

Supporting Information

Ligand functionalization as a deactivation pathway in a *fac*-Ir(ppy)₃ mediated radical addition

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1.0 General Information

Chemicals were either used as received or purified according to the procedures outlined in *Purification of Common Laboratory Chemicals*. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp and stained with an ethanolic solution of potassium permanganate, ceric ammonium molybdate, or anisaldehyde. Column flash chromatography was performed using 230-400 mesh silica gel or via automated column chromatography. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted. LED lights were purchased from Creative Lighting Solutions (<http://www.creativelightings.com>).

^1H , ^{13}C and ^{19}F NMR spectra were recorded using an internal deuterium lock on Varian Unity Plus 400, Varian 500, or a Varian 700 spectrometers. All signals are reported in ppm with the internal reference of the specified solvent. J couplings are reported in Hz. Data are presented as follows: integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent, dd = doublet of doublet, dt = doublet of triplet, etc) and coupling constant (J/Hz).

Photocatalysts were assigned via comparison to those assigned by Watts¹ and by the coordination-induced shift calculation as described by Watts.¹ For *fac*-Ir(*p*-CF₃Ph)(*p*-MePy)₃ and related complex's *p*- is defined as the substituent position relative to the carbon-iridium or carbon-nitrogen bond. The numbering scheme for the ligands and the photocatalysts is based on that reported by Watts¹ for 2-phenylpyridine and has remained consistent throughout for ease of comparison.

Infrared spectra were recorded on a Perkin Elmer BX FT-IR fitted with an ATR accessory. Absorptions are given in wavenumbers (cm⁻¹). High resolution mass spectra were obtained on a Waters® Micromass® AutoSpec Ultima™ high resolution mass spectrometer. Photocatalyst quenching was conducted on a Fluoromax-2 fluorimeter and the values represent an average of 3 samples. UPLC analysis was conducted on a Waters® Acuity H-Class UPLC with a Acquity UPLC BEH C18 column 1.7 μm 2.1 x 50mm. GC-MS was performed on a Shimadzu QP2010 SE fitted with a AOC-20i auto injector.

¹ Grace, F. O.; Watts, R. J. *Magn. Reson. Chem.* **1993**, *31*, 529.

2.0 Model Reaction

Ethyl 2-(3-methyl-1H-indol-2-yl)acetate **4**

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with *fac*-Ir(ppy)₃ (5 mg, 1.0 μmol, 0.00375 equiv), NaHCO₃ (0.16 g, 2.0 mmol, 1.0 equiv), 3-methyl indole (0.26 g, 2.0 mmol, 1.0 equiv), ethyl bromoacetate (0.66 mL, 6.0 mmol, 3.0 equiv), DMA (10.0 mL). The heterogeneous mixture was sparged with N₂ gas while stirring for 15 minutes. The flask was then irradiated with a 1 W blue LED strip. After the reaction was complete (12 h, as judged by TLC analysis), the solution was washed with 5% aqueous LiCl (50 mL) and extracted with diethyl ether (2 x 25 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated. The residue was purified via Combiflash using silica gel and a hexanes-EtOAc gradient to provide **4** (0.37 g, 85%) as colorless oil with spectroscopic properties in accordance with those reported in the literature.²

¹H NMR (CDCl₃, 400 MHz): δ_H 1.29 (3H, t, *J* 7.6), 3.76 (2H, s), 2.56 (3H, s), 4.20 (2H, q, *J* 7.2), 7.09 (1H, t, *J* 8.0), 7.16 (1H, t, *J* 8.0), 7.31 (1H, d, *J* 8.0), 7.50 (1H, d, *J* 8.0) and 8.49 (1H, br s).

3.0 Procedure for Kinetic Analysis

A 25 mL recovery flask equipped with a magnetic stir bar was charged with **1**, **2**, and NaHCO₃. 10 mL DMA was added to the flask and it was sealed with a rubber septum. **3** was added via syringe. The slurry was sparged with N₂ for 15 min. The reaction was then illuminated with a 1W blue LED strip and stirred under N₂ atmosphere. 0.05 mL aliquots were sampled via syringe. 10 μL reaction solution was dissolved 990 μL 2:1 MeCN:H₂O containing 10 μL of 5 mg/mL acetophenone in 2:1 MeCN:H₂O. Samples were analyzed via reverse-phase UPLC.

² Kapur, A.; Kumar, K.; Singh, L.; Singh, P.; Elango, M.; Subramanian, V.; Gupta, V.; Kanwai, P.; Ishar, M. P. S. *Tetrahedron* **2009**, *65*, 4593.

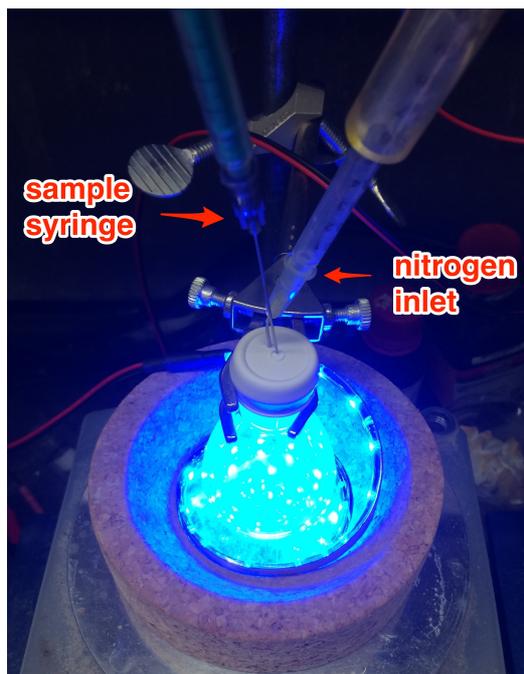


Figure S1. Set up for kinetic analysis

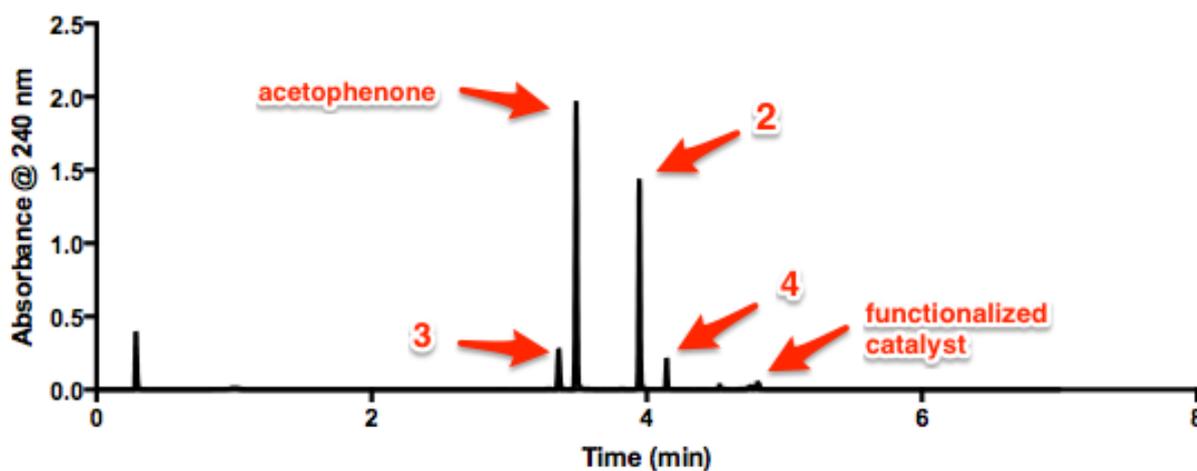


Figure S2. Representative UPLC trace.

4.0 Method for Graphical Analysis

The concentration of the limiting substrate is measured as a function of time and plotted. The rate of reaction is calculated from the slope of this curve. The raw data is approximated using mathematical curve-fitting software to determine an equation that represents the full data set over the time observed. The resulting function, $f(\text{time})$, is used to determine the concentration of substrate for all times measured. The derivative of this function ($f'(\text{time})$) is a mathematical approximation of the rate of reaction for all times measured. Then, $f'(\text{time})$ and $f(\text{time})$ are treated as parametric equations for all times measured over the course of the experiment, where $y = f'(\text{time})$ and $x = f(\text{time})$.

The data are then fit to a first order exponential decay in Prism 6 software using the following equation:

$$f(\text{time}) = [\mathbf{2}] = y_0 + Ae^{-k_{obs}(\text{time})}$$

where constants A , k_{obs} , and y_0 are calculated by the software. A R^2 value ≥ 0.99 was required to determine an accurate approximation of the data. The standard deviation with respect to $[\mathbf{2}]$ was determined using the following equation and standard deviations determined by the software:

$$\sigma_{[\mathbf{3}]} = Ae^{-k_{obs}(\text{time})} \sqrt{(-k_{obs}e^{-k_{obs}(\text{time})}(\text{time})(\sigma_{k_{obs}}))^2 + \left(\frac{\sigma_A}{A}\right)^2 + \sigma_{y_0}^2}$$

The derivative $[\mathbf{2}]$ provided the equation for rate of reaction as follows:

$$f'(\text{time}) = -\frac{d[\mathbf{2}]}{dt} = k_{obs}Ae^{-k_{obs}(\text{time})}$$

where the uncertainty with respect to rate is defined as

$$\sigma_{\frac{d[\mathbf{2}]}{dt}} = k_{obs}Ae^{-k_{obs}(\text{time})} \sqrt{(-k_{obs}e^{-k_{obs}(\text{time})}(\text{time})(\sigma_{k_{obs}}))^2 + \left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_{k_{obs}}}{k_{obs}}\right)^2}$$

5.0 Supplementary Rate Data

Functionalization of 1

An initial UPLC trace of **1** was obtained (Figure S3, blue). In the absence of **2**, **1** and **3** were irradiated under reaction conditions for 2 h (Figure S3, black). We sampled this mixture and obtained a UPLC trace that displayed no obvious peak corresponding to **1** and a variety of other peaks. We then added the typical **2** (2 mmol) to the reaction mixture and irradiated this system with light. After 2 h, the mixture was sampled and a UPLC trace obtained which displayed 0.030 mmol conversion of **2** (Figure S3, red).

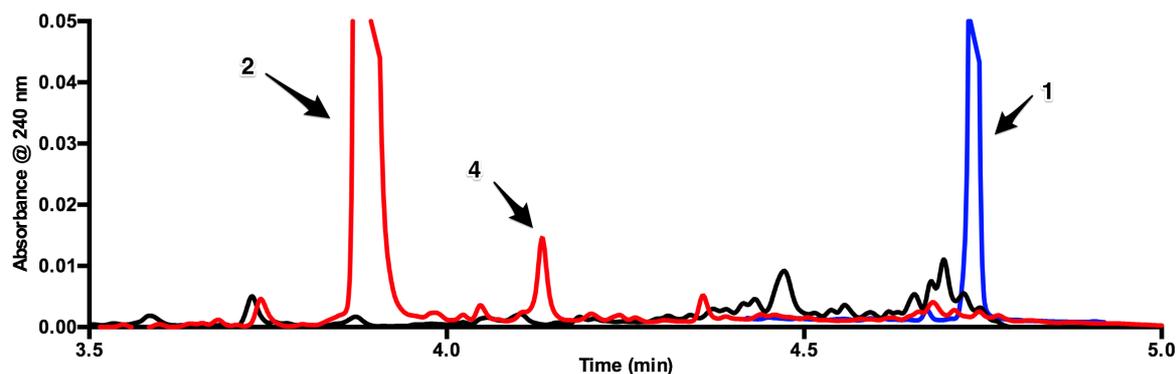


Figure S3. UPLC trace of **1** before irradiation (blue). UPLC trace of **1** after 2 h irradiation (black). UPLC trace of reaction mixture after 2 h of irradiation (red).

Deactivation of 5

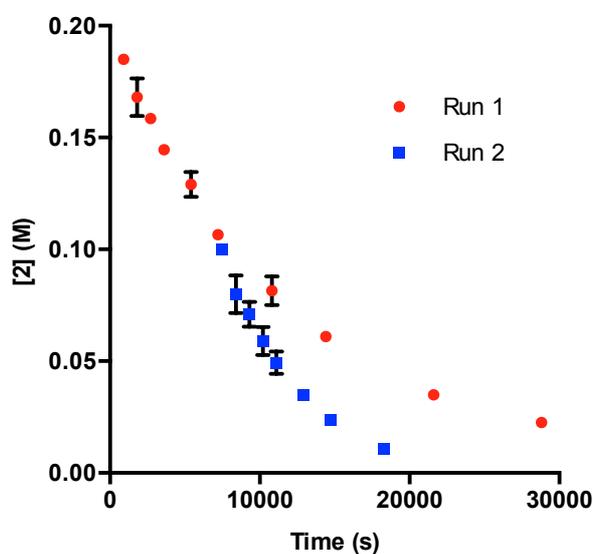


Figure S4. Profile of Run 1 as $[2]$ vs time and the time-adjusted profile of Run 2 as $[2]$ vs adjusted time for the **5**-catalyzed system. Run 1: **5** = 7.5 μmol . **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL. Run 2: **5** = 7.5 μmol . **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO_3 = 3.00 mmol, DMA = 10 mL. All points are averaged from three reactions.

Initial consumption of 5

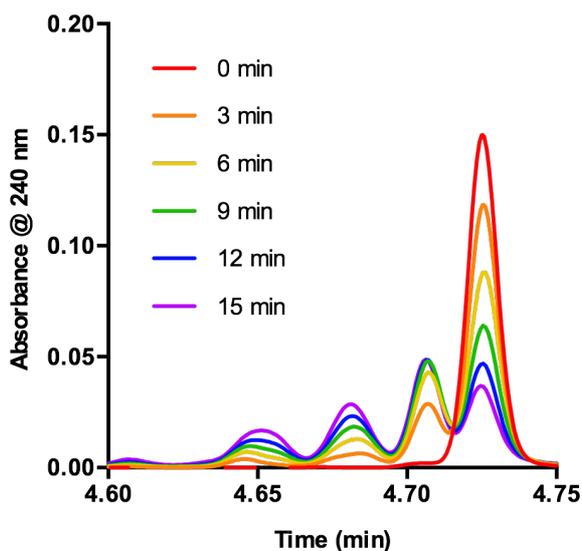


Figure S5. Consumption of **5** during the first 15 min of the reaction displayed as an overlay of UPLC traces. Conditions: **5** = 7.5 μmol . **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL.

Rate Order of **1**

We considered the impact of [**1**] on the rate of reaction. Surprisingly, when the amount of **1** added to the reaction mixture was doubled from 7.50 μmol to 15.00 μmol , no change in rate occurred. Decrease in the amount of **1** to 3.75 μmol resulted in a slight decrease in the rate of reaction. While not visually apparent, these data suggest that when 7.50 μmol of **1** are added to the reaction mixture, not all of the catalyst is in solution. As a result, when additional **1** is added to the system, the [**1**] remains constant, providing no rate enhancement. A decrease in the amount of **1** to 3.75 μmol provided a minimal decrease in reaction rate. Because we know that the system must be near saturation based on the result at higher amounts of **1**, a further decrease in **1** is necessary to accurately observe homogenous concentration effects with respect to **1**. A reaction performed with 1.88 μmol yielded a more significant decrease in the rate of reaction. It is important to note that below this catalyst loading, the reaction does not proceed through three half-lives. The combined kinetic data suggest that the reaction is positive order in catalyst.

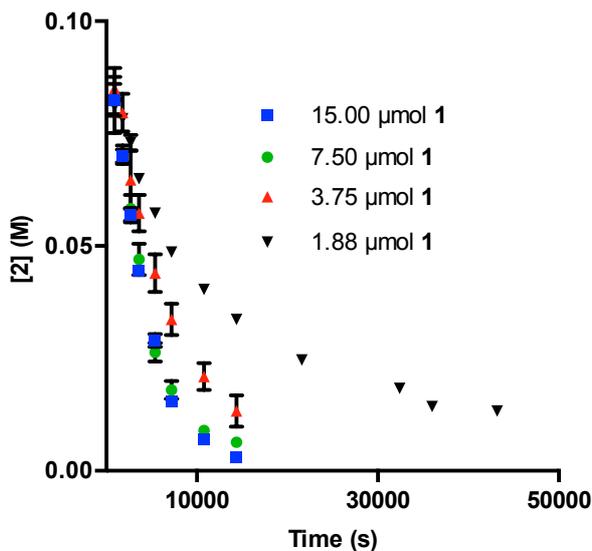
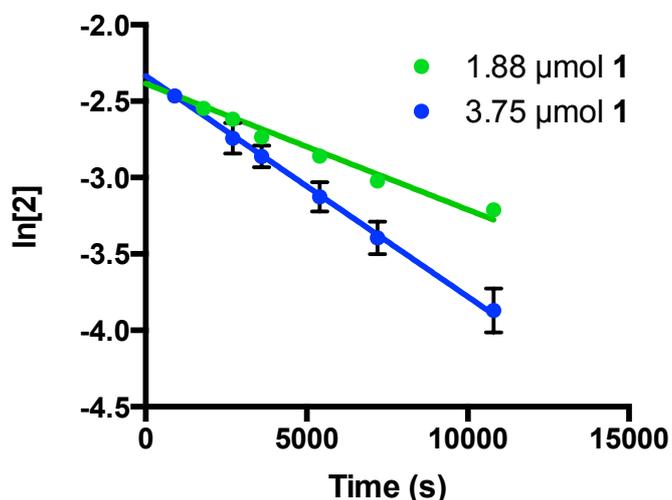


Figure S6. Effect of **1** on rate plotted as $[2]$ vs time. General conditions: **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO_3 = 3.00 mmol, DMA = 10 mL. All points are averaged from three reactions.

Three different methods were utilized to determine the rate order of **1**. All three methods utilized **1** in 10 mL DMA.

Method 1: initial rates

Using the initial 6 points of decays determined measured for 3.75 μmol **1** and 1.88 μmol **1**, the slopes of the lines were determined using Prism 6 software and are given as follows:



3.75 μmol **1**: R^2 fit = 0.9420; slope = $-1.05 \times 10^{-5} \pm 7 \times 10^{-7}$

1.88 μmol **1**: R^2 fit = 0.9066; slope = $-7.2 \times 10^{-6} \pm 6 \times 10^{-7}$

These data were used to determine the rate order as follows:

$$order = \frac{\log\left(\frac{slope_1}{slope_2}\right)}{\log\left(\frac{concentration_1}{concentration_2}\right)} = \frac{\log\left(\frac{-1.05 \times 10^{-5}}{-7.2 \times 10^{-6}}\right)}{\log\left(\frac{0.00075}{0.000375}\right)} = 0.54$$

Method 2: Graphical analysis of normalized rate

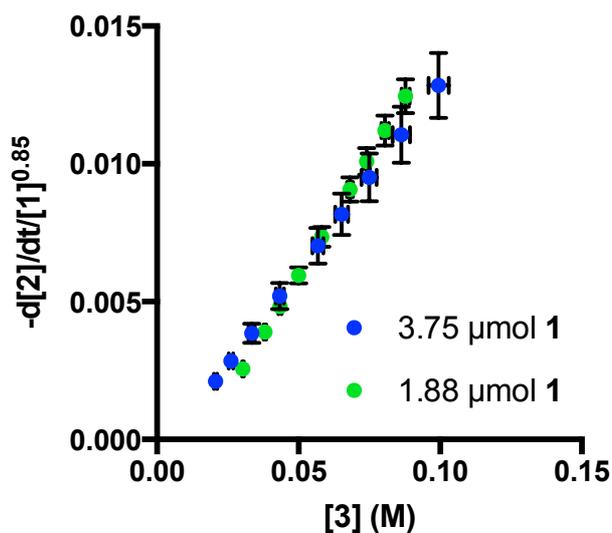
Using the typical method, the data were approximated using Prism 6. Then considered according to the rate equation

$$-\frac{d[2]}{dt} = -k_{obs}[2][1]^x$$

The rate data can be directly compared through normalization of the reaction rate by the $[1]^x$

$$-\frac{\frac{d[2]}{dt}}{[1]^x} = -k_{obs}[2]$$

where x is the rate order of 1. Overlay of the two decays occurs when $x = 0.85$.



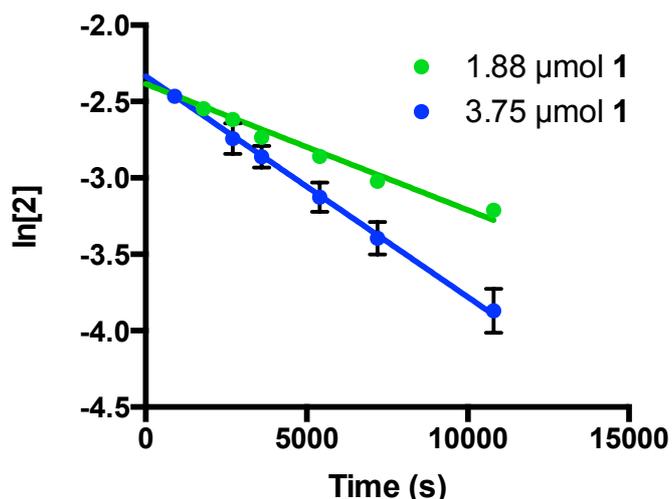
Method 3: $\ln(k_{obs})$ vs $\ln([1])$

Values for k_{obs} can be determined through determination of the slope of $\ln[2]$ vs time because

$$[2] = [2]_0 e^{-k_{obs}(time)}$$

therefore,

$$\ln([2]) = \ln([2]_0) - k_{obs}(time)$$



3.75 $\mu\text{mol 1}$: $R^2 = 0.9791$; slope = $-1.45 \times 10^{-4} \pm 5 \times 10^{-6}$

1.88 $\mu\text{mol 1}$: $R^2 = 0.9688$; slope = $-8.3 \times 10^{-5} \pm 3 \times 10^{-6}$

A rate order of 1.3 was determined through the following equation:

$$\text{order} = \frac{\ln(k_{obs1}) - \ln(k_{obs2})}{\ln(\text{concentration}_1) - \ln(\text{concentration}_2)} = \frac{\ln(1.45 \times 10^{-4}) - \ln(8.3 \times 10^{-5})}{\ln(0.00075) - \ln(0.000375)} = 1.3$$

On/Off Experiment

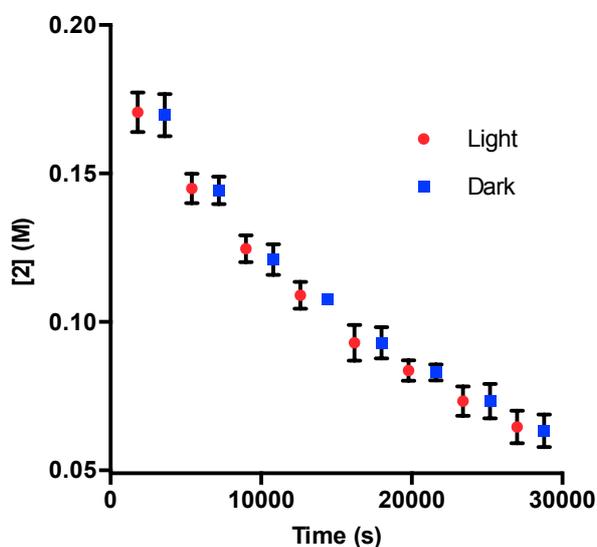


Figure S7. Analysis of the role of light plotted as [3] vs time. Concentrations designated as Light (red) were sampled after 30 min of irradiation. Concentrations designated as Dark (blue) were sampled after 30 min of darkness. Conditions: **1** = 7.5 μmol , **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL. Data consistent with propagation not being the dominant mechanism.

Degree of Deactivation of 6

Figure S8 displays a direct comparison of the reaction profiles for the **1**- and **6**-catalyzed systems. Figure S8a compares the Run 1 conditions for both systems while Figure S8b compares Run 2 conditions. Examination of Run 1 shows that **6** provides a

higher overall rate than **1**. However, under Run 2 conditions, **1** and **6** provide statistically similar rates. The difference in Figure S8a is consistent with a decrease in the degree of deactivation of the complex.

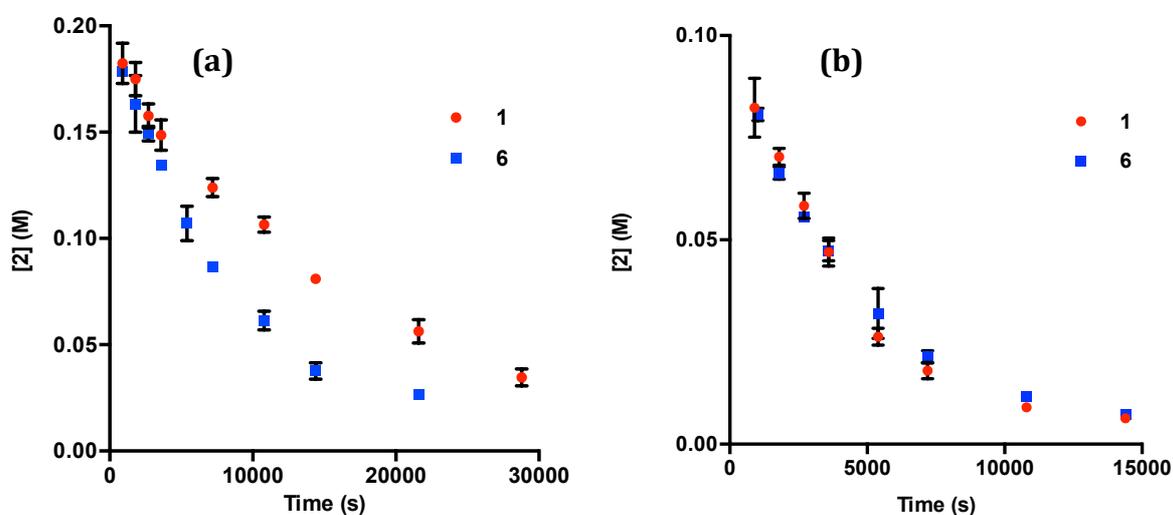


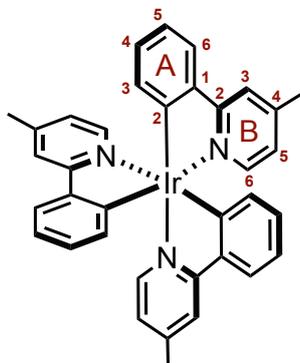
Figure S8. (a) Profile of Run 1 as [2] vs time for the **1**- and **6**-catalyzed systems Run 1: catalyst = 7.5 μmol, **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO₃ = 4.00 mmol, DMA = 10 mL. (b): Profile of Run 2 as [2] vs time for the **1**- and **6**-catalyzed systems Run 2: catalyst = 7.5 μmol, **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO₃ = 3.00 mmol, DMA = 10 mL. All points are averaged from three reactions.

6.0 General Procedure for the Synthesis of the Photocatalysts

IrCl₃ hydrate (1 equiv), ligand (9 equiv), KI (9 equiv) and ethylene glycol (39 mM) were combined in a microwave vial equipped with a magnetic stir bar and microwaved at 200 °C for 50 min. The crude mixture was diluted with H₂O. The slurry was vacuum filtered through a medium fritted funnel to isolate a solid. The solid was washed with H₂O and then dissolved with CH₂Cl₂ and filtered. The frit was washed with CH₂Cl₂ until the filtrate was colorless. The filtrate was dried with sodium sulfate and concentrated via rotary evaporation to give a solid.

The solid was combined with ligand (5 equiv relative to initial IrCl₃ hydrate) in H₂O (0.12 M) in an acid digestion bomb equipped with a magnetic stir bar. The bomb was then heated in a sand bath to 250 °C for 12 h. Upon cooling to ambient temperature, the crude mixture was diluted with H₂O. The slurry was vacuum filtered through a medium fritted funnel to isolate a solid. The solid was washed with H₂O and then dissolved with CH₂Cl₂ and filtered. The frit was washed with CH₂Cl₂ until the filtrate was colorless. The filtrate was dried with sodium sulfate and concentrated via rotary evaporation to give a solid. This crude solid was purified via Combiflash using silica gel and a hexanes-CH₂Cl₂ gradient.

fac-Ir(Ph(*p*-MePy))₃ **6**



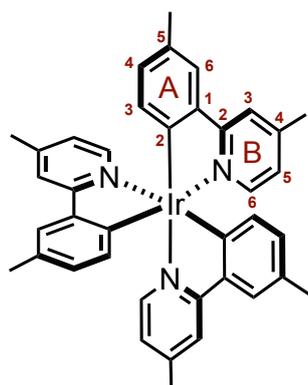
Prepared via the general procedure (110 mg, 28% yield) with spectroscopic properties in accordance with those reported in the literature.³

¹H NMR (700 MHz, CD₂Cl₂) δ_H 2.41 (9H, s, Py-CH₃), 6.71 (3H, d, *J* 7.3, *H*-A3), 6.74-6.78 (6H, m, *H*-B5 and *H*-A4), 6.85 (3H, t, *J* 7.1, *H*-A5), 7.42 (3H, d, *J* 5.6, *H*-B6), 7.64 (3H, d, *J* 7.9, *H*-A6) and 7.72 (3H, s, *H*-B3);

¹³C NMR (176 MHz, CD₂Cl₂) δ_C 21.4 (Py-CH₃), 119.8 (*C*-B3), 119.9 (*C*-A5), 123.5 (*C*-B5), 124.1 (*C*-A6), 129.7 (*C*-A4), 137.1 (*C*-A3), 144.3 (*C*-A2), 146.9 (*C*-B6), 148.1 (*C*-B4), 161.8 (*C*-A1) and 166.2 (*C*-B2).

³ Yang, C.-H., Fang, K.-H.; Chen, C.-H.; Sun, I.-W. *Chem. Comm.* **2004**, 2232.

fac-Ir((*p*-MePh)(*p*-MePy))₃ 7

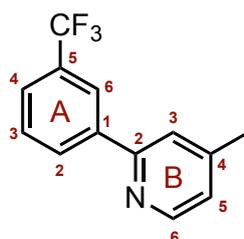


Prepared via the general procedure (70 mg, 17% yield) with spectroscopic properties in accordance with those reported in the literature.⁴

¹H NMR (700 MHz, CD₂Cl₂) δ_H 2.26 (9H, s, Ph-CH₃), 2.40 (9H, s, Py-CH₃), 6.57 (3H, d, *J* 7.6, *H*-A3), 6.62 (3H, dd, *J* 7.6, 1.4, *H*-A4), 6.70 (3H, dd, *J* 5.6, 1.1, *H*-B5), 7.37 (3H, d, *J* 5.6, *H*-B6), 7.47 (3H, s, *H*-A6) and 7.70 (3H, s, *H*-B3);

¹³C NMR (176 MHz, CD₂Cl₂) δ_C 21.2 (Ph-CH₃), 21.4 (Py-CH₃), 119.7 (*C*-B3), 123.4 (*C*-B5), 124.7 (*C*-A6), 128.8 (*C*-A5), 130.9 (*C*-A4), 137.0 (*C*-A3), 144.4 (*C*-A2), 146.9 (*C*-B6), 147.8 (*C*-B4), 157.4 (*C*-A1) and 166.3 (*C*-B2).

4-methyl-2-(3-(trifluoromethyl)phenyl)pyridine S1



To two identical 20 mL microwave vials was added (3-(trifluoromethyl)phenyl)boronic acid (360 mg, 1.88 mmol, 1.2 equiv), K₂CO₃ (430 mg, 3.14 mmol, 2.0 equiv), Bis(triphenylphosphine)palladium(II) dichloride (11.0 mg, 0.02 mmol, 0.01 equiv), 1,4-dioxane (10.5 mL), water (4.50 mL) and 2-bromo-4-methylpyridine (170 μL, 1.57 mmol, 1.0 equiv) and the heterogeneous solution sparged with nitrogen for 5 mins. The vials were sealed and heated in a microwave at 150 °C for 50 mins before cooling to rt,

⁴ Jung, S.; Kang, Y.; Kim, H.-S.; Kim, Y.-H.; Lee, C.-L.; Kim, J.-J.; Lee, S.-K.; Kwon, S.-K. *Eur. J. Inorg. Chem.* **2004**, 3415.

combining and diluting with Et₂O (50 mL). The black heterogeneous solution was filtered through celite to give a light orange solution that was washed twice with water (50 mL), dried (Na₂SO₄), filtered and concentrated *in vacuo* to give an orange oil. This crude material was purified via automated column chromatography (12 g silica column, eluting with 5% EtOAc:hexanes) to give 4-methyl-2-(3-(trifluoromethyl)phenyl)pyridine **S1** (370 mg, 76%) as a colorless crystalline solid.

¹H NMR (700 MHz, CDCl₃) δ_H 2.45 (3H, s, Py-CH₃), 7.12 (1H, dd, *J* 5.0, 0.7, *H*-B5), 7.57-7.60 (2H, m, *H*-B3, *H*-A3), 7.66-7.67 (1H, m, *H*-A4), 8.18 (1H, d, *J* 7.8, *H*-A2), 8.26 (1H, s, *H*-A6) and 8.58 (1H, dd, *J* 5.0, 0.4, *H*-B6);

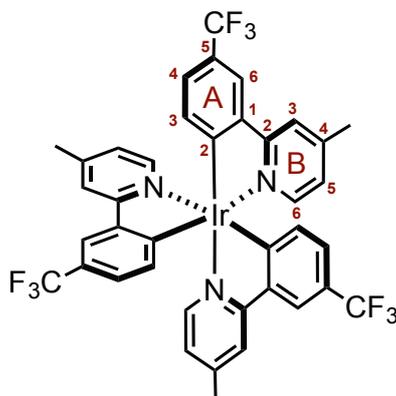
¹³C NMR (176 MHz, CDCl₃) δ_C 21.3 (Py-CH₃), 121.6 (*C*-B3), 123.9 (q, *J* 3.9, *C*-A6), 123.9 (*C*-B5), 124.3 (q, *J* 272, CF₃), 125.5 (q, *J* 3.7, *C*-A4), 129.2 (*C*-A3), 130.2 (*C*-A2), 131.2 (q, *J* 32.3, *C*-A5), 140.4 (*C*-A1), 148.2 (*C*-B4), 149.7 (*C*-B6) and 155.8 (*C*-B2);

¹⁹F NMR (376 MHz, CDCl₃) δ_F -62.3;

ν_{max} (ATR)/cm⁻¹ 2921, 2182, 1606, 1429, 1335, 1285, 1153, 1102, 1091, 1077, 910, 804, 700 and 670;

m/z: (ESI+) HRMS [M+H] C₁₃H₁₀F₃N⁺: found 238.0848; calcd 238.0838.

fac-Ir((*p*-CF₃Ph)(*p*-MePy))₃ 8



Prepared via the general procedure (270 mg, 53% yield).

¹H NMR (700 MHz, CDCl₃) δ_H 2.47 (9H, s, Py-CH₃), 6.81 (3H, d, *J* 5.4, *H*-B5), 6.85 (3H, d, *J* 7.8, *H*-A3), 7.01 (3H, d, *J* 8.1, *H*-A4), 7.37 (3H, d, *J* 5.6, *H*-B6), 7.76 (3H, s, *H*-A6) and 7.82 (3H, s, *H*-B3);

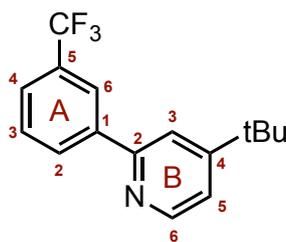
¹³C NMR (176 MHz, CDCl₃) δ_C 21.6 (Py-CH₃), 120.19 (*C*-B3) overlapping 120.20 (app s, *C*-A6), 122.4 (q, *J* 32, *C*-A5), 124.2 (*C*-B5), 125.7 (q, *J* 271, Ph-CF₃), 126.0 (q, *J* 3.3, *C*-A4), 137.1 (*C*-A3), 144.2 (*C*-A2), 146.7 (*C*-B6), 148.5 (*C*-B4), 164.9 (*C*-B2) and 166.2 (*C*-A1);

¹⁹F NMR (376 MHz, CDCl₃) δ_F -62.6;

ν_{max} (ATR)/cm⁻¹ 2158, 1615, 1599, 1328, 1269, 1103, 1075, 1029, 820 and 683;

m/z: (ESI⁺) HRMS [M+H] C₃₉H₂₇F₉IrN₃⁺: found 902.1741; calcd 902.1763.

4-(tert-butyl)-2-(3-(trifluoromethyl)phenyl)pyridine **S2**



To a 20 mL microwave vial was added (3-(trifluoromethyl)phenyl)boronic acid (4.20 g, 22.1 mmol, 1.5 equiv), K_2CO_3 (6.11 g, 44.2 mmol, 3.0 equiv), Tetrakis(triphenylphosphine)palladium(0) (510 mg, 0.442 mmol, 0.03 equiv), THF (9.0 mL), water (3.0 mL) and 2-chloro-4-tertbutylpyridine⁵ (2.5 g, 14.7 mmol, 1.0 equiv) and the heterogeneous solution sparged with nitrogen for 5 mins. The vials were sealed and heated in a microwave at 150 °C for 50 mins before cooling to rt, combining and diluting with Et_2O (50 mL). The black heterogeneous solution was filtered through celite to give a light orange solution that was washed twice with water (50 mL) once with Na_2CO_3 , dried (Na_2SO_4), filtered and concentrated *in vacuo*. This crude material was purified via automated column chromatography (40 g silica column, eluting with 0% to 100% EtOAc:hexanes) to give 4-(tert-butyl)-2-(3-(trifluoromethyl)phenyl)pyridine **S2** (4.12 g, 62%) as a pale yellow oil.

1H NMR (700 MHz, $CDCl_3$) δ_H 1.37 (9H, s, Py- $C(CH_3)_3$), 7.28 (1H, dd, J 5.2, 1.8, $H-B5$), 7.58 (1H, t, J 7.7, $H-A3$), 7.65 (1H, d, J 7.8, $H-A4$), 7.71 (1H, app t, J 0.9, $H-B3$), 8.15 (1H, d, J 7.8, $H-A2$), 8.23 (1H, s, $H-A6$) and 8.61-8.62 (1H, m, $H-B6$);

^{13}C NMR (176 MHz, $CDCl_3$) δ_c 30.5 (Py- $C(CH_3)_3$), 34.9 (Py- $C(CH_3)_3$), 117.8 ($C-B3$), 120.1 ($C-B5$), 123.9 (d, J 3.7, $C-A6$), 124.2 (q, J 272, Ph- CF_3), 125.3 (d, J 3.6, $C-A4$), 129.1 ($C-A3$), 130.2 ($C-A2$), 131.1 (q, J 32, $C-A5$), 140.7 ($C-A1$), 149.7 ($C-B6$), 155.9 ($C-B2$), and 161.2 ($C-B4$);

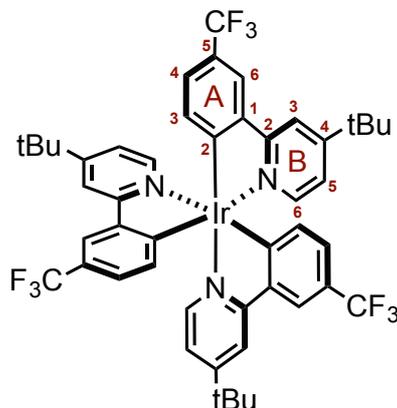
^{19}F NMR (376 MHz, $CDCl_3$) δ_F -62.6;

ν_{max} (ATR)/ cm^{-1} 2965, 2243, 1600, 132, 1162, 1120, 1063, 801, 697 and 663;

m/z : (ESI+) HRMS $[M+H]^+$ $C_{16}H_{16}F_3N^+$: found 280.1318; calcd 280.1308.

⁵ Fu, R.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **2011**, *30*, 6751.

***fac*-Ir((*p*-CF₃Ph)(*p*-^tBuPy))₃ 9**



Prepared via the general procedure (20 mg, 11% yield).

¹H NMR (700 MHz, CDCl₃) δ_H 1.35 (9H, s, Py-C(CH₃)₃), 6.87 (3H, br s, *H*-A3), 7.00 (3H, dd, *J* 5.9, 1.6, *H*-B5), 7.02 (3H, d, *J* 7.6, *H*-A4), 7.37 (3H, d, *J* 5.9, *H*-B6), 7.83 (3H, s, *H*-A6) and 7.89 (3H, d, *J* 1.6, *H*-B3);

¹³C NMR (176 MHz, CDCl₃) δ_C 30.5 (Py-C(CH₃)₃), 35.1 (Py-C(CH₃)₃), 116.0 (*C*-B3), 119.9 (app d, *J* 3.0, *C*-A6), 120.5 (*C*-B5), 122.2 (q, *J* 33.0, *C*-A5), 125.5 (q, *J* 271, Ph-CF₃), 125.7 (app d, *J* 2.5, *C*-A4), 137.1 (*C*-A3), 144.4 (*C*-A2), 146.6 (*C*-B6), 161.0 (*C*-B4), 164.6 (*C*-B2) and 166.1 (*C*-A1);

¹⁹F NMR (376 MHz, CDCl₃) δ_F -61.5;

ν_{max} (ATR)/cm⁻¹ 2360, 1327, 1276, 1117, 1072, 1060, 1031, 835 and 606;

m/z: (ESI⁺) HRMS [M+H] C₄₈H₄₅F₉IrN₃⁺: found 1027.3088; calcd 1027.3094.

7.0 Synthesis of *fac*-Ir[*(p*-(CH₂C(O)OEt)PhPy)(ppy)₂] 5

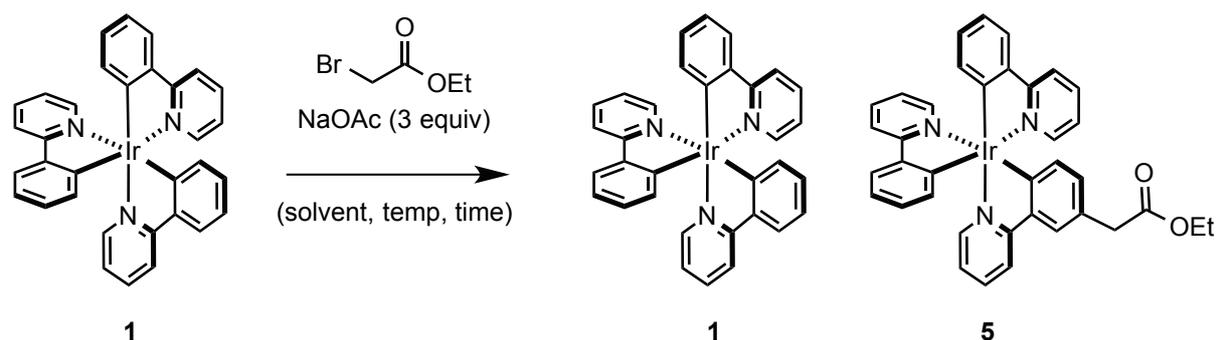


Table S1: Synthesis of 5; optimization

Equiv of ethyl-bromoacetate ^a	Scale/mg	Solvent	Temp/°C	Time/h	Yield of Ir(ppy) ₃	Yield of 5
10	20	DMA	22	4	-	18
2	25	DMA	10	5	52	4
3	25	DCM	10	5	48	14
3	50	DCM	5	13	30	27
3	200	DCM	5	13.5	13	24
3	200	DCM	5	9.5	35	29
3 ^b	20	DCM	5	9.5	>95	

^a The use of higher equivalents of ethylbromoacetate representative of the reaction conditions led to an intractable mixture of products within 1h. ^b Reaction performed in the dark.

A heterogeneous solution of *fac*-Ir(ppy)₃ (200 mg, 0.305 mmol, 1.0 equiv), sodium acetate (75.1 mg, 0.916 mmol, 3.0 equiv) and ethylbromoacetate (101 μL, 0.916 mmol, 3.0 equiv) in CH₂Cl₂ (40 mL) in a 100 mL RBF was cooled to 5 °C in a 100 mL jacketed beaker connected to a circulating chiller with *i*-PrOH as the internal beaker coolant (see picture for details). The heterogeneous solution was sparged with N₂ for 15 minutes resulting in minimal solvent loss and a color change from yellow to bright luminous green consistent with *fac*-Ir(ppy)₃. Two 1W LED strips were turned on and the heterogeneous solution stirred at 5 °C for 9.5 h. The solution was then diluted with CH₂Cl₂ (25 mL) and washed with water (25 mL), the organic portion was dried (Na₂SO₄), filtered and concentrated *in vacuo* to give a bright yellow crude material that was purified via automated column chromatography (40 g silica column, eluting with 30% hexanes:CH₂Cl₂ to CH₂Cl₂ to 1% MeOH:CH₂Cl₂) to give *fac*-Ir(ppy)₃ (70 mg, 35% yield), **5**

(66 mg, 29% yield) and a second mono alkylated *fac*-Ir(ppy)₃ complex **S3** (12 mg, 5% yield).

Data for *fac*-Ir[[(*p*-(CH₂C(O)OEt)PhPy)(ppy)]₂] **5**

¹H NMR (700 MHz, DMSO) δ_H 1.16 (3H, t, *J* 7.1, CH₂CH₃), 3.49 (2H, s, ArCH₂C(O)) 4.05 (2H, q, *J* 7.1, CH₂CH₃), 6.58-6.61 (2H, m, *H*-C3 and *H*-C4), 6.65 (1H, dd, *J* 3.2, 1.2, *H*-A3), 6.67-6.70 (2H, m, *H*-A4), 6.79-6.81 (2H, m, *H*-A5), 7.11-7.14 (3H, m, *H*-B5, *H*-D5), 7.47-7.49 (3H, m, *H*-B6, *H*-D6), 7.64, (1H, d, *J* 1.2, *H*-C6), 7.75(2H, d, *J* 7.8, *H*-A6), 7.77-7.81 (3H, m, *H*-B4, *H*-D4), 8.09(1H, d, *J* 8.3, *H*-D3) and 8.12-8.13 (2H, m, *H*-B3);

¹³C NMR (176 MHz, DMSO) δ_C 14.1 (CH₂CH₃), 40.3 (ArCH₂C(O)), 60.0 (CH₂CH₃), 119.0 (*C*-D3), 119.05 and 119.07 (2 × *C*-B3), 119.57 and 119.58 (2 × *C*-A5), 122.85 and 122.87 (2 × *C*-B5 and *C*-D5), 124.1 (2 × *C*-A6), 125.09 and 125.11 (*C*-C5, *C*-C6) 129.08 and 129.09 (2 × *C*-A4), 130.3 (*C*-C4), 136.23 and 136.24 and 136.27 (2 × *C*-A3, *C*-C3), 136.87 (*C*-D4), 136.91 (*C*-B4), 143.77 and 143.78 (2 × *C*-A2), 143.9 (*C*-C2), 146.76 and 146.78 (2 × *C*-B6), 146.9 (*C*-D6), 158.6 (*C*-C1), 160.56 and 160.63 (2 × *C*-A1), 165.3 (*C*-D2), 165.52 and 165.56 (2 × *C*-B2) and 171.5 (*C*=O);

ν_{max} (ATR)/cm⁻¹ 2359, 2336, 1733, 1652, 1558, 1471, 1261, 1030 and 750;

m/z: (EI⁺) HRMS [M⁺] C₃₇H₃₀IrN₃O₂⁺: found 741.1973; calcd 741.1970.

Data for mono alkylated *fac*-Ir(ppy)₃ complex **S3**

The complex **S3** could not be assigned beyond reasonable doubt via NMR spectroscopy but is highly consistent with alkylation at the 3-position of the phenyl ring. Further to this, attempts to perform a hydrolysis/decarboxylation/oxidation sequence to give the formyl complex failed. Under both the conditions used for **5** (*vide Infra*) and more forcing conditions (Dioxane/NaOH, 80 °C) the starting material was recovered.

¹H NMR (700 MHz, DMSO) δ_H 0.99 (3H, t, *J* 7.1, CH₂CH₃), 3.13 (1H, d, *J* 16.8, ArCH_AH_BC(O)) 3.27 (1H, d, *J* 16.8, ArCH_AH_BC(O)), 3.65-3.74 (2H, m, CH₂CH₃), 6.54 (1H, dd, *J* 7.6, 1.1), 6.56-6.58 (1H, m), 6.60-6.61 (1H, m), 6.69-6.72 (2H, m), 6.82-6.84 (2H,

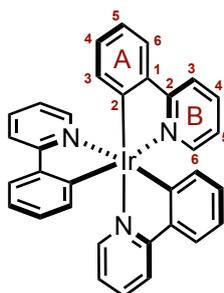
m), 6.88 (1h, t, J 7.6), 7.04-7.09 (3H, m), 7.21-7.22 (2H, m), 7.25-7.26 (1H, m), 7.69-7.70 (1H, m), 7.76-7.82 (5H, m), 8.11 (2H, dd, J 13.4, 8.3) and 8.20 (1H, d, J 8.3);

^{13}C NMR (176 MHz, DMSO) δ_{c} 13.9 (CH_2CH_3), 44.5 ($\text{ArCH}_2\text{C}(\text{O})$), 59.1 (CH_2CH_3), 119.0, 119.2, 119.7, 119.7, 120.7, 122.3, 122.6, 122.9, 123.0, 124.1, 124.4, 128.5, 129.2, 129.9, 136.3, 136.7, 136.9, 137.1, 137.4, 142.5, 143.5, 144.1, 145.3, 146.2, 146.2, 159.4, 159.4, 165.5, 165.6, 166.3 and 172.6;

ν_{max} (ATR)/ cm^{-1} 2360, 2335, 1733, 1599, 1471, 1161 and 749;

m/z : (EI+) HRMS $[\text{M}^+]$ $\text{C}_{37}\text{H}_{30}\text{IrN}_3\text{O}_2^+$: found 741.1956; calcd 741.1970.

8.0 Assignment for *fac*-Ir(ppy)₃ and comparison with 5



^1H NMR (700 MHz, DMSO) δ_{H} 6.62 (3H, d, J 6.8, H -A3), 6.64-6.66 (3H, m, H -A4), 6.76-6.78 (3H, m, H -A5), 7.09-7.10 (3H, m, H -B5), 7.45 (3H, d, J 5.0, H -B6) 7.72 (3H, d, J 7.5, H -A6), 7.76 (3H, t, J 8.5, H -B4) and 8.10 (3H, d, J 8.2, H -B3);

^{13}C NMR (176 MHz, DMSO) δ_{c} 119.0 (C -B3), 119.6 (C -A5), 122.8 (C -B5), 124.1 (C -A6), 129.1 (C -A4), 136.3 (C -A3), 136.9 (C -B4), 143.8 (C -A2), 146.8 (C -B6), 160.7 (C -A1) and 165.6 (C -B2).

^1H NMR (700 MHz, CD_2Cl_2) δ_{H} 6.75 (3H, dd, J 7.8, 1.1, H -A3), 6.79 (3H, td, J 7.3, 1.4, H -A4), 6.89 (3H, ddd, J 7.8, 7.1, 1.4, H -A5), 6.93 (3H, ddd, J 7.2, 5.6, 1.4, H -B5), 7.57 (3H, ddd, J 5.6, 1.6, 0.80, H -B6) 7.65-7.68 (3H, m, H -A6 and H -B4) and 7.93 (3H, d, J 8.2, H -B3);

^{13}C NMR (176 MHz, CD_2Cl_2) δ_c 118.8 (C-B3), 119.8 (C-A5), 122.1 (C-B5), 124.0 (C-A6), 129.6 (C-A4), 136.2 (C-B4), 136.7 (C-A3), 143.8 (C-A2), 147.1 (C-B6), 160.9 (C-A1) and 166.4 (C-B2)

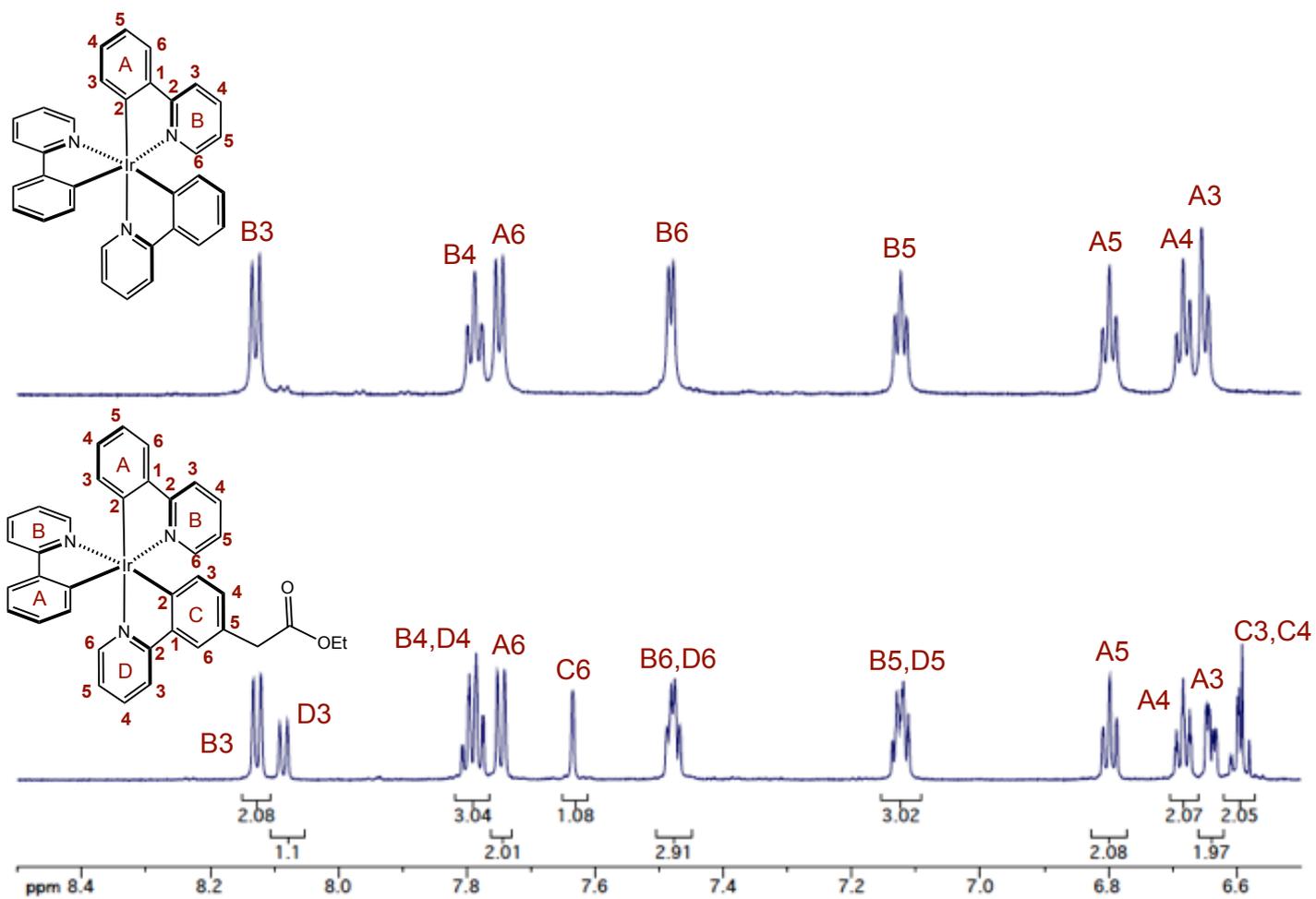


Fig. S7: Comparison of ¹H NMR of 1 and 5 in *D*₆-DMSO

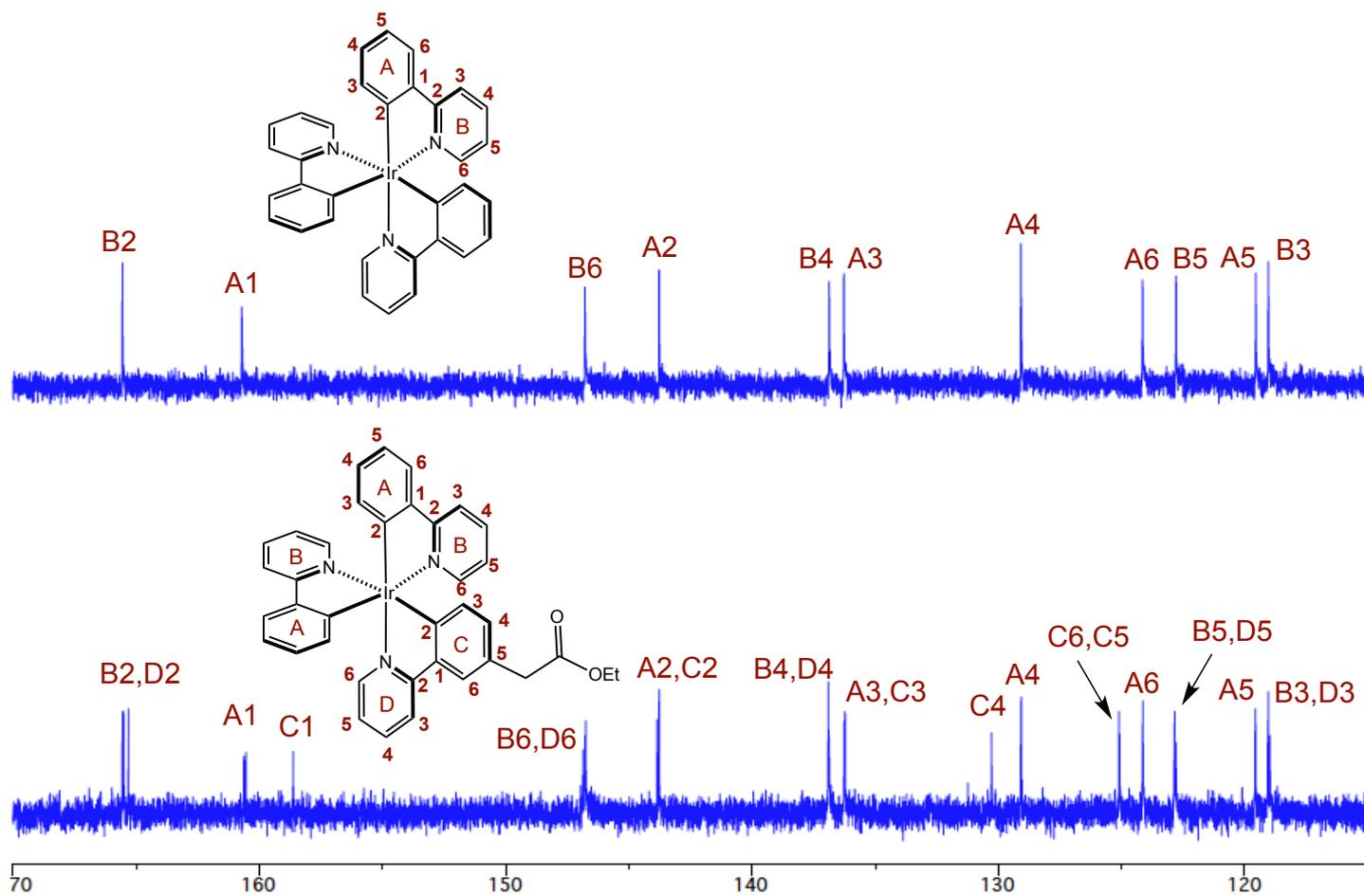


Figure S9. Comparison of ^{13}C NMR of 1 and 5 in D_6 -DMSO

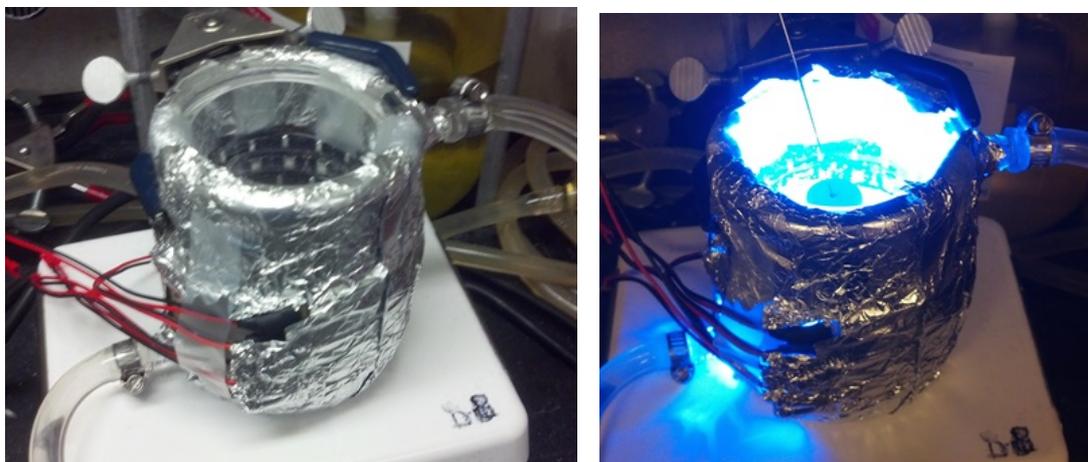
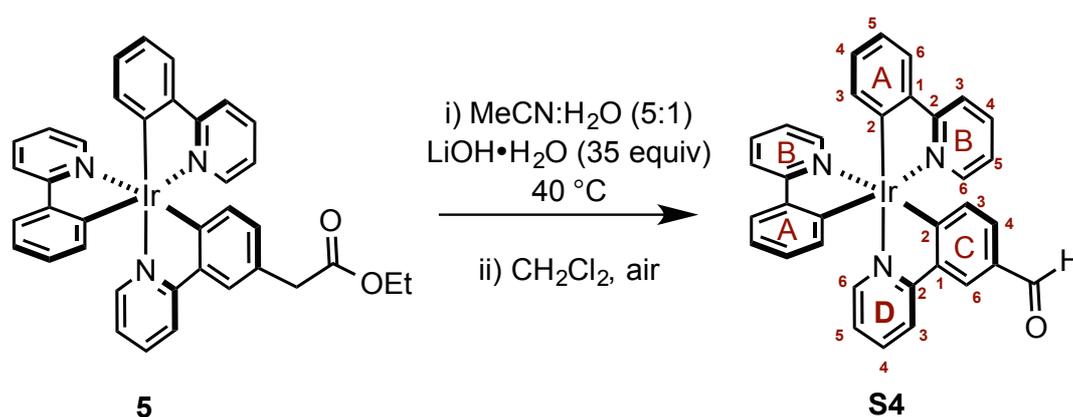


Figure S10. Reaction set up for the synthesis of **5**

9.0 Transformation of **6** to to *fac*-Ir[*[(p-C(O)H)Ph]Py*](ppy)₂ **S4**

To further confirm the structural assignment of **5** it was transformed to the known aldehyde **S4** via a hydrolysis/decarboxylation/oxidation sequence.



To a screw cap vial was added **5** (10.0 mg, 0.013 mmol, 1.0 equiv), MeCN (2.5 ml), water (0.5 ml) and LiOH.H₂O (20.0 mg, 0.477 mmol, 35 equiv) and the solution was stirred at 40 °C for 12 h forming a bright yellow precipitate. The solvent was pipetted away from the solids and water (2 ml) was added. The slurry was transferred to a separatory funnel containing CH₂Cl₂ (10 ml). 1N HCl (10 ml) was added, the layers separated and

the aqueous solution was extracted with CH₂Cl₂ (10 ml). The combined organic portions were left to stand open to the air for 2 h. The solution was dried (Na₂SO₄), filtered and concentrated *in vacuo* to give a bright yellow crude material that was purified *via* flash column chromatography (CH₂Cl₂ to 1% MeOH: CH₂Cl₂) to give **S4** (3 mg, 34% yield). The data was inconsistent with that reported in the patent literature,⁶ which appears poorly resolved e.g. 6.65-6.92 (12H, m).^{12a} However, the data was consistent with the major product (13% yield) isolated from the formylation of *fac*-Ir(ppy)₃ with POCl₃/DMF following the specified literature procedure^{12b} (see comparison spectrum).

¹H NMR (700 MHz, DMSO) δ_H 6.53 (1H, d, *J* 7.5, *H*-A3), 6.65 (1H, d, *J* 7.1, *H*-A3), 6.70 (1H, t, *J* 7.1, *H*-A4), 6.73 (1H, td, *J* 7.4, 1.0, *H*-A4), 6.81-6.86 (2H, m, *H*-A5), 6.94 (1H, d, *J* 7.8, *H*-C3), 7.14-7.18 (3H, m, *H*-C4, *H*-B5), 7.24 (1H, t, *J* 6.5, *H*-D5), 7.46 (1H, d, *J* 5.4, *H*-B6), 7.48 (1H, d, *J* 5.5, *H*-B6), 7.55 (1H, d, *J* 5.3, *H*-D6), 7.79 (2H, t, *J* 6.5, *H*-A6), 7.83 (2H, td, *J* 7.7, 0.6, *H*-B4), 7.89 (1H, td, *J* 7.8, 1.4, *H*-D4), 8.17 (2H, d, *J* 8.2, *H*-B3), 8.27 (1H, d, *J* 1.5, *H*-C6), 8.27 (1H, d, *J* 8.1, *H*-D3) and 9.78 (1H, s, C(O)H);

¹³C NMR (176 MHz, DMSO) δ_C 119.7 (*C*-B3), 119.8 (*C*-B3), 120.1 (*C*-D3), 120.5 (*C*-A5), 120.6 (*C*-A5), 123.4 and 123.5 (2 × *C*-B5 and *C*-D5), 124.3 (2 × *C*-A6), 124.8 (*C*-C6 and *C*-C5), 129.79 and 129.83 and 129.89 (2 × *C*-A4 and *C*-C4), 136.4 (*C*-A3), 136.6 (*C*-A3), 137.3 (*C*-C3), 137.7 and 137.85, and 137.90 (2 × *C*-B4 and *C*-D4) 144.1 (*C*-A2), 144.3 (*C*-A2), 145.8 (*C*-C2), 147.1 and 147.4 and 147.5 (2 × *C*-B6 and *C*-D6) 159.6 (*C*-A1), 159.9 (*C*-A1), 164.5 (*C*-C1), 165.5 (*C*-B2), 165.8 (*C*-B2), 177.2(*C*-D2) and 192.3 (*C*(O)H);

ν_{max} (ATR)/cm⁻¹ 2160, 1675, 1598, 1576, 1471, 1413, 1261, 1186, 1059, 749 and 732;

m/z: (EI+) HRMS [M⁺] C₃₄H₂₄IrN₃O⁺: found 684.1602; calcd 684.1621.

⁶ (a) Evans, C. E. B.; Crutchley, R. J.; Derosa, M. C.; Mosher, P. J. From PCT Int. Appl. (2004), WO 2004031321 A1 20040415. (b) Stoessel, P.; Spreitzer, H.; Becker, H. From PCT Int. Appl. (2003), WO 2003040160 A1 20030515.

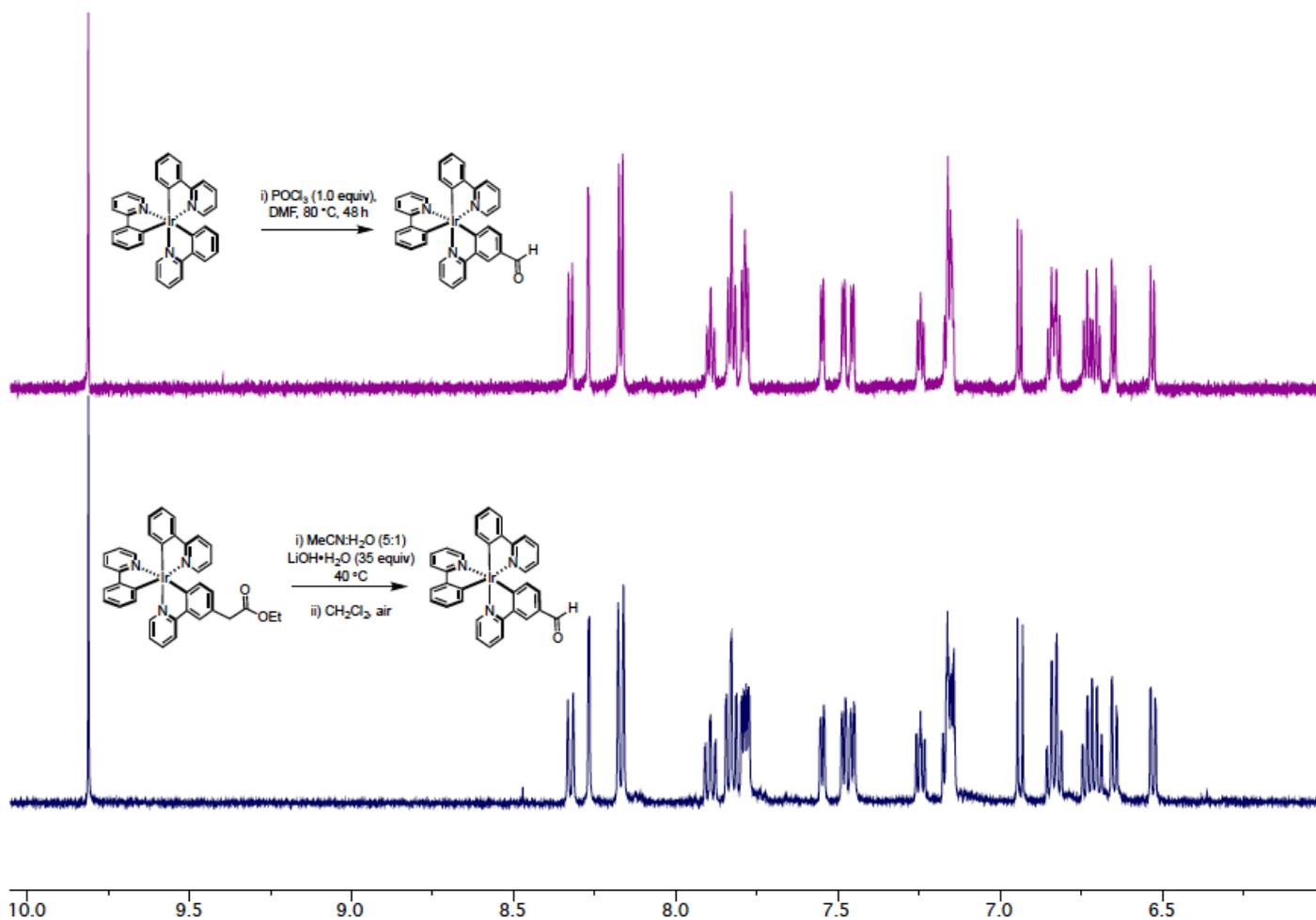


Figure S11. Comparison of ^1H NMR of S4 formed via formylation and via hydrolysis/decarboxylation/oxidation

10.0 ¹³C Coordination-Induced Shift Calculations

Following the precedent of Watts¹ shifts are calculated as [CIS, $\delta(\text{complex}) - \delta(\text{free ligand})$] in ppm and serve as an effective tool to aid and verify assignments. Calculated shifts (table S2 and Fig.S11) are similar to those reported for the heteroleptic complexes [Ir(ppy-*R*)₂(bpy)].

Table S2: ¹³C Coordination-induced shifts [CIS, $\delta(\text{complex}) - \delta(\text{free ligand})$] in ppm

Position	<i>fac</i> -Ir(ppy) ₃ 1	<i>fac</i> -Ir(Ph(<i>p</i> -MePy)) ₃ 6	<i>fac</i> -Ir((<i>p</i> -MePh)(<i>p</i> -MePy)) ₄ 7	<i>fac</i> -Ir((<i>p</i> -CF ₃ Ph)(<i>p</i> -MePy)) ₃ 8	<i>fac</i> -Ir((<i>p</i> -CF ₃ Ph)(<i>p</i> - ^t BuPy)) ₃ 9
	CD ₂ Cl ₂	CD ₂ Cl ₂	CD ₂ Cl ₂	CDCl ₃	CDCl ₃
A1	21.3	22.4	17.7	25.8	25.4
A2	16.7	17.6	20.2	14.0	14.2
A3	7.7	8.5	8.2	7.9	8.0
A4	0.4	1.0	1.1	0.5	0.4
A5	-9.2	-8.7	-9.9	-8.8	-8.9
A6	-3.2	-2.6	-3.2	-1.5	-4.0
B2	9.0	9.4	8.9	9.1	8.7
B3	-1.8	-1.4	-1.9	-1.4	-1.8
B4	-0.9	0.2	-0.4	0.3	-0.2
B5	-0.4	0.4	-0.1	0.3	0.4
B6	-2.8	-2.3	-2.7	-3.0	-3.1

Table S2 continued: ¹³C Coordination-induced shifts [CIS, $\delta(\text{complex}) - \delta(\text{free ligand})$] in ppm

	<i>fac</i> -Ir(ppy) ₃ 1	<i>fac</i> -Ir[((<i>p</i> -C(O)H)Ph)Py)(ppy) ₂] S4
Position	DMSO	DMSO
A1	22.1	21.0
A2	17.3	19.1
A3	7.5	7.8
A4	0.1	0.8
A5	-9.2	-8.1
A6	-2.4	-2.2
B2	9.6	9.7
B3	-1.2	-0.4
B4	-0.3	0.7
B5	0.2	0.8
B6	-2.7	-2.0

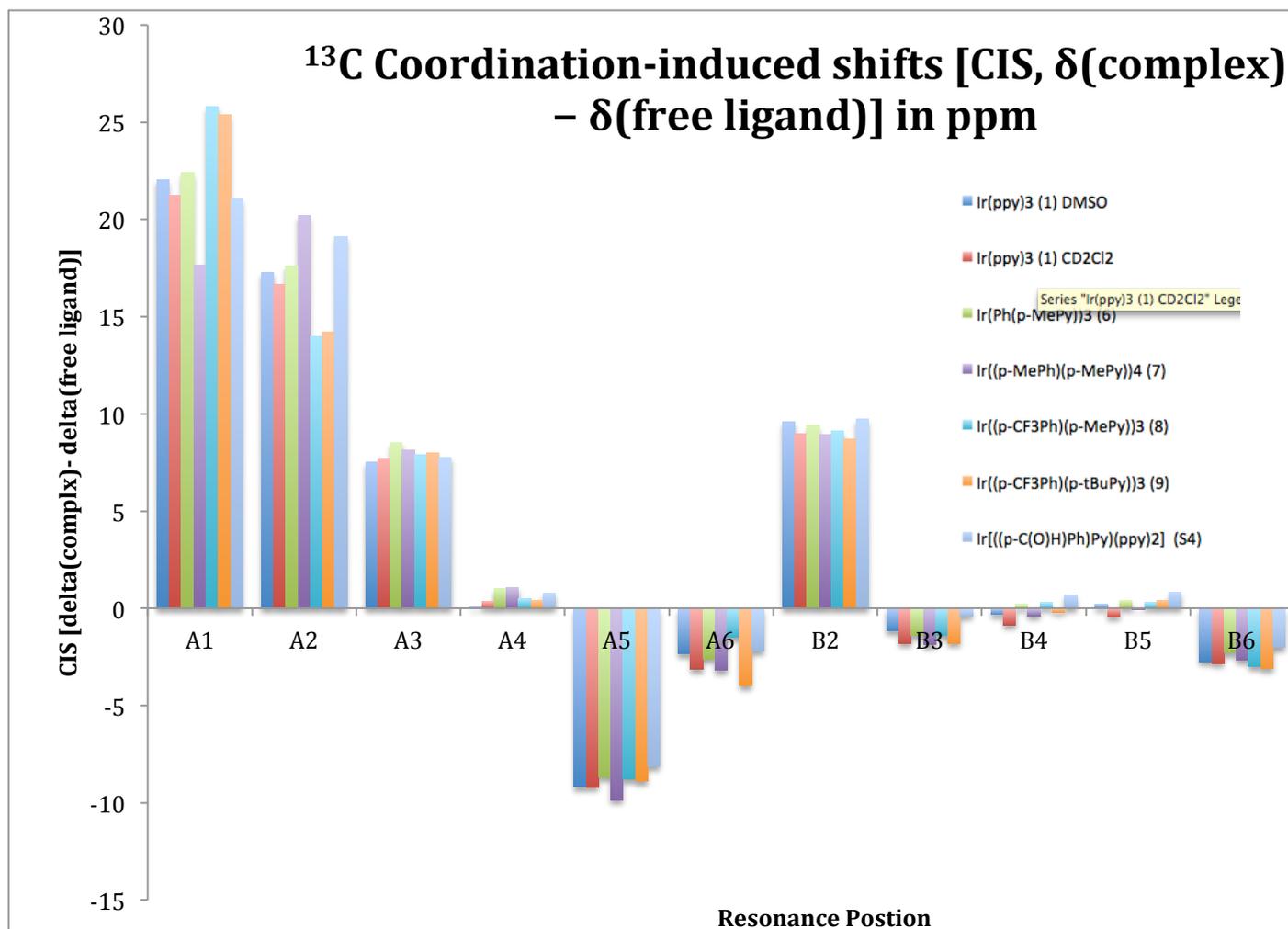


Figure S12. ^{13}C Coordination-induced shifts [CIS, $\delta(\text{complex}) - \delta(\text{free ligand})$] in ppm

11.0 Photocatalyst Quenching Studies

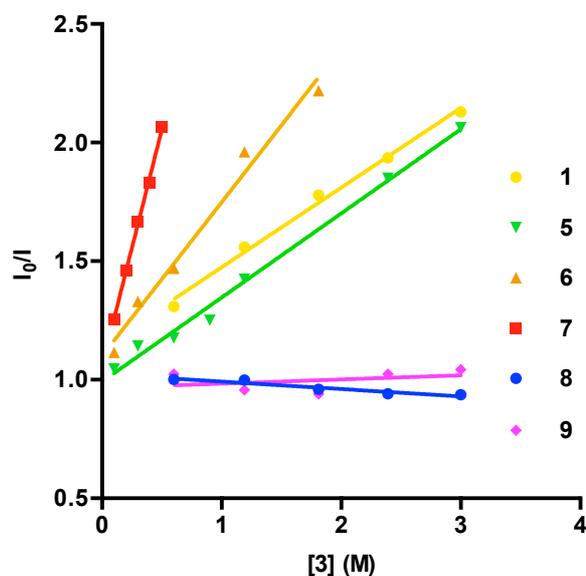


Figure S13.

All quenching data was recorded in a quartz cuvette with a stir bar at 25 °C with DMA as the solvent. Excitation was at 450 nm with emission measured at the maximum as stated. All values are the average of 3 measurements.

Photocatalyst		Concentration/ M	Emission Maximum/nm
Ir(ppy) ₃	1	2.85E-06	520
Ir[<i>p</i> -(CH ₂ C(O)OEt)PhPy](ppy) ₂	5	3.24E-06	516
Ir(Ph(<i>p</i> -MePy)) ₃	6	3.25E-06	517
Ir((<i>p</i> -MePh)(<i>p</i> -MePy)) ₃	7	3.61E-06	520
Ir((<i>p</i> -CF ₃ Ph)(<i>p</i> -MePy)) ₃	8	2.96E-06	516
Ir((<i>p</i> -CF ₃ Ph)(<i>p</i> - ^t BuPy)) ₃	9	1.82E-06	490

Table S3: Photocatalyst Quenching Data

12.0 Full Page Versions of Manuscript Figures

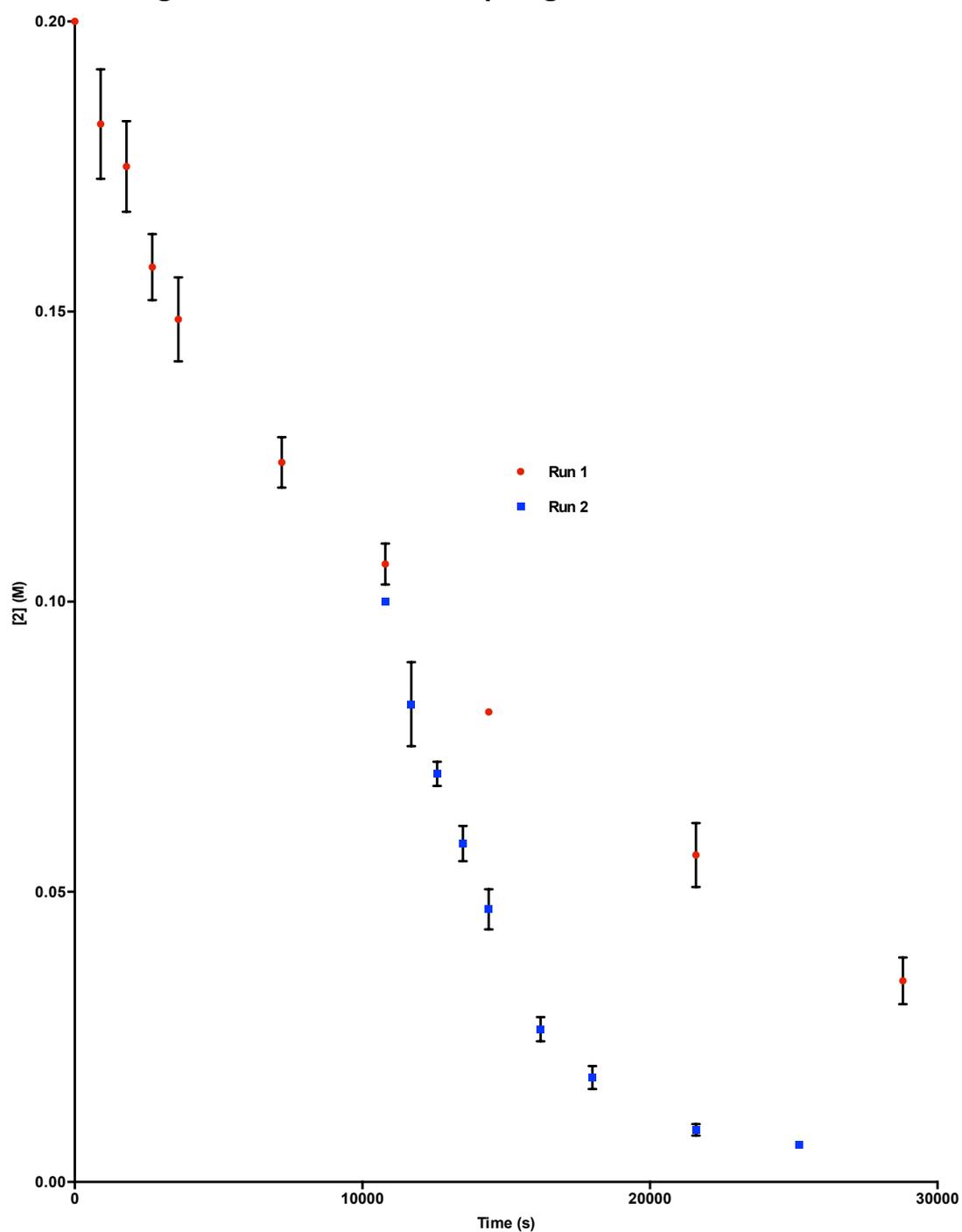


Figure S14. Profile of Run 1 as [2] vs time and the time-adjusted profile of Run 2 as [2] vs adjusted time. Run 1: **1** = 7.5 μmol . **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL. Run 2: **1** = 7.5 μmol . **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO_3 = 3.00 mmol, DMA = 10 mL.

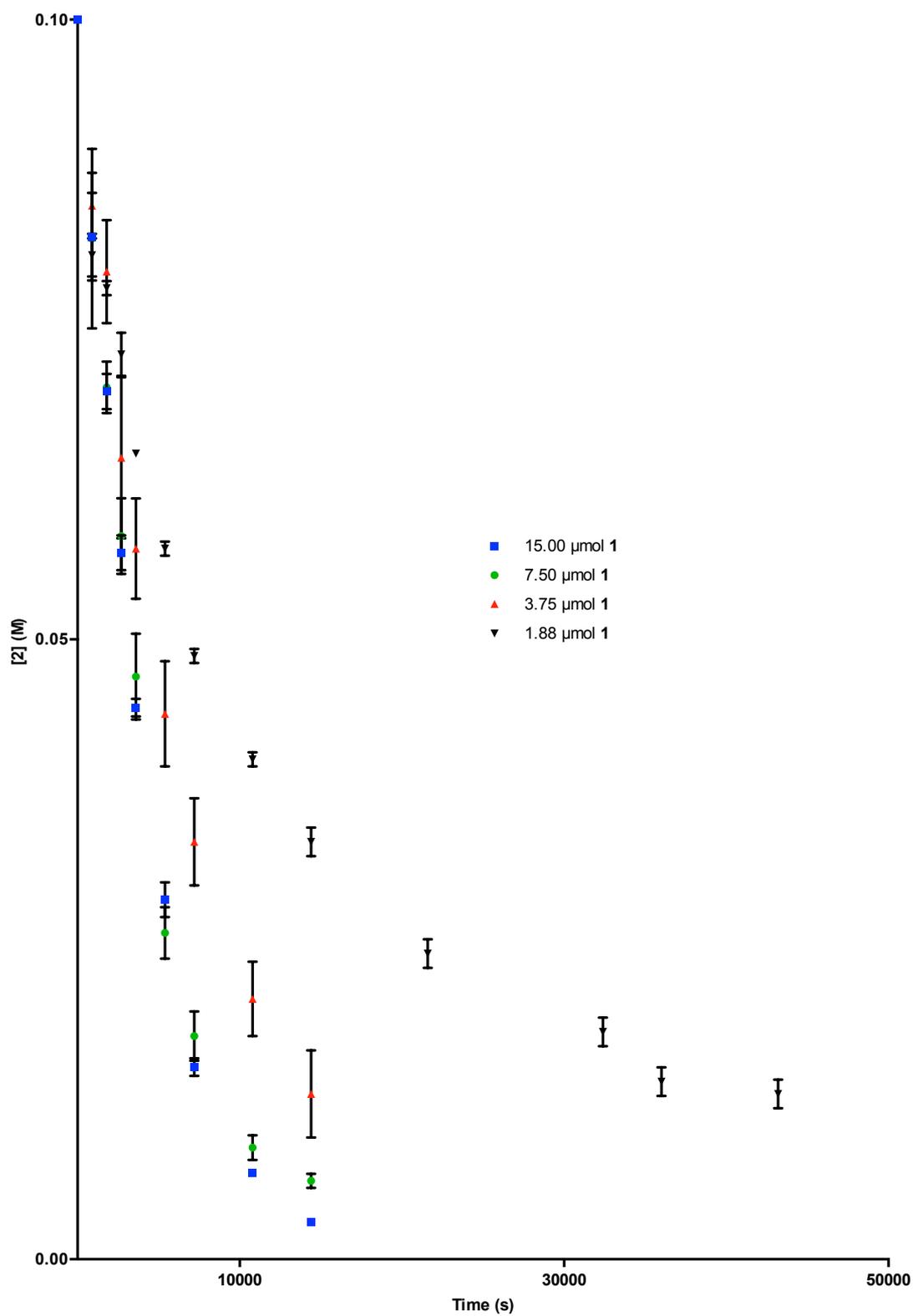


Figure S15. Effect of **1** on rate plotted as **[2]** vs time. General conditions: **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO₃ = 3.00 mmol, DMA = 10 mL.

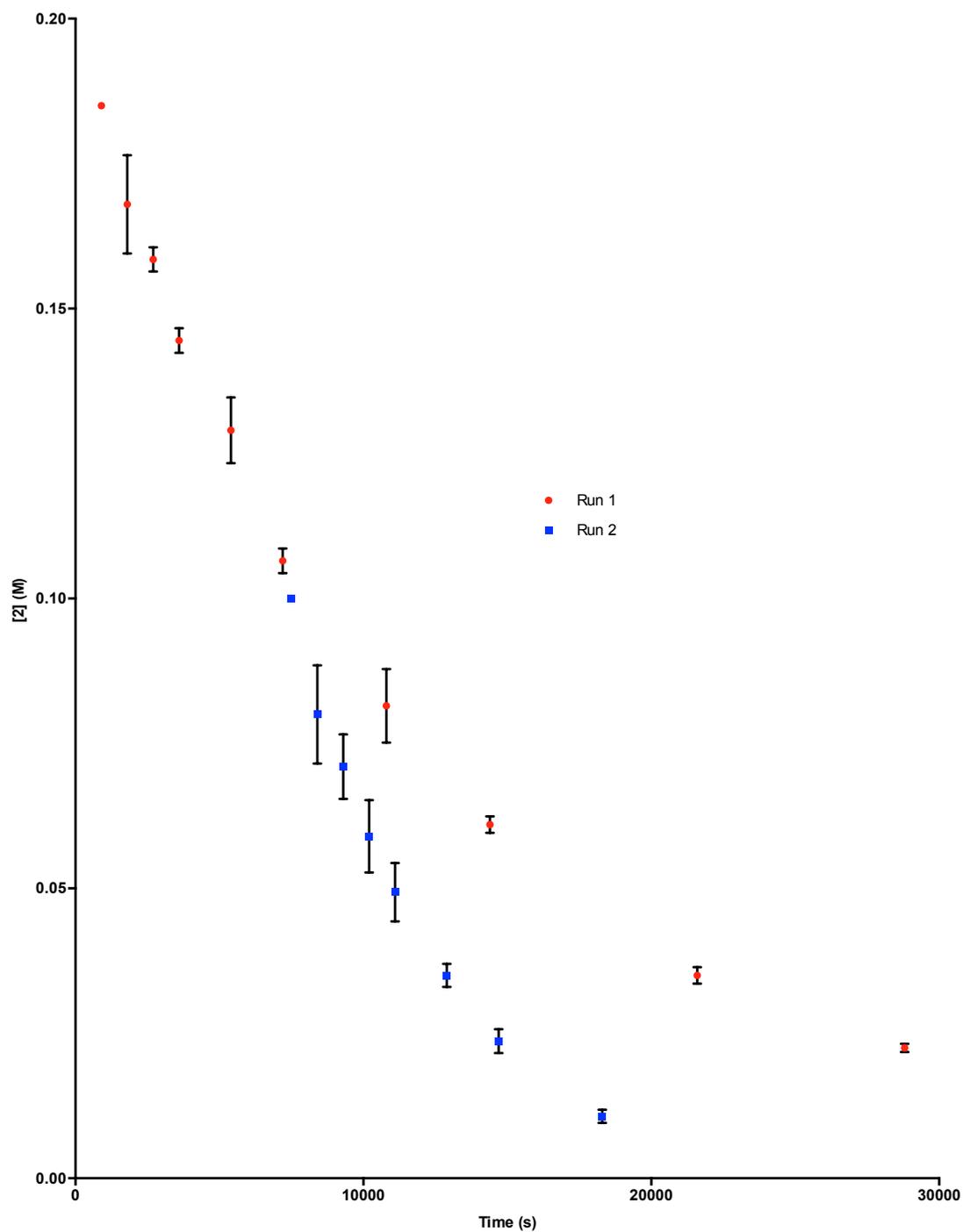


Figure S16. Profile of Run 1 as [2] vs time and the time-adjusted profile of Run 2 as [2] vs adjusted time for the **5**-catalyzed system. Run 1: **5** = 7.5 μmol . **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL. Run 2: **5** = 7.5 μmol . **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO_3 = 3.00 mmol, DMA = 10 mL.

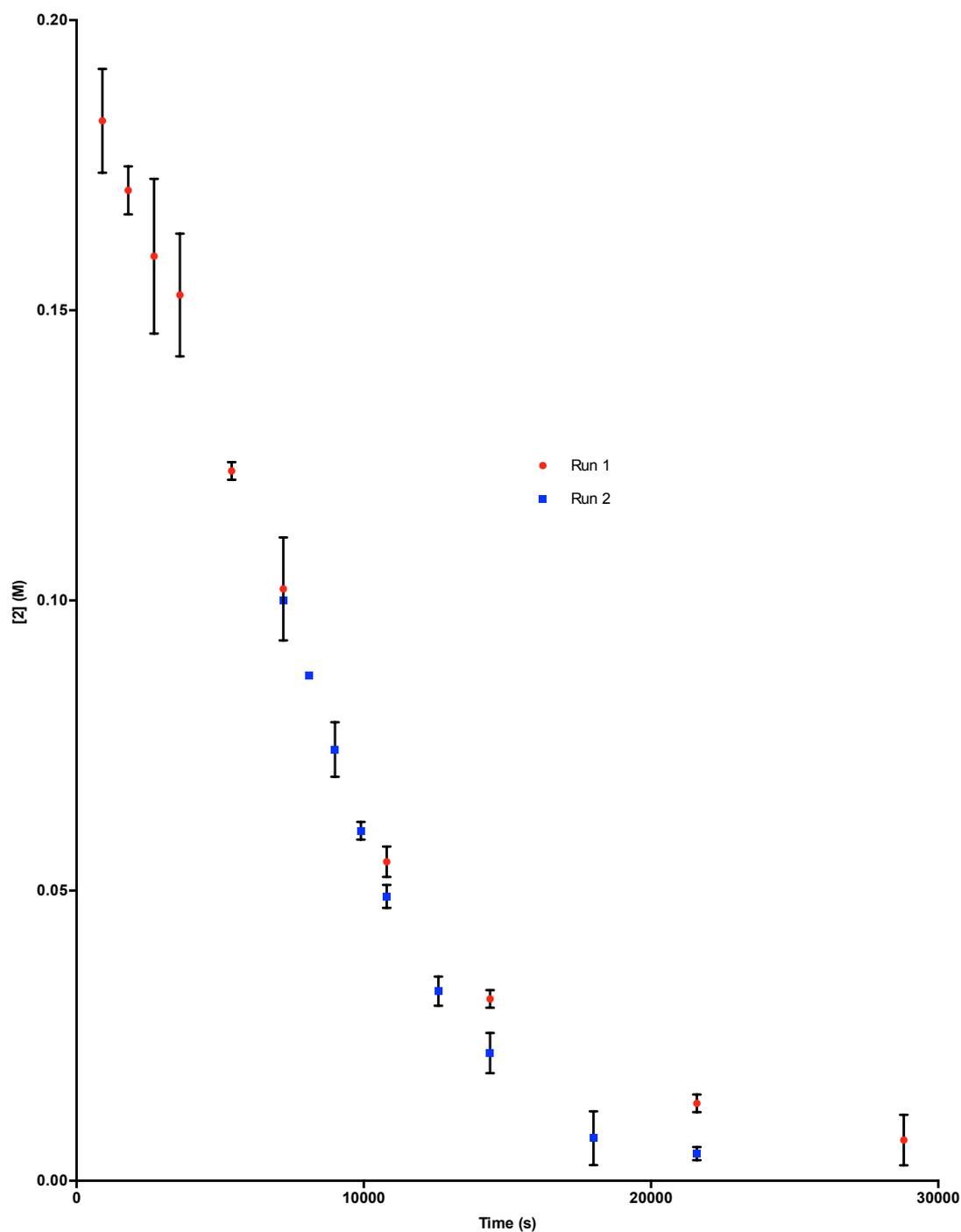


Figure S17. Figure 4. Profile of Run 1 as [2] vs time and the time-adjusted profile of Run 2 as [2] vs adjusted time for the **2**-catalyzed reaction at 2 mol% catalyst. Run 1: **1** = 40.0 μ mol, **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO₃ = 4.00 mmol, DMA = 10 mL. Run 2: **1** = 40.0 μ mol, **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO₃ = 3.00 mmol, DMA = 10 mL.

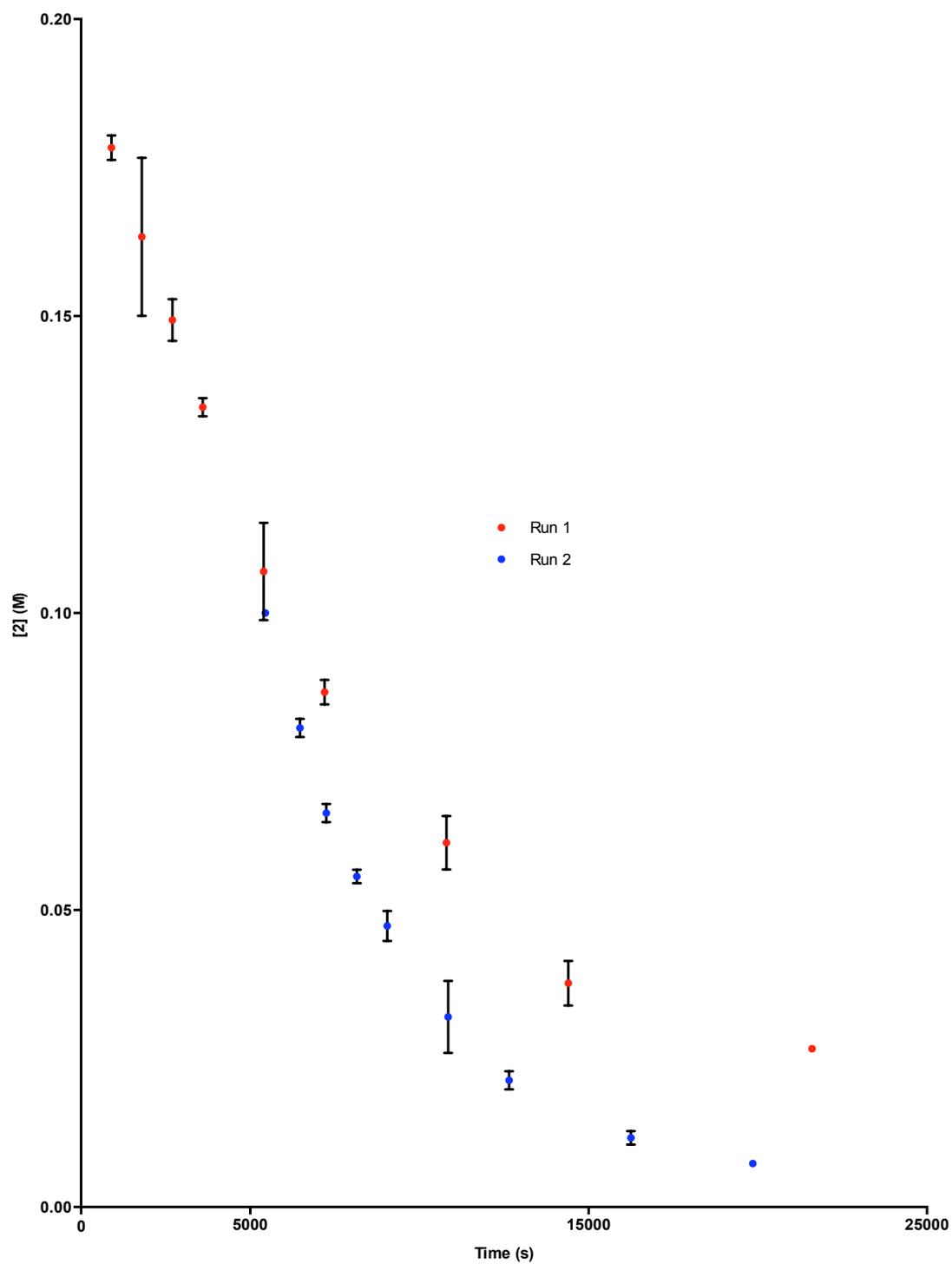
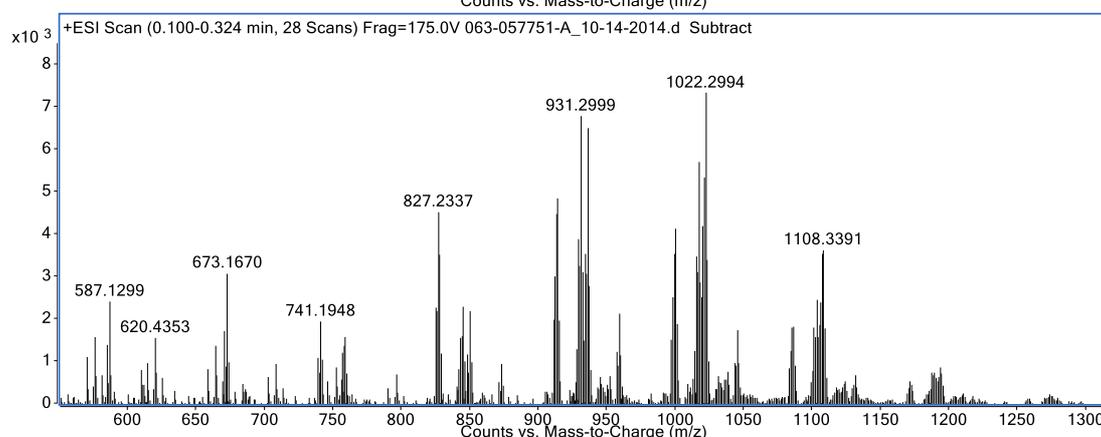
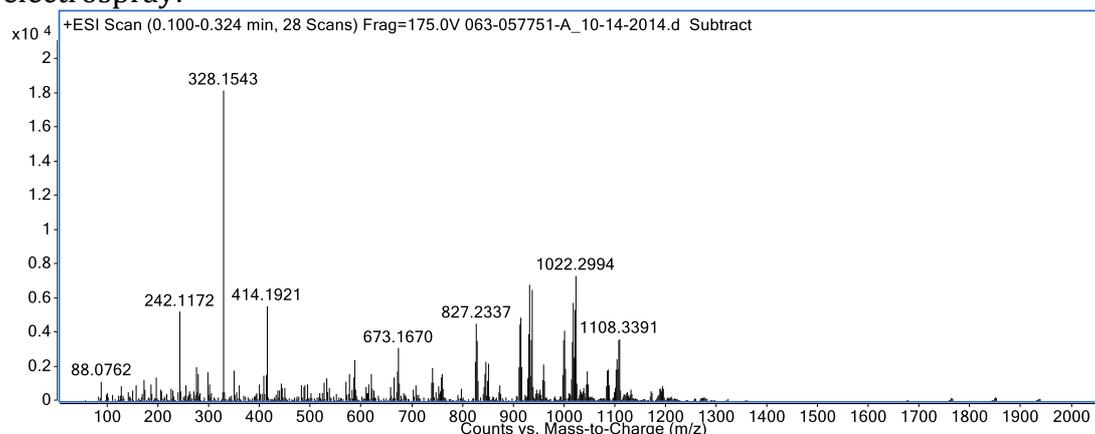


Figure S18. Profile of Run 1 as [2] vs time and the time-adjusted profile of Run 2 as [2] vs adjusted time for the **6**-catalyzed system. Run 1: **6** = 7.5 μmol . **2** = 2.00 mmol, **3** = 6.00 mmol, NaHCO_3 = 4.00 mmol, DMA = 10 mL. Run 2: **6** = 7.5 μmol . **2** = 1.00 mmol, **3** = 5.00 mmol, NaHCO_3 = 3.00 mmol, DMA = 10 mL.

13.0 MS Data

Intractable mixture resulting from irradiation of **1** and **3** by positive ion electrospray:



m/z	Abund	Abund %
81.9379	260.71	1.44
88.0762	1139.03	6.27
97.9682	343.78	1.89
98.9624	477.47	2.63
99.971	295.1	1.63
110.0575	355.81	1.96
122.9638	319.29	1.76
124.9642	294.4	1.62
128.0702	837.96	4.62
130.0855	295.41	1.63
141.9585	524.42	2.89
143.0318	259.73	1.43
144.0098	232.93	1.28
149.023	630.51	3.47
156.0792	931.13	5.13
168.0805	420	2.31
172.0276	1223.91	6.74
174.1117	663.41	3.65
186.2213	955.67	5.26
187.9993	427.43	2.35
196.0938	1363.81	7.51

204.1221	651.37	3.59
207.0885	569.87	3.14
214.0862	266.86	1.47
216.1951	386.51	2.13
226.0964	683.86	3.77
226.1788	465.08	2.56
228.1958	626.79	3.45
229.0749	322.92	1.78
230.2467	259.74	1.43
240.0153	489.49	2.7
242.1172	5193.39	28.61
242.2835	414.47	2.28
243.1206	988.39	5.44
244.19	562.61	3.1
250.177	241.54	1.33
252.9729	295.93	1.63
254.1145	886.89	4.88
258.2775	231.69	1.28
259.0998	355.97	1.96
261.1302	580.65	3.2
264.0989	381.14	2.1
270.096	544.51	3
274.2738	362.19	1.99
276.1438	1967.96	10.84
277.1216	489.74	2.7
279.0933	1551.19	8.54
279.1563	434.44	2.39
280.1141	208.67	1.15
280.1264	298.91	1.65
282.1128	456.16	2.51
283.1595	451.67	2.49
290.1584	221.02	1.22
298.1258	1012.78	5.58
298.3463	1683.77	9.27
299.3496	348.92	1.92
301.0744	365.93	2.02
301.1404	955.21	5.26
302.144	226.19	1.25
305.1574	478.13	2.63
309.139	214.92	1.18
318.2994	203.31	1.12
327.0842	526.72	2.9
327.1764	396.17	2.18
328.1543	18155.5	100
329.1575	3697.89	20.37
330.1603	488.85	2.69
340.1462	257.44	1.42

344.1488	299.84	1.65
344.2254	218.5	1.2
349.1806	359.38	1.98
350.1365	1773.99	9.77
350.3248	240.43	1.32
351.1399	356.82	1.97
355.2804	514.29	2.83
359.2034	925.76	5.1
368.15	286.01	1.58
371.3126	246.45	1.36
388.2521	258.41	1.42
391.2818	267.04	1.47
393.2112	260.29	1.43
393.2949	374.22	2.06
394.3501	470.01	2.59
399.3074	946.41	5.21
400.3091	394.64	2.17
405.2604	421.8	2.32
408.3089	1491.26	8.21
409.3117	383.36	2.11
413.2109	1508.39	8.31
414.1921	5536.02	30.49
415.1945	1435.11	7.9
416.1977	209.82	1.16
429.3178	219.07	1.21
431.3824	365.36	2.01
432.2802	219.92	1.21
436.1739	628.68	3.46
438.3788	618.17	3.4
443.3331	1008.99	5.56
444.3328	769.19	4.24
449.2869	748.98	4.13
468.3875	206.35	1.14
473.3509	227.93	1.26
476.3074	237.07	1.31
482.4033	889.84	4.9
483.4057	221.3	1.22
487.3601	803.47	4.43
488.3584	896.73	4.94
489.3608	275.85	1.52
493.3126	948.88	5.23
494.3176	253.55	1.4
500.2303	452	2.49
501.0918	233.96	1.29
512.4159	222.35	1.22
517.3635	209.76	1.16
518.3684	461.44	2.54

523.3224	458.1	2.52
526.43	1060.52	5.84
527.4316	325.59	1.79
531.3846	555.51	3.06
532.3834	1341.07	7.39
533.3863	487.08	2.68
537.3389	748.49	4.12
546.3974	276.46	1.52
550.6273	391.67	2.16
556.4426	223.34	1.23
570.4562	1093.6	6.02
571.4579	347.15	1.91
575.41	415.75	2.29
576.41	1568.51	8.64
577.4125	643.56	3.54
581.3649	668.5	3.68
582.3695	213.96	1.18
585.1268	1383.23	7.62
586.1321	491.61	2.71
587.1299	2402.99	13.24
588.1323	678.5	3.74
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600.4677	233.25	1.28
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611.1833	457.31	2.52
612.1776	455.21	2.51
614.4822	963.35	5.31
615.4847	324.94	1.79
619.4373	348.03	1.92
620.4353	1546.25	8.52
621.4374	725.13	3.99
625.3909	609.62	3.36
634.447	306.55	1.69
658.5083	815.92	4.49
659.5114	311.71	1.72
664.4613	1377.32	7.59
665.4632	681.21	3.75
669.4178	527.01	2.9
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671.1642	1714.44	9.44
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673.167	3069.53	16.91
674.1697	988.86	5.45
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703.5375	241.45	1.33
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709.4955	352.22	1.94
713.4446	367.78	2.03
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740.1942	740.81	4.08
741.1948	1933.44	10.65
742.1979	1047.31	5.77
743.2004	226.87	1.25
746.5596	525.54	2.89
747.5629	207.72	1.14
752.5137	864.88	4.76
753.5178	412.33	2.27
755.1886	213.58	1.18
756.2099	579.63	3.19
757.2001	1198.74	6.6
757.4688	281.51	1.55
758.2144	1362.03	7.5
759.2074	1564.76	8.62
760.209	714.9	3.94
761.208	207.74	1.14
764.1851	225.3	1.24
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797.5442	271.65	1.5
825.23	2273.67	12.52
826.233	2191.27	12.07
827.2337	4513.13	24.86
828.2371	3516.57	19.37
829.241	1174.84	6.47
830.2424	238.68	1.31
834.6137	217.1	1.2
840.5661	398.1	2.19
841.2314	333.04	1.83
842.2387	814.8	4.49
843.2543	1545.1	8.51
844.25	1593.15	8.78
845.2614	2280.01	12.56
846.2656	1003.24	5.53
847.2638	304.96	1.68
848.2222	1172.16	6.46
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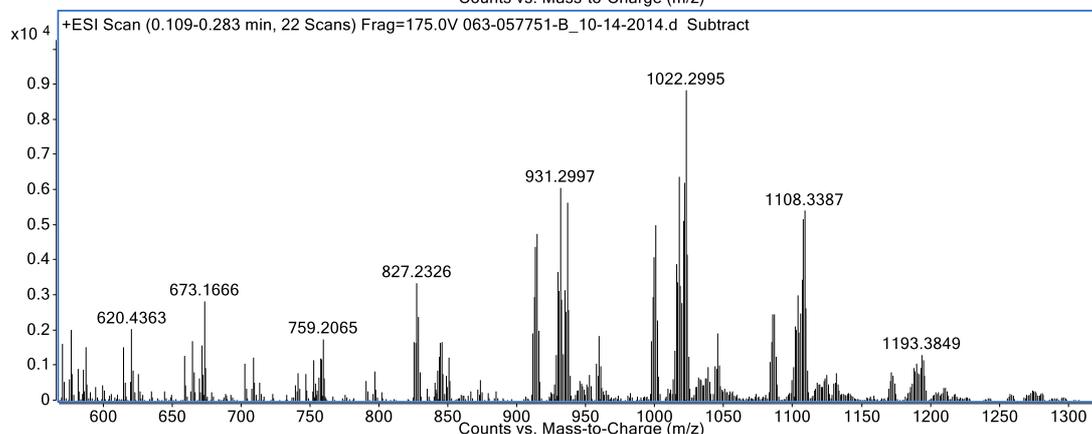
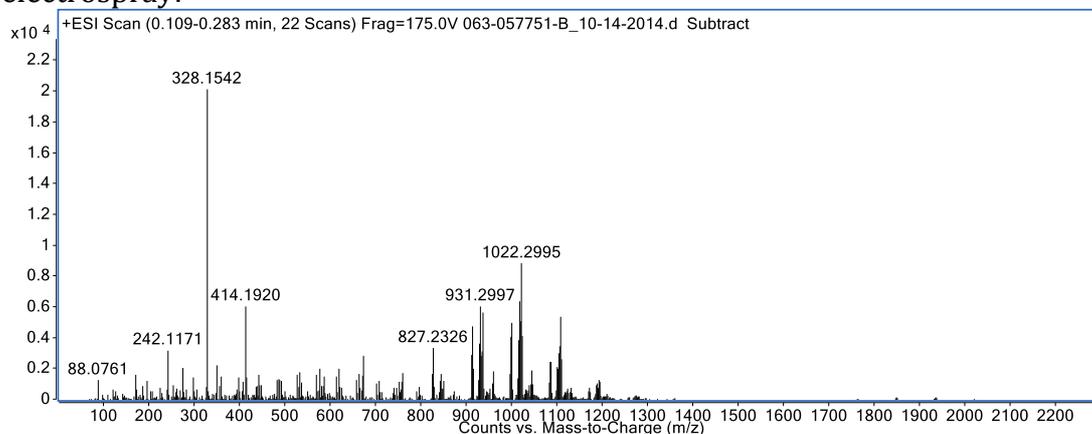
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874.2943	421.46	2.32
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907.1492	229.45	1.26
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915.2796	1958.59	10.79
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923.1669	333.34	1.84
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928.2735	1291.66	7.11
929.2956	3881.25	21.38
930.13	216.94	1.19
930.2904	3252.03	17.91
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932.3039	3105.36	17.1
933.2895	1482.09	8.16
934.2588	3529.2	19.44
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936.2597	6486.3	35.73
937.2611	2785.67	15.34
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951.2454	355.35	1.96
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960.3328	1142.95	6.3
961.3231	406.36	2.24
962.2661	205.83	1.13
964.2542	212.29	1.17
982.293	250.52	1.38
991.1998	268.68	1.48
992.2013	240.43	1.32
993.2011	239.33	1.32
996.3185	245.75	1.35
997.3203	1501.08	8.27
998.3157	2519.35	13.88
999.3216	3539.64	19.5
1000.3175	4127.04	22.73
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1002.32	556.57	3.07
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1011.2094	391.26	2.16
1011.3009	215.67	1.19
1012.2065	226.69	1.25
1013.1833	306.24	1.69
1013.3132	588.25	3.24
1014.1737	338.38	1.86
1014.3107	1244.84	6.86
1015.1803	270.33	1.49
1015.3315	3466.26	19.09
1016.3264	3098.96	17.07
1017.3358	5698.03	31.38
1018.3378	2860.51	15.76
1019.318	2519.5	13.88
1020.3001	4174.88	23
1021.3065	5336.39	29.39
1022.2994	7316.81	40.3
1023.3007	3383.45	18.64
1024.3009	994.85	5.48
1025.303	252.26	1.39
1029.3307	349.06	1.92
1030.3264	348.21	1.92
1031.3399	647.21	3.56
1032.3297	518.84	2.86
1033.3296	483.34	2.66
1034.3194	382.74	2.11
1035.3086	325.64	1.79
1036.2928	563.57	3.1
1037.2911	562.15	3.1
1038.2879	760.97	4.19

1039.2873	448.12	2.47
1042.3728	210.19	1.16
1043.3656	961.56	5.3
1044.3742	905.78	4.99
1045.3684	1740.37	9.59
1046.3699	965.13	5.32
1047.3529	379.5	2.09
1048.3085	210.23	1.16
1050.2934	239.78	1.32
1052.2895	211.74	1.17
1054.2911	231.23	1.27
1056.2997	210.38	1.16
1083.361	844.45	4.65
1084.3581	1237.78	6.82
1085.3624	1793.46	9.88
1086.3567	1818.59	10.02
1087.3597	891.04	4.91
1088.3589	303.6	1.67
1097.3334	212.05	1.17
1099.2209	286.72	1.58
1099.3539	501.77	2.76
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1101.3663	1799.4	9.91
1102.3648	1569.19	8.64
1103.3722	2443.62	13.46
1104.3735	1567.28	8.63
1105.3529	1858.94	10.24
1106.3431	2392.49	13.18
1107.3458	3525.34	19.42
1108.3391	3616.4	19.92
1109.3412	1776.11	9.78
1110.344	615.26	3.39
1115.3614	205.51	1.13
1116.3654	261.78	1.44
1117.3679	381.7	2.1
1118.3656	336.24	1.85
1119.3703	341.21	1.88
1120.356	270.08	1.49
1121.3464	293.64	1.62
1122.3346	391.22	2.15
1123.3376	473.05	2.61
1124.3315	523.42	2.88
1125.334	298.52	1.64
1129.4027	372.52	2.05
1130.4118	451.53	2.49
1131.4053	665.48	3.67
1132.4031	396.52	2.18

1133.3742	220.21	1.21
1169.3958	243.61	1.34
1170.4008	357.58	1.97
1171.4011	539.48	2.97
1172.3918	440.75	2.43
1173.4007	297.7	1.64
1183.3944	219.57	1.21
1184.3969	224.43	1.24
1185.3943	300.25	1.65
1186.3978	352.04	1.94
1187.4017	724.85	3.99
1188.4061	668.22	3.68
1189.4107	726.79	4
1190.4099	606.94	3.34
1191.3934	533.89	2.94
1192.388	624.8	3.44
1193.3856	854.8	4.71
1194.3831	718.09	3.96
1195.3858	432.45	2.38
1209.3841	207.22	1.14
1210.3743	243.24	1.34
1273.4415	226.98	1.25

Intractable mixture resulting from irradiation of **5** and **3** by positive ion electrospray:



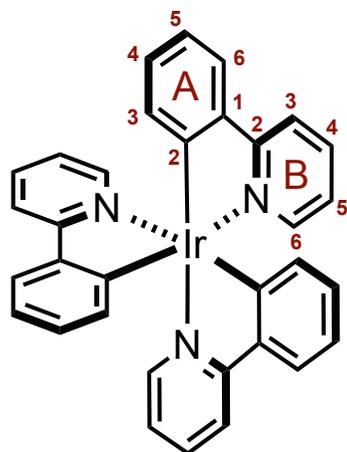
m/z	Abund	Abund %	
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196.0937	1240.17	6.16	
242.1171	3206.42	15.92	
276.144	2046.28	10.16	
298.1257	1433.42	7.12	
298.3461	1240.92	6.16	
328.1542	20138.53	100	
329.1575	4013.59	19.93	
350.1364	2217.66	11.01	
359.2033	1486.74	7.38	
399.3074	1467.95	7.29	
408.3082	1164.16	5.78	
413.2116	2286.92	11.36	
414.192	6061.92	30.1	
415.195	1479.46	7.35	
443.3336	1600.43	7.95	
482.4045	1273.16	6.32	
487.3591	1369.45	6.8	
488.3584	1284.62	6.38	
493.3133	1250.2	6.21	
526.4302	1627.63	8.08	
532.3839	1774.23	8.81	
537.3396	1111.9	5.52	
570.4568	1628.04	8.08	
576.4101	2005.33	9.96	
587.1303	1531.78	7.61	
614.483	1516.11	7.53	
620.4363	2033.1	10.1	
658.5078	1272.64	6.32	
664.4613	1709.26	8.49	
671.1641	1571.58	7.8	
673.1666	2831.12	14.06	
702.5339	1050.49	5.22	
708.4915	1239.94	6.16	
752.5144	1156.09	5.74	
757.1998	1200.45	5.96	
758.2132	1182.93	5.87	
759.2065	1750.42	8.69	
825.2298	1673.49	8.31	
826.2328	1643.11	8.16	
827.2326	3349.08	16.63	
828.2369	2389.39	11.86	
843.2495	1245.4	6.18	
844.248	1651.64	8.2	
845.2584	1671.01	8.3	

850.2217	1225.84	6.09	
911.271	1923.82	9.55	
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914.2764	4747.84	23.58	
915.2791	1998.64	9.92	
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930.2885	3129.54	15.54	
931.2997	6062.93	30.11	
932.3024	2871.08	14.26	
933.2905	1324.69	6.58	
934.2582	3139.23	15.59	
935.2654	2527.22	12.55	
936.2596	5640.16	28.01	
937.2609	2571.95	12.77	
957.3283	1066.96	5.3	
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997.3202	1703.98	8.46	
998.315	2945.01	14.62	
999.3208	4094.69	20.33	
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1017.335	6383.63	31.7	
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1021.306	6209.89	30.84	
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1024.3019	1253.48	6.22	
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1045.3688	1927.27	9.57	
1046.3668	1019.97	5.06	
1083.3604	1099.41	5.46	
1084.3569	1674.52	8.32	
1085.3617	2465.35	12.24	
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1087.3597	1265.67	6.28	
1101.3669	2123.41	10.54	
1102.3638	2010.16	9.98	
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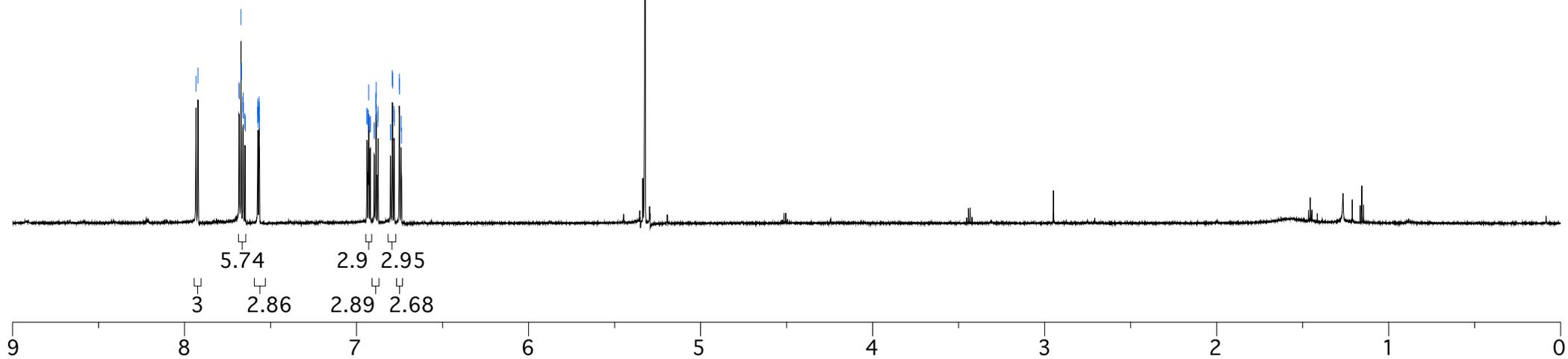
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1107.3456	5171.77	25.68	
1108.3387	5401.08	26.82	
1109.3403	2635.81	13.09	
1189.41	1067.88	5.3	
1193.3849	1302.8	6.47	
1194.3803	1151.42	5.72	

14.0 NMR Spectra

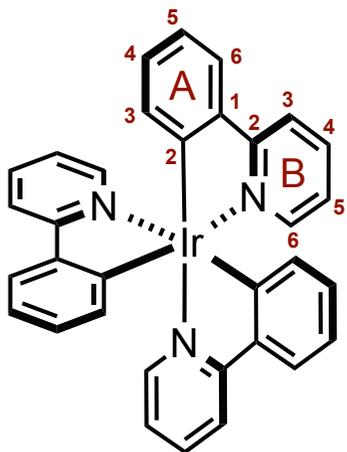
7.933
7.922
7.684
7.682
7.672
7.671
7.670
7.661
7.660
7.659
7.658
7.650
7.647
7.576
7.574
7.573
7.572
7.566
7.565
7.564
6.940
6.938
6.932
6.930
6.928
6.922
6.920
6.898
6.896
6.888
6.887
6.886
6.885
6.877
6.875
6.803
6.801
6.792
6.790
6.782
6.780
6.752
6.750
6.741
6.739



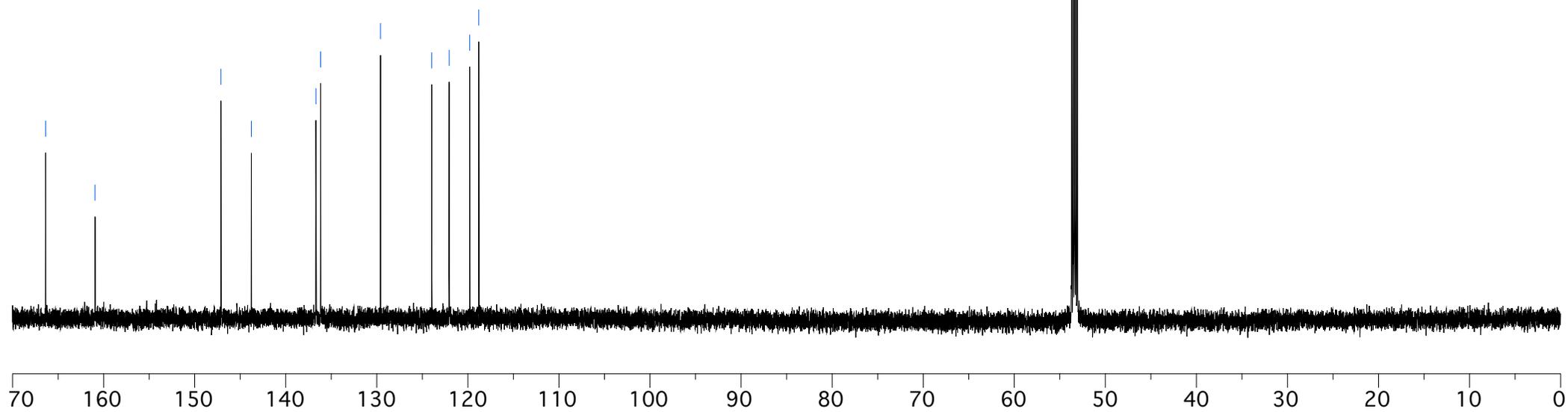
1, ^1H , 700 MHz, CD_2Cl_2



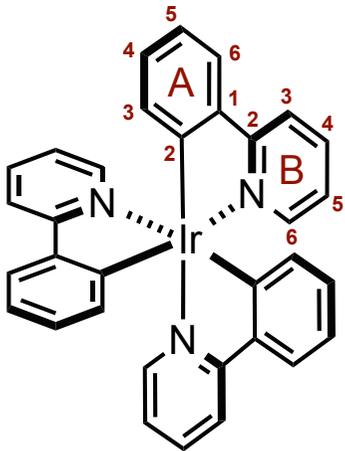
166.375
160.937
147.116
143.779
136.690
136.173
129.592
123.964
122.052
119.794
118.804



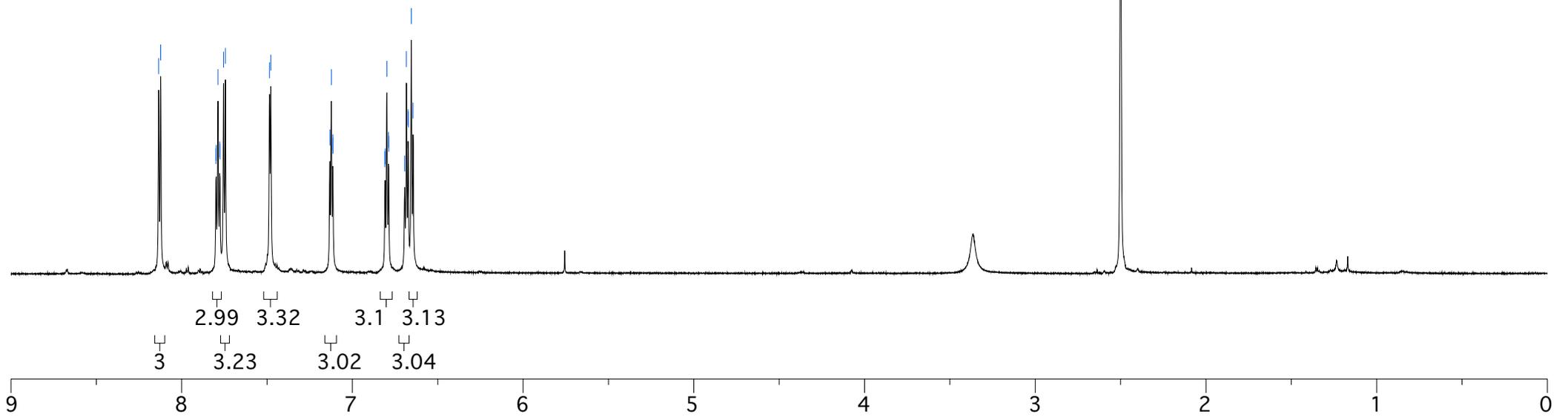
1, ^{13}C , 176 MHz, CD_2Cl_2



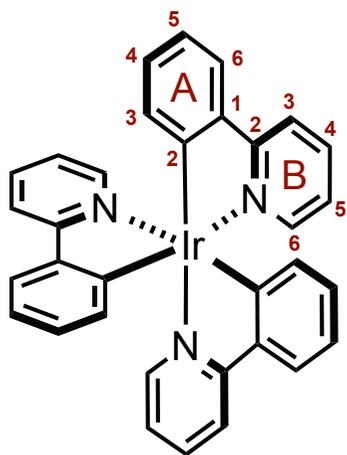
8.135
8.123
7.800
7.798
7.787
7.777
7.775
7.755
7.744
7.485
7.478
7.132
7.123
7.115
7.114
6.810
6.808
6.798
6.789
6.787
6.693
6.684
6.674
6.673
6.654
6.645



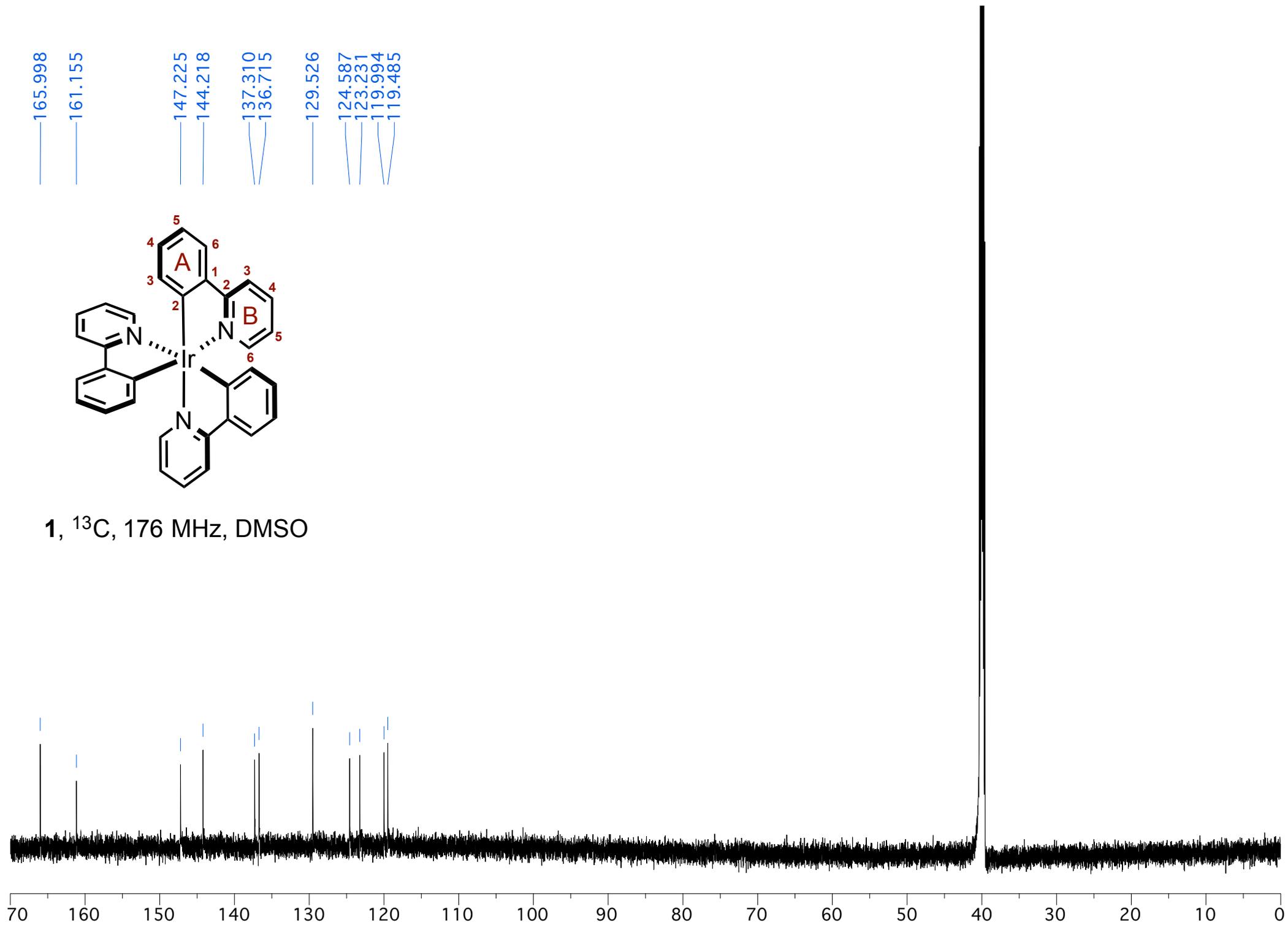
1, ^1H , 700 MHz, DMSO

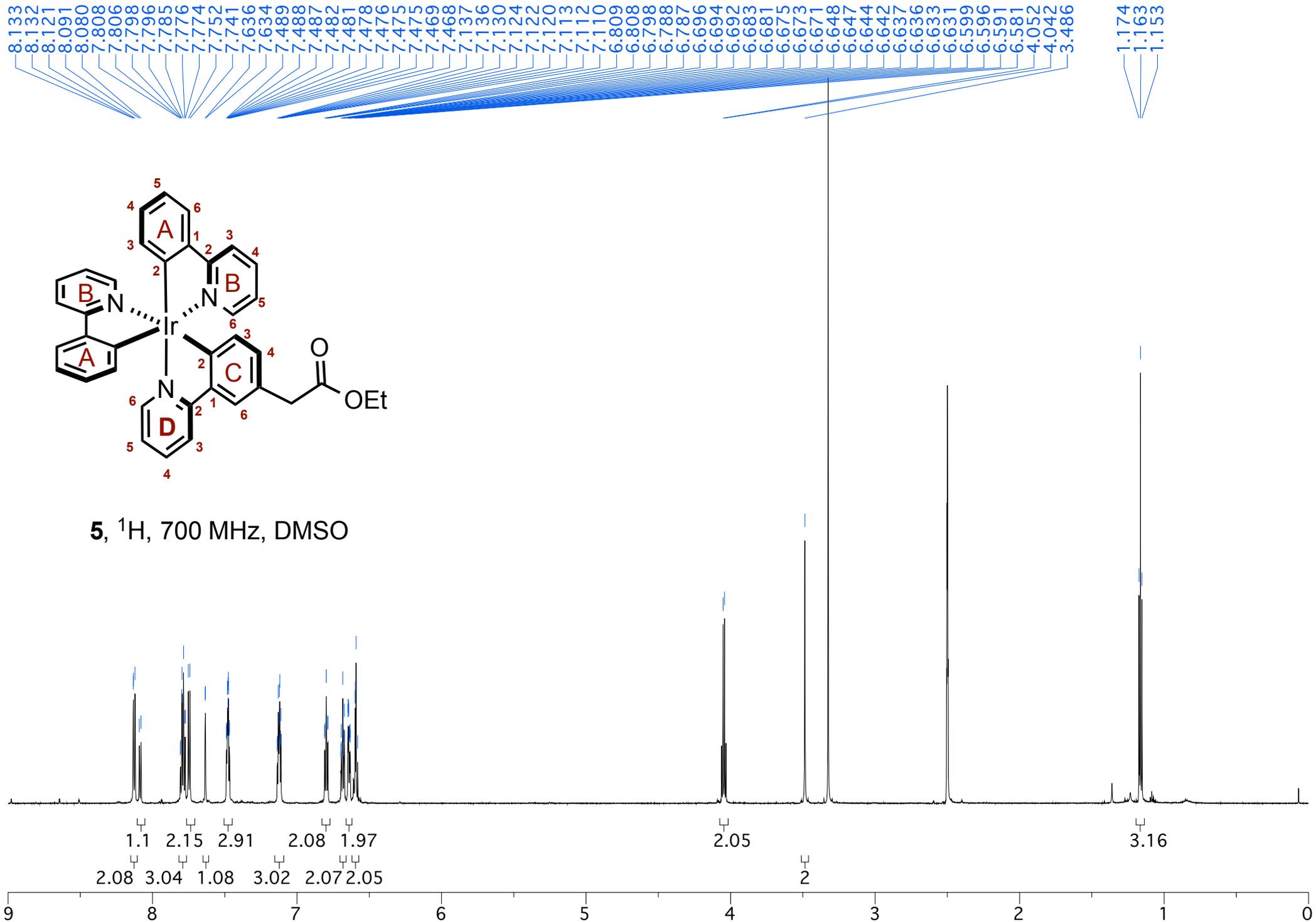


165.998
161.155
147.225
144.218
137.310
136.715
129.526
124.587
123.231
119.994
119.485



1, ^{13}C , 176 MHz, DMSO



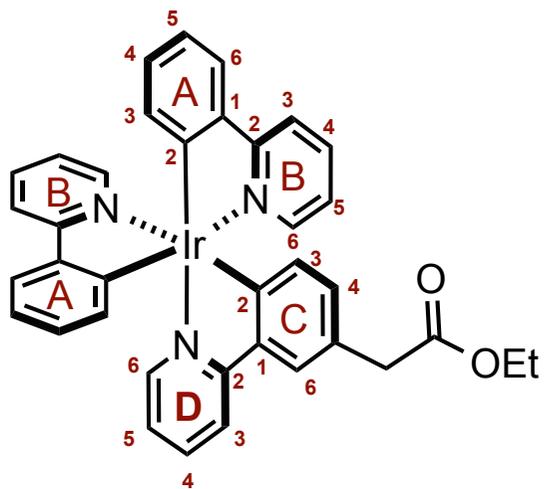


171.515
165.556
165.514
165.316
160.627
160.547
158.628
146.863
146.777
146.750
143.857
143.769
136.903
136.867
136.263
136.227
130.278
129.082
129.072
125.106
125.083
124.138
122.847
122.793
119.565
119.061
119.042
118.981

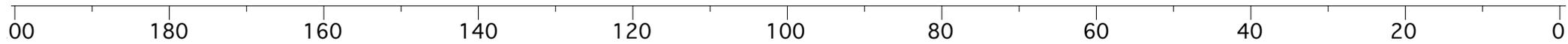
60.004

40.250

14.098

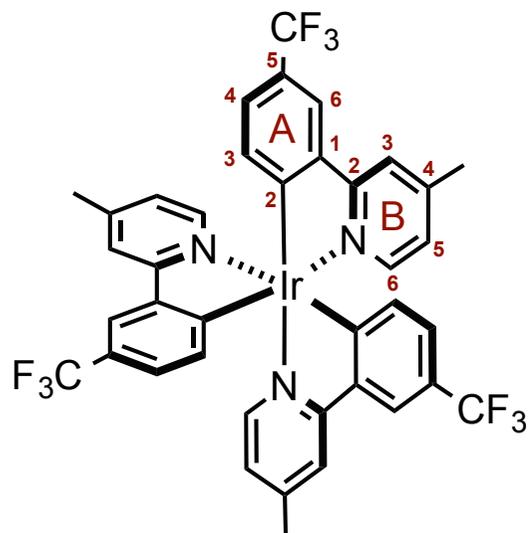


5, ^{13}C , 176 MHz, DMSO

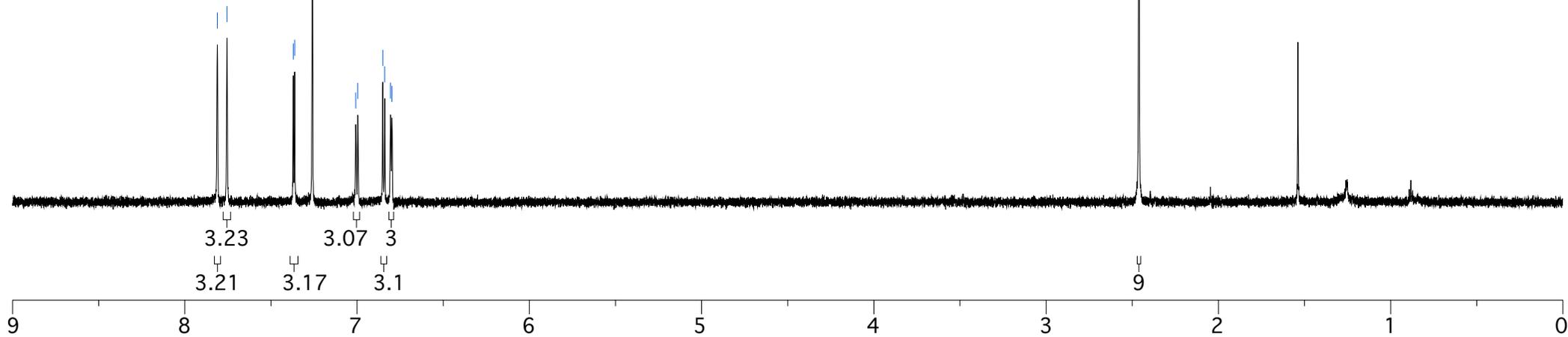


7.811
7.755
7.370
7.362
7.008
6.996
6.851
6.840
6.806
6.798

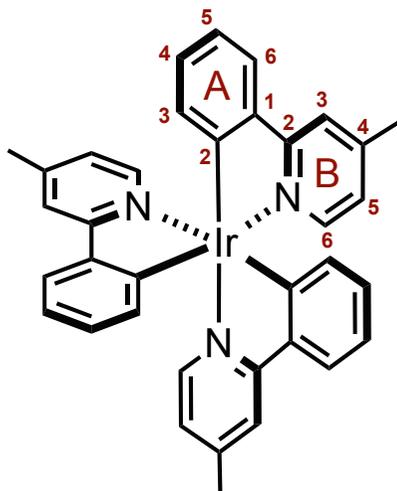
2.461



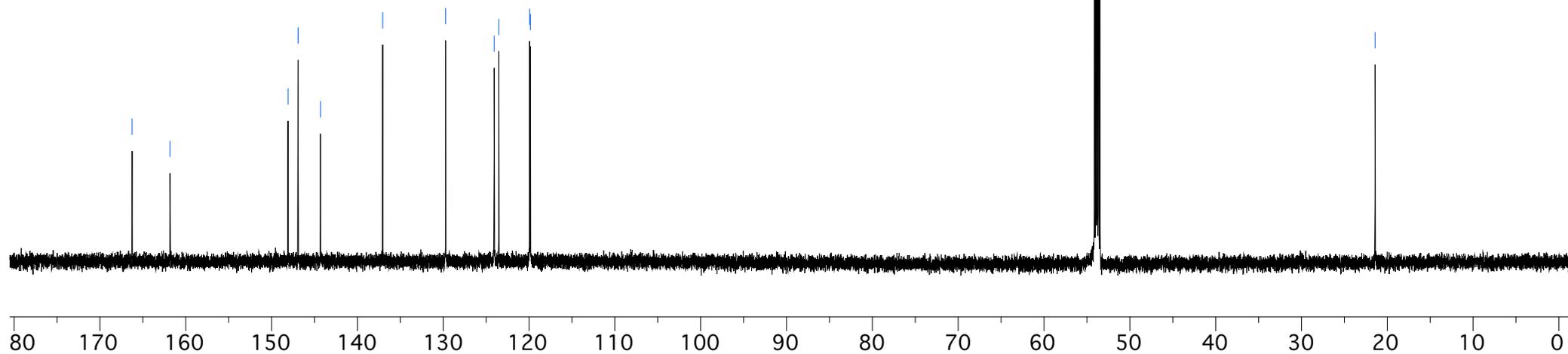
8, ¹H, 700 MHz, CDCl₃

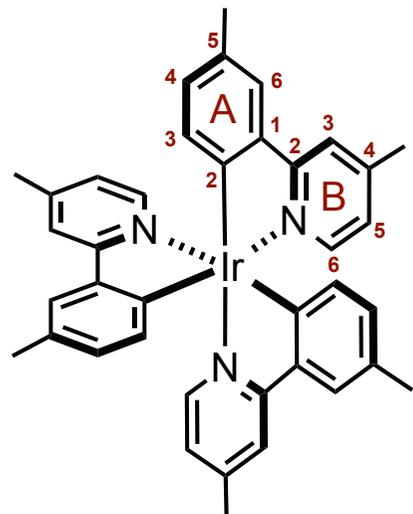


166.246
161.835
148.083
146.914
144.302
137.051
129.715
124.060
123.519
119.941
119.841
21.425

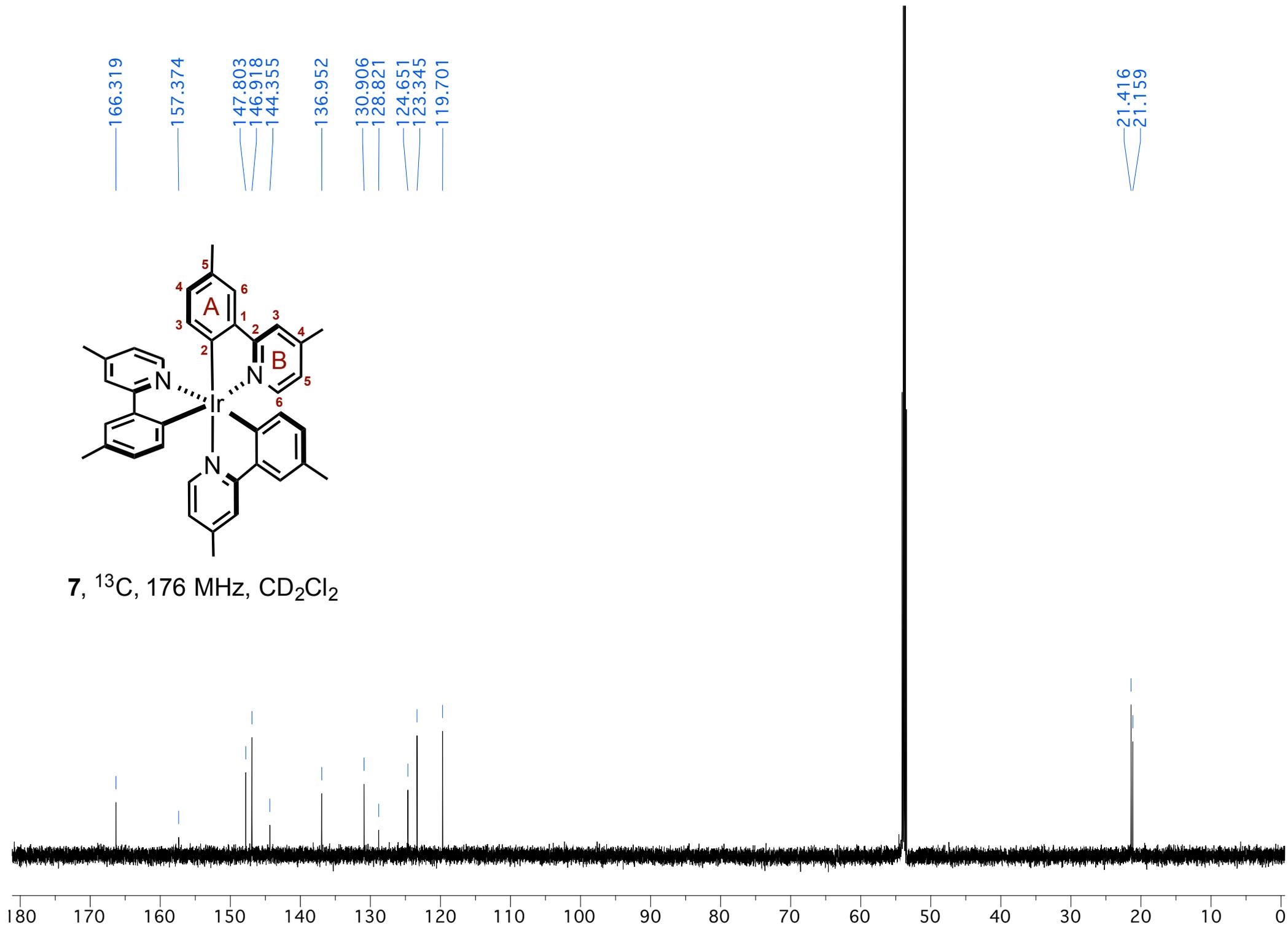


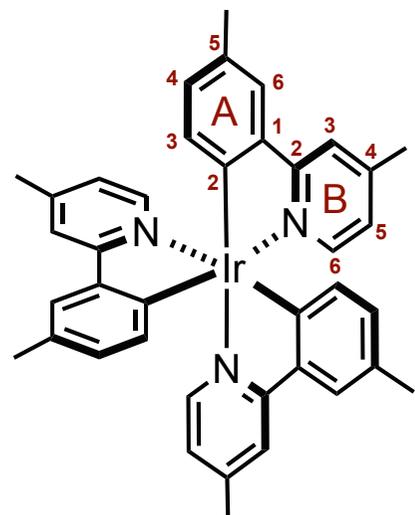
6, ^{13}C , 176 MHz, CD_2Cl_2



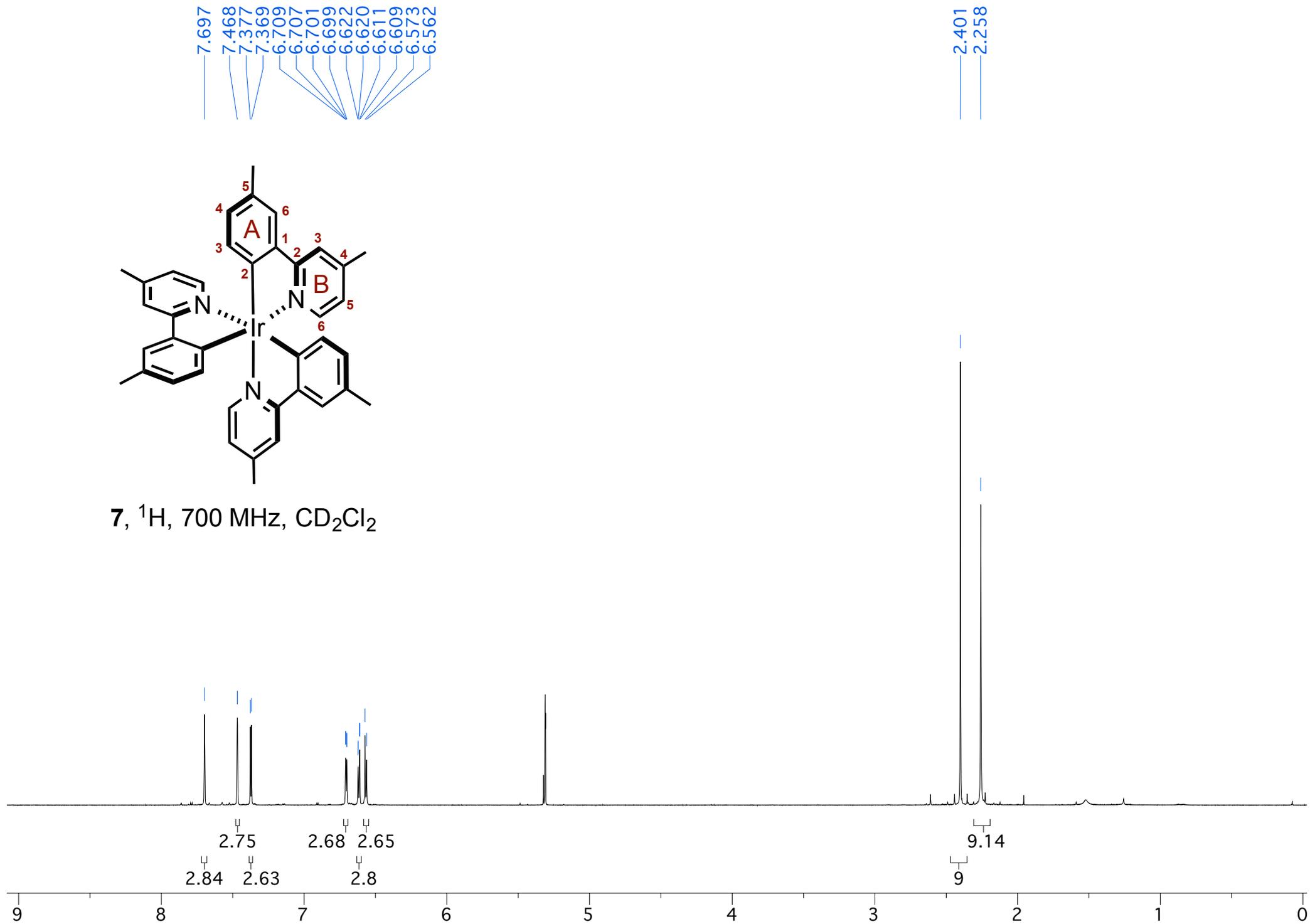


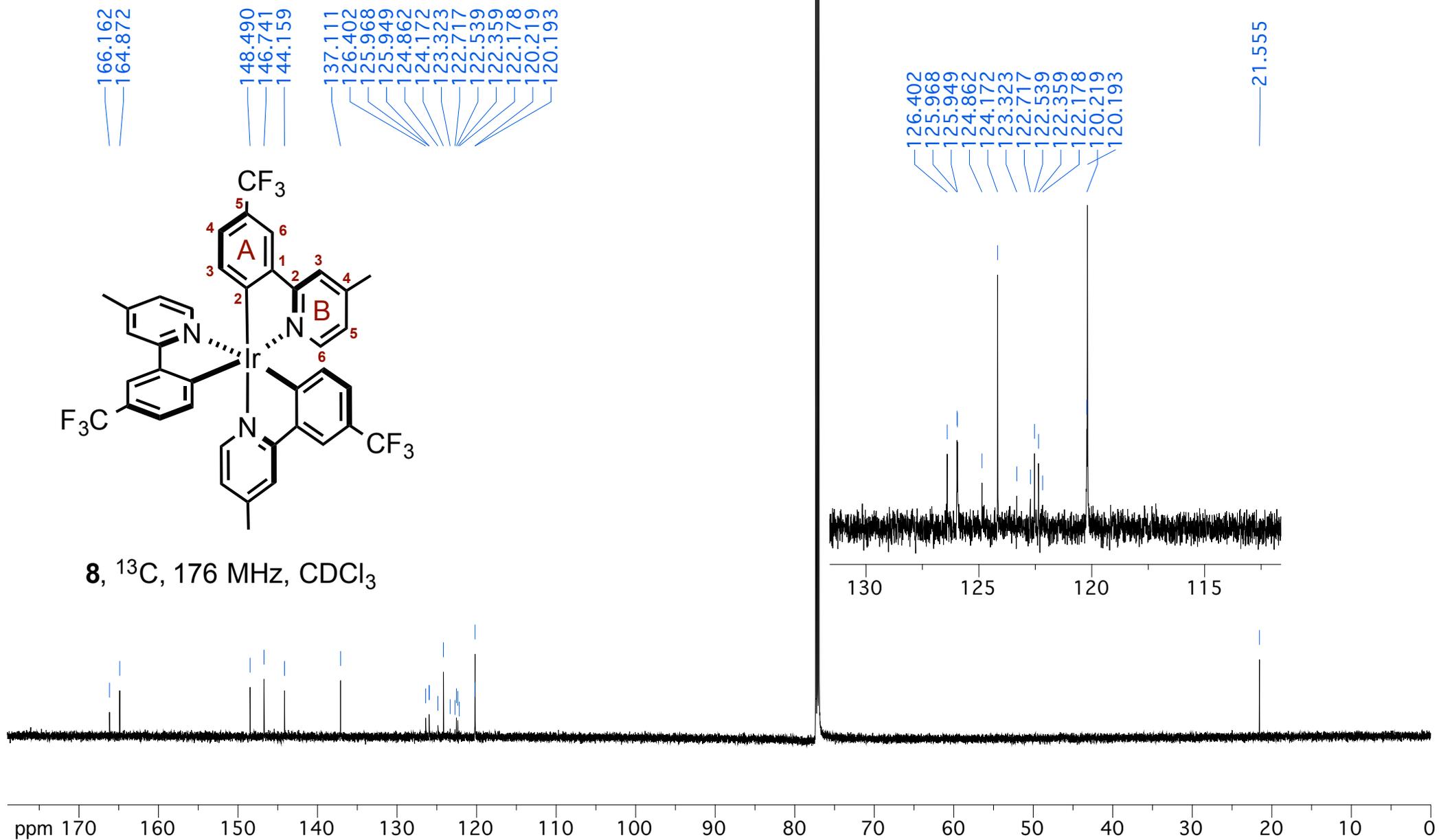
7, ^{13}C , 176 MHz, CD_2Cl_2





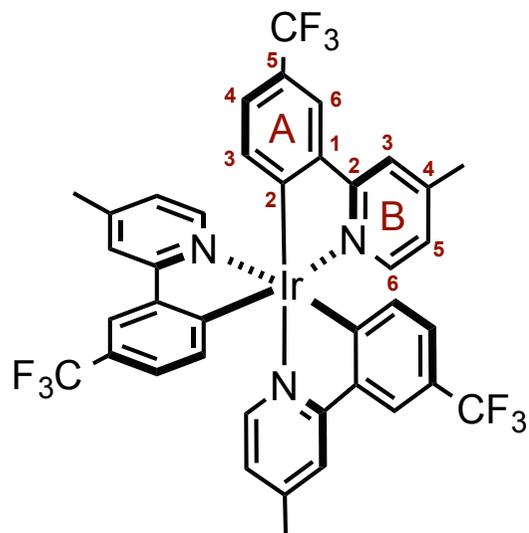
7, ^1H , 700 MHz, CD_2Cl_2



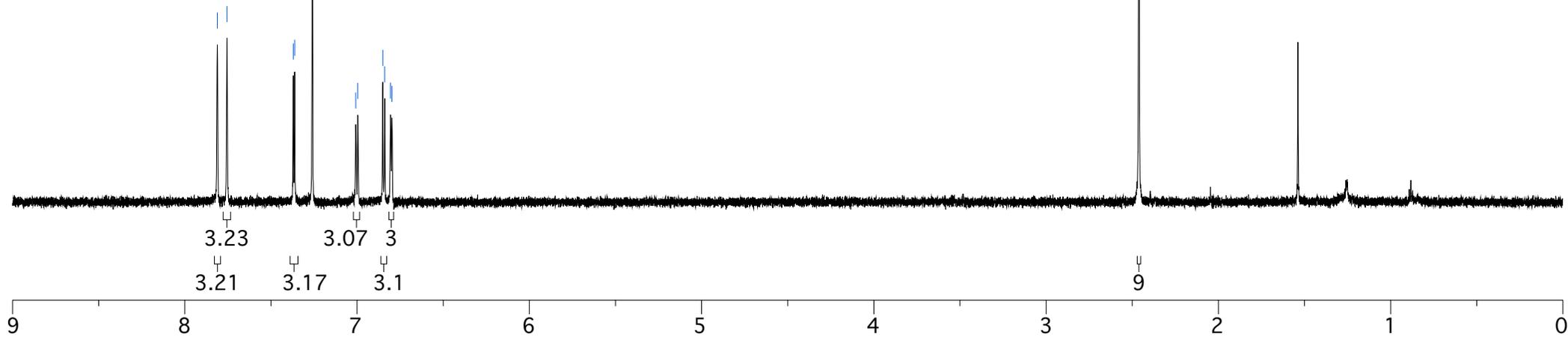


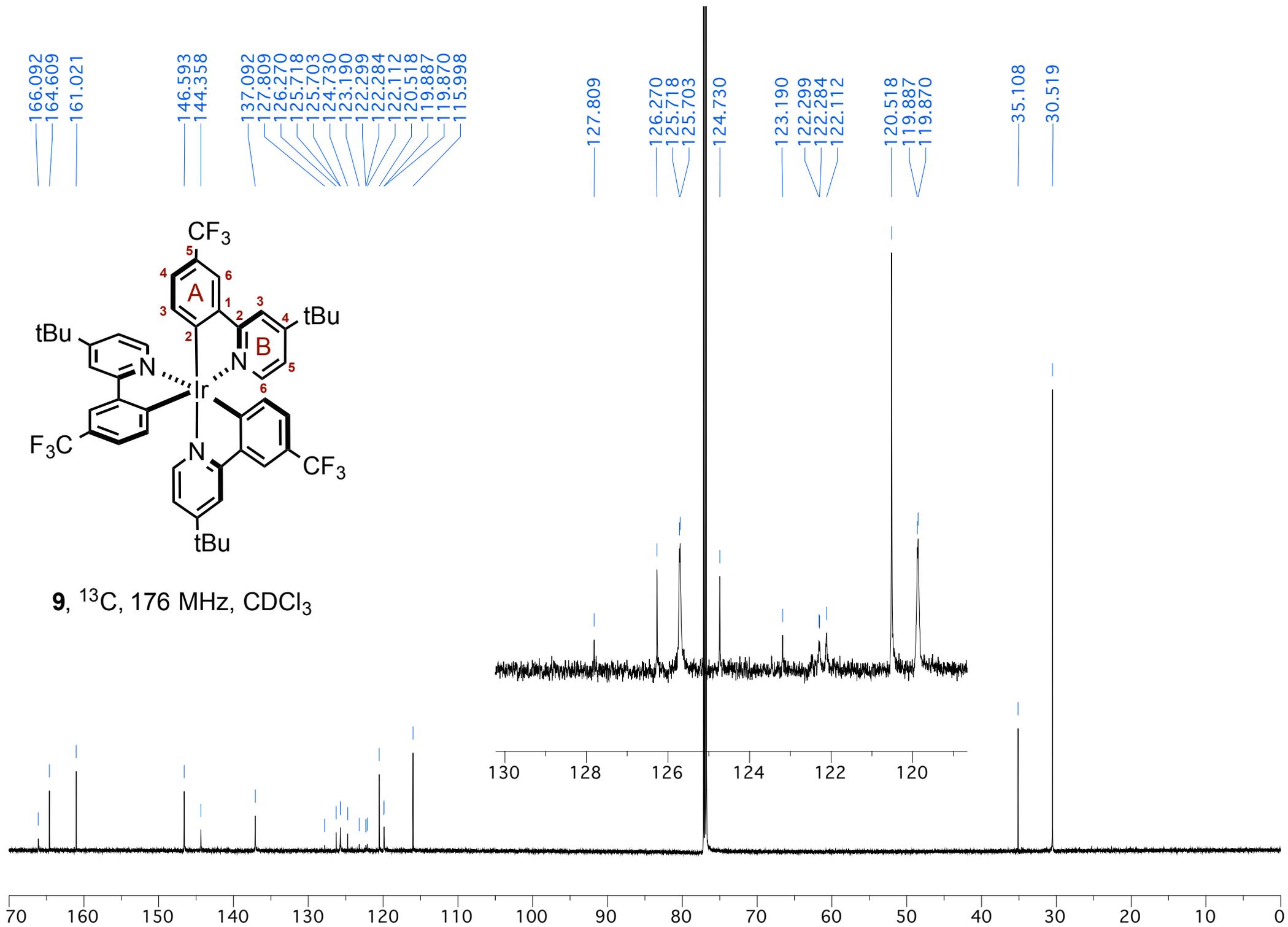
7.811
7.755
7.370
7.362
7.008
6.996
6.851
6.840
6.806
6.798

2.461

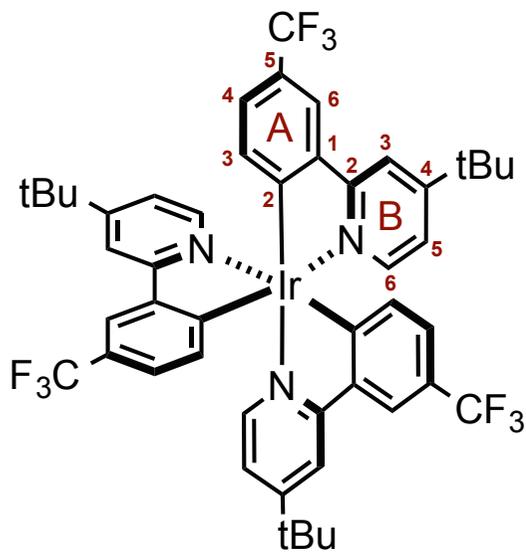


8, ¹H, 700 MHz, CDCl₃

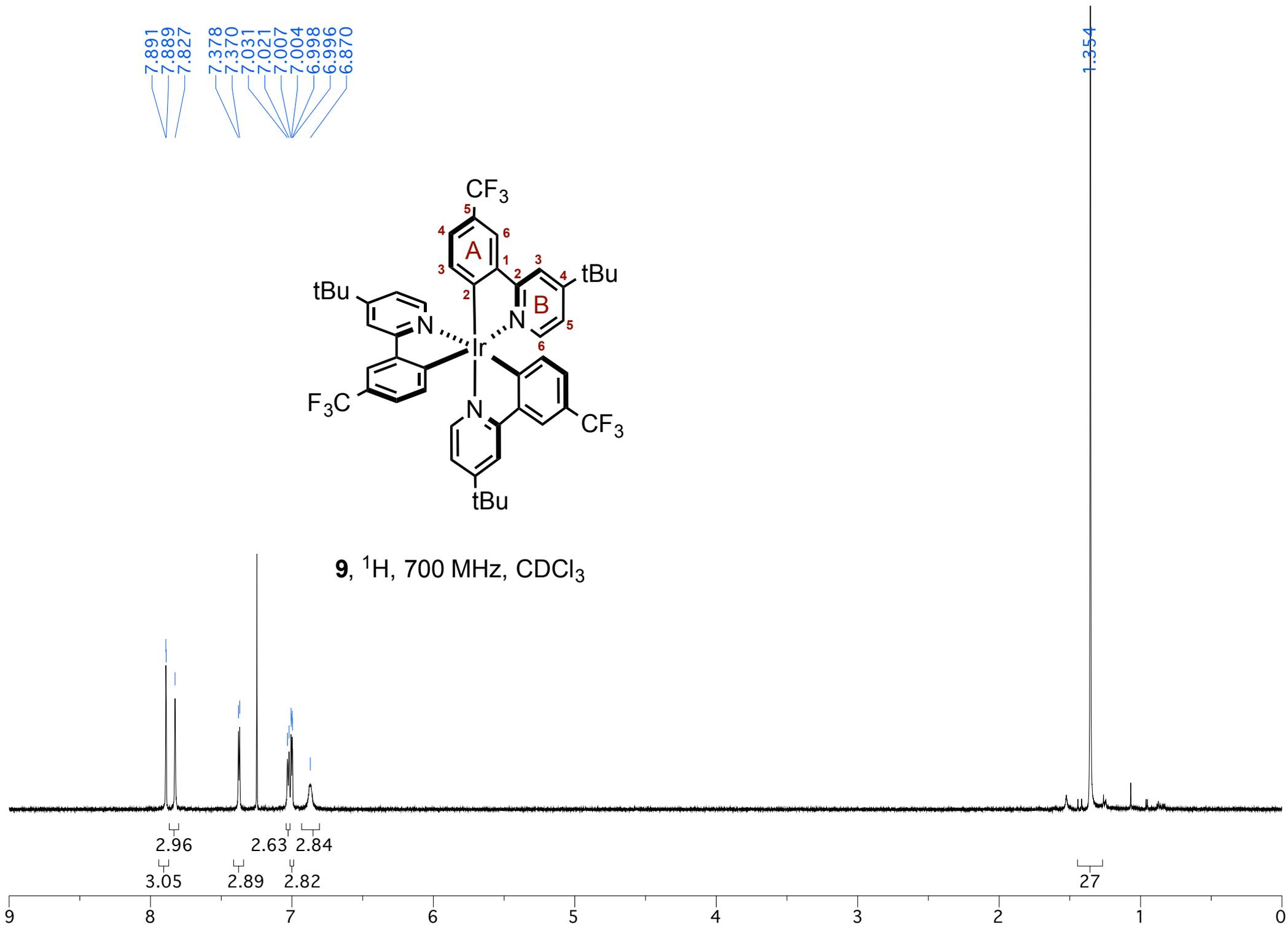




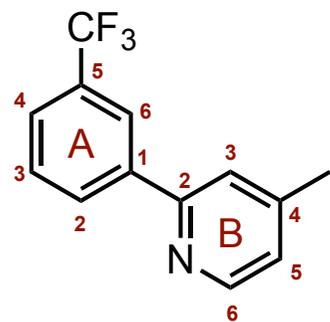
7.891
7.889
7.827
7.378
7.370
7.031
7.021
7.007
7.004
6.998
6.996
6.870



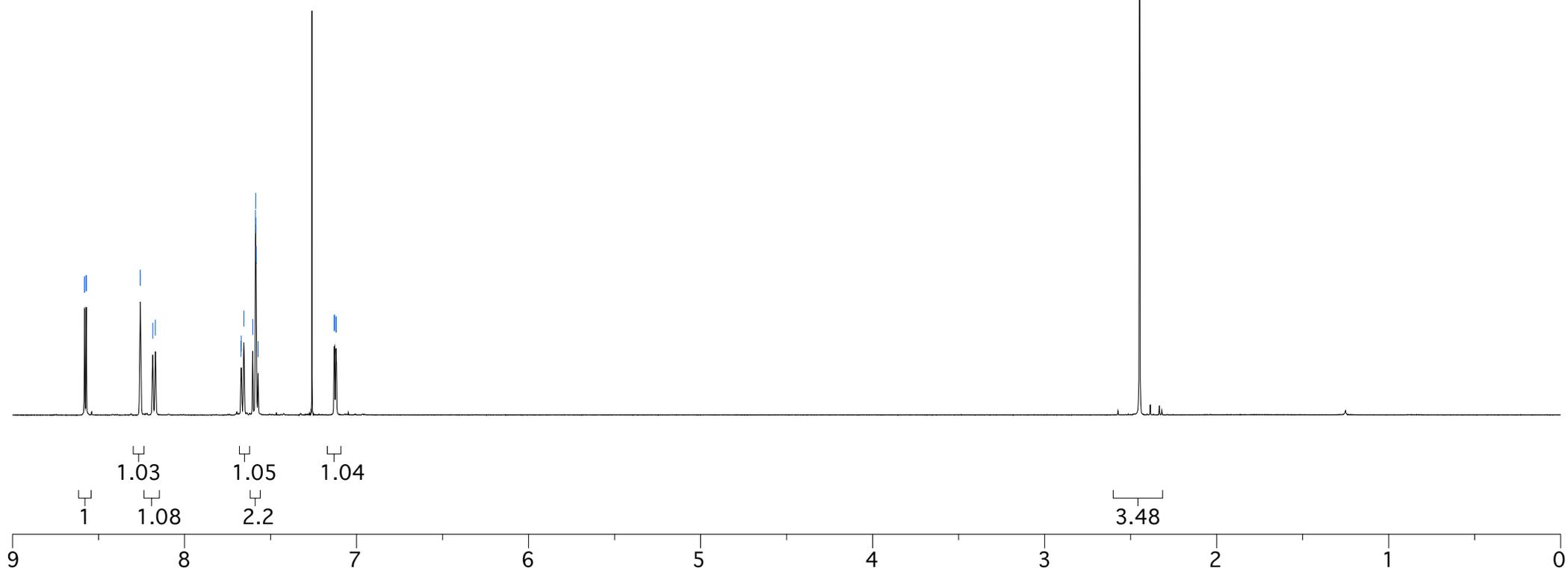
9, ^1H , 700 MHz, CDCl_3



8.582
8.581
8.572
8.571
8.257
8.185
8.169
7.672
7.655
7.604
7.588
7.587
7.585
7.573
7.130
7.128
7.120
7.118

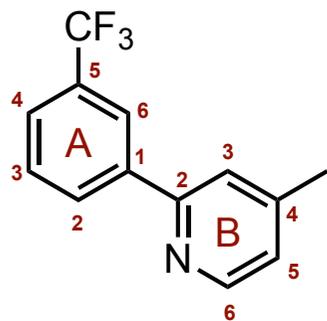


S1, ^1H , 500 MHz, CDCl_3

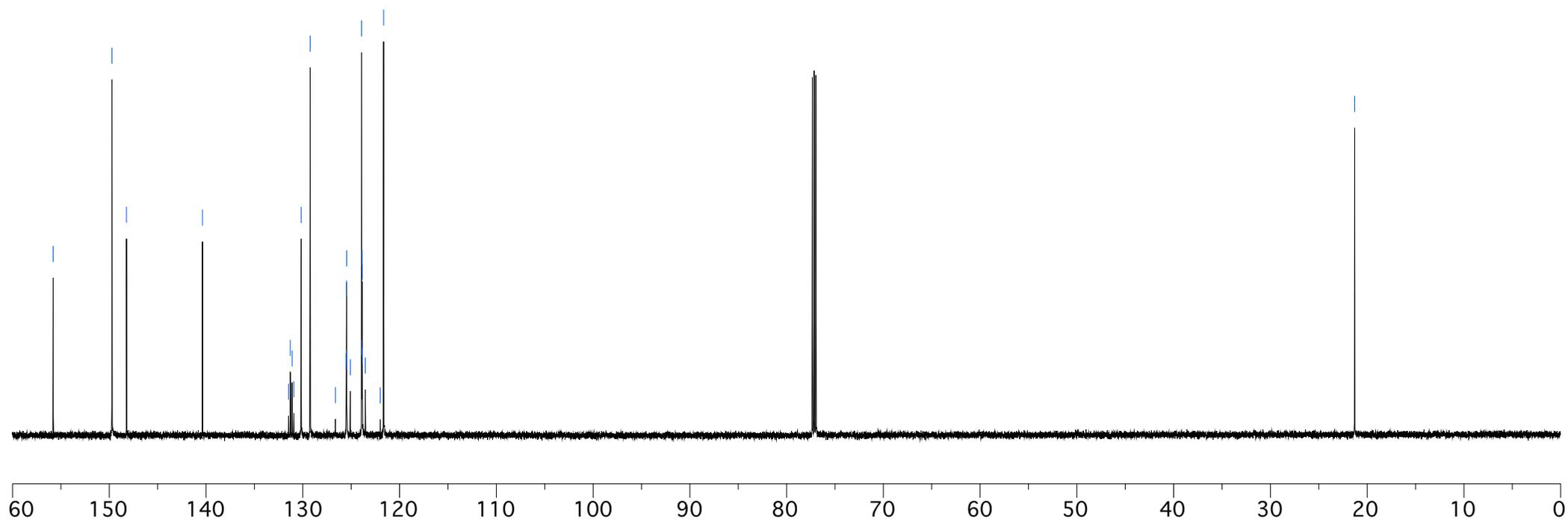


155.803
149.726
148.224
140.369
131.478
131.295
131.112
130.928
130.178
129.245
126.639
125.512
125.492
125.470
125.450
125.092
123.930
123.909
123.886
123.864
123.843
123.545
121.997
121.649

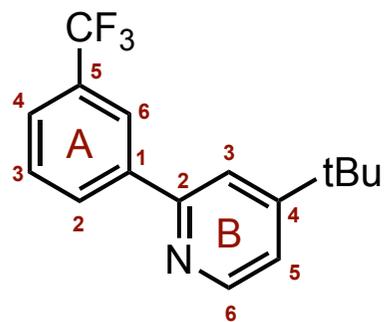
21.289



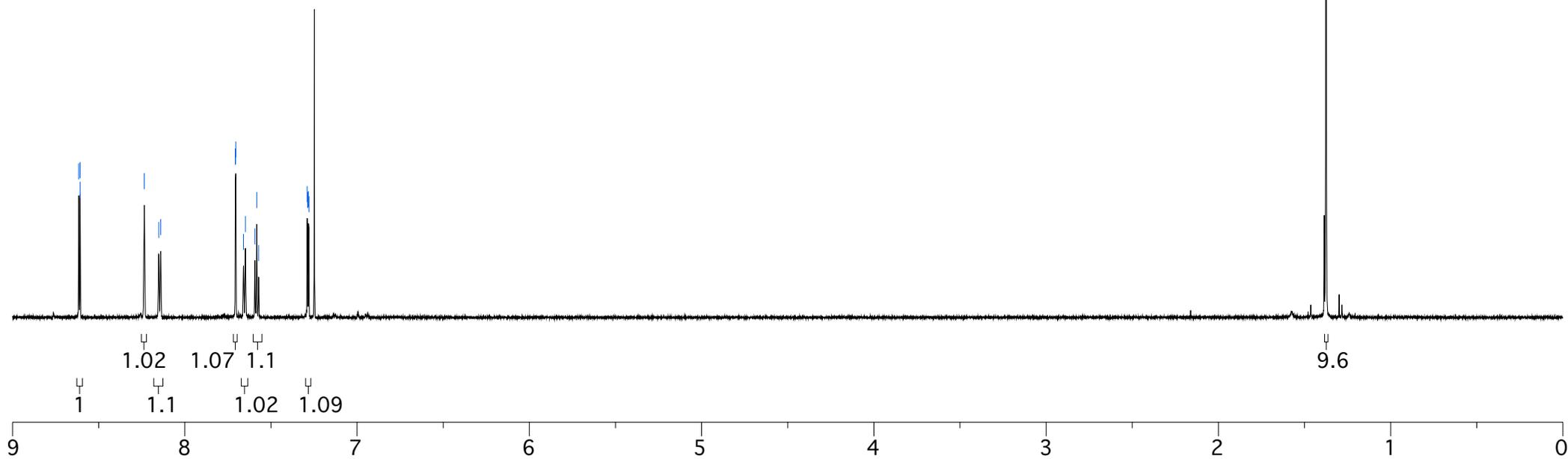
S1, ¹³C, 176 MHz, CDCl₃

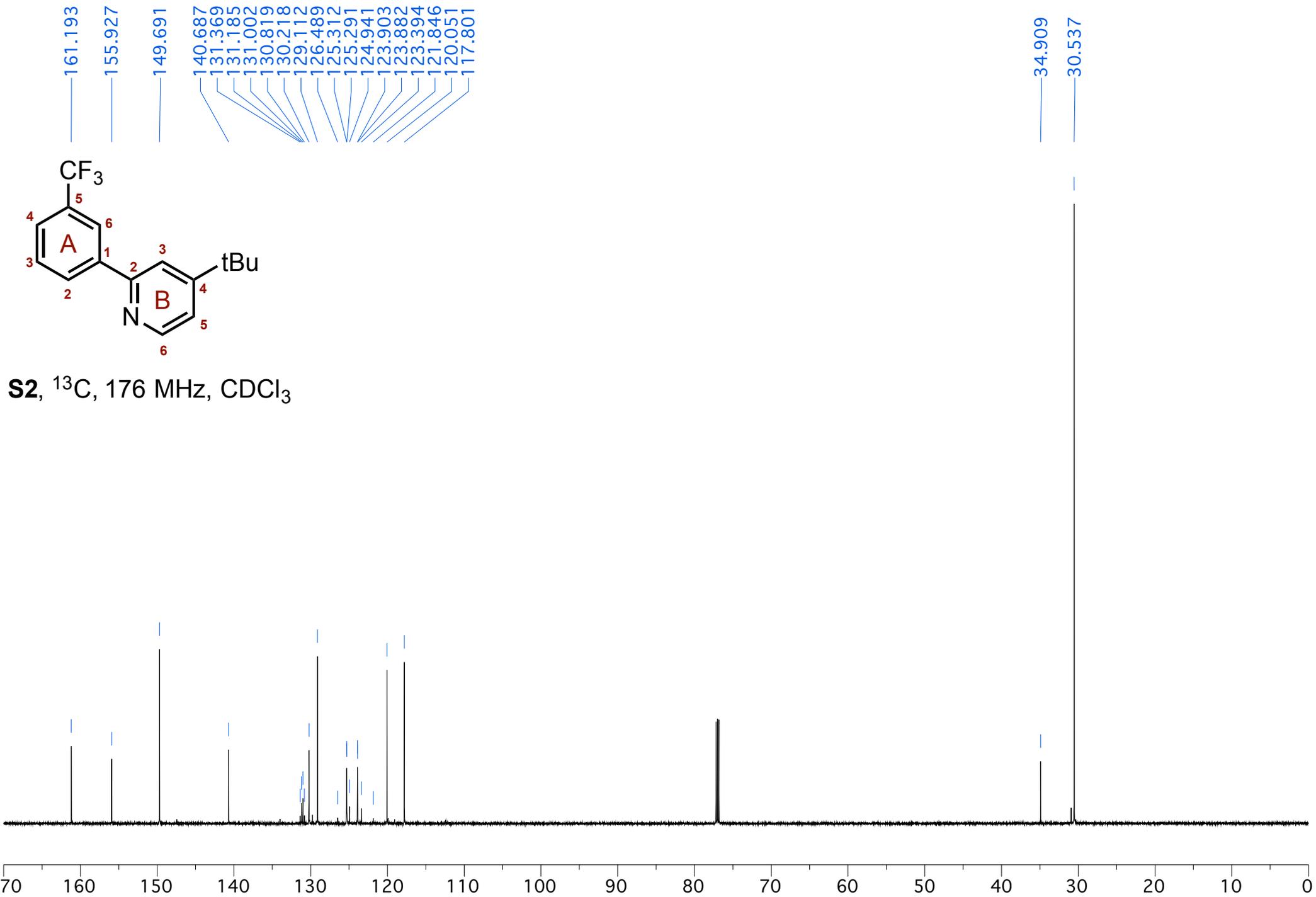


8.616
8.608
8.607
8.235
8.151
8.140
7.707
7.706
7.704
7.659
7.648
7.593
7.582
7.571
7.290
7.287
7.282
7.280

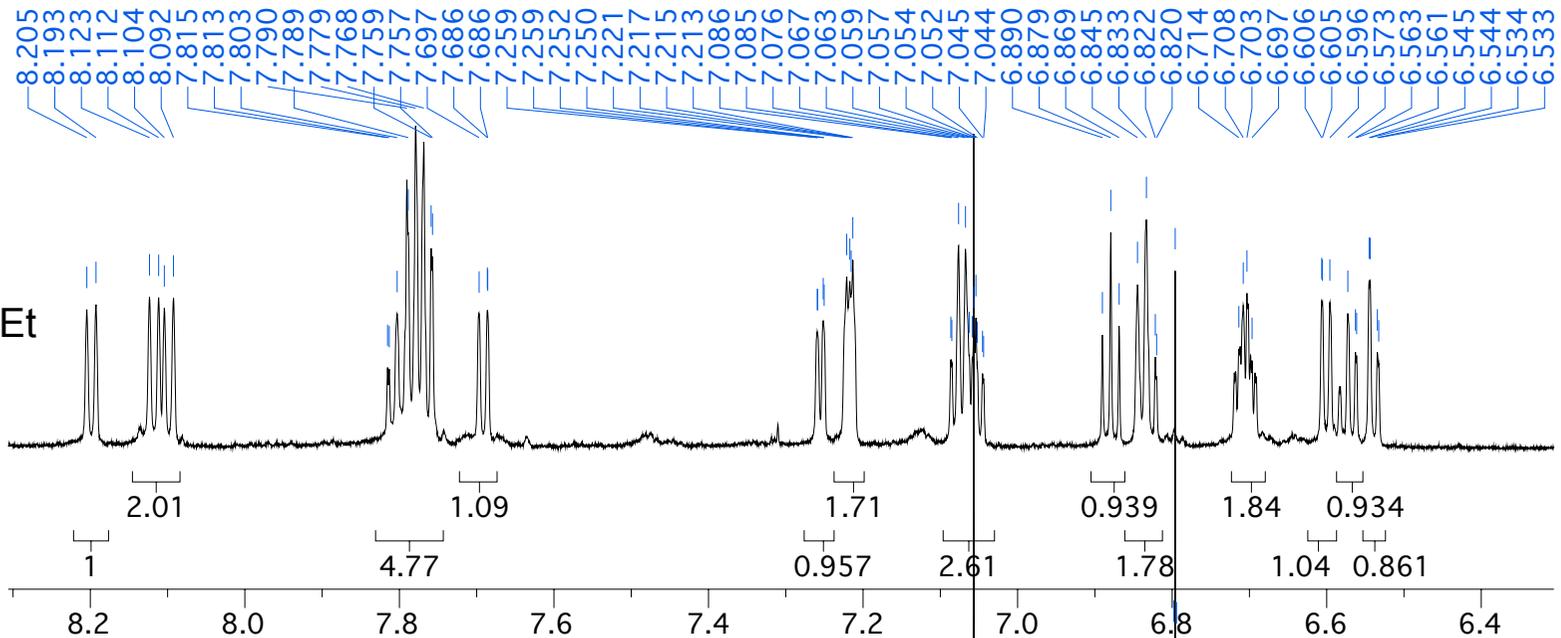
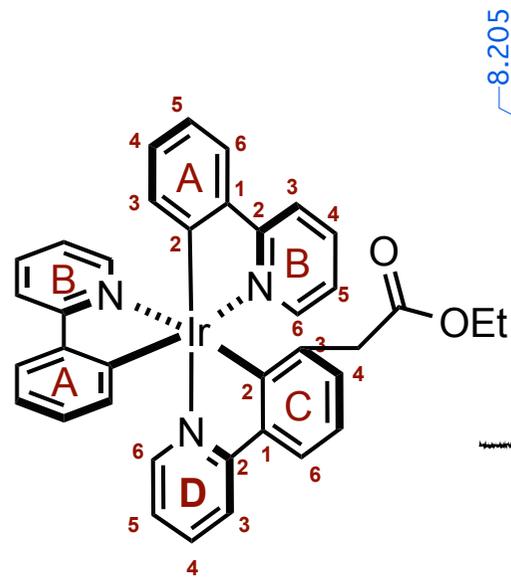


S2, ¹H, 700 MHz, CDCl₃

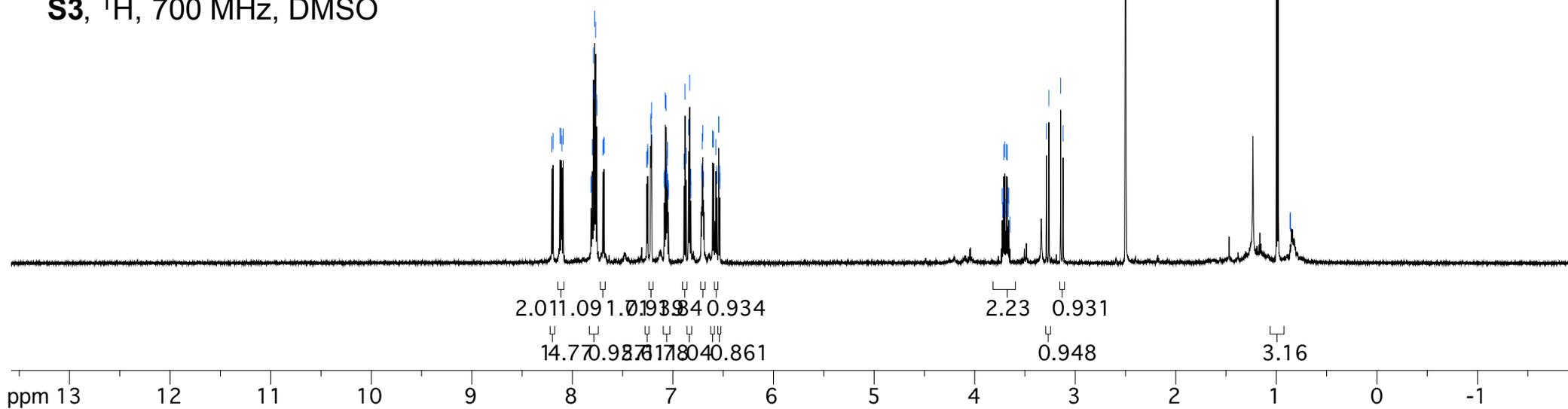


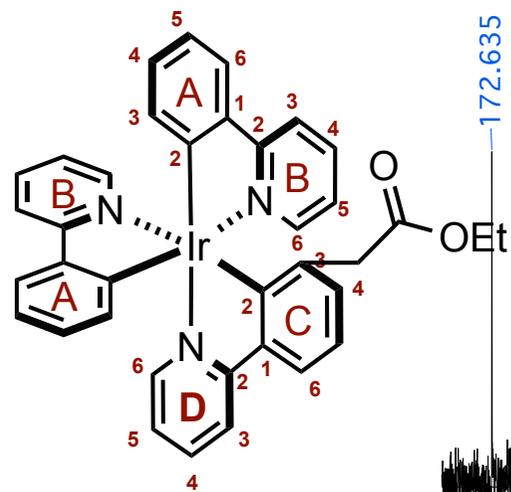


8.205
8.193
8.123
8.112
8.104
8.092
7.815
7.813
7.803
7.790
7.789
7.779
7.768
7.759
7.757
7.697
7.686
7.686
7.259
7.259
7.252
7.250
7.221
7.217
7.215
7.213
7.086
7.085
7.076
7.067
7.063
7.059
7.057
7.054
7.052
7.045
7.044
6.890
6.879
6.869
6.845
6.833
6.822
6.820
6.714
6.708
6.703
6.697
6.606
6.605
6.596
6.573
6.563
6.561
6.545
6.544
6.534
6.533
3.726
3.721
3.716
3.710
3.700
3.696
3.690
3.685
3.675
3.670
3.665
3.660
3.649
3.286
3.262
3.144
3.120
1.001
0.991
0.862
0.861
0.859

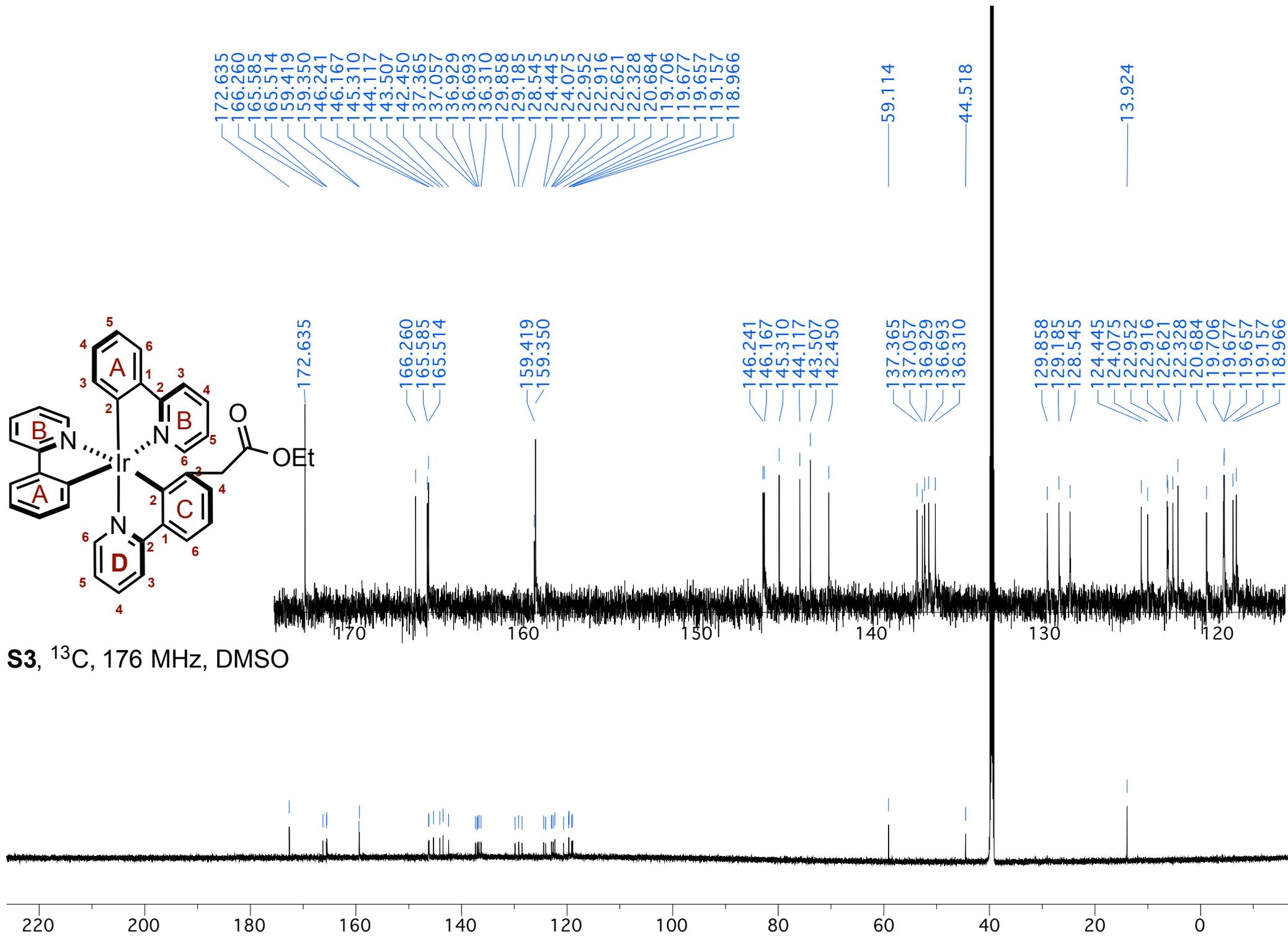


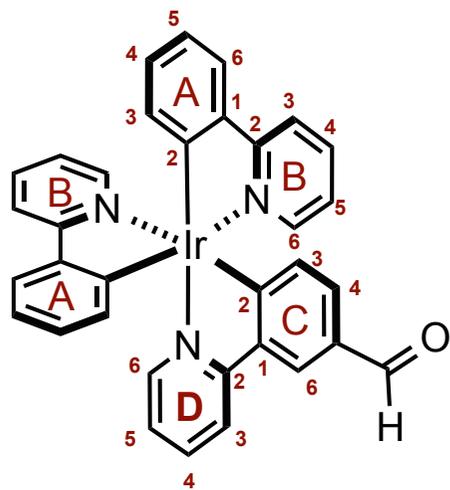
S3, ^1H , 700 MHz, DMSO



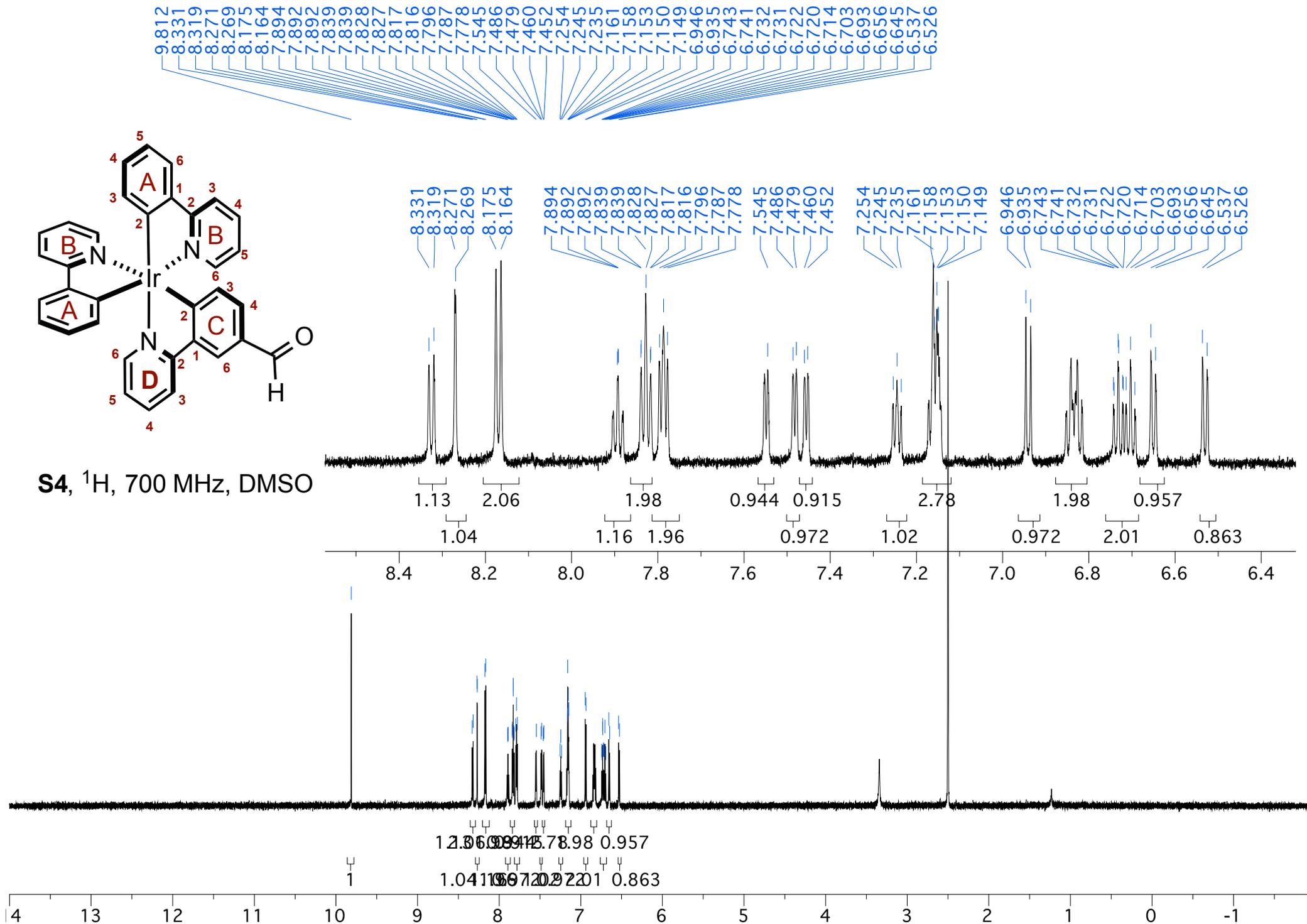


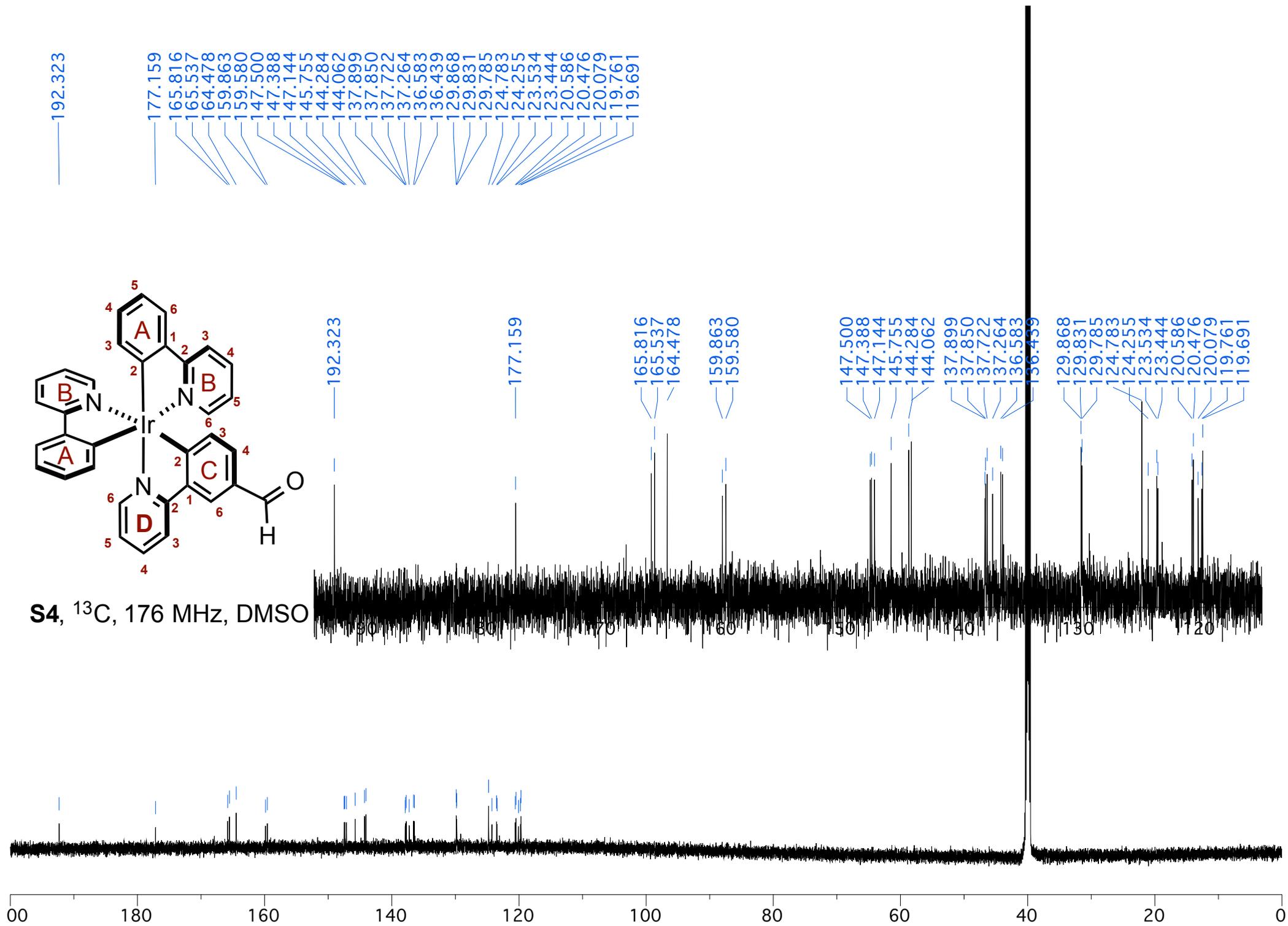
S3, ^{13}C , 176 MHz, DMSO





S4, ¹H, 700 MHz, DMSO





Intractable mixture obtained after 1h irradiation of 1 under reaction conditions in the absence of indole

