

***Intermolecular 2+2 Carbonyl-Olefin Photocycloadditions  
Enabled by Cu(I)-Norbornene MLCT***

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*Supporting Information*

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## I. Experimental Section

**A. General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.<sup>1</sup>

<sup>1</sup>H and <sup>13</sup>C NMR were recorded on Bruker 300 MHz or Varian 500 MHz spectrometers at 300 and 126 MHz, respectively. All chemical shifts are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) chemical shifts of the solvent as a secondary standard. GC analyses were performed using an Agilent Technologies 7890B gas chromatograph equipped with an Agilent 7693 autosampler and Agilent HP-5 capillary column (30 m x 0.320mm x 250µm). Standard method parameters: 1.2 mL/min flow rate with oven program 80 – 250 °C with a ramp rate of 25 °C/min and hold time of 8.7 minutes at 250 °C. High-resolution mass spectra were measured using a Thermo LCQdeca APCI-MS.

**Photophysical Methods.** Electronic absorption and fluorescence experiments were conducted using sealable 1-cm path length fused quartz cuvettes (Starna Cells, catalog number 3-Q-10-GL14-C, 3.5 mL volume) using a Shimadzu UV-2450 UV-Vis spectrometer and a HORIBA Scientific Fluoromax-4 fluorometer. Samples were prepared in a dry nitrogen glove box. Filter experiments were conducted using a long pass UV filter with a cut-on wavelength of 300 nm (Asahi Spectra XUL0300).

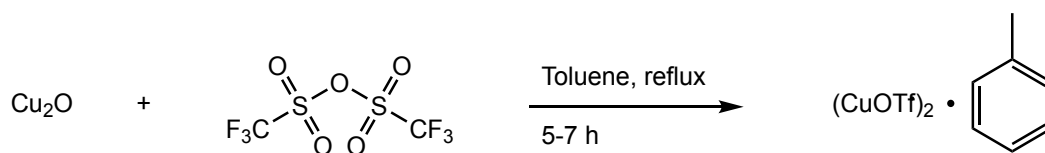
**Photochemical Reactions.** Photochemical reactions were carried out using a 100-W Blak-Ray Long Wave Ultraviolet Lamp (Hg). Temperature control was maintained with a fan, with the ambient temperature within the setup measured at 55 °C. The light source was placed approximately 20 cm from the sample and the reaction mixture was stirred vigorously using a magnetic stir bar. All reactions were

performed in VWR 13 x 100 mm borosilicate culture tubes that were capped then sealed with electrical tape.



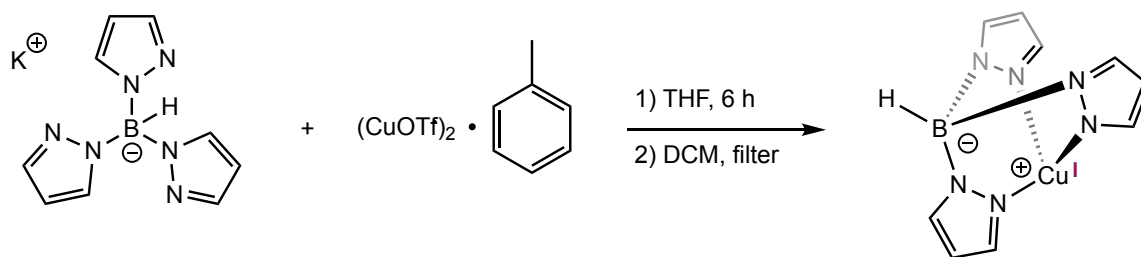
**Figure S1.** Photoreactor set-up for 2+2 COPC reactions.

## B. Preparation of TpCu



In a glovebox a 100 mL Schlenk flask was charged with a stir bar, copper(I) oxide (1.000 g, 6.989 mmol, 1.0 equiv), 40 mL of toluene, and fitted with a reflux condenser with a duck adapter sealing the flask. The apparatus was brought out of the glovebox and put under nitrogen atmosphere from a Schlenk line. Freshly prepared triflic anhydride (9.74 mmol, 1.4 equiv) was added via syringe through the side arm (triflic anhydride can be made from the mixing of triflic acid and P<sub>2</sub>O<sub>5</sub> neat, followed by distillation). The solution was stirred vigorously and gently refluxed for 5-7 hr. In our hands, heating above 130 °C lead to decomposition. Reaction completion was judged upon full dissolution of copper(I) oxide, when a clear solution was obtained. It should be noted residual copper(II) oxide does not dissolve, and remains as a black precipitate. Under a positive flow of N<sub>2</sub>, the reflux

condenser was replaced with a medium porosity Schlenk frit capped with a 100 mL round bottom flask. The reaction was filtered hot and the filtrate was allowed to cool in an ice bath for several hours, resulting in the precipitation of copper(I) triflate toluene. The mixture was filtered back through the Schlenk frit, collecting  $(\text{CuOTf})_2 \cdot \text{PhMe}$  on the frit and the supernatant back into the reaction flask. Under a positive flow of nitrogen the Schlenk flask was removed and replaced with a 50 mL round bottom flask and the product was dried under vacuum overnight producing copper (I) triflate toluene complex as an off-white powder (4.486 g, 62% yield). This compound immediately undergoes a yellow discoloration upon exposure to air and should be handled and stored in an oxygen free environment.<sup>2</sup>



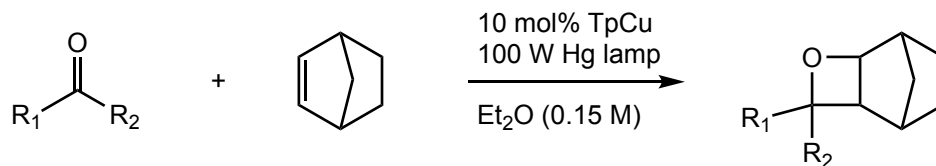
In a nitrogen filled glovebox a 20 mL vial was charged with copper(I) triflate toluene complex (0.250 g, 1 equiv), potassium trispyrazolylborate (0.244 g, 2 equiv), and a stir bar. THF (4 mL) was added and the solution was allowed to stir vigorously for 6 h. The solvent was removed under vacuum, and DCM (5 mL) was added. The solution was filtered through a thin pad of celite on a fritted funnel and DCM removed under vacuum to provide **TpCu** (0.267 g, 98% yield) as a faint blue solid. Copper(I) chloride can alternatively be used as a source of Cu(I): In a nitrogen filled glovebox, a 20 mL vial was charged with CuCl (0.125g, 1 equiv), potassium trispyrazolylborate (0.318 g, 1 equiv) and a magnetic stir bar. A mixture of THF (4 mL) and dried, degassed acetone (4 mL) was added and the mixture was stirred vigorously for 6 h. The solvent was removed under reduced pressure, the resultant solid extracted with dichloromethane (5 mL), and the suspension filtered through a thin pad of celite on a fritted funnel. Removal of the solvent under reduced pressure provided **TpCu** (0.349 g, 98% yield) as a faint blue solid. Analytical data for **TpCu**:

**<sup>1</sup>H-NMR** (300 MHz; C<sub>6</sub>D<sub>6</sub>): δ 7.58 (d, J=1.8 Hz, 3H), 7.09 (d, J=1.2 Hz 3H), 5.96 (t, J=1.8 Hz, 3H).

**<sup>13</sup>C-NMR** (126 MHz; C<sub>6</sub>D<sub>6</sub>): δ 141.8, 135.9, 104.9.

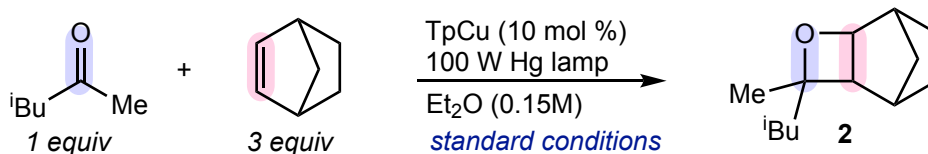
**HRMS** (ESI-TOFMS): Calc. for [C<sub>9</sub>H<sub>10</sub>BCuN<sub>6</sub>]<sup>+</sup> =276.0352, Found = 276.0354.

### C. General 2+2 COPC Reaction Procedures.



In a glovebox to a borosilicate culture tube charged with a magnetic stir bar was added ketone (30 mg, 1.0 equiv), TpCu (0.1 equiv), norbornene (3.0 equiv), and diethyl ether (0.15M). The vial was capped, sealed with electrical tape, and irradiated with a UVP Blak-Ray B-100A UV lamp in an assembled photoreactor fitted with an exhaust fan and 20" box fan. After 12 h, or otherwise indicated, the reaction mixture was filtered through a glass filter, rinsed with an additional 1 mL Et<sub>2</sub>O, and solvent removed under reduced pressure. A 0.6M solution of durene in C<sub>6</sub>D<sub>6</sub> added (100 μL) before diluting with additional C<sub>6</sub>D<sub>6</sub> for <sup>1</sup>H-NMR analysis. The sample was then concentrated under reduced pressure and purified by flash chromatography.

*We note that <sup>1</sup>H-NMR yields differ from isolated yields for some products and attribute this to observed oxetane degradation on silica during purification compounded with the challenging removal of the NMR silent, Tp<sub>2</sub>Cu, byproduct of TpCu degradation when exposed to O<sub>2</sub>.*

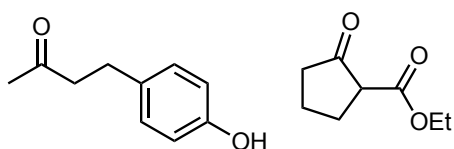
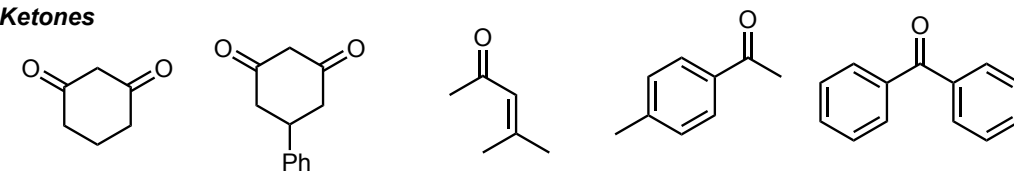
**Table S1.** Expanded reaction condition optimization

Entry	Deviation from above	Reaction time (h)	Yield of <b>2</b> <sup>a</sup>	dr (exo:endo) <sup>b</sup>
1	None	12	53%	55:45
2	No TpCu	12	<i>n.d.</i>	---
3	No light, heated to 43 °C	12	<i>n.d.</i>	---
4	1 equiv norbornene	36	33%	55:45
5	5.0 equiv norbornene	9	56%	55:45
6	3.0 equiv ketone (+1 equiv norbornene)	12	<10%	62:38
7	5.0 equiv ketone (+1 equiv norbornene)	12	<i>n.d.</i>	---
8	0.5M Et <sub>2</sub> O	60	24%	55:45
9	0.01M Et <sub>2</sub> O	48	<10%	55:45
10	2.5 mol % TpCu	48	21%	50:50
11	5 mol % TpCu	24	36%	55:45
12	Benzene solvent	12	50% conv.	55:45
13	Dichloromethane solvent	12	<i>n.d.</i>	---
14	CuOTf in place of TpCu	12	13% <sup>c</sup>	55:45
15	CuOTf + KTp (10 mol % each)	12	31%	55:45
16	AgOTf + KTp (10 mol % each)	12	<i>n.d.</i>	---
17	Zn(OTf) <sub>2</sub> + KTp (10 mol % each)	12	<i>n.d.</i>	---
18	Sc(OTf) <sub>3</sub> + KTp (10 mol % each)	12	<i>n.d.</i>	---

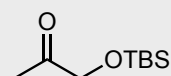
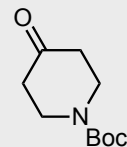
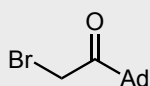
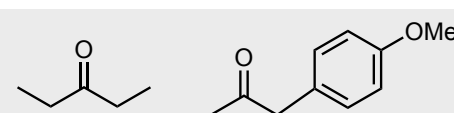
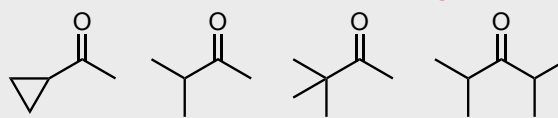
<sup>a</sup>Yields determined based on analysis of crude reaction mixtures by <sup>1</sup>H-NMR using durene as internal standard; *n.d.* = not detected. <sup>b</sup>Diastereomeric ratios were determined via gas chromatography of crude reaction mixtures. <sup>c</sup>11% yield of norbornene dimers also isolated

**Scheme S1.** Failed carbonyl substrates using standard conditions.

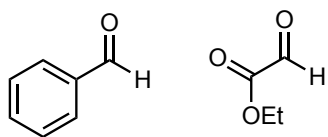
**Ketones**



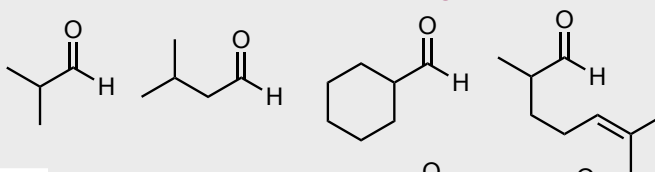
*Trace oxetane formation observed using norbornene*



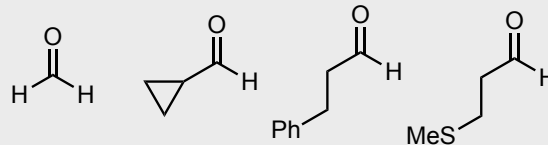
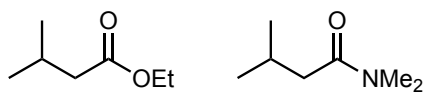
**Aldehydes**



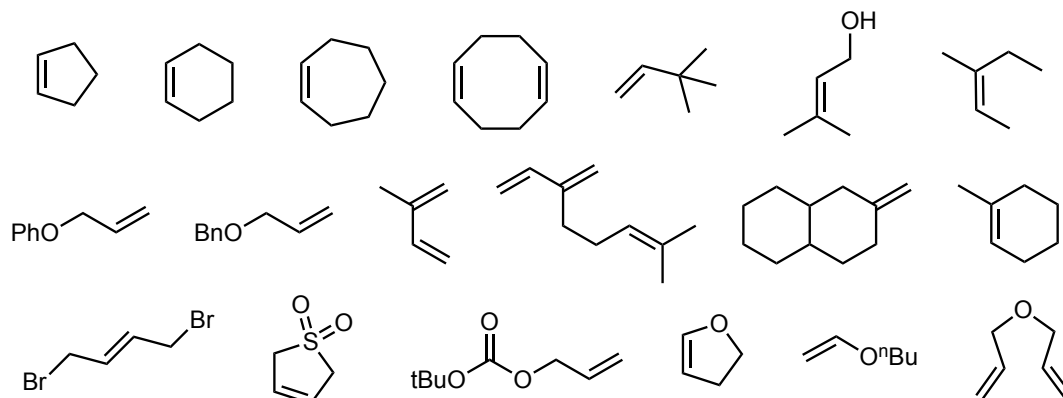
*Trace oxetane formation observed using norbornene*



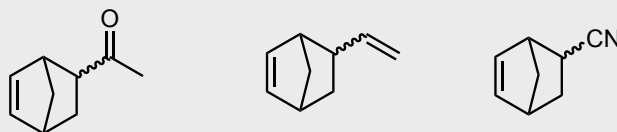
**Other carbonyls**



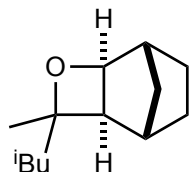
**Scheme S2.** Failed olefin substrates using standard conditions.



*Trace oxetane formation observed using methyl isobutyl ketone*



**D. Characterization of Oxetane Products.**



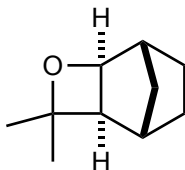
**1** was synthesized via general COPC procedure in 49% NMR yield determined using durene as an internal standard as an average of 3 independent trials (51%, 49% and 46% yield each) and 24% isolated yield (55:45 diastereomeric mixture at C2, > 95:5 *exo:endo*). See S23-24) as a white solid. Analytical data for **1**:

**<sup>1</sup>H-NMR** (300 MHz; C<sub>6</sub>D<sub>6</sub>): δ 4.42 (d, J=4.5 Hz, 1H), 2.50 (m, 1H), 2.15 (s, 1H), 2.09 (s, 1H), 2.01 (s, 1H), 1.77 (d, J = 4.7 Hz, 1H), 1.72-1.63 (m, 2H), 1.51-1.34 (m, 3H), 1.22 (d, J = 6.0 Hz, 2H), 1.15 (s, 2H), 1.04 (d, J=6.0 Hz, 2H), 0.97 (d, J=6.0 Hz, 1H), 0.91 (d, J=6.0 Hz, 2H), 0.81 (d, J=6.0 Hz, 1H), 0.74 (m, 1H), 0.62 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; C<sub>6</sub>D<sub>6</sub>): δ 86.16, 86.09, 81.2, 51.8, 51.3, 50.4, 43.1, 38.5, 35.46, 35.30, 33.7, 33.4, 28.0, 27.4, 24.61, 24.48, 23.93, 23.81, 23.4, 22.33, 22.19, 19.2.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>13</sub>H<sub>22</sub>O+H<sup>+</sup>]<sup>+</sup> = 195.1744, Found = 195.1744.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.5.



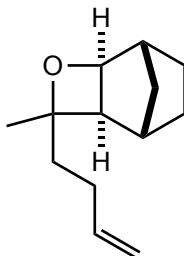
**2** was synthesized via general COPC procedure in 51% NMR yield determined using durene as an internal standard and 21% isolated yield (>95:5 *exo:endo* as determined by a series of multidimensional NMR experiments. See S25-27) as a white solid. Analytical data for **2**:

**<sup>1</sup>H-NMR** (300 MHz; C<sub>6</sub>D<sub>6</sub>): δ 4.42 (d, J=2.4 Hz, 1H), 2.47 (d, J=5.7 Hz, 1H), 2.16 (s, 1H), 1.97 (s, 1H), 1.66 (d, J= 3.6 Hz, 1H), 1.36 (m, 4H), 1.21 (d, J=4.0 Hz, 2H), 1.13 (m, 4H), 0.67 (m, 2H).

**<sup>13</sup>C-NMR** (126 MHz; C<sub>6</sub>D<sub>6</sub>): δ 84.1, 80.9, 50.4, 38.8, 35.8, 33.6, 31.2, 28.3, 22.6, 22.2.

**HRMS** (ESI-TOFMS) Calc. for [C<sub>10</sub>H<sub>16</sub>O+H<sup>+</sup>]<sup>+</sup> = 153.1275 Found = 153.1275.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.5.



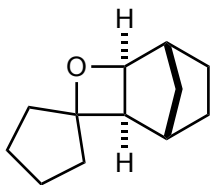
**3** was synthesized via general COPC procedure in 45% NMR yield determined using durene as an internal standard and 25% isolated yield (55:45 diastereomeric mixture at C2, > 95:5 *exo:endo* as determined by analogy to **1** and **2** above) as a white solid. Analytical data for **3**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 5.84 (m, 1H), 5.07-4.92 (m, 2H), 4.53 (d, J=4.2 Hz, 1 H), 2.33 (s, 1H), 2.23 (s, 2H), 2.17-2.07 (m, 1H), 2.01 (dd, J=4.8 Hz, J=11.6 Hz, 1H), 1.94-1.60 (m, 3H), 1.43 (m, 3H), 1.28 (m, 1H), 1.20 (s, 2H), 0.97 (m, 1H), 0.83 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 138.92, 138.74, 114.50, 114.43, 86.96, 86.88, 82.2, 81.7, 50.4, 49.4, 42.9, 38.56, 38.45, 35.56, 35.36, 34.1, 33.7, 28.21, 28.09, 28.01, 27.96, 27.7, 22.5, 22.3, 19.6.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>13</sub>H<sub>20</sub>O+H<sup>+</sup>]<sup>+</sup> = 193.1586, Found = 193.1587.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.6.



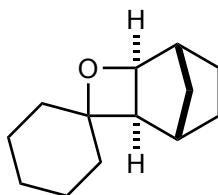
**4** was synthesized via general COPC procedure in 66% NMR yield determined using durene as an internal standard and 33% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **4**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.51 (d, J=4.5 Hz, 1H), 2.21 (m, 4H), 2.08 (m, 1H), 1.88-1.22 (m, 10H), 0.96 (m, 1H), 0.84 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 95.45, 82.06, 49.89, 42.43, 39.30, 35.95, 33.22, 32.94, 27.60, 23.86, 23.07, 22.46.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>12</sub>H<sub>18</sub>O+H<sup>+</sup>]<sup>+</sup> = 179.1430, Found = 179.1429.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.6.



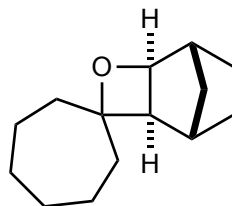
**5** was synthesized via general COPC procedure in 81% NMR yield determined using durene as an internal standard and 33% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **5**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.53 (d, J=4.5 Hz, 1H), 2.33 (d, J=9.9 Hz, 1H), 2.19 (m, 3H), 1.96 (m, 1H), 1.83 (m, 2H), 1.67-0.81 (m, 13).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 86.99, 82.01, 48.85, 39.85, 38.60, 34.90, 33.78, 31.83, 28.23, 25.57, 23.14, 22.88, 22.34.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>13</sub>H<sub>20</sub>O+H<sup>+</sup>]<sup>+</sup> = 193.1586, Found = 193.1587.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.6.



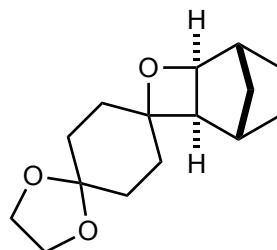
**6** was synthesized via general COPC procedure in 67% NMR yield determined using durene as an internal standard and 32% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **6**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.47 (d, J=4.8 Hz, 1H), 2.21-1.79 (m, 7 H), 1.47-0.97 (m, 15H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 90.1, 81.7, 51.0, 42.4, 38.6, 35.6, 34.2, 33.7, 29.3, 28.8, 28.1, 22.5, 22.04, 21.94.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>14</sub>H<sub>22</sub>O+H<sup>+</sup>]<sup>+</sup> = 207.1743, Found = 207.1743.

**R<sub>f</sub>** (5% Acetone in Pentane): 0.6.



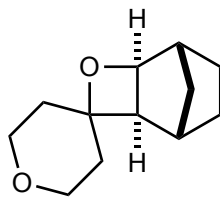
**7** was synthesized via general COPC procedure in 96% NMR yield determined using durene as an internal standard and 76% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **7**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.57 (d, J=4.2 Hz, 1H), 3.92 (s, 4H), 2.33 (d, J=9.9 Hz, 1H), 2.25 (m, 2H), 2.02 (m, 2H), 1.92-1.72 (m, 5H), 1.71-1.56 (m, 2H), 1.53-1.43 (m, 4H), 1.32-1.24 (m, 3H), 1.11 (d, J=12.3 Hz, 1H), 0.98 (m, 1H), 0.87-0.84 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 108.3, 85.7, 82.3, 64.53, 64.44, 48.5, 38.6, 36.7, 35.2, 33.8, 31.01, 30.94, 28.6, 28.3, 22.4.

**HRMS** (ESI-TOFMS) Calc. for [C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>+H<sup>+</sup>]<sup>+</sup> = 251.1642 Found = 251.1642.

**R<sub>f</sub>** (5 % Acetone in Pentane): 0.75.



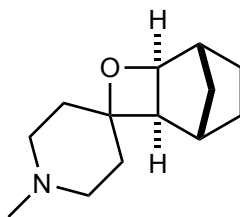
**8** was synthesized via general COPC procedure, irradiating for 24 h, in 75% NMR yield determined using durene as an internal standard and 22% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **8**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.63 (d, J=4.8 Hz, 1H), 3.85 (m, 1H), 3.72 (m, 1H), 3.61 (m, 1H), 3.49 (m, 1H), 2.32 (m, 3H), 2.08 (d, J=4.8 Hz, 1H), 1.89 (m, 4H), 1.70 (m, 1H), 1.51-1.48 (m, 3H), 1.35 (m, 2H), 1.06-0.99 (m, 1H), 0.89 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 83.8, 82.4, 64.52, 64.48, 49.0, 40.0, 38.7, 34.8, 33.7, 32.7, 28.1, 22.3.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>+H<sup>+</sup>]<sup>+</sup> = 195.1380 Found = 195.1379.

**R<sub>f</sub>** (5 % Acetone in Pentane): 0.5.



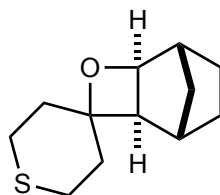
**9** was synthesized via general COPC procedure, irradiating for 24 h, in 69% NMR yield determined using durene as an internal standard and 14% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **9**:

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.42 (s, 1H – apparent singlet due to broadening), 2.52-2.36 (m, 4H), 2.19-1.68 (m, 8H), 1.21-1.08 (m, 4H), 0.75-0.70 (m, 1H), 0.61-0.57 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 83.4, 81.3, 54.9, 52.1, 48.4, 45.9, 39.1, 38.6, 34.6, 33.6, 31.5, 28.0, 22.1.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>13</sub>H<sub>21</sub>NO]<sup>+</sup> = 217.1199 Found = 217.1197.

**R<sub>f</sub>** (5 % Acetone in Pentane): 0.25.



**10** was synthesized via general COPC procedure, irradiating for 24 h, in 89% NMR yield determined using durene as an internal standard and 60% isolated yield (> 95:5 *exo:endo* as determined by analogy to **2**) as a white solid. Analytical data for **10**:

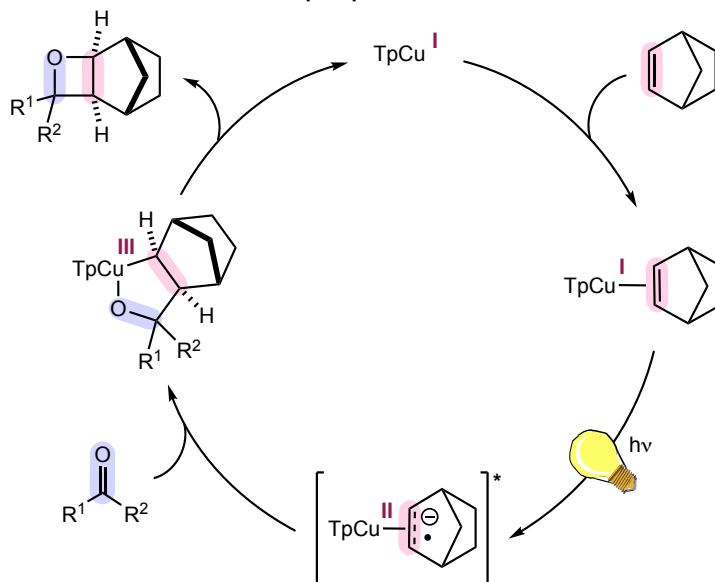
**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 4.55 (d, J=3.0 Hz, 1H), 2.94-2.39 (m, 5H), 2.26 (s, 3H), 2.14 (m, 1H), 2.05 (m, 2H), 1.96 (m, 2H), 1.45 (m, 2H), 1.30 (d, J=9.9 Hz, 1H), 1.13 (m, 1H) 0.97-0.94 (m, 1H), 0.86-0.82 (m, 1H).

**<sup>13</sup>C-NMR** (126 MHz; CDCl<sub>3</sub>): δ 85.1, 82.5, 49.2, 40.3, 38.5, 34.7, 34.1, 33.0, 28.2, 25.3, 25.0, 22.0.

**HRMS** (APCI-TOFMS) Calc. for [C<sub>12</sub>H<sub>18</sub>OS+H<sup>+</sup>]<sup>+</sup> = 211.1151 Found = 211.1151.

**R<sub>f</sub>** (5 % Acetone in Pentane): 0.4.

**Scheme S3.** Additional mechanistic proposal



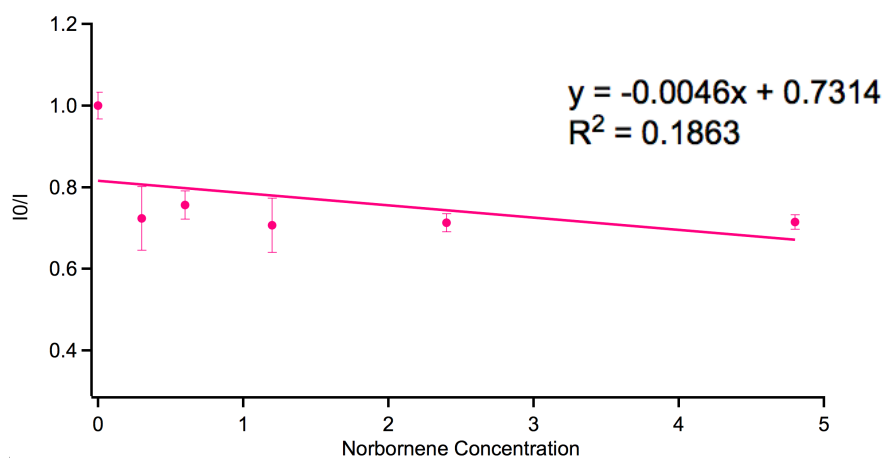
While our or existing data and data from the literature does not entirely exclude nor solely support the formation of a Cu(III) oxametallacycle as an on-cycle intermediate, it is plausible that it may be the penultimate species prior to oxetane formation.

### **E. Stern-Volmer Quenching Studies.**

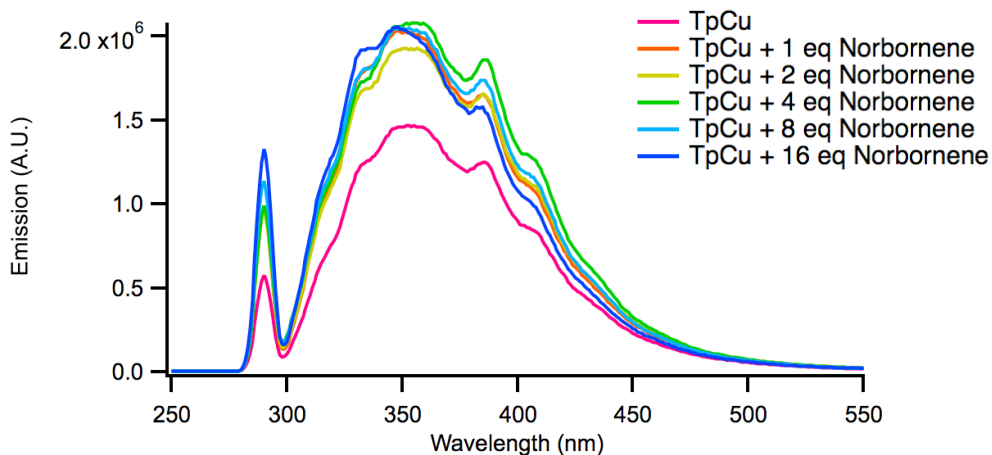
Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of  $3.0 \times 10^{-4}$  M **TpCu** or **TpCu(Norb)** as indicated in diethyl ether at room temperature under an inert atmosphere. The solutions were irradiated at 294 nm and luminescence was measured at 350 nm. Each sample was prepared three times, the luminescence was acquired and averaged. The average of the results was used for the graphical representation and determination of  $K_{SV}$ . The data show that norbornene and methyl isobutyl ketone are shown to be unable to quench the excited state of **TpCu** or **TpCu(Norb)**. For all tabular and graphical data, see **Tables S2- S3** and **Figures S2-S7** below.

**Table S2.** Luminescence quenching data with solution of **TpCu(Norb)** and norbornene. See **Figures S2-S3**.

Sample	1	2	3	4	5	6
Molarity (mM)	0	3.00E-04	6.00E-04	1.20E-03	2.40E-03	4.80E-03
Trial 1	1425270	2151096	1913457	2038849	2014523	1995782
Trial 2	1520302	1931018	1987233	2001444	2038714	2043452
Trial 3	1462478	1986729	1891140	2186087	2078013	2038556
Average	1469350	2023281	1930610	2075460	2043750	2025930



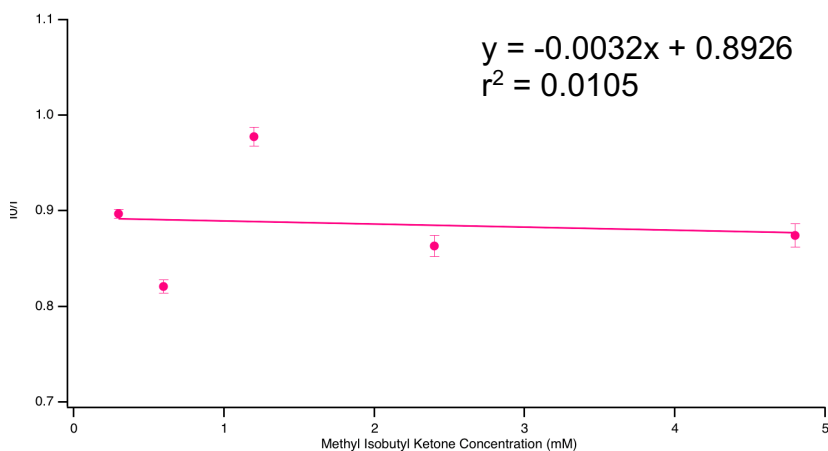
**Figure S2.** Stern-Volmer plot of **TpCu(Norb)** quenching with varying concentration of norbornene.



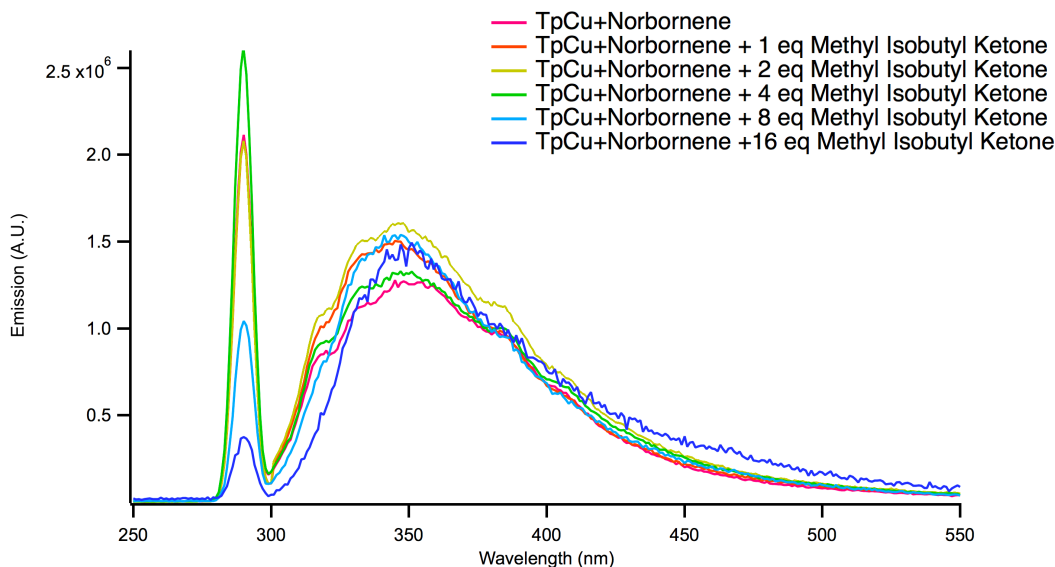
**Figure S3.** Emission plot of **TpCu(Norb)** with varying concentration of methyl isobutyl ketone.

**Table S3.** Luminescence quenching data with solution of **TpCu(Norb)** and methyl isobutyl ketone. See **Figures S4-S5**.

Sample	1	2	3	4	5	6
<b>Molarity (mM)</b>	0	3.00E-04	6.00E-04	1.20E-03	2.40E-03	4.80E-03
<b>Trial 1</b>	1276513	1406580	1537320	1290420	1479531	1432788
<b>Trial 2</b>	1258921	1417320	1552500	1287420	1461456	1448654
<b>Trial 3</b>	1261126	1409460	1536480	1305420	1455855	1461958
<b>Average</b>	1265520	1411120	1542100	1294420	1465614	1447800

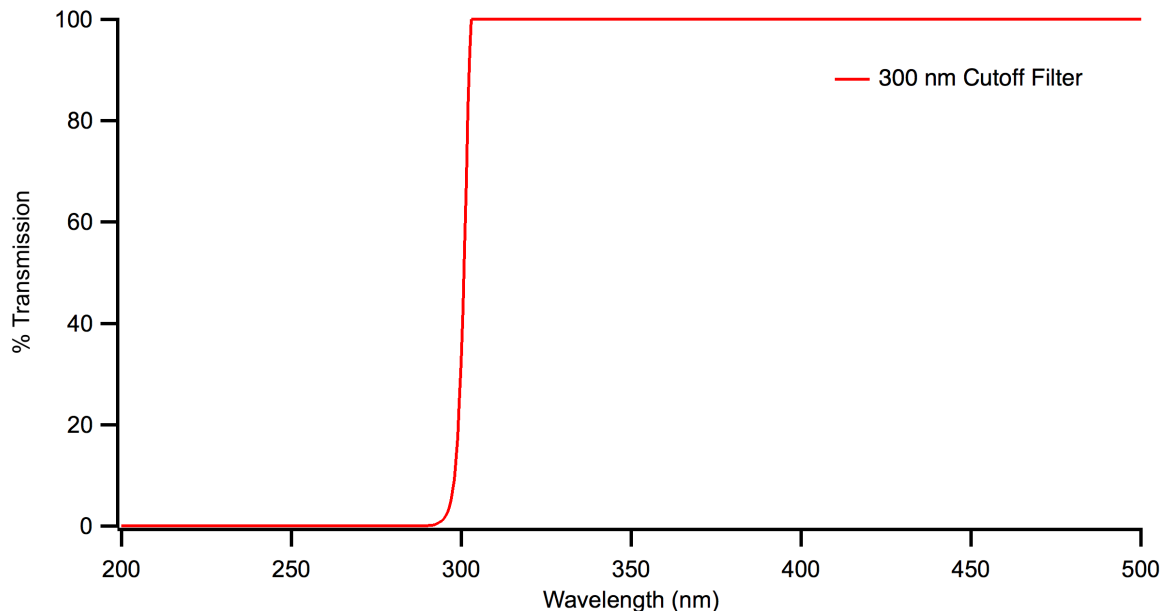


**Figure S4.** Stern-Volmer plot of **TpCu(Norb)** quenching with varying concentration of methyl-isobutyl ketone.

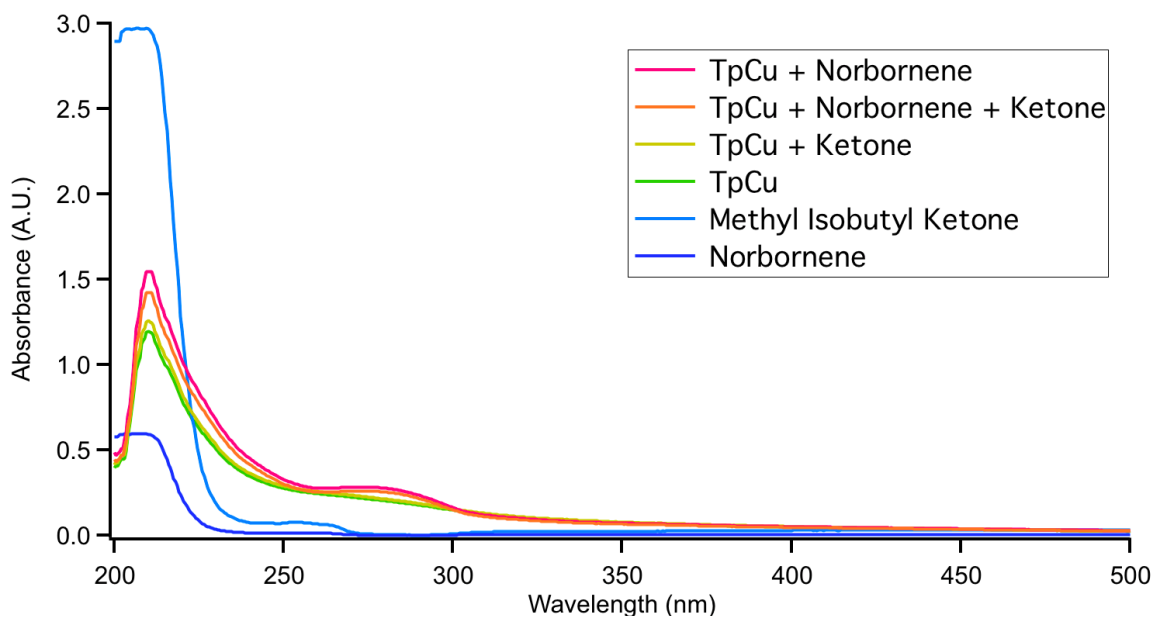


**Figure S5.** Emission plot of **TpCu(Norb)** with varying concentration of methyl-isobutyl ketone.

## F. Electronic Absorption Spectra.



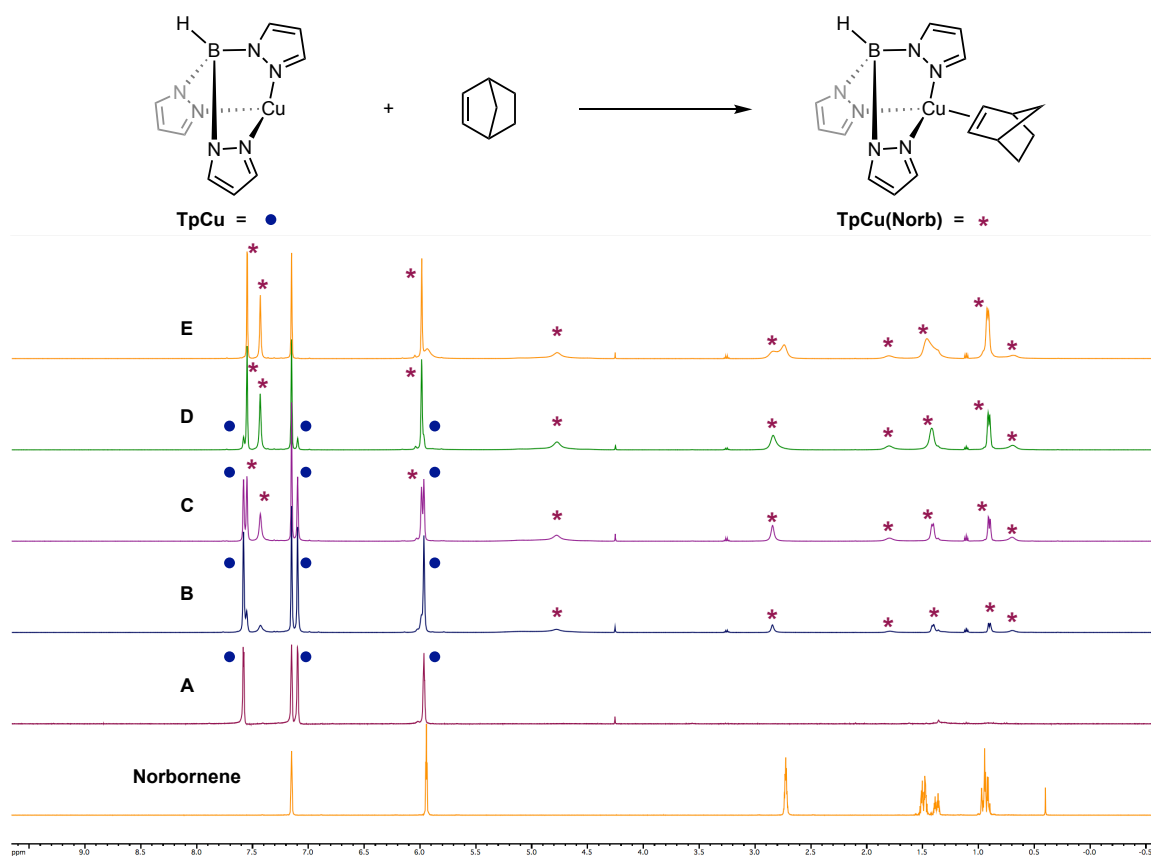
**Figure S6.** Transmission spectrum of Asahi Spectra long pass 300 nm cut-on filter.



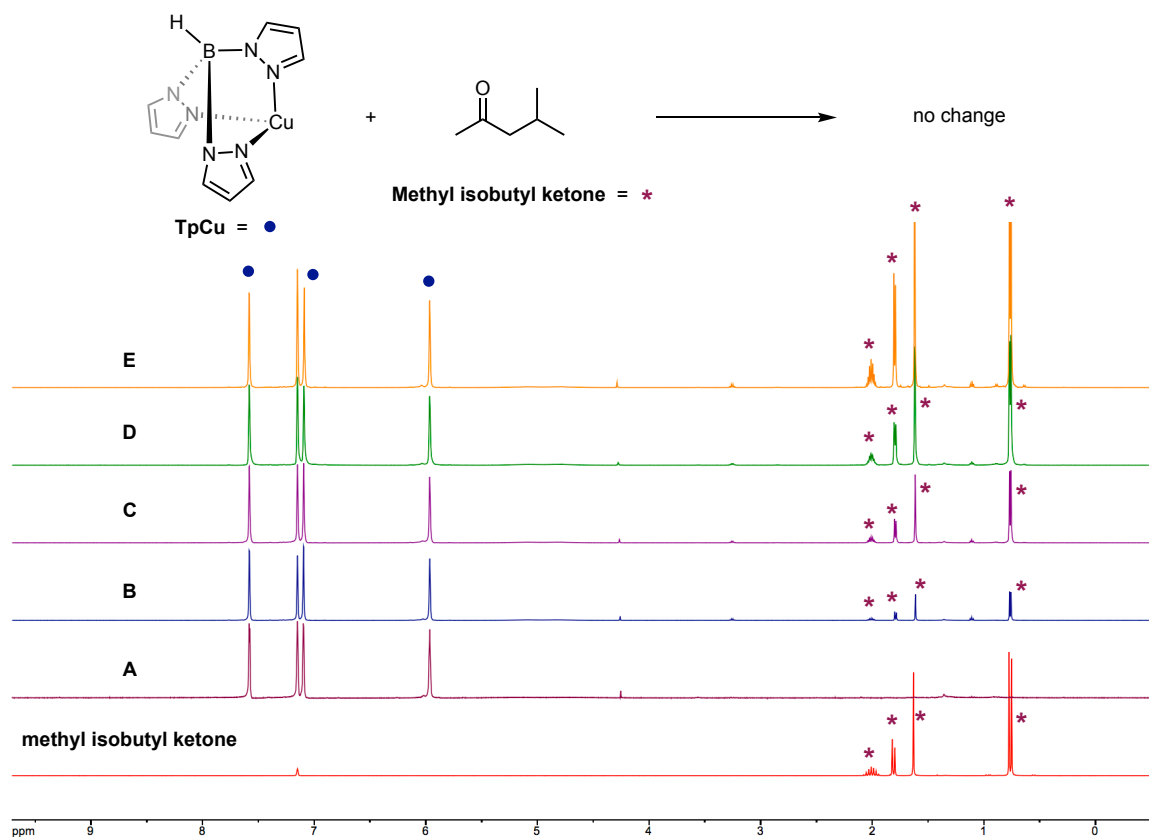
**Figure S7.** Electronic absorption spectra. All samples were collected as equimolar mixtures as indicated at 0.5 mM in diethyl ether.

## G. NMR Studies.

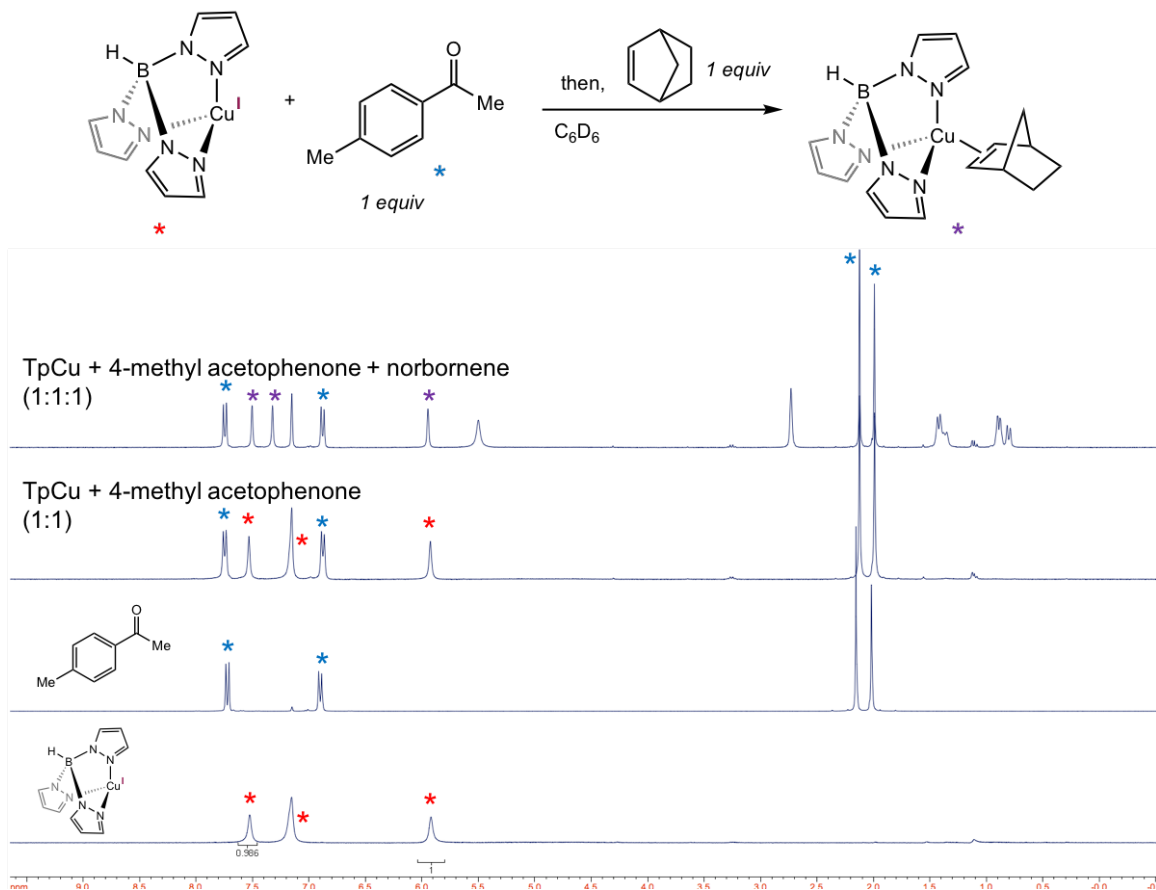
NMR coordination experiments were conducted with freshly prepared solutions of 0.11M TpCu in dry, degassed C<sub>6</sub>D<sub>6</sub> at room temperature under an inert atmosphere. From a stock solution, methyl isobutyl ketone or norbornene were added into the NMR tube. The sample was sealed with electrical tape, and spectra obtained. Samples were brought back into the glove box and the process was repeated. For all graphical data see **Figures S10-S11**.



**Figure S8.** <sup>1</sup>H-NMR spectrum of TpCu with varying equivalents of norbornene. *Spectrum A* = **TpCu** only (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum B* = 1 equiv **TpCu** + 0.25 equiv norbornene (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum C* = 1 equiv **TpCu** + 0.5 equiv norbornene (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum D* = 1 equiv **TpCu** + 1 equiv norbornene (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum E* = 1 equiv **TpCu** + 2 equiv norbornene (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**).



**Figure S9.** <sup>1</sup>H-NMR spectrum of TpCu with varying equivalents of methyl isobutyl ketone. *Spectrum A* = **TpCu** only (0.11M in C<sub>6</sub>D<sub>6</sub>). *Spectrum B* = 1 equiv **TpCu** + 0.25 equiv methyl isobutyl ketone (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum C* = 1 equiv **TpCu** + 0.5 equiv methyl isobutyl ketone (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum D* = 1 equiv **TpCu** + 1 equiv methyl isobutyl ketone (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**). *Spectrum E* = 1 equiv **TpCu** + 2 equiv methyl isobutyl ketone (0.11M in C<sub>6</sub>D<sub>6</sub> with respect to **TpCu**).



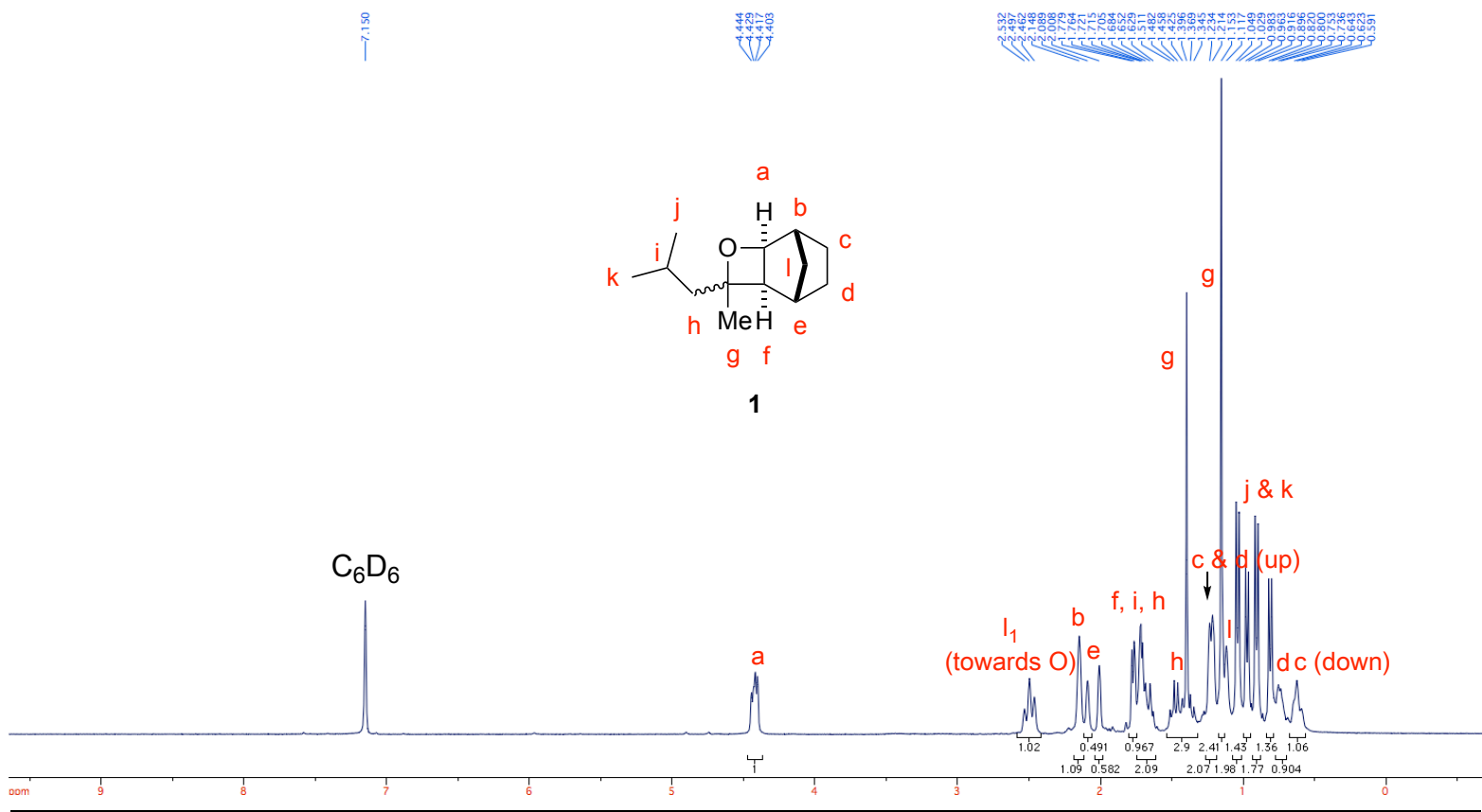
**Figure S10.** <sup>1</sup>H-NMR spectra mixing **TpCu** with 4-methyl acetophenone (1:1) at 0.11M in C<sub>6</sub>D<sub>6</sub> (with respect to each component).

## H. References.

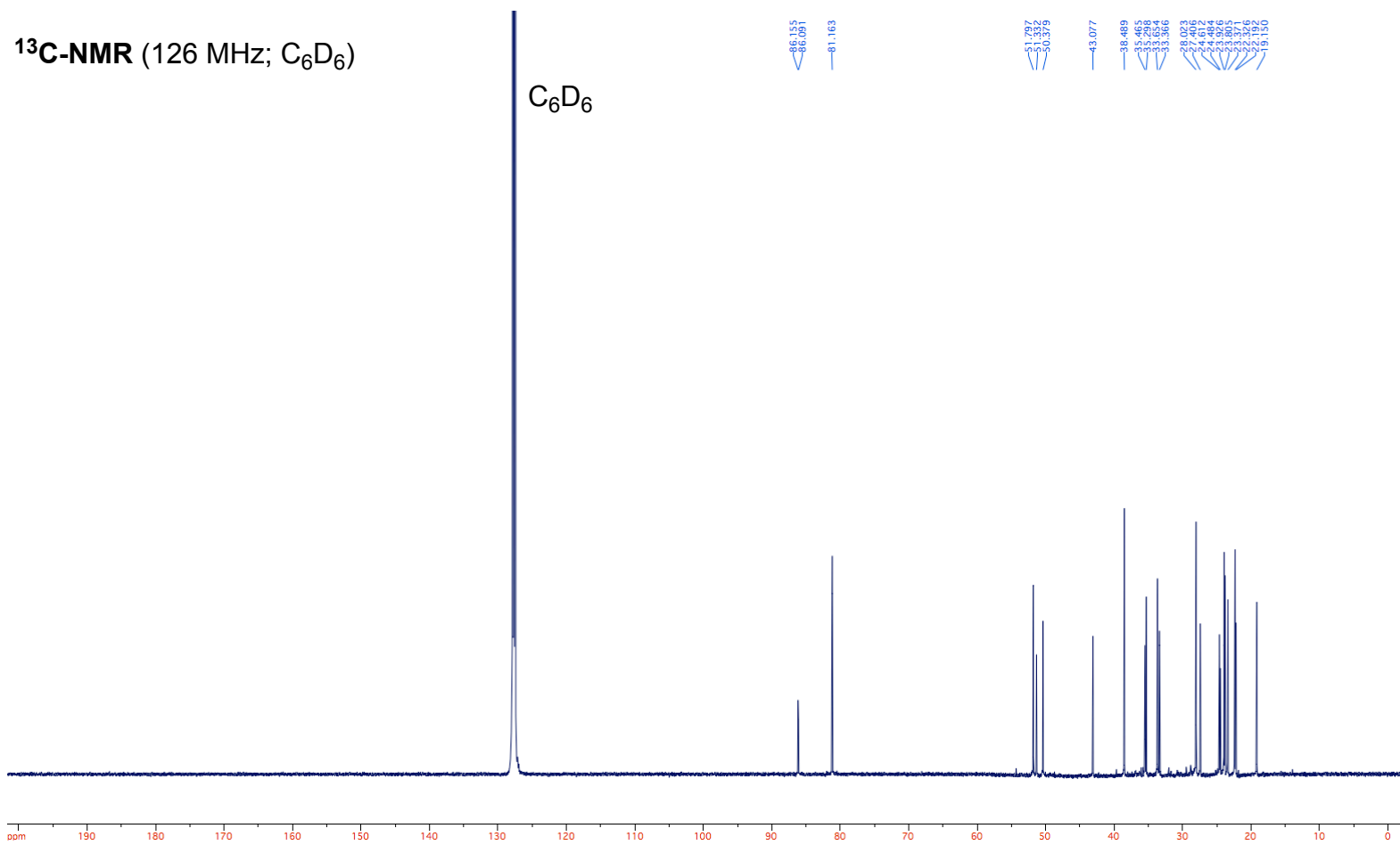
- 
- <sup>1</sup> Salvi, L.; Davis, N. R.; Ali, S. Z.; Buchwald, S. L. *Org. Lett.* **2012**, *14*, 170.
- <sup>2</sup> Salomon, R. G.; Kochi, J. K.; *J. Am. Chem. Soc.* **1972**, *95*, 1889.

## II. $^1\text{H}$ , $^{13}\text{C}$ , and 2-D NMR Spectra

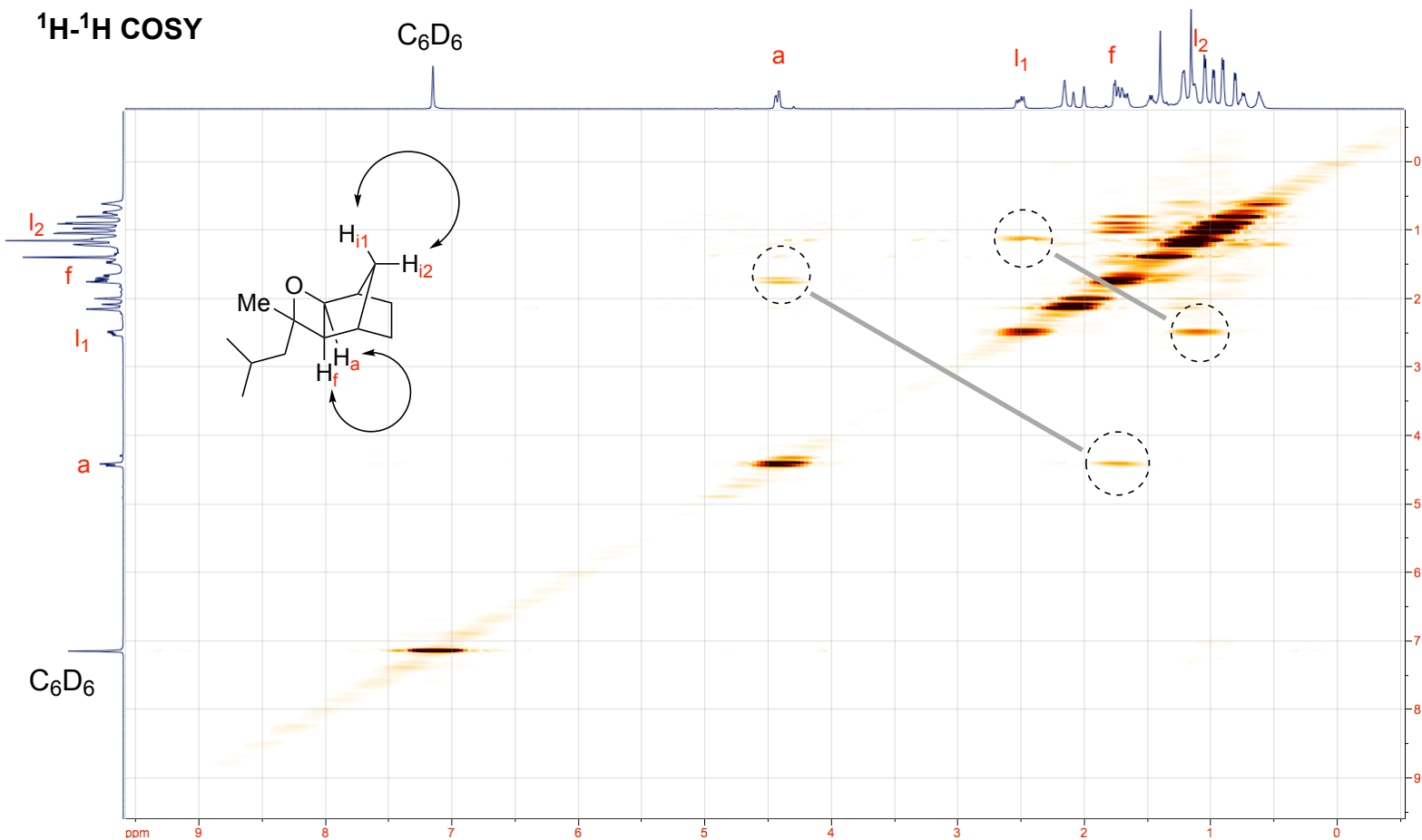
### $^1\text{H}$ -NMR (300 MHz; $\text{C}_6\text{D}_6$ )



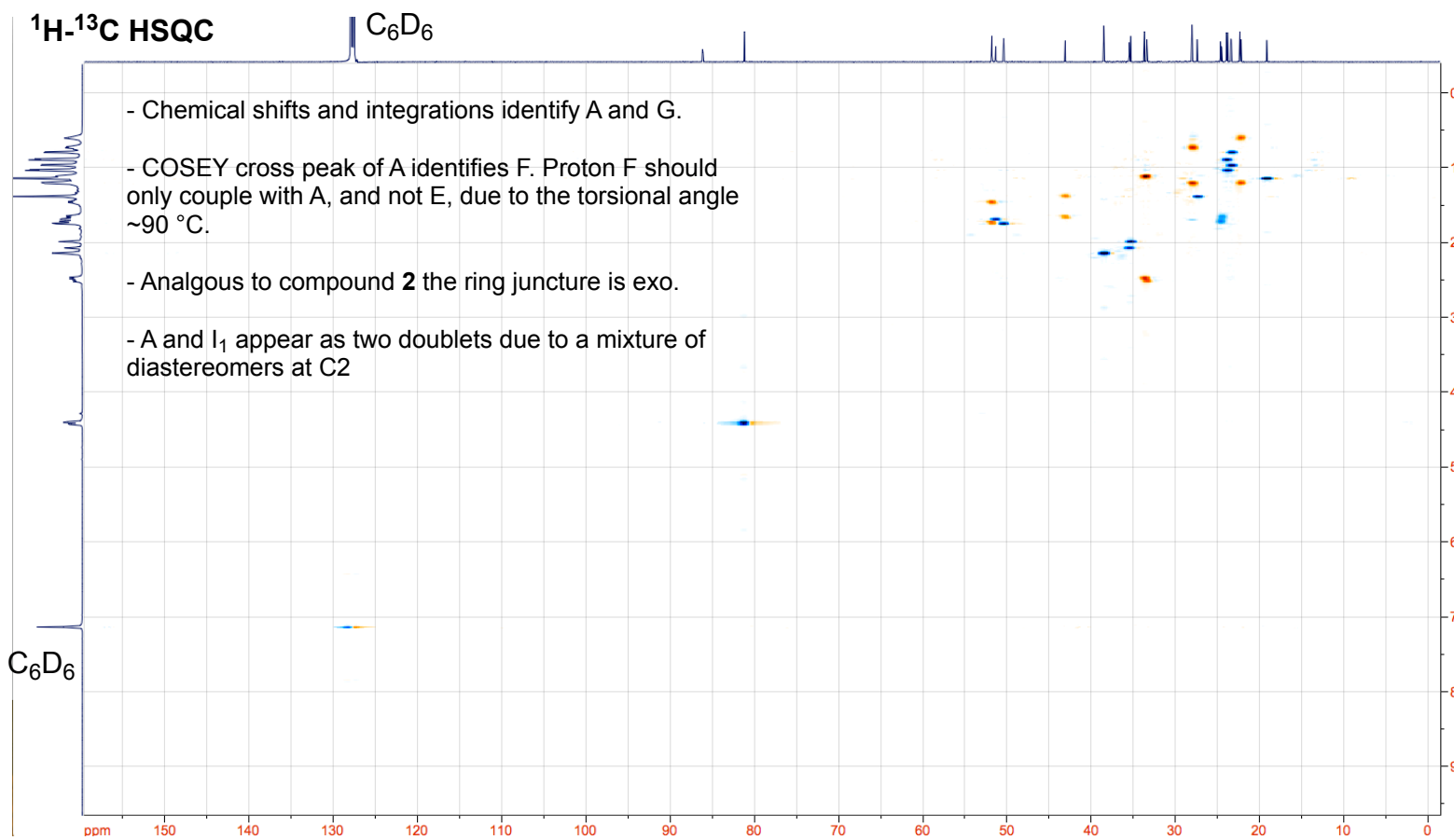
### $^{13}\text{C}$ -NMR (126 MHz; $\text{C}_6\text{D}_6$ )



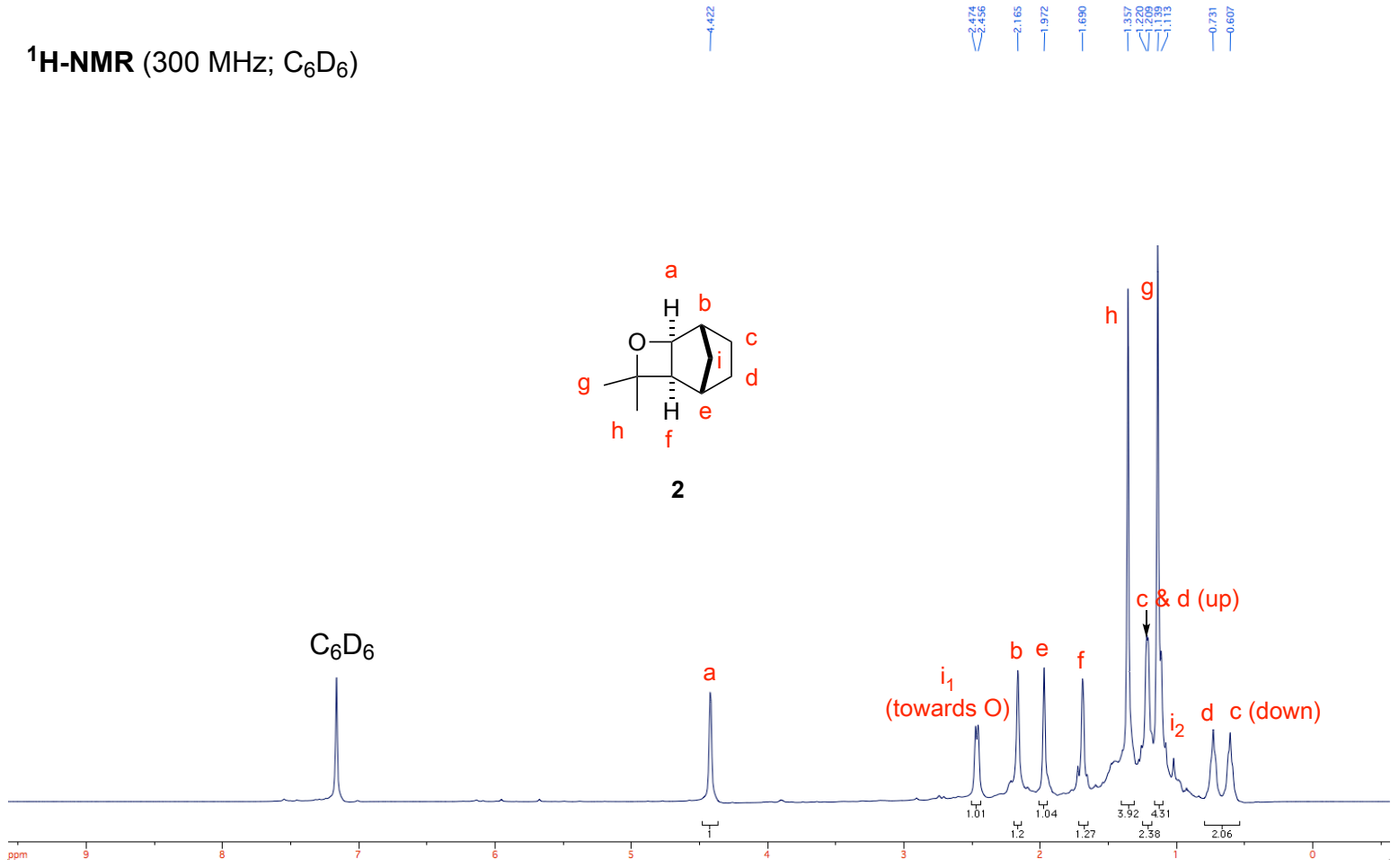
# $^1\text{H}$ - $^1\text{H}$ COSY



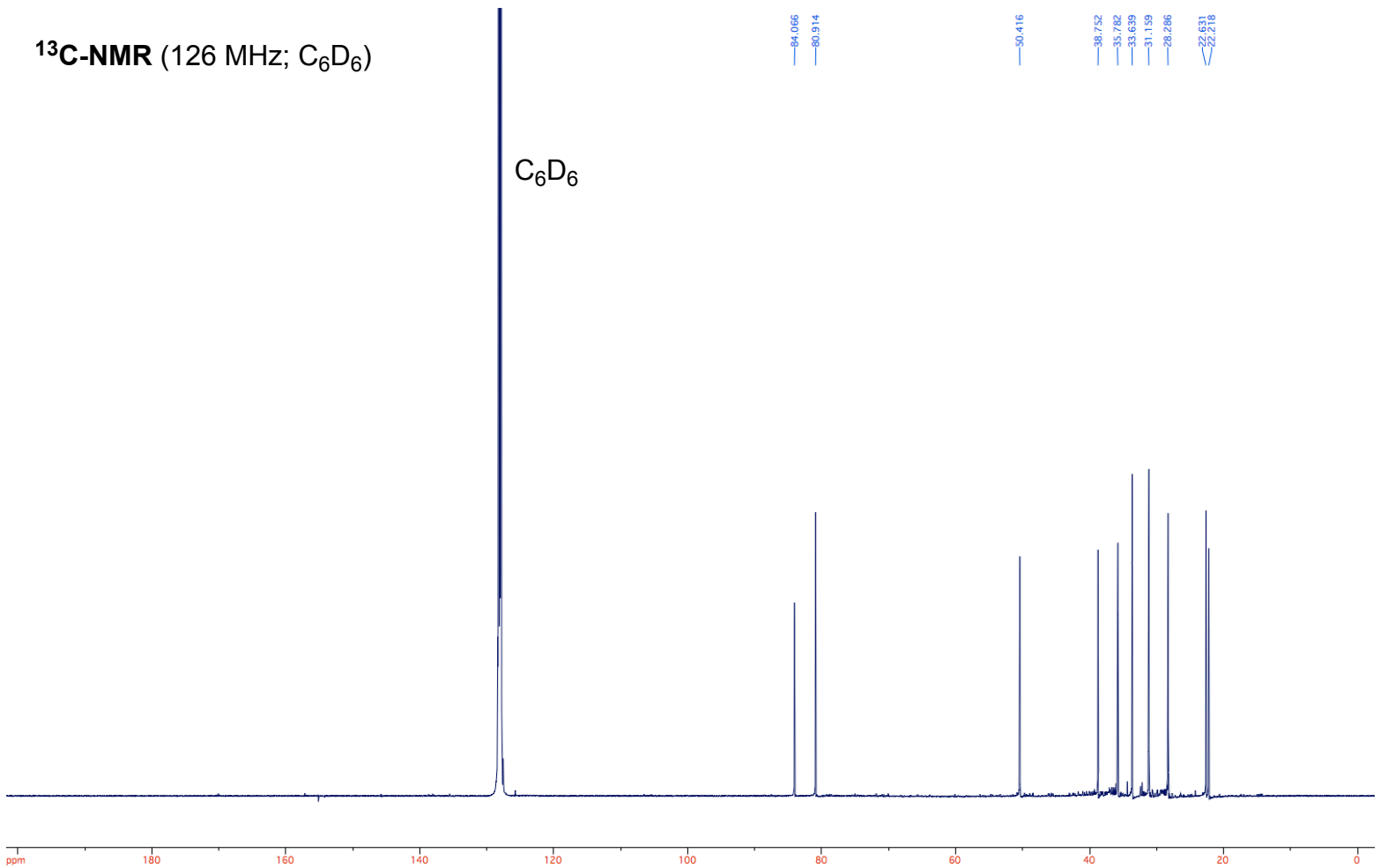
# $^1\text{H}$ - $^{13}\text{C}$ HSQC



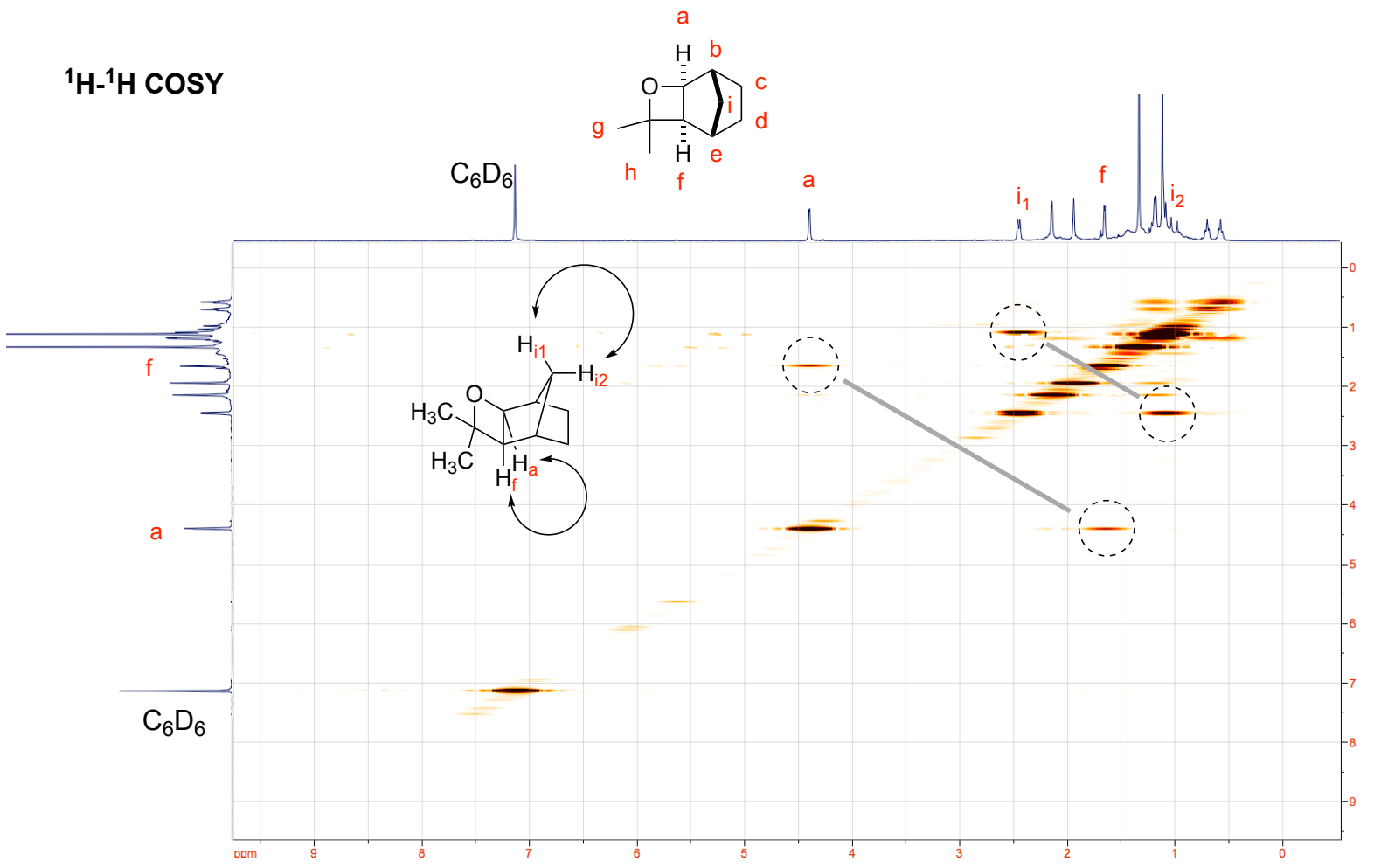
**$^1\text{H-NMR}$  (300 MHz;  $\text{C}_6\text{D}_6$ )**



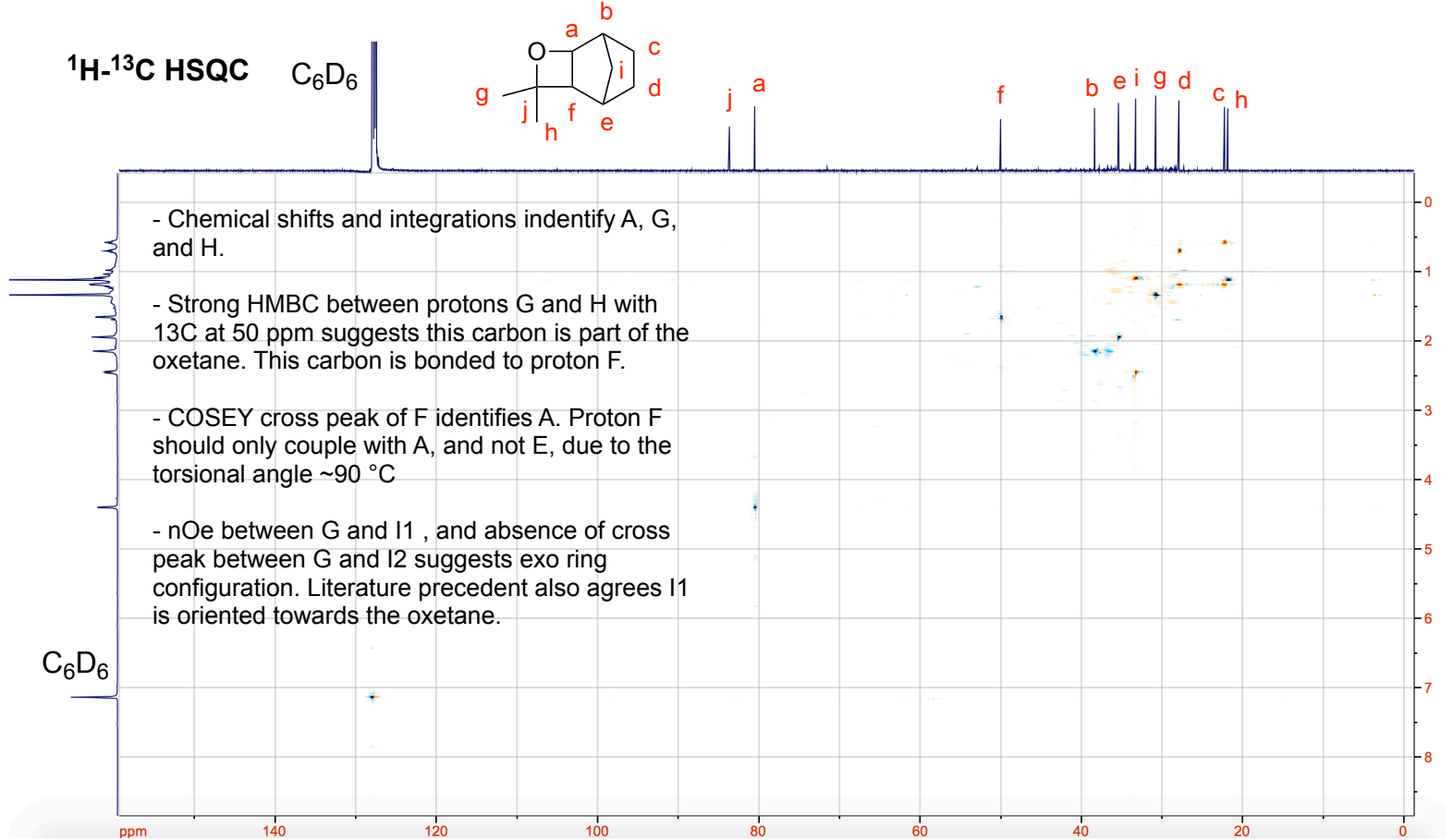
**$^{13}\text{C-NMR}$  (126 MHz;  $\text{C}_6\text{D}_6$ )**



# $^1\text{H}$ - $^1\text{H}$ COSY

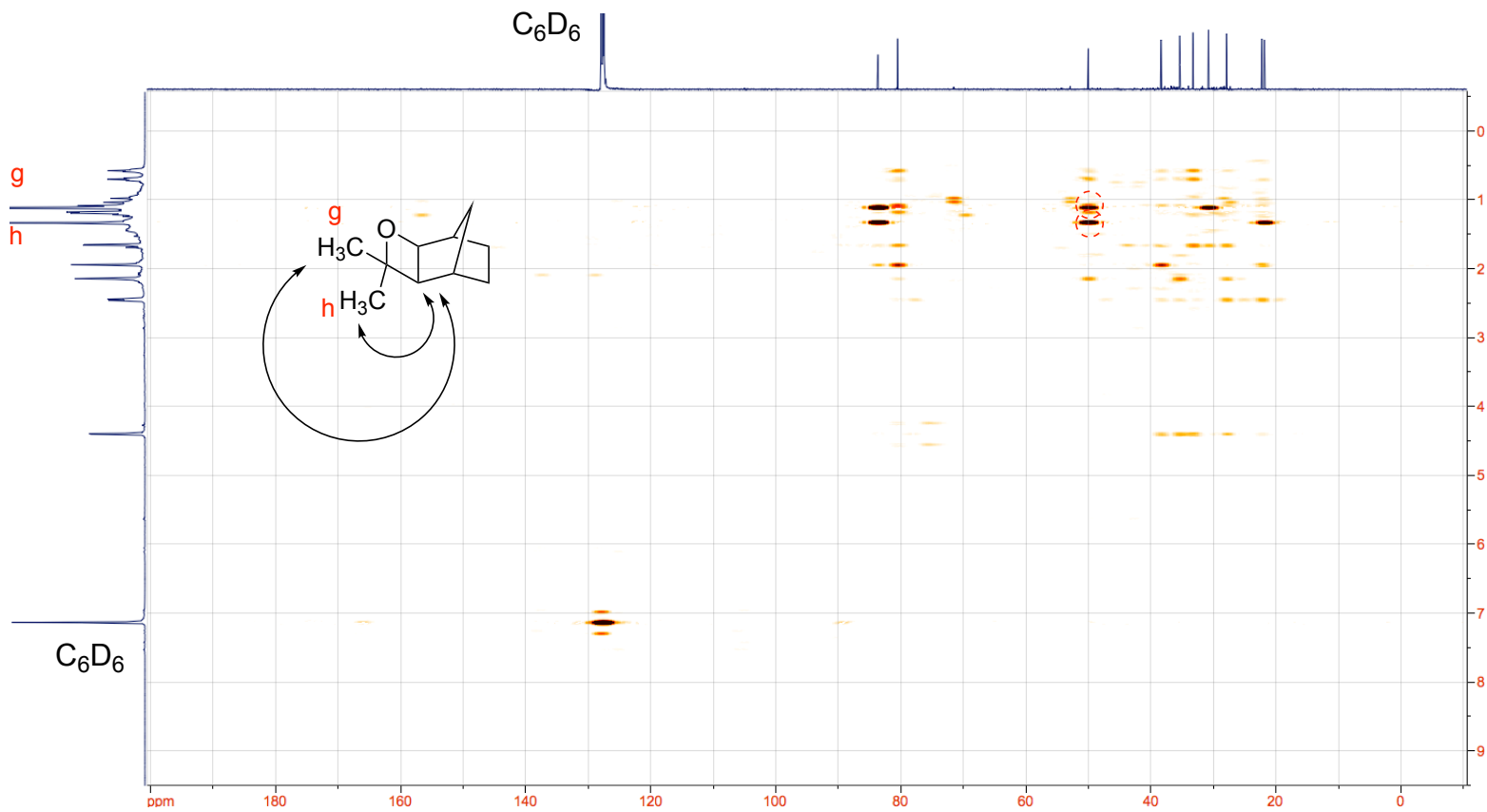


# $^1\text{H}$ - $^{13}\text{C}$ HSQC

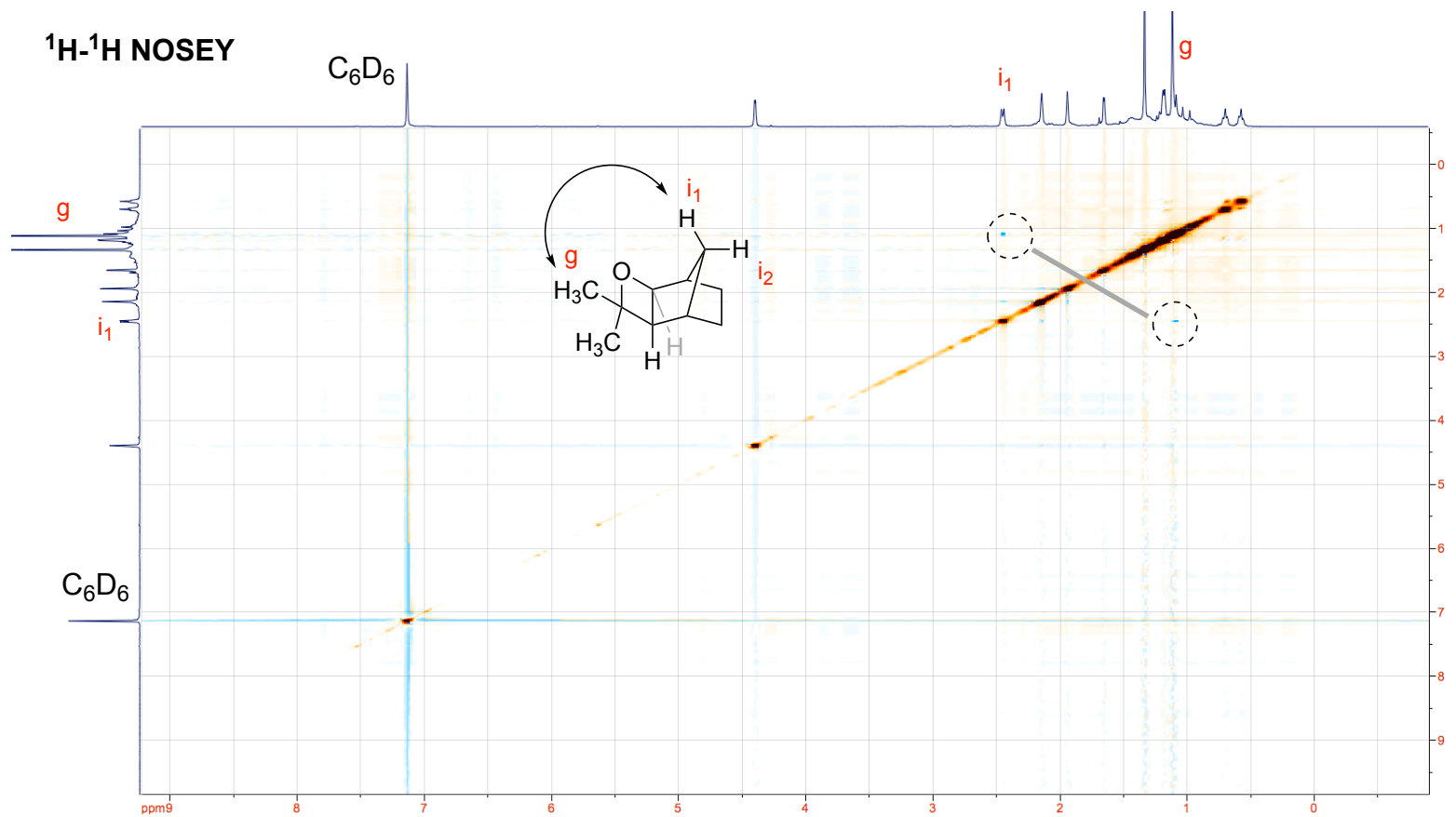


- Chemical shifts and integrations identify A, G, and H.
- Strong HMBC between protons G and H with  $^{13}\text{C}$  at 50 ppm suggests this carbon is part of the oxetane. This carbon is bonded to proton F.
- COSEY cross peak of F identifies A. Proton F should only couple with A, and not E, due to the torsional angle  $\sim 90^\circ$ .
- nOe between G and I1, and absence of cross peak between G and I2 suggests exo ring configuration. Literature precedent also agrees I1 is oriented towards the oxetane.

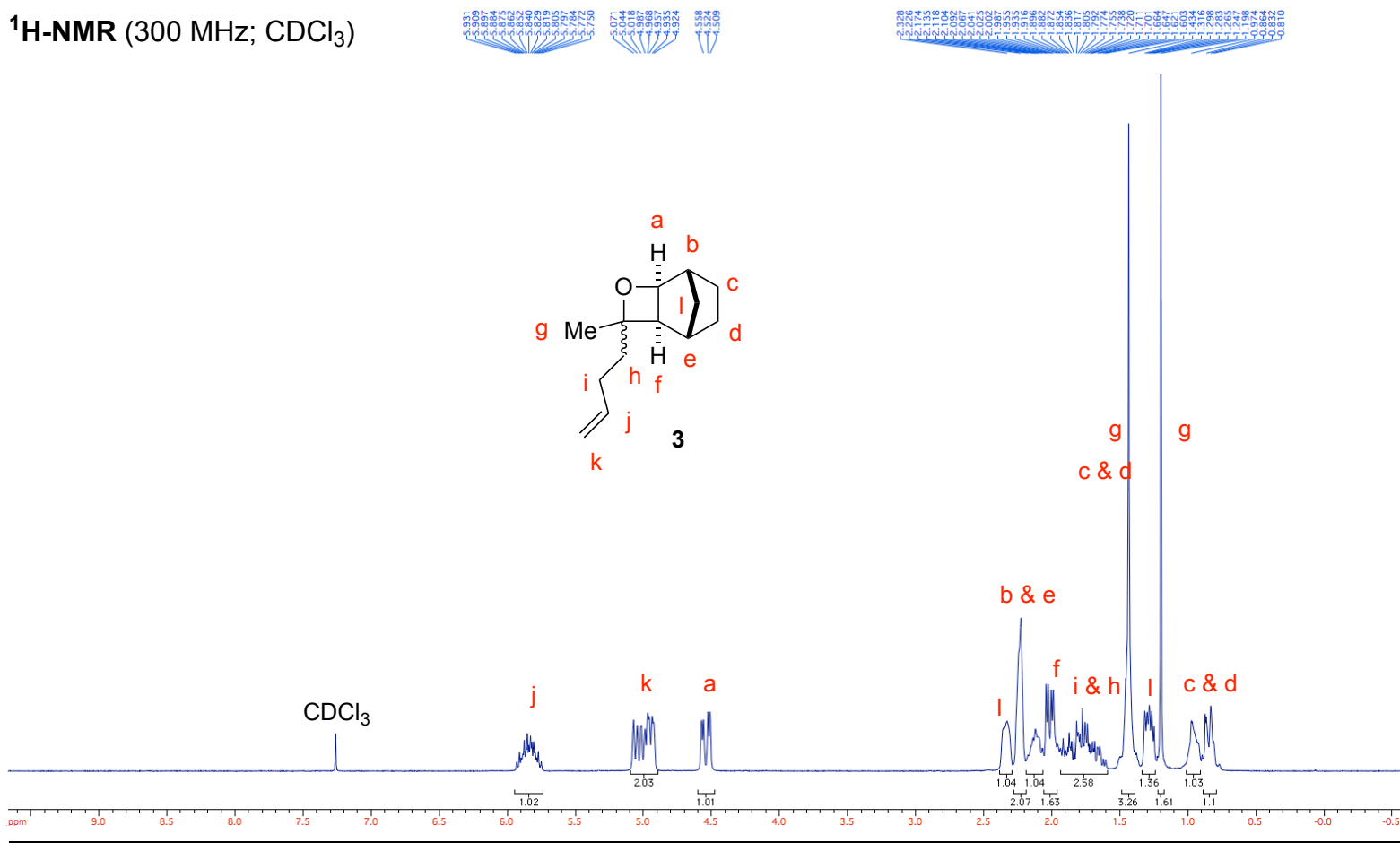
# $^1\text{H}$ - $^{13}\text{C}$ HMBC



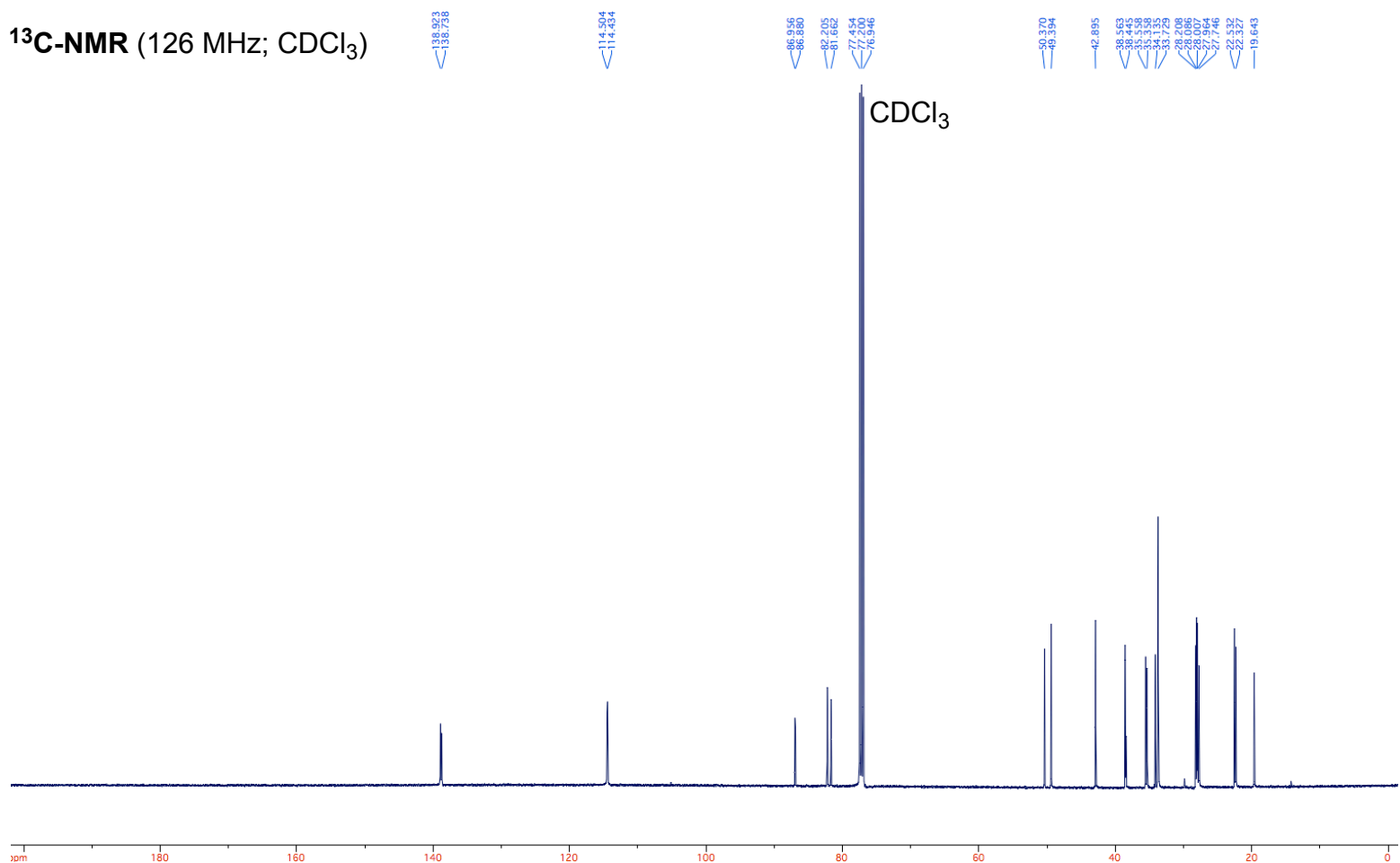
# $^1\text{H}$ - $^1\text{H}$ NOSEY



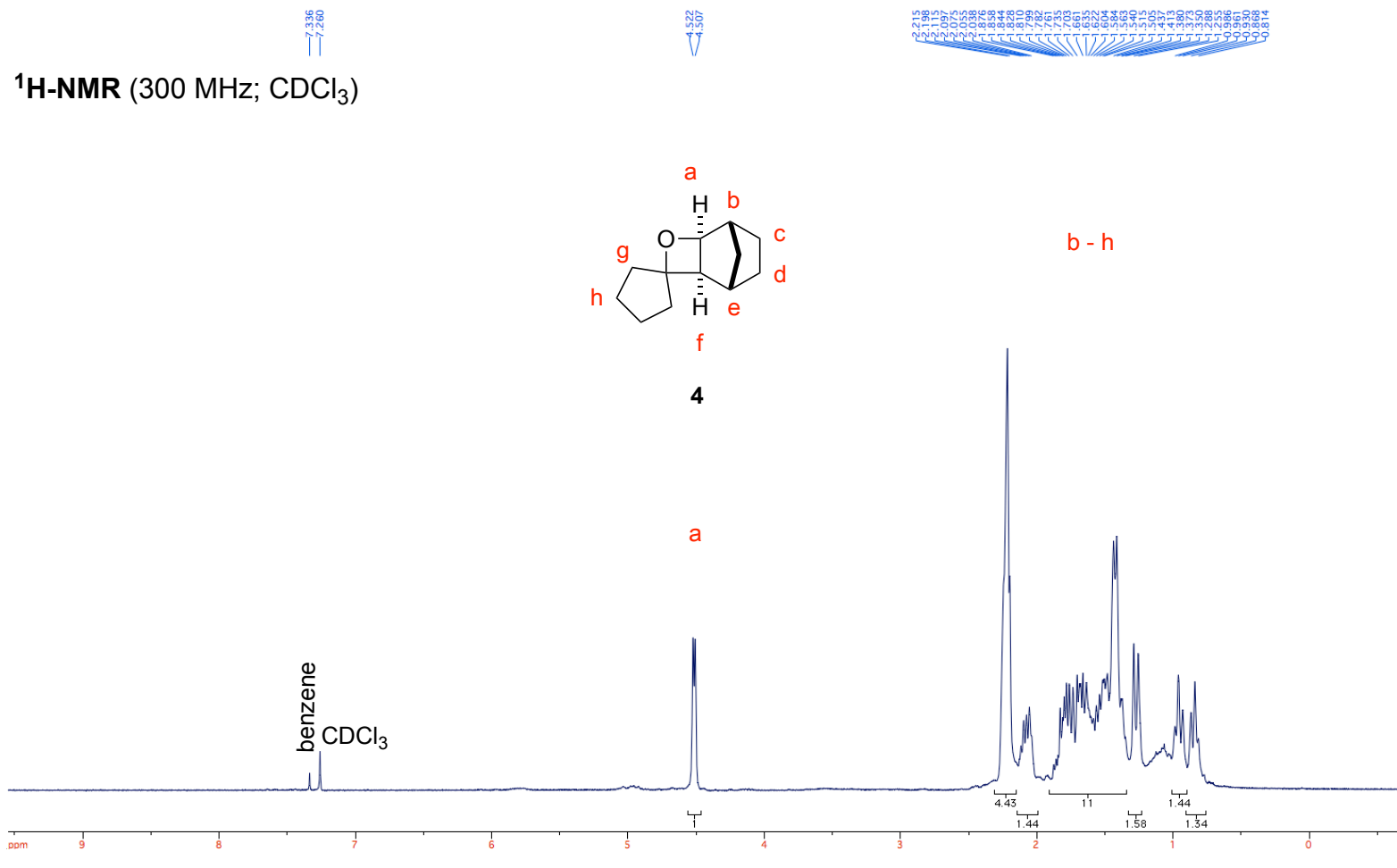
<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)



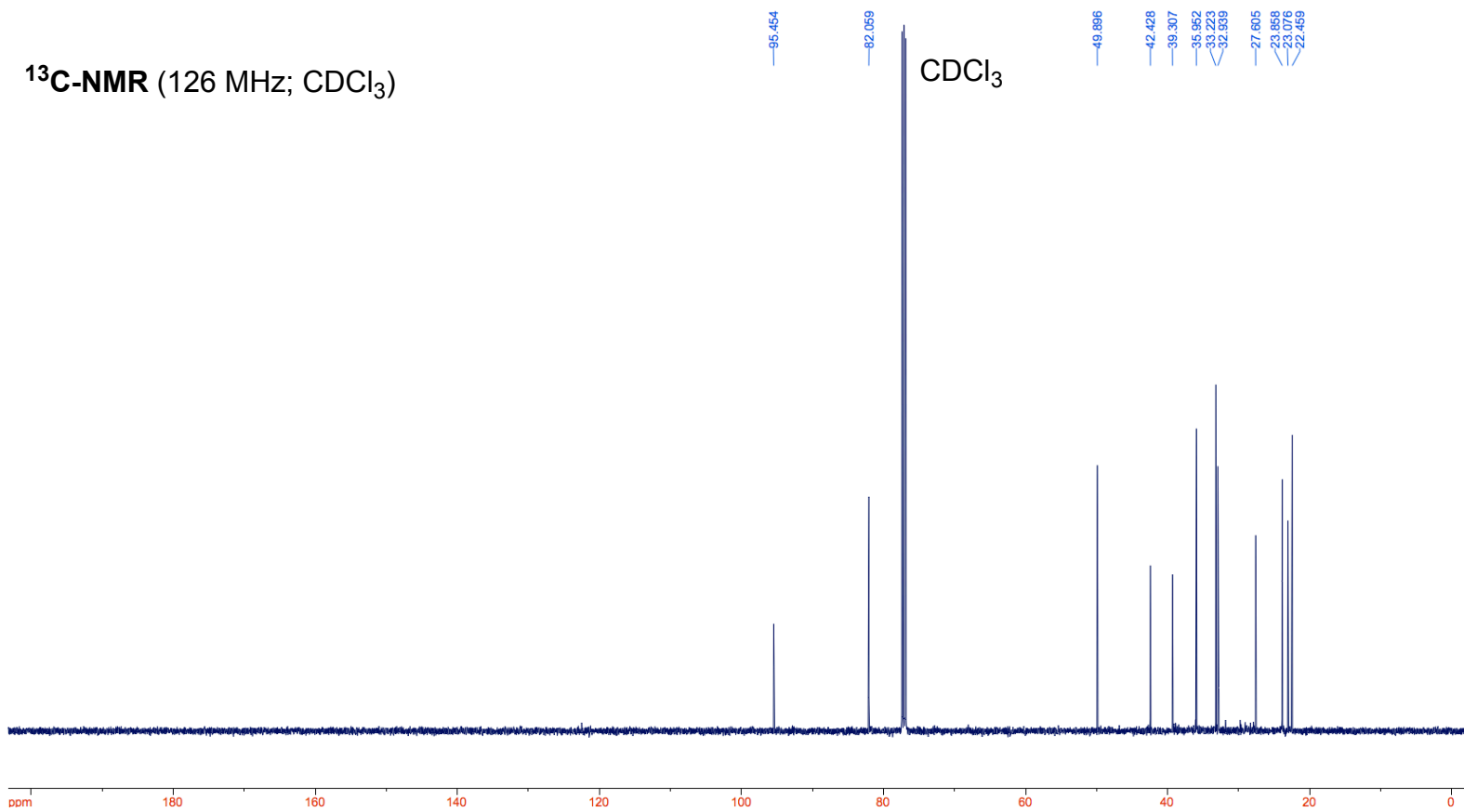
<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)



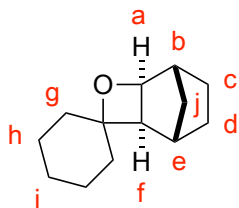
**<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)**



**<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)**



**<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)**



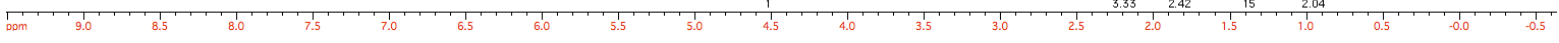
**5**

**a**

**a - i**

**j**

CDCl<sub>3</sub>



**<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)**

87.088

82.002

48.844

38.845

36.596

34.896

33.770

31.826

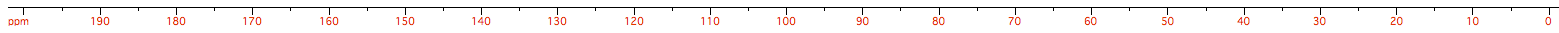
28.274

23.185

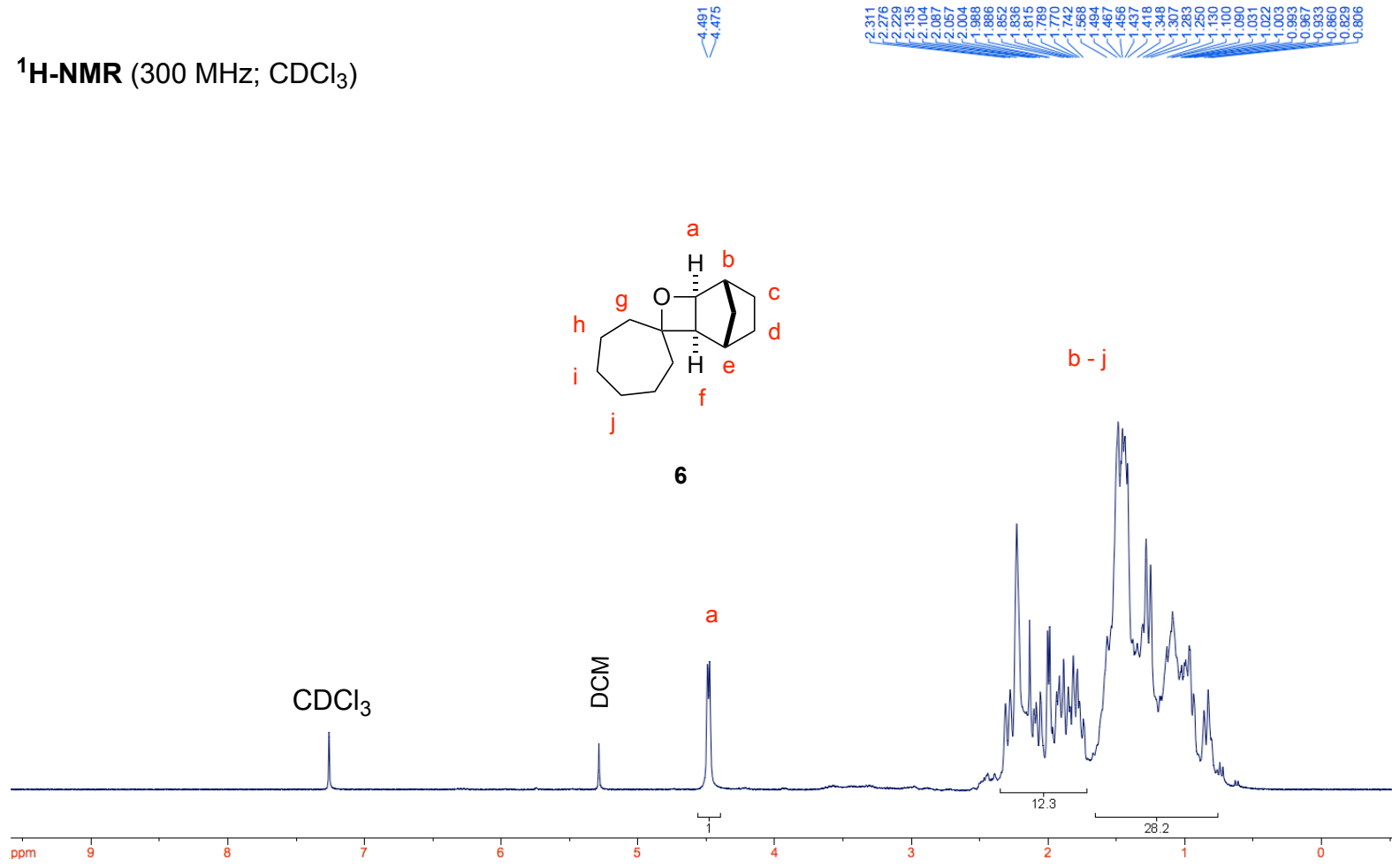
22.875

22.352

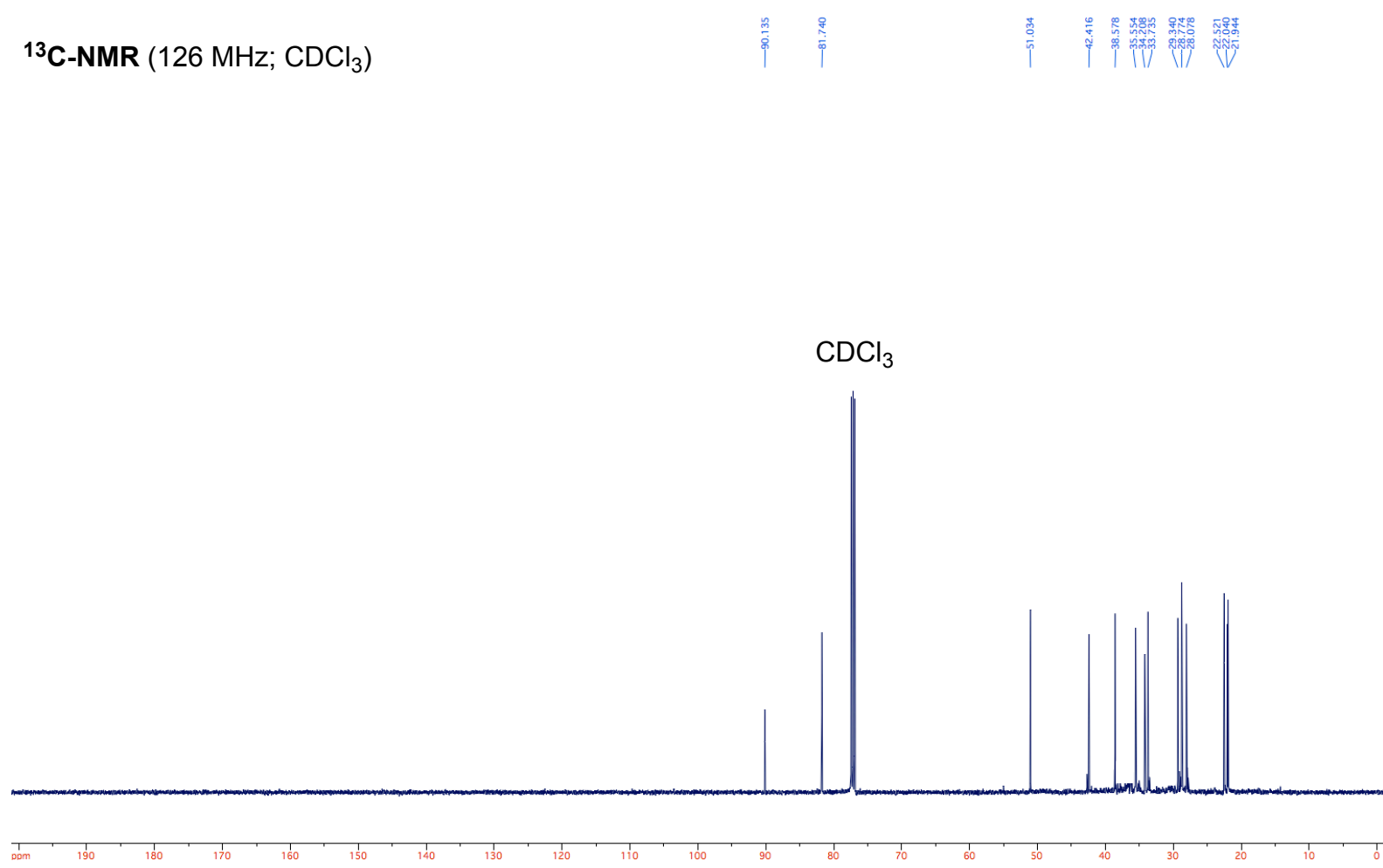
CDCl<sub>3</sub>



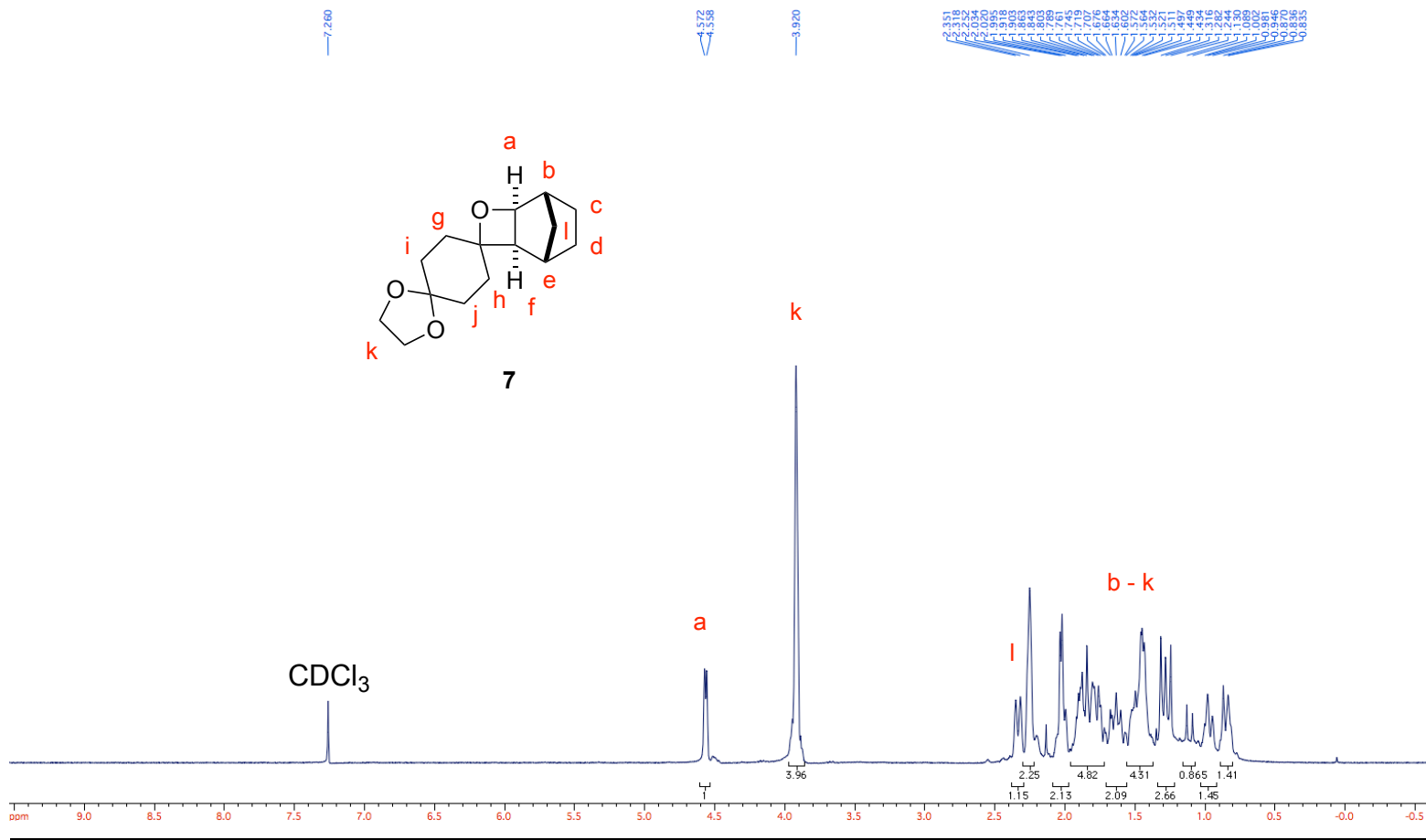
**<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)**



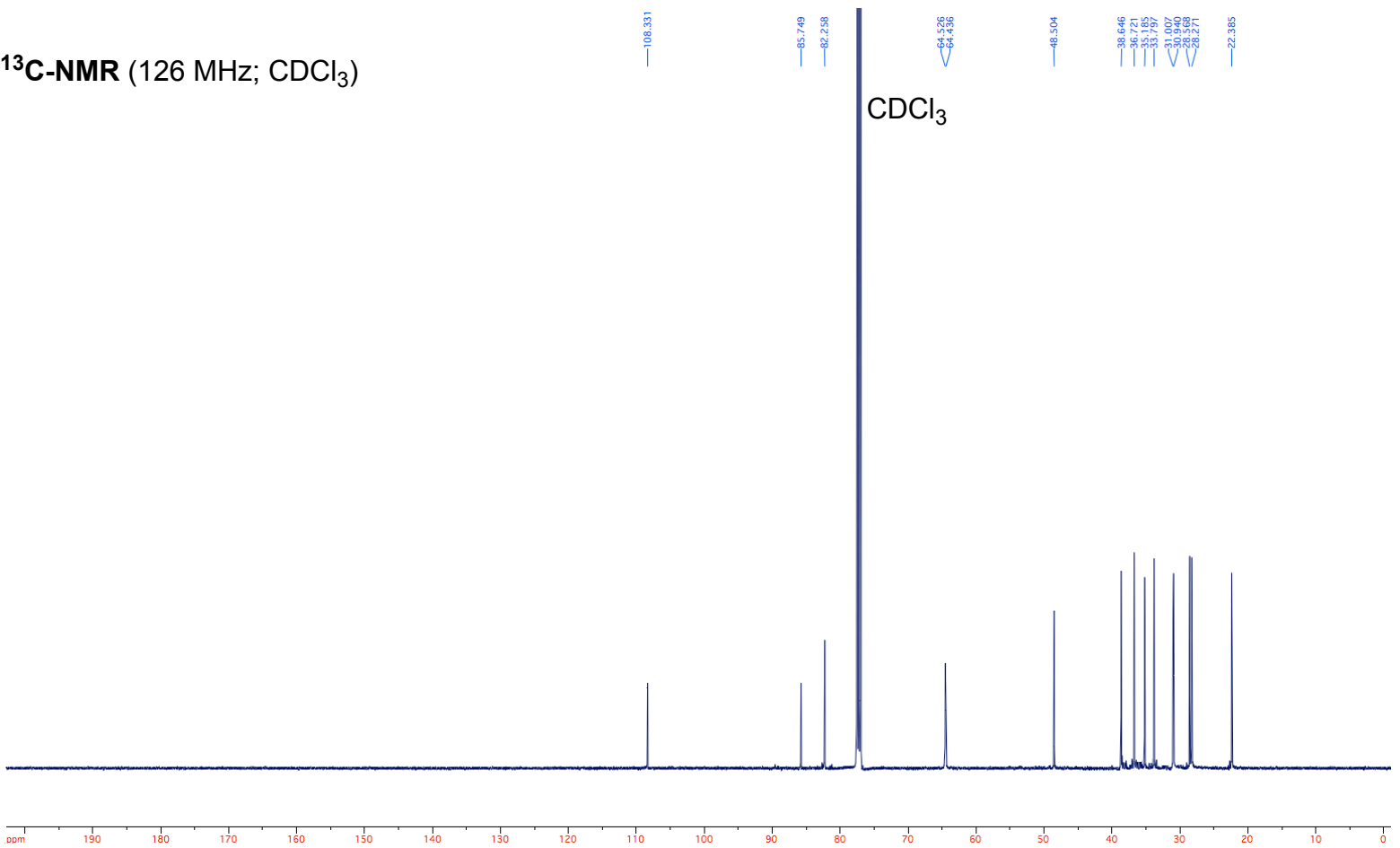
**<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)**



<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)

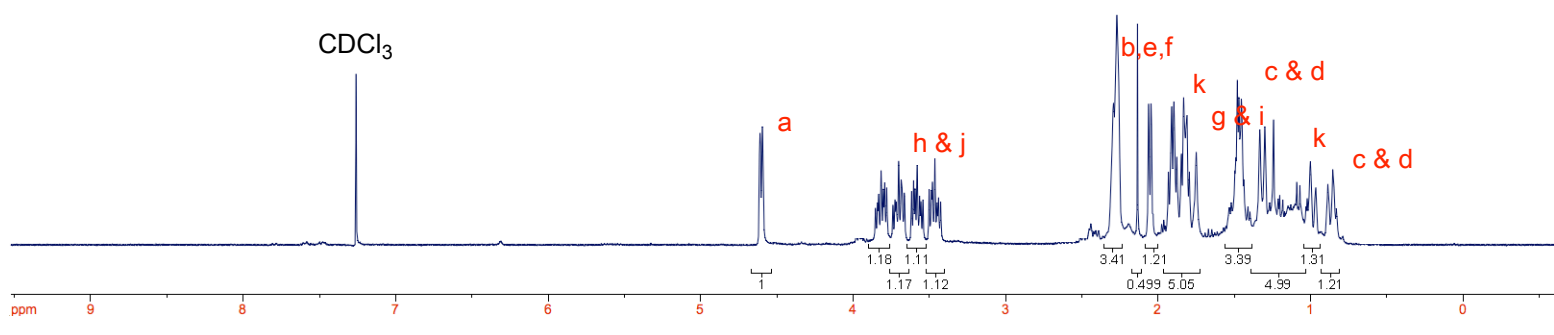
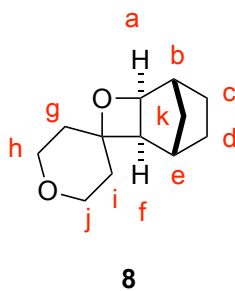


<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)

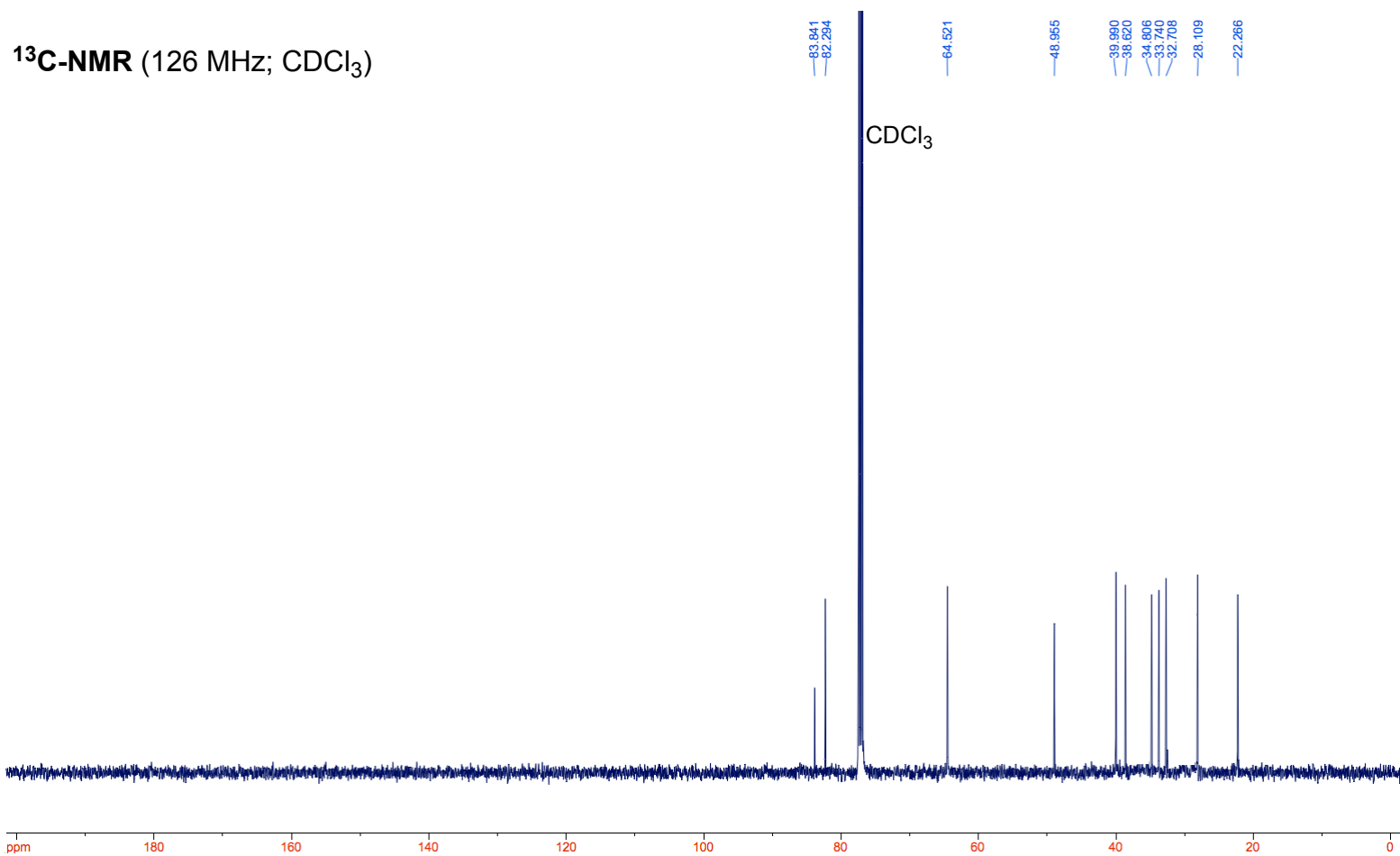


<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)

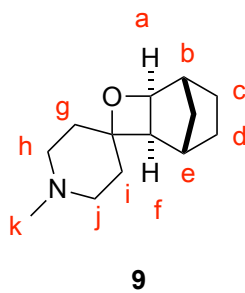
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3.701  
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0.880  
0.854  
0.851



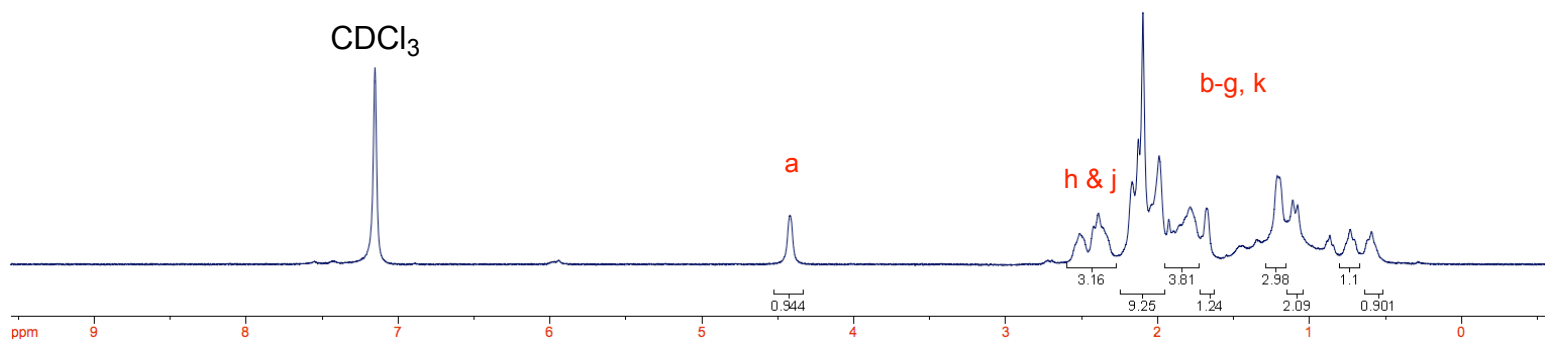
<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)



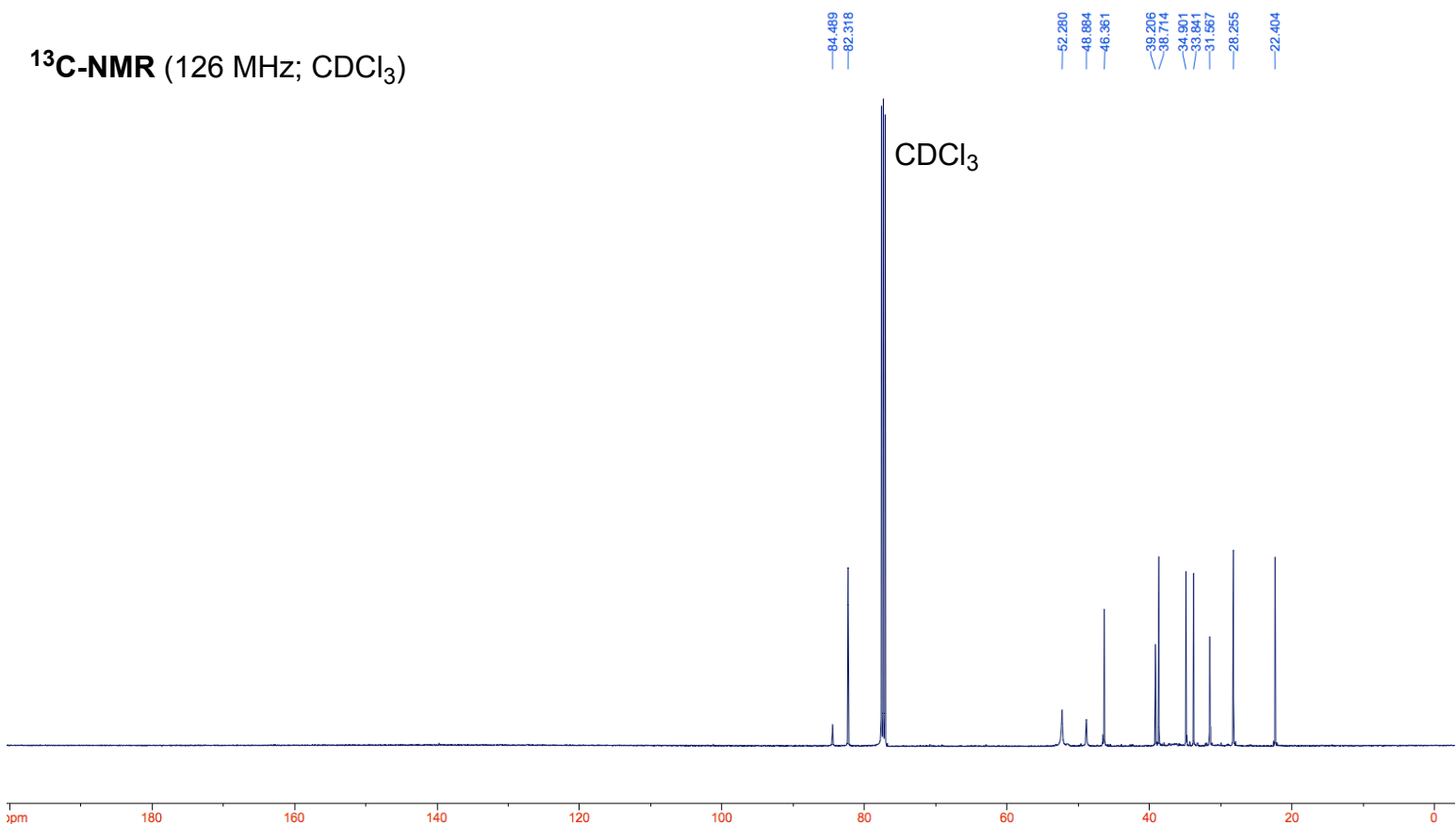
**<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)**



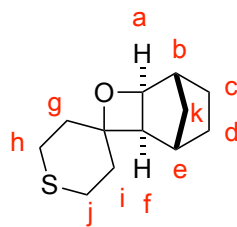
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2.506  
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1.852  
1.832  
1.798  
1.678  
1.213  
1.208  
1.109  
1.079  
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0.865  
0.888  
0.752  
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0.703  
0.617  
0.583  
0.571



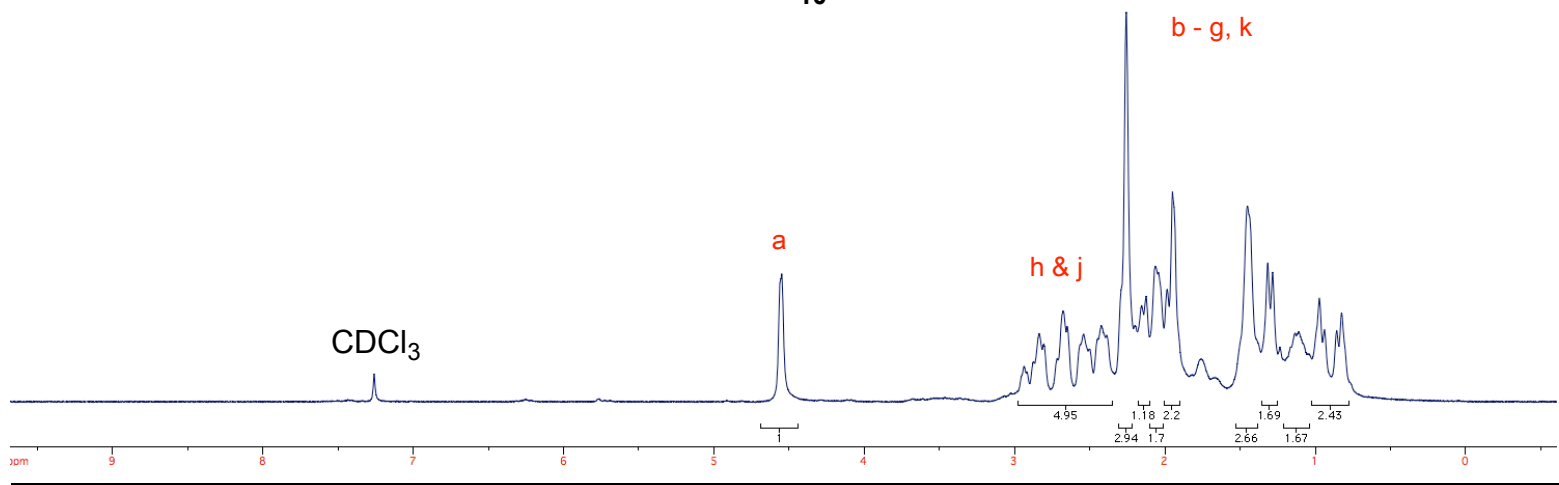
**<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)**



**<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)**



**10**



**<sup>13</sup>C-NMR (126 MHz; CDCl<sub>3</sub>)**

