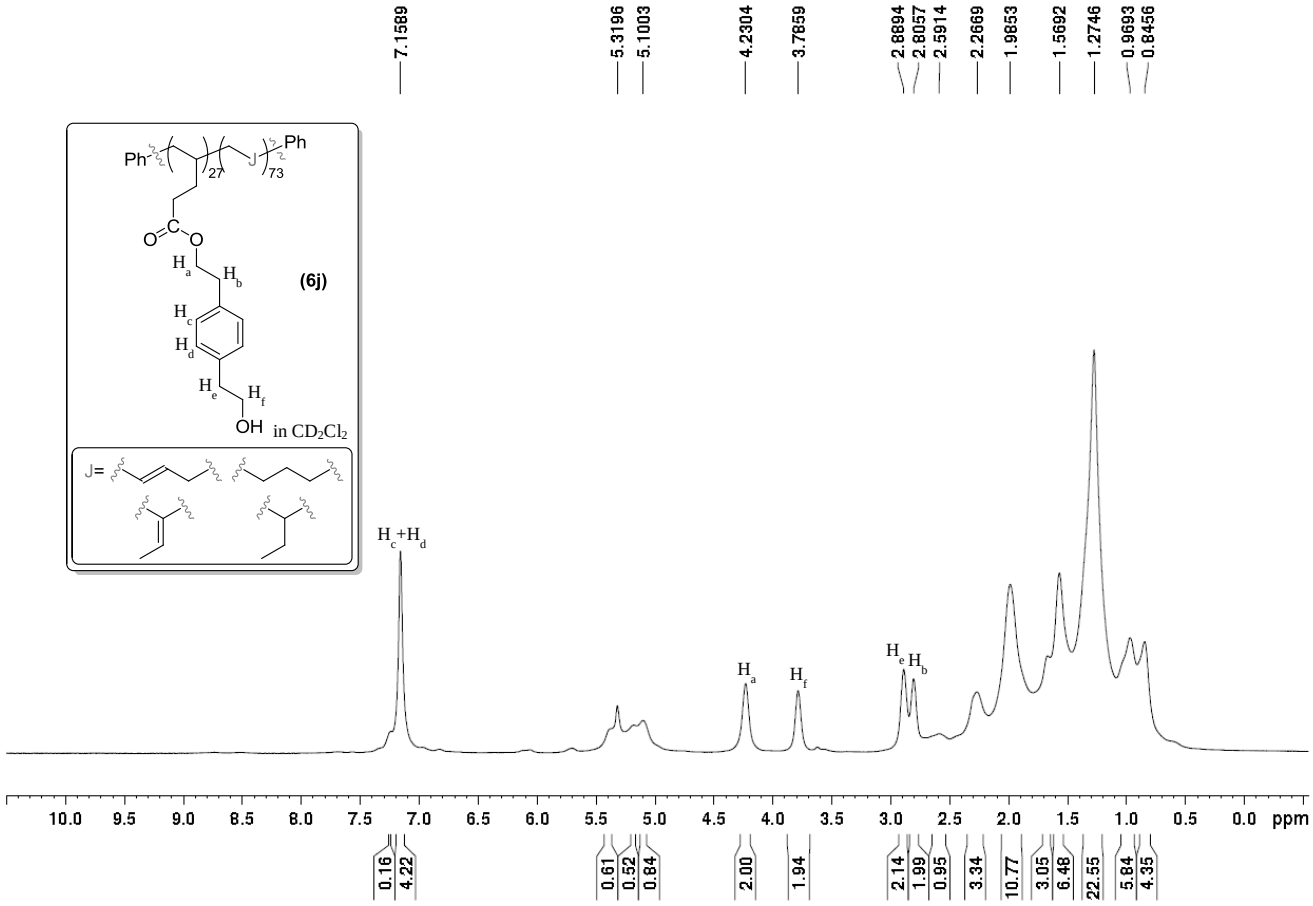

8.5518
7.6947
7.3400
7.2147
5.3195
5.1908
2.6018
2.4153
1.9927
1.5758
1.2808
0.9666
0.8574
Ph
23
77
Ph
O
C
O
H a
H e
H d
H c
H b
(6g)
in CD2Cl2
J=
H b
H d
H e
H c
H a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.87
1.00
1.03
1.42
0.74
2.29
0.71
2.37
8.51
9.20
30.54
3.97
6.50

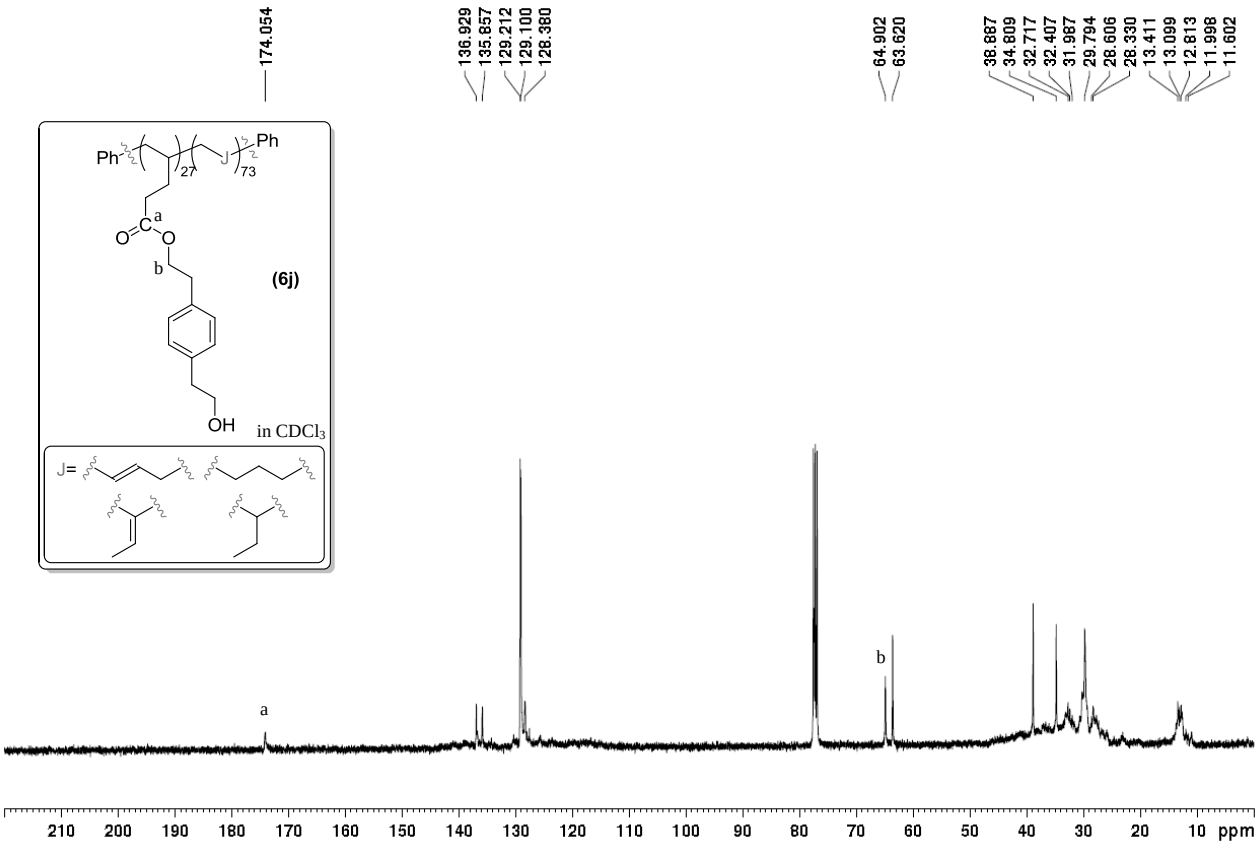

173.552
156.054
149.506
140.997
136.732
130.384
128.359
125.938
125.589
123.609
122.821
121.765
66.693
38.786
38.264
37.079
36.665
36.055
35.299
32.723
32.333
31.892
30.246
29.789
29.633
28.617
28.308
27.773
26.791
25.919
13.635
Ph
23
77
Ph
O
C
a
O
b
(6g)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

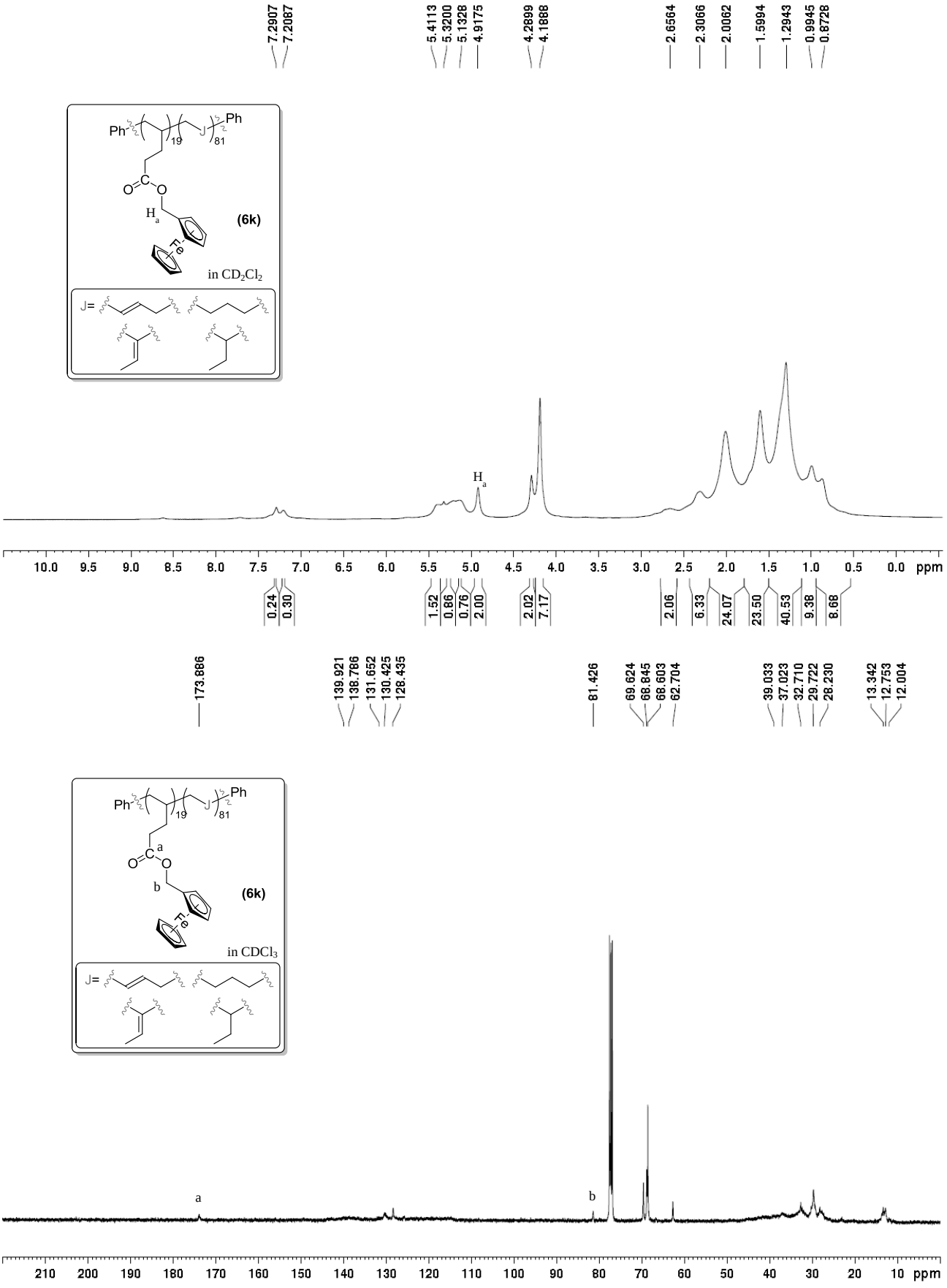

7.2518
7.1621
6.9356
6.8657
5.3899
5.3190
5.1971
4.9540
4.2551
3.1370
2.7045
2.6316
2.3019
1.9770
1.5645
1.2715
0.9536
0.8451
(6h)
in CD2Cl2
J=
He Hd Hc
Hf
Ha
Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.25 1.35 0.86 0.80 1.95 0.99 0.81 0.94 2.00 2.05 1.36 3.98 9.21 9.14 17.32 2.79 4.01

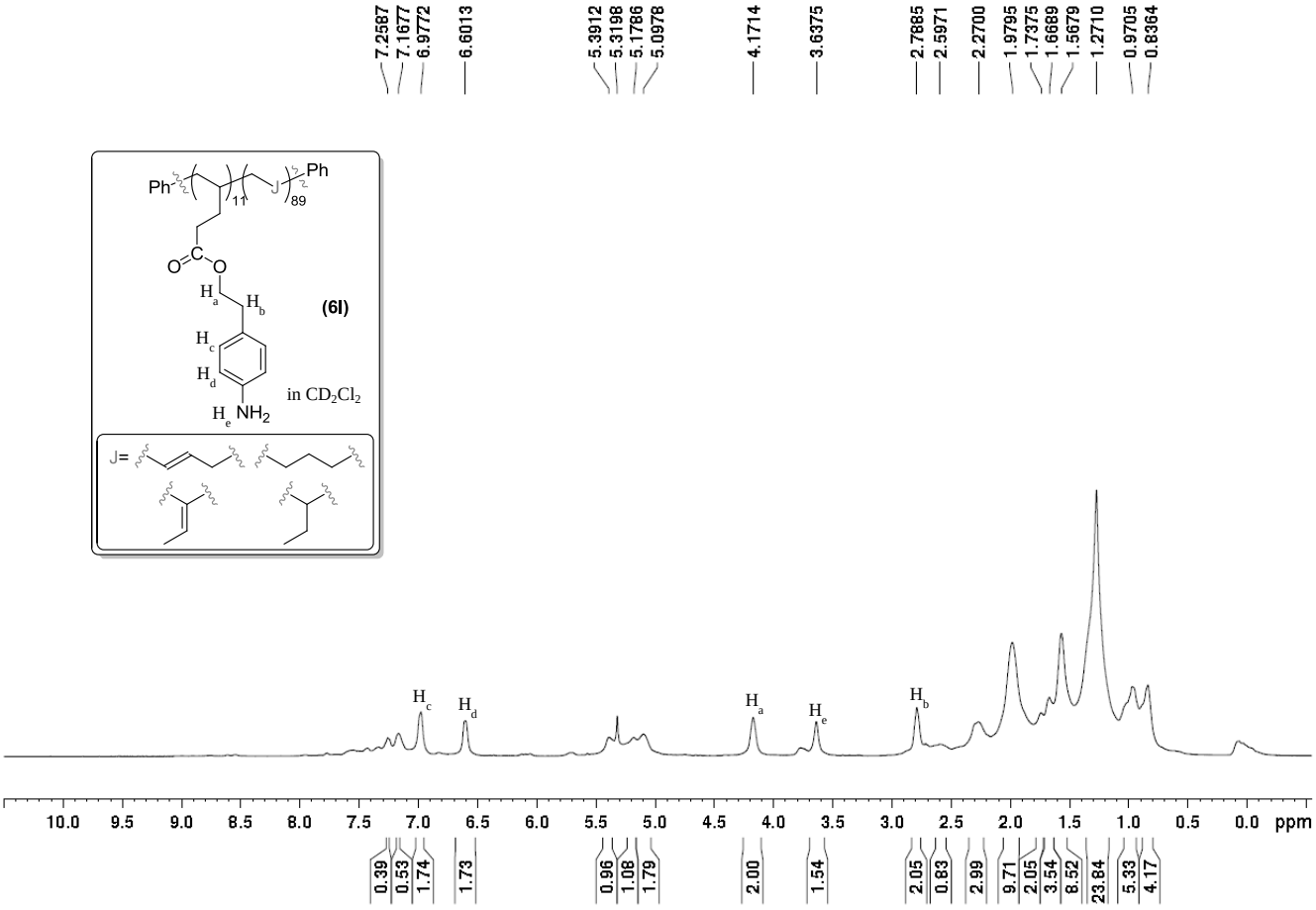

173.7715
139.9718
128.3596
126.8554
125.5012
124.0061
64.4897
44.6490
41.0298
38.8640
37.0735
36.6722
32.7068
32.3247
31.9309
30.6683
29.7874
29.3842
28.5860
28.3063
27.7587
26.8087
25.9513
23.0678
14.2623
(6h)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

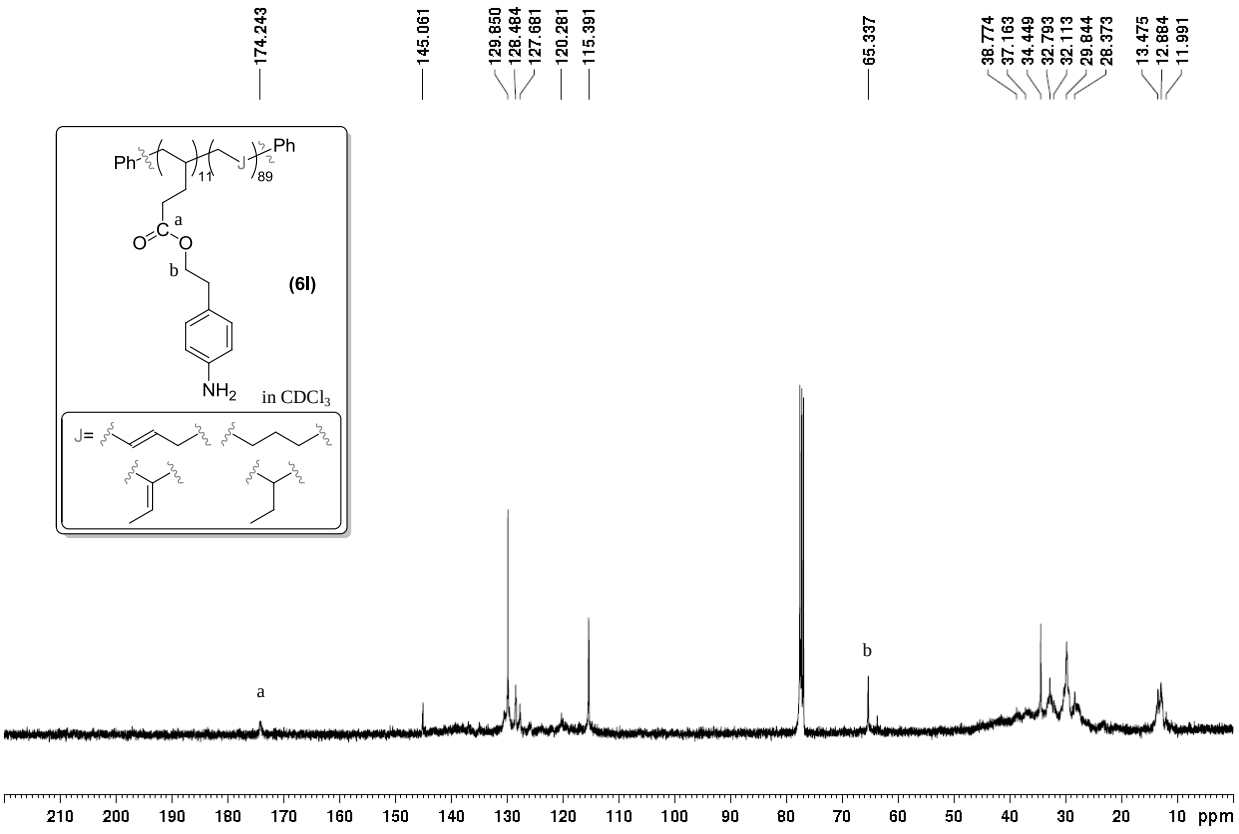

8.4545
7.2341
7.1711
7.1196
5.3884
5.3186
5.1754
4.9497
4.0586
2.6797
2.2965
1.9698
1.7816
1.5599
1.2828
0.8494
(6i)
in CD2Cl2
J=
Hd
Hc
Ha
Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.81
0.55
0.50
1.71
4.94
2.55
0.94
2.11
2.00
2.28
5.01
18.22
4.90
13.70
22.37
7.84
174.187
150.328
149.934
130.509
129.920
128.479
123.983
63.356
32.774
31.716
29.821
29.275
28.321
27.762
27.389
26.801
13.363
12.845
12.001
11.664
(6i)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

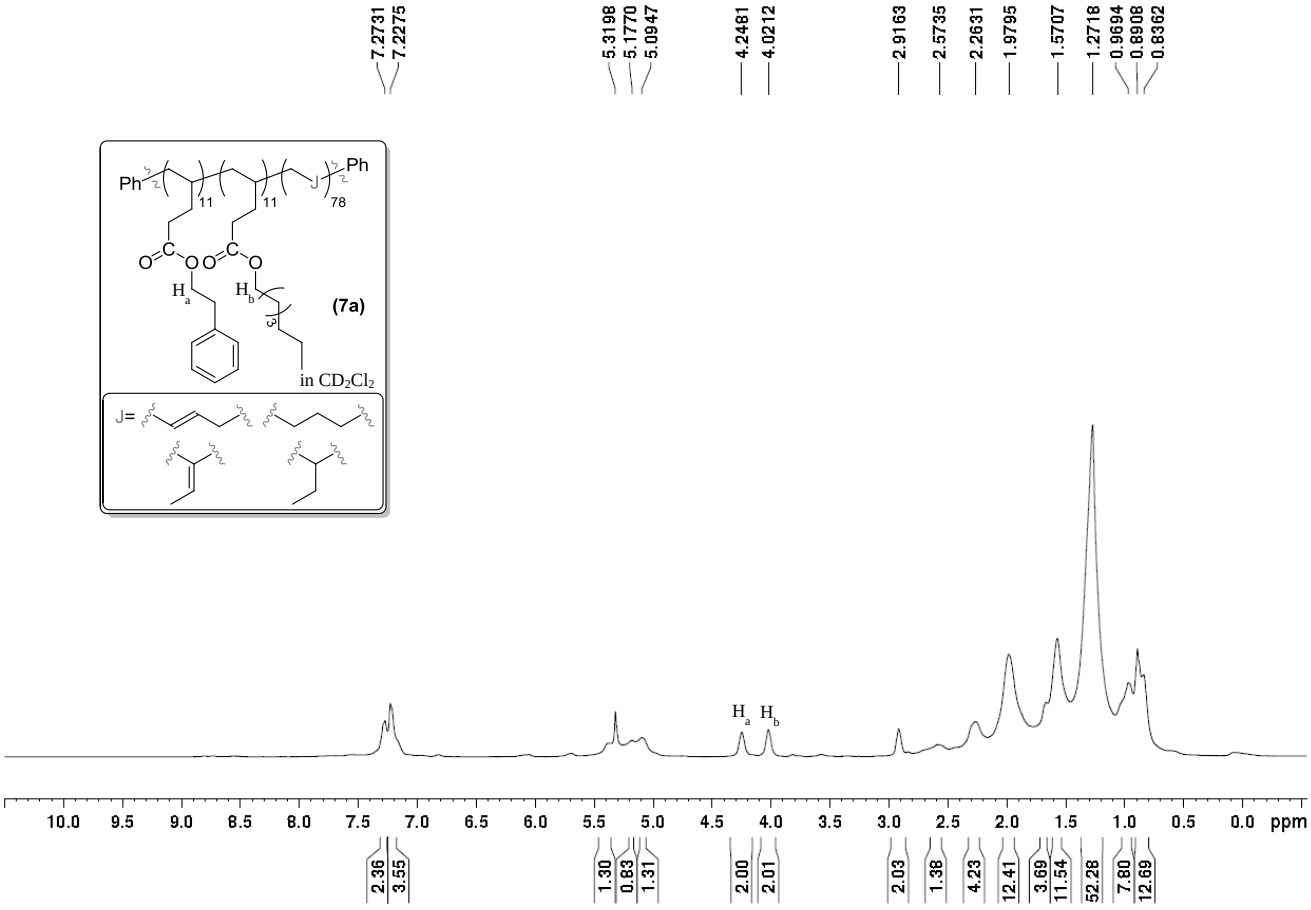

7.1589
5.3196
5.1003
4.2304
3.7859
2.8894
2.8057
2.5914
2.2669
1.9853
1.5692
1.2746
0.9693
0.8456
(6j)
in CD2Cl2
J=
Hc+Hd
Ha
Hf
He
Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.16
4.22
0.61
0.52
0.84
2.00
1.94
2.14
1.99
0.95
3.34
10.77
3.05
6.48
22.55
5.84
4.35

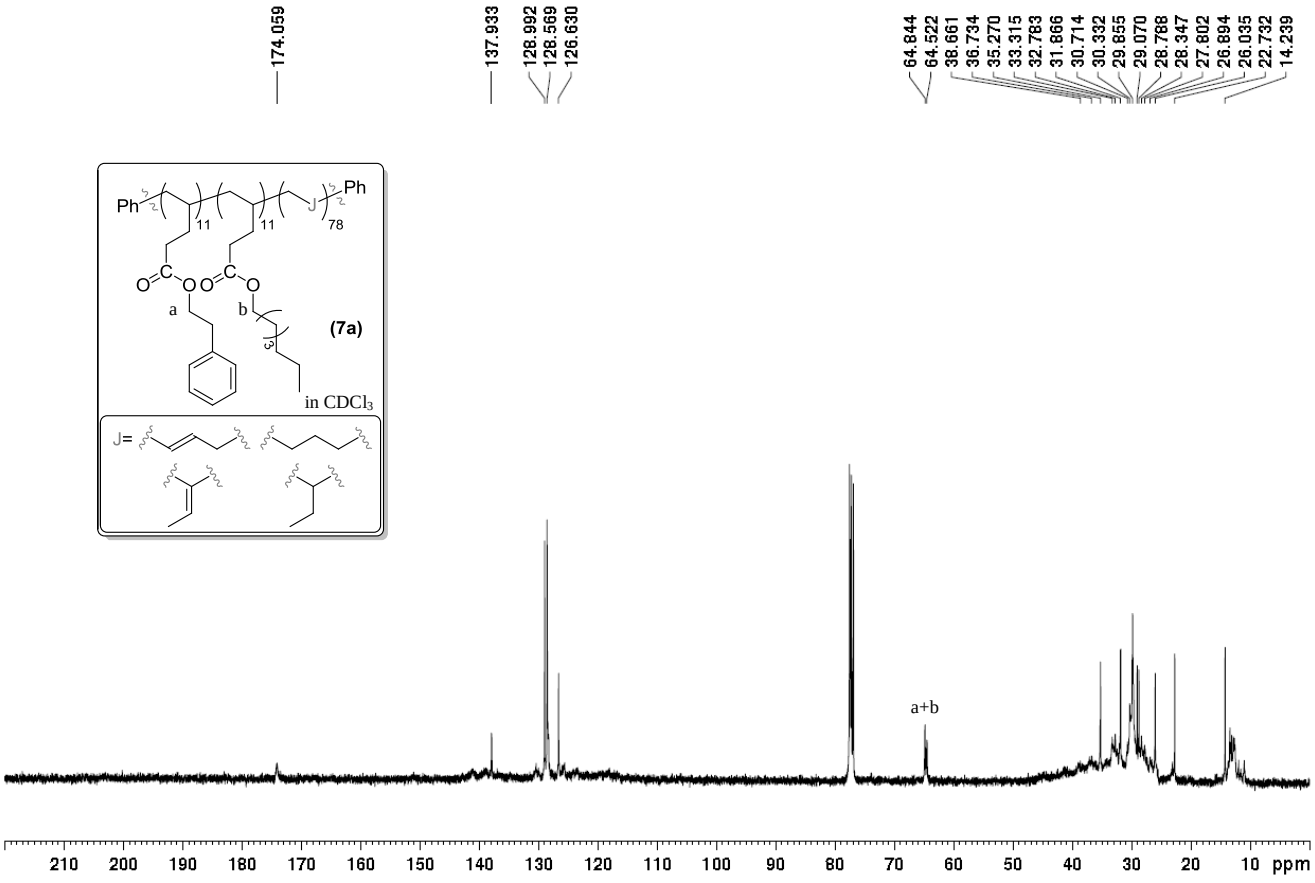

174.054
136.929
135.857
129.212
129.100
128.380
64.902
63.620
38.887
34.809
32.717
32.407
31.987
29.794
28.606
28.330
13.411
13.099
12.813
11.998
11.602
(6j)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

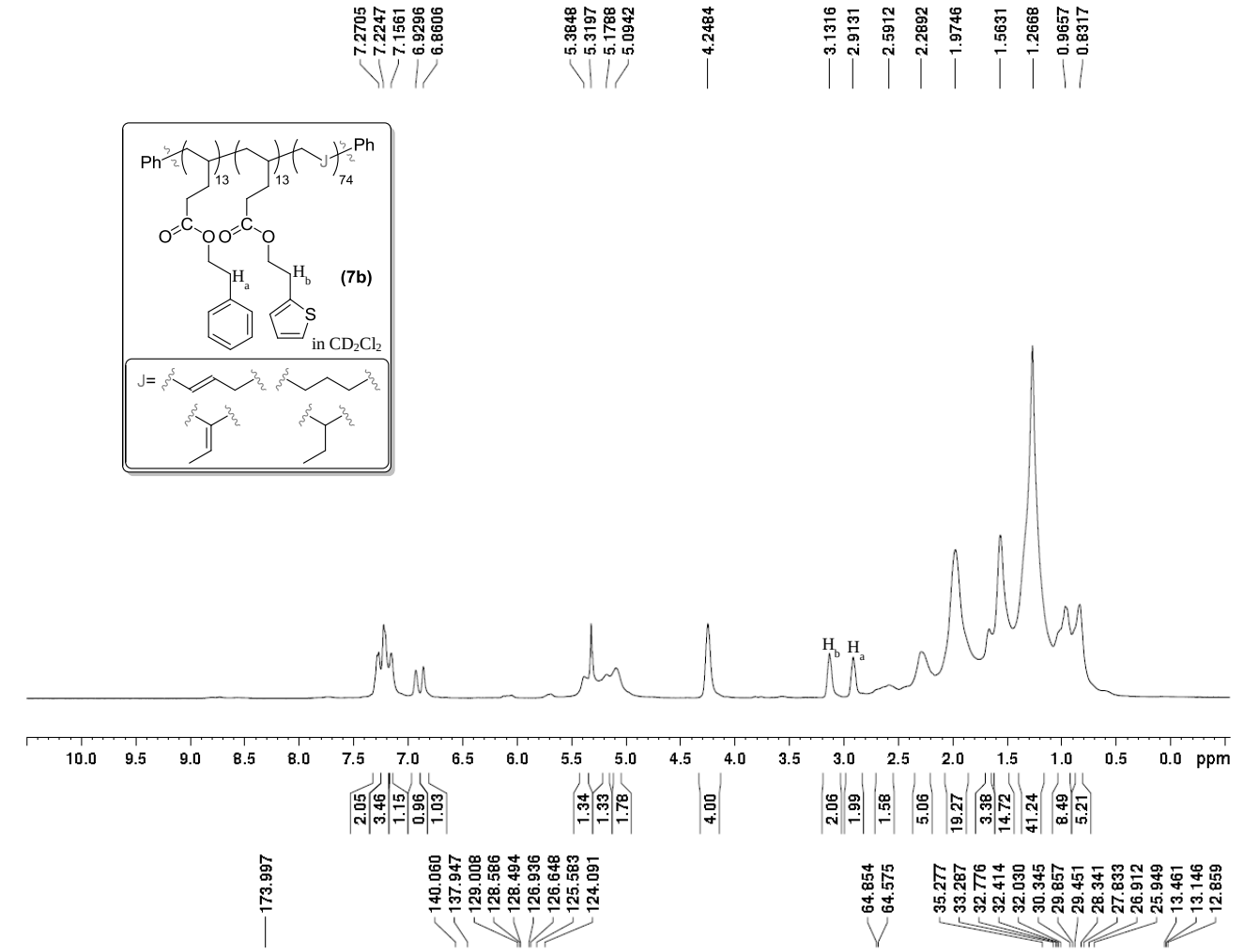

7.2907
7.2087
5.4113
5.3200
5.1328
4.9175
4.2899
4.1888
2.6564
2.3066
2.0062
1.5994
1.2943
0.9945
0.8728
Ph
19
J
81
Ph
O
C
O
Ha
(6k)
Tp
in CD2Cl2
J=
Ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.24
0.30
1.52
0.86
0.76
2.00
2.02
7.17
2.06
6.33
24.07
23.50
40.53
9.38
8.68
173.886
139.921
138.786
131.652
130.425
128.435
81.426
69.624
68.845
68.603
62.704
39.033
37.023
32.710
29.722
28.230
13.342
12.753
12.004
Ph
19
J
81
Ph
a
O
C
O
b
(6k)
Tp
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

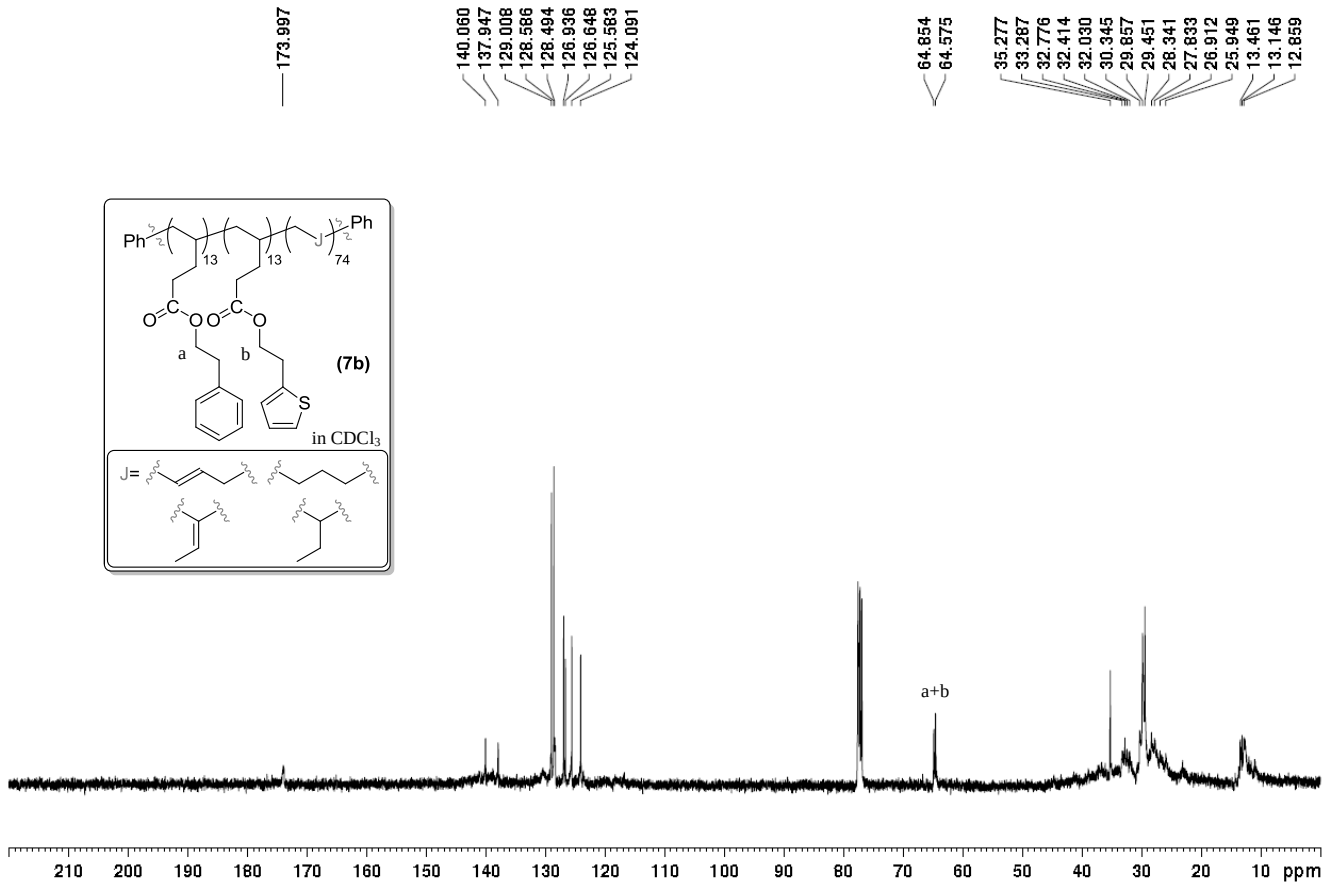

7.2587
7.1677
6.9772
6.6013
5.3912
5.3198
5.1786
5.0978
4.1714
3.6375
2.7885
2.5971
2.2700
1.9795
1.7375
1.6689
1.5679
1.2710
0.9705
0.8364
(6l)
in CD2Cl2
J=
Hc
Hd
Ha
He
Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.39
0.53
1.74
1.73
0.96
1.08
1.79
2.00
1.54
2.05
0.83
2.99
9.71
2.05
3.54
8.52
23.84
5.33
4.17

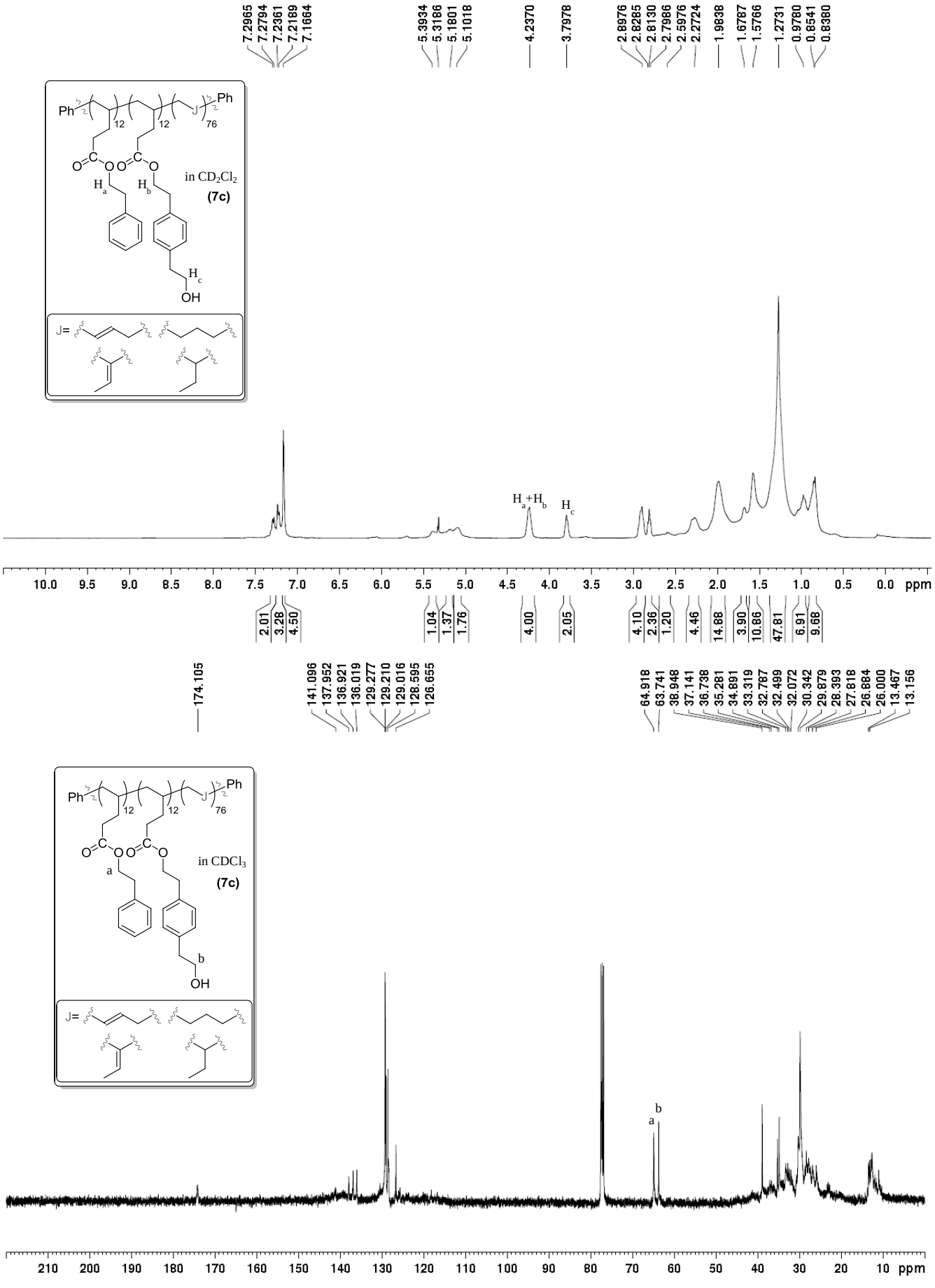

174.243
145.061
129.850
128.484
127.681
120.281
115.391
65.337
38.774
37.163
34.449
32.793
32.113
29.844
28.373
13.475
12.884
11.991
(6l)
in CDCl3
J=
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

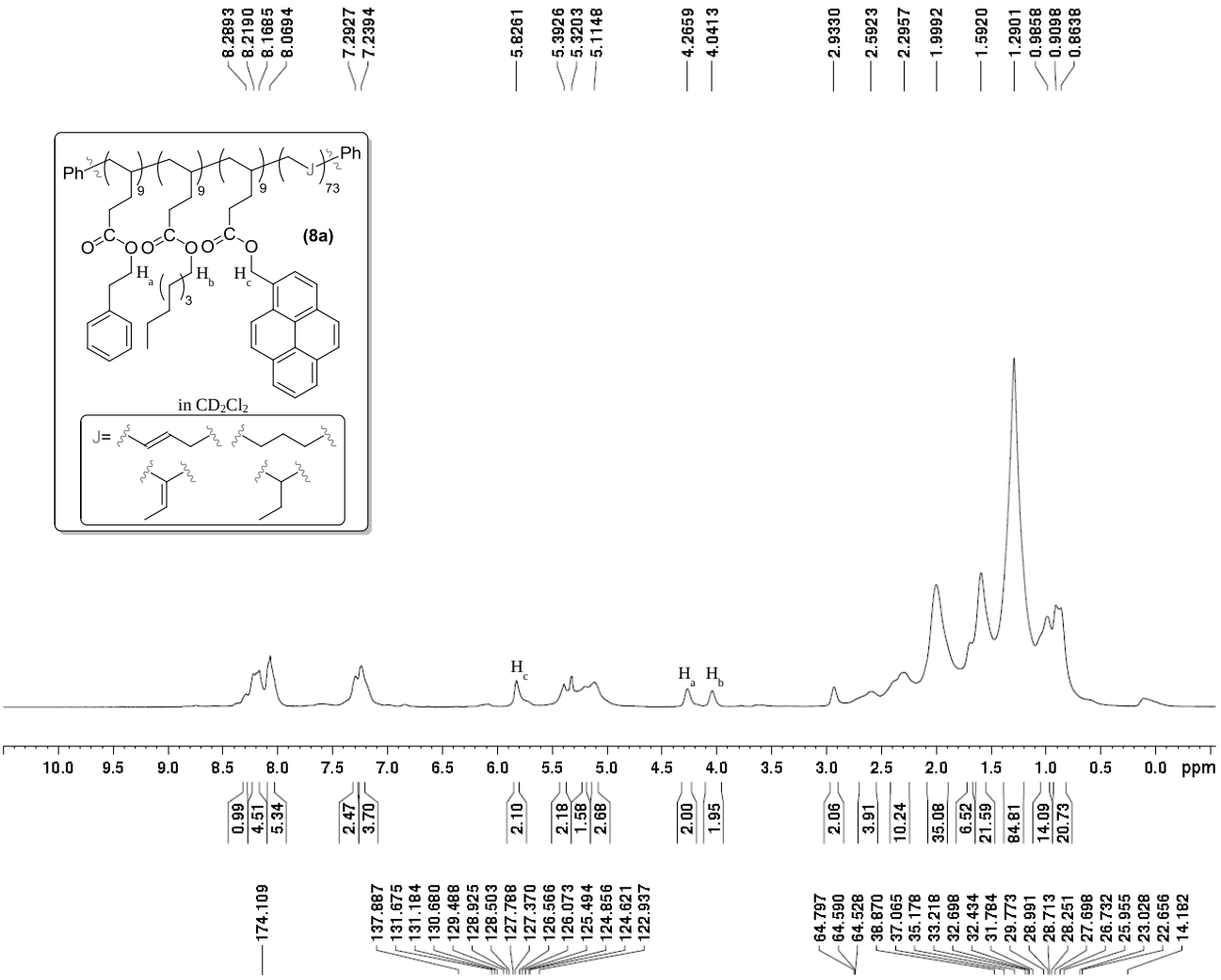

7.2731
7.2275
5.3198
5.1770
5.0947
4.2481
4.0212
2.9163
2.5735
2.2631
1.9795
1.5707
1.2718
0.9694
0.8908
0.8362
Ph
11
11
J
78
Ph
(7a)
in CD2Cl2
J=
Ha Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.36
3.55
1.30
0.83
1.31
2.00
2.01
2.03
1.38
4.23
12.41
3.69
11.54
52.28
7.80
12.69

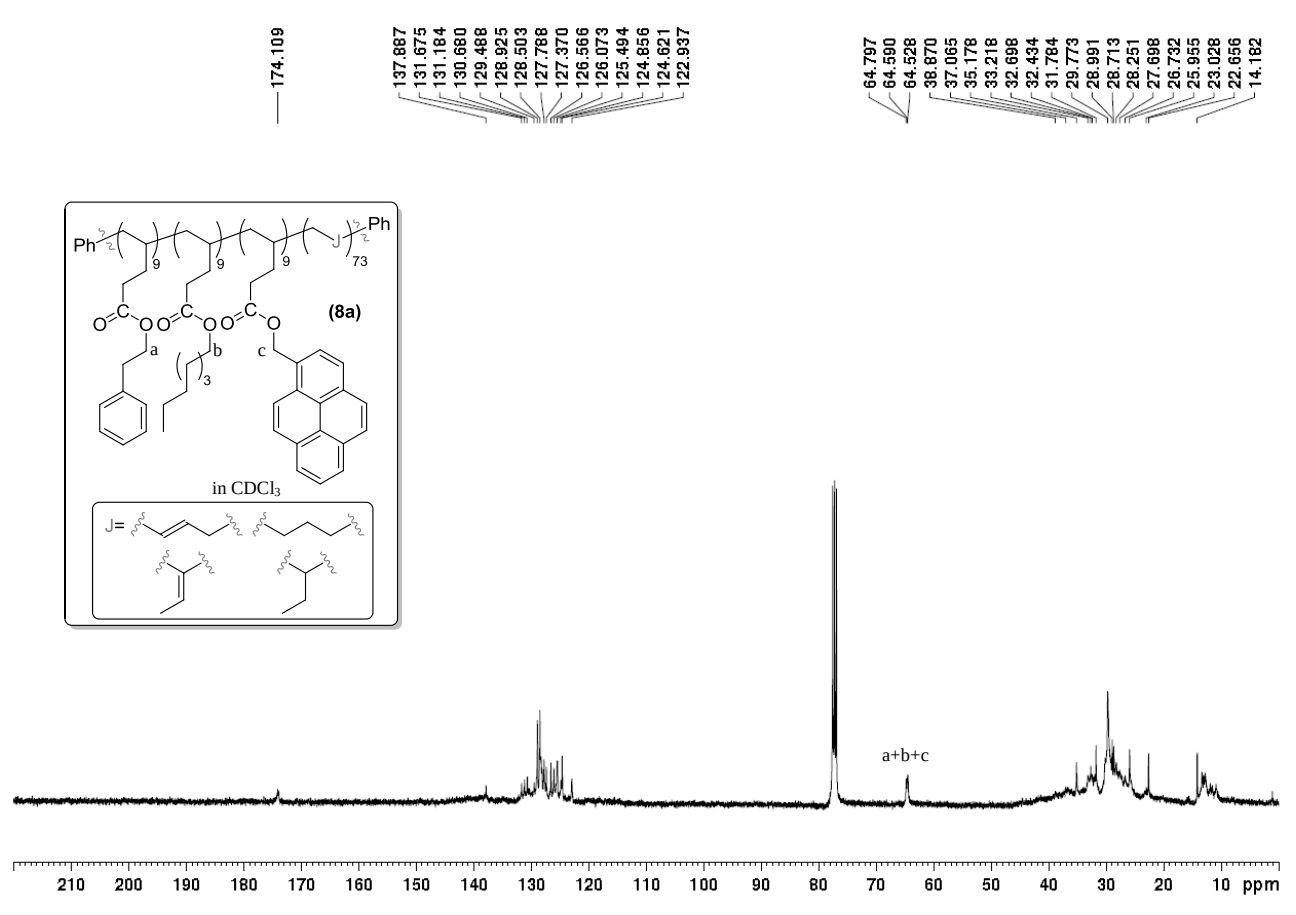

174.059
137.933
128.992
128.569
126.630
64.844
64.522
38.661
36.734
35.270
33.315
32.783
31.866
30.714
30.332
29.855
29.070
28.788
28.347
27.802
26.894
26.035
22.732
14.239
Ph
11
11
J
78
Ph
(7a)
in CDCl3
J=
a
b
a+b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

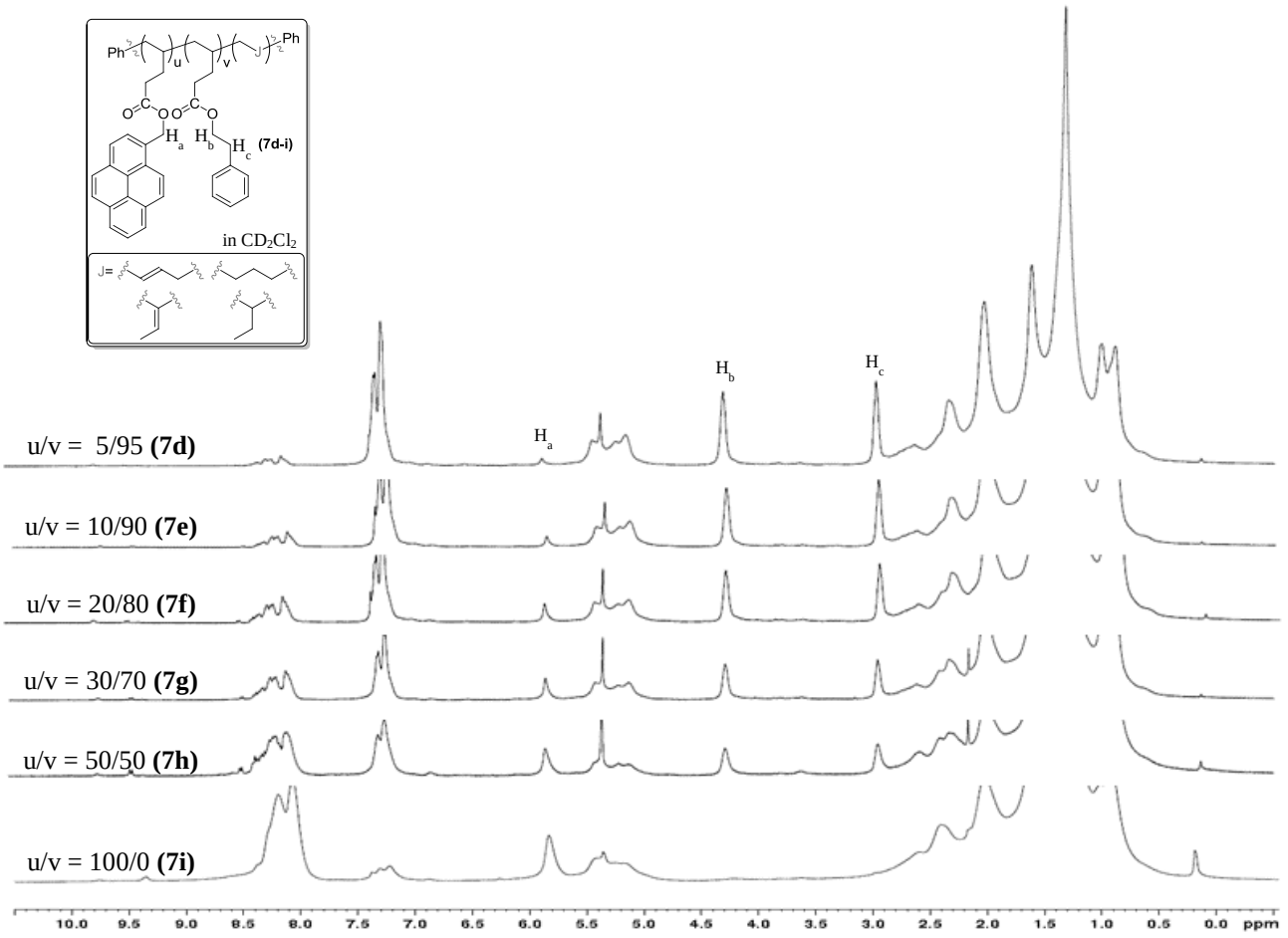

7.2705
7.2247
7.1561
6.9296
6.8606
5.3848
5.3197
5.1788
5.0942
4.2484
3.1316
2.9131
2.5912
2.2892
1.9746
1.5631
1.2668
0.9657
0.8317
Ph
13
13
J
74
Ph
(7b)
in CD2Cl2
J=
Hb Ha
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
3.46
1.15
0.96
1.03
1.34
1.33
1.78
4.00
2.06
1.99
1.58
5.06
19.27
3.38
14.72
41.24
8.49
5.21

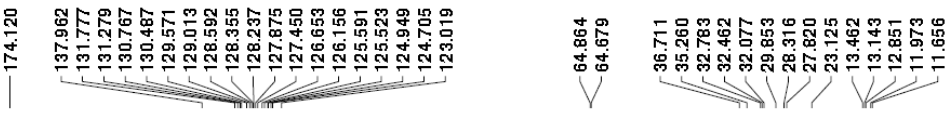

173.997
140.060
137.947
129.008
128.586
128.494
126.936
126.648
125.583
124.091
64.854
64.575
35.277
33.267
32.776
32.414
32.030
30.345
29.857
29.451
28.341
27.833
26.912
25.949
13.461
13.146
12.859
Ph
13
13
J
74
Ph
a
b
(7b)
in CDCl3
J=
a+b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

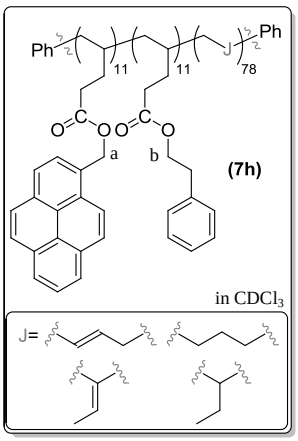

7.2965
7.2794
7.2361
7.2189
7.1664
5.3934
5.3186
5.1801
5.1018
4.2370
3.7978
2.8976
2.8285
2.8130
2.7986
2.5976
2.2724
1.9838
1.6787
1.5766
1.2731
0.9780
0.8541
0.8380
Ph
12
12
76
Ph
in CD2Cl2
(7c)
Ha
Hb
Hc
OH
Ha+Hb
Hc
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
3.28
4.50
1.04
1.37
1.76
4.00
2.05
4.10
2.36
1.20
4.46
14.88
3.90
10.86
47.81
6.91
9.68
174.105
141.096
137.952
136.921
136.019
129.277
129.210
129.016
128.595
126.655
64.918
63.741
38.948
37.141
36.738
35.281
34.891
33.319
32.787
32.499
32.072
30.342
29.879
28.393
27.818
26.884
26.000
13.467
13.156
Ph
12
12
76
Ph
in CDCl3
(7c)
a
b
OH
a
b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

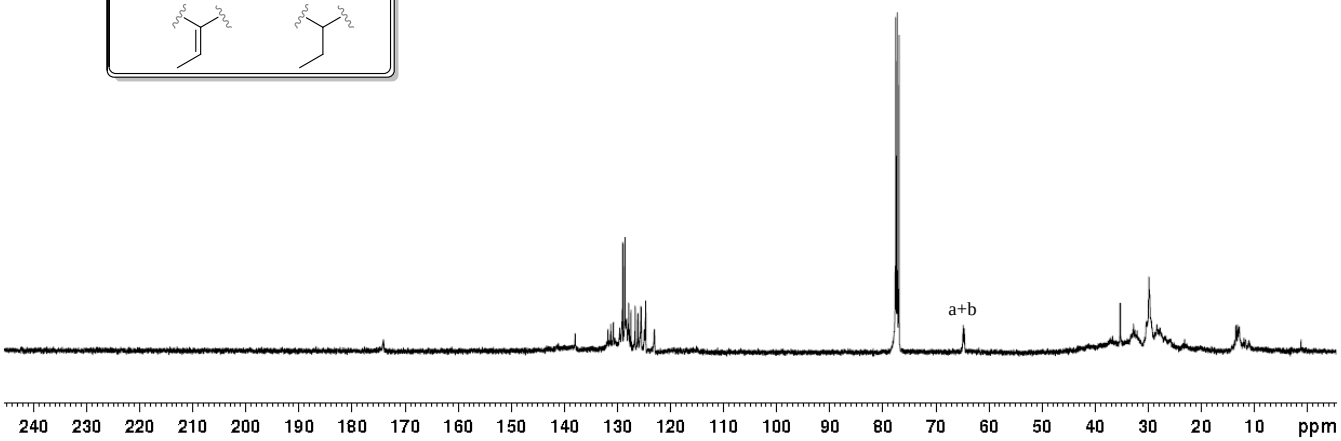

8.2893
8.2190
8.1685
8.0694
7.2927
7.2394
5.6261
5.3926
5.3203
5.1148
4.2659
4.0413
2.9330
2.5923
2.2957
1.9992
1.5920
1.2901
0.9858
0.9098
0.8638
(8a)
in CD2Cl2
J=
Hc
Ha Hb
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.99 4.51 5.34 2.47 3.70 2.10 2.18 1.58 2.68 2.00 1.95 2.06 3.91 10.24 35.08 6.52 21.59 84.81 14.09 20.73


174.109
137.887
131.675
131.184
130.680
129.488
128.925
128.503
127.788
127.370
126.566
126.073
125.494
124.856
124.621
122.937
64.797
64.590
64.528
38.870
37.065
35.178
33.218
32.698
32.434
31.784
29.773
28.991
28.713
28.251
27.698
26.732
25.955
23.028
22.656
14.182
(8a)
in CDCl3
J=
a+b+c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

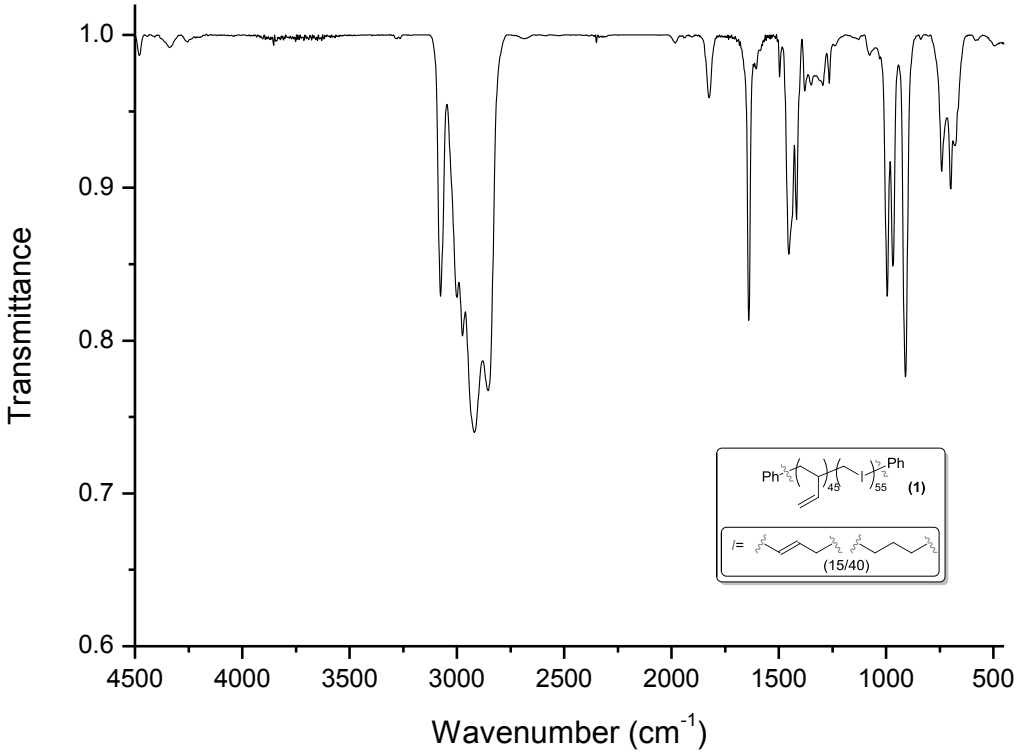

Ph
u
v
J
Ph
H_a H_b H_c (7d-i)
in CD_2Cl_2
J=
u/v = 5/95 (7d)
u/v = 10/90 (7e)
u/v = 20/80 (7f)
u/v = 30/70 (7g)
u/v = 50/50 (7h)
u/v = 100/0 (7i)
H_a
H_b
H_c
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

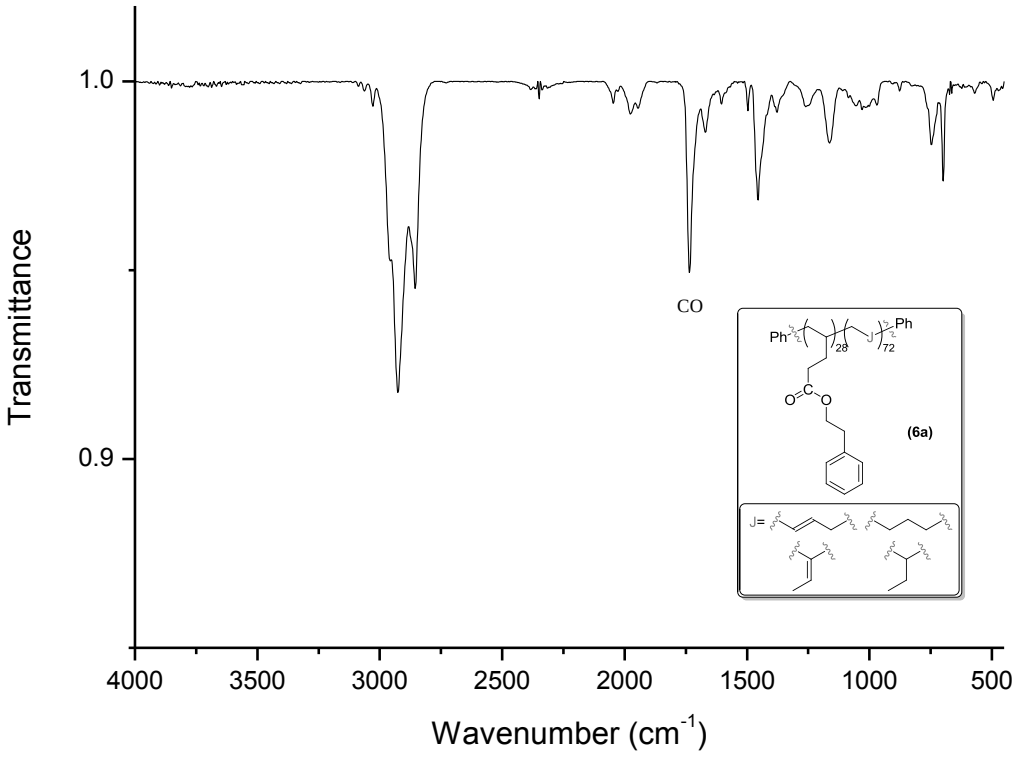

174.120
137.962
131.777
131.279
130.767
130.487
129.571
129.013
128.592
128.355
128.237
127.875
127.450
126.653
126.156
125.591
125.523
124.949
124.705
123.019
64.864
64.679
36.711
35.260
32.783
32.462
32.077
29.853
28.316
27.820
23.125
13.462
13.143
12.851
11.973
11.656

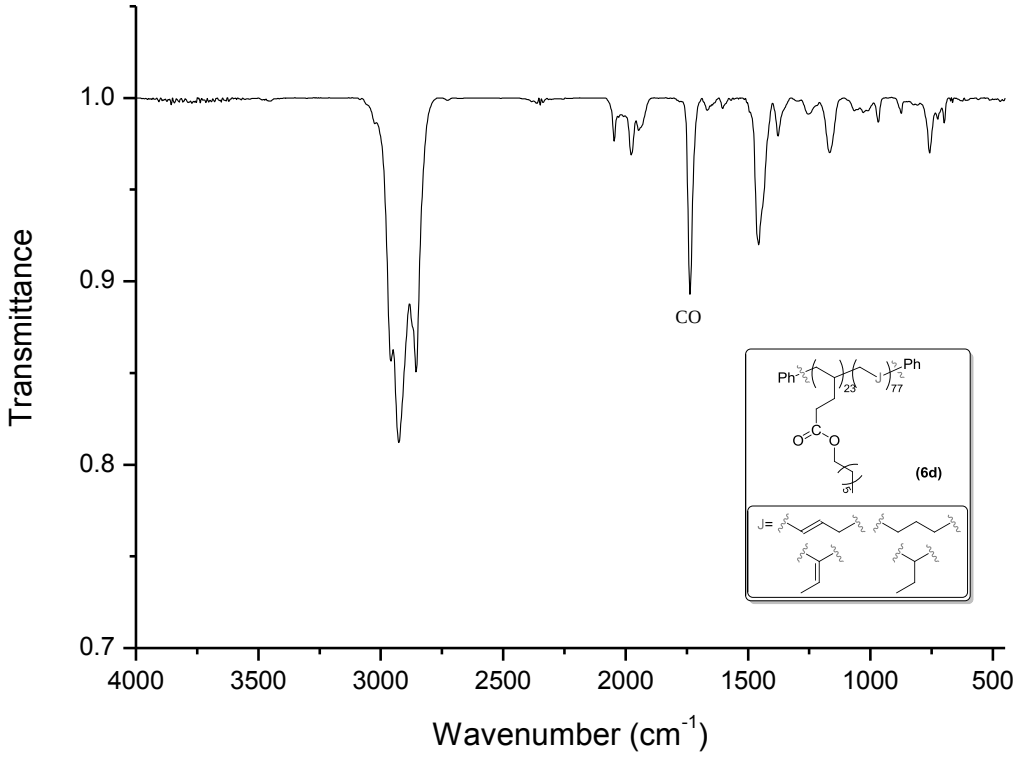

Ph
11
11
J
78
Ph
a
b
(7h)
in $CDCl_3$
J=

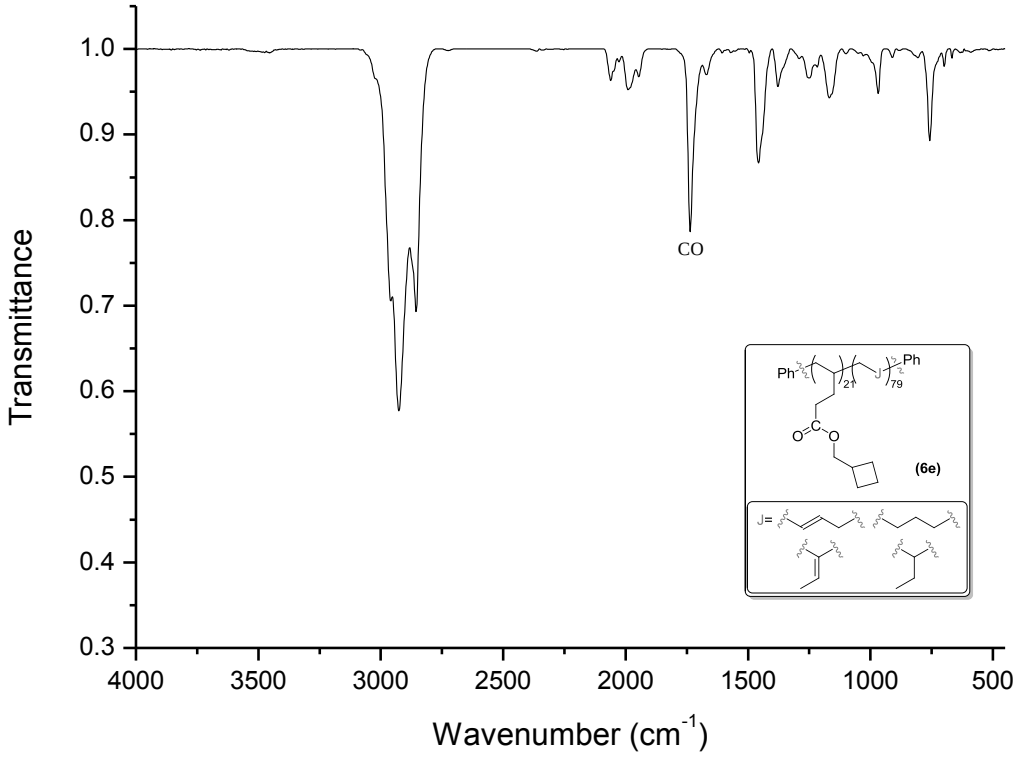

a+b
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

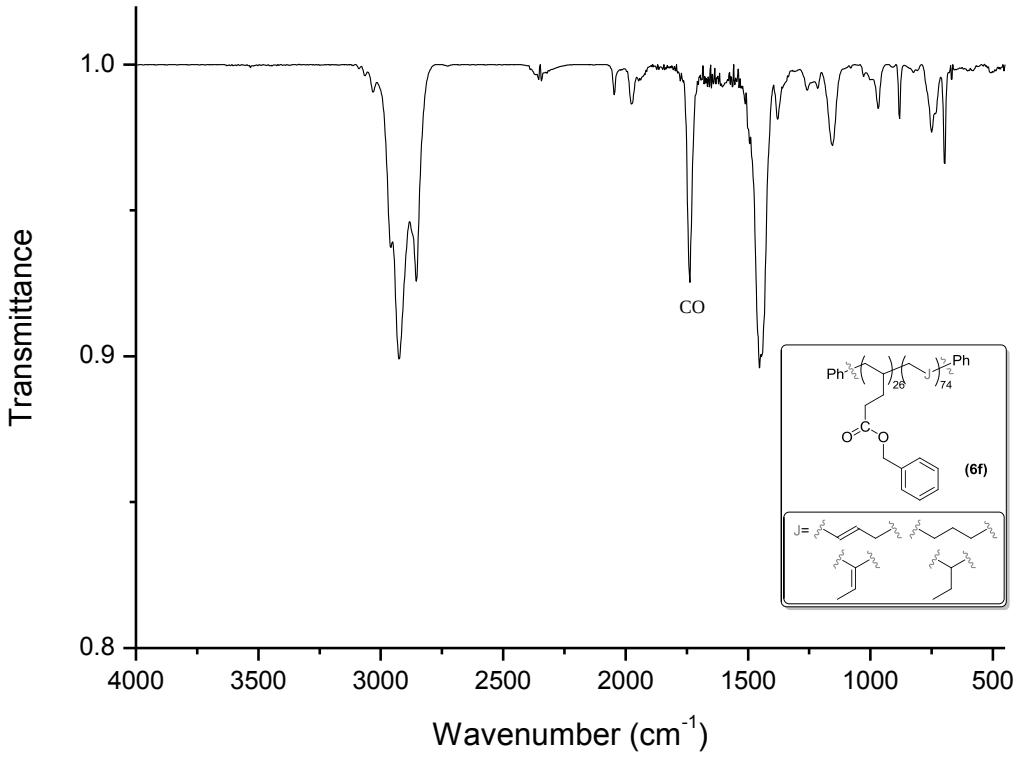
IR SPECTRA

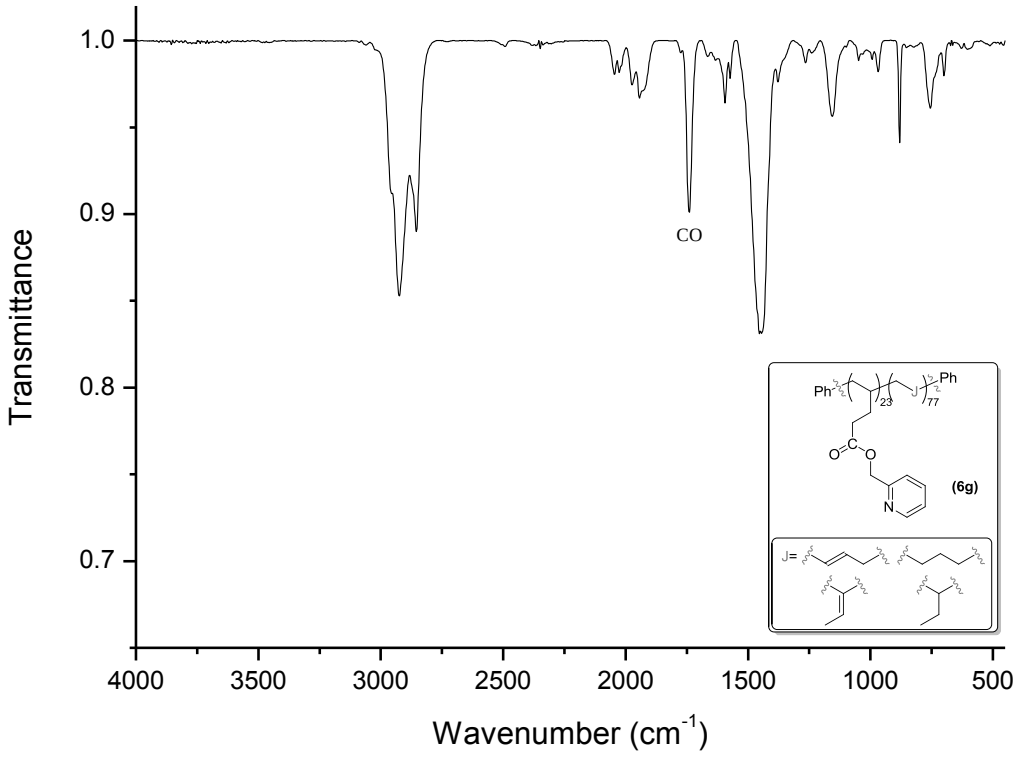

Transmittance
1.0
0.9
0.8
0.7
0.6
4500
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
Ph
Ph
49
55
(1)
/=
(15/40)

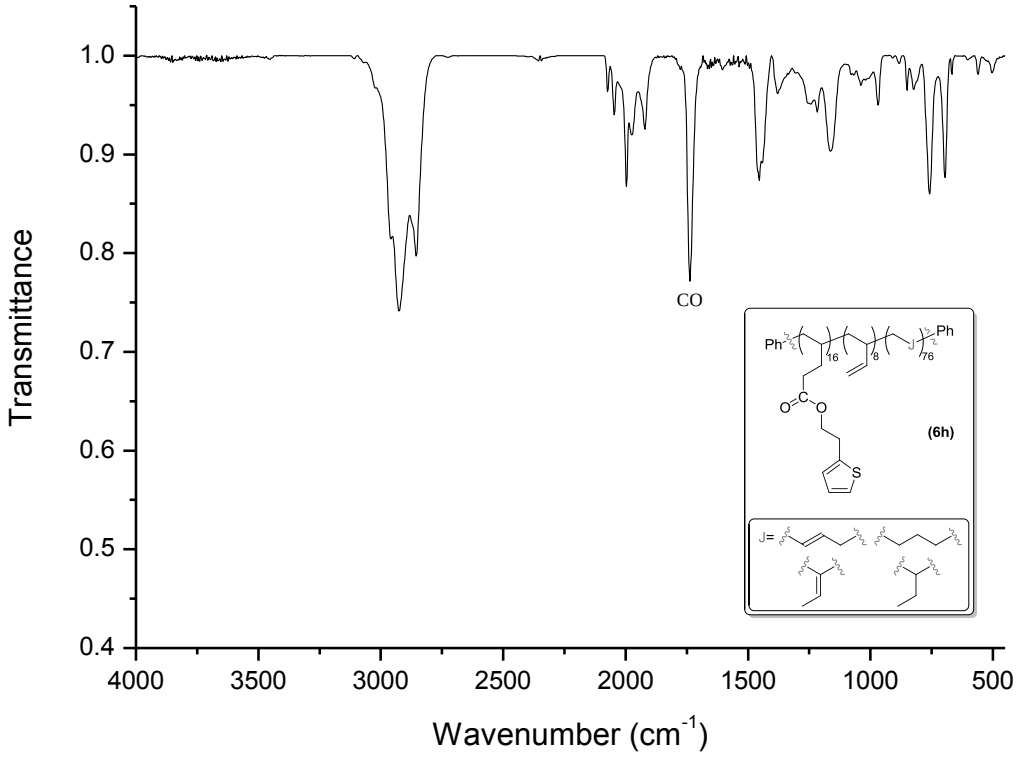

Transmittance
1.0
0.9
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
Ph
28
72
O
C
O
(6a)
J=

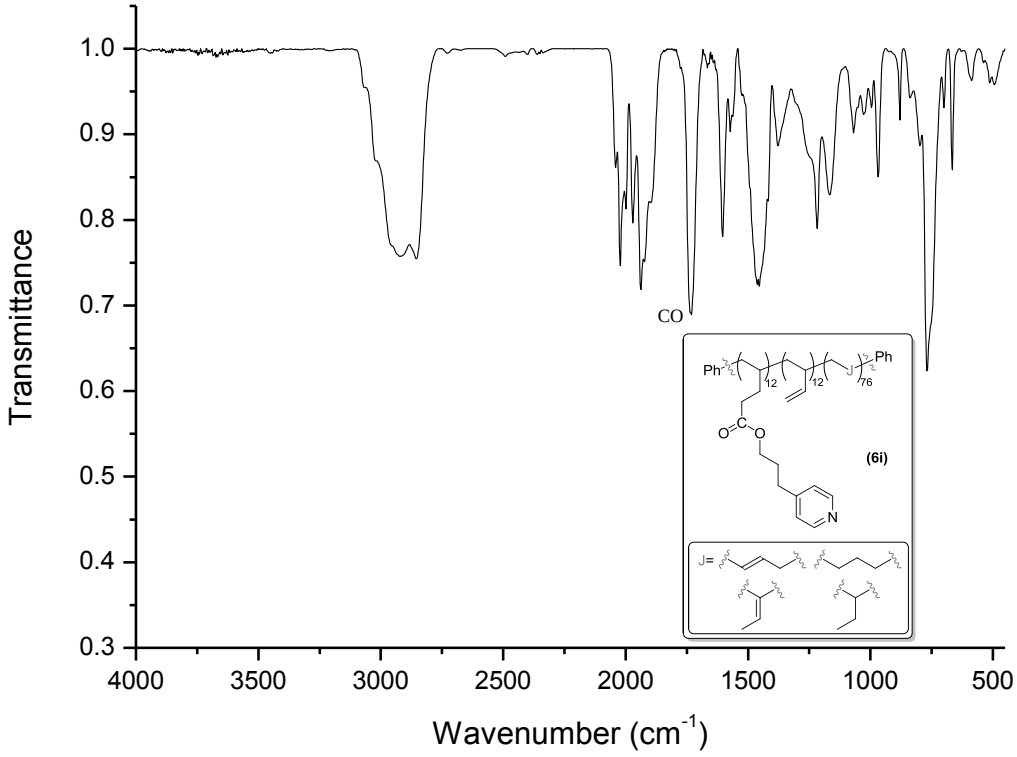

Transmittance
1.0
0.9
0.8
0.7
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
23
77
Ph
(6d)
J=

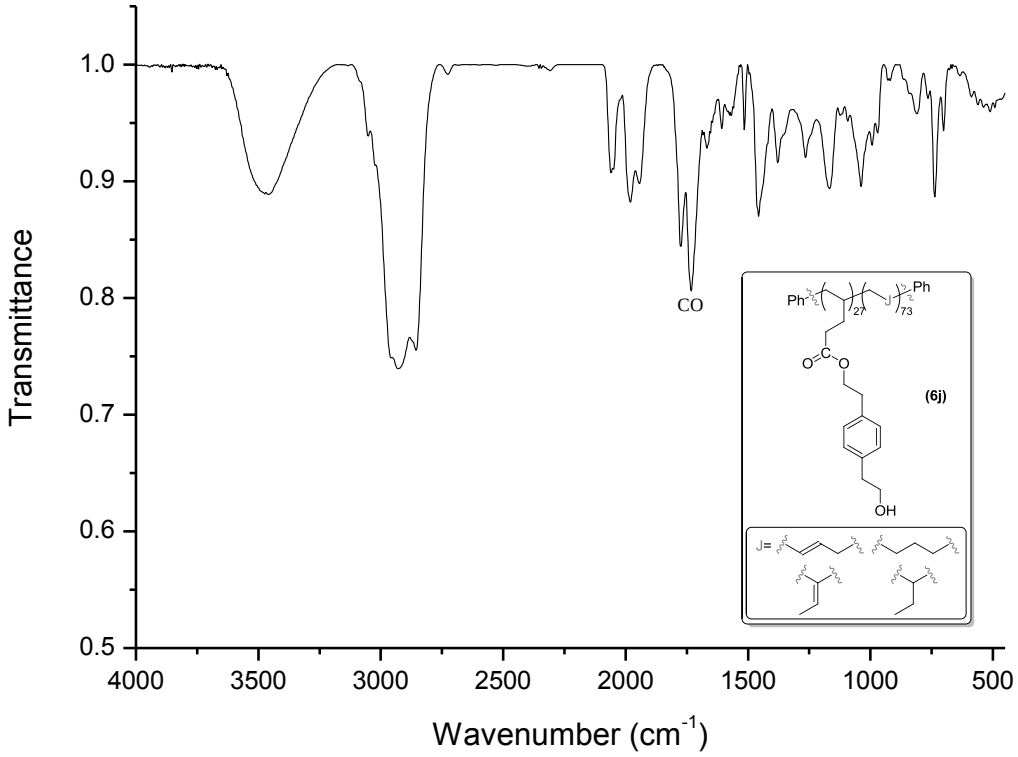

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
21
79
Ph
(6e)
J=

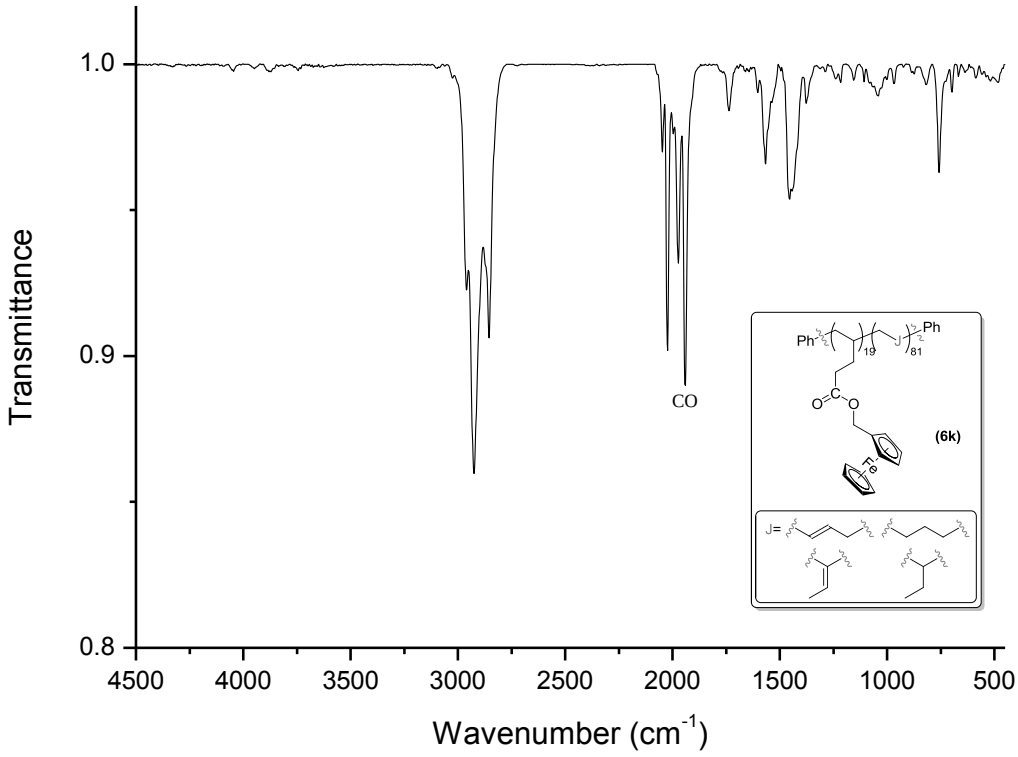

1.0
0.9
0.8
Transmittance
CO
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
Ph
26
J
74
Ph
(6f)
J=

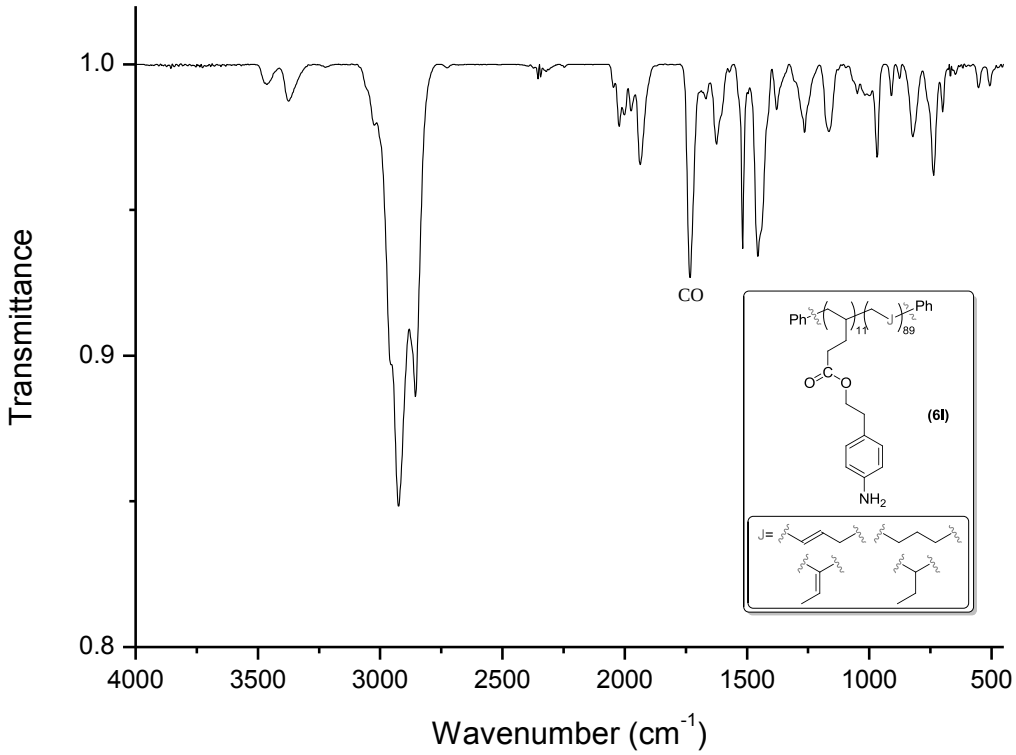

1.0
0.9
0.8
0.7
Transmittance
CO
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
Ph
23
J
77
Ph
(6g)
N
J=

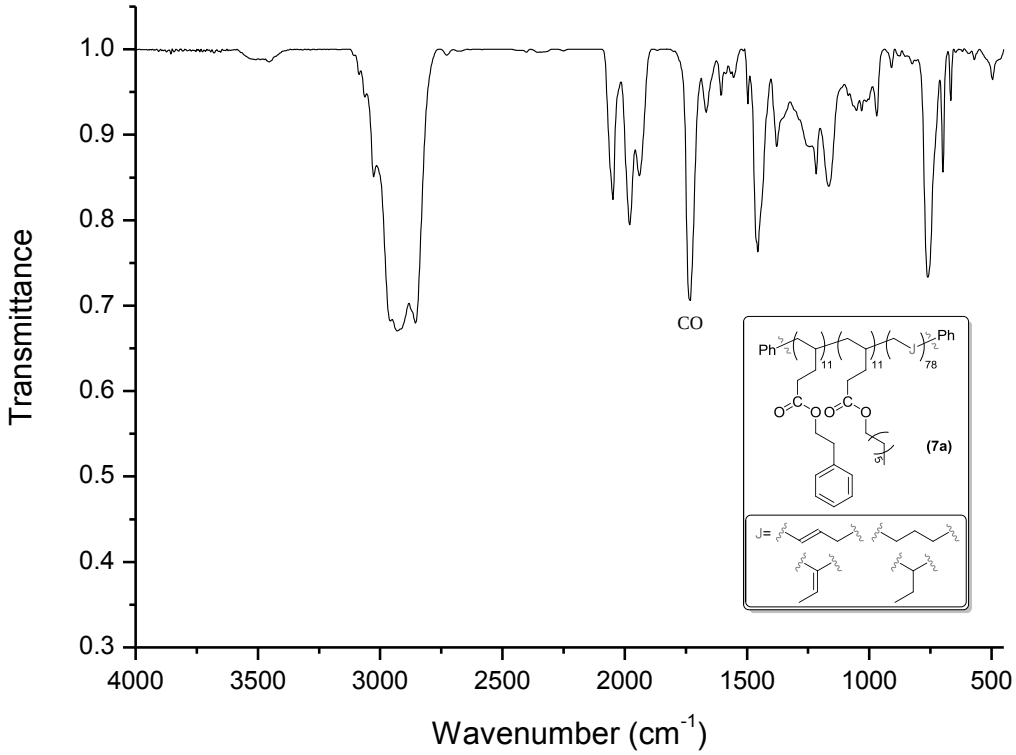

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
(6h)

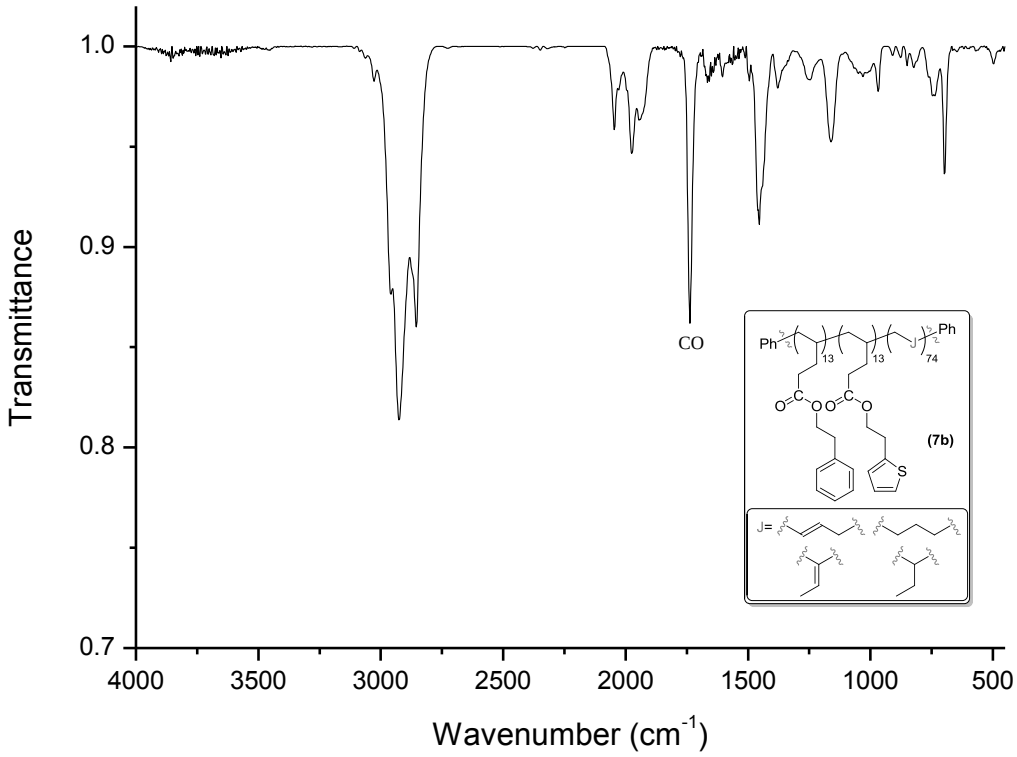

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
(6i)

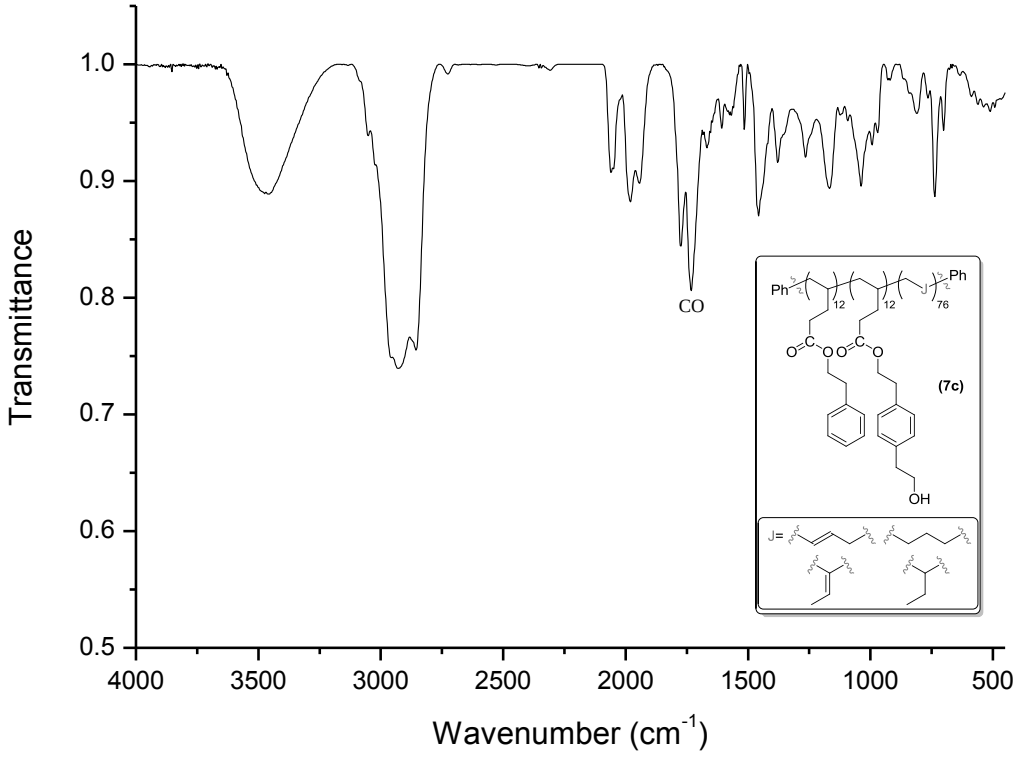

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
27
J
73
Ph
O
O
(6j)
OH
J=

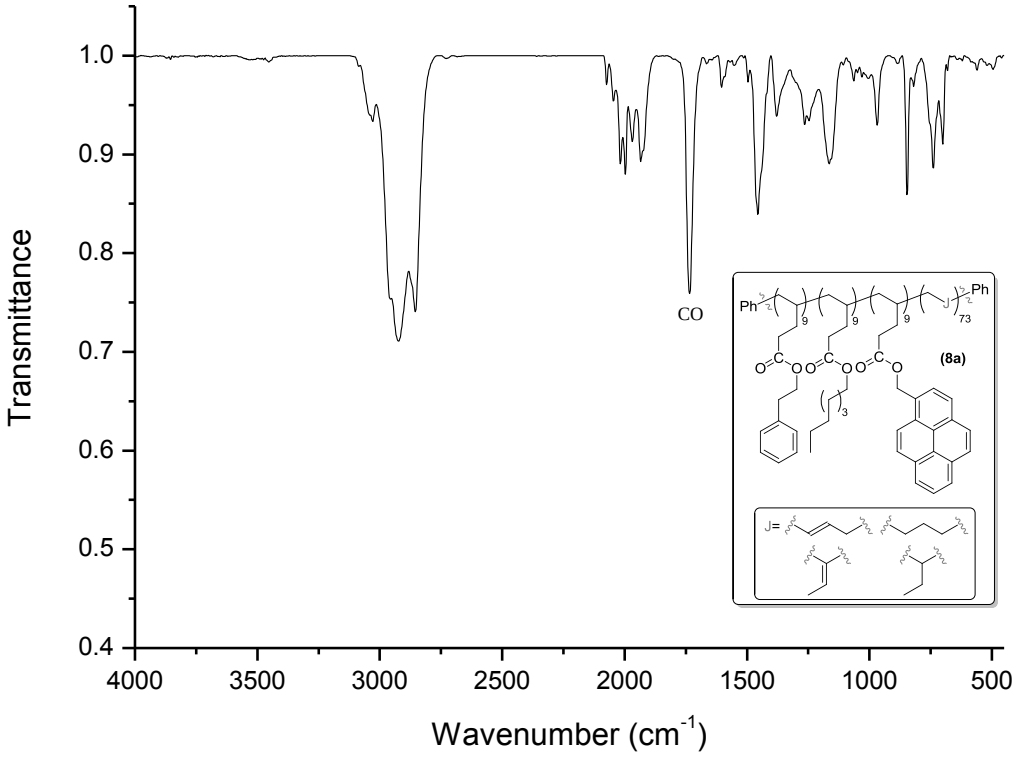

Transmittance
1.0
0.9
0.8
4500
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
19
J
81
Ph
O
O
(6k)
Fe
J=

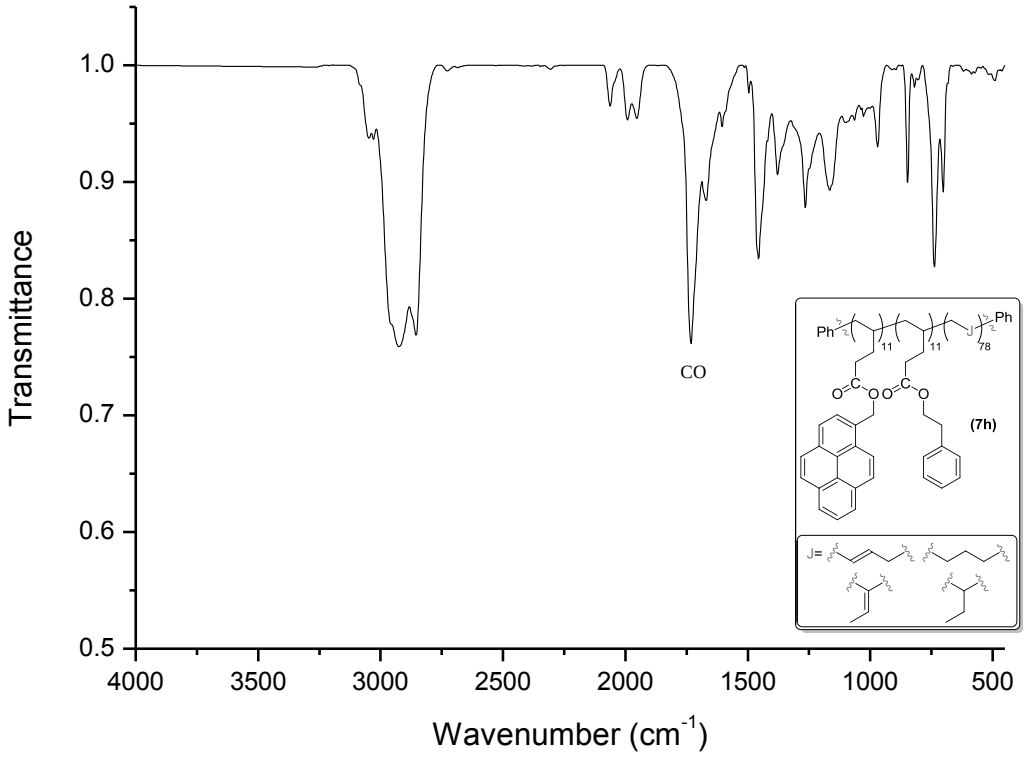

Transmittance
1.0
0.9
0.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
(6l)


Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
(7a)


Transmittance
1.0
0.9
0.8
0.7
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
13
13
74
Ph
(7b)
S
J=


Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
CO
Ph
12
12
76
Ph
(7c)
OH
J=


Transmittance
Wavenumber (cm-1)
CO
(8a)
J=


Transmittance
Wavenumber (cm-1)
CO
(7h)
J=

TGA and DSC thermograms

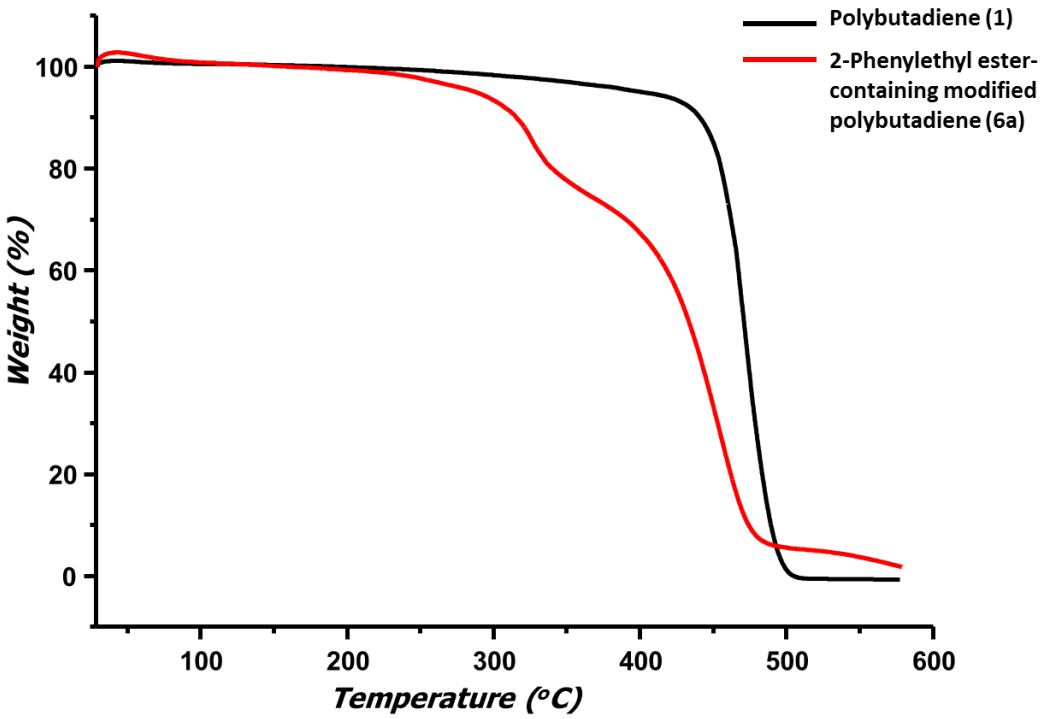


Fig S2. TGA plots of polybutadiene (**1**) and 2-phenylethyl ester-containing modified polybutadiene (**6a)**

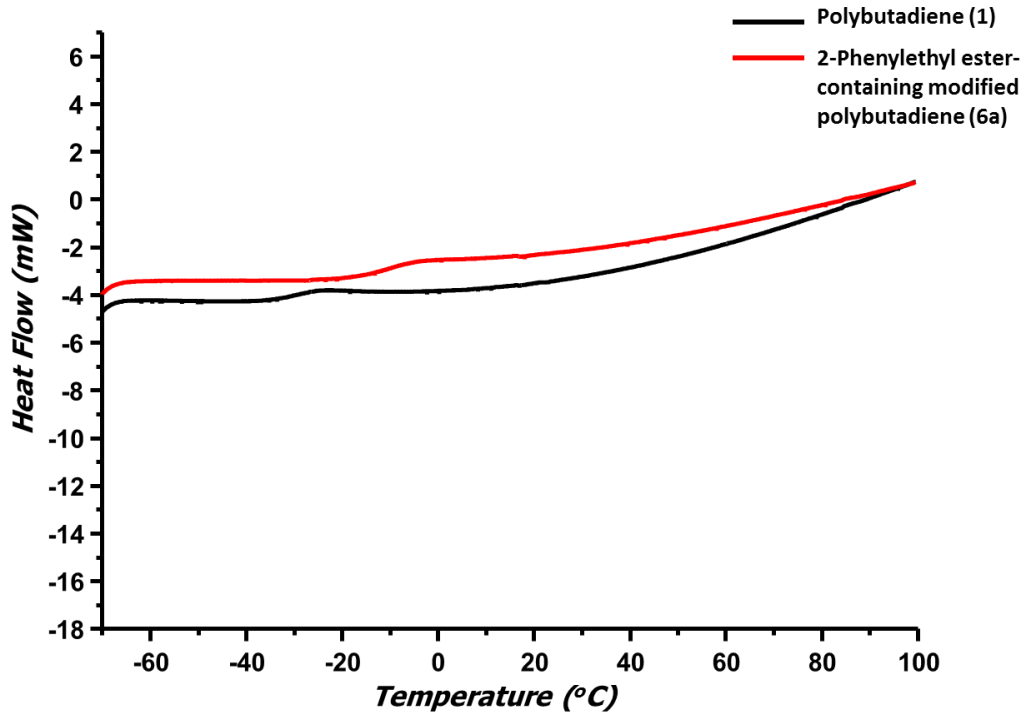


Fig S3. DSC trace of polybutadiene (**1**) and 2-phenylethyl ester-containing modified polybutadiene (**6a)**