Heterogeneous Carbon Nitrides Photocatalysis C-C Bond Oxidative Cleavage of Vicinal Diols in Aerobic Micellar Medium

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General Methods

All chemicals were commercially available and used without further purification. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm). The plates were visualized by exposure to ultraviolet light. ^{1}H NMR spectra were recorded on Bruker DRX (400 MHz) and ^{13}C NMR spectra on Bruker DRX (100 MHz) spectrometer. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. X-ray diffraction (XRD) pattern was recorded with a diffractometer (Bruker D8 Advance) using Cu Ka radiation. The catalysts were examined at room temperature at a range of 10-80° on 2θ. The N_2 adsorption–desorption isotherms were measured using a Quantachrome Autosorb iQ instrument. UV–vis di□use reflectance spectroscopy (UV–vis DRS) of the samples were measured using a UV-3600 plus spectrometer (Shimadzu, Japan) and the spectra were collected at 300–800nm using $BaSO_4$ as a reference.

Experimental Section

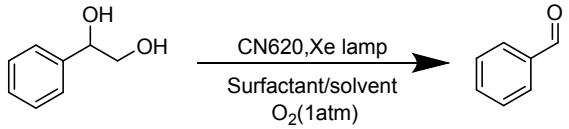
Table S1 Optimization of reaction conditions for internal 1,2-diols

Entry	Catalyst	solvent	Conv./%	Sel./%[b]
1	CN620 (20 mg)	CH_3OH	87	70
2	CN620 (20 mg)	MeCN	82	73
3	CN620 (20 mg)	CH_2Cl_2	32	57
4	CN620 (20 mg)	DMF	76	43
5	p-g-C_3N_4 (20 mg)	CH_3OH	88	55
6	Fe_2O_3@g-C_3N_4 (20 mg)	CH_3OH	78	50
7	CuO@g-C_3N_4 (20 mg)	CH_3OH	82	52
8	Acr^+–Mes (2 mol%)	CH_3OH	100	37
9	Eosin Y (2 mol%)	CH_3OH	74	68
10	$Ru(bpy)_3Cl_2$ (2 mol%)	CH_3OH	40	100
11	Rhodamine B (2 mol%)	CH_3OH	51	53
12	CN620 (20 mg)	H_2O	8	75
13	CN620 (20 mg)	2wt% Brij L4/H_2O	84	90
14	CN620 (20mg)	2wt% Brij O20/H_2O	62	13
15	CN620 (20mg)	2wt% Brij C20/H_2O	74	66
16	CN620 (20mg)	2wt% Brij SDS/H_2O	66	47
17	CN620 (20mg)	2wt% CTAB/H_2O	94	90
18	CN620 (20mg)	1wt% CTAB/H_2O	92	77
19	CN620 (20mg)	4wt% CTAB/H_2O	86	90
20	CN620 (30mg)	2wt% CTAB/H_2O	95	79

21[c]	CN620 (20mg)	2wt% CTAB/H_2O	84	85
22	p-g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	84	61
23	Fe_2O_3@g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	73	54
24	CuO@g-C_3N_4 (20 mg)	2wt% CTAB/H_2O	80	63
25	Acr+–Mes (2 mol%)	2wt% CTAB/H_2O	Trace	-
26	Eosin Y (2 mol%)	2wt% CTAB/H_2O	Trace	-
27	$Ru(bpy)_3Cl_2$ (2 mol%)	2wt% CTAB/H_2O	Trace	-
28	Rhodamine B (2 mol%)	2wt% CTAB/H_2O	Trace	-
29	NO	2wt% CTAB/H_2O	NR	NR
30[d]	CN620 (20mg)	2wt% CTAB/H_2O	NR	NR

[a] Reaction conditions: substrate **1a** (1 mmol), CN620 under Xe lamp (250 W) irradiation or homogeneous PC under blue LED (5W), at room temperature, solvent (3 mL), O_2 atmosphere, reaction for 5 hours. [b] Conversion and selectivity determined by HPLC. [c] reaction carried out at open air. [d] reaction without light.

Table S2 Optimization of reaction conditions for monosubstituted 1,2-diols

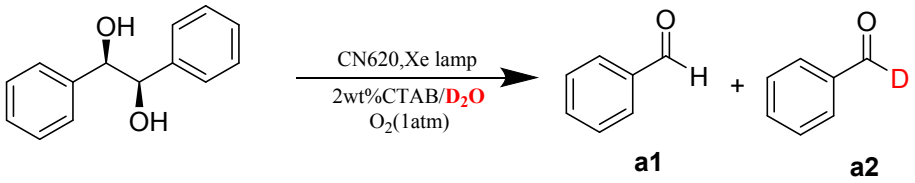


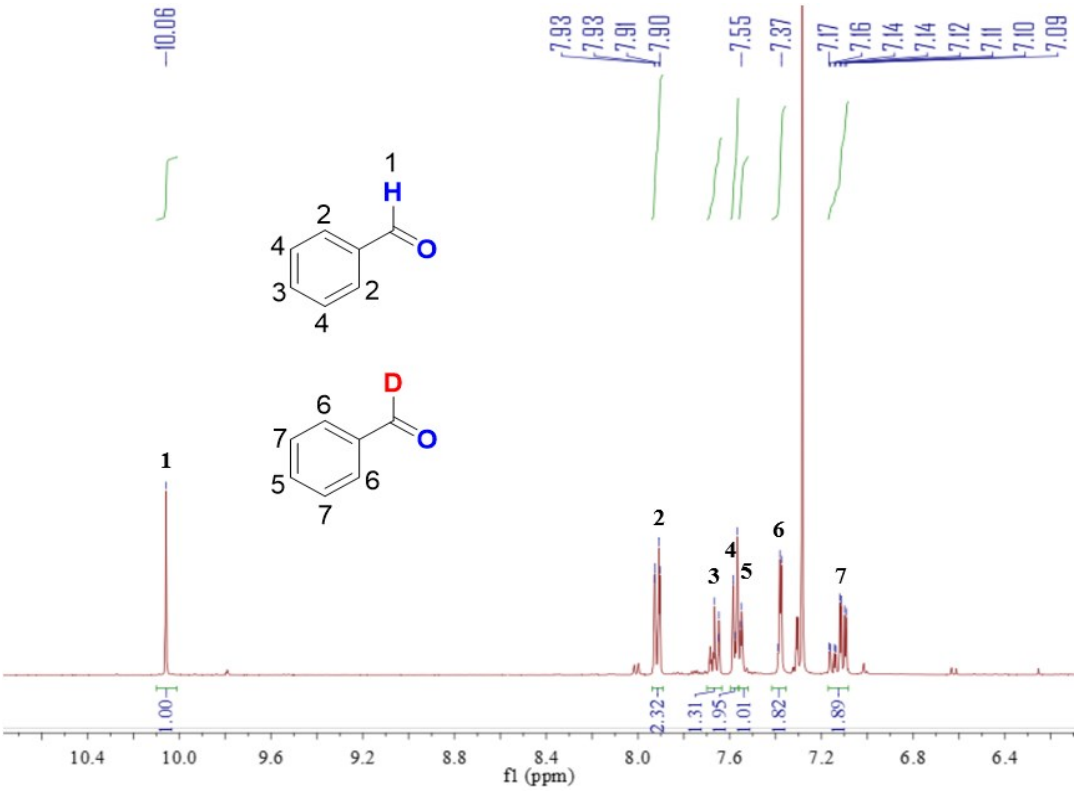
3a **2a**

Entry	Base (eq)	Surfactant/solvent	Conversion/%	Yield(%)[b]
1	—	CH_3CN: H_2O(1:1)	83	37
2	Na_2CO_3 (2)	CH_3CN: H_2O(1:1)	71	68
3	$NaHCO_3$ (2)	CH_3CN: H_2O(1:1)	37	37
4	$CaCO_3$ (2)	CH_3CN: H_2O(1:1)	58	21
5	Cs_2CO_3 (2)	CH_3CN: H_2O(1:1)	46	43
6	Na_2CO_3 (1)	CH_3CN: H_2O(1:1)	53	42
7	Na_2CO_3 (4)	CH_3CN: H_2O(1:1)	36	12
8	Na_2CO_3 (4)	H_2O	Trace	Trace
9	Na_2CO_3 (2)	2wt%CTAB/H_2O	78	78
10	Na_2CO_3 (2)	2wt%Brij L4/H_2O	88	88
11	Na_2CO_3 (2)	2WT% Brij C20/H_2O	68	72
12	Na_2CO_3 (2)	2WT% Brij SDS/H_2O	65	63

[a] Reaction conditions: 1-Phenyl-1,2-ethanediol (1mmol), CN620 (20 mg), solvent (3 mL), the reaction filled with oxygen (1 atm), at room temperature, Xe lamp (250 W), 5 h irradiation. [b] Conversion and yield determined by HPLC. [c] reaction carried out at open air. [d] reaction without light.

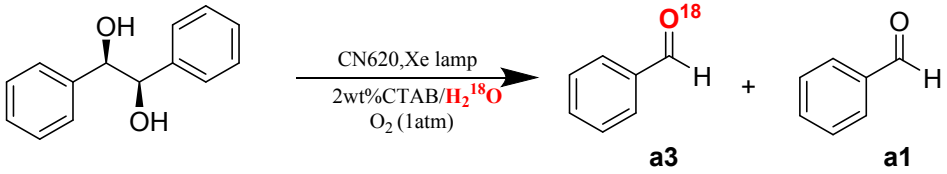
The D_2O isotope experiment.

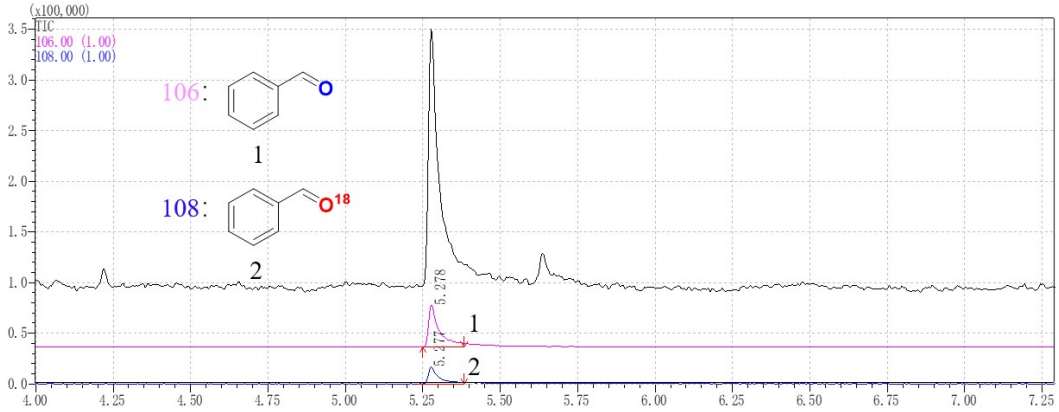




Sa1:Sa2≈1:1.1

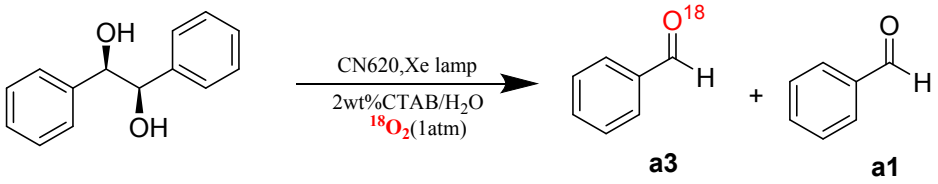
The H_2O^{18} isotope experiment.

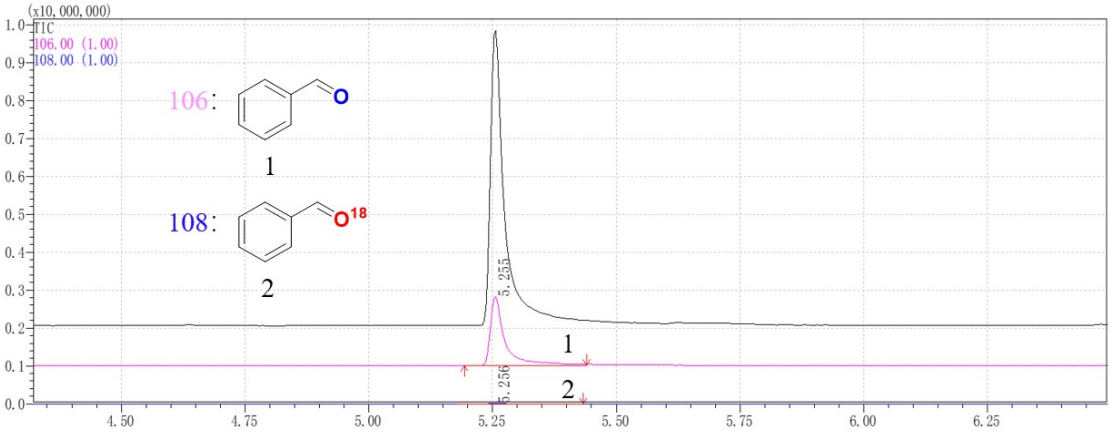




Sa3:Sa1=40282:103381≈1:2.57

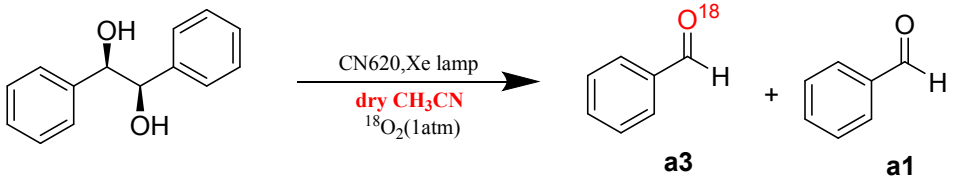
The O_2^{18} isotope experiment.

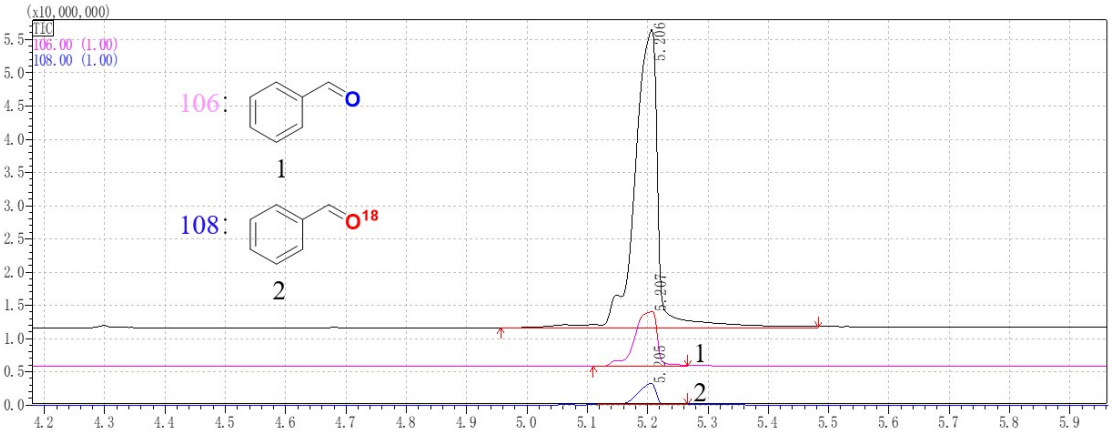




Sa3:Sa1=23496:3752891≈1:159.72

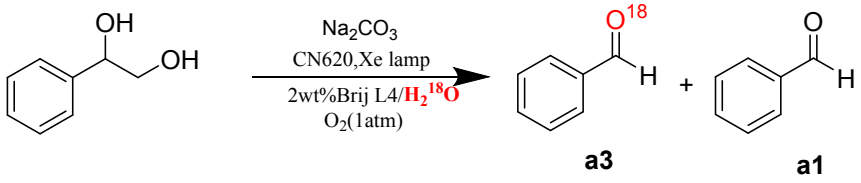
The O_2^{18} isotope experiment in dry CH_3CN.

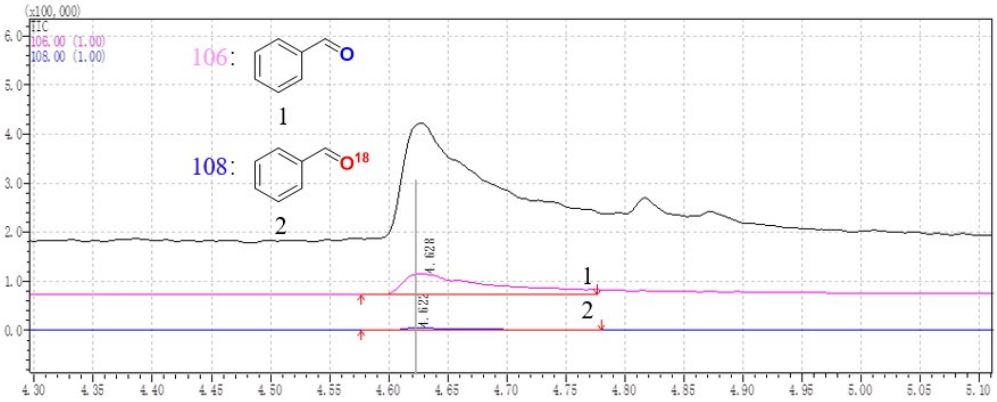




Sa3:Sa1=6925663:21078363≈1:3.04

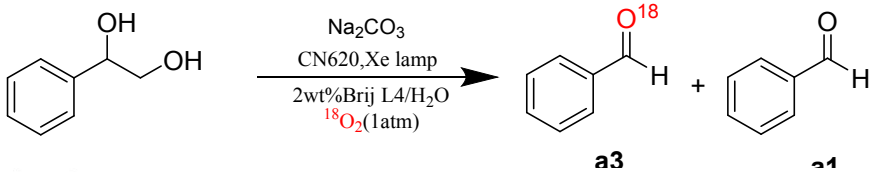
The H_2O^{18} isotope experiment.

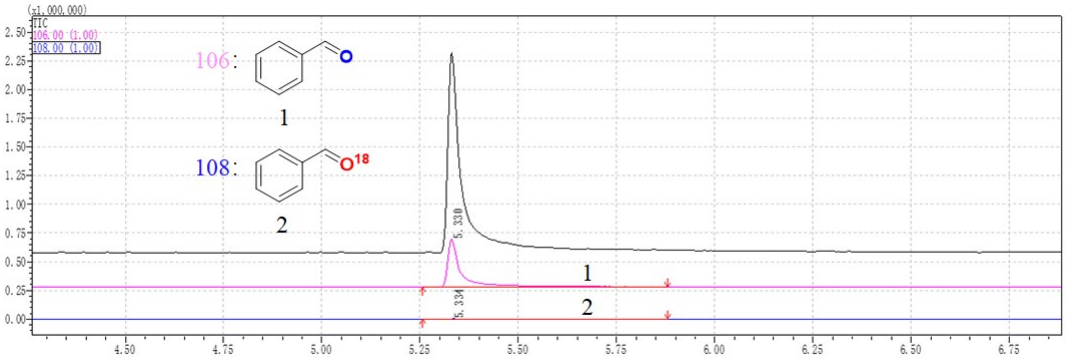




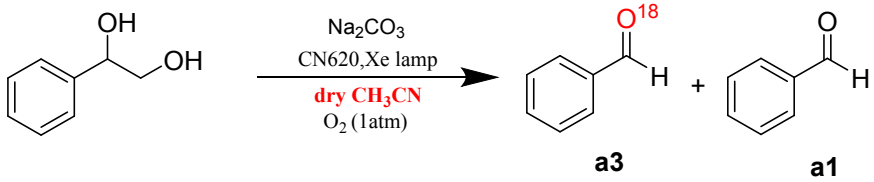
Sa3:Sa1=24237:228890≈1:9.44

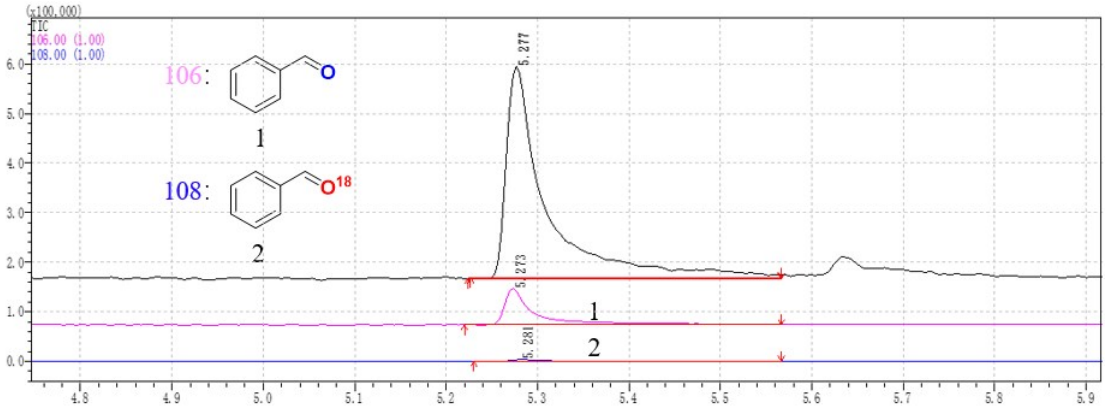
The O_2^{18} isotope experiment.





Sa3:Sa1=11144:2108853≈1:189.2





Sa3:Sa1=11982:177455≈1:14.81

Synthesis of CN620[1]:

5g of dicyandiamide was put into a covered crucible, heated to 500℃ at a ramp rate of 5℃ min^{-1} in a tube furnace under air condition and then maintained at this temperature for additional 4h, noted as CN. 1g of CN was put into a crucible, heated to 620℃ at a ramp rate of 5℃ min^{-1} in a tube furnace under N_2 condition, respectively, and maintained at the corresponding temperature for 2h.

Representative procedure for oxidative cleavage of (R, R)-hydrobenzoin to Benzaldehyde:

A 25 mL reaction vessel with a magnetic stirring bar was equipped with (R, R)-hydrobenzoin (1 mmol), CN620 (20 mg), CTAB (60mg) and distilled water (3 mL). The mixture was irradiated with a Xe lamp (250 W) and stirred at r.t. in an oxygen atmosphere for 5 h. The distance of the reaction vial from the light is about 10 centimeters. After the reaction, the solvent was extracted with EtOAc (3×10mL). The extracted solution was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (5:1~10:1) as eluent.

Representative procedure for oxidative cleavage of 1-phenyl-1,2-ethanediol to benzaldehyde:

A 25 mL reaction vessel with a magnetic stirring bar was equipped with benzaldehyde (1 mmol), CN620 (20 mg), Na_2CO_3 (2 mmol), Brij L4 (60mg) and distilled water (3 mL). The mixture was irradiated with a Xe lamp (250 W) and stirred at r.t. in an oxygen atmosphere for 5 h. The distance of the reaction vial from the light is about 10 centimeters. After the reaction, the solvent was extracted with EtOAc (3×10mL). The extracted solution was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (5:1~10:1) as eluent.

Representative procedure for photocatalyst recycling

A 25 mL reaction vessel with a magnetic stirring bar was equipped with (R, R)-hydrobenzoin (1 mmol), CN620 (20 mg), CTAB (60mg) and distilled water (3 mL). The mixture was irradiated with a Xe lamp (250 W) and stirred at r.t. in an oxygen atmosphere for 5 h. The distance of the reaction vial from the light is about 10 centimeters. Once the reaction was finished, the solvent was extracted with EtOAc (3×6mL). The extracted solution was tested by HPLC. Then another (R, R)-

hydrobenzoin (1 mmol) was added in the separated aqueous medium without fresh portion of surfactant or catalyst for recycle reaction.

Characterization data

Characterization of the catalyst

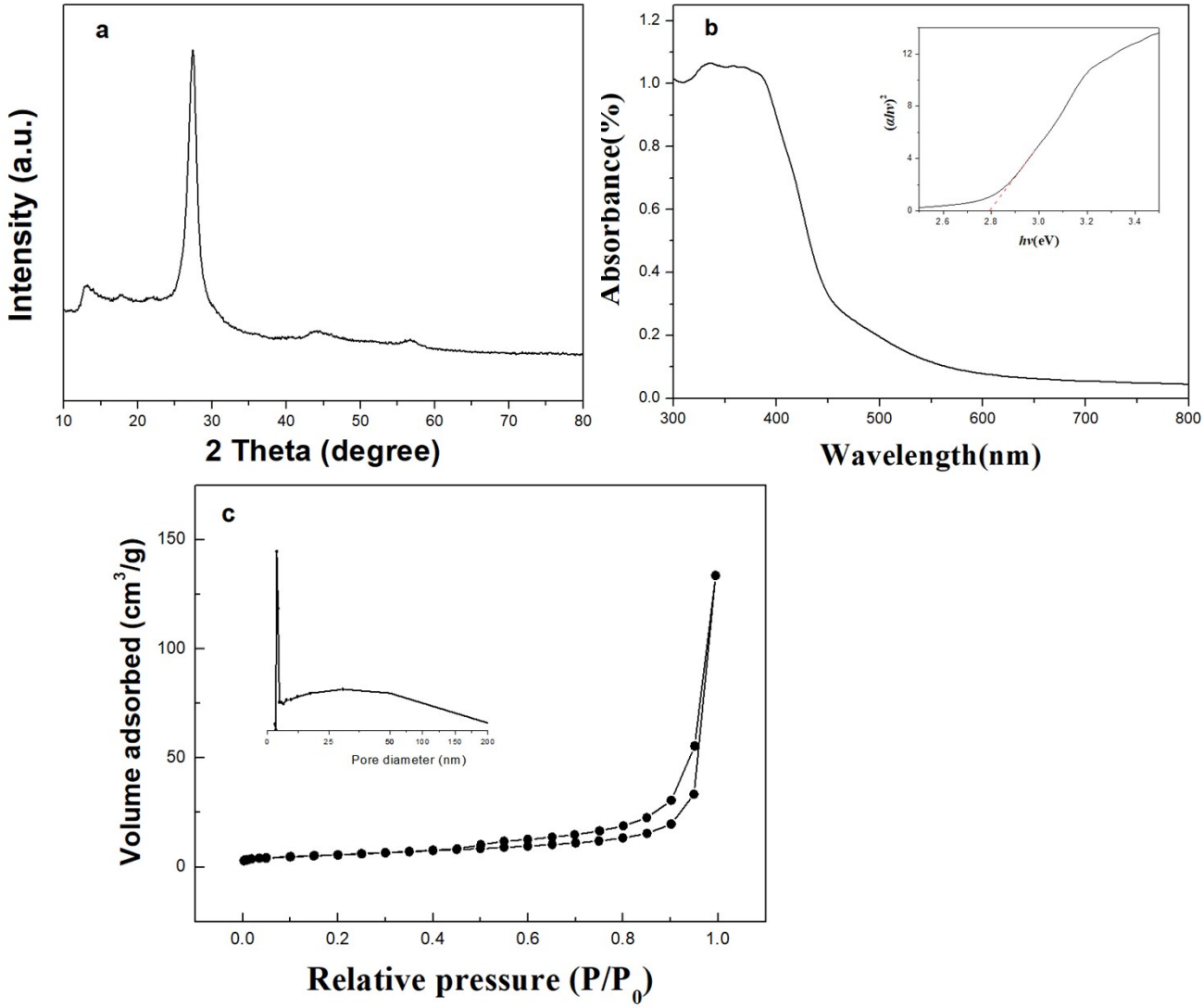


Figure S1. (a) XRD patterns and (b) diffuse reflectance UV-vis spectra (c) Nitrogen adsorption–desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution plots (inset) of CN620.

The XRD patterns of CN620 show two diffraction peaks at 13.2° and 27.4°, which correspond to the (100) and (002) crystal planes of the graphitic carbon nitride, respectively. Figure S1 (b) shows UV–vis diffuse reflectance spectra (DRS) and calculated bandgaps for CN620 samples. The calculated band gaps were approximately2.79 eV for CN620. The Brunauer-Emmett-Teller (BET) specific surface areas of CN620 were calculated to be 19.961 m^2g^{-1}.

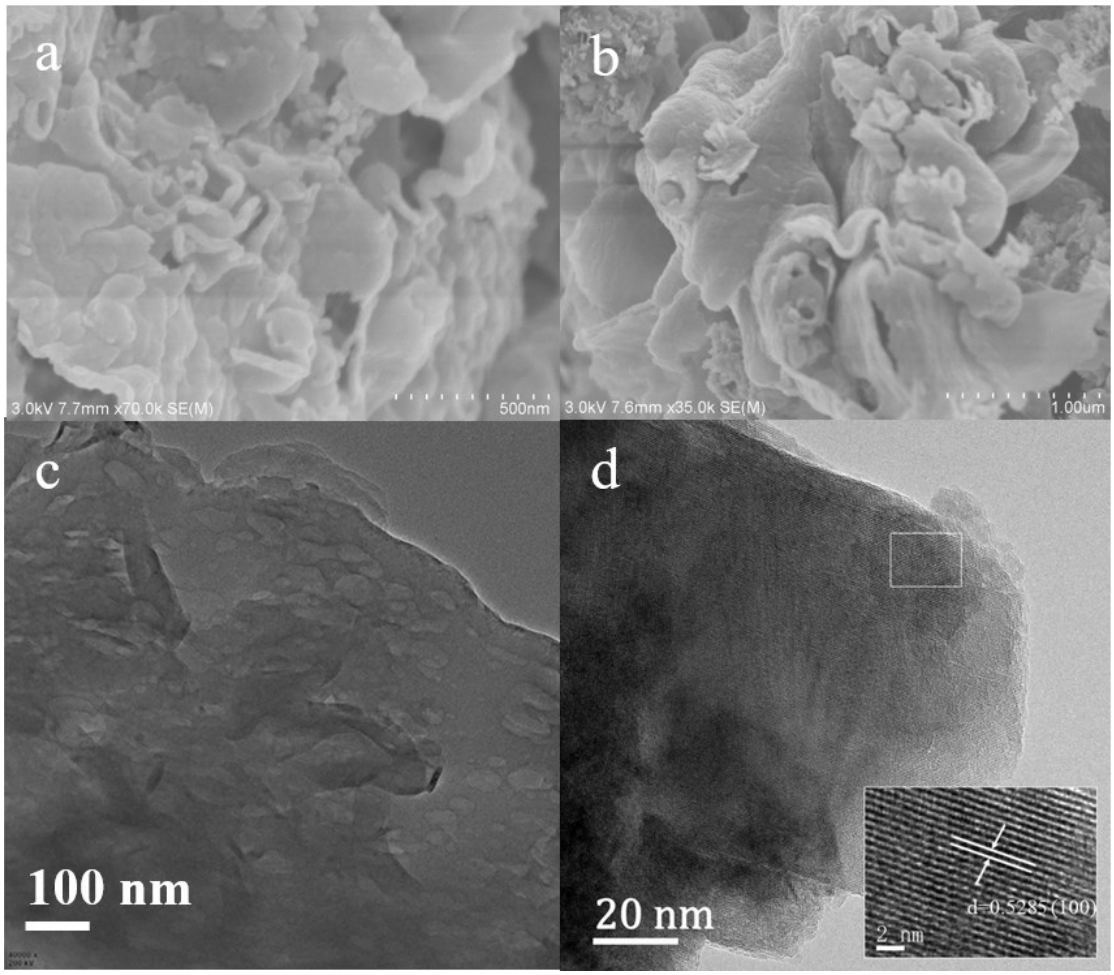


Figure S2. (a,b) SEM, (c) TEM and (d) HRTEM image of CN620.

The morphology of the sample was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). SEM and TEM spectra show that CN620 has a lamellar stacking structure, and some crack holes are generated while stacking. The high-resolution TEM image reveals well-defined lattice fringes with an interplanar spacing of 0.5285 nm, corresponding to the (100) plane of CN620.

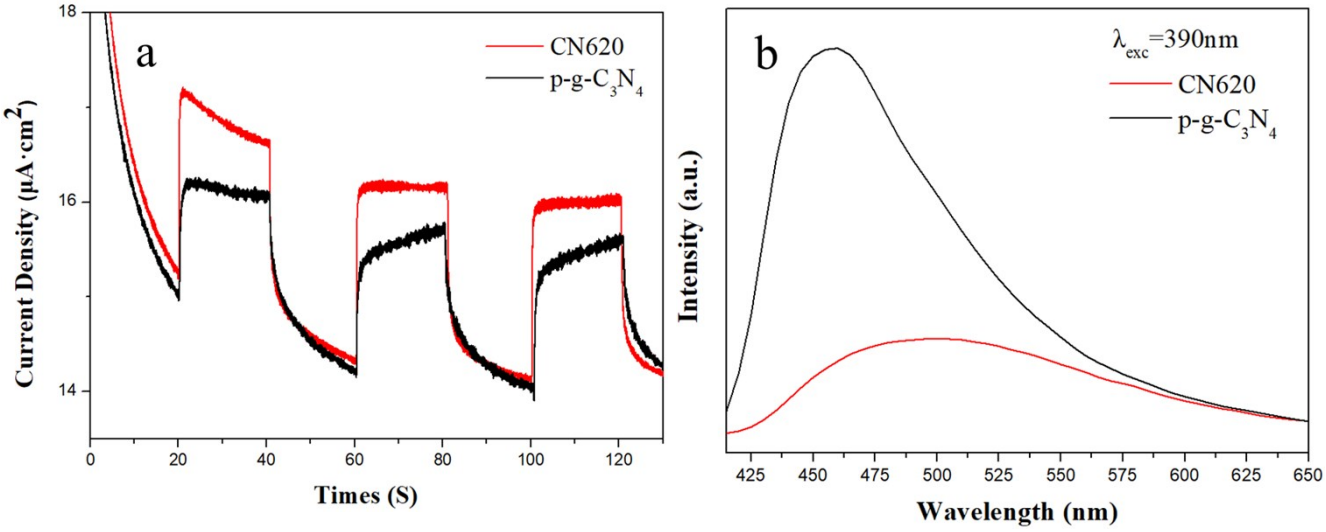


Figure S3. (a) Photocurrent responses and (b) PL emission spectra of CN620.

To prove the positive impact of nitrogen vacancies on separation and transportation of photogenerated electron–hole pairs under irradiation, the periodic on/off photocurrent response was measured over the samples. CN620 enhancement in photocurrent response as compared to p-g-C_3N_4. The charge separation efficiency was also investigated by photoluminescence spectra (PL) at an excitation wavelength of 390 nm. From p-g-C_3N_4 to CN620, the PL intensity is significantly reduced, which indicates that the reorganization of the photogenerated electron-hole pairs of CN620 is reduced compared to p-g-C_3N_4.

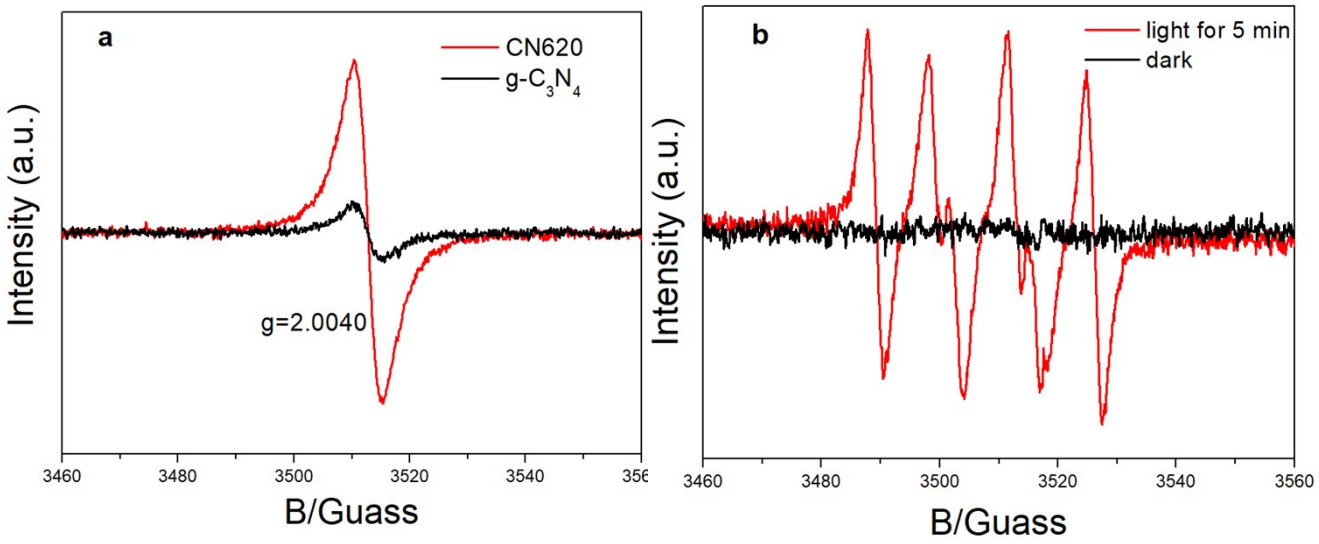


Figure S4. (a) EPR spectra of CN620 and g-C_3N_4. (b) ESR measurement for $^{\bullet}O_2^-$over CN620 composite.

The electron paramagnetic resonance (EPR) spectroscopy can provide fingerprint evidence for probing the surface vacancies in semiconductor photocatalysts.[2] As shown in Figure S4 (a), the EPR signal strength of CN620 is significantly higher than that of g-C_3N_4, revealing the increase of nitrogen vacancies generated in CN620. Figure S4 (b) shows, superoxide radical was detected by electron paramagnetic resonance (ESR).[3]

Characterization of micelles

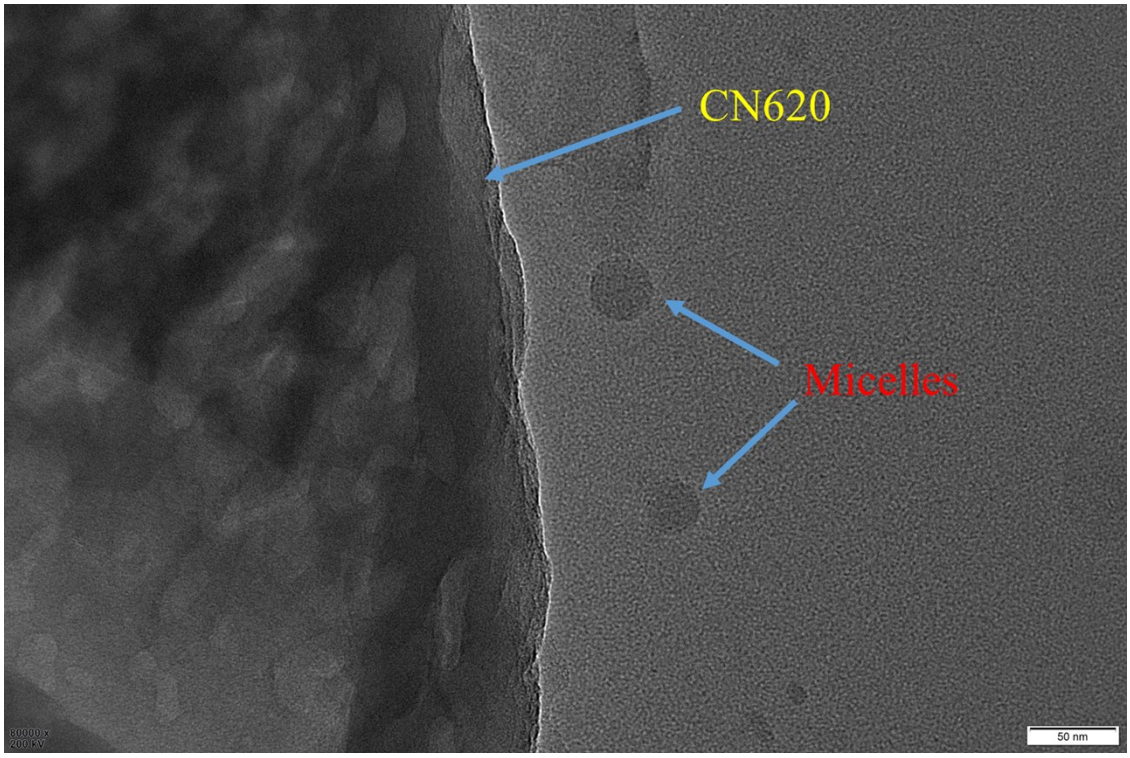


Figure S5. TEM images of CN620 and CTAB mixed solution

As can be seen from TEM, the nature of the micelles formed by CTAB was found to be spherical in shape. TEM also revealed that the micelle size distribution of CTAB aqueous solution is within 50 nm and CN620 is much larger than the micelle size. Therefore, the micelle is probably on the surface of the catalyst rather than the catalyst in the micelle.

Figure S6. The photograph of outdoor equipment of sunlight-driven.

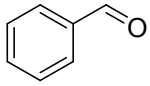
References

1 P. Zhou, X. Hou, Y. Chao, W. Yang, W. Zhang, Z. Mu, J. Lai, F. Lv, K. Yang, Y. Liu, J. Li, J. Ma, J. Luo and S. Guo, *Chem Sci*., 2019, **10**, 5898-5905.

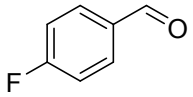
2 W. Tu, Y. Xu, J. Wang, B. Zhang, T. Zhou, S. Yin, S. Wu, C. Li, Y. Huang, Y. Zhou, Z. Zou, J. Robertson, M. Kraft and R. Xu, *ACS Sustainable Chem. Eng*., 2017, **5**, 7260-7268.

3 L. Wang, X. Zhang, X. Yu, F. Gao, Z. Shen, X. Zhang, S. Ge, J. Liu, Z. Gu and C. Chen, *Adv. Mater.*, 2019, **31**, 1901965.

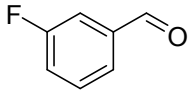
NMR data for characteristic compounds



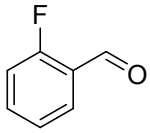
Benzaldehyde (**2a**). Colorless liquid (159mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.97 – 7.84 (m, 2H), 7.70 – 7.58 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 136.4, 134.5, 129.7, 129.0. ESI-MS: m/z =107 $[M+1]^+$.



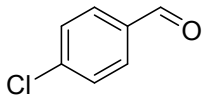
4-Fluorobenzaldehyde (**2b**). Colorless liquid (174mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.02 – 7.82 (m, 2H), 7.22 (dd, *J* = 11.9, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 167.8, 133.0, 133.0, 132.3, 132.2, 116.5, 116.2. ESI-MS: m/z =125 $[M+1]^+$.



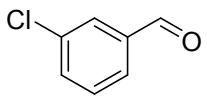
3-Fluorobenzaldehyde (**2c**). Colorless liquid (166mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 1.9 Hz, 1H), 7.69 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.35 (tdd, *J* = 8.3, 2.7, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 190.9, 164.3, 161.9, 138.4, 138.4, 130.8, 130.8, 126.1, 126.1, 121.7, 121.5, 115.4, 115.2. ESI-MS: m/z =125 $[M+1]^+$.



2-Fluorobenzaldehyde (**2d**). Colorless liquid (184mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (d, *J* = 0.5 Hz, 1H), 7.93 – 7.82 (m, 1H), 7.61 (dddd, *J* = 8.4, 7.3, 5.4, 1.9 Hz, 1H), 7.34 – 7.22 (m, 1H), 7.18 (ddd, *J* = 10.4, 8.4, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 187.2, 166.0, 163.4, 136.4, 136.3, 128.7, 128.7, 124.7, 124.6, 116.6, 116.4. ESI-MS: m/z =125 $[M+1]^+$.

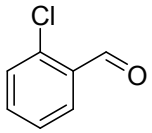


4-Chlorobenzaldehyde (**2e**). Colorless solid (204mg, 73%); m.p. 48℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.89 – 7.80 (m, 2H), 7.61 – 7.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 144.6, 140.1, 136.4, 134.5. ESI-MS: m/z =141 $[M+1]^+$.

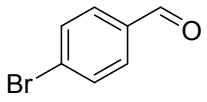


3-Chlorobenzaldehyde (**2f**). Colorless liquid (207mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.77 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.0, 2.2, 1.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$)

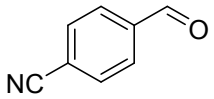
δ 190.8, 137.8, 135.4, 134.4, 130.4, 129.3, 128.0. ESI-MS: m/z =141 $[M+1]^+$.



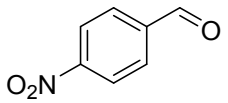
2-Chlorobenzaldehyde (**2g**). Colorless liquid (182mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (d, *J* = 0.8 Hz, 1H), 7.92 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.1, 7.2, 1.8 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 137.9, 135.1, 132.5, 130.6, 129.4, 127.3. ESI-MS: m/z =141 $[M+1]^+$.



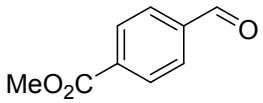
4-Bromobenzaldehyde (**2h**). Colorless solid (313mg, 85%); m.p. 55-58℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.82 – 7.74 (m, 2H), 7.74 – 7.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 135.1, 132.4, 131.0, 129.7. ESI-MS: m/z =185 $[M+1]^+$.



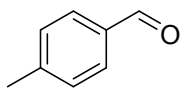
4-Formylbenzonitrile (**2i**). White crystalline Powder (228mg, 87%); m.p. 100-102℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.04 – 7.96 (m, 2H), 7.90 – 7.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 138.7, 132.9, 129.9, 117.7, 117.6. ESI-MS: m/z =132 $[M+1]^+$.



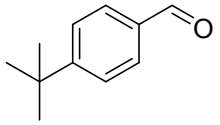
4-Nitrobenzaldehyde (**2j**). Yellow powder (269mg, 89%); m.p. 103-106℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.41 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 151.1, 140.1, 130.5, 124.3. ESI-MS: m/z =152 $[M+1]^+$.



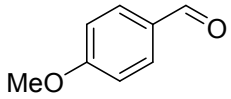
Methyl 4-formylbenzoate (**2k**). White solid (207mg, 63%); m.p. 59-63℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 8.01 – 7.89 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 166.0, 139.2, 135.1, 130.2, 129.5, 52.5. ESI-MS: m/z =165 $[M+1]^+$.



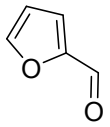
4-Methylbenzaldehyde (**2l**). Colorless liquid (161mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.86 – 7.69 (m, 2H), 7.41 – 7.24 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 145.5, 134.2, 130.2, 129.8, 129.7, 129.2, 21.8. ESI-MS: m/z =121 $[M+1]^+$.



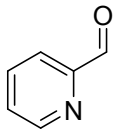
4-(Tert-butyl)benzaldehyde (**2m**). Faint yellow liquid (204mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 158.4, 134.1, 129.7, 126.0, 35.4, 31.1. ESI-MS: m/z =163 $[M+1]^+$.



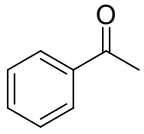
4-Methoxybenzaldehyde (**2n**). Colorless liquid (95mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 164.6, 132.0, 130.0, 114.3, 55.6. ESI-MS: m/z =137 $[M+1]^+$.



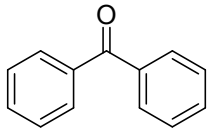
Furan-2-carbaldehyde (**2o**). Brown liquid (159mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 0.4 Hz, 1H), 7.74 – 7.53 (m, 1H), 7.23 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 152.9, 148.1, 121.2, 112.6. ESI-MS: m/z =97 $[M+1]^+$.



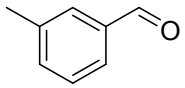
Picolinaldehyde (**2p**). Brown liquid (178mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 0.8 Hz, 1H), 8.72 (ddd, *J* = 4.8, 1.5, 1.0 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.82 (tdd, *J* = 7.8, 1.6, 0.8 Hz, 1H), 7.47 (ddd, *J* = 7.5, 4.8, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 152.7, 150.2, 137.0, 127.8, 121.6. ESI-MS: m/z =108 $[M+1]^+$.



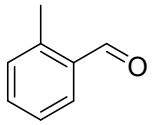
Acetophenone (**2q**). Colorless liquid (199mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 140.6, 132.9, 132.2, 128.6, 127.7, 127.1, 32.5. ESI-MS: m/z =121 $[M+1]^+$.



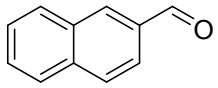
Benzophenone (**2r**). White solid (313mg, 86%); m.p. 47-51℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.67 – 7.59 (m, 2H), 7.56 – 7.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3. ESI-MS: m/z =183 $[M+1]^+$.



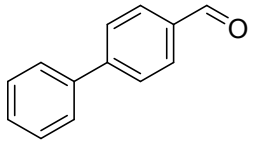
3-Methylbenzaldehyde (**4a**). Colorless liquid (95mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.70 (dd, *J* = 6.9, 1.1 Hz, 2H), 7.54 – 7.36 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2. ESI-MS: m/z =121 $[M+1]^+$.



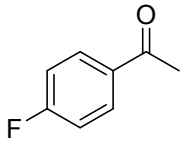
2-Methylbenzaldehyde (**4b**). Colorless liquid (88mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.80 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 140.6, 134.1, 133.7, 132.1, 131.8, 126.3, 19.6. ESI-MS: m/z =121 $[M+1]^+$.



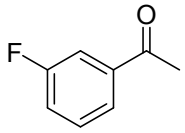
2-Naphthaldehyde (**4c**). Off-white to yellow solid (125mg, 80%); m.p. 58-61℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.37 (s, 1H), 8.10 – 7.89 (m, 4H), 7.65 (dddd, *J* = 22.8, 8.1, 6.9, 1.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 136.5, 134.6, 134.1, 132.7, 129.5, 129.1, 129.1, 128.1, 127.1, 122.8. ESI-MS: m/z =157 $[M+1]^+$.



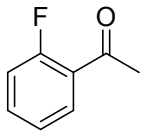
[1,1'-Biphenyl]-4-carbaldehyde (**4d**). Colorless solid (133mg, 73%); m.p. 57-59℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.02 – 7.94 (m, 2H), 7.83 – 7.74 (m, 2H), 7.71 – 7.62 (m, 2H), 7.55 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 147.2, 139.7, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4. ESI-MS: m/z =183$[M+1]^+$.



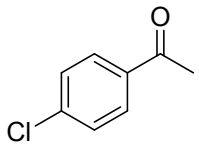
1-(4-Fluorophenyl)ethan-1-one (**4e**). Colorless liquid (89mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.20 – 6.97 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 167.0, 164.5, 133.6, 133.6, 131.0, 130.9, 115.7, 115.5, 26.5. ESI-MS: m/z =139 $[M+1]^+$.



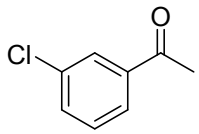
1-(3-Fluorophenyl)ethan-1-one (**4f**). Colorless liquid (86mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.62 (ddd, *J* = 9.5, 2.4, 1.6 Hz, 1H), 7.43 (td, *J* = 8.0, 5.5 Hz, 1H), 7.30 – 7.20 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 196.6, 164.1, 161.6, 139.2, 139.2, 130.3, 130.2, 124.1, 124.1, 120.2, 119.9, 115.0, 114.8, 26.6. ESI-MS: m/z =139 $[M+1]^+$.



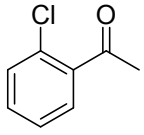
1-(2-Fluorophenyl)ethan-1-one (**4g**). Colorless liquid (70mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (td, *J* = 7.7, 1.9 Hz, 1H), 7.51 (dddd, *J* = 8.3, 7.1, 5.0, 1.9 Hz, 1H), 7.26 – 7.16 (m, 1H), 7.12 (ddd, *J* = 11.2, 8.3, 0.8 Hz, 1H), 2.63 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 195.8, 163.5, 160.9, 134.7, 134.6, 130.6, 130.5, 125.8, 125.7, 124.4, 124.3, 116.7, 116.5, 31.4, 31.3. ESI-MS: m/z =139 $[M+1]^+$.



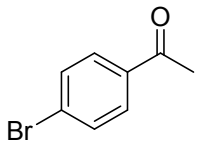
1-(4-Chlorophenyl)ethan-1-one (**4h**). Colorless liquid (108mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.82 (m, 2H), 7.57 – 7.37 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 139.6, 135.5, 129.7, 128.9, 26.5. ESI-MS: m/z =155 $[M+1]^+$.



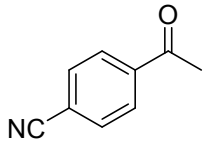
1-(3-Chlorophenyl)ethan-1-one (**4i**). Faint yellow liquid (103mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 1.8 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.53 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 138.6, 134.9, 133.0, 129.9, 128.4, 126.4, 26.6. ESI-MS: m/z =155 $[M+1]^+$.



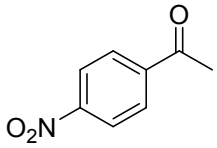
1-(2-Chlorophenyl)ethan-1-one (**4j**). Colorless liquid (72mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.45 – 7.36 (m, 2H), 7.36 – 7.28 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 139.2, 132.0, 131.3, 130.6, 129.4, 126.9, 30.7. ESI-MS: m/z =155 $[M+1]^+$.



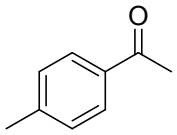
1-(4-Bromophenyl)ethan-1-one (**4k**). Colorless solid (123mg, 62%); m.p. 108-110℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.65 – 7.55 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 135.8, 131.9, 129.8, 128.3, 26.5. ESI-MS: m/z =199 $[M+1]^+$.



4-Acetylbenzonitrile (**4l**). Faint yellow crystalline powder (101mg, 70%); m.p. 56-59℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.95 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 139.9, 132.5, 128.7, 117.9, 116.4, 26.7. ESI-MS: m/z =146 $[M+1]^+$.



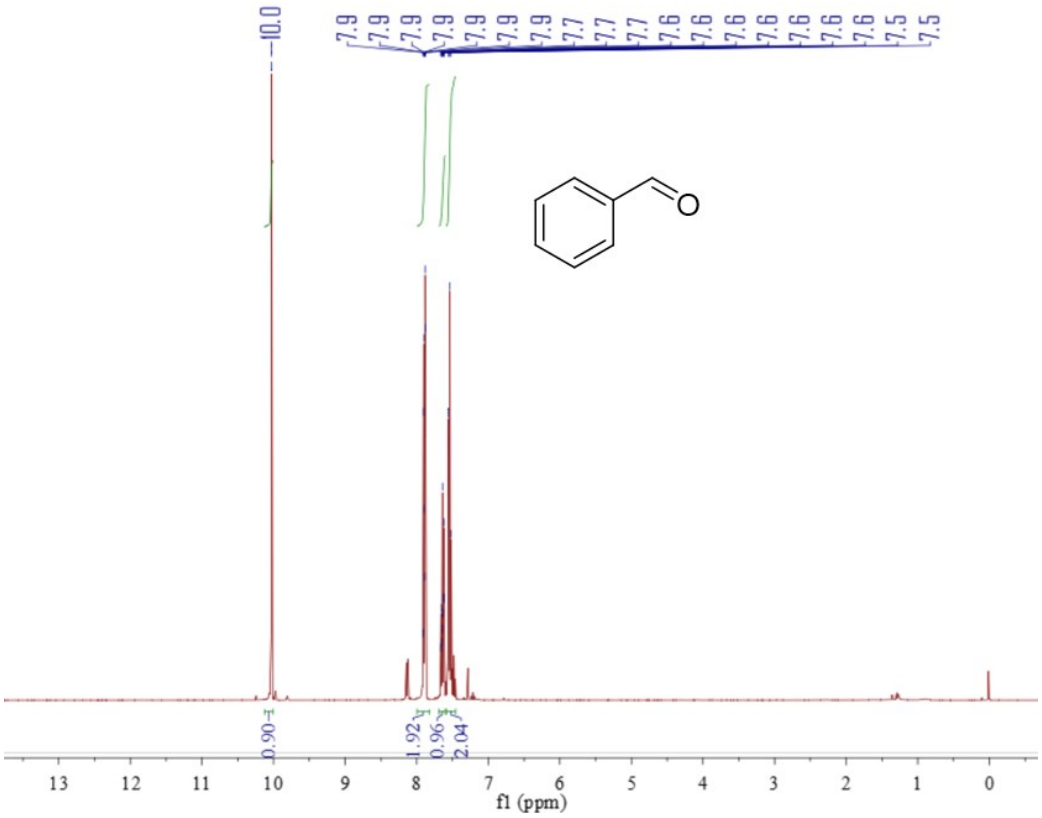
1-(4-Nitrophenyl)ethan-1-one (**4m**). Light yellow crystal (119mg, 72%); m.p. 75-78℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.18 – 8.02 (m, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 150.4, 141.4, 129.3, 123.8, 26.9. ESI-MS: m/z =166 $[M+1]^+$.

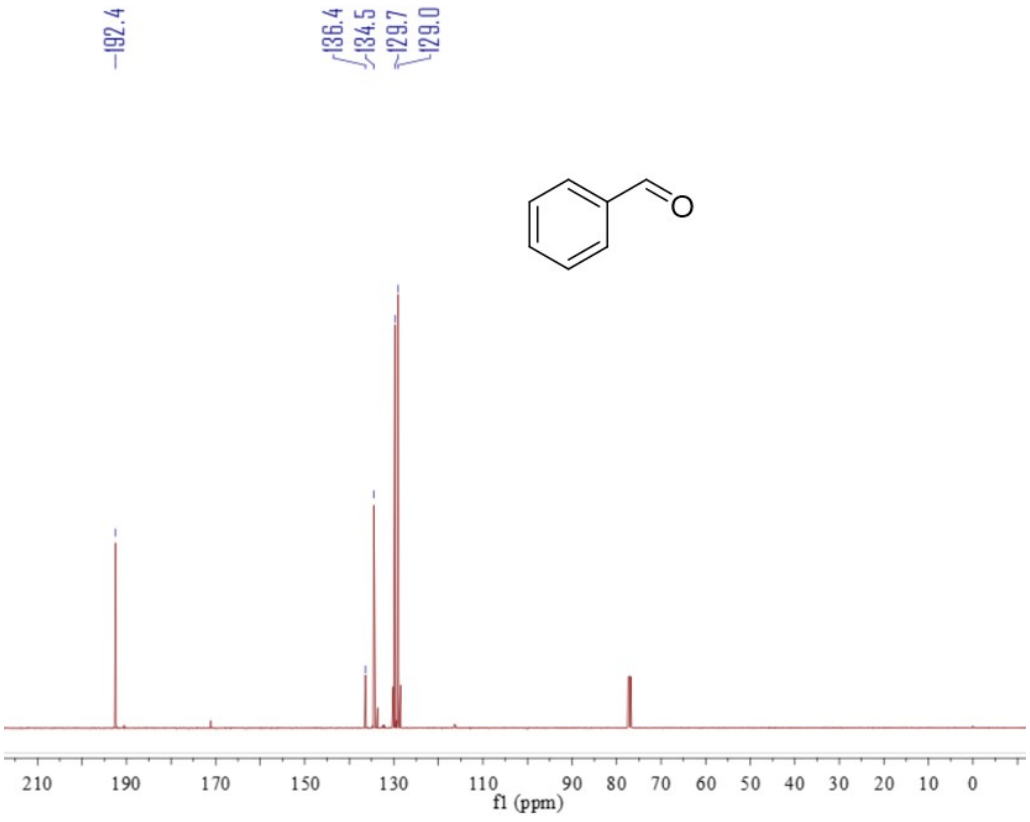


1-(P-tolyl)ethan-1-one (**4n**). Colorless liquid (75mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.20 (m, 2H), 2.61 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 143.9, 134.8, 129.2, 128.4, 26.5, 21.6. ESI-MS: m/z =135 $[M+1]^+$.

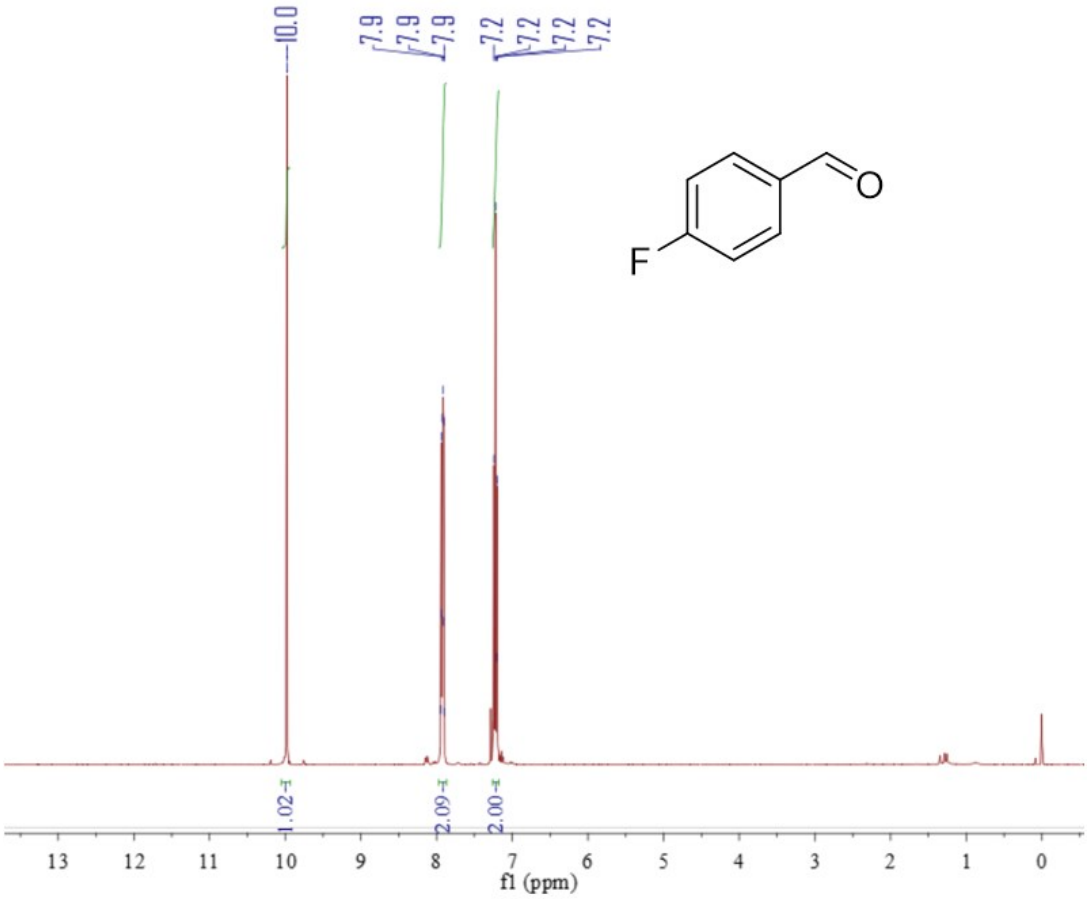
NMR Spectra

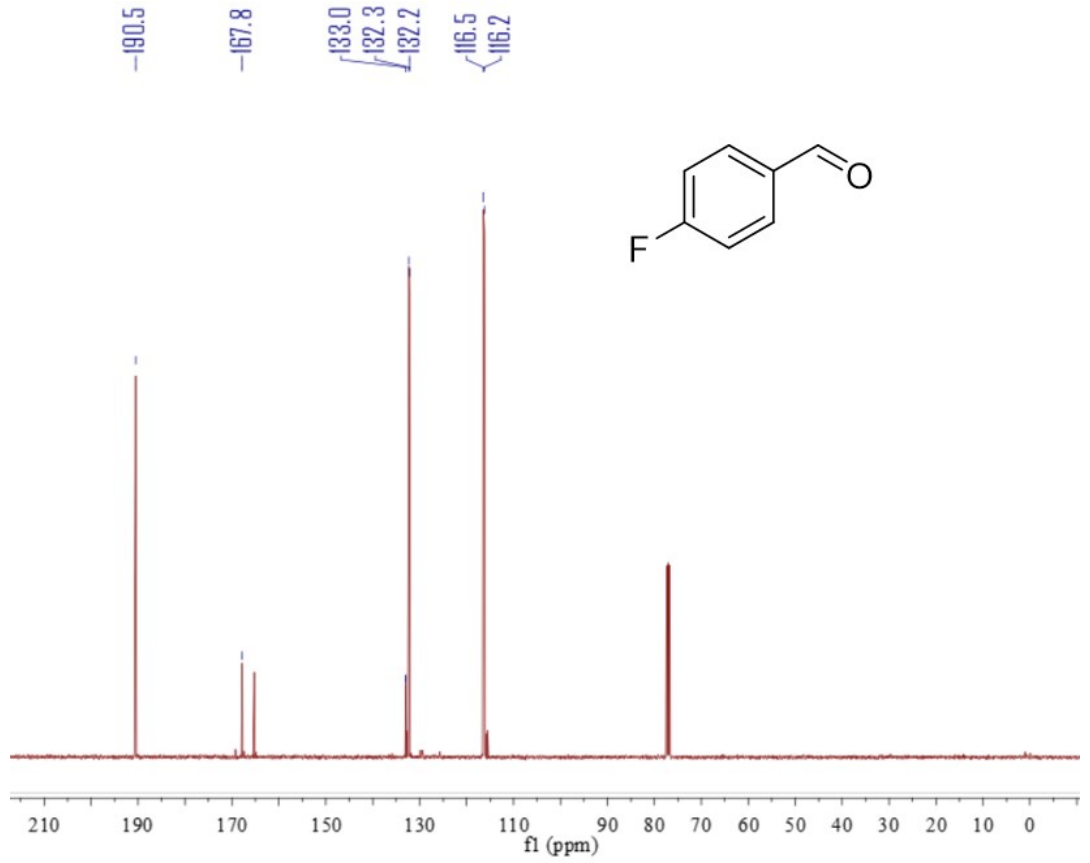
Compound 2a



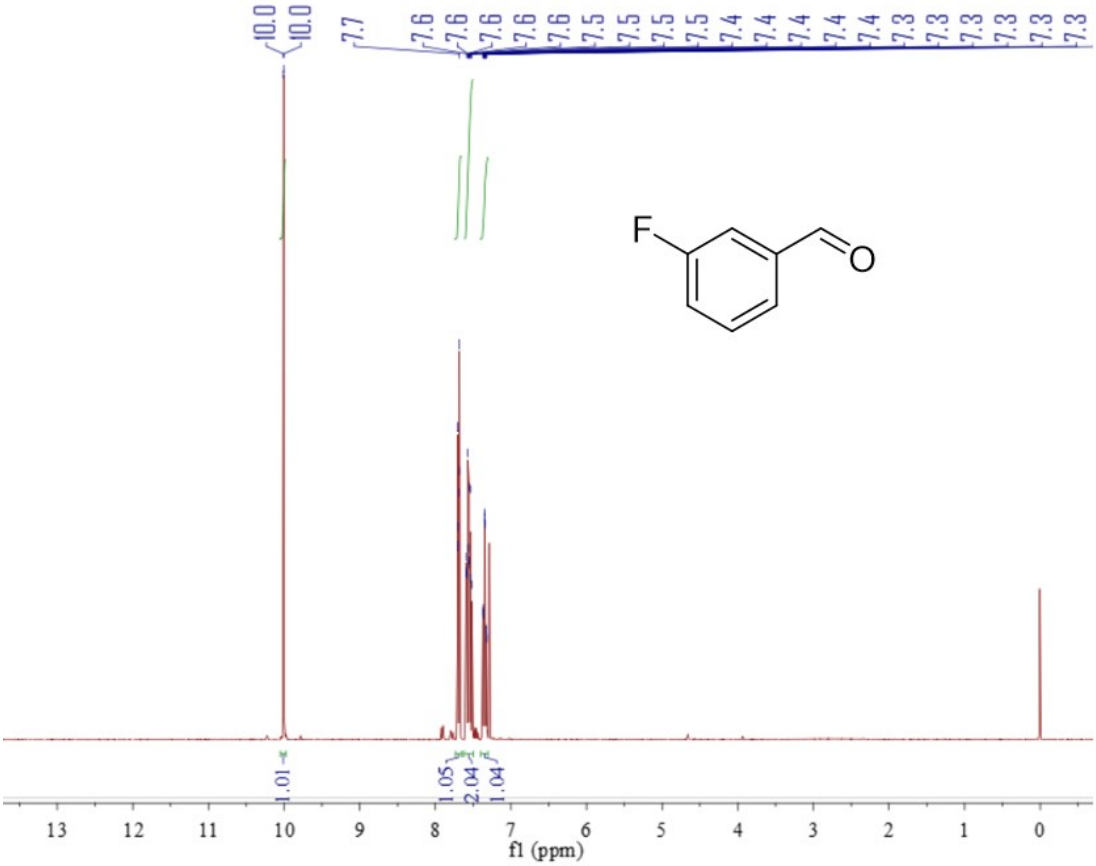


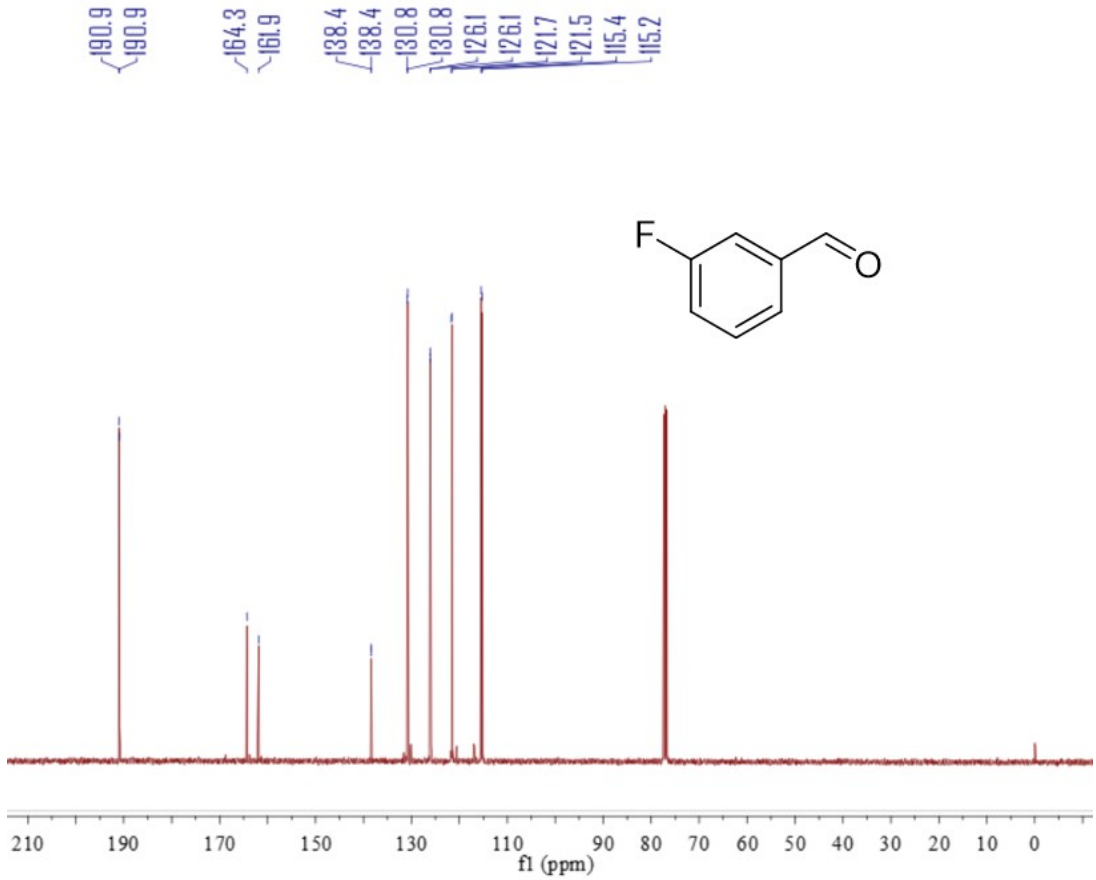
Compound 2b


10.0
7.9
7.9
7.9
7.2
7.2
7.2
7.2
O
F
1.02
2.09
2.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

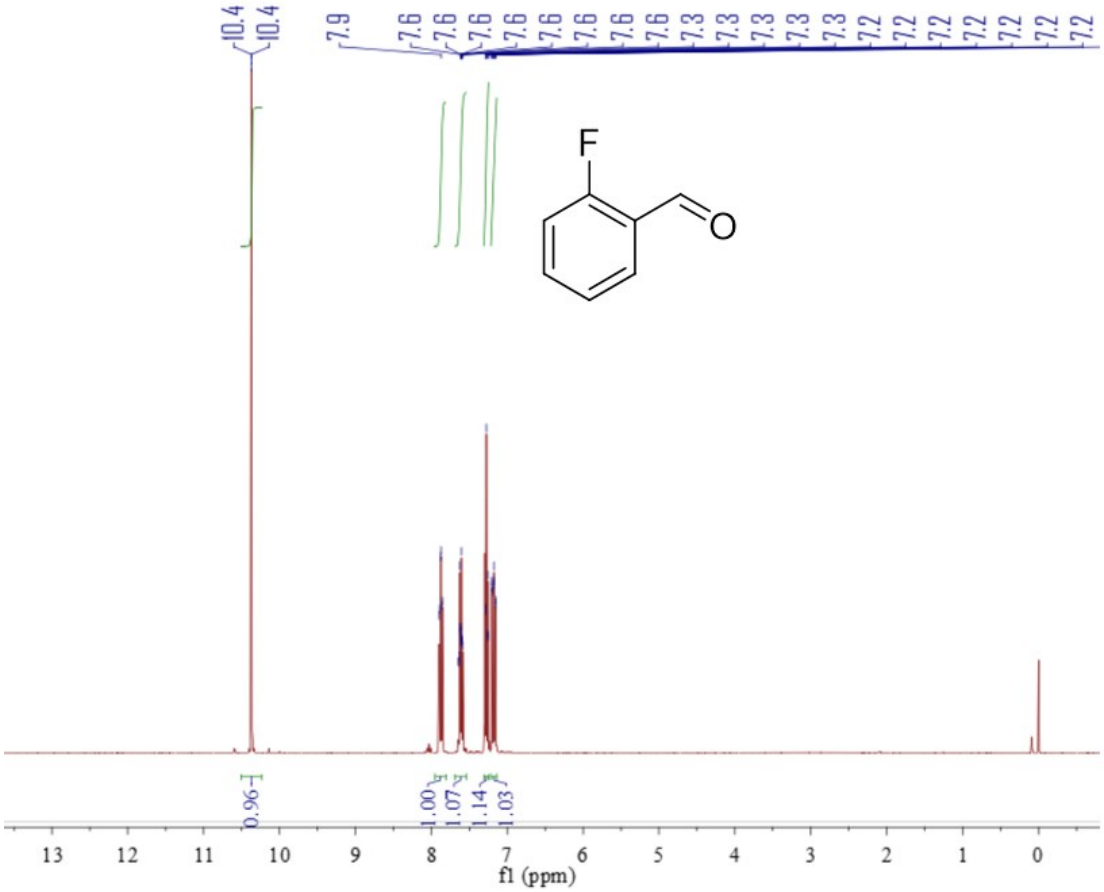

190.5
167.8
133.0
132.3
132.2
116.5
116.2
O
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

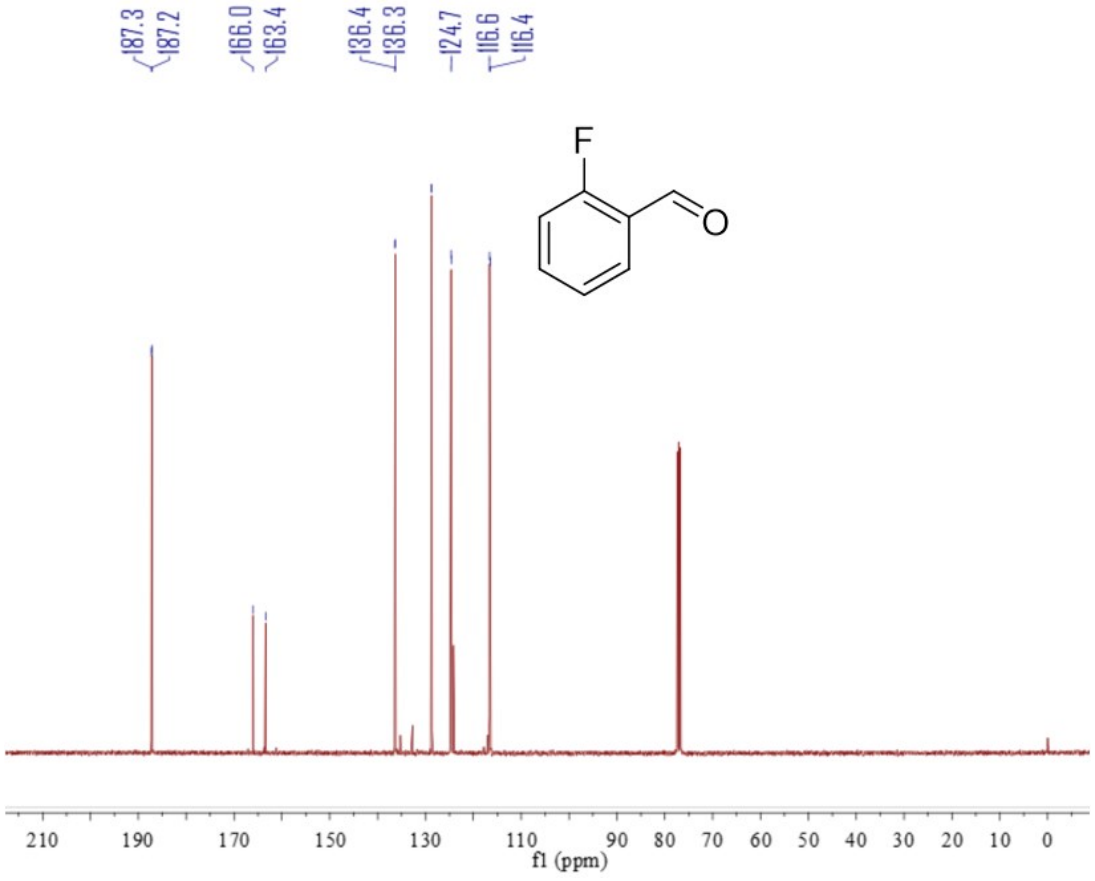
Compound 2c


10.0
10.0
7.7
7.6
7.6
7.6
7.6
7.6
7.5
7.5
7.5
7.5
7.4
7.4
7.4
7.4
7.4
7.3
7.3
7.3
7.3
7.3
7.3
F
O
1.01
1.05
2.04
1.04
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

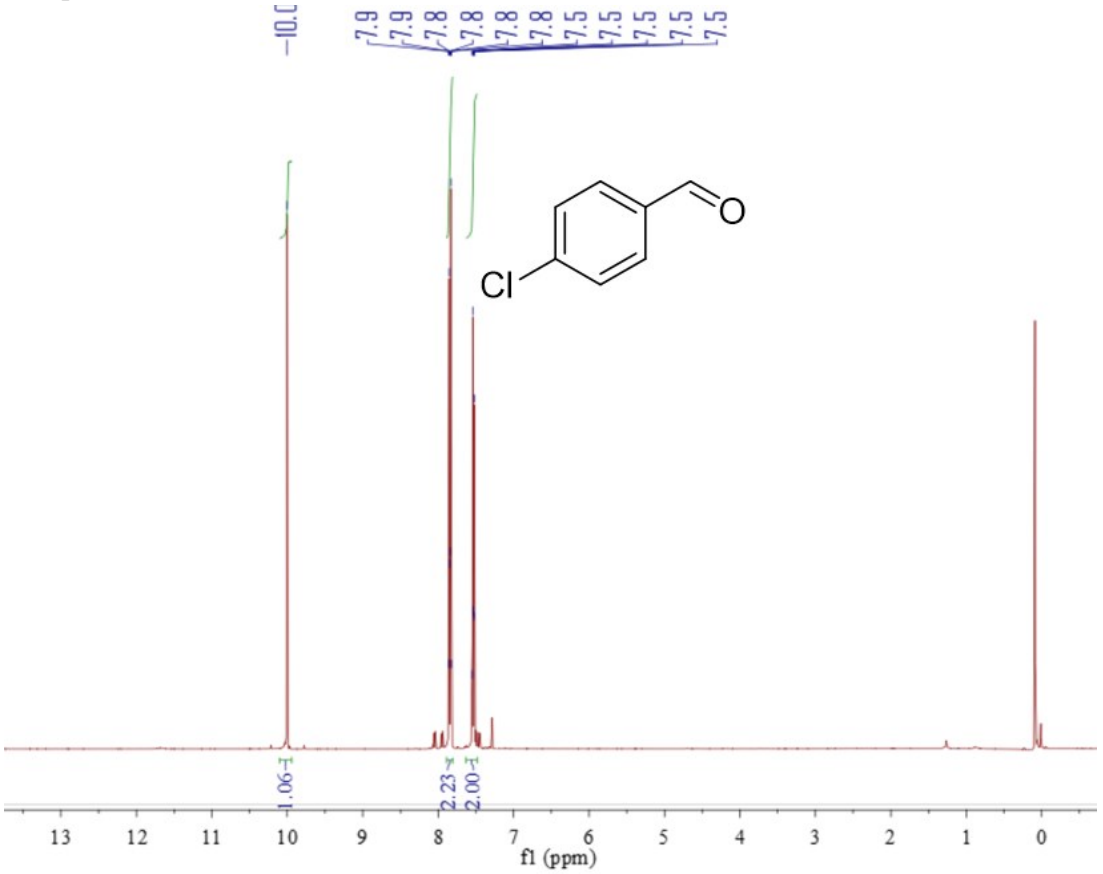

190.9
190.9
164.3
161.9
138.4
138.4
130.8
130.8
126.1
126.1
121.7
121.5
115.4
115.2
F
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

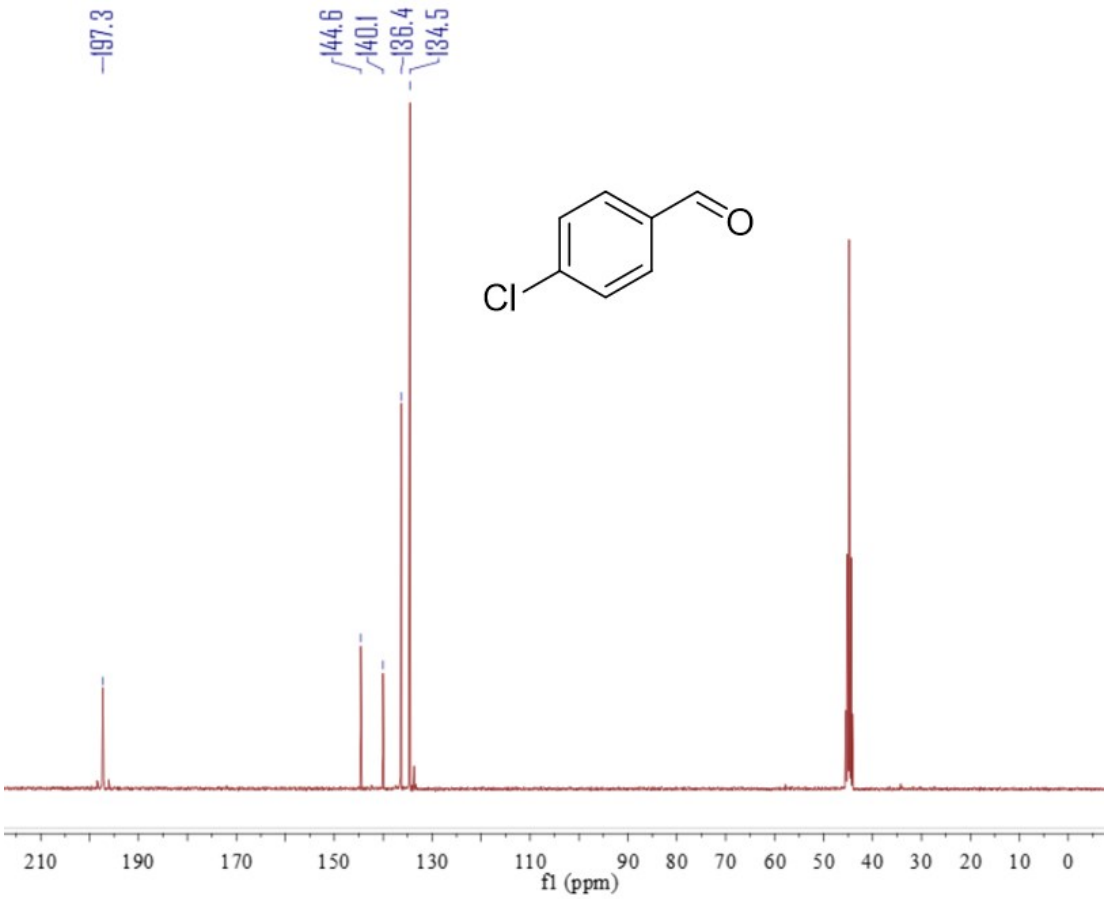
Compound 2d


10.4
10.4
7.9
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.2
7.2
7.2
F
O
0.96
1.00
1.07
1.14
1.03
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

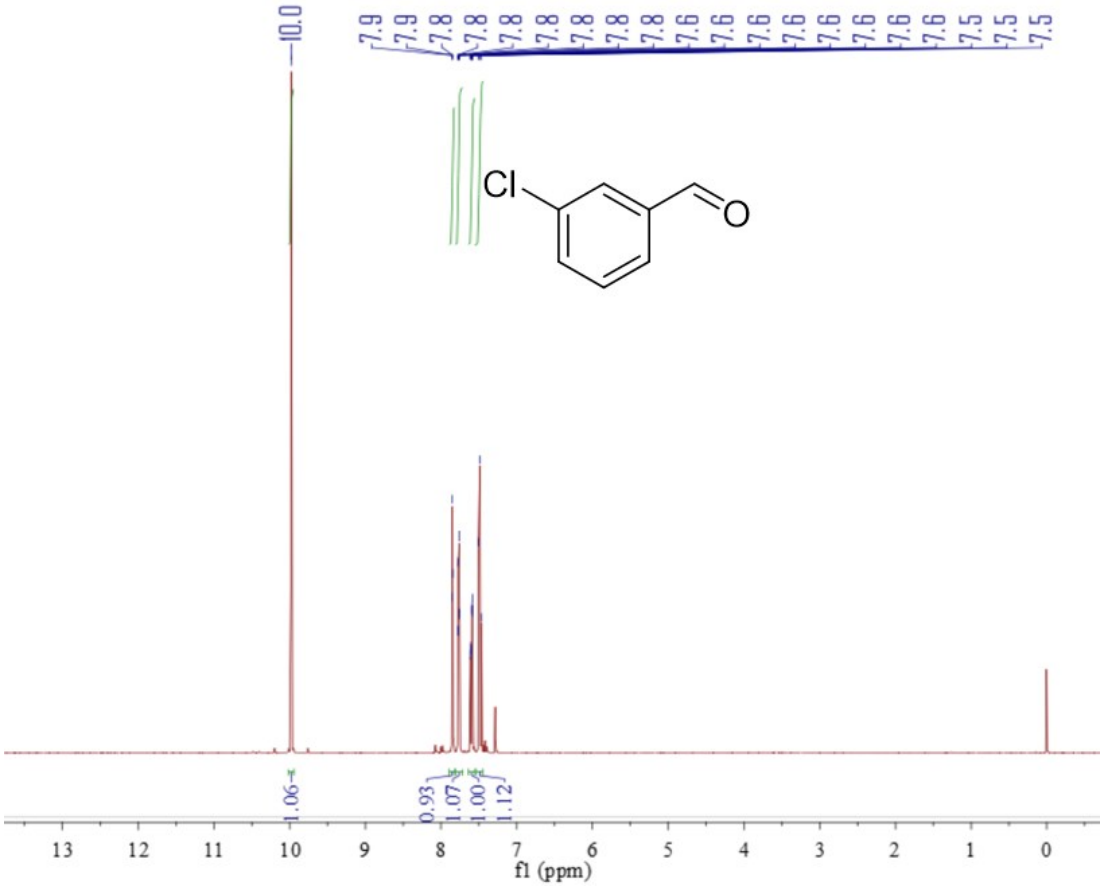

187.3
187.2
166.0
163.4
136.4
136.3
124.7
116.6
116.4
F
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

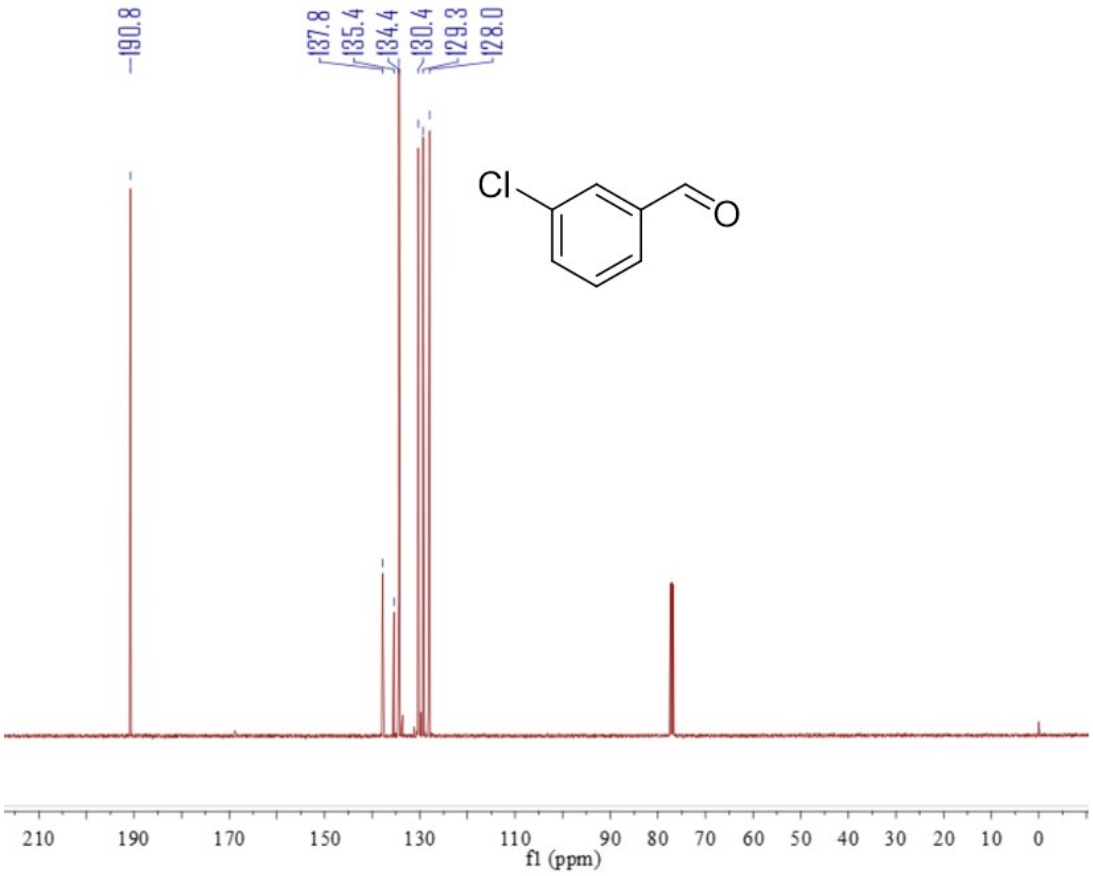
Compound 2e


10.0
7.9
7.9
7.8
7.8
7.8
7.8
7.5
7.5
7.5
7.5
7.5
O
Cl
1.06
2.23
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

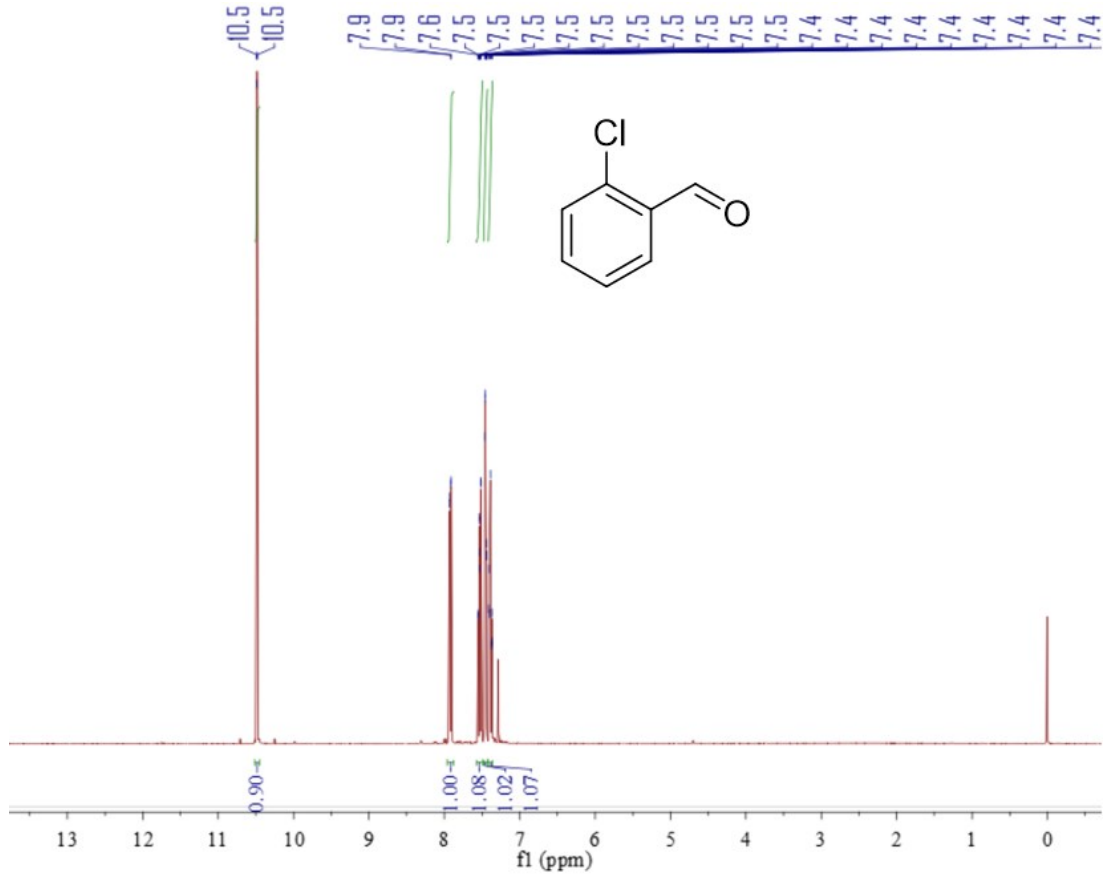

197.3
144.6
140.1
136.4
134.5
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

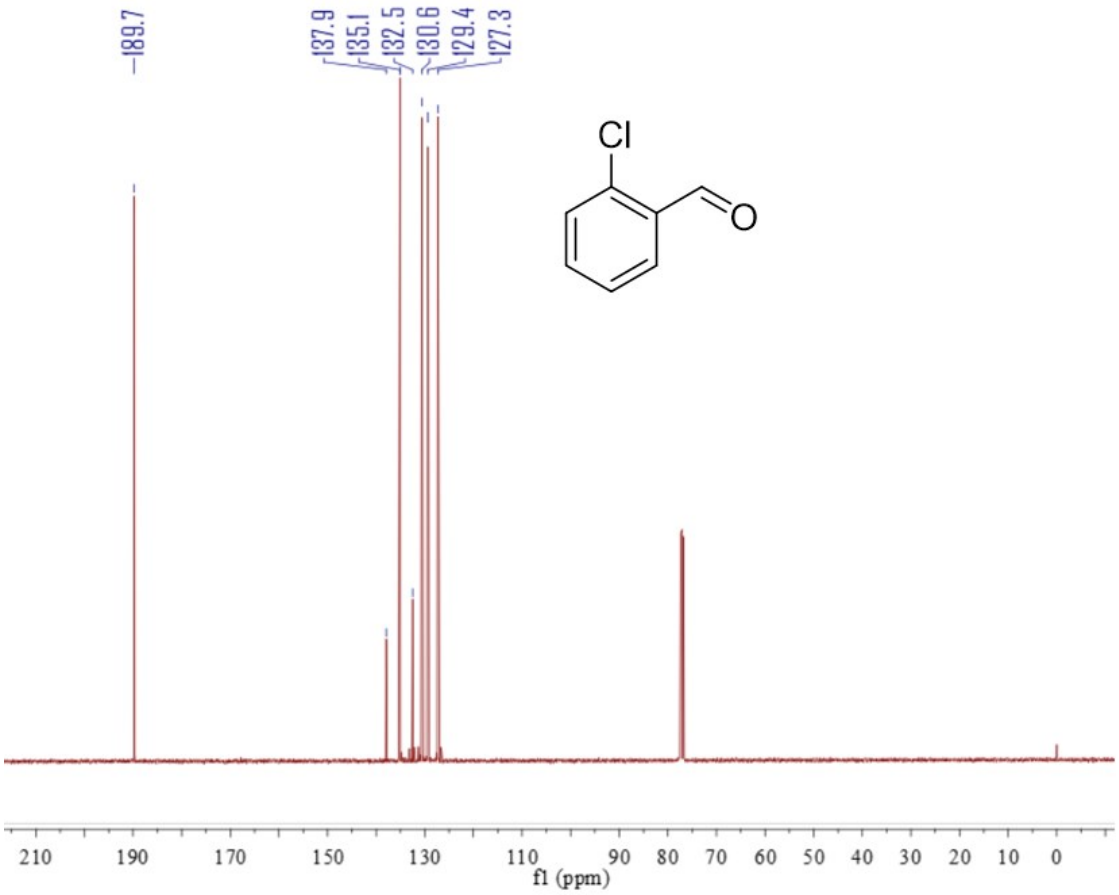
Compound 2f


10.0
7.9
7.9
7.8
7.8
7.8
7.8
7.8
7.8
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.5
7.5
7.5
Cl
O
1.06
0.93
1.07
1.00
1.12
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

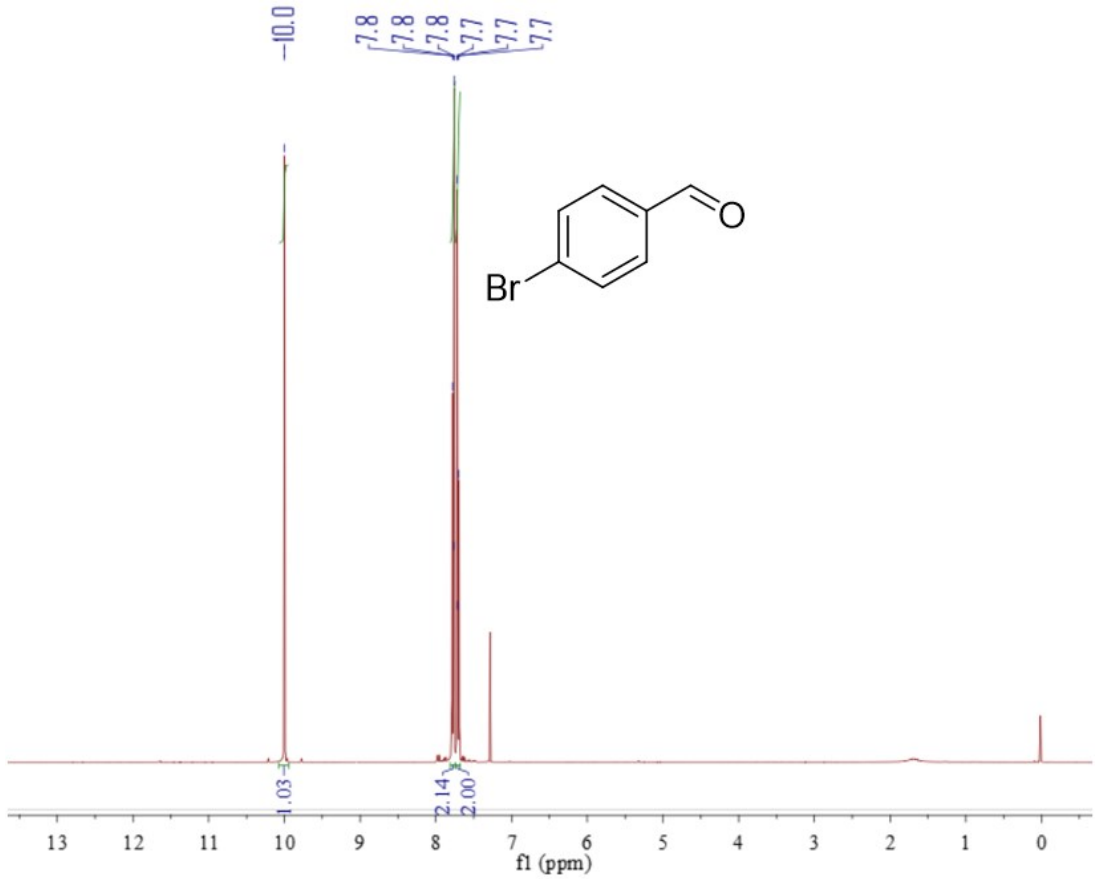

190.8
137.8
135.4
134.4
130.4
129.3
128.0
Cl
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

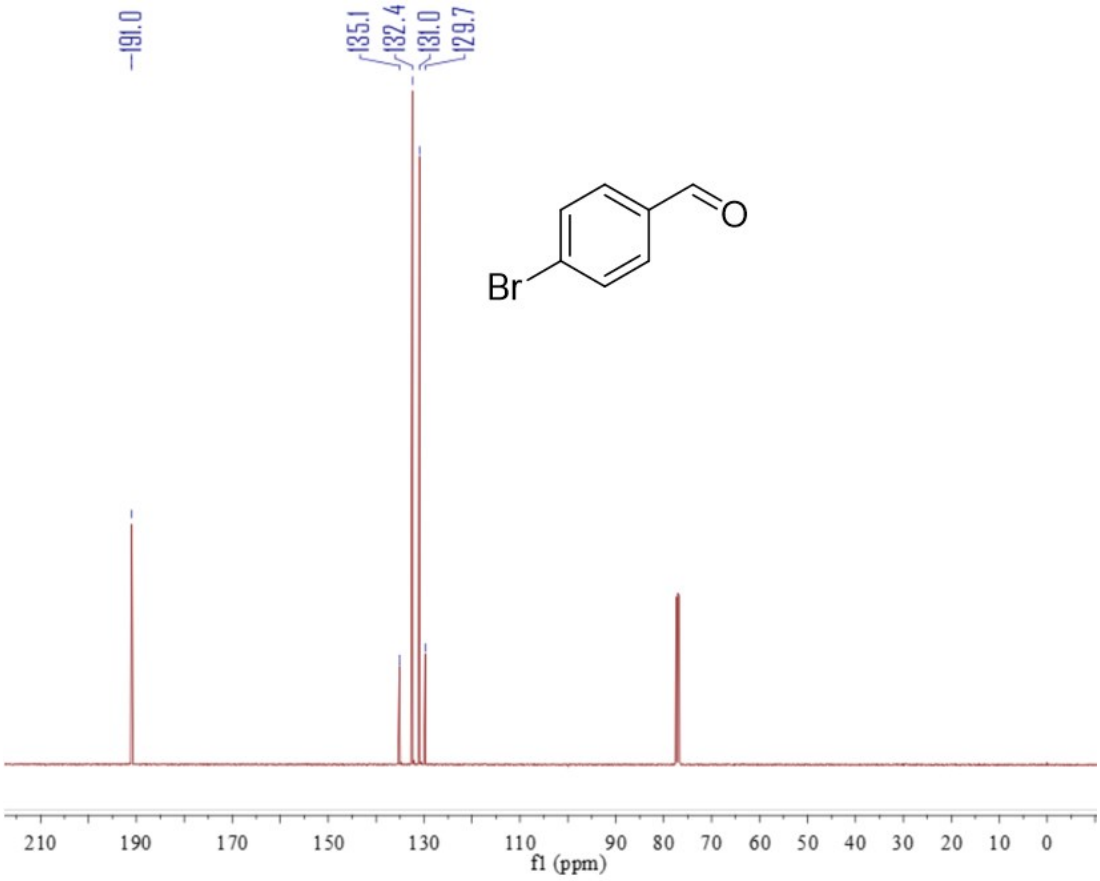
Compound 2g


10.5
10.5
7.9
7.9
7.6
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.4
7.4
7.4
7.4
7.4
7.4
7.4
7.4
Cl
O
0.90
1.00
1.08
1.02
1.07
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

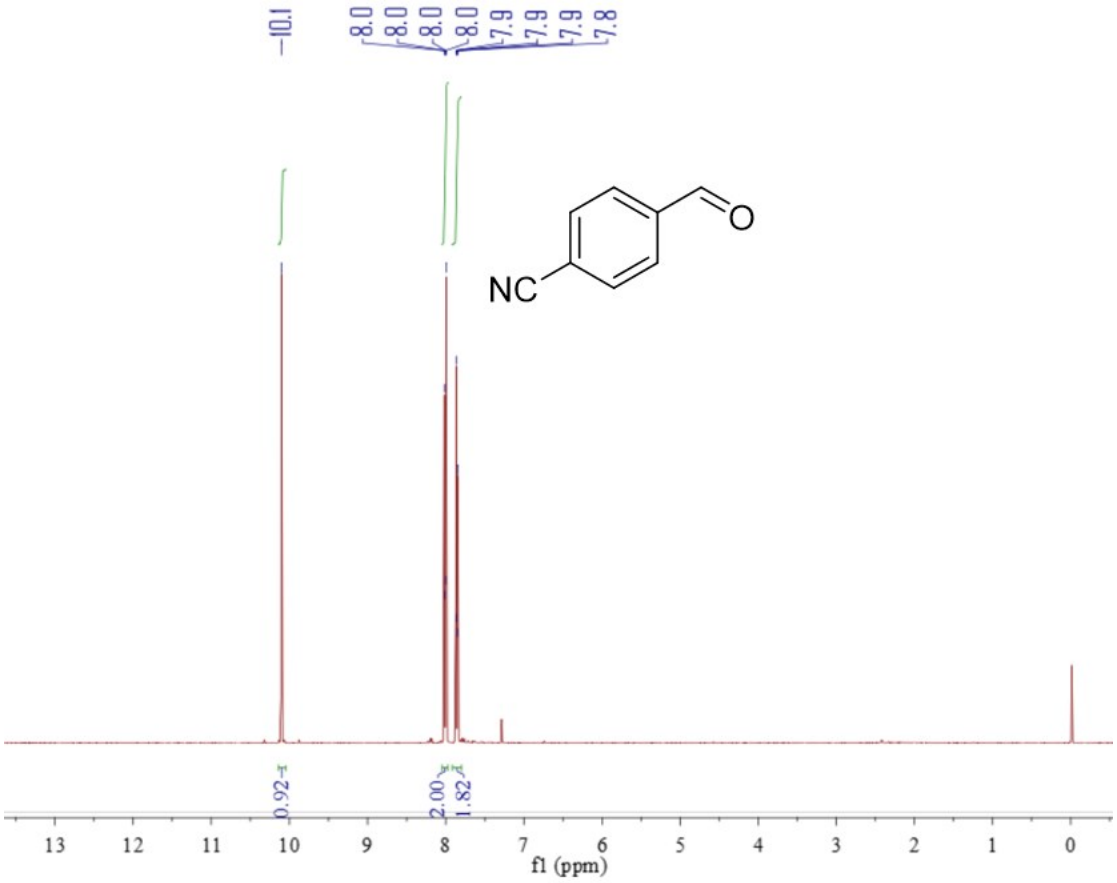

189.7
137.9
135.1
132.5
130.6
129.4
127.3
Cl
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

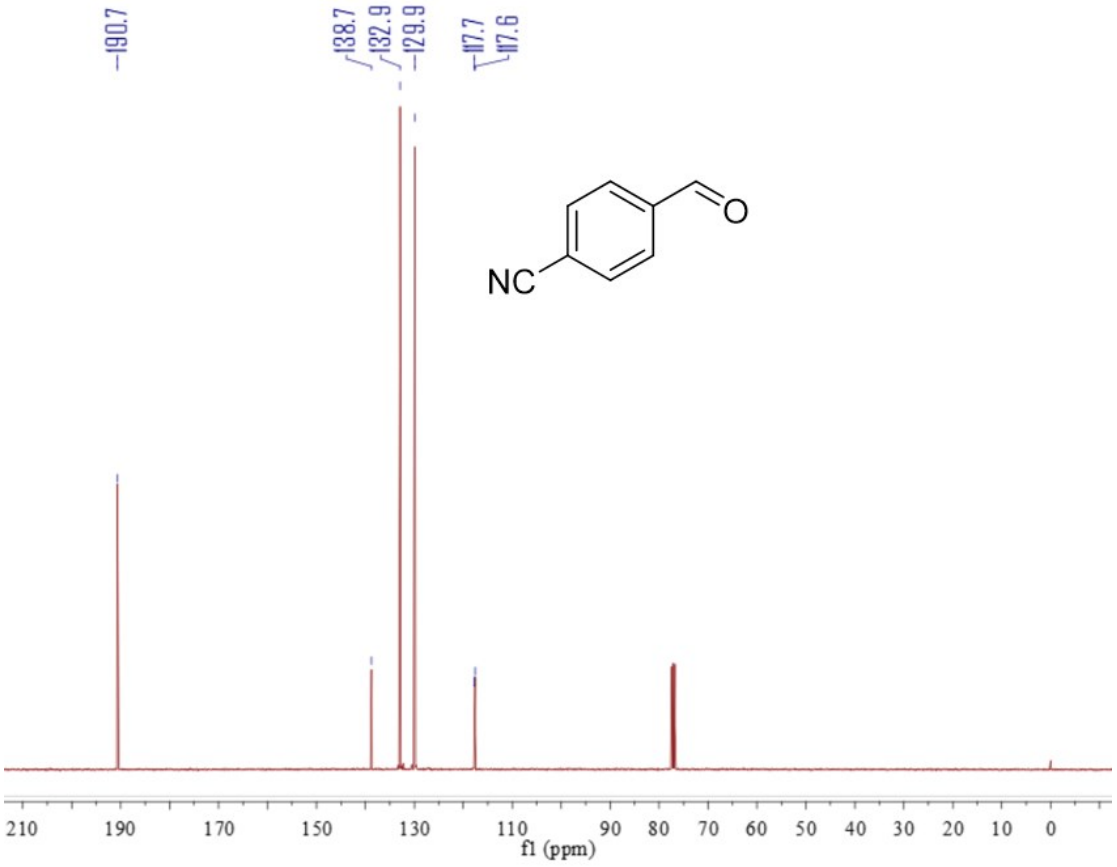
Compound 2h


10.0
7.8
7.8
7.8
7.7
7.7
7.7
O
Br
1.03
2.14
2.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

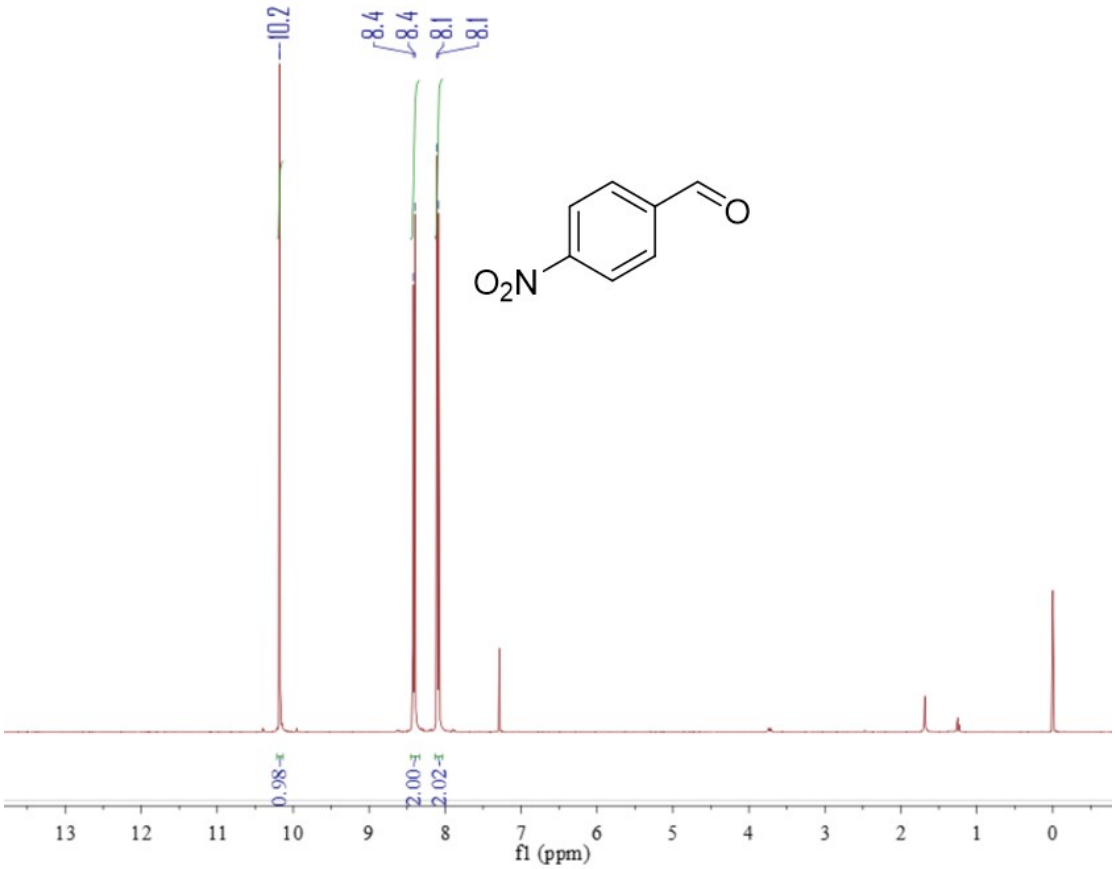

191.0
135.1
132.4
131.0
129.7
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

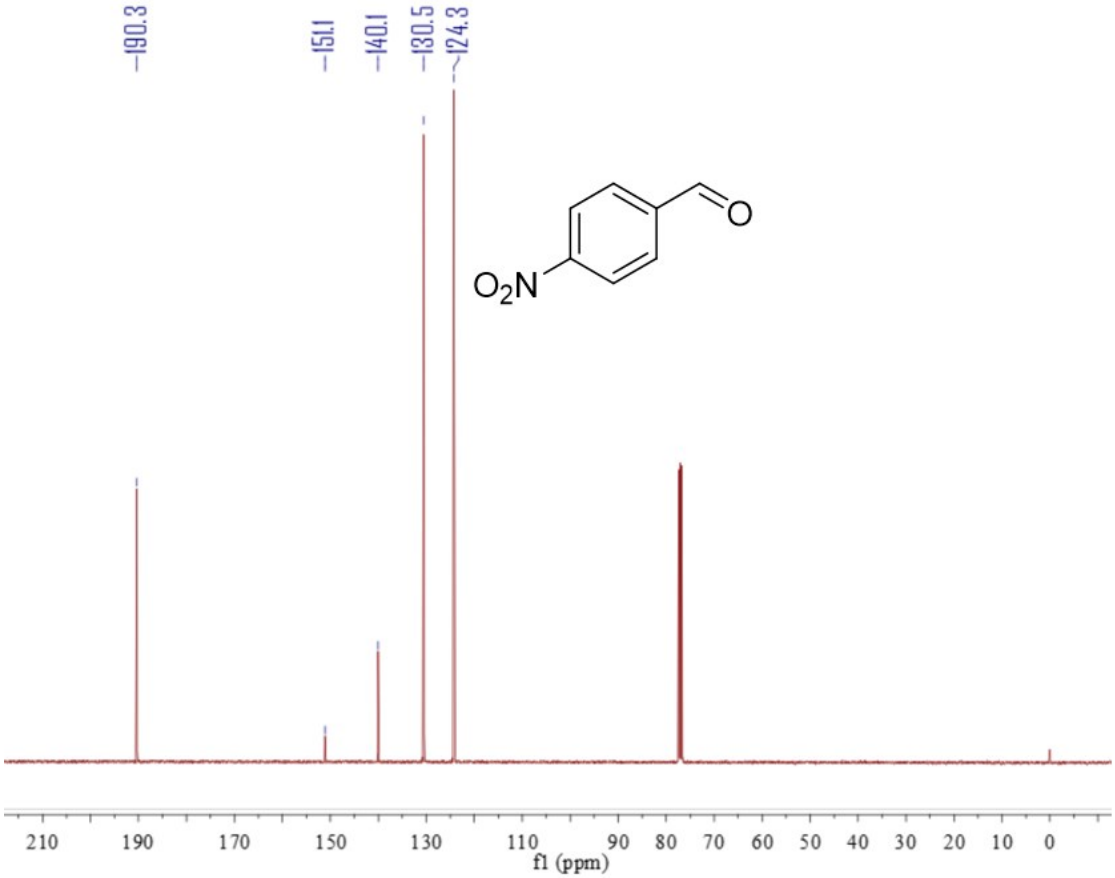
Compound 2i


10.1
8.0
8.0
8.0
8.0
7.9
7.9
7.9
7.8
O
NC
0.92
2.00
1.82
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

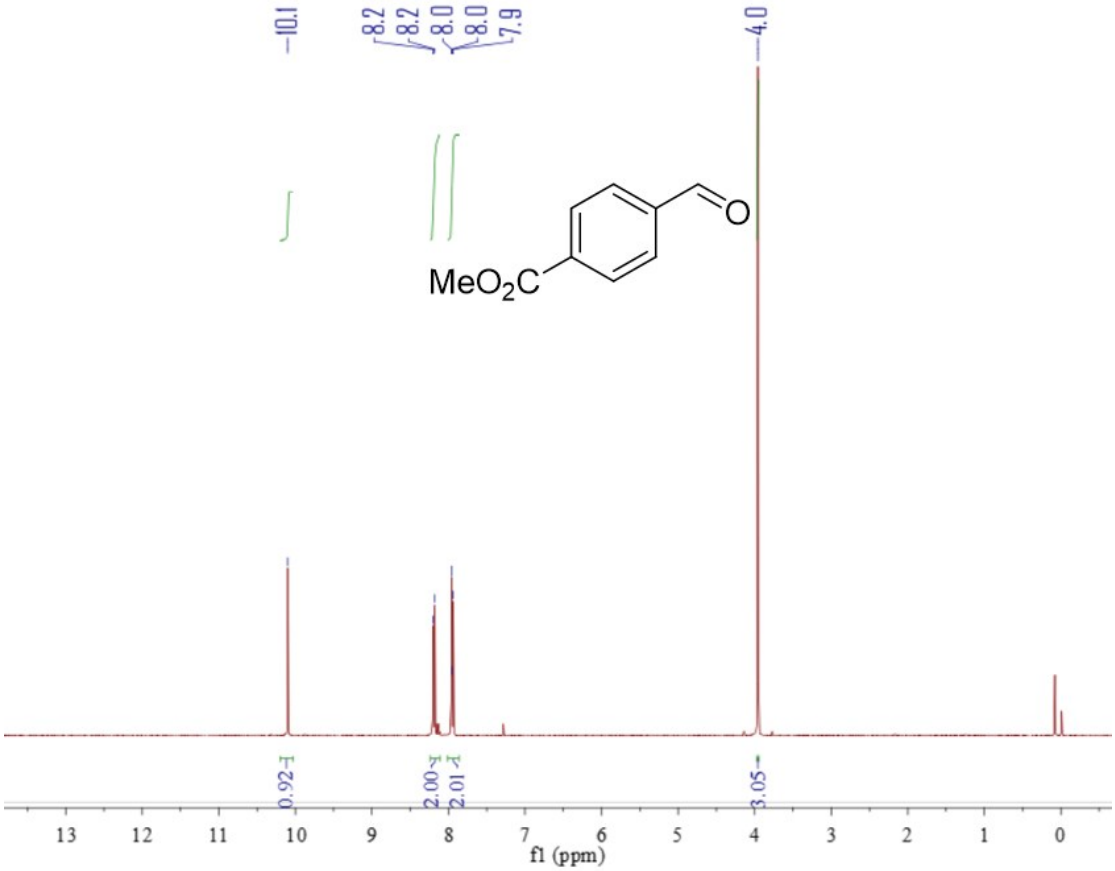

190.7
138.7
132.9
129.9
117.7
117.6
O
NC
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

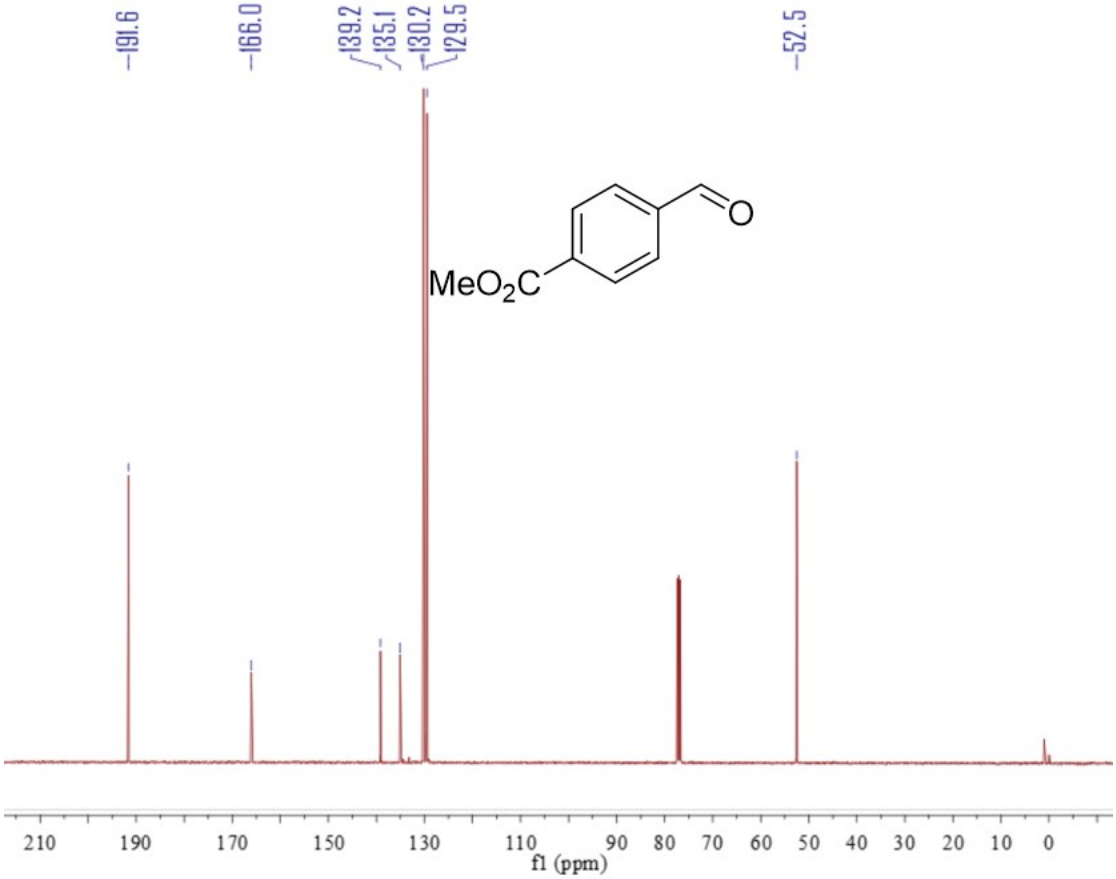
Compound 2j


10.2
8.4
8.4
8.1
8.1
O
O2N
0.98
2.00
2.02
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

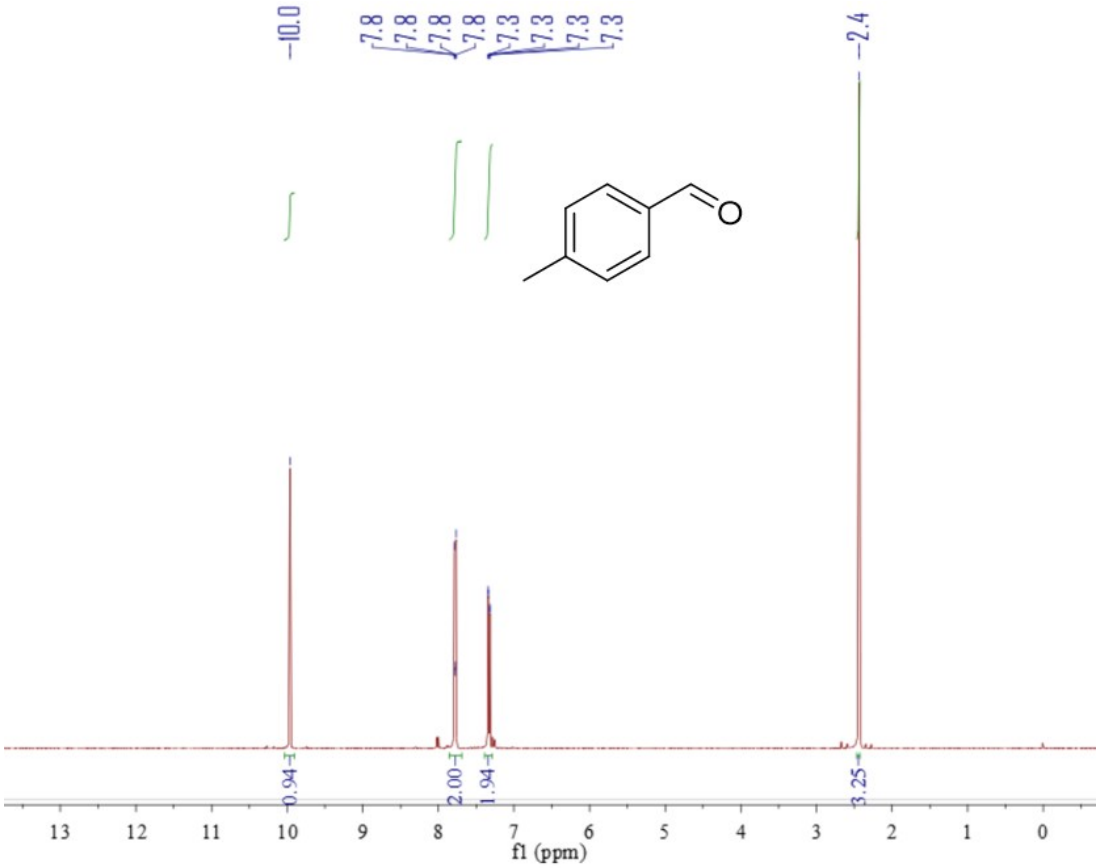

190.3
151.1
140.1
130.5
124.3
O
O2N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

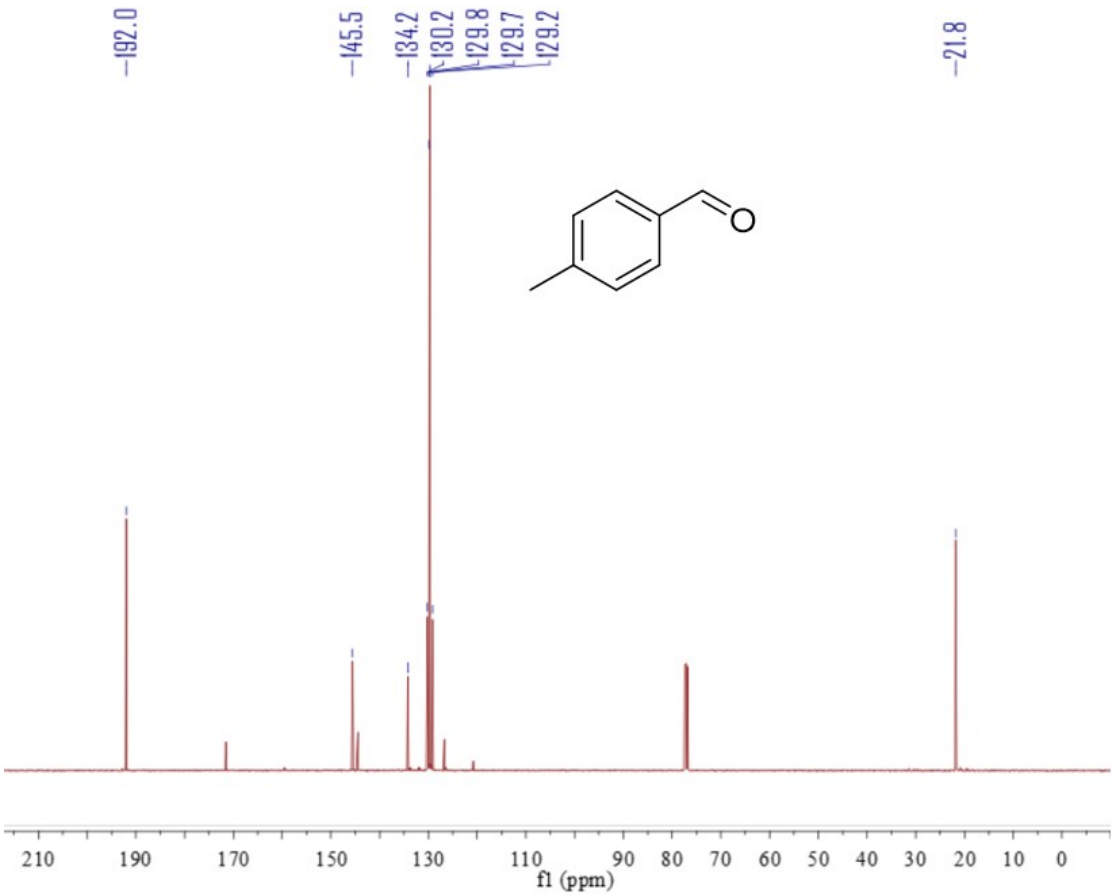
Compound 2k


10.1
8.2
8.2
8.0
8.0
7.9
4.0
O
MeO2C
0.92
2.00
2.01
3.05
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

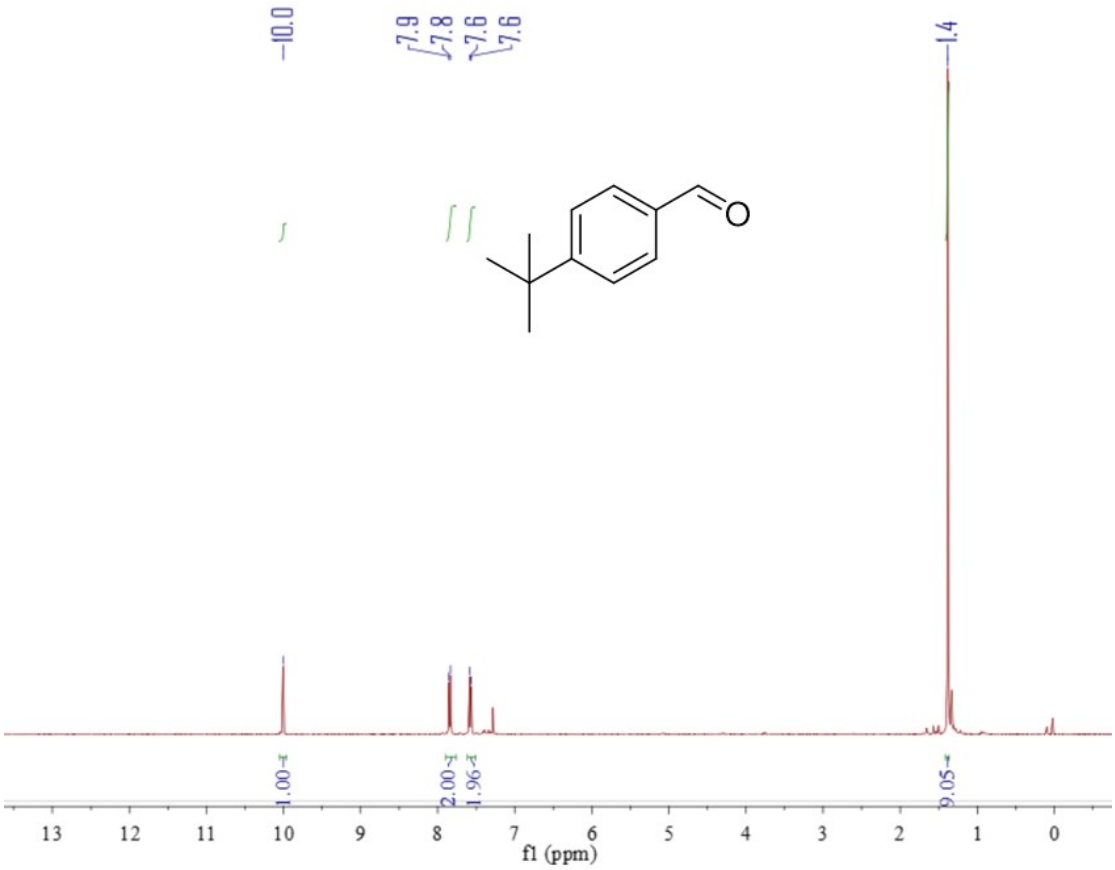

191.6
166.0
139.2
135.1
130.2
129.5
52.5
O
MeO2C
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

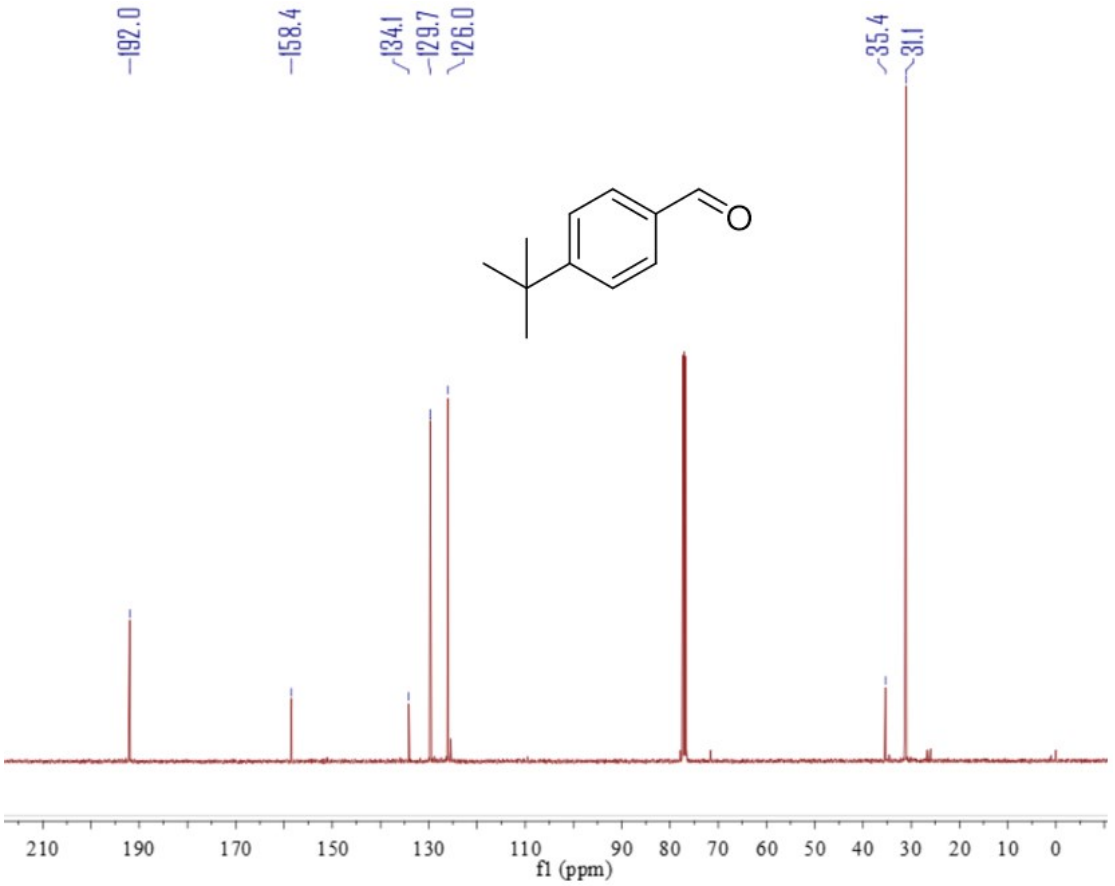
Compound 2l


10.0
7.8
7.8
7.8
7.8
7.3
7.3
7.3
7.3
2.4
0.94
2.00
1.94
3.25
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

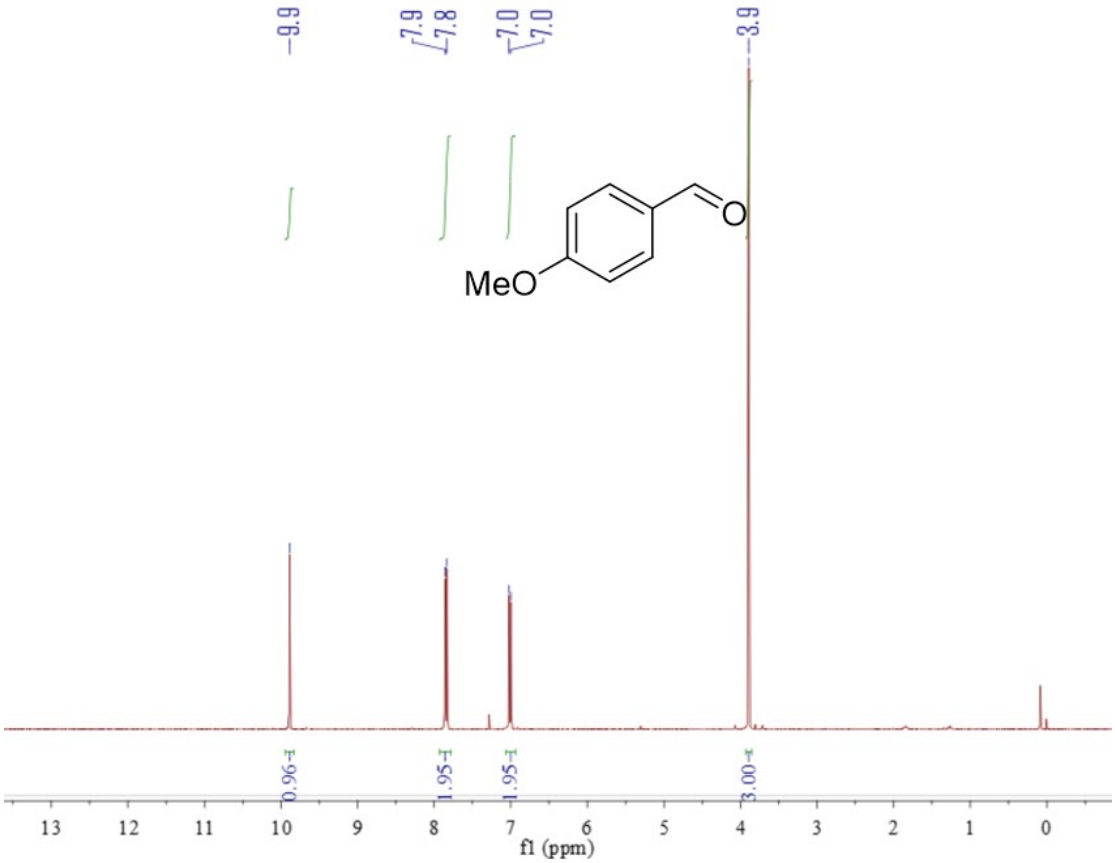

192.0
145.5
134.2
130.2
129.8
129.7
129.2
21.8
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

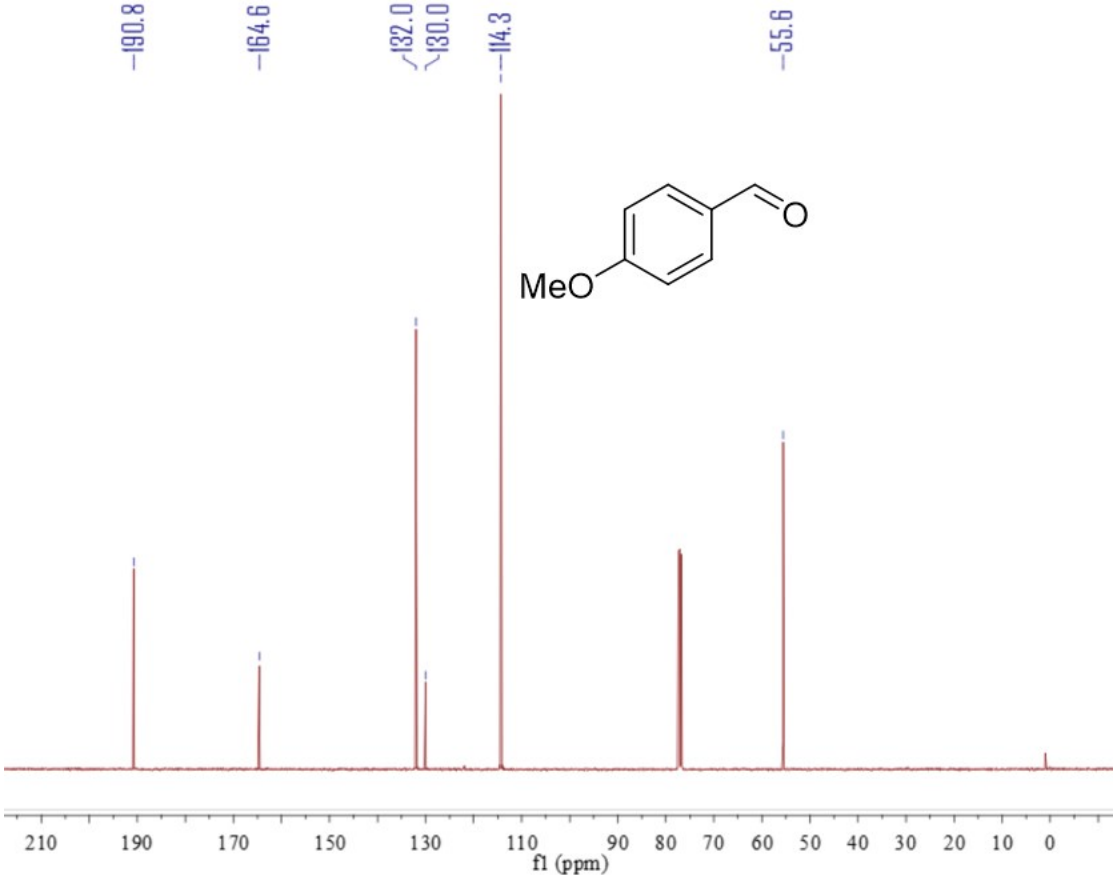
Compound 2m


10.0
7.9
7.8
7.6
7.6
1.4
1.00
2.00
1.96
9.05
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

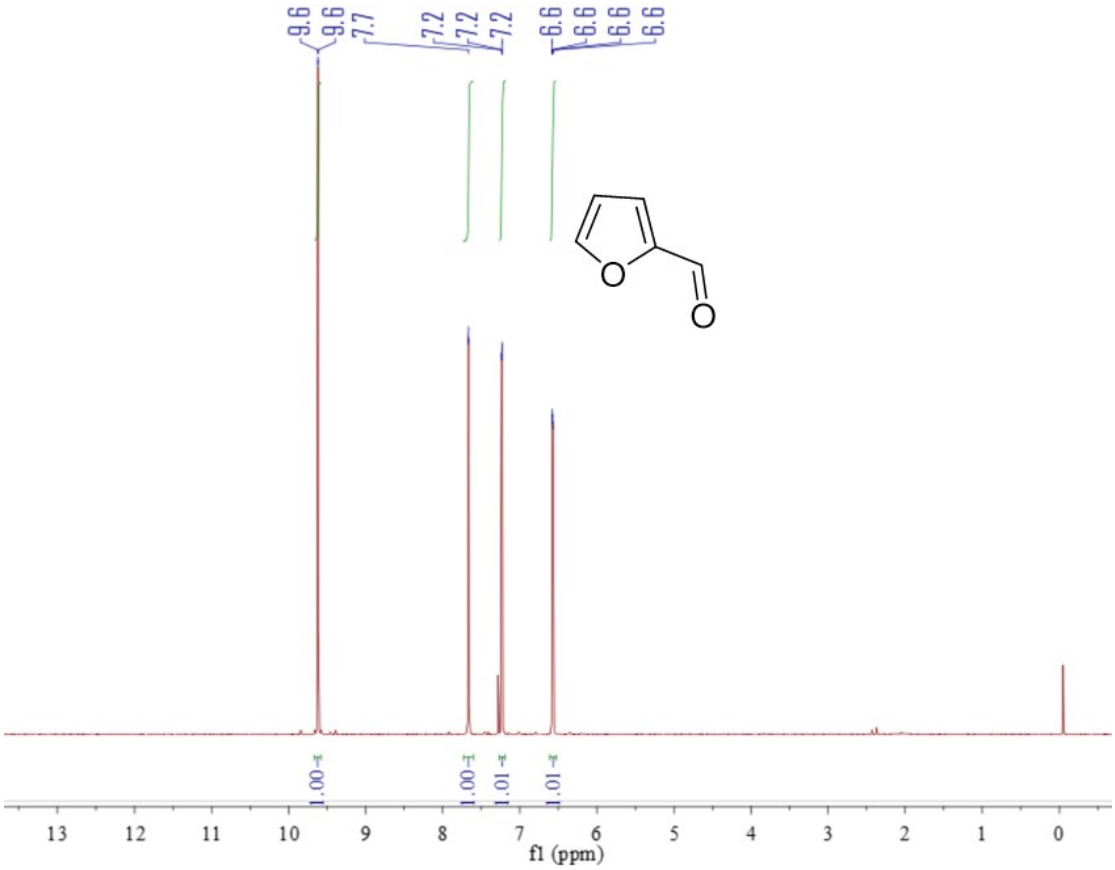

192.0
158.4
134.1
129.7
126.0
35.4
31.1
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

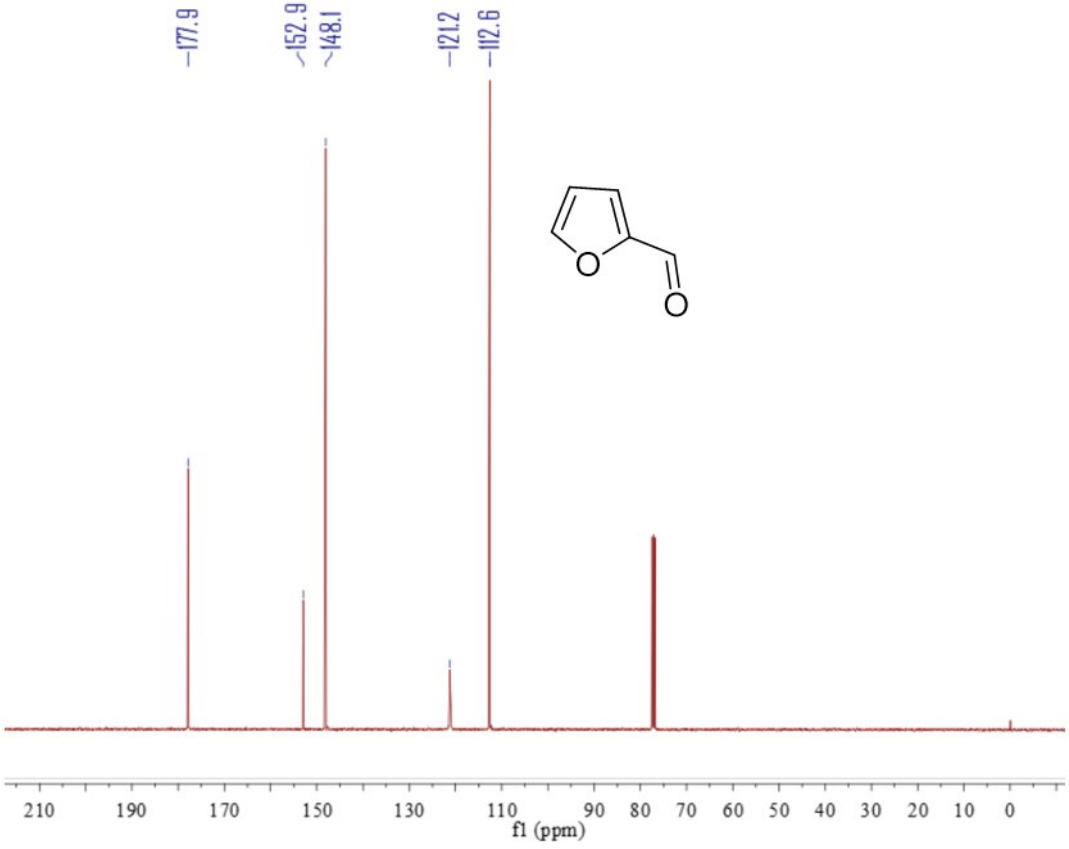
Compound 2n


9.9
7.9
7.8
7.0
7.0
3.9
O
MeO
0.96
1.95
1.95
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

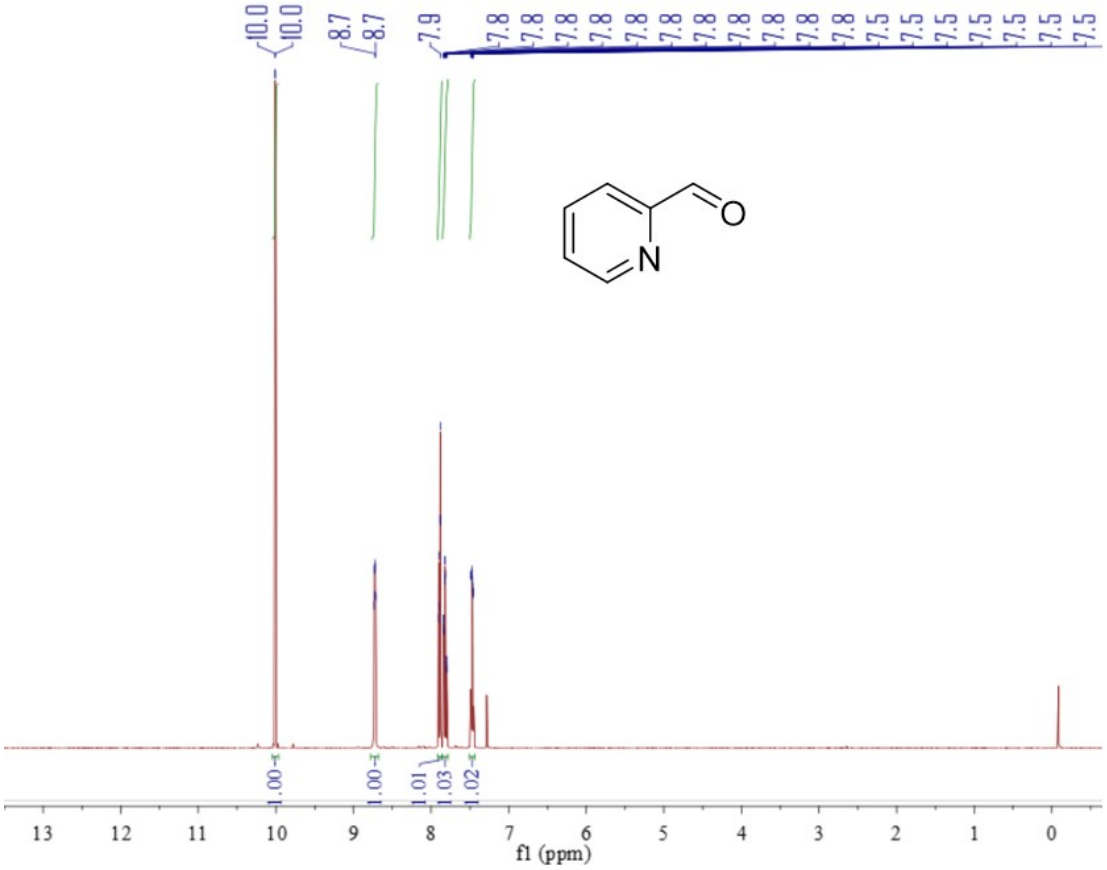

190.8
164.6
132.0
130.0
114.3
55.6
O
MeO
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

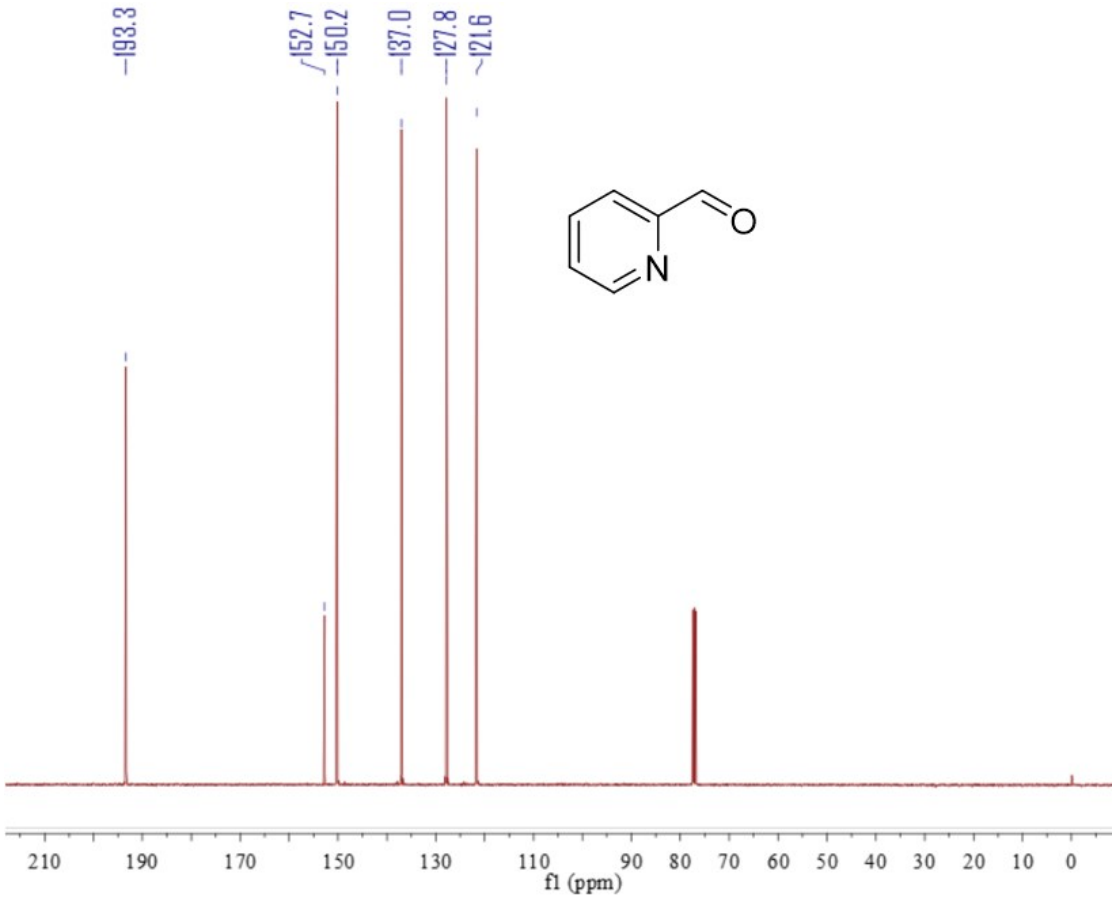
Compound 2o


9.6
9.6
7.7
7.2
7.2
7.2
6.6
6.6
6.6
6.6
1.00
1.00
1.01
1.01
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

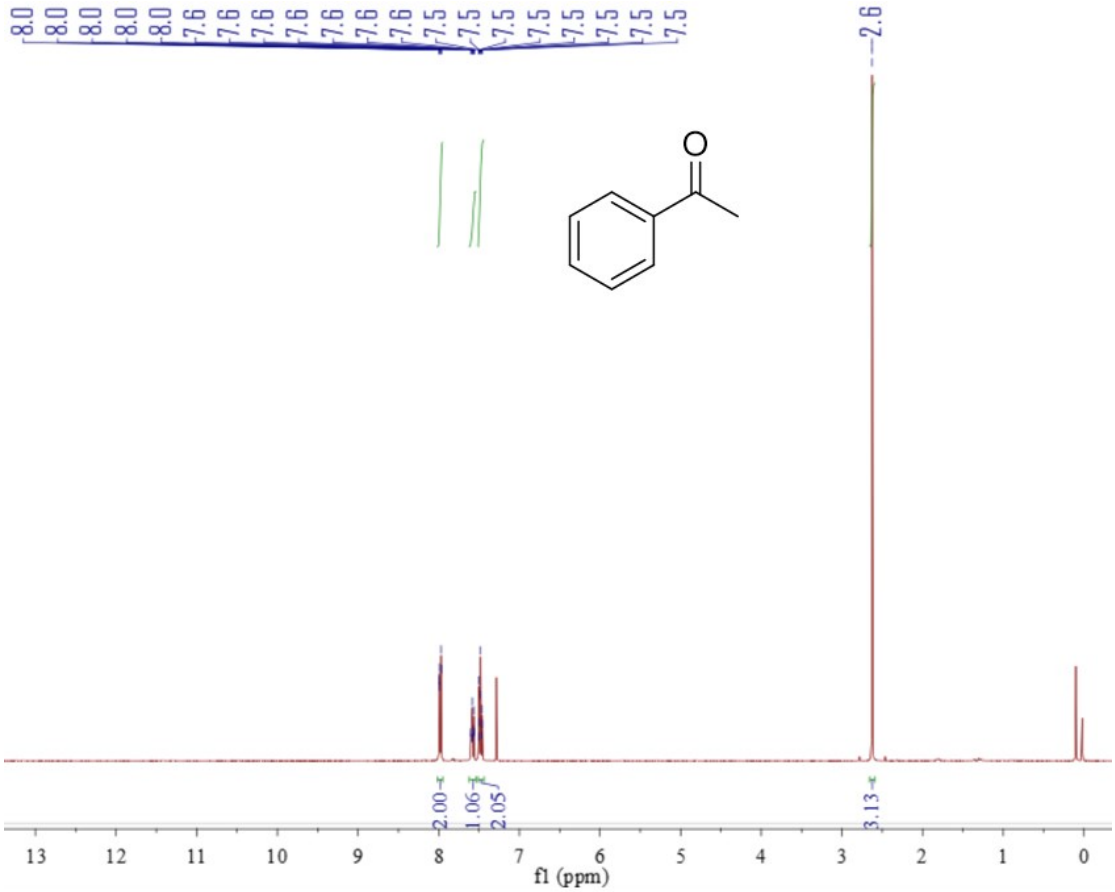

177.9
152.9
148.1
121.2
112.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

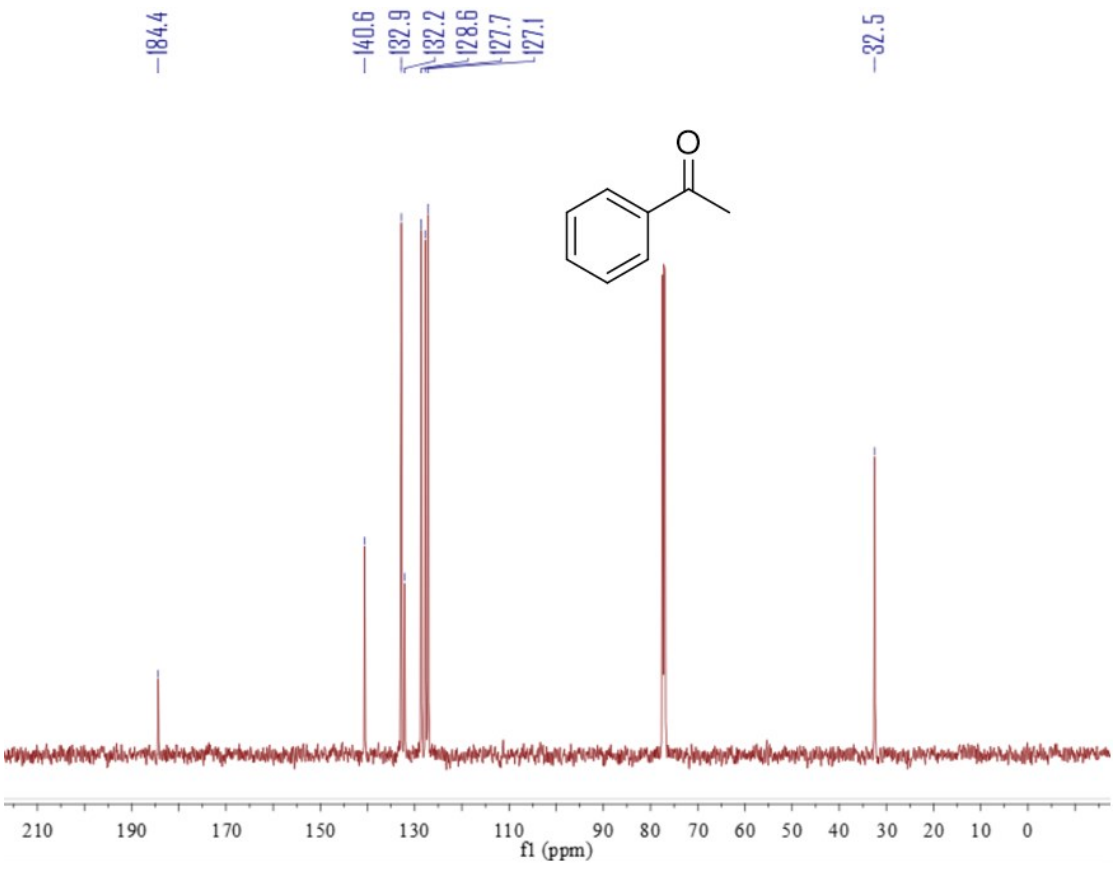
Compound 2p


10.0
10.0
8.7
8.7
7.9
7.8
7.8
7.8
7.8
7.8
7.8
7.8
7.8
7.8
7.5
7.5
7.5
7.5
7.5
7.5
7.5
O
N
1.00
1.00
1.01
1.03
1.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

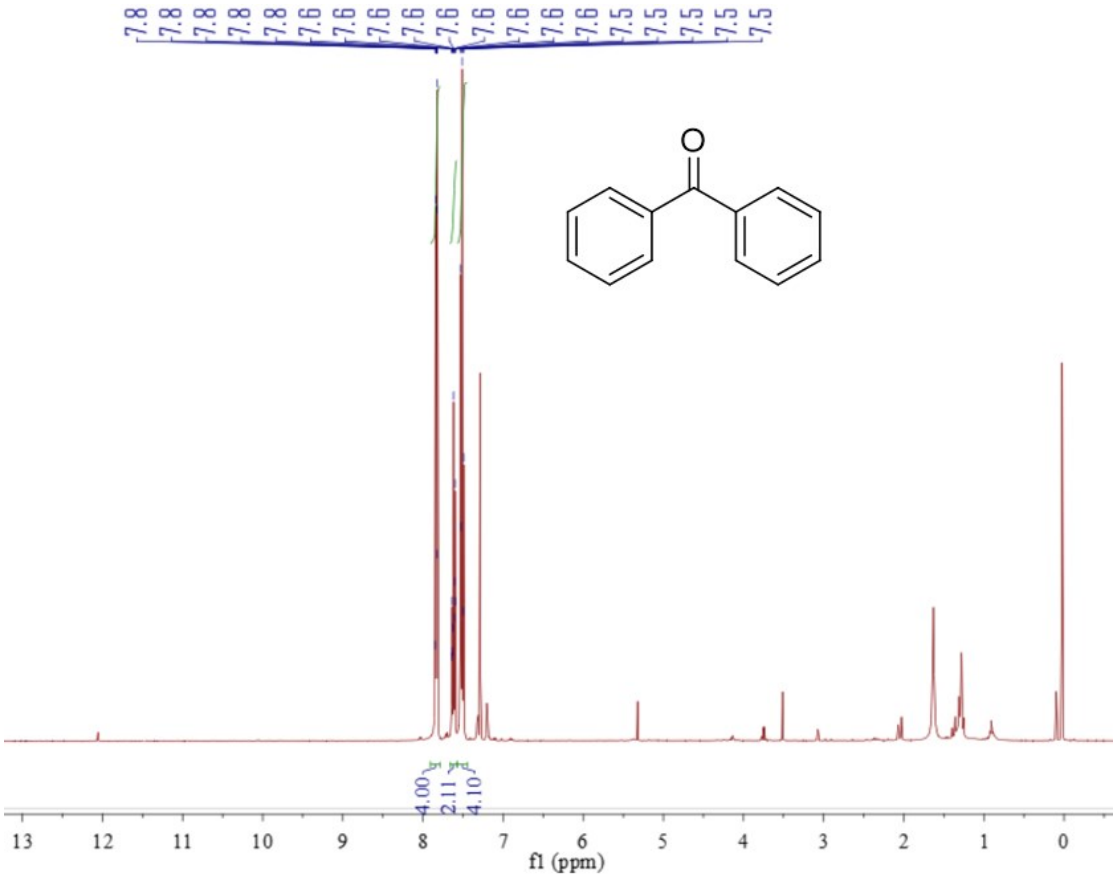

193.3
152.7
150.2
137.0
127.8
121.6
O
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

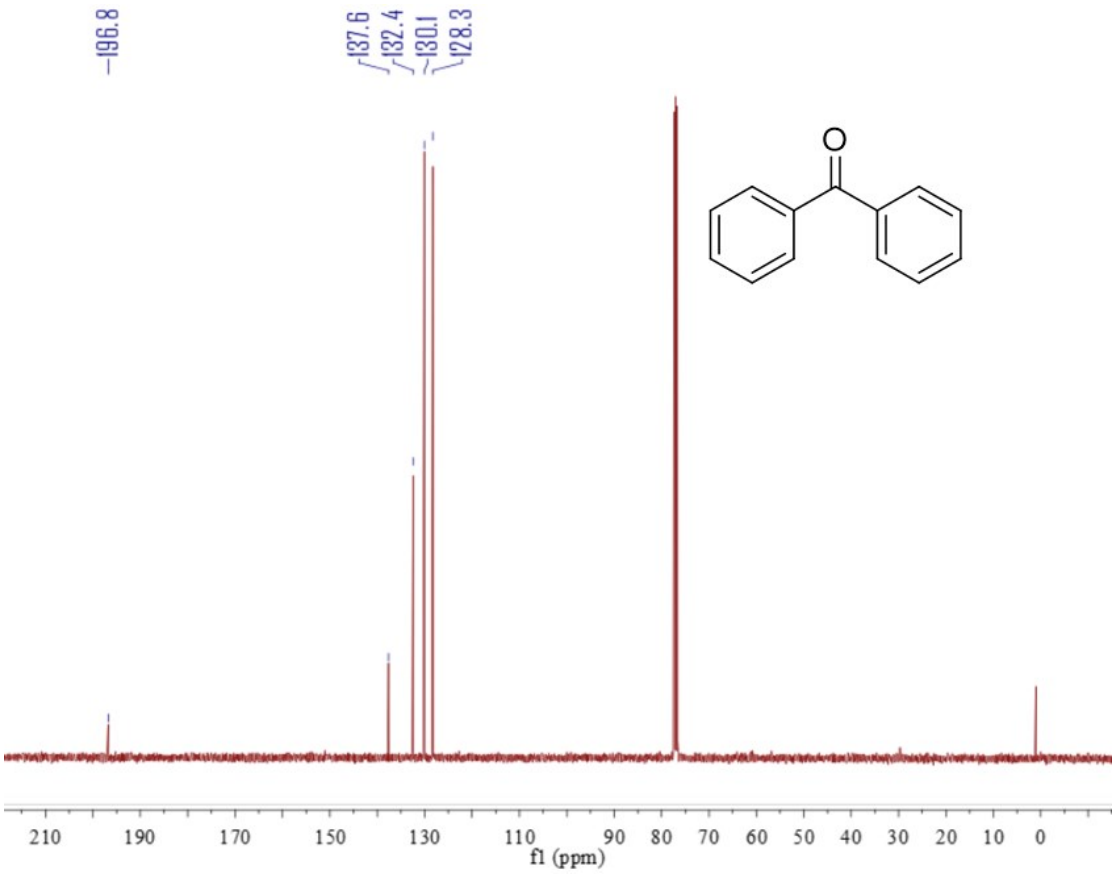
Compound 2q


8.0
7.6
7.5
2.6
2.00
1.06
2.05
3.13
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

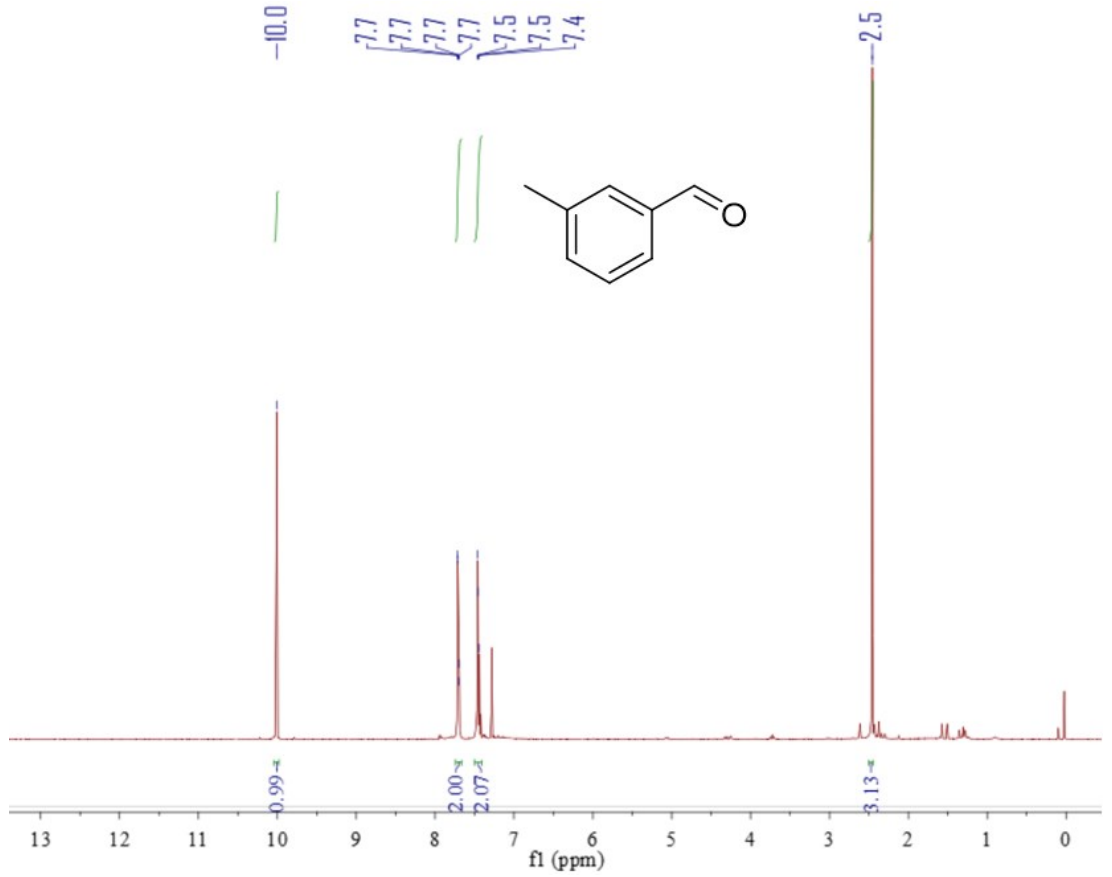

184.4
140.6
132.9
132.2
128.6
127.7
127.1
32.5
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

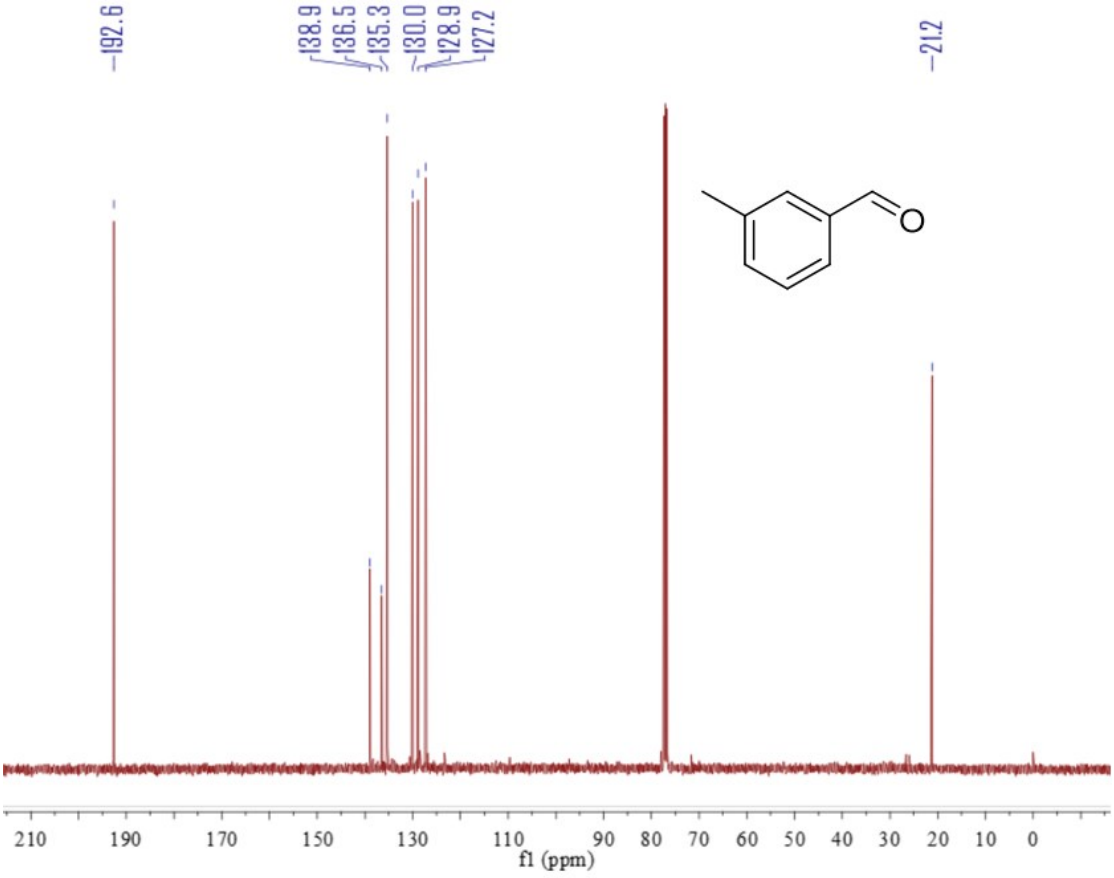
Compound 2r


7.8
7.8
7.8
7.8
7.8
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.6
7.5
7.5
7.5
7.5
4.00
2.11
4.10
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

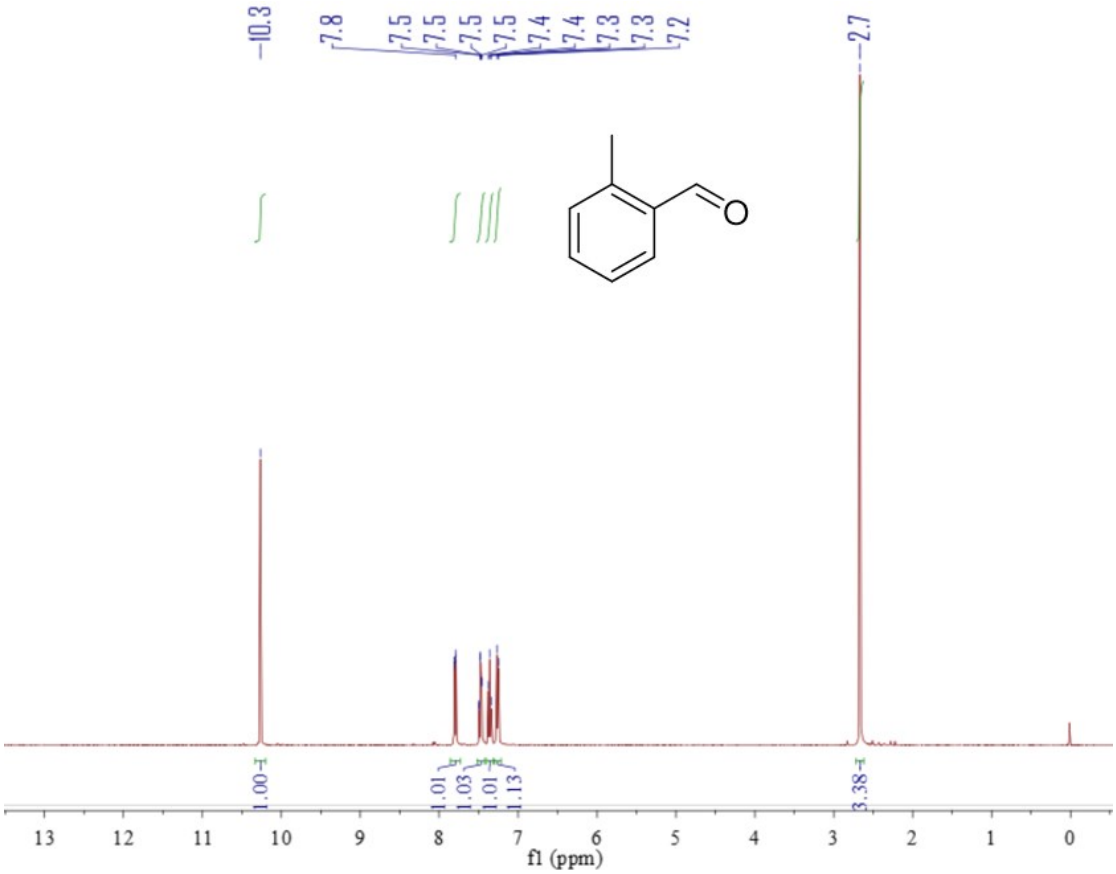

196.8
137.6
132.4
130.1
128.3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

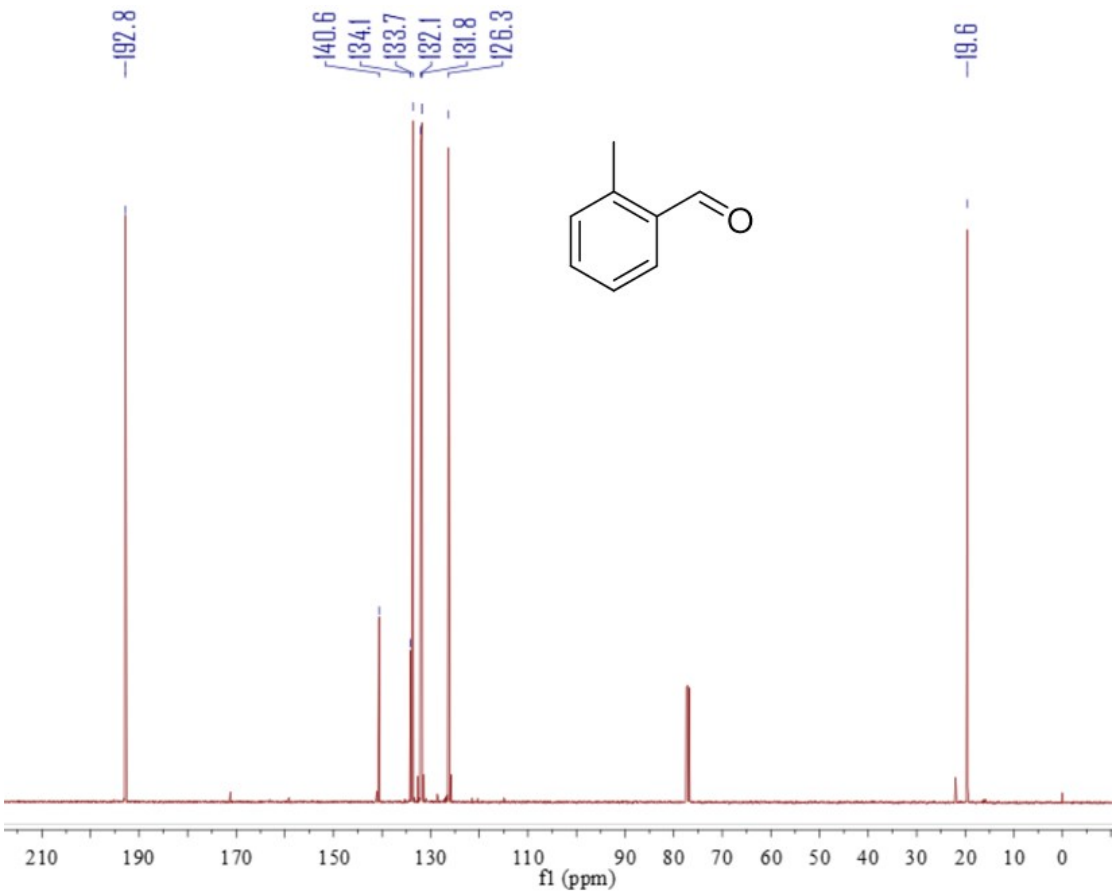
Compound 4a


10.0
7.7
7.7
7.7
7.7
7.5
7.5
7.4
2.5
0.99
2.00
2.07
3.13
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

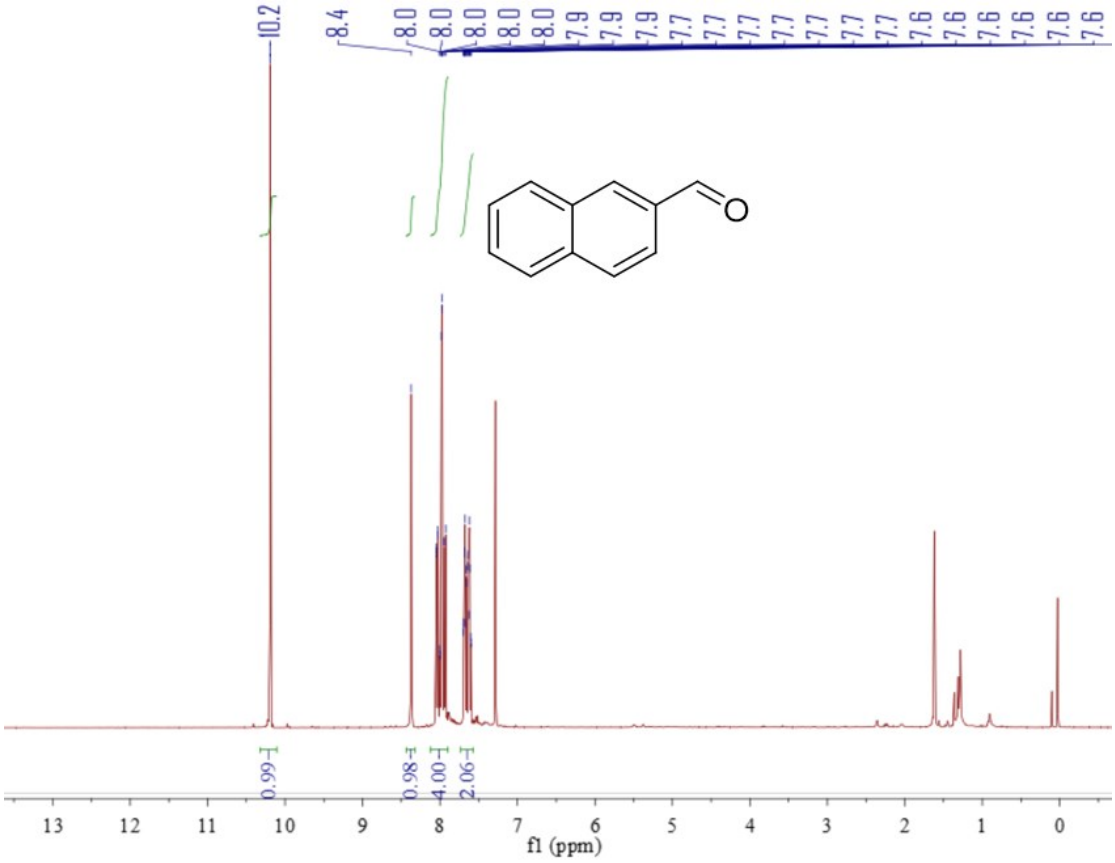

192.6
138.9
136.5
135.3
130.0
128.9
127.2
21.2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

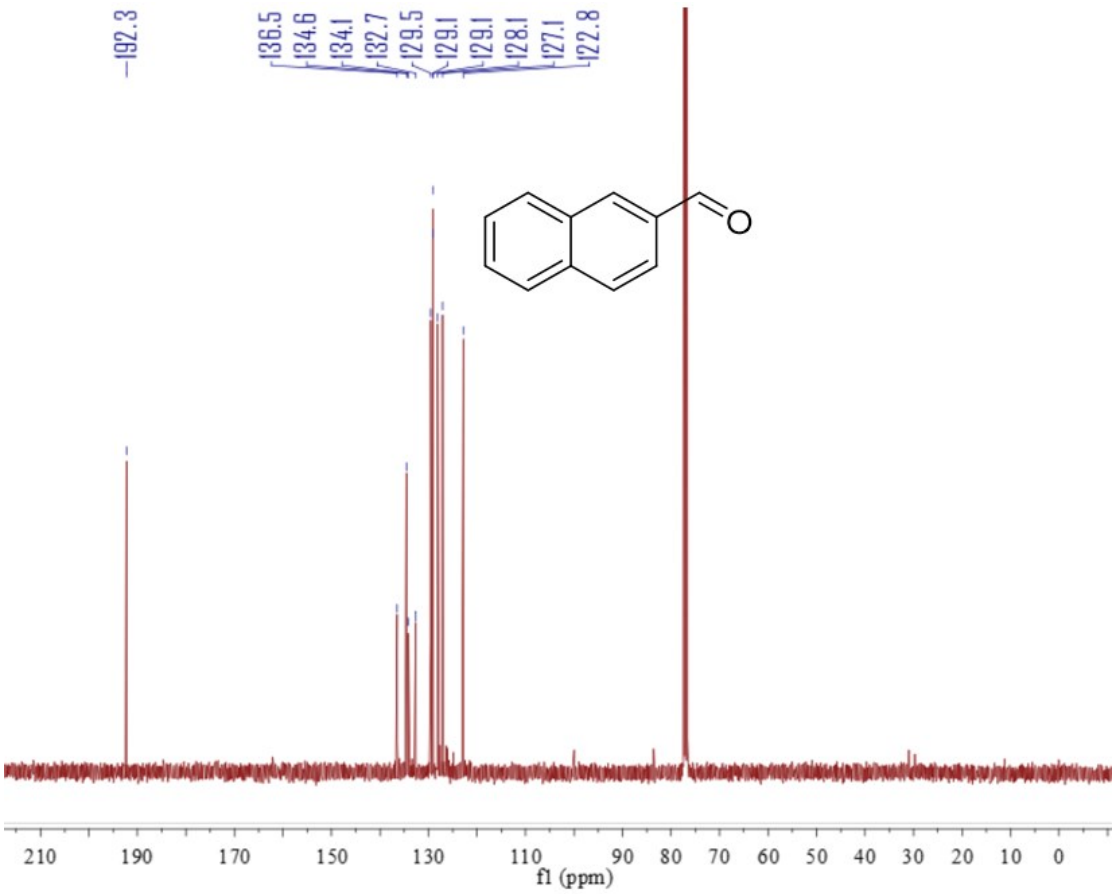
Compound 4b


10.3
7.8
7.5
7.5
7.5
7.5
7.4
7.4
7.3
7.3
7.2
2.7
1.00
1.01
1.03
1.01
1.13
3.38
f1 (ppm)

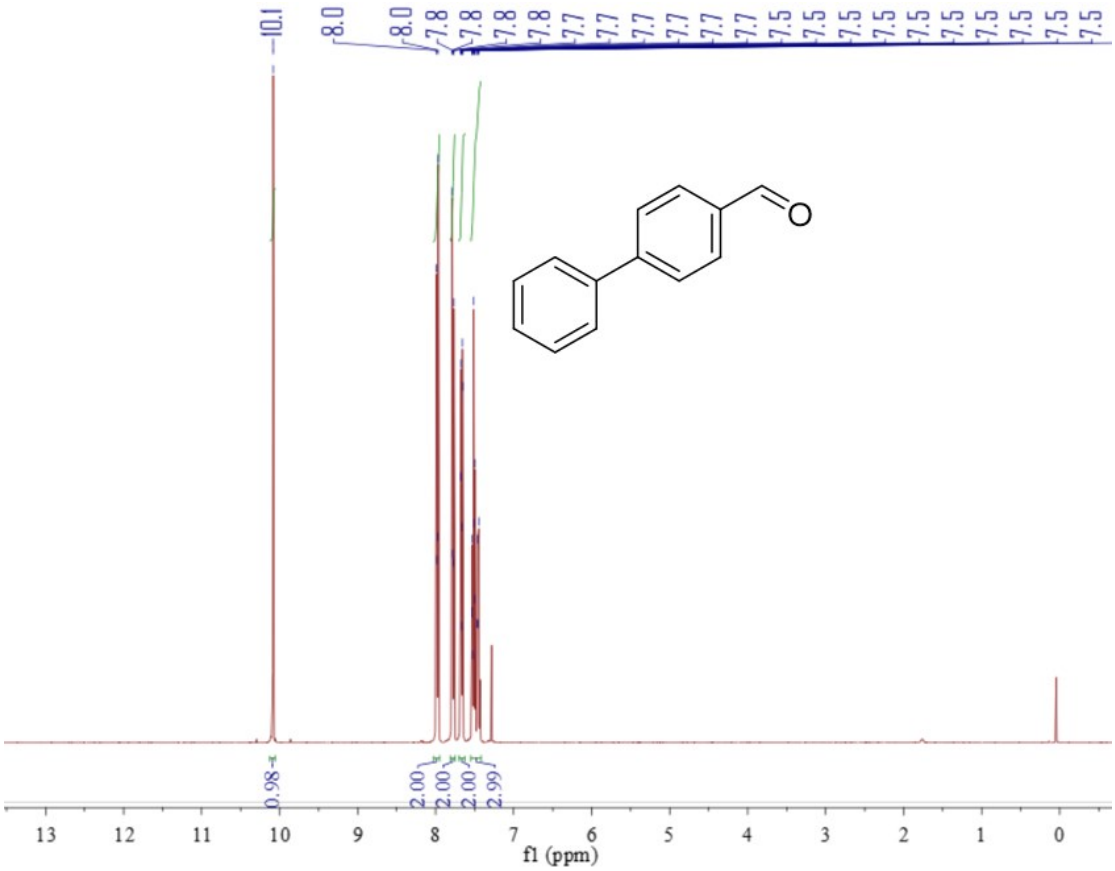

192.8
140.6
134.1
133.7
132.1
131.8
126.3
19.6
f1 (ppm)

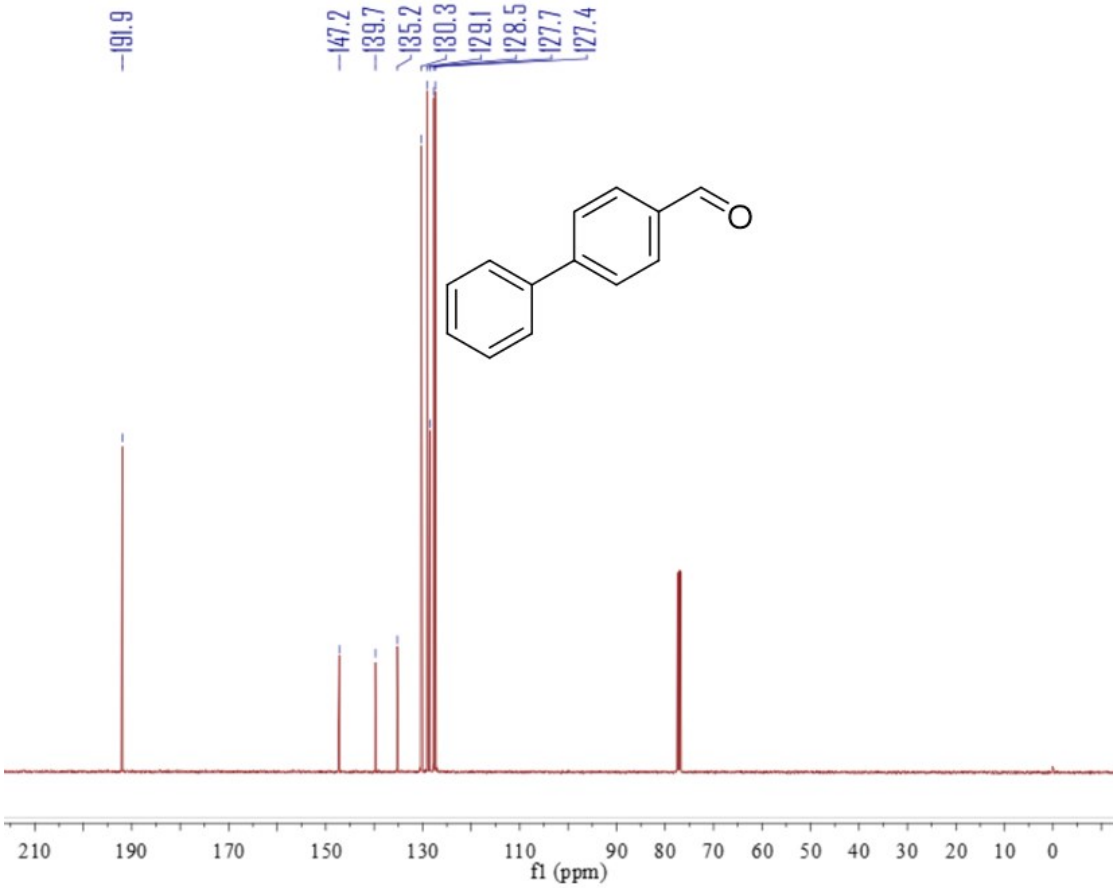
Compound 4c


10.2
8.4
8.0
8.0
8.0
8.0
8.0
7.9
7.9
7.9
7.7
7.7
7.7
7.7
7.7
7.7
7.7
7.6
7.6
7.6
7.6
7.6
7.6
0.99
0.98
4.00
2.06
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

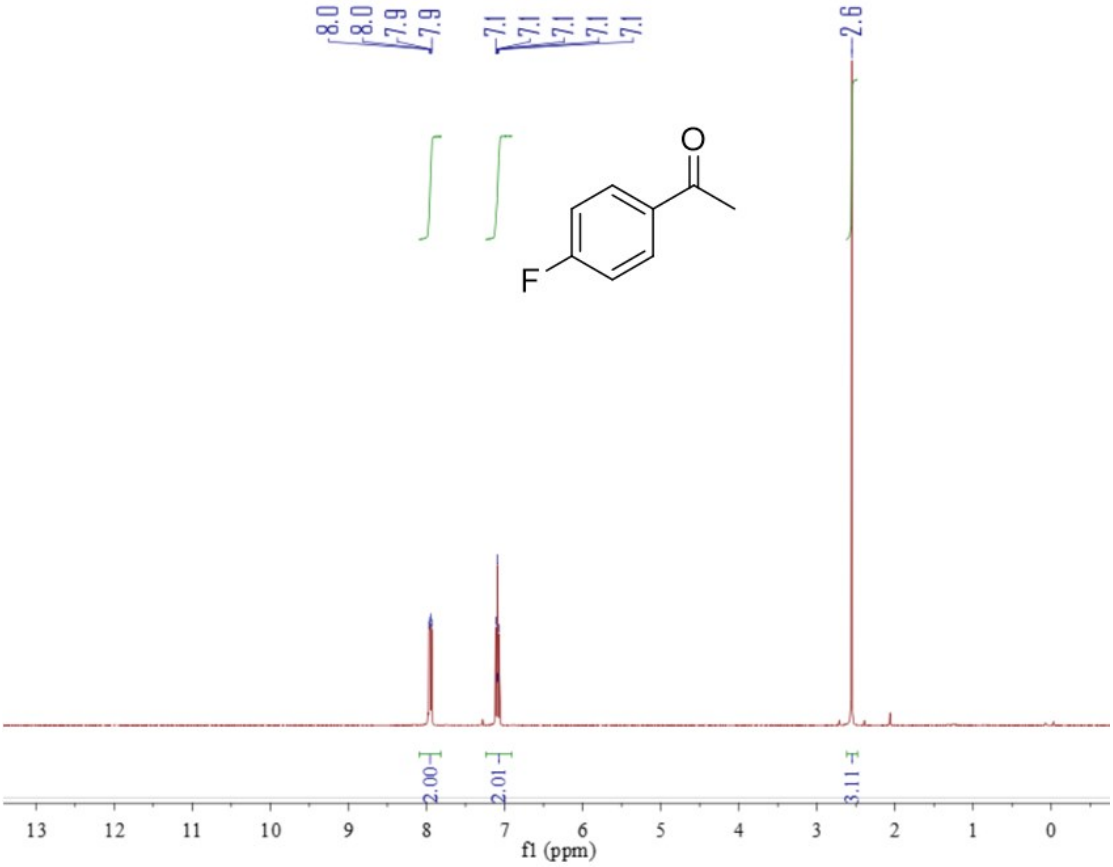

192.3
136.5
134.6
134.1
132.7
129.5
129.1
129.1
128.1
127.1
122.8
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

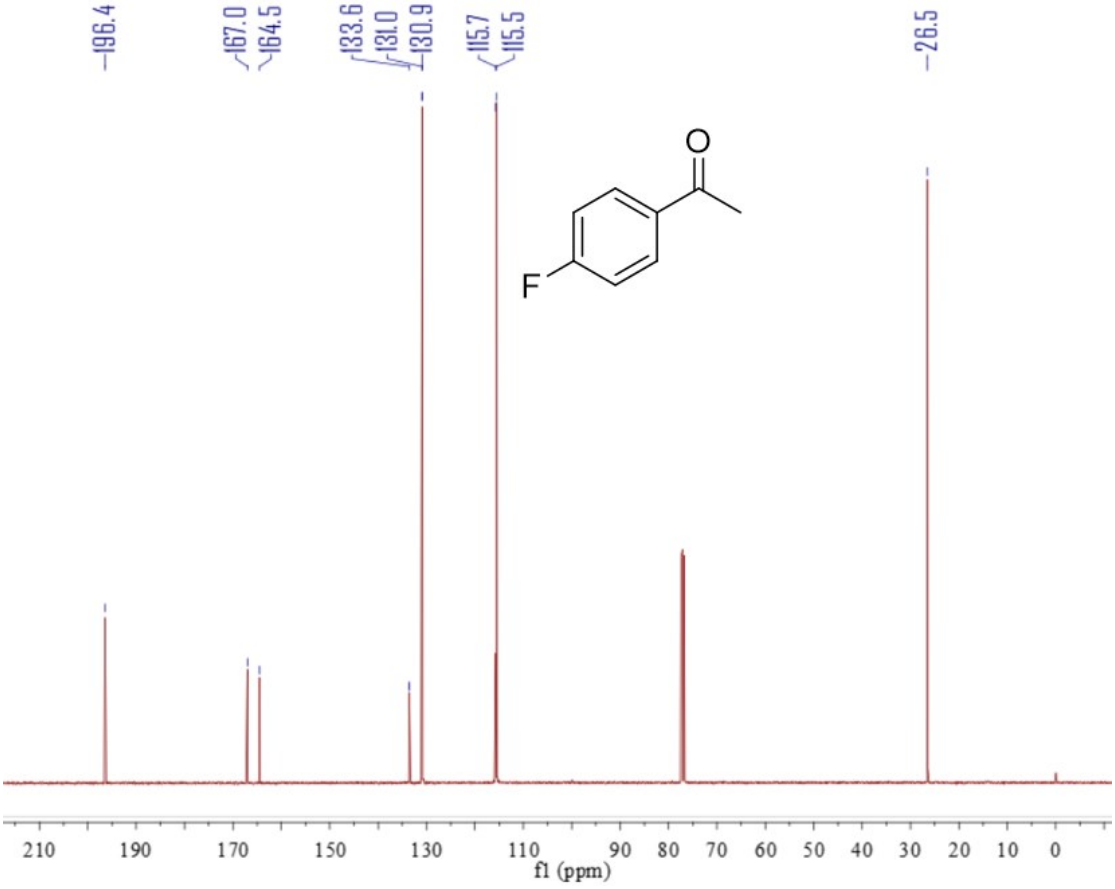
Compound 4d


10.1
8.0
8.0
7.8
7.8
7.8
7.8
7.7
7.7
7.7
7.7
7.7
7.7
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.5
O
0.98
2.00
2.00
2.00
2.99
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

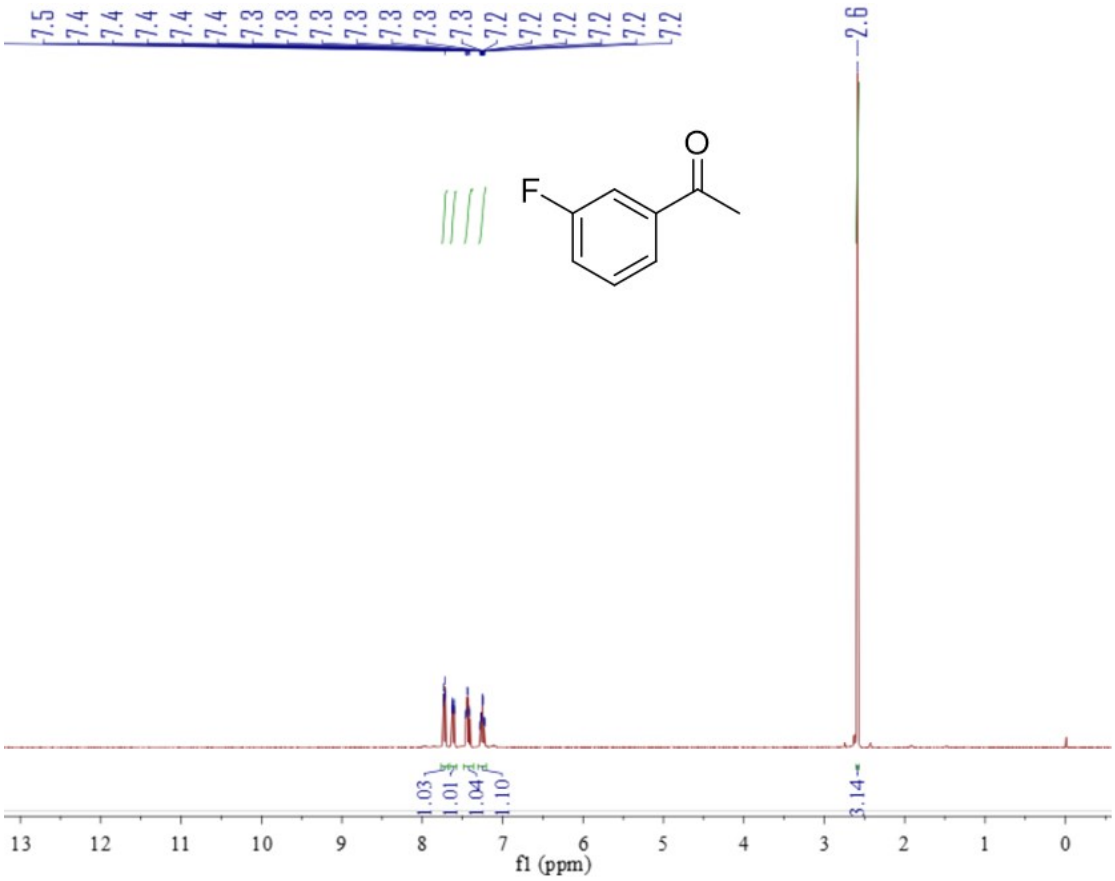

191.9
147.2
139.7
135.2
130.3
129.1
128.5
127.7
127.4
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

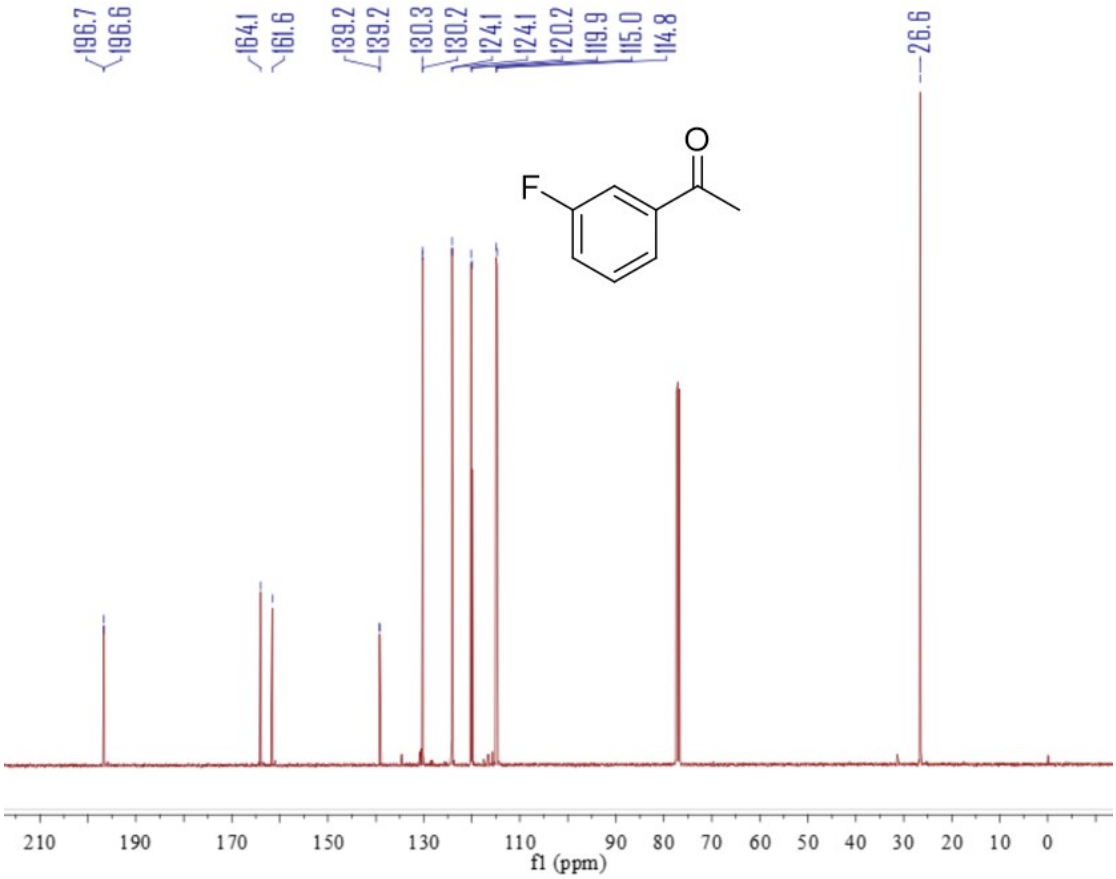
Compound 4e


8.0
8.0
7.9
7.9
7.1
7.1
7.1
7.1
7.1
2.6
O
F
2.00
2.01
3.11
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

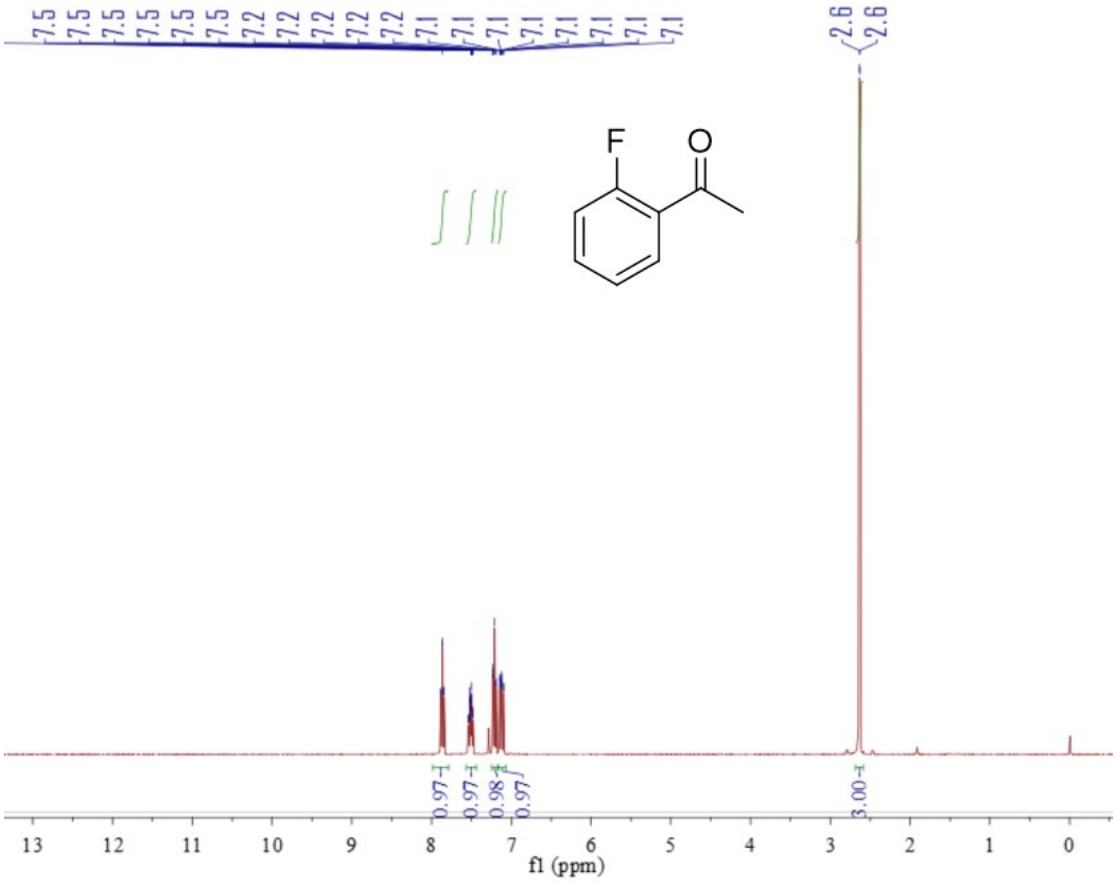

196.4
167.0
164.5
133.6
131.0
130.9
115.7
115.5
26.5
O
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

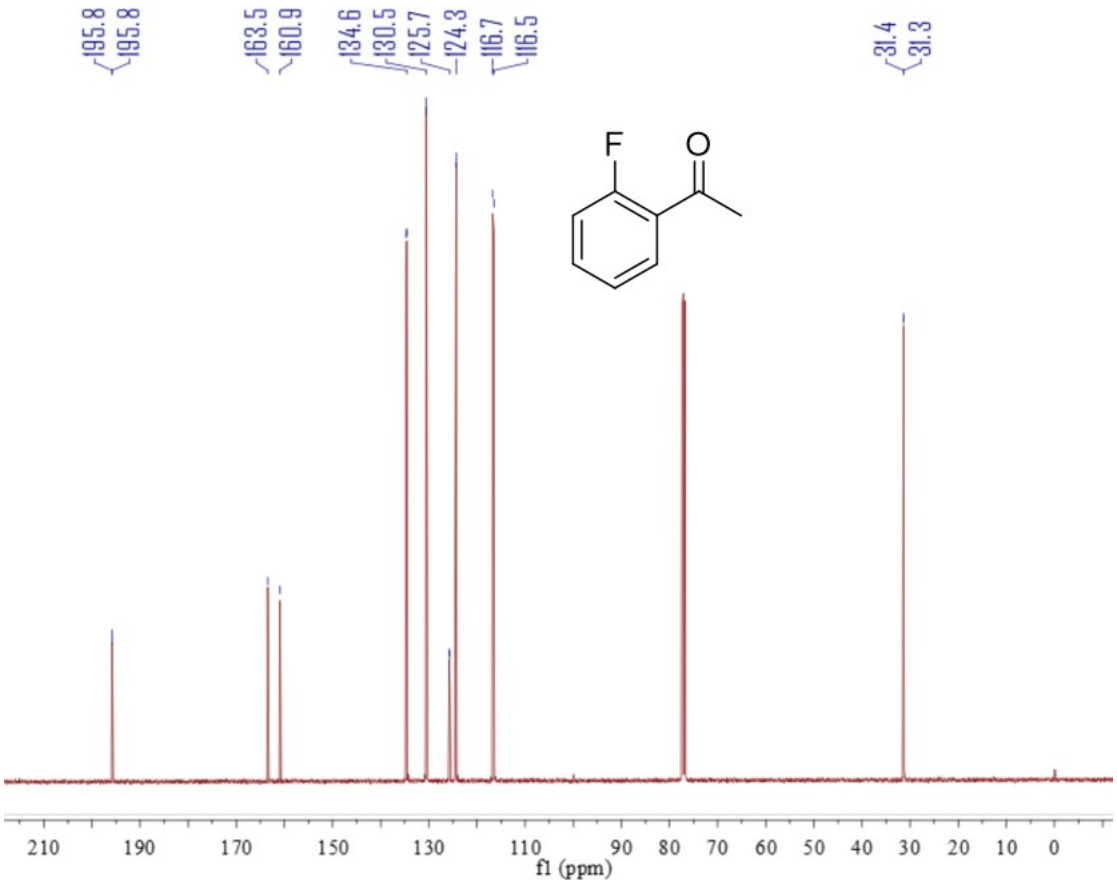
Compound 4f


7.5
7.4
7.4
7.4
7.4
7.4
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.2
7.2
2.6
O
F
1.03
1.01
1.04
1.10
3.14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

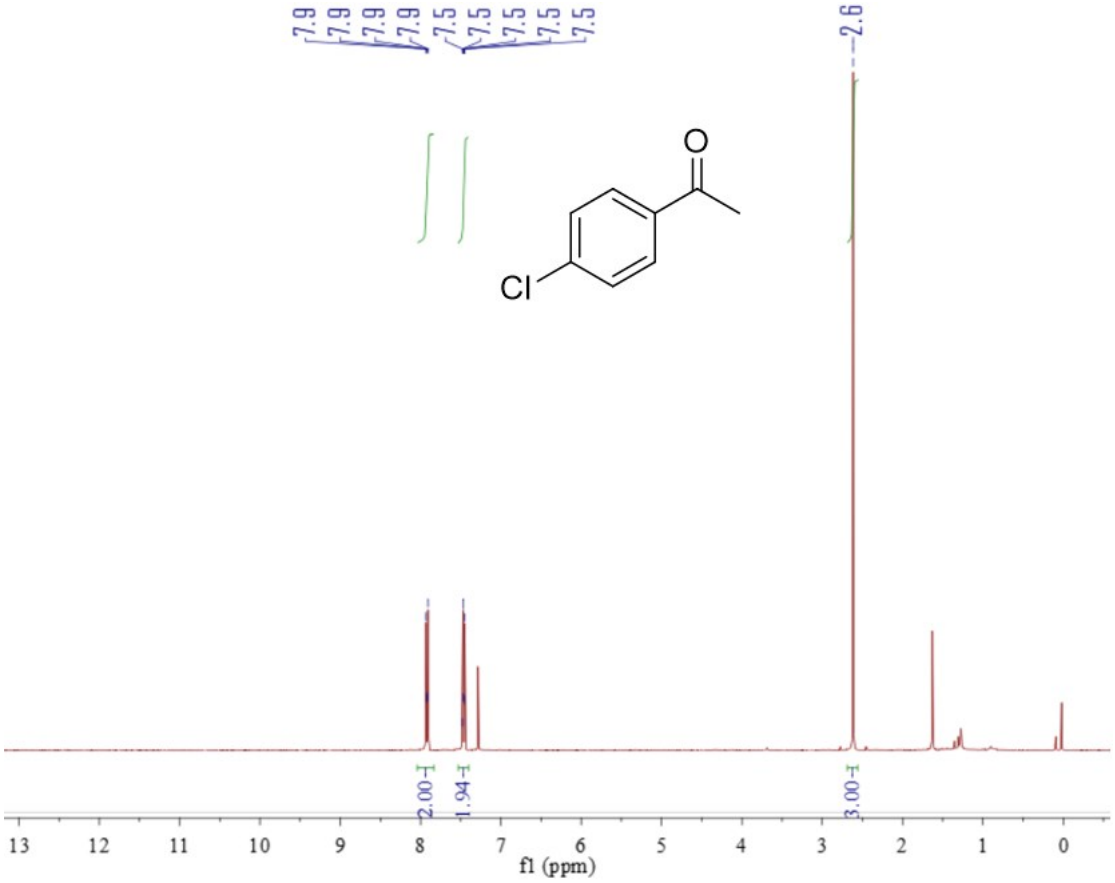

196.7
196.6
164.1
161.6
139.2
139.2
130.3
130.2
124.1
124.1
120.2
119.9
115.0
114.8
26.6
O
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

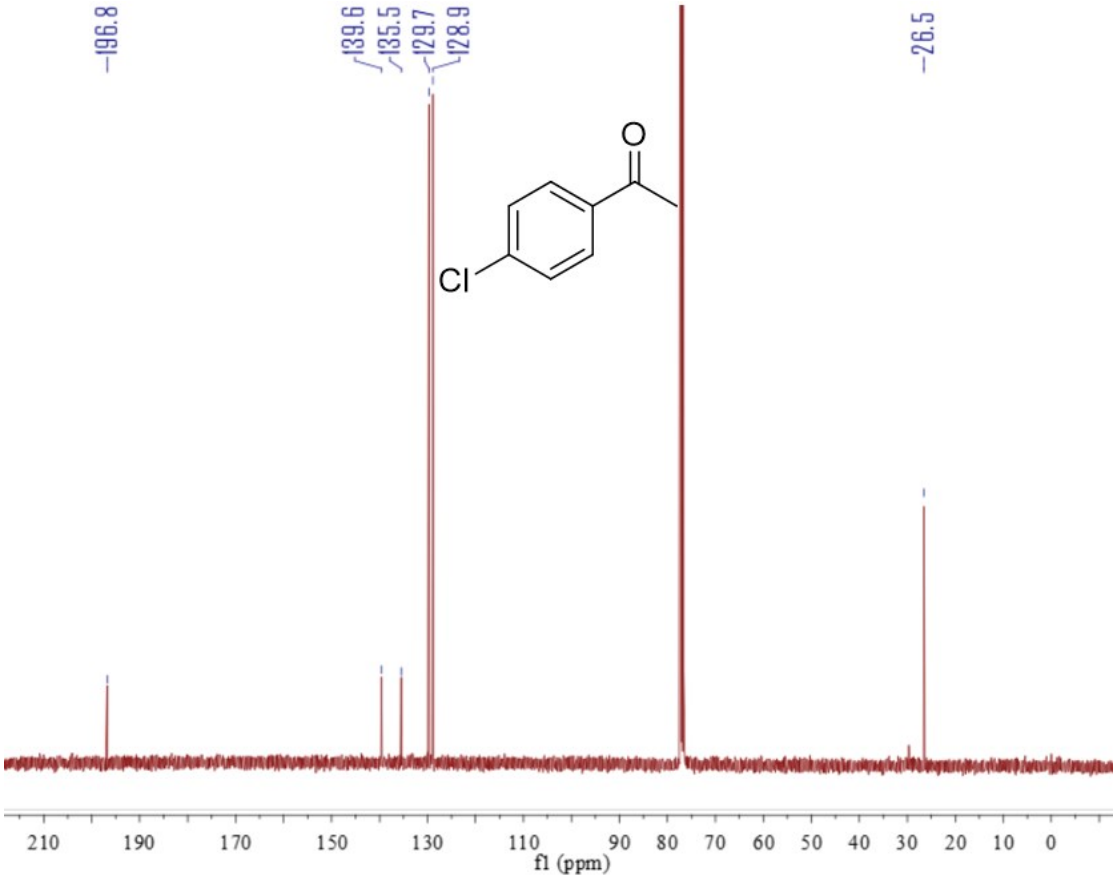
Compound 4g


7.5
7.5
7.5
7.5
7.5
7.5
7.2
7.2
7.2
7.2
7.2
7.1
7.1
7.1
7.1
7.1
7.1
7.1
7.1
2.6
2.6
F
O
0.97
0.97
0.98
0.97
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

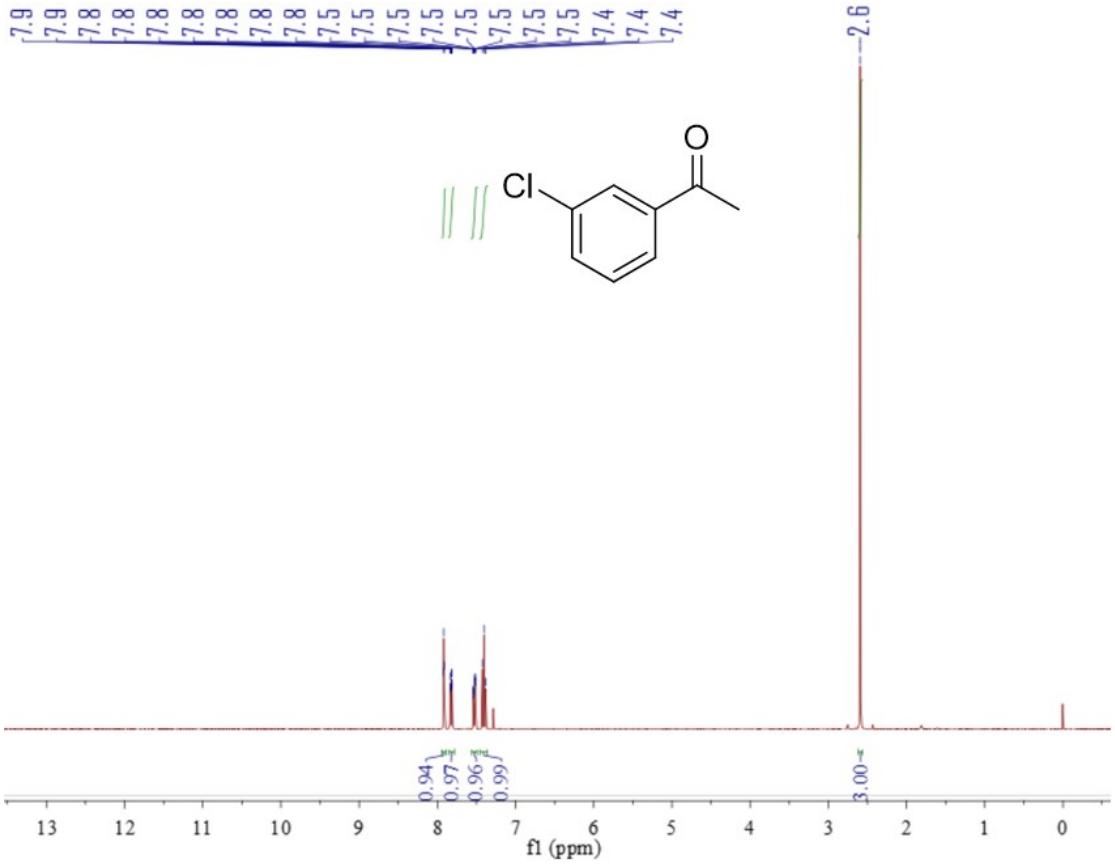

195.8
195.8
163.5
160.9
134.6
130.5
125.7
124.3
116.7
116.5
31.4
31.3
F
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

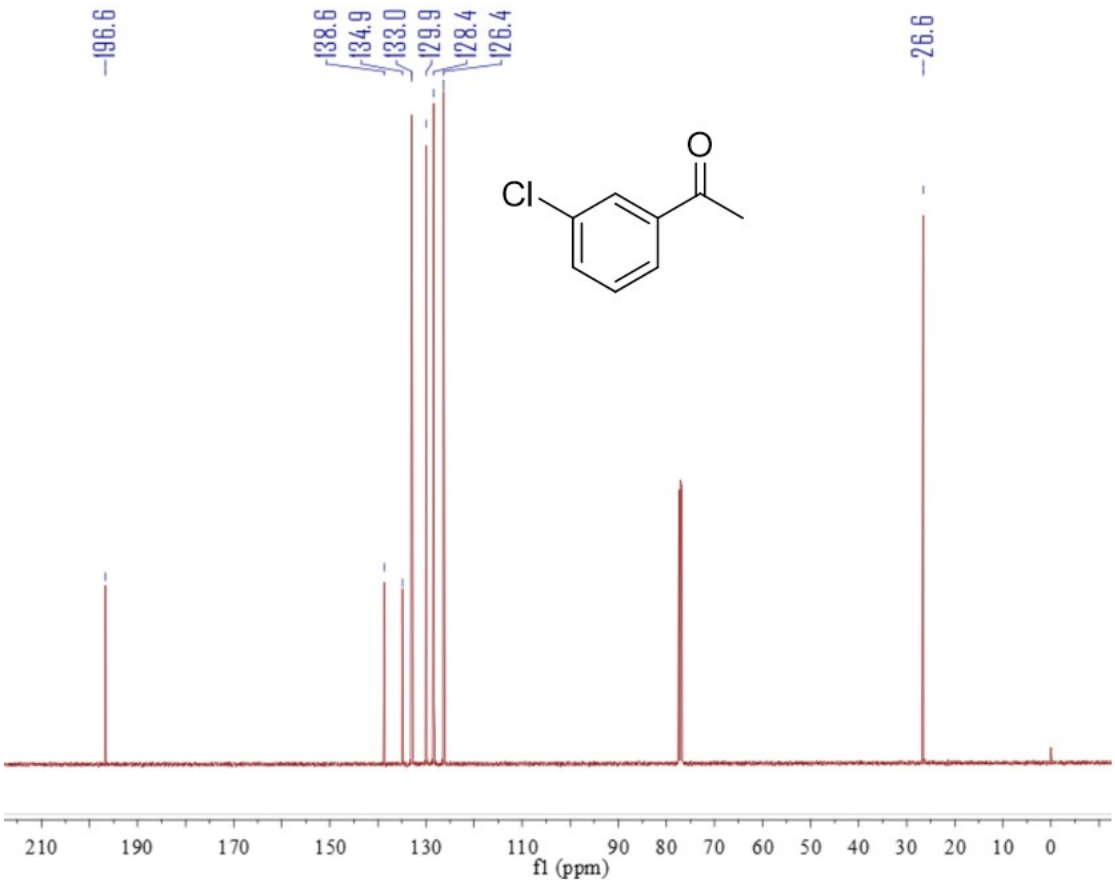
Compound 4h


7.9
7.9
7.9
7.9
7.5
7.5
7.5
7.5
7.5
2.6
O
Cl
2.00
1.94
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

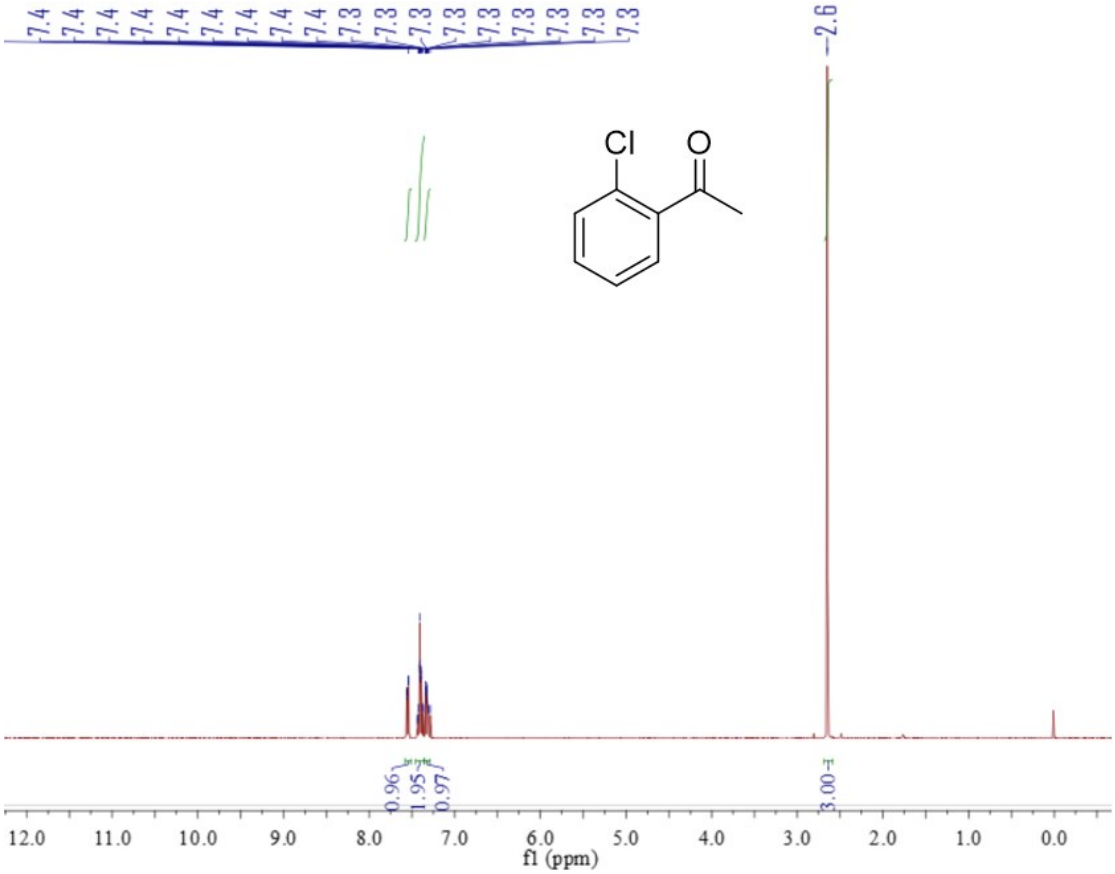

196.8
139.6
135.5
129.7
128.9
26.5
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

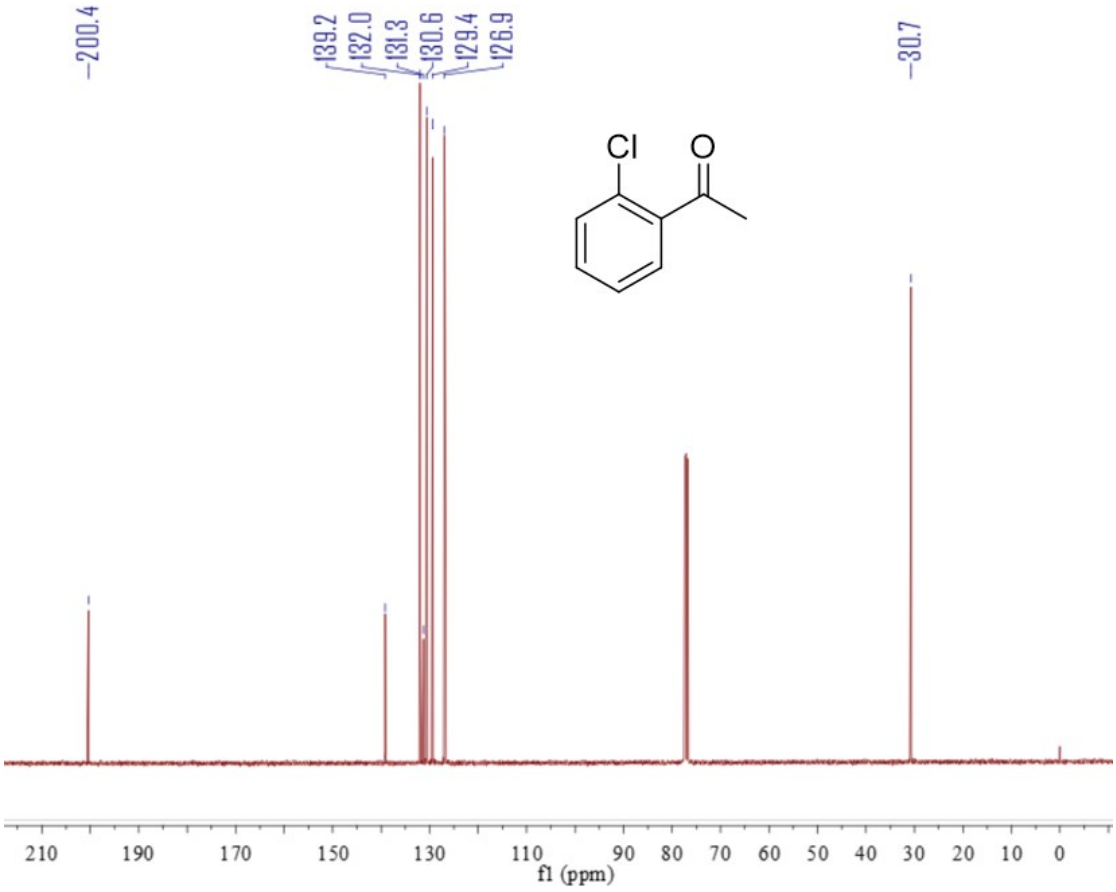
Compound 4i


7.9
7.9
7.8
7.8
7.8
7.8
7.8
7.8
7.8
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.5
7.4
7.4
7.4
2.6
Cl
O
0.94
0.97
0.96
0.99
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

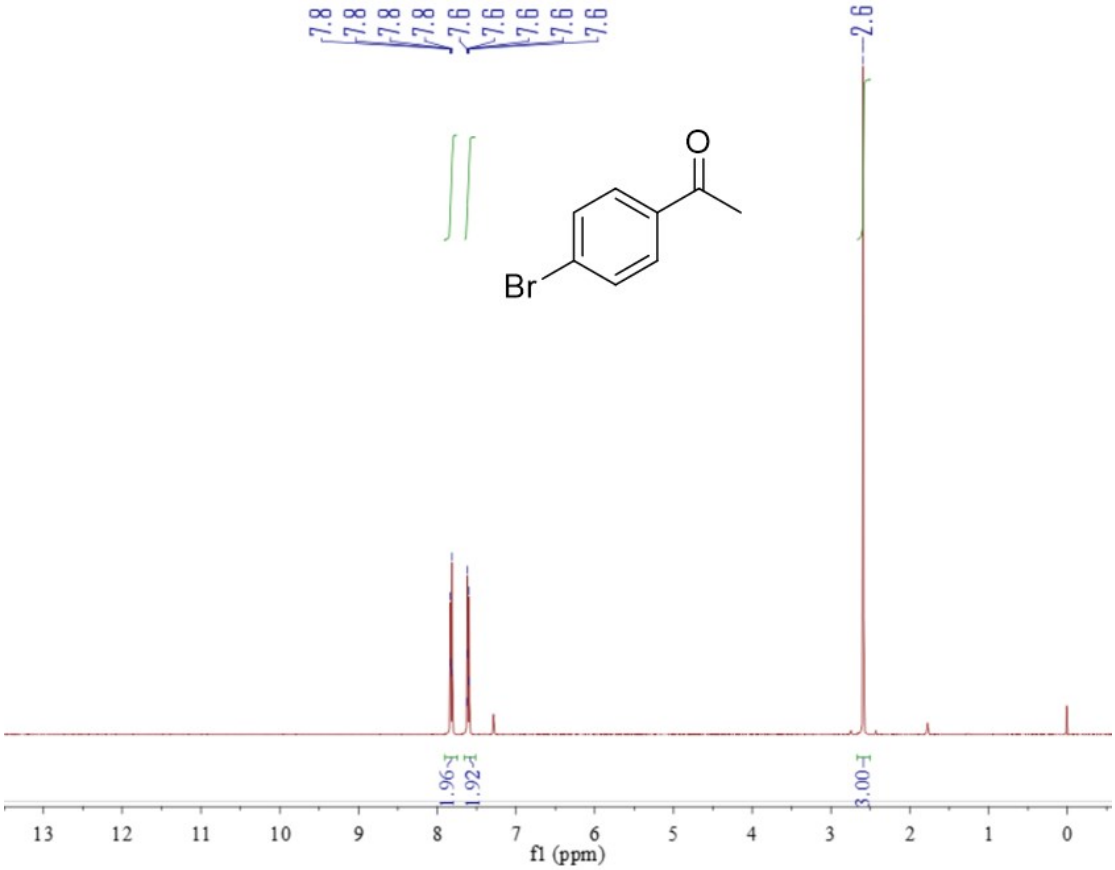

196.6
138.6
134.9
133.0
129.9
128.4
126.4
26.6
Cl
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

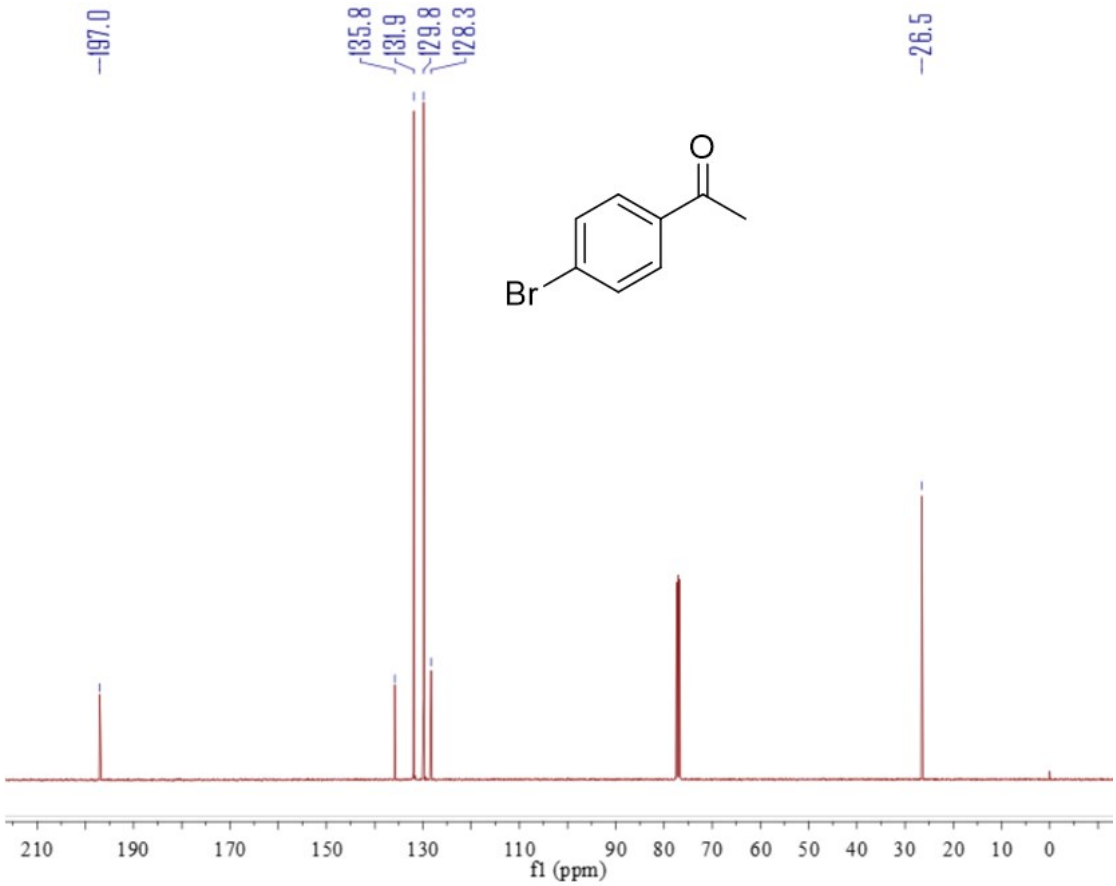
Compound 4j


7.4
7.3
2.6
Cl
O
0.96
1.95
0.97
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

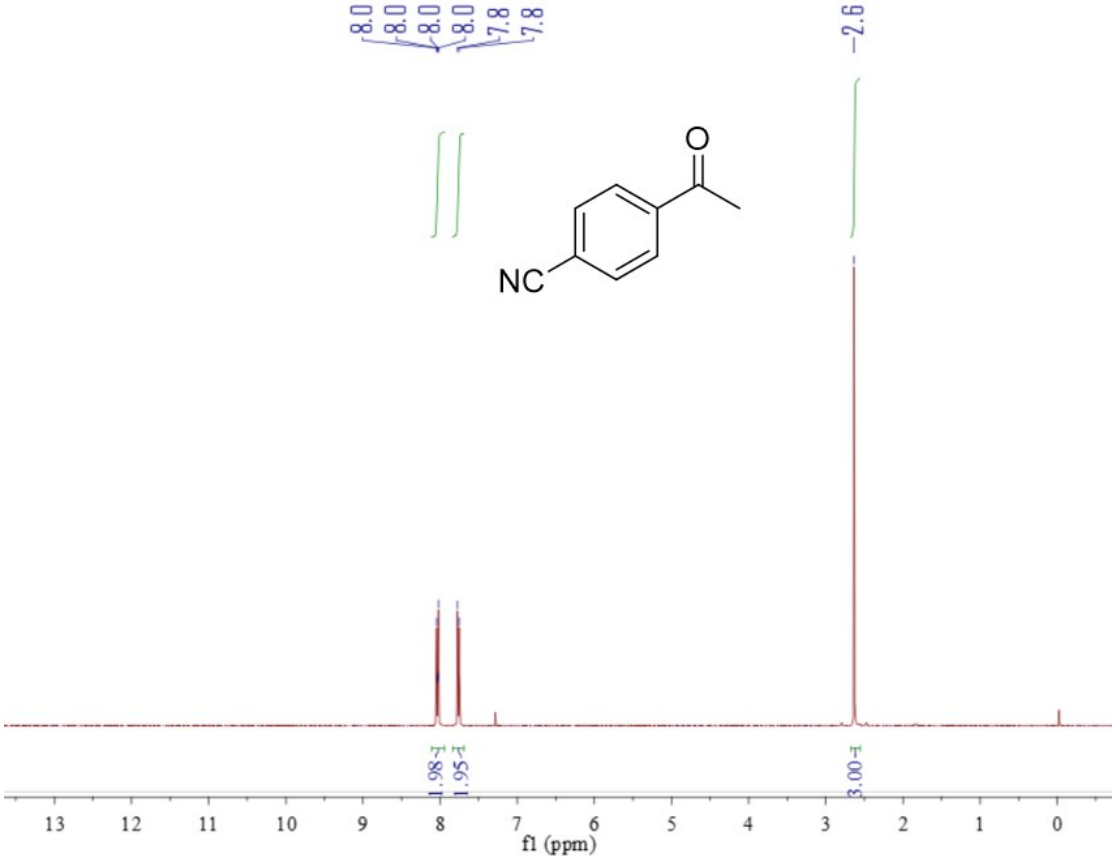

200.4
139.2
132.0
131.3
130.6
129.4
126.9
30.7
Cl
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

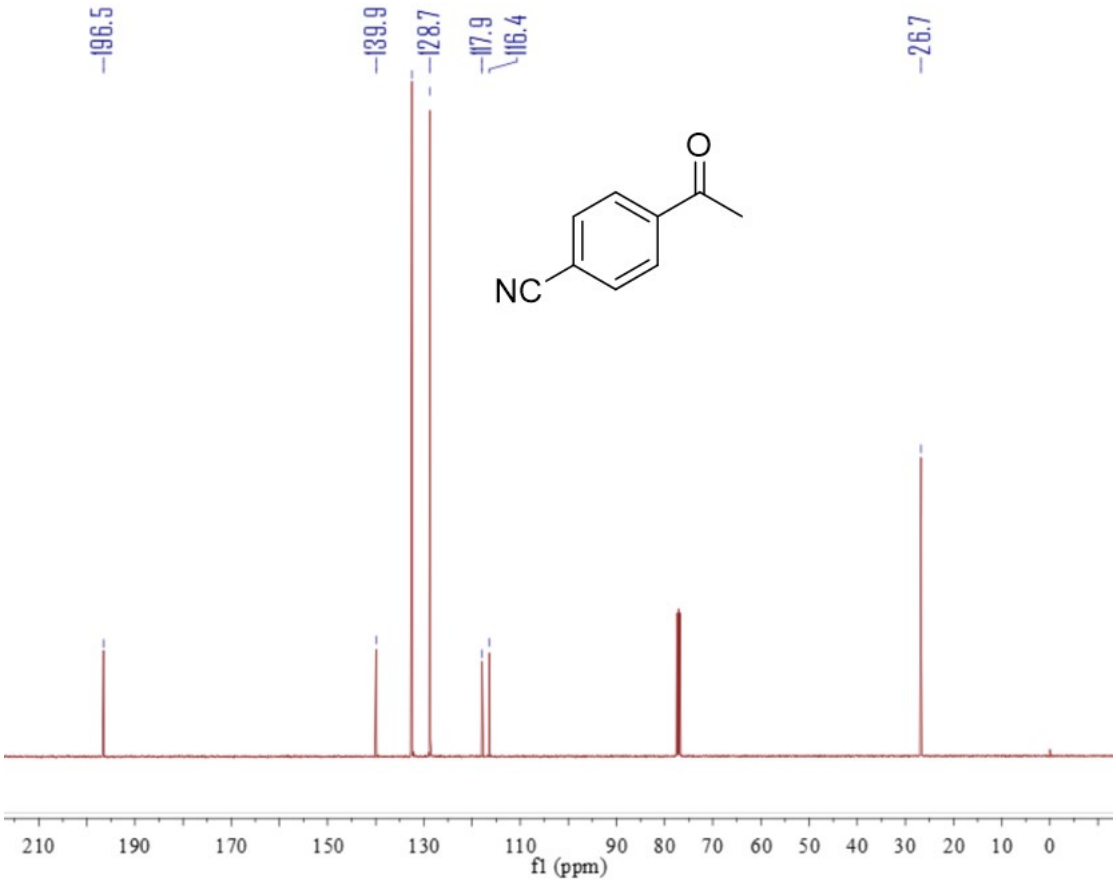
Compound 4k


7.8
7.8
7.8
7.8
7.6
7.6
7.6
7.6
7.6
2.6
O
Br
1.96
1.92
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

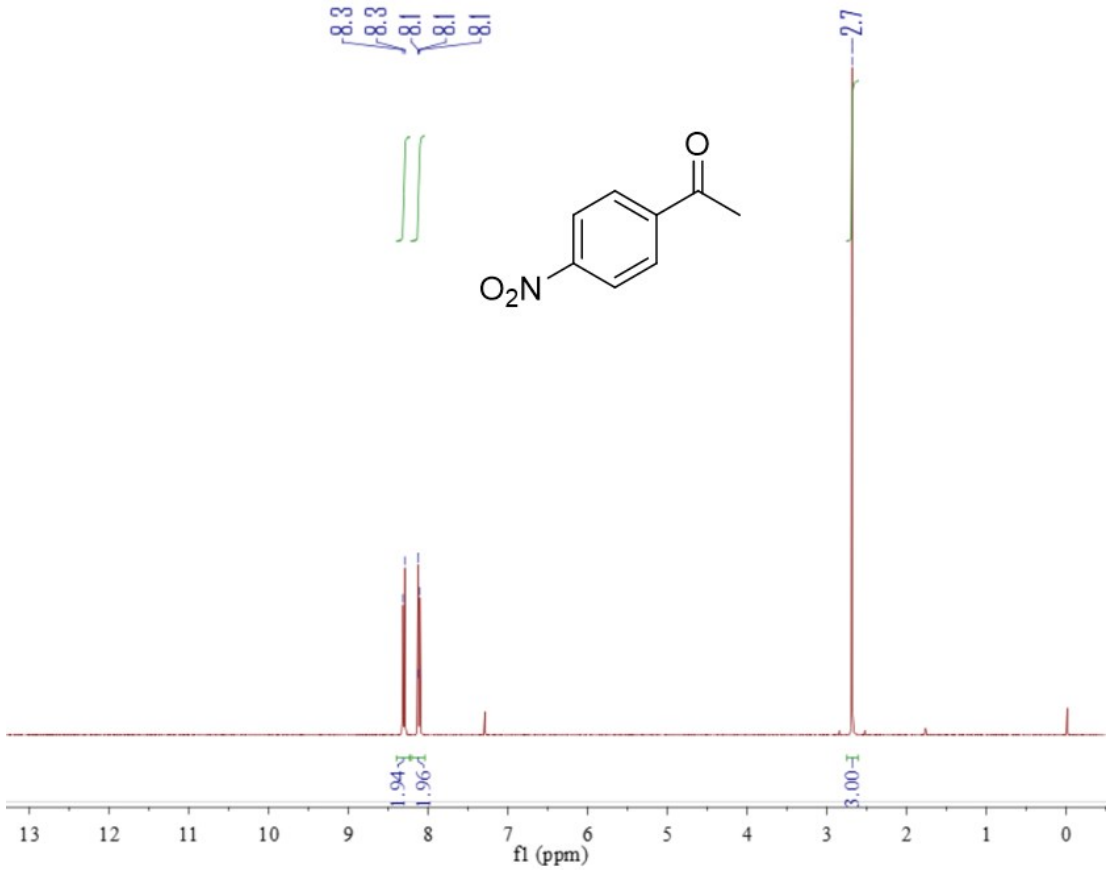

197.0
135.8
131.9
129.8
128.3
26.5
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

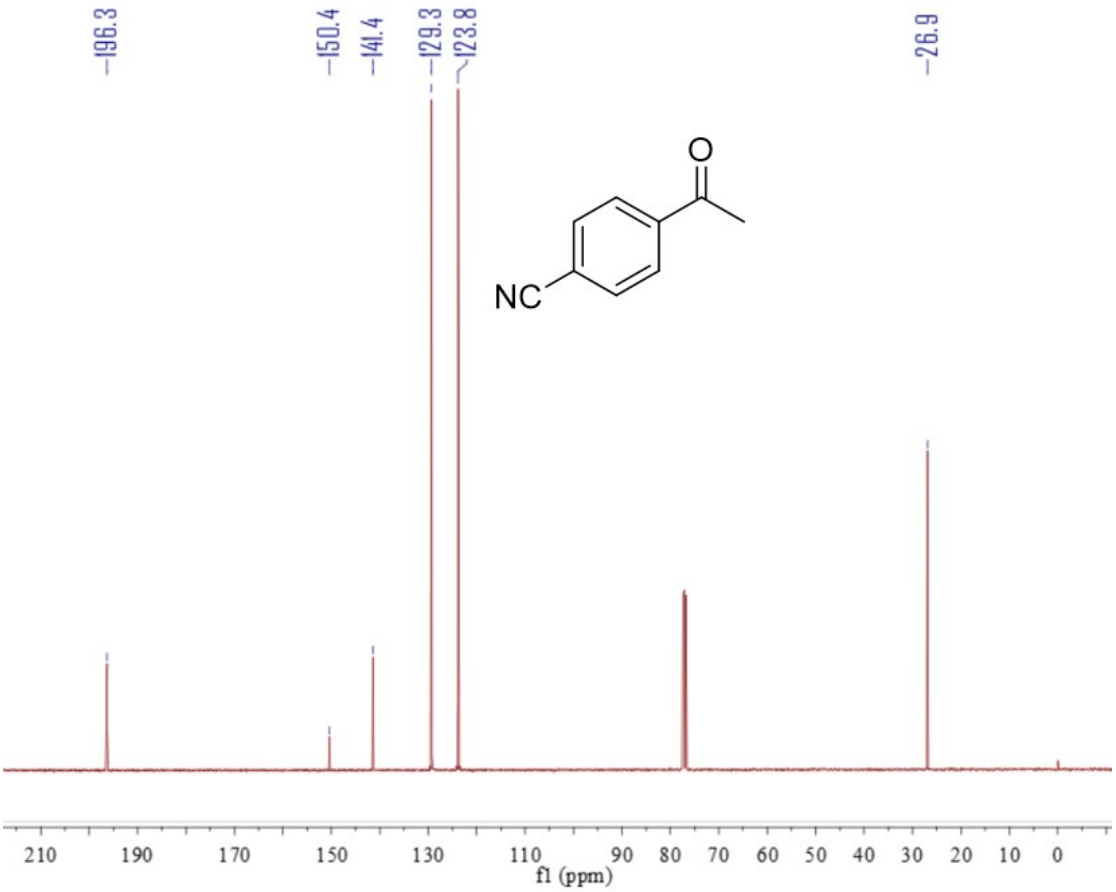
Compound 4l


8.0
8.0
8.0
8.0
7.8
7.8
2.6
O
NC
1.98
1.95
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

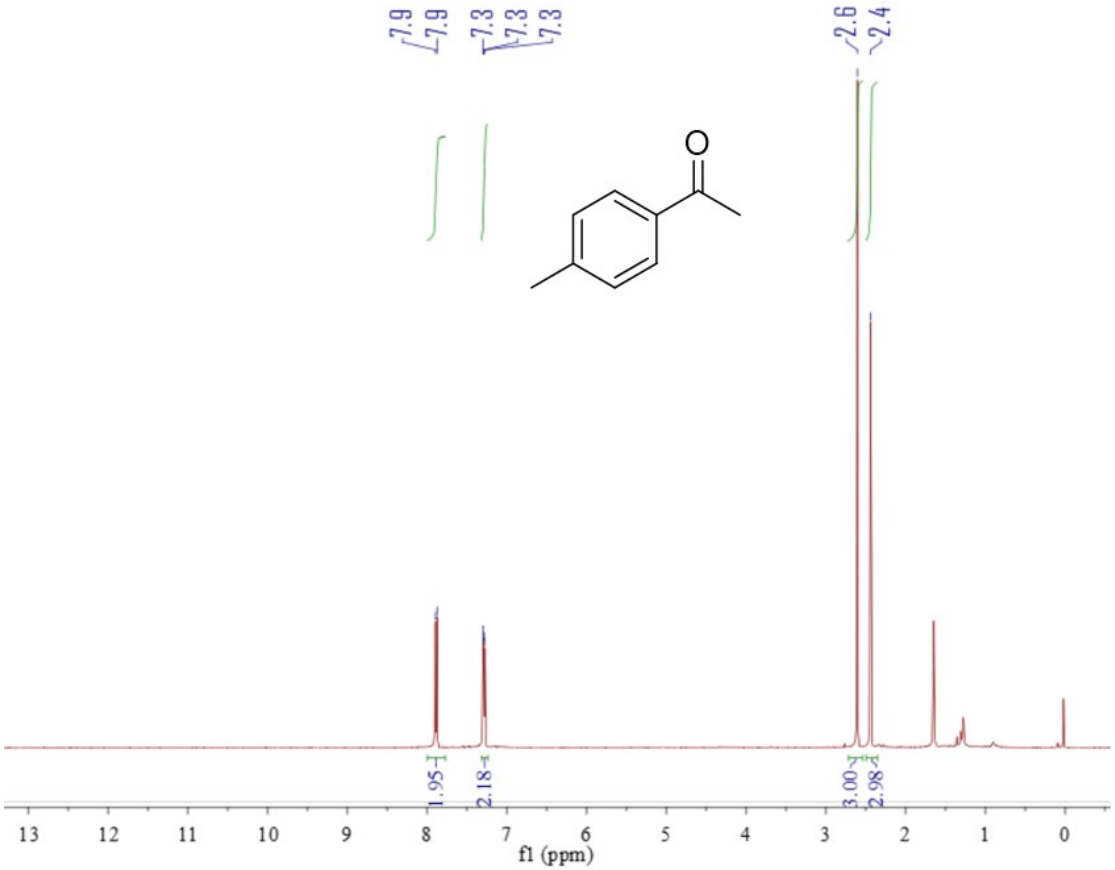

196.5
139.9
128.7
117.9
116.4
26.7
O
NC
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

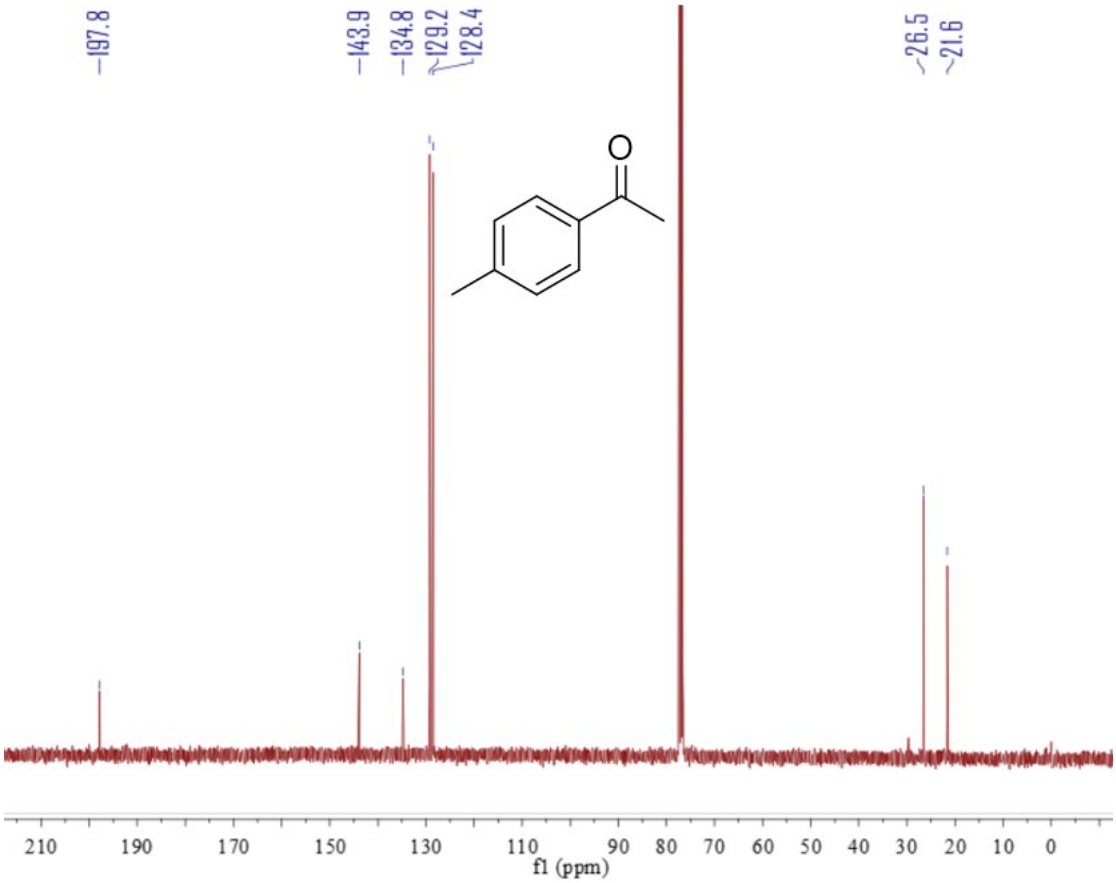
Compound 4m


8.3
8.3
8.1
8.1
8.1
2.7
O
O2N
1.94
1.96
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


196.3
150.4
141.4
129.3
123.8
26.9
O
NC
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Compound 4n


7.9
7.9
7.3
7.3
7.3
2.6
2.4
O
1.95
2.18
3.00
2.98
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


197.8
143.9
134.8
129.2
128.4
26.5
21.6
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)