

SUPPORTING INFORMATION

Facile Photochemical/Thermal Assisted Hydration of Alkynes Catalysed under Aqueous media by a Chalcogen Stabilized, Robust, Economical, and Reusable $\text{Fe}_3\text{Se}_2(\text{CO})_9$ Cluster

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Experimental Details: The ^1H , ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ^1H and 100 MHz for ^{13}C).

Chemicals and reagents: Reactants, reagents, chemicals and solvents available commercially within the country were used.

Experimental

Procedure for the synthesis of $\text{Fe}_3\text{E}_2(\text{CO})_9$ Complex¹: In an ice cold bath 2 neck R.B. flask equipped nitrogen inlet. 1 ml of 50% KOH solution was added followed by the addition of 10 ml of MeOH. The mixture was stirred for 20 minutes. To the above solution (6.525 mmol) of FeCO_5 was added and the solution was further stirred for 30 minutes while maintaining the temperature 0°C subsequently 80 ml aq. solution of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ / $\text{Na}_2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ / Na_2TeO_3 (7.6 mmol) was added and the ice bath surrounding the R.B. was removed after 20 minutes. The solution was allowed stirring at room temperature for 30 min. The solution was cooled to 0°C and the mixture was acidified with HCl (6M, 11.25ml) till completion. The content was filtered through the celite pad under N_2 atmosphere. The solid on the celite pad was thoroughly washed with distilled water (100 ml) and dried under vacuum and extracted with 6-50 ml portion of pure CH_2Cl_2 . The combined extracts was filtered through a celite pad and the filtrate was evaporated to dryness.

General Procedure for the Catalytic Reaction: To a 100 mL capacity borosilcate immersion well of UV reactor 80 mL, water is used as solvent, alkyne (1 mmol), Fe catalyst (5 mol%) was added, The reaction mixture was first cool down at -5°C then it was exposed to the Hg vapour UV lamp, 125 W, 289 nm for 25 min with continuous stirring. After completion of the reaction, catalyst was separated through filtration and product was extracted through solvent extraction with ethyl acetate. The extracted solvent is dried over anhydrous Na_2SO_4 , concentrated at reduced pressure, and purified by flash column chromatography with hexanes/ethyl acetate as eluent to obtain the corresponding product.

Characterisation Data

Acetophenone ²

¹H NMR (400 MHz, CDCl₃): δ = 7.87 – 7.85 (m, 2H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 2H), 2.50 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 198.34, 137.26, 133.32, 128.77, 128.50, 26.81.

1-(4-(tert-butyl)phenyl)ethan-1-one ³

¹H NMR (400 MHz, CDCl₃): δ = 7.82 – 7.80(m, 2H), 7.39 – 7.37 (m, 2H), 2.48 (s, 3H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ = 197.66, 156.52, 134.27, 131.55, 129.75, 128.02, 125.21, 34.79, 30.78, 26.25

1-(p-tolyl)ethan-1-one ⁴

¹H NMR (400 MHz, CDCl₃): δ = 7.87 - 7.85 (m, 2H), 7.26 – 7.24 (m, 2H), 2.57 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 197.50, 143.54, 134.33, 128.91, 128.10, 26.18, 21.28.

1-(m-tolyl)ethan-1-one ⁴

¹H NMR (400 MHz, CDCl₃): δ = 7.75 – 7.72 (m, 2H), 7.34 – 7.32 (m, 2H), 2.56 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 198.21, 138.21, 137.01, 133.77, 128.67, 128.35, 125.49, 26.55, 21.21.

1-(o-tolyl)ethan-1-one ³

¹H NMR (400 MHz, CDCl₃): δ = 7.68 – 7.67 (m, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.20 (m, 2H), 2.55 (s, 3H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 201.60, 138.38, 137.44, 132.02, 131.52, 129.40, 125.70, 29.48, 21.60.

1-(4-ethylphenyl)ethan-1-one ⁴

¹H NMR (400 MHz, CDCl₃): δ = 7.89 – 7.87 (m, 2H), 7.29 – 7.27 (m, 2H), 2.73 – 2.67 (q, 2H), 2.57 (s, 3H), 1.27 – 1.23 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 198.07, 150.26, 135.12, 128.76, 128.27, 29.15, 26.76, 15.43.

1-(4-methoxyphenyl)ethan-1-one ⁴

¹H NMR (400 MHz, CDCl₃): δ = 7.93 – 7.91 (m, 2H), 6.92 – 6.90 (m, 2H), 3.84 (s, 3H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 196.88, 163.63, 130.72, 130.42, 113.82, 55.58, 26.46.

1-(2-methoxyphenyl)ethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 7.71 - 7.69$ (m, 1H), $7.43 - 7.39$ (m, 1H), $6.95 - 6.90$ (m, 2H), 3.84 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 199.83, 159.11, 133.91, 130.41, 128.26, 120.63, 111.80, 55.59, 32.01$.

1-(4-fluorophenyl)ethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 8.0 - 7.97$ (m, 2H), $7.15 - 7.11$ (m, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.67, 165.94$ (d, $J_{\text{C-F}} = 254$ Hz), 133.76 (d, $J_{\text{C-F}} = 3.0$ Hz), 131.13 (d, $J_{\text{C-F}} = 9.0$ Hz), 115.83 (d, $J_{\text{C-F}} = 22$ Hz), 26.71 .

1-(4-chlorophenyl)ethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 7.93 - 7.91$ (m, 2H), $7.47 - 7.45$ (m, 2H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.71, 139.40, 135.26, 129.62, 128.75, 26.45$.

1-(2-chlorophenyl)ethan-1-one

^1H NMR (400 MHz, CDCl_3): $\delta = 7.55 - 7.53$ (m, 1H), $7.41 - 7.29$ (m, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 200.32, 138.94, 131.91, 131.13, 130.52, 129.29, 126.83, 30.58$.

1-(4-bromophenyl)ethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 7.83 - 7.81$ (m, 2H), $7.61 - 7.59$ (m, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 197.26, 136.00, 132.11, 130.07, 128.53, 26.79$.

1-(3-aminophenyl)ethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 7.32 - 7.20$ (m, 3H), $6.87 - 6.85$ (m, 1H), 3.88 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 198.53, 146.78, 138.08, 129.35, 119.60, 118.67, 113.91, 26.65$.

Acetyl Ferrocene ⁵

^1H NMR (400 MHz, CDCl_3): $\delta = 4.77$ (s, 2H), 4.51 (s, 2H), 4.21 (s, 5H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 202.16, 72.29, 69.80, 69.54, 27.38$.

1,2-diphenylethan-1-one ⁴

^1H NMR (400 MHz, CDCl_3): $\delta = 8.01 - 7.99$ (m, 2H), $7.54 - 7.51$ (m, 1H), $7.45 - 7.41$ (m, 2H), $7.33 - 7.21$ (m, 5H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 197.37, 136.27, 134.25, 132.91, 129.20, 128.39, 128.37, 128.34, 126.01, 45.21$.

2-phenyl-1-(p-tolyl)ethan-1-one ⁶

^1H NMR (400 MHz, CDCl_3): δ = 2.30 (s, 3H), 4.22 (s, 2H), 7.10 – 7.15 (m, 4H), 7.40 – 7.44 (m, 2H), 7.50 – 7.52 (m, 1H), 7.98 – 8.00 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 197.79, 136.52, 136.42, 133.05, 131.35, 129.34, 129.25, 128.56, 45.07, 21.03

1-(4-chlorophenyl)-2-phenylethan-1-one ⁷

^1H NMR (400 MHz, CDCl_3): δ = 4.25 (s, 2H), 7.24 – 7.35 (m, 5H), 7.41 – 7.44 (m, 2H), 7.93 – 7.96 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 196.46, 139.65, 134.83, 134.18, 130.07, 129.40, 128.99, 128.79, 127.07, 45.56



Figure S1. Photochemical reactor (Capacity 100 mL)



Figure S2. Reaction setup for photochemical reactor

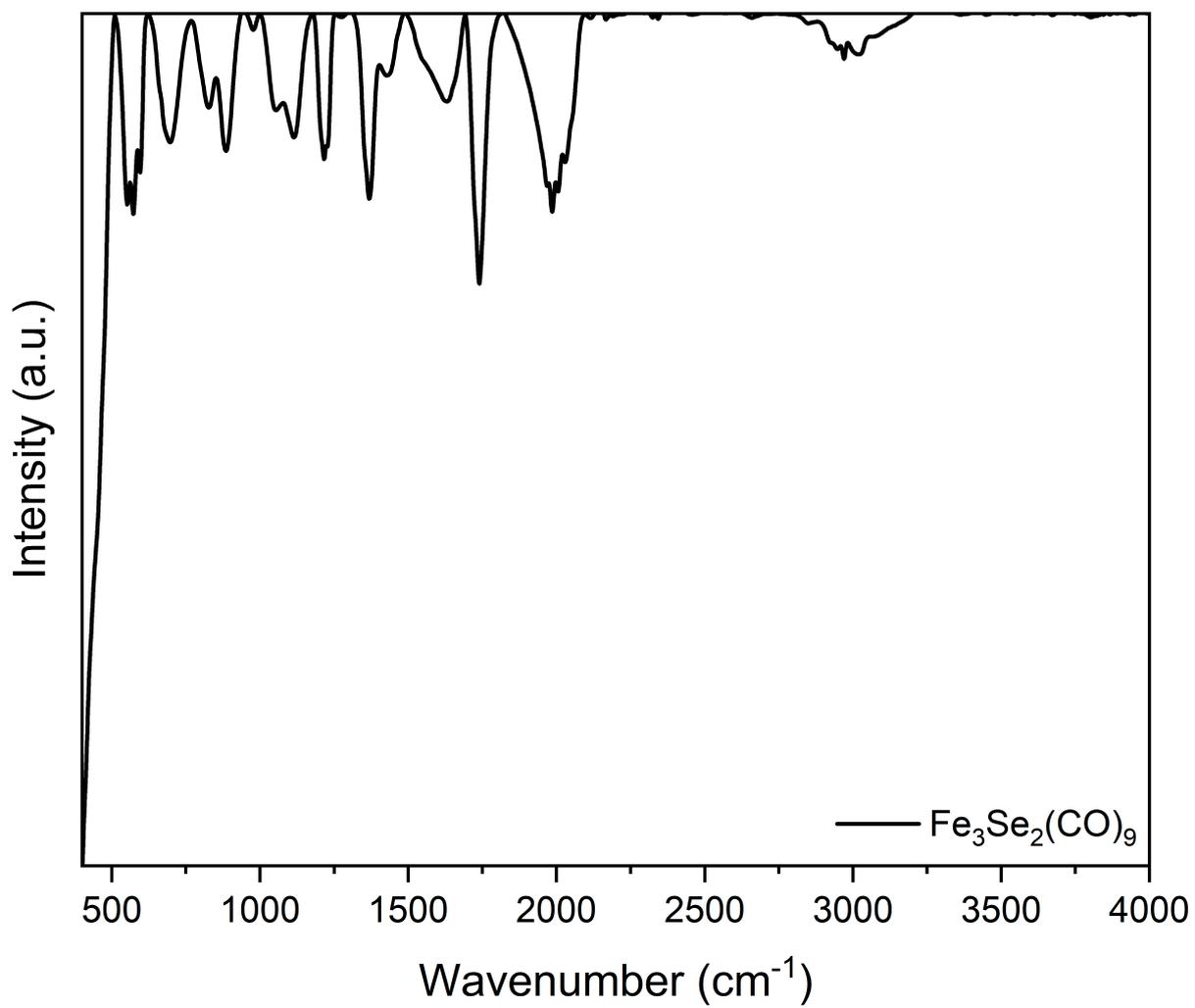
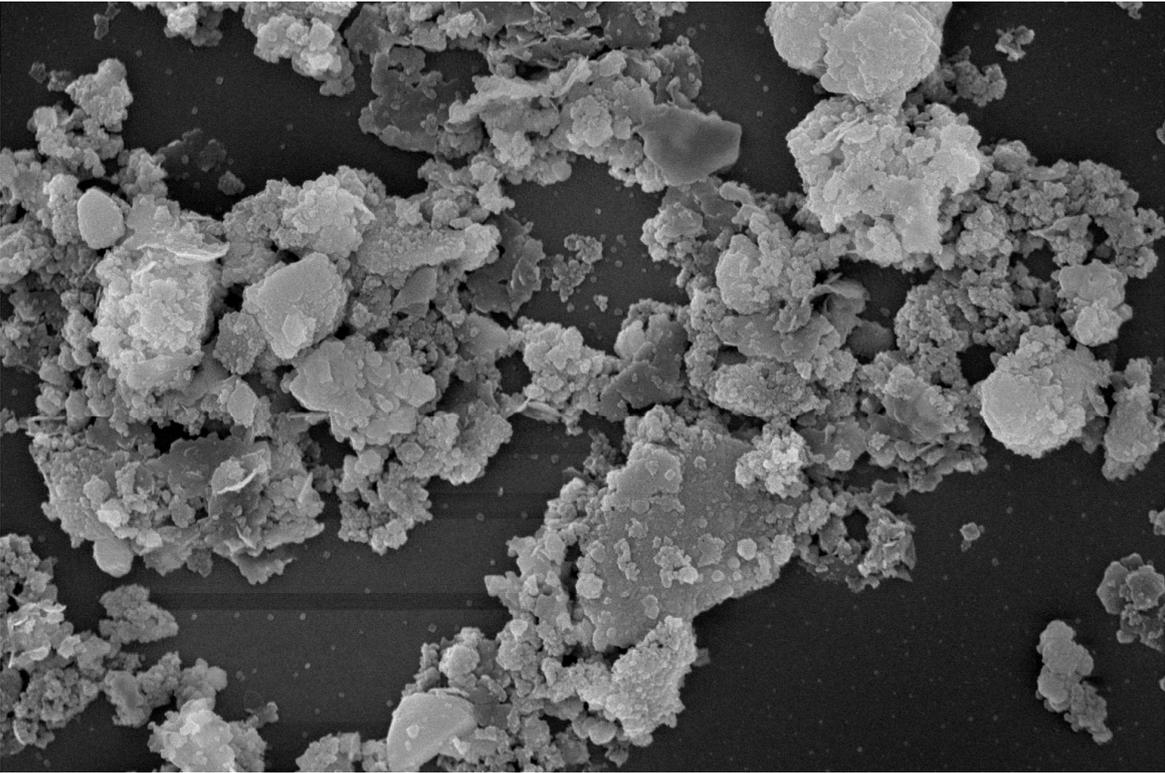


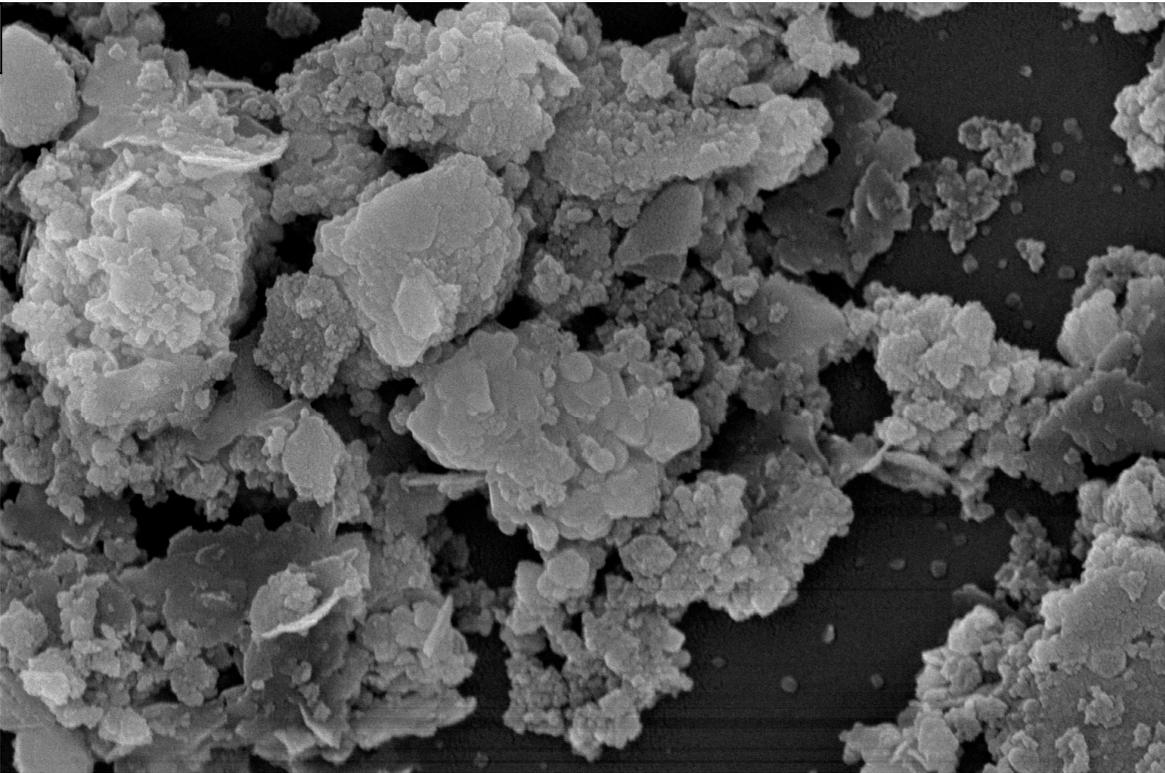
Figure S3. FTIR of $\text{Fe}_3\text{Se}_2(\text{CO})_9$ catalyst

a



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b



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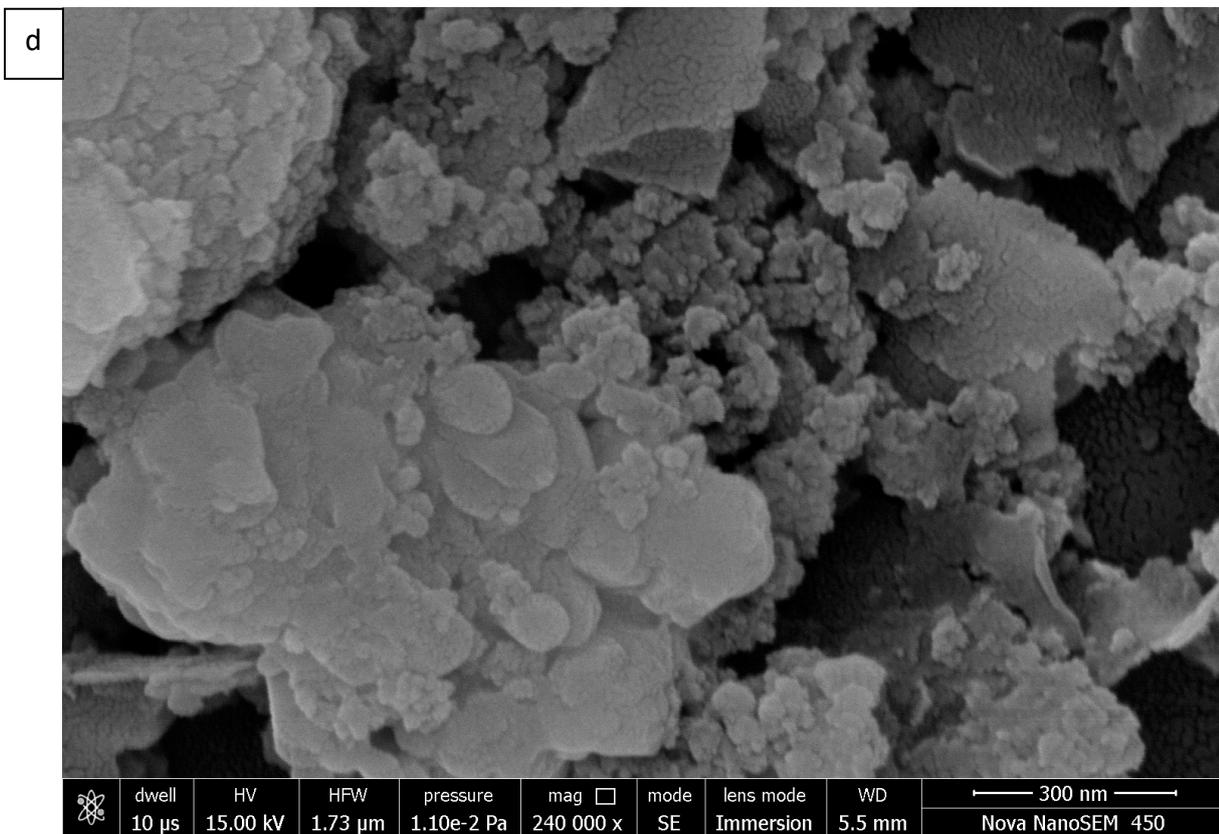
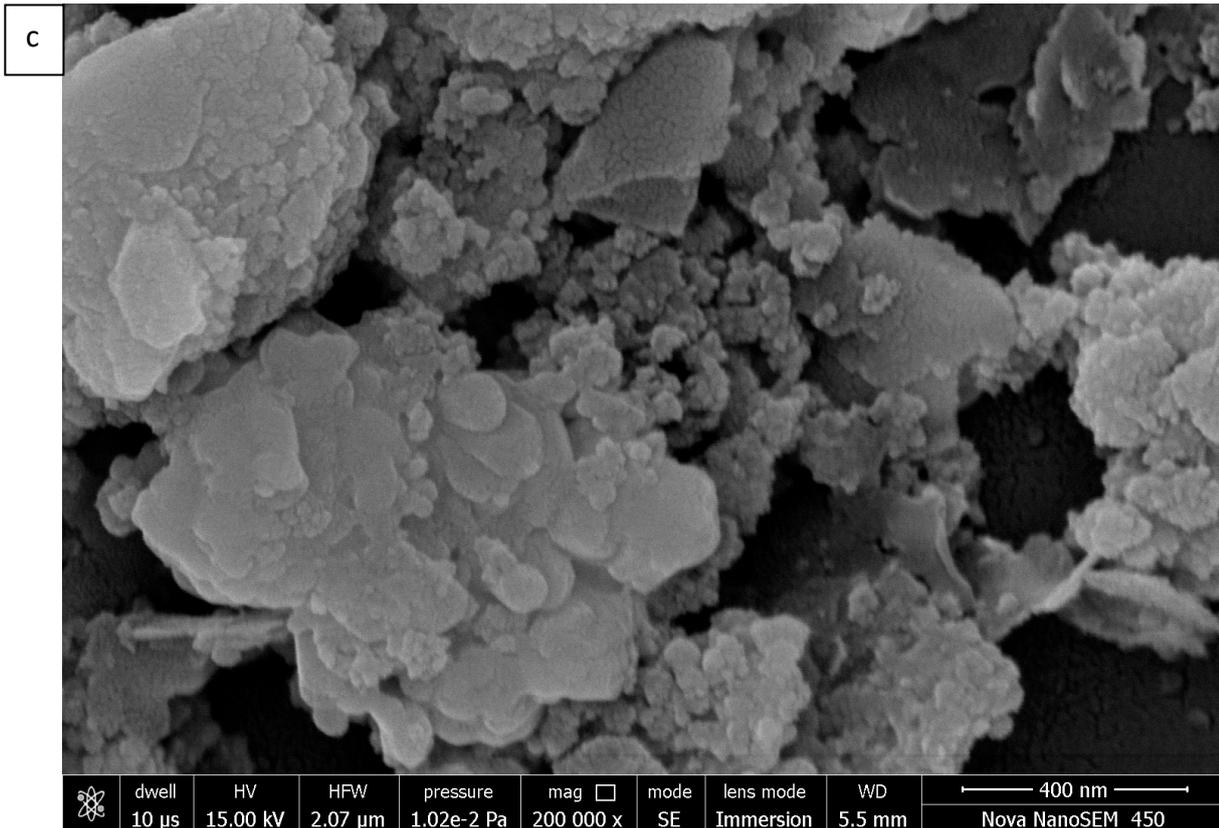
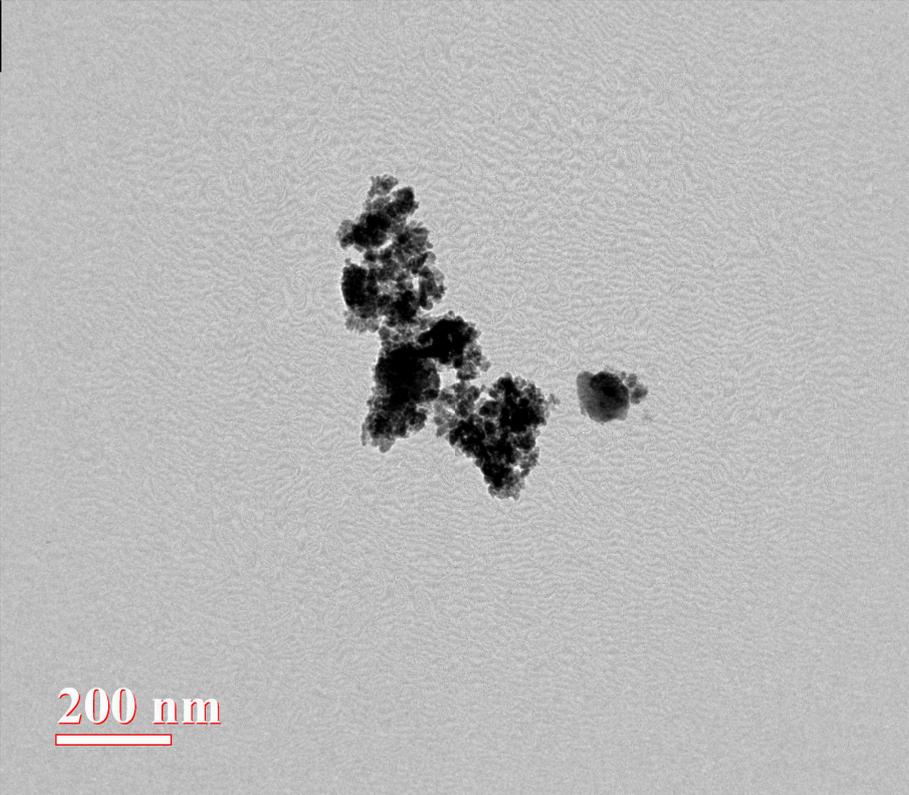
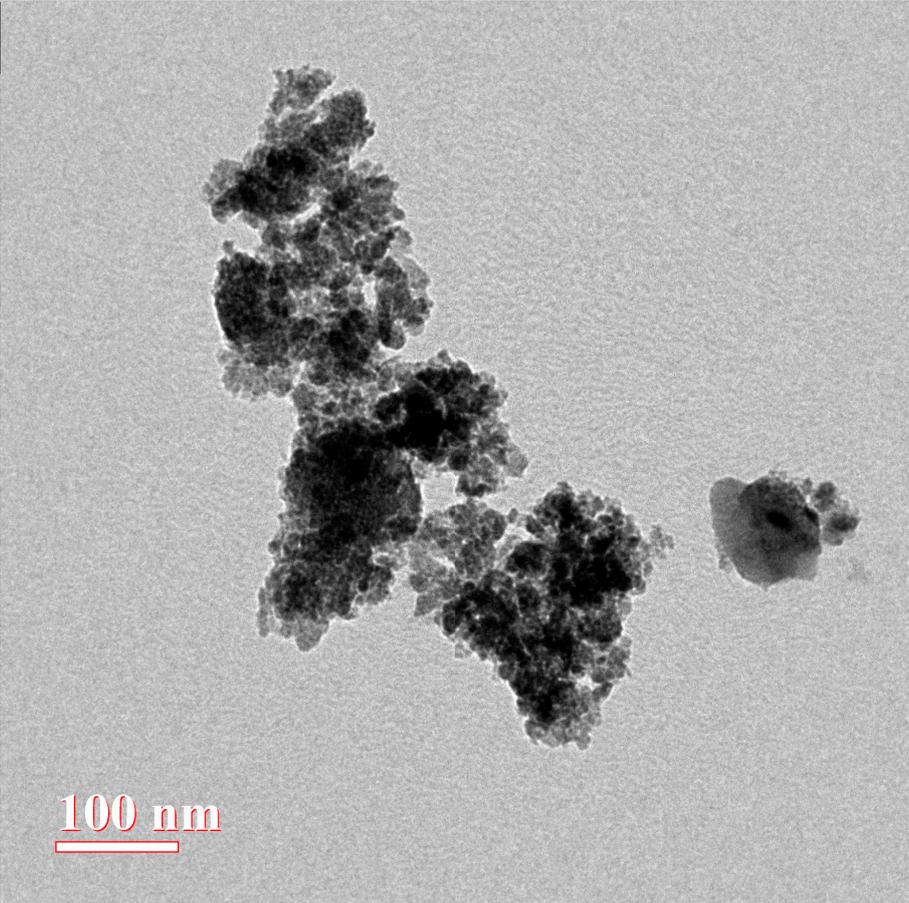


Figure S4 (a - d). FESEM images of FeSe nanoparticles.

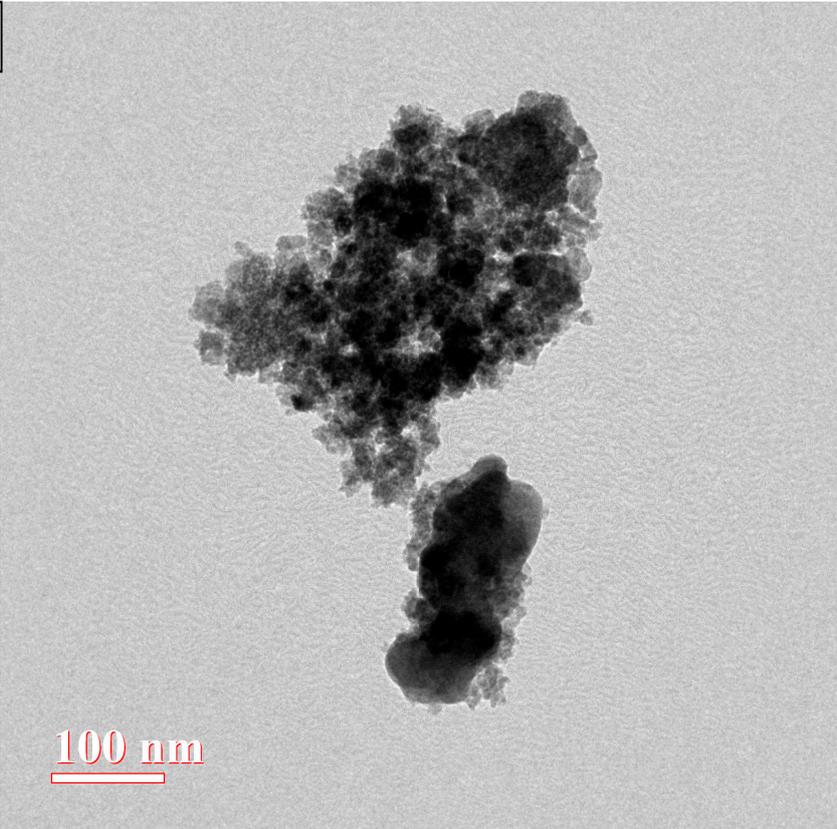
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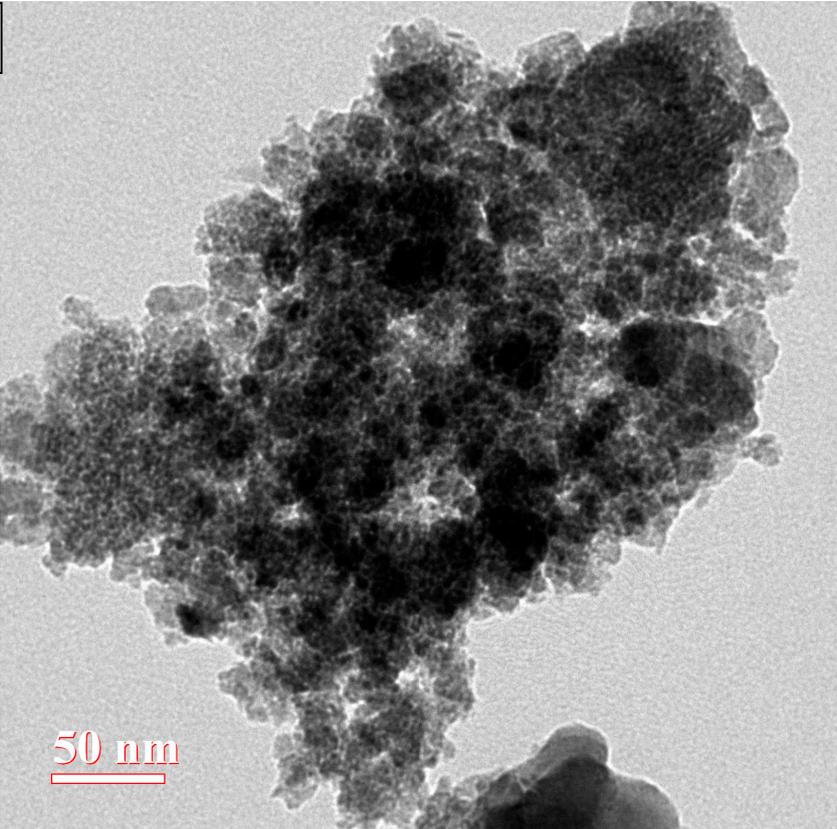
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c



d



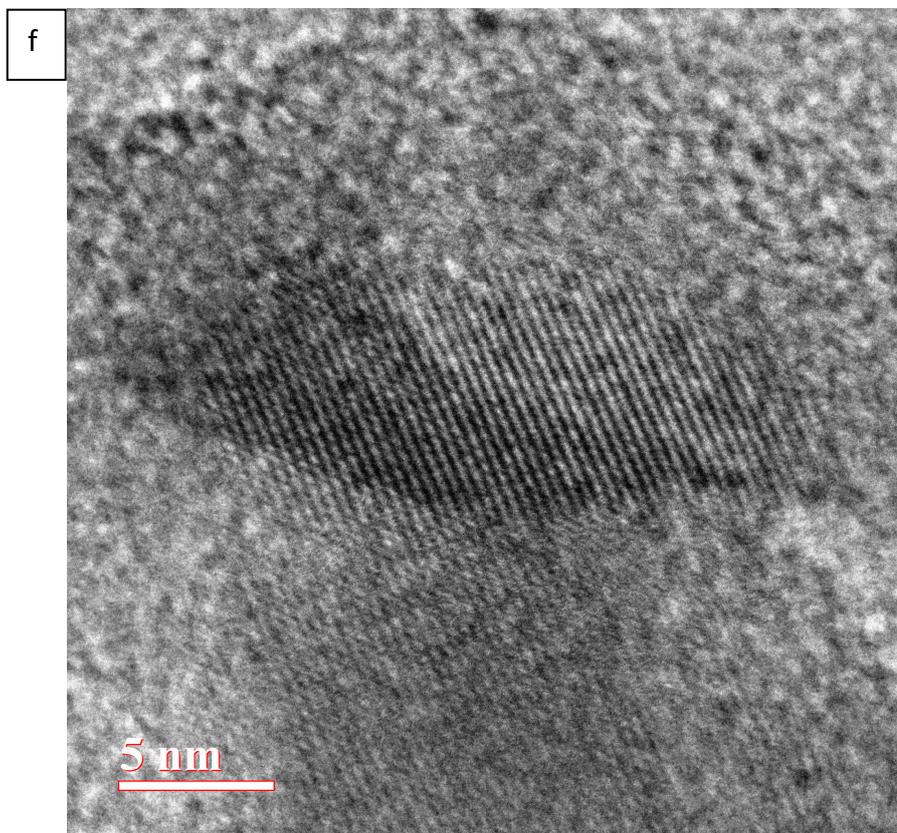
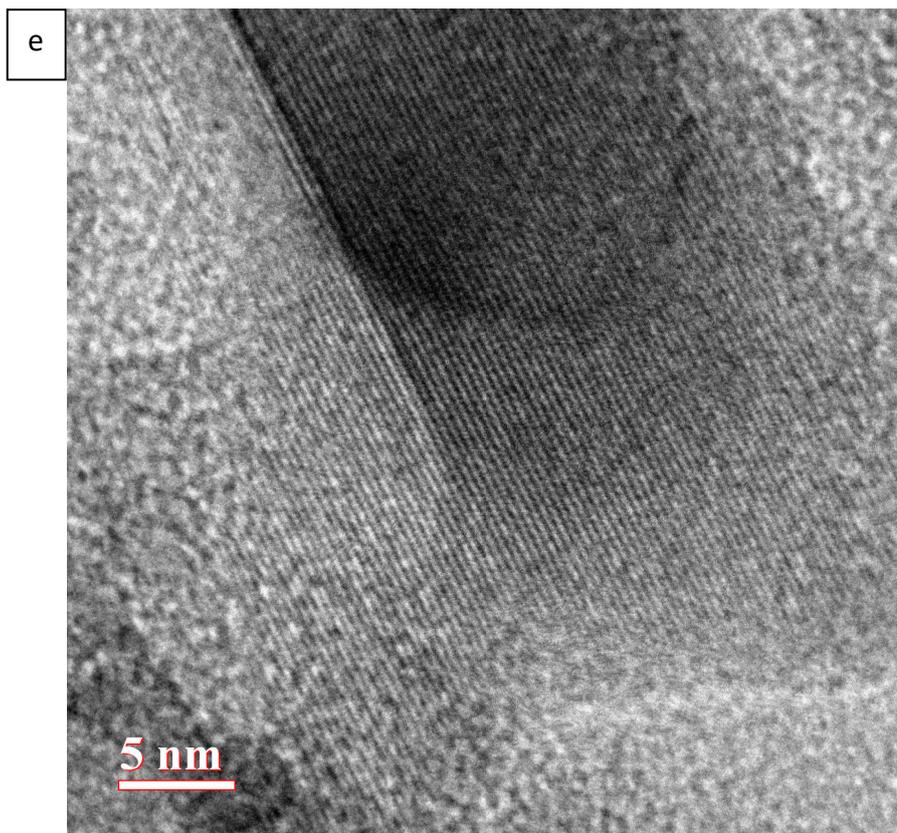


Figure S5 (a - f). TEM images of FeSe nanoparticles

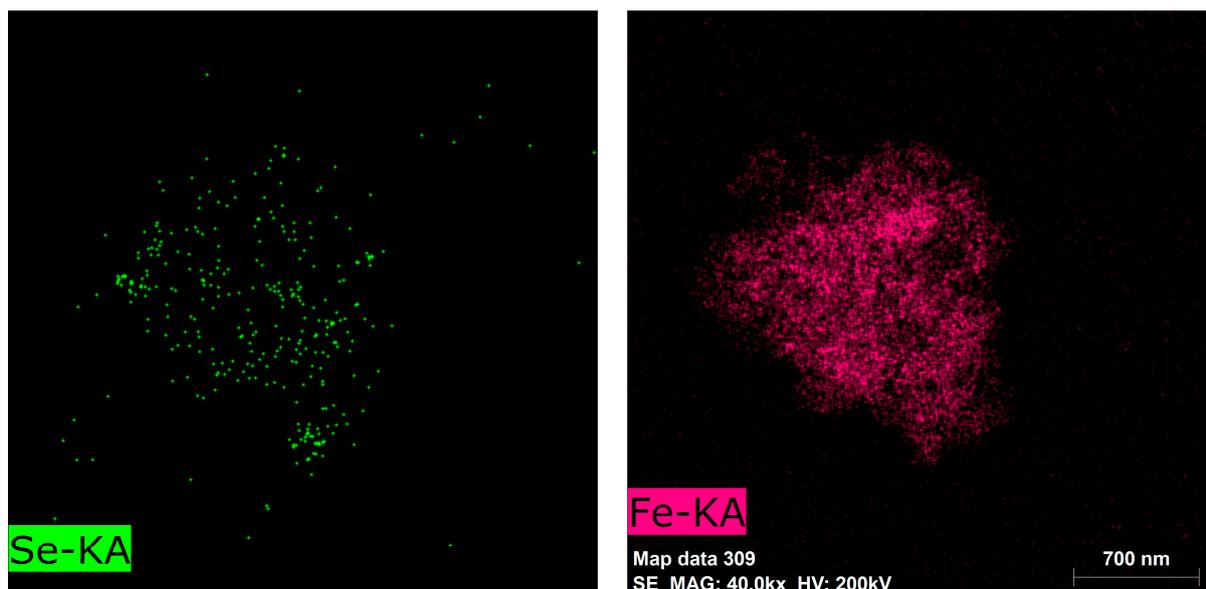


Figure S6. Elemental mapping of FeSe nanoparticles

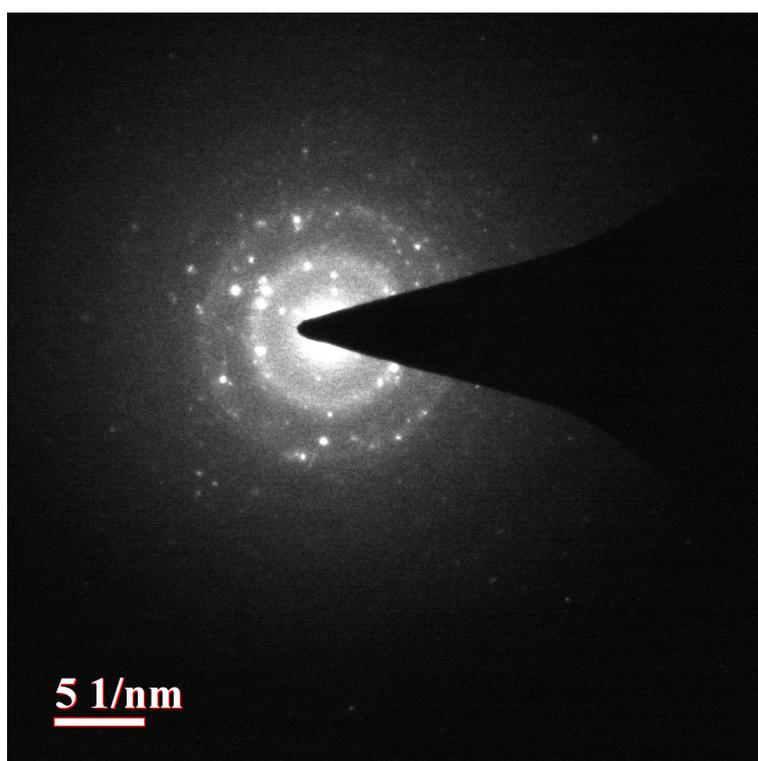


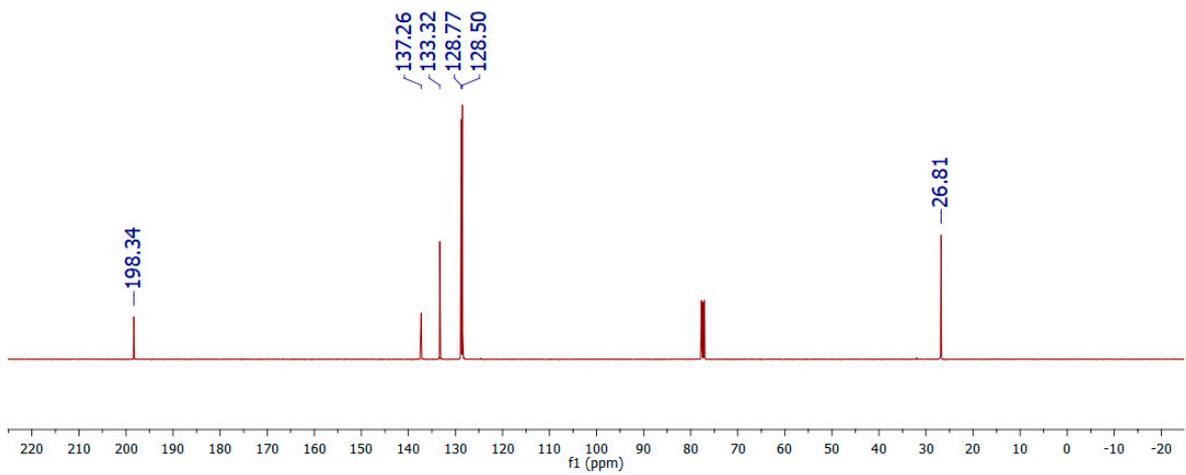
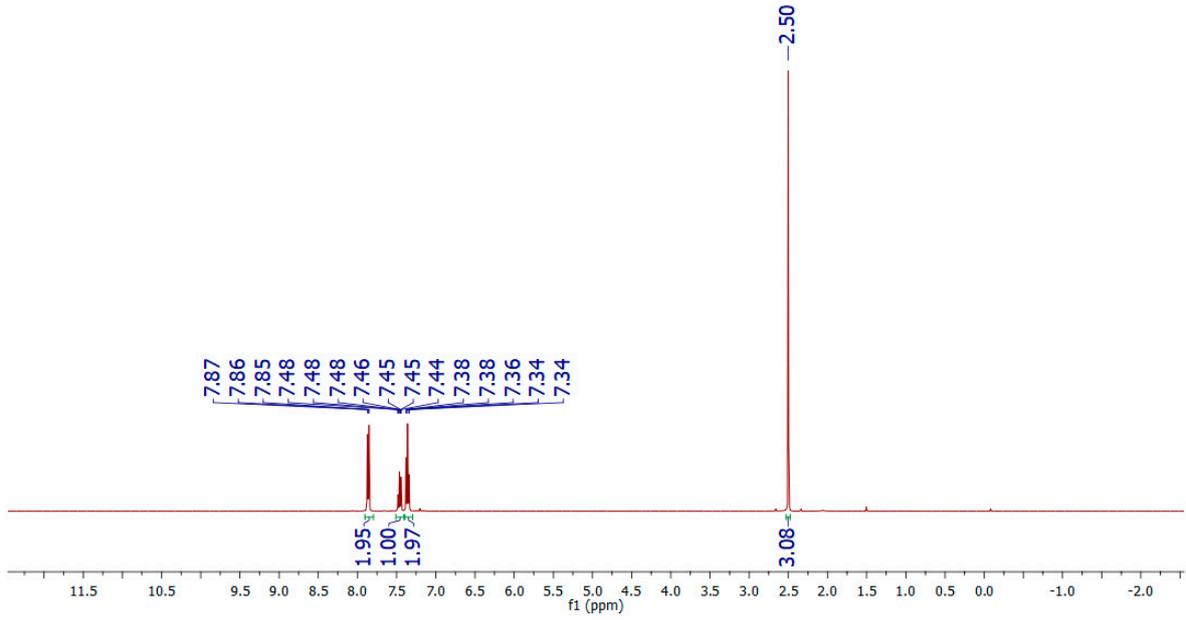
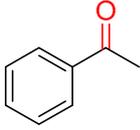
Figure S7. SAED pattern FeSe nanoparticles

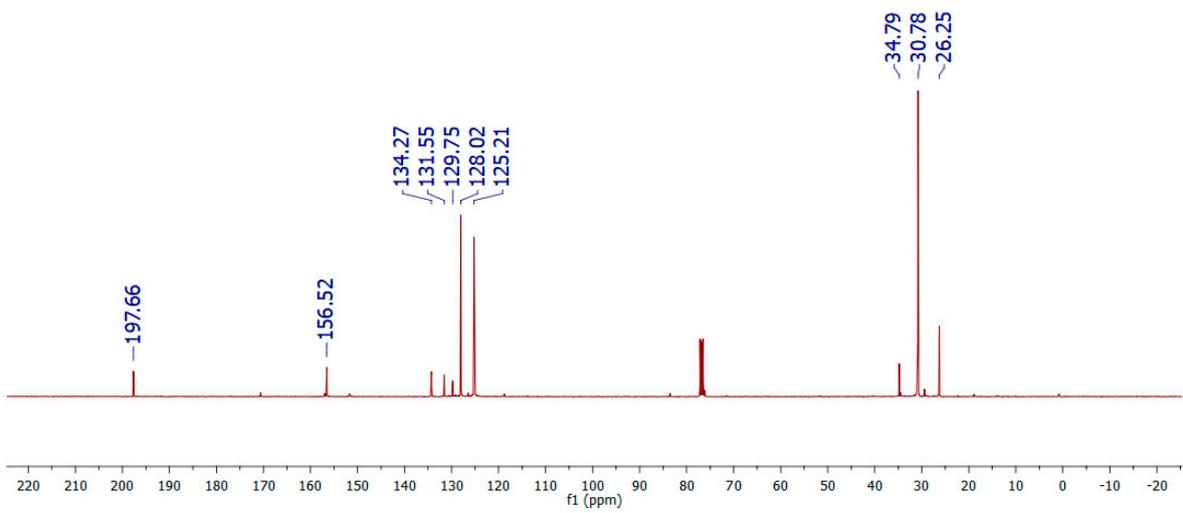
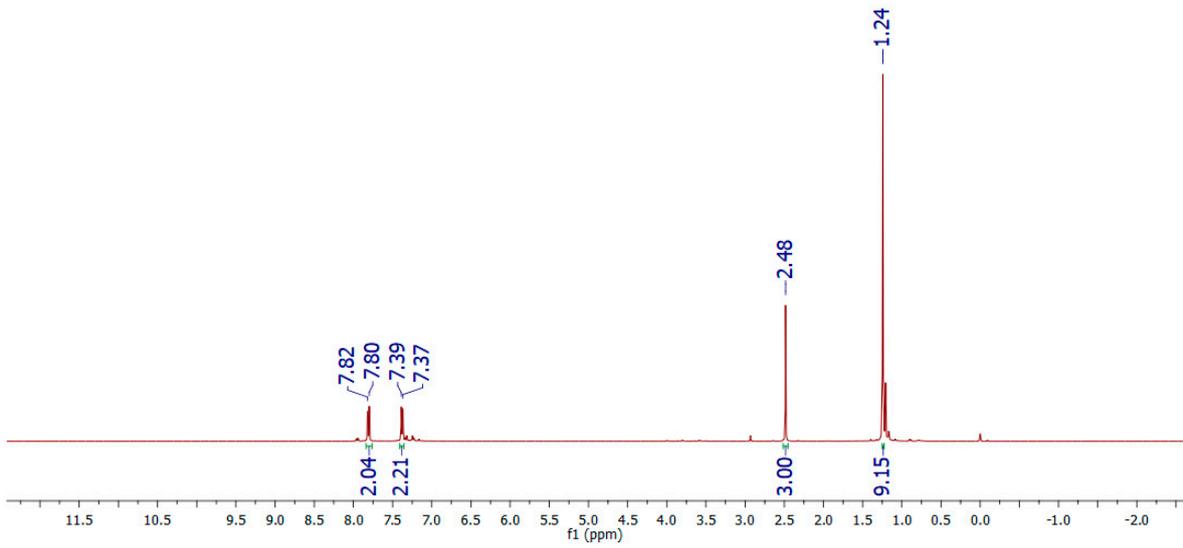
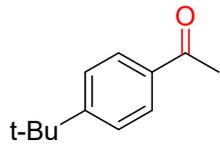
Table S1: Comparison Table

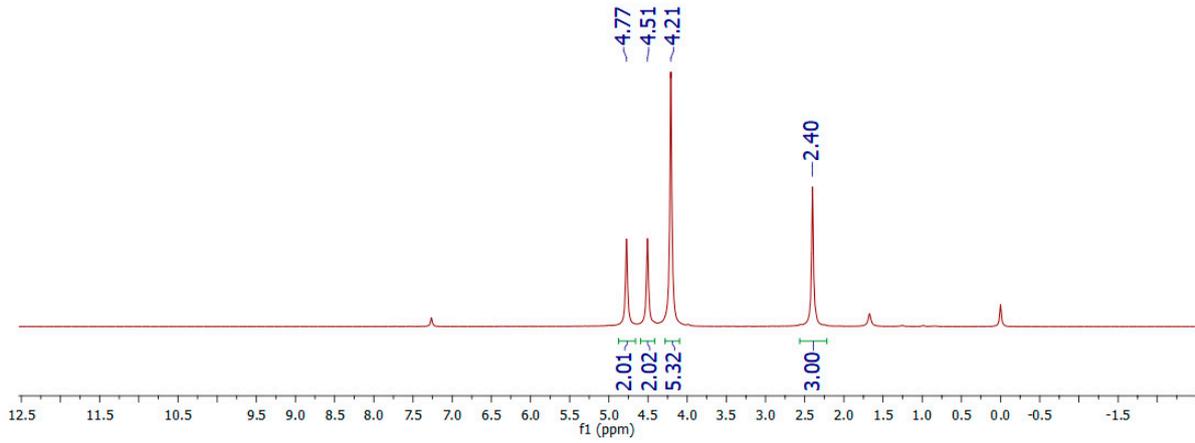
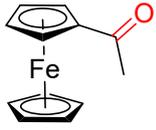
Entry	Metal catalyst	Catalyst (mol%)	Solvent	Temp. (°C)	Time (h)	condition (Δ , hv, MW)	Yield (%)	Ref.
1.	Hg(II)	5	MeCN	rt	12	Δ	100	7
2.	Sn-W	50	cycloocatane	100	0.5 - 24	Δ	91	4
3.	Co(III)	2	MeOH	80	5 – 36	Δ	99	9
4.	Fe(III)	10	DCE	75	67	Δ	96	2
5.	Ag(I)	10	MeOH	75	36 – 48	Δ	94	10
6.	Pt(II)	0.8	THF	60	12	Δ	55:45	11
7.	Rh(III)	4	THF	110	16 – 24	Δ	93	12
8.	Rh(I)	5	THF	110	2	Δ	100	13
9.	Rh(III)	20	MeOH	rt	12	hv	91	14
10.	Ru(I)	1 – 5	IPA	100	12 – 36	Δ	99	15
11.	Ru(II)	5	PEG-400	rt	12 – 48	Δ	89	16
12.	Pd(II)	5	MeOH	50	1 – 51	Δ	99	17
13.	Au(I)	0.1	Dioxane	120	18	Δ	97	18
14.	Au-TiO ₂	1	Dioxane	120	1	mw	97	19
15.	Au(III)	1.6 – 4.5	MeOH	70	1.5 – 4	Δ	98	20
16.	Rh(I)	1.5	MeOH	-5	0.5	hv	85	21
17.	Fe(III)	100	DCM	rt	24	Δ	92	22
18.	Fe(II)	5	DCE	60	1	Δ	92	23
19.	Fe(III)	10	Dioxane	80	20	Δ	96	24
20.	Fe(III)	9	AcOH	95	24	Δ	99	25
21.	Cu(I)	1	HCl	rt	24	hv	91	26
22.	Fe(0)	5	Water	-5	0.42	hv	86	--

In comparison to the previous reports this presented catalyst have shown better activity in many terms. This catalyst required in comparatively low quantity for the presented reaction. This catalyst produces excellent yields with wide functional group compatibility at very low temperature and takes minimum time in comparison to other catalysts. Moreover, this catalysis methodology is time and energy efficient. The presented catalyst behaves as a heterogeneous catalyst in aqueous media. While comparing the reusability of the present catalyst, there were two heterogeneous (Table 4, Entry 2 and Entry 14) and one homogeneous (Table 4, Entry 16) reusable catalyst are reported earlier, this catalyst is an example of heterogeneous reusable catalyst in aqueous media. This will be the first report presenting iron chalcogenide carbonyl complex as a catalyst for hydrations of alkynes, which can produce promising results up to four straight catalytic cycles, it can be easily separated through filtration and no activation is required for the next catalytic cycle. While the previous catalysts had shown activity up to 3, 4 and 7 cycles respectively. (Table 3 Entry 2, 14 and 16)

Most of the iron-based catalysts reported earlier are non-reusable and performs reaction in organic media. While, this catalyst is the first ever example of performing alkyne hydration under neat reaction condition. Moreover, highly stable iron chalcogenide carbonyl complex was used for catalysis.



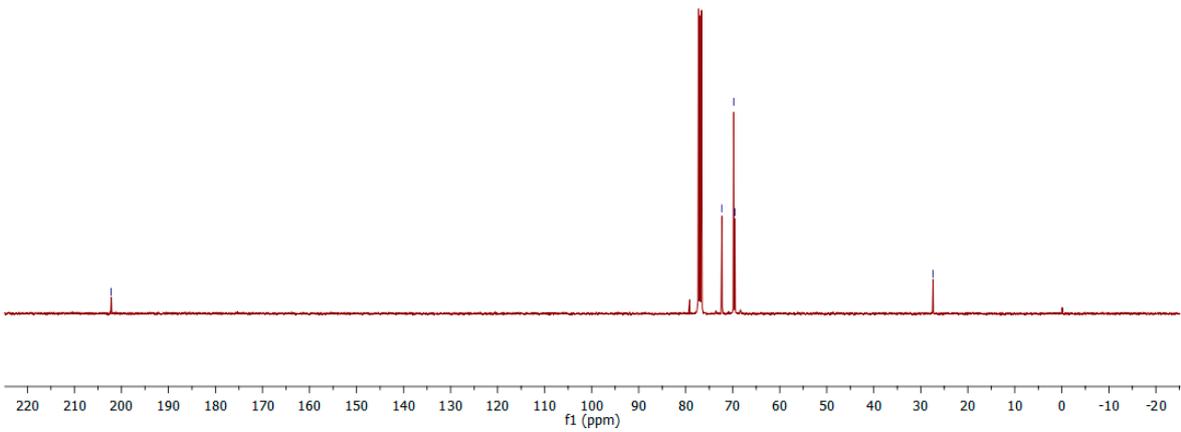


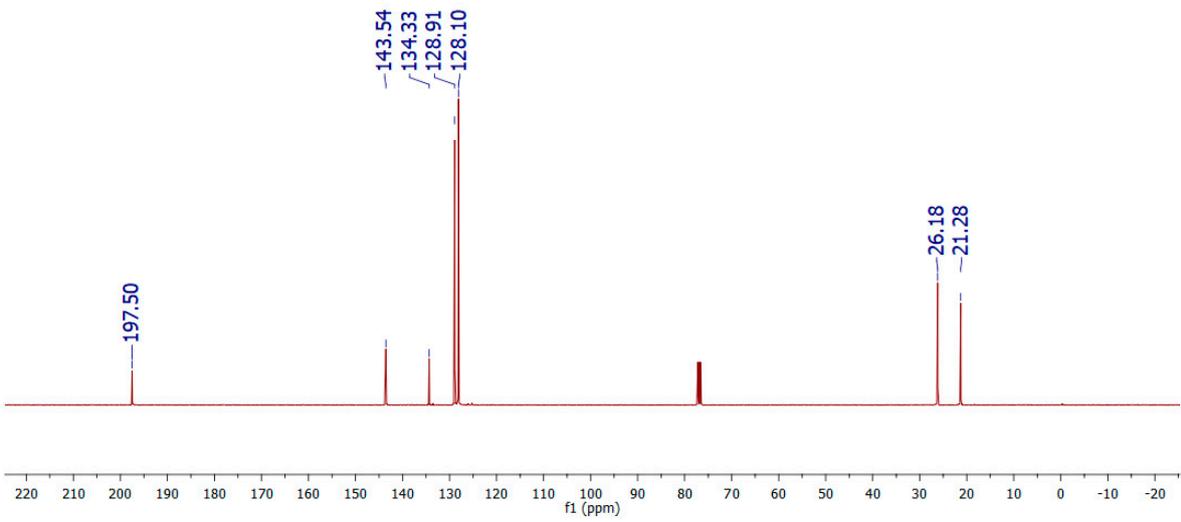
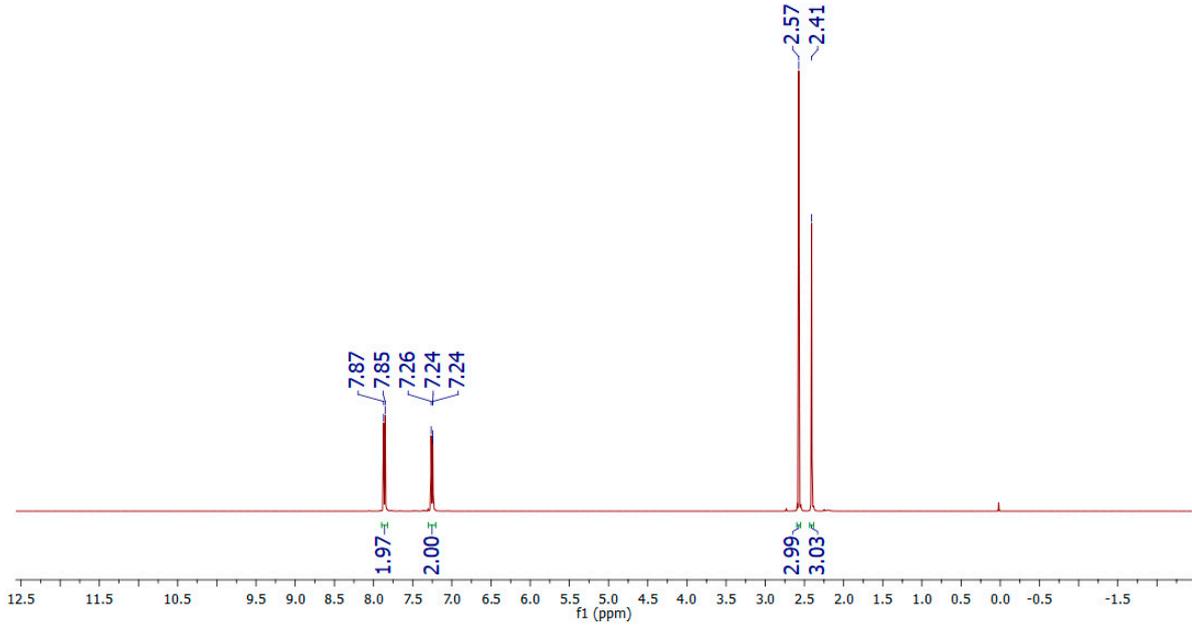
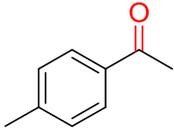


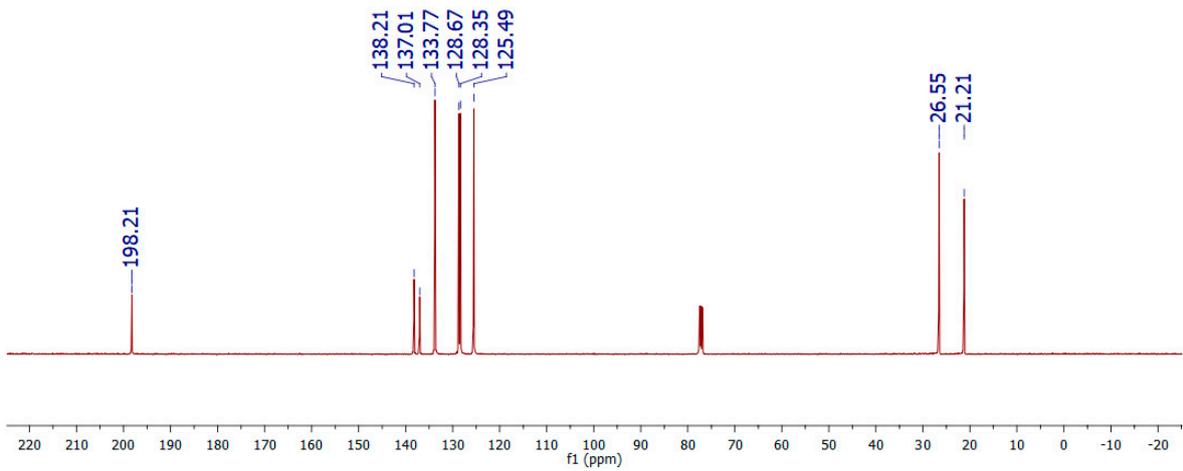
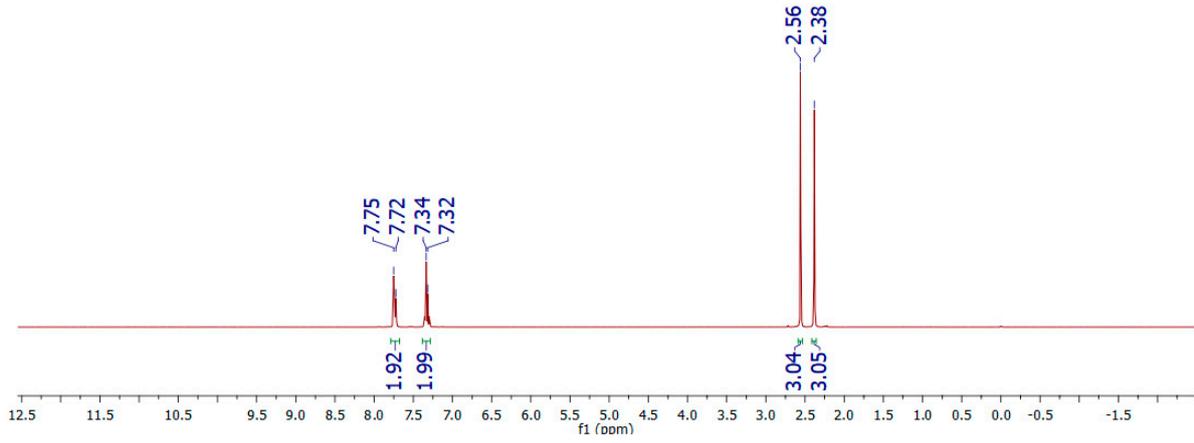
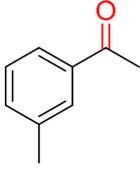
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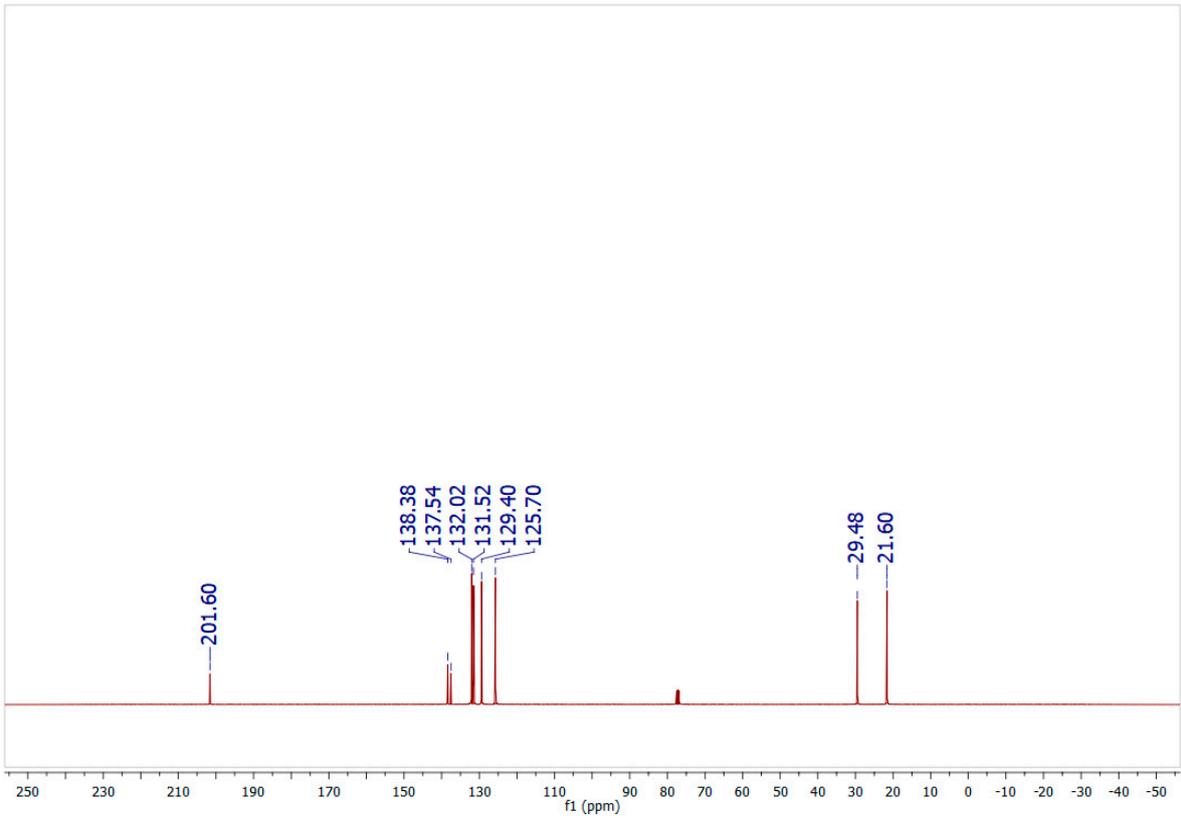
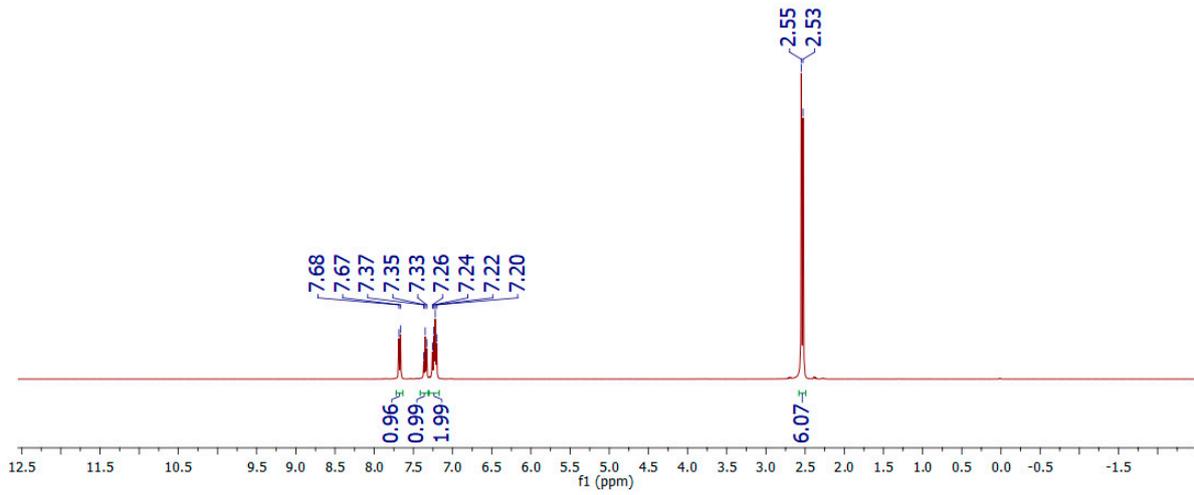
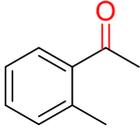
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69.54

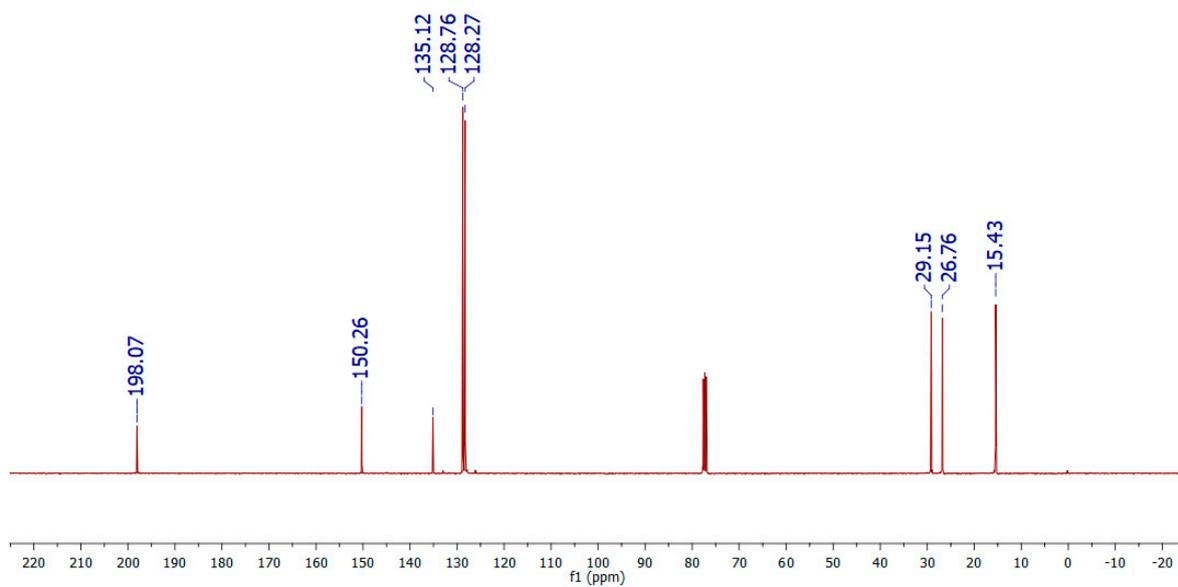
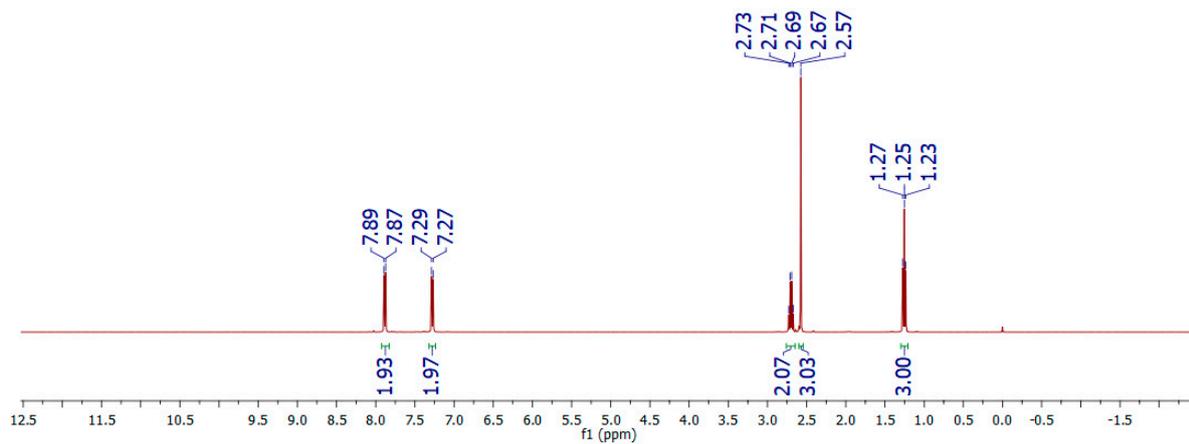
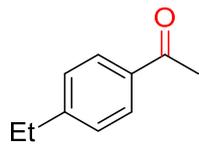
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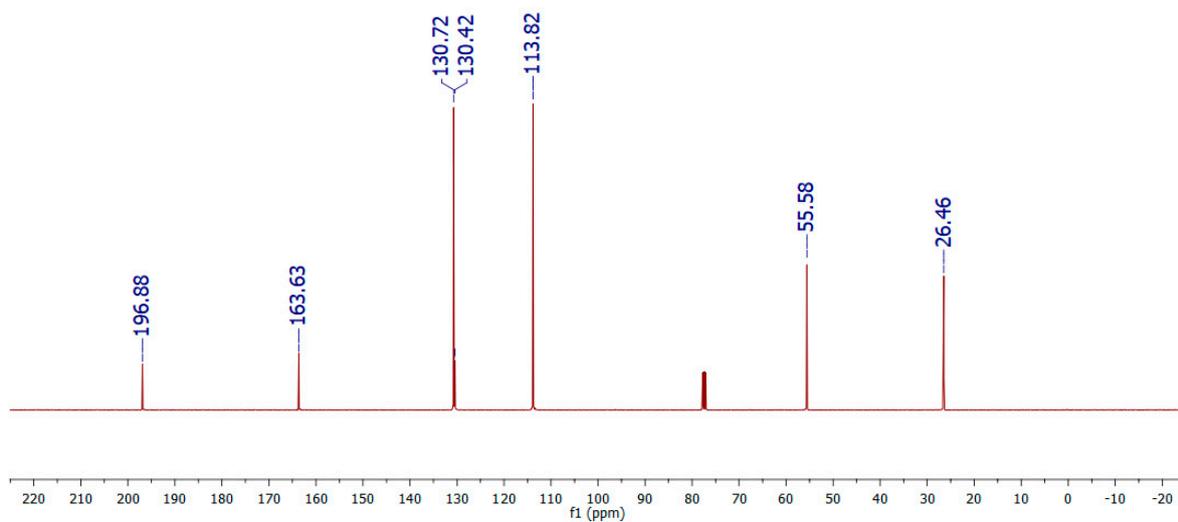
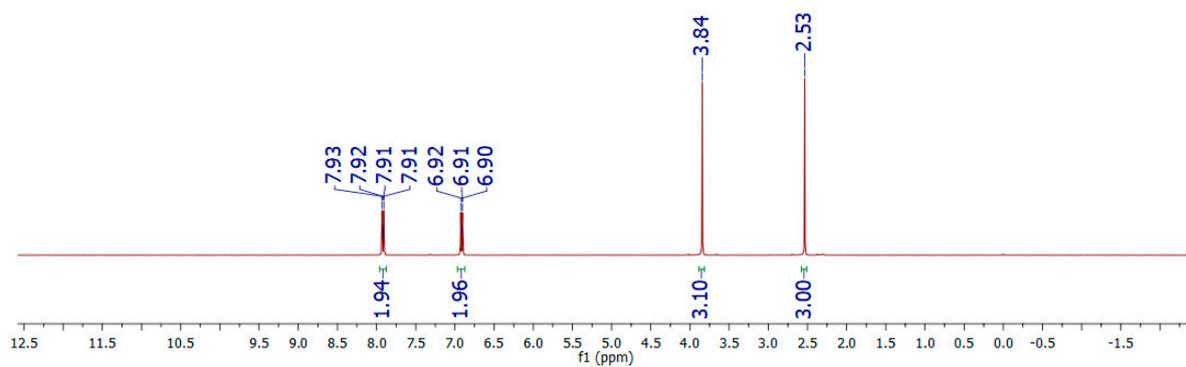
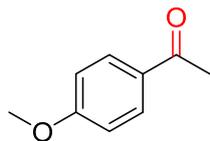


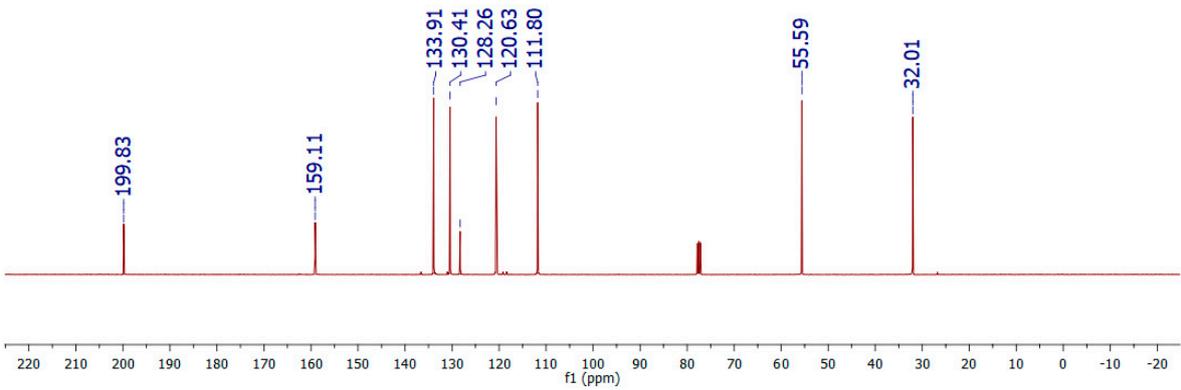
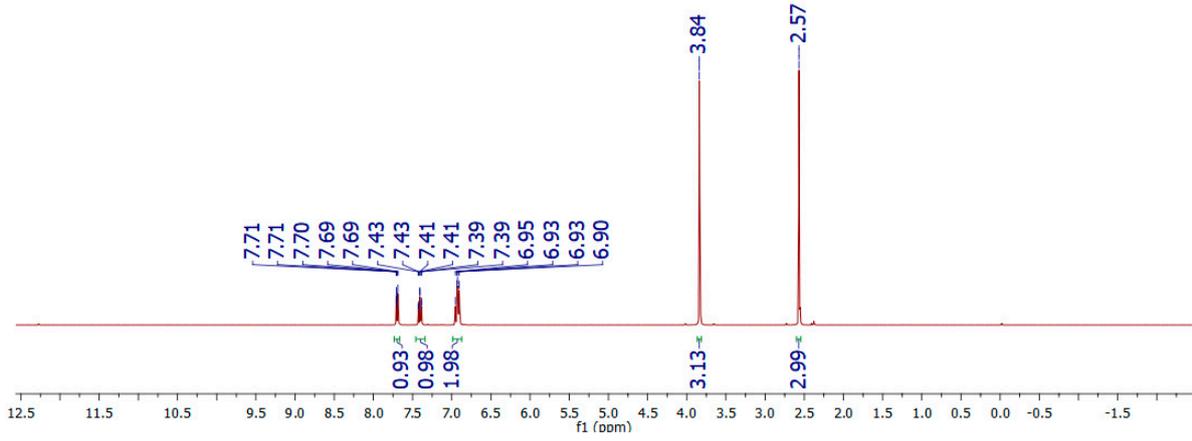
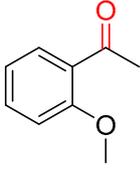


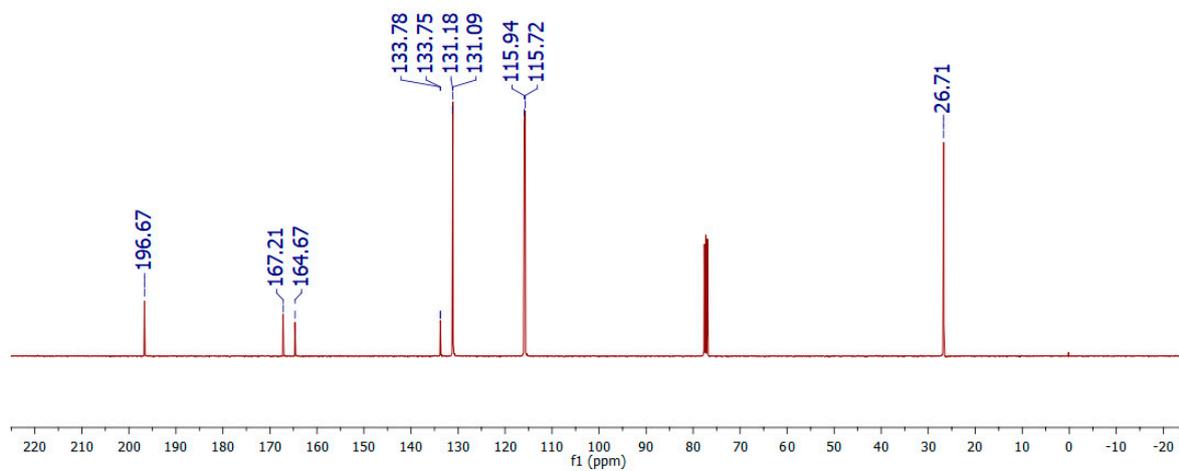
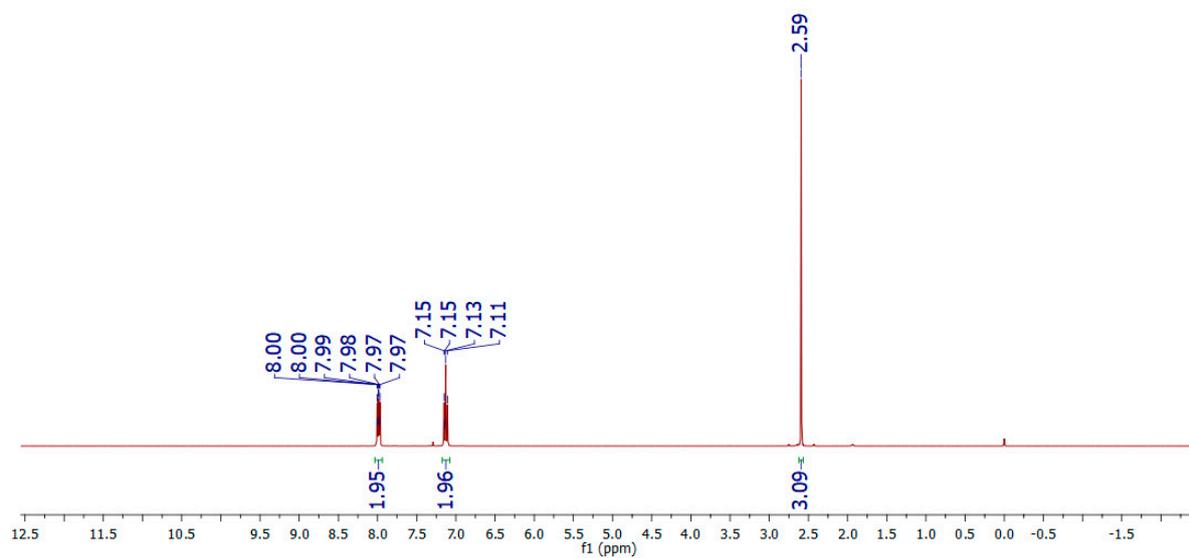
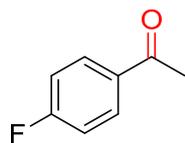


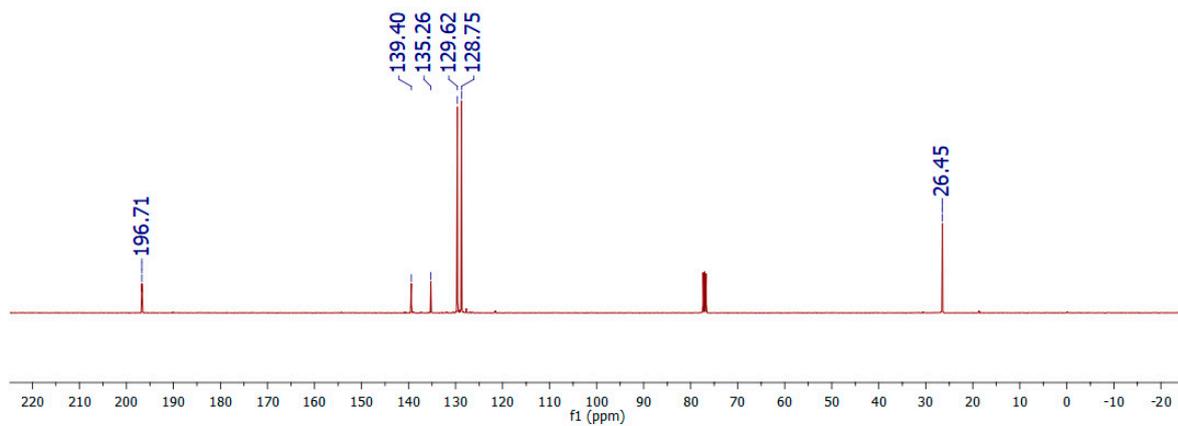
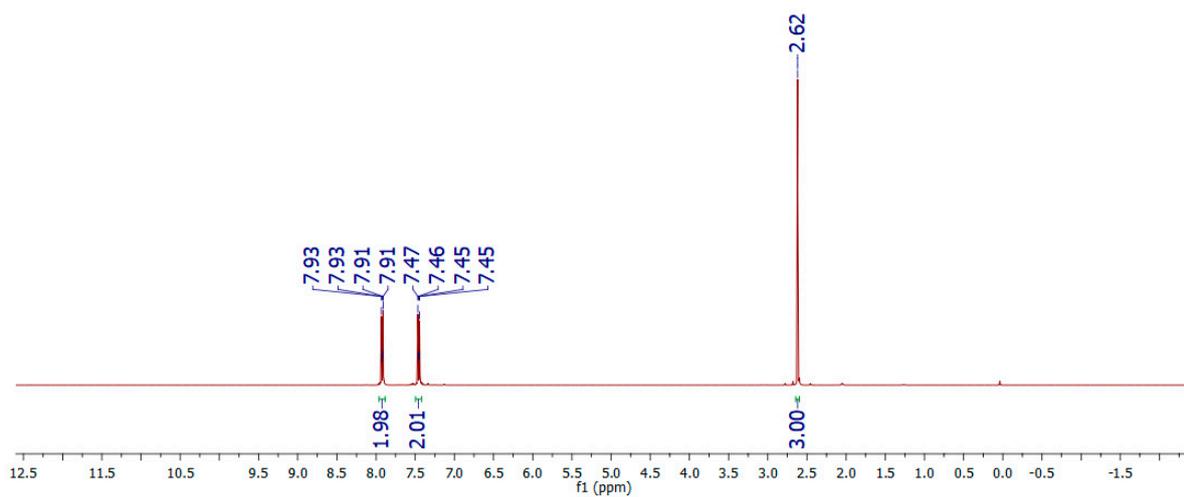
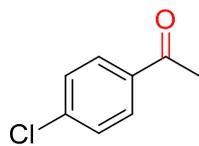


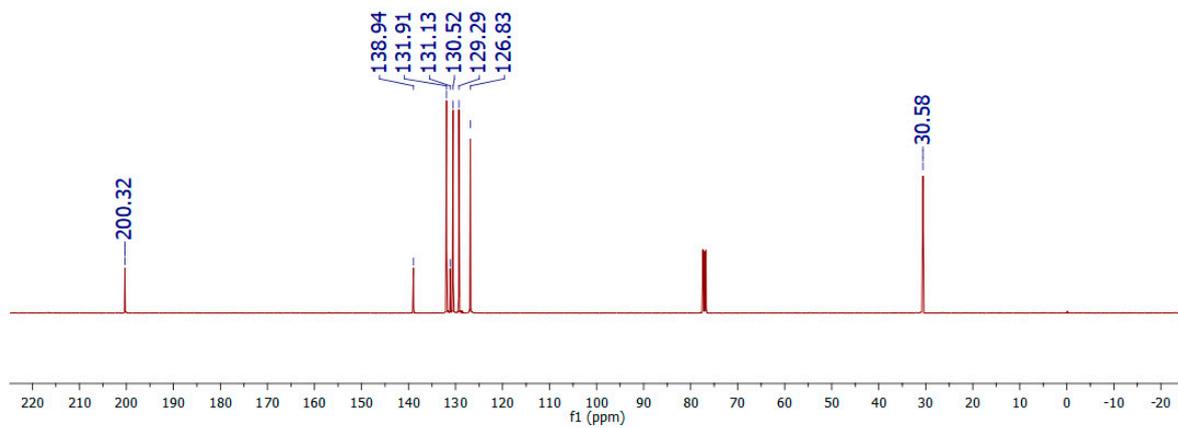
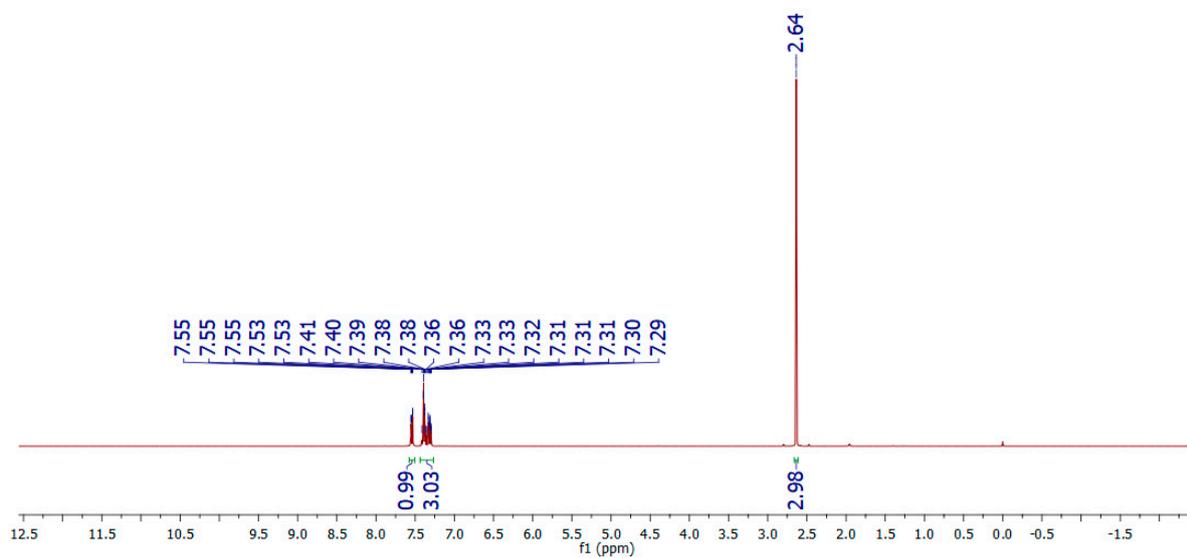
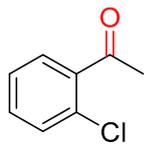


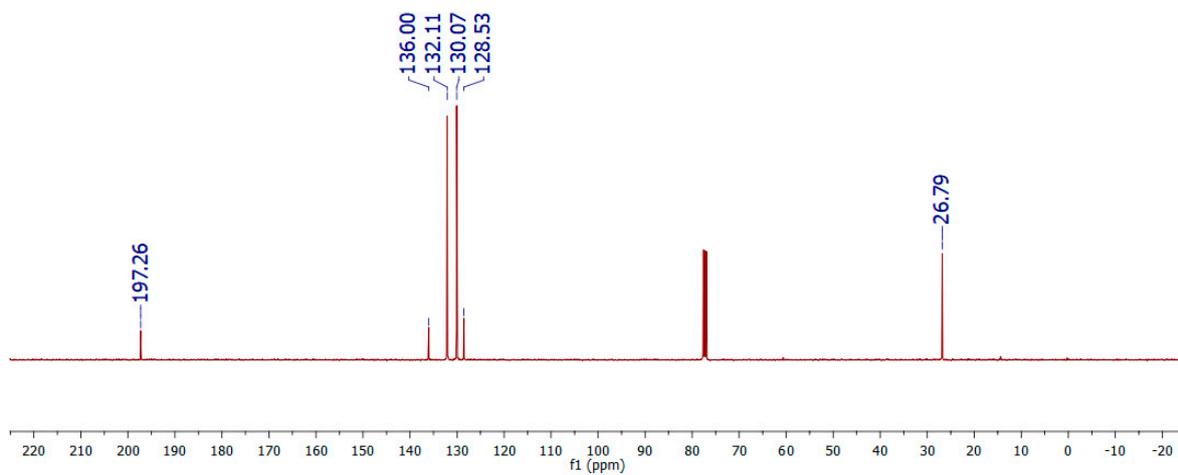
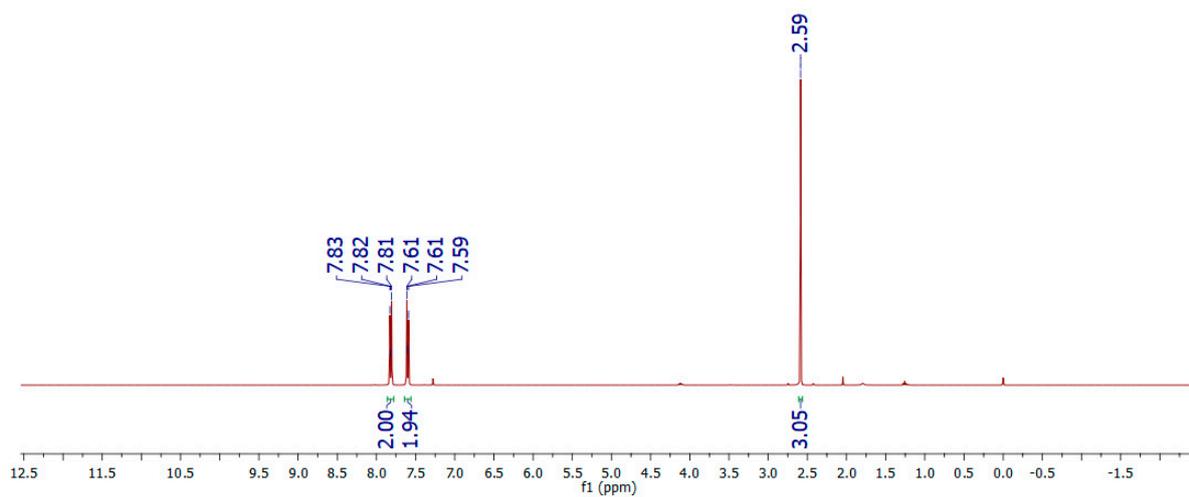
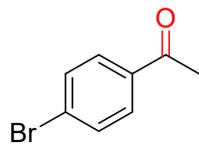


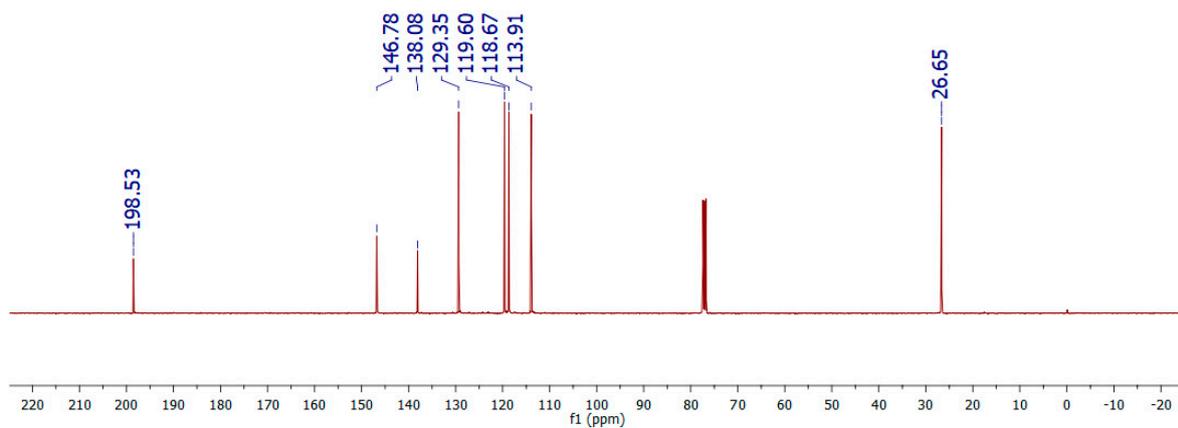
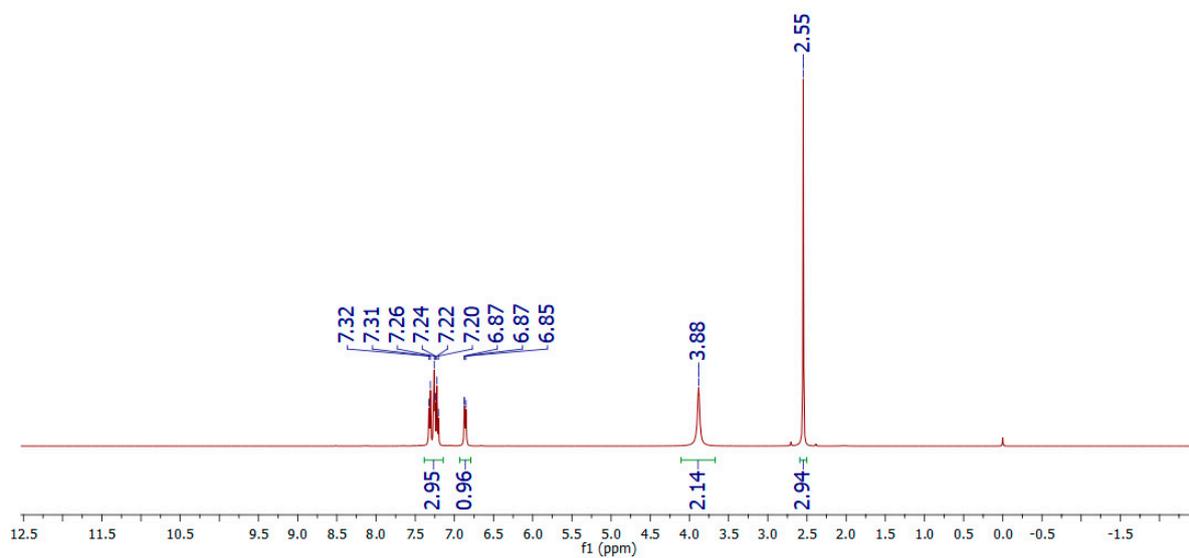
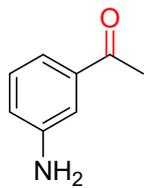


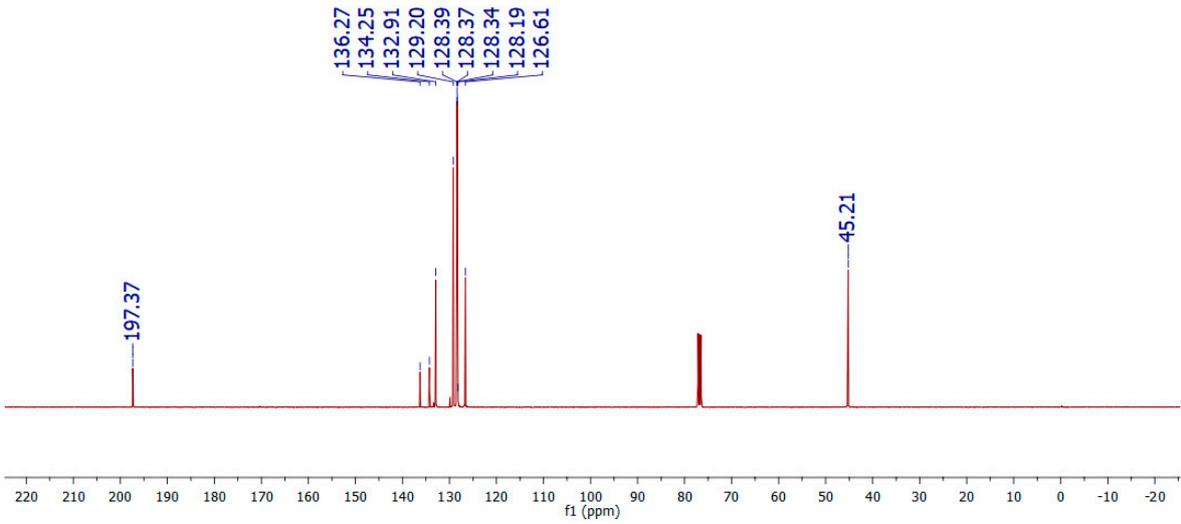
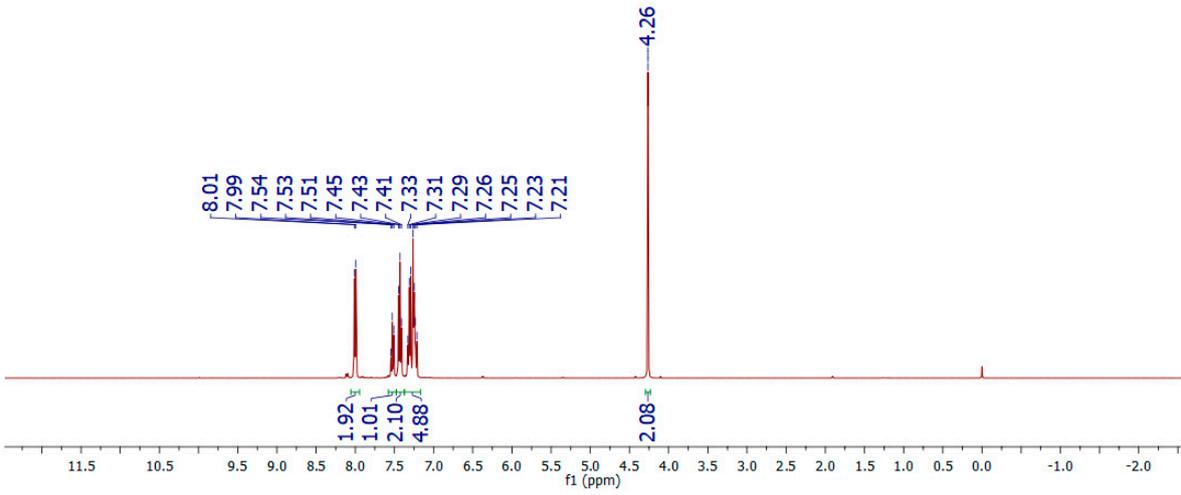
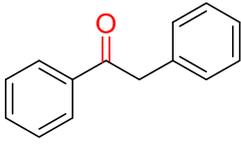


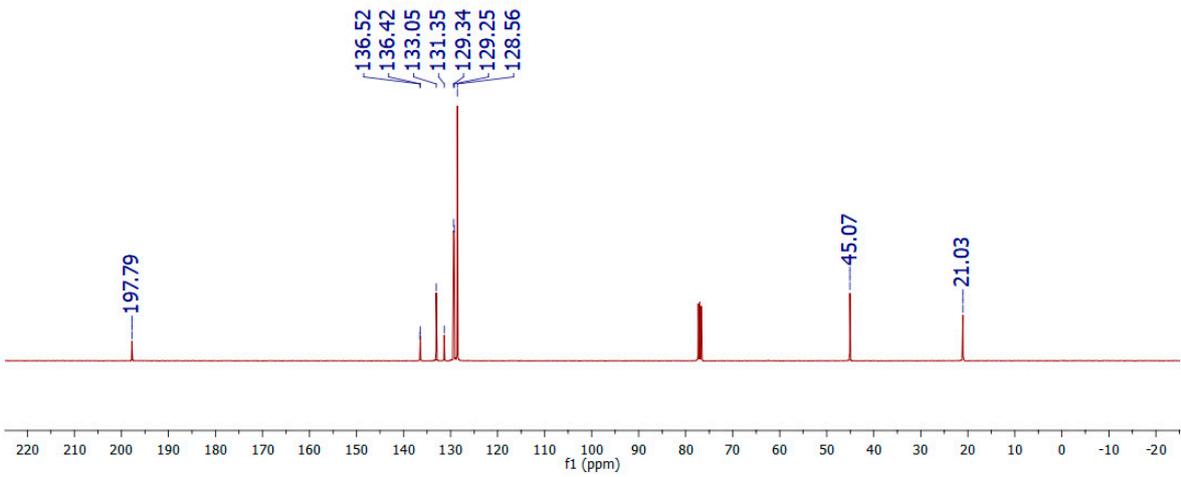
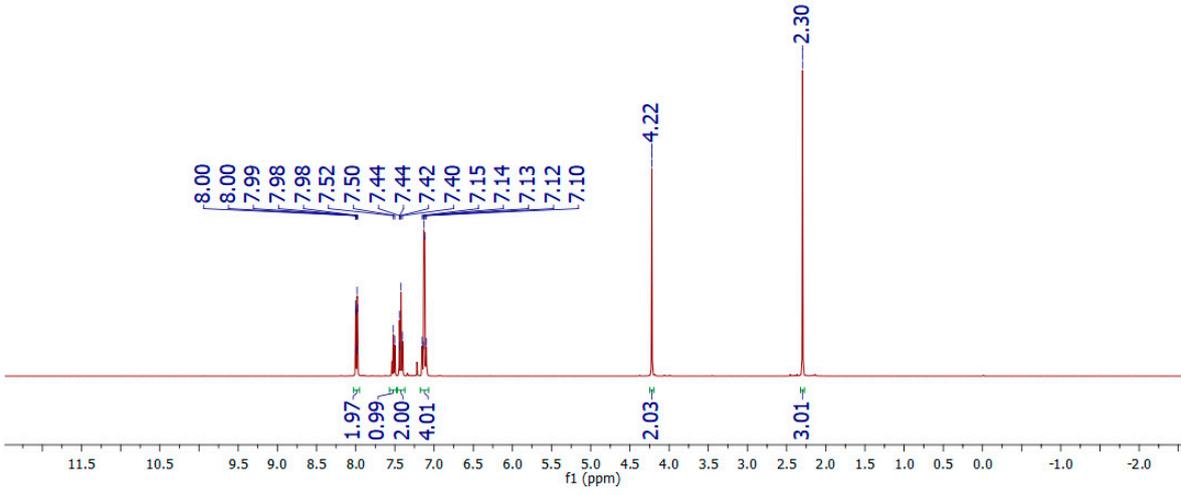
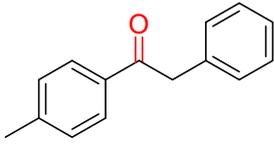


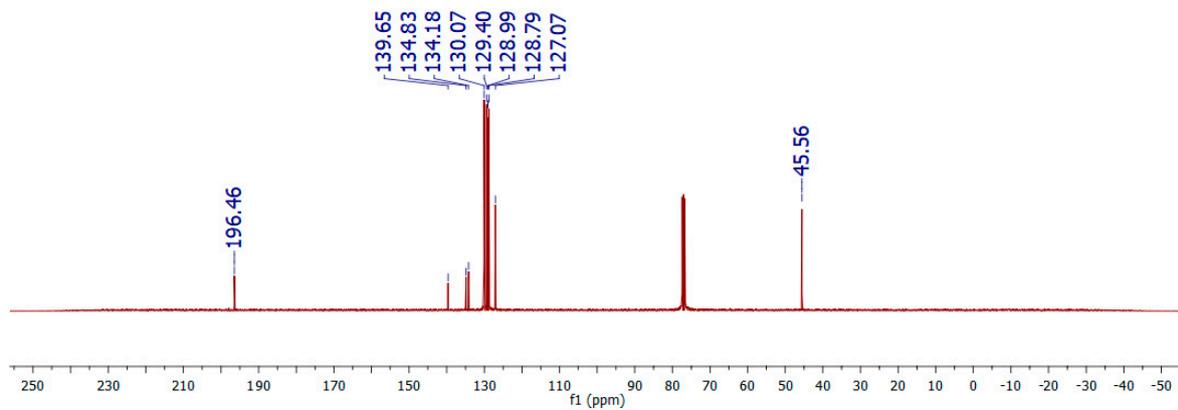
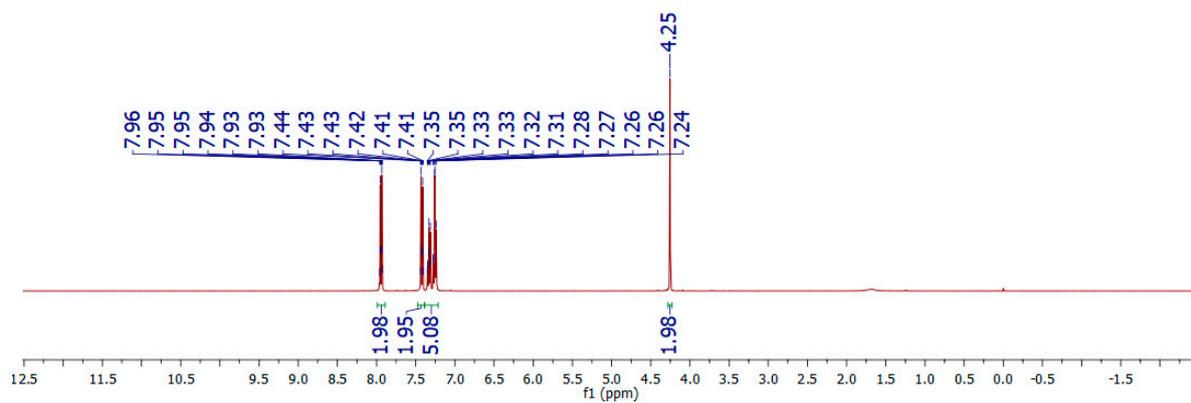
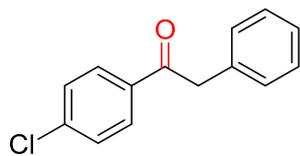












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