

# Supplementary Information

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## **CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-SO<sub>3</sub>H nano composite as a magnetically recoverable catalyst for oxidative bromination of alkynes**

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### **Experimental Data:**

<sup>1</sup>H NMR and <sup>13</sup>C spectra were recorded in Bruker Avance 300 MHz instrument. Chemical shifts are given in  $\delta$  units relative to the tetramethylsilane (TMS) signal as an internal reference in CDCl<sub>3</sub>. Coupling constants ( $J$ ) are reported in hertz (Hz). IR spectra were recorded in Perkin – Elmer Spectrum RXI FT-IR spectrometer. Silica gel (230-400 mesh) was used for column chromatography.

### Characterization:

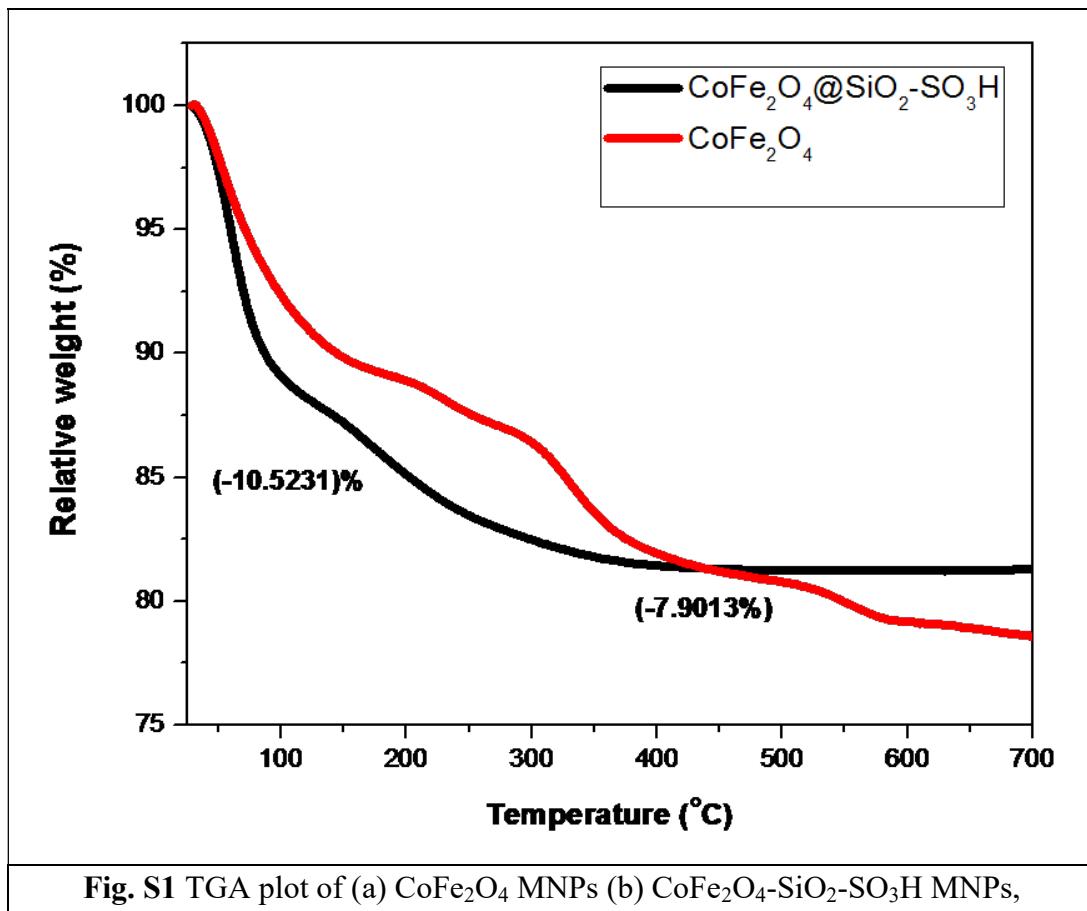


Fig. S1 TGA plot of (a)  $\text{CoFe}_2\text{O}_4$  MNPs (b)  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-SO}_3\text{H}$  MNPs,

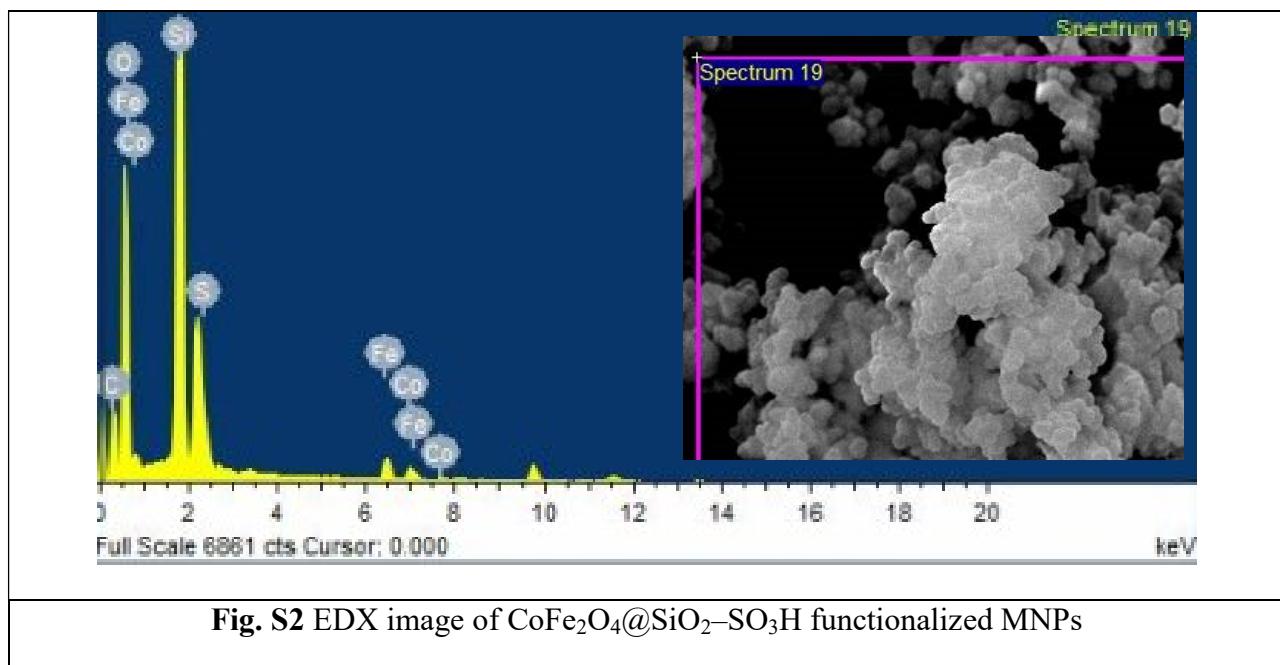
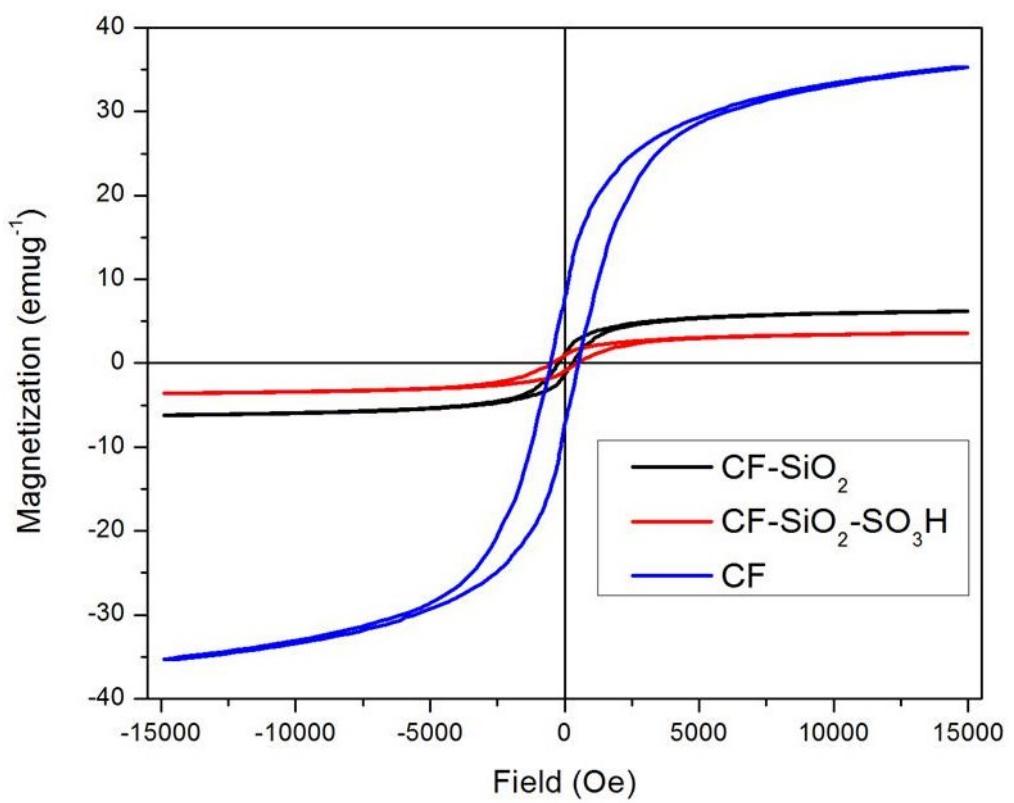
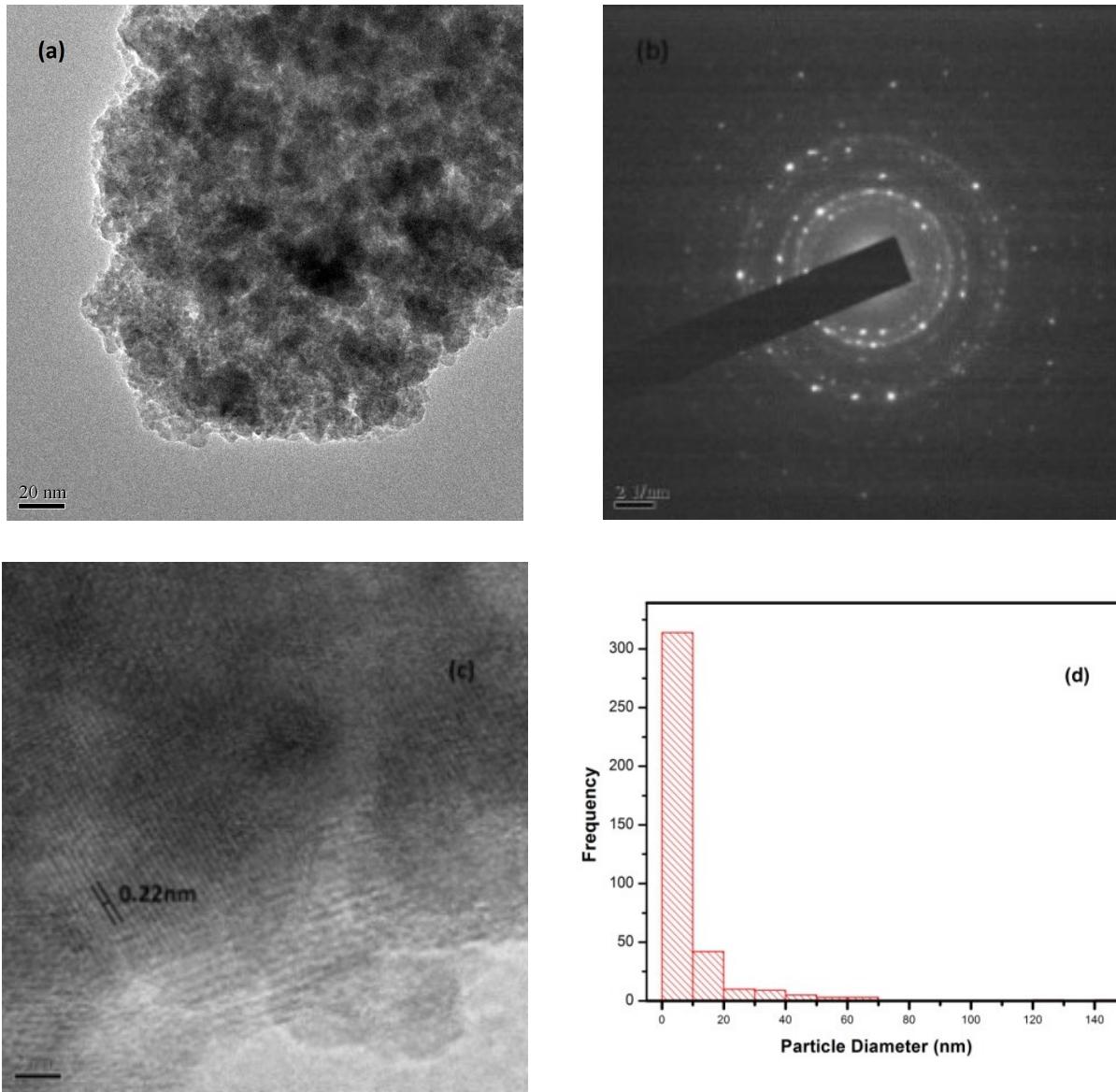


Fig. S2 EDX image of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$  functionalized MNPs



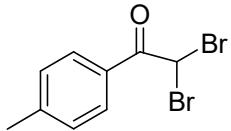
**Fig.S3** M-H loop in VSM measurement of for CoFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>, and CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H



**Fig. S4** TEM images. (a) TEM image of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$  MNPs, (b) SAED pattern of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$  MNPs. (c) HRTEM images of  $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$  MNPs. (d) Particle size distribution of  $\text{CoFe}_2\text{O}_4-\text{SO}_3\text{H}$  MNPs.

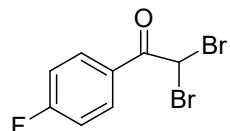
### Spectroscopic Data:

#### 1. 2,2-dibromo-1-p-tolyethanone (3b)<sup>1</sup>



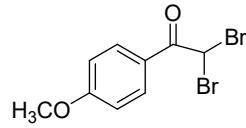
Yield: 86%; Pale yellow crystals, m.p. 96-98° C; IR (KBr, cm<sup>-1</sup>):  $\nu_{\max}$ . 3452, 3026, 3014, 2928, 2850, 1708, 1684, 1426, 1271, 993, 966, 758, 689; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm) : 7.98 (d, 2H, *J* = 9 Hz), 7.31 (d, 2H, *J* = 6 Hz) 6.71 (s, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ (ppm) : 185.6, 145.7, 129.8, 129.6, 128.1, 39.9, 21.8.

#### 2. 2,2-dibromo-1-(4-fluorophenyl)ethanone (4b)<sup>3,5</sup>



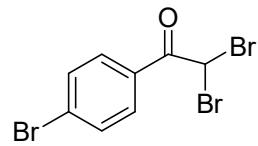
Yield: 80%; Pale yellow oil; IR (KBr, cm<sup>-1</sup>):  $\nu_{\max}$ . 3446, 3026, 2983, 2922, 2850, 2366, 2331, 1707, 1677, 1648, 1599, 1548, 1464, 1407, 1372, 1323, 1265, 1187, 1135, 1073, 980, 857, 597; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm): 8.12-8.18 (m, 2H), 7.08-7.27 (m, 2H), 6.64 (s, 1H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ(ppm): 184.5, 167.3, 165.3, 132.7, 132.6, 127.1, 116.3, 116.1, 39.3.

#### 3. 2,2-dibromo-1-(4-methoxyphenyl)ethanone (5b)<sup>4</sup>



Yield: 87%; White solid m.p. 86-88° C; IR (KBr, cm<sup>-1</sup>):  $\nu_{\max}$ . 3460, 3042, 2970, 2934, 2839, 1684, 1599, 1492, 1464, 1442, 1288, 1260, 1168, 1109, 1048, 1015, 981, 857, 815, 747, 702, 632, 597, 532, 504; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 8.06 (d, 2H, *J* = 9.3 Hz), 6.96 (d, 2H, *J* = 9 Hz), 6.69 (s, 1H), 3.88 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ (ppm): 184.5, 164.4, 132.1, 123.2, 114.1, 55.6, 39.9.

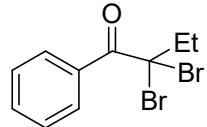
#### 4. 2,2-dibromo-1-(4-bromophenyl)ethanone (6b)<sup>1,5</sup>



Yield: 84%; Colourless solid m.p. 92-93° C; IR (KBr, cm<sup>-1</sup>):  $\nu_{\max}$ . 3074, 1698, 1600, 1501,

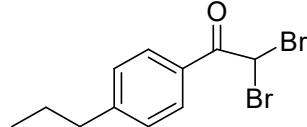
1426, 1281, 1204, 1132, 1096, 1015, 996, 885, 738, 689, 650, 582;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300MHz)  $\delta$  (ppm): 7.98 (d, 2H,  $J = 8.7$  Hz), 7.67 (d, 2H,  $J = 8.1$  Hz), 6.61 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  (ppm): 185.1, 132.3, 131.2, 129.9, 129.4, 39.2.

**5. 2,2-dibromo-1-phenylbutan-1-one (7b)<sup>4a, 5</sup>**



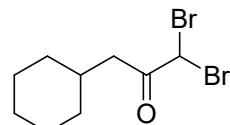
Yield: 84%; Colourless oil; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  3460, 3055, 3026, 2932, 1698, 1455, 1257, 1188, 981, 804;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  (ppm): 8.37 (d, 2H,  $J = 7.8$  Hz), 7.45-7.61 (m, 3H), 2.75-2.68 (q, 2H), 1.30 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  (ppm): 188.6, 133.2, 132.6, 131.1, 127.9, 68.2, 40.1, 11.9.

**6. 2,2-dibromo-1-(4-propylphenyl) ethanone(8b)<sup>5</sup>**



Yield: 85%; Pale yellow oil; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  3406, 3022, 2939, 2856, 2334, 1692, 1591, 1418, 1262, 1161, 997, 832, 712, 574;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  (ppm): 8.00 (d, 2H,  $J = 8.1$  Hz), 7.31 (d, 2H,  $J = 8.4$  Hz), 6.73 (s, 1H), 2.67 (t, 2H,  $J = 7.5$  Hz), 1.61-1.74 (m, 2H), 0.96 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  (ppm): 185.5, 150.3, 129.7, 128.9, 128.2, 39.8, 38.0, 24.0, 13.7.

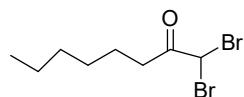
**7. 1,1-dibromo-3-cyclohexyl-propan-2-one (9b)**



Yield: 77%; Pale yellow oil; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  2920, 2864, 2358, 2331, 1727, 1649, 1542, 1464, 1407, 1378, 1294, 1243, 1158, 1072, 1029, 874;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  (ppm):

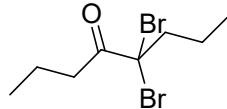
5.76 (s, 1H), 2.78 (d, 2H,  $J$  = 6.6 Hz), 1.68-1.72 (m, 5H), 1.12-1.30 (m, 4H), 0.84-1.04 (m, 2H);  $^{13}$  C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 196.1, 43.5, 42.4, 33.8, 32.8, 26.0, 25.9. GCMS (M/Z %): 217 (3) (M<sup>+</sup>-Br), 201 (2), 173 (12), 160 (2), 149 (2), 137 (5 ), 126 (38) , 125 (63.51), 120 (8), 107, 98 (36), 97 (60), 95 (11), 83 (50), 79 (24), 77 (12), 67 (43), 57 (7), 56 (16), 55 (55), 54 (100), 53 (34), 51 (12), 43 (26), 41 (74), 39 (62), 38 (11), 29 (36), 27 (42), 26 (8).

**8. 1,1-dibromooctan-2-one (10b)**<sup>1b,4</sup>



Yield: 75%; Pale yellow oil; IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{max}}$ . 3458, 2936, 2840, 1656, 1458, 1118, 1030, 760, 625;  $^1$ H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ (ppm): 5.79 (s, 1H), 2.92 (t, 2H,  $J$  = 7.5 Hz), 1.64-1.69 (m, 2H), 1.25-1.36 (m, 6H), 0.89 ( t, 3H,  $J$  = 6.3 Hz);  $^{13}$  C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 196.7, 43.0, 34.8, 31.3, 28.4, 24.1, 22.3, 13.9.

**11. 5,5-dibromooctan-4-one (11b)**<sup>2,4</sup>



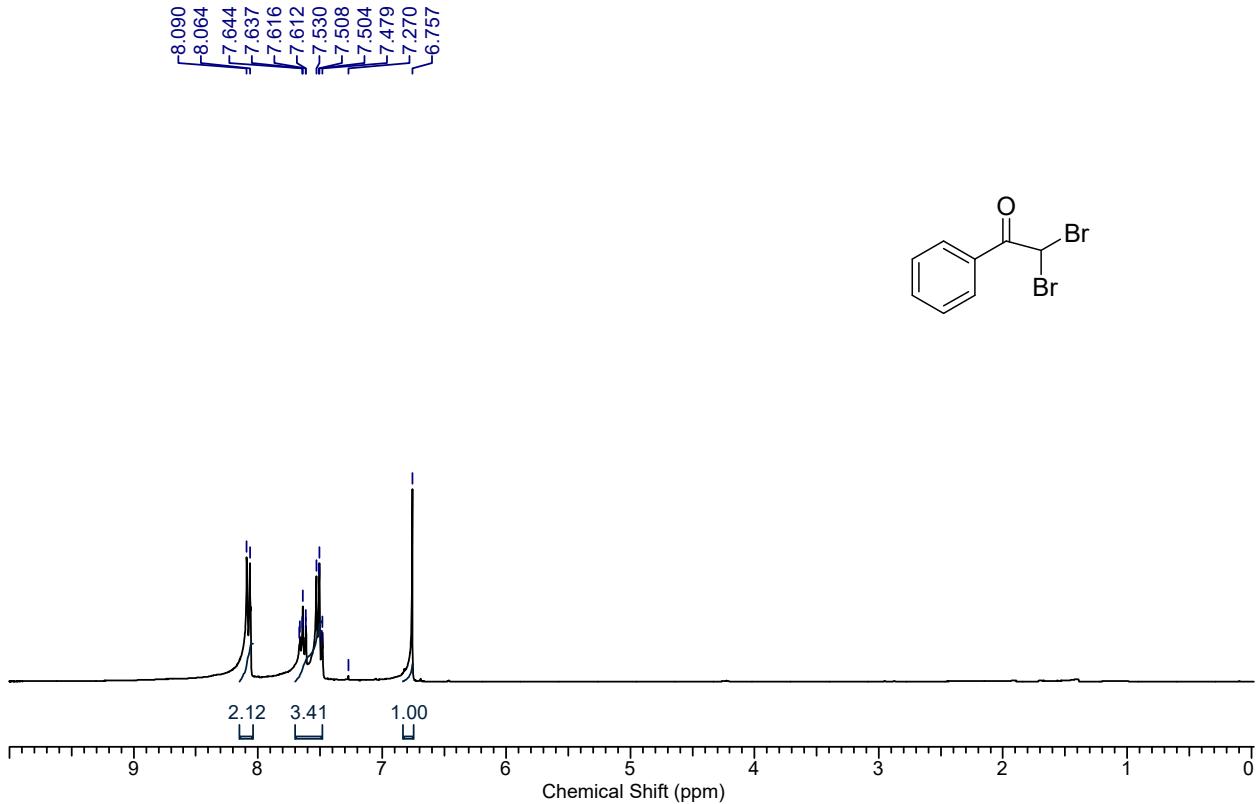
Yield: 70%; Pale yellow oil; IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{max}}$ . 3455, 2940, 2845, 1660, 1456, 1120, 1033, 761, 624;  $^1$ H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ (ppm): 3.06 (t, 2H,  $J$  = 7.2 Hz), 2.41-2.46 (m, 2H), 1.62-1.76 (m, 4H), 0.96-1.04 (m, 6H);  $^{13}$  C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ (ppm): 198.1, 46.7, 38.1, 21.0, 18.7, 13.4.

## References

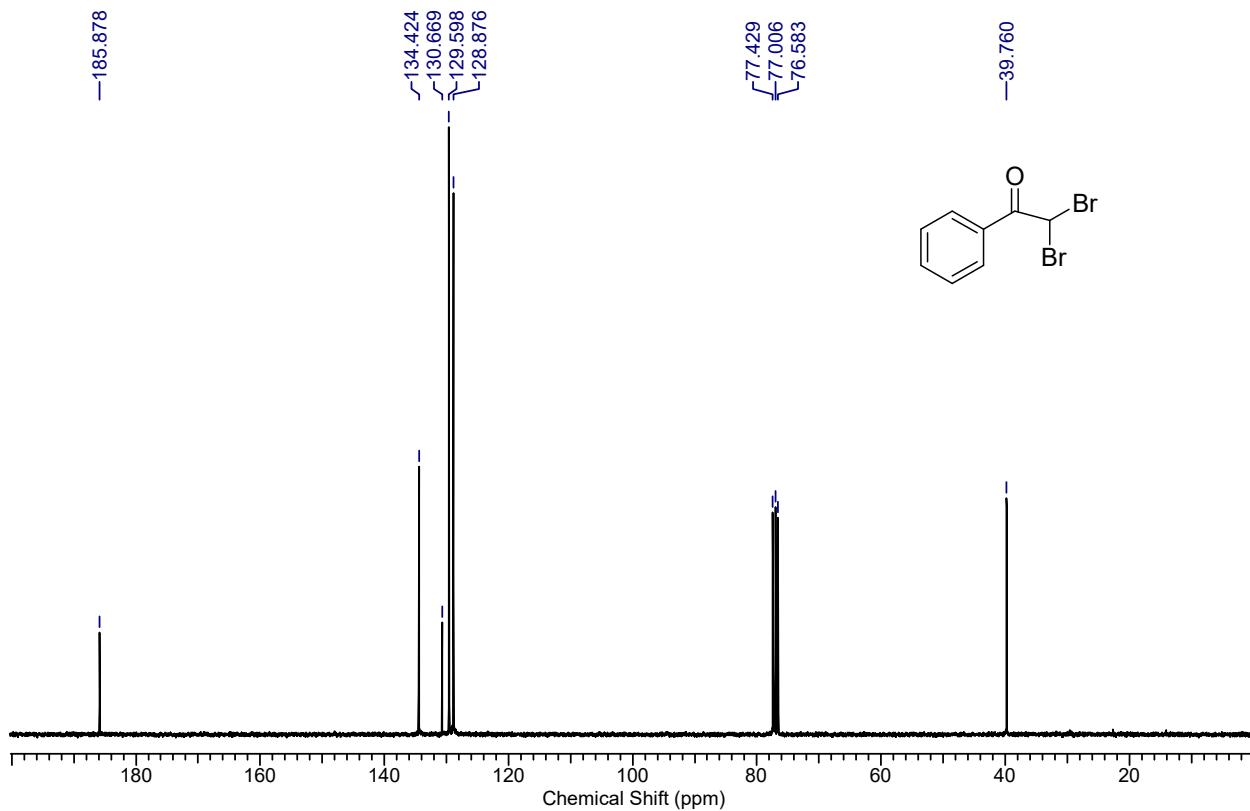
1. (a) Terent'ev, A. O.; Krylov, I. B.; Vil, V. A. Pastukhova, Z. Y.; Fastov, S. A.; Nikishin, G. *Eur. J. Chem.* **2012**, 10, 360-369; (b) Madabhushi, S.; Jillella, R.; Mallu, K. K. R.; Godala, K. R.; Vangipuram, V. S. *Tetrahedron Lett.* **2013**, 54, 3993.
2. Chawla, R.; Singh, A. K.; Yadav, L. D. S. *Synlett.* **2013**, 24, 1558.
3. Jucai, D.; Songlin, Z. *Synlett.* **2008**, 10, 1491-1494.
4. (a) Liu, J.; Li, W.; Li, Z. *Tetrahedron Lett.* **2011**, 52, 4320; (b) Vražič, D.; Jereb, M.; Laali, K. K.; Starber, S. *Molecules.* **2013**, 18, 74-96.
5. Wang, J-Y.; Jiang, Q.; Guo, C-C. *Synth Commun.* **2014**, 0, 1.

**$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of Compounds (1b, 2b, 3b, 4b, 5b, 6b, 7b, 8b, 9b, 10b and 11b)**

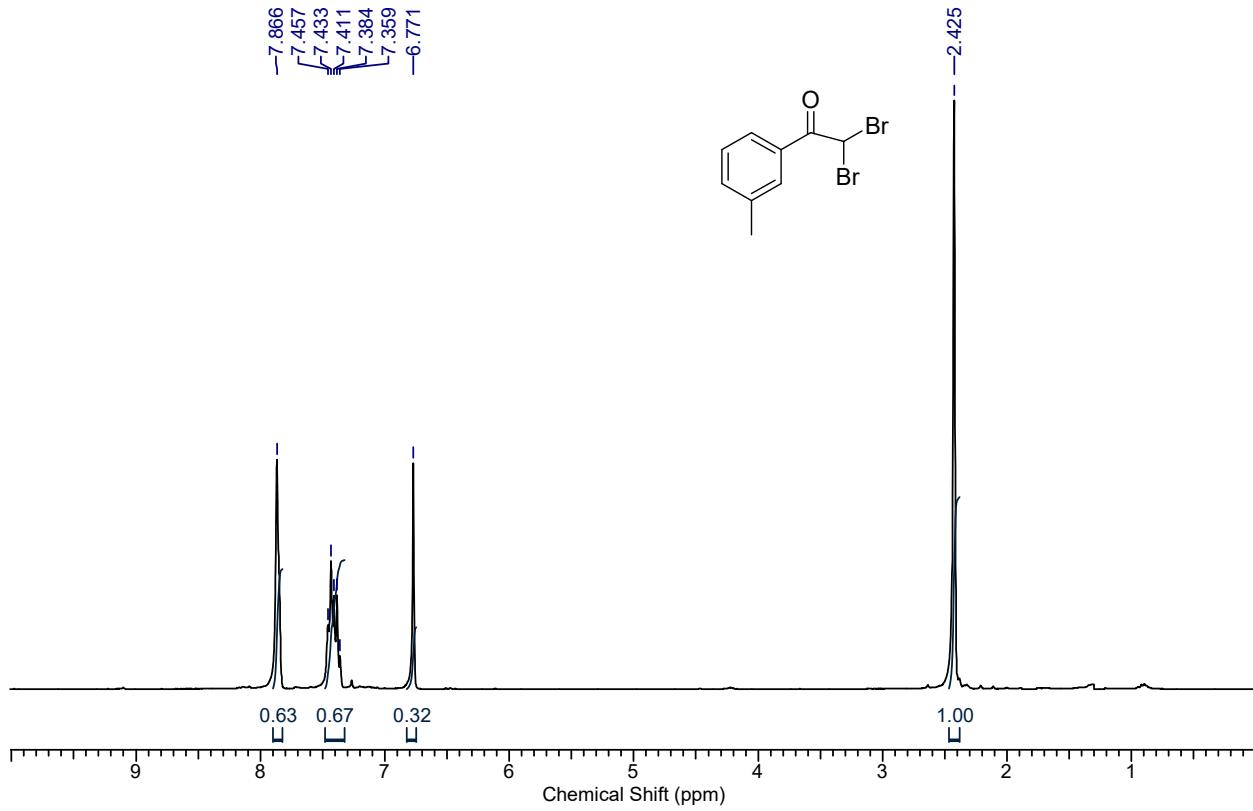
**2,2-dibromo-1-phenylethanone (1b)  $^1\text{H-NMR}$  spectrum**



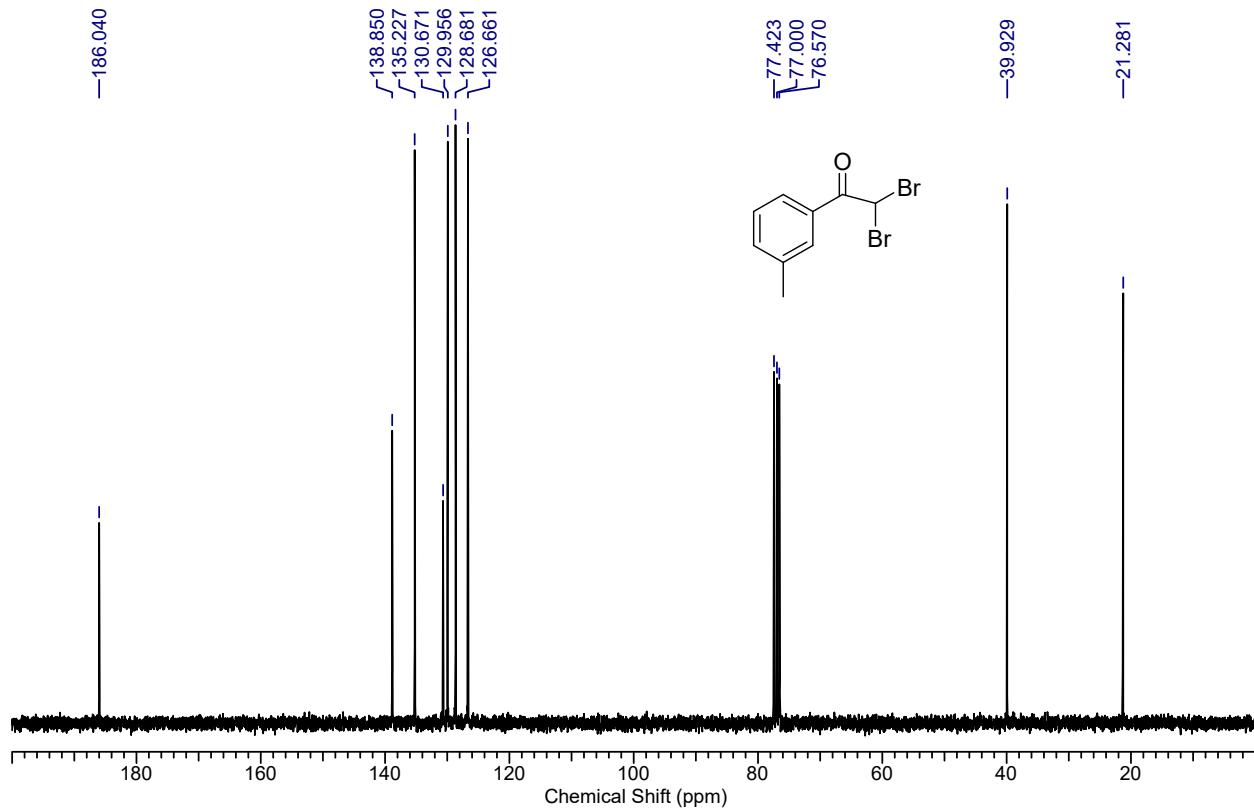
**2,2-dibromo-1-phenylethanone (1b)  $^{13}\text{C}$ -NMR spectrum**



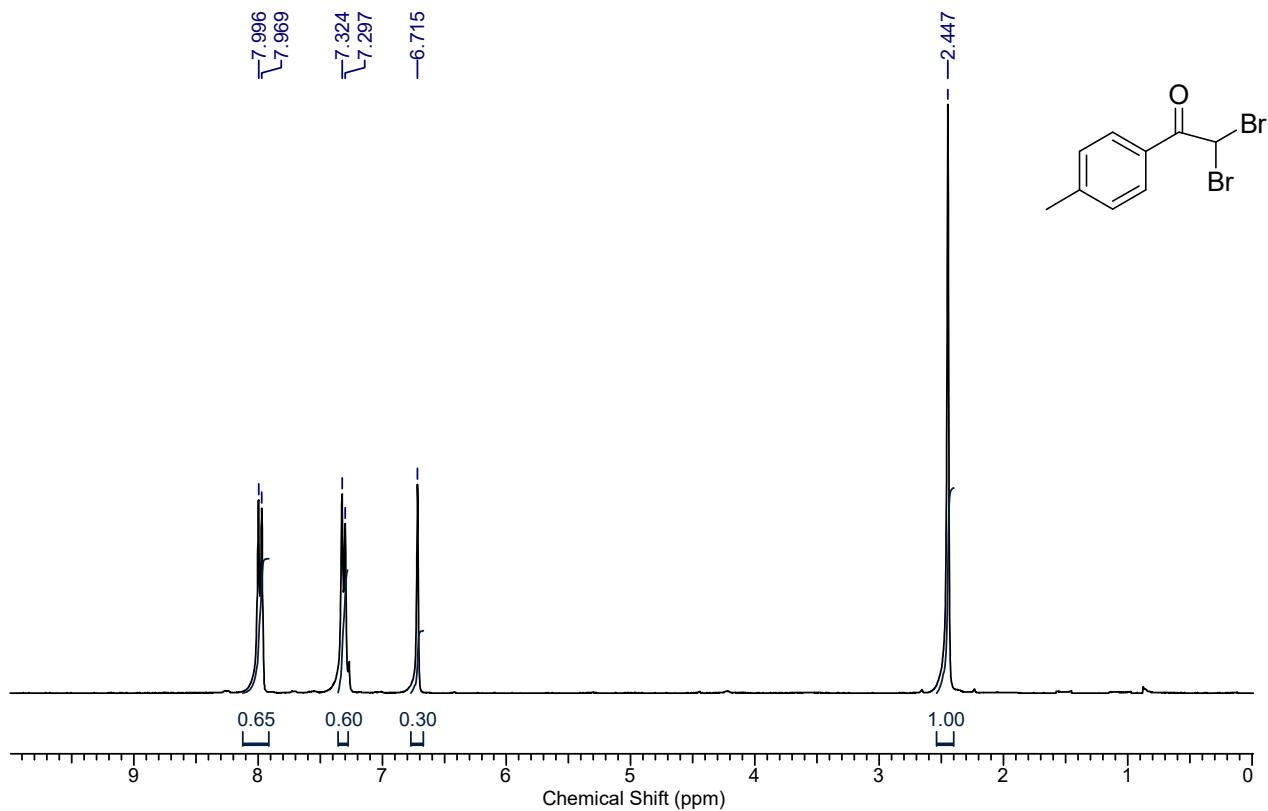
**2,2-dibromo-1-m-tolylethanone (2b)  $^1\text{H}$ -NMR spectrum**



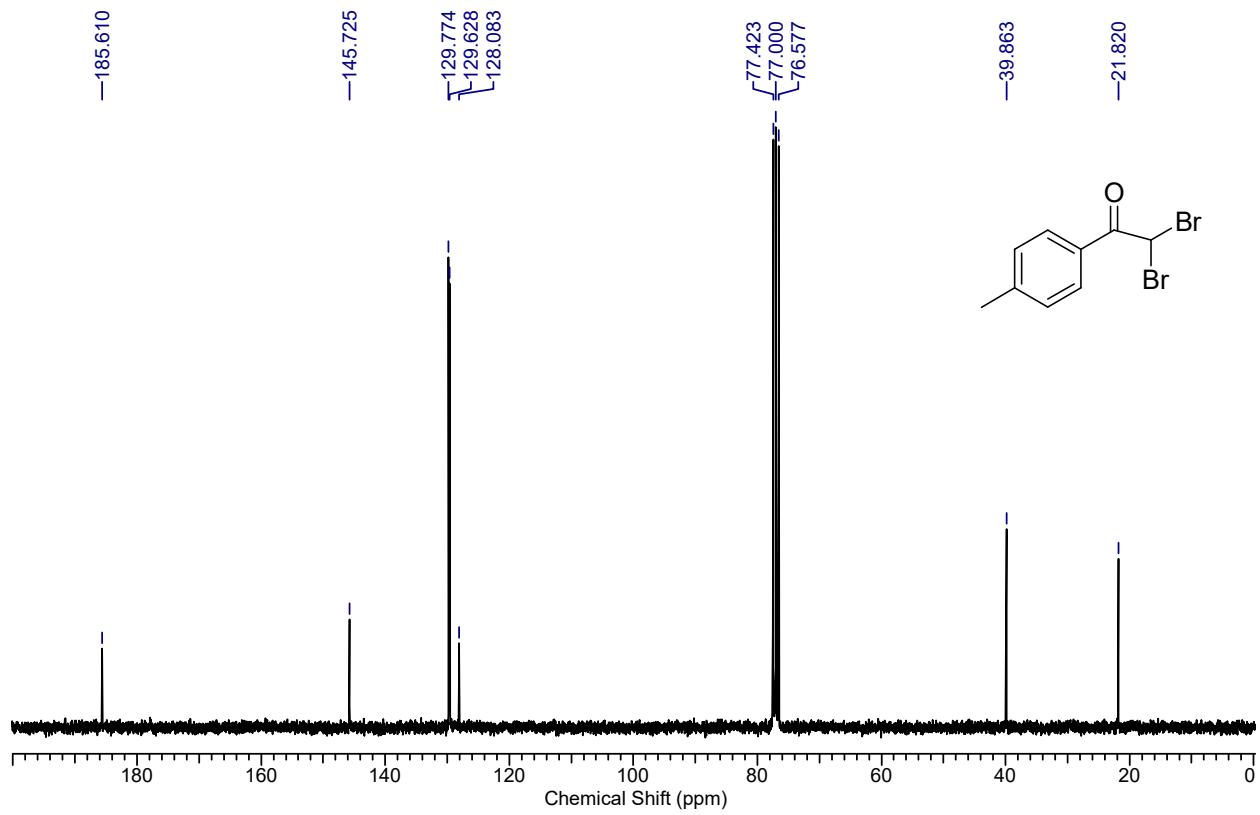
**2,2-dibromo-1-m-tolylethanone (2b)  $^{13}\text{C}$ -NMR spectrum**



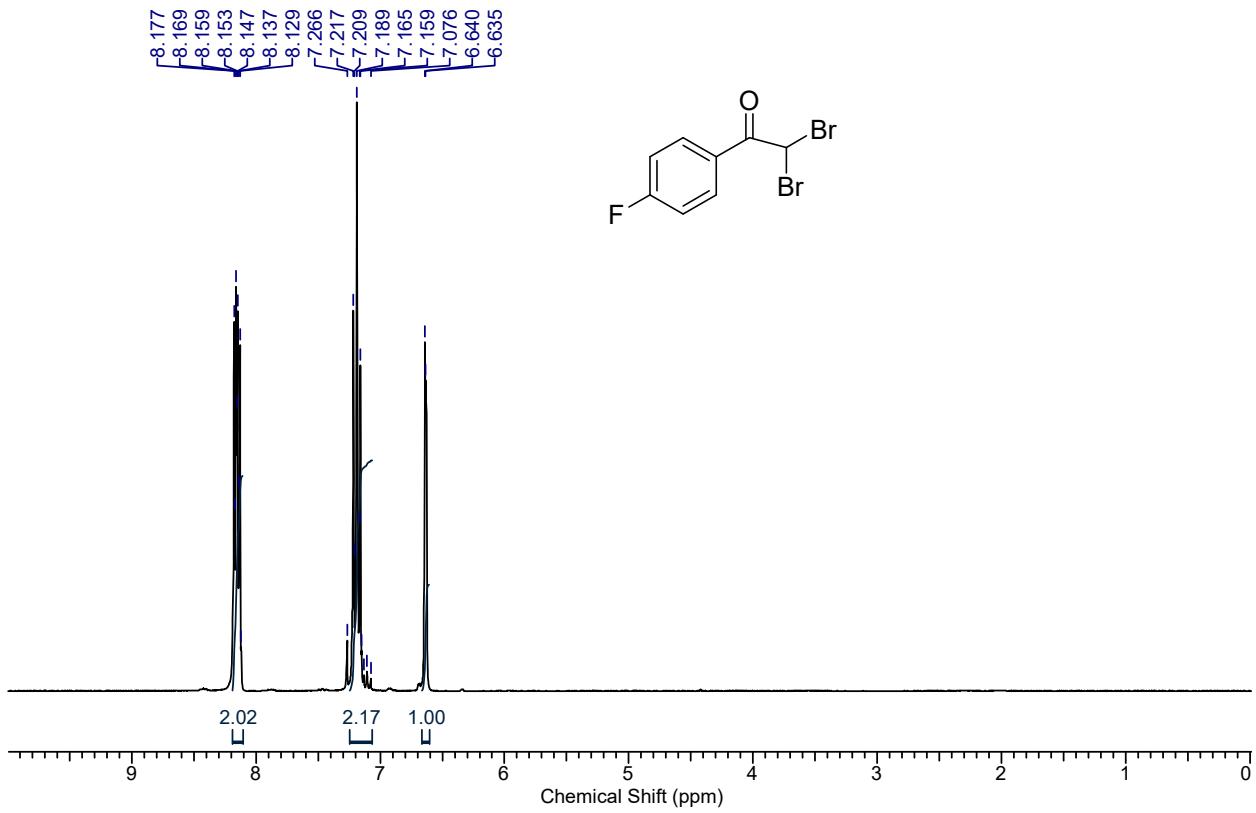
**2,2-dibromo-1-p-tolylethanone (3b)  $^1\text{H}$ -NMR spectrum**



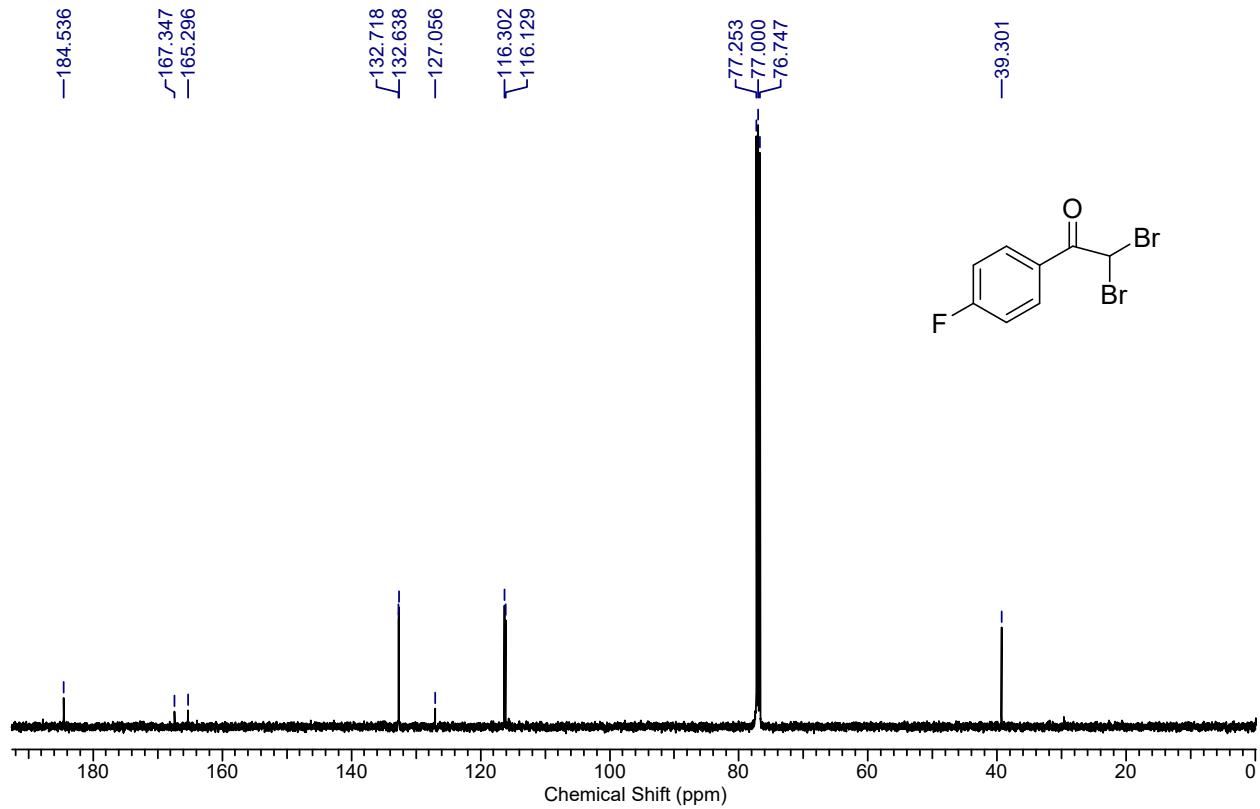
**2,2-dibromo-1-p-tolyethanone (3b)  $^{13}\text{C}$ -NMR spectrum**



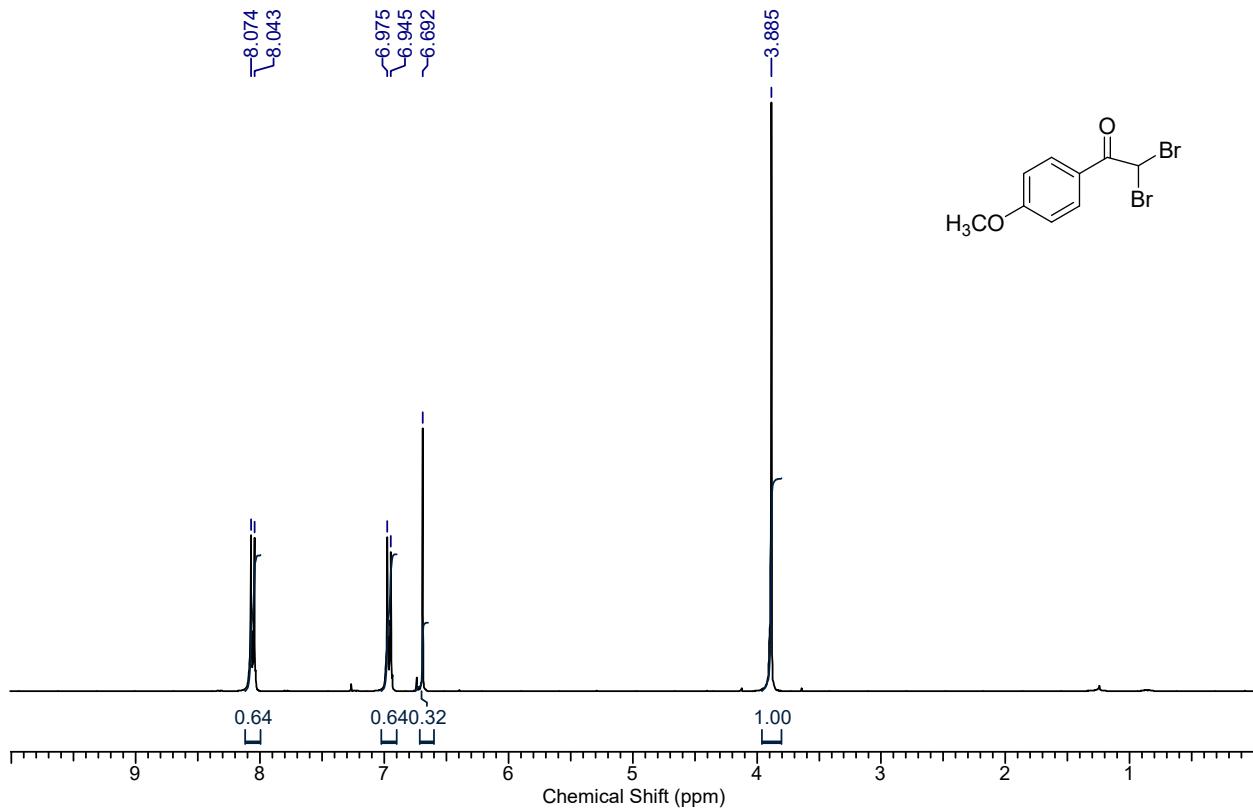
**2,2-dibromo-1-(4-fluorophenyl)ethanone (4b)  $^1\text{H-NMR}$  spectrum**



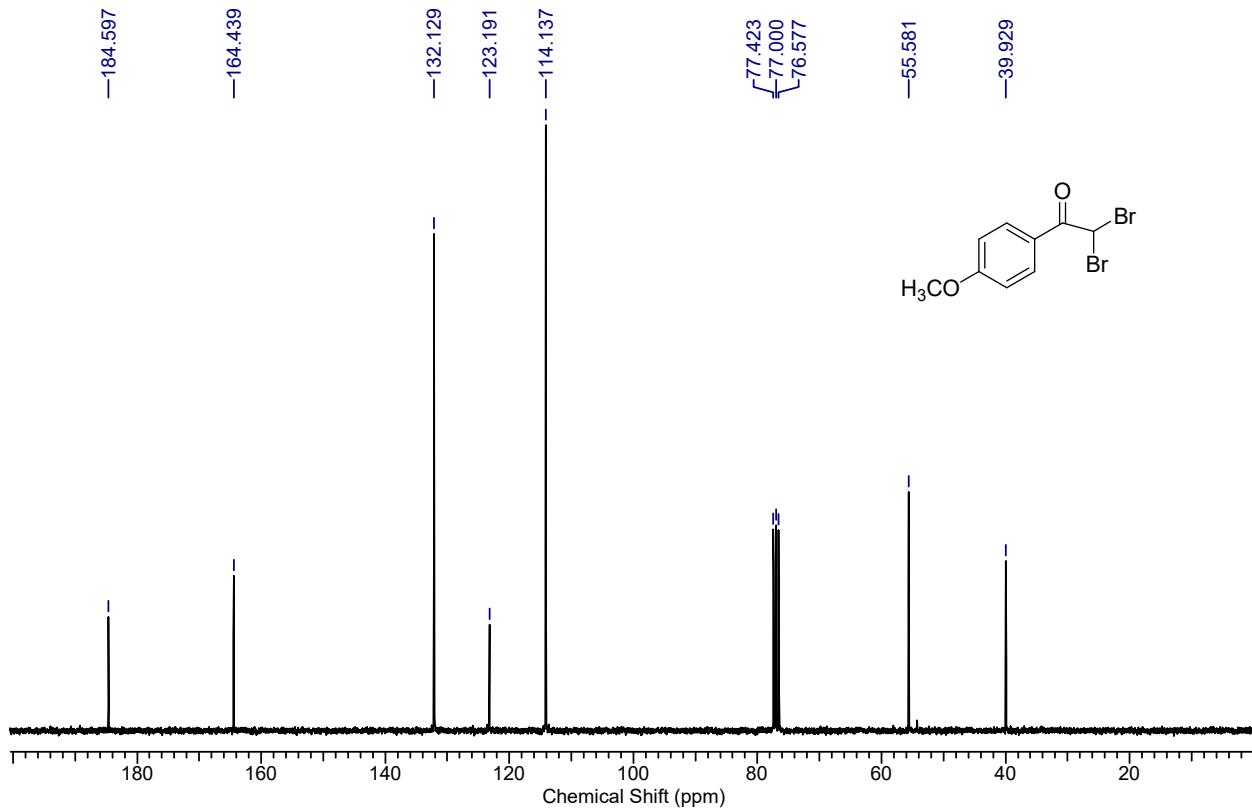
**2,2-dibromo-1-(4-fluorophenyl)ethanone (4b)  $^{13}\text{C}$ -NMR spectrum**



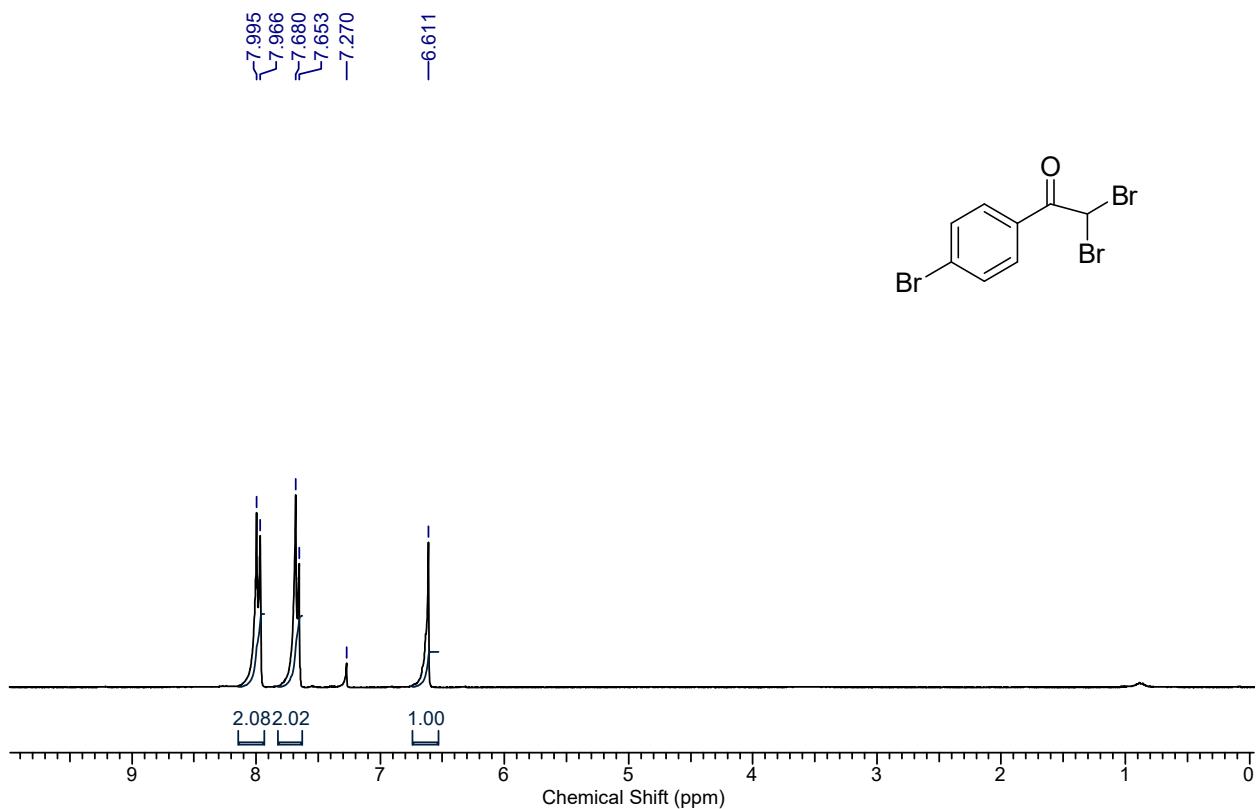
**2,2-dibromo-1-(4-methoxyphenyl)ethanone (5b)  $^1\text{H-NMR}$  spectrum**



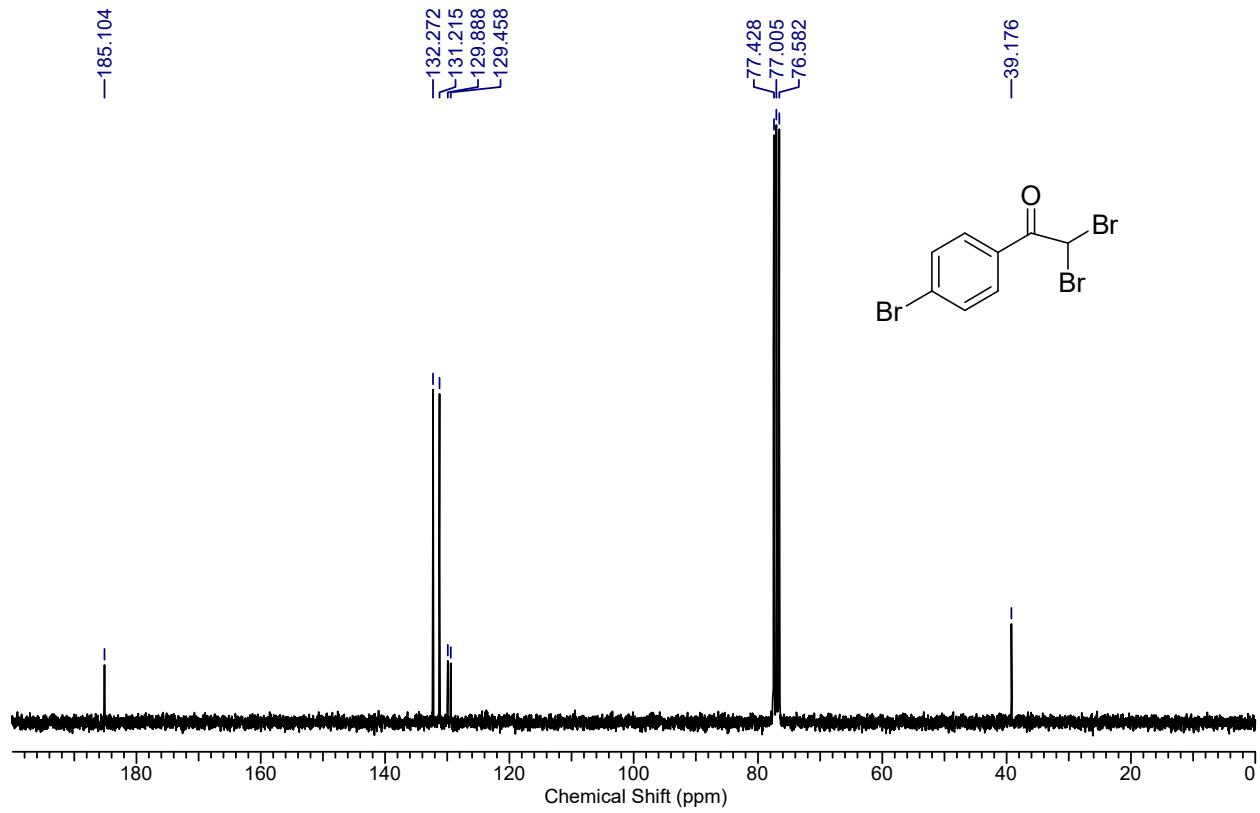
**2,2-dibromo-1-(4-methoxyphenyl)ethanone (**5b**)  $^{13}\text{C}$ -NMR spectrum**



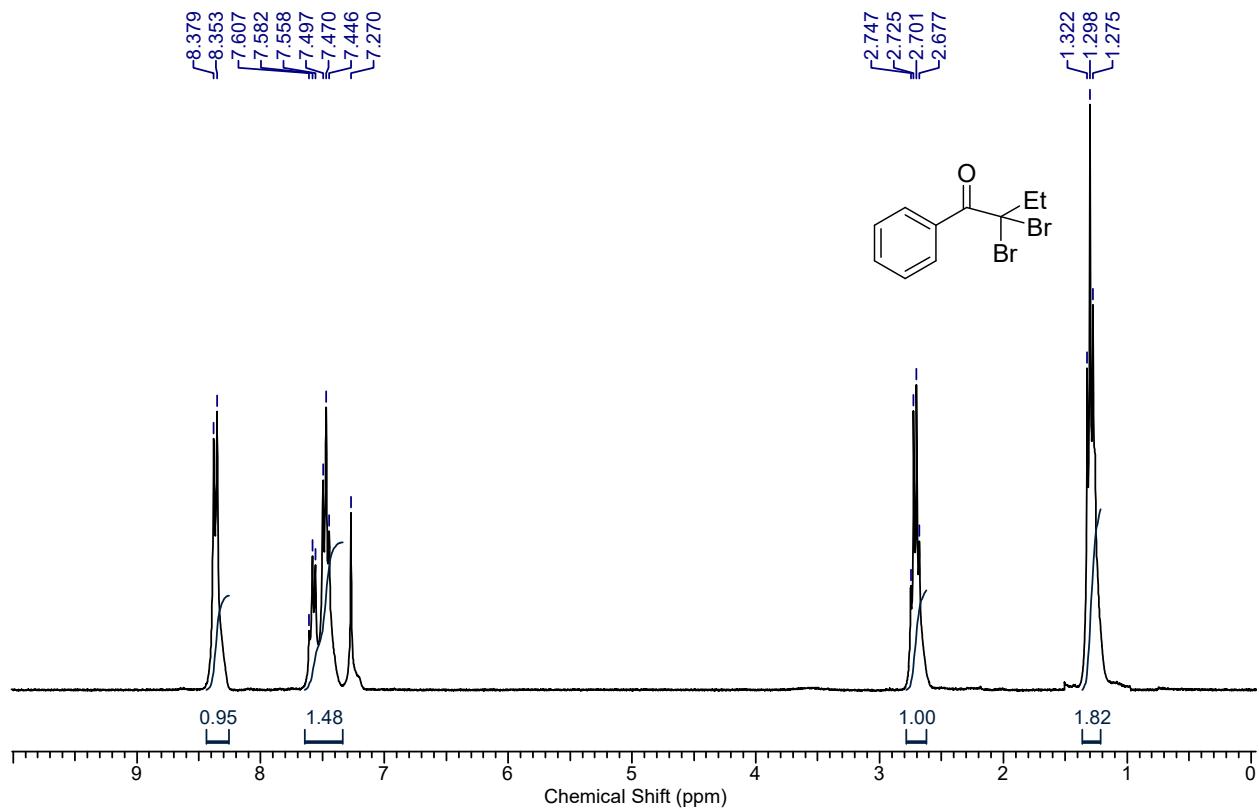
**2,2-dibromo-1-(4-bromophenyl)ethanone (6b)  $^1\text{H-NMR}$  spectrum**



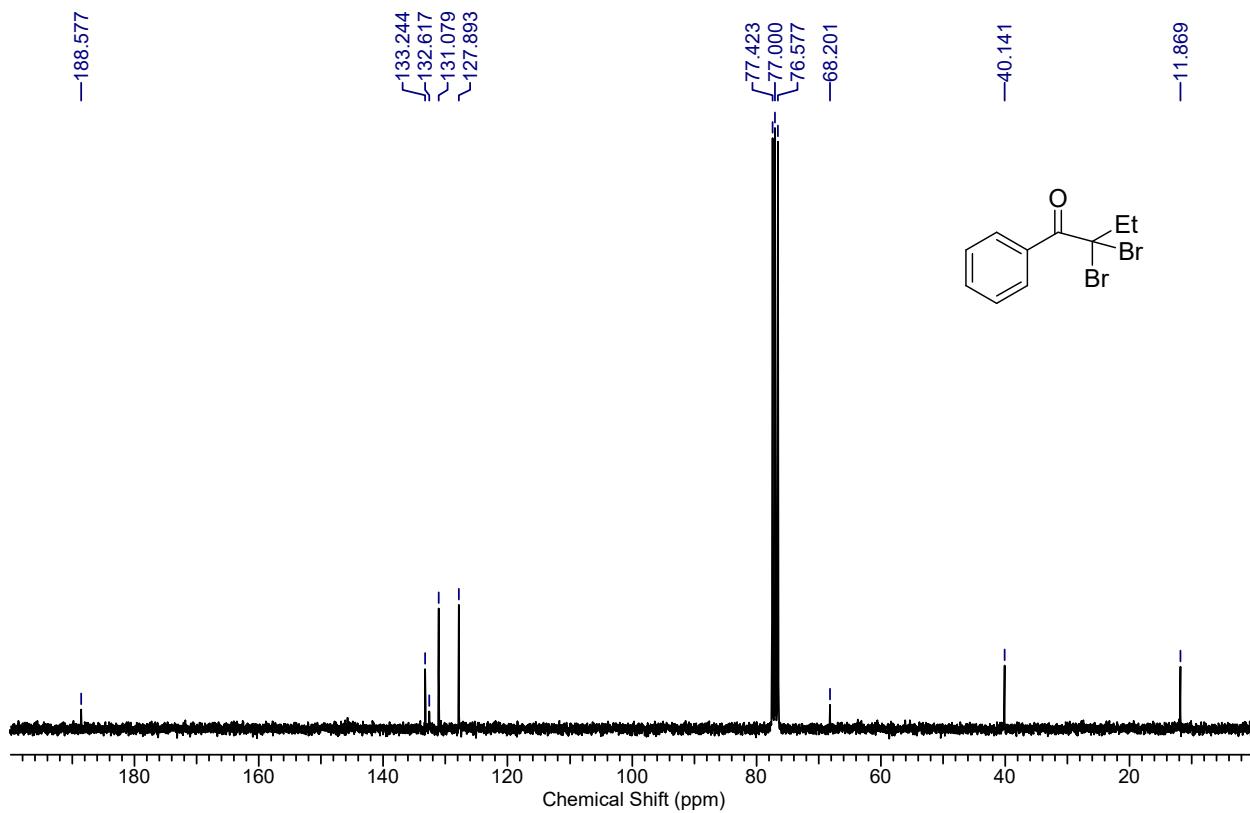
**2,2-dibromo-1-(4-bromophenyl)ethanone (6b)  $^{13}\text{C}$ -NMR spectrum**



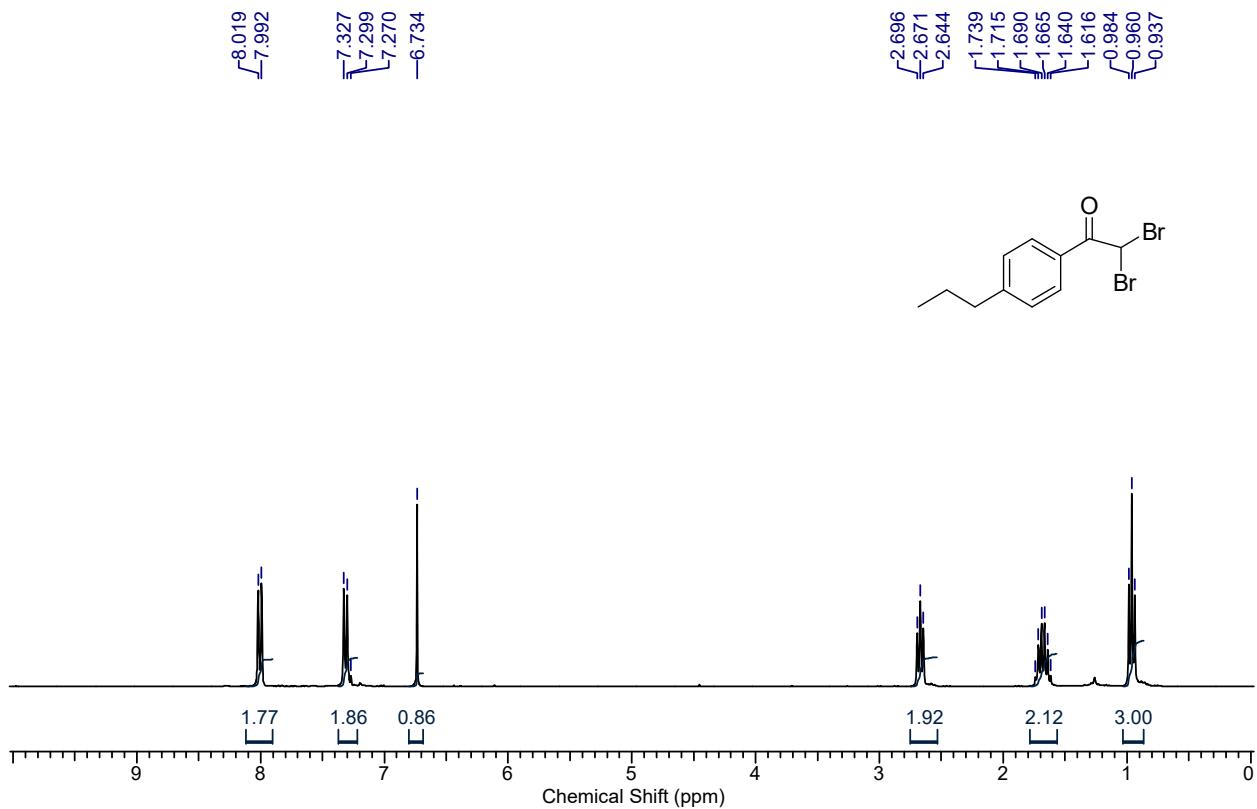
**2,2-dibromo-1-phenylbutan-1-one (7b)  $^1\text{H}$ -NMR spectrum**



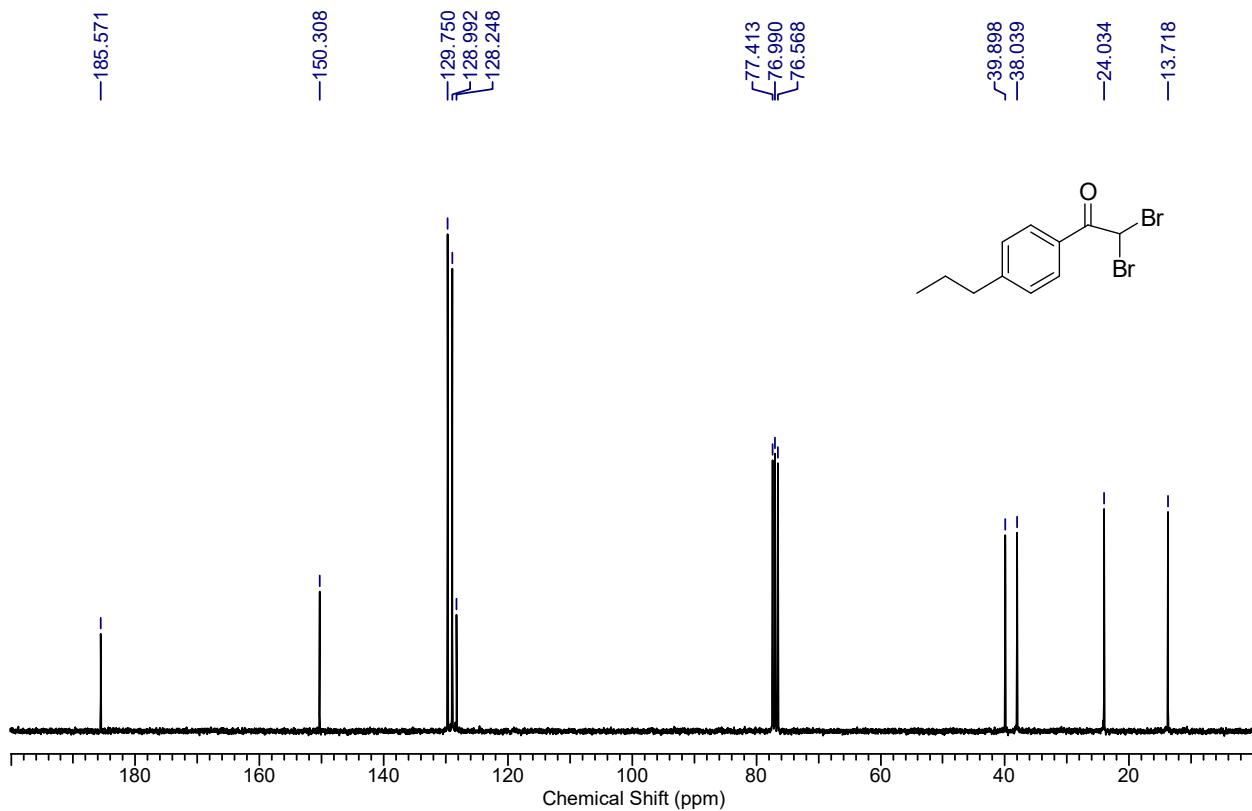
**2,2-dibromo-1-phenylbutan-1-one (7b)  $^{13}\text{C}$ -NMR spectrum**



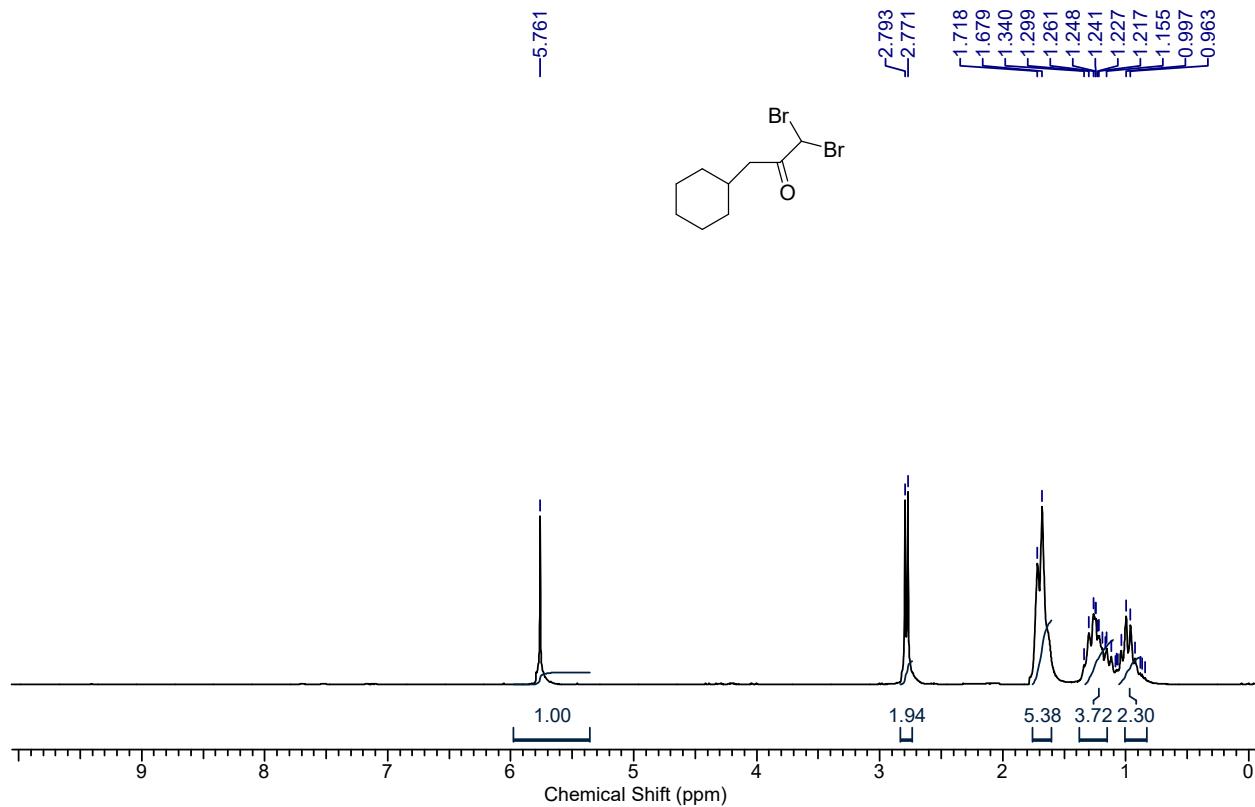
**2,2-dibromo-1-(4-propylphenyl) ethanone (8b)  $^1\text{H-NMR}$  spectrum**



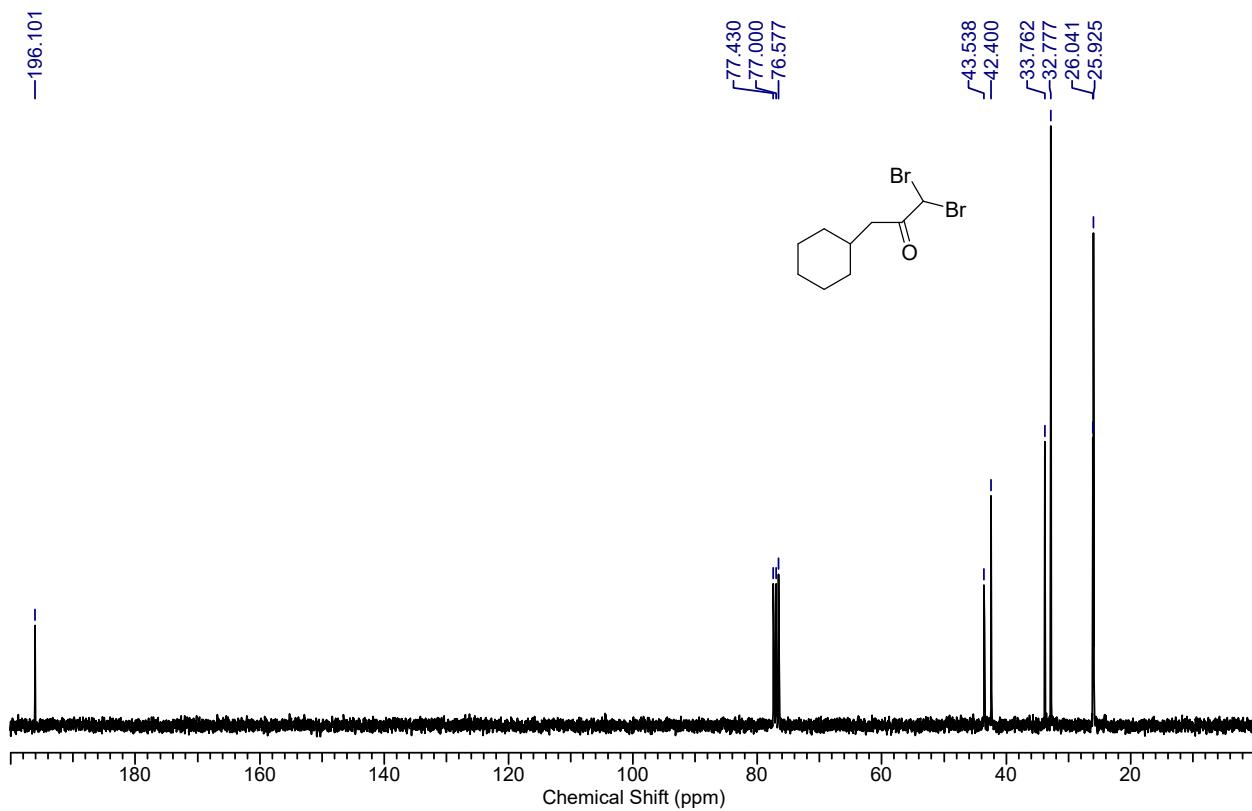
**2,2-dibromo-1-(4-propylphenyl)ethanone(8b)  $^{13}\text{C}$ -NMR spectrum**



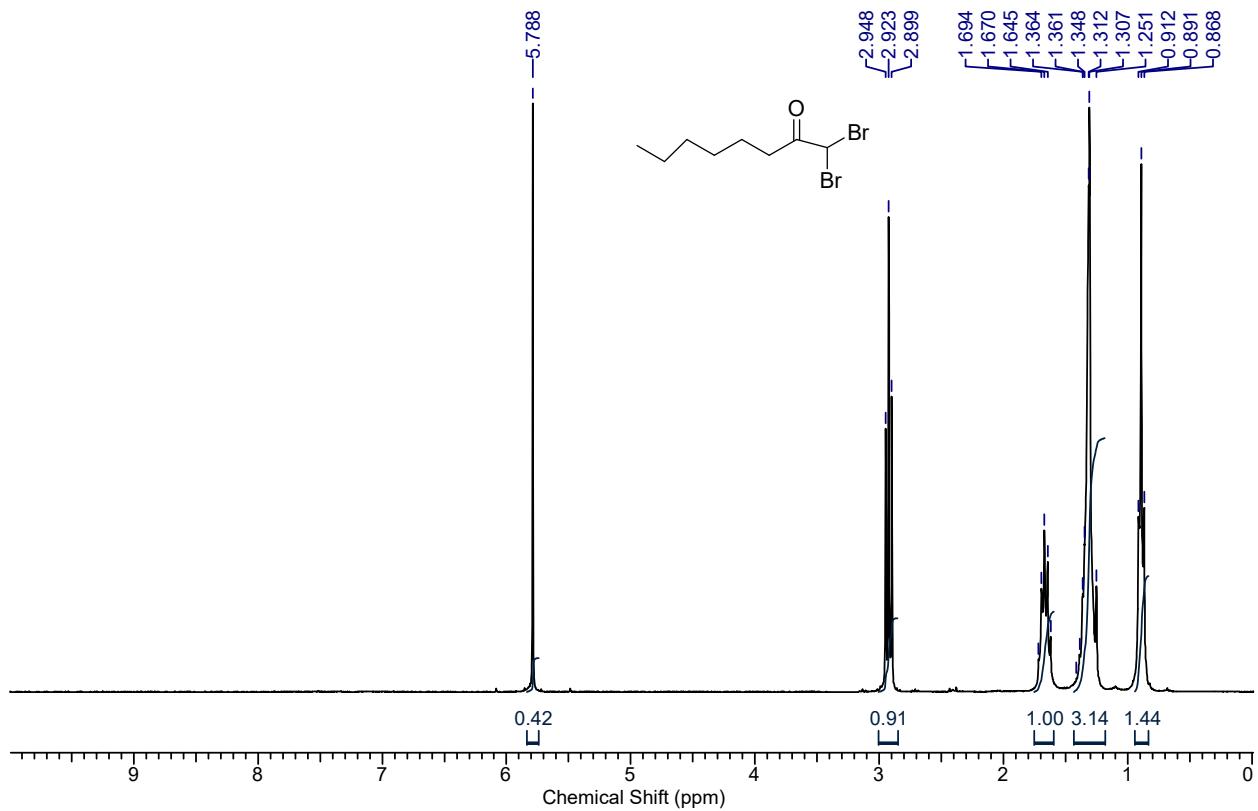
**1,1-dibromo-3-cyclohexylpropan-2-one (9b)  $^1\text{H-NMR}$  spectrum**



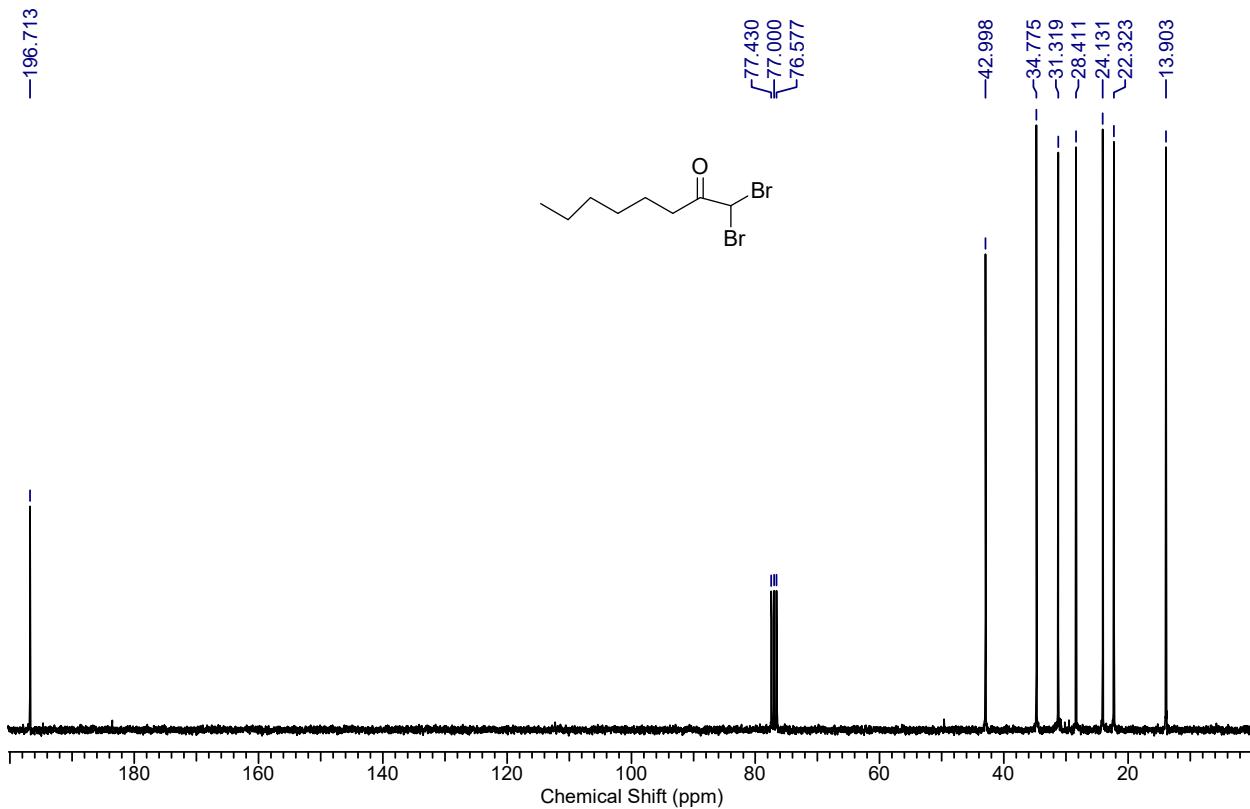
**1,1-dibromo-3-cyclohexylpropan-2-one (9b)  $^{13}\text{C}$ -NMR spectrum**



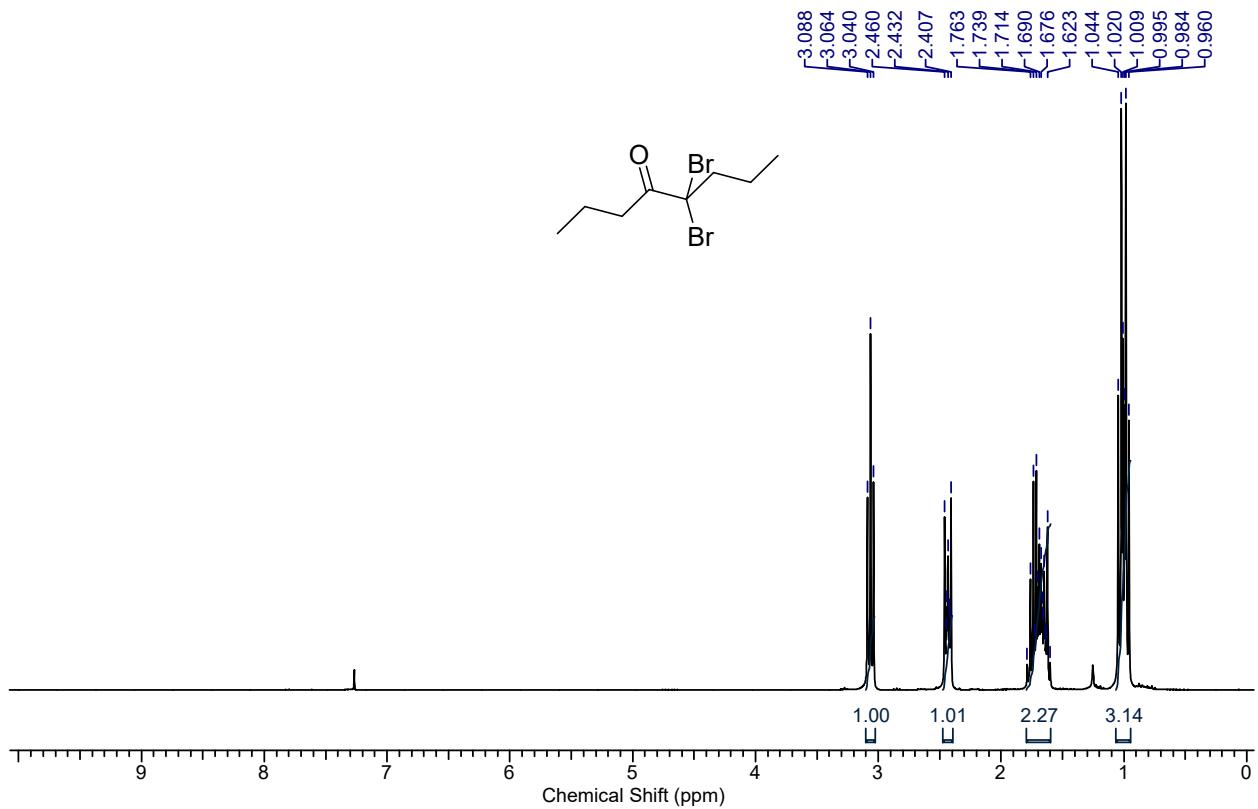
**1,1-dibromo-octan-2-one (10b)  $^1\text{H}$ -NMR spectrum**



**1,1-dibromoocan-2-one (10b)  $^{13}\text{C}$ -NMR spectrum**



**5,5-dibromo-*octan*-4-one (11b)  $^1\text{H}$ -NMR spectrum**



**5,5-dibromoocan-4-one (11b)  $^{13}\text{C}$ -NMR spectrum**

