



Supporting Information

for

Light on the sustainable preparation of aryl-cored dibromides

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Additional figures and tables and copies of spectra

Table S1 – Preparation of **3a** from **3**, using variable H₂O₂ amounts.

entry	H ₂ O ₂ 35 wt% (mL)	unconverted 3	3am (%)	3a (%)	3at (%)
1	1.0	9	11	80	-
2	1.2	8	8	84	-
3	1.5	5	3	86	-
4	2.0	-	1	90	6
5	2.2	-	1	90	9

Reaction conditions: *p*-xylene (531 mg, 5 mmol), H₂O (2.0 mL), HBr (48 wt% aqueous solution, 1.24 mL, 11 mmol), Osram white LED lamp 6.5 W, H₂O₂ (35 wt% aqueous solution, dropped at 1.0 mL/h by a syringe pump), CH₂Cl₂ (0.5 mL).

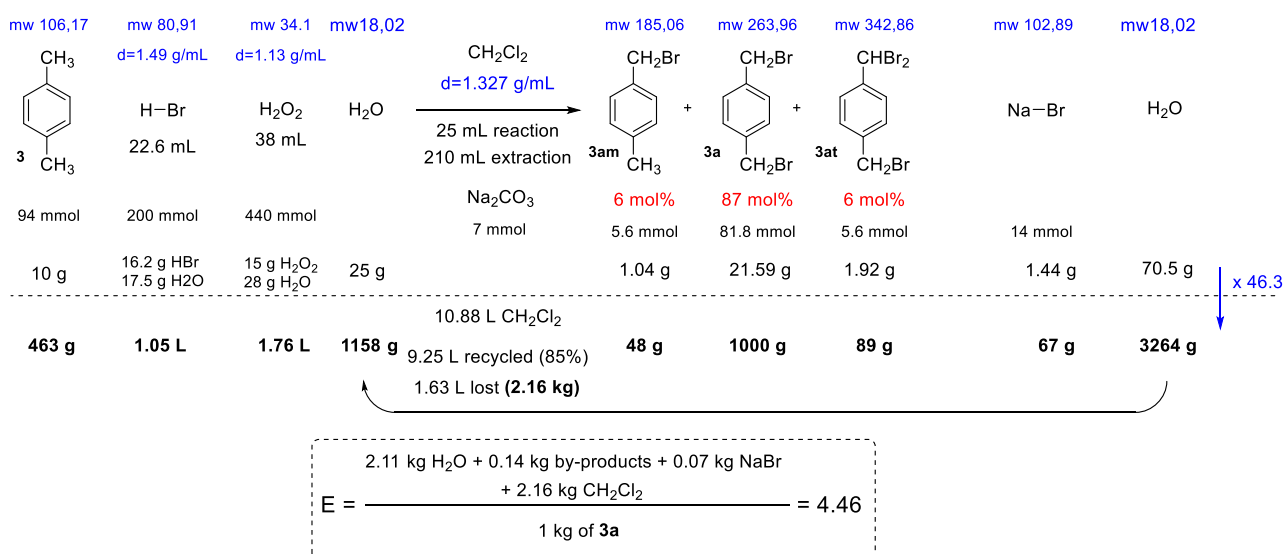


Figure S1. Evaluation of E factor for the conversion (benzylic bromination) of **3** into **3a**, based on the 10-gram scale procedure: In a 150 mL Schlenk tube with screw cap, equipped with a magnetic stirring bar, substrate (10 g, 94 mmol, 1.0 equiv), CH₂Cl₂ (25 mL), H₂O (25 mL) and HBr (48 wt % aqueous solution, *d* = 1.49 g/mL, 22.6 mL, 200 mmol, 2.13 equiv) were inserted. The mixture was kept under stirring at rt and irradiated with a LED lightbulb placed at 10 cm from the side of the reaction tube. Aqueous H₂O₂ (35 wt % solution, *d* = 1.13 g/mL, 38 mL, 440 mmol, 4.7 equiv) was added over 2 h using a syringe pump, through a small PTFE tube inserted through the side arm of the Schlenk. After the addition was over, the mixture was irradiated under stirring for 1 h and 30 min. Once the mixture was neutralized with solid Na₂CO₃ (0.74 g, 7 mmol) the product was extracted with CH₂Cl₂ (3 × 70 mL). The combined organic layers were concentrated to dryness to give the crude product as white-yellowish solid in 87% yield. The solvent recovery efficiency was set at 85 wt %.

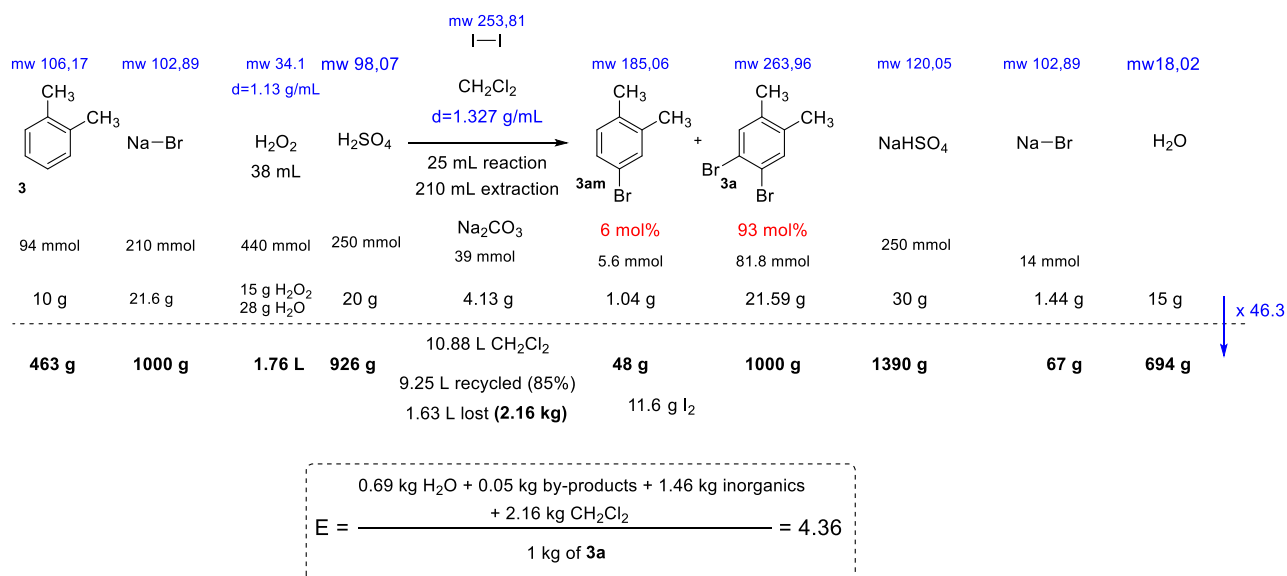
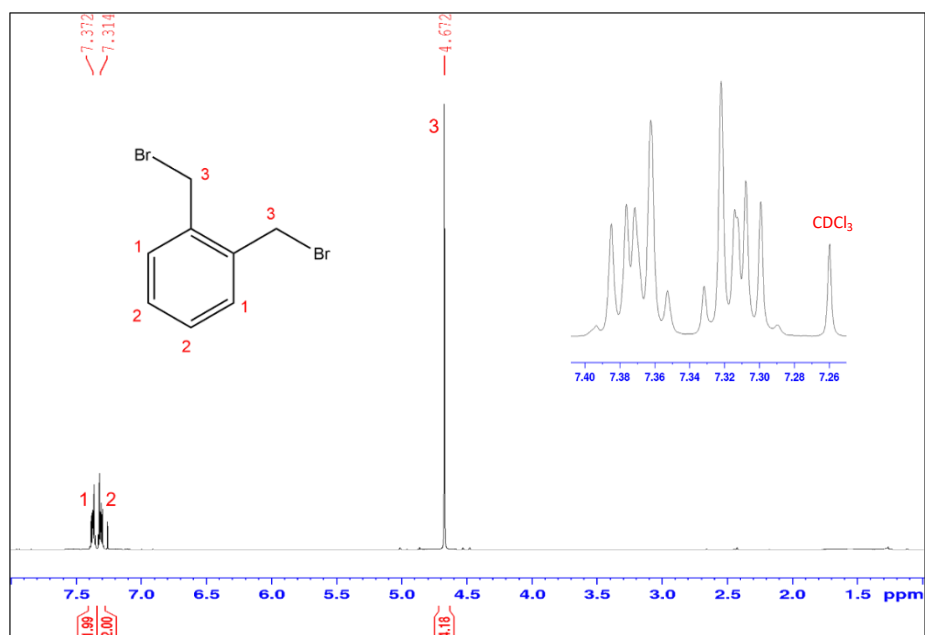


Figure S2. Evaluation of E factor for the conversion (ring bromination) of **1** into **1b**, based on the 10-gram scale procedure: In a 100 mL round-bottom flask, equipped with a magnetic stirring bar, substrate (10 g, 94 mmol, 1.0 equiv), H₂SO₄ (96 wt %, 20.0 g, 235 mmol, 2.4 equiv), I₂ (0.25 g, 1 mol %) and CH₂Cl₂ (25 mL) were inserted. The flask, kept under stirring at rt, was light-shielded with aluminium foil and a water-cooled condenser was installed on its top. A solution of NaBr (2.88 g, 28 mmol, 2.33 equiv) in H₂O₂ (35 wt % aqueous solution, 38 mL, 440 mmol, 4.7 equiv) was added to the mixture over 20 min with a syringe pump, through a PTFE tube inserted in the top of the condenser. The system was then refluxed for 48 h. Once cooled to RT, the reaction mixture was neutralized with solid Na₂CO₃ (4.13 g, 39 mmol), and the product was extracted with CH₂Cl₂ (3 × 70 mL). The combined organic layers were concentrated to dryness to give the crude product as brown solid in 93% yield. The solvent recovery efficiency was set at 85 wt %.

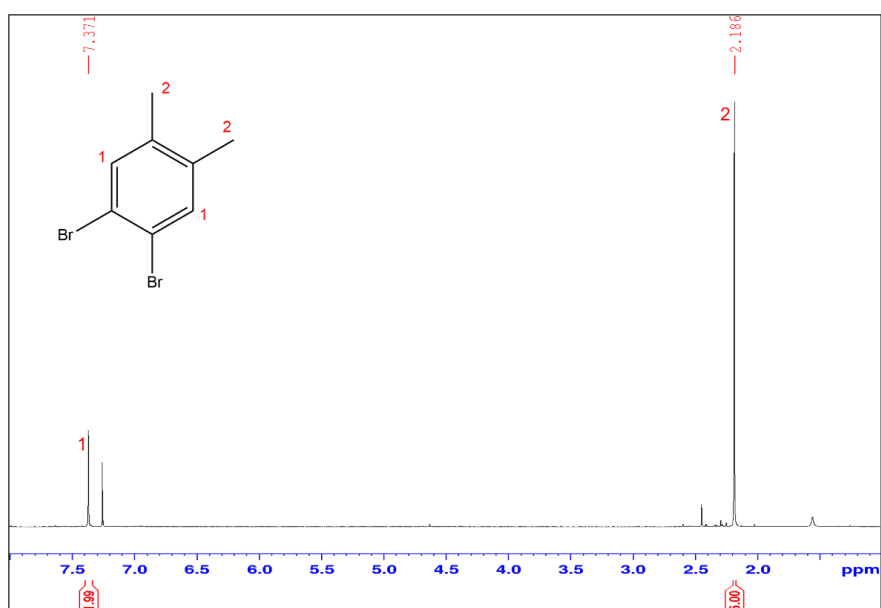
¹H NMR spectra (400 MHz, 298 K, CDCl₃)

All the synthesized compounds correspond to well-known structures. In the following, the ¹H NMR spectra of the extracted reaction mixture are reported. For compound **3a**, the spectrum for the crystallized product is reported. Compound **4a** from the raw reaction mixture was strongly contaminated by aryl bromides by-products (see main text). The reported spectrum is that obtained after the first chromatographic purification. A purer version is obtainable after a second purification, resulting in 42% yield (see main text).

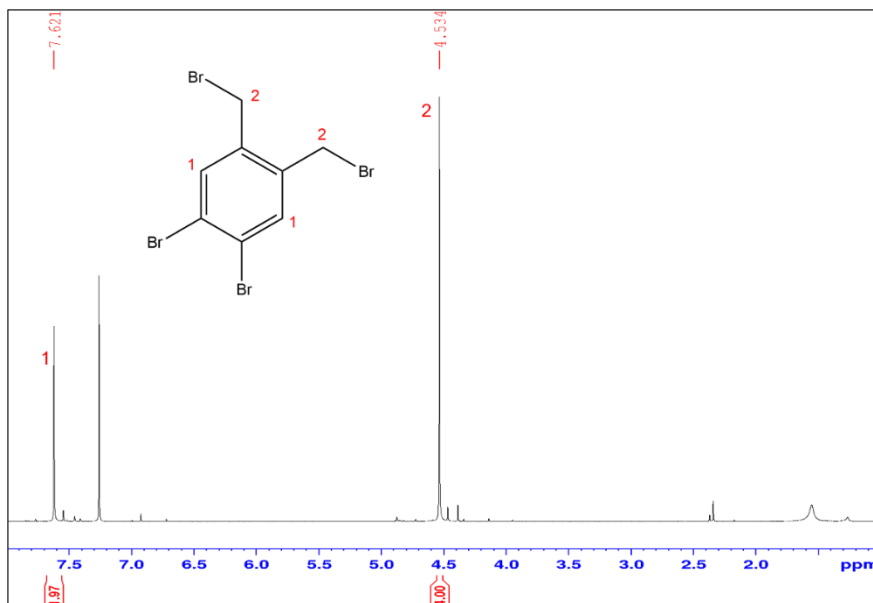
1,2-Bis(bromomethyl)benzene (1a): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.37 (m, 2H), 7.31 (m, 2H), 4.67 (s, 4H) ppm.



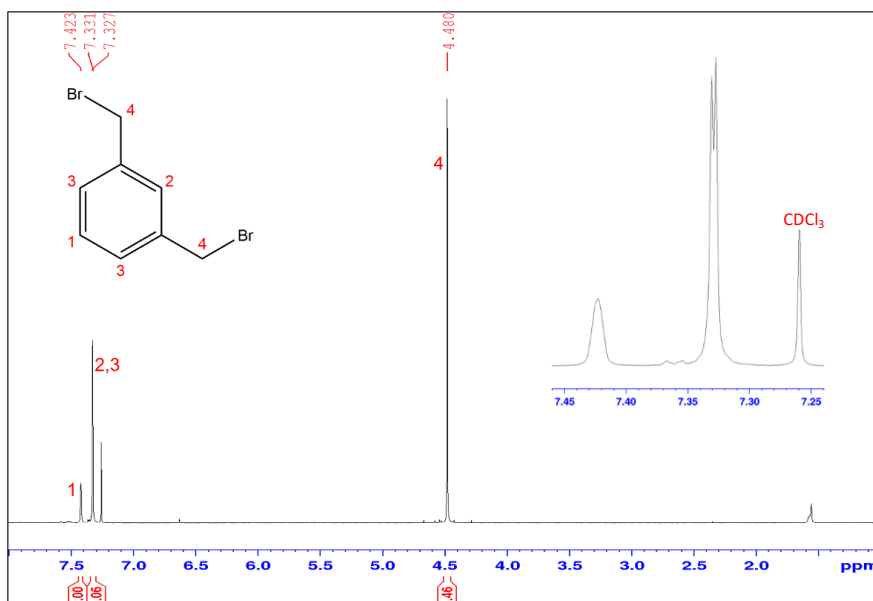
1,2-Dibromo-4,5-dimethylbenzene (1b): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3) δ 7.37 (s, 2H), 2.19 (s, 6H) ppm.



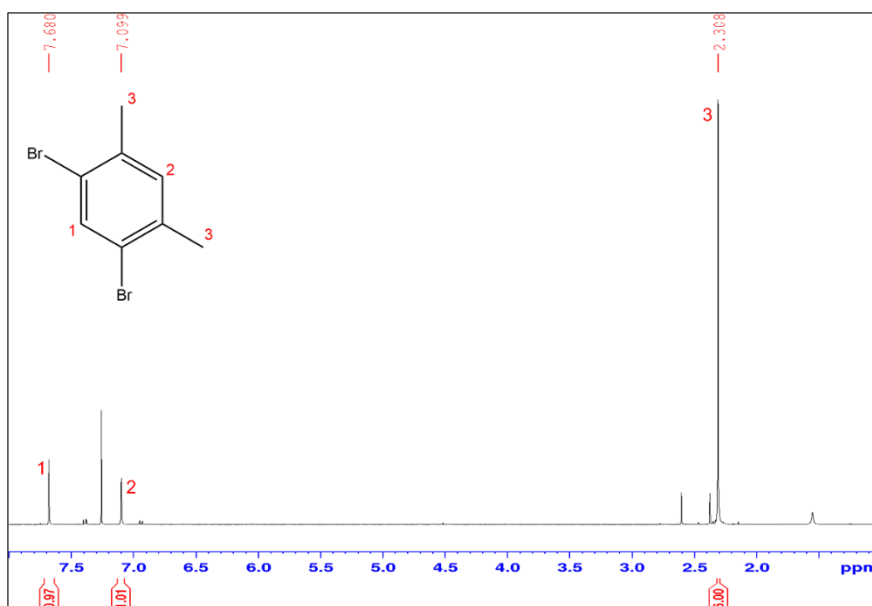
1,2-Dibromo-4,5-bis(bromomethyl)benzene (1c): ^1H NMR (400 MHz, 298 K, CDCl_3): δ 7.62 (m, 2H), 4.53 (s, 4H) ppm.



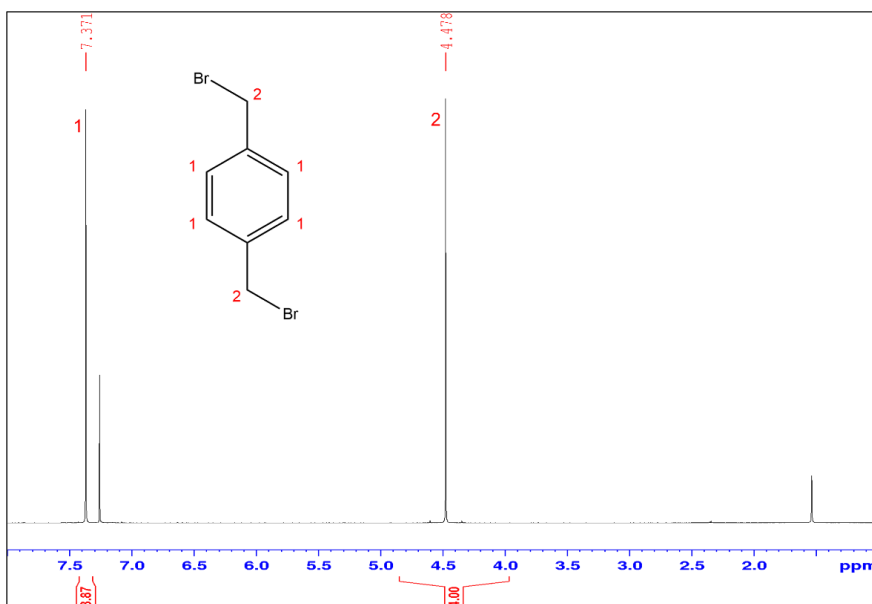
1,3-Bis(bromomethyl)benzene (2a): ^1H NMR (400 MHz, 298 K, CDCl_3): δ 7.42 (m, 1H), 7.33 (m, 1H), 7.32 (m, 2H), 4.48 (s, 4H) ppm.



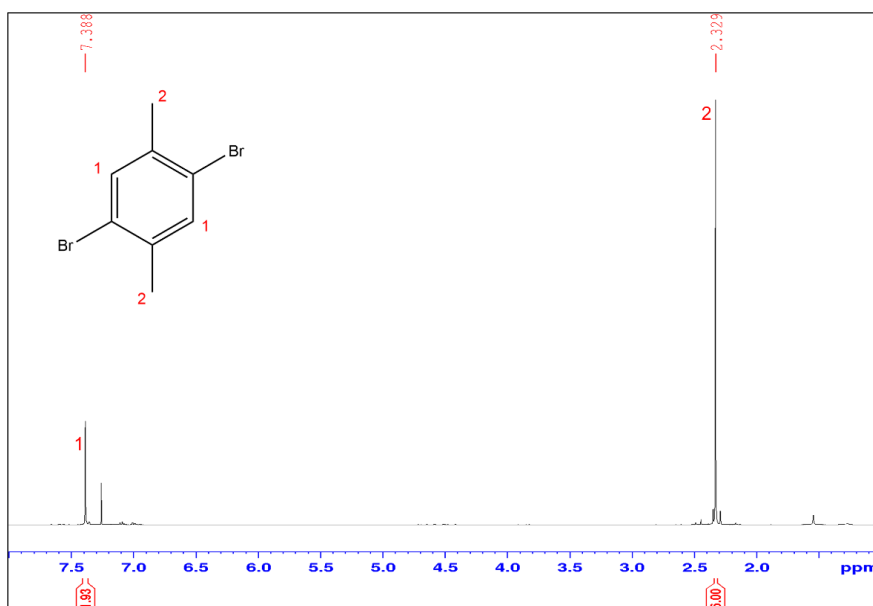
1,5-Dibromo-2,4-dimethylbenzene (2b): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.68 (s, 1H), 7.10 (s, 1H), 2.31 (s, 6H) ppm.



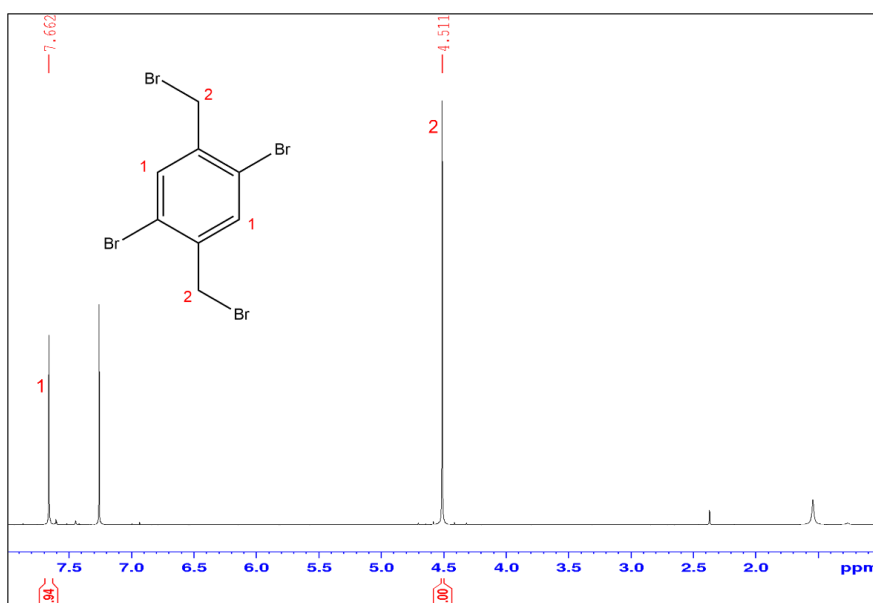
1,4-Bis(bromomethyl)benzene (3a) (crystallized from toluene): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.37 (s, 4H), 4.48 (s, 4H) ppm.



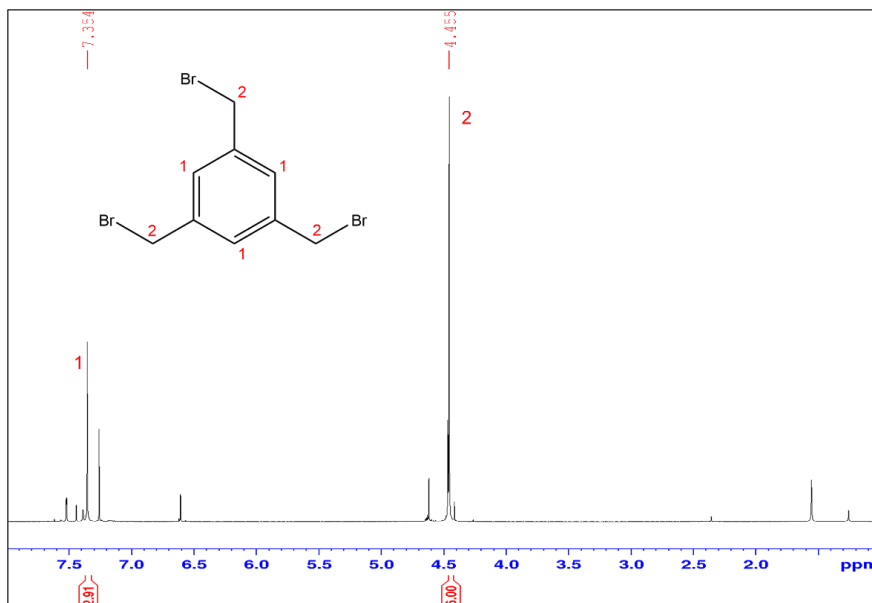
1,4-Dibromo-2,5-dimethylbenzene (3b): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.39 (s, 2H), 2.33 (s, 6H) ppm.



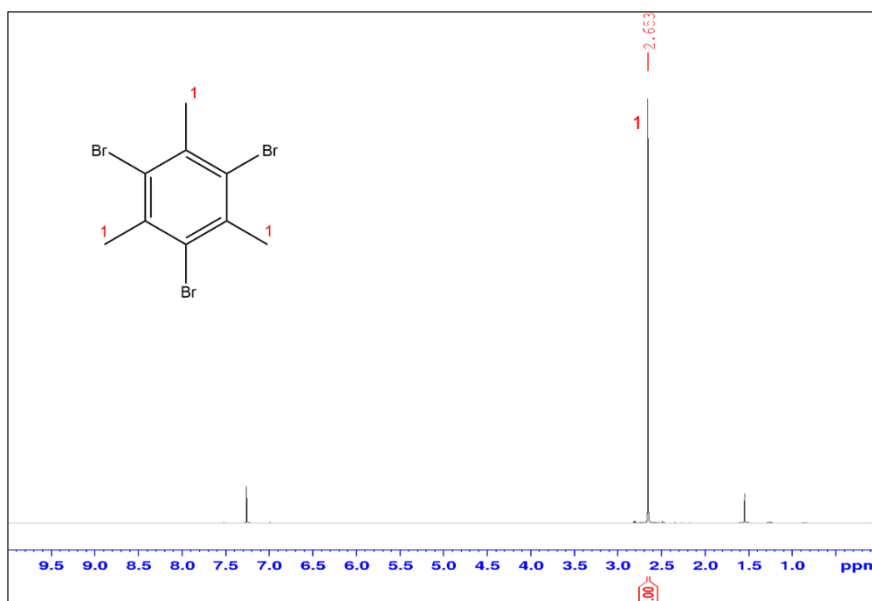
1,4-Dibromo-2,5-bis(bromomethyl)benzene (3c): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.66 (s, 2H), 4.51 (s, 4H) ppm.



1,3,5-Tris(bromomethyl)benzene (4a) (after column chromatography): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 7.35 (s, 3H), 4.45 (s, 6H) ppm.



1,3,5-Tribromo-2,4,6-trimethylbenzene (4b): $^1\text{H NMR}$ (400 MHz, 298 K, CDCl_3): δ 2.65 (s, 9H) ppm.



1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene (4c): ^1H NMR (400 MHz, 298 K, CDCl_3): δ 4.92 (s, 6H) ppm.

