Supporting Information for: Bifunctional, Conjugated Oligomers for Orthogonal Self-Assembly: Selectivity Varies from Planar Substrates to Nanoparticles

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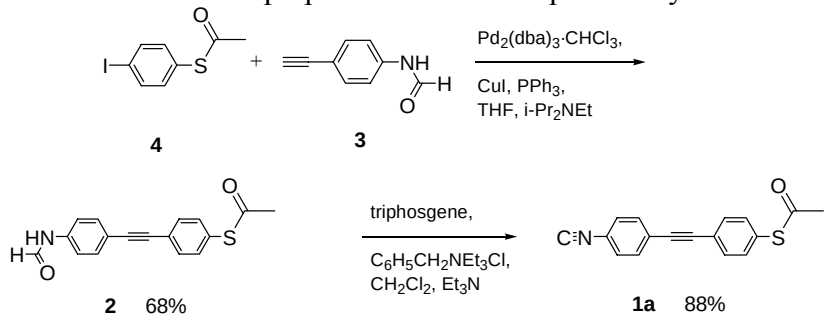
Experimental Details for the Synthesis of New Compounds.

Molecule **4** was prepared as described previously.[1] Molecule **3** was prepared as described previously[2] except that iodoaniline was used as the starting material instead of bromoaniline. Molecule **1b** was prepared as described previously.



4 **3** **2** 68% **1a** 88%

Molecule **2** Inside a N_2-filled dry box, **4** (0.99 g, 3.57 mmol), **3** (0.45 g, 3.10 mmol), tris(dibenylideneacetone) bispalladium (0) (0.09 g, 0.09 mmol), triphenylphosphine (0.12 g, 0.46 mmol), and copper iodide (0.07 g, 0.37 mmol) were weighed into an oven-dried Schlenk flask. THF (8 mL) and diisopropylethylamine (3 mL) were then added. The

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[1] Pearson, D. L.; Tour, J. M., *J. Org. Chem.* **1997**, *62*, 1376-1387.

[2] Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem.-Eur. J.* **2001**, *7*, 5118-5134.

flask was sealed, removed from dry box, and heated to 50°C with stirring for 48 hours. The flask was then cooled to room temperature and the solvents were removed on a rotatory evaporator. The remaining residue was dissolved in dichloromethane and filtered through a Celite plug. The filtrate was dried and purified using flash chromatography (1:1 hexanes:ethyl acetate) to yield 0.63 g of the desired product (68%). IR (neat) 1687, 1606, 1587, 1523, 1407, 1294, 1118, 831 cm^{-1}. FAB-MS (matrix: NBA); m/z Calcd 295.0667 (M+); found 295.0672 (Δ = 1.7 ppm). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.75 (d, J = 11.2 Hz, 0.5H), 8.39 (d, J = 1.6 Hz, 0.5H), 7.67 (d, J = 11.6 Hz, 0.5 H), 7.42 (m, 7H), 7.06 (d, J = 8.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 194.66, 194.34, 162.49, 159.44, 137.48, 137.19, 135.30, 134.57, 133.43, 133.36, 132.78, 132.72, 132.61, 132.40, 131.94, 131.83, 128.22, 127.95, 124.90, 124.65, 119.88, 119.84, 119.76, 119.07, 118.35, 118.29, 91.16, 90.57, 89.16, 88.60, 30.60.

Molecule **1a** This molecule was prepared using a procedure adapted from Tour et al.[3] Into an oven-dried Schlenk flask, **2** (0.10 g, 0.35 mmol) and triphosgene (0.07 g, 0.25 mmol) were weighed. The flask was evacuated and back-filled with argon four times then cooled to 0°C. Dichloromethane (5 mL) and TEA (2 mL) were then added followed by benzyltriethyl ammonium chloride (0.02 g, 0.08 mmol) in 2 mL of dichloromethane. The flask was allowed to warm to room temperature and stir for 5 hours. The solution was then diluted with water and extracted with dichloromethane. The organic phase was washed with water and dried with magnesium sulfate. The filtrate was dried and purified using flash chromatography (10:1 hexanes:ethyl acetate) to yield 86 mg of the desired product (88%). IR (neat) 2124, 1711, 1508, 844, 820 cm^{-1}. FAB-MS (matrix: NBA); m/z Calcd 277.0561 (M+); found 277.0564 (Δ = 1.1 ppm). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 (d, J = 3.0 Hz, 2H), 7.53 (d, J = 3.3 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 9.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 193.54, 166.03, 135.32, 134.53, 132.90, 132.69, 132.47, 131.38, 131.33, 129.05, 126.74, 124.62, 123.87, 91.56, 89.48, 30.59.

Experimental Details for the Preparation and Characterization of Monolayers.

SAM Preparation. Evaporated gold on glass with a titanium adhesion layer was purchased from Evaporated Metals Inc. (Ithaca NY). Evaporated Platinum on glass with a titanium adhesion layer was fabricated in the North Carolina State University Engineering Graduate Research Facility. Pt foil was purchased from Alfa Aesar (Ward Hill, Ma Stock # 11509) and was used for ellipsometry measurements. Prior to monolayer deposition for use in ellipsometry the substrates were cleaned in piranha solution (3:1 H_2SO_4:H_2O_2 (30%) by volume) for 30 seconds, rinsed with deionized water and dried under a N_2 stream. (*Caution: Piranha solution is corrosive and can explode violently when contacted with organics In addition, care should be taken to not store piranha solution for extended lengths of time due to the formation of explosive oxides*). Gold slides for use in FT-IR studies were cleaned via UV / O_3 for 20 minute sand then

[3] Price, D. W.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tet.* **2003**, *59*, 2497-2518.

immersed in ethanol for 15 minutes. Platinum slides for use in FT-IR studies were cleaned using piranha solution. All clean Gold and platinum substrates were incubated in a 10 mM solution of **1a** or **1b** in tetrahydrofuran for 24 hours at room temperature to form a self-assembled monolayer. After copious rinsing in ethanol the slides were then dried in a dinitrogen stream and used immediately.

Ellipsometry Measurements were performed with a VASE spectroscopic ellipsometer using a 75W Xe lamp as its source and a HS-190 monochromator. Thicknesses were calculated assuming a refractive index of 1.45. The angle of incidence in all studies on gold was 68° and 70° and the wavelength was swept from 400 to 800 nm at 1 nm/s. For platinum an angle of incidence of 55° was used and the wave length was swept from 400 to 800 at 1nm/s.

Surface FT-IR The IR spectra of molecules **1a** and **1b** on Pt and Au slides were recorded on a Veemax II Variable-angle Reflectance Attachment connected to a Digilab FTS-3000 FTIR with a liquid nitrogen cooled MCT detector. The spectra were recorded at room temperature at a resolution of 4 cm^{-1} and were the results of 3 spectra averaged together. Each spectrum was the product of 2048 scans. Spectra were recorded over a range of 4000 to 400cm^{-1}. A freshly cleaned gold slide was used as a background.

Experimental Details for the Preparation and Characterization of Nanoparticle/molecule conjugates.

A solution of **1b** was prepared by dissolving 1.5 mg in 5 mL of tetrahydrofuran (THF). A solution of gold nanoparticles was prepared by dissolving 4.5 mg of dodecanethiol-capped gold nanoparticles (~3-5 nm) in 5 mL of THF. A solution of platinum nanoparticles was prepared by dissolving 6.9 mg of hexane-thiol capped platinum nanoparticles (~3-4 nm) in 5 mL of THF. Then, 1 mL of the gold nanoparticle solution was combined with 1 mL of solution the solution of **1b**. Separately, 1 mL of the platinum nanoparticle solution was combined with 1 mL of solution the solution of **1b**. The samples were allowed to incubate for 30 minutes before analysis. The two sample-nanoparticle solutions as well as a neat sample of **1b** were evaporated on KBr plates and analyzed using a Mattson Genesis II FTIR. Spectra were recorded at room temperature with a resolution of 8 cm^{-1} over 16 scans. Spectra were recorded over a range of 4000 to 400 cm^{-1}.

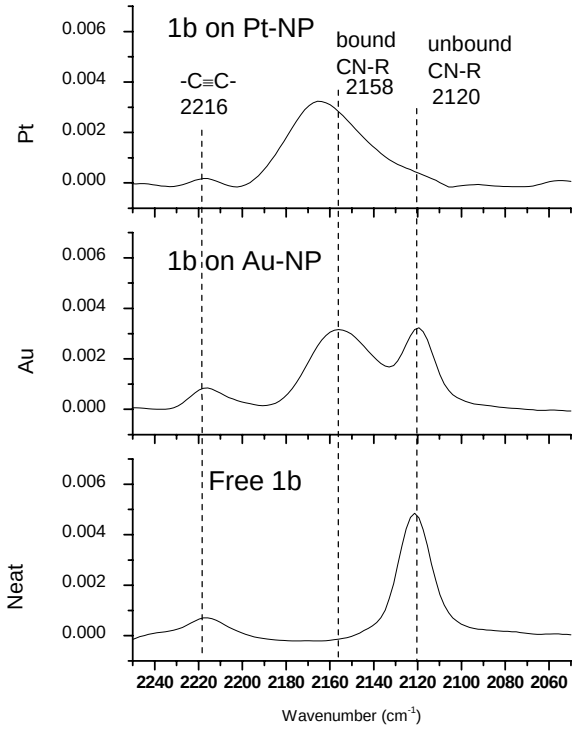
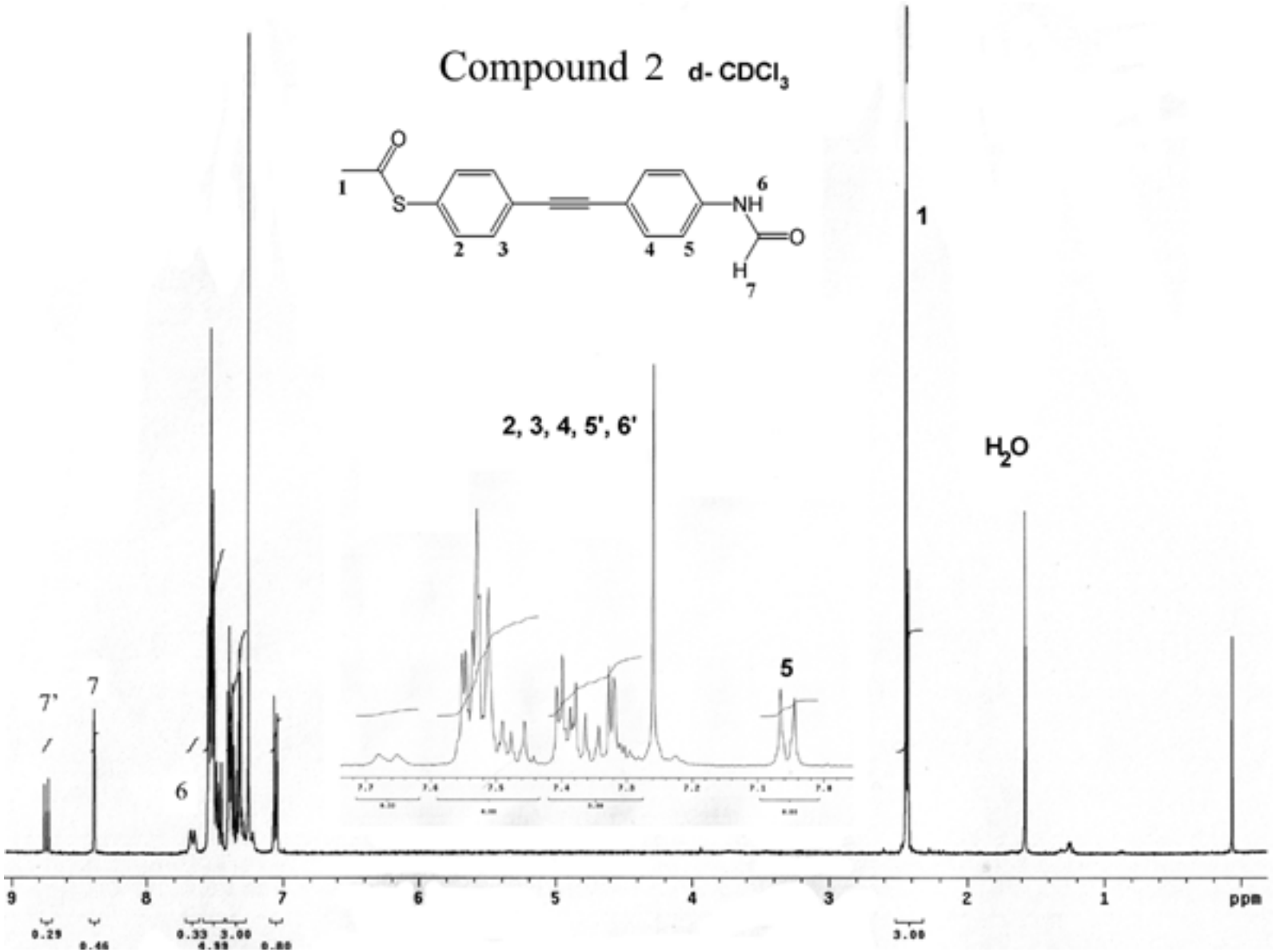


Figure S1. Interaction of compound **1b** and Pt and Au nanoparticles (NP). For Pt-NP, essentially all isonitrile is bound. For Au-NP only partial interaction with the isonitrile is observed, suggesting some non-specific interaction is present.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1
S
O
2 3
4 5
NH
6
O
H
7
2, 3, 4, 5', 6'
5
1
H2O
7'
7
6
9
8
7
6
5
4
3
2
1
ppm
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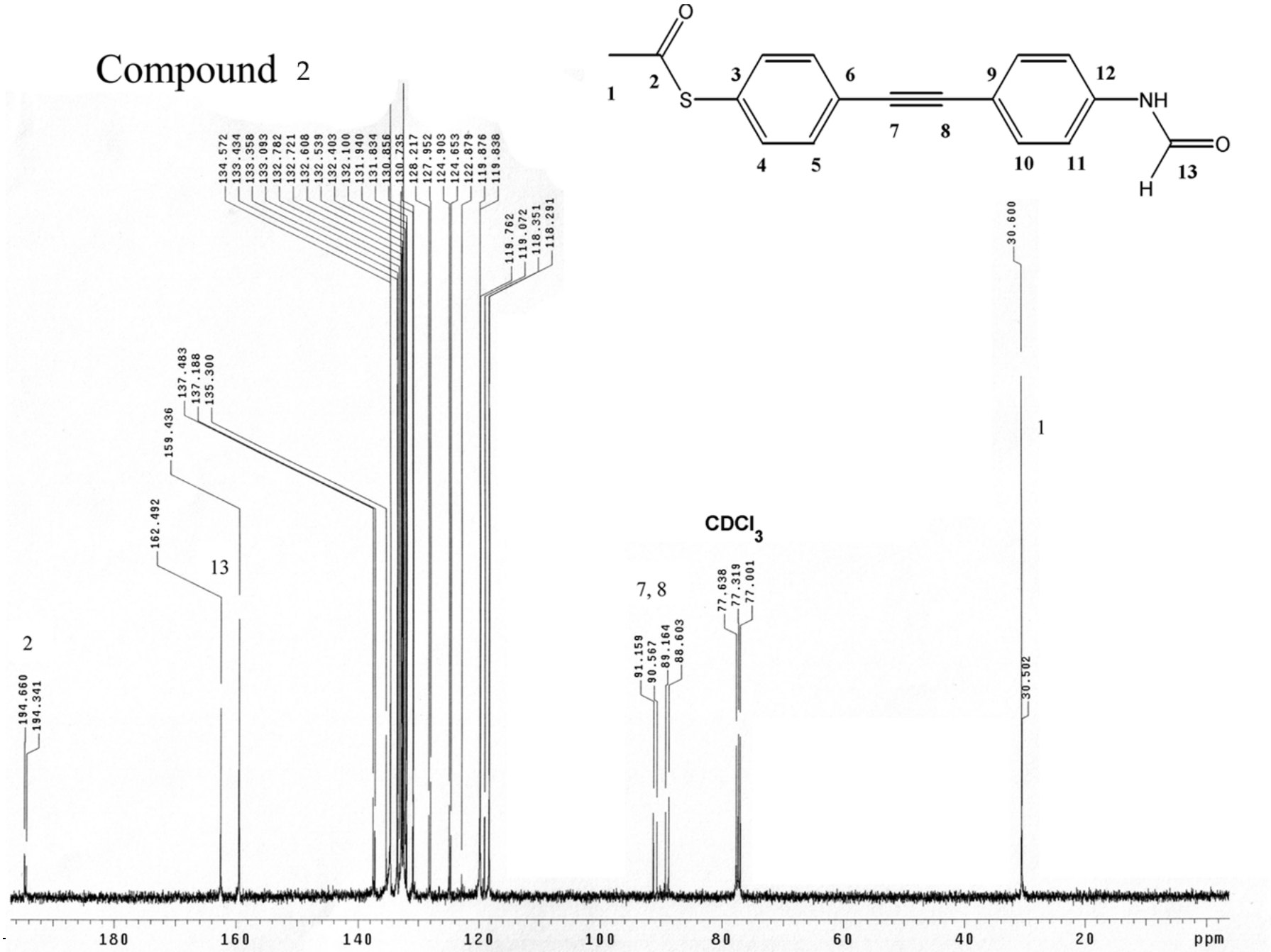
0.33
3.00
3.00


Compound 2
O
1
2
S
3
4
5
6
7
8
9
10
11
12
NH
O
13
H
134.572
133.434
133.358
133.093
132.782
132.721
132.608
132.539
132.403
132.100
131.940
131.834
130.856
130.735
128.217
127.952
124.903
124.653
122.879
119.876
119.838
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137.188
135.300
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162.492
13
2
194.660
194.341
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91.159
90.567
89.164
88.603
CDCl3
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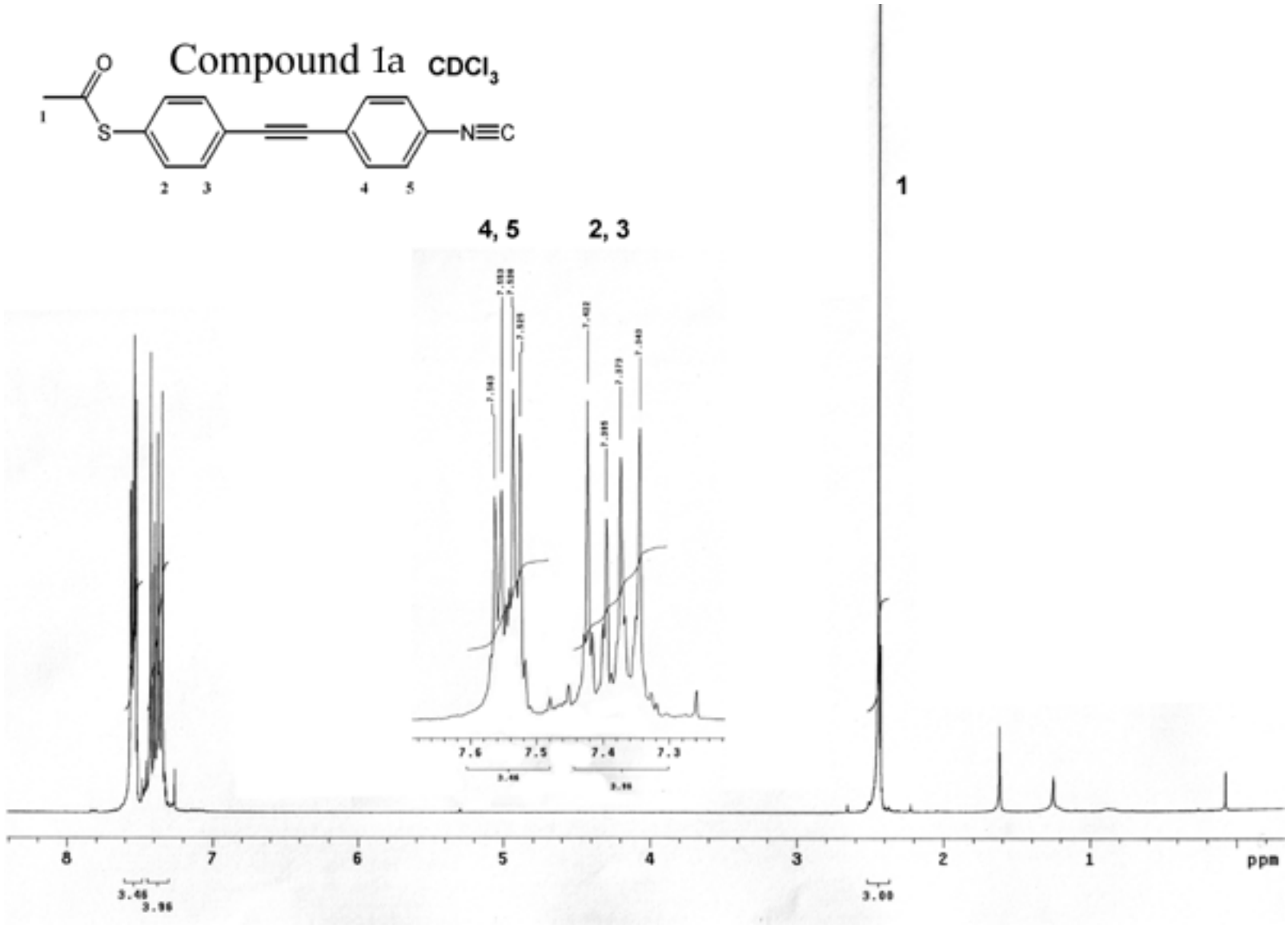
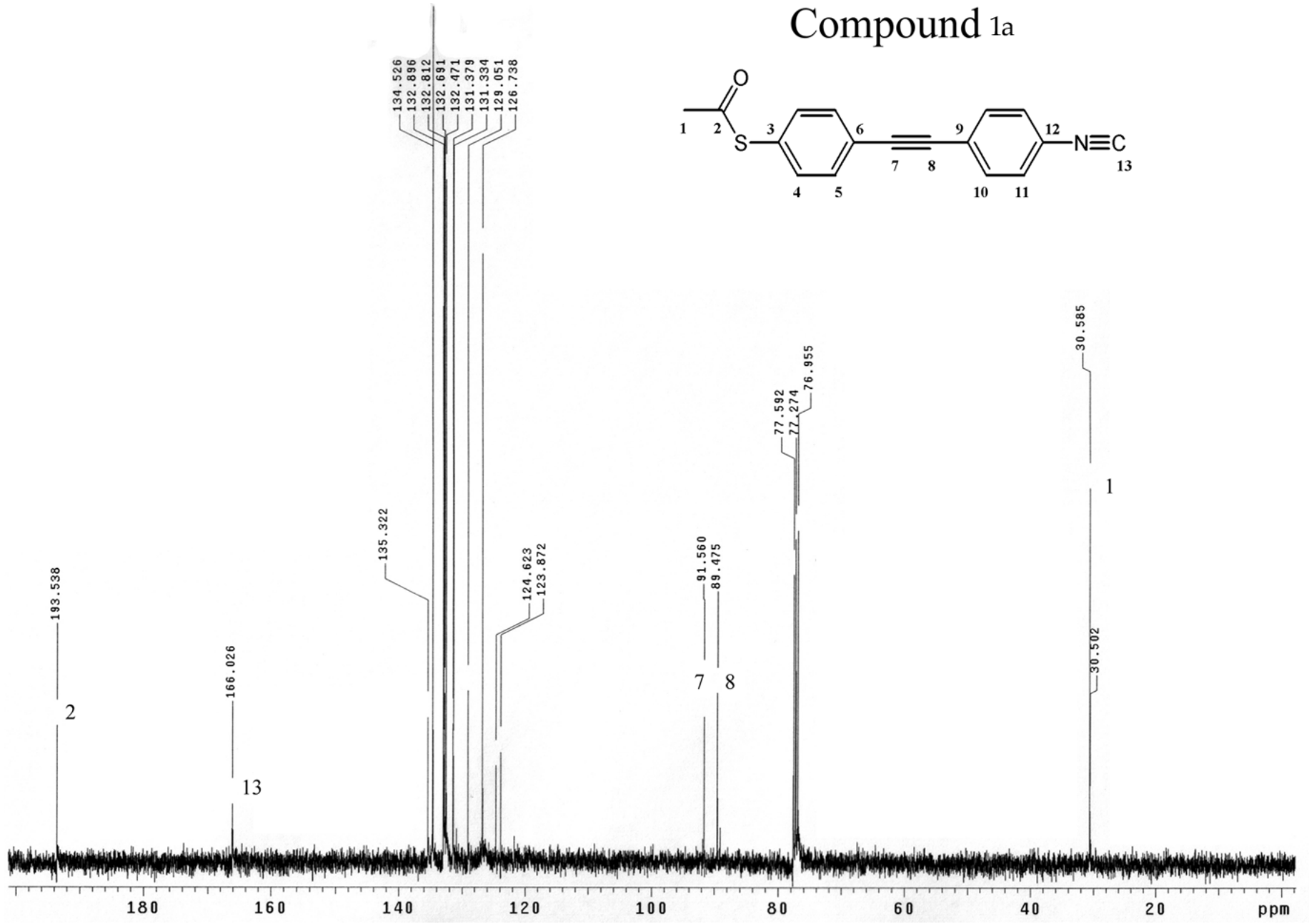
77.001
30.600
1
30.502
180
160
140
120
100
80
60
40
20
ppm


Compound 1a CDCl3
O
1
S
N≡C
2 3
4 5
4, 5
2, 3
1
7.6
7.5
7.4
7.3
8
7
6
5
4
3
2
1
ppm
3.46
3.96
3.00


Compound 1a
O
S
N≡C
1
2
3
4
5
6
7
8
9
10
11
12
13
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132.896
132.812
132.691
132.471
131.379
131.334
129.051
126.738
193.538
166.026
135.322
124.623
123.872
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89.475
77.592
77.274
76.955
30.585
30.502
2
13
7
8
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140
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80
60
40
20
ppm