Supporting Information

Metal-free Synthesis of 1,3-Dichloro-1,5-diarylpentan-5-ones *via* Cascade Oxidative Radical Addition of Styrenes with $CHCl_3$

Min Liu[a,b], Bifu Liu[a,b,*], Qian Wang[a], Kejun Feng[a], Yuanhua Li [a], Lixin Liu[a] and Jiaen Tong[a]

a School of Chemistry and Materials Engineering, Huizhou University, Huizhou, 516007, Guangdong, China

b Guangdong Provincial Key Laboratory of Electronic Functional Materials and Devices, Huizhou University, Huizhou 516001, Guangdong, P. R. China

E-mail: liubf@hzu.edu.cn;

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1. General information

All the reactions were carried out at room temperature for 24 h in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvent were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker model Bruker AV-400 spectrometer in solutions of $CDCl_3$ using tetramethyl silane as the internal standard; δ values are given in ppm, and coupling constants (*J*) in Hz. HR-MS were obtained on a Q-TOF micro spectrometer.

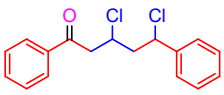
2. General experimental procedure for the synthesis of 1,3-Dichloro-1,5-diarylpentan-5-ones

Typical procedure: 1,3-dichloro-1,5-diphenylpentan-5-one (2a).

A mixture of styrene (1a) (104 mg, 1.0 mmol), TBHP (643 mg, 5.0 mmol, 70% in water), $CHCl_3$ (1.0 mL) and NEt_3 (1.0 mL) were added in a round-bottom flask, and the resulting solution was stirred at 70 °C for 12 h. The mixture was purified by column chromatography on silica gel to afford product **2a** with PE/EA = 20/1 as the eluent.

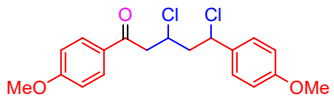
3. Characterization and analytical data of products

1,3-dichloro-1,5-diphenylpentan-5-one (2a)



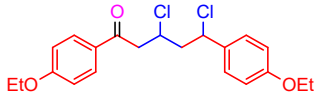
Yield: 78%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.90 (d, *J* = 7.2Hz,2H),7.56 (t, *J* = 7.2Hz,1H),7.44 (t, *J* = 7.2Hz,2H),7.34 (t, *J* = 7.2Hz,2H),7.26 (m, 3H),5.30 (dd, *J* = 10.0Hz,*J* = 3.6Hz, 1H),3.71 (m, 1H),3.31 (m, 2H),2.67 (m, 1H),2.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.6, 141.6, 136.8, 133.2, 129.0, 128.6, 128.0, 127.5, 127.2, 71.6, 49.6, 44.9, 38.6; HRMS (ESI): calcd for $C_{17}H_{17}Cl_2O$: $[M+H^+]$ 307.0651, found 307.0667.

1,3-dichloro-1,5-bis(4-methoxyphenyl)pentan-5-one (2b)



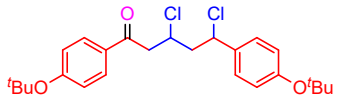
Yield: 77%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.29 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.62 (m, 1H), 3.25 (m, 2H), 2.64 (m, 1H), 2.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.3, 163.5, 158.6, 133.6, 130.3, 129.9, 128.5, 114.3, 113.7, 71.8, 55.4, 55.2, 49.8, 44.8, 38.1; HRMS (ESI): calcd for $C_{19}H_{21}Cl_2O_3$: [M+H$^+$] 367.0862, found 367.0865.

1,3-dichloro-1,5-bis(4-ethoxyphenyl)pentan-5-one (2c)



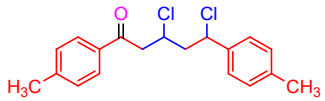
Yield: 81%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.29 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.63 (m, 1H), 3.23 (m, 2H), 2.64 (m, 1H), 2.46 (m, 1H), 1.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.1,, 162.9, 157.8, 138.4, 130.3, 129.7, 128.5, 114.8, 114.1, 71.8, 63.7, 63.4, 49.8, 44.8, 38.1, 14.8, 14.6; HRMS (ESI): calcd for $C_{21}H_{25}Cl_2O_3$: [M+H$^+$] 395.1175, found 395.1171.

1,5-bis(4-tert-butoxyphenyl)-1,3-dichloropentan-5-one (2d)



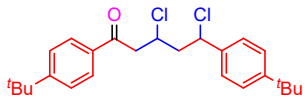
Yield: 76%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.29 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.64 (m, 1H), 3.24 (m, 2H), 2.67 (m, 1H), 2.48 (m, 1H), 1.41 (s, 9H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.7, 160.5, 154.4, 136.3, 131.4, 129.5, 127.9, 124.4, 122.2, 78.4, 77.3, 71.7, 49.6, 44.8, 38.2, 28.9, 28.8; HRMS (ESI): calcd for $C_{25}H_{33}Cl_2O_3$: [M+H$^+$] 451.1801, found 451.1807.

1,3-dichloro-1,5-dip-tolylpentan-5-one (2e)



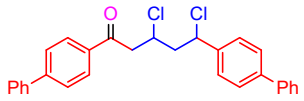
Yield: 80%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.28 (d, *J* = 8.4Hz, 2H),7.24 (d, *J* = 8.4 Hz, 2H),7.16 (m, 4H), 5.30 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.65 (m, 1H), 3.25 (m, 2H), 2.66 (m, 1H), 2.50 (m, 1H), 2.41 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.3, 144.0, 138.6, 136.8, 134.3, 129.6, 129.3, 128.1, 127.4, 71.8, 49.6, 44.9, 38.3, 21.6, 21.0; HRMS (ESI): calcd for $C_{19}H_{21}Cl_2O$: [M+H$^+$] 335.0964, found 335.0977.

1,5-bis(4-tert-butylphenyl)-1,3-dichloropentan-5-one (2f)



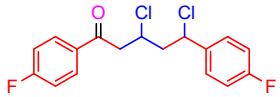
Yield: 75%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.31 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.67 (m, 1H), 3.29 (m, 2H), 2.67 (m, 1H), 2.51 (m, 1H), 1.34 (s, 9H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.4, 156.9, 150.0, 138.5, 134.3, 128.0, 127.1, 125.8, 125.5, 71.9, 49.6, 44.9, 38.1, 35.1, 34.4, 31.3, 31.0; HRMS (ESI): calcd for $C_{25}H_{33}Cl_2O$: [M+H$^+$] 419.1903, found 419.1906.

1,5-bis(4-phenylphenyl)-1,3-dichloropentan-5-one (2g)



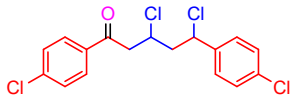
Yield: 82%, *d.r* > 20:1; Pale yellowpowder solid;mp: 60-62°C;^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.00 (d, *J* = 8.4 Hz,2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.60 (m, 6H), 7.42 (m, 8H), 5.38 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.79 (m, 1H), 3.38 (m, 2H), 2.75 (m, 1H), 2.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.9, 145.9, 140.6, 140.5, 140.2,139.7, 135.4, 128.9, 128.7, 128.6, 128.3, 128.0, 127.7, 127.3, 127.29, 127.26, 127.0, 71.6, 49.6, 45.0, 38.4; HRMS (ESI): calcd for $C_{29}H_{25}Cl_2O$: [M+H$^+$] 459.1277, found 459.1263.

1,3-dichloro-1,5-bis(4-fluorophenyl)pentan-5-one (2h)



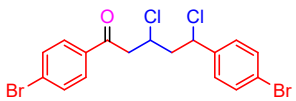
Yield: 66%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.91 (dd, *J* = 4.2 Hz,*J* = 8.8 Hz, 2H), 7.25 (dd, *J* = 4.2 Hz,*J* = 8.8 Hz, 2H), 7.12 (t, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.29 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.70 (m, 1H), 3.28 (m, 2H), 2.66 (m, 1H), 2.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 195.7, 165.2 (d, $^{1}J_{C\text{-}F}$ = 253.0 Hz), 162.6 (d, $^{1}J_{C\text{-}F}$ = 247.0 Hz),137.1(d, $^{4}J_{C\text{-}F}$ = 3.9 Hz),133.1 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz),130.5 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz),130.5 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz),115.9 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz),115.9 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 71.3, 49.6, 44.8, 38.0; HRMS (ESI): calcd for $C_{17}H_{15}Cl_2F_2O$: [M+H$^+$] 343.0463, found 343.0481.

1,3-dichloro-1,5-bis(4-chlorophenyl)pentan-5-one (2i)



Yield: 70%, *d.r* > 20:1;Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.30 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.70 (m, 1H), 3.29 (m, 2H), 2.67 (m, 1H), 2.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.0, 139.9, 134.9, 133.1, 129.3, 129.2, 129.0, 128.9, 71.2, 49.4, 44.7, 38.0; HRMS (ESI): calcd for $C_{17}H_{15}Cl_4O$: [M+H$^+$] 374.9872, found 374.9899.

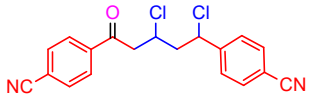
1,5-bis(4-bromophenyl)-1,3-dichloropentan-5-one (2j)



Yield: 77%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.75 (d, *J* = 8.8Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.29 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.69 (m, 1H), 3.27 (m, 2H), 2.66 (m, 1H), 2.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ196.1, 140.4, 135.3, 132.1, 132.0, 129.4, 129.3, 128.6, 121.2, 71.2, 49.4, 44.6, 38.1; HRMS (ESI): calcd for $C_{17}H_{15}Br_2Cl_2O$:

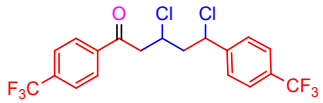
[M+H$^+$] 462.8861, found 462.8865.

4,4'-(1,3-dichloro-5-oxopentane-1,5-diyl)dibenzonitrile (2k)



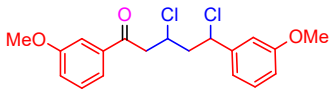
Yield: 47%, *d.r* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.30 (dd, *J* = 9.5, 3.8 Hz, 1H), 3.83 (d, *J* = 7.0 Hz, 1H), 3.39 (dd, *J* = 9.4, 6.9 Hz, 2H), 2.70 (d, *J* = 9.7 Hz, 1H), 2.60 (d, *J* = 10.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 195.37, 146.83, 139.18, 132.89, 132.66, 128.56, 128.36, 118.37, 117.66, 116.90, 111.58, 70.71, 49.03, 44.69, 38.48.

1,3-dichloro-1,5-bis(4-(trifluoromethyl)phenyl)pentan-5-one (2l)



Yield: 43%, *d.r* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.31 (dd, *J* = 9.8, 3.7 Hz, 1H), 3.88 – 3.80 (m, 1H), 3.45 (dd, *J* = 17.5, 7.3 Hz, 1H), 3.36 (dd, *J* = 17.5, 6.6 Hz, 1H), 2.73 (ddd, *J* = 14.2, 9.8, 4.4 Hz, 1H), 2.60 (ddd, *J* = 14.3, 10.7, 3.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 196.01, 145.49, 139.11, 135.26, 134.93, 134.61, 134.28, 130.30, 129.97, 129.65, 129.32, 128.29, 128.05, 126.11, 126.07, 126.03, 126.00, 125.87, 125.84, 125.80, 125.76, 125.29, 124.81, 122.59, 122.10, 70.97, 49.28, 44.90, 38.35.

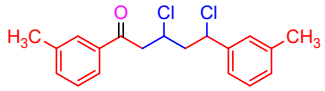
1,3-dichloro-1,5-bis(3-methoxyphenyl)pentan-5-one (2m)



Yield: 84%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.48 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.11 (m, 1H), 8.78 (m, 3H), 5.32 (dd, *J* = 10.0 Hz,*J* = 3.2 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.327 (m, 2H), 2.67 (m, 1H), 2.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.4, 159.9, 159.7, 143.2, 138.1, 130.0,

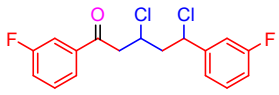
129.6, 120.6, 119.8, 119.7, 113.7, 112.2, 71.6, 55.4, 55.2, 49.5, 44.9, 38.7; HRMS (ESI): calcd for $C_{19}H_{21}Cl_2O_3$: [M+H$^+$] 367.0862, found 367.0869.

1,3-dichloro-1,5-dim-tolylpentan-5-one (2n)



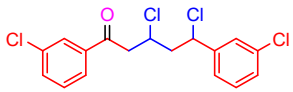
Yield: 82%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.71 (m, 2H), 7.35 (m, 2H), 7.22 (m, 2H), 7.06 (br, 3H), 5.32 (dd, *J* = 10.0 Hz,*J* = 3.2 Hz, 1H), 3.66 (m, 1H), 3.32 (m, 2H), 2.67 (m, 1H), 2.51 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.8, 141.6, 138.6, 138.4, 136.8, 133.9, 128.8, 128.5, 128.4, 128.3, 128.0, 125.2, 124.5, 71.7, 49.6, 45.0, 38.6, 21.5, 21.3; HRMS (ESI): calcd for $C_{19}H_{21}Cl_2O$: [M+H$^+$] 335.0964, found 335.0969.

1,3-dichloro-1,5-bis(3-fluorophenyl)pentan-5-one (2o)



Yield: 68%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.68 (m, 1H), 7.57 (m, 1H), 7.43 (m, 1H), 7.29 (m, 1H), 7.25 (m, 1H), 7.07 (m, 1H), 6.97 (m, 2H), 5.31 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.72 (m, 1H), 3.31 (m, 2H), 2.66 (m, 1H), 2.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 195.8, 162.9 (d, $^1J_{C\text{-}F}$ = 254.7 Hz), 162.6 (d, $^1J_{C\text{-}F}$ = 253.8 Hz), 144.0 (d, $^3J_{C\text{-}F}$ = 6.7 Hz), 138.6 (d, $^3J_{C\text{-}F}$ = 6.1 Hz), 130.5 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 130.3 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 123.7 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 123.3 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 120.4 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 114.7 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 114.5 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 114.6 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 71.1, 49.4, 44.8, 38.3; HRMS (ESI): calcd for $C_{17}H_{15}Cl_2F_2O$: [M+H$^+$] 343.0463, found 343.0453.

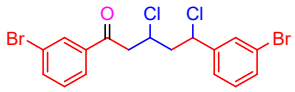
1,3-dichloro-1,5-bis(3-chlorophenyl)pentan-5-one (2p)



Yield: 73%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.86 (m, 1H),

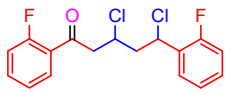
7.67 (m, 1H), 7.54 (m, 1H), 7.41 (m, 1H), 7.25 (m, 3H), 7.18 (m, 1H), 5.31 (dd, J = 10.0 Hz,J = 3.6 Hz, 1H), 3.71 (m, 1H), 3.31 (m, 2H), 2.67 (m, 1H), 2.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ195.8, 143.5, 138.1, 135.0, 134.9, 133.3, 130.3, 130.0, 128.1, 127.6, 127.5, 126.0, 71.1, 49.3, 44.7, 38.2; HRMS (ESI): calcd for $C_{17}H_{15}Cl_4O$: [M+H$^+$] 374.9872, found 374.9858.

1,5-bis(3-bromophenyl)-1,3-dichloropentan-5-one (2q)



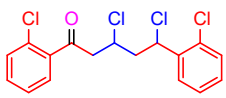
Yield: 71%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ8.01 (t, J = 1.6 Hz,1H), 7.82 (d, J = 8.0 Hz,1H), 7.68 (d, J = 8.0 Hz,1H), 7.40 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H),7.22 (m, 2H), 5.31 (dd, J = 10.0 Hz,J = 3.6 Hz, 1H), 3.69 (m, 2H), 3.28 (m, 2H), 2.65 (m, 1H), 2.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ195.7, 143.8, 138.2, 136.2, 130.62, 130.60, 130.4, 130.3, 126.5, 126.4, 123.1, 123.0, 71.1, 49.3, 44.7, 38.2; HRMS (ESI): calcd for $C_{17}H_{15}Br_2Cl_2O$: [M+H$^+$] 462.8861, found 462.8874.

1,3-dichloro-1,5-bis(2-fluorophenyl)pentan-5-one (2r)



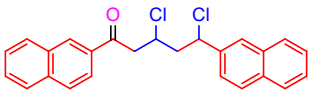
Yield: 71%, *d.r* > 20:1; Colorless powder solid;mp: 58-60°C;^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.79 (m, 1H), 7.52 (m, 1H), 7.24 (m, 3H), 7.08 (m, 3H), 5.37 (dd, J = 9.6 Hz,J = 4.0 Hz, 1H), 3.89 (m, 1H), 3.43 (m, 2H), 2.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 195.8, 162.7(d, $^1J_{C\text{-}F}$ = 254.0 Hz), 160.2 (d, $^1J_{C\text{-}F}$ = 253.8 Hz), 134.7(d, $^3J_{C\text{-}F}$ = 9.1 Hz), 130.6(d, $^4J_{C\text{-}F}$ = 2.5 Hz), 130.3(d, $^3J_{C\text{-}F}$ = 5.2 Hz), 128.8(d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.0(d, $^2J_{C\text{-}F}$ = 16.4 Hz), 125.3 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 124.5 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 124.4 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 21.2 Hz),71.6, 48.1, 47.9, 34.3; HRMS (ESI): calcd for $C_{17}H_{15}Cl_2F_2O$: [M+H$^+$] 343.0463, found 343.0466.

1,3-dichloro-1,5-bis(2-chlorophenyl)pentan-5-one (2s)



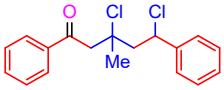
Yield: 63%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (m, 3H), 7.24 (m, 1H), 7.41 (m, 5H), 5.44 (dd, *J* = 8.8 Hz,*J* = 4.8 Hz, 1H), 4.14 (m, 1H), 3.38 (d, *J* = 7.2 Hz, 2H), 2.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ200.7, 138.9, 138.4, 134.0, 131.8, 130.49, 130.44, 130.1, 128.9, 128.4, 127.3, 126.9, 71.2, 47.9, 47.7, 36.2; HRMS (ESI): calcd for $C_{17}H_{15}Cl_4O$: [M+H$^+$] 374.9872, found 374.9867.

1,3-dichloro-1,5-di(naphthalen-3-yl)pentan-5-one (2u)



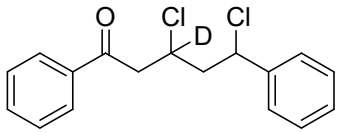
Yield: 80%, *d.r* > 20:1; Pale yellow powder solid;mp: 72-74°C;^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.42 (s, 1H), 7.97 (m, 2H), 7.86 (m, 5H), 7.77 (s, 1H), 7.51 (m, 5H), 5.34 (dd, *J* = 10.0 Hz,*J* = 3.6 Hz, 1H), 3.96 (m, 1H), 3.57 (m, 2H), 2.83 (m, 1H), 2.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.4, 139.0, 135.6, 134.1, 133.5, 132.6, 132.4, 129.7, 129.5, 128.9, 128.5, 128.4, 127.78, 127.72, 127.67, 126.8, 126.6, 126.3, 125.9, 125.2, 123.7, 71.6, 49.6, 45.0, 38.9; HRMS (ESI): calcd for $C_{25}H_{21}Cl_2O$: [M+H$^+$] 407.0964, found 407.0971.

1,3-dichloro-3-methyl-1,5-diphenylpentan-5-one (2w)



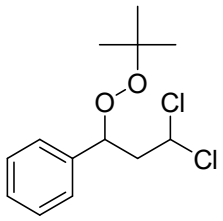
Yield: 66%, *d.r* > 20:1; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.30 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 3.86 (m, 1H), 3.40 (m, 2H), 2.78 (m, 2H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ197.9, 144.1, 136.8, 133.1, 128.7, 128.5, 128.0, 127.8, 126.7, 89.9, 54.8, 46.6, 39.0, 37.7; HRMS (ESI): calcd for $C_{18}H_{19}Cl_2O$: [M+H$^+$] 321.0807, found 321.0814.

3-deuterium-1,3-dichloro-1,5-diphenylpentan-5-one (2a')



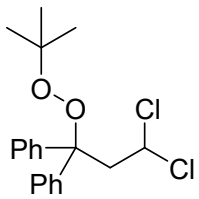
Yield: 78%; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.90 (d, *J* = 7.2Hz, 2H), 7.56 (t, *J* = 7.2Hz, 1H), 7.45 (t, *J* = 7.2Hz, 2H), 7.34 (t, *J* = 7.2Hz, 2H), 7.25 (m, 3H), 3.72 (m, 1H), 3.34 (m, 2H), 2.68 (m, 1H), 2.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 197.6, 141.6, 136.8, 133.2, 129.0, 128.6, 128.0, 127.5, 127.2, 49.4, 44.9, 38.6; HRMS (ESI): calcd for $C_{17}H_{16}DCl_2O$: [M+H$^+$] 308.0714, found 308.0731.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (3a)



Colorless oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (m, 5H), 5.84 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.13 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.87 (m, 1H), 2.52 (m, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 139.0, 128.5, 128.3, 126.9, 82.3, 80.7, 70.4, 49.4, 26.4; HRMS (ESI): calcd for $C_{13}H_{18}Cl_2NaO_2$: [M+Na$^+$] 299.0576, found 299.0579.

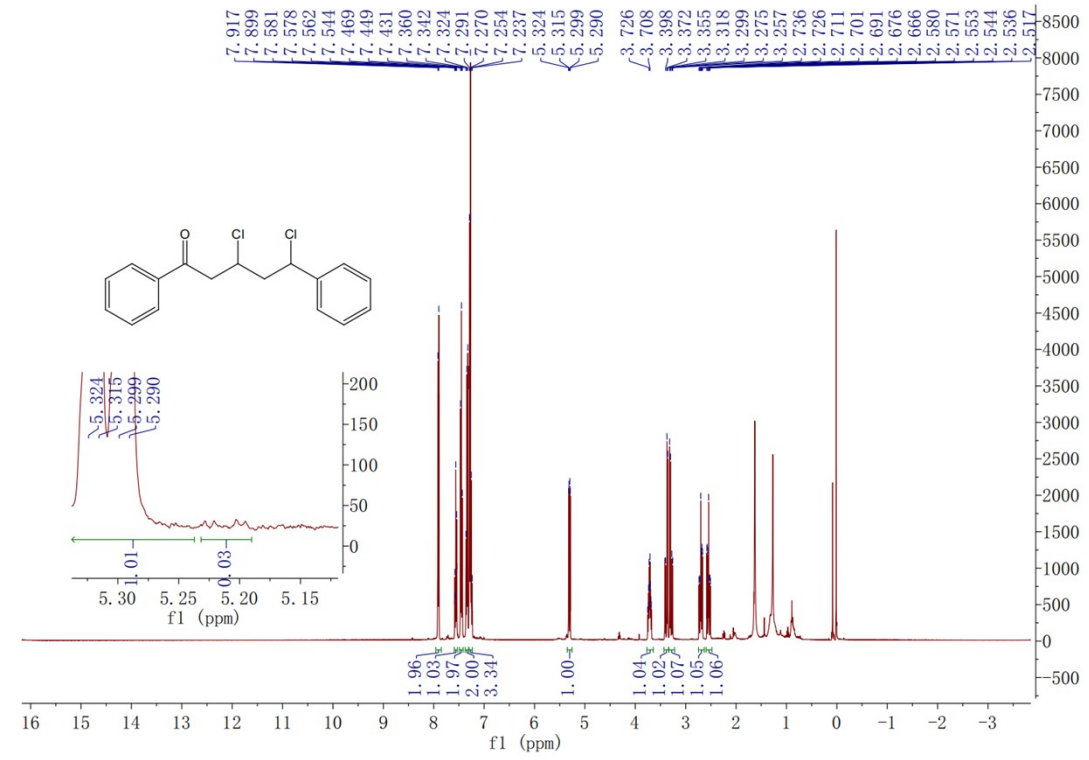
1-(tert-butylperoxy)-3,3-dichloro-1,1-diphenylpropane (4a)

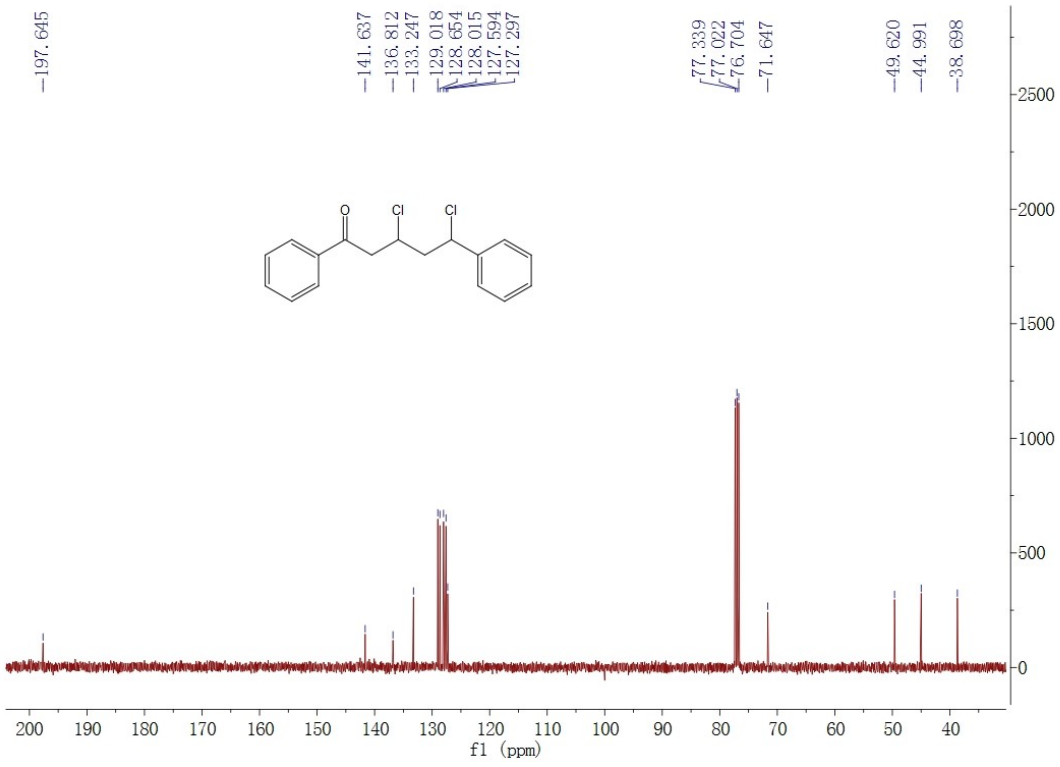


Colorless oily liquid; ^{1}H NMR (CDCl3, 400 Hz) δ 7.35 (m, 10H), 5.96 (dd, J =8.4 Hz, J = 8.4 Hz, 1H), 3.67 (d, J = 8.4 Hz, 2H), 1.28 (s, 9H); 13C NMR (CDCl3, 100 Hz) δ 143.1,127.9, 127.4, 126.8, 85.1, 76.8, 69.6, 50.5, 26.6; HRMS (ESI): calcd for C19H22Cl2NaO2: [M+Na+]375.0889, found 375.0888.

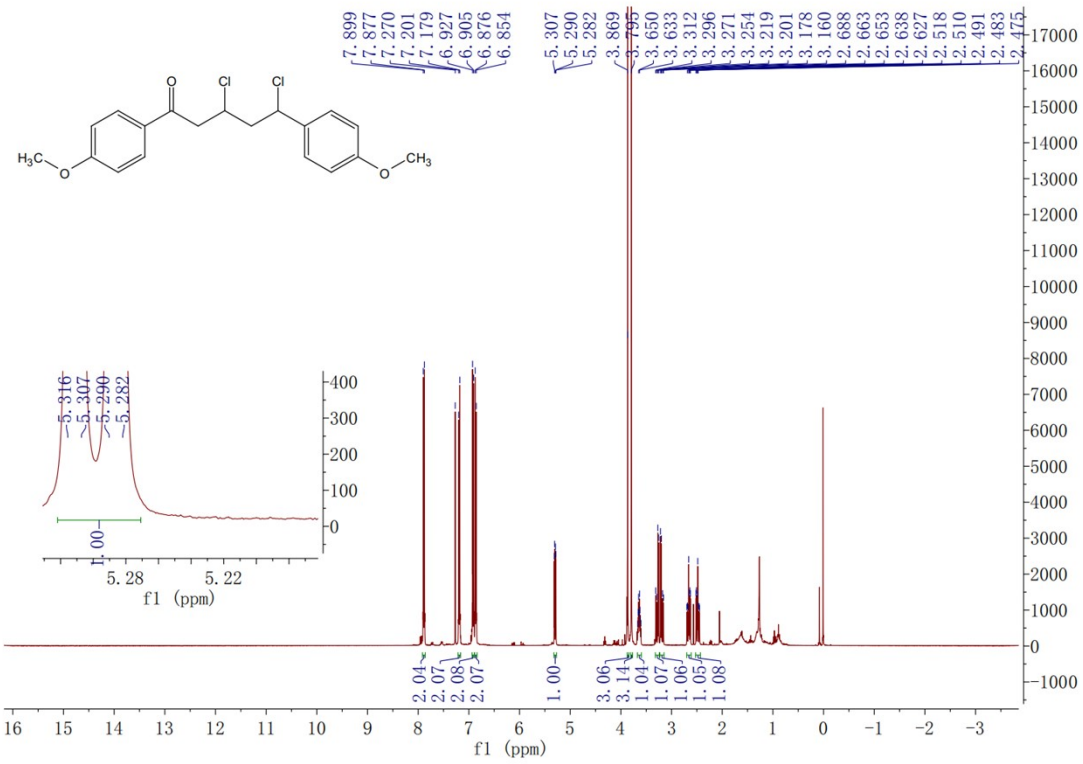
4. ^{1}H and ^{13}C-NMR spectrum of products

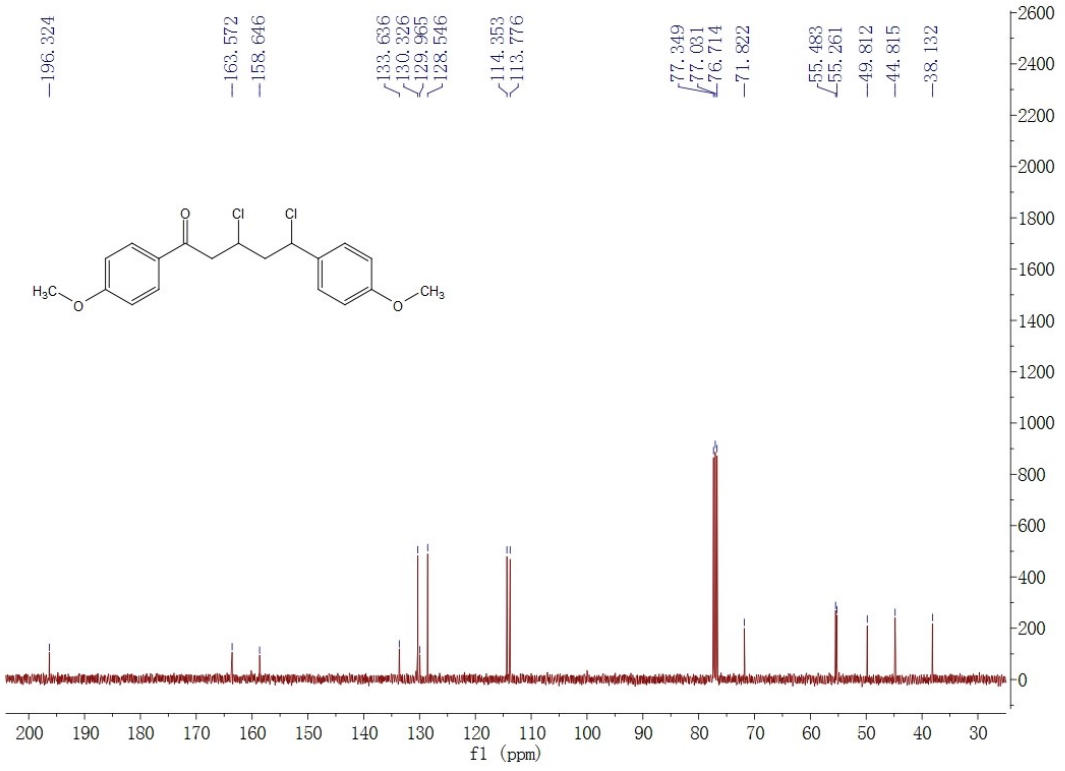
1,3-dichloro-1,5-diphenylpentan-5-one (2a)



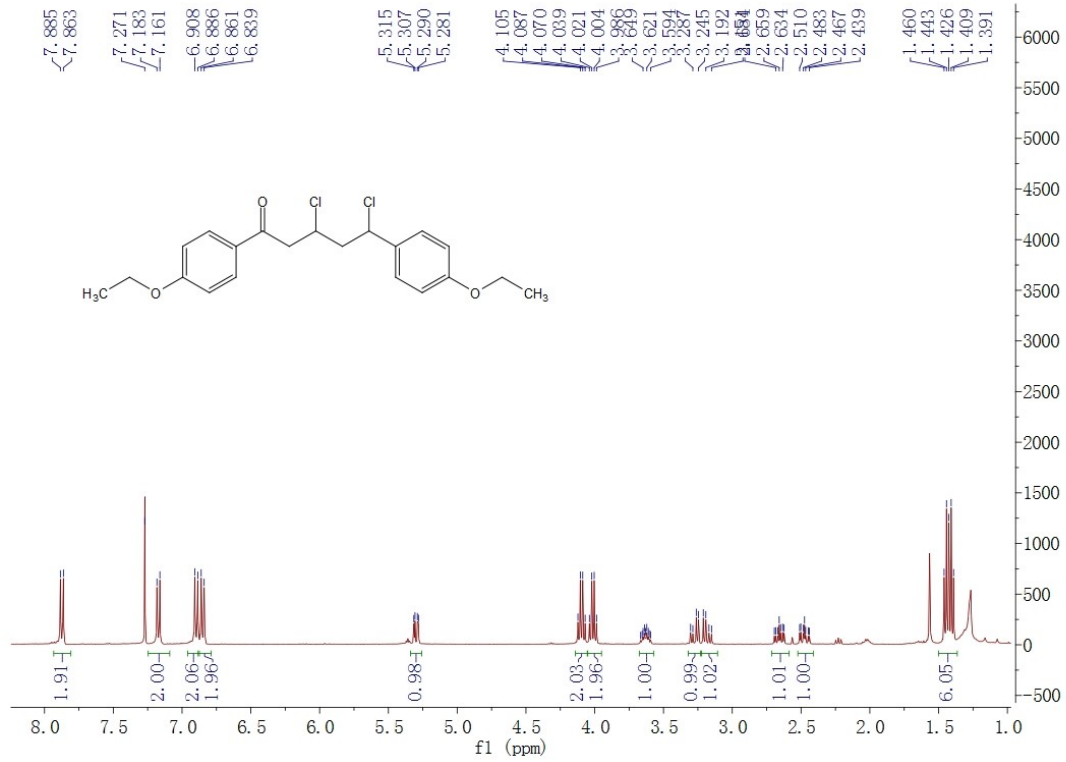


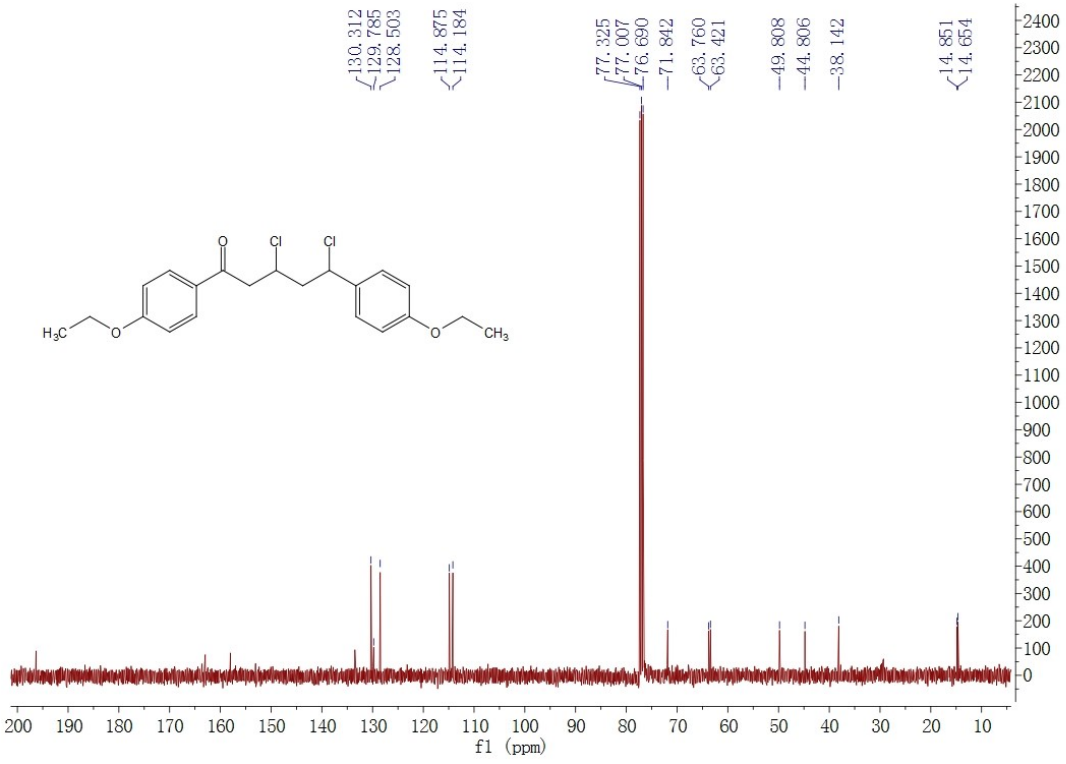
1,3-dichloro-1,5-bis(4-methoxyphenyl)pentan-5-one (2b)



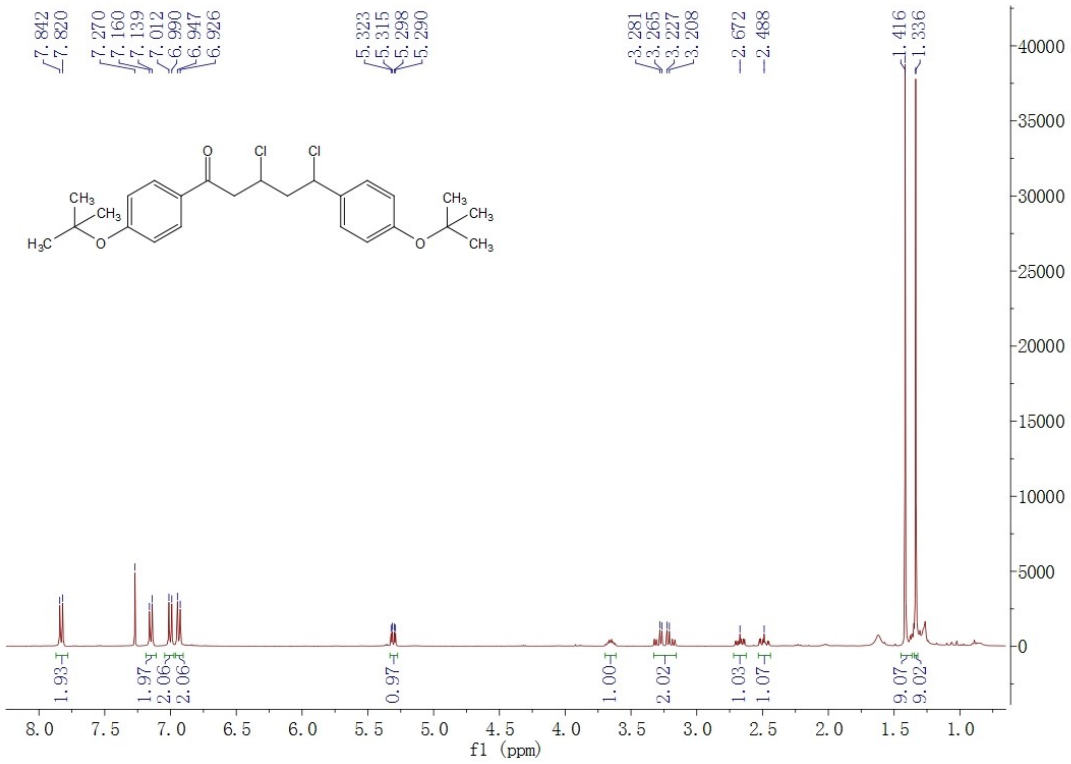


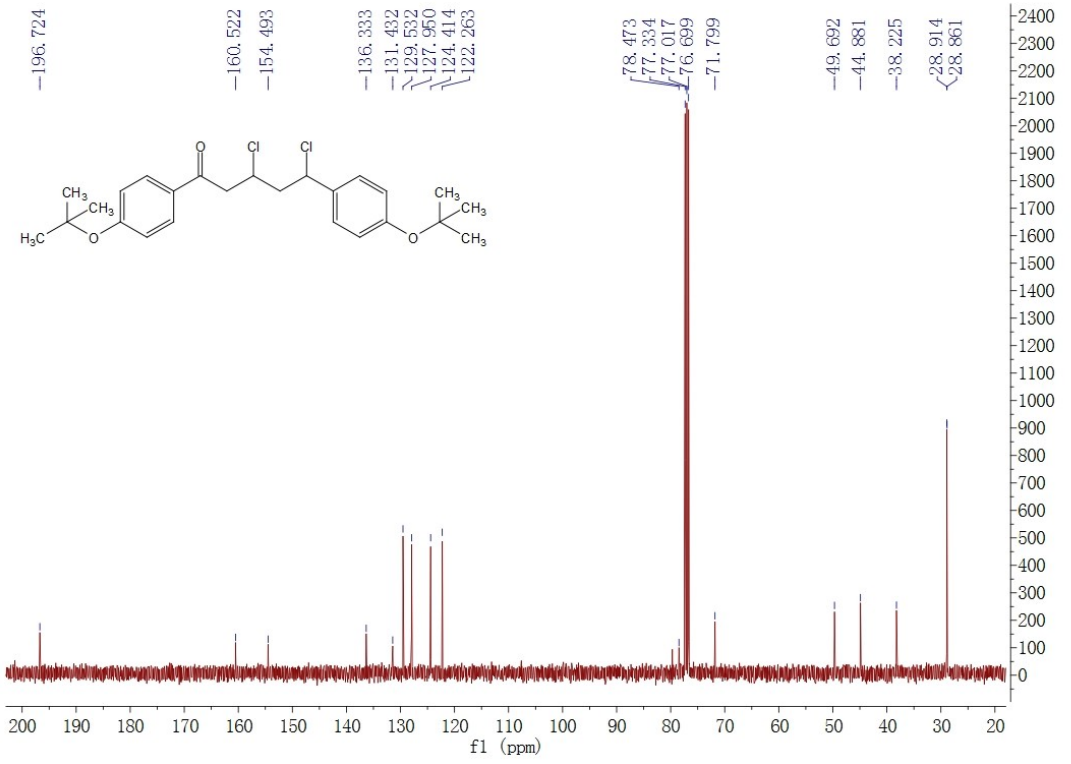
1,3-dichloro-1,5-bis(4-ethoxyphenyl)pentan-5-one (2c)



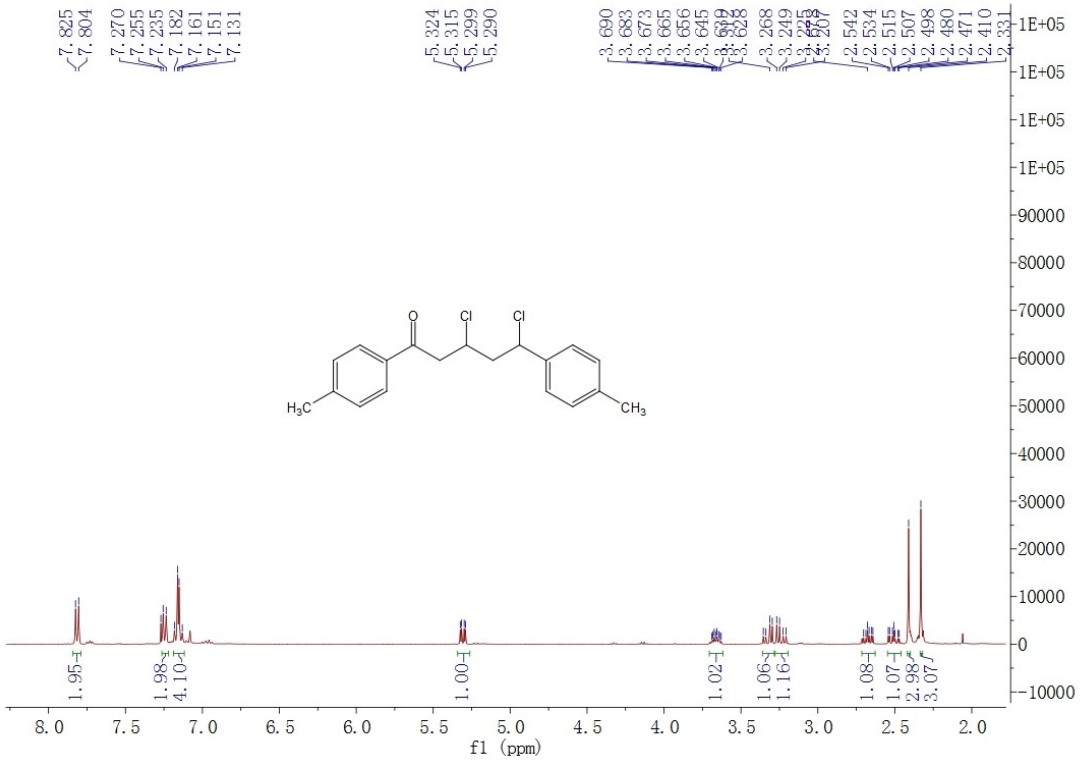


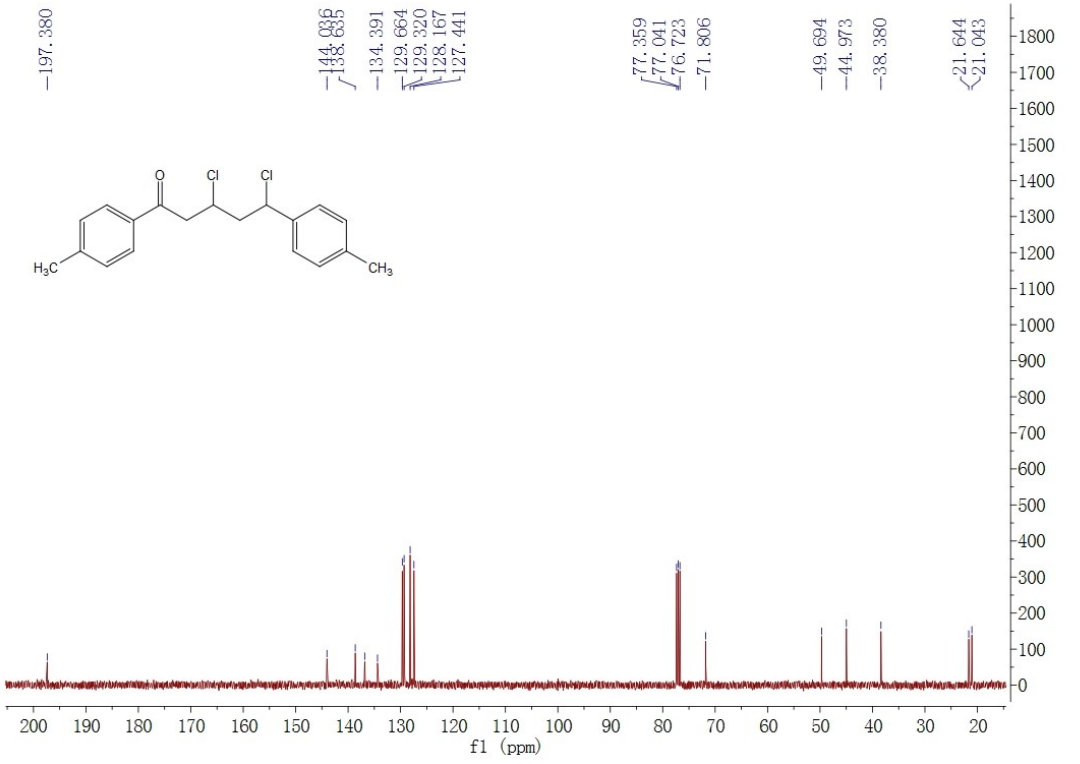
1,5-bis(4-tert-butoxyphenyl)-1,3-dichloropentan-5-one (2d)



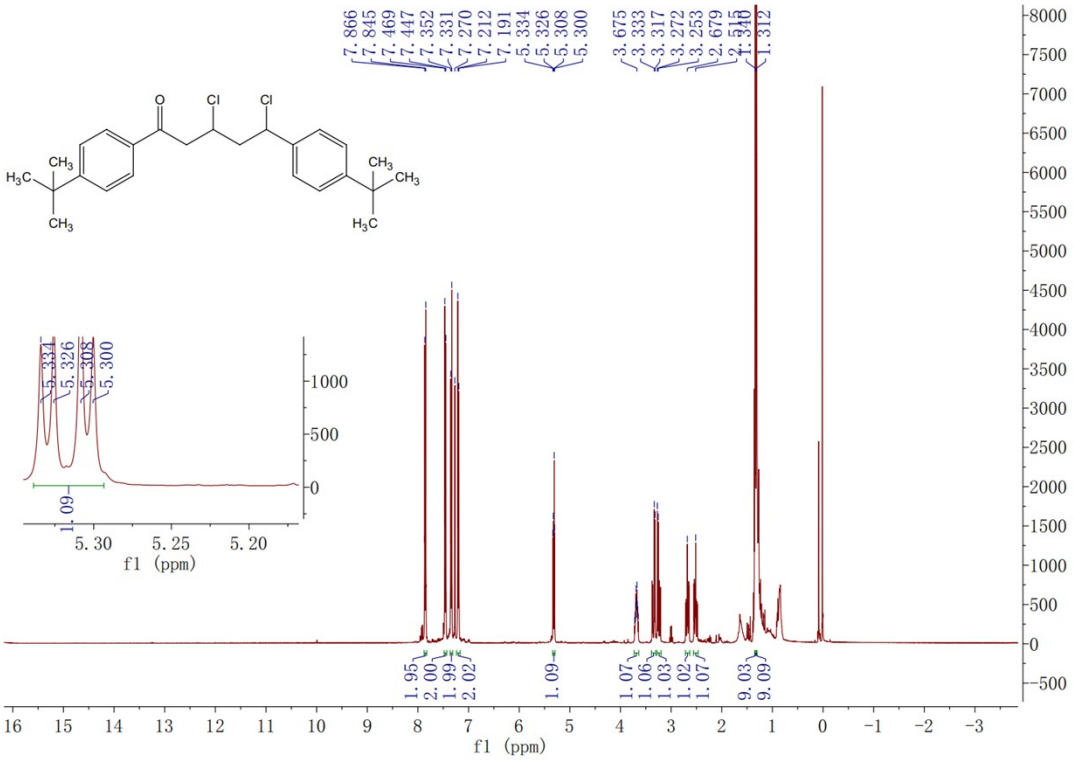


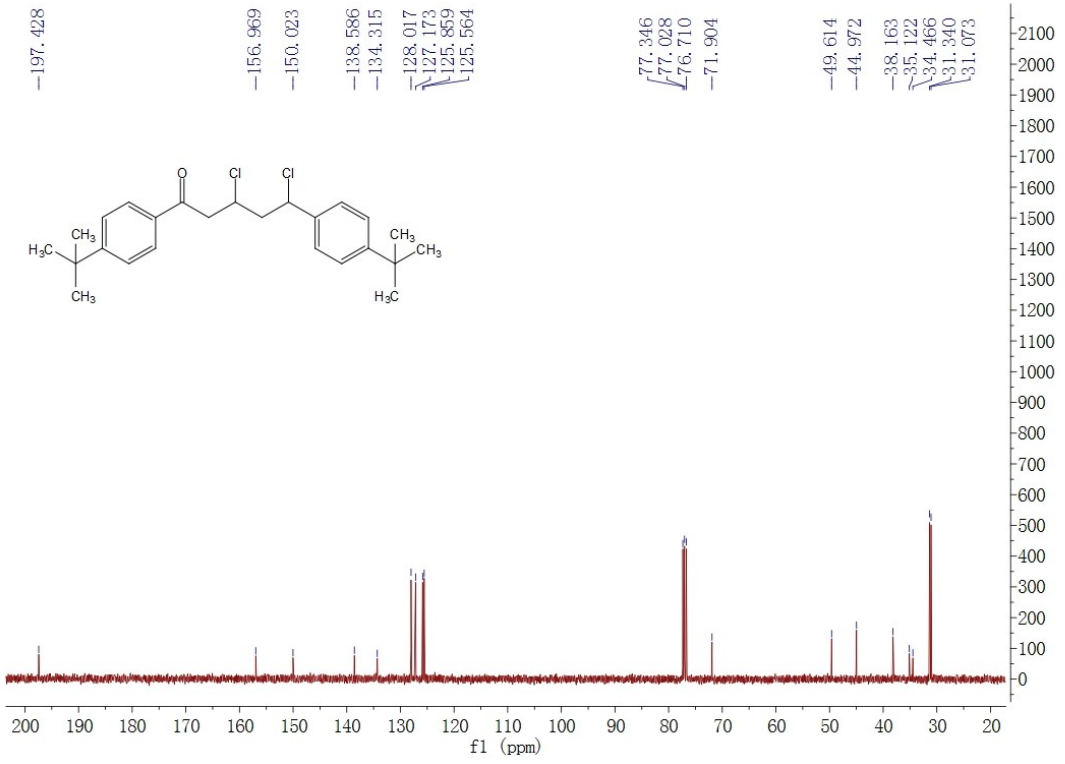
1,3-dichloro-1,5-dip-tolylpentan-5-one (2e)



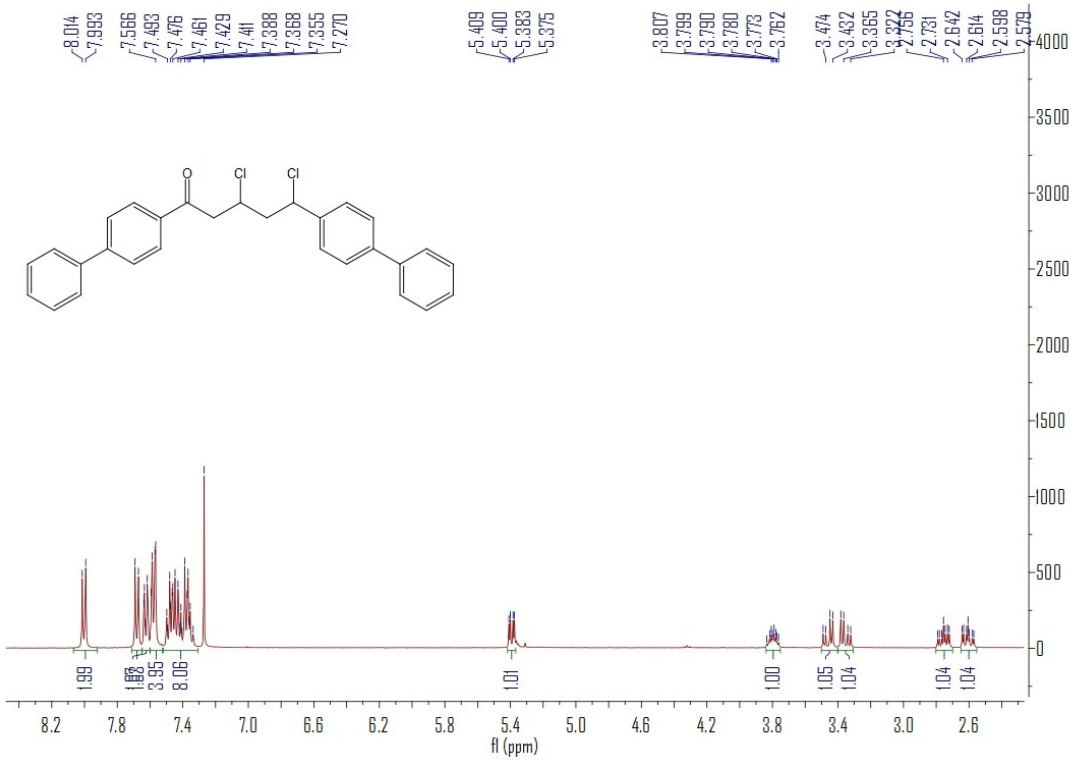


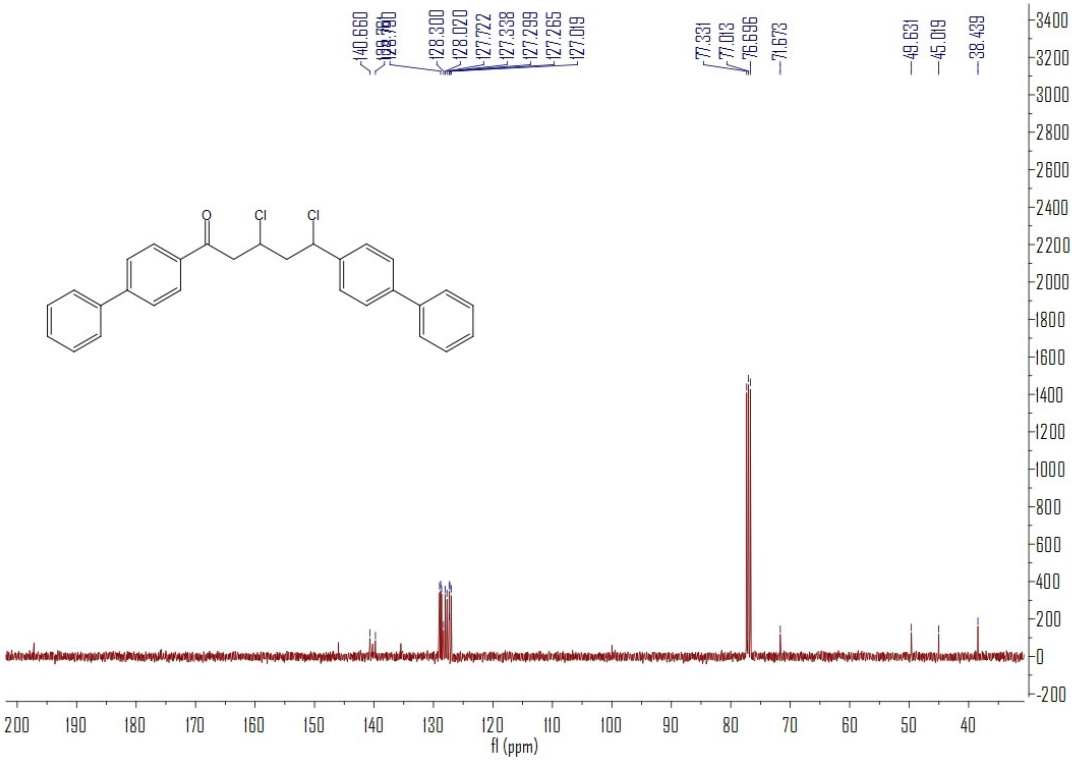
1,5-bis(4-tert-butylphenyl)-1,3-dichloropentan-5-one (2f)



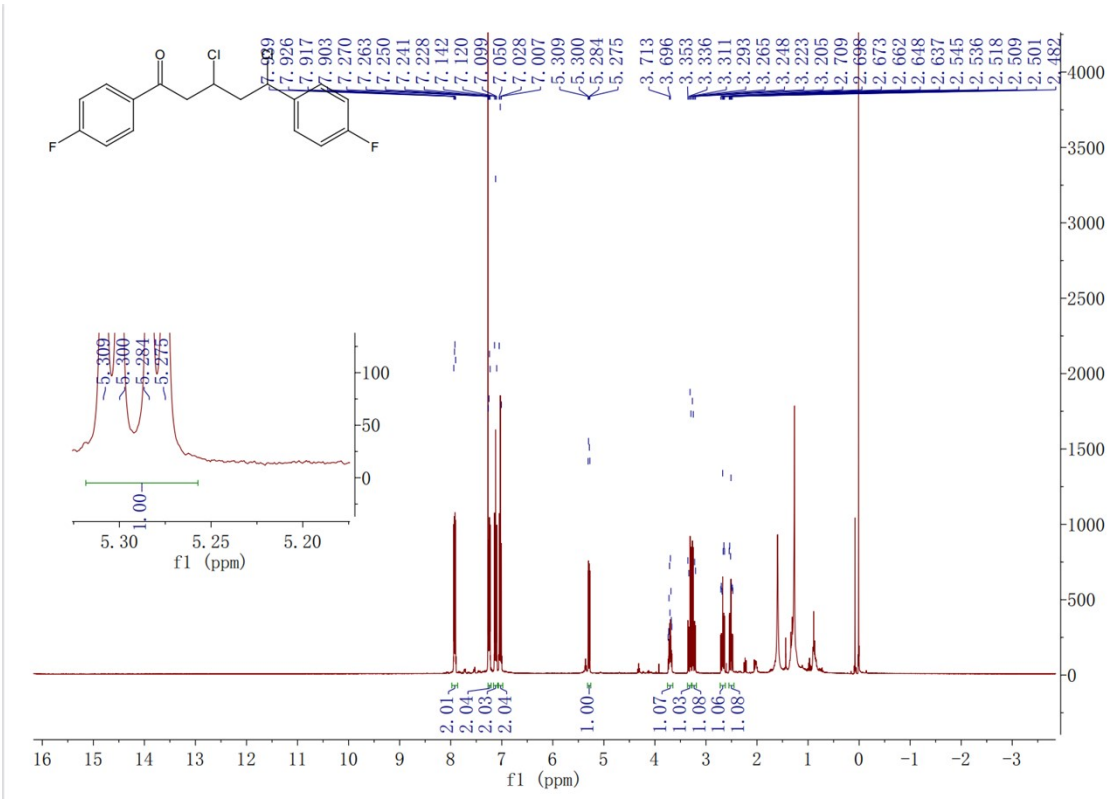


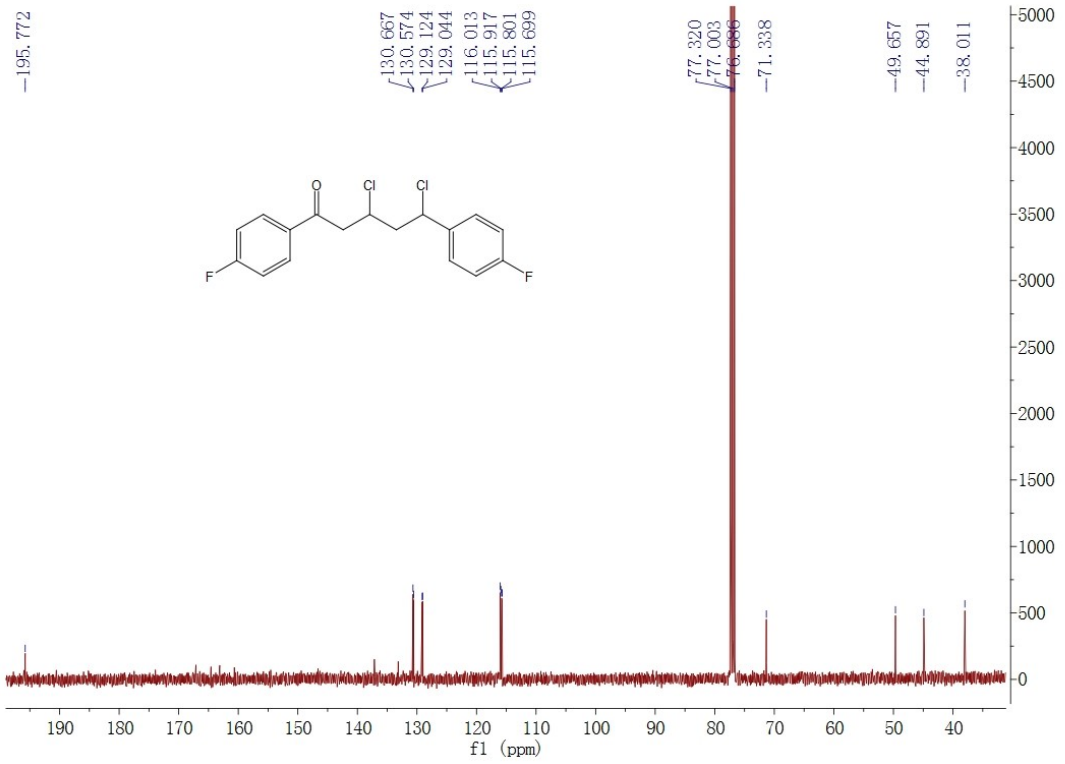
1,5-bis(4-phenylphenyl)-1,3-dichloropentan-5-one (2g)



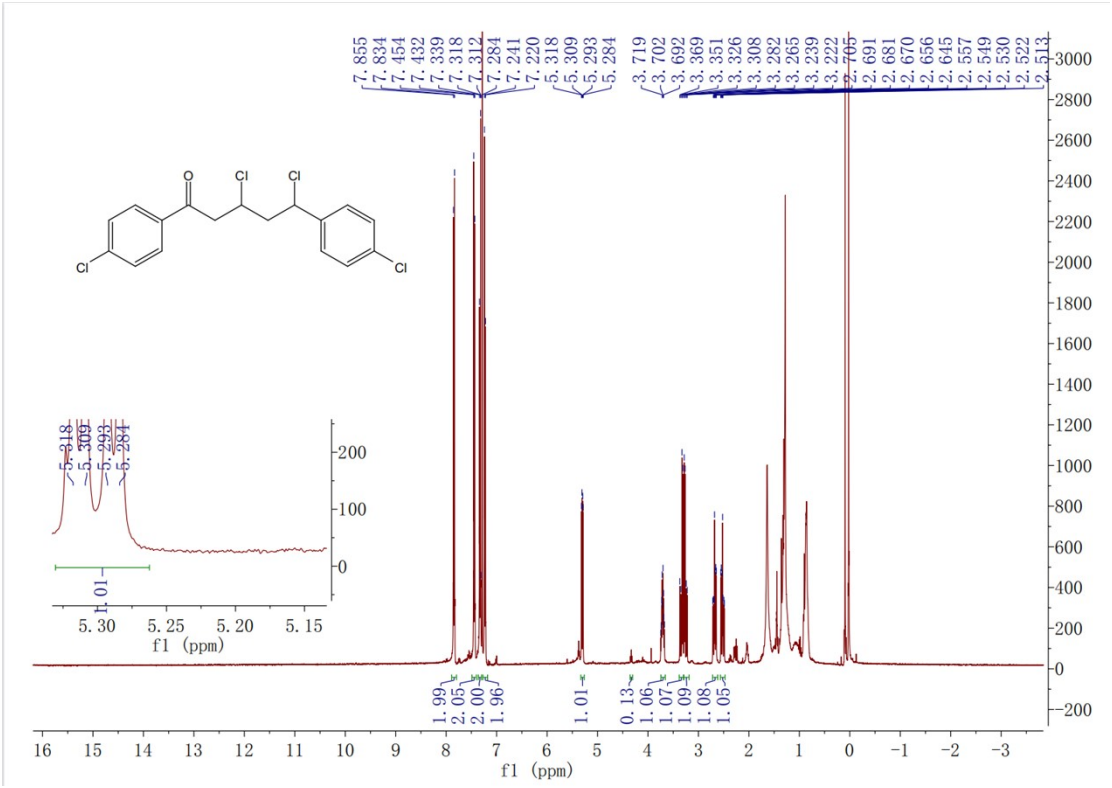


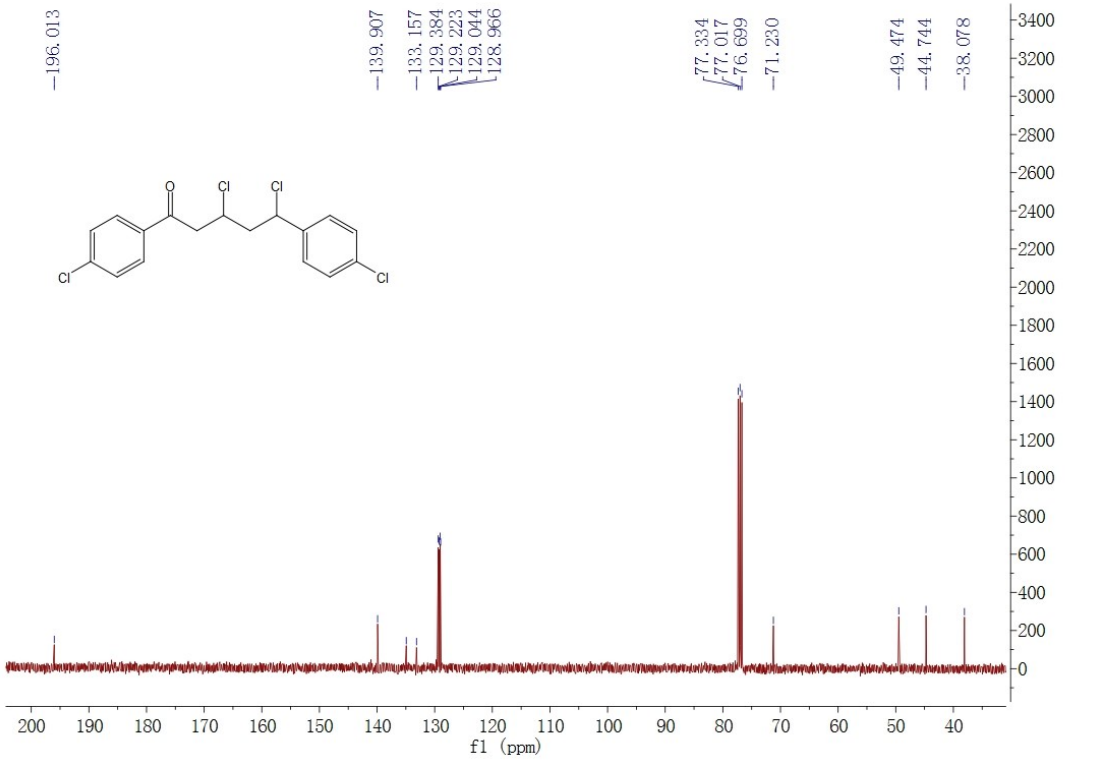
1,3-dichloro-1,5-bis(4-fluorophenyl)pentan-5-one (2h)



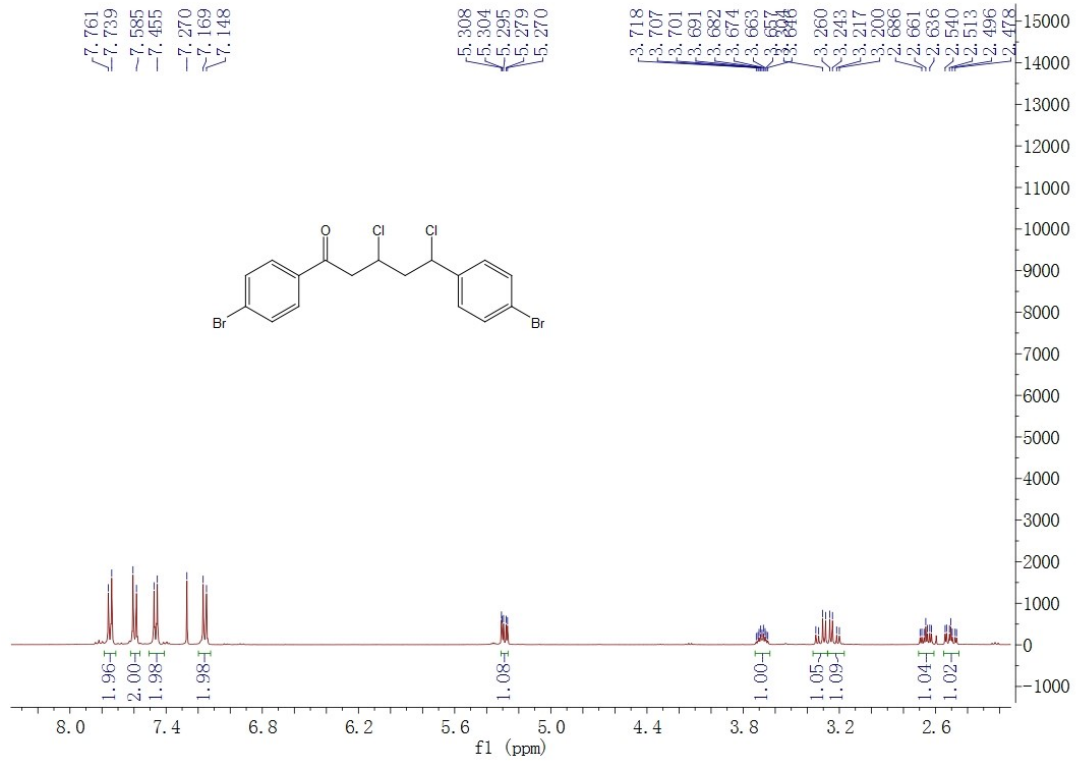


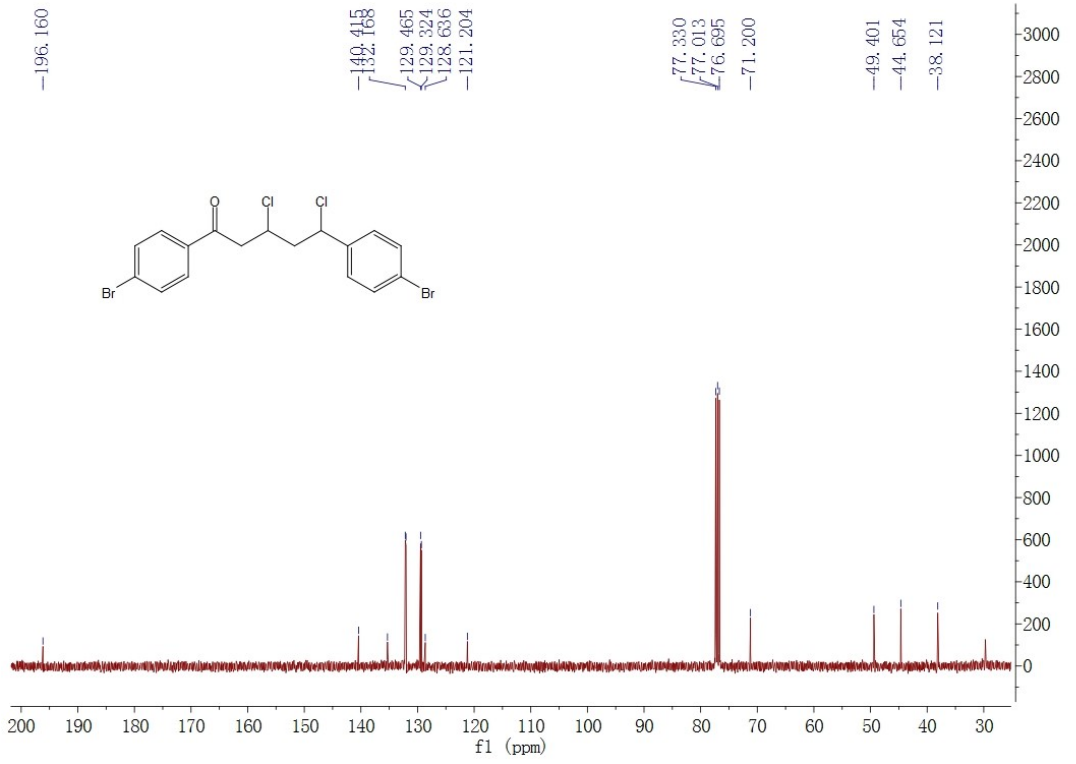
1,3-dichloro-1,5-bis(3-chlorophenyl)pentan-5-one (2i)



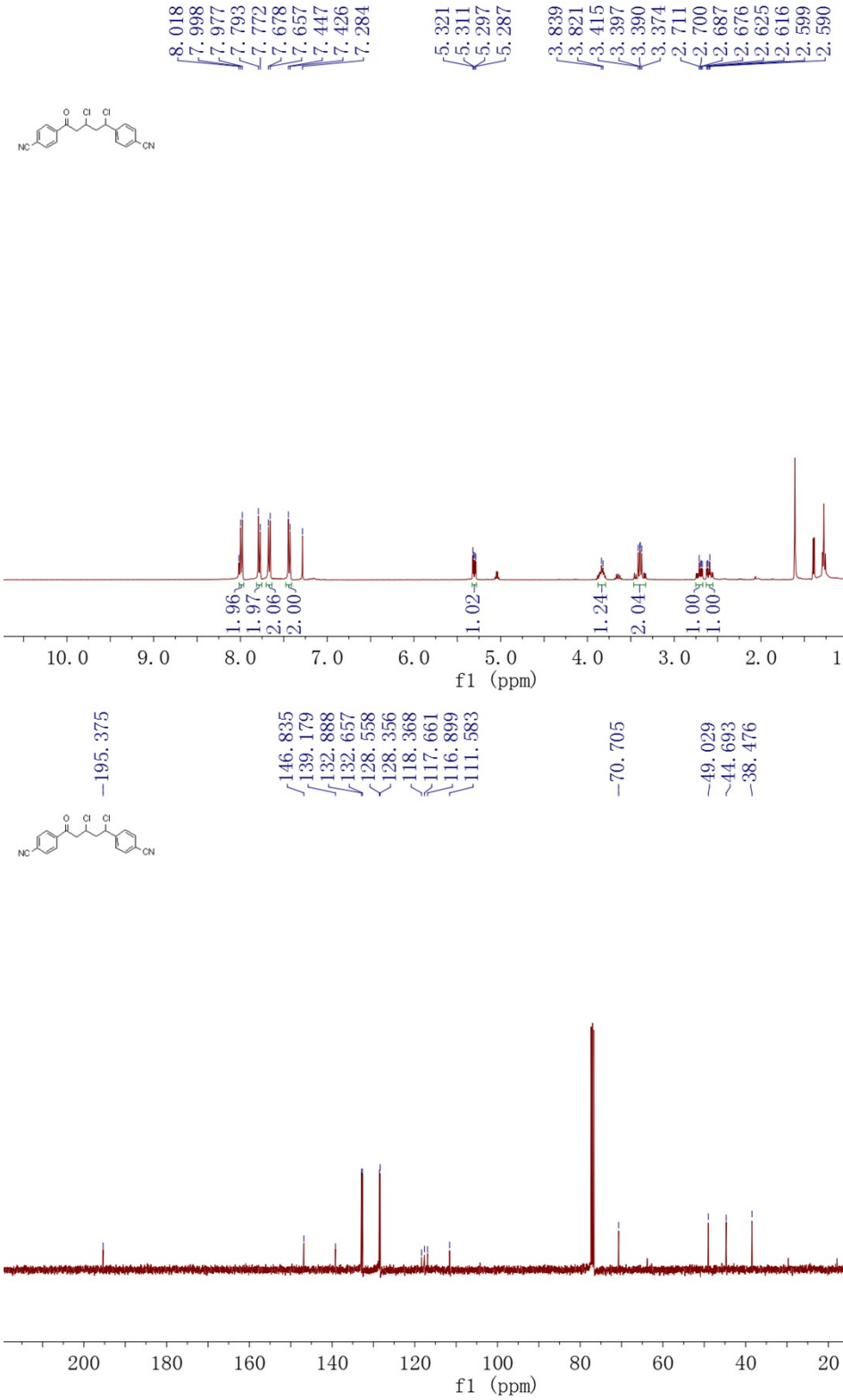


1,5-bis(4-bromophenyl)-1,3-dichloropentan-5-one (2j)

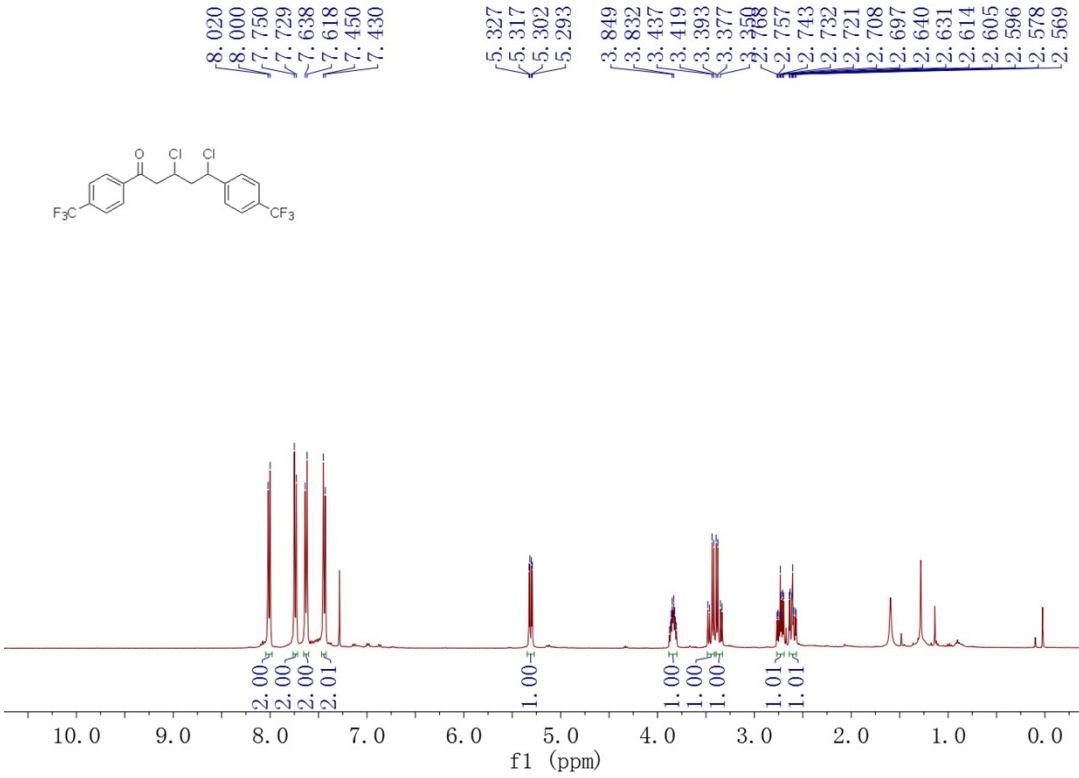


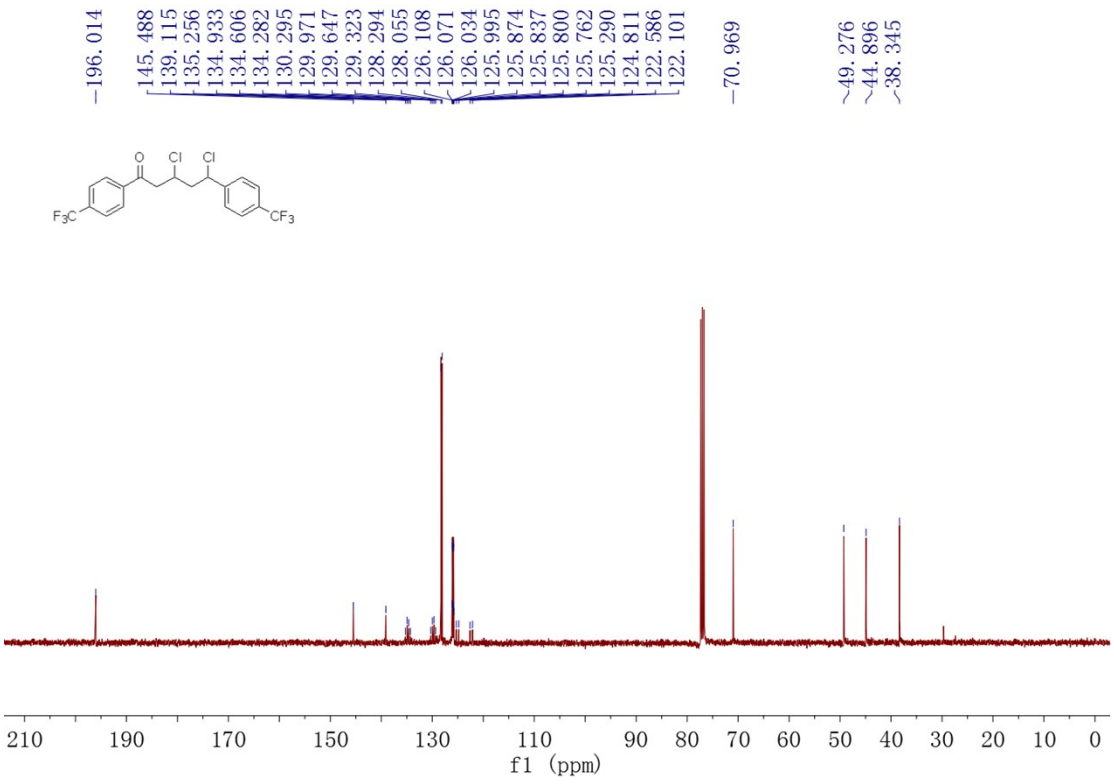


4,4'-(1,3-dichloro-5-oxopentane-1,5-diyl)dibenzonitrile (2k)

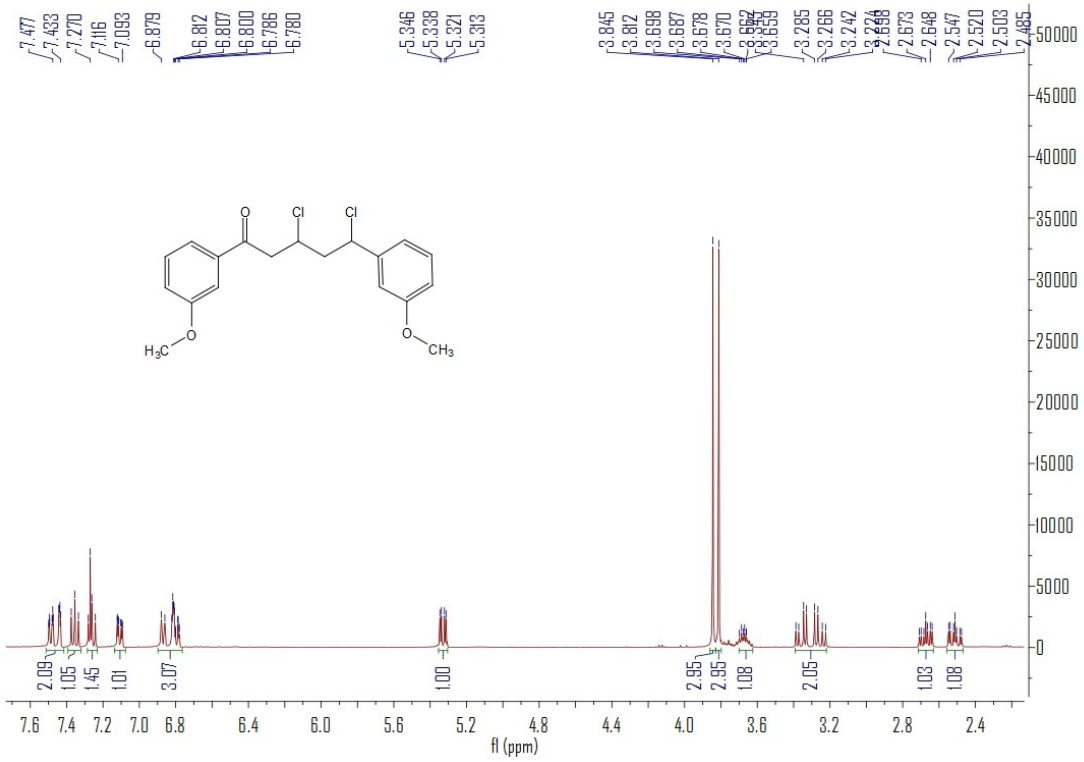


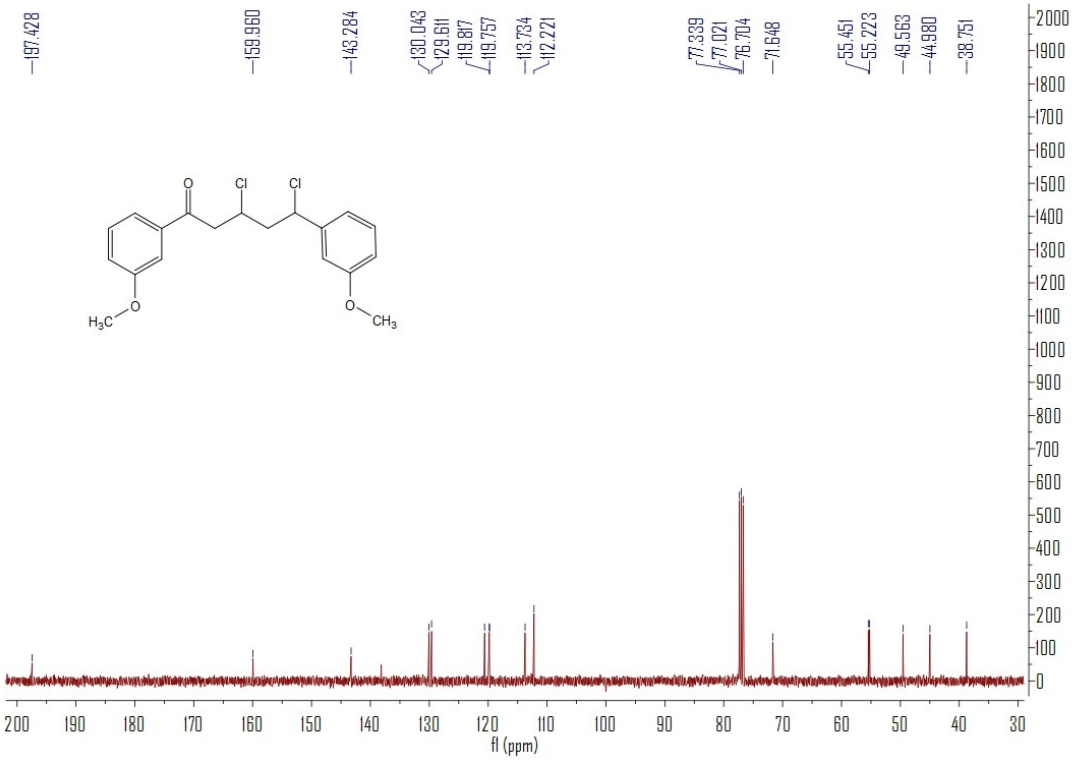
1,3-dichloro-1,5-bis(4-(trifluoromethyl)phenyl)pentan-5-one (2l)



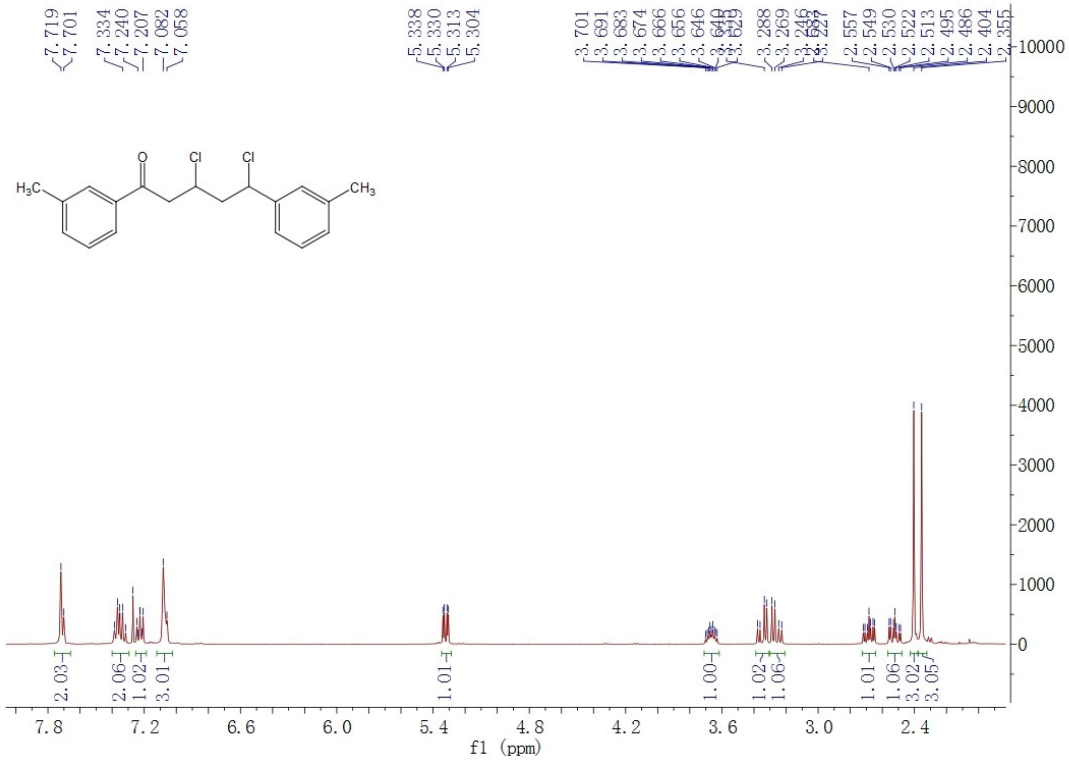


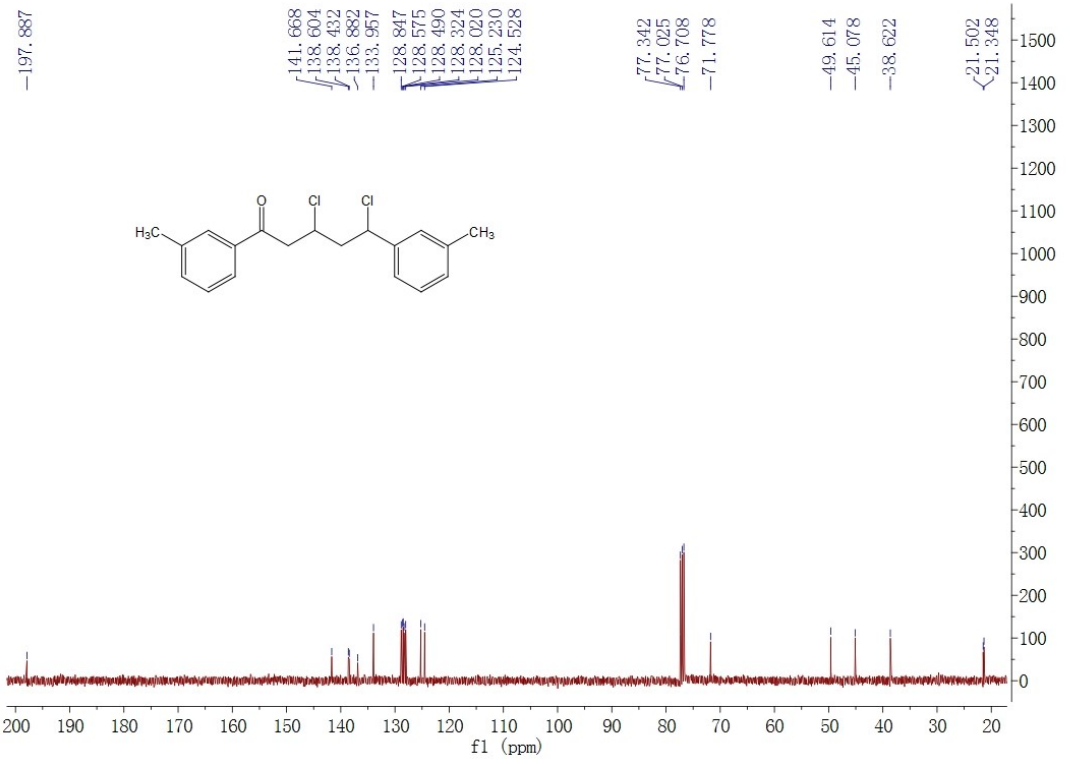
1,3-dichloro-1,5-bis(3-methoxyphenyl)pentan-5-one (2m)



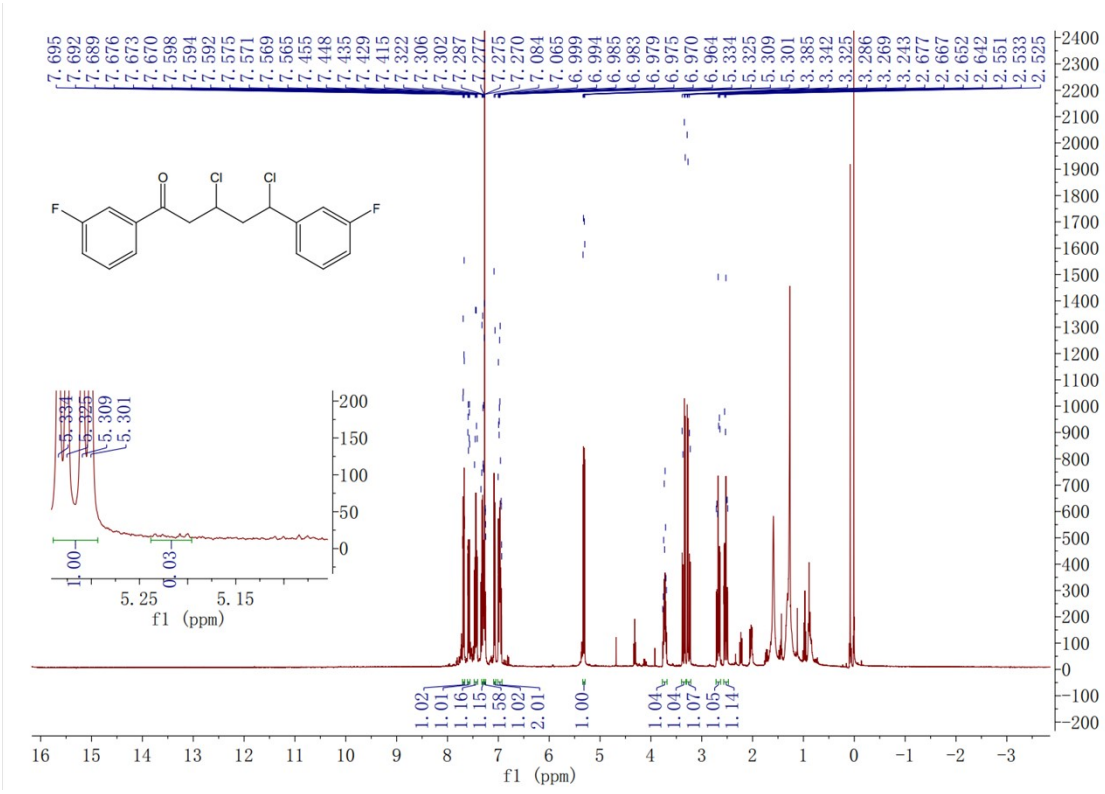


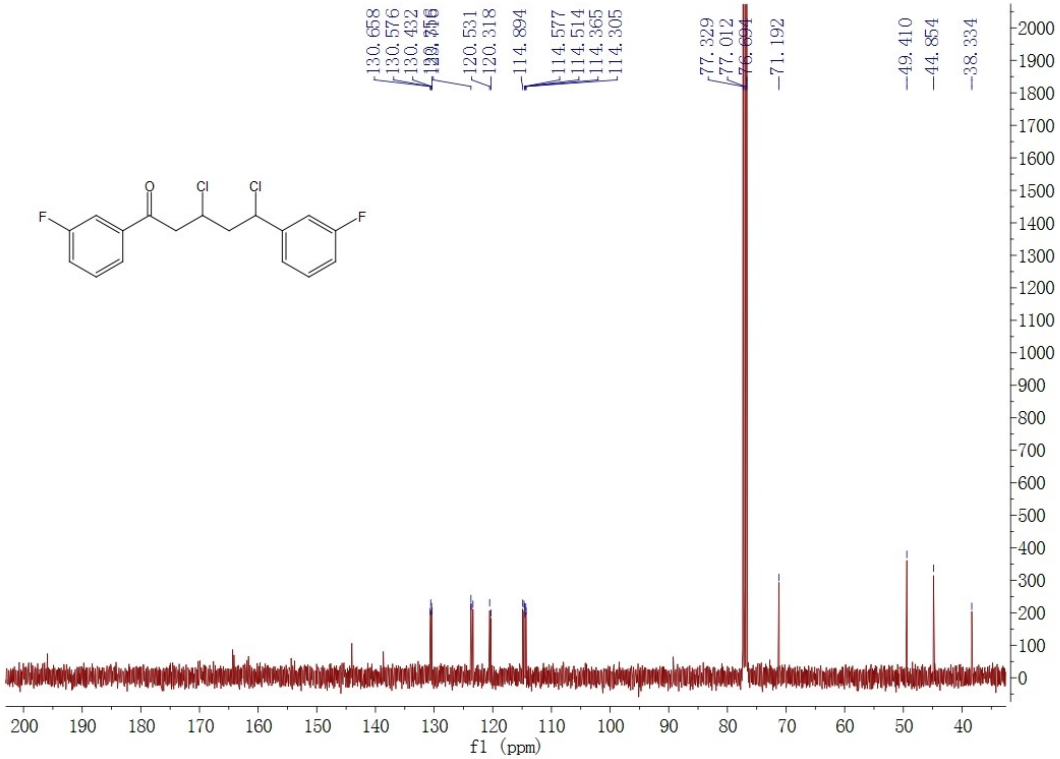
1,3-dichloro-1,5-dim-tolylpentan-5-one (2n)



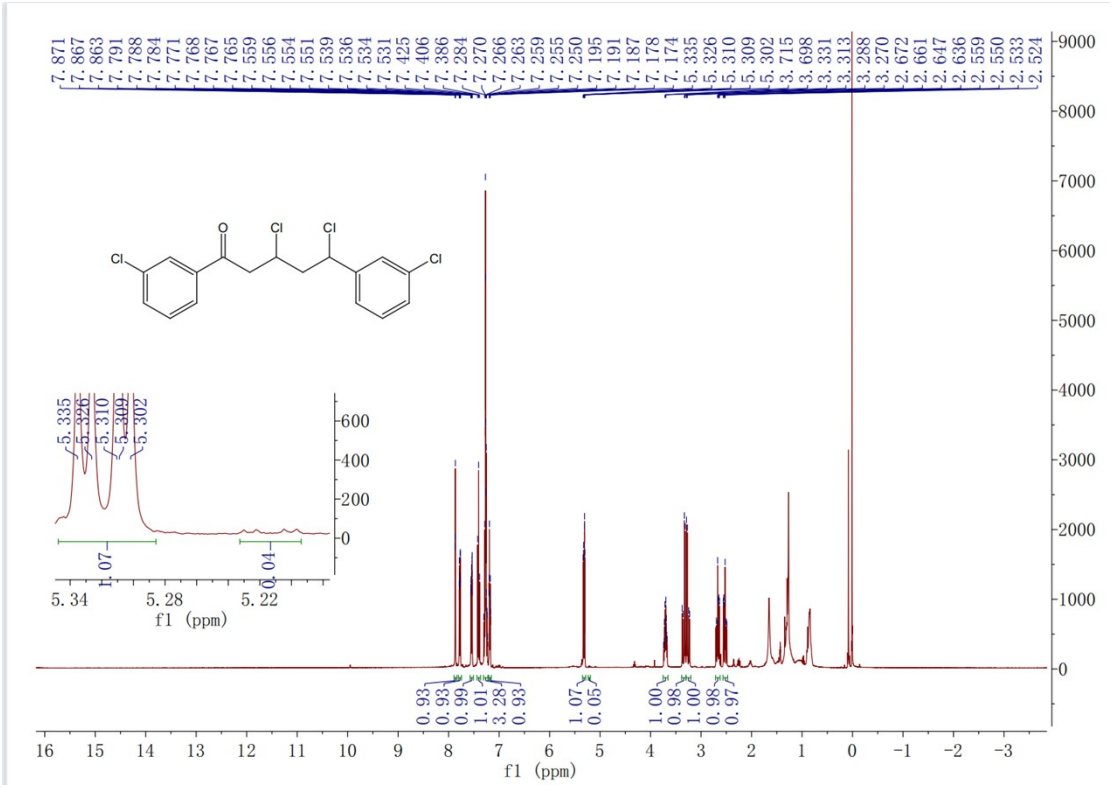


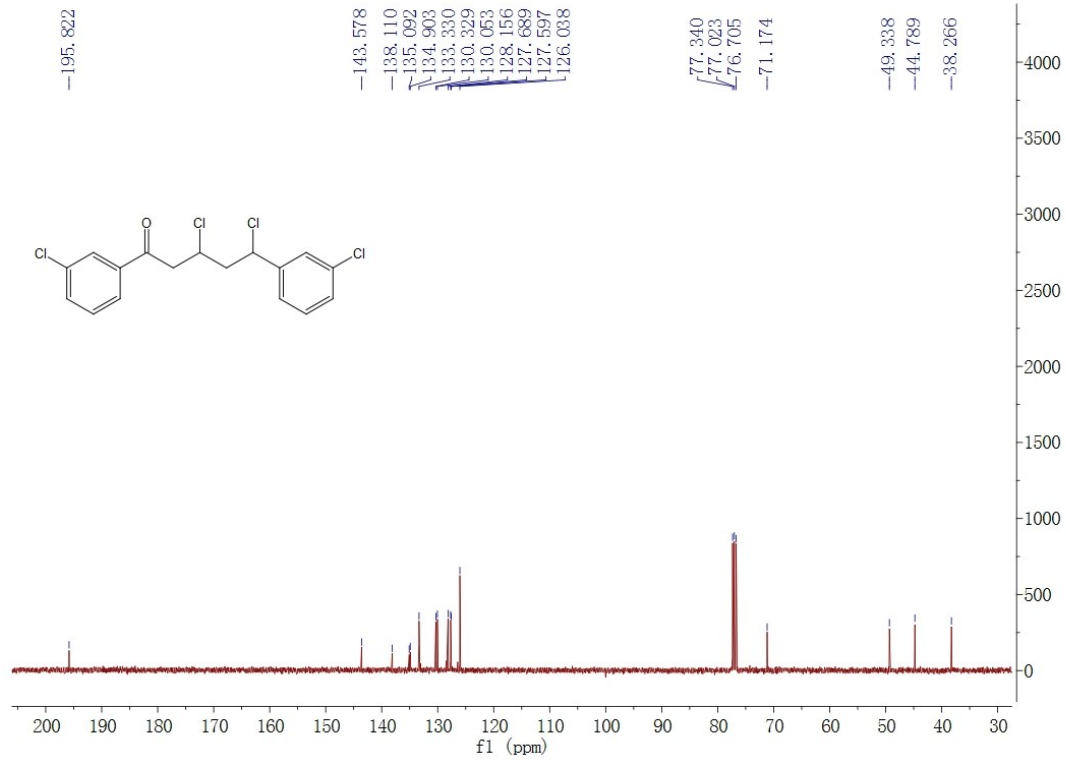
1,3-dichloro-1,5-bis(3-fluorophenyl)pentan-5-one (2o)



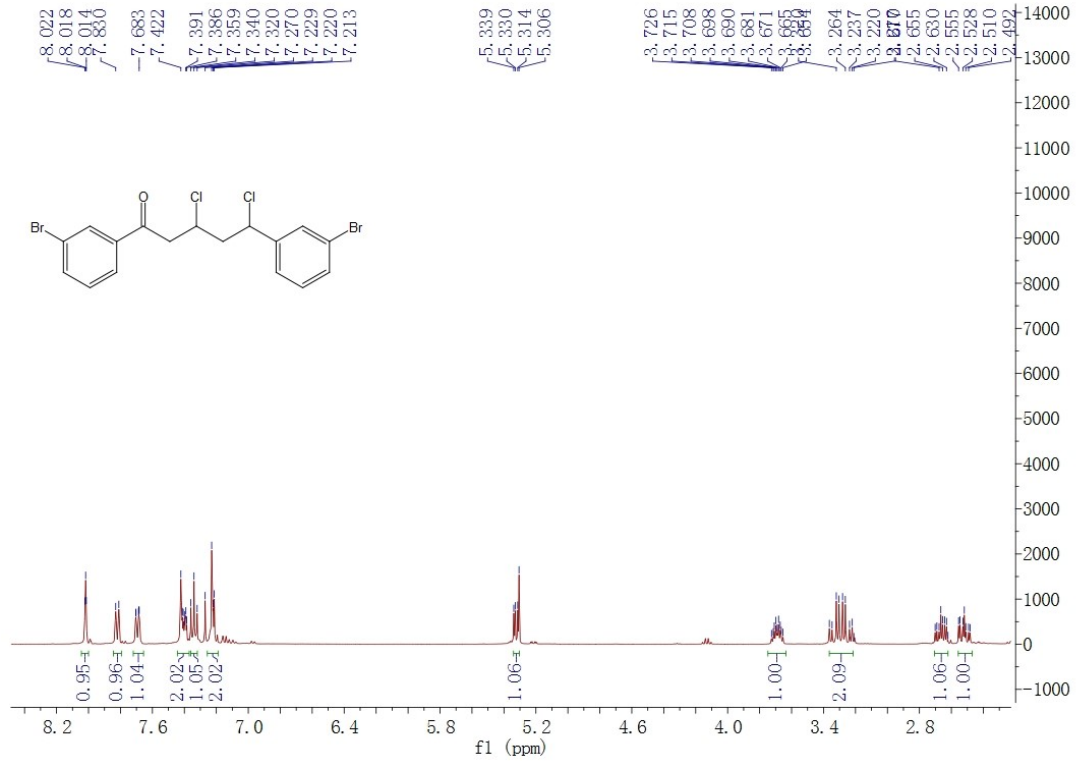


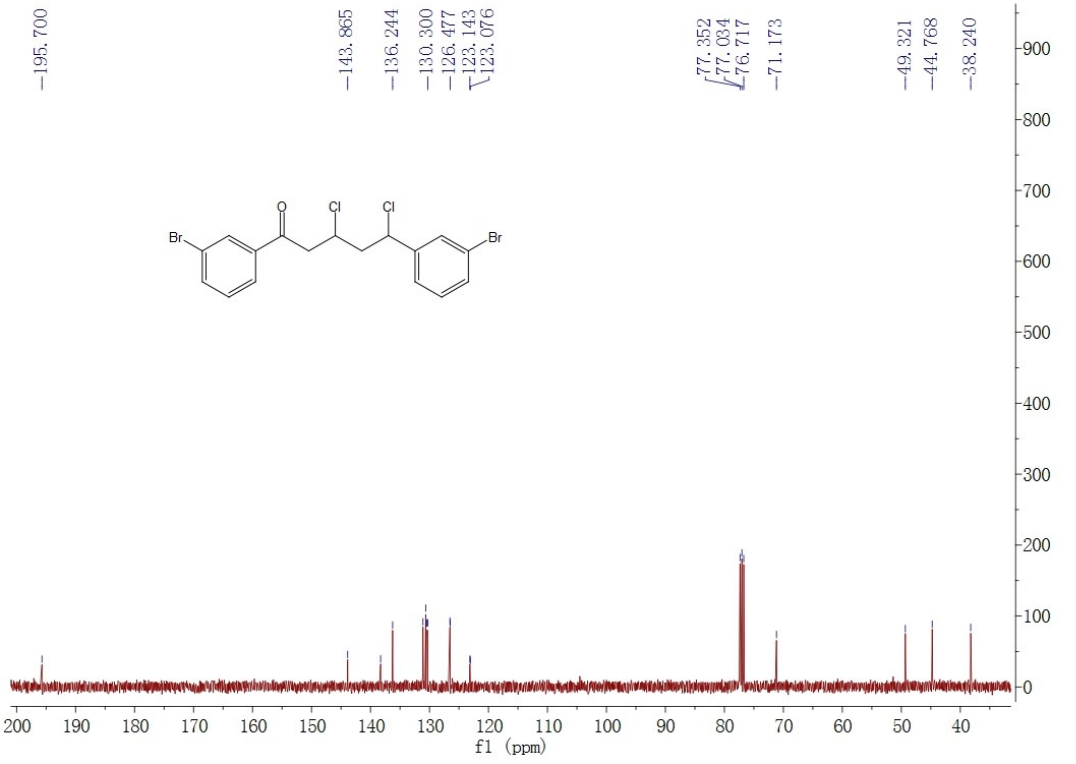
1,3-dichloro-1,5-bis(4-chlorophenyl)pentan-5-one (2p)



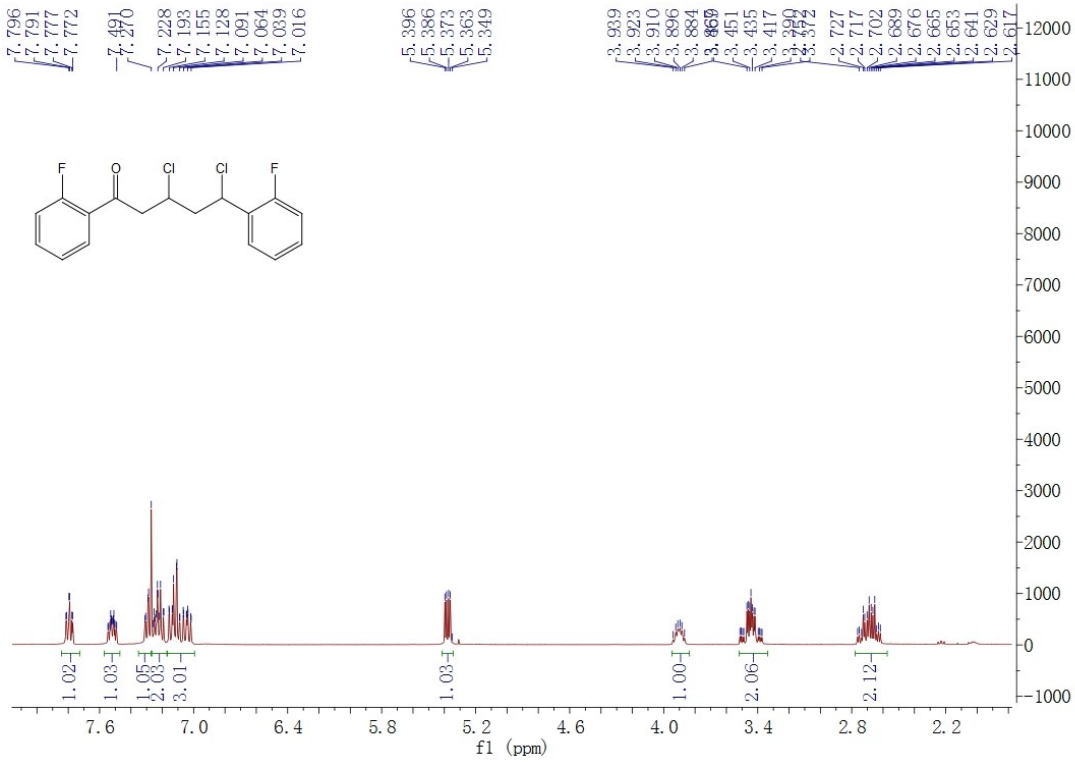


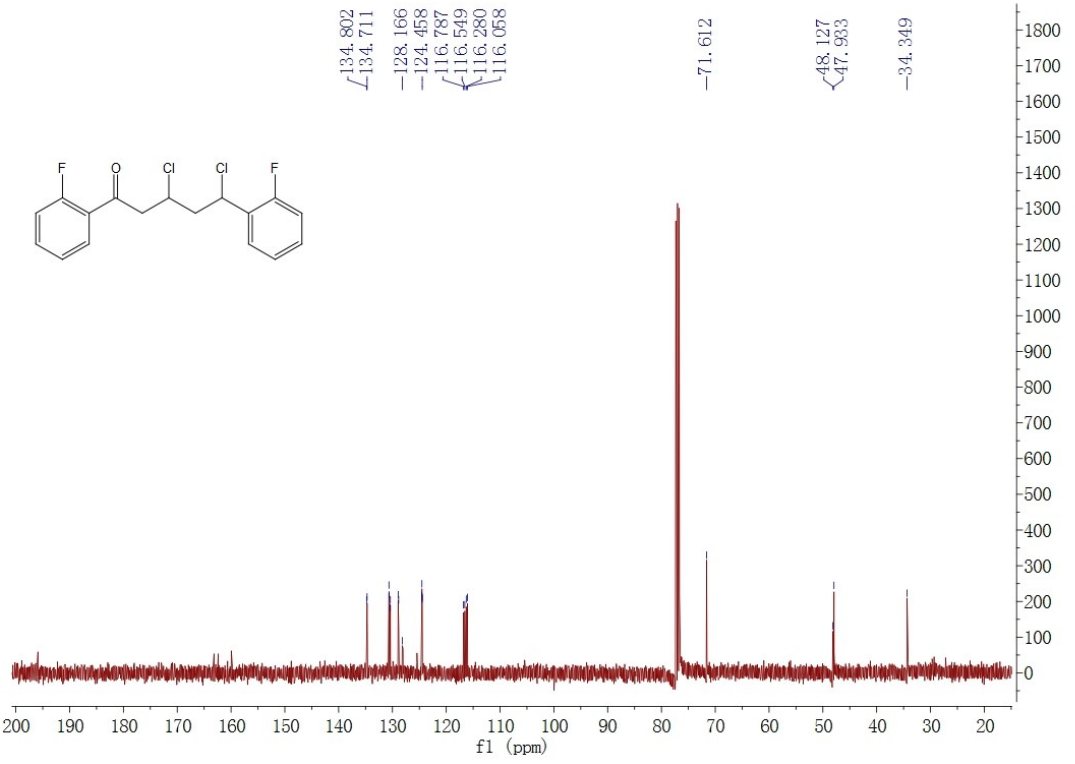
1,5-bis(3-bromophenyl)-1,3-dichloropentan-5-one (2q)



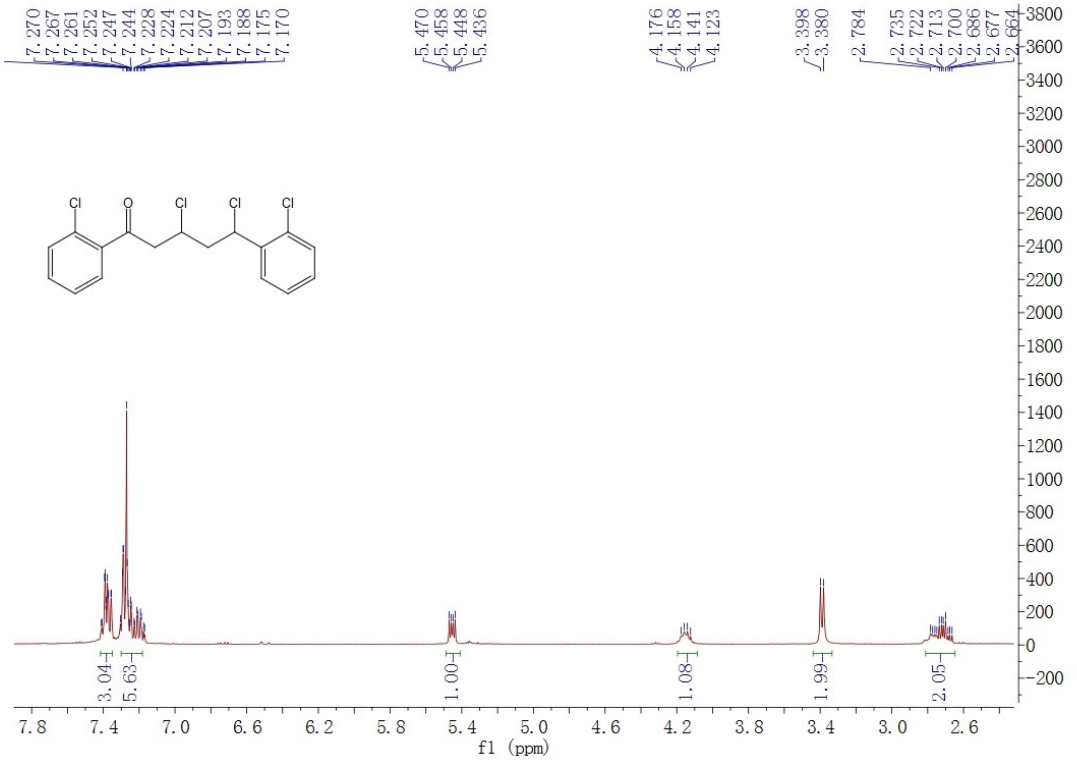


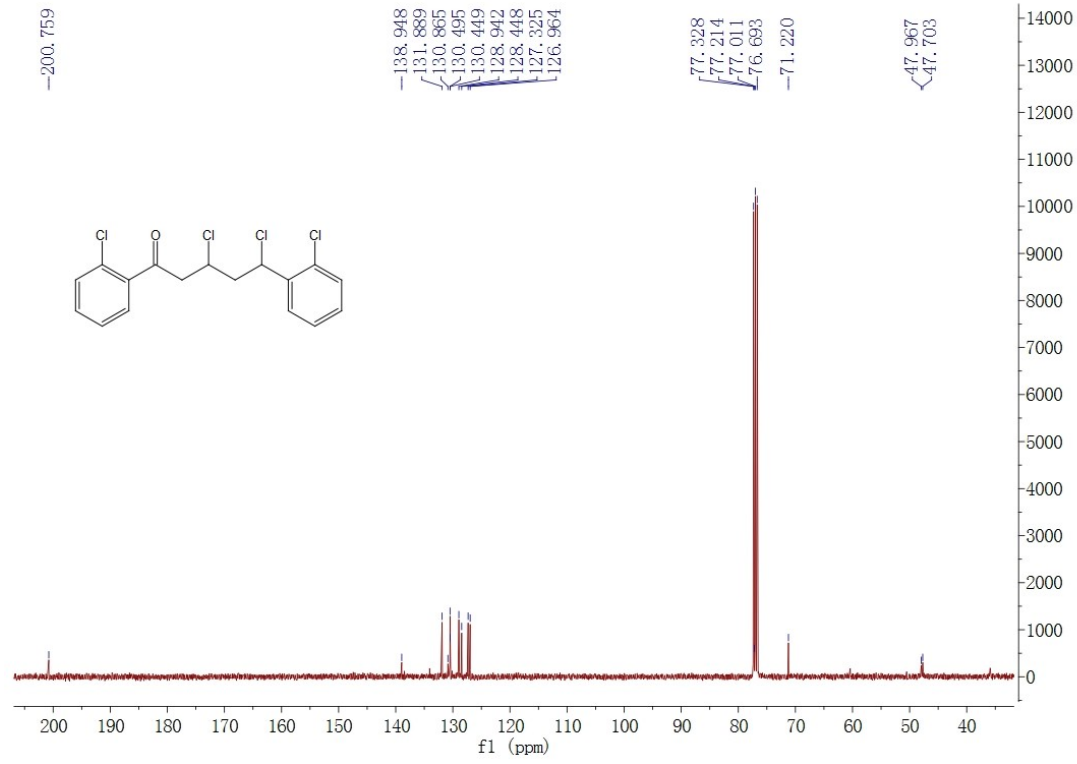
1,3-dichloro-1,5-bis(2-fluorophenyl)pentan-5-one (2r)



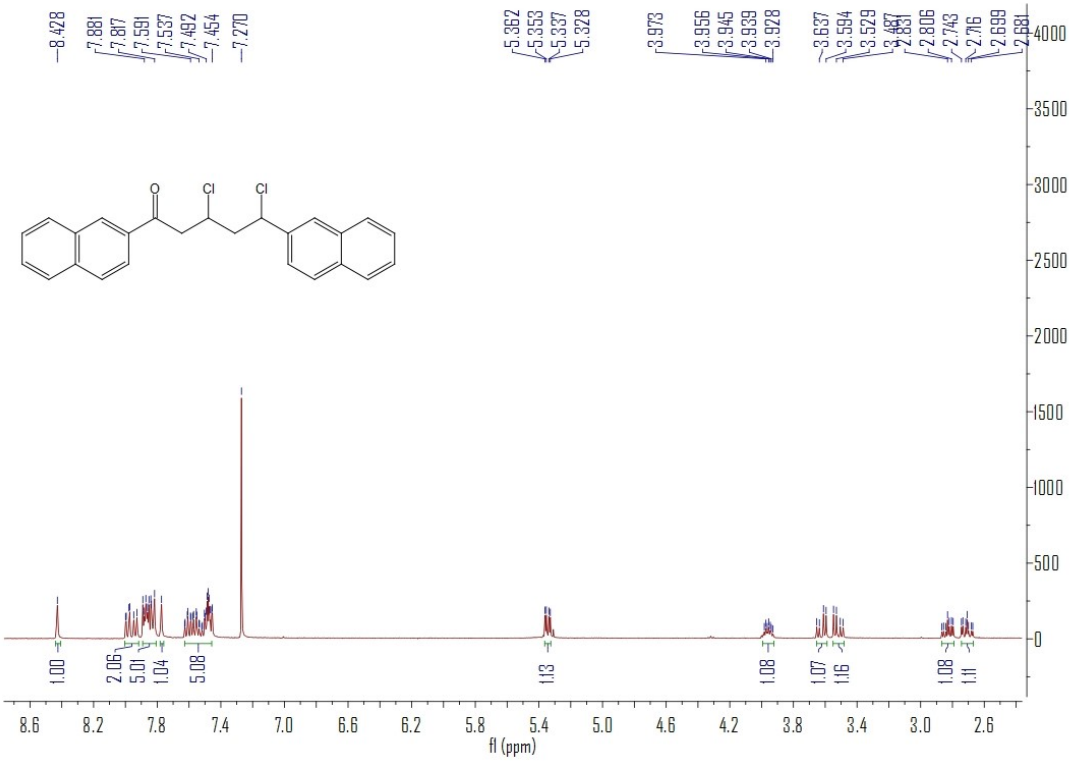


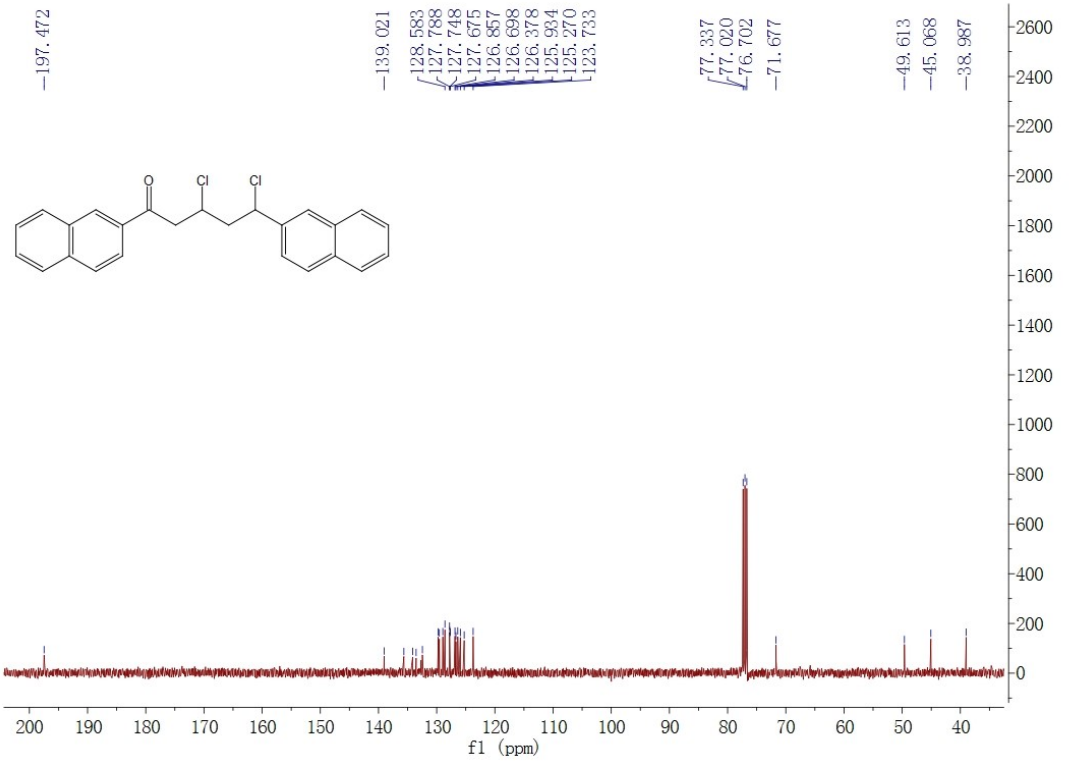
1,3-dichloro-1,5-bis(2-chlorophenyl)pentan-5-one (2s)



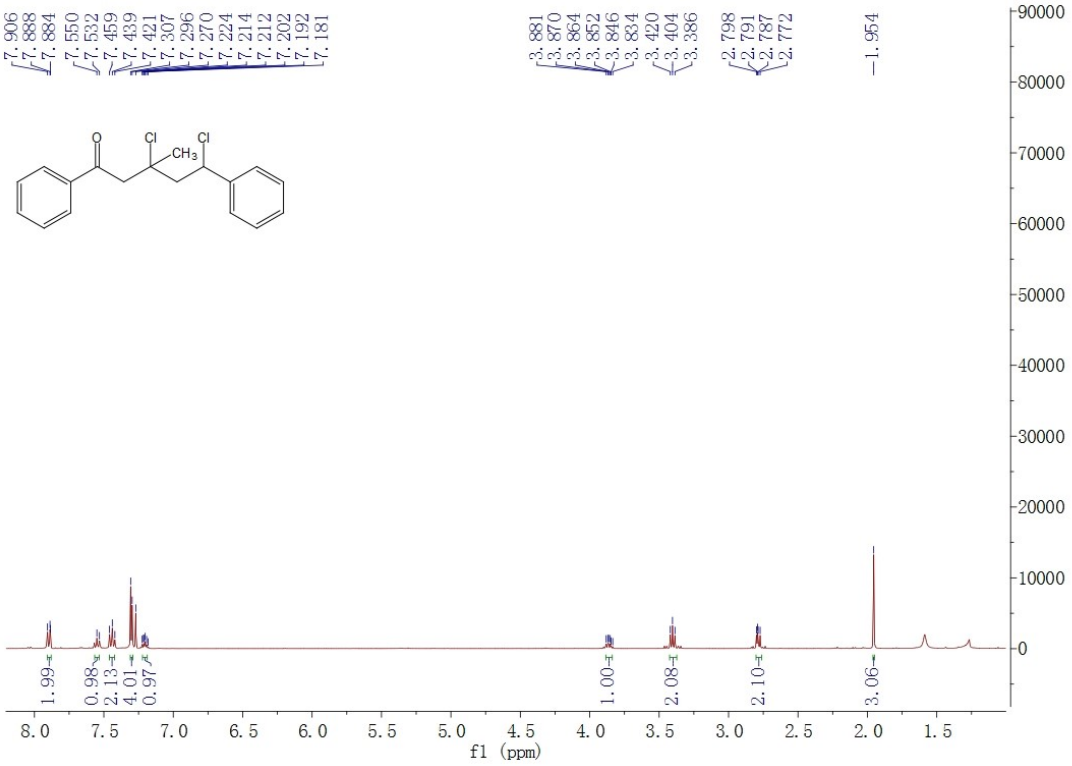


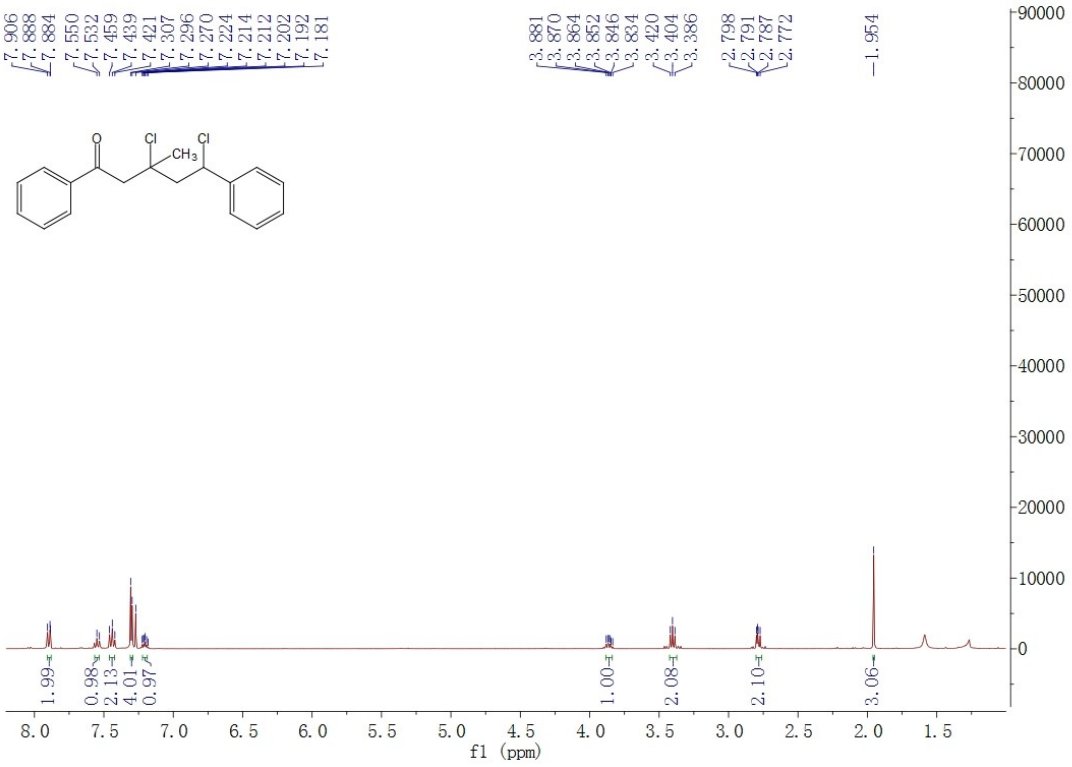
1,3-dichloro-1,5-di(naphthalen-3-yl)pentan-5-one (2u)



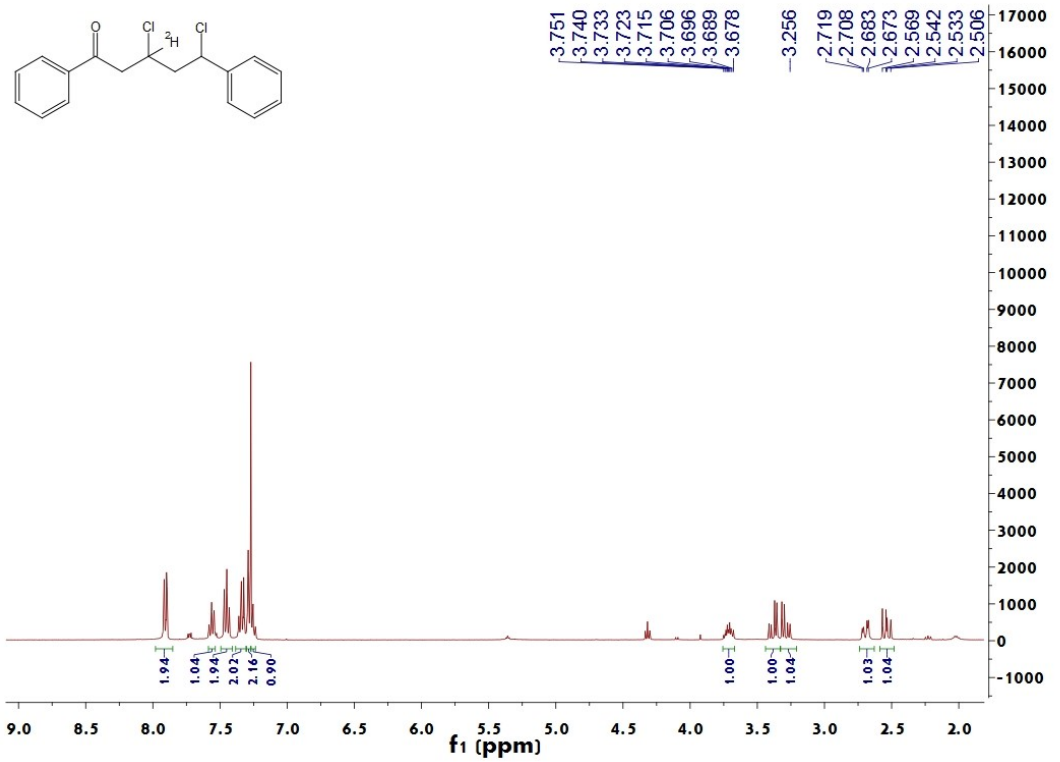


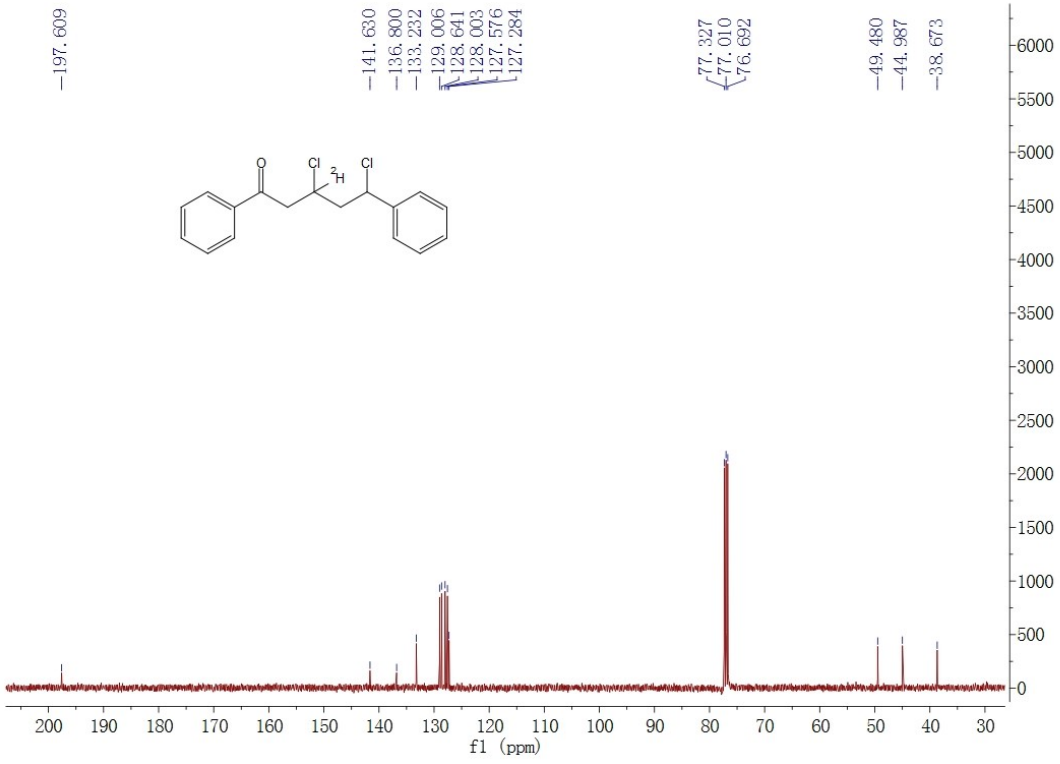
1,3-dichloro-3-methyl-1,5-diphenylpentan-5-one (2w)



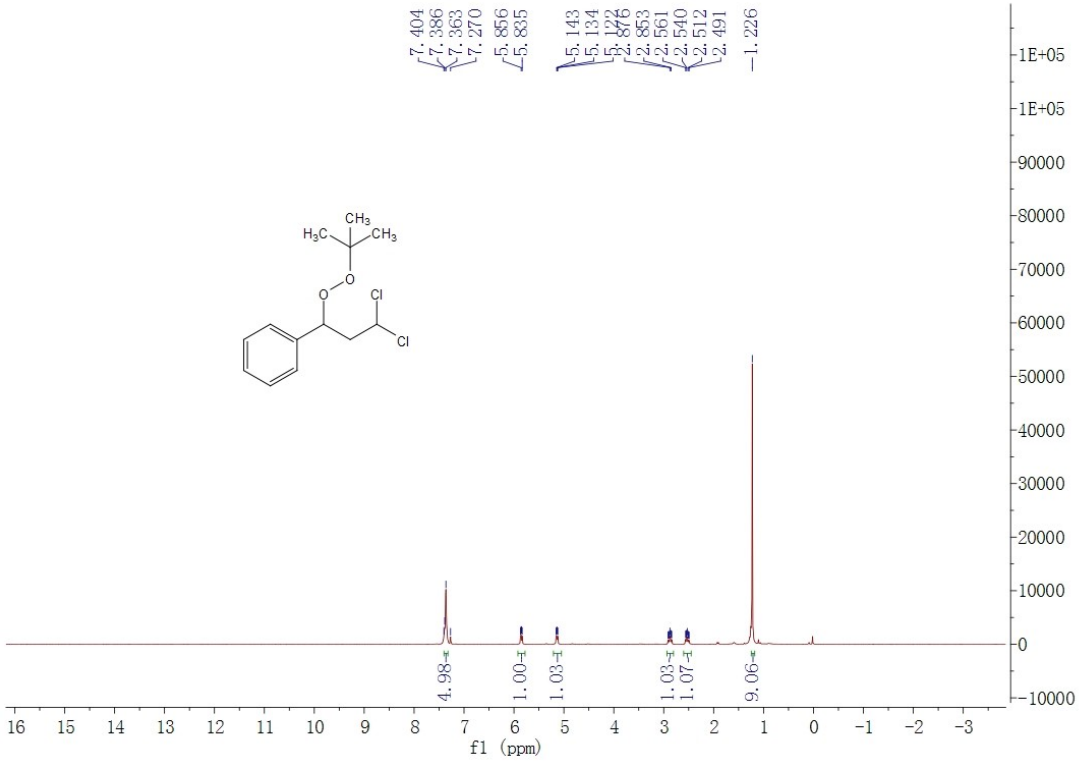


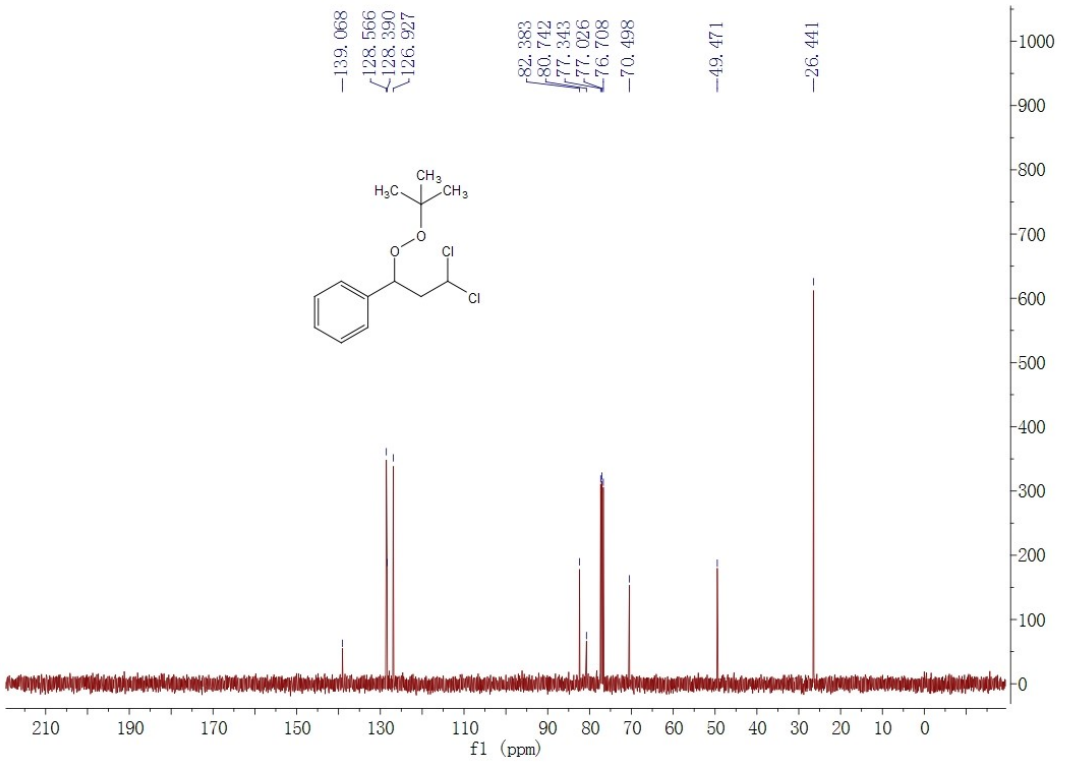
3-deuterium-1,3-dichloro-1,5-diphenylpentan-5-one (2a')





1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (3a)





1-(tert-butylperoxy)-3,3-dichloro-1,1-diphenylpropane (4a)