

Supporting Information

**Efficient and eco-friendly oxidative cleavage C–C bonds of 1,2-diols
to ketones: electrochemistry vs thermochemistry**

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1. Materials and methods

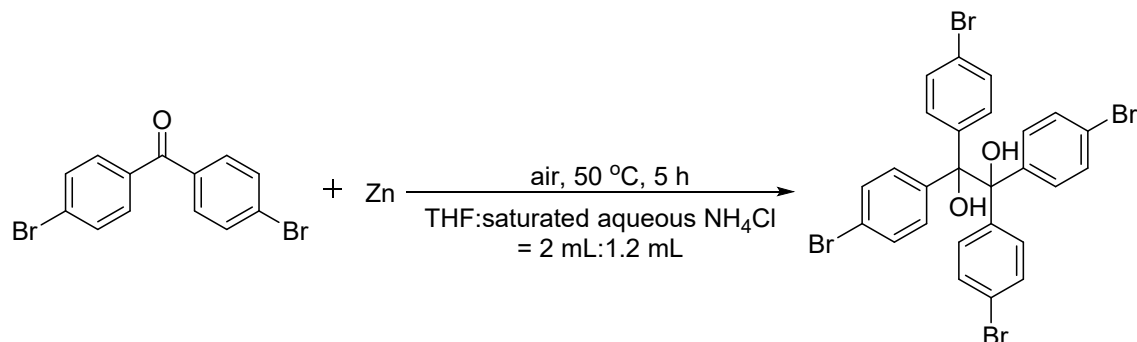
General. ^1H , ^{13}C NMR spectra were recorded on a Varian Inova-400 (400 and 100 MHz, respectively) spectrometer. ^1H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm or CDCl_3 ($\delta(^1\text{H})$, 7.26 ppm; $\delta(^{13}\text{C})$, 77.16 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel. Electrochemical cleavage reactions were performed on IKA ElectraSyn 2.0 pro. H_2 detection experiment was conducted on a ES20B- H_2 gas detector (Shenzhen Eyesky Technology Co., Ltd). Continuous-flow reaction was performed in the microfluidic electrolysis cell and its components were purchased from Hangzhou Saiao Electrochemical Technology Co. Ltd., China.

Materials. All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. 1,2-Diols are known compounds and synthesized according to the reported method^[1].

2. Experimental procedures

2.1 General procedure for synthesis of 1,2-diols

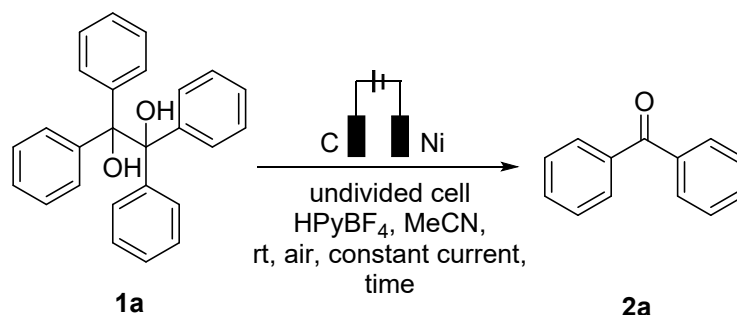
(taking 1,1,2,2-tetrakis(4-bromophenyl)ethane-1,2-diol as an example)



Under atmosphere, bis(4-bromophenyl)methanone (0.5 mmol, 1.0 equiv.) and Zn powder (1 mmol, 2.0 equiv.) were slurried in 1.2 mL saturated aqueous NH₄Cl and 2 mL THF. The mixture was stirred at 50 °C for 5 h, until Zn powder disappeared. The reaction was then quenched by the hydrochloric acid solution (1 M). After cooling to ambient temperature, the resulting mixture was extracted with ethyl acetate. The combined organic layer dried over anhydrous Na₂SO₄. After filtration and concentration, the pure product 1,1,2,2-tetrakis(4-bromophenyl)ethane-1,2-diol was obtained by flash column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/EtOAc= 10:1, v/v).

2.2 Optimization of electrooxidative cleavage C–C bonds of 1,2-diols

Table S1 Screening of constant current^a

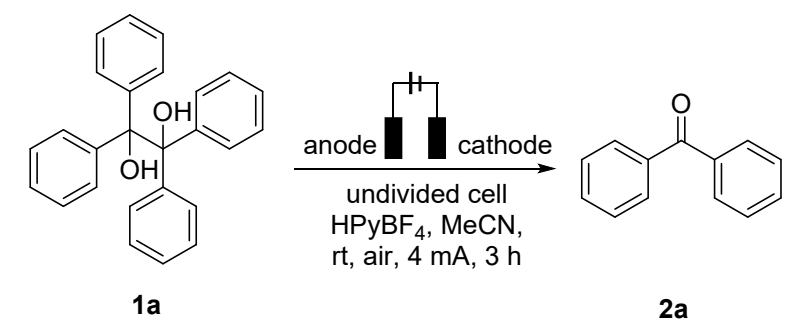


Entry	Constant current (mA)	Yield (%) ^b
1	6	88
2	4	87
3	2	38
4	0	n.r.

^a Reaction conditions: **1a** (0.2 mmol), HPyBF₄ (20 mol%), MeCN (4.0 mL), carbon plate anode

(immersed surface area $8 \times 5 \text{ mm}^2$), nickel plate cathode (immersed surface area $8 \times 5 \text{ mm}^2$), the distance between the electrodes (5 mm), constant current, 3 h, room temperature, under air, undivided cell, reactions were performed using ElectraSyn 2.0. ^b Isolated yields. HPyBF₄: *N*-Hexylpyridinium tetrafluoroborate. n.r.: no reaction.

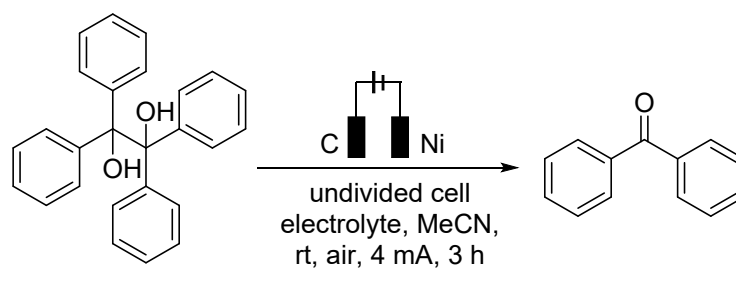
Table S2 Screening of electrodes^a



Entry	Anode	Cathode	Yield (%) ^b
1	C	Ni	87
2	C	C	n.r.
3	C	Pt	90
4	RVC	Ni	85
5	Ni	Ni	n.r.

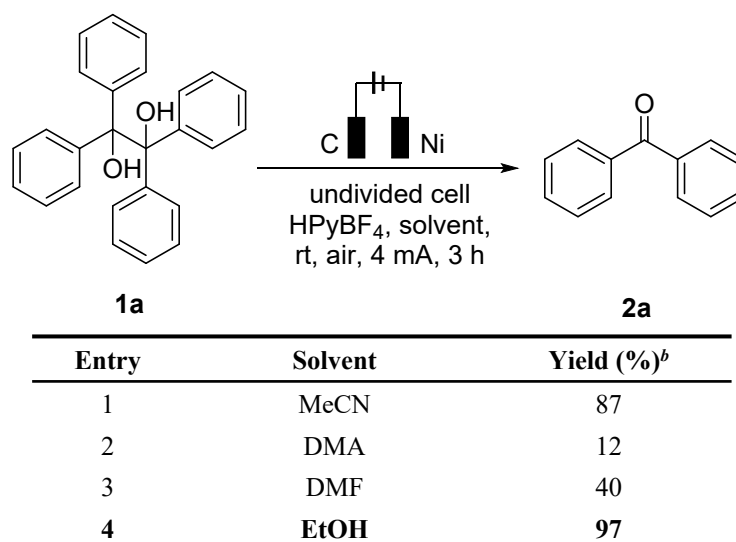
^a Reaction conditions: **1a** (0.2 mmol), HPyBF₄ (20 mol%), MeCN (4.0 mL), anode (immersed surface area $8 \times 5 \text{ mm}^2$), cathode (immersed surface area $8 \times 5 \text{ mm}^2$), the distance between the electrodes (5 mm), constant current = 4 mA, 3 h, room temperature, under air, undivided cell, reactions were performed using ElectraSyn 2.0. ^b Isolated yields.

Table S3 Screening of electrolytes^a



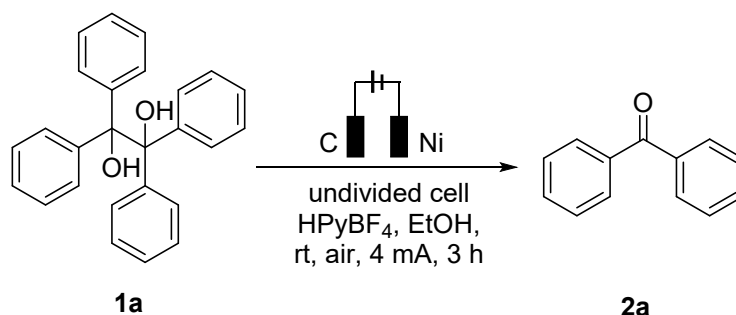
Entry	Electrolyte	Yield (%) ^b
1	HPyBF ₄	87
2	Bu ₄ NClO ₄	82
3	Bu ₄ NPF ₆	79
4	NaCl	n.r.
5	LiClO ₄	n.r.
6	/	n.r.

^a Reaction conditions: **1a** (0.2 mmol), electrolyte (20 mol%), MeCN (4.0 mL), carbon plate anode (immersed surface area $8 \times 5 \text{ mm}^2$), nickel plate cathode (immersed surface area $8 \times 5 \text{ mm}^2$), the distance between the electrodes (5 mm), constant current = 4 mA, 3 h, room temperature, under air, undivided cell, reactions were performed using ElectraSyn 2.0. ^b Isolated yields.

Table S4 Screening of solvents^a

^a Reaction conditions: **1a** (0.2 mmol), HPyBF₄ (20 mol%), solvent (4.0 mL), carbon plate anode (immersed surface area 8 × 5 mm²), nickel plate cathode (immersed surface area 8 × 5 mm²), the distance between the electrodes (5 mm), constant current = 4 mA, 3 h, room temperature, under air, undivided cell, reactions were performed using ElectraSyn 2.0. ^b Isolated yields. DMA: *N,N*-Dimethylacetamide. DMF: *N,N*-Dimethylformamide.

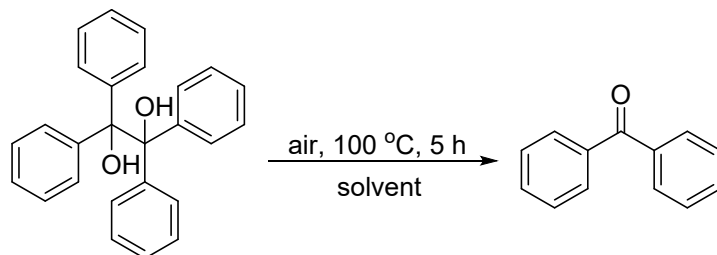
2.3 General procedure for electrooxidative cleavage C–C bonds of 1,2-diols (taking **1a** as an example)



Under atmosphere, a mixture of benzopinacol **1a** (73 mg, 0.2 mmol), HPyBF₄ (100 mg, 20 mol%), and EtOH (4.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with carbon plate as the anode and nickel plate as the cathode. The resulting mixture was stirred and electrolyzed at a constant current mode with a constant current 4 mA at ambient temperature for 3 h. When the reaction was finished, the resulting mixture was the reaction mixture was diluted with ethyl acetate and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v/v) to afford the desired product **2a** as light yellow oily liquid (71 mg, 97% yield).

2.4 Optimization of thermoxidative cleavage C–C bonds of 1,2-diols

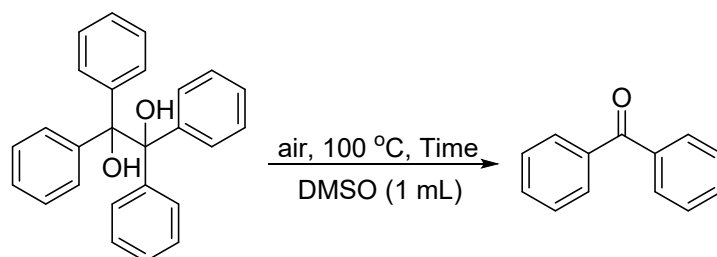
Table S5 Screening of solvents^a



Entry	Solvent	Yield (%) ^b
1	NMP	75
2	DMF	85
3	DMSO	94
4	H ₂ O	n.r.
5	1,4-Dioxane	23
6	THF	n.r.

^a Reaction conditions: **1a** (0.2 mmol), 100 °C, 5 h, solvent (1.0 mL), under air. ^b Isolated yields. NMP: 1-Methyl-2-pyrrolidinone. DMSO: Dimethyl sulfoxide. THF: Tetrahydrofuran.

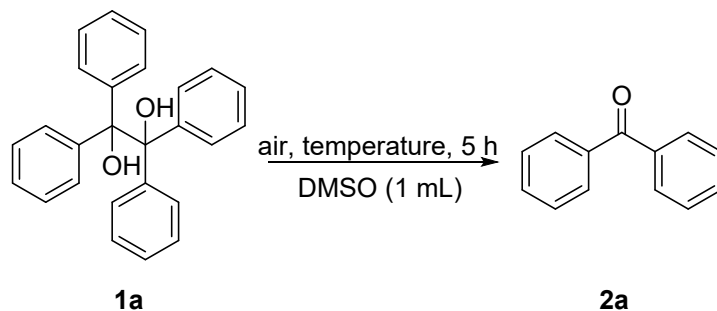
Table S6 Screening of reaction time^a



Entry	Time (h)	Yield (%) ^b
1	24	94
2	5	97
3	4	83

^a Reaction conditions: **1a** (0.2 mmol), 100 °C, time, DMSO (1.0 mL), under air. ^b Isolated yields.

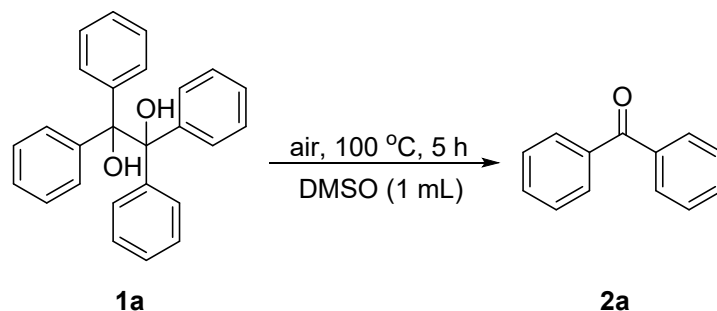
Table S7 Screening of temperature^a



Entry	Temperature (°C)	Yield (%) ^b
1	100	97
2	80	41

^a Reaction conditions: **1a** (0.2 mmol), temperature, 5 h, DMSO (1.0 mL), under air. ^b Isolated yields.

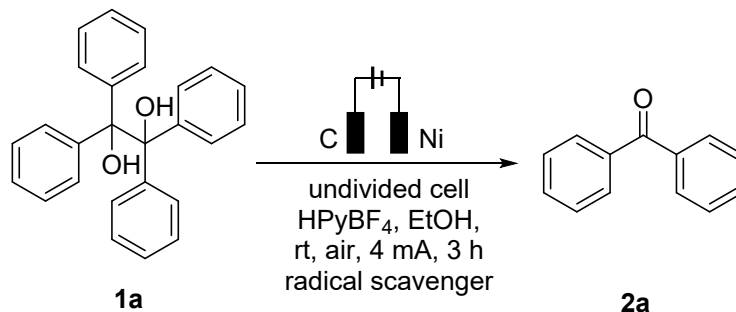
2.5 General procedure for thermoxidative cleavage C–C bonds of 1,2-diols (taking **1a** as an example)



Under atmosphere, benzopinacol **1a** (73 mg, 0.2 mmol), and DMSO (1.0 mL) were added to a 10 mL reaction tube equipped with magneton. Then the reaction mixture was stirred in an oil bath at 100 °C for 5 h. After cooling to ambient temperature, the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer washed with saturated sodium chloride solution (10 mL) and dried over anhydrous Na₂SO₄, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc= 100:1, v/v) to afford the desired product **2a** as light yellow oily liquid (71 mg, 97% yield).

3. Mechanistic studies

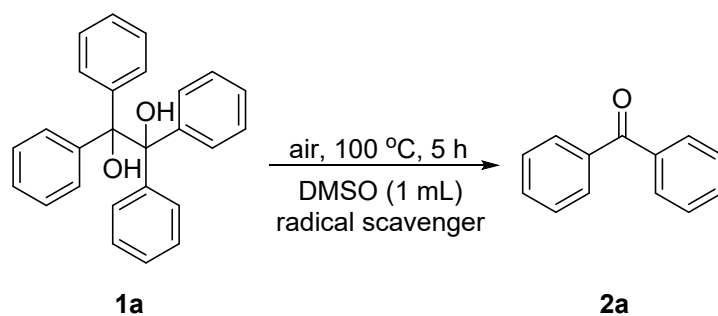
3.1 Radical trapping experiments of electrooxidative cleavage C–C bonds of 1,2-diols



Entry	Radical scavenger (equiv.)	Isolated yield of 2a (%)
1	No radical scavenger	97
2	TEMPO (4.0)	5
3	BHT (4.0)	4

Under atmosphere, a mixture of benzopinacol **1a** (73 mg, 0.2 mmol), radical scavenger TEMPO or BHT (0.8 mmol), HPyBF₄ (100 mg, 20 mol%), and EtOH (4.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with carbon plate as the anode and nickel plate as the cathode. The resulting mixture was stirred and electrolyzed at a constant current mode with a constant current 4 mA at ambient temperature for 3 h. When the reaction was finished, the resulting mixture was the reaction mixture was diluted with ethyl acetate and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v/v) to afford the desired product **2a** in 5% and 4% yield, respectively.

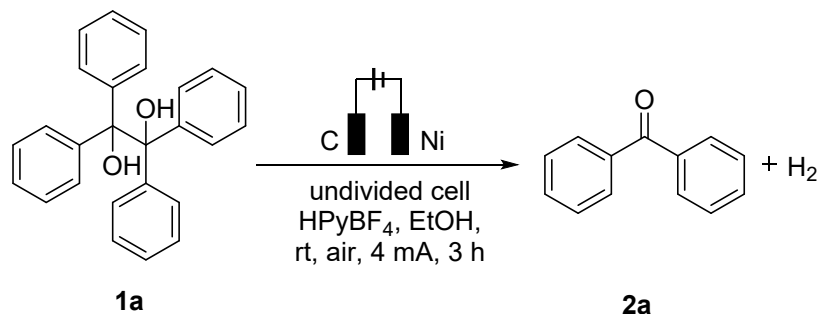
3.2 Radical trapping experiments of thermoxidative cleavage C–C bonds of 1,2-diols



Entry	Radical scavenger (equiv.)	Isolated yield of 2a (%)
1	No radical scavenger	97
2	TEMPO (4.0)	96
3	BHT (4.0)	97

Under atmosphere, benzopinacol **1a** (73 mg, 0.2 mmol), radical scavenger TEMPO or BHT (0.8 mmol), and DMSO (1.0 mL) were added to a 10 mL reaction tube equipped with magneton. Then the reaction mixture was stirred in an oil bath at 100 °C for 5 h. After cooling to ambient temperature, the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer washed with saturated sodium chloride solution (10 mL) and dried over anhydrous Na₂SO₄, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc= 100:1, v/v) to afford the desired product **2a** in 96% and 97% yield, respectively.

3.3 H₂ detection experiment



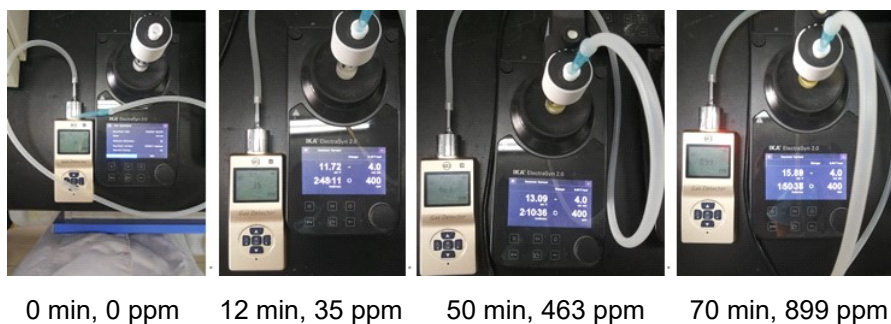


Figure S1 H₂ detection experiment by a H₂ detector at different reaction time

In order to demonstrate the release of H₂ during this electrochemical oxidative cleavage C—C bonds of 1,2-diols procedure, the model reaction of benzopinacol (**1a**) was monitored by a H₂ detector under standard conditions. Just as shown in **Figure S1**, as the reaction proceeded, the H₂ was observed clearly and the concentration increased gradually.

3.4 Cyclic voltammetry experiments

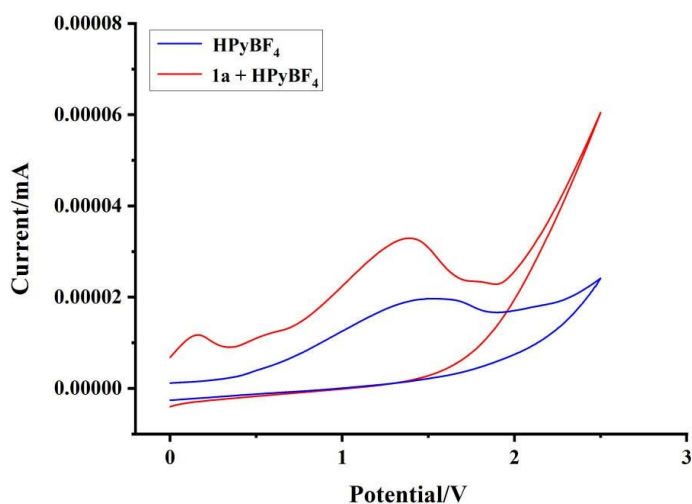
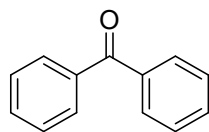


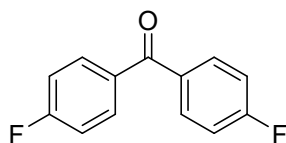
Figure S2 Cyclic voltammograms

Cyclic voltammograms were recorded with a CHI660E electrochemical workstation at room temperature in EtOH. A glassy carbon-disk (R = 5.5 mm, h = 10 mm) was used as the working electrode. The Pt disk (R = 5.5 mm, h = 10 mm) and Ag/AgCl (R = 5.0 mm, h = 10 mm) was used as counter and reference electrode, respectively. The scan rate was 100 mV/s.

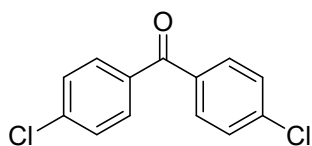
4. Analytical data



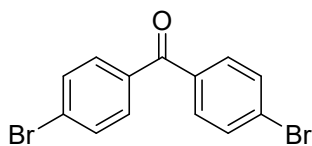
benzophenone (2a)^[2]: Known compound. Light yellow oily liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.49-7.51 (t, 4H, *J* = 7.8 Hz), 7.58-7.61 (t, 2H, *J* = 7.4 Hz), 7.80-7.82 (d, 4H, *J* = 7.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 196.8, 137.8, 132.5, 130.2, 128.4.



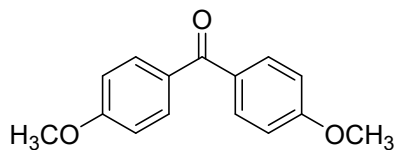
bis(4-fluorophenyl)methanone (2b)^[2]: Known compound. White solid. m.p.: 106.2-108.0 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.84-7.79 (m, 4H), 7.20-7.14 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.9, 166.8, 164.3, 133.8 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 22 Hz).



bis(4-chlorophenyl)methanone (2c)^[2]: Known compound. White solid. m.p.: 145.9-147.3 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.72 (d, 4H, *J* = 8.4 Hz), 7.47 (d, 4H, *J* = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 194.3, 139.3, 135.7, 131.4, 128.9.

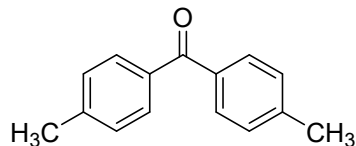


bis(4-bromophenyl)methanone (2d)^[3]: Known compound. White solid. m.p.: 162.4-166.1 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (s, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 194.6, 136.0, 131.9, 131.5, 127.9.

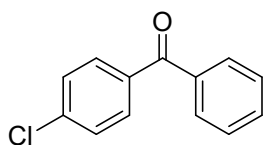


bis(4-methoxyphenyl)methanone (2e)^[2]: Known compound. White solid. m.p.:

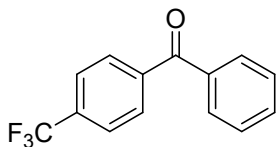
147.1-149.0 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.79 (d, 4H, $J = 8.1$ Hz), 6.96 (d, 4H, $J = 8.9$ Hz), 3.88 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 194.6, 162.9, 132.3, 130.8, 113.6, 55.6.



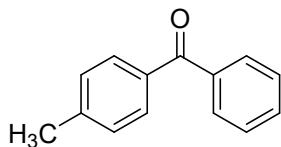
di-*p*-tolylmethanone (2f)^[2]: Known compound. White solid. m.p.: 91.5-93.2 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.70 (d, 4H, $J = 8.2$ Hz), 7.27 (d, 4H, $J = 7.8$ Hz), 2.44 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 196.4, 143.0, 135.3, 130.3, 129.0, 21.7.



(4-chlorophenyl)(phenyl)methanone (2h)^[4]: Known compound. White solid. m.p.: 76.1-77.2 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.77 (t, 4H, $J = 7.0$ Hz), 7.60 (t, 1H, $J = 7.4$ Hz), 7.51-7.45 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 195.6, 139.0, 137.4, 136.0, 132.8, 131.6, 130.0, 128.8, 128.5.

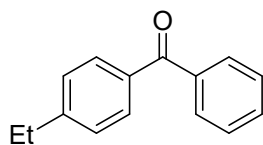


phenyl(4-(trifluoromethyl)phenyl)methanone (2i)^[5]: Known compound. White solid. m.p.: 117.4-117.9 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.91-7.88 (m, 2H), 7.82-7.75 (m, 4H), 7.66-7.61 (m, 1H), 7.54-7.49 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 195.7, 140.9, 136.9, 134.0, 133.7, 133.2, 130.3 (d, $J = 3.4$ Hz), 128.6, 125.6-125.4 (m), 125.2, 122.5.

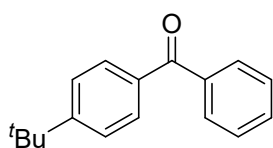


phenyl(*p*-tolyl)methanone (2j)^[4]: Known compound. Yellow solid. m.p.: 51.6-52.8 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.79 (d, 2H, $J = 7.6$ Hz), 7.73 (d, 2H, $J = 8.2$ Hz), 7.57 (t, 1H, $J = 7.4$ Hz), 7.48 (t, 2H, $J = 7.7$ Hz), 7.29 (d, 2H, $J = 8.4$ Hz), 2.45 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 196.5, 143.3, 138.1, 135.0, 132.2, 130.4, 130.0,

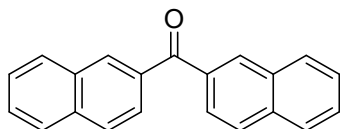
129.1, 128.3, 21.7.



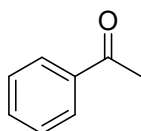
(4-ethylphenyl)(phenyl)methanone (2k)^[5]: Known compound. Light yellow oily liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.81-7.74 (m, 4H), 7.58 (t, 1H, *J* = 7.4 Hz), 7.48 (t, 2H, *J* = 7.8 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 2.74 (q, 2H, *J* = 7.6 Hz), 1.29 (t, 3H, *J* = 7.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 196.7, 149.6, 138.1, 135.2, 132.3, 130.5, 130.1, 128.3, 128.0, 29.1, 15.4.



(4-tert-butylphenyl)(phenyl)methanone (2l)^[5]: Known compound. Yellow oily liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.82-7.76 (m, 4H), 7.60-7.56 (m, 1H), 7.52-7.46 (m, 4H), 1.37 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 196.6, 156.3, 138.0, 135.0, 132.3, 130.3, 130.1, 128.3, 125.4, 35.2, 31.3.



di(naphthalen-2-yl)methanone (2n)^[6]: Known compound. White solid. m.p.: 162.7-166.2 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.33 (s, 2H), 8.03-7.92 (m, 8H), 7.66-7.55 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 196.9, 135.4, 135.3, 132.4, 132.0, 129.6, 128.5, 128.4, 128.0, 127.0, 126.0.



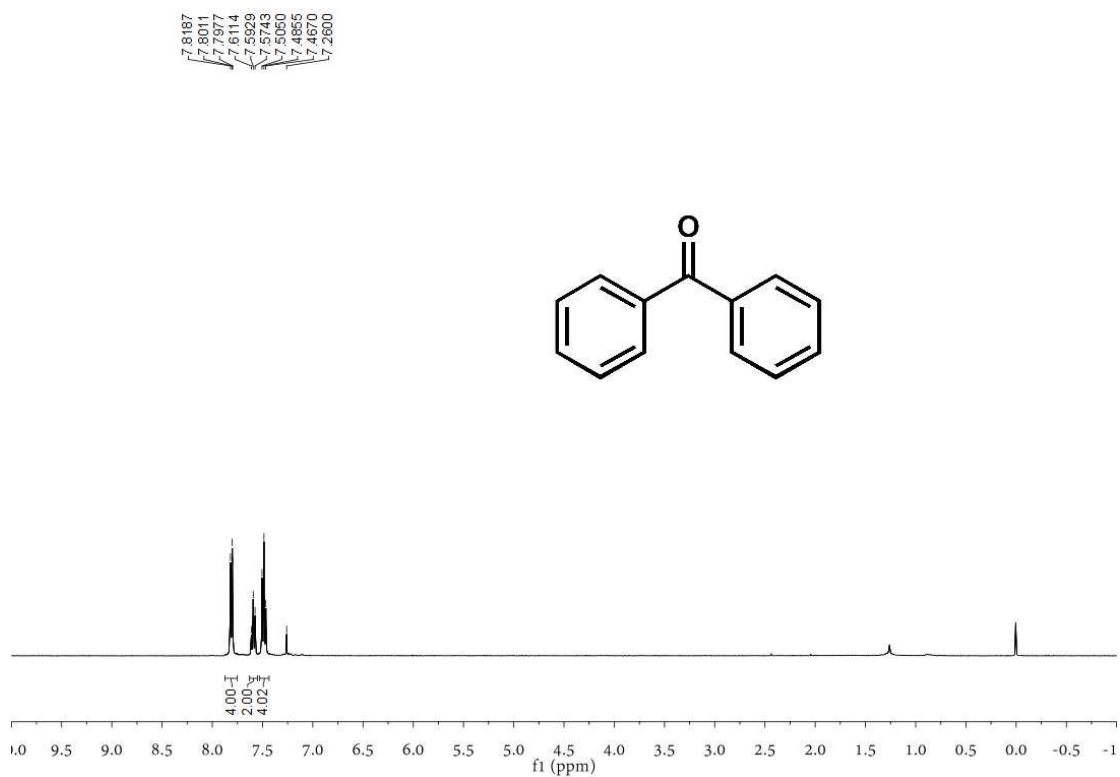
acetophenone (2o)^[7]: Known compound. Colorless oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.86-7.84 (m, 2H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 2H), 2.47 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 197.7, 136.8, 132.9, 128.3, 128.0, 26.3.

5. References

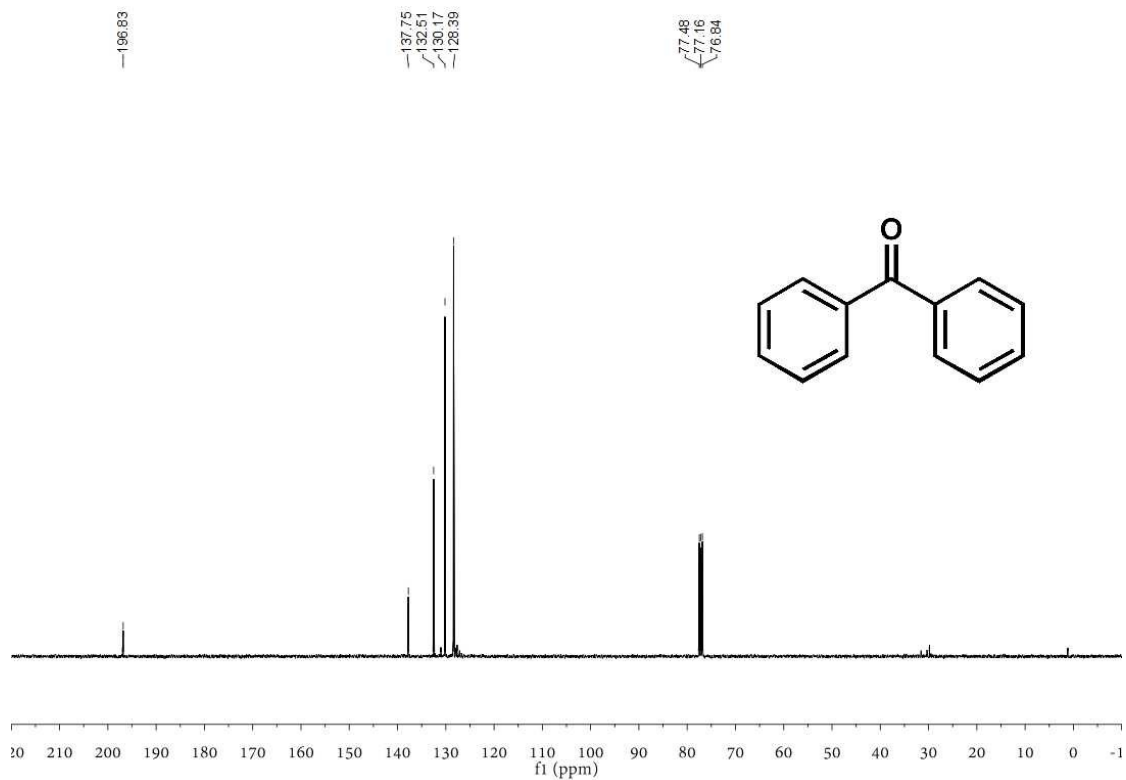
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- [7] J. Xiao, A. Gonzalez-de-Castro, *J. Am. Chem. Soc.* **2015**, *137*, 8206-8218.

6. Copies of NMR spectra

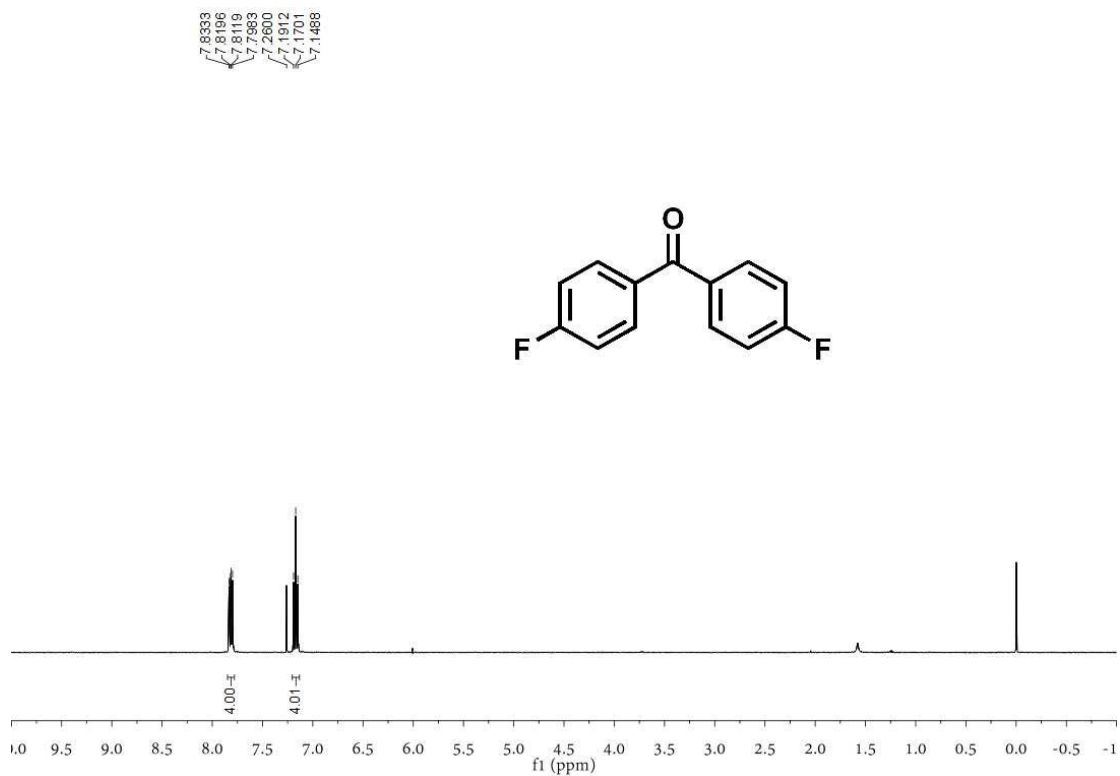
^1H NMR of product 2a in CDCl_3 (400 MHz)



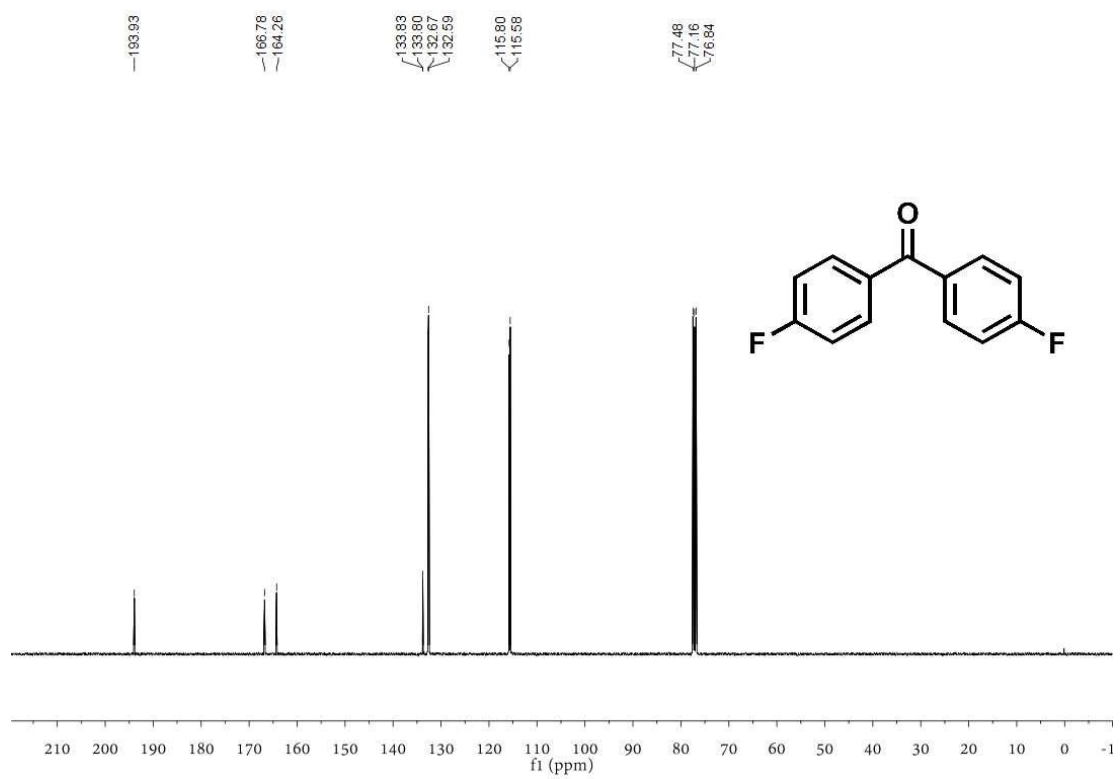
^{13}C NMR of product 2a in CDCl_3 (100 MHz)



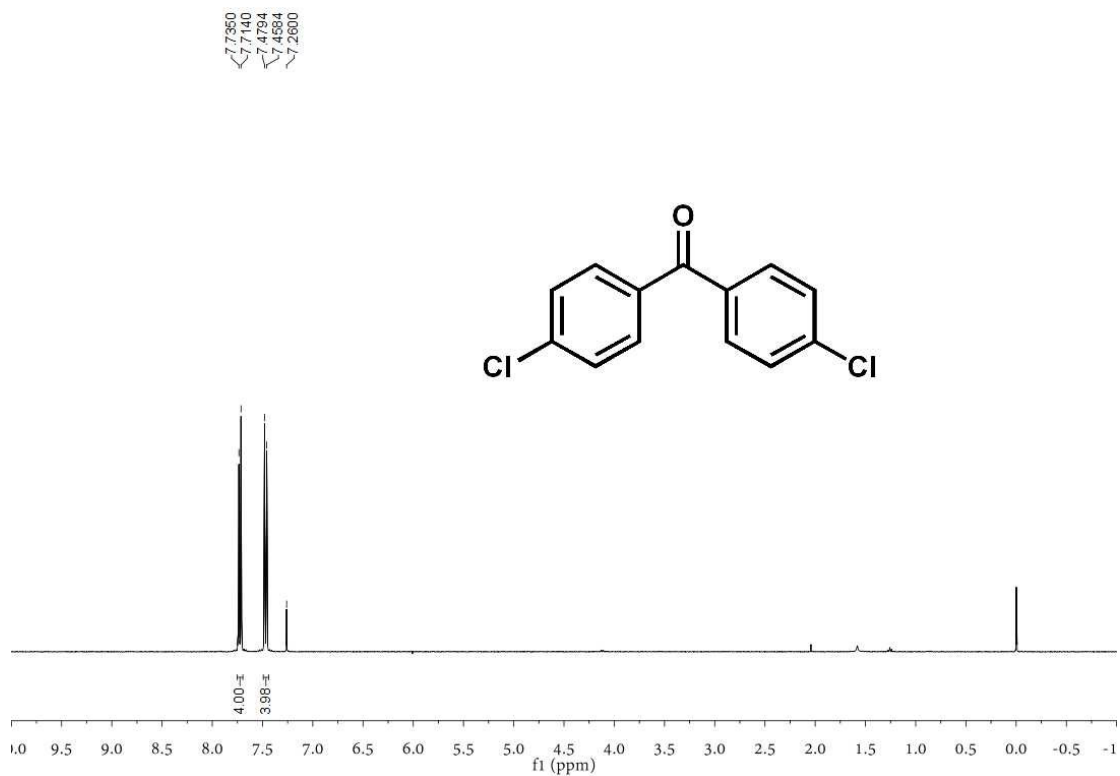
¹H NMR of product 2b in CDCl₃ (400 MHz)



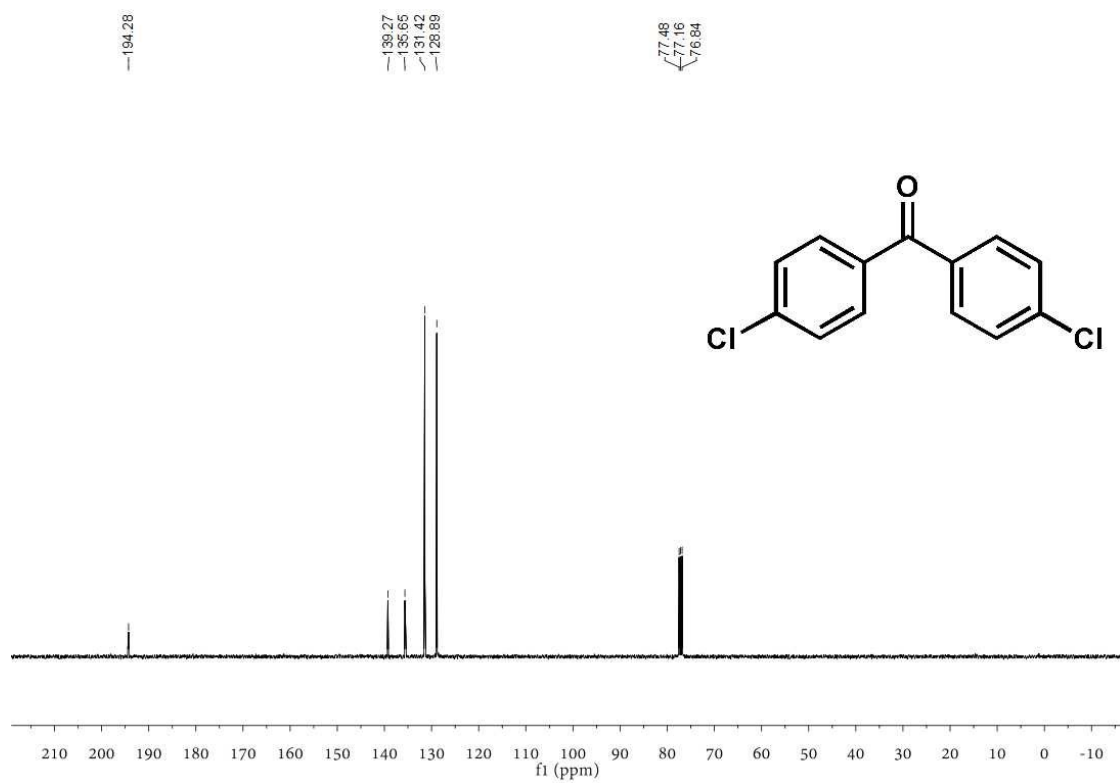
¹³C NMR of product 2b in CDCl₃ (100 MHz)



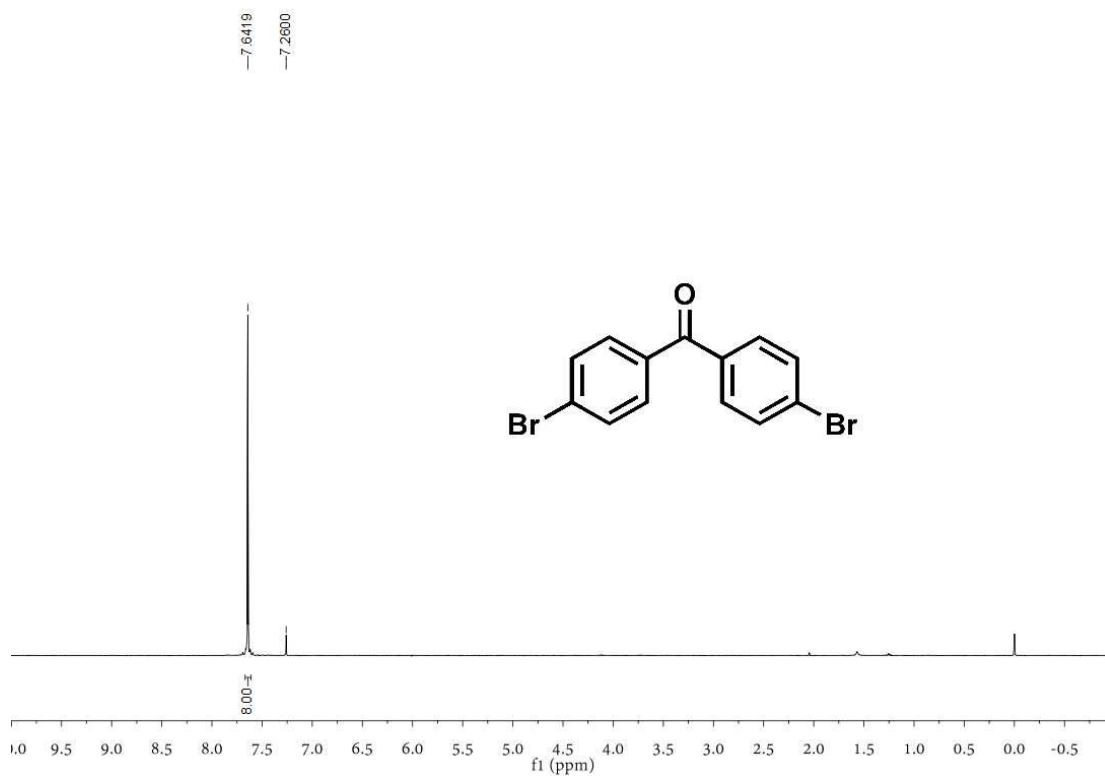
¹H NMR of product 2c in CDCl₃ (400 MHz)



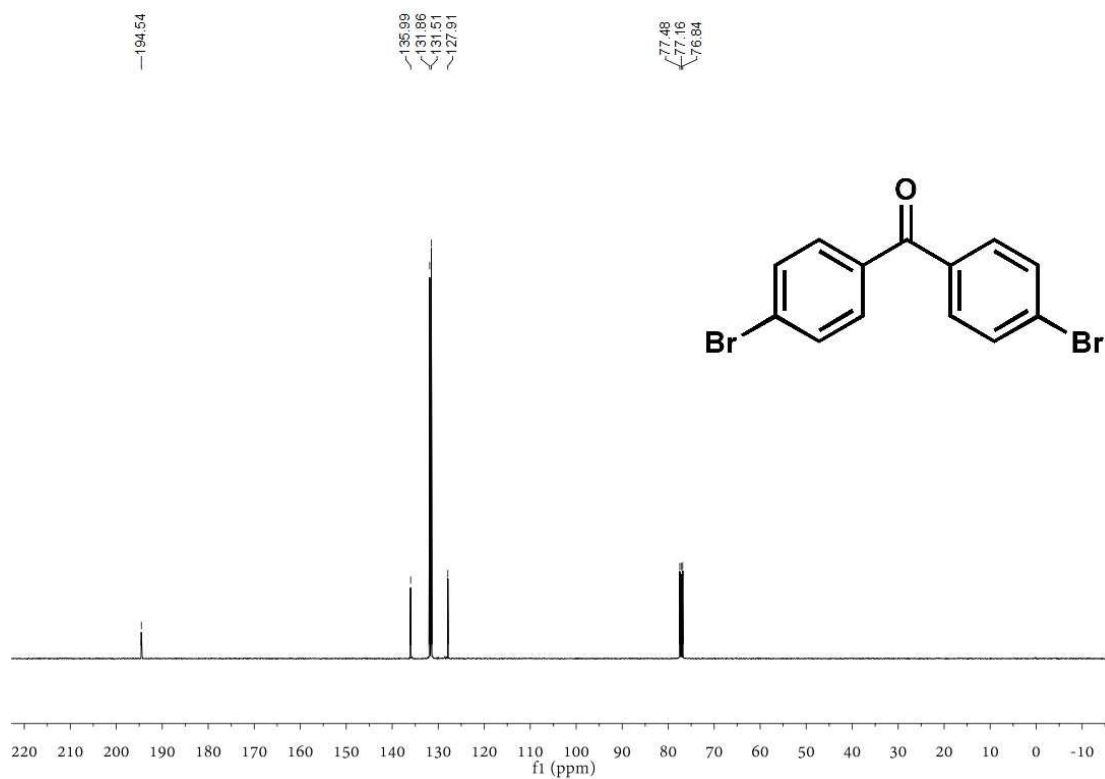
¹³C NMR of product 2c in CDCl₃ (100 MHz)



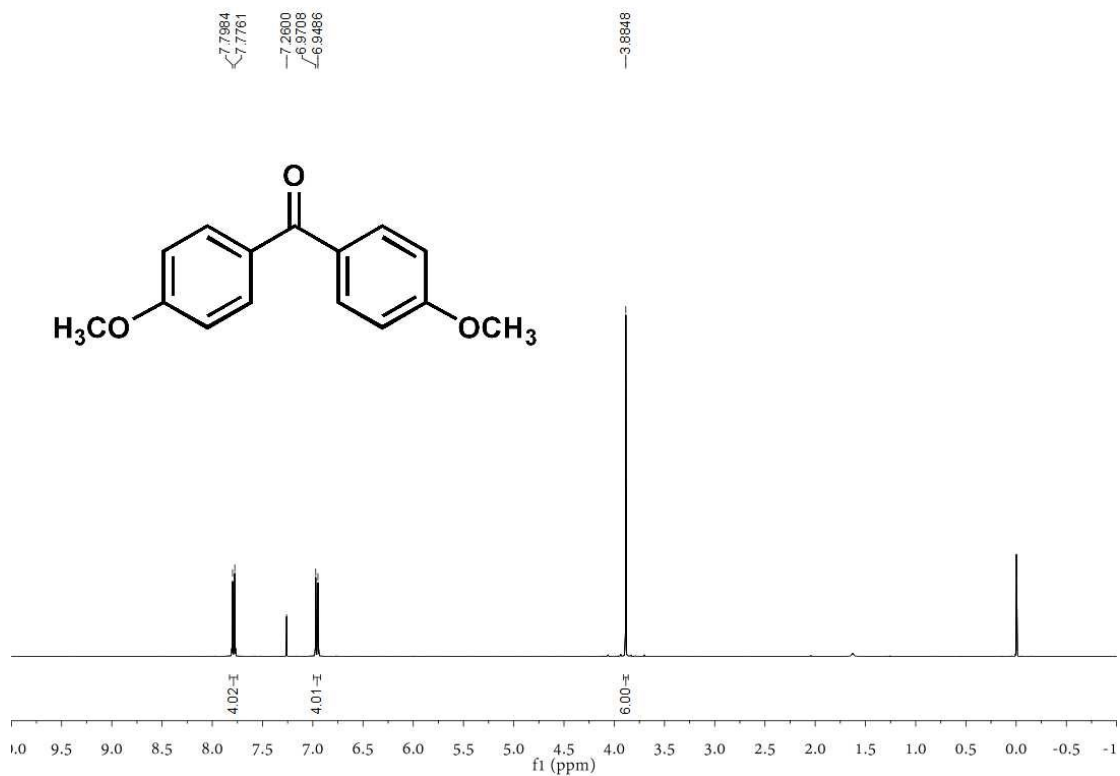
¹H NMR of product 2d in CDCl₃ (400 MHz)



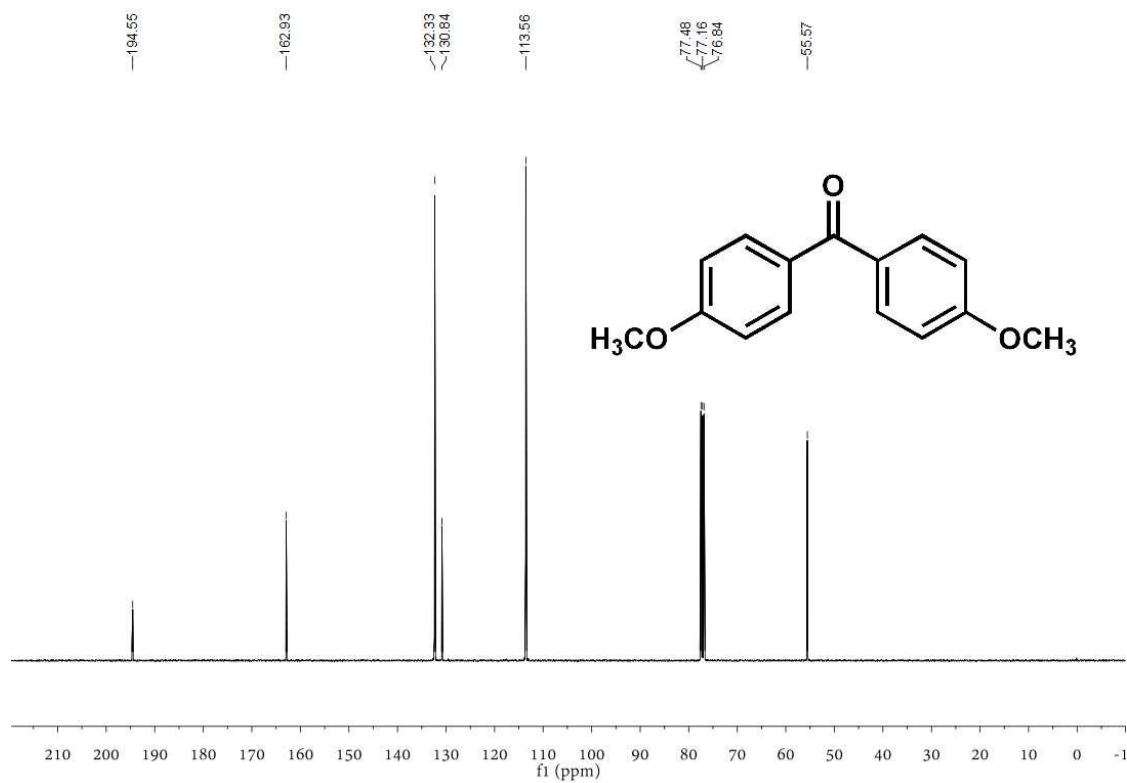
¹³C NMR of product 2d in CDCl₃ (100 MHz)



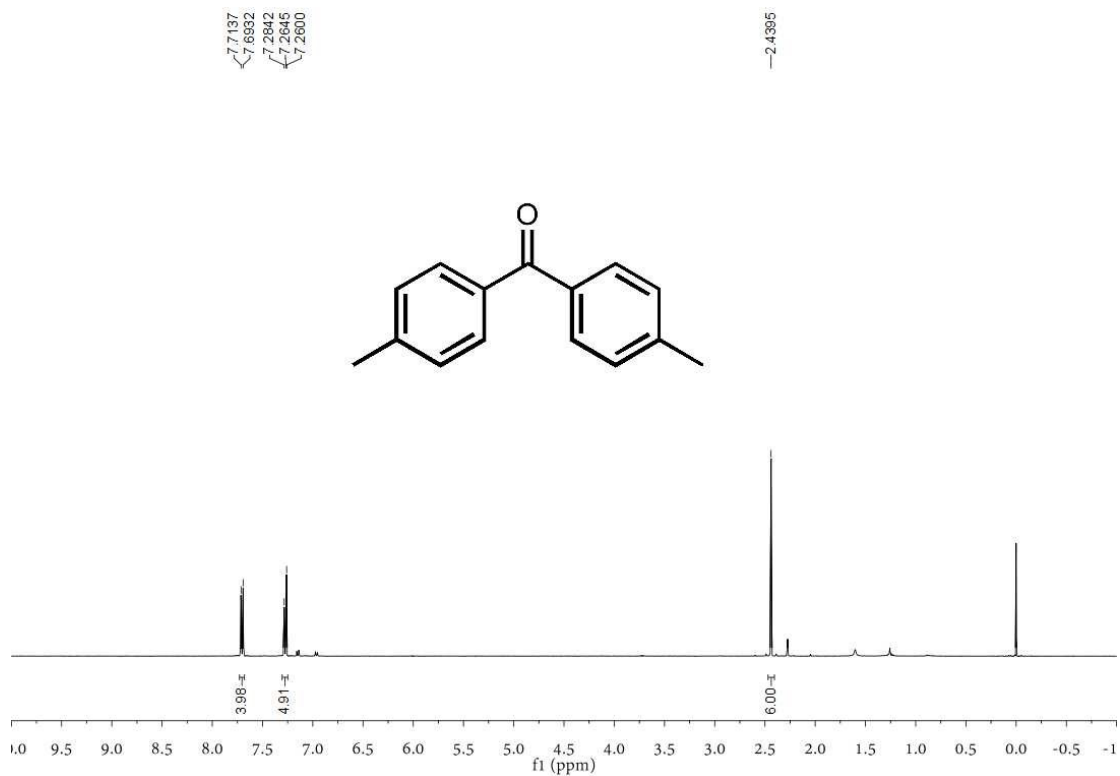
¹H NMR of product 2e in CDCl₃ (400 MHz)



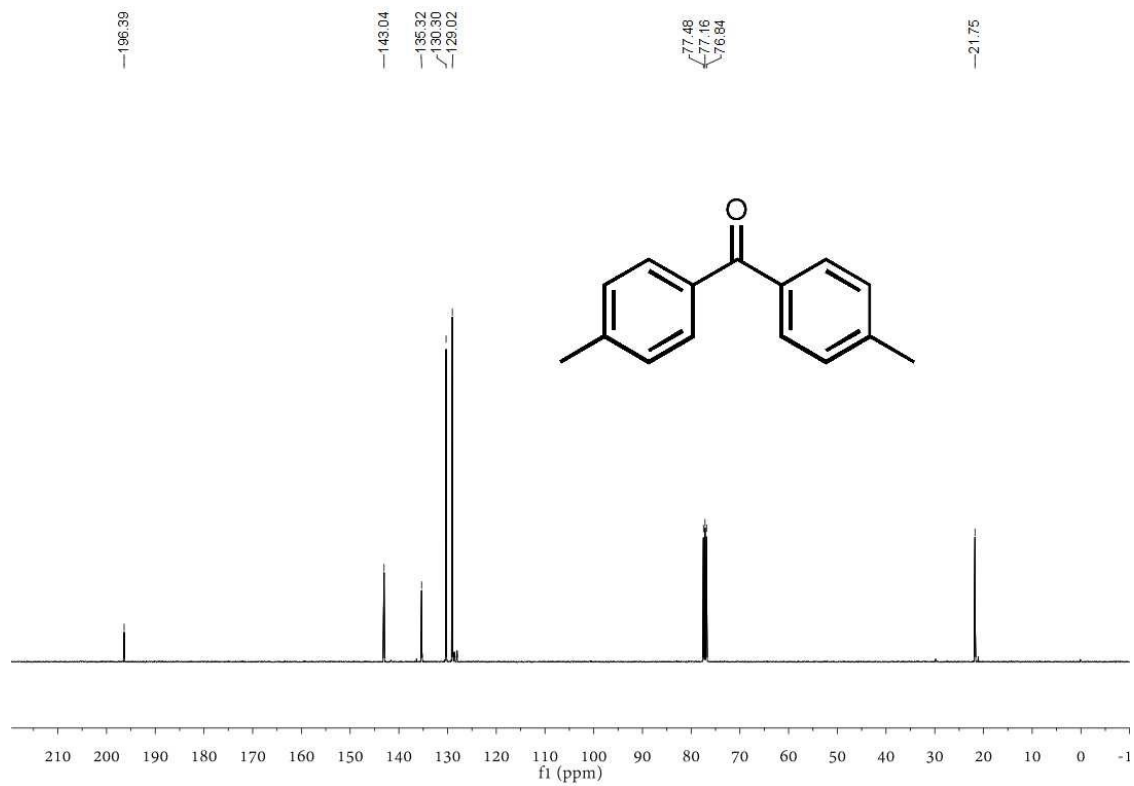
¹³C NMR of product 2e in CDCl₃ (100 MHz)



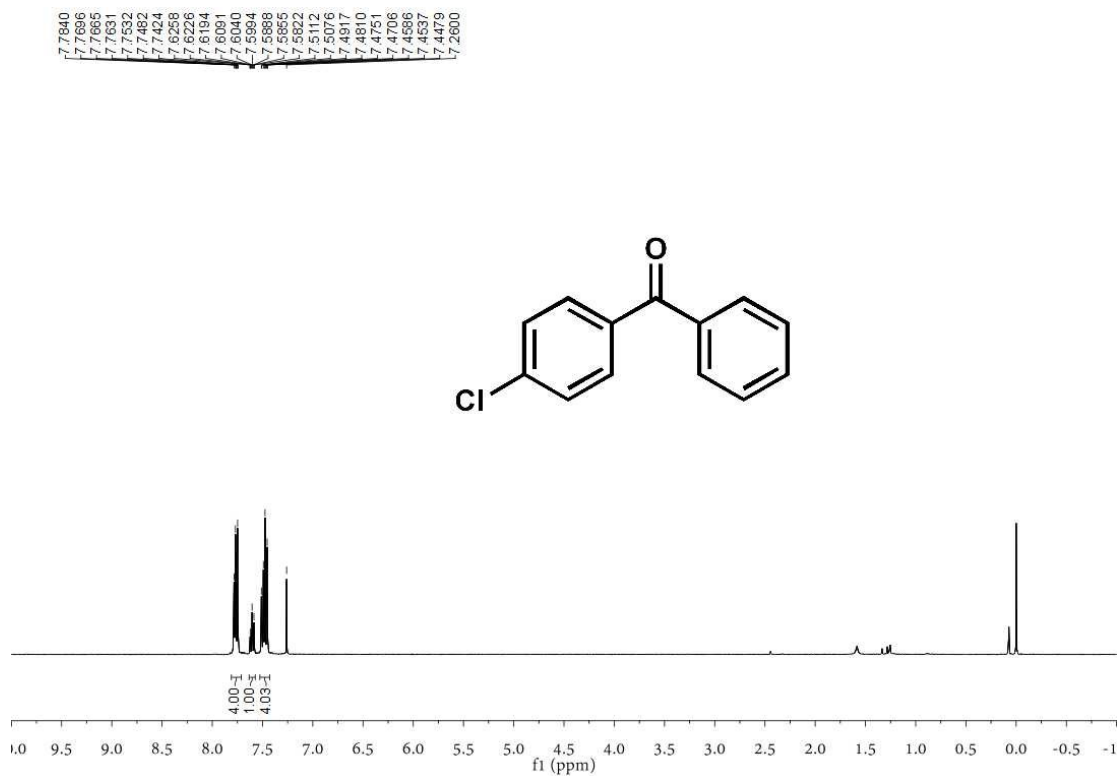
¹H NMR of product 2f in CDCl₃ (400 MHz)



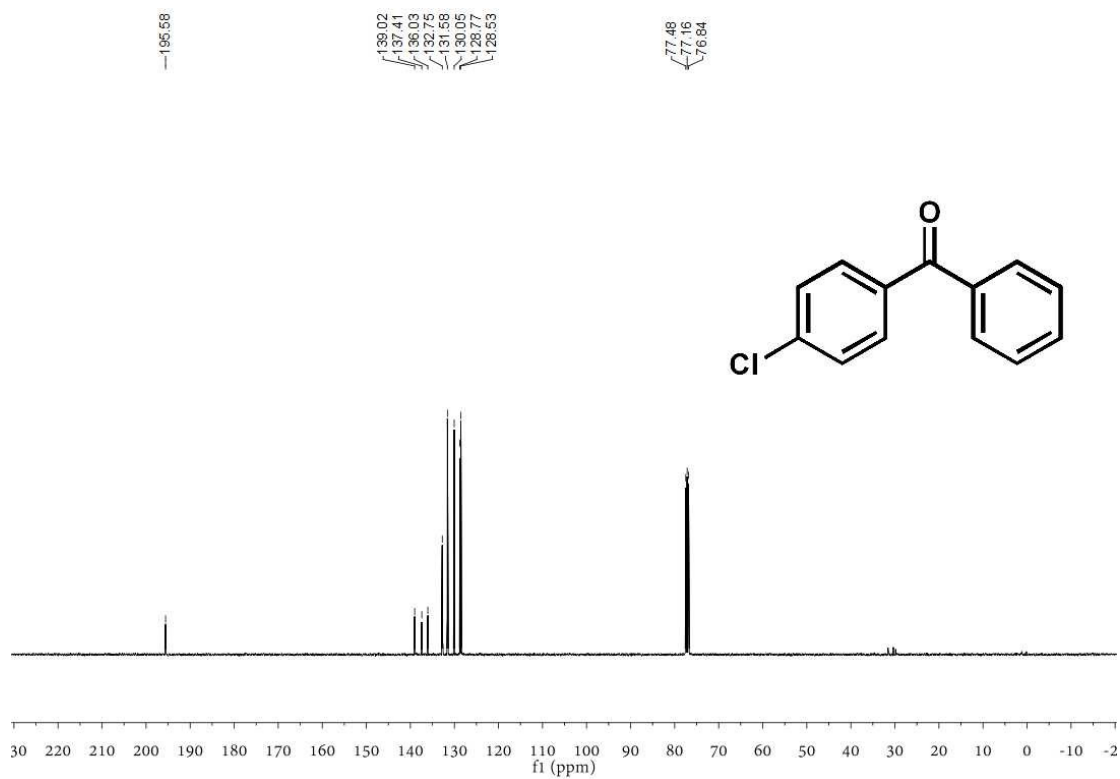
¹³C NMR of product 2f in CDCl₃ (100 MHz)



¹H NMR of product 2h in CDCl₃ (400 MHz)

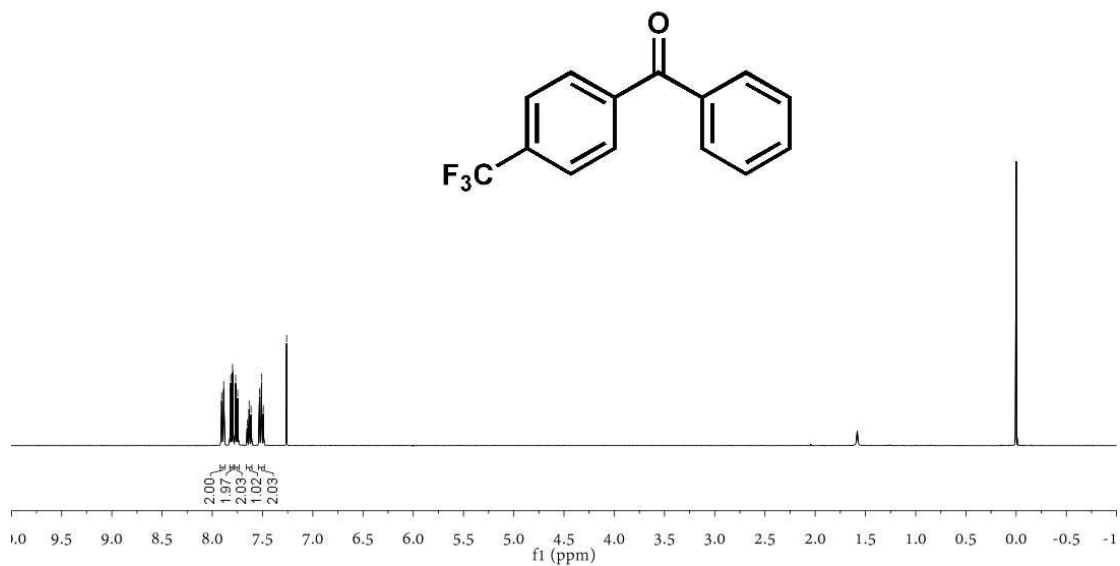


¹³C NMR of product 2h in CDCl₃ (100 MHz)

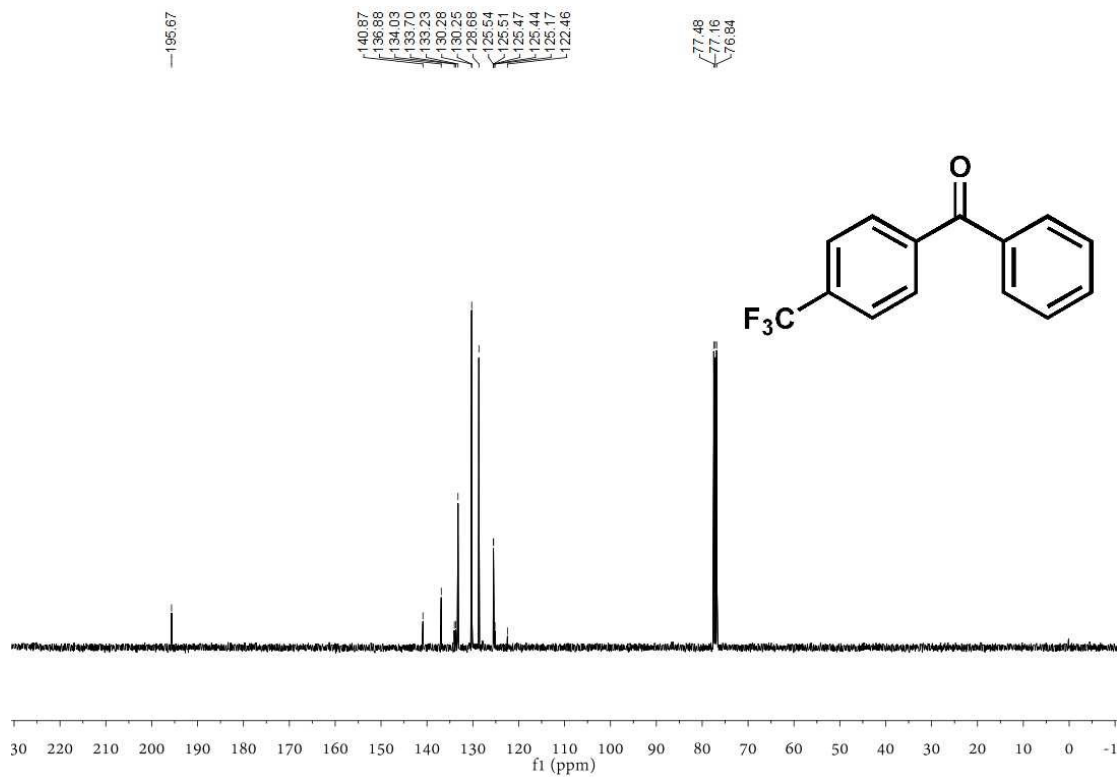


¹H NMR of product 2i in CDCl₃ (400 MHz)

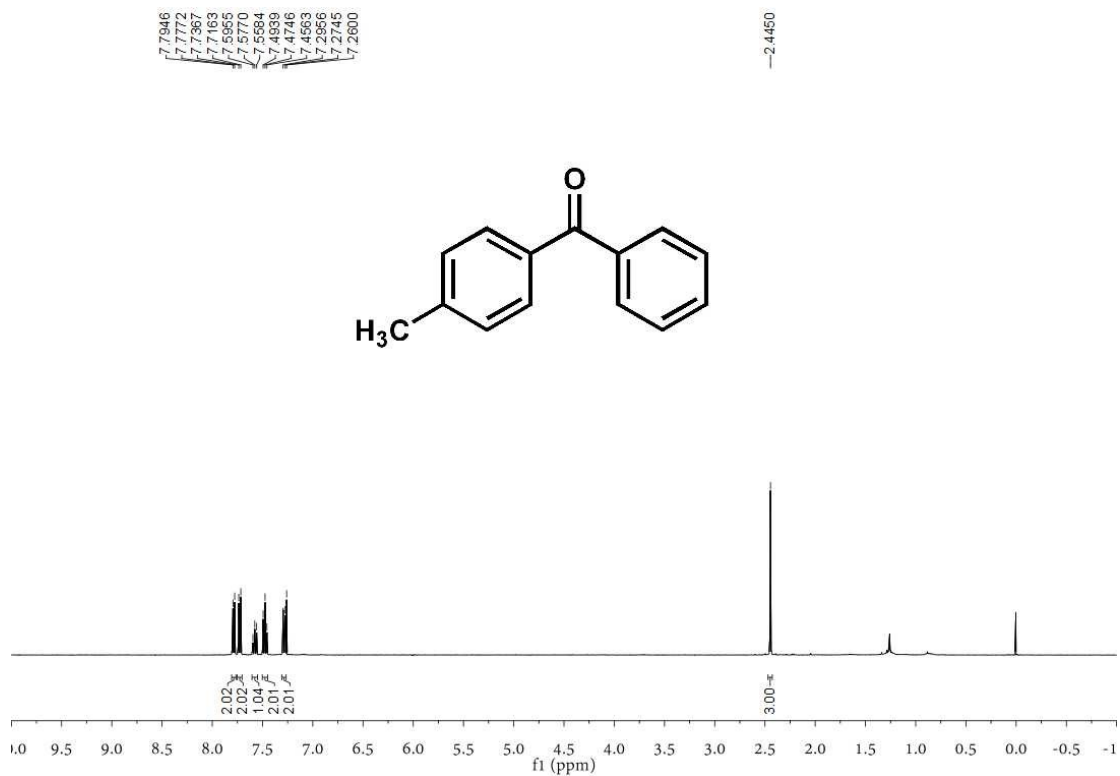
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7.4821
7.4862
7.2600



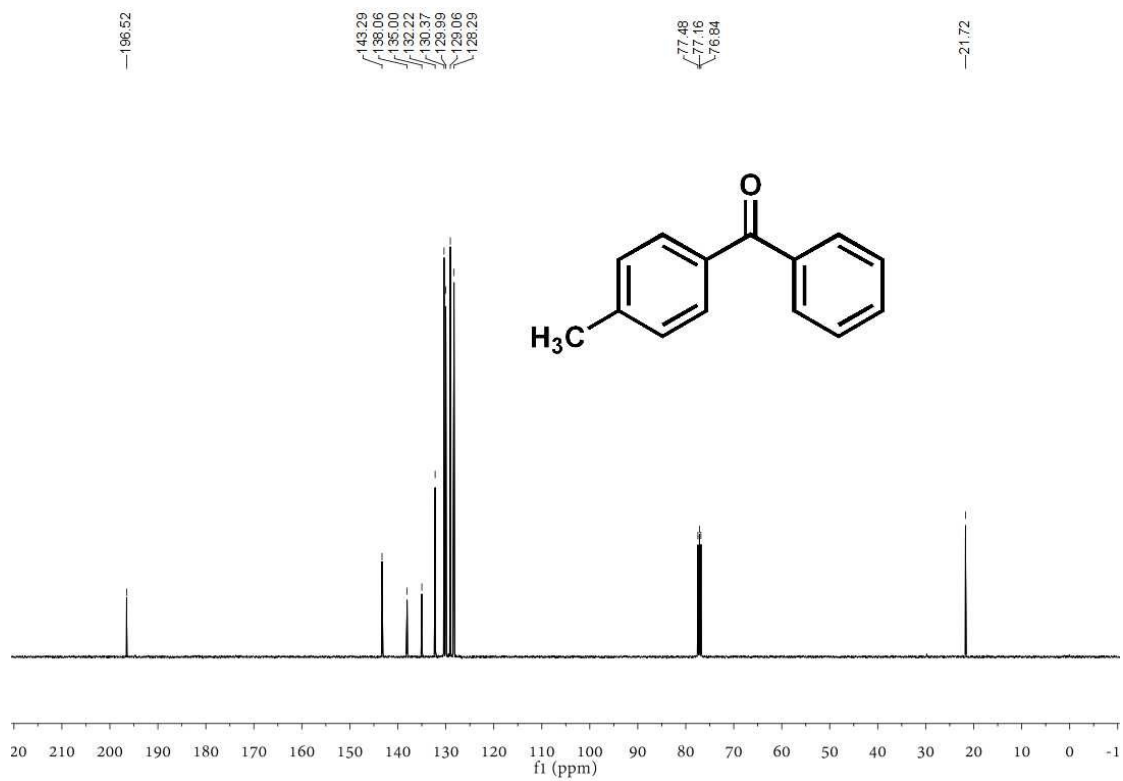
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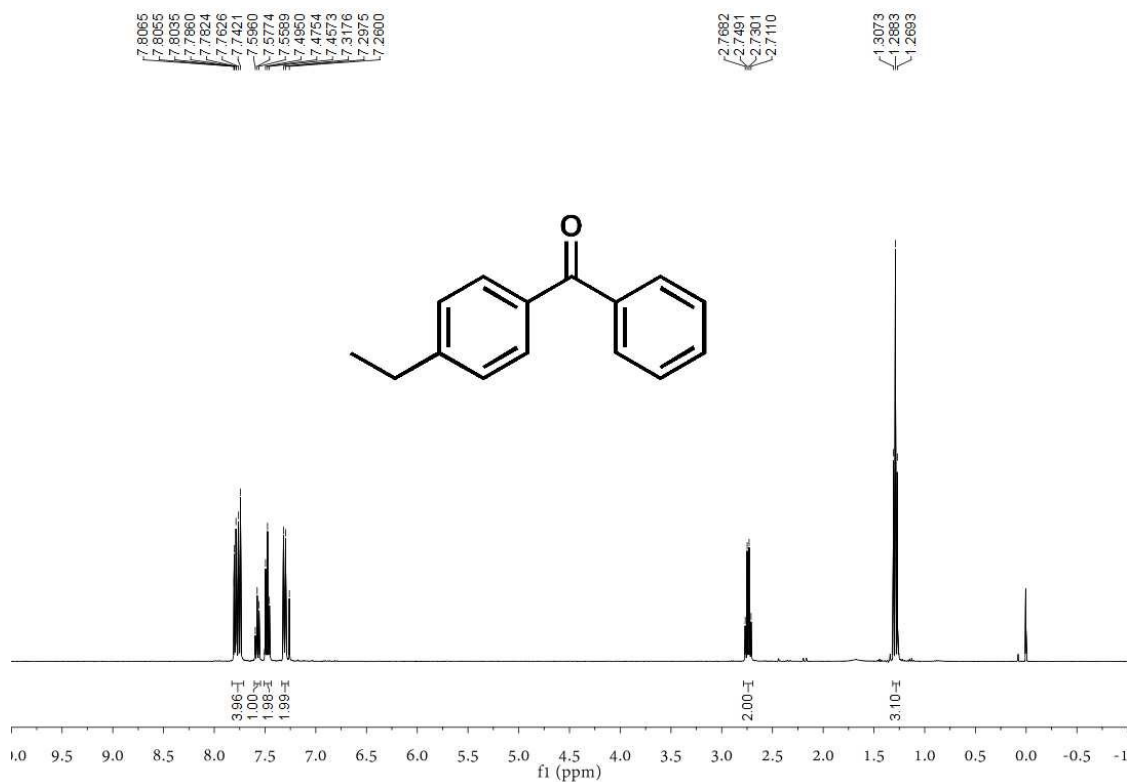
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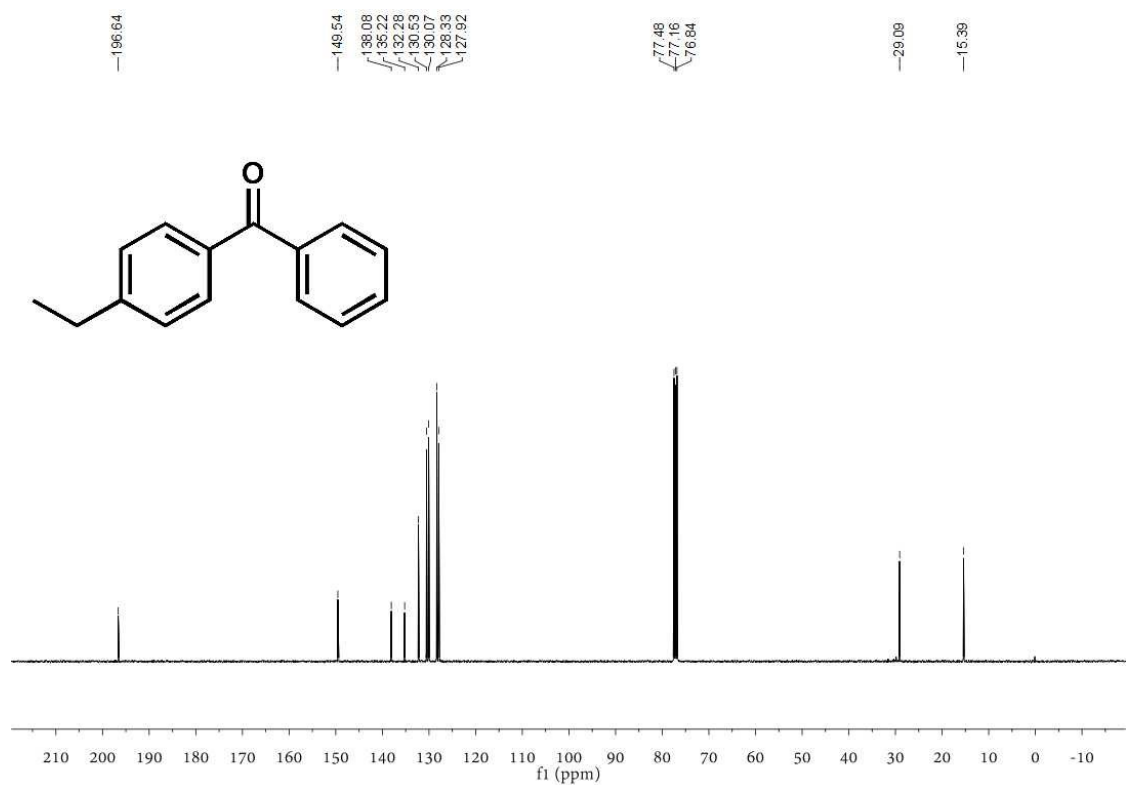
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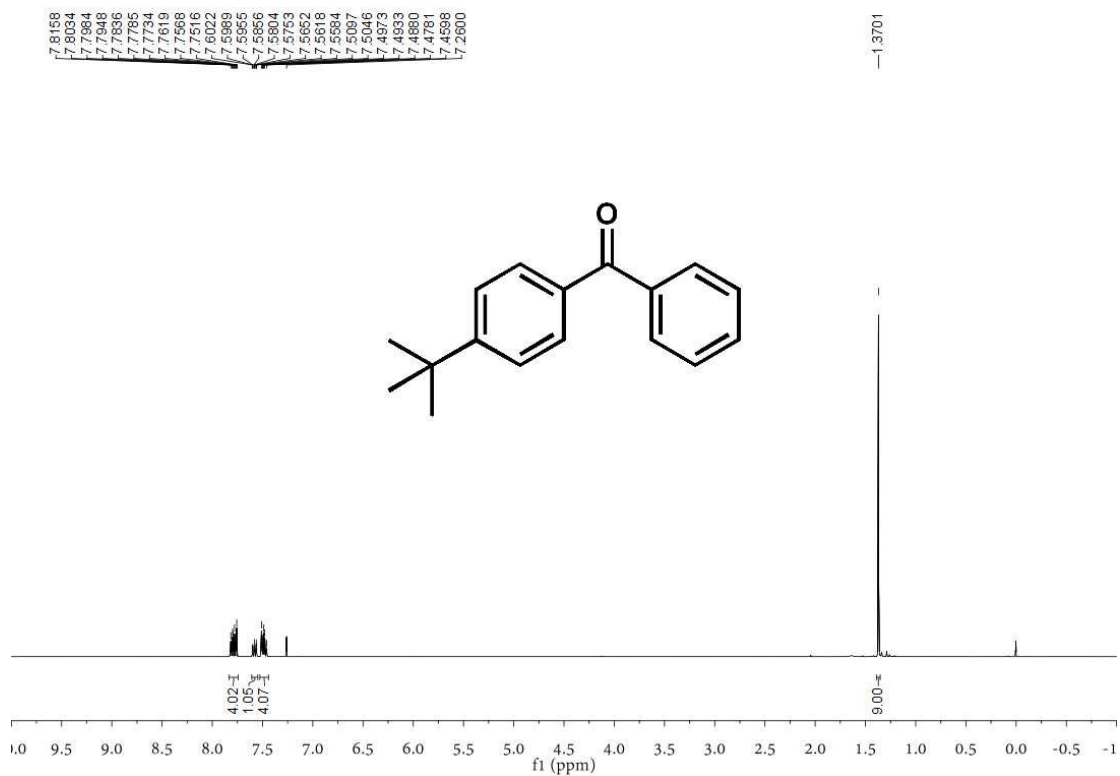
¹H NMR of product 2k in CDCl₃ (400 MHz)



¹³C NMR of product 2k in CDCl₃ (100 MHz)



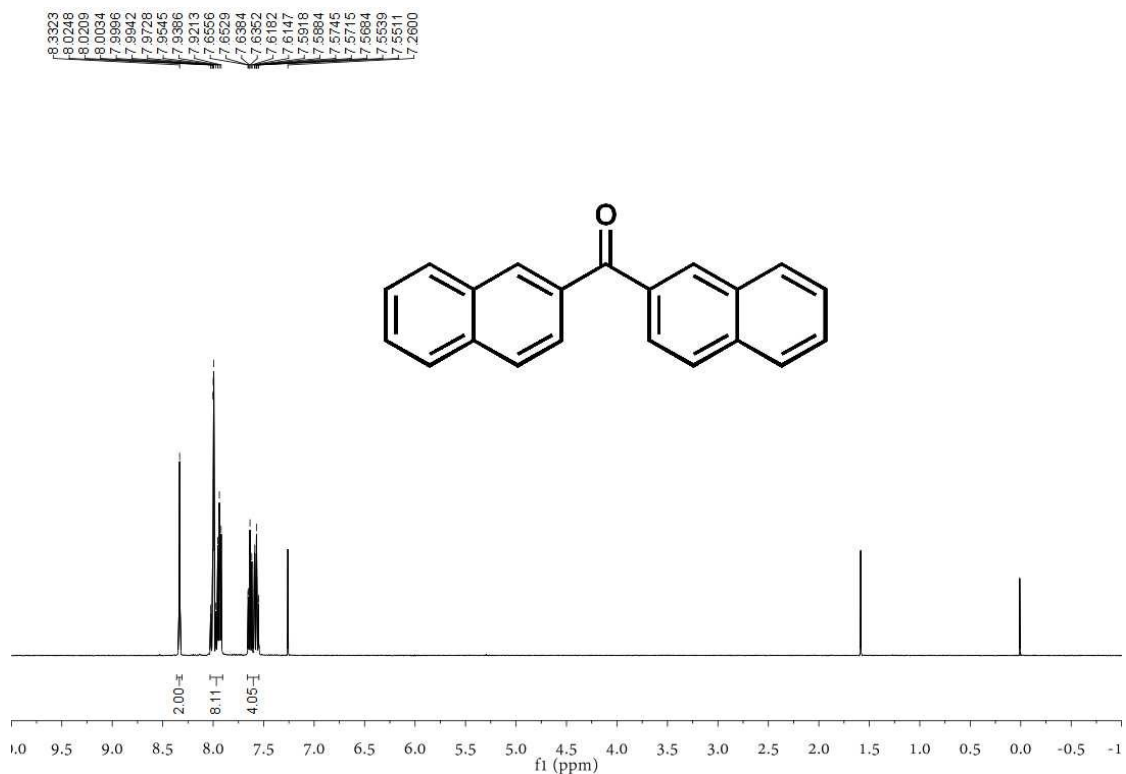
¹H NMR of product 2l in CDCl₃ (400 MHz)



¹³C NMR of product 2l in CDCl₃ (100 MHz)



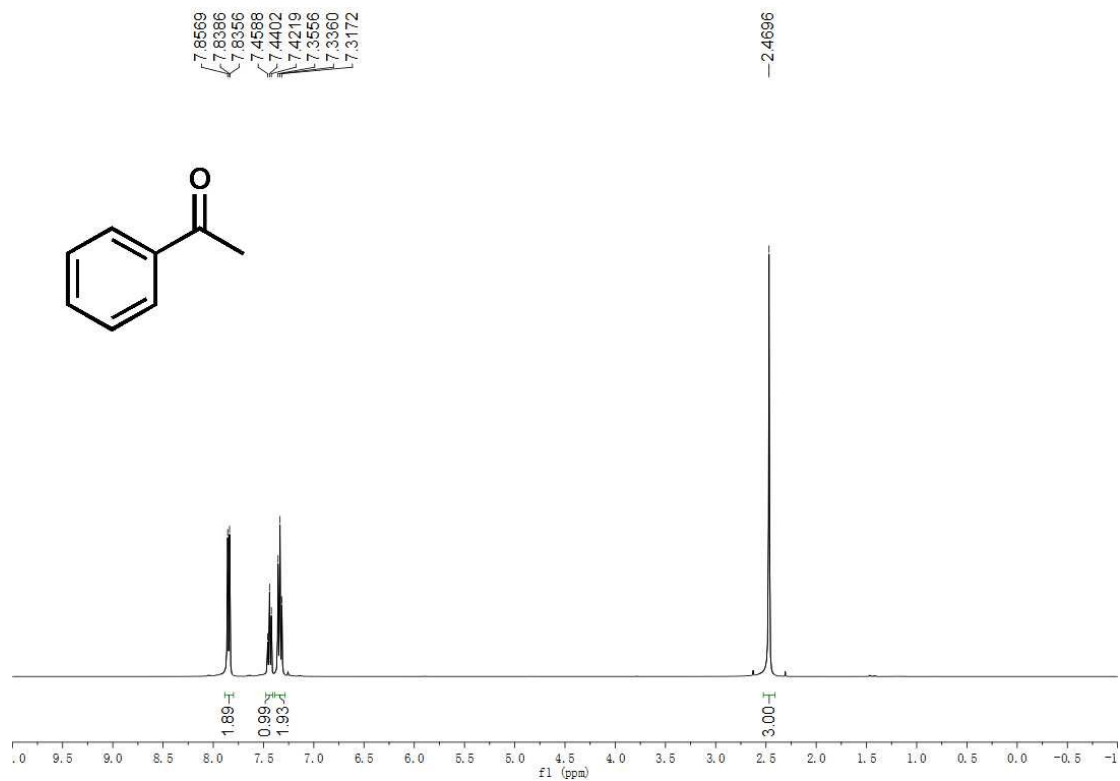
¹H NMR of product 2n in CDCl₃ (400 MHz)



¹³C NMR of product 2n in CDCl₃ (100 MHz)



¹H NMR of product 2o in CDCl₃ (400 MHz)



¹³C NMR of product 2o in CDCl₃ (100 MHz)

