

Electronic Supplementary Information

**Ring-Opening Iodination and Bromination of Unstrained
Cycloalkanols through β -Scission of Alkoxy Radicals**

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1. General information

1.1 Analytic methods

¹H, ¹³C NMR data were obtained on AVANCE III Bruker 400 M Hz nuclear resonance spectrometers unless otherwise noted. CDCl₃ was used as solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ¹H NMR spectrum as 0.00 ppm. The data of ¹H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ¹³C NMR spectra were recorded in ppm from TMS using the central peak of CDCl₃ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Photochemical reactions were carried with 10 W white LED. The LED lamp were purchased from Taobao. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CHI630E. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI and EI) by the Analytical Center of Peking University.

1.2 Reagents

PhI(OAc)₂ was purchased from Ouhe chemical company (China). MeCN was used after distillation. Other reagents were purchased and used directly without further purification. PE: petroleum ether; EA: ethyl acetate.

2. Experimental section

2.1 Standard reaction procedures

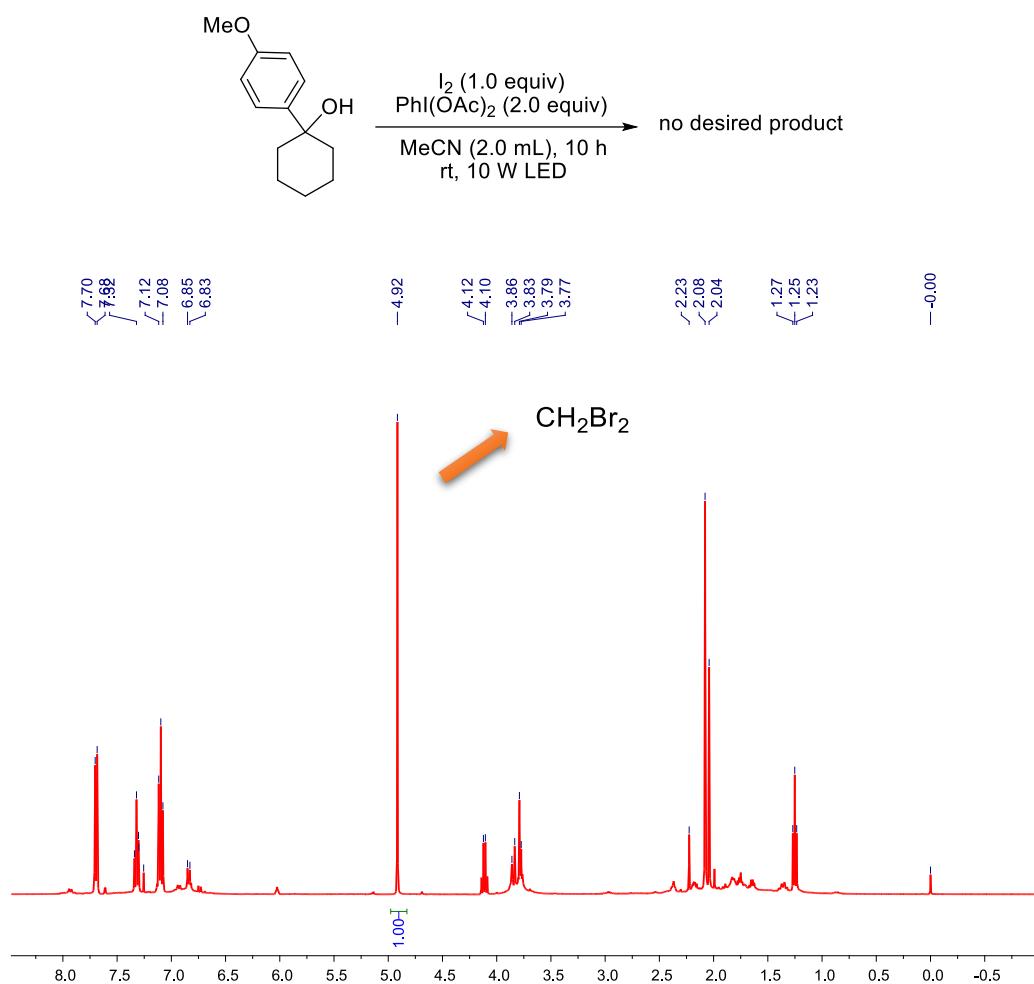
General procedure A (when cycloalkanols is solid). Cycloalkanol (0.2 mmol, 1.0 equiv), PhI(OAc)₂ (0.4 mmol, 2.0 equiv), and NaI or NaBr (2.0 equiv) were weighted and added to a 10 mL colorless transparent glass vial. The vial was degassed and refilled with N₂ for three times before 2.0 mL MeCN was added. Then the vial was irradiated by a 10 W white LED at room temperature with stirring for the appropriate time. Upon completion of the reaction, the solution was diluted with ethyl acetate, and was washed with aqueous sodium thiosulfate (20% w/w). The separated aqueous layer was further extracted with ethyl acetate and the combined organic fractions were dried over magnesium sulfate. Upon removal of magnesium sulfate the organic solution was concentrated in *vacuo* to yield the crude product. This crude product was purified using flash column chromatography on silica gel with gradient eluent (PE:EA = 40:1-10:1).

General Procedure B (when cycloalkanols is liquid) To a 10 mL colorless transparent glass vial was added PhI(OAc)₂ (0.4 mmol, 2.0 equiv), and NaI or NaBr (2.0 equiv). The vial was degassed and refilled with N₂ for three times. Then a solution of cycloalkanol (0.2 mmol, 1.0 equiv) in MeCN (2.0

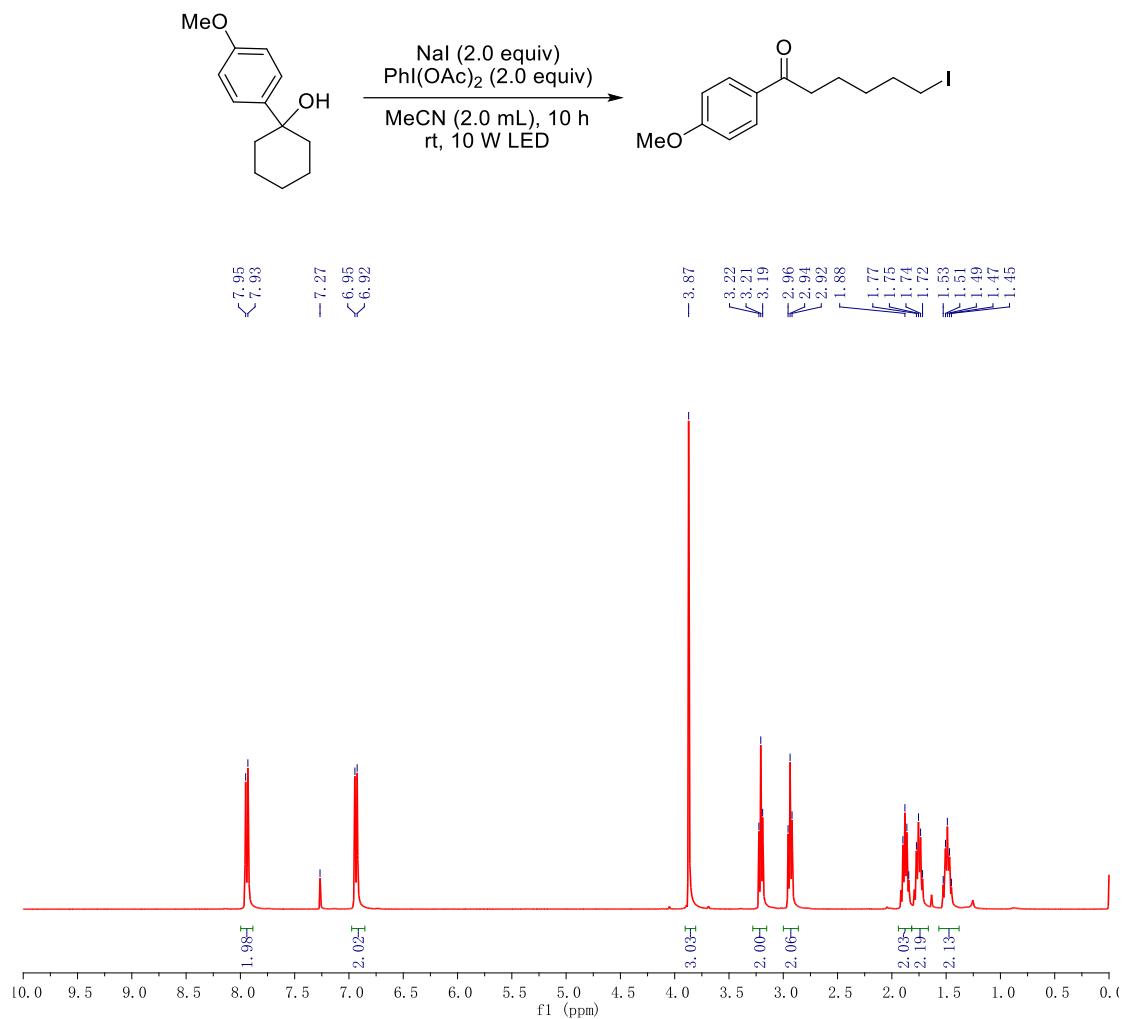
mL) was added to the vial. Subsequently the vial was irradiated by 10 W white LED at room temperature with stirring for appropriate time. Upon completion of the reaction, the solution was diluted with ethyl acetate, and washed with aqueous sodium thiosulfate (20% w/w). The separated aqueous layer was further extracted with ethyl acetate and the combined organic fractions were dried over magnesium sulfate. Upon removal of magnesium sulfate the organic solution was concentrated in vacuo to yield the crude product. This crude product was purified using flash column chromatography on silica gel with gradient eluent (PE:EA = 40:1-10:1).

2.2 Control experiments

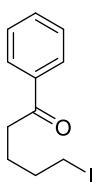
2.2.1 The reaction with Suárez reagent



2.2.2 The reaction under the conditions of this work.

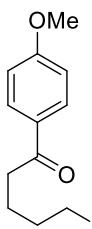


3. Characterization data of the products



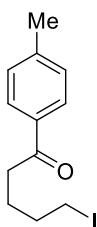
5-Iodo-1-phenylpentan-1-one **2**¹

¹H NMR (400 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.59-7.55 (m, 1H), 7.45-7.49 (m, 2H), 3.24 (t, *J* = 6.7 Hz, 2H), 3.01 (t, *J* = 6.7 Hz, 2H), 1.97-1.83 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 199.6, 136.8, 133.1, 128.7, 128.0, 37.3, 33.0, 25.1, 6.3.



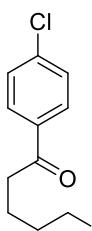
5-Iodo-1-(4-methoxyphenyl)pentan-1-one **3**

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 4H), 3.23 (t, *J* = 6.7 Hz, 2H), 2.95 (t, *J* = 6.9 Hz, 2H), 1.94-1.82 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 198.2, 163.5, 130.3, 129.9, 113.8, 55.5, 36.9, 33.1, 25.3, 6.4. HRMS (ESI): caclcd. for C₁₂H₁₆IO₂ ([M+H]⁺) 318.0195, found: 319.0189.



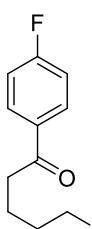
5-Iodo-1-(*p*-tolyl)pentan-1-one **4**

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 3.22 (t, *J* = 6.7 Hz, 2H), 2.97 (t, *J* = 6.7 Hz, 4H), 2.41 (s, 4H), 1.94-1.83 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 143.9, 134.4, 129.3, 128.2, 37.1, 33.03, 25.2, 21.7, 6.4. HRMS (ESI): caclcd. for C₁₂H₁₆IO ([M+H]⁺) 303.0246, found: 303.0241.



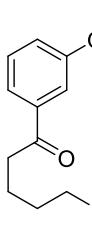
1-(4-Chlorophenyl)-5-iodopentan-1-one **5**

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 3.22 (t, *J* = 6.3 Hz, 2H), 2.97 (t, *J* = 6.7 Hz, 2H), 1.93-1.85 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 198.24, 139.53, 135.10, 129.46, 128.96, 37.24, 32.89, 24.96, 6.23. HRMS (ESI): caclcd. for C₁₁H₁₃ClIO ([M+H]⁺) 322.9700, found: 322.9692.



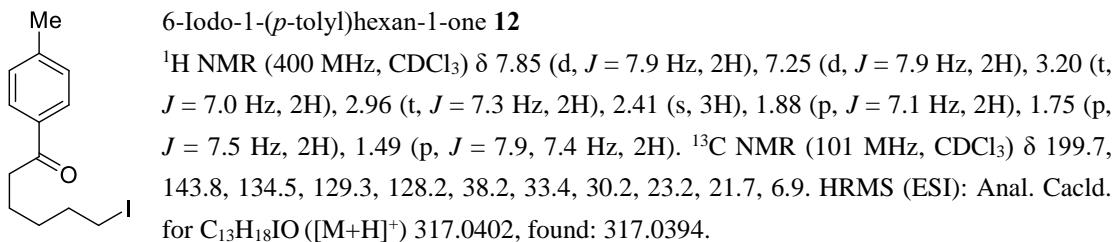
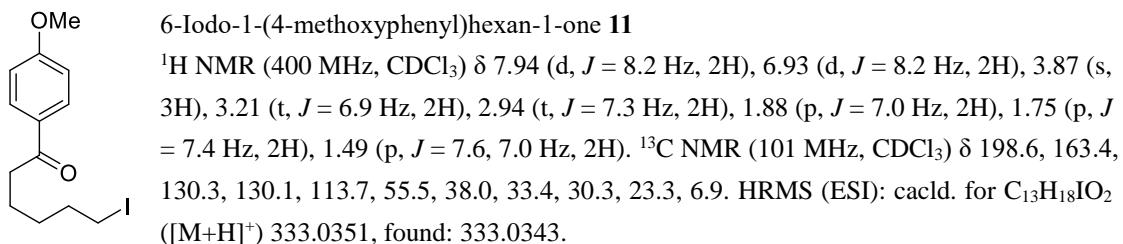
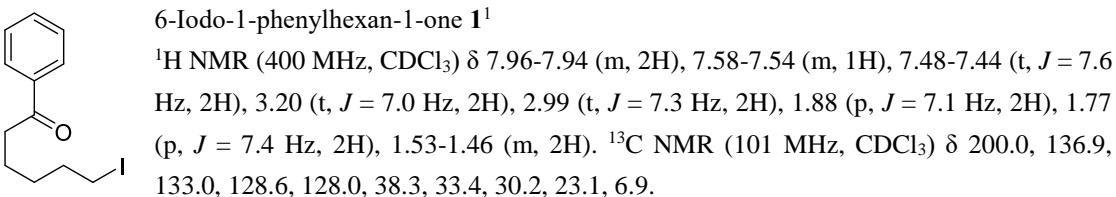
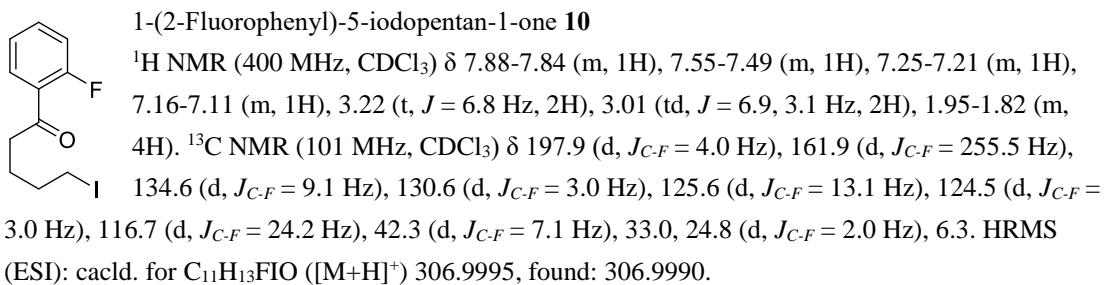
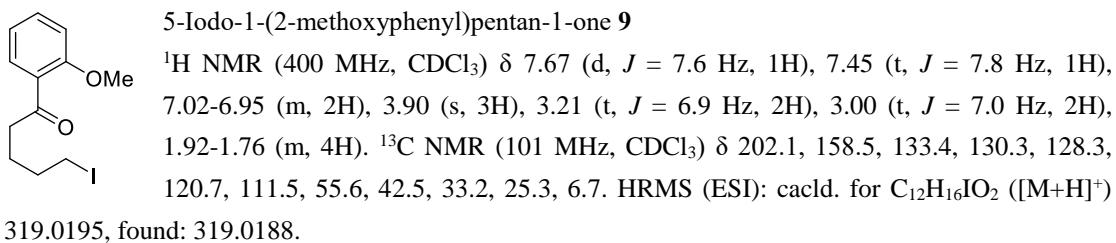
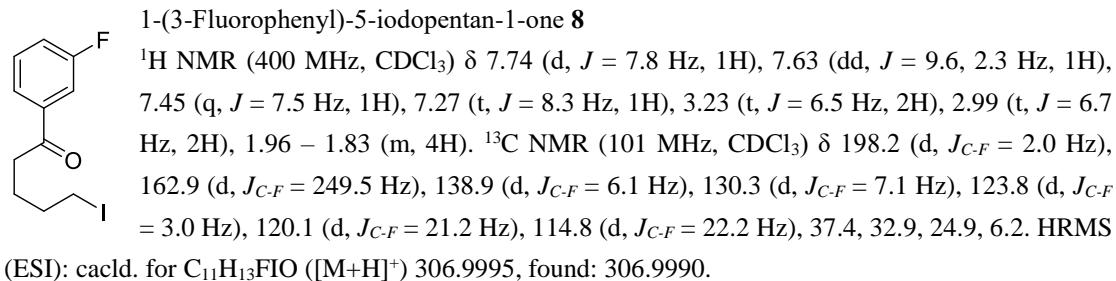
1-(4-Fluorophenyl)-5-iodopentan-1-one **6**

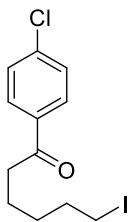
¹H NMR (400 MHz, CDCl₃) δ 8.00-7.97 (m, 2H), 7.13 (t, *J* = 8.5 Hz, 2H), 3.23 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 1.94-1.84 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 165.7 (d, *J*_{C-F} = 255.5 Hz), 133.2 (d, *J*_{C-F} = 3.0 Hz), 130.7 (d, *J*_{C-F} = 10.1 Hz), 115.7 (d, *J*_{C-F} = 21.2 Hz), 37.2, 32.9, 25.0, 6.2. HRMS (ESI): caclcd. for C₁₁H₁₃FIO ([M+H]⁺) 306.9995, found: 306.9995.



5-Iodo-1-(3-methoxyphenyl)pentan-1-one **7**

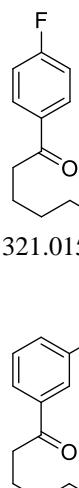
¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.22 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 1.94-1.83 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 199.35, 159.85, 138.19, 129.64, 120.66, 119.51, 112.31, 55.48, 37.4, 33.0, 25.1, 6.34. HRMS (ESI): caclcd. for C₁₂H₁₆IO₂ ([M+H]⁺) 319.0195, found: 319.0194.





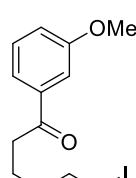
1-(4-Chlorophenyl)-6-iodohexan-1-one **13**

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.49 (p, *J* = 7.9, 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.7, 139.4, 135.2, 129.5, 128.9, 38.3, 33.3, 30.2, 23.0, 6.8. HRMS (ESI): caclcd. for C₁₂H₁₅ClIO ([M+H]⁺) 336.9856, found: 336.9849.



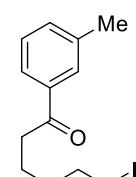
1-(4-Fluorophenyl)-6-iodohexan-1-one **14**

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.50 (p, *J* = 7.8, 7.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.3, 165.7 (d, *J*_{CF} = 255.5 Hz), 133.4 (d, *J*_{CF} = 3.0 Hz), 130.6 (d, *J*_{CF} = 9.1 Hz), 115.7 (d, *J*_{CF} = 22.2 Hz), 38.2, 33.3, 30.2, 23.1, 6.8. HRMS (ESI): caclcd. for C₁₂H₁₅FIO ([M+H]⁺) 321.0152, found: 321.0143.



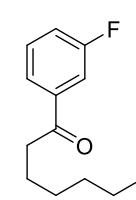
6-Iodo-1-(3-methoxyphenyl)hexan-1-one **15**

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.49 (p, *J* = 7.7, 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.8, 159.8, 138.3, 129.6, 120.7, 119.4, 112.3, 55.5, 38.4, 33.4, 30.2, 23.2, 6.8. HRMS (ESI): caclcd. for C₁₃H₁₈IO₂ ([M+H]⁺) 333.0351, found: 333.0342.



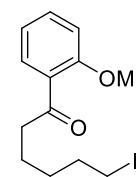
6-Iodo-1-(*m*-tolyl)hexan-1-one **16**

¹H NMR (400 MHz, CDCl₃) δ 7.76-7.73 (m, 2H), 7.38-7.32 (m, 2H), 3.20 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.53-1.45 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 200.2, 138.4, 137.0, 133.8, 128.6, 128.5, 125.3, 38.3, 33.4, 30.2, 23.2, 21.4, 6.9. HRMS (ESI): caclcd. for C₁₃H₁₈IO ([M+H]⁺) 317.0402, found: 317.0392.



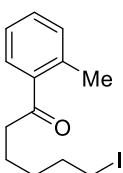
1-(3-Fluorophenyl)-6-iodohexan-1-one **17**

¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 9.5, 2.4 Hz, 1H), 7.45 (q, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 8.2 Hz, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.50 (p, *J* = 7.9, 7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.6 (d, *J*_{CF} = 2.0 Hz), 162.9 (d, *J*_{CF} = 249.5 Hz), 139.0 (d, *J*_{CF} = 6.1 Hz), 130.3 (d, *J*_{CF} = 7.1 Hz), 123.8 (d, *J*_{CF} = 3.0 Hz), 120.0 (d, *J*_{CF} = 21.2 Hz), 114.7 (d, *J*_{CF} = 22.2 Hz), 38.4, 33.3, 30.1, 22.9, 6.8. HRMS (ESI): caclcd. for C₁₂H₁₅FIO ([M+H]⁺) 321.0152, found: 321.0143.



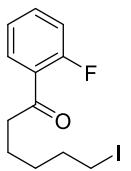
6-Iodo-1-(2-methoxyphenyl)hexan-1-one **18**

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.01-6.95 (m, 2H), 3.90 (s, 3H), 3.20 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.86 (p, *J* = 7.2 Hz, 2H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.46 (p, *J* = 8.0, 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 202.7, 158.4, 133.3, 130.2, 128.5, 120.7, 111.5, 55.6, 43.5, 33.4, 30.2, 23.3, 7.1. HRMS (ESI): caclcd. for C₁₃H₁₈IO₂ ([M+H]⁺) 333.0351, found: 333.0342.



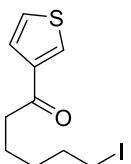
6-Iodo-1-(*o*-tolyl)hexan-1-one **19**

¹H NMR (400 MHz, CDCl₃) δ 7.63-7.61 (m, 1H), 7.39-7.35 (m, 1H), 7.28-7.24 (m, 2H), 3.20 (t, *J* = 7.0 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.49 (s, 3H), 1.87 (p, *J* = 7.1 Hz, 2H), 1.73 (p, *J* = 7.4 Hz, 2H), 1.51-1.44 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 204.3, 138.1, 137.9, 132.0, 131.2, 128.3, 125.7, 41.3, 33.3, 30.2, 23.3, 21.3, 6.8. HRMS (ESI): caclcd. for C₁₃H₁₈IO ([M+H]⁺) 317.0402, found: 317.0395.



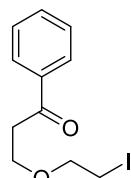
1-(2-Fluorophenyl)-6-iodohexan-1-one **20**

¹H NMR (400 MHz, CDCl₃) δ 7.85 (td, *J* = 7.6, 1.8 Hz, 1H), 7.54-7.49 (m, 1H), 7.27-7.21 (m, 1H), 7.16 -7.11 (m, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.99 (td, *J* = 7.3, 3.0 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.75 (p, *J* = 7.4 Hz, 2H), 1.52-1.45 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.4 (d, *J*_{C-F} = 4.0 Hz), 161.9 (d, *J*_{C-F} = 252.0 Hz), 134.4 (d, *J*_{C-F} = 9.1 Hz), 130.6 (d, *J*_{C-F} = 2.0 Hz), 125.7 (d, *J*_{C-F} = 13.1 Hz), 124.5 (d, *J*_{C-F} = 3.0 Hz), 116.7 (d, *J*_{C-F} = 24.2 Hz), 43.3 (d, *J*_{C-F} = 7.1 Hz), 33.3, 30.1, 22.8 (d, *J*_{C-F} = 2.0 Hz), 6.8. HRMS (ESI): caclcd. for C₁₂H₁₅FIO ([M+H]⁺) 321.0152, found: 321.0141.



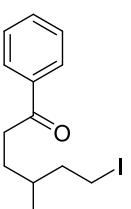
6-Iodo-1-(thiophen-3-yl)hexan-1-one **21**

¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.54 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.32 (dd, *J* = 5.1, 2.9 Hz, 1H), 3.20 (t, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 1.87 (p, *J* = 7.1 Hz, 2H), 1.75 (p, *J* = 7.4 Hz, 2H), 1.52-1.45 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.4, 142.3, 131.8, 127.0, 126.4, 39.6, 33.3, 30.2, 23.1, 6.8. HRMS (ESI): caclcd. for C₁₀H₁₄IOS ([M+H]⁺) 308.9810, found: 308.9799.



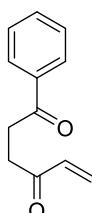
3-(2-Iodoethoxy)-1-phenylpropan-1-one **22**

¹H NMR (400 MHz, CDCl₃) δ 7.98-7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.75 (t, *J* = 6.8 Hz, 2H), 3.29-3.23 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 136.9, 133.3, 128.7, 128.2, 71.8, 66.0, 38.7, 3.0. HRMS (ESI): caclcd. for C₁₁H₁₄IO₂ ([M+H]⁺) 305.0038, found: 305.0039.



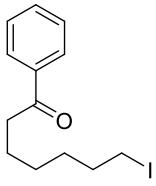
6-Iodo-4-methyl-1-phenylhexan-1-one **23**

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.31-3.16 (m, 2H), 3.02-2.97 (m, 2H), 1.97-1.89 (m, 1H), 1.85-1.54 (m, 4H), 0.95 (d, *J* = 6.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.2, 137.0, 133.0, 128.6, 128.1, 40.7, 36.1, 33.7, 30.4, 18.7, 4.9. HRMS (ESI): caclcd. for C₁₃H₁₈IO ([M+H]⁺) 317.0402, found: 317.0391.



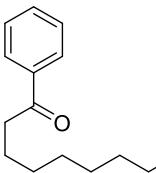
1-Phenylhex-5-ene-1,4-dione **24³**

¹H NMR (400 MHz, CDCl₃) δ 8.02-7.99 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 6.44 (dd, *J* = 17.7, 10.4 Hz, 1H), 6.33 (dd, *J* = 17.7, 1.0 Hz, 1H), 5.90 (dd, *J* = 10.4, 1.1 Hz, 1H), 3.35 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 198.5, 136.7, 136.4, 133.2, 128.6, 128.5, 128.1, 33.3, 32.3.



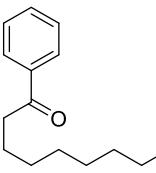
7-Iodo-1-phenylheptan-1-one **25**¹

¹H NMR (400 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.3 Hz, 2H), 1.84 (p, *J* = 7.0 Hz, 2H), 1.75 (p, *J* = 7.3 Hz, 2H), 1.50-1.36 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 137.0, 133.0, 128.6, 128.1, 38.4, 33.3, 30.4, 28.2, 24.0, 7.2.



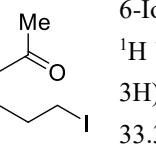
8-Iodo-1-phenyloctan-1-one **26**¹

¹H NMR (400 MHz, CDCl₃) δ 7.95-7.97 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.71 (m, 4H), 1.45-1.39 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 200.4, 137.1, 132.9, 128.6, 128.1, 38.5, 33.5, 30.4, 29.1, 28.4, 24.2, 7.2.



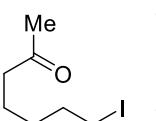
12-Iodo-1-phenyldodecan-1-one **27**

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.85-1.69 (m, 4H), 1.39-1.28 (m, 14H). ¹³C NMR (101 MHz, CDCl₃) δ 200.6, 137.1, 132.9, 128.6, 128.1, 38.6, 33.6, 30.5, 29.5, 29.4, 29.3, 29.2, 28.6, 24.4, 7.4. HRMS (ESI): cacl. for C₁₈H₂₈IO ([M+H]⁺) 387.1185, found: 387.1172.



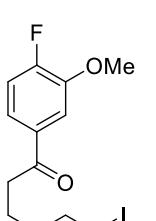
6-Iodohexan-2-one **28**²

¹H NMR (400 MHz, CDCl₃) δ 3.41 (t, *J* = 6.6 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.90-1.83 (m, 2H), 1.76-1.68 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 208.1, 42.5, 33.3, 32.0, 29.9, 22.2.



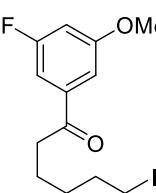
7-Iodoheptan-2-one **29**²

¹H NMR (400 MHz, CDCl₃) δ 3.41 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.14 (s, 3H), 1.90-1.83 (m, 2H), 1.64-1.58 (m, 2H), 1.48-1.40 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 208.6, 43.3, 33.6, 32.5, 29.9, 27.6, 22.8.



1-(4-Fluoro-3-methoxyphenyl)-6-iodohexan-1-one **30**

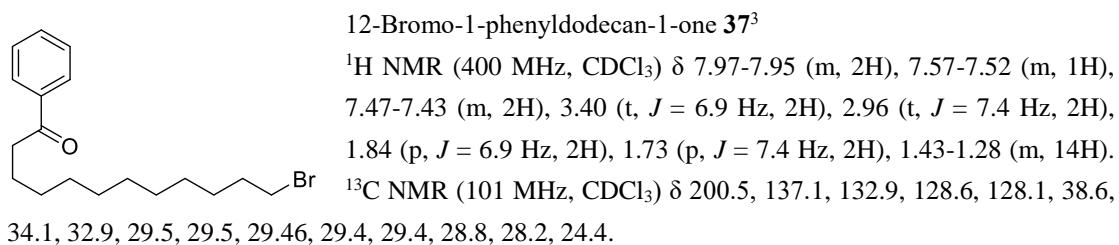
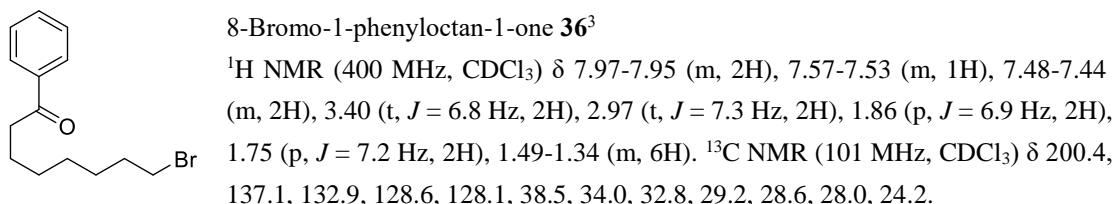
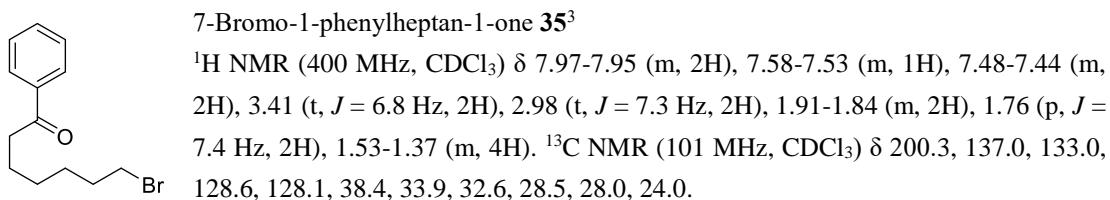
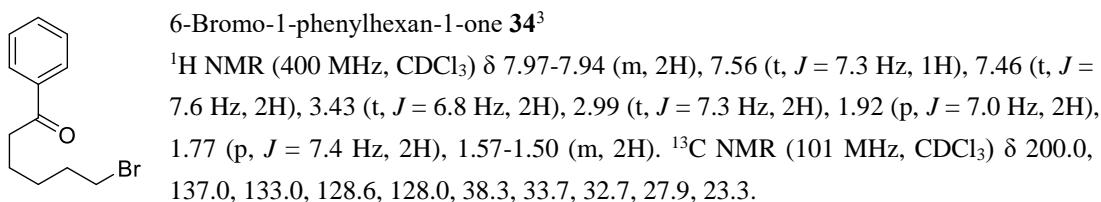
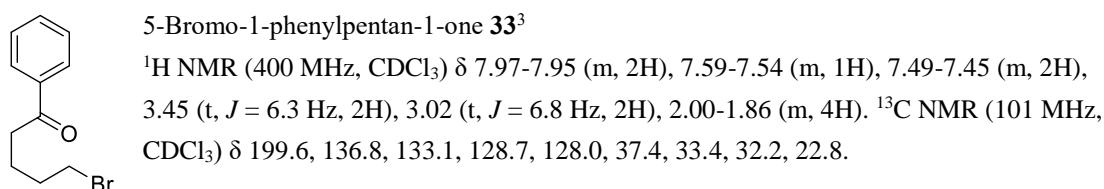
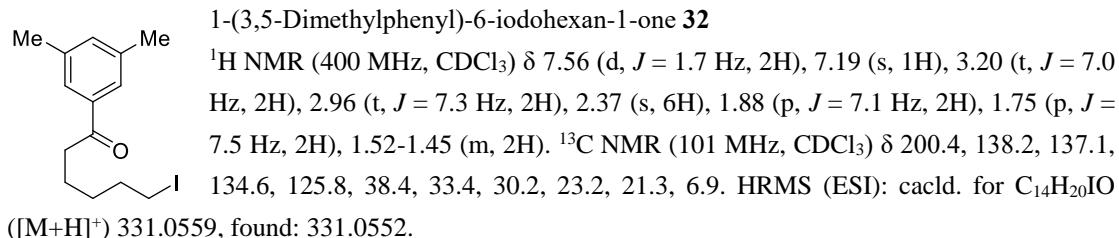
¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.53 (ddd, *J* = 8.3, 4.3, 2.1 Hz, 1H), 7.13 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.95 (s, 3H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.80-1.72 (m, 2H), 1.53-1.46 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.5 (d, *J*_{C-F} = 2.0 Hz), 163.5 (d, *J*_{C-F} = 247.5 Hz), 161.1 (d, *J*_{C-F} = 11.1 Hz), 139.3 (d, *J*_{C-F} = 8.1 Hz), 109.1 (d, *J*_{C-F} = 2.0 Hz), 107.3 (d, *J*_{C-F} = 23.2 Hz), 106.3 (d, *J*_{C-F} = 25.2 Hz), 55.9, 38.4, 33.3, 30.1, 23.0, 6.7. HRMS (ESI): cacl. for C₁₃H₁₇FIO₂ ([M+H]⁺) 351.0257, found: 351.0248.

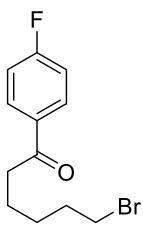


1-(3-Fluoro-5-methoxyphenyl)-6-iodohexan-1-one **31**

¹H NMR (400 MHz, CDCl₃) δ 7.28-7.27 (m, 1H), 7.23-7.20 (m, 1H), 6.82-6.79 (m, 1H), 3.85 (s, 3H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.0 Hz, 2H), 1.75 (p, *J* = 7.4 Hz, 2H), 1.53-1.45 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.5 (d, *J*_{C-F} = 2.0 Hz), 163.5 (d, *J*_{C-F} = 247.5 Hz), 161.1 (d, *J*_{C-F} = 11.1 Hz),

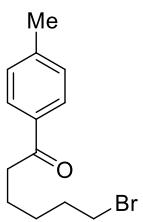
139.3 (d, $J_{C-F} = 8.1$ Hz), 109.1 (d, $J_{C-F} = 2.0$ Hz), 107.3 (d, $J_{C-F} = 23.2$ Hz), 106.3 (d, $J_{C-F} = 25.2$ Hz), 55.9, 38.4, 33.3, 30.1, 23.0, 6.7. HRMS (ESI): caclcd. for $C_{13}H_{17}FIO_2$ ($[M+H]^+$) 351.0257, found: 351.0253.





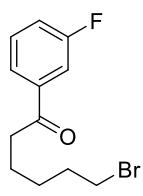
6-Bromo-1-(4-fluorophenyl)hexan-1-one **38**³

¹H NMR (400 MHz, CDCl₃) δ 8.01-7.96 (m, 2H), 7.16-7.10 (m, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.92 (p, *J* = 6.9 Hz, 2H), 1.77 (p, *J* = 7.3 Hz, 2H), 1.57-1.50 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.3, 165.7 (d, *J_{C-F}* = 255.5 Hz), 133.4 (d, *J_{C-F}* = 3.0 Hz), 130.6 (d, *J_{C-F}* = 9.1 Hz), 115.7 (d, *J_{C-F}* = 22.2 Hz), 38.2, 33.6, 32.61, 27.9, 23.3.



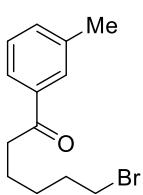
6-Bromo-1-(*p*-tolyl)hexan-1-one **39**

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.27-7.25 (m, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.92 (p, *J* = 7.0 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.57-1.49 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.7, 143.8, 134.5, 129.3, 128.2, 38.2, 33.7, 32.7, 27.9, 23.4, 21.7. HRMS (ESI): caclcd. for C₁₃H₁₈BrO ([M+H]⁺) 269.0541, found: 269.0534.



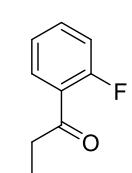
6-Bromo-1-(3-fluorophenyl)hexan-1-one **40**

¹H NMR (400 MHz, CDCl₃) δ 7.75-7.72 (m, 1H), 7.65-7.62 (m, 1H), 7.47-7.42 (m, 1H), 7.29-7.24 (m, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 1.92 (p, *J* = 6.9 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.58-1.50 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.6 (d, *J_{C-F}* = 2.0 Hz), 162.9 (d, *J_{C-F}* = 248.5 Hz), 139.0 (d, *J_{C-F}* = 6.1 Hz), 130.3 (d, *J_{C-F}* = 8.1 Hz), 123.8 (d, *J_{C-F}* = 3.0 Hz), 120.0 (d, *J_{C-F}* = 22.2 Hz), 114.8 (d, *J_{C-F}* = 22.2 Hz), 38.4, 33.6, 32.6, 27.8, 23.2. HRMS (ESI): caclcd. for C₁₂H₁₅BrFO ([M+H]⁺) 273.0290, found: 273.0283.



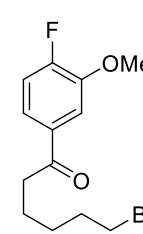
6-Bromo-1-(*m*-tolyl)hexan-1-one **41**

¹H NMR (400 MHz, CDCl₃) δ 7.77-7.73 (m, 2H), 7.38-7.32 (m, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.95-1.88 (m, 2H), 1.77 (p, *J* = 7.3 Hz, 2H), 1.57-1.49 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 138.4, 137.0, 133.8, 128.6, 128.5, 125.3, 38.4, 33.7, 32.7, 27.9, 23.4, 21.4. HRMS (ESI): caclcd. for C₁₃H₁₈BrO ([M+H]⁺) 269.0541, found: 269.0534.



6-Bromo-1-(2-fluorophenyl)hexan-1-one **42**³

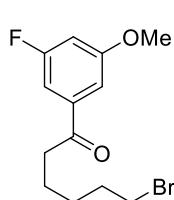
¹H NMR (400 MHz, CDCl₃) δ 7.85 (td, *J* = 7.6, 1.9 Hz, 1H), 7.54-7.48 (m, 1H), 7.27-7.21 (m, 1H), 7.16-7.11 (m, 1H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.00 (td, *J* = 7.3, 3.0 Hz, 2H), 1.91 (p, *J* = 7.0 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.56-1.49 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.4 (d, *J_{C-F}* = 4.0 Hz), 161.9 (d, *J_{C-F}* = 254.5 Hz), 134.5 (d, *J_{C-F}* = 9.1 Hz), 130.6 (d, *J_{C-F}* = 2.0 Hz), 125.7 (d, *J_{C-F}* = 13.1 Hz), 124.5 (d, *J_{C-F}* = 3.0 Hz), 116.7 (d, *J_{C-F}* = 14.1 Hz), 43.3 (d, *J_{C-F}* = 7.1 Hz), 33.7, 32.6, 27.8, 23.0 (d, *J_{C-F}* = 2.0 Hz).



6-Bromo-1-(4-fluoro-3-methoxyphenyl)hexan-1-one **44**

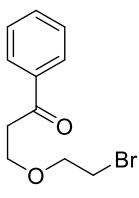
¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.53 (ddd, *J* = 8.4, 4.3, 2.0 Hz, 1H), 7.13 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.95 (s, 3H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.92 (p, *J* = 6.9 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.57-1.50 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.4, 155.6 (d, *J_{C-F}* = 255.5 Hz), 148.0 (d, *J_{C-F}* = 11.1 Hz), 133.7 (d, *J_{C-F}* = 4.0 Hz), 121.8 (d, *J_{C-F}* = 8.1 Hz), 115.8 (d, *J_{C-F}* = 19.2

Hz), 112.5 (d, $J_{C-F} = 3.0$ Hz), 56.3, 38.1, 33.7, 32.6, 27.8, 23.4. HRMS (ESI): caclcd. for $C_{13}H_{17}BrFO_2$ ($[M+H]^+$) 303.0396, found: 303.0389.



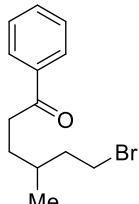
6-Bromo-1-(3-fluoro-5-methoxyphenyl)hexan-1-one **45**

1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.27 (m, 1H), 7.23-7.20 (m, 1H), 6.83-6.79 (m, 1H), 3.85 (s, 3H), 3.43 (t, $J = 6.7$ Hz, 2H), 2.94 (t, $J = 7.3$ Hz, 2H), 1.92 (p, $J = 6.9$ Hz, 2H), 1.76 (p, $J = 7.4$ Hz, 2H), 1.57-1.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5 (d, $J_{C-F} = 3.0$ Hz), 163.5 (d, $J_{C-F} = 247.5$ Hz), 161.1 (d, $J_{C-F} = 11.1$ Hz), 139.3 (d, $J_{C-F} = 8.1$ Hz), 109.1 (d, $J_{C-F} = 3.0$ Hz), 107.3 (d, $J_{C-F} = 22.2$ Hz), 106.3 (d, $J_{C-F} = 25.2$ Hz), 55.8, 38.4, 33.6, 32.6, 27.8, 23.2. HRMS (ESI): caclcd. for $C_{13}H_{17}BrFO_2$ ($[M+H]^+$) 303.0396, found: 303.0385.



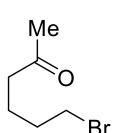
3-(2-Bromoethoxy)-1-phenylpropan-1-one **46**

1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J = 7.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 3.95 (t, $J = 6.5$ Hz, 2H), 3.81 (t, $J = 6.1$ Hz, 2H), 3.46 (t, $J = 6.2$ Hz, 2H), 3.28 (t, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 136.9, 133.3, 128.7, 128.1, 71.1, 66.3, 38.7, 30.4. HRMS (ESI): caclcd. for $C_{11}H_{14}BrO_2$ ($[M+H]^+$) 257.0177, found: 257.0169.



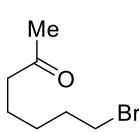
6-Bromo-4-methyl-1-phenylhexan-1-one **47³**

1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 3.52-3.40 (m, 2H), 3.06-2.93 (m, 2H), 1.99-1.69 (m, 4H), 1.63-1.54 (m, 1H), 0.96 (d, $J = 6.0$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 137.0, 133.0, 128.6, 128.0, 39.8, 36.1, 31.8, 31.4, 30.6, 18.9.



6-Bromohexan-2-one **48⁴**

1H NMR (400 MHz, $CDCl_3$) δ 3.18 (t, $J = 6.9$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 2.15 (s, 3H), 1.86-1.79 (m, 2H), 1.72-1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 42.3, 32.8, 30.0, 24.6, 6.2.

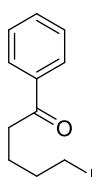
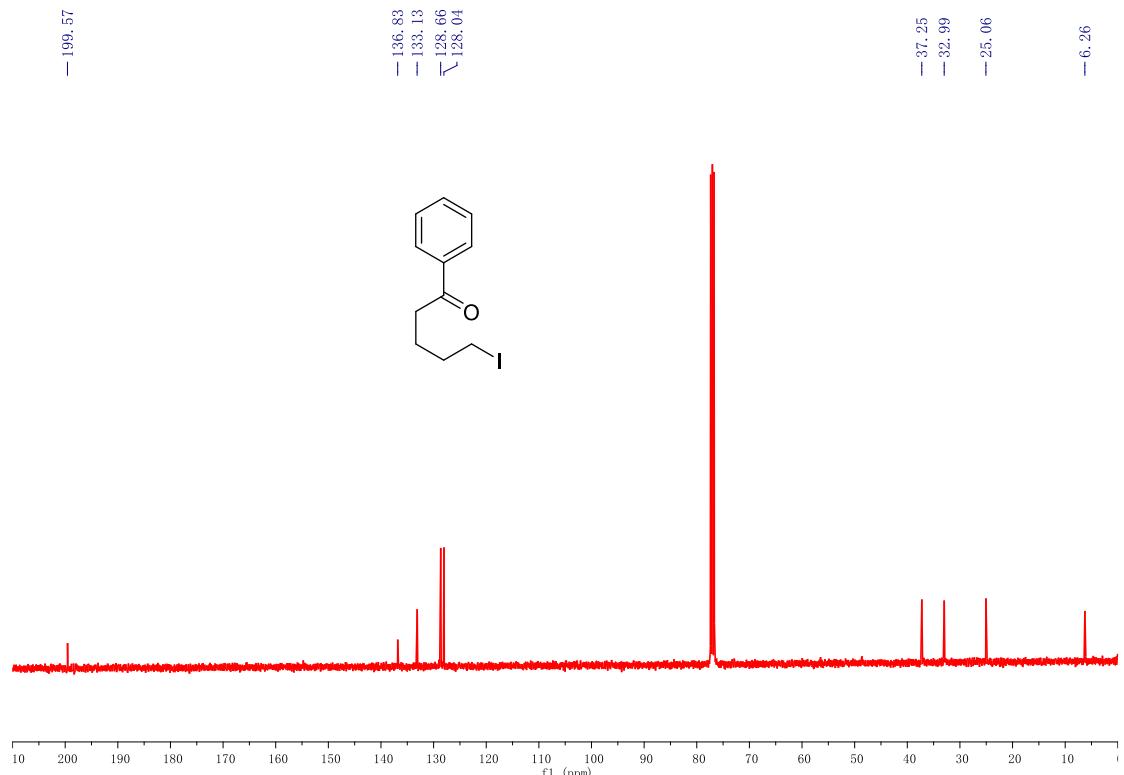
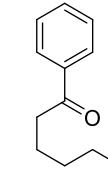
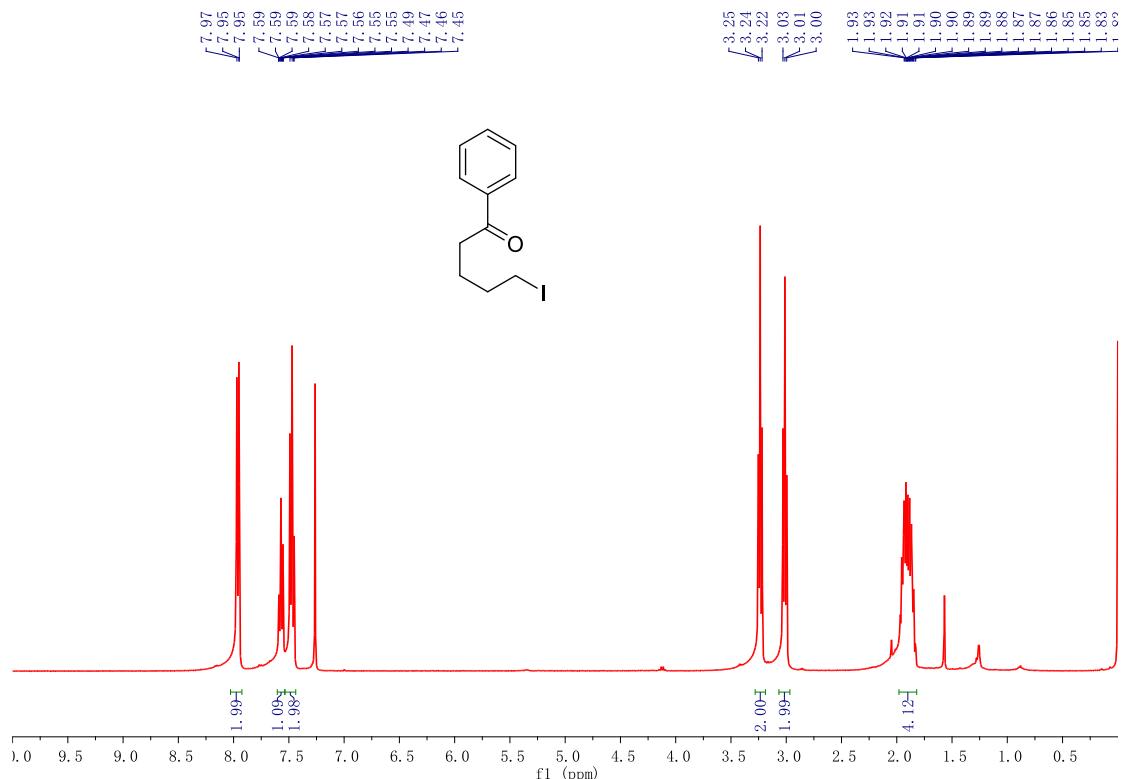


7-Bromohexan-2-one **49⁴**

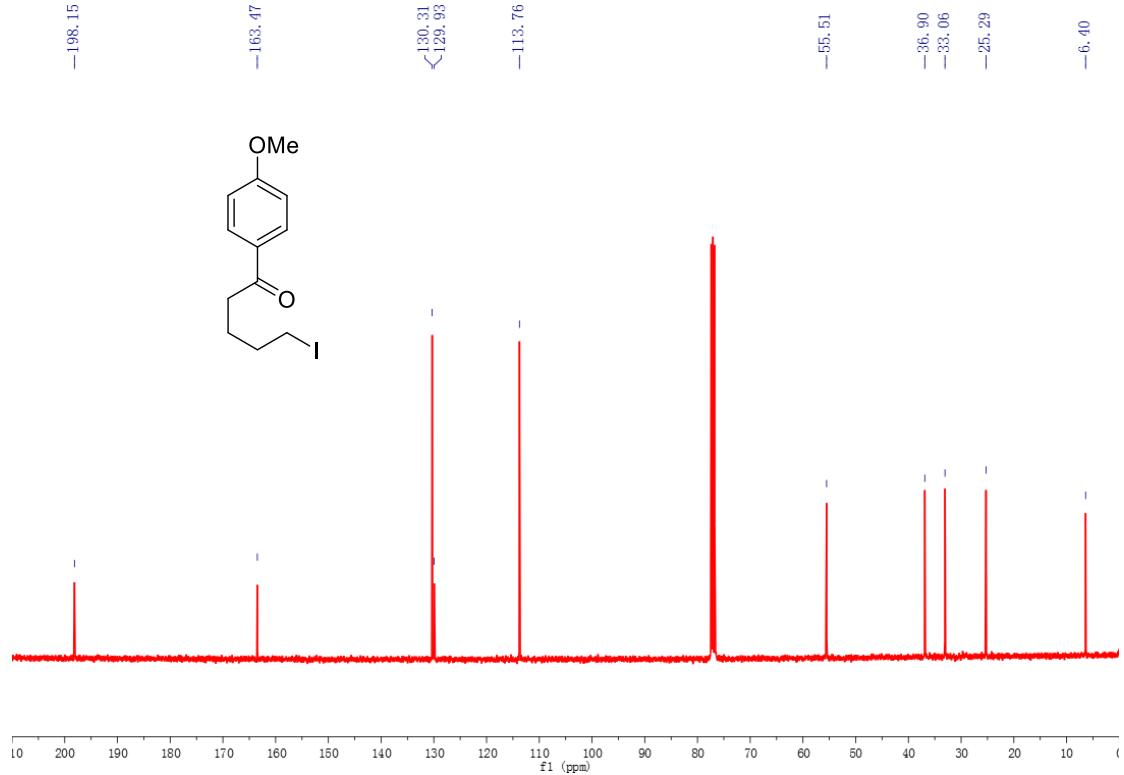
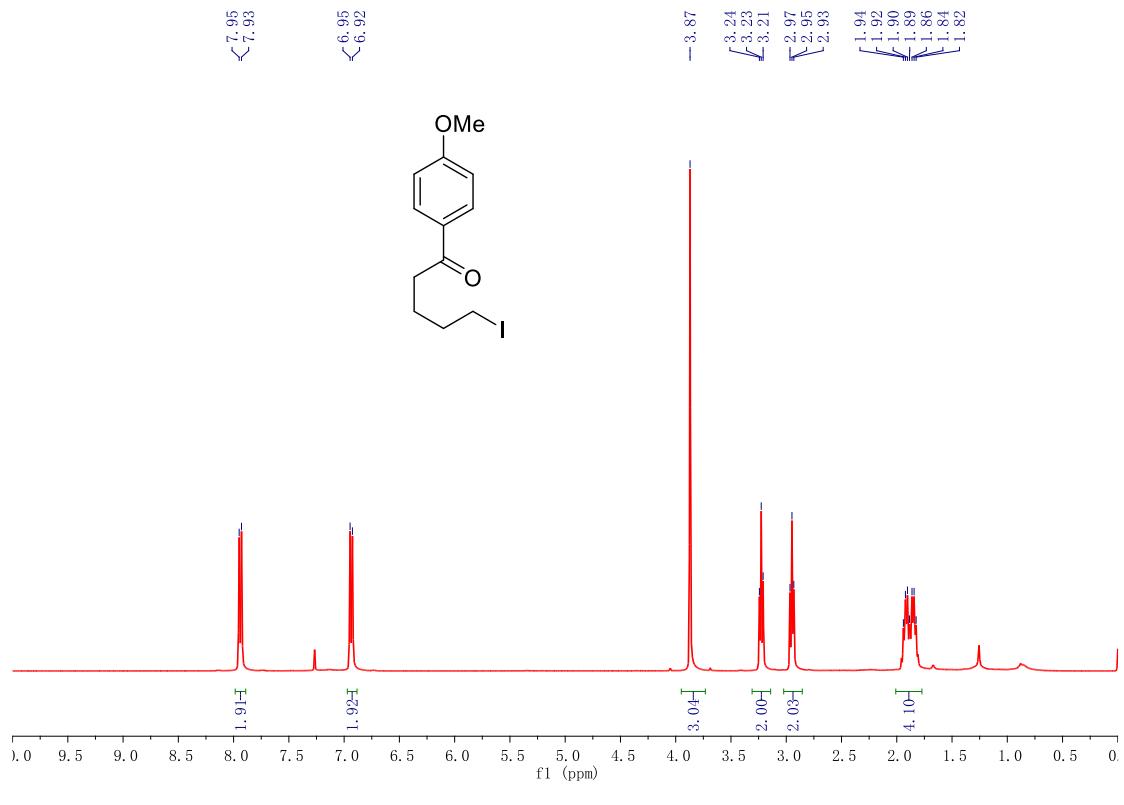
1H NMR (400 MHz, $CDCl_3$) δ 3.19 (t, $J = 6.9$ Hz, 2H), 2.45 (t, $J = 7.3$ Hz, 2H), 2.15 (s, 3H), 1.87-1.80 (m, 2H), 1.63-1.56 (m, 2H), 1.44-1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 43.4, 33.2, 30.0, 22.6, 6.8.

4. ^1H and ^{13}C NMR spectra of the products

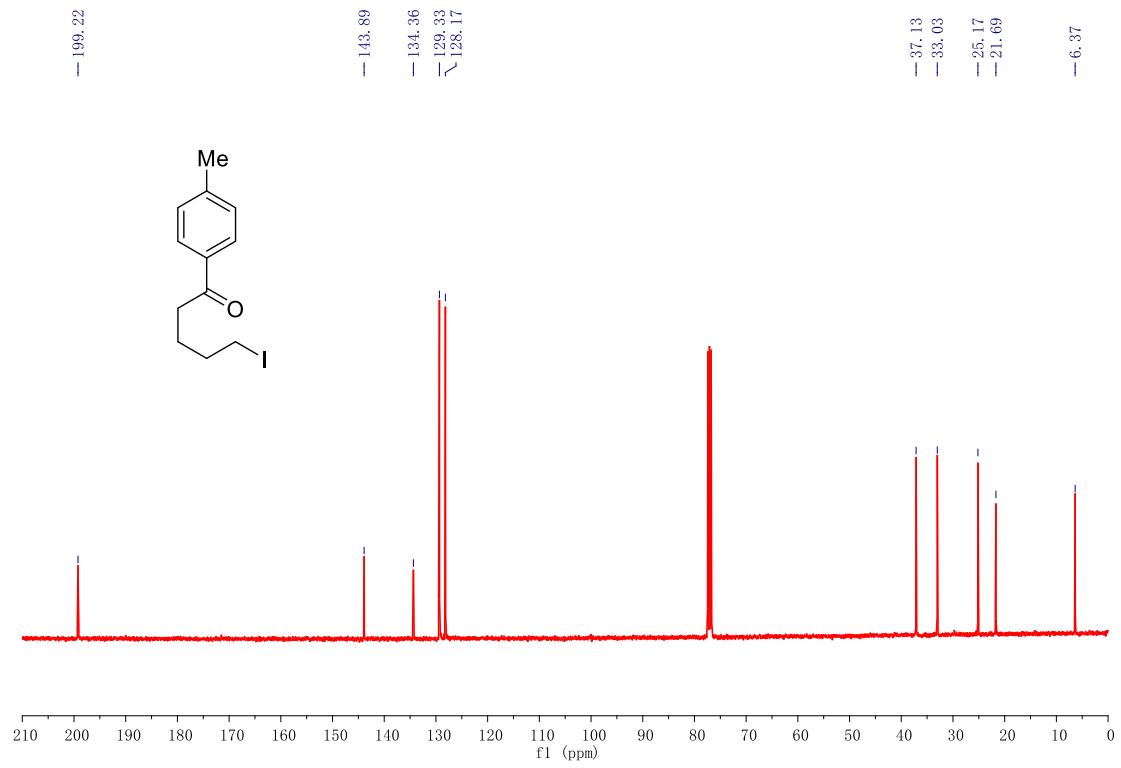
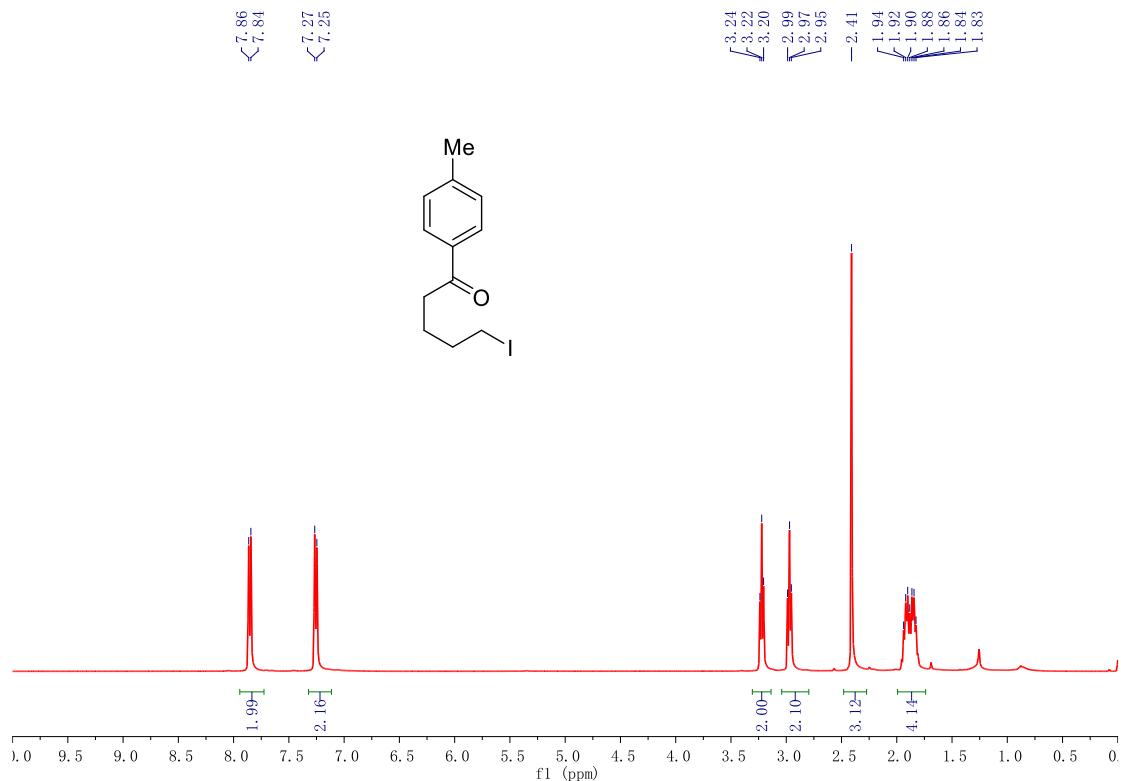
5-Iodo-1-phenylpentan-1-one **2**



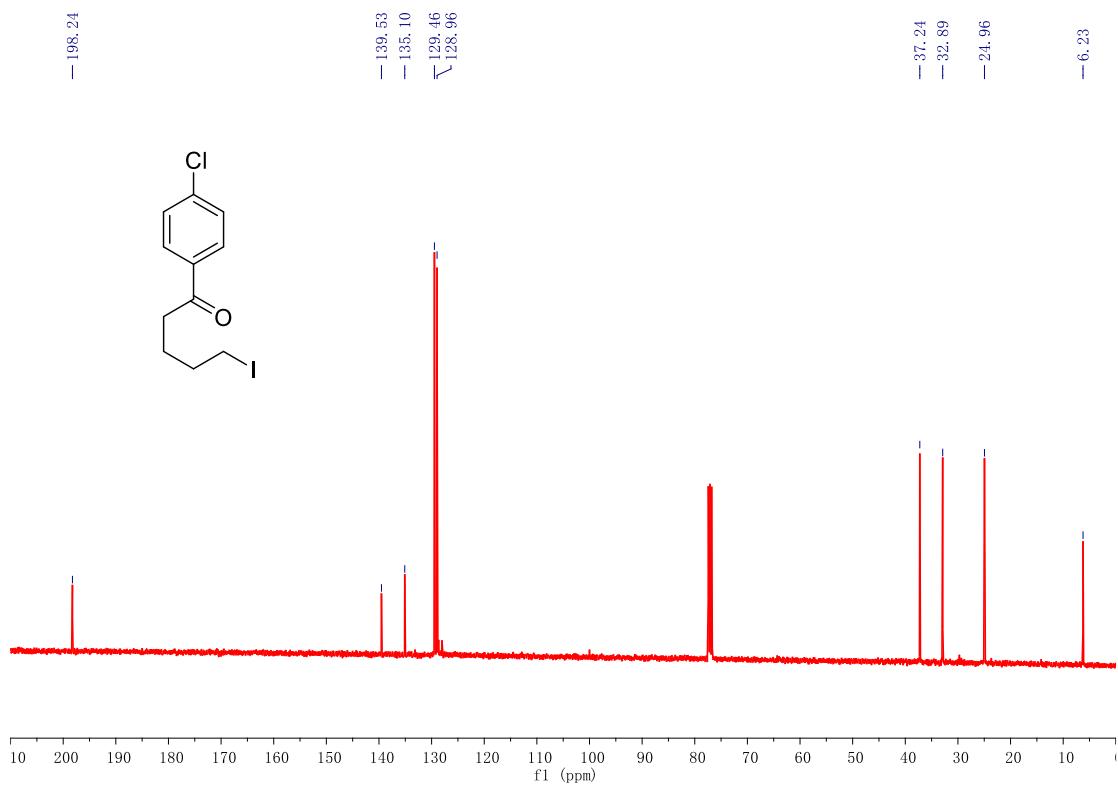
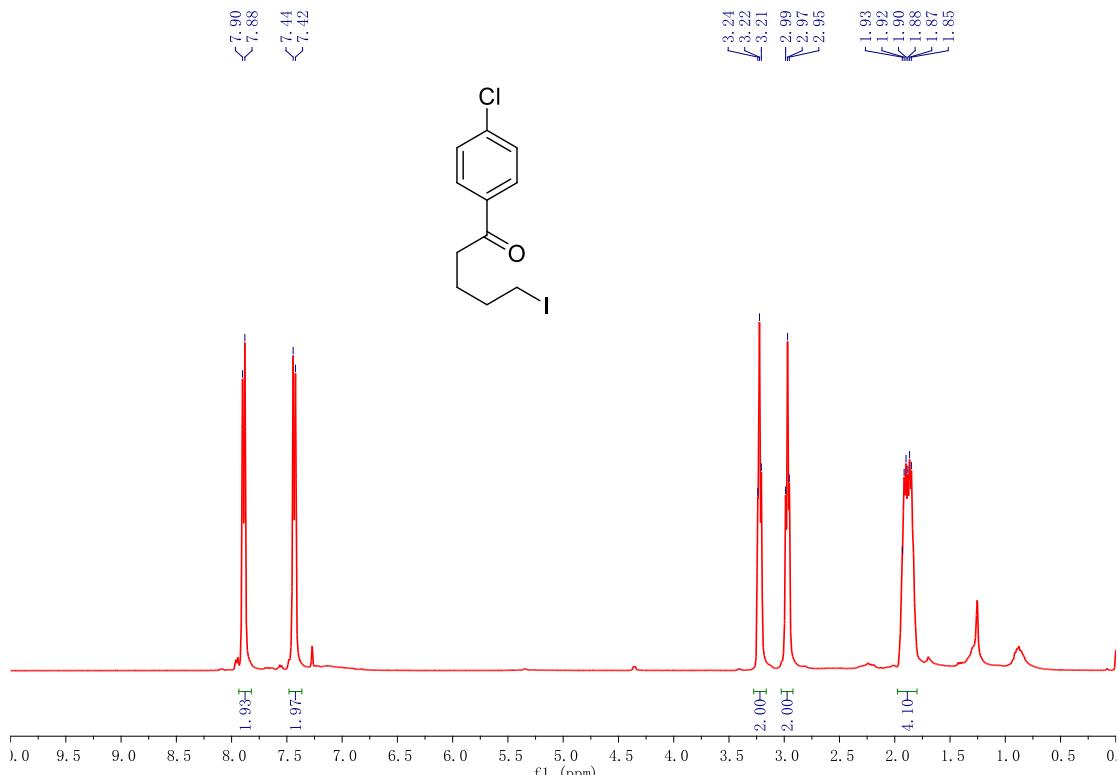
5-Iodo-1-(4-methoxyphenyl)pentan-1-one **3**



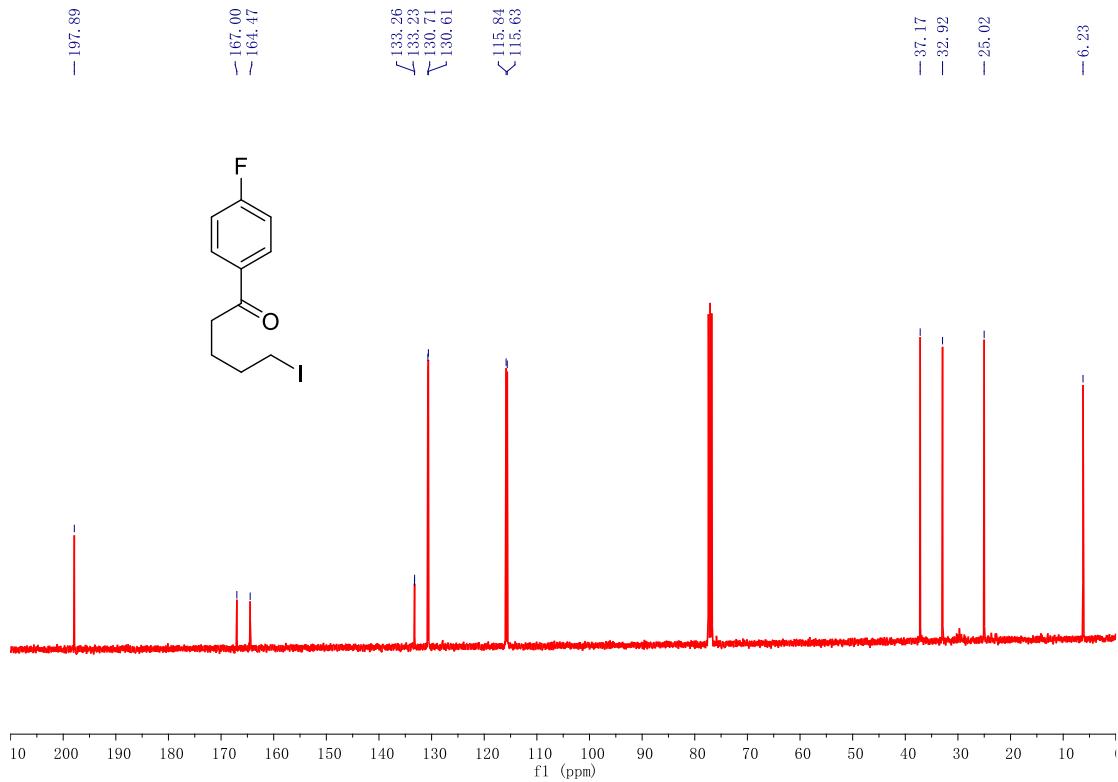
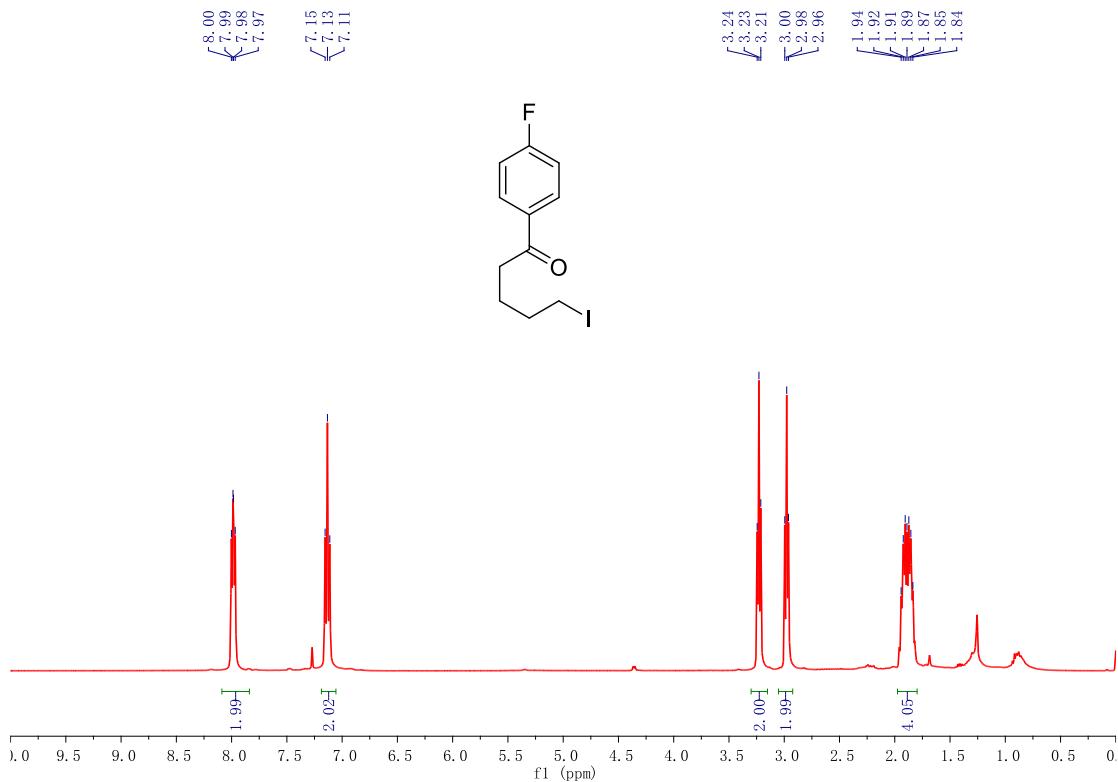
5-Iodo-1-(*p*-tolyl)pentan-1-one **4**



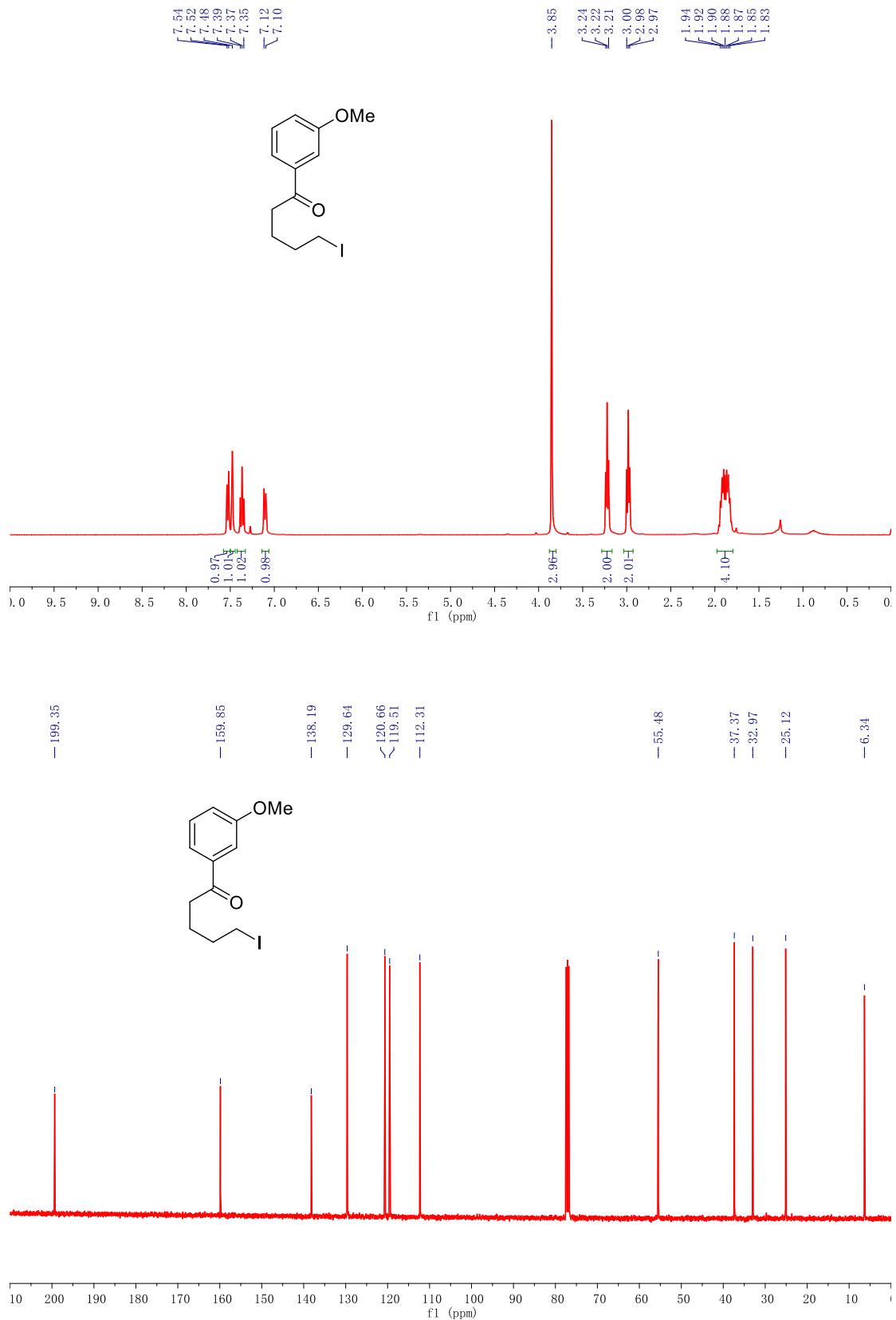
1-(4-Chlorophenyl)-5-iodopentan-1-one **5**



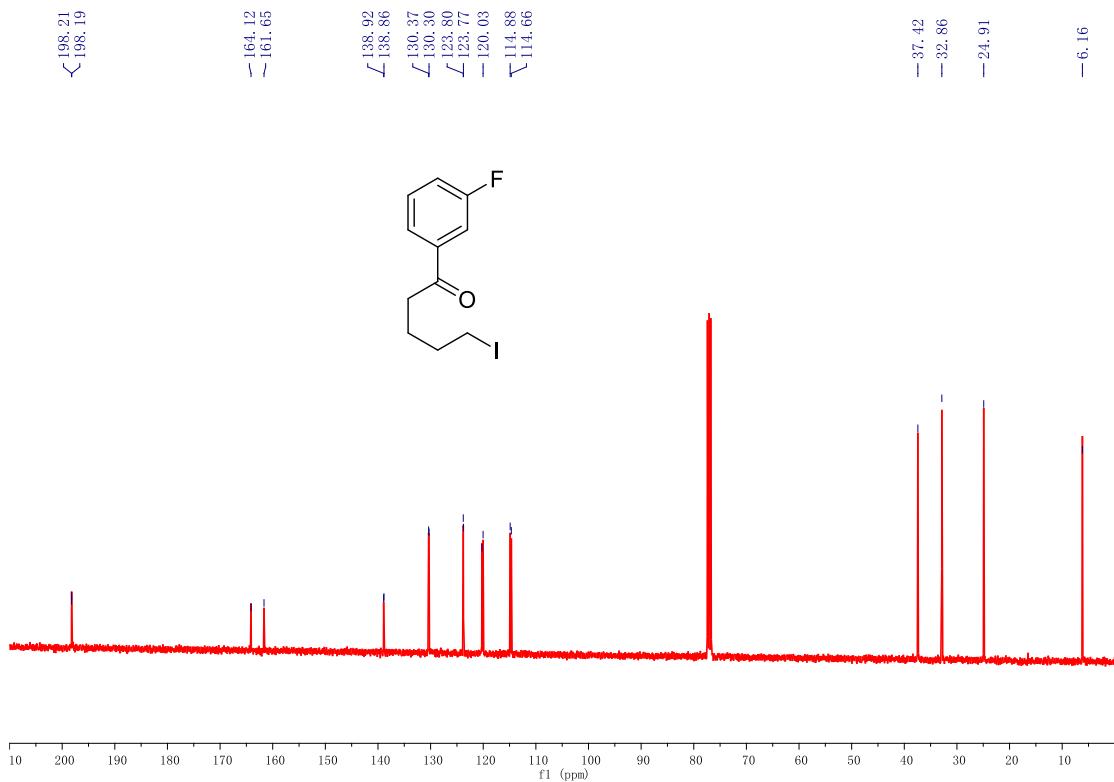
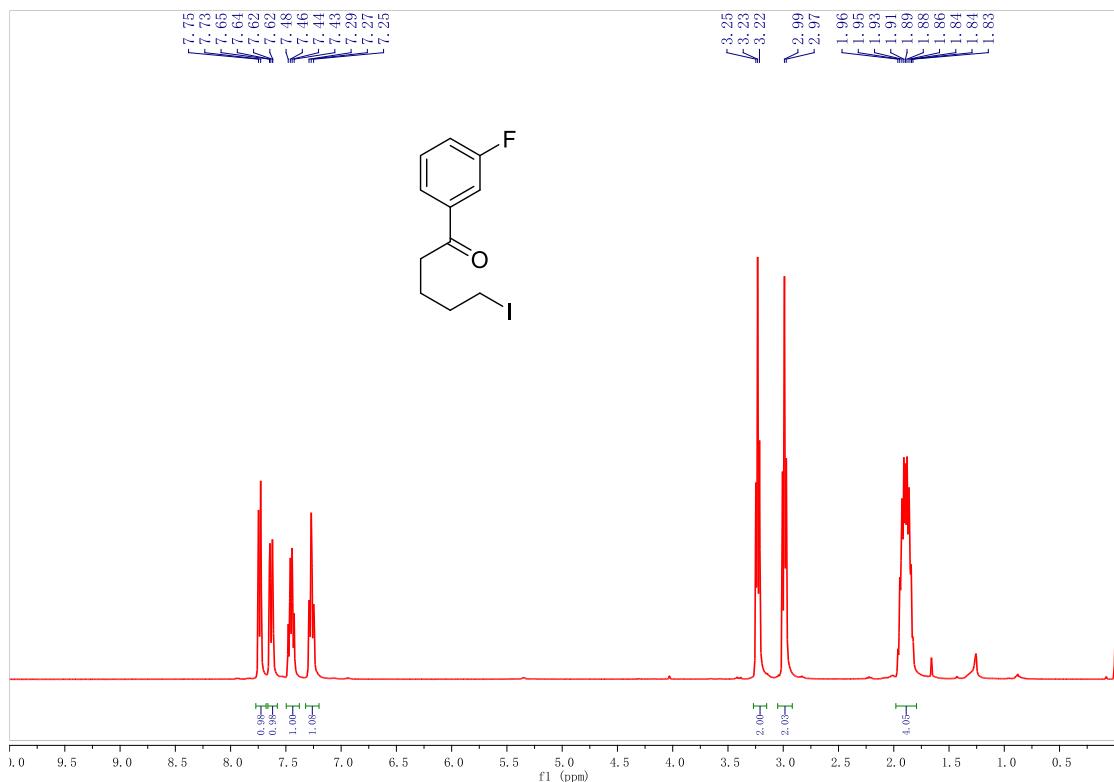
1-(4-Fluorophenyl)-5-iodopentan-1-one **6**



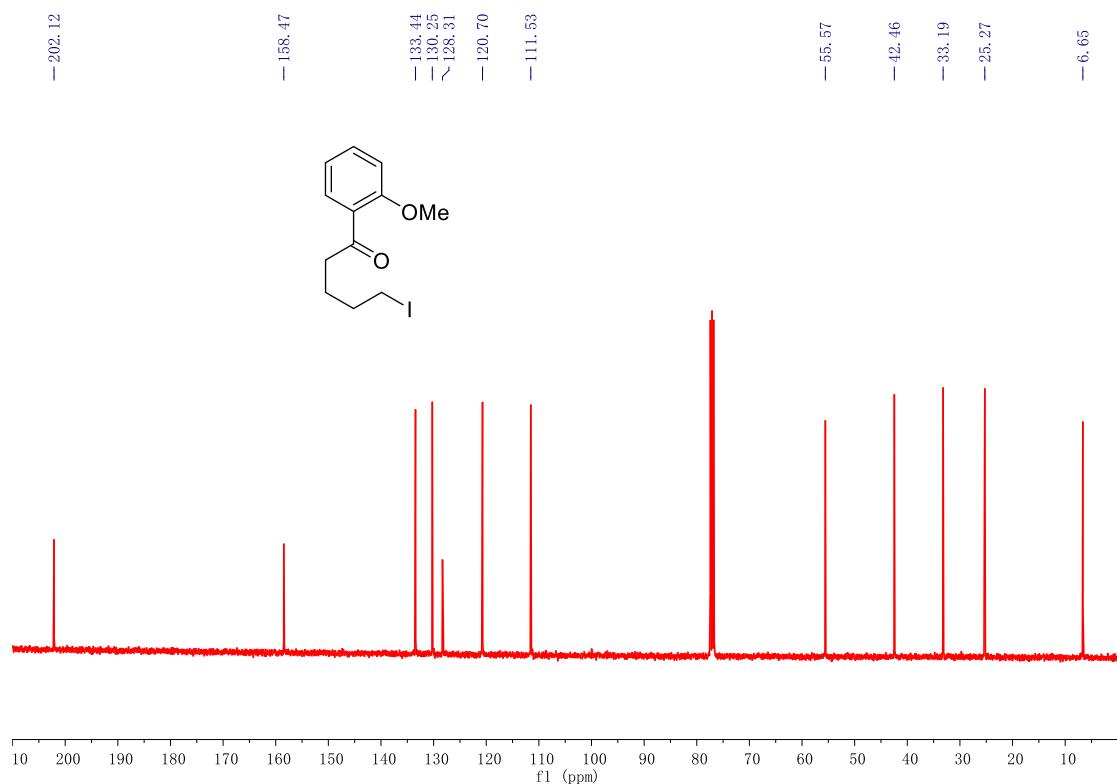
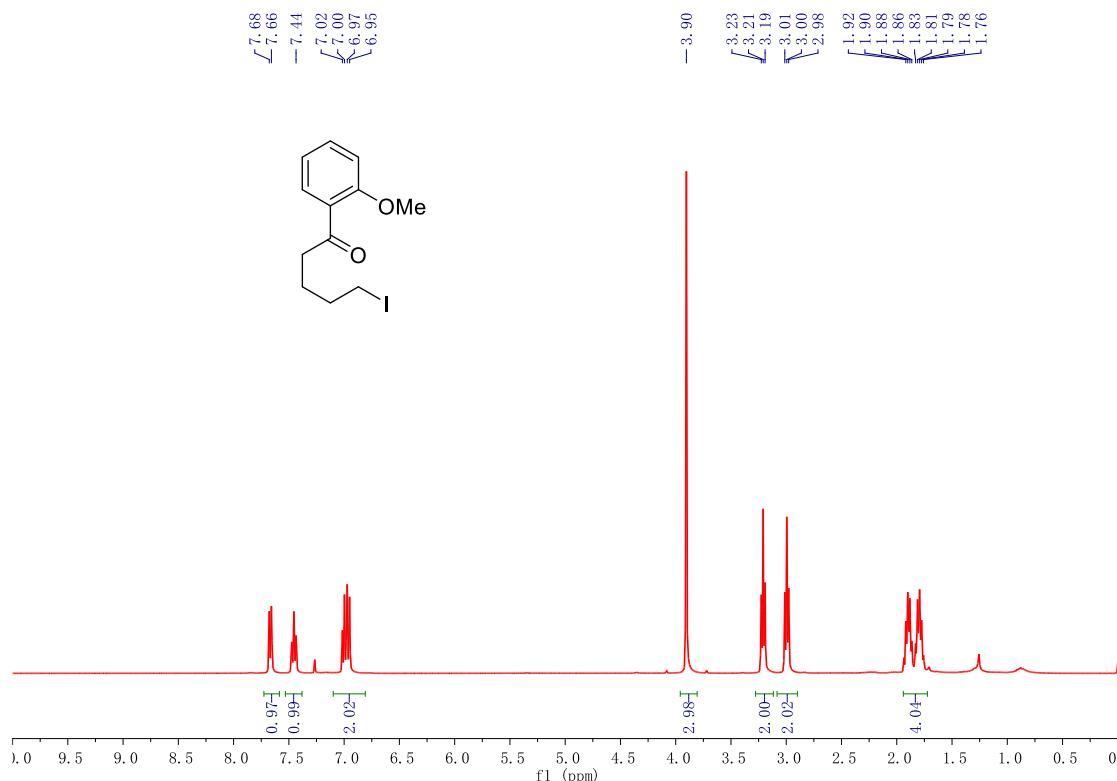
5-Iodo-1-(3-methoxyphenyl)pentan-1-one **7**



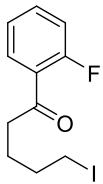
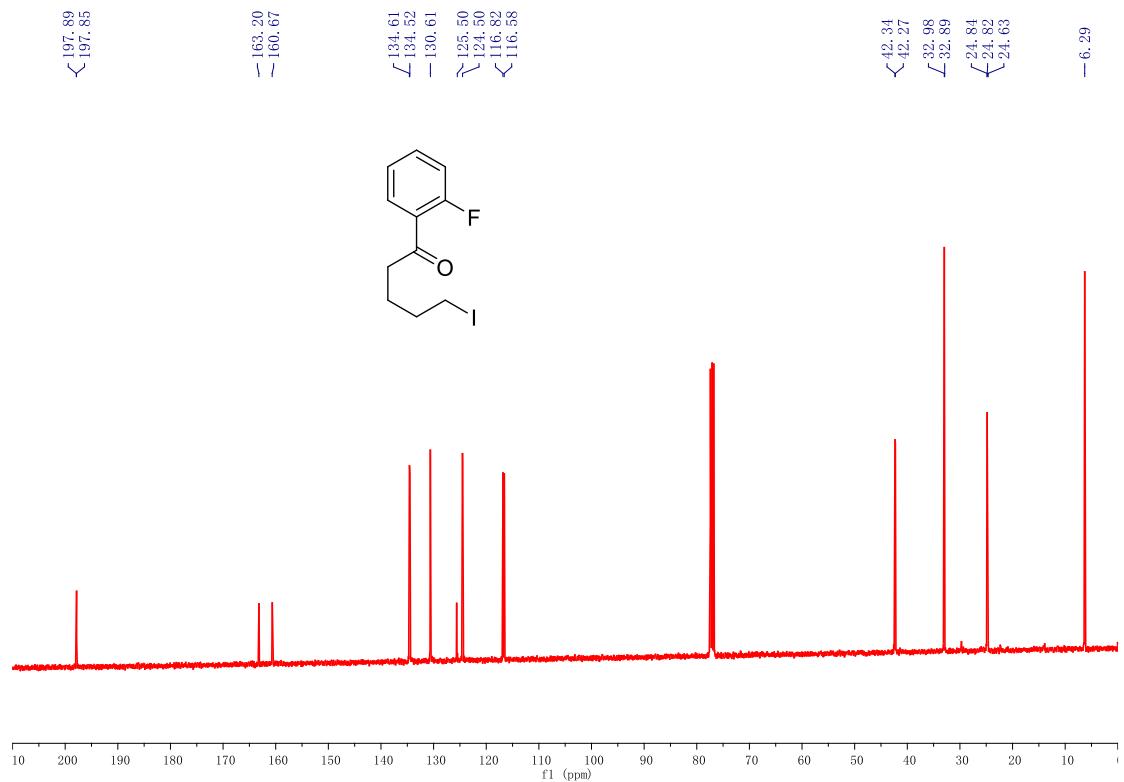
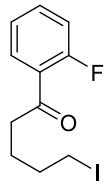
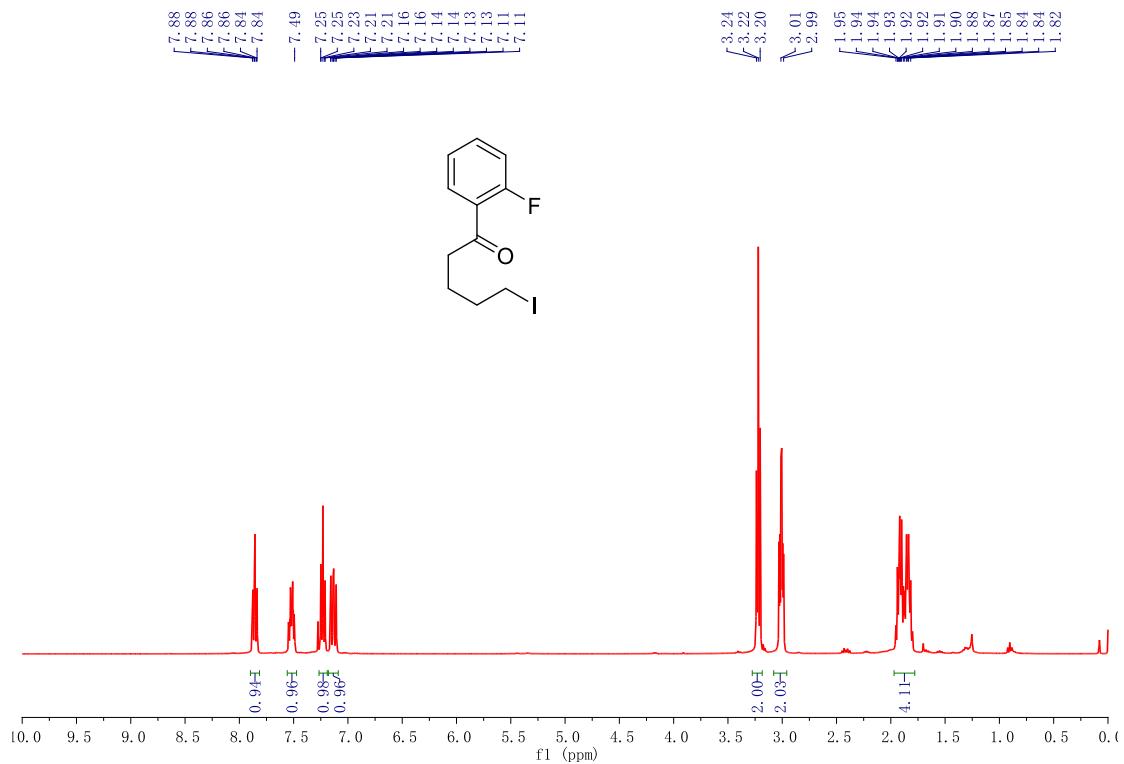
1-(3-Fluorophenyl)-5-iodopentan-1-one **8**



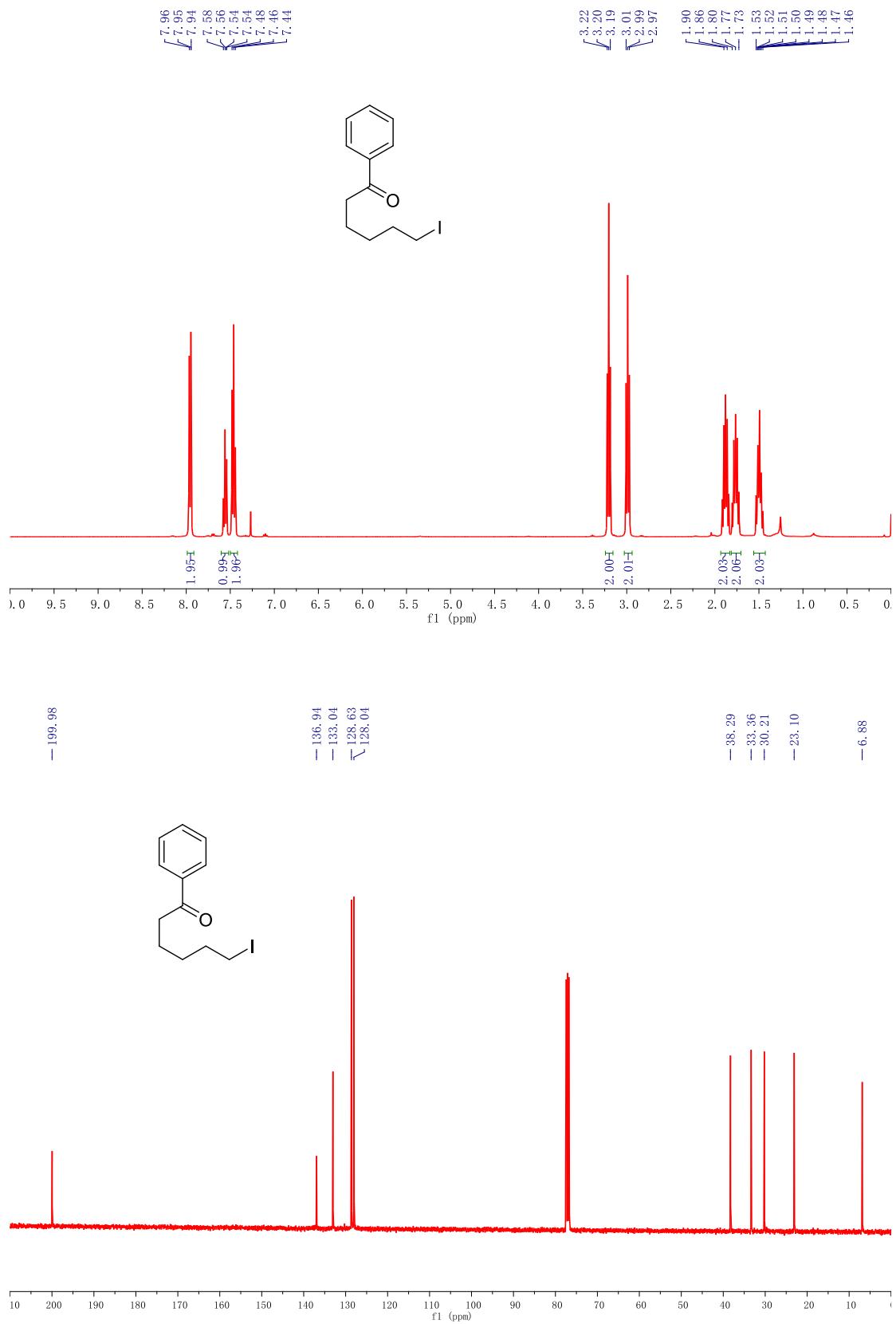
5-Iodo-1-(2-methoxyphenyl)pentan-1-one **9**



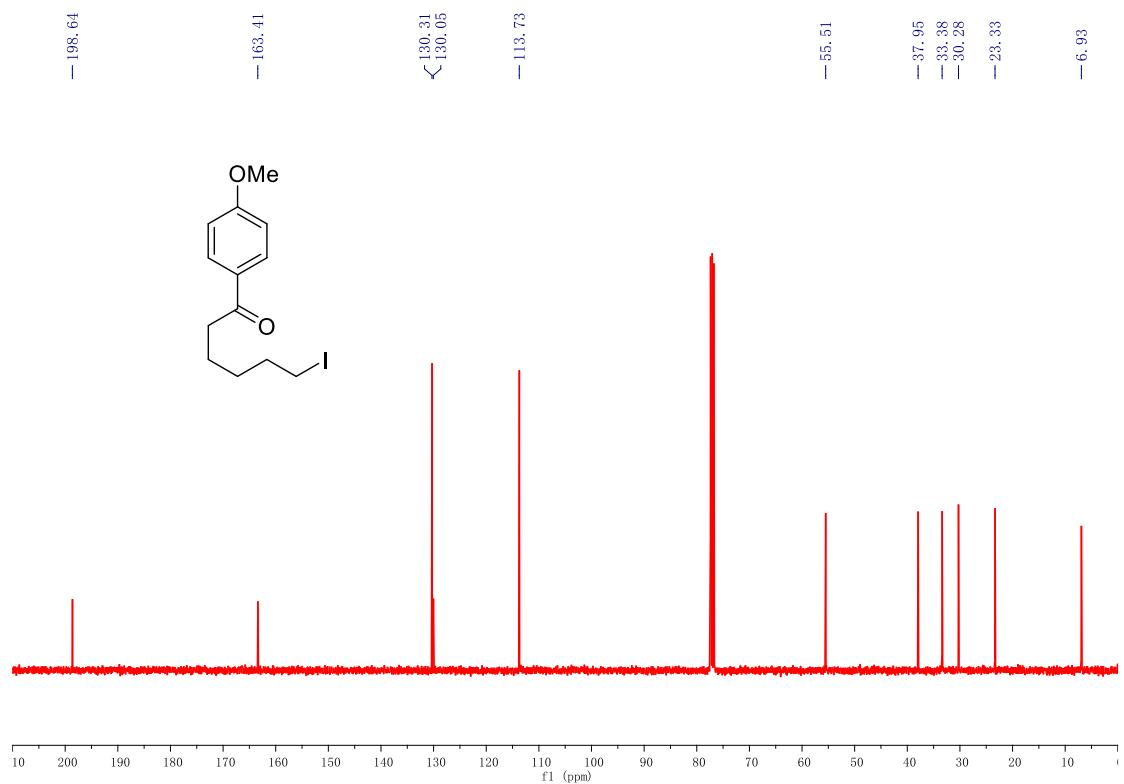
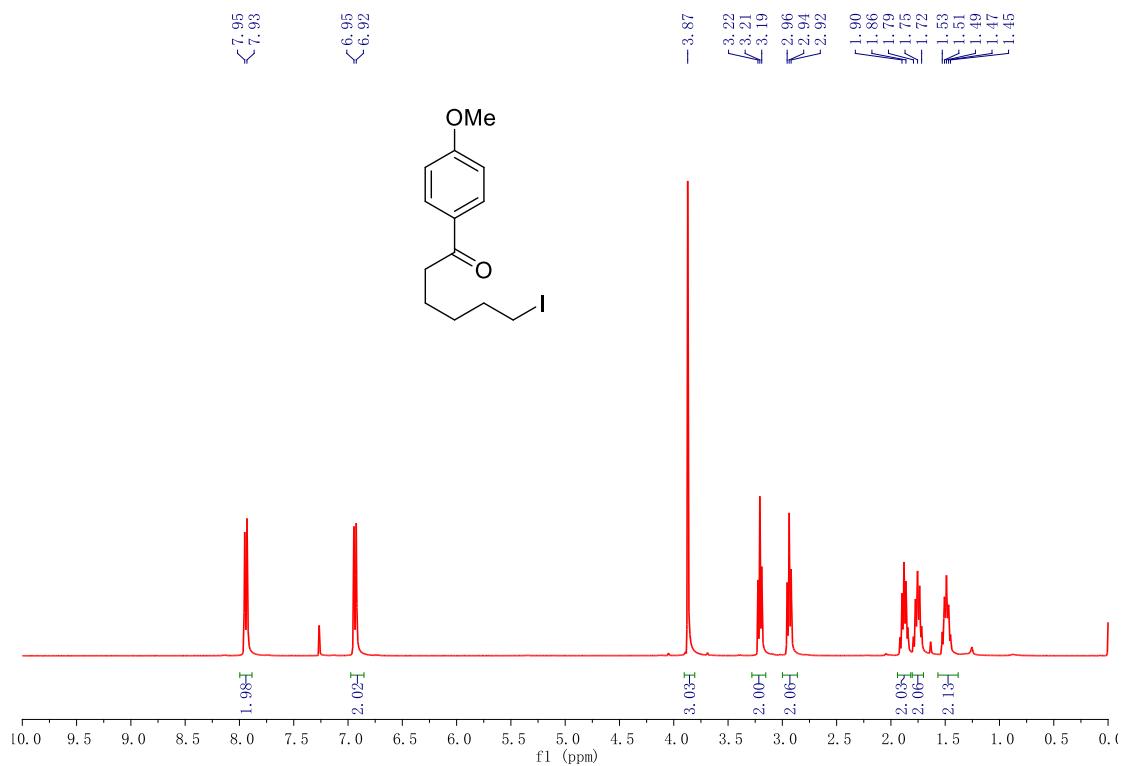
1-(2-Fluorophenyl)-5-iodopentan-1-one **10**



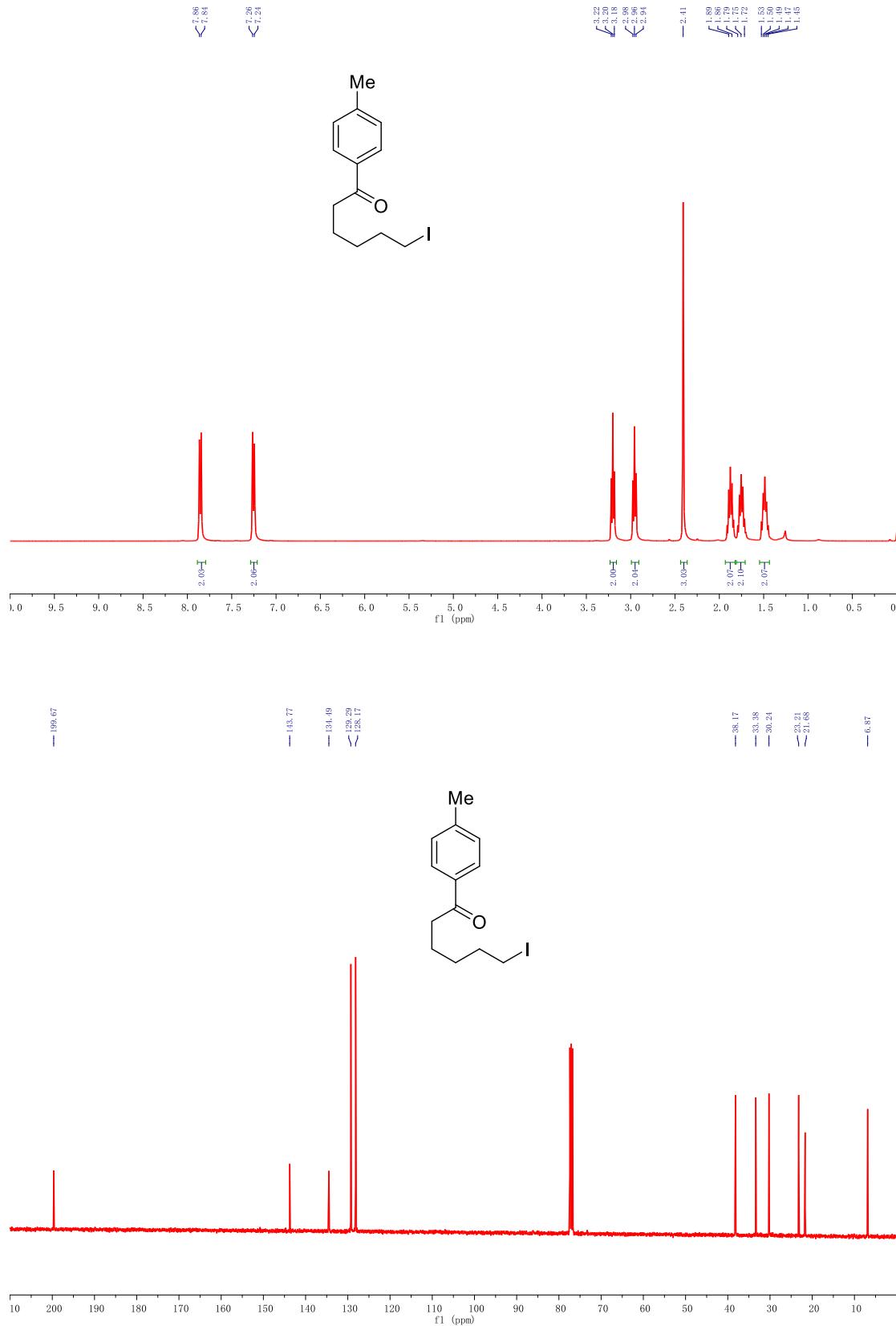
6-Iodo-1-phenylhexan-1-one **1**



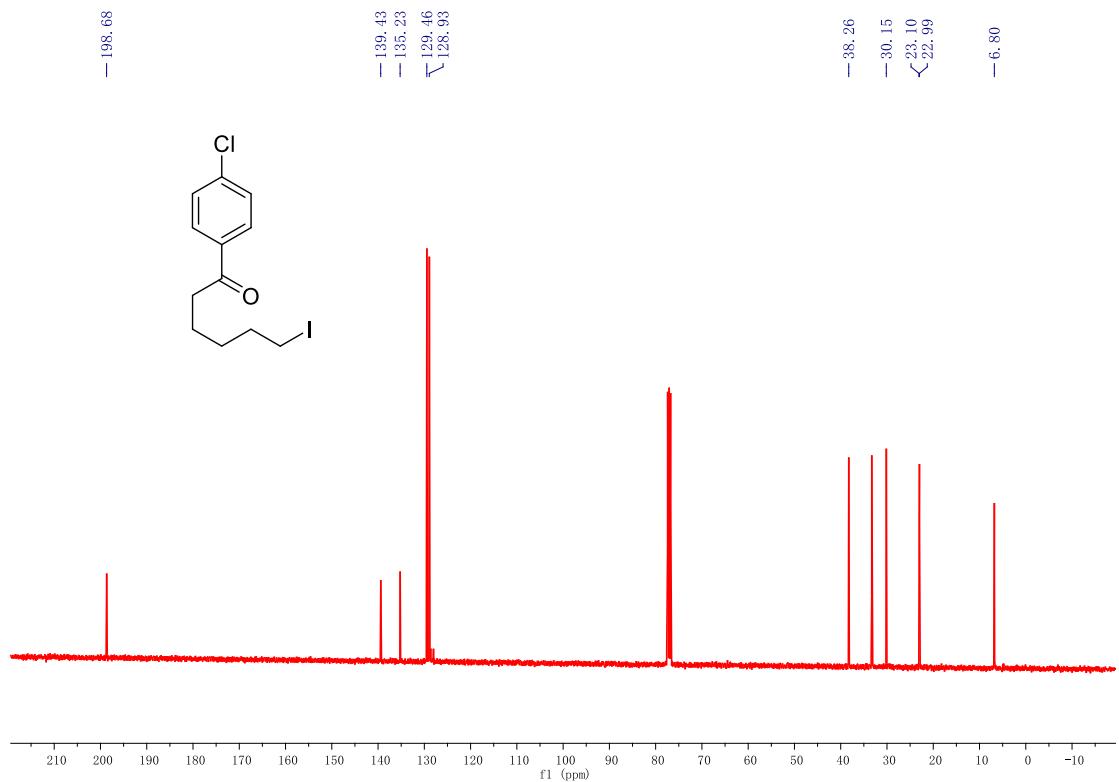
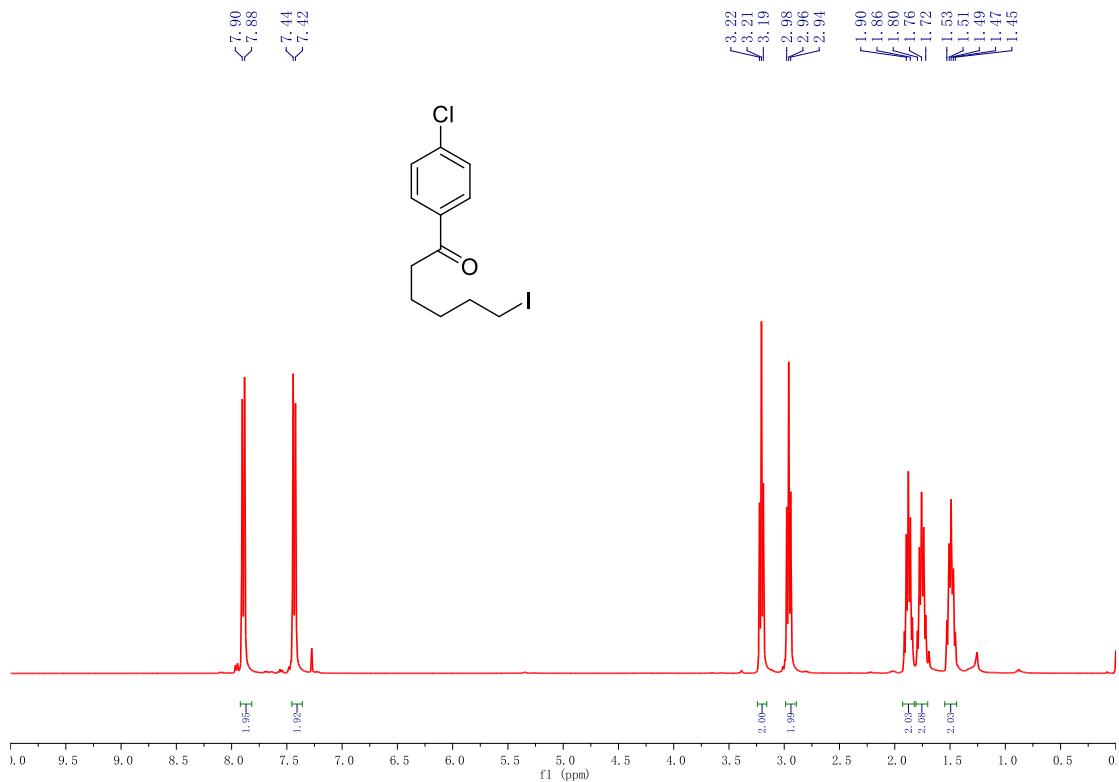
6-Iodo-1-(4-methoxyphenyl)hexan-1-one **11**



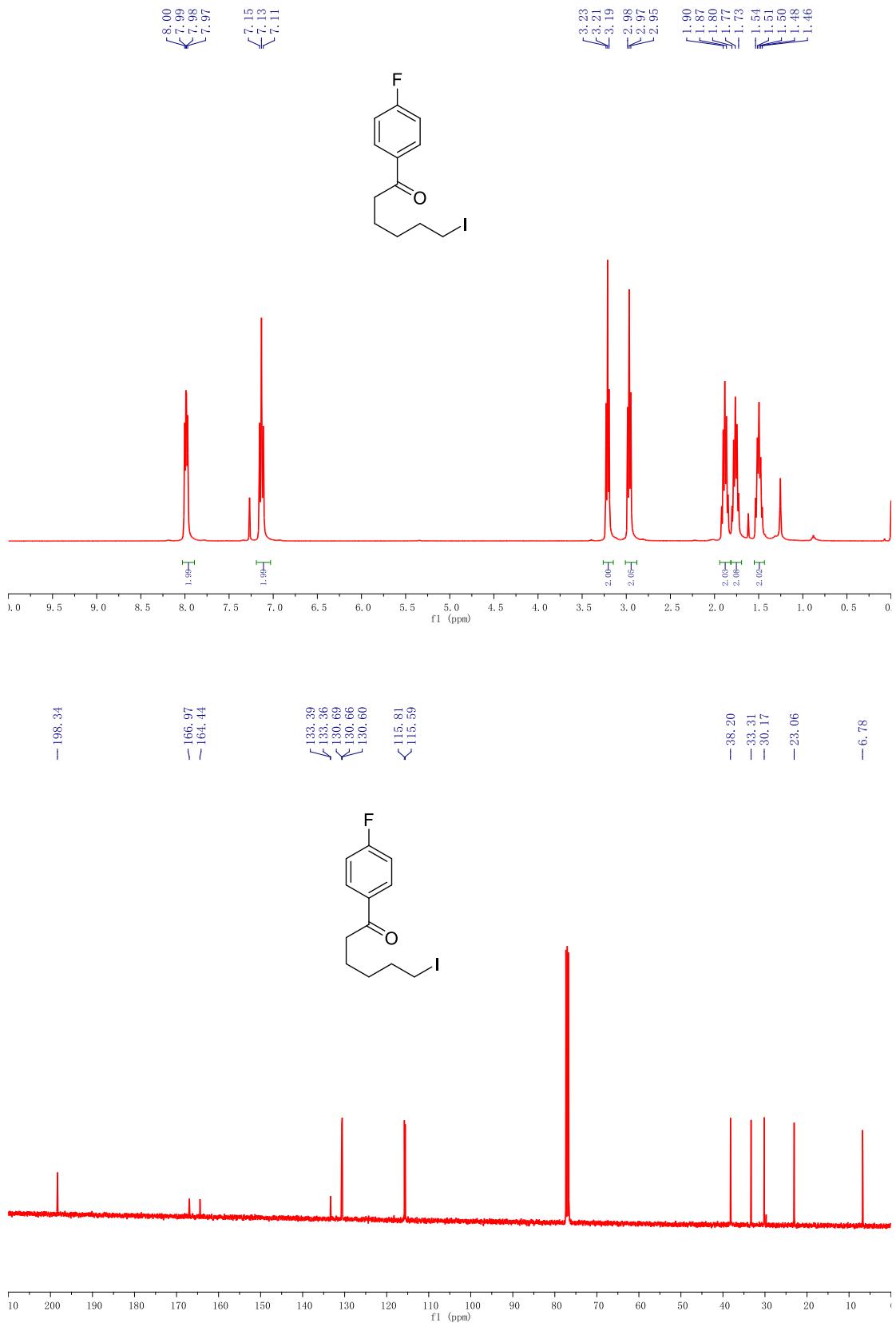
6-Iodo-1-(p-tolyl)hexan-1-one **12**



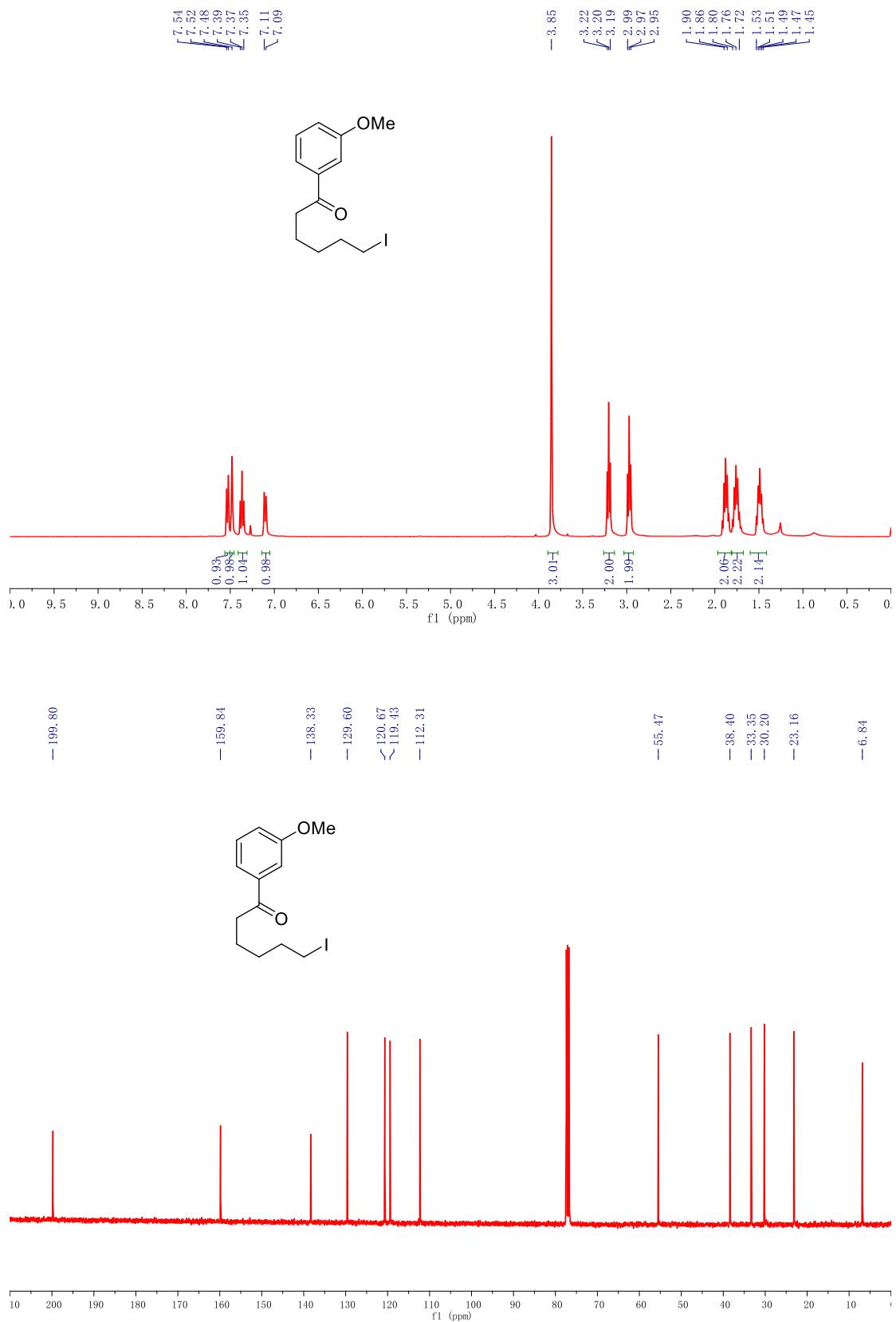
1-(4-Chlorophenyl)-6-iodohexan-1-one **13**



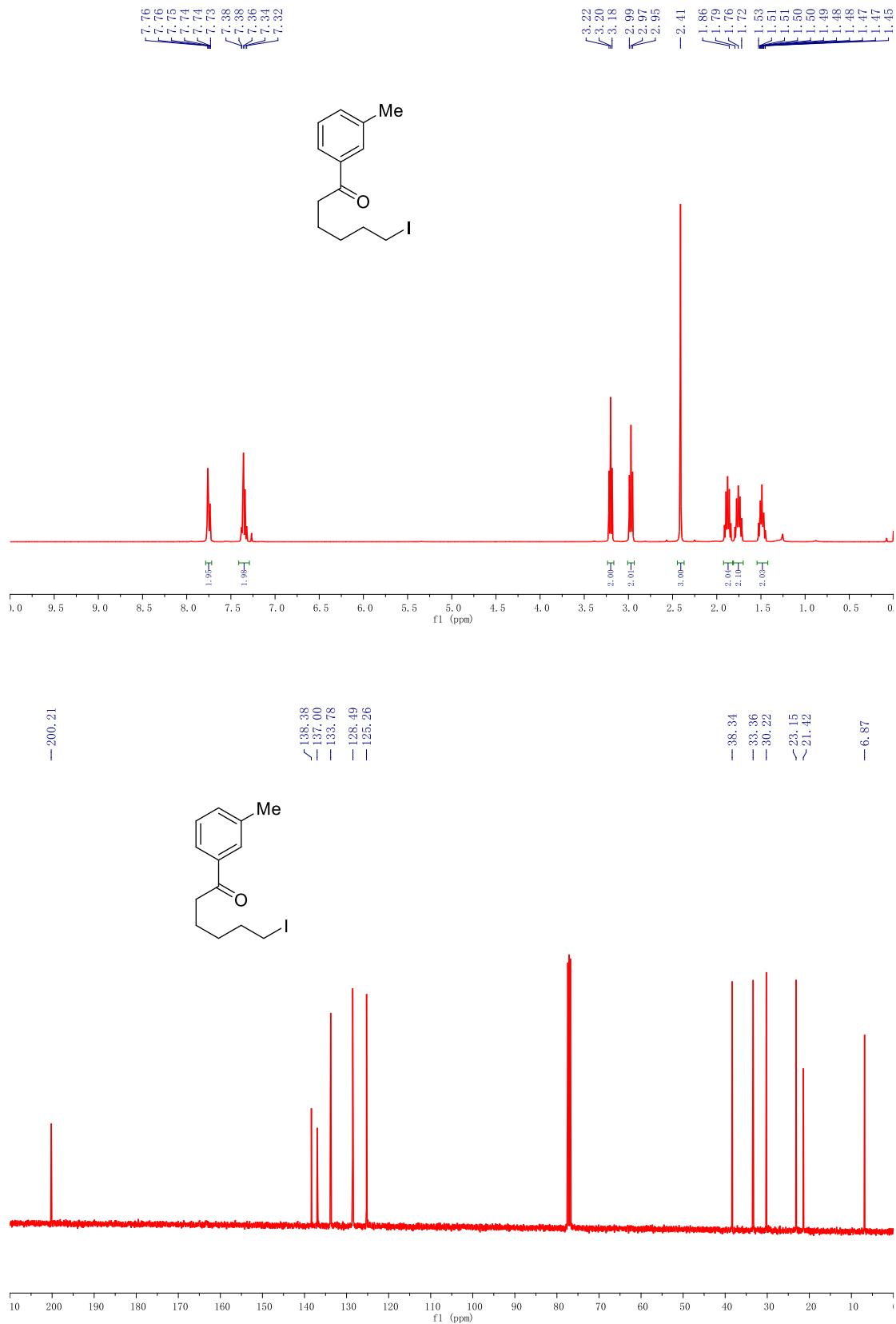
1-(4-Fluorophenyl)-6-iodohexan-1-one **14**



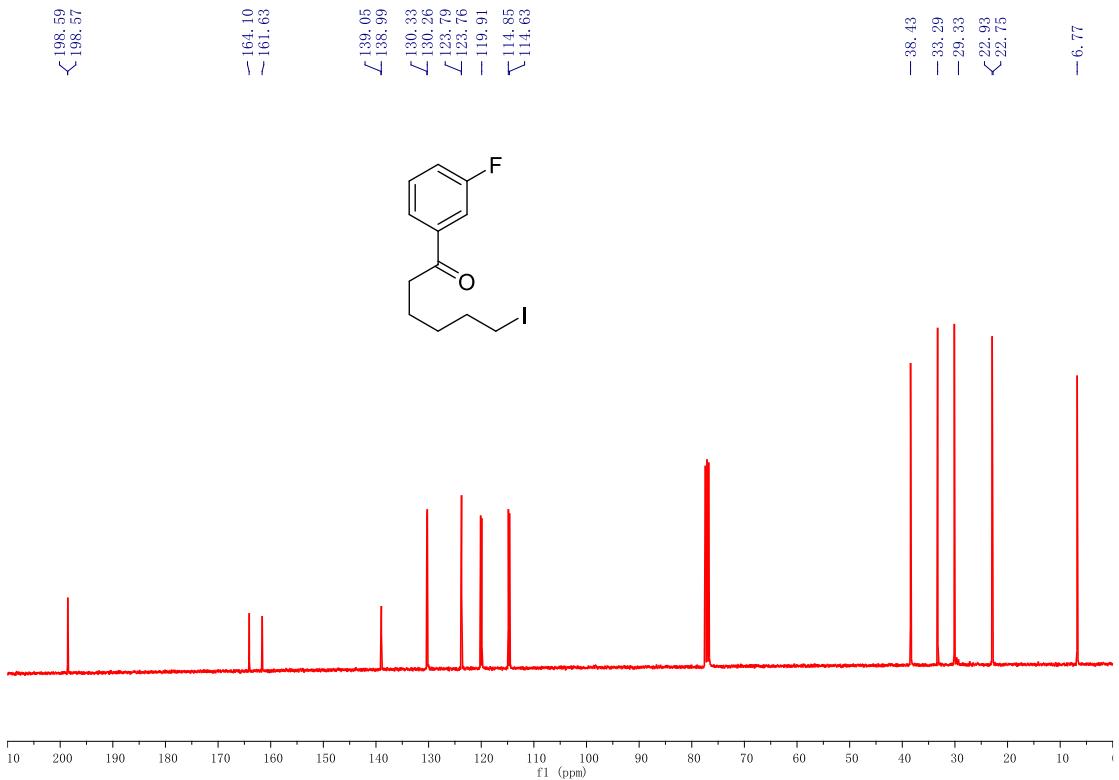
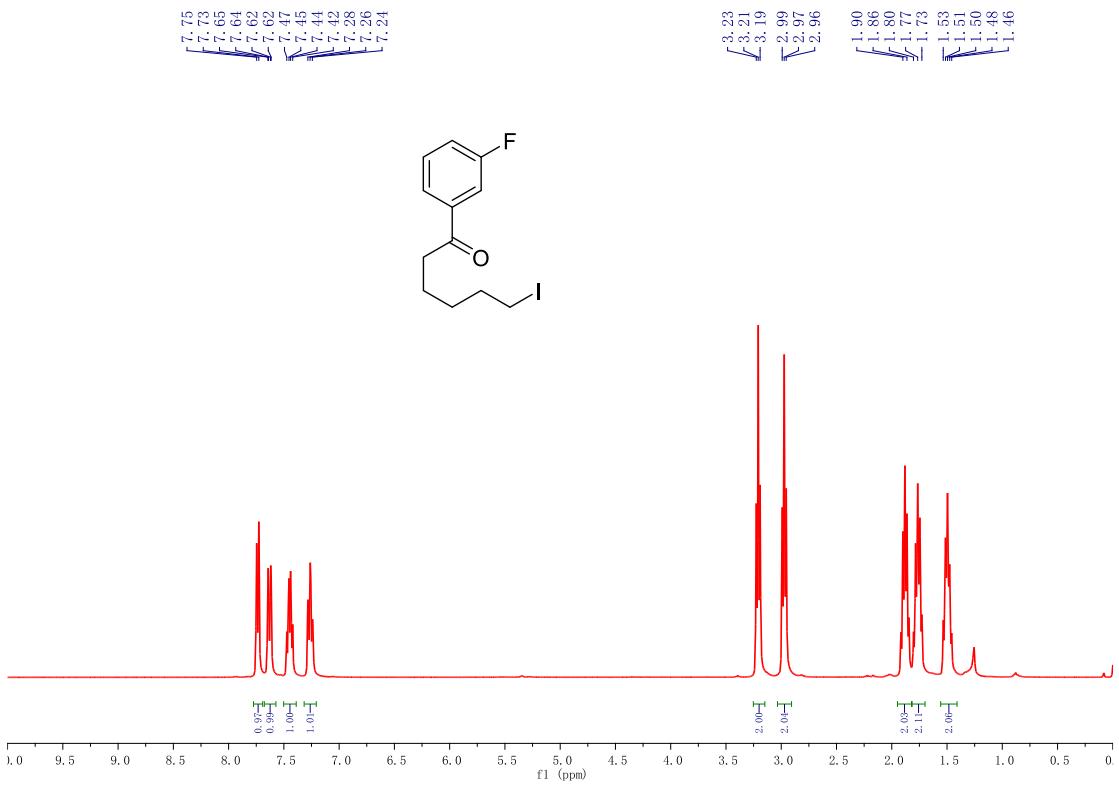
6-Iodo-1-(3-methoxyphenyl)hexan-1-one **15**



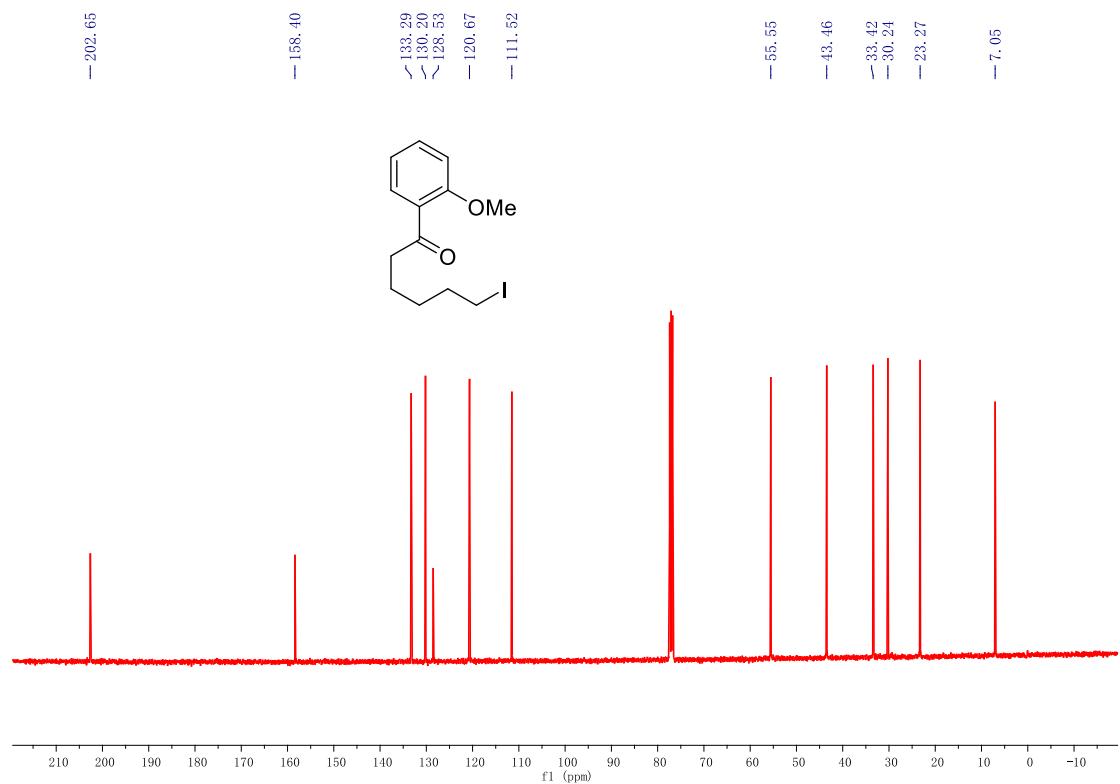
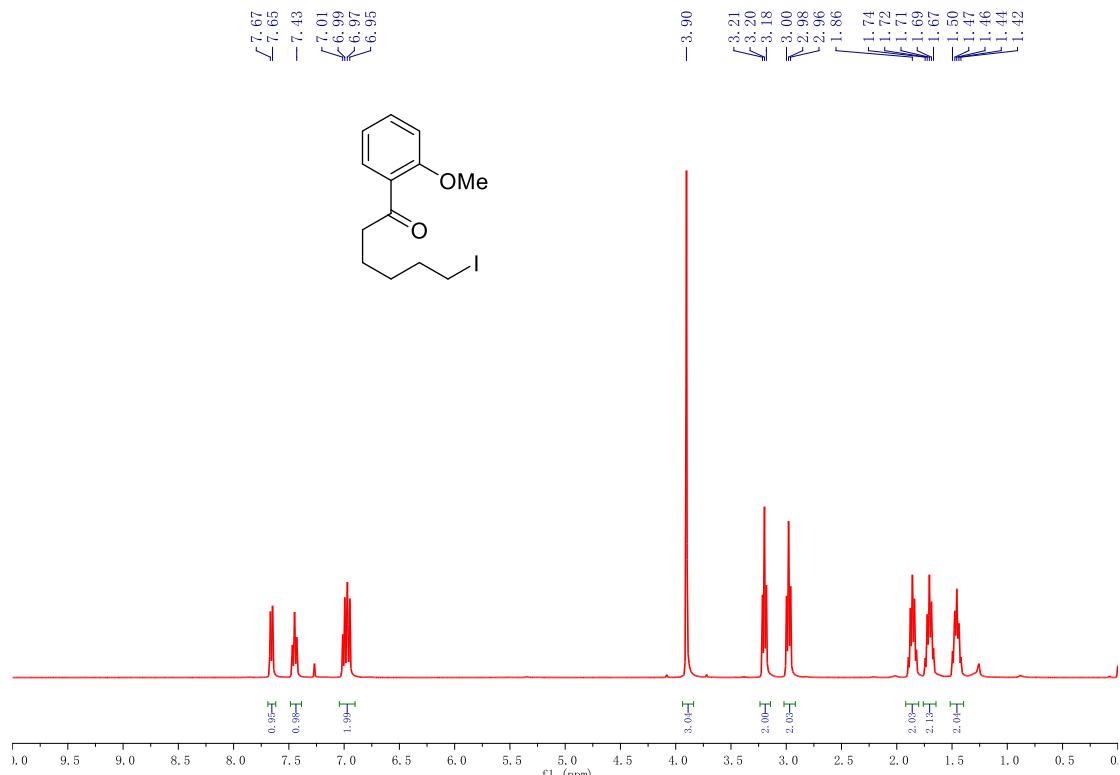
6-Iodo-1-(*m*-tolyl)hexan-1-one **16**



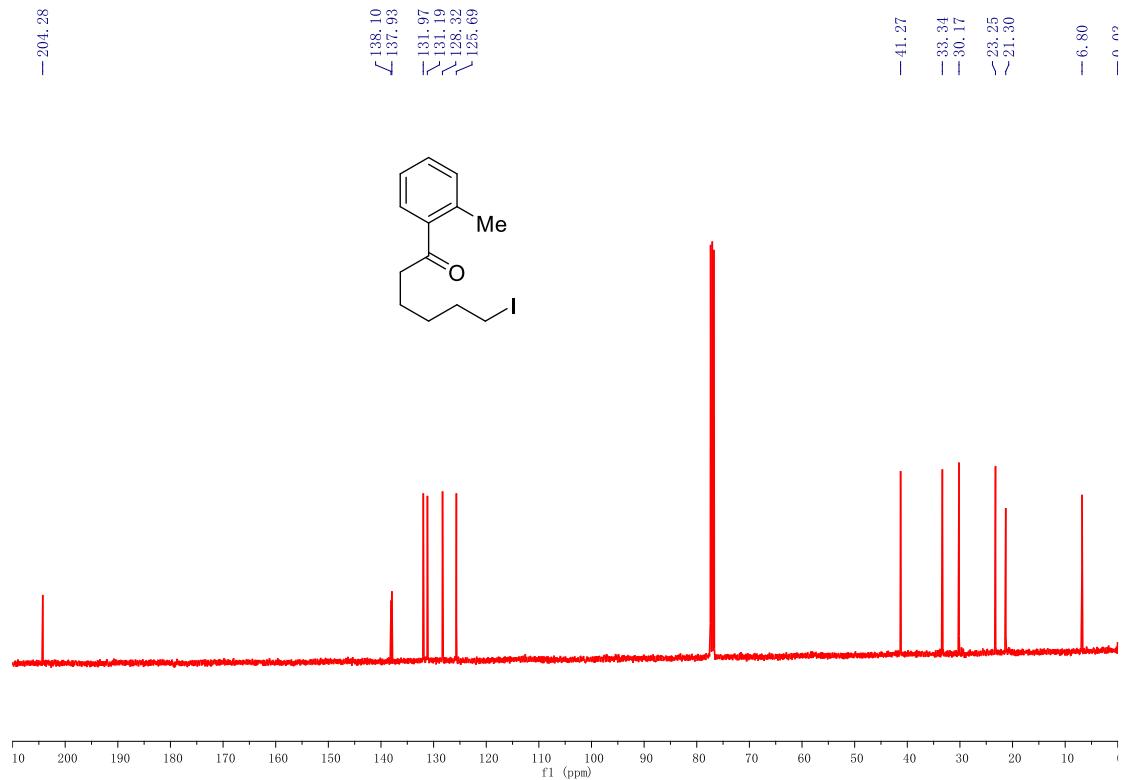
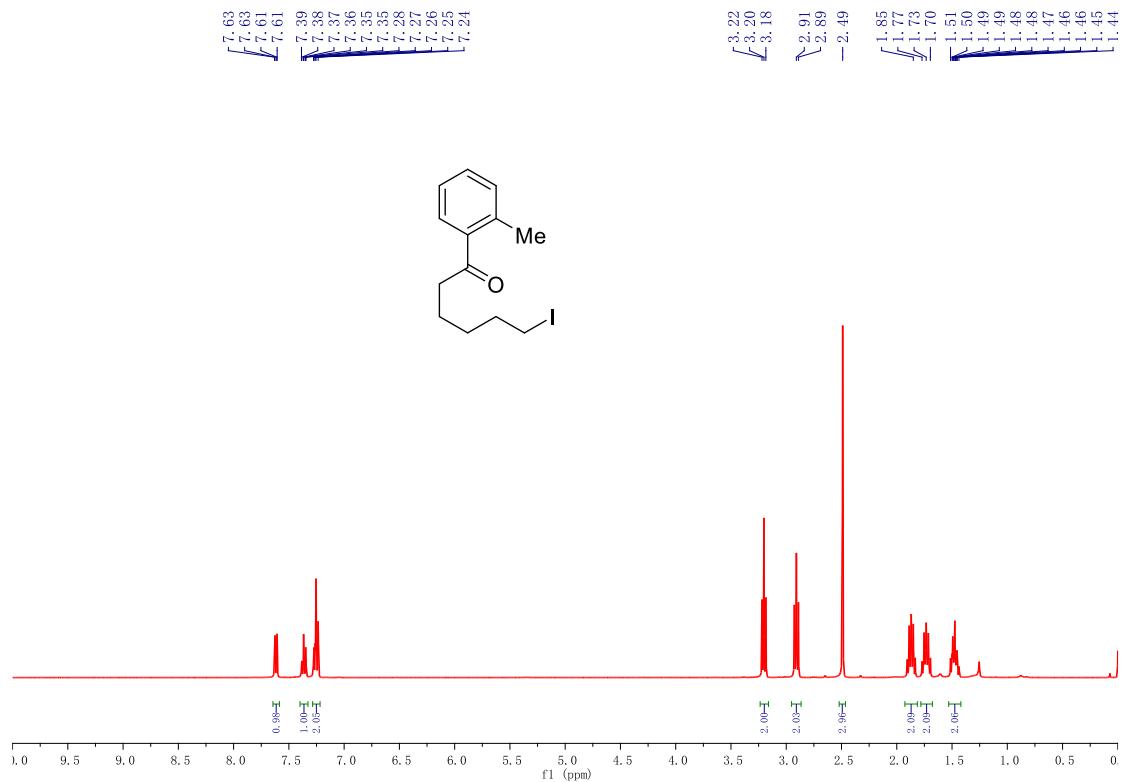
1-(3-Fluorophenyl)-6-iodohexan-1-one **17**



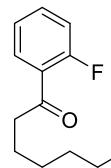
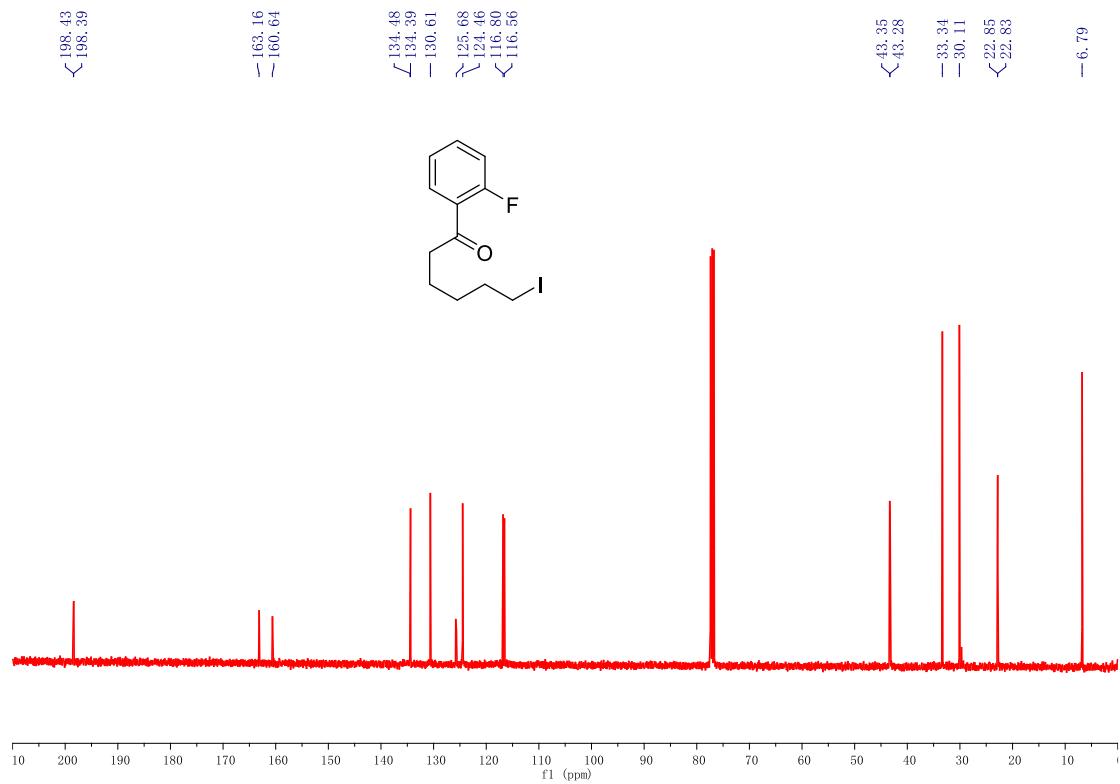
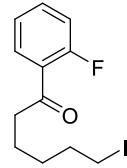
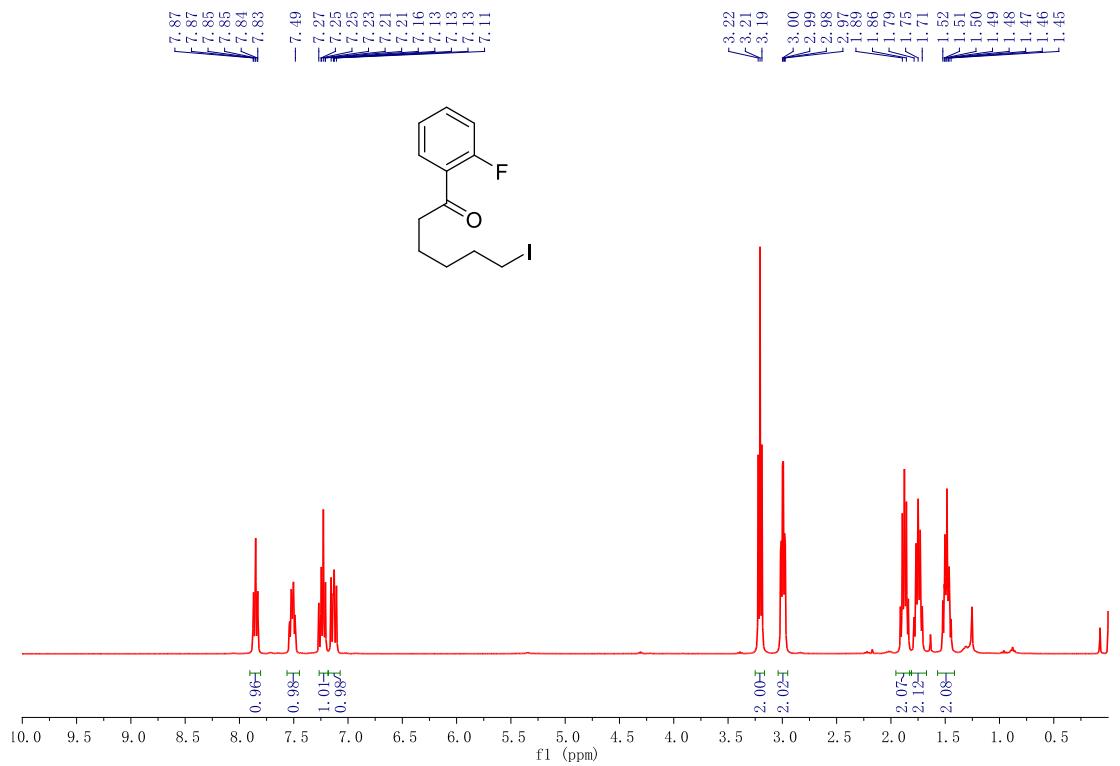
6-Iodo-1-(2-methoxyphenyl)hexan-1-one **18**



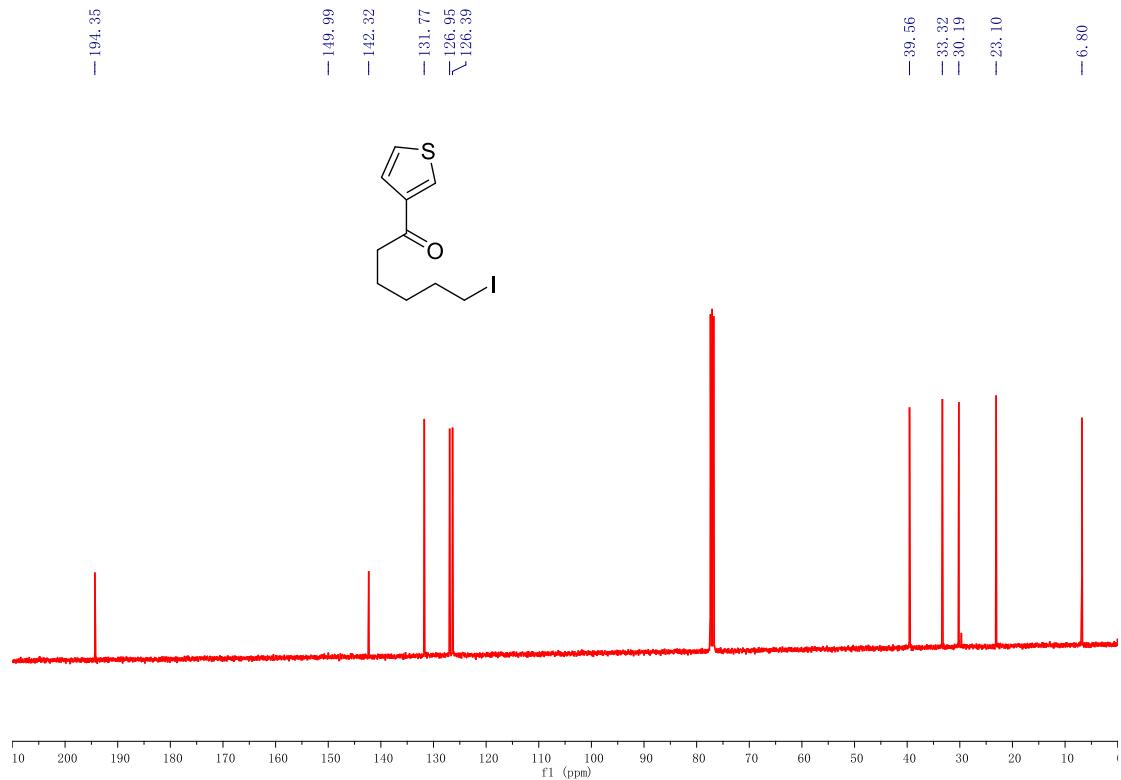
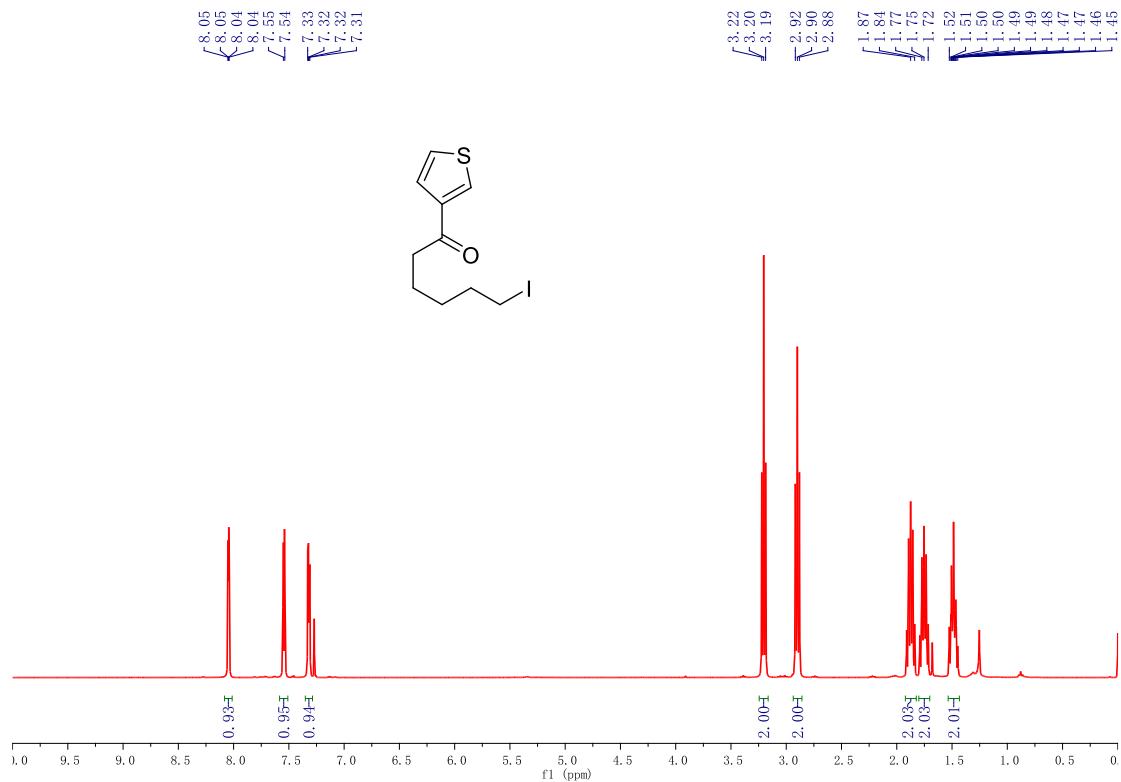
6-Iodo-1-(o-tolyl)hexan-1-one **19**



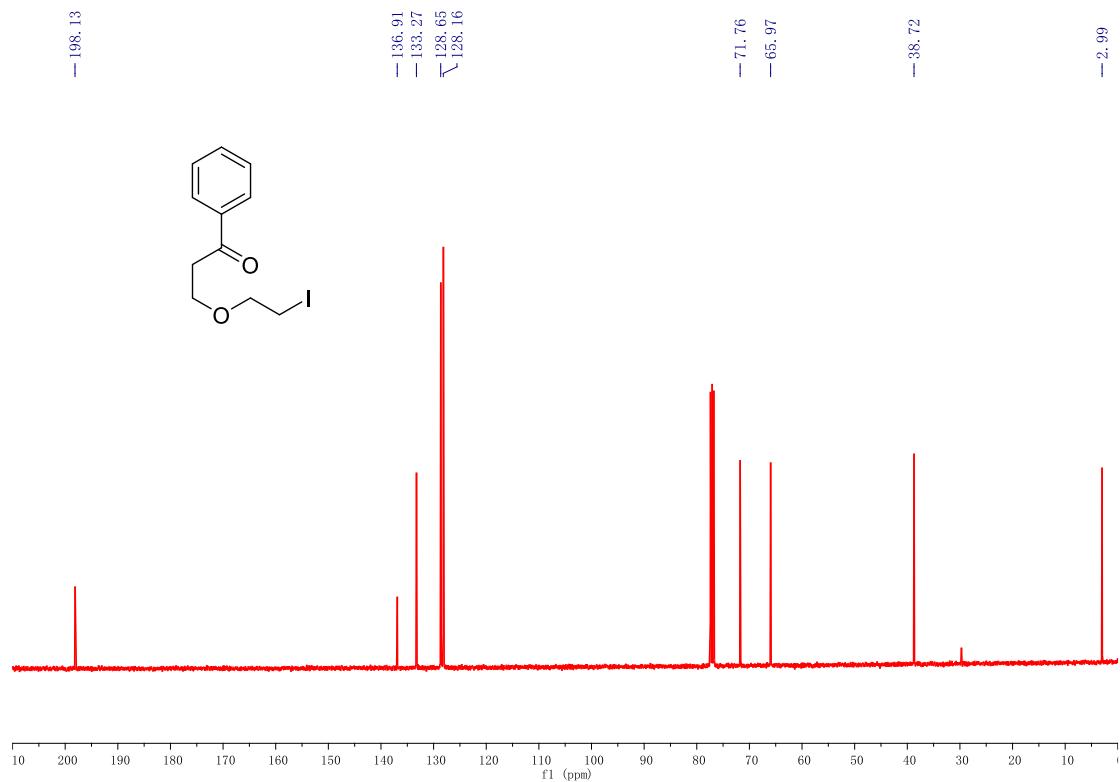
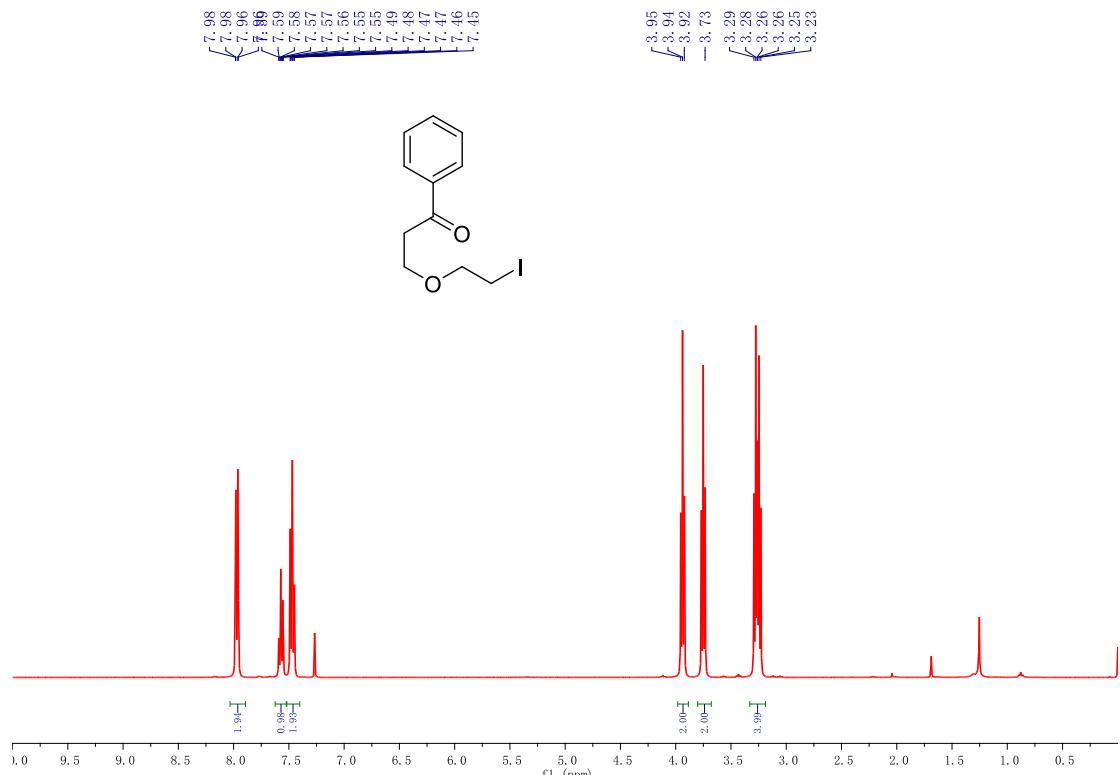
1-(2-Fluorophenyl)-6-iodohexan-1-one **20**



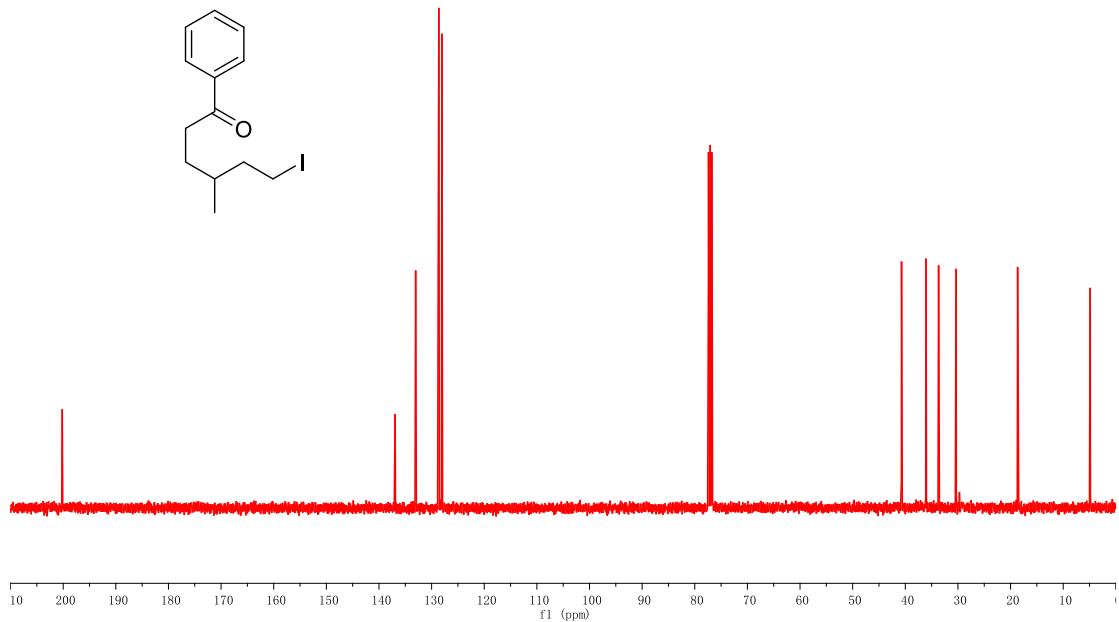
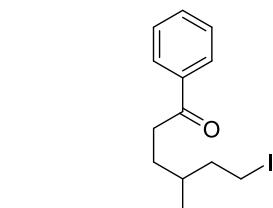
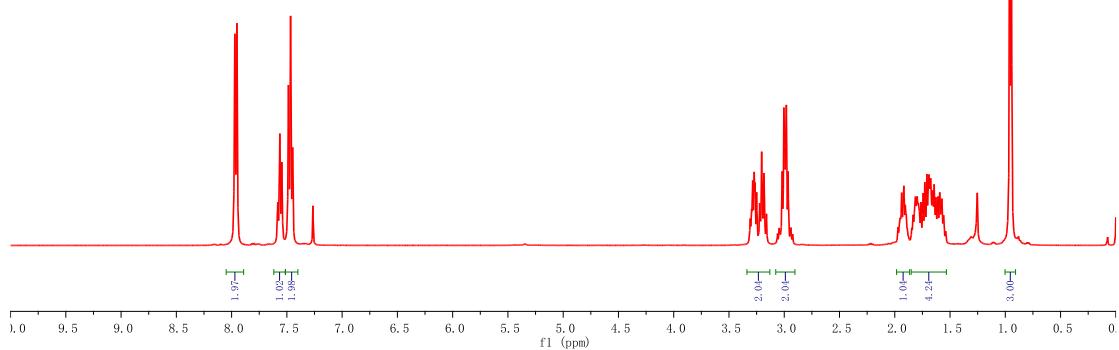
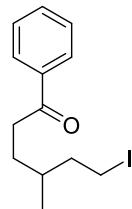
6-Iodo-1-(thiophen-3-yl)hexan-1-one **21**



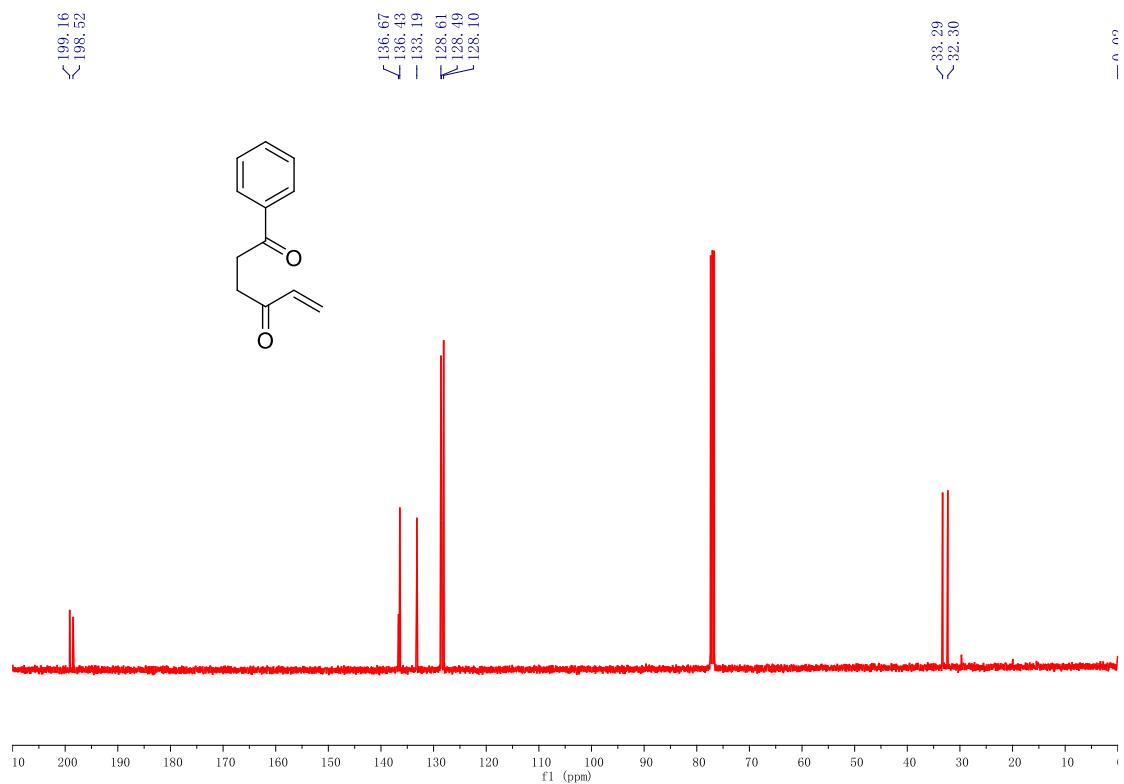
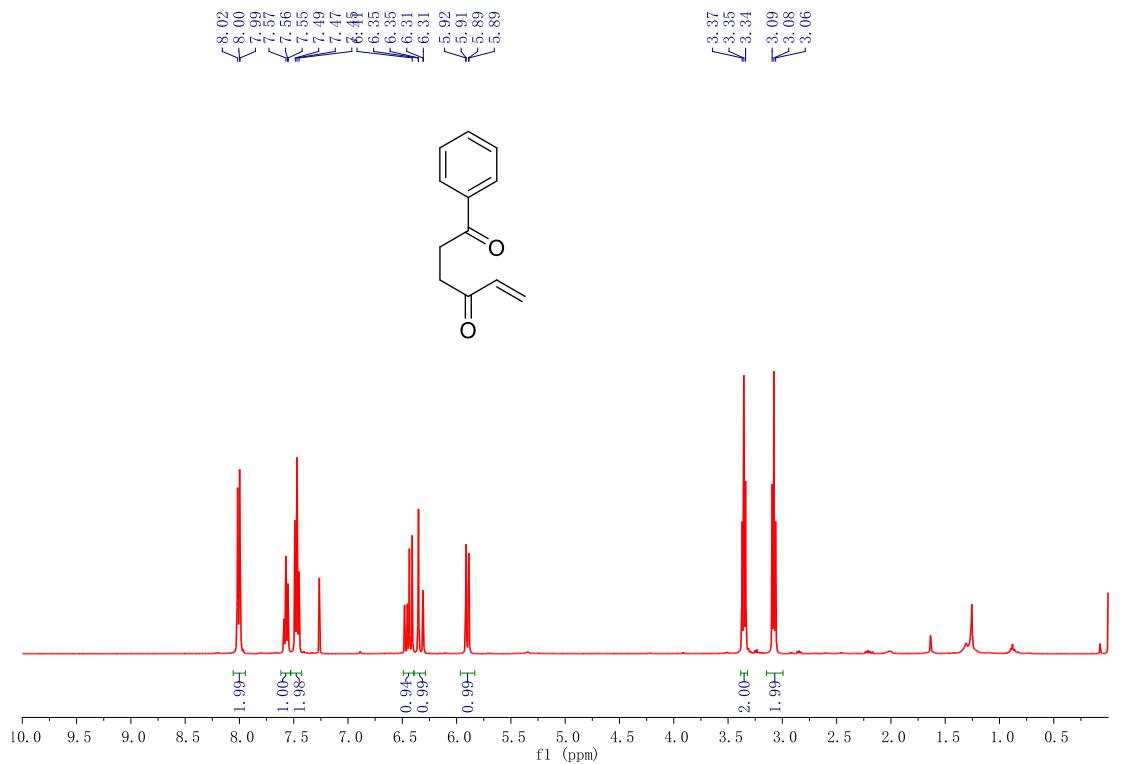
3-(2-Iodoethoxy)-1-phenylpropan-1-one **22**



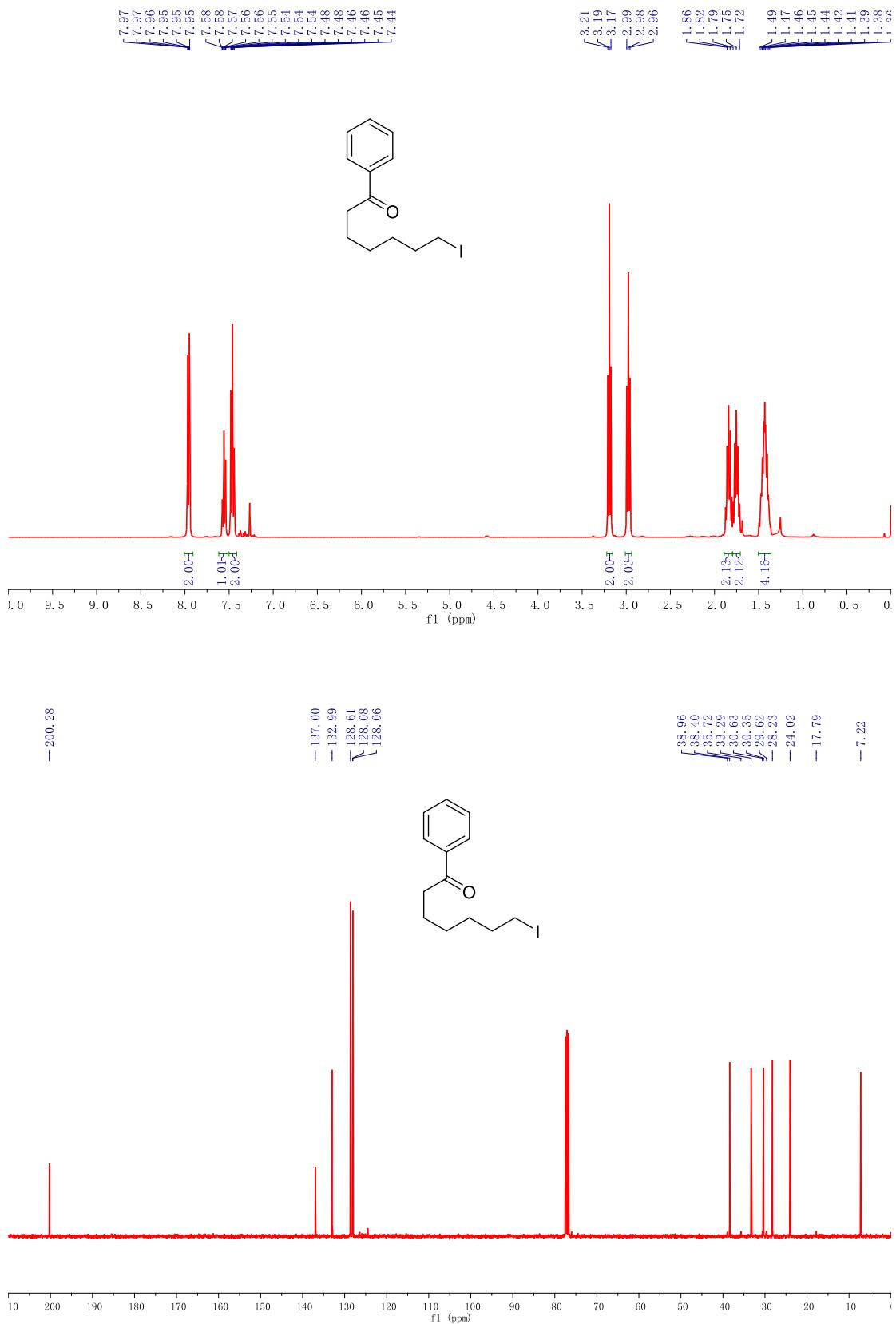
6-Iodo-4-methyl-1-phenylhexan-1-one **23**



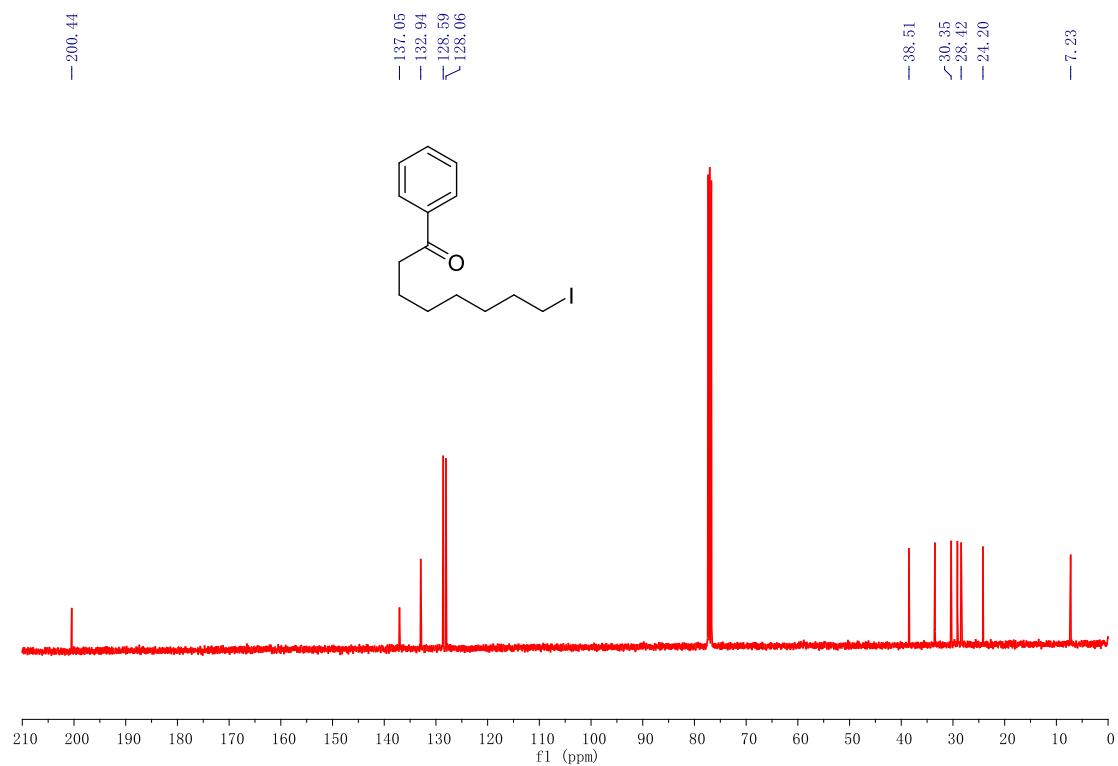
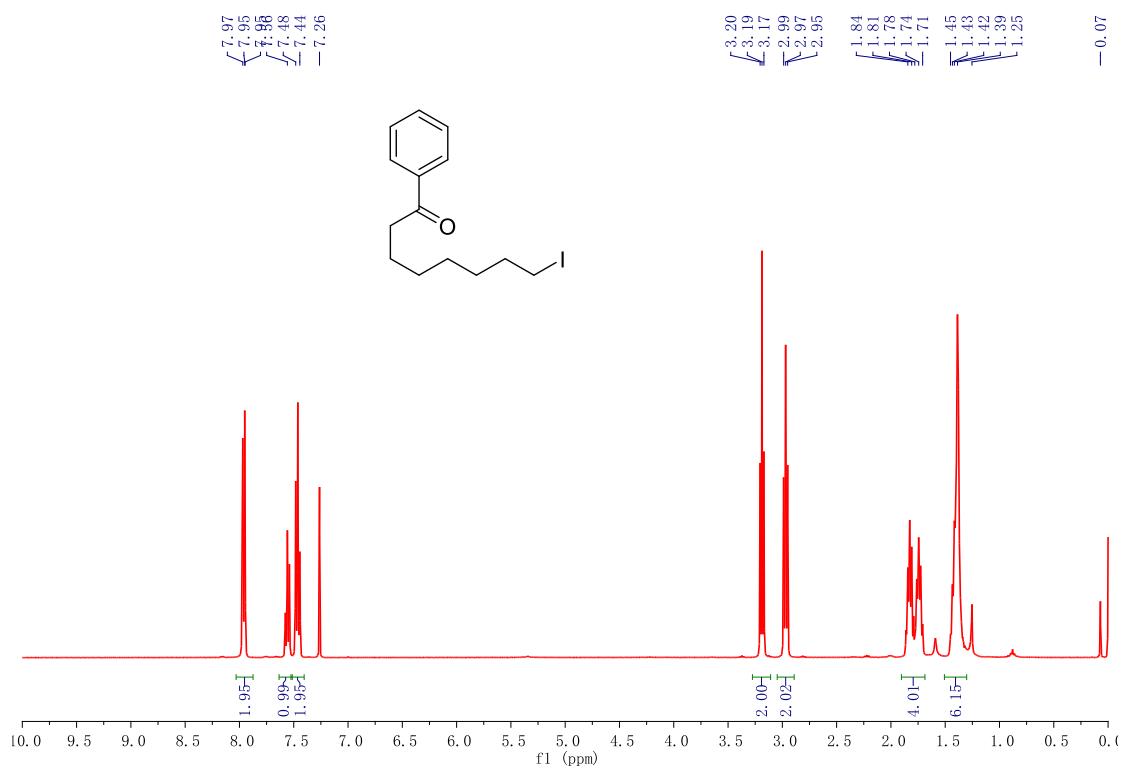
1-Phenylhex-5-ene-1,4-dione 24



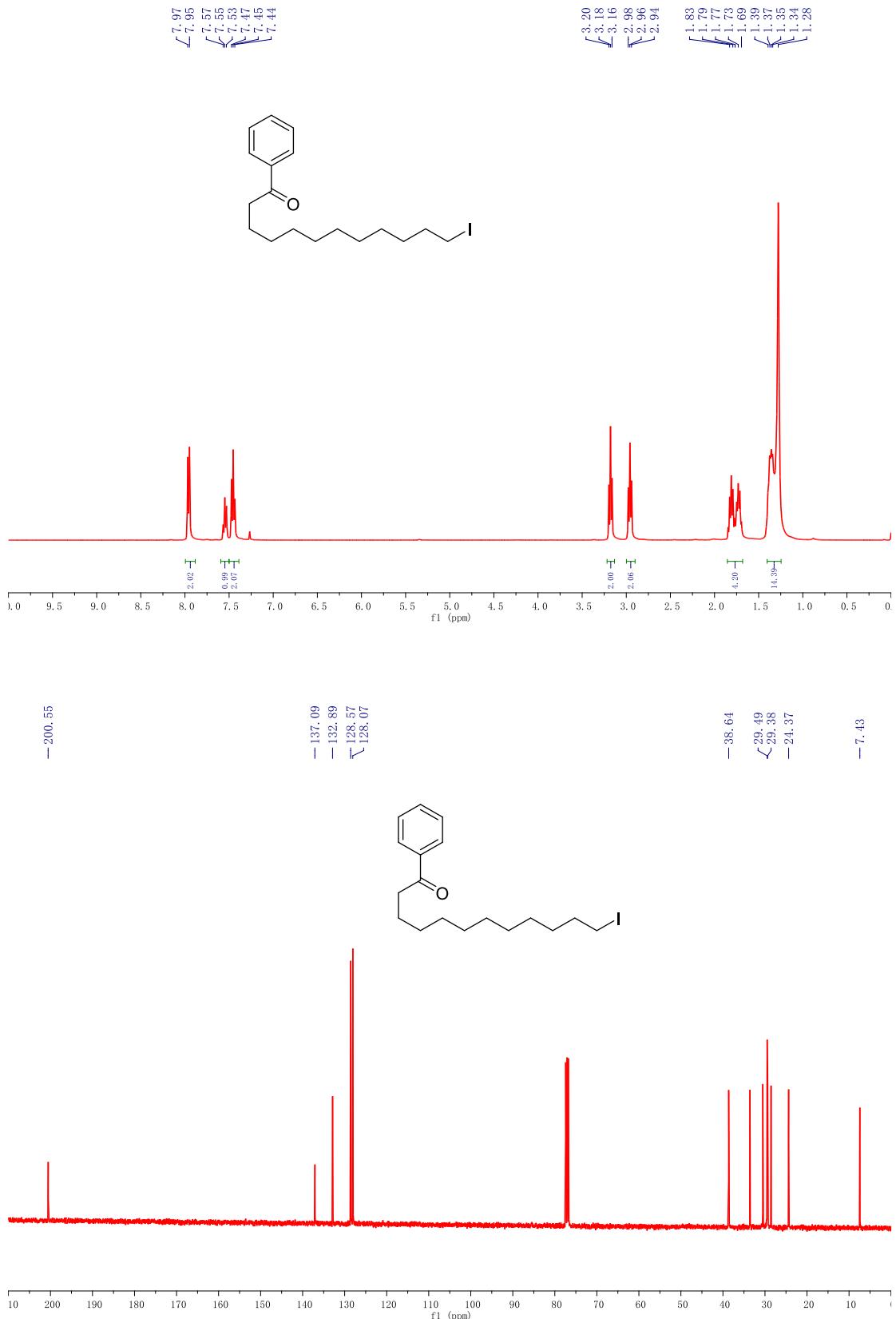
7-Iodo-1-phenylheptan-1-one **25**



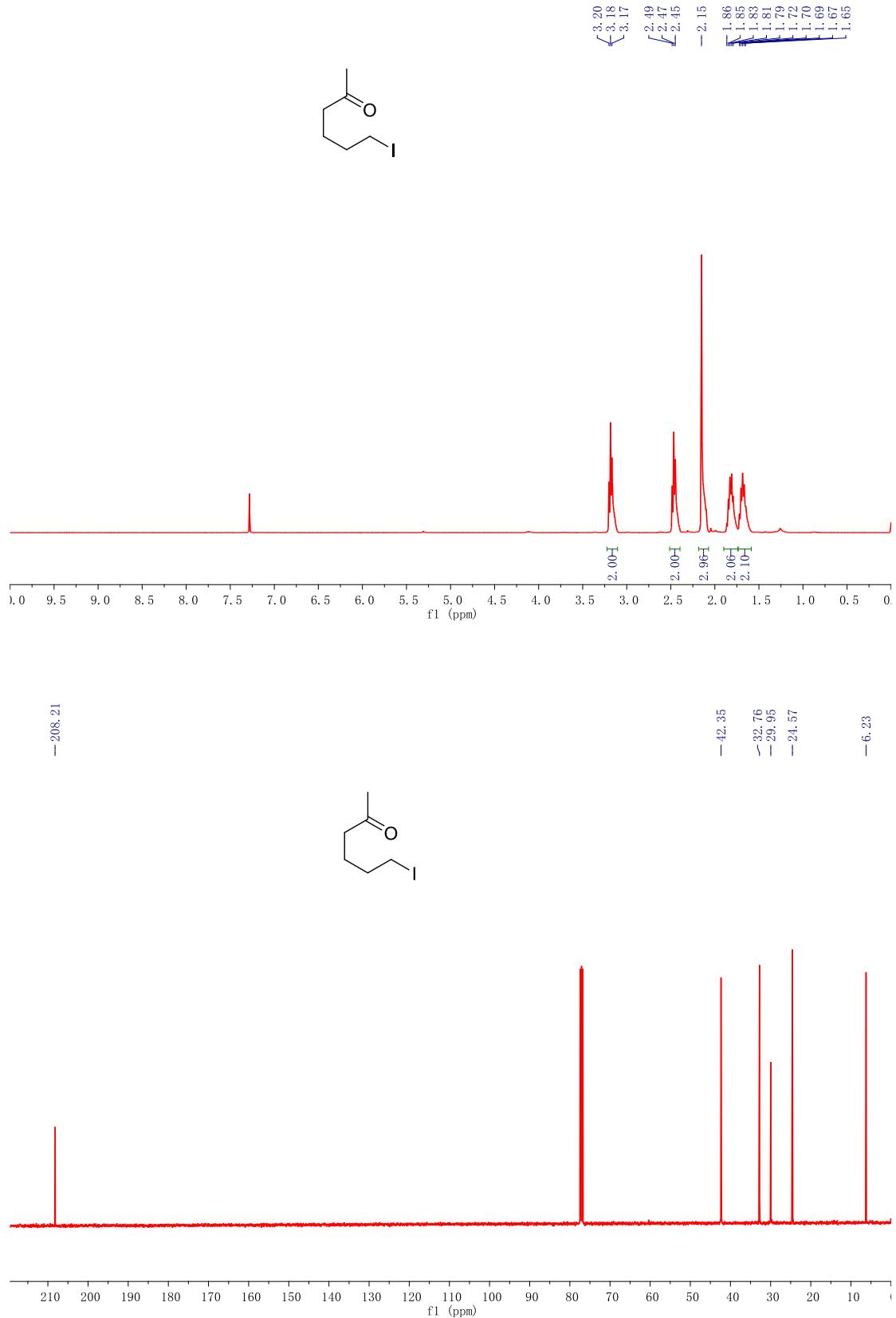
8-Iodo-1-phenyloctan-1-one **26**



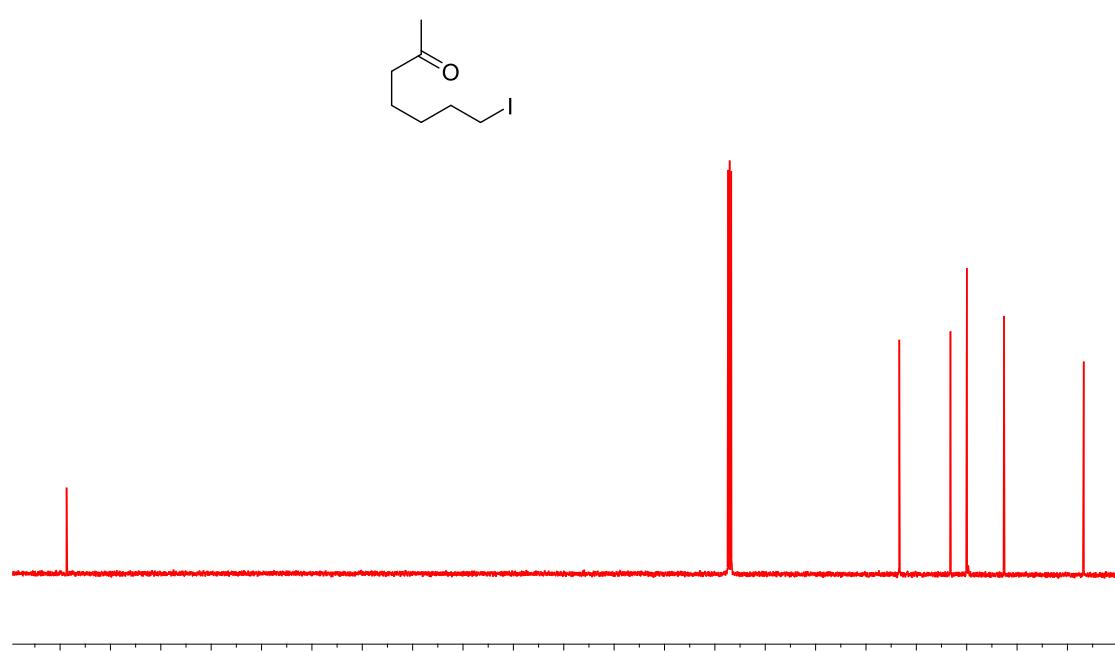
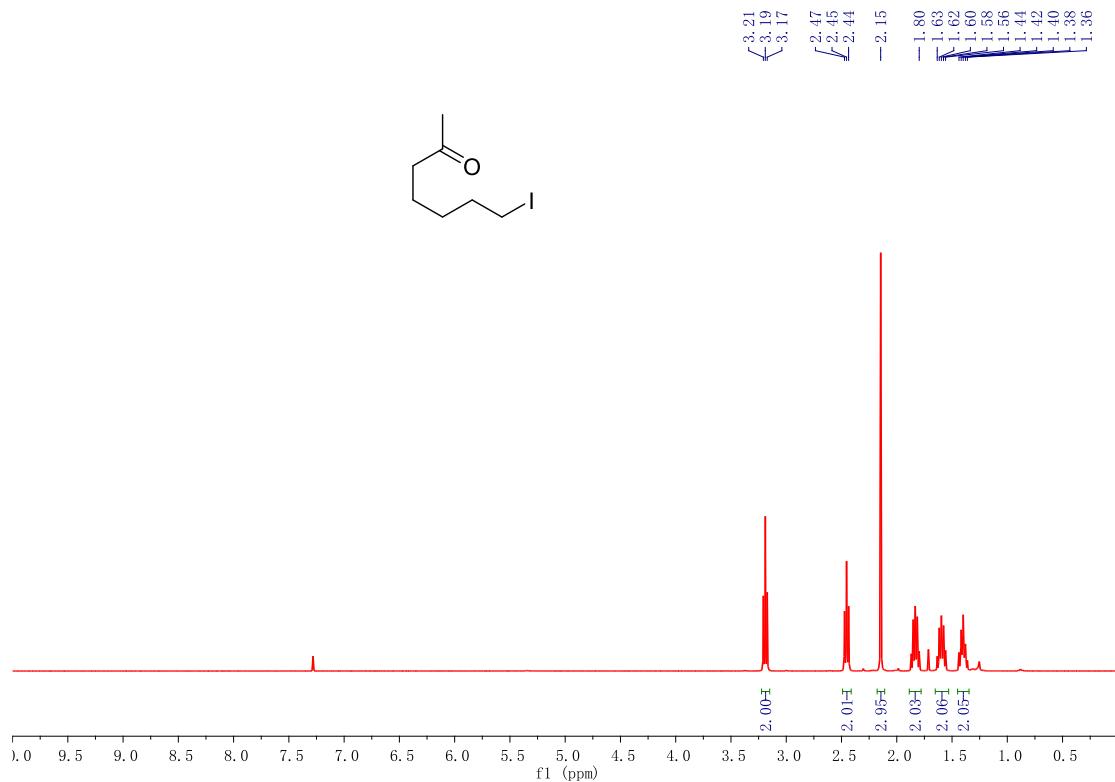
12-Iodo-1-phenyldodecan-1-one **27**



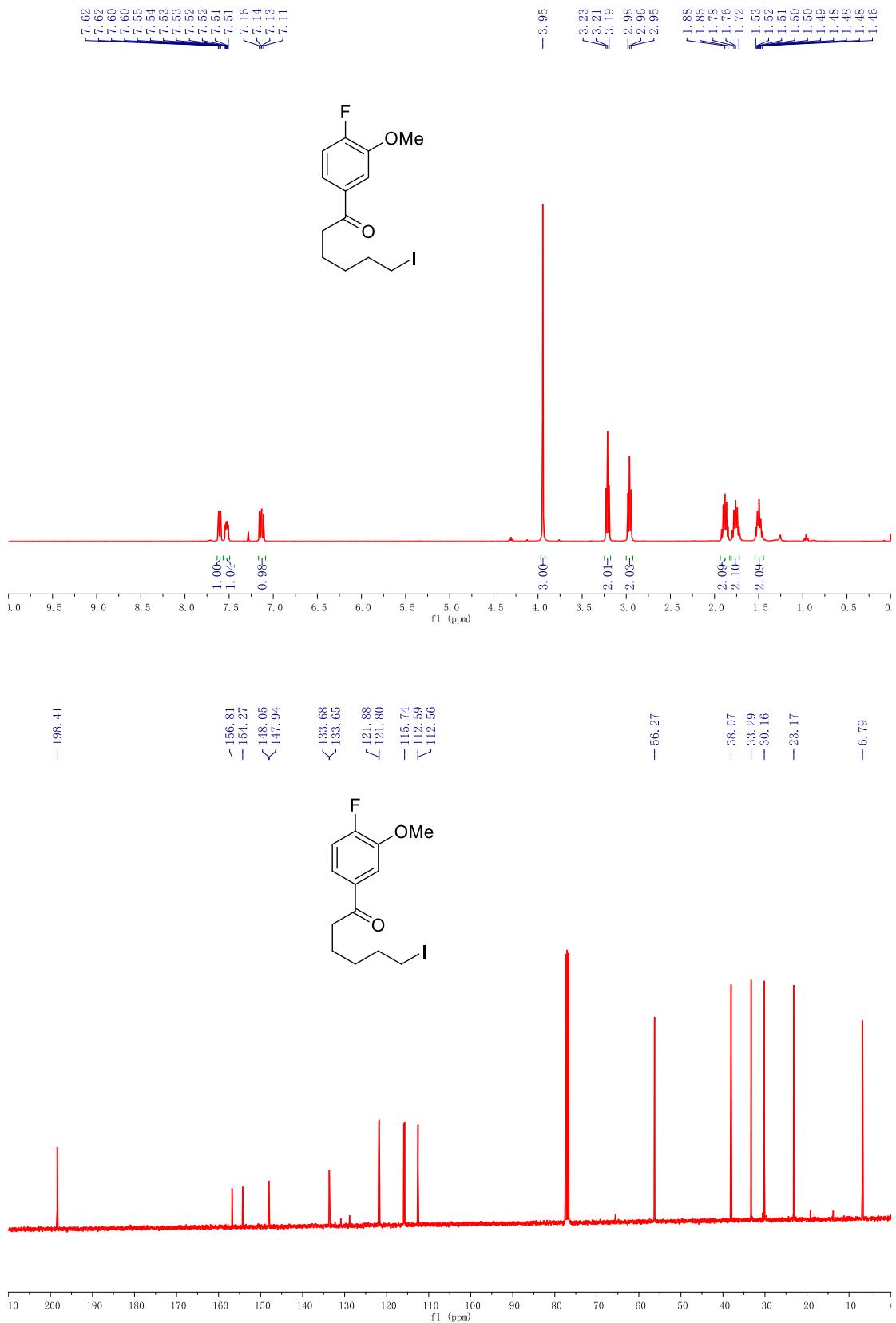
6-Iodohexan-2-one **28**



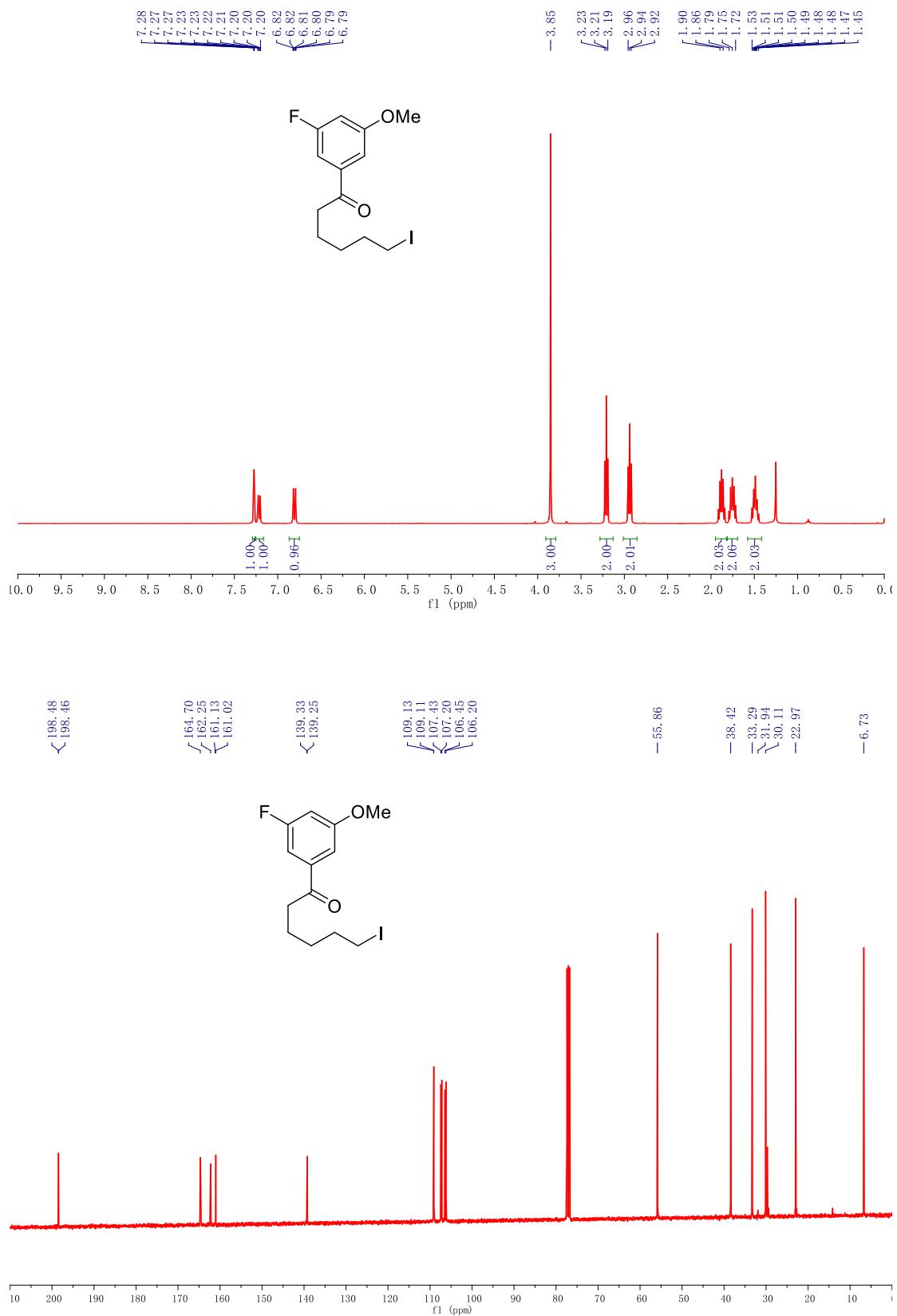
7-Iodoheptan-2-one **29**



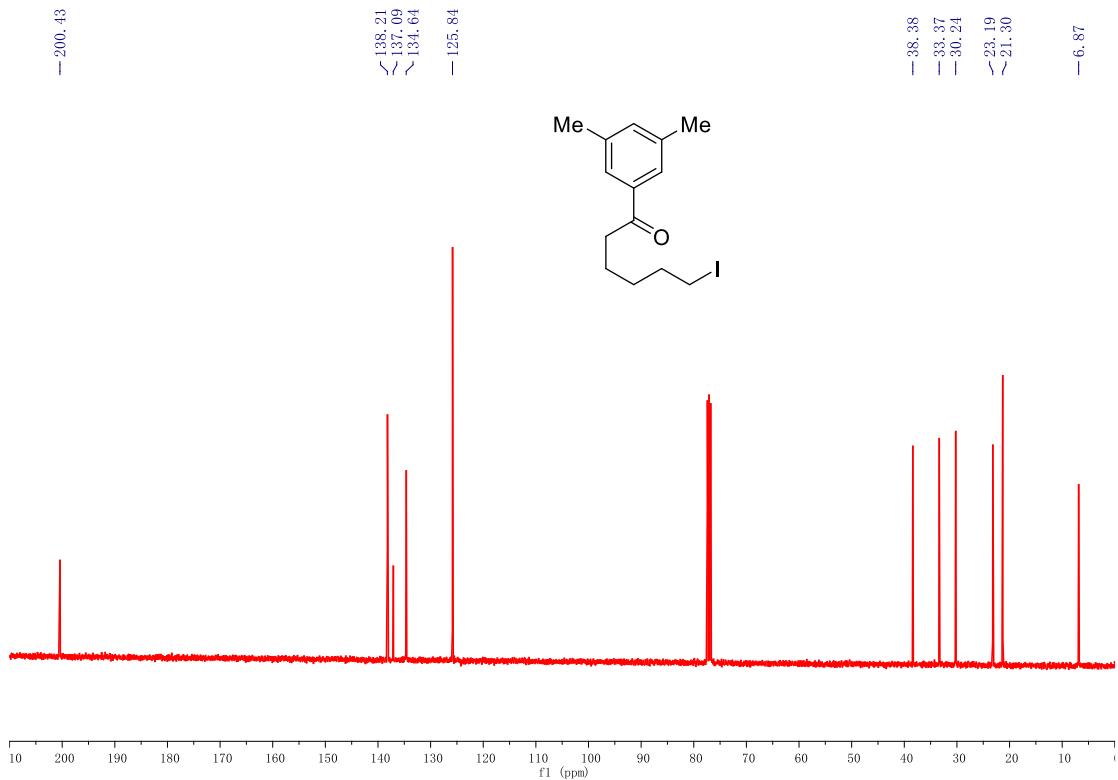
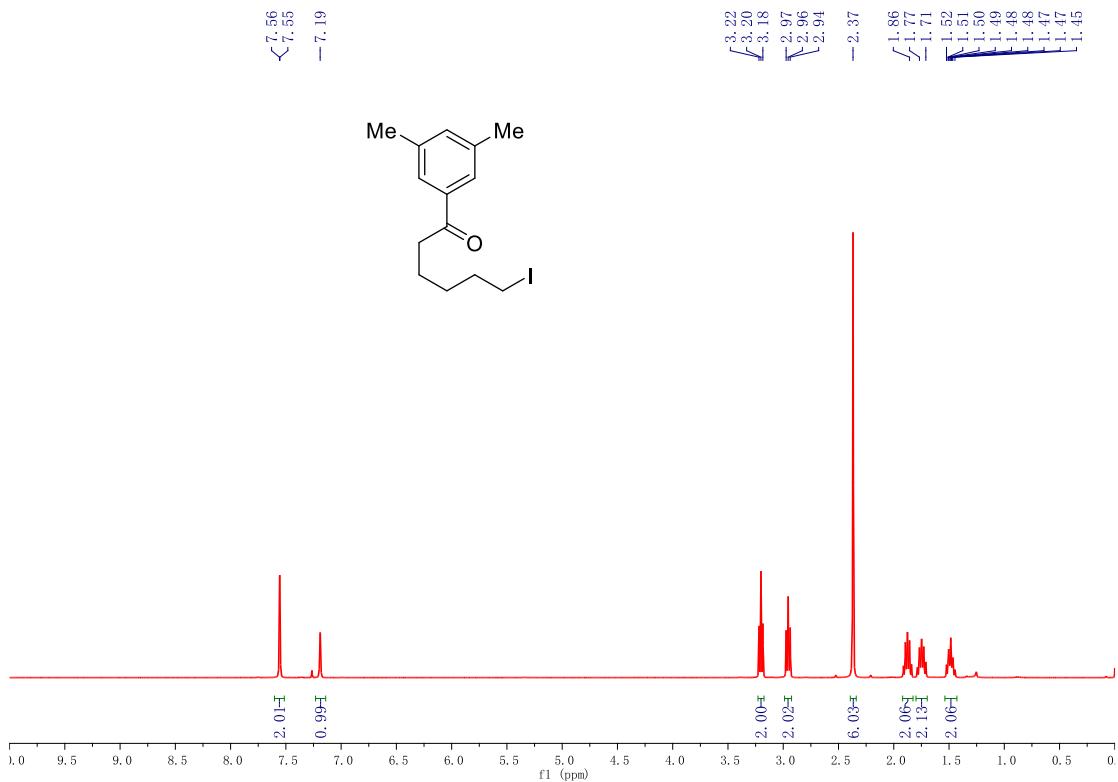
1-(4-Fluoro-3-methoxyphenyl)-6-iodohexan-1-one **30**



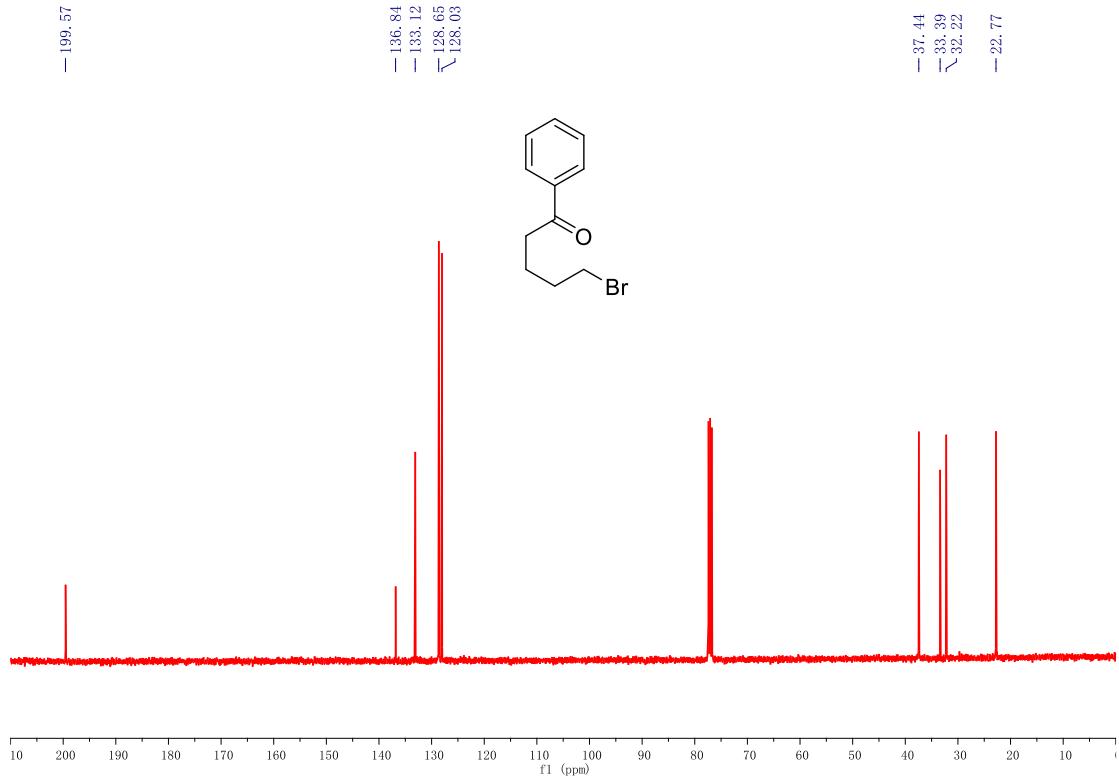
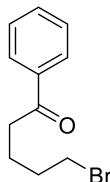
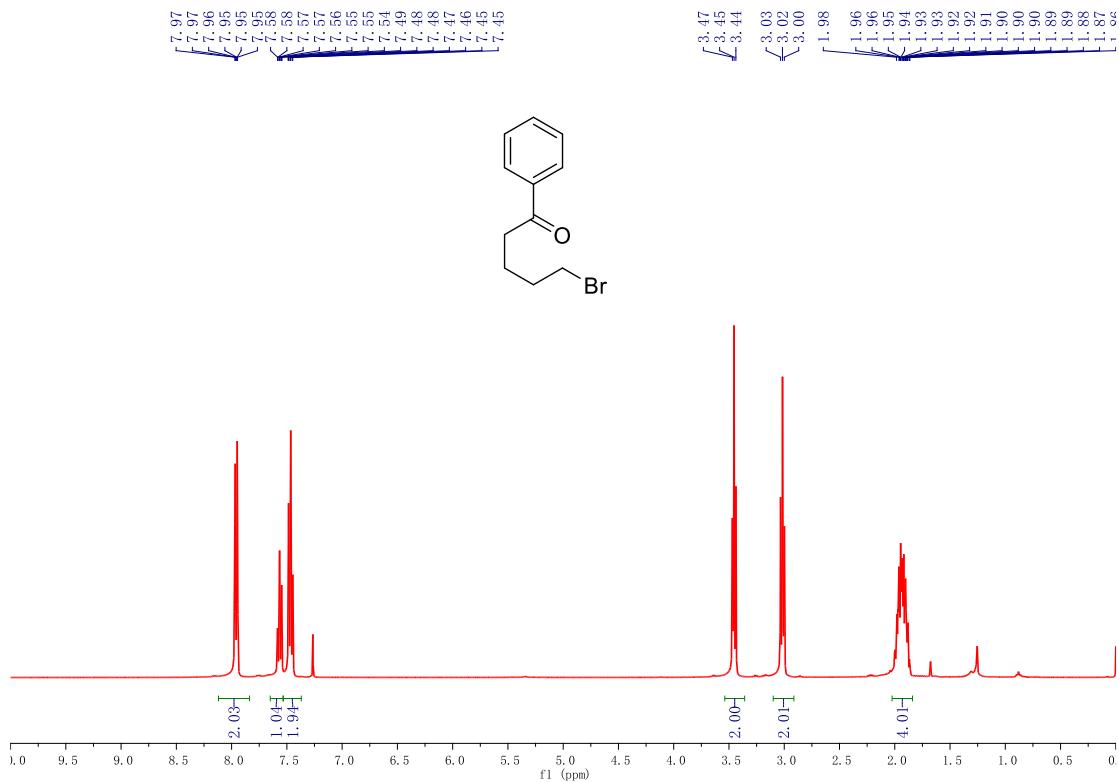
1-(3-Fluoro-5-methoxyphenyl)-6-iodohexan-1-one **31**



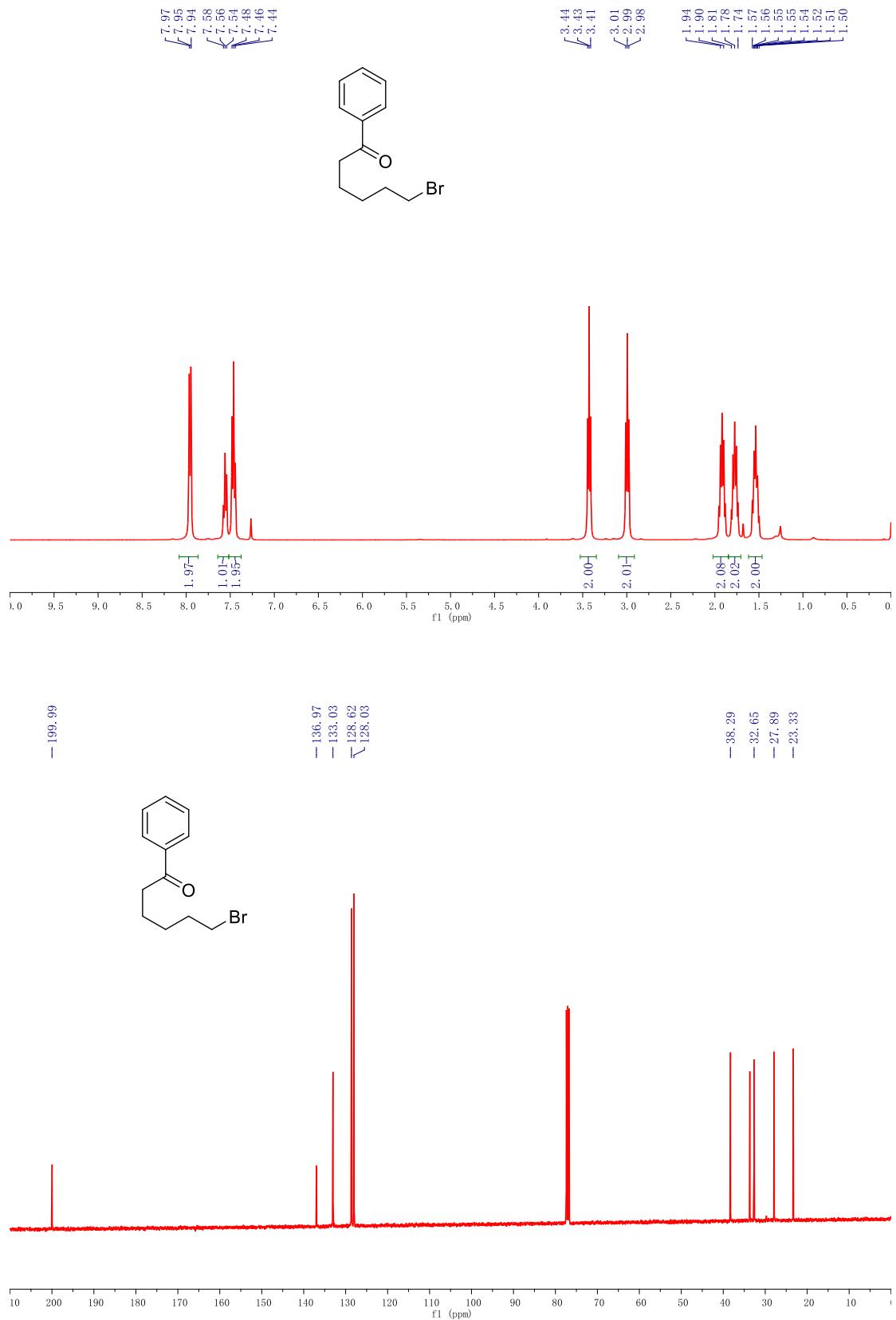
1-(3,5-Dimethylphenyl)-6-iodohexan-1-one **32**



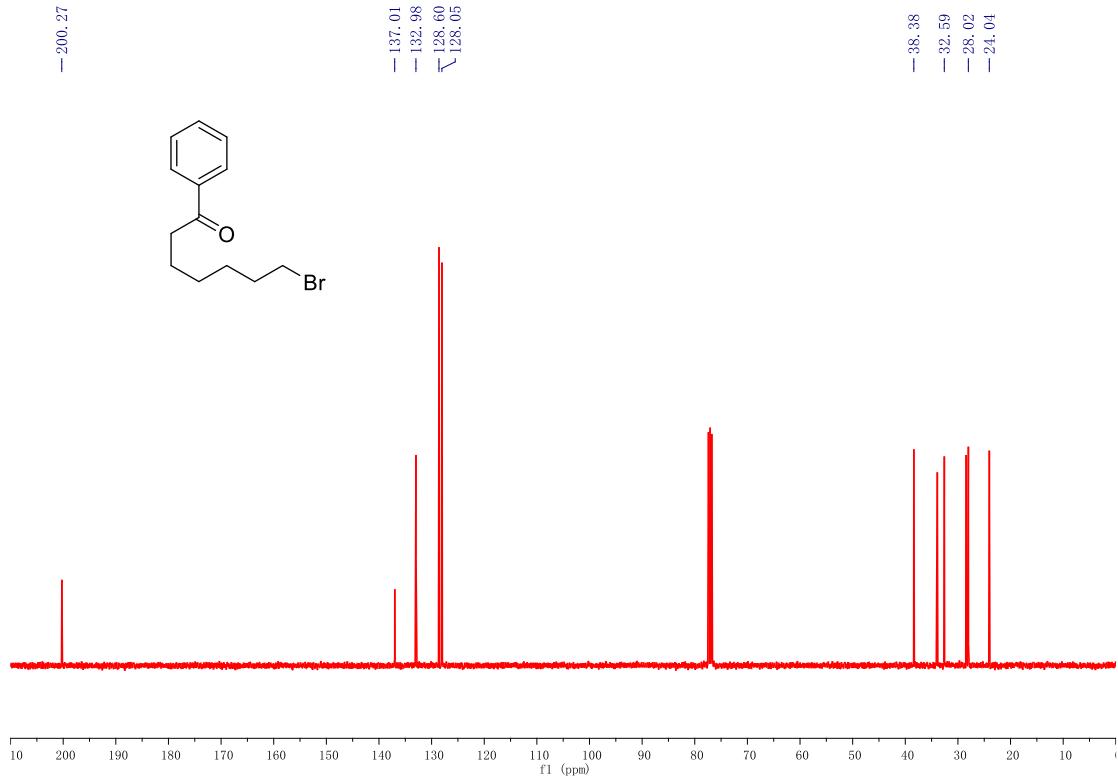
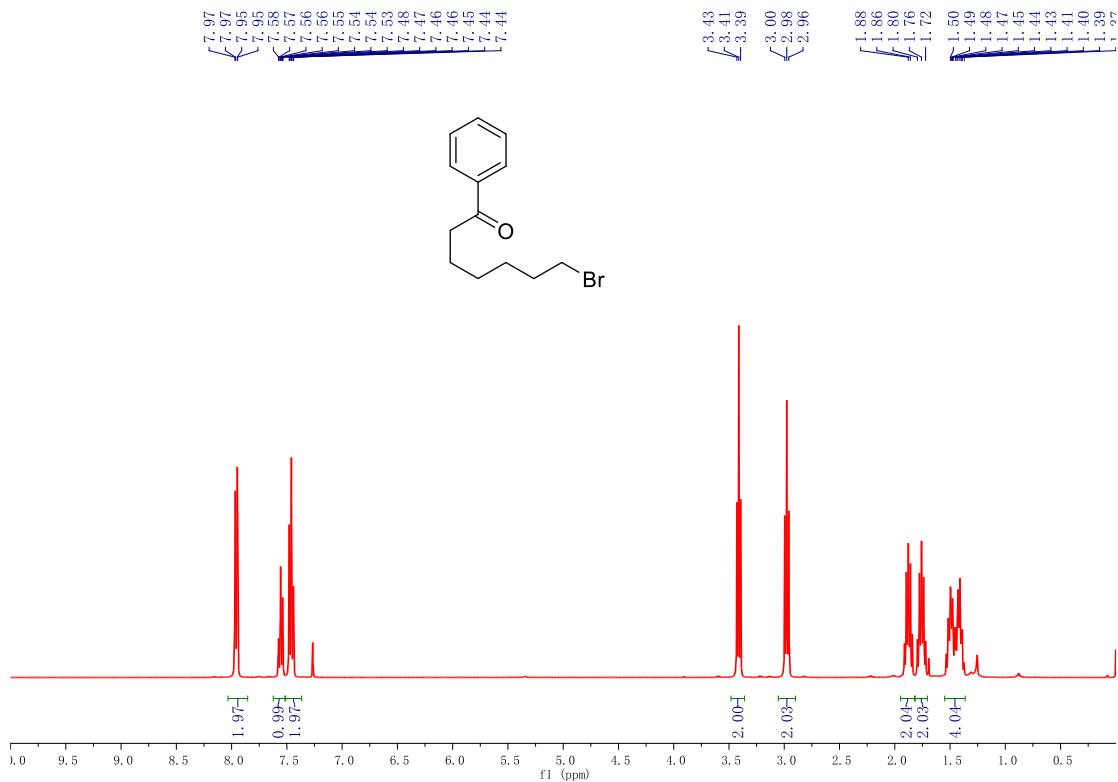
5-Bromo-1-phenylpentan-1-one 33



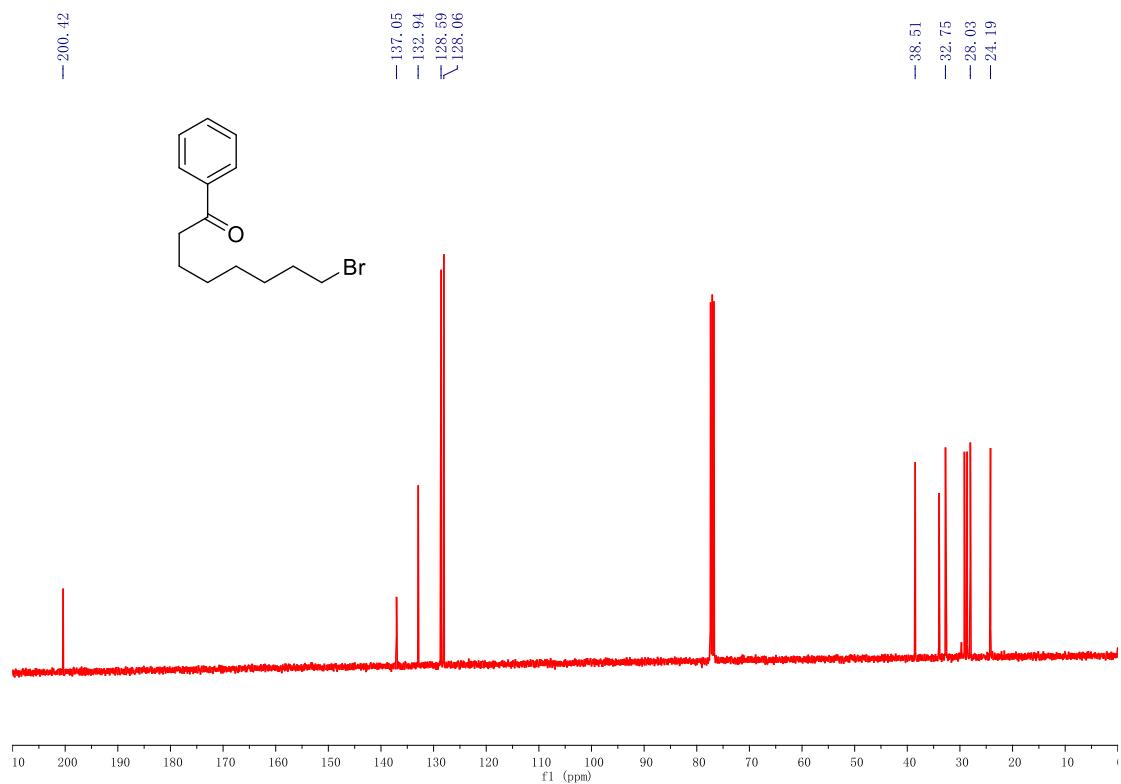
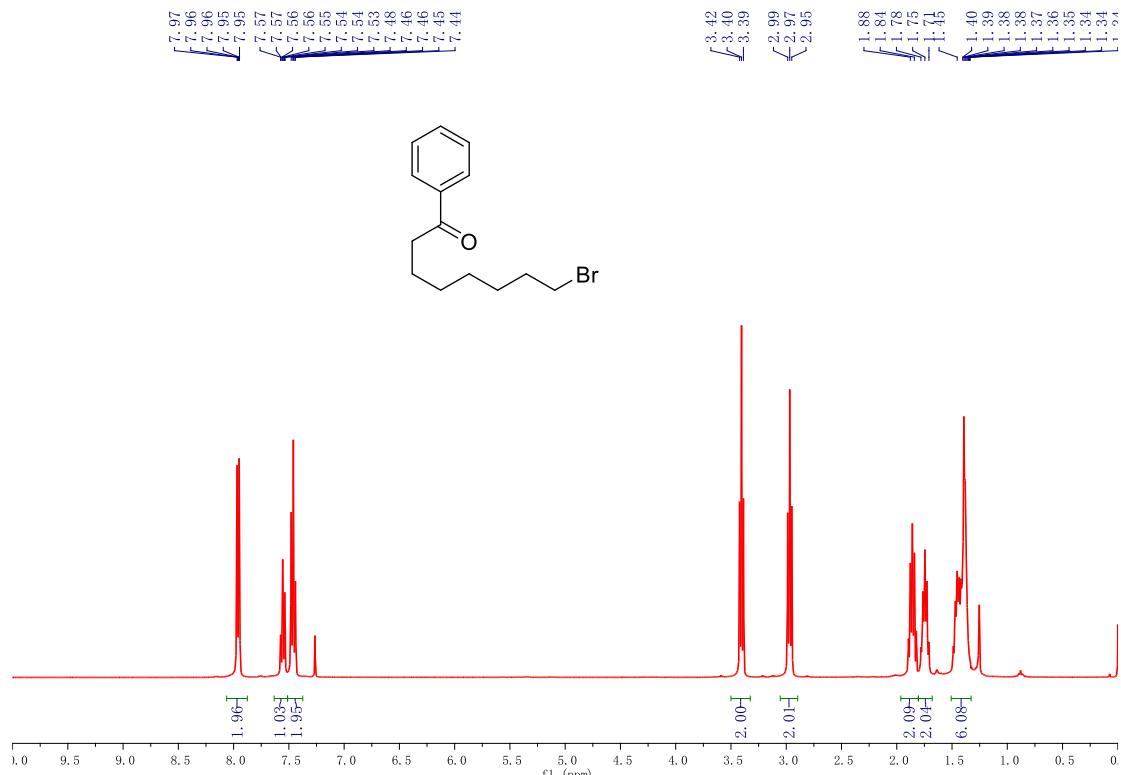
6-Bromo-1-phenylhexan-1-one **34**



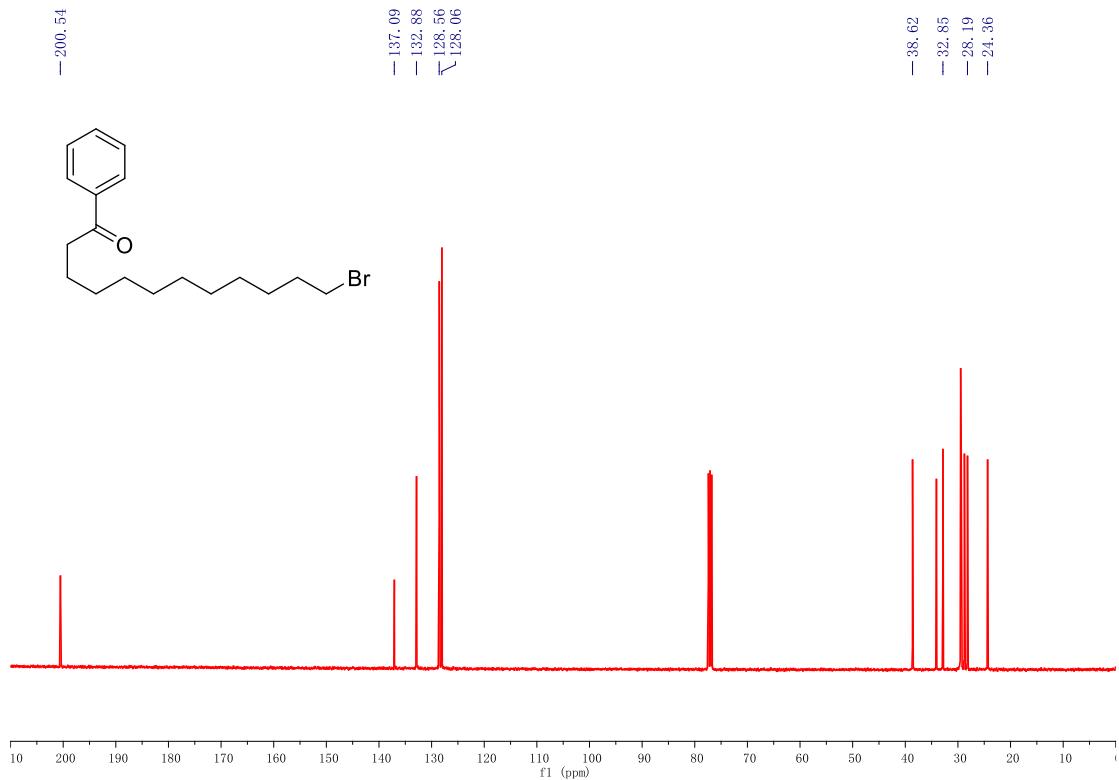
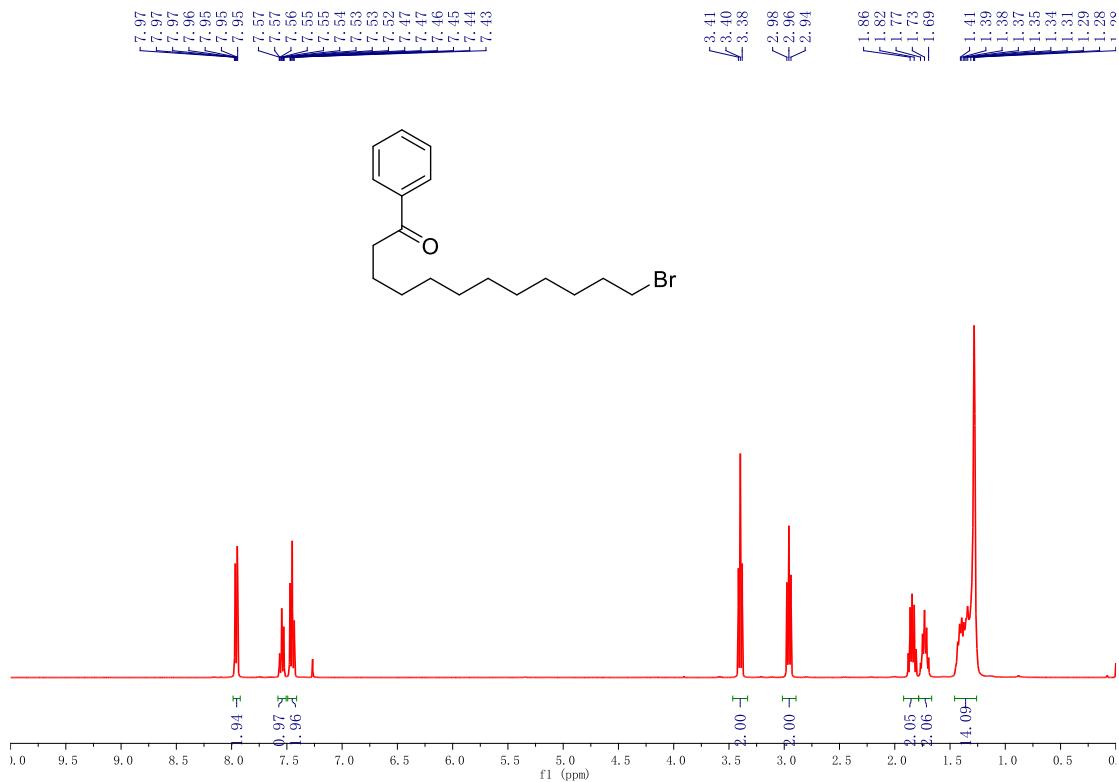
7-Bromo-1-phenylheptan-1-one **35**



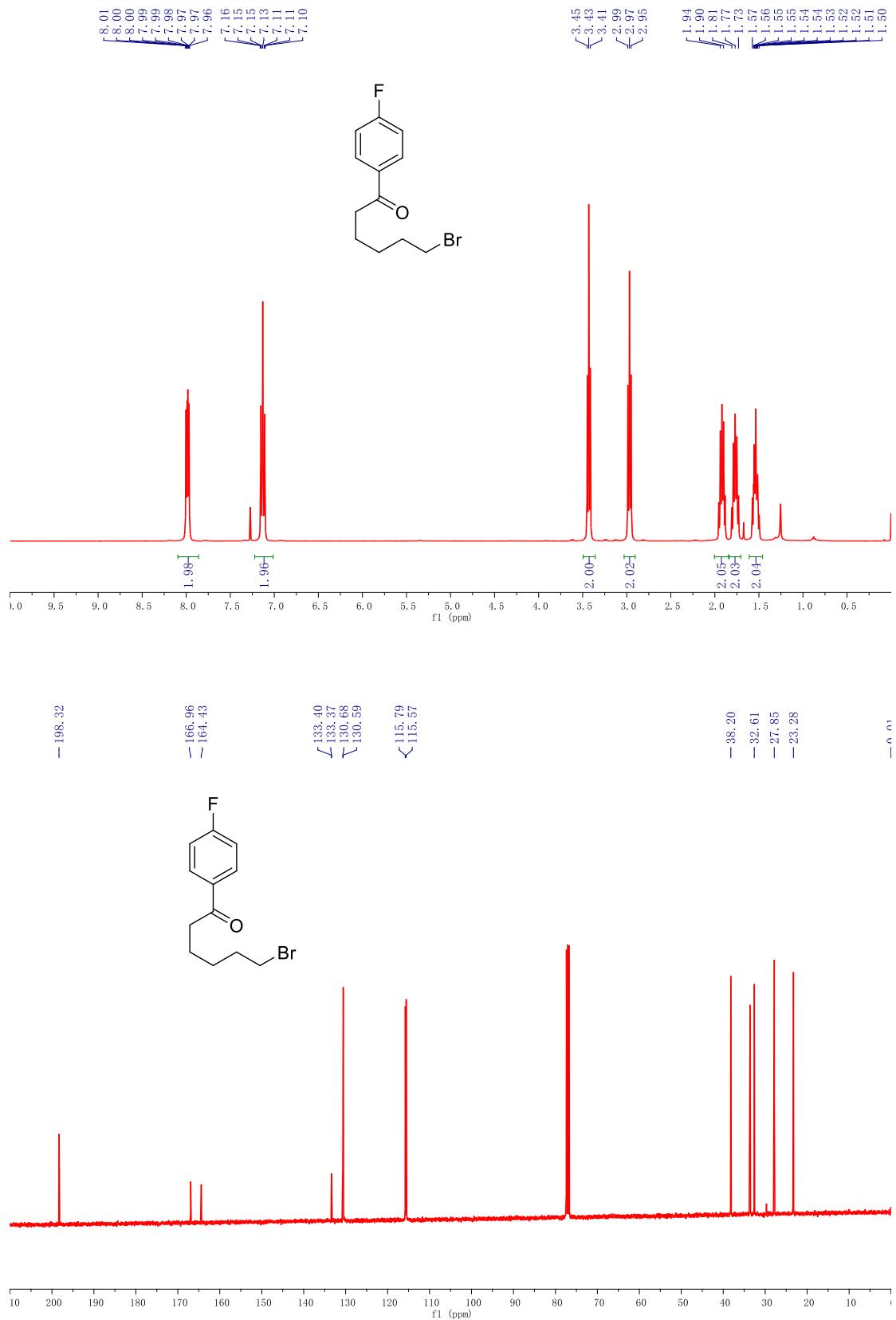
8-Bromo-1-phenyloctan-1-one **36**



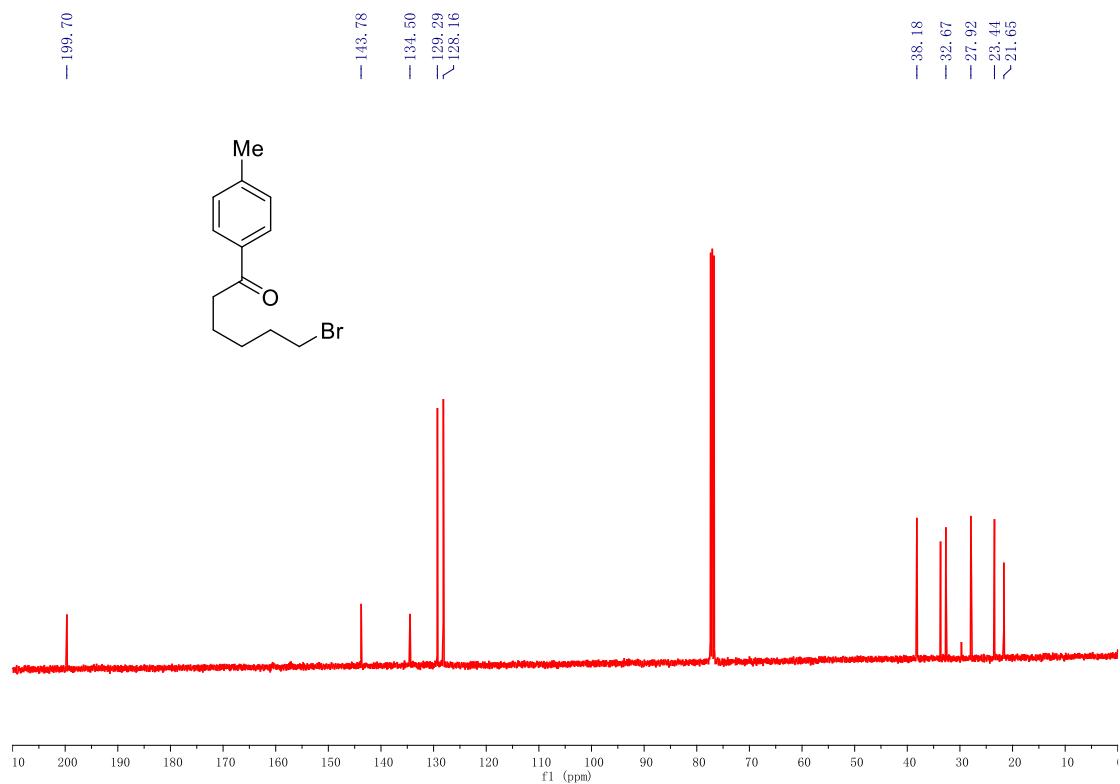
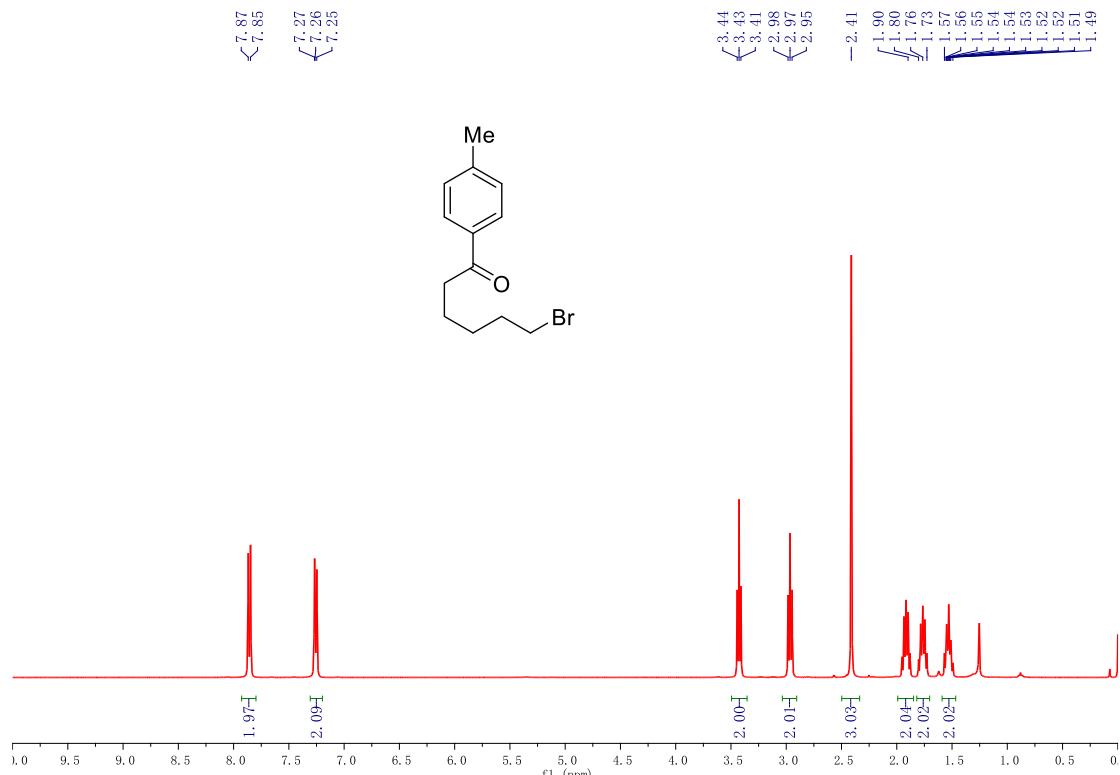
12-Bromo-1-phenyldodecan-1-one **37**



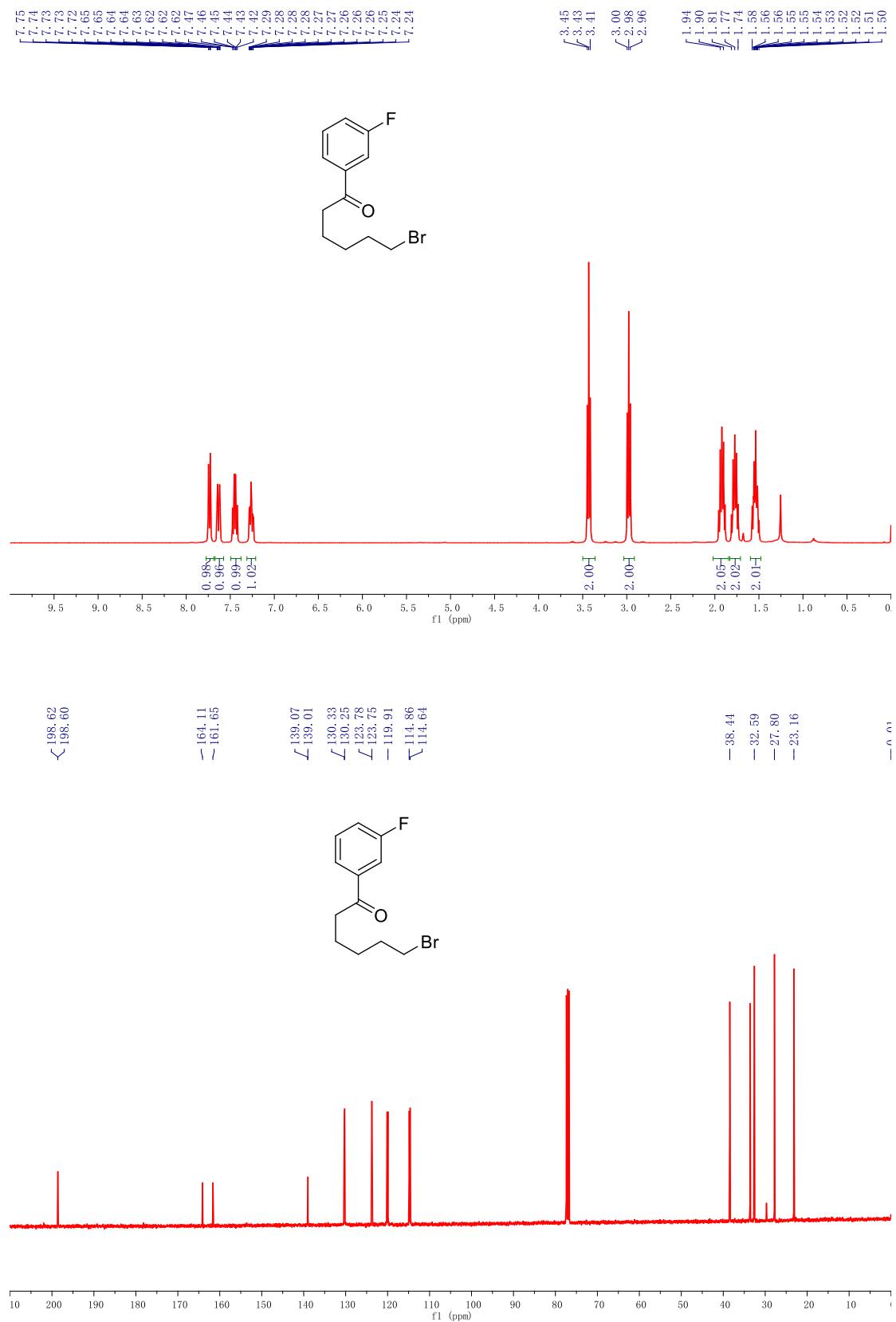
6-Bromo-1-(4-fluorophenyl)hexan-1-one **38**



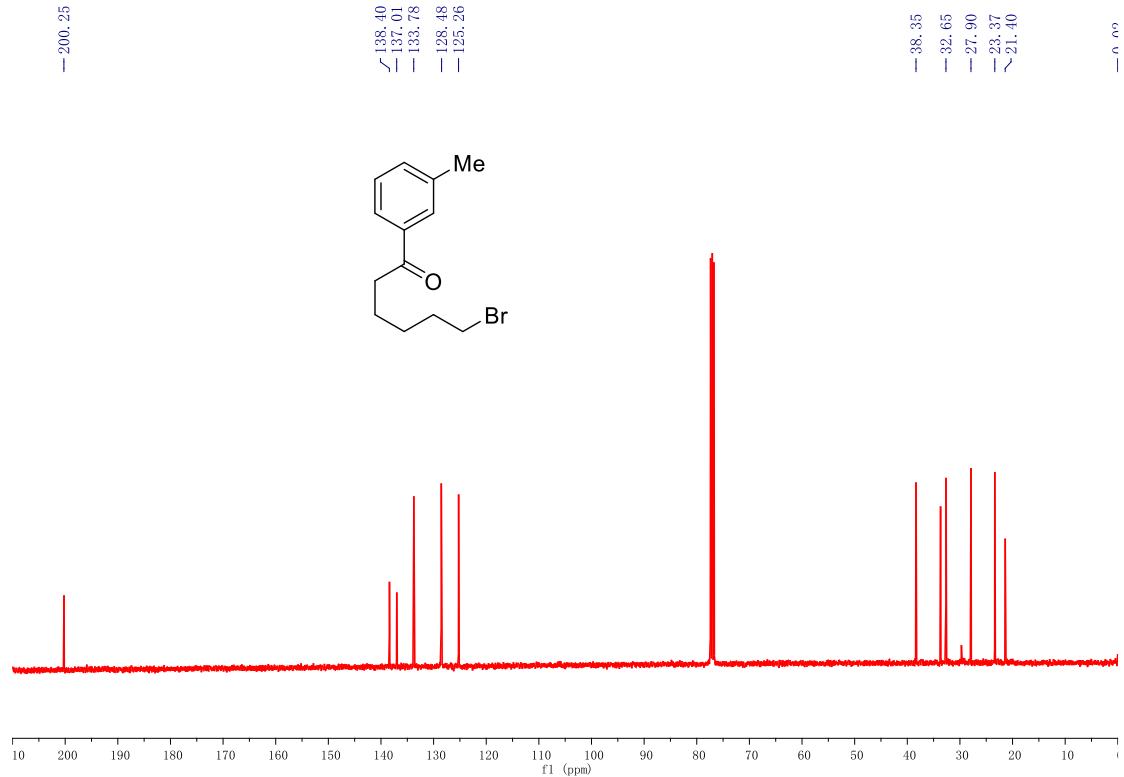
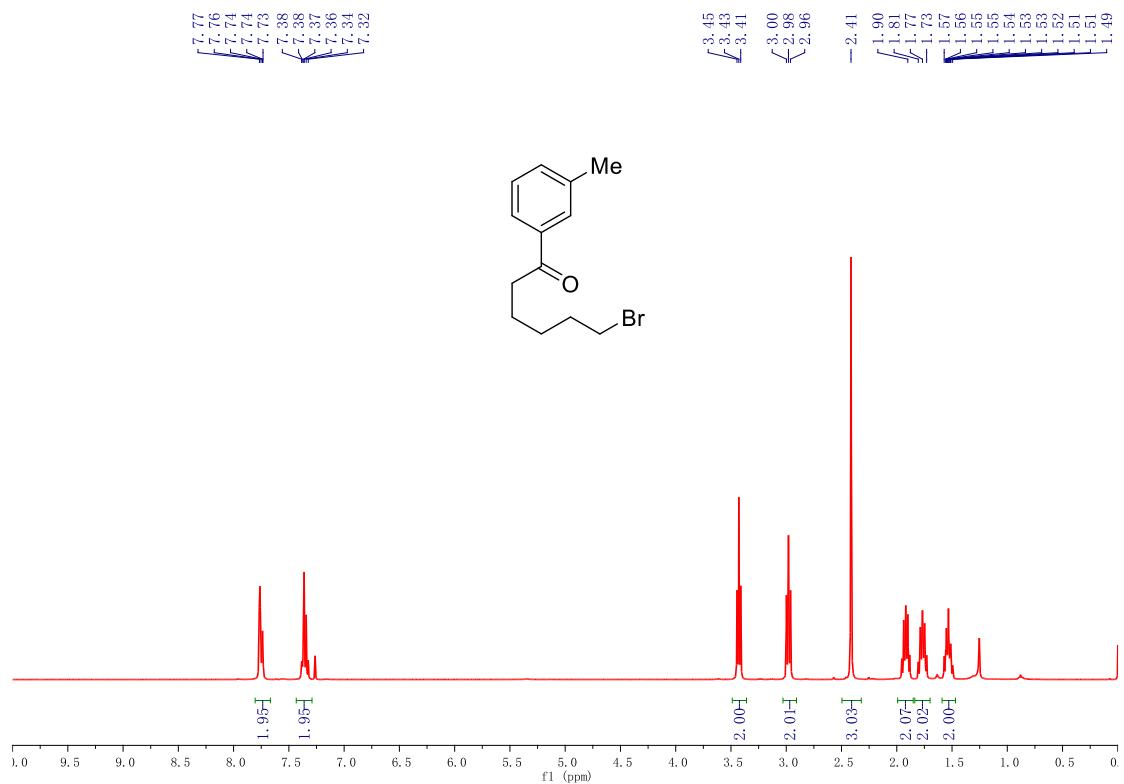
6-Bromo-1-(*p*-tolyl)hexan-1-one **39**



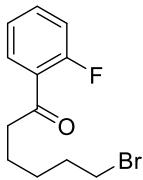
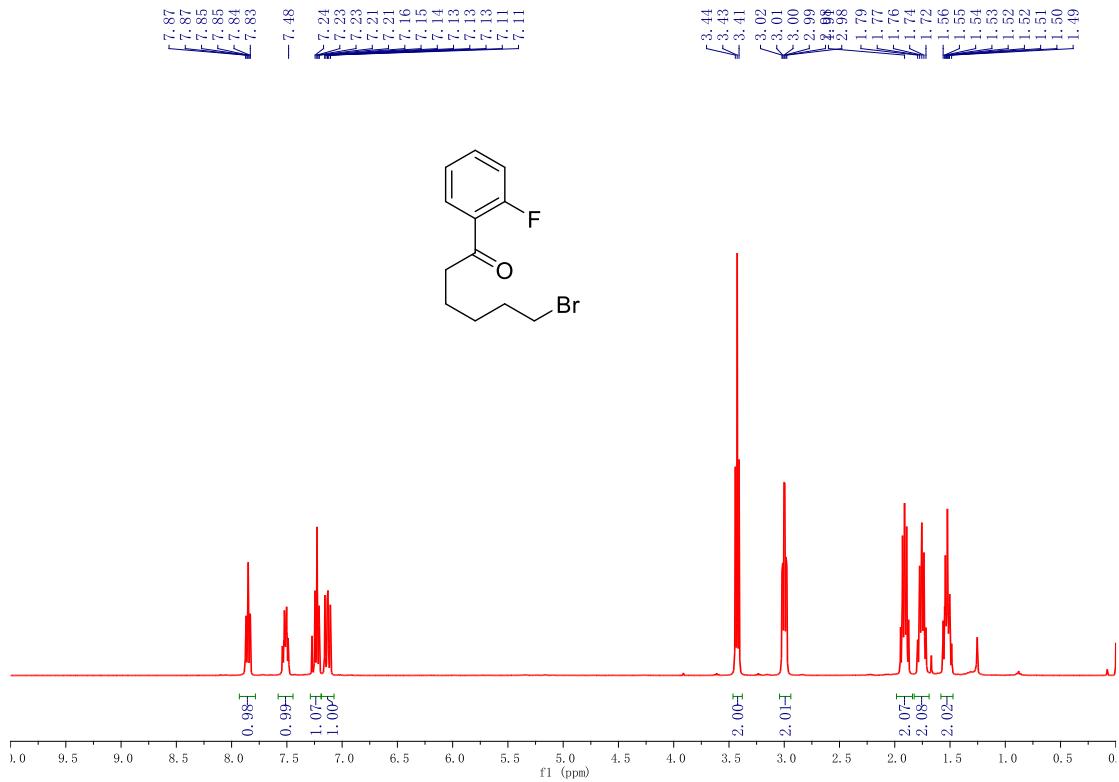
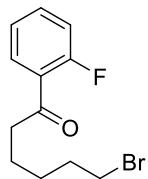
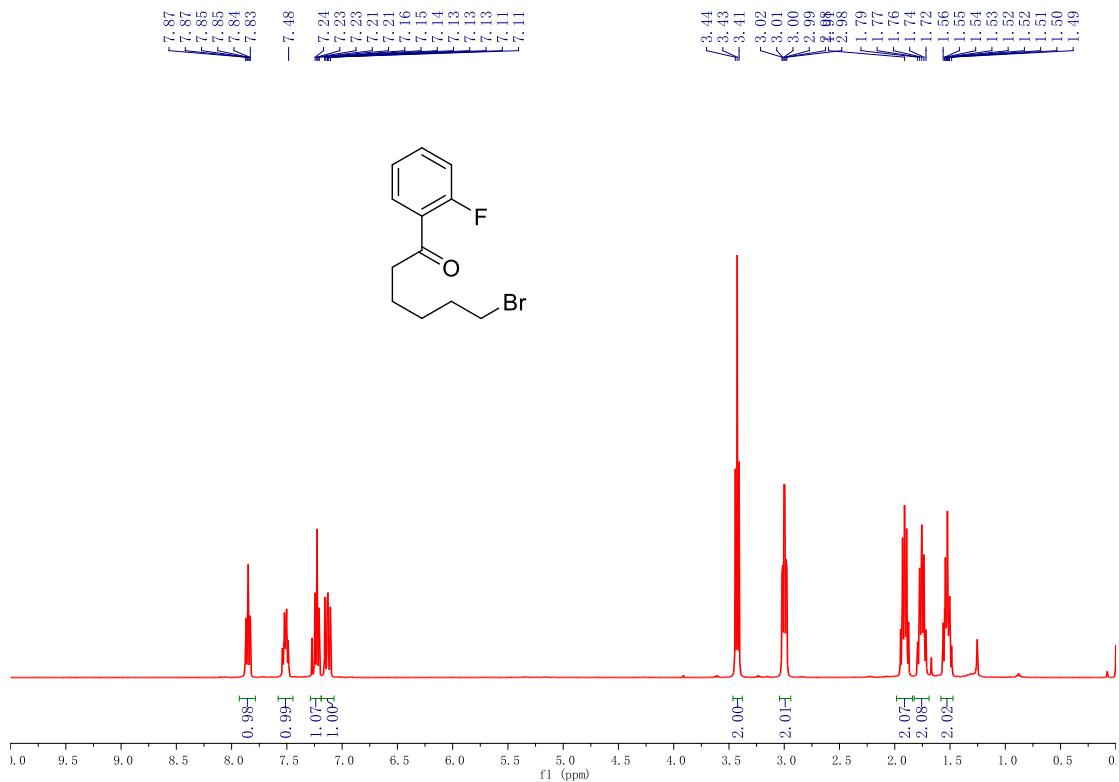
6-Bromo-1-(3-fluorophenyl)hexan-1-one **40**



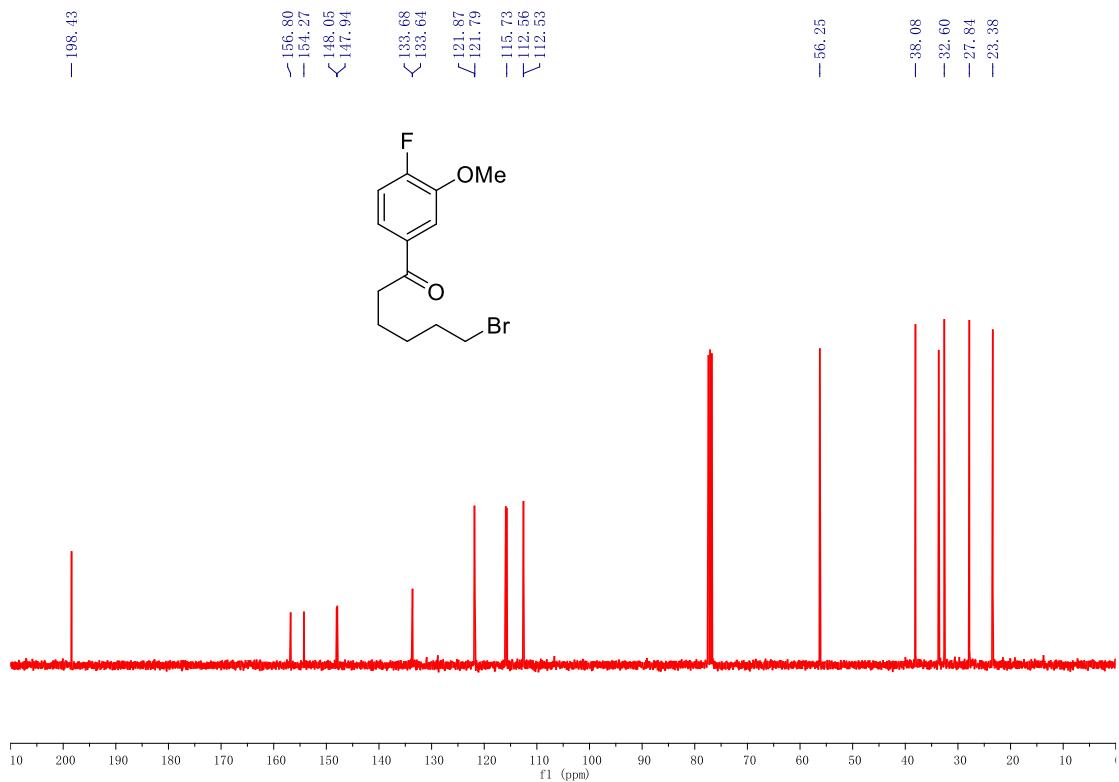
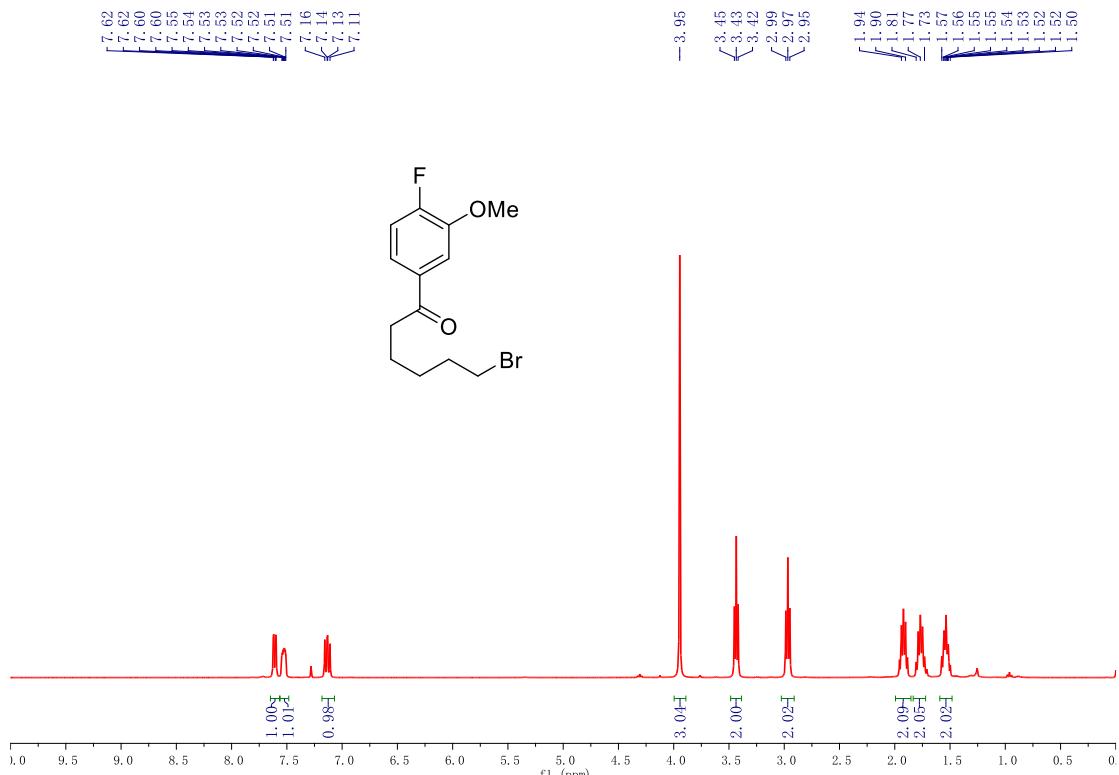
6-Bromo-1-(m-tolyl)hexan-1-one **41**



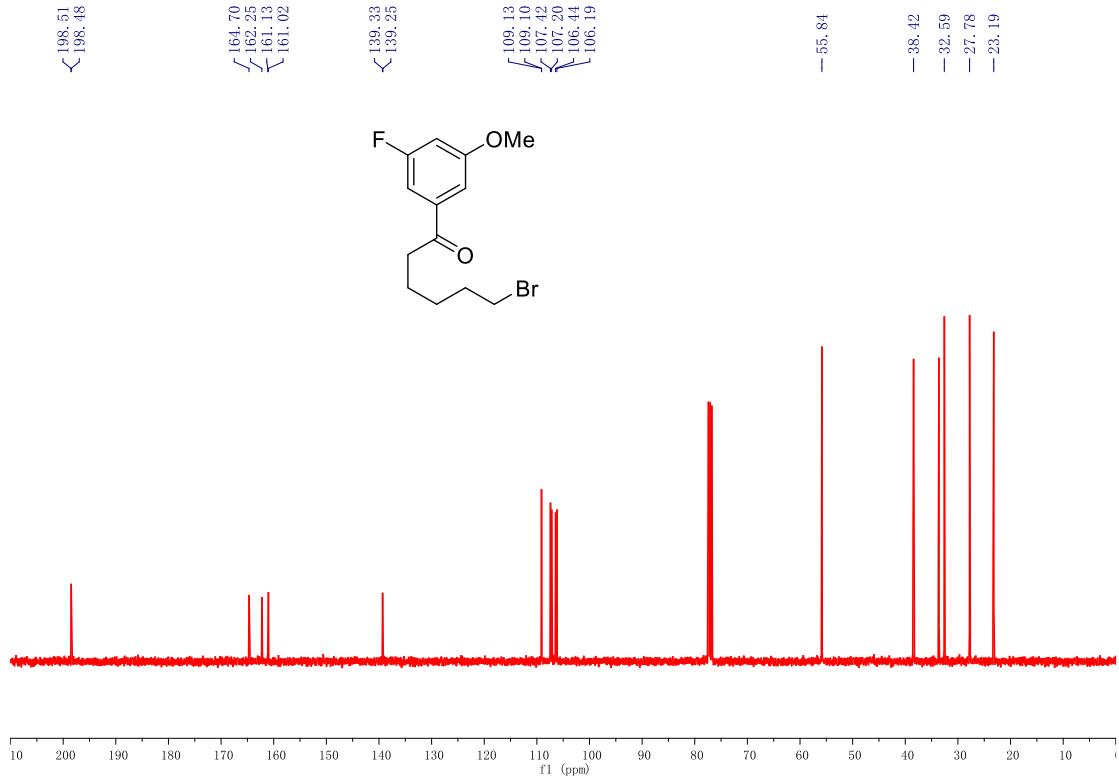
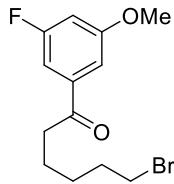
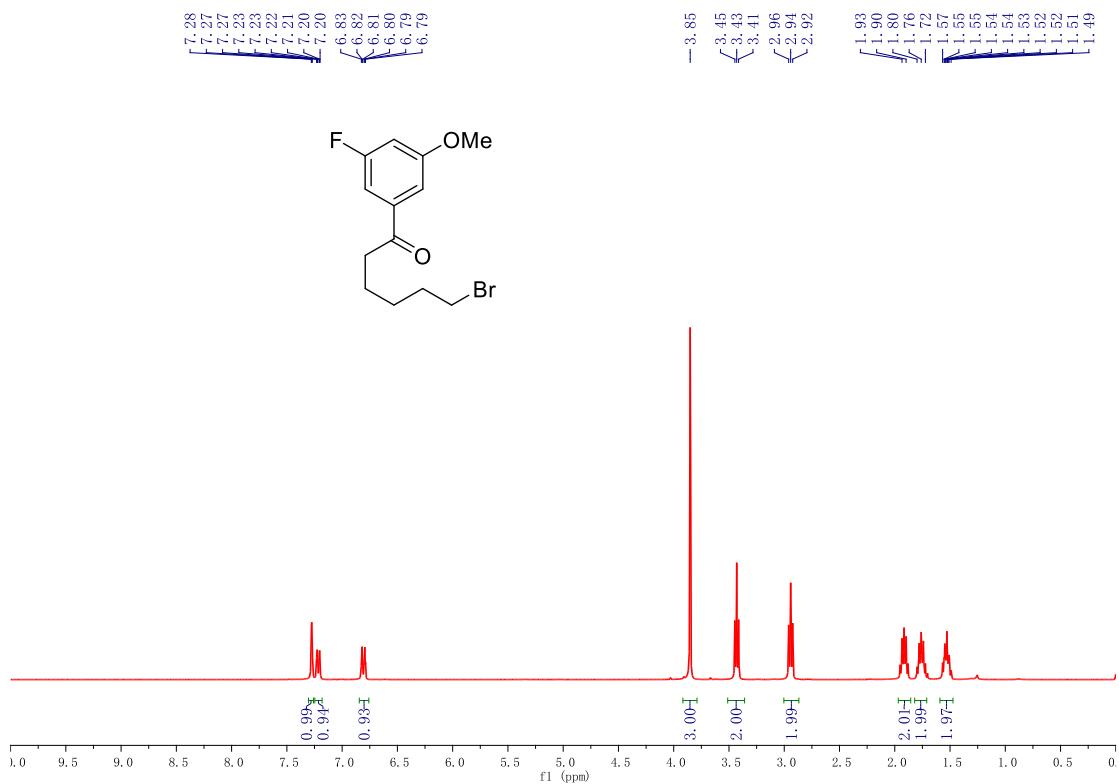
6-Bromo-1-(2-fluorophenyl)hexan-1-one **42**



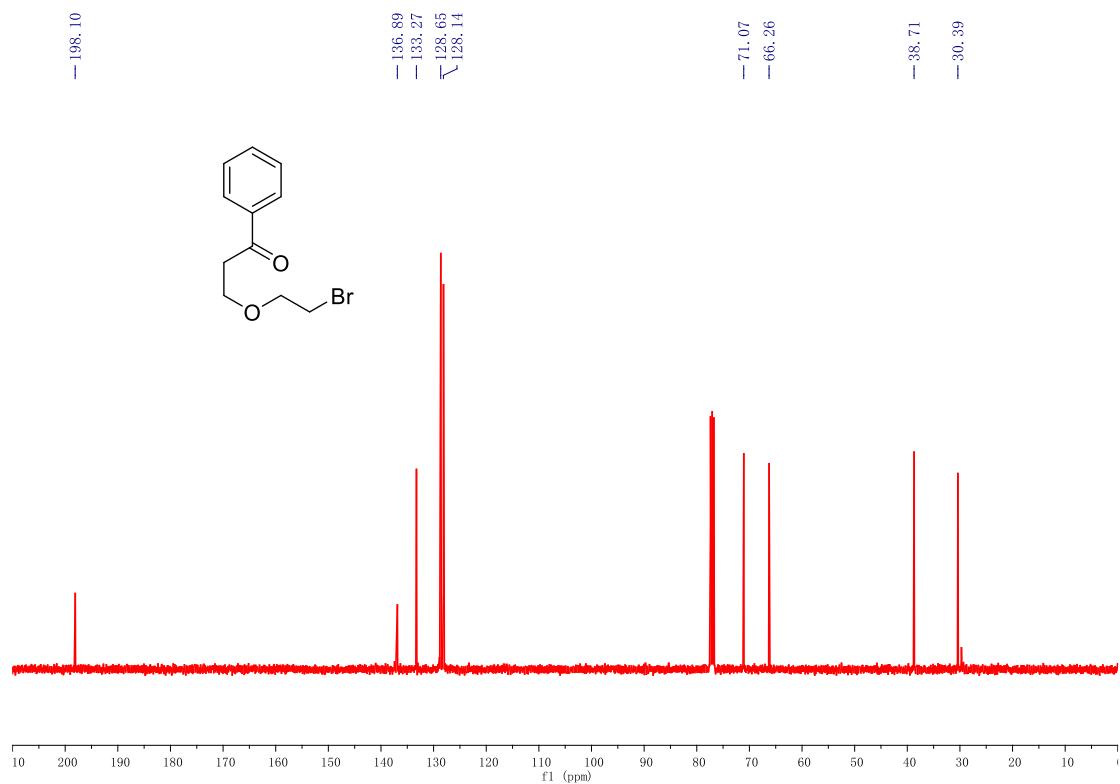
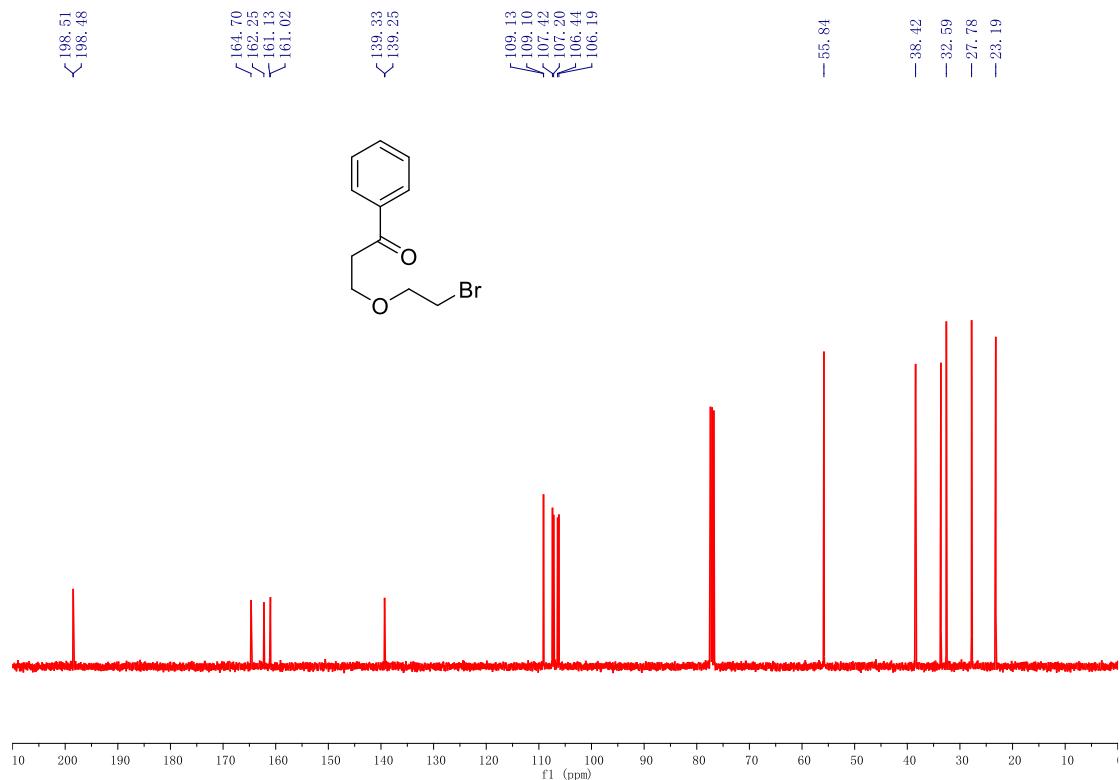
6-Bromo-1-(4-fluoro-3-methoxyphenyl)hexan-1-one **44**



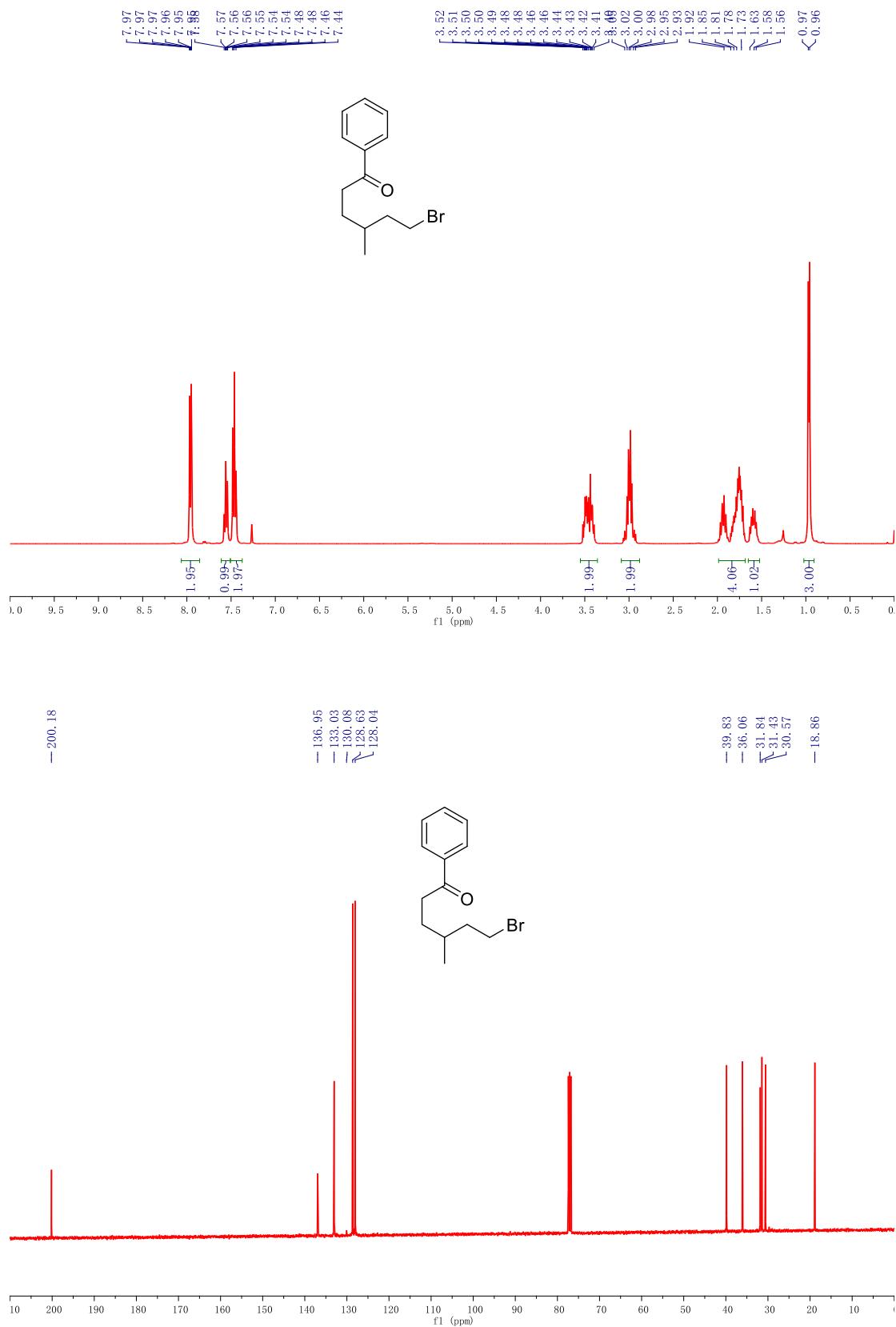
6-Bromo-1-(3-fluoro-5-methoxyphenyl)hexan-1-one **45**



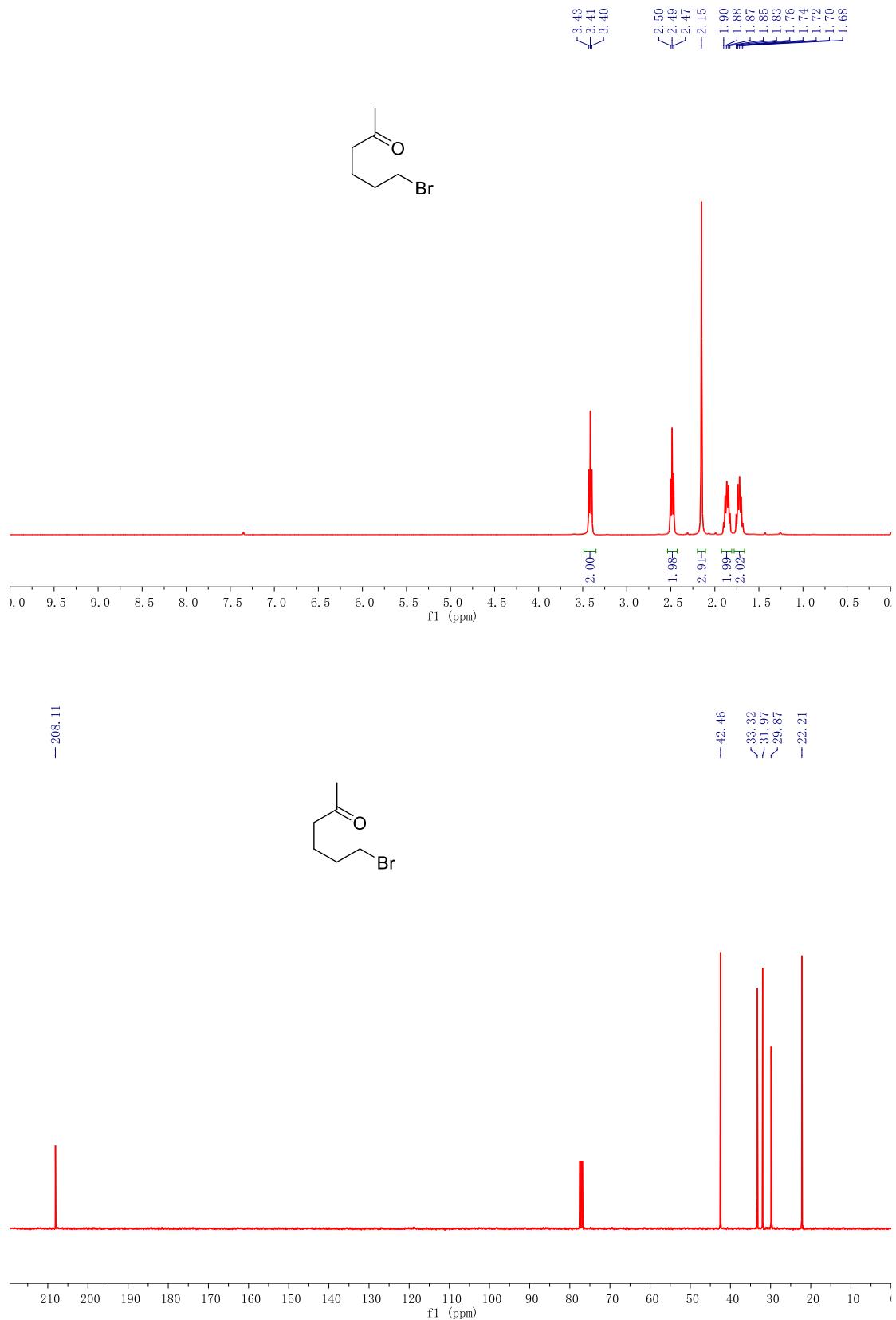
3-(2-Bromoethoxy)-1-phenylpropan-1-one **46**



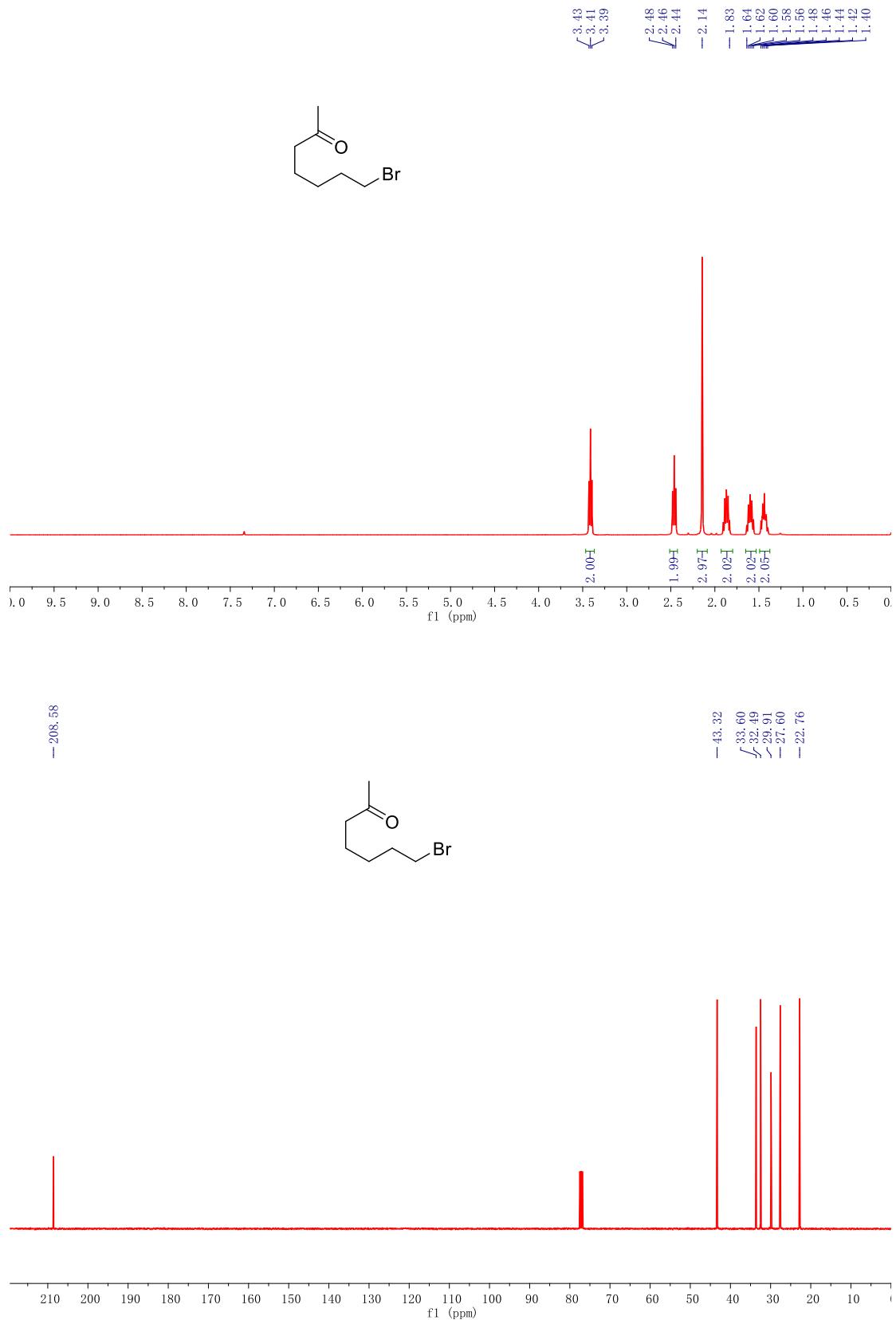
6-Bromo-4-methyl-1-phenylhexan-1-one **47**



6-Bromohexan-2-one **48**



7-Bromoheptan-2-one **49**



5. References

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