

A Metal-Free Heterogeneous Photocatalyst for the Selective Oxidative Cleavage of C=C Bonds in Aryl Olefins via Harvesting Direct Solar Energy

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Contents:

- 1. Materials and methods**
- 2. Setup for photocatalytic reactions**
- 3. General procedure for the cleavage of olefins using Blue LED**
- 4. General procedure for the cleavage of olefins using Sunlight**
- 5. General procedure for the synthesis and characterization of the catalyst**
- 6. Mechanistic investigations**
- 7. Characterization of starting material**
- 8. Characterization of the products**
- 9. References**
- 10. NMR spectra**

1. Materials and methods

Commercial reagents were used without the purification and reactions were carried out under air/oxygen. Solvents used for this reaction, workup or TLC were distilled. TLC plates with a 0.20 mm silica gel 60 layer on alumina containing a fluorescent indicator F₂₅₄ from MACHEREY NAGEL by MERCK were used for reaction monitoring, retardation factor determination and isolation. ¹H NMR spectra (300, 500 MHz) and ¹³C NMR spectra (75.58, and 125.71 MHz) were recorded using Bruker spectrometers AVANCE III 300, AVANCE III 400, AVANCE III HD 500 and Varian spectrometers Mercury VX 300, VNMRS 300 and Inova 500 with CDCl₃ or DMSO-*d*₆ as solvent. NMR spectra were calibrated using the solvent residual signals (CDCl₃: δ ¹H = 7.26, δ ¹³C = 77.16; DMSO-*d*₆: δ ¹H = 2.50, δ ¹³C = 39.52). NMR spectra were calibrated using the solvent residual signals (CDCl₃: ¹H (s) δ = 7.26 ppm, ¹³C(t) δ = 77.16 ppm). ESI mass spectra were recorded on BRUKER Daltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). GC-MS mass spectra were recorded on THERMO FINNIGAN spectrometers TRACE (Varian GC Capillary Column; wcot fused silica coated CP-SIL 8 CB; 30 m x 0.25 mm x 0.25 μ m) and DSQ (Varian FactorFour Capillary Column; VF-5ms 30 m x 0.25 mm x 0.25 μ m). FTIR was measured Jasco-FTIR-4100), SEM (Nova NanoSem 650, detail in part 5), TEM (Phillips CM12, detail in part 5), UV/Vis spectra were recorded on a Jasco V-770 Spectrophotometer. Absorption-emission spectra were recorded on a Jasco FP-6500 Spectrofluorometer. The catalyst was synthesized using GERO carbolite oven to 635 °C (type F70-200, power: 1.5 kW). Several substrates were purified with Recycling preparative HPLC (Japan Analytical Industry).

2. Setup for photocatalytic reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of a self-constructed light source configuration, made up of a crystallizing dish with a diameter of 140 mm. Inside of the crystallizing dish, commercially available 5 m LED-Strip is glued with separable LED elements. In total, 3 m LED strip is used in a crystallizing dish, with a total power of 24 W. Light intensity of the light source can be adjusted by a self-constructed dimmer. Construction of the reaction setup and the dimmer was performed by the electronic services of the faculty for chemistry of the Georg-August-Universität Göttingen. Cooling of the setup is performed by a commercially available 120 mm computer fan. To ensure the constant room temperature, the dimmer setting was used at 50 % (12 W). During the first experiment the temperature was monitored inside the crystallizing dish and did not exceed the room temperature (25–30 °C). Magnetic stirring was performed with 250 rpm.

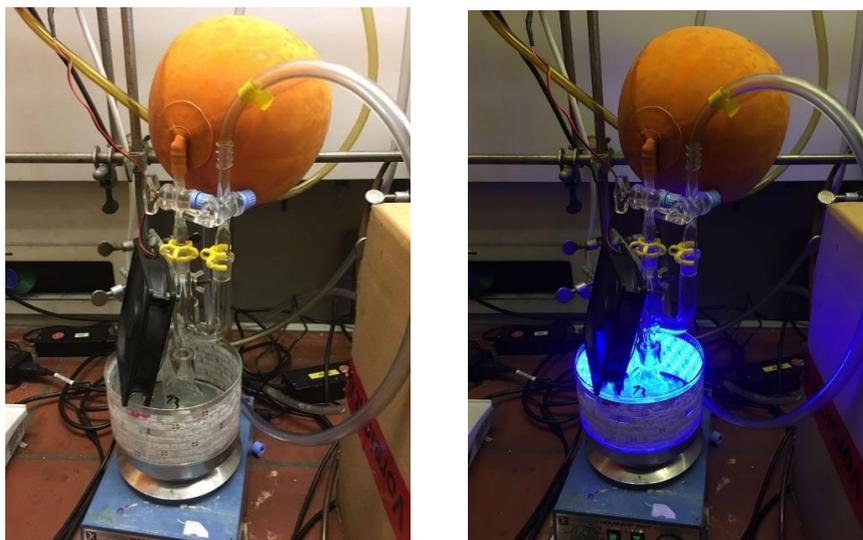


Figure S1: LED reaction setup for photocatalytic reactions.

3. General procedure for the cleavage of olefins using Blue LED

A 10 mL two-necked flask containing a stirring bar was charged with 0.25 mmol of substrate, 8 mg of g-C₃N₄ and 20 mol% of *N*-hydroxysuccinimide. After purging the flask three times with vacuum and two times with nitrogen, oxygen atmosphere was incorporated through an O₂ balloon. Finally dry acetonitrile (1.0 mL) was added. The resulting mixture was stirred for 9–40 h under 12 W blue LED irradiation (the progress can be monitored *via* GC-MS or TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Products were purified *via* silica gel chromatography or GPC (see details of products) with ethyl acetate and *n*-hexane as solvents.

4. General procedure for the cleavage of olefins using Sunlight

A 50 mL two-necked flask containing a stirring bar was charged with 1.0 g of substrate, 80 mg or 50 mg of g-C₃N₄ and 20 mol% of *N*-hydroxysuccinimide depending on the amount of starting material. After purging the flask three times with vacuum and two times with nitrogen, oxygen atmosphere was incorporated through an O₂ balloon. Finally, dry acetonitrile (12.0 mL or 10.0 mL) was added. The resulting mixture was stirred under sunlight (the setup was put on the roof of building, seeing the **Figure S2**). And the progress was monitored *via* GC-MS). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Products were purified *via* silica gel chromatography with ethyl acetate and *n*-hexane as solvents.

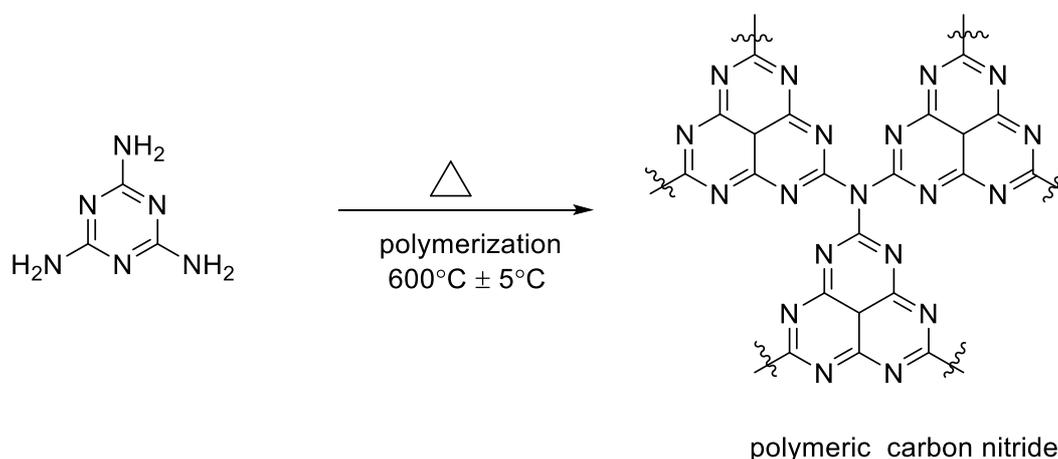


Figure S2: Cleavage of olefins using Sunlight.

5. General procedure for synthesis and characterization of catalyst

Melamine (15 g), was loaded in a stainless-steel chamber with a semi closed lid. Prepared chamber inserted into a stainless-steel heating chamber, which was heated to 00 °C (inside chamber temperature) by setting the temperature of the GERO carbolite oven to 35 °C (outside temperature at the heating coil) (type F70-200, power: 1.5 kW). The heating ramp was set to achieve target temperature in 30 minutes. The temperature was maintained for about two hours, followed by cooling the chamber to room temperature in 6 hours (**Figure S3**).

Figure S3. The synthesis of polymeric carbon nitride (PCN).



An aqueous hydrochloric acid (HCl) solution (18 %) was used to neutralize the formed ammonia gas leaving the reaction chamber.^{1,2} Afterwards, the synthesized PCN was characterized by *Infrared Spectroscopy* (IR) and *Scanning Electron Microscope* (SEM) (**Figure S4**).

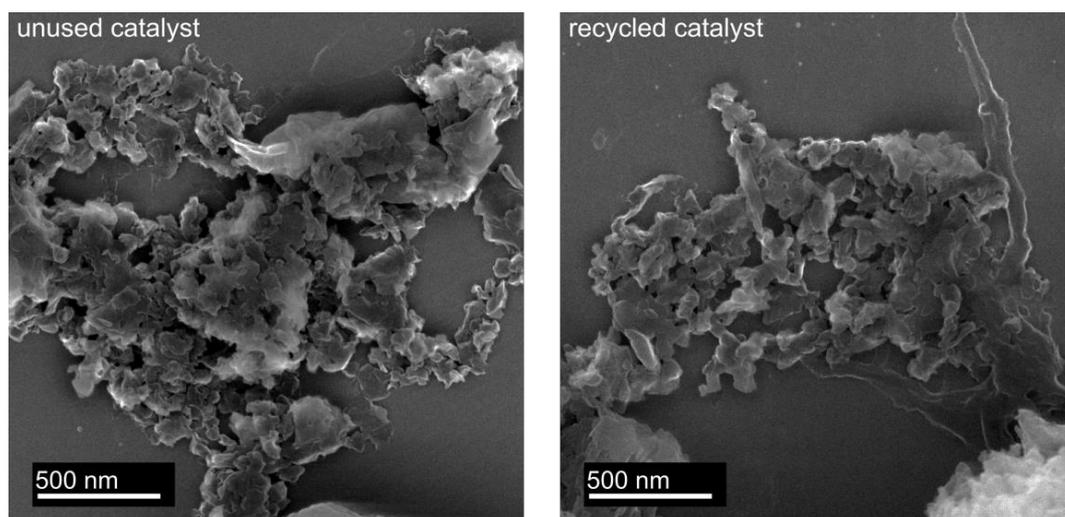
IR (FTIR): ν (cm⁻¹) = 1635, 1397, 1316, 1234, 808. Compared to the reference³ the morphology of g-C₃N₄ is similar but our particles have relatively more branches.

For the TEM an SEM analysis 5 mg of the catalyst was mixed with 1 ml of THF and treated with ultrasonic sound. One drop of this mixture was applied to a TEM Grid. The TEM analysis including electron diffraction was carried out a Phillips CM12 at 120 kV. For the HRTEM analysis an aberration corrected FEI Titan electron microscope with 300 keV electrons was deployed. The information limit in high vacuum is about 0.08 nm for this

microscope.

SEM analysis was carried out at the same Grids which were used for the TEM analysis. Here a Nova NanoSem 650 in-situ SEM from FEI was employed. At an acceleration voltage of 15 kV a “through the lens” (TTL) detector was used to take images.

Figure S4. SEM of synthesized of PCN. (left) unused catalyst; (right) recycled catalyst.



Element analysis (**Table S1**) also clearly show the constituents of fresh and reused catalyst have no difference.

Name	C (%)	H (%)	N (%)
New catalyst	35.18	2.00	62.00
Reused catalyst	35.26	2.01	61.36

Figure S5. Reusability of PCN for the C=C bond cleavage of 4-fluoro- α -methylstyrene.

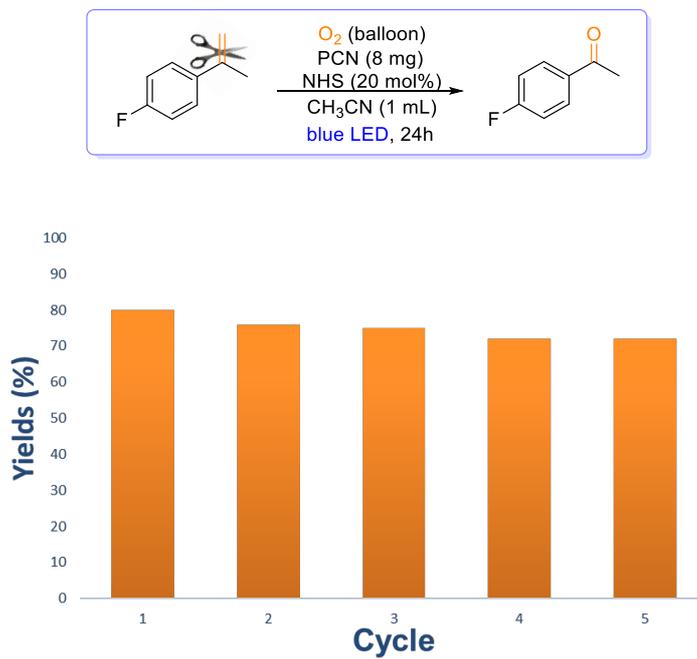
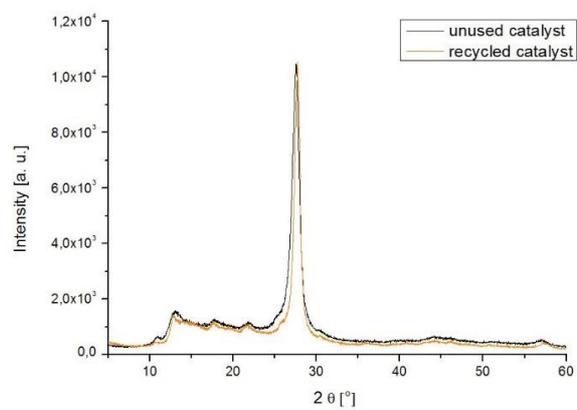


Figure S6. Analysis of new and recovered PCN by powder XRD.



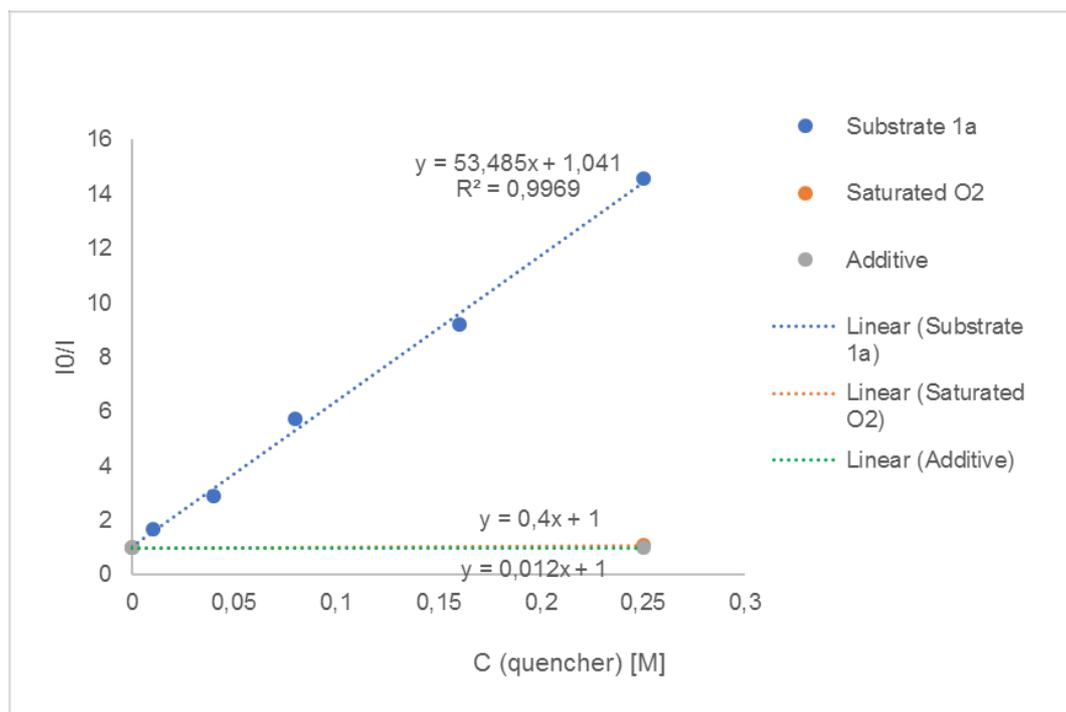
6. Mechanistic investigations

Stern-Volmer Plot

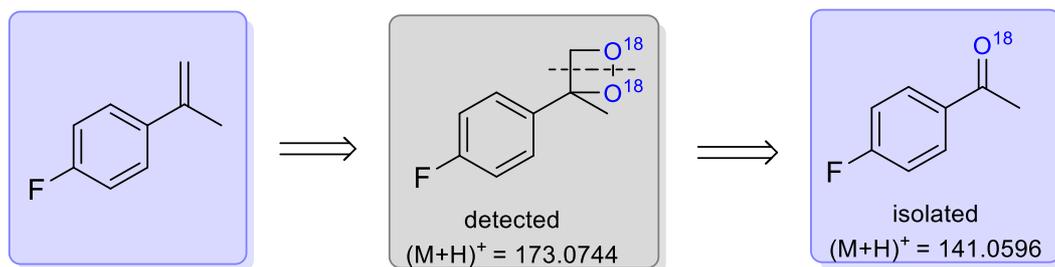
To find the suitable excitation and emission, several wavelengths were tested and the excitation maximum at 300 nm with corresponding emission maximum at 600 nm gave the best signal.

A blank sample was recorded without the substrate and the received intensity was set as I_0 . The effect of varied amounts of 4-fluoro- α -methylstyrene were investigated. **Figure S7** shows a summary of investigations. Depending on the concentration of 4-fluoro- α -methylstyrene, emission decreases significantly. The concentration of additive and oxygen atmosphere had no measurable effect on the emission of the photocatalyst.

Figure S7: Stern-Volmer plot for different concentrations of substrates (blue).



Oxidation of 4-fluoro- α -methylstyrene in presence of ^{18}O -labeled oxygen



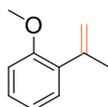
The ^{18}O -labeling experiment was performed with $^{18}\text{O}_2$ (Sigma Aldrich, ^{18}O atom 99.7%), and analyzed with ESI-HRMS and NMR showing the ^{18}O -labeled product with a isolated yield of 72%. The result showed that the origin of the oxygen atom in the desired product was only from oxygen gas since no ^{16}O -labeled product was found.

ESI-HRMS: m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{N}^{18}\text{O}$ $[\text{M}+\text{H}]^+$: 141.0559, found 141.0596.

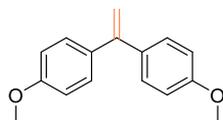
The intermediate also detected with **ESI-HRMS:** m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{N}^{18}\text{O}$ $[\text{M}+\text{H}]^+$: 173.0665, found 173.0744.

7. Characterization of the starting materials⁴

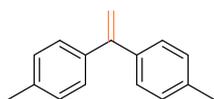
Most of starting materials are commercially available, the following starting materials were synthesized according to the reported literature under 10 mmol scale.



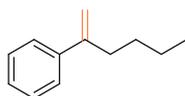
2-(2'-Methoxy-phenyl)-propene (5a). ¹H NMR (300 MHz, CDCl₃): δ 7.26 – 7.17 (m, 2H), 6.94 – 6.86 (m, 2H), 5.19 – 5.08 (m, 1H), 5.09 – 5.02 (m, 1H), 3.83 (s, 3H), 2.11 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.5, 144.3, 132.8, 129.4, 128.3, 120.5, 115.1, 110.6, 55.4, 23.1; **MS (GC-MS):** m/z 148 (M⁺);⁴ Yield: 50%.



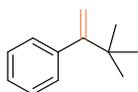
4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (8a). ¹H NMR (300 MHz, CDCl₃): δ 7.31 – 7.25 (m, 4H), 6.89 – 6.86 (m, 4H), 5.31 (s, 2H), 3.84 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 159.3, 148.9, 134.2, 129.4, 113.4, 111.6, 55.3. **MS (GC-MS):** m/z 240 (M⁺);⁴ Yield: 55%.



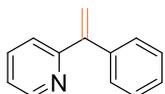
4,4'-(Ethene-1,1-diyl)bis(methylbenzene) (9a). ¹H NMR (300 MHz, CDCl₃): δ 7.25 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 5.39 (s, 2H), 2.38 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ 149.5, 138.6, 137.2, 128.7, 128.1, 113.0, 21.2. **MS (GC-MS):** m/z 208 (M⁺);⁵ Yield: 58%.



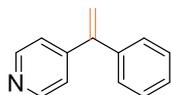
hex-1-en-2-ylbenzene (10a). ¹H NMR (300 MHz, CDCl₃): δ 7.3 (d, *J* = 6.9 Hz, 2 H), 7.2–7.0 (m, 2 H), 7.1 (d, *J* = 6.9 Hz, 1 H), 5.1 (d, *J* = 1.2 Hz, 1 H), 4.9 (d, *J* = 1.2 Hz, 1 H), 2.4 (t, *J* = 7.1 Hz, 2 H), 1.2–1.4 (m, 4 H), 0.8 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 148.6, 141.4, 128.2, 127.2, 126.2, 112.0, 35.0, 30.4, 22.4, 13.9. **MS (GC-MS):** m/z 160 (M⁺);⁶ Yield: 48%.



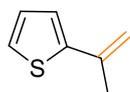
(3,3-Dimethylbut-1-en-2-yl)benzene (12a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.25 – 7.15 (m, 3H), 7.08 (dd, $J = 7.6, 1.5$ Hz, 2H), 5.11 (d, $J = 1.7$ Hz, 1H), 4.70 (d, $J = 1.7$ Hz, 1H), 1.08 (s, 9H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 159.8, 143.4, 129.0, 127.2, 126.2, 111.5, 29.6. **MS (GC-MS):** m/z 160;⁷ Yield: 55%.



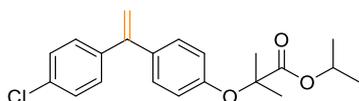
2-(1-phenylvinyl)pyridine (16a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.66 (s, 1H), 7.39 – 7.37 (m, 5H), 7.24 (d, $J = 8.0$ Hz, 1H), 6.02 (s, 1H), 5.63 (s, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 158.5, 149.4, 149.1, 140.4, 136.4, 128.5, 128.3, 127.9, 122.9, 122.5, 117.9. **MS (GC-MS):** m/z 181;⁸ Yield: 50%.



4-(1-phenylvinyl)pyridine (17a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.56 (d, $J = 4.0$ Hz, 2H), 7.35 – 7.33 (m, 3H), 7.28-7.24 (m, 2H), 7.22 – 7.21 (m, 2H), 5.60 (s, 1H), 5.59 (s, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 149.9, 148.9, 147.9, 139.8, 128.5, 128.3, 128.2, 122.8, 117.0. **MS (GC-MS):** m/z 181;⁹⁸Yield: 45%.

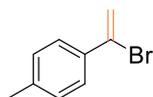


2-(Prop-1-en-2-yl)thiophene (15a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.17 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.03 (dd, $J = 3.6, 1.2$ Hz, 1H), 6.98 (dd, $J = 5.1, 3.6$ Hz, 1H), 5.38 (s, 1H), 4.95 (t, $J = 1.4$ Hz, 1H), 2.15 (dd, $J = 1.5, 0.8$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 145.8, 137.2, 127.3, 124.2, 123.5, 111.2, 21.8. **MS (GC-MS):** m/z 124;⁴Yield: 60%.

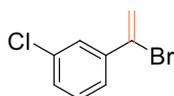


1-(1-bromovinyl)-3-chlorobenzene (29a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.29–7.22 (m, 4H), 7.17 (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 5.38 (s, 1H), 5.32 (s, 1H), 5.13–5.03 (m, 1H), 1.60 (s, 6H), 1.21 (d, $J = 6.0$ Hz, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 173.6, 155.4, 148.3, 140.0, 134.3, 133.4, 129.6, 128.8, 128.1, 118.2, 113.6, 79.0, 69.0, 25.3, 21.5. **MS (GC-MS):** m/z 358;⁹ Yield: 59%.

α -Bromostyrene derivatives was synthesized according to the literature.^{10, 11}

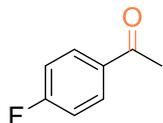


1-(1-Bromovinyl)-4-methylbenzene (28a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.50 (d, $J = 7.0$ Hz, 2H), 7.12 (d, $J = 7.0$ Hz, 2H), 6.11 (d, $J = 1.8$ Hz, 1H), 6.78 (d, $J = 1.8$ Hz, 1H), 2.40 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 139.1, 135.7, 131.0, 128.9, 125.9, 116.8, 21.1. **MS (GC-MS):** m/z 196;¹² Yield: 65%.

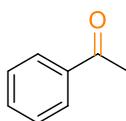


1-(1-Bromovinyl)-3-chlorobenzene (29a). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.59–7.57 (m, 1H), 7.48–7.46 (m, 1H), 7.31–7.26 (m, 2H), 6.13 (d, $J = 2.3$ Hz, 1H), 5.81 (d, $J = 2.3$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 140.2, 134.3, 129.5, 129.2, 129.1, 127.4, 125.4, 118.8. **MS (GC-MS):** m/z 196;¹² Yield: 61%.

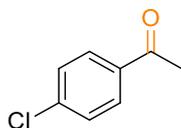
8. Characterization of the products



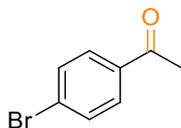
24h, **4-Fluoroacetophenone (1b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.84 (dd, $J = 8.9, 5.4$ Hz, 2H), 7.14 – 7.08 (m, 2H), 2.57 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 196.4, 167.4, 133.6, 130.9 (d, $J = 9.3$ Hz), 115.6 (d, $J = 21.9$ Hz), 26.5; **MS (GC-MS)**: m/z 138 (M^+);¹⁴ Yield: 80%.



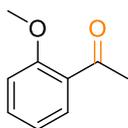
24h, **Acetophenone (2b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.98 – 7.95 (m, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 198.1, 137.1, 133.1, 128.6, 128.3, 26.6; **MS (GC-MS)**: m/z 120 (M^+);¹³ Yield: 78%.



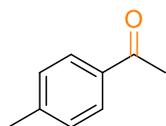
40h, **4-Chloroacetophenone (3b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.91 – 7.88 (m, 2H), 7.45 – 7.42 (m, 2H), 2.59 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 196.8, 139.5, 135.4, 129.7, 128.9, 26.5; **MS (GC-MS)**: m/z 154 (M^+);¹³ Yield: 90%.



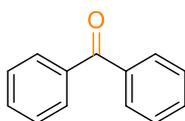
24h, **4-Bromoacetophenone (4b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.84 (dd, $J = 8.2, 1.0$ Hz, 2H), 7.64 (d, $J = 0.9$ Hz, 2H), 2.59 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 197.0, 135.8, 131.9, 129.8, 128.3, 26.5; **MS (GC-MS)**: m/z 197 (M^+);¹³ Yield: 68%.



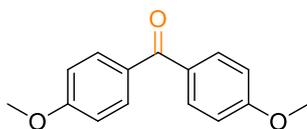
40h, **2-Methoxyacetophenone (5b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.76 – 7.73 (m, 1H), 7.50 – 7.44 (m, 1H), 7.03 – 6.96 (m, 1H), 3.90 (s, 3H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 199.9, 158.9, 133.6, 130.3, 128.3, 120.5, 111.6, 55.5, 26.5; **MS (GC-MS)**: m/z 150 (M^+);¹⁵ Yield: 71%.



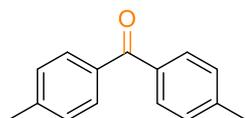
24h, **4-Methylacetophenone (6b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.88 (d, $J = 7.4$ Hz, 2H), 7.27 (d, $J = 7.4$ Hz, 2H), 2.58 (s, 3H), 2.42 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 197.8, 143.9, 134.7, 129.2, 128.4, 26.5, 21.6; **MS (GC-MS)**: m/z 134 (M^+);¹² Yield: 78%.



24h, **Benzophenone (7b, 34b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.85 – 7.81 (m, 4H), 7.64 – 7.59 (m, 2H), 7.54–7.48 (m, 4H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 196.8, 137.6, 132.4, 130.1, 128.3; **MS (GC-MS)**: m/z 182 (M^+);⁴ 90% yield for **1b**, 68% yield for **34b**.

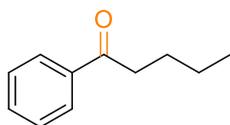


24h, **4,4'-Dimethoxybenzophenone (8b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.83 – 7.74 (m, 4H), 6.99-6.91 (m, 4H), 3.89 (s, 6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 194.42, 162.83, 132.20, 130.78, 113.45, 55.45; **MS (GC-MS)**: m/z 242 (M^+);¹⁶ 75% yield.

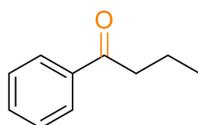


24h, **4,4'-Dimethylbenzophenone (9b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.74 – 7.71 (m, 4H),

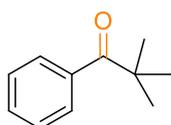
7.31 – 7.28 (m, 2H), 2.46 (s, 6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 196.3, 142.9, 135.2, 130.2, 128.9, 21.6; **MS (GC-MS)**: m/z 210 (M^+);¹⁶ Yield: 81%.



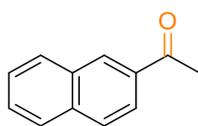
40h, **1-Phenylpentan-1-one (10b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.99–7.96 (m, 2H), 7.59–7.55 (m, 1H), 7.50–7.45 (m, 2H), 3.00 (t, $J = 7.4$ Hz, 2H), 1.76 (m, 2H), 1.44 (m, 2H), 1.03 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 200.6, 137.1, 132.9, 128.5, 128.1, 38.3, 26.5, 22.5, 14.0; **MS (GC-MS)**: m/z 162 (M^+);¹⁷ Yield: 75%.



40h, **1-Phenylbutan-1-one (11b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.99–7.96 (m, 2H), 7.60–7.54 (m, 1H), 7.50–7.45 (m, 2H), 2.97 (t, $J = 7.3$ Hz, 2H), 1.80 (q, $J = 7.4$ Hz, 2H), 1.03 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 200.4, 137.1, 132.9, 128.5, 128.0, 40.5, 17.8, 13.9; **MS (GC-MS)**: m/z 148 (M^+);¹⁸ Yield: 72%.

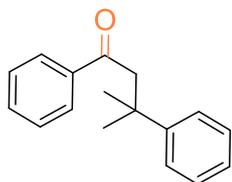


40h, **2,2-dimethyl-1-phenylpropan-1-one (12b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.71 –7.64 (m, 2H), 7.51–7.39 (m, 3H), 1.37 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 209.3, 138.6, 130.8, 128.0, 127.8, 44.2, 28.0; **MS (GC-MS)**: m/z 162 (M^+);¹² Yield: 61%.

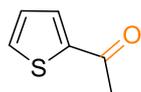


24h, **2'-Acetonaphthone (13b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.50 (br-s, 1H), 8.09-7.98 (m, 2H), 7.94-7.89 (m, 2H), 7.67-7.56 (m, 2H), 2.76 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7; **MS (GC-MS)**: m/z

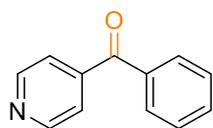
170 (M⁺);¹⁴ Yield: 75%.



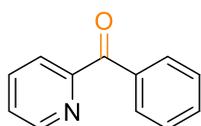
40h, **3,3-dimethyl-1,4-diphenylbutan-1-one (14b)**. ¹H NMR (300 MHz, CDCl₃): δ 7.85-7.82 (m, 2H), 7.54-7.49 (m, 1H), 7.42-7.37 (m, 4H), 7.32-7.30 (m, 2H), 7.20-7.15 (m, 1H), 3.33 (s, 2H), 2.76 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ ¹³C NMR (75 MHz, CDCl₃) δ 199.0, 148.9, 138.2, 132.7, 128.4, 128.2, 128.1, 125.8, 125.4, 50.9, 37.5, 29.1, 15.3; **ESI-HRMS**: *m/z* calcd. for C₁₇H₁₈O [M+H]⁺: 239.1436, found 239.1428; Yield: 53%. Purified with GPC.



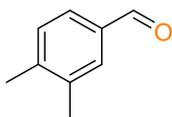
40h, **2-Acetylthiophene (15b)**. ¹H NMR (300 MHz, CDCl₃): δ 7.69 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.12 (td, *J* = 5.0, 3.8 Hz, 1H), 2.55 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 190.7, 144.5, 133.8, 132.5, 128.1, 26.9; **MS (GC-MS)**: *m/z* 126 (M⁺);¹⁹ Yield: 70%.



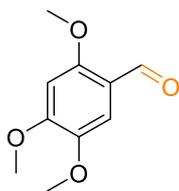
40h, **Phenyl(pyridin-4-yl)methanone (16b)**. ¹H-NMR (300 MHz, CDCl₃): δ 8.81 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.89-7.77 (m, 2H), 7.64 (s, 1H), 7.58 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz): δ 195.1, 150.4, 144.4, 135.9, 133.50, 130.1, 128.7, 122.8; **MS (GC-MS)**: *m/z* 183 (M⁺);²⁰ Yield: 71%.



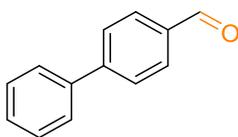
40h, **Phenyl(pyridine-2-yl)methanone (17b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.74 (ddd, $J = 4.8, 1.7, 0.9$ Hz, 1H), 8.09 – 8.02 (m, 3H), 7.91 (td, $J = 7.7, 1.7$ Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.45 (m, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 194.0, 155.1, 148.6, 137.1, 136.3, 132.9, 131.0, 128.2, 126.2, 124.6; **MS (GC-MS)**: m/z 183 (M^+);²⁰ Yield: 75%.



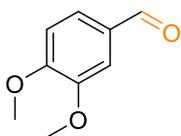
16h, **3, 4-Dimethylbenzaldehyde (18b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.95 (s, 1H), 7.66-7.61 (m, 2H), 7.32-7.29 (m, 1H), 2.29 (s, 6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.3, 144.3, 137.5, 134.6, 130.6, 130.2, 127.7, 20.3, 19.7.; **MS (GC-MS)**: m/z 134 (M^+);²¹ Yield: 60%.



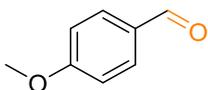
9h, **2, 4, 5-Trimethoxybenzaldehyde (19b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.3 (s, 1H), 7.34 (s, 1H), 6.51 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 188.0, 158.3, 155.8, 143.6, 117.4, 109.0, 96.0, 56.3, 56.2, 56.2; **MS (GC-MS)**: m/z 196 (M^+);¹⁵ Yield: 52%.



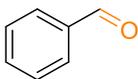
24h, **Biphenyl-4-carboxaldehyde (20b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.09 (s, 1H), 8.00-7.97 (m, 2H), 7.80-7.77 (m, 2H), 7.69-7.64 (dd, $J = 1.8, 8.4$ Hz, 2H), 7.54-7.41 (m, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.9, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4; **MS (GC-MS)**: m/z 182 (M^+);¹² Yield: 56%.



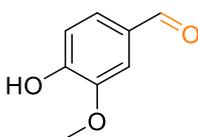
9h, **3,4-Dimethoxybenzaldehyde (21b, 24b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.81 (s, 1H), 7.41 (dd, $J = 8.2, 1.9$ Hz, 1H), 7.36 (d, $J = 1.9$ Hz, 1H), 6.94 (d, $J = 8.2$ Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 190.9, 154.5, 149.6, 130.1, 126.9, 110.4, 108.9, 56.18, 56.2; **MS (GC-MS)**: m/z 166 (M^+);¹⁵ 41% yield for **21b**, 52% for **24b**.



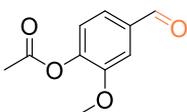
16h, **4-Methoxybenzaldehyde (22b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.88 (s, 1H), 7.82 (m, 2H), 6.99 (m, 2H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 190.8, 164.6, 132.0, 130.0, 114.3, 55.6; **MS (GC-MS)**: m/z 136 (M^+);¹² Yield: 62%.



16h, **Benzaldehyde (23b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.00 (s, 1H), 7.91 – 7.83 (m, 2H), 7.67 – 7.59 (m, 1H), 7.55 – 7.46 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 192.4, 136.4, 134.5, 129.7, 129.0; **MS (GC-MS)**: m/z 106 (M^+);¹² Yield: 65%.

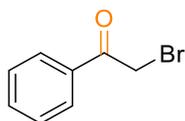


40h, **Vanillin (25b)**: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.85 (s, 1H), 7.47 – 7.44 (m, 2H), 7.07 (br-d, $J = 8.8$ Hz, 1H), 6.28 (br-s, 1H), 3.99 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 13C NMR (75 MHz, CDCl_3) δ 190.89, 151.68, 147.14, 129.89, 127.53, 114.38, 108.76, 56.13; **MS (GC-MS)**: m/z 152 (M^+);²² Yield: 39%.

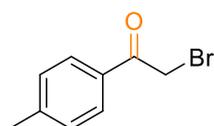


16h, **Methyl 4-formyl-2-methoxybenzoate (26b)**: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.97 (s,

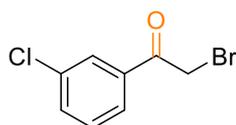
1H), 7.55 – 7.46 (m, 2H), 7.24 (d, $J = 8.2$ Hz, 1H), 3.92 (s, 3H), 2.37 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 191.0, 168.3, 152.0, 144.9, 135.2, 124.7, 123.4, 110.8, 56.1, 20.6. **MS (GC-MS):** m/z 194 (M^+);²³ Yield: 42%



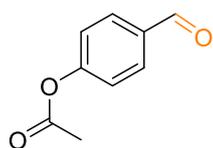
16h, **2-Bromo-1-phenylethan-1-one (27b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.03-8.00 (m, 2H), 7.67-7.61 (m, 1H), 7.54-7.50 (m, 2H), 4.49 (s, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.3, 134.0, 133.9, 130.0, 128.9, 30.9; **MS (GC-MS):** m/z 197 (M^+);¹² Yield: 70%.



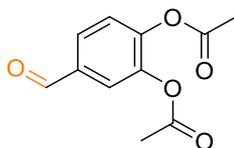
16h, **2-Bromo-1-(p-tolyl)ethan-1-one (28b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.29-7.27 (m, 2H), 4.41 (s, 2H), 2.42 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 190.9, 145.0, 131.5, 31.2, 21.8; **MS (GC-MS):** m/z 211 (M^+);¹² Yield: 64%.



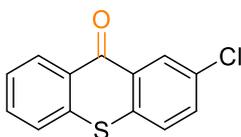
16h, **2-Bromo-1-(3-chlorophenyl)ethan-1-one (29b)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.06-7.92 (m, 1H), 7.88 (ddd, $J = 7.7, 1.7, 1.1$ Hz, 1H), 7.61 (ddd, $J = 8.0, 2.1, 1.1$ Hz, 1H), 7.53-7.39 (m, 1H), 4.44 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 190.1, 135.5, 135.3, 133.9, 130.2, 129.0, 127.0, 30.5; **MS (GC-MS):** m/z 231 (M^+);²⁴ Yield: 61%.



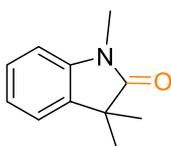
40h, **4-Acetoxybenzaldehyde (30b-1)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.02 (s, 1H), 7.97-7.92 (m, 2H), 7.32-7.28 (m, 2H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 190.9, 168.7, 155.3, 134.0, 131.2, 122.4, 21.2; **MS (GC-MS):** m/z 164 (M^+);²⁶ Yield: 57%.



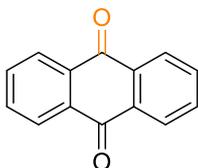
40h, **3,4-Diacetoxybenzaldehyde (30b-2)**. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.98 (s, 1H), 7.88 (dd, $J = 2.3, 0.6$ Hz, 2H), 7.23 (m, 1H), 2.32 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 190.0, 168.6, 151.6, 138.1, 121.4, 119.9, 21.0; **MS (GC-MS)**: m/z 222 (M^+);²⁶ Yield: 57%.



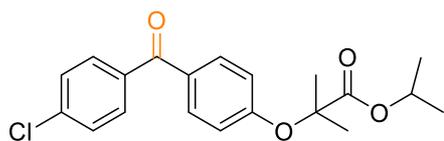
40h, **2-Chlorothioxanthone (31b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.65–8.63 (m, 2H), 7.70–7.29 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 178.9, 136.9, 135.4, 132.6, 132.6, 132.5, 130.3, 130.0, 129.3, 128.8, 127.4, 126.6, 126.0; **MS (GC-MS)**: m/z 208 (M^+);²⁹ Yield: 62%.



24h, **1,3,3-Trimethylindolin (32b)**: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.26 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.21 (dd, $J = 7.2, 0.4$ Hz, 1H), 7.06 (dt, $J = 7.6, 0.8$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): δ 181.3, 142.5, 135.7, 127.6, 122.4, 122.2, 107.9, 44.1, 26.1, 24.3; **MS (GC-MS)**: m/z 175 (M^+);²⁷ Yield: 71%.



24h, **Anthraquinone (33b)**. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.7–7.82 (m, 4 H), 8.24–8.36 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): 183.2, 134.1, 133.5, 127.2; **MS (GC-MS)**: m/z 208 (M^+);²⁸ Yield: 68%.



18h, **Fenofibrate (35b)**. **¹H NMR** (300 MHz, CDCl₃) δ 7.74 (s, 4H), 7.50 – 7.39 (m, 2H), 6.93 – 6.81 (m, 2H), 5.11 (hept, $J = 6.2$ Hz, 1H), 1.66 (s, 6H), 1.20 (d, $J = 6.5$ Hz, 6H); **¹³C NMR** (CDCl₃, 75 MHz): δ 194.2, 173.1, 159.7, 138.3, 136.4, 131.9, 131.1, 130.2, 128.5, 117.2, 79.4, 69.3, 25.4, 21.5; **MS (GC-MS)**: m/z 360 (M⁺);²⁵ Yield: 75%.

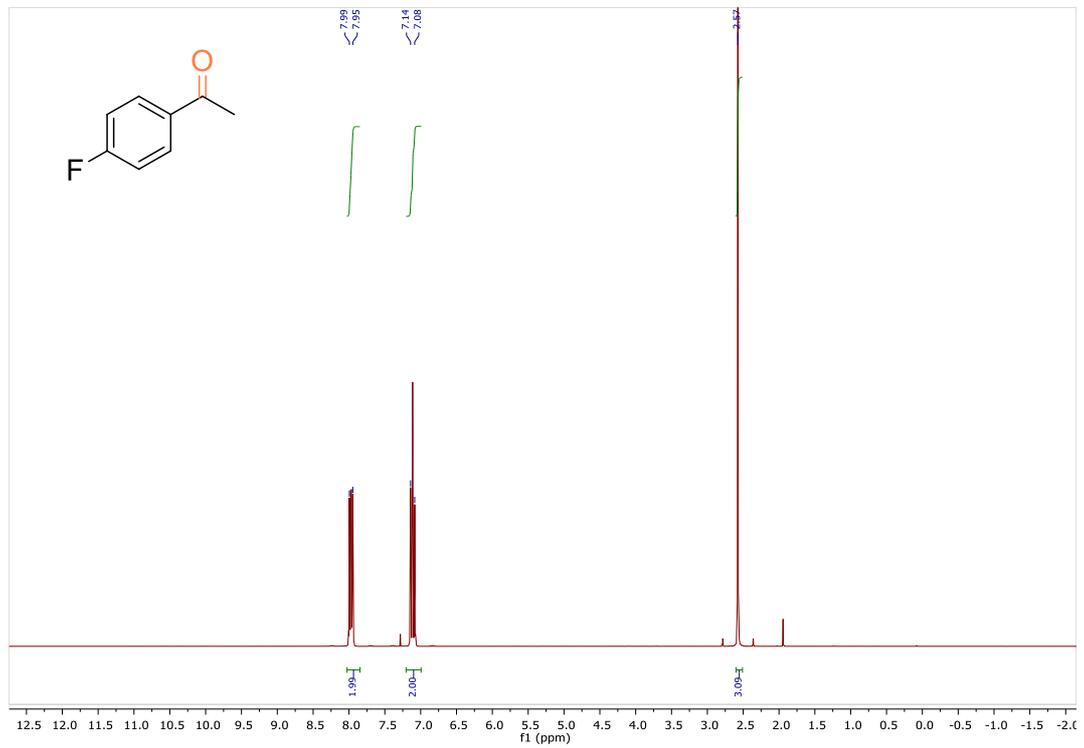
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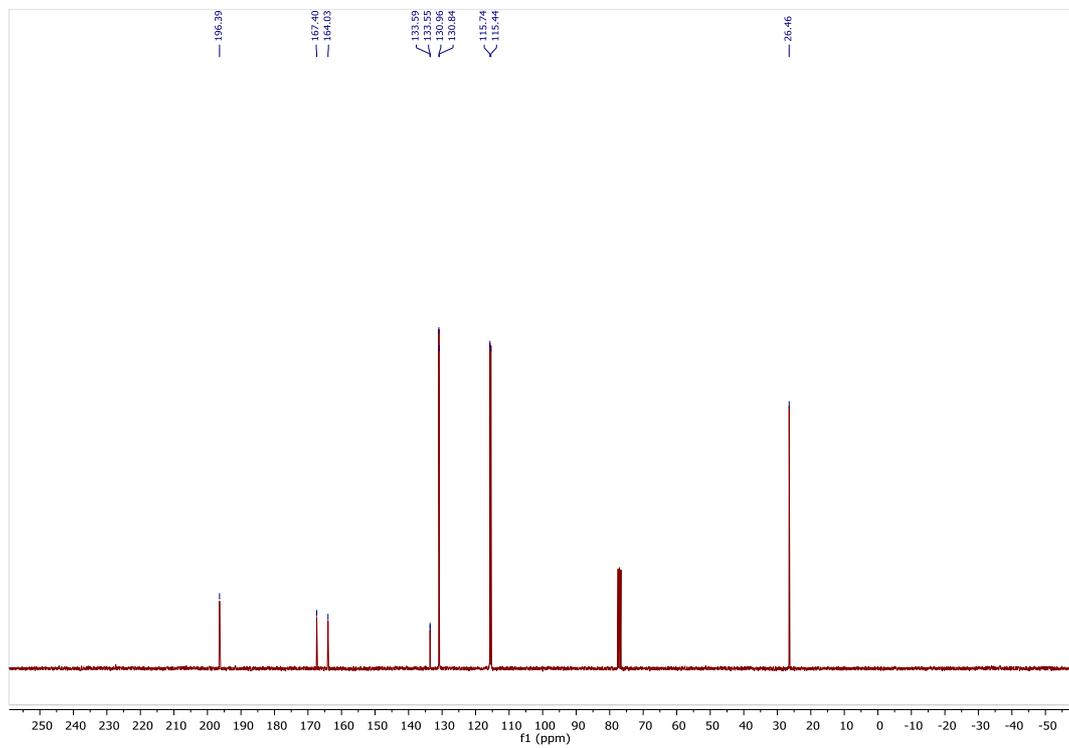
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10. NMR spectra

1b

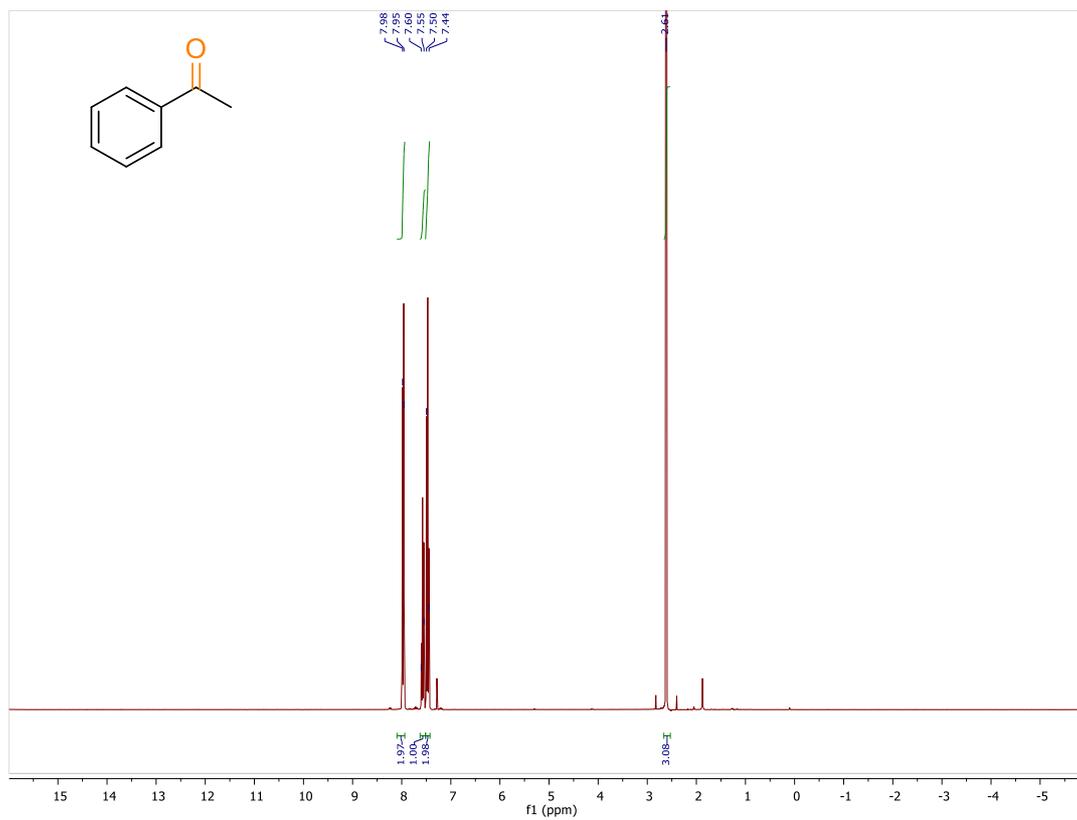


^1H NMR spectrum in CDCl_3 .

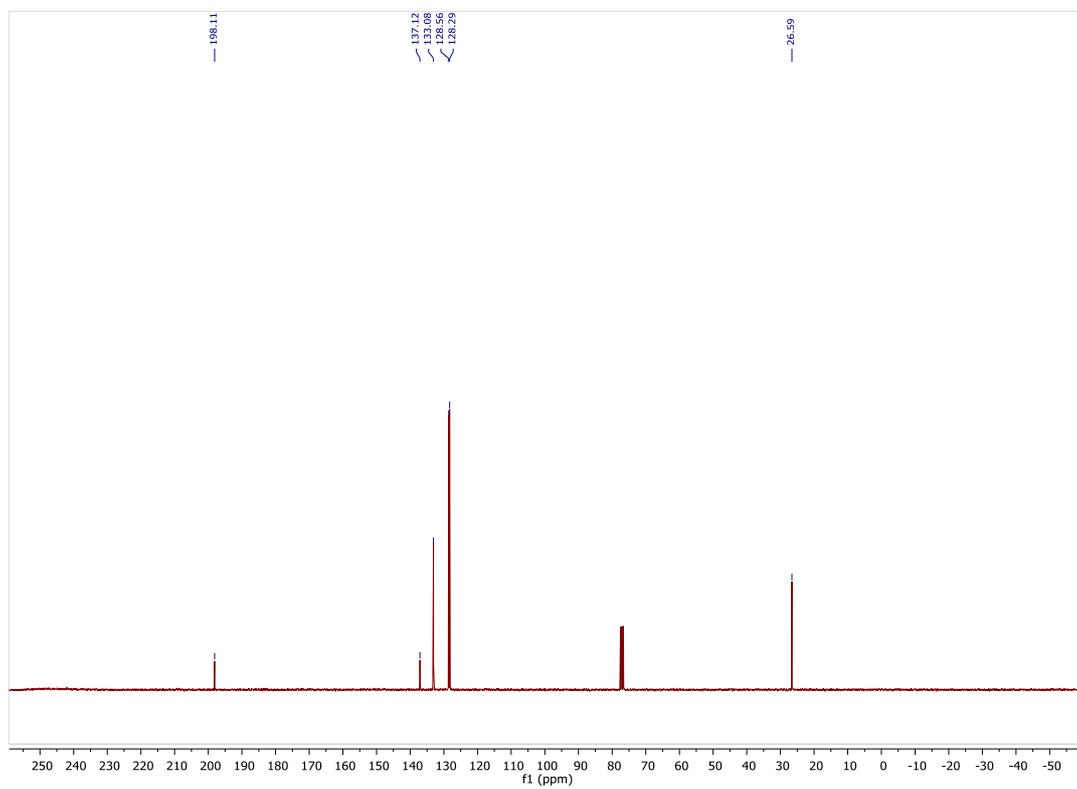


^{13}C NMR spectrum in CDCl_3 .

2b

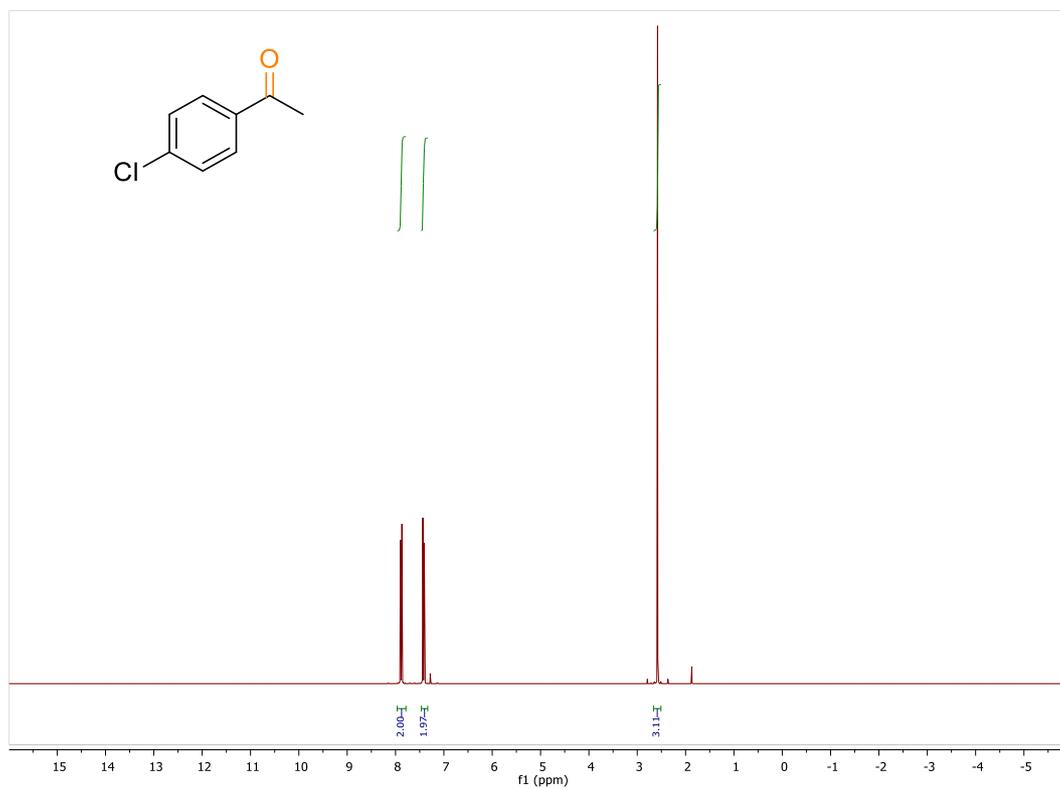


^1H NMR spectrum in CDCl_3

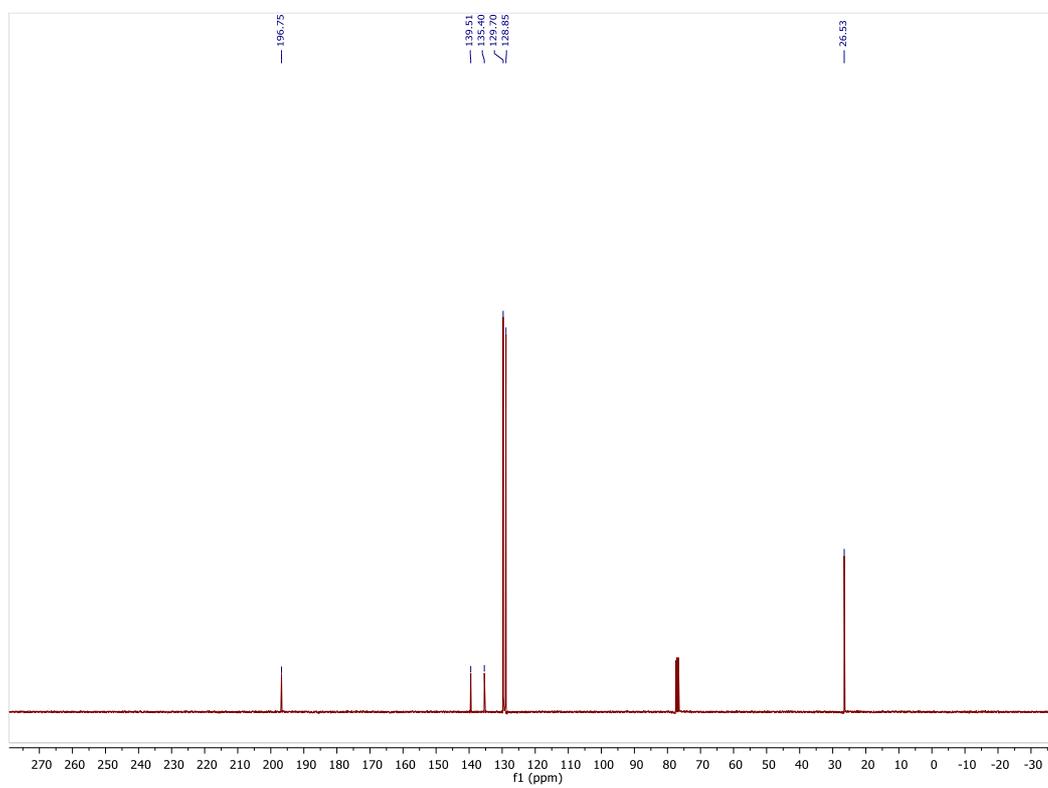


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3b

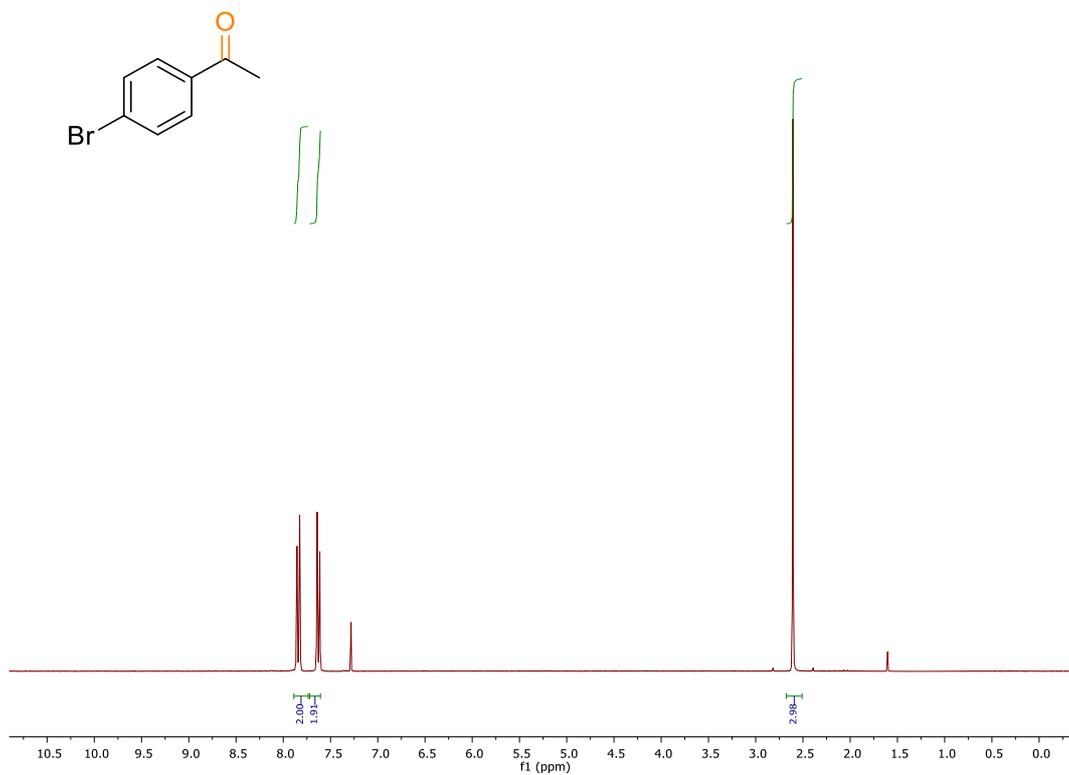


^1H NMR spectrum in CDCl_3 .

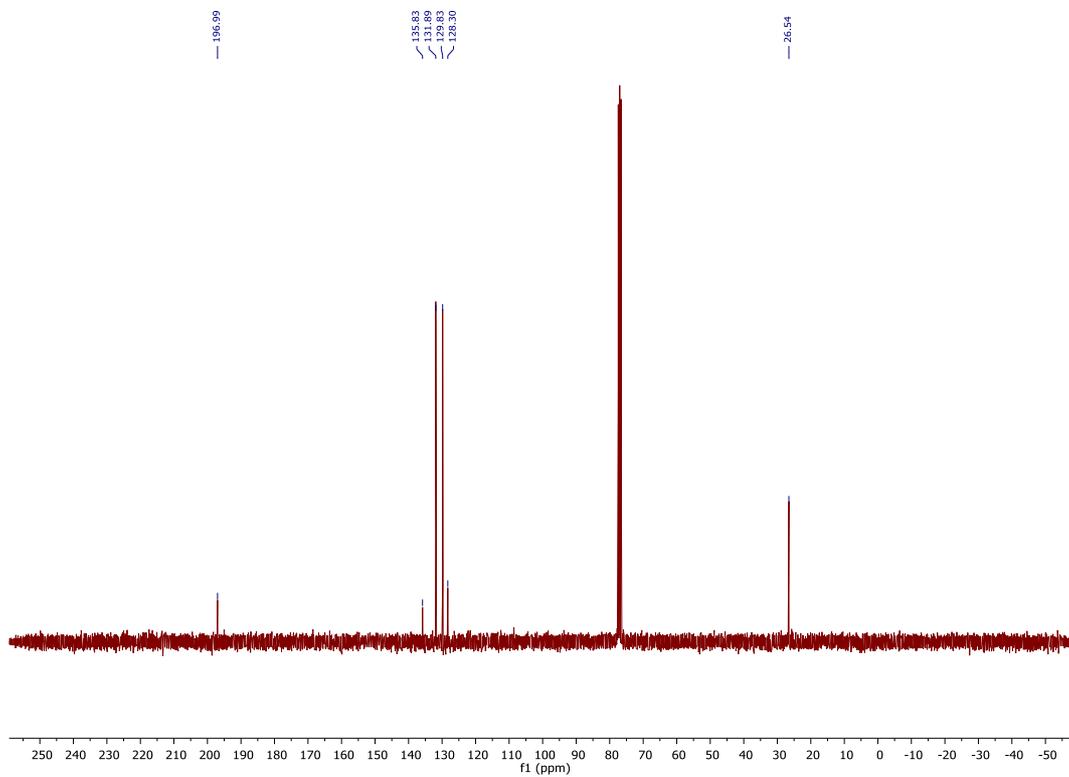


^{13}C NMR spectrum in CDCl_3 .

4b

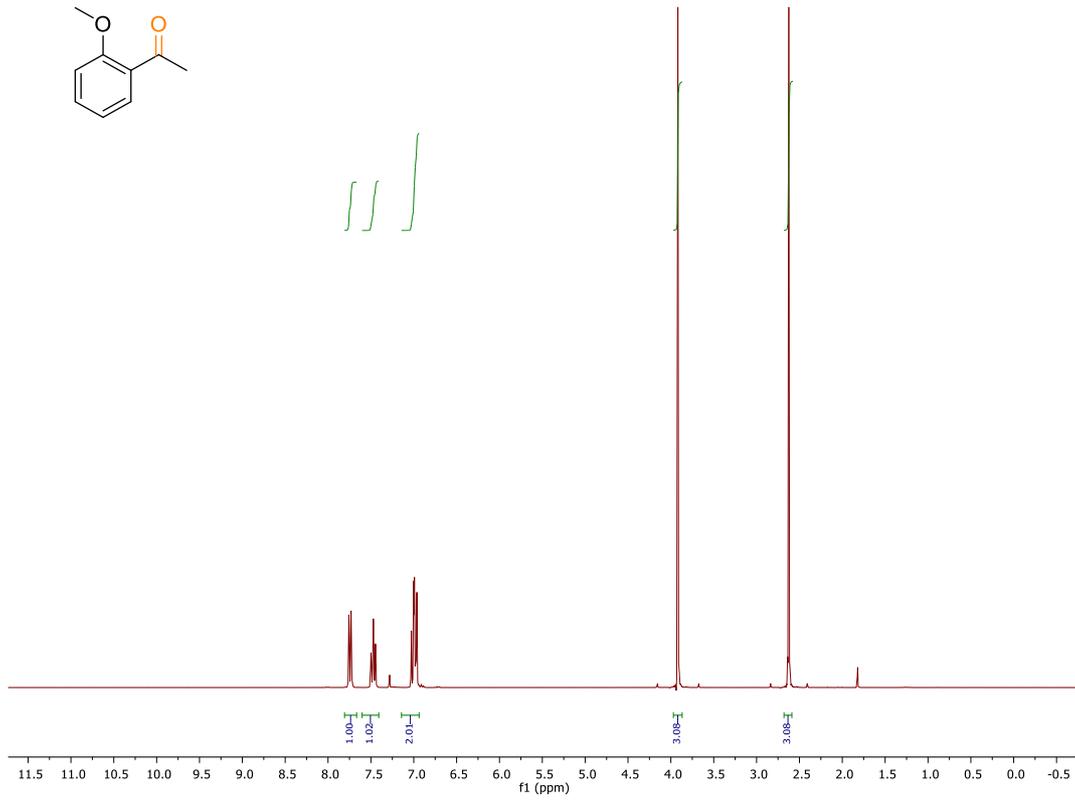
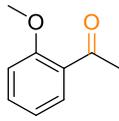


¹H NMR spectrum in CDCl₃.

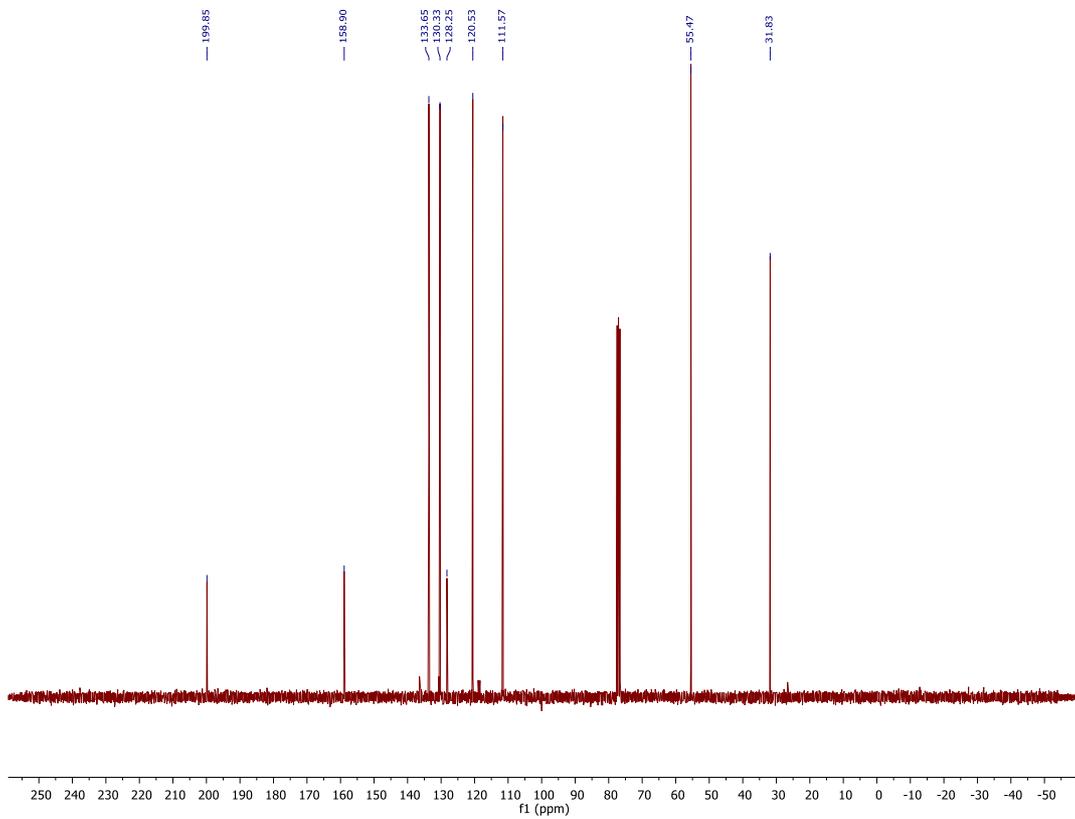


¹³C NMR spectrum in CDCl₃.

5b

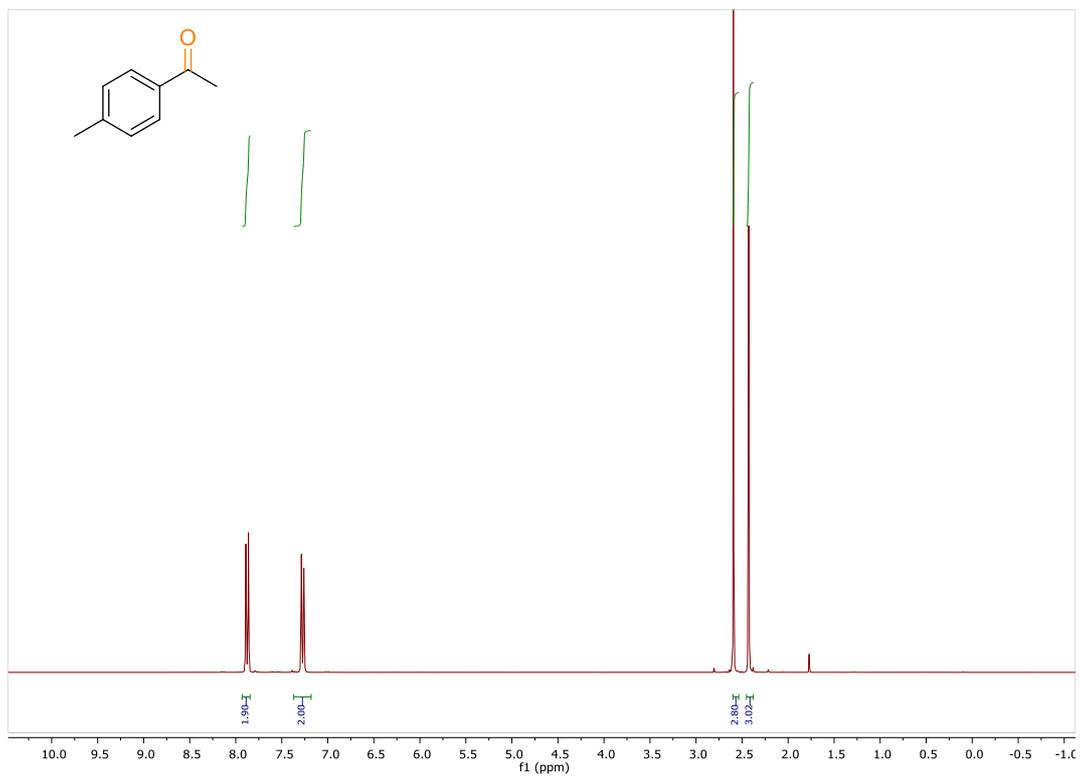


¹H NMR spectrum in CDCl₃.

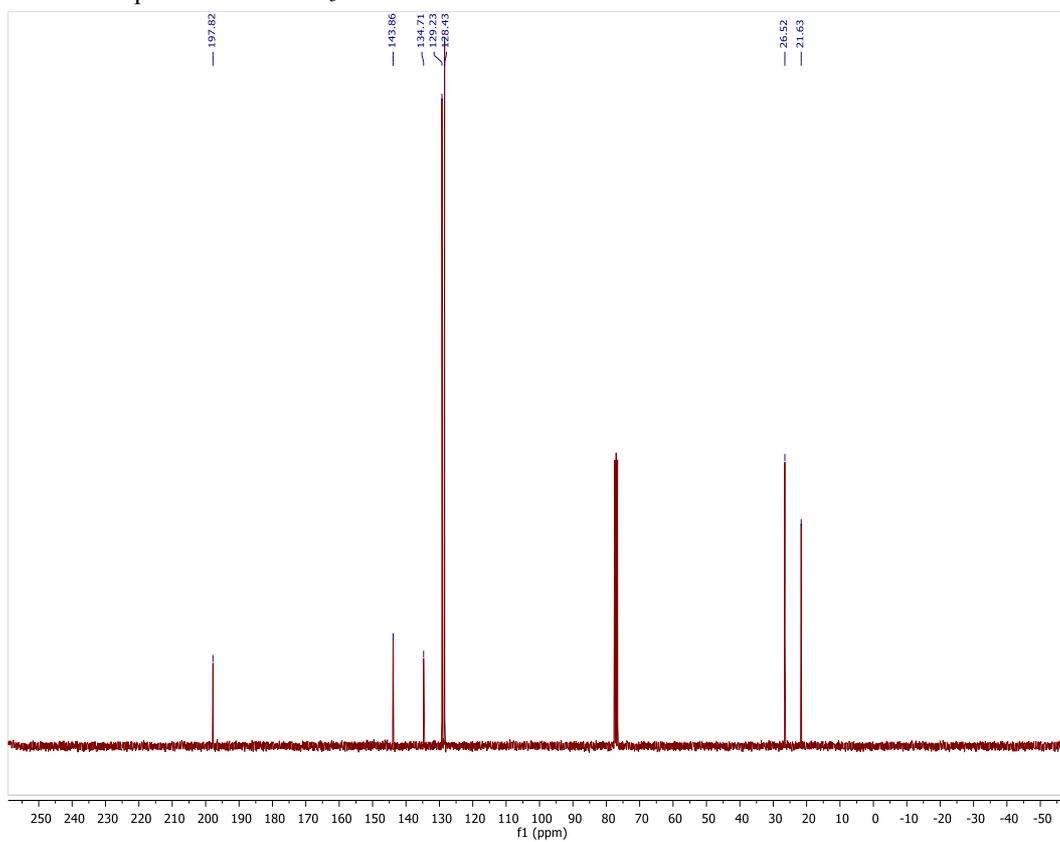


¹³C NMR spectrum in CDCl₃.

6b

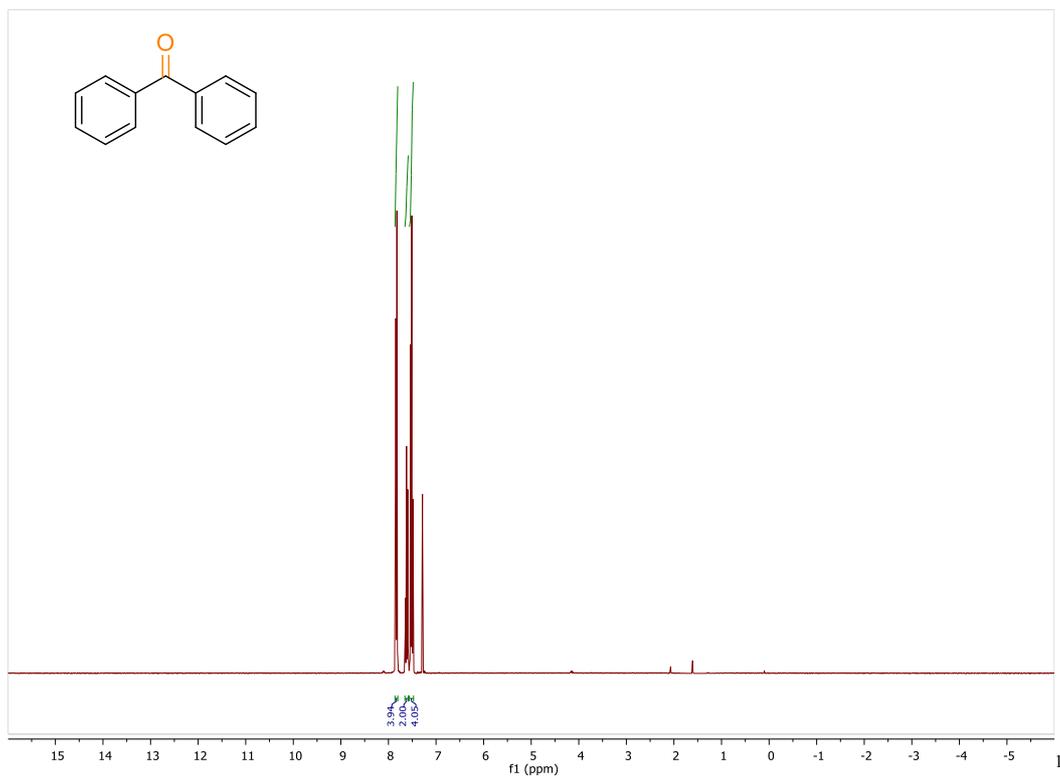


¹³C NMR spectrum in CDCl₃.

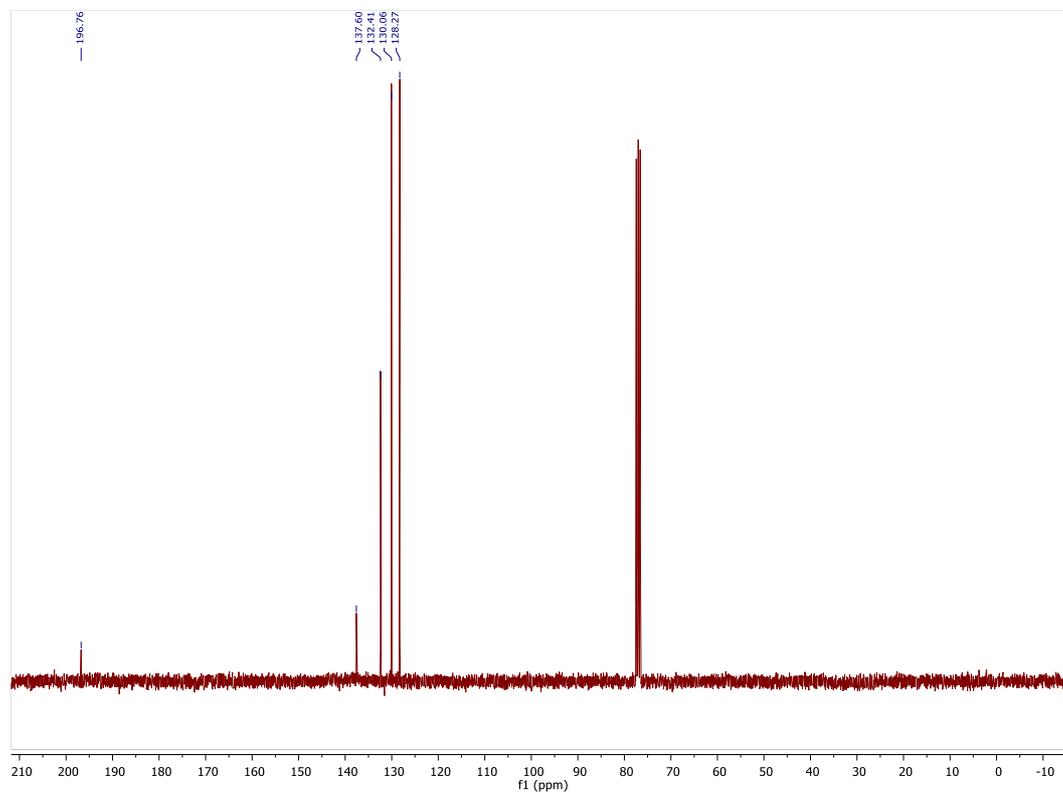


¹H NMR spectrum in CDCl₃.

7b

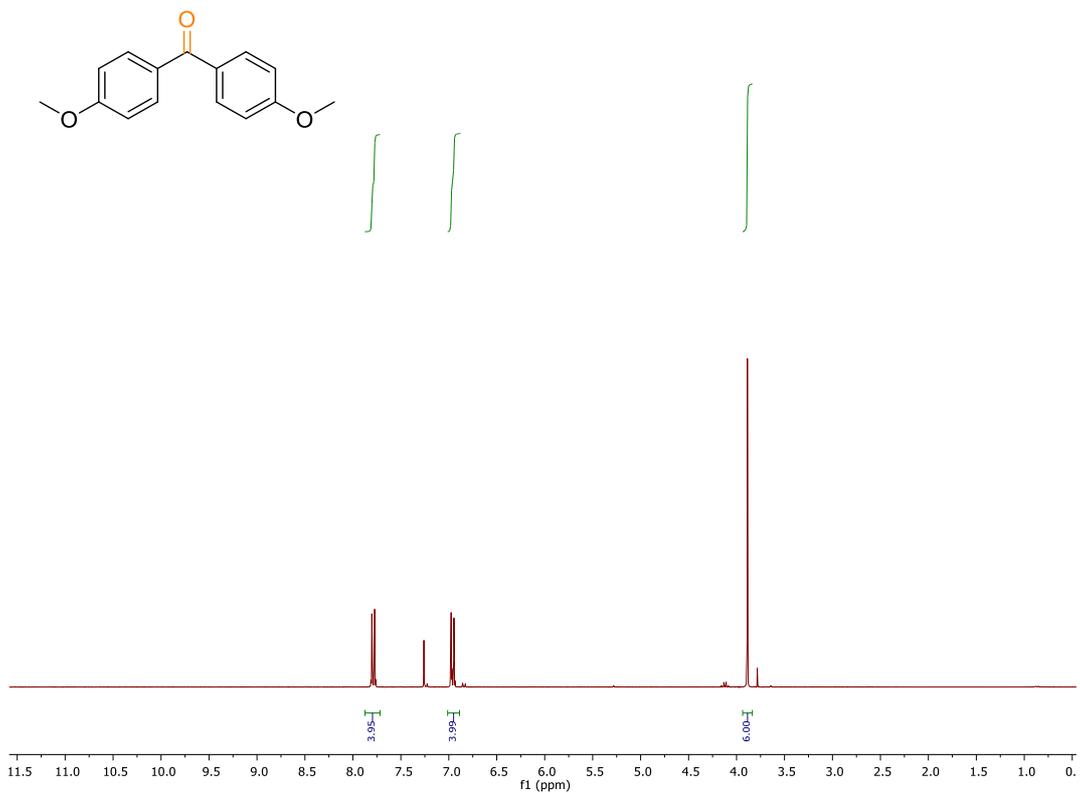


¹H NMR spectrum in CDCl₃

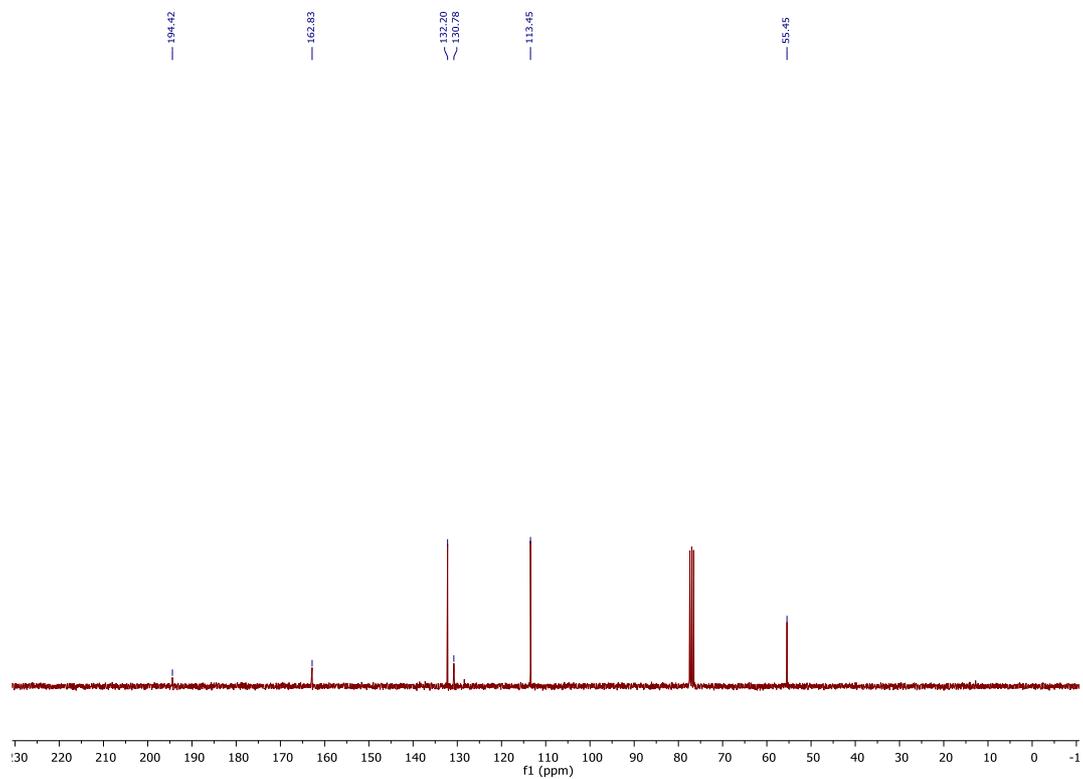


¹³C NMR spectrum in CDCl₃.

8b

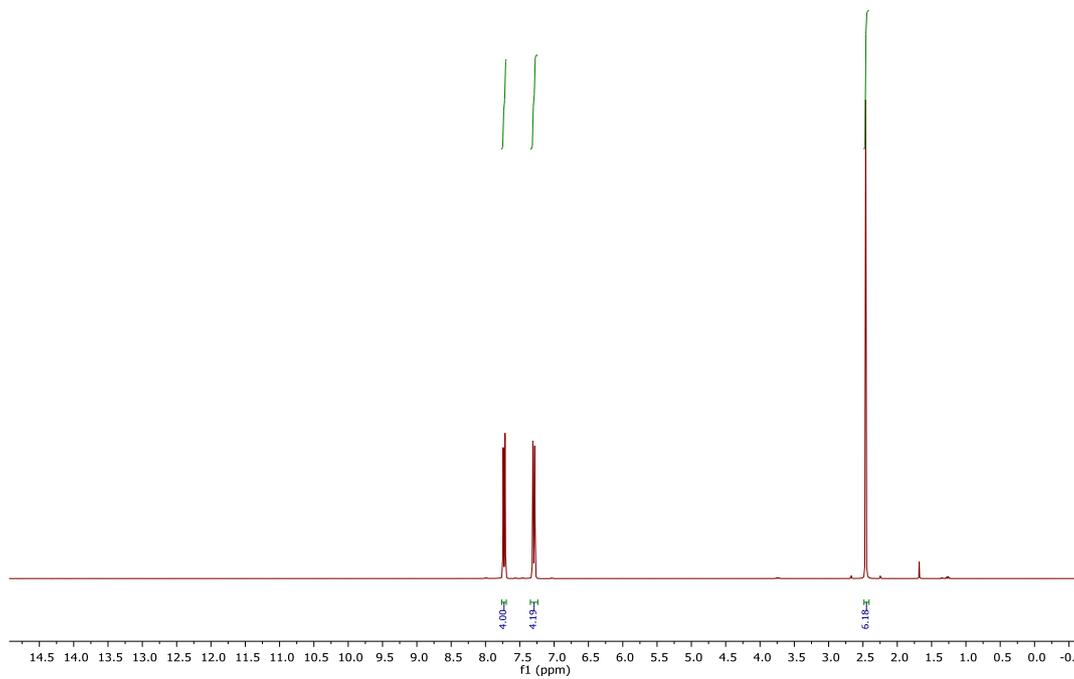
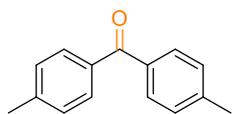


¹H NMR spectrum in CDCl₃.

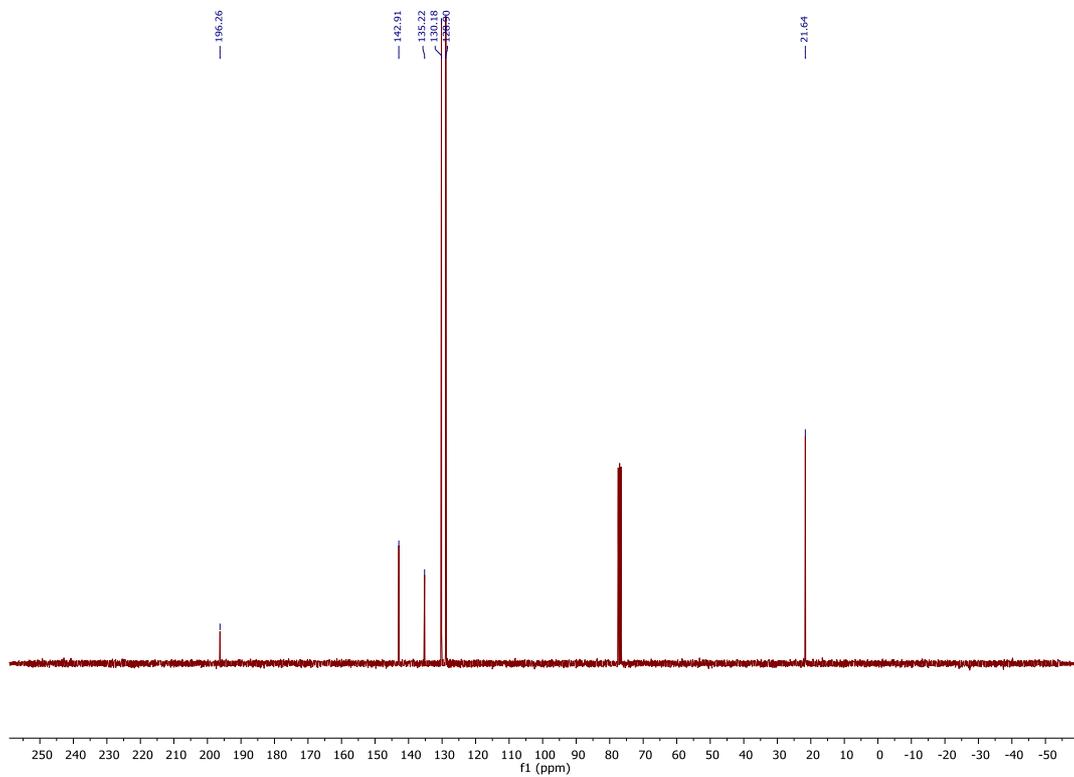


¹³C NMR spectrum in CDCl₃.

9b

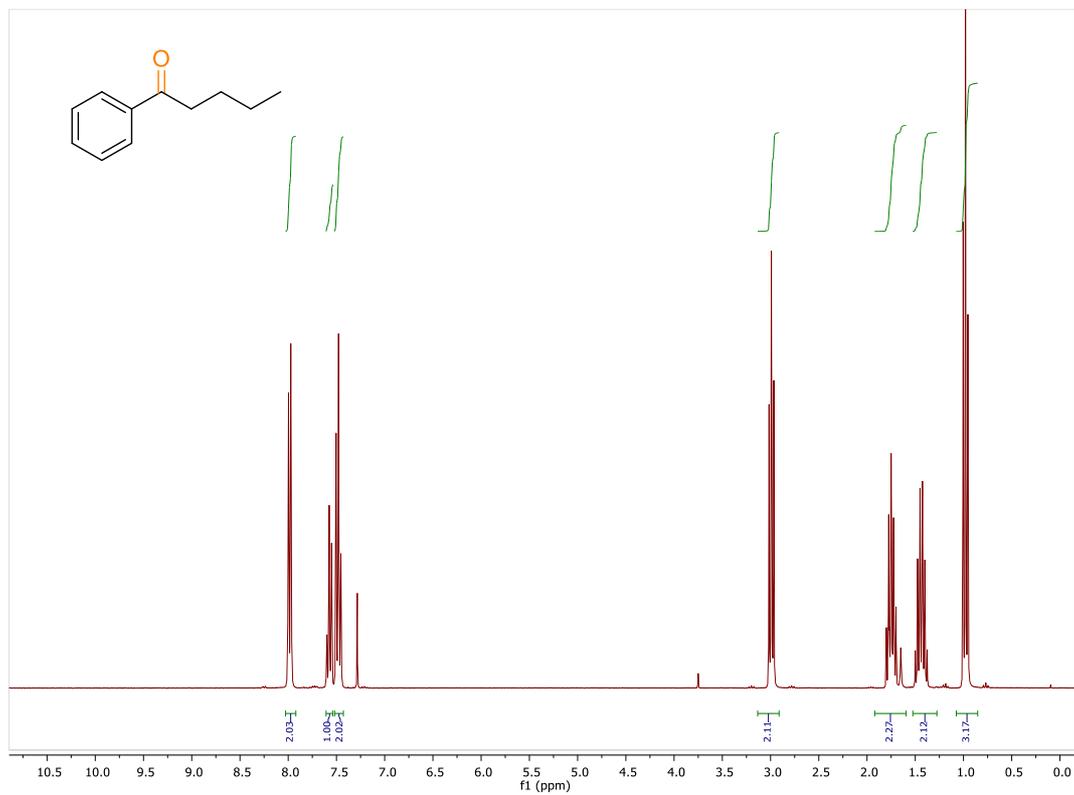


^1H NMR spectrum in CDCl_3 .

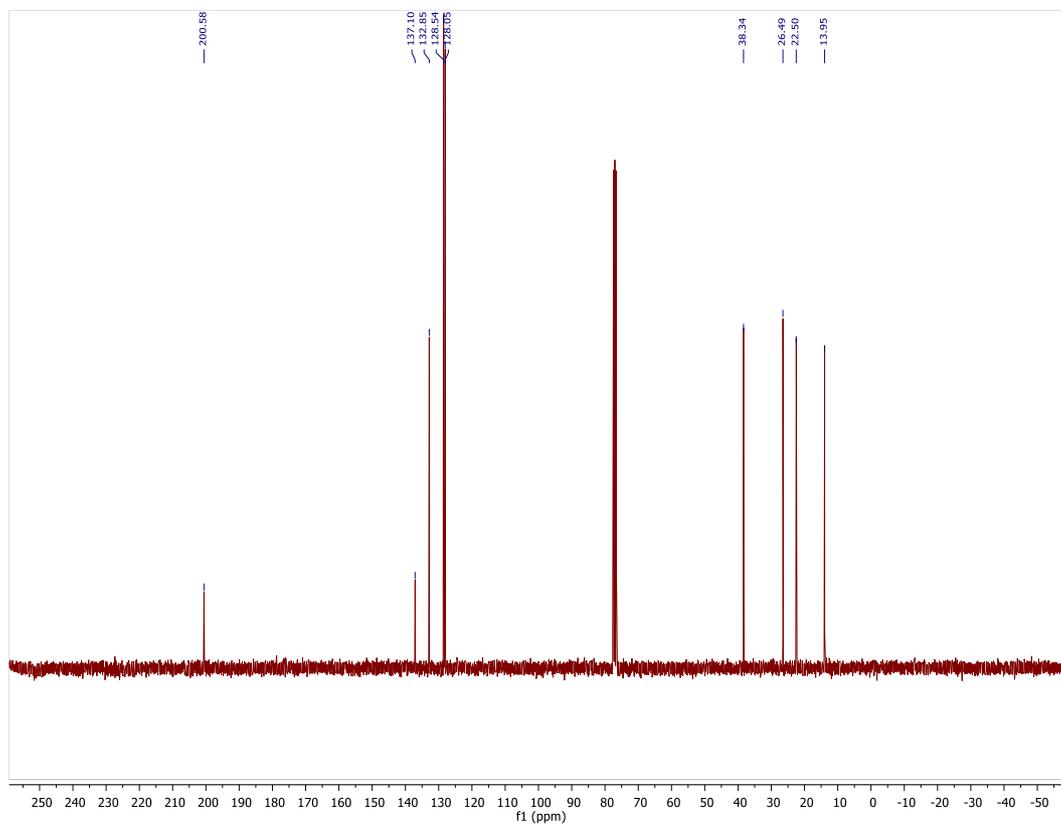


^{13}C NMR spectrum in CDCl_3 .

10b

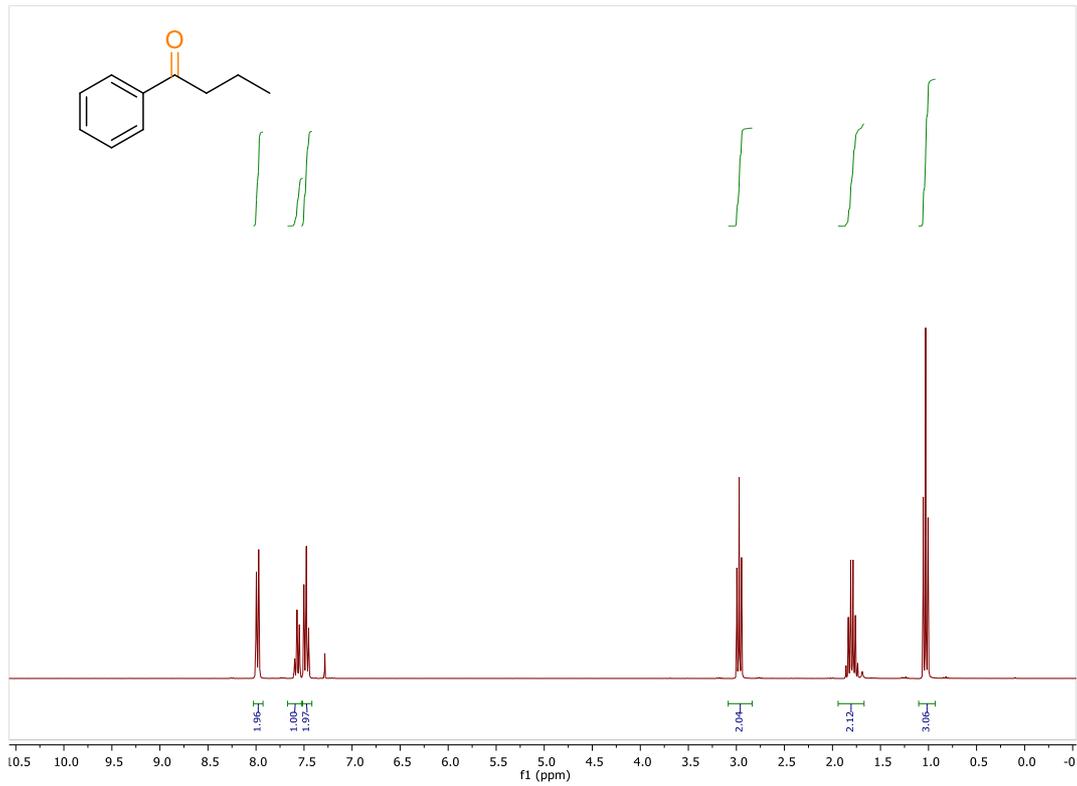


¹H NMR spectrum in CDCl₃.

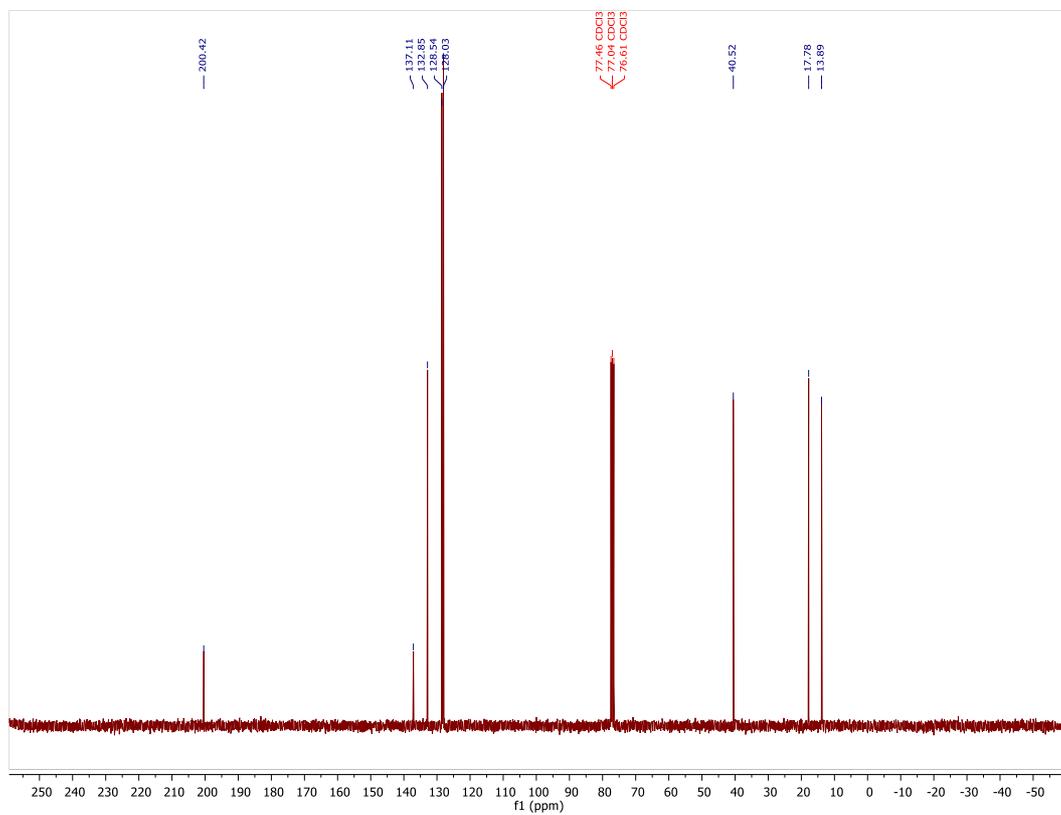


¹³C NMR spectrum in CDCl₃.

11b

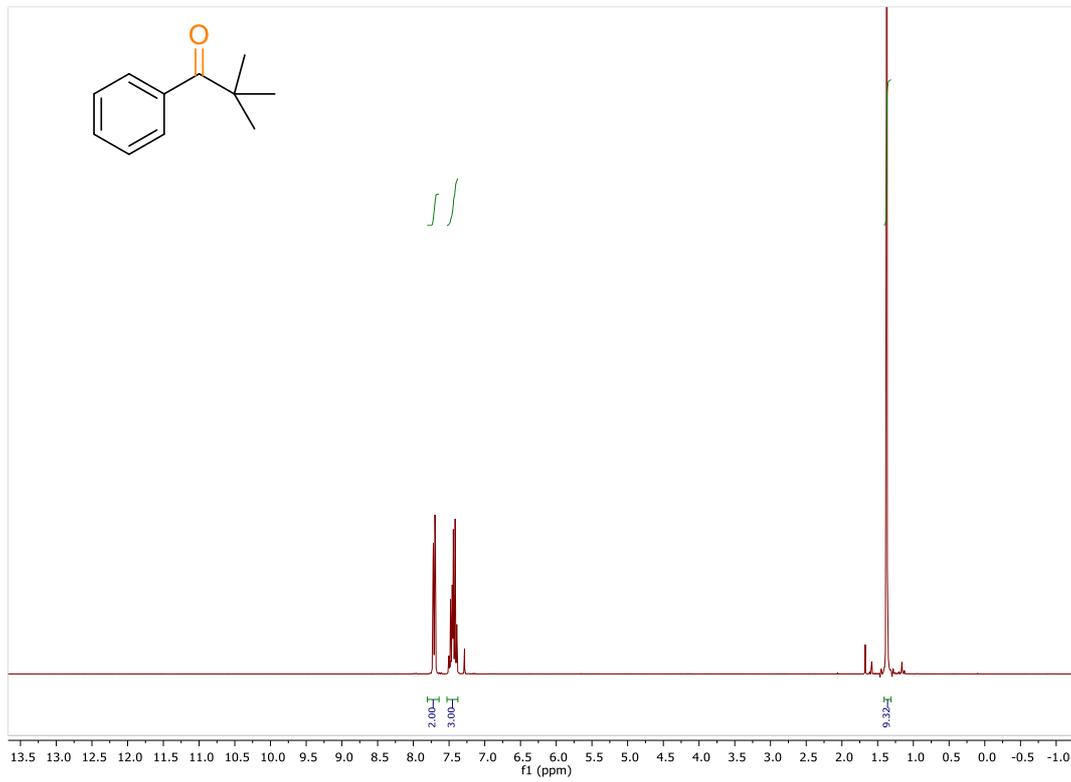


^1H NMR spectrum in CDCl_3 .

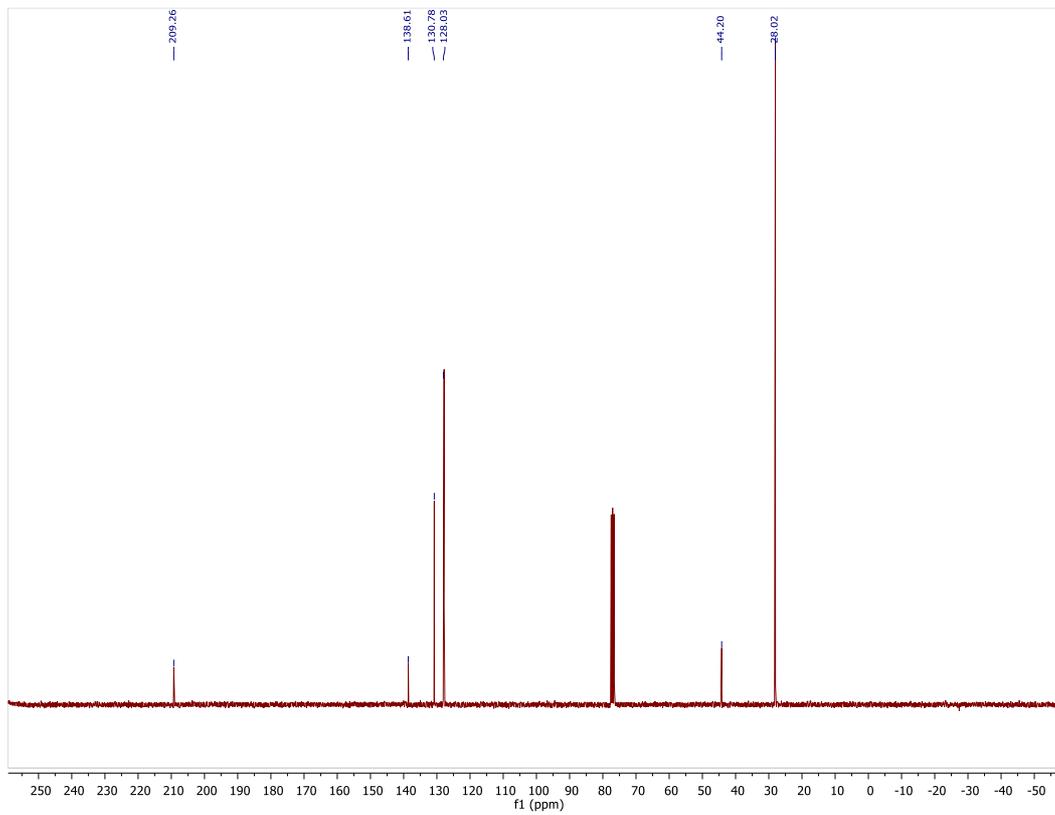


^{13}C NMR spectrum in CDCl_3 .

12b

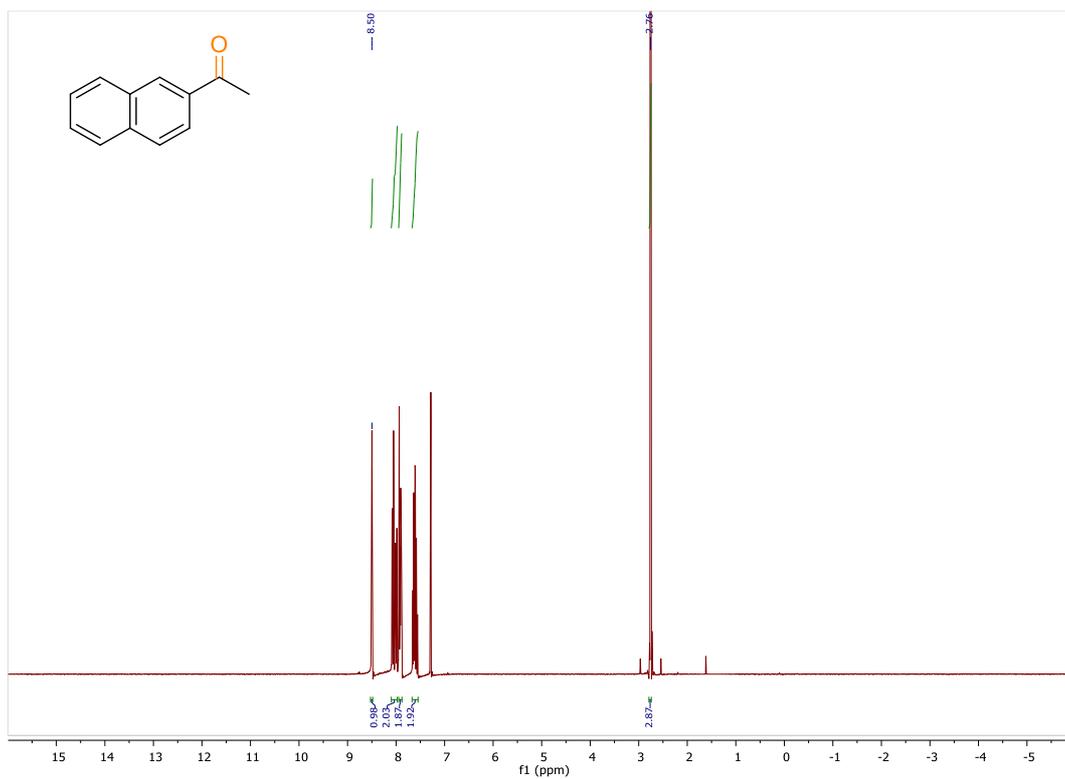


¹H NMR spectrum in CDCl₃.

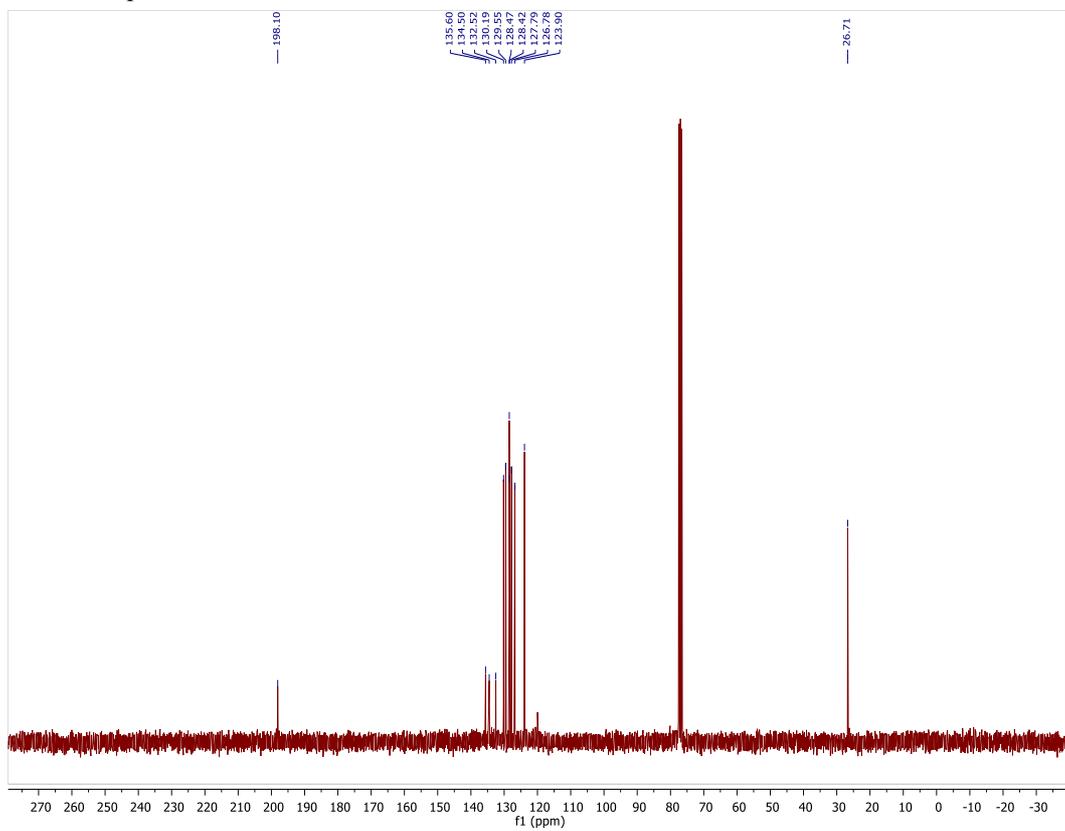


¹³C NMR spectrum in CDCl₃.

13b

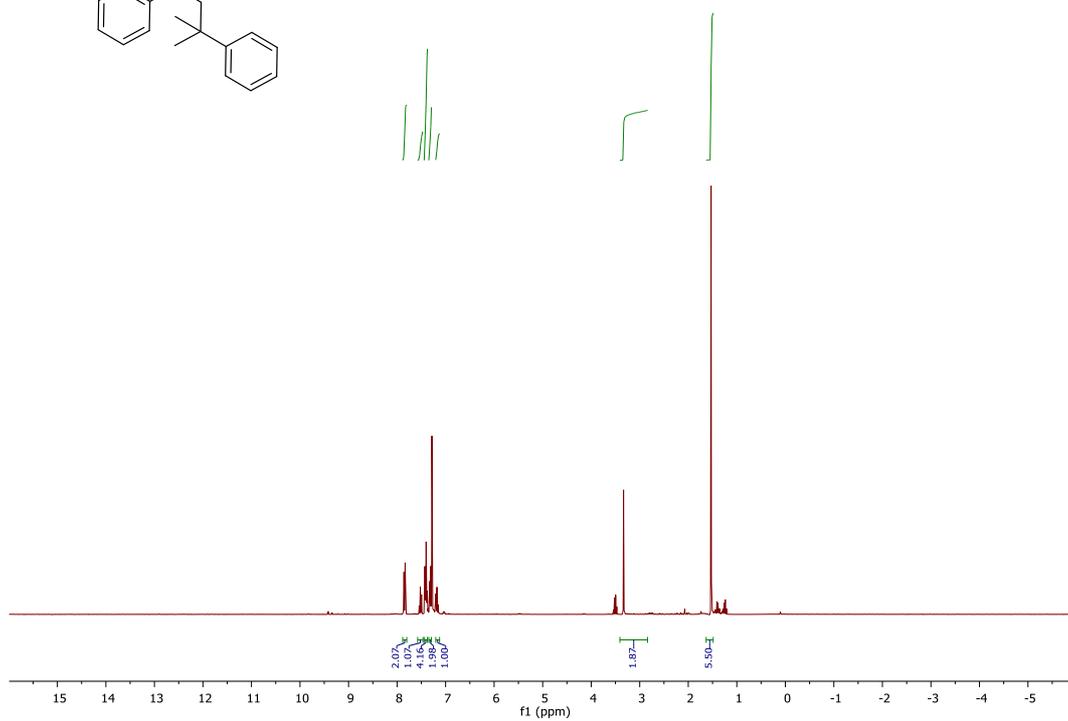
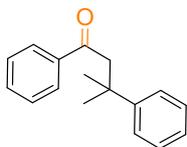


¹H NMR spectrum in CDCl₃.

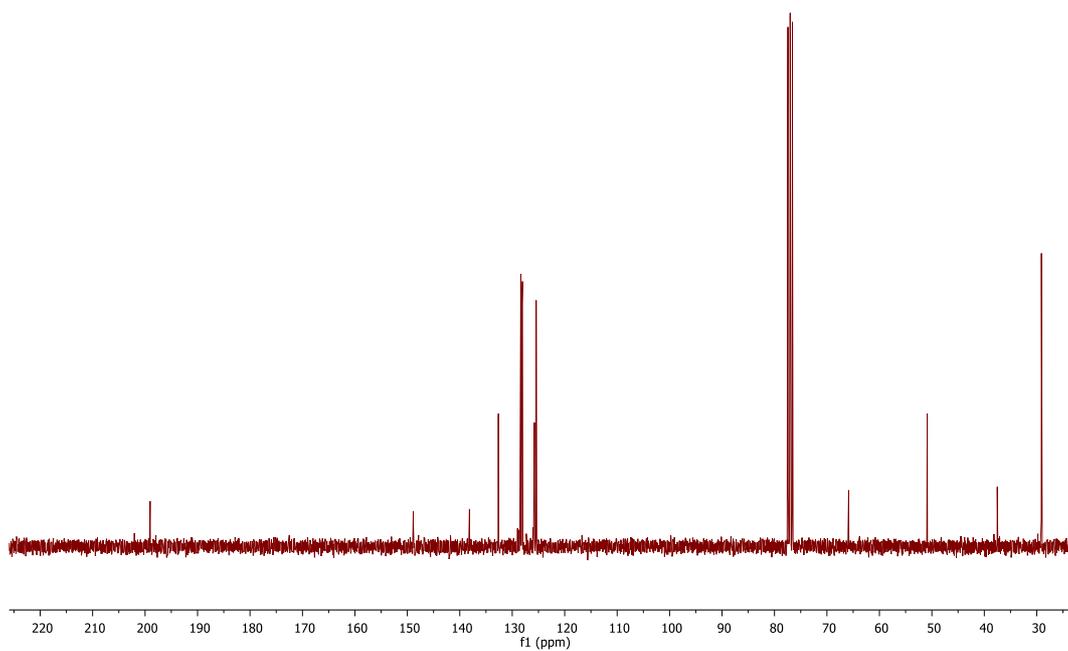


¹³C NMR spectrum in CDCl₃.

14b

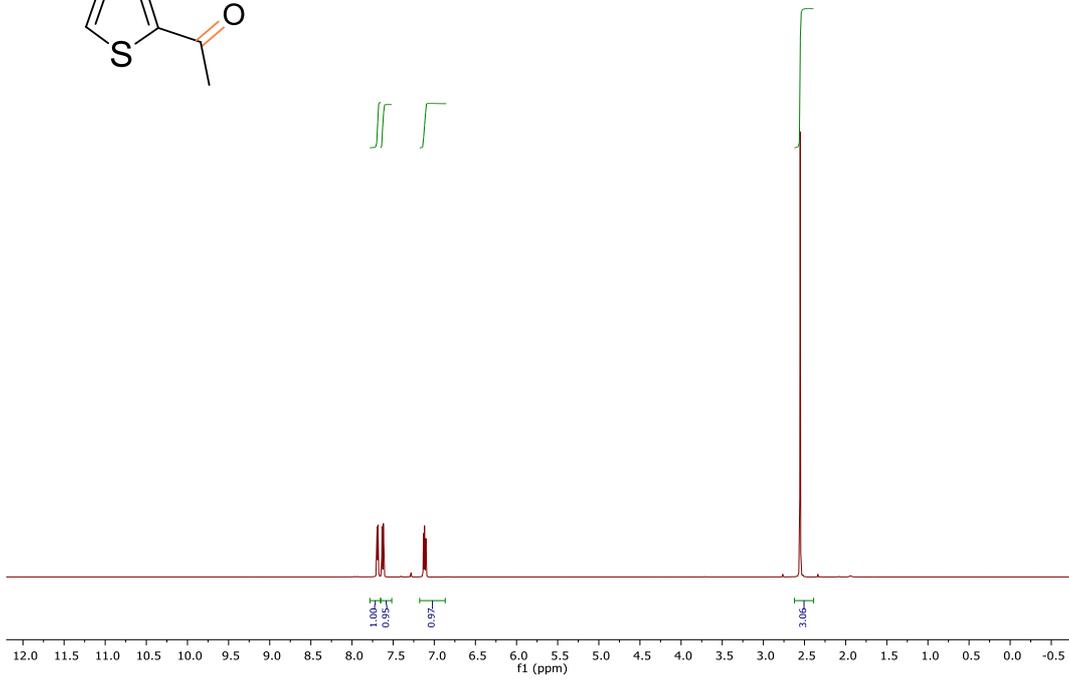
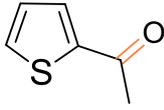


^1H NMR spectrum in $\text{DMSO}-d_6$.

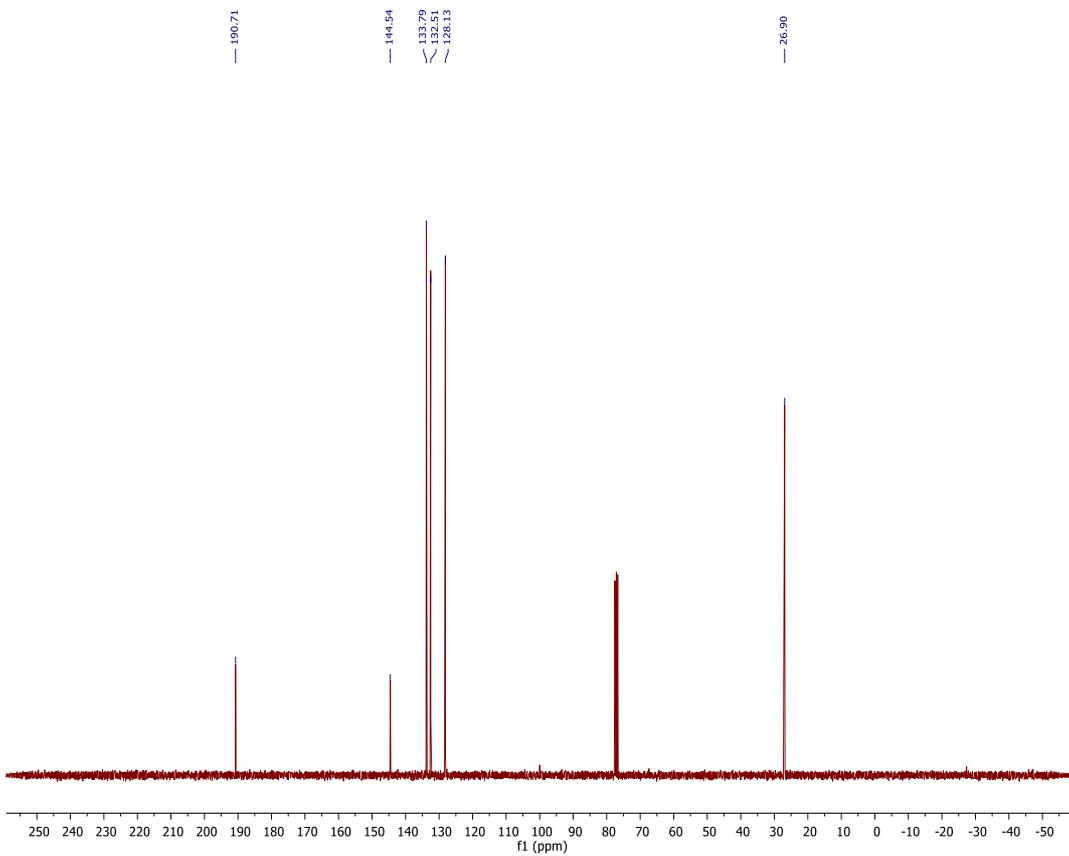


^{13}C NMR spectrum in $\text{DMSO}-d_6$.

15b

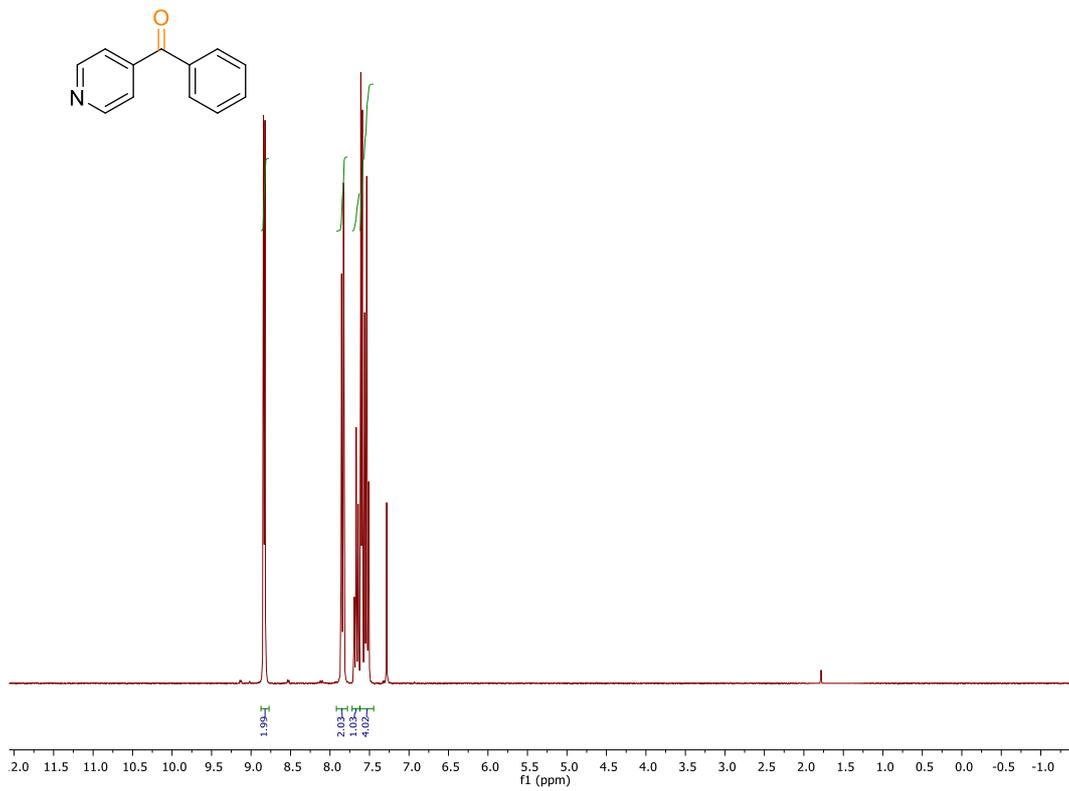


^1H NMR spectrum in CDCl_3 .

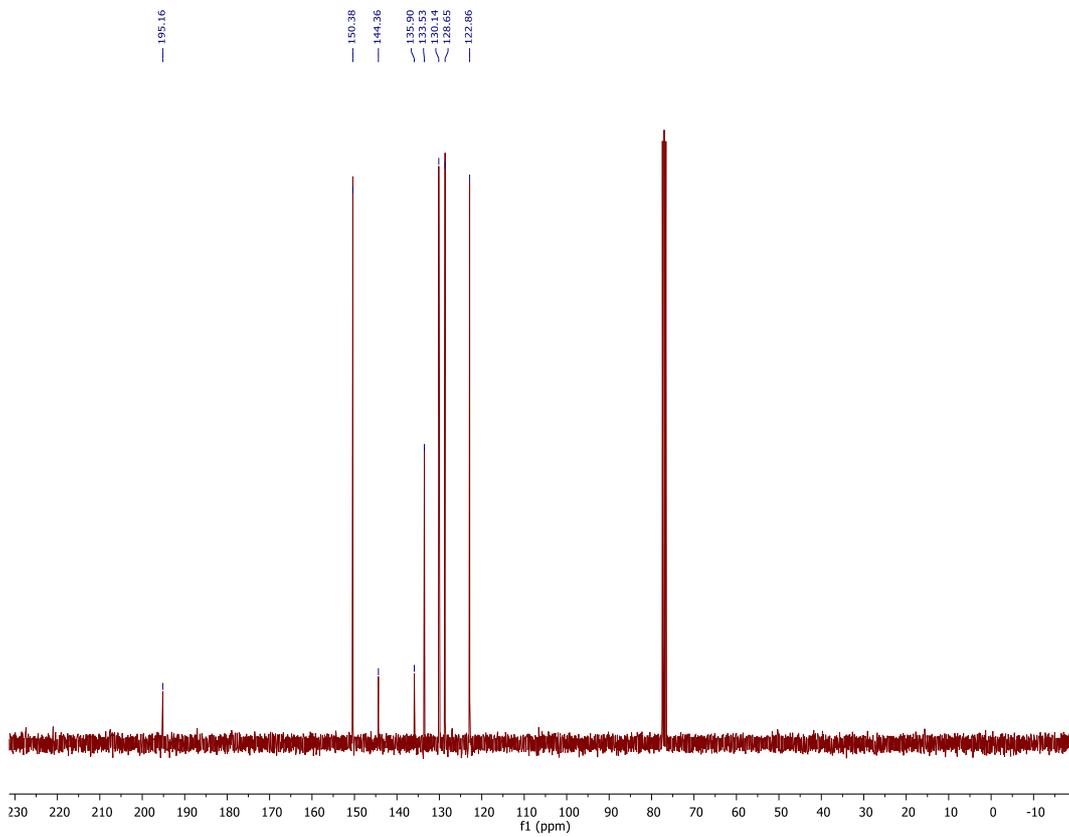


^{13}C NMR spectrum in CDCl_3 .

16b

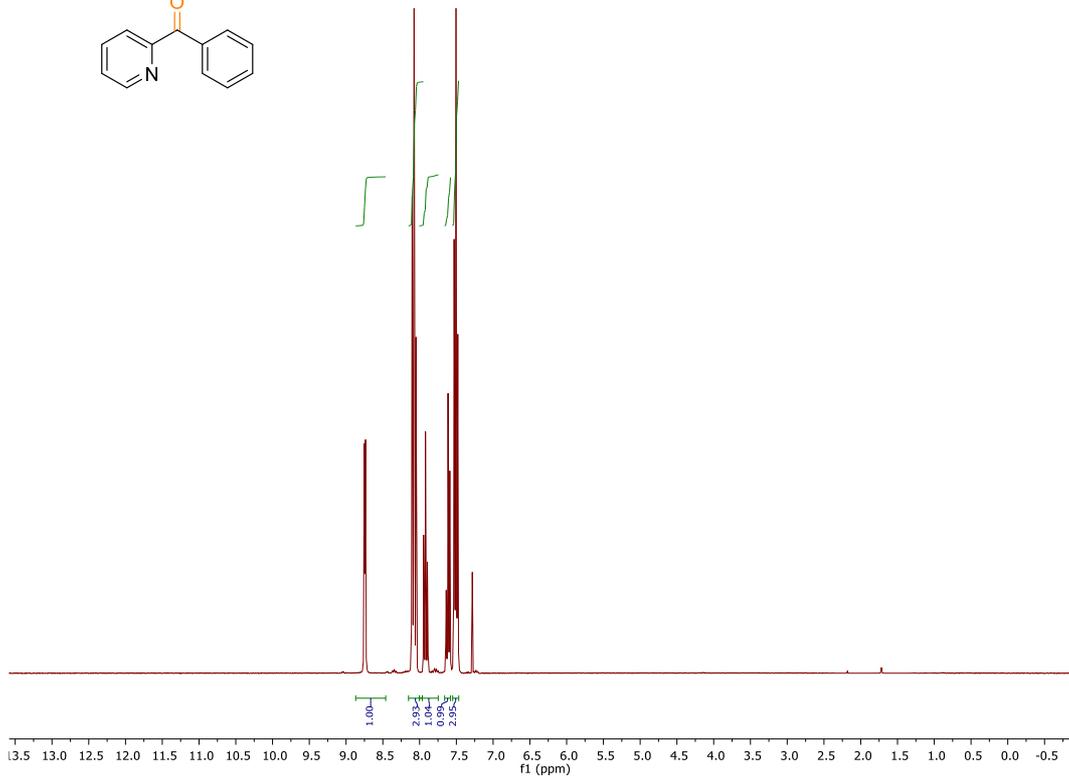
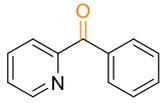


¹H NMR spectrum in CDCl₃.

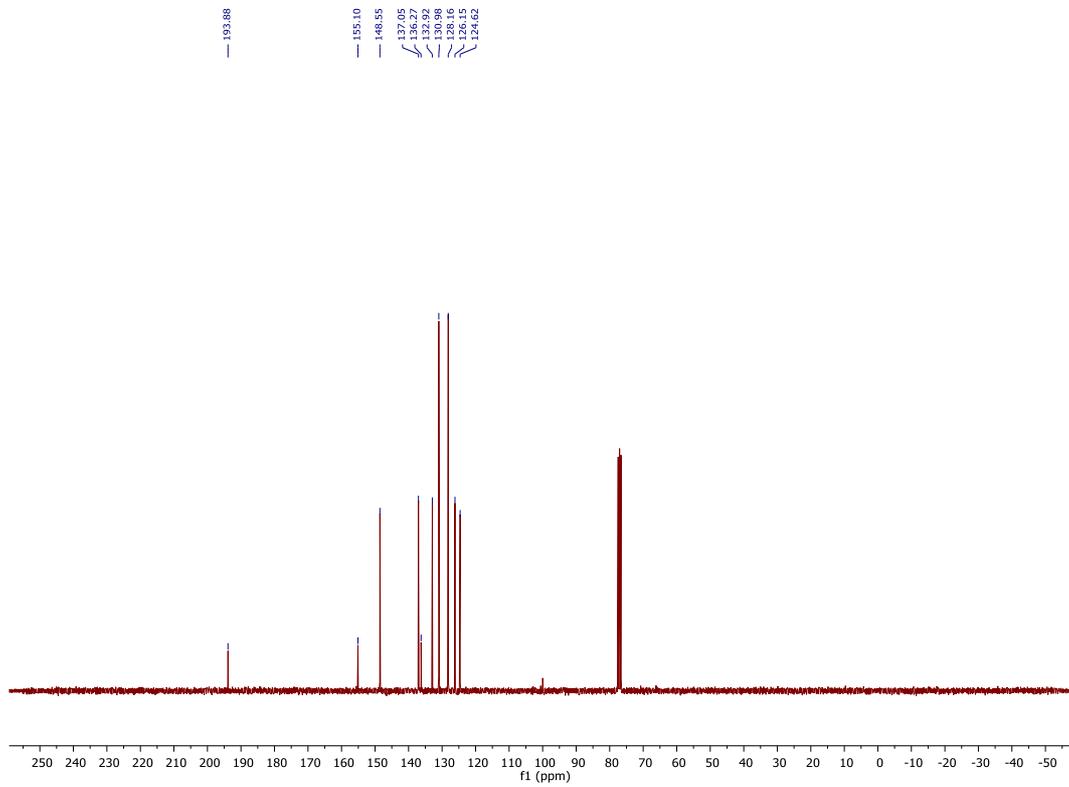


¹³C NMR spectrum in CDCl₃.

17b

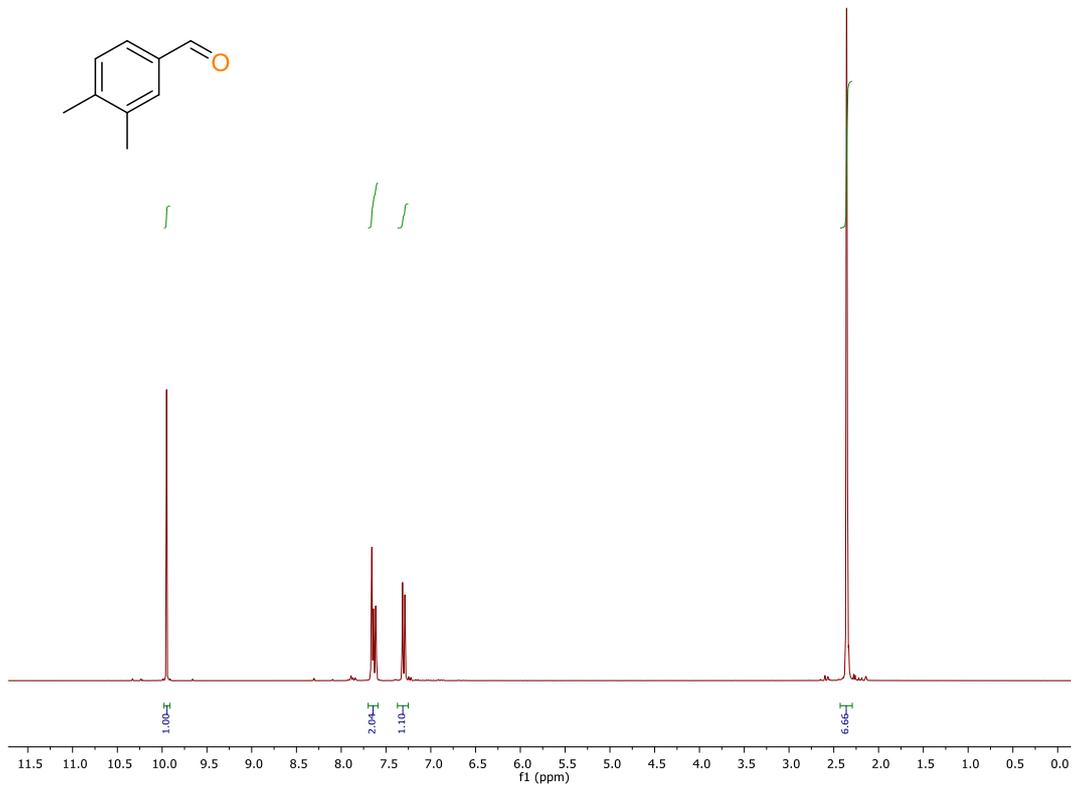
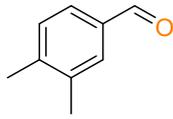


¹H NMR spectrum in CDCl₃.

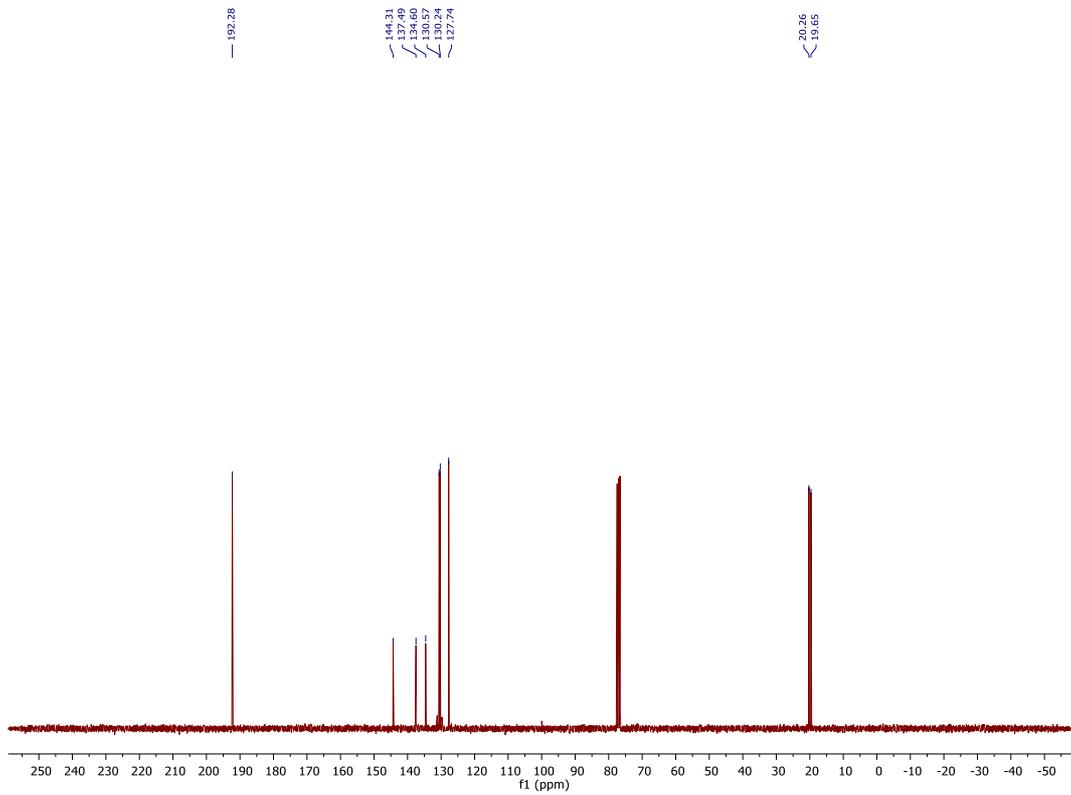


¹³C NMR spectrum in CDCl₃.

18b

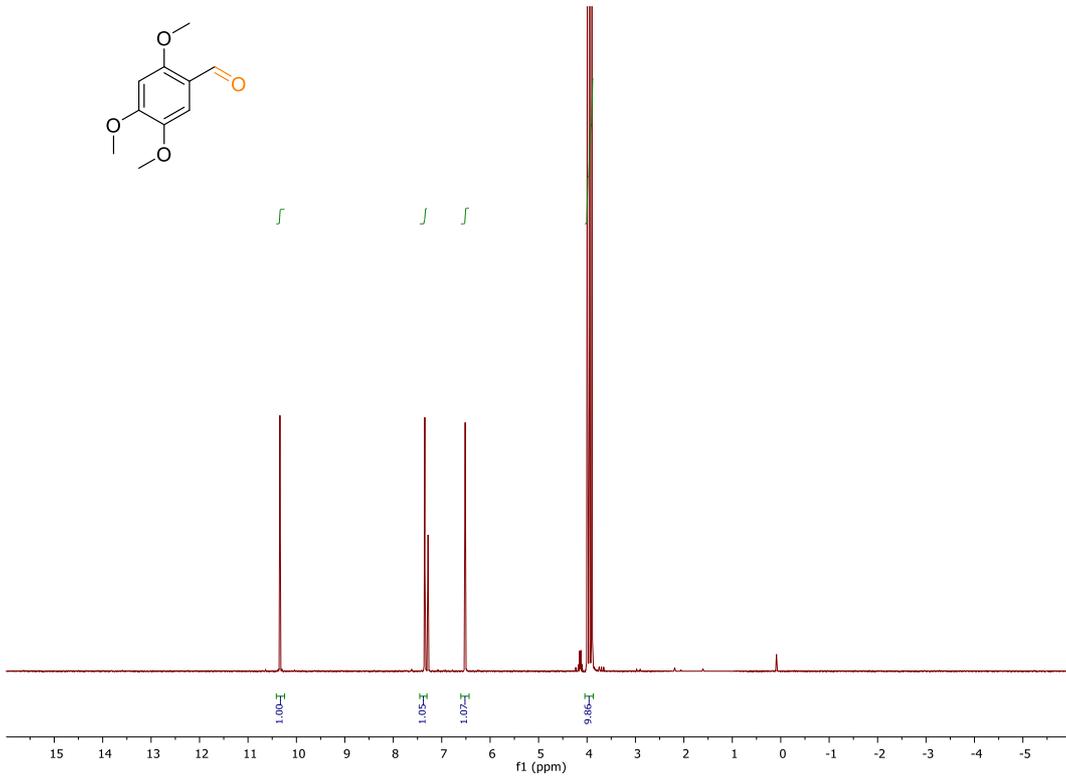
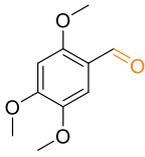


^1H NMR spectrum in CDCl_3 .

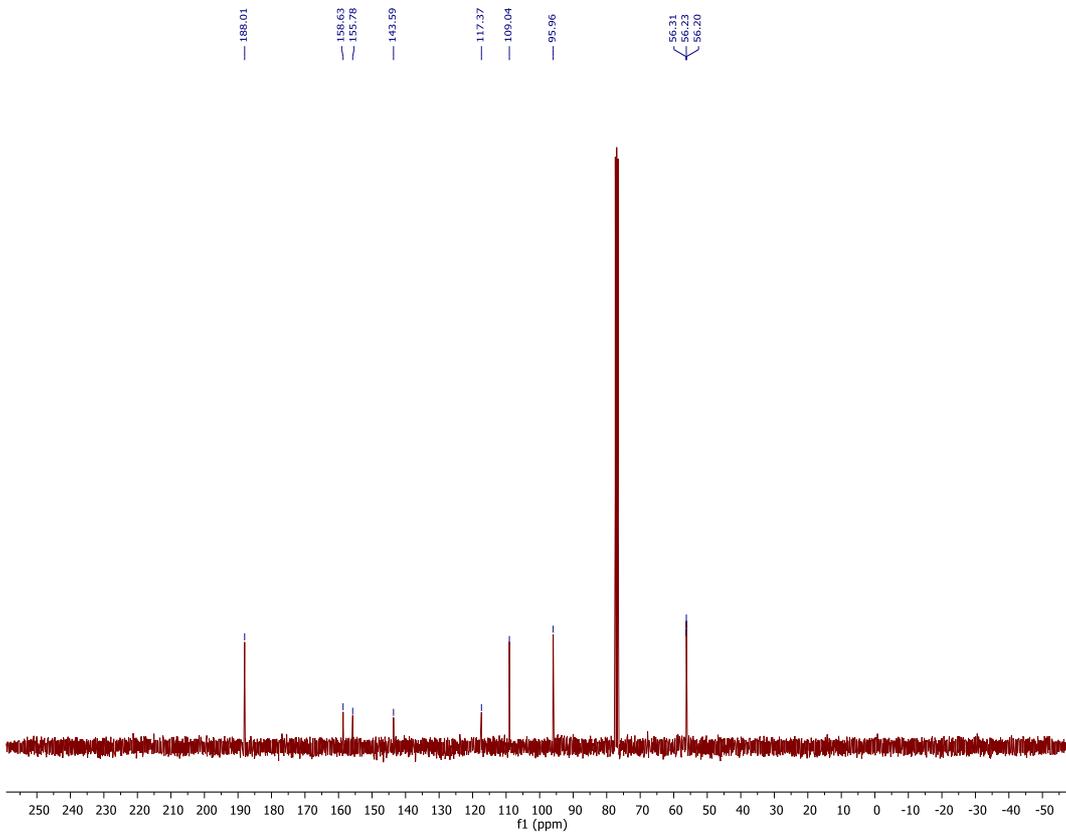


^{13}C NMR spectrum in CDCl_3 .

19b

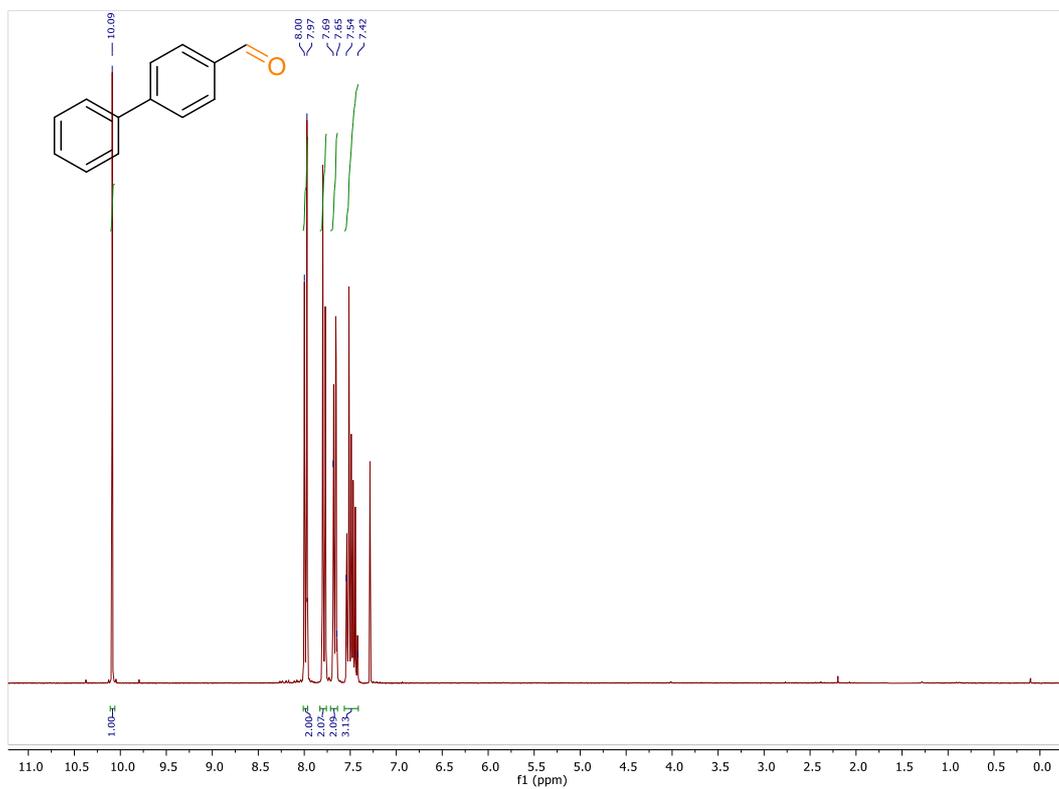


^1H NMR spectrum in CDCl_3 .

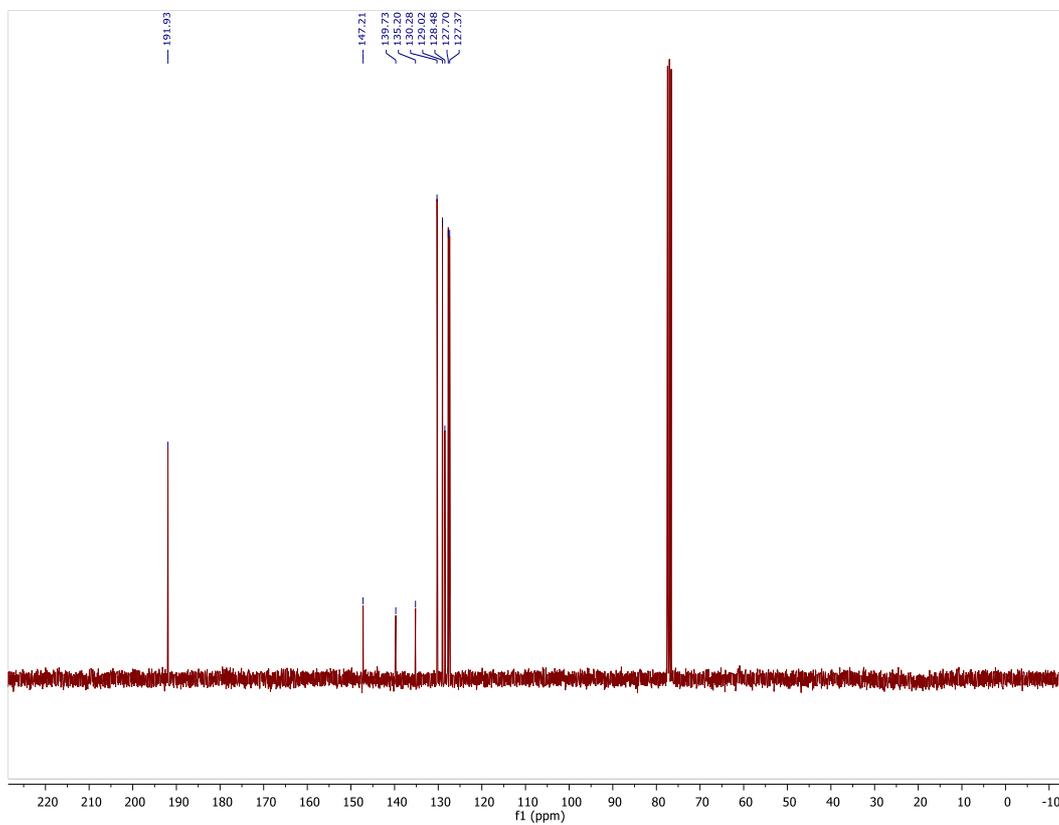


^{13}C NMR spectrum in CDCl_3 .

20b

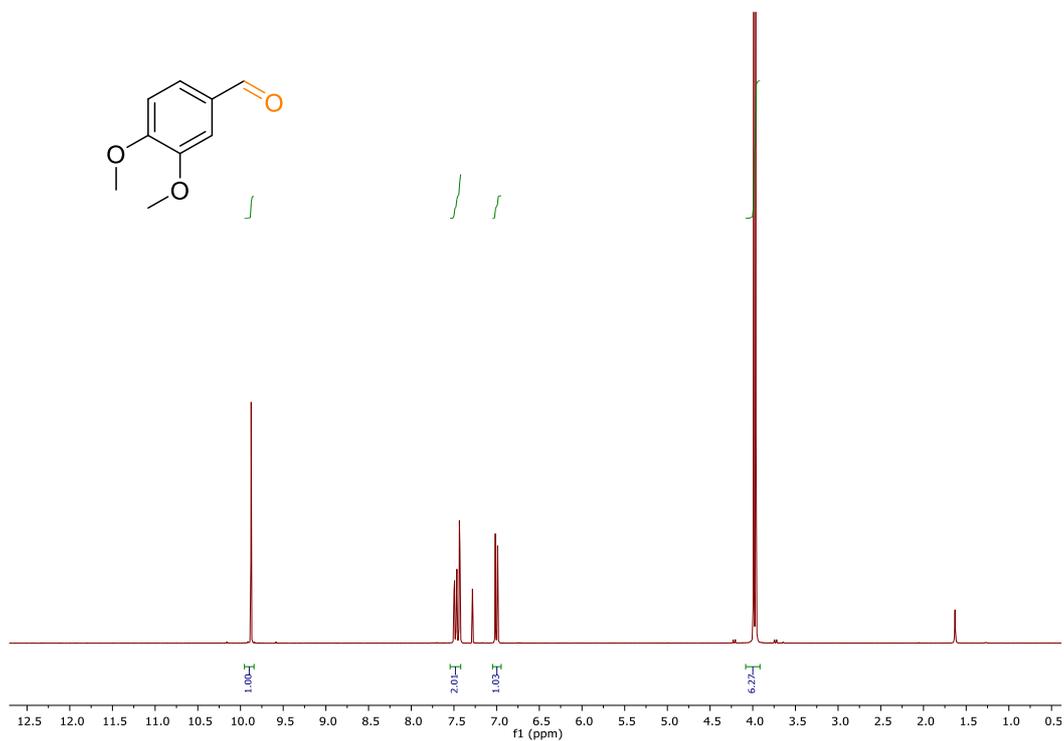


¹H NMR spectrum in CDCl₃.

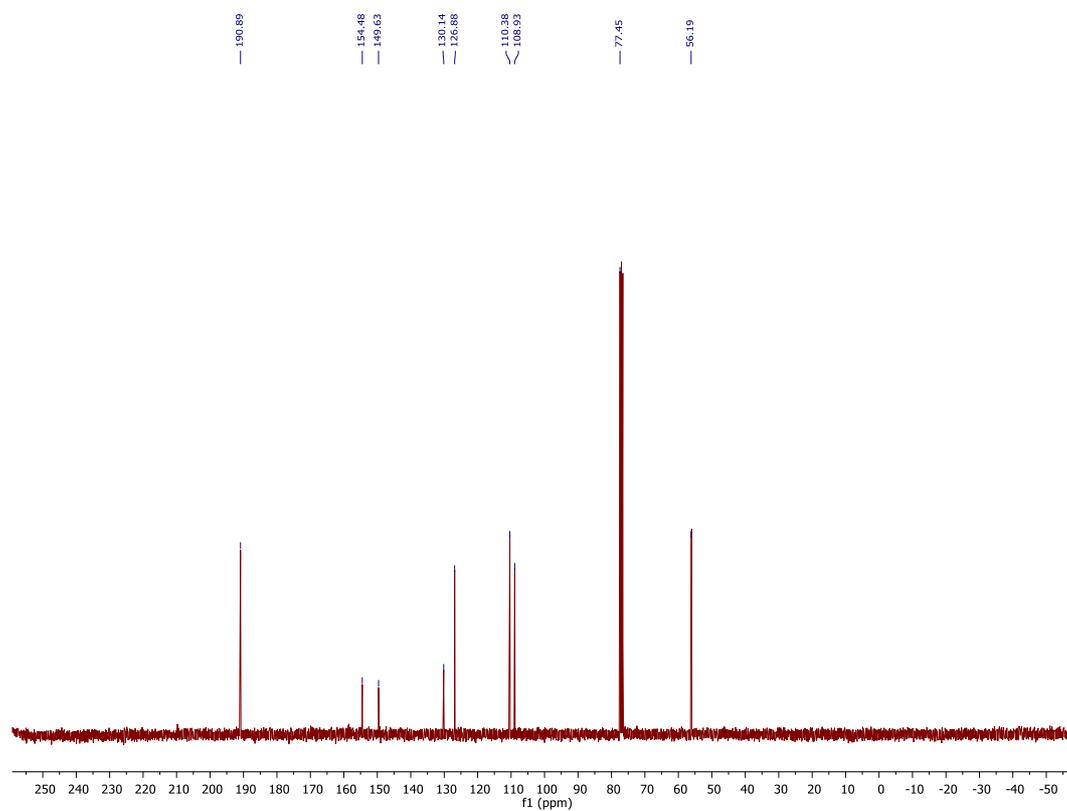


¹³C NMR spectrum in CDCl₃.

21b

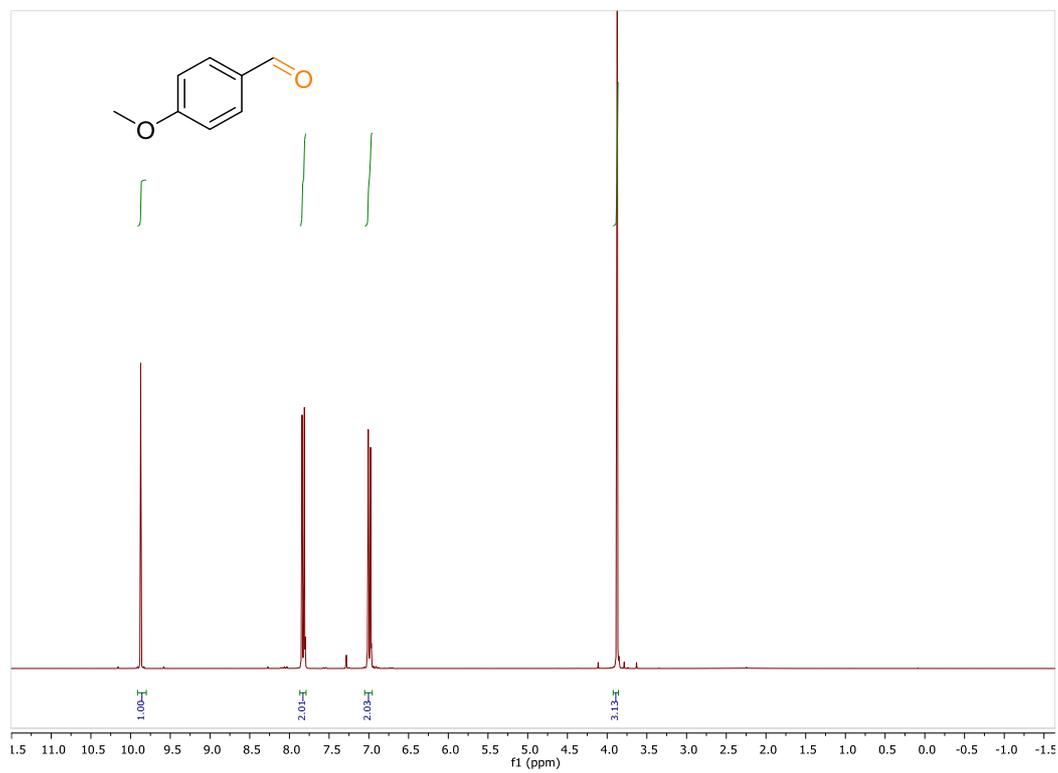


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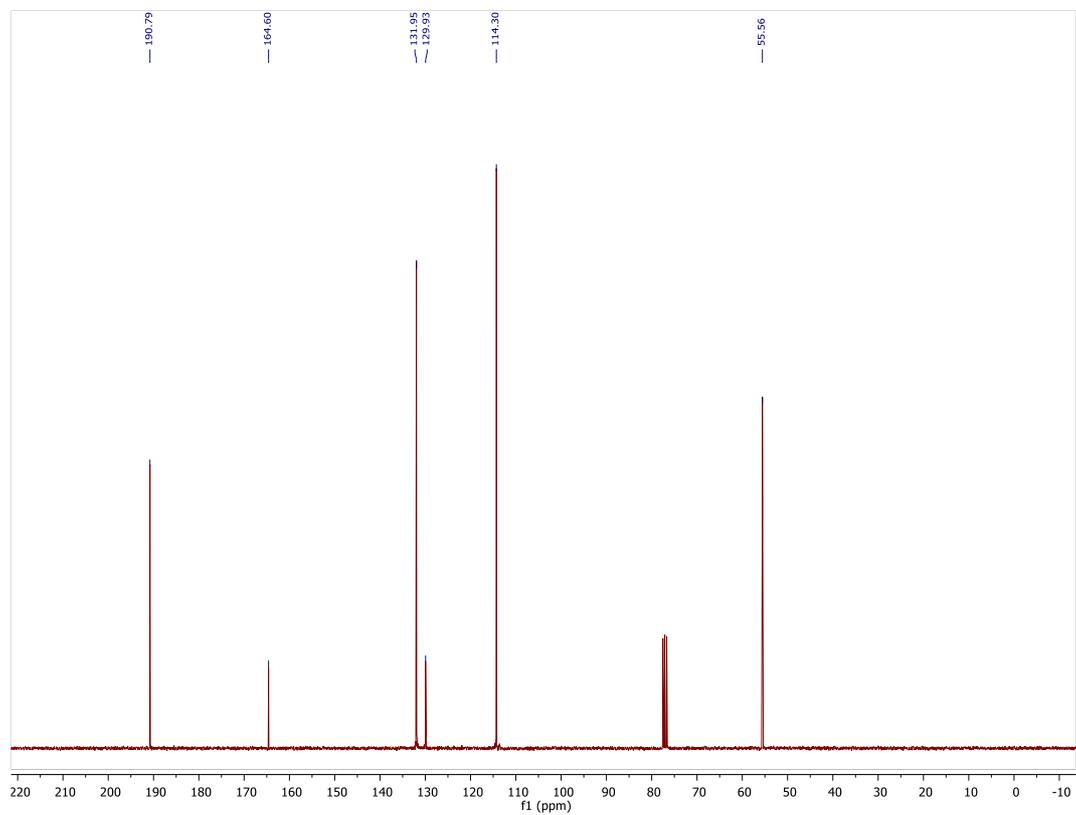


¹³C NMR spectrum in CDCl₃.

22b

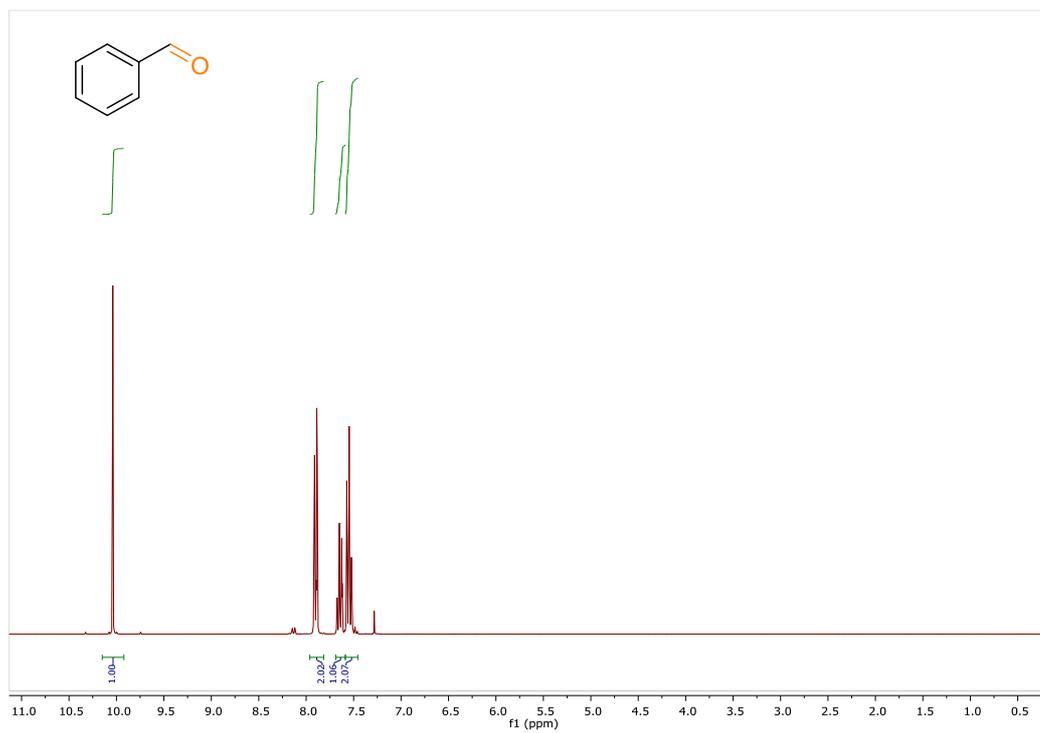


¹H NMR spectrum in CDCl₃.

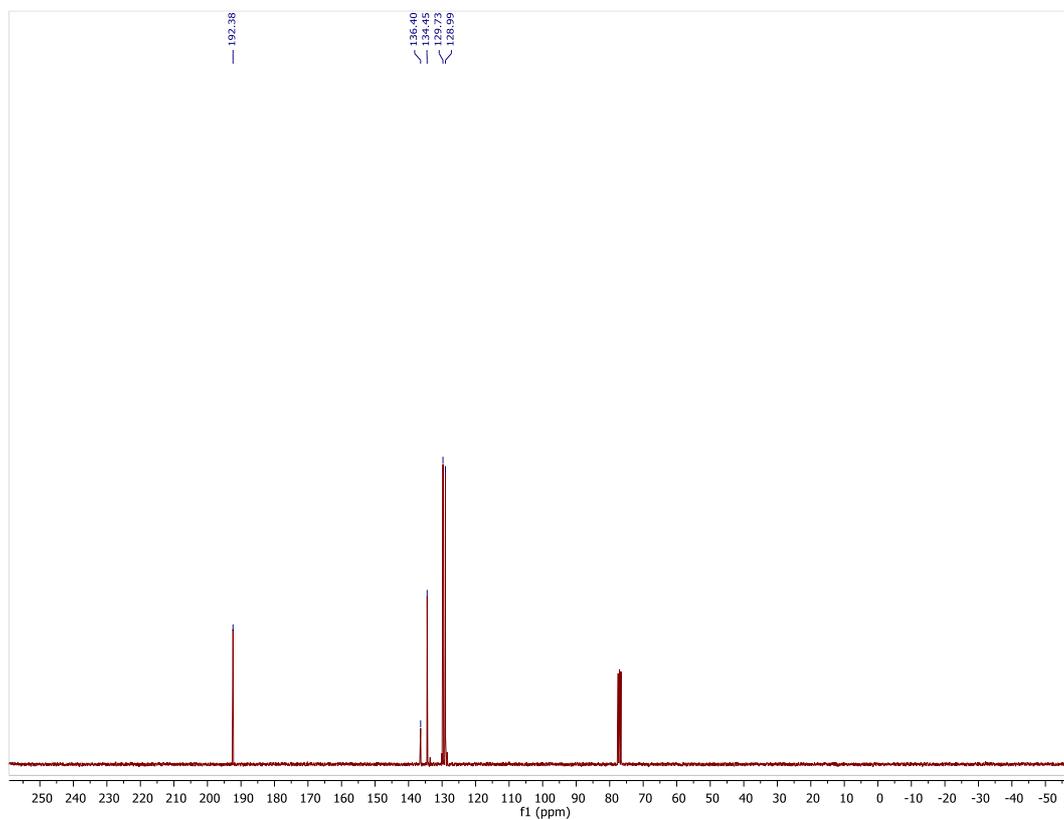


¹³C NMR spectrum in CDCl₃.

23b

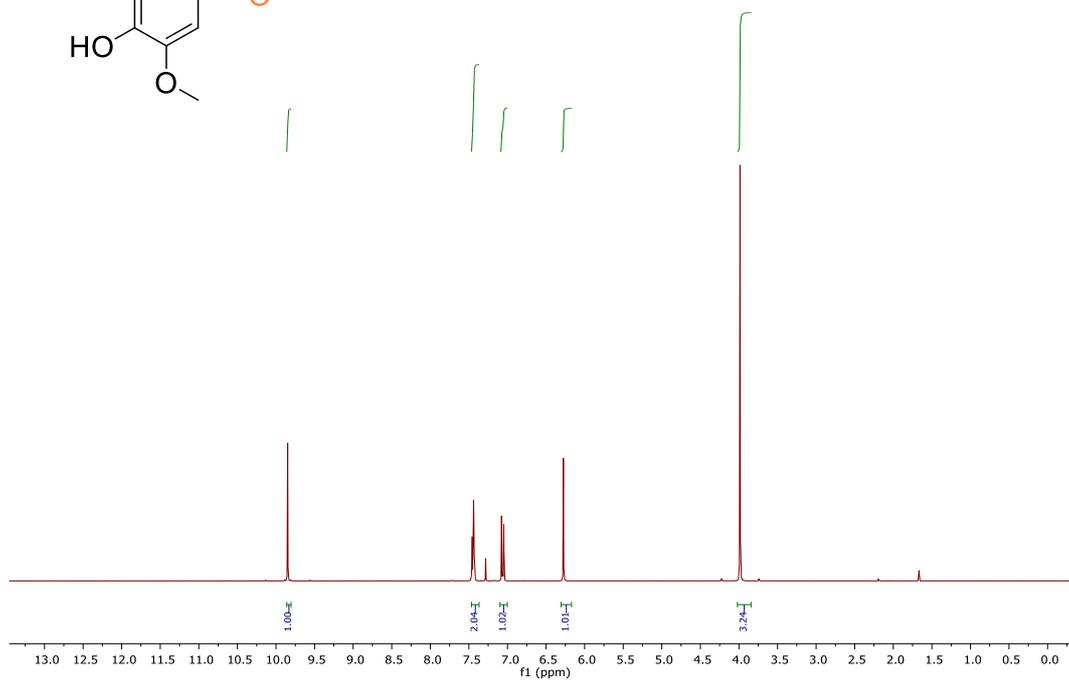
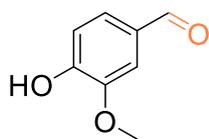


^1H NMR spectrum in CDCl_3 .

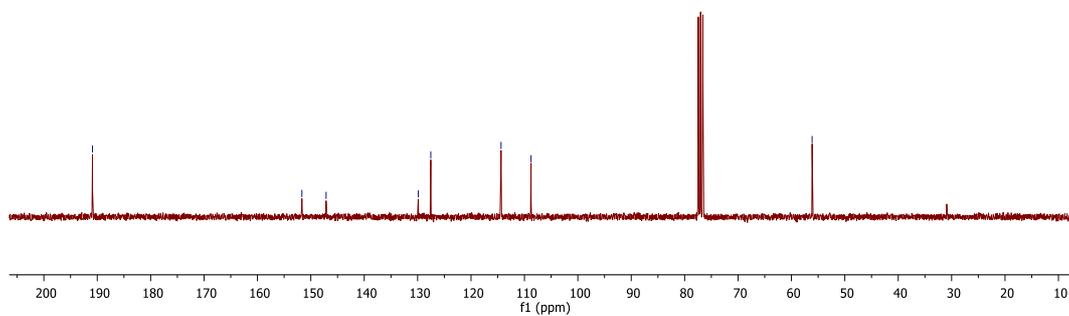


^{13}C NMR spectrum in CDCl_3 .

25b

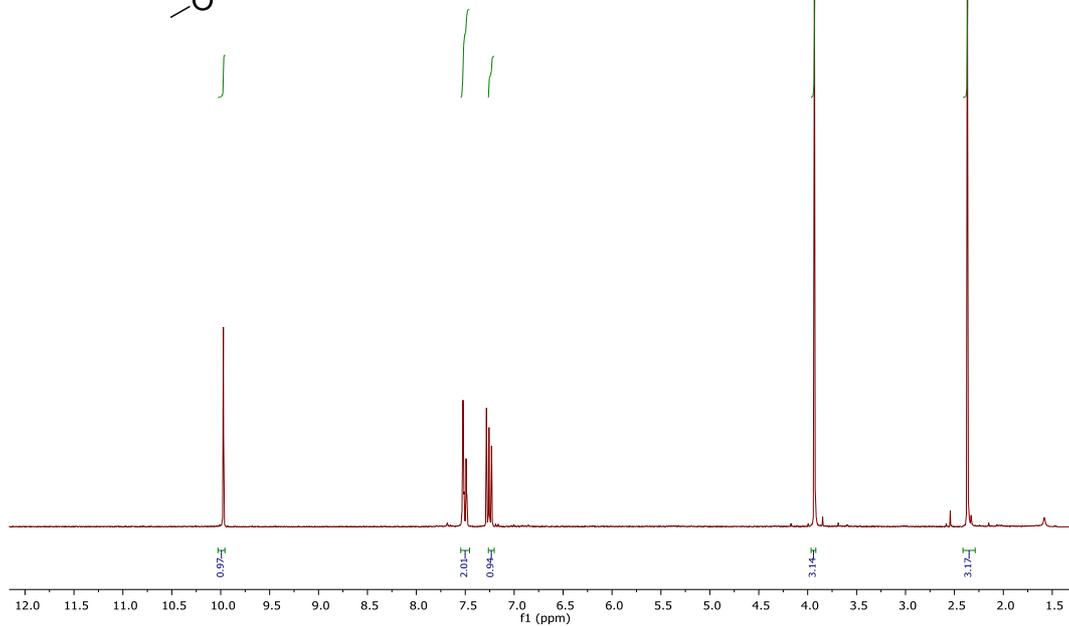
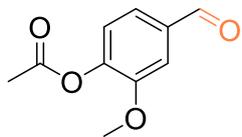


^1H NMR spectrum in CDCl_3 .

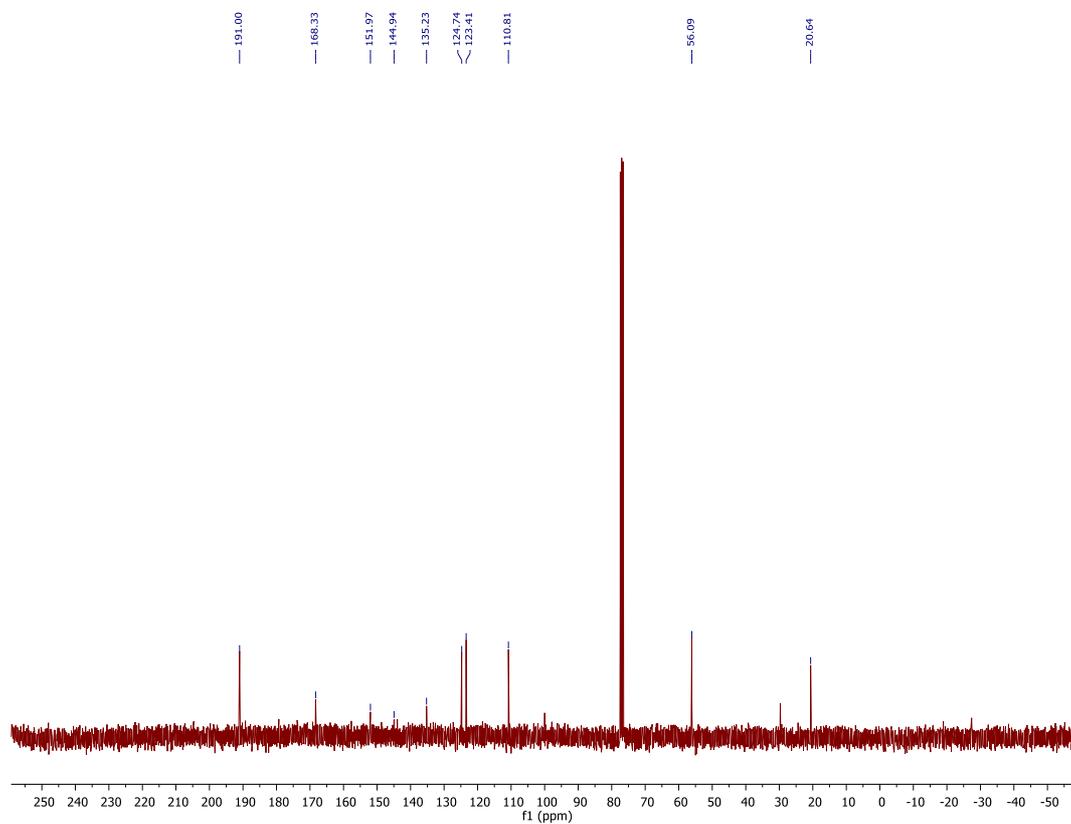


^{13}C NMR spectrum in CDCl_3 .

26b

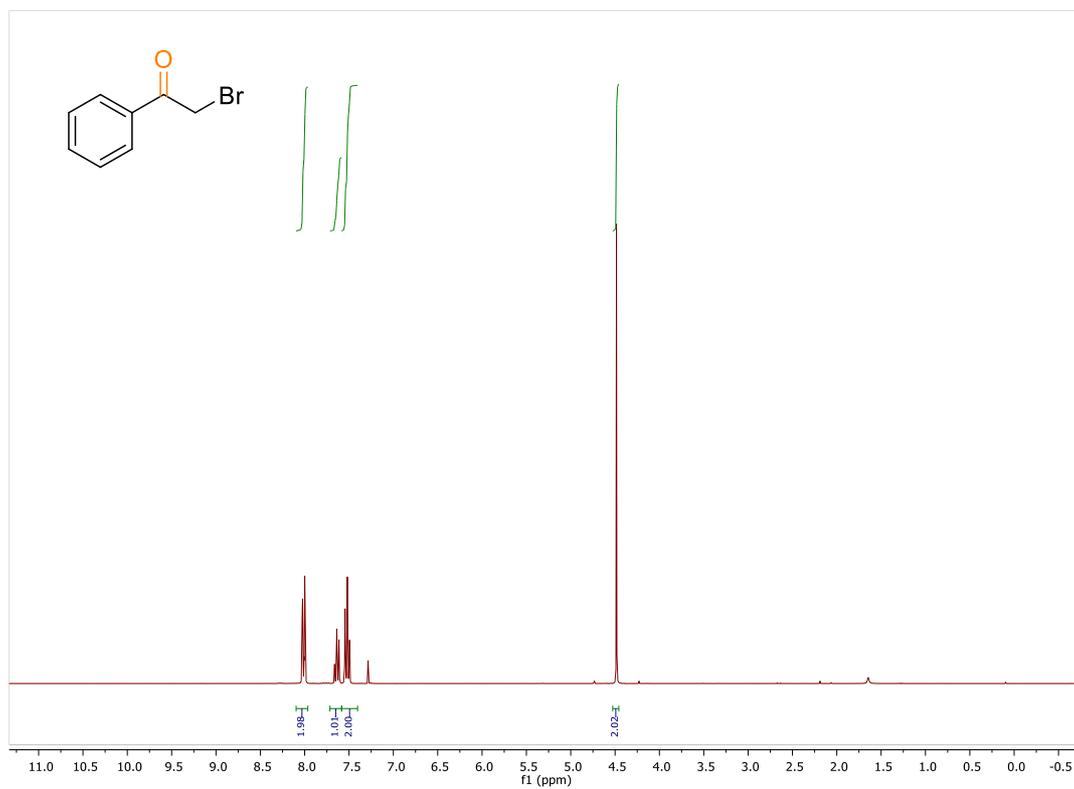


^1H NMR spectrum in CDCl_3 .

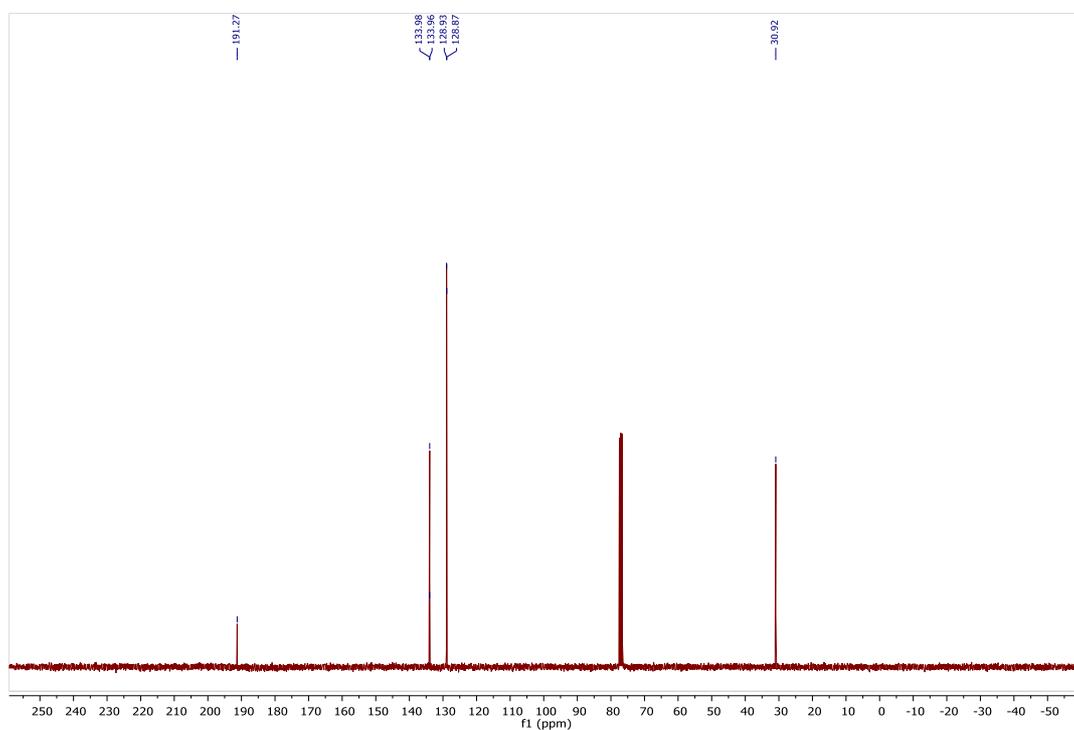


^{13}C NMR spectrum in CDCl_3 .

27b

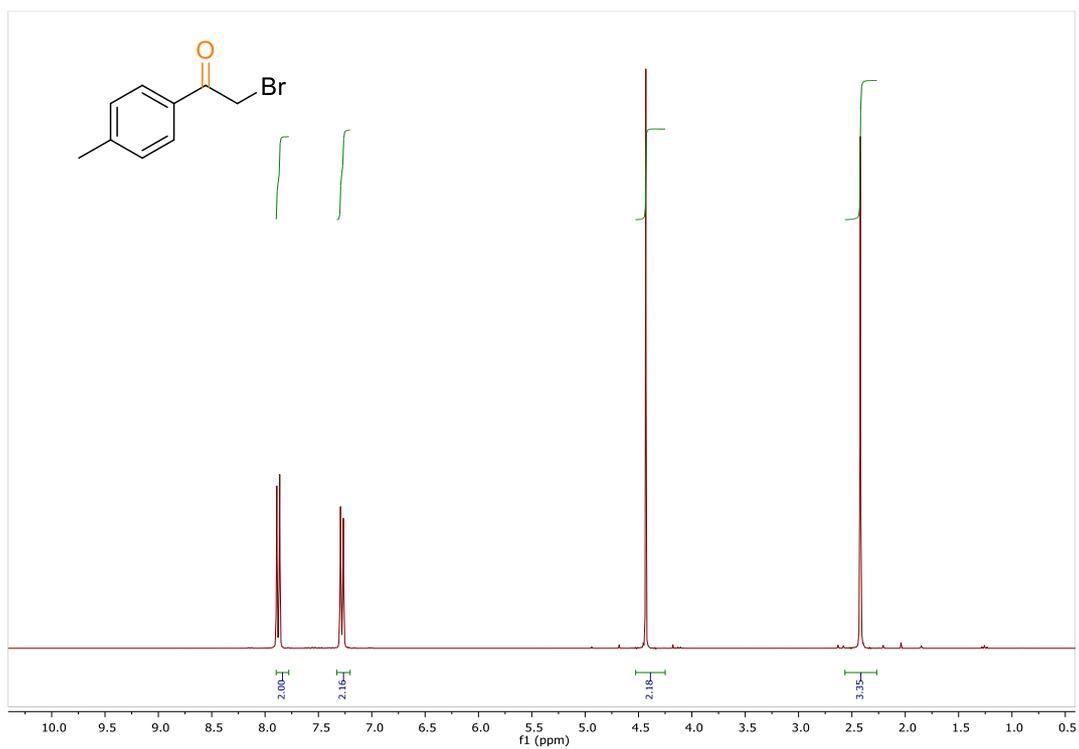


¹H NMR spectrum in CDCl₃.

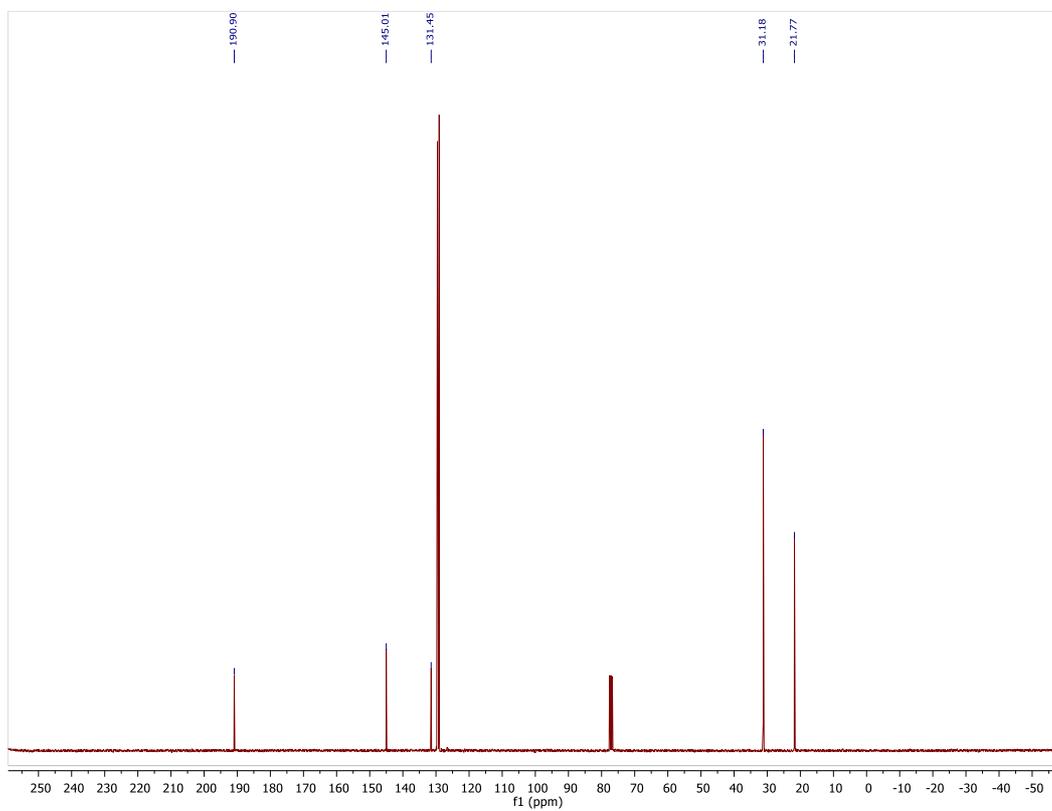


¹³C NMR spectrum in CDCl₃.

28b

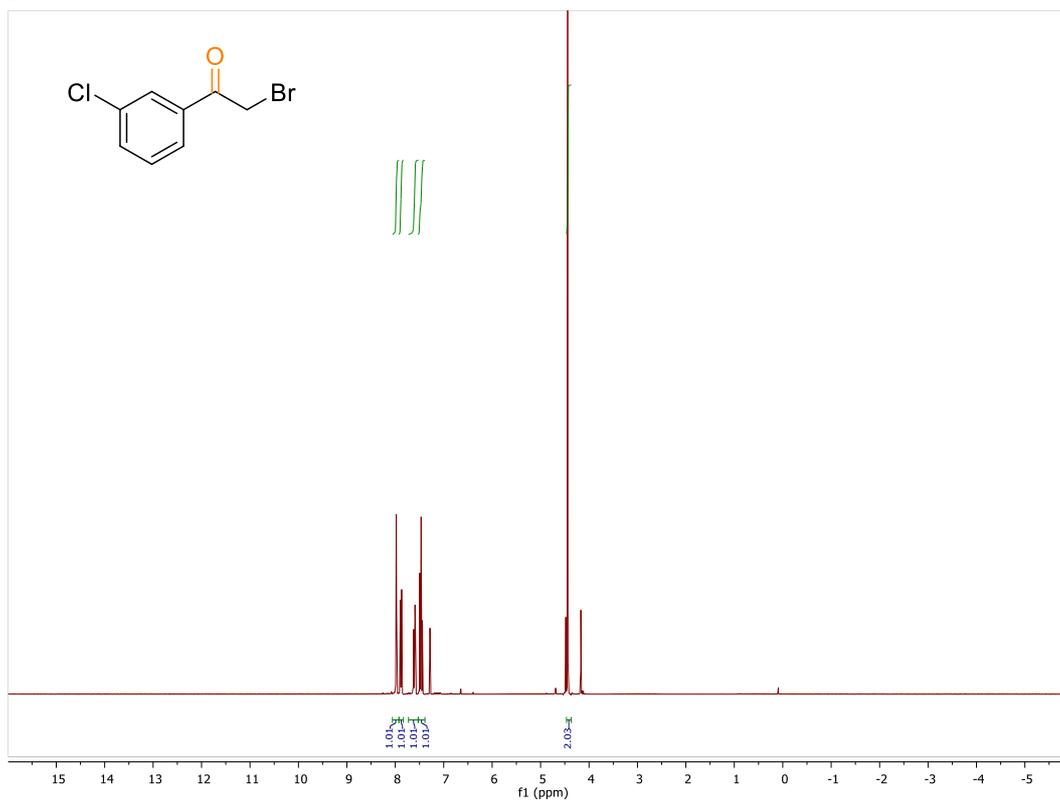


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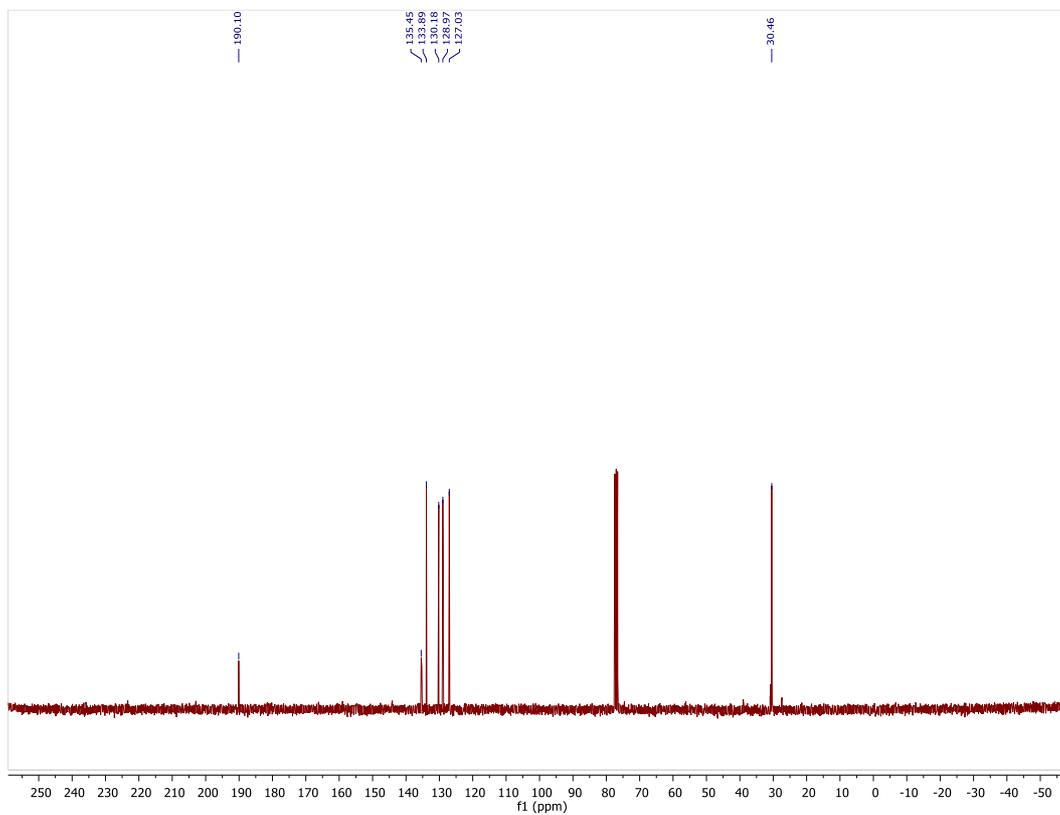


¹³C NMR spectrum in CDCl₃.

29b

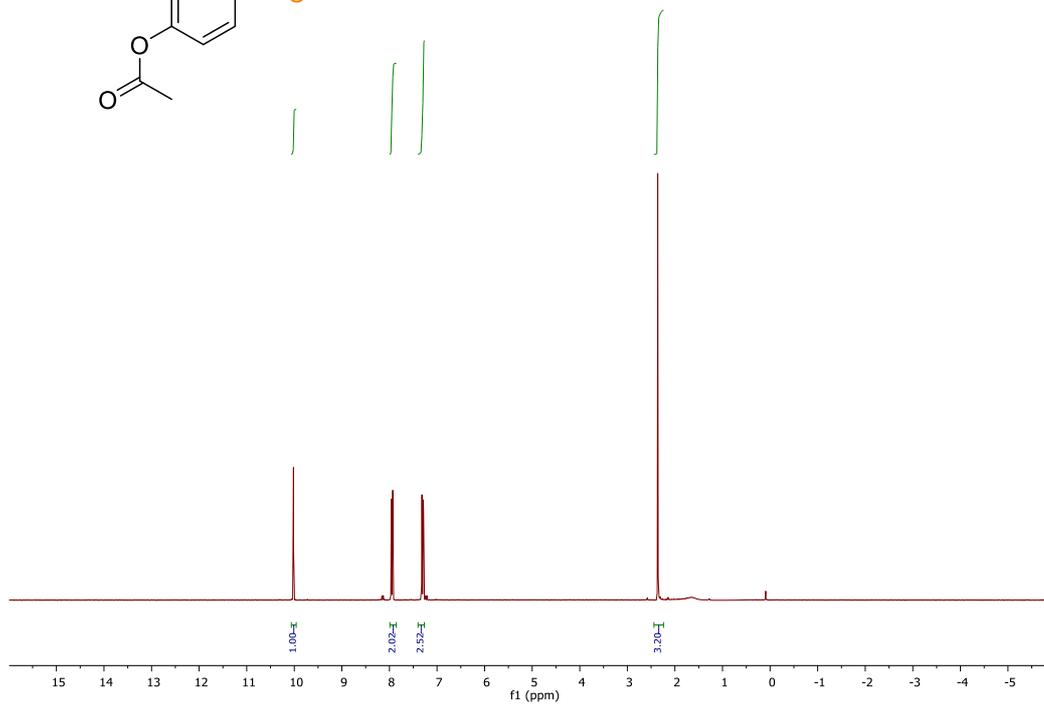
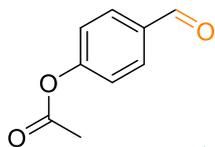


¹H NMR spectrum in CDCl₃.

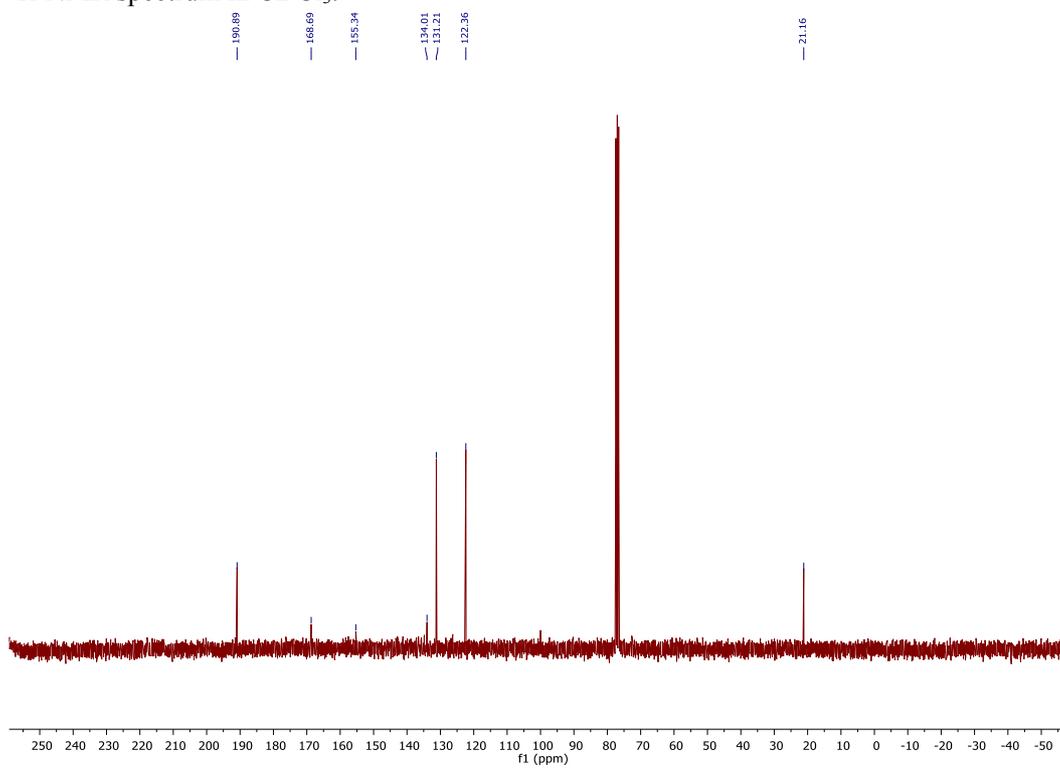


¹³C NMR spectrum in CDCl₃.

30b-1

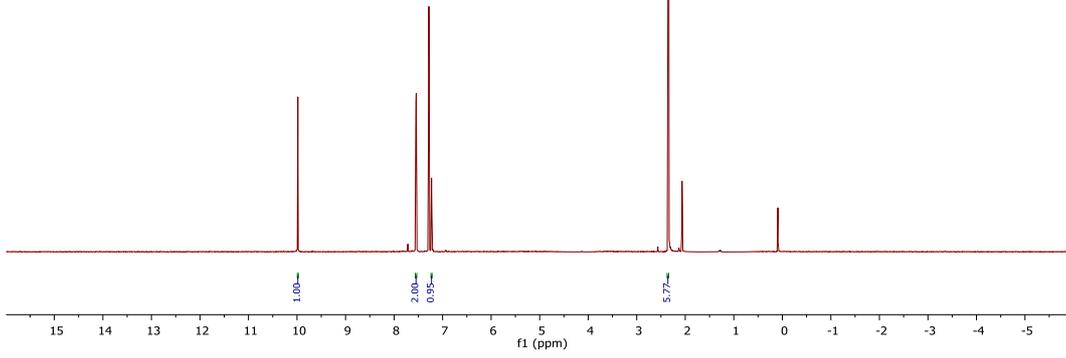
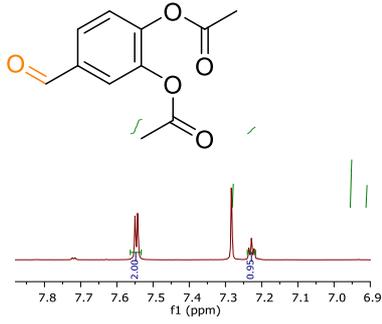


^1H NMR spectrum in CDCl_3 .



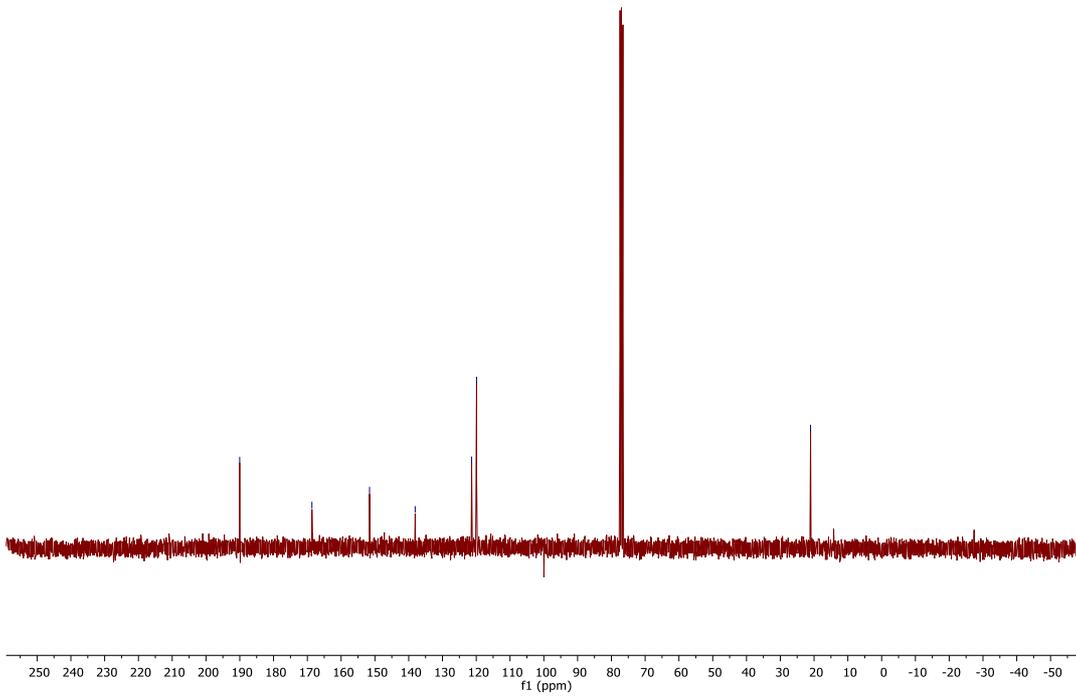
^{13}C NMR spectrum in CDCl_3 .

30b-2



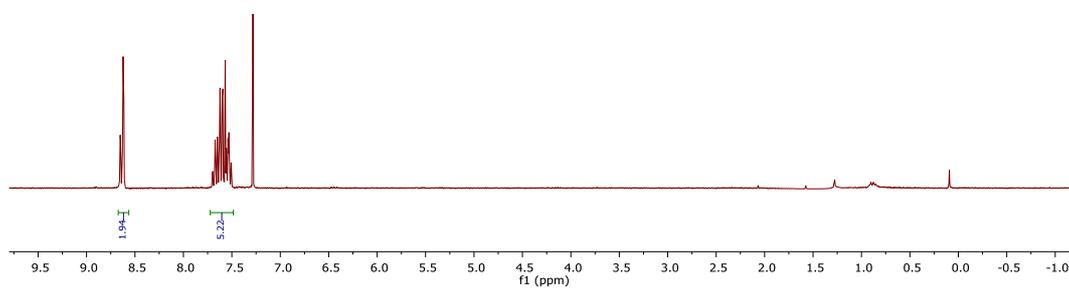
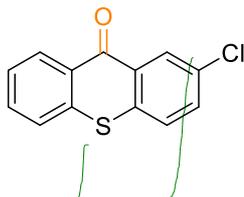
¹H NMR spectrum in CDCl₃.

190.03
168.64
151.99
138.08
121.36
119.91
21.04

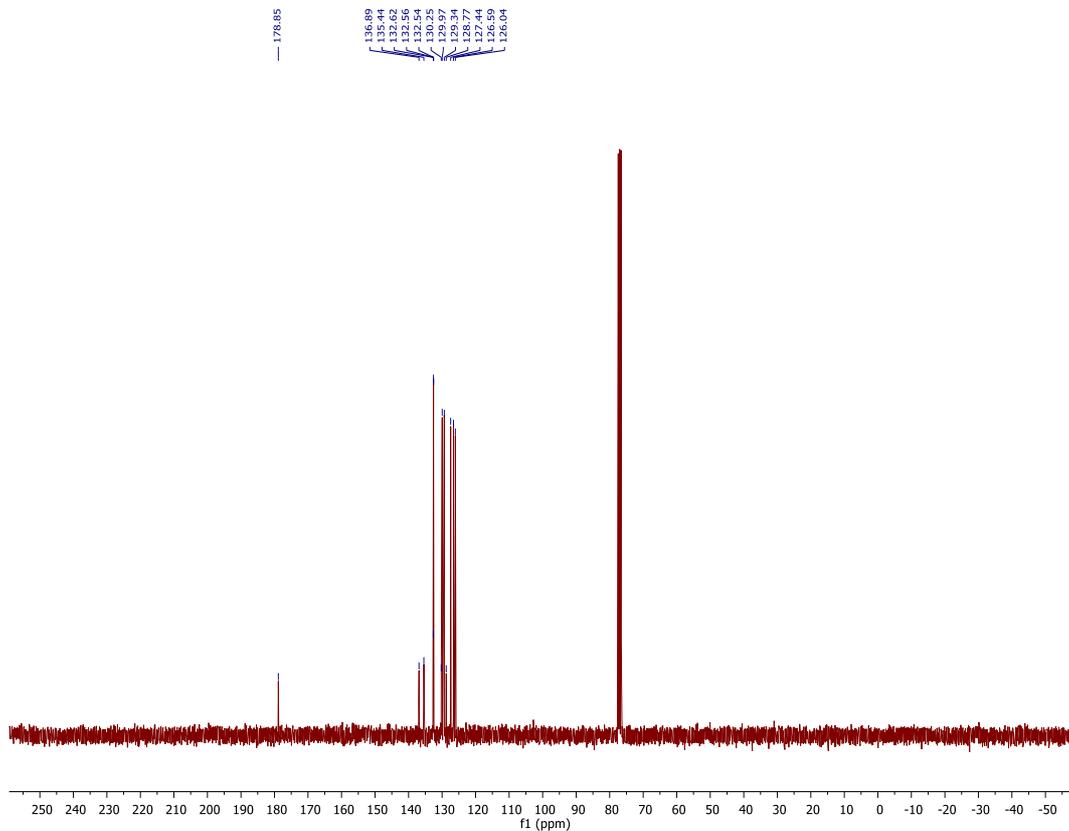


¹³C NMR spectrum in CDCl₃.

31b

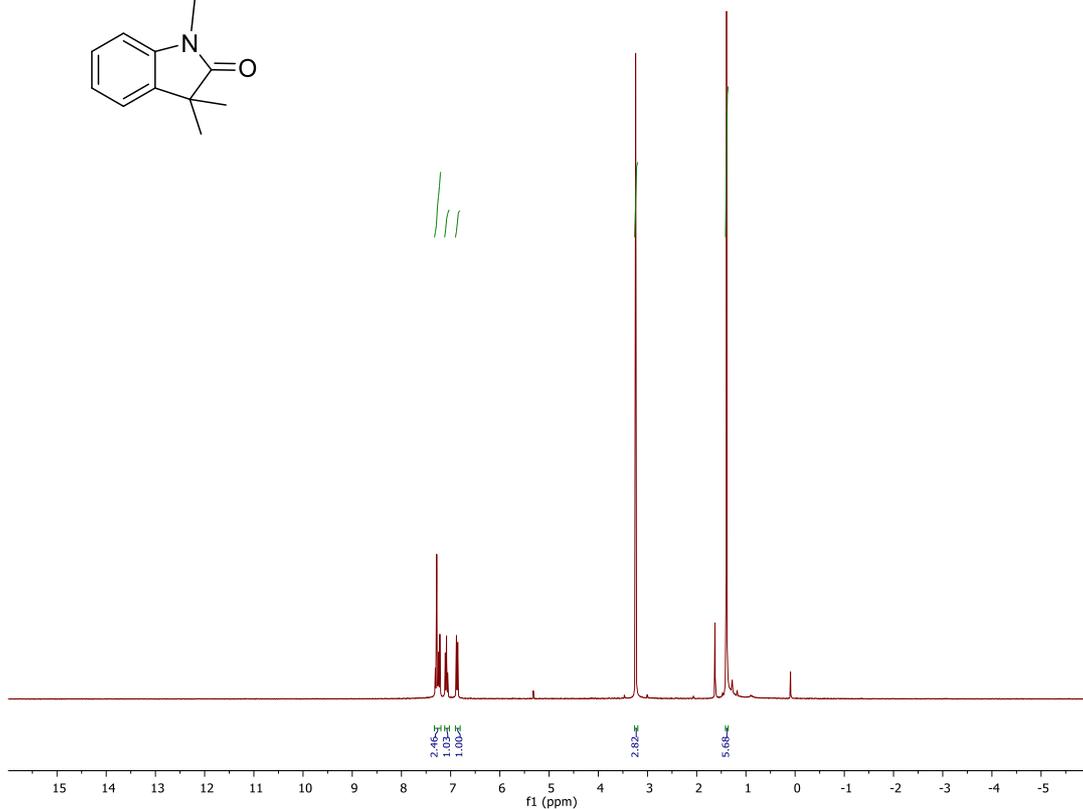
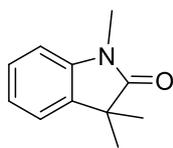


^1H NMR spectrum in CDCl_3 .

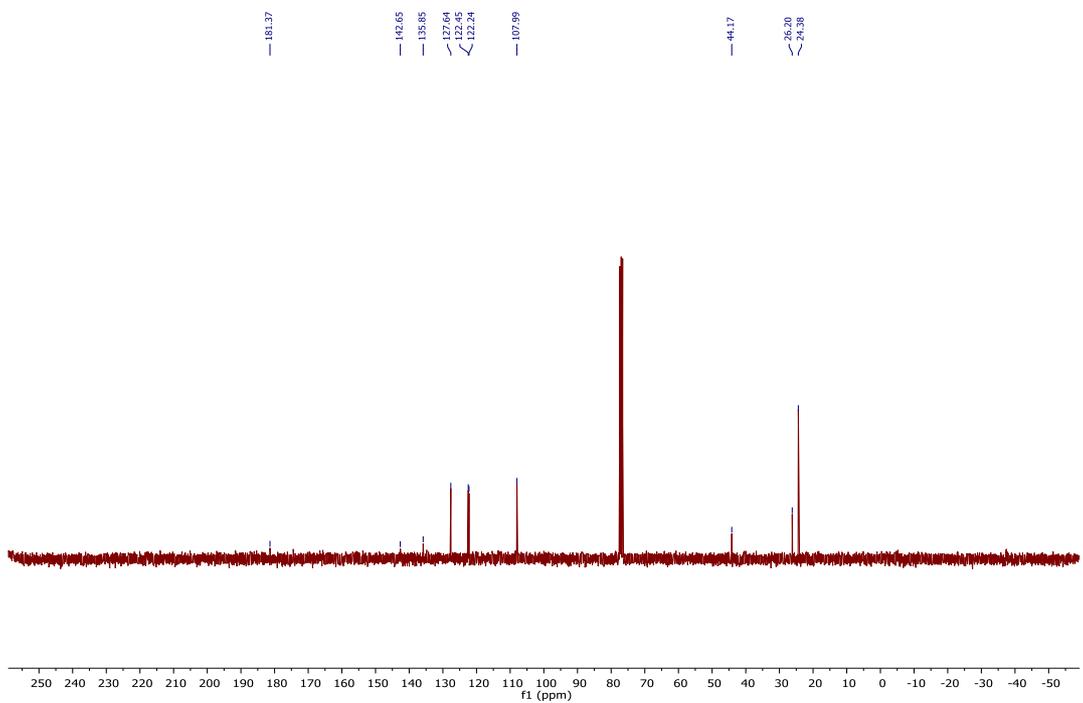


^{13}C NMR spectrum in CDCl_3 .

32b

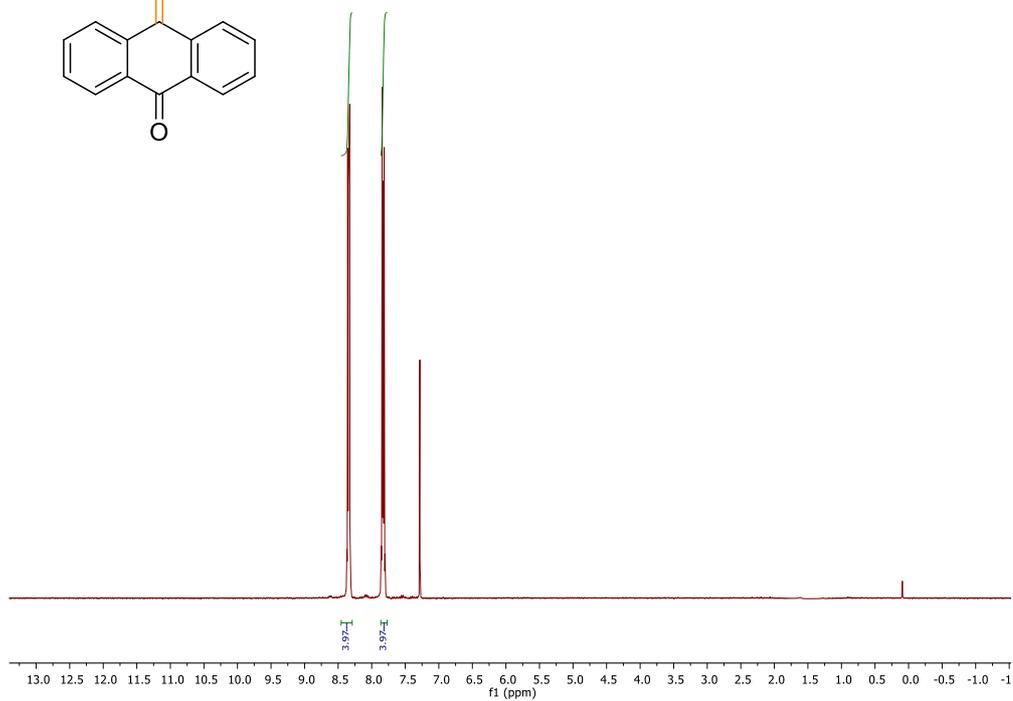
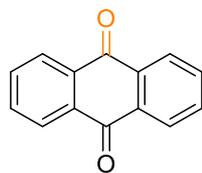


¹H NMR spectrum in CDCl₃.

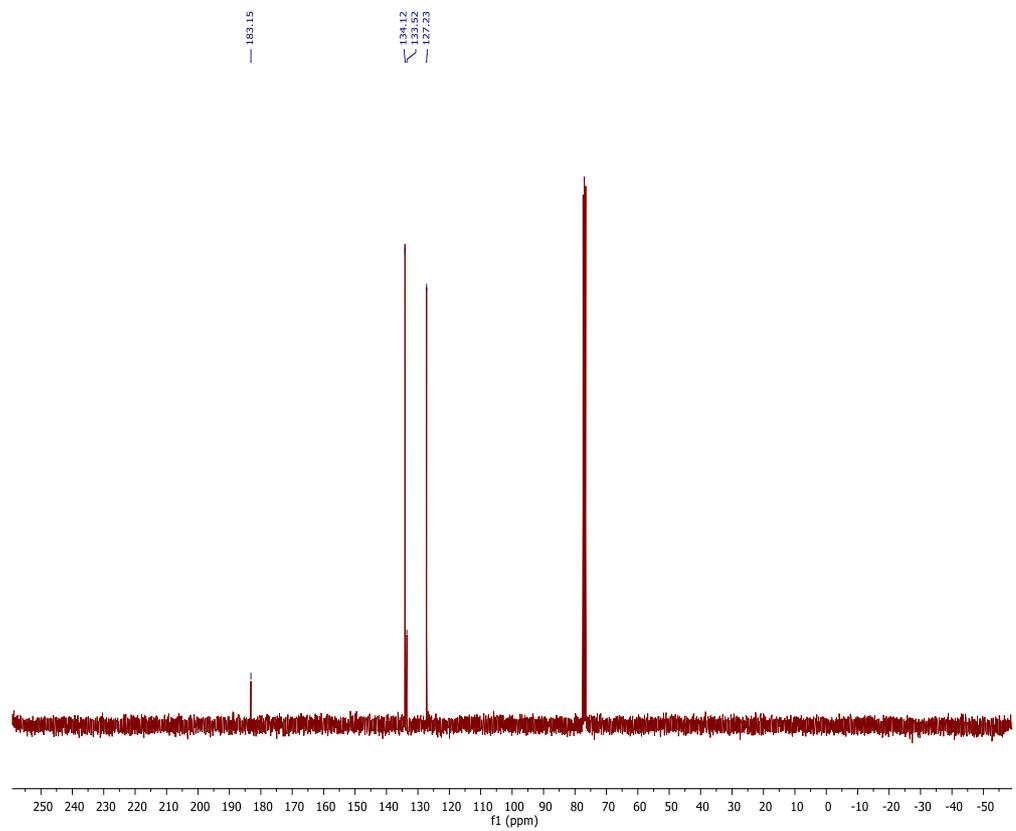


¹³C NMR spectrum in CDCl₃.

33b

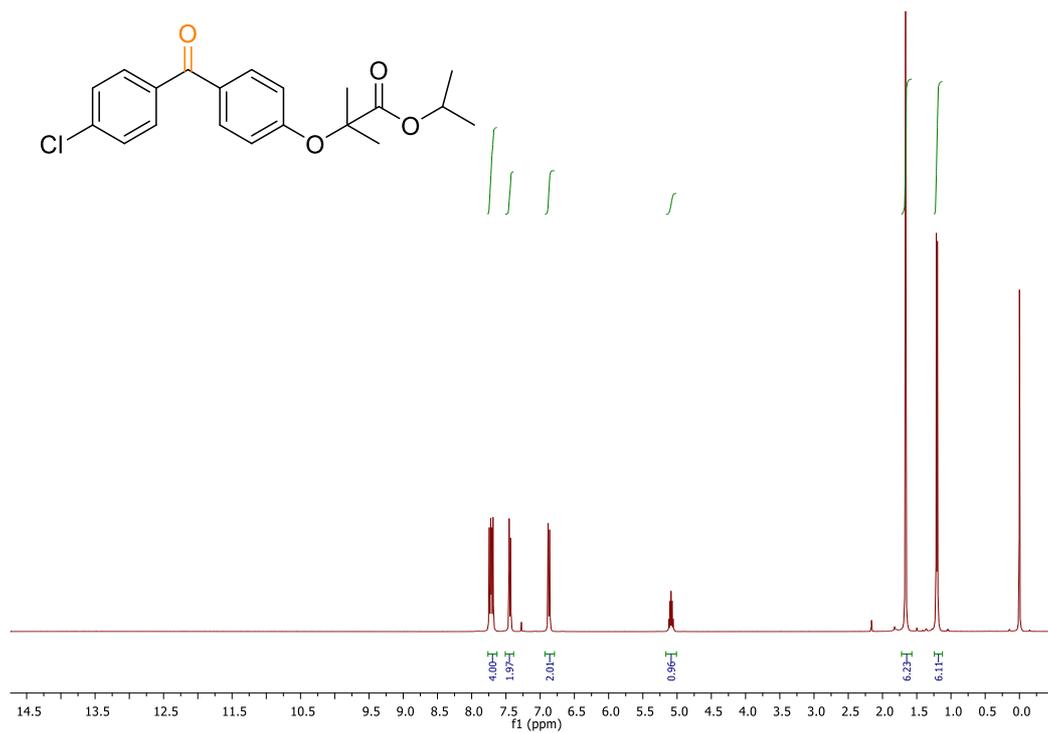


^1H NMR spectrum in CDCl_3 .

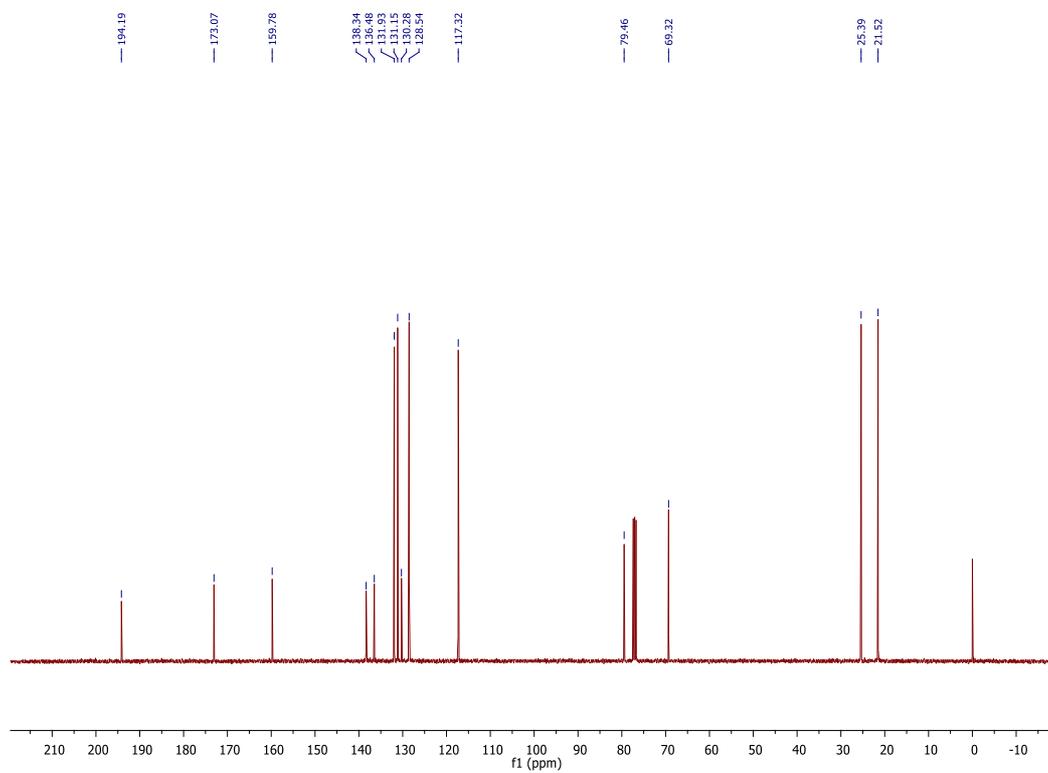


^{13}C NMR spectrum in CDCl_3 .

35b



¹H NMR spectrum in CDCl₃.



¹³C NMR spectrum in CDCl₃.