Supporting Information

Effect of spacer stiffness on the properties of hyperbranched polymers

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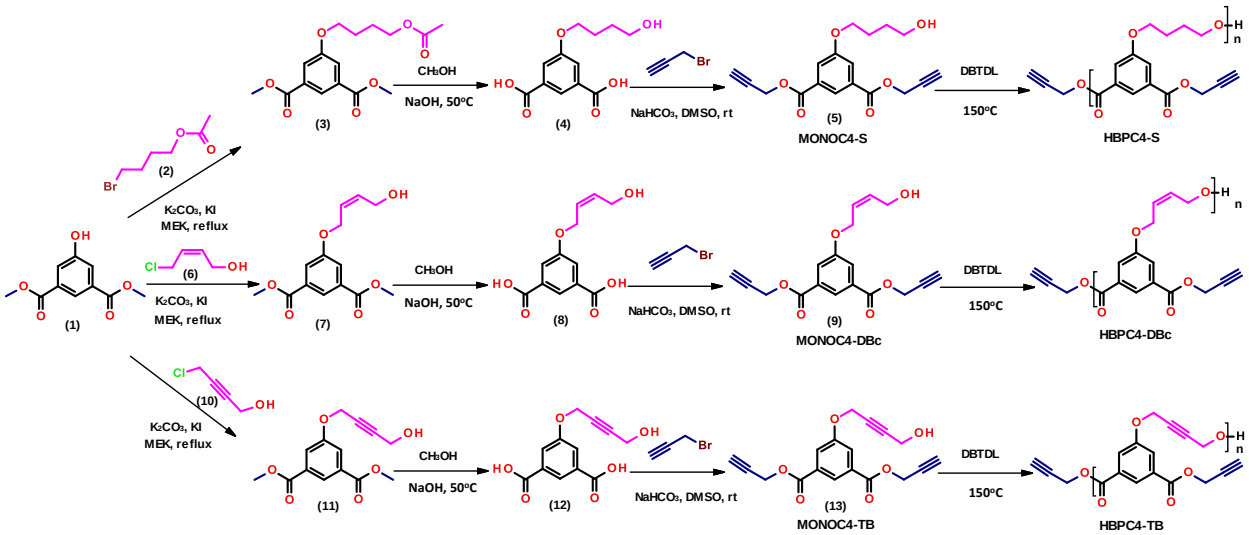
EXPERIMENTAL SECTION

Scheme-SI1: Synthetic routes for the preparation of hyperbranched polymers



Synthesis of Monomers

Synthesis of MONOC4-S

Dimethyl 5-hydroxyisophthalate (1) (yield = 96%), 4-Bromobutylacetate (2) (71%), Dimethyl 5-(4-acetoxybutoxy) isophthalate (3) (85%) and 5-(4-hydroxybutoxy) isophthalic acid (4) (75%) were synthesized via the same procedure as shown in reference RS1.

Reference RS1: Samuel, A. Z.; Ramakrishnan, S. Janus Hybramers: Self-Adapting Amphiphilic Hyperbranched Polymers. *Macromolecules* **2012**, *45*, 2348-2358.

Di (prop-2-yn-1-yl) 5-(4-hydroxybutoxy) isophthalate (MONOC4-S) (5)

5-(4-Hydroxybutoxy) isophthalic acid (3.5g, 13.77 mmol), and $NaHCO_3$ (4.6g, 55.11 mmol) were taken in DMSO (50 mL) and stirred for 1h at room temperature under nitrogen atmosphere. Then, propargyl bromide (4.09g, 34.42 mmol) was added to it. After 24 h, $CHCl_3$ was added to it and washed with water few times to remove DMSO and salts. The $CHCl_3$ layer was passed through Na_2SO_4 and concentrated under reduced pressure to yield the product as a light brownish white color solid. This was further purified by using silica gel column chromatography where the EtOAc and pet ether (20:80) was used as the eluent. Yield = 90%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.75-1.80 (m, 2H, -OCH_2CH2**CH_2**CH2-); 1.88-1.95 (m, 2H, -OCH_2**CH2**CH_2CH2-); 2.54 (t, 2H, -$COOCH_2C$**CH**); 3.74 (t, 2H, -OCH_2CH2CH_2**CH2**-); 4.09 (t, 2H, -O**CH_2**CH2CH_2CH2-); 4.93-4.94 (d, 2H, -COO**CH_2**CCH); 7.77 (d, 2H, -**ArH**); 8.31 (t, 1H, -**ArH**).

Synthesis of MONOC4-DB*c*

4-Chlorobut-2-en-1-ol (6) (90%) was synthesized via the same procedure as shown in reference RS2

Reference RS2: Ravikumar, V. T.; Cheruvallath, Z. S. A Convenient Large-scale Synthesis of 4-Cyno-2-Butene-1-ol. *Synthetic Communications* **1996**, *26*, 1815-1819.

Dimethyl 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalate (7)

Dimethyl 5-hydroxyisophthalate (6g, 28.57 mmol), K_2CO_3 (15.7g, 114.28 mmol), catalytic amount of KI were taken in 130 mL of dry MEK. 4-Chlorobut-2-en-1-ol (3.65g, 34.28 mmol) was added to it and nitrogen was purged into it for 10 min. The reaction mixture was refluxed for 72h under nitrogen atmosphere. Then the solvent was removed under reduced pressure, and water was added to the residue. It was extracted with ethyl acetate, and the ethyl acetate layer was washed with brine solution. The organic layer was passed through Na_2SO_4 and the solvent was removed under reduced pressure to get the product as a white color solid. This was further purified by using silica gel column chromatography where the EtOAc and pet ether (15:85) was used as the eluent. Yield = 76%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.94 (s, 6H, -COO**CH_3**); 4.22-4.23 (dd, 2H, -OCH_2CHCH**CH_2**OH); 4.62-4.64 (dd, 2H, -O**CH_2**$CHCHCH_2OH$); 5.75-5.80 (m, 1H, -OCH_2CH**CH**CH_2OH); 5.89-5.98 (m, 1H, -OCH_2**CH**$CHCH_2OH$); 7.74 (t, 2H, -**ArH**); 8.26 (t, 1H, -**ArH**).

5-((4-Hydroxybut-2-en-1-yl) oxy) isophthalic acid (8)

Dimethyl 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalate (6g, 21.42 mmol) and methanol (120 mL) were taken in 250 mL of round bottom flask. NaOH (3.42g, 85.71 mmol) was dissolved in 10 mL of water and added to the reaction mixture. The reaction mixture was stirred for 48h at 50^{o}C. Then, the methanol was removed under reduced pressure. Then the residue was dissolved in small amount of water. It was acidified with dil. HCl and it was kept in freeze (0^{o}C) for 10h to get a white precipitate. The precipitate was filtered and dried by using Buchner funnel to get the product as a white crystalline solid. Yield = 73%.

^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 3.44 (d, 2H, -O**CH$_2$**CHCHCH$_2$OH); 3.94 (d, 2H, -OCH$_2$CHCH**CH$_2$**OH); 4.93-5.20 (m, 2H, -OCH$_2$**CHCH**CH$_2$-); 6.94 (s, 2H, -**ArH**); 7.43 (s, 1H, -**ArH**)

Di (prop-2-yn-1-yl) 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalate (MONOC4-DB*c*) (9)

5-((4-Hydroxybut-2-en-1-yl) oxy) isophthalic acid (3.3g, 13 mmol), and $NaHCO_3$ (4.36g, 52 mmol) were taken in DMSO (50 mL) and stirred for 1h at room temperature under nitrogen atmosphere. Propargyl bromide (4.64g, 39 mmol) was added dropwise to it. After 24 h, $CHCl_3$ was added to the reaction mixture and washed with water few times to remove DMSO and salts. Then the $CHCl_3$ layer was passed through Na_2SO_4 and concentrated under reduced pressure to yield the product as a viscous brownish color liquid. This was further purified by using silica gel column chromatography where the EtOAc and pet ether (30:70) was used as the eluent. Yield = 88%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.54 (t, 2H, -COOCH$_2$C**CH**); 4.34-4.35 (d, 2H, -OCH$_2$CHCH**CH$_2$**OH); 4.73-4.74 (d, 2H, -O**CH$_2$**CHCHCH$_2$OH); 4.94 (s, 2H, -COO**CH$_2$**CCH); 5.73-5.80 (m, 1H, -OCH$_2$CH**CH**CH$_2$OH); 5.88-6.09 (m, 1H, -OCH$_2$**CH**CHCH$_2$OH); 7.78 (t, 2H, -**ArH**); 8.31 (t, 1H, -**ArH**).

Synthesis of MONOC4-TB

4-Chlorobut-2-yn-1-ol (10) was synthesized via the same procedure as shown in reference RS3.

Reference RS3: Cuyamendous, C.; Leung, K. S.; Durand, T.; Lee, J. C. Y.; Oger, C.; Galano, J. M. Synthesis and Discovery of Phytofurans: Metabolites of α-Linolenic acid Peroxidation. *Chem. Commun.* **2015**, *51*, 15696-15699.

Dimethyl 5-((4-hydroxybut-2-yn-1-yl) oxy) isophthalate (11)

Dimethyl 5-hydroxyisophthalate (10g, 47.61 mmol), K_2CO_3 (39.4g, 285.7 mmol), catalytic amount of KI were taken in 200 mL of dry MEK. Then, 4-Chlorobut-2-yn-1-ol (5.97g, 57.14 mmol) was added to it and nitrogen was purged for 10 min. Then the reaction mixture was refluxed under N_2 atmosphere for 72h. Then the solvent was removed under reduced pressure, to this residue, cold water was added and extracted with ethyl acetate. Organic layer was passed through Na_2SO_4, concentrated under reduced pressure to obtain the product as a white color solid. Yield = 73%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.78 (s, 1H, -CCCH_2**OH**); 3.94 (s, 6H, -COO**C**$\mathbf{H_3}$); 4.30 (t, 2H, -CC**C**$\mathbf{H_2}$OH); 4.82 (s, 2H, -O**C**$\mathbf{H_2}$CCCH_2OH); 7.81 (t, 2H, -**ArH**); 8.31 (t, 1H, -**ArH**).

5-((4-(Hydroxybut-2-yn-1-yl) oxy) isophthalic acid (12)

Compound (11) (3g, 10.79 mmol), NaOH (1.72g, 43.16 mmol) were taken in 25 mL of methanol and 5 mL of water was added to it. The reaction mixture was stirred for 48h at 50^{o}C. Then the solvent was removed under reduced pressure, diluted HCl (2N) was added to it to get white precipitate. It was kept in freeze for few hours, it was filtered and dried to get the product as a white crystalline solid. Yield = 86%.

^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 2.54 (s, 2H, -CC**C**$\mathbf{H_2}$OH); 3.40 (t, 2H, -O**C**$\mathbf{H_2}$CCCH_2OH); 7.0 (d, 2H, -**ArH**); 7.46 (t, 1H, -**ArH**).

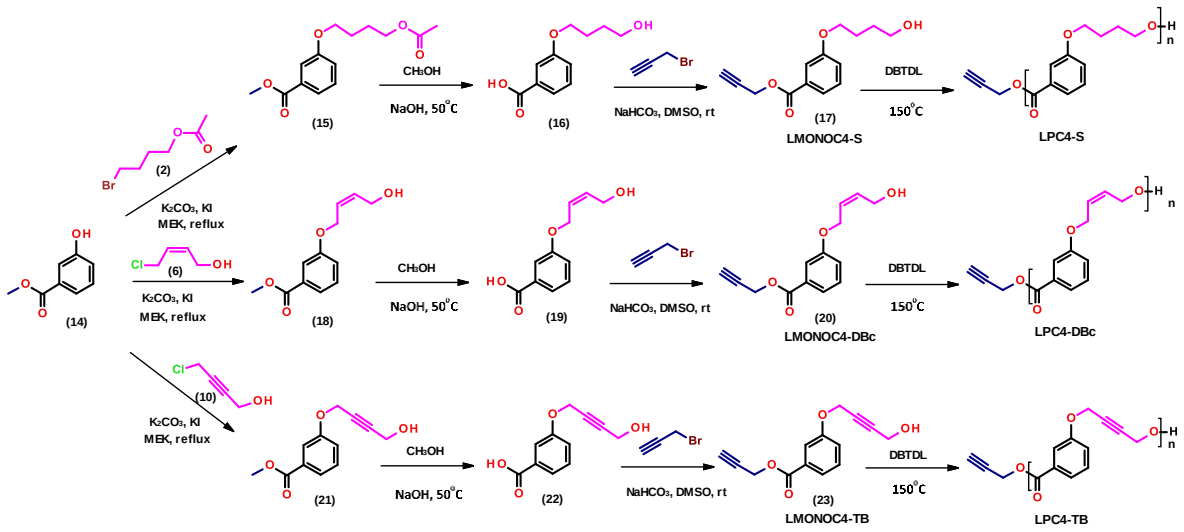
Di (prop-2-yn-1-yl) 5-((4-hydroxybut-2-yn-1-yl) oxy) isophthalate (MONOC4-TB) (13)

5-((4-(Hydroxybut-2-yn-1-yl) oxy) isophthalic acid (2g, 8 mmol), $NaHCO_3$ (2.68g, 32 mmol) were taken in 35 mL of DMSO and it was stirred for 1h at room temperature under nitrogen atmosphere. Then, propargyl bromide (2.85g, 24 mmol) was added to it and it was stirred for 24h at room temperature under nitrogen atmosphere. To this, 100 mL of $CHCl_3$ was added, it was washed with water few times to remove DMSO and salts. Then it was passed through anhydrous Na_2SO_4 and concentrated under reduced pressure to get the product as a viscous brownish liquid; the product was became solid after few hours. It was purified by using silica gel column chromatography where the EtOAc and pet ether (30:70) was used as the eluent. Yield = 90%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.54 (t, 2H, -$COOCH_2C$**CH**); 4.30-4.31 (d, 2H, -OCH_2CC**CH_2**OH); 4.82-4.83 (t, 2H, -O**CH_2**$CCCH_2OH$); 4.94-4.95 (d, 2H, -COO**CH_2**CCH); 7.86 (d, 2H, -**ArH**); 8.37 (t, 1H, -**ArH**).

Docosyl tosylate (87%) and Docosyl azide (86%) were prepared via the same procedure as shown in reference RS1.

Scheme-SI2: Synthetic routes for the preparation of linear polymers



LMONOC4-S (90%), LMONOC4-DB*c* (85%) and LMONOC4-TB (88%) monomers were synthesized via the same procedure as MONOC4-S (90%), MONOC4-DB*c* (88%) and MONOC4-TB (90%) respectively.

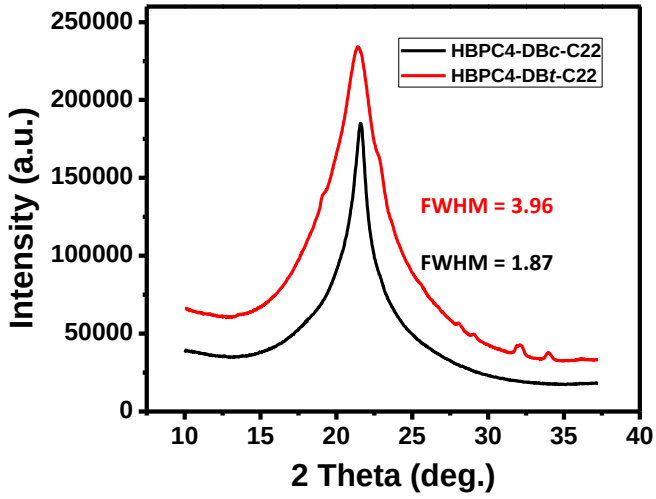
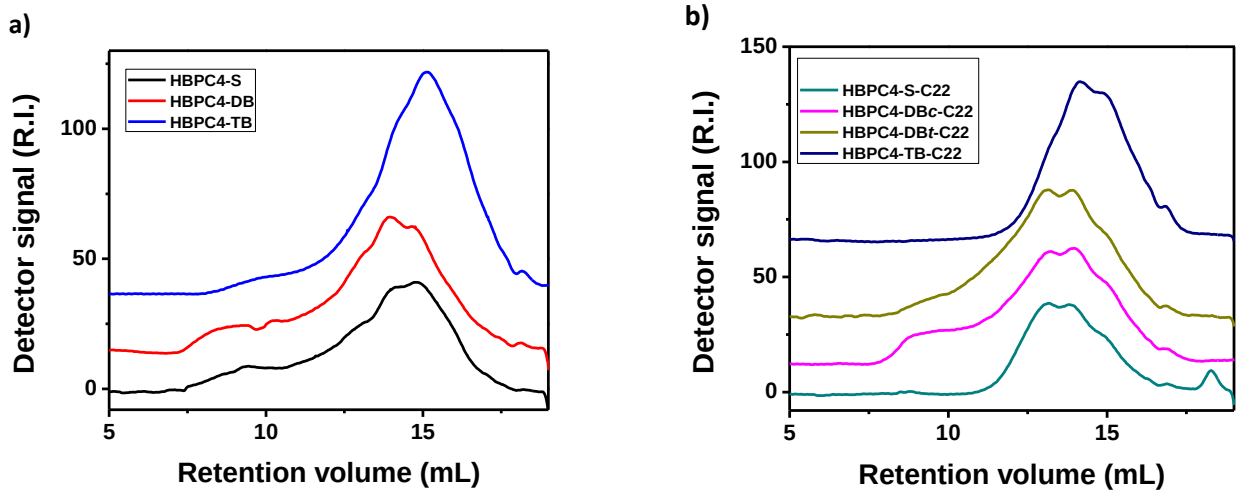


Figure S1: WAXS profiles of *cis* and *trans* HBPs.



c)

Polymer	M_n
HBPC4-S	10000
HBPC4-DB	10000
HBPC4-TB	5000
HBPC4-S-C22	16000
HBPC4-DB*c*-C22	16700
HBPC4-DB*t*-C22	17500
HBPC4-TB-C22	8500

Figure S2: GPC profiles of different parent HB polyesters (a), C22-derivatized HB polyesters (b) and M_n values of all the HBPs (c). The broad multi-modal distribution is often seen for such HBPs.

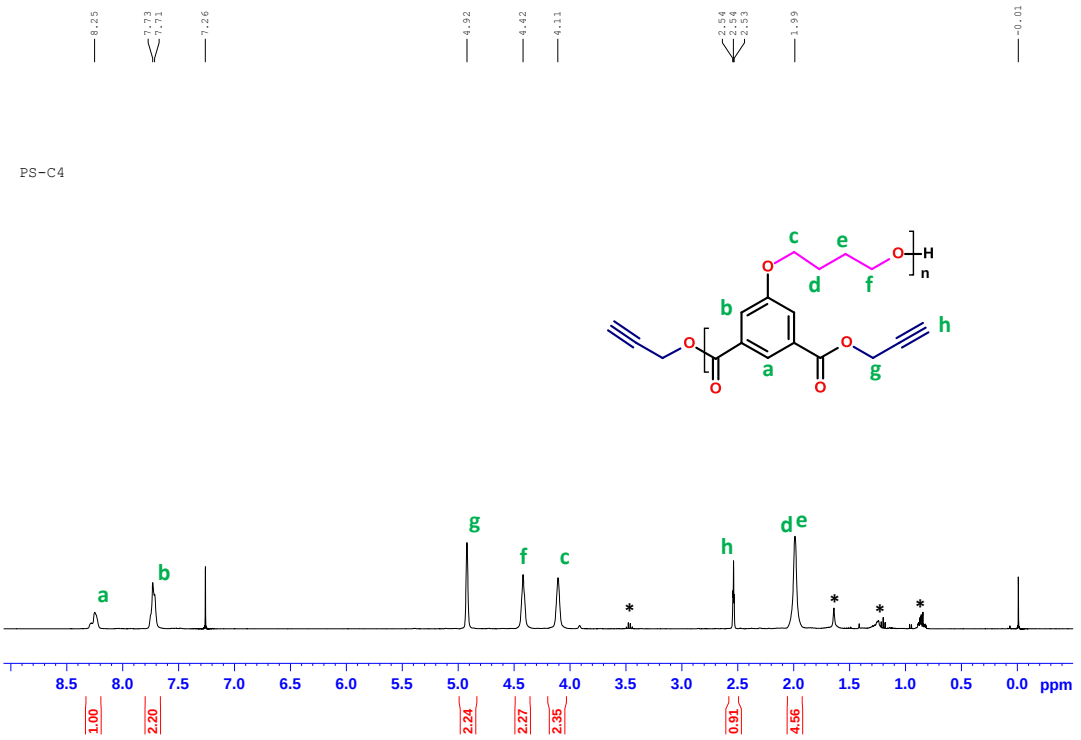


Figure-S3: ^{1}H NMR spectrum of di (prop-2-yn-1-yl) 5-(4-hydroxybutoxy) isophthalate (MONOC4-S)

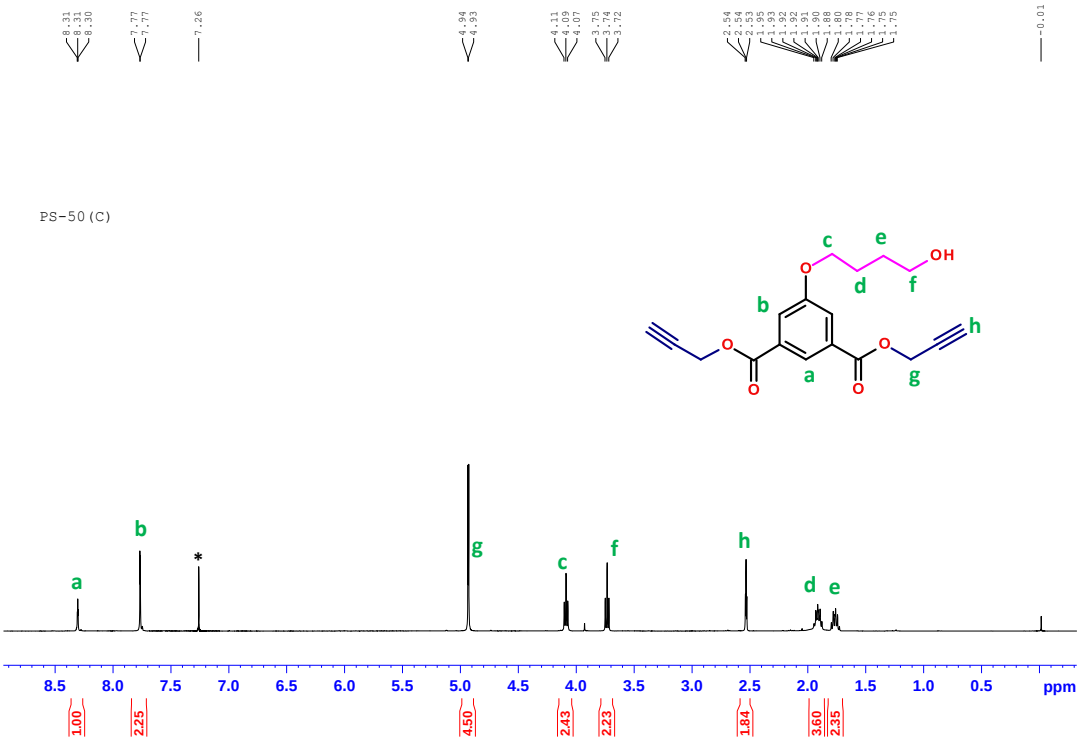


Figure-S4: ^{1}H NMR spectrum of HBPC4-S

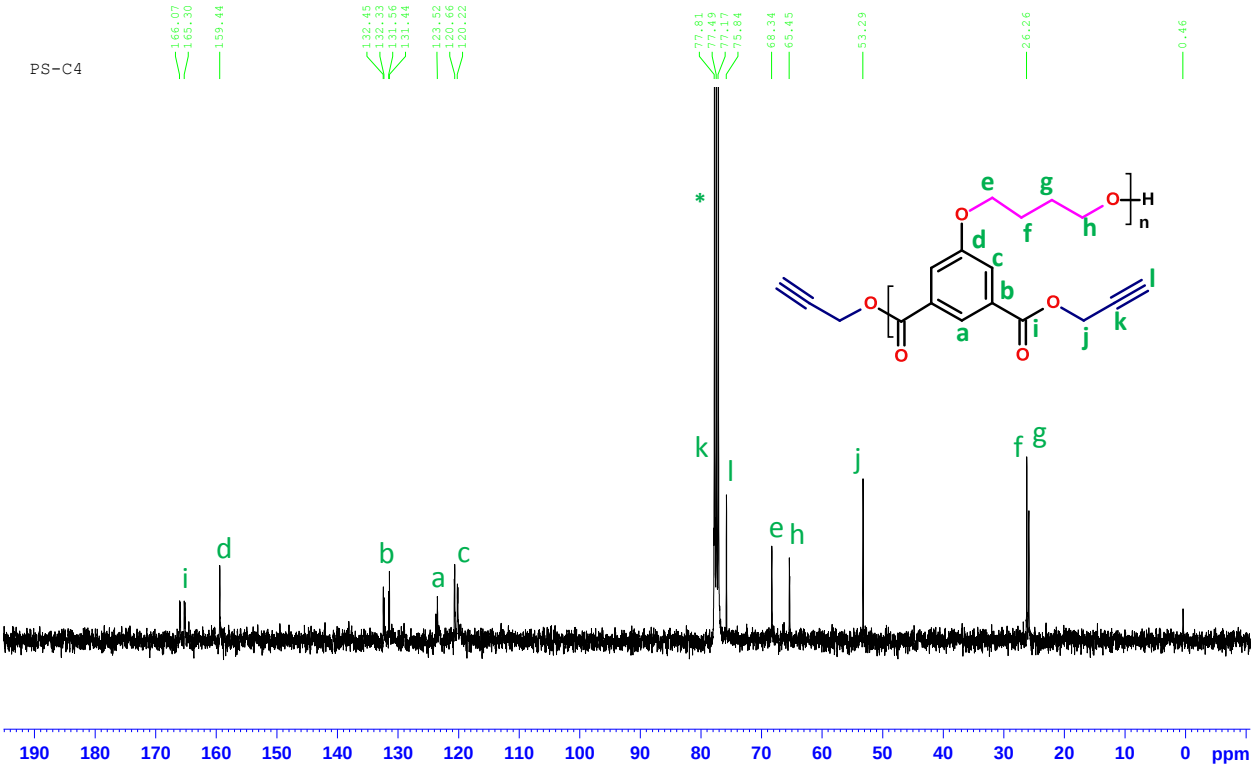


Figure-S5: ^{13}C NMR spectrum of HBPC4-S

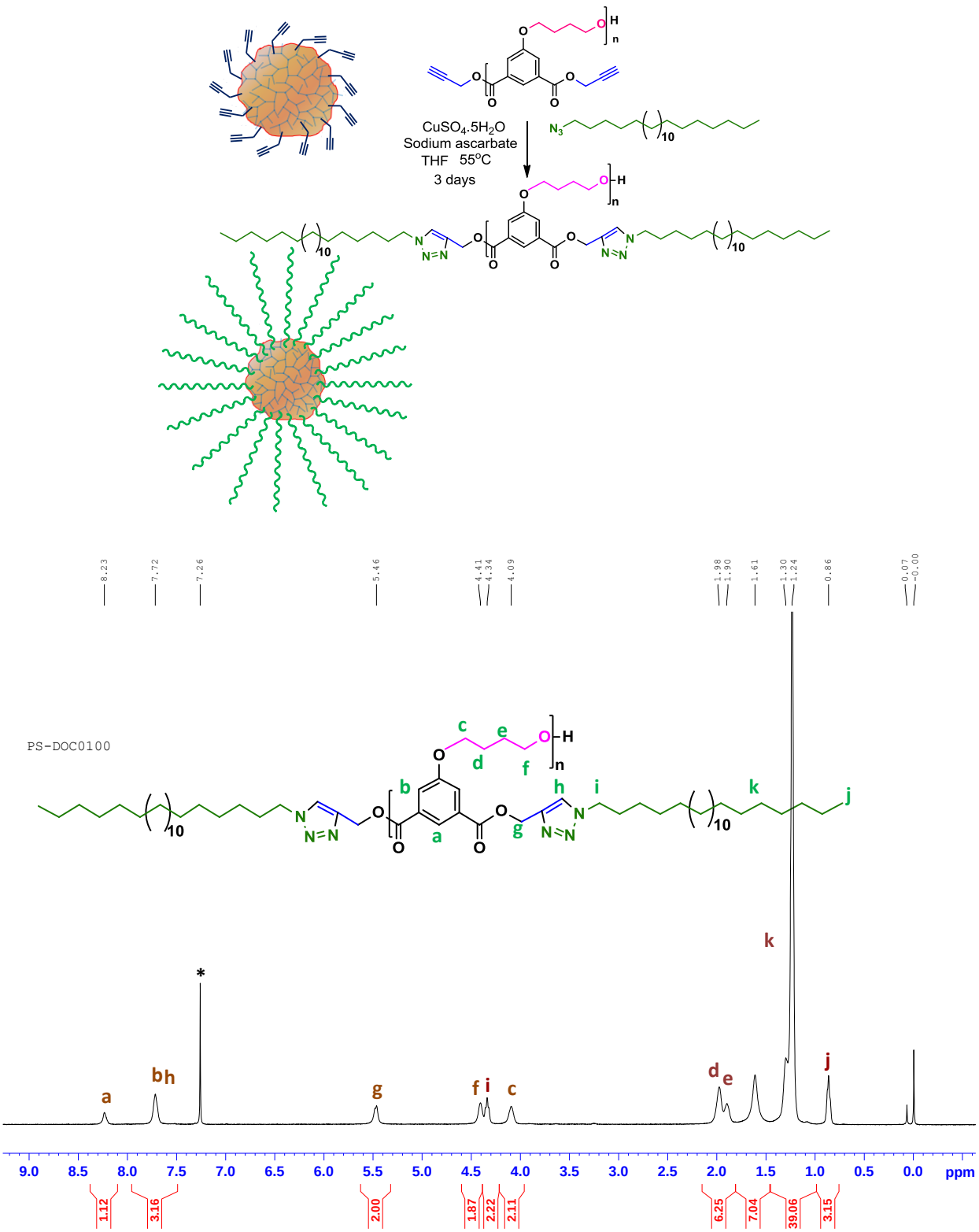


Figure-S6: Installation of crystallizable segments (C22 alkyl chains) on periphery of the HBPC4-S and ^{1}H NMR spectra of HBPC4-S-C22

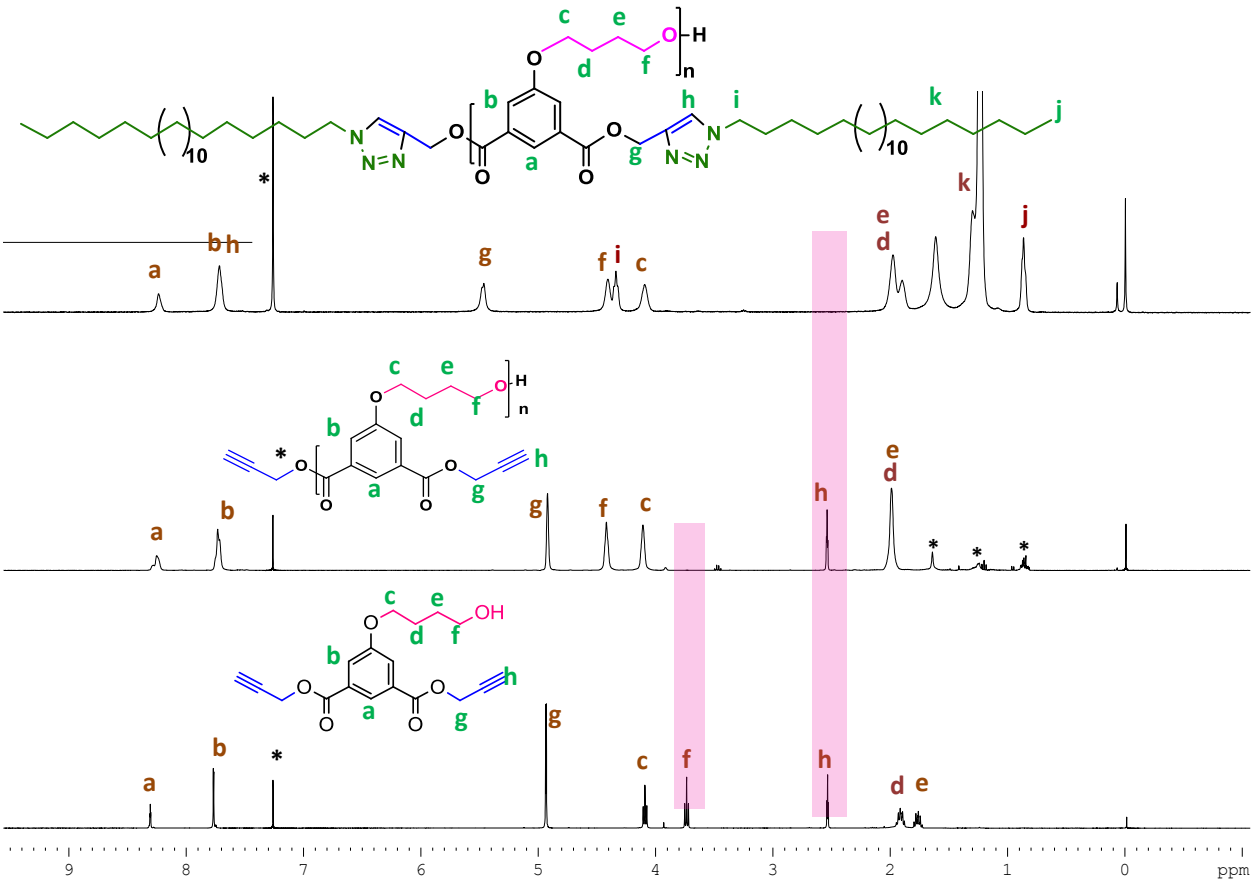


Figure-S7: Stacked ^{1}H NMR spectra of MONOC4-S, HBPC4-S and HBPC4-S-C22. Peak (f) is shifted from upfield to downfield is clearly indicating the polymer formation; the complete disappearance of the propargyl group proton peaks and the appearance of the traizole proton peak along with docosyl segment peaks confirm the completion of the click reaction.

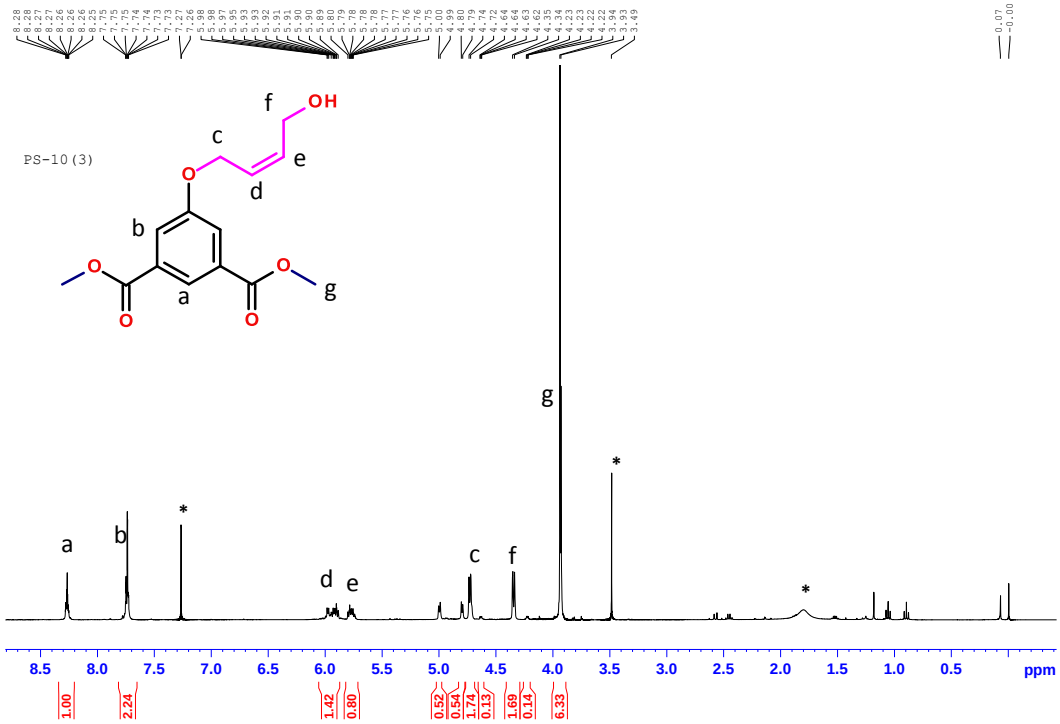


Figure-S8: [1]H NMR spectrum of dimethyl 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalate

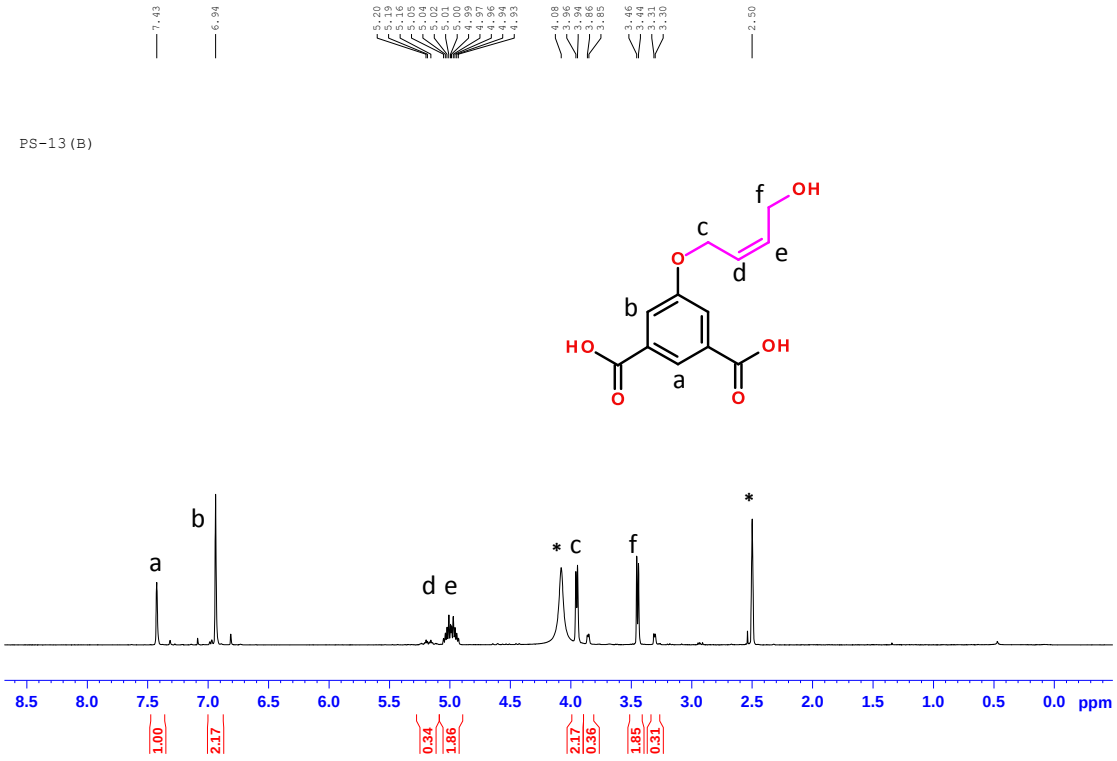


Figure-S9: [1]H NMR spectrum of 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalic acid

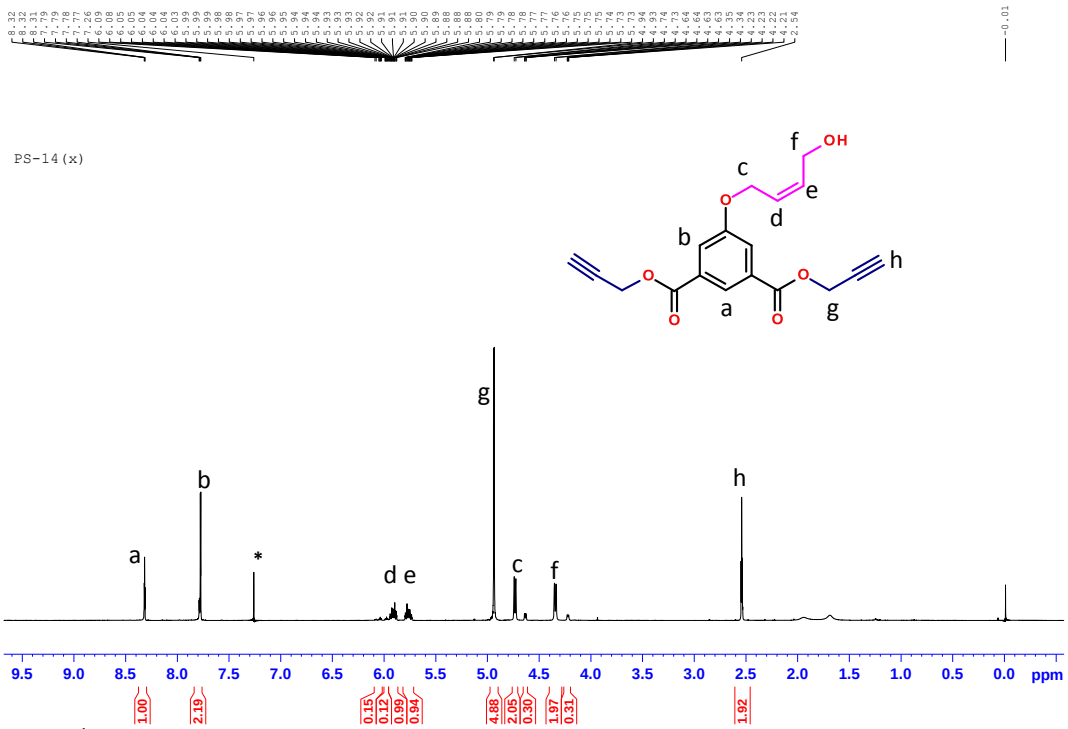


Figure-S10: ^{1}H NMR spectrum of di (prop-2-yn-1-yl) 5-((4-hydroxybut-2-en-1-yl) oxy) isophthalate (MONOC4-DB*c*)

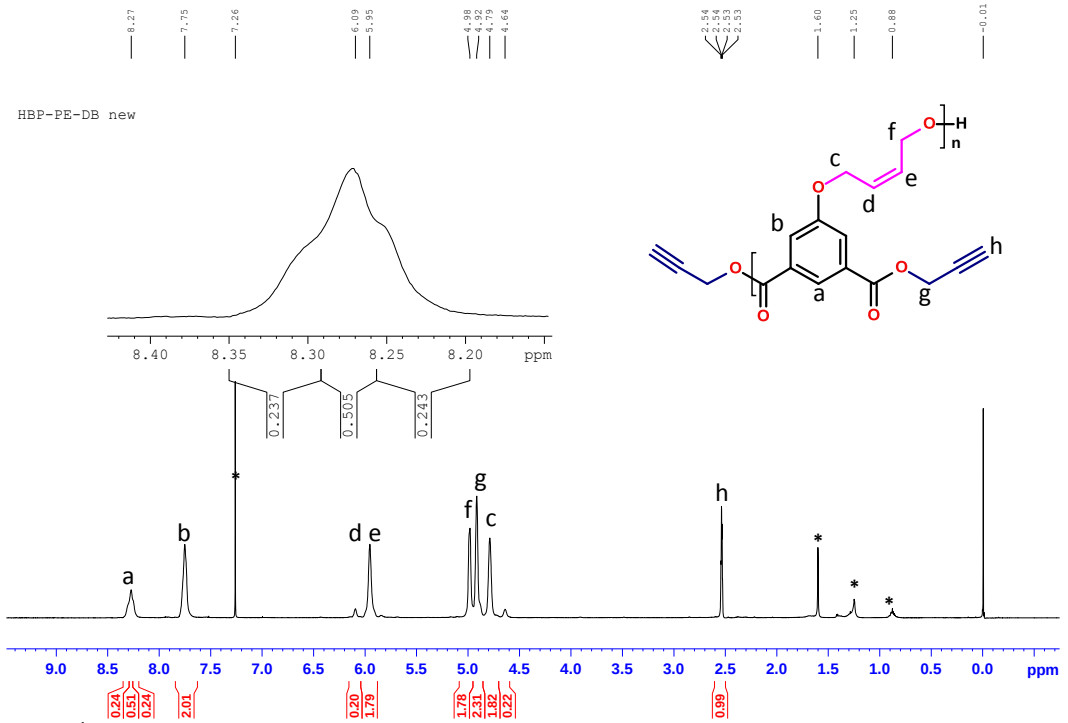


Figure-S11: ^{1}H NMR spectrum of HBPC4-DB*c;* The aromatic single peak (a) in the polymer split it into 3 peaks (not well resolved) suggesting that HBP was formed. Approximately those peaks intensity ratio is 1:2:1. These three peaks belongs to dendritic, linear and terminals units in the HBP. The degree of branching is 48.7 %.

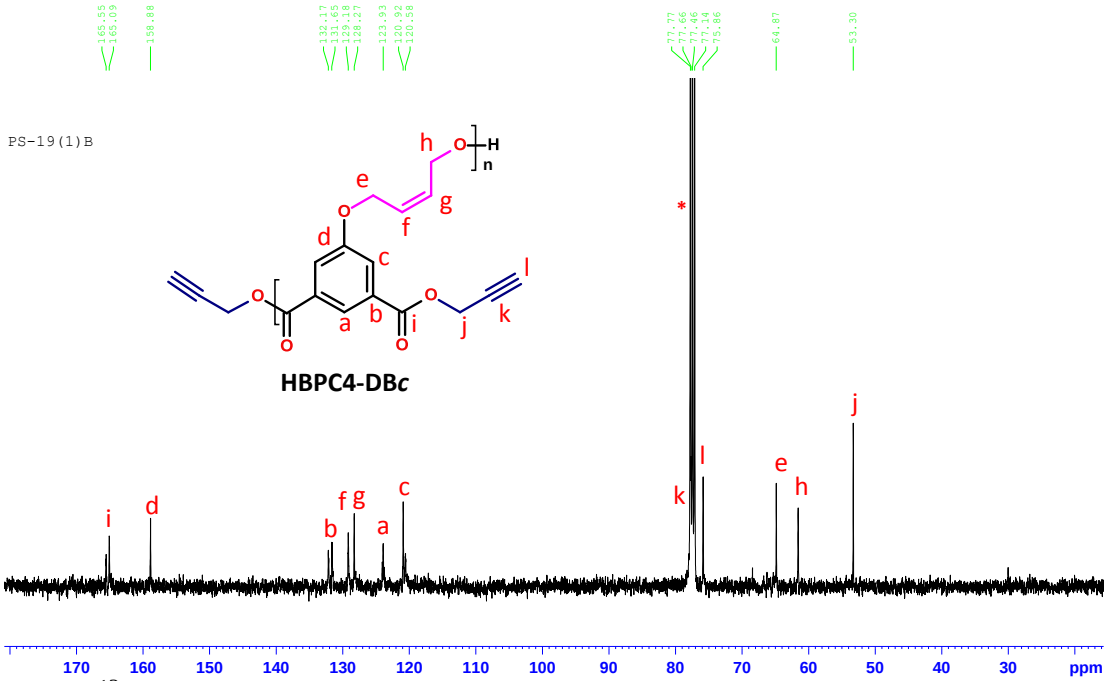


Figure-S12: ^{13}C NMR spectrum of HBPC4-DB*c*

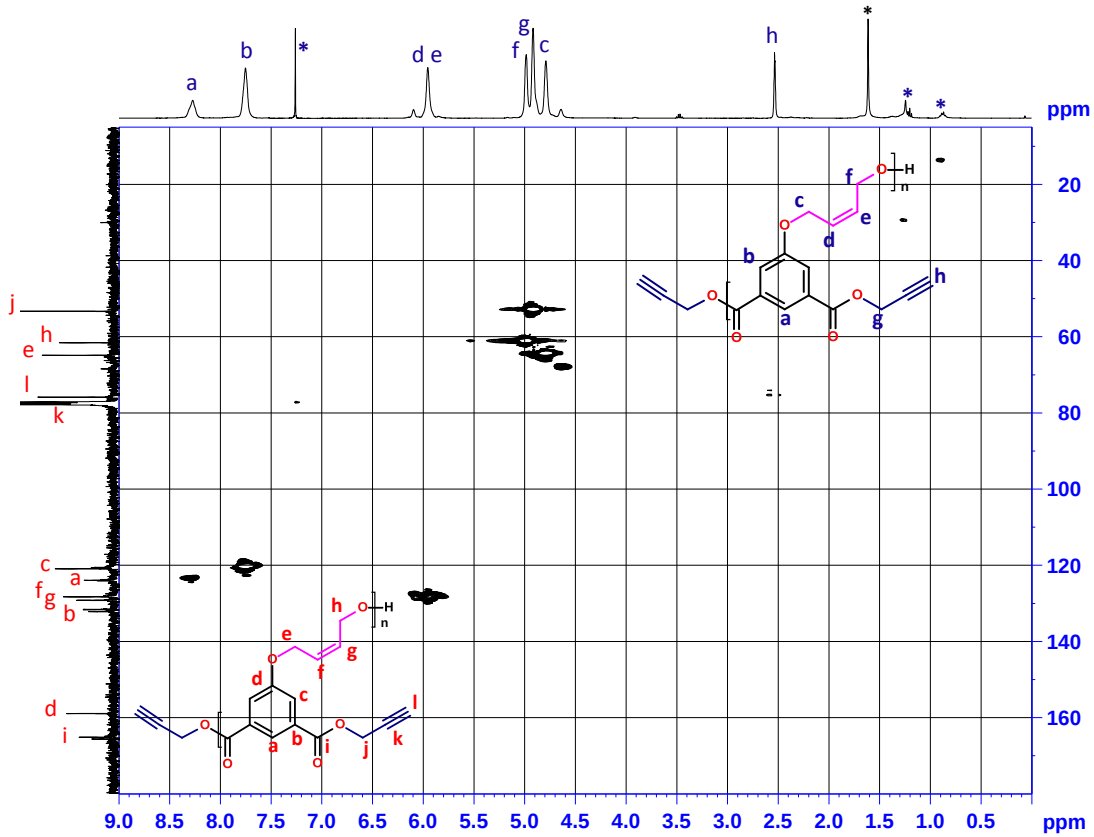


Figure-S13: Hetero COSY NMR spectrum of HBPC4-DB*c*.

Hetero COSY NMR was carried out to confirm the peaks belongs to *cis* and *trans* isomers of HBP.

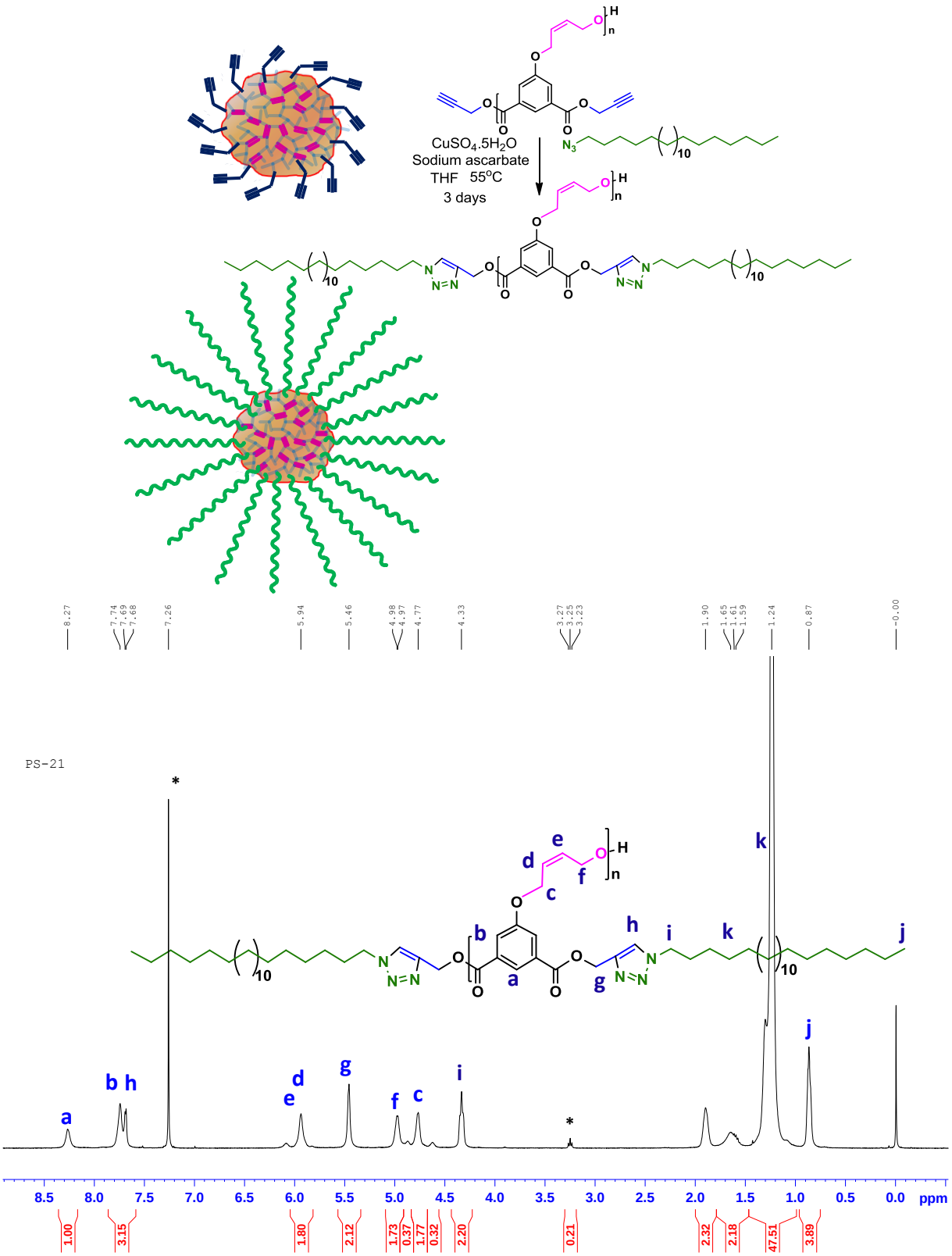


Figure-S14: Installation of crystallizable segments (C22 alkyl chains) on periphery of the HBPC4-DB*c* and ^{1}H NMR spectrum of HBPC4-DB*c*-C22

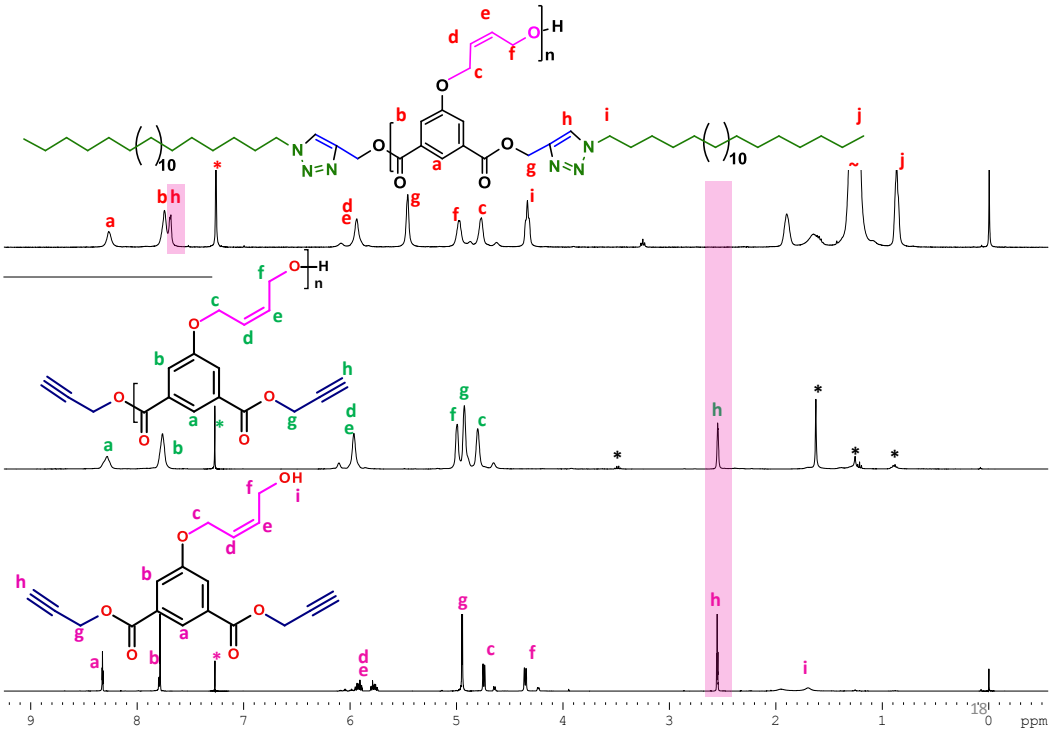


Figure-S15: Stacked ^{1}H NMR spectra of MONOC4-DB*c*, HBPC4-DB*c* and HBPC4-DB*c*-C22. Peak (f) is shifted from upfield to downfield is clearly indicating that the polymer was formed; the complete disappearance of the propargyl group proton peak (h) and the appearance of the traizole proton peak along with docosyl segment peaks confirm the completion of the click reaction.

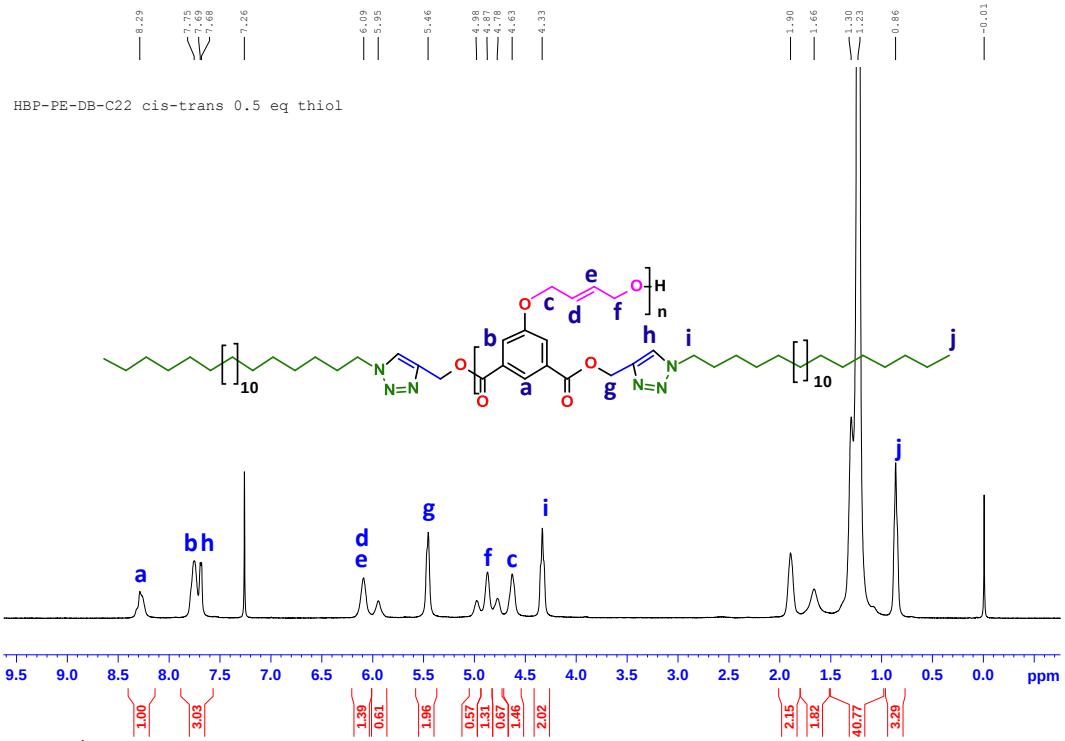


Figure-S16: ^{1}H NMR spectra of HBPC4-DB*t*-C22

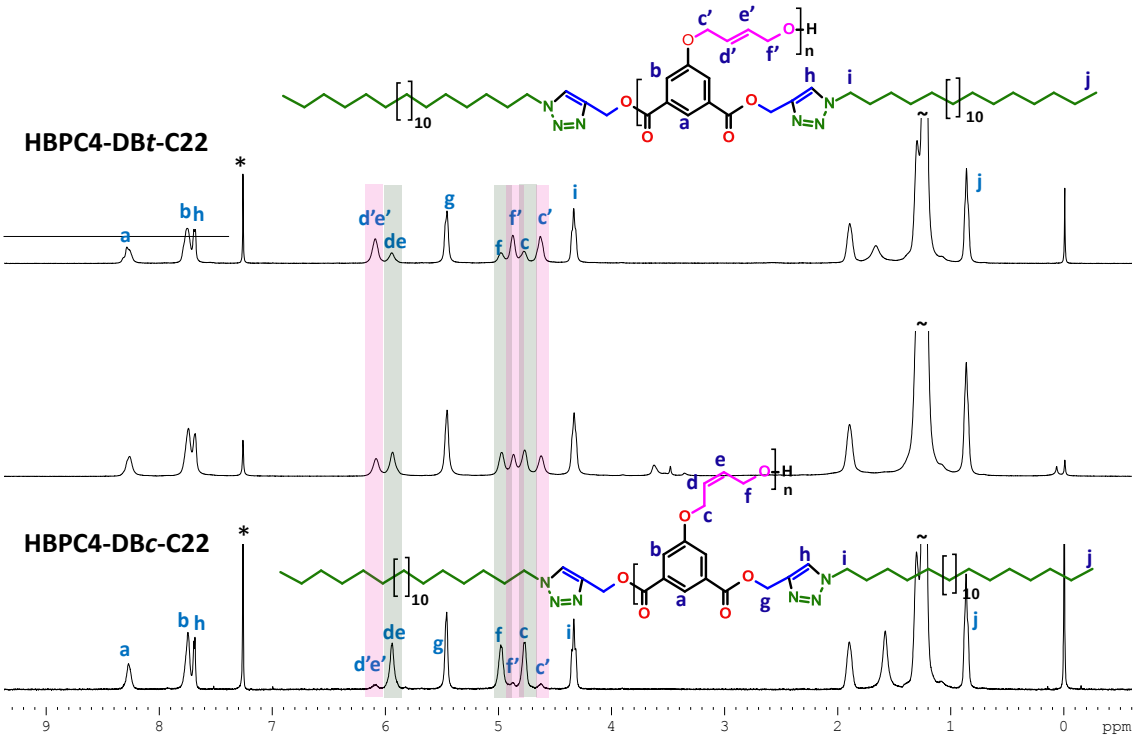


Figure-S17: Stacked ^{1}H NMR spectra of HBPC4-DB*c* and intermediate time interval spectra and HBPC4-DB*t*-C22. The peaks belongs to cis isomer intensity decreases and trans isomer intensity increases is clearly reveals that the formation of trans isomer from cis.

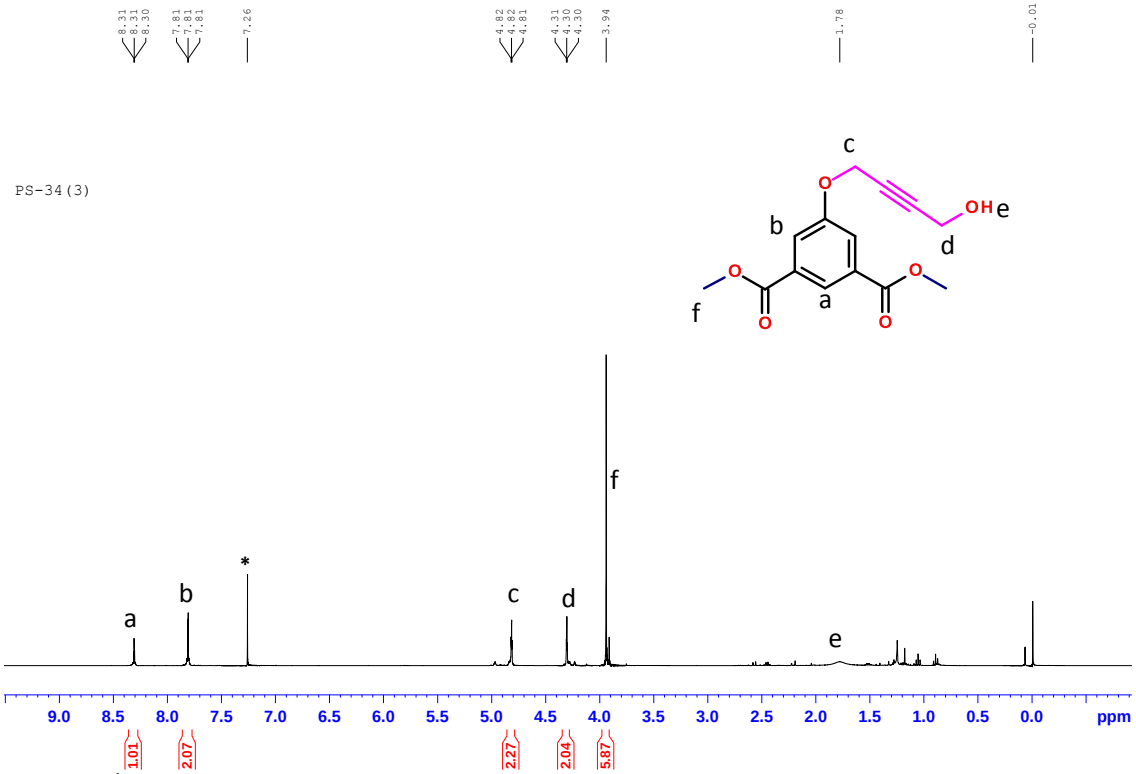


Figure-S18: ^{1}H NMR spectrum of dimethyl 5-((4-hydroxybut-2-yn-1-yl) oxy) isophthalate

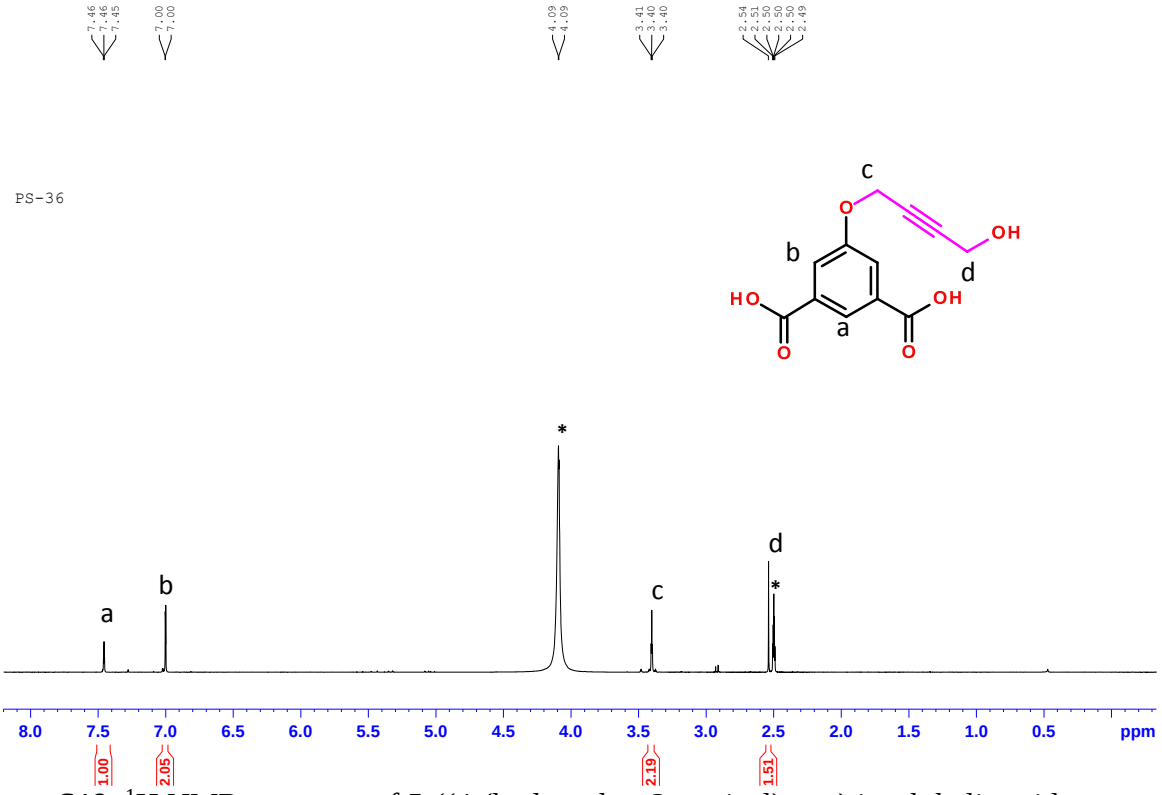


Figure-S19: ^{1}H NMR spectrum of 5-((4-(hydroxybut-2-yn-1-yl) oxy) isophthalic acid

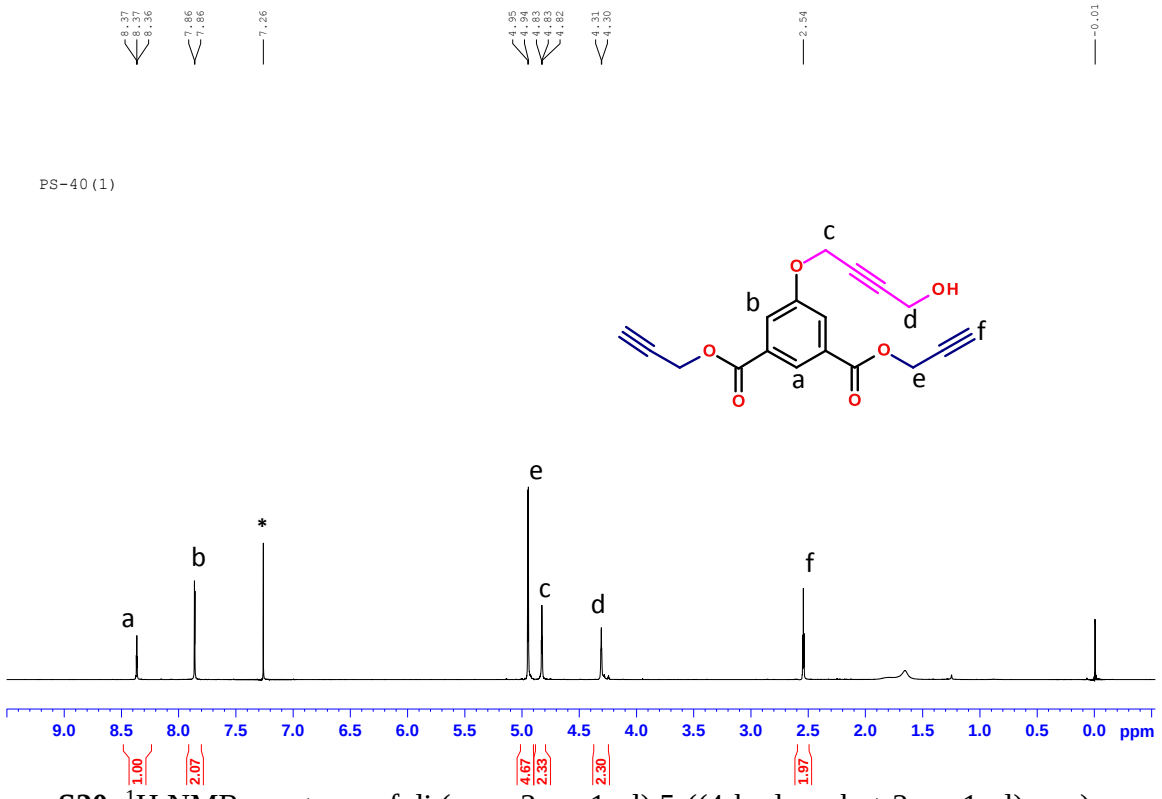


Figure-S20: ^{1}H NMR spectrum of di (prop-2-yn-1-yl) 5-((4-hydroxybut-2-yn-1-yl) oxy) isophthalate (MONOC4-TB)

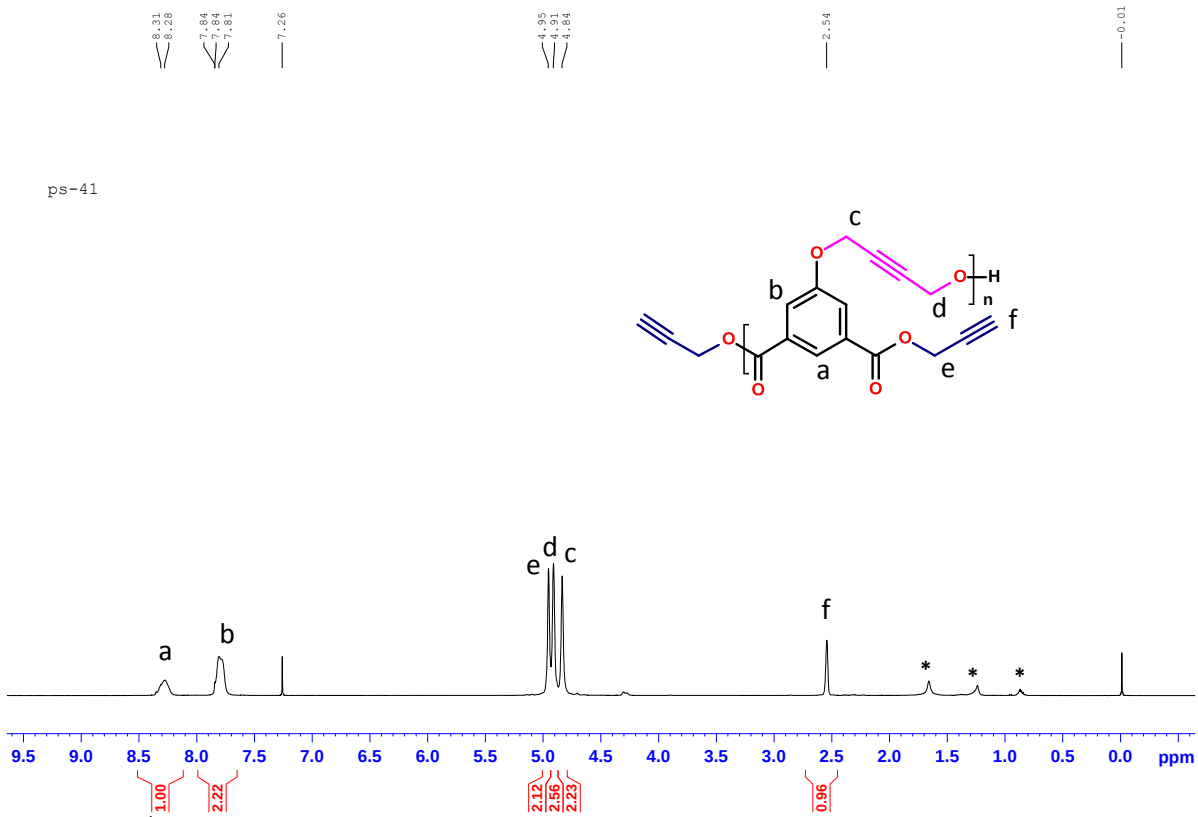


Figure-S21: ^{1}H NMR spectrum of HBPC4-TB

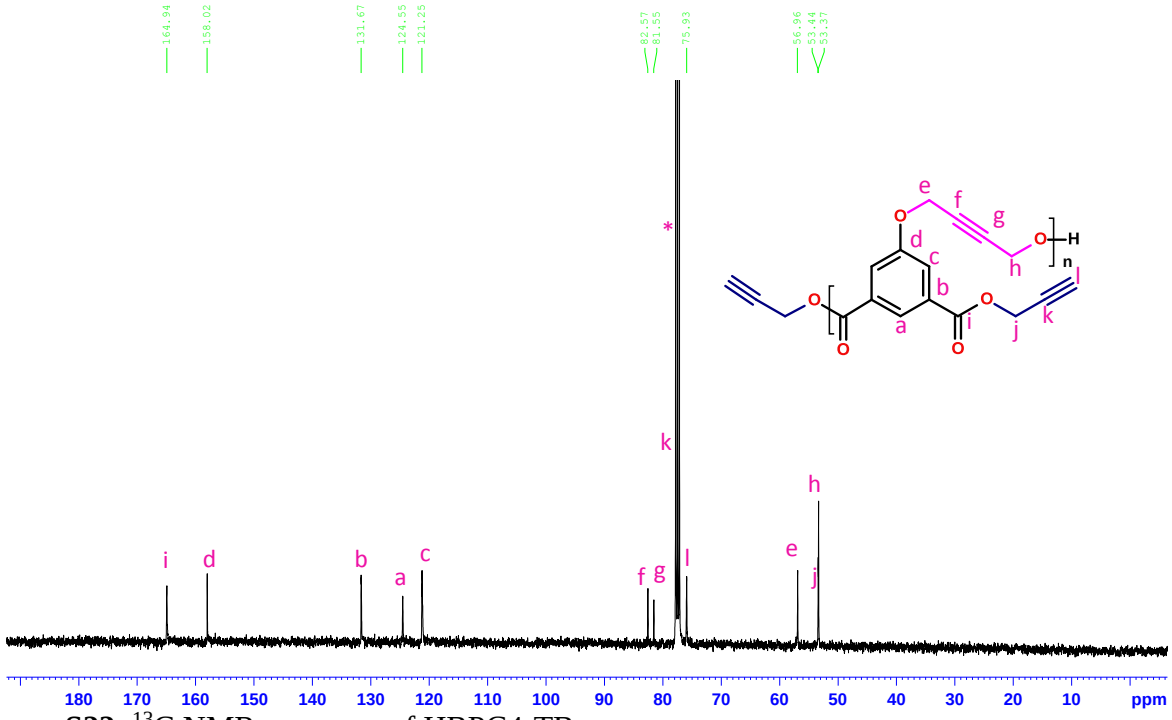


Figure-S22: ^{13}C NMR spectrum of HBPC4-TB

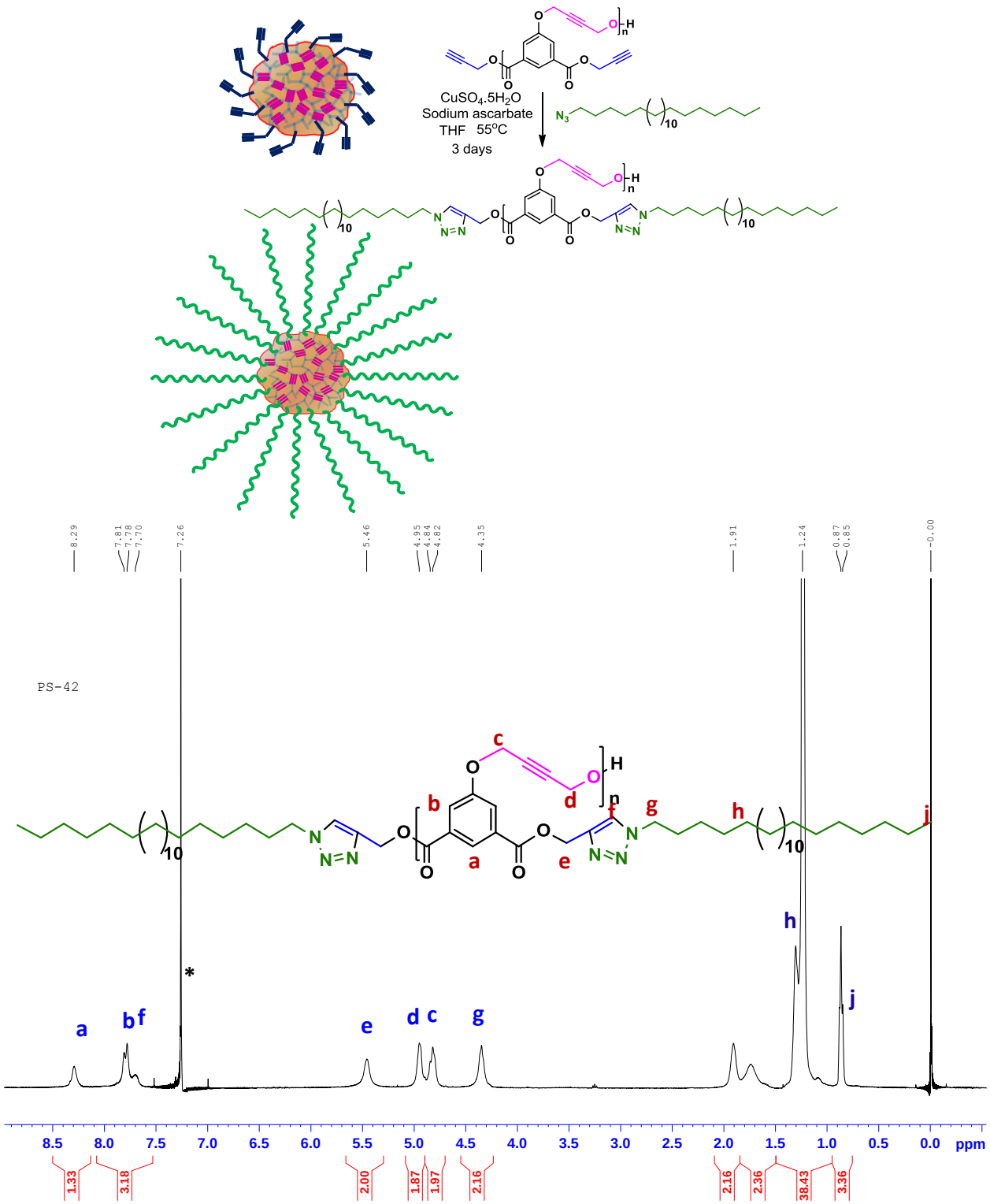


Figure-S23: Installation of crystallizable segments (C22 alkyl chains) on periphery of the HBPC4-TB and ^{1}H NMR spectrum of HBPC4-TB-C22

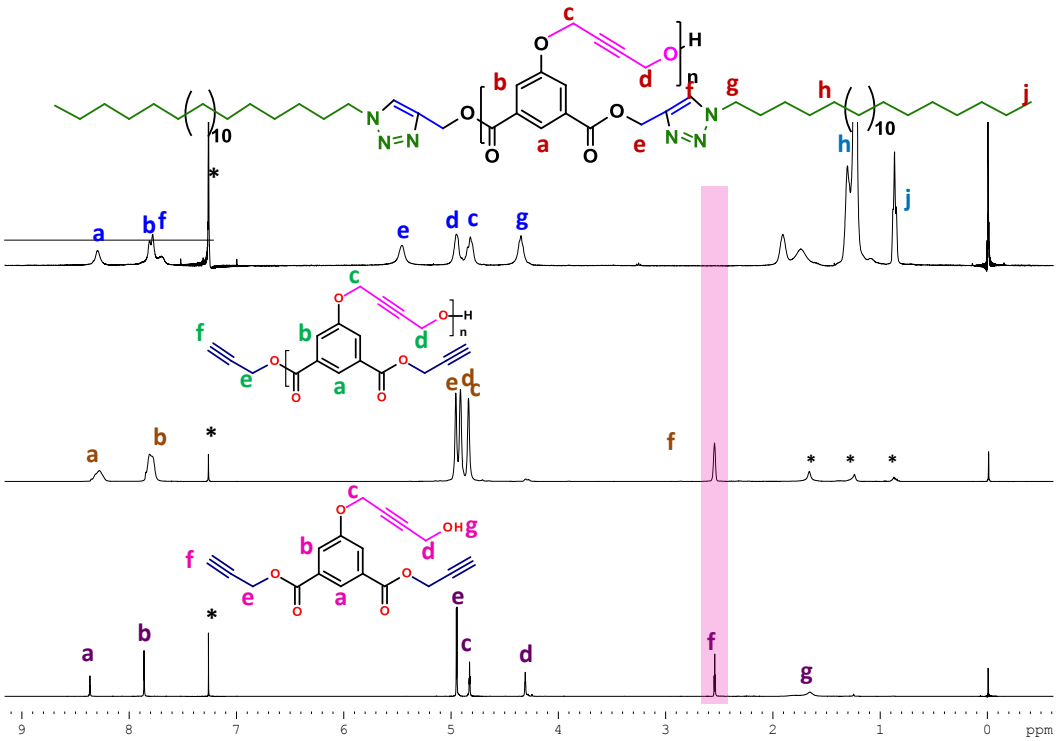


Figure-S24: Stacked ^{1}H NMR spectra of MONOC4-TB, HBPC4-TB and HBPC4-TB-C22. Peak (d) is shifted from upfield to downfield is clearly reveals that the polymer was formed; the complete disappearance of the propargyl group proton peak (f) and the appearance of the traizole proton peak along with docosyl segment peaks confirm the completion of the click reaction.

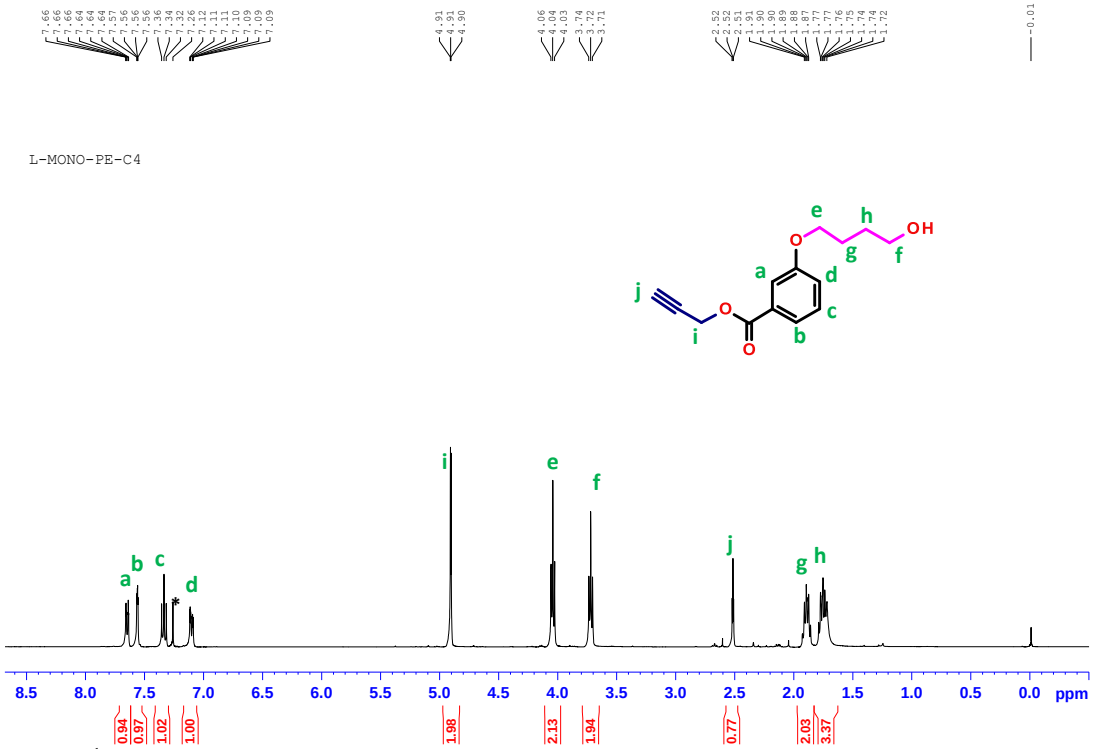


Figure-S25: ^{1}H NMR spectrum of prop-2-yn-1-yl 3-(4-hydroxybutoxy)benzoate (LMONOC4-S)

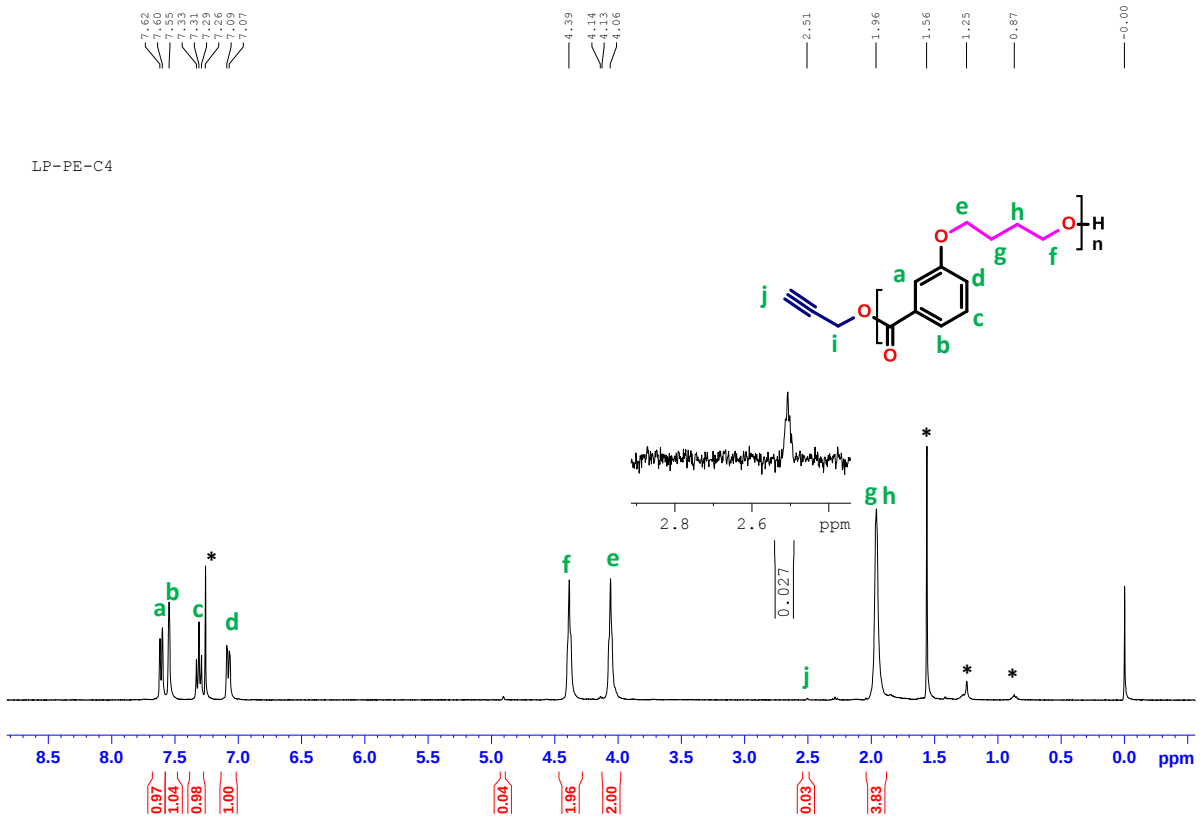


Figure-S26: ^{1}H NMR spectrum of LPC4-S. From end group analysis, DP of the polymer is 28.

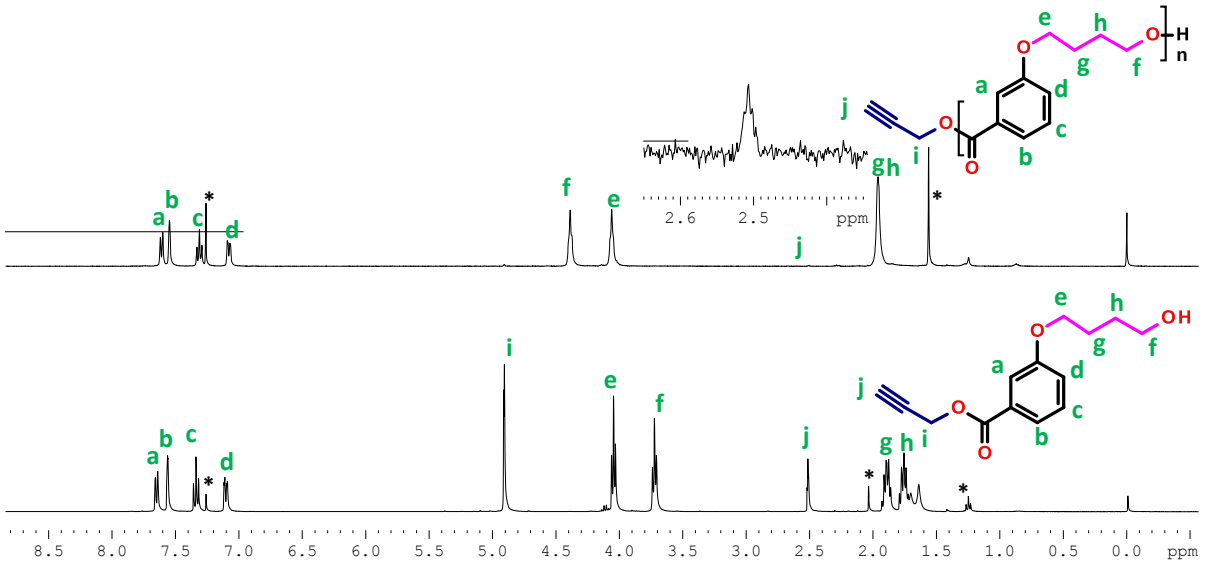


Figure-S27: Stacked plot of LMONOC4-S and LPC4-S. The peak (f) is shifted from upfield to downfield is clearly reveals the polymer formation.

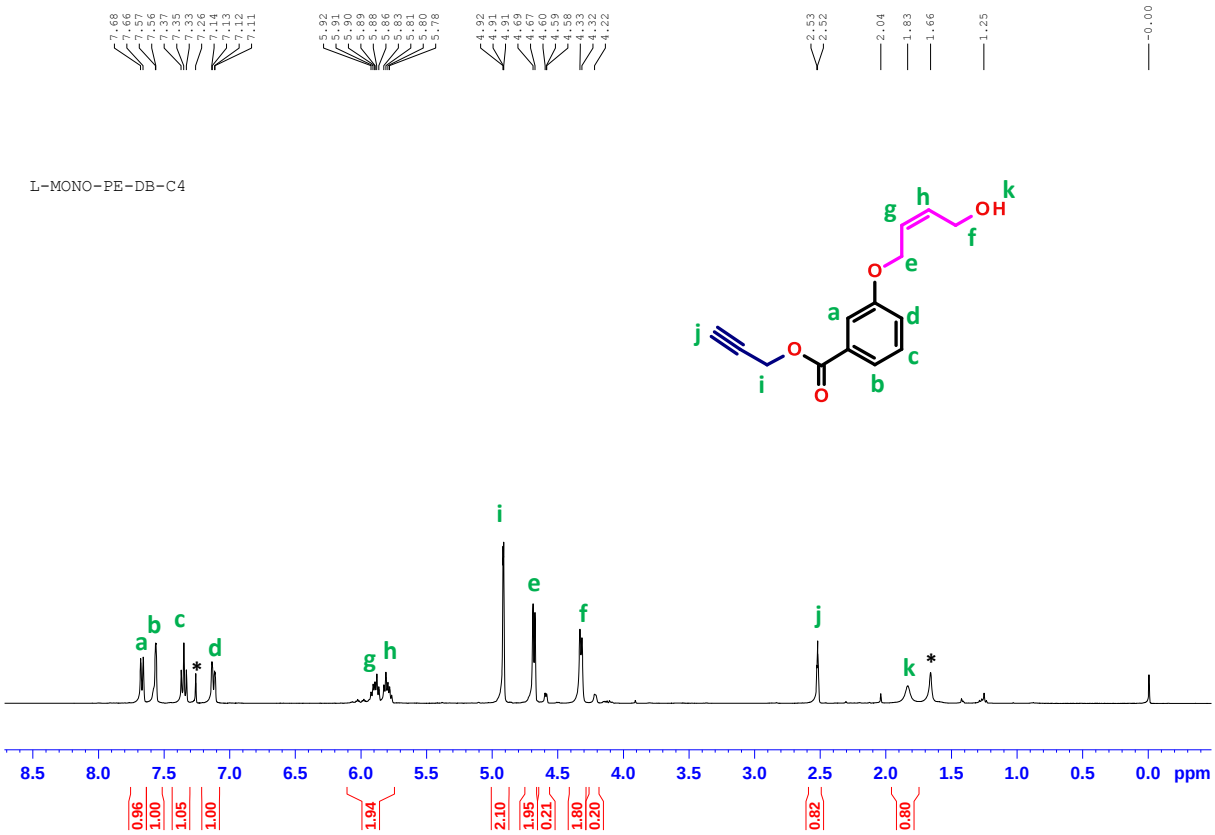


Figure-S28: [1]H NMR spectrum of (Z)-prop-2-yn-1-yl 3-((4-hydroxybut-2-en-1-yl) oxy) benzoate (LMONOC4-DB*c*)

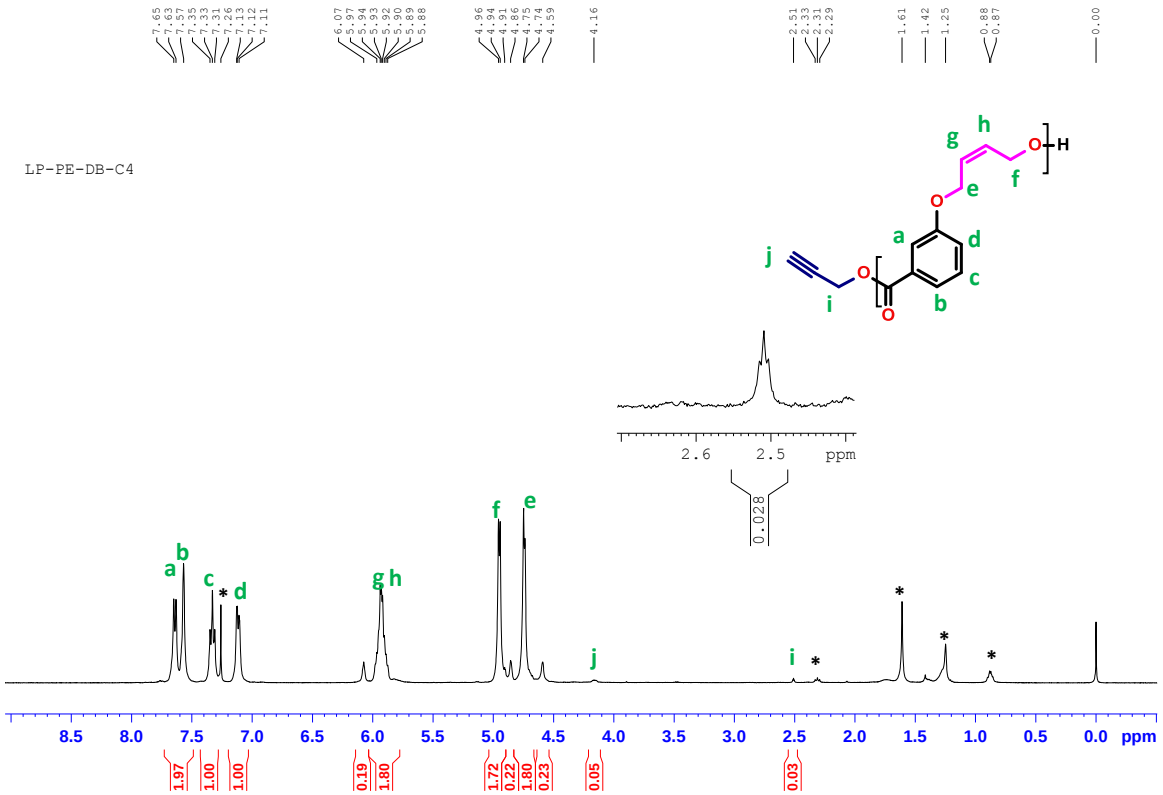


Figure-S29: ^{1}H NMR spectrum of LPC4-DB*c*. From end group analysis, DP of the polymer is 29.

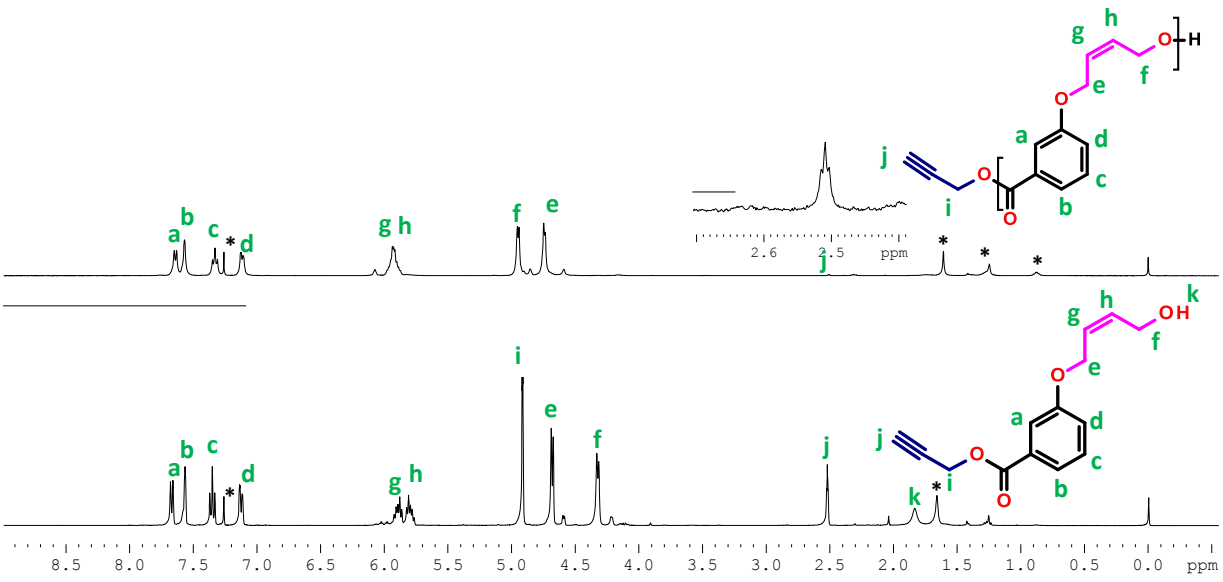


Figure-S30: Stacked plot of LMONOC4- DB*c* and LPC4-DB*c*. The peak (f) is shifted from upfield to downfield is clearly reveals the polymer formation.

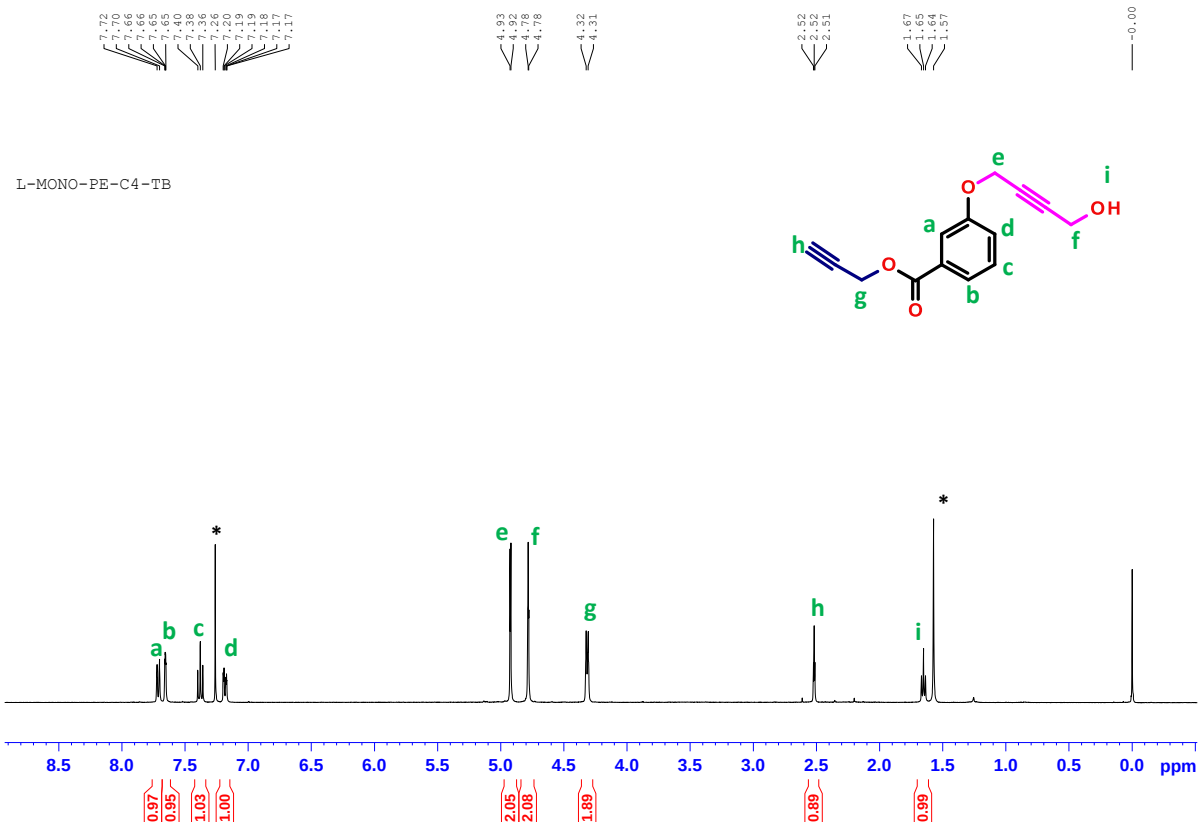


Figure-S31: ^{1}H NMR spectrum of prop-2-yn-1-yl 3-((4-hydroxybut-2-yn-1-yl) oxy) benzoate (LMONOC4-TB)

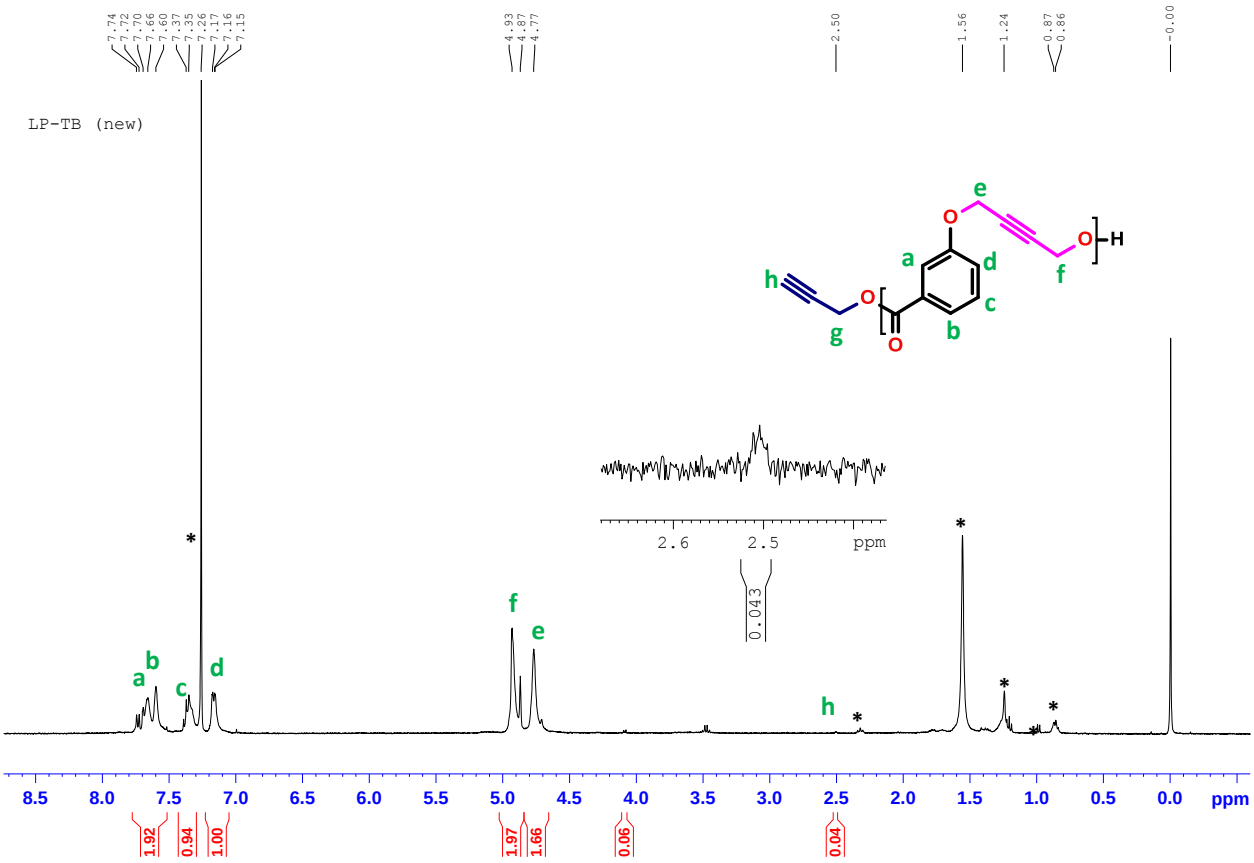


Figure-S32: ^{1}H NMR spectrum of LPC4-TB. From end group analysis, DP of the polymer is 21.

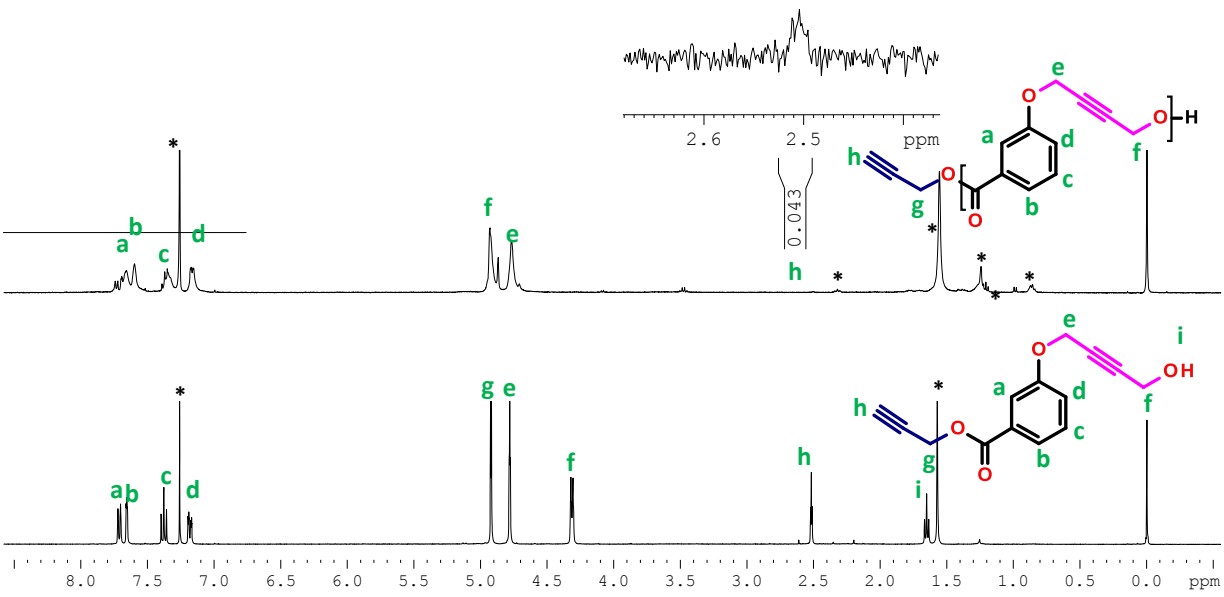


Figure-S33: Stacked plot of LMONOC4-TB and LPC4-TB. The peak (f) is shifted from upfield to downfield is clearly reveals the polymer formation.

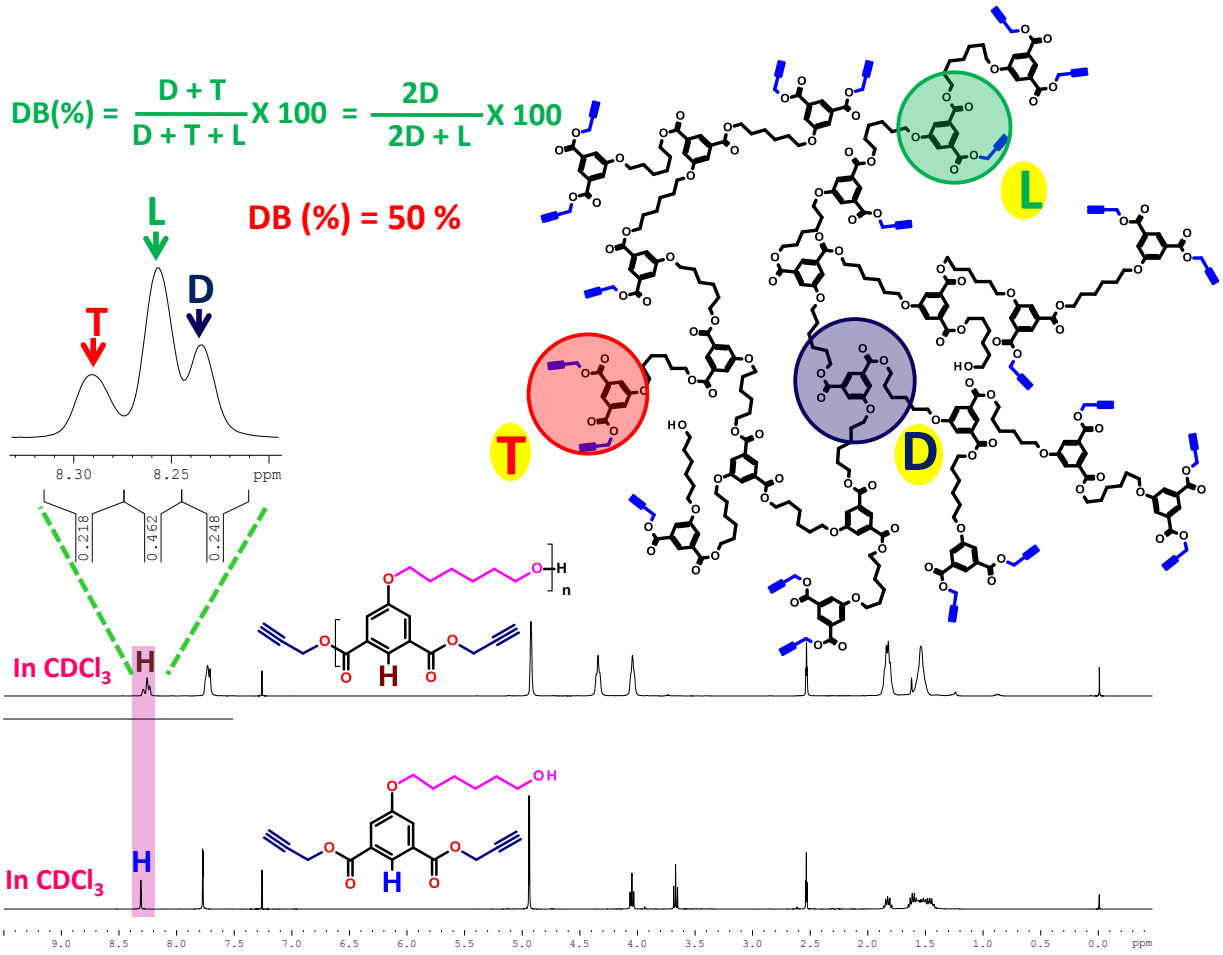


Figure-S34: Stacked ^{1}H NMR plot of MONOC6-S and HBPC6-S. In the case of HBP, the aromatic proton peak (singlet) was split into 3 peaks indicates the formation of HBP. Those 3 peaks belongs to dendritic (D), linear (L) and terminal (T) units. The degree of branching (DB) is 50%.