# Dendritic Effect and Magnetic Permeability in Dendron Coated Nickel and Manganese Zinc Ferrite Nanoparticles

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## Experimental Section

### Materials

Ni (II) acetylacetonate (96%), manganese (II) acetylacetonate, zinc (II) acetylacetonate (≥98%), iron (III) acetylacetonate (99+%), 1-octadecene (technical grade, 90%) were purchased from Acros Organics. Nickel (II) acetylacetonate (95%), trioctylphosphine (97%), benzyl ether (98%), oleic acid (technical grade, 90%) and oleylamine (technical grade, 70%) were purchased from Sigma-Aldrich. All the chemicals were used as received.

12-Azidododecylphosphonic acid **6** was purchased from Alfa-Aesar. 2,2-Dimethoxypropane (98+%), bis-MPA (98%), propargyl bromide (80% soln. in toluene), propargyl alcohol (99%), pyridine (reagent), Dowex $H^+$ ion exchange resin (200-400 mesh), p-toluenesulfonyl chloride (TsCl, 99+%), copper (II) sulfate pentahydrate (98+), triethylamine ($Et_3N$, 99%) and oleylamine (80-90%) were purchased from Acros. N,N'-Dicyclohexylcarbodiimide (DCC, 99%), $NaN_3$ (≥99.5%), 4-dimethylaminopyridine (DMAP, 99%), stearic anhydride (≥97%), sodium L-ascorbate (≥99%) and 11-bromo-1-undecanol (98%) were purchased from Aldrich. All chemicals were used as received without further purification. Solvents were ACS grade or higher. $CH_2Cl_2$ was dried over $CaH_2$ and freshly distilled before used. $HAuCl_4 \cdot 3H_2O$ is stored in a 4 ºC refrigerator.

**Synthesis of Ni NPs**

For the synthesis of 5.0 nm Ni NPs, 1 mmol of Ni (II) acetylacetonate were dissolved in a solution of 15 mL benzyl ether and 30 mmol oleylamine. The mixture was evacuated at room temperature for 5 minutes before the injection of 30 mmol of trioctylphosphine. The reaction mixture was heated to 80 °C and kept under vacuum for 30 minutes. Then, the temperature was increased to 230 °C at a rate of 10 °C/min. After 30 minutes, the reaction mixture was cooled down to the room temperature and Ni NPs were precipitated by adding acetone. Ni NPs were redispersed in toluene and washed with acetone for three times.

**Synthesis of $Mn_{0.08}Zn_{0.33}Fe_{2.59}O_4$ (MZF) NPs**

For the synthesis of 11.0 nm MZF NPs, 3 mmol of Mn (II) acetylacetonate, 6 mmol of zinc (II) acetylacetonate, 12 mmol of iron (III) acetylacetonate, 100 mmol of oleic acid, 112 mmol of oleylamine, and 72 mL of 1-octadecene were mixed in a 250 mL flask. The reaction mixture was heated to 110 °C and kept under vacuum for two hours. Then, the temperature was increased to 300 °C at a rate of 11 °C/min. After two hours, the reaction mixture is cooled down to the room

temperature and zinc ferrite NPs are precipitated by adding isopropanol. Manganese zinc ferrite NPs were redispersed in hexane and washed further using isopropanol three times. The ratio between zinc and iron is measured by Inductive Coupling Plasma-Optical Emission spectrometry (ICP-OES) performed on a Spectro Genesis spectrometer with a concentric nebulizer.

**Ligand Exchange with Dendrimers**

Ligand exchange of Ni NPs was performed using 10 mg of L-COOH (L = G0-G3) dissolved in 5 mL of chloroform added to 1 mL of Ni NPs in toluene (10 mg/mL). The reaction was stirred for 30 minutes at room temperature and stopped by precipitation of the Ni NPs with acetone. The Ni NPs were redispersed in toluene and washed with acetone for two times.

For ligand exchange of MZF NPs, 150 mg of G2-$PO_3H_2$ was first dissolved in 5 mL of hexane at 40 °C. When the solution became transparent and colorless, 150 mg of NPs in 5 mL of hexane was added into the solution with G2-$PO_3H_2$ and kept at 40 °C. After overnight stirring, 30 mL of isopropanol was added into the solution to precipitate out the ligand exchanged NPs. The precipitate was redispersed in 5 mL of hexane. Then, 20 mL of isopropanol was added into the NP solution again to get rid of the extra amount of the dendrimers. The final product was dissolved and kept in hexane.

**Techniques**

**NMR.** $^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra were recorded on Bruker UNI500 or BIODRX500 NMR spectrometer. $^{1}$H and $^{13}$C chemical shifts ($\delta$) are reported in ppm while coupling constants ($J$) are reported in Hertz (Hz). The multiplicity of signals in $^{1}$H NMR spectra is described as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet),“p” (pentet), “dd” (doublet of doublets) and “m” (multiplet). All spectra were referenced using solvent residual signals ($CDCl_3$: $^{1}$H, $\delta$ 7.27 ppm; $^{13}$C, $\delta$ 77.2 ppm).[1] Heteronuclear single quantum coherence ($^{1}$H-$^{13}$C HSQC)

experiment was used to confirm NMR peak assignments. Reaction progress was monitored by thin-layer chromatography using silica gel coated plates or $^{1}$H NMR. Compounds were purified by filtration, precipitation, crystallization or flash column chromatography using silica gel (Acros Organics, 90 Å, 35-70 μm) as indicated in corresponding procedures.

**Thermal Analysis.** Thermal transitions were determined on a TA Instruments Q2000 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling system with 10 ºC/min heating and cooling rates.

**Mass Spectroscopy**. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed on Bruker Ultraflex III (Maldi-Tof-Tof) mass spectrometer using dithranol as matrix.

**Electron Microscopy.** TEM micrographs were collected using a JEOL JEM-1400 microscope operating at 120 kV. The TEM was calibrated using a MAG*I*CAL® TEM calibration standard.

**DC Magnetic Characterization.** Zero-field-cooling (ZFC) curves were collected by a Quantum Design MPMS-XL 7T superconducting quantum interference device (SQUID). First, the samples were cooled to 15 K without an external field. Then, the magnetization of the samples were taken under an applied field of 0.01 T from 15 to 300 K. The magnetization hysteresis curves were taken from 3 to -3 T at 300 K and 15 K.

**AC Magnetic Characterization.** The susceptibility ($\chi$) of NPs is measured by a 4395A Agilent network analyzer and a 16454A Agilent magnetic material test fixture. MZF NPs dispersed in hexane was deposited into a toroidal-shaped sample holder (8 mm OD, 3.2 mm ID, 3mm height and 2.5 mm depth) and dried. The reactance and resistance of the test fixture were measured in the frequency range of 10 – 500 MHz in log frequency and converted into the real ($\chi'$) and imaginary ($\chi''$) parts of the susceptibility using equation (1),

$$\chi = \left(\frac{X_m}{f\mu_0 h \ln\frac{c}{b}}\right) - i\frac{R_m}{f\mu_0 h \ln\frac{c}{b}} = \chi' - i\chi'' \quad (1)$$

$X_m$ is the reactance, $R_m$ is the resistance, $f$ is the frequency of the ac field, $\mu_0$ is the vacuum permeability, $h$ is the height, $c$ is the outer diameter and $b$ is the inner diameter of the toroidal sample.

**Additional data**

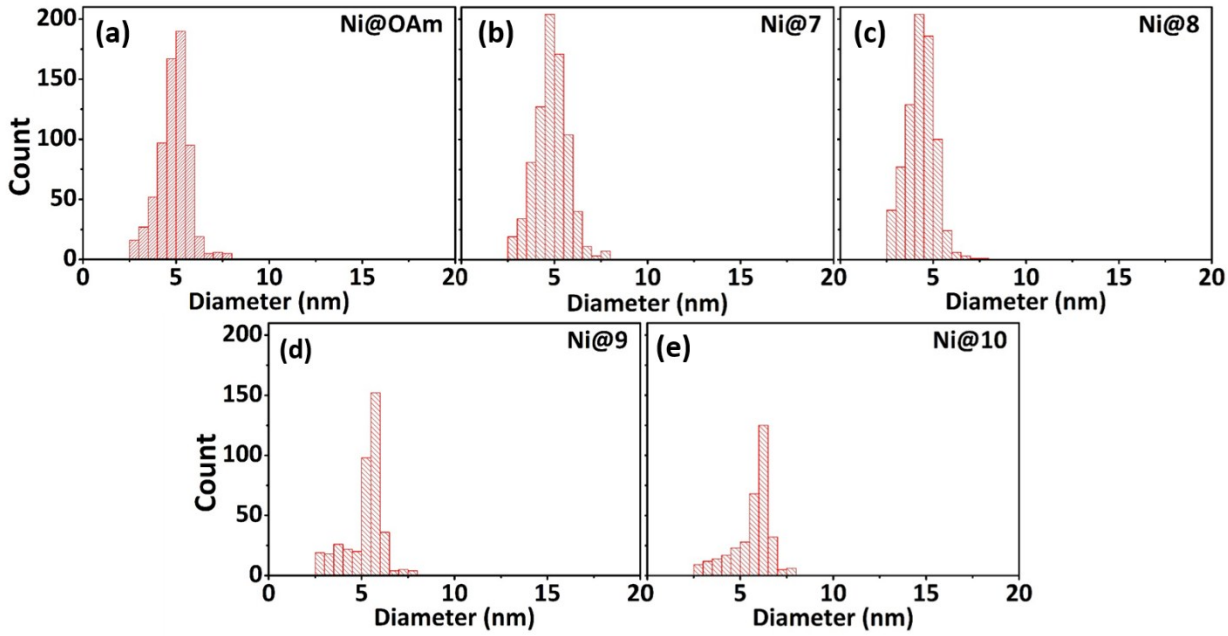



Figure S1. The size distribution of Ni NPs before (OAm) and after ligand exchange (dendron **7-10**).

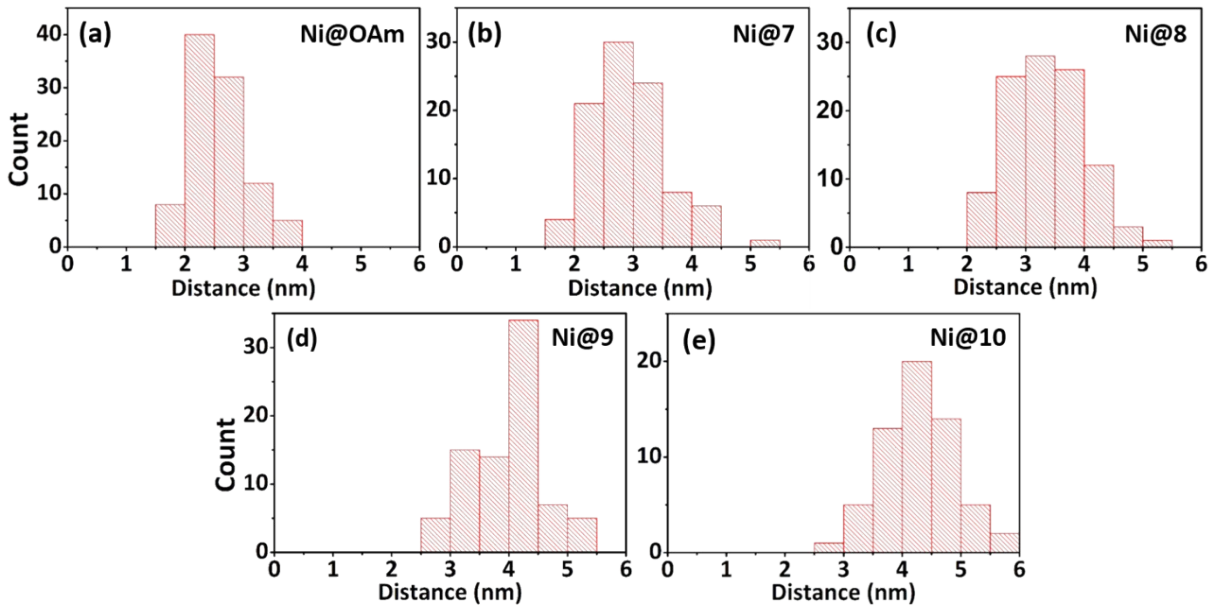



Figure S2. The inter-particle (surface to surface) spacing distribution in dendron-coated Ni NPs.

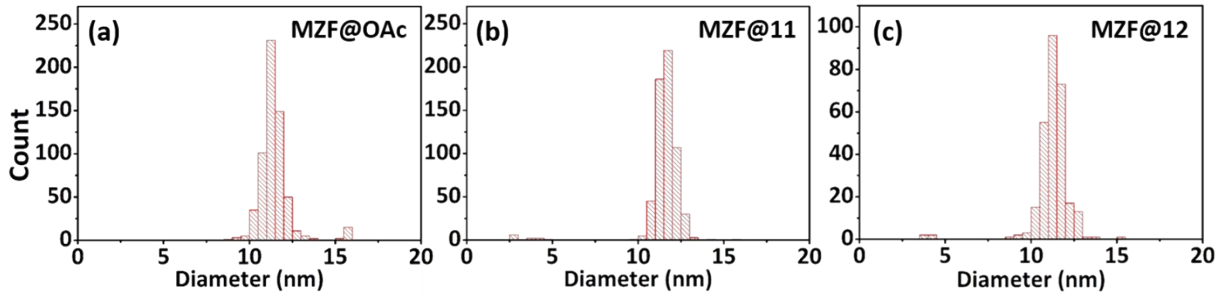



Figure S3. The size distribution of MZF NPs before (OAc) and after ligand exchange (dendron **11** and **12**).

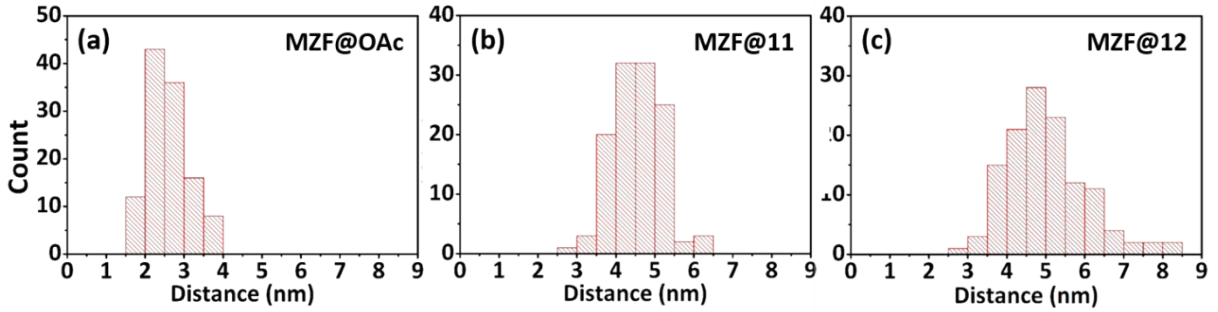



Figure S4. The inter-particle (surface to surface) spacing distribution in dendron-coated MZF NPs.

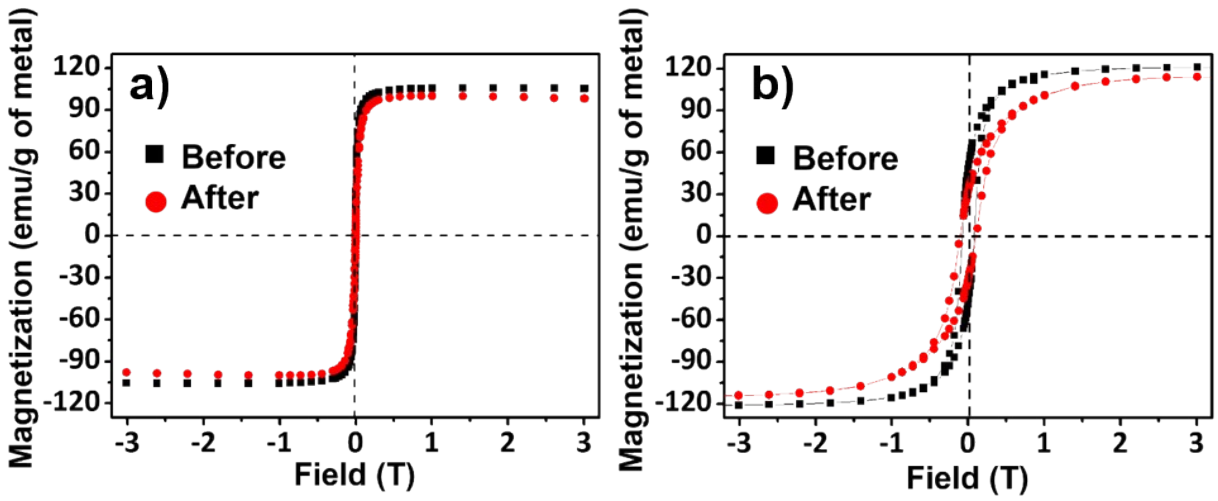



**Figure S5.** Hysteresis curves of MZF NPs before (black) and after (red) the ligand exchange with dendron **12** at a) 300 K and b) 15K.

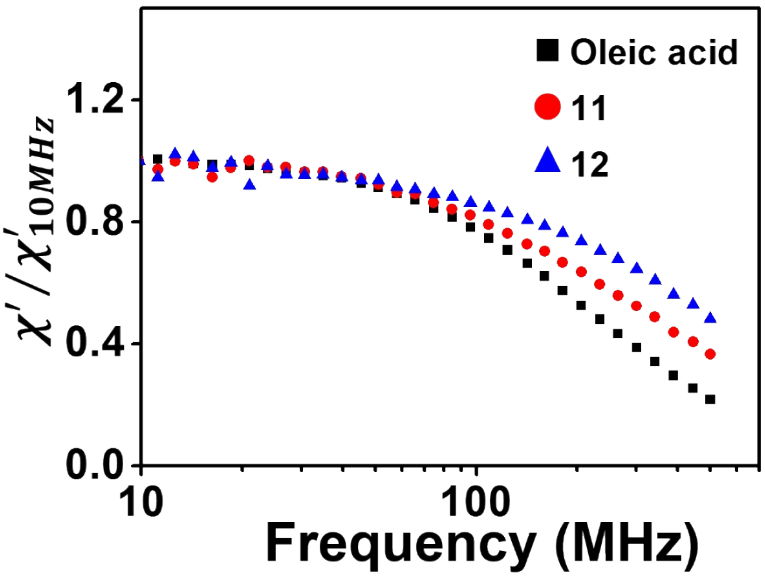
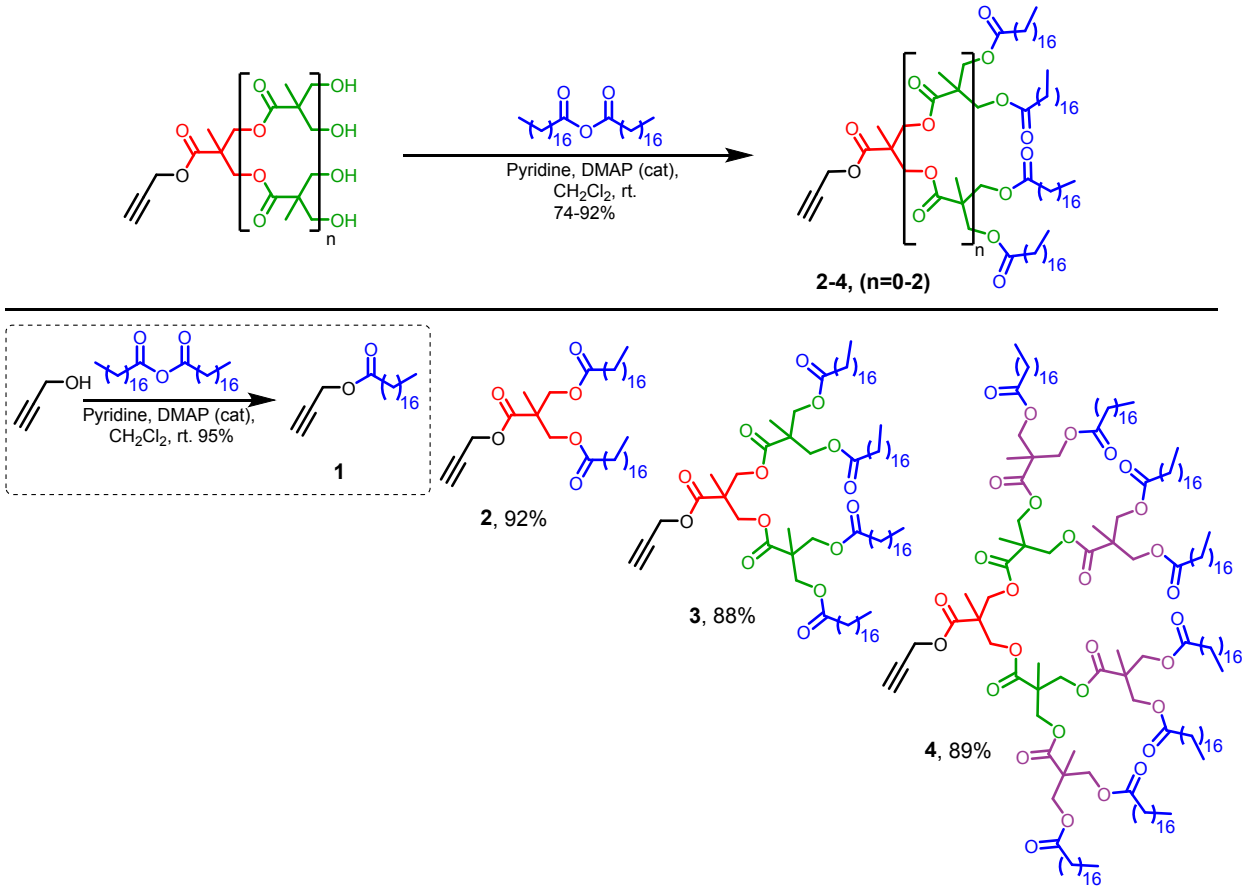



**Figure S6.** The normalized real part of the susceptibility of MZF NPs before (black) and after the ligand exchange with dendron **11** (red) and **12** (blue) from 10 MHz to 500 MHz.

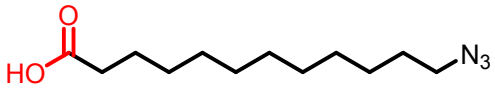
## Synthesis

### Synthesis of intermediates 1-4.

Intermediates **1-4** were prepared using the strategy that utilizes the late stage end-group functionalization of bis-MPA derived dendrons via stearic anhydride. The general reaction scheme is shown below, however, all synthetic procedures and characterization details can be found in our previous report.[2]

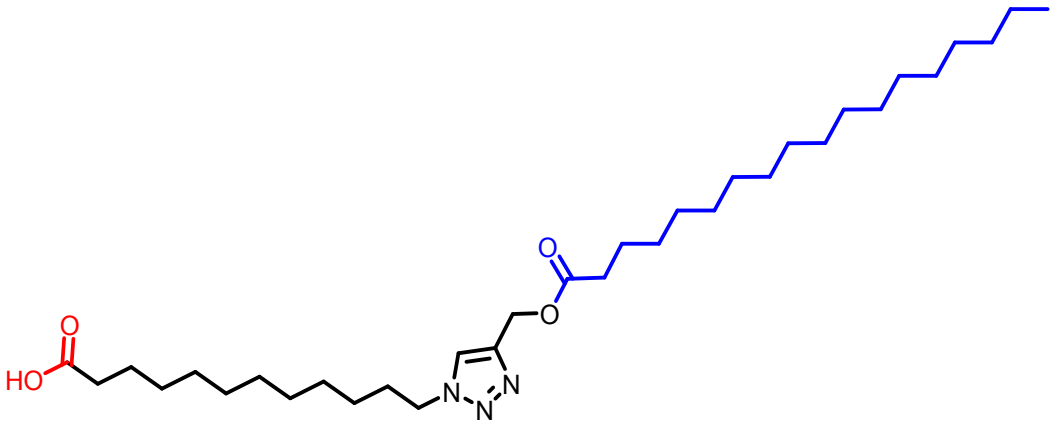



**Scheme S1.** The synthesis of **1-4**



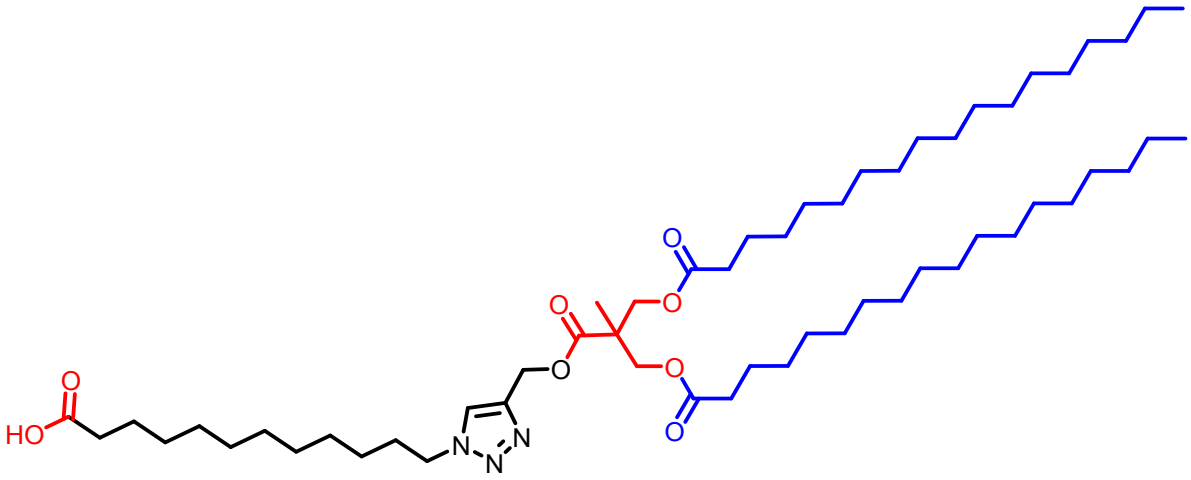
**12-Azidododecanoic acid 5**.[3] To a stirred solution of 12-bromododecanoic acid (10g, 19.2 mmol) in DMF (50 mL) at room temperature was added $NaN_3$ (3.74g, 57.6 mmol) as one portion and the resulting mixture was stirred at 90 °C for additional 12h. The mixture was allowed to cool to room temperature, diluted with EtOAc (200 mL) and washed with water (3 x 100 mL), 1N HCl (2 x 100 mL) and Brine (50 mL). Organic fraction was dried over $Na_2SO_4$ and concentrated under reduced pressure to afford pure 12-azidododecanoic acid **5** as white solid (4.4g, 95%). $^1$H NMR ($CDCl_3$) $\delta$ 3.25 (t, $J$ = 7.0 Hz, 2H), 2.34 (t, $J$ = 7.5 Hz, 2H), 1.68 – 1.53 (m, 4H), 1.39 – 1.24 (m, 14H); $^{13}$C NMR ($CDCl_3$) $\delta$ 180.39, 51.62, 34.20, 29.56, 29.49, 29.33, 29.26, 29.16, 28.96, 26.84, 24.78.

**General Procedure for the Synthesis of 7-11 through azido alkyne Huisgen cycloaddition**.

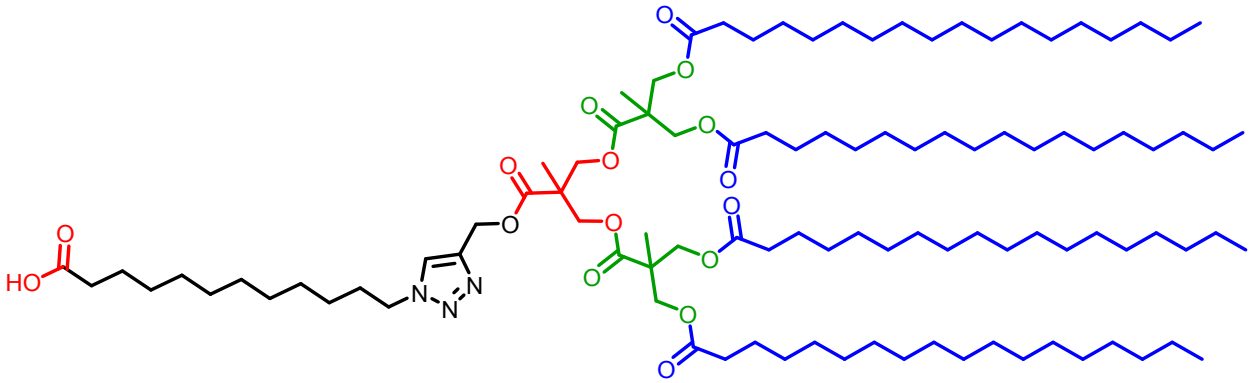


**12-(4-((Stearoyloxy)methyl)-1H-1,2,3-triazol-1-yl)dodecanoic acid 7**. To a stirred solution of 12-azidododecanoic acid (1.0g, 4.14 mmol), prop-2-yn-1-yl stearate (1.33g, 4.14 mmol) and CuSO4•5H2O (0.42g, 1.66 mmol) in THF/$H_2O$ = 4:1 (8 mL) was added sodium ascorbate (0.44g, 2.22 mmol) and the resulting mixture stirred at 65 °C for 6 h under microwave irradiation (constant temperature mode). The solvent was evaporated, residue was dissolved in $CHCl_3$ (100 mL) and washed with 1N HCl (3 x 100 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered and the filtrate concentrated under reduced pressure to afford pure 12-(4-((Stearoyloxy)methyl)-

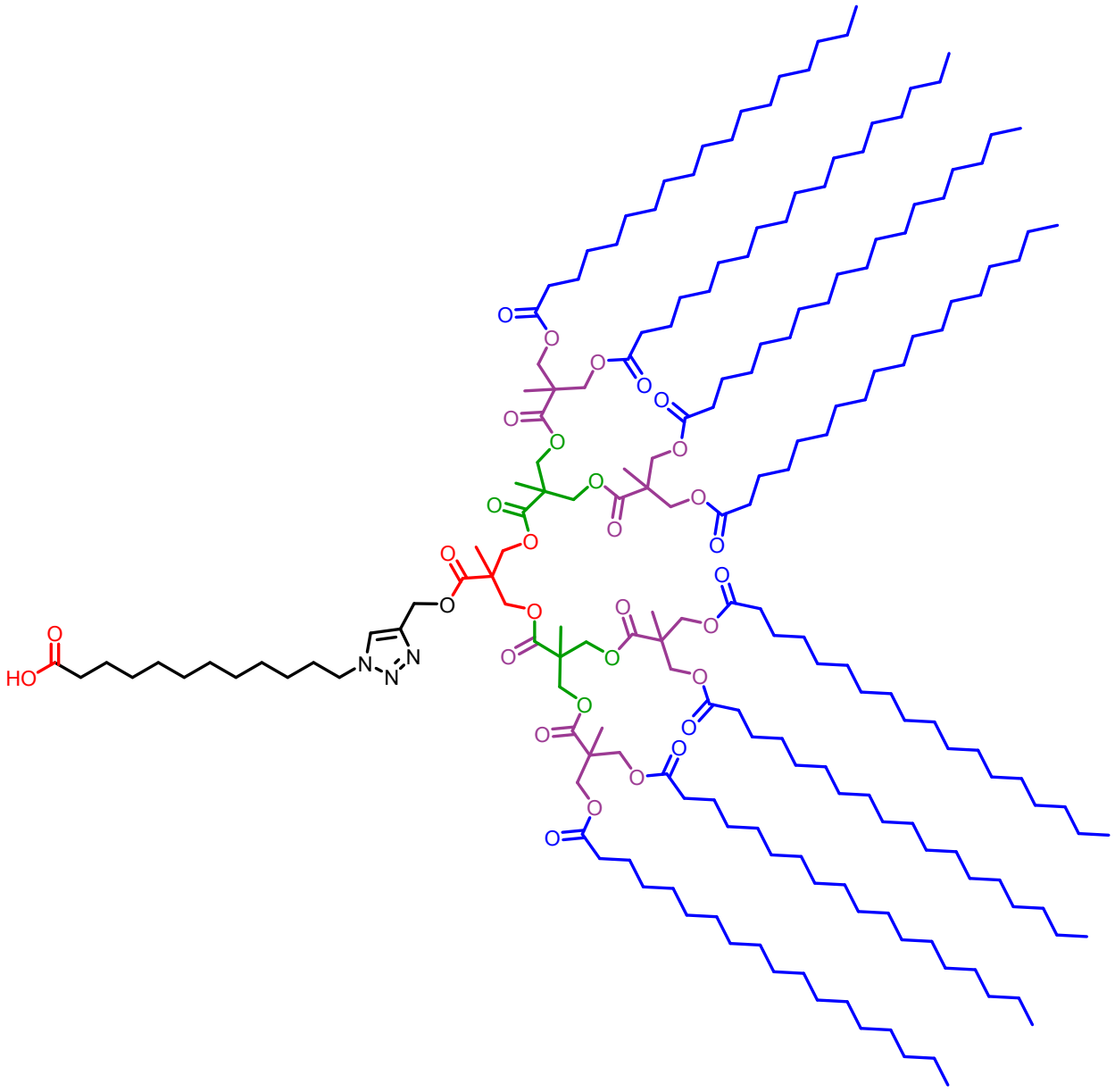
1H-1,2,3-triazol-1-yl)dodecanoic acid **7** as white solid (2.12g, 91%). In case of **9-11** the residue was redissolved in smallest possible amount of warm $CHCl_3$ and mixed with MeOH to induce the precipitation. The precipitate was collected by filtration and dried to obtain the corresponding compound. $^1$H NMR ($CDCl_3$) $\delta$ 7.58 (s, 1H), 5.21 (s, 2H), 4.33 (t, $J$ = 7.3 Hz, 2H), 2.34 (t, $J$ = 7.5 Hz, 2H), 2.31 (t, $J$ = 7.7 Hz, 2H), 1.89 (p, $J$ = 7.1 Hz, 2H), 1.67 – 1.56 (m, 4H), 1.34 – 1.22 (m, 43H), 0.87 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 178.97, 173.99, 143.06, 123.70, 57.63, 50.56, 34.30, 34.03, 32.07, 30.37, 29.84, 29.82, 29.80, 29.75, 29.60, 29.51, 29.45, 29.41, 29.39, 29.26, 29.25, 29.11, 29.05, 26.55, 24.99, 24.81, 22.84, 14.27; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{33}H_{61}N_3O_4Na$, 586.4560; found 586.528.



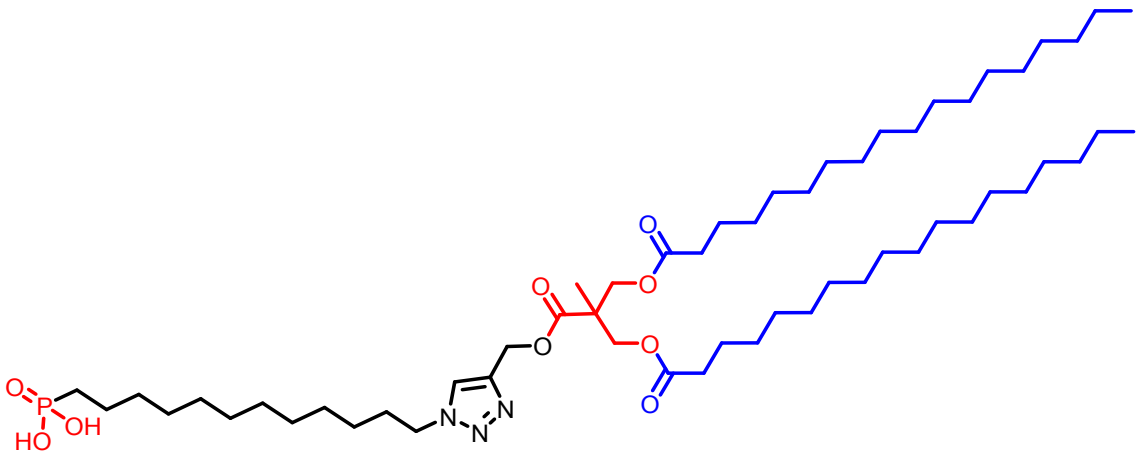

**12-(4-(((2-Methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)methyl)-1H-1,2,3-triazol-1-yl)dodecanoic acid 8**. Prepared according to the general procedure. White solid (0.9g, 93%). $^1$H NMR ($CDCl_3$) $\delta$ 7.57 (s, 1H), 5.25 (s, 2H), 4.33 (t, $J$ = 7.4 Hz, 2H), 4.21 (q, $J$ = 11.0 Hz, 4H), 2.35 (t, $J$ = 7.5 Hz, 2H), 2.24 (t, $J$ = 7.6 Hz, 4H), 1.94 – 1.85 (m, 2H), 1.63 (p, $J$ = 7.4 Hz, 2H), 1.56 (p, $J$ = 7.4 Hz, 4H), 1.34 – 1.23 (m, 70H), 1.21 (s, 3H), 0.87 (t, $J$ = 6.9 Hz, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 178.85, 173.39, 172.94, 142.49, 123.73, 77.42, 77.16, 76.91, 65.23, 58.57, 50.59, 46.48, 34.21, 34.01, 32.07, 30.39, 29.85, 29.81, 29.77, 29.64, 29.51, 29.47, 29.42, 29.27, 29.12, 29.06, 26.58, 24.99, 24.82, 22.83, 17.87, 14.26; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{56}H_{103}N_3O_8Na$, 968.7643; found 969.021.



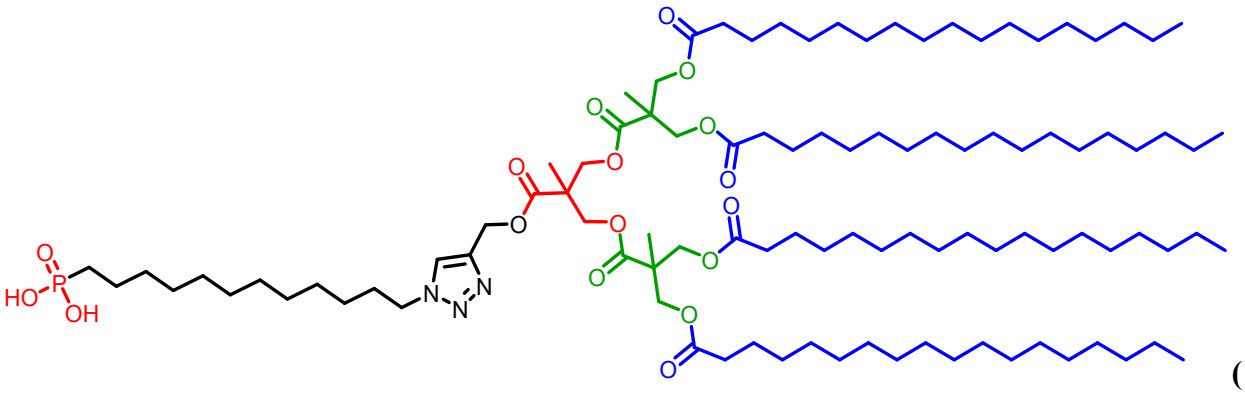
**12-(4-(((2-Methyl-3-((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)-2-(((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)methyl)propanoyl) oxy)methyl)-1H-1,2,3-triazol-1-yl)dodecanoic acid 9**. Prepared according to the general procedure. White solid (1.2g, 88%). $^{1}$H NMR ($CDCl_3$) $\delta$ 7.69 (s, 1H), 5.25 (s, 2H), 4.36 (t, $J$ = 7.3 Hz, 2H), 4.25 (d, $J$ = 11.0 Hz, 2H), 4.21 (d, $J$ = 11.1 Hz, 2H), 4.17 – 4.09 (m, 7H), 2.33 (t, $J$ = 7.5 Hz, 2H), 2.28 (t, $J$ = 7.6 Hz, 8H), 1.97 – 1.85 (m, 2H), 1.66 – 1.52 (m, 10H), 1.34 – 1.22 (m, 126H), 1.22 (s, 3H), 1.17 (s, 6H), 0.87 (t, $J$ = 6.9 Hz, 12H); $^{13}$C NMR (CDCl3) $\delta$ 178.53, 173.39, 172.28, 172.14, 65.66, 65.08, 58.54, 50.61, 46.79, 46.47, 34.17, 33.97, 32.07, 30.39, 29.86, 29.83, 29.81, 29.79, 29.66, 29.51, 29.47, 29.45, 29.43, 29.29, 29.12, 29.08, 26.60, 25.00, 24.81, 22.83, 17.90, 17.65, 14.26; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{102}H_{187}N_3O_{16}Na$, 1733.3809; found 1733.595.



**10**. Prepared according to the general procedure. White solid (0.6g, 79%). $^{1}$H NMR ($CDCl_3$) $\delta$ 7.71 (s, 1H), 5.25 (s, 2H), 4.36 (t, $J$ = 7.3 Hz, 2H), 4.32 – 4.09 (m, 28H), 2.34 (t, $J$ = 7.4 Hz, 2H), 2.28 (t, $J$ = 7.6 Hz, 16H), 1.96 – 1.85 (m, 2H), 1.65 – 1.54 (m, 18H), 1.33 – 1.22 (m, 241H), 1.21 (s, 12H), 1.19 (s, 6H), 0.87 (t, $J$ = 6.8 Hz, 24H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 178.78, 173.33, 172.18, 172.14, 171.56, 66.27, 65.33, 65.02, 58.68, 50.59, 46.80, 46.74, 46.50, 34.17, 33.75, 32.08, 30.42, 29.88, 29.87, 29.83, 29.69, 29.52, 29.49, 29.38, 29.32, 29.21, 29.06, 26.56, 25.02, 24.82, 22.85, 17.95, 17.60, 14.27; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{194}H_{355}N_3O_{32}Na$, 3262.6141; found 3262.661.



**(12-(4-(((2-Methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)methyl)-1H-1,2,3-triazol-1-yl)dodecyl)phosphonic acid 11**. Prepared according to the general procedure. White solid (0.1g, 85%). $^{1}$H NMR ($CDCl_3$) $\delta$ 8.37 (s, 1H), 7.58 (s, 1H), 5.25 (s, 2H), 4.33 (t, $J$ = 7.3 Hz, 2H), 4.21 (q, $J$ = 11.1 Hz, 4H), 2.24 (t, $J$ = 7.6 Hz, 4H), 1.98 – 1.83 (m, 2H), 1.83 – 1.68 (m, 2H), 1.68 – 1.48 (m, 6H), 1.41 – 1.23 (m, 72H), 1.22 (s, 3H), 0.87 (t, $J$ = 6.9 Hz, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 173.37, 172.93, 65.23, 58.48, 50.69, 46.52, 34.22, 32.08, 30.38, 29.86, 29.82, 29.78, 29.65, 29.56, 29.51, 29.42, 29.29, 29.13, 29.06, 26.60, 25.01, 22.84, 17.88, 14.26. MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{56}H_{106}N_3O_9PNa$, 1018.7564; found 1019.04.



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**11-(4-(((2-Methyl-3-((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)-2-(((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)methyl)propanoyl)oxy)**

**methyl)-1H-1,2,3-triazol-1-yl)undecyl)phosphonic acid 12.** Prepared according to the general procedure. White solid (0.5g, 90%). $^{1}$H NMR ($CDCl_3$) $\delta$ 7.72 (s, 1H), 5.25 (s, 2H), 4.36 (t, $J$ = 7.3 Hz, 2H), 4.23 (q, $J$ = 11.1 Hz, 4H), 4.14 (t, $J$ = 8.4 Hz, 8H), 2.27 (t, $J$ = 7.5 Hz, 8H), 1.98 – 1.83 (m, 2H), 1.83 – 1.67 (m, 2H), 1.57 (p, $J$ = 7.3 Hz, 11H), 1.47 – 1.18 (m, 133H), 1.17 (s, 6H), 0.87 (t, $J$ = 6.7 Hz, 12H); $^{13}$C NMR ($CDCl_3$) δ 173.34, 172.27, 172.13, 65.64, 65.09, 58.48, 50.71, 46.79, 46.49, 34.16, 32.06, 30.71, 30.60, 30.39, 29.84, 29.82, 29.80, 29.78, 29.64, 29.61, 29.52, 29.49, 29.44, 29.28, 29.21, 29.14, 26.67, 25.00, 22.82, 22.24, 17.89, 17.65, 14.24; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{102}H_{190}N_3O_{17}Na$, 1783.3731; found 1783.696.

# THERMAL ANALYSIS OF DENDRITIC LIGANDS

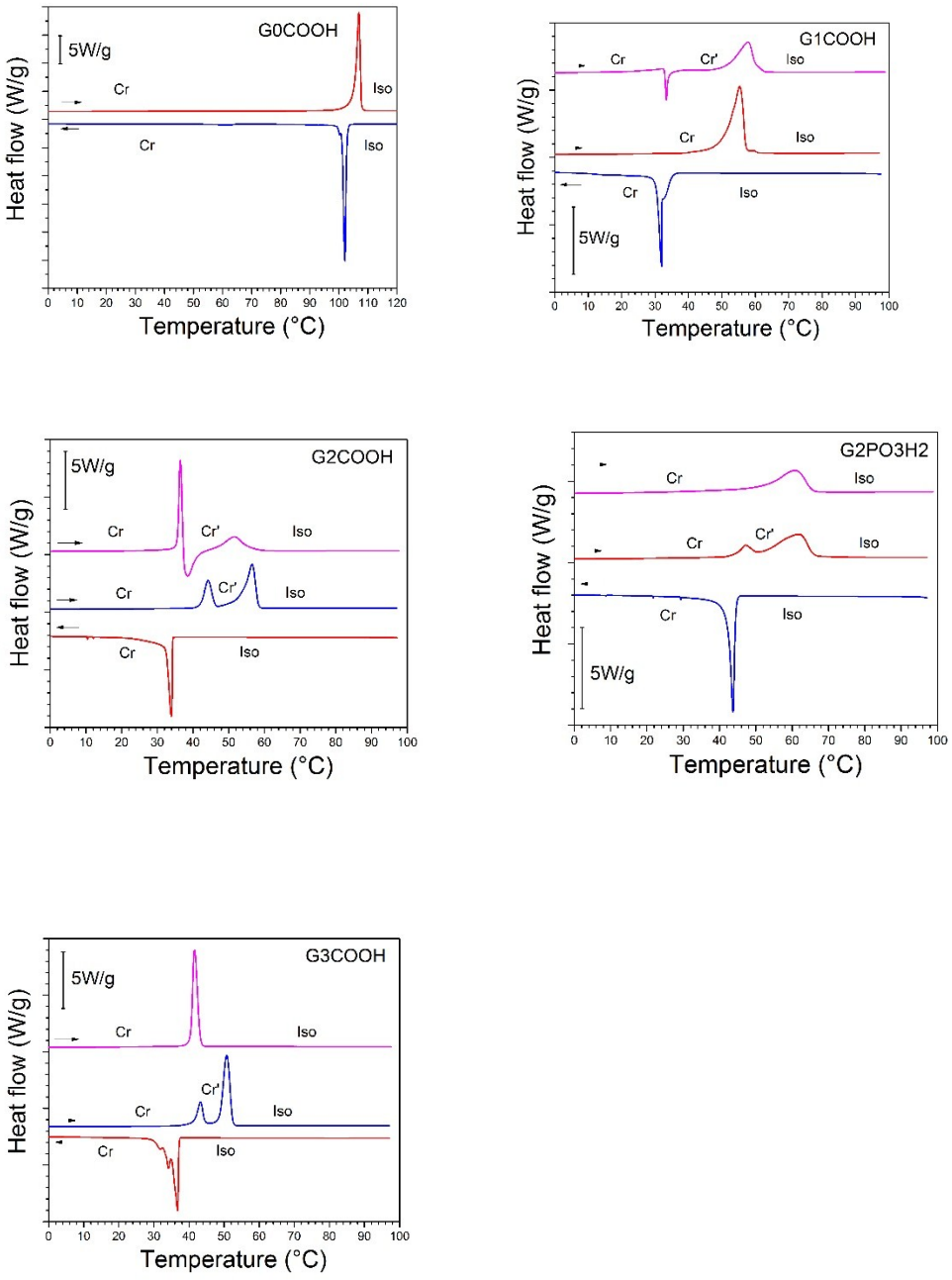



Figure S36. DSC traces of the dendritic ligands. Cr: crystalline phase; Iso: isotropic liquid.

**Table S1. DSC analysis of dendritic ligands**

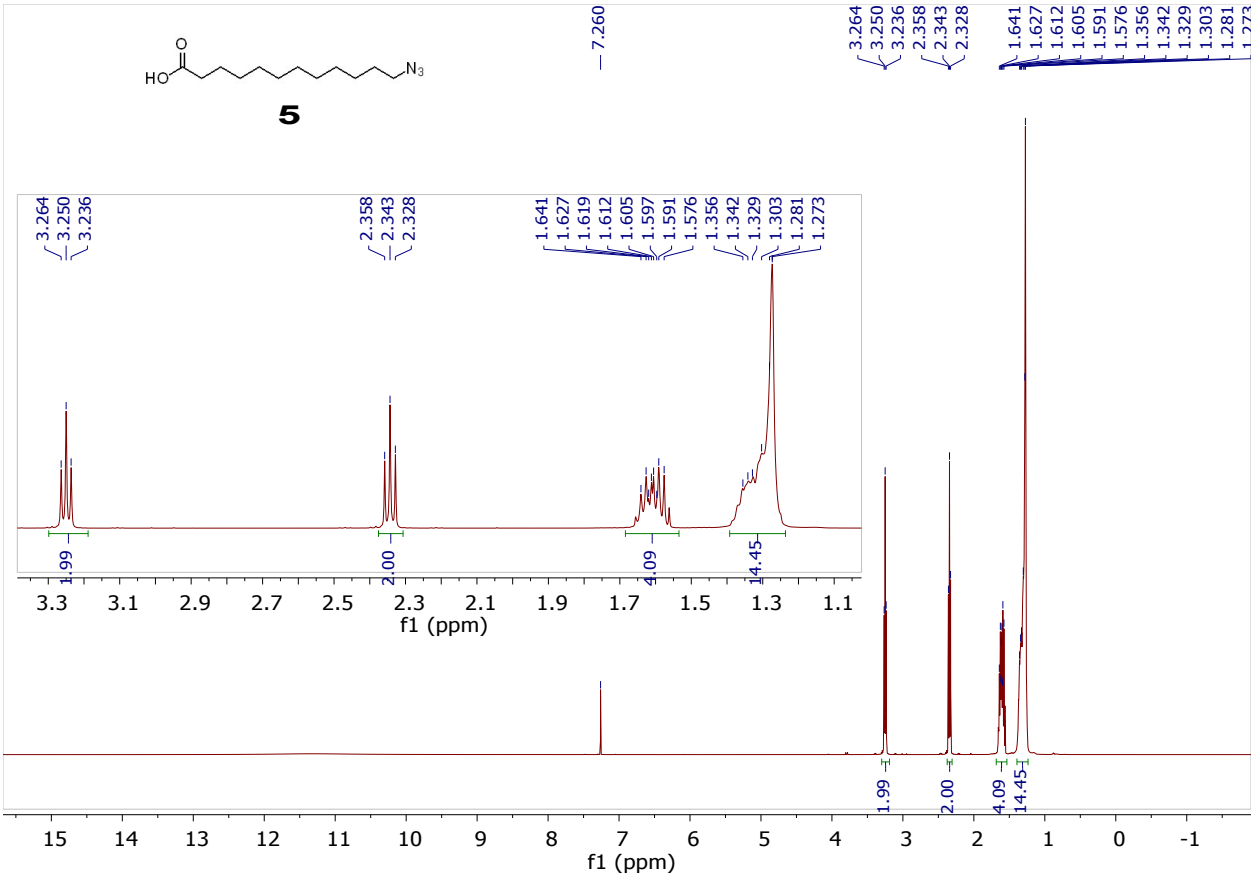
| Compounds | First heating/Second heating | First cooling |
|---|---|---|
| G0COOH | Cr 105.3 (106.9) [207.5] Iso | Iso 102.1 (102.8] [202.5] Cr |
| G1COOH | i) Cr 51.1 (55.3) [147.1] Iso<br><br>ii) Cr 32.9 (33.4 [-9.6] Cr' 51.3 (57.9) [74.9] Iso | Iso 34.5 (32.0) [76.3) Cr |
| G2COOH | i) Cr 42.1 (44.2) [36.4] Cr' 53.7 (56.5) [75.8] Iso<br><br>ii) Cr 36.4 (35.7] [63.7] Cr' 38.5 (38.5) [32.1] 45.6 (51.6) [54.1] Iso | Iso 33.9 (34.3) [73.6] Cr |
| G2PO3H2 | i) Cr 44.5 (47.1) [-] Cr' 53.3 (62.3) [98.1] Iso<br><br>ii) Cr 52.6 (61.3) [59.7] Iso | Iso 43.7 (44.4) [86.1] Cr |
| G3COOH | i) Cr 41.5 (43.3) [-] Cr' 48.8 (50.7) [125.8] Iso<br><br>ii) Cr 40.6 (41.6) [97.8] Iso | Iso 36.7 (37.1) [96.8] Cr |
| ONSET temperature: $T_{ONSET}$/°C; Peak temperature: ($T_{PEAK}$/°C); Melting enthalpy: [$\Delta$H/J $g^{-1}$] | | |

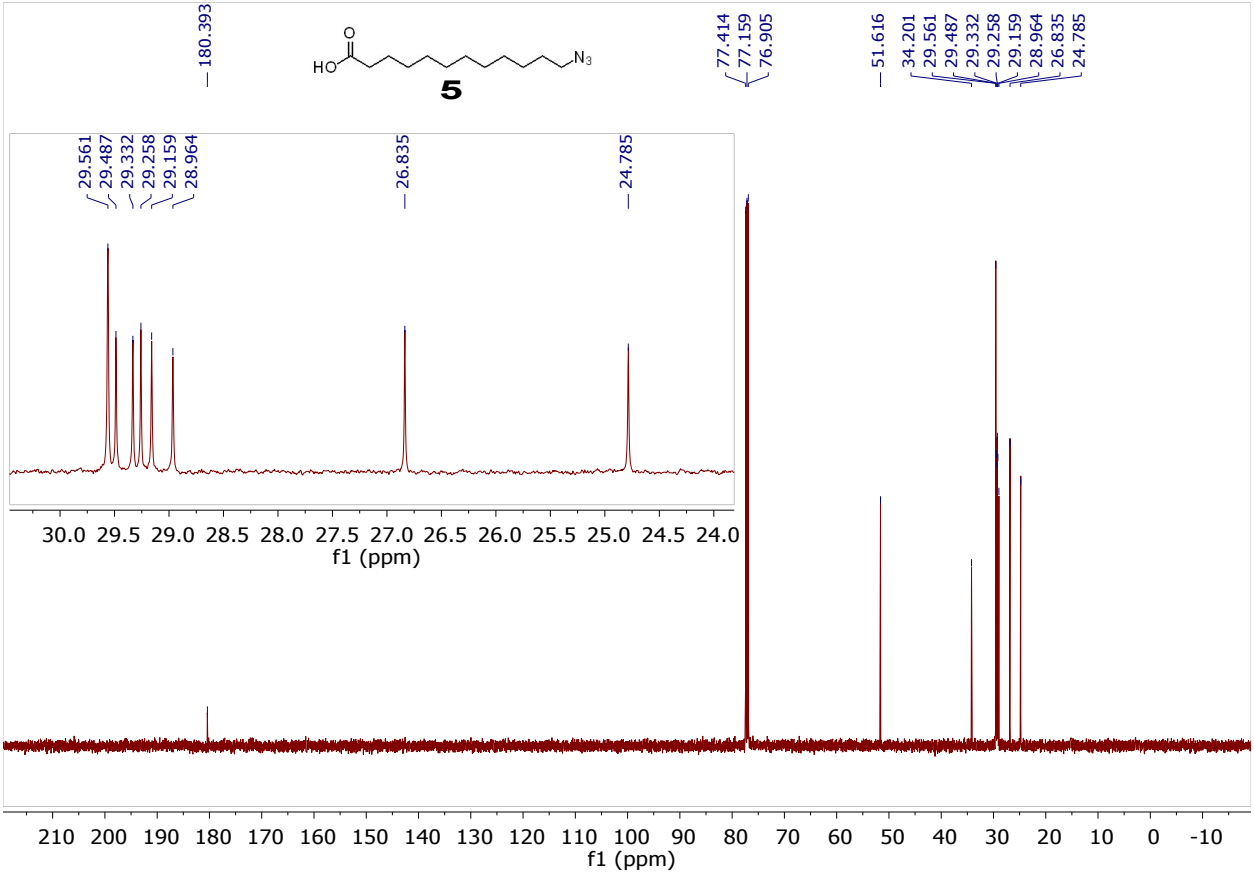
References:

(1) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62* (21), 7512.

(2) Jishkariani, D.; Diroll, B. T.; Cargnello, M.; Klein, D. R.; Hough, L. A.; Murray, C. B.; Donnio, B. *J. Am. Chem. Soc.* **2015**, *137* (33), 10728.

(3) Eising, R.; Elias, W. C.; Albuquerque, B. L.; Fort, S.; Domingos, J. B. *Langmuir* **2014**, *30* (21), 6011.


HO
O
N3
5
7.260
3.264
3.250
3.236
2.358
2.343
2.328
1.641
1.627
1.619
1.612
1.605
1.597
1.591
1.576
1.356
1.342
1.329
1.303
1.281
1.273
1.99
2.00
4.09
14.45
f1 (ppm)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O
N3
5
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77.159
76.905
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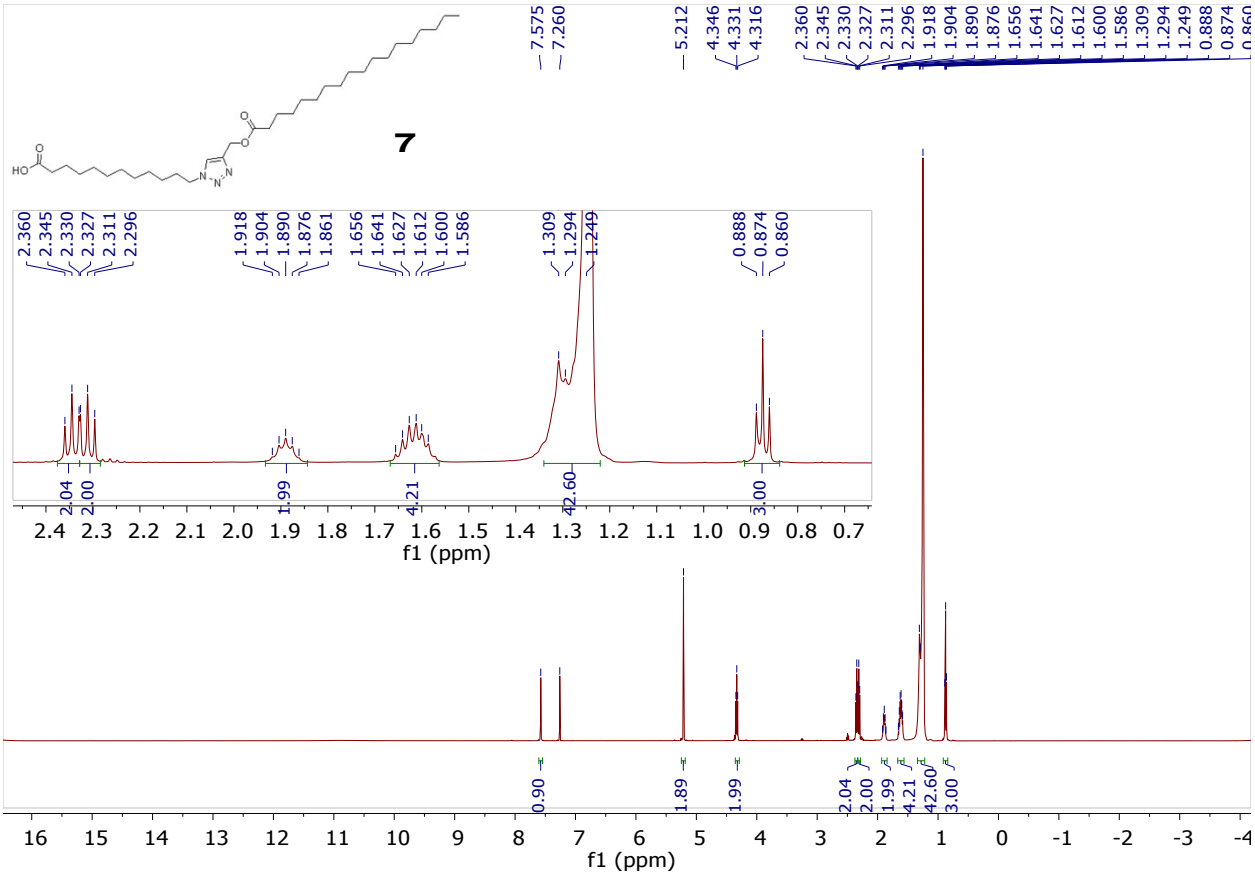
29.159
28.964
26.835
24.785
f1 (ppm)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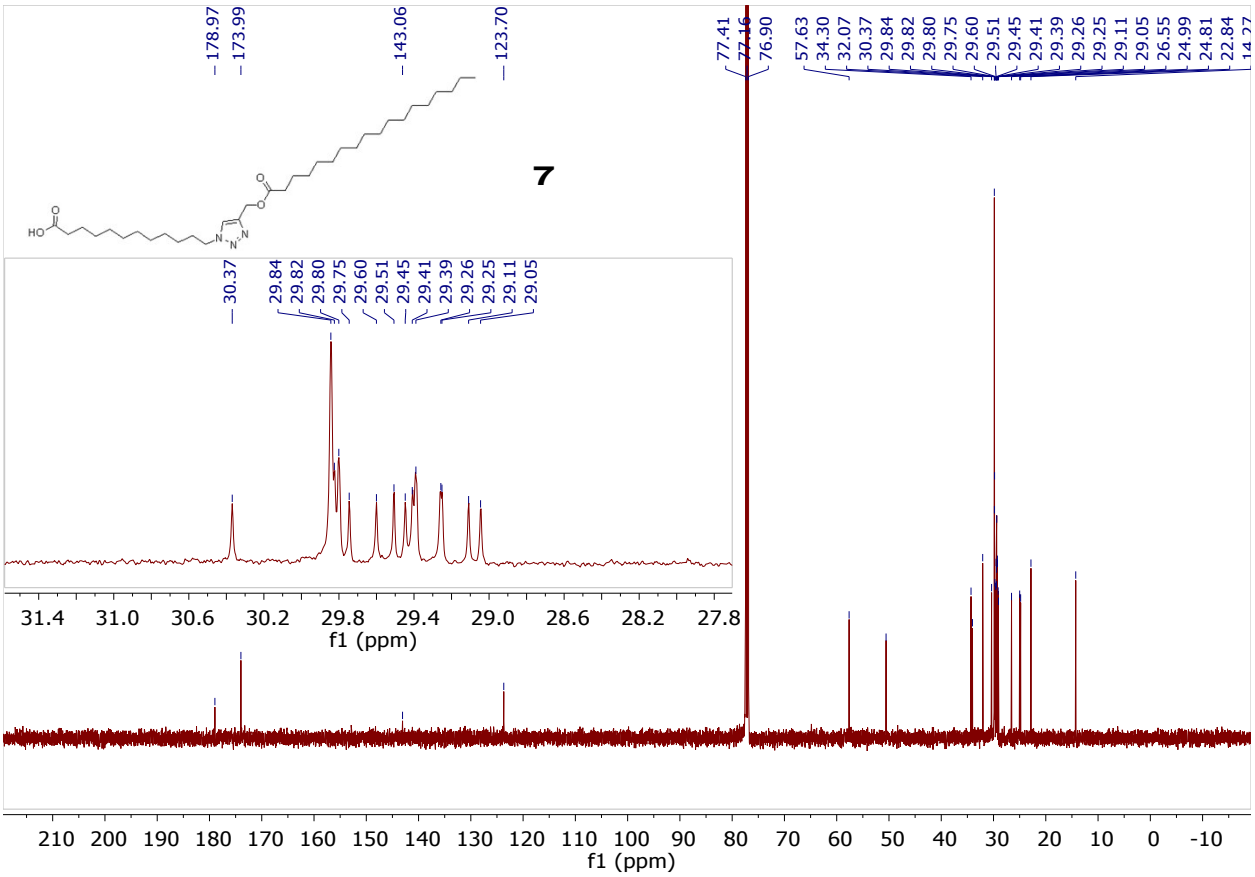
7
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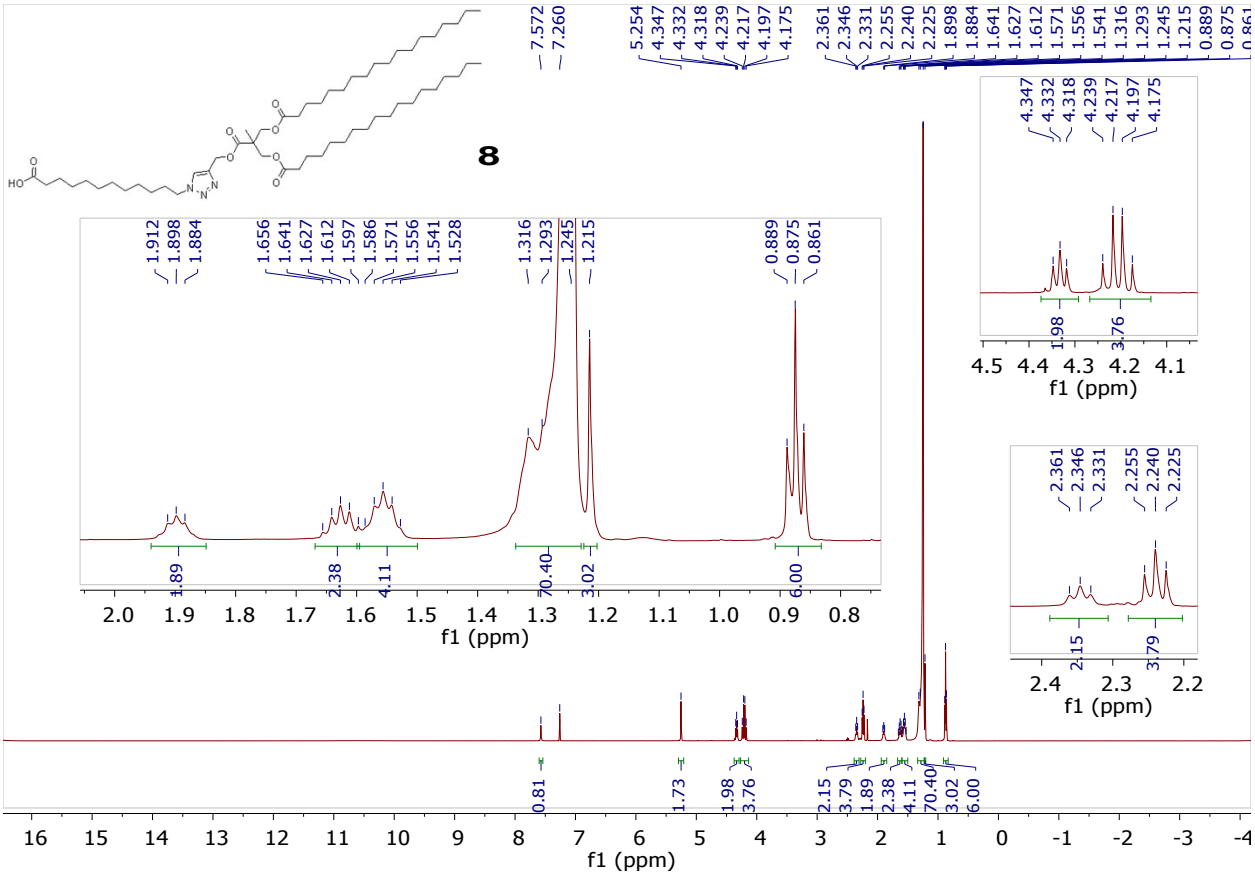
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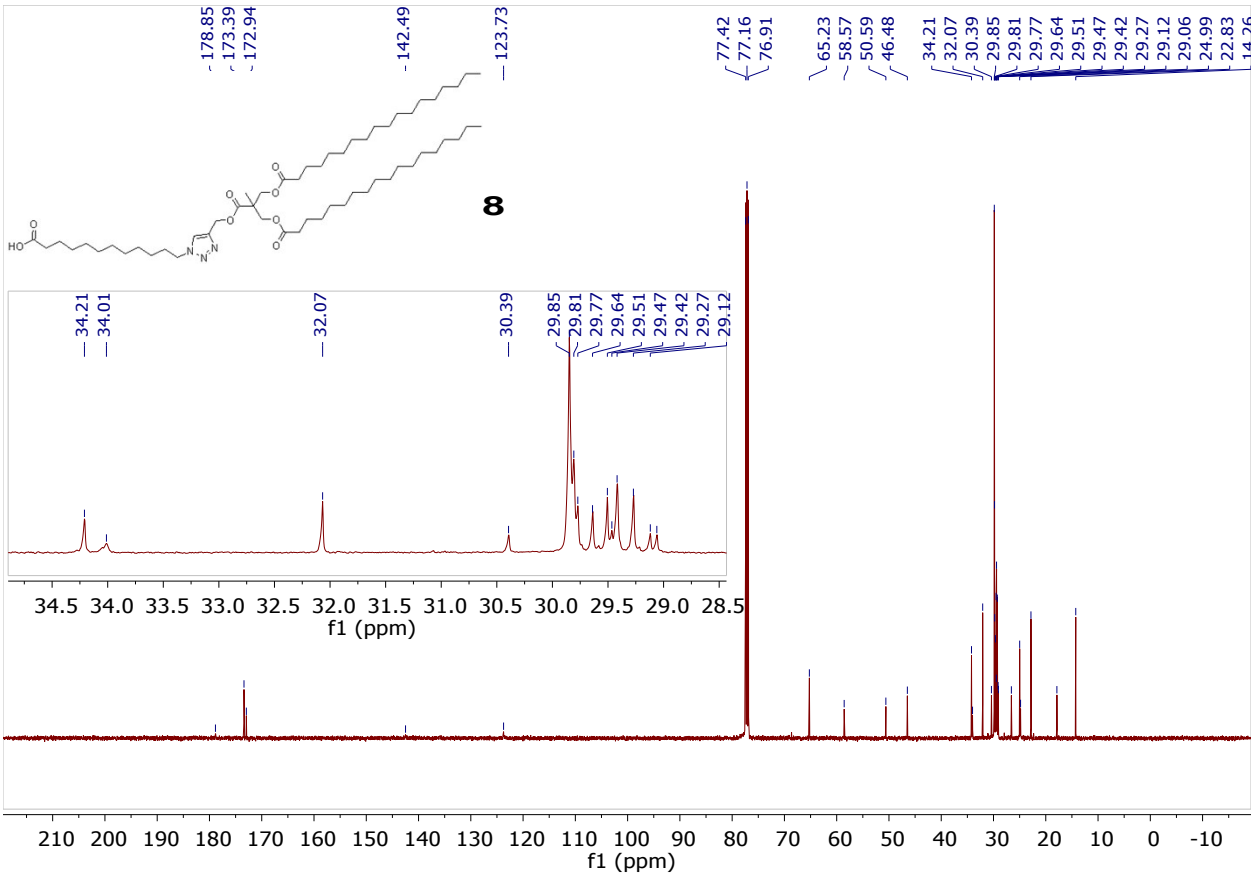
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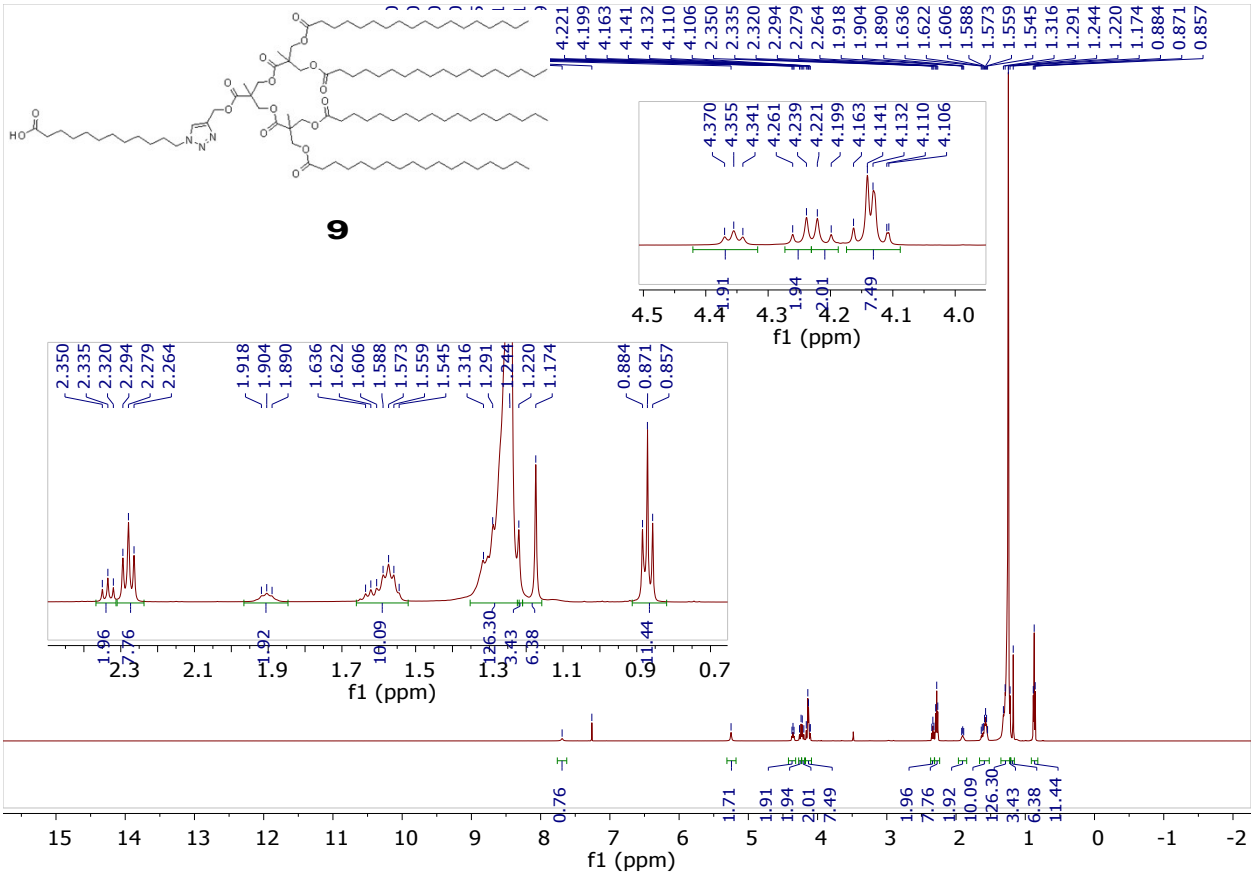
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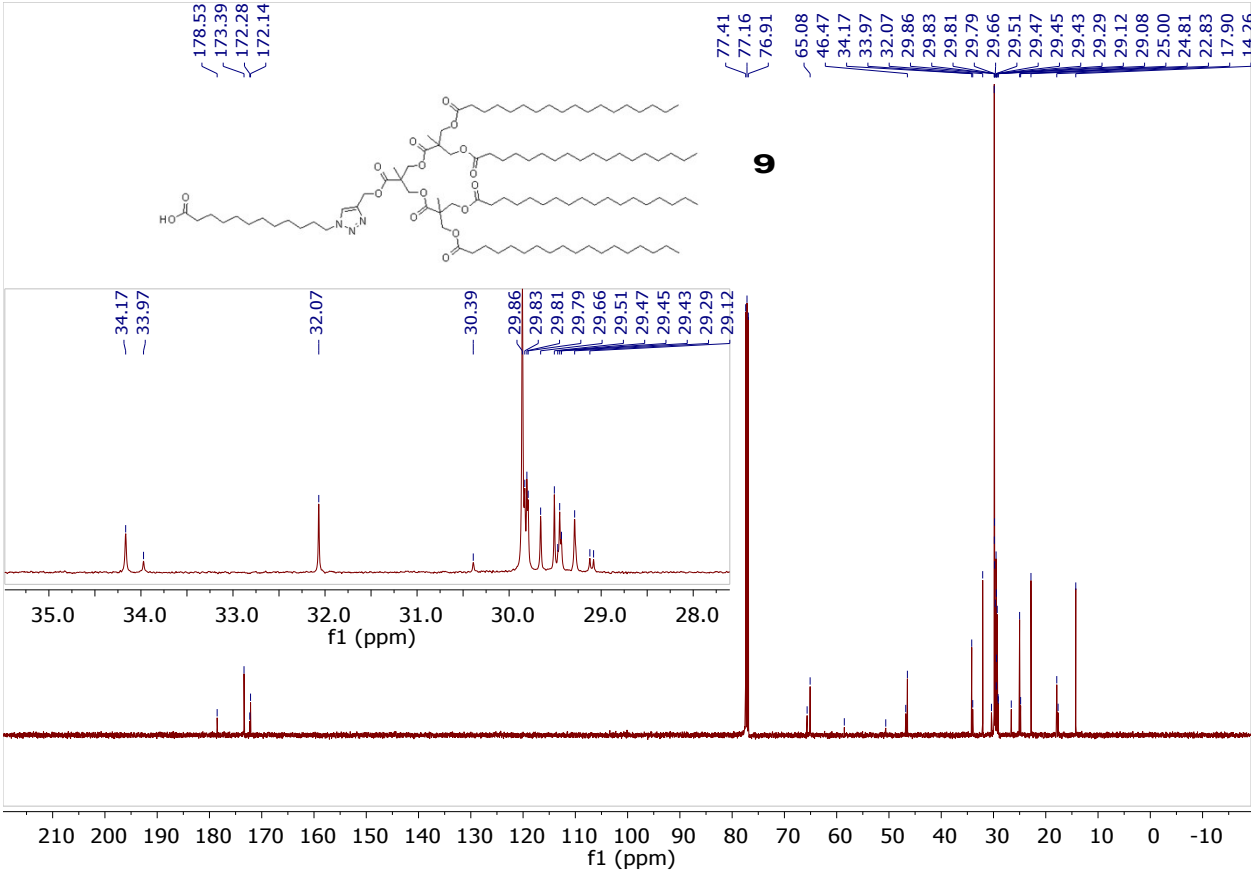
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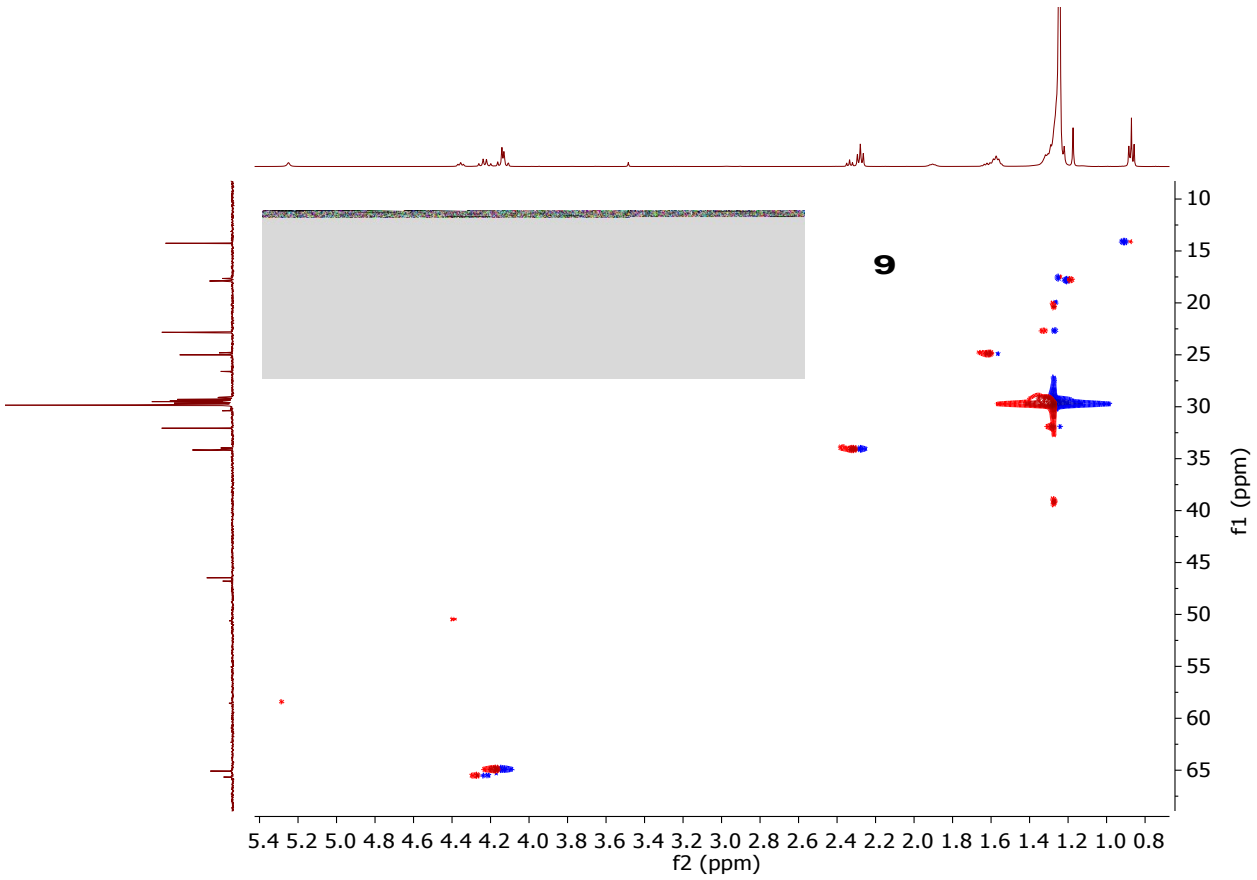
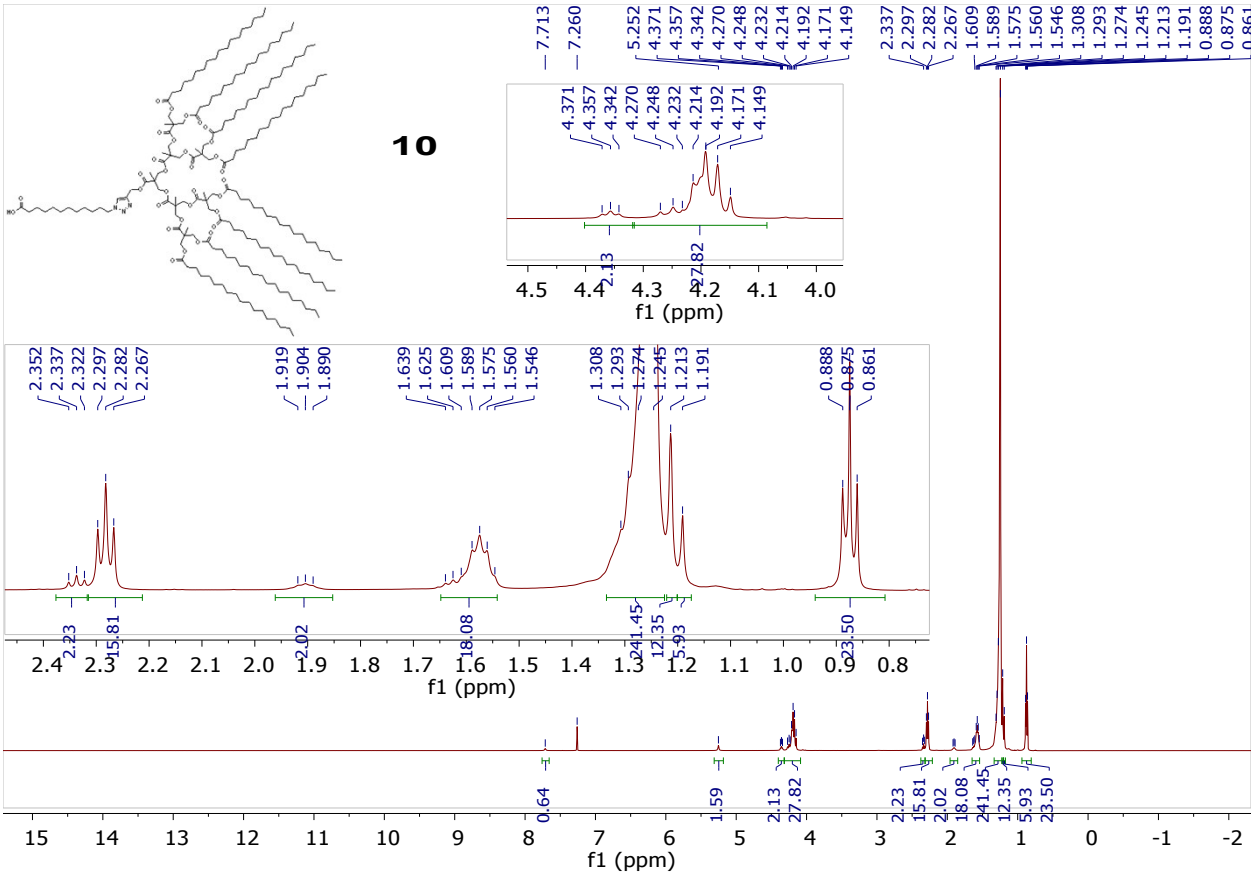
f1 (ppm)


9
10
15
20
25
30
35
40
45
50
55
60
65
f1 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)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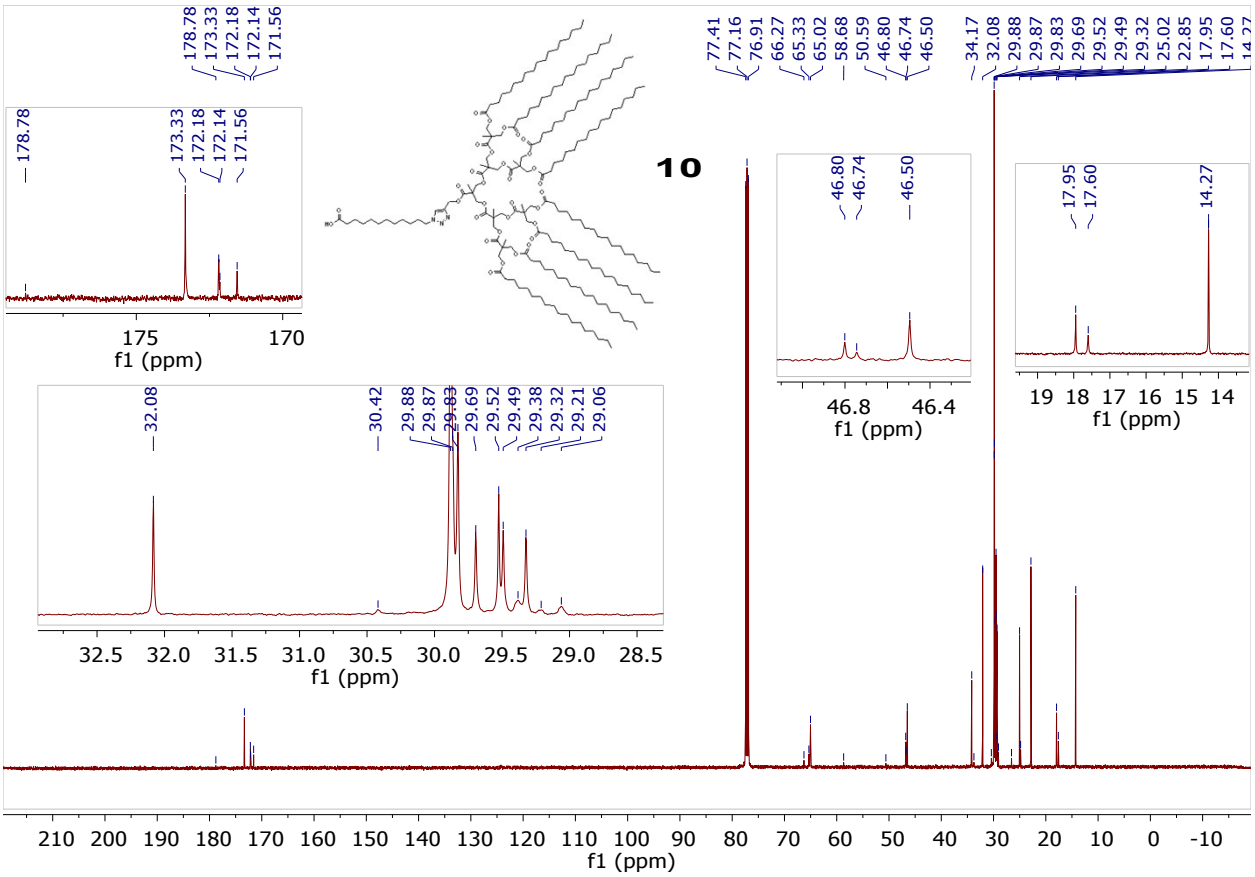
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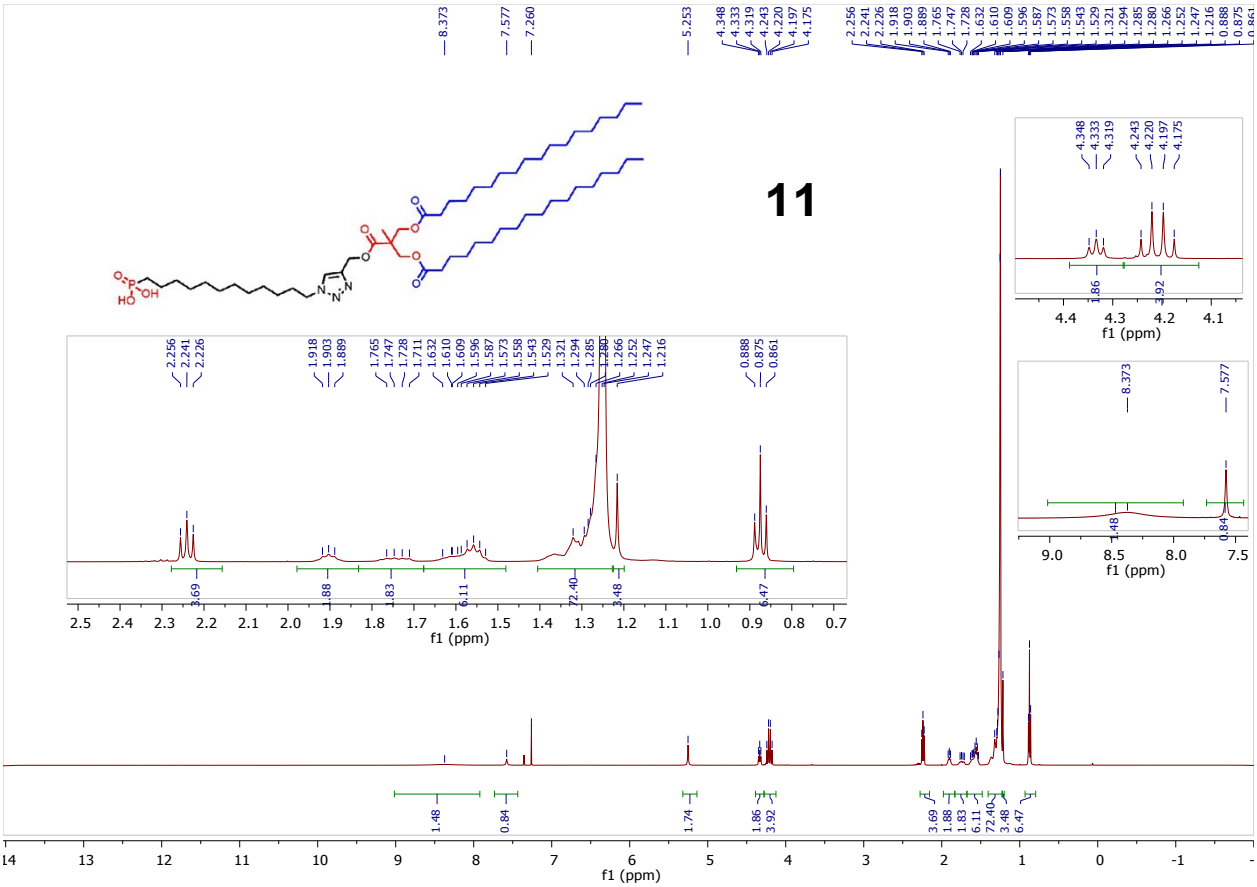
f1 (ppm)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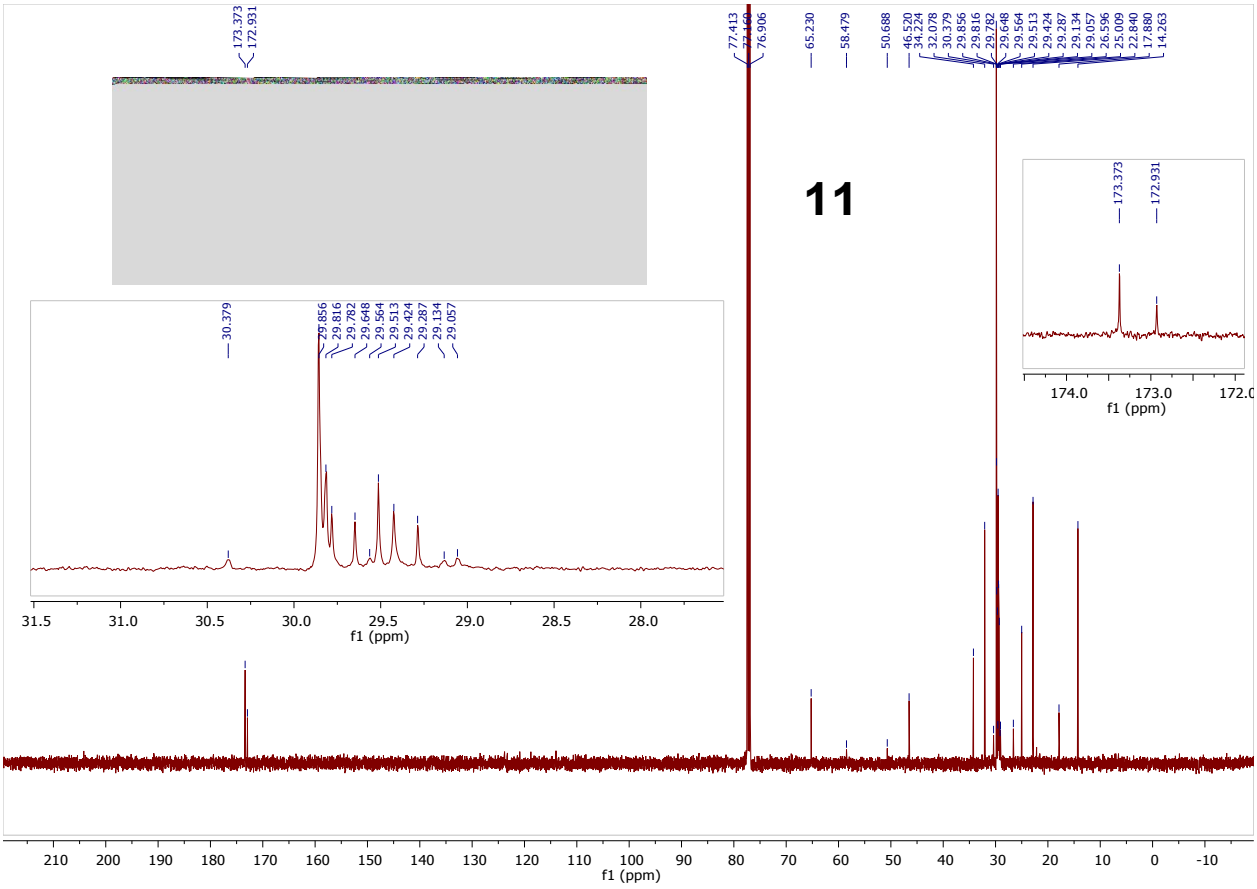
11
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172.931
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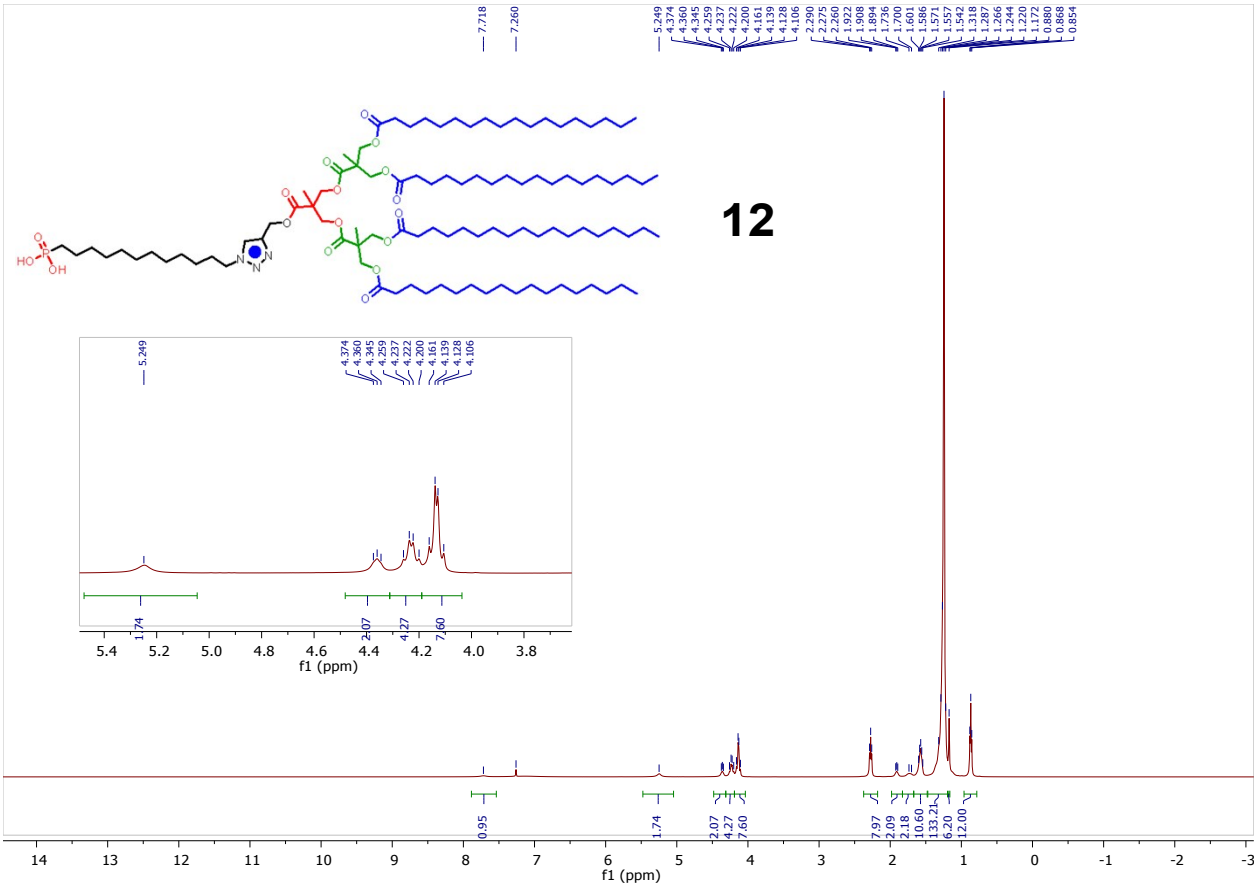
77.160
76.906
65.230
58.479
50.688
46.520
34.224
32.078
30.379
29.856
29.816
29.782
29.648
29.564
29.513
29.424
29.287
29.134
29.057
26.596
25.009
22.840
17.880
14.263
30.379
29.856
29.816
29.782
29.648
29.564
29.513
29.424
29.287
29.134
29.057
31.5
31.0
30.5
30.0
29.5
29.0
28.5
28.0
f1 (ppm)
173.373
172.931
174.0
173.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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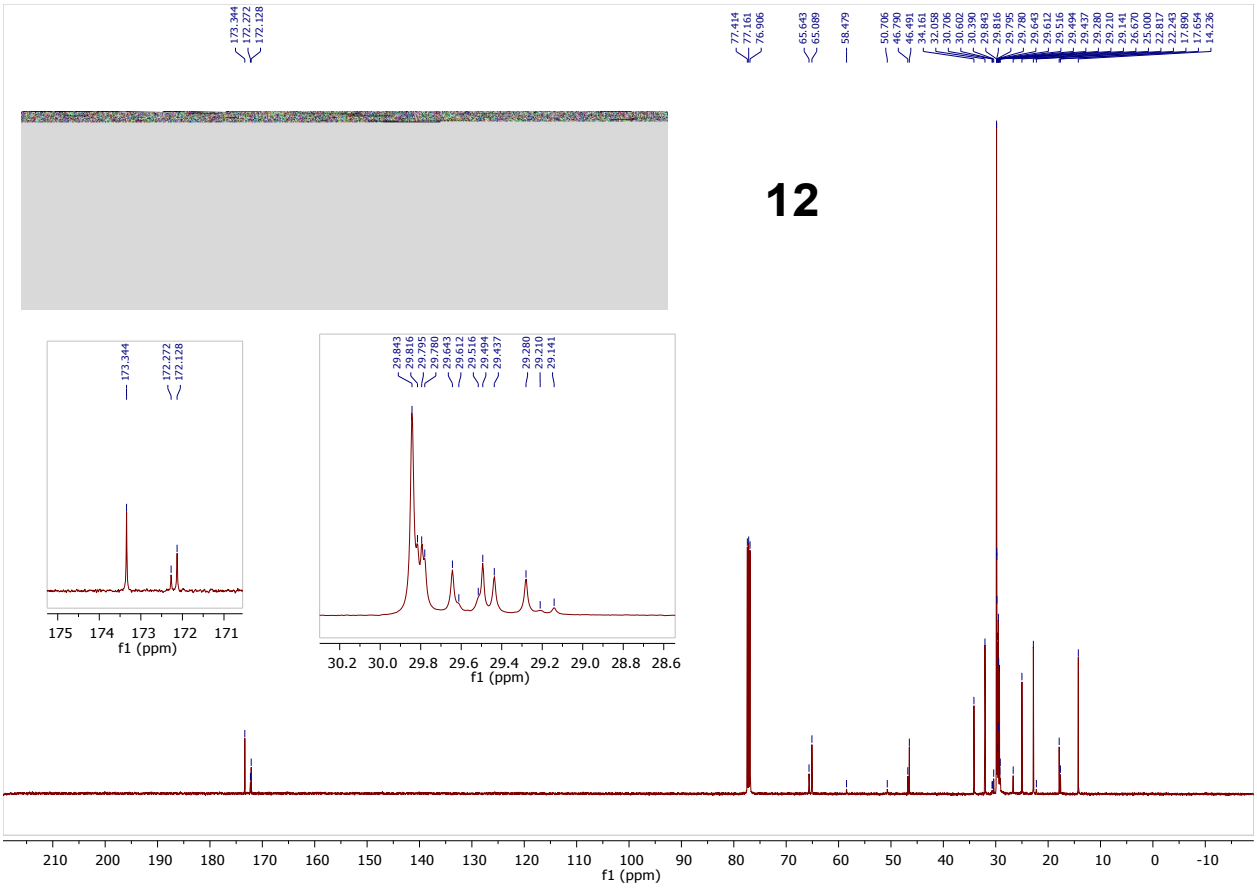
f1 (ppm)


12
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172.272
172.128
77.414
77.161
76.906
65.643
65.089
58.479
50.706
46.790
46.491
34.161
32.058
30.706
30.602
30.390
29.843
29.816
29.795
29.780
29.643
29.612
29.516
29.494
29.437
29.280
29.210
29.141
26.670
25.000
22.817
22.243
17.890
17.654
14.236
f1 (ppm)