

Molecular Machinery: Synthesis of a "Nanodragster"

Supporting Information

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General Synthetic Methods. ¹H NMR and ¹³C NMR spectra were recorded at 400 and 500 MHz, respectively, on a Bruker Avance 400 and Avance 500 spectrometer. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). Mass spectroscopy was performed at the Rice University Mass Spectrometry Laboratory or at the University of South Carolina Mass Spectrometry Laboratory. IR spectra were obtained on a Nicolet Avatar 360 FTIR. All Reagent grade tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled under nitrogen over sodium benzophenone ketyl. Triethylamine and CH₂Cl₂ were distilled over CaH₂ under nitrogen unless otherwise stated. THF and triethylamine were well-degassed with a stream of argon for 1 h before being used in the Castro-Stephens-Sonogashira coupling. All other reagents were purchased from commercial suppliers and used without further purification. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. or Petra Research Inc. Flash chromatography was carried out using silica gel (230-400 mesh from EM science). Thin layer chromatography (TLC) was carried out on glass plates coated with silica gel 40 F254 purchased from EM Science. All reactions were conducted under a dry oxygen-free atmosphere using oven-dried glassware unless otherwise stated. PdCl₂(PPh₃)₂, ¹**2**, ²**3**, ⁷**3** and ⁹**2** were prepared using literature procedures.

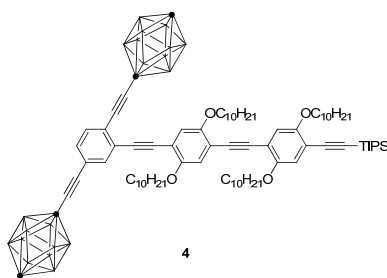
¹ Itatani, H.; Bailar, J. C., *J. Am. Oil Chem. Soc.* **1967**, *44*, 147.

² Shirai, Y.; Zhao, Y.; Cheng, L.; Tour, J. M. *Org. Lett.* **2004**, *6*, 2129-2132.

³ Morin, J.-F.; Sasaki, T.; Shirai, Y.; Guerrero, J. M.; Tour, J. M. *J. Org. Chem.* **2007**, *72*, 9481-9490.

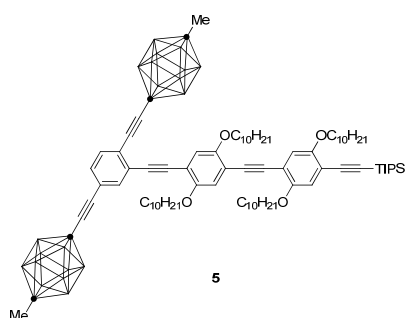
General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Using a Palladium-Catalyzed Sonogashira Coupling. To an oven-dried round-bottom flask equipped with a magnetic stir bar were added the aryl halide, the terminal alkyne, $\text{PdCl}_2(\text{PPh}_3)_2$ (ca. 2 mol % per aryl halide), and CuI (ca. 4 mol % per aryl halide). A solvent system of Et_3N and/or THF was added depending on the substrates. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl . The organic layer was then diluted with hexanes, diethyl ether, or CH_2Cl_2 and was washed with water or saturated NH_4Cl (1 \times). The combined aqueous layers were extracted with hexanes, diethyl ether, or CH_2Cl_2 (2 \times). The combined organic layers were dried over MgSO_4 , filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each compound.

General procedure for the removal of TMS/TIPS protecting groups. To an oven-dried round-bottom flask equipped with a magnetic stir bar were added the TMS-protected compound dissolved in THF. Then to the stirred solution TBAF (ca. 1.5~2 equiv. per TMS/TIPS) was added and the mixture was stirred for ~1 h (completion monitored by TLC). Upon completion, the reaction was diluted with 20% CH_2Cl_2 in hexane and the mixture was passed through a short silica plug. The column was washed with 75% CH_2Cl_2 in hexane until the entire product was removed. The solvent was removed in vacuo to afford the product.

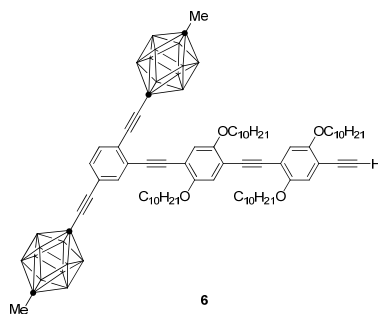


Compound 4. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **2** (200 mg, 0.20 mmol), **3** (130 mg, 0.24 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 0.02 mmol), CuI (8.0 mg, 0.04 mmol), THF (10 mL), and Et_3N (10 mL) at RT overnight. The crude product was purified by column chromatography (silica gel, Hexanes / CH_2Cl_2 8:2) to yield a yellow solid (250 mg, 88%). FTIR 2924, 2854, 2615, 2148, 1505, 1466, 1424, 1385, 1214, 1064 cm^{-1} ; ^1H NMR (400 MHz CDCl_3) δ 7.38 (dd, $J = 1.6$ Hz, $J = 0.5$ Hz, 1H), 7.21 (dd, $J = 8.1$ Hz, $J = 0.5$ Hz, 1H), 7.12 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.03 (s, 1H), 7.02 (s,

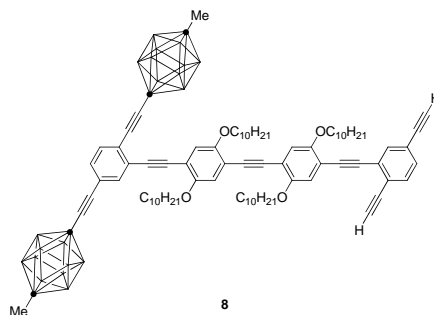
1H), 6.96 (s, 1H), 6.94 (s, 1H), 4.11 (t, $J = 6.3$ Hz, 2H), 4.03 (t, $J = 6.3$ Hz, 2H), 4.01 (t, $J = 6.3$ Hz, 2H), 3.95 (t, $J = 6.3$ Hz, 2H), 3.2-1.7 (m broad, 30H), 1.50 (m, 8H), 1.27 (m, 48H), 1.15 (s broad, 21H), 0.87 (m, 12H); ^{13}C NMR (100 MHz CDCl_3) δ 154.5, 154.0, 153.6, 153.4, 135.3, 132.2, 130.9, 127.0, 123.8, 122.1, 118.2, 117.2, 117.0, 116.7, 115.0, 114.5, 114.2, 113.4, 103.2, 96.7, 92.1, 91.7, 91.4, 91.4, 87.9, 70.1, 69.8, 69.4, 32.1, 29.9, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 26.4, 26.3, 26.2, 26.2, 22.9, 18.9, 14.3, 11.6; MALDI-TOF (sulfur as the matrix): calculated for $\text{C}_{81}\text{H}_{134}\text{B}_{20}\text{O}_4\text{Si}$: 1416.2 found: 1416.5.



Compound 5. In a Schlenk tube, *n*-BuLi (0.2 ml, 0.5 mmol, 2.5 M) was added dropwise to a solution of **4** (215 mg, 0.15 mmol) in THF at -78°C . The solution was stirred at -78°C for 1 h, then MeI (0.1 ml, 1.6 mmol) was added. The mixture was stirred another 30 min at -78°C , then allowed to warm to RT and was stirred for an additional 2 h. The solvent was evaporated and the mixture purified by column chromatography (silica gel, hexanes / CH_2Cl_2 8:2) to yield **5** as a yellow solid (215 mg, 98%). FTIR 2924, 2854, 2611, 2149, 1505, 1466, 1424, 1385, 1275, 1214, 1022 cm^{-1} ; ^1H NMR (400 MHz CDCl_3) δ 7.35 (d, $J = 1.6$ Hz, 1H), 7.18 (d, $J = 8.1$ Hz, 1H), 7.09 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 6.95 (s, 1H), 6.94 (s, 1H), 4.11 (t, $J = 6.3$ Hz, 2H), 4.02 (t, $J = 6.3$ Hz, 2H), 4.00 (t, $J = 6.3$ Hz, 2H), 3.95 (t, $J = 6.3$ Hz, 2H), 3.2-1.7 (m broad, 28H), 1.50 (m, 8H), 1.39 (s, 6H), 1.27 (m, 48H), 1.14 (s broad, 21H), 0.87 (m, 12H); ^{13}C NMR (100 MHz CDCl_3) δ 154.56, 153.98, 153.67, 153.47, 135.37, 132.24, 130.92, 126.99, 123.90, 122.21, 118.17, 117.21, 117.06, 116.71, 114.95, 114.56, 114.22, 113.52, 103.25, 96.73, 92.08, 91.85, 91.51, 91.33, 90.79, 87.67, 70.11, 69.80, 69.79, 69.43, 32.17, 32.14, 29.97, 29.94, 29.88, 29.85, 29.79, 29.77, 29.75, 29.73, 29.66, 29.63, 29.57, 26.48, 26.38, 26.31, 26.28, 26.25, 22.94, 18.97, 14.37, 11.62; 11.6; MALDI-TOF (sulfur as the matrix): calculated for $\text{C}_{83}\text{H}_{138}\text{B}_{20}\text{O}_4\text{Si}$: 1444.3 found: 1444.5.

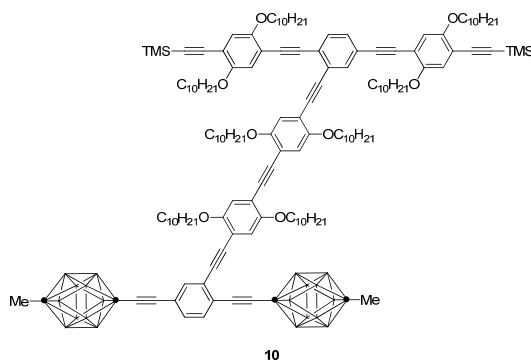


Compound 6. **5** was deprotected with TBAF (see the general procedure for the removal of TMS/TIPS protecting groups). The materials used were **5** (200 mg, 0.13 mmol), THF (10 mL), and TBAF (0.30 mL, 0.30 mmol) at RT. The resulting reaction mixture was passed through a plug of silica gel, and concentrated to afford the title compound **6** as a yellow solid (169 mg, 95%). FTIR 2923, 2853, 2610, 1506, 1467, 1423, 1385, 1215, 1022 cm^{-1} ; ^1H NMR (400 MHz CDCl_3) δ 7.35 (d, $J = 1.6$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H), 7.10 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 4.12 (t, $J = 6.3$ Hz, 2H), 4.01 (m, 6H), 3.35 (s, 1H), 3.2-1.7 (m broad, 28H), 1.50 (m, 8H), 1.41 (s, 6H), 1.27 (m, 48H), 0.87 (m, 12H); ^{13}C NMR (100 MHz CDCl_3) δ 154.37, 153.98, 153.70, 153.53, 135.38, 132.25, 130.94, 126.96, 123.90, 122.22, 118.23, 117.25, 117.22, 117.07, 115.19, 114.80, 113.67, 112.77, 91.91, 91.77, 91.67, 91.28, 90.80, 82.53, 80.29, 78.30, 78.18, 70.00, 69.80, 32.16, 29.98, 29.94, 29.87, 29.84, 29.81, 29.77, 29.74, 29.70, 29.63, 29.59, 29.53, 29.43, 26.38, 26.31, 26.28, 26.23, 26.20, 22.94, 18.38, 17.94, 14.37, 13.63, 12.51; MALDI-TOF (sulfur as the matrix): calculated for $\text{C}_{74}\text{H}_{118}\text{B}_{20}\text{O}_4$: 1287.9 found:1288.4.



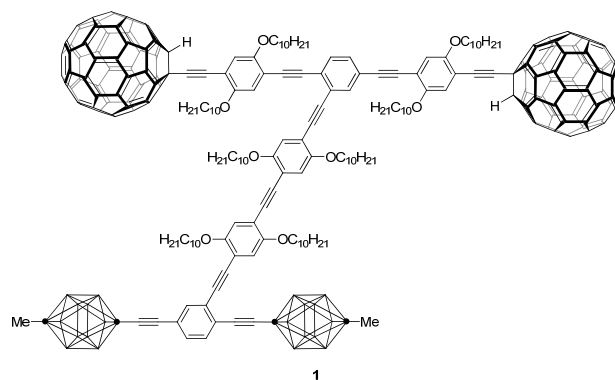
Compound 8. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **6** (170 mg, 0.13 mmol), **7** (45 mg, 0.11 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (8 mg, 0.001 mmol), CuI (4 mg, 0.002 mmol), THF (10 mL), and Et_3N (10 mL) at RT overnight. The crude product was purified by column chromatography (silica gel, hexanes / CH_2Cl_2 7:3) to yield a yellow solid. The product was immediately deprotected (see the general procedure for the removal of TMS/TIPS protecting groups) with K_2CO_3 (100 mg), MeOH (5mL) and THF (5 mL) at RT for 2 h. The resulting reaction mixture was passed through a plug of silica

gel, and concentrated to afford the title compound **8** as a fluorescent yellow solid (75 mg, 48% two steps). FTIR 2923, 2853, 2610, 1423, 1216, 1022 cm^{-1} ; ^1H NMR (400 MHz CDCl_3) δ 7.67 (d, $J = 1.6$ Hz, 1H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.38 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.37 (d, $J = 1.6$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H), 7.10 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.04 (s, 1H), 7.03 (s broad, 2H), 7.02 (s, 1H), 4.12 (t, $J = 6.3$ Hz, 2H), 4.01 (m, 6H), 3.43 (s, 1H), 3.18 (s, 1H), 3.2-1.7 (m broad, 28H), 1.50 (m, 8H), 1.41 (s, 6H), 1.27 (m, 48H), 0.87 (m, 12H); ^{13}C NMR (100 MHz CDCl_3) δ 154.06, 154.01, 153.73, 153.68, 135.70, 135.38, 132.85, 132.25, 131.44, 130.93, 127.05, 126.98, 124.71, 123.91, 122.81, 122.22, 117.92, 117.40, 117.28, 117.11, 115.25, 114.88, 113.71, 113.69, 92.38, 91.97, 91.91, 91.31, 91.16, 90.81, 87.69, 83.02, 82.54, 82.05, 79.66, 78.31, 78.20, 70.09, 69.92, 69.85, 69.82, 32.16, 32.14, 29.98, 29.94, 29.90, 29.88, 29.84, 29.77, 29.75, 29.73, 29.66, 29.63, 29.60, 29.58, 26.38, 26.31, 26.29, 26.26, 22.93, 14.36; MALDI-TOF (sulfur as the matrix): calculated for $\text{C}_{84}\text{H}_{122}\text{B}_{20}\text{O}_4$: 1412.1 found:1412.5.



Compound 10. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **8** (75 mg, 0.053 mmol), **9** (100 mg, 0.16 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 0.02 mmol), CuI (8.0 mg, 0.04 mmol), THF (10 mL), and Et_3N (5 mL) at RT overnight. The crude product was purified by column chromatography (silica gel, Hexanes / CH_2Cl_2 7:3) to yield **10** as a fluorescent yellow solid (50 mg, 39%). FTIR 2924, 2853, 2611, 1502, 1466, 1425, 1379, 1275, 1216, 1022, 843 cm^{-1} ; ^1H NMR (500 MHz CDCl_3) δ 7.70 (d, $J = 1.6$ Hz, 1H), 7.50 (d, $J = 8.1$ Hz, 1H), 7.42 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.37 (d, $J = 1.6$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H), 7.10 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 7.00 (s, 2H), 6.95 (s, 2H), 6.94 (s, 1H), 6.93 (s, 1H), 4.12 (t, $J = 6.3$ Hz, 2H), 4.02-3.93 (m, 12H), 3.82 (t, $J = 6.3$ Hz, 2H), 3.72 (t, $J = 6.3$ Hz, 2H), 3.2-1.7 (m broad, 36H), 1.50 (m, 16H), 1.41 (s, 6H), 1.27 (m, 96H), 0.87 (m, 24H), 0.27 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (126 MHz CDCl_3) δ 154.48, 154.36, 154.00, 153.84, 153.81, 153.78, 153.70, 153.68, 153.58, 135.39, 132.26, 131.73, 131.06, 130.91, 127.00, 126.57, 125.95, 123.87, 123.43, 122.21, 117.80,

117.57, 117.44, 117.23, 117.20, 117.06, 117.04, 117.03, 114.96, 114.84, 114.49, 114.27, 114.21, 114.01, 113.59, 101.36, 101.30, 100.55, 100.43, 94.16, 93.89, 93.19, 92.35, 91.97, 91.94, 91.88, 91.35, 91.11, 90.77, 88.43, 87.68, 70.22, 70.12, 69.79, 69.74, 69.72, 69.70, 69.44, 32.17, 32.15, 29.90, 29.85, 29.66, 29.61, 29.59, 26.29, 22.93, 14.38, 0.21; MALDI-TOF (sulfur as the matrix): calculated for $C_{146}H_{226}B_{20}O_8Si_2$: 2381.7 found: 2382.6

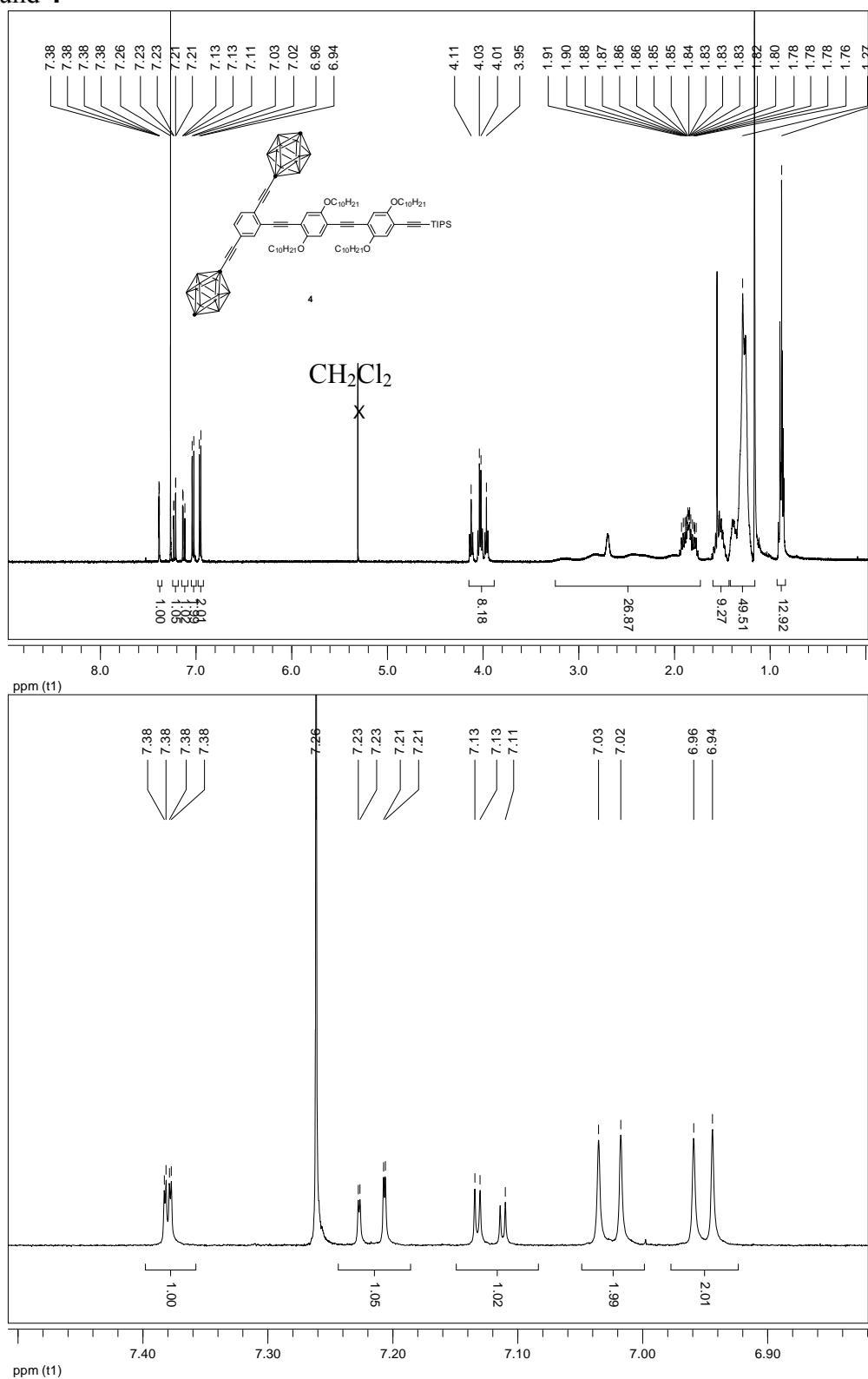


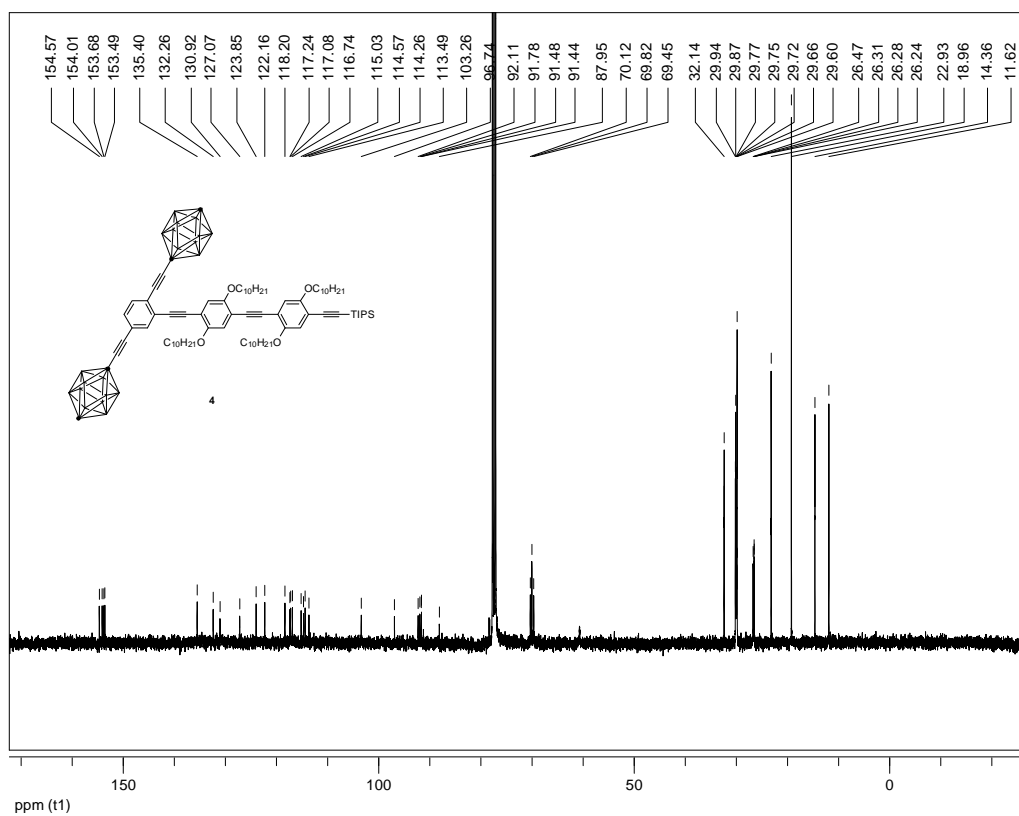
Nanodragster 1. To a solution of **10** (24 mg, 0.010 mmol) in THF (5 mL) was added dropwise TBAF (0.1 mL, 0.1 mmol). 30 min after the addition of TBAF, the resulting reaction mixture was passed through a plug of silica gel, and concentrated to a yellow solid (22 mg, 98%). This material was pure enough to carry on to the next reaction. To an oven-dried 250 mL round-bottom flask equipped with a magnetic stir bar were added the deprotected product (22 mg, 0.0098 mmol) and C_{60} (28 mg, 0.038 mmol). After adding THF (120 mL), the mixture was sonicated for 3 h. To the greenish-brown suspension formed after sonication was added LHMDS (0.1 mL, 0.1 mmol) dropwise at room temperature over 0.5 h. As the reaction progressed, the mixture turned into a deep greenish-black solution. During the addition of LHMDS, small aliquots from the reaction were extracted and quenched with trifluoroacetic acid (TFA), dried and redissolved in CS_2 for TLC analysis (developed in a mixture of CS_2 , CH_2Cl_2 , and hexanes 5:2:3). Completion of the reaction was confirmed by the disappearance of the starting materials. Upon completion, the reaction was quenched with TFA to give a brownish slurry. Excess TFA and solvent were then removed in vacuo to afford a crude product which was then dissolved in CS_2 and directly loaded onto a column (SiO_2). The column was eluted with CS_2 to remove unreacted C_{60} , followed by CS_2 /Hexanes/ CH_2Cl_2 (5:3:2) to afford the nanodragster **1** as a brown solid (14 mg, 41 %). FTIR 2923, 2852, 2609, 1504, 1464, 1423, 1377, 1275, 1216, 1021 cm^{-1} ; 1H NMR (500 MHz $CDCl_3$) δ 7.79 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.52 (dd, J = 8.1 Hz, J = 1.6 Hz, 1H), 7.34 (d, J = 1.6 Hz, 1H), 7.31 (s, 1H), 7.28 (s, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.19 (s,

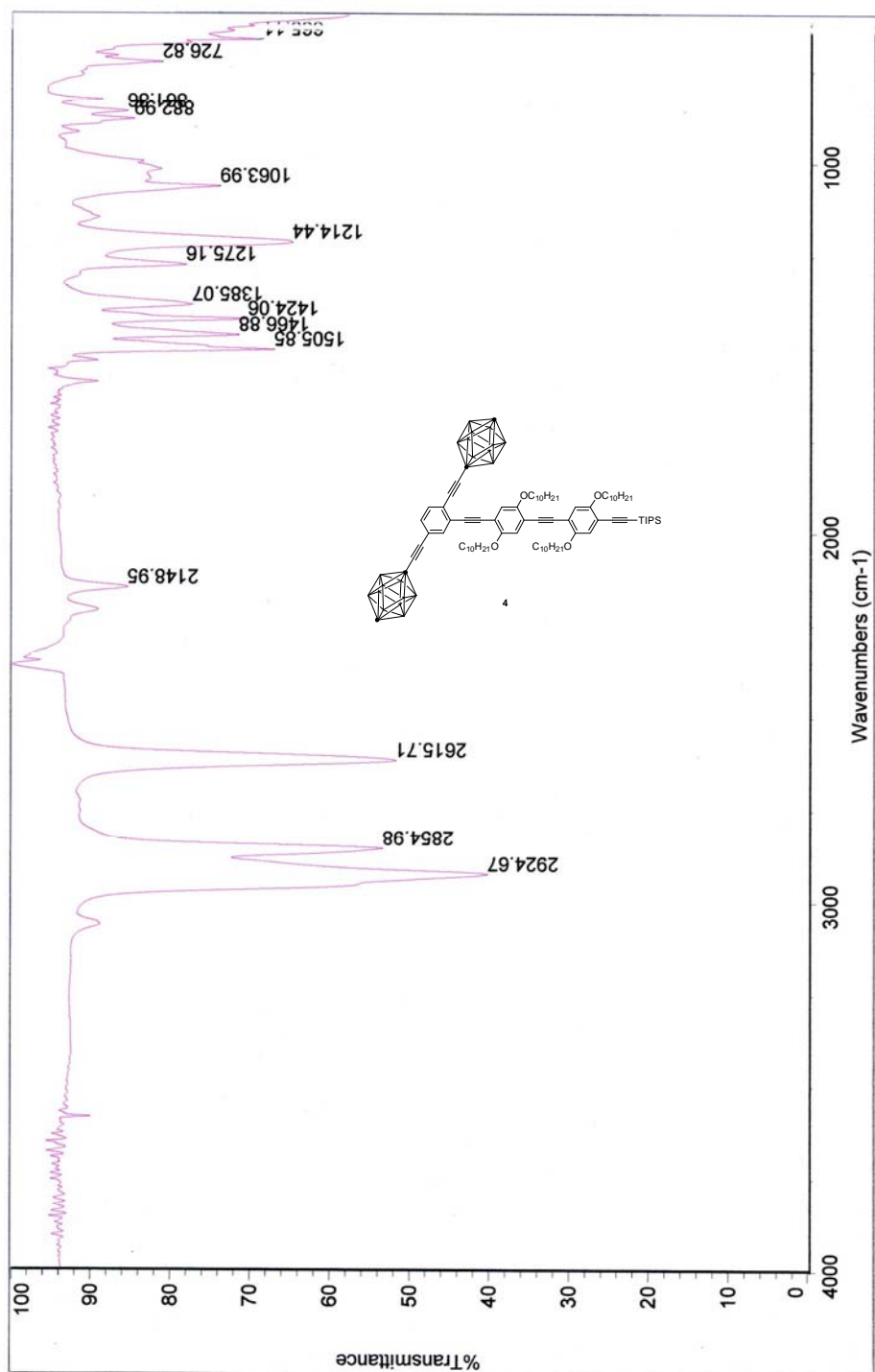
1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.10 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, 1H), 7.09 (s, 1H), 7.07 (s, 1H), 7.01 (s, 1H), 7.00 (s, 1H), 4.18 (m; 4H), 4.11 (m; 4H), 4.04 (t, $J = 6.3$ Hz, 2H), 3.99 (t, $J = 6.3$ Hz, 2H), 3.89 (m, 4H), 3.2-1.7 (m broad, 36H), 1.50 (m, 16H), 1.41 (s, 6H), 1.27 (m, 96H), 0.87 (m, 24H); ^{13}C NMR (126 MHz CDCl_3) δ 154.89, 154.76, 154.05, 154.03, 153.99, 153.95, 153.91, 153.86, 153.84, 153.81, 153.70, 151.88, 151.84, 151.80, 151.72, 147.95, 147.67, 146.97, 146.93, 146.90, 146.88, 146.70, 146.61, 146.54, 146.15, 146.12, 146.08, 146.04, 146.01, 145.95, 145.92, 145.87, 145.76, 145.68, 145.00, 144.97, 144.82, 144.81, 143.50, 143.32, 142.91, 142.88, 142.85, 142.44, 142.41, 142.36, 142.30, 142.28, 142.20, 141.99, 141.97, 141.92, 140.69, 140.68, 140.62, 140.61, 136.40, 136.37, 135.50, 135.46, 135.39, 134.58, 132.25, 131.76, 131.19, 130.92, 130.90, 126.97, 126.95, 126.79, 126.10, 123.86, 123.53, 123.00, 122.21, 118.19, 117.85, 117.65, 117.61, 117.60, 117.55, 117.29, 117.26, 117.23, 117.17, 117.09, 117.07, 117.03, 116.99, 116.97, 115.98, 115.95, 115.56, 115.35, 115.29, 115.05, 114.98, 114.86, 114.79, 114.58, 114.28, 113.68, 113.65, 113.52, 113.38, 113.12, 100.21, 98.03, 94.53, 94.29, 93.25, 92.46, 92.07, 91.94, 91.91, 91.31, 91.29, 90.75, 88.49, 87.68, 70.29, 70.02, 69.83, 69.79, 69.71, 69.54, 62.22, 62.18, 55.81, 32.26, 32.20, 32.18, 32.15, 30.24, 30.18, 30.15, 30.07, 30.04, 29.97, 29.96, 29.93, 29.90, 29.87, 29.79, 29.76, 29.72, 29.68, 29.63, 29.57, 26.38, 26.36, 26.32, 26.31, 22.99, 22.96, 14.45, 14.41; MALDI-TOF (sulfur as the matrix): calculated for $\text{C}_{260}\text{H}_{210}\text{B}_{20}\text{O}_8$: 3678.7 found: 3678.9

^1H and ^{13}C NMR spectra for compounds 1, 4-6, 8, 10

Compound 4







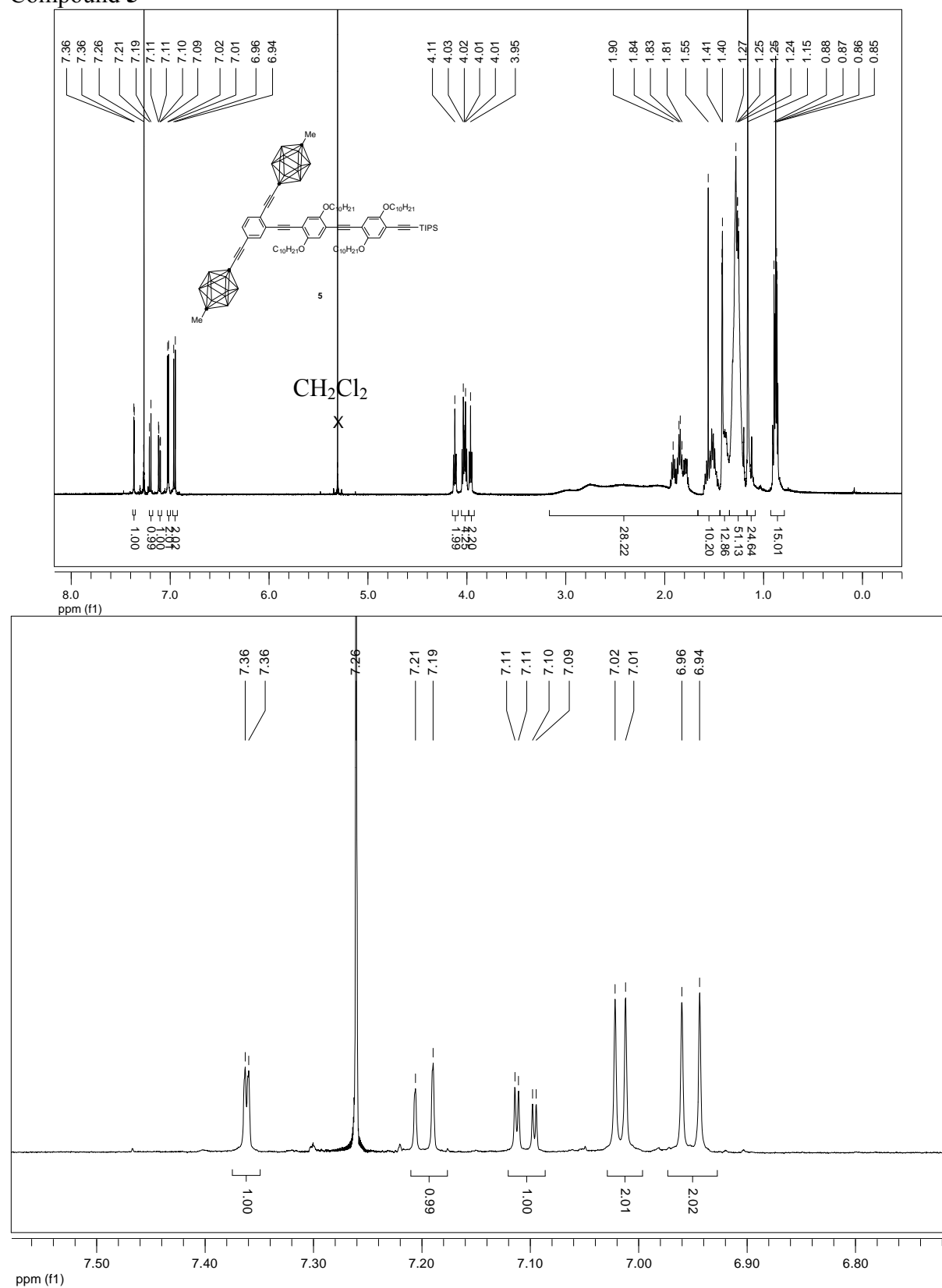
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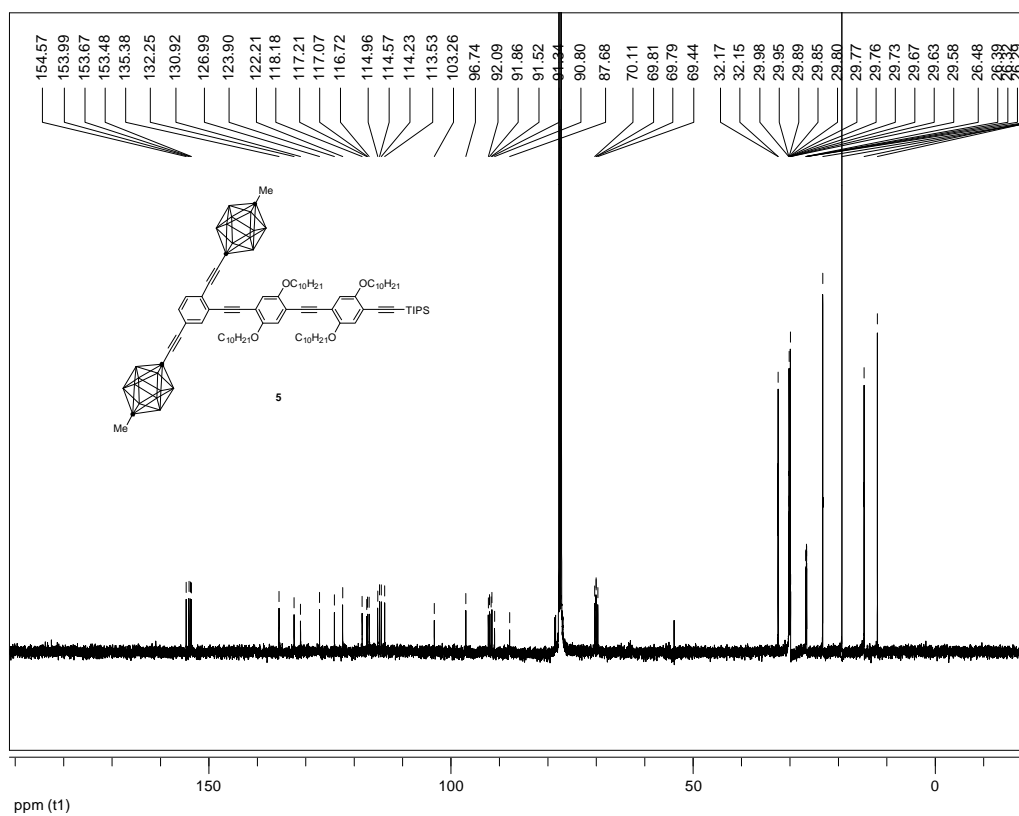
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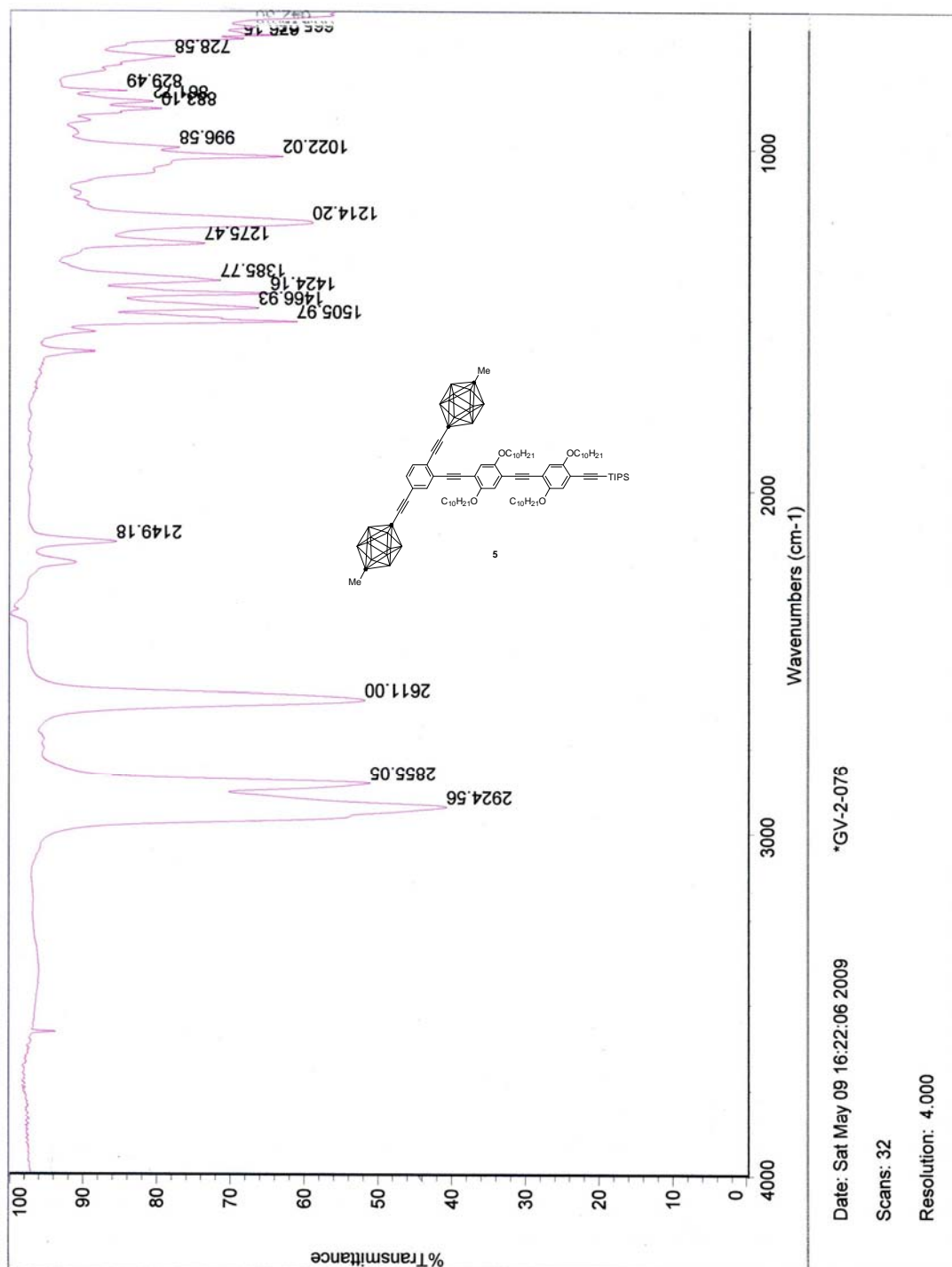
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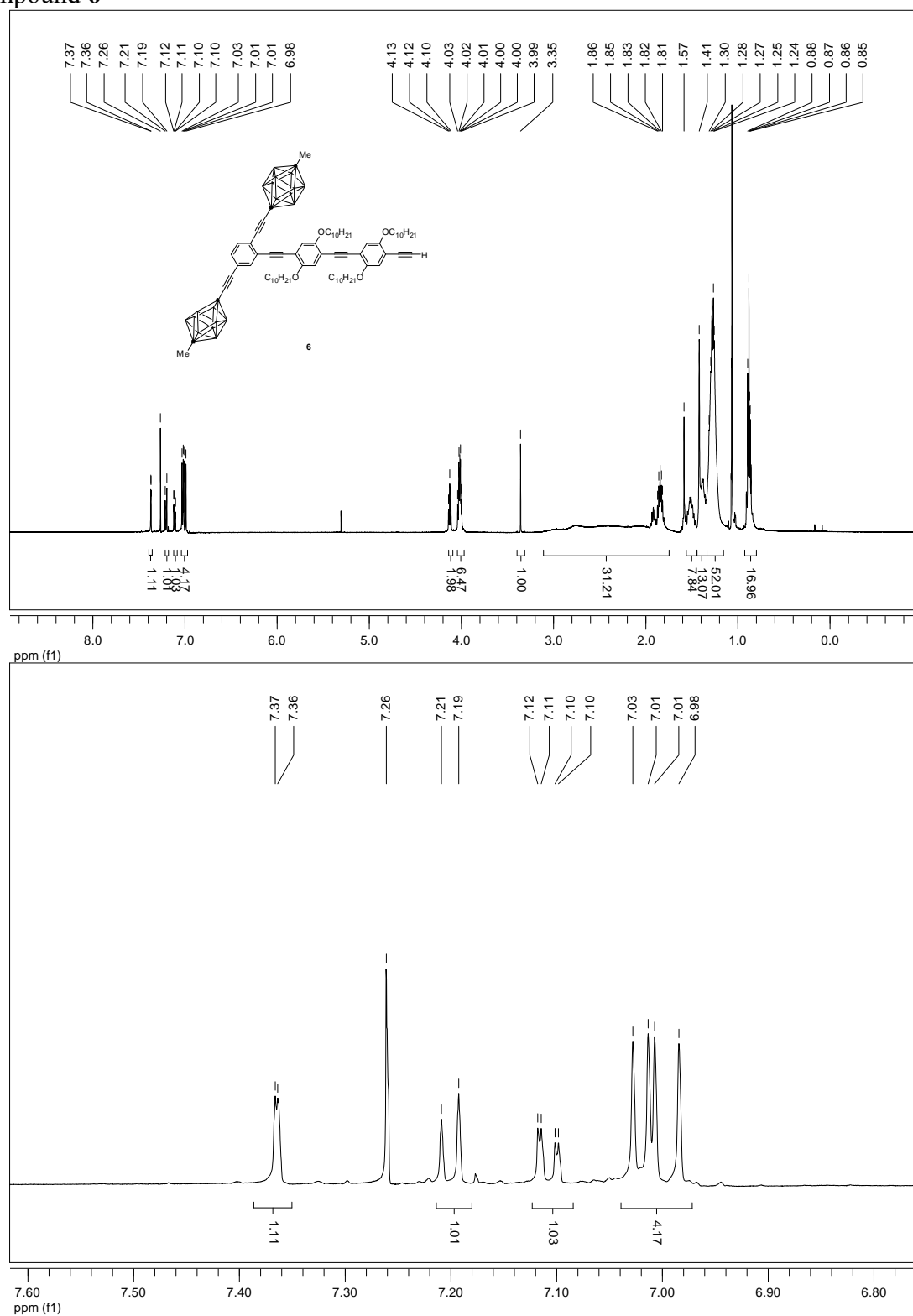
S11

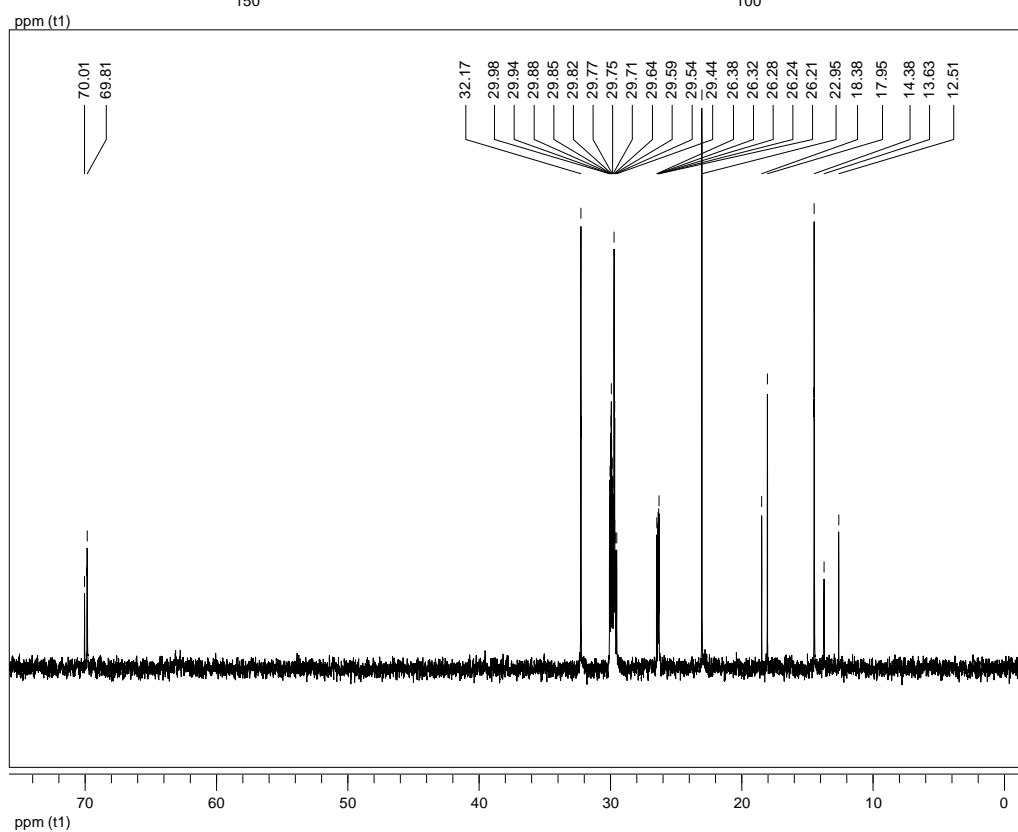
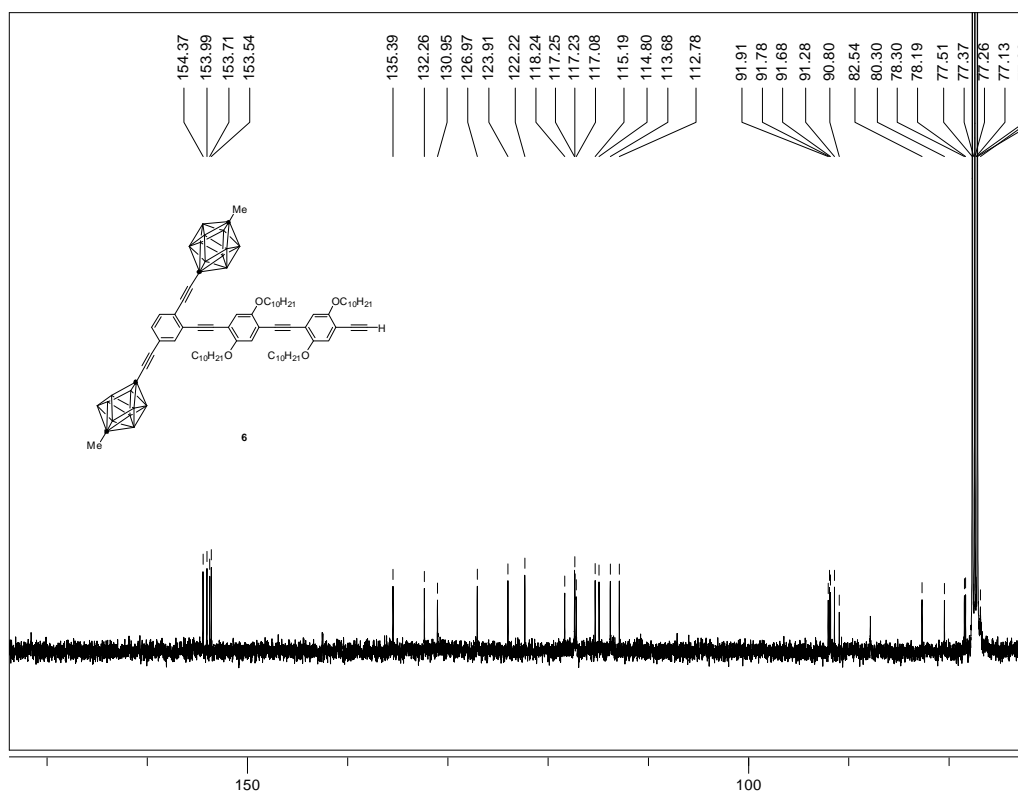


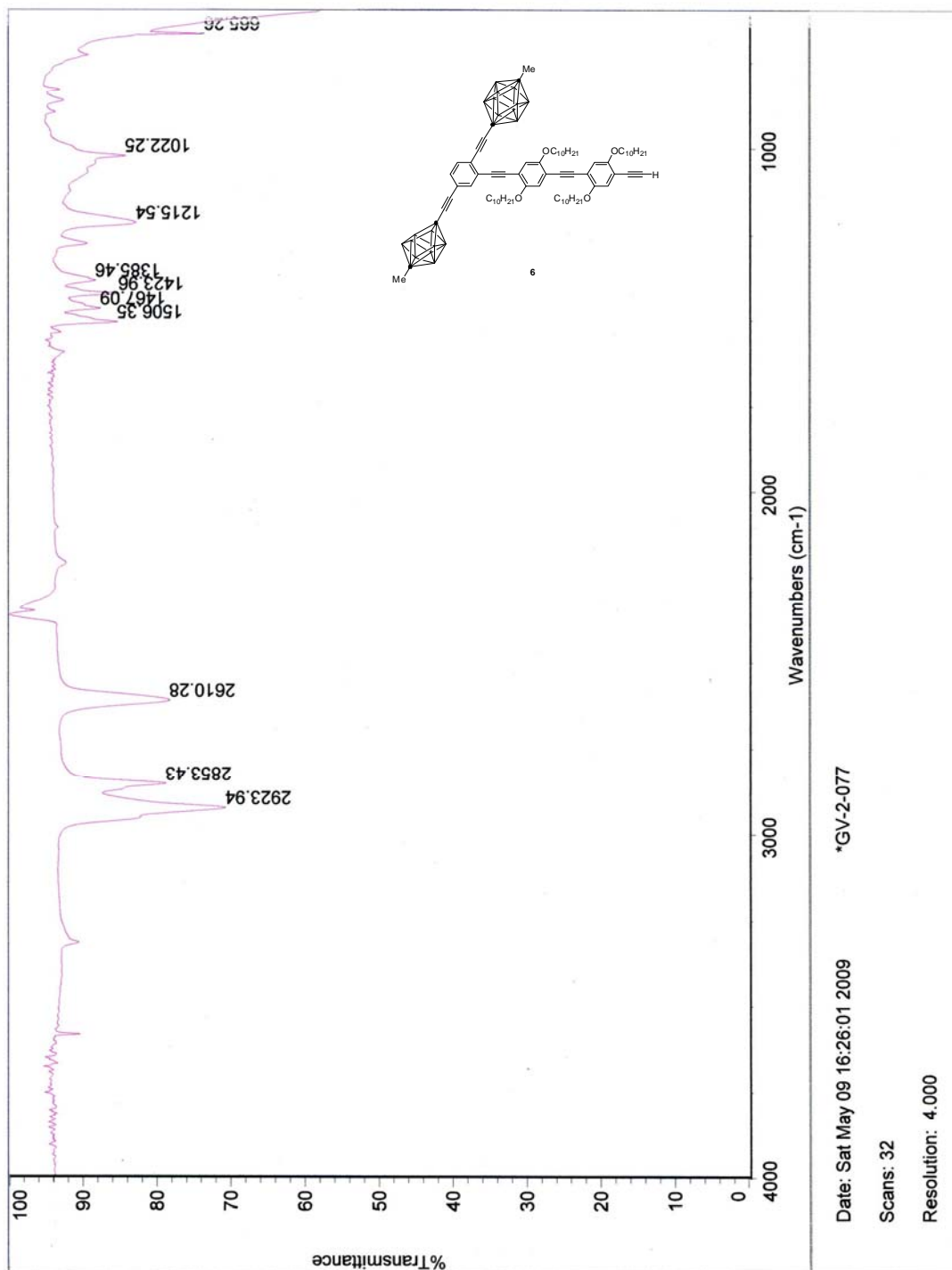




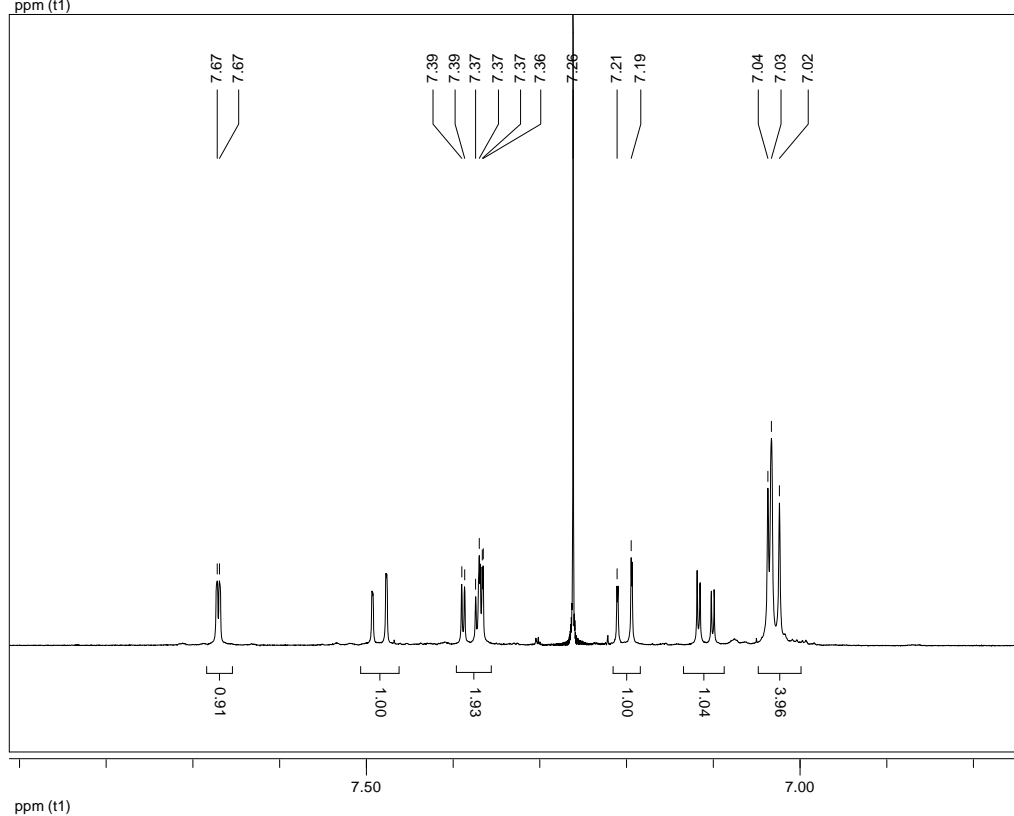
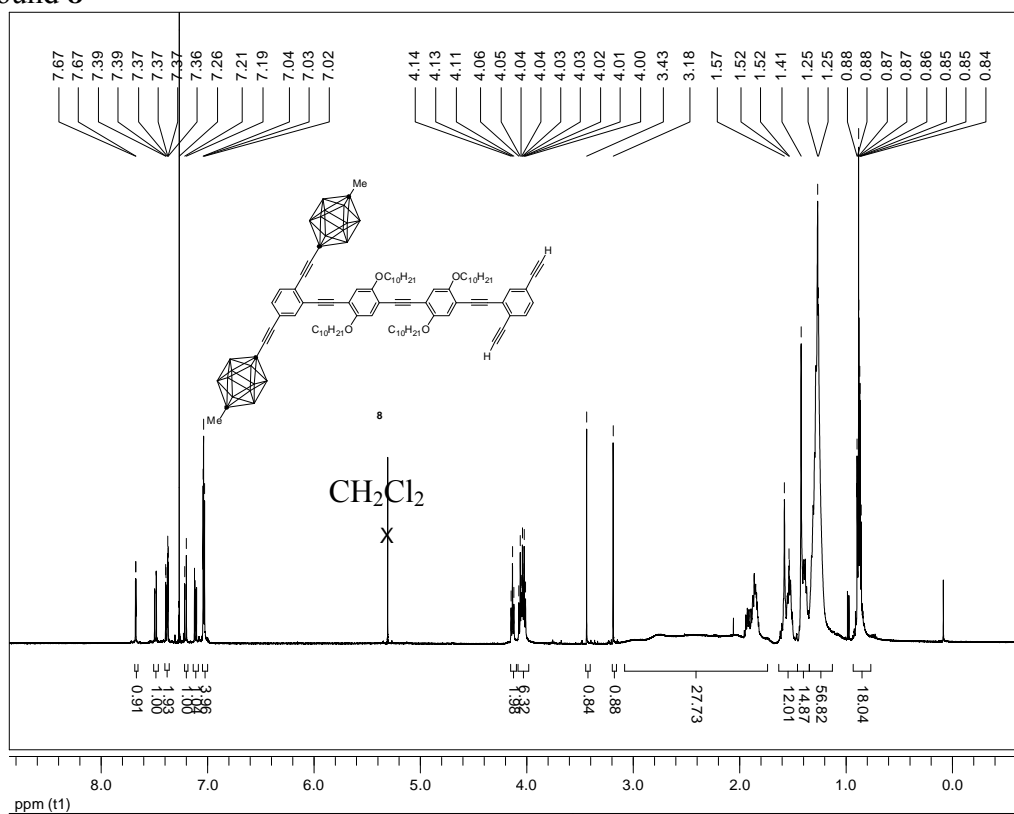
Compound 6

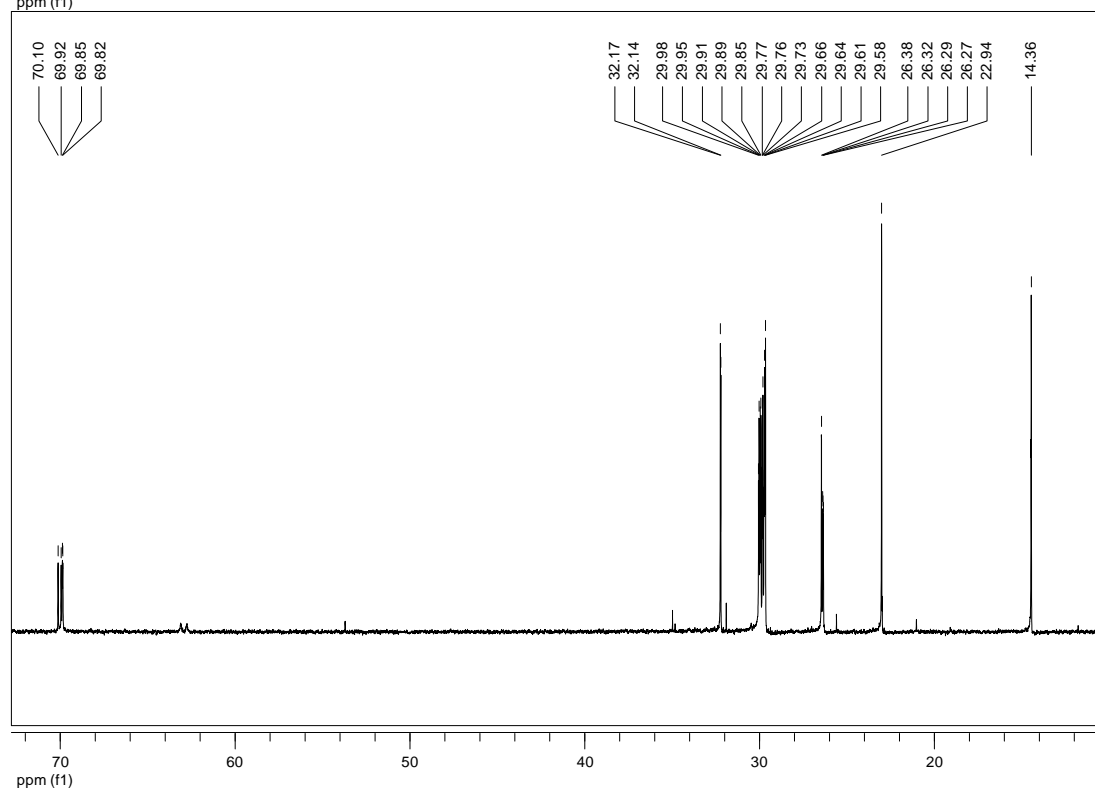
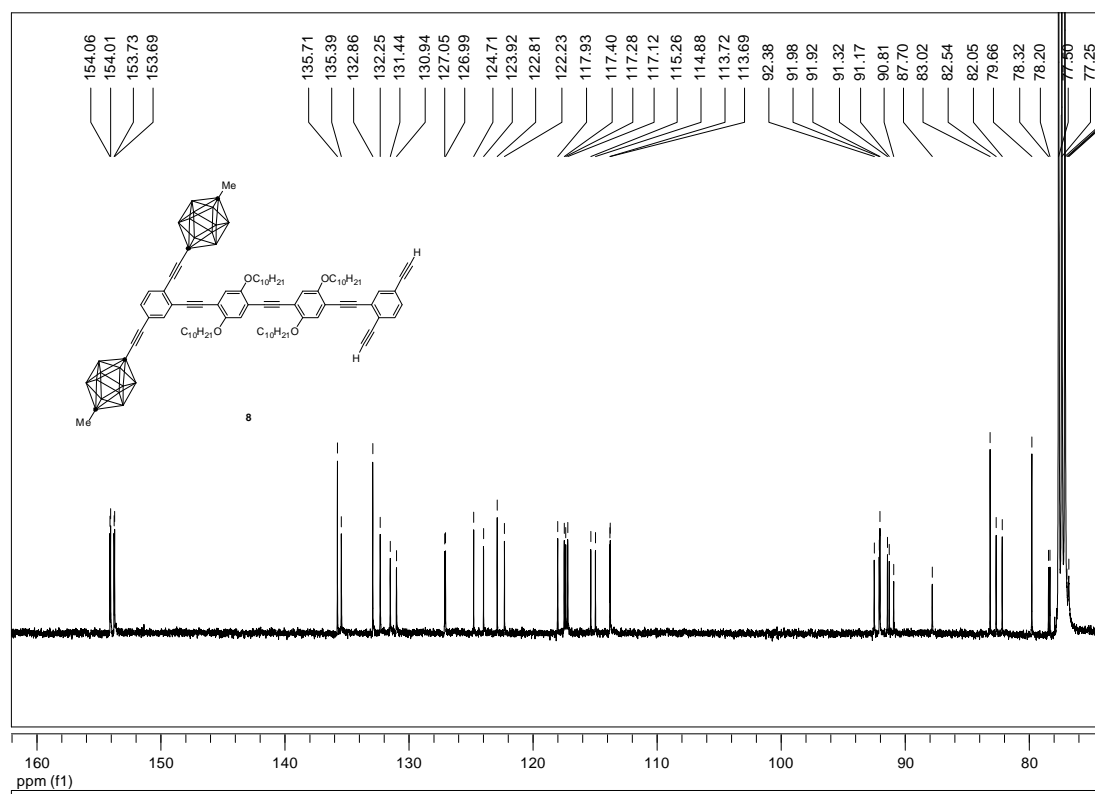


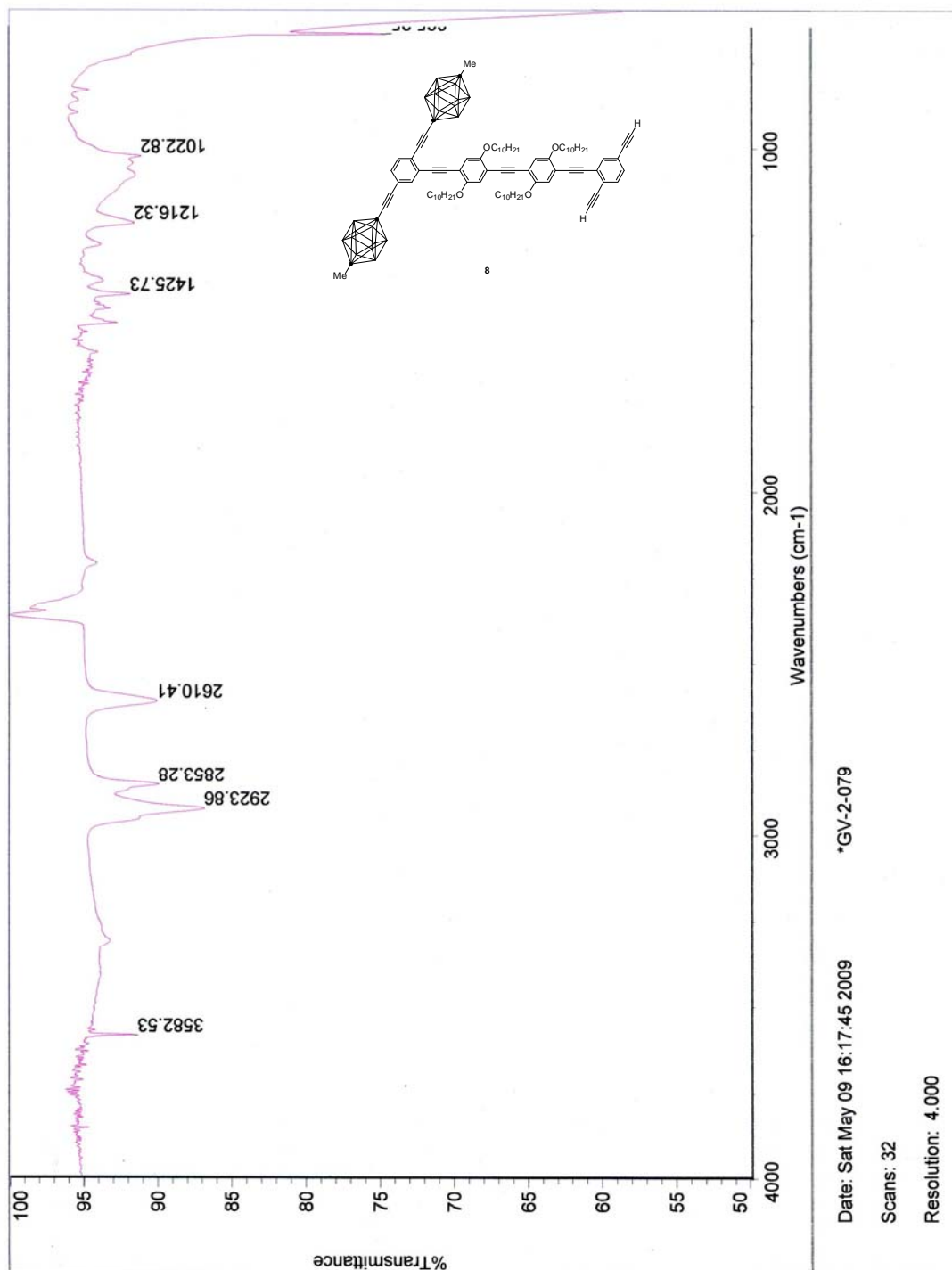




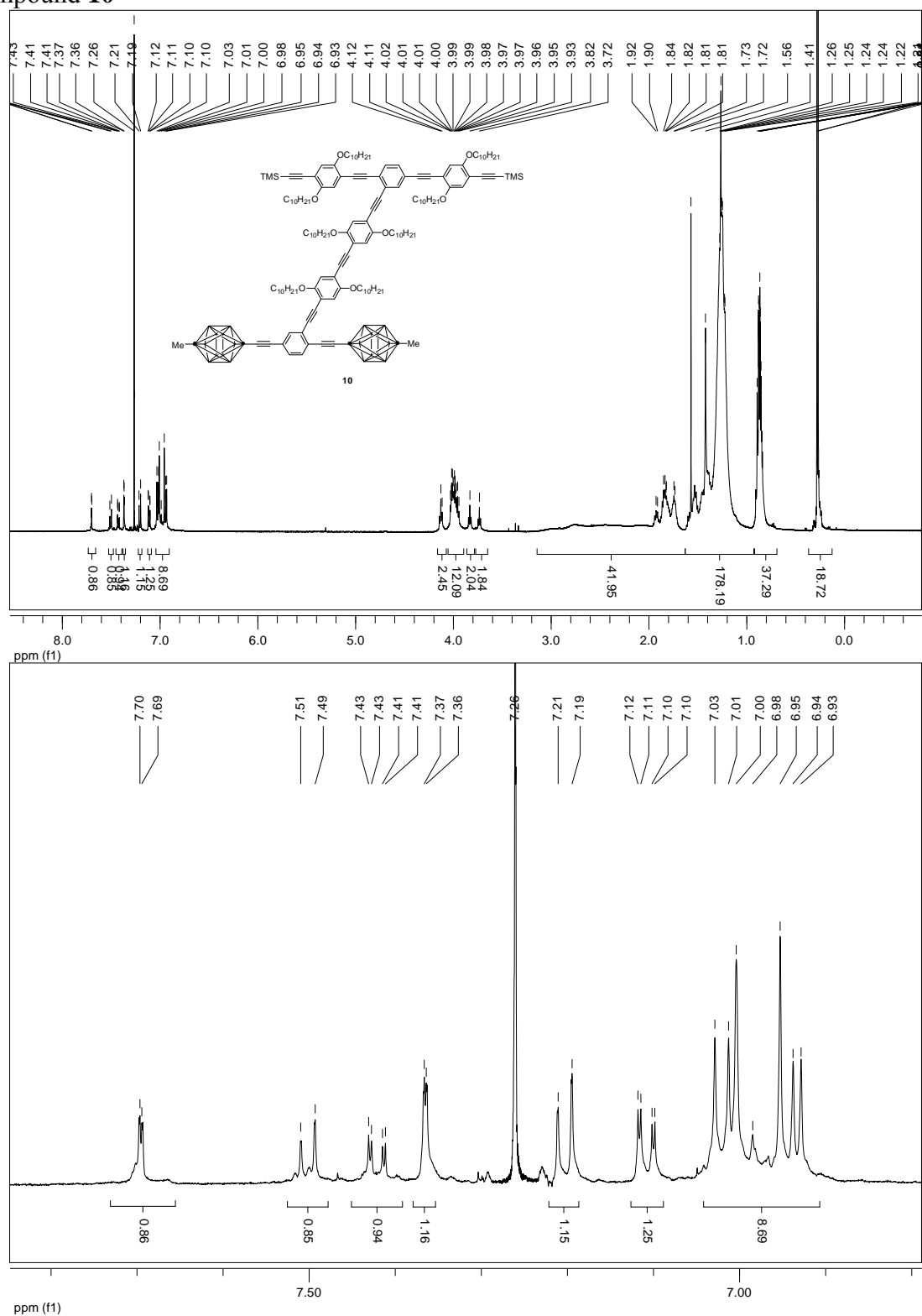
Compound 8

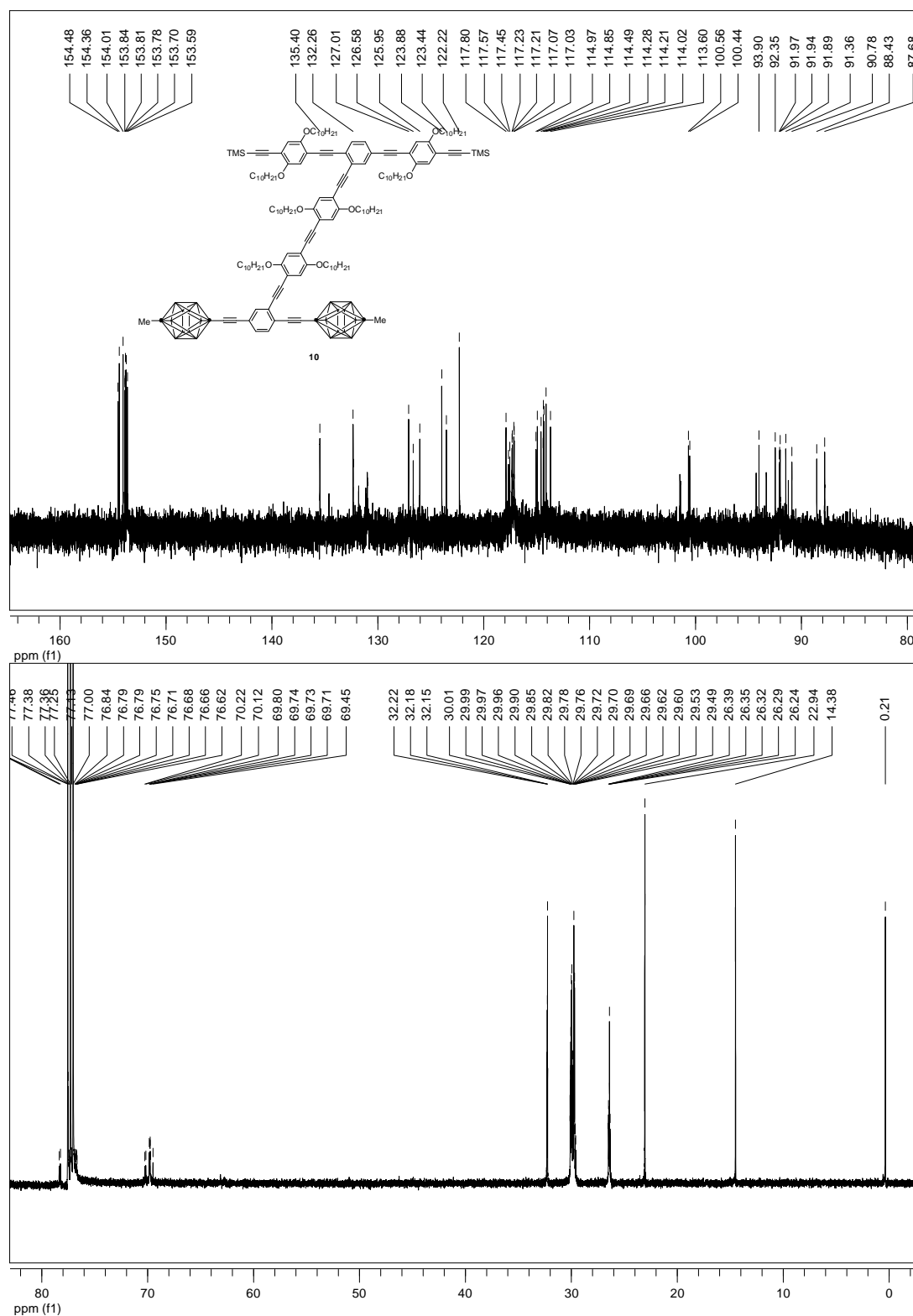


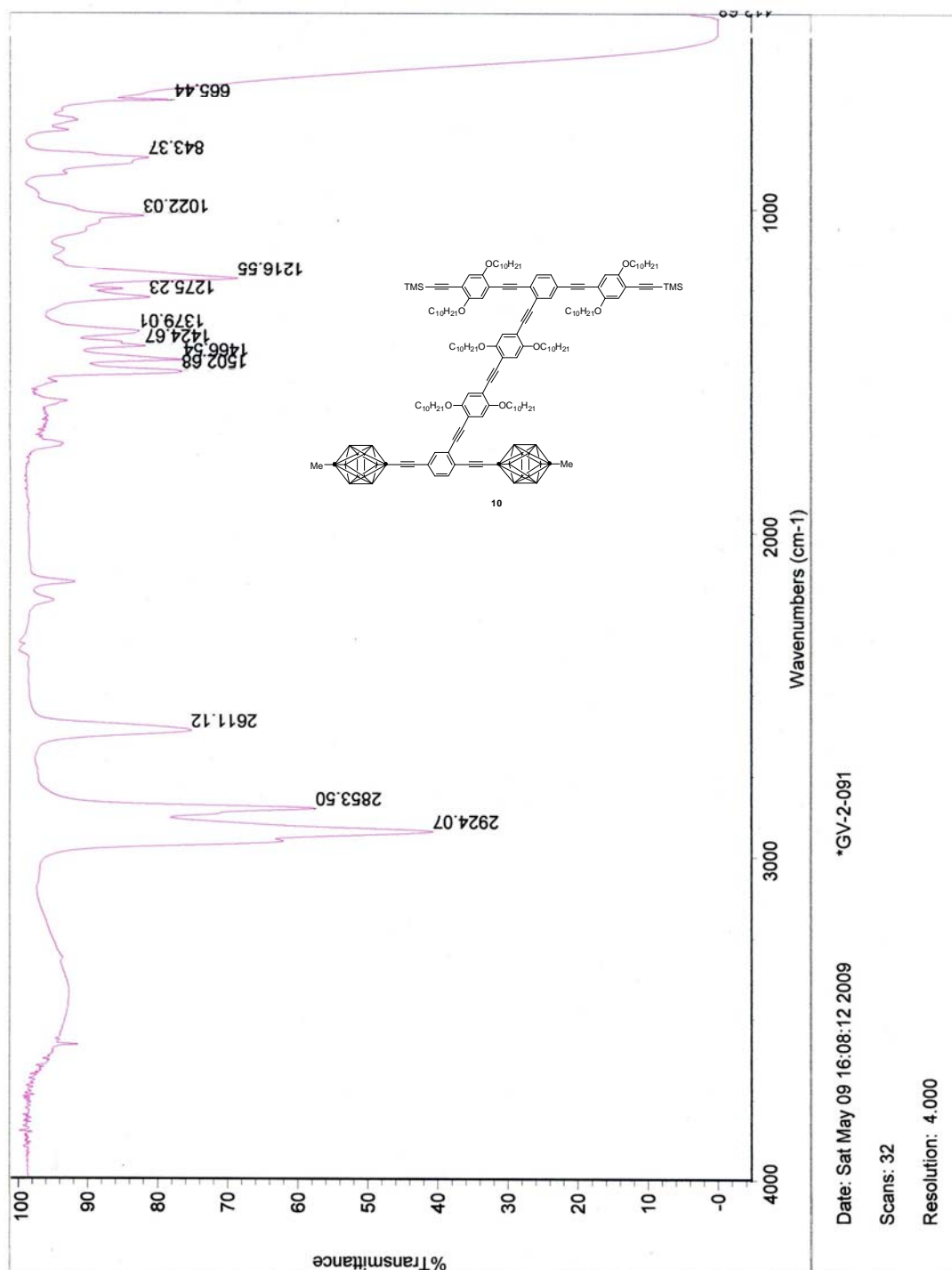




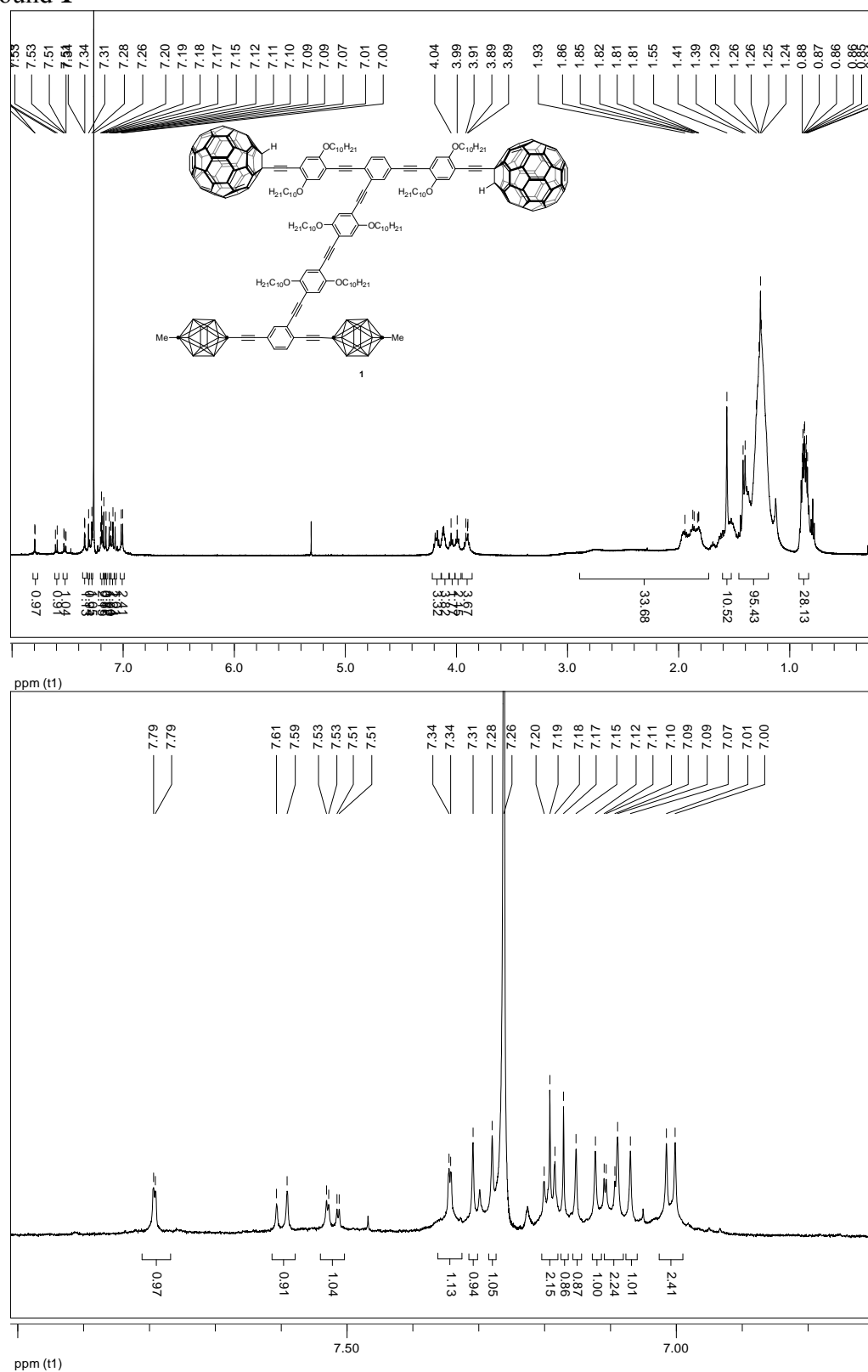
Compound 10

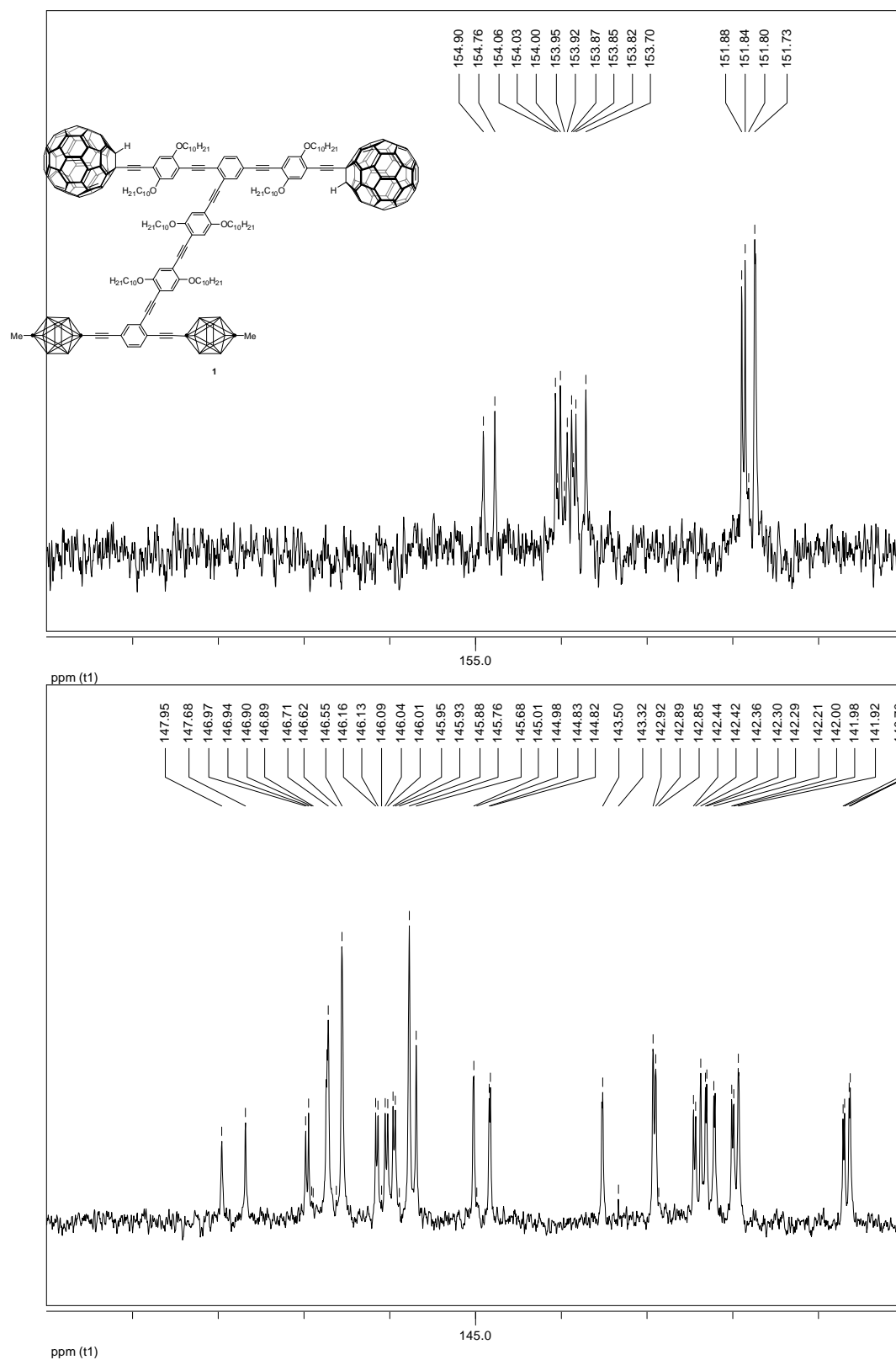


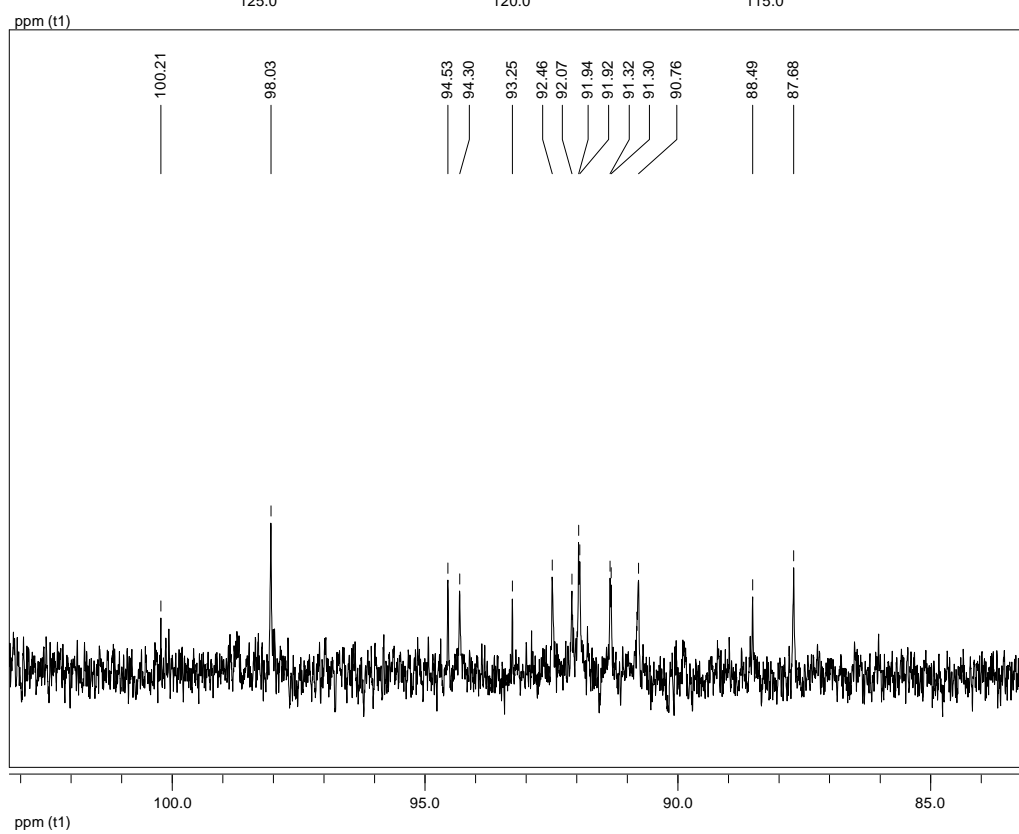
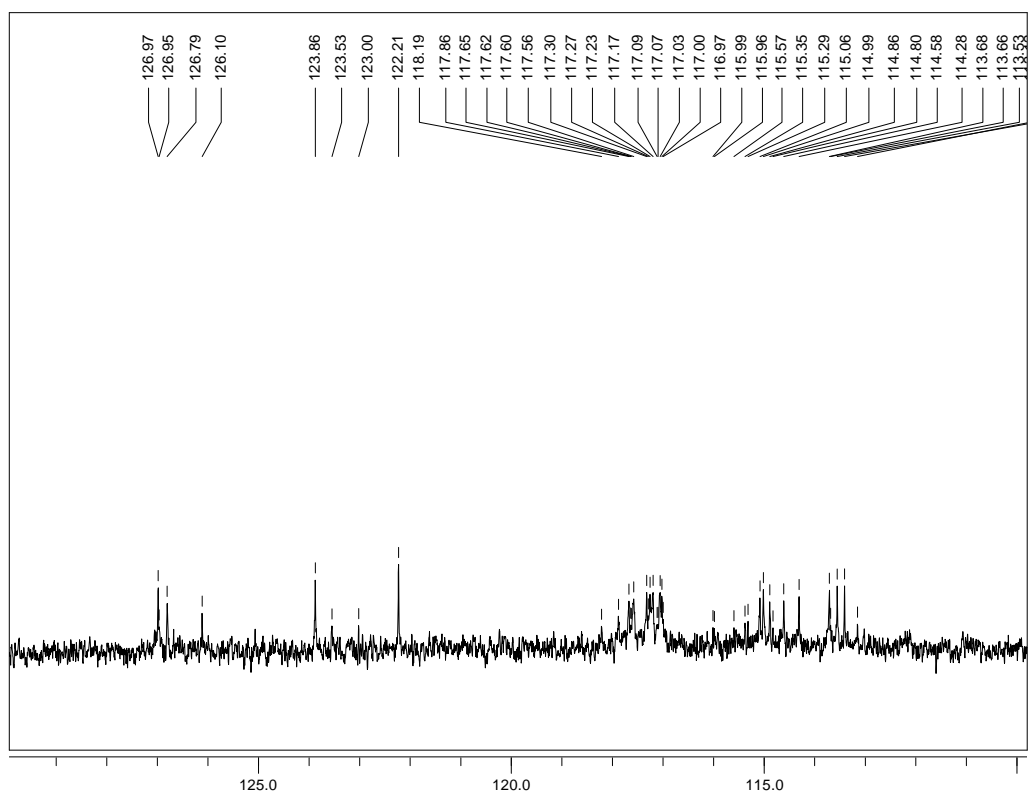


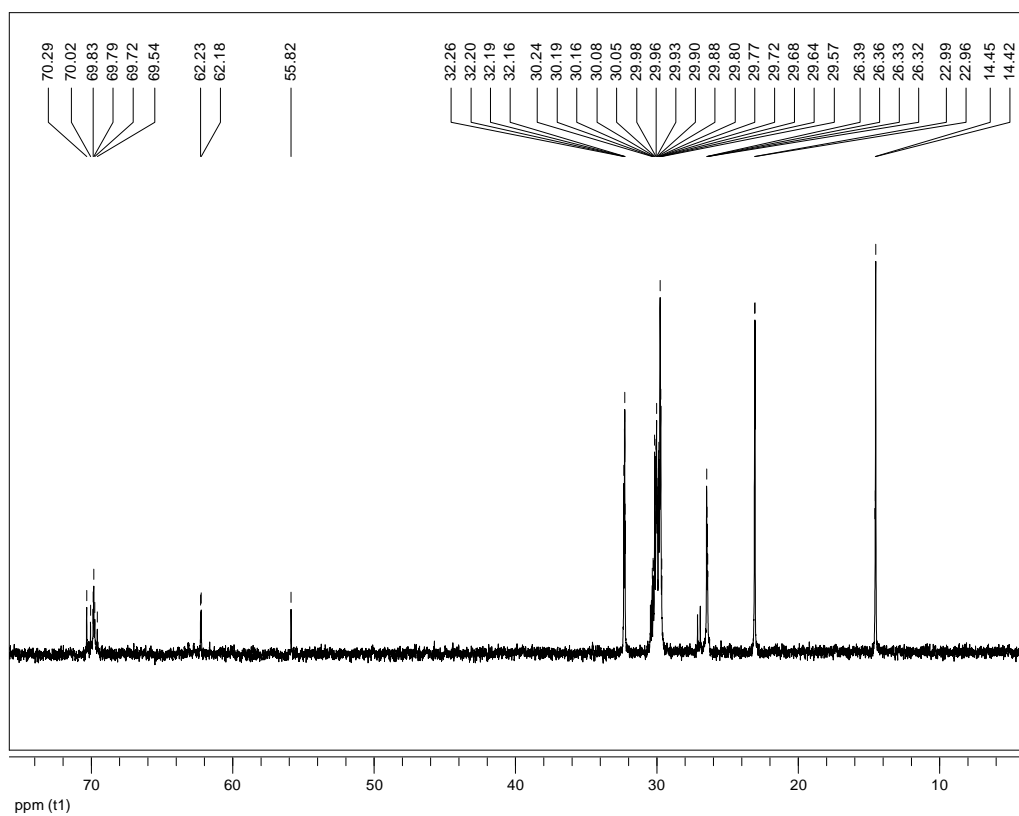


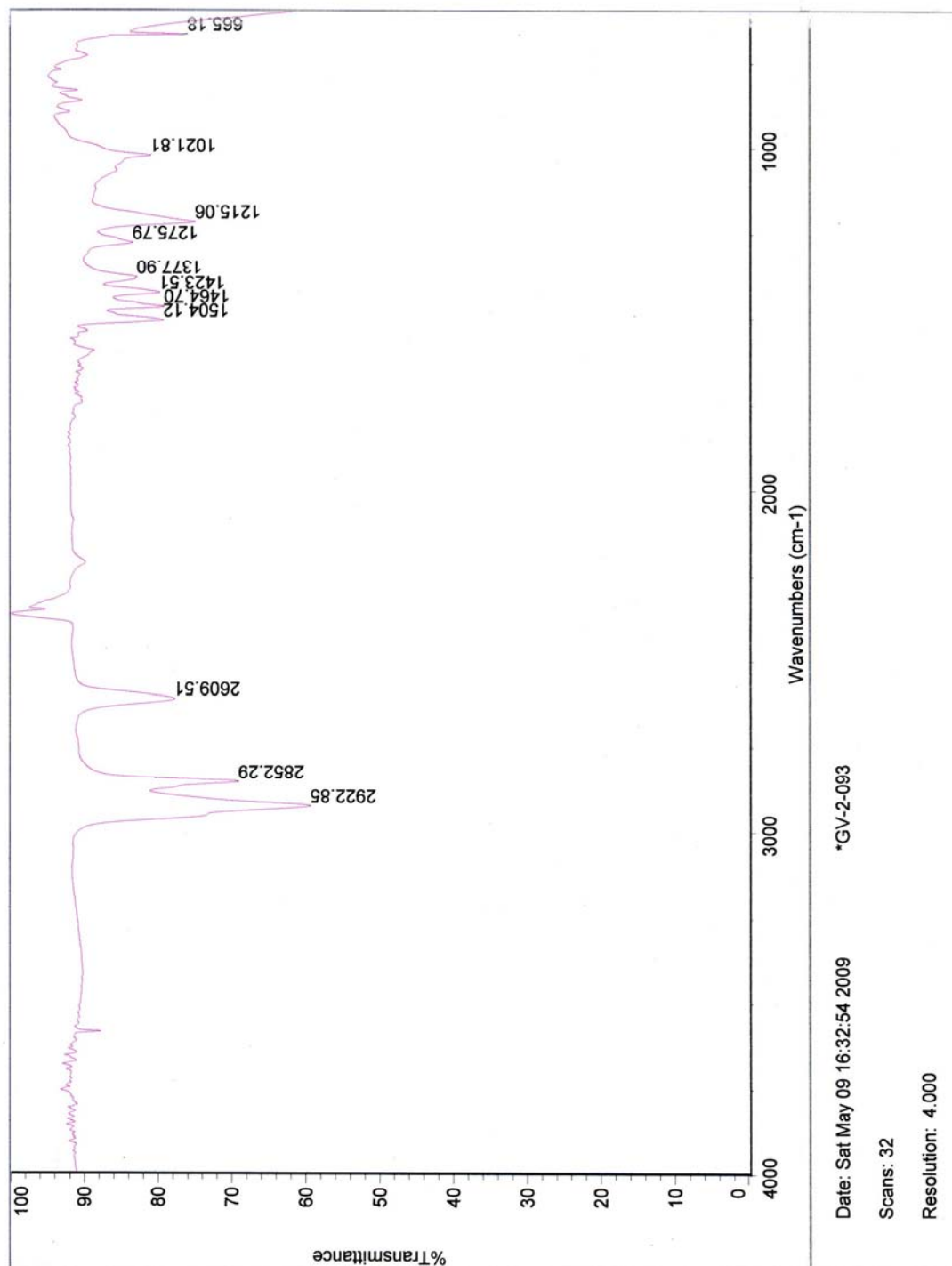
S23



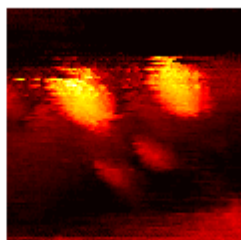
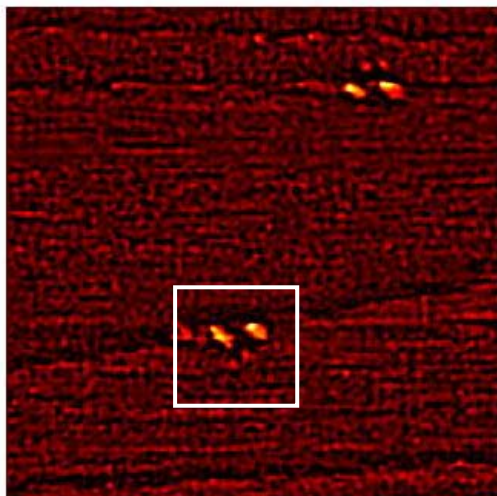








Zoomed-in image of Figure 2A



STM image of the bottom nanodragsters (bias voltage [V_{bias}] = -75 mV, tunneling current [I_t] = 0.3 nA, image size : 7.8 x 7.8 nm²).