Photoacid-catalyzed acetalization of carbonyls with alcohols

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I. General information:

^{1}H NMR spectra were recorded on a Varian Inova (500 MHz) spectrometer, and chemical shifts were reported in ppm relative to tetramethylsilane (TMS). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet; d = doublet; dd = doublet of doublets; ddd = doublet of doublet of doublets; m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR spectra were recorded on a Varian Inova (125 MHz) spectrometer, chemical shifts are reported in ppm relative to the solvent ($CDCl_3$ as d = 77.2 ppm). High-resolution mass spectra (HRMS) were obtained using a Waters Q-TOF Ultima ESI (electrospray ionization) and are reported in m/z. Silica gel high-purity, pore size 60, particle size 40–63 µm, 230–400 mesh was used for flash column chromatography. Rotary evaporation was performed using a Buchi R-300 rotary evaporator and Welch Model 2027 dry vacuum pump. Carbonyl reagents and catalysts **3**, **4**, **5**, **F₂Irpic**, and **S2** were purchased from commercial sources and used without further purification. Thiourea **2** was prepared according to literature.[1]

II. General procedures for the photoacid catalyzed acetalization of carbonyls:

Procedure **A**:

To an 8 mL vial fitted with a magnetic stir bar was added 6-bromo-2-naphthol (0.011g, 0.05 mmol, 0.1 equiv.) and the corresponding alcohol (1 mL). Next, the carbonyl compound was added (0.5 mmol, 1.0 equiv.) The reaction mixture was then sparged for 5 min, sealed, and placed 4.0 cm from a 40 W Blue LED light (Kessil Tuna Blue) for 18 h. Cooling fans were used to maintain room temperature. To the reaction was then added 5,6-dibromo-1,2-benzodioxole (0.5. mmol) and 250 µL of dioxane (to solubilize the std.). An aliquot was then taken up, dissolved in $CDCl_3$, and analyzed by ^{1}H NMR.

Column free acetal isolation and catalyst recovery:

Procedure **B**:

Acetal isolation:
The reaction mixture was transferred into a separatory funnel using 5 mL of diethyl ether. Saturated aqueous sodium bisulfite (10 mL) was added, and the mixture was shaken vigorously for approximately 1 min (Figure S1, A). The organic layer was washed with 3 X 10 mL 1 M NaOH, dried over $MgSO_4$, filtered, and concentrated in vacuo to give the acetal (Figure S1, B).

Recovery of catalyst **3**:
Concentrated HCl was added to NaOH (aq) layer (from Figure S1, B) until pH 7 (Figure S1, C). Afterward, 2 X 10 mL of diethyl ether was added. Then the organic layer was collected and dried over MgSO4, filtered, and concentrated in vacuo to give **3** as a white solid in up to 96% yield. Note: If needed **3** can be run through a SiO_2 plug with hexanes/ethyl acetate to remove trace impurities.

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[1] Larsen, D.; Langhorn, L. M.; Akselsen, O. M.; Nielsen, B. E.; Pittelkow, M. *Chem. Sci.* **2017**, *8*, 7978.
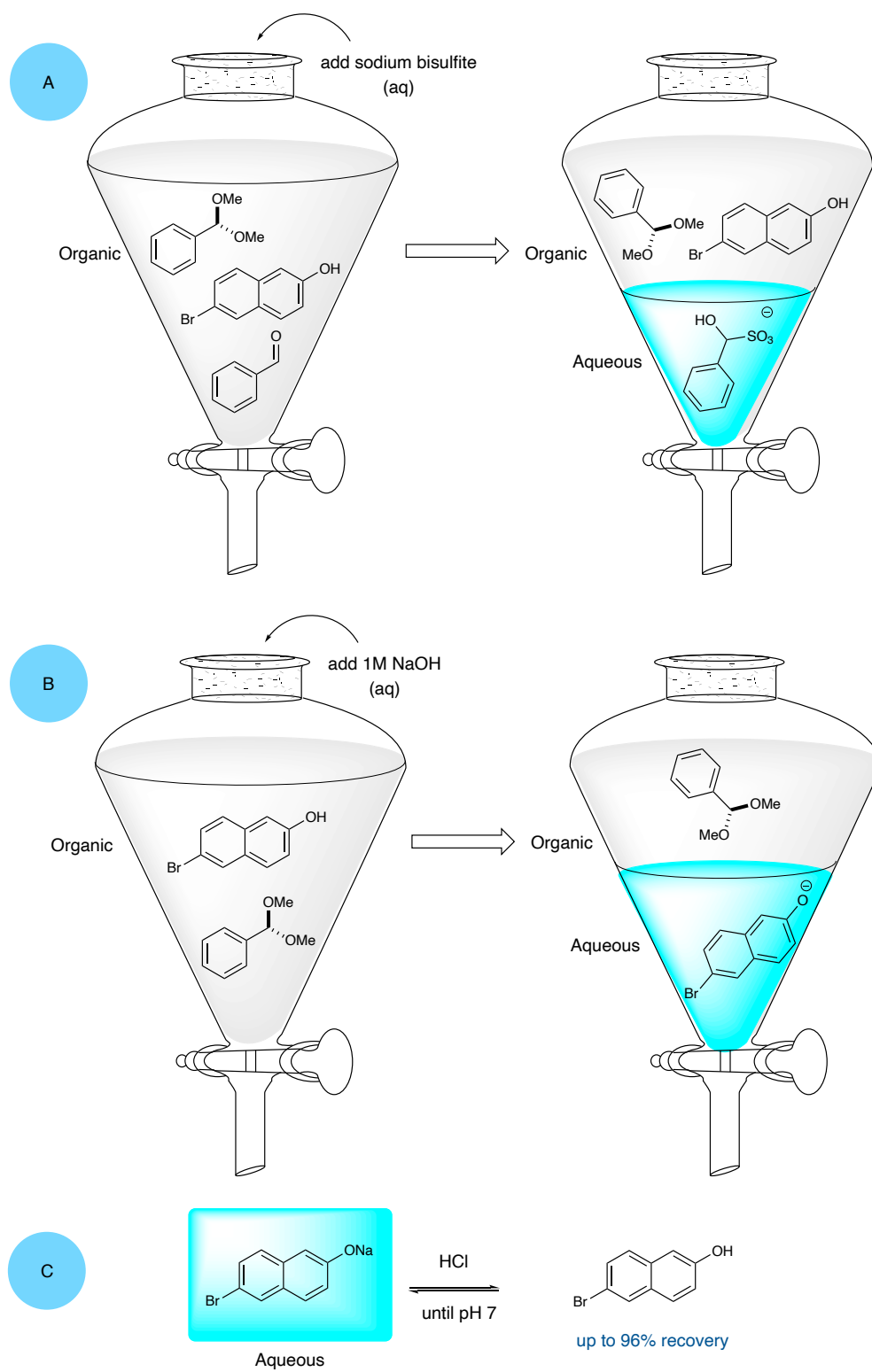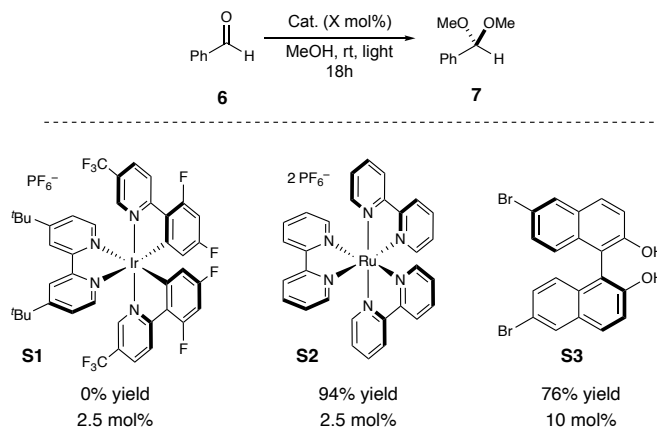
Figure S1: Column free isolation of acetals and recovery of catalyst **3**.

III. Additional catalyst, substrate, and control reactions:

Iridium catalyst **S1** gives no product (Scheme S1). Ruthenium catalyst **S2** gives **7** in 94% yield and dibromo-BINOL **S3** gives **7** in 76% yield. Note: **S1** gives up to 40% yield of acetal **13** via triplet energy transfer with **5** (vide infra).

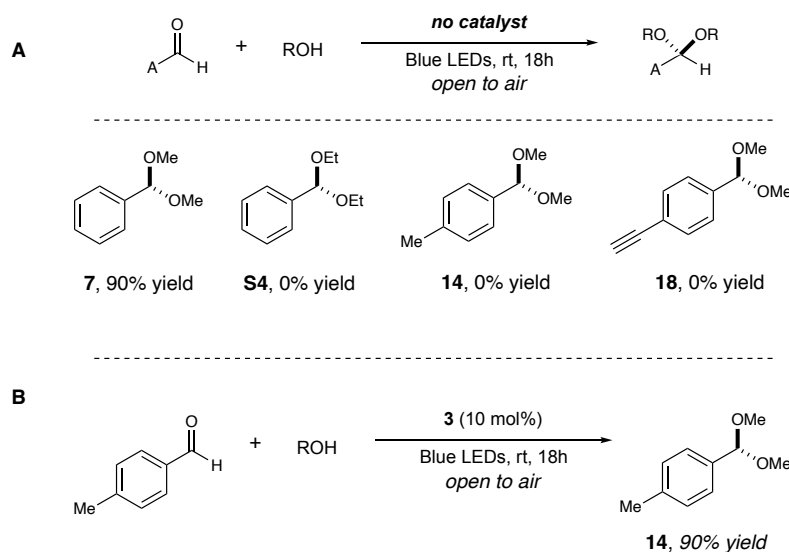**Scheme S1:** Reactions run according to modified procedure **A**.

In general, sterically hindered and more complicated alcohol substrates did not work well using photocatalyst **3**. (Scheme S2).
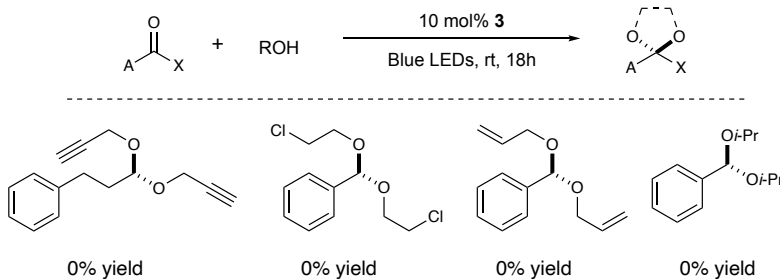
Scheme S2: Unsuccessful substrates run according to procedure **A**.

In the case of benzaldehyde (**6**) aerobic (reaction run open to air) photoirradiation in the absence of a catalyst provides **7** in 90% efficiency (Scheme S3, A). This phenomenon is only observed for benzaldehyde with methanol, when ethanol is used compound **S4** is not observed. Additionally, acetals **14** and **18** are not formed in the absence of catalyst with methanol. Also, acetal **14** was formed in 90% yield with 10 mol% **3** left open to air, suggesting that the triplet excited state of **3** may not be important for the rection to proceed (Scheme S3, B). Note that purification of benzaldehyde by washing with $NaOH_{(aq)}$, Sat. Na_2SO_3, drying over $MgSO_4$, and freshly distilling had no effect on reaction efficiency with 10 mol% **3** under argon or without catalyst open to air, **7** was formed in 80-90% efficiency.[2]

[2] Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals, 5th Edition*; Butterworth-Heinemann, 2003.

A

7, 90% yield   **S4**, 0% yield   **14**, 0% yield   **18**, 0% yield

B

14, *90% yield*

Scheme S3: Reactions run according to modified procedure **A**, no sparge, and left open to air. [a]Run with 390 nm LEDs. [b]Run with 370 nm LEDs.

It is possible that benzoic acid is being generated under the reaction conditions, however, when 10 mol% benzoic acid was used with and without light only 40 and 50% yield was observed, respectively (Table S1, Entries 1 and 2). The addition of 5 mol% triethylamine (TEA) shut down the standard reaction (with 10 mol% **3**), however 4-chlorobenzaldehyde proceeds in 68% yield with 5 mol% TEA in the absence of a catalyst (Entries 3 and 4). The addition of 15 mol% triethylamine shut down the reaction with 4-chlorobenzaldehyde in the absence of **3**, suggesting that the mechanism is indeed acid-catalyzed (Entry 5). Finally, the addition of 5 mol% sodium bicarbonate shut down the standard reaction and the reaction with 4-chlorobenzaldehyde (Entries 6 and 7).

Entry	X	Cat.	additive	light	%yield
1	H	—	10 mol% benzoic acid	Blue LEDs	40
2	H	—	10 mol% benzoic acid	—	50
3	H	**3**	5 mol% NEt$_3$	Blue LEDs	0
4	Cl	—	5 mol% NEt$_3$	Blue LEDs	68
5	Cl	—	15 mol% NEt$_3$	Blue LEDs	0
6	H	**3**	5 mol% NaHCO$_3$	Blue LEDs	0
7	Cl	—	5 mol% NaHCO$_3$	Blue LEDs	0

Table S1: Reactions run with 0.5 mmol aldehyde in MeOH (0.5 M), under argon atmosphere, % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

To better understand the catalyst free formation of halogen containing acetals we purified 4-bromobenzaldehyde via recrystallization. Regardless of whether the reaction contained catalyst or was open to air, product was formed in 90-92% yield (Entries 1-4, Table S2).
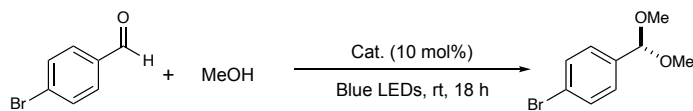
Entry	Cat.	Conditons	%yield
1	**3**	Open to Air	90
2	**3**	Under Argon	90
3	—	Open to Air	90
4	—	Under Argon	92

Table S2: Reactions run with 0.5 mmol 4-bromobenzaldehyde (freshly recrystallized) in MeOH (0.5 M), % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

It is worth noting that we observed inconsistent results depending on the batch of methanol used (Table S3). Several "dry" bottles of AcroSeal® methanol were shipped from the vendor leaking, and thus were assumed not to be dry, and provided no product (Entries 1 and 2). Others appeared to be sealed, however, no reaction was observed, even after subsequent drying with 5 Å mol sieves (Entries 3 and 4). Ultimately, it was determined that methanol dried over activated 5 Å MS and subsequent bulb-to-bulb distillation under argon via a short path condenser provided consistent results, Entry 7.
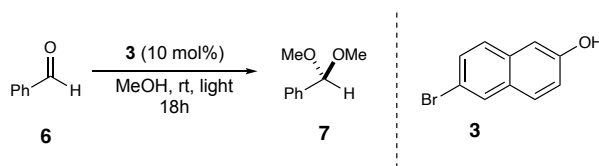
Entry	MeOH Source	Part - Lot #	% yield	Comments
1	AcroSeal®	36439-B0539396A[b]	0	Shipped from vendor leaking
2	AcroSeal®	36439-B0538002A[b]	0	Shipped from vendor leaking
3	AcroSeal®	36439-B0539396A[b]	0	Not leaking
4	AcroSeal®	61098-B0535263	0	Dried over 5 Å mol sieves
5	AcroSeal®	61098-B0542325C	91	Not leaking
6	Macron	3016-16-0000178672	13	Dried over 5 Å mol sieves
7	Macron	3016-16-0000178672	90	Distilled over 5 Å mol sieves

Table S3: [a]Conditions: Carbonyl compound (0.5 mmol) in the corresponding alcohol (0.5 M), under argon atmosphere, % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole. [b]LOT #s: B0539396A and B0538002A shipped over mol sieves from vendor.

IV. Compound characterization:

All compounds are consistent with the reported literature.[3,4,5,6,7,8,9,10,11,12]
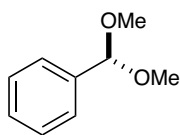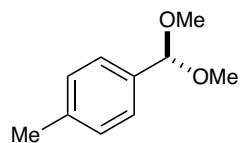

(dimethoxymethyl)benzene **7**: Compound **7** was prepared according to the general procedure **A** and purified according to procedure **B** to give a pale-yellow oil, 0.067g, 83% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.29 (m, 3H), 5.39 (s, 1H), 3.33 (s, 6H).
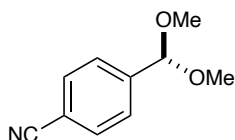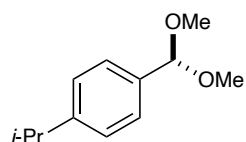

4-(dimethoxymethyl)benzonitrile **8**: Compound **8** was prepared according to the general procedure **A**, 86% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. give 8^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 5.43 (s, 1H), 3.33 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.31, 132.22, 127.71, 118.84, 112.43, 101.85, 52.83.
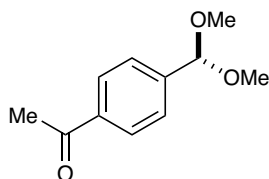
1-(4-(dimethoxymethyl)phenyl)ethan-1-one **9**: Compound **9** was prepared according to modified general procedure **A**, using 0.25 mmol aldehyde, 20 mol% **3**, 0.33 M MeOH:dioxane (2:1), to give 44% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, J = 7.4 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H), 5.45 (s, 1H), 3.34 (s, 6H), 2.62 (s, 3H).

[3] Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. *Science* **2010**, *328*, 1679.

[4] Fujioka, H.; Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T. *Chem. Commun.* **2011**, *47*, 9894.

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[8] Sakai, N.; Moritaka, K.; Konakahara, T. *Eur. J. Org. Chem.* **2009**, 4123.

[9] Zhao, Y.-J.; Chng, S.-S.; Loh, T.-P. *J. Am. Chem. Soc.* **2007**, *129*, 492.

[10] Spiliopoulou, N.; Nikitas, N. F.; Kokotos, C. G. *Green Chem.* **2020**, *22*, 3539.

[11] De, S. K.; Gibbs, R. A. *Tetrahedron Lett.* **2004**, *45*, 8141.

[12] Kumar, R.; Chakraborti, A. K. C. *Tetrahedron Lett.* **2005**, *46* (48), 8319-8323.
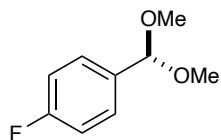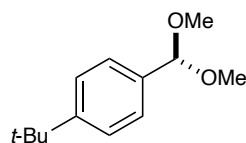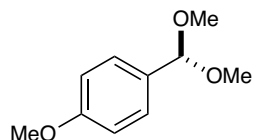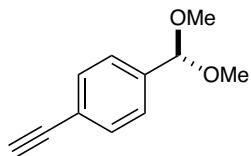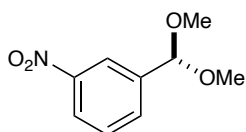
1-(dimethoxymethyl)-4-fluorobenzene **10**: Compound **10** was prepared according to the general procedure **A**, 76% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 – 7.38 (m, 2H), 7.05 (t, J = 8.7 Hz, 2H), 5.37 (s, 1H), 3.32 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.91 (d, J_{FC} = 246.3 Hz), 134.11 (d, J_{FCCCC} = 3.2 Hz), 128.63 (d, J_{FCCC} = 8.2 Hz), 115.21 (d, J_{FCC} = 21.2 Hz), 102.63, 52.76.
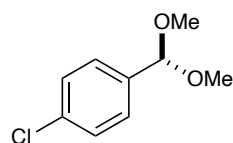
1-chloro-4-(dimethoxymethyl)benzene **11**: Compound **11** was prepared according to the general procedure **A** and purified according to procedure **B** to give a pale-yellow oil, 0.060g, 64% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 5.37 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 136.73, 134.32, 128.45, 128.26, 102.34, 52.60. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{12}$ClO$_2$, 186.0451 found 186.0448.
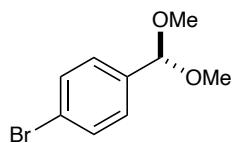
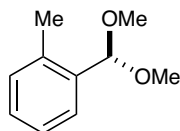1-bromo-4-(dimethoxymethyl)benzene **12**: Compound **12** was prepared according to the general procedure **A**, 90% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.35 (s, 1H), 3.30 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.25, 131.45, 128.63, 122.61, 102.40, 52.67. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{11}$BrO$_2$, 229.9942; found 229.9932.
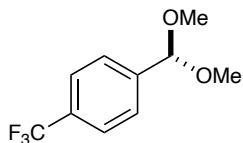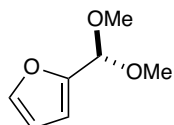

1-(dimethoxymethyl)-4-(trifluoromethyl)benzene **13**: Compound **13** was prepared according to the general procedure **A**, 94% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 5.44 (s, 1H), 3.33 (s, 6H). ^{13}C NMR (125 MHz, CDCl3$_3$) δ 142.14, 130.73 (q, J_{FCC} = 32.3 Hz), 127.30, 125.26 (q, J_{FCCC} = 3.5 Hz), 124.29 (q, J_{FC} = 272.0 Hz, CF$_3$), 102.27, 52.70.

1-(dimethoxymethyl)-4-methylbenzene **14**: Compound **14** was prepared according to the general procedure **A** and purified according to procedure **B** to give a pale-yellow oil, 0.065g, 74% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 (d, J = 7.4 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 5.36 (s, 1H), 3.32 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 138.27, 135.25, 128.99, 126.72, 103.33, 52.75, 21.32. HRMS (ESI) m/z [M + H] calcd for C$_{10}$H$_{15}$O$_2$, 166.0994 found 166.0994.

1-(dimethoxymethyl)-4-isopropylbenzene **15**: Compound **15** was prepared according to the general procedure **A**, 77% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, J = 6.9 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.35 (s, 1H), 3.33 (s, 6H), 3.00 – 2.80 (m, 1H), 1.25 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.31, 135.65, 126.76, 126.40, 103.53, 52.95, 34.03, 24.11. HRMS (ESI) m/z [M + H] calcd for C$_{12}$H$_{19}$O$_2$, 194.1307 found 194.1303.

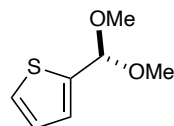1-(*tert*-butyl)-4-(dimethoxymethyl)benzene **16**: Compound **16** was prepared according to the general procedure **A**, 75% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.32 (m, 4H), 5.36 (s, 1H), 3.33 (s, 6H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.54, 135.25, 126.47, 125.25, 103.52, 52.97, 34.72, 31.47.

1-(dimethoxymethyl)-4-methoxybenzene **17**: Compound **17** was prepared according to the general procedure **A**, 56% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 5.35 (s, 1H), 3.81 (s, 3H), 3.31 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.79, 130.49, 128.04, 113.65, 103.18, 55.37, 52.72. HRMS (ESI) m/z [M + H] calcd for C$_{10}$H$_{15}$O$_3$, 182.0943 found 182.0948.

1-(dimethoxymethyl)-4-ethynylbenzene **18**: Compound **18** was prepared according to modified general procedure **A**, using 20 mol% **3**, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 78% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 5.39 (s, 1H), 3.32 (s, 6H), 3.08 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 138.87, 132.14, 126.87, 122.31, 102.61, 83.56, 77.59, 52.75. HRMS (ESI) m/z [M + H] calcd for C$_{11}$H$_{13}$O$_2$, 176.0837 found 176.0835.

1-(dimethoxymethyl)-3-nitrobenzene **19**: Compound **19** was prepared according to the general procedure **A**, 72% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.35 (s, 1H), 8.22 – 8.16 (m, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 5.48 (s, 1H), 3.35 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.32, 140.40, 132.91, 129.26, 123.44, 122.07, 101.44, 52.72. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{12}$NO$_4$, 197.0688 found 197.0691.

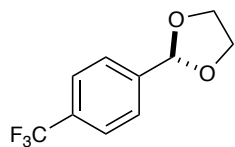1-(dimethoxymethyl)-2-methylbenzene **20**: Compound **20** was prepared according to the general procedure **A**, 50% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 (d, J = 6.2 Hz, 1H), 7.31 – 7.10 (m, 3H), 5.46 (s, 1H), 3.32 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 136.39, 135.77, 130.66, 128.51, 126.65, 125.56, 101.89, 53.16, 19.02.
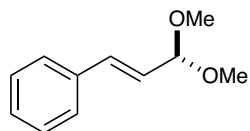
(*E*)-(3,3-dimethoxyprop-1-en-1-yl)benzene **21**: Compound **21** was prepared according to the general procedure **A** to give 72% yield as a 91:9 mixture of *E:Z* isomers as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard, and purified by column chromatography (98% hexanes/2% triethylamine) to give a 70:30 mixture of *E:Z* isomers, the isolated yield was not determined. Peaks corresponding to the *E*-isomer are as follows: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.23 (m, 5H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 16.3, 4.7 Hz, 2H), 4.96 (d, *J* = 4.8 Hz, 1H), 3.38 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 136.23, 133.73, 128.73, 128.25, 126.87, 125.83, 103.06, 52.87. Peaks corresponding to the *Z*-isomer are as follows: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.76 (dd, *J* = 11.9, 7.4 Hz, 1H), 5.11 (d, *J* = 7.3 Hz, 1H), 3.36 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 99.66, 52.42.

2-(dimethoxymethyl)furan **22**: Compound **22** was prepared according to modified general procedure **A**, using 20 mol% **3**, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 64% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.37 (m, 1H), 7.29 – 7.24 (m, 1H), 6.44 – 6.41 (m, 1H), 6.39 – 6.35 (m, 1H), 5.44 (s, 1H), 3.36 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.99, 142.64, 110.20, 108.58, 98.10, 52.99.

2-(dimethoxymethyl)thiophene **23**: Compound **23** was prepared according to modified general procedure **A**, using 20 mol% **3**, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 92% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29 (d, *J* = 5.1 Hz, 1H), 7.07 (dd, *J* = 2.8, 1.7 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.64 (s, 1H), 3.36 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.61, 126.76, 125.78, 125.52, 100.18, 52.64. HRMS (ESI) m/z [M + H] calcd for C$_7$H$_{11}$O$_2$S, 159.0474 found 159.0475.
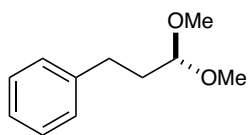
(3,3-dimethoxypropyl)benzene **24**: Compound **24** was prepared according to modified general procedure **A**, using 20 mol% **3**, to give 62% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.09 (m, 5H), 4.37 (t, 1H), 3.33 (s, 6H), 2.68 (t, J = 8.0 Hz, 2H), 1.97 – 1.89 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.77, 128.74, 128.54, 126.02, 103.90, 52.87, 34.23, 31.01. HRMS (ESI) m/z [M + H] calcd for C$_{11}$H$_{17}$O$_2$, 181.1229 found 181.1184
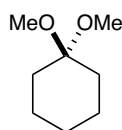
1,1-dimethoxycyclohexane **25**: Compound **25** was prepared according to the general procedure **A**, 75% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.17 (s, 6H), 1.91 – 1.30 (m, 11H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 100.09, 47.43, 32.81, 25.72, 22.95. HRMS (ESI) m/z [M + H] calcd for C$_8$H$_{17}$O$_2$, 145.1229 found 145.1184.
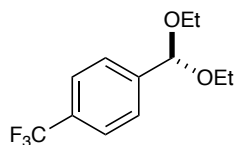
1-(diethoxymethyl)-4-(trifluoromethyl)benzene **26**: Compound **26** was prepared according to modified general procedure **A** using 20 mol% **3** and purified according to procedure **B** to give a pale-yellow oil, 0.079g, 64% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 – 7.58 (m, 4H), 5.57 (s, 1H), 3.69 – 3.48 (m, 4H), 1.33 – 1.18 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.17, 130.58 (q, J_{FCC} = 32.2 Hz), 127.23, 125.26 (q, J_{FCCC}= 3.8 Hz), 124.29 (q, J_{FC} = 272.0 Hz, CF$_3$), 100.78, 61.28, 15.23.
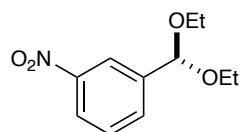
1-(diethoxymethyl)-3-nitrobenzene **27**: Compound **27** was prepared according to modified general procedure **A** using 20 mol% **3**, to give 70% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.40 – 8.31 (m, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.58 – 7.52 (m, 1H), 5.59 (s, 1H), 3.70 – 3.48 (m, 4H), 1.27 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.41, 141.53, 133.00, 129.33, 123.42, 122.09, 100.14, 61.41, 15.27.

2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane **28**: Compound **28** was prepared according to modified general procedure **A** using 20 mol% **3**, 62% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 5.86 (s, 1H), 4.16 – 4.01 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.05, 131.36 (q, J_{FCC} = 32.2 Hz), 125.47 (q, J_{FCCC} = 3.8 Hz), 124.16 (q, J_{CF} = 272.3 Hz, CF$_3$), 126.96, 102.90, 65.52.
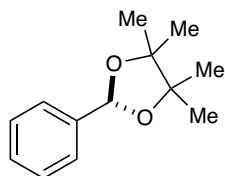
4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolane **29**: Compound **29** was prepared was prepared according to modified general procedure **A**, using 20 mol% **3** and 0.33 M MeOH:dioxane (2:1). Compound **29** was purified according to procedure **B** to give a pale-yellow oil, 0.069g, 67% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, J = 7.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.98 (s, 1H), 1.32 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (125 MHz) δ 139.76, 128.70, 128.34, 126.36, 100.00, 82.73, 24.43, 22.29.
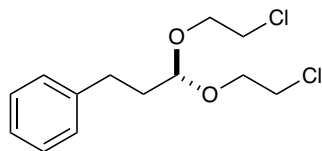
(3,3-bis(2-chloroethoxy)propyl)benzene **30**: Compound **30** was prepared according to the general procedure **A**, 53% yield as determined by ^{1}H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.63 (t, J = 5.9 Hz, 1H), 3.86 (dt, J = 11.0, 5.6 Hz, 2H), 3.75 (dt, J = 11.0, 5.7 Hz, 2H), 3.65 (t, J = 5.6 Hz, 4H), 2.75 – 2.69 (m, 2H), 2.03 – 1.95 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.28, 128.54, 128.51, 126.11, 102.47, 65.44, 43.41, 34.55, 30.93.

V. Photosensitizer procedure and mechanistic studies:

General procedure for sensitizer reaction:

To an 8 mL vial fitted with a magnetic stir bar was added **F₂Irpic** {bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III)} (0.005g, 0.0065 mmol, 0.025 equiv.), 2-naphthol (0.018g, 0.125 mmol, 0.5 equiv.), and methanol (1 mL). Next, the carbonyl compound was added (0.25 mmol, 1.0 equiv.). The reaction mixture was then sparged for 5 min, sealed, and placed 4.0 cm from a 40 W Blue LED light (Kessil Tuna Blue) for 18 h. Cooling fans were used to maintain room temperature. To the reaction was then added 5,6-dibromo-1,2-benzodioxole (0.5. mmol) and 250 µL of dioxane. An aliquot was then taken up, dissolved in CDCl₃, and analyzed by ¹H NMR.

Photosensitizer mechanistic studies:

Emission quenching studies showed that **F₂Irpic** emission was 34% quenched in the presence of 2-naphthol (**5**) with and without benzaldehyde (**6**) and 4-trifluoromethyl benzaldehyde (**S5**), suggesting efficient energy transfer between **F₂Irpic** and **5** (Figure S2). No **F₂Irpic** emission quenching was observed in the presence of **6** and **S5** in the absence of **5**.
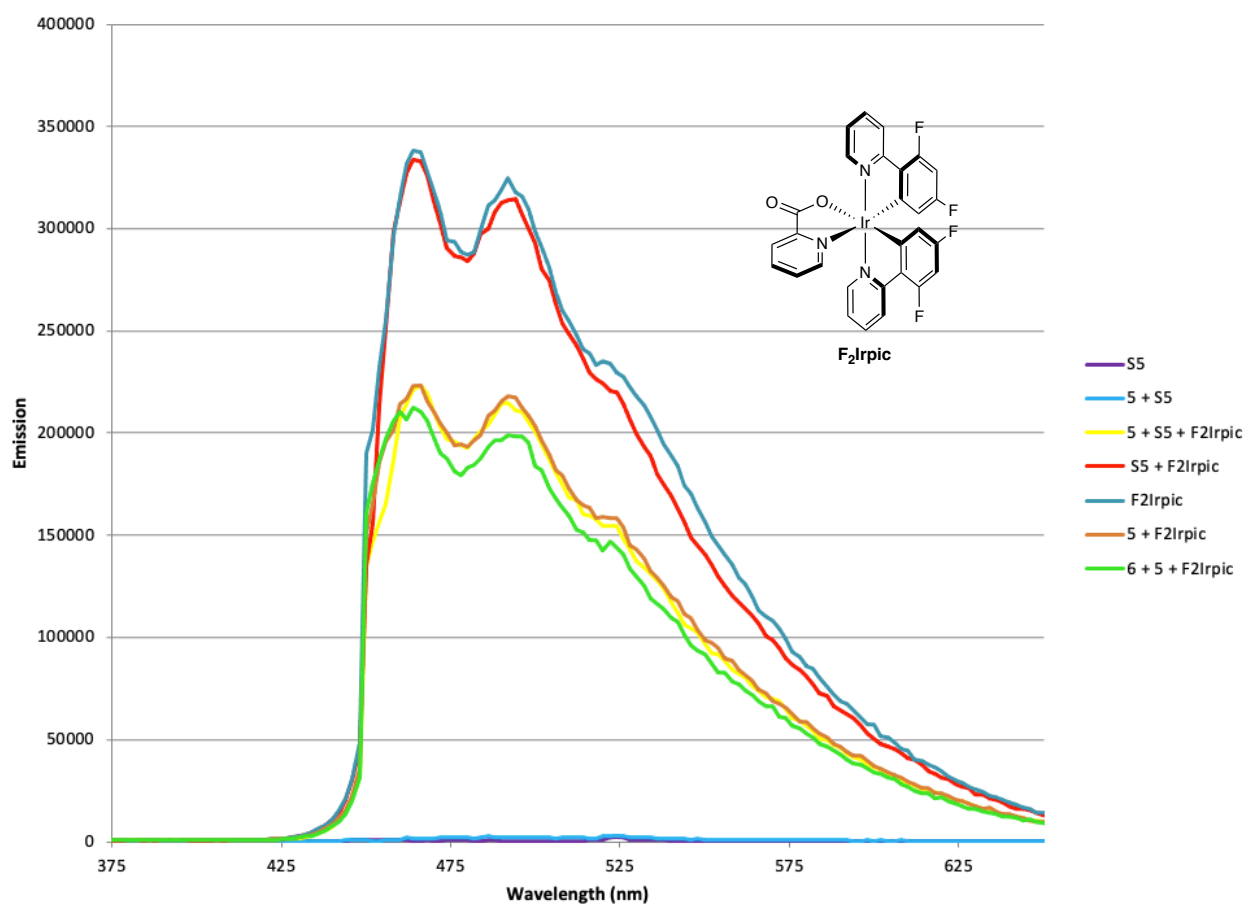
Figure S2: Emission spectra of **F₂Irpic** [bis(4,6-difluorophenyl-pyridine)(picolinate) iridium(III)] (0.8 mM in methanol) with and without 25 equivalents of the corresponding aldehydes (**6** or **S5**) and/or 2-naphthol (**5**) [Excitation wavelength: 454 nm].

Emission quenching studies showed that **S1** emission was 80% quenched in the presence of 2-naphthol (**5**) with and without 4-trifluoromethyl benzaldehyde (**S5**) (Figure S3). No **S1** emission quenching was observed in the presence of **S5** in the absence of **5**.
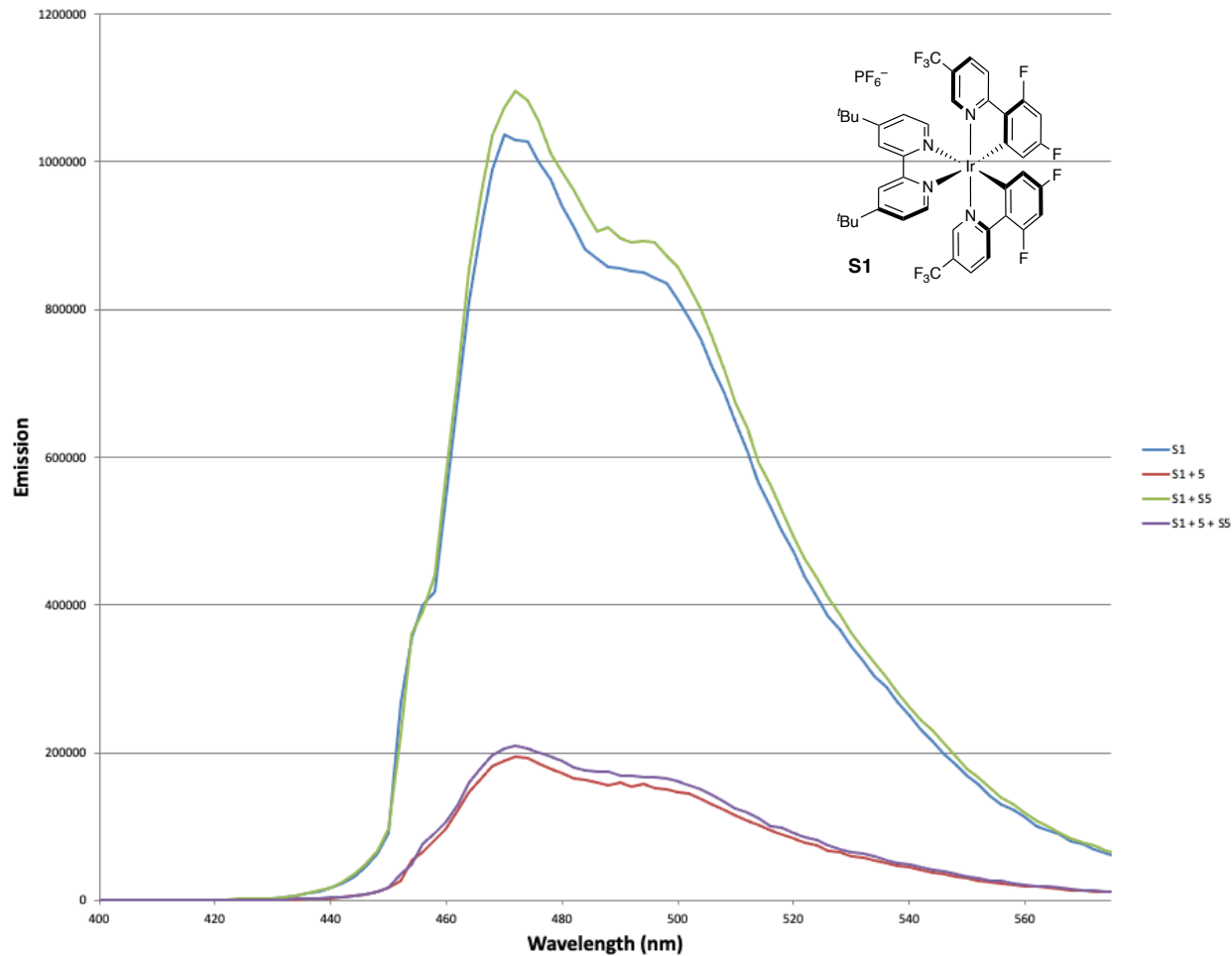
Figure S3: Emission spectra of [Ir{dF(CF$_3$)ppy}2(dtbpy)]PF$_6$](**S1**) [0.8 mM in methanol] with and without 25 equivalents of the corresponding aldehyde (**S5**) and/or 2-naphthol (**5**) [Excitation wavelength: 454 nm].

Emission quenching studies showed that the emission of ruthenium complex **S2** was not quenched by either aldehyde **S5** or 2-naphthol (**5**) [Figure S4].
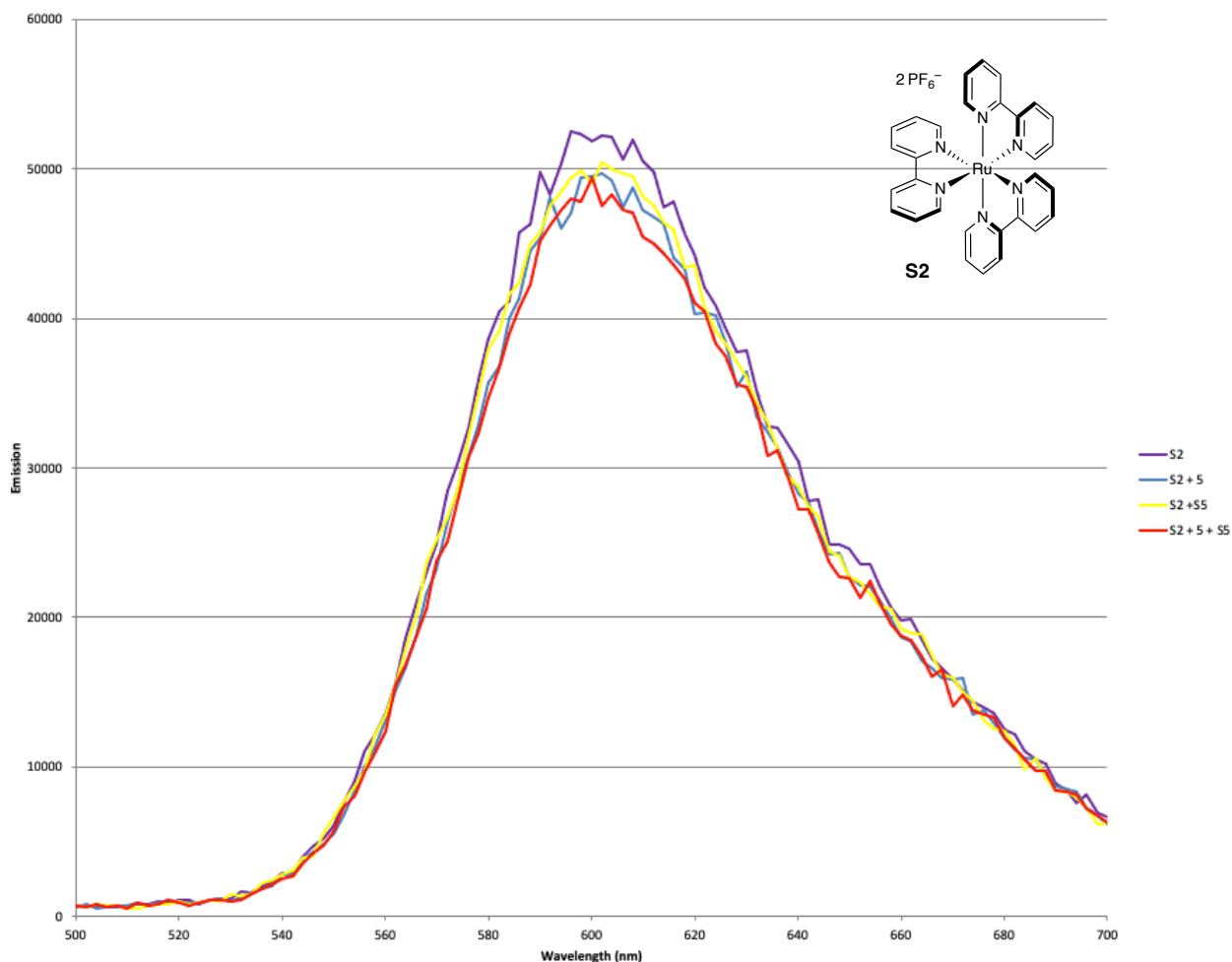
Figure S4: Emission spectra of **S2** [Ru(bby)₃(PF₆)₂], {0.8 mM in methanol} with and without 25 equivalents of the aldehyde **S5** and/or 2-naphthol (**5**) [Excitation wavelength: 450 nm].

A possible mechanism for the formation of **13** is shown in Scheme S4. Photoexcitation of **F₂Irpic** results in formation of singlet ^{1}**F₂Irpic***, intersystem crossing (ISC), and metal to ligand charge transfer (MLCT) gives rise to triplet excited state ^{3}**F₂Irpic***. Triplet energy transfer (TET) from ^{3}**F₂Irpic*** to **5**, gives rise to **5*** which is sufficiently acidic to protonate aldehyde **S5** to afford oxonium **S6**. Subsequent reaction of **S6** or hydrogen bonding complex **S6*** with 2 equivalents of methanol results in formation of acetal product **13** and regenerates a proton. The resulting in situ generated proton can either protonate an additional equivalent of aldehyde or protonate **S7** to reconstitute **5**. The addition of 5 mol% sodium bicarbonate shut down acetal formation in the presence of **F₂Irpic** with and without **5**, suggesting that the reaction involves generation of a Brønsted acid. Notably, unlike in the case of 6-bromo-2-naphthol (**3**), overnight irradiation of **F₂Irpic** and **5**, followed by the addition of **S5** and placement in the dark resulted in no product formation. There does not appear to be generation of a persistent in situ generated acidic species (vide infra). The reaction is completely shut down if left open to air with **F₂Irpic** with and without **5**. It is also worth noting that the use of 1 equiv. of **5** does not provided and increase in reaction efficiency.

5	F$_2$Irpic	5 mol% NaHCO$_3$	*yield*
×	×	—	0
√	×	—	0
×	√	—	25
√	√	—	*74*
×	√	√	0
√	√	√	0
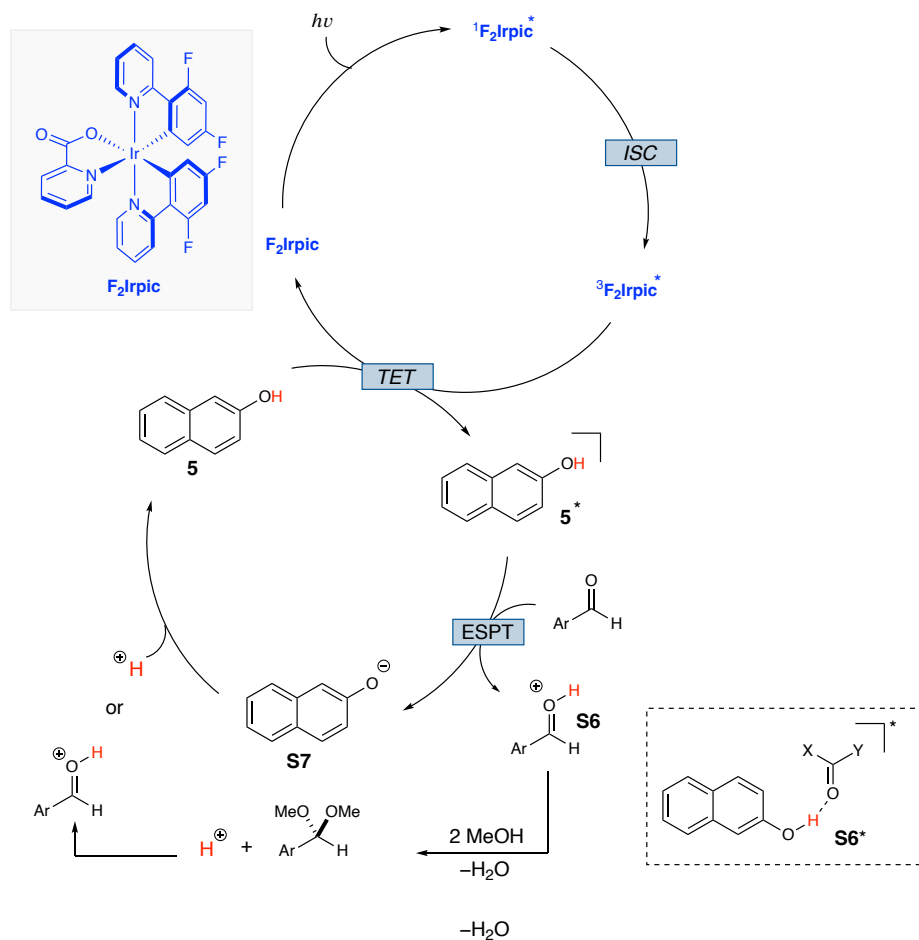
Scheme S4: Potential mechanism for triplet energy transfer and photoactivation of naphthol. Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

When iridium photocatalyst **S1** in combination with **5** is used, 40% yield of **13** is obtained in (Scheme S5). No product is observed with **S1** in the absence of **5**.

5	S1	yield
✗	✗	0
✓	✗	0
✗	✓	0
✓	✓	*40*
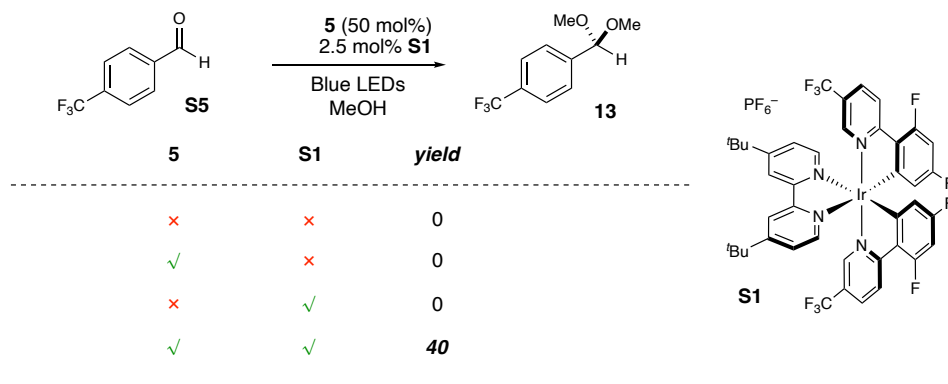
Scheme S5: Run according to the general procedure for sensitizer reactions: **(**0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

With iridium photocatalyst **S2**, >90% yield of **13** is observed with and without 2-naphthol **5**. This suggests that a different mechanism may be operable (Scheme S6). Notably, the addition of 5 mol% NaHCO$_3$ shuts down the reaction with **S2** and with (**S2** + **5**), suggesting that in both cases there is photogeneration of a Brønsted acidic species.

5	S2	5 mol% NaHCO$_3$	yield
✗	✗	—	0
✓	✗	—	0
✗	✓	—	94
✓	✓	—	*95*
✗	✓	✓	0
✓	✓	✓	0
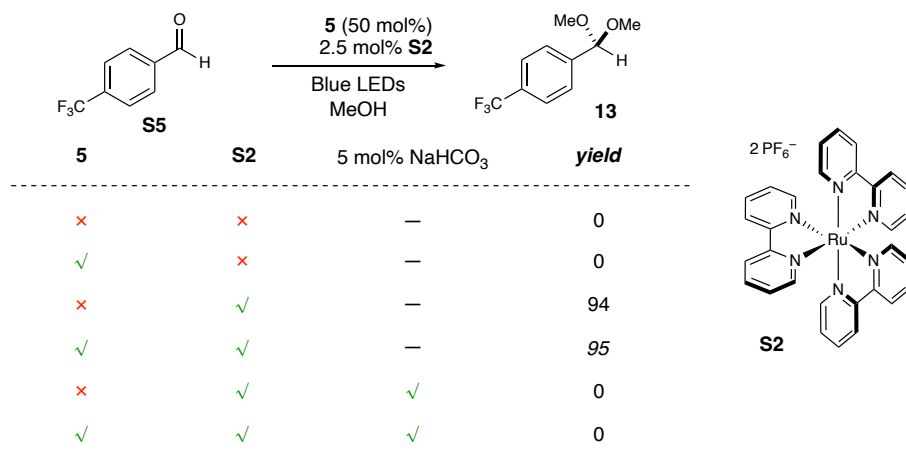
Scheme S6: Run according to the general procedure for sensitizer reactions: **(**0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on ^{1}H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

It was observed that electron-withdrawing groups are required for the sensitization reaction to proceed. When benzaldehyde (**6**) was investigated only 6% product **7** was observed in the presence of **F₂Irpic**, with and without **5** (Scheme S7). For the reaction of electron-rich *p*-tolualdehyde (**S8**) in the presence of **F₂Irpic**, with or without **5**, 57 and 54% yield of **12** was observed, respectively (Scheme S8).

5	F₂Irpic	*yield*
✗	√	6
√	√	6
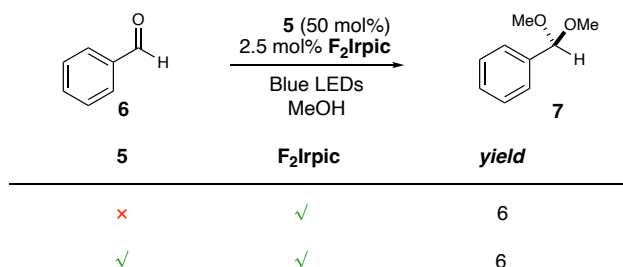
Scheme S7: Photosensitizer and 2-naphthol with benzaldehyde. Run according to the general procedure for sensitizer reactions: **(**0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on ¹H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

5	F₂Irpic	*yield*
✗	√	54
√	√	57
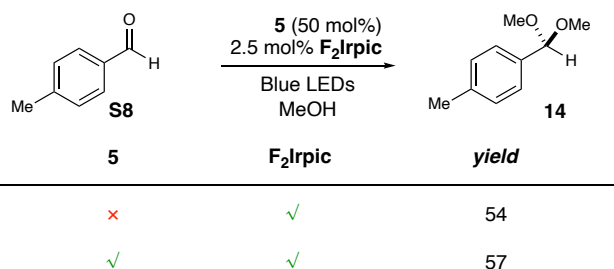
Scheme S8: Photosensitizer and 2-naphthol with *p*-tolualdehyde. Run according to the general procedure for sensitizer reactions: **(**0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on ¹H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

IV. Initiation kinetics and NMR evidence for photogenerated strong acid:

The standard reaction was monitored under constant irradiation with Blue LEDs (Figure S5). A 2 h induction period was observed, after which the reaction reached 90% conversion after 6 h.
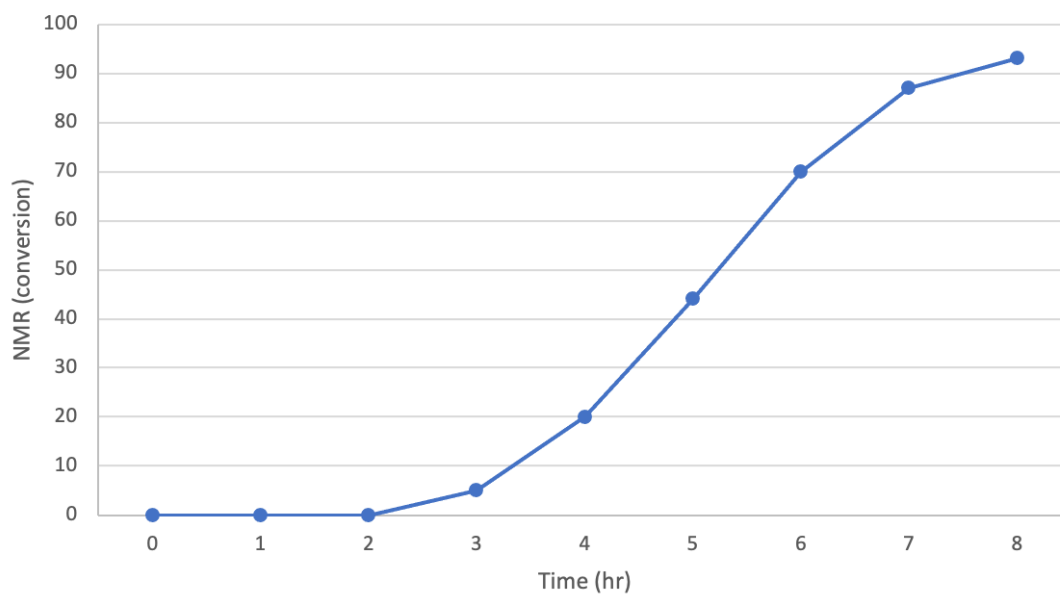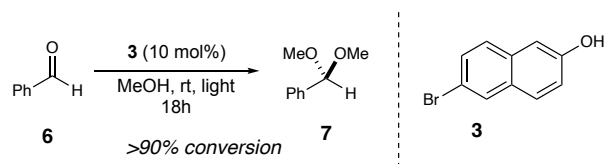
Figure S5: Reaction run according to standard procedure A. Aliquots were taken every 1 h using a BD spinal needle and %conversion of **6** to **7** was determined by NMR spectroscopy.

To further probe the initiation kinetics, catalyst **3** in methanol was irradiated with Blue LEDs for 17 h (Figure S6). Next, aldehyde **6** was added and the reaction was placed in the dark. The reaction reached completion in less than 2 h. This suggests that a strongly acidic species is generated and persists in the absence of further irradiation.
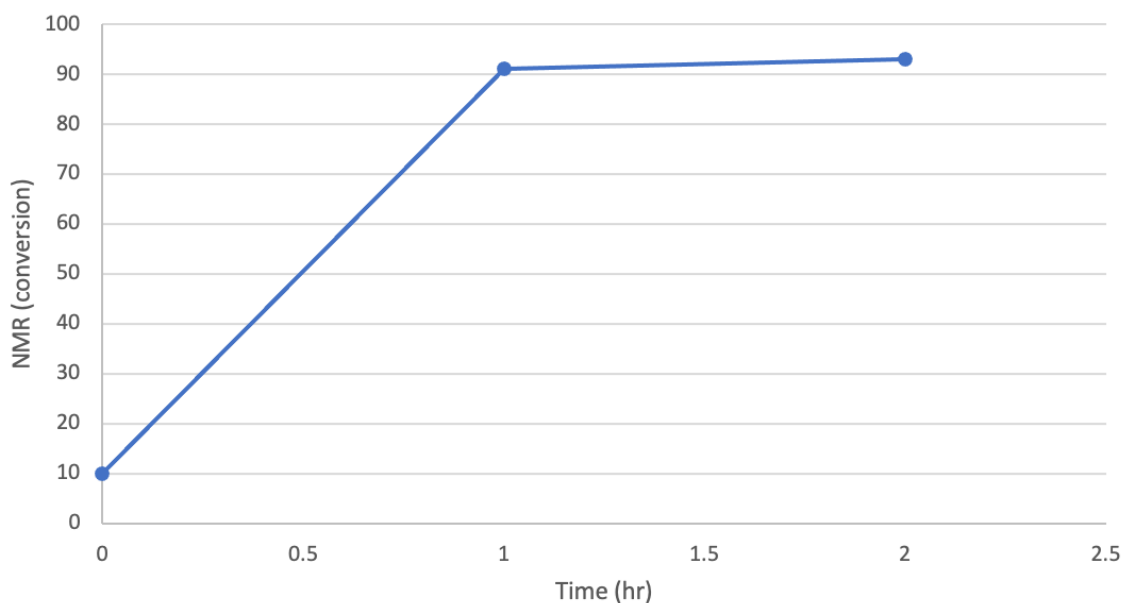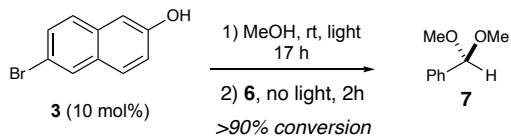
Figure S6: Reaction run with 0.05 mmol **3** and 0.5 mmol **6** in methanol (0.5 M) under argon atmosphere. Aliquots were taken using a BD spinal needle and %conversion of **6** to **7** was determined by NMR spectroscopy.

To test the reversibility of strong acid formation, catalyst **3** was irradiated in methanol for 24 h (Figure S7). The reaction was then placed in the dark for 26 h. Next, **6** was added, and the reaction was left to stir in the dark until complete. Despite having stirred in the dark for 26 h, the reaction still finished in less than 2 h, indicating the formation of a persistent strongly acidic species is not reversible.
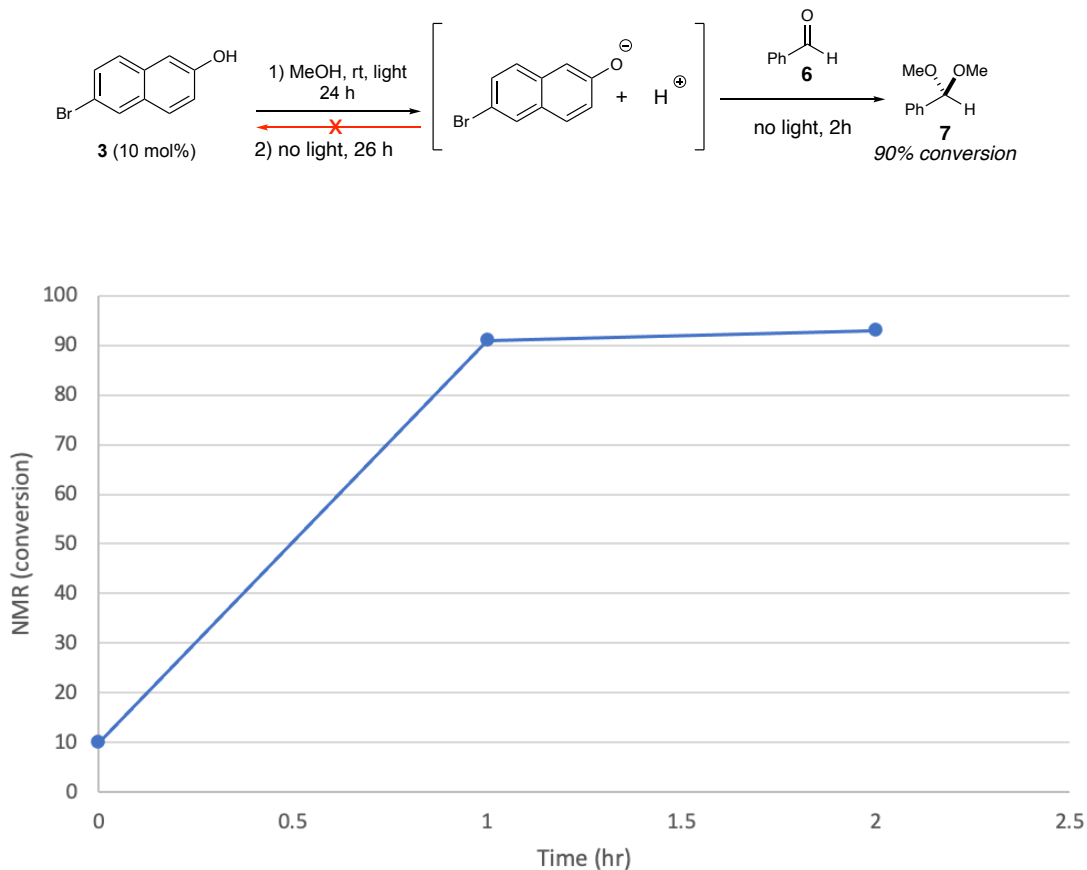
Figure S7: Reaction run with 0.05 mmol **3** and 0.5 mmol **6** in methanol (0.5 M) under argon atmosphere. Aliquots were taken using a BD spinal needle and %conversion of **6** to **7** was determined by NMR spectroscopy.

The hydroxyl peak of catalyst **3** in the absence of aldehyde **6** is shown in Figure S8, A. Upon the addition of **6** the OH-peak broadens slightly and shifts downfield from 5.17 ppm to 6.13, suggesting the formation of an H-bonding complex between **3** and **6** (Figure S8, B). After 5 h irradiation with Blue LEDs, the OH-peak of **3** significantly broadens and shifts from 6.13 to 6.20 ppm, suggesting enhanced hydrogen bonding upon irradiation (Figure S8, C). Finally, after 21 h irradiation, the OH-peak further shifts to 6.31 ppm (Figure S8, D). This is evidence that prolonged irradiation results in further generation of a strongly acidic species.
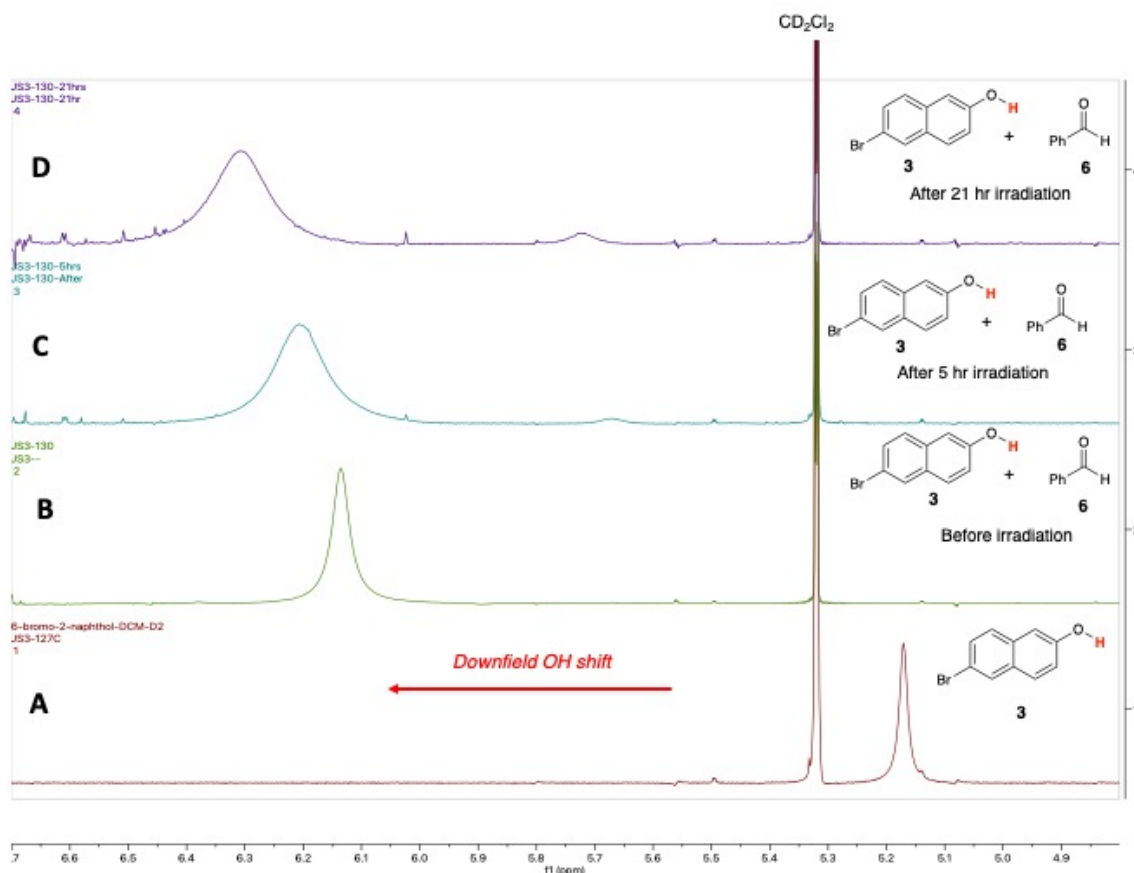
Figure S8: ^{1}H NMR spectra showing the hydroxy chemical shift of **3** compared to a 1:1 mixture of **3** and **6** before and after 5 h and 21 h irradiation with Blue LEDs (0.25 M in CD$_2$Cl$_2$).

The aromatic region for catalyst **3** and aldehyde **6** is shown in Figure S9, A and B. Up mixing of **3** and **6**, the peaks broaden, suggesting formation of an H-bonding complex (Figure S9, C). Notably, the catalyst peaks at 7.11 ppm shift down filed by ~0.05 ppm. After 18 h irradiation with Blue LEDs, the aromatic region shows little change (Figure S9, D).
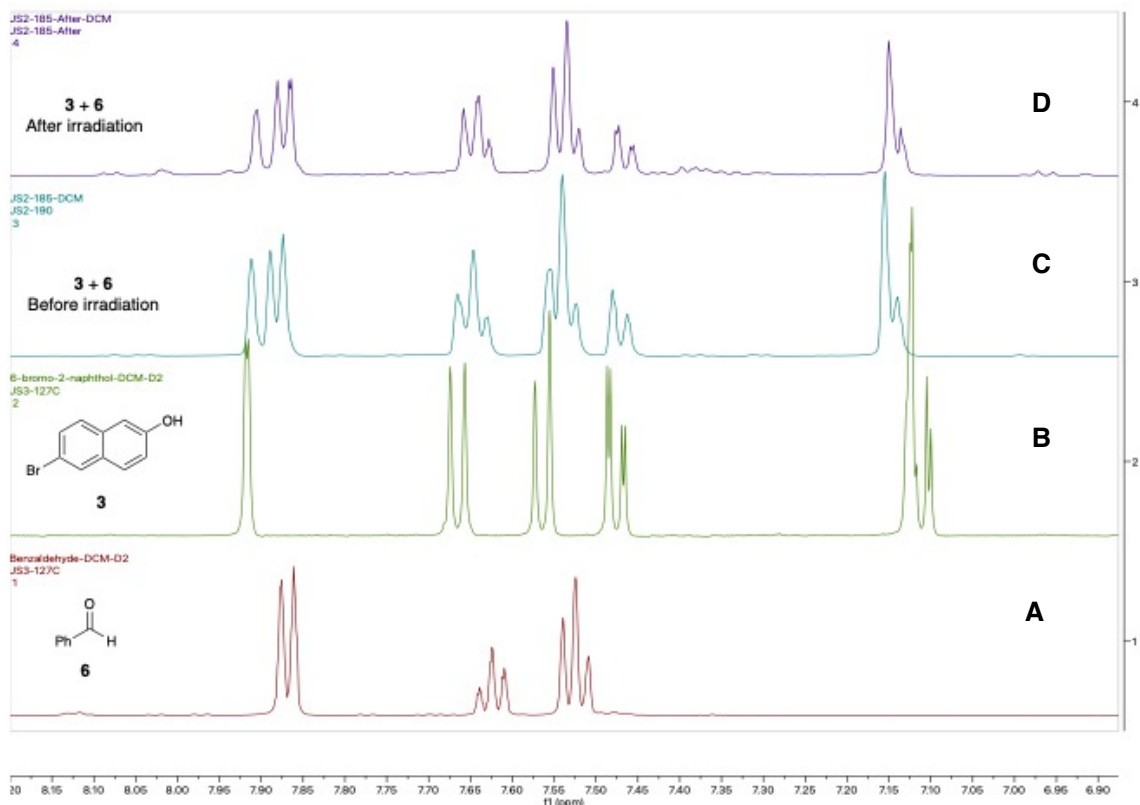
Figure S9: NMR spectra showing the aromatic region of **3** and **6** compared to of a 1:1 mixture of **3** and **6** before and after 18 h irradiation with Blue LEDs (0.25 M in CD_2Cl_2).

VII. Determination of the excited state pKas and excited state lifetimes for catalysts 3 and 5:[13,14,15]

<u>2-naphthol (**5**):</u>

The following aqueous stock solutions were prepared:
- 1 mg in 50 mL; 2-naphthol (2-Nap) solution
- 0.10 M HCl
- 0.10 M NaOH
- 0.20 M 1:1 NH_3-NH_4Cl buffer solution

Afterward, the solutions being analyzed were prepared in the following ratio:
- Acidic Solution: 10 mL of HCl solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water
- Basic Solution: 10 mL of NaOH solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water
- Buffer Solution: 10 mL of Buffer solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water

The pH for those solutions were as follows (measured by Vernier Go Direct™ Electrode Amplifier):
- Acidic: 1.7
- Basic: 12.33
- Buffer: 9.48

[13] Marciniak, B.; Kozubek, H.; Paszyc, S. *J. Chem. Ed.* **1992**, *69*, 247.
[14] Park, H.-R.; Mayer, B.; Wolschann, P.; Koehler, G. *J. Phys. Chem.* **1994**, *98*, 6158.
[15] Rosenberg, J. L.; Brinn, I. *J. Phys. Chem.* **1972**, *76*, 3558.

The three solutions were analyzed using UV-Vis (Figure S10) and fluorometer (Figure S11).
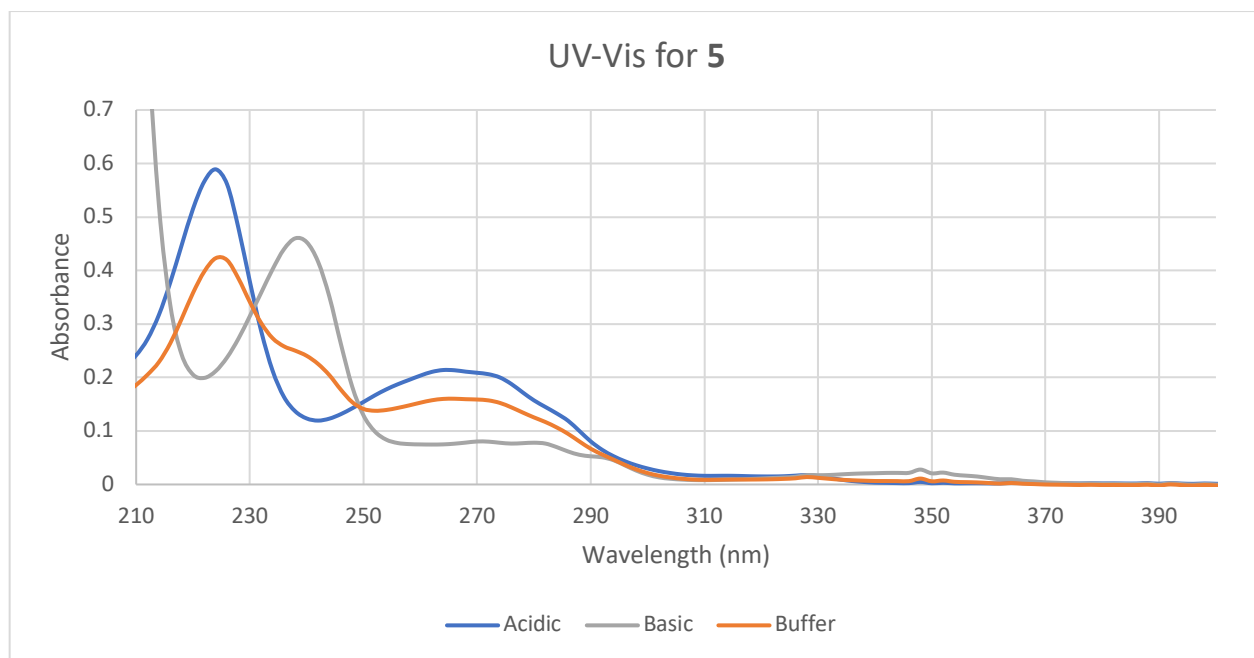
Figure S10: UV-Vis for the acidic, basic, and buffer solutions of **5**.
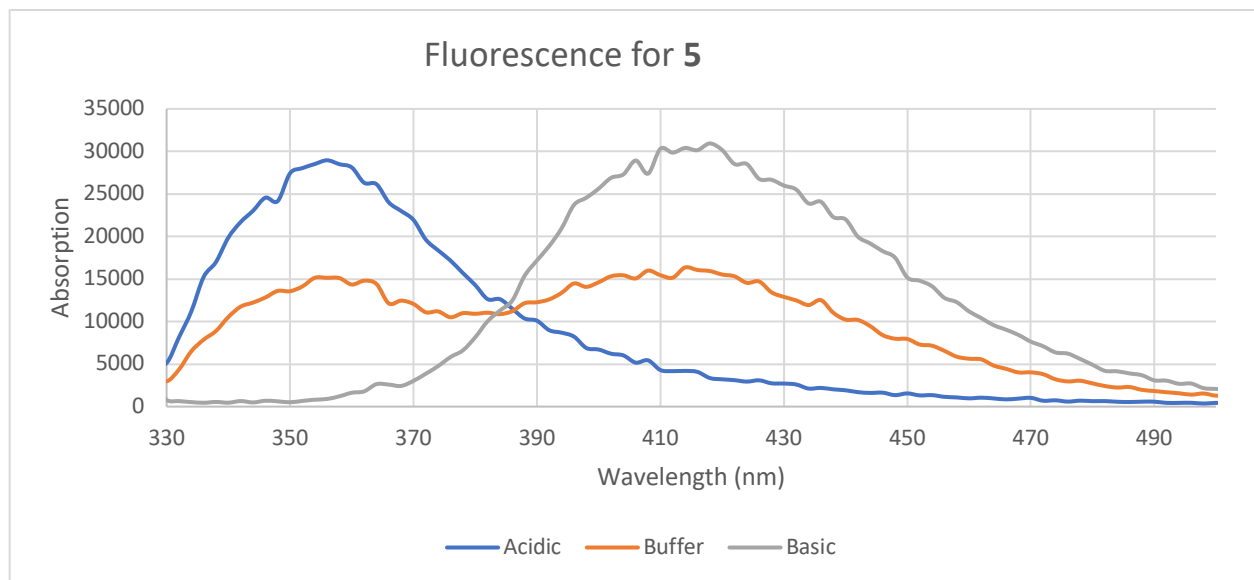
Figure S11: Fluorescence spectra for the acidic, basic, and buffer solutions of **5** (Excitation wavelength: 331 nm).

From the acidic and basic solutions, the 0-0 energy was able to be calculated by overlaying the UV-Vis and fluorometer graphs (Figures S12 and S13).
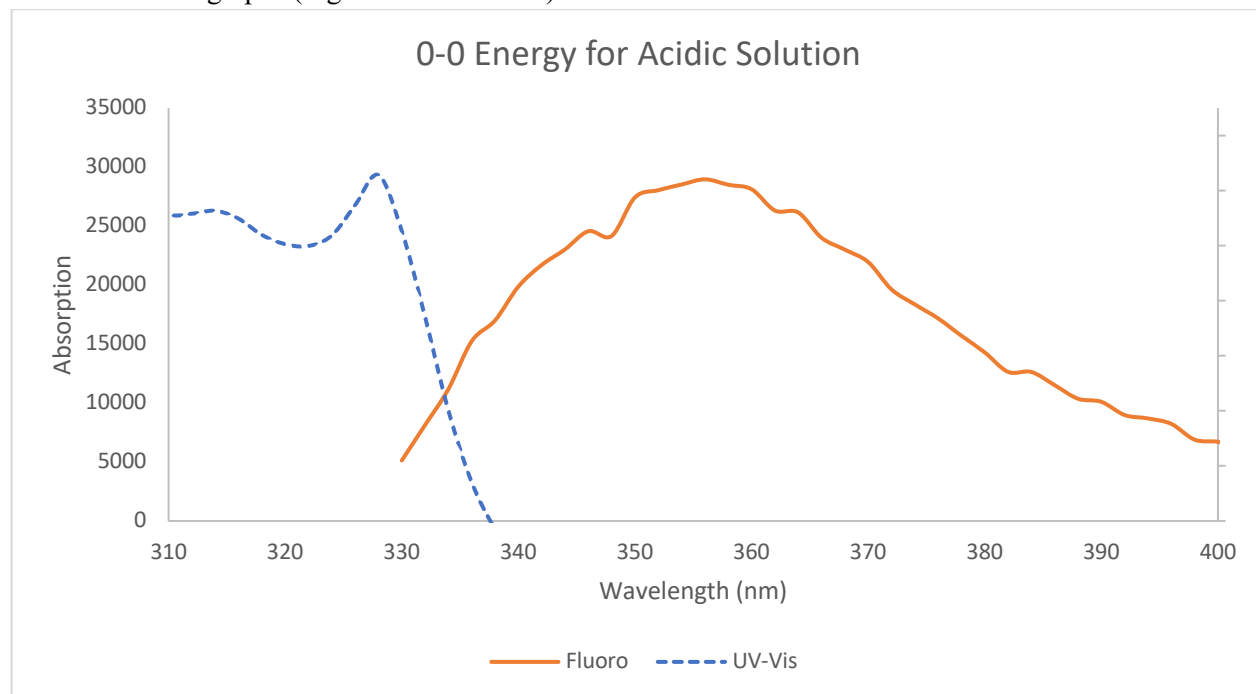
Figure S12: Fluorescence and UV-Vis overlay of the acidic solution for **5** (Excitation wavelength: 331 nm).

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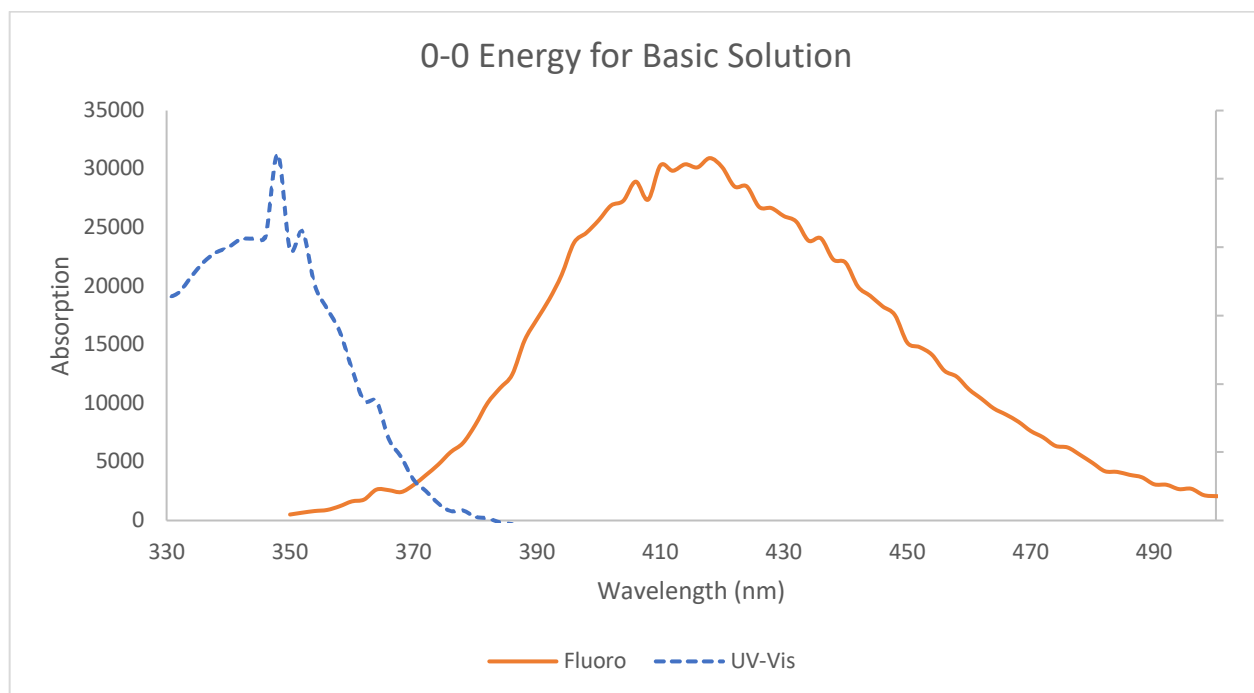
Figure S13: Fluorescence and UV-Vis spectra overlay of the basic solution for **5** (Excitation wavelength: 331 nm).

The following calculations were performed to determine pKa and pKa*:

To begin we must figure out the concentration of the analyte in the three solutions being tested;

$$M_1V_1=M_2V_2$$
$$(1.388x10^{-4}M)(5 \text{ mL})=M_2(50 \text{ mL})$$
$$M_2= 1.388x10^{-5}M=c_o$$

We must also calculate the molar absorptivity (ε) of the acidic and basic forms of 2-naphthol at the wavelength of maximum absorbance for the **conjugate base** form from UV-Vis graphs:

$$A=\varepsilon bc_o$$

$c_o= 1.388x10^{-5}M$

$b = 1$ cm

$A_{238(NOH)}=.137$

$A_{238(NO-)}=.460$

$$\varepsilon_{(NOH)}= \frac{.137}{(1.388x10^{-5})}= 9876.317$$

$$\varepsilon_{(NO-)}= \frac{.460}{(1.388x10^{-5})}= 33141.21$$

Afterward, we can calculate the concentration of the (NOH) and (NO⁻) in the buffer using the absorbance at the wavelength used previously and the following equations:

$$A = (\varepsilon_{NOH} - \varepsilon_{NO^-})\,[NOH] + (\varepsilon_{NO^-})c_o$$

and

$$c_o = [NOH] + [NO^-]$$

$A_{238(Buffer)} = .250$

$\varepsilon_{(NOH)} = 9876.317$

$\varepsilon_{(NO^-)} = 33141.21$

$c_o = 1.388x10^{-5}M$

$$[NOH] = \frac{A - ((\varepsilon NO-)co)}{(\varepsilon NOH - \varepsilon NO-)}$$

$$[NOH] = \frac{.25 - ((33141.21)(1.388x10^{-5}))}{(9876.317 - 33141.21)}$$

$$[NOH] = (9.026x10^{-6}M)$$

$$c_o - [NOH] = [NO^-]$$

$$(1.388x10^{-5}M) - (9.026x10^{-6}M) = (4.854x10^{-6}M)$$

pK_a for the buffered solution was determined using the following equation:

$$pK_a = pH + \log\left(\frac{[NOH]}{[NO^-]}\right)$$

$$pK_a = 9.48 + \log\left(\frac{[9.026x10^{-6}M]}{[4.854x10^{-6}M]}\right)$$

$$pK_a = 9.75$$

Next you must first determine the wavelength at which the two graphs intersect in the overlay for both the acidic and basic solutions:

0-0 energy of acidic solution: 332 nm

0-0 energy of basic solution: 370 nm

Afterward, use this equation to determine the corresponding wavenumbers (ϑ_{OH} & ϑ_{NO^-}):

$$\vartheta = \left(\frac{10^7}{wavelength\ (nm)}\right)$$

$\vartheta_{OH} = 30120\ \text{cm}^{-1}$

$\vartheta_{NO^-} = 27027\ \text{cm}^{-1}$

To calculate the $pK_a{}^*$ the following forster equation was used:

$$pK_a{}^* = pK_a - \left(\frac{[N_o hc]}{[2.303RT]}\right)(\vartheta_{OH} - \vartheta_{NO^-})$$

ϑ = wavenumber based on 0-0 energy for acidic and basic solutions

N_o = Avagrado's number = $(6.022 x 10^{23})$

h = Planck's constant = $(6.626 x 10^{-34})$

c = speed of light (cm) = $(3 x 10^{10})$

R = Gas Constant = 8.3145

T = Room Temp (K) = 298

$$pK_a{}^* = 9.75 - \left(\frac{[(6.022 x 10^{23})(6.626 x 10^{-34})(3 x 10^{10})]}{[2.303(8.3145)(298)]} \right)(30120 - 27027)$$

$$pK_a{}^* = 3.26$$

6-bromo-2-naphthol (**3**):

The following aqueous stock solutions were prepared:
- 1 mg in 50 mL; 6-Bromo-2-Naphthol (6-Bromo) solution
- 0.10 M HCl
- 0.10 M NaOH
- 0.20 M 1:1 NH_3-NH_4Cl buffer solution

Afterward, the solutions being analyzed were prepared in the following ratio:
- Acidic Solution: 10 mL of HCl solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water
- Basic Solution: 10 mL of NaOH solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water
- Buffer Solution: 10 mL of Buffer solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water

The pH for those solutions were as follows:
- Acidic: 1.73
- Basic: 12.45
- Buffer: 9.51

The three solutions were analyzed using UV-Vis and Fluorometer (Figures S14 and S15):
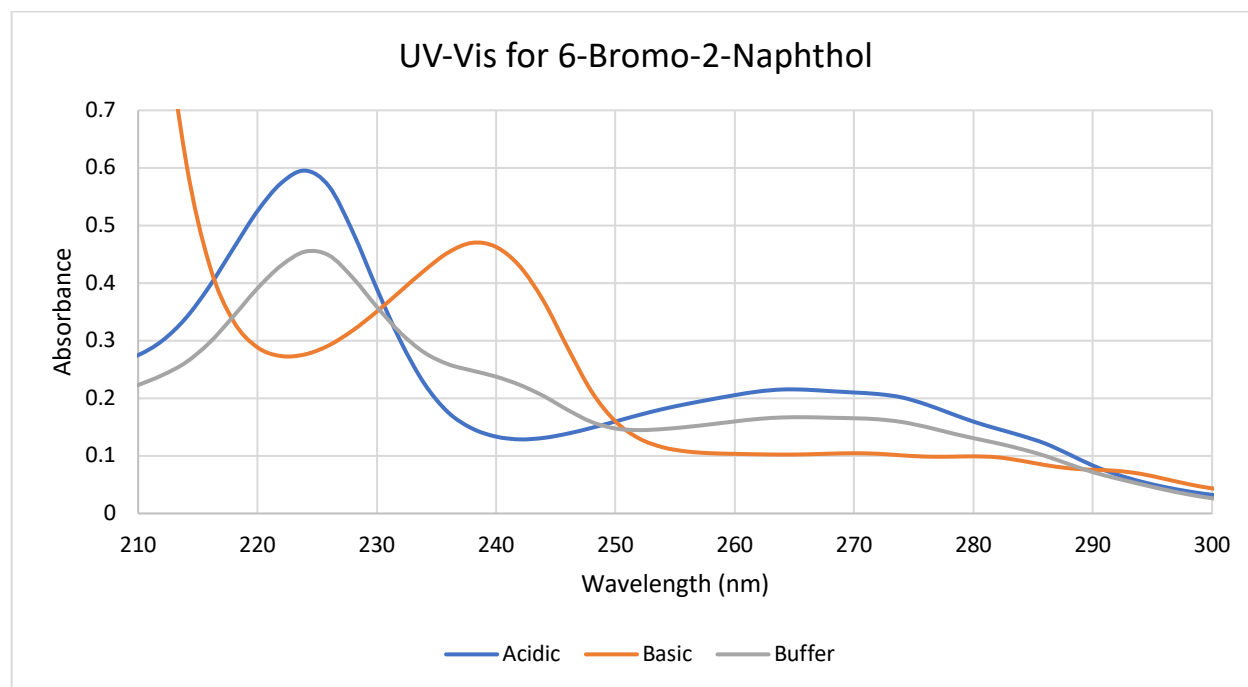
Figure S14: UV-Vis for the Acidic, Basic, and Buffer solutions of **3**.
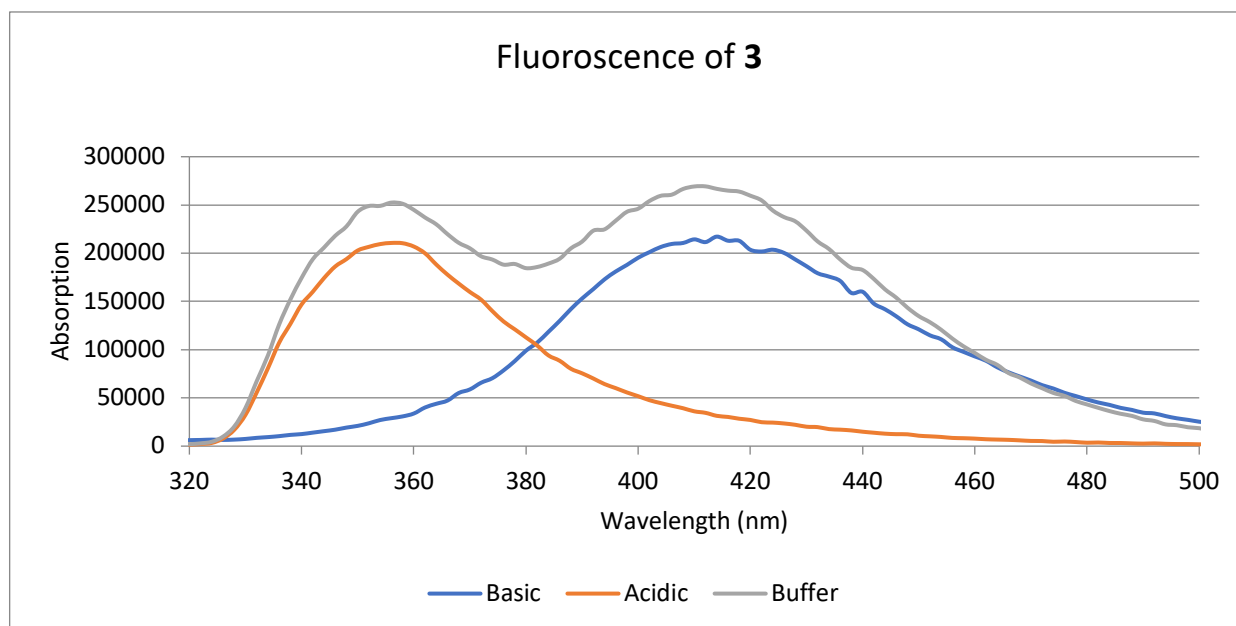
Figure S15: Fluorescence spectra for the acidic, basic, and buffer solutions of **3**.

The 0-0 energy was calculated by overlaying the UV-Vis and fluorometer graphs for the acidic (Figure S16) and basic (Figure S17) solutions (Excitation wavelength: 274 nm).
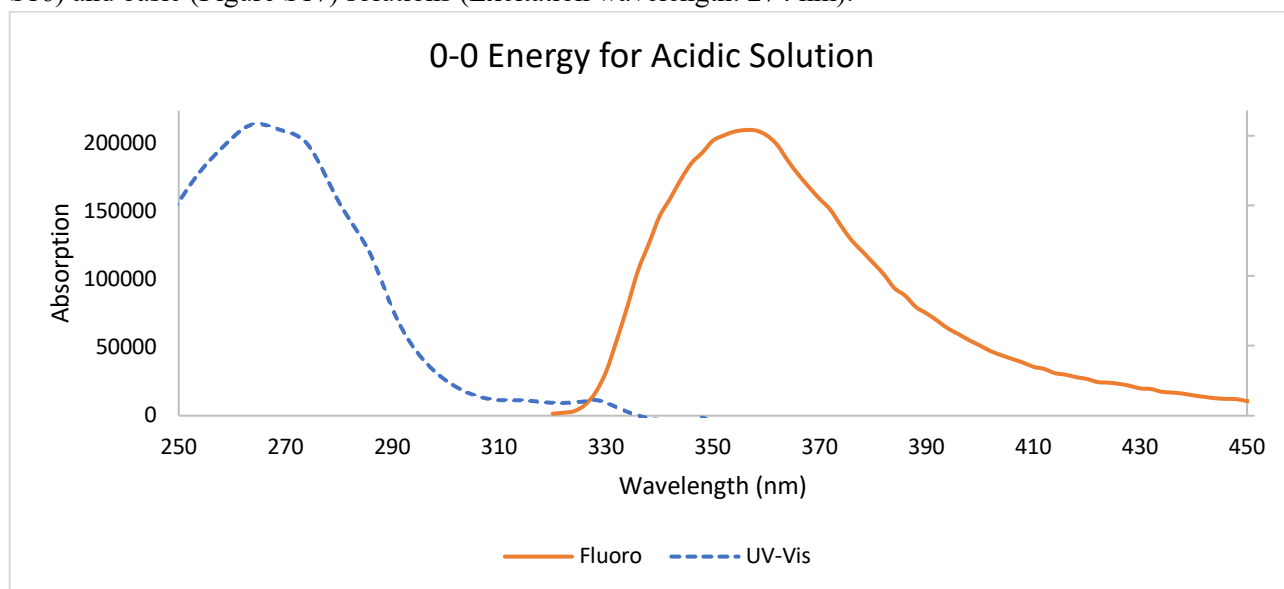
Figure S16: Fluorescence and UV-Vis overlay of the acidic solution for **3** (Excitation wavelength: 274 nm).
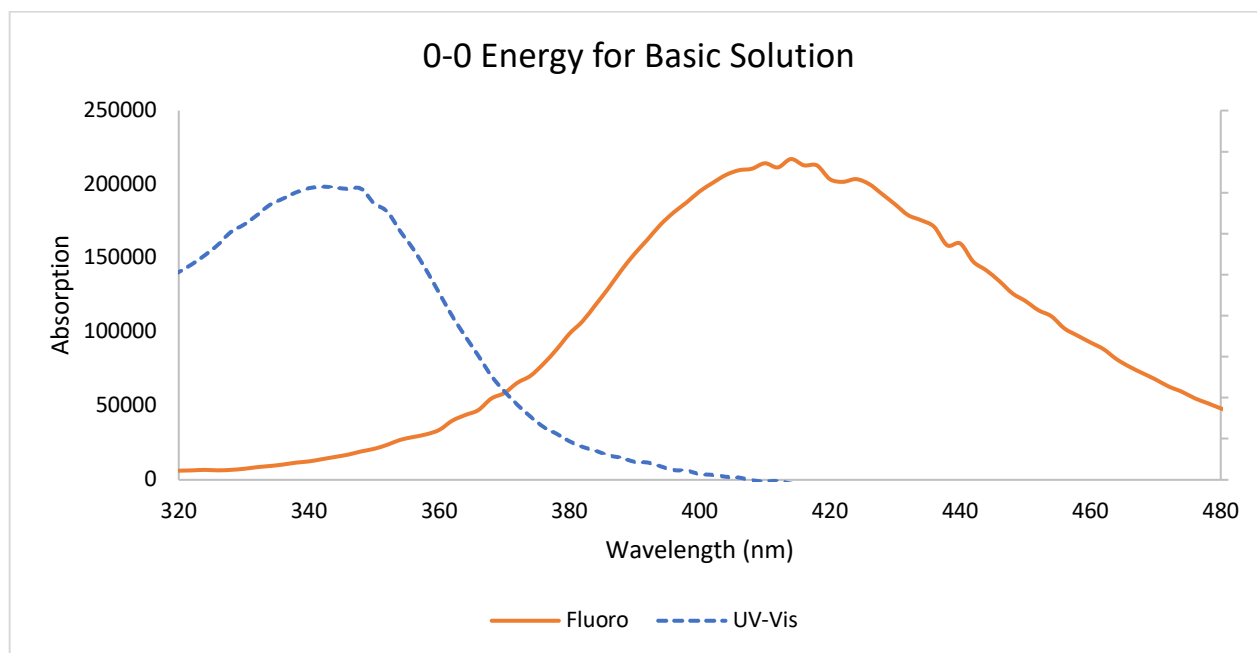
Figure S17: Fluorescence and UV-Vis spectra overlay of the basic solution for **3** (Excitation wavelength: 274 nm).

The following calculations were performed to determine pKa and pKa*:

To begin we must figure out the concentration of the analyte in the three solutions being tested;

$$M_1V_1=M_2V_2$$
$$(8.97 \times 10^{-4}M)(5 \text{ mL})=M_2(50 \text{ mL})$$
$$M_2= 8.97 \times 10^{-5}M=c_o$$

We must also calculate the molar absorptivity (ε) of the acidic and basic forms of 6-Bromo-2-naphthol at the wavelength of maximum absorbance for the **conjugate base** form from UV-Vis graphs:

$$A=\varepsilon b c_o$$

$c_o= 8.97 \times 10^{-5}M$
$b = 1 \text{ cm}$
$A_{238(NOH)}=.147$
$A_{238(NO-)}=.469$

$$\varepsilon_{(NOH)}= \frac{.147}{(8.97 x 10^{-5})} = 1638.796$$

$$\varepsilon_{(NO-)}= \frac{.469}{(8.97 x 10^{-5})} = 5228.539$$

Afterwards we can calculate the concentration of the (NOH) and (NO⁻) in the buffer using the absorbance at the wavelength used previously and the following equations:

$$A = (\varepsilon_{NOH} - \varepsilon_{NO^-})[NOH] + (\varepsilon_{NO^-})c_o$$

and

$$c_o = [NOH] + [NO^-]$$

$A_{238(Buffer)} = .250$
$\varepsilon_{(NOH)} = 1638.796$
$\varepsilon_{(NO^-)} = 5228.539$
$c_o = 8.97x10^{-5}M$

$$[NOH] = \frac{A - ((\varepsilon NO-)co)}{(\varepsilon NOH - \varepsilon NO-)}$$

$$[NOH] = \frac{.25 - ((5228.539)(8.97x10^{-5}))}{(1638.796 - 5228.539)}$$
$$[NOH] = (6.101x10^{-5}M)$$

$$c_o - [NOH] = [NO^-]$$
$$(8.97x10^{-5}M) - (6.101x10^{-5}M) = (2.87x10^{-5}M)$$

pKₐ for the buffered solution was determined using the following equation:

$$pK_a = pH + \log\left(\frac{[NOH]}{[NO^-]}\right)$$

$$pK_a = 9.51 + \log\left(\frac{[6.101x10^{-5}M]}{[2.87x10^{-5}M]}\right)$$

$$pK_a = 9.84$$

Next, you must first determine the wavelength at which the two graphs intersect in the overlay for both the acidic and basic solutions:

1-0 energy of acidic solution: 328 nm

1-0 energy of basic solution: 374 nm

Afterwards use this equation to determine the corresponding wavenumbers (ϑ_{OH} & ϑ_{NO^-}):

$$\vartheta = \left(\frac{10^7}{wavelength\ (nm)}\right)$$

$\vartheta_{OH} = 30487.8$ cm^{-1}

$\vartheta_{NO^-} = 26737.97$ cm^{-1}

To calculate the pK$_a$* the following forster equation was used:

$$pK_a{}^* = pK_a - \left(\frac{[N_o hc]}{[2.303RT]}\right)(\vartheta_{OH} - \vartheta_{NO^-})$$

ϑ = wavenumber based on 0-0 energy for acidic and basic solutions

N$_o$ = Avagrado's number = $(6.022x10^{23})$

h = Planck's constant = $(6.626x10^{-34})$

c = speed of light (cm) = $(3x10^{10})$

R = Gas Constant = 8.3145

T = Room Temp (K) = 298

$$pK_a{}^* = 9.84 - \left(\frac{[(6.022x10^{23})(6.626x10^{-34})(3x10^{10})]}{[2.303(8.3145)(298)]}\right)(30487.8 - 26737.97\,)$$

$$pK_a{}^* = 1.976$$

The singlet excited-state lifetimes for 2-naphthol (**5**, τ = 6.8 ns) and 6-bromo-2-naphthol (**3**, τ = 0.049 ns) were measurements in 80% ethanol (Figures S18 and S19). The short-lived S_1 excited state for **3** is attributed to rapid intersystem crossing into a triplet excited state (not measured) due to the heavy atom effect (bromine).
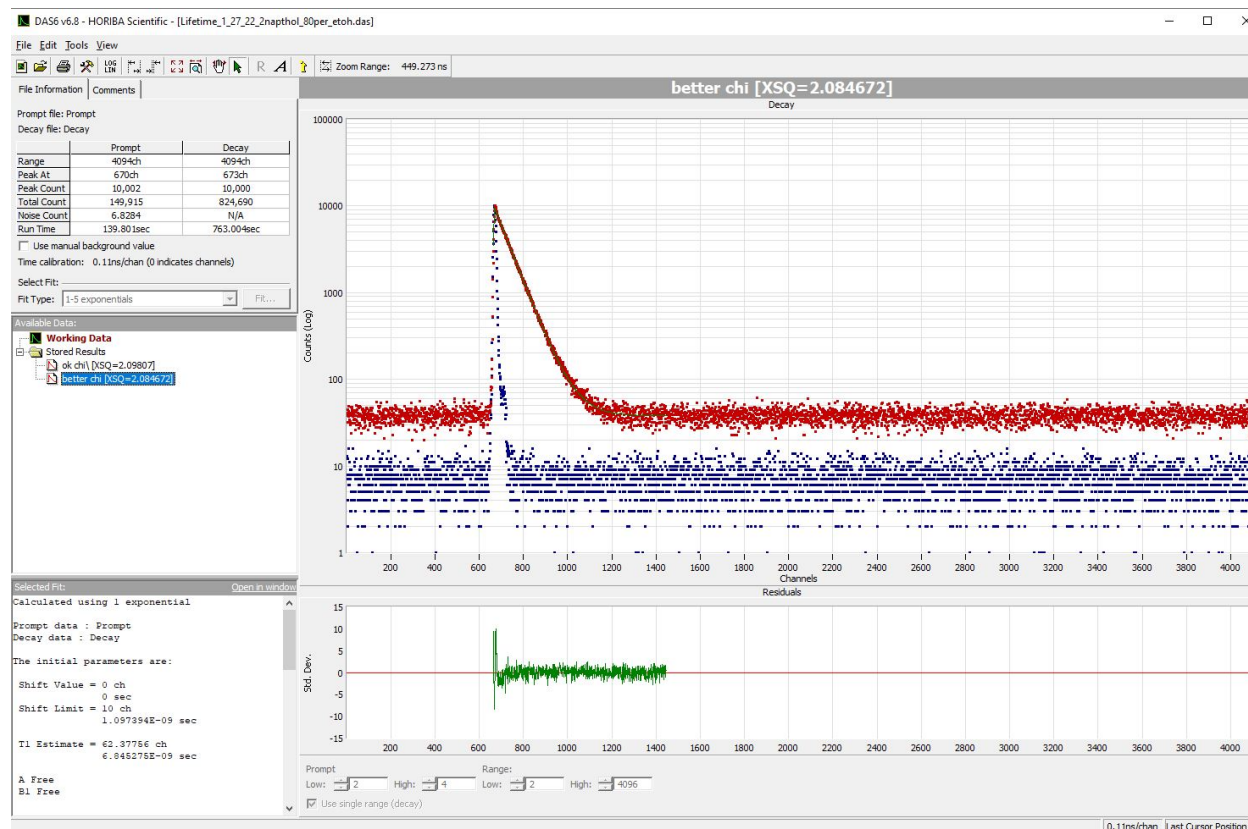
Scheme S18: Singlet excited-state spectrum for 2-naphthol (**5**) in 80% ethanol.
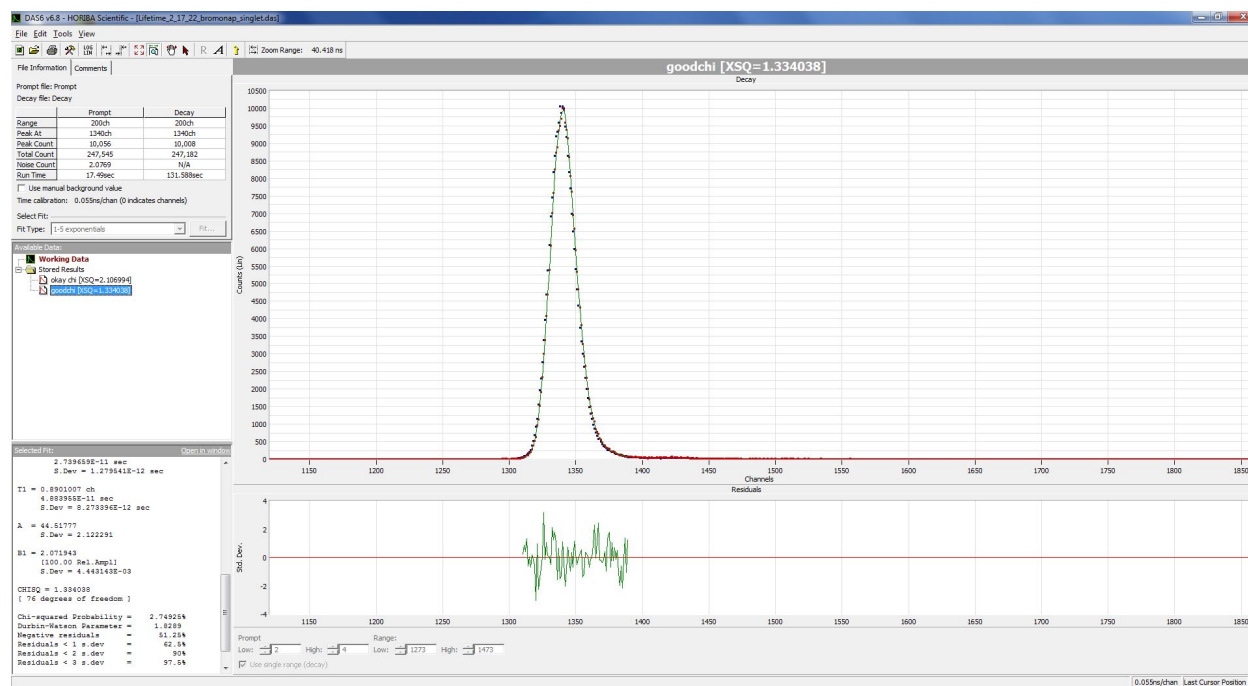
Scheme S19: Singlet excited-state spectrum for 6-bromo-2-naphthol (**3**) in 80% ethanol.

VIII. Kessil LED set-up and emission spectra:

The general setup for the photoacid catalyzed procedure is shown in Figure S20.
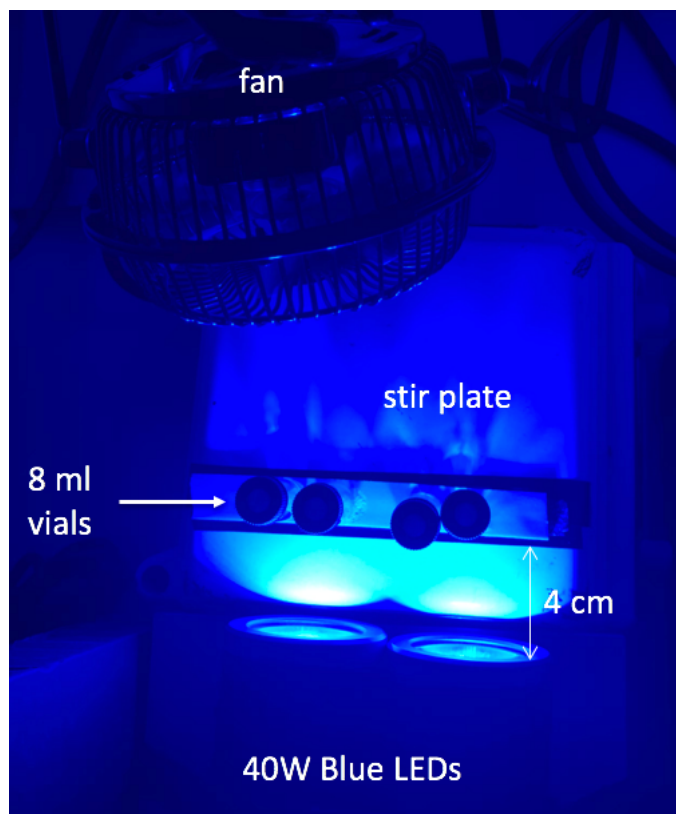
Figure S20: General reaction setup.

We thank Kessil (https://kessil.com/science/PR160L.php) for providing the emission spectra for the PR160L - 370 nm, 456 nm, 390 nm, and 160WE 40W Tuna Blue LEDs shown in Figures S21- S24, respectively. The Tuna Blue LEDs used in this study emit strongly from 408-535 nm with weak emission from 372-390 nm. Note: Tuna Blue LEDs are used with %blue and intensity settings maximized.

PR160L- 370 nm Spectrum
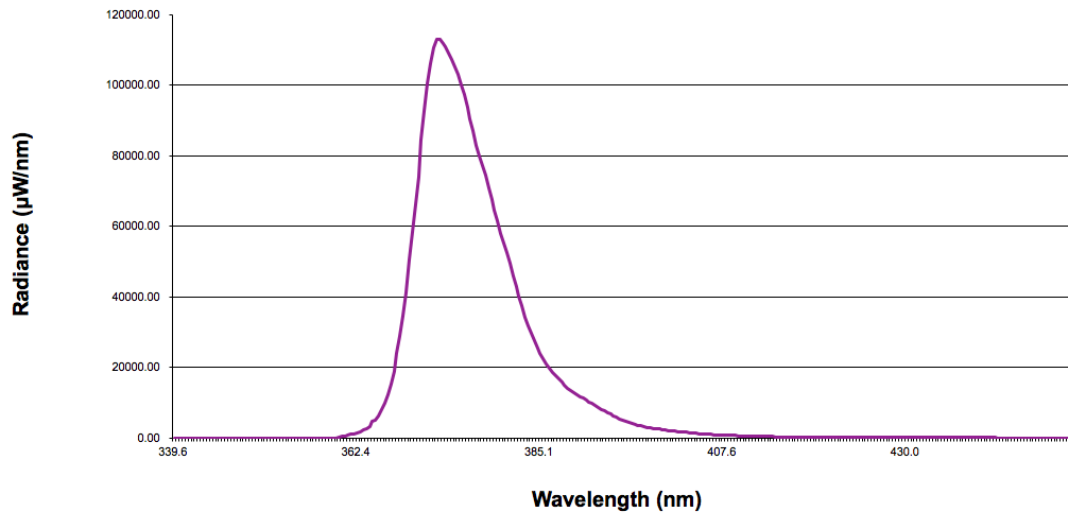
Figure S21: Emission spectrum for Kessil 370 nm LEDs.

PR160L-456 Spectrum
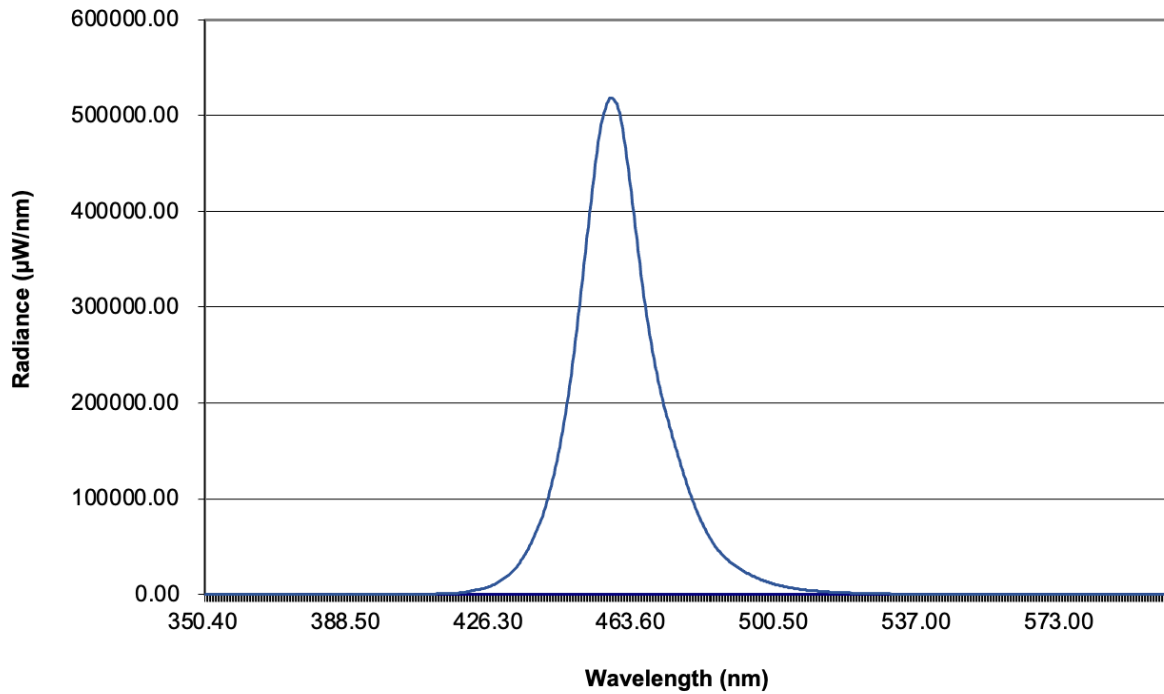
Figure S22: Emission spectrum for Kessil 456 nm LEDs.

PR160L-390 Spectrum
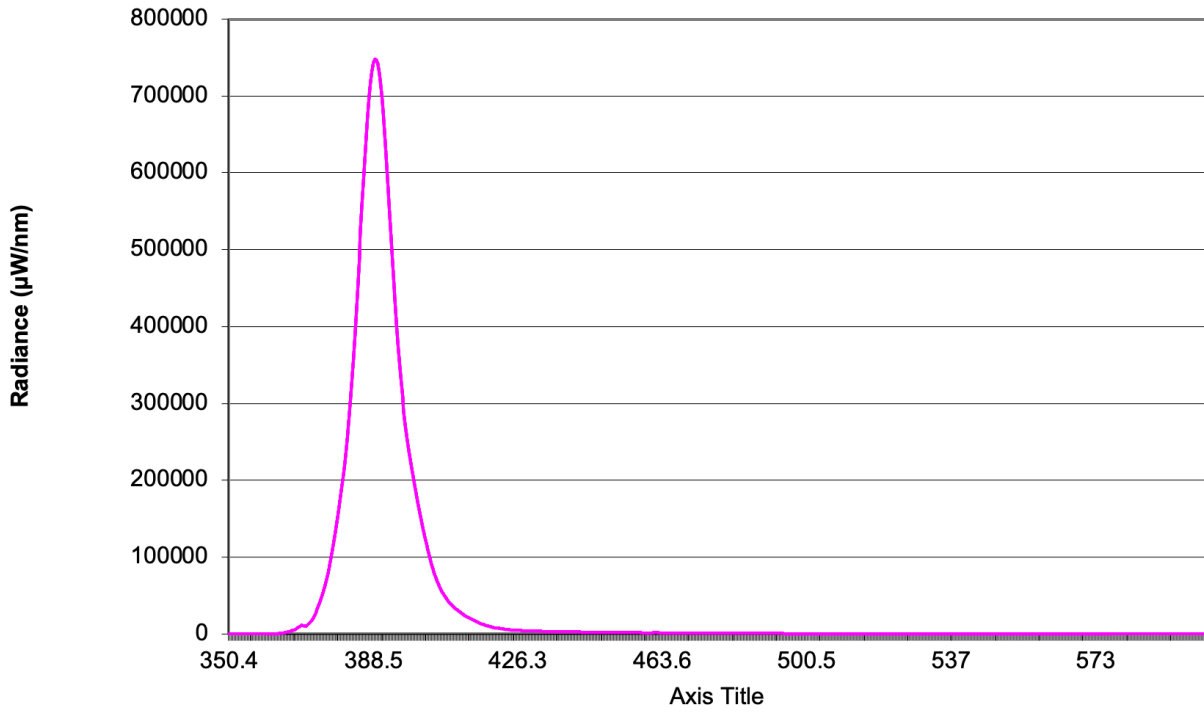
Figure S23: Emission spectrum for Kessil 390 nm LEDs.

A160WE 40W Tuna Blue LED Emission Spectrum
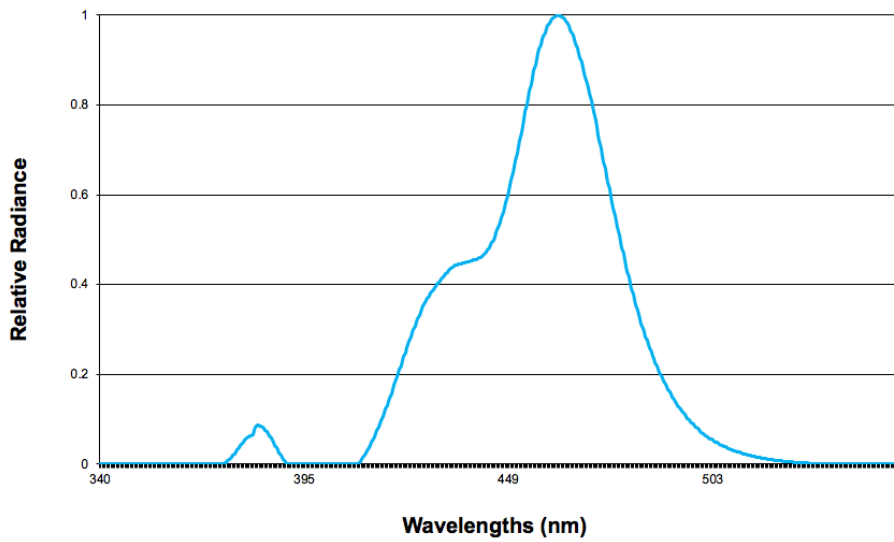
Figure S24: Emission spectrum for Kessil Tuna Blue LEDs. Note: This is the "deep ocean" emission spectrum provided by Kessil.

IX. Spectra:

OMe

OMe

500 MHz, CDCl$_3$

7

1.97 3.08 1.00 6.33

f1 (ppm)

13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
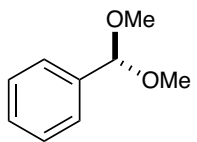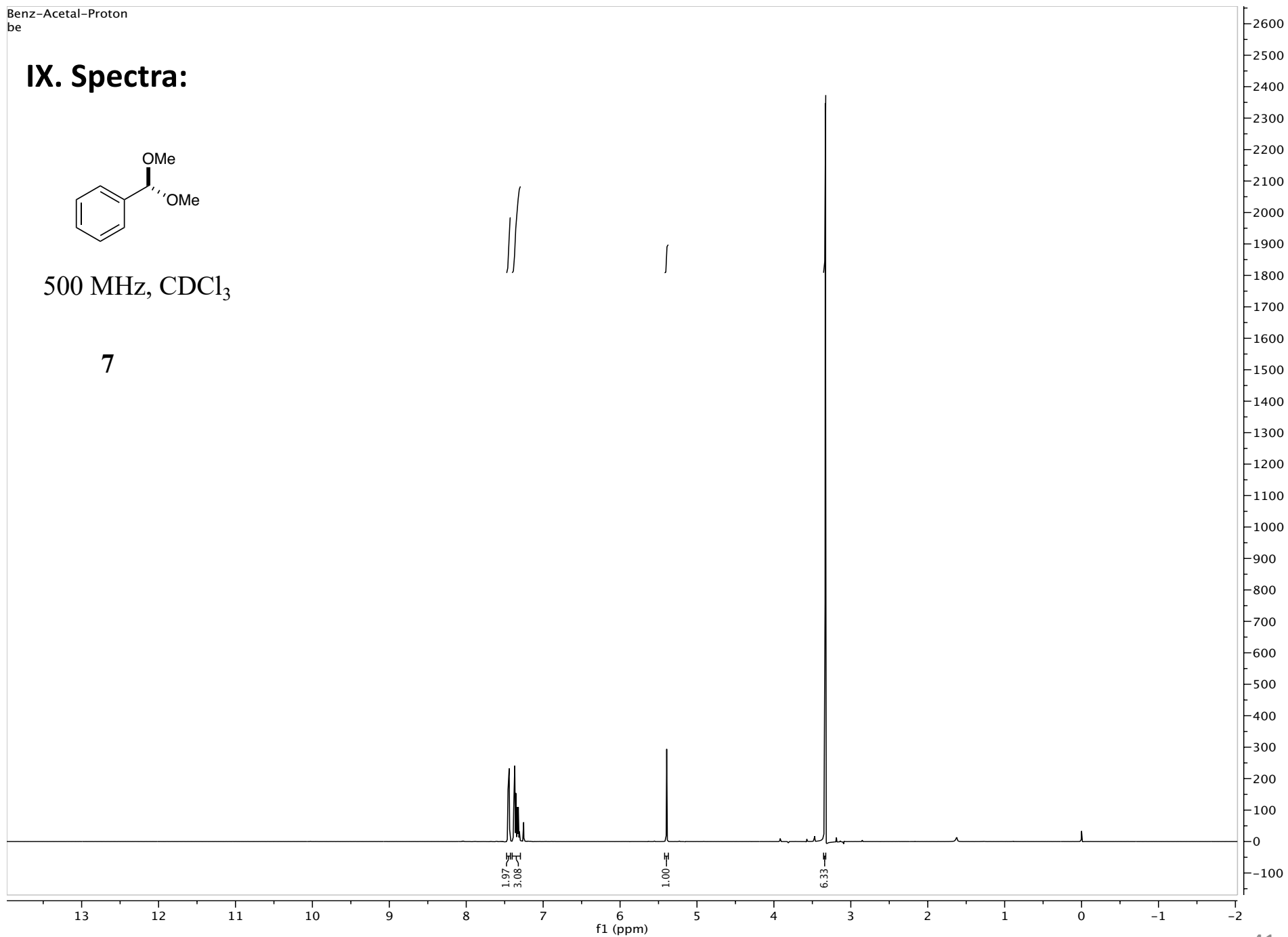
Cyano–Acetal–Retake
Cyano

500 MHz, CDCl$_3$

OMe
OMe

NC

8

Cyano–Acetal–Carbon–Final

125 MHz, CDCl$_3$

143.31
132.22
127.71
118.84
112.43
101.85
52.83

8

f1 (ppm)
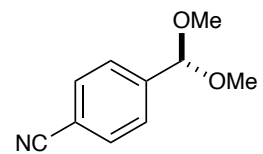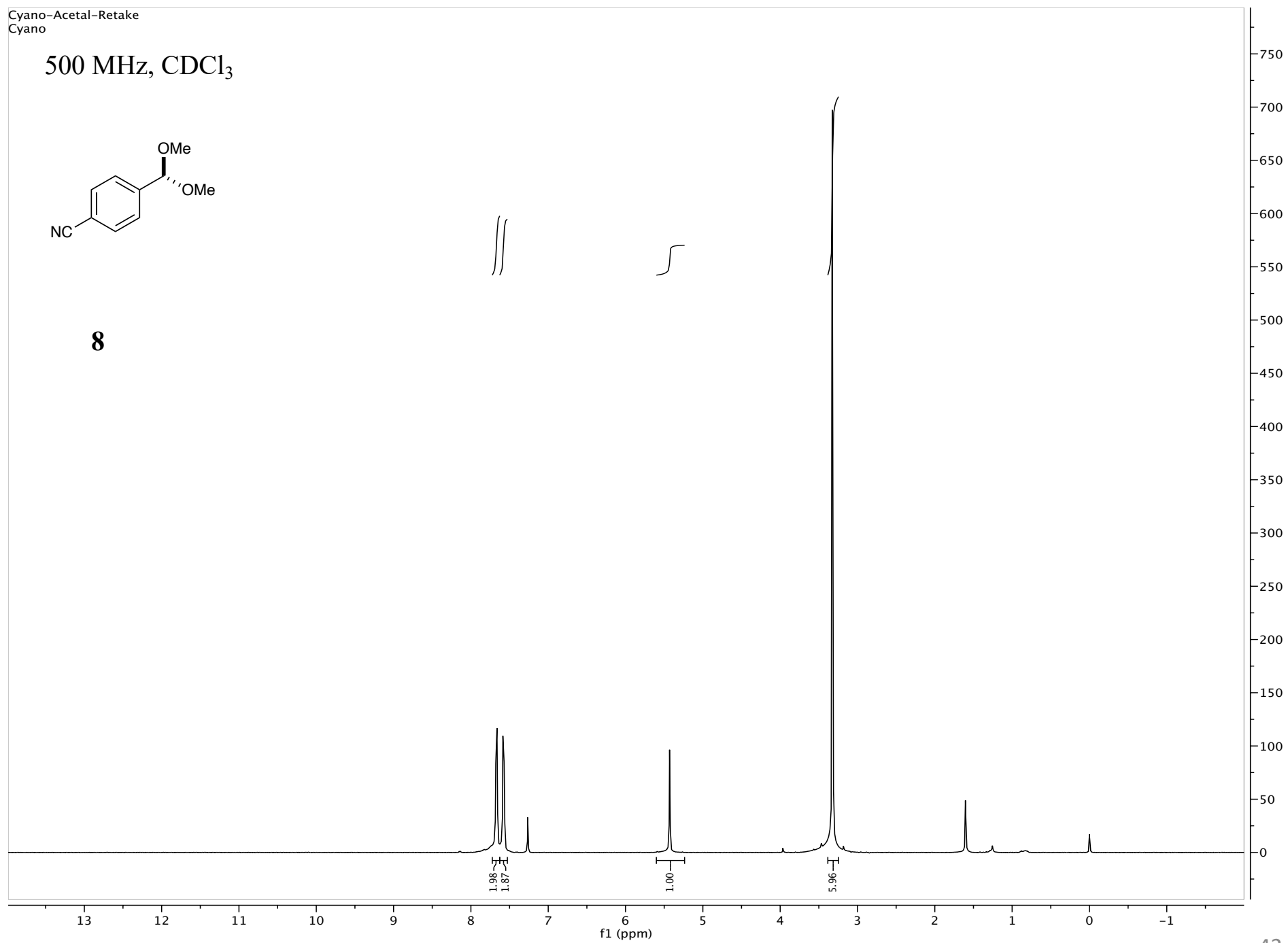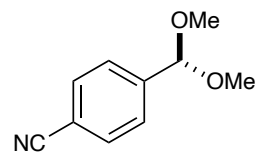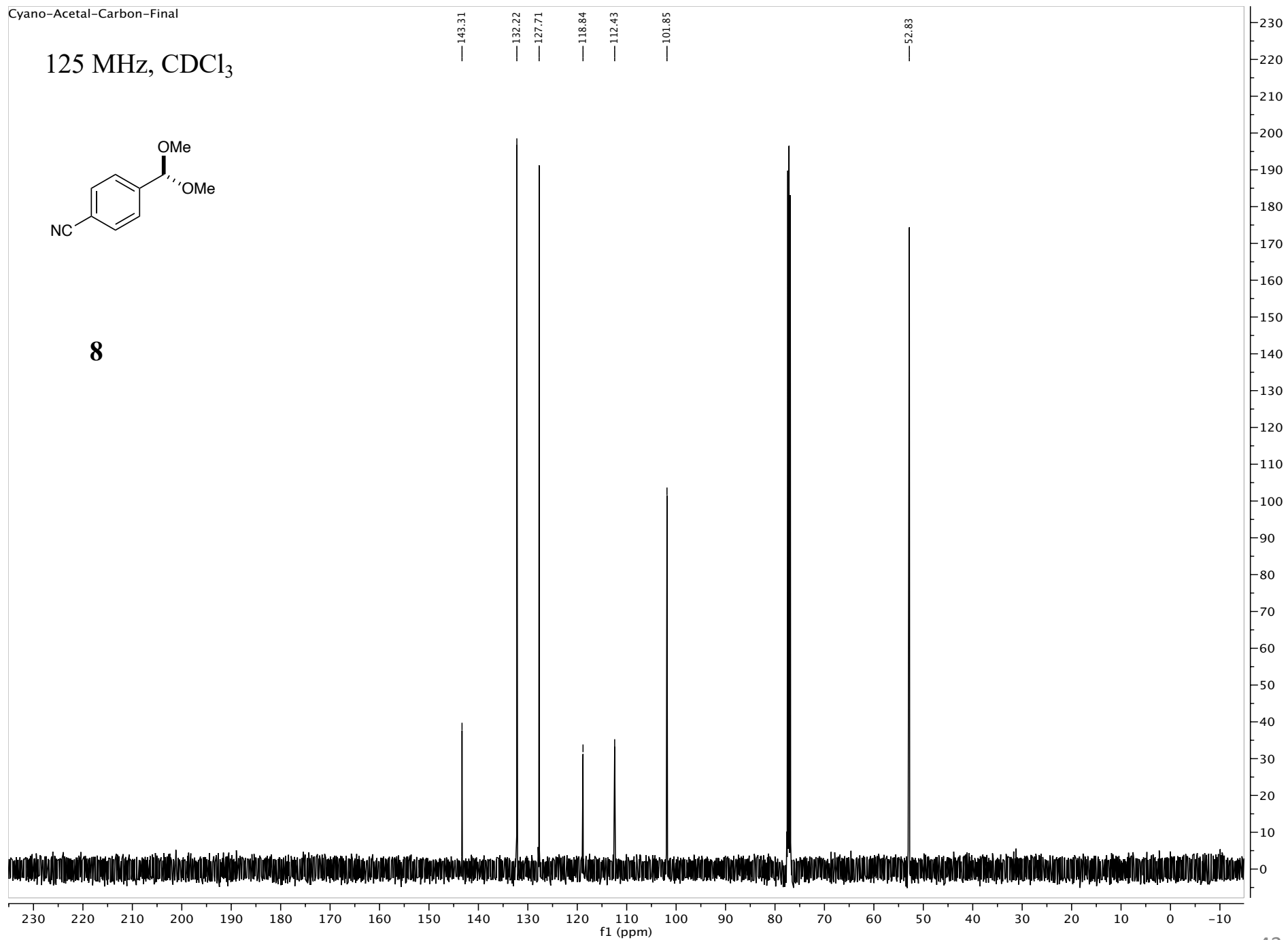
Keto–Acetal–Proton–New
Ke

500 MHz, CDCl$_3$

9

2.04 2.00 1.00 6.53 3.22

f1 (ppm)
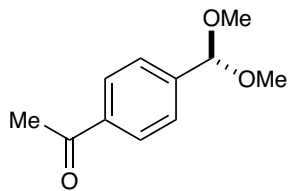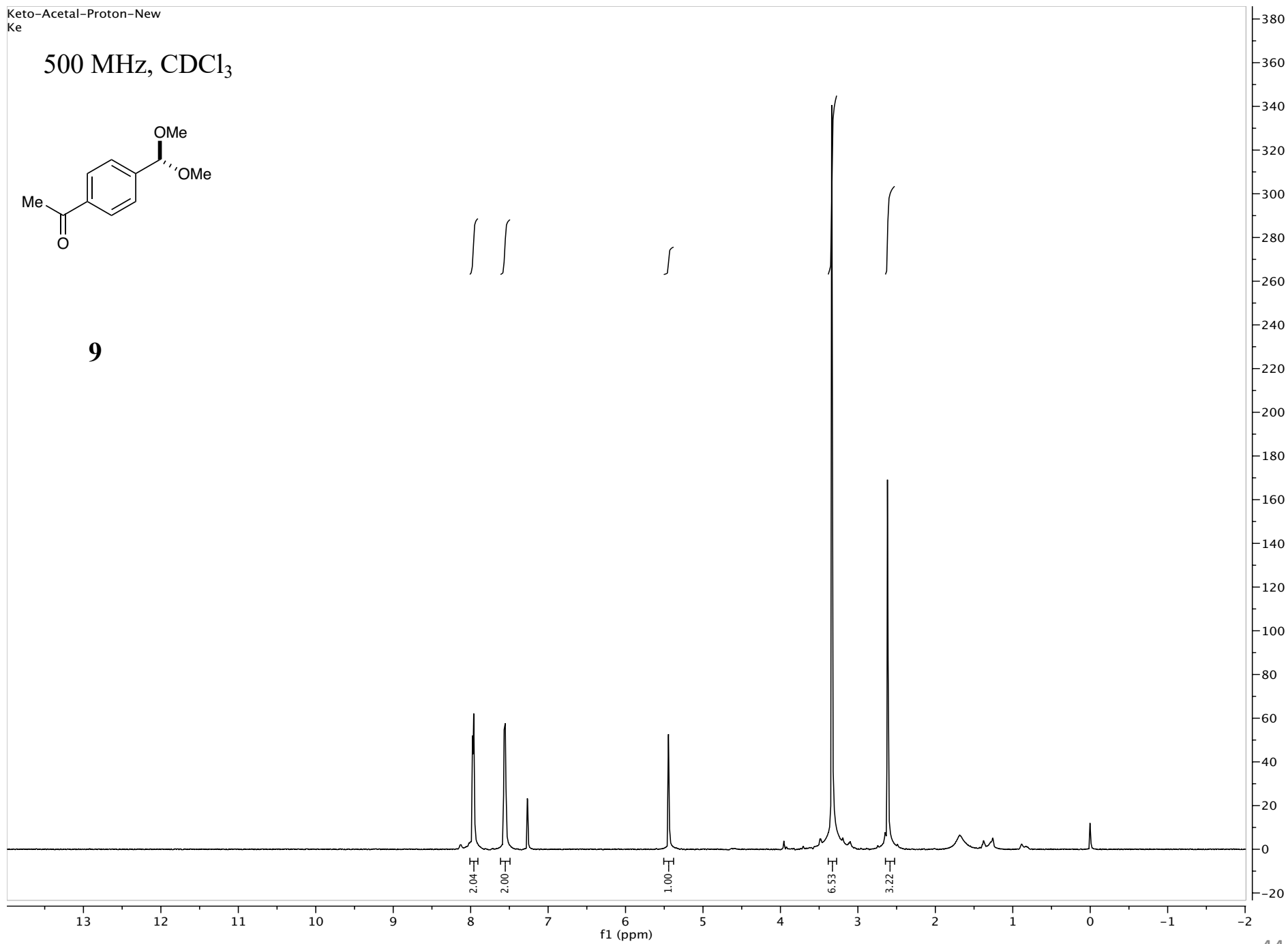
Fluoro–Acetal
F-2

500 MHz, CDCl$_3$

10

2.16 2.16 1.00 5.95

13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)
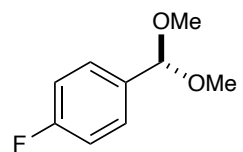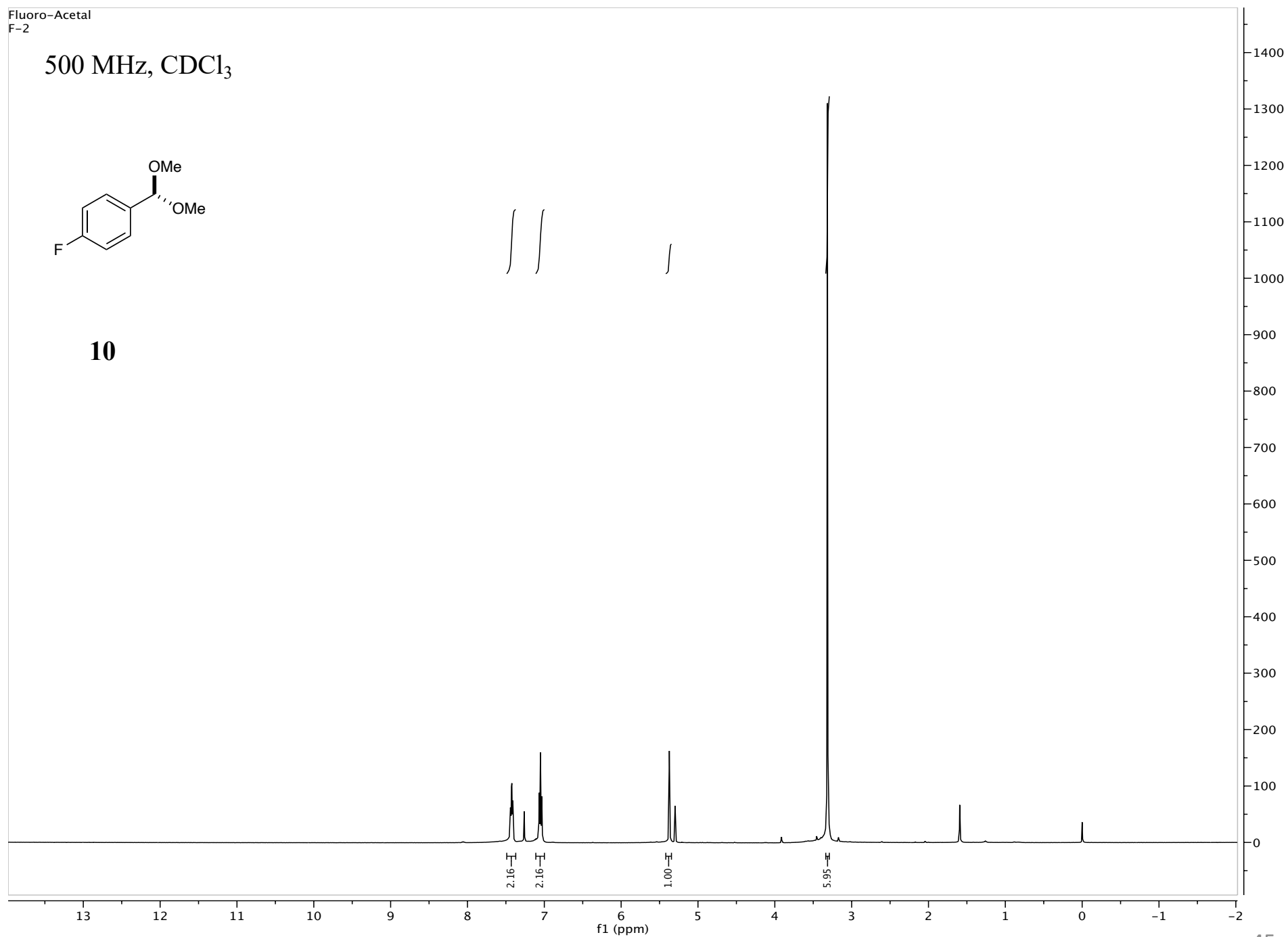
F-Benz-Carbon
F-Benz-Proton

125 MHz, CDCl$_3$

163.89
161.93
134.12
134.09
128.66
128.60
115.29
115.12
102.63
52.76

10

JS2-130A-Cl-Acetal-Proton
JS2-130-tt-3-4

500 MHz, CDCl$_3$

11

1.98
2.01
1.00
6.00

13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

JS2-130-tt-3-4
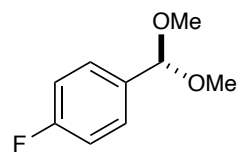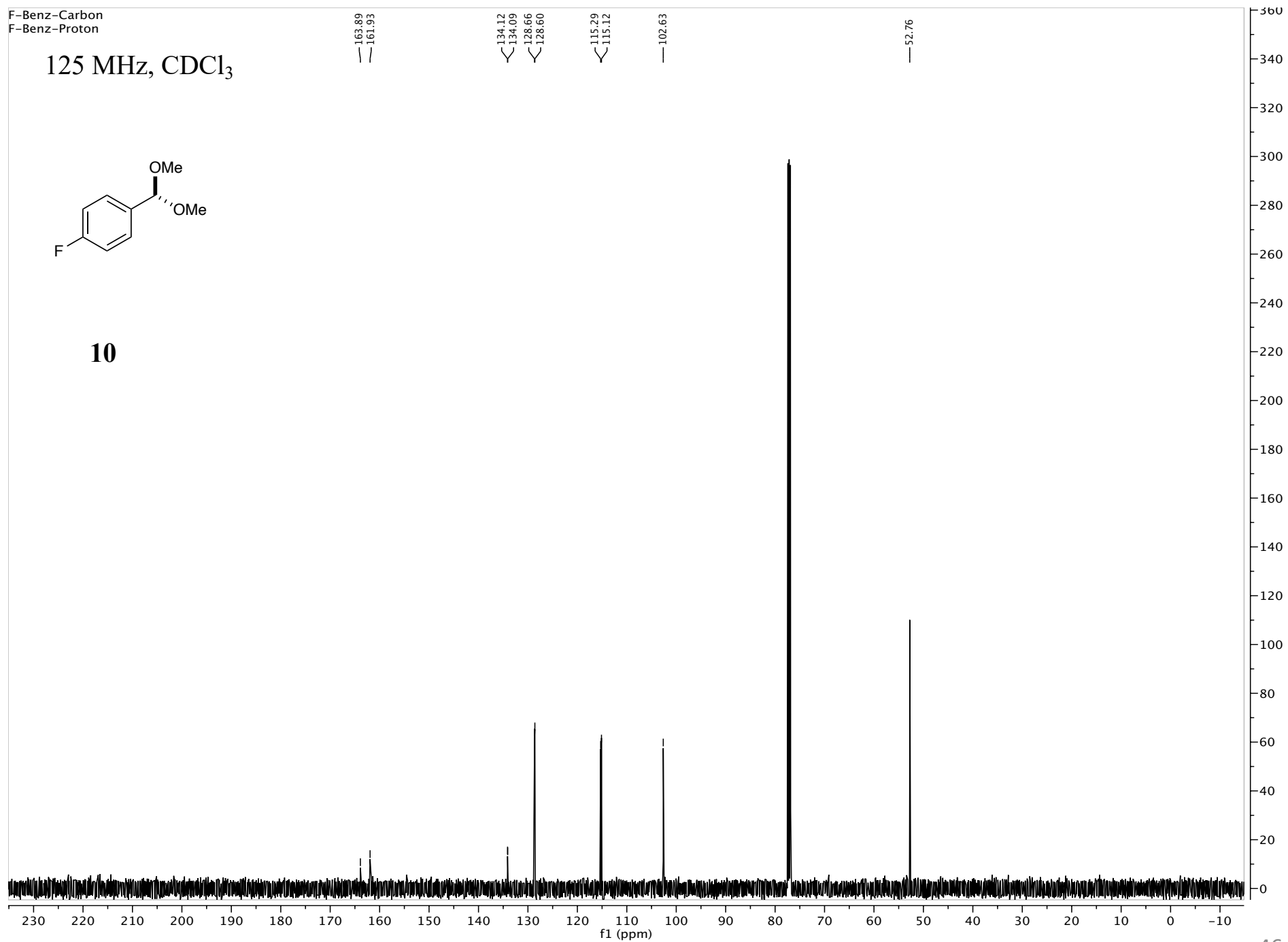
125 MHz, CDCl₃

11

136.
134.
128.
128.
102.
52.6

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

JS2-Br-Acetal-Proton
Br-Benz-Acetal
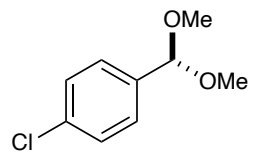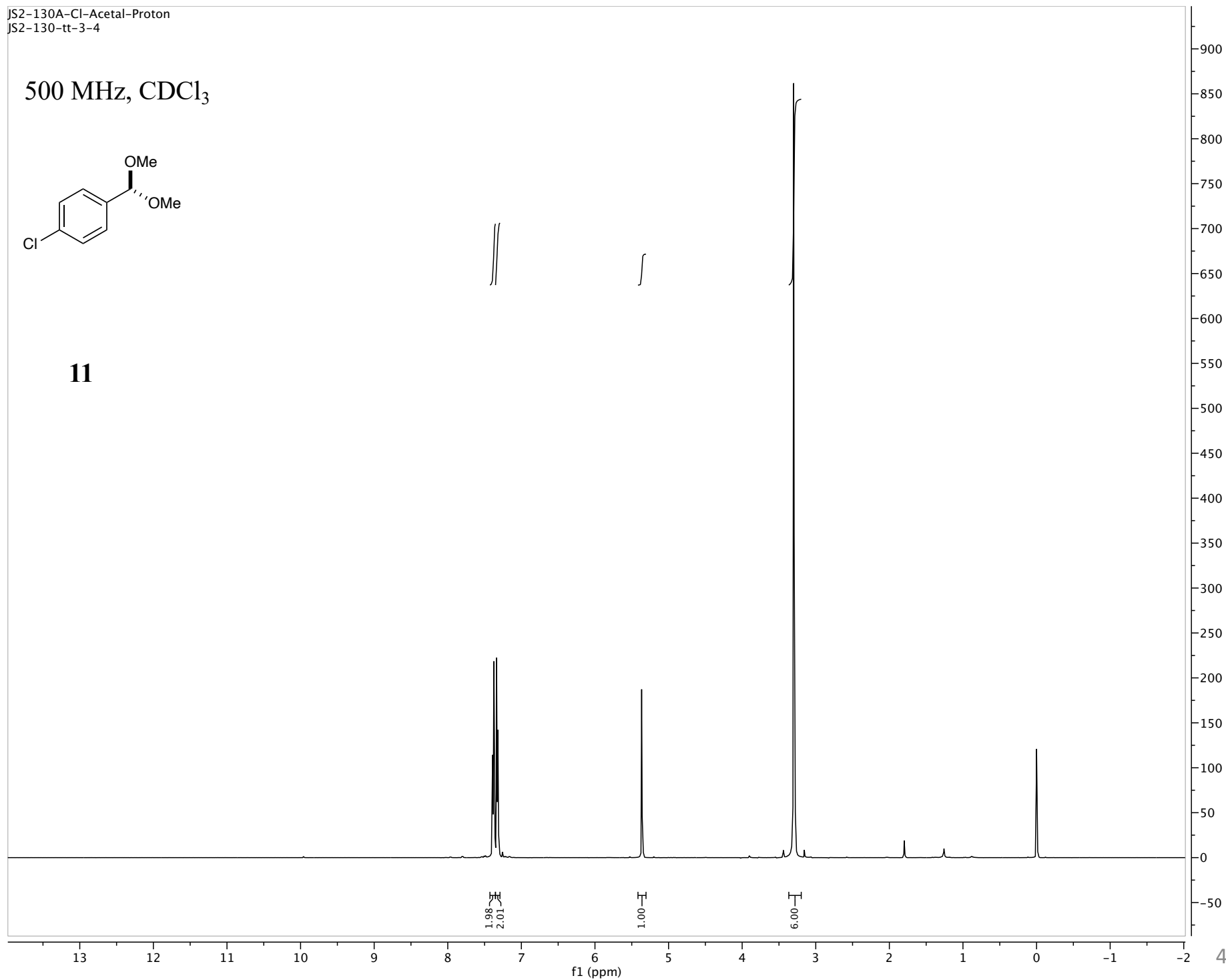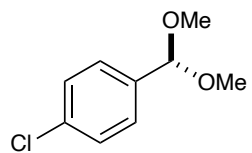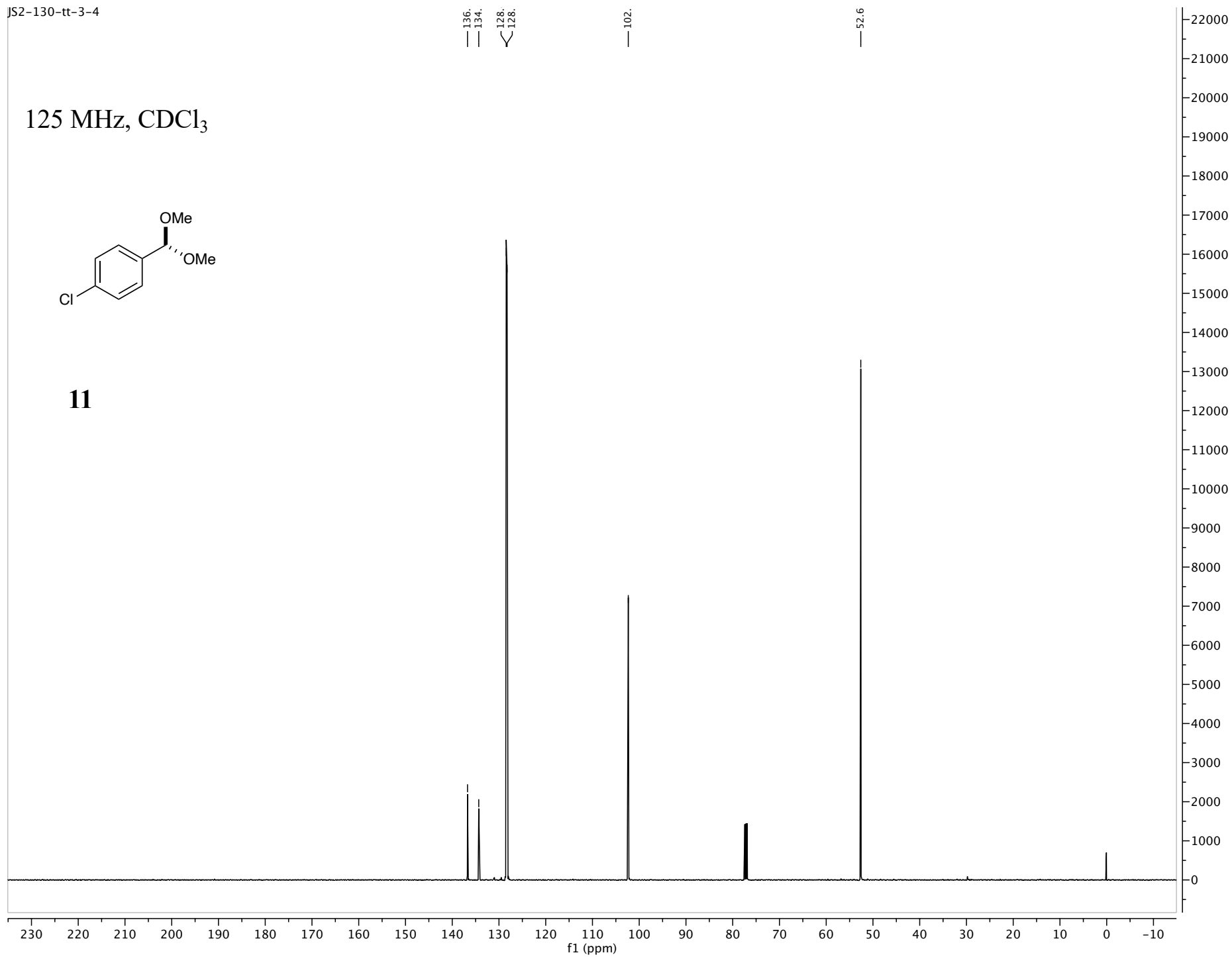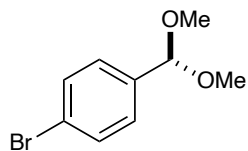
500 MHz, CDCl$_3$

12
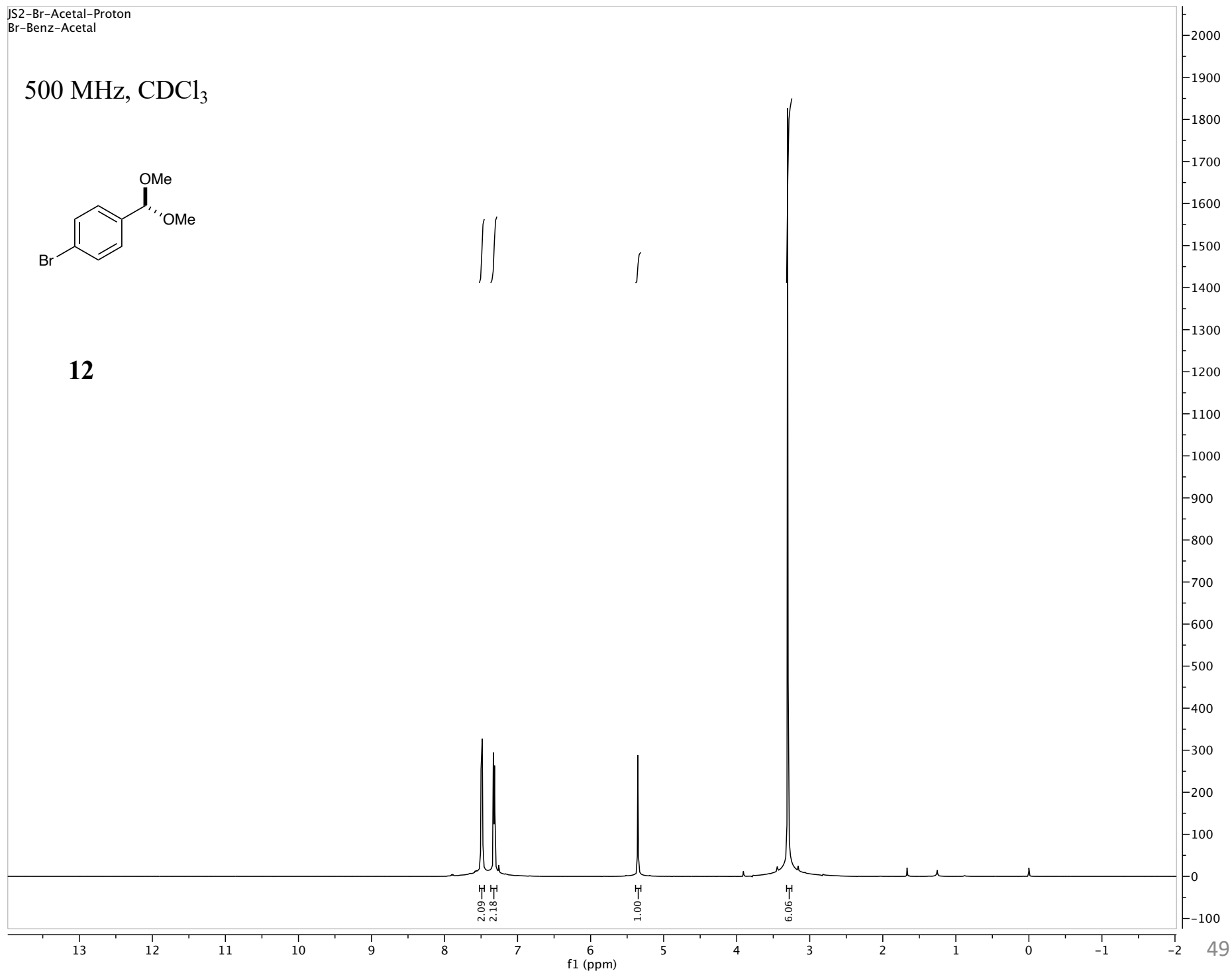
JS2-Br-Acetal-Carbon
Br-Benz-Acetal

125 MHz, CDCl$_3$

137.25
131.45
128.63
122.61
102.40
52.67

12

f1 (ppm)

50

500 MHz, CDCl$_3$

13

2.35
2.07
1.00
6.58

13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)

500 MHz, CDCl$_3$

14

2.20
2.11
1.00
6.34
3.17

13   12   11   10   9   8   7   6   5   4   3   2   1   0   -1   -2

f1 (ppm)
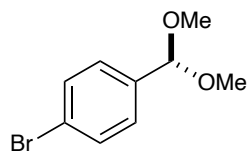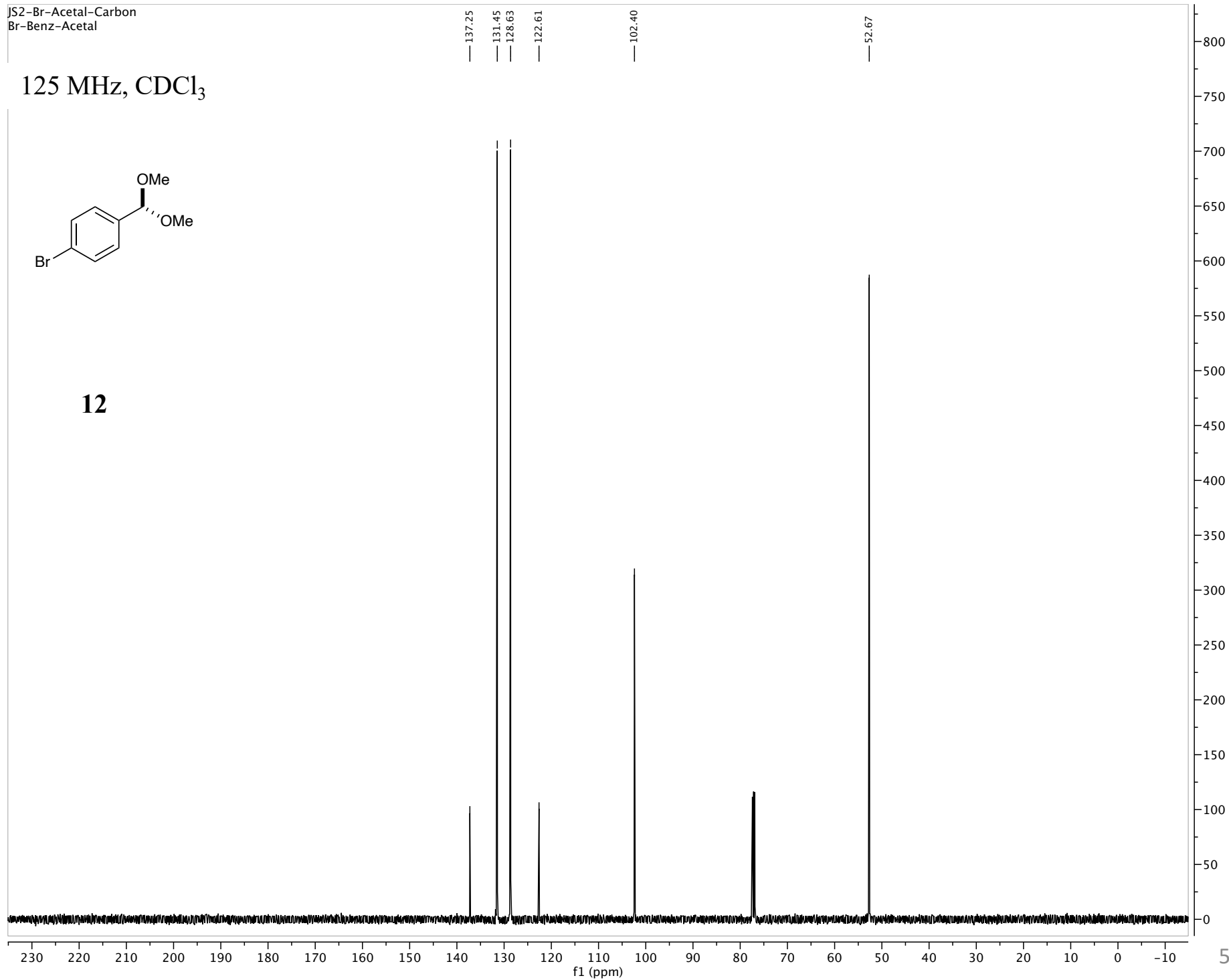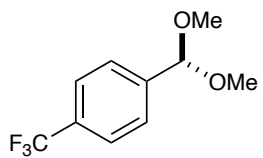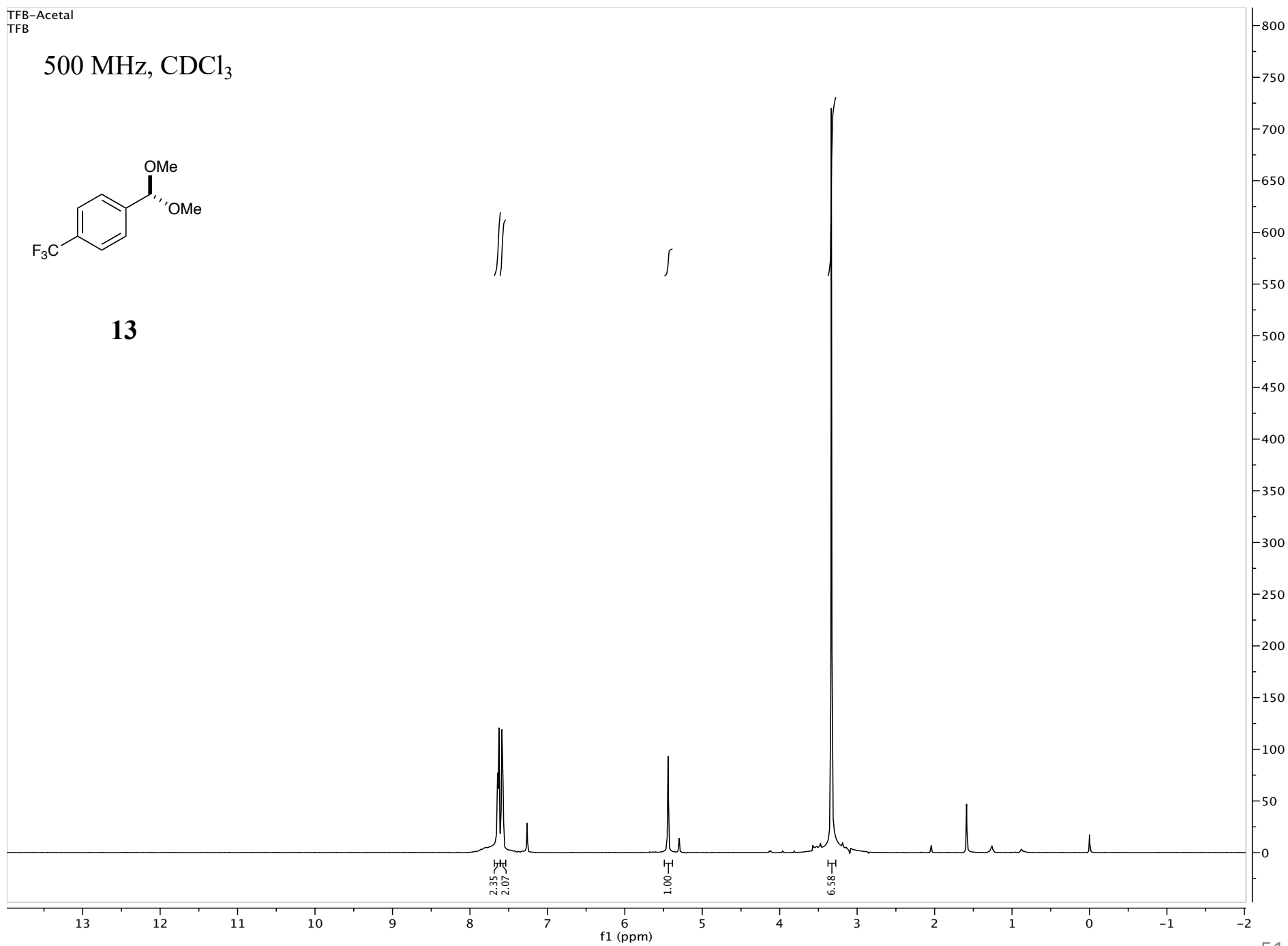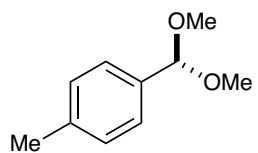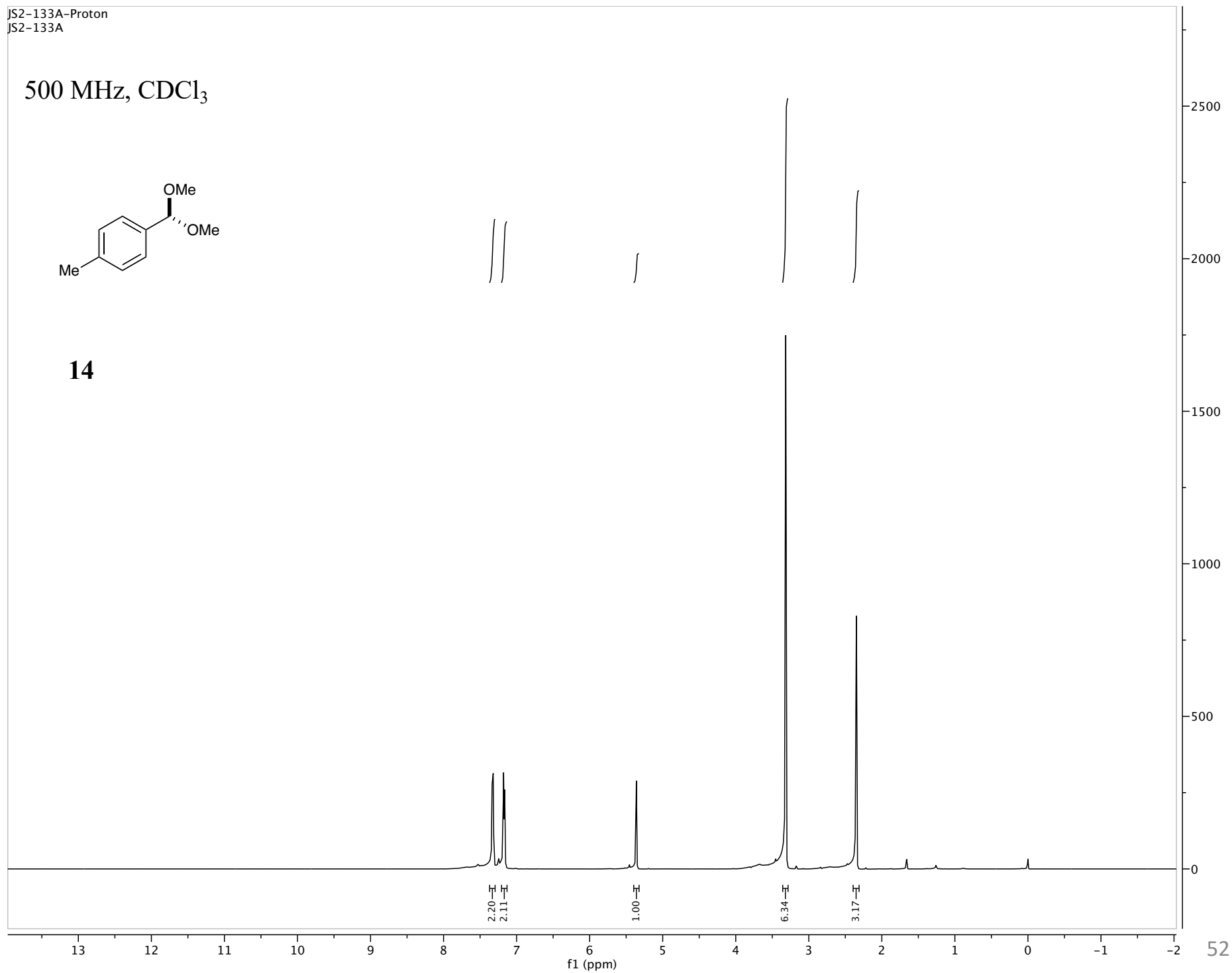
JS2–133A–Carbon
JS2–133A

125 MHz, CDCl$_3$
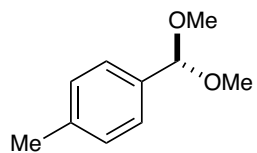
138.27
135.25
128.99
126.72
103.33
52.75
21.32
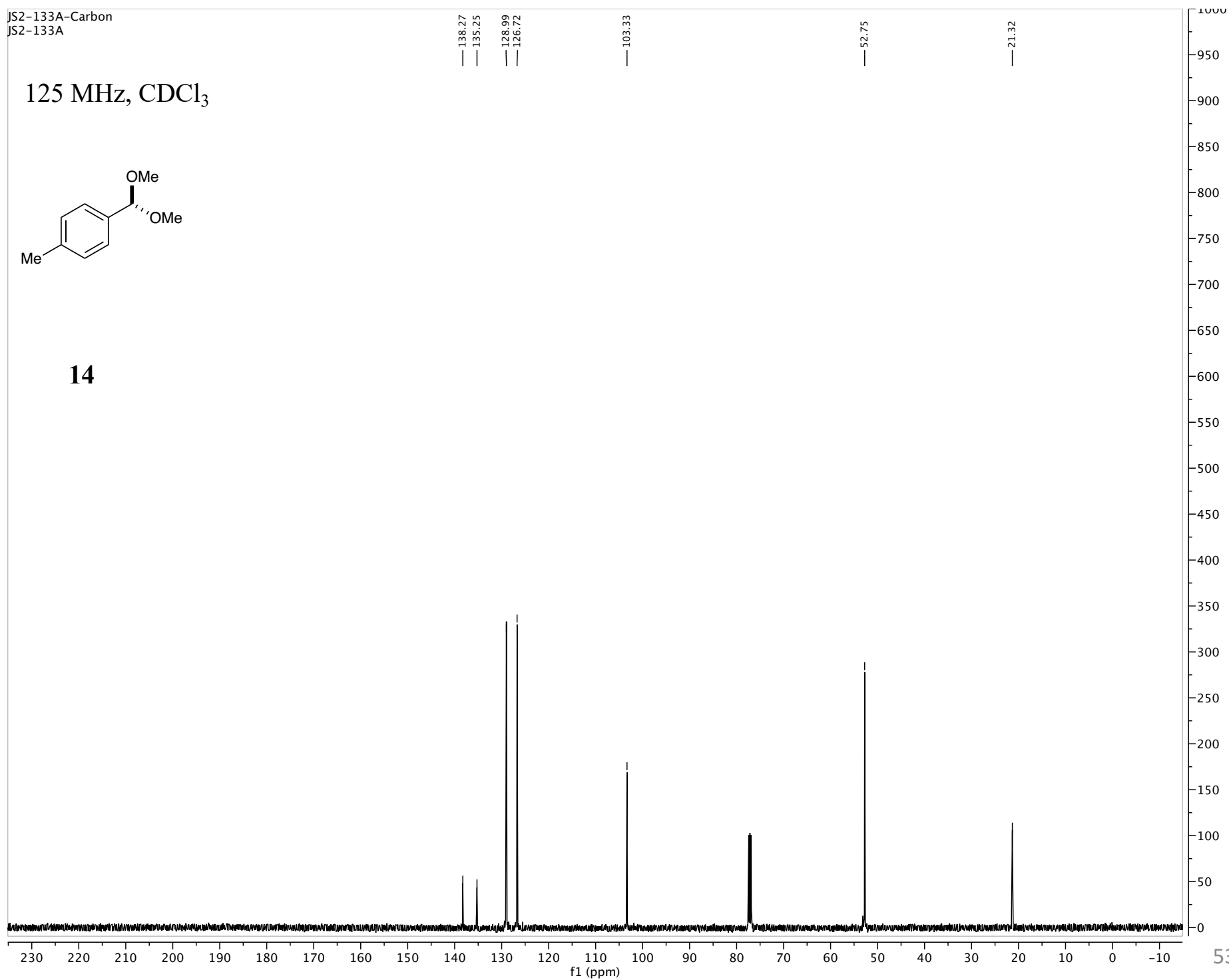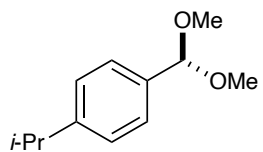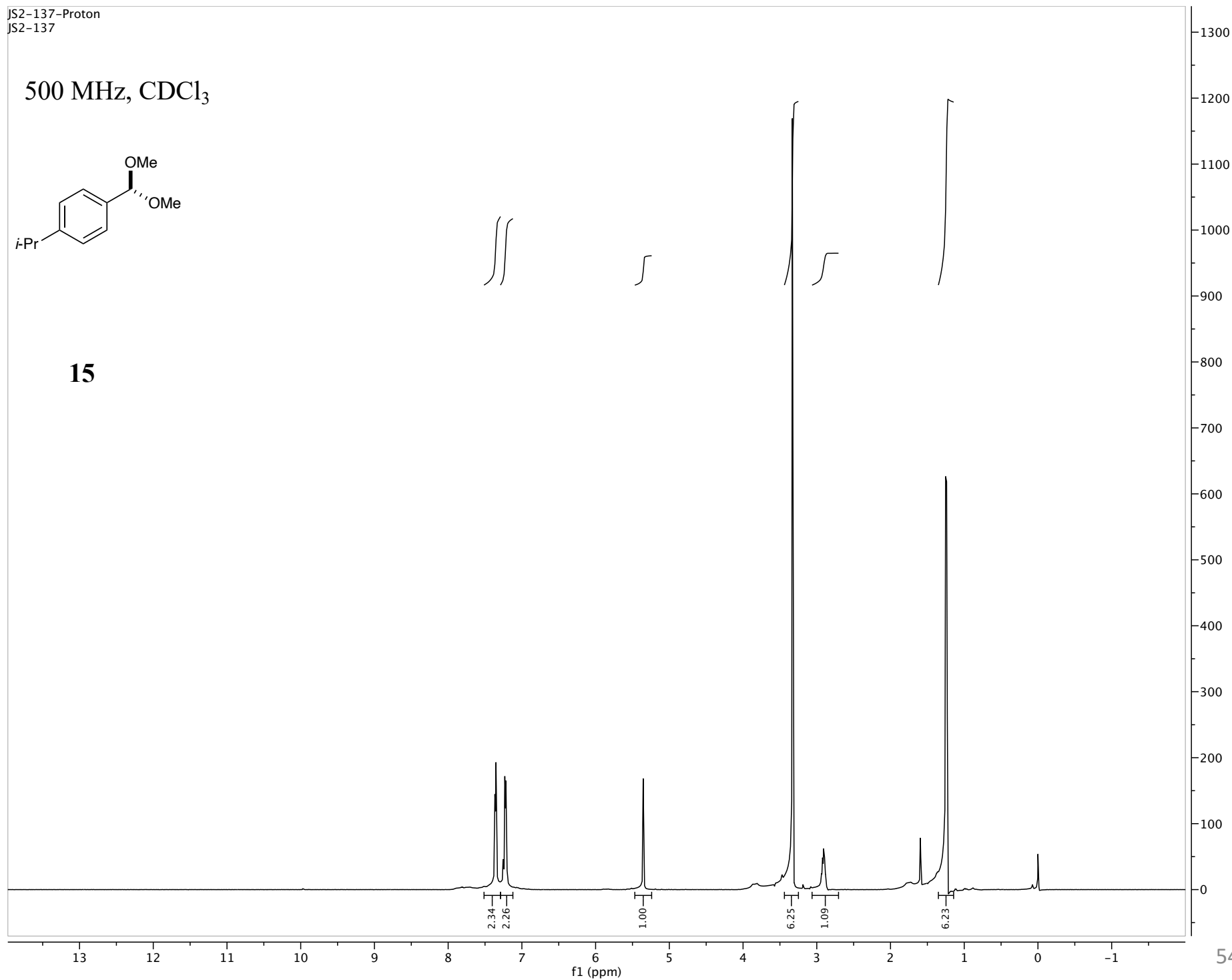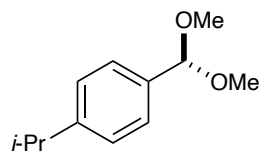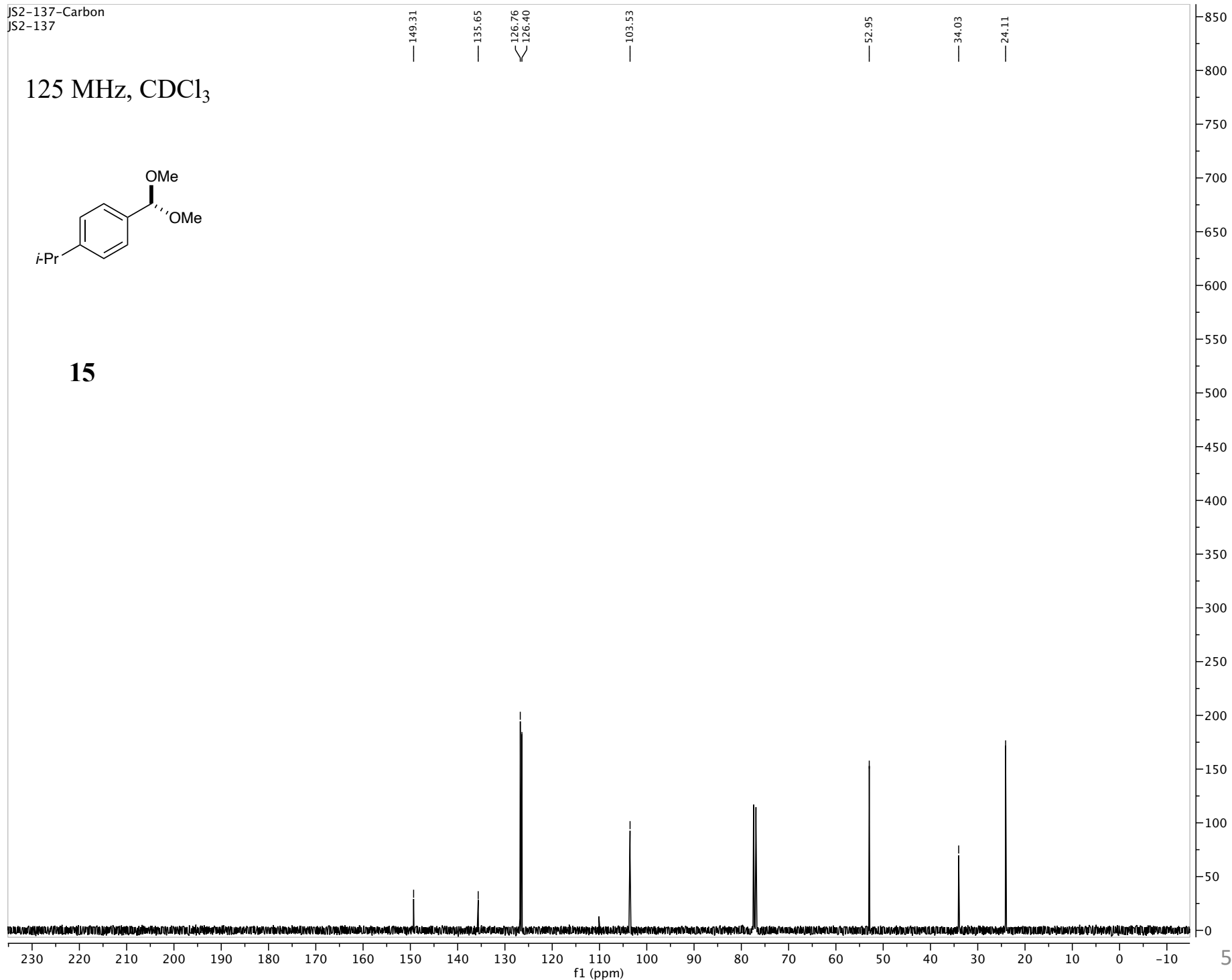
14

f1 (ppm)

500 MHz, CDCl$_3$

15

2.34 2.26   1.00   6.25 1.09   6.23

13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

125 MHz, CDCl$_3$

15

149.31
135.65
126.76
126.40
103.53
52.95
34.03
24.11

OMe

''OMe

i-Pr

500 MHz, CDCl$_3$

16

125 MHz, CDCl$_3$

151.54
135.25
126.47
125.25
103.52
52.97
34.72
31.47

OMe
OMe

t-Bu

16

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

500 MHz, CDCl$_3$

17

2.35 2.01 1.00 3.23 6.11

13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2

f1 (ppm)
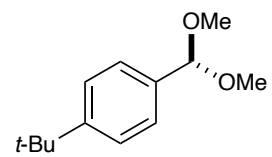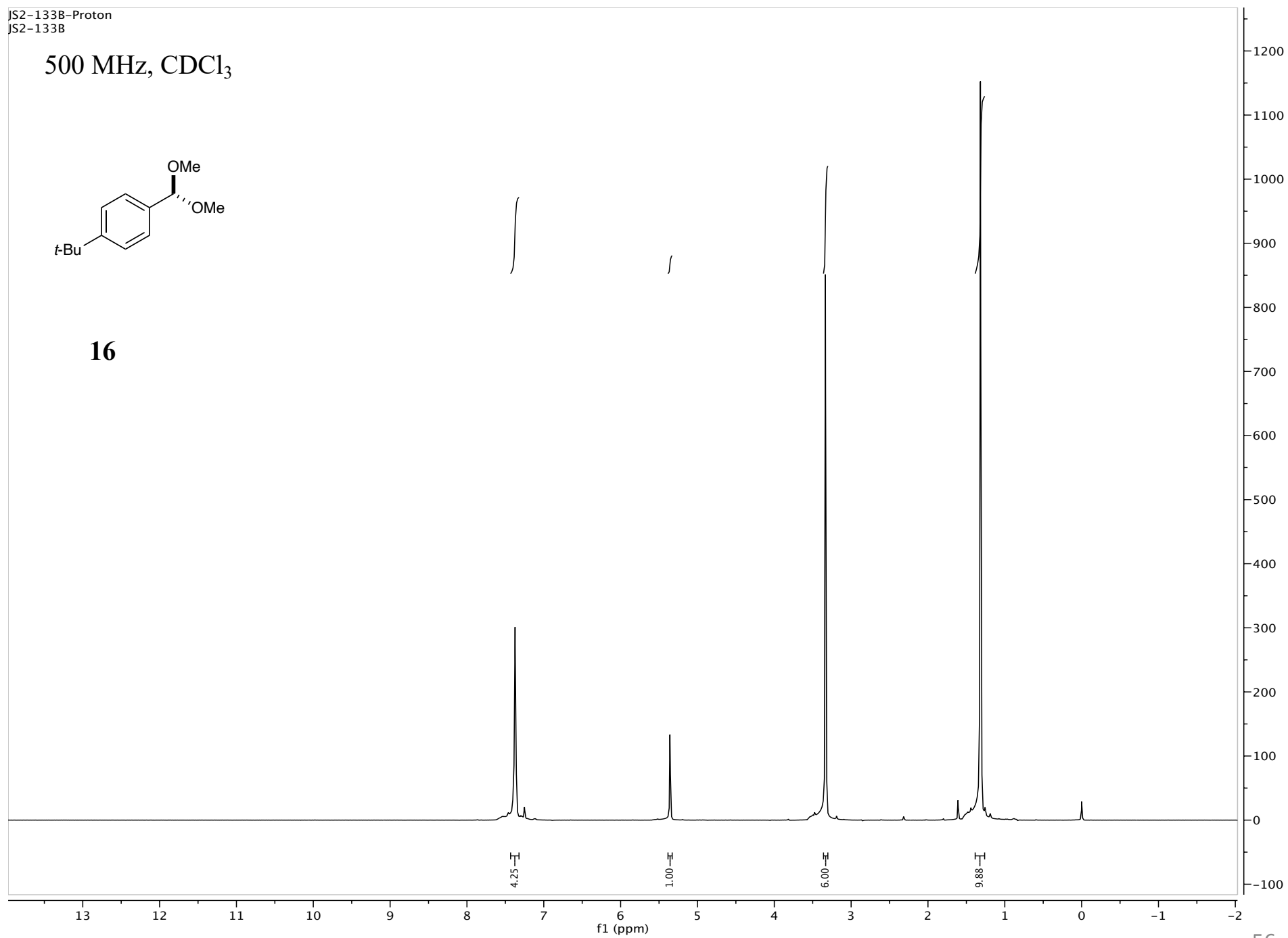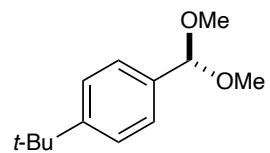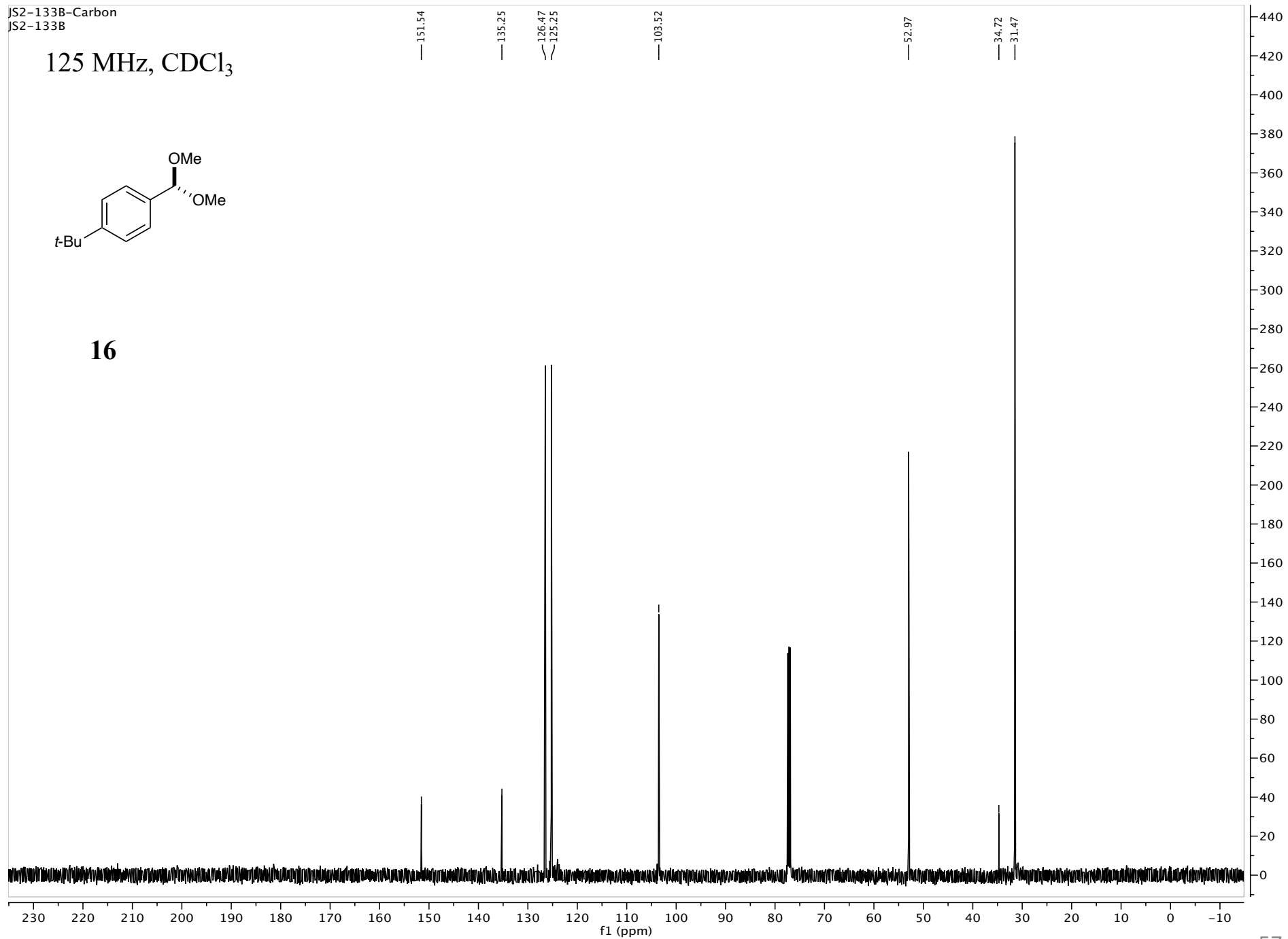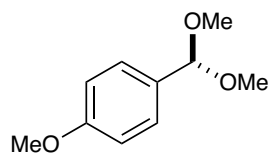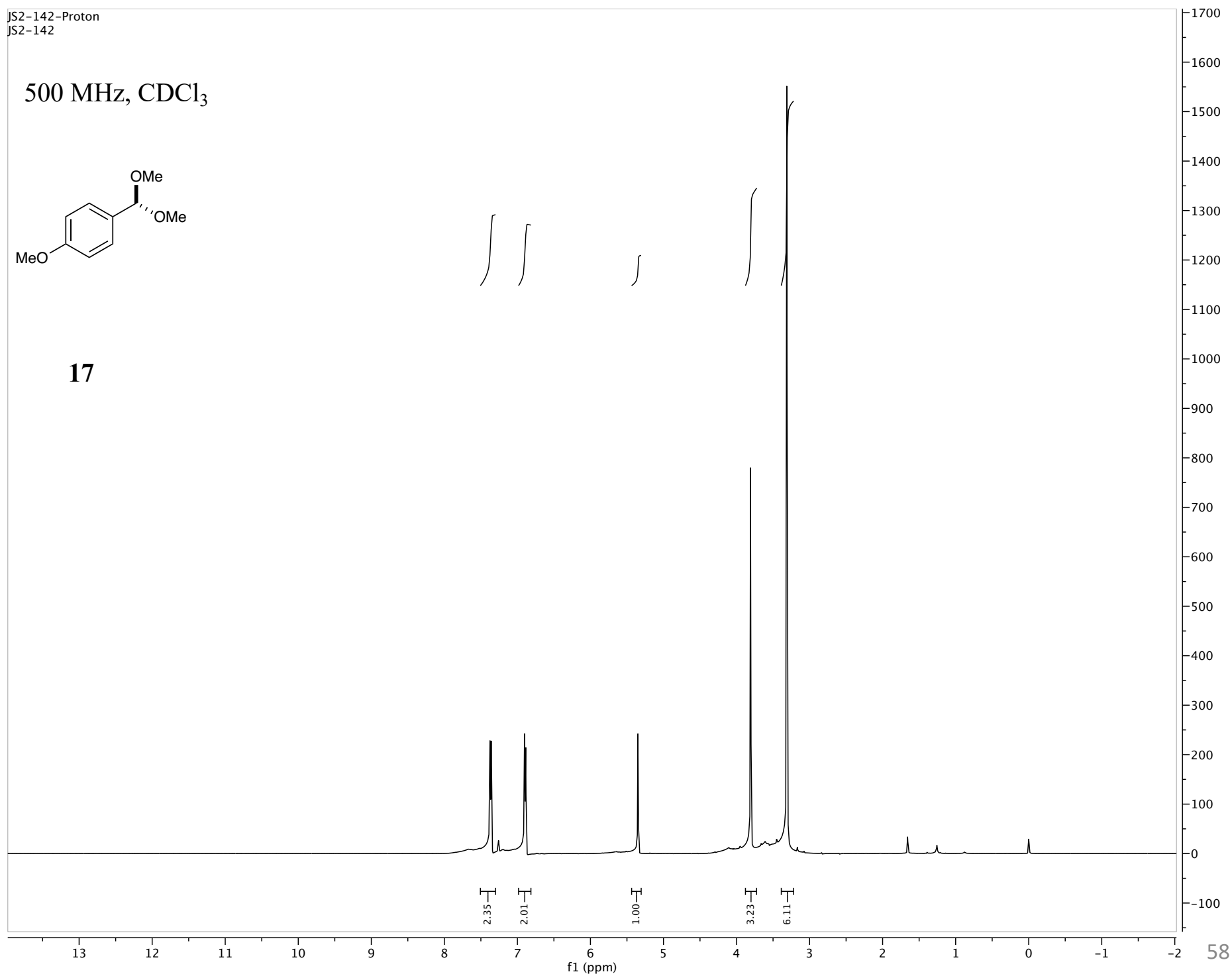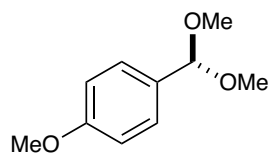
125 MHz, CDCl$_3$

17
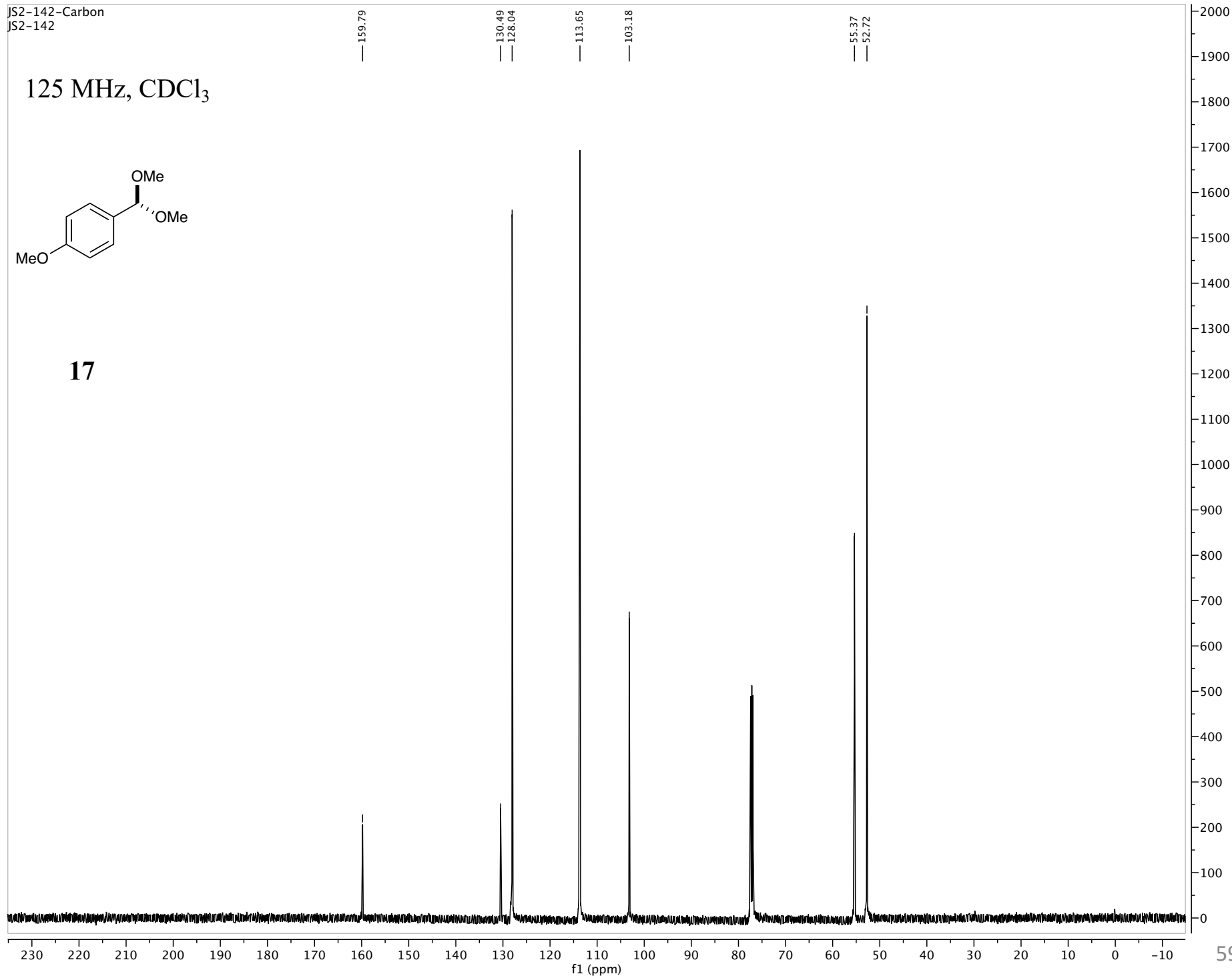
500 MHz, CDCl$_3$
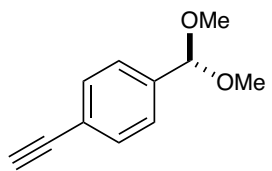
18
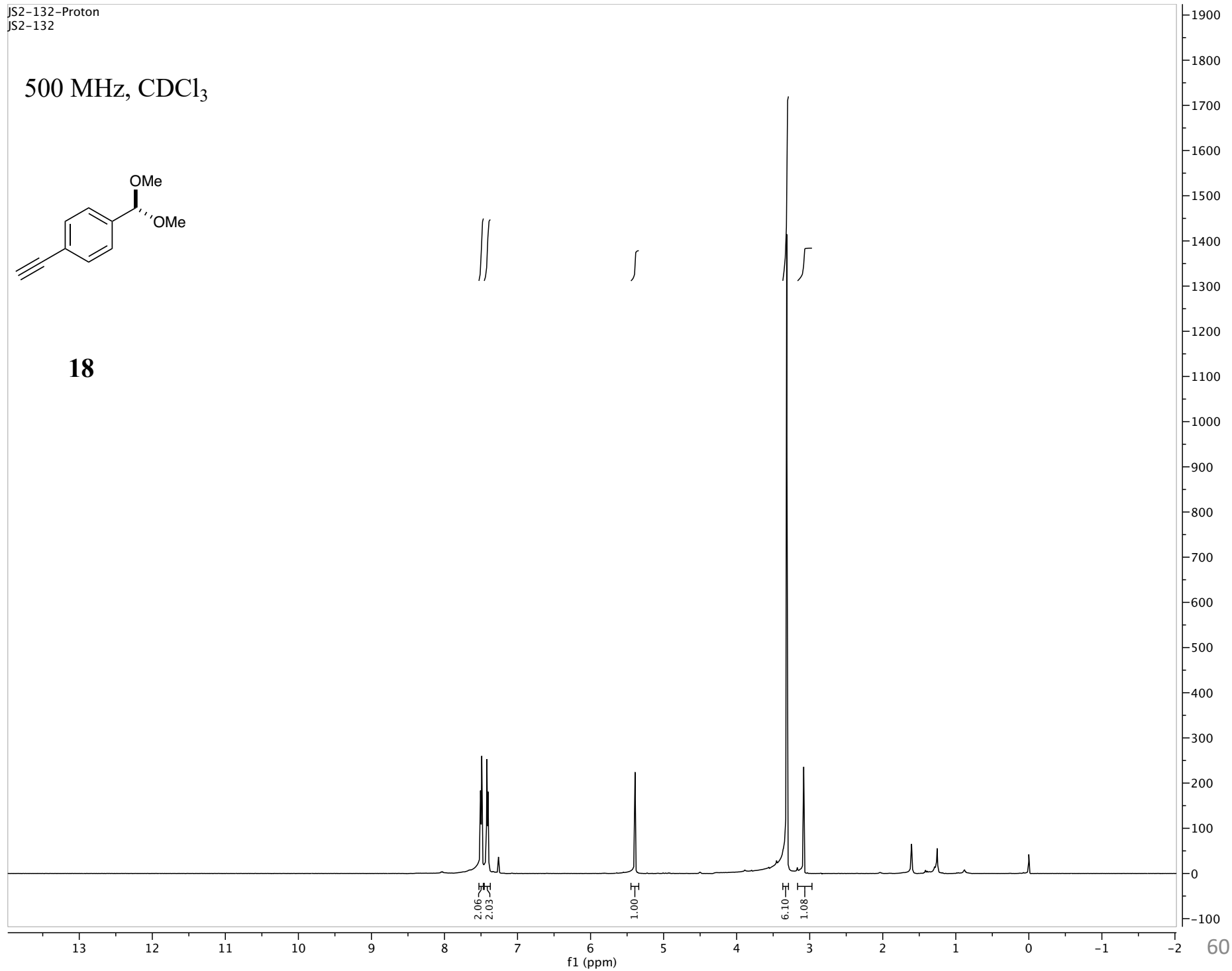
JS2-132-Carbon
JS2-132

125 MHz, CDCl$_3$

138.87
132.14
126.87
122.31
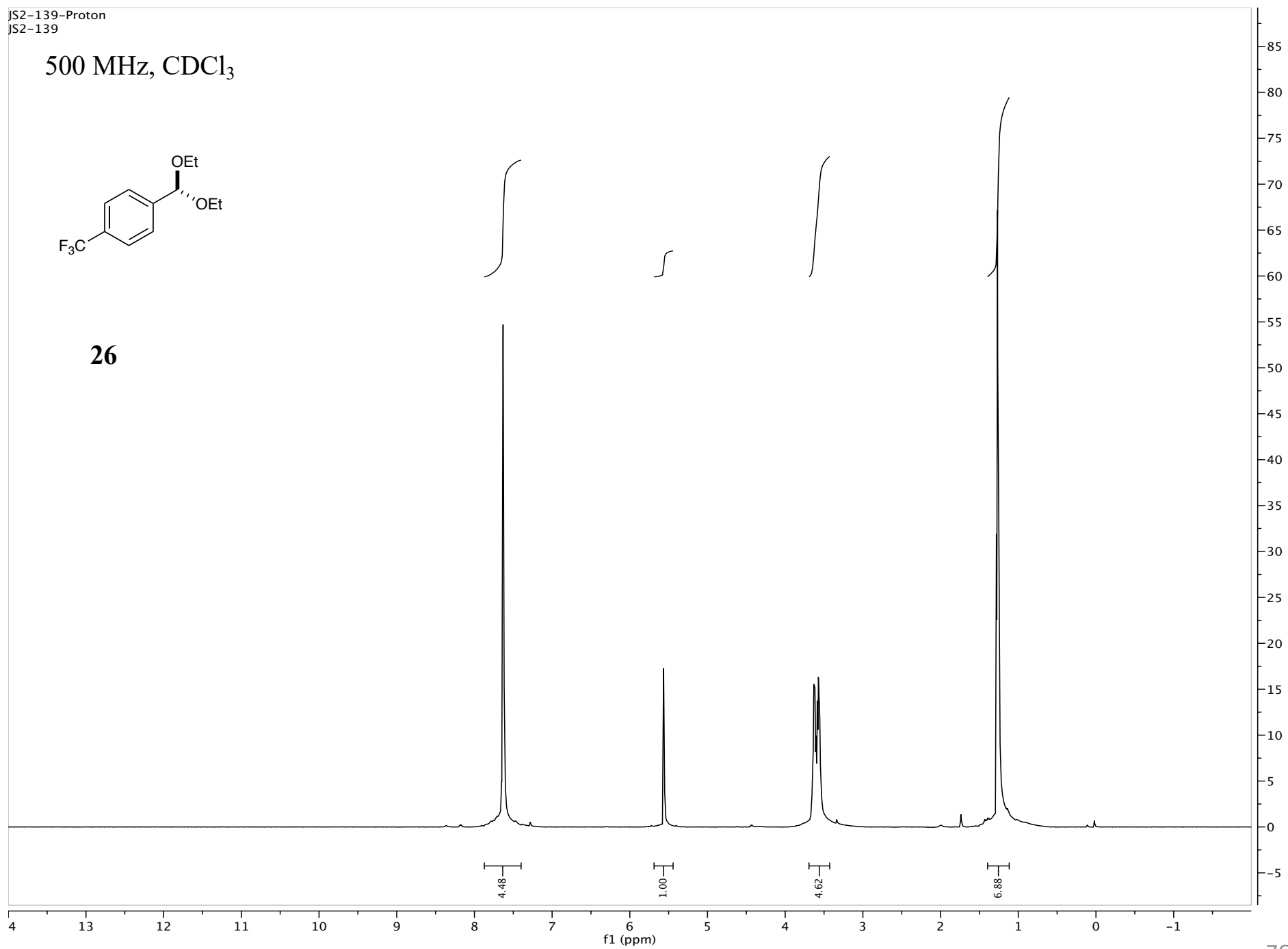102.61
83.56
77.59
52.75

18

f1 (ppm)
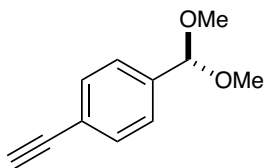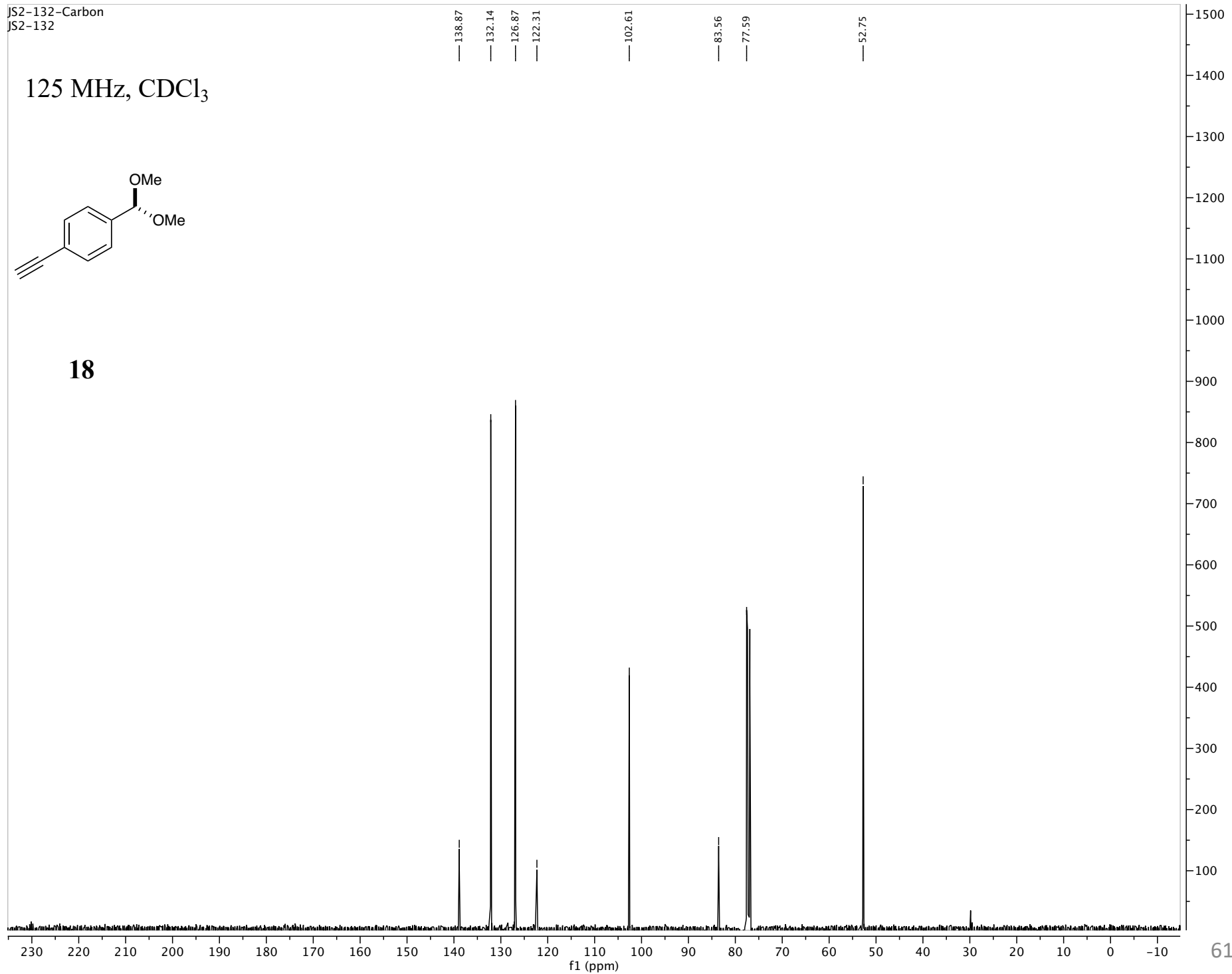
JS2-136-Proton
JS2-136

500 MHz, CDCl$_3$
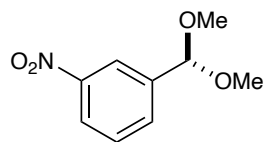
19
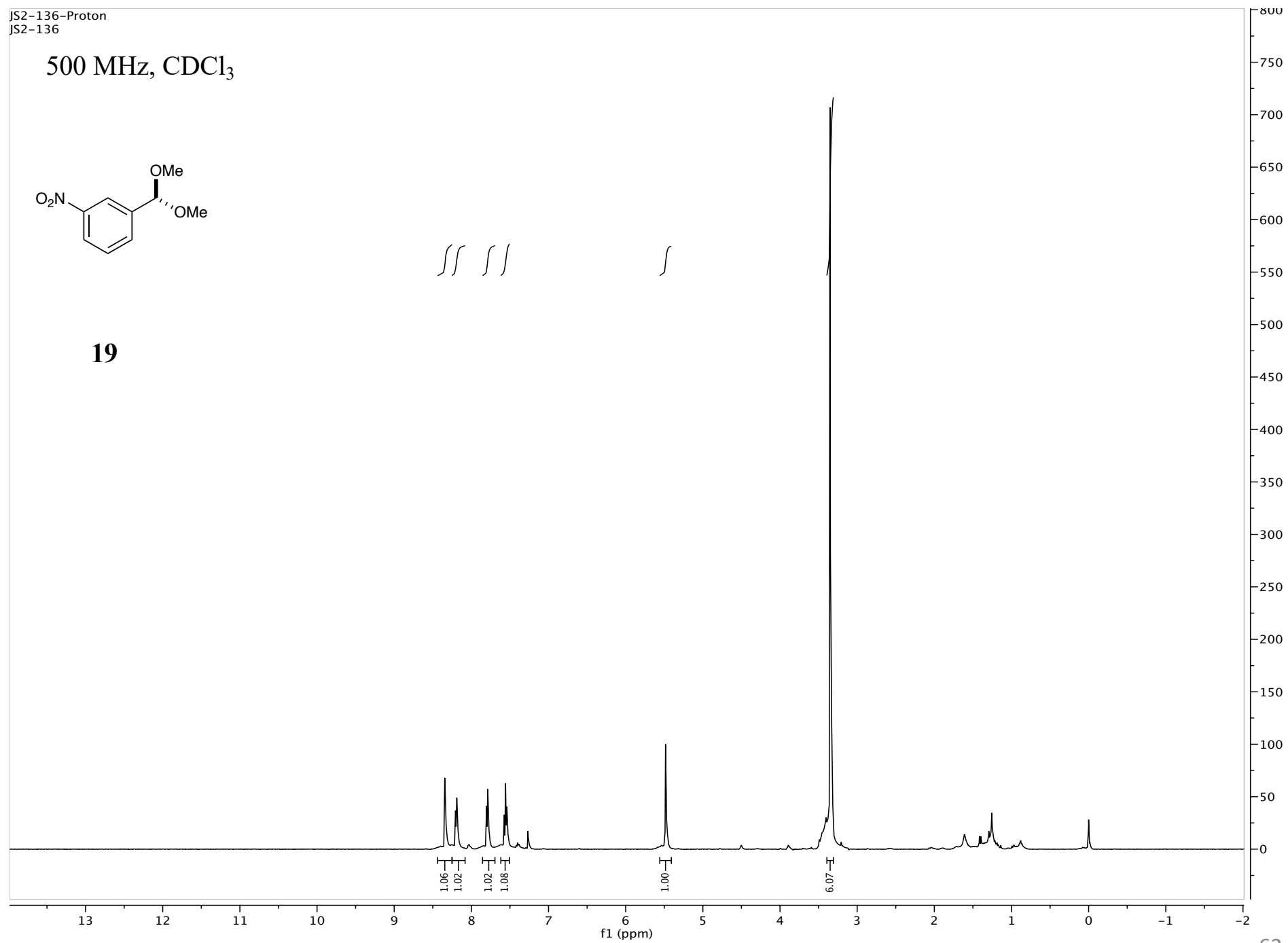
JS2-136-Carbon
JS2-136

125 MHz, CDCl$_3$

148.32
140.40
132.91
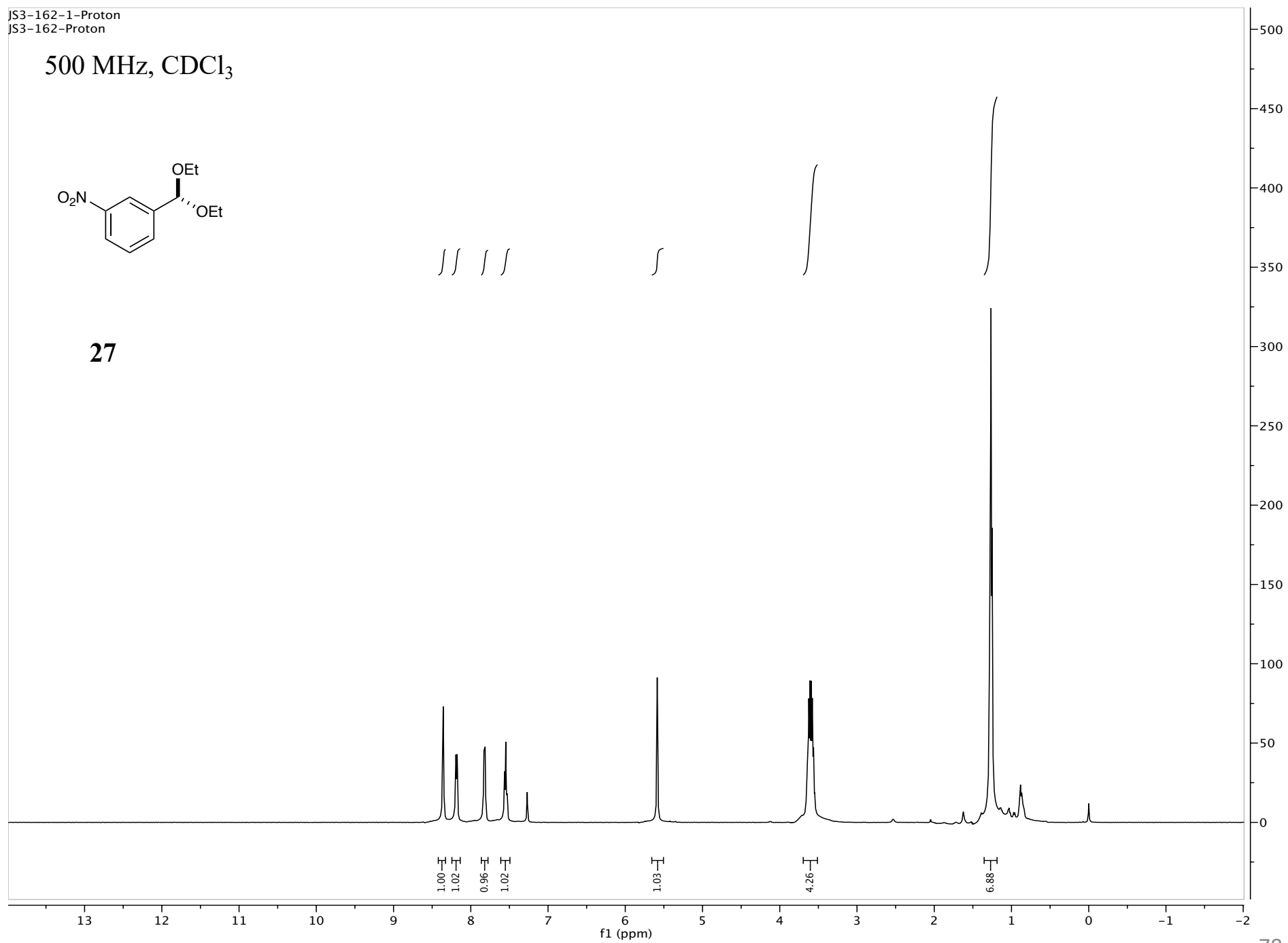129.26
123.44
122.07
101.44
52.72
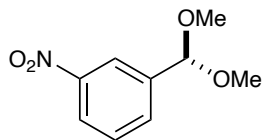
19
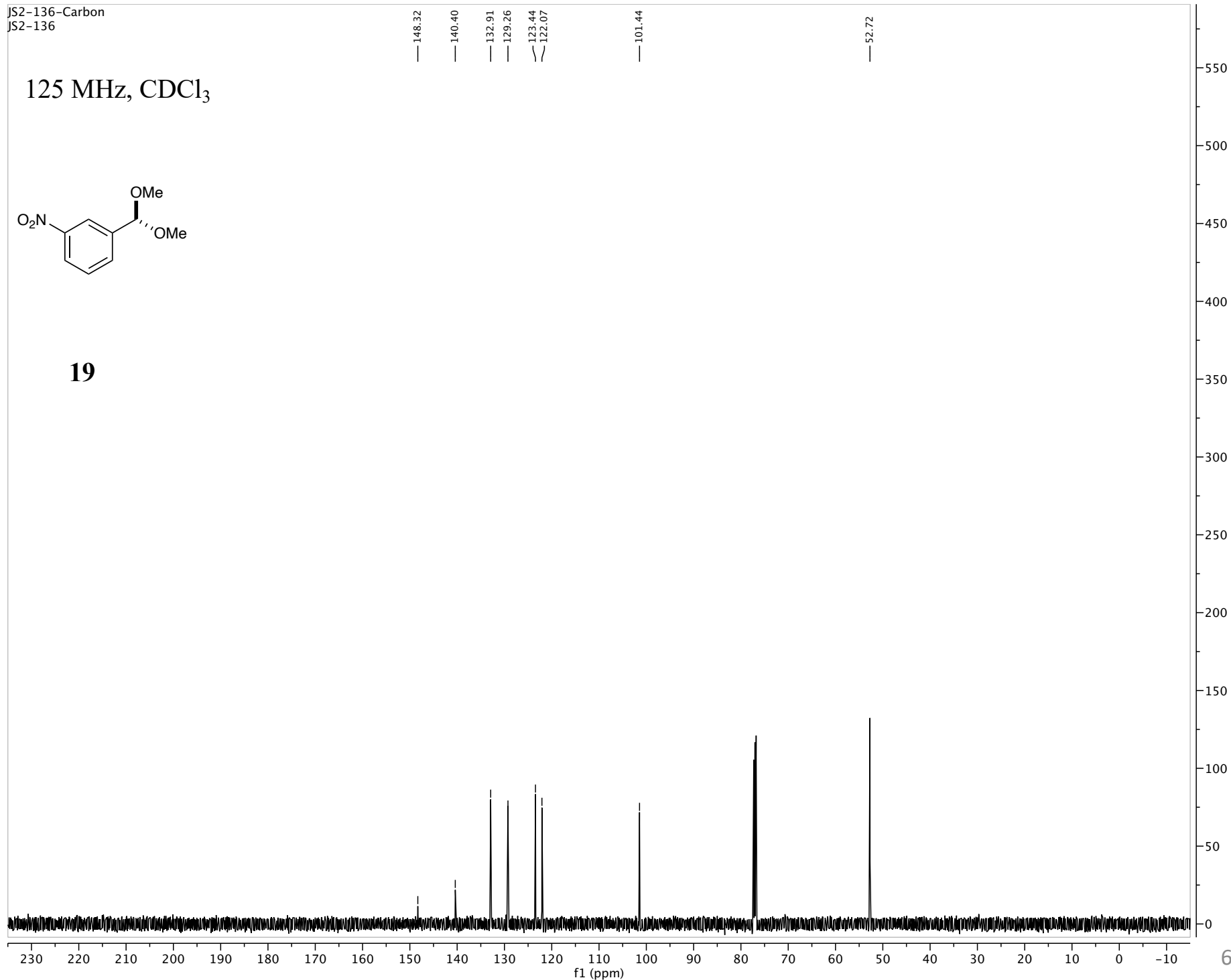
Ortho–toulic–acetal–Proton
Ortho

500 MHz, CDCl$_3$

20

f1 (ppm)
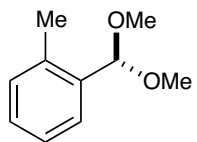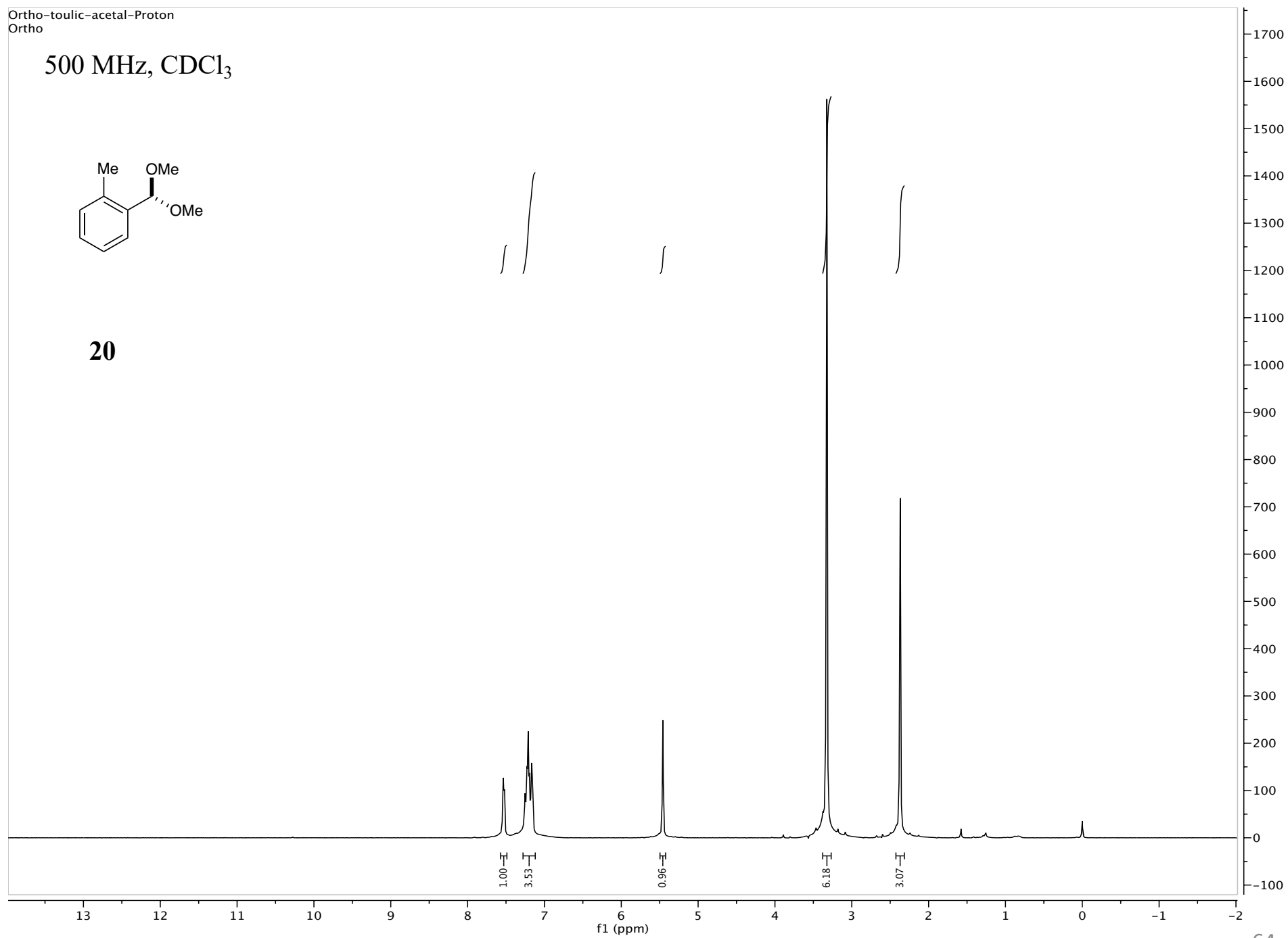
Ortho–toulic–Acetal–Carbon
Ortho

125 MHz, CDCl$_3$
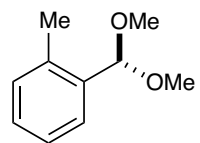
136.39
135.77
130.66
128.51
126.65
125.56
101.89
53.16
19.02

Me   OMe

OMe

20

f1 (ppm)

500 MHz, CDCl$_3$

OMe

OMe

(70:30 mixture of *E:Z* isomers)

21
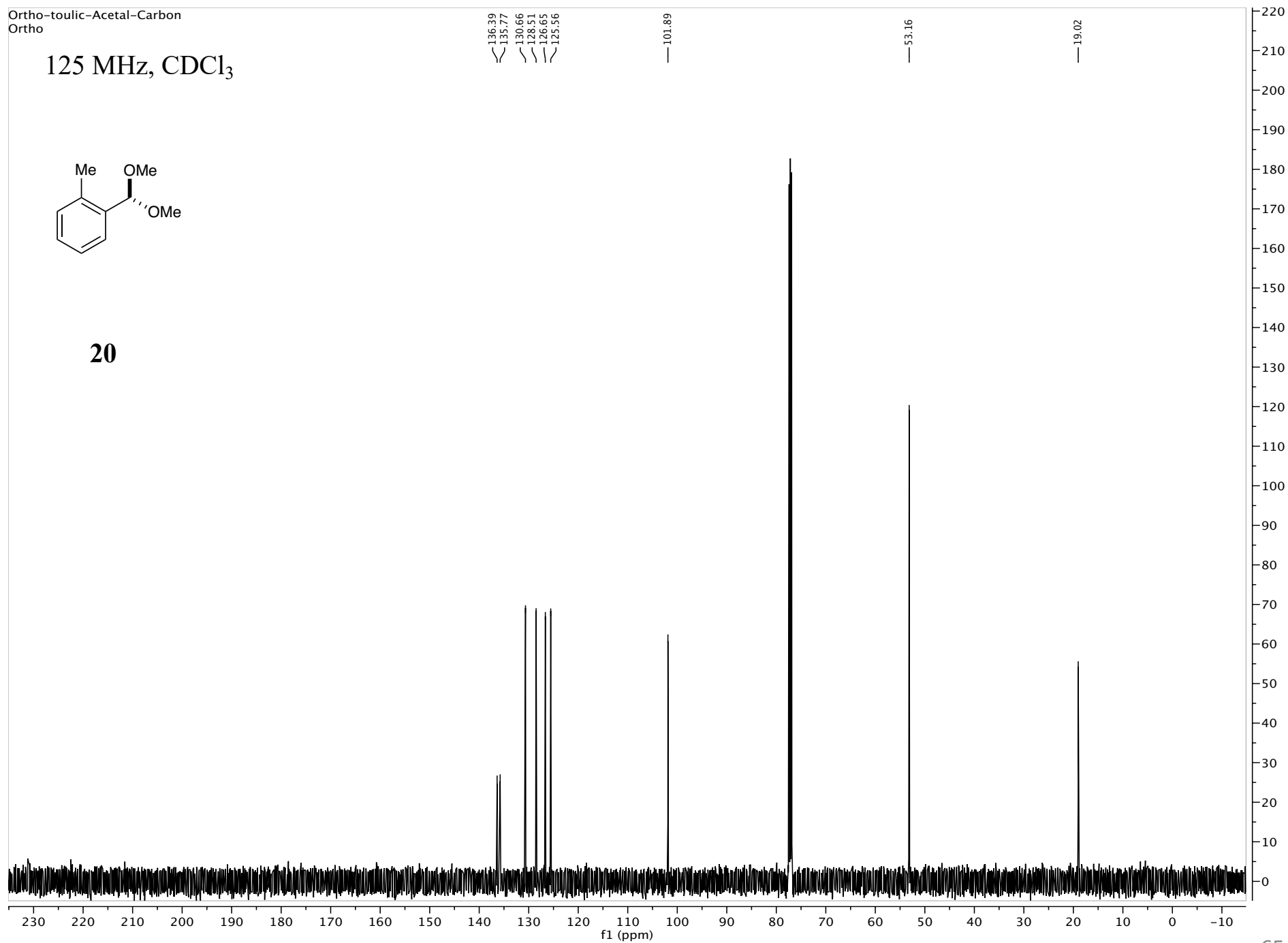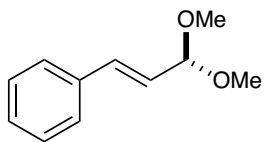
125 MHz, CDCl$_3$

(70:30 mixture of *E:Z* isomers)
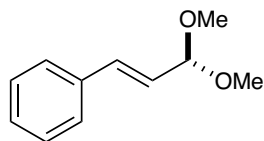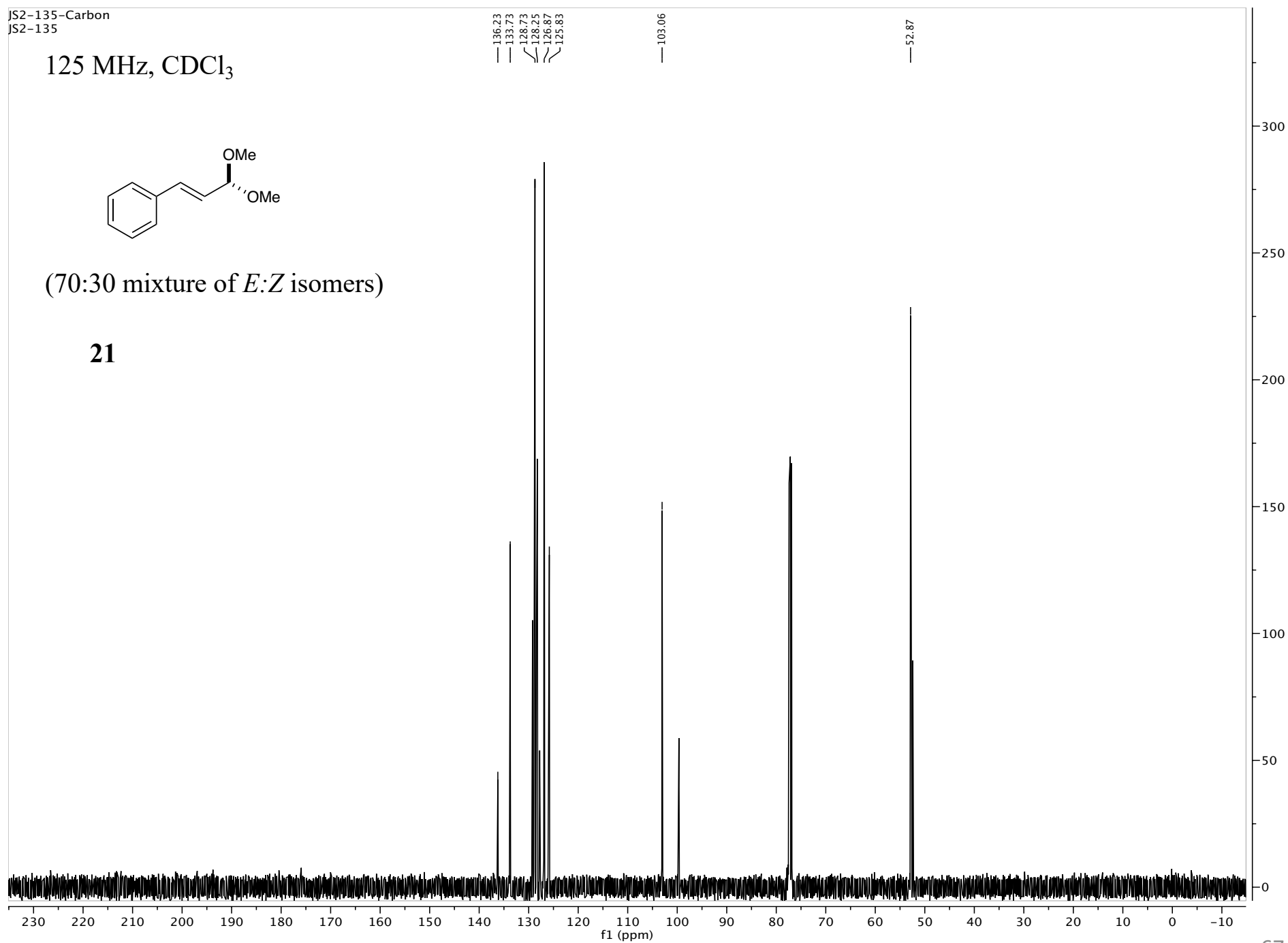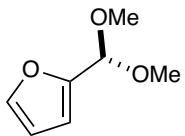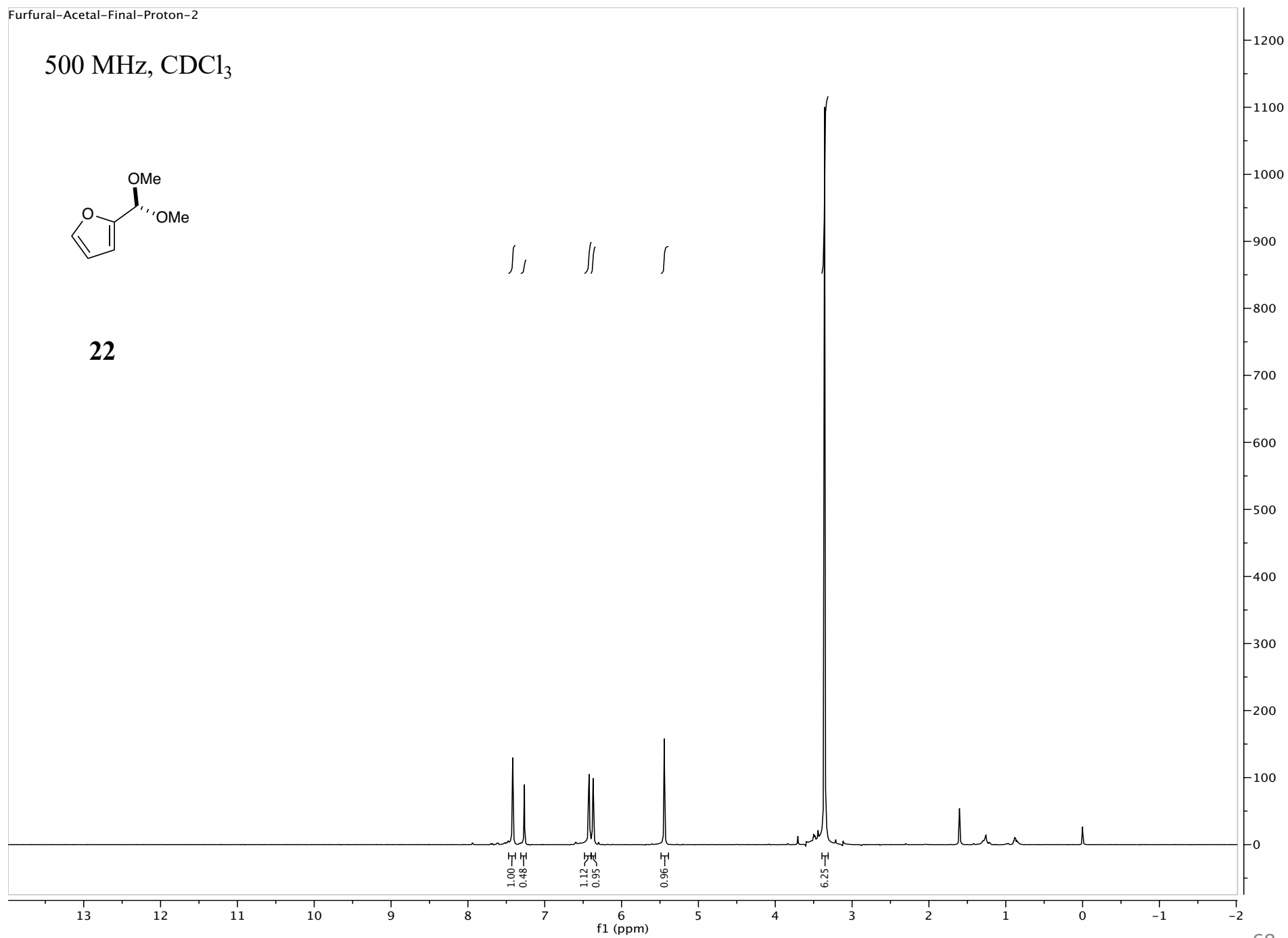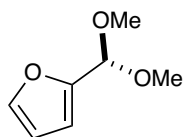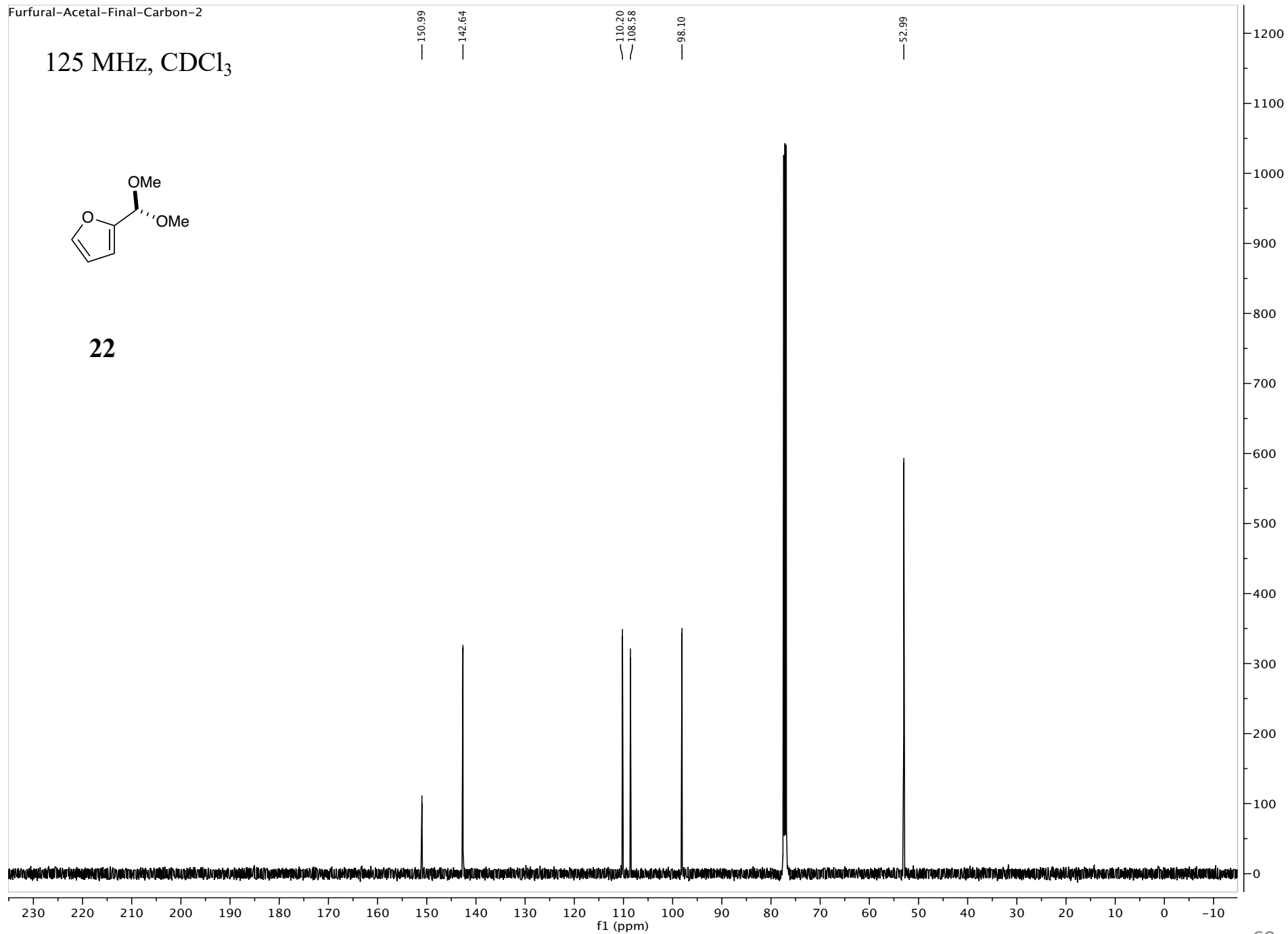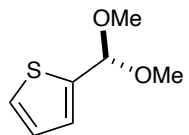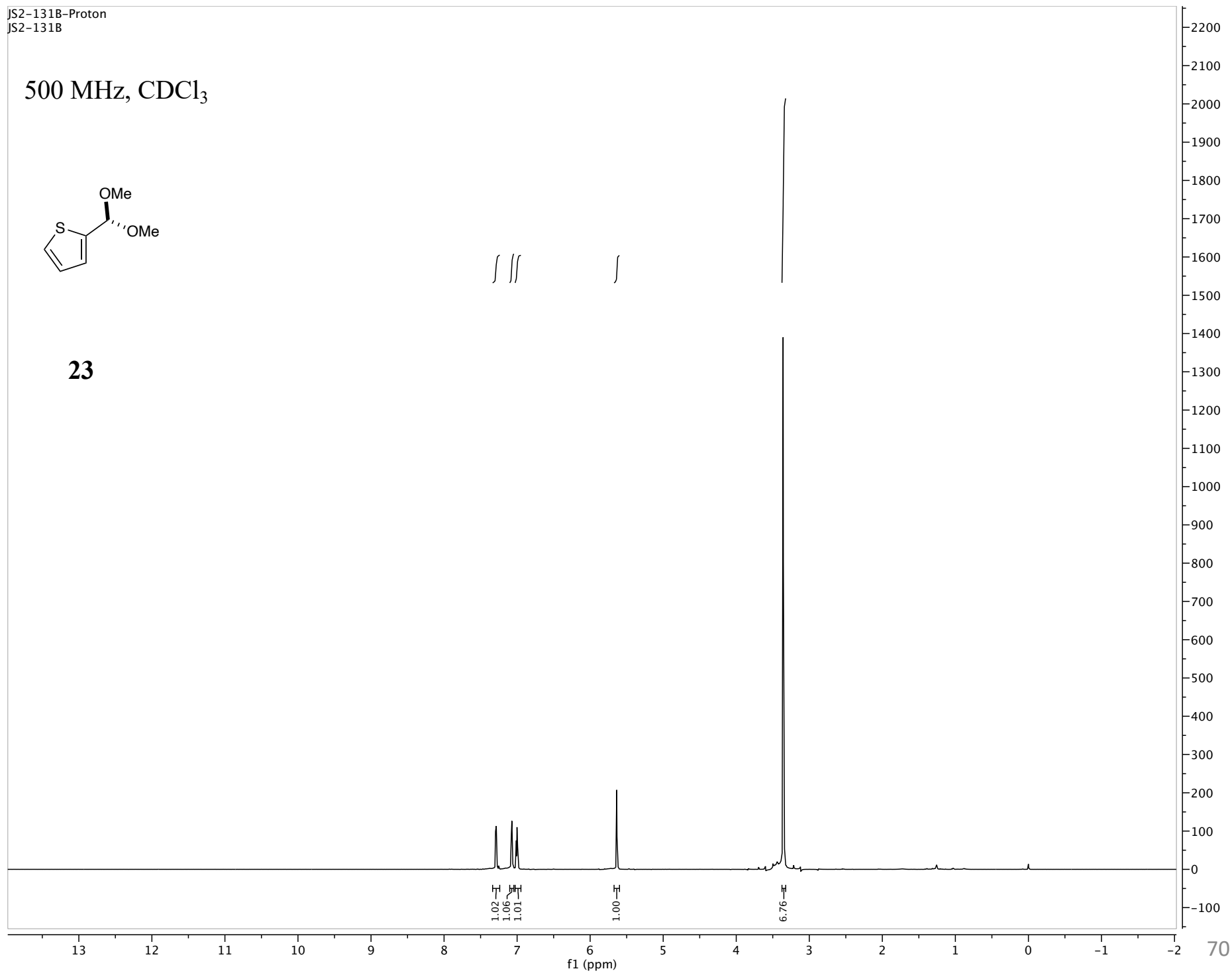
21

136.23
133.73
128.73
128.25
126.87
125.83
103.06
52.87

f1 (ppm)

Furfural–Acetal–Final–Proton–2

500 MHz, CDCl$_3$

22

1.00 0.48 1.12 0.95 0.96 6.25

f1 (ppm)

Furfural–Acetal–Final–Carbon–2

125 MHz, CDCl$_3$

22

150.99
142.64
110.20
108.58
98.10
52.99

f1 (ppm)

JS2-131B-Proton
JS2-131B

500 MHz, CDCl$_3$

23

1.02
1.06
1.01
1.00
6.76

13   12   11   10   9   8   7   6   5   4   3   2   1   0   −1   −2

f1 (ppm)

70

125 MHz, CDCl$_3$

141.61 126.76 125.78 125.52 100.18 52.64

23

f1 (ppm)

500 MHz, CDCl$_3$

OMe

OMe

24

5.10   1.00   6.34   2.30   2.25

13   12   11   10   9   8   7   6   5   4   3   2   1   0   −1   −2

f1 (ppm)
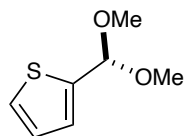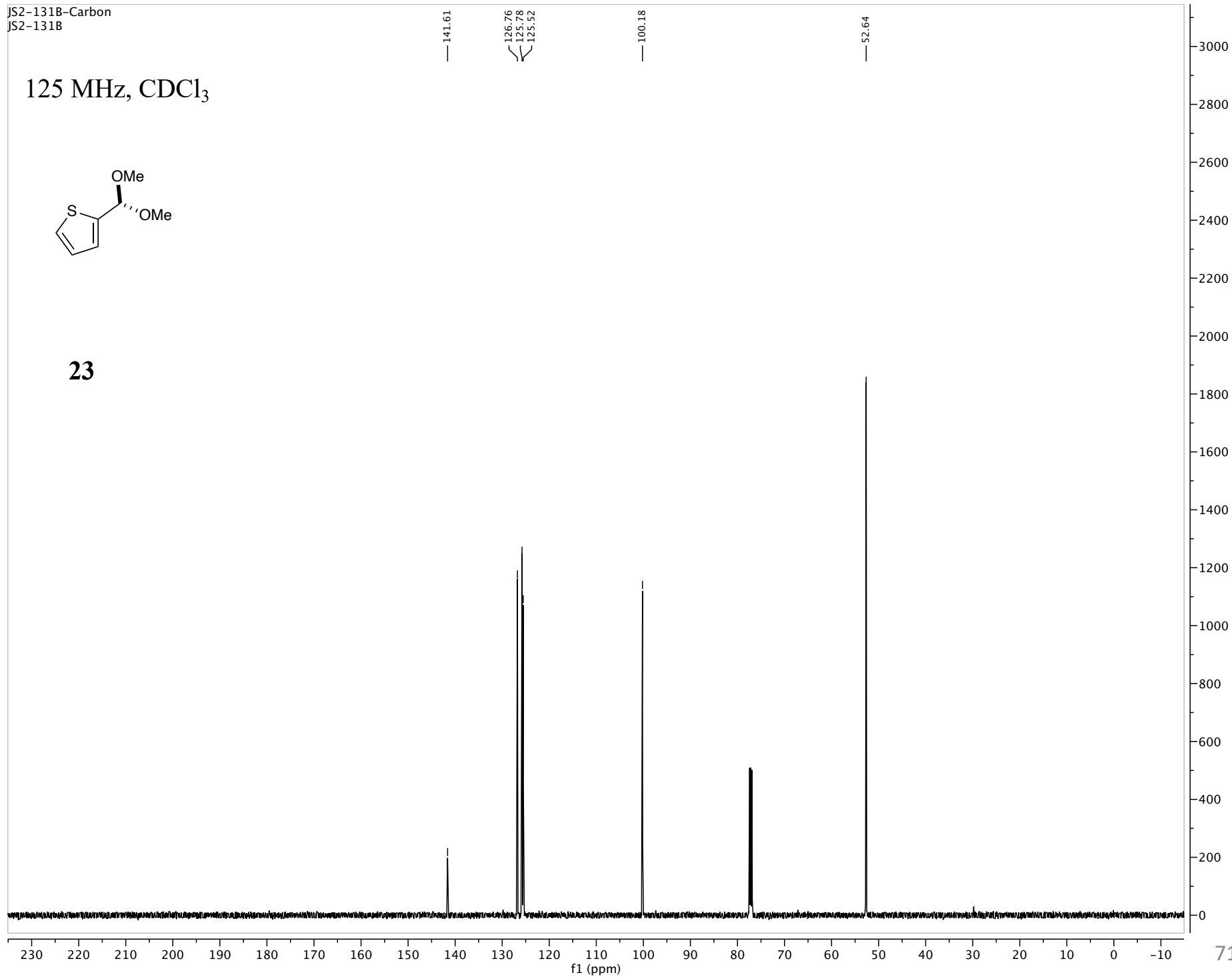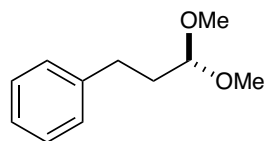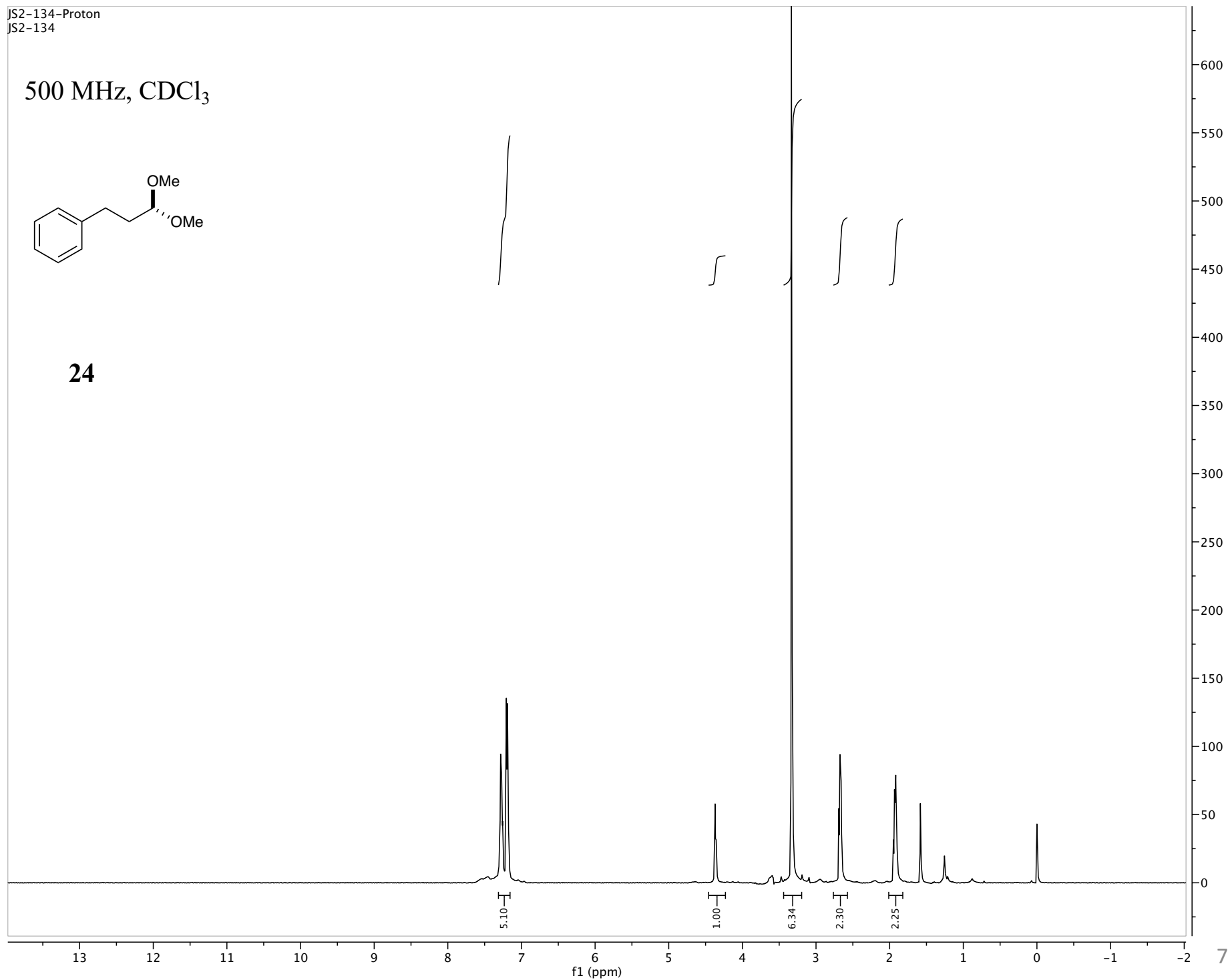
JS2-134-Carbon
JS2-134

125 MHz, CDCl$_3$

141.77
128.74
128.54
126.02
103.90
52.87
34.23
31.01

24

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
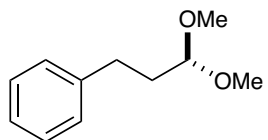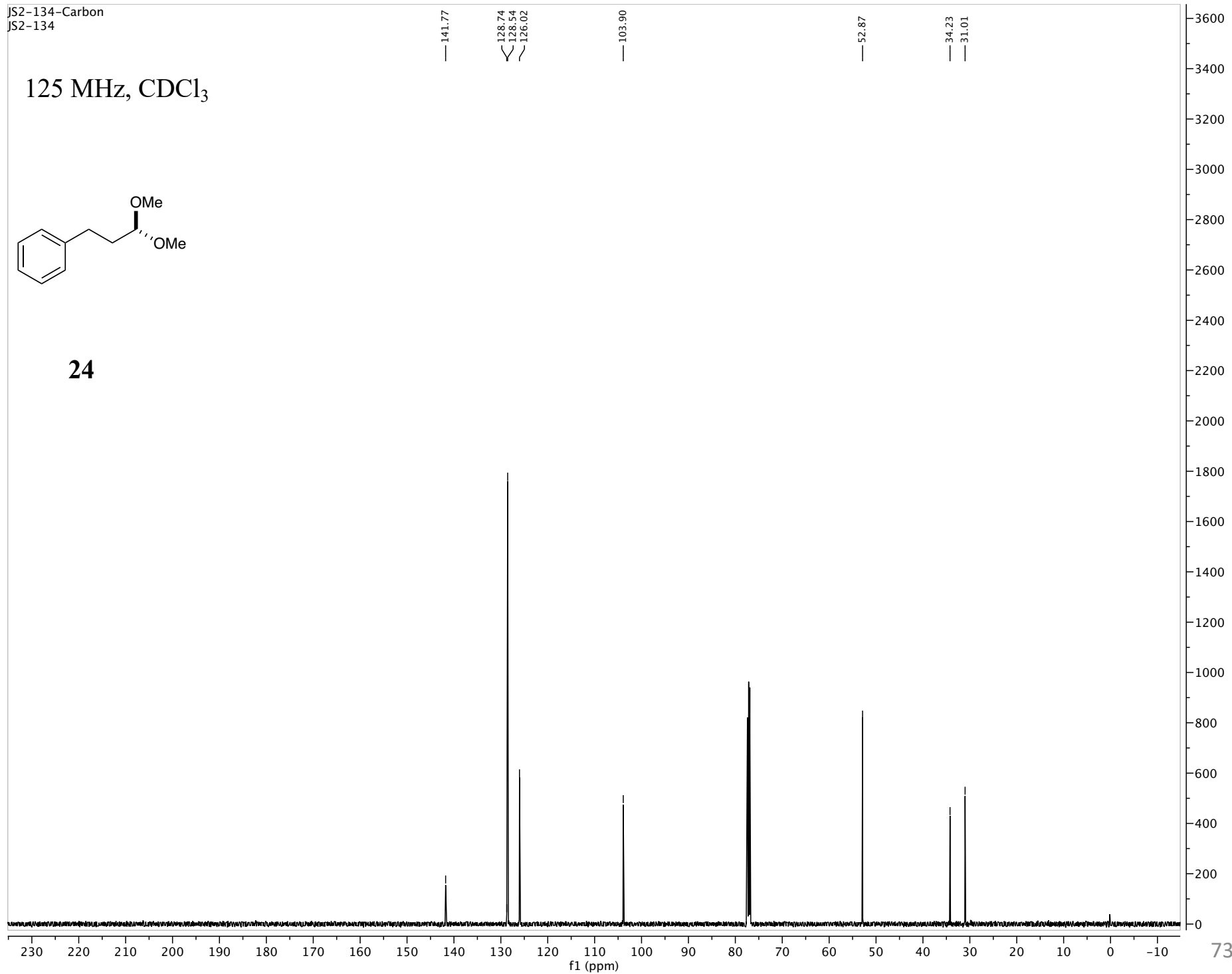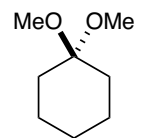
500 MHz, CDCl₃

25
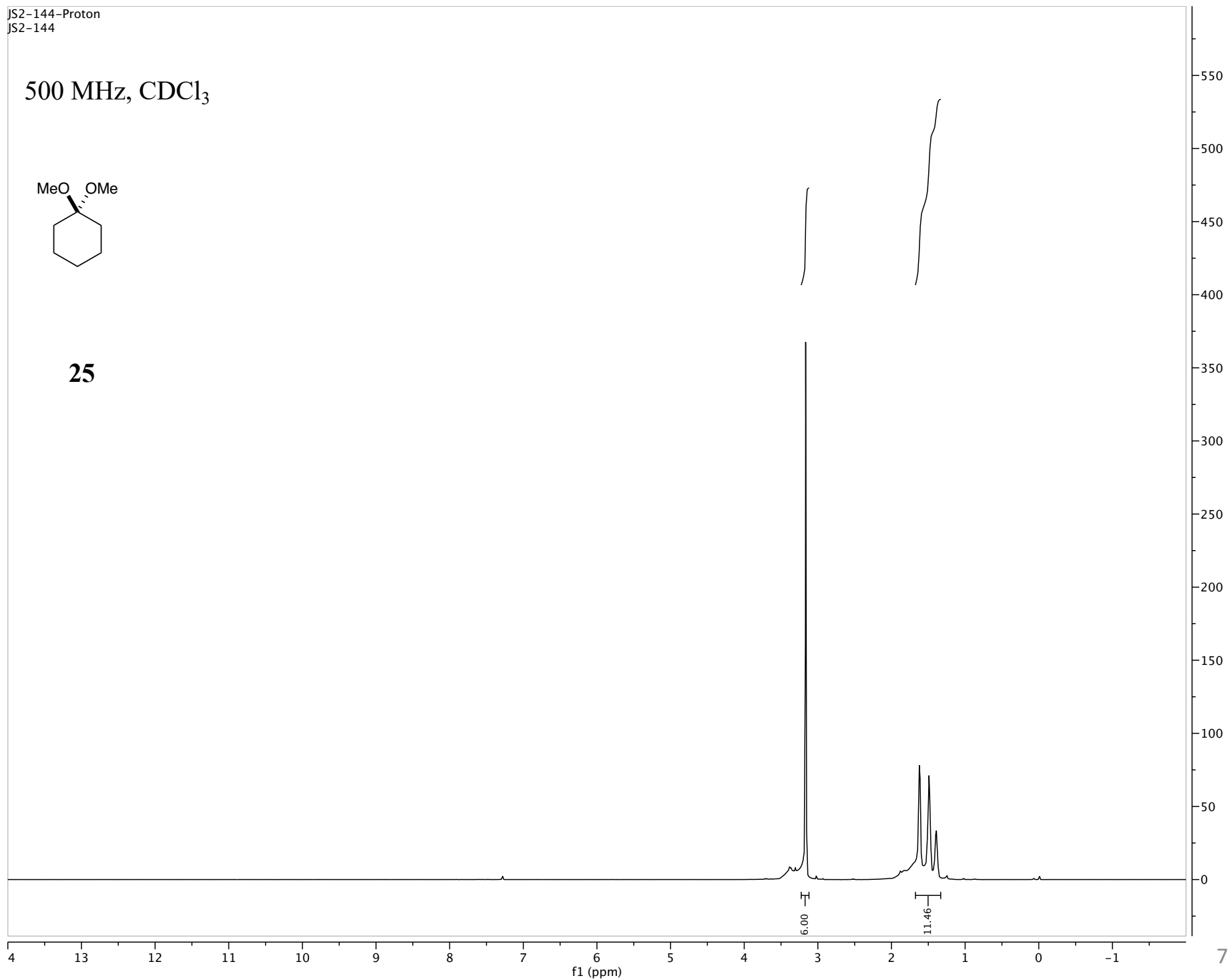
JS2-144-Carbon
JS2-144

125 MHz, CDCl$_3$
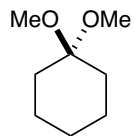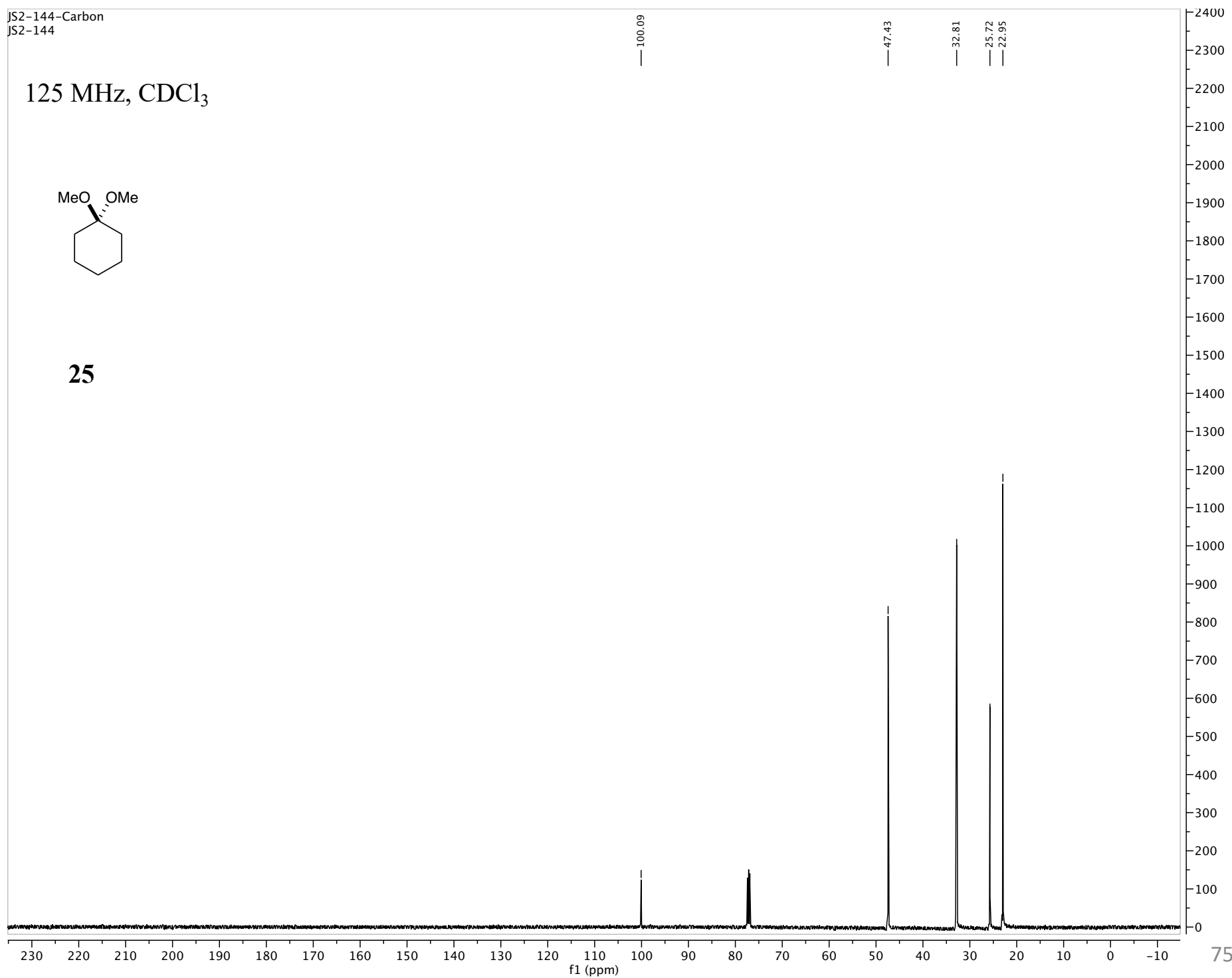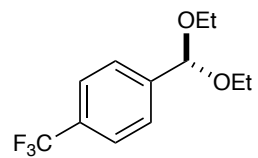
MeO OMe

25

100.09   47.43   32.81   25.72   22.95

f1 (ppm)

500 MHz, CDCl$_3$

26

4.48 1.00 4.62 6.88

f1 (ppm)

125 MHz, CDCl$_3$

26

500 MHz, CDCl$_3$

27

1.00 1.02 0.96 1.02 1.03 4.26 6.88

f1 (ppm)

125 MHz, CDCl₃

27

500 MHz, CDCl$_3$

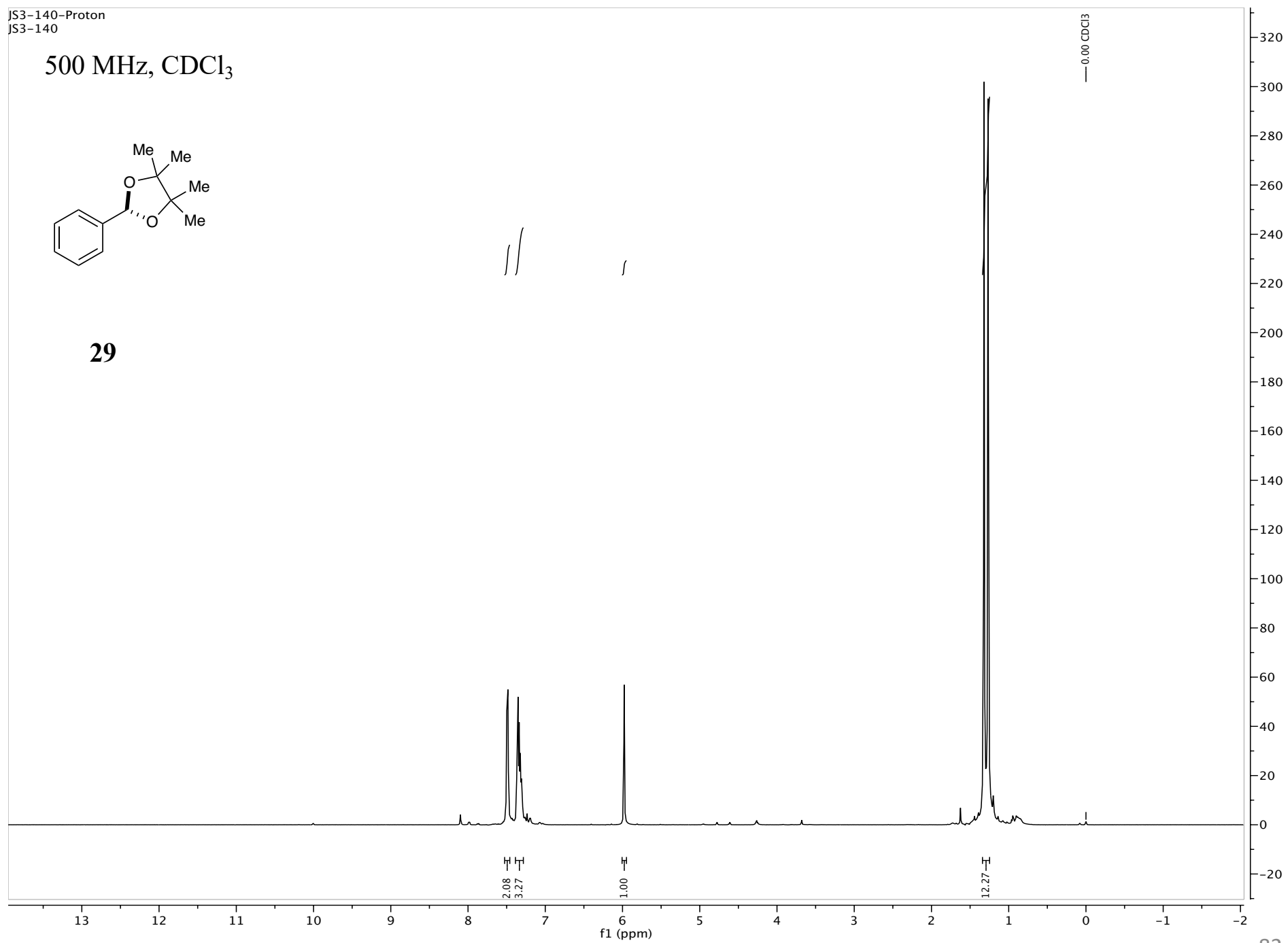**28**

f1 (ppm)

80
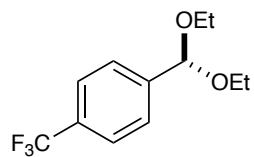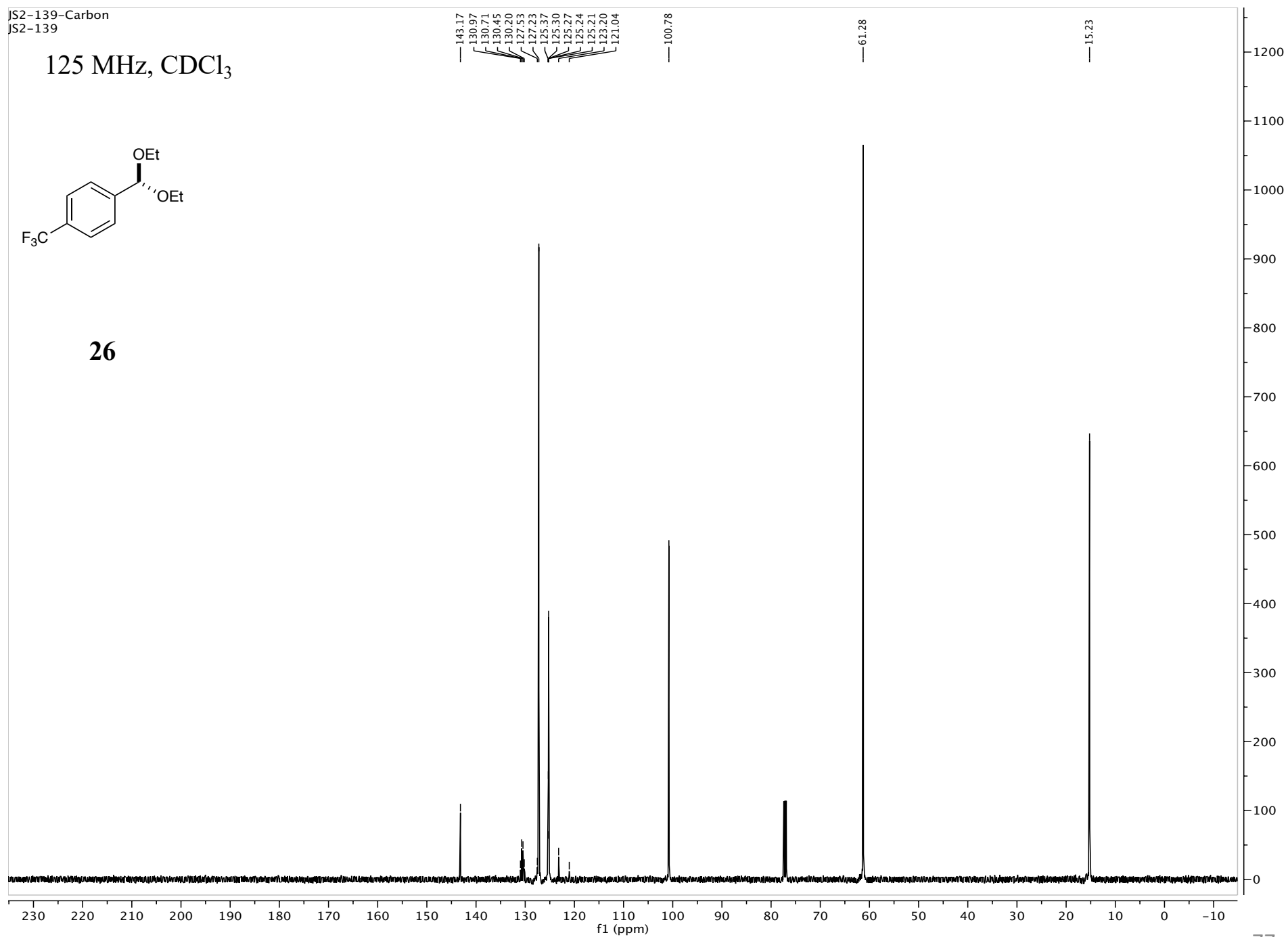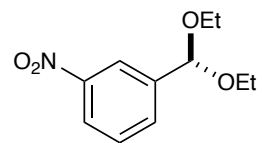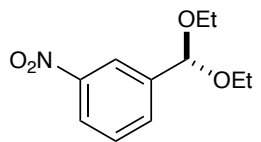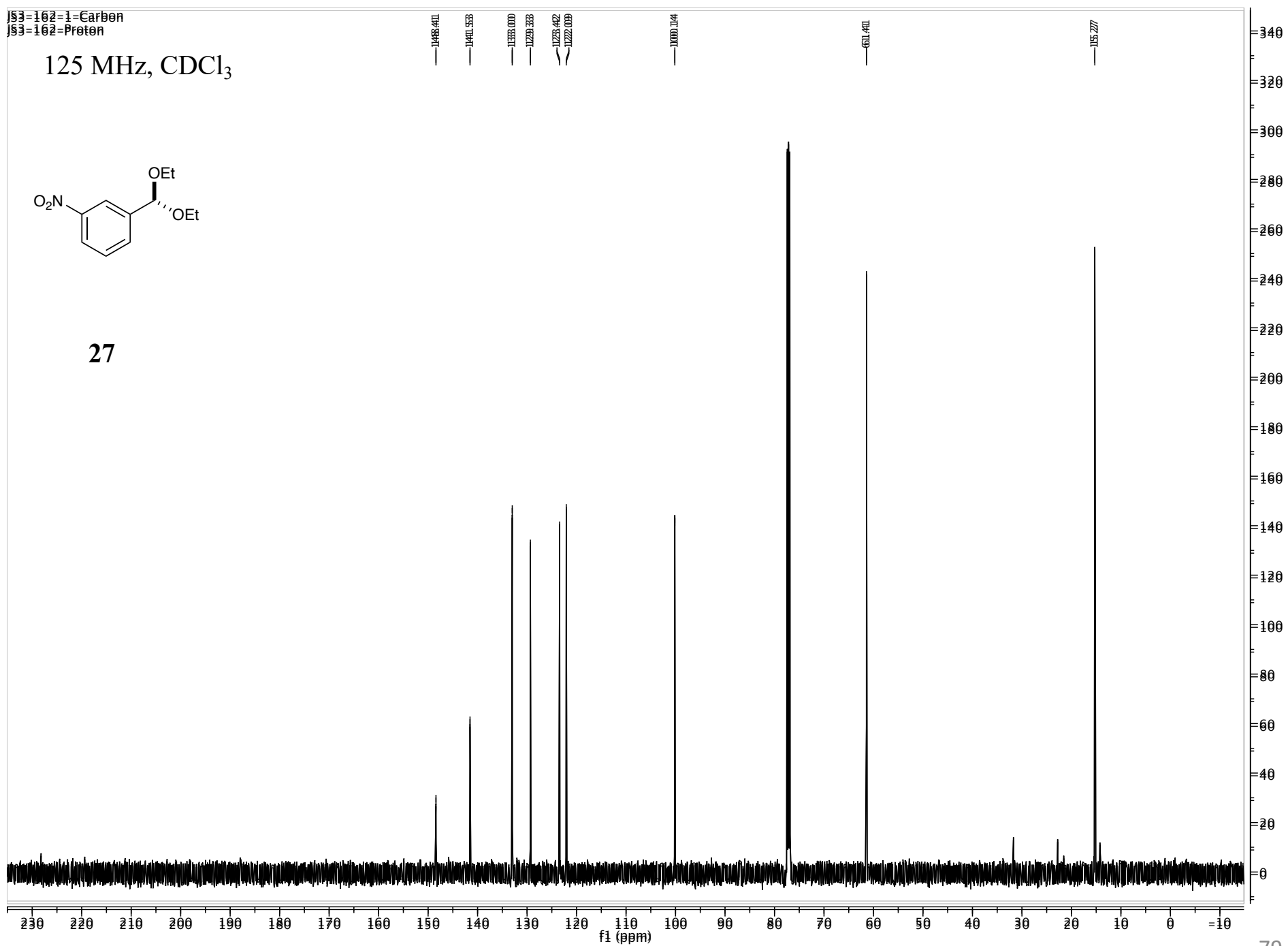
TFB–Glycol–Carbon
TFB–Glycol–Proton

125 MHz, CDCl₃
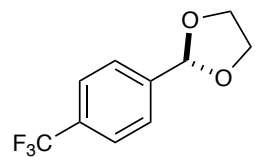
28
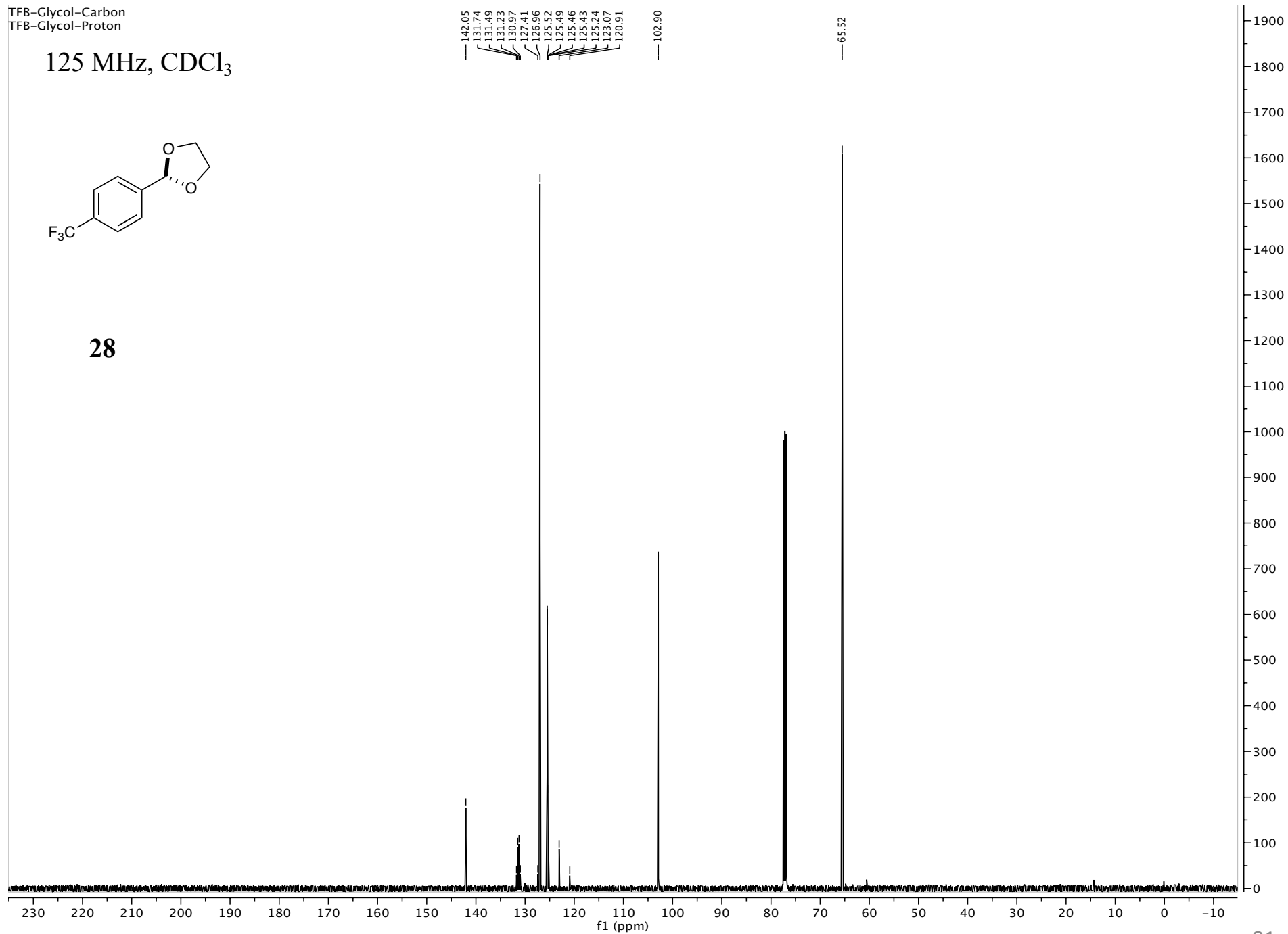
142.05
131.74
131.49
131.23
130.97
127.41
126.96
125.52
125.49
125.46
125.43
125.24
123.07
120.91
102.90
65.52

500 MHz, CDCl$_3$

29

125 MHz, CDCl$_3$

29

139.76
128.70
128.34
126.36
100.00
82.73
77.16 CDCl3
24.43
22.29

f1 (ppm)
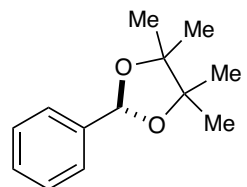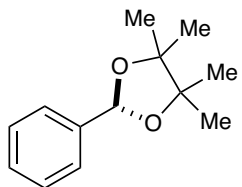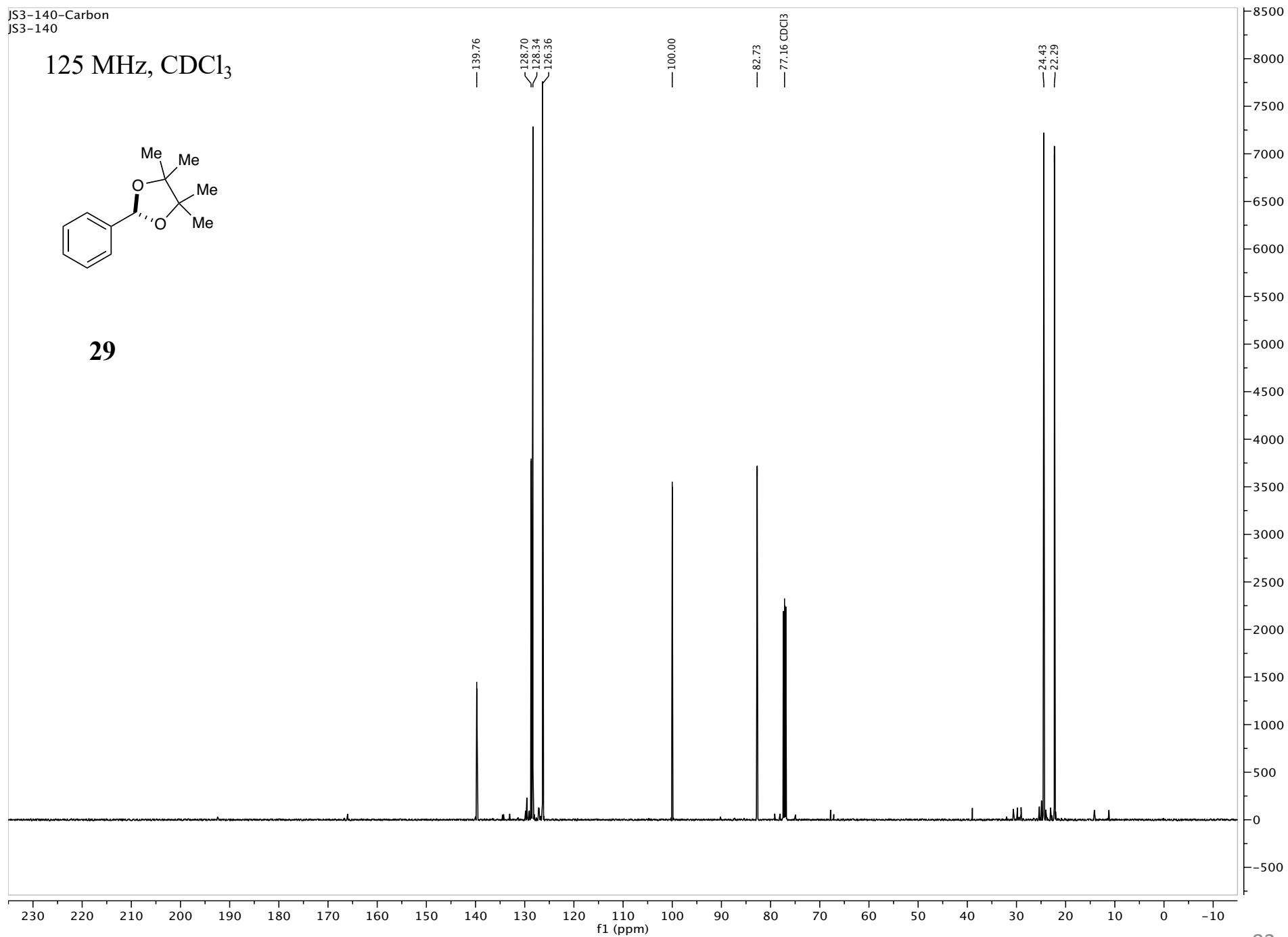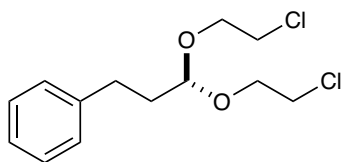
500 MHz, CDCl$_3$
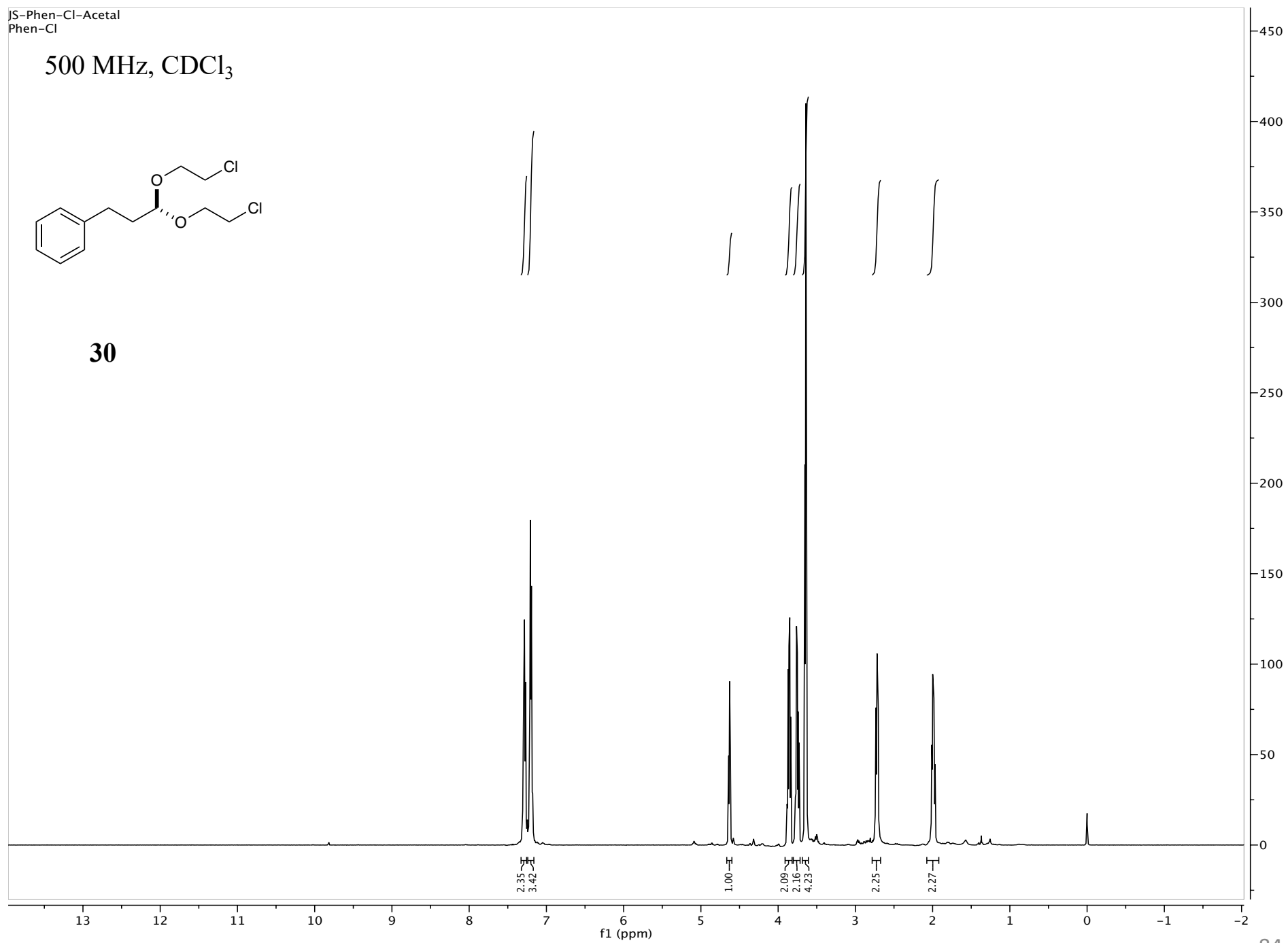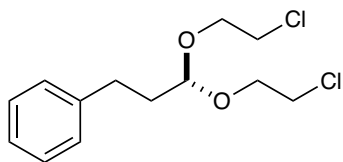

30

JS3-164-Acetal-Carbon
JS3-164-Acetal

125 MHz, CDCl$_3$

30