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Supplementary Material

Microreactor mediated benzylic bromination in concentrated solar radiation

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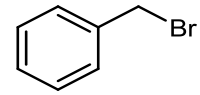
General Information: All chemicals were purchased from Sigma-Aldrich and/or Alfa Aesar and were used without any further purification. The NMR spectra were recorded on a JNM-AL400, a Fourier and a Bruker Advance 300. The proton chemical shifts were reported in ppm (δ) relative to TMS with a solvent resonance employed as internal standard ($CDCl_3$, δ = 7.26 ppm). The data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet and doublet dt = doublet and triplet, m = multiplet), coupling constants (Hz) and integration. A GC-MS analysis was performed with an Agilent 5975C GC/MSD System (Agilent Tech., USA/Germany). FEP tubing and T-junctions (thru-hole: 0.5 mm, ETFE) were purchased from Upchurch, USA. Legato 210 (KD Scientific, USA) syringe pump, PHD 2000 (Harvard Apparatus, USA) syringe pump, and 323S 400 rpm Drive (Watson Marlow, UK) peristaltic pump were used in the microchemical reactions.

General description of the microreactor mediated benzylic bromination in concentrated solar radiation: $CHCl_3$ solution of alkylbenzene (0.5 M) was placed in one syringe, and $CHCl_3$ solution of Br_2 (0.6 M) was placed in another syringe wrapped with aluminum foil. The reaction streams were introduced to each of the inlets of the capillary microreactor through a 25 cm FEP tubing segment. The injection rates for toluene and Br_2 varied but were equal for both solutions. Sunlight was focused with a fresnel lens, and solar tracking was conducted manually every 15 min. The results of the reaction were collected into a brown vial containing an aqueous solution of $Na_2S_2O_3$. After extraction with additional $CHCl_3$, the organic layer was analyzed. The crude yield and selectivity were calculated through a GC/MSD analysis or ^1H NMR analysis. The mixtures were purified via column chromatography.

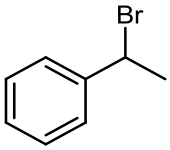
NMR spectral data of monobrominated products

(bromomethyl)benzene[1]



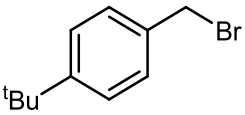
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.35 (m, 5H), 4.53 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.82, 129.04, 128.81, 128.42, 33.54.

(1-bromoethyl)benzene[1]



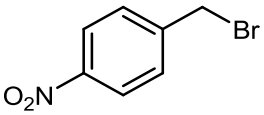
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, J = 7.36Hz, 2H), 7.40-7.31 (m, 3H), 5.23 (q, J = 6.89 Hz, 20.69 Hz, 1H), 2.09 (d, J = 6.97 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.27, 128.68, 128.33, 126.81, 49.52, 29.71, 26.83.

1-(bromomethyl)-4-tert-butylbenzene[2]



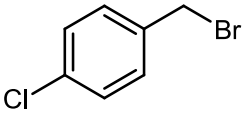
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.34 (m, 4H), 4.52 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.59, 134.77, 128.76, 125.77, 34.65, 33.57, 31.25.

1-(bromomethyl)-4-nitrobenzene[3]



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.43 Hz 2H), 4.54 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.74, 144.75, 129.90, 124.04, 30.86.

1-(bromomethyl)-4-chlorobenzene[2]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (s, 4H), 4.48 (s 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.32, 134.33, 130.37, 129.01, 32.34.

References

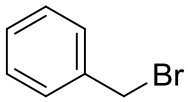
[1] R. M. Denton, et al. *J. Org. Chem.* **2011**, *76*, 6749-6767.

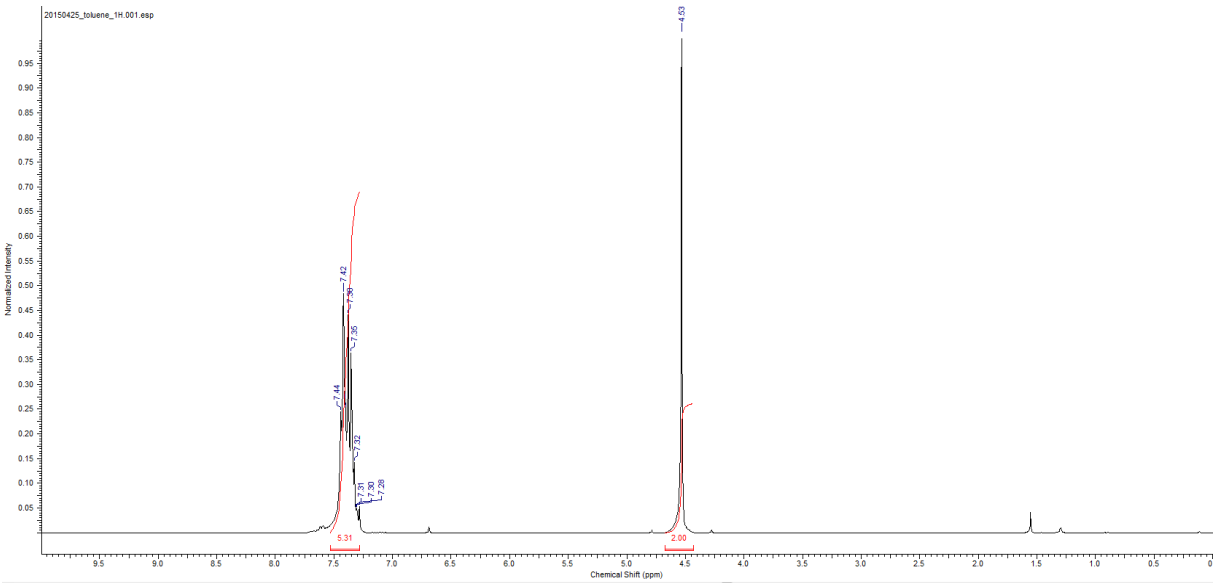
[2] J. J. Campbell et al. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2067-2079.

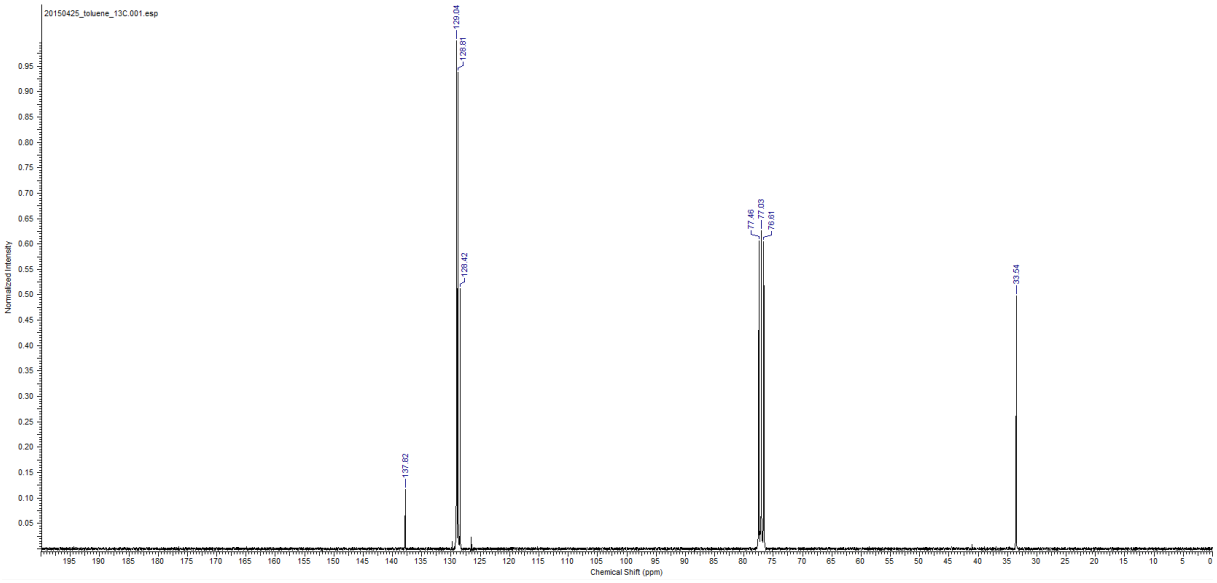
[3] A. Podgoršek, et al. *Tetrahedron* **2009**, *65*, 4429-4439.

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

(bromomethyl)benzene

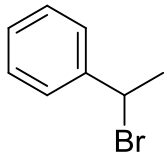


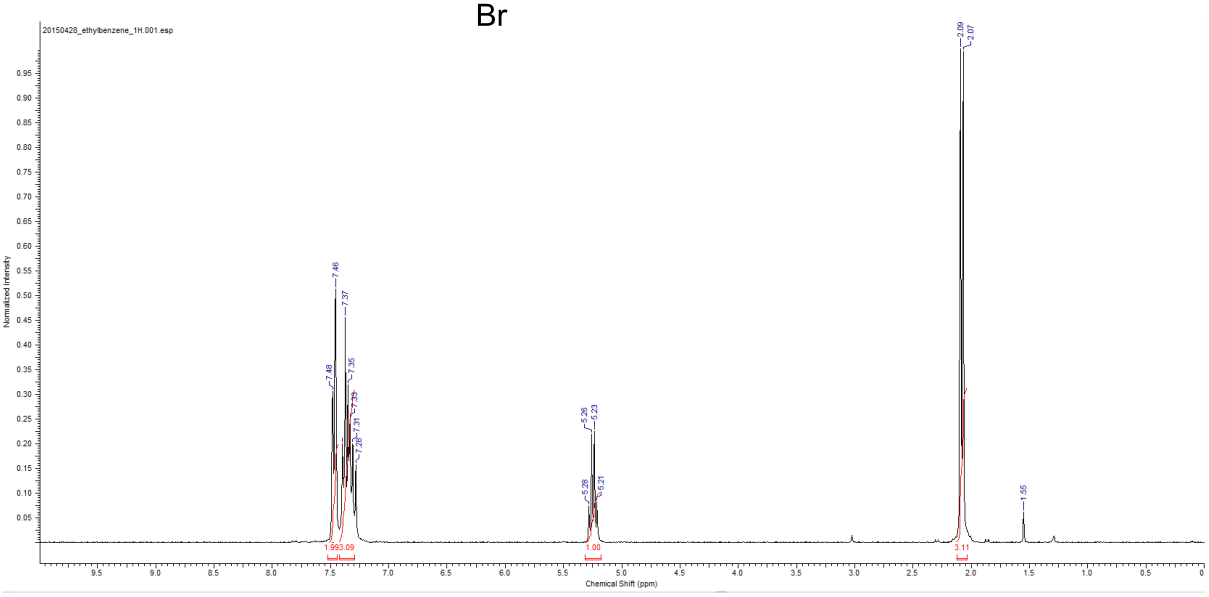


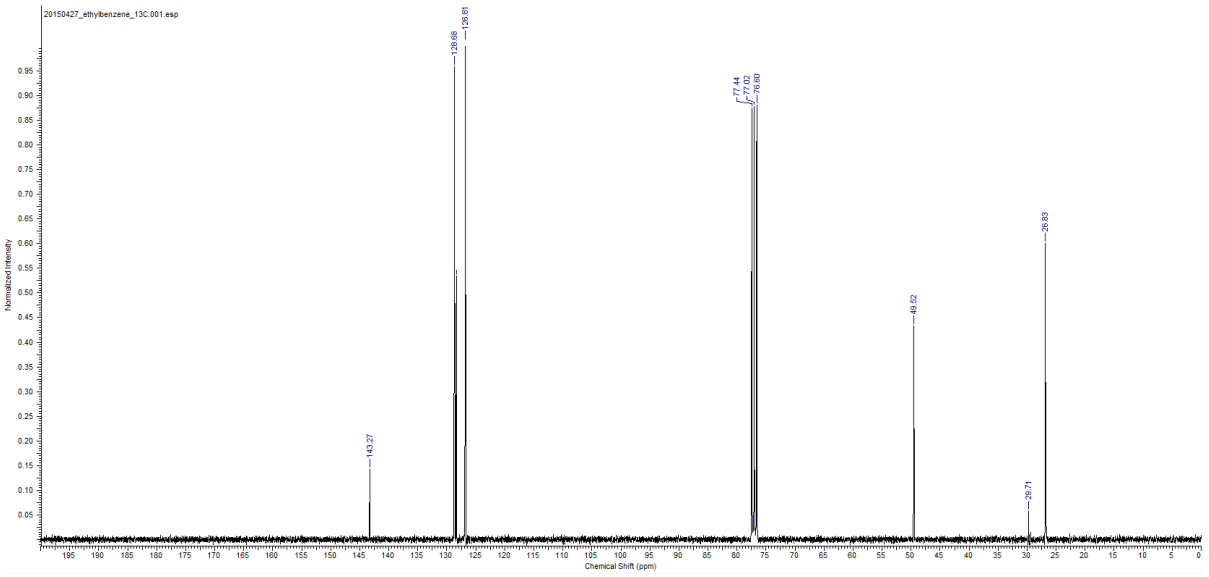


^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (75 MHz, $CDCl_3$) (down)

(1-bromoethyl)benzene

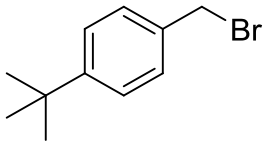


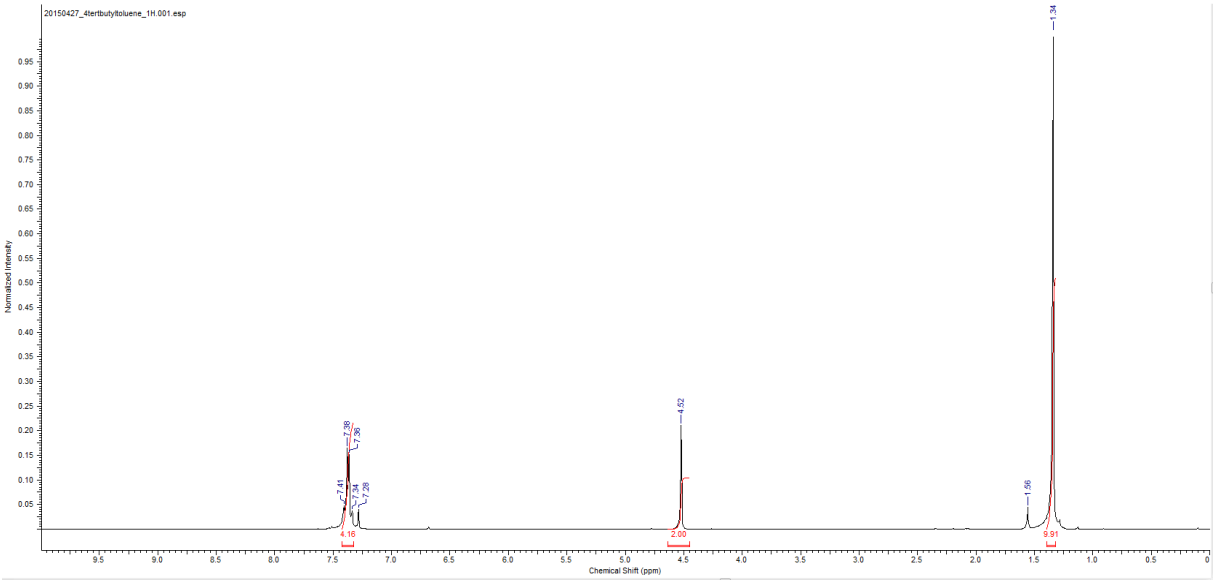


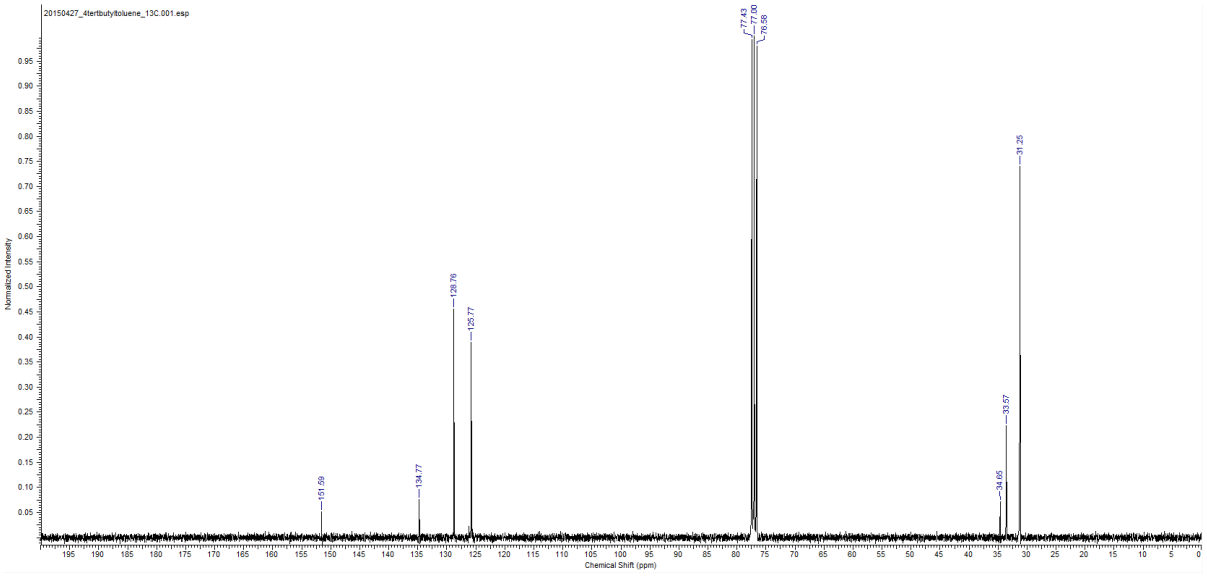


^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (75 MHz, $CDCl_3$) (down)

1-(bromomethyl)-4-tert-butylbenzene

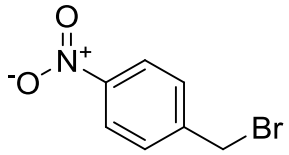


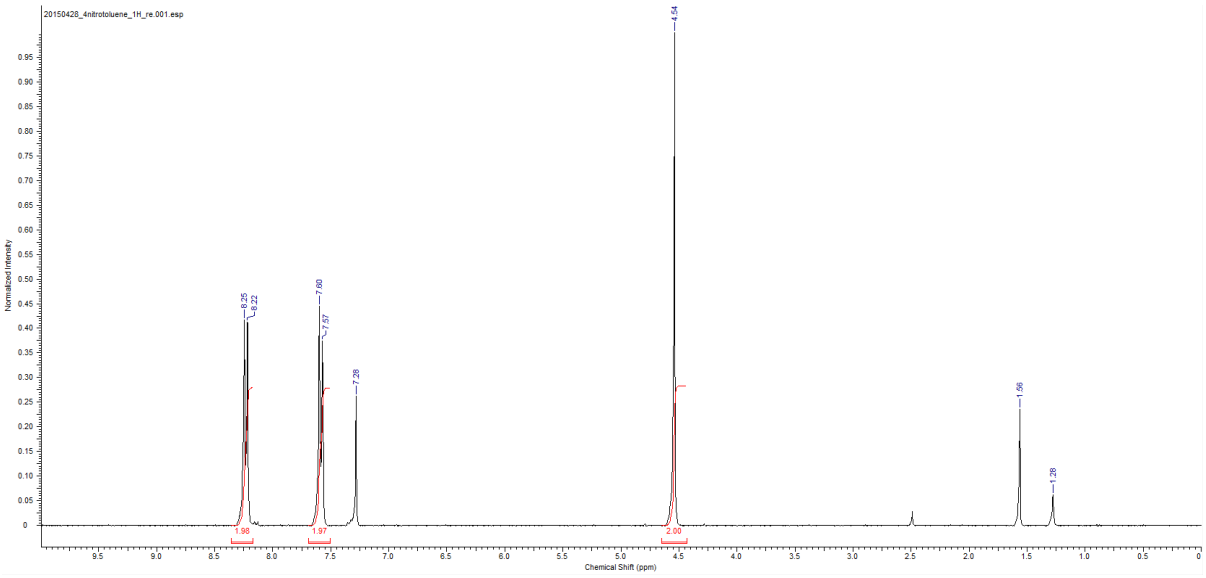


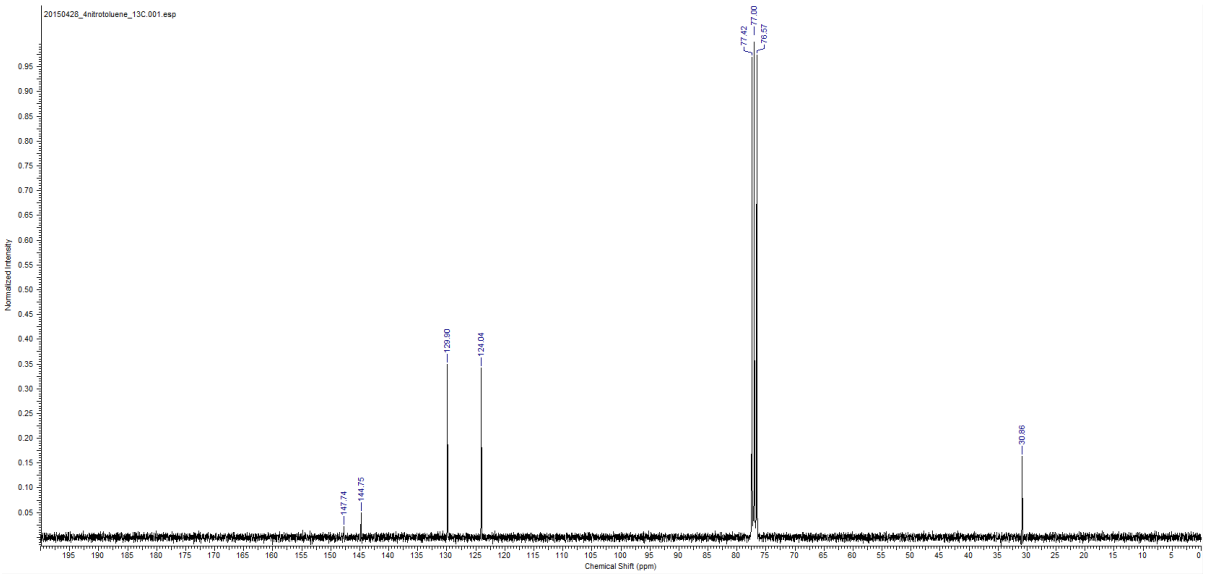


^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (75 MHz, $CDCl_3$) (down)

1-(bromomethyl)-4-nitrobenzene

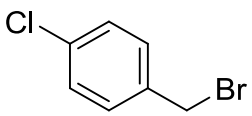


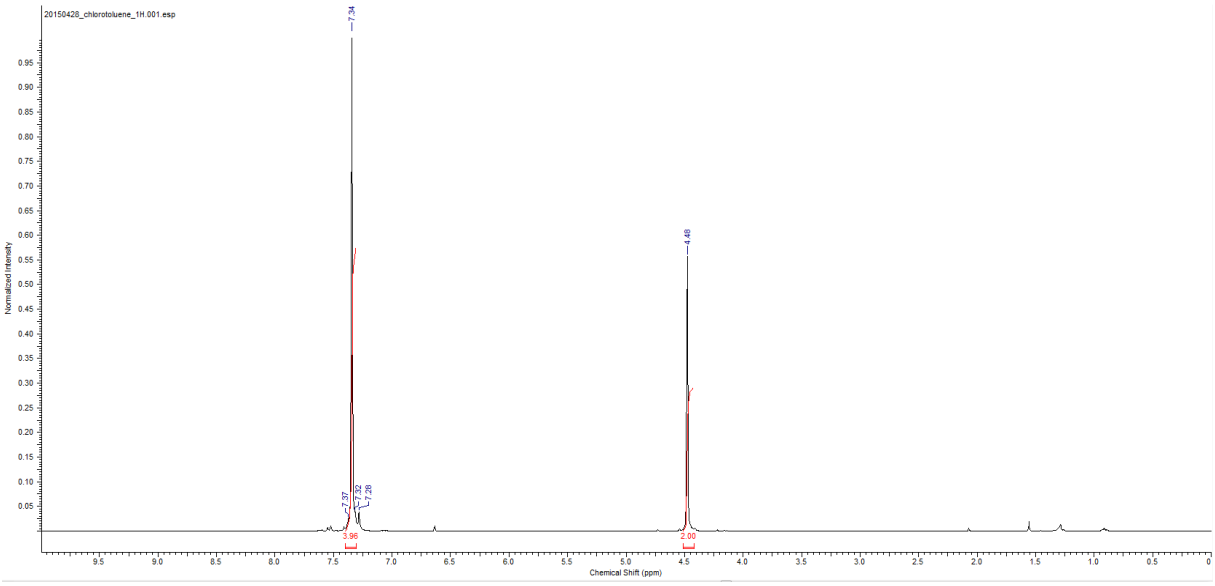


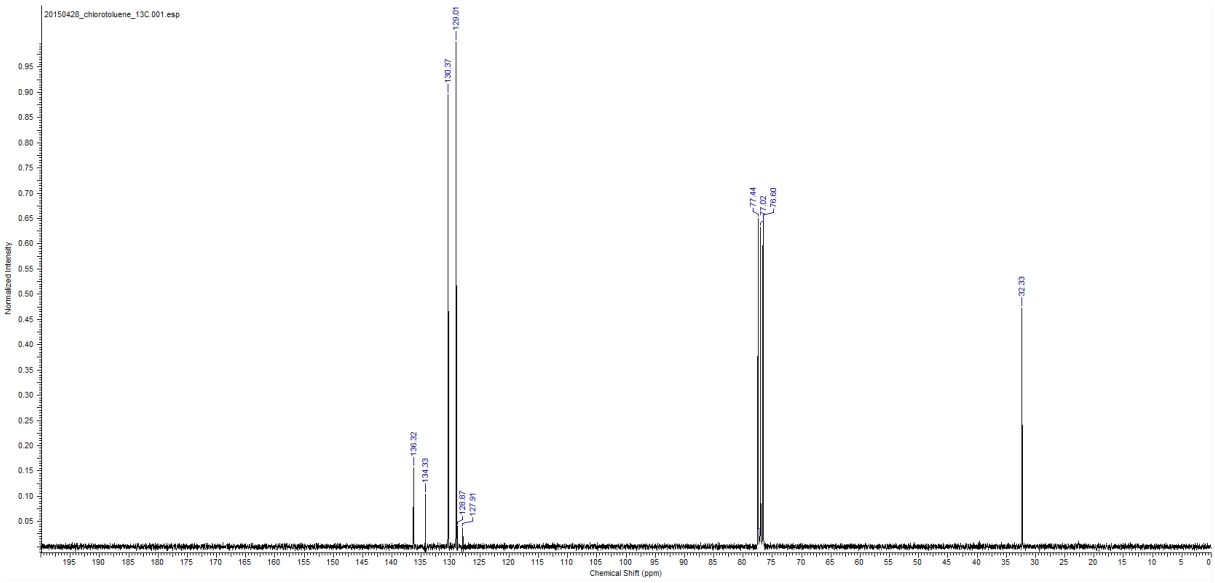


^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (75 MHz, $CDCl_3$) (down)

1-(bromomethyl)-4-chlorobenzene







^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (75 MHz, $CDCl_3$) (down)