Electronic Supplementary Material (ESI) for ChemComm.

Expanding the Scope of Strained-Alkyne Chemistry: a Protection-Deprotection Strategy *via* the Formation of a Dicobalt-Hexacarbonyl Complex

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Materials and Methods

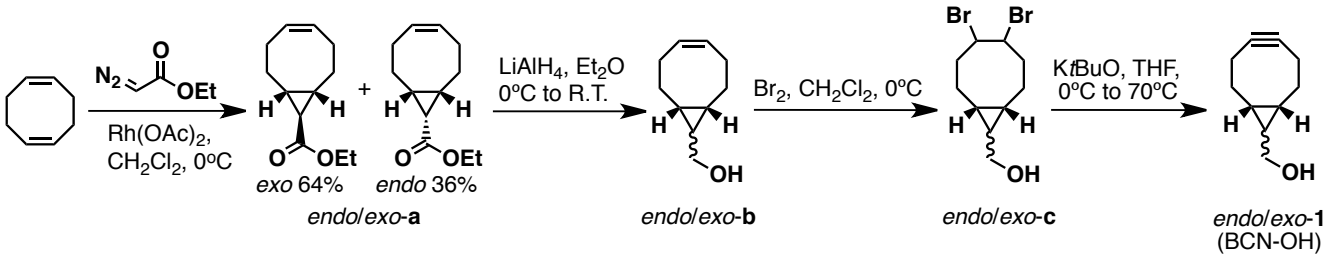
All reagents were used as received. Cyclooctadiene, rhodium tetracetate dimer [$(Rh_2(OAc)_4)$], ethyl diazoacetate, lithium aluminum hydride ($LiAlH_4$), bromine (Br_2), potassium tertbutoxide (K*t*BuO) 1M solution in THF, dicobalt-octacarbonyl [$Co_2(CO)_8$], *p*-nitrophenyl chloroformate [(*p*-NO_2PhOC(O)Cl)], pyridine, sodum azide (NaN_3), 2-bromoethylamine hydrobromide, phenylacetylene, triethylamine (NEt_3), and trimethylamine *N*-oxide (Me_3NO) were purchased from Sigma-Aldrich. All common solvents, anhydrous sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), anhydrous magnesium sulfate ($MgSO_4$), sodium thiosulfate ($Na_2S_2O_3$), ammonium chloride (NH_4Cl), and all common solvents were purchased from Caledon. Solvents were dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves.

^1H and ^{13}C NMR spectra were recorded on an Inova 400 MHz spectrometer. ^1H NMR spectra are reported as δ in units of parts per million (ppm) relative to chloroform (δ 7.26, s). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintuplet), dd (doublet of doublets), m (multiplet), and bs (broad signal). Coupling constants are reported as *J* values in Hertz (Hz). The number of protons (n) for a given resonance is indicated as nH, and is based on spectral integration values. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) relative to $CDCl_3$ (δ 77.23, t).

Infrared spectra were recorded using a Bruker Vector33 spectrometer by making a thin film of each sample onto a KBr disk. The background was subtracted from each spectrum.

UV-Vis spectra were collected employing a Varian UV-Vis spectrophotometer model Cary 300 Bio, and dissolving the sample in spectroscopic grade CH_2Cl_2 to obtain a $1 \cdot 10^{-5}$M solution. The background was subtracted from each spectrum.

Synthesis of BCN-OH *endo/exo*-1[1]



Synthesis of bicycle[6.1.0]-nonyne-methanol (BCN-OH) *endo*-1 and *exo*-1

In a typical synthesis, $Rh_2(OAc)_4$ (0.776 g, 1.76 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under argon atmosphere. Cyclooctadiene (40 mL, 0.33 mol) was then added to the solution. In a separate flask, ethyl diazoacetate (4.3 mL, 41 mmol) was also dissolved in dry CH_2Cl_2 (20 mL) and then slowly added to the cyclooctadiene solution. Evolution of nitrogen gas was observed right away. The dark green solution was stirred at room temperature for two days. CH_2Cl_2 was evaporated, then excess cyclooctadiene was recovered by column chromatography on silica gel using hexanes as the eluent. After elution of cyclooctadiene, the *endo*/*exo*-**a** isomers were separated using hexanes/Et_2O 9:0.5 as the eluent. The two isomers were obtained as a colorless oil (6.979 g, 88% overall yield, 36% *endo* and 64% *exo*). R_f *exo* = 0.6, R_f *endo* = 0.4 in hexanes/Et_2O 9:0.5.

The syntheses of *endo*-**1** and *exo*-**1** isomers were carried out separately by reacting the two separate isomers according to the following procedures. A suspension of $LiAlH_4$ (1.371 g, 36.11 mmol) in dry Et_2O (80 mL) was cooled to 0 ºC. Compound *endo*/*exo*-**a** from the previous step (7.85 g, 40.4 mmol) was also dissolved in dry Et_2O (90 mL) and cooled to 0 ºC before dropwise addition to the reaction flask. The gray solution was stirred for 15 min at room temperature, then it was cooled again to 0 ºC and distilled water was added dropwise under normal atmosphere until formation of a white precipitate was observed. The mixture was dried over Na_2SO_4, and the solids were filtered off and washed with Et_2O. The solvent was evaporated to obtain intermediate *endo/exo* alcohol. No further purification was performed.

Compound *endo*/*exo*-**b** from the previous step was dissolved in CH_2Cl_2 (250 mL) and cooled to 0 ºC. A solution of Br_2 (2.6 mL, 51 mmol) in CH_2Cl_2 was added dropwise at 0 ºC to the alkene solution until a light yellow color persisted. The reaction mixture was quenched with a 10% $Na_2S_2O_3$ solution (70 mL). After vigorous stirring for a few minutes the solution turned colorless and was then extracted with CH_2Cl_2 (4 x 15 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo* to give *endo/exo* as a thick yellow oil in 90% yield over the two last steps. No further purification was performed.

The *endo*/*exo*-**c** from the previous step was dissolved in dry THF (80 mL) and cooled to 0 ºC. A 1 M solution of KO*t*Bu in THF (120 mL) was added dropwise into the reaction flask. After addition the solution turned orange. At this point the ice-bath was removed, the temperature was raised to 70 ºC, and the reaction mixture was refluxed for 2 h. After cooling to room temperature the reaction mixture was quenched with saturated NH_4Cl (200 mL) and the product was extracted with CH_2Cl_2. The collected organic fractions were dried with $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (3:1 Et_2O/hexanes) to give *endo*/*exo*-**1** as a white solid (2.579 g, 62% yield).

BCN-OH *exo*-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.57 (d, J = 4.0 Hz, 2H), 2.45-2.41 (m, 2H), 2.34-2.27 (m, 2H), 2.20-2.15 (m, 2H), 1.45-1.36 (m, 3H), 0.73-0.67 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 98.8, 67.2, 33.4, 27.3, 22.6, 21.5. IR (KBr, cm^{-1}): 3349, 2980, 2922, 2844, 2723, 2621, 2263, 2187, 2021, 1700, 1441, 1311, 1292, 1238, 1199, 1167, 1128, 1088, 1023, 995, 942, 922, 896, 843, 803,757, 716. CI-HRMS: calculated for $C_{10}H_{15}O^+$ [M+1] 151.1123, found 151.1118.

BCN-OH *endo*-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.74 (d, J = 8.0 Hz, 2H), 2.35-2.20 (m, 6H), 1.66-1.56 (m, 2H), 1.39- 1.30 (m, 2H), 0.99-0.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 98.9, 60.0, 29.0,

21.47, 21.38, 20.0 IR (KBr, cm^{-1}): 3350, 2987, 2924, 2845, 2726, 2621, 2177, 2005, 1699, 1479, 1439, 1366, 1336, 1303, 1212, 1197, 1176, 1125, 1089, 1048, 1017, 990, 934, 955, 907, 894, 875, 820, 767, 735. CI-HRMS: calculated for $C_{10}H_{15}O^{+}$ [M+1] 151.1123, found 151.1118.

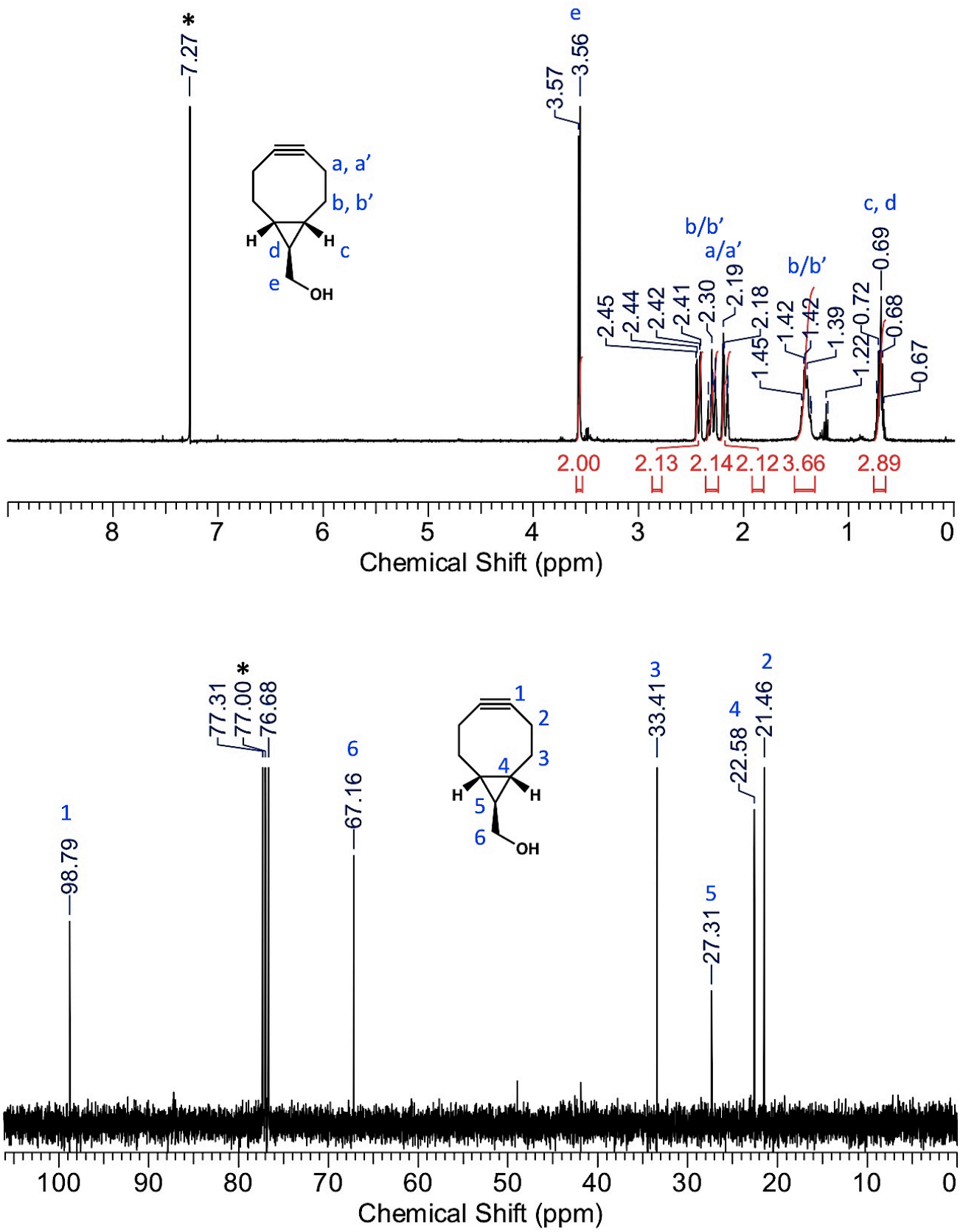


Figure SI1: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**1** isomer. * denotes residual solvent signals.

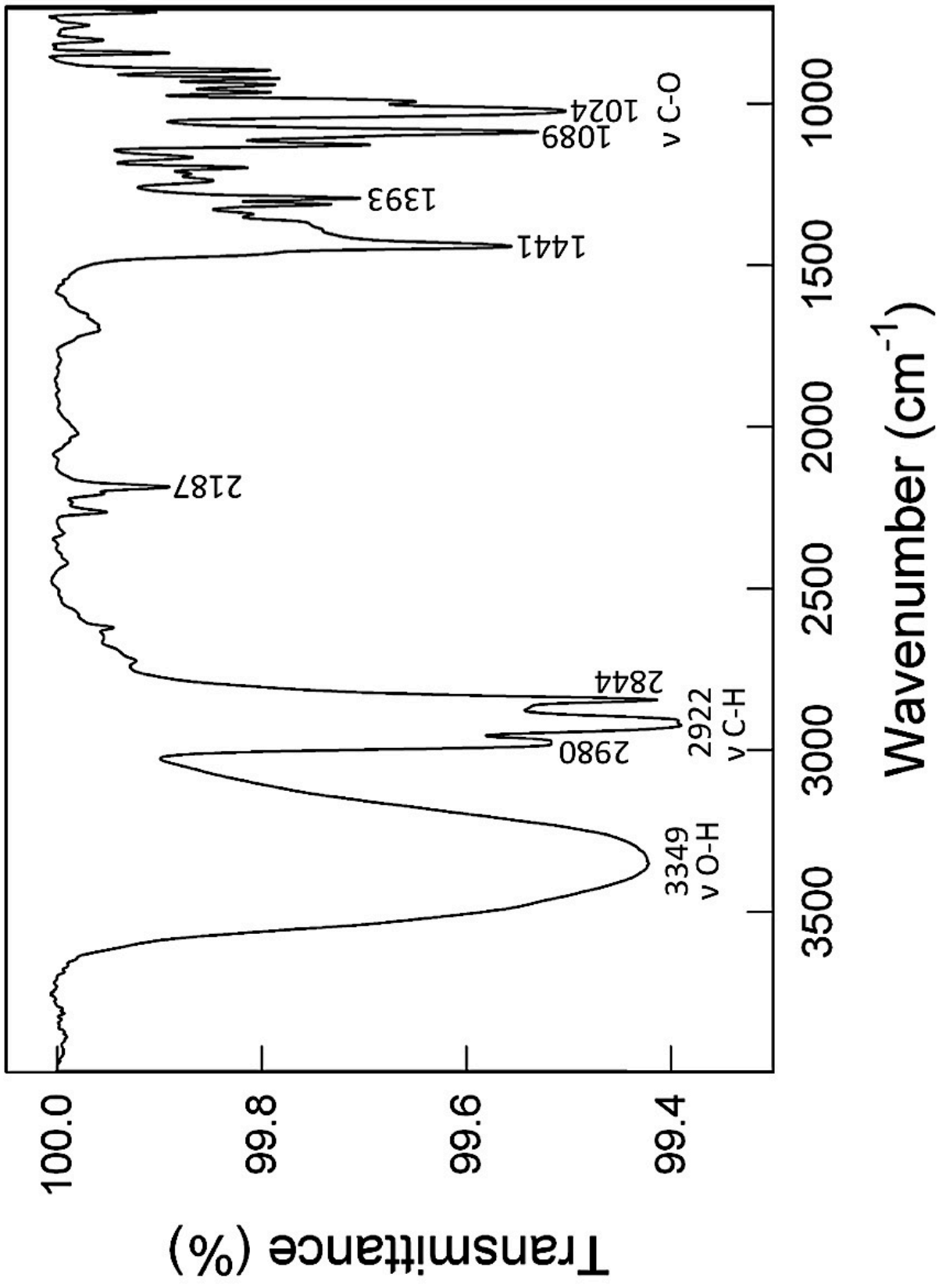


Figure SI2: IR absorption spectrum of *exo*-**1** isomer.

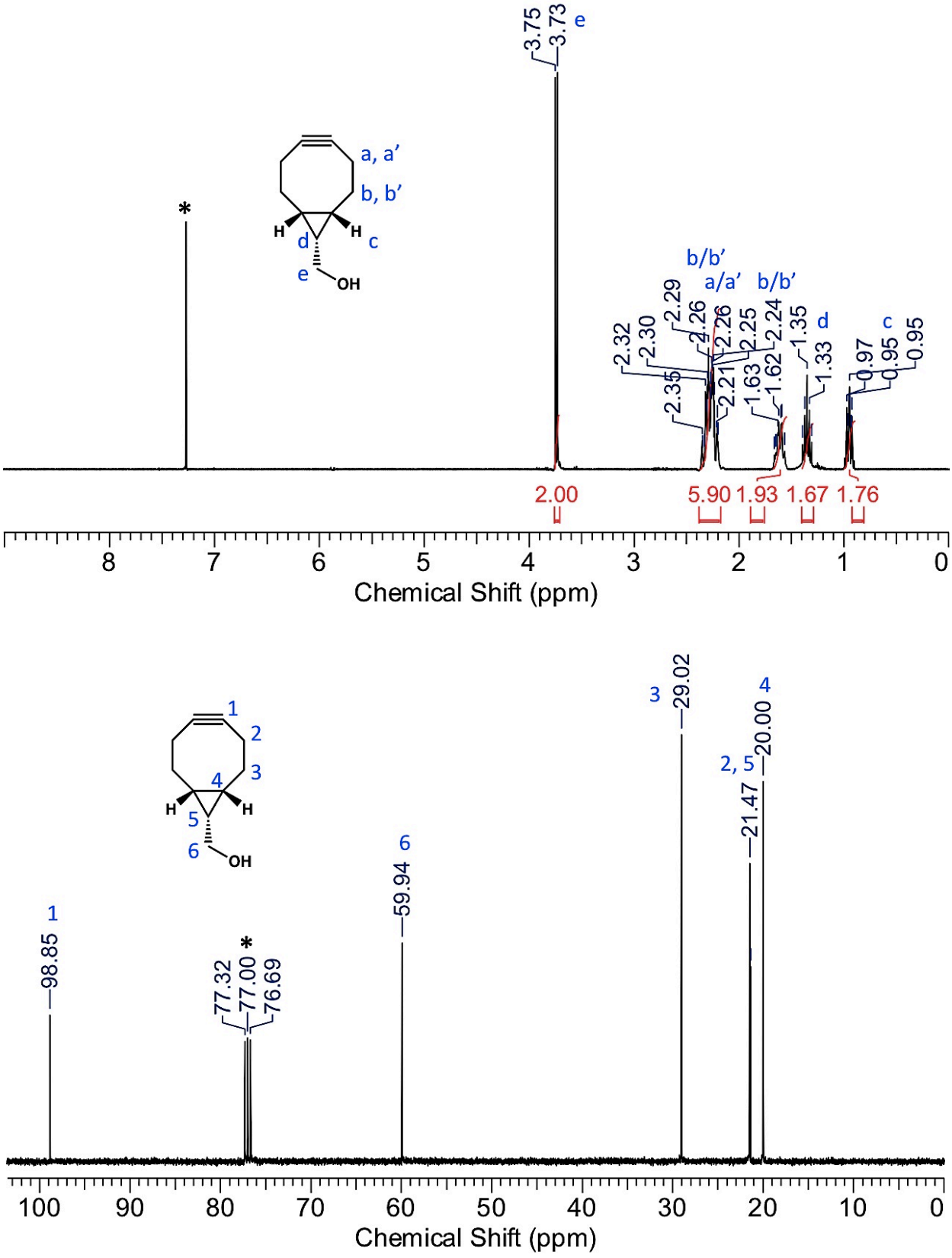


Figure SI3: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *endo*-**1** isomer. * denotes residual solvent signals.

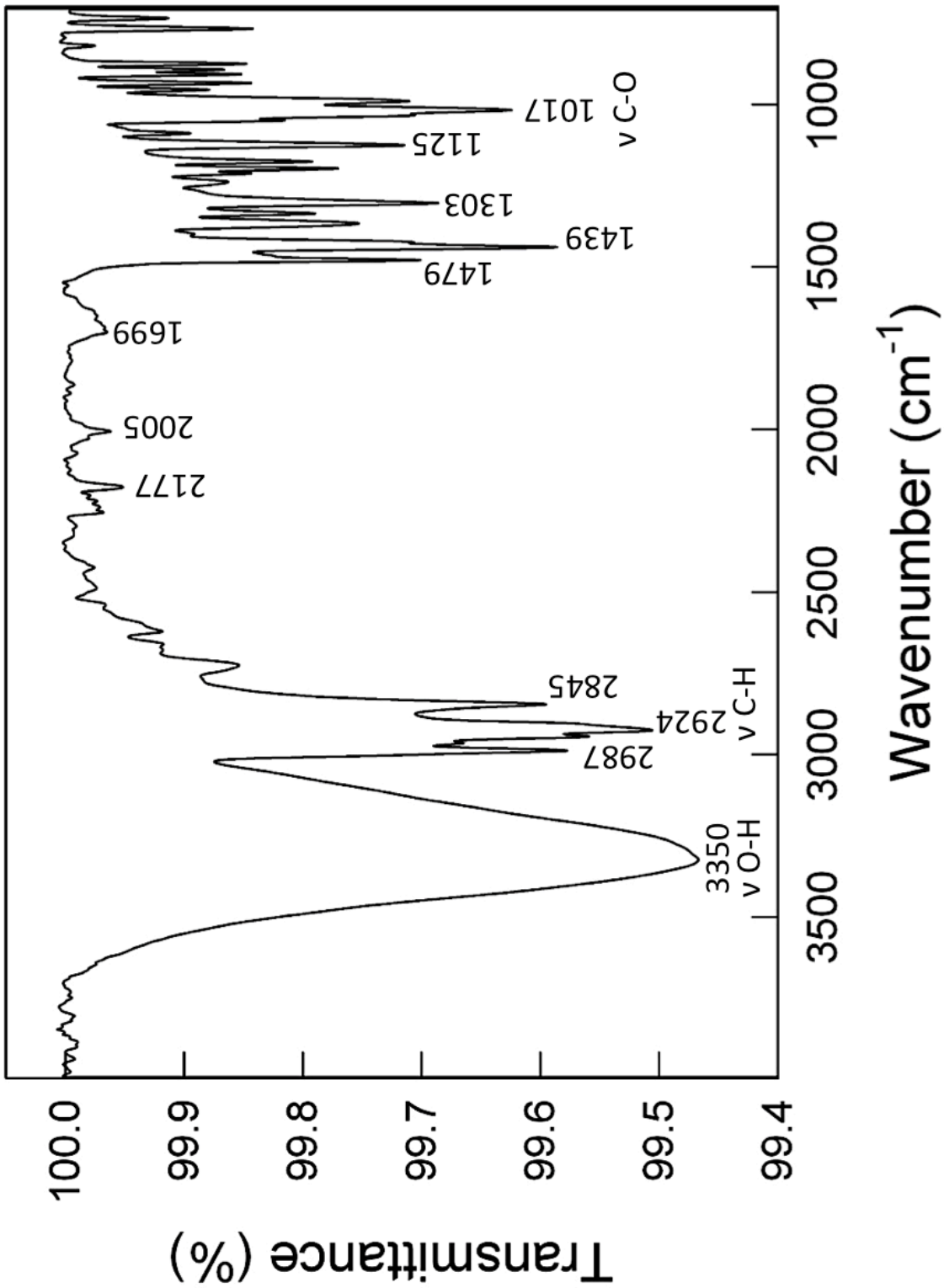
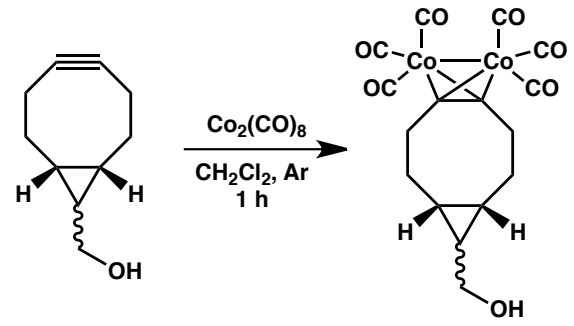


Figure SI4: IR absorption spectrum of *endo*-**1** isomer.

Representative protection of BCN-OH *endo/exo*-1 with dicobalt-octacarbonyl



endo/exo-**1** *endo/exo*-**2**

In a glove box BCN-OH *endo/exo*-**1** (0.481 g, 3.20 mmol) was dissolved in 10 ml of dry CH_2Cl_2. To this solution, $Co_2(CO)_8$ (1.163 g, 3.400 mmol) was quickly added and right away $CO_{(g)}$ evolution was observed. The reaction was monitored by TLC (EtOAc/hexanes 1:1), which indicated the reaction had gone to completion after 1 h. The solvent was evaporated and product *endo/exo*-**2** was purified by column chromatography on silica gel in air using EtOAc/hexanes 1:1 as the eluent. Compound *endo/exo*-**2** was obtained as a red solid in quantitative yield, and could be stored in the freezer at normal atmosphere for months with negligible decomposition. The reaction can be safely performed without the use of a glove box, but extra care needs to be taken in handling $Co_2(CO)_8$ because it is pyrophoric.

Protected BCN-OH *exo*-**2**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.57 (2H), 3.25-3.18 (2H), 3.05-2.98 (2H), 2.39-2.36 (2H), 1.29-1.26 (3H), 0.86-0.73 (3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.5, 98.2, 66.6, 36.7, 29.6, 26.4, 22.9. IR (KBr, cm^{-1}): 3277, 2964, 2963, 2915, 2884, 2845, 2467, 2085, 2039, 1993, 1963, 1627, 1446, 1430, 1361, 1320, 1297, 1234,1206, 1169, 1123, 1091, 1028, 999, 961, 939, 909, 891,851, 795, 747, 717. UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 263 (19,671), 360 (5,262), 430 (1,228). ESI-HRMS: calculated for $C_{16}H_{14}Co_2O_7$ [M] 435.9404, found 435.9403.

Protected BCN-OH *endo*-**2**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.76 (2H), 3.31-3.27 (2H), 3.07-3.00 (2H), 2.24-2.21 (2H), 1.49-1.46 (2H), 1.28-1.10 (4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.5, 98.2, 60.0, 36.8, 30.9, 25.1, 20.5. IR (KBr, cm^{-1}): 3289, 3297, 2981, 2917, 2890, 2851, 2082, 2035, 1982, 1624, 1431, 1448, 1364, 1321, 1250, 1234, 1204, 1176, 1121, 1093, 1054, 1019, 972, 943, 907, 873, 824, 757, 724. UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 263 (19,671), 360 (5,262), 430 (1,228). ESI-HRMS: calculated for $C_{16}H_{14}Co_2O_7$ [M] 435.9404, found 435.9416.

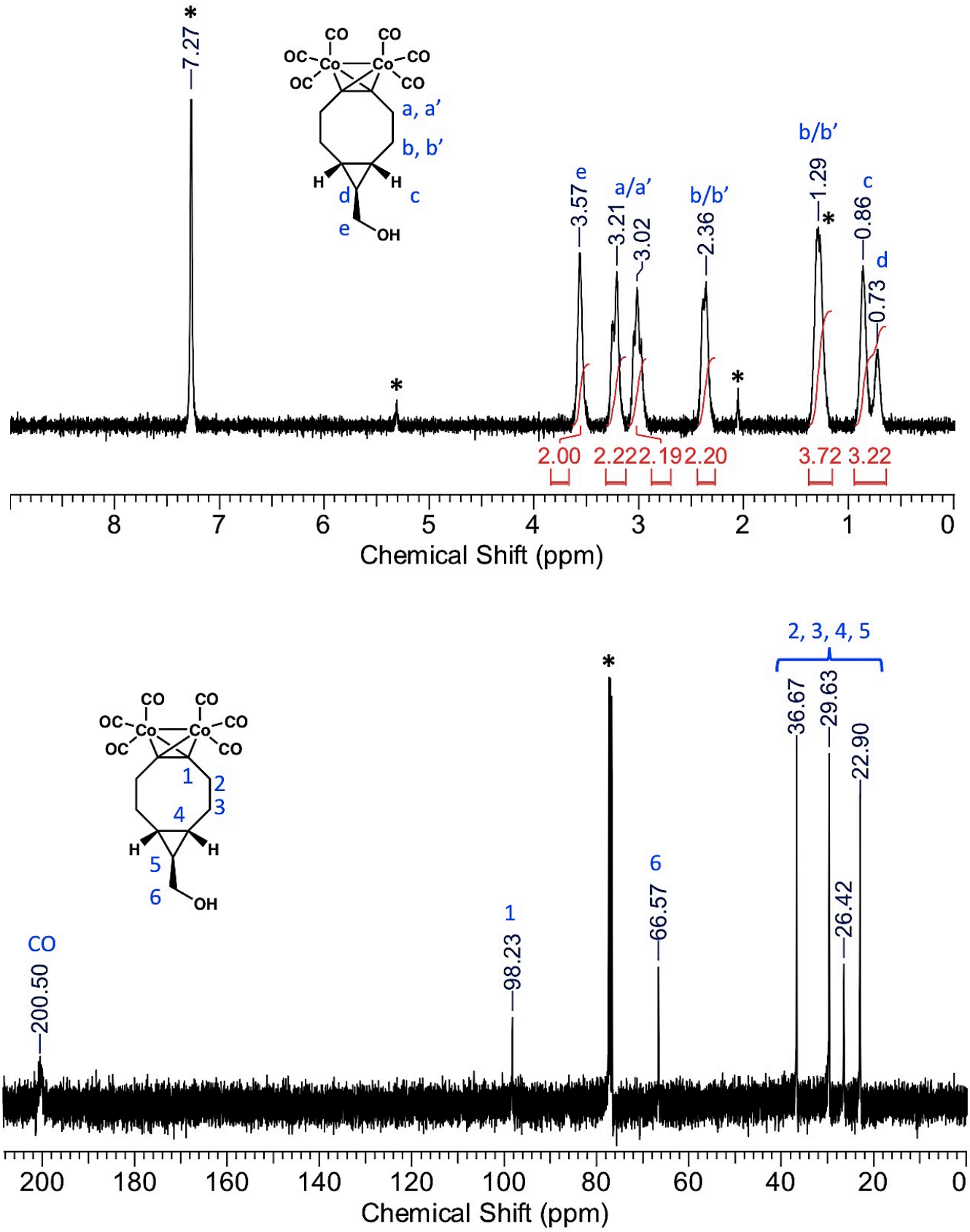


Figure SI5: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**2** isomer. * denotes residual solvent signals.

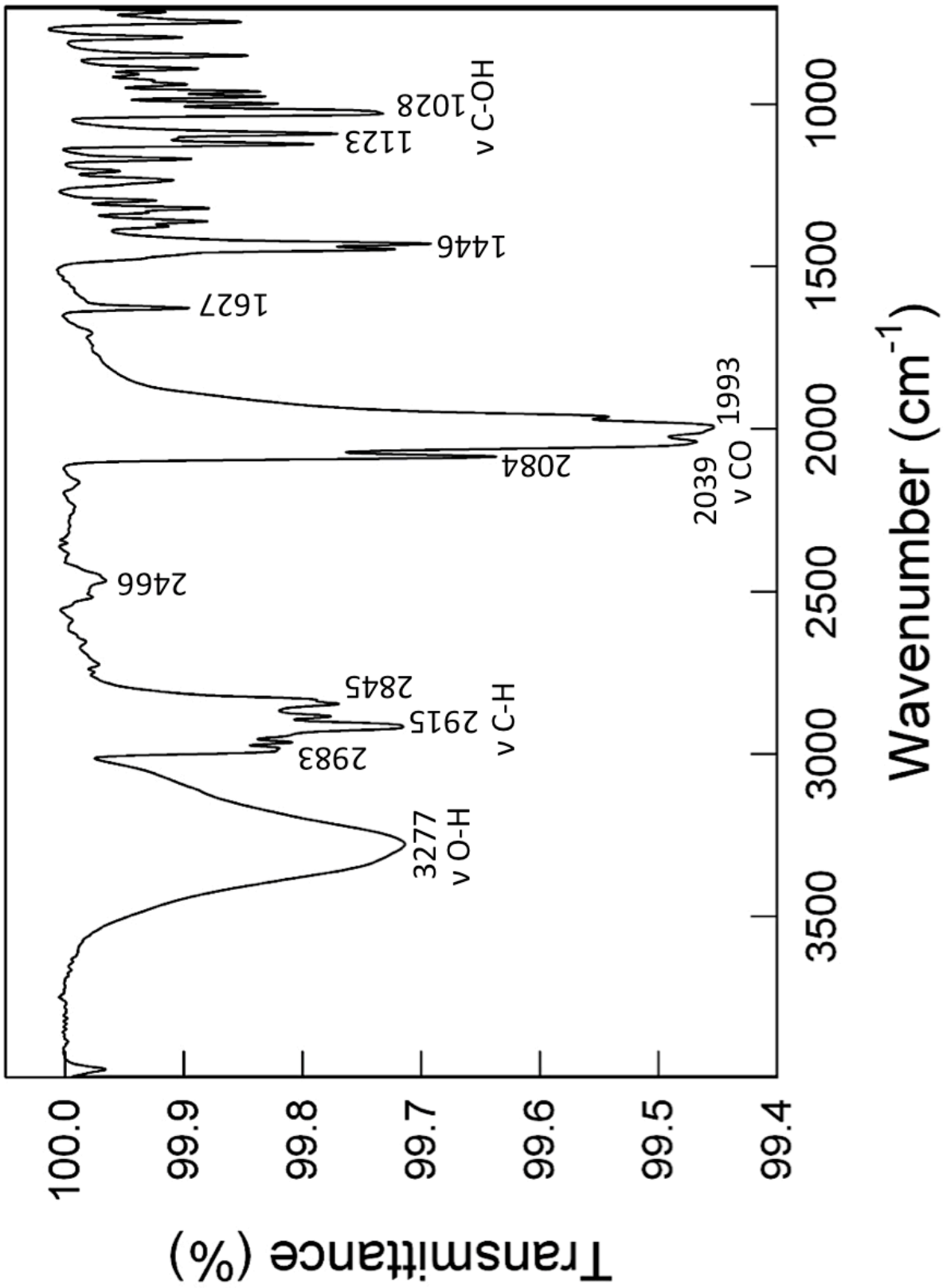


Figure SI6: IR absorption spectrum of complex *exo*-**2** isomer.

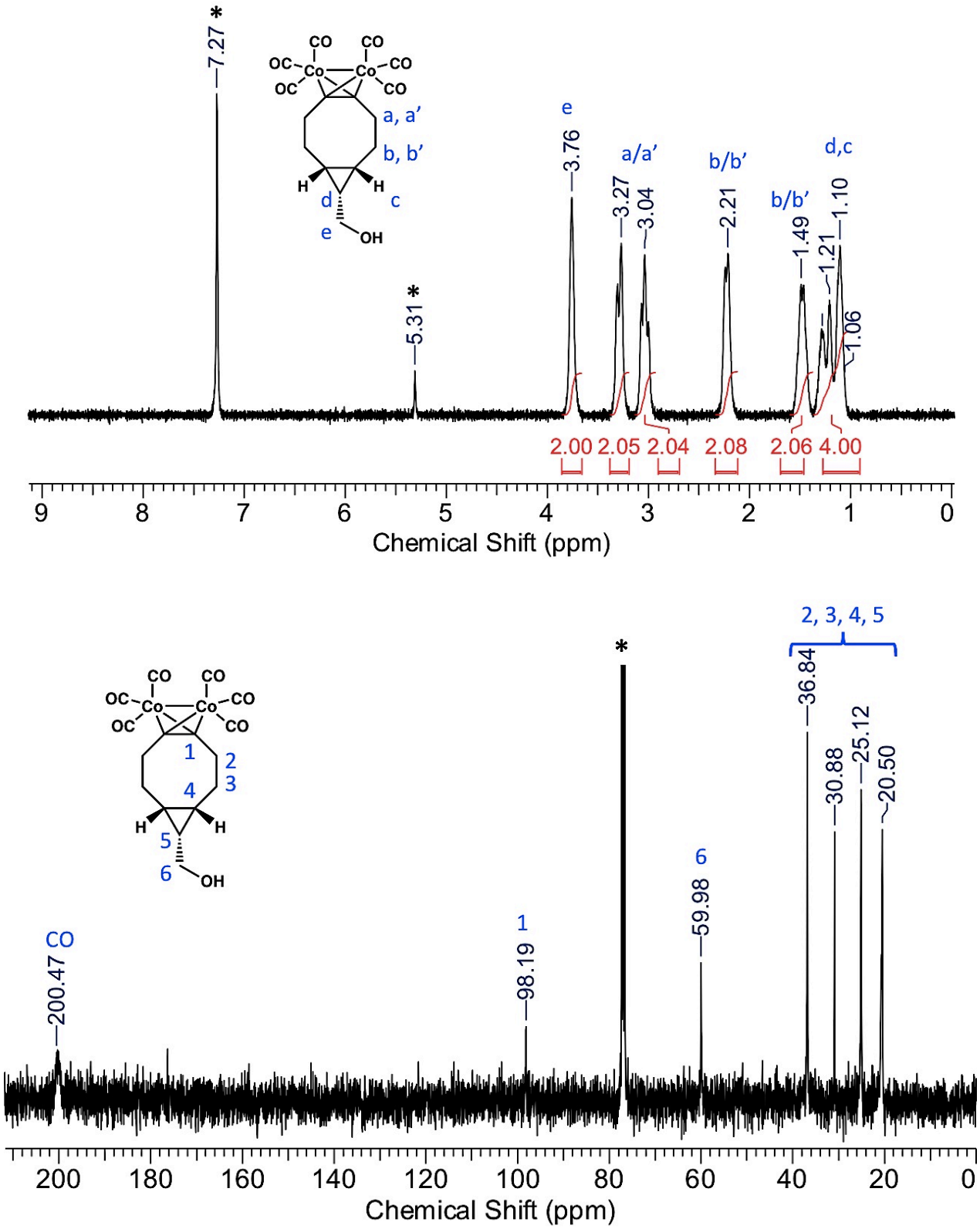


Figure SI7: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *endo*-**2** isomer. * denotes residual solvent signals.

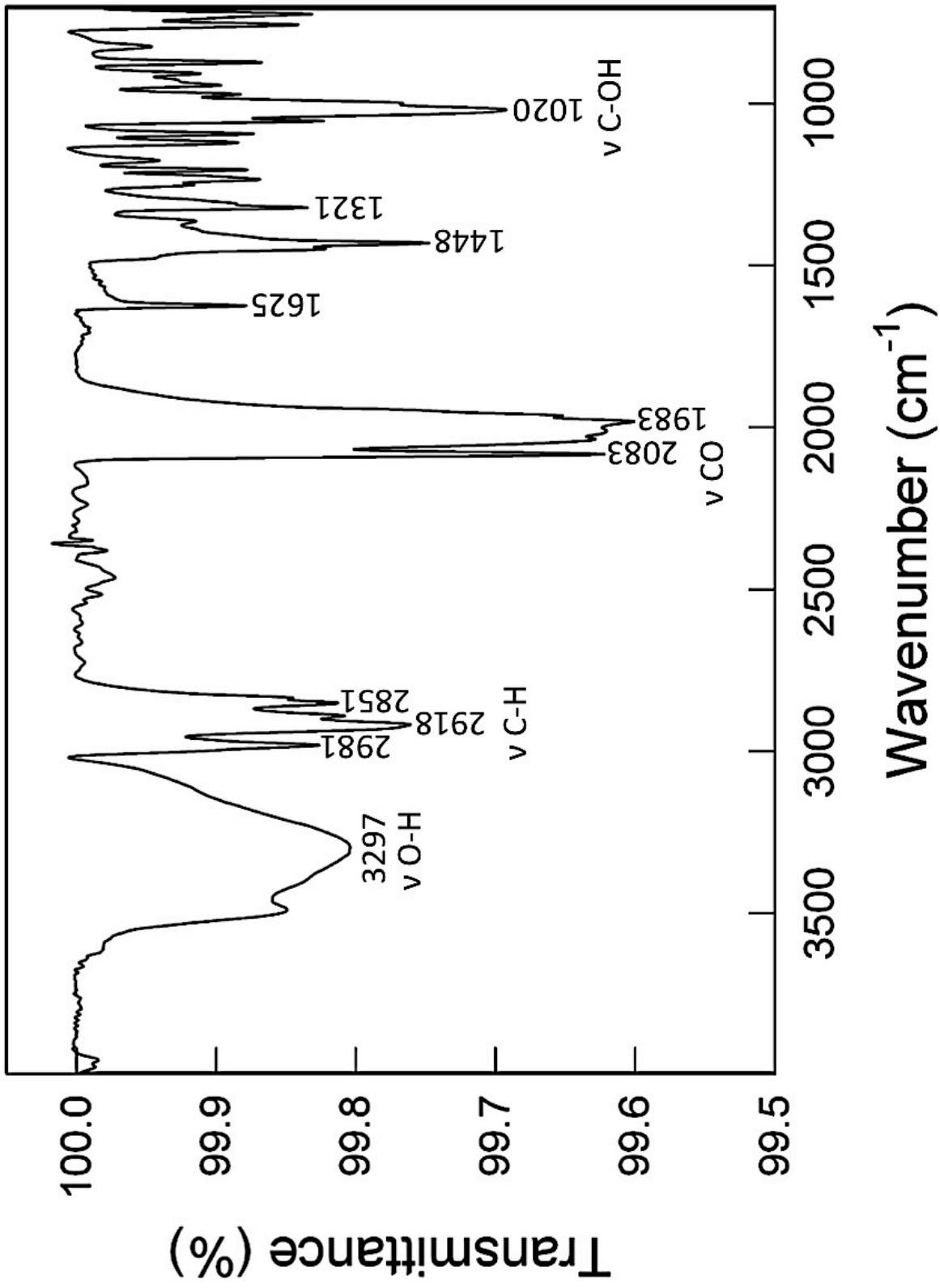


Figure SI8: IR absorption spectrum of complex *endo*-**2** isomer.

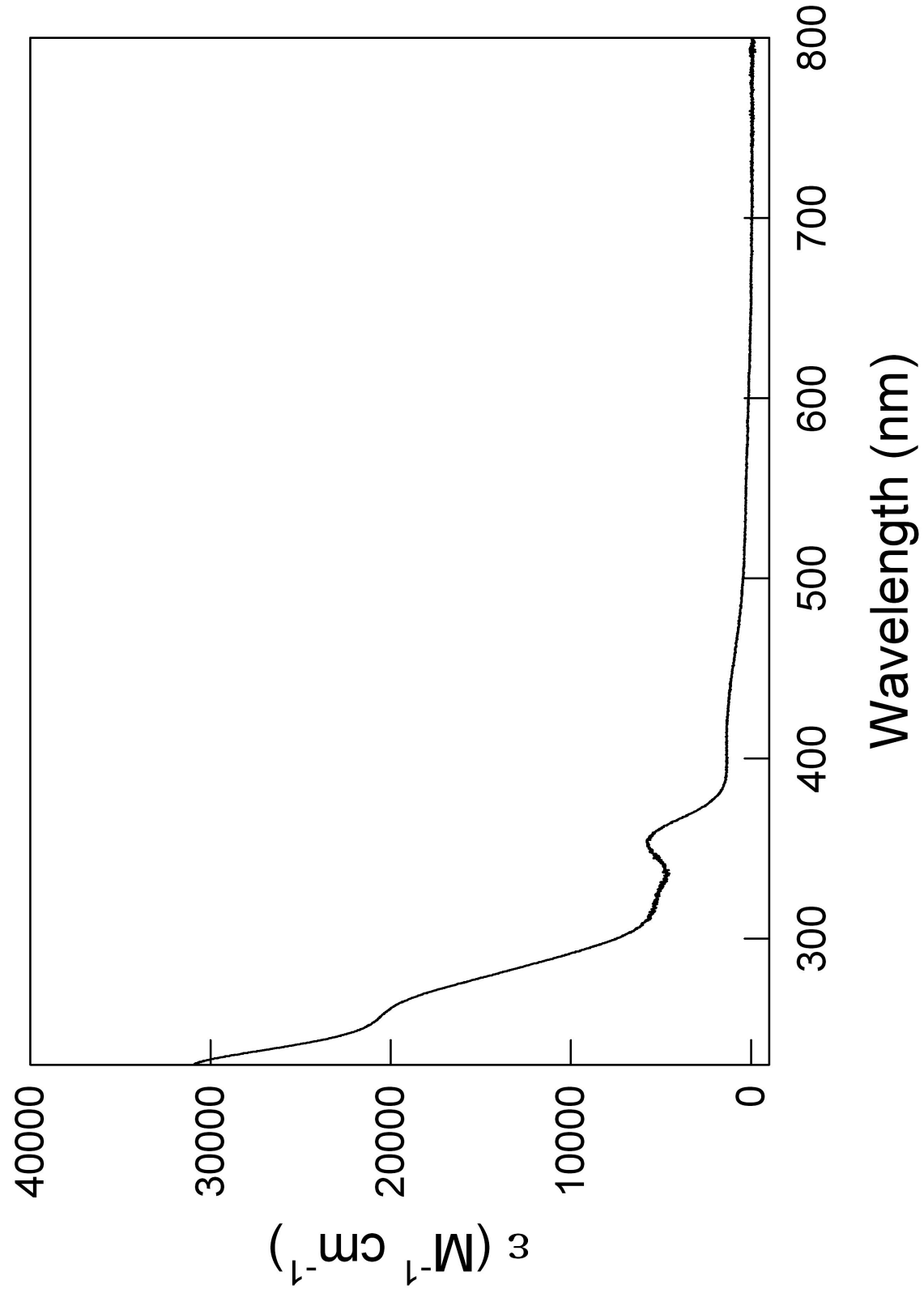
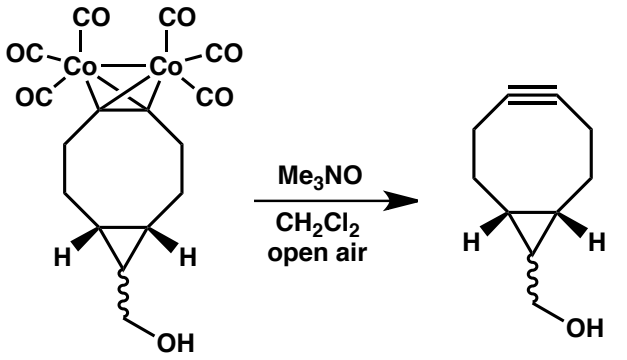


Figure SI9: UV-Vis absorption spectrum of complex *endo/exo*-**2** measured in CH_2Cl_2.

Representative deprotection of *endo/exo*-2

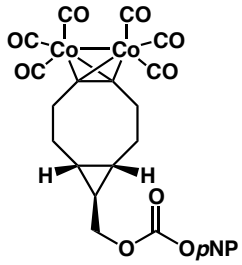


endo/exo-**2** *endo/exo*-**1**

To deprotect compound *endo/exo*-**2** and regenerate *endo/exo*-**1**, compound *endo/exo*-**2** (0.102 g, 0.230 mmol) was dissolved in dry CH_2Cl_2in a round bottom flask equipped with a calcium chloride drying tube, and Me_3NO (0.131 g, 1.18 mmol) was added to the solution. During the decomplexation, formation of a gray-green precipitate was observed. The reaction was monitored by TLC (silica gel) using EtOAc/Et_2O 1:6 as the eluent and was completed in 4 h. The solvent was removed *in vacuo*, and the reaction mixture was purified through column chromatography using EtOAc/Et_2O 1:6 as the eluent and *endo/exo*-**1** was isolated in 85% yield.

Functionalization of *exo*-2 complex

Synthesis of compound *exo*-4



Compound *exo*-**2** (0.113 g, 0.260 mmol) was dissolved in 8 mL dry CH_2Cl_2 under argon atmosphere. To this solution pyridine (53 μL, 0.66 mmol) was added at 0˚C. Subsequently, *p*-NO_2PhOC(O)Cl (0.070 g, 0.35 mmol) dissolved in 2 mL dry CH_2Cl_2 was added dropwise to reaction flask at 0˚C. The reaction was stirred at room temperature for 75 min. The solvent was evaporated and the product was purified by column chromatography (4:1 hexane/EtOAc) to give a dark brown solid (0.145 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 4.23 (d, J = 8 Hz, 2H), 3.28-3.23 (m,

2H), 3.07-3.00 (m, 2H), 2.43-2.40 (m, 2H); 1.36-1.30 (m, 2H), 1.04-1.01 (m, 2H), 0.91-0.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.4, 155.6, 152.3, 145.4, 125.3, 121.8, 97.8, 73.4, 36.4, 29.3, 23.6, 22.2. IR (KBr, cm^{-1}): 3085, 3031, 2924, 2852, 2084, 2040, 2009, 1765, 1559, 1526, 1455, 1215, 1102, 1042, 1005, 927, 859, 750, 718, 672. UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 268 (22,226), 360 (3,643), 430 (693).

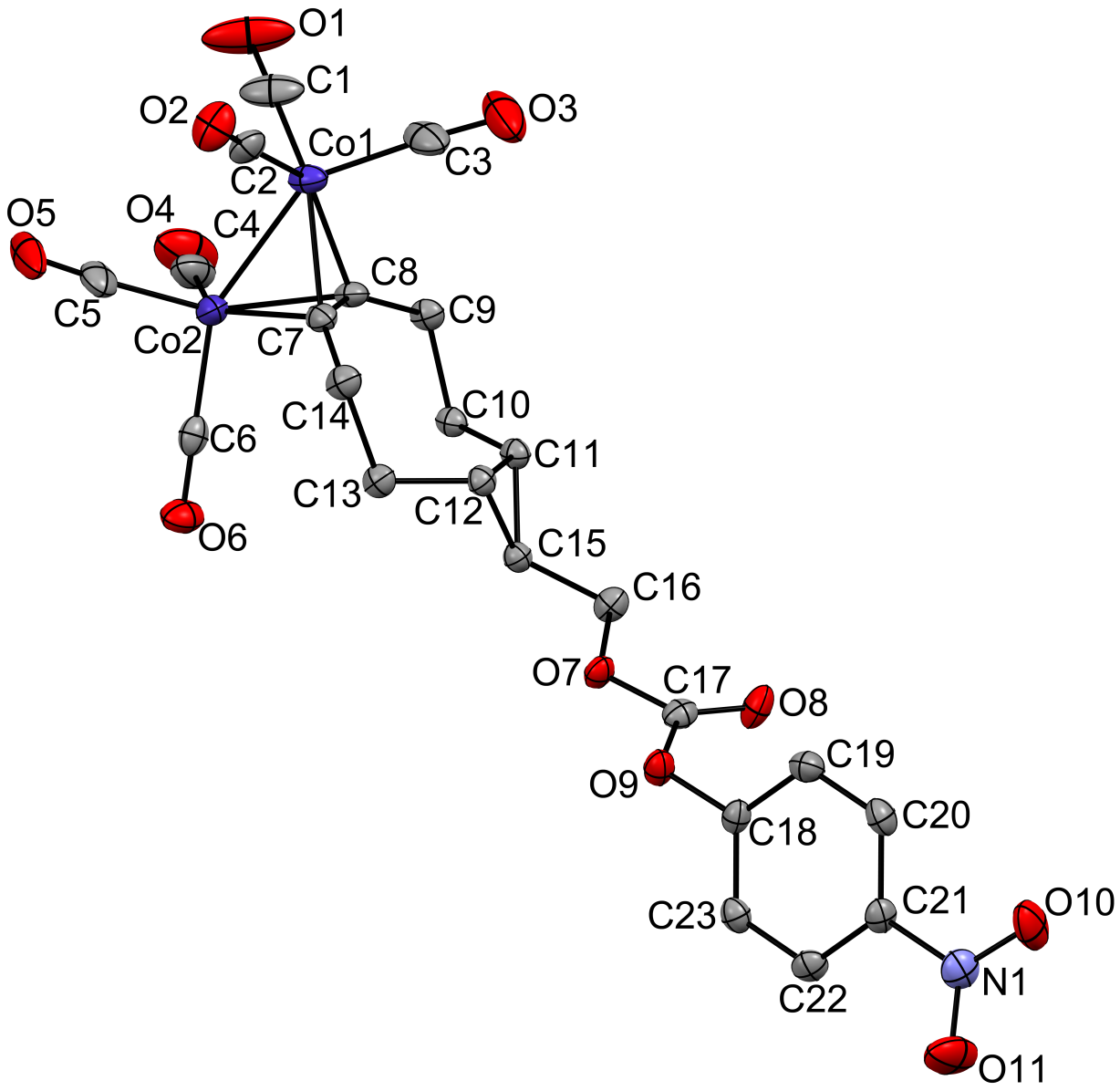


Figure SI10: Solid-state structure of *exo*-**4**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been removed for clarity.

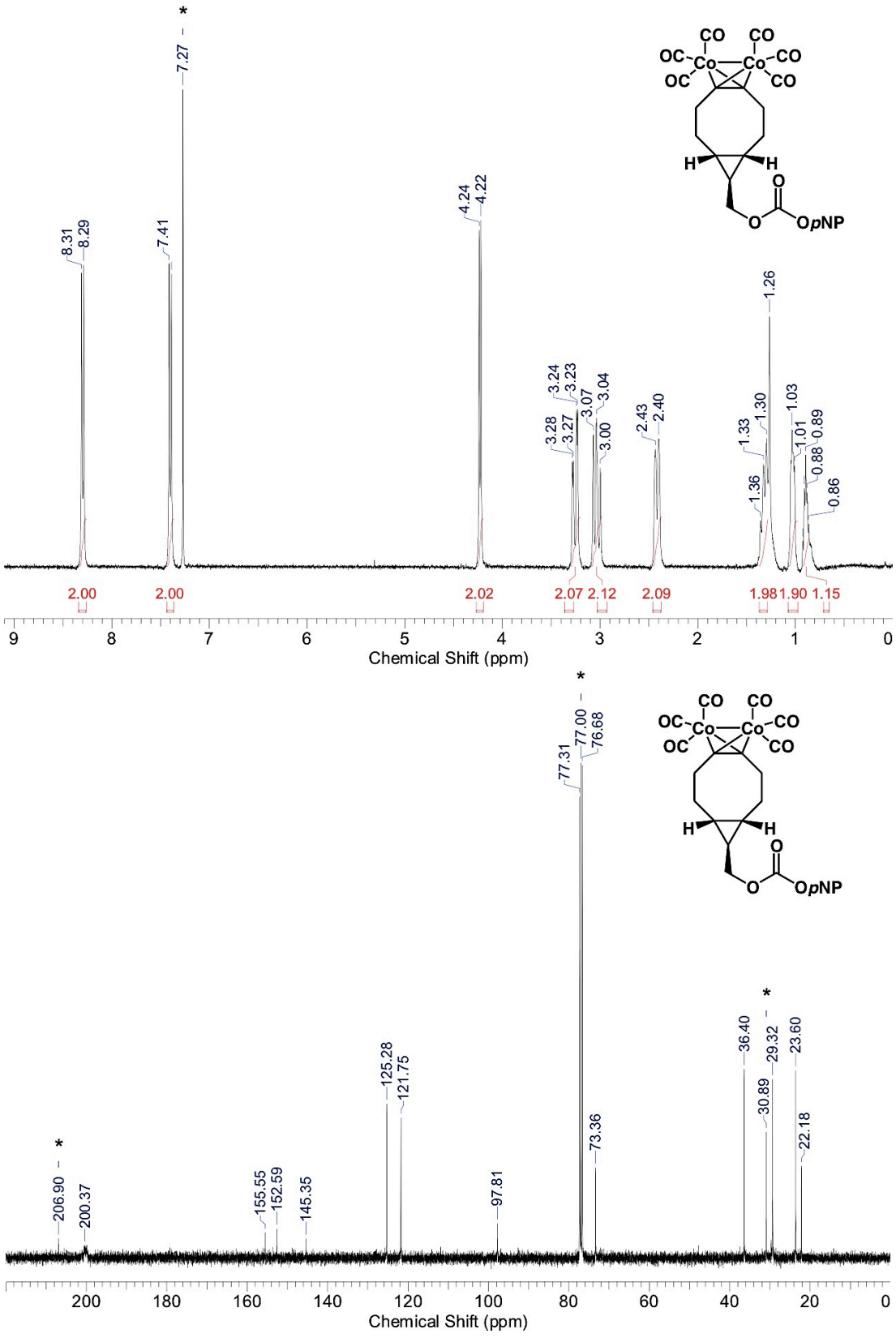


Figure SI11: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**4** isomer. * denotes residual solvent signals.

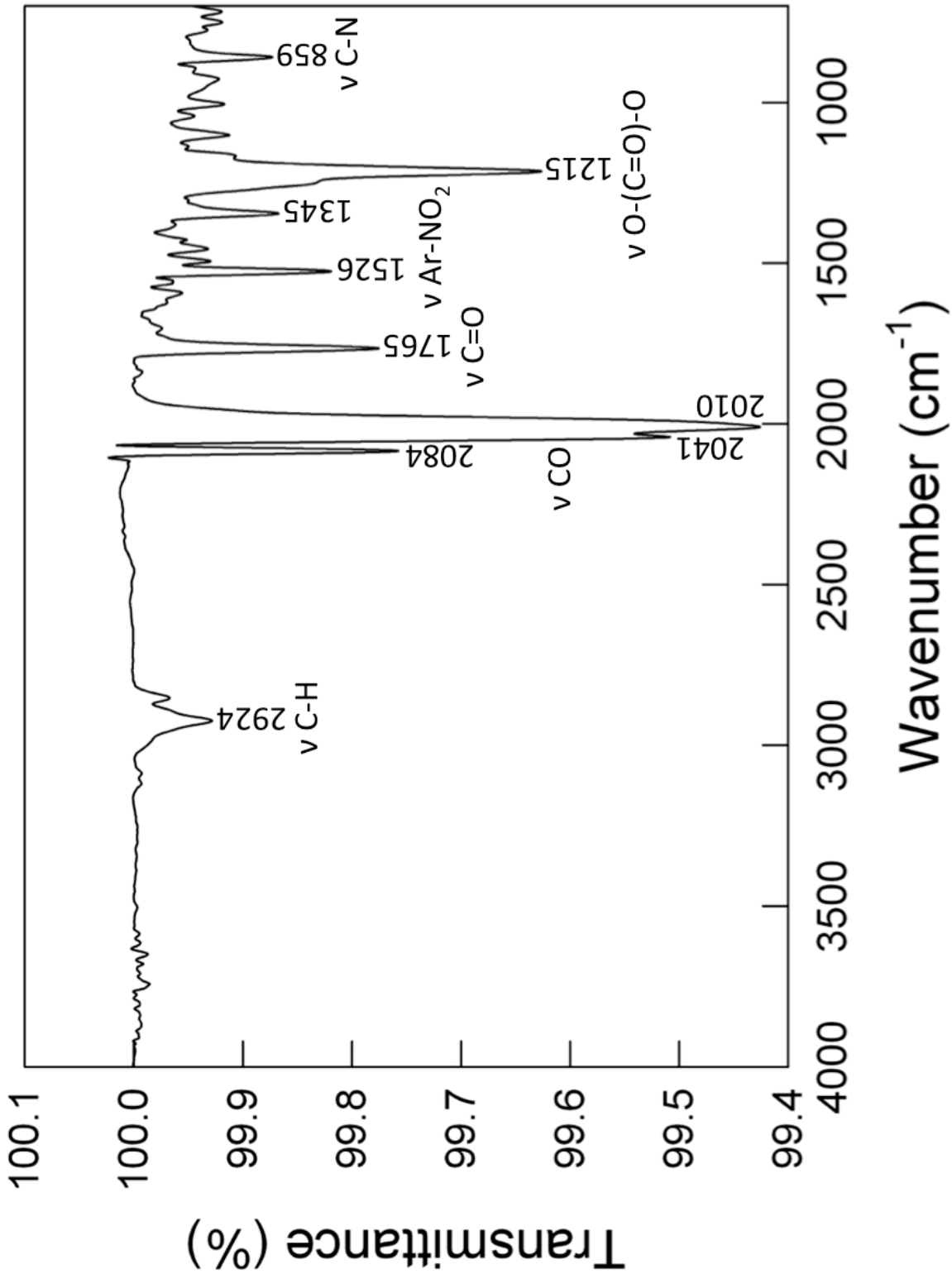
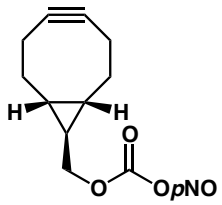


Figure SI12: IR absorption spectrum of complex *exo*-**4** isomer.

Synthesis of unprotected compound *exo*-3



The synthesis of compound *exo*-**3** was carried out under the same reaction conditions as for the synthesis of compound *exo*-**4**, but in the absence of the dicobalt-hexacarbonyl protecting group. To a solution of *exo*-**1** (0.500 g, 3.33 mmol) in 25 mL of dry CH_2Cl_2 and at 0 ºC was added pyridine (229 µL, 8.31 mmol) and subsequently a solution of *p*-NO_2PhOC(O)Cl (0.838 g, 4.16 mmol) in 20 mL of CH_2Cl_2. The ice-bath was removed and the reaction was carried out at room temperature. The reaction was complete after 15 min. Subsequently, the reaction mixture was quenched with saturated NH_4Cl-solution (75 mL) and extracted with 3 x 20 mL of CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography using Et_2O/hexanes 1:1 as the eluent to afford product **(10)** as a white solid in 73% yield. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.29 (d, *J* = 12 Hz, 2H), 7.40 (d, *J* = 12 Hz, 2H), 4.23 (d, *J* = 8 Hz, 2H), 2.48-2.17 (m, 6H), 1.47-1.38 (m, 2H), 0.89-0.83 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 152.5, 145.3, 125.3, 121.7, 98.7, 68.0, 29.0, 21.3, 20.5, 17.2. ESI-HRMS: Calc. for $C_{11}H_{13}O_2$ [M] 315.1107, found 315.1223.

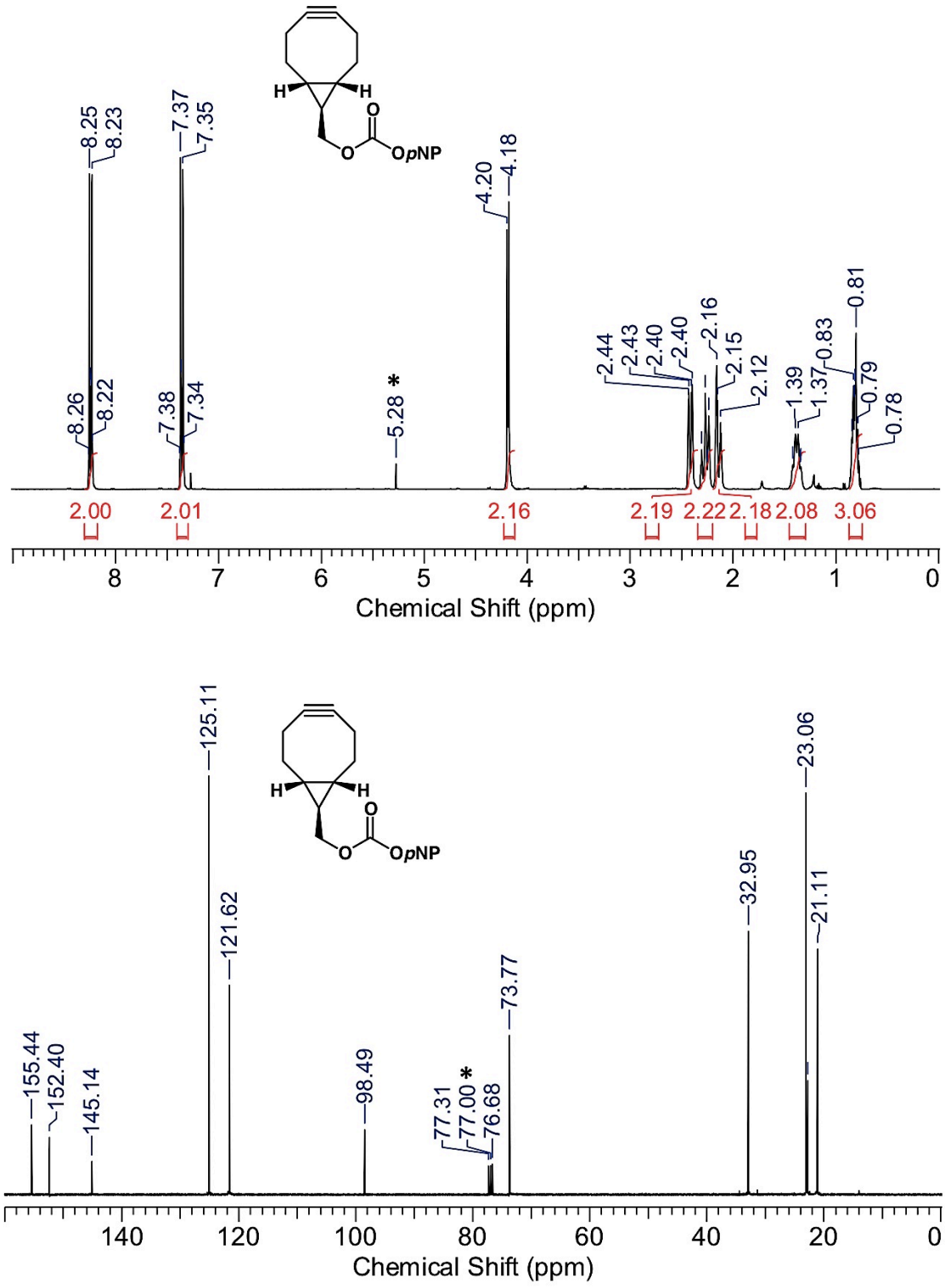


Figure SI13: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**3** isomer. * denotes residual solvent signals.

Synthesis of 2-azidoethanamine

2-bromoethylamine hydrobromide (2.00 g, 9.76 mmol) was dissolved in 10 mL water, then NaN_3 (1.91 g, 29.3 mmol) was added to reaction flask. The reaction mixture was heated to 80 ºC and stirred overnight. The reaction mixture was let to cool down to room temperature, and it was quenched by the addition of 4 equivalents of NaOH. The crude product was extracted with CH_2Cl_2 (3 x 50 mL) then dried with anhydrous Na_2SO_4. The solvent was evaporated then the final product was concentrated *in vacuo* to give a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (t, J = 8 Hz, 2H), 2.89 (t, J = 8 Hz, 2H), 1.42 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.6, 41.3. IR (KBr, cm^{-1}): 3275, 2928, 2098, 2020, 1746, 1663, 1575, 1455, 1347, 1293, 1130, 974, 912, 809.

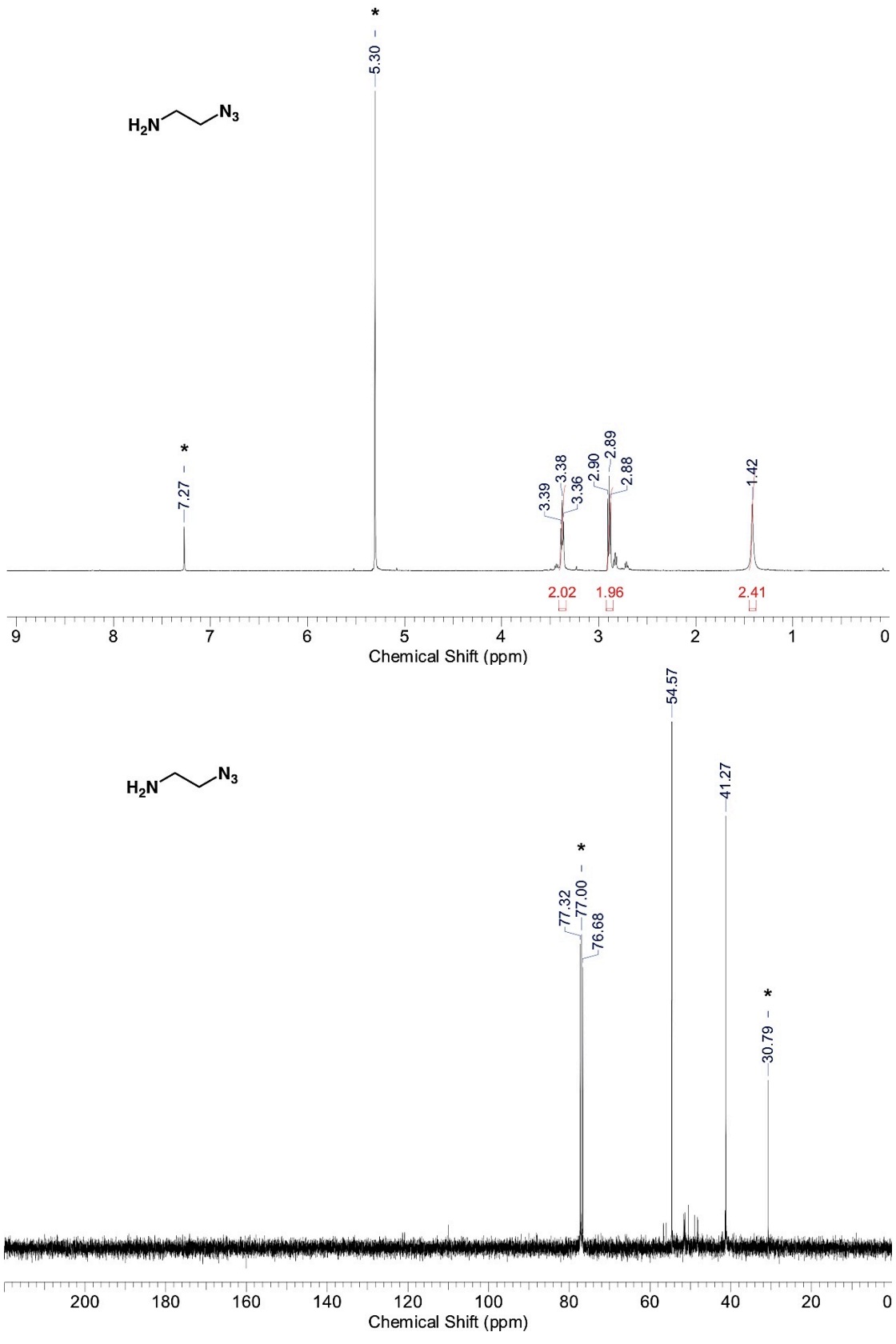


Figure SI14: ^{1}H (top) and ^{13}C NMR (bottom) spectra of 2-azidoethanamine. * denotes residual solvent signals.

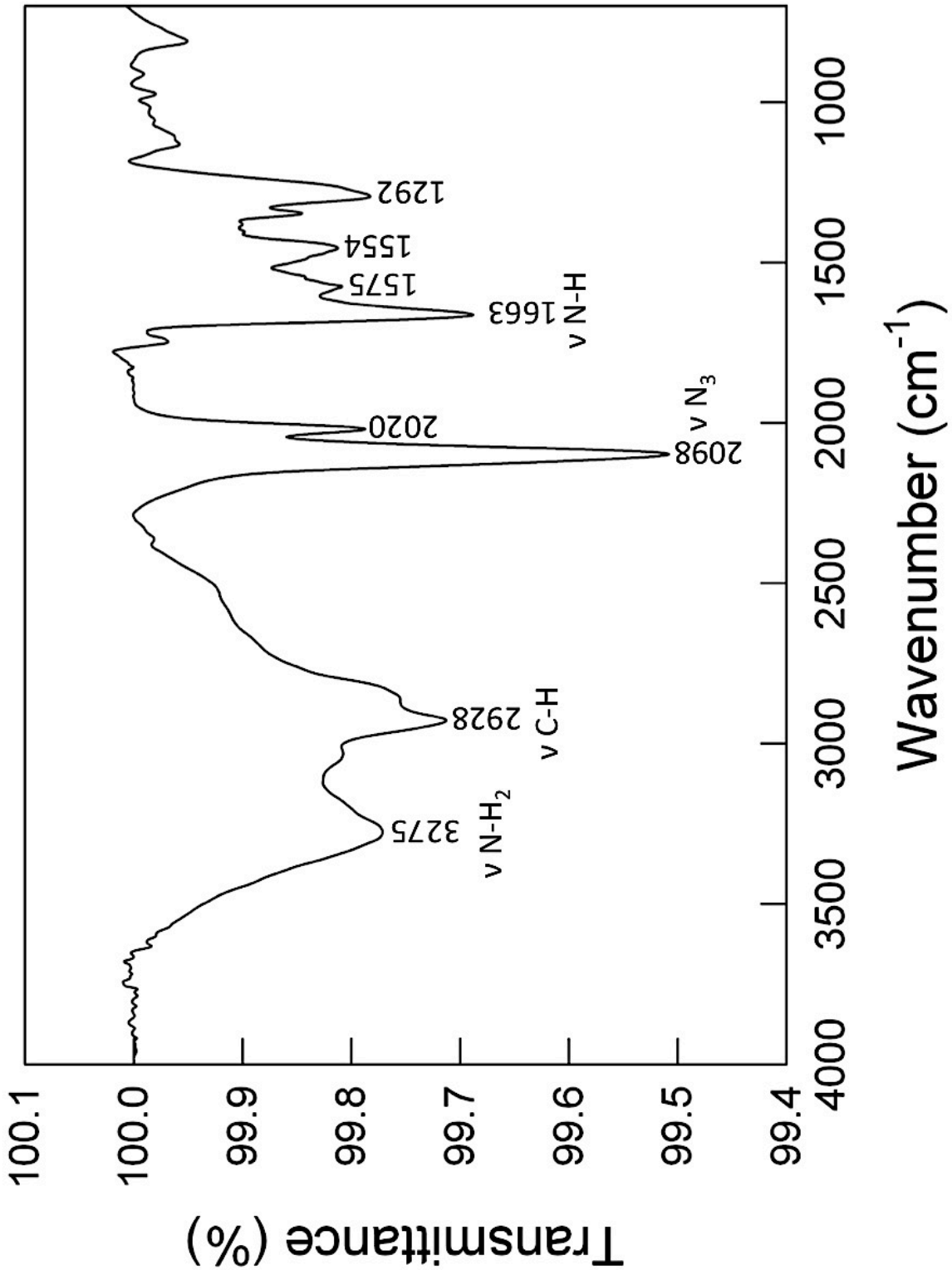
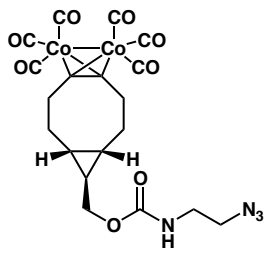


Figure SI15: IR absorption spectrum of complex 2-azidoethanamine.

Synthesis of compound *exo*-5



Compound *exo*-**4** (0.0888 g, 0.148 mmol) was dissolved in 1.0 mL of dry DMF under argon atmosphere and at 0 ºC. To this solution, a solution of 2-azidoethanamine (0.0272 g, 0.316 mmol) and Et_3N (44 μL, 0.315 mmol) in 0.5 mL DMF was added under argon atmosphere and at 0˚C. The reaction was stirred at room temperature for 30 min. The solvent was evaporated and the crude product was purified by column chromatography (4:1 hexane/EtOAc) to give a dark brown oil (0.0639 g, 80% yield). R_f = 0.31 in 4:1 hexane/EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (m, 1H), 3.99 (m, 2H), 3.46-3.38 (m, 4H), 3.24-3.20 (m, 2H), 3.04-2.97 (m, 2H), 2.38-2.34 (m, 2H), 1.26 (m, 2H), 0.91 (m, 2H), 0.74 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.4, 156.6, 98.2, 68.8, 51.2, 40.4, 36.5, 29.5, 23.3, 22.9. IR (KBr, cm^{-1}): 3328, 2924, 2852, 2103, 2085, 2040, 2007, 1708, 1517, 1450, 1431, 1249, 1145, 1097, 1015. UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 263 (13,3166), 360 (3,397), 430 (839).

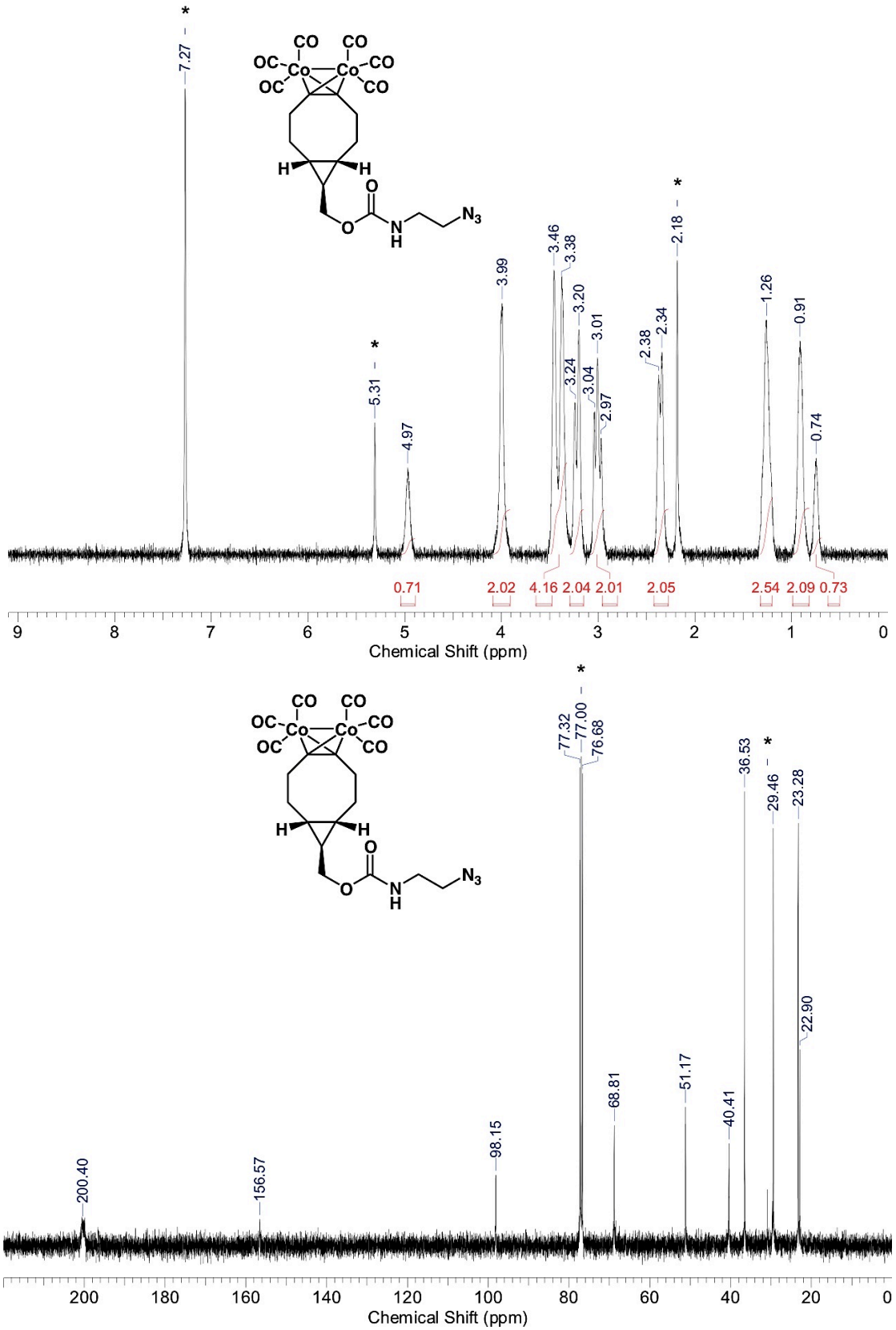


Figure SI16: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**5** isomer. * denotes residual solvent signals.

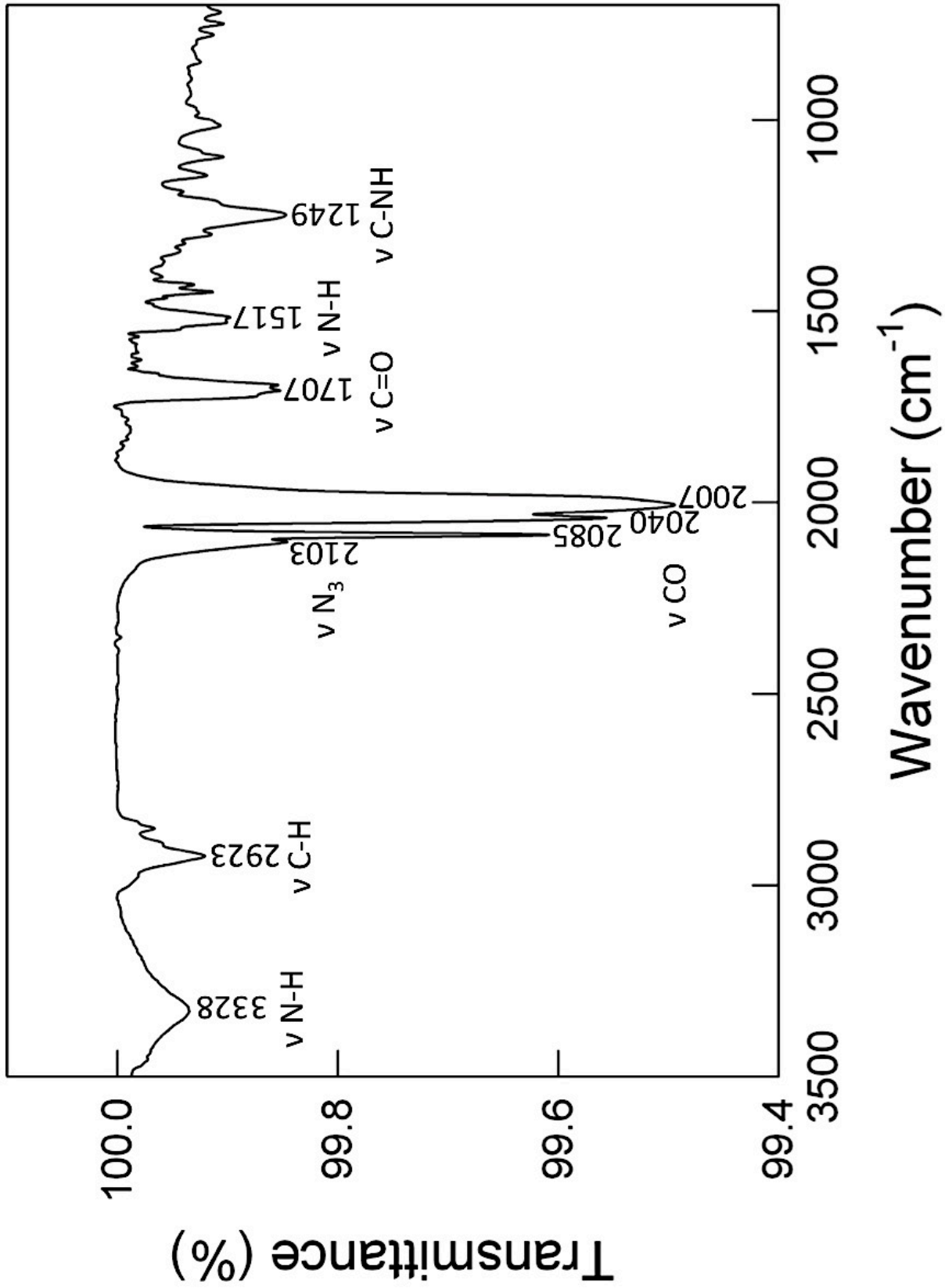
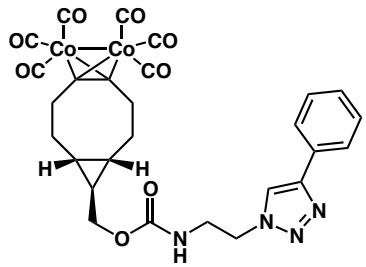


Figure SI17: IR absorption spectrum of complex *exo*-**5** isomer.

Synthesis of compound *exo*-6



In a glove box, phenylacetylene (40 μL, 0.3642 mmol) and CuI (0.075 g, 0.39 mmol) were dissolved in 5 mL of dry MeCN to give a colorless solution with a white precipitate. To this mixtue, Et_3N (56 μL, 0.40 mmol) was added to reaction flask and and a bright yellow precipitate quickly formed. Finally, azide *exo*-**5** (0.127 g, 0.2318 mmol) was added to the reaction mixture and let stir for 4 h. The crude product was purified by column chromatography (2:1 EtOAc/hexane) to give a dark brown solid (0.105 g, 70% yield). R_f = 0.38 in 2:1 EtOAc/hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.79 (m, 2H), 7.45-7.43 (m, 2H), 7.36 (m, 1H), 5.08 (m, 1H), 4.55 (m, 2H), 3.97 (m, 2H), 3.78 (m, 2H), 3.20-3.15 (m, 2H), 3.00-2.93 (m, 2H), 2.33-2.29 (m, 2H), 1.24 (m, 2H), 0.88 (m, 2H), 0.71 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.4, 156.7, 147.9, 130.3, 128.9, 128.3, 125.9, 120.4, 98.1, 69.0, 49.9, 40.8, 36.5, 29.5, 23.3, 22.8. IR (KBr, cm^{-1}): 3335, 3117, 3085, 3031, 2921, 2886, 2848, 2083, 1985, 1690, 1529, 1464, 1448, 1427, 1363, 1331, 1278, 1256, 1228, 1171, 1148, 1080, 1005, 969, 938, 847, 763, 693, 668. UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 243 (32,299), 360 (3,659), 430 (880).

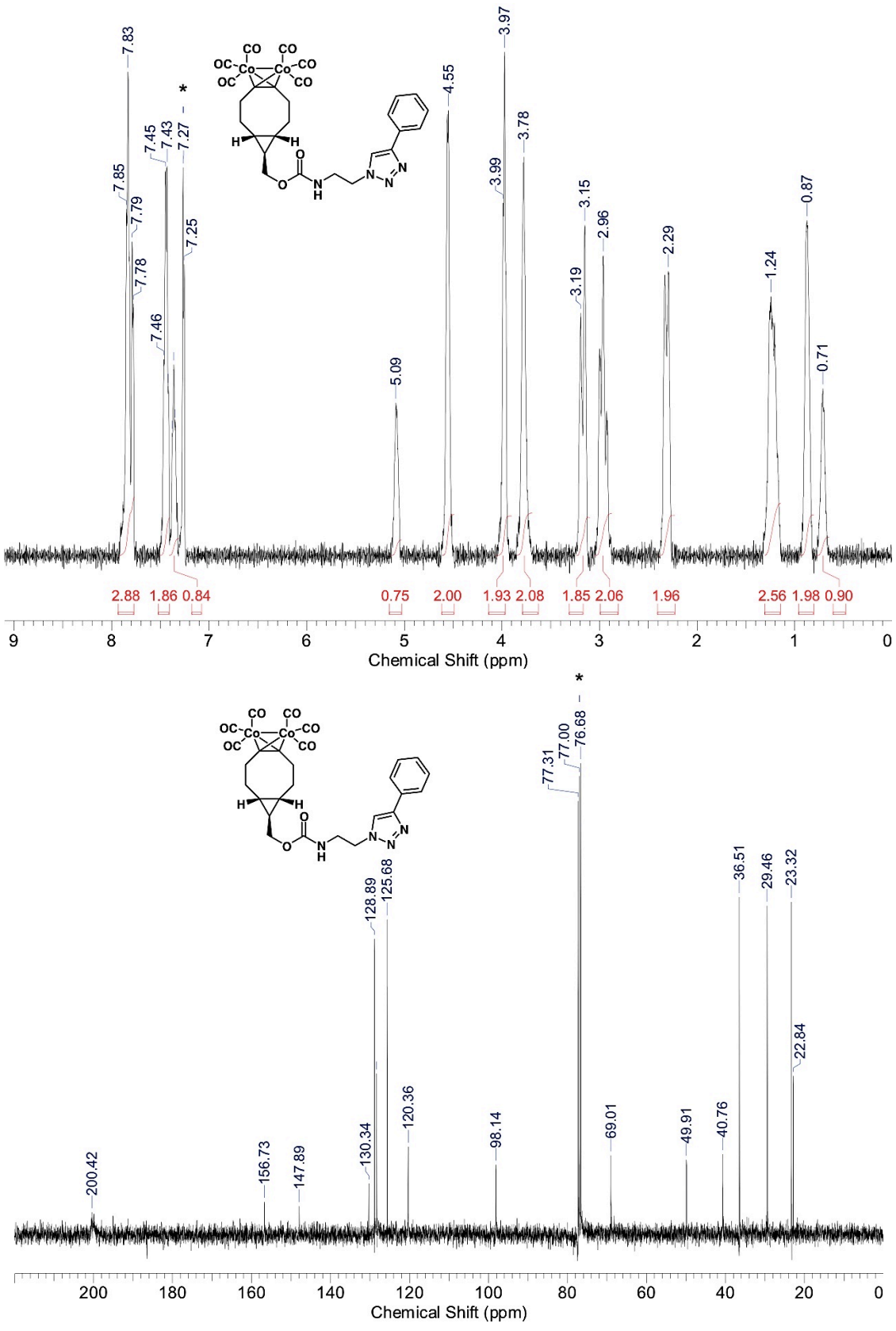


Figure SI18: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**6** isomer. * denotes residual solvent signals.

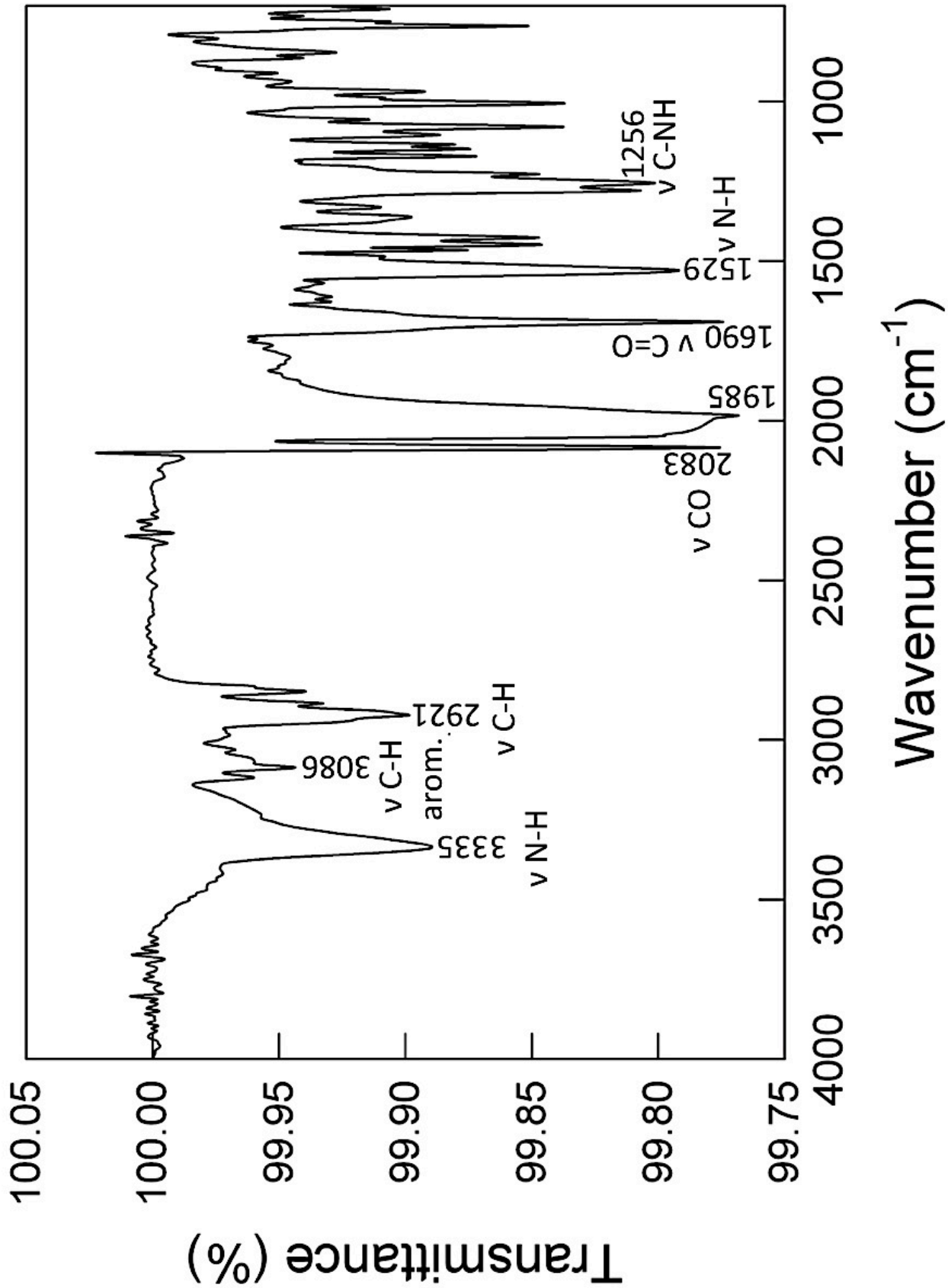
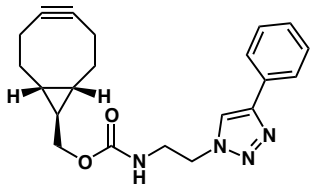


Figure SI19: IR absorption spectrum of complex *exo*-**6** isomer.

Synthesis of compound *exo*-7



Compound *exo*-**6** (0.0503 g, 0.0773 mmol) was dissolved in 5 mL dry CH_2Cl_2 in a flask equipped with a calcium chloride drying tube. To this solution, Me_3NO (0.0454 g, 0.409 mmol) was added, and the reaction was stirred at room temperature for 4 h. Upon removal of the solvent, the crude product was purified by column chromatography (4:1 EtOAc/hexane) to give the final product as a yellow oil (0.0169 g, 60 %). R_f = 0.37 in 2:1 EtOAc/hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.79 (m, 3H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 2H), 5.16 (bs, 1H), 4.56-4.54 (m, 2H), 4.00-3.98 (d, 2H, 8 Hz), 3.79-3.75 (m, 2H), 2.39-2.36 (m, 2H), 2.31-2.24 (m, 2H), 2.16-2.12 (m, 2H), 1.40-1.34 (m, 2H), 0.90-0.84 (bs, 2H), 0.74-0.71 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.8, 147.8, 130.3, 128.9, 128.3, 125.7, 120.5, 98.7, 69.5, 49.9, 40.8, 33.2, 23.6, 22.9, 21.3. CI-HRMS: Calculated for $C_{21}H_{25}N_4O_2$ [M+1]: 365.1972, found 365.1974.

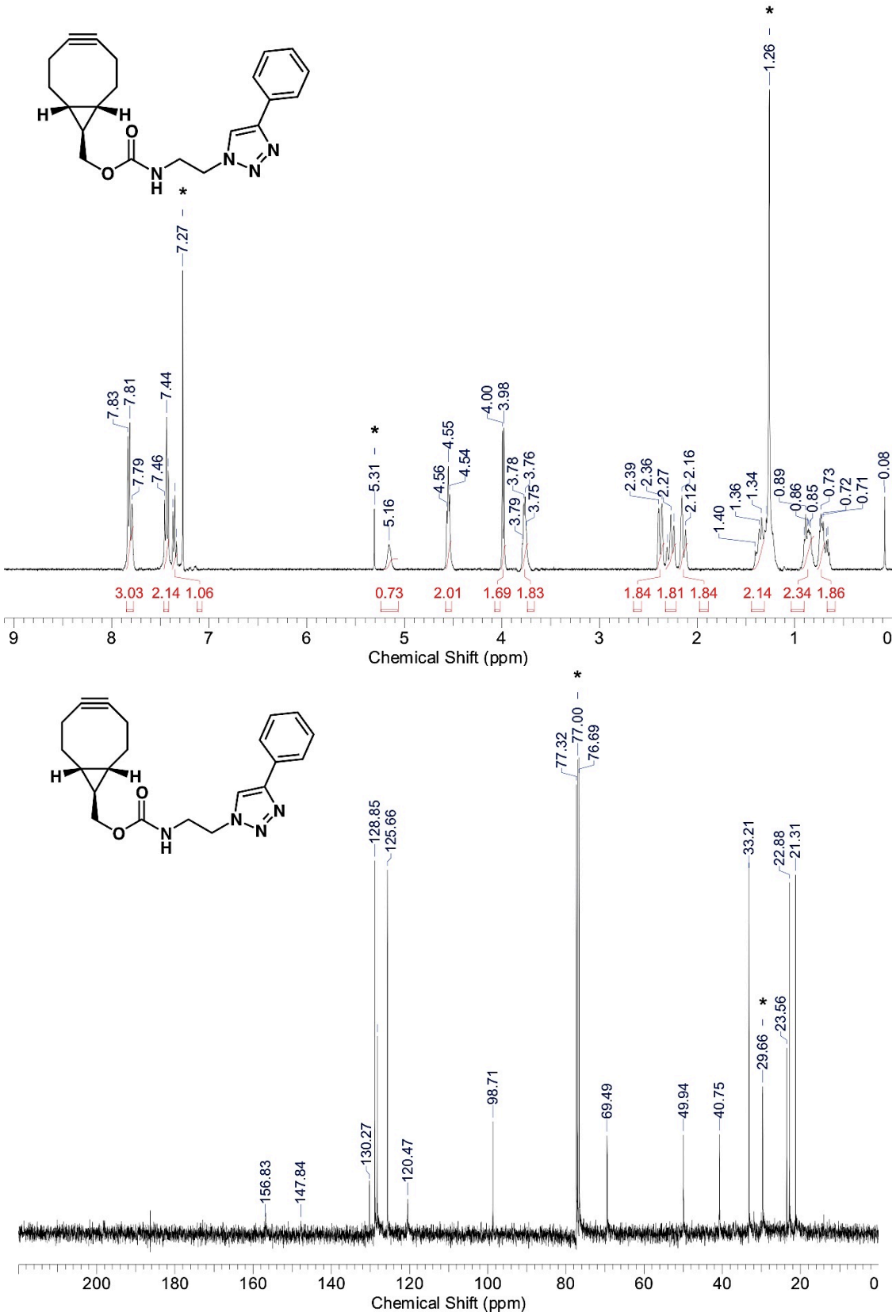
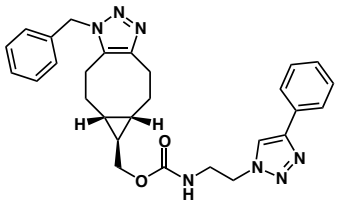


Figure SI20: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**7** isomer. * denotes residual solvent signals.

Synthesis of compound *exo*-8



Compound *exo*-**7** (0.0150 g, 0.0412 mmol) was dissolved in 2 mL of CH_2Cl_2. To this solution was added benzyl azide (5.1 uL, 0.041 mmol) and the reaction was stirred for 10 min. Solvent and any residual benzyl azide were removed *in vacuo*, and compound *exo*-**8** could be obtained pure in a mixture of 1,4- and 1,5-substituted regioisomers in essentially quantitative yield by NMR (0.020 g). R_f = 0.33 in EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.79 (m, 3H), 7.45-7.42 (m, 2H), 7.37-7.31 (m, 4H), 7.13-7.11 (m, 2H), 5.49 (s, 2H), 5.14 (bs, 1H), 4.55-4.53 (m, 2H), 3.94-3.82 (m, 2H), 3.78-3.74 (m, 2H), 3.16-3.12 (bs, 1H), 2.92-2.86 (bs, 1H), 2.75-2.72 (bs, 1H), 2.54-2.48 (bs, 1H), 2.40-2.35 (bs, 1H), 2.20-2.15 (bs, 1H), 1.36-1.30 (bs, 2H), 0.89-0.85 (bs, 2H), 0.69-0.68 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2, 148.0, 145.4, 135.9, 134.4, 131.3, 129.44, 129.38, 129.30, 128.77,128.67, 128.63, 127.5, 126.1, 121.1, 69.1, 55.3, 52.6, 50.5, 41.4, 32.48, 32.42, 32.25, 30.2, 30.08, 30.02, 29.99, 29.91, 29.83, 29.79, 29.76, 29.64, 27.50, 27.14, 26.64, 26.02, 24.56, 23.46, 23.24, 23.22, 23.17, 23.10, 23.03, 22.9, 14.43, 14.41. CI-HRMS: Calculated for $C_{28}H_{32}N_7O_2$ [M+1]: 498.2617, found 498.2638.

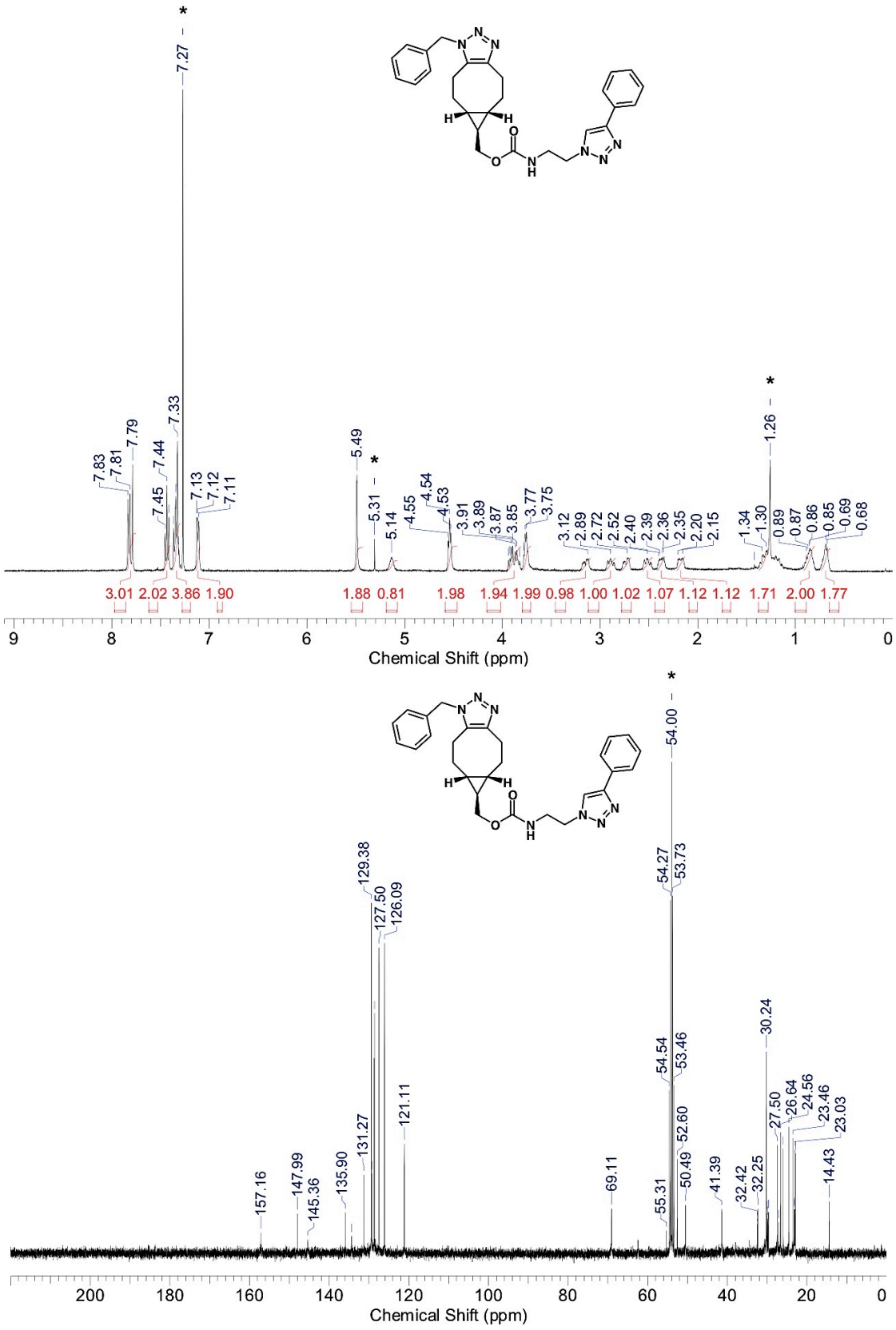


Figure SI21: ^{1}H (top) and ^{13}C NMR (bottom) spectra of *exo*-**8** isomer. * denotes residual solvent signals.

X-ray Crystallography

Single crystals of complexes *exo*-**2,** *endo*-**2**, and *exo*-**4** suitable for X-ray diffraction studies were grown by slow evaporation of a concentrated solution of each compound in dichloromethane. The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The data collection strategy included a number of ω and φ scans which collected data over a range of angles, 2θ. The frame integration was performed using SAINT.[2] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[3] The structures were solved by direct methods using the SIR92 program (*exo*-**2**)[4] or XS program **(***endo*-**2**),[5] and by a dual space methodology using the SHELXT program (*exo*-**4**)[6]. All non-hydrogen atoms were obtained from the initial solution. Atoms H7 and H7A (*exo*-**2**) and atoms H7A, H7B, H7C (*endo*-**2**) were disordered over two positions. The disorder arises because of close H···H contacts across a crystallographic inversion centre. The O—H bond lengths for the disordered hydrogen atoms were fixed to 0.84 Å and the isotropic displacement parameter was set to 1.5 times the value of U_{equiv} for the parent oxygen atom. Each of the disordered hydrogen atoms forms O—H···O hydrogen bonds with neighbouring oxygen atoms. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from SHELXTL.[7] See Table SI1 for additional crystallographic data.

Table SI1. X-ray diffraction data collection and refinement details for complexes *exo*-**2,** *endo*-**2**, and *exo*-**4**.

	exo-**2**	*endo*-**2**	*exo*-**4**
Chemical Formula	$C_{16}H_{14}Co_2O_7$	$C_{16}H_{14}Co_2O_7$	$C_{23}H_{17}Co_2NO_{11}$
Formula Weight (g/mol)	436.13	436.13	601.23
Crystal Habit	red block	red block	orange needle
Crystal System	triclinic	triclinic	monoclinic
Space Group	P -1	P -1	C 2/c
λ (Å)	0.71073	0.71073	0.71073
T (K)	110	110	110
a (Å)	9.074(3)	8.893(3)	39.343(20)
b (Å)	12.983(6)	16.495(6)	8.101(4)
c (Å)	16.699(5)	19.797(9)	16.720(6)
α (deg)	110.879(17)	101.280(16)	90
β (deg)	96.205(8)	102.130(12)	110.966(13)
γ (deg)	98.023(9)	103.697(12)	90
V ($Å^3$)	1793.4(11)	2664.9(18)	4976(4)
Z	4	6	8
ρ (g/cm)	1.615	1.631	1.605
μ, (cm^{-1})	1.883	1.900	1.394
R_1,[a] wR_2[b] [I > 2σ]	0.0285, 0.0668	0.0231, 0.0571	0.0360, 0.0636
R_1, wR_2 (all data)	0.0360, 0.0701	0.0296, 0.0600	0.0672, 0.0724
GOF[c]	1.029	1.046	1.011

[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$, [b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$, [c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns. - No. of params.})]^{½}$

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[3] Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA.

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[7] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.