Electronic Supplementary Material (ESI) for ChemComm.

Mechanochemical Reduction of Alkyl and Aryl Halides Using Mesoporous Zinc Oxide

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Supporting Information

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1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. Ball milling experiment were performed using 1.5 mL stain-less steel jar with 5 mm stain-less steel ball in Retsch MM400 (Figure S1-S2). Reactions were monitored by thin layer chromatography (TLC) and visualized by a dual short wave UV lamp and stain with potassium permanganate solution or iodine tank. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai, 22040C). ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers (AvanceIII HD-400, Bruker). Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). High resolution mass spectra (HR-MS) were obtained on a Waters® GCT Primier high resolution mass spectrometer. The structures of the m-ZnO were characterized by X-ray diffraction (XRD) employing an X-ray diffractometer (D8 Advance, Bruker Inc.). The morphology of m-ZnO was observed with scanning electron microscope (SEM) (Regulus 8100, Hitachi) and transmission electron microscope (TEM) (Talos F200X G2, FEI). The specific surface areas were carried by the Bruanuer-Emmett-Teller (BET) method with the Micrometrics ASAP 2460 according to N_2 physisorption isotherms at 77 K. The pretreatment was done for 12 h through heat degradation at 573 K under vacuum condition. Gas chromatography-mass spectrometry (GC-MS) were recorded on Agilent 8860-5977C under helium atmosphere.

2. Synthesis of m-ZnO

m-ZnO material was synthesized via a hydrothermal method using F-127 as the template reagent. In a typical experiment, a solution containing 0.025 mol of $Zn(CH_3COO)\cdot 2H_2O$ and 0.5 mol of $CO(NH_2)_2$ was prepared in 150 mL of deionized water at room temperature. Subsequently, F-127 (0.025×10^{-3} mol) was added to the solution with continuous stirring, resulting in a transparent solution. The solution was further stirred at the same temperature for 2 hours. Then, it was transferred to teflon-lined sealed stainless-steel autoclaves and subjected to hydrothermal treatment at 90°C for 24 hours. After natural cooling to room temperature (R.T.), the obtained product was washed several times with deionized water to neutrality and dried at 80°C in ambient air overnight. Finally, the template was removed by calcination in static air at 400°C for 2 hours.

3. PFM characterization of c-ZnO

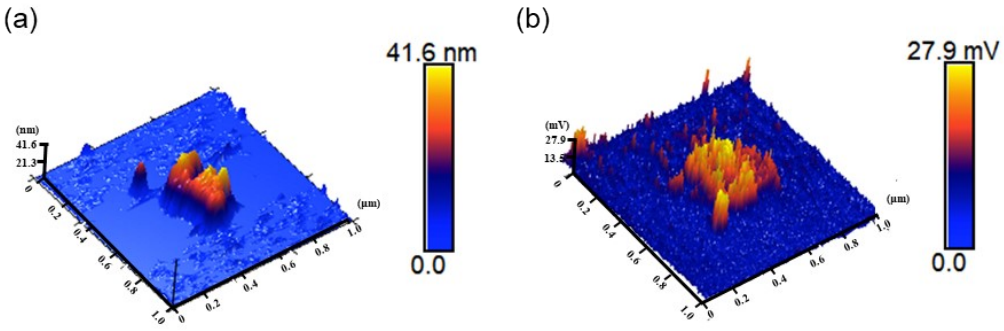


Figure S1 (a) 3D topographic image of c-ZnO. (b) 3D potential distribution diagram of c-ZnO.

4. XRD pattern of m-ZnO nanoparticles.

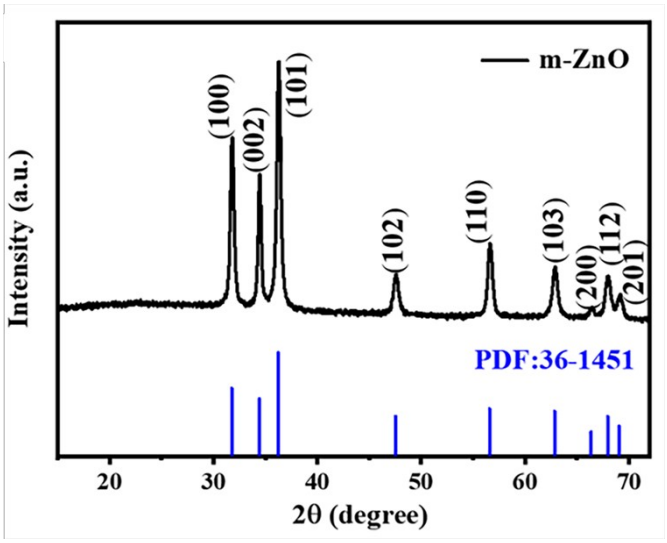


Figure S2. XRD pattern of m-ZnO nanoparticles.

5. BET characterization of m-ZnO before reaction

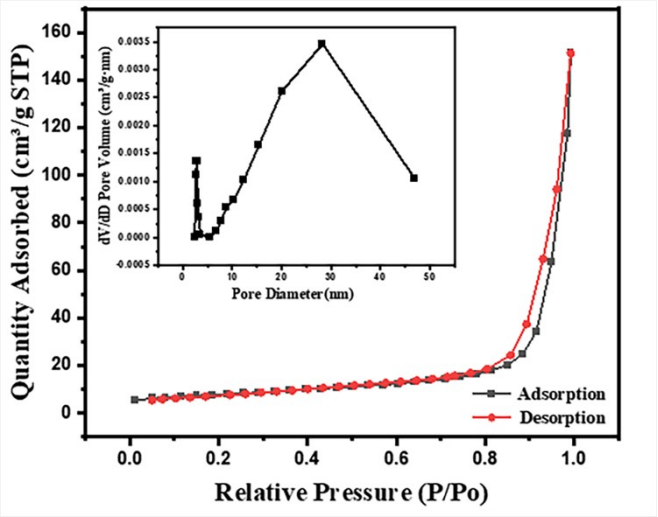


Figure S3 N_2 isotherm and pore-size distribution of m-ZnO before reaction.

6. Instruments and experimental steps

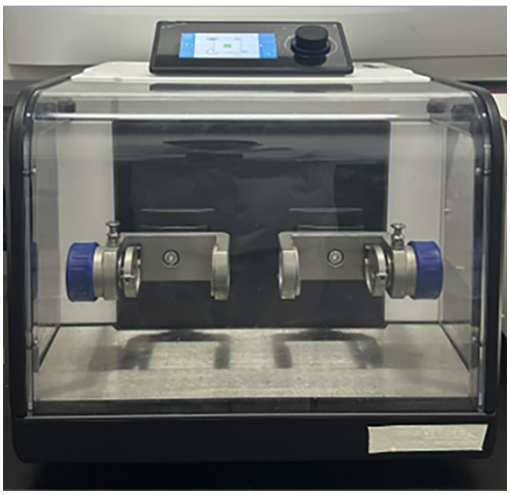


Figure S4. Retsch MM400 used in this study.

Figure S5. Stain-less and ZrO_2 jars and balls used in this study.

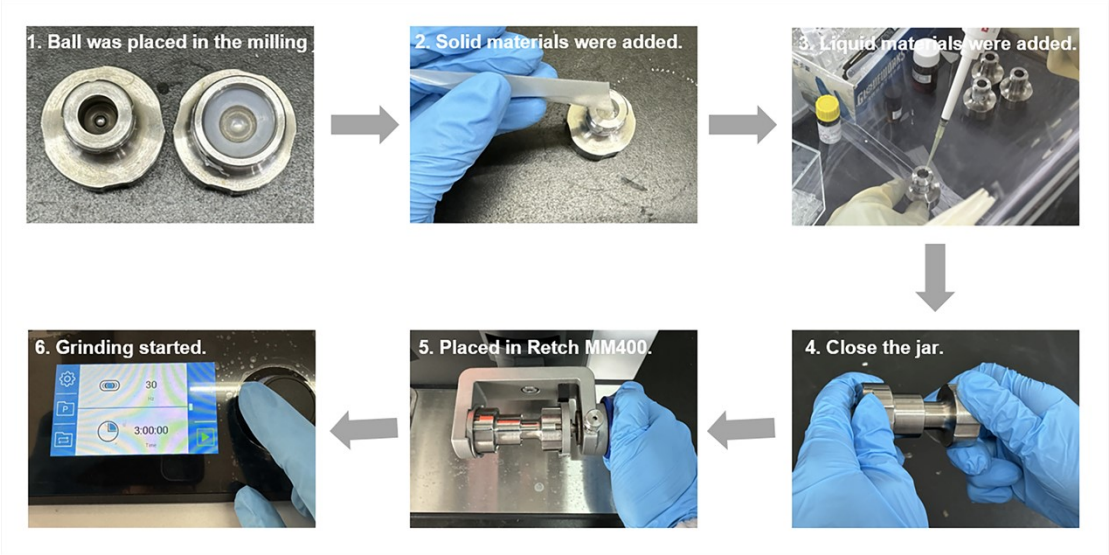


Figure S6. Procedures and experimental setup for mechanoredox reactions.

7. Gram-scale synthesis

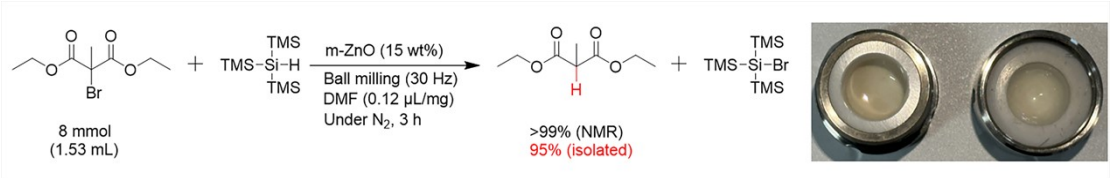
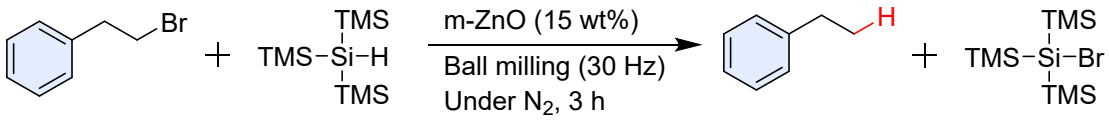


Figure S7. Exploration of a gram-scale synthesis.

8. Reaction kinetics of alkyl bromide



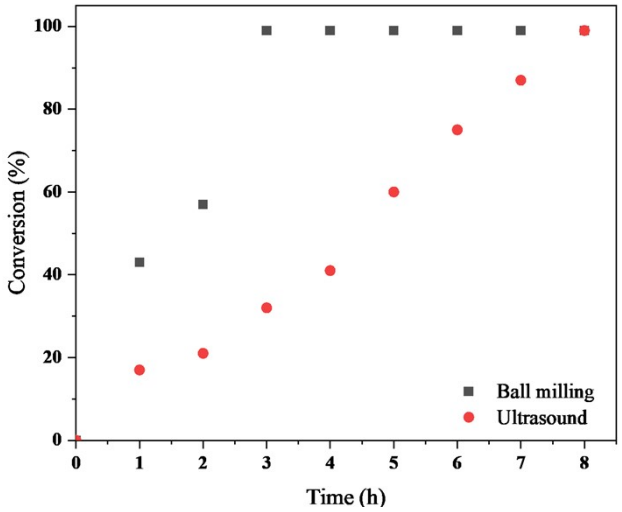


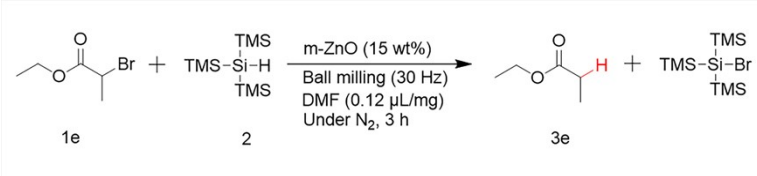
Figure S8. The comparison of reaction kinetics under ball milling and ultrasound conditions (25 °C, 40 kHz, 110 W).

Table S1. The summary of reaction times required for the complete reaction under different conditions.

Entry	Method	Conditions	Reaction time (h)	Yield (%)[b]	Ref.
1	Solid-state	Ball milling	3	99	This work
2[a]	Solution-state	Ultrasound	8	99	This work
3	Solution-state	Visible light	10	99	21

[a]Reaction condition: Phenethyl bromide (0.4 mmol), TTMSS (0.8 mmol) and m-ZnO (15 wt%) were combined in DMF (0.5 mL) and under ultrasound for 8 hours (25 °C, 40 kHz, 110 W). [b]Yields were determined by ^{1}H NMR.

9. Characterization of recycled mechanoredox catalyst



Entry	Number of run	Yield (%)
1	1st run	>99
2	2nd run	>95
3	3rd run	>95
4	4th run	>95
5	5th run	>95

Figure S9. m-ZnO recycling experiments.

10.BET characterization of m-ZnO after reaction

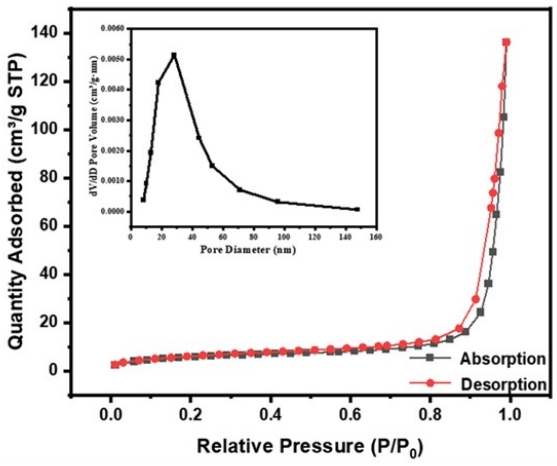


Figure S10. N_2 isotherm and pore-size distribution of m-ZnO after reaction.

11.SEM and TEM characterization of m-ZnO before and after reaction

The m-ZnO sample after ball milling was prepared by using Retsch MM 400 (1.5 mL jar, 5 mm ball, 30 Hz, 3 h). Additional images were shown in Figure S5 and Figure S6.

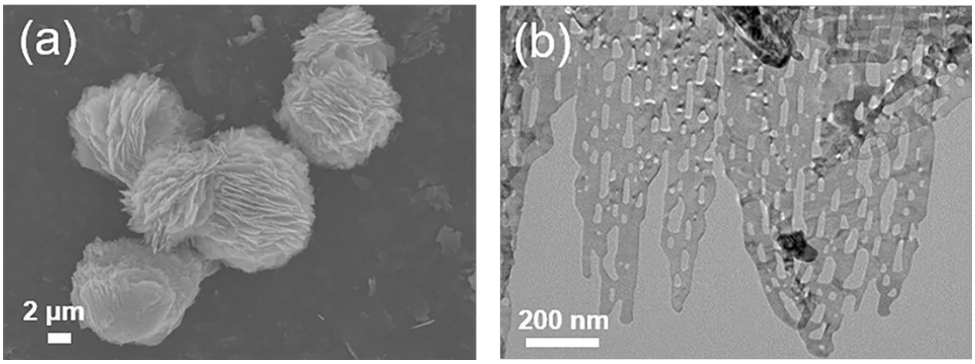


Figure S11. (a) SEM and (b) TEM image of m-ZnO before ball milling.

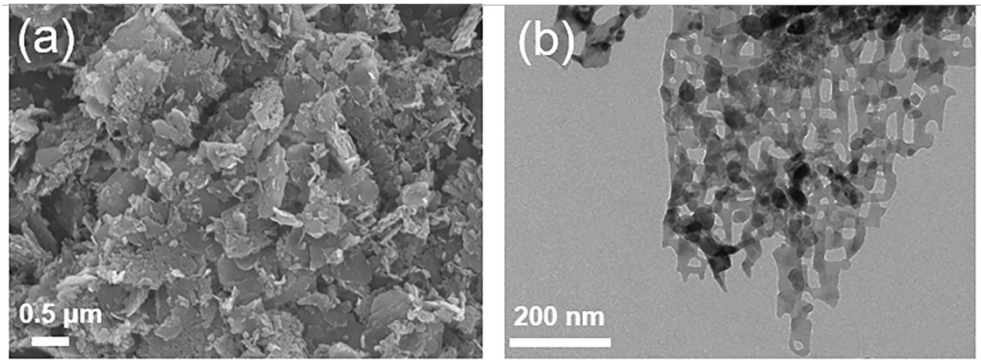


Figure S12. (a) SEM and (b) TEM image of m-ZnO after ball milling (30 Hz, 3 h).

12.XRD characterization of m-ZnO before and after reaction

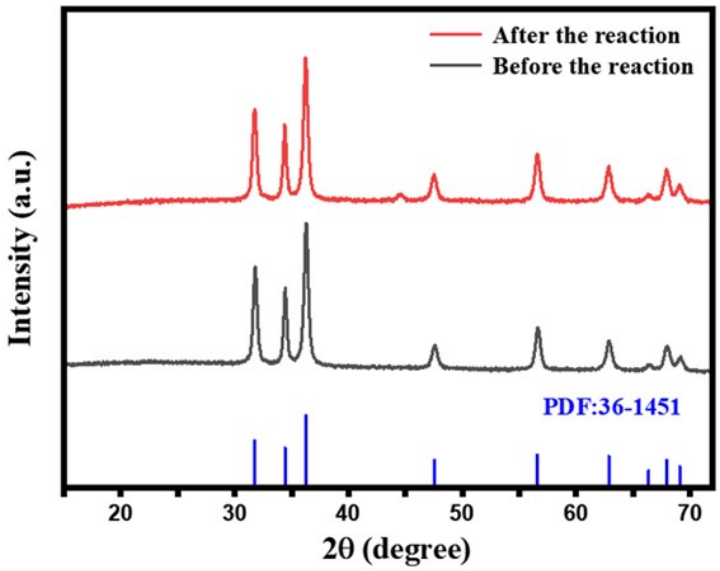


Figure S13. XRD patterns of m-ZnO before and after the reaction.

13.Reaction temperature confirmed by thermography

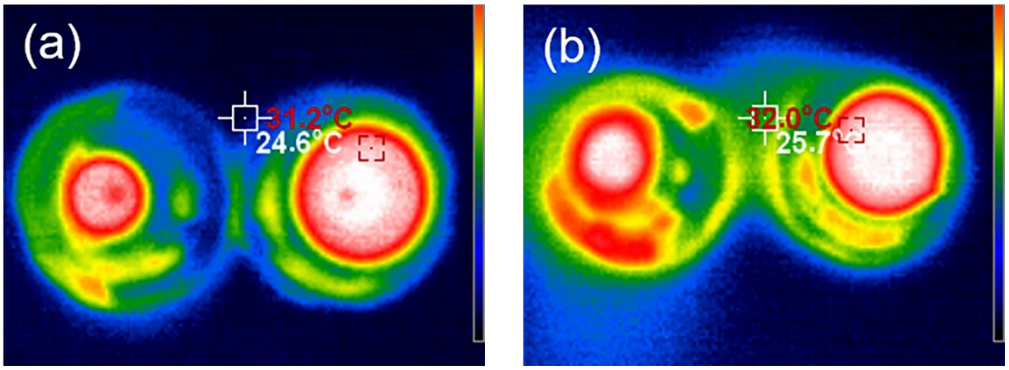
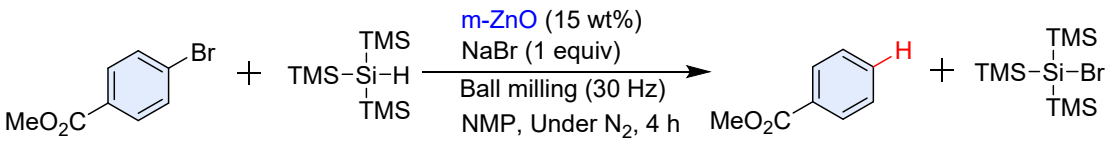


Figure S14. Temperature inside the milling jar (a) after reaction 90 min and (b) 180 min confirmed by thermography.

14.Optimization of reaction conditions

Table S2. Impact of catalyst loading.



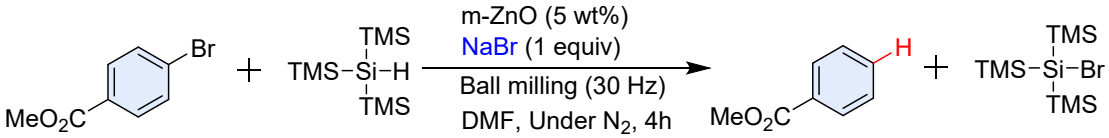
1j 2 3j

Entry	Variation from initial conditions[a]	Yield(%)[b]
1	None	51
2	5 wt% catalyst loading	83
3	1 wt% catalyst loading	24

[a]Initial conditions: 1j (0.4 mmol), TTMSS (0.8 mmol), NaBr (0.4 mmol), NMP as LAG (1 μL/mg) and m-ZnO (15 wt%) were added in a stain-less steel milling jar (1.5 mL) with a stain-

less steel ball (diameter, 5 mm) and react in N_2 atmosphere for 4 h. [b]Yields were determined by ^{1}H NMR.

Table S3. Impact of bromide ions.

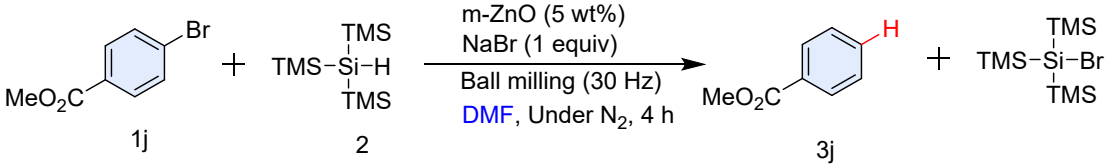


1j 2 3j

Entry	Variation from initial conditions[a]	Yield(%)[b]
1	No additive	<10
2	NaBr as additive	31
3	KBr as additive	22
4	LiBr as additive	<10

[a]Initial conditions: 1j (0.4 mmol), TTMSS (0.8 mmol), bromide salts (0.4 mmol), DMF as LAG (0.12 μL/mg) and m-ZnO (5 wt%) were added in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (diameter, 5 mm) and react in N_2 atmosphere for 3h.[b] Yields were determined by ^{1}H NMR.

Table S4. Evaluation the effects of LAG.

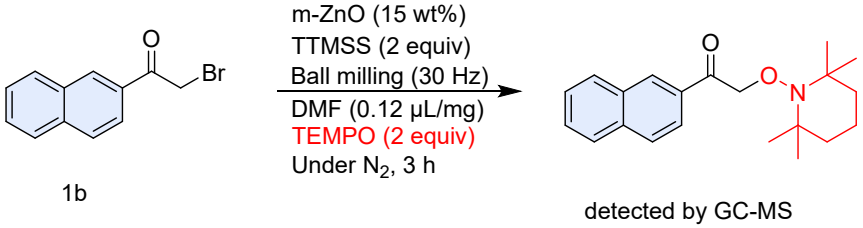


1j 2 3j

Entry	Variation from initial conditions[a]	Yield (%)[b]
1	None	28
2	MeCN	Trace
3	DMA	37
4	NMP	83
5	1,4-Dioxane	7
6	THF	Trace
7	DMSO	11

[a]Initial conditions: 1j (0.4 mmol), TTMSS (0.8 mmol), NaBr (0.4 mmol), DMF as LAG (1 μL/mg) and m-ZnO (5 wt%) were added in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (diameter, 5 mm) and react in N_2 atmosphere for 4 h. [b]Yields were determined by ^{1}H NMR.

15.Radical trapping experiment



2-Bromo-2′-acetonaphthone (99.6 mg, 0.4 mmol), DMF as LAG (0.12 μl/mg), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 125 mg, 0.8 mmol) and m-ZnO (63.1 mg, 15 wt%) were placed in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (5.0 mm, diameter) in glove box. Then TTMSS (2, 248.66 μL, 0.8 mmol) was added to the mixture. After the jar was closed with the purge with inert gas, it was placed in the ball mill (Retsch MM 400, 3 h, 30 Hz) for reaction. The adduct of aryl radical with TEMPO (3) were detected by GC-MS (Figure S11).

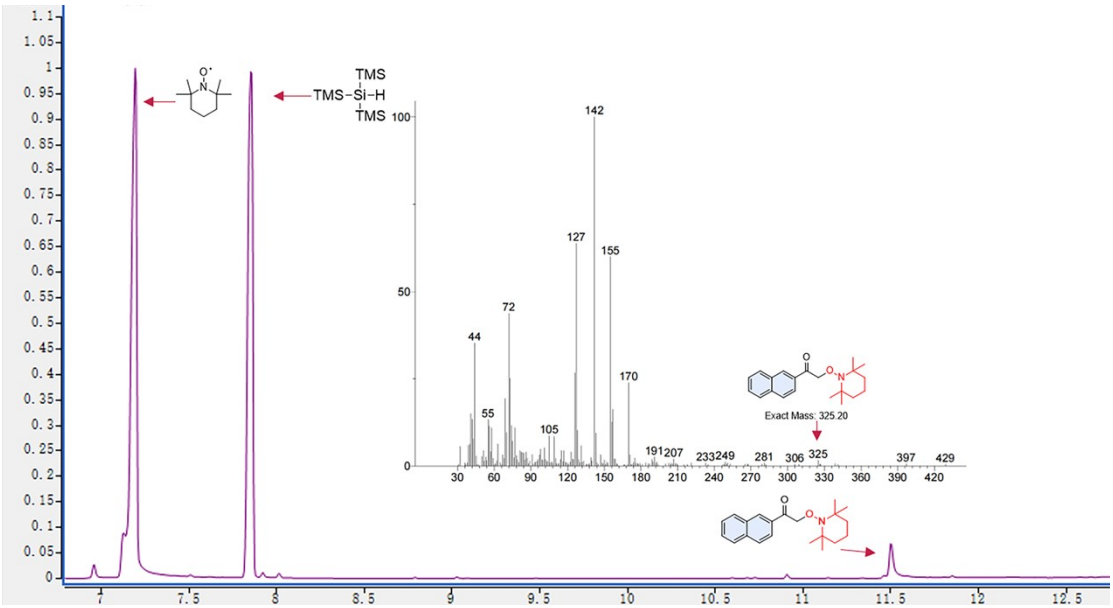
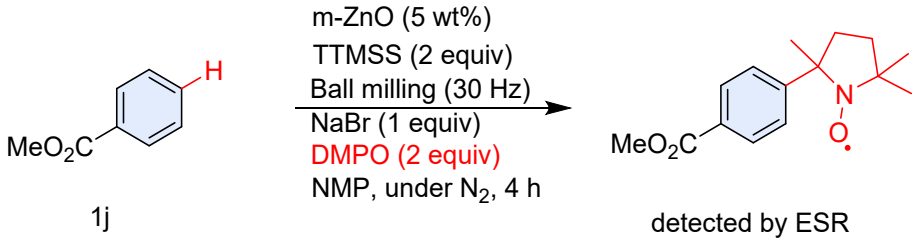


Figure S15. GC-MS spectra of radical trapping experiment with TEMPO.



Methyl 4-bromobenzoate (1j, 0.4 mmol), ZnO nanoparticles (32.1 mg, 5 wt%), NMP as LAG (1 µl/mg), 5,5 dimethyl-1-pyrroline-N-oxide (DMPO, 0.8mmol) and 0.4 mmol NaBr were placed in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (5.0 mm, diameter) in glove box. Then TTMSS (**2**, 0.8 mmol 248.66 µL) was added to the mixture. After the jar was closed with the purge with inert gas, it was placed in the ball mill (Retsch MM 400, 4 h, 30 Hz) for reaction. The adduct of aryl radical with DMPO were detected by ESR.

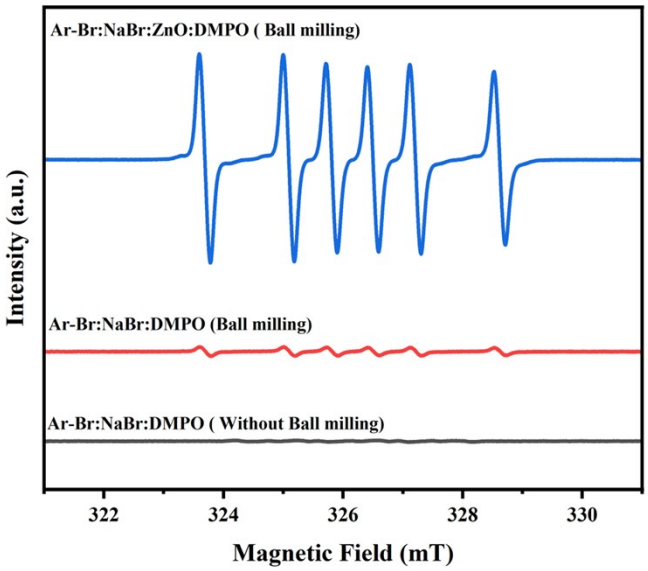
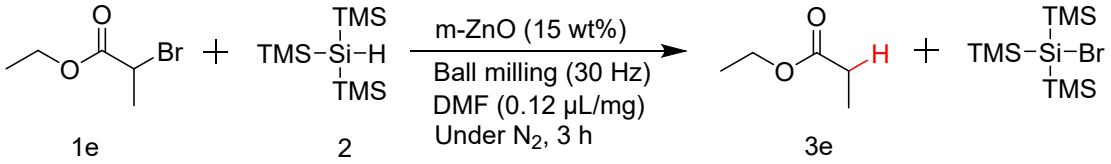


Figure S16. ESR spectra of alkyl radicals trapped by DMPO.

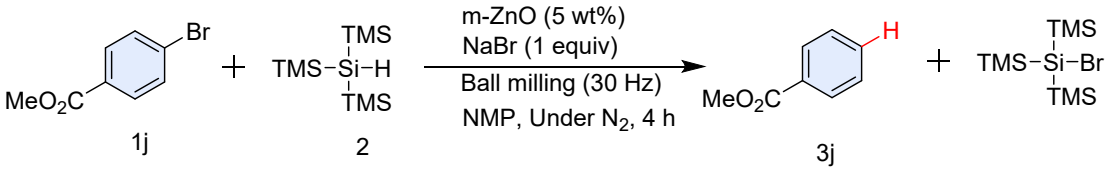
16.General procedure for mechanoredox reaction

General procedure A:



Ethyl 2-bromopropionate (**1e**, 0.40 mmol), DMF as LAG (0.12 µl/mg) and ZnO nanoparticles (45.6 mg, 15 wt%) were placed in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (5.0 mm, diameter) in glove box. Then TTMSS (**2**, 0.8 mmol 248.66 µL) was added to the mixture. After the jar was closed with the purge with inert gas, it was placed in the ball mill (Retsch MM 400, 3 h, 30 Hz) for reaction. After reaction, 5 g of KF on Alumina (37 wt%) were added and stirred for 30 min. The crude material was purified by flash chromatography (SiO_2, hexane/ethyl acetate) to give the arylation product **3e**.

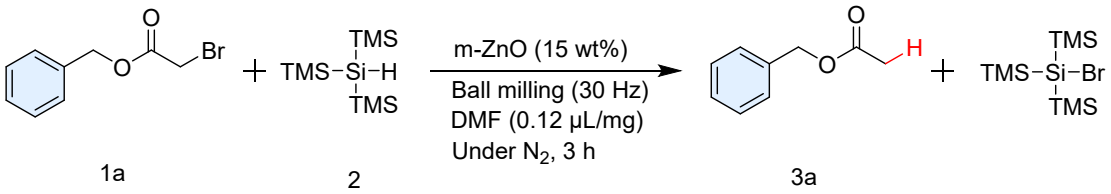
General procedure B:



Methyl 4-bromobenzoate (1j, 0.4 mmol), ZnO nanoparticles (32.1 mg, 5 wt%), NMP as LAG (1 µl/mg) and 0.4 mmol NaBr were placed in a stain-less steel milling jar (1.5 mL) with a stain-less steel ball (5.0 mm, diameter) in glove box. Then TTMSS (**2**, 0.8 mmol 248.66 µL) was added to the mixture. After the jar was closed with the purge with inert gas, it was placed in the ball mill (Retsch MM 400, 4 h, 30 Hz) for reaction. After reaction, 5 g of KF on Alumina (37 wt%) were added and stirred for 30 min. The crude material was purified by flash chromatography (SiO_2, hexane/ethyl acetate) to give the arylation product **3j**.

17.Characterization of hydrodebromination products

Benzyl acetate (3a)

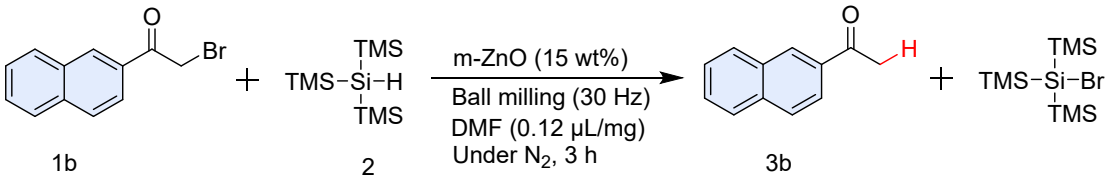


1a 2 3a

According to general procedure A, benzyl 2-bromoacetate (65.4 µL, 0.4 mmol) afforded benzyl acetate in 94% yield (53.6 µL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 – 7.33 (m, 4H), 7.36 – 7.25 (m, 1H), 5.10 (s, J = 0.6 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 170.83, 136.31, 128.54, 128.44, 128.22, 66.35, 20.88. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_{10}O_2$, 150.0681; found, 150.0684.

2-Acetonaphthone (3b)

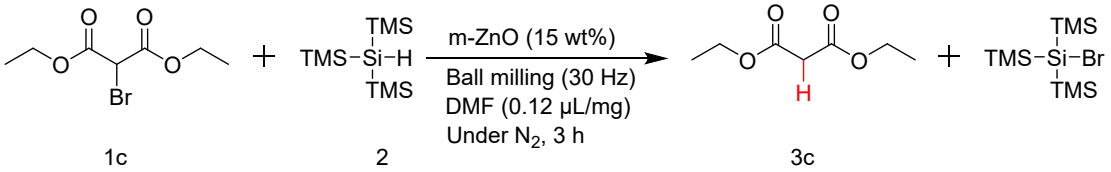


1b 2 3b

According to general procedure A, 2-Bromo-2′-acetonaphthone (99.6 mg, 0.4 mmol) afforded 2-Acetonaphthone in 72% yield (49.5 mg, 0.28 mmol) as white fine crystal powder by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.40 (dd, J = 2.8, 1.3 Hz, 1H), 8.21 (dt, J = 7.8, 1.7 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.74 (dd, J = 8.5, 1.7 Hz, 1H), 7.65 – 7.52 (m, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 197.55, 135.59, 134.63, 133.51, 130.64, 130.21, 128.20, 128.08, 127.28, 126.75, 124.79, 26.61. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{10}O$, 170.0732; found, 170.0729.

Diethyl malonate (3c)

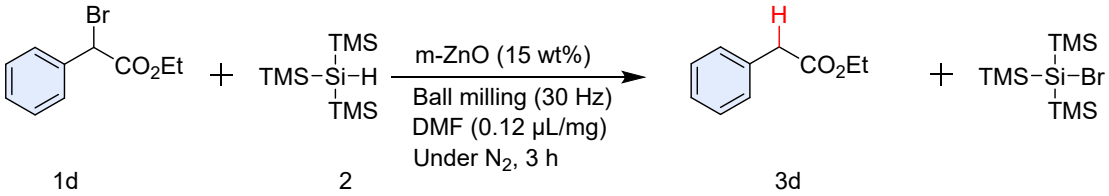


1c 2 3c

According to general procedure A, diethyl 2-bromomalonate (68.3 µL, 0.4 mmol) afforded diethyl malonate in 92% yield (55.2 µL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.18 (dd, J = 6.6 Hz, 4H), 3.38 (s, 2H), 1.25 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.19, 61.37, 41.61, 14.06. HRMS-EI (m/z): $[M]^+$ calcd for $C_7H_{12}O_4$, 160.0736; found, 160.0737.

Ethyl 2-phenylacetate (3d)

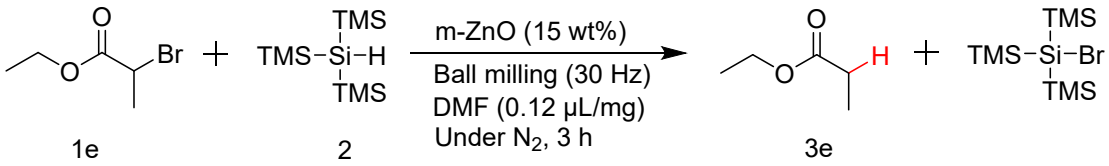


1d 2 3d

According to general procedure A, ethyl 2-bromo-2-phenylacetate (70.4 μL, 0.4 mmol) afforded ethyl 2-phenylacetate in 94% yield (57.0 μL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 – 7.20 (m, 4H), 4.14 (dd, J = 6.6 Hz, 2H), 3.56 (d, J = 0.7 Hz, 2H), 1.24 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.33, 134.80, 129.46, 129.03, 127.28, 60.77, 41.44, 14.15. HRMS-EI (m/z): $[M]^+$ calcd for $C_{10}H_{12}O_2$, 164.0837; found, 164.0840.

Ethyl 2-bromopropionate (3e)

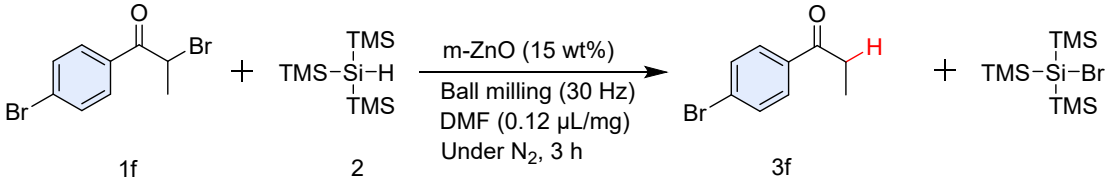


1e 2 3e

According to general procedure A, ethyl 2-bromopropionate (55.6 μL, 0.4 mmol) afforded ethyl propionate in 94% yield (58.9 μL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.15 (dd, J = 6.6 Hz, 2H), 2.37 (dd, J = 8.0 Hz, 2H), 1.24 (t, J = 6.6 Hz, 3H), 1.13 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.79, 60.05, 27.76, 14.26, 9.18. HRMS-EI (m/z): $[M]^+$ calcd for $C_5H_{10}O_2$, 102.0681; found, 102.0680.

4-Bromopropiophenone (3f)

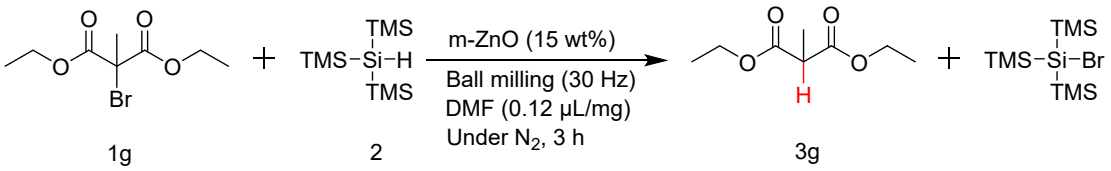


1f 2 3f

According to general procedure A, 2,4'-Dibromopropiophenone (116.8 mg, 0.4 mmol) afforded 4-Bromopropiophenone in 95% yield (81.03 mg, 0.38 mmol) as white light yellow powder by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.84 – 7.78 (m, 2H), 7.65 – 7.59 (m, 2H), 3.32 (dd, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 200.02, 135.38, 131.86, 130.08 , 129.07, 31.72, 8.37. HRMS-EI (m/z): $[M]^+$ calcd for C_9H_9BrO, 211.9837; found, 211.9836.

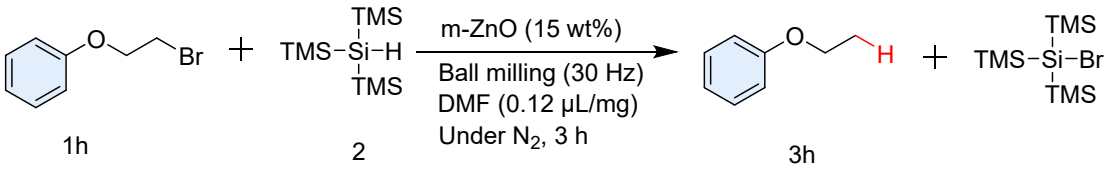
Diethyl 2-methylmalonate (3g)



According to general procedure A, diethyl 2-bromomalonate (68.3 μL, 0.4 mmol) afforded diethyl malonate in 95% yield (57.8μL, 0.38mmol) as a colorless transparent liquid by flash column chromatography (hexane).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.22 – 4.09 (m, 4H), 3.41 (q, J = 8.4 Hz, 1H), 1.37 (d, 3H), 1.23 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.94, 61.14, 46.07, 14.18, 13.66. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_{14}O_4$, 174.0892; found, 174.0890.

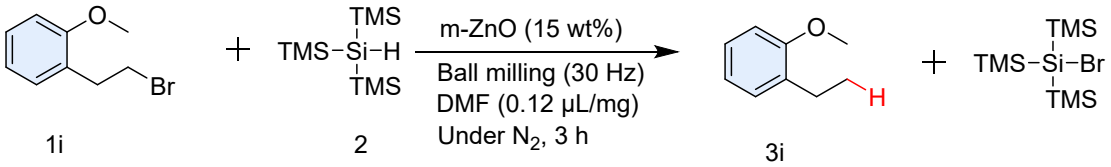
Phenetole (3h)



According to general procedure A, 2-Phenoxyethylbromide (55.4 μL, 0.4 mmol) afforded Phenetole in 94% yield (47.6 μL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 – 7.27 (dd, 2H), 7.01 – 6.98 (tt, 1H), 6.89- 6.87 (m, 2H), 4.01- 4.03 (q, 2H), 1.42 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.96, 129.73, 121.37, 114.67, 63.67, 14.69. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_{10}O$, 122.0732; found, 122.0733.

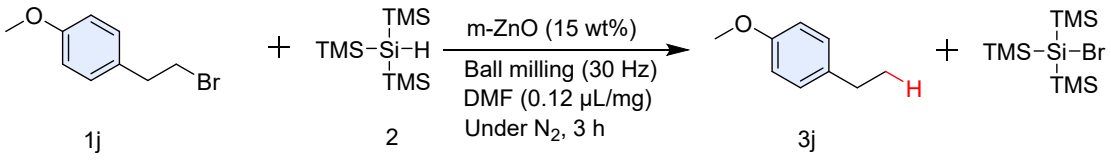
2-Ethylanisole (3i)



According to general procedure A, 2-Methoxyphenethyl bromide (63.7 μL, 0.4 mmol) afforded 2-Ethylanisole in 92% yield (52.2 μL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24 - 7.20 (dd, 1H), 7.17 -7.15 (ddt, 1H), 6.99- 6.96 (td, 1H), 6.86- 6.84 (dd, 1H), 3.78 (s, 3H), 2.69- 2.64 (qd, 2H), 1.21-1.18 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.34, 132.58, 128.94, 126.90, 120.59,110.27, 55.21, 23.36, 14.22. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_9H_{12}O$, 136.0888; found, 136.0891.

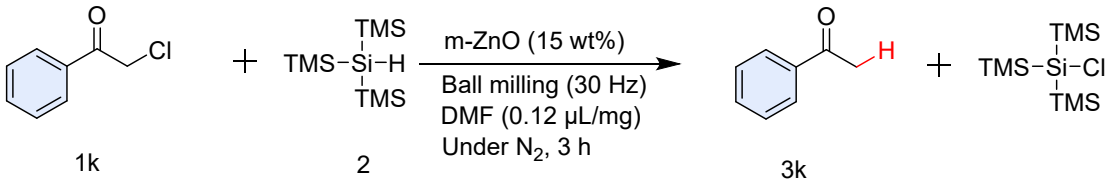
4-Ehylanisole (3j)



According to general procedure A, 4-Methoxyphenethyl bromide (63.7 μL, 0.4 mmol) afforded 4-Ethylanisole in 93% yield (50.2 μL, 0.37 mmol) as a colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.12 - 7.10 (m, 2H), 6.83 -6.80 (m, 2H), 3.80 (s, 3H), 2.65-2.60 (qt, 2H), 1.23-1.20 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.69, 138.74, 129.18, 110.64, 55.35, 28.47, 15.47. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_{12}O$, 136.0888; found, 136.0890.

Acetophenone (3k)

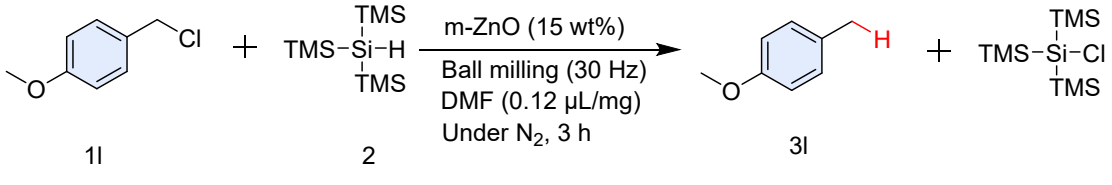


1k 2 3k

According to general procedure A, 2-Chloroacetophenone (47.3 μL, 0.4 mmol) afforded 1-methoxy-4-methylbenzene in 94% yield (44.4 μL, 0.37 mmol) as light yellow transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.94 – 7.92 (m, 2H), 7.58 – 7.55 (m, 1H), 7.48 – 7.45 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.00, 136.63, 134.45, 129.07, 128.83, 26.38. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_8H_{10}O$, 120.0568; found, 120.0574.

1-methoxy-4-methylbenzene (3l)

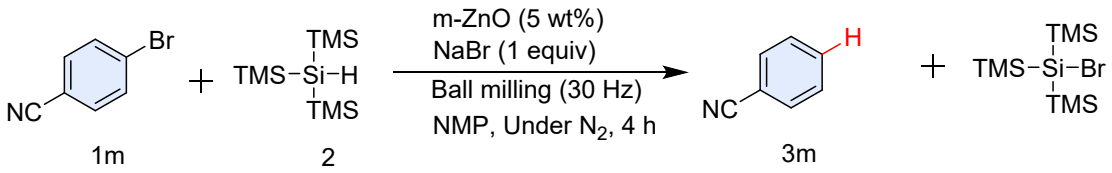


1l 2 3l

According to general procedure A, 4-Methoxybenzylchloride (56.9 μL, 0.4 mmol) afforded 1-methoxy-4-methylbenzene in 83% yield (42.3 μL, 0.33 mmol) as light yellow transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.11 – 7.05 (m, 2H), 6.83 – 6.77 (m, 2H), 3.80 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.15, 130.28, 129.75, 113.79, 55.35, 20.63. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_8H_{10}O$, 122.0732; found, 122.0731.

Benzonitrile (3m)

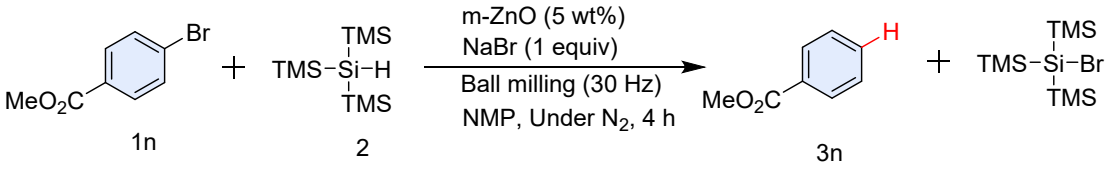


1m 2 3m

According to general procedure B, 4-bromobenzonitrile (72.8 mg, 0.4 mmol) afforded benzonitrile in 53% yield(21.9 μL, 0.21 mmol) as light yellow transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 – 7.64 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 132.63, 132.47, 128.83, 118.85, 112.68. HRMS-EI (*m/z*): $[M]^+$ calcd for C_7H_5N, 103.0422; found, 103.0423.

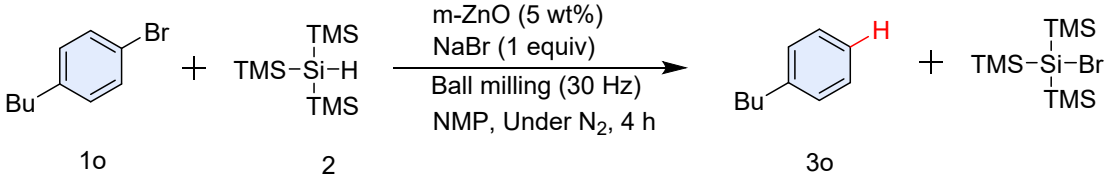
Methyl benzoate (3n)



According to general procedure B, methyl 4-bromobenzoate (86.0 mg, 0.4 mmol) afforded methyl benzoate in 71% yield(38.5 μL, 0.28 mmol) as light yellow transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.06 – 7.99 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.08, 133.40, 130.50, 129.92, 128.67, 52.10. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_8O_2$, 136.0524; found, 136.0527.

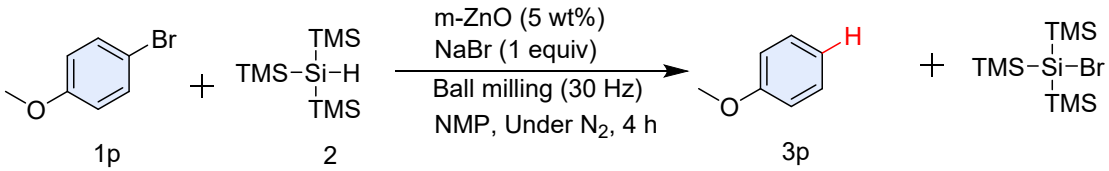
Butylbenzene (3o)



According to general procedure B, 1-bromo-4-butylbenzene (85.2 mg, 0.4 mmol) afforded benzonitrile in 52% yield (30.5 μL, 0.22 mmol) as colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 – 7.19 (m, 3H), 7.14 (ddt, J = 7.8, 1.7, 0.9 Hz, 2H), 2.61 (tt, J = 8.2, 0.9 Hz, 2H), 1.62 – 1.52 (tt, 2H), 1.34 (hept, J = 6.8 Hz, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.15, 128.74, 128.45, 126.53, 35.97, 33.93, 22.84, 13.85. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{14}$, 134.1096; found, 134.1100.

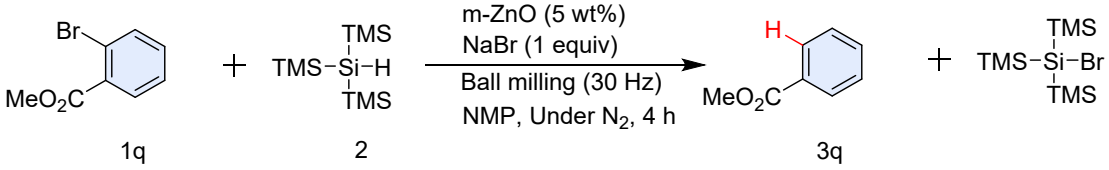
Anisole (3p)



According to general procedure B, 1-bromo-4-methoxybenzene (50.2 μL, 0.4mmol) afforded benzonitrile in 51% yield (22.3 μL, 0.20 mmol) as colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 – 7.24 (m, 2H), 7.00 (tt, J = 7.3, 1.4 Hz, 1H), 6.93 – 6.87 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 160.15, 129.70, 121.16, 114.48, 54.96. HRMS-EI (*m*/*z*): $[M]^+$ calcd for C_7H_8O, 108.0575; found, 108.0580.

Methyl benzoate (3q)

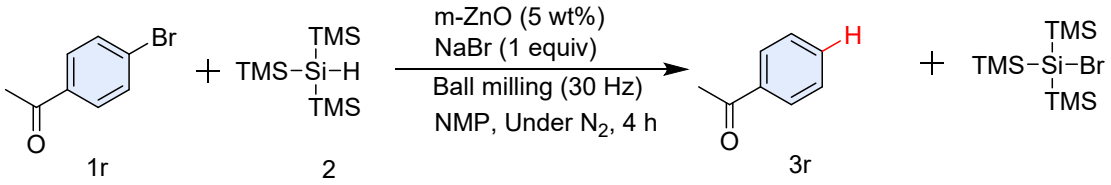


According to general procedure B, methyl 2-bromobenzoate (57.3 μL, 0.4 mmol) afforded

methyl benzoate in 70% yield (35.3 μL, 0.28 mmol) as colorless transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.06 – 7.99 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.08, 133.40, 130.50, 129.92, 128.67, 52.10. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_8O_2$, 136.0524; found, 136.0527.

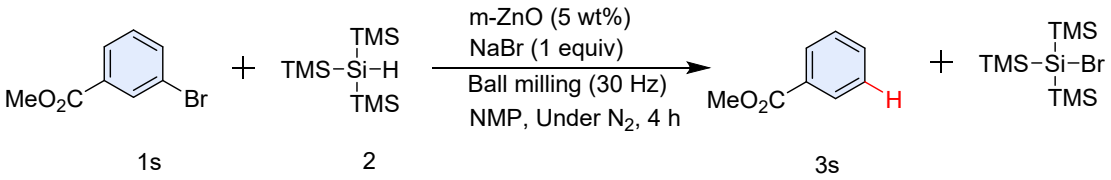
Acetophenone (3r)



According to general procedure B, 4-bromoacetophenone (48.5 μL, 0.4 mmol) afforded methyl benzoate in 51% yield (24.5 μL, 0.20 mmol) as slightly yellowish transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96 – 7.90 (m, 2H), 7.60 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.00, 136.63, 134.45, 129.07, 128.83, 26.36. HRMS-EI (*m*/*z*): $[M]^+$ calcd for C_8H_8O, 120.0575; found, 120.0574.

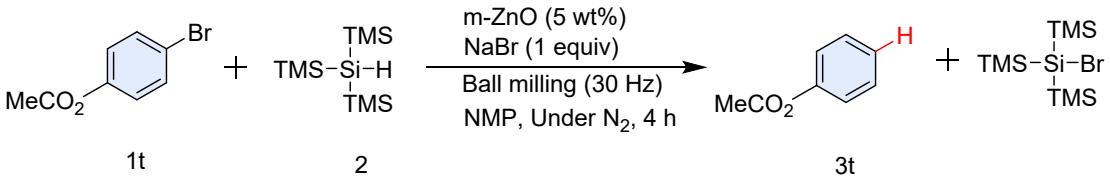
Phenyl acetate (3s)



According to general procedure B, 3-bromophenyl acetate (86.1 mg, 0.4 mmol) afforded phenyl acetate in 74% yield (41.3 μL, 0.30 mmol) as slightly brown transparent liquid by flash column chromatography (hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.64 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.12 – 7.05 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 169.48, 151.25, 129.88, 125.07，121.99, 21.08. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_8O_2$, 136.0524; found, 136.0528.

Phenyl acetate (3t)

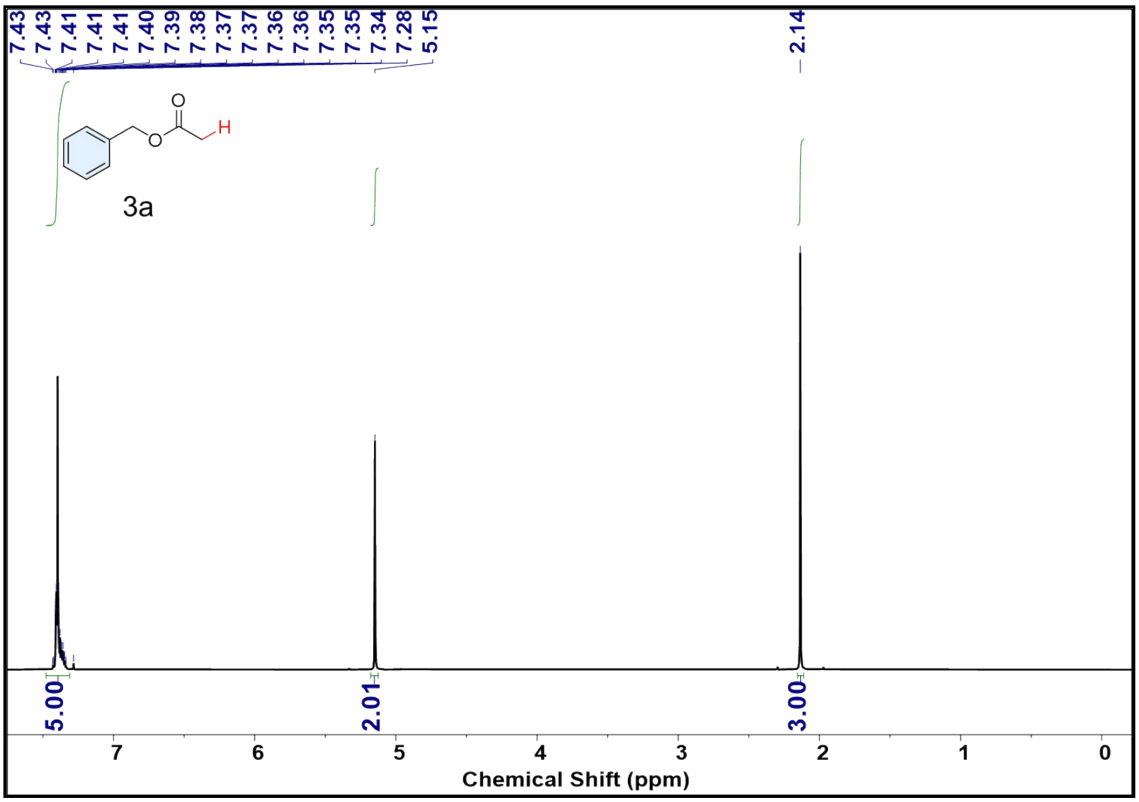


According to general procedure B, 4-bromophenyl acetate (57.3 μL, 0.4 mmol) afforded phenyl acetate in 50% yield (27.3 μL, 0.20 mmol) as slightly brown transparent liquid by flash column chromatography (hexane/ethyl acetate).

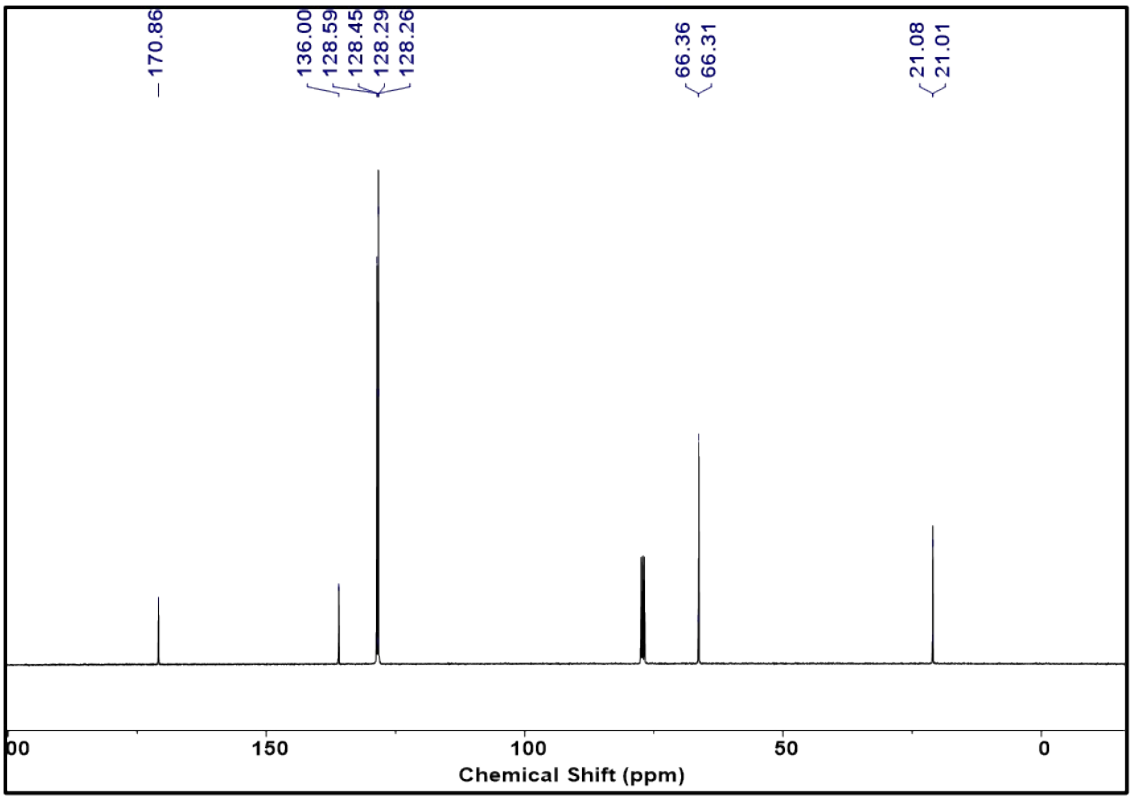
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.64 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.12 – 7.05 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.48, 151.25, 129.88, 125.07, 121.99, 21.08. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_8H_8O_2$, 136.0524; found, 136.0528.

18.NMR Spectra of hydrodebromination products

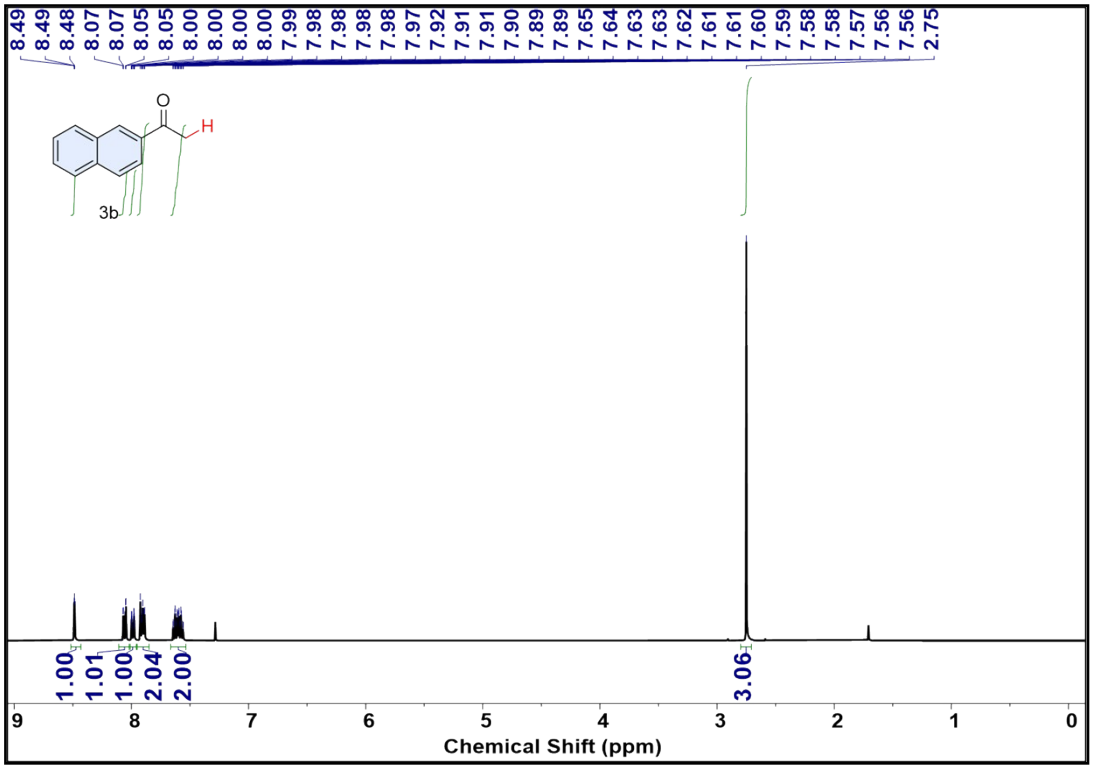
^{1}H-NMR



^{13}C-NMR



^{1}H-NMR



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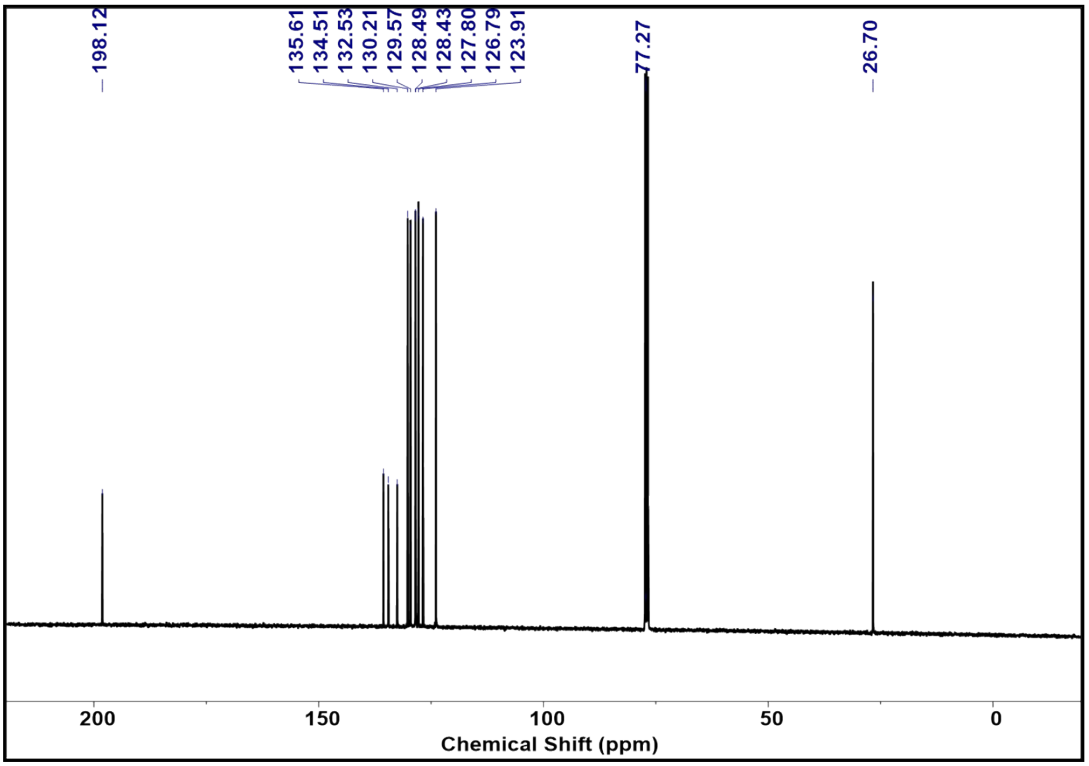
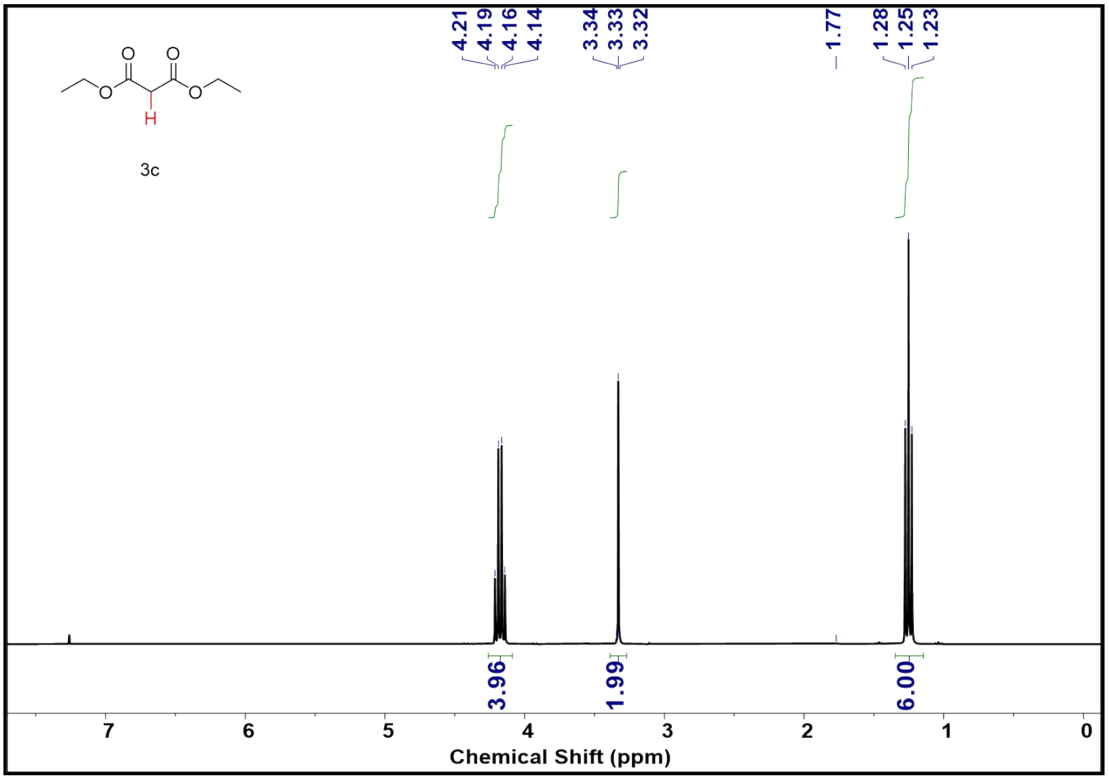


^{1}H-NMR



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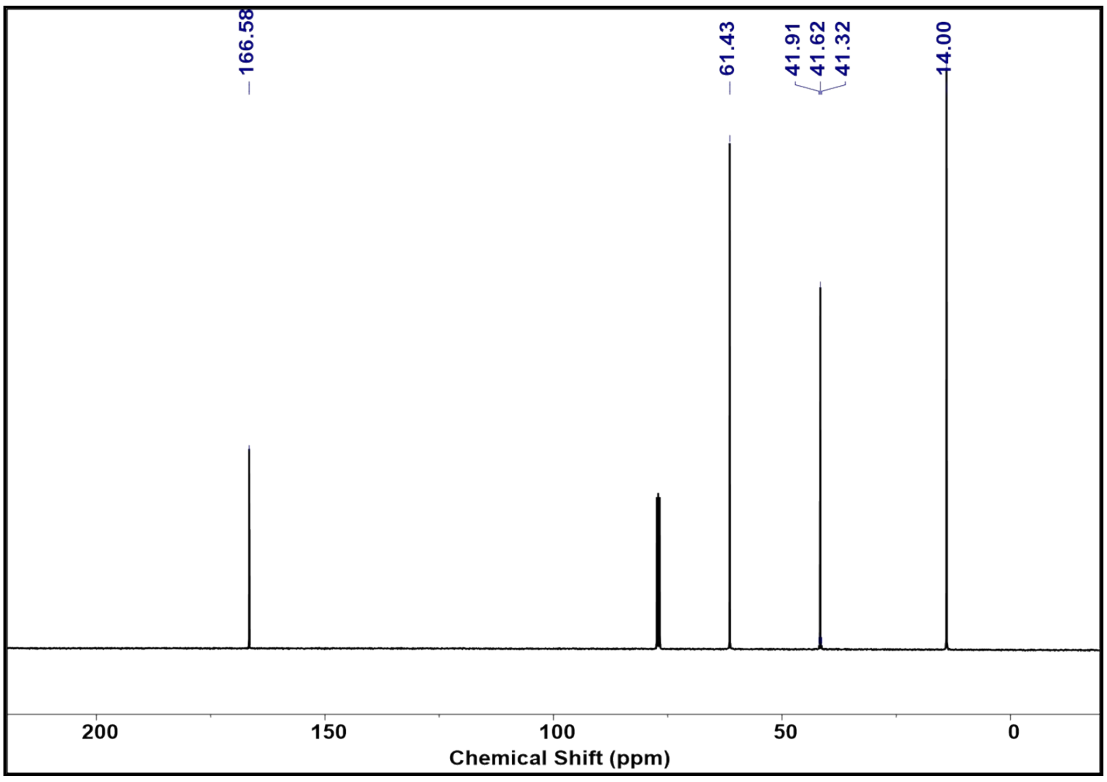

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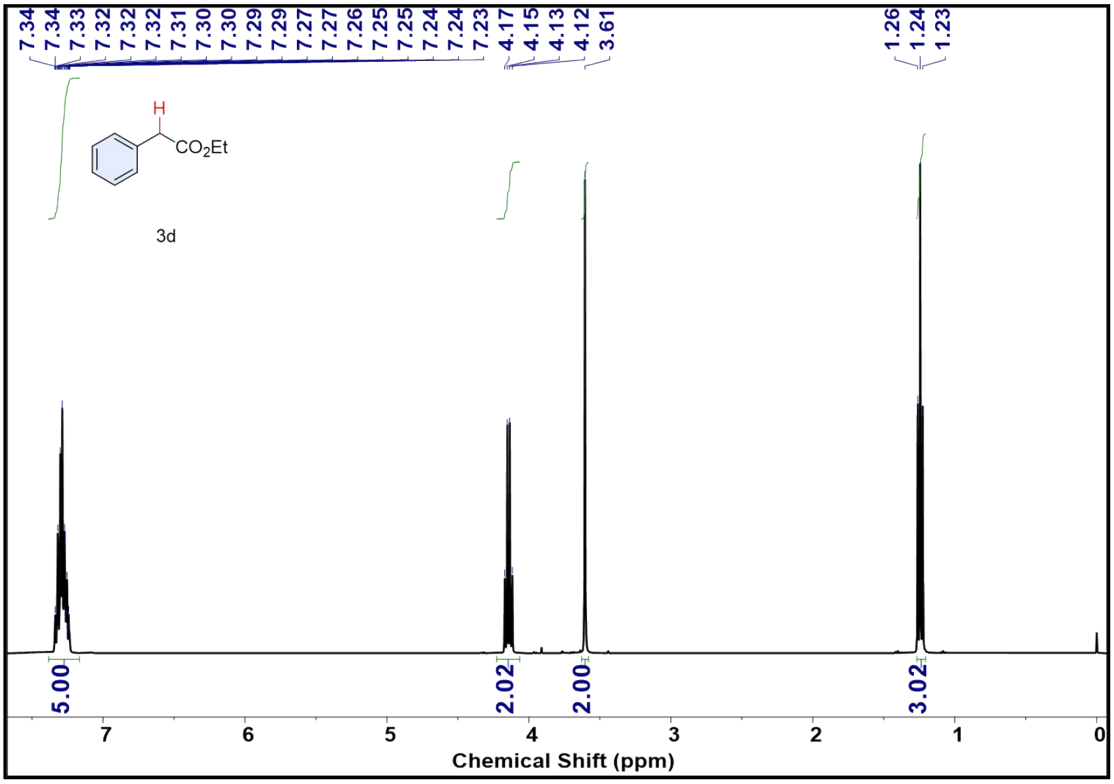
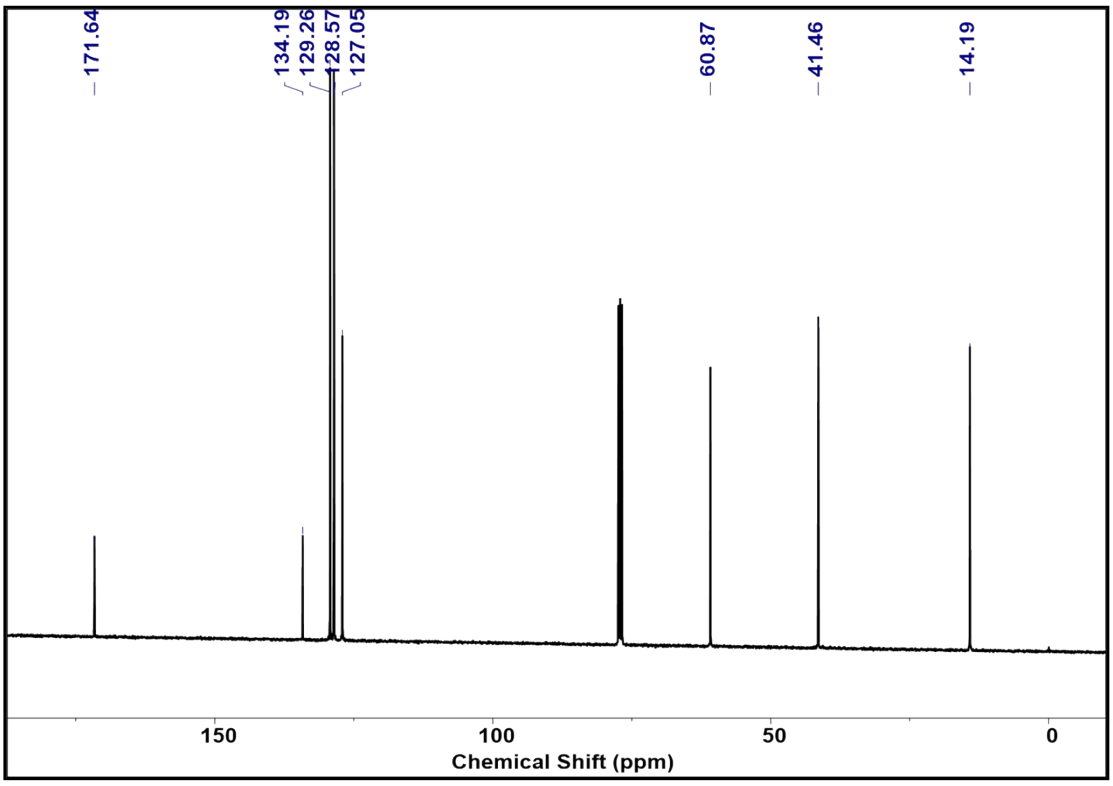
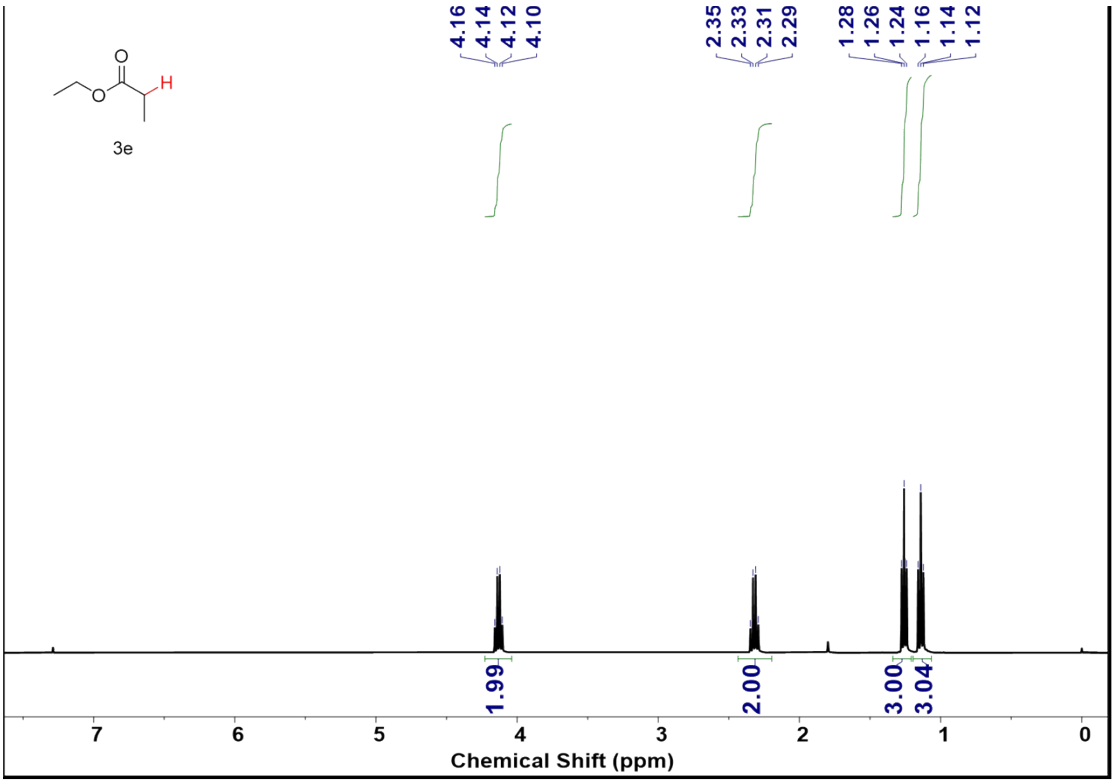


^{13}C-NMR



^{1}H-NMR



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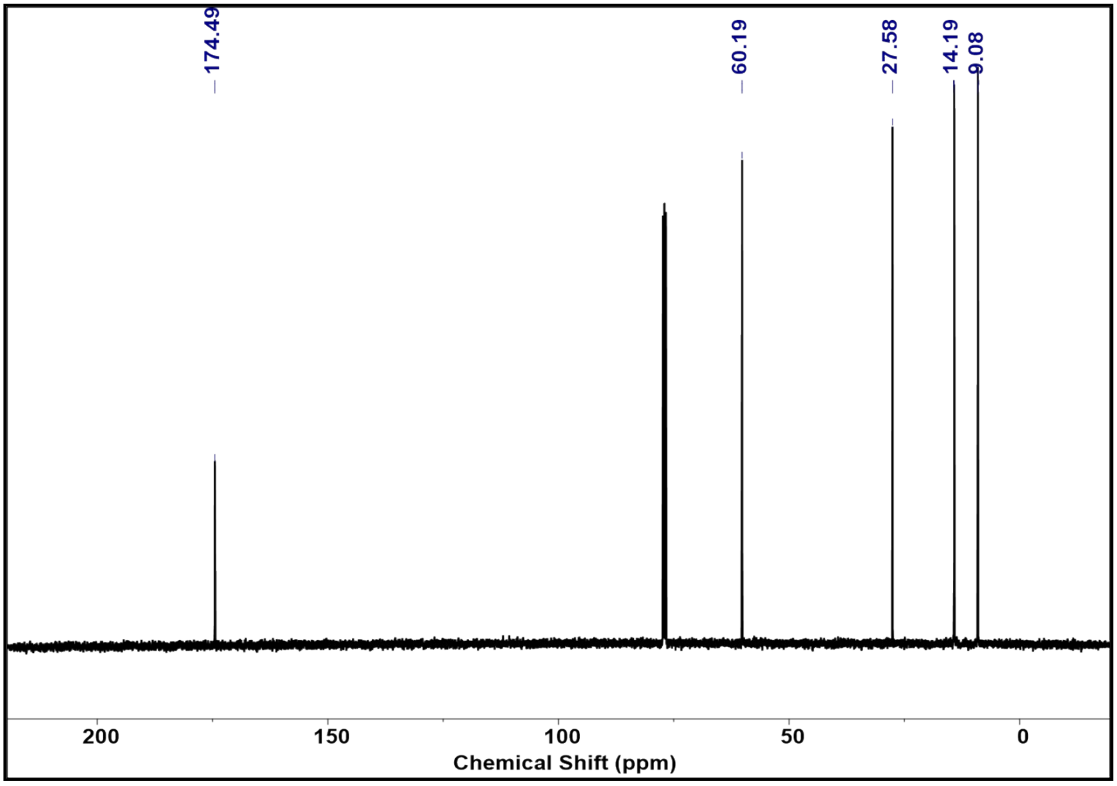
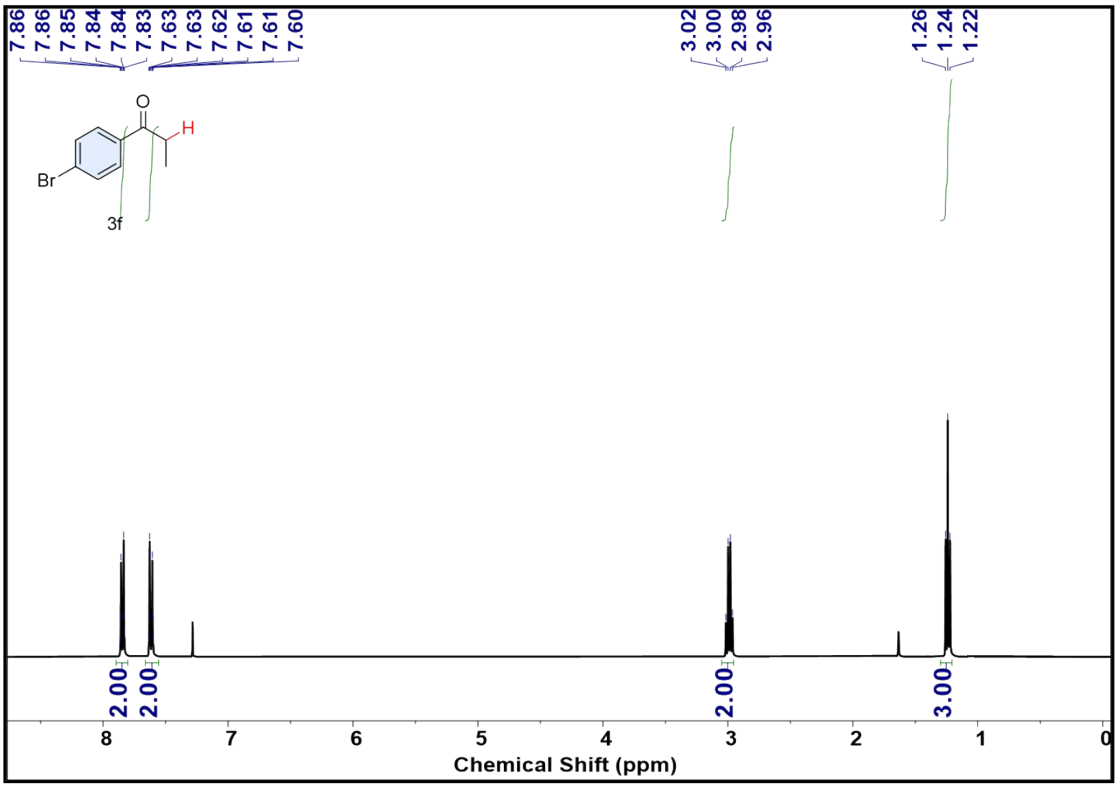
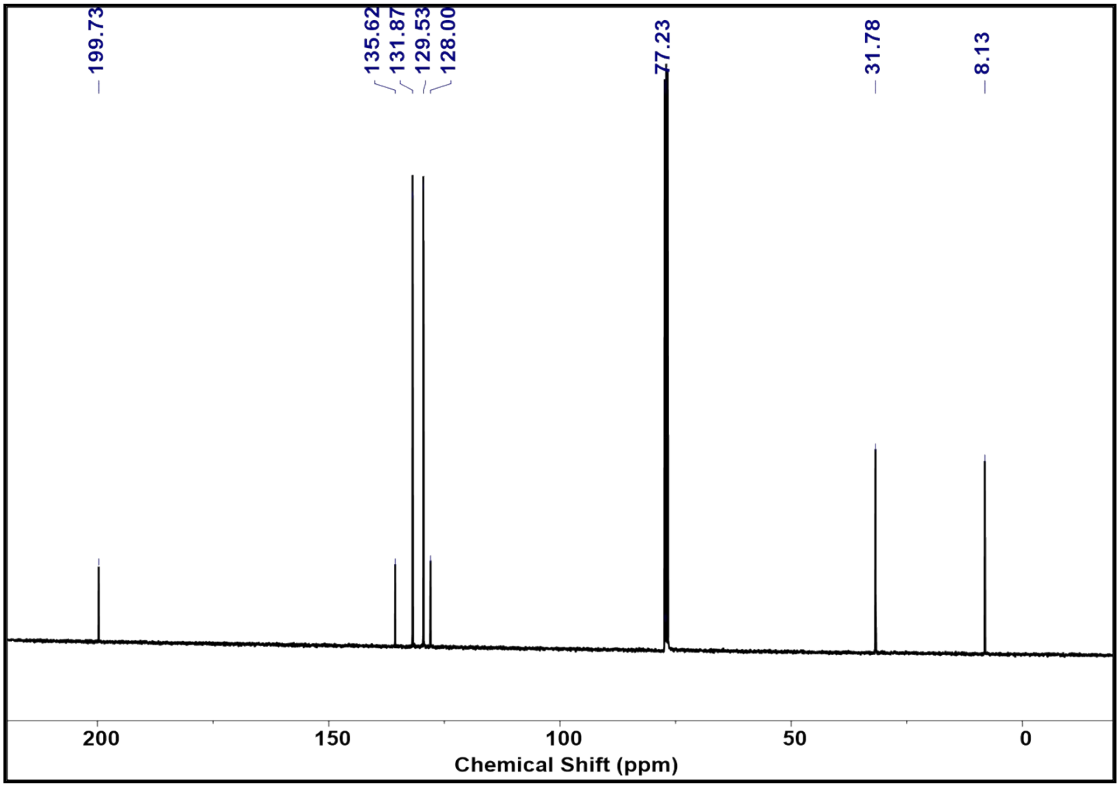


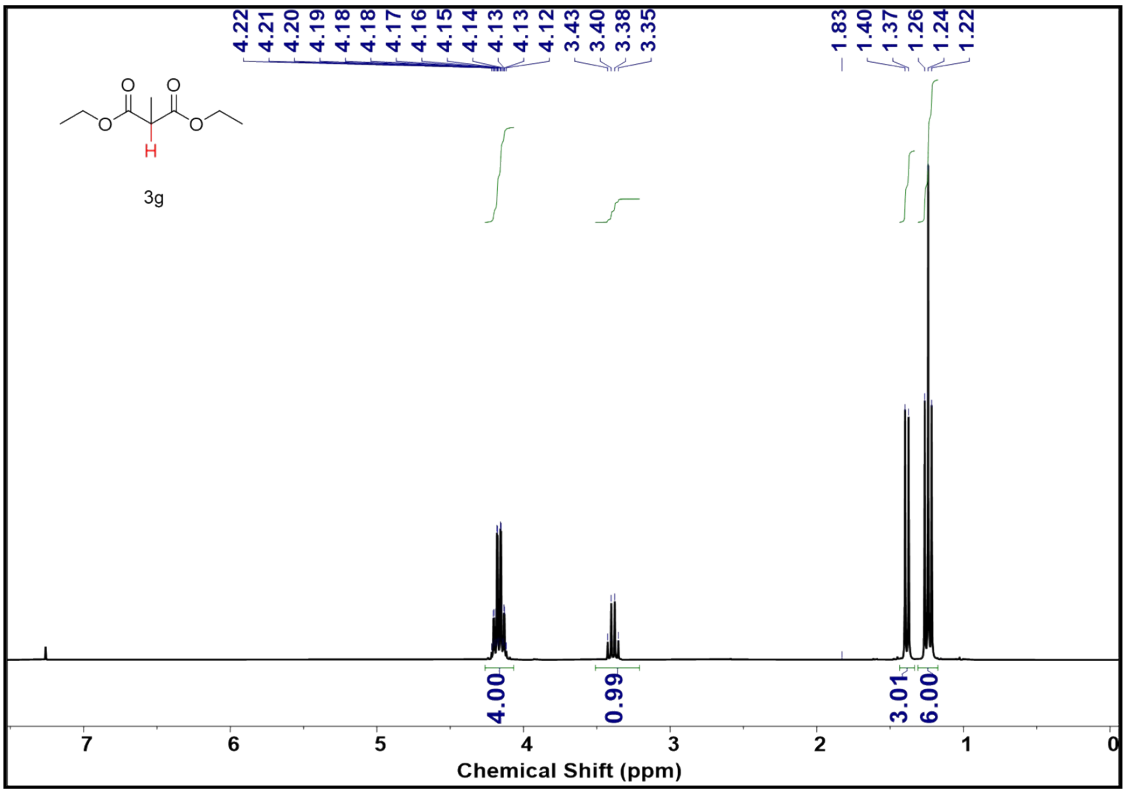
^{1}H-NMR



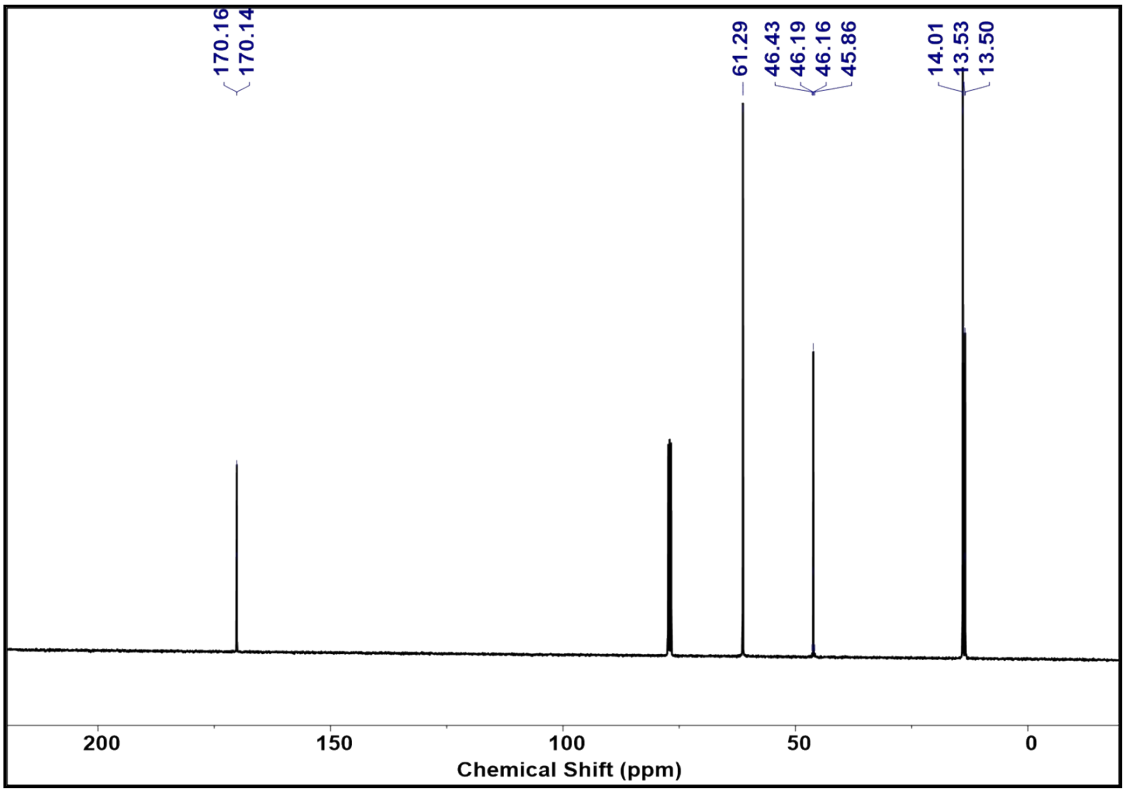
^{13}C-NMR



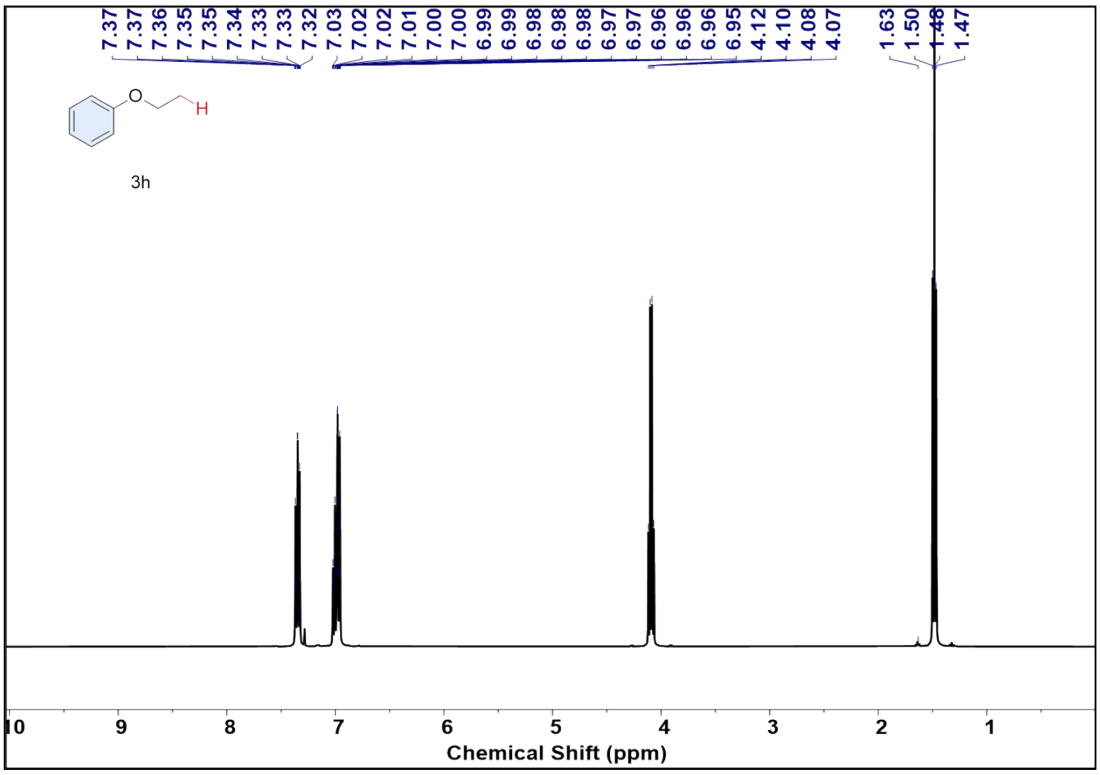
^{1}H-NMR



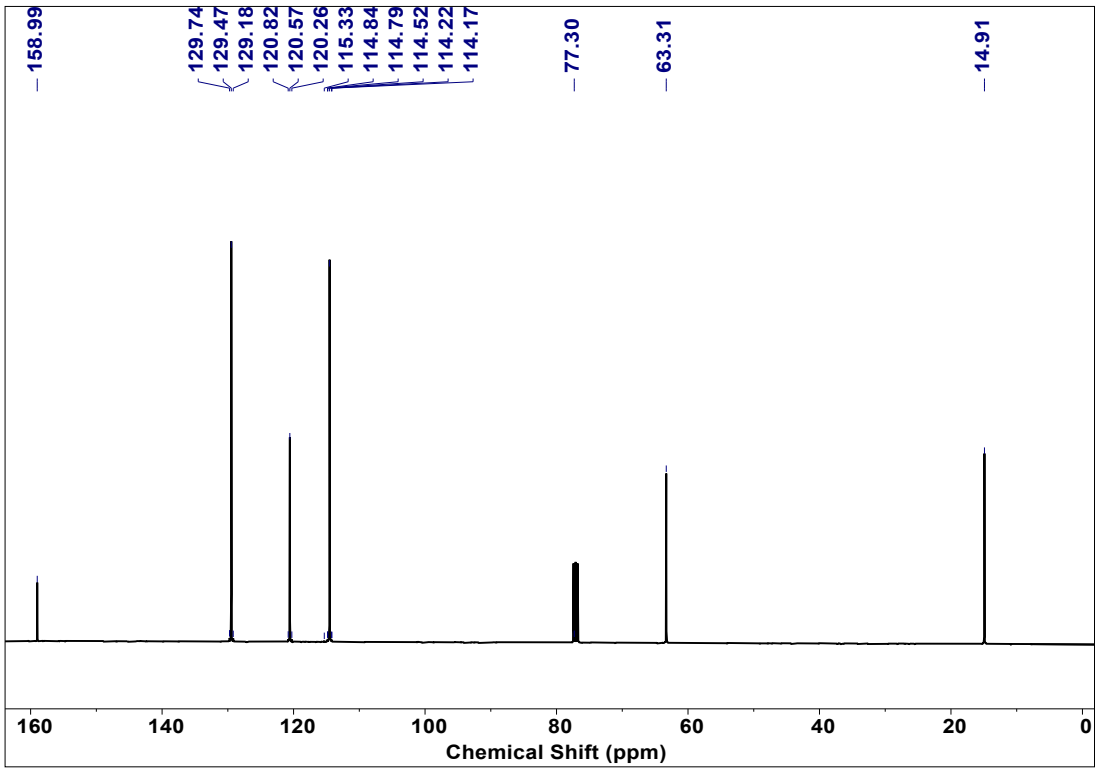
^{13}C-NMR



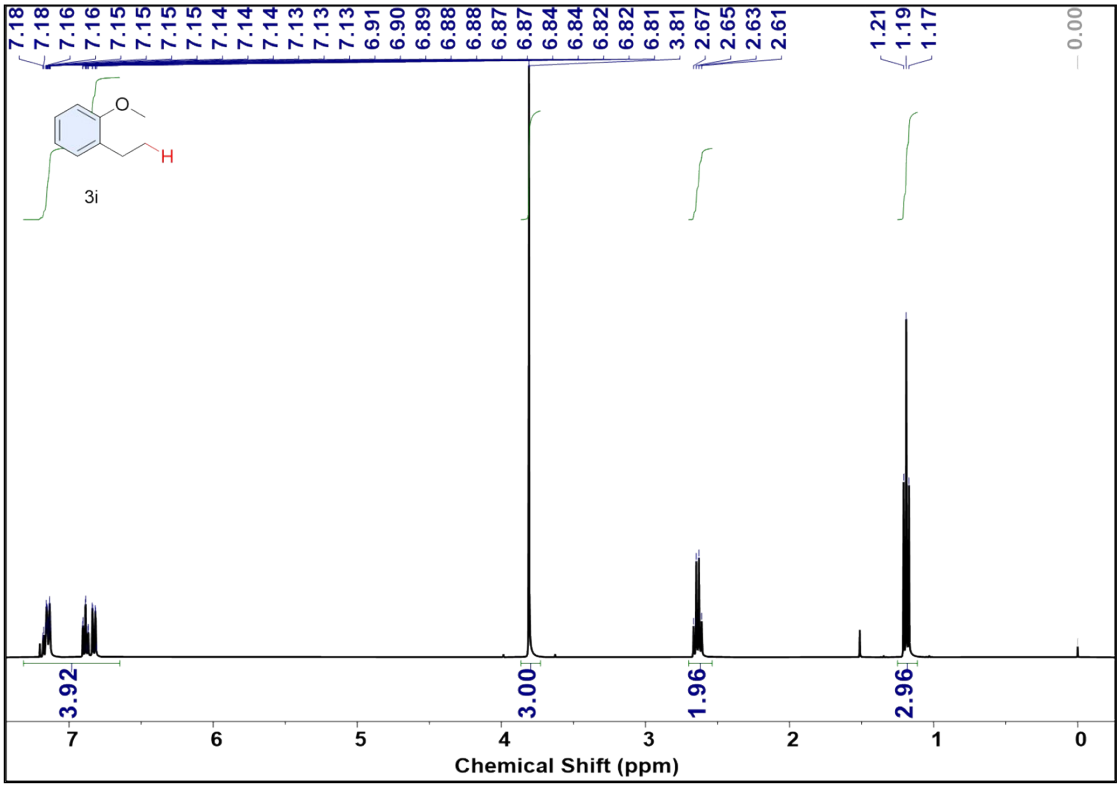
^{1}H-NMR



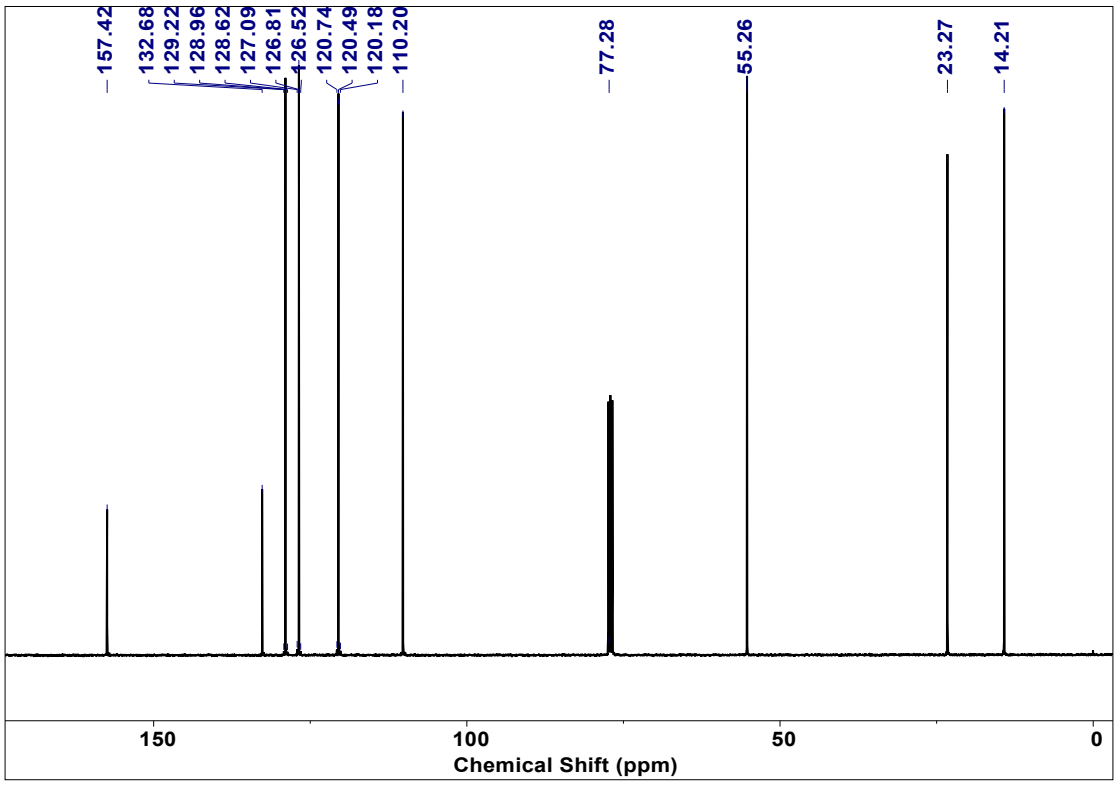
^{13}C-NMR



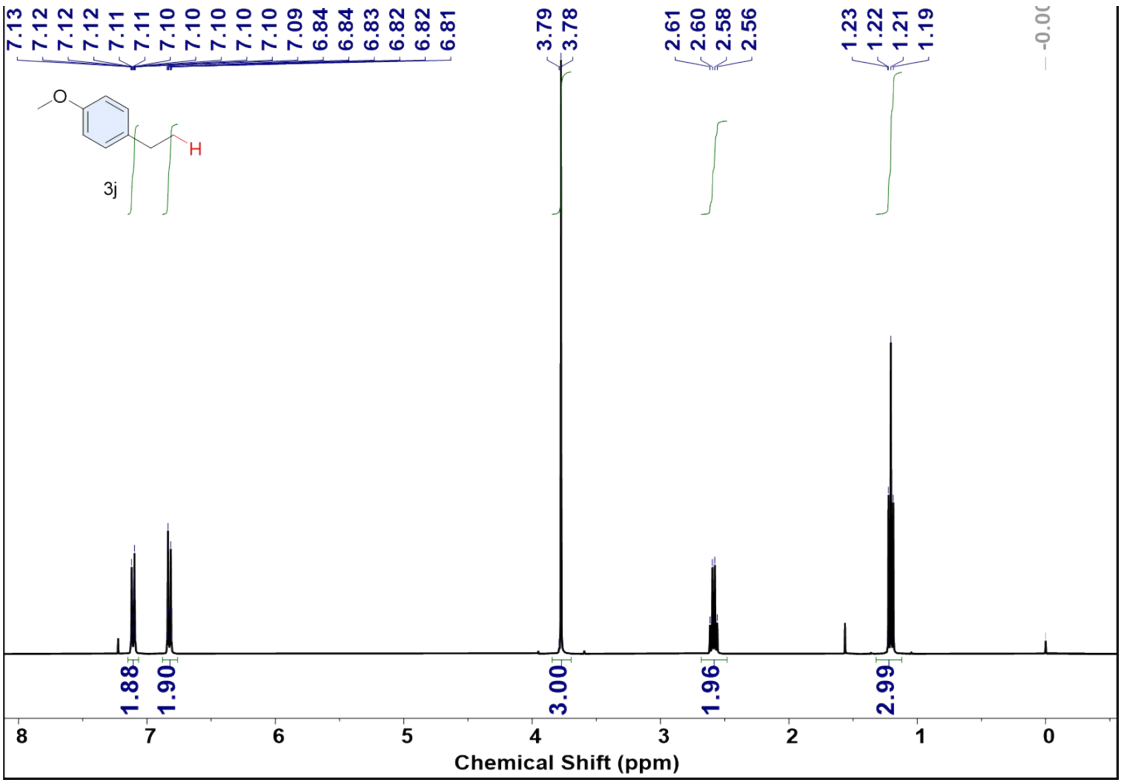
^{1}H-NMR



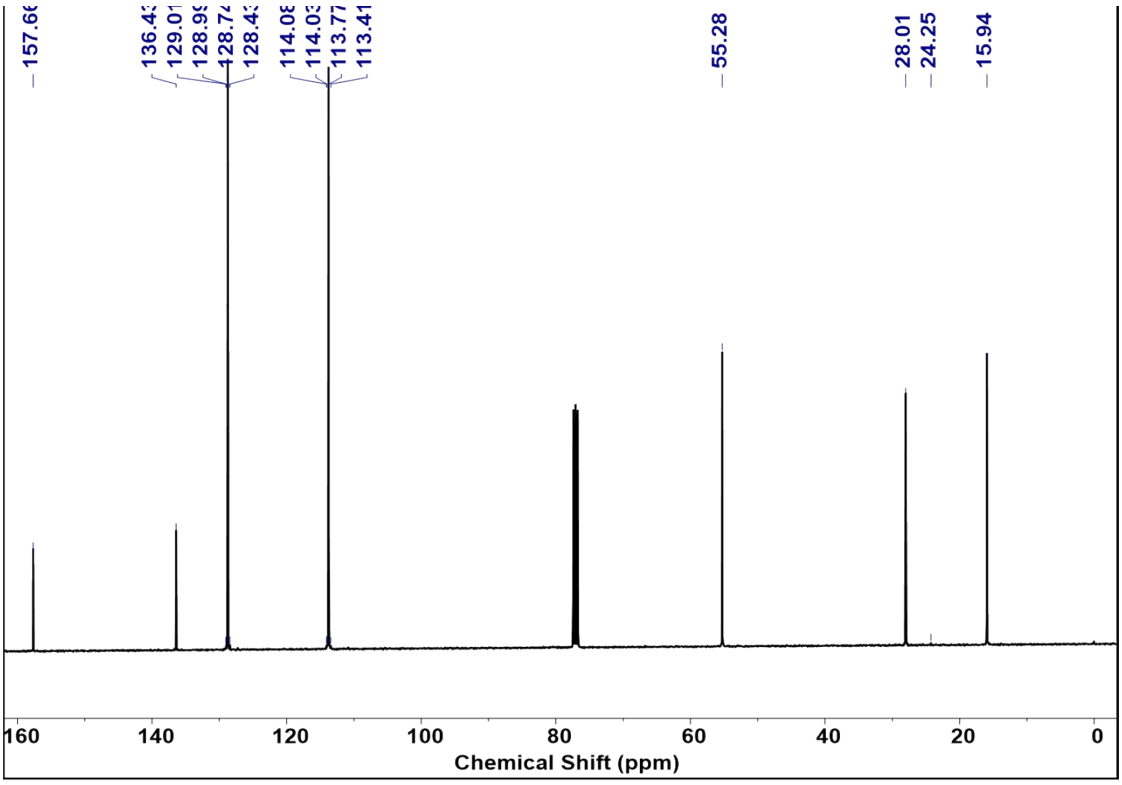
^{13}C-NMR



^{1}H-NMR



^{13}C-NMR



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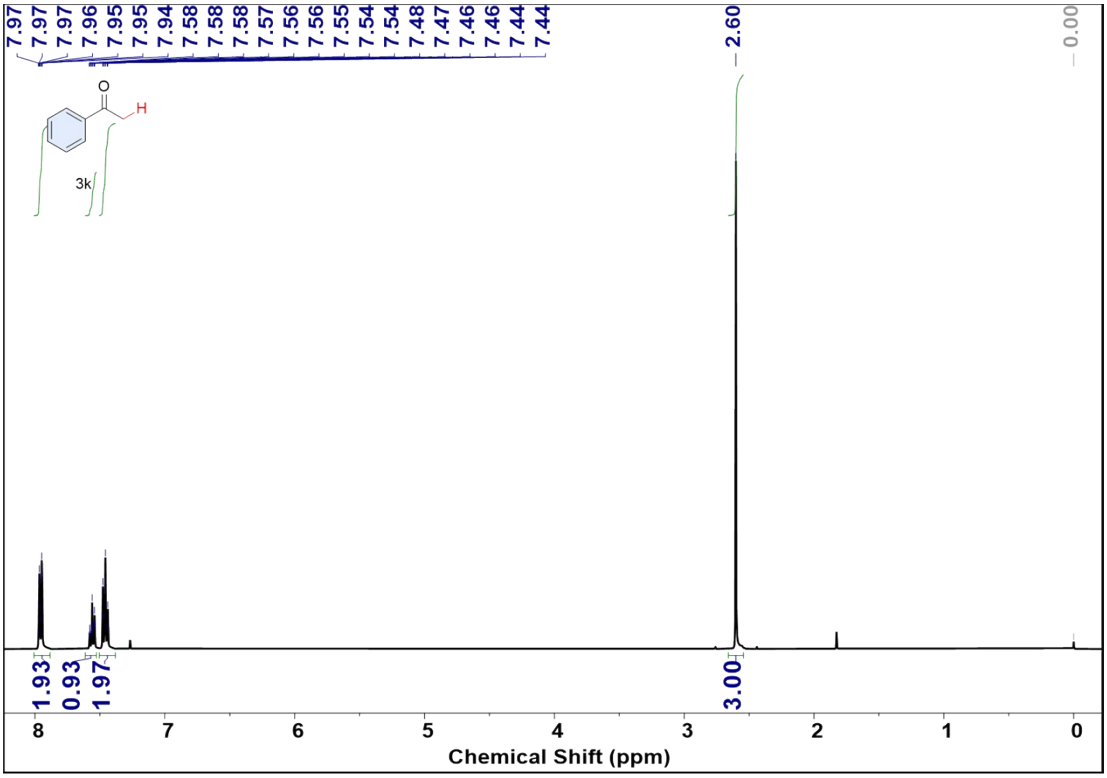

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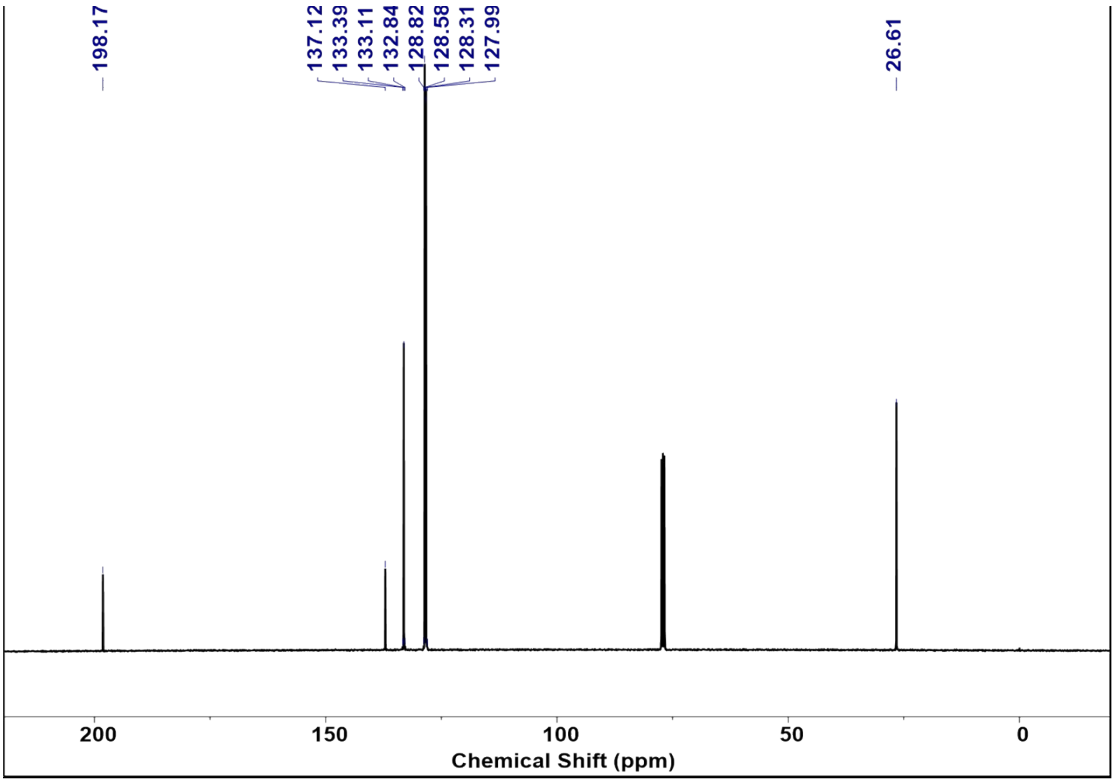

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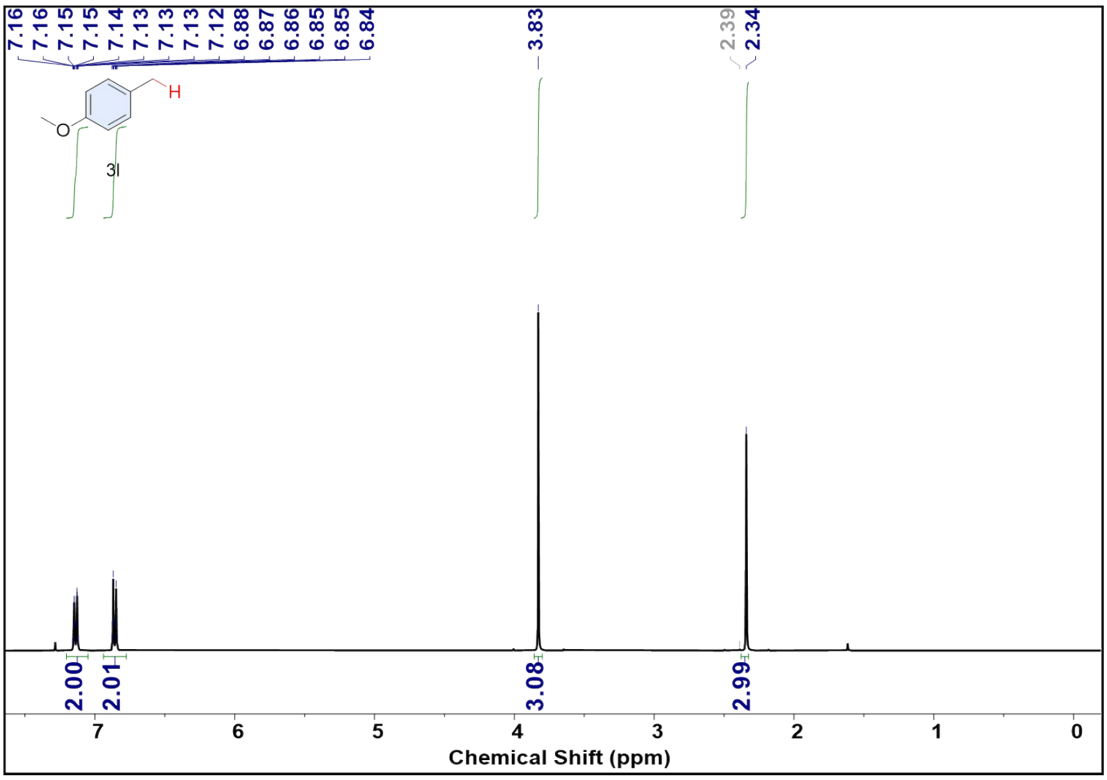

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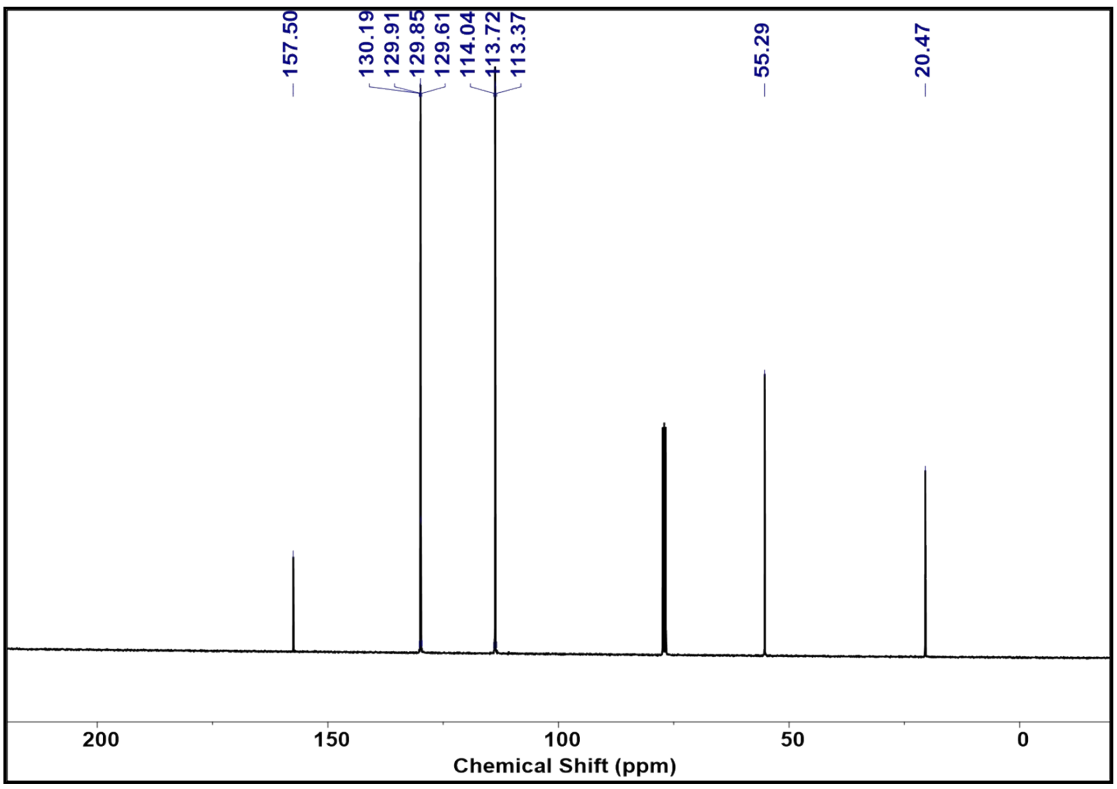

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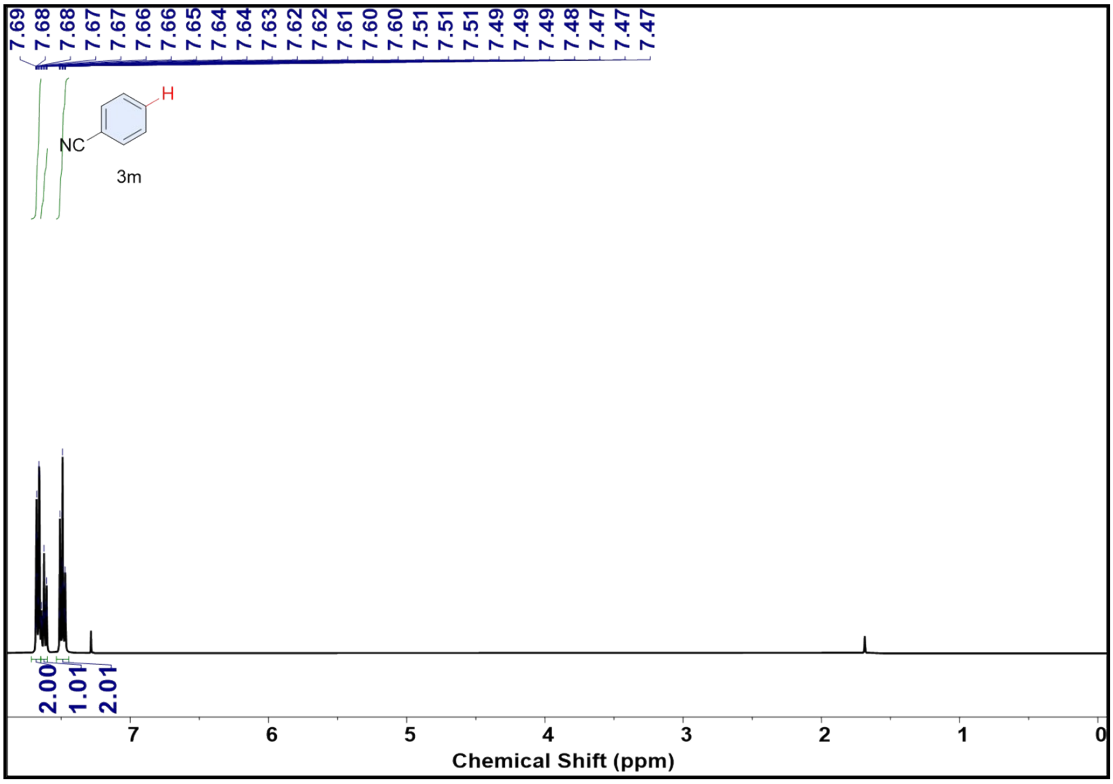

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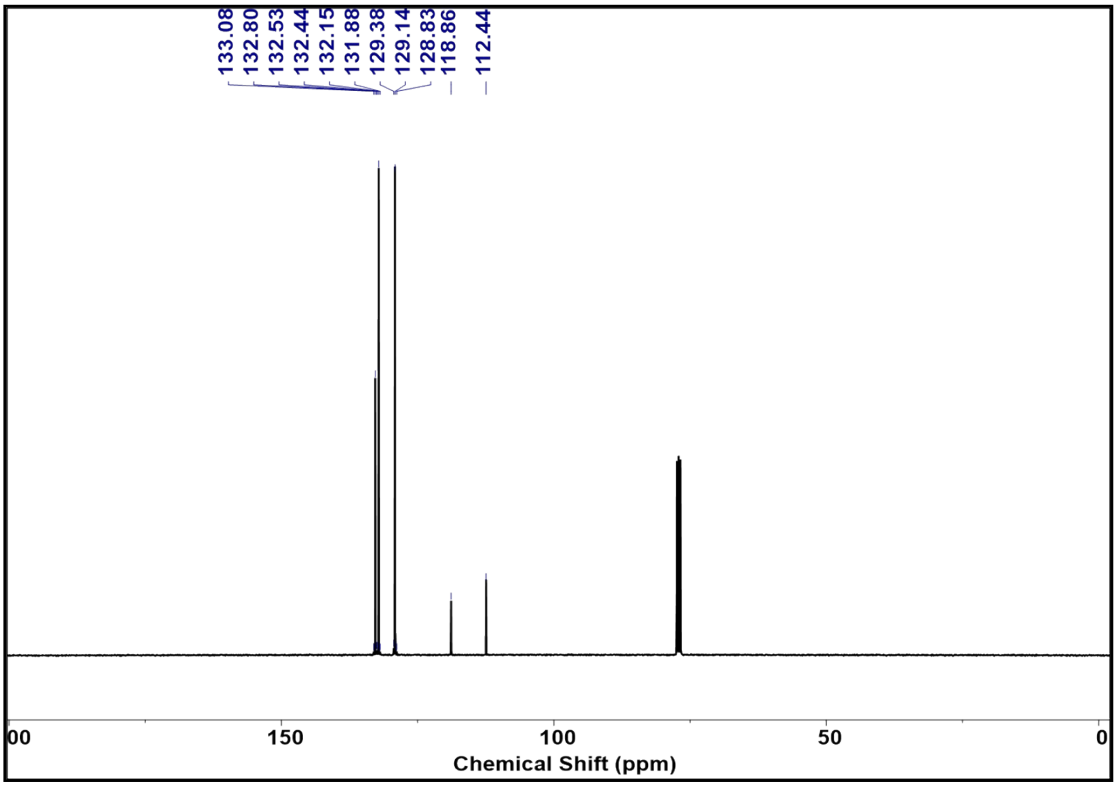

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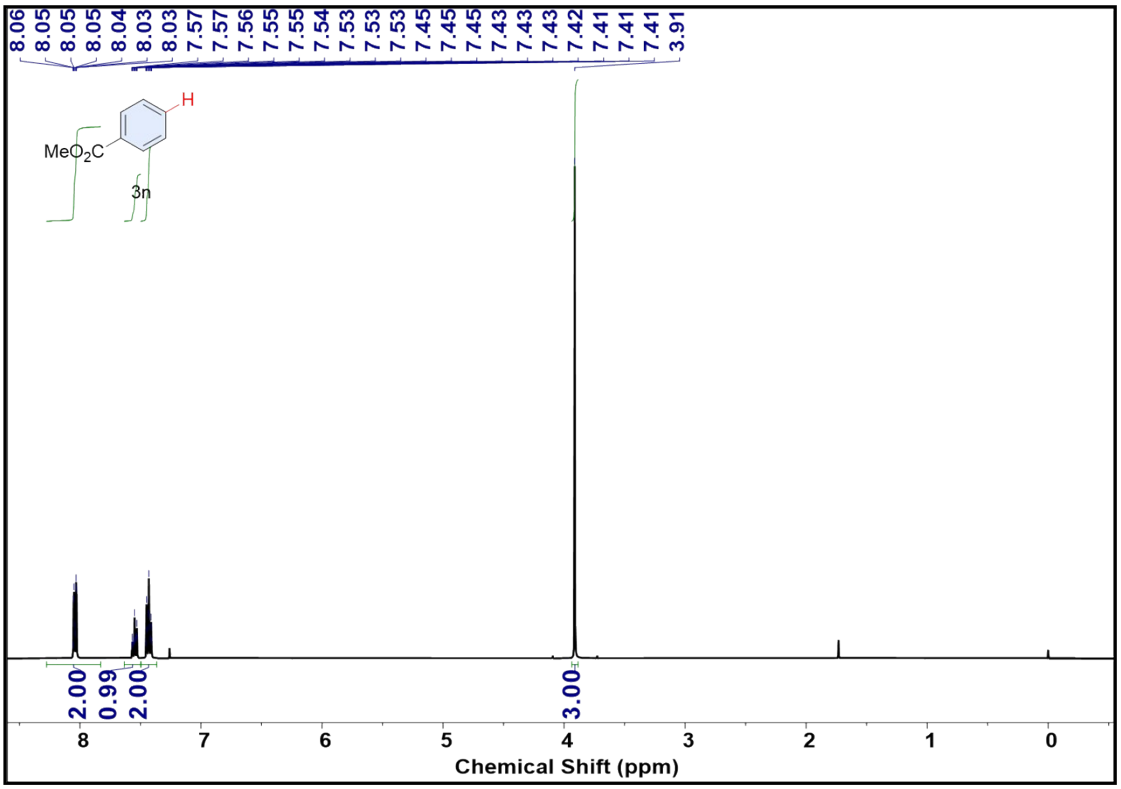

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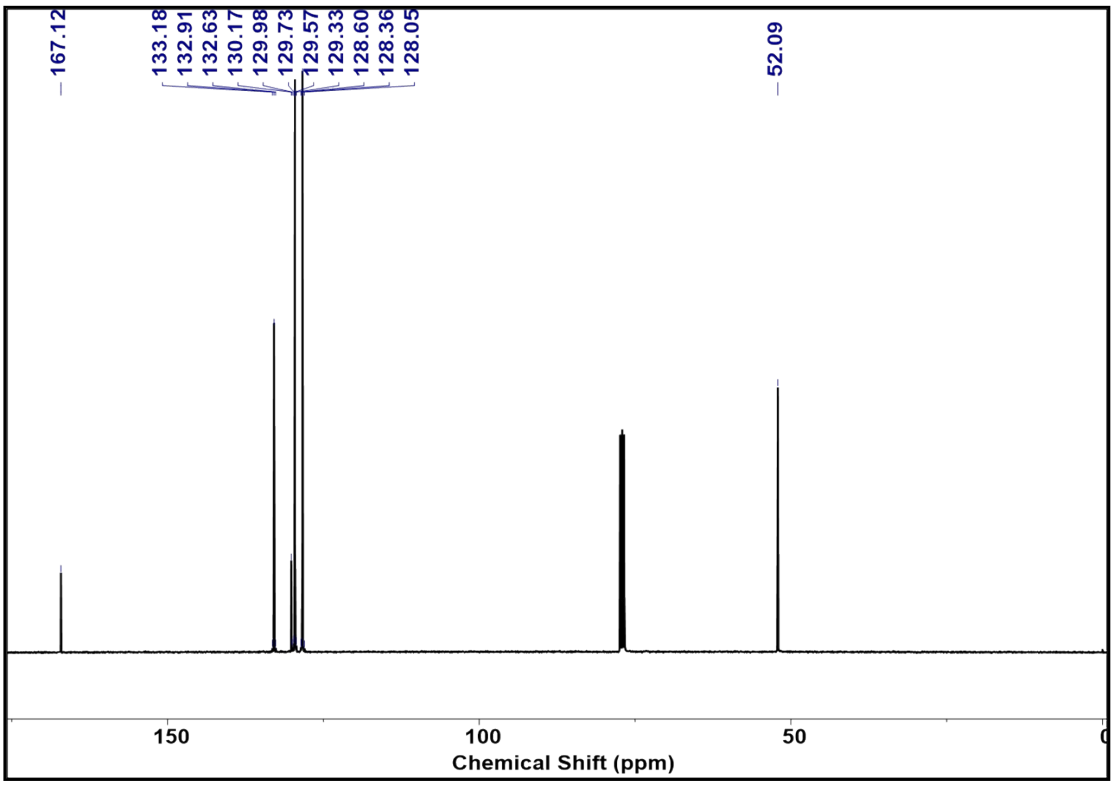

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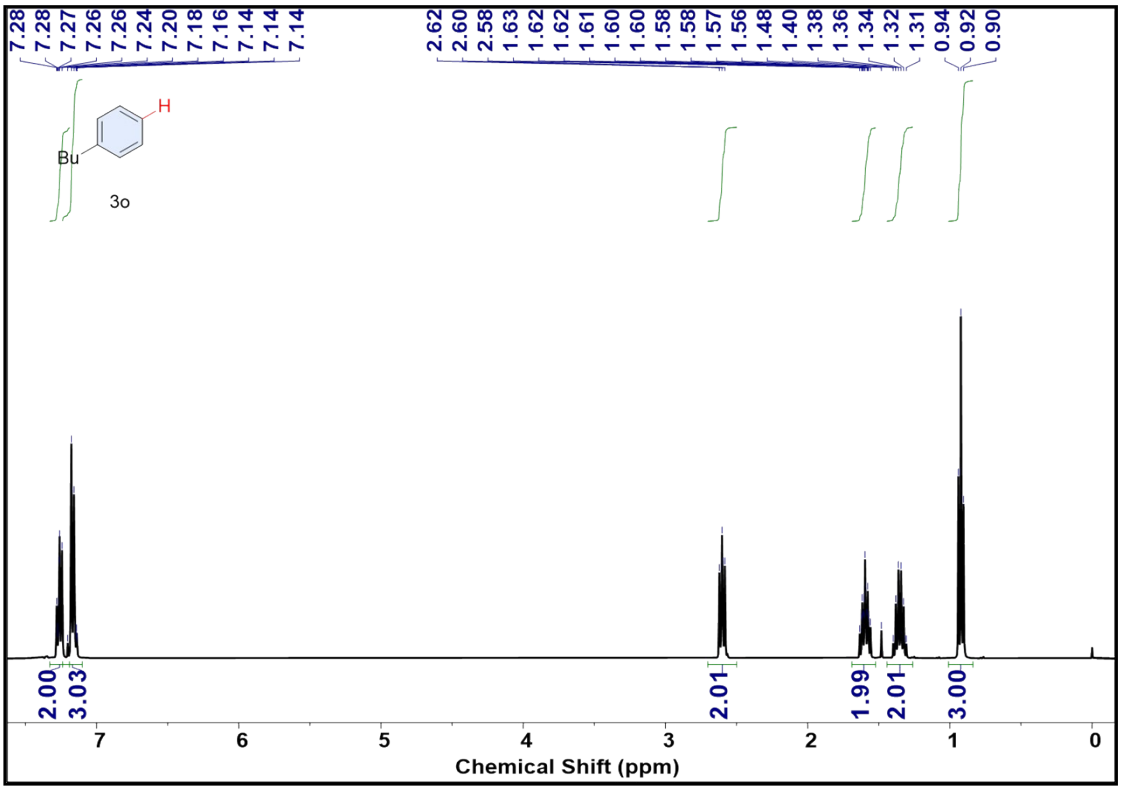

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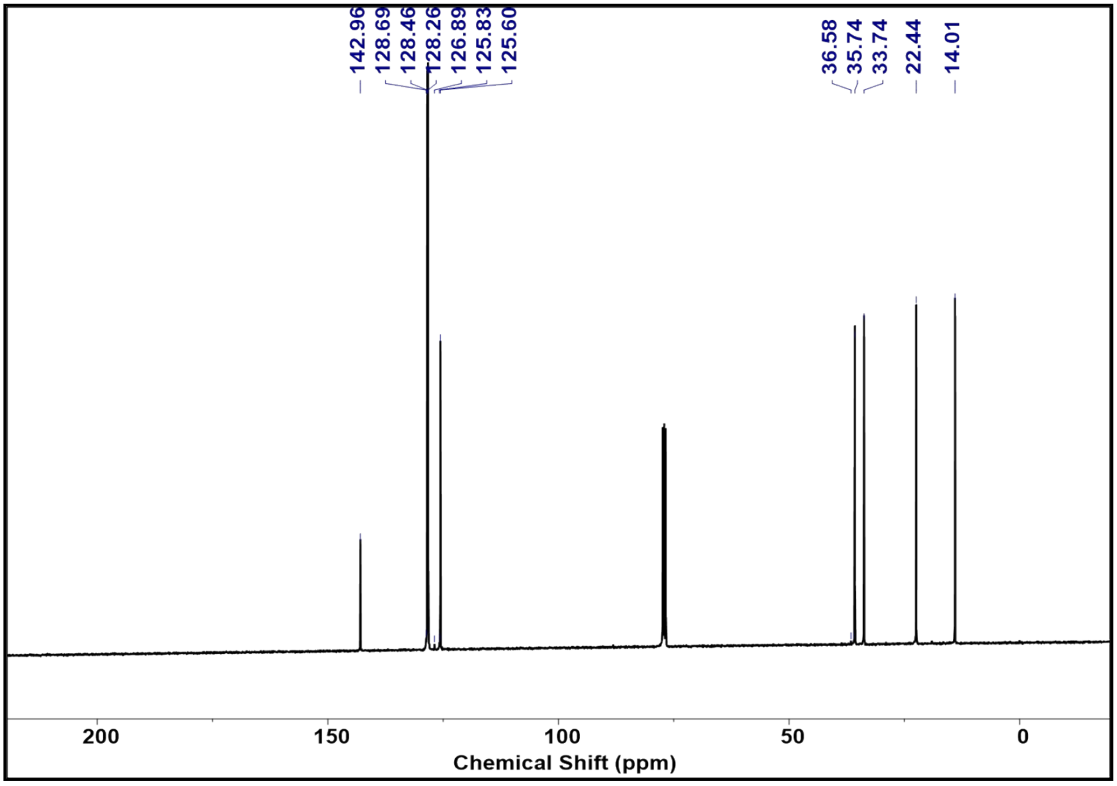

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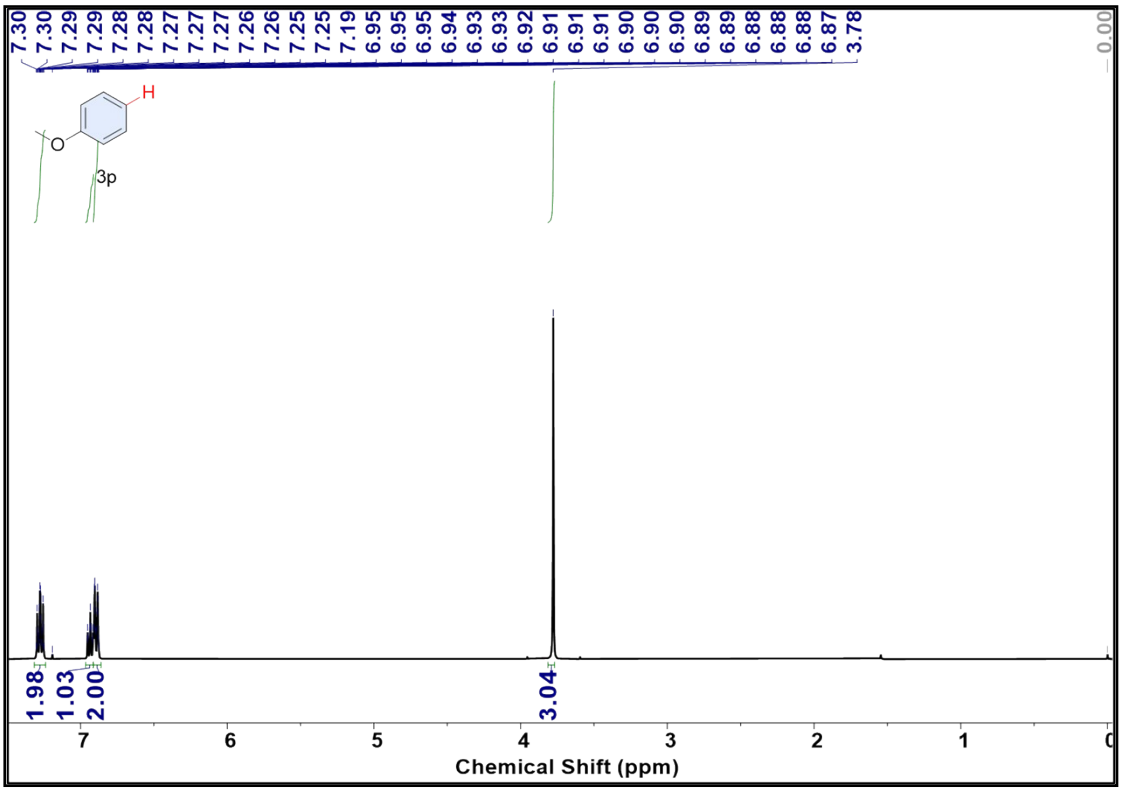

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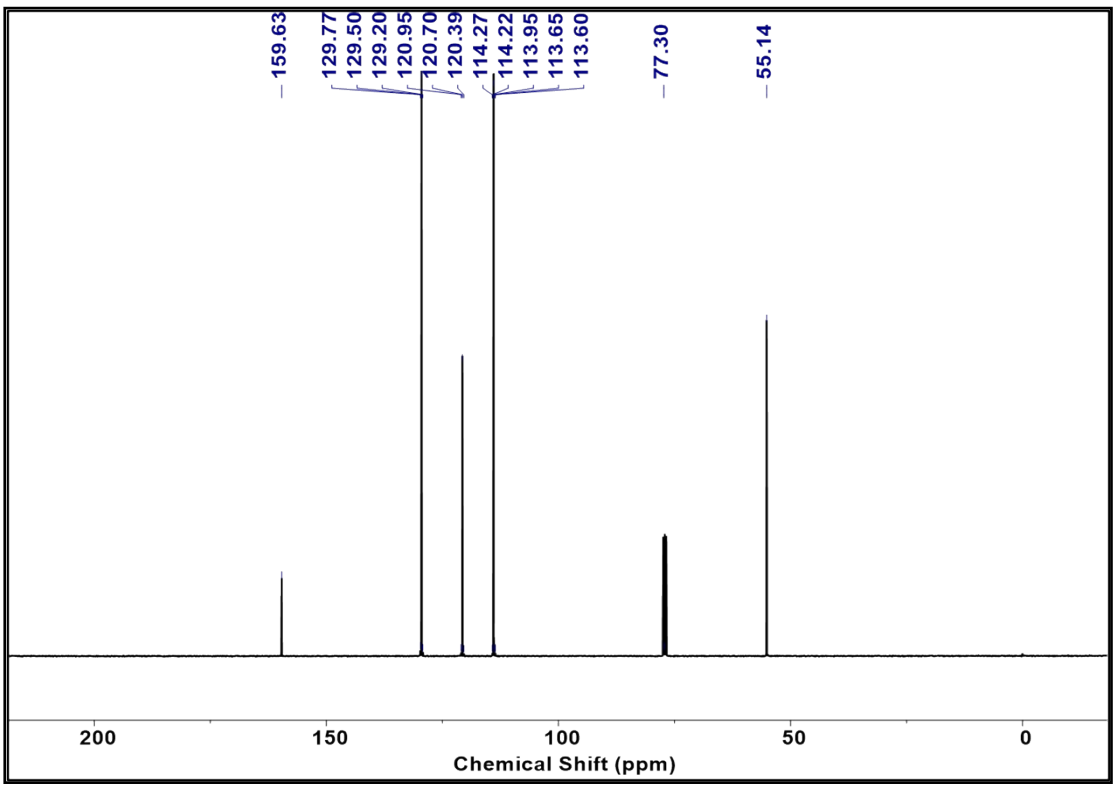

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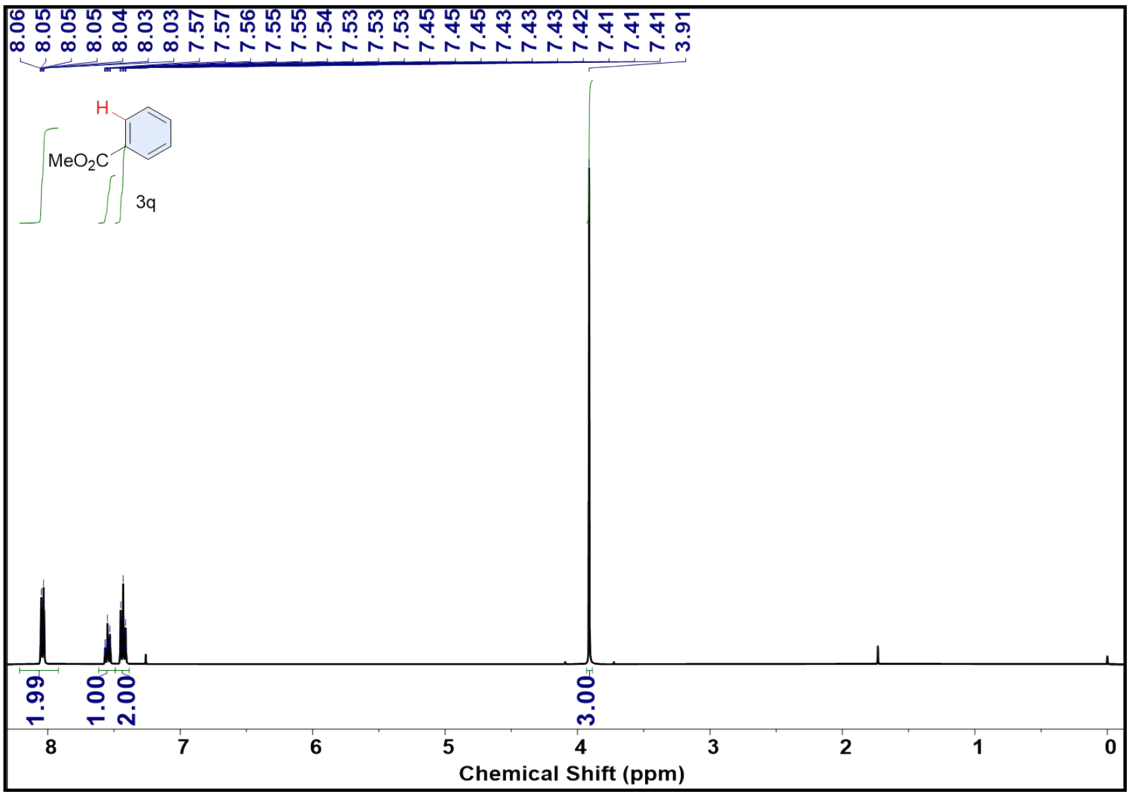

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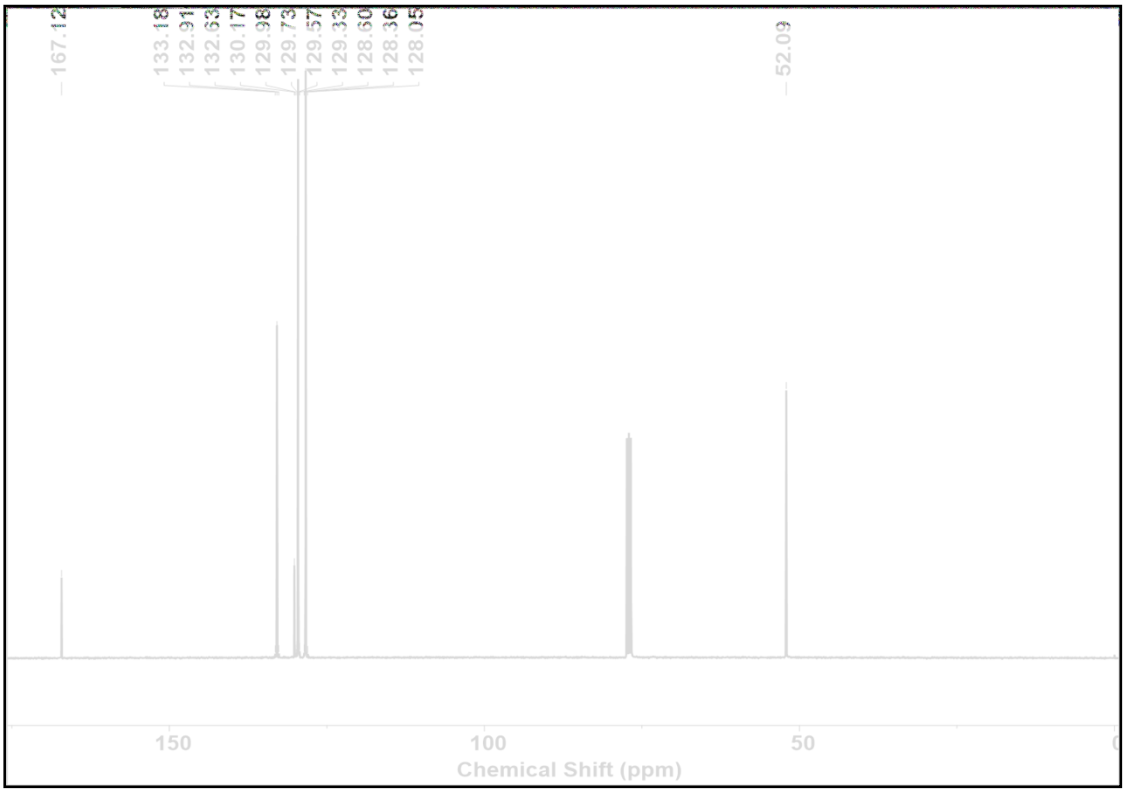

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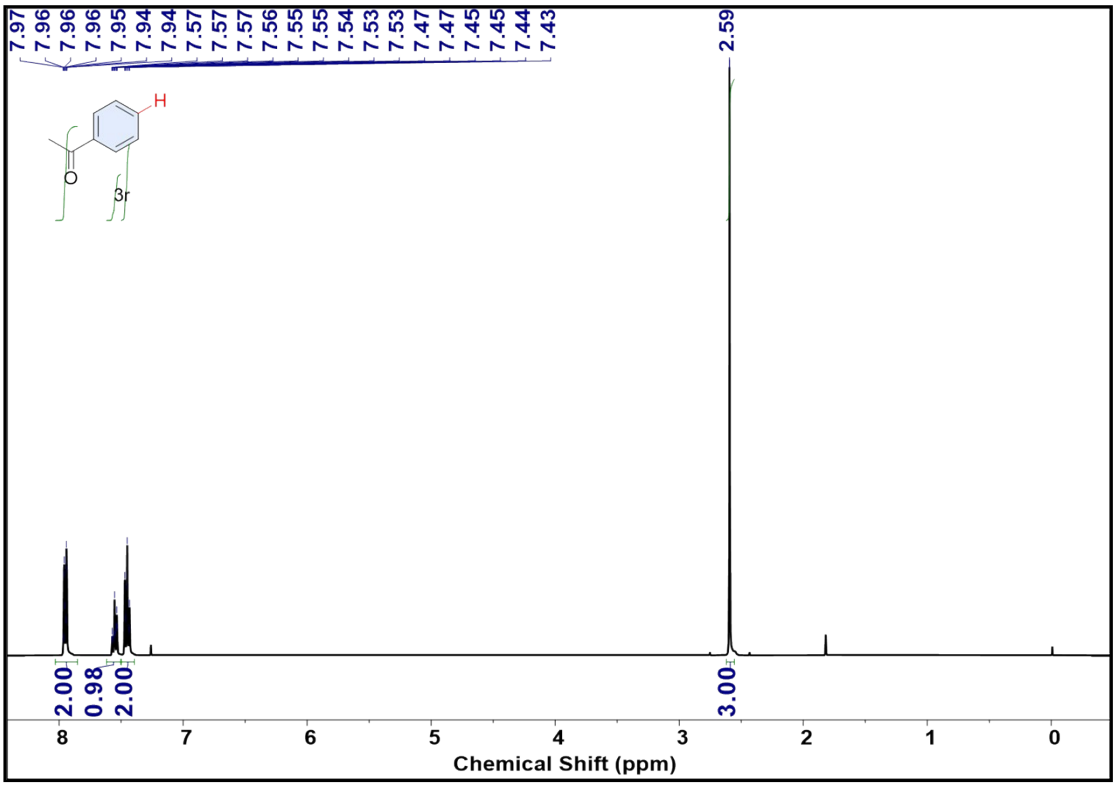

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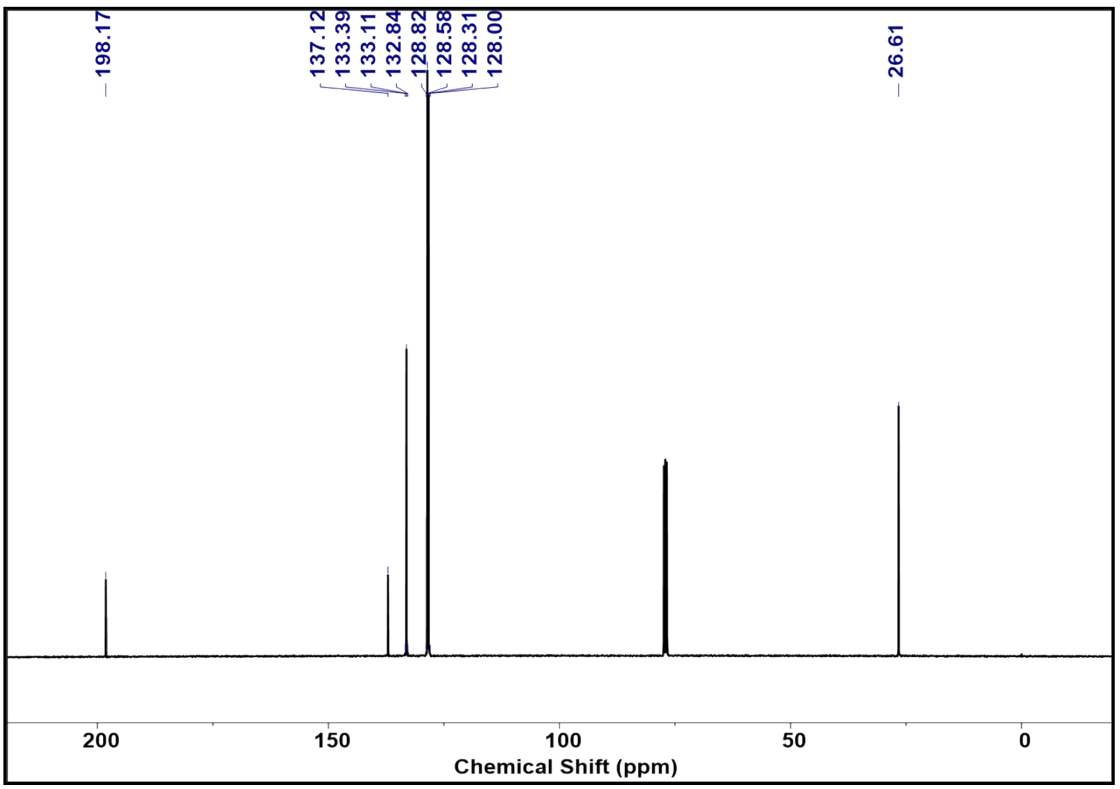

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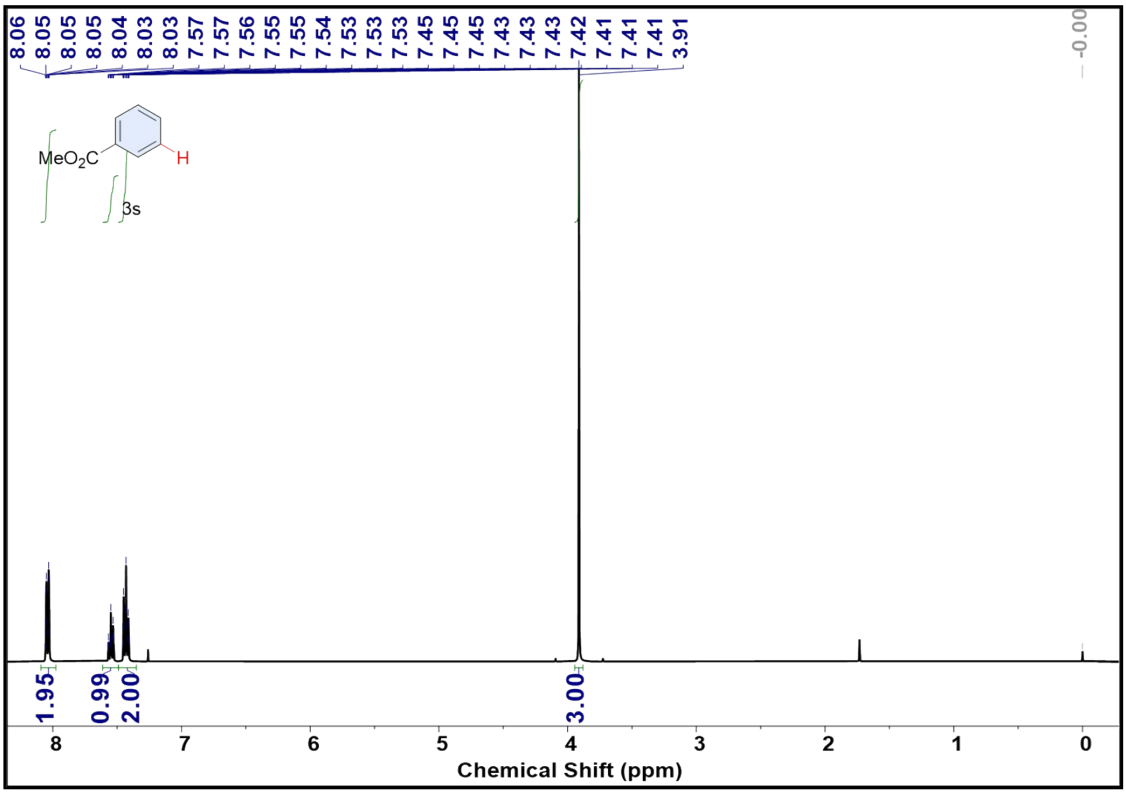

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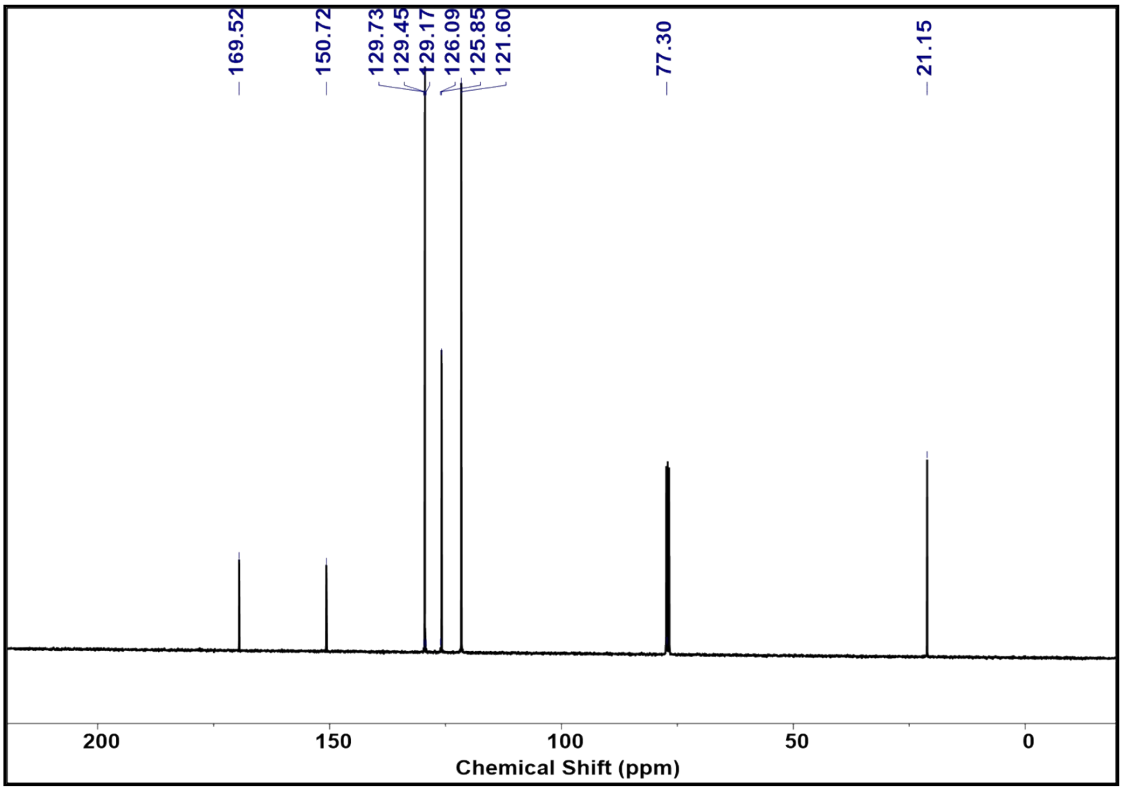

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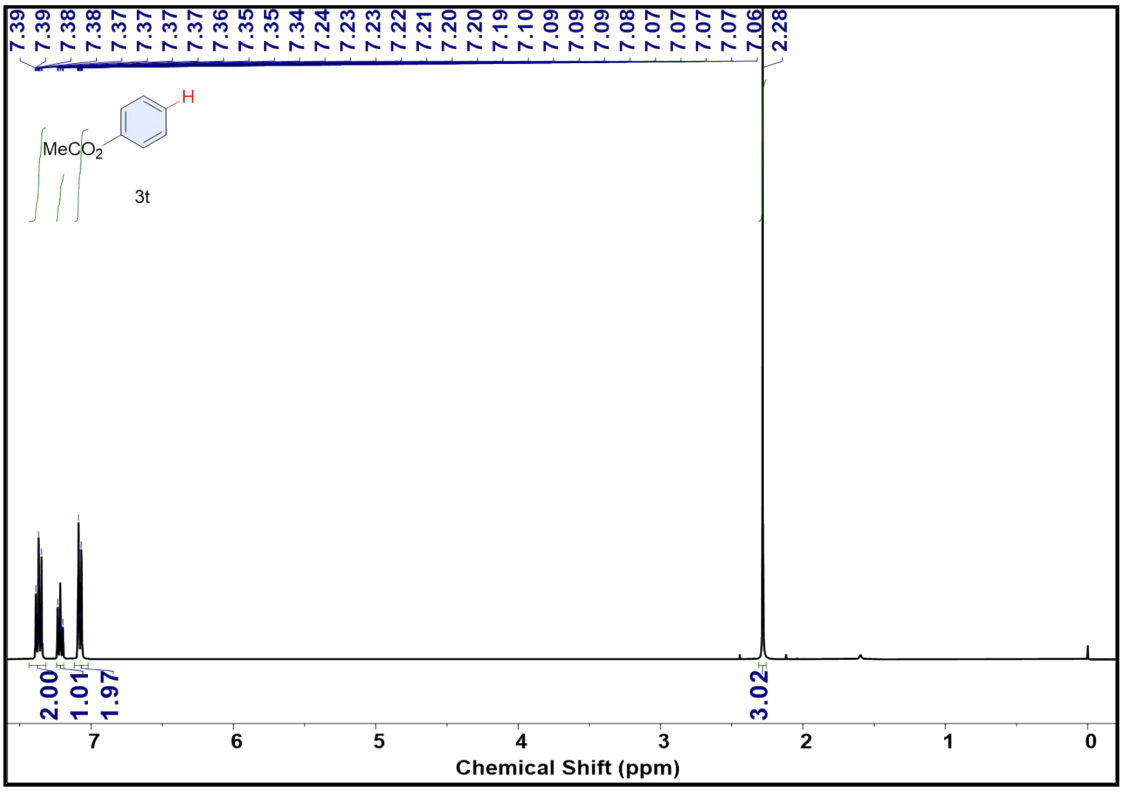
7.39
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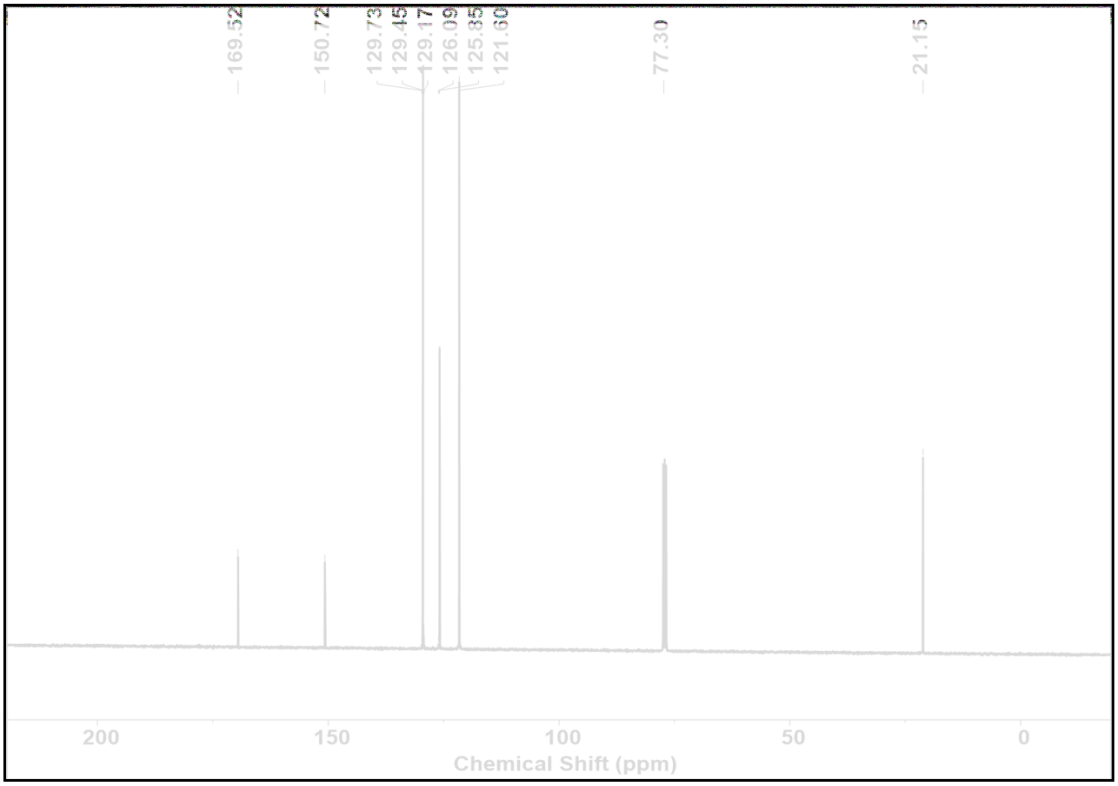
2.28
H
MeCO2
3t
2.00
1.01
1.97
3.02
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{13}C-NMR


169.52
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129.45
129.17
126.09
125.85
121.60
77.30
21.15
200
150
100
50
0
Chemical Shift (ppm)