Electronic Supplementary Information

Dual-fixations of europium cation and TEMPO species on metal-organic frameworks for aerobic oxidation of alcohols

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General materials and methods

Concentration of solution was performed using rotary evaporator, and followed by followed by vacuum drying at 0.1-1 torr. All commercial reactants, reagents and solvents used without additional purification unless otherwise stated. All chemicals were purchased from Sigma-Aldrich, TCI, Alfa Aesar chemical company.

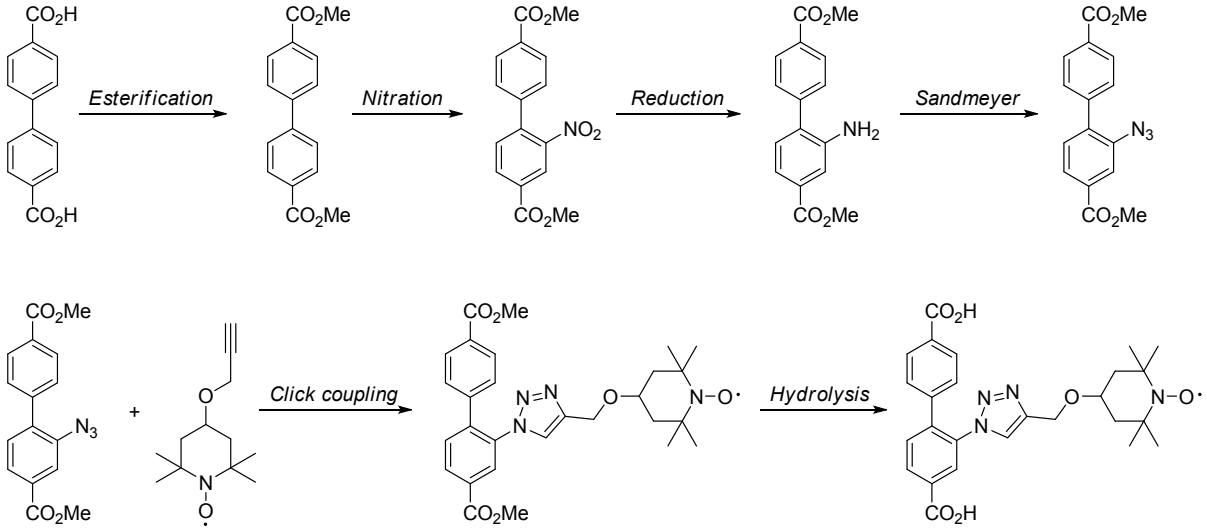
Thin layer chromatography (TLC) analysis was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H and ^{13}C NMR (nuclear magnetic resonance) spectra were recorded on a FT AM 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or FT AM 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d =doublet, t = triplet, q = quartet, quin = quintet and m = multiplet. Coupling constants, J, were reported in Hertz unit (Hz).

Approximately 10 mg of MOFs were dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of HF (48% aqueous solution). Powder X-ray diffraction (PXRD) data were collected on Bruker AXS D8 Discover (at 40 kV, 40 mA for CuKa (λ = 1.5406 Å)) and Rigaku Miniflex 600 (at 40 kV, 15 mA) with a scan speed of 1.0 min/step, a step size of 0.02^{o} in 2θ, and a 2θ range of 3-50^{o}. N_2 sorption isotherms of samples were obtained using a BELSORP-max at 77K. Thermogravimetric analysis (TGA) were performed under N_2 atmosphere at a scan rate of 5 ^{o}C/min using Q50 from TA instruments. PL measurements (examined by Fluoromax-4P Luminescence Spectrophotometer from HORIBA, λ_{ex} = 395 nm) for Eu species, Eu-based MOFs and Eu-loaded MOFs were in degassed aqueous solution at ambient temperature. ICP-OES analysis were collected on Perkin Elmer Optima 7300DV, with pretreatment 20 mg of sample in HF-HNO_3(1:1=v/v) at 200 ^{o}C for 1 h. GC (Gas Chromatography) analysis for determination of conversions was performed on an Younglin YL-6500. All quantum chemical calculations were performed using the optimized molecular geometry functional B3LYP/6-311G+g(d,p) as implemented in the Gaussian 09 software suite.[S1,S2]

Synthesis of $Eu(Me\text{-}BPY)_2(NO_3)_3$

To a solution of 5,5'-dimethyl-2,2'-bipyridine (37 mg, 0.20 mmol) in CH_3CN (2 mL) was added to a solution of $Eu(NO_3)_3 \cdot 5H_2O$ (86 mg, 0.20 mmol) in CH_3CN (2 mL). The clear solution mixture was heated 60 ^oC for 12 h, a colorless precipitate was collected, washed with 3 times CH_3CN (2 mL) then dried under high vacuum for 12 h yielded $Eu(Me\text{-}BPY)_2(NO_3)_3$ as a colorless solid (60 mg, 85%).

Synthesis of BPDC-TEMPO



BPDC-TEMPO was synthesized according to the reported literature.[S3]

MOF characterizations

PXRD (Powder X-ray diffraction): PXRD data was collected at ambient temperature on a Bruker D8 Discover at 40 kV, 40 mA and a Rigaku Miniflex at 40 kV, 15 mA for CuKa (λ = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02^{o} in 2θ, and a 2θ range of 5-30^{o}.

N_2 full isotherm for UiO-67-bpy and UiO-67-bpy-Eu: Approximately 30-60 mg of MOF sample was evacuated under vacuum for a moment at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 120 ^{o}C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 6 h or until the outgas rate was <5 μmHg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials. BET surface area (m^2/g) measurements were collected at 77 K by N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.

N_2 full isotherm for UiO-67-TEMPO, UiO-67-(bpy&TEMPO), UiO-67-(bpy-Eu&TEMPO): These MOFs were measured according to activation at 50 ^{o}C for 24 h.

TGA (Thermogravimetric analysis): Approximately 10 mg of MOF was used for TGA measurements, after BET analysis (activated). Sample was analyzed under a stream of N_2 using a TGA/DSC 1 running from room temperature to 700 ^{o}C with a scan rate of 5 ^{o}C/min.

PL (Photoluminescence) Measurements: PL measurements (examined by Fluoromax-4P Luminescence Spectrophotometer from HORIBA, λ_{ex} = 395 nm) for Eu species, Eu-based MOFs and Eu-loaded MOFs were in degassed aqueous solution at ambient temperature.

Chemical stability of MOFs: Approximately 20 mg of MOF was placed in 4 mL vials containing 2 mL of acetone, DCM, pyridine, H_2O, 0.1 M HCl, 0.1 M NaOH. Samples were allowed to sit statically at 25 ^{o}C for 24 h. The samples were filtered and recovered for analysis.

Procedures for aerobic oxidations

Condition I in Tables 2 and 3 (Eu-fixed): Alcohol (0.25 mmol), UiO-67-bpy-Eu (2 mg, 0.0025 mmol), TEMPO (0.4 mg, 0.0025 mmol), sodium nitrate (0.2 mg, 0.0025 mmol) and toluene (1 mL) were added to a scintillation vial. Acetic acid (0.1 mL) was added to solution, and then the mixture was stirred at 60 ^{o}C under air. Resulting mixture was filtered by syringe filter and checked by conversion ratio with GC column or the desired product was isolated by a silica gel column chromatography.

Condition II in Table 3 (TEMPO-fixed): Alcohol (0.25 mmol), $Eu(NO_3)_3$ (1 mg, 0.0025 mmol), UiO-67-TEMPO (3 mg, 0.0025 mmol), sodium nitrate (0.2 mg, 0.0025 mmol) and toluene (1 mL) were added to a scintillation vial. Acetic acid (0.1 mL) was added to solution, and then the mixture was stirred at 60 ^{o}C under air. Resulting mixture was filtered by syringe filter and checked by conversion ratio with GC column or the desired product was isolated by a silica gel column chromatography.

Condition III in Table 3 (Eu & TEMPO-fixed): Alcohol (0.25 mmol), UiO-67-bpy-Eu (2 mg, 0.0025 mmol), UiO-67-TEMPO (3 mg, 0.0025 mmol), sodium nitrate (0.2 mg, 0.0025 mmol) and toluene (1 mL) were added to a scintillation vial. Acetic acid (0.1 mL) was added to solution, and then the mixture was stirred at 60 ^{o}C for 18 h under air. Resulting mixture was filtered by syringe filter and checked by conversion ratio with GC column or the desired product was isolated by a silica gel column chromatography.

Condition IV in Table 3 (Eu-fixed + TEMPO-fixed): Alcohol (0.25 mmol), UiO-67-(bpy-Eu)(TEMPO) (6 mg, 0.0025 mmol), sodium nitrate (0.2 mg, 0.0025 mmol) and toluene (1 mL) were added to a scintillation vial. Acetic acid (0.1 mL) was added to solution, and then the mixture was stirred at 60 ^{o}C for 18 h under air. Resulting mixture was filtered by syringe filter and checked by conversion ratio with GC column or the desired product was isolated by a silica gel column chromatography.

General GC conditions

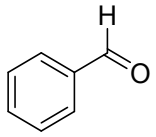
GC-Condition #1: GsBP-5 column, 30m x 0.32mm (id); FID detector, 300 °C; injection: 200 °C; carrier gas: nitrogen; carrier gas rate: 1 mL / min; area normalization:

- Reaction condition optimization experiments (Table 1), and the detection of benzyl alcohol (**1a**), 4-chlorobenzylalcohol (**1d**), 3-chlorobenzylalcohol (**1e**), 2-chlorobenzylalcohol (**1f**), 2-thiophene methanol (**1k**), and 3-thiophene methanol (**1l**) were performed under a Condition Is column temperature: 120 °C for 2 minutes, increasing to 190 °C in a rate of 10 °C / min.
- 4-Nitrobenzylalcohol (**1b**), 4-bromobenzylalcohol (**1c**), 4-methylbenzylalcohol (**1g**), 4-methoxybenzylalcohol (**1h**), 3-methoxybenzylalcohol (**1i**), 2-methoxybenzylalcohol (**1j**) were detected under a Condition Is column temperature: 150 °C for 2 minutes, raising to 210 °C in a rate of 10 °C / min.
- 1-Hexanol (**1m**) and 2-heptanol (**1n**) were detected under a Condition Is column temperature: 80 °C for 1 minutes, raising to 100 °C in a rate of 1 °C / min
- Diphenyl ketone (**2o**) was detected under a Condition Is column temperature: 120 °C for 1 minutes, raising to 190 °C in a rate of 2 °C / min.

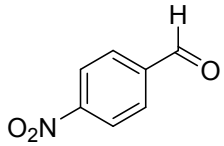
GC-Condition #2: DB-5 column, 30m x 0.32mm (id); FID detector, 350 °C; injection: 250 °C; carrier gas: nitrogen; carrier gas rate: 1 mL / min; area normalization.

- Pyrenyl aldehyde (**2p**) was detected under a Condition Is column temperature: 120 °C for 2 minutes, raising to 330 °C in a rate of 15 °C / min.

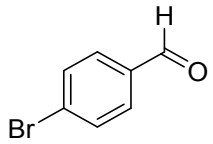
Characterizations of aldehydes or ketones from aerobic oxidations



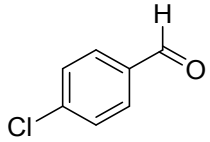
Benzaldehyde (**2a**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/30, v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.90-7.88 (m, 2H), 7.64-7.62 (m, 1H), 7.56-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 136.5, 134.6, 129.9, 129.1.
Condition I in Tables 1 and 2: Isolation yield (98%, 26 mg), obtained as a colorless liquid.
Condition II in Table 3: GC conversion (99%, 9 h).
Condition III in Table 3: GC conversion (65%, 18 h).
Condition IV in Table 3: GC conversion (70%, 18 h).



4-Nitrobenzaldehyde (**2b**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/10, v/v) as the eluent, obtained as a pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.40-8.37 (m, 2H), 8.09-8.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 151.3, 140.2, 130.6, 124.4.
Condition I: GC conversion (99%, 9 h).



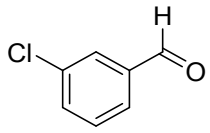
4-Bromobenzaldehyde (**2c**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:20 v/v) as the eluent, obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.75-7.73 (m, 2H), 7.69-7.67 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 135.2, 132.6, 131.1, 129.9.
Condition I: GC conversion (99%, 11 h).



4-Chlorobenzaldehyde (**2d**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:20 v/v) as the eluent, obtained as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ

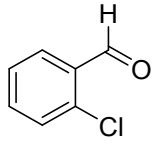
9.98 (s, 1H), 7.84-7.82 (m, 2H), 7.53-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 141.1, 134.8, 131.1, 129.6.

Condition I: GC conversion (99%, 11 h).



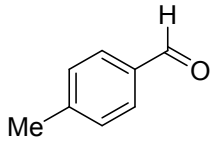
3-Chlorobenzaldehyde (**2e**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/30 v/v) as the eluent, obtained as a light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.92-7.90 (m, 1H), 7.78-7.76 (m, 1H), 7.45-7.43 (m, 1H), 7.39-7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 138.0, 135.2, 132.6, 130.7, 129.5, 127.4.

Condition I: GC conversion (99%, 8 h).



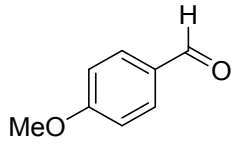
2-Chlorobenzaldehyde (**2f**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:30 v/v) as the eluent, obtained as a light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85-7.85 (m, 1H), 7.77-7.75 (m, 1H), 7.61-7.58 (m, 1H), 7.50-7.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 137.9, 135.6, 134.5, 130.5, 129.4, 128.1.

Condition I: GC conversion (99%, 13 h).



4-Methylbenzaldehyde (**2g**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/20, v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.78-7.77 (m, 2H), 7.34-7.32 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 145.7, 134.4, 130.0, 129.9, 22.0.

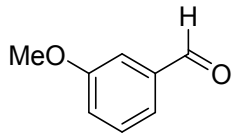
Condition I: GC conversion (99%, 11 h).



4-Methoxybenzaldehyde (**2h**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/30, v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ

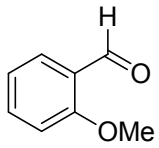
9.88 (s, 1H), 7.84-7.82 (m, 2H), 7.00-6.99 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9, 164.7, 132.1, 130.1, 114.4, 55.7.

Condition I: GC conversion (99%, 18 h).



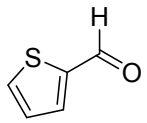
3-Methoxybenzaldehyde (**2i**)[S3]: Desire product was isolated by flash column purification with ethyl acetate/*n*-hexane (1/30, v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.46-7.44 (m, 2H), 7.40-7.39 (m, 1H), 7.20-7.17 (m, 1H) 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 160.3, 137.9, 130.2, 123.7, 121.7, 112.2, 55.6.

Condition I: GC conversion (99%, 8 h).



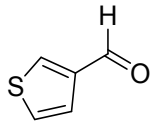
2-Methoxybenzaldehyde (**2j**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:30 v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.84-7.82 (dd, 1H, *J* = 9.6, 2.3 Hz), 7.58-7.53 (ddd, 1H, *J* = 10.6, 9.2, 2.3 Hz), 7.05-6.98 (m, 2H) 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.0, 136.1, 128.7, 125.0, 120.8, 111.7, 55.8.

Condition I: GC conversion (99%, 14 h).

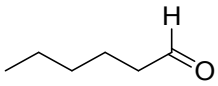


2-Thiophenecarboxaldehyde (**2k**)[S4]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:30 v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.79-7.78 (dd, 1H, *J* = 3.8, 1.2 Hz), 7.78-7.78 (m, 1H), 7.23-7.21 (dd, 1H, *J* = 4.9, 3.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1, 144.2, 136.4, 135.3, 128.4.

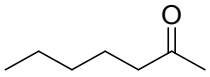
Condition I: GC conversion (99%, 9 h).



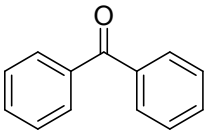
3-Thiophenecarboxaldehyde (**2l**)[S4]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:30 v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.13-8.12 (dd, 1H, *J* = 2.9, 1.2 Hz), 7.56-7.54 (dd, 1H, *J* = 5.1, 1.1 Hz), 7.39-7.37 (ddd, 1H, *J* = 5.1, 2.9, 0.9 Hz); ^{13}C NMR (125 zMHz, $CDCl_3$) δ 185.1, 143.2, 136.8, 127.5, 125.5.
Condition I: GC conversion (99%, 12 h).



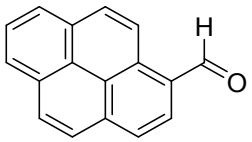
1-Hexanal (**2m**)[S4]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:40 v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1H), 2.43-2.40 (td, 2H, *J* = 7.4, 1.9 Hz), 1.66-1.61 (m, 2H), 1.35-1.29 (m, 4H) 0.91-0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 44.0, 31.5, 22.5, 21.9, 14.0.
Condition I: GC conversion (99%, 15 h).



2-Heptanone (**2n**)[S4]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:40 v/v) as the eluent, obtained as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43-2.40 (t, 3H, *J* = 7.5 Hz), 2.13 (s, 3H), 1.60-1.54 (quint, 2H, *J* = 7.6 Hz) 1.32-1.24 (m, 4H), 0.90-0.87 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 43.9, 34.5, 30.0, 23.7, 22.6, 14.1.
Condition I: GC conversion (99%, 18 h).



Diphenyl ketone (**2o**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:40 v/v) as the eluent, obtained as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 4H), 7.59-7.57 (m, 2H), 7.51-7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 137.7, 132.6, 130.2, 128.4.
Condition I: GC conversion (99%, 11 h).
Condition II: GC conversion (99%, 11 h).
Condition III: GC conversion (49%, 18 h).
Condition IV: GC conversion (48%, 18 h).



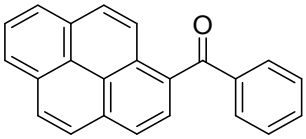
1-Pyrenecarboxaldehyde (**2p**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:40 v/v) as the eluent, obtained as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.62 (s, 1H), 9.18-9.16 (d, 1H, *J* = 9.3 Hz), 8.21-8.20 (d, 1H, *J* = 7.9 Hz), 8.15-8.13 (d, 1H, *J* = 7.6 Hz), 8.09-8.07 (d, 1H, *J* = 9.25 Hz), 8.04-8.02 (d, 1H, J = 8.9 Hz), 8.00-7.96 (m, 2H), 7.87-7.85 (d, 1H, J = 8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 135.2, 131.0, 130.8, 130.7, 130.5, 130.5, 130.2, 127.1, 127.0, 126.9, 126.7, 126.4, 124.3, 124.3, 123.8, 122.7.

Condition I: GC conversion (99%, 11 h).

Condition II: GC conversion (68%, 18 h).

Condition III: GC conversion (42%, 18 h).

Condition IV: GC conversion (45%, 18 h).



phenyl(pyren-1-yl)methanone (**2q**)[S3]: Desire product was isolated by flash column purification with ethyl acetate-hexane (1:40 v/v) as the eluent. Isolation yield (85%, 18 h), obtained as a light yellow solid. ^{1}H NMR (500 MHz, DMSO) δ 8.40-8.09 (m, 9H), 7.81-7.79 (dd, 2H, *J* = 8.1, 1.3 Hz), 7.72-7.69 (dt, 1H, *J* = 8.6, 1.1 Hz), 7.58-7.54 (t, 2H, *J* = 7.9 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 138.1, 133.7, 132.9, 132.5, 130.8, 130.1, 130.1, 129.1, 128.9, 128.9, 128.7, 127.3, 126.9, 126.7, 126.4, 126.1, 124.2, 124.2, 123.9, 123.6.

Condition I: Isolation yield (85%, 65 mg, 18 h), obtained as a light yellow solid.

Condition II: Isolation yield (60%, 46 mg, 18 h), obtained as a light yellow solid.

Condition III: Isolation yield (30%, 23 mg, 18 h), obtained as a light yellow solid.

Condition IV: Isolation yield (28%, 21 mg, 18 h), obtained as a light yellow solid.

Table S1. Crystal data and structure refinement for $Eu(Me\text{-}BPY)_2(NO_3)_3$.

Identification code	$Eu(Me\text{-}BPY)_2(NO_3)_3$	
Empirical formula	$C_{24}\ H_{24}\ EuN_7\ O_9$	
Formula weight	706.47	
Temperature	293(2) K	
Wavelength	0.71073Å	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 16.643(3) Å	α = 90°.
	b = 9.4200(19)Å	β = 90°.
	c = 17.491(4)Å	γ = 90°.
Volume	2742.2(9)$Å^3$	
Z	4	
Density (calculated)	1.745Mg/m^3	
Absorption coefficient	2.354mm^{-1}	
F(000)	1436	
Crystal size	0.3 x 0.2 x 0.1mm^3	
Theta range for data collection	3.379 to 27.497°.	
Index ranges	-21<=h<=21,-12<=k<=12, -22<=l<=22	
Reflections collected	25638	
Independent reflections	3154[R(int) = 0.0642]	
Completeness to theta= 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.790 and 0.574	
Refinement method	Full-matrixleast-squares on F^2	
Data / restraints / parameters	3154 / 0 / 189	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0986	
R indices (all data)	R1 = 0.0579, wR2 = 0.1227	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.020 and -1.123 e.$Å^{-3}$	

Table S2. Calculated BET surface area, pore volume, and pore size of UiO-67-bpy, UiO-67-bpy-Eu, UiO-67-(bpy&TEMPO), and UiO-67-(bpy-Eu&TEMPO).

Entry	MOF	BET surface area (m^2/g)	Pore volume (cm^3/g)	NLDFT pore size (nm)
1	UiO-67-bpy	1828	0.96	1.12
2	UiO-67-bpy-Eu	671	0.36	1.05
3	UiO-67-(bpy&TEMPO)	1372	0.73	1.12
4	UiO-67-(bpy-Eu&TEMPO)	609	0.33	0.97

Table S3. Molecular formula and ICP-OES data of UiO-67-bpy-Eu and UiO-67-(bpy-Eu&TEMPO).

Entry	MOF	Molecular formula of MOFs from ideal structures	ICP-OES element	Amount (ppm [μmol])
1	UiO-67-bpy-Eu	Zr_6O_4(bpydc-Eu)$_{4.5}$(bpydc)$_{1.5}$	Zr	113050 [1239]
			Eu	144710 [952]
2	UiO-67-(bpy-Eu&TEMPO)	Zr_6O_4(bpydc-Eu)$_{2.5}$(bpydc)$_{1.1}$(bpdc-TEMPO)$_{2.4}$	Zr	142672 [1564]
			Eu	99167 [653]

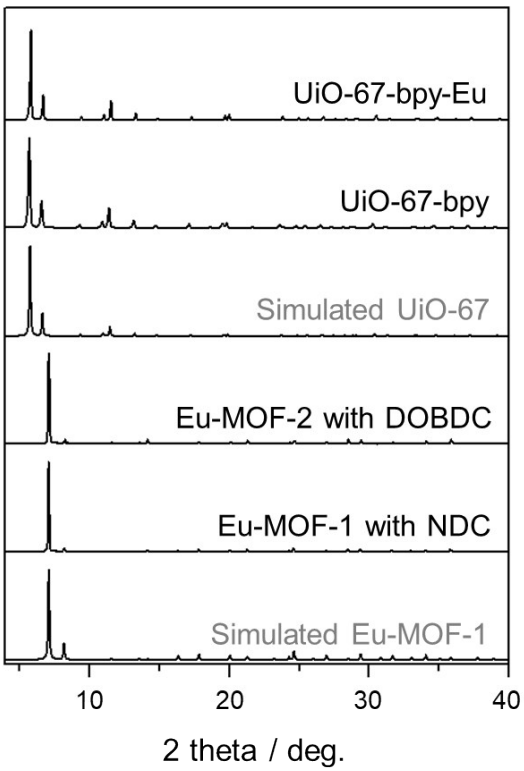


Fig. S1 PXRD of Eu-MOF-1, Eu-MOF-2, UiO-67-bpy and UiO-67-bpy-Eu.

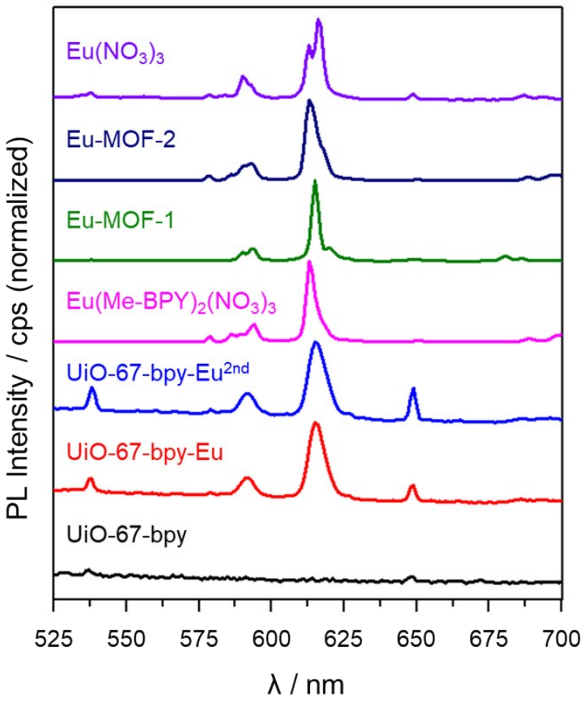


Fig. S2 PL spectra of Eu species, Eu-based MOFs and Eu-loaded MOFs.

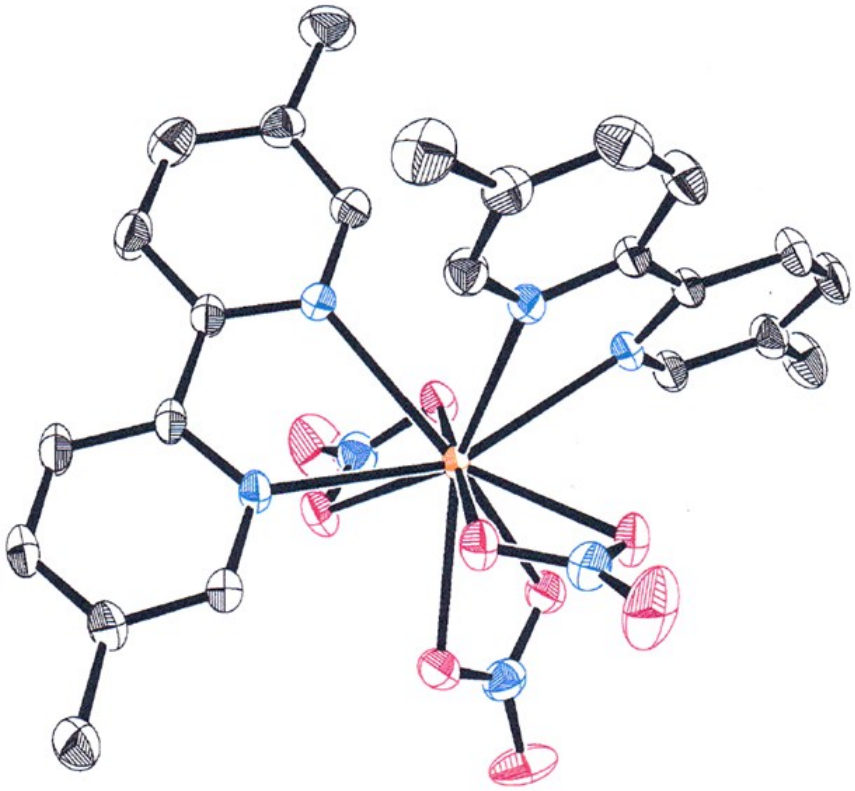


Fig. S3 X-ray structure of $Eu(Me\text{-}BPY)_2(NO_3)_3$.

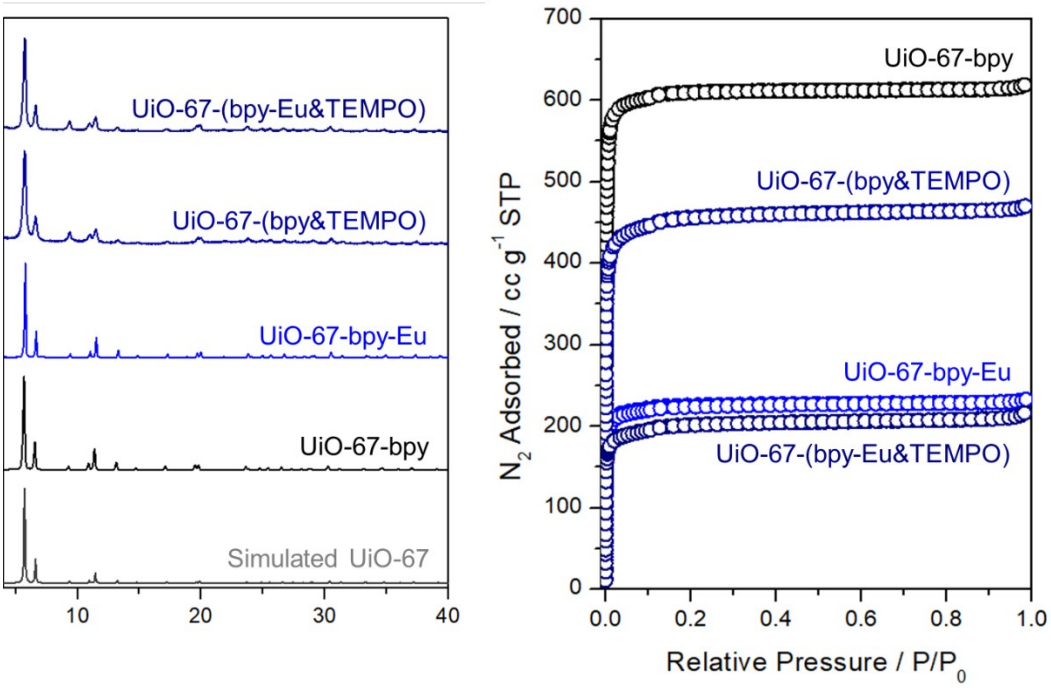


Fig. S4 PXRD patterns and N_2 full isotherms of Eu-loaded or/and TEMPO-functionalized UiO-67s

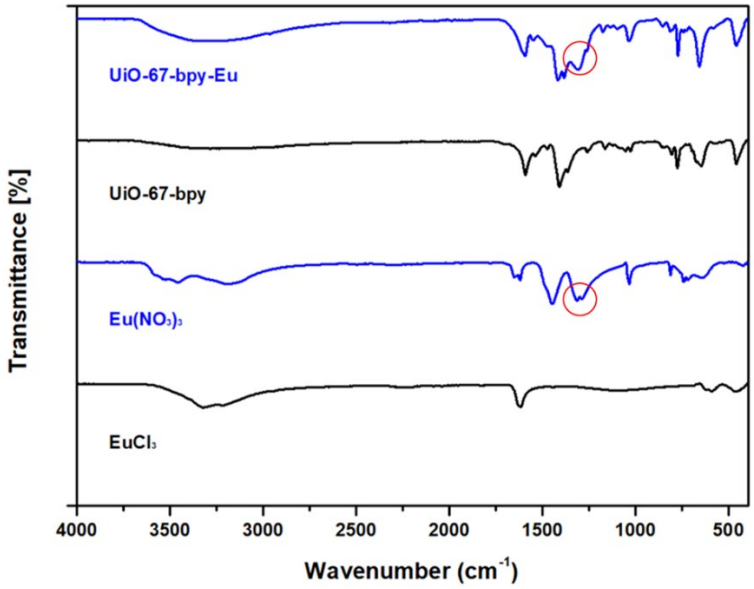


Fig. S5 IR spectra of UiO-67-bpy and UiO-67-Eu after metalation with $Eu(NO_3)_3$ to confirm the existence of NO_3^- in the framework (reference IR peaks of nitrate anion: 1410-1340 for antisymmetric stretch.[S15]

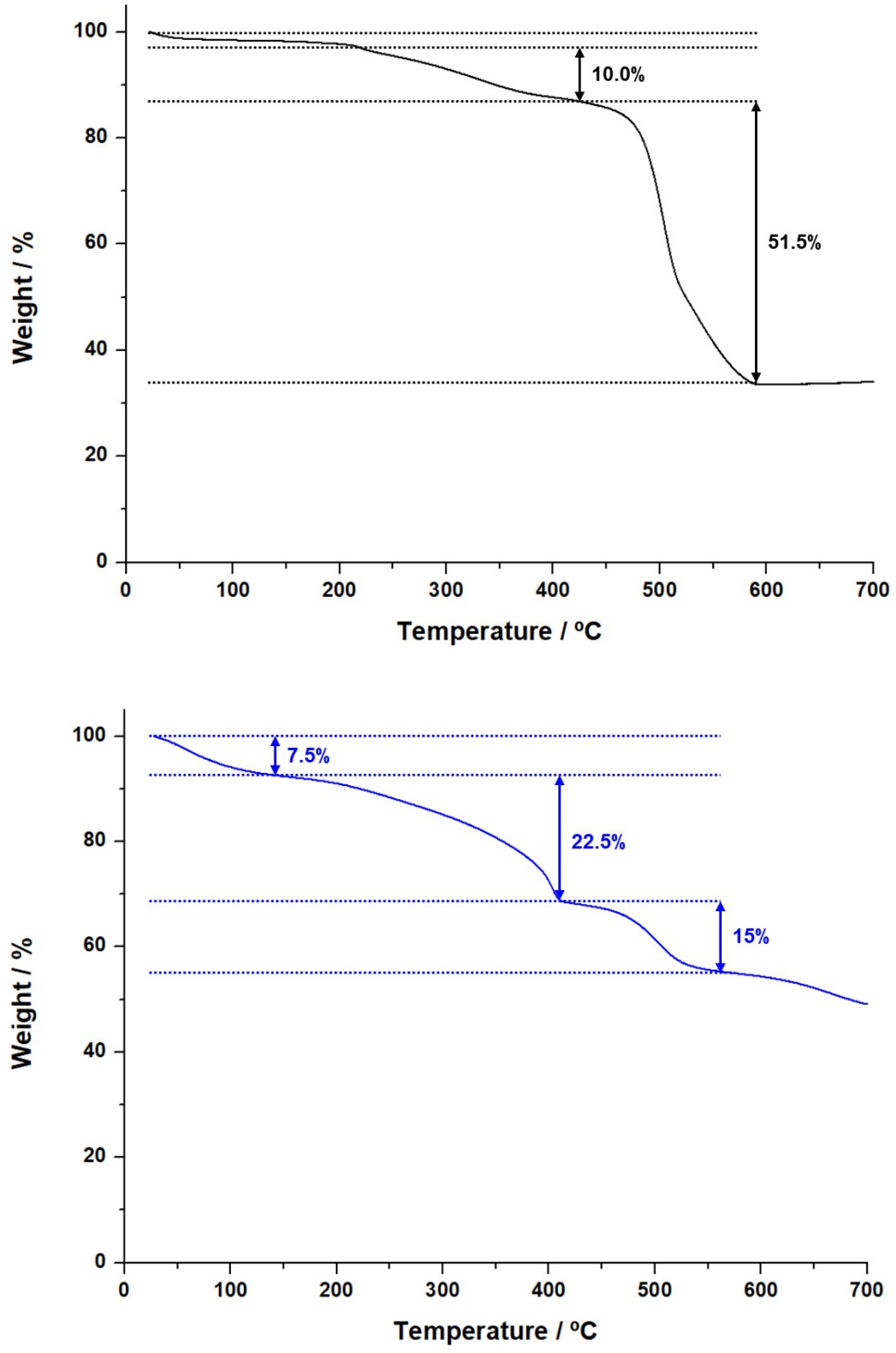


Fig. S6 TGA of UiO-67-bpy (top, black line) and UiO-67-bpy-Eu (bottom, blue line).

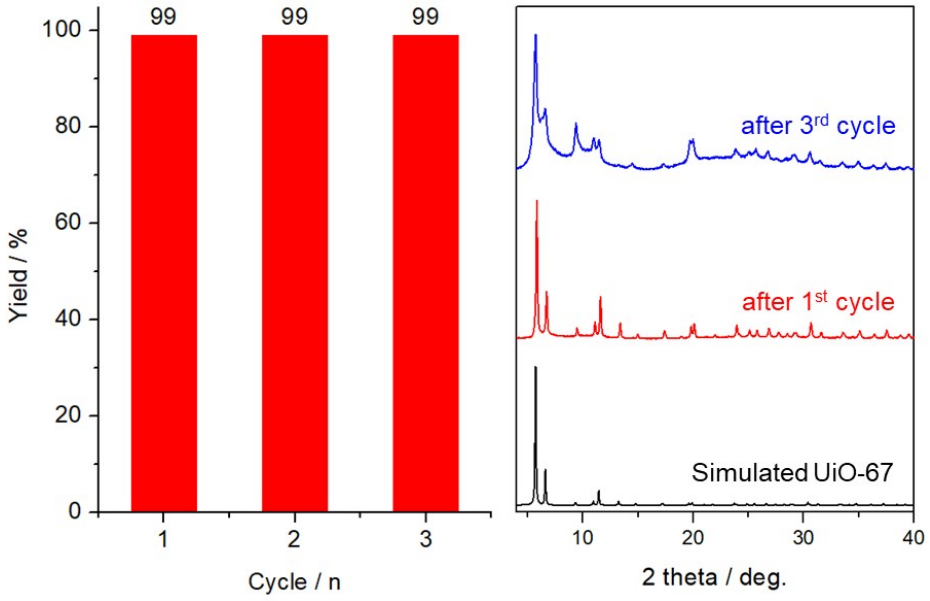


Fig. S7 Reusable test and PXRD of recovered UiO-67-bpy-Eu after aerobic oxidation reaction.

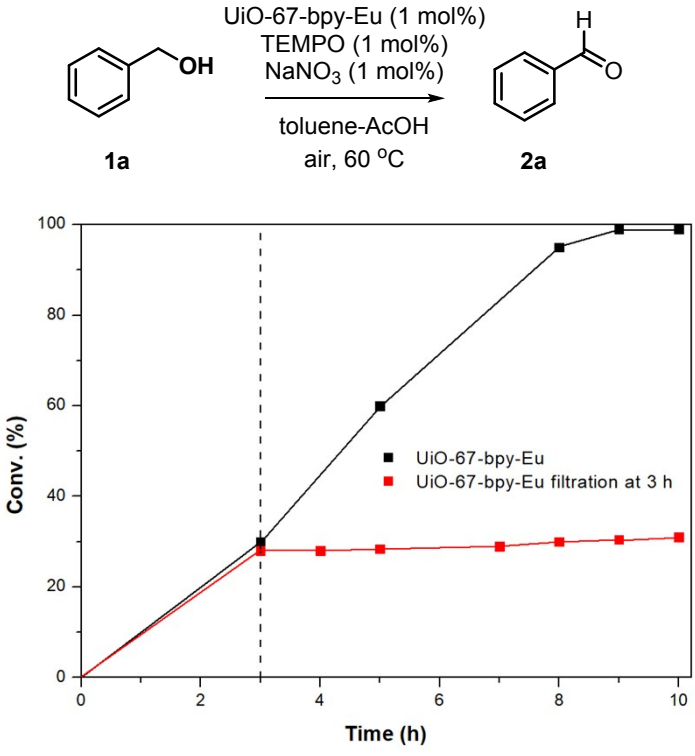


Fig. S8 Hot filtration test for the aerobic oxidation of benzyl alcohol with UiO-67-bpy-Eu.

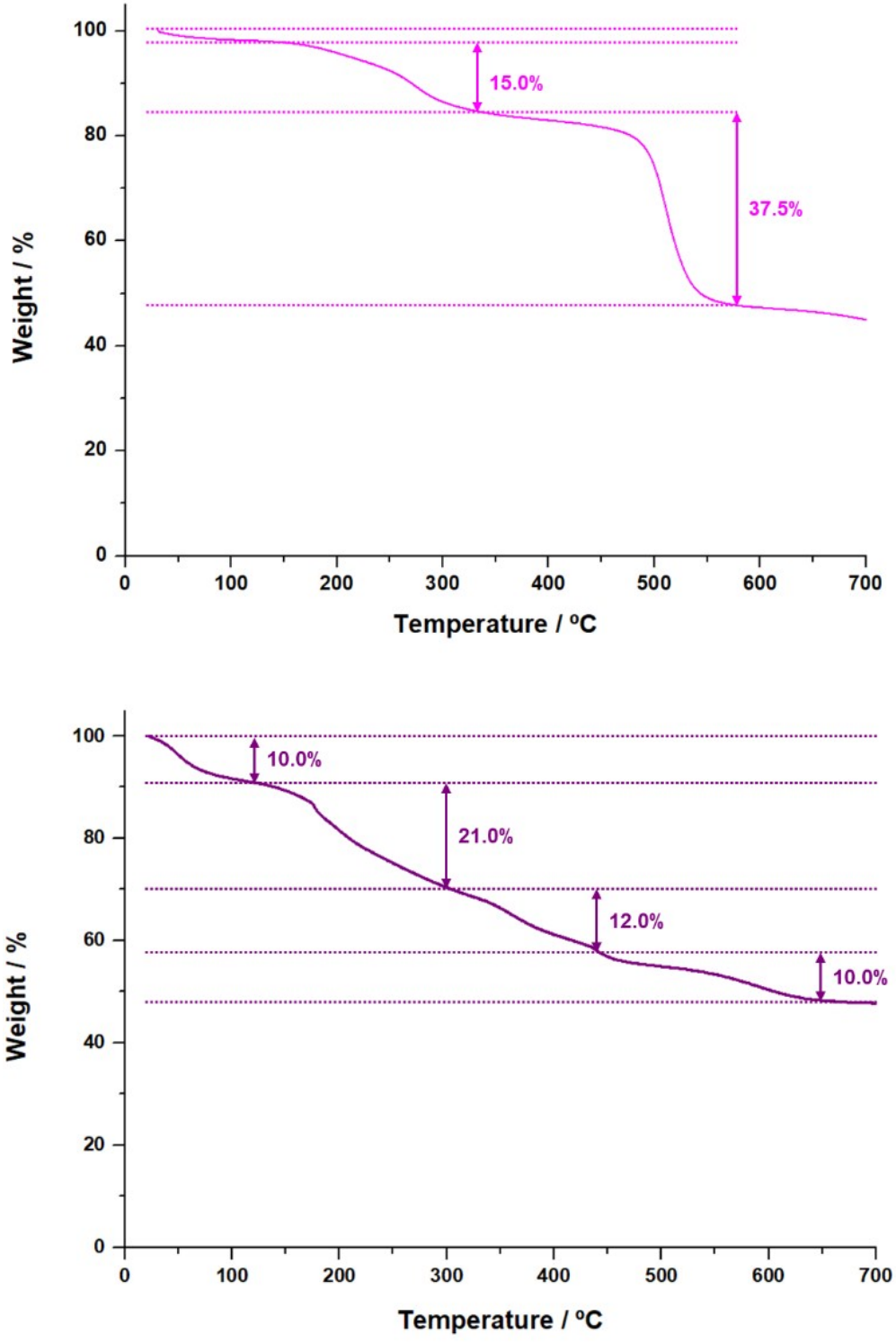


Fig. S9 TGA of UiO-67-(bpy&TEMPO) (middle, pink line) and UiO-67-(bpy-Eu&TEMPO) (bottom, purple line).

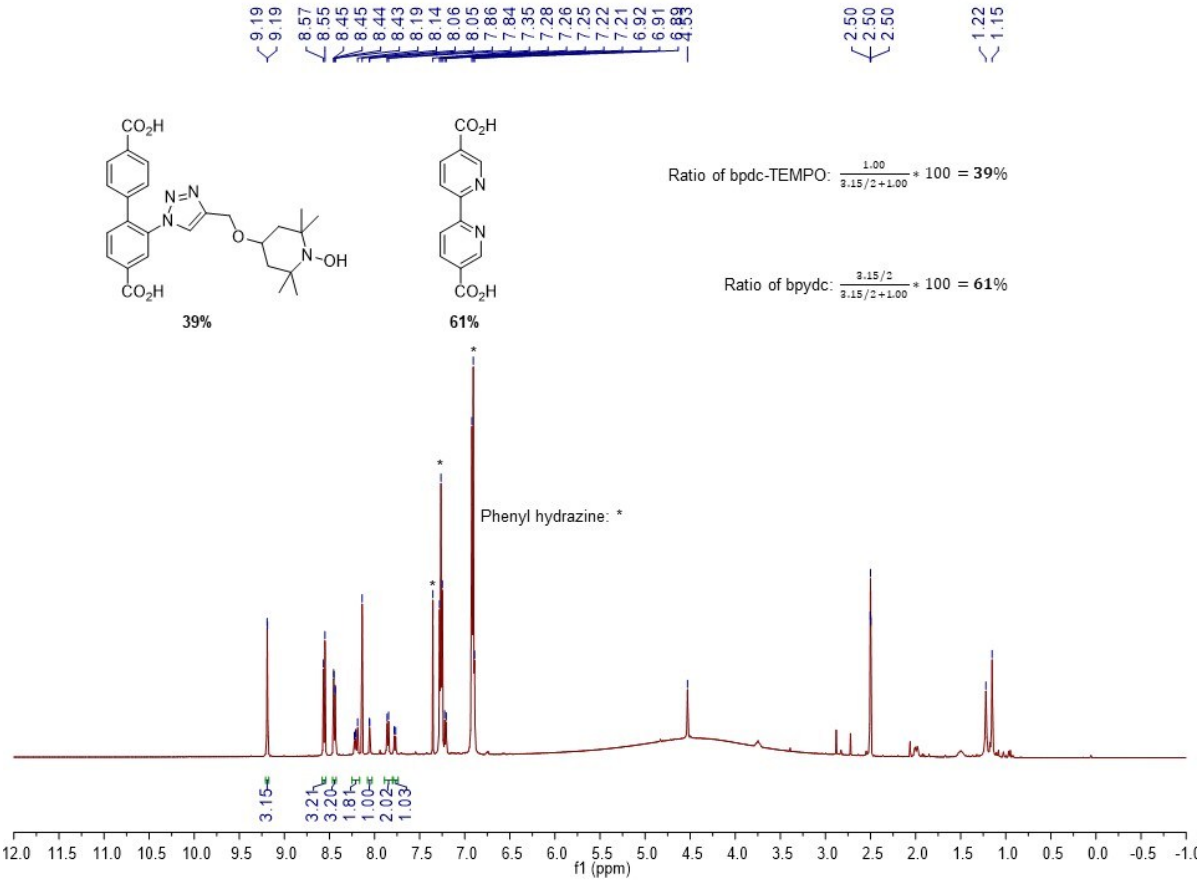


Fig. S10 ^{1}H NMR spectra of UiO-67-(bpy-Eu&TEMPO) after acid digestion.

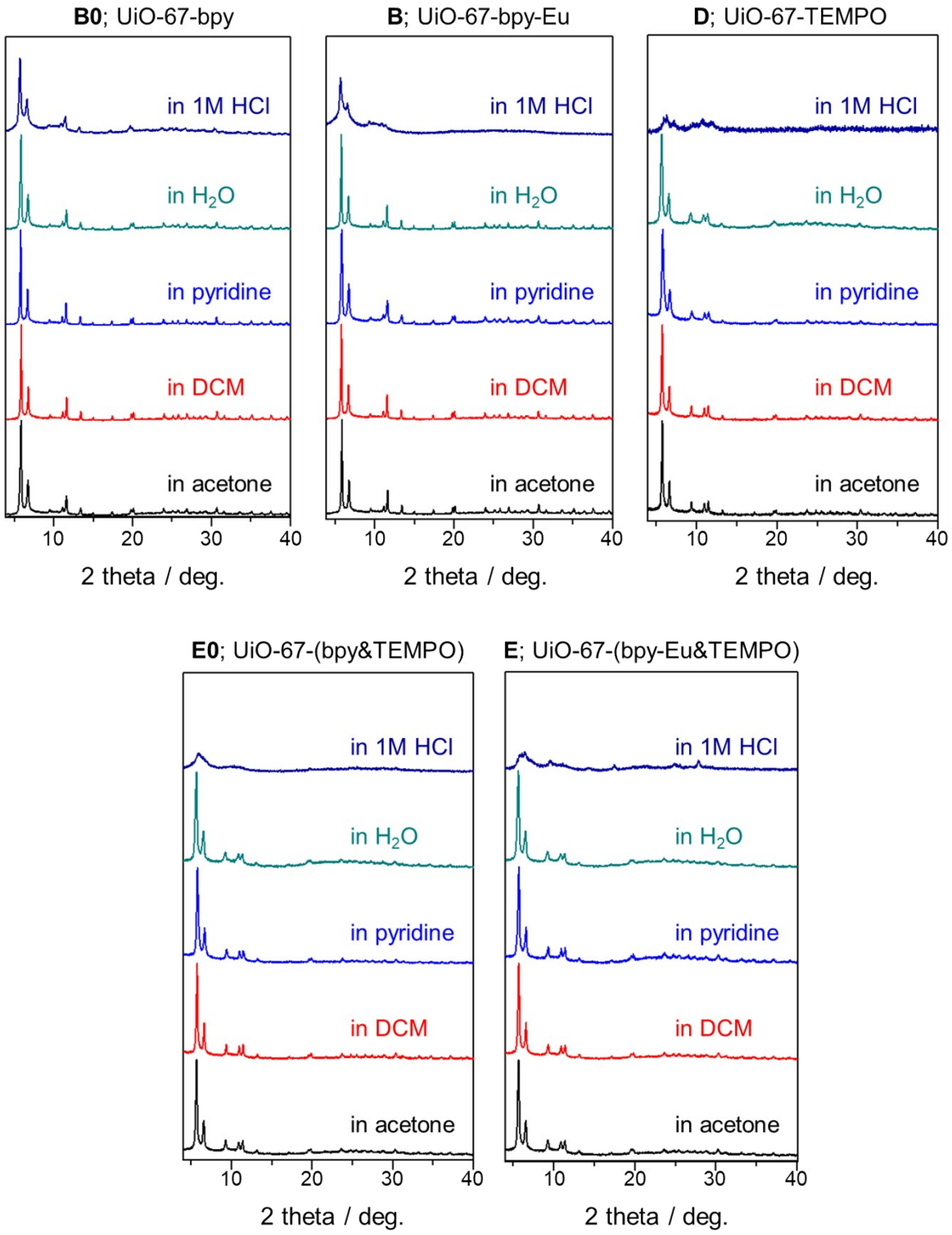


Fig. S11 PXRD patterns of UiO-67-bpy (**B0**), UiO-67-bpy-Eu (**B**), UiO-67-TEMPO (**D**), UiO-67-(bpy&TEMPO) (**E0**), and UiO-67-(bpy-Eu&TEMPO) (**E**) after exposure to a variety of chemicals.

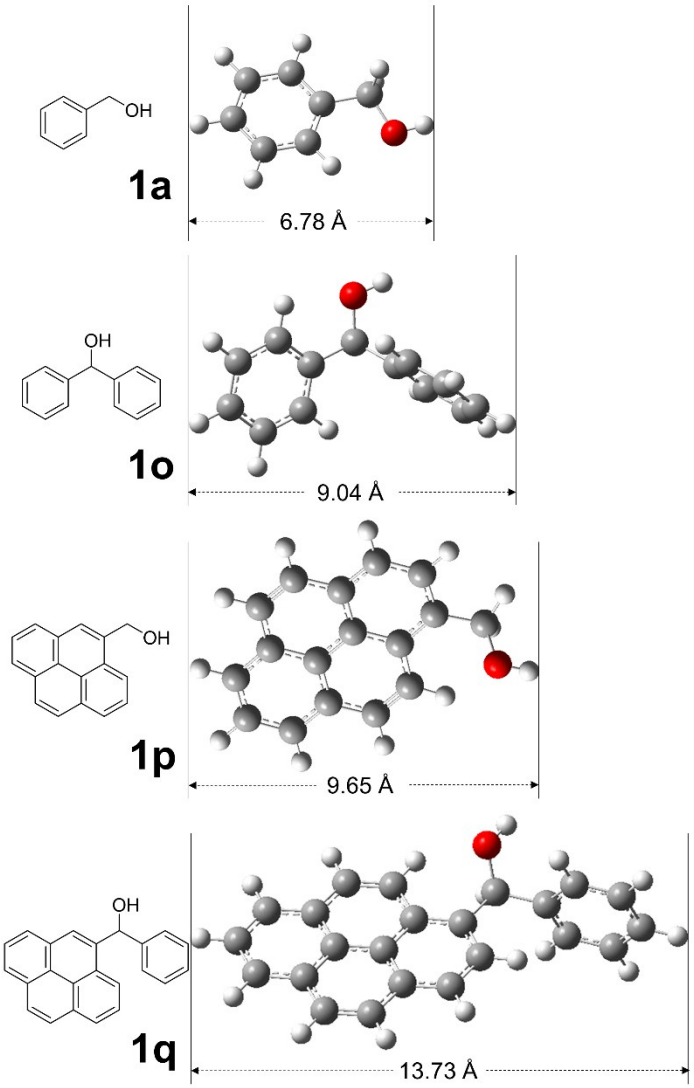
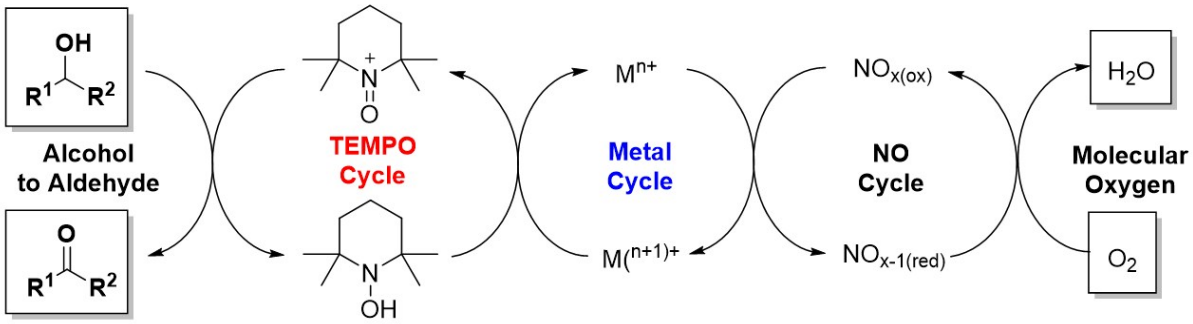


Fig. S12 B3LYP/6-311G(d,p) optimized molecular geometry of substrates and molecular sizes.

Scheme S1. General mechanism for transition metal-catalyzed aerobic oxidation with TEMPO moiety



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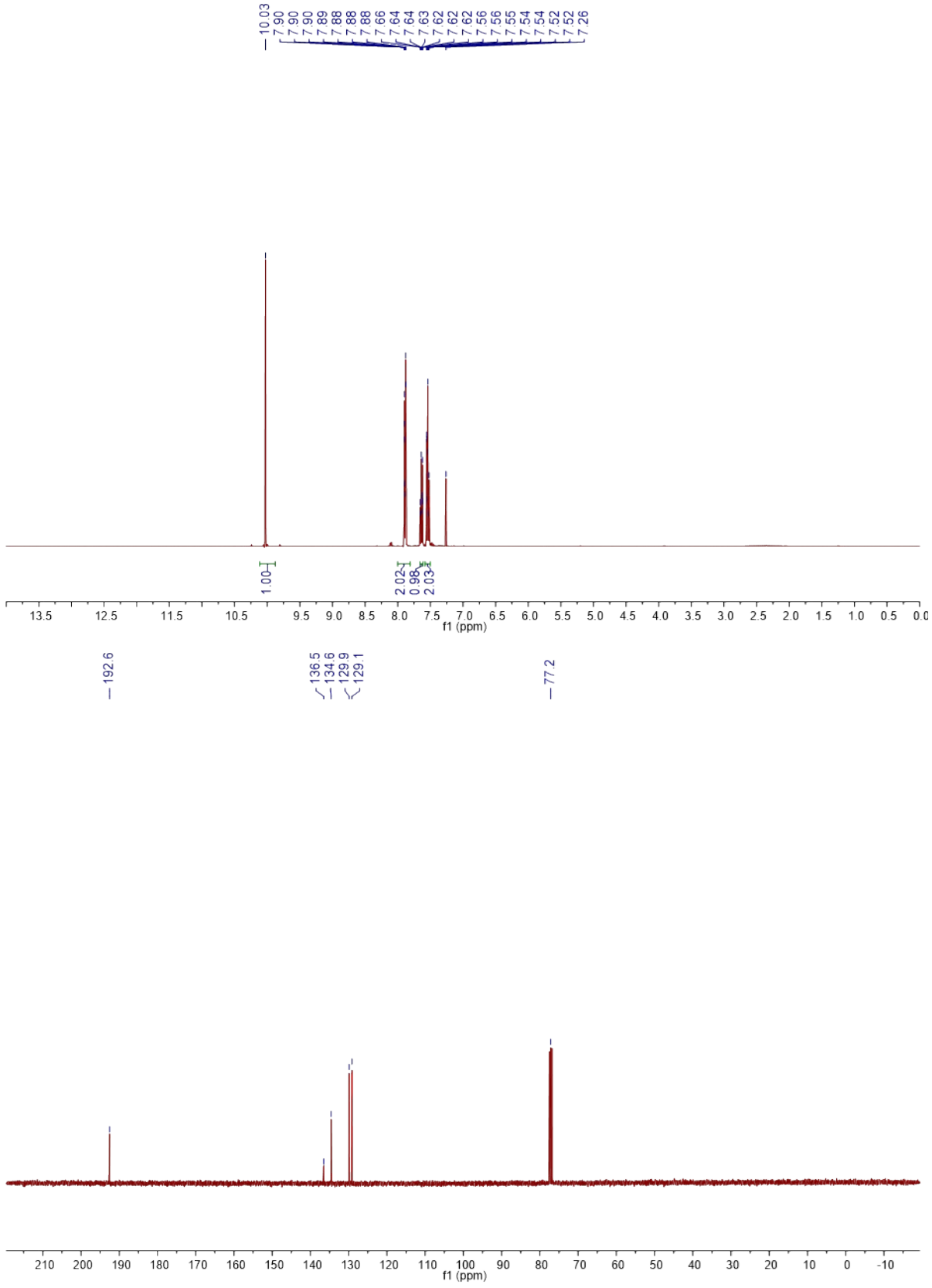
S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.01; Gaussian, Inc.: Wallingford, CT, **2010**.
S2 T. Zhang, K. Manna and W. Lin *J. Am. Chem. Soc.* **2016**, 138, 3241.
S3 S. Kim, J. Lee, S. Jeoung, H. R. Moon and M. Kim, *Chem. Eur. J.* **2020**, DOI:10.1002/chem.202000933.
S4 S. Kim, Y. Kim, H. Jin, M. H. Park, Y. Kim, K. M. Lee and M. Kim *Adv. Synth. Catal.* **2019**, 361, 1259.

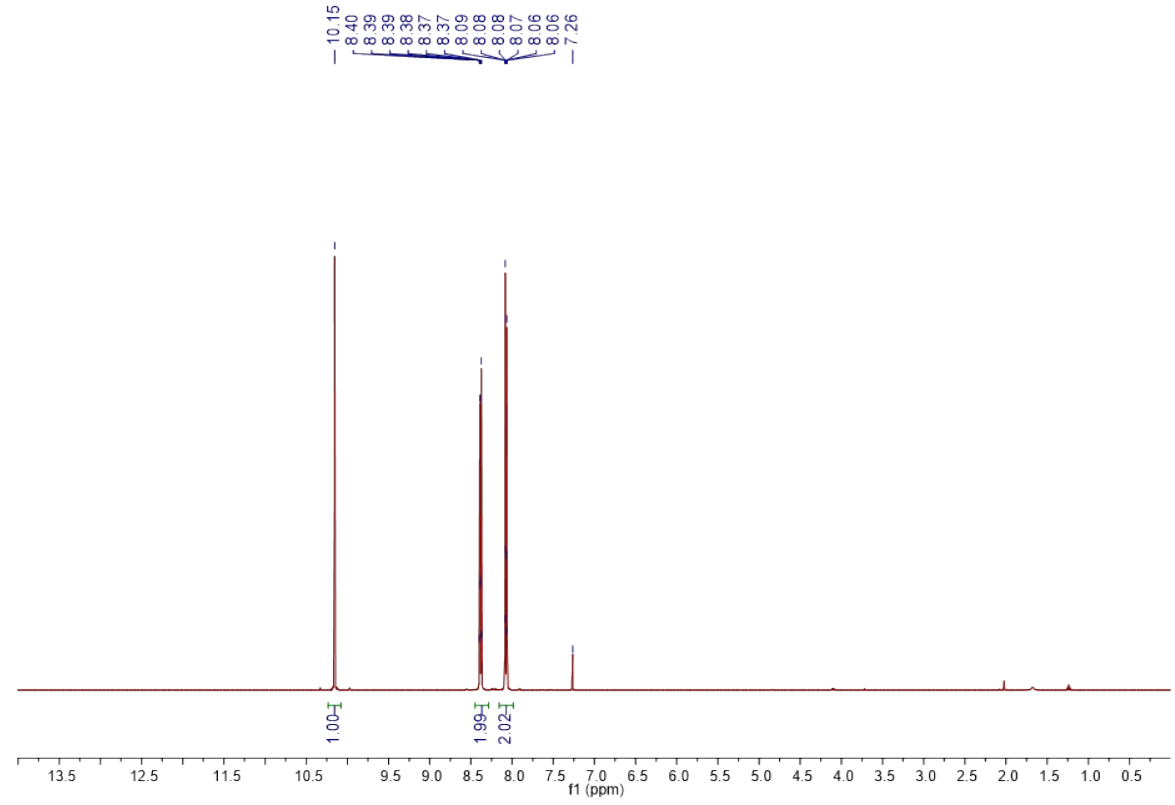
Appendix

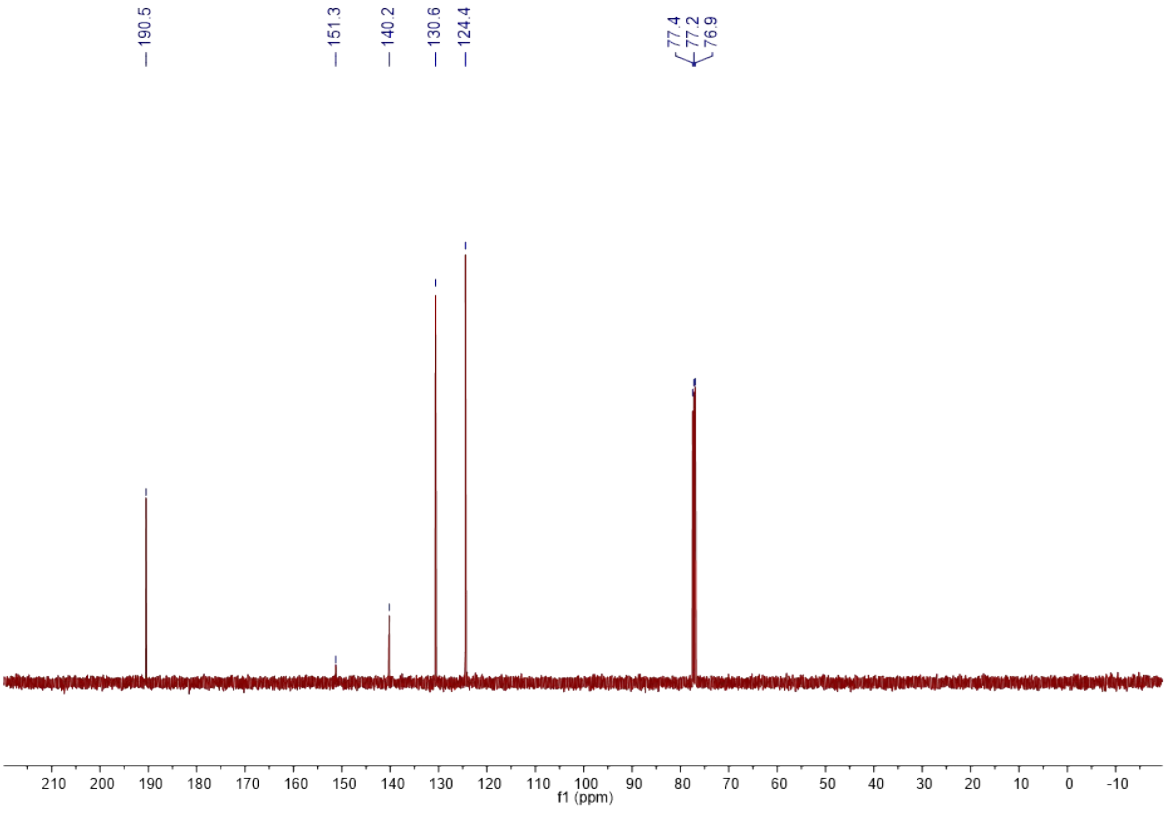
Spectral copies of ^{1}H and ^{13}C NMR of the obtained compounds

Benzaldehyde (2a)

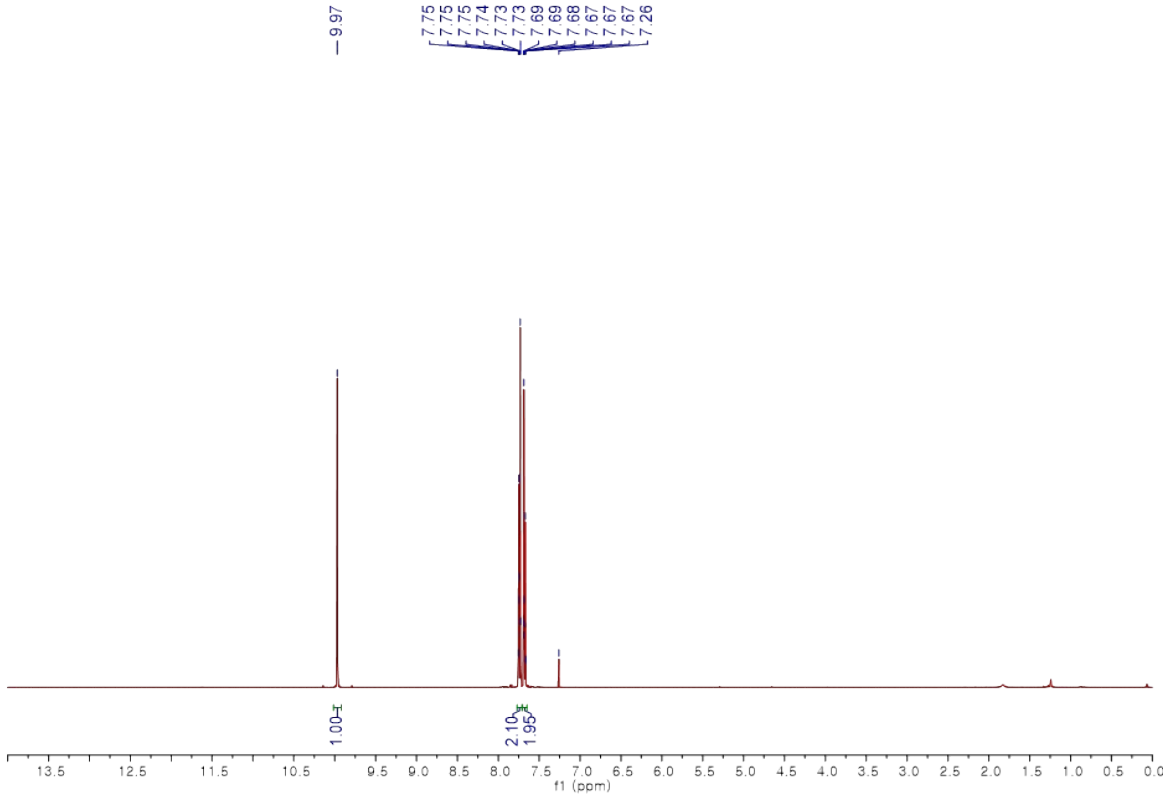


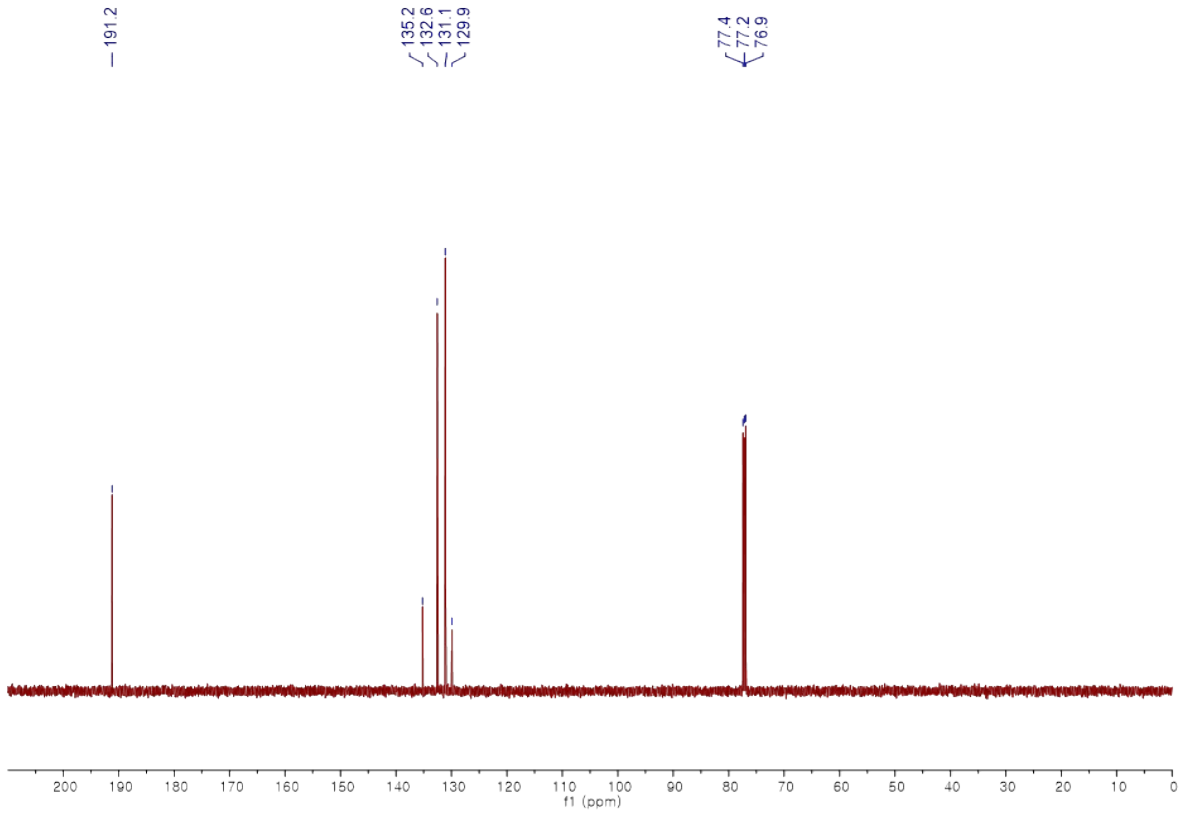
4-Nitrobenzaldehyde (2b)



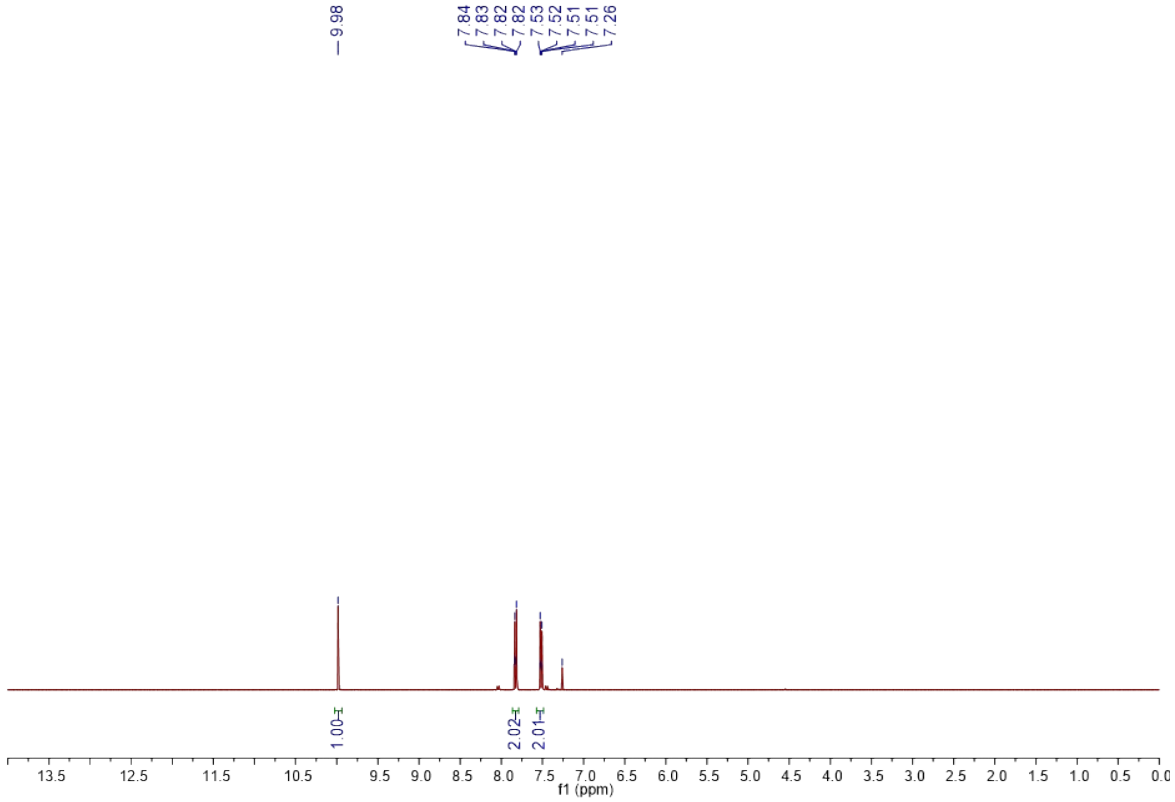


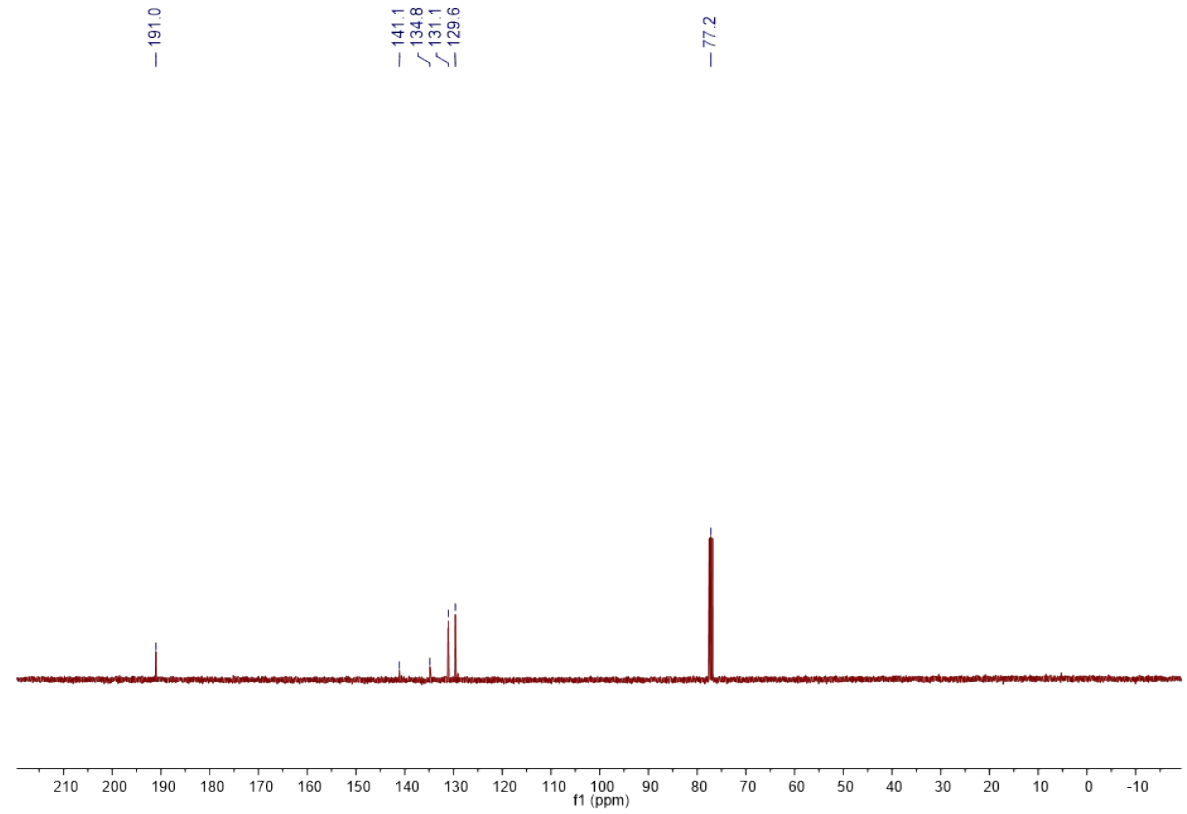
4-Bromobenzaldehyde (2c)



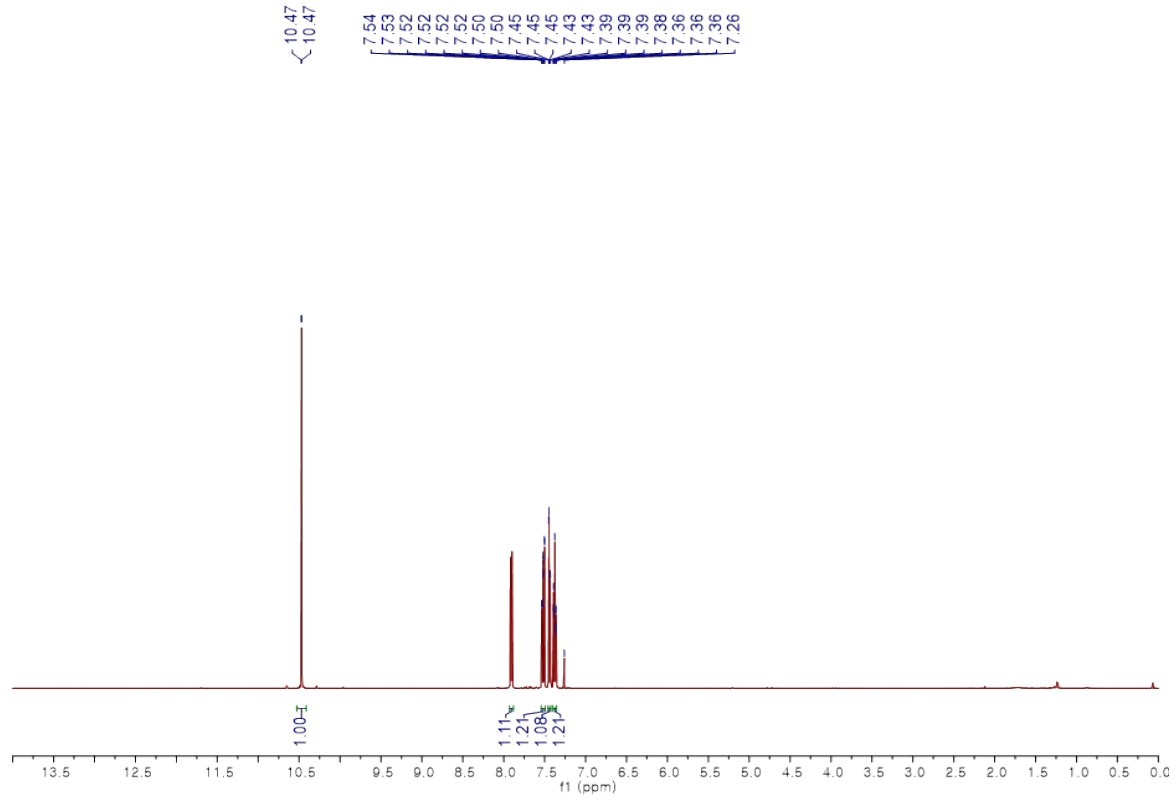


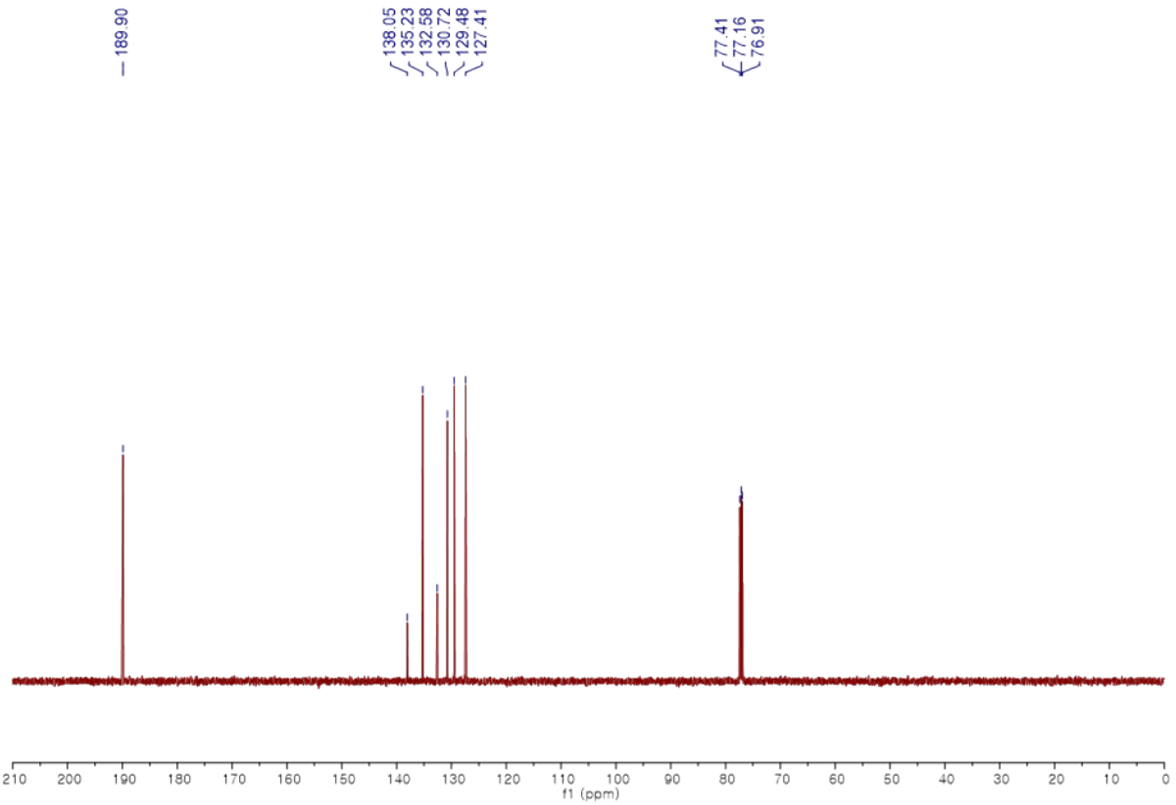
4-Chlorobenzaldehyde (2d)



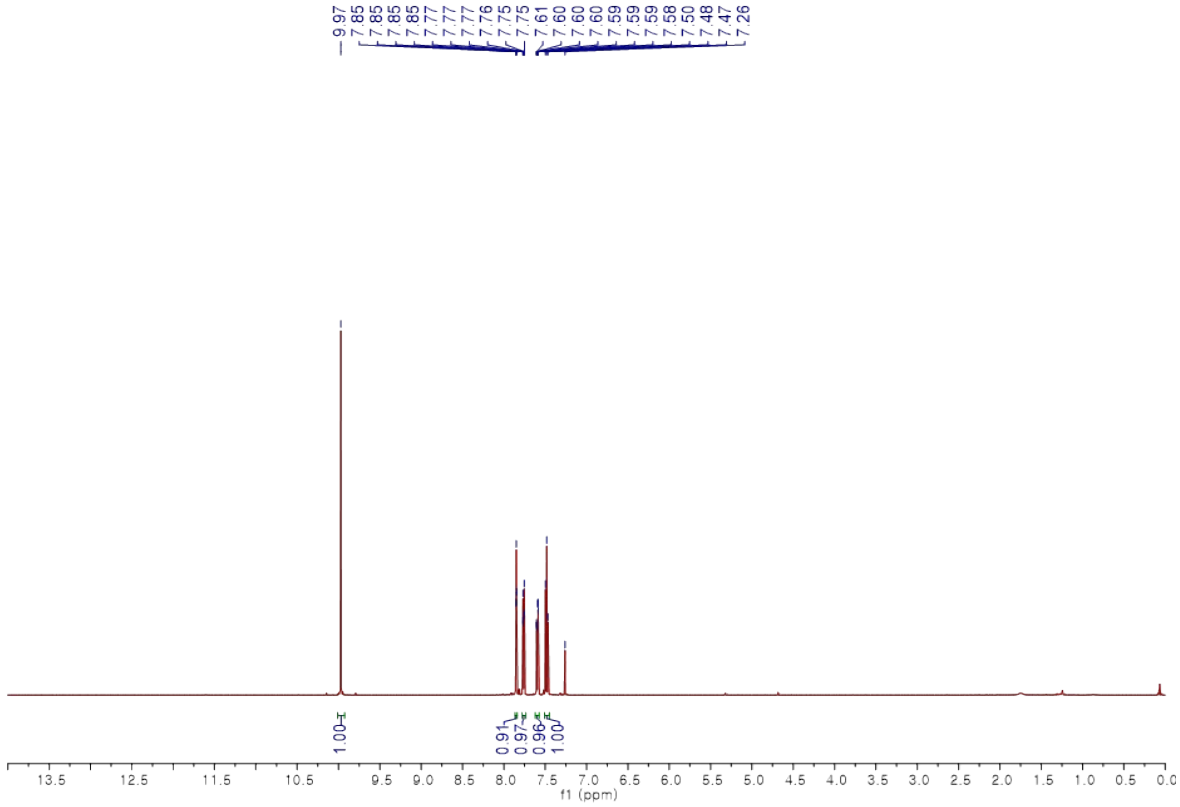


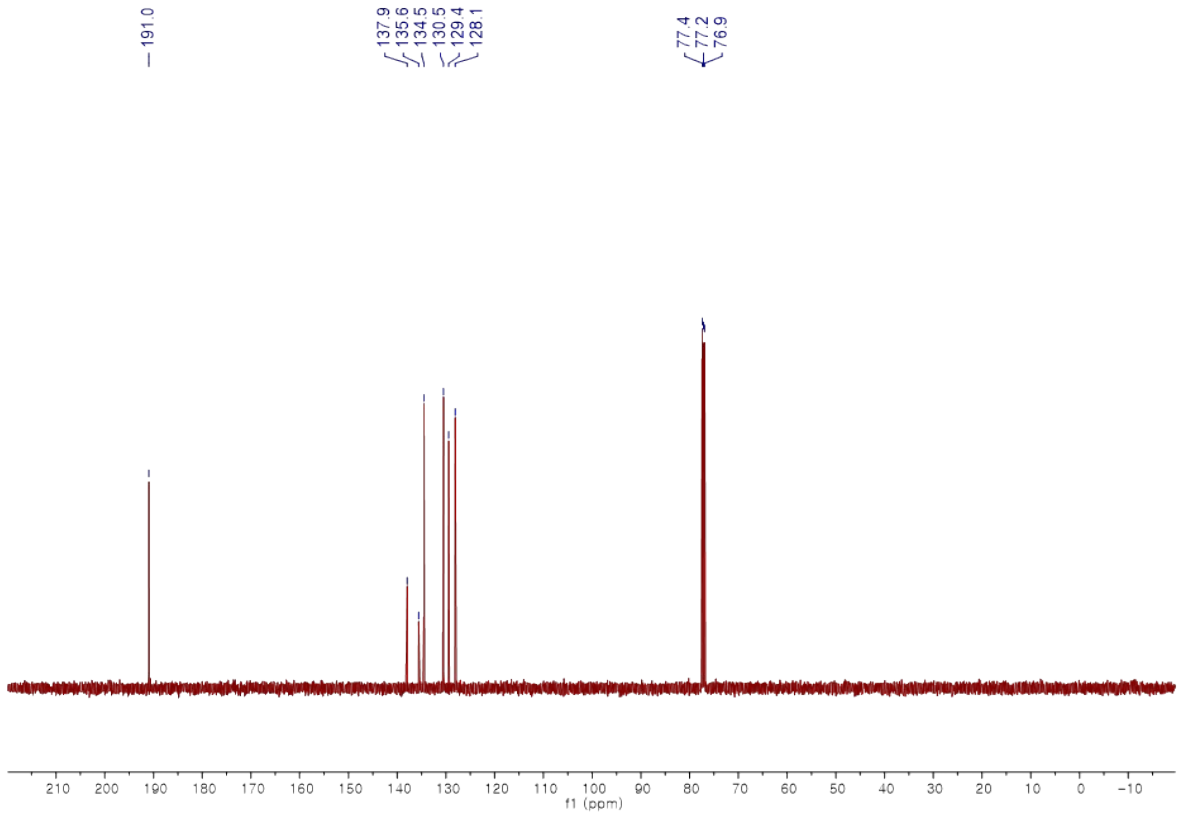
3-Chlorobenzaldehyde (2e)



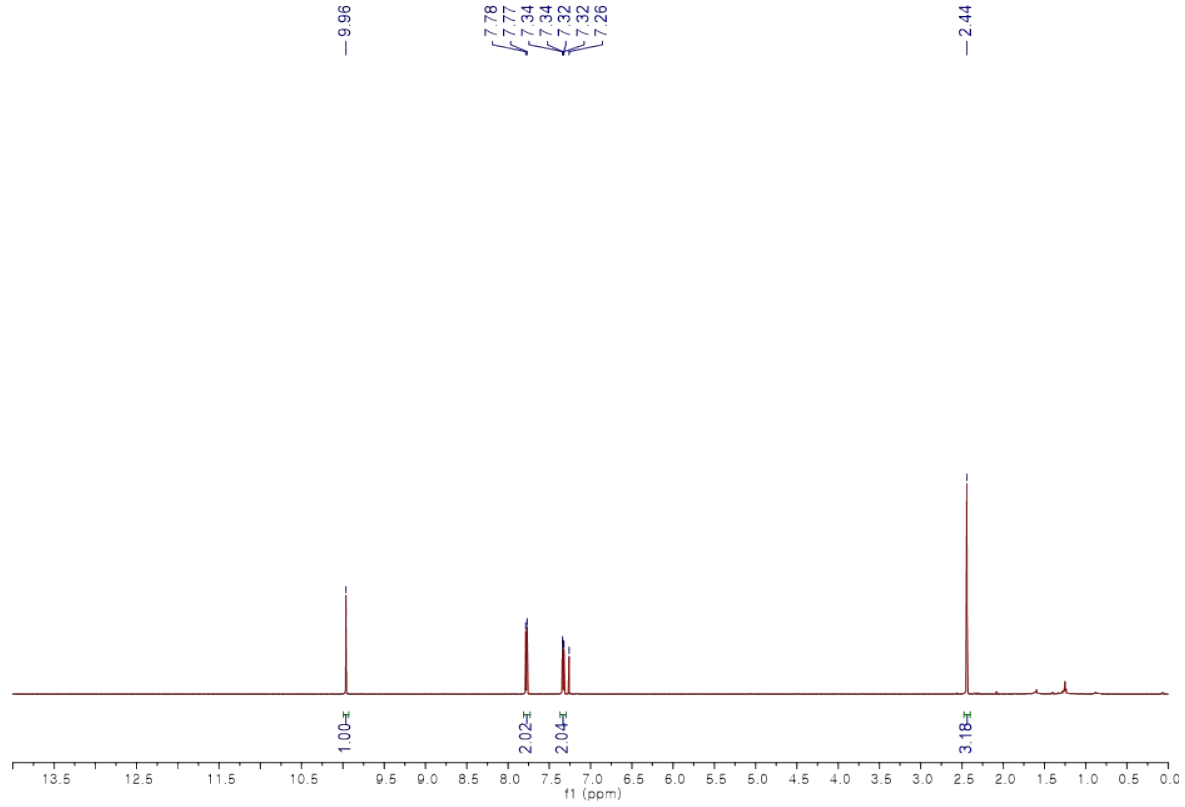


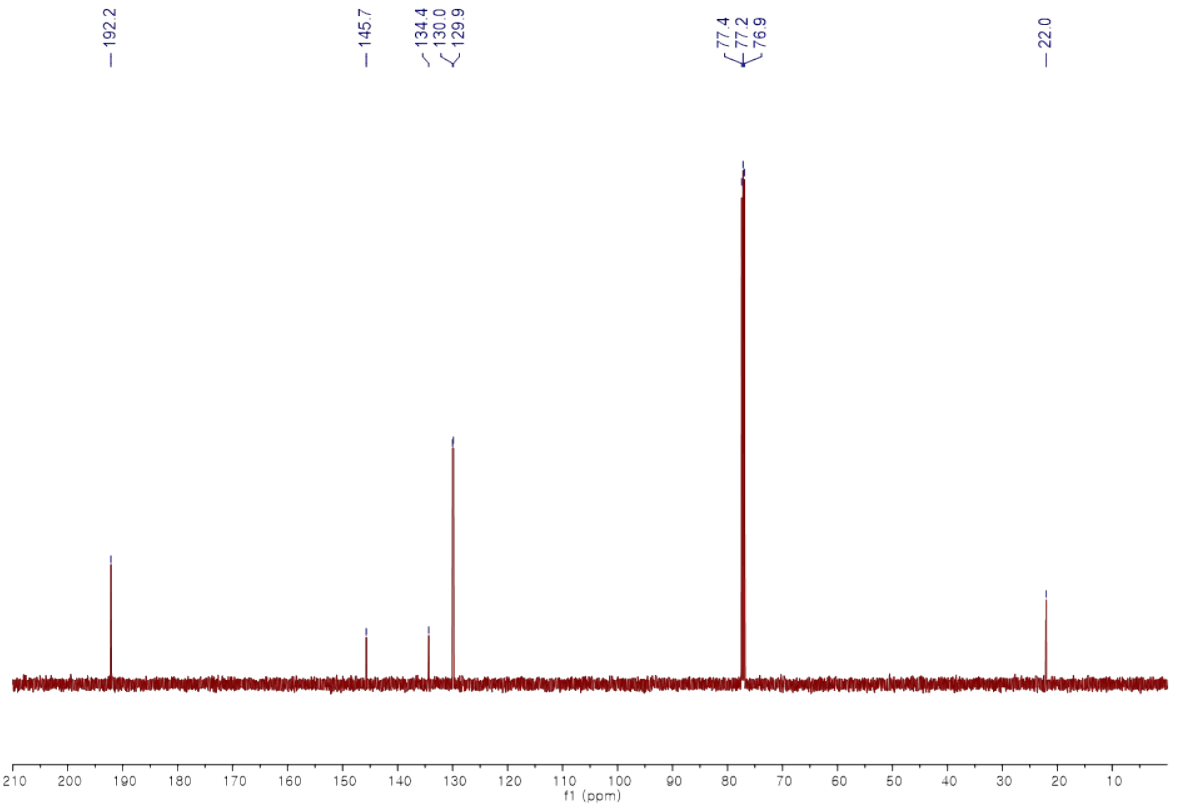
2-Chlorobenzaldehyde (2f)



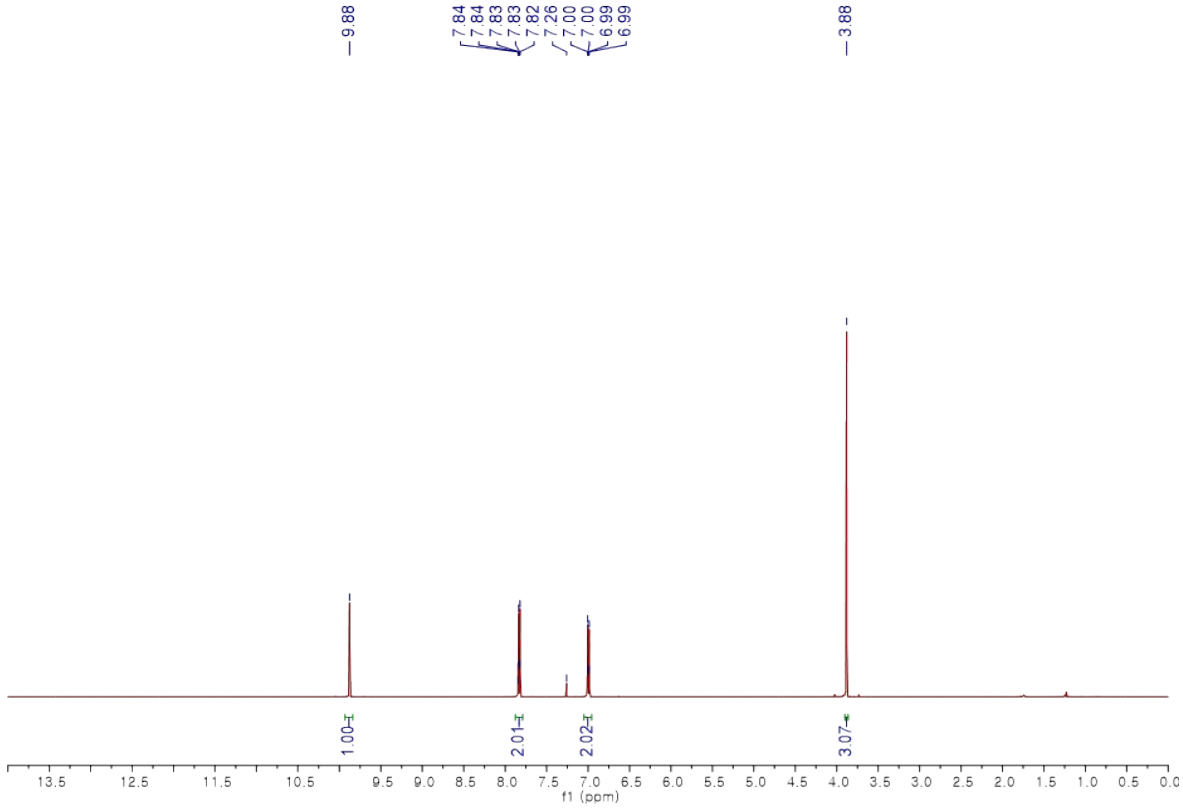


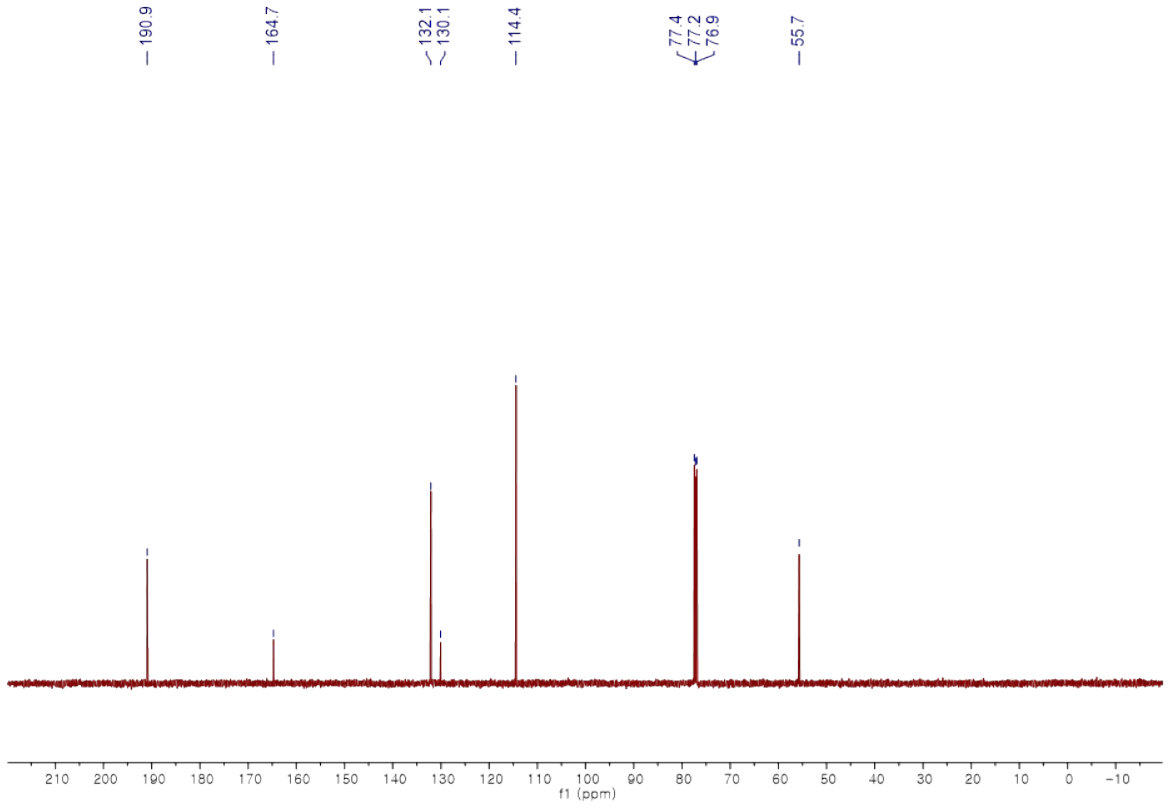
4-Methylbenzaldehyde (2g)



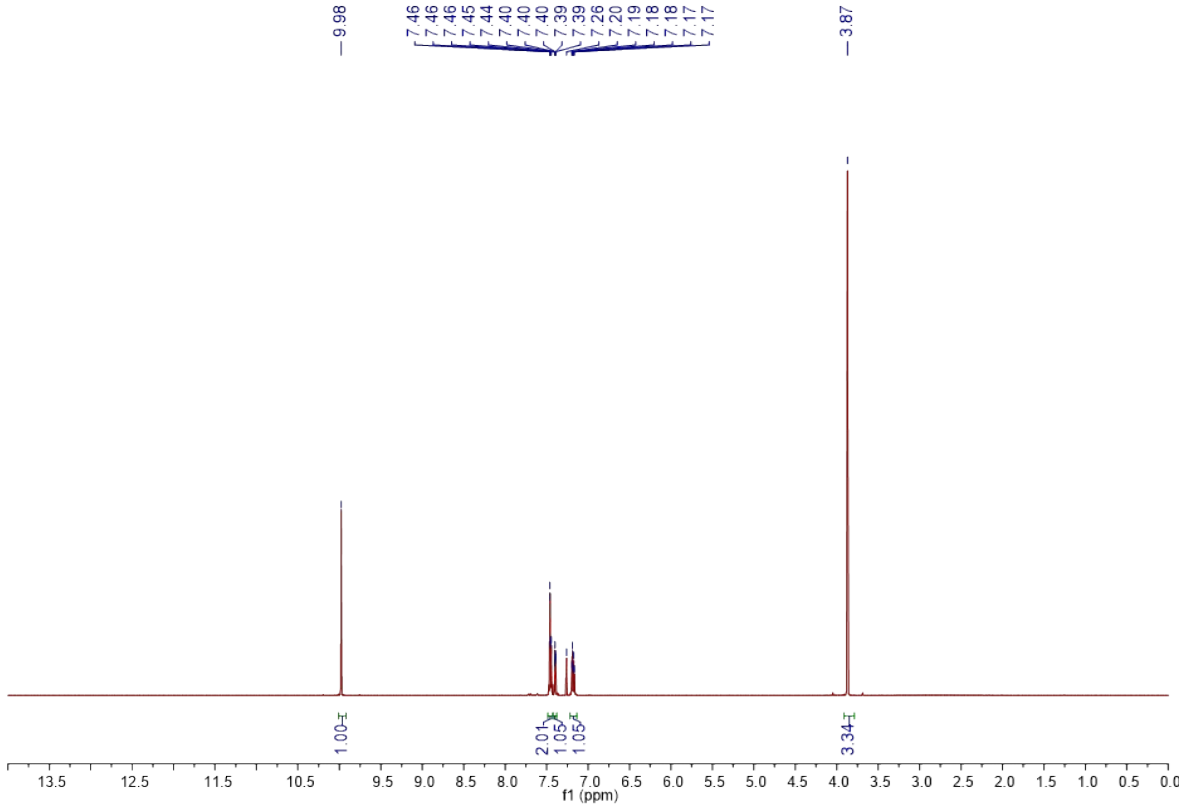


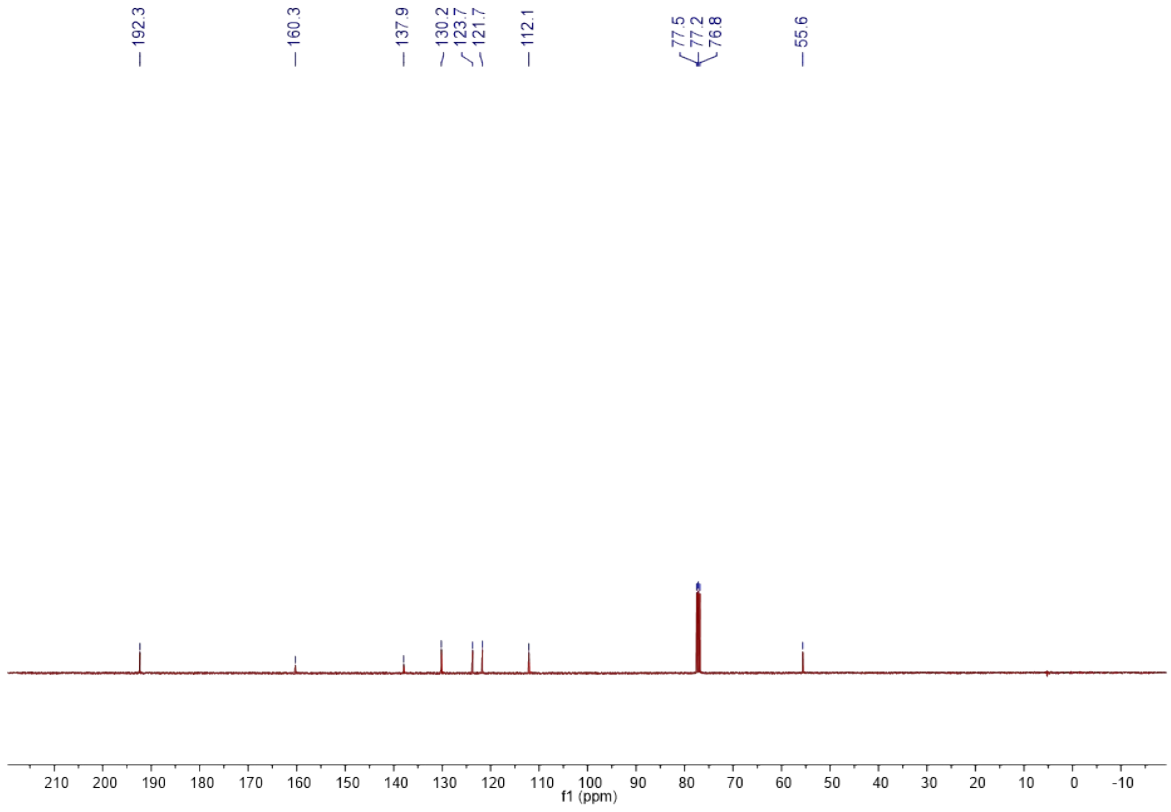
4-Methoxybenzaldehyde (2h)



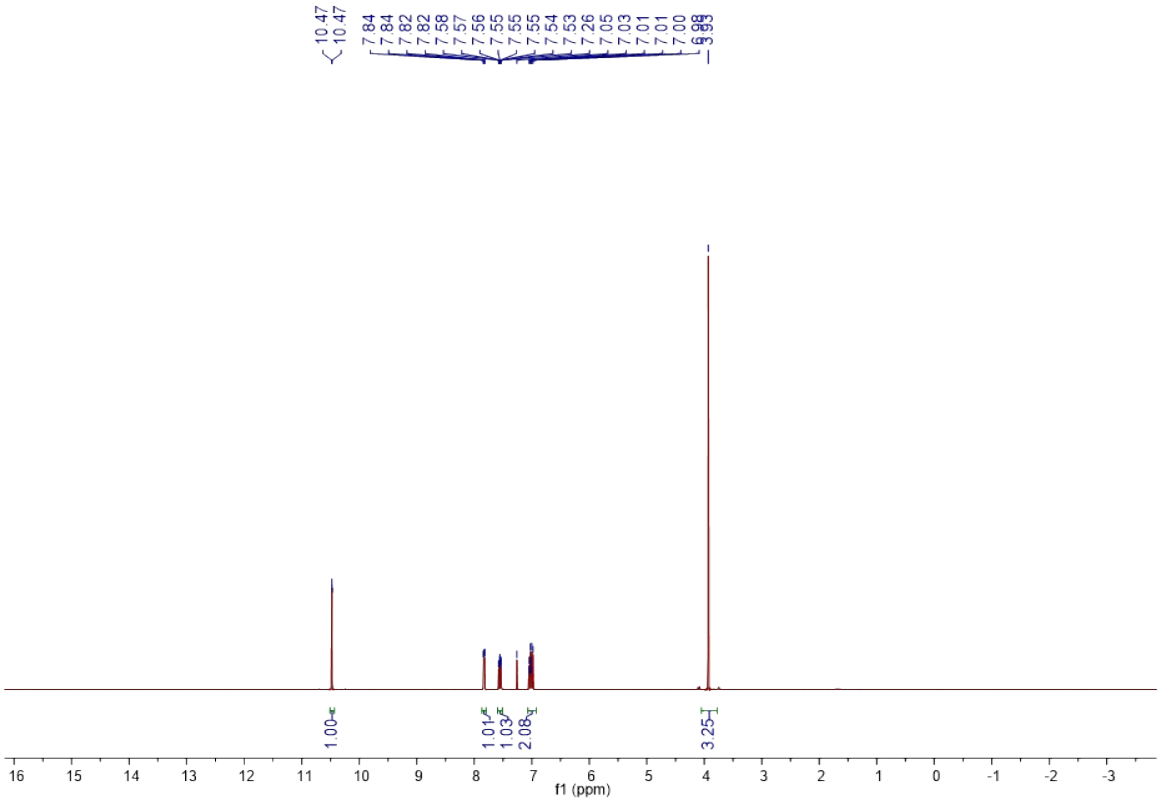


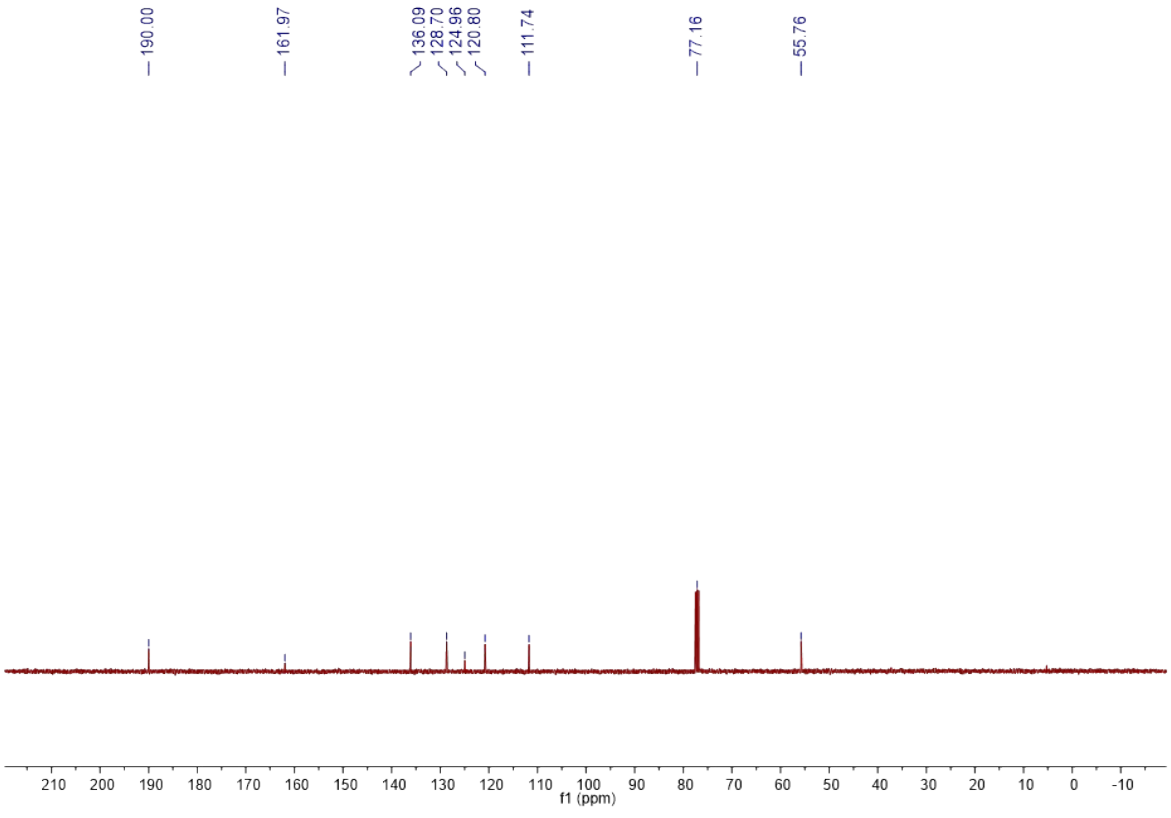
3-Methoxybenzaldehyde (2i)



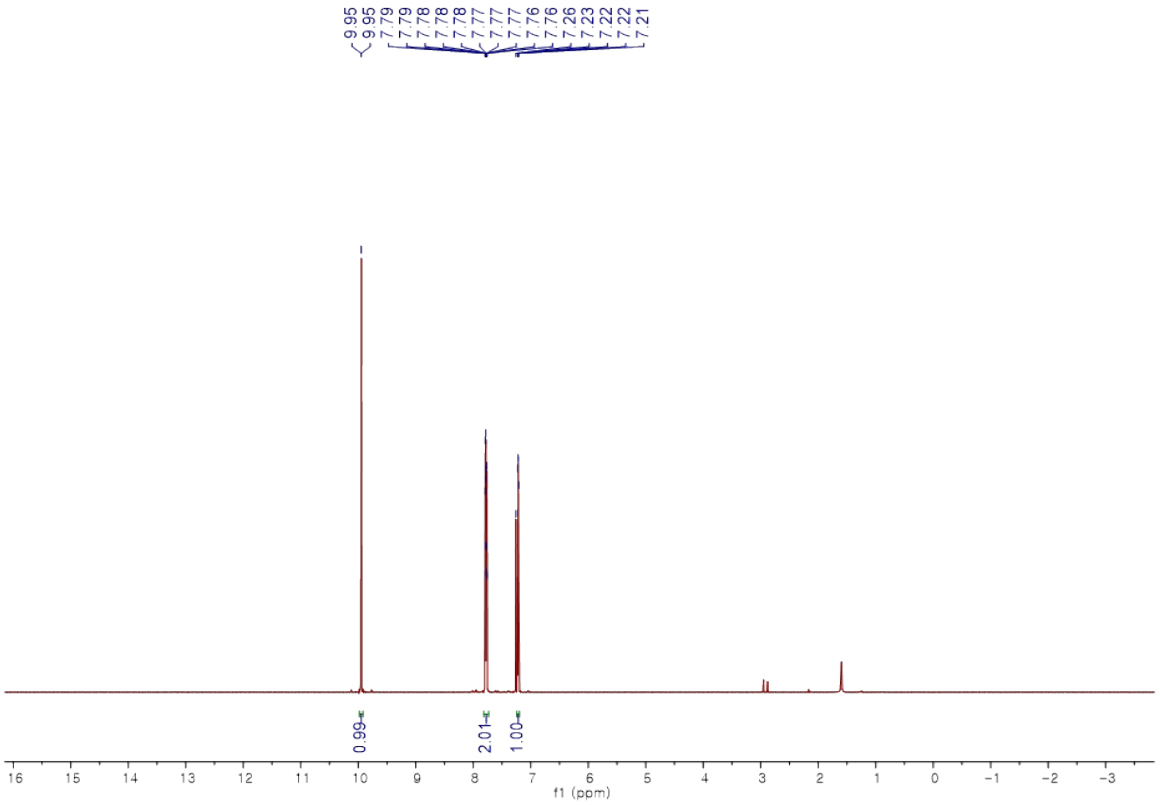


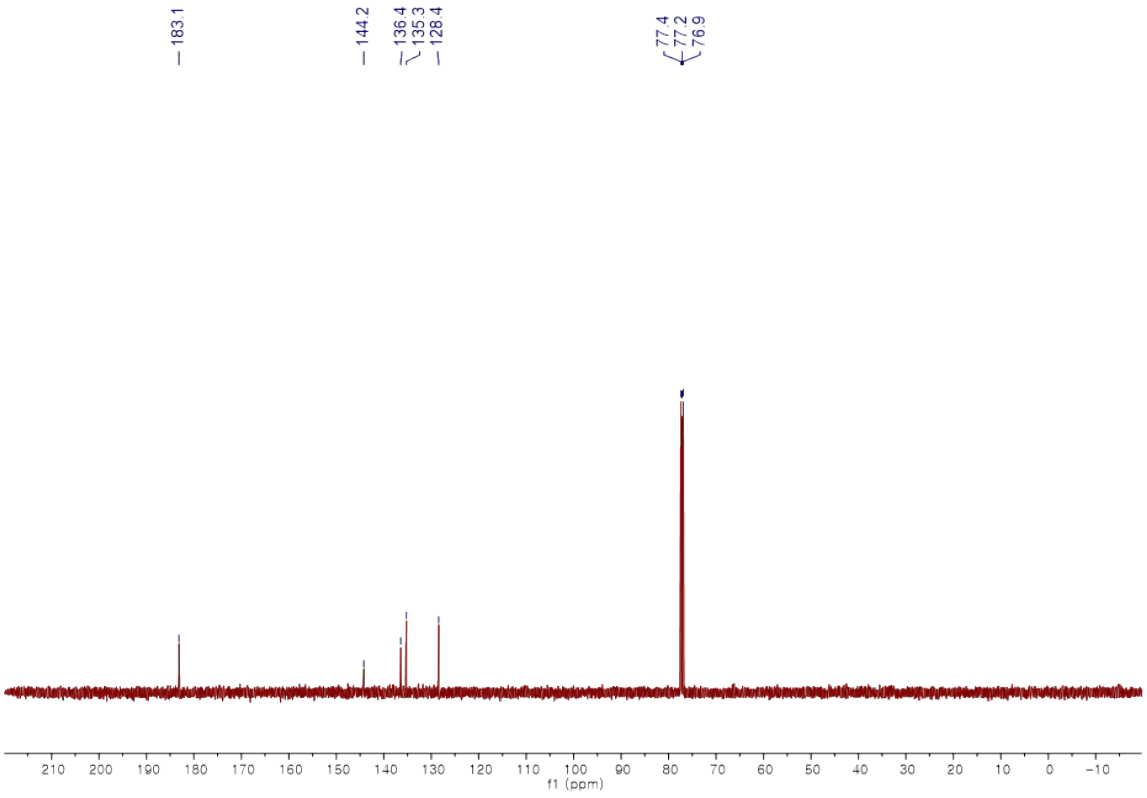
2-Methoxybenzaldehyde (2j)



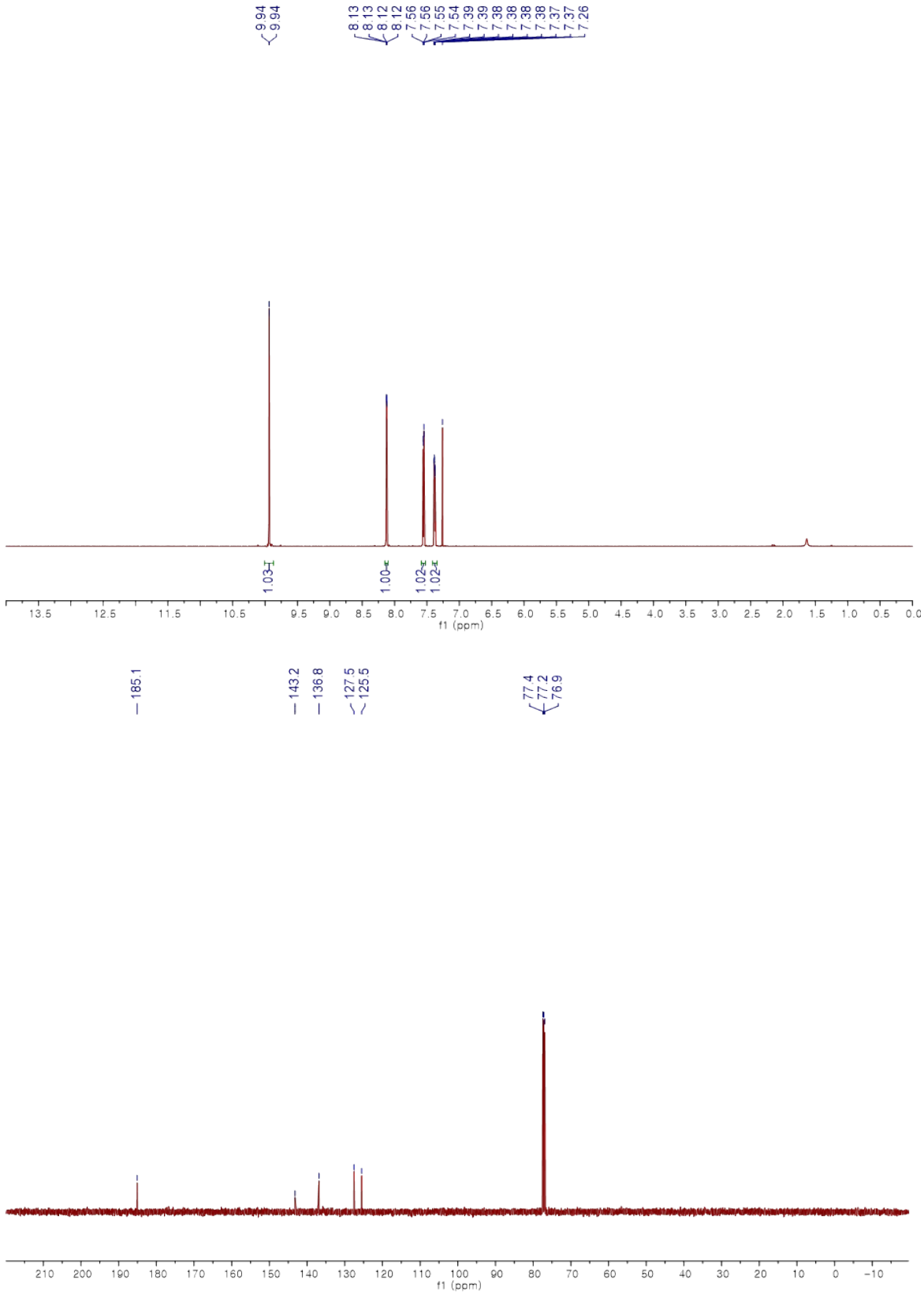


2-Thiophenecarboxaldehyde (2k)

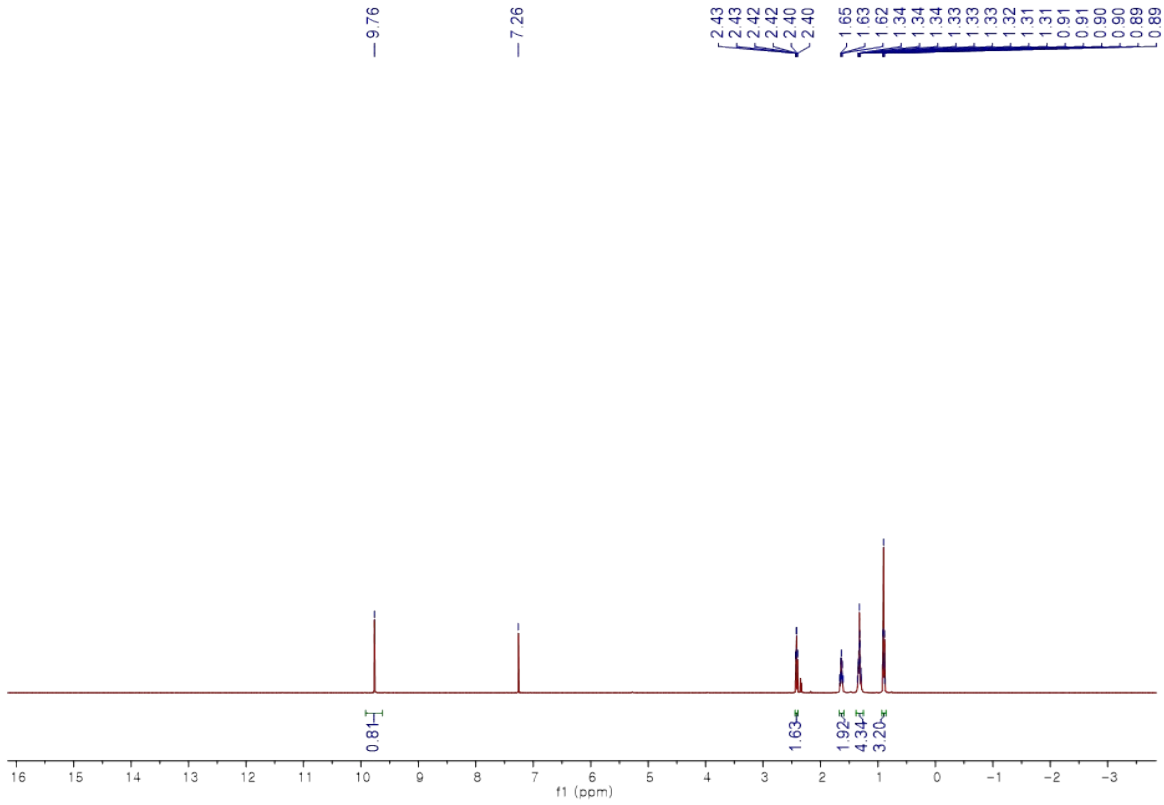


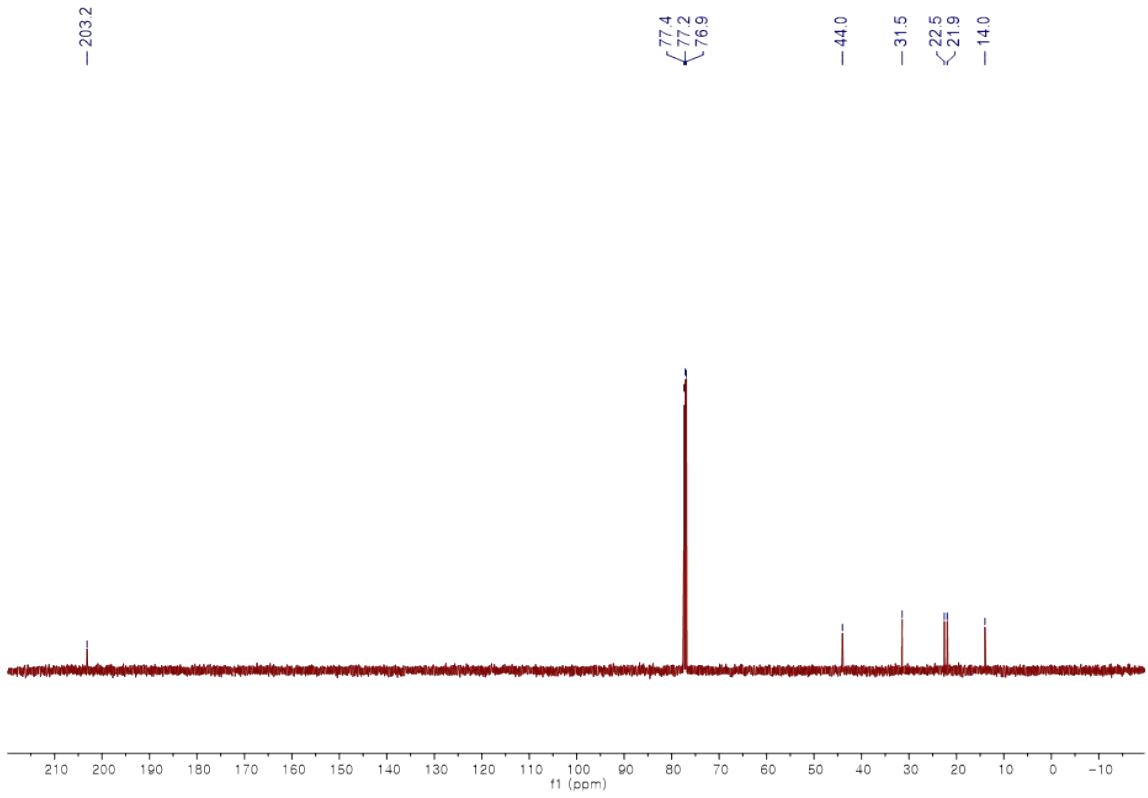


3-Thiophenecarboxaldehyde (2l)

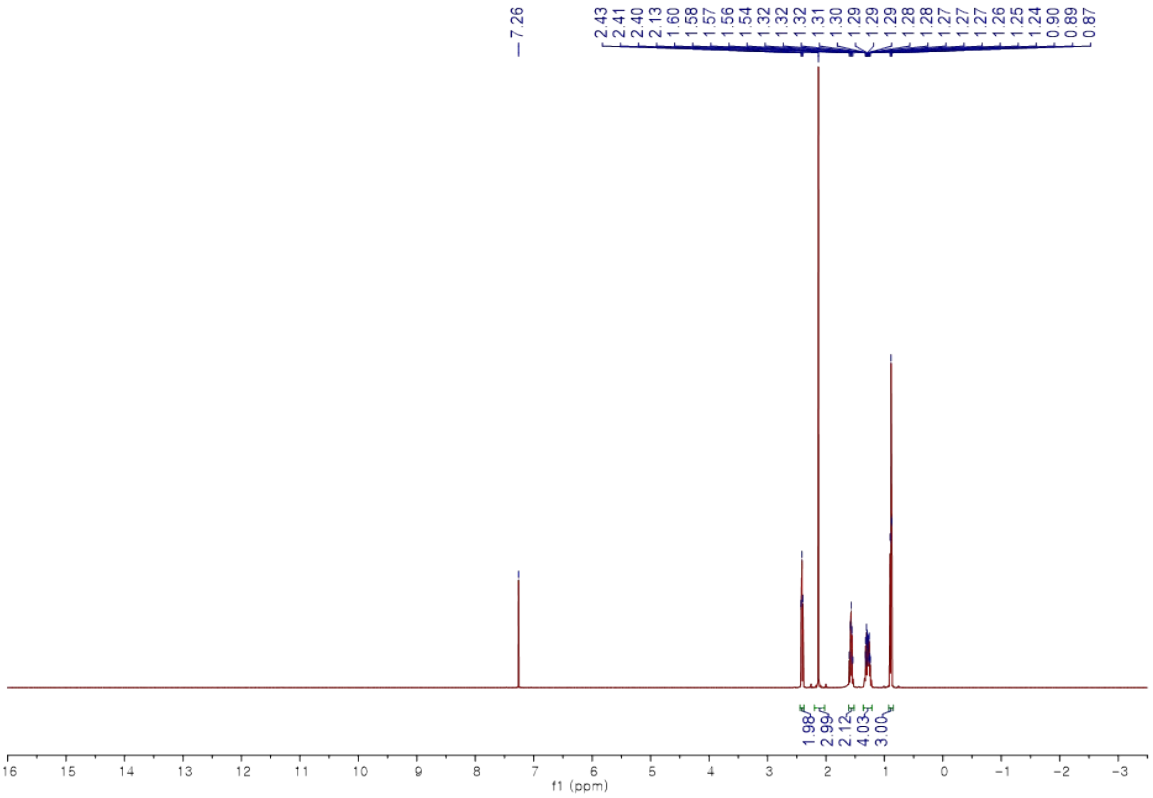


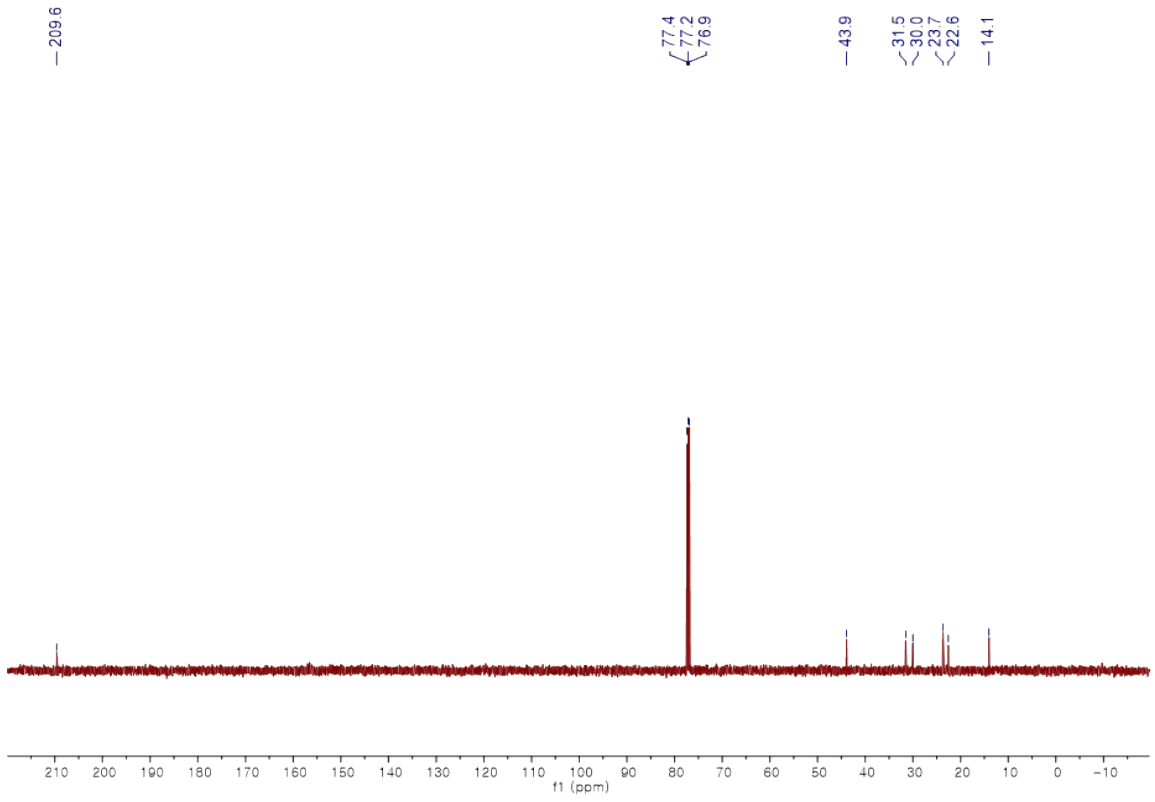
1-Hexanal (2m)


9.76
7.26
2.43
2.43
2.42
2.42
2.40
2.40
1.65
1.63
1.62
1.34
1.34
1.34
1.33
1.33
1.33
1.32
1.31
1.31
0.91
0.91
0.90
0.90
0.89
0.89
0.81
1.63
1.92
4.34
3.20
f1 (ppm)

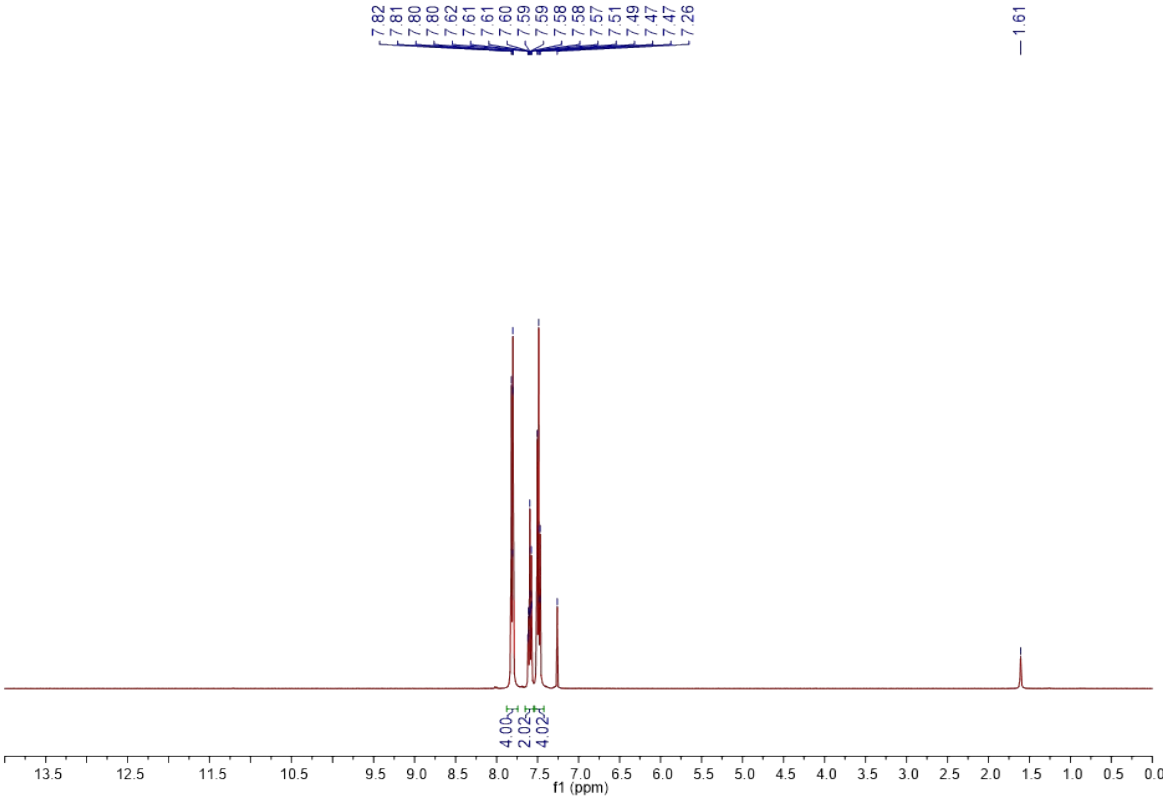

203.2
77.4
77.2
76.9
44.0
31.5
22.5
21.9
14.0
f1 (ppm)

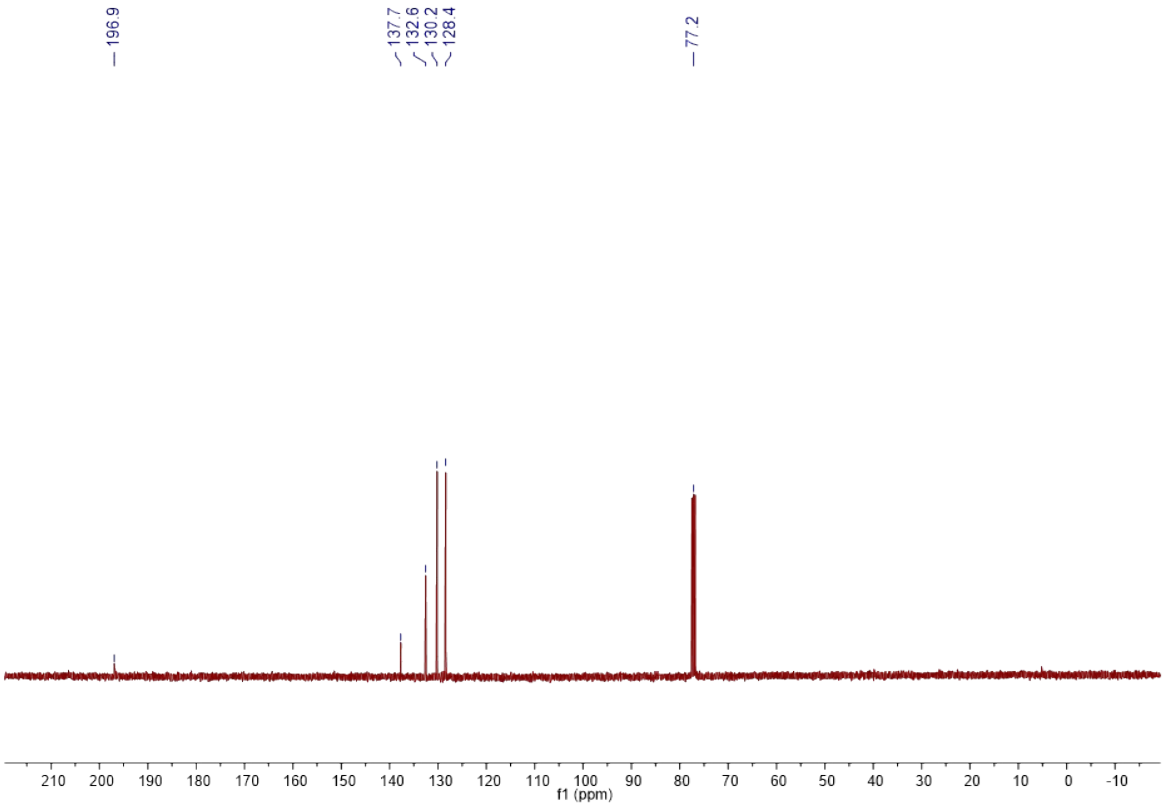
2-Heptanone (**2n**)



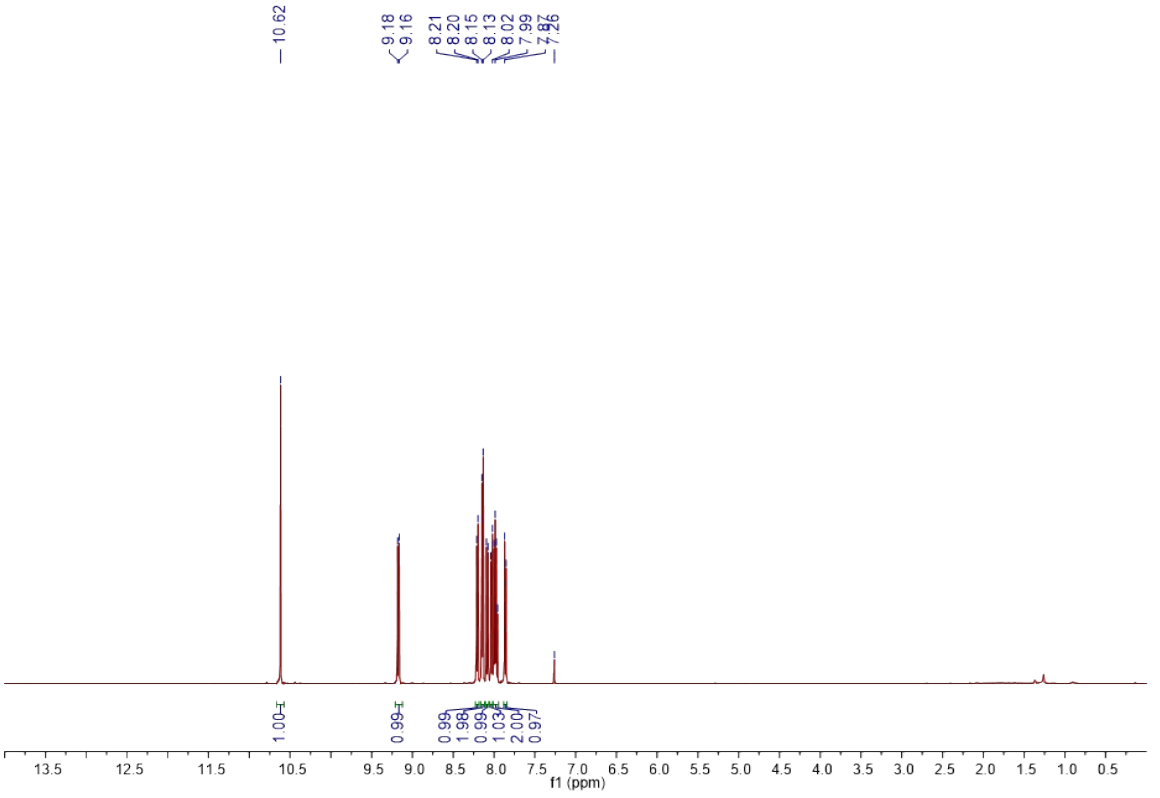


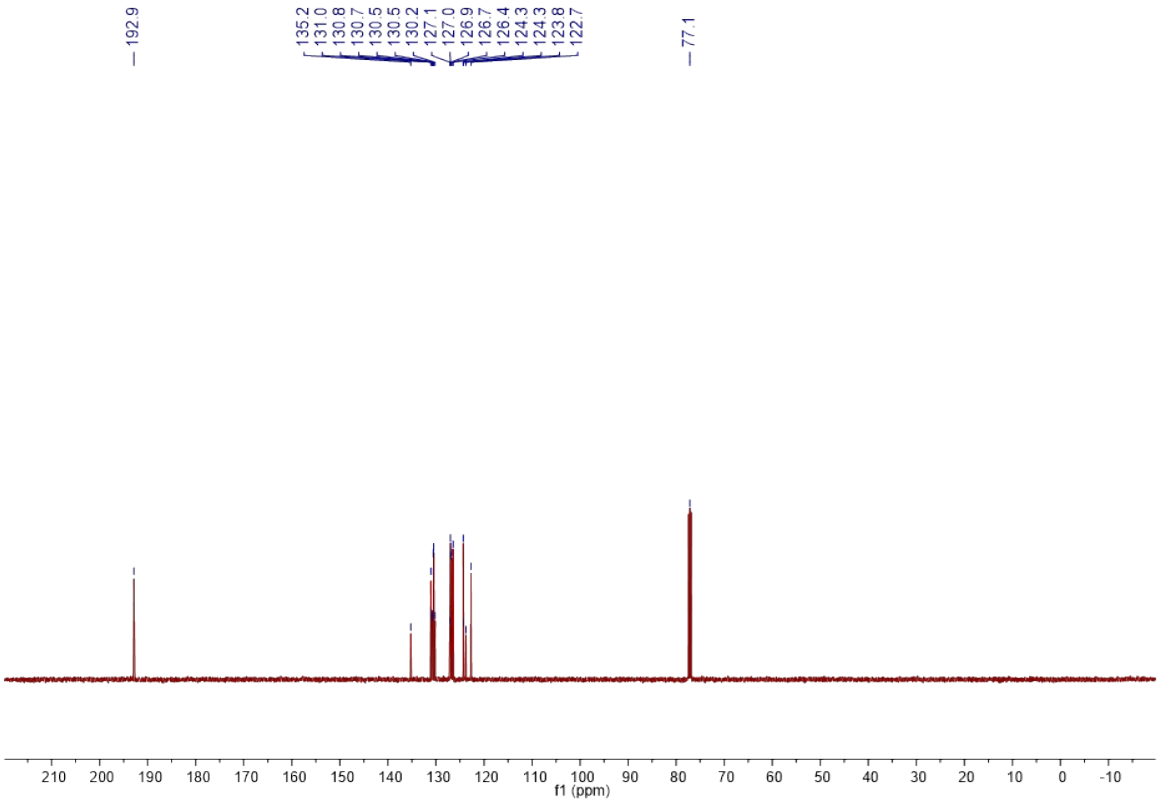
Diphenyl ketone (2o)





1-Pyrenylaldehyde (2p)





Phenyl pyrenyl ketone (2q)