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Supporting Information

Multifunctional “Clickates” as Versatile Extended Heteroaromatic Building Blocks: Efficient Synthesis via Click Chemistry, Conformational Preferences, and Metal Coordination

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General Methods. Solvents and starting materials were used as received. 2,6-Dibromopyridine, citrazinic acid, the aryl azide precursors, and europium(III)triflate are commercially available as a bulk chemical and were used without further purification. Toluene and THF, were distilled under an inert gas (Ar) atmosphere over $NaAl(C_2H_5)_4$, CH_2Cl_2 over CaH_2 and acetonitrile and triethylamine (TEA) over KOH, prior to use. Triethylene glycol monomethyl ether was stored over activated molecular sieves in inert gas atmosphere (Ar) and distilled prior to use. $Pd(PPh_3)_4$ was freshly prepared.[1] All reactions requiring inert gas were performed under Ar atmosphere. Column chromatography was carried out with 130 – 400 mesh silica gel using the eluents specified (Hex = hexane, EA = ethyl acetate). NMR spectra were recorded on a 400 MHz (100.6 MHz for ^{13}C) Bruker AV 400 or on a 300 MHz (75.6 MHz for ^{13}C) Bruker DPX 300 spectrometer at 27 °C using residual protonated solvent signals as internal standard (^1H: $\delta(CHCl_3)$ = 7.26 ppm, $\delta(CH_2Cl_2)$ = 5.30 ppm, $\delta((CH_3)_2SO)$ = 2.50 ppm, $\delta(CH_3OH)$ = 3.31 ppm and ^{13}C: $\delta(CHCl_3)$ = 77.16 ppm, $\delta(CH_2Cl_2)$ = 53.52 ppm, $\delta((CH_3)_2SO)$ = 39.52 ppm, $\delta(CH_3OH)$ = 49.00 ppm). Assignments are based on chemical shifts and/or DEPT as well as COSY spectra (Ar is used as abbreviation for assigning both aromatic as well as triazole moieties). NOE NMR experiments were performed with degassed and argon saturated samples in CD_2Cl_2 at 27 °C using the *noesygpph* pulse program. Mixing times (D8) were adjusted to 1.0 sec to assure for maximum NOE sensitivity. Mass spectrometry was performed on Bruker-Esquire 3000 (ESI, Ionentrap-MS, potential 4500 V) or Bruker-Apex III (FTICR-MS, ESI-HRMS) and Finnigan MAT 8200 (EI, double focusing sector field, resolution of 3000, 70 eV ionization), respectively. The BTP metal ion complexes were measured on a QSTARXL Applied Biosystems ESI Q-TOF with a ISV of 950 V. HPLC separations were performed with Shimadzu LC-10A systems equipped with a photodiode array detector (PAD or DAD), specific measuring and system conditions are described at the corresponding substances. GC was performed on a Carlo Erba HRGC instrument equipped with a achiral 30 m DB-1 column using FID detection and employing 0.8 bar of H_2 as the carrier gas. UV-visible absorption and fluorescence emission spectra were recorded in quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorimeter, respectively, each equipped with a Peltier thermostated cell holder at 25 ± 0.05 °C using spectrophotometric grade solvents. Emission spectra were corrected for variations in photomultiplier response and lamp intensity over wavelength using correction curves generated on the instrument, followed by

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[1] D. R. Coulson, *Inorg. Syn.* **1971**, *13*, 121-124.

normalization considering the optical density of the sample at the excitation wavelength. The samples were excited at λ = 265 nm, slit widths were set to 10 nm bandpass for excitation and 10 nm bandpass for emission.

Crystal structure determinations 4a-4d, 5b, 5d, 10a, $[Fe(5c)_2](OTf)_2$, $[Eu(5a)_3](OTf)_3$. Crystals were transferred to the respective diffractometers and cooled to the denoted temperatures by a stream of cold N_2 gas. In order to increase the signal to noise ratio for the diffracted intensities a data collection strategy involving phi scans and multiple omega scans at different phi values and constant chi was employed. The resulting high redundancy intensity data were averaged using the programs *SADABS* (Sheldrick/Bruker-AXS, 2005) or *SCALEPACK* (Otwinowski, 1997). $R_{int} = \Sigma \mid F_o^2 - F_o^2(\text{mean}) \mid / \Sigma [F_o^2]$, $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$ and $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{½}$. Structures were solved using direct methods (*SHELXS-97*) and refined by least-squares (*SHELXL-97*) on F_o^2, both programs from G. Sheldrick, University of Göttingen, 1997.

Crystal data for **4a**: $[C_{31}H_{33}N_7O_5]$, from ethanol, M_r = 583.64, colourless plate, crystal size: 0.07×0.10×0.36 mm^3; a = 10.3510(2), b = 28.1832(5), c = 19.7683(3) Å, β = 93.773(1)°, U = 5754.4(2) Å^3, T = 100 K, monoclinic, space group $P2_1/c$ (No. 14), Z = 8, ρ_{calcd} = 1.35 g cm^{-3}, $F(000)$ = 2464, Nonius KappaCCD diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 0.094 mm^{-1}, 110005 measured and 21878 independent reflections (R_{int} = 0.077), 15145 with $I > 2\sigma(I)$, θ_{max} = 33.1°, T_{min} = 0.4333, T_{max} = 0.7464, Chebyshev type weights, 779 parameters, H atoms riding, R_1 = 0.0766 [$I > 2\sigma(I)$], wR_2 = 0.1851 (all data), $\Delta\rho_{max/min}$ = 0.898/-1.048 (0.95 Å from C47) eÅ^{-3}.

Crystal data for **4b**: $[C_{29}H_{27}I_2N_7O_5]$, from dichloromethane/diethylether, M_r = 807.38, yellow prism, crystal size: 0.13×0.13×0.26 mm^3; a = 10.1000(3), b = 10.2657(3), c = 16.5979(5) Å, α = 78.308(1), β = 80.254(1), γ = 65.085(1)°, U = 1521.55(8) Å^3, T = 100 K, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, ρ_{calcd} = 1.76 g cm^{-3}, $F(000)$ = 792, Bruker-AXS X8 Proteum diffractometer, λ(Cu K_α) = 1.54178 Å, μ = 16.66 mm^{-1}, 31640 measured and 5202 independent reflections (R_{int} = 0.039), 4993 with $I > 2\sigma(I)$, θ_{max} = 67.9°, T_{min} = 0.460, T_{max} = 1.0, Chebyshev type weights, 388 parameters, H atoms riding, R_1 = 0.0250 [$I > 2\sigma(I)$], wR_2 = 0.0623 (all data), $\Delta\rho_{max/min}$ = 0.760/-0.732 eÅ^{-3}.

Crystal data for **4c**: $[C_{29}H_{27}N_9O_9]\cdot[CH_2Cl_2]$, from dichloromethane, M_r = 730.52, colourless prism, crystal size: 0.08×0.19×0.29 mm^3; a = 8.2392(1), b = 11.4777(2), c = 17.9104(3) Å, α = 74.439(1), β = 86.064(1), γ = 87.025(1)°, U = 1626.81(4) Å^3, T = 100 K, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, ρ_{calcd} = 1.49 g cm^{-3}, $F(000)$ = 756, Nonius KappaCCD diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 0.269 mm^{-1}, 40896 measured and 10508 independent reflections (R_{int} = 0.038), 9317 with $I > 2\sigma(I)$, θ_{max} = 31.3°, T_{min} = 0.872, T_{max} = 1.0, Chebyshev type weights, 452 parameters, H atoms riding, R_1 = 0.0370 [$I > 2\sigma(I)$], wR_2 = 0.0949 (all data), $\Delta\rho_{max/min}$ = 0.435/-0.356 eÅ^{-3}.

Crystal data for **4d**: $[C_{33}H_{39}N_9O_5]$, from tetrahydrofuran, M_r = 641.73, yellow prism, crystal size: 0.04×0.12×0.13 mm^3; a = 9.9892(3), b = 11.4054(4), c = 16.2683(6) Å, α = 75.622(2), β = 84.255(2), γ = 77.826(2)°, U = 1752.8(1) Å^3, T = 100 K, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, ρ_{calcd} = 1.22 g cm^{-3}, $F(000)$ = 680, Bruker-AXS X8 Proteum diffractometer, λ(Cu K_α) = 1.54178 Å, μ = 0.693 mm^{-1}, 36210 measured and 5976 independent reflections (R_{int} = 0.058), 4569 with $I > 2\sigma(I)$, θ_{max} = 67.9°, T_{min} = 0.7828, T_{max} = 1.0. The 3,6,9-trioxadeca-1-yloxycarbonyl side-chain is severly disordered. Disordered atoms were refined with isotropic displacement parameters and occupancies fixed to give the correct total molecular formula. It cannot be ruled out that part of the disordered chain is occupied by a tetrahydrofuran solute molecule since the crystals effloresce when removed from the mother liquor. Hydrogen atoms were calculated for carbon atoms with unambiguous locations. Chebyshev type weights, 463 parameters, H atoms riding, R_1 = 0.0872 [$I > 2\sigma(I)$], wR_2 = 0.2666 (all data), $\Delta\rho_{max/min}$ = 0.909/-0.814 eÅ^{-3}.

Crystal data for **5b**: $[C_{28}H_{27}I_2N_7O_4]\cdot[C_2H_3N]$, from acetonitrile, M_r = 820.42, colourless prism, crystal size: 0.06×0.06×0.08 mm^3; a = 9.4669(2), b = 11.4080(3), c = 15.9200(5) Å, α = 83.838(1), β = 80.301(1), γ = 82.816(1)°, U = 1674.9(1) Å^3, T = 100 K, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, ρ_{calcd} = 1.63 g cm^{-3}, $F(000)$ = 808, Nonius KappaCCD diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 1.924 mm^{-1}, 46536 measured and 10238 independent reflections (R_{int} = 0.054), 8119 with $I > 2\sigma(I)$, θ_{max} = 31.6°, T_{min} = 0.8425, T_{max} = 1.0. Both the 3,6,9-trioxadeca-1-yloxy side-chain and the acetonitrile solute molecule are disordered (0.5:0.5). The disordered C and N atoms were refined with isotropic displacement parameters. The H atoms on the solute acetonitrile molecules could not be located. Otherwise

H atoms were calculated and refined using a riding model. Chebyshev type weights, 412 parameters, R_1 = 0.0640 [$I > 2\sigma(I)$], wR_2 = 0.1322 (all data), $\Delta\rho_{max/min}$ = 2.351 (0.26 Å from I2) /-4.185 (0.79 Å from I2) eÅ^{-3}.

Crystal data for **5d**: [$C_{32}H_{39}N_9O_4$], from tetrahydrofuran, M_r = 613.72, colourless prism, crystal size: 0.02×0.04×0.07 mm^3; a = 11.2373(1), b = 20.8946(3), c = 13.2267(2) Å, β = 95.219(1)°, U = 3092.7(1) Å^3, T = 100 K, monoclinic, space group $P2_1$ (No. 4), Z = 4, ρ_{calcd} = 1.32 g cm^{-3}, F(000) = 1304, Nonius KappaCCD diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 0.090 mm^{-1}, 104070 measured and 7593 independent reflections (no significant anomalous signal so Friedel pairs merged, R_{int} = 0.106), 5585 with $I > 2\sigma(I)$, θ_{max} = 28.0°, T_{min} = 0.5883, T_{max} = 0.7454, Chebyshev type weights, 819 parameters, H atoms riding, R_1 = 0.0511 [$I > 2\sigma(I)$], wR_2 = 0.1040 (all data), $\Delta\rho_{max/min}$ = 0.247/-0.229 eÅ^{-3}.

Crystal data for **10a**: [$C_{42}H_{55}N_7O_4$]·[C_2D_6OS], from dimethylsulfoxide-d6, M_r = 806.09, colourless prism, crystal size: 0.02×0.04×0.06 mm^3; a = 8.3323(4), b = 10.6037(7), c = 26.829(2) Å, α = 93.652(2), β = 98.126(4), γ = 109.518(4)°, U = 2196.1(2) Å^3, T = 100 K, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, ρ_{calcd} = 1.21 g cm^{-3}, F(000) = 860, Nonius KappaCCD diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 0.125 mm^{-1}, 29212 measured and 9635 independent reflections (R_{int} = 0.076), 5722 with $I > 2\sigma(I)$, θ_{max} = 27.1°, T_{min} = 0.317, T_{max} = 0.744. The isonicotinic acid carboxylic acid H atom was located in a difference Fourier synthesis and its position and isotropic atomic displacement parameter were refined (U_{Hiso} = 0.048(14) Å^2, O-H 0.81(4) Å). Otherwise H atoms were calculated and refined using a riding model. Chebyshev type weights, 518 parameters, R_1 = 0.0860 [$I > 2\sigma(I)$], wR_2 = 0.2165 (all data), $\Delta\rho_{max/min}$ = 0.905/-0.606 eÅ^{-3}.

Crystal data for [Fe(**5c**)$_2$](OTf)$_2$ (cocrystallized with Fe(OTf)$_2$(H_2O)($MeCN$)$_4$): [$C_{143.5}H_{140}F_{18}Fe_3N_{40}O_{51}S_6$], from acetonitrile/toluene, M_r = 3942.87, red prism, crystal size: 0.50×0.40×0.15 mm^3, a = 25.7798(7), b = 29.8435(6), c = 26.7631(8) Å, α = 90, β = 118.492(2), γ = 90 °, U = 18096.6(8) Å^3, T = 116(2) K, monoclinic, space group P 2_1/n, Z = 4, ρ_{calcd} = 1.45 g cm^{-3}, F_{000} = 8100, μ = 0.415 mm^{-1}, Θ = 3.20-26.00°, reflections collected 139307, independent reflections 35500 [R_{int} = 0.1245], *GoF* = 0.963, R = 0.0995, wR_2 = 0.2130, largest diffraction peak and hole 1.613/-0.573 eÅ^{-3}. The data were collected on a

STOE IPDS2T using $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, and the structures were solved with anisotropic atomic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model.

Crystal data for [Eu(**5a**)$_3$](OTf)$_3$ (cocrystallized with MeCN): [$C_{188}H_{201}Eu_2F_{18}N_{43}O_{42}S_6$], from acetonitrile/diethylether, M_r = 4573.20, colorless cubes, crystal size: 0.48×0.48×0.42 mm^3, a = 16.9855(6), b = 22.8044(11), c = 29.5181(12) Å, α = 104.320(4), β = 96.527(3), γ = 90.858(3) °, U = 10995.6(8) Å^3, T = 100(2) K, triclinic, space group $P\bar{1}$, Z = 2, ρ_{calcd} = 1.38 g cm^{-3}, F_{000} = 4700, μ = 0.717 mm^{-1}, Θ = 3.13-25.80°, reflections collected 78576, independent reflections 41557 [R_{int} = 0.1332], *GoF* = 1.033, R = 0.1150, wR_2 = 0.2804, largest diffraction peak and hole 3.229/-2.903 eÅ^{-3}. The data was collected on a STOE IPDS2T using $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, and the structures were solved with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model.

The crystallographic data (apart from structure factors) of **4a-4d**, **5b**, **5d**, **10a**, [Fe(**5c**)$_2$](OTf)$_2$, and [Eu(**5a**)$_3$](OTf)$_3$ have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 650303-650309, 650835, and 659662. Copies of the data (cif files) can be ordered free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis. The preparation and characterization of the compounds outlined in the manuscript's schemes are provided below:

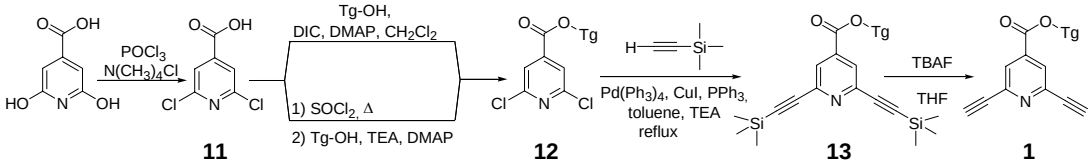
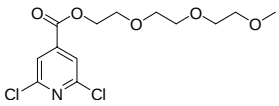


Figure 1. Synthesis of 2,6-Di(ethynyl)-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine **1**.

2,6-Dichloro-isonicotinic acid **11** was prepared as described by Gu.[2]

2,6-Dichloro-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 12. There are two possible procedures to obtain this compound. Procedure *2)* is the preferred one:



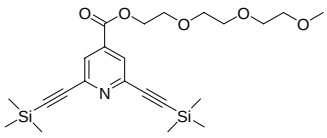
1) In a two necked flask equipped with a condenser 20.07 g **11** (104.55 mmol, 1 equiv.) were suspended in 364 mL of thionyl chloride (ρ = 1.64 g/mL, 5018 mmol, 48 equiv.) and refluxed for 2 h. Excess thionyl chloride was removed in vacuum and the remaining residue was dried in vacuum over night (oil pump) to afford the crude acid chloride as a brown solid. After dissolving it in dry CH_2Cl_2 it was transferred to a stirring mixture of 3,6,9-trioxadecyl-1-ol (36 mL, 230 mmol, ρ = 1.026 g/mL, 2.2 equiv.), triethylamine (65 mL, 460.02 mmol, ρ = 0.72 g/mL, 4.4 equiv.) and 4-dimethylaminopyridine (1.022 g, 8.36 mmol, 0.08 equiv.) in 100 mL of CH_2Cl_2 at 0°C. The mixture was then allowed to warm up to room temperature and stirred for 30 h. The CH_2Cl_2 phase was washed with sat NaHCO3 (3 x), with brine (1 x) and afterwards dried over $MgSO_4$. Purification by column chromatography (Hex/EA 6/4) gave 12.13 g (34%) of a yellow oil that crystallizes in the fridge.

2) 10.08 g **11** (52.5 mmol, 1 equiv.), 16.8 mL of 3,6,9-trioxadecyl-1-ol (105.0 mmol, ρ = 1.026 g/mL, 2.0 equiv.) and 1.28 g 4-dimethylaminopyridine (10.5 mmol, 0.2 equiv.) were dissolved in 50 mL of THF under heating. After cooling down to 0 °C *N,N′*-Diisopropylcarbodiimide (12.27 mL, 78.75 mmol, ρ = 0.81 g/mL, 1.5 equiv.) was dropped to the mixture. The reaction was stirred for 10 min at 0 °C and then allowed to warm up to rt and stirred over night. After consumption of all starting material indicated by TLC

[2] K. E. Henegar, S. W. Ashford, T. A. Baughman, J. C. Sih, R.-L. Gu, *J. Org. Lett.* **1997**, *62*, 6588-6597.

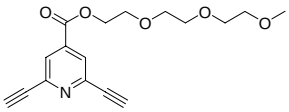
monitoring the solvent was removed *in vacuo* and the residue diluted with toluene and filtered. The filtrate was concentrated and filtered again and after removing the solvent purification by column chromatography (Hex/EA 6/4) gave 16.05 g (90%) of a yellow oil that crystallizes in the fridge.

R_f (Hex 7/3 EA) = 0.3. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.82 (s, 2H, Ar*H*), 4.53 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.83 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.72-3.64 (m, 6H, OC*H*$_2$), 3.54 (m, 2H, OC*H*$_2$), 3.37 (s, 3H, OC*H*$_3$). **^{13}C-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 162.92 (*C*O_2), 151.62 (Cl*C*$_{Ar}$), 142.62 (CO_2*C*$_{Ar}$), 122.87 (H*C*$_{Ar}$), 72.07 (O*C*H$_2$), 70.84 (O*C*H$_2$), 70.78 (O*C*H$_2$), 70.6 (O*C*H$_2$), 68.89 (O*C*H$_2$), 65.65 (O*C*H$_2$), 59.21 (O*C*H$_3$). **MS** (EI, T = 65 °C): m/z = 337 ([M]$^+$), 302 ([M]$^+$ - Cl), 218 ([M]$^+$ - $C_5H_{10}O_3$), 192 ($C_8H_{16}O_5^+$), 174, 146 ($C_5H_2Cl_2N^+$), 89 ($C_4H_9O_2^+$), 59 ($C_3H_7O^+$, 100%), 45 ($C_2H_5O^+$). **HRMS (**ESI): *m/z* = 360.0373, (calcd 360.0375 for [M] + Na^+).



2,6-Bis([Trimethylsilyl]ethynyl)-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 13. 12 (12.13 g, 35.86 mmol, 1 equiv.), CuI (137 mg, 0.717 mmol, 0.02 equiv.) and PPh_3 (0.941 g, 3.587 mmol, 0.1 equiv.) were suspended in 160 mL of a mixture of dry toluene/TEA (1/1), the solution evacuated at rt and flushed with argon (4 cycles), freeze degassed (1 x) and $Pd(PPh_3)_4$ (83 mg, 0.717 mmol, 0.02 equiv.) added under argon. After freeze degassing (1 x) TMS-acetylene (25.53 mL, ρ = 0.69 g/mL, 179.33 mmol, 5 equiv.) was added via a syringe in the counterflow of argon. The reaction mixture was stirred at 70 °C for 2 d and after consumption of all starting material indicated by TLC monitoring (CH_2Cl_2/acetone 8/2) the mixture was cooled down to rt and the solvent was removed. Purification using column chromatography (EA/Hex 2/8) gave 8.45 g (72%) of a yellow oil. R_f (Hex/EA 1/1)= 0.4. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.91 (s, 2H, Ar*H*), 4.5 (t, ^{3}J = 4.8 Hz, 2H, OC*H*$_2$), 3.83 (t, ^{3}J = 4.8 Hz, 2H, OC*H*$_2$), 3.85 - 3.63 (m, 6H, OC*H*$_2$), 3.54 (m, 2H, OC*H*$_2$), 3.53 (s, 3H, OC*H*$_3$), 0.25 (s, 18H, SiC*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.07 (*C*O_2), 144.24 (C≡C*C*$_{Ar}$), 138.47 (CO_2*C*$_{Ar}$), 126.05 (H*C*$_{Ar}$), 102.85 (C≡*C*), 97.31 (C≡*C*), 77.62 (O*C*H$_2$), 72.33 (O*C*H$_2$), 71.04 (O*C*H$_2$), 69.29 (O*C*H$_2$), 65.46 (O*C*H$_2$), 59.45 (O*C*H$_2$), 53.82 (O-*C*H$_3$), 0.00 (Si*C*H$_3$). **MS (**ESI): *m/z* = 462 ([M] + H^+), 484 ([M] + Na^+). **HRMS (**ESI): *m/z* = 484.1942 (calcd 484.1946 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 2.0 mm i.D., methanol/water 85/15, 0.2 mL/min, 8.2 MPa, 308 K, det. UV 285 nm, ret. time 6.13 min.): 96.1 area %.

2,6-Di(ethynyl)-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 1.



1.787 g **13** (3.87 mmol, 1 equiv.) were dissolved in 500 mL of THF and the solution cooled to 0 °C. To the rapidly stirred reaction mixture was added a solution of TBAF (9.7 mL, 1 M solution in THF, 2.5 equiv.) using a syringe. The mixture immediately turned dark. The reaction was stirred 2 min at 0 °C and then filtered through a silica plug with THF. Removal of the solvent *in vacuo* gave a brown oil. Purification using column chromatography (CH_2Cl_2/acetone 9/1) gave 1.14 g (93%) of a yellow solid. R_f (CH_2Cl_2/acetone 8/2) = 0.6. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.96 (s, 2H, Ar*H*), 4.49 (m, 2H, OCH_2), 3.94 (m, 2H, OCH_2), 3.81 - 3.66 (m, 6H, OCH_2), 3.51 (m, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 3.21 (s, 2H, C≡C*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 163.83 (*C*O_2), 143.76 (CO_2C_{Ar}), 138.58 (C≡CC_{Ar}), 126.50 (HC_{Ar}), 81.68 (C≡*C*), 79.00 (C≡*C*), 72.07 (O*C*H_2), 70.83 (O*C*H_2), 70.76 (O*C*H_2), 68.04 (O*C*H_2), 65.4 (O*C*H_2), 59.22 (O*C*H_3). **MS (**ESI): *m/z* = 318 ([M] + H^+), 340 ([M] + Na^+). **HRMS (**ESI): *m/z* = 340.1151 (calcd 340.1155 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 2.0 mm i.D., methanol/water 40/60, 0.2 mL/min, 9.0 MPa, 308 K, det. UV 254 nm, ret. time 21.81 min.): 97.6 area %.

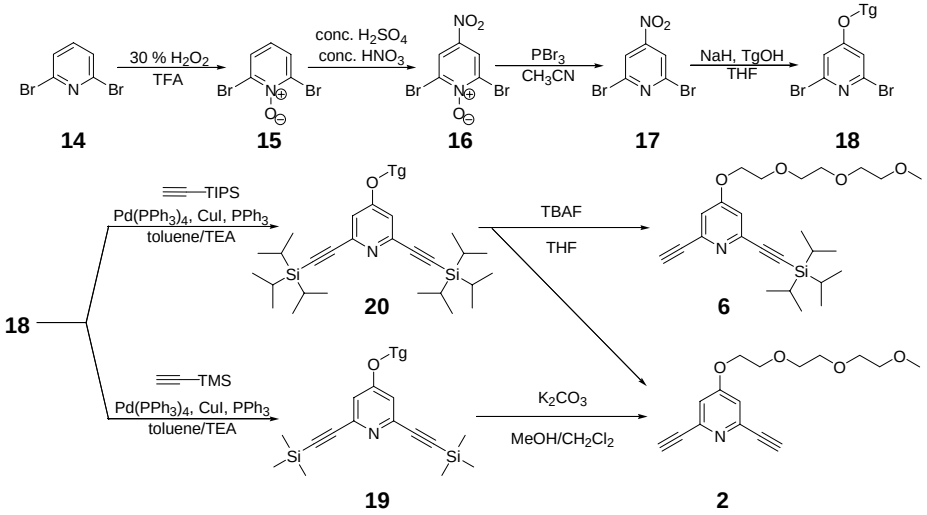


Figure 2. Preparation of the acetylene compounds **2** and **6**.

2,6-Dibromo-4-nitropyridine-1-oxide **16** was prepared as illustrated in **Figure 2** and described by Jenny.[3] Reduction to the 2,6-Dibromo-4-nitropyridine **17** was achieved by treatment with PBr_3 in dry acetonitrile as described by Vögtle.[4]

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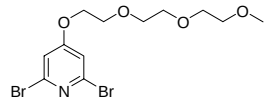
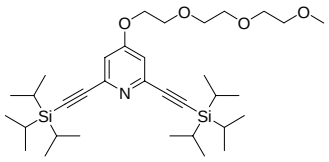
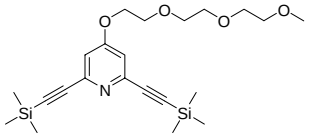
[3] M. Nettekoven, C. Jenny, *Org. Process Res. Dev.* **2003**, *7*, 38-43.
[4] U. Neumann, F. Vögtle, *Chem. Ber.* **1989**, *122*, 589-591.

2,6-Dibromo-4-(3,6,9-trioxadec-1-yloxy)pyridine 18.  In a dry two necked flask NaH (0.953 g, 39.7 mmol, 1.07 equiv.) was suspended in 400 mL of dry THF. After cooling the mixture down to 0 °C dry triethylenglycol mono methyl ether (5.82 mL, ρ = 1.026 g/mL, 36.36 mmol, 0.98 equiv.) was added slowly using a syringe and the reaction mixture was allowed to warm up to rt. The solution was stirred for 1.5 h and then **17** (10.46 g, 37.1 mmol, 1 equiv.) was added under stirring in one portion at 0 °C. The reaction mixture was allowed to warm up to rt and stirred for 3 h. After consumption of all starting material indicated by TLC monitoring (Hex/EA 6/4) the reaction mixture was poured onto ice water and the product extracted with CH_2Cl_2 (3 x). The combined CH_2Cl_2 phases were washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo* purification by column chromatography (Hex/EA 6/4) gave 13.0 g of a colorless oil (89%). R_f (EA) = 0.46. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.97 (s, 2H, Ar*H*), 4.13 (t, ^{3}J = 5.9 Hz, 2H, OCH_2), 3.80 (m, 2H, OCH_2), 3.65-3.53 (m, 6H, OCH_2), 3.48 (m, 2H, OCH_2), 3.33 (s, 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 165.95 (OC_{Ar}), 140.02 (BrC_{Ar}), 112.97 (HC_{Ar}), 70.91 (OCH$_2$), 69.97 (OCH$_2$), 69.64 (OCH$_2$), 69.61 (OCH$_2$), 68.09 (OCH$_2$), 67.52 (OCH$_2$), 58.06 (OCH$_3$). **MS (**EI, T = 90 °C): m/z = 352 ([M]$^+$ - $C_2H_5O^+$), 318 ([M]$^+$ - Br), 280, 254, 200, 156, 89 ($C_4H_9O_2^+$), 76 ($C_3H_8O_2^+$), 59 ($C_3H_7O^+$, 100%), 45 ($C_2H_5O^+$). **HRMS (**ESI): m/z = 419.9414, (calcd 419.9416 for [M] + Na$^+$). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 50/50, 0.8 mL/min, 9.4 MPa, 308 K, det. UV 220 nm, ret. time 11.9 min.): 99.8 area %.

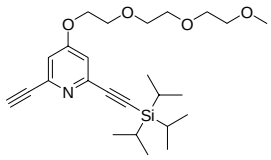
2,6-Bis-[(triisopropylsilanyl)-ethynyl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 20.  In a dry three necked flask equipped with a condenser 1.14 g of **18** (2.856 mmol, 1 equiv.), copper iodide (11 mg, 0.057 mmol, 0.02 equiv.) and triphenylphosphine (37 mg, 0.14 mmol, 0.05 equiv.) were suspended in 80 mL of a mixture of dry toluene/TEA (3/1). The solution was evacuated at rt and flushed with argon (4 cycles), freeze degassed (1 x) and tetrakistriphenylphosphine palladium (66 mg, 0.057 mmol, 0.02 equiv.) added under argon. After freeze degassing (1 x) TIPS-acetylene (1.92 mL, ρ = 0.813 g/mL, 8.56 mmol, 3 equiv.) was added in the counterflow of argon using a syringe. The reaction mixture was stirred at 70 °C for 28 h. After consumption of starting material **18** indicated by TLC monitoring (Hex/EA 8/2) the solvent was removed *in vacuo*. Purification by column chromatography (Hex/EA 8/2) gave 1.71 g of a yellow oil (quant. yield). R_f (Hex/EA 8/2) = 0.56. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.94 (s, 2H, Ar*H*), 4.18 (t, ^{3}J = 4.5 Hz, 2H,

OCH_2), 3.84 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.70-3.62 (m, 6H, OCH_2), 3.51 (m, 2H, OCH_2), 3.36 (s, 3H, OCH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.79 (OC_{Ar}), 144.74 (C≡CC_{Ar}), 114.34 (HC_{Ar}), 105.53, (*C*≡C), 92.00 (*C*≡C), 72.04 (O*C*H$_2$), 71.05 (O*C*H$_2$), 70.78 (O*C*H$_2$), 70.73 (O*C*H$_2$), 69.33 (O*C*H$_2$), 67.71 (O*C*H$_2$), 59.16 (O*C*H$_3$), 18.77 (SiCH*C*H$_3$), 11.37 (Si*C*H). **MS (**EI, T = 155 °C): *m/z*= 601 ([M]$^+$), 558 ([M]$^+$ - C_3H_7, 100%), 516, 444, 412, 145, 115, 59 ($C_3H_7O^+$). **HRMS (**ESI): *m/z*= 624.3871, (calcd 624.3874 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 9/1, 0.8 mL/min, 5.5 MPa, 308 K, det. UV 220 nm, ret. time 31.5 min.): 99.5 area %.

2,6-Bis[(trimethylsilyl)ethynyl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 19. 

In a dry three necked flask equipped with a condenser 8.982 g **18** (22.50 mmol, 1 equiv.), copper iodide (86 mg, 0.45 mmol, 0.02 equiv.) and triphenylphosphine (0.295 g, 1.12 mmol, 0.05 equiv.) were suspended in 80 mL of a mixture of dry toluene/TEA (8/2). The solution was degassed at rt by evacuating and flushing with argon (4 cycles), freeze degassed (1 x) and tetrakistriphenylphosphine palladium (520 mg, 0.45 mmol, 0.02 equiv.) added under argon. After freeze degassing (1 x) TMS-acetylene (16.02 mL, ρ = 0.69 g/mL, 112.54 mmol, 5 equiv.) was added in the counterflow of argon using a syringe. The reaction mixture was stirred at 65 °C for 3 d. After consumption of starting material **18** indicated by TLC monitoring (Hex/EA 1/1) the solvent was removed *in vacuo*. Purification by column chromatography (Hex/EA 6/4) gave 9.51 g of a yellow oil (70%). R_f (Hex/EA 6/4) = 0.4. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.90 (s, 2H, Ar*H*), 4.12 (t, ^{3}J = 4.8 Hz, 2H, OCH_2), 3.80 (t, ^{3}J = 4.8 Hz, 2H, OCH_2), 3.68- 3.58 (m, 6H, OCH_2), 3.51-3.48 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 0.19 (s, 18H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.94 (OC_{Ar}), 144.37 (C≡CC_{Ar}), 113.72 (HC_{Ar}), 103.22 (C≡*C*), 94.80 (C≡*C*), 71.95 (O*C*H$_2$), 71.0 (O*C*H$_2$), 70.68 (O*C*H$_2$), 70.63 (O*C*H$_2$), 69.21 (O*C*H$_2$), 67.78 (O*C*H$_2$), 59.05 (O*C*H$_3$), -0.30 (Si*C*H$_3$). **MS** (EI, T = 130 °C): *m/z* = 433 ([M]$^+$), 403, 360, 345, 330, 287 (100%), 272, 259, 97, 83, 73, 59 ($C_3H_7O^+$), 45 ($C_2H_5O^+$). **HRMS** (ESI): *m/z*= 434.2178, (calcd 434.2177 for [M] + H^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 75/25, 0.8 mL/min, 9.9 MPa, 308 K, det. UV 220 nm, ret. time 13.83 min.): 98.4 area %.

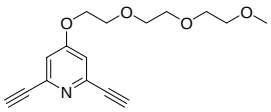
6-Ethynyl-2-[(triisopropylsilanyl)ethynyl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 6. 1.339 g of **20** (2.24 mmol, 1 equiv.) were dissolved in 500 mL of THF, 0.1 mL of acetic acid (1.89 mmol, 0.85 equiv.) were added and the mixture was cooled down to 0 °C.



To the rapidly stirred reaction mixture was added a solution of TBAF (1.89 mL, 1 M solution in THF, 0.85 equiv.) via a syringe dropwise and while stirring for 10 min the mixture was allowed to reach rt. The mixture was filtered through a short silica plug and the solvent was removed *in vacuo.* Purification by column chromatography gave 0.338 mg of colorless oil (34%). Starting material **20** could be recovered and **2** isolated. R_f (Hex/EA 1/1) = 0.3. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.95 (dd, ^{3}J = 2.5 Hz, 2H, Ar*H*), 4.14 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.82 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.70-3.59 (m, 6H, OCH_2), 3.51-3.48 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 3.08 (s, 1H, C≡C*H*), 1.09 (d, ^{3}J = 2.2 Hz, 21H, SiCHCH_3, SiC*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.89 (OC_{Ar}), 144.74 (C≡CC_{Ar}), 143.53 (C≡CC_{Ar}), 114.63 (HC_{Ar}), 113.61 (HC_{Ar}), 105.21 (C≡*C*), 91.9 (C≡*C*), 82.39 (C≡*C*), 77.2 (C≡*C*), 71.91 (O*C*H$_2$), 70.93 (O*C*H$_2$), 70.63 (O*C*H$_2$), 70.59 (O*C*H$_2$), 69.18 (O*C*H$_2$), 67.74 (O*C*H$_2$), 69.18 (O*C*H$_3$), 18.63 (SiCH*C*H$_3$), 11.22 (SiC*H*). **MS (**EI, T = 130 °C): *m/z* = 445([M]$^+$), 558 ([M]$^+$ - C_3H_7, 100%), 288 ([M]$^+$ - $C_9H_{21}Si$), 145, 117, 89 ([$C_4H_9O_2$]$^+$), 75 ([$C_3H_7O_2$]$^+$), 59 ([C_3H_7O]$^+$), 45 ([C_2H_5O]$^+$). **HRMS (**ESI): *m/z* = 446.2723, (calcd 446.2721 [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 8/2, 0.8 mL/min, 9.1 MPa, 308 K, det. UV 220 nm, ret. time 11.67 min.): 100 area %.

2,6-Di(ethynyl)-4-(3,6,9-trioxadec-1-yloxy)pyridine 2.

1) The reaction to afford **6** gave **2** as side product.



2) Using the reaction conditions to afford **6** but with 2.5 equiv. TBAF instead of 0.85 equiv. gave compound **2** in yields ranging from 80- 90%.

3) A one necked flask was charged with **19 (**0.841 g, 1.94 mmol, 1 equiv.), 100 mL of a mixture of CH_2Cl_2/MeOH 9/1 and 0.839 mg K_2CO_3 (6.07 mmol, 3.1 equiv.). The suspension was stirred for 10 h at rt and after consumption of starting material **19** indicated by TLC monitoring the mixture was filtered and transferred into a separation funnel. CH_2Cl_2 was added and the organic phase was washed with sat. NH_4Cl (3 x) and brine (1 x). After drying over $MgSO_4$ the solvent was evaporated to give a brown oil. Purification by column chromatography gave 0.54 g of a pale yellow oil (96%). R_f (Hex/EA 4/6) = 0.3. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.96 (s, 2H, Ar*H*), 4.13 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.81 (t, ^{3}J =

4.5 Hz, 2H, OCH_2), 3.68-3.62 (m, 6H, OCH_2), 3.57-3.50 (m, 2H, OCH_2), 3.32 (s, 3H, OCH_3), 3.09 (s, 2H, C≡C*H*). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.06 (OC_{Ar}), 143.62 (CC_{Ar}), 114.13 (HC_{Ar}), 82.12 (C≡*C*), 77.31 (C≡*C*H), 71.86 (O*C*H$_2$), 70.89 (O*C*H$_2$), 70.59 (O*C*H$_2$), 70.54 (O*C*H$_2$), 69.13 (O*C*H$_2$), 67.84 (O*C*H$_2$), 58.97 (O*C*H$_3$). **MS** (ESI): *m/z*= 290 ([M] + H^+), 312 ([M] + Na^+), 328 ([M] + K^+). **HRMS** (ESI): *m/z*= 312.1210, (calcd 312.1206 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 50/50, 0.8 mL/min, 11.5 MPa, 308 K, det. UV 220 nm, ret. time 5.23 min.): 100 area %.

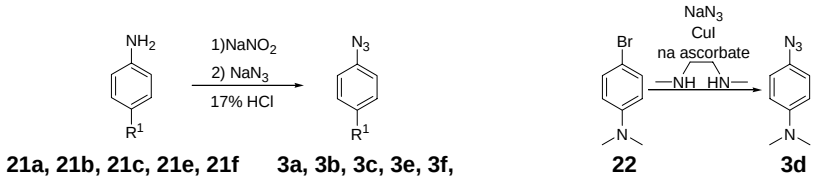


Figure 3. Preparation routes used for generation of aryl azides.

Aryl azides depicted in the table were prepared by the diazotation reaction of the corresponding amine as described for the preparation of 4-Azido-benzoic acid ethyl ester. (4-Azido-phenyl)-dimethyl-amine was prepared using the cross coupling reactions conditions with CuI described by Liang.[5]

CAUTION: As organic azides are potentially explosive, all aryl azides have been stored in the freezer in the dark!

Table 1. Yield, color, and aggregation state of the used aromatic azides.

compound	R^1	Yield [%]	color /aggregate state
3a	Me [b]	37	Brown oil
3b	I [b]	96	Yellow solid
3c	NO_2 [b]	98	Orange solid
3d	NMe_2 [a, b]	99	Yellow solid
3e	CO_2Et [d]	Quantitative	Yellow oil
3f	OMe [c]	88	Red-brown oil

[5] J. Andersen, U. Madsen, F. Bjorkling, X. Liang, *Synlett* **2005**, 2209-2213.

[a] Synthesis proceeded as described by Liang.[5] [b] Characterization see literature.[6] [c] Characterization see literature.[7] [d] Characterization see experimental part.

[6] N. Faucher, Y. Ambroise, J.-C. Cintrat, E. Doris, F. Pillon, B. Rousseau, *J. Org. Chem.* **2002**, *67*, 932-934.
[7] Q. Liu, Y. Tor, *Org. Lett.* **2003**, *5*, 2571-2572.

4-Azido-benzoic acid ethyl ester 3e. 4.29 g (26.0 mmol, 1 equiv.) 4-Amino-benzoic acid ethyl ester were suspended in 170 mL of 17% HCl at rt and under gentle warming ethanol was added until a clear solution was obtained. The mixture was cooled to 0°C, $NaNO_2$ (2.87 g, 41.6 mmol, 1.6 equiv.) added in small portions (Attention! release of toxic gas!) and the reaction mixture was stirred for 15 min at 0°C. Then NaN_3 (2.7 g, 41.6 mmol, 1.6 equiv.) was added in small portions and the mixture stirred for 20 min at 0°C. The solution was transferred into a separation funnel, water added and the aqueous phase was extracted with 150 mL of diethyl ether (4 x). The combined organic phases were washed with sat. aqueous $NaHCO_3$ solution (3 x) and brine. After drying over $MgSO_4$ and filtration removal of the solvent gave 4.95 g of a yellow solid (quant. yield). **TLC** (Hex/EE 8/2) R_f = 0.7. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.05 (d, ^3J = 8.7 Hz, 2H, Ar*H*), 7.08 (d, ^3J = 8.7 Hz, 2H, Ar*H*), 4.38 (q, ^3J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.39 (t, ^3J = 7.1 Hz, 3H, $CO_2CH_2CH_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.96 ($CO_2CH_2CH_3$), 144.75 (N_3C_{Ar}), 131.5 (HC_{Ar}), 127.19 ($C_{Ar}CO_2CH_2CH_3$), 118.92 (HC_{Ar}), 61.19 ($CO_2CH_2CH_3$), 14.47 ($CO_2CH_2CH_3$). **MS** (EI, T = 10 °C): m/z = 191 ($[M]^+$), 163 ($[M]^+$ - N_2, 100%), 146 ($[M]^+$ - C_2H_4O), 135 ($[M]^+$ - N_2 - C_2H_4), 117, 107, 90 ($C_6H_4N^+$), 79, 63, 39, 29 ($C_2H_5^+$). **MS** (High-resolution EI-MS, T = 10 °C): *m/z* = 191.0696, (calcd 191.0694 for $[M]^+$). **GC** (achiral, device: split injector 220 °C, FID, gas carrier: 0.8 bar H_2, column: 30 m DB-1, start-T: 80°C, up to 350 °C with 8 °C per minute): 98.5 area %.

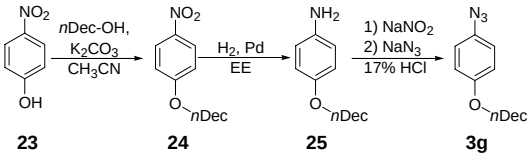


Figure 4. Preparation of 1-azido-4-decyloxy-benzene **3g** via diazotation reaction.

1-Decyloxy-4-nitro-benzene 24. In a two necked flask equipped with a condenser 1.11 g (8 mmol, 1 equiv.) 4-nitrophenol were dissolved in 50 mL of acetonitrile, 1.93 g 1-iododecane (7.2 mmol, 0.9 equiv.), 0.1 g 18-crown-6 (0.4 mmol, 0.05 equiv.) and 2.21 g (16 mmol, 2 equiv.) K_2CO_3 were added and the mixture was degassed at rt by evacuating under stirring and flushing with argon (4 cycles). The suspension was stirred at 50 °C over night and after consumption of 4-nitrophenol indicated by TLC monitoring the yellow solution was transferred into a separation funnel and diluted with EA. The organic phase was washed with sat. aq. $NaHCO_3$ solution (3 x), water (3 x) and brine. After drying over $MgSO_4$ and filtration the solvent was removed *in vacuo*. Purification by

column chromatography (Hex → Hex/EA 1/1) gave 0.753 g of a yellow solid (37%). R_f (Hex/EE 8/2) = 0.7. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.13 (d, ^{3}J = 9.3 Hz, 2H, Ar*H*), 6.88 (d, ^{3}J = 9.3 Hz, 2H, Ar*H*), 3.99 (t, ^{3}J = 6.5 Hz, 2H, OCH_2), 1.78 (tt, ^{3}J = 6.6 Hz, ^{3}J = 6.5 Hz, 2H, OCH_2CH_2), 1.43-1.36 (m, 2H, CH_2), 1.21 (m, 12H, CH_2), 0.83 (t, ^{3}J = 6.7 Hz, 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.34 (OC_{Ar}), 141.37 (NO_2-C_{Ar}), 125.95 (HC_{Ar}), 114.46 (HC_{Ar}), 68.98 (OCH_2), 31.96 (CH_2), 29.60 (CH_2), 29.38 (CH_2), 29.04 (CH_2), 25.98 (CH_2), 22.74 (CH_2), 14.17 (CH_3). **MS** (EI, T = 75 °C): m/z = 279 ($[M]^+$), 140 ($[C_{10}H_{20}]^+$), 123, 111, 97, 85 ($[C_6H_{13}]^+$), 71 ($[C_5H_{11}]^+$), 57 $[C_4H_9]^+$), 43 ($[C_3H_7]^+$, 100%). **HRMS** (ESI): *m/z*= 302.1728, (calcd 302.1726 for [M] + Na^+).

4-Decyloxyaniline 25. In a one necked flask 0.754 mg **24** (2.7 mmol, 1 equiv.) were dissolved in 50 mL of ethyl acetate, 75 mg Pd on charcoal (10% wt) were added, the stirred mixture was degassed at rt *in vacuo* and flushed with H_2 (3 cycles). After stirring for 24 h at rt in H_2 atmosphere (ca. 2 bar) the mixture was filtered through a celite pad and the solvent removed *in vacuo*. Purification by column chromatography (Hex/EE 8/2) gave 0.67 g of a red solid (quant. yield). R_f (Hex/EE 8/2) = 0.2. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.76 (d, ^{3}J = 8.8 Hz, 2H, Ar*H*), 6.65 (d, ^{3}J = 8.9 Hz, 2H, Ar*H*), 3.88 (t, ^{3}J = 6.7 Hz, 2H, OCH_2), 3.29 (br s, 2H, NH_2), 1.74 (tt, ^{3}J = 6.6 Hz,^{3}J = 6.8 Hz, 2H, OCH_2CH_2), 1.44 (tt, ^{3}J = 7.0 Hz, ^{3}J = 6.7 Hz, 2H, OCH_2CH_2 CH_2), 1.32-1.28 (m, 12H, CH_2), 0.89 (t, ^{3}J = 6.7 Hz, 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.45 (OC_{Ar}), 139.80 (NC_{Ar}), 116.52 (HC_{Ar}), 115.74 (HC_{Ar}), 68.79 (OCH_2), 31.97 (CH_2), 29.67 (CH_2), 29.64 (CH_2), 29.51 (CH_2), 29.40 (CH_2), 26.14 (CH_2), 22.75 (CH_2), 14.18 (CH_3). **MS** (EI, T = 75 °C): m/z = 249 ($[M]^+$), 109 ($[C_6H_7NO]^+$, 100%), 92 ($[C_6H_6N]^+$), 80, 55, 41, 29 ($[C_2H_5]^+$).

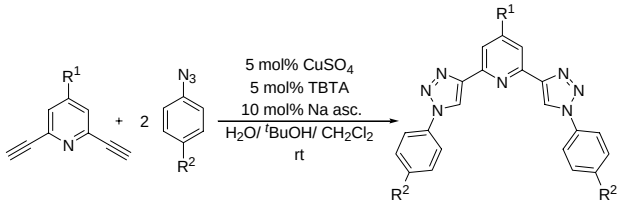
1-Azido-4-decyloxy-benzene 3g. 671 mg **25** (2.69 mmol, 1 equiv.) were dissolved in 40 mL of 17% HCl under help of addition of EtOH and gentle warming. The mixture was cooled down to 0 °C, $NaNO_2$ (0.353 g, 5.11 mmol, 1.9 equiv.) was added in small portions (ATTENTION: Release of toxic gas!). After the mixture was stirred for 15 min at 0 °C 50 mg NaN_3 (5.38 mmol, 2 equiv.) were added in small portions and the stirring was continued for 15 min at 0 °C. The solution was transferred into a separation funnel, water added and the aqueous phase was extracted with EA (4 x). The combined organic phases were washed with sat. aqueous $NaHCO_3$ solution (3 x) and brine. After drying over $MgSO_4$ and filtration, removal of the solvent gave 596 mg of a yellow oil

(80%). R_f (Hex/EE 8/2) = 0.4. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.92 (dd, ^{3}J = 2.9 Hz, ^{3}J = 2.1 Hz, 4H, Ar*H*), 3.94 (t, ^{3}J = 6.6 Hz, 2H, OCH_2), 1.80 (tt, ^{3}J = 6.6 Hz,^{3}J = 7.0 Hz, 2H, OCH_2CH_2), 1.44 (tt, ^{3}J = 7.0 Hz, ^{3}J = 8.1 Hz, 2H, $OCH_2CH_2CH_2$), 1.38-1.27 (m, 12H, CH_2), 0.88 (t, ^{3}J = 7.8 Hz, 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 156.61 (OC_{Ar}), 132.09 (N_3C_{Ar}), 119.87 (HC_{Ar}), 115.68 (HC_{Ar}), 68.33 (OCH_2), 31.96 (CH_2), 29.64 (CH_2), 29.61 (CH_2), 29.45 (CH_2), 29.38 (CH_2), 29.30, 26.07 (CH_2), 22.72 (CH_2), 14.09 (CH_3). **MS** (EI, T = 75 °C): m/z = 275 ($[M]^+$), 247 ($[M]^+ - N_2$), 107 ($[C_6H_4NOH]^+$, 100%), 99 ($[C_7H_{15}]^+$), 90 ($[C_6H_4N]^+$), 85 ($[C_6H_{13}]^+$), 71 ($[C_5H_{11}]^+$), 57 ($[C_4H_9]^+$]), 43 ($[C_3H_7]^+$]). **HRMS** (EI): *m/z*= 275.1998, (calcd 275.1997 for $[M]^+$).

General procedure of the copper catalyzed 1,3-dipolar cycloaddition

A three necked flask was charged with bisacetylenes **1** and **2**, respectively, (1 equiv.), the aryl azides **3** (1.0- 1.5 equiv. per acetylene functionality), sodium ascorbate (0.1-0.2 equiv.), TBTA (0.05 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 1/2/1. The flask was evacuated and flushed with argon repeatedly (3 cycles). $CuSO_4$ was added (stock solution, 10 mg $CuSO_4$ per 0.3 mL of water) and the mixture was stirred for 3 d at r.t. in the dark. In case of an appearing precipitate additional CH_2Cl_2 was added. After the acetylene starting material was consumed indicated by TLC monitoring the mixture was transferred into a separation funnel and CH_2Cl_2 was added. The aqueous phase was extracted with CH_2Cl_2 (3x), the organic phases were combined and washed once with brine. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* a colored solid was obtained that was purified by column chromatography (CH_2Cl_2/acetone) to yield the respective products in high analytical purities.

Table 2. Synthesis of 2,6-bis(1,2,3-triazol-4-yl)pyridines.

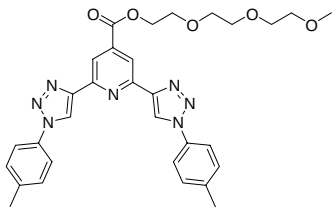


1 $R^1 = CO_2Tg$ **3a-g** **4a-g**

2 $R^1 = OTg$ **5a-d, 9**

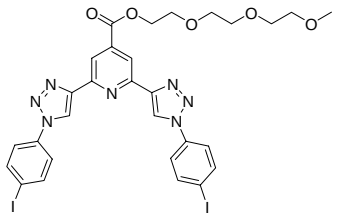
Compound	R^1	R^2	Yield [%][a]	Equiv. Na asc	Equiv. azide
4a	CO_2Tg[b]	CH_3	quant.	0.2 [c]	2.3[d]
4b	CO_2 Tg	I	98	0.1	2.0
4c	CO_2 Tg	NO_2	95	0.1	2.0
4d	CO_2 Tg	$N(CH_3)_2$	95	0.1	2.0
4e	CO_2 Tg	CO_2Et	quant.	0.1	2.0
4f	CO_2 Tg	OCH_3	88	0.2[c]	3.0
4g	CO_2 Tg	$(CH_2)_9CH_3$	96	0.1	2.2
5a	O Tg[b]	CH_3	quant.	0.2[c]	2.5
5b	O Tg	I	85	0.1	2.1
5c	O Tg	NO_2	86	0.1	2.3
5d	O Tg	$N(CH_3)_2$	94	0.1	2.1
9	OTg	$N(CH_3)_2/NO_2$ [e]	98 (overall)	0.1 (each)	1.3 (each)

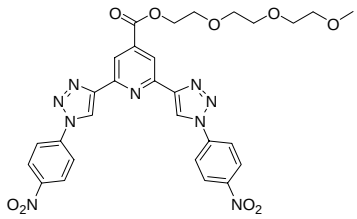
[a] Isolated yield. [b] Tg = $-(CH_2CH_2O)_3CH_3$. [c] Due to the low boiling point of the aryl azide 3a thoroughly degassing procedure wasn't performed and therefore the double amount of Na ascorbate was used as reducing agent. [d] Due to the degassing procedure and the low boiling point of the aryl azide an increased amount of azide was used. [e] Reaction sequence: cycloaddition with (4-Azido-phenyl)-dimethyl-amine, cleavage of the TIPS protecting group and cycloaddition with 1-Azido-4-nitro-benzene with an overall yield of 98%. Both cycloaddition reactions have been run with 1.3 equiv. aryl azide and 0.1 equiv. Na ascorbate.

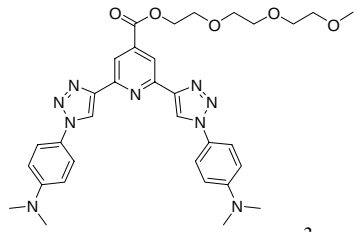


2,6-Bis[1-(4-methylphenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4a. R_f (CH_2Cl_2/acetone 9/1) = 0.32. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.47 (s, 2H, Ar*H*), 8.45 (s, 2H, Ar*H*), 7.54 (d, ^{3}J = 8.2 Hz, 4H, Ar*H*), 7.16 (d, ^{3}J = 8.1 Hz, 4H, Ar*H*), 4.42 (t, ^{3}J = 4.7 Hz, 2H, OCH_2), 3.77 (t, ^{3}J = 3.8 Hz, 2H, OCH_2), 3.71-3.69 (m, 4H, OCH_2), 3.67 (m, 2H, OCH_2), 3.46 (m, 2H, OCH_2), 3.25 (s, 3H, OCH_3), 2.28 (s, 6H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.52 (CO_2), 150.55 (C_{Ar}), 147.77 (C_{Ar}), 138.93 (C_{Ar}), 138.81 (C_{Ar}), 134.24 (C_{Ar}), 130.02 (HC_{Ar}), 120.21 (C_{Ar}), 119.91 (HC_{Ar}), 118.42 (C_{Ar}), 71.14 (OCH_2), 70.55 (OCH_2), 70.44 (OCH_2), 70.41 (OCH_2), 68.69 (OCH_2), 64.74 (OCH_2), 58.79 (OCH_3), 20.91 (CH_3). **HRMS (**ESI): *m/z* = 584.2612, (calcd 584.2615 for [M]

+ H^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 8/2, 0.8 mL/min, 7.1 MPa, 308 K, det. UV 240 nm, ret. time 15.78 min.): 99.9 area %.

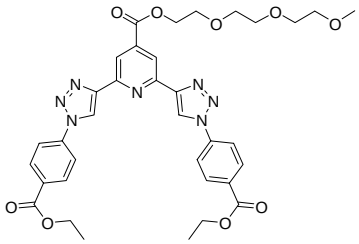
2,6-Bis[1-(4-iodophenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4b.  R_f (CH_2Cl_2/acetone 9/1) = 0.46. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.72 (s, 2H, triazol*H*), 8.66 (s, 2H, Ar*H*), 7.94 (d, ^{3}J = 8.7 Hz, 4H, Ar*H*), 7.65 (d, ^{3}J = 8.7 Hz, 4H, Ar*H*), 4.58 (t, ^{3}J = 4.8 Hz, 2H, OCH_2), 3.90 (t, ^{3}J = 4.8 Hz, 2H, OCH_2), 3.71-3.65 (m, 4H, OCH_2), 3.60 (m, 2H, OCH_2), 3.49 (m, 2H, OCH_2), 3.30 (s, 3H, OCH_3). **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ (ppm) = 165.15 (*C*O_2), 151.27 (C_{Ar}), 148.81 (C_{Ar}), 140.17 (C_{Ar}), 139.40 (HC_{Ar}), 137.06 (C_{Ar}), 122.39 (C_{Ar}), 120.76 ($C_{triazol}$), 119.19 (HC_{Ar}), 94.14 (C_{Ar}), 72.29 (O*C*H_2), 71.14 (O*C*H_2), 70.90 (O*C*H_2), 70.86 (O*C*H_2), 69.26 (O*C*H_2), 65.53 (O*C*H_2), 58.96 (O*C*H_3). **HRMS (**ESI): *m/z* = 808.0231, (calcd 808.0235 for [M] + H^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 2.0 mm i.D., methanol/water 85/15, 0.2 mL/min, 5.8 MPa, 308 K, det. UV 254 nm, ret. time 7.71 min.): 98.9 area %.

2,6-Bis[1-(4-nitrophenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4c.  R_f (CH_2Cl_2/acetone 9/1) = 0.32. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.8 (s, 2H, Ar*H*), 8.75 (s, 2H, Ar*H*), 8.49 (d, ^{3}J = 8.9 Hz, 4H, Ar*H*), 8.12 (d, ^{3}J = 9.0 Hz, 4H, Ar*H*), 4.6 (t, ^{3}J = 4.9 Hz, 2H, OCH_2), 3.91 (m, 2H, OCH_2), 3.75-3.65 (m, 6H, OCH_2), 3.55 (m, 2H, OCH_2), 3.35 (s, 3H, OCH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$ + CD_3OD): δ (ppm) = 164.61 (*C*O_2-), 150.2 (C_{Ar}), 148.50 (C_{Ar}), 147.32 (C_{Ar}), 140.91 (C_{Ar}), 139.71 (C_{Ar}), 125.53 (C_{Ar}), 121.17 (C_{Ar}), 120.48 (C_{Ar}), 119.27 (C_{Ar}), 71.71 (O*C*H_2), 70.52 (O*C*H_2), 70.43 (O*C*H_2), 70.34 (O*C*H_2), 68.79 (O*C*H_2), 65.08 (O*C*H_2), 58.73 (O*C*H_3). **MS** (ESI): *m/z*= 646 ([M] + H^+), 668 ([M] + Na^+). **HRMS (**ESI): *m/z* = 668.1825, (calcd 668.1823 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 75/25, 0.8 mL/min, 7.2 MPa, 308 K, det. UV 254 nm, ret. time 8.74 min.): 97.6 area %.

2,6-Bis[1-(4-{dimethylamino}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4d.  R_f (CH_2Cl_2/acetone 85/15) = 0.34. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.68 (s, 2H, Ar*H*), 8.52 (s, 2H, Ar*H*), 7.64 (d, ^{3}J = 9.1 Hz, 4H, Ar*H*), 6.79 (d, ^{3}J = 9.6 Hz, 4H, Ar*H*), 4.57 (t, ^{3}J = 4.9 Hz, 2H, OCH_2), 3.89 (t, ^{3}J = 4.4 Hz, 2H, OCH_2), 3.73-3.66 (m, 6H, OCH_2), 3.56 (m, 2H, OCH_2), 3.35 (s, 3H, OCH_3), 3.02

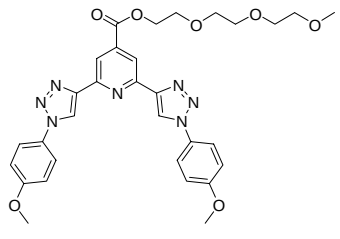
(s, 12H, NC*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.13 (*C*O$_2$-), 150.25 (*C*$_{Ar}$), 149.78 (*C*$_{Ar}$), 146.97 (*C*$_{Ar}$), 138.47 (*C*$_{Ar}$), 125.64 (*C*$_{Ar}$), 121.0 (H*C*$_{Ar}$), 119.57 (H*C*$_{Ar}$), 117.85 (H*C*$_{Ar}$), 111.37 (H*C*$_{Ar}$), 71.04 (O*C*H$_2$), 69.89 (O*C*H$_2$), 69.76 (O*C*H$_2$), 69.73 (O*C*H$_2$), 68.06 (O*C*H$_2$), 64.06 (O*C*H$_2$), 58.13 (O*C*H$_3$), 39.56 (N*C*H$_3$). **MS (**EI, T = 310 °C): *m/z* = 641 ([M]$^+$), 613 ([M]$^+$-N$_2$), 585 ([M]$^+$ - 2 N$_2$), 570 ([M]$^+$ - 2 N$_2$ - CH$_3$, 100%), 478 ([M]$^+$ - C$_7$H$_{15}$O$_4$), 424, 395, 209, 159, 119 ([C$_5$H$_{11}$O$_3$]$^+$), 59 ([C$_3$H$_7$O]$^+$). **HRMS (**ESI): *m/z* = 642.3143, (calcd 642.3146 for [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C$_{18}$, 4.0 mm i.D., methanol/water 75/25, 0.8 mL/min, 4.2 MPa, 308 K, det. UV 220 nm, ret. time 17.19 min.): 92 area %.

2,6-Bis[1-(4-{ethoxycarbonyl}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4e.



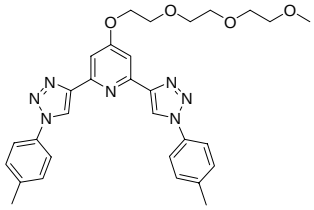
R$_f$ (CH_2Cl_2/acetone 95/5) = 0.3. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.72 (s, 2H, Ar*H*), 8.66 (s, 2H, Ar*H*), 8.23 (d, ^{3}J = 8.7 Hz, 4H, Ar*H*), 7.94 (d, ^{3}J = 8.7 Hz, 4H, Ar*H*), 4.54 (t, ^{3}J = 4.8 Hz, 2H, OC*H*$_2$), 4.43 (q, ^{3}J = 7.1 Hz, 4H, C*H*$_2$CH$_3$), 3.88 (t, ^{3}J = 4.8 Hz, 2H, O*C*H$_2$), 3.75 - 3.65 (m, 6H, O*C*H$_2$), 3.54 (m, 2H, O*C*H$_2$), 3.33 (s, 3H, O*C*H$_3$), 1.43 (t, ^{3}J = 7.1 Hz, 6H, CH$_2$*C*H$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 165.39 (*C*O$_2$-), 164.69 (*C*O$_2$-), 150.6 (*C*$_{Ar}$), 148.49 (*C*$_{Ar}$), 139.83 (*C*$_{Ar}$), 139.67 (*C*$_{Ar}$), 131.4 (*C*$_{Ar}$), 130.91 (*C*$_{Ar}$), 120.41 (*C*$_{Ar}$), 119.93 (*C*$_{Ar}$), 119.36 (*C*$_{Ar}$), 71.98 (O*C*H$_2$), 70.80 (O*C*H$_2$), 70.70 (O*C*H$_2$), 70.66 (O*C*H$_2$), 68.97 (O*C*H$_2$), 65.12 (O*C*H$_2$), 61.57 (O*C*H$_2$), 59.04 (O*C*H$_3$), 14.38 (CH$_2$*C*H$_3$). **MS (**ESI): *m/z* = 722 (M + Na$^+$), 738 (M + K$^+$). **HRMS (**ESI): *m/z* = 722.2550 (calcd 722.2545 for [M] + Na$^+$). **HPLC** (125 mm Nucleodur 100-5-C$_{18}$, 4.0 mm i.D., methanol/water 8/2, 0.8 mL/min, 7.1 MPa, 308 K, det. UV 240 nm, ret. time 11.2 min.): 98.9 area %.

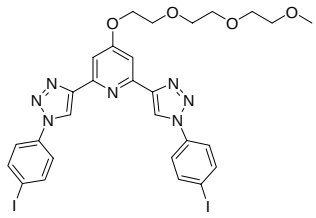
2,6-Bis[1-(4-{methoxy}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4f.

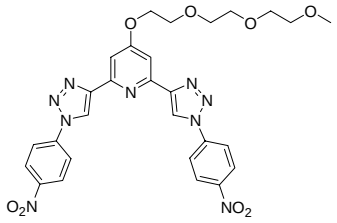


R$_f$ (CH_2Cl_2/acetone 9/1) = 0.16. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.62 (s, 2H, Ar*H*), 8.53 (s, 2H, Ar*H*), 7.69 (d, ^{3}J = 8.9 Hz, 4H, Ar*H*), 7.00 (d, ^{3}J = 8.9 Hz, 4H, Ar*H*), 4.55 (t, ^{3}J = 4.9 Hz, 2H, OC*H*$_2$), 3.86 (m, 2H, OC*H*$_2$), 3.84 (s, 6H, ArOC*H*$_3$), 3.71 - 3.61 (m, 6H, OC*H*$_2$), 3.54 (m, 2H, OC*H*$_2$), 3.33 (s, 3H, OC*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.97 (*C*O$_2$-), 160.11 (*C*$_{Ar}$), 151.0 (*C*$_{Ar}$), 148.13 (*C*$_{Ar}$), 139.57 (*C*$_{Ar}$), 130.4 (*C*$_{Ar}$), 122.24.00 (H*C*$_{Ar}$), 120.78 (H*C*$_{Ar}$), 119.01 (H*C*$_{Ar}$), 114.93 (H*C*$_{Ar}$), 72.03 (O*C*H$_2$), 70.87 (O*C*H$_2$), 70.75 (O*C*H$_2$), 70.72 (O*C*H$_2$), 69.04

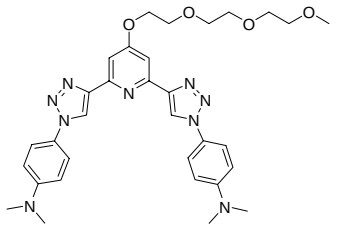
(O*C*H$_2$), 65.10 (O*C*H$_2$), 59.12 (OCH$_3$), 55.77 (OCH$_3$). **MS** (EI, T = 290 °C): m/z = 615 ([M]$^+$), 587 ([M]$^+$ - N$_2$), 559 ([M]$^+$ - 2N$_2$), 398, 369 (100%), 354, 196, 149, 59 ($C_3H_7O^+$). **HRMS (**ESI): *m/z* = 616.2509, (calcd 616.2514 for [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C$_{18}$, 4.0 mm i.D., methanol/water 75/25, 0.8 mL/min, 4.2 MPa, 308 K, det. UV 220 nm, ret. time 9.0 min.): 98.2 area %.

2,6-Bis[1-(4-methylphenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 5a.  R_f (CH_2Cl_2/acetone 9/1) = 0.4. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.62 (s, 2H, triazole*H*), 7.70 (s, 2H, Ar*H*), 7.59 (d, ^{3}J = 7.7 Hz, 4H, Ar*H*), 7.24 (d, ^{3}J = 8.0 Hz, 4H, Ar*H*), 4.32 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.91 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.76-3.63 (m, 6H, OC*H*$_2$), 3.54-3.52 (m, 2H, OC*H*$_2$), 3.34 (s, 3H, OC*H*$_3$), 2.38 (s, 6H, C*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.47 (O*C*$_{Ar}$), 151.34 (*C*$_{Ar}$), 148.52 (*C*$_{Ar}$), 138.88 (*C*$_{Ar}$), 134.57 (*C*$_{Ar}$), 130.19 (*C*$_{Ar}$), 120.25 (*C*$_{Ar}$), 120.14 (*C*$_{Ar}$), 106.11 (*C*$_{Ar}$), 71.90 (O*C*H$_2$), 70.95 (O*C*H$_2$), 70.63 (O*C*H$_2$), 70.56 (O*C*H$_2$), 69.29 (O*C*H$_2$), 67.88 (O*C*H$_2$), 58.98 (O*C*H$_3$), 21.04 (*C*H$_3$). **MS** (ESI): *m/z*= 556 ([M] + H$^+$), 578 ([M] + Na$^+$), 694 ([M] + K$^+$). **HRMS** (ESI): *m/z*= 556.2670, (calcd 556.2666 for [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C$_{18}$, 4.0 mm i.D., methanol/0.1% TFA 75/25, 0.8 mL/min, 10.7 MPa, 308 K, det. UV 220 nm, ret. time 10.8 min.): 98.5 area %.

2,6-Bis[1-(4-iodophenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 5b.  R_f (CH_2Cl_2/acetone 1/1) = 0.3. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.65 (s, 2H, triazole*H*), 7.85 (d, ^{3}J = 8.8 Hz, 4H, Ar*H*), 7.71 (s, 2H, Ar*H*), 7.56 (d, ^{3}J = 8.8 Hz, 4H, Ar*H*), 4.36 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.94 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.78-3.65 (m, 6H, OC*H*$_2$), 3.56-3.54 (m, 2H, OC*H*$_2$), 3.36 (s, 3H, OC*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.71 (O*C*$_{Ar}$), 150.97 (*C*$_{Ar}$), 148.72 (*C*$_{Ar}$), 138.95 (*C*$_{Ar}$), 136.56 (*C*$_{Ar}$), 121.91 (*C*$_{Ar}$), 120.14 (*C*$_{Ar}$), 106.59 (*C*$_{Ar}$), 93.88 (*C*$_{Ar}$), 72.01 (O*C*H$_2$), 71.06 (O*C*H$_2$), 70.74 (O*C*H$_2$), 70.67 (O*C*H$_2$), 69.37 (O*C*H$_2$), 68.10 (O*C*H$_2$), 59.11 (O*C*H$_3$). **MS** (ESI): *m/z*= 780 ([M] + H$^+$), 802 ([M] + Na$^+$). **HRMS** (ESI): *m/z*= 780.0279, (calcd 780.0286 for [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C$_{18}$, 4.0 mm i.D., methanol/water 80/20, 0.8 mL/min, 10.1 MPa, 308 K, det. UV 220 nm, ret. time 11.0 min.): 99.9 area %.

2,6-Bis[1-(4-nitrophenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 5c. R_f (CH_2Cl_2/acetone 9/1) = 0.3. 

^{1}H-NMR (400 MHz, DMSO-D_6): δ (ppm) = 9.50 (s, 2H, triazole*H*), 8.52 (d, ^{3}J = 9.1 Hz, 4H, Ar*H*), 8.34 (d, ^{3}J = 9.2 Hz, 4H, Ar*H*), 7.63 (s, 2H, Ar*H*), 4.43 (t, ^{3}J = 4.1 Hz, 2H, OCH_2), 3.87 (t, ^{3}J = 4.3 Hz, 2H, OCH_2), 3.66-3.52 (m, 6H, OCH_2), 3.44 (m, 2H, OCH_2), 3.38 (s, 3H, OCH_3). **^{13}C-NMR** (75 MHz, DMSO-D_6, T = 373 K): δ (ppm) = 169.75 (OC_{Ar}), 154.23 (C_{Ar}), 151.77 (C_{Ar}), 150.57 (C_{Ar}), 144.15 (C_{Ar}), 128.63 (C_{Ar}), 125.49 (C_{Ar}), 124.39 (C_{Ar}), 109.49 (C_{Ar}), 74.64 (OCH$_2$), 73.46 (OCH$_2$), 73.18 (OCH$_2$), 72.98 (OCH$_2$), 72.05 (OCH$_2$), 71.37 (OCH$_2$), 61.22 (OCH$_3$). **MS** (ESI): *m/z*= 618 ([M] + H^+), 640 ([M] + Na^+). **HRMS** (ESI): *m/z*= 618.2050, (calcd 618.2055 for [M] + H^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 70/30, 0.8 mL/min, 12.1 MPa, 308 K, det. UV 220 nm, ret. time 11.80 min.): 97.5 area %.

2,6-Bis[1-(4-{dimethylamino}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 5d. R_f (CH_2Cl_2/acetone 85/15) = 0.2. 

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.56 (s, 2H, triazole*H*), 7.68 (s, 2H, Ar*H*), 7.49 (d, ^{3}J = 9.1 Hz, 4H, Ar*H*), 6.63 (d, ^{3}J = 9.1 Hz, 4H, Ar*H*), 4.30 (t, ^{3}J = 4.3 Hz, 2H, OCH_2), 3.88 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.74-3.61 (m, 6H, OCH_2), 3.52-3.50 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 2.90 (s, 12H, NCH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.32 (OC_{Ar}), 151.51 (C_{Ar}), 150.36 (C_{Ar}), 148.12 (C_{Ar}), 126.39 (C_{Ar}), 121.41 (HC_{Ar}), 120.17 (C_{Ar}), 112.06 (HC_{Ar}), 105.73 (C_{Ar}), 71.81 (OCH$_2$), 70.85 (OCH$_2$), 70.53 (OCH$_2$), 70.47 (OCH$_2$), 69.22 (OCH$_2$), 67.75 (OCH$_2$), 58.90 (OCH$_3$), 40.23 (NCH$_3$). **HRMS** (ESI): *m/z*= 614.3192, (calcd 614.3197 for [M] + H^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/10 mmol triethylammonium acetate pH 7 75/25, 0.8 mL/min, 11.3 MPa, 308 K, det. UV 220 nm, ret. time 13.10 min.): 99.2 area %.

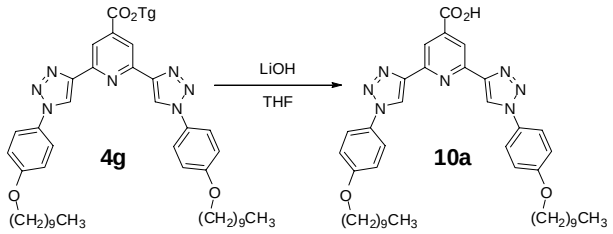
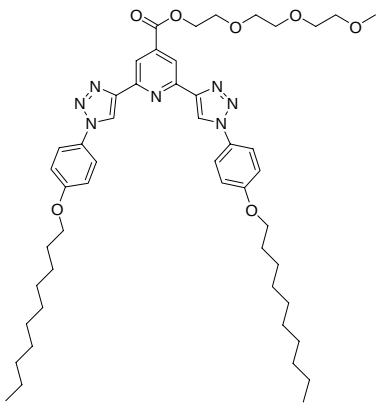
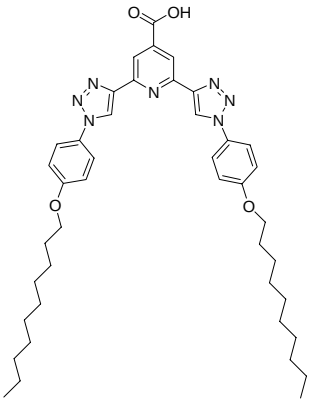


Figure 5. Saponification of compound **4g** to give carboxylic acid **10a**.

2,6-Bis[1-(4-{decyloxy}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 4g.  R_f (CH_2Cl_2/acetone 9/1) = 0.4. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.50 (s, 2H, Ar*H*), 8.47 (s, 2H, Ar*H*), 7.61 (d, ^{3}J = 8.6 Hz, 4H, Ar*H*), 6.91 (d, ^{3}J = 8.8 Hz, 4H, Ar*H*), 4.46 (t, ^{3}J = 4.4 Hz, 2H, OC*H*$_2$CH$_2$O), 3.92 (t, ^{3}J = 6.5 Hz, 4H, OC*H*$_2$CH$_2$CH$_2$), 3.81 (t, ^{3}J = 4.6 Hz, 2H, OC*H*$_2$), 3.69-3.59 (m, 6H, OC*H*$_2$), 3.49-3.47 (m, 2H, OC*H*$_2$), 3.28 (s, 3H, OC*H*$_3$), 1.77 (tt, ^{3}J = 6.6 Hz, ^{3}J = 7.0 Hz, 4H, OCH$_2$C*H*$_2$ CH$_2$), 1.41-1.22 (m, 28H, CH$_2$C*H*$_2$), 0.85 (t, ^{3}J = 6.9 Hz, 6H, CH$_2$C*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.61 (*C*O$_2$-), 159.40 (*C*$_{Ar}$), 150.72 (*C*$_{Ar}$), 147.85 (*C*$_{Ar}$), 139.09 (*C*$_{Ar}$), 129.90 (*C*$_{Ar}$), 121.76 (H*C*$_{Ar}$), 120.44 (*C*$_{Ar}$), 118.51 (*C*$_{Ar}$), 115.12 (H*C*$_{Ar}$), 71.82 (O*C*H$_2$CH$_2$CH$_2$), 70.64 (O*C*H$_2$), 70.52 (O*C*H$_2$), 70.48 (O*C*H$_2$), 68.78 (O*C*H$_2$), 68.35 (O*C*H$_2$), 64.80 (O*C*H$_2$), 58.84 (O*C*H$_3$), 31.81 (*C*H$_2$), 29.48 (*C*H$_2$), 29.32 (*C*H$_2$), 29.24 (*C*H$_2$), 29.09 (*C*H$_2$), 25.92 (*C*H$_2$), 22.59 (*C*H$_2$), 14.03 (*C*H$_3$). **MS** (ESI): m/z = 868 ([M] + H$^+$), 890 ([M] + Na$^+$). **HRMS** (ESI): *m/z*= 890.5149, (calcd 890.5150 for [M] + Na$^+$). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.6 mm i.D., methanol/water 95/5, 0.8 mL/min, 5.6 MPa, 308 K, det. DAD 220 nm, ret. time 15.3 min.): 95.2 area %.

4-Carboxy-2,6-bis[1-(4-{decyloxy}phenyl)-*1H*-1,2,3-triazol-4-yl]-pyridine 10a.  100 mg **4g** (0.11 mmol) were dissolved in mixture of 10 mL of THF, 2 mL of water and 2 mL of an aqueous solution of LiOH (1 M). After complete consumption of starting material (20 min) indicated by TLC monitoring (CH_2Cl_2/acetone 9/1), the mixture was poured into 200 mL of diluted aqueous HCl (5%) and the colourless precipitate was filtered and washed thoroughly with water. Drying *in vacuo* gave 62 mg of a yellow solid (75%). **^{1}H-NMR** (400 MHz, DMSO-D_6): δ (ppm) = 9.31 (s, 2H, Ar*H*), 8.42 (s, 2H, Ar*H*), 7.90 (d, ^{3}J =

9.1 Hz, 4H, Ar*H*), 7.17 (d, ^{3}J = 9.0 Hz, 4H, Ar*H*), 4.05 (t, ^{3}J = 6.3 Hz, 4H, OCH_2), 3.40 (br s, 1H, CO_2H), 1.77 (tt, ^{3}J = 6.8 Hz, ^{3}J = 7.2 Hz, 4H, OCH_2CH_2), 1.46-1.25 (m, 28H, CH_2), 0.87 (t, ^{3}J = 6.4 Hz, 6H, CH_2CH_3). **^{13}C-NMR** (75 MHz, DMSO-D_6): δ (ppm) = 165.78 (CO_2H), 159.02 (C_{Ar}), 150.66 (C_{Ar}), 147.38 (C_{Ar}), 141.22 (C_{Ar}), (129.70 (C_{Ar}), 122.15 (C_{Ar}), 121.98 (C_{Ar}), 117.48 (C_{Ar}),115.40 (C_{Ar}), 67.98 (OCH_2), 31.32 (CH_2), 29.00 (CH_2), 28.95 (CH_2), 28.76 (CH_2), 28.69 (CH_2), 28.59 (CH_2), 25.47 (CH_2), 22.08 (CH_2), 13.94 (CH_3). **HRMS** (ESI): *m/z*= 720.4242, (calcd 720.4242 for [M] - H^+). **HPLC** (250 mm Asahipak ODP-50, 4.6 mm i.D., acetonitrile/0.1% TFA 95/5, 0.8 mL/min, 5.8 MPa, 308 K, det. DAD 220 nm, ret. time 31.0 min.): 99.9 area %.

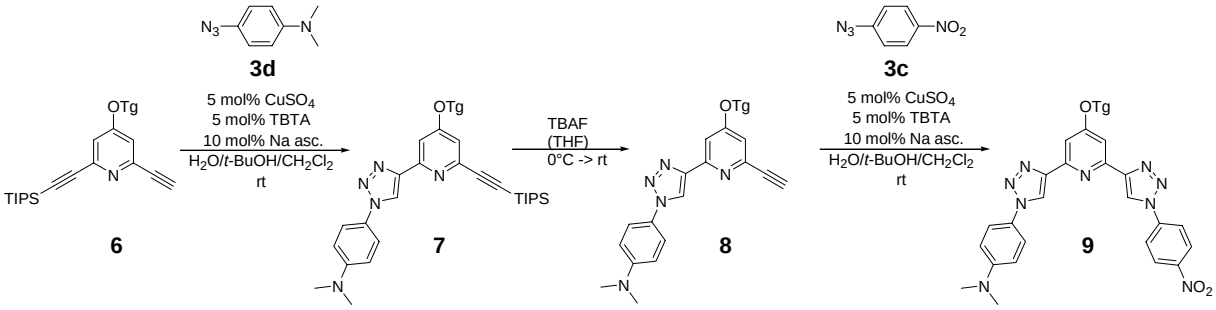
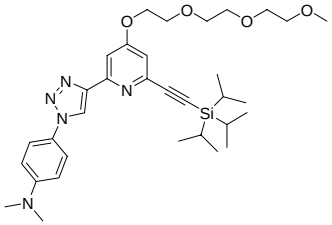


Figure 6. Reaction sequence to give non-symmetrical BTP **9**.

2-[1-(4-{dimethylamino}phenyl)-*1H*-1,2,3-triazol-4-yl]-6-[(triisopropylsilanyl)-ethynyl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 7. R_f (EE/Hex 6/4) = 0.2. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.51 (s, 1H, triazole*H*), 7.73 (d, ^{3}J = 2.4 Hz, 1H, Ar*H*), 7.59 (d, ^{3}J = 9.1 Hz, 2H, Ar*H*), 6.97 (d, ^{3}J = 2.4 Hz, 1H, Ar*H*), 6.74 (d, ^{3}J = 9.1 Hz, 2H, Ar*H*), 4.26 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.87 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.72-3.61 (m, 6H, OCH_2), 3.52-3.50 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 2.96 (s, 6H, NCH_3), 1.12 (d, ^{3}J = 2.8 Hz, 21H, C*H*, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 165.46 (OC_{Ar}), 152.15 (C_{Ar}), 150.53 (C_{Ar}), 147.86 (C_{Ar}), 143.98 (C_{Ar}), 126.56 (C_{Ar}), 121.70 (C_{Ar}), 120.72 (C_{Ar}), 114.83 (C_{Ar}), 112.23 (C_{Ar}), 105.99 (C≡*C*), 105.33 (C_{Ar}), 91.08 (C≡*C*), 71.88 (OCH_2), 70.89 (OCH_2), 70.61 (OCH_2), 70.55 (OCH_2), 69.23 (OCH_2), 67.70 (OCH_2), 58.97 (OCH_3), 40.37 (NCH_3), 18.65 ($SiCHCH_3$), 11.25 (Si*C*H). **MS** (ESI): *m/z*= 608 ([M] + H^+), 630 ([M] + Na^+), 646 ([M] + K^+). **HRMS** (ESI): *m/z*= 630.3447, (calcd 630.3445 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 85/15, 0.8 mL/min, 8.8 MPa, 308 K, det. UV 220 nm, ret. time 18.65 min.): 100 area %.



2-[1-(4-{dimethylamino}phenyl)-*1H*-1,2,3-triazol-4-yl]-6-(ethynyl)-4-(3,6,9-trioxadec-1-yloxy)pyridine 8. Compound **7** (161 mg, 0.265 mmol, 1 equiv.) was dissolved in 50 mL of THF and the mixture was cooled down to 0 °C. To the rapidly stirred reaction mixture was added a solution of TBAF (0.53 mL, 1 M solution in THF, 2 equiv.) via a syringe and while stirring for 10 min the mixture was allowed to reach rt. The mixture was filtered through a short silica plug and the solvent removed *in vacuo.* Purification by column chromatography (EA/Hex 7/3) gave 0.118 mg of colorless oil (quant. yield). R_f (EE/Hex 7/3) = 0.2. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.41 (s, 1H, triazole*H*), 7.65 (d, ^{3}J = 2.4 Hz, 1H, Ar*H*), 7.47 (d, ^{3}J = 9.1 Hz, 2H, Ar*H*), 6.87 (d, ^{3}J = 2.4 Hz, 1H, Ar*H*), 6.61 (d, ^{3}J = 9.1 Hz, 2H, Ar*H*), 4.16 (t, ^{3}J = 4.4 Hz, 2H, OCH_2), 3.77 (t, ^{3}J = 4.5 Hz, 2H, OCH_2), 3.62-3.51 (m, 6H, OCH_2), 3.42 -3.40 (m, 2H, OCH_2), 3.23 (s, 3H, OCH_3), 3.15 (s, 1H, C≡C*H*), 2.83 (s, 6H, NCH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 165.31 (OC_{Ar}), 151.96 (C_{Ar}), 150.18 (C_{Ar}), 147.35 (C_{Ar}), 142.64 (C_{Ar}), 126.10 (C_{Ar}), 121.17 (C_{Ar}), 120.17 (C_{Ar}), 113.89 (C_{Ar}), 111.91 (C_{Ar}), 105.65 (C_{Ar}), 82.58 (C≡*C*), 76.81 (C≡*C*), 71.57 (O*C*H$_2$), 70.57 (O*C*H$_2$), 70.28 (O*C*H$_2$), 70.22 (O*C*H$_2$), 68.90 (O*C*H$_2$), 67.53 (O*C*H$_2$), 58.64 (O*C*H$_3$), 40.00 (N*C*H$_3$). **MS** (ESI): *m/z*= 452 ([M] + H$^+$), 474 ([M] + Na$^+$), 690 ([M] + K$^+$). **HRMS** (ESI): *m/z*= 452.2293, (calcd 452.2292 for [M] + H$^+$). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 65/35, 0.8 mL/min, 12.7 MPa, 308 K, det. UV 220 nm, ret. time 10.56 min.): 97.4 area %.

6-[1-(4-{dimethylamino}phenyl)-*1H*-1,2,3-triazol-4-yl]-2-[1-(4-Nitrophenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxy)pyridine 9. R_f (CH_2Cl_2/acetone 8/2) = 0.5. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.73 (s, 1H, triazole*H*), 8.45 (s, 1H, triazole*H*), 8.30 (d, ^{3}J= 9.0 Hz, 2H, Ar*H*), 7.96 (d, ^{3}J= 9.0 Hz, 2H, Ar*H*), 7.61 (d, ^{3}J= 2.3 Hz, 2H, pyridine*H*), 7.50 (d, ^{3}J= 9.0 Hz, 2H, Ar*H*), 6.65 (d, ^{3}J= 9.1 Hz, 2H, Ar*H*), 4.26 (t, ^{3}J = 4.1 Hz, 2H, OCH_2), 3.88 (t, ^{3}J = 4.3 Hz, 2H, OCH_2), 3.75-3.62 (m, 6H, OCH_2), 3.54-3.51 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 2.94 (s, 6H, NCH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.38 (OC_{Ar}), 151.72 (C_{Ar}), 150.49 (C_{Ar}), 150.37 (C_{Ar}), 149.43 (C_{Ar}), 148.03 (C_{Ar}), 147.04 (C_{Ar}), 140.94 (C_{Ar}), 126.30 (C_{Ar}), 125.38 (C_{Ar}), 121.47 (C_{Ar}), 120.22 (C_{Ar}), 120.16 (C_{Ar}), 120.10 (C_{Ar}), 112.09 (C_{Ar}), 106.34 (C_{Ar}), 106.02 (C_{Ar}), 71.88 (O*C*H$_2$), 70.91 (O*C*H$_2$), 70.61 (O*C*H$_2$), 70.54 (O*C*H$_2$), 69.24 (O*C*H$_2$), 67.88 (O*C*H$_2$), 58.96

(OCH_3), 40.30 (NCH_3). **MS** (ESI): m/z = 616.3 ([M] + H^+), 638.4 ([M] + Na^+), 654.3 ([M] + K^+). **HRMS** (ESI): *m/z*= 638.2452, (calcd 638.2446 for [M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 2.0 mm i.D., methanol/10 mmol TEAA pH = 7, 8/2, 0.2 mL/min, 8.1 MPa, 308 K, det. DAD 220 nm, ret. time 6 min.): 98.4 area %.

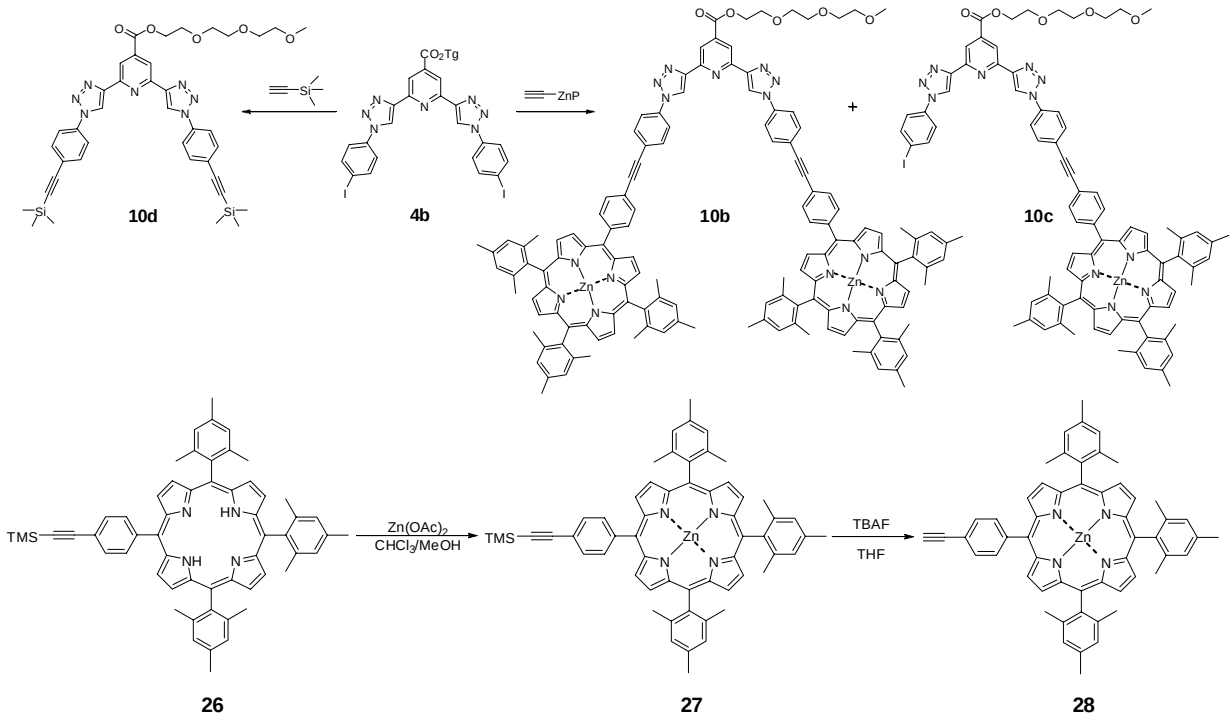
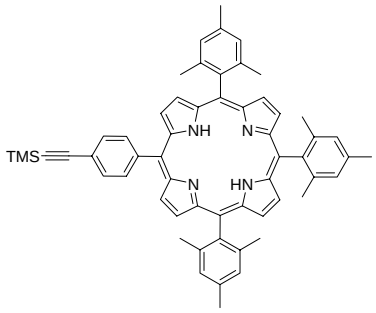
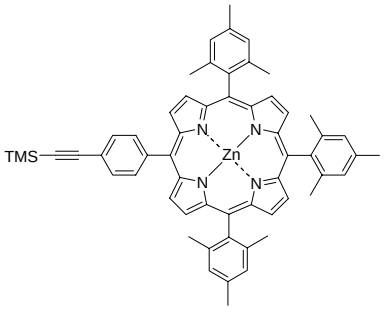


Figure 7. Synthesis of Zn porphyrine **28** and postfunctionalization of BTP **4b**.



5,10,15-Trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl} porphyrin 26.

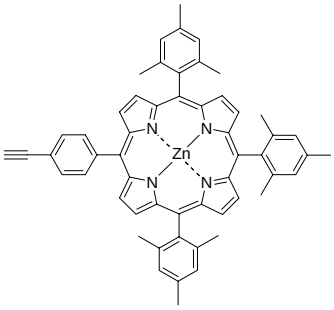
Synthesis has been done following the method of Lindsey.[8]



Zinc(II) 5,10,15-Trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}-porphyrin 27. Synthesis has been done following the common method of preparation of Zn(II) porphyrine derivatives described by Lindsey.[9] The spectroscopic data were in common with those described therein.

[8] J. S. Lindsey, S. Prathapan, T. E. Johnson, R. W. Wagner, *Tetrahedron* **1994**, *50***,** 8941-8968.
[9] R. W. Wagner, T. E. Johnson, F. Li, J. S. Lindsey, *J. Org. Chem.* **1995**, *60*, 5266-5273.

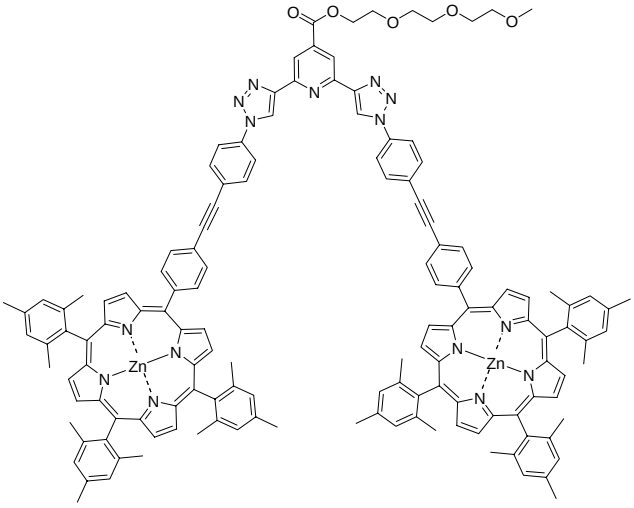
Zinc(II) 5,10,15-trimesityl-20-(4-ethynylphenyl)-porphyrin 28.



115 mg **27** were dissolved in 50 mL of THF, cooled down to 0 °C, 0.26 mL of a TBAF solution of THF (1 M, 2 equiv.) were added via a syringe to the stirred reaction mixture, the mixture was allowed to reach rt and stirred for 1 h. After complete consumption of the starting material indicated by TLC monitoring the mixture was filtered through a short silica pad which was washed with THF thoroughly. Removal of the solvent *in vacuo* gave a purple solid which was purified by preparative TLC (Hex/CH_2Cl_2 1/1) to give 105 mg of a purple solid (99%).

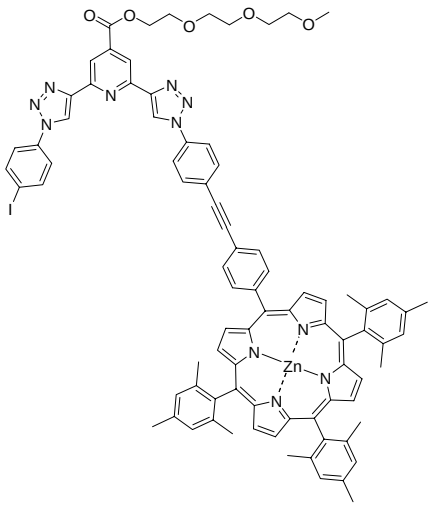
The spectroscopic data were in common with the data described by Lindsey.[9]

2,6-Bis[1-(4-{Zinc(II) 5,10,15-tri(2,4,6-trimethylphenyl)-porphyrinyl-20-(phenyl-4-ethynyl)}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 10b.

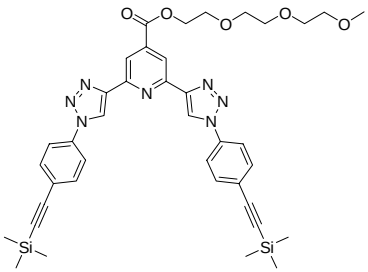


In a three necked flask equipped with a reflux condenser 24 mg **4b** (0.03 mmol, 1 equiv.) and 80 mg **28** (0.096 mmol, 3.2 equiv.) were dissolved in 60 mL of a mixture of toluene/TEA (5/1), the mixture was degassed at rt and flushed with argon (4 cycles), a tip of spatula of $Pd(PPh_3)_4$ (ca. 1 mg) was added under a counterflow of argon and the solution was freeze degassed. The reaction was stirred at 40 °C for 3 d under argon and after consumption of all starting material **4b** indicated by TLC monitoring (Hex/CH_2Cl_2 1/1) the solvent was removed *in vacuo*. Purification by column chromatography (CH_2Cl_2 + 2% MeOH) gave 40 mg (60%) of compound **10b** and compound **10c** (11 mg, 24%) both as a purple solids. R_f (CH_2Cl_2/acetone 9/1) = 0.7. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.88, 8.86 (s, s, 4H, triazole*H*/pyridine*H*), 8.79 (m, 8H, pyrrole*H*), 8.71 (s, 8H, pyrrole*H*), 8.27 (d, ^{3}J = 8.0 Hz, 4H, Ar*H*), 7.97 - 7.9 (m, 12H, Ar*H*), 7.28 (s, 12H, Ar*H*), 4.62 (t, ^{3}J = 4.8 Hz, 2H, OCH_2), 3.93 (t, ^{3}J = 4.4 Hz, 2H, OCH_2), 3.76 - 3.63 (m, 6H, OCH_2), 3.51 (m, 2H, OCH_2), 3.32 (s, 3H, OCH_3), 2.63 (s, 18H, para-ArCH_3), 1.85 (s, 36H, ortho-ArCH_3). **MS** (ESI): *m/z* = 2204 ($M + H^+$). **GPC** (Det at 254 nm and 420 nm, THF, standart: PS, 30°C): M_n: $5.706 \cdot 10^3$, M_w: $5.734 \cdot 10^3$, M_v: $5.760 \cdot 10^3$, D: 1.005. **HPLC** (125 mm Nucleodur 100-5-C_{18},

4.0 mm i.D., methanol, 0.8 mL/min, 4.5 MPa, 308 K, det. UV 425 nm, ret. time 14.7 min.): 96.0 area %. λ_{abs} ($CHCl_3$) = 309, 406, 426, 557, 597 nm.

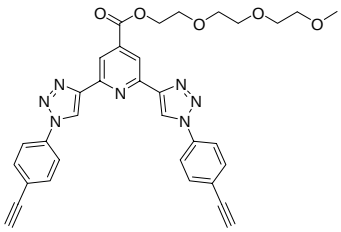


2-[1-(4-iodophenyl)-*1H*-1,2,3-triazol-4-yl]-6-[1-(4-{Zinc(II) 5,10,15-tri(2,4,6-trimethylphenyl)-porphyrinyl-20-(phenyl-4-ethynyl)}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 10c. Yield: 24%; **TLC** (CH_2Cl_2/acetone 9/1) R_f = 0.52. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.87 (s, 1H, pyridine*H*), 8.86 (s, 1H, pyridine*H*), 8.76 (m, 5H, pyrrole*H*, triazole*H*), 8.71 (s, 5H, pyrrole*H*, triazole*H*), 8.27 (d, ^{3}J = 8.0 Hz, 2H, Ar*H*), 7.97 - 7.67 (m, 8H, Ar*H*), 7.65 (d, ^{3}J = 8.8 Hz, 2H, Ar*H*), 7.28 (s, 6H, Ar*H*), 4.61 (t, ^{3}J = 4.4 Hz, 2H, OCH_2), 3.91 (t, ^{3}J = 4.7 Hz, 2H, OCH_2), 3.76-3.63 (m, 6H, OCH_2), 3.51 (t, ^{3}J = 4.4 Hz 2H, OCH_2), 3.31 (s, 3H, OCH_3), 2.63 (s, 9H, para-ArCH_3), 1.85 (s, 18H, ortho-ArCH_3). **MS** (ESI): *m/z* = 1505 ([M] + Na^+). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 2.0 mm i.D., methanol, 0.2 mL/min, 3.6 MPa, 308 K, det. DAD 425 nm, ret. time 21.5 min.): 94.7 area %. λ_{abs} ($CHCl_3$) = 307, 405, 426, 557, 596 nm.



2,6-Bis[1-(4-{(trimethylsilyl)ethynyl}phenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 10d. A flame dried three necked flask equipped with a reflux condenser was charged with 41 mg **4b** (0.051 mmol, 1 equiv.), CuI (1 mg, 0.001 mmol, 0.02 equiv.) and PPh_3 (0.001 g, 0.005 mmol, 0.1 equiv.) and the mixture was suspended in 5 mL of dry TEA, the solution freeze degassed (2 x) and $Pd(PPh_3)_4$ (1 mg, 0.001 mmol, 0.02 equiv.) was added in the counterflow of argon. After the suspension was freeze degassed again (1 x) TMS-acetylene was added to the mixture using a syringe in the counterflow of argon. The reaction mixture was stirred at 70 °C for 3 d and after consumption of all starting material indicated by TLC monitoring (CH_2Cl_2/acetone 8/2) the solvent was removed. Purification by column chromatography (CH_2Cl_2/MeOH 95/5 → 9/1) gave 34 mg (89%) of a yellow solid. R_f (CH_2Cl_2/acetone 8/2) = 0.6. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.69 (s, 4H, Ar*H*), 7.82 (d, ^{3}J = 7.9 Hz, 4H, Ar*H*), 7.65 (d, ^{3}J = 7.9 Hz, 4H, Ar*H*), 4.56 (t, ^{3}J = 4.6 Hz, 2H, OCH_2), 3.9 (t, ^{3}J = 4.2 Hz, 2H, OCH_2), 3.74-3.67 (m, 6H, OCH_2), 3.54 (m, 2H, OCH_2), 3.34 (s, 3H,

OC*H*$_3$), 0.28 (s, 18H, SiC*H*$_3$). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.78 (*C*O_2), 150.68 (*C*$_{Ar}$), 148.29 (*C*$_{Ar}$), 139.88 (*C*$_{Ar}$), 136.37 (*C*$_{Ar}$), 133.54 (H*C*$_{Ar}$), 124.19 (*C*$_{Ar}$), 120.52 (*C*$_{Ar}$), 120.20 (H*C*$_{Ar}$), 119.41 (*C*$_{Ar}$), 103.54 (C≡*C*), 95.78 (C≡*C*), 72.04 (OC*H*$_2$), 70.86 (OC*H*$_2$), 70.76 (OC*H*$_2$), 70.72 (OC*H*$_2$), 69.03 (OC*H*$_2$), 65.17 (OC*H*$_2$), 58.11 (OC*H*$_3$), 0.0 (SiC*H*$_3$). **MS** (ESI): *m/z*= 748 ([M] + H^+), 770 ([M] + Na^+). **HRMS (**ESI): *m/z* = 770.2903, (calcd 770.2912 for [M] + Na^+). **IR (**KBr**):** 3136 (triazole), 2957 (TMS-C≡C), 2897 (CH_2), 2159 (TMS-C≡C), 1732 (-CO_2-), 1619, 1604, 1573, 1516 (C=C, C=N), 1249 (-CO_2-), 1107 (C-O-C), 865, 843, 769, 677 (TMS-C≡C). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 9/1, 0.8 mL/min, 5.8 MPa, 308 K, det. UV 285 nm, ret. time 11.38 min.): 93.7 area %.



2,6-Bis[1-(4-ethynylphenyl)-*1H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadec-1-yloxycarbonyl)pyridine 10e. 10d (34 mg, 0.05 mmol, 1 equiv) was dissolved in 35 mL of THF and the solution cooled down to 0 °C. To the rapidly stirred reaction mixture was added a solution of TBAF (90.3 mL, 1 M solution in THF, 2.8 equiv.) via a syringe. The mixture immediately turned red. The mixture was stirred for 2 min at 0 °C and then filtered through a short plug of silica gel which was washed with THF and EA thoroughly. After removing the solvent *in vacuo* a brown oil was obtained. Purification by column chromatography (CH_2Cl_2/acetone 9/1) gave 26 mg (96%) of a pale yellow solid. R_f (CH_2Cl_2/acetone 8/2) = 0.46. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.67 (m, 4H, Ar*H*), 7.83 (d, ^{3}J = 8.4 Hz, 4H, Ar*H*), 7.67 (d, ^{3}J = 8.4 Hz, 4H, Ar*H*), 4.57 (t, ^{3}J = 4.7 Hz, 2H, OC*H*$_2$), 3.89 (t, ^{3}J = 3.8 Hz, 2H, OC*H*$_2$), 3.74-3.66 (m, 6H, OC*H*$_2$), 3.54 (m, 2H, OC*H*$_2$), 3.34 (s, 3H, OC*H*$_3$), 3.21 (s, 2H, C≡C*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.77 (*C*O_2), 150.64 (*C*$_{Ar}$), 148.28 (*C*$_{Ar}$), 139.83 (*C*$_{Ar}$), 136.69 (*C*$_{Ar}$), 133.74 (H*C*$_{Ar}$), 123.17 (*C*$_{Ar}$), 120.53 (*C*$_{Ar}$), 120.29 (H*C*$_{Ar}$), 119.42 (*C*$_{Ar}$), 82.32 (C≡*C*), 79.47 (C≡*C*), 72.05 (O*C*H$_2$), 70.87 (O*C*H$_2$), 70.76 (O*C*H$_2$), 70.72 (O*C*H$_2$), 69.04 (O*C*H$_2$), 65.20 (O*C*H$_2$), 59.11 (O*C*H$_3$). **MS** (ESI): *m/z*= 604 ([M] + H^+), 626 ([M] + Na^+), 642 ([M] + K^+). **HRMS (**ESI): *m/z* = 626.2128, (calcd 626.2122 for [M] + Na^+). **IR (**KBr**):** 3249 (HC≡C), 3135 (triazolring), 2879 (CH_2), (OCH_3), 2106 (HC≡C), 1728 (CO_2-), 1554, 1429, 1394 (C=C, C=N), 1619, 1607, 1572, 1515 (C=C aryl), 1241 (CO_2-), 1106 (C-O-C), 840 (arylring). **HPLC** (125 mm Nucleodur 100-5-C_{18}, 4.0 mm i.D., methanol/water 75/25, 0.8 mL/min, 8.0 MPa, 308 K, det. UV 285 nm, ret. time 13.37 min.): 85.1 area %.

Synthesis of complexes $[Fe(5c)_2](OTf)_2$ and $[Eu(5b)_3](OTf)_3$. All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere and dry, degassed and argon saturated solvents.

$[Fe(5c)_2](OTf)_2$. Compound **5c** (60.0 mg, 97.2 µmol) was suspended in 5 mL of acetonitrile and a solution of $Fe(OTf)_2(MeCN)_2$[10] (45.0 mg, 103 µmol) in 5 mL of acetonitrile was added. The resulting red solution was stirred for 10 min., and subsequently all volatiles were removed in vacuum. Washing the residue with THF (3 x 2 mL) and drying it in vacuum led to $[Fe(\mathbf{5c})_2](OTf)_2$ (38.4 mg, 24.2 µmol, 50%) in form of a pure orange red solid. All attempts to crystallize pure $[Fe(\mathbf{5c})_2](OTf)_2$ failed, but single crystals containing $[Fe(\mathbf{5c})_2](OTf)_2$ together with co-crystallized $Fe(OTf)_2(H_2O)(MeCN)_4$ (ratio 2:1), which could be obtained after slow diffusion of toluene into a solution of the corresponding complex mixture in acetonitrile, proved suitable for X-ray diffraction (Figure 8).

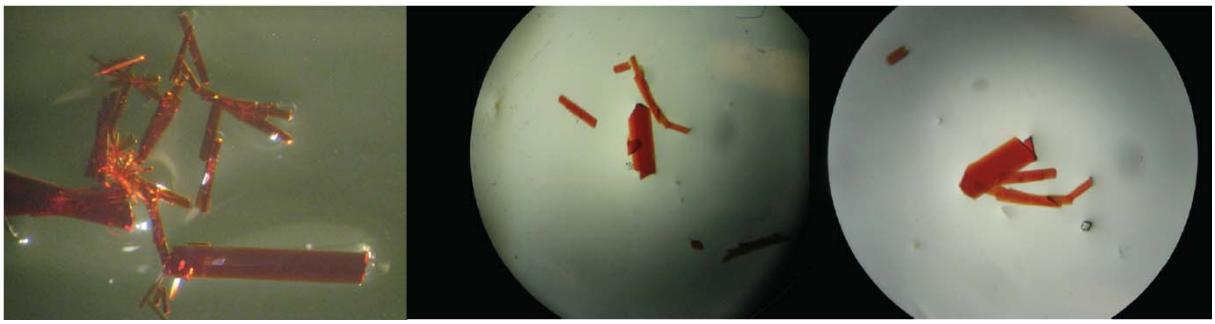


Figure 8. Pictures of crystals obtained by co-crystallization of $[Fe(\mathbf{5c})_2](OTf)_2$ and $Fe(OTf)_2(H_2O)(MeCN)_4$ as recorded by optical microscopy at room temperature.

EA: C 43.61, H 3.65, N 15.68, S 3.96 (calcd. for $[Fe(\mathbf{5c})_2](OTf)_2$, $C_{58}H_{54}F_6FeN_{18}O_{22}S_2$: C 43.84, H 3.43, N 15.87, S 4.04). **^{1}H NMR** (400 MHz, CD_3CN, 25 °C, see Figure 9): δ=9.96 (s, 2H, Ar*H*), 9.09 (s, 2H, Ar*H*), 8.36 (d, ^3J = 8.8 Hz, 4H, Ar*H*), 7.92 (d, ^3J = 8.8 Hz, 4H, Ar*H*), 4.73 (s, 2H, CH_2), 4.01 (s, 2H, CH_2), 3.75 (m, 2H; CH_2), 3.65 (m, 2H, CH_2), 3.58 (m, 2H, CH_2), 3.48 (m, 2H, CH_2), 3.26 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, CD_3CN, 25 °C): δ=149.0 (C_{Ar}), 126.8 (C_{Ar}), 125.0 (C_{Ar}), 122.6 (C_{Ar}), 72.5 (CH_2), 71.4 (CH_2), 71.1 (CH_2), 70.9 (CH_2), 70.6 (CH_2), 69.8 (CH_2), 58.8 (CH_3). **IR** (KBr): $\tilde{\upsilon}$ =3099 (m), 2878 (m), 1622 (m), 1596 (s), 1531 (vs), 1505 (s), 1452 (m), 1410 (m), 1346 (vs), 1257 (vs), 1163 (m), 1030 (vs), 989 (m), 949 (w), 855 (s), 750 (m), 685 (w), 638 (s), 574 (w), 518 (m). **HRMS** (ESI, CH_3OH/CH_3CN): *m/z* = 645.1647, (calcd for $[C_{56}H_{44}FeN_{18}O_{16}]^{2+}$ 645.1657).

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[10] $Fe(OTf)_2(MeCN)_2$ was synthesized according to the following literature: R. A. Heintz, J. A. Smith, P. S. Szalay, A. Weisgerber, K. R. Dunbar, K. Beck, D. Coucouvanis, *Inorg. Synth.* **2002**, *33*, 75 and A. M. Tait, D. H. Busch, *Inorg. Synth.* **1978**, *18*, 2.

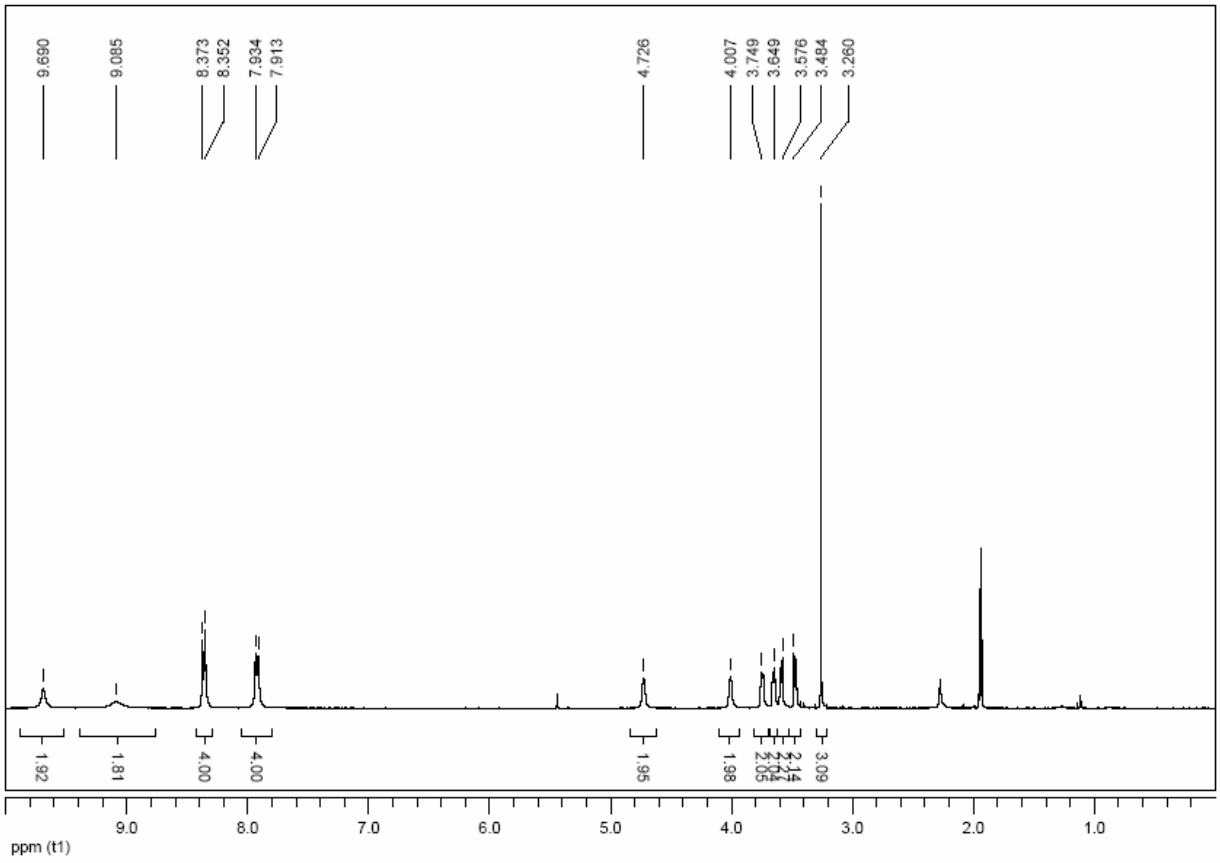


Figure 9. ^{1}H-NMR spectrum of complex [Fe(**5c**)$_2$](OTf)$_2$ in CD_3CN at 27 °C.

[Eu(5b)$_3$](OTf)$_3$. A solution of Eu(OTf)$_3$ (12.0 mg, 20.0 µmol) in 3 mL of THF was added to a solution of **5b** (50.0 mg, 64.2 µmol) in 3 mL of THF. After 10 minutes a white solid started to precipitate from the colorless solution and the reaction mixture was stirred at room temperature for 24 hours. After filtration the residue was dried in vacuum and the resulting white powder consisted of pure [Eu(**5b**)$_3$](OTf)$_3$ (33.7 mg, 11.5 µmol, 57%). Single crystals of [Eu(**5b**)$_3$](OTf)$_3$ (see MS Figure 6) could be grown by slow evaporation of the solvent from a THF solution. The result of a single crystal X-ray diffraction study is shown in Figure 10.

EA: C 35.37, H 3.16, N 9.88, S 2.88 (calcd for $C_{87}H_{81}EuF_9I_6N_{21}O_{21}S_3$: C 35.57, H 2.78, N 10.01, S 3.27). **IR** (KBr): $\tilde{\upsilon}$ =3098 (m), 2962 (m), 2877 (m), 1623 (s), 1620 (s), 1616 (s), 1590 (s), 1576 (s), 1494 (vs), 1465 (s), 1405 (w), 1310 (m), 1260 (vs), 1223 (s), 1200 (m), 1147 (s), 1096 (vs), 1110 (s), 1074 (s), 1061 (s), 1054 (s), 1049 (s), 1029 (vs), 1013 (s), 990 (s), 950 (w), 862 (m), 821 (s), 800 (s), 756 (w), 697 (w), 638 (vs), 573 (w), 519 (m), 460 (w). **HRMS** (ESI-TOF): *m/z* = 830.0101, (calcd. for $[C_{84}H_{81}EuI_6N_{21}O_{12}]^{3+}$ 829.9951).

[Eu(5a)$_3$](OTf)$_3$ can be synthesized in close analogy to the procedure described above for [Eu(**5b**)$_3$](OTf)$_3$. Single crystals of [Eu(**5a**)$_3$](OTf)$_3$ could be grown by slow diffusion of diethylether into a solution of [Eu(**5a**)$_3$](OTf)$_3$ in acetonitrile.

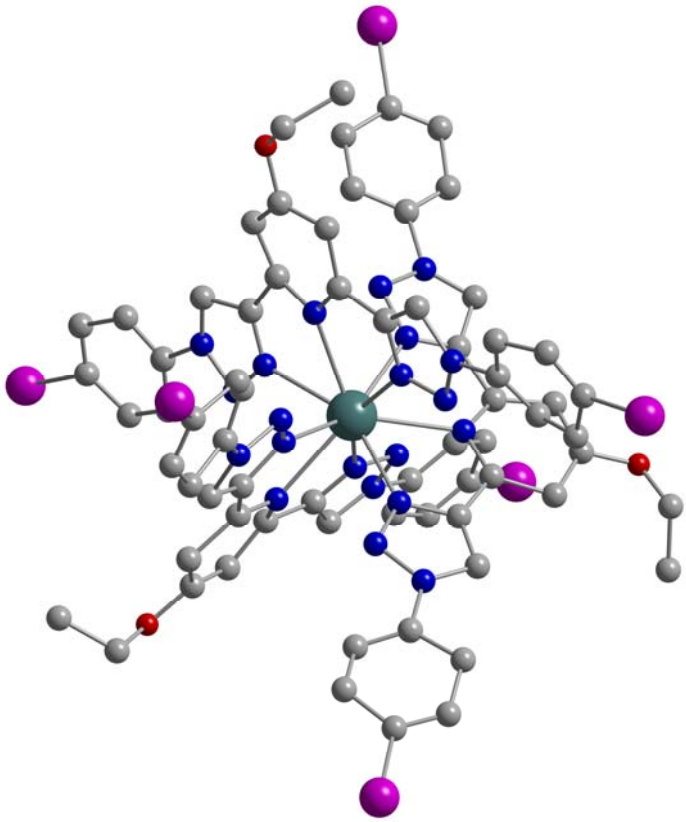


Figure 10. An extract of one of the disordered [Eu(**5b**)$_3$]$^{3+}$ ions found in the crystals of complex [Eu(**5b**)$_3$](OTf)$_3$ in course of a single crystal X-ray diffraction study. The solution of this complex could not be refined to an adequate level. Nevertheless it clearly shows the coordination of the europium atom by nine nitrogen atoms from three BTP ligands **5b** with a three-fold symmetry (OTg residues are only shown partly), as deduced for the properly solved structure of [Eu(**5a**)$_3$](OTf)$_3$ (see MS Figure 5).

UV-vis titration of BTP ligand **4b**.

In a UV-vis titration experiment, the chelating ability of BTP **4b** towards Fe(II) was studied. A stock solution of **4b** in $CHCl_3$ with an optical density OD(λ_{max}) ~0.9 was used and a methanolic $Fe(BF_4)_2$ solution was added in portions of 0.2 equiv. Upon complexation of the metal ion a remarkable change in BTP absorption was observed and clear isosbestic points were found as can be seen on the left side of Figure 11. This resulting titration curve and the corresponding extinction difference diagram (R = 0.99917) indicate that only a single equilibrium between the free and complexed BTP exists during the titration experiment. The inset in the titration curve shows a sharp endpoint at a metal/ligand ratio of 1:1. Excess of Fe(II) leads to no further change in absorption, indicating the formation of a 1:1 Fe-BTP complex in contrast to the crystal structure of $[Fe(\mathbf{5c})_2](OTf)_2$ (1:2 Fe(II)-BTP complex). As both oxygen and water have not been excluded during the titration experiment a reasonable explanation for the formation of the 1:1 Fe-BTP complex might be the oxidation of Fe(II) to Fe(III) before or during complexation and the role of water as a competing ligand.

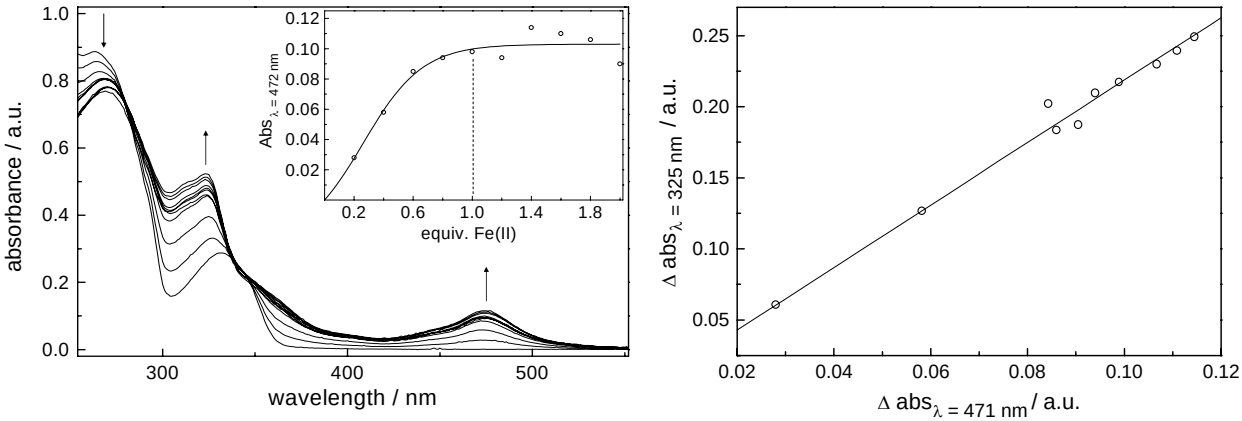


Figure 11. Absorption spectrum of titration of $Fe(BF_4)_2$ to BTP **4b** and the linear fit of the corresponding extinction difference diagram (R = 0.99917).

Computation. The relative stability of the *anti* and *syn* conformers was calculated at both semiempirical and DFT levels of theory by varying the dihedral angle in a 4-(2-pyridyl)-1,2,3-triazole model system (Figure 12). The results indicate the anticipated thermodynamic stability of the *anti* over the *syn* conformer:

$$\Delta H_f^o \text{ (DFT)} = 6.4 \text{ kcal/mol} \quad \{\Delta H_f^o \text{ (AM1)} = 3.2 \text{ kcal/mol}\}$$

and a barrier for rotation *anti* → *syn* conformer (*syn* → *anti* conformer):

$$\Delta H^{\ddagger} \text{ (DFT)} = 7.8 \text{ (1.4) kcal/mol} \quad \{\Delta H^{\ddagger} \text{ (AM1)} = 3.7 \text{ (0.5) kcal/mol}\}.$$

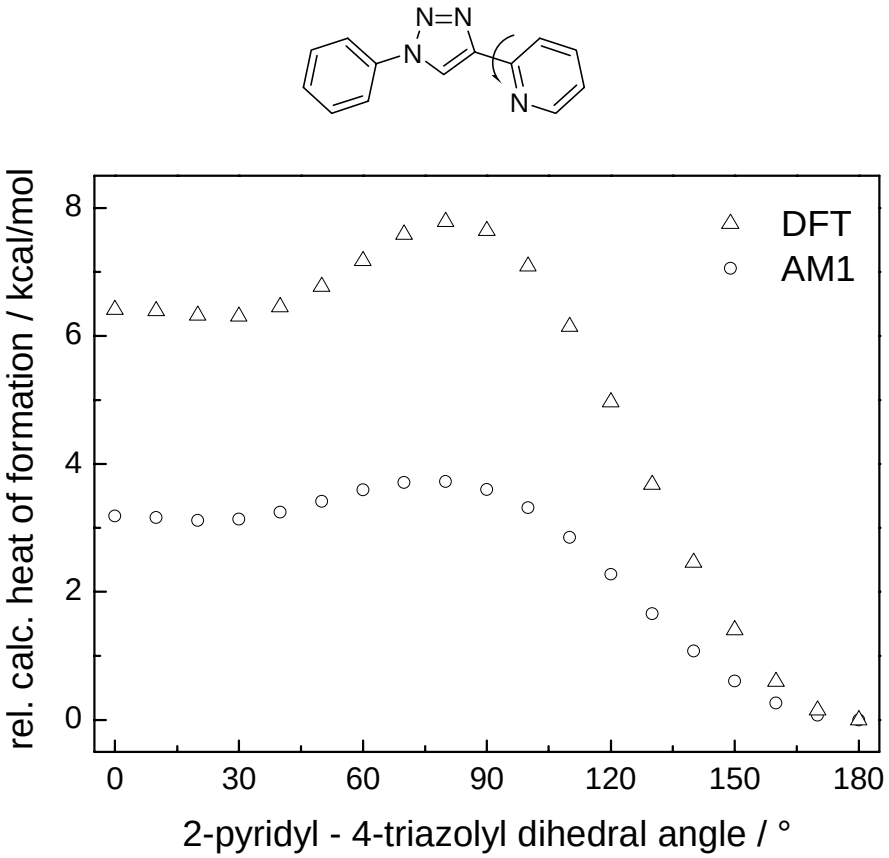
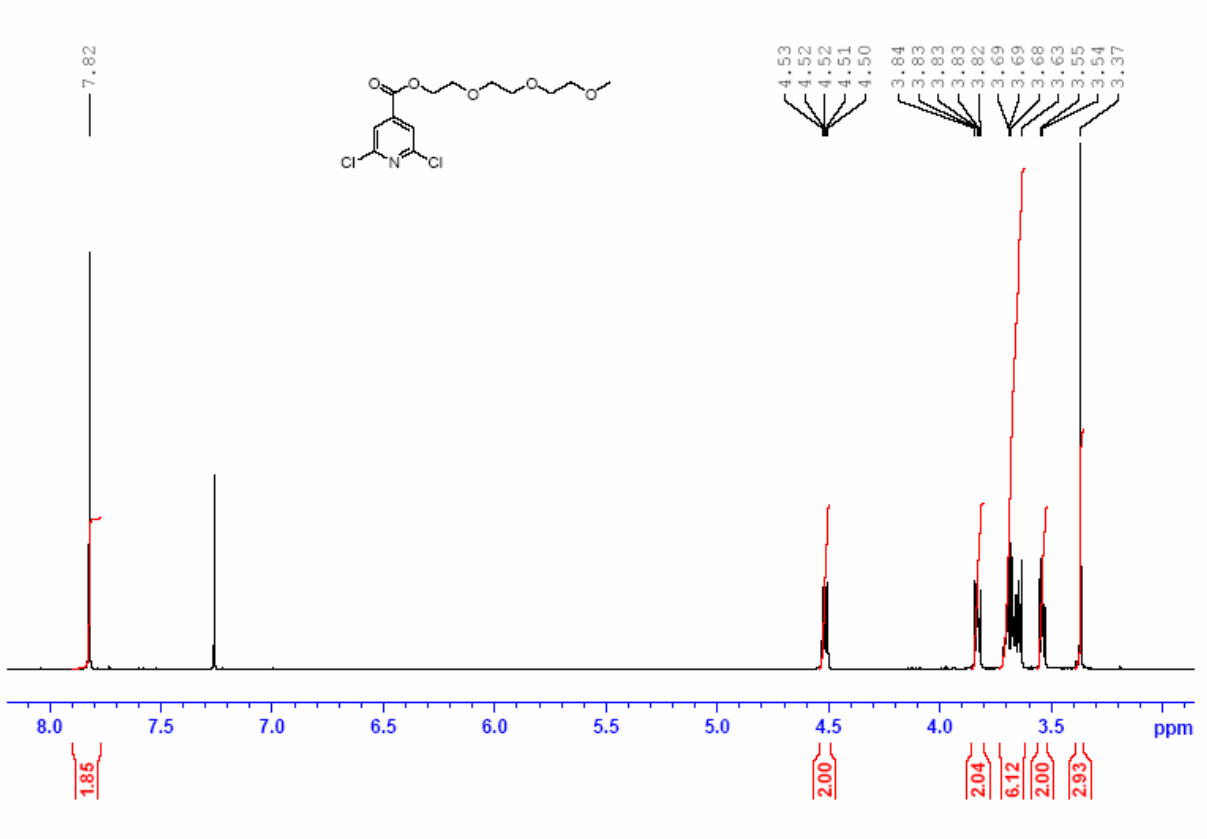


Figure 12. The relative heat of formation calculated using semiempirical (AM1) and DFT theories indicating the preferred *anti* conformation.

Appendix

Please see the following pages for copies of ^{1}H-NMR, ^{13}C-NMR, and NOE spectra of the described compounds.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3.83
3.83
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3.68
3.63
3.55
3.54
3.37
Cl
N
Cl
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7.5
7.0
6.5
6.0
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4.0
3.5
ppm
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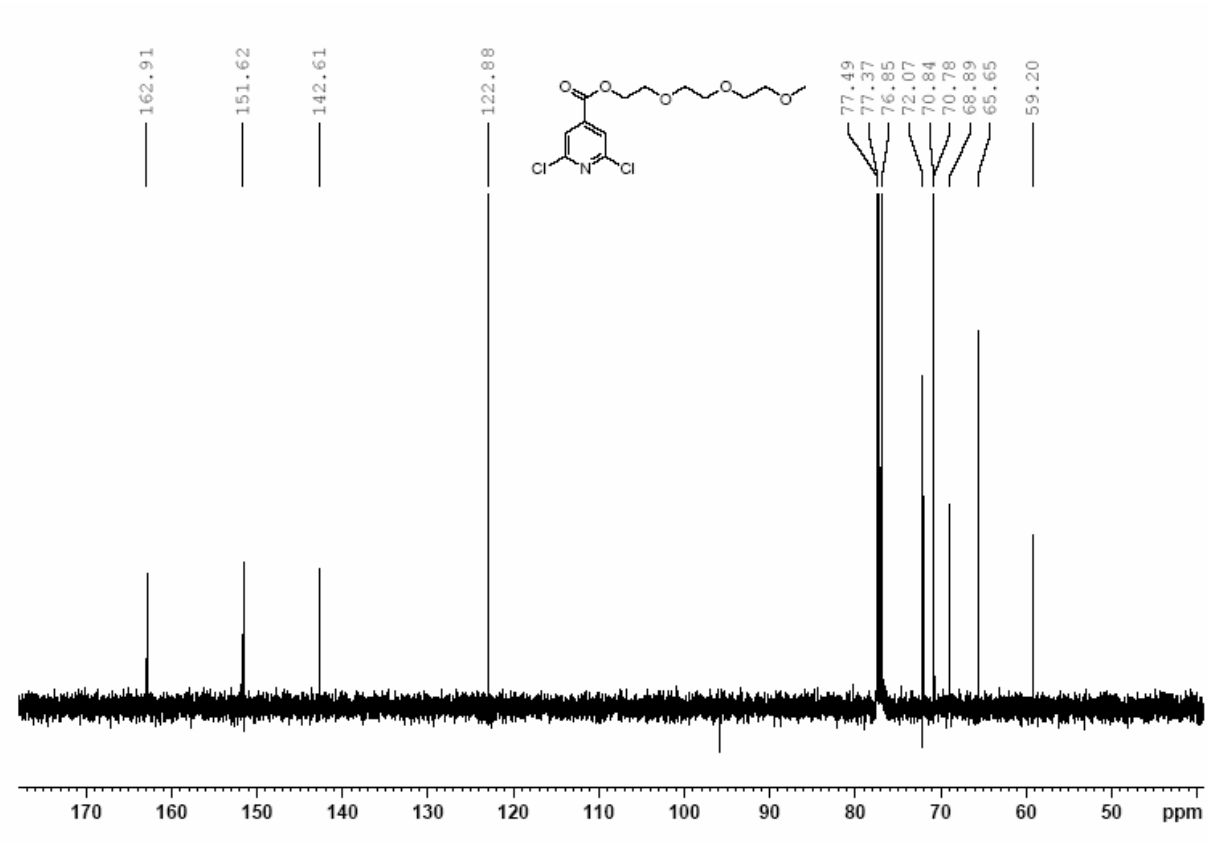
2.00
2.04
6.12
2.00
2.93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142.61
122.88
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77.37
76.85
72.07
70.84
70.78
68.89
65.65
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N
Cl
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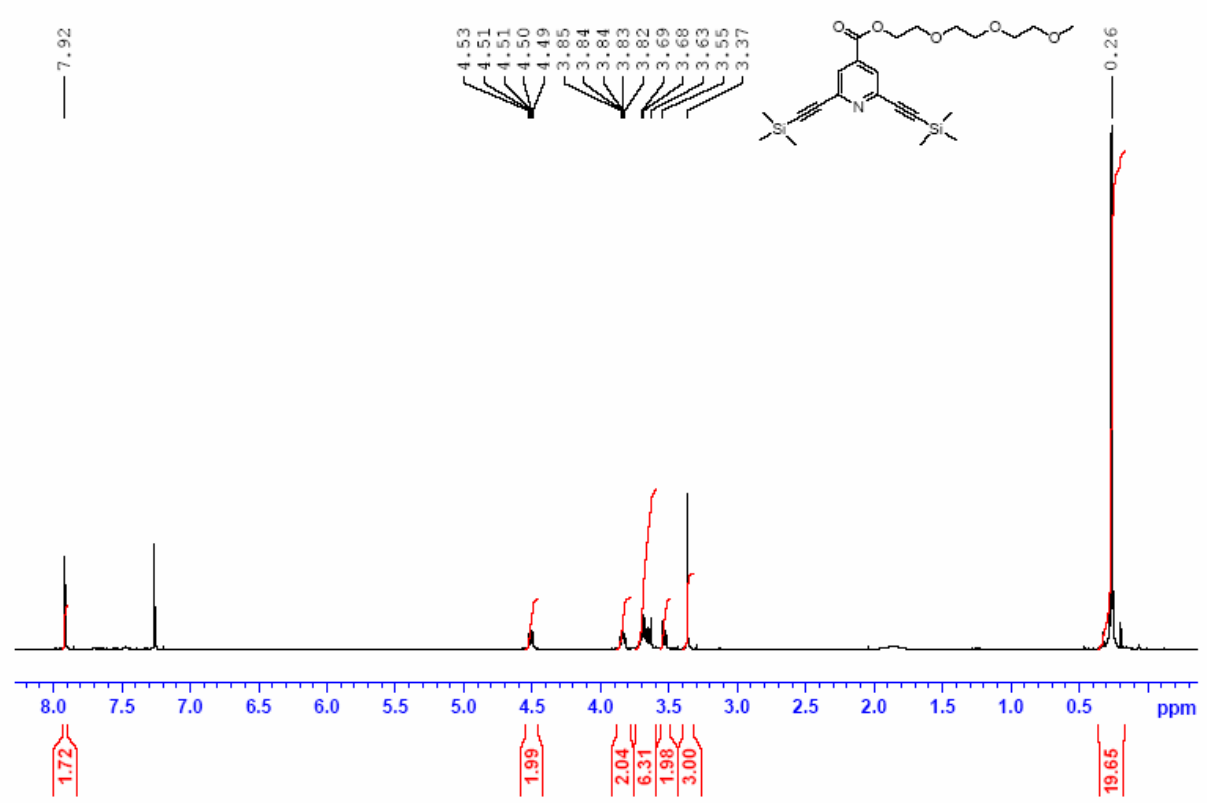
150
140
130
120
110
100
90
80
70
60
50
ppm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3.84
3.84
3.83
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3.68
3.63
3.55
3.37
0.26
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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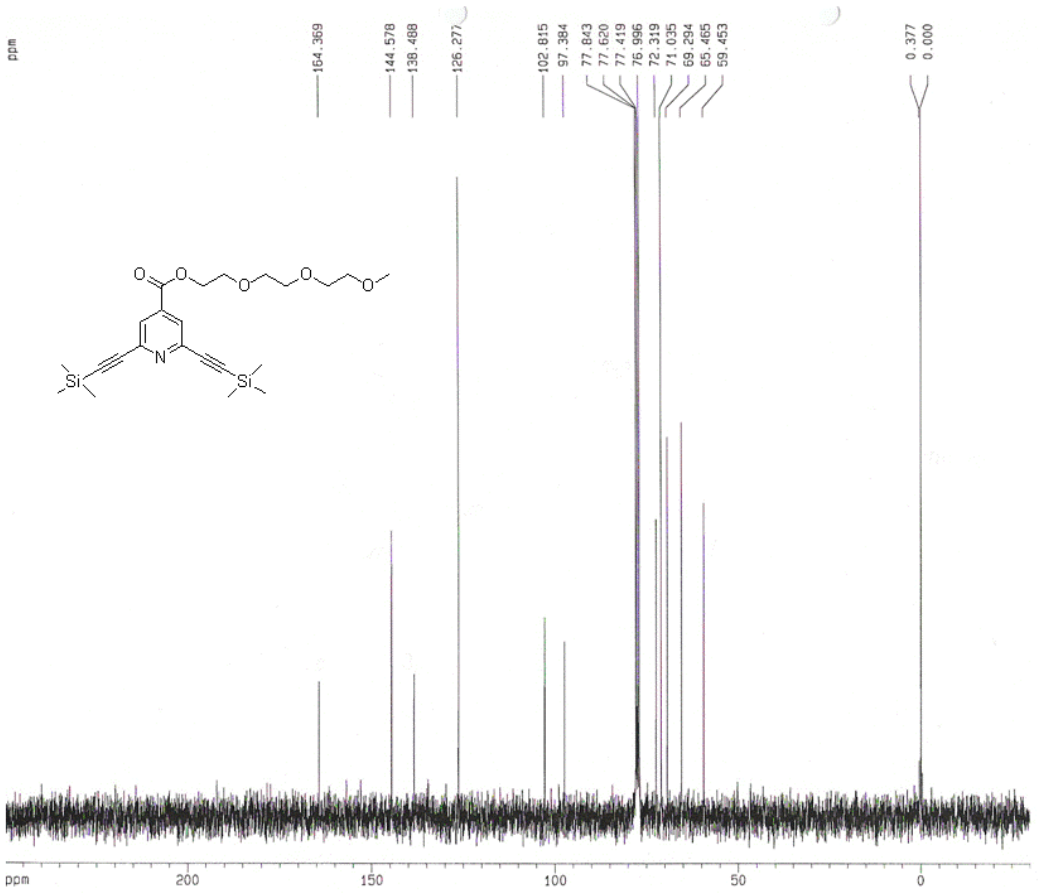
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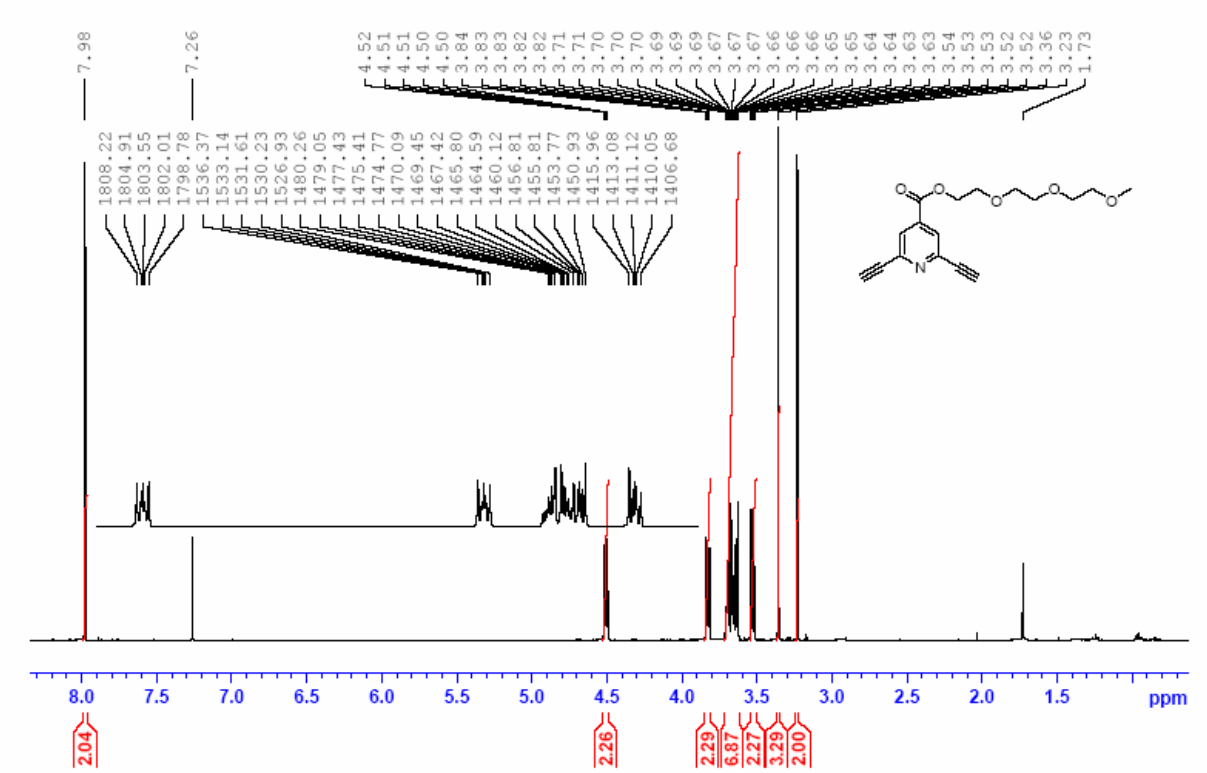
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3.23
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1804.91
1803.55
1802.01
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1526.93
1480.26
1479.05
1477.43
1475.41
1474.77
1470.09
1469.45
1467.42
1465.80
1464.59
1460.12
1456.81
1455.81
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1415.96
1413.08
1411.12
1410.05
1406.68
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O
O
O
O
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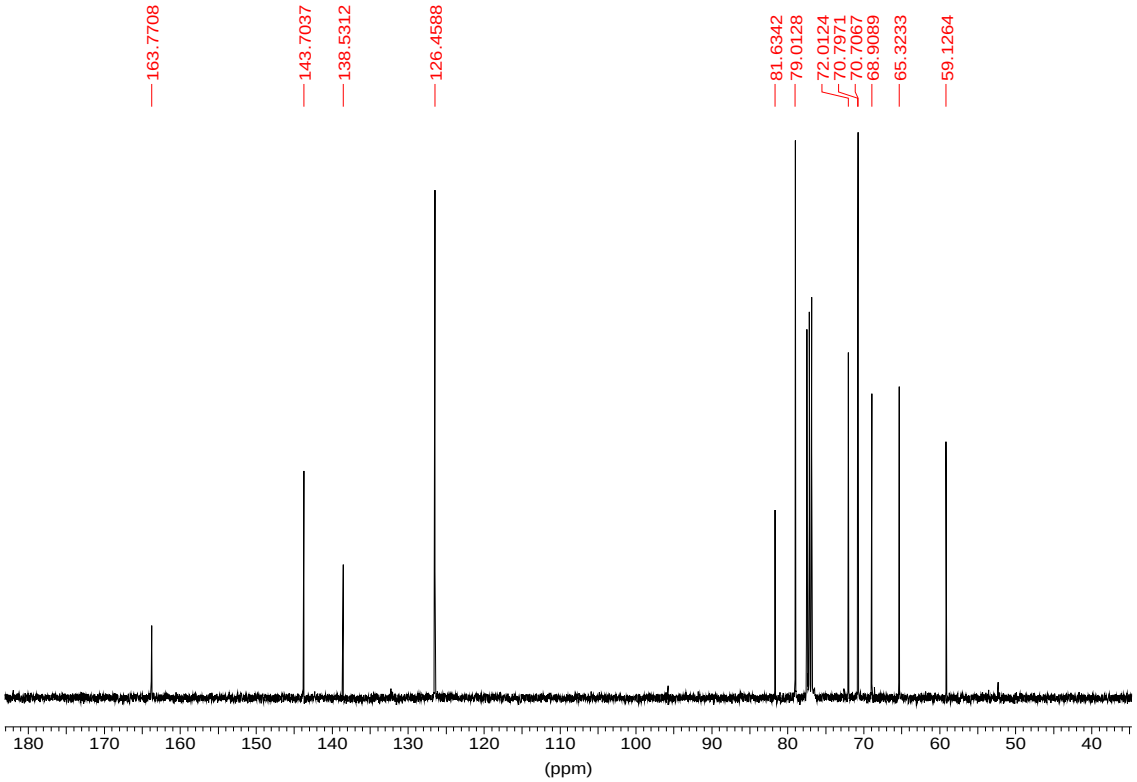
2.00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90
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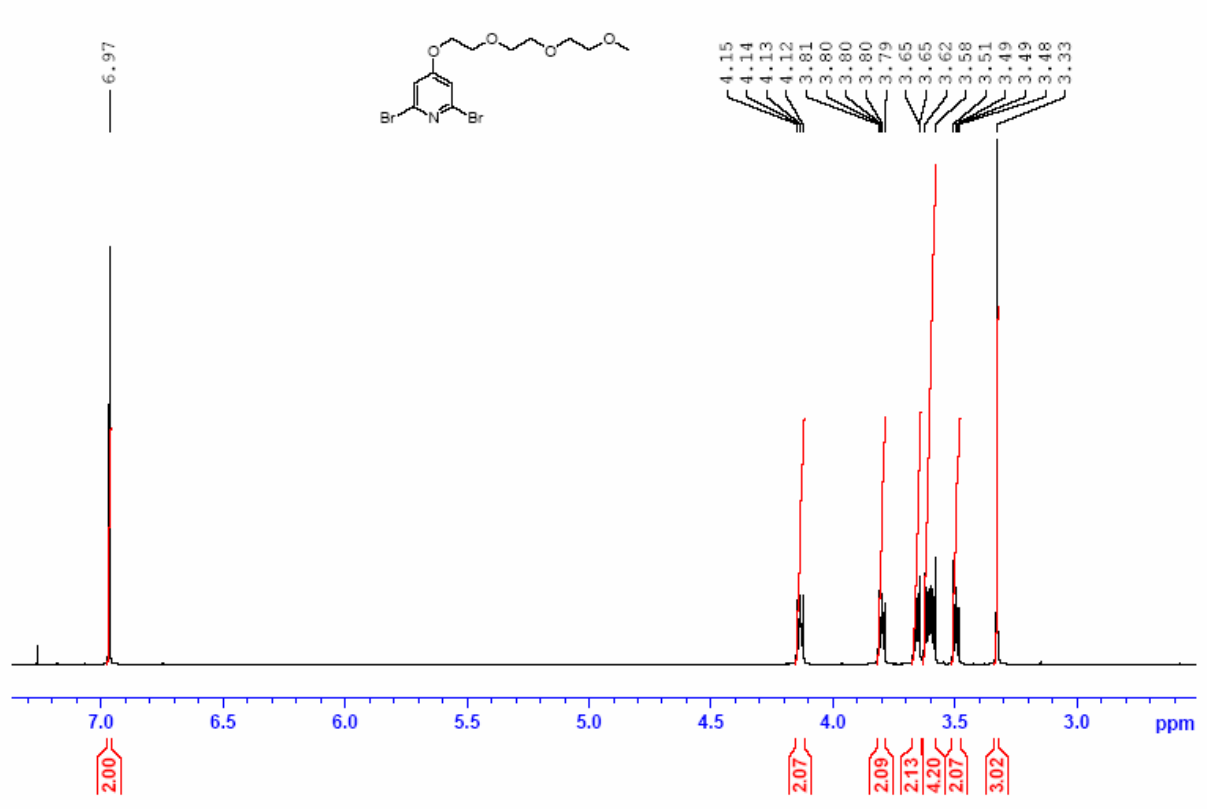
50
40
(ppm)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3.62
3.58
3.51
3.49
3.49
3.48
3.33
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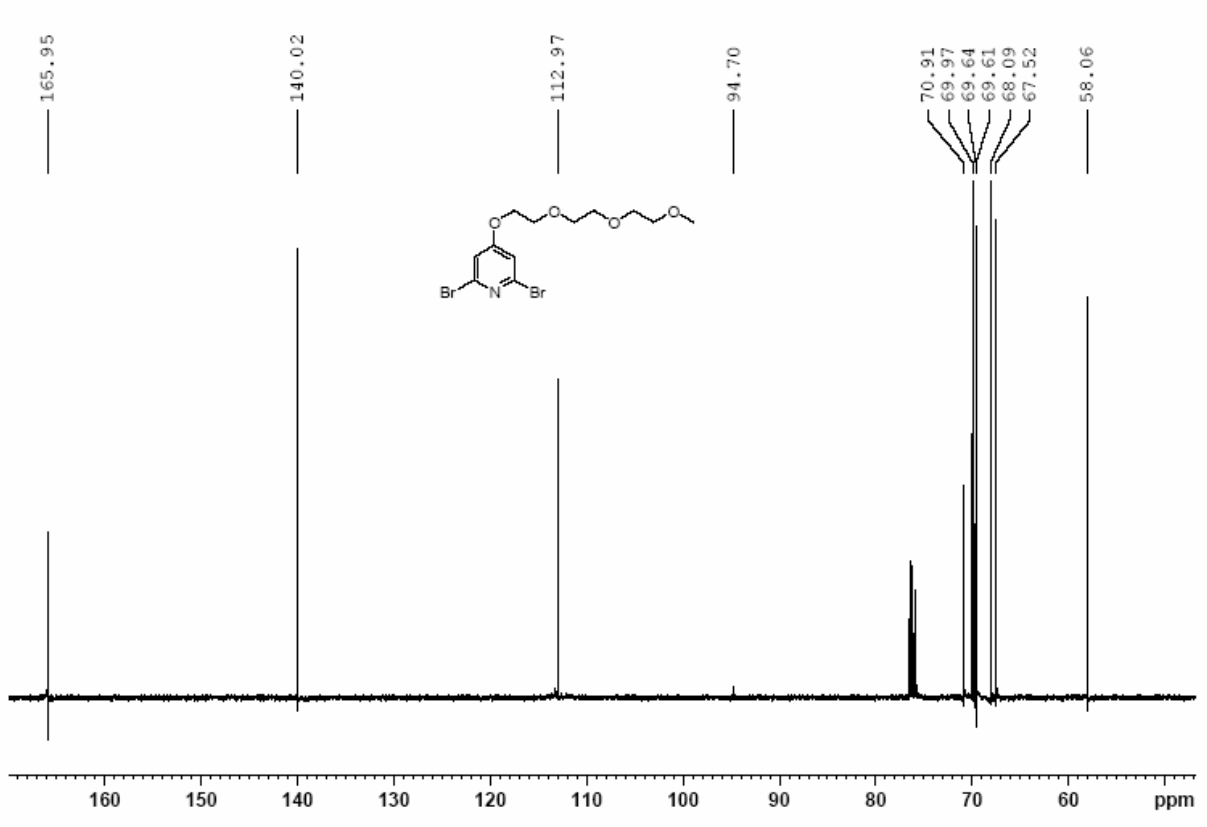
2.07
3.02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69.61
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Br
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120
110
100
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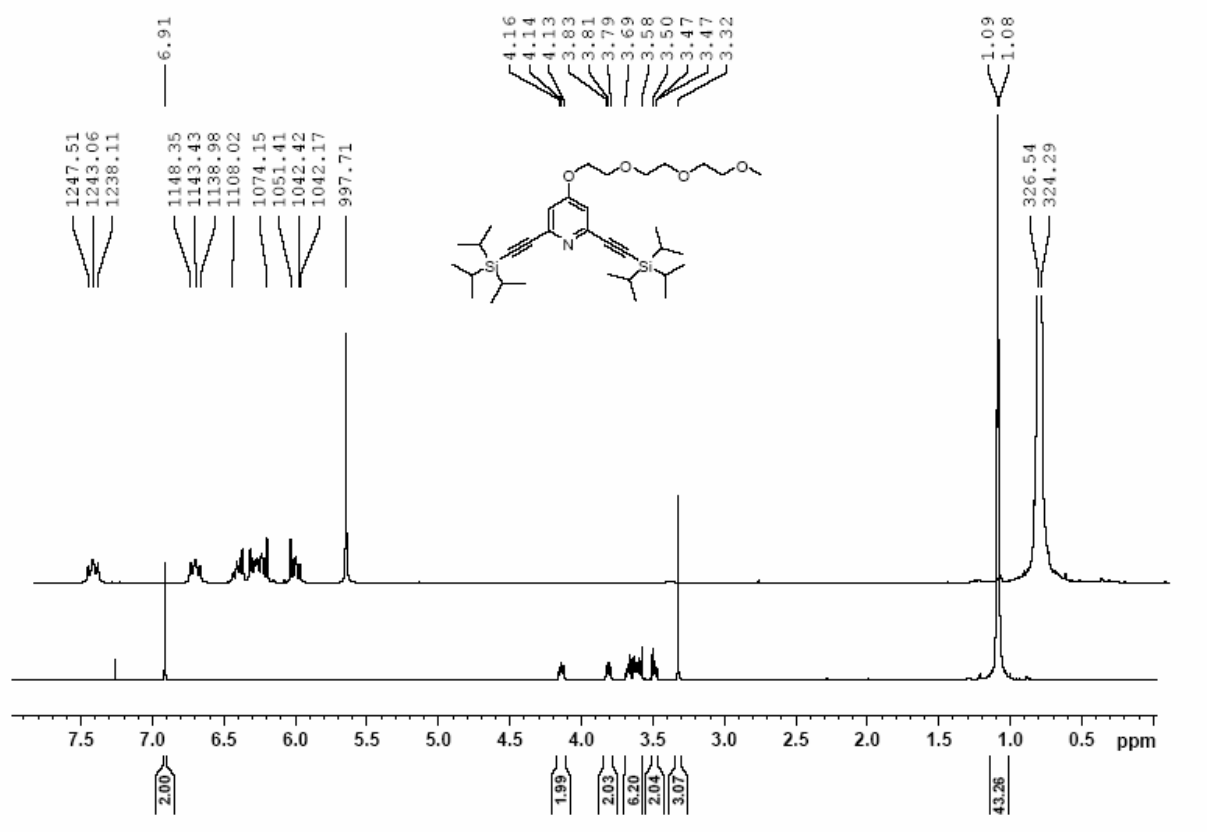
80
70
60
ppm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3.69
3.58
3.50
3.47
3.32
1.09
1.08
1247.51
1243.06
1238.11
1148.35
1143.43
1138.98
1108.02
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1051.41
1042.42
1042.17
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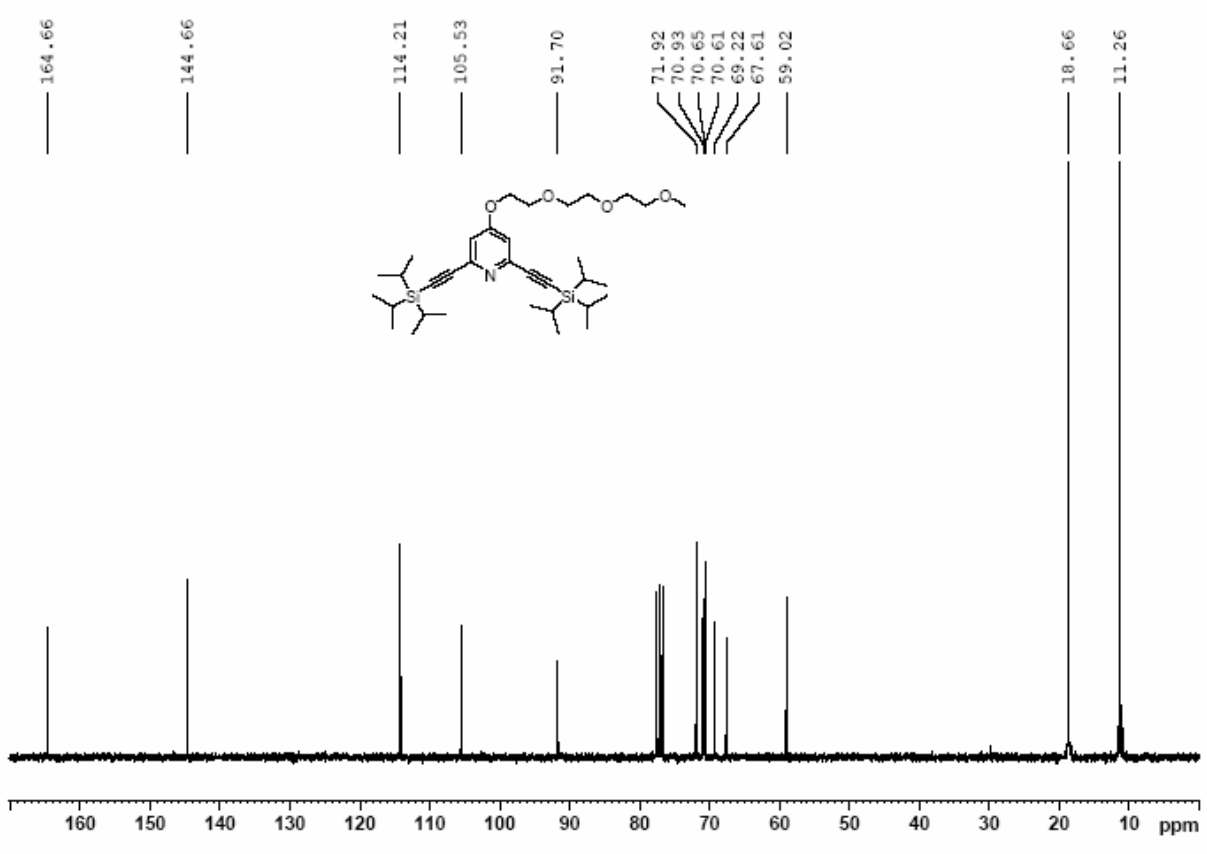
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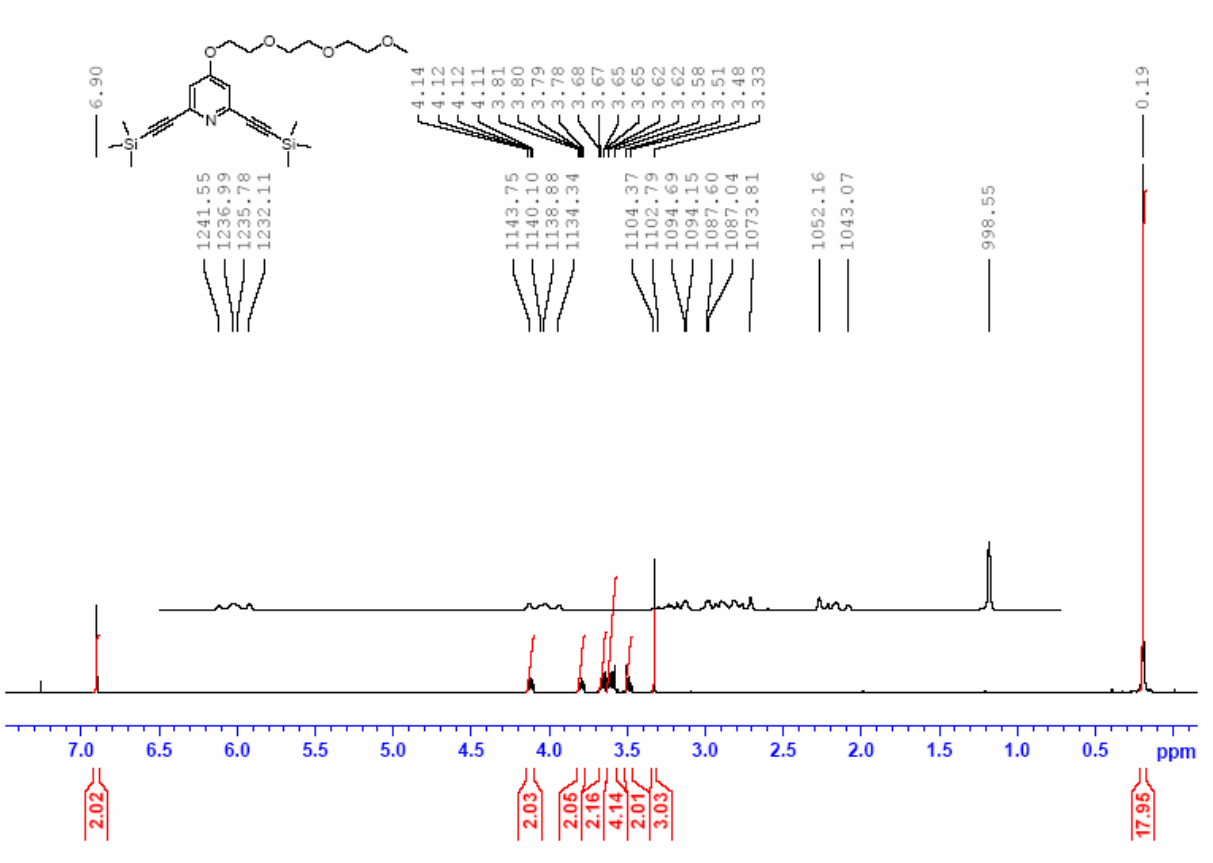
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3.79
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3.68
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3.65
3.62
3.62
3.58
3.51
3.48
3.33
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1235.78
1232.11
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5.5
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3.0
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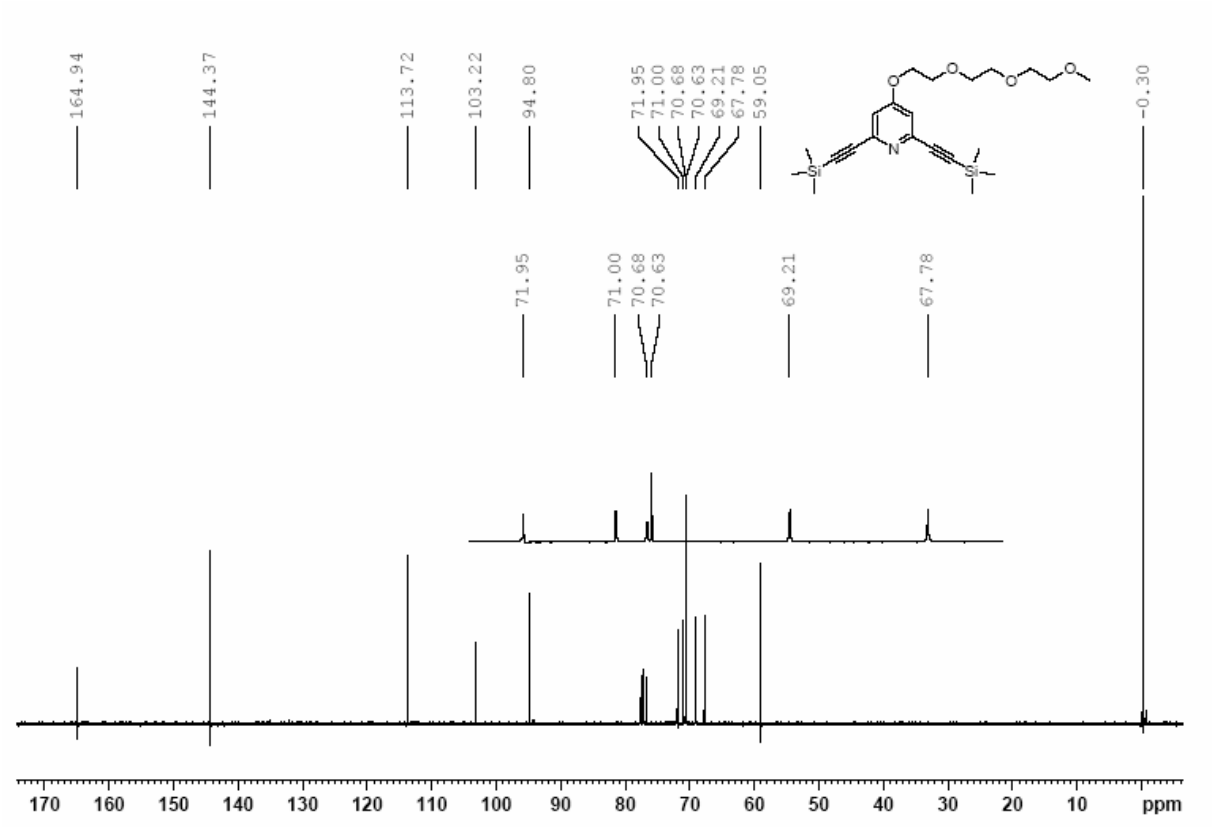
17.95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71.00
70.68
70.63
69.21
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150
140
130
120
110
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30
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10
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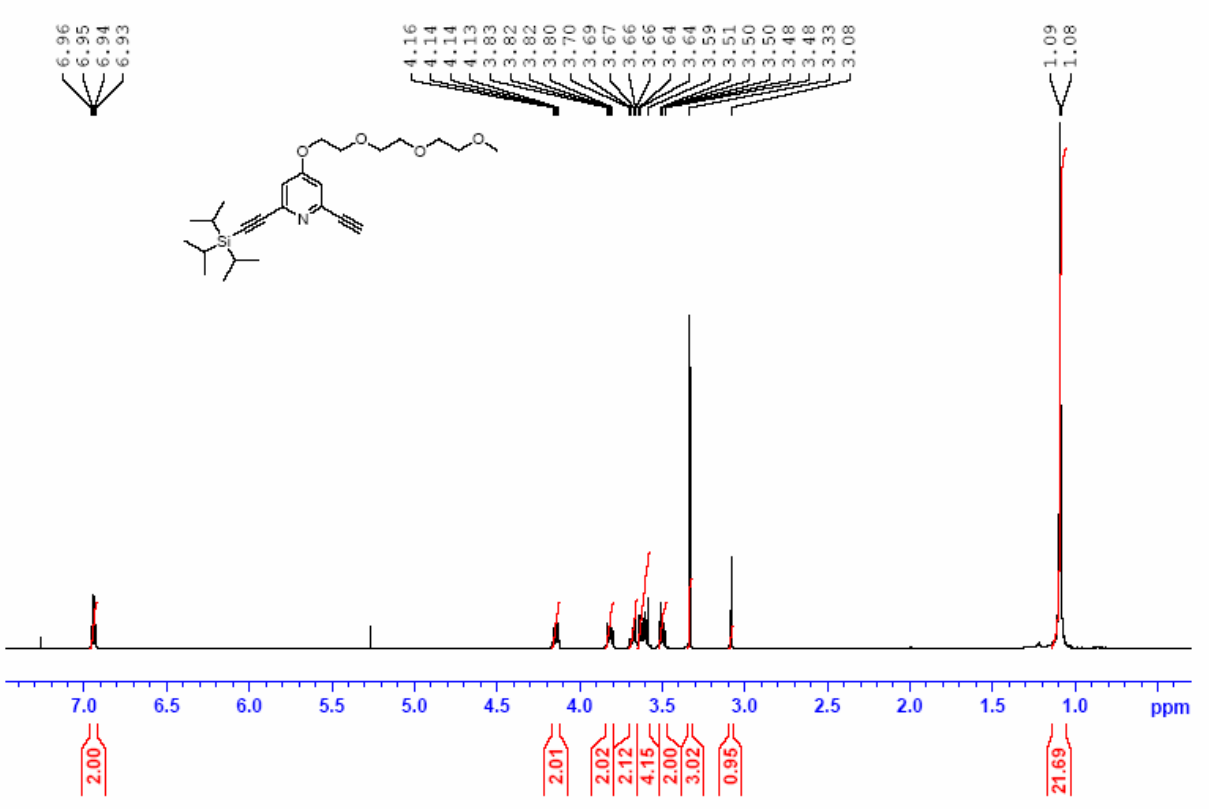
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6.94
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4.14
4.13
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3.69
3.67
3.66
3.66
3.64
3.64
3.59
3.51
3.50
3.50
3.48
3.48
3.33
3.08
1.09
1.08
7.0
6.5
6.0
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5.0
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3.0
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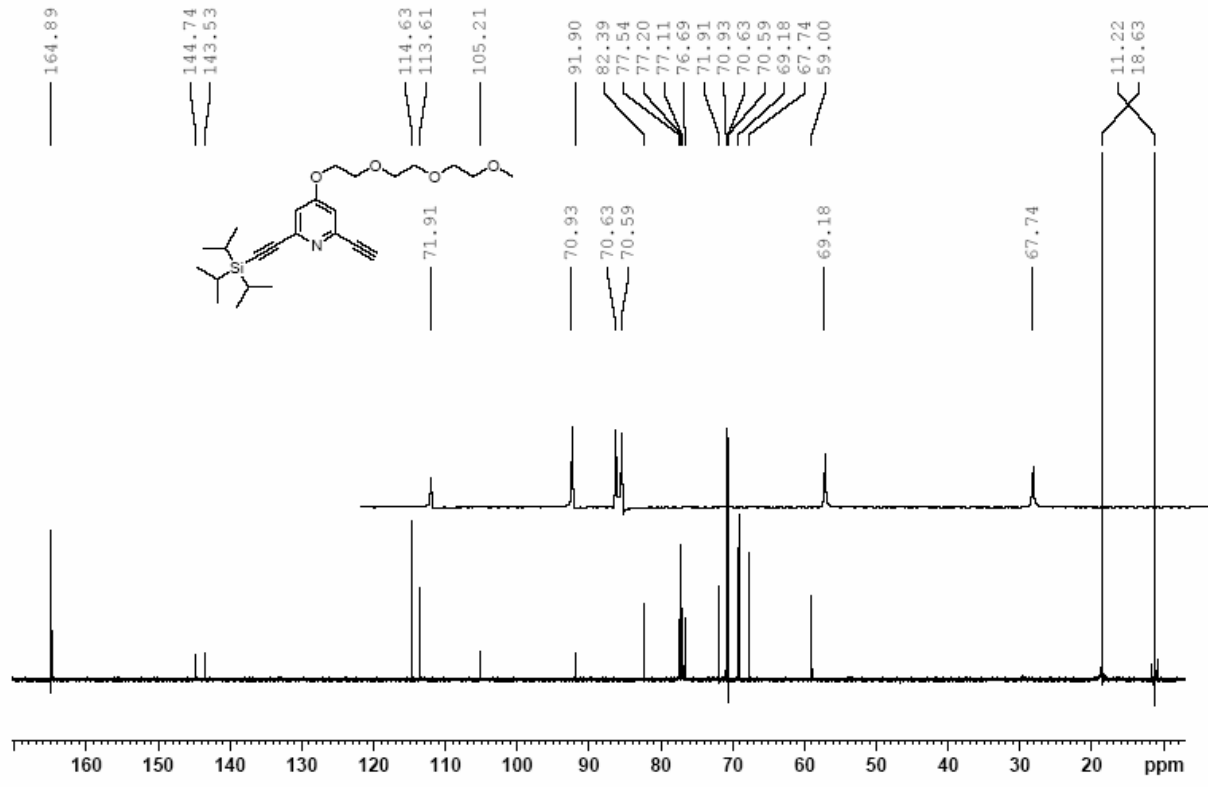
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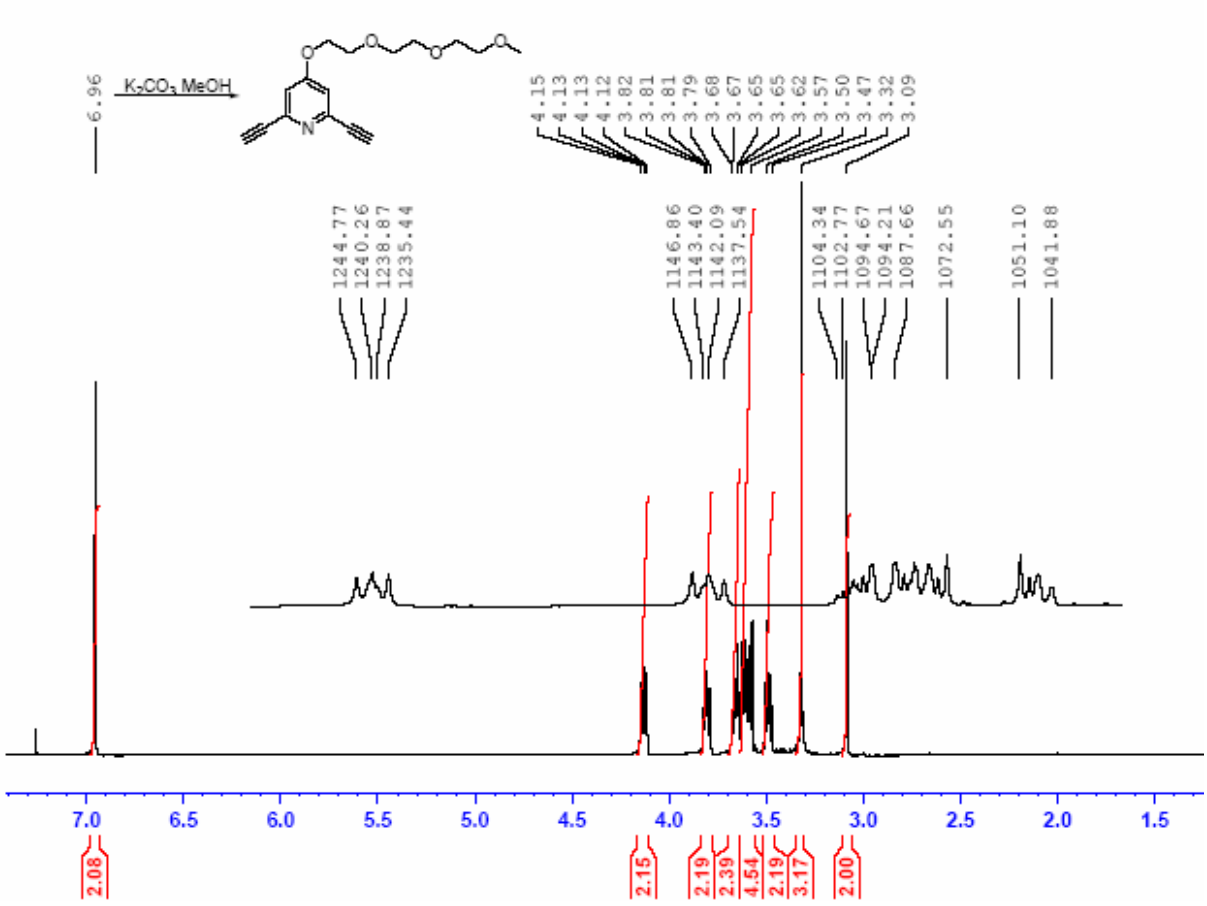
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1142.09
1137.54
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1102.77
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4.5
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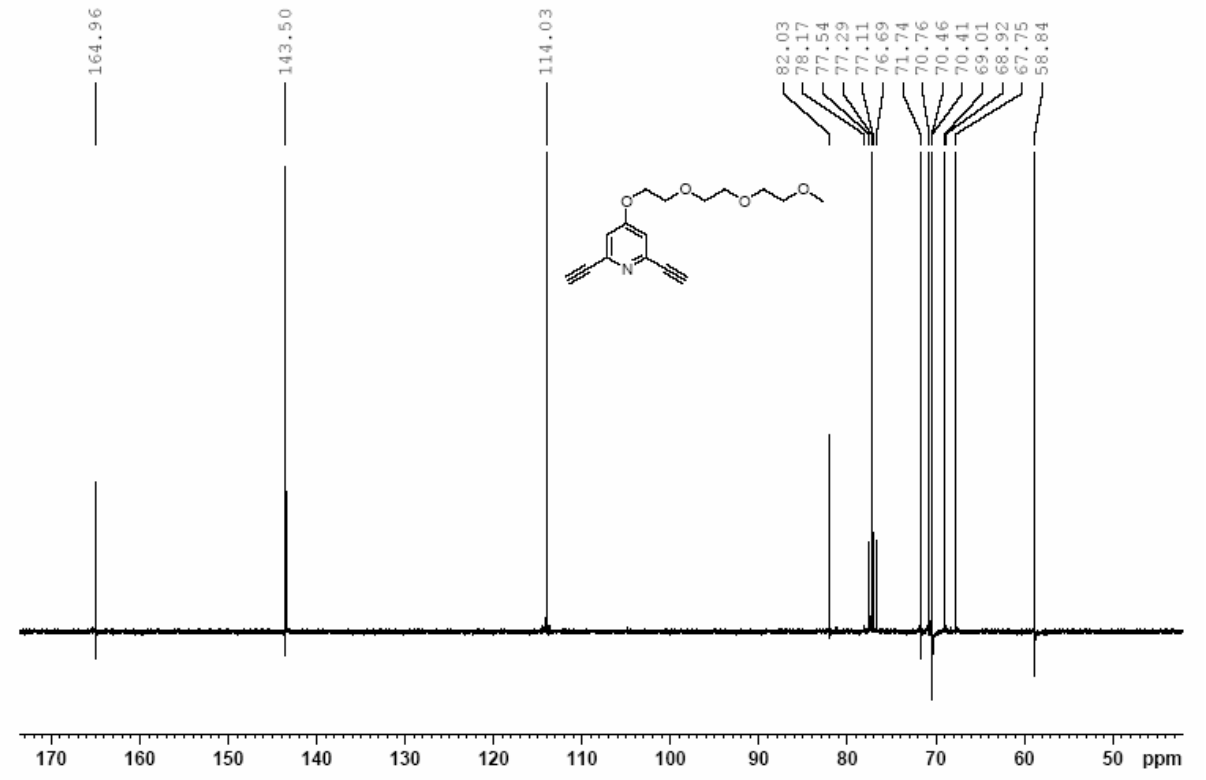
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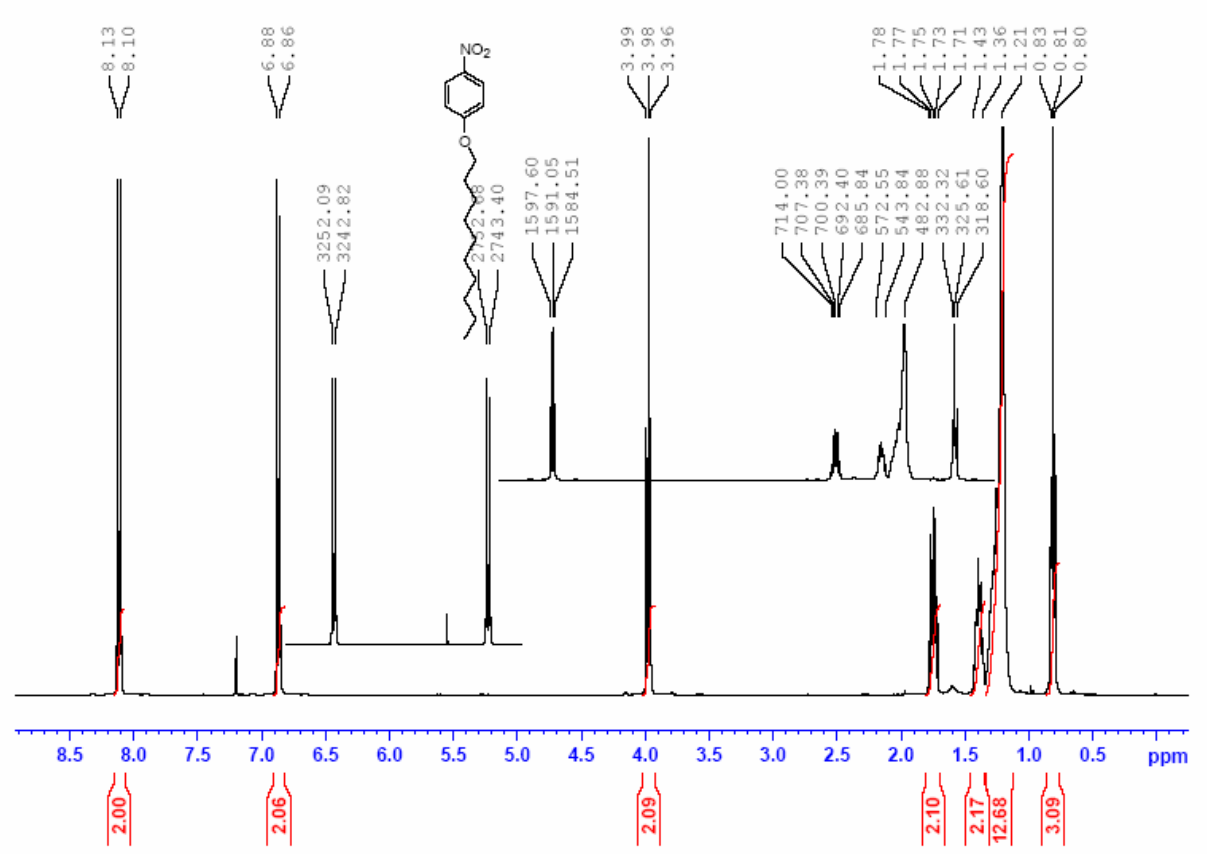
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1.36
1.21
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0.81
0.80
3252.09
3242.82
2922.68
2743.40
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1584.51
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700.39
692.40
685.84
572.55
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482.88
332.32
325.61
318.60
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7.0
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5.5
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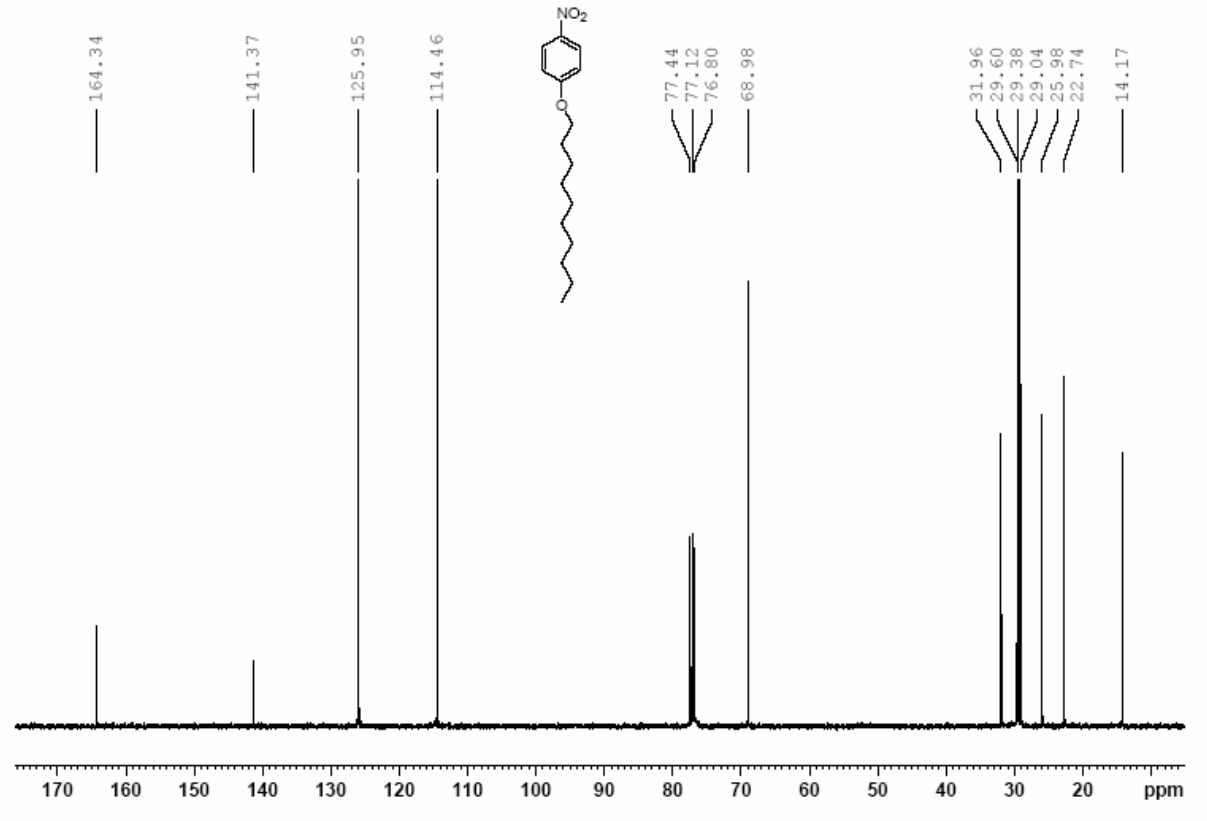
3.09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68.98
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25.98
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150
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120
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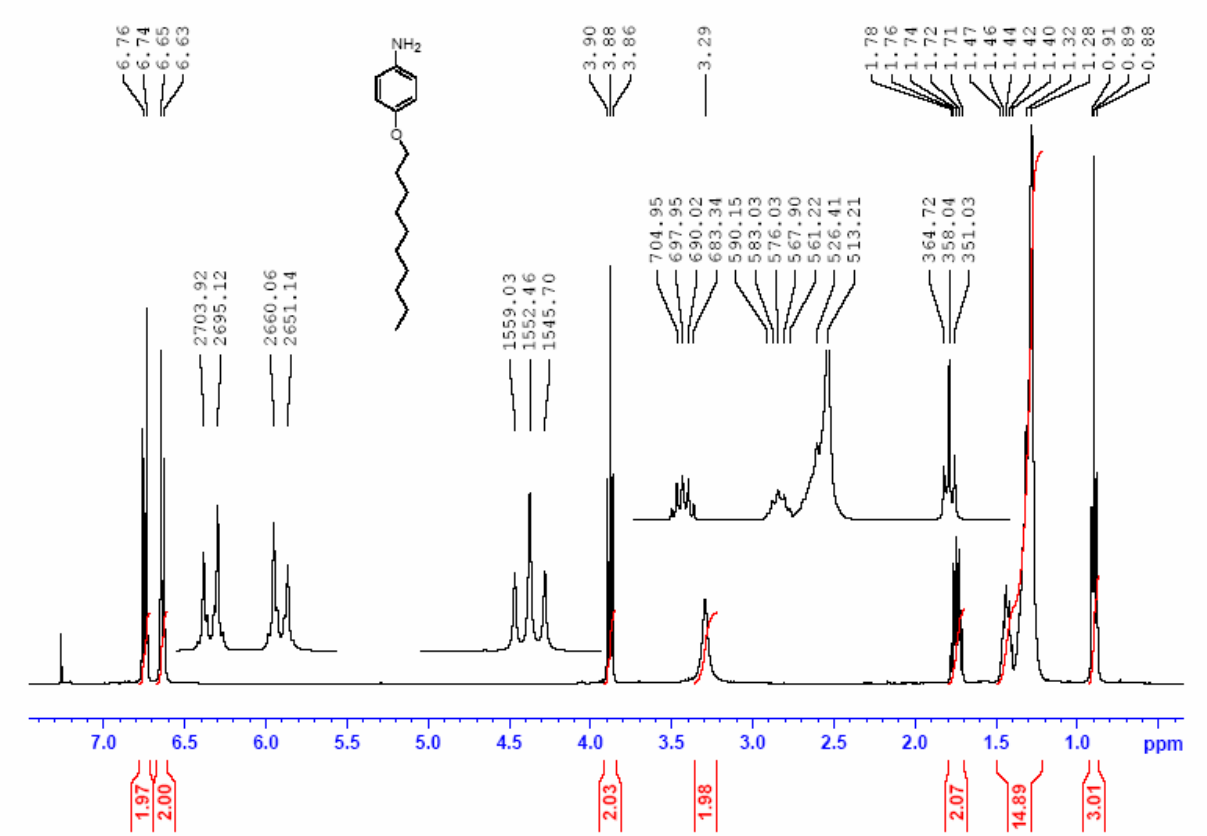
30
20
ppm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1.71
1.47
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1.40
1.32
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0.89
0.88
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697.95
690.02
683.34
590.15
583.03
576.03
567.90
561.22
526.41
513.21
364.72
358.04
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6.0
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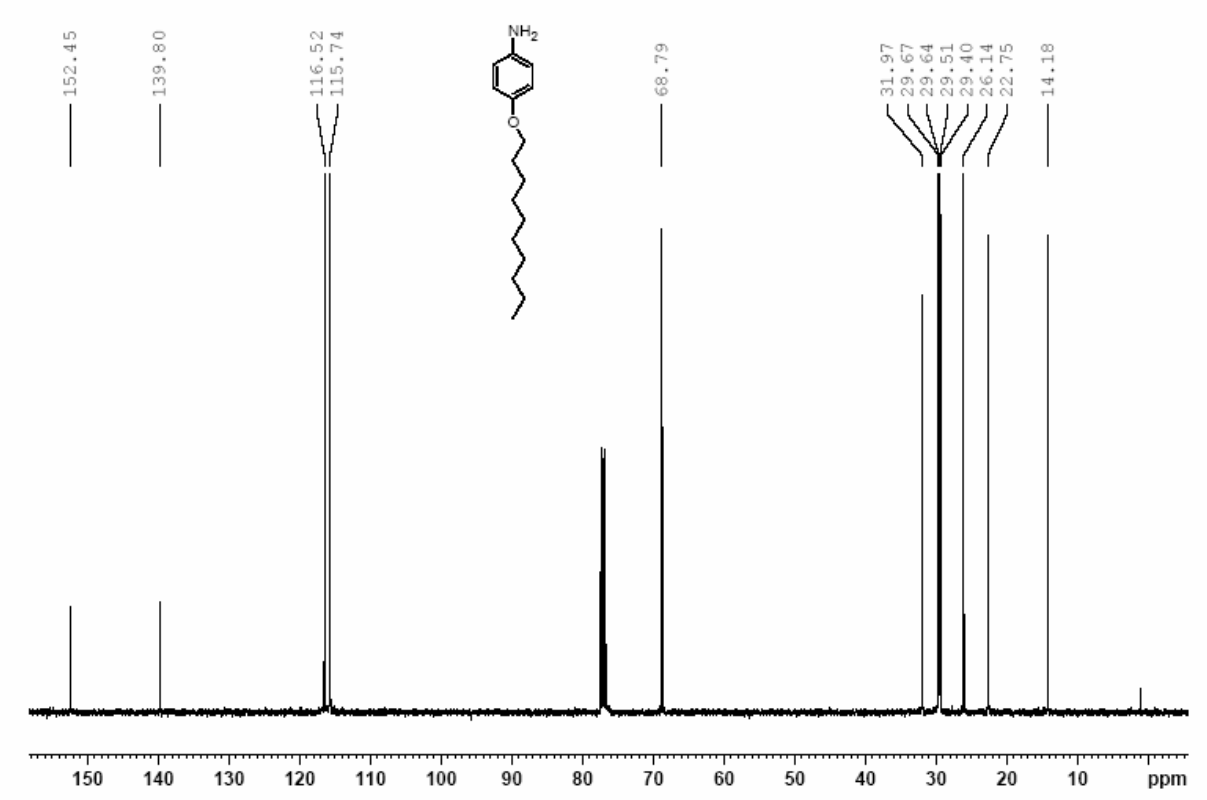
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O
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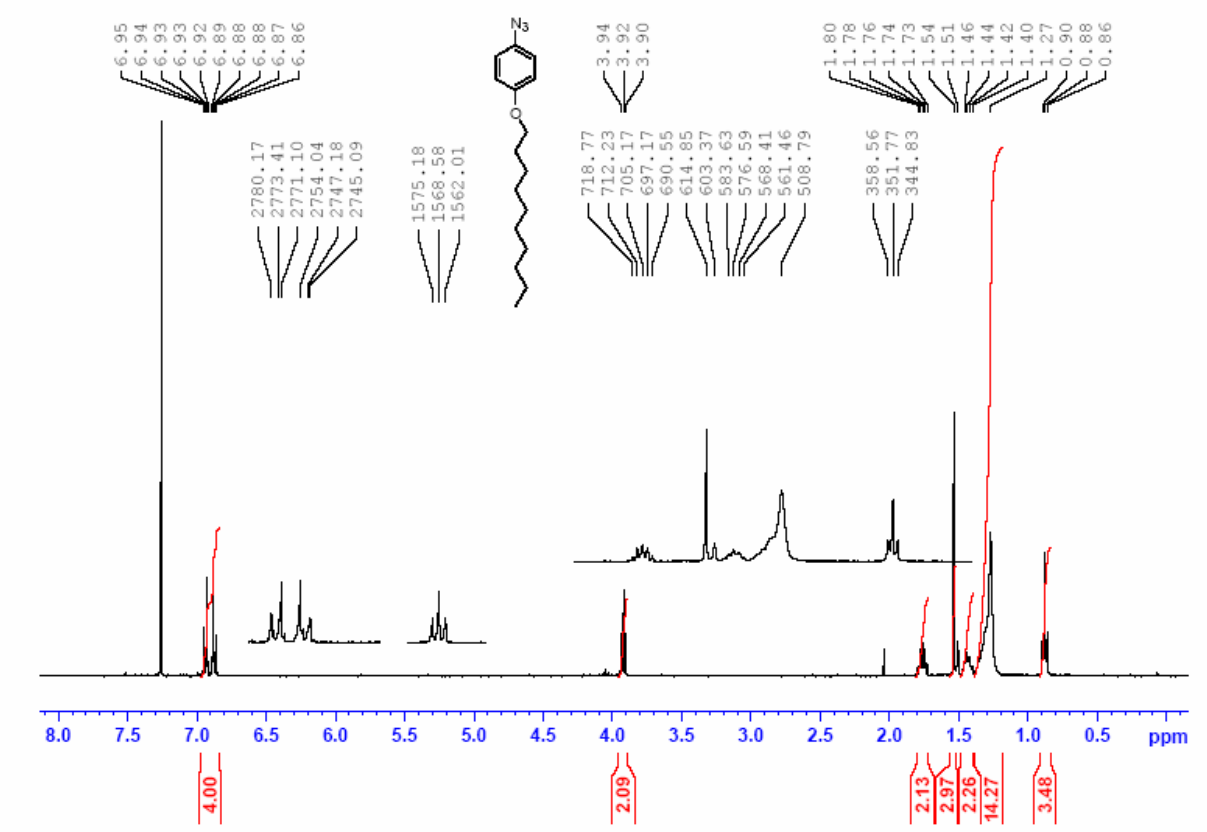
10
ppm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6.88
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1.78
1.76
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1.46
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1.42
1.40
1.27
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0.88
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2771.10
2754.04
2747.18
2745.09
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1568.58
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718.77
712.23
705.17
697.17
690.55
614.85
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561.46
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7.0
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5.5
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4.0
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2.0
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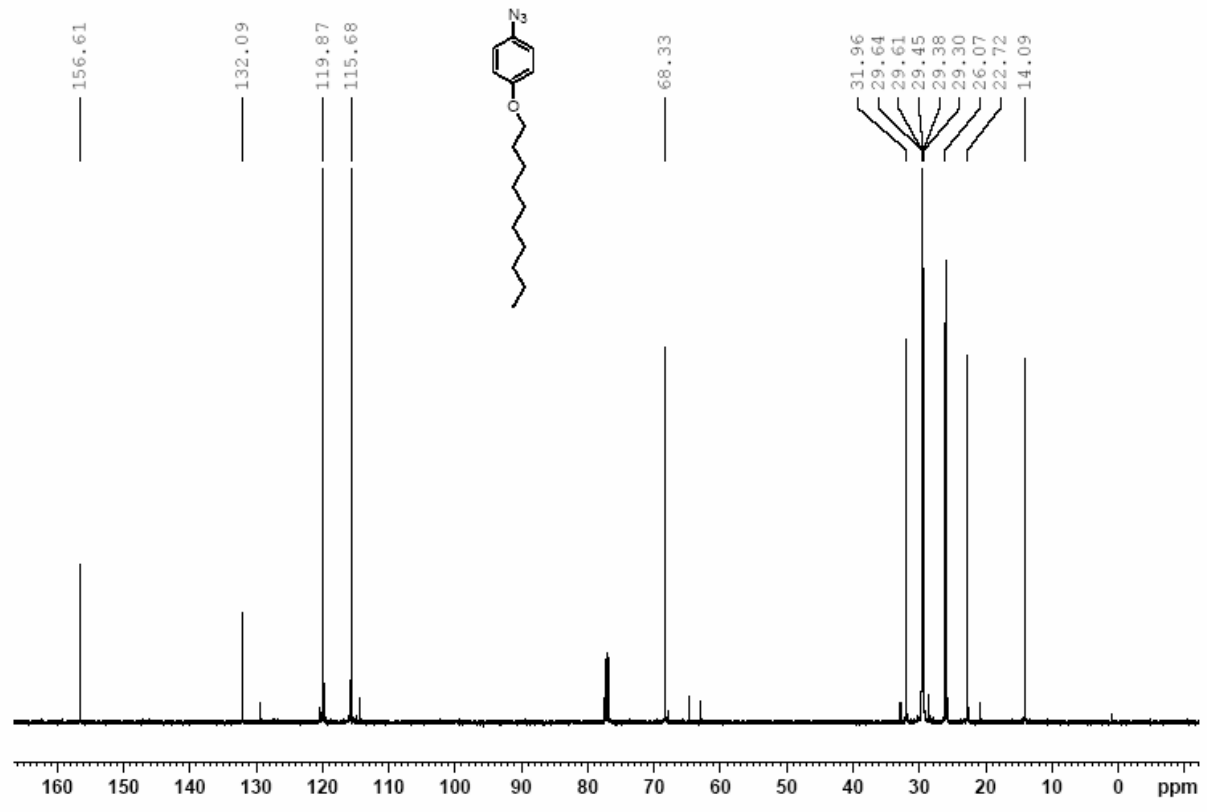
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31.96
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29.38
29.30
26.07
22.72
14.09
N3
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130
120
110
100
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20
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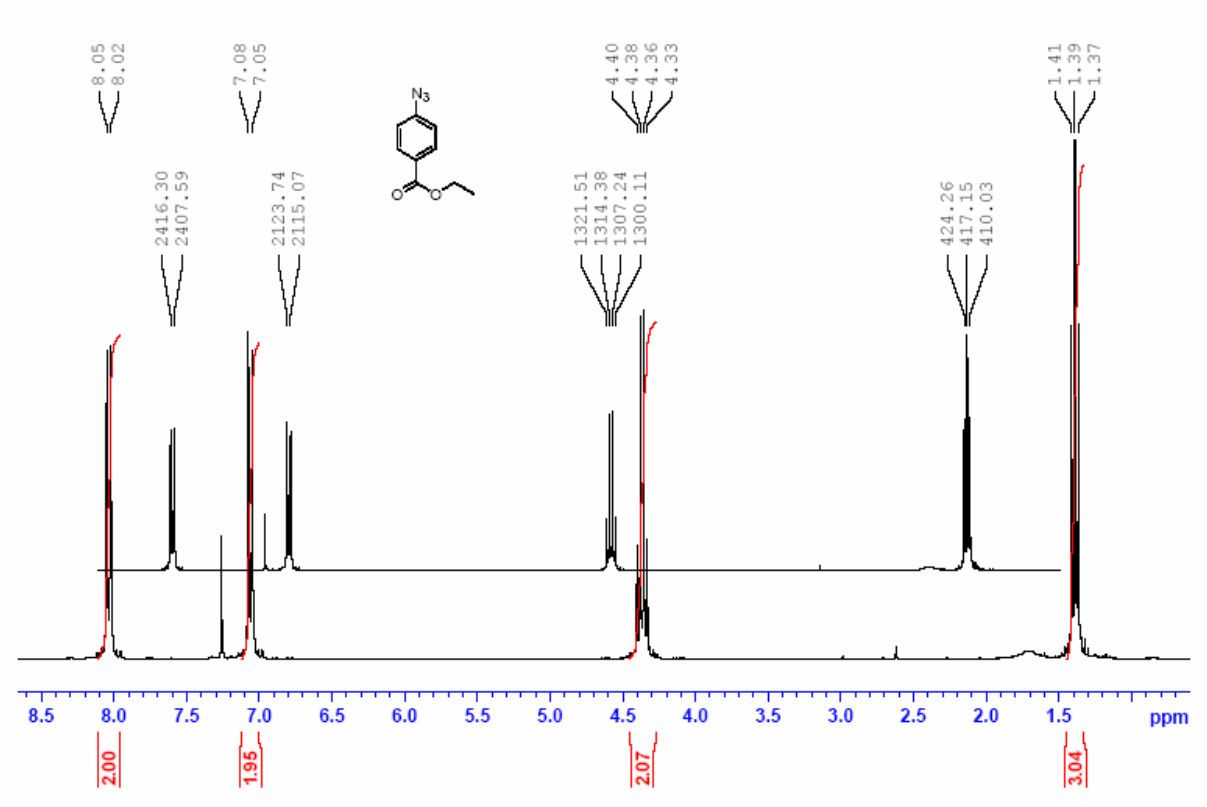
0
ppm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1.39
1.37
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2407.59
2123.74
2115.07
1321.51
1314.38
1307.24
1300.11
424.26
417.15
410.03
N3
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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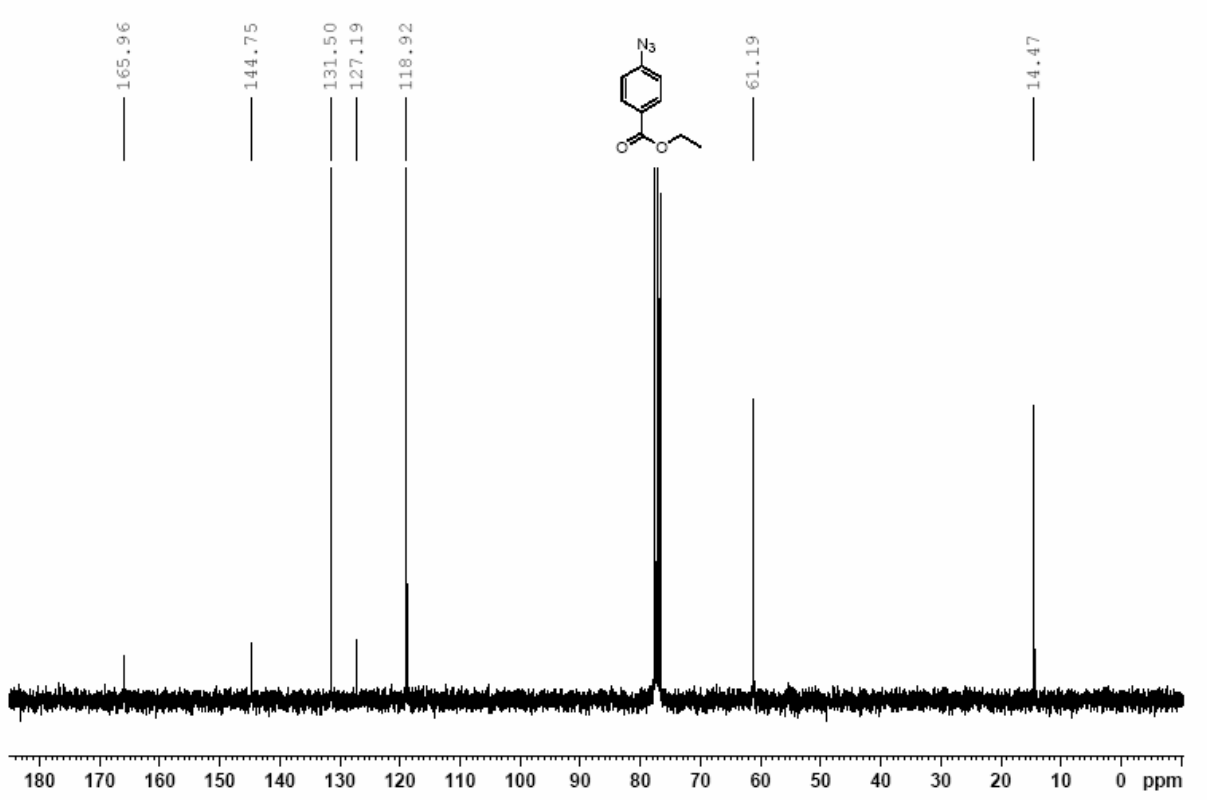
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N3
O
O
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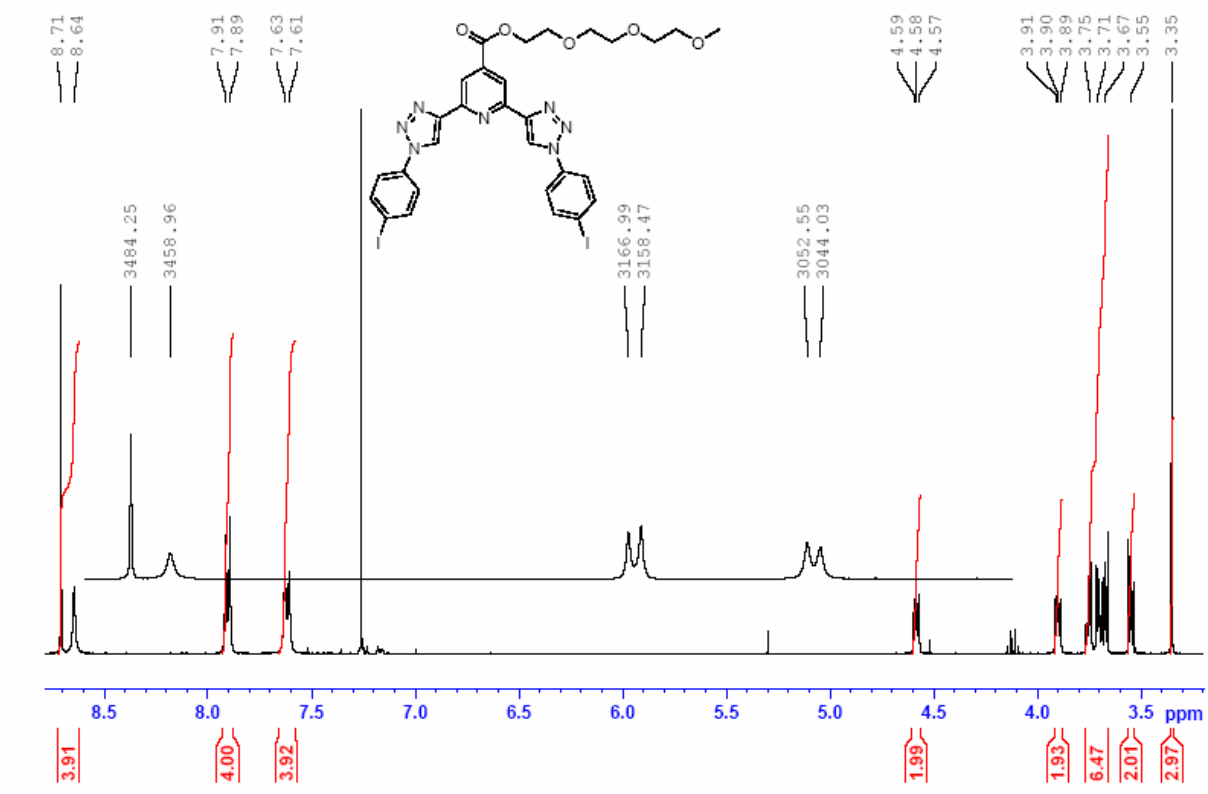
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3.75
3.71
3.67
3.55
3.35
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3166.99
3158.47
3052.55
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8.5
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7.5
7.0
6.5
6.0
5.5
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ppm
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1.99
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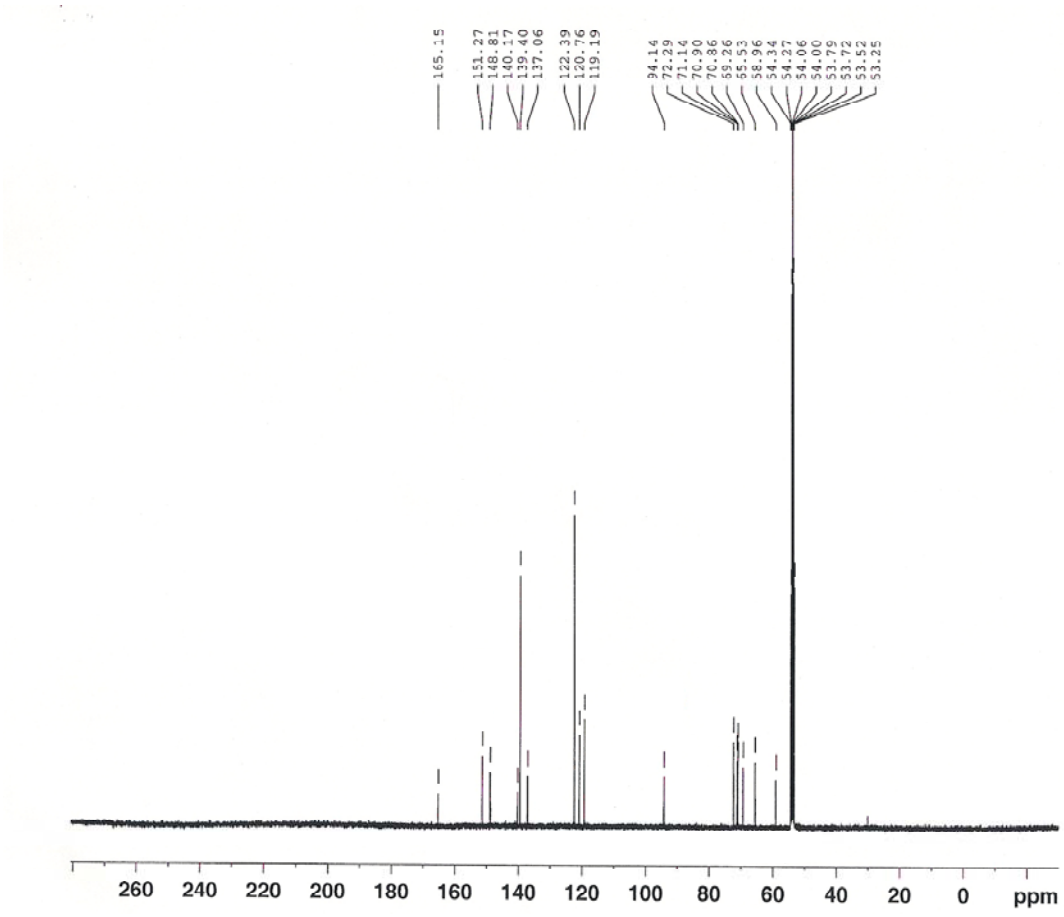
2.01
2.97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120.76
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72.29
71.14
70.90
70.86
59.26
55.53
54.96
54.34
54.27
54.06
54.00
53.79
53.72
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53.25
260
240
220
200
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160
140
120
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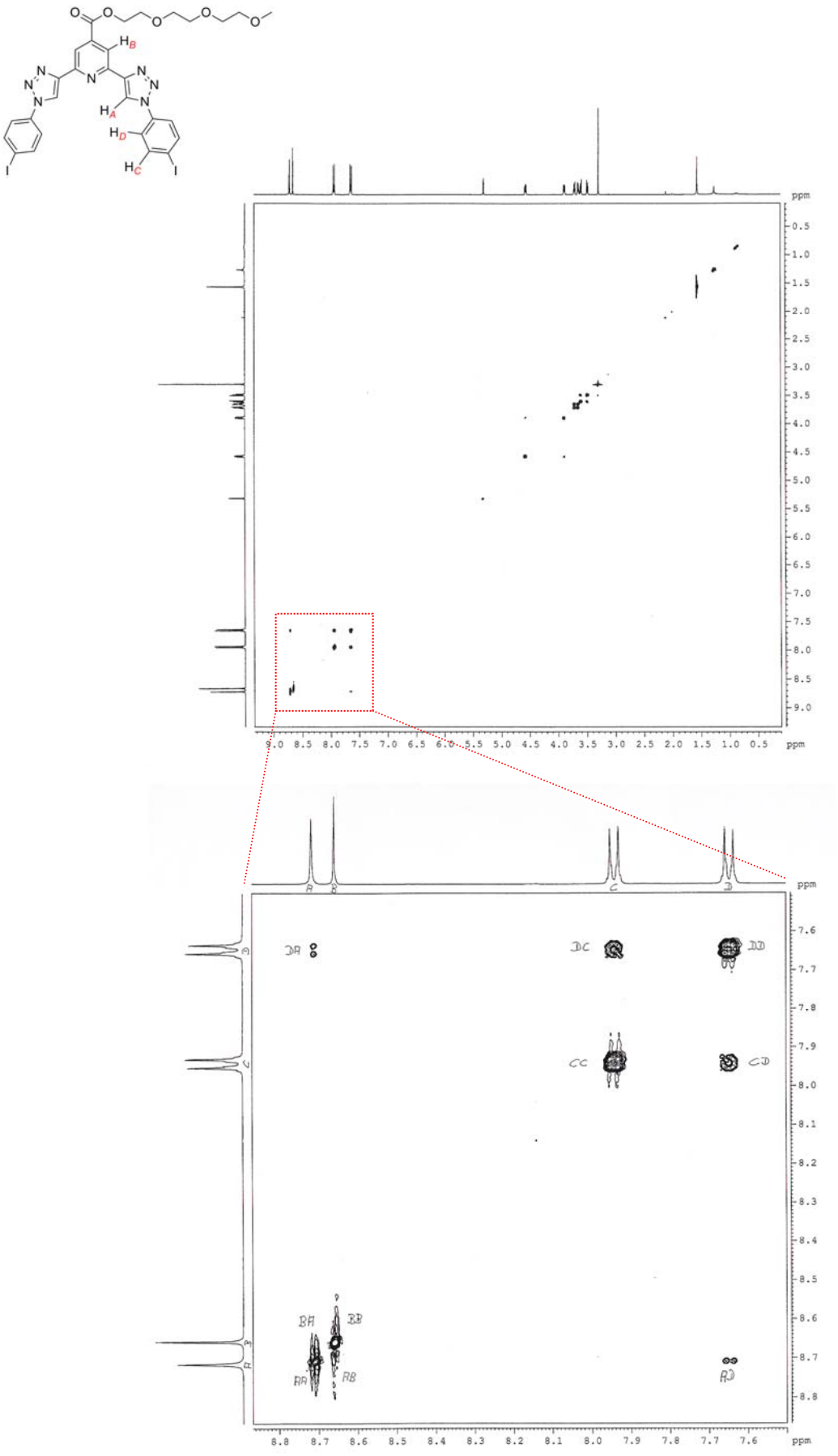
60
40
20
0
ppm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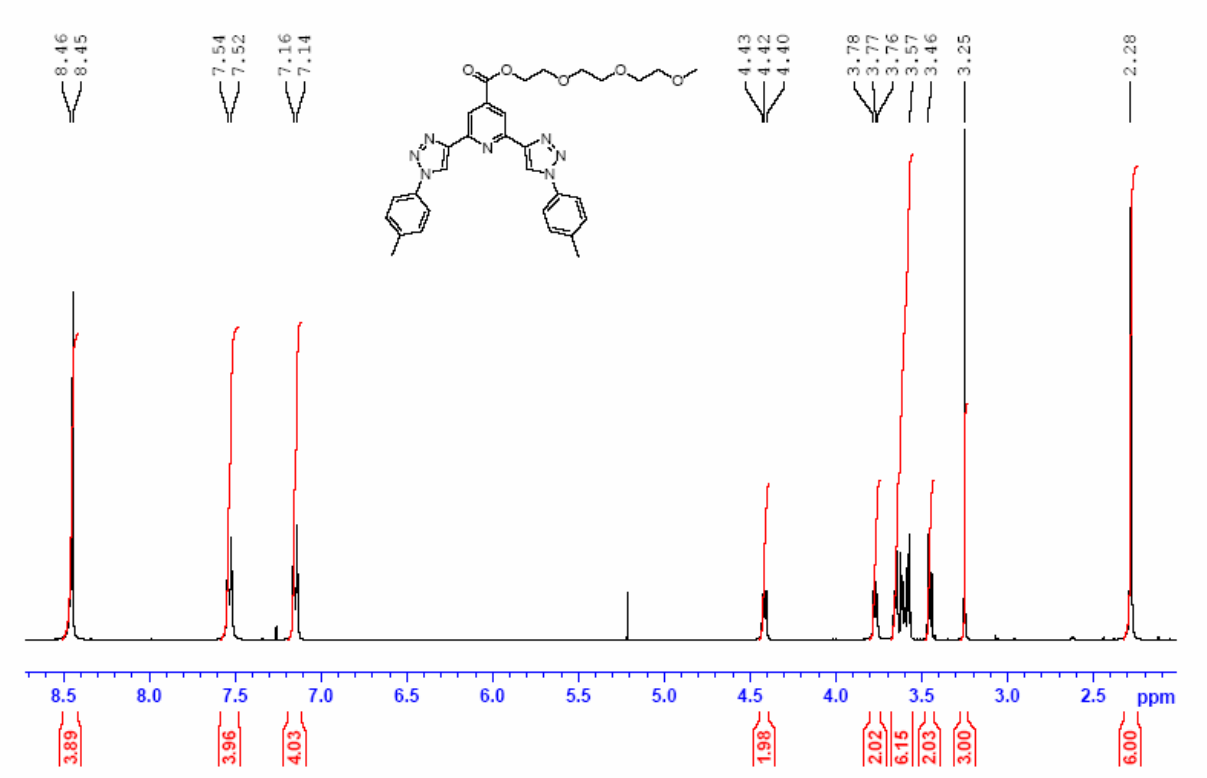
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6
ppm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4.42
4.40
3.78
3.77
3.76
3.57
3.46
3.25
2.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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ppm
3.89
3.96
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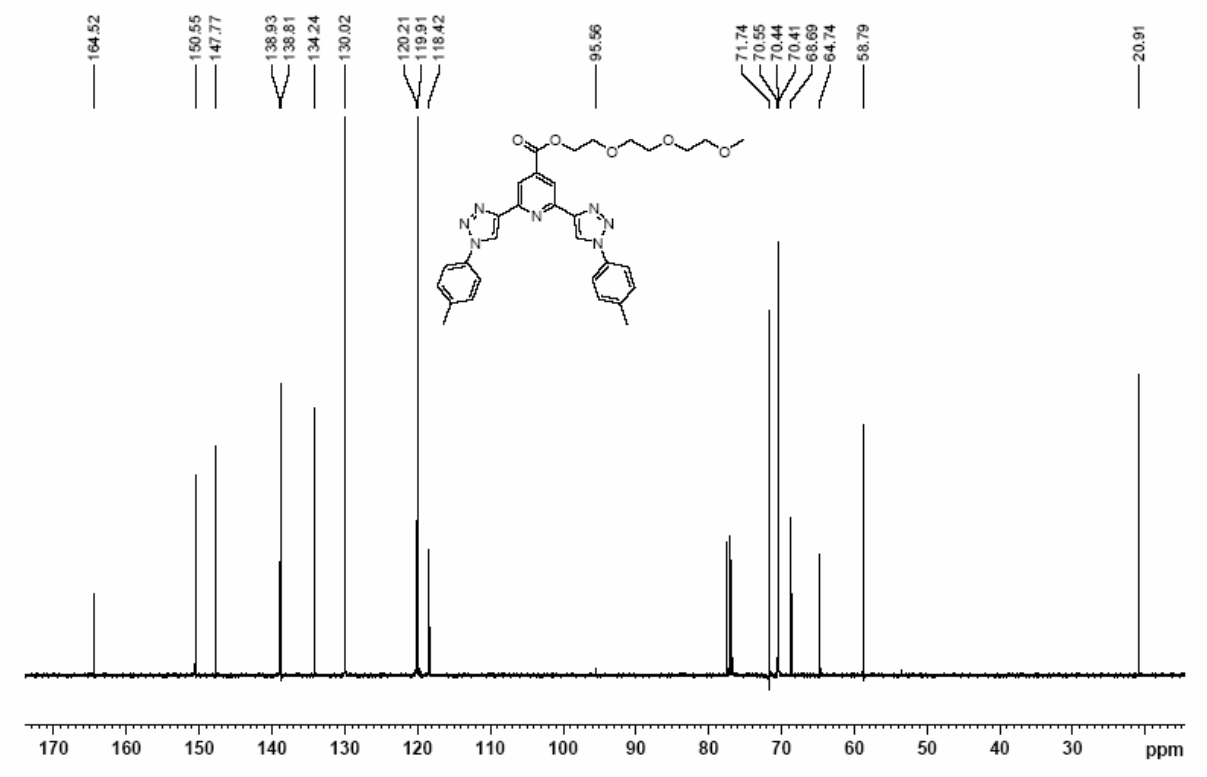
1.98
2.02
6.15
2.03
3.00
6.00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120.21
119.91
118.42
95.56
71.74
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70.44
70.41
68.69
64.74
58.79
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160
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100
90
80
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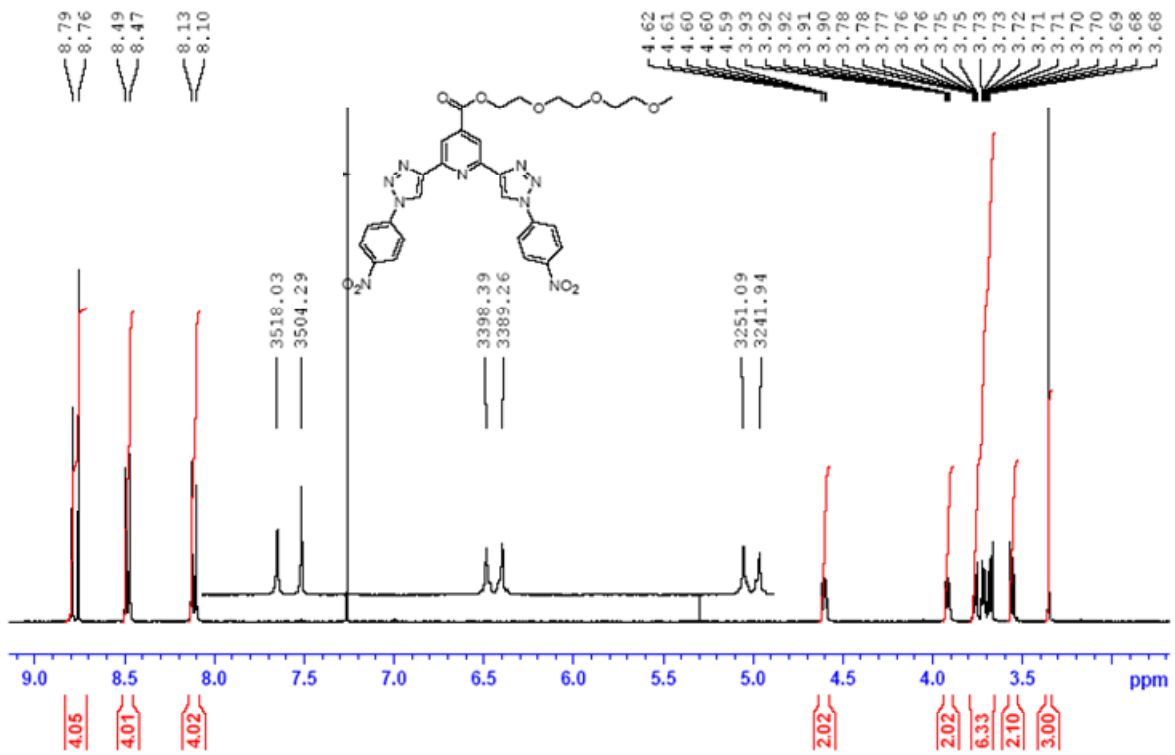
ppm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3.92
3.91
3.90
3.78
3.78
3.77
3.76
3.76
3.75
3.75
3.73
3.73
3.72
3.71
3.71
3.70
3.70
3.69
3.68
3.68
3518.03
3504.29
3398.39
3389.26
3251.09
3241.94
9.0
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8.0
7.5
7.0
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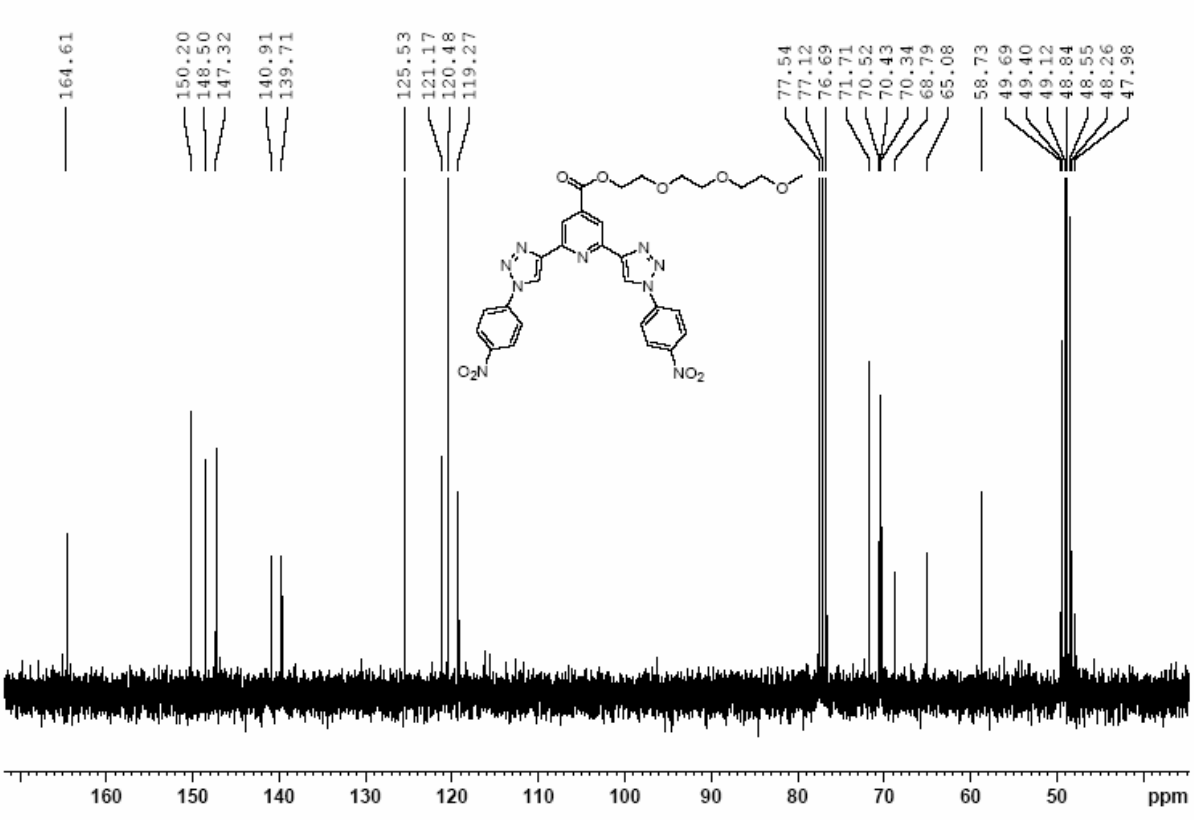
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71.71
70.52
70.43
70.34
68.79
65.08
58.73
49.69
49.40
49.12
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48.26
47.98
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110
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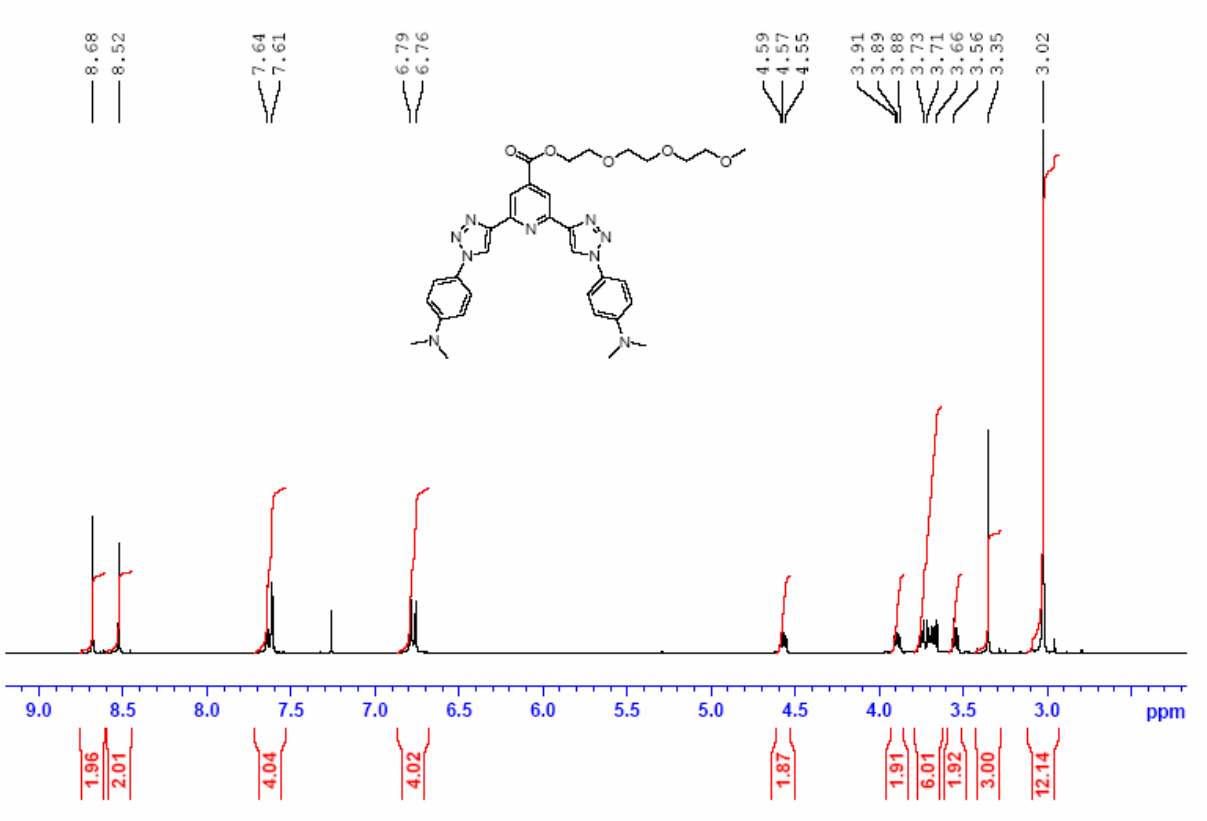
70
60
50
ppm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3.88
3.73
3.71
3.66
3.56
3.35
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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4.02
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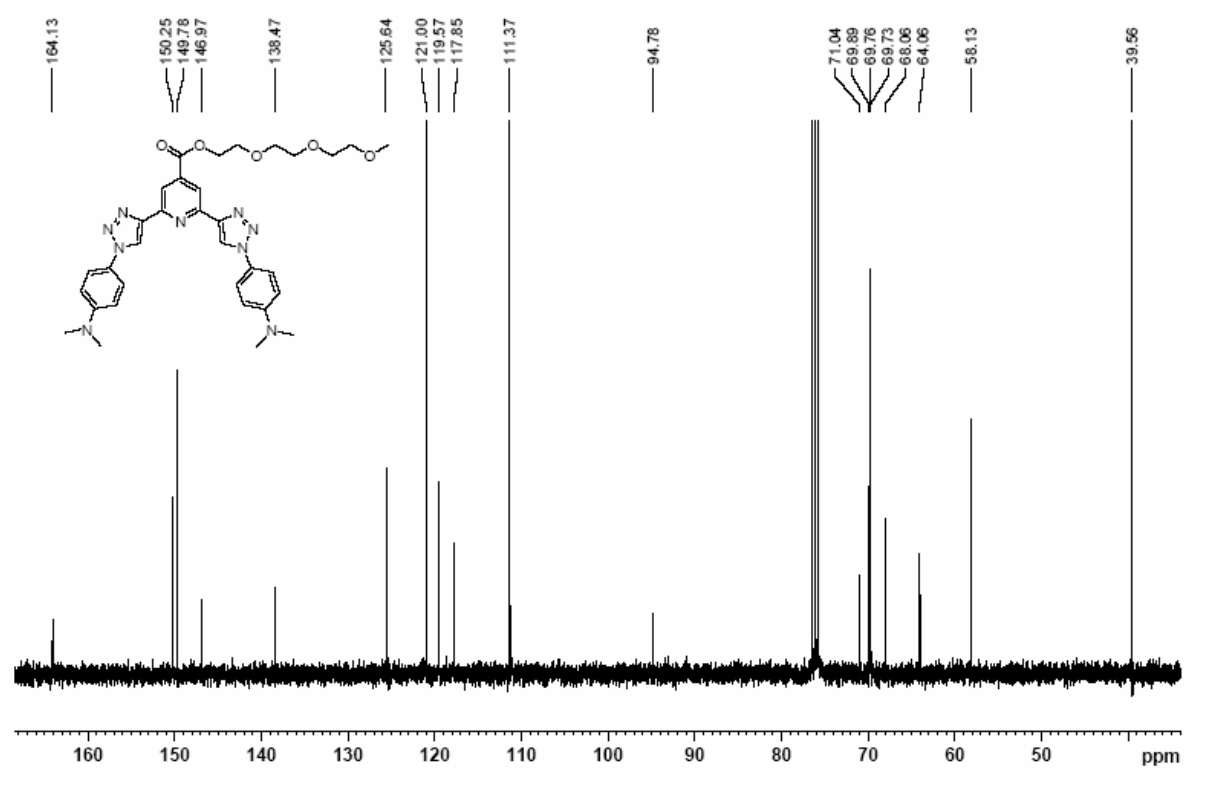
1.91
6.01
1.92
3.00
12.14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94.78
71.04
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69.73
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39.56
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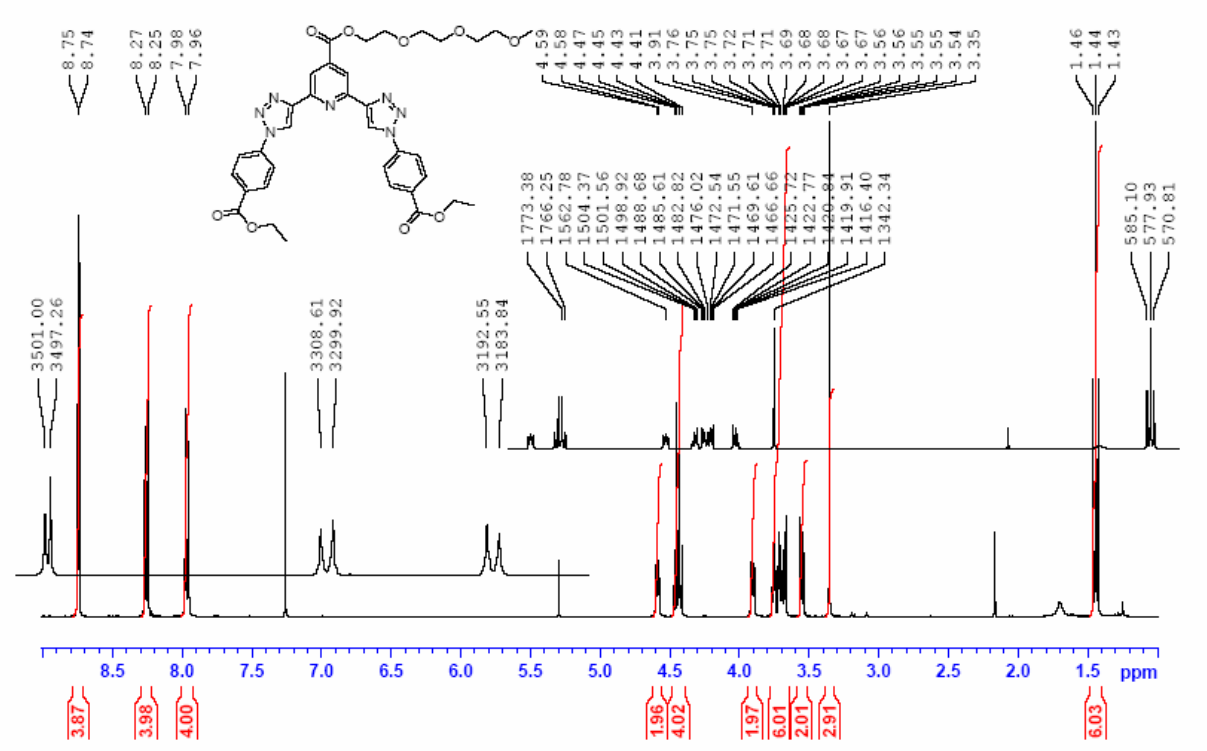
60
50
ppm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3.75
3.72
3.71
3.69
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3.67
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3.55
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3.35
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1.43
1773.38
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3.98
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1.97
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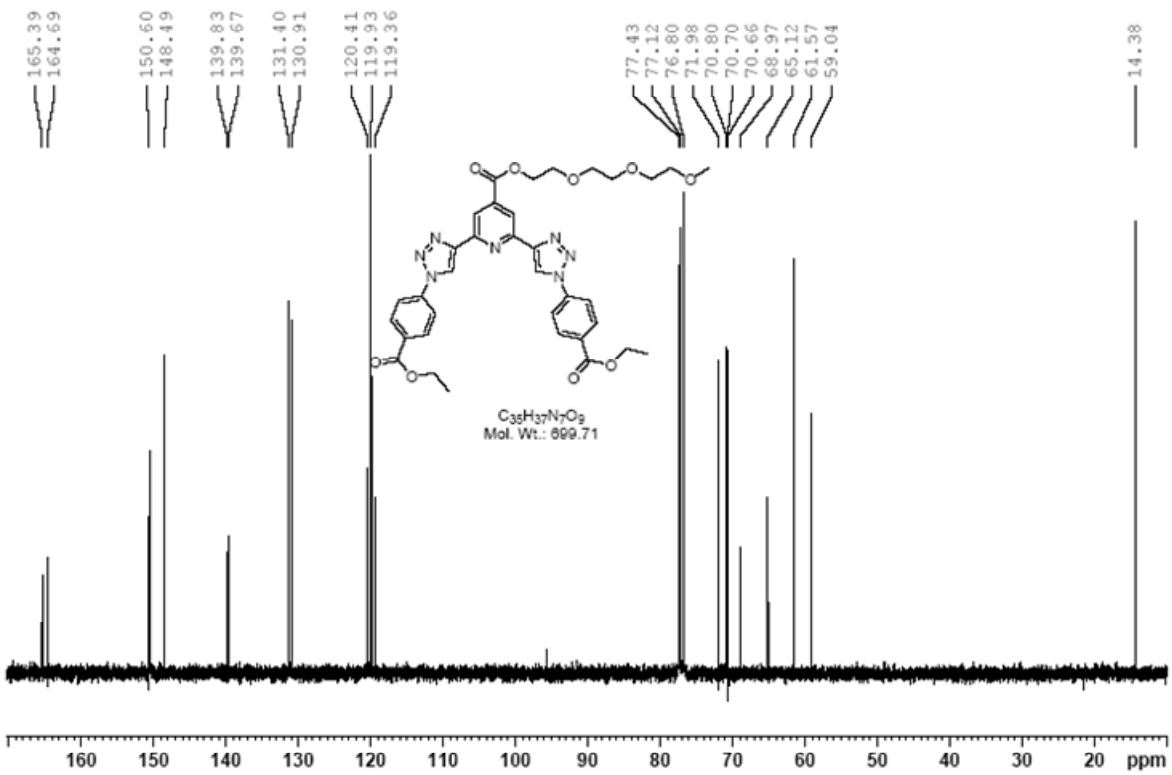
2.91
6.03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76.80
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70.70
70.66
68.97
65.12
61.57
59.04
14.38
C35H37N7O9
Mol. Wt.: 699.71
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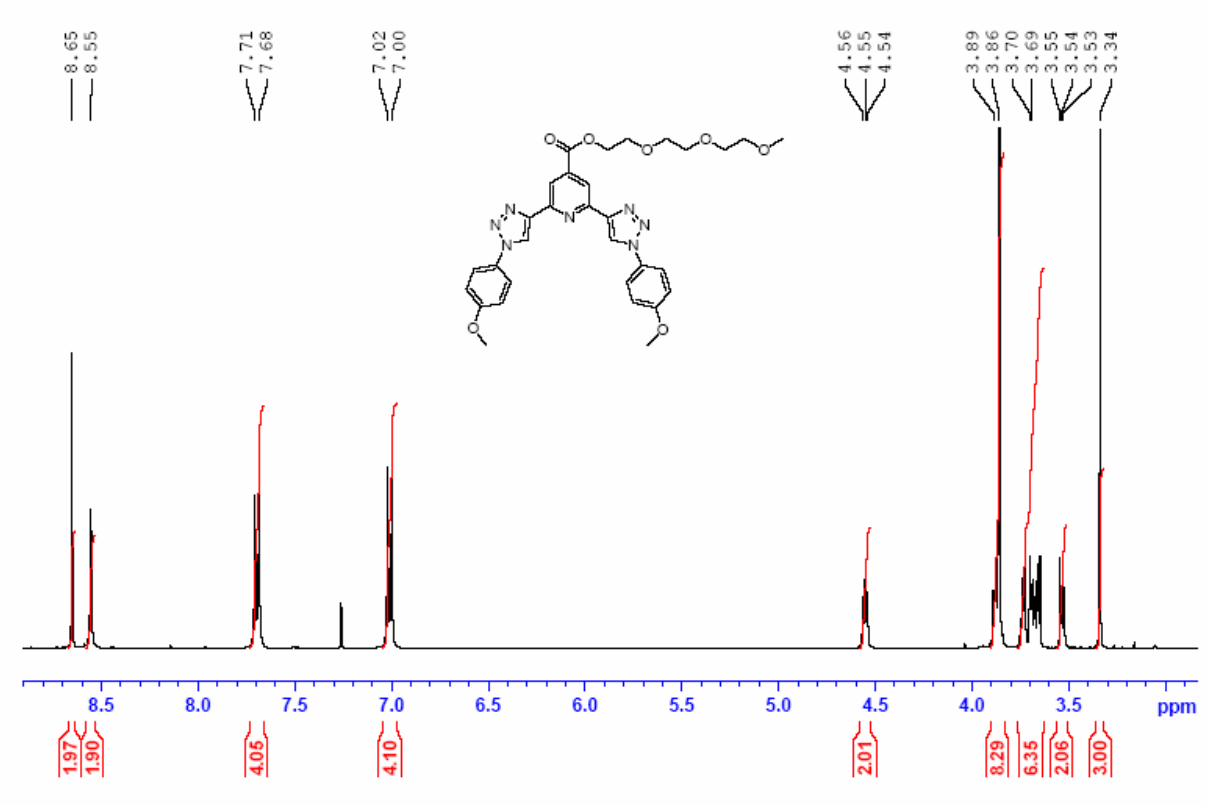
20
ppm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3.70
3.69
3.55
3.54
3.53
3.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.01
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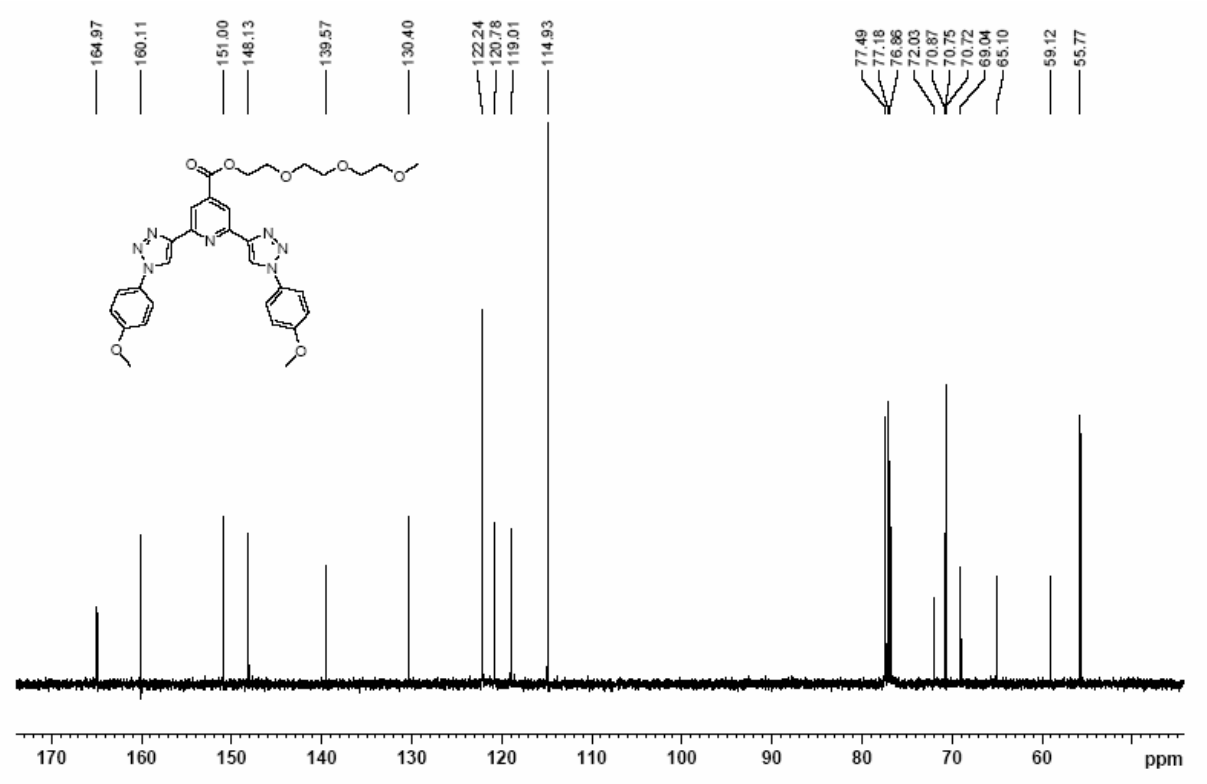
2.06
3.00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70.72
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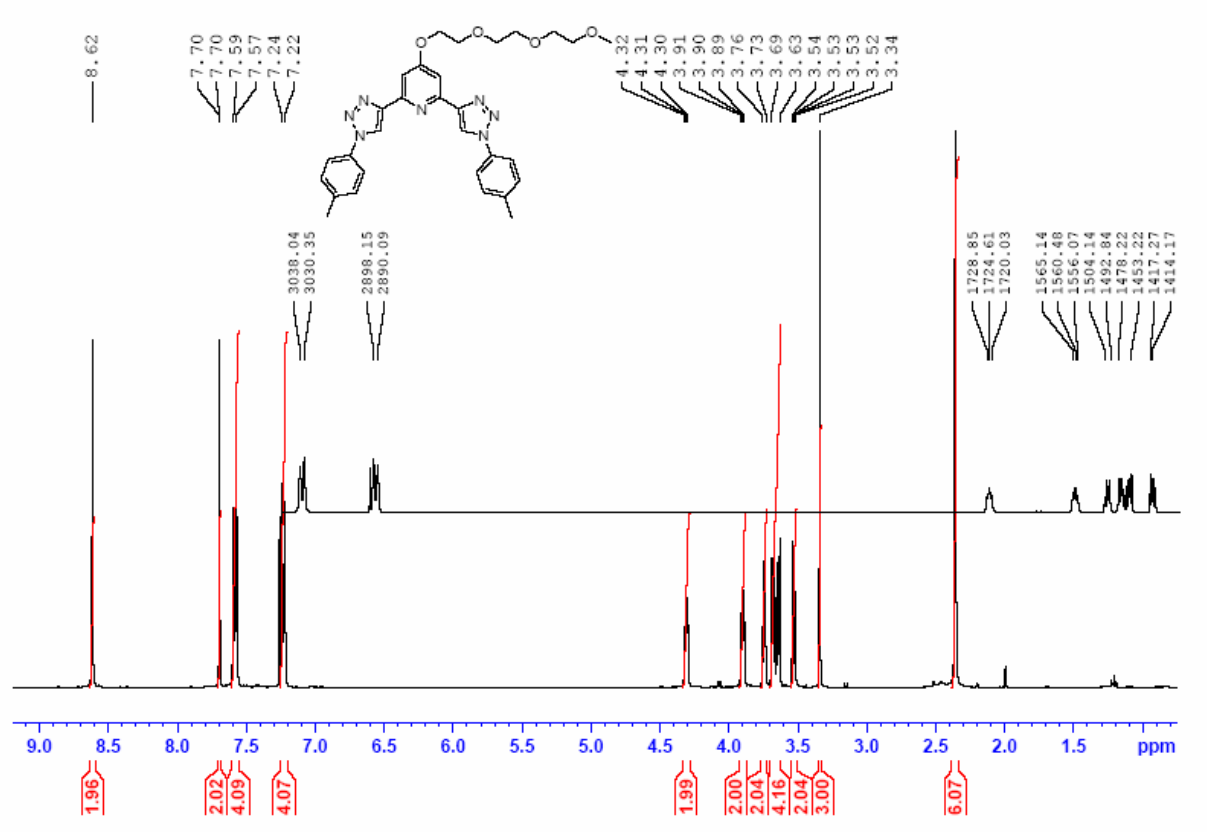
ppm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3.73
3.69
3.63
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3.53
3.53
3.52
3.34
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3030.35
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1724.61
1720.03
1565.14
1560.48
1556.07
1504.14
1492.84
1478.22
1453.22
1417.27
1414.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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2.0
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4.07
1.99
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2.04
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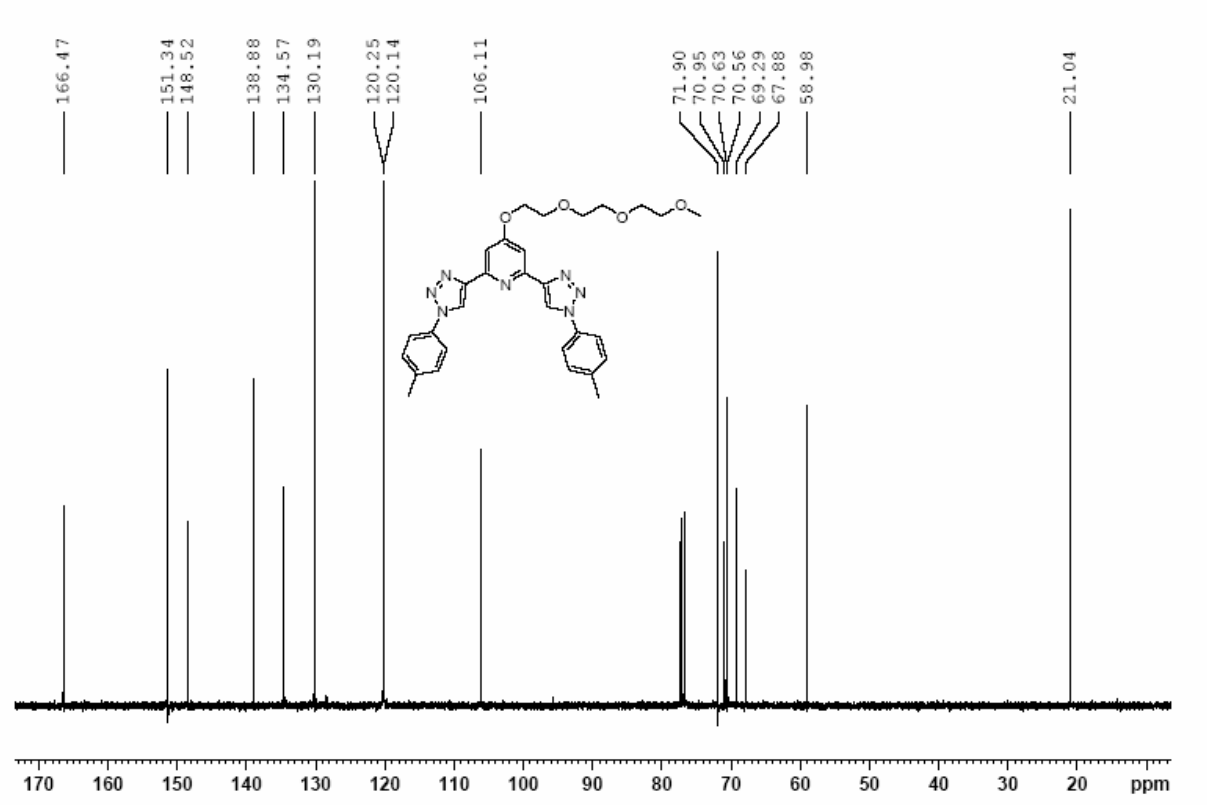
3.00
6.07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120.14
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71.90
70.95
70.63
70.56
69.29
67.88
58.98
21.04
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160
150
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120
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80
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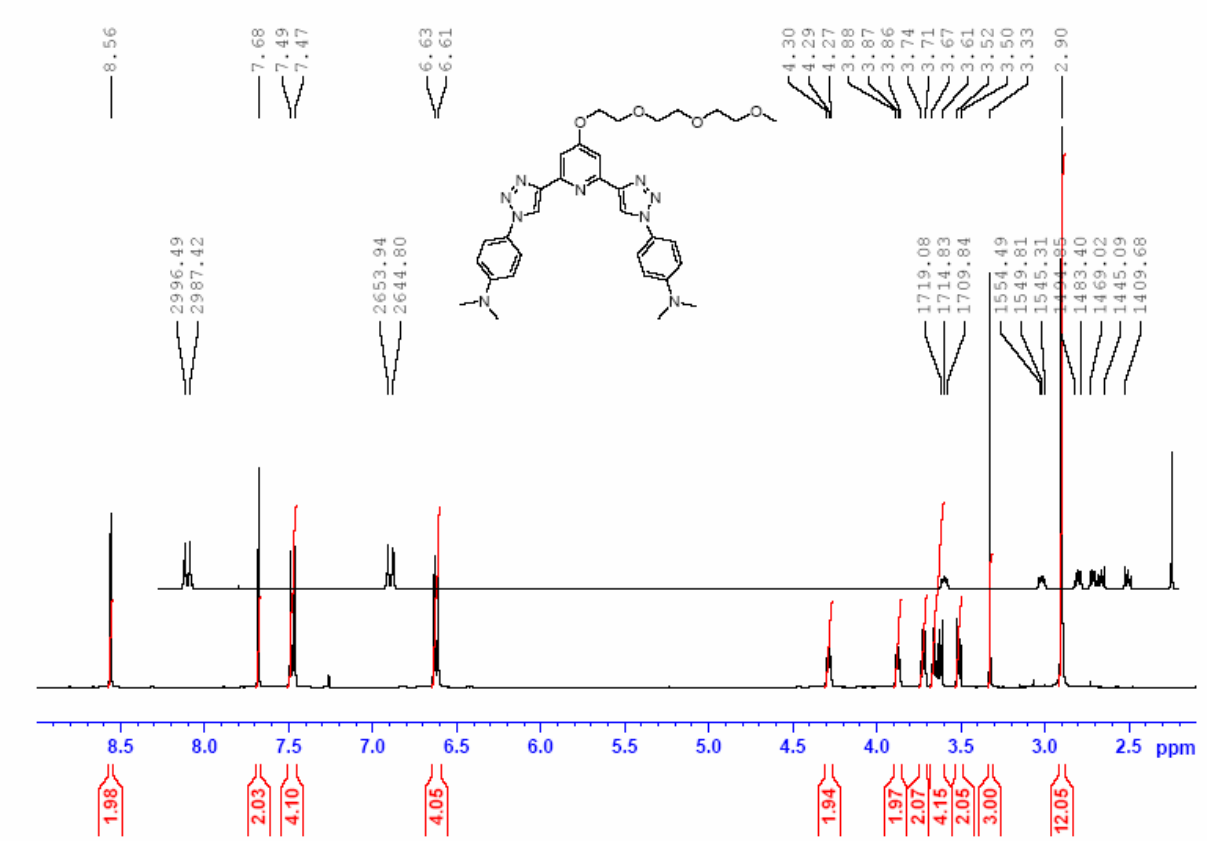
20
ppm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4.29
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3.74
3.71
3.67
3.61
3.52
3.50
3.33
2.90
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2644.80
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1714.83
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7.5
7.0
6.5
6.0
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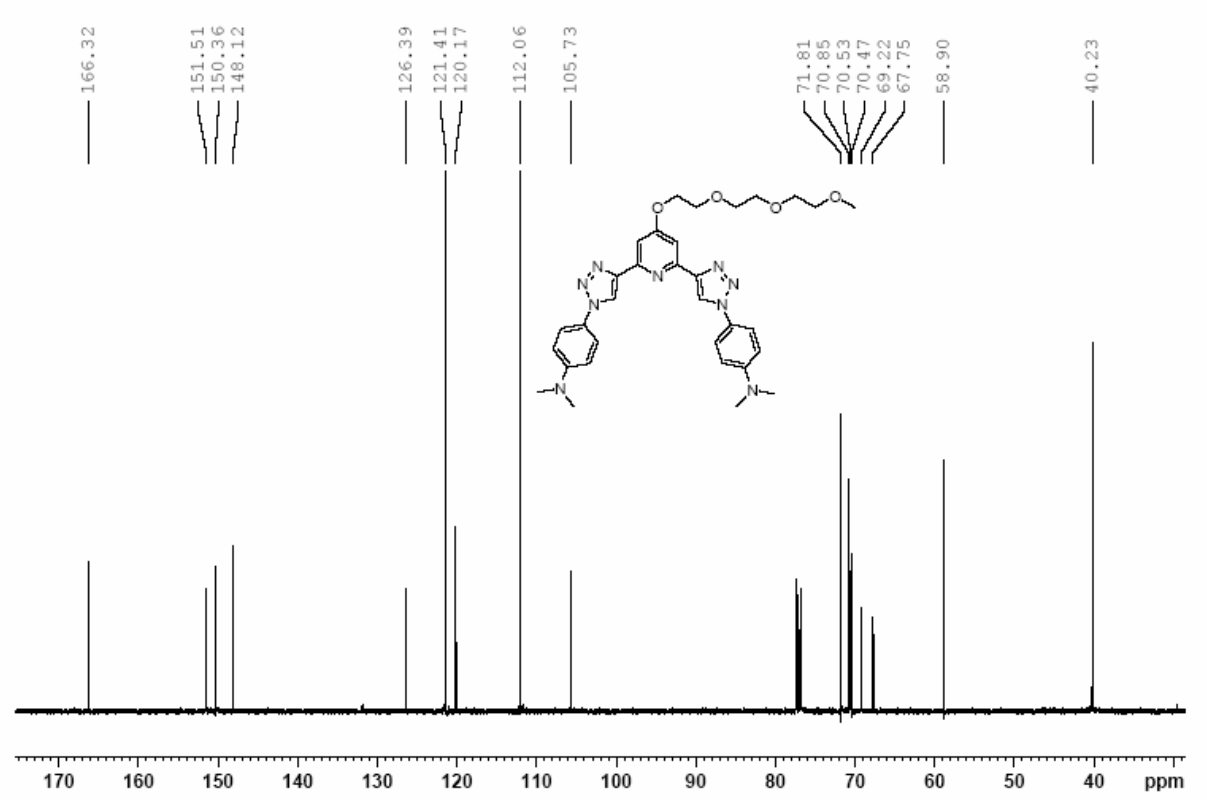
2.07
4.15
2.05
3.00
12.05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112.06
105.73
71.81
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70.53
70.47
69.22
67.75
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40.23
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130
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100
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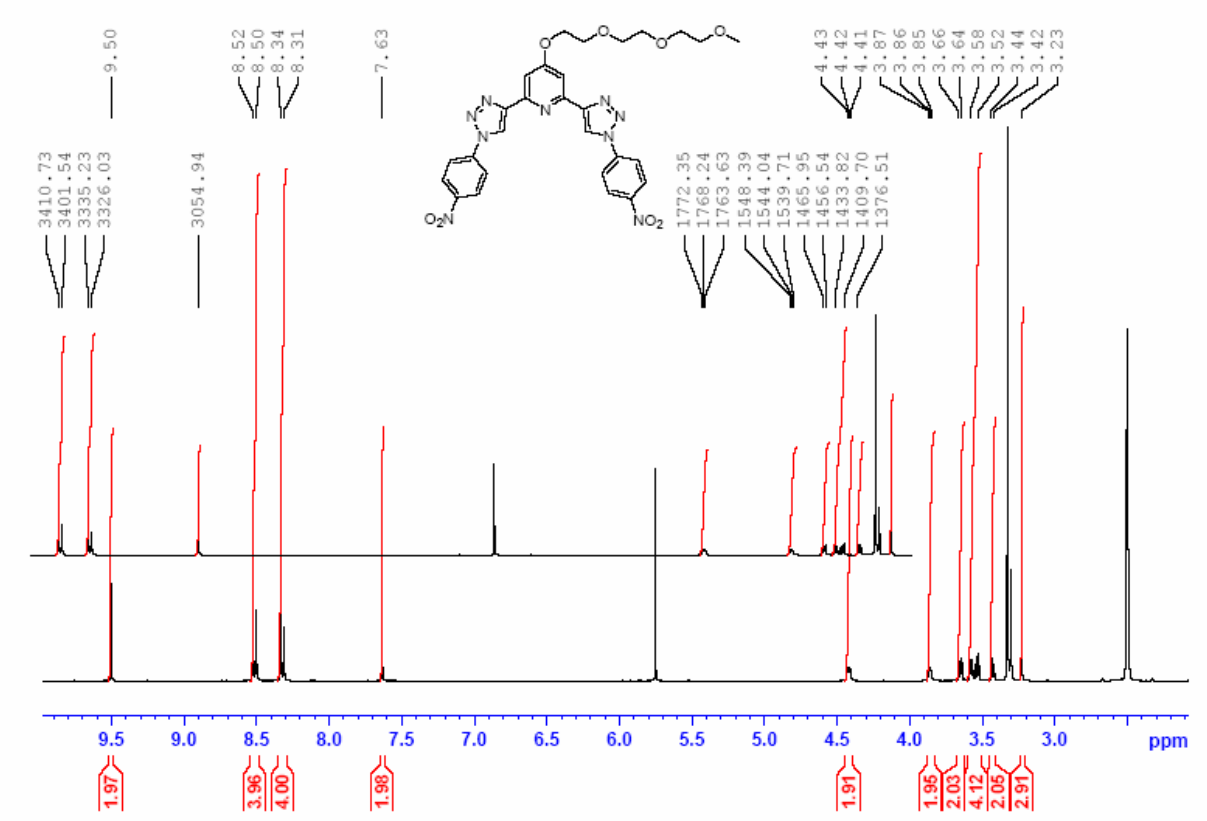
70
60
50
40
ppm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4.43
4.42
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3.87
3.86
3.85
3.66
3.64
3.58
3.52
3.44
3.42
3.23
3410.73
3401.54
3335.23
3326.03
3054.94
1772.35
1768.24
1763.63
1548.39
1544.04
1539.71
1465.95
1456.54
1433.82
1409.70
1376.51
O2N
NO2
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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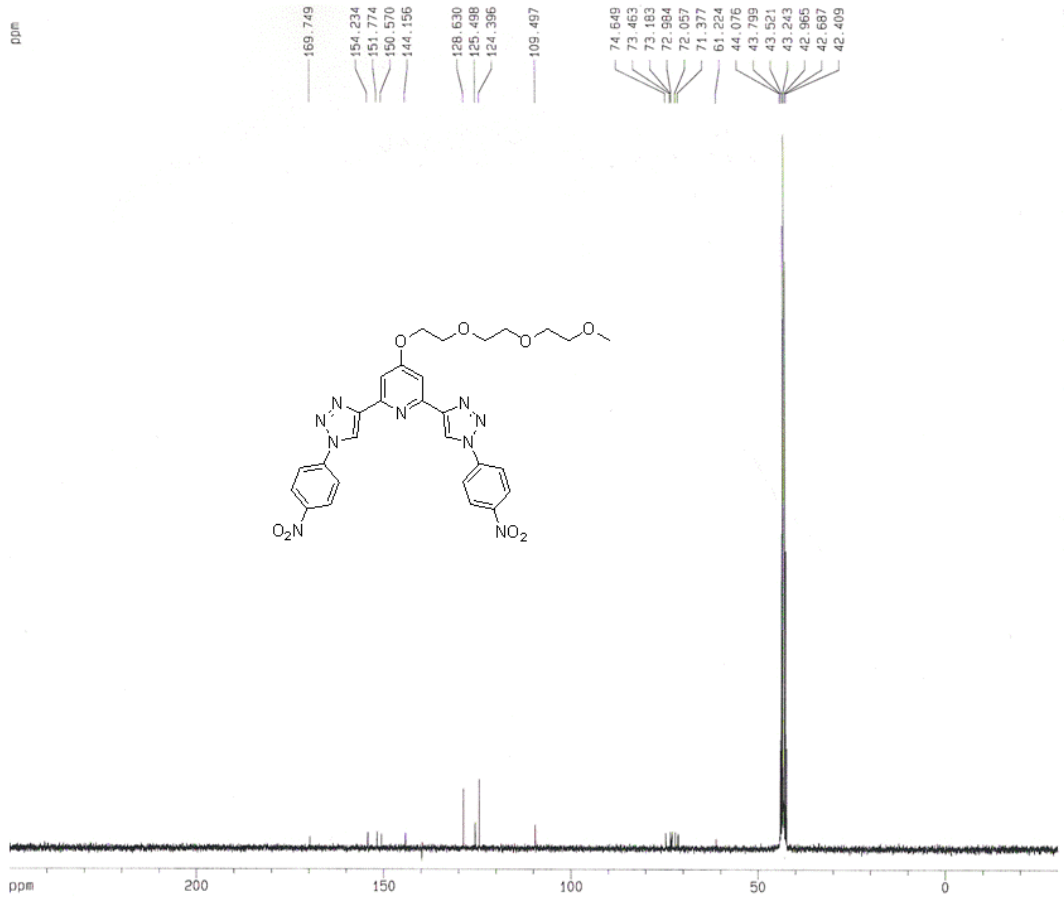
1.98
1.91
1.95
2.03
4.12
2.05
2.91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72.984
72.057
71.377
61.224
44.076
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43.521
43.243
42.965
42.687
42.409
O2N
NO2
ppm
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150
100
50
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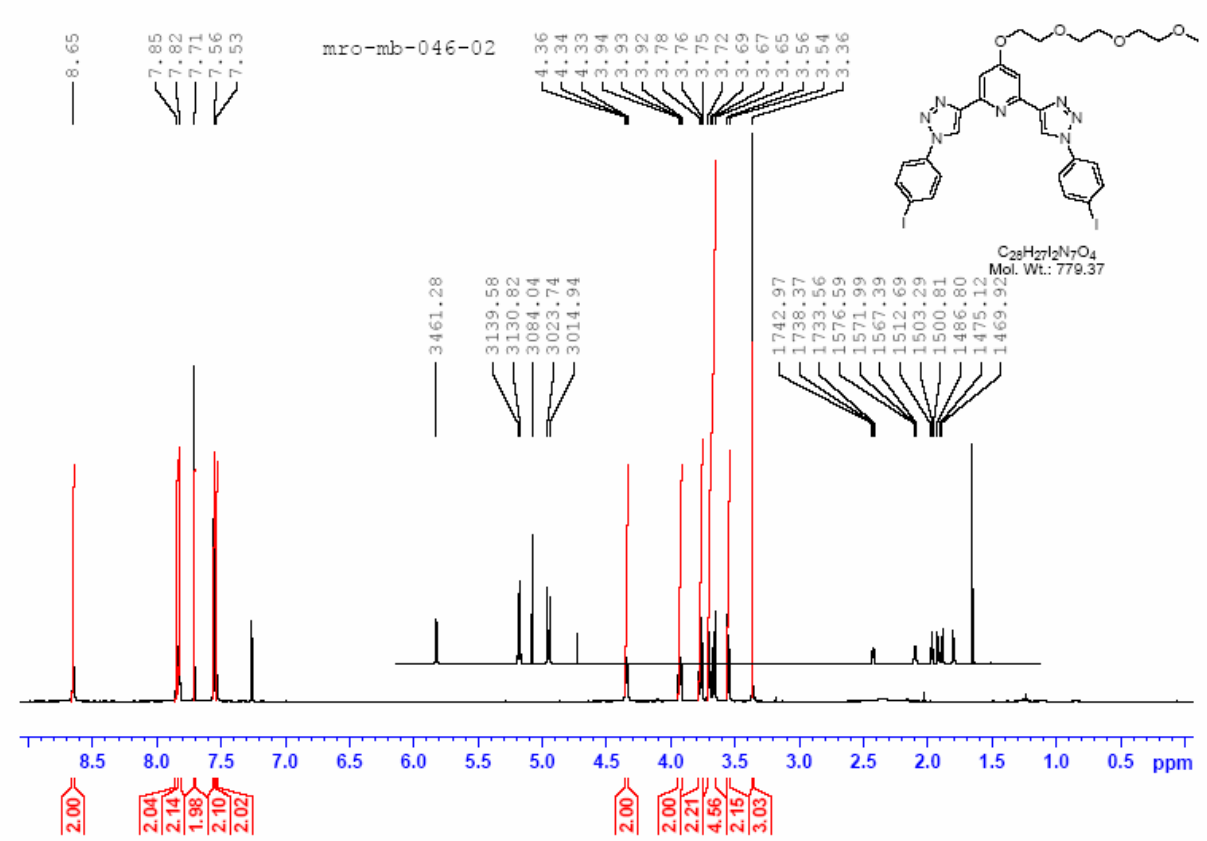
mro-mb-046-02
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4.34
4.33
3.94
3.93
3.92
3.78
3.76
3.75
3.72
3.69
3.67
3.65
3.56
3.54
3.36
3461.28
3139.58
3130.82
3084.04
3023.74
3014.94
1742.97
1738.37
1733.56
1576.59
1571.99
1567.39
1512.69
1503.29
1500.81
1486.80
1475.12
1469.92
C28H27I2N7O4
Mol. Wt.: 779.37
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 ppm
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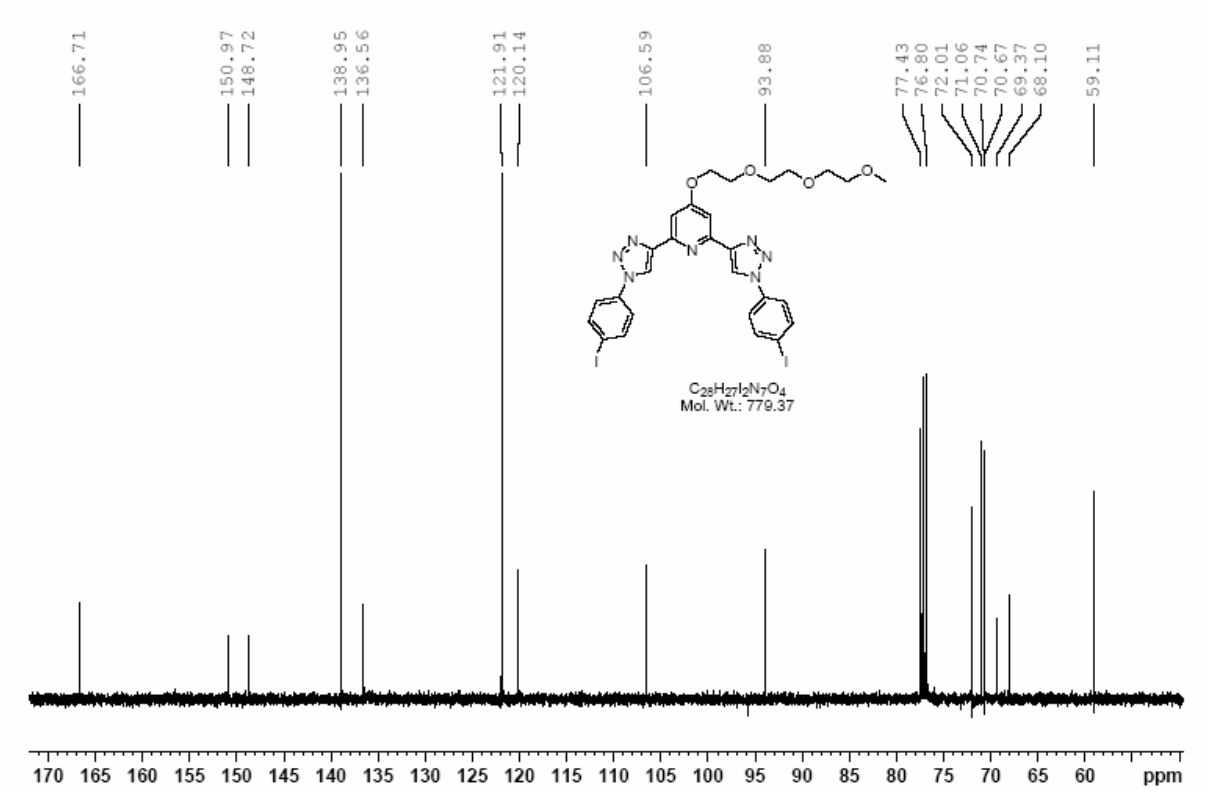
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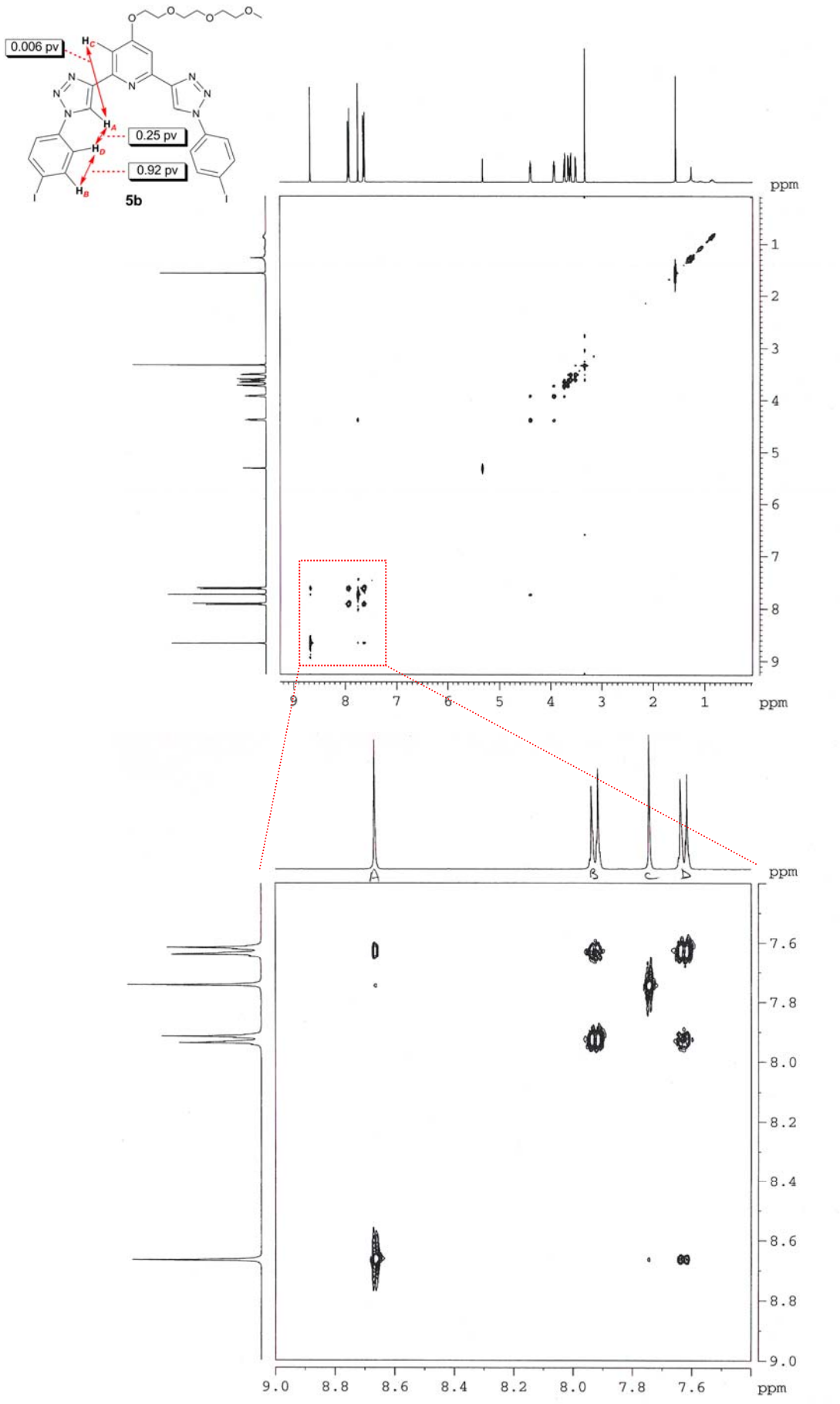
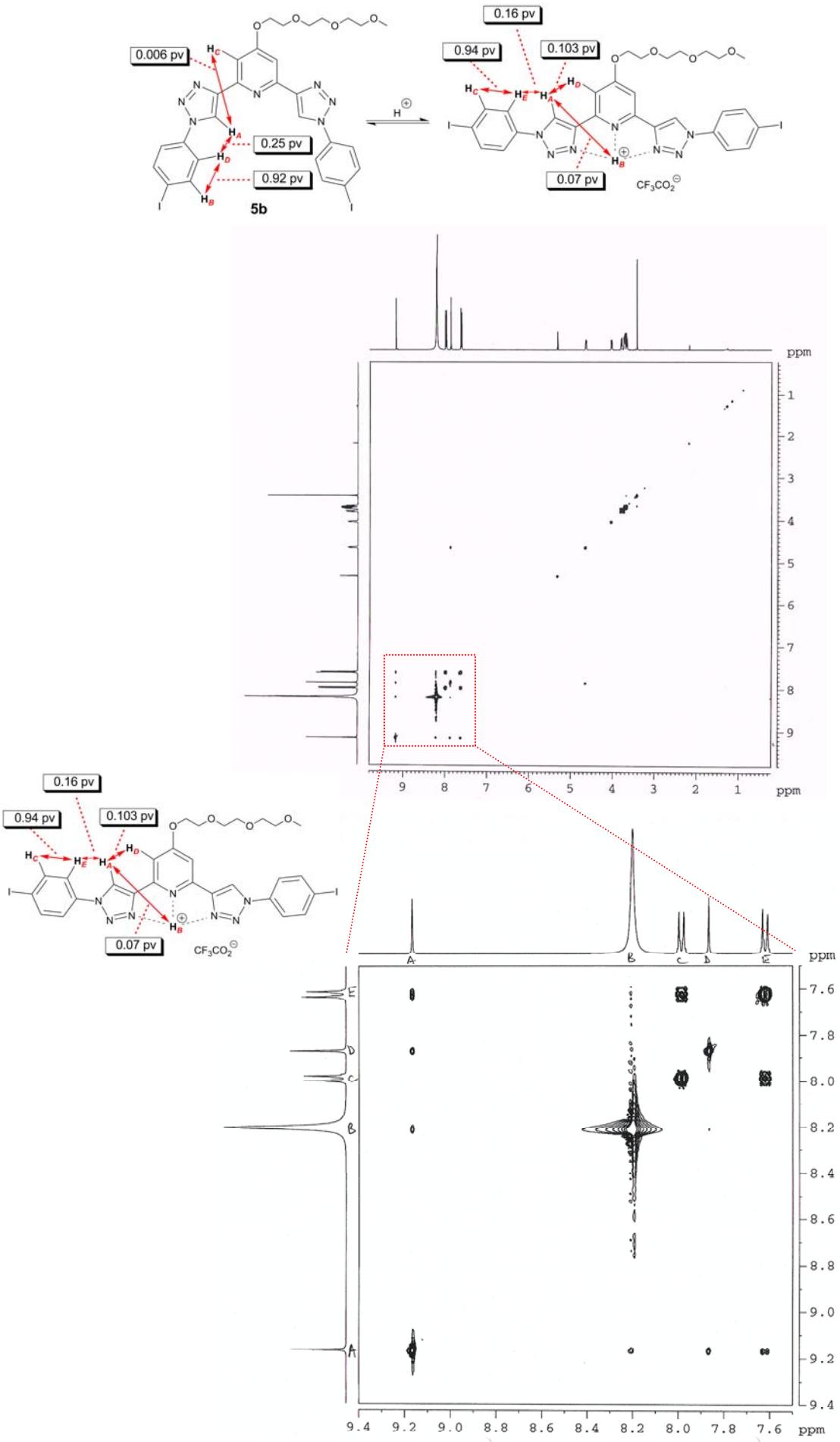
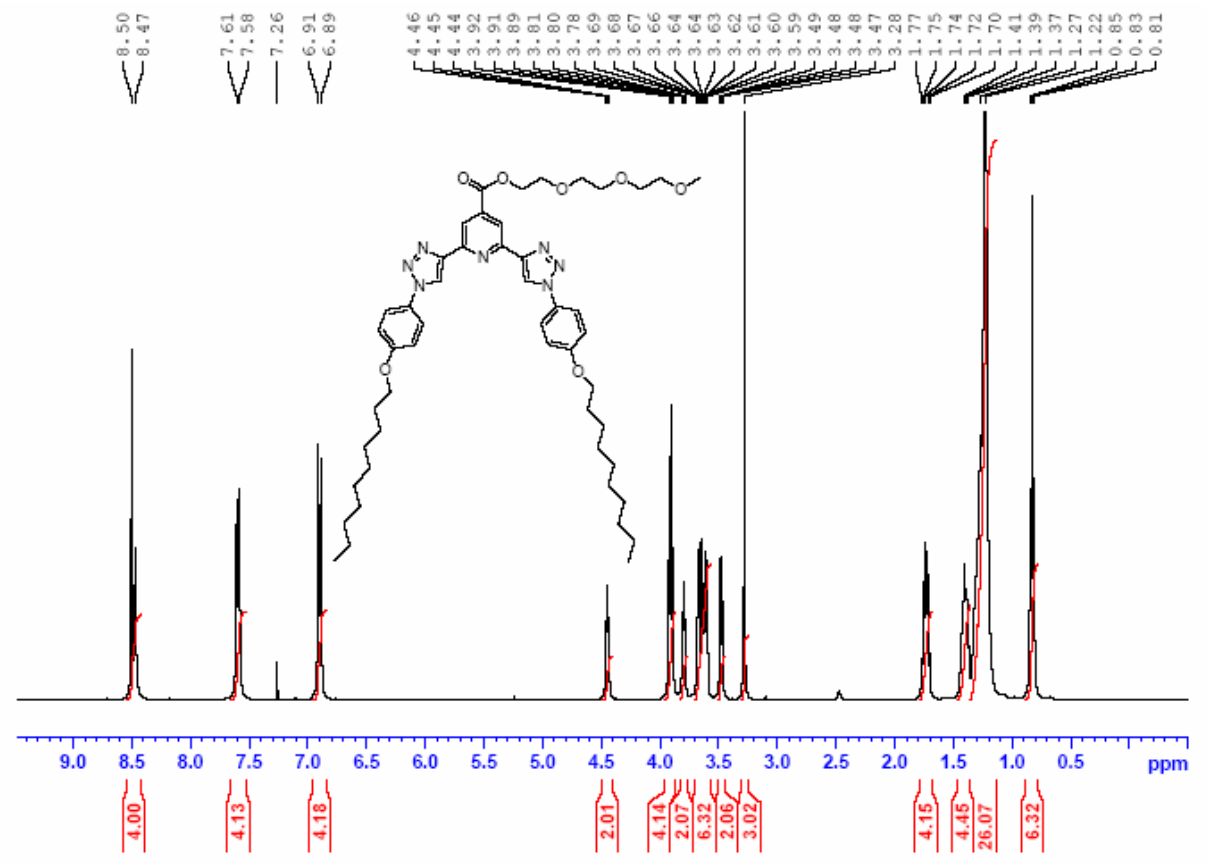
106.59
93.88
77.43
76.80
72.01
71.06
70.74
70.67
69.37
68.10
59.11
C28H27I2N7O4
Mol. Wt.: 779.37
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 ppm


0.006 pv
0.25 pv
0.92 pv
5b
ppm
A
B
C
D


0.006 pv
0.25 pv
0.92 pv
5b
0.16 pv
0.94 pv
0.103 pv
0.07 pv
$CF_3CO_2^-$
ppm
ppm
ppm
ppm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8.47
7.61
7.58
7.26
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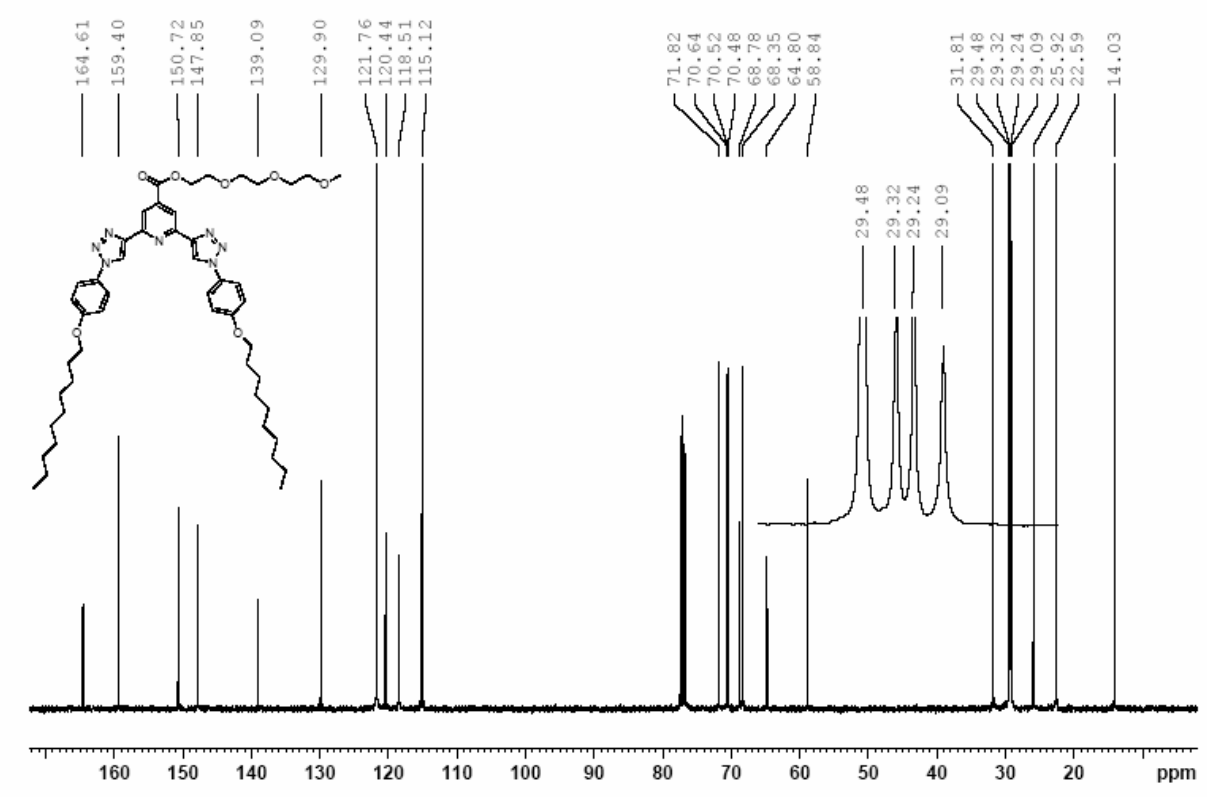
6.89
4.46
4.45
4.44
3.92
3.91
3.89
3.81
3.80
3.78
3.69
3.68
3.67
3.66
3.64
3.64
3.63
3.62
3.61
3.60
3.59
3.49
3.48
3.47
3.28
1.77
1.75
1.74
1.72
1.70
1.41
1.39
1.37
1.27
1.22
0.85
0.83
0.81
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
4.13
4.18
2.01
4.14
2.07
6.32
2.06
3.02
4.15
4.45
26.07
6.32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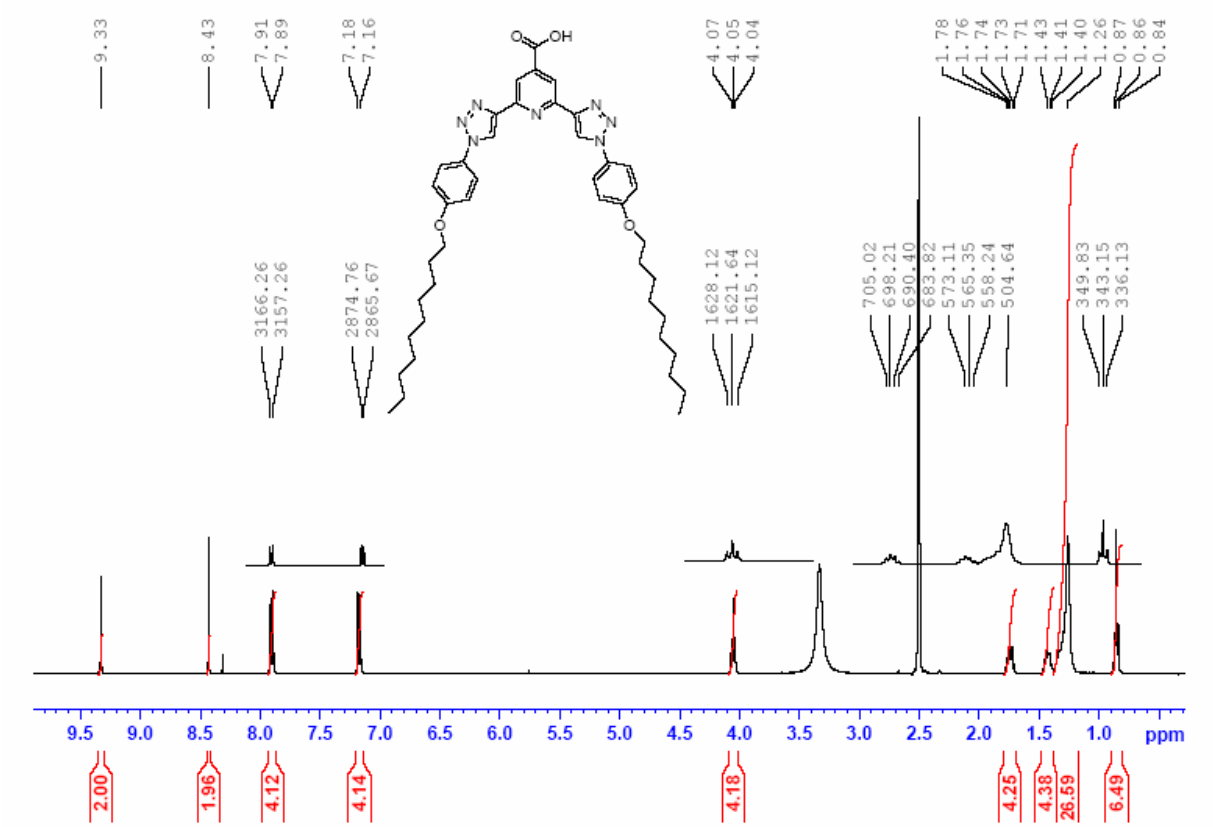
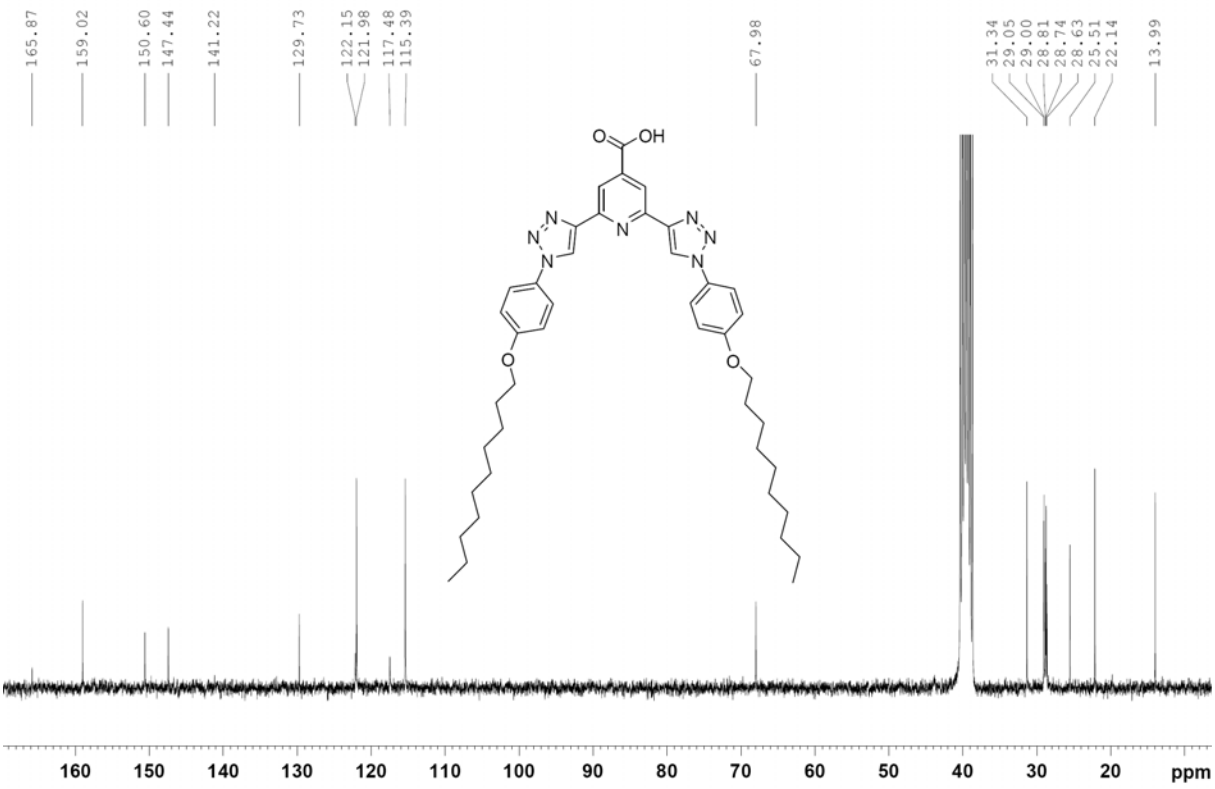
159.40
150.72
147.85
139.09
129.90
121.76
120.44
118.51
115.12
71.82
70.64
70.52
70.48
68.78
68.35
64.80
58.84
31.81
29.48
29.32
29.24
29.09
25.92
22.59
14.03
29.48
29.32
29.24
29.09
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


9.33
8.43
7.91
7.89
7.18
7.16
4.07
4.05
4.04
1.78
1.76
1.74
1.73
1.71
1.43
1.41
1.40
1.26
0.87
0.86
0.84
3166.26
3157.26
2874.76
2865.67
1628.12
1621.64
1615.12
705.02
698.21
690.40
683.82
573.11
565.35
558.24
504.64
349.83
343.15
336.13
OH
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 ppm
2.00
1.96
4.12
4.14
4.18
4.25
4.38
26.59
6.49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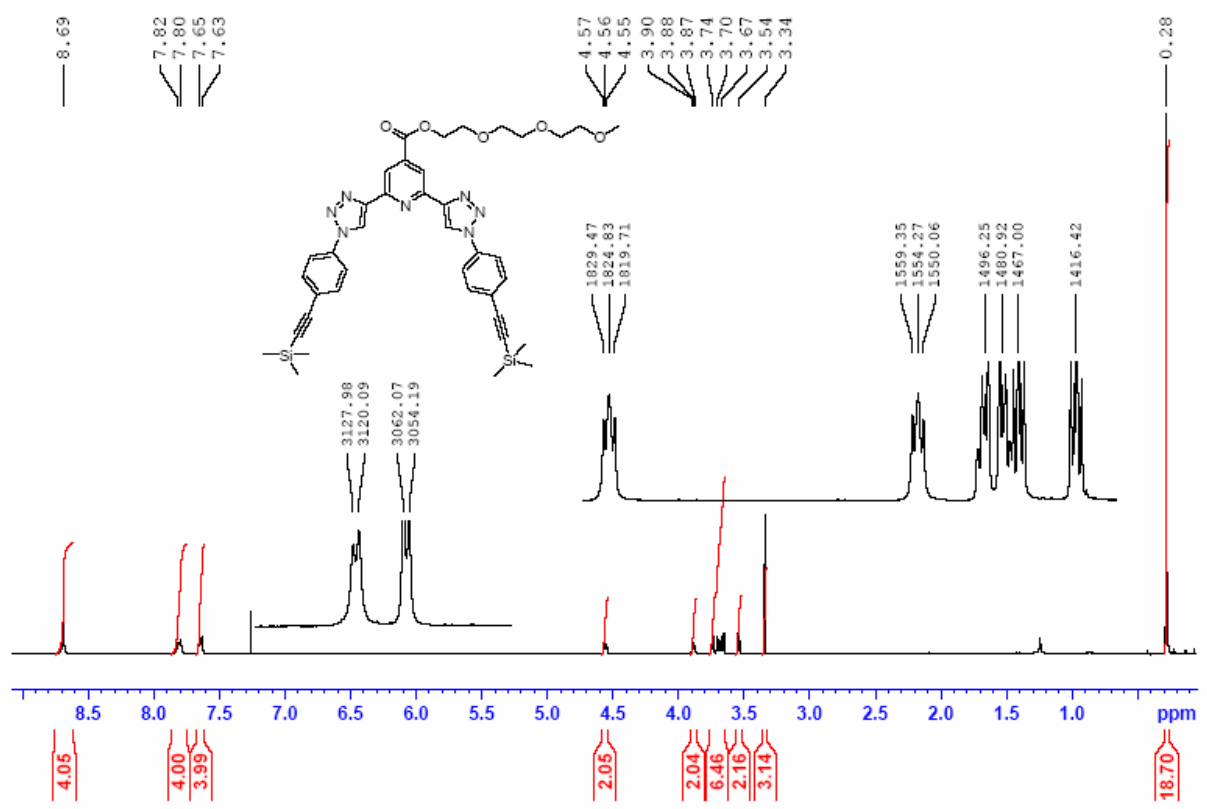
159.02
150.60
147.44
141.22
129.73
122.15
121.98
117.48
115.39
67.98
31.34
29.05
29.00
28.81
28.74
28.63
25.51
22.14
13.99
OH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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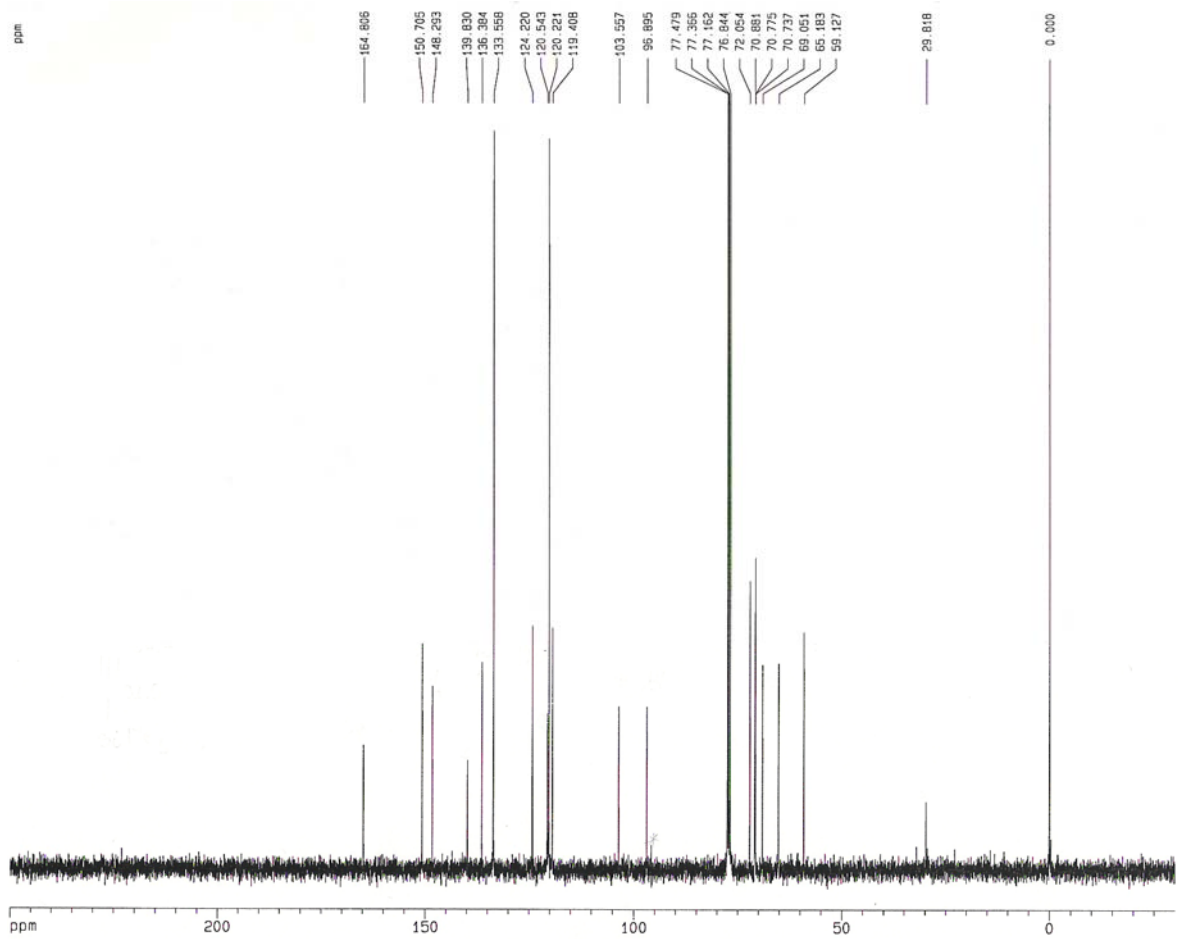
7.82
7.80
7.65
7.63
4.57
4.56
4.55
3.90
3.88
3.87
3.74
3.70
3.67
3.54
3.34
0.28
1829.47
1824.83
1819.71
1559.35
1554.27
1550.06
1496.25
1480.92
1467.00
1416.42
3127.98
3120.09
3062.07
3054.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.05
4.00
3.99
2.05
2.04
6.46
2.16
3.14
18.70


ppm
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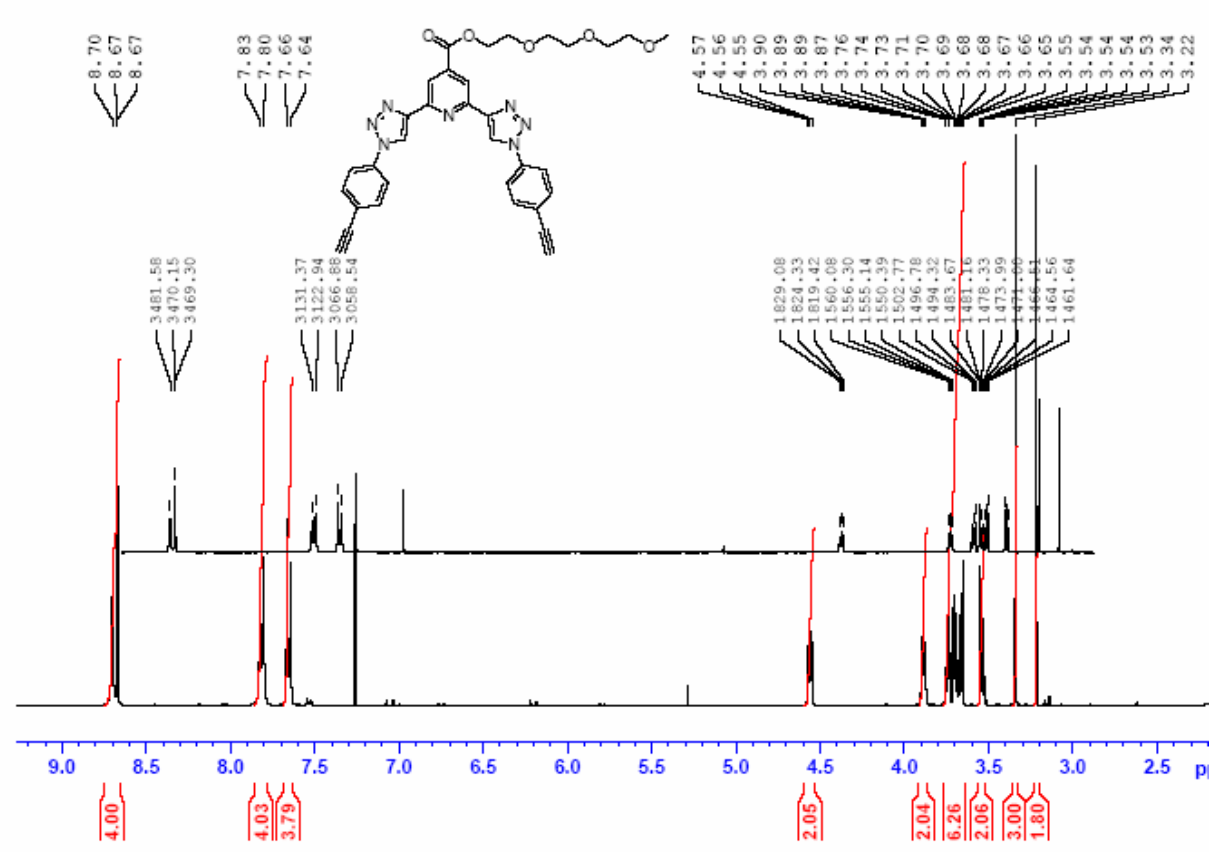
150.705
148.293
139.830
136.384
133.558
124.220
120.543
120.221
119.408
103.557
96.895
77.479
77.366
77.162
76.844
72.054
70.881
70.775
70.737
69.051
65.183
59.127
29.818
0.000
ppm
200
150
100
50
0


8.70
8.67
8.67
7.83
7.80
7.66
7.64
4.57
4.56
4.55
3.90
3.89
3.89
3.87
3.76
3.74
3.73
3.71
3.70
3.69
3.68
3.68
3.67
3.66
3.65
3.55
3.54
3.54
3.54
3.53
3.34
3.22
3481.58
3470.15
3469.30
3131.37
3122.94
3066.88
3058.54
1829.08
1824.33
1819.42
1560.08
1556.30
1555.14
1550.39
1502.77
1496.78
1494.32
1483.67
1481.16
1478.33
1473.99
1471.00
1466.61
1464.56
1461.64
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
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4.00
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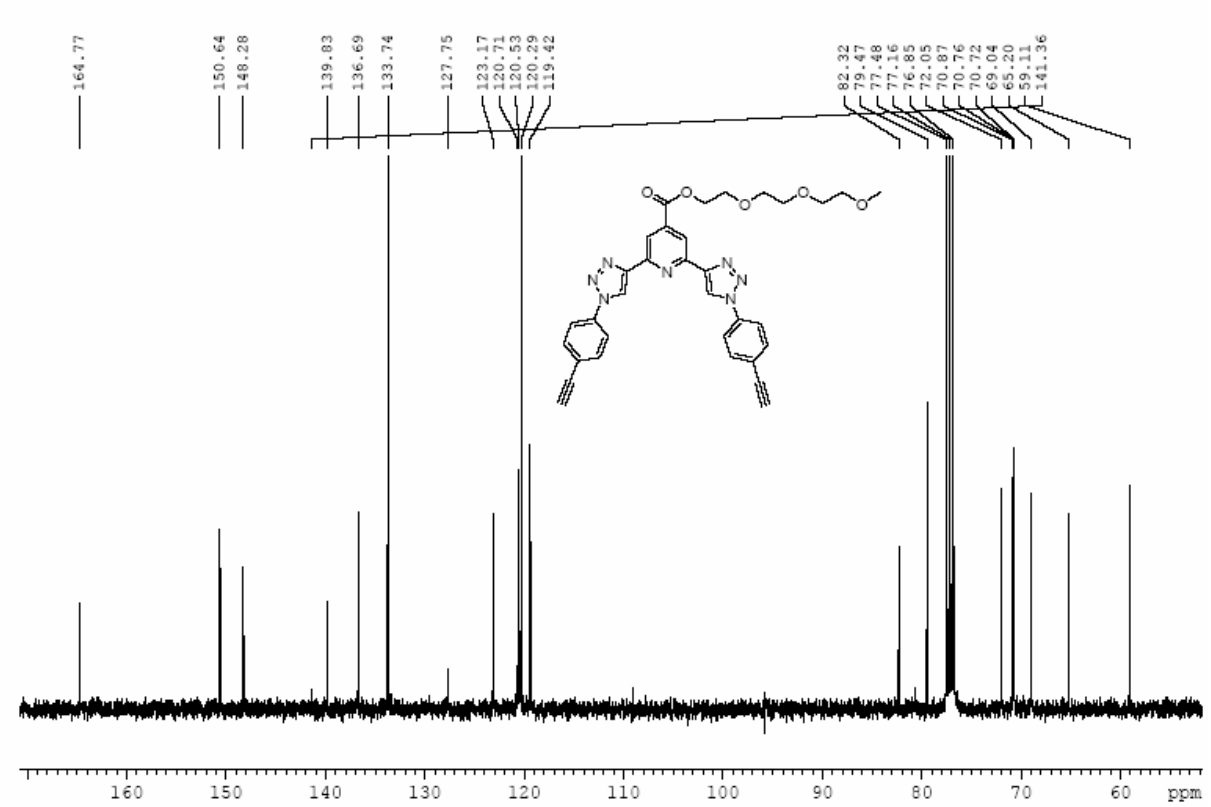
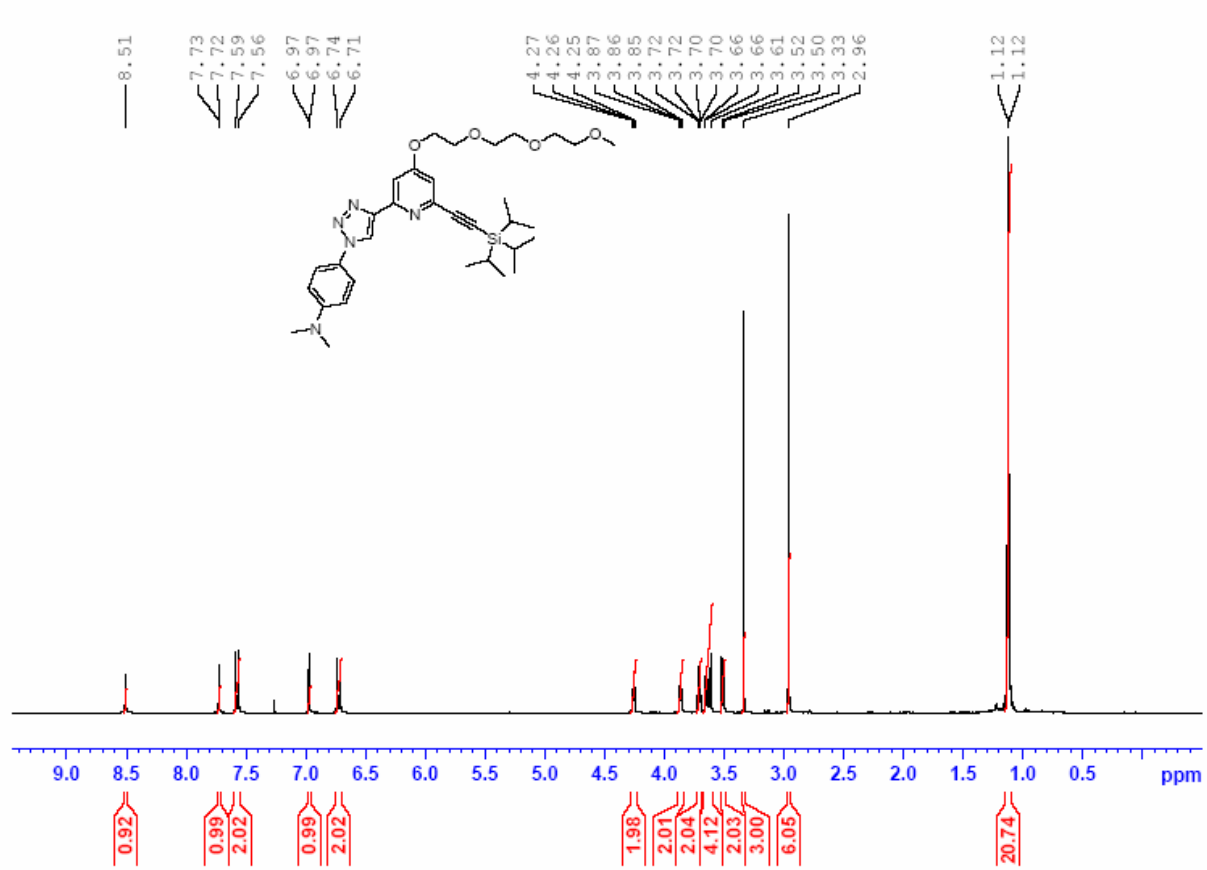
2.05
2.04
6.26
2.06
3.00
1.80


164.77
150.64
148.28
139.83
136.69
133.74
127.75
123.17
120.71
120.53
120.29
119.42
82.32
79.47
77.48
77.16
76.85
72.05
70.87
70.76
70.72
69.04
65.20
59.11
141.36
160
150
140
130
120
110
100
90
80
70
60
ppm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7.73
7.72
7.59
7.56
6.97
6.97
6.74
6.71
4.27
4.26
4.25
3.87
3.86
3.85
3.72
3.72
3.70
3.70
3.66
3.66
3.61
3.52
3.50
3.33
2.96
1.12
1.12
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
ppm
0.92
0.99
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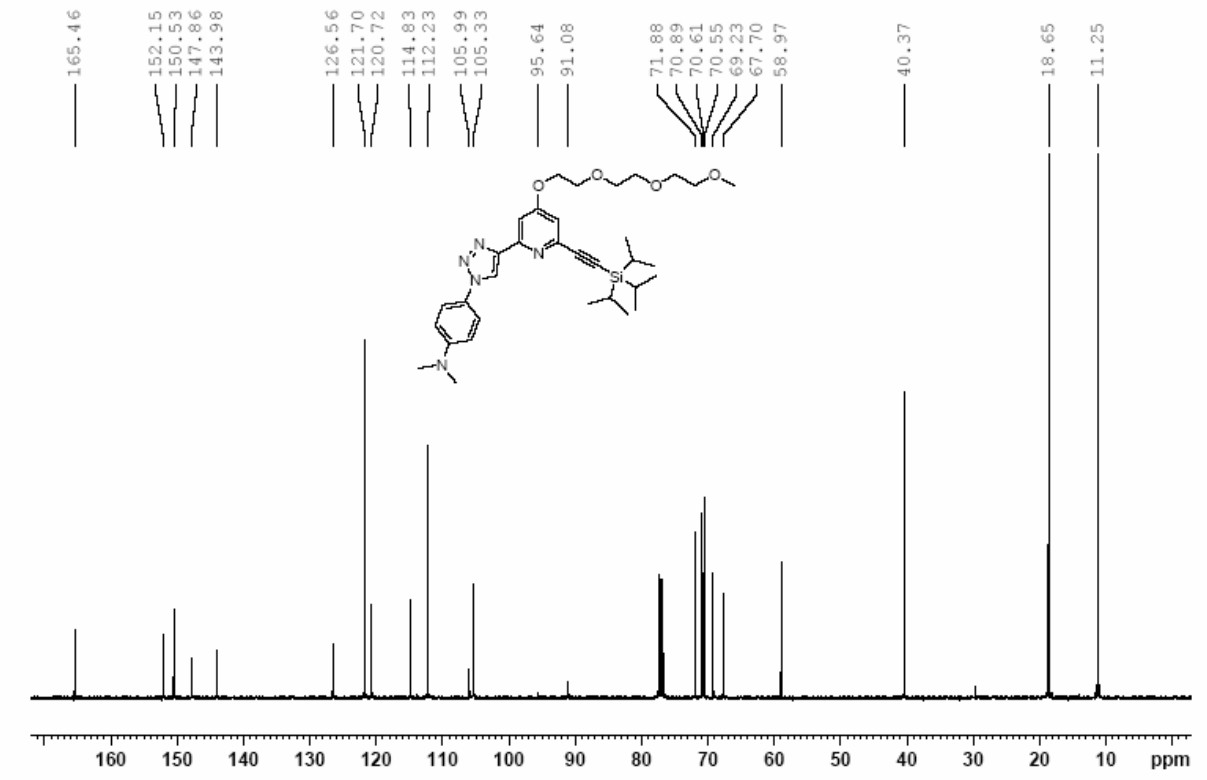
0.99
2.02
1.98
2.01
2.04
4.12
2.03
3.00
6.05
20.74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150.53
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121.70
120.72
114.83
112.23
105.99
105.33
95.64
91.08
71.88
70.89
70.61
70.55
69.23
67.70
58.97
40.37
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150
140
130
120
110
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70
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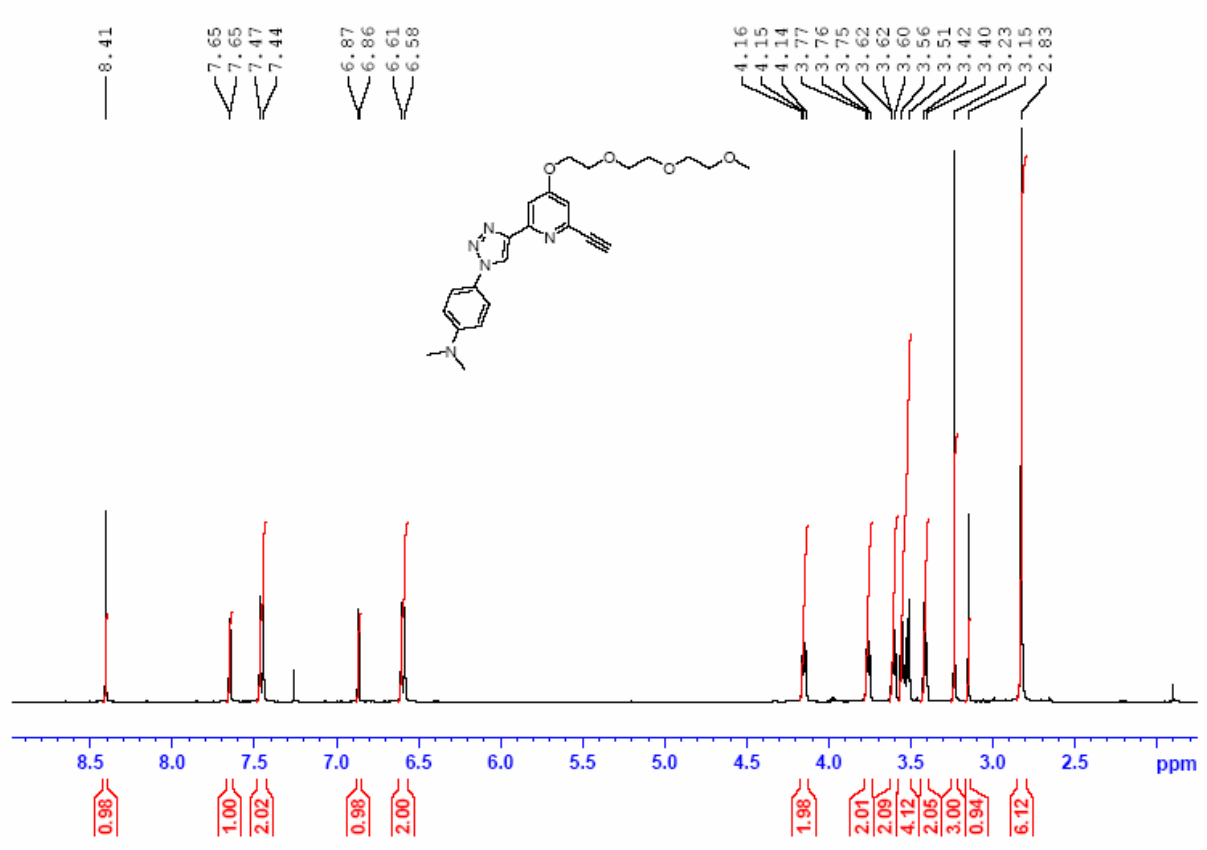
40
30
20
10
ppm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7.65
7.47
7.44
6.87
6.86
6.61
6.58
4.16
4.15
4.14
3.77
3.76
3.75
3.62
3.62
3.60
3.56
3.51
3.42
3.40
3.23
3.15
2.83
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
0.98
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2.02
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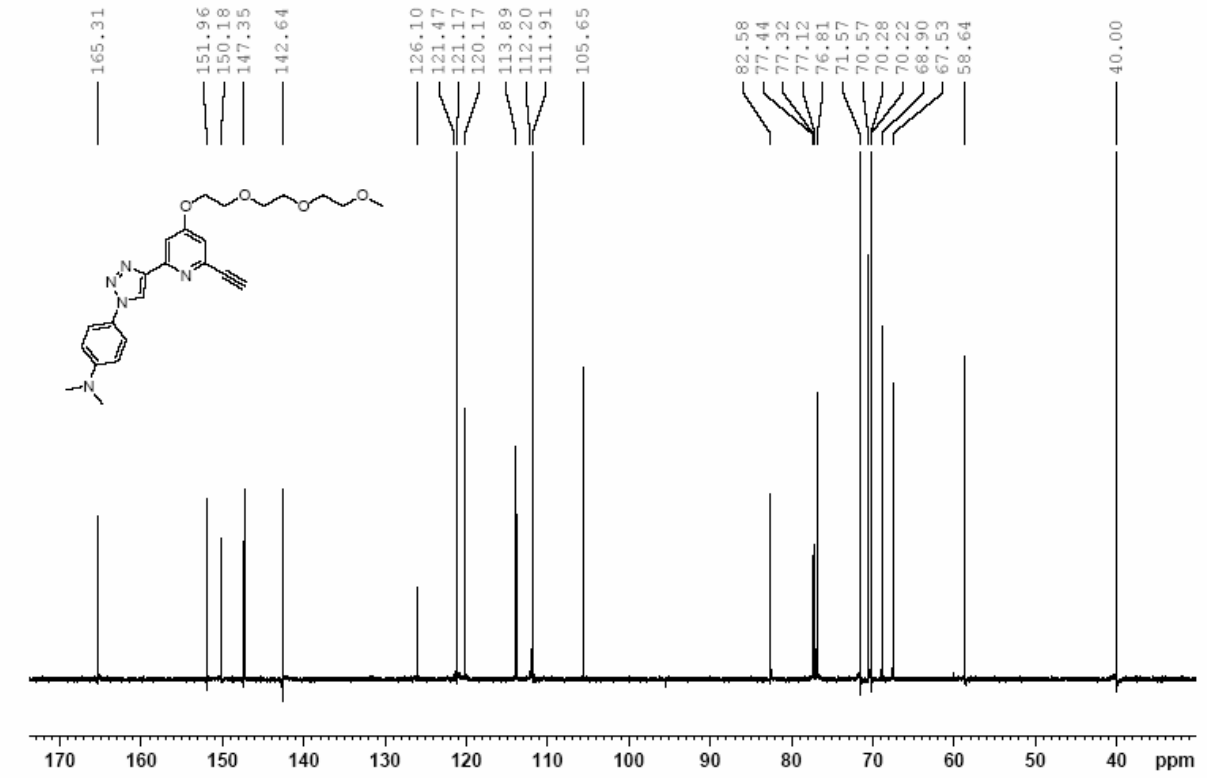
2.00
1.98
2.01
2.09
4.12
2.05
3.00
0.94
6.12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121.17
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113.89
112.20
111.91
105.65
82.58
77.44
77.32
77.12
76.81
71.57
70.57
70.28
70.22
68.90
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40.00
170
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150
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100
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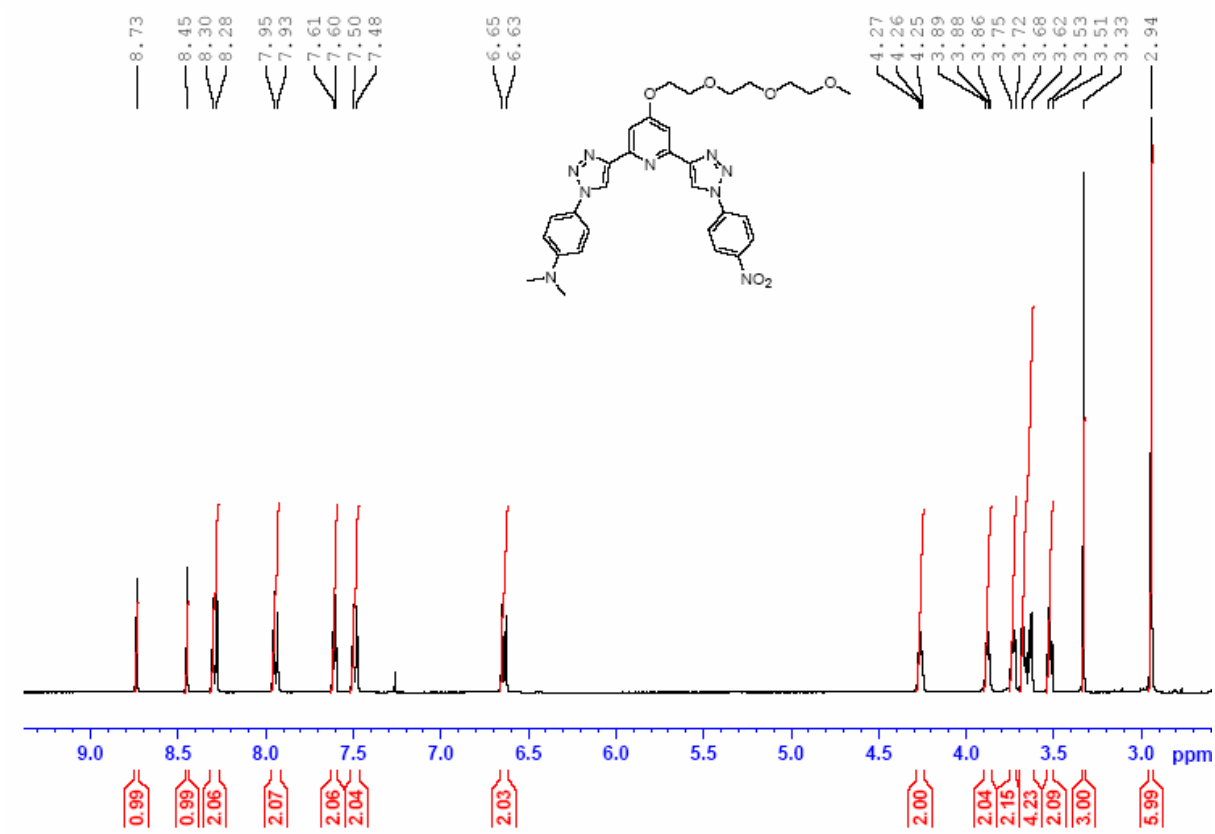
60
50
40
ppm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6.63
4.27
4.26
4.25
3.89
3.88
3.86
3.75
3.72
3.68
3.62
3.53
3.51
3.33
2.94
NO2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.99
0.99
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2.06
2.04
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2.15
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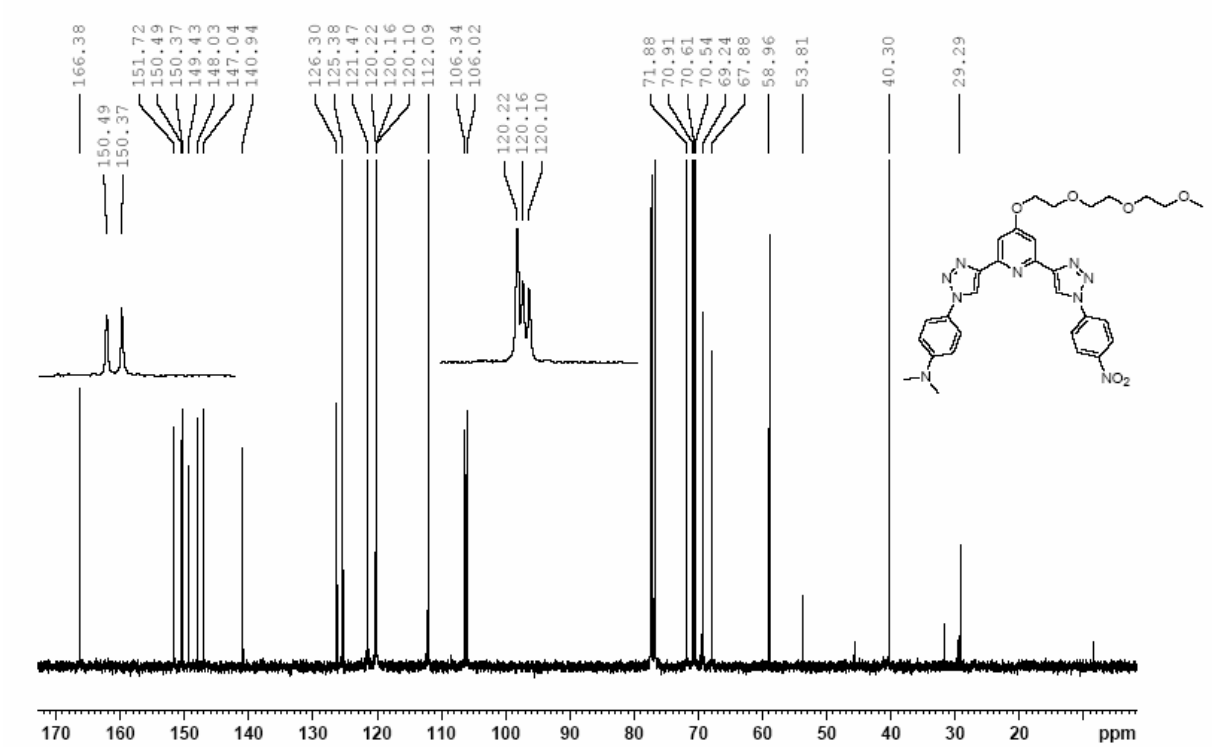
5.99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148.03
147.04
140.94
126.30
125.38
121.47
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120.16
120.10
112.09
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120.22
120.16
120.10
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70.61
70.54
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53.81
40.30
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120
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80
70
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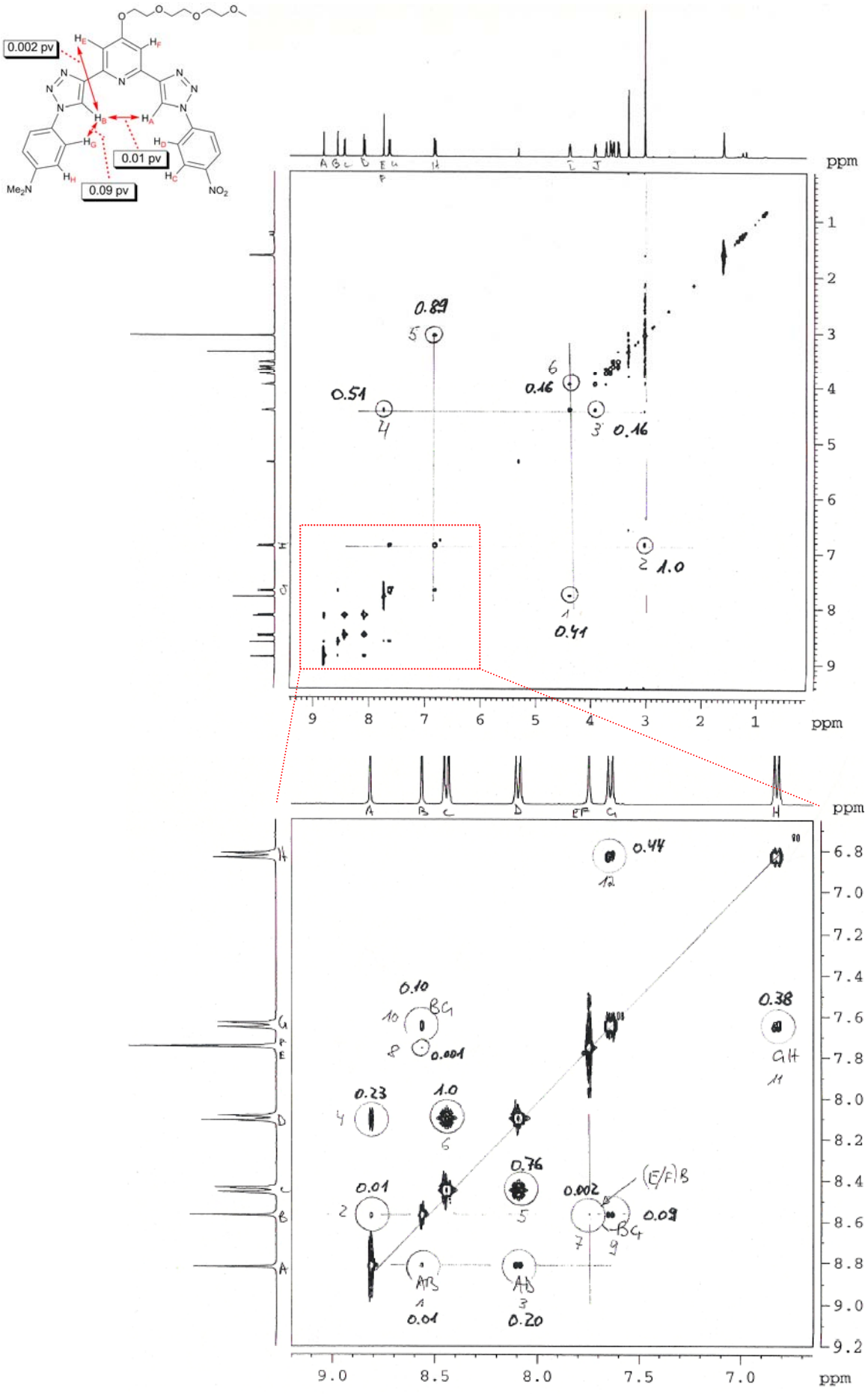
50
40
30
20
ppm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0.01 pv
0.09 pv
Me2N
NO2
ppm
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0.38
0.23
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0.01
0.76
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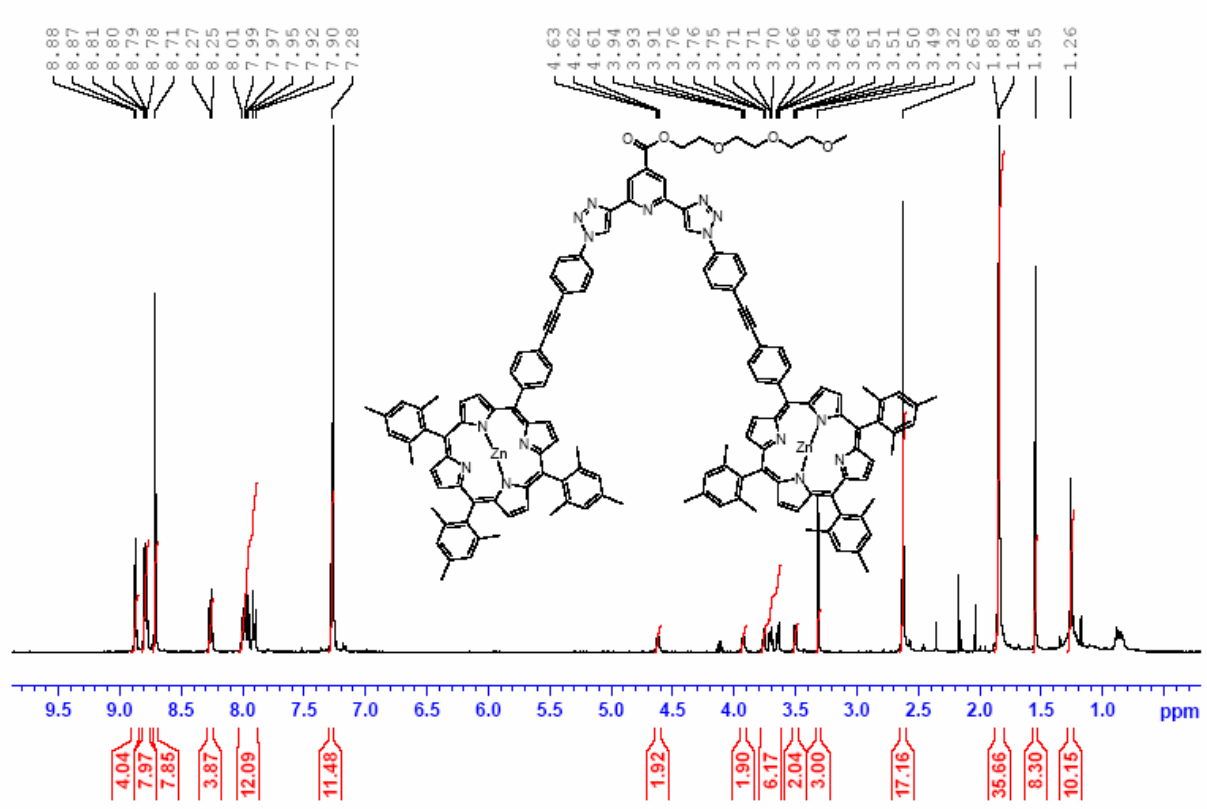
0.01
0.20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8.27
8.25
8.01
7.99
7.97
7.95
7.92
7.90
7.28
4.63
4.62
4.61
3.94
3.93
3.91
3.76
3.76
3.75
3.71
3.71
3.70
3.66
3.65
3.64
3.63
3.51
3.51
3.50
3.49
3.32
2.63
1.85
1.84
1.55
1.26
Zn
Zn
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8.0
7.5
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
ppm
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7.97
7.85
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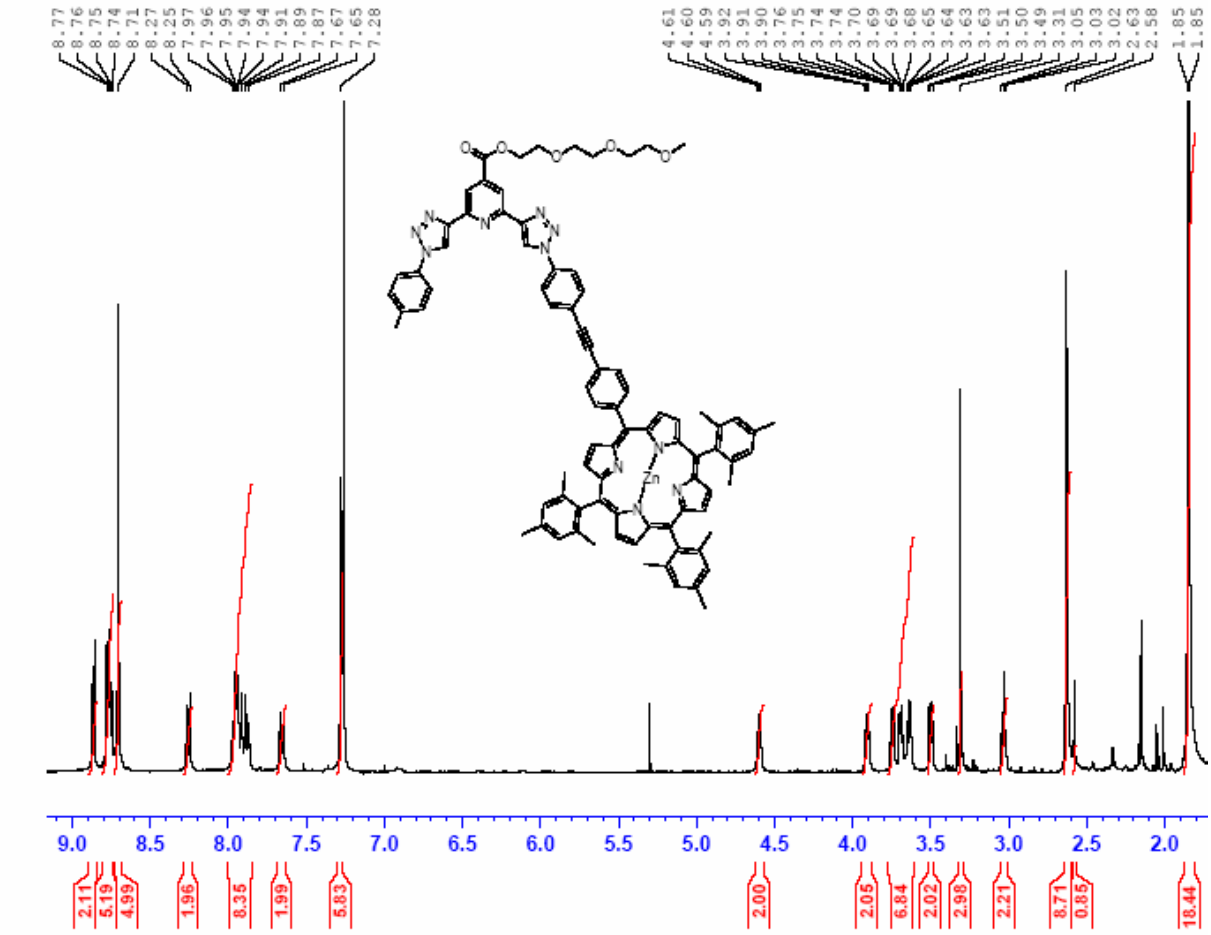
10.15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7.89
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7.65
7.28
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4.60
4.59
3.92
3.91
3.90
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3.69
3.68
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3.51
3.50
3.49
3.31
3.05
3.03
3.02
2.63
2.58
1.85
1.85
Zn
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
2.11
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4.99
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0.85
18.44