Supporting Information for

A simple and highly diastereoselective approach for the vicinal dichlorination of functional olefins

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1.Experimental section

General Information. All reactions were carried out in tubes under argon. All the β,γ-unsaturated α-ketoesters were prepared according to literature.[1] All the other reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on silica gel 300−400 mesh. The ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz spectrometer with $CDCl_3$ as the solvent using tetramethylsilane (TMS) as the internal standard. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruker solariX FT-ICR mass spectrometer. GC-MS was measured on an Agilent 7890A/5975C spectrometer.

General Procedure for the Synthesis of 2a-p, 4a-h. Esters or ketones (0.2 mmol), SO_2Cl_2 (0.21 mmol), Ph_3PO (5 mol %) and $CHCl_3$ (1.0 mL) were added to a thick-walled pressure tube. The mixture was stirred at room temperature for 1h. Then the reaction was quenched with water and extracted with dichloromethane for three times. The organic layers were then combined, washed with brine, dried (anhydrous Na_2SO_4), and concentrated under vacuum. The residue was purified by flash chromatography (EtOAc/ petroleum ether = 1:20) on silica gel to give the desired product.

2. Crystallography

Suitable crystal of **2o**, **2p** and **4j** were collected on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293 K during data collection. Using Olex2,[2] the structure was solved with the Superflip[3] structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation.

Crystallographic data and structure refinements for (Trans)-methyl 3,4-dichloro-4-(3,4-dichlorophenyl)-2-oxobutanoate (**2o**), $C_{11}H_8Cl_4O_3$, M_r = 329.99 g mol^{-1}, colorless block, triclinic, space group $P\bar{1}$, a = 6.5579(7), b = 7.6349(6), c = 15.6331(14) Å, α = 84.549(7), β = 86.322(8), γ = 78.859(8) °, V = 763.67(12) Å^3; Z = 2; ρ = 1.435 g cm^{-3}; λ(Mo-K$_\alpha$) = 0.71073 Å; 4489 reflections measured, 2890 unique (R_{int} = 0.0710), 155 refined parameters; GOOF = 1.065; final R_1 = 0.3172, wR_2 = 0.7473 (all data). CCDC: 1417743.

(Trans)-methyl 3,4-dichloro-4-(naphthalen-2-yl)-2-oxobutanoate (**2p**), $C_{15}H_{12}Cl_2O_3$, M_r = 311.15 g mol^{-1}, colorless block, orthorhombic, space group *P*bca, a = 7.1786(3), b = 20.0394(12), c = 20.1954(8) Å, V = 2905.2(2) Å^3; Z = 8; ρ = 1.423 g cm^{-3}; λ(Cu-K$_\alpha$) = 1.5418 Å; 5886 reflections measured, 2295 unique (R_{int} = 0.1576), 183 refined parameters; GOOF = 1.083; final R_1 = 0.1305, wR_2 = 0.3637 (all data). CCDC: 1417744.

5α,6β-Dichlorocholestan-3β-yl acetate (**4j**), $C_{29}H_{48}Cl_2O_2$, *M*r = 499.57 g mol^{-1}, colorless block, monoclinic, space group $P2_1$, a = 10.2490(6), b = 7.6979(4), c = 19.7126(11) Å, α = 90, β = 95.778(6), γ = 90 °, V = 1547.35(15) Å^3; Z = 2; ρ = 1.072 g cm^{-3}; λ (Cu-Kα) = 1.54184 Å; 5564 reflections measured, 3527 unique (R_{int} = 0.0214), 304 refined parameters; GOOF = 1.046; final R_1 = 0.0654, wR$_2$ = 0.1649 (all data). CCDC: 1495828.

Note: Although the authors tried to grow the single crystals of **2o**/**2p** with good crystallinity for many times, the weakness of diffraction is responsible for the elevated agreement values (*R* values) found for its structure. However, the atomic positions of **2o**/**2p** are well resolved in the crystal structure analysis.

3.The NMR datum of products.

(Trans)-methyl 3,4-dichloro-2-oxo-4-phenylbutanoate (**2a**)**:** Colorless oil (50 mg, 96%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41-7.48 (m, 5H), 5.39 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.4, 159.6, 136.2, 129.6, 128.9, 128.1, 59.3, 58.1, 53.8. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1689 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_{10}Cl_2NaO_3$ ([M+Na]$^+$): 282.9899, Found 282.9905.

(Trans)-ethyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2b) : Colorless oil (52 mg, 95%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41-7.47 (m, 5H), 5.39 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 4.43 (q, J =7.2 Hz, 2H), 1.41-1.45 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.8, 159.2, 136.2, 129.6, 128.9, 128.2, 63.6, 59.4, 58.1, 13.9. IR (thin film) $\upsilon_{(C=O)}$: 1734, 1691 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{12}H_{12}Cl_2NaO_3$ ([M+Na]$^+$): 297.0056, Found 297.0060.

(Trans)-isopropyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2c): Colorless oil (53 mg, 91%, dr=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41-7.47 (m, 5H), 5.37 (d, J = 10.0 Hz, 1H), 5.35 (d, J = 8.0 Hz, 1H), 5.21-5.31 (m, 1H), 1.41 (s, 3H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 184.1, 158.8, 136.3, 131.4, 129.6, 128.8, 128.1, 72.1, 59.5, 58.2, 21.5. IR (thin film) $\upsilon_{(C=O)}$: 1729, 1692 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{13}H_{14}Cl_2NaO_3$ ([M+Na]$^+$): 311.0212, Found 311.0215.

(Trans)-sec-butyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2d): Colorless oil (56 mg, 93%, dr=11:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41-7.45 (m, 5H), 5.36 (d, J = 10.8 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 4.15-4.16 (m, 2H), 2.08-2.14 (m, 1H), 1.02 (s, 3H), 1.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.7, 159.3, 136.3, 129.6, 129.5, 128.8, 128.1, 73.2, 59.4, 58.3, 27.6,19.2, 18.9. IR (thin film) $\upsilon_{(C=O)}$: 1734, 1694 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{14}H_{16}Cl_2NaO_3$ ([M+Na]$^+$): 325.0369, Found 325.0375.

(Trans)-butyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2e): Colorless oil (56 mg, 92%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.39-7.48 (s, 5H), 5.37 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 4.37 (t, J = 6.8 Hz, 2H), 1.73-1.78 (m, 2H) , 1.40-1.49 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.7, 159.3, 136.3, 131.4, 129.6, 128.9, 128.2, 67.2, 59.5, 58.3, 30.3, 18.9, 13.6. IR (thin film) $\upsilon_{(C=O)}$: 1734, 1691 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{14}H_{16}Cl_2NaO_3$ ([M+Na]$^+$): 325.0369, Found 325.0371.

(Trans)-2-methoxyethyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2f): Colorless oil (55 mg, 90%, dr=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.39-7.49 (m, 5H), 5.37 (d, J = 10.8 Hz, 1H), 5.35 (d, J = 11.2 Hz, 1H), 4.50-4.53 (m, 2H), 3.71-3.74 (m, 2H), 3.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.3, 159.1, 136.2, 131.5, 129.6, 128.8, 128.1, 69.6, 66.1, 59.4, 59.1, 58.3. IR (thin film) $\upsilon_{(C=O)}$: 1737, 1689 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{13}H_{14}Cl_2NaO_4$ ([M+Na]$^+$): 327.0161, Found 327.0167.

(Trans)-benzyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2g): Colorless oil (64 mg, 95%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.24-7.45 (m, 10H), 5.33-5.40 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.5, 159.1, 136.2, 133.9, 131.5, 129.6, 128.9, 128.6, 128.2, 68.9, 59.5, 58.4. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1690 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{17}H_{14}Cl_2NaO_3$ ([M+Na]$^+$): 359.0212, Found 359.0212.

(Trans)-methyl 3,4-dichloro-2-oxo-4-(p-tolyl)butanoate (2h): Colorless oil (53 mg, 94%, dr=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.35 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.38 (d, J = 10.8 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H), 3.98 (s, 3H) , 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.5, 159.6, 139.7, 133.2, 129.6, 128.0, 59.4, 58.1, 53.8, 21.3. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1688 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{12}H_{12}Cl_2NaO_3$ ([M+Na]$^+$): 297.0056, Found 297.0059.

(Trans)-methyl 3,4-dichloro-4-(4-ethylphenyl)-2-oxobutanoate (2i): Colorless oil (52 mg, 90%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.37 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz,1H), 7.25 (d, J = 7.6 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H),

5.32 (d, J = 11.2 Hz, 1H), 3.98 (s, 3H) , 2.65-2.70 (m, 2H), 1.24-1.28 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.5, 159.6, 145.9, 133.4, 131.8, 128.4, 128.1, 59.4, 58.1, 53.6, 28.6, 15.2. IR (thin film) $\upsilon_{(C=O)}$: 1739, 1687 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{13}H_{14}Cl_2NaO_3$ ([M+Na]$^+$): 311.0212, Found 311.0217.

(Trans)-methyl 3,4-dichloro-2-oxo-4-(m-tolyl)butanoate (2j): Colorless oil (55 mg, 96%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.26-7.32 (m, 3H), 7.20-7.24 (m, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 10.8Hz, 1H), 3.98 (s, 3H) , 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.4, 159.6, 138.8, 136.1, 130.4, 128.8, 128.7, 59.4, 58.0, 53.8, 21.4. IR (thin film) $\upsilon_{(C=O)}$: 1733, 1689 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{12}H_{12}Cl_2NaO_3$ ([M+Na]$^+$): 297.0056, Found 297.0058.

(Trans)-methyl 3,4-dichloro-4-(4-chlorophenyl)-2-oxobutanoate (2k): Colorless oil (55 mg, 93%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41 (s, 4H), 5.34 (d, J = 10.8 Hz, 1H), 5.31 (d, J = 10.8 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.1, 159.5, 135.6, 134.7, 129.5, 129.1, 58.5, 57.9, 53.9. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1692 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_9Cl_3NaO_3$ ([M+Na]$^+$): 316.9510, Found 316.9513.

(Trans)-methyl 3,4-dichloro-4-(3-chlorophenyl)-2-oxobutanoate (2l): Colorless oil (54 mg, 92%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.46 (s, 1H), 7.35-7.38 (m, 3H),5.34 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 10.8 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.0, 160.3, 137.9, 134.8, 130.1, 129.8, 128.3, 126.4, 58.3, 57.8, 53.8. IR (thin film) $\upsilon_{(C=O)}$: 1739, 1693 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_9Cl_3NaO_3$ ([M+Na]$^+$): 316.9510, Found 316.9517.

(Trans)-methyl 4-(4-bromophenyl)-3,4-dichloro-2-oxobutanoate (2m): Colorless oil (64 mg, 95%, dr=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.56 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.33 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 10.8 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.1, 159.5, 135.2, 132.1, 129.7,

123.8, 58.6, 57.8, 53.9. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1691 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_9BrCl_2NaO_3$ ($[M+Na]^+$): 360.9004, Found 360.9008.

(Trans)-methyl 4-(3-bromophenyl)-3,4-dichloro-2-oxobutanoate (2n): Colorless oil (61 mg, 90%, dr>25:1). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.63 (s, 1H), 7.53-7.55 (m, 1H), 7.39-7.41 (m, 1H), 7.30-7.32 (m, 1H), 5.33 (d, J = 10.8 Hz, 1H), 5.28 (d, J = 11.2 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.2, 159.4, 138.2, 132.7, 131.2, 130.4, 126.9, 122.7, 58.3, 57.8, 53.8. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1693 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_9BrCl_2NaO_3$ ($[M+Na]^+$): 360.9004, Found 360.9005.

(Trans)-methyl 3,4-dichloro-4-(3,4-dichlorophenyl)-2-oxobutanoate (2o): White solid (59 mg, 90%, dr>25:1). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.57-7.58 (m, 1H), 7.49-7.52 (m, 2H), 7.30-7.33 (m, 1H), 5.32 (d, J = 10.8 Hz, 1H), 5.28 (d, J = 10.8 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 183.4, 159.6, 133.3, 133.2, 128.8, 128.4, 127.9, 127.6, 126.9, 126.0, 125.1, 123.5, 58.9, 57.1, 54.6. IR (thin film) $\upsilon_{(C=O)}$: 1733, 1688 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{11}H_8Cl_4NaO_3$ ($[M+Na]^+$): 350.9119, Found 350.9134.

(Trans)-methyl 3,4-dichloro-4-(naphthalen-2-yl)-2-oxobutanoate (2p): White solid (57 mg, 92%, dr>25:1). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.87-7.92 (m, 2H), 7.84-7.86 (m, 2H), 7.51-7.55 (m, 3H), 5.52 (s, 2H), 3.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 182.8, 159.4, 136.3, 133.1, 131.7, 129.9, 128.2, 126.7, 58.4, 56.9, 54.7. IR (thin film) $\upsilon_{(C=O)}$: 1738, 1692 cm^{-1}. HRMS *m/z* (ESI): Calcd for $C_{15}H_{12}Cl_2NaO_3$ ($[M+Na]^+$): 333.0056, Found 333.0055.

(Trans)-methyl 2,3-dichloro-3-phenylpropanoate (4a)[4]: Colorless oil (42 mg, 90%, dr>25:1). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.43-7.35 (m, 5H), 5.31 (d, J = 8.0 Hz, 1H), 4.66 (d, J =8.0 Hz, 1H), 3.62(s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.1, 136.6, 129.5, 128.8, 127.7, 63.5, 62.5, 53.2. HRMS: m/z (ESI), calcd for $C_{10}H_{10}Cl_2O_2Na$ $[M+Na]^+$ 254.9950, found 254.9959.

(Trans)-ethyl 2,3-dichloro-3-phenylpropanoate (4b)[5]: Colorless oil (43 mg, 87%, dr=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.42-7.39 (m, 5H), 5.18 (d, J = 10.4 Hz, 1H), 4.60 (d, J =10.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.5, 136.5, 129.5, 128.8, 128.1, 62.7, 61.1, 59.0, 14.0. GC/MS (m/z): 246.0.

(Trans)-4-nitrophenyl 2,3-dichloro-3-phenylpropanoate (4c): Colorless oil (53 mg, 78%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.20 (d, J = 9.2 Hz, 2H), 7.47-7.38 (m, 7H), 5.37 (d, J = 8.4 Hz, 1H), 4.91 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 164.4, 155.6, 145.3, 139.9, 129.1, 128.5, 125.3, 122.5, 63.4, 62.1. IR (thin film) $\upsilon_{(C=O)}$: 1695 cm^{-1}.HRMS: m/z (%), calcd for $C_{15}H_{11}Cl_2NO_4Na$ $[M+Na]^+$ 361.9957, found 361.9960.

Methyl 2,3-dichloropropanoate (4d) [6]: Colorless oil (1.9 g, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.47-4.44 (m, 1H), 3.99-3.95 (m, 1H), 3.85-3.82 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.6, 54.9, 53.4, 43.9. GC/MS (m/z): 156.0.

Methyl 2,3-dichloro-2-methylpropanoate (4e) [6]: Colorless oil (1.8 g, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.09 (d, J = 11.2 Hz, 1H), 3.84 (s, 3H), 3.76 (d, J = 11.2 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.1, 65.5, 53.5, 50.1, 24.9. GC/MS (m/z): 170.0.

(Trans)-2,3-dichloro-1,3-diphenylpropan-1-one (4f)[7]: White powder (51 mg, 91%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.09 (d, J = 7.2 Hz, 2H), 7.49-7.38 (m, 6H), 7.25-7.16 (m, 2H), 5.52-5.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 191.4, 139.8, 134.3, 130.7, 129.6, 129.0, 128.8, 128.7, 128.4, 63.6, 57.0. GC/MS (m/z): 278.0.

(Trans)-3,4-dichloro-4-phenylbutan-2-one (4g)[8]: White powder (35 mg, 80%, dr=7:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.43-7.39 (m, 5H), 5.15 (d, J = 10.4 Hz, 1H), 4.59 (d, J = 10.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 199.2, 136.6, 129.4, 128.8, 128.1, 63.5, 60.2, 26.9. GC/MS (m/z): 216.0

(Trans)-4,5-dichloro-1,5-diphenylpent-1-en-3-one (4h): White powder (54 mg, 88%, dr=3.3:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.84 (d, J = 16.0 Hz, 1H), 7.62 (d, J = 9.6 Hz, 2H), 7.47-7.40 (m, 8H), 6.99 (d, J = 16.0 Hz, 1H), 5.32 (d, J = 10.4 Hz, 1H), 4.91 (d, J= 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 190.4, 146.3, 136.9, 131.3, 129.3, 129.1, 128.8, 128.8, 128.8, 128.2, 122.0, 62.0, 60.2. IR (thin film) $\upsilon_{(C=O)}$: 1698 cm^{-1}.HRMS: m/z (%), calcd for $C_{17}H_{14}Cl_2ONa$ $[M+Na]^+$ 327.0314, found 327.0314.

(8,9-Dichloro-p-menth-6-en-2-one (4i): Colorless oil (33 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.26-5.32 (m, 1H), 5.10 (d, J = 1.2 Hz, 1H), 4.55 (t, J = 1.2 Hz, 1H), 4.04 (d, J = 0.8 Hz, 1H), 3.62-3.71 (m, 1H), 3.16-3.20 (m, 1H), 3.05 (t, J= 13.6 Hz, 1H), 2.72-2.76 (m, 1H), 2.49-2.51 (m, 1H), 2.14-2.20 (m, 1H), 1.76 (d, J = 1.6 Hz, 3H), 1.61-1.66 (m, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 200.9, 145.9, 115.8, 68.3, 65.9, 46.9, 40.7, 35.2, 34.4, 24.2. IR (thin film) $\upsilon_{(C=O)}$: 1710 cm^{-1}.HRMS: m/z (%), calcd for $C_{17}H_{14}Cl_2ONa$ $[M+Na]^+$ 243.0314, found 243.0310.

5α,6β-Dichlorocholestan-3β-yl acetate (4j): White powder (85 mg, 91%, dr=15:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.29-5.34 (m, 1H), 4.31 (d, J = 2.4 Hz, 1H), 2.52 (dd, J = 2.8 Hz, 10.8 Hz, 1H), 2.07-2.09 (m, 1H), 2.00-2.02 (m, 6H), 1.80-1.85 (m, 3H), 1.48-1.53 (m, 5H), 1.22-1.34 (m, 12H), 2.00-2.02 (m, 6H), 1.08-1.12, 0.82-0.88 (m, 9H), 0.67(s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.3, 84.4, 70.7, 63.6, 56.1, 55.2, 45.8, 42.7, 40.7, 39.5, 35.7, 34.2, 30.2, 28.1, 27.9, 24.0, 23.8, 22.8, 22.5, 21.3, 21.1, 19.5, 18.6, 12.1. IR (thin film) $\upsilon_{(C=O)}$: 1721 cm^{-1}.HRMS: m/z (%), calcd for $C_{27}H_{44}Cl_2O_2Na$ $[M+Na]^+$ 493.2611, found 493.2609.

Ethyl 4,5-dichlorohex-2-enoate(6): Cololess oil (904 mg, 86%, dr>25:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.87 (dd, J = 8.0, 15.6 Hz, 1H), 6.06 (dd, J = 0.8, 15.6 Hz, 1H), 4.45.07-4.48 (m, 1H), 4.16-4.22 (m, 2H), 4.11-4.14 (m, 1H), 1.60 (d, J = 6.4 Hz, 3H), 1.17 (t, 3 J =7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.28, 142.02, 125.30, 63.67, 60.87, 58.75, 21.88, 14.15. IR (thin film) $\upsilon_{(C=O)}$: 1723 cm^{-1}.HRMS m/z (%), calcd for $C_8H_{12}Cl_2O_2Na$ $[M+Na]^+$, 233.0107; found, 233.0105.

3,4-dichloro-4-phenylbutane-1,2-diol (7): White powder (912 mg, 78%, dr=20:1). ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.45 (d, J = 5.6 Hz, 1H), 7.30-7.33 (m, 3H), 5.61 (d, J = 4.2 Hz, 1H), 3.46-3.49 (m, 5H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 137.4, 129.1, 128.9, 128.5, 72.1, 67.4, 62.6, 62.1. HRMS: m/z (%), calcd for $C_{10}H_{12}Cl_2O_2Na$ $[M+Na]^+$ 257.0107, found 257.0106.

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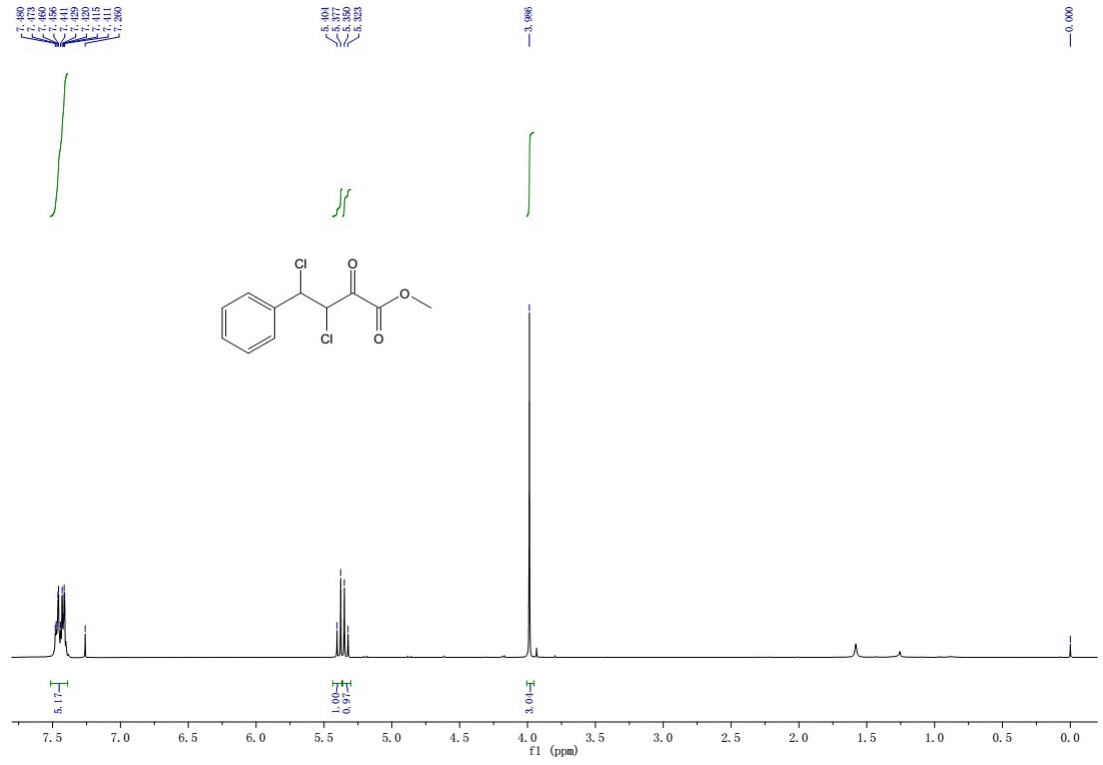
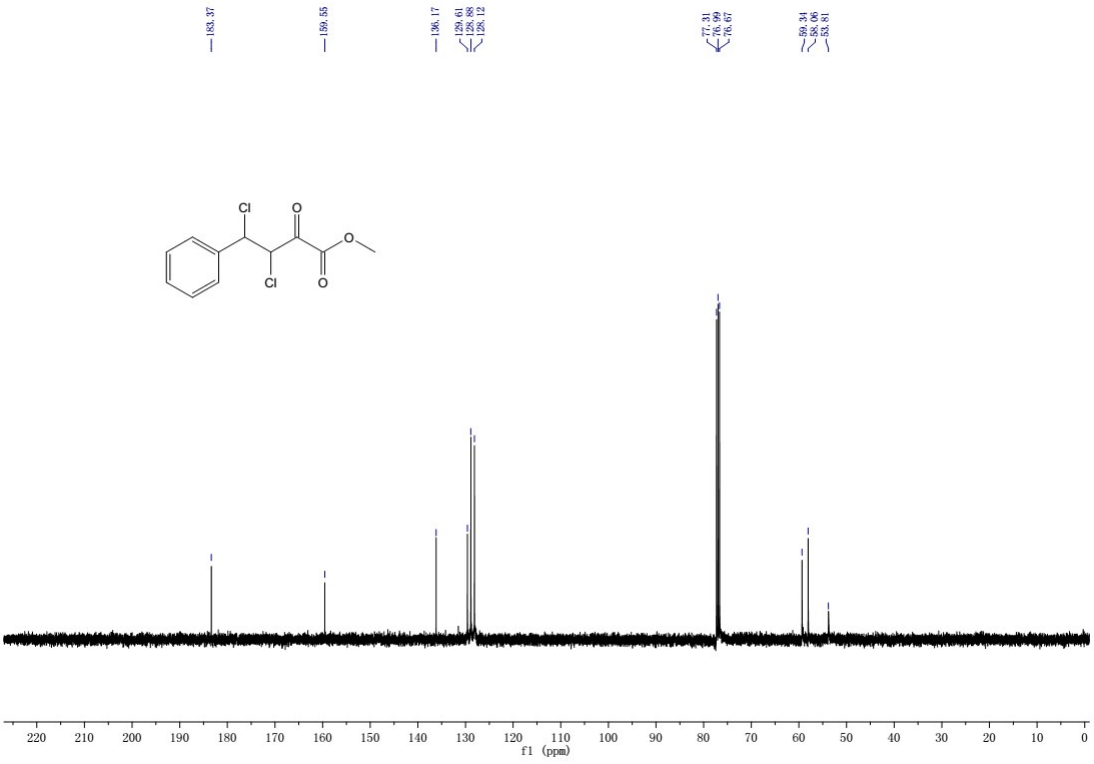
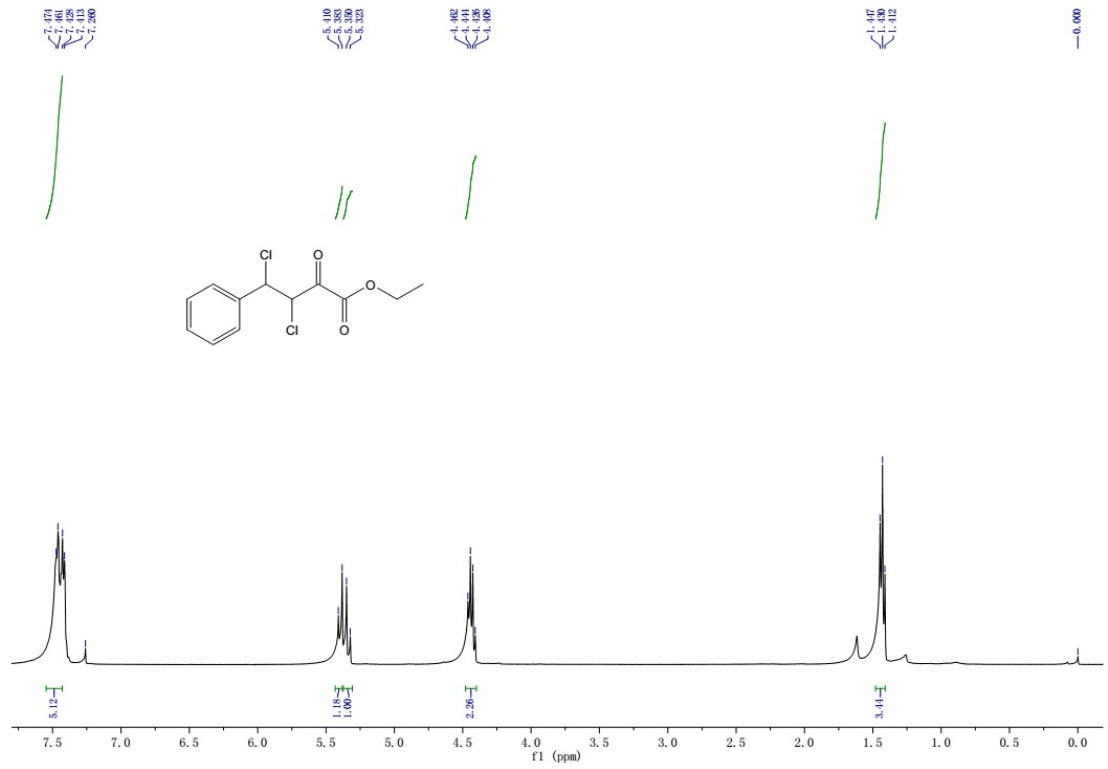
4. ^{1}H (up) and ^{13}C (bottom) NMR Spectra of 2a-p, 4a-h

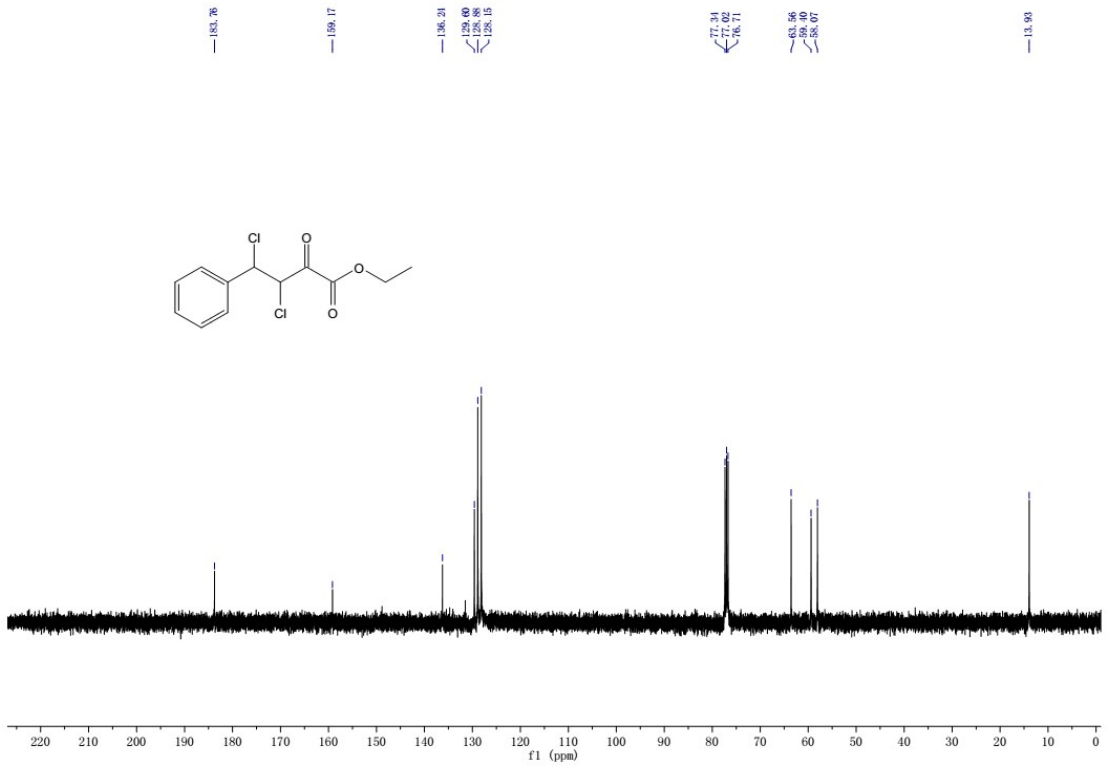
(trans)-methyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2a):



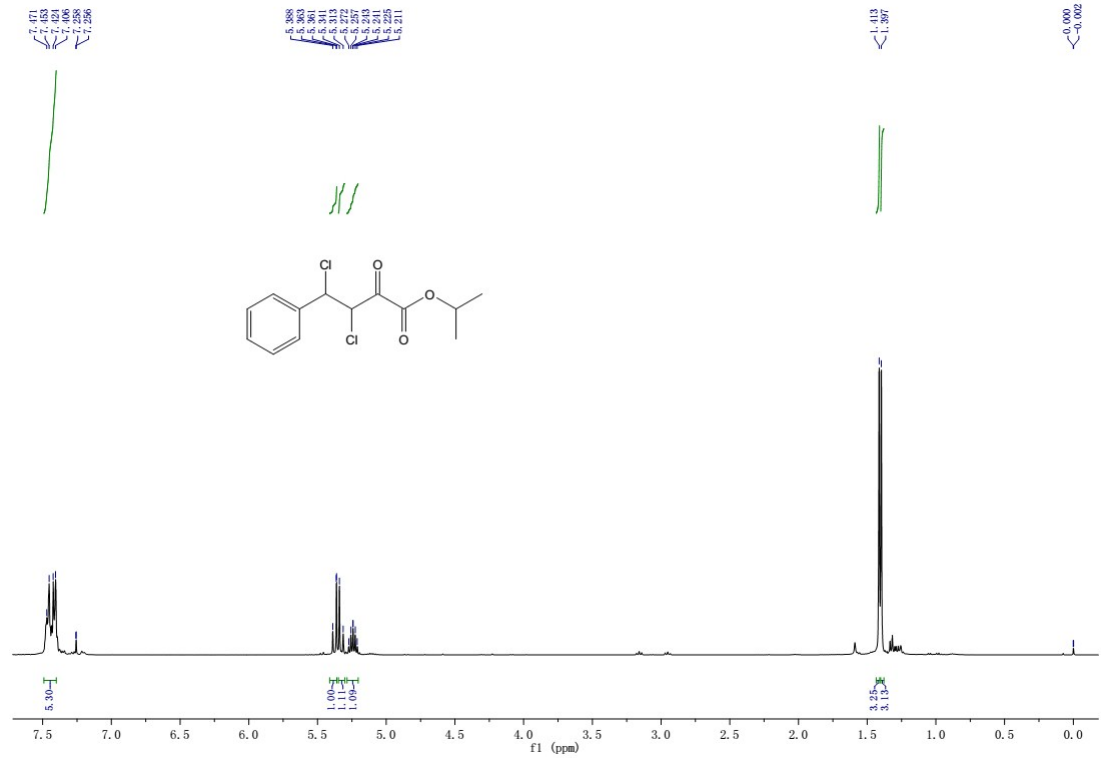


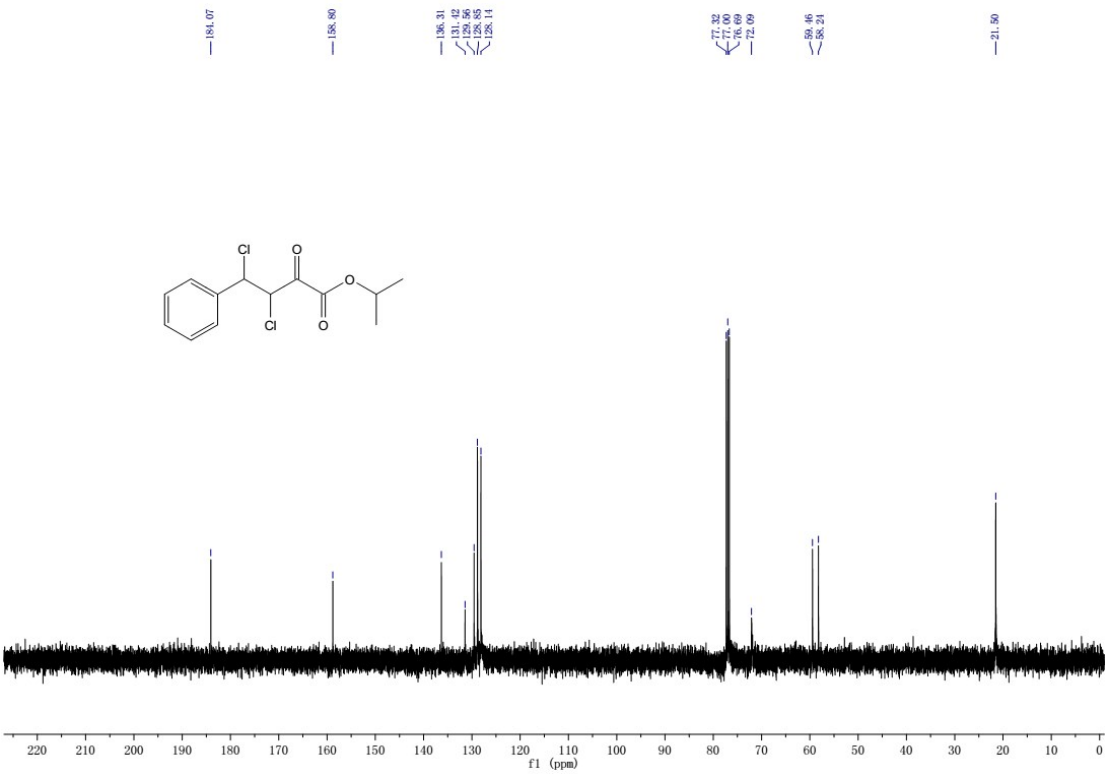
(trans)-ethyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2b):



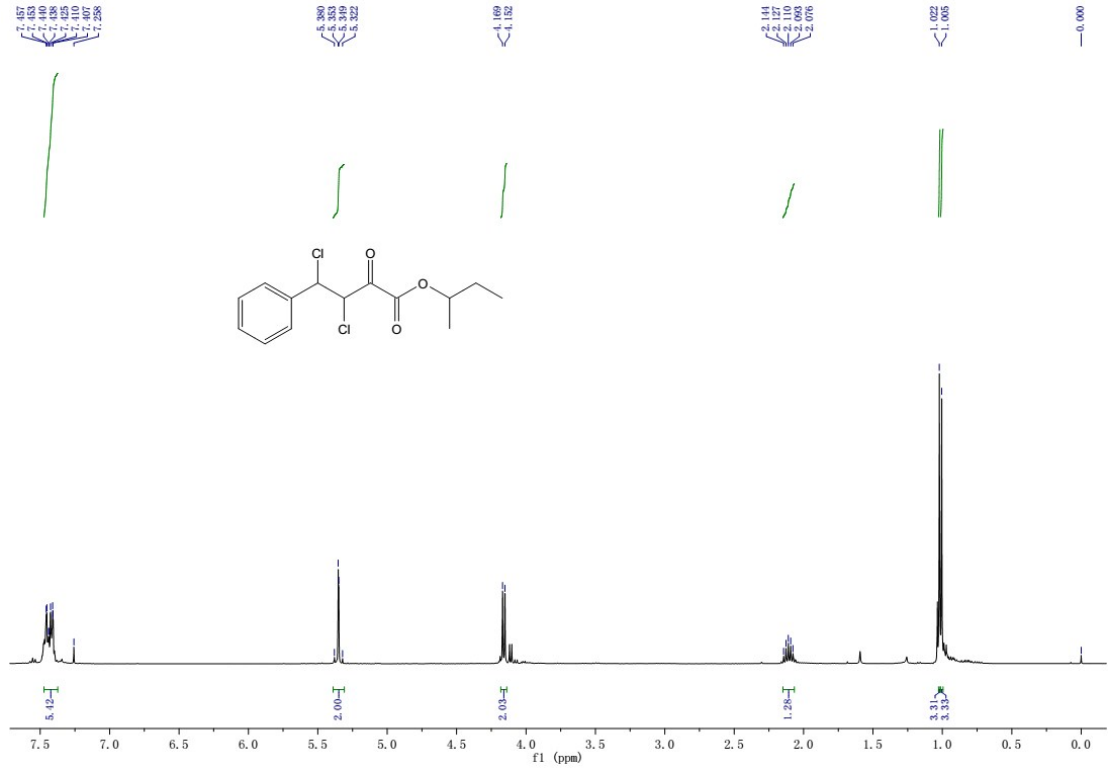


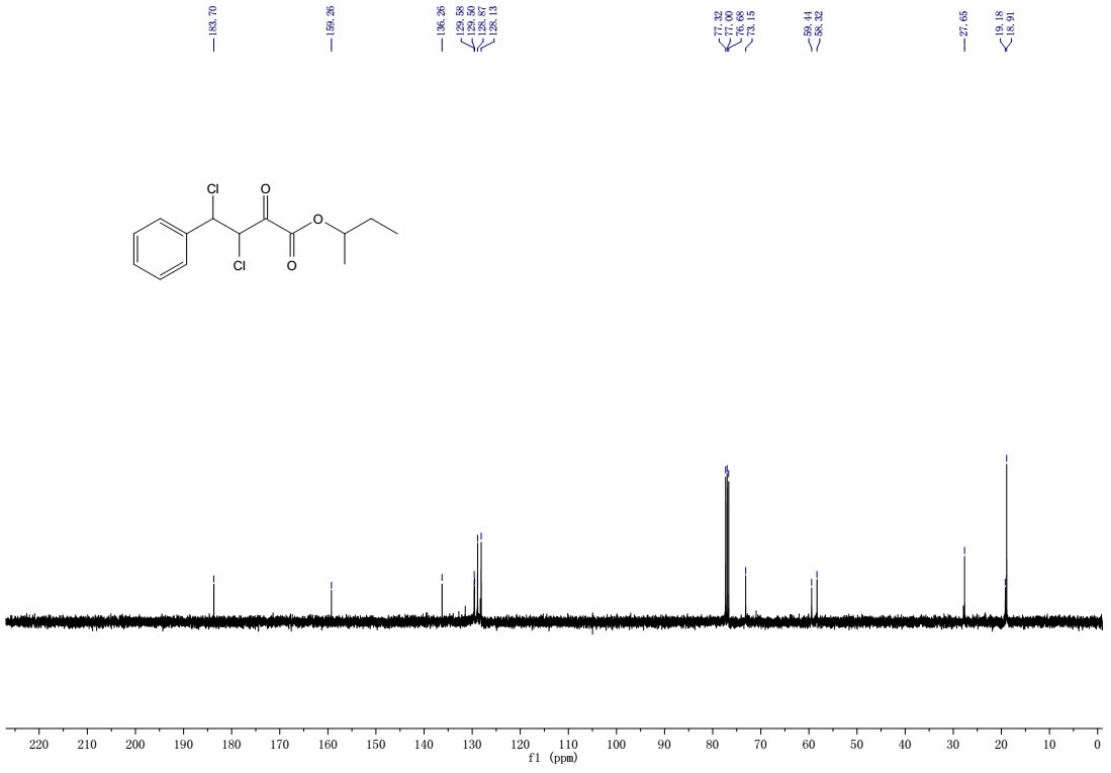
(trans)-isopropyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2c):



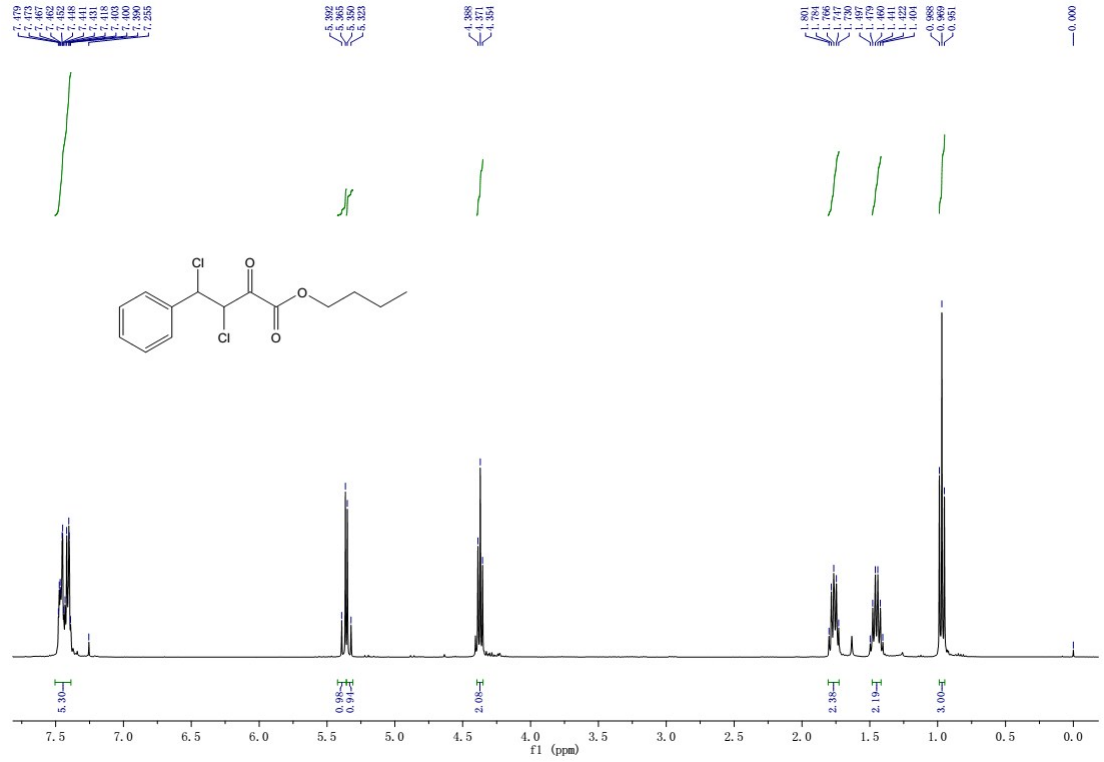


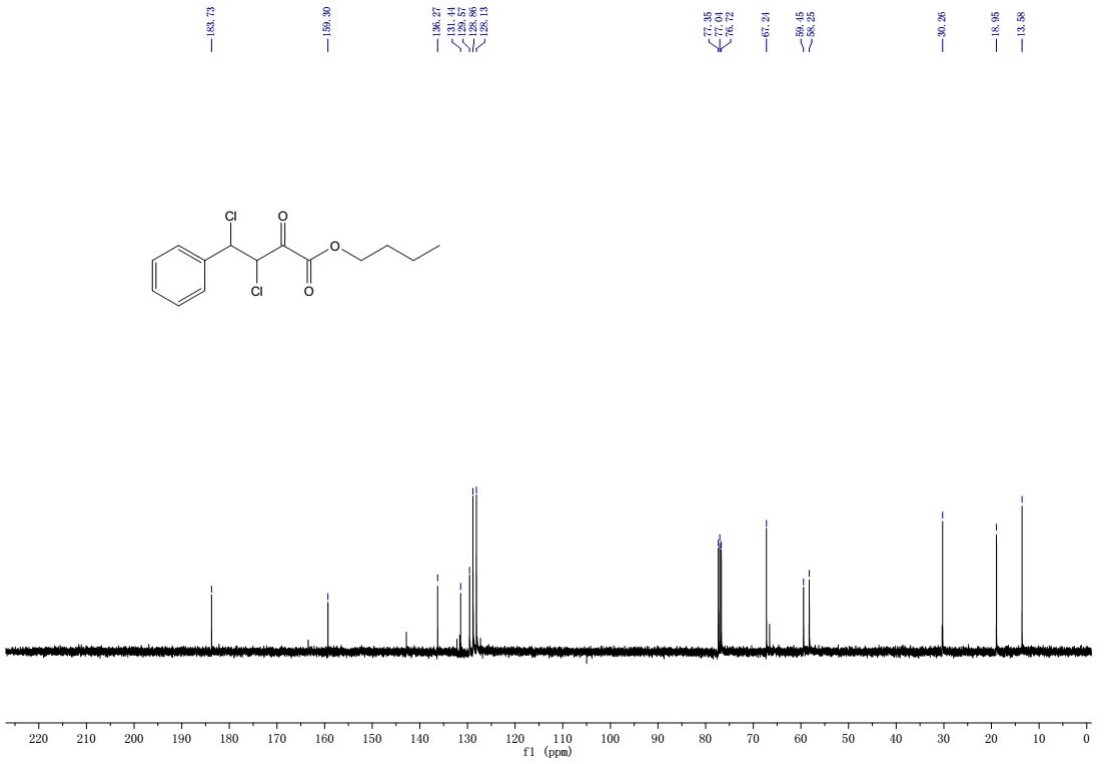
(trans)-sec-butyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2d):



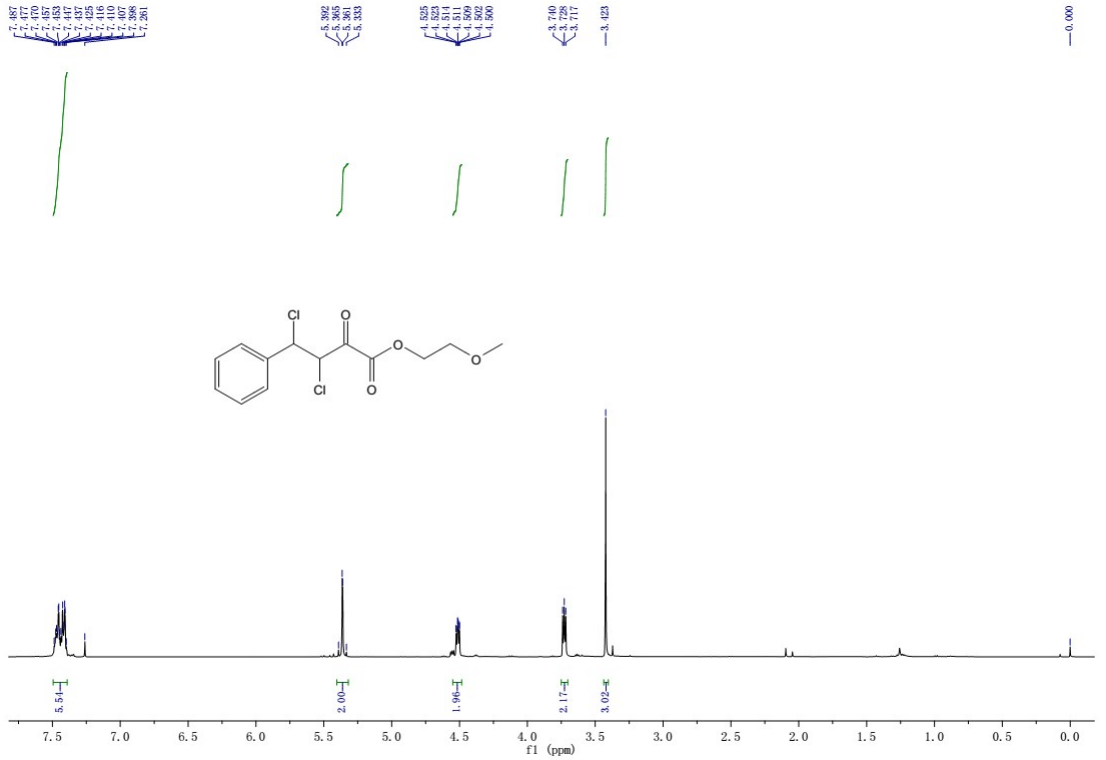


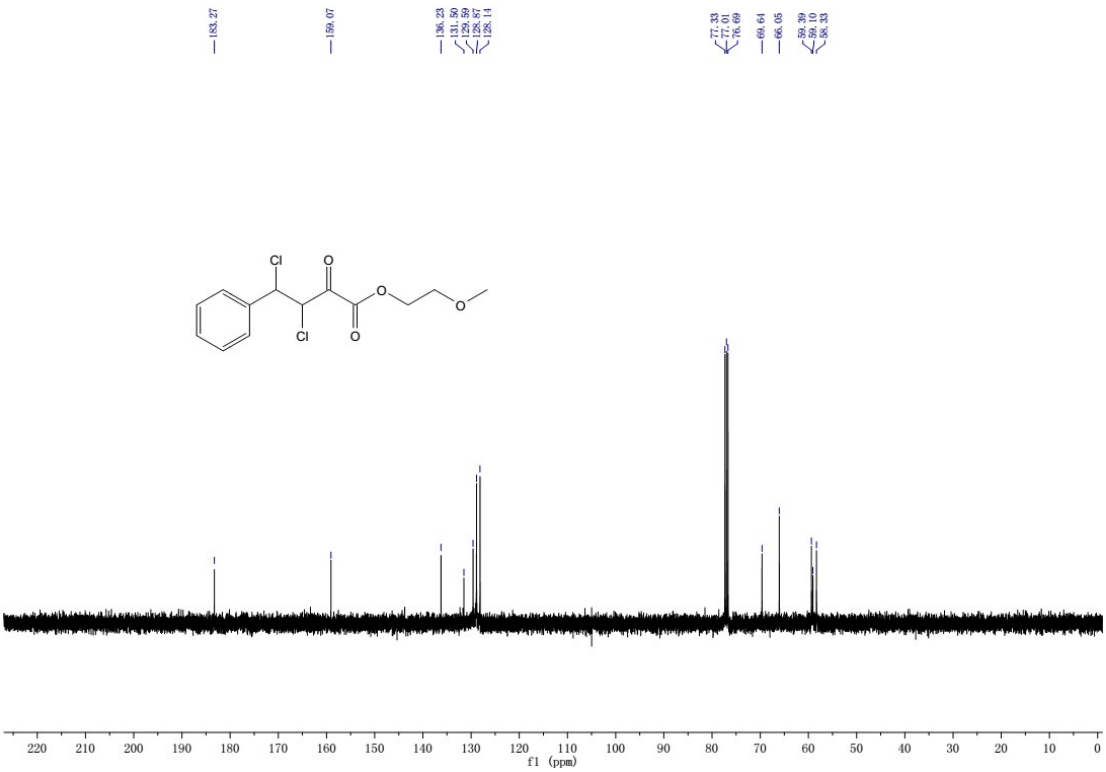
(trans)-butyl 3,4-dichloro-2-oxo-4-phenylbutanoate(2e):



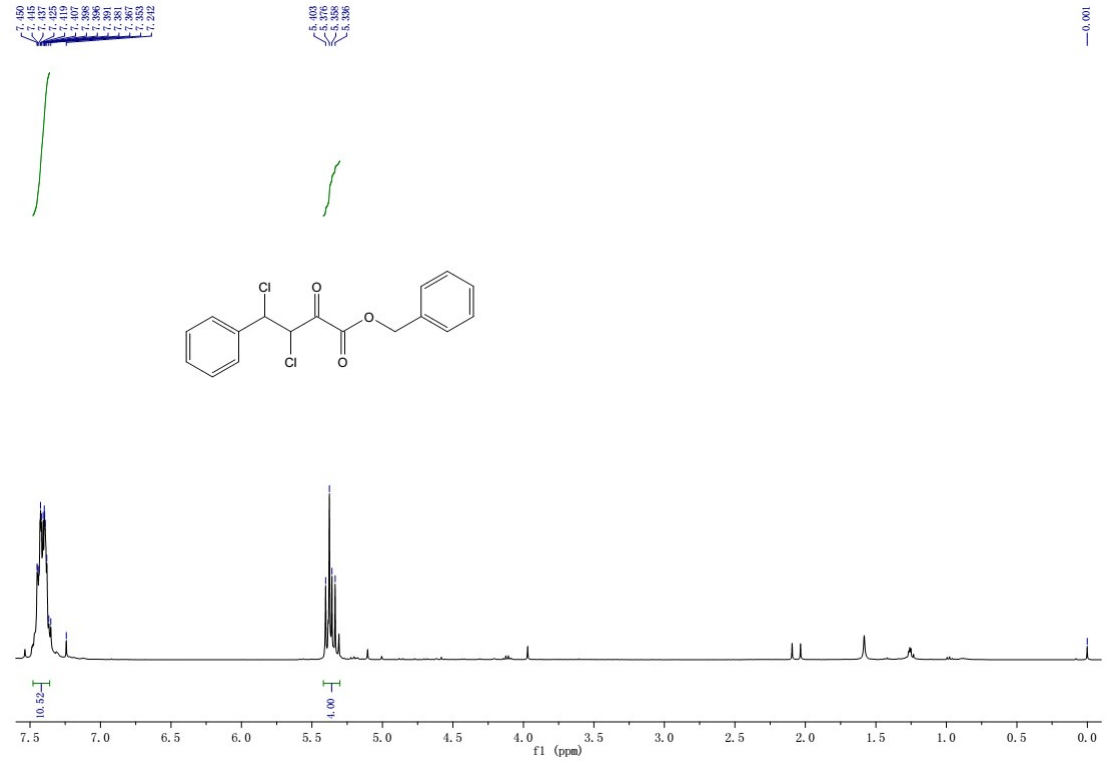


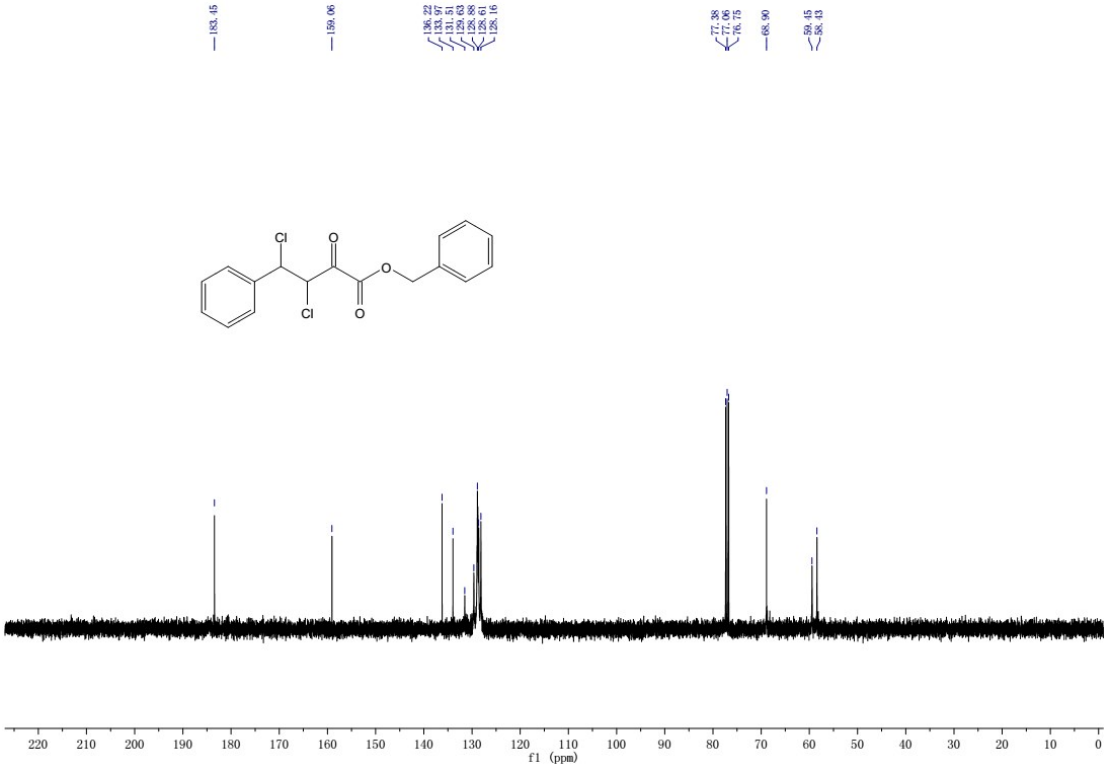
(trans)-2-methoxyethyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2f):



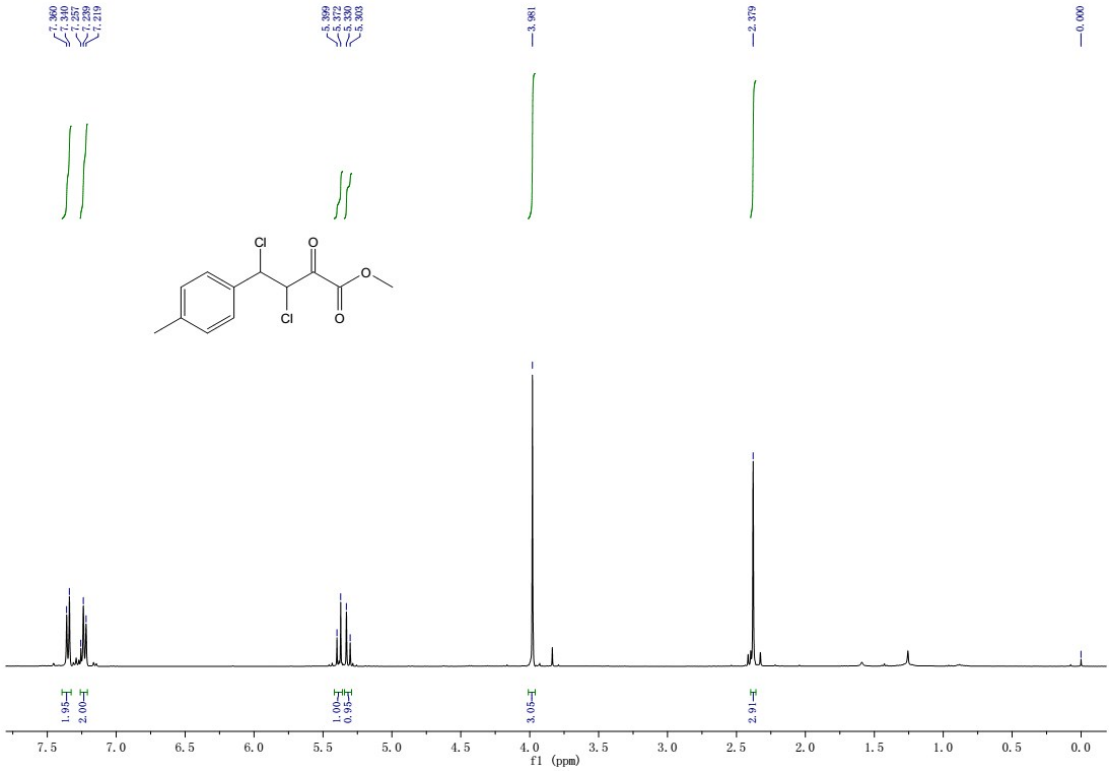


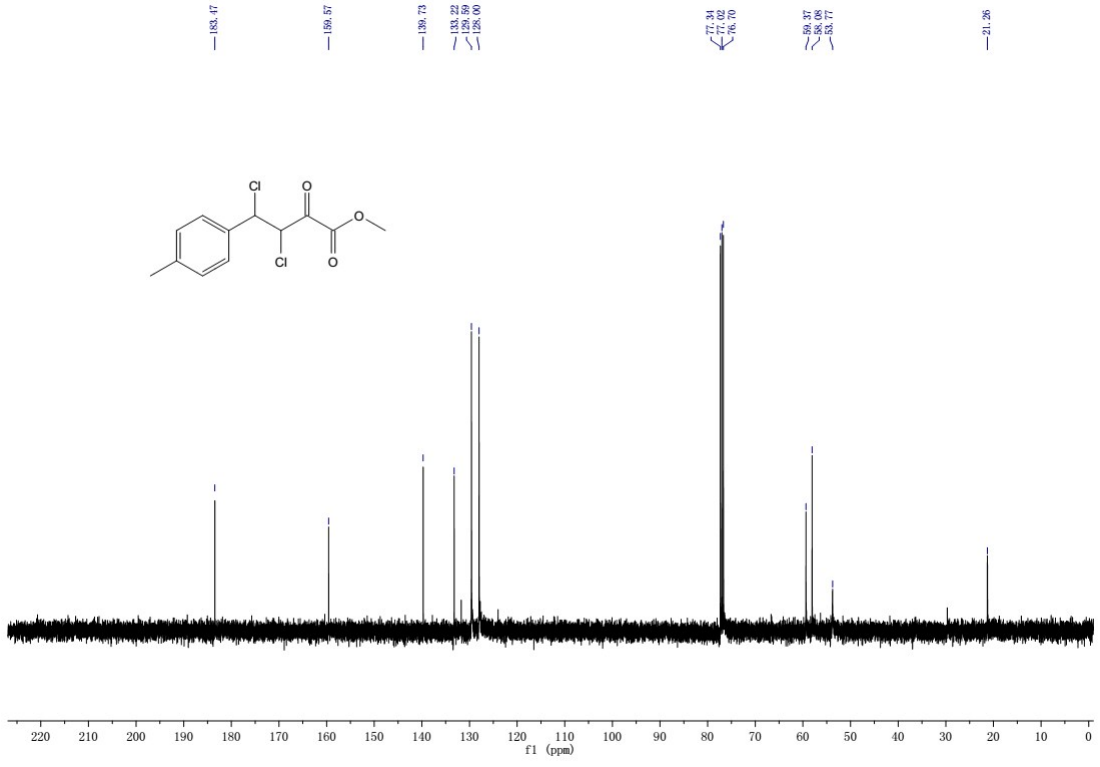
(trans)-benzyl 3,4-dichloro-2-oxo-4-phenylbutanoate (2g):



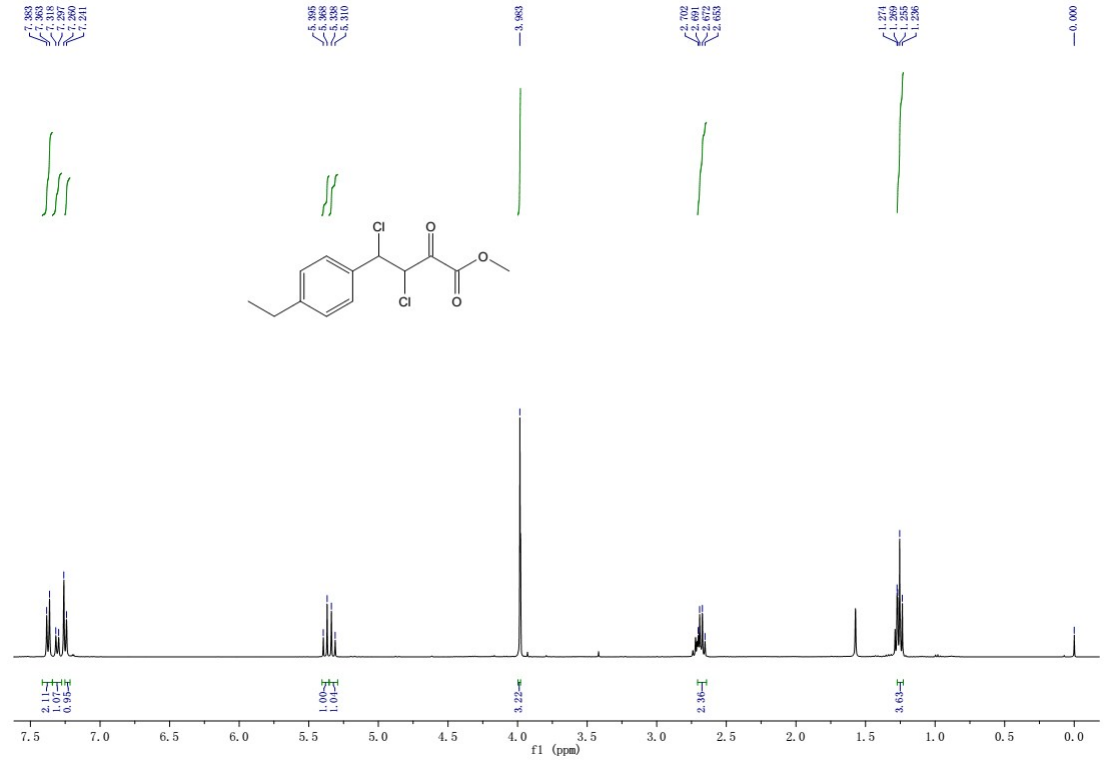


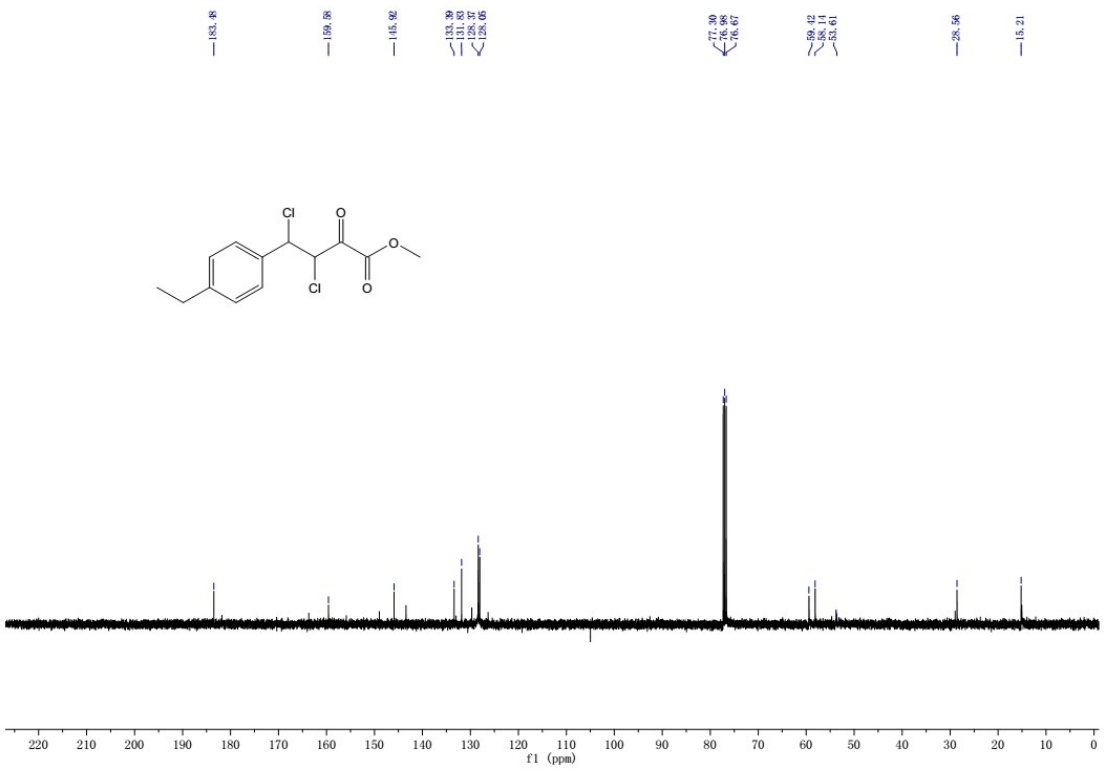
(trans)-methyl 3,4-dichloro-2-oxo-4-(p-tolyl)butanoate (2h):



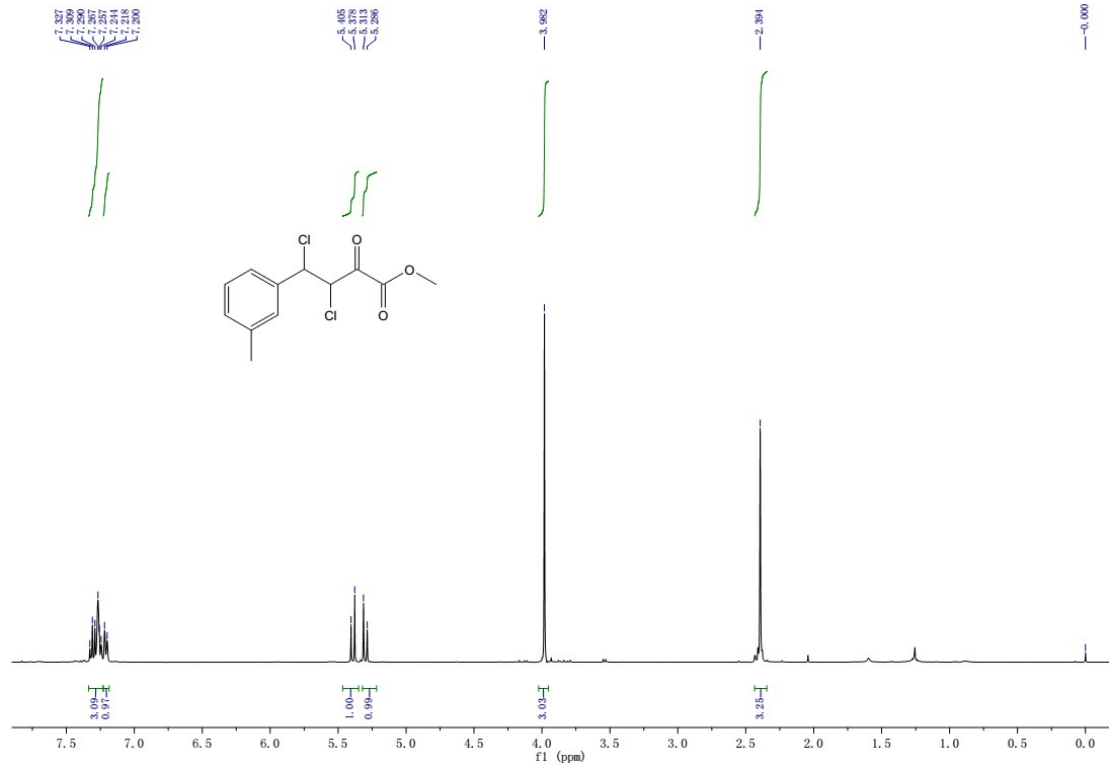


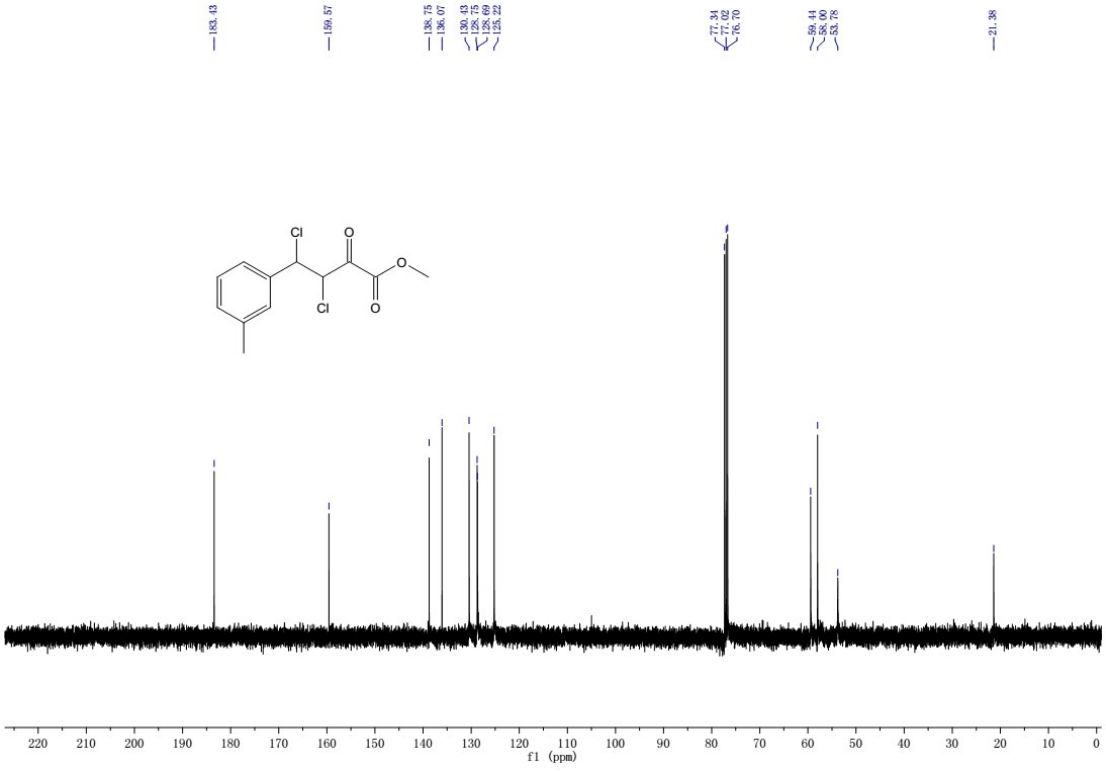
(trans)-methyl 3,4-dichloro-4-(4-ethylphenyl)-2-oxobutanoate (2i):



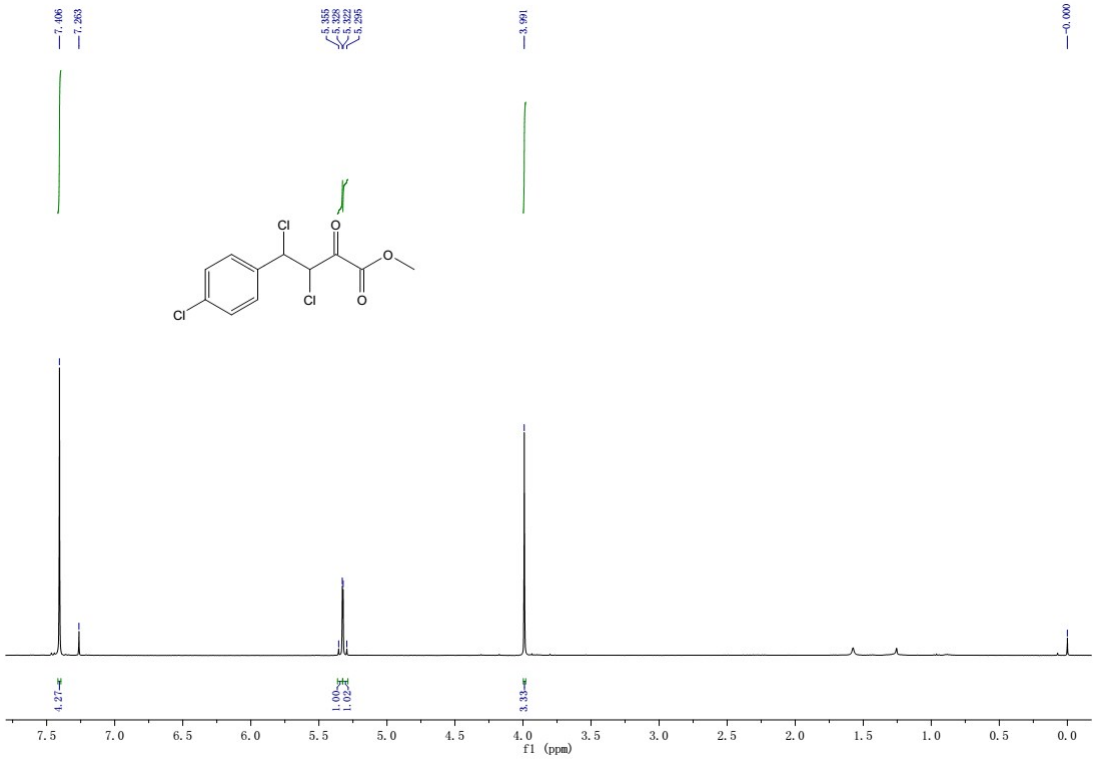


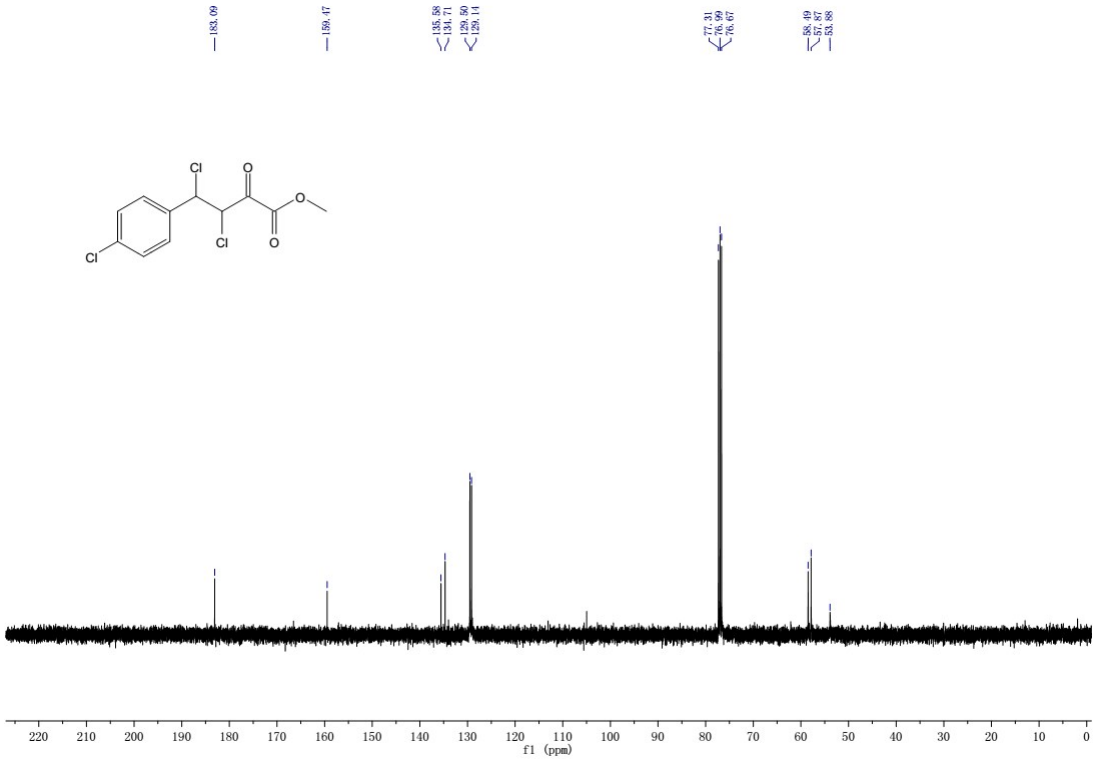
(trans)-methyl 3,4-dichloro-2-oxo-4-(m-tolyl)butanoate (2j):



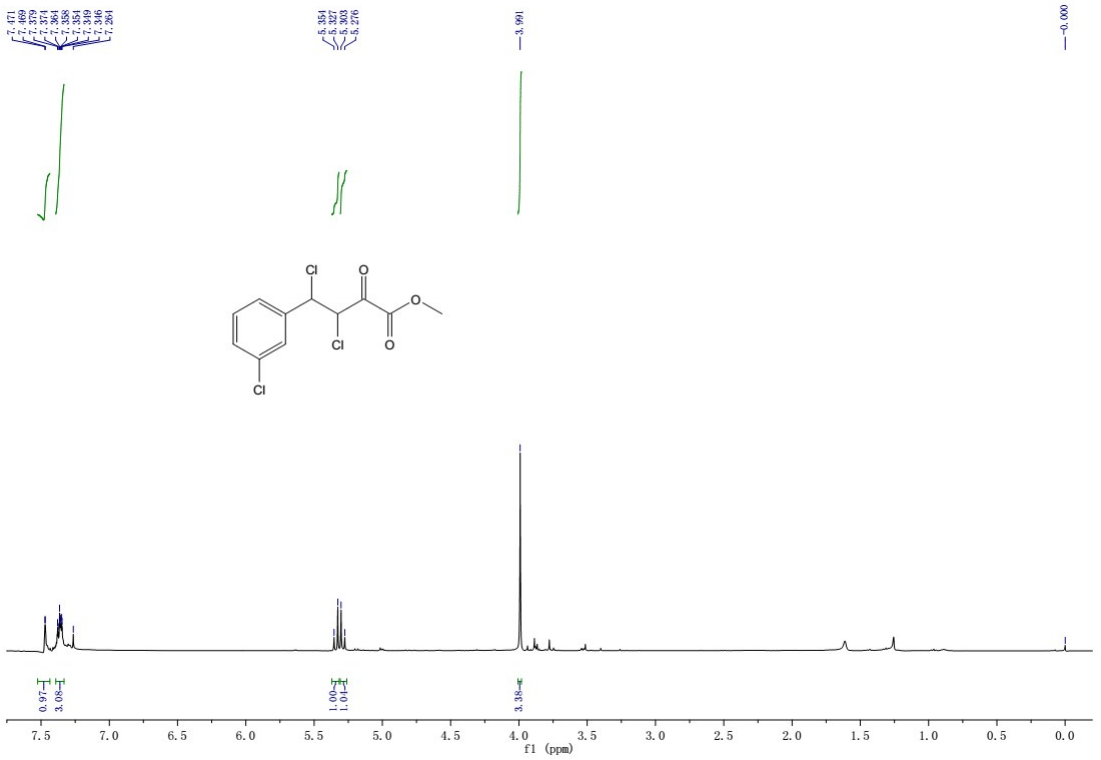


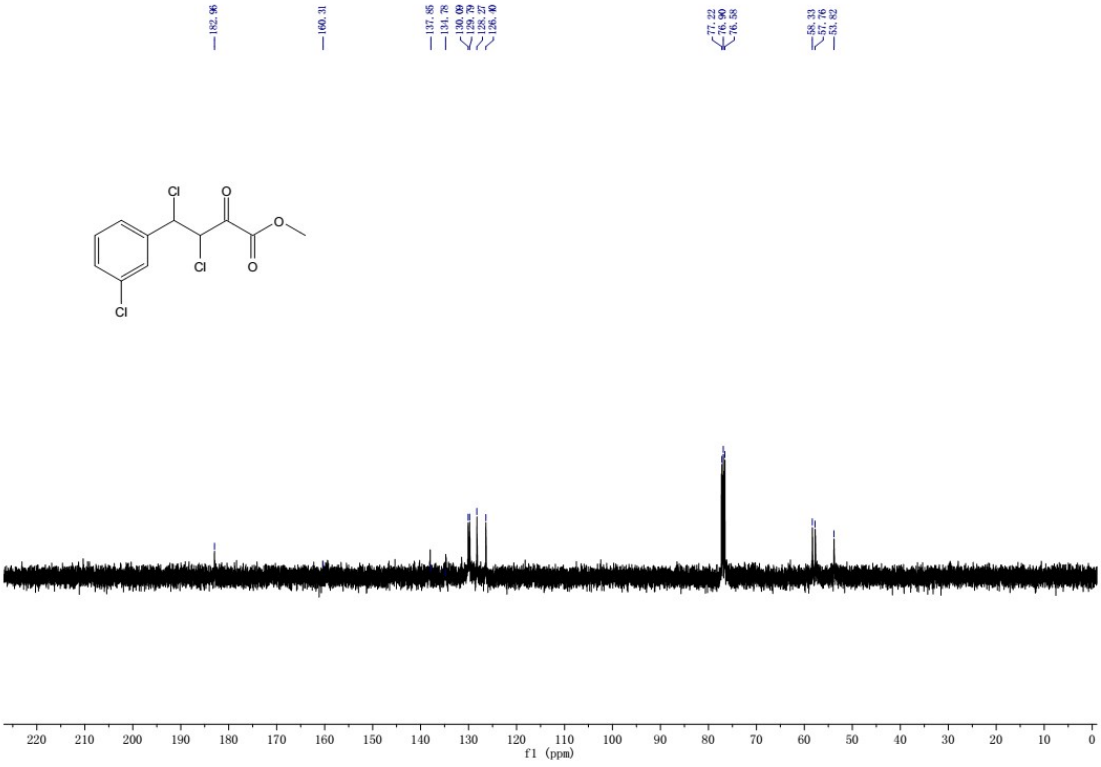
(trans)-methyl 3,4-dichloro-4-(4-chlorophenyl)-2-oxobutanoate (2k):



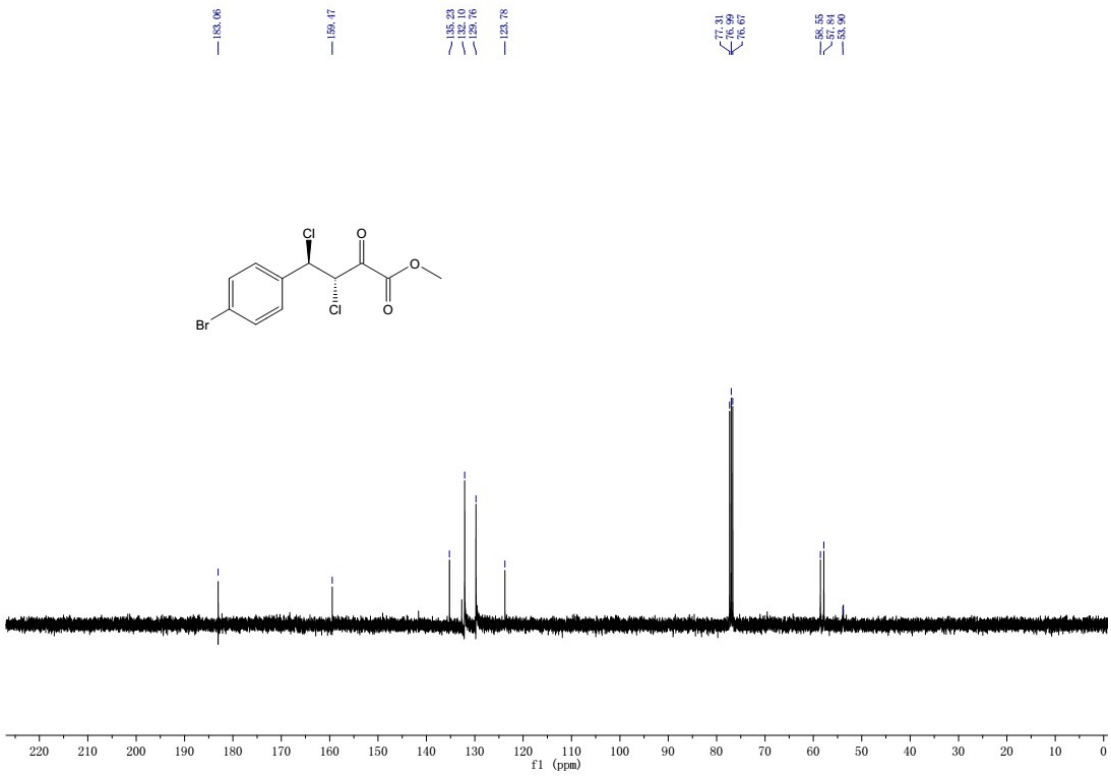


(trans)-methyl 3,4-dichloro-4-(3-chlorophenyl)-2-oxobutanoate (2l):





(trans)-methyl 4-(4-bromophenyl)-3,4-dichloro-2-oxobutanoate (2m):



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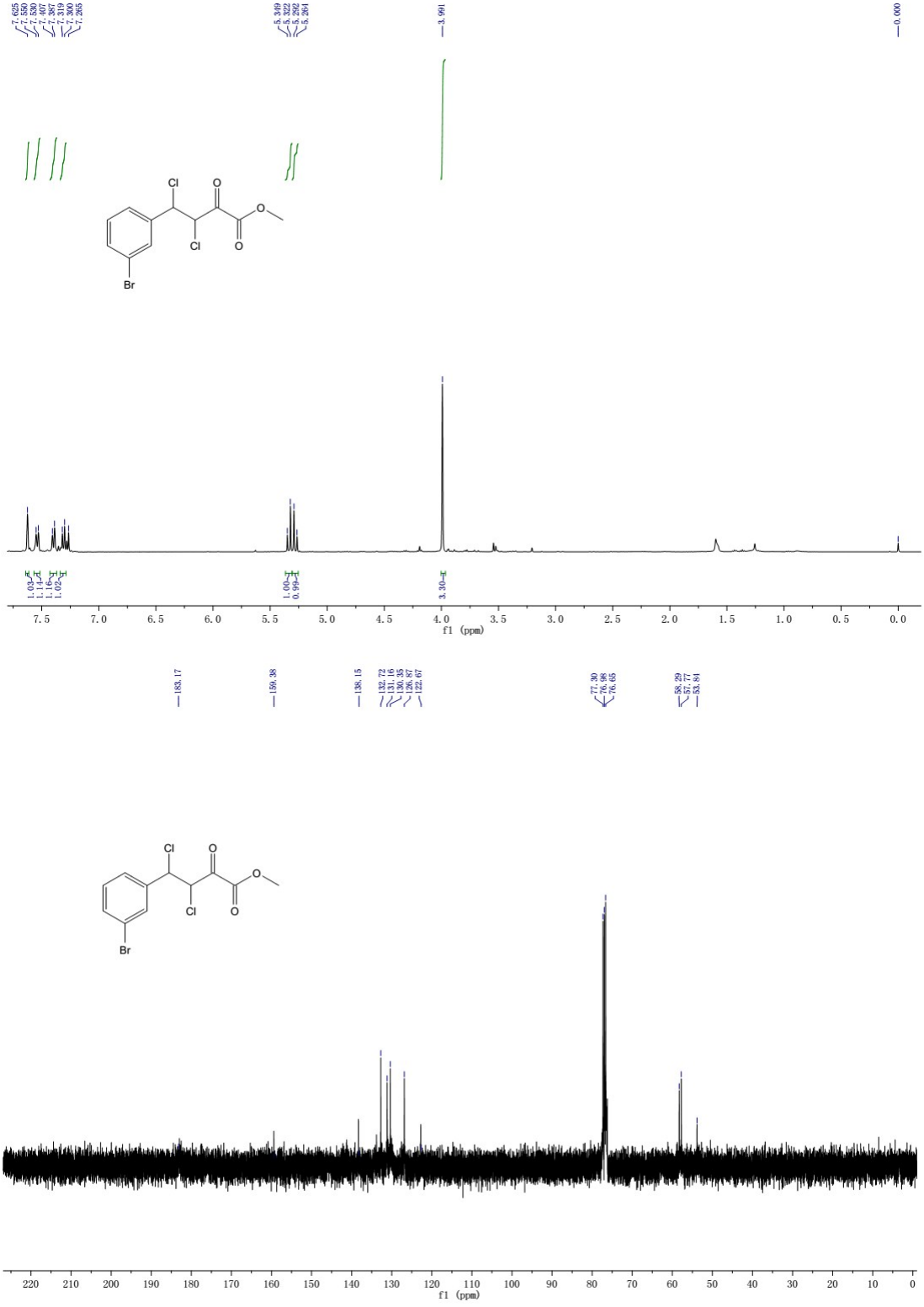

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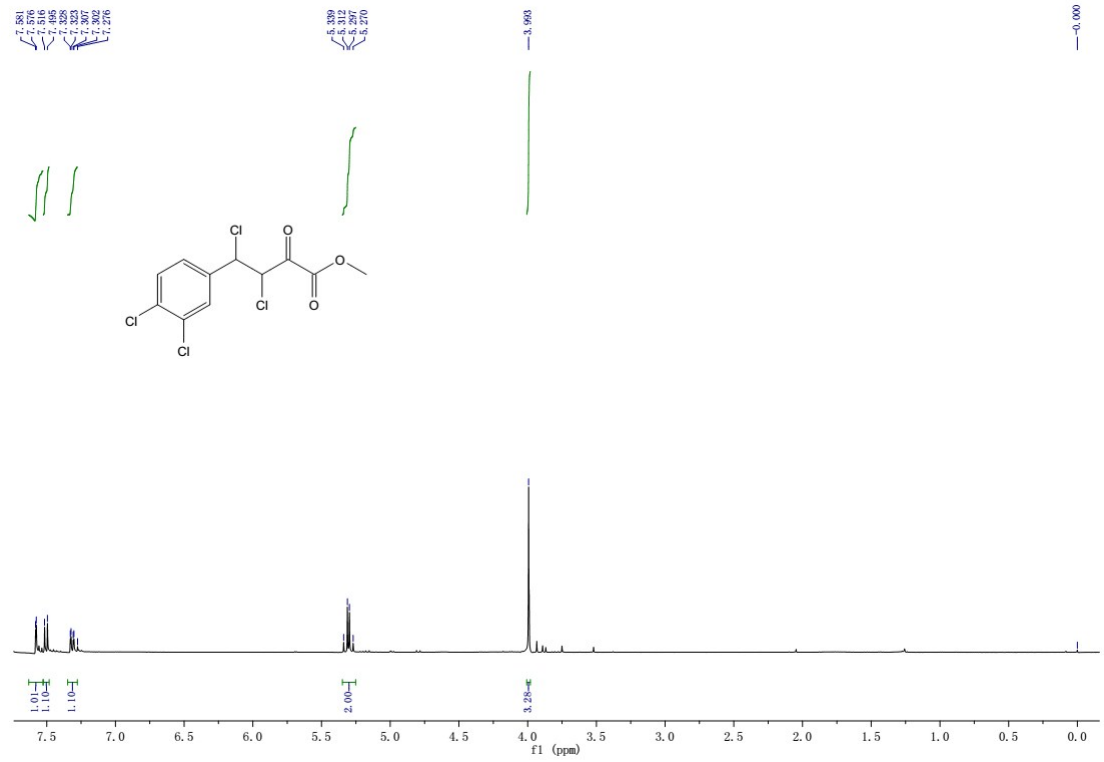
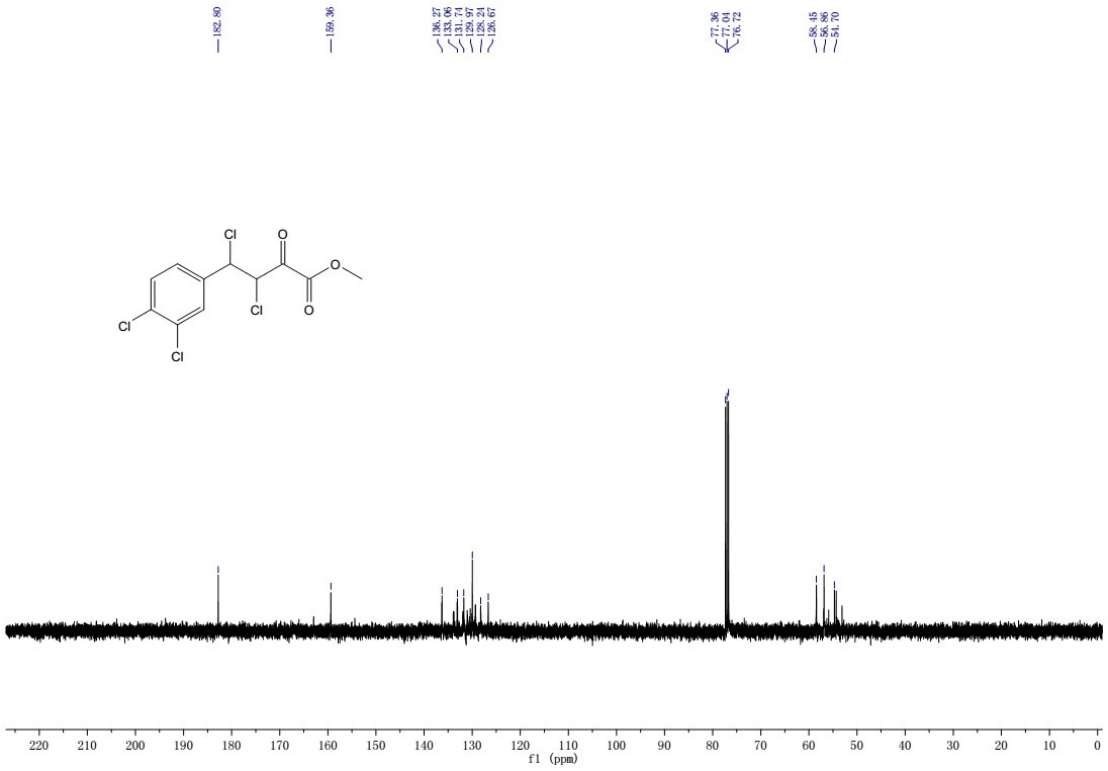
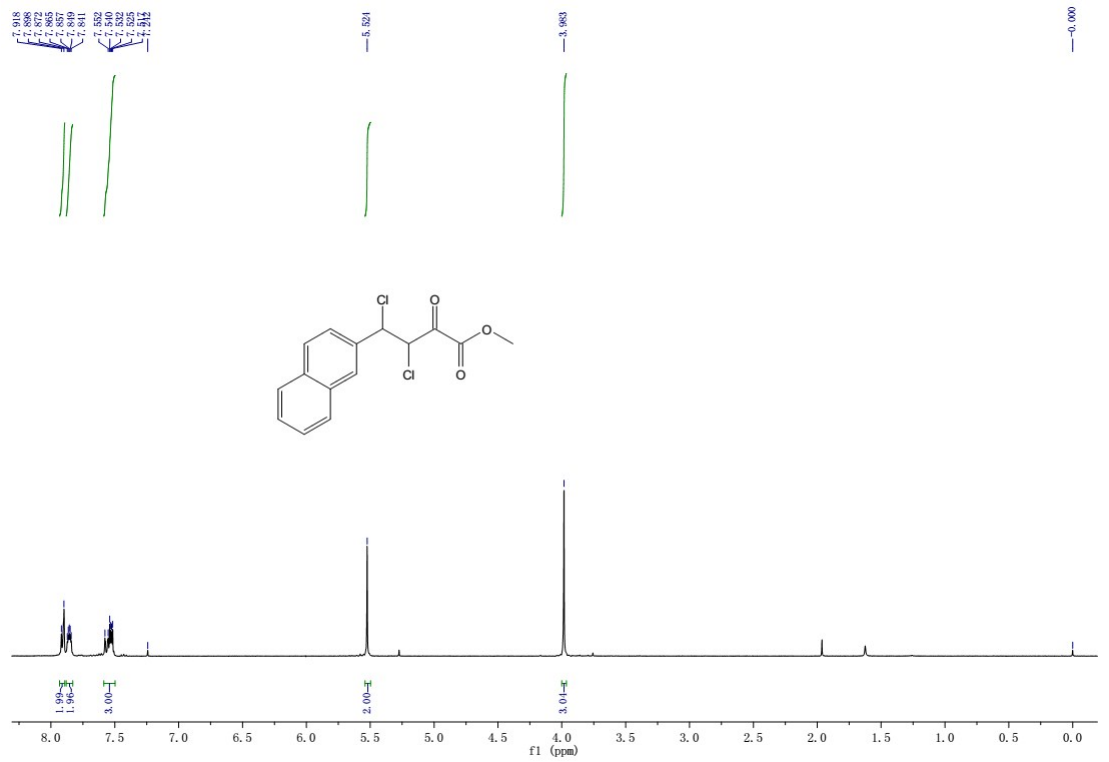
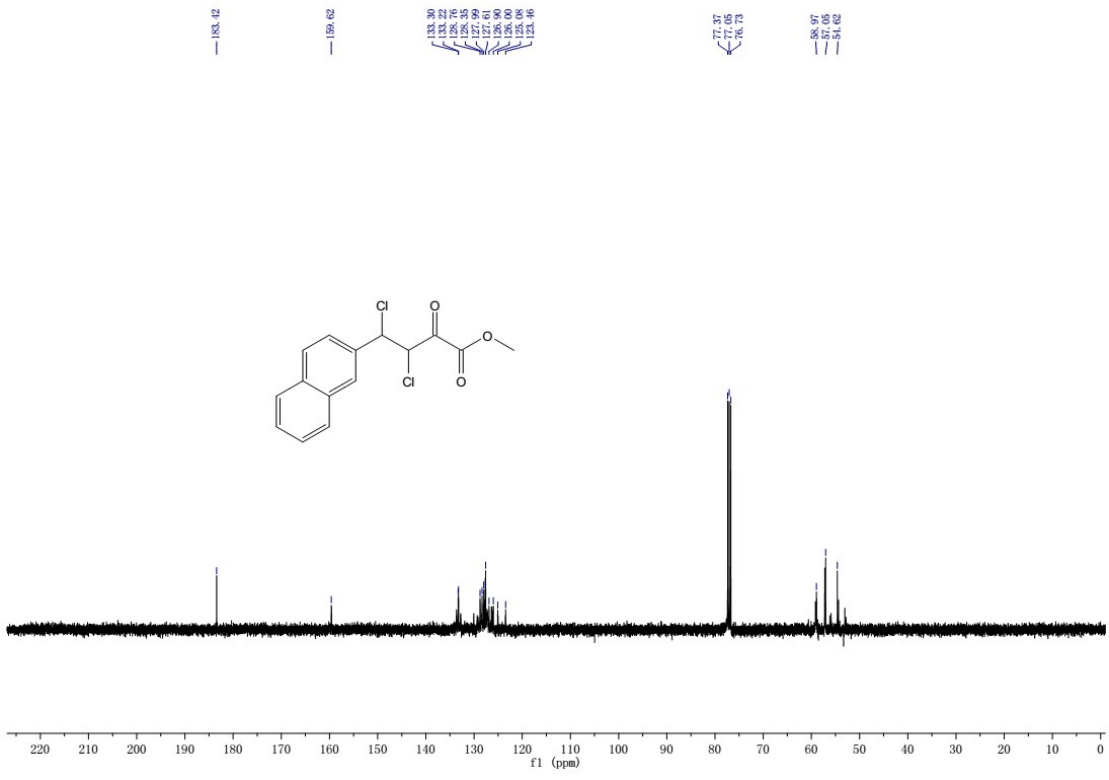


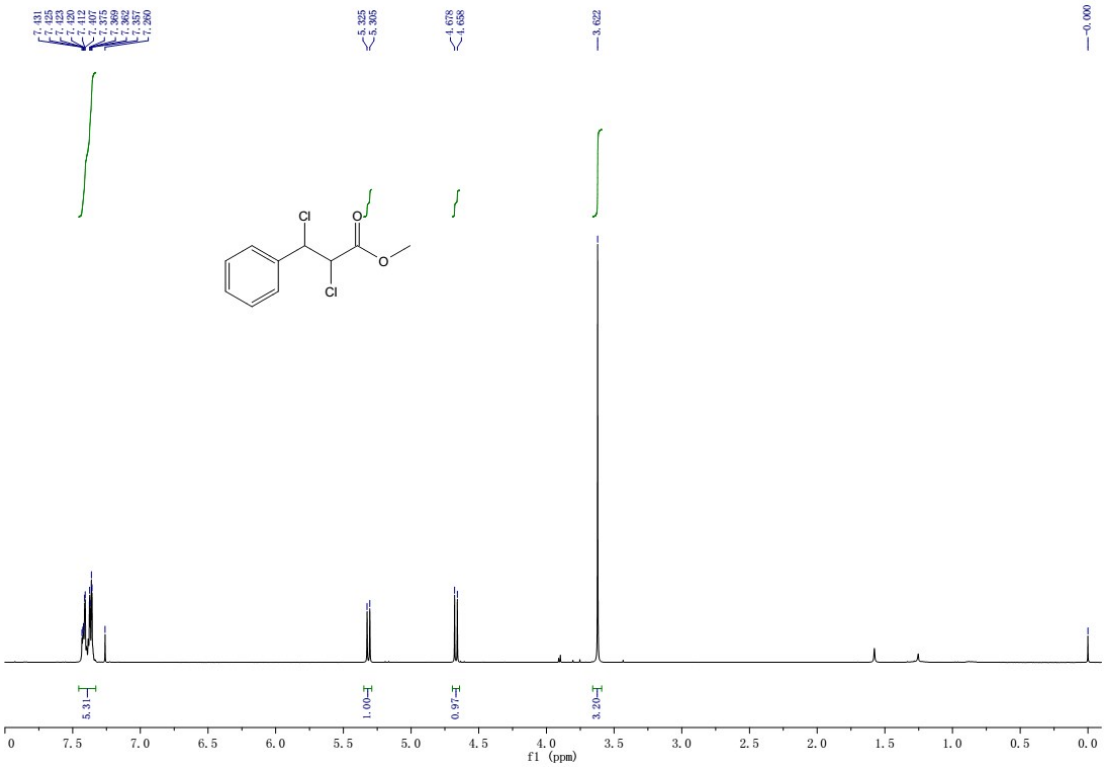


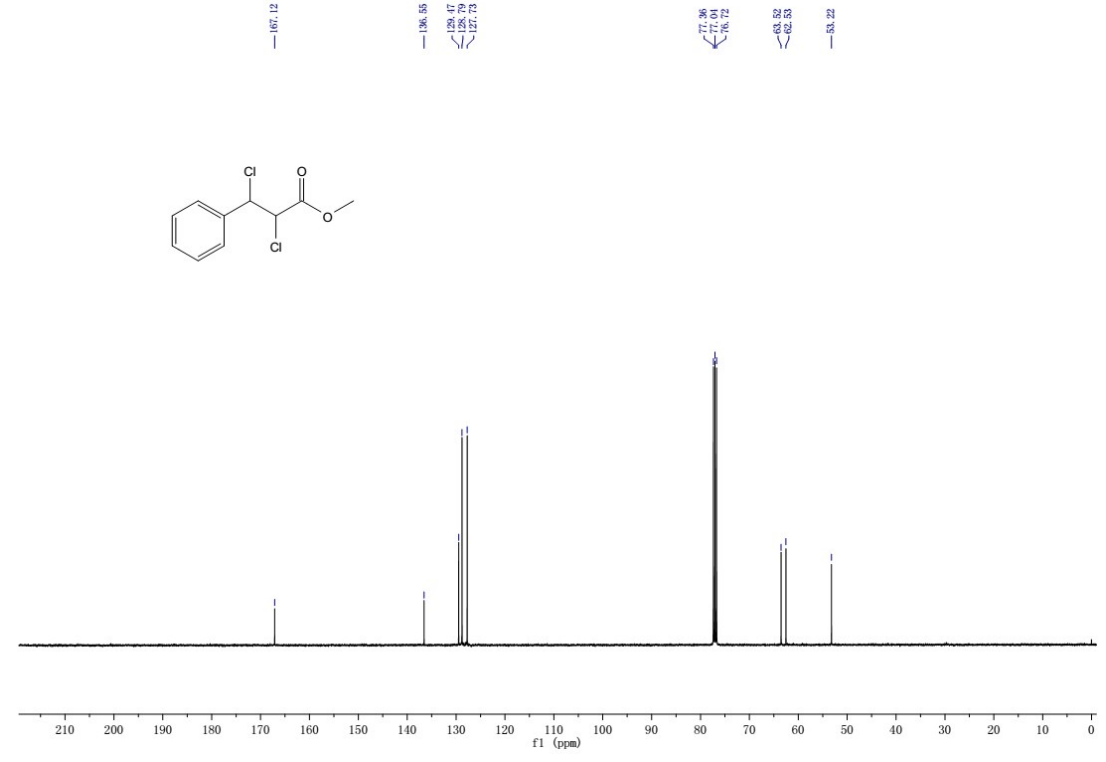
(trans)-methyl 3,4-dichloro-4-(naphthalen-2-yl)-2-oxobutanoate (2p):



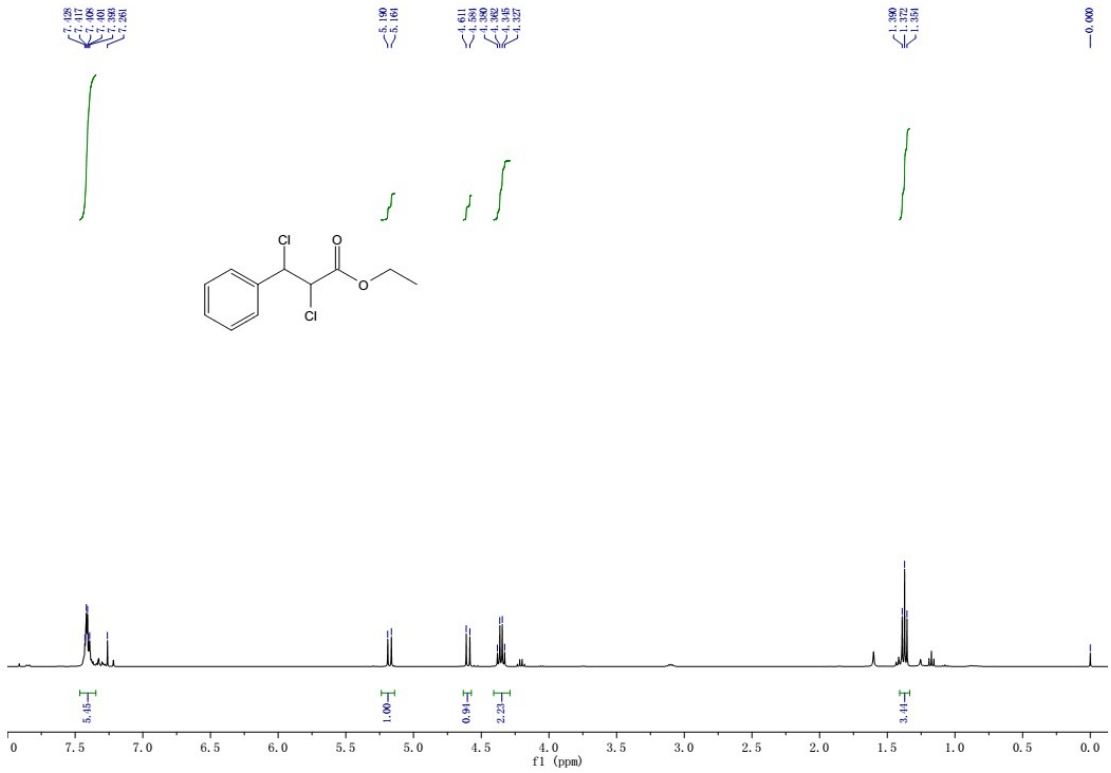


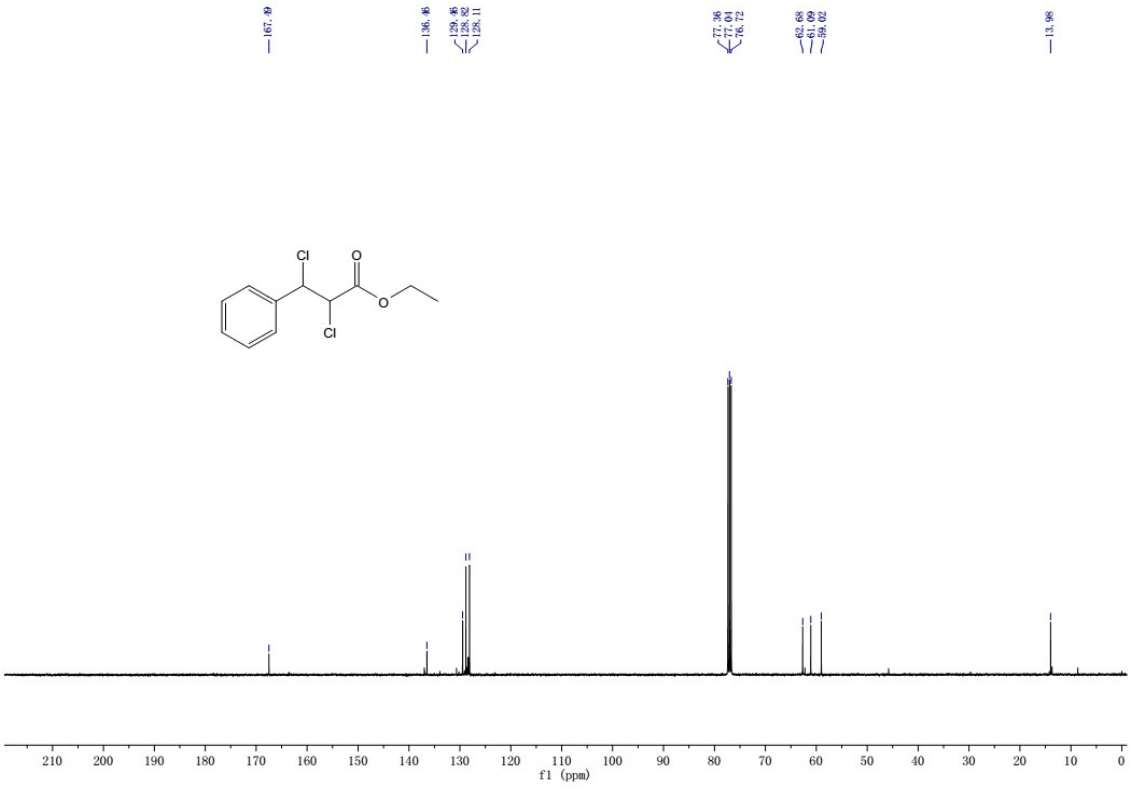
(trans)-methyl 2,3-dichloro-3-phenylpropanoate (4a)



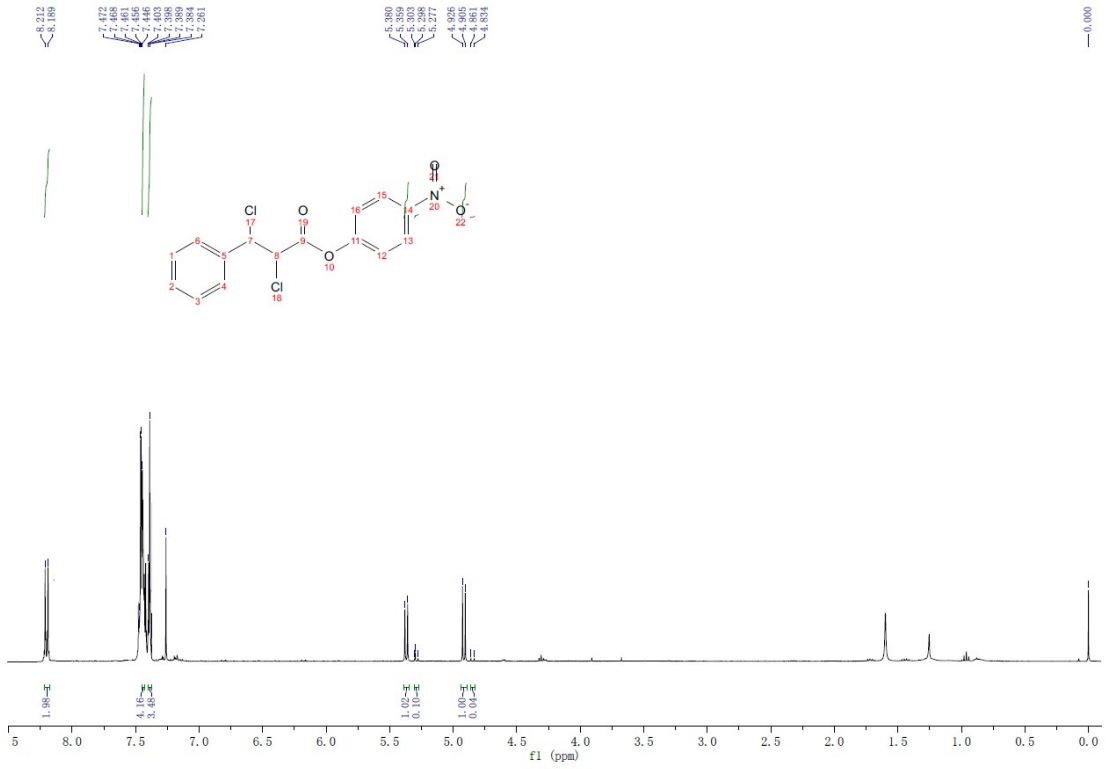


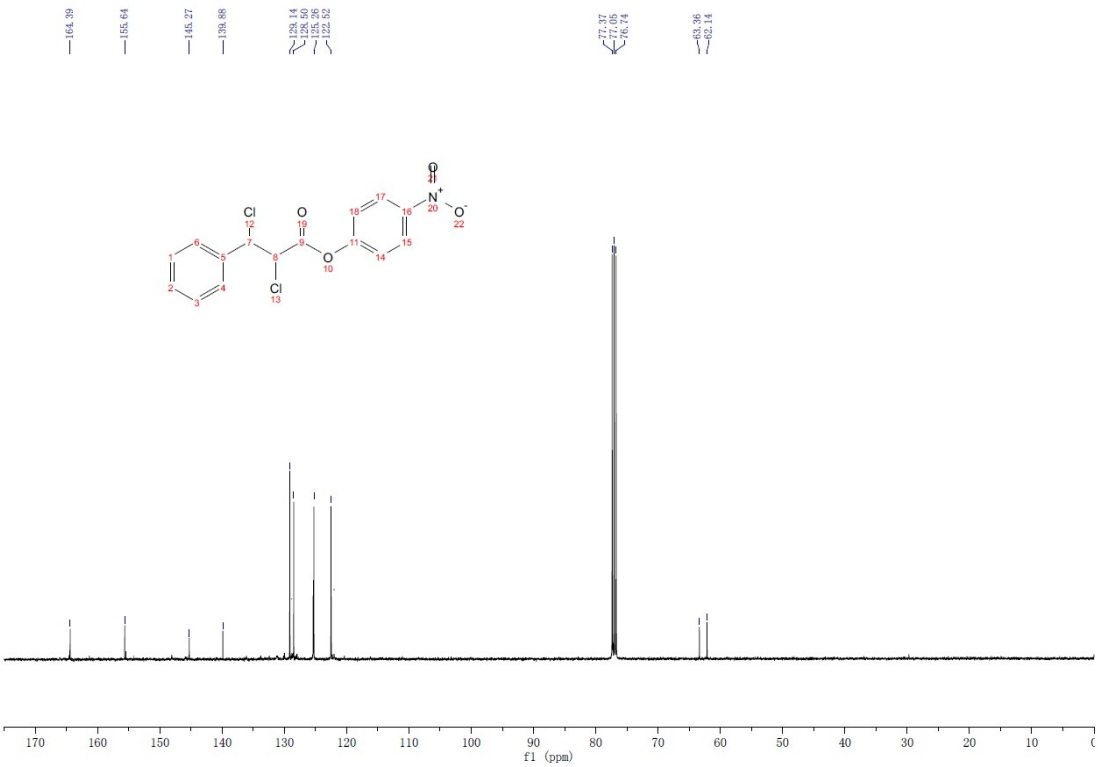
(trans)-ethyl 2,3-dichloro-3-phenylpropanoate (4b)



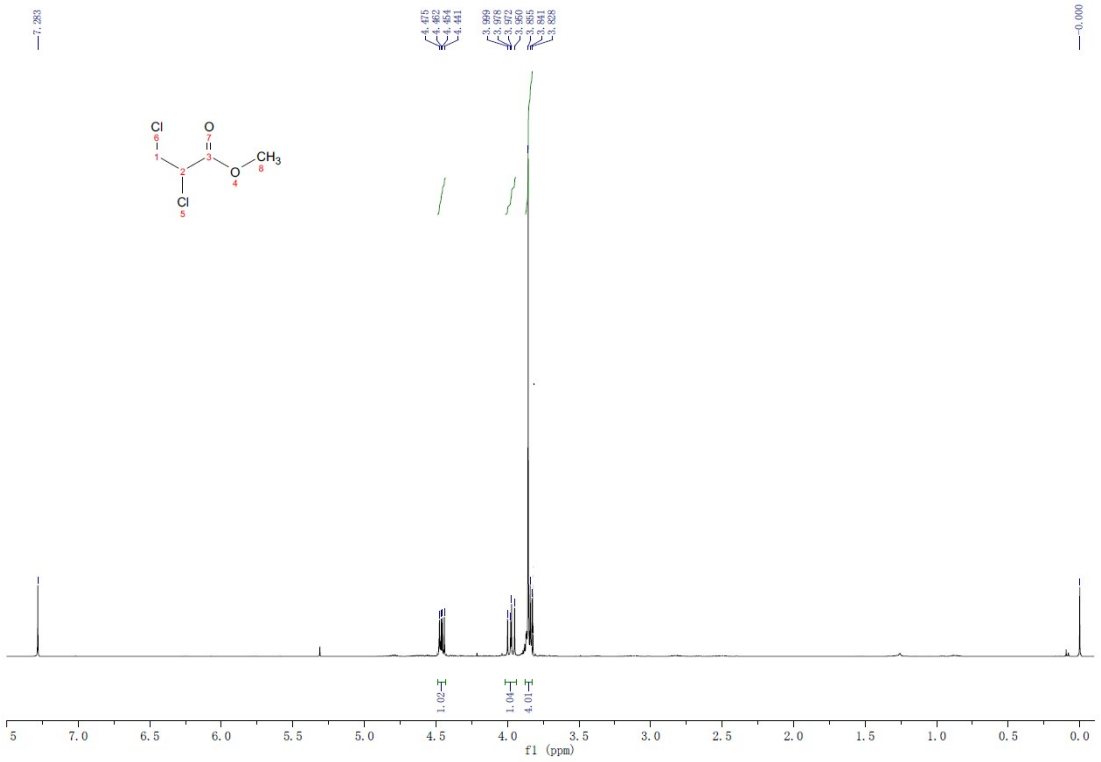


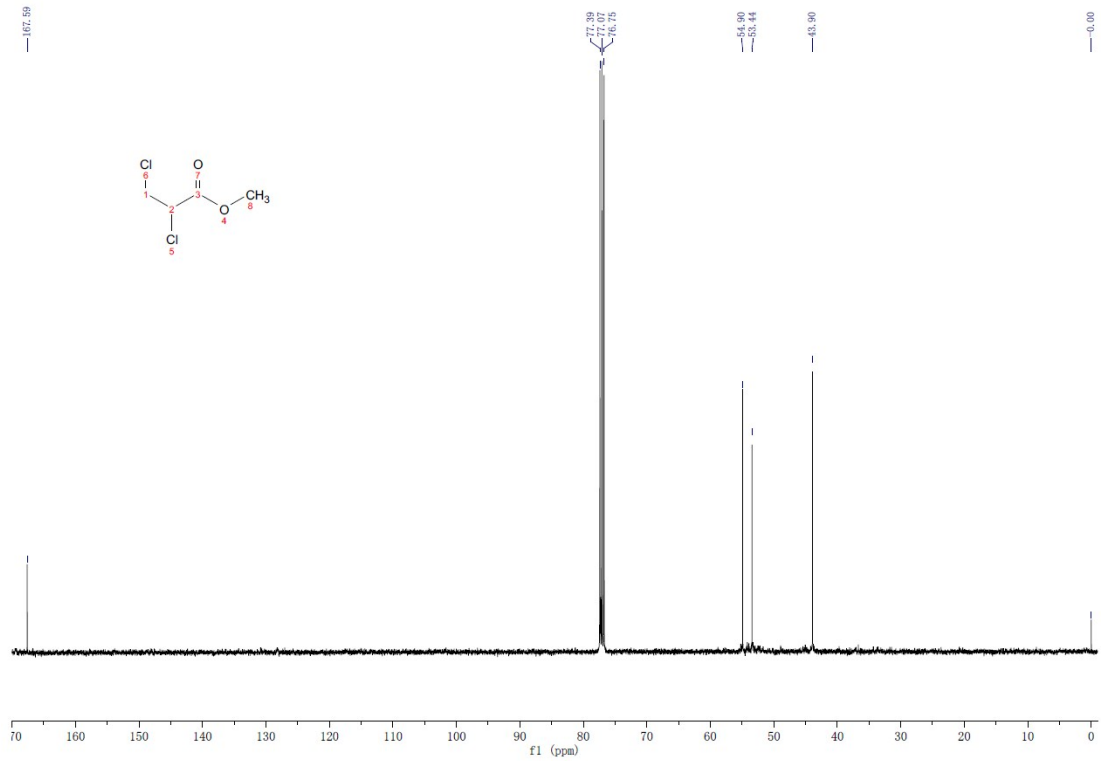
(trans)-4-nitrophenyl 2,3-dichloro-3-phenylpropanoate (4c)



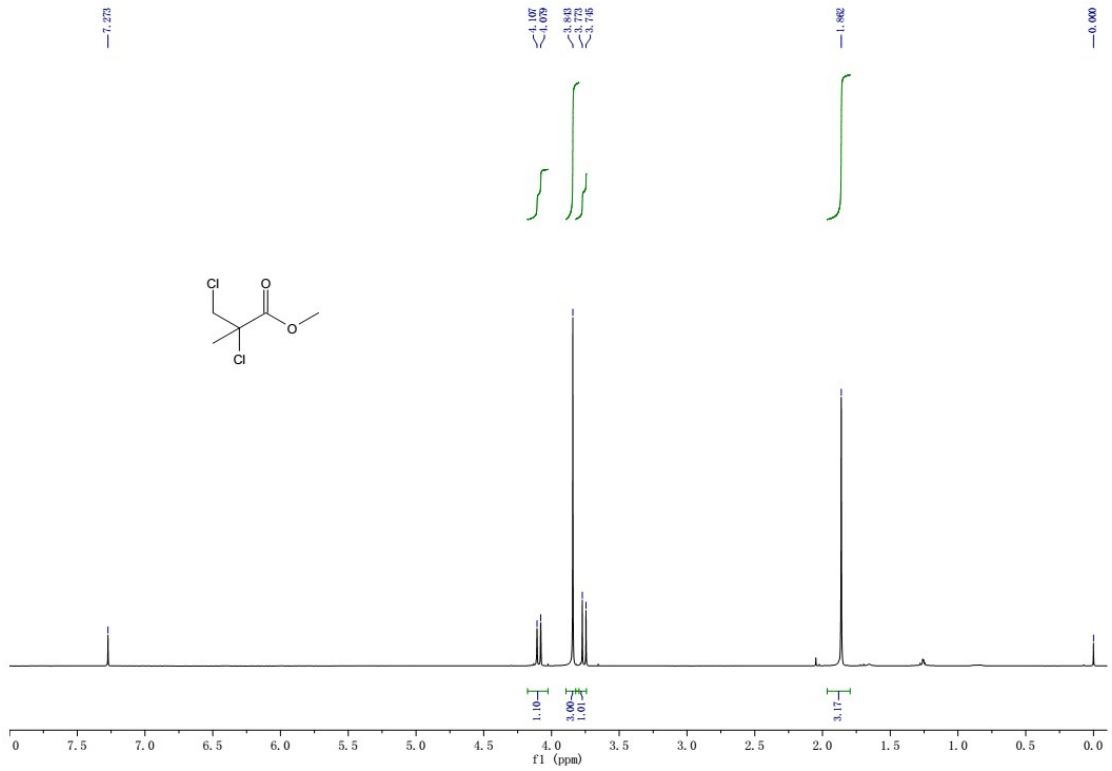


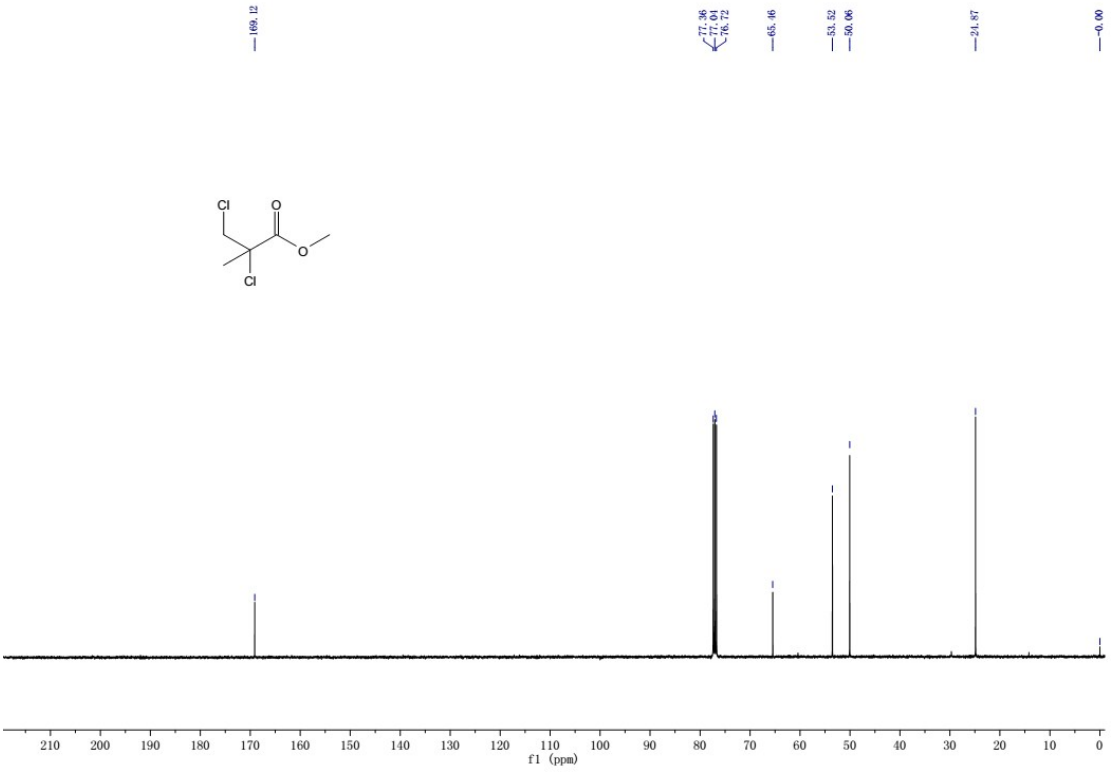
methyl 2,3-dichloropropanoate (4d)



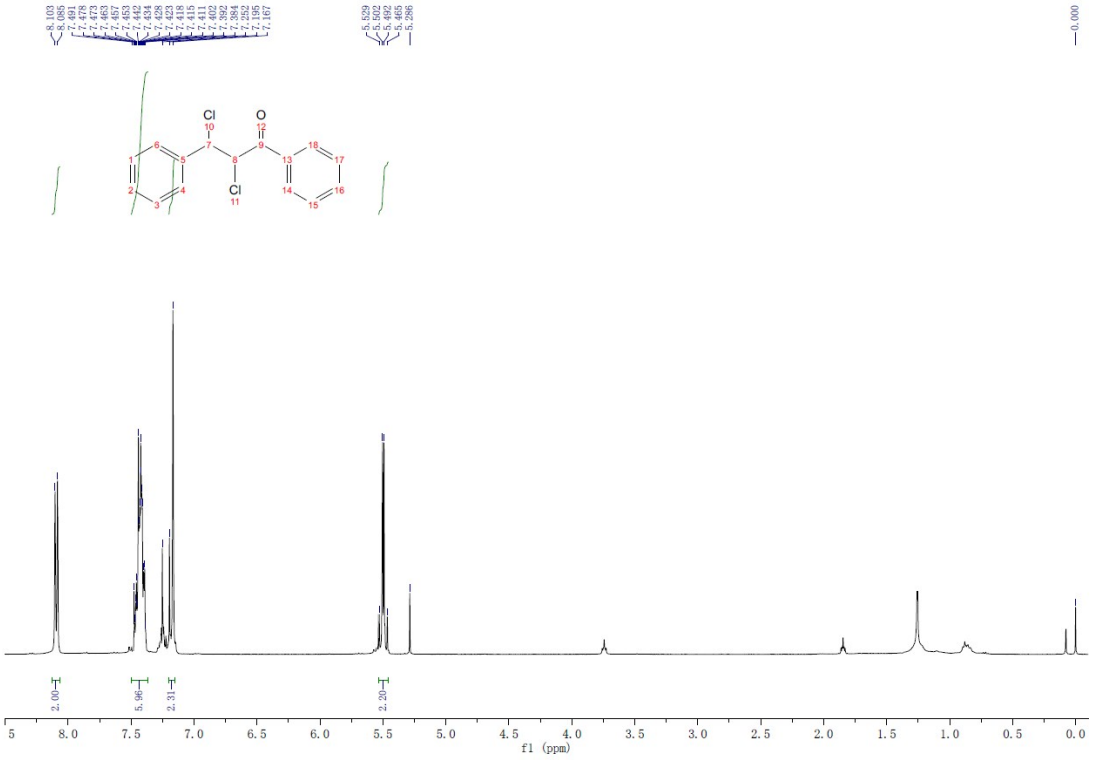


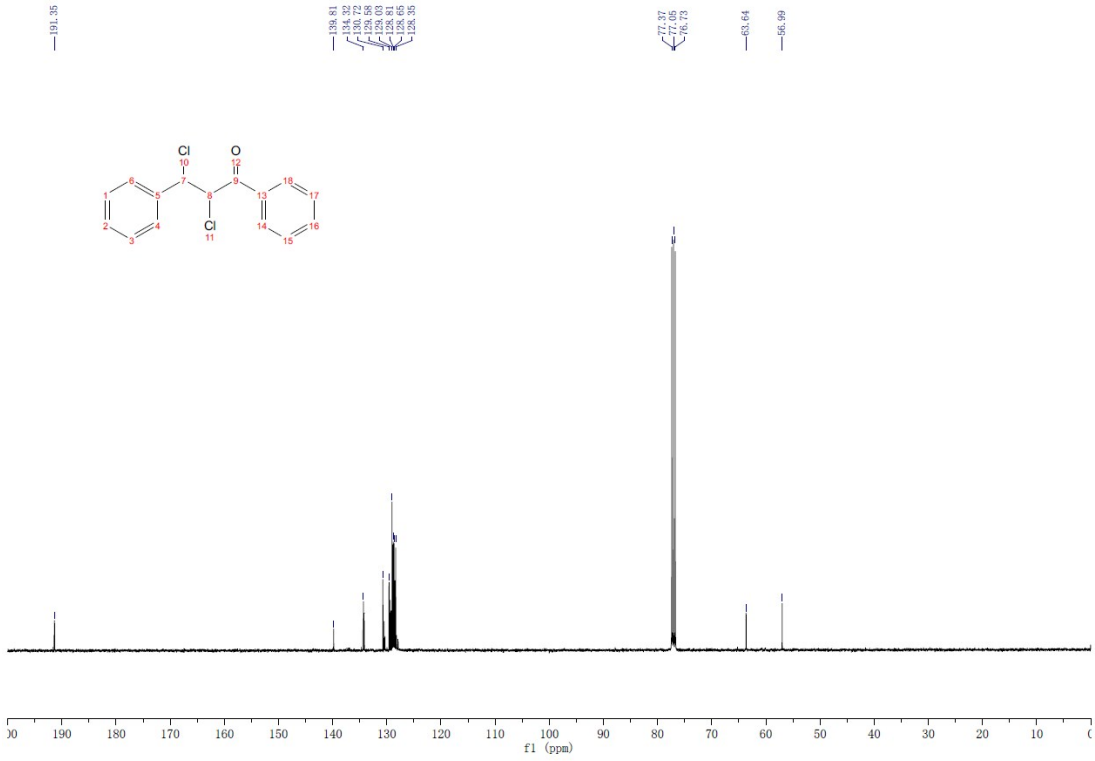
methyl 2,3-dichloro-2-methylpropanoate (4e)



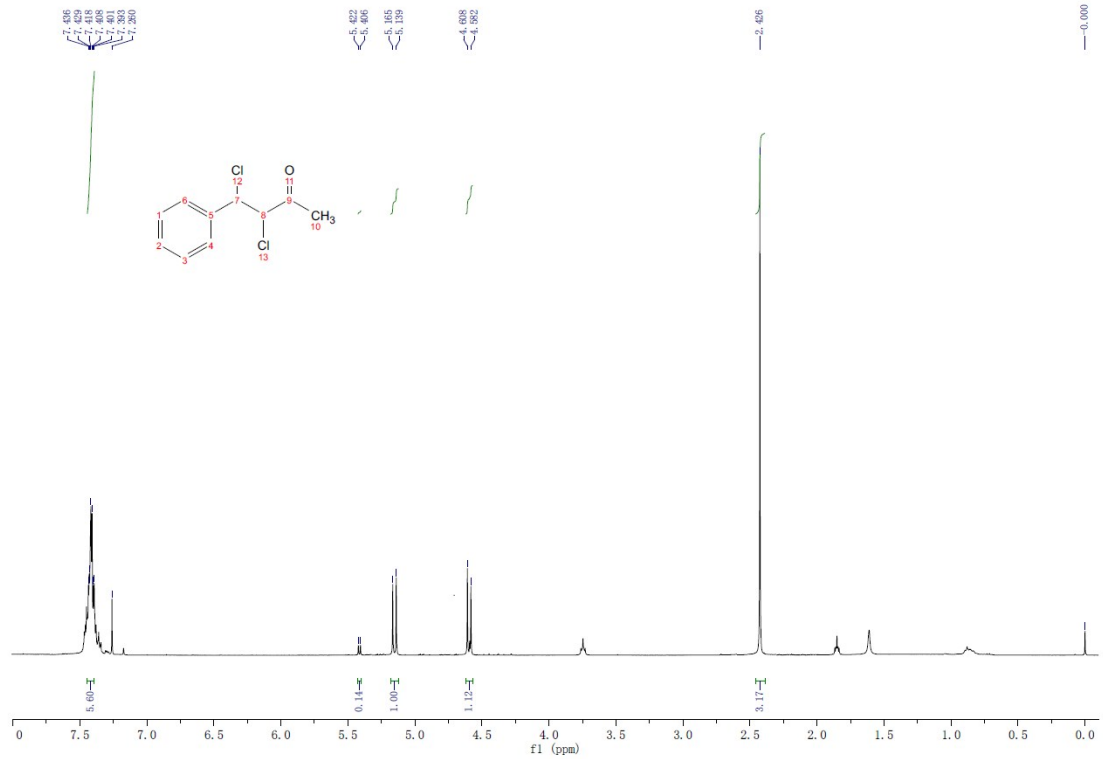


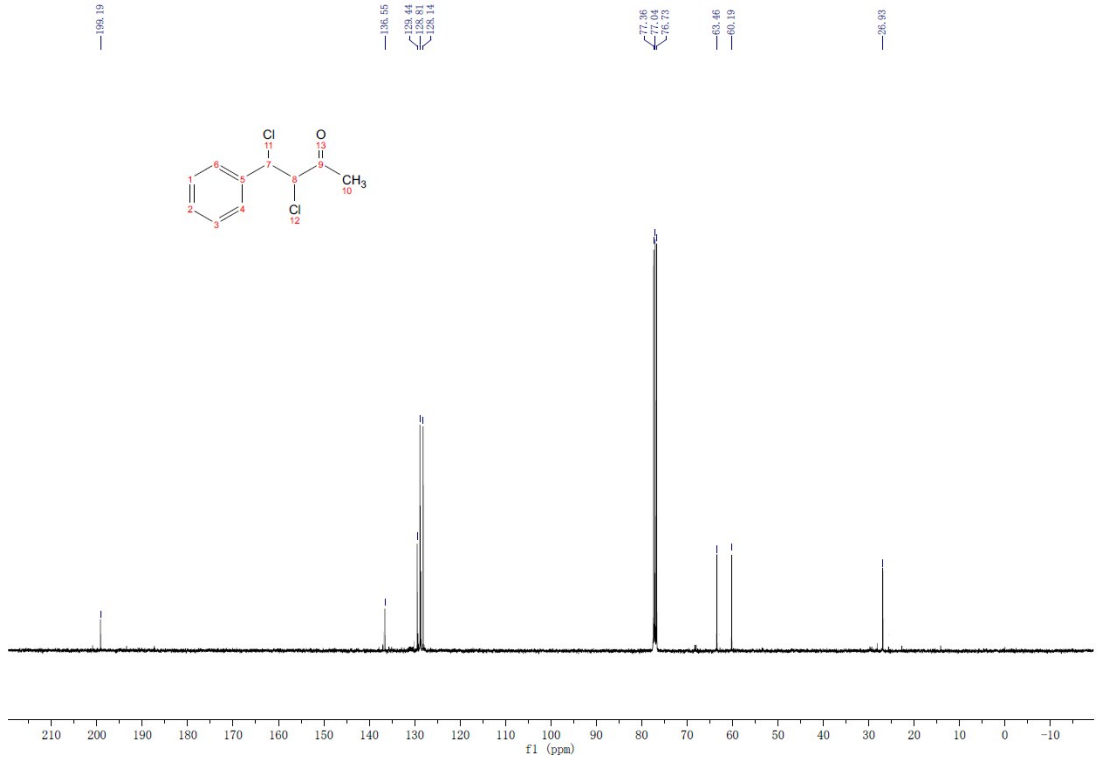
(trans)-2,3-dichloro-1,3-diphenylpropan-1-one (4f)



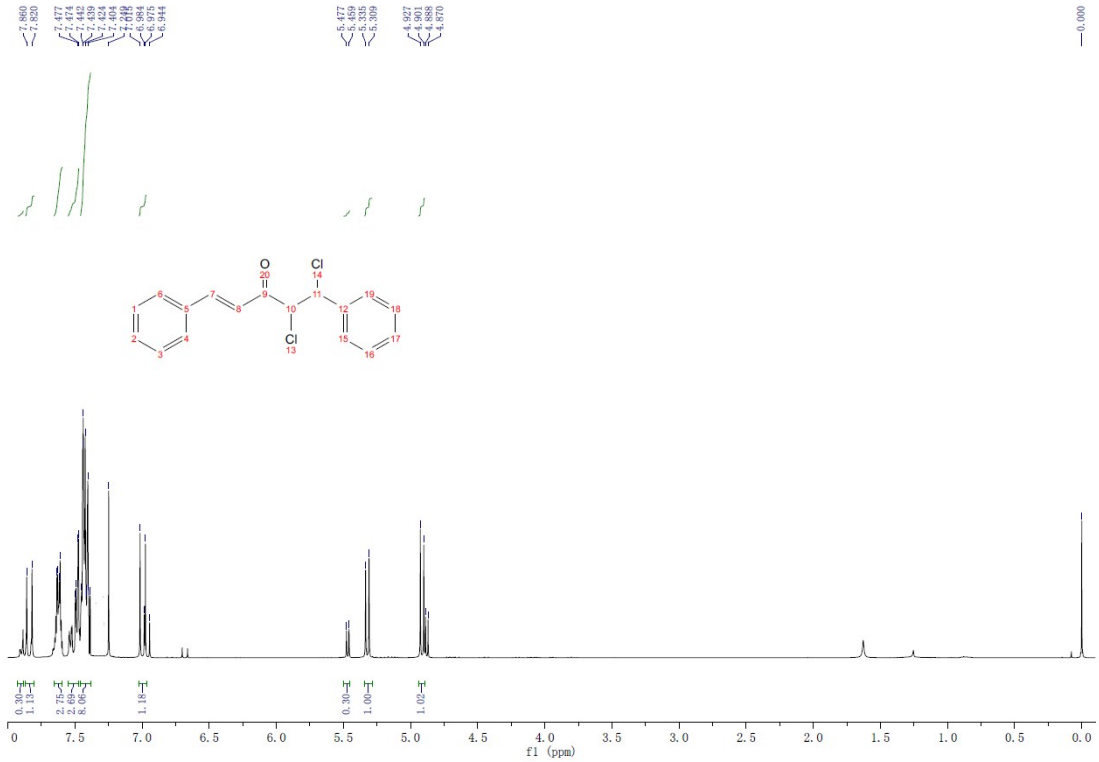


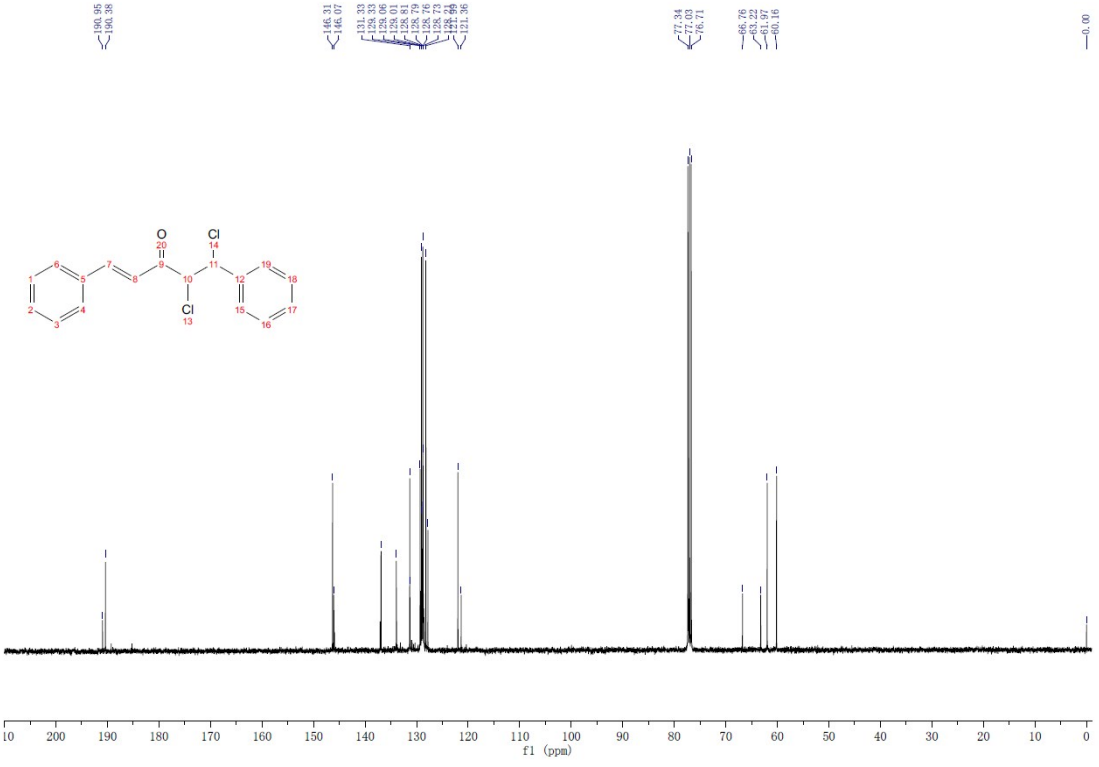
(trans)-3,4-dichloro-4-phenylbutan-2-one (4g)



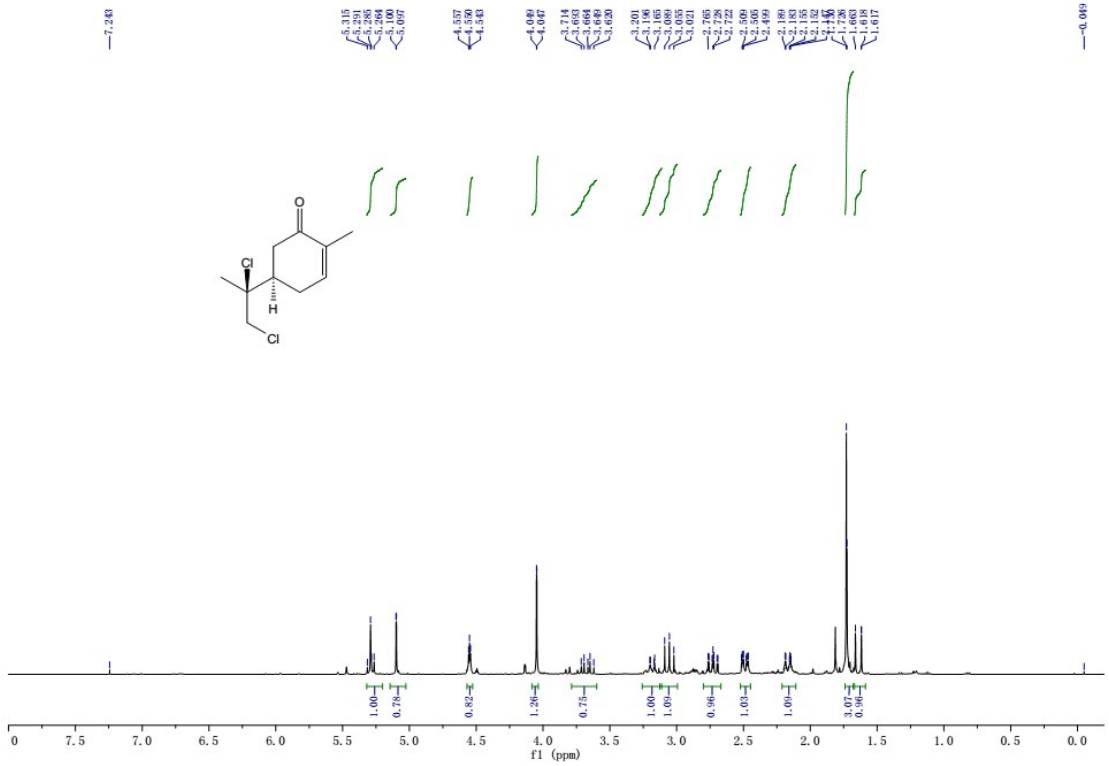


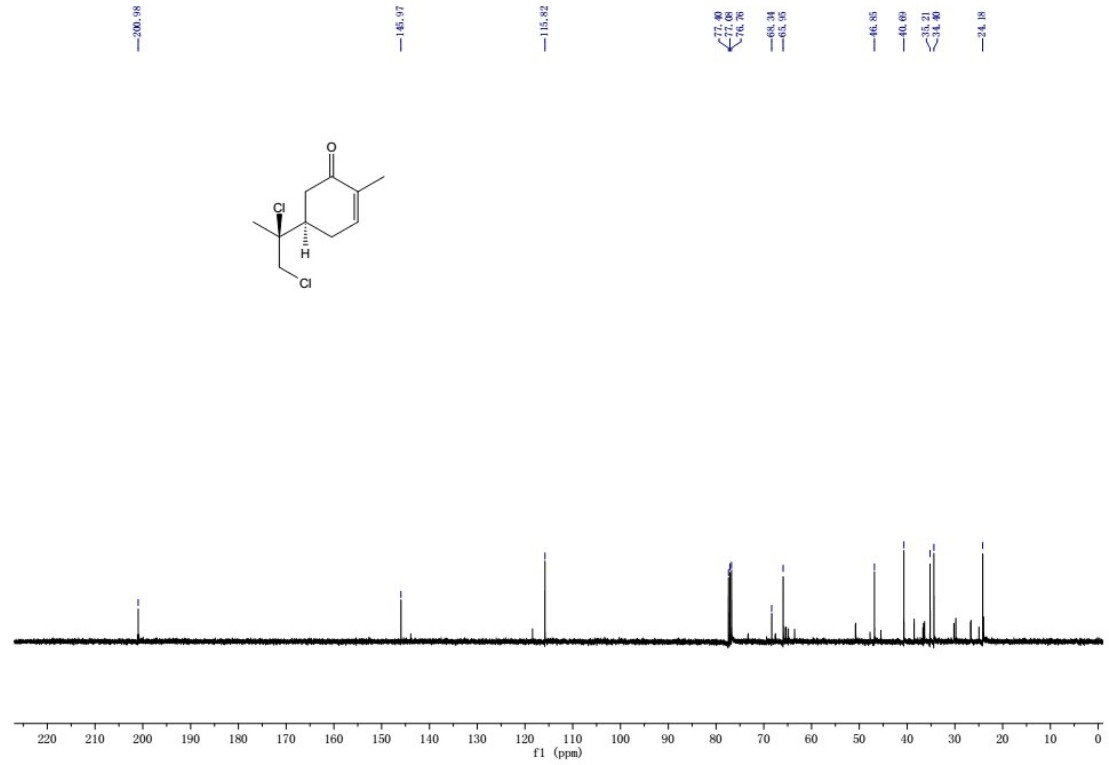
(trans)-4,5-dichloro-1,5-diphenylpent-1-en-3-one (4h)



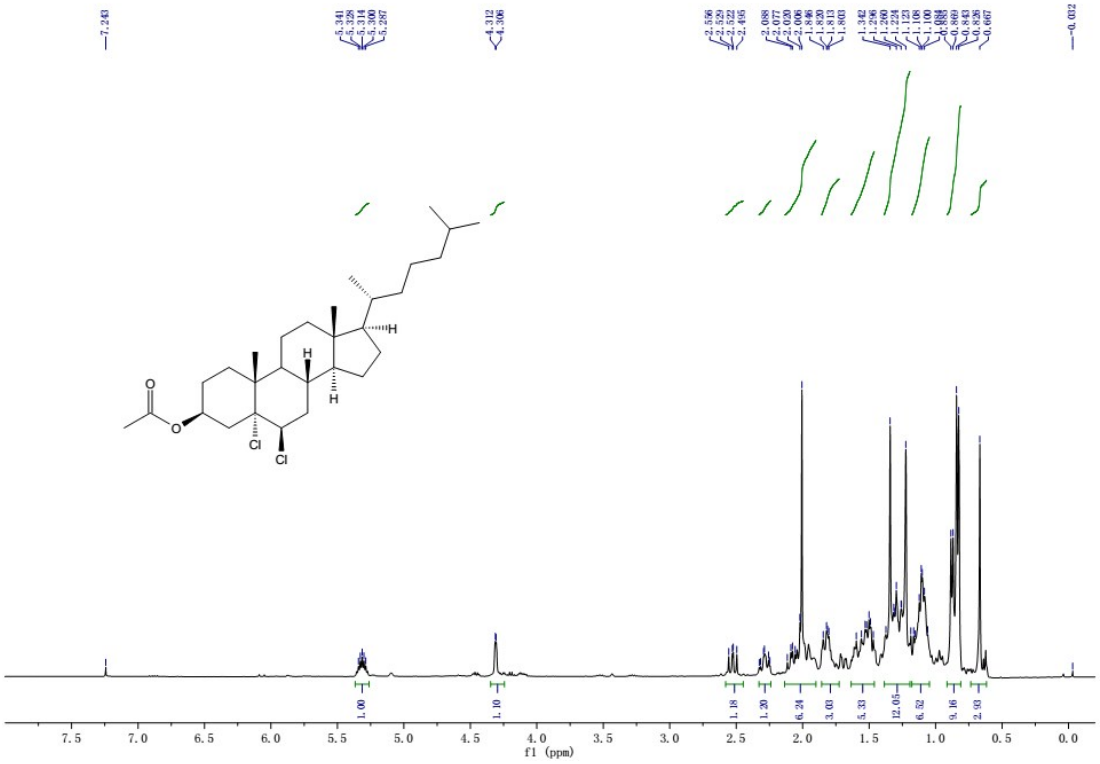


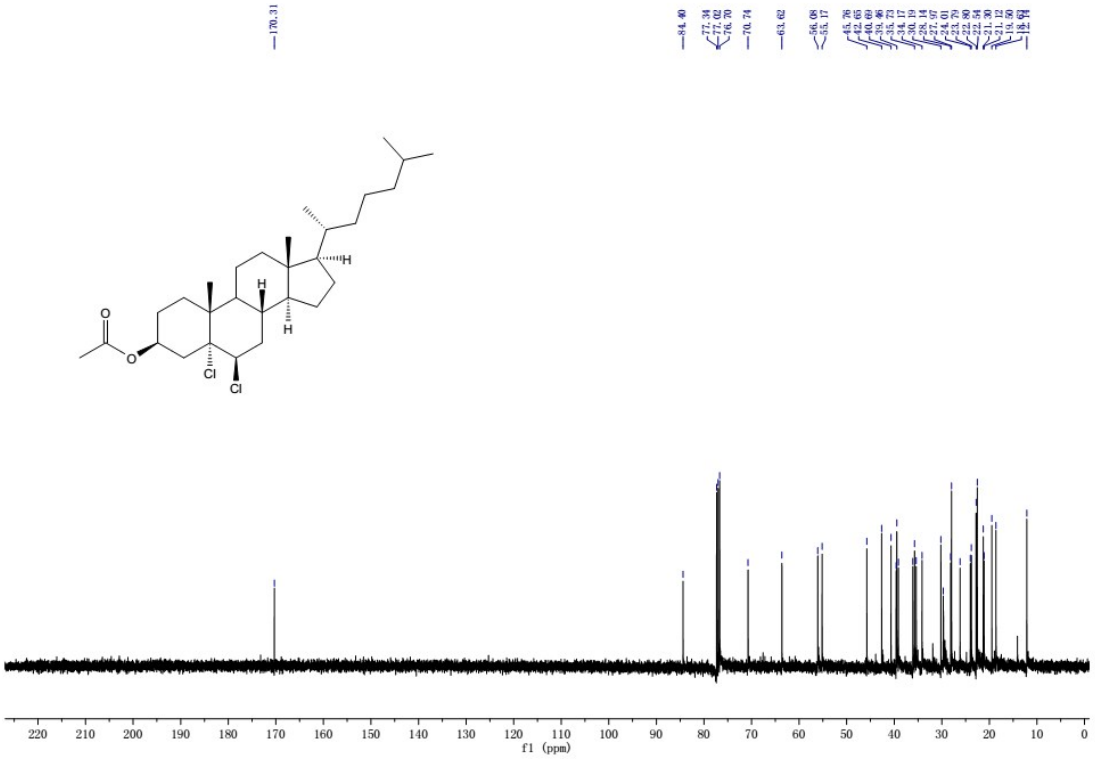
(8,9-Dichloro-p-menth-6-en-2-one (4i)



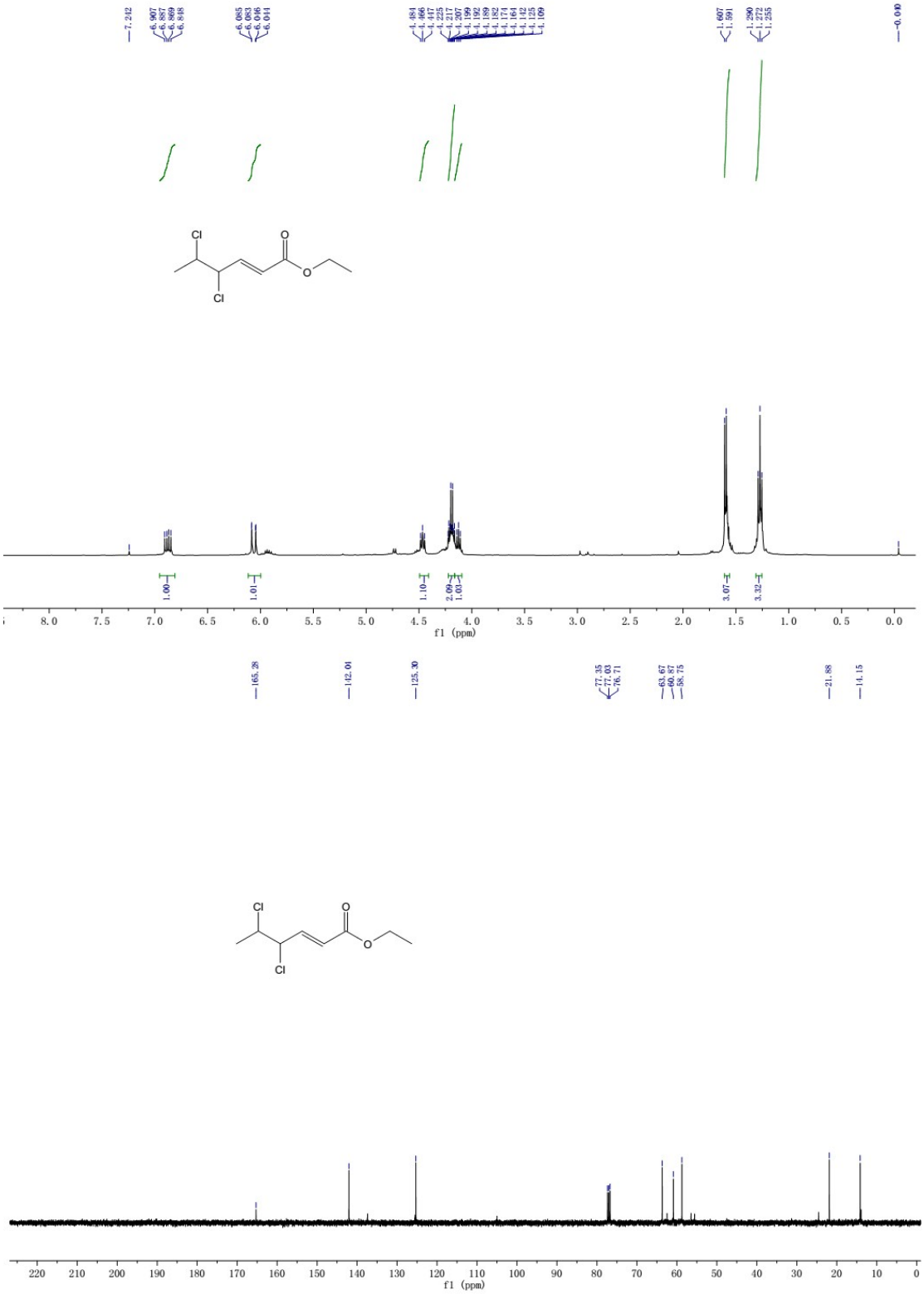


5α,6β-Dichlorocholestan-3β-yl acetate (4j)





ethyl 4,5-dichlorohex-2-enoate(5)



3,4-dichloro-4-phenylbutane-1,2-diol (6)