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Supporting information

A metal free, eco-friendly protocol for the oxidative halogenation of aromatic compound using Highly Efficient and Reusable Graphene Oxide Carbocatalyst

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General:

Experimental section:

Materials and methods

All the reagents and reactants were purchased from commercial suppliers and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 GF245 precoated sheets and component were visualized using a UV-lamp at a wavelength of 254 nm. Column chromatography was performed using silica gel (60-120 mesh).^{1}H and ^{13}C NMR spectra were recorded using an Agilent 500 MHz spectrometer with $CDCl_3$ as the solvent (with TMS as the internal standard). Powder XRD analysis was carried out using a Shimadzu (Maxima 7000 S) using CuKα (λ=1.5418 Å and 1.6 kW X-ray tube with applied voltage and current values as 40 kV and 40 mA) radiation from 20 to 80° 2θ range at scanning speed of 2 min-1. FTIR spectra were recorded with KBr pellets using a Bruker Tensor 27 instrument. The TGA thermograms were recorded on schimadzu 60H DTG apparatus in the range of 30-600°C with a heating rate 10°C/min under nitrogen atmosphere. UV-Visible spectra were recorded on a Perkin Elmer Lambda 25 UV–VIS spectrophotometer. Morphology was investigated on scanning electron microscope (SEM) using Hitachi S-4800, and Transmission Electron Microscopy (TEM) analysis using a S3 PHILIPS model CM 200. Raman analysis was carried out on a STR 500 confocal micro-raman spectrometer.

Preparation of Graphene oxide by improved Hummer's method (IHM):

Graphene Oxide was prepared by improved hummer`s method: In 9:1 a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL), natural graphite flakes (3g,) were suspended and then $KMnO_4$ (18.0 g,) was added slowly with a slight exotherm of 35-40 °C. The reaction mixture was heated to 50-60 °C and stirred for 12 h. The reaction mixture was cooled to RT and poured on ice cubes (400g) followed by the addition of H_2O_2 (30 %, 3 mL). The resultant suspension was filtered and centrifuged for 4 h (4000 rpm). The supernatant layer was decanted and the residual solid material

was washed sequentially using water (2 x 200 mL), 30% HCl (2 x 200 mL), and ethanol (2 x 200 mL). After this, the remaining solid material was coagulated using ether (200 mL), and the resulting suspension was filtered. The processed dark brown oxidized material is graphite oxide. Graphite oxide was further exfoliated into graphene oxide using ultrasonic probe VCX 750, Sonics & Materials, USA (tip diameter: 13 mm, intensity: 50%, time: 30 minutes). The obtained solid mass was vacuum-dried overnight, 6 g of graphene oxide was obtained and was thoroughly characterized using various spectral techniques.

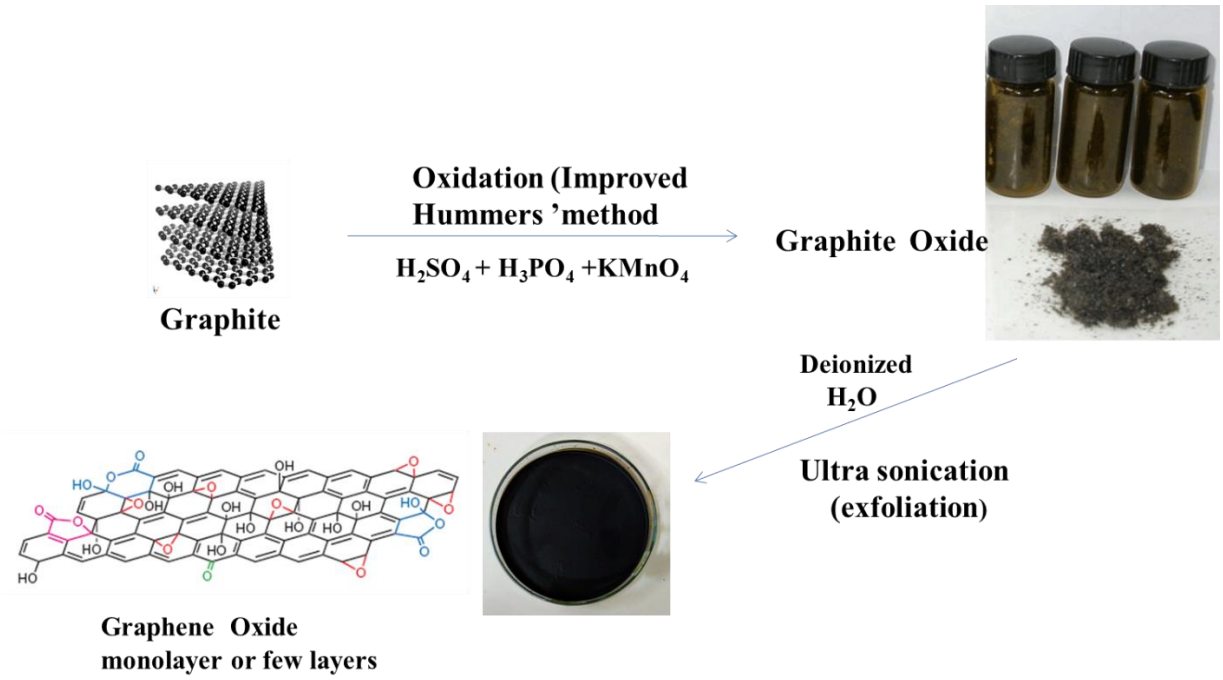


Figure S1: Preparation of Graphene oxide by improved Hummer's method (IHM)[1]

Characterization of Graphene Oxide (GO) and recycled Graphene Oxide

The powder XRD pattern of GO **(Figure S2a)** showed a sharp diffraction peak at 2θ =9.4 and a small intensity peak at 42.14 which correspond to (001) and (101) planes respectively indicating the oxidation of graphite to graphene oxide. [2]

The powder XRD pattern of reused GO showed a sharp diffraction peak at 2θ=10.0 and a small intensity peak at 42.58 which correspond to (001) and (101) planes respectively of GO. We observed peak around 26 which corresponds to formation of rGO in small amounts. But from the obtained yields the catalytic activity of GO was found unaltered **(Figure S2b).**

The presence of various oxygenated functionalities on the surface of GO was confirmed by FTIR analysis. **Figure S2c** shows the IR spectrum of GO, the peaks at 3386, 1727, 1638, 1211, 1055 cm^{-1} should be attributed to O–H stretching vibrations, C=O stretching vibrations from carbonyl and carboxylic groups, skeletal vibrations from unoxidized graphene domains, C–OH stretching vibrations and C–O stretching vibrations respectively.[1]

The presence of oxygenated functionalities (like carboxyl, epoxy, and hydroxyl) on the surface of recycled GO was confirmed from the FTIR study. The peak present at 1722 cm^{-1} corresponds to the stretching vibration of carbonyl (C=O) and the C-O stretching vibration of the epoxy group appeared at 1192 cm^{-1}. The skeletal vibration of the graphitic domains emerged around 1631 cm^{-1} and a peak at 1045 cm^{-1} can be assigned as C-O stretching vibration. **(Figure S2d).**

The synthesized GO was further analysed by Raman spectroscopy **(Figure S2e).** Since it is a very helpful method for the characterization of carbon-based materials, it revealed two prominent characteristic peaks. One is a G-band at around 1596.0 cm^{-1} which is because of stretching of C−C bonds common to sp^2 carbon network and the other one is a D-band at around 1349.8 cm^{-1} which is due to the chaos in that network ID/IG, the intensity ratio of D and G bands was also calculated, and its value was found to be 1.06 which designates the introduction of anarchy in the π-network of graphite. [1]

Raman analysis of the reused GO was also performed. In Raman spectra of GO, two peaks around 1357.31 and 1596.79 cm^{-1} are characteristic of D and G band respectively (Figure 5). The intensity ratio of two characteristic bands (ID/IG) was found to be ~0.90 and it indicated little or inconsequential changes over that of fresh GO **(Figure S2f).**

The UV-Vis spectrum of graphene oxide **(Figure S2g)** displays a strong absorption peak at 220 nm, which is the attribute to the π→π* transition of graphitic C–C bonds and a shoulder at ~305 nm is assigned to the n → π* transitions of C=O bonds. [3]

The recovered GO was further characterized by UV–Vis spectrum as shown in **Figure S2h.** The UV-Vis spectrum of graphene oxide exhibits a strong absorption peak at 222 nm, which is attributable to the π→π*transition of graphitic C–C bond and a shoulder at 305 nm are assigned to the n → π* transitions of C=O bond**.**

TGA analysis of synthesized GO shows weight loss in two steps **(Figure S2i).** First, Weight loss of around 10% at 100°C due to the loss of the intercalated water molecules is displayed, and the second drastic weight loss of around 85% at above 180 °C signifies decomposition of various oxygenated functional groups decorated on graphite oxide nanosheet. [3]

Further to check the quality of the recovered GO, Thermal gravimetric analysis (TGA) was performed (Figure S2j). A Major weight loss was observed at ~100 °C, signifying the loss of water molecules, and minor weight loss was observed around 190 °C due to the removal of oxygenated functional groups. From the results, it was concluded that GO maintained its original catalytic activity even after repeated use **(Figure S2j).**

To further gain information regarding the structure of catalyst we took TEM images of GO, and it showed the presence of distinct multi-layered GO sheet **(Figure S2k).**[3]

The TEM image reveals the morphology of reused GO remains unchanged as the layer structure of the GO sheet was found intact, with little amount of reduction in oxygen functionalities of the recovered GO after fourth recycle also supports the preservation of the catalytic activity **(Figure S3l).**

Then to get a fair idea regarding the structure and shape of GO, SEM images were taken. **Figure S2m** shows the SEM image of graphite oxide which indicates that it possesses a sheet-like structure.

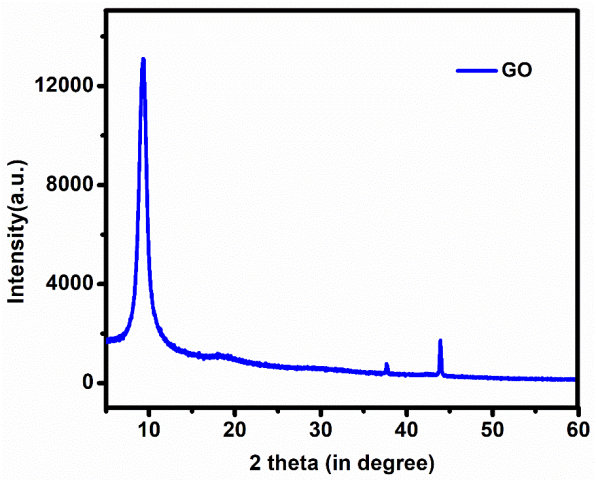


Figure S2a. X-ray diffraction pattern of GO

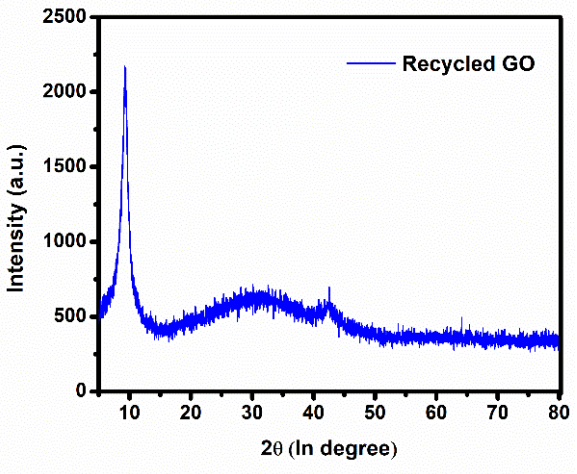


Figure S2b. X-ray diffraction pattern of recycled GO

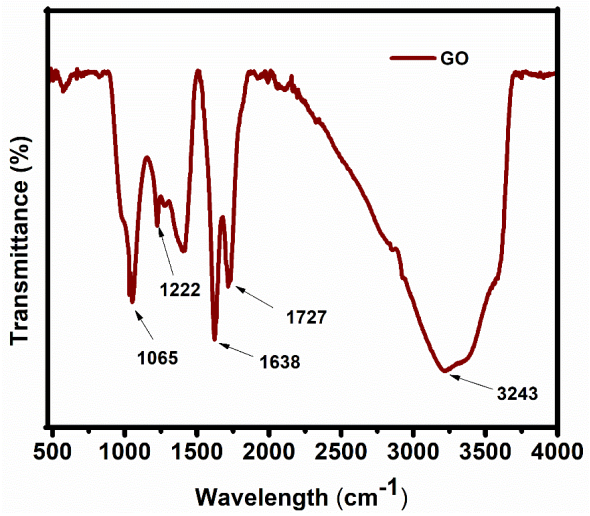


Figure S2c. FTIR spectra of GO

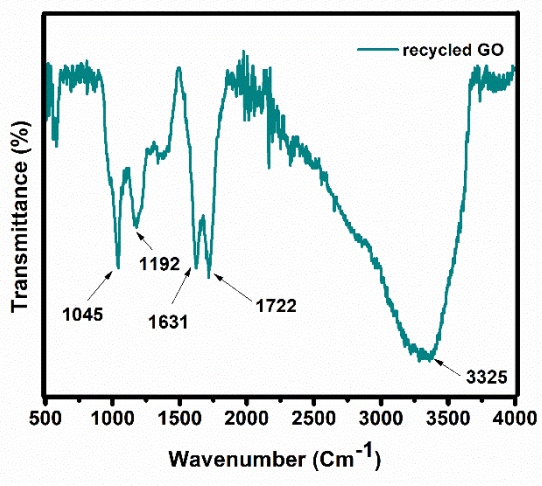


Figure S2d FTIR spectrum of Recycled GO

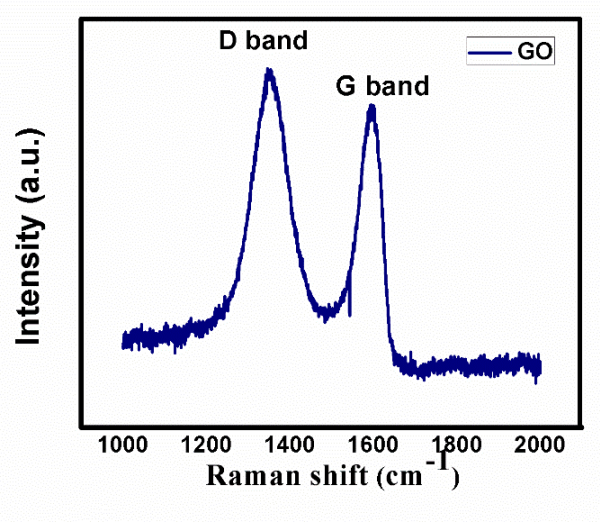


Figure S2e. Raman spectra of GO

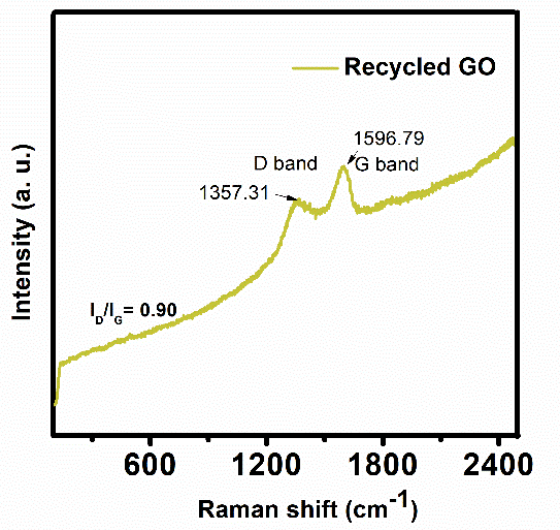


Figure S2f. Raman spectra of recycled GO

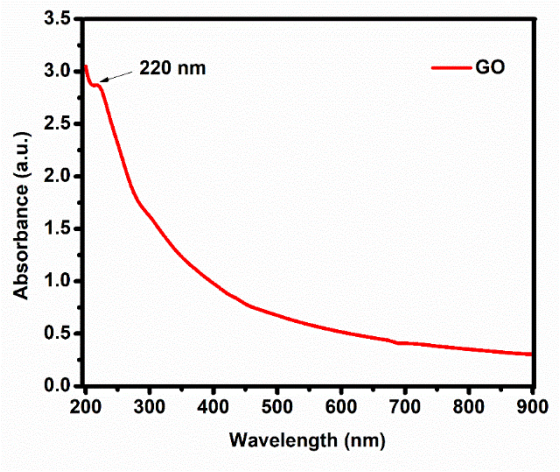


Figure S2g. UV−visible spectra of GO

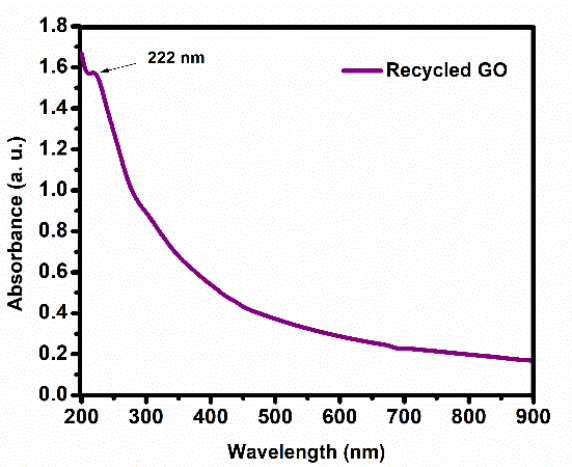


Figure S2h. UV−visible spectrum of recycled GO

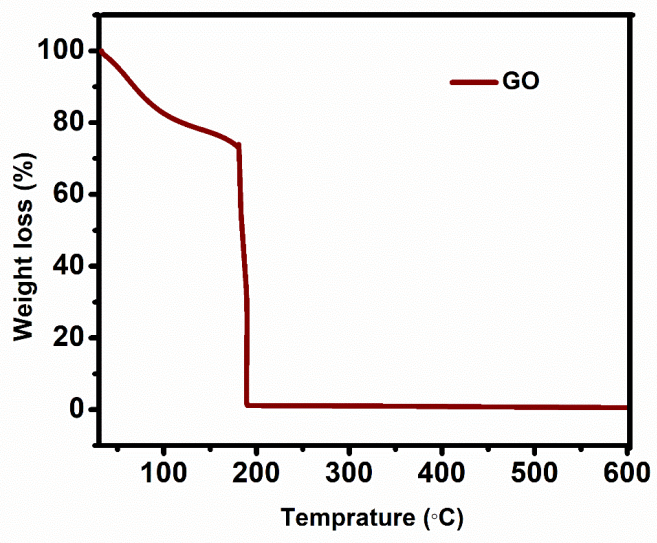


Figure S2i. Thermogravimetric analysis (TGA) of GO

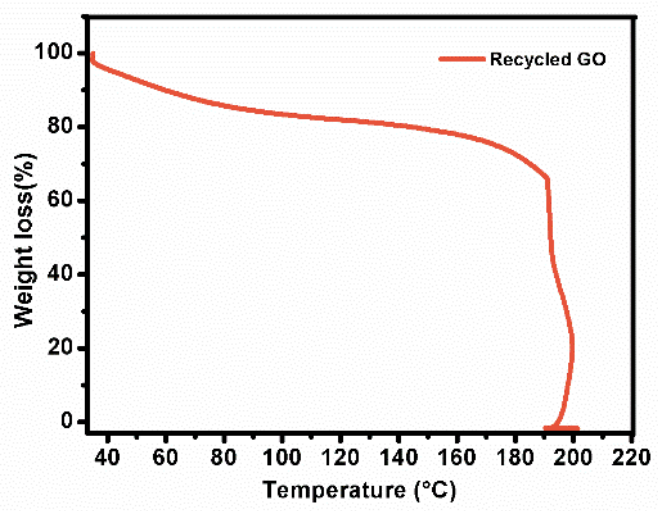


Figure S2j. (TGA) of recycled GO

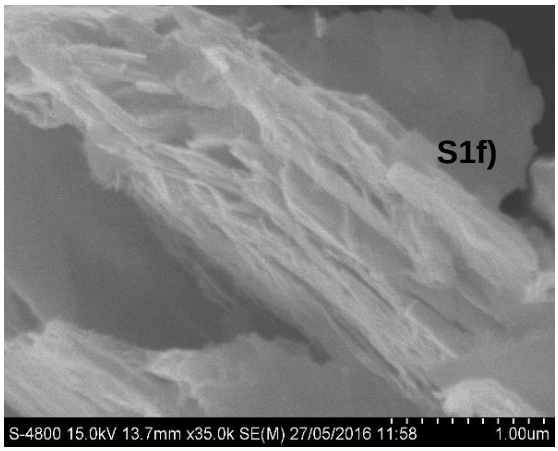


Figure S2k. Scanning electron microscope (SEM) images of GO, scale bar 1µm;

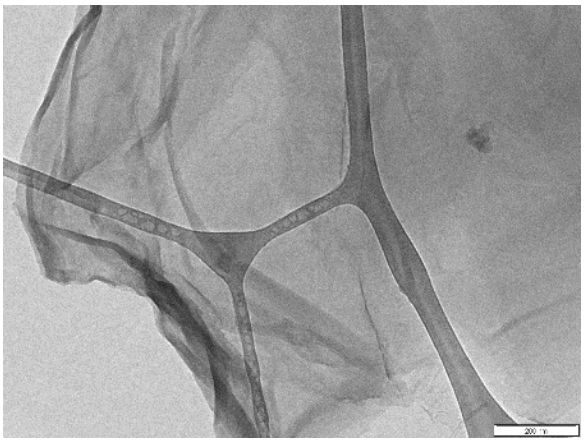


Figure S2l. TEM analysis of GO

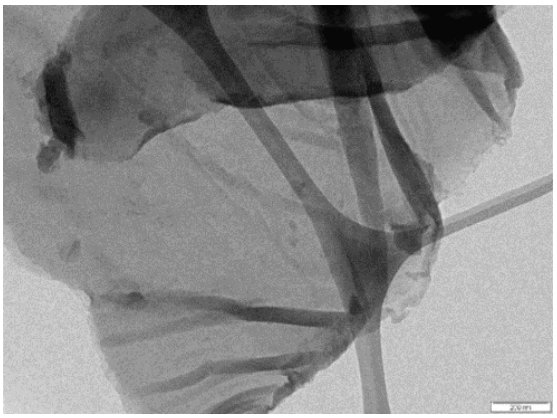


Figure S2m. TEM analysis of recycled GO

The catalytic activities of cyclohexane oxidation over different catalyst

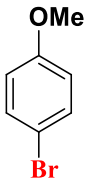
The effectiveness of the various catalysts in bromination of anisole was shown in **Table S1.** Graphene Oxide catalytic system demonstrated a high yield of p-bromoanisole in comparison to other catalysts, the metal free strong catalytic performance over safe halogenating agent and reusability upto four cycle. Graphene oxide might be viewed as a notable metal free heterogeneous catalyst for the bromination of aromatic compounds as a results.

Table S1: The catalytic activities of cyclohexane oxidation over different catalyst

Catalyst	Brominating Agent	Time(h)	Yield	Reference
CAN	LiBr	1	99	[4]
HZSM-5	KBr	2	98	[5]
NH_4VO_3	AlBr3	8	96	[6]
NH_4VO_3	HBr	24	48	[7]
Graphene oxide	KBr	12	99	Present Work

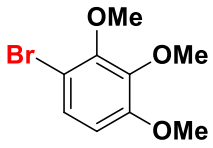
Spectral data of selected brominated compounds:

1] 1-bromo-4-methoxybenzene(2b)



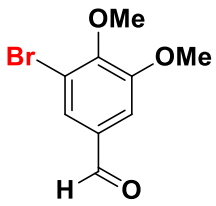
^{1}H NMR (500 MHz, cdcl$_3$) δ 7.38 – 7.34 (m, 2H), 6.78 – 6.75 (m, 2H), 3.76 (s, 3H).^{13}C NMR (126 MHz, cdcl$_3$) δ 158.67 (s), 132.22 (s), 115.75 (s), 112.79 (s), 55.41 (s).

2] 1-bromo-2,3,4-trimethoxybenzene(2c)



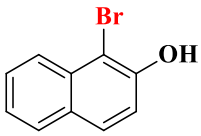
^{1}H NMR (500 MHz, cdcl$_3$) δ 7.18 (d, *J* = 9.0 Hz, 1H), 6.56 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H).^{13}C NMR (126 MHz, cdcl$_3$) δ 150.94 (s), 143.49 (s), 126.81 (s), 108.61 (s), 61.02 (d, *J* = 9.5 Hz), 56.13 (s).

3] 3-bromo-4,5-dimethoxybenzaldehyde(2d)



^{1}H NMR (500 MHz, cdcl$_3$) δ 10.18 (s, 1H), 7.41 (s, 1H), 7.05 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 190.79 (s), 154.74 (s), 148.85 (s), 126.64(s), 120.39 (s), 115.43 (s), 110.10 (s), 56.57 (s), 56.15 (s).

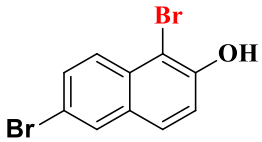
4] 1-bromonaphthalen-2-ol (2e)



^{1}H NMR (500 MHz, cdcl$_3$) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 5.95 (s, 1H). ^{13}C NMR

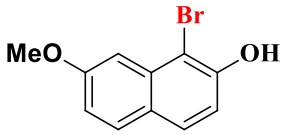
(126 MHz, cdcl$_3$) δ 150.57 (s), 132.28 (s), 129.67 (s), 129.32 (s), 128.26 (s), 127.83 (s), 125.32 (s), 124.13 (s), 117.15 (s), 106.13 (s).

5] 1,6-dibromonaphthalen-2-ol (2f)



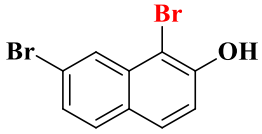
^{1}H NMR (500 MHz, cdcl$_3$) δ 7.92 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.27 (s, 1H), 5.94 (s, 1H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 150.90 (s), 130.97 (d, *J* = 9.5 Hz), 130.59 (s), 130.05 (s), 128.35 (s), 127.20 (s), 118.34 (s), 117.99 (s), 106.08 (s).

6] 1-bromo-7-methoxynaphthalen-2-ol (2g)



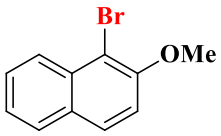
^{1}H NMR (500 MHz, dmso) δ 10.46 (s, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, dmso) δ 159.35 (s), 153.40 (s), 134.67 (s), 130.59 (s), 129.03 (s), 124.29 (s), 115.95 (s), 104.38 (s), 103.93 (s), 55.55 (s).

7] 1,7-dibromonaphthalen-2-ol (2h)



^{1}H NMR (500 MHz, dmso) δ 10.81 (s, 1H), 8.12 (d, *J* = 1.9 Hz, 1H), 7.82 (ddd, *J* = 8.4, 5.3, 3.1 Hz, 2H), 7.47 (dd, *J* = 10.2, 2.3 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, dmso) δ 153.92 (s), 134.47 (s), 131.06 (s), 129.54 (s), 127.58 (s), 126.99 (s), 126.84 (s), 122.09 (s), 119.31 (s), 103.37 (s).

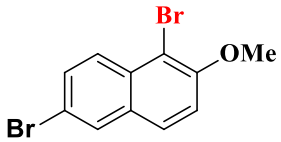
8] 1-bromo-2-methoxynaphthalene (2i)



^{1}H NMR (500 MHz, cdcl$_3$) δ 8.23 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 14.8, 8.6 Hz, 2H), 7.57 (t, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.26 (s, 1H), 4.02 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz,

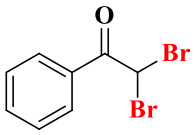
cdcl$_3$) δ 153.82 (s), 133.11 (s), 129.79 (s), 128.96 (s), 128.03 (s), 127.73 (s), 126.10 (s), 124.30 (s), 113.58 (s), 108.62 (s), 57.04 (s).

9] 1,6-dibromo-2-methoxynaphthalene (2j)



^{1}H NMR (500 MHz, cdcl$_3$) δ 8.01 (d, *J* = 9.1 Hz, 1H), 7.85 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.18 (s, 1H), 3.95 (s, 3H).^{13}C NMR (126 MHz, cdcl$_3$) δ 153.98 (s), 131.72 (s), 131.01 (s), 130.53 (s), 129.81 (s), 128.03 (s), 127.98 (s), 118.15 (s), 114.45 (s), 108.64 (s), 56.93 (s).

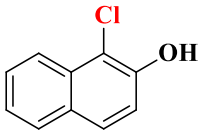
10] 2,2-dibromo-1-phenylethanone (2k)



^{1}H NMR (500 MHz, dmso) δ 8.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.90 (s, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.62 – 7.57 (m, 2H). ^{13}C NMR (126 MHz, dmso) δ 187.30 (s), 135.01 (s), 131.25 (s), 129.83 (s), 129.54 (s), 43.74 (s).

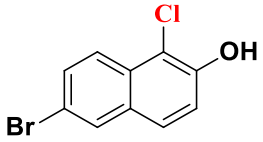
Spectral data of selected chlorinated compounds:

1] 1-chloronaphthalen-2-ol



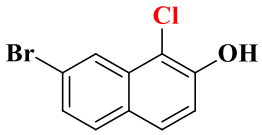
^{1}H NMR (500 MHz, cdcl$_3$) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.28 (s, 1H), 5.96 (s, 1H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 149.34 (s), 131.05 (s), 129.45 (s), 128.43 (s), 128.21 (s), 127.57 (s), 124.14 (s), 122.77 (s), 117.23 (s), 113.32 (s).

2] 6-bromo-1-chloronaphthalen-2-ol



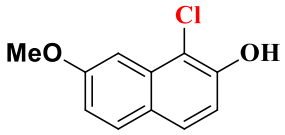
^{1}H NMR (500 MHz, cdcl$_3$) δ 7.94 – 7.90 (m, 2H), 7.62 (dd, *J* = 12.8, 5.4 Hz, 2H), 7.28 (s, 1H), 5.95 (s, 1H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 149.73 (s), 130.78 (s), 130.43 (s), 130.09 (s), 129.67 (s), 127.46 (s), 124.64 (s), 118.41 (s), 117.99 (s), 113.49 (s).

3] 7-bromo-1-chloronaphthalen-2-ol



^{1}H NMR (500 MHz, dmso) δ 10.77 (s, 1H), 8.16 (d, *J* = 1.7 Hz, 1H), 7.85 (dd, *J* = 15.7, 8.8 Hz, 2H), 7.52 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H).^{13}C NMR (126 MHz, dmso) δ 152.67 (s), 133.16 (s), 131.01 (s), 128.69 (s), 127.33 (s), 126.87 (s), 124.48 (s), 121.80 (s), 119.53 (s), 111.65 (s).

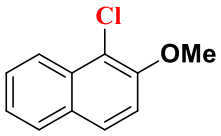
4] 1-chloro-7-methoxynaphthalen-2-ol



^{1}H NMR (500 MHz, dmso) δ 10.40 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 2.7 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.91 (s, 3H).

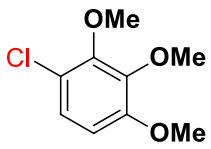
^{13}C NMR (126 MHz, dmso) δ 159.18 (s), 152.08 (s), 133.38 (s), 130.45 (s), 128.17 (s), 124.08 (s), 116.07 (d, *J* = 9.0 Hz), 111.92 (s), 101.59 (s), 55.64 (s).

5] 1-chloro-2-methoxynaphthalene



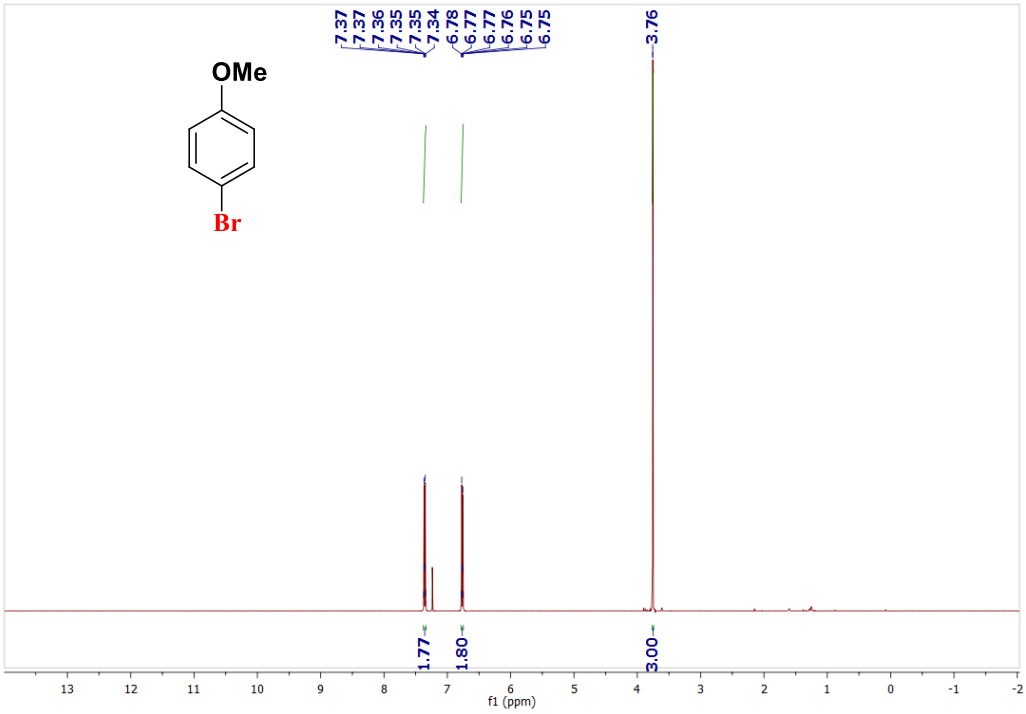
^{1}H NMR (500 MHz, cdcl$_3$) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.63 (dd, *J* = 18.9, 8.6 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 152.52 (s), 131.85 (s), 129.49 (s), 128.02 (s), 127.99 (s), 127.47 (s), 124.31 (s), 123.42 (s), 116.78 (s), 113.62 (s), 56.92 (s).

6] 1-chloro-2,3,4-trimethoxybenzene

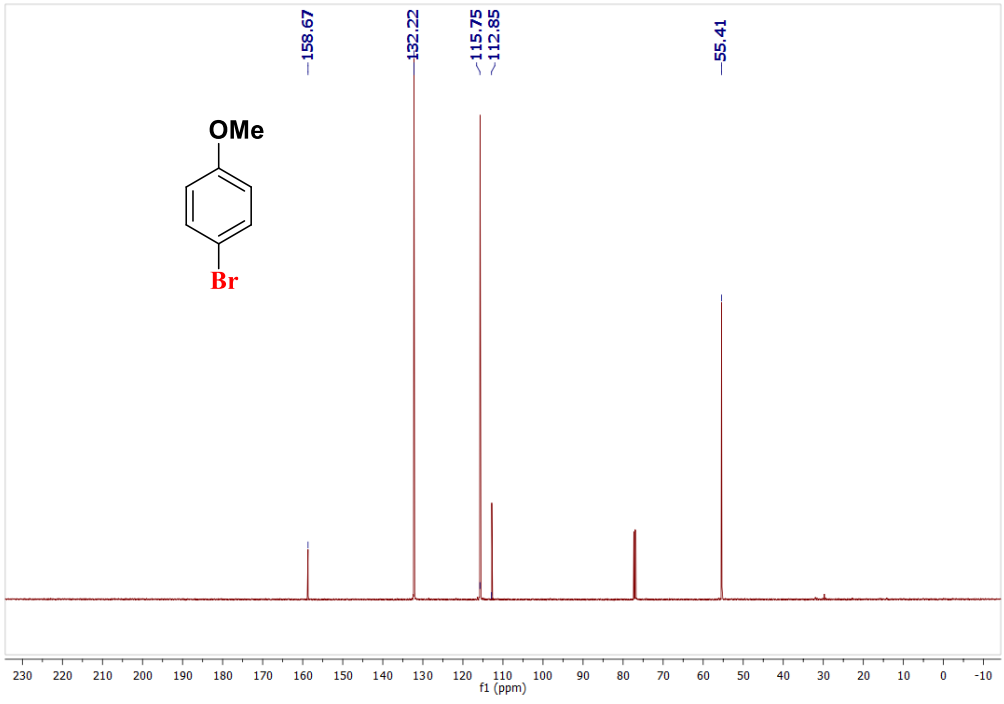


^{1}H NMR (500 MHz, cdcl$_{3}$) δ 7.15 (d, *J* = 9.0 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H), 3.96 (s, 3H).

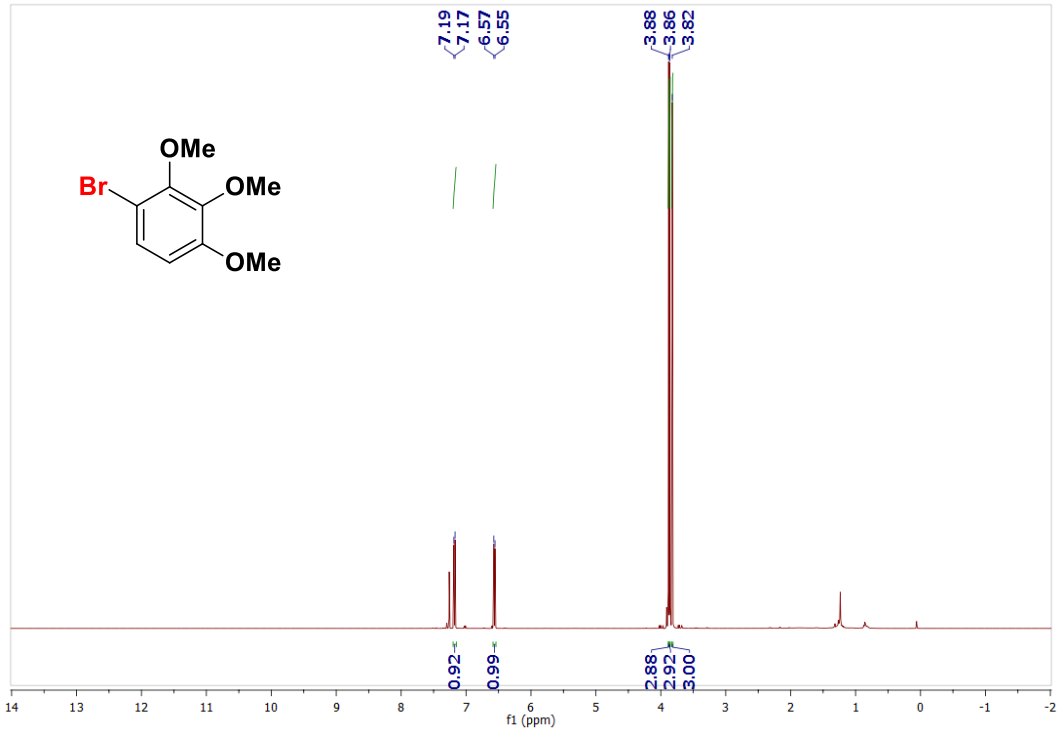
^{1}H and ^{13}C NMR Spectra



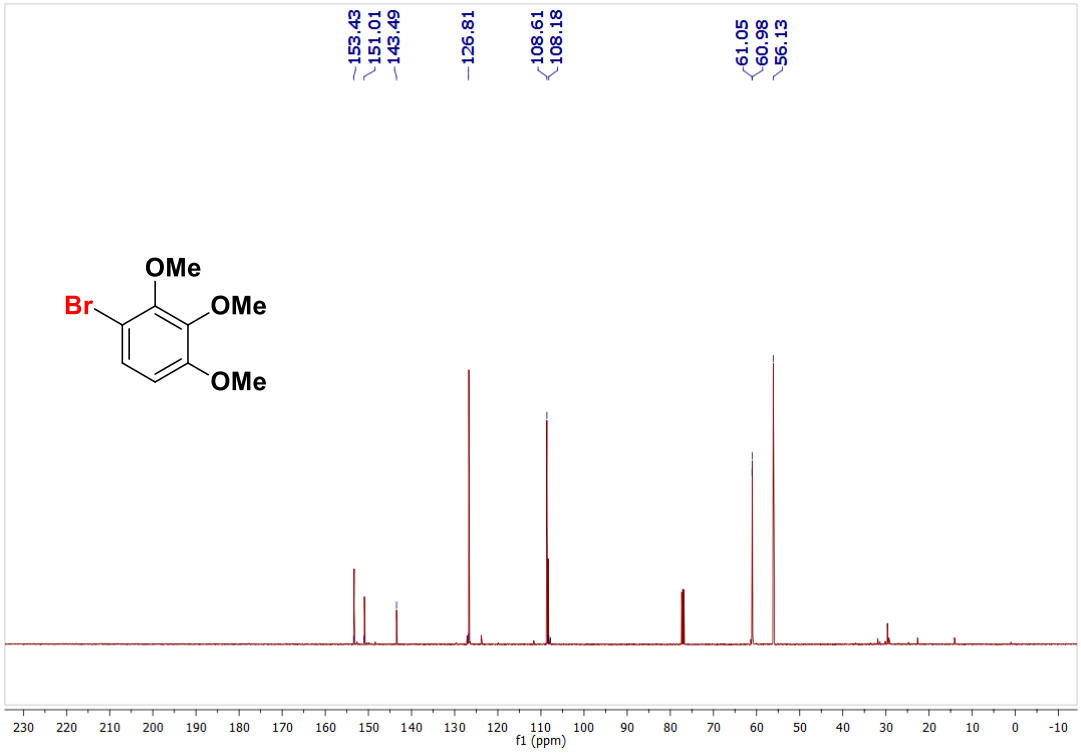
^{1}H NMR 1-bromo-4-methoxybenzene (2b)



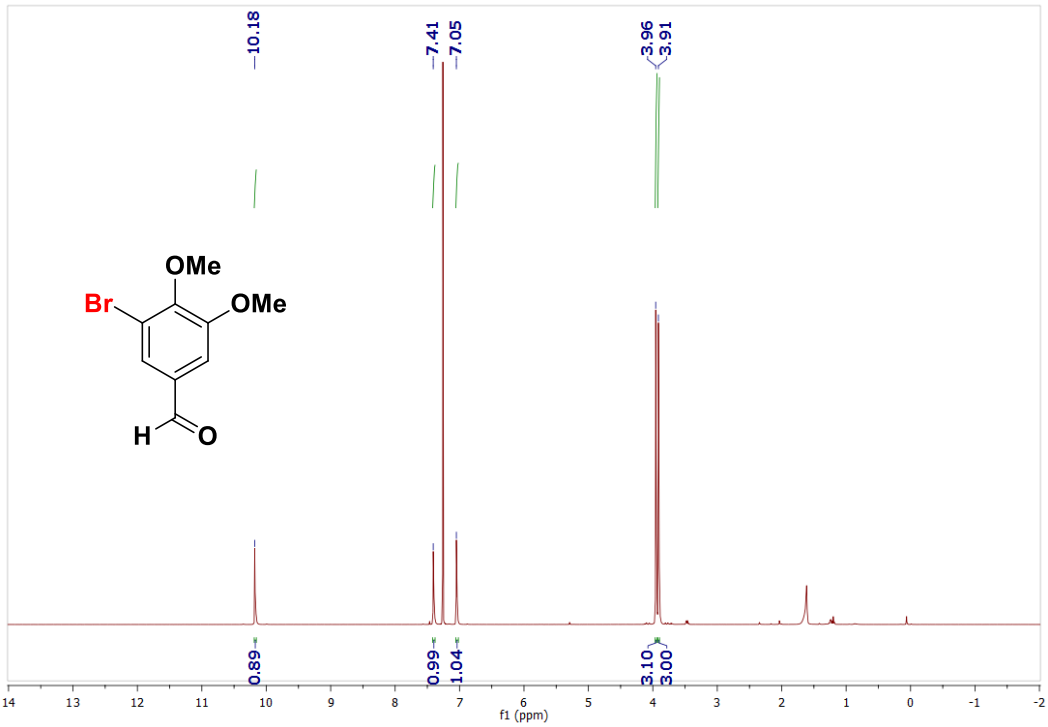
^{13}C NMR 1-bromo-4-methoxybenzene (2b)



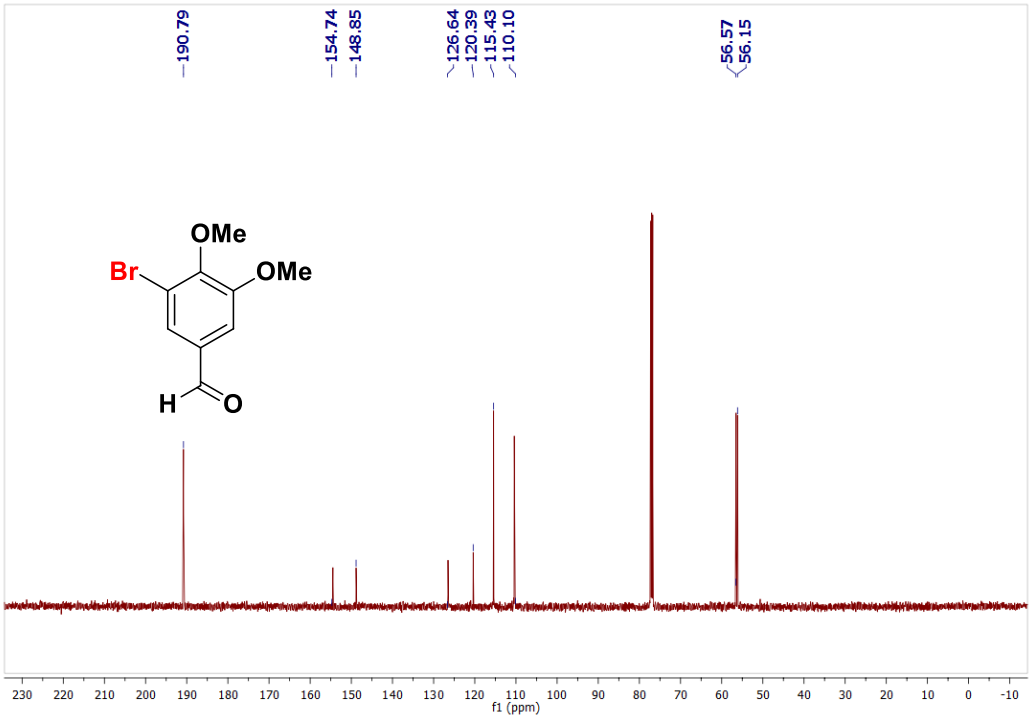
[1] H NMR 1-bromo-2,3,4-trimethoxybenzene(2c)



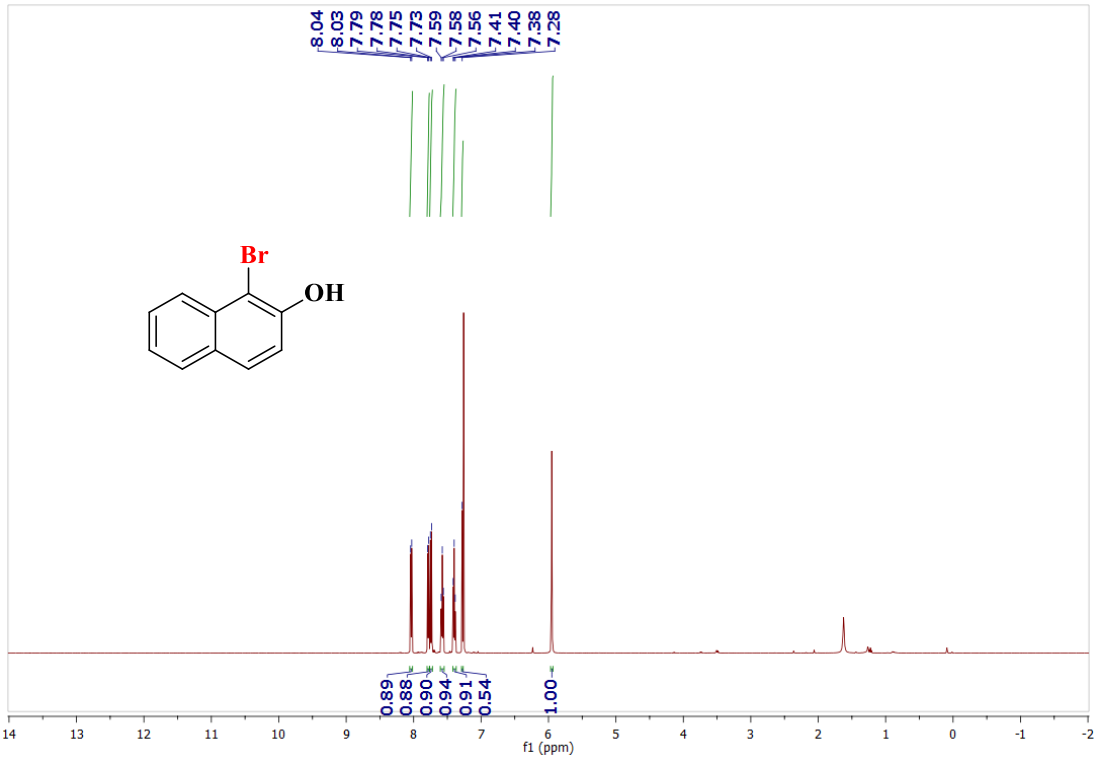
[13]C NMR 1-bromo-2,3,4-trimethoxybenzene (2c)



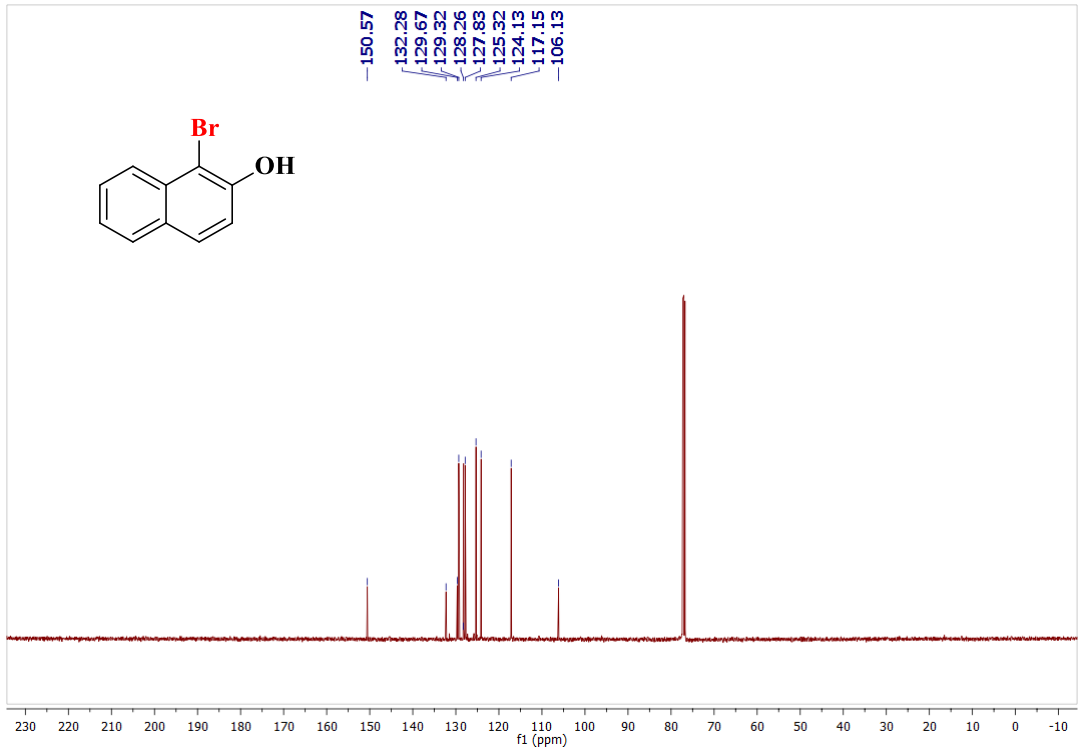
^{1} H NMR 3-bromo-4,5-dimethoxybenzaldehyde



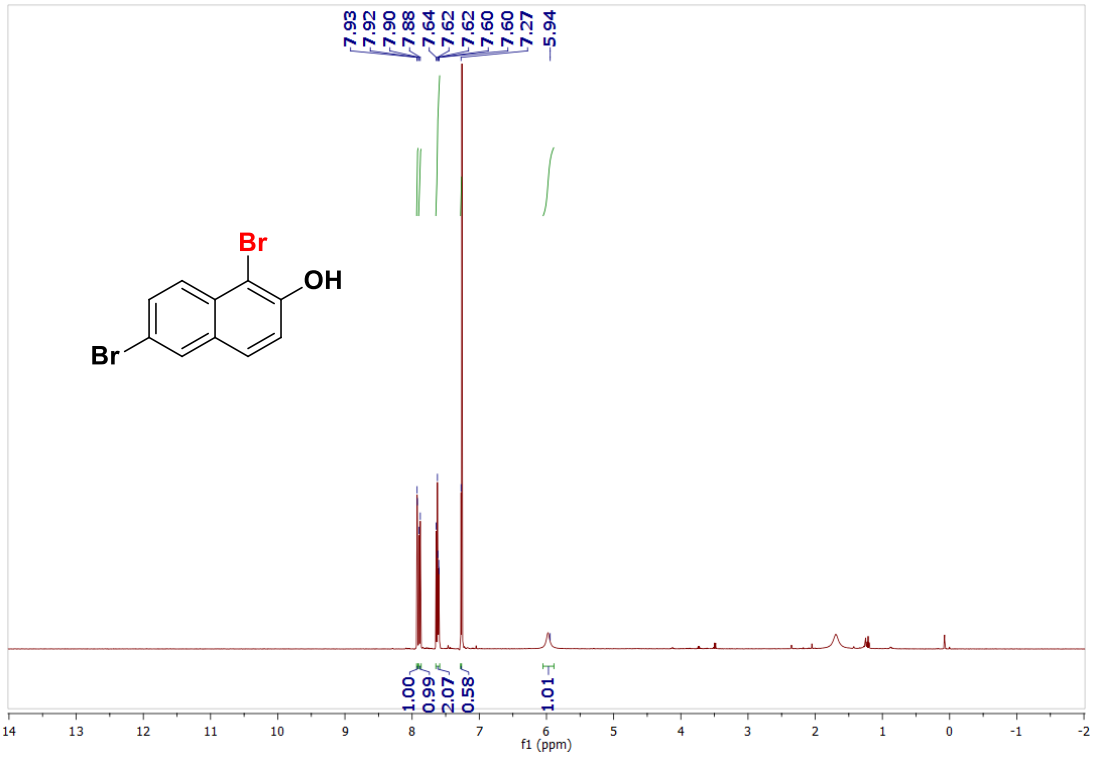
^{13}C NMR 3-bromo-4,5-dimethoxybenzaldehyde



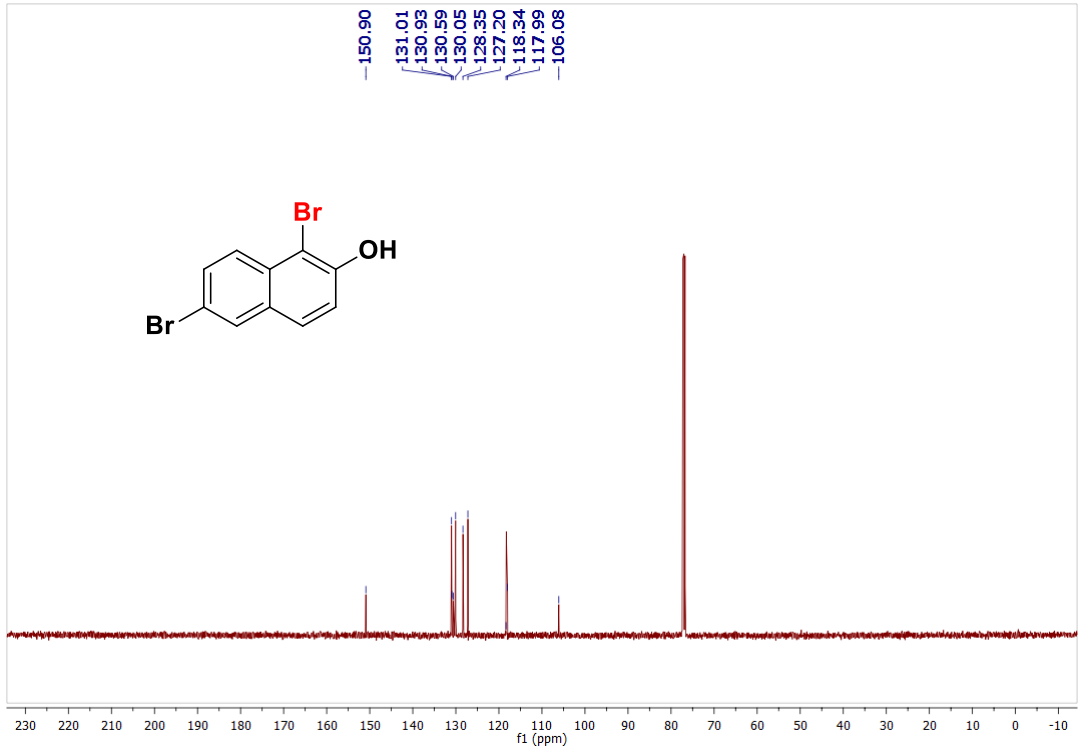
[1] H NMR 1-bromonaphthalen-2-ol



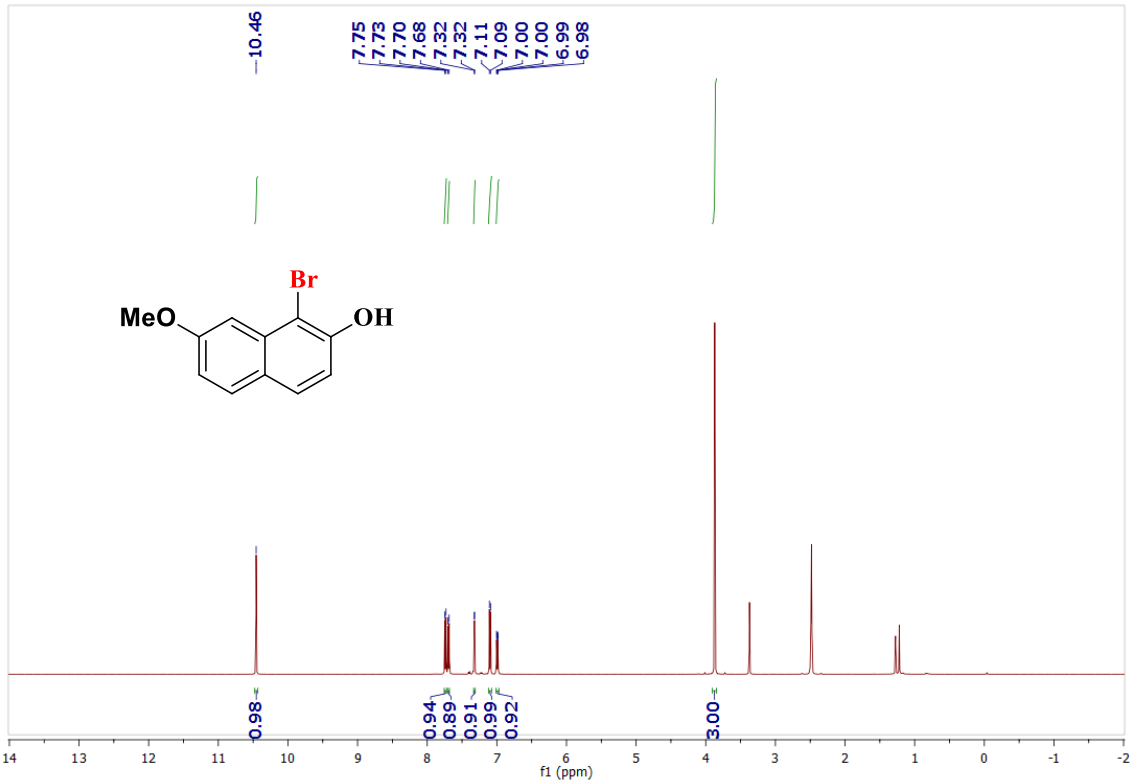
[13]C NMR 1-bromonaphthalen-2-ol



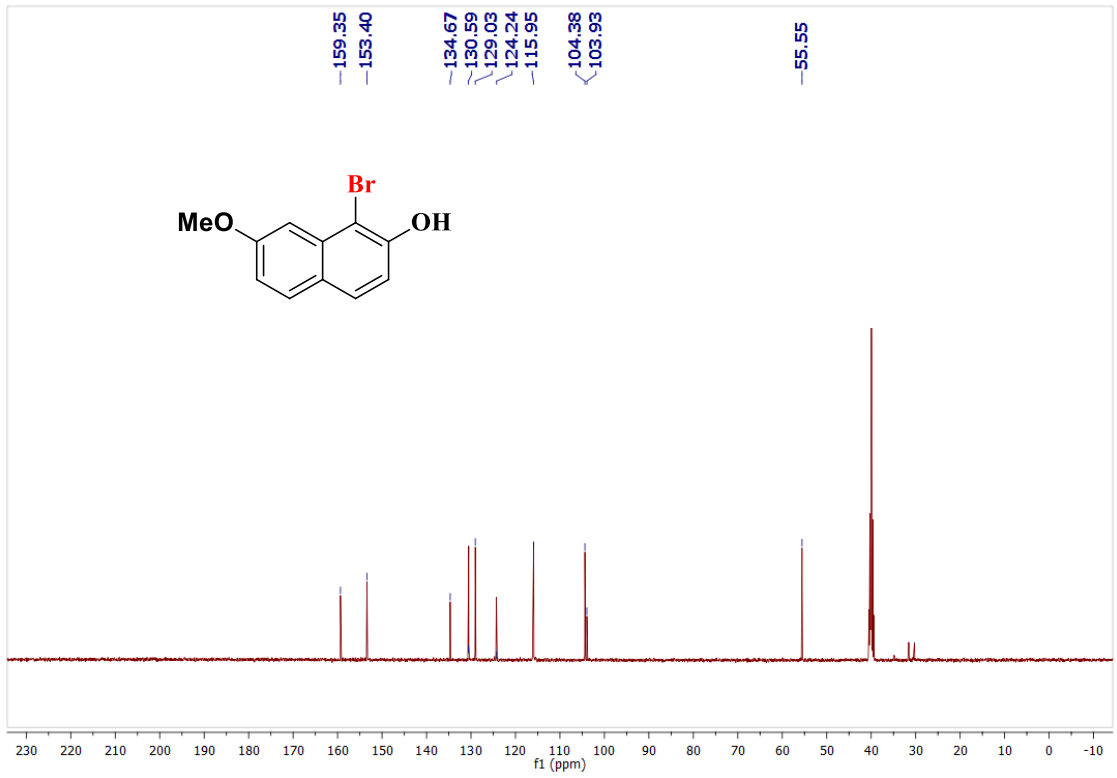
[1] H NMR 1,6-dibromonaphthalen-2-ol



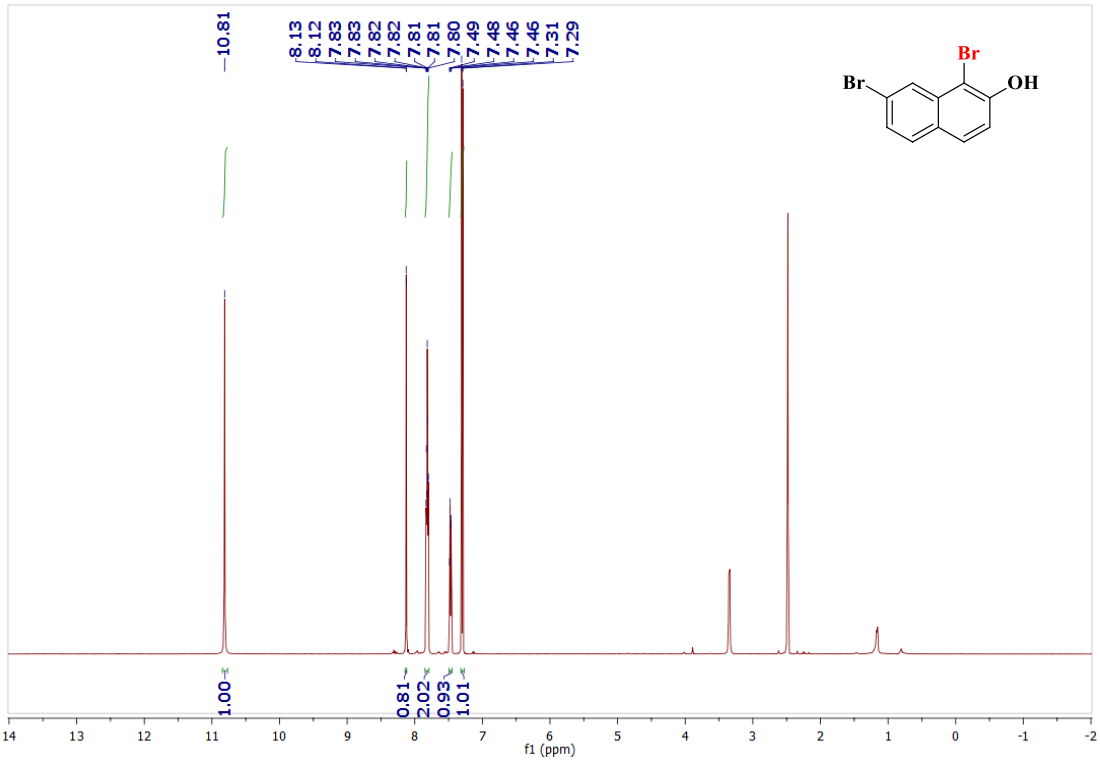
[13]C NMR 1,6-dibromonaphthalen-2-ol



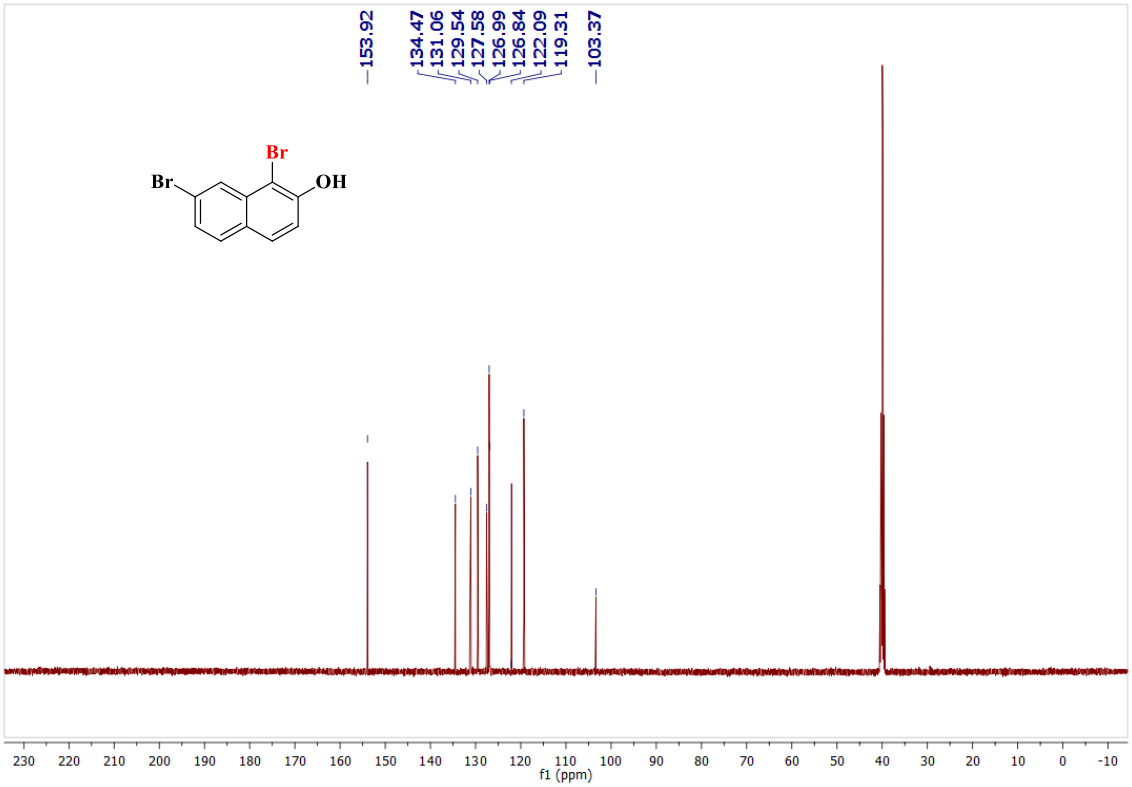
[1] H NMR 1-bromo-7-methoxynaphthalen-2-ol



[13]C NMR 1-bromo-7-methoxynaphthalen-2-ol



[1] H NMR 1,7-dibromonaphthalen-2-ol



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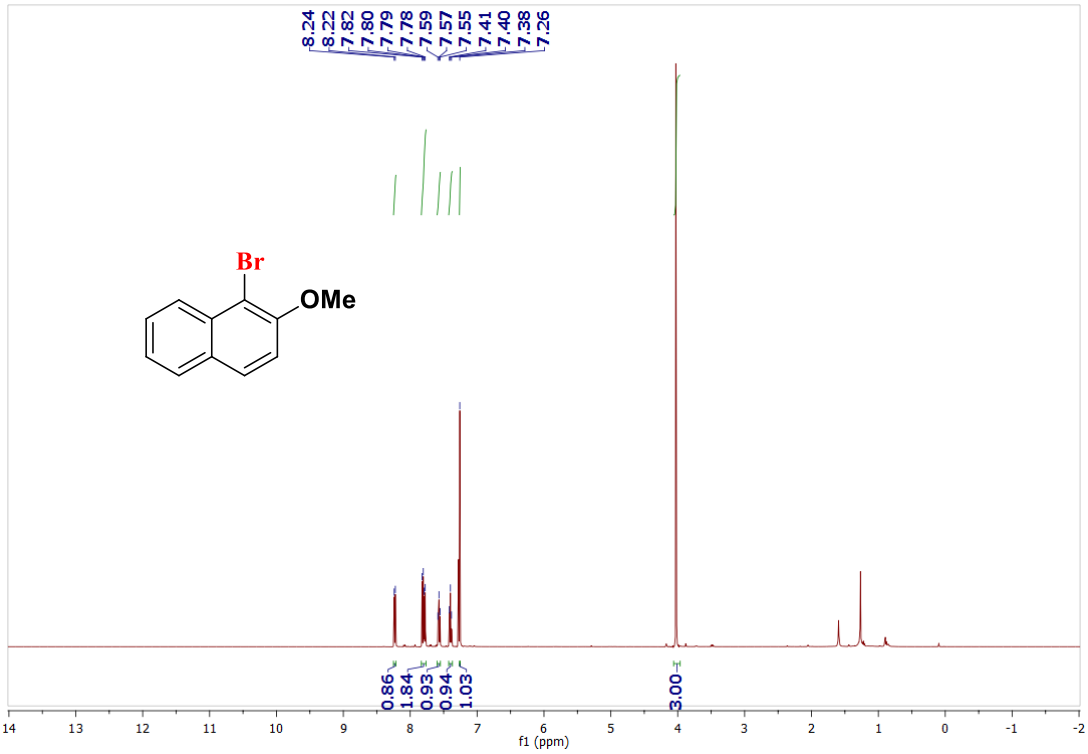
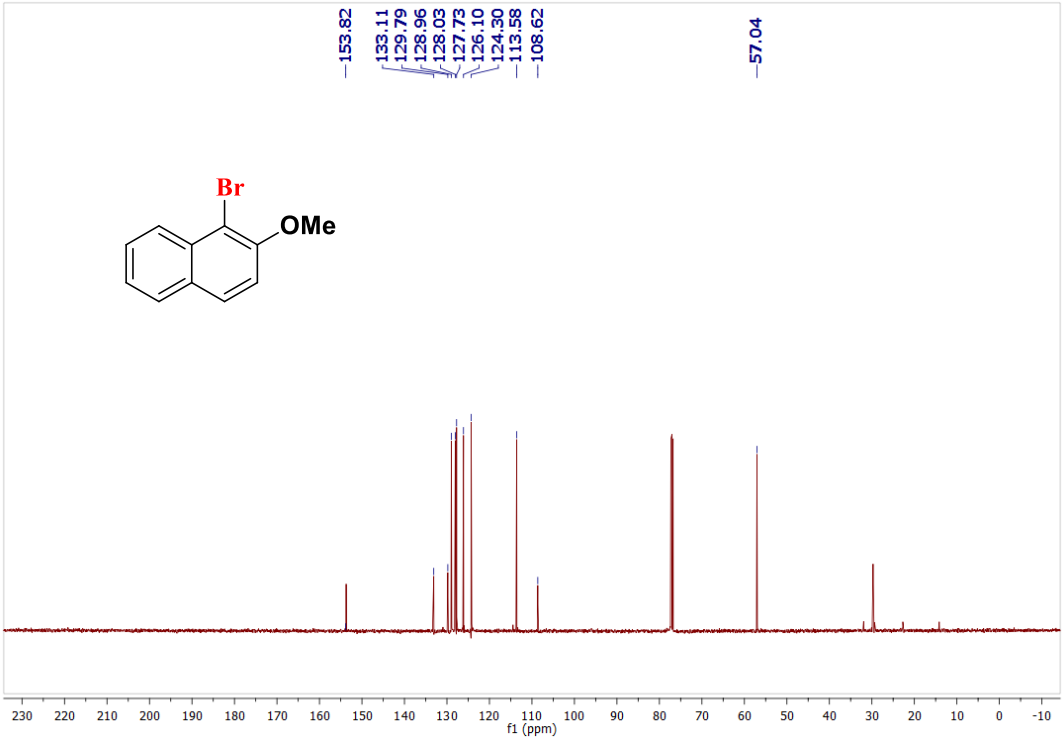
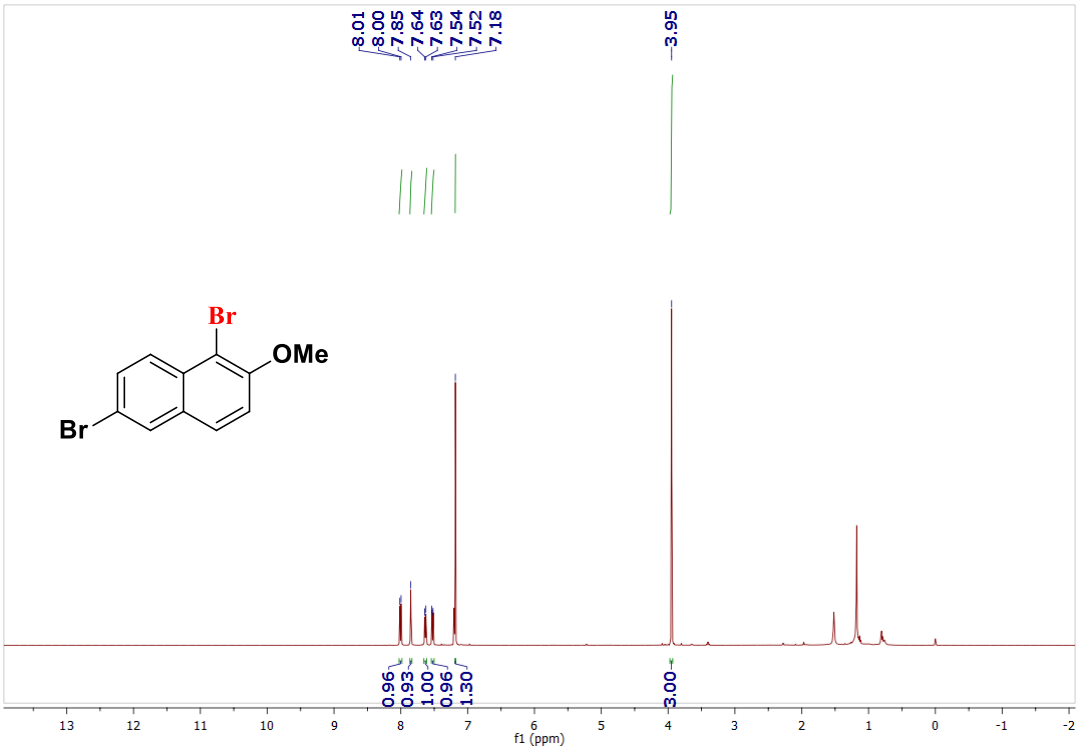


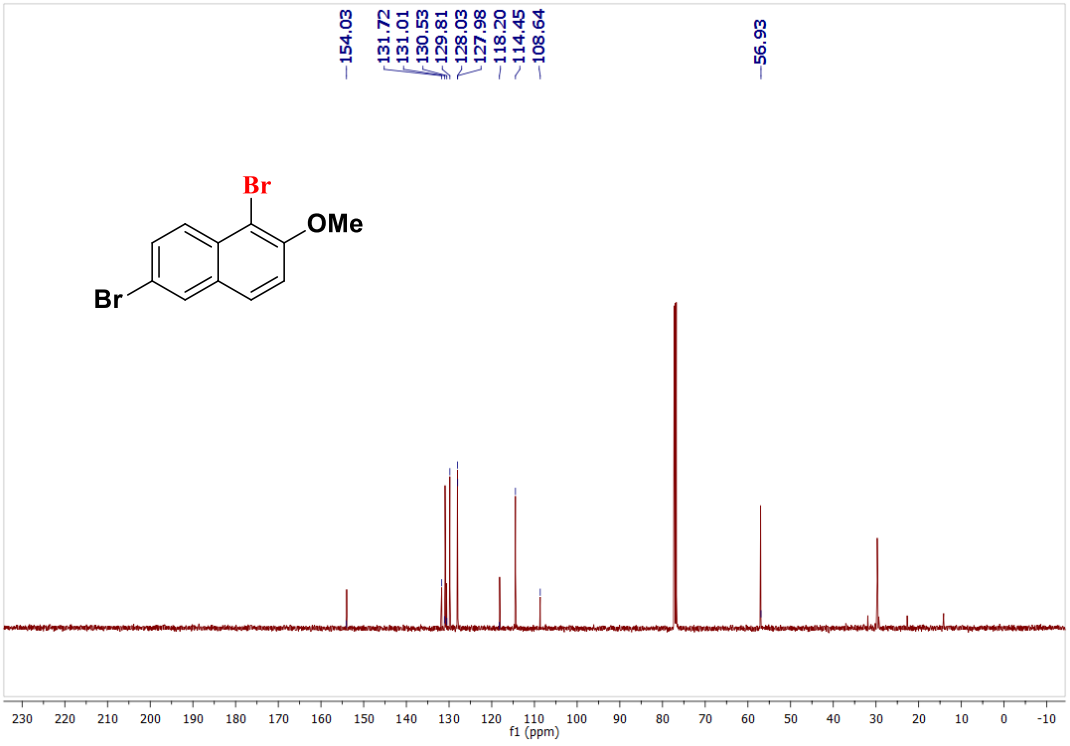
^{1} H NMR 1-bromo-2-methoxynaphthalene



^{13}C NMR 1-bromo-2-methoxynaphthalene



[1] H NMR 1,6-dibromo-2-methoxynaphthalene



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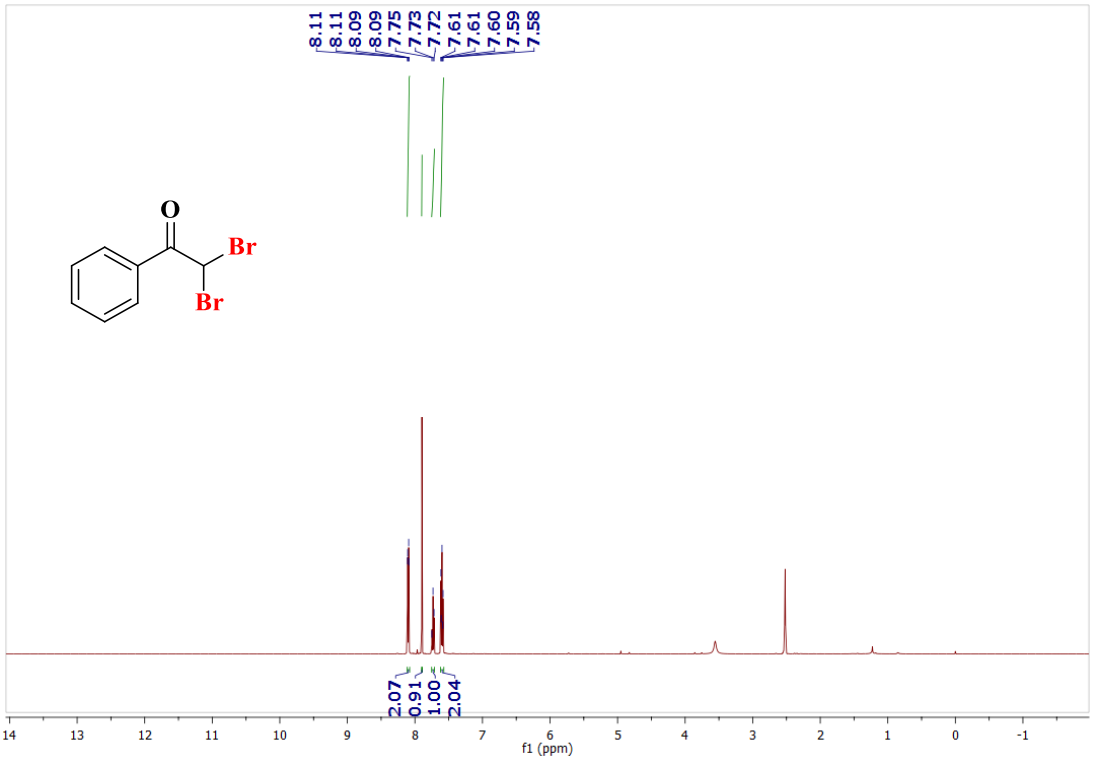
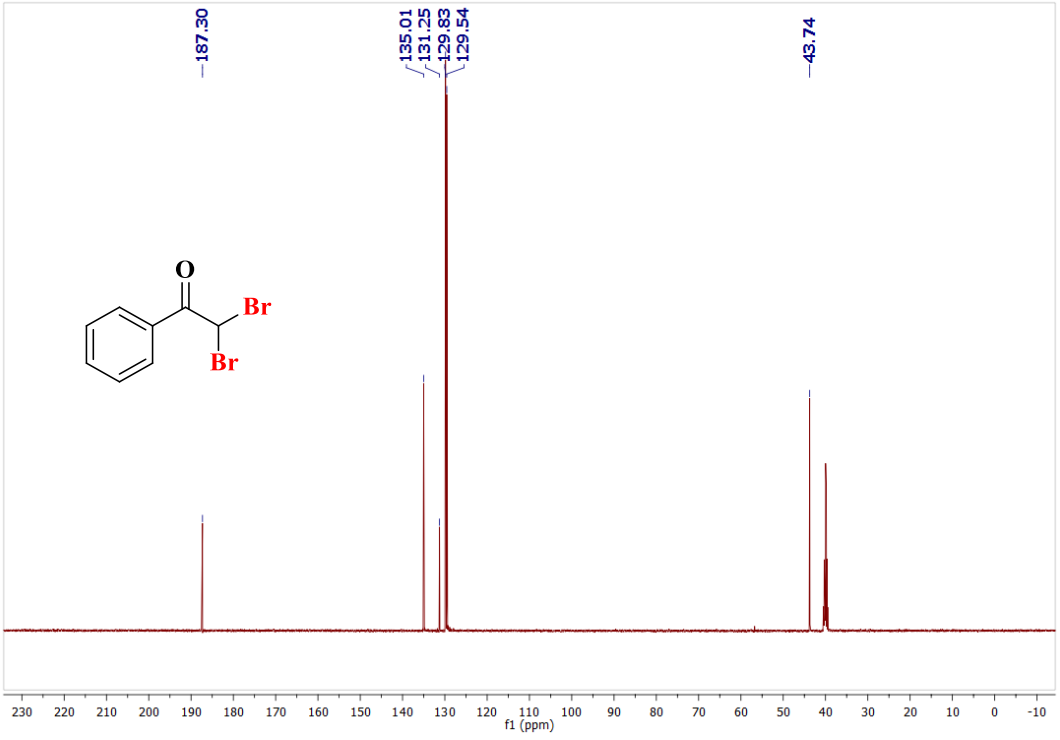
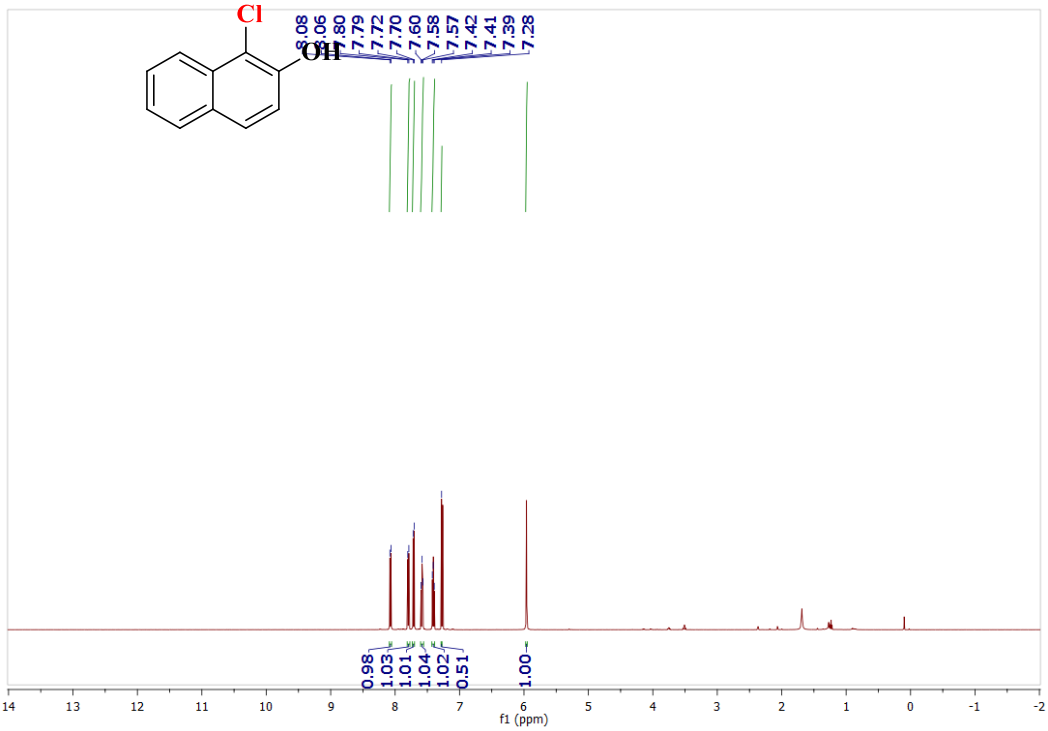


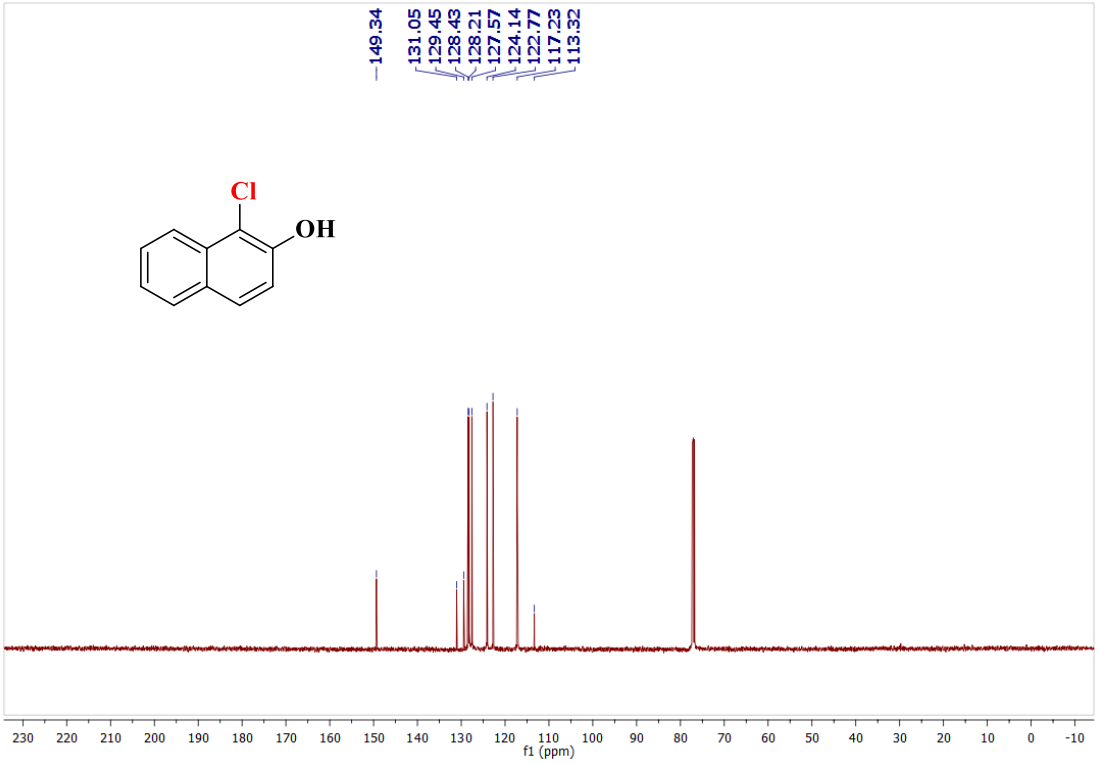
[1] H NMR 2,2-dibromo-1-phenylethanone



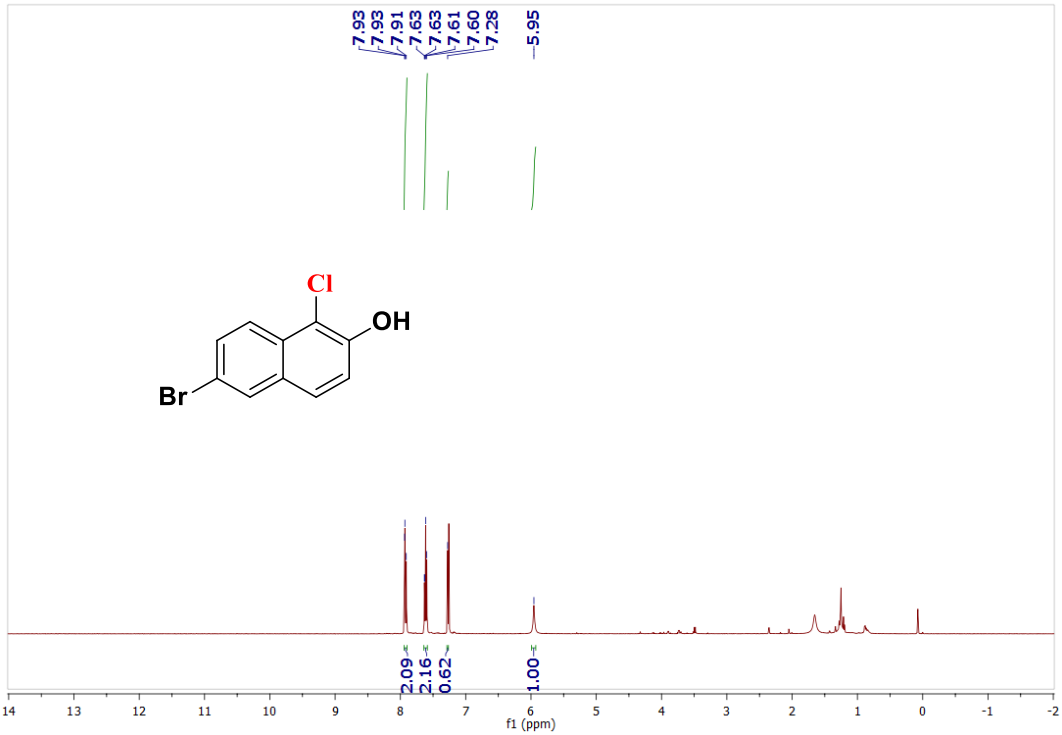
[13]C NMR 2,2-dibromo-1-phenylethanone



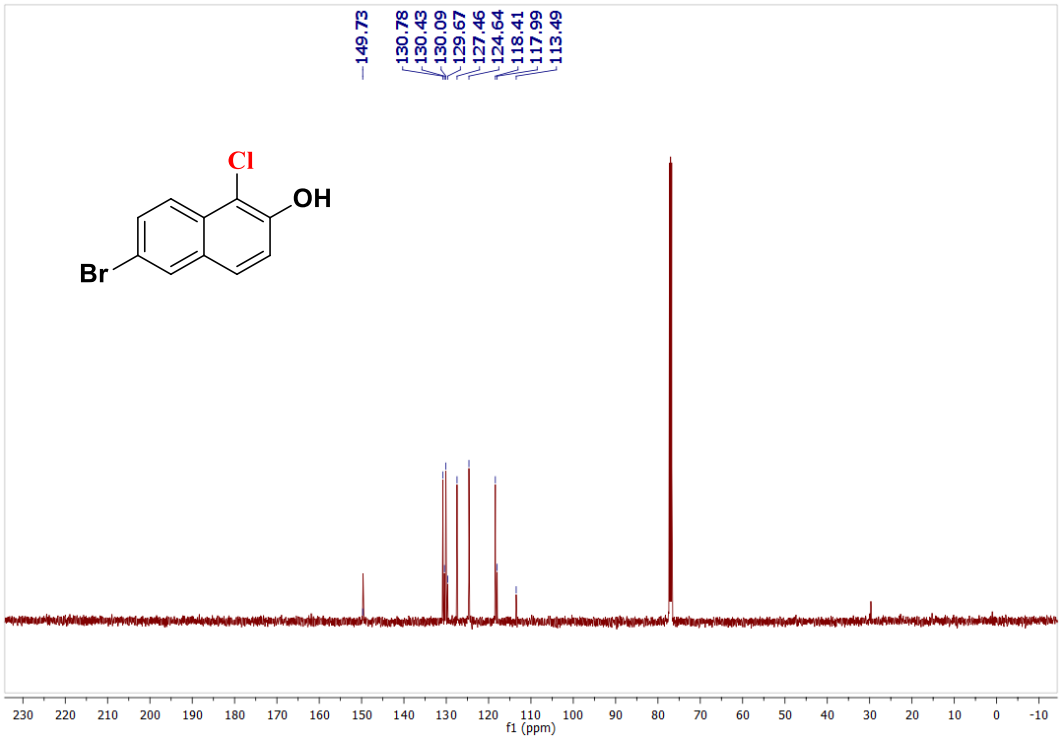
^{1}H NMR 1-chloronaphthalen-2-ol



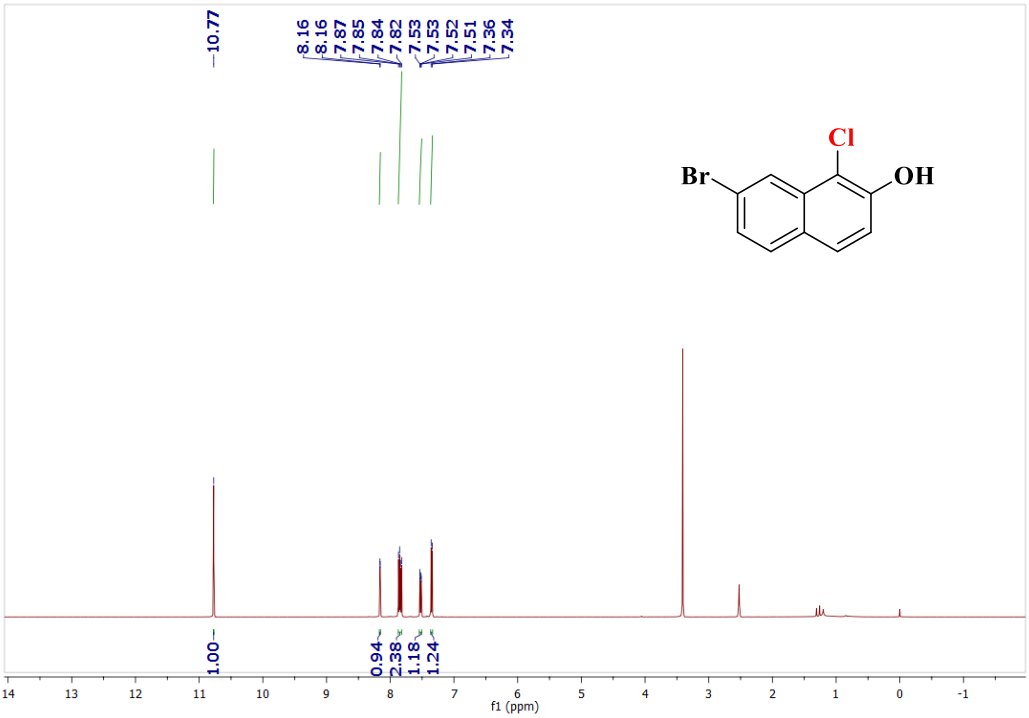
^{13}C NMR 1-chloronaphthalen-2-ol



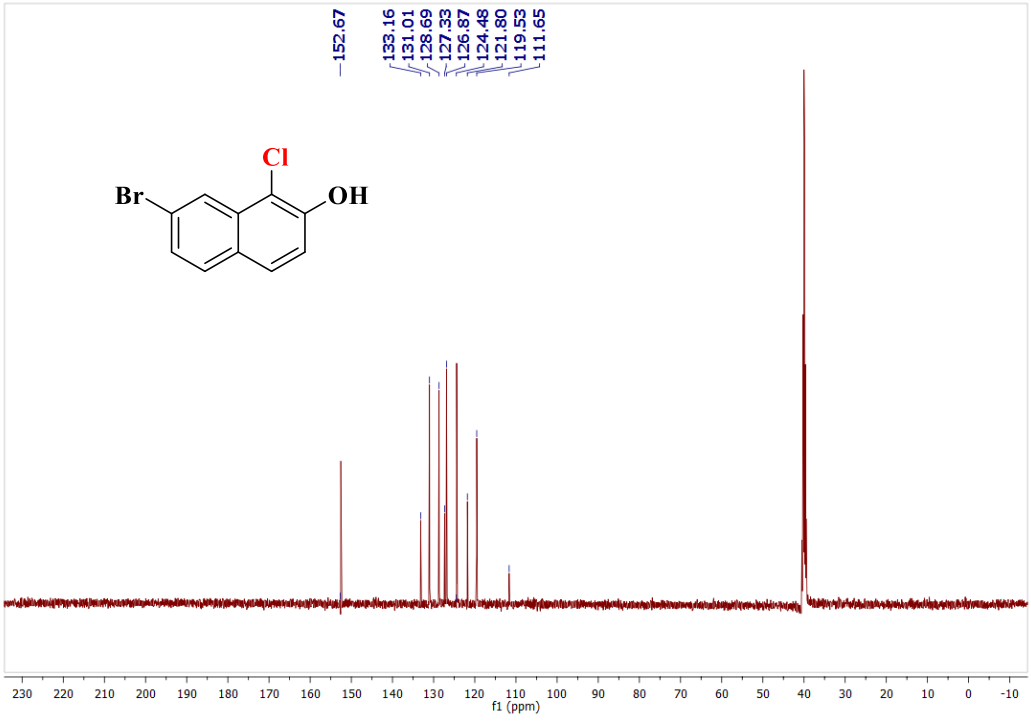
[1]H NMR 6-bromo-1-chloronaphthalen-2-ol



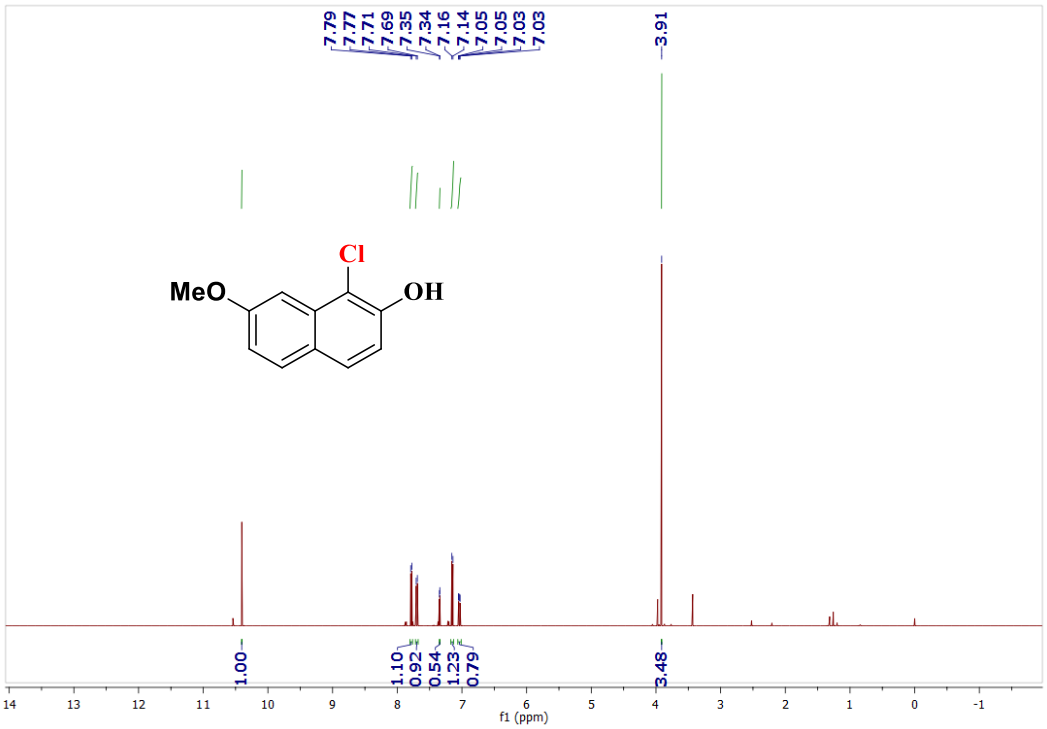
[13] C NMR 6-bromo-1-chloronaphthalen-2-ol



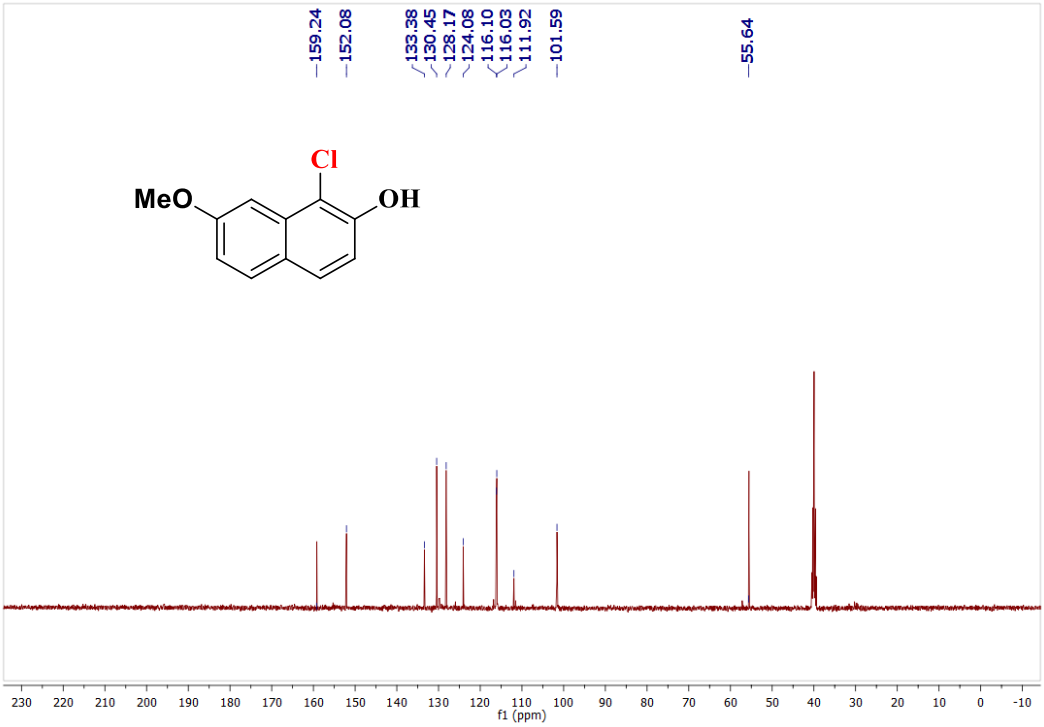
[1]H NMR 7-bromo-1-chloronaphthalen-2-ol



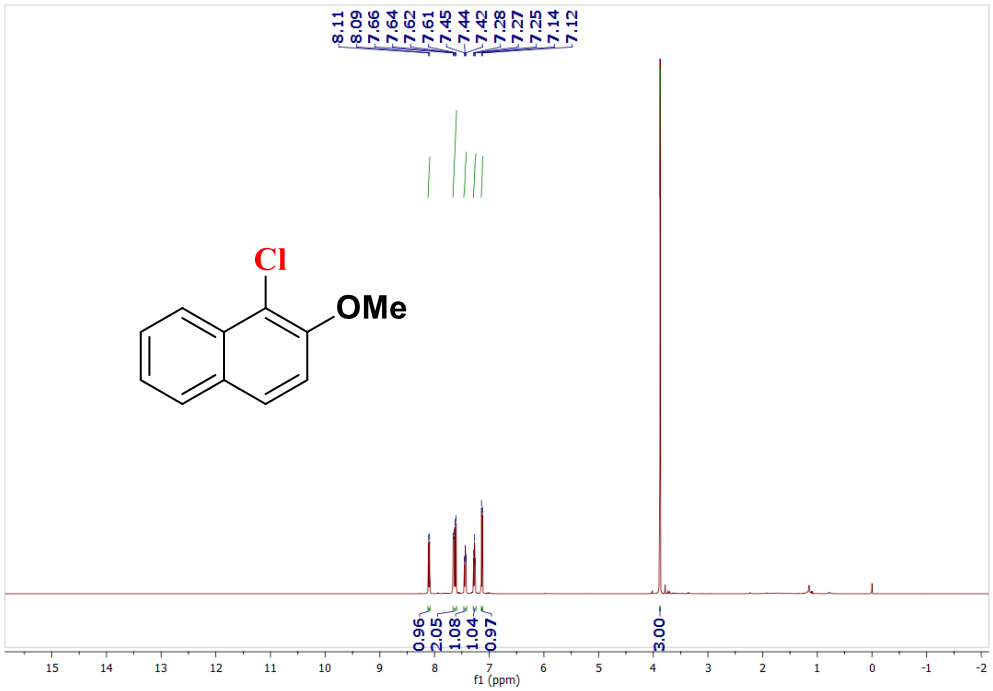
[13] C NMR 7-bromo-1-chloronaphthalen-2-ol



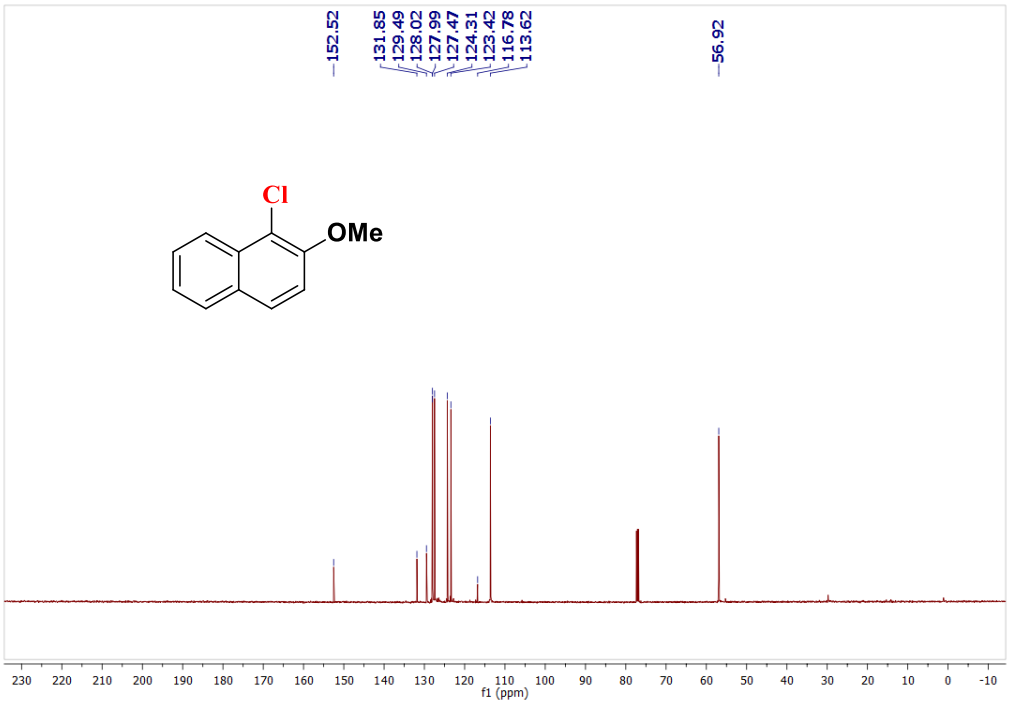
[1]H NMR 1-chloro-7-methoxynaphthalen-2-ol



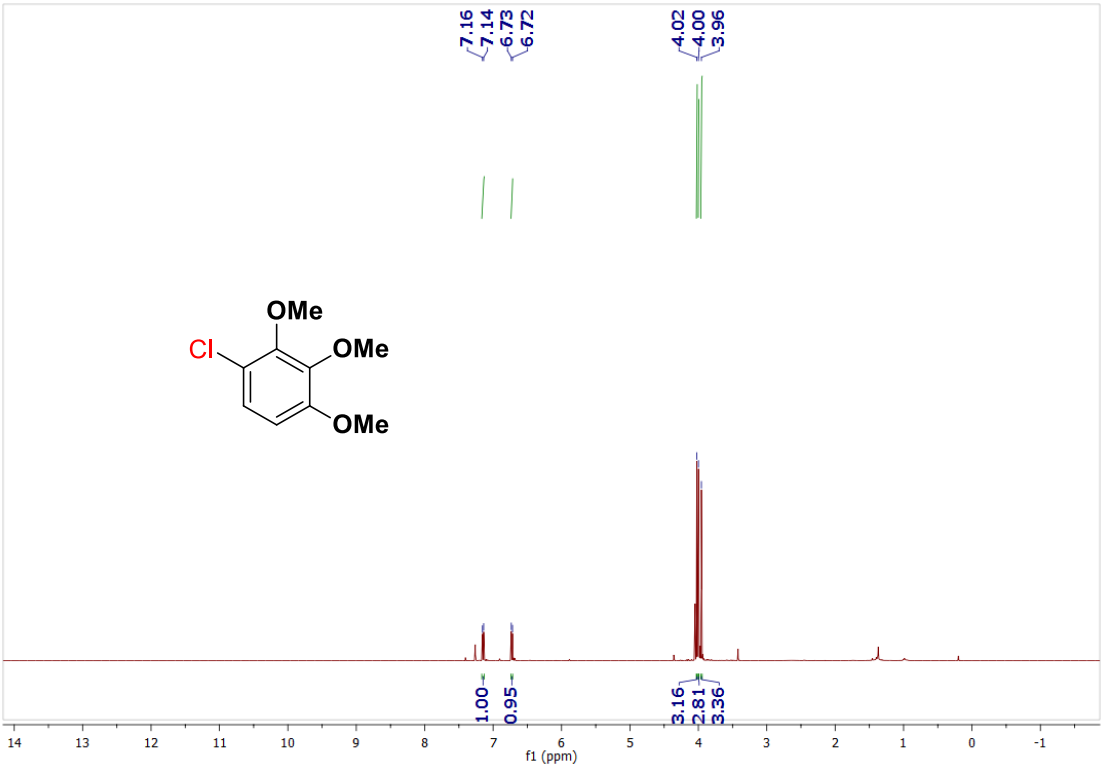
[13] C NMR 1-chloro-7-methoxynaphthalen-2-ol



^{1}H NMR 1-chloro-2-methoxynaphthalene



^{13}C NMR 1-chloro-2-methoxynaphthalene



^{1}H NMR 1-chloro-2,3,4-trimethoxybenzene

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[2] X. Leng, R. Liu, J. Zou, X. Xiong, H. He, *J. Cent. South Univ.* **2016**, *23*, 1823–1830.

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[7] T. Moriuchi, M. Yamaguchi, K. Kikushima, T. Hirao, **2007**, *48*, 2667–2670.