Polychloromethylation/acyloxylation of 1,6-enynes with chloroalkanes and diacyl peroxides through dual roles designs

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Supporting Information

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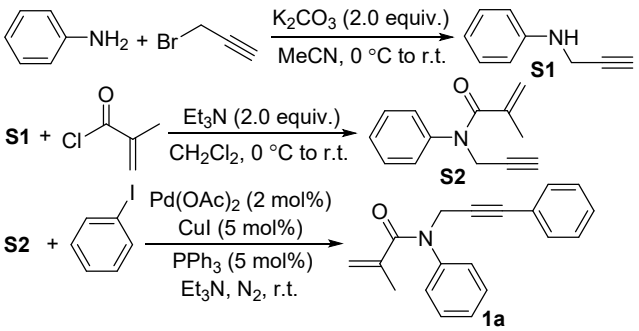
(A) General information

Unless otherwise noted, all starting materials and solvents were commercially available and used without further purification. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz/500 MHz spectrometer, chemical shift (δ) values were given in ppm. Chemical shifts of ^{1}H NMR are reported downfield from TMS (= 0). Chemical shifts of ^{13}C NMR are reported in the scale relative to $CDCl_3$ (= 77.0). Coupling constants (J) were reported in hertz (Hz). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

(B) Typical experimental procedures

(1) General procedure for the synthesis of substrate 1a



Step I: To a round bottom flask were added with aniline (1.2 equiv.), K_2CO_3 (2.0 equiv.), and MeCN (10.0 mL), then cooled to 0 ^{o}C in the ice water bath. 3-Bromo-1-propyne (3.0 mmol) was slowly added to the solution at 0 ^{o}C and then the mixture was stirred at room temperature for 7 h. The solution was concentrated under reduced

pressure, and the mixture was purified by flash column chromatography over silica gel to afford *N*-(prop-2-yn-1-yl)aniline **S1** (petroleum ether/ethyl acetate = 5:1).

Step II To a round bottom flask were added with *N*-(prop-2-yn-1-yl)aniline **S1** (1.0 equiv.), Et_3N (2.0 equiv.), and CH_2Cl_2 (10.0 mL). Then the solution was cooled to 0 °C in the ice water bath. Methacryloyl chloride (3.0 mmol) was slowly added to the solution at 0 °C and then the mixture was stirred at room temperature for 7 h. The solution was concentrated under reduced pressure and purified by flash column chromatography over silica gel to afford *N*-phenyl-*N*-(prop-2-yn-1-yl)methacrylamide **S2** (petroleum ether/ethyl acetate = 10:1).

Step III Under a nitrogen atmosphere, to a triethylamine solution (8.0 mL) of $Pd(OAc)_2$ (2 mol%), CuI (5 mol%), and PPh_3 (5 mol%) was added *N*-phenyl-*N*-(prop-2-yn-1-yl)methacrylamide **S2** (1.0 equiv.) and stirred for 10 mins, then added iodobenzene (1.2 equiv.) dropwise over 30 mins. The resulting system was then stirred at room temperature for 3 h. After completion of the reaction, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel to afford *N*-phenyl-*N*-(3-phenylprop-2-yn-1-yl)methacrylamide **1a** (petroleum ether/ethyl acetate = 10:1).

(2) Typical procedure for the synthesis of aryl acylperoxides[1]

Hydrogen peroxide (0.84 g, 35 wt. % in H_2O, 8.5 mmol) was added dropwise over 10 mins to a cold (ice bath) solution of acid chloride (15.0 mmol) in diethyl ether (3.5 mL), followed by dropwise addition of an aqueous solution of NaOH (0.76 g, 19.0 mmol, 5.0 mL) over 20 mins. The resulting white precipitate was collected by filtration.

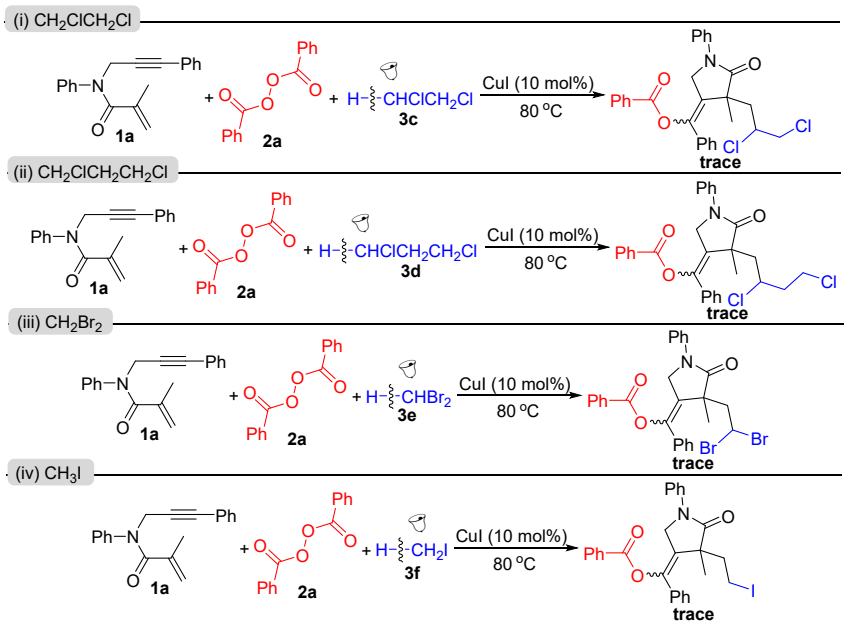
After washing with water (3 × 5.0 mL) and diethyl ether (3 × 5.0 mL), the solid was crystallized from a cold acetone/water mixture (*v*/*v* 1: 3).

(3) Typical experimental procedure for the polychloromethylation/acyloxylation of 1,6-enynes

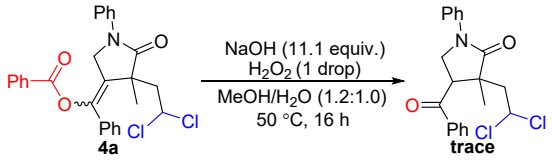
To a Schlenk tube were added 1,6-enynes **1** (0.2 mmol), diacyl peroxides **2** (0.4 mmol), CuI (10 mol%), and dichloromethane or trichloromethane **3** (1.0 mL). Then the tube was stirred at 80 °C sealed in air for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, filtration and evaporation of the solvent. The mixture was purified by flash column chromatography over silica gel (petroleum ether /ethyl acetate = 8:1) to afford the desired products **4**.

(C) Supplementary experiments

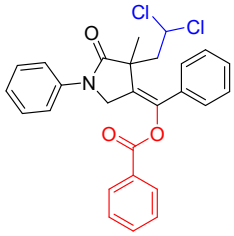
(1) Substrate scope of haloalkanes



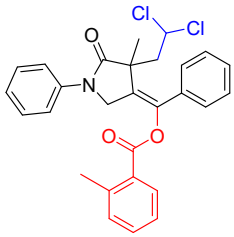
(2) The application about the hydrolysis of ester moiety[2-3]



(D) Analytical data

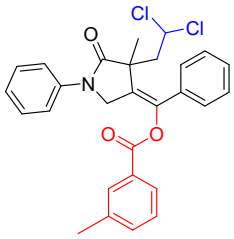


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow solid (0.0834 g, 87% yield, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 2H), 7.64-7.61 (m, 3H), 7.57-7.55 (m, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.46-7.45 (m, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 6.21-6.18 (m, 1H), 4.64 (d, J = 15.0 Hz, 1H), 4.51 (d, J = 14.5 Hz, 1H), 2.86-2.81 (m, 1H), 2.18-2.15 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 174.8, 164.2, 143.7, 138.5, 133.9, 133.7, 130.1, 129.9, 129.7, 129.0, 128.8, 128.7, 128.6, 125.6, 125.3, 120.5, 70.3, 50.1, 49.7, 47.6, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{24}Cl_2NO_3$ ($[M+H]^+$) 480.1128, found 480.1136.

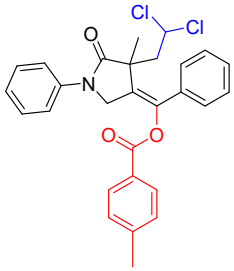


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 2-methylbenzoate (4b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0789 g, 80% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.03 (m, 1H), 7.66-7.63 (m, 2H), 7.58-7.55 (m, 2H), 7.49-7.45 (m, 4H), 7.38 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H),

6.21-6.18 (m, 1H), 4.65 (d, J = 14.8 Hz, 1H), 4.53 (d, J = 14.8 Hz, 1H), 2.87-2.81 (m, 1H), 2.62 (s, 3H), 2.19-2.14 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 164.6, 143.7, 141.5, 138.5, 133.8, 133.0, 132.0, 131.1, 129.8, 129.7, 129.0 (2), 128.6, 127.8, 126.0, 125.3, 120.5, 70.4, 50.0, 49.8, 47.6, 26.8, 22.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_3$ ($[M+H]^+$) 494.1284, found 494.1280.

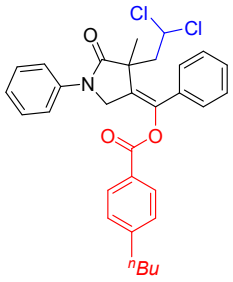


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 3-methylbenzoate (4c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0838 g, 85% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.87 (m, 2H), 7.64-7.61 (m, 2H), 7.57-7.54 (m, 2H), 7.45-7.42 (m, 4H), 7.38-7.34 (m, 3H), 7.16 (t, J = 7.6 Hz, 1H), 6.22-6.19 (m, 1H), 4.64 (d, J = 14.4 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.86-2.80 (m, 1H), 2.41 (s, 3H), 2.18-2.13 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 164.4, 143.7, 138.6, 138.5, 134.7, 133.7, 130.6, 129.9, 129.7, 129.0, 128.6 (3), 127.3, 125.4, 125.3, 120.5, 70.3, 50.1, 49.7, 47.6, 26.7, 21.2; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_3$ ($[M+H]^+$) 494.1284, found 494.1290.

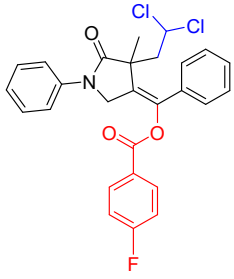


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-methylbenzoate (4d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0868 g, 88% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J = 8.4 Hz, 2H), 7.63-7.61 (m, 2H), 7.56-7.54 (m, 2H), 7.46-7.43 (m, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.29-7.27 (m, 2H), 7.16

(t, J = 7.6 Hz, 1H), 6.21-6.18 (m, 1H), 4.63 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.86-2.80 (m, 1H), 2.43 (s, 3H), 2.17-2.13 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 164.3, 144.9, 143.7, 138.5, 133.8, 130.2, 129.9, 129.7, 129.4, 129.0, 128.6, 126.0, 125.4, 125.3, 120.5, 70.4, 50.1, 49.7, 47.6, 26.7, 21.7; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_3$ ($[M+H]^+$) 494.1284, found 494.1276.

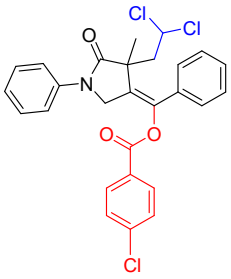


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-butylbenzoate (4e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0867 g, 81% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.56-7.54 (m, 2H), 7.44 (t, J = 3.2 Hz, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 6.22-6.19 (m, 1H), 4.63 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.86-2.80 (m, 1H), 2.68 (t, J = 7.6, 2H), 2.18-2.13 (m, 1H), 1.61 (t, J = 7.6, 2H), 1.40-1.36 (m, 1H), 1.35 (s, 3H), 1.33-1.30 (m, 1H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 164.3, 149.8, 143.7, 138.5, 133.8, 130.2, 129.8, 129.7, 129.0, 128.8, 128.6, 126.1, 125.4, 125.3, 120.5, 70.4, 50.1, 49.7, 47.6, 35.7, 33.2, 26.7, 22.2, 13.8; HRMS *m/z* (ESI) calcd for $C_{31}H_{32}Cl_2NO_3$ ($[M+H]^+$) 536.1754, found 536.1750.

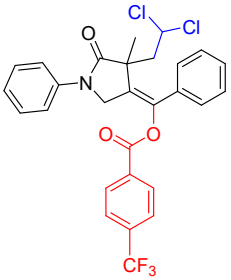


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-fluorobenzoate (4f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0726 g, 73% yield, *Z/E*

>20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ： 8.14-8.10 (m, 2H), 7.63-7.61 (m, 2H), 7.56-7.53 (m, 2H), 7.47-7.45 (m, 3H), 7.38-7.34 (m, 2H), 7.19-7.13 (m, 3H), 6.20-6.16 (m, 1H), 4.62 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.85-2.79 (m, 1H), 2.18-2.13 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.4, 166.2 (d, J_{C-F} = 257.0 Hz), 163.3, 143.6, 138.4, 133.5, 132.8 (d, J_{C-F} = 9.5 Hz), 130.0, 129.7, 129.0, 128.6, 125.7, 125.4, 124.9, 120.6, 115.9 (d, J_{C-F} = 22.2 Hz), 70.3, 50.0, 49.7, 48.1, 26.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ: -103.5; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_2FNO_3$ ($[M+H]^+$) 498.1034, found 498.1038.

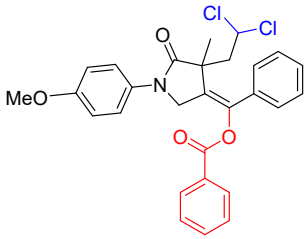


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-chlorobenzoate (4g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0698 g, 68% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04-8.02 (m, 2H), 7.63-7.61 (m, 2H), 7.56-7.53 (m, 2H), 7.47-7.45 (m, 4H), 7.39-7.35 (m, 3H), 7.18 (t, J = 7.6 Hz, 1H), 6.18-6.15 (m, 1H), 4.62 (d, J = 14.4, 1H), 4.49 (d, J = 14.4, 1H), 2.85-2.79 (m, 1H), 2.17-2.13 (m, 1H), 1.35(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.8, 163.4, 143.5, 140.6, 138.4, 133.4, 131.5, 130.0, 129.7, 129.1, 129.0, 128.7, 127.2, 125.8, 125.4, 120.5, 70.3, 50.0, 49.7, 47.6, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_3NO_3$ ($[M+H]^+$) 514.0738, found 514.0746.

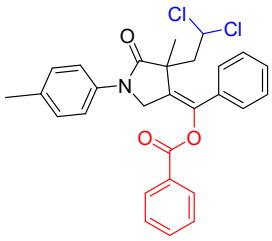


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-(trifluoromethyl)benzoate (4h). The product was purified by silica gel column chromatography with

petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0777 g, 71% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, J = 8.0 Hz, 2H), 7.76-7.73 (m, 2H), 7.63-7.60 (m, 2H), 7.57-7.55 (m, 2H), 7.48-7.46 (m, 3H), 7.37 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 6.18-6.15 (m, 1H), 4.63 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.4 Hz, 1H), 2.86-2.80 (m, 1H), 2.19-2.14 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.7, 163.1, 143.5, 138.4, 133.3, 130.5, 130.1, 129.8, 129.0, 128.9, 128.7, 128.5, 126.0, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.4, 121.0, 120.5, 70.2, 50.0, 49.6, 47.6, 26.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -63.2; HRMS *m/z* (ESI) calcd for $C_{28}H_{23}Cl_2F_3NO_3$ ($[M+H]^+$) 548.1002, found 548.1006.

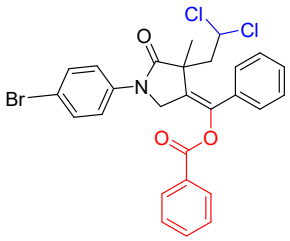


(4-(2,2-Dichloroethyl)-1-(4-methoxyphenyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4j). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v). Yellow oil (0.0886 g, 87% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71-7.69 (m, 2H), 7.60-7.53 (m, 3H), 7.51-7.44 (m, 5H), 7.31-7.28 (m, 2H), 6.96-6.93 (m, 2H), 6.90-6.87 (m, 1H), 5.66-5.63 (m, 1H), 4.61-4.44 (m, 1H), 3.82 (s, 3H), 3.28-3.23 (m, 1H), 3.04-2.97 (m, 1H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.5, 164.2, 158.9, 146.6, 138.9, 133.9, 131.9, 130.1, 129.7, 128.7, 128.3, 124.4, 123.0, 122.4, 114.7, 114.2, 70.8, 55.6, 50.4, 49.1, 47.4, 24.4; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_4$ ($[M+H]^+$) 510.1233, found 510.1227.

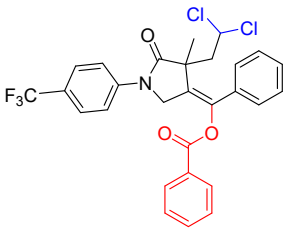


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-(*p*-tolyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4k). The product was

purified by silica gel column chromatography with petroleum ether/ethyl acetate (9:1, v/v). Yellow oil (0.0828 g, 84% yield, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.10 (d, J = 7.5 Hz, 2H), 7.61-7.55 (m, 3H), 7.50-7.44 (m, 7H), 7.15 (d, J = 8.0 Hz, 2H), 6.21-6.19 (m, 1H), 4.61 (d, J = 14.5 Hz, 1H), 4.48 (d, J = 14.5 Hz, 1H), 2.85-2.80 (m, 1H), 2.31 (s, 3H), 2.17-2.14 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 174.6, 164.2, 143.6, 135.9, 135.0, 133.9, 133.6, 130.1, 129.8, 129.7, 129.4, 128.7, 128.6, 128.5, 125.6, 120.5, 70.3, 50.1, 49.8, 47.5, 26.6, 20.8; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_3$ ([M+H]$^+$) 494.1284, found 494.1288.

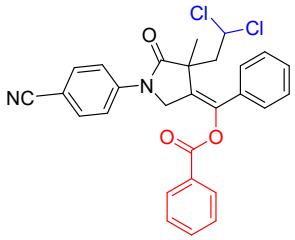


(1-(4-Bromophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4l). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow solid (0.0880g, 79% yield, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.11-8.09 (m, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.56-7.53 (m, 4H), 7.51-7.44 (m, 7H), 6.20-6.17 (m, 1H), 4.60 (d, J = 14.5 Hz, 1H), 4.46 (d, J = 14.5 Hz, 1H), 2.84-2.79 (m, 1H), 2.17-2.13 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.0, 164.2, 143.9, 137.6, 134.0, 133.5, 131.9, 130.1, 130.0, 129.7, 128.7 (2), 128.6, 125.1, 121.7, 118.1, 70.3, 50.2, 49.5, 47.6, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}BrCl_2NO_3$ ([M+H]$^+$) 558.0233, found 558.0227.

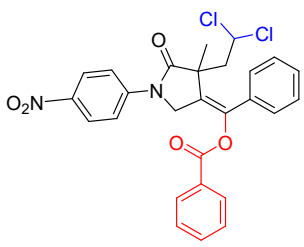


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4m). The product was purified by silica gel column chromatography with petroleum

ether/ethyl acetate (8:1, v/v). Yellow oil (0.0886 g, 81% yield, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.13-8.11 (m, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.65-7.60 (m, 3H), 7.56-7.54 (m, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.46-7.45 (m, 3H), 6.23-6.20 (m, 1H), 4.67 (d, J = 14.0 Hz, 1H), 4.52 (d, J = 14.5, 1H), 2.87-2.82 (m, 1H), 2.18-2.15 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.5, 164.2, 144.1, 141.4, 134.0, 133.4, 130.1, 130.0, 129.6, 128.7, 128.6 (2), 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.0, 124.7, 122.8, 119.7, 70.2, 50.2, 49.3, 47.7, 26.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{23}Cl_2F_3NO_3$ ([M+H]$^+$) 548.1002, found 548.1008.

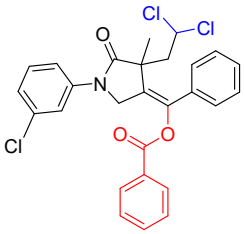


(1-(4-Cyanophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4n). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v). Yellow oil (0.0756 g, 75% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 2H), 7.83-7.81 (m, 2H), 7.66-7.63 (m, 3H), 7.55-7.51 (m, 4H), 7.47-7.45 (m, 3H), 6.21-6.18 (m, 1H), 4.65 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.86-2.80 (m, 1H), 2.18-2.13 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.9, 164.1, 144.3, 142.2, 134.1, 133.3, 133.1, 130.2, 130.1, 129.6, 128.7 (2), 128.5, 124.3, 119.7, 118.6, 107.9, 70.1, 50.2, 49.1, 47.8, 26.7; HRMS *m/z* (ESI) calcd for $C_{28}H_{23}Cl_2N_2O_3$ ([M+H]$^+$) 505.1080, found 505.1084.

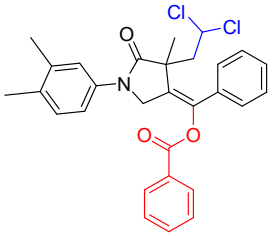


(4-(2,2-Dichloroethyl)-4-methyl-1-(4-nitrophenyl)-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4o). The product was purified by silica gel column

chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0839 g, 80% yield, *Z*/*E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (d, J = 9.5 Hz, 2H), 8.13-8.11 (m, 2H), 7.89-7.87 (m, 1H), 7.66-7.59 (m, 2H), 7.54-7.45 (m, 7H), 6.23-6.20 (m, 1H), 4.70 (d, J = 14.5 Hz, 1H), 4.55 (d, J = 14.5 Hz, 1H), 2.87-2.83 (m, 1H), 2.19-2.16 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 176.1, 164.2, 144.4, 143.8, 134.1, 133.7, 133.3, 130.2, 130.1, 129.5, 128.7 (2), 128.4, 124.7, 124.2, 119.3, 70.1, 50.3, 49.3, 47.8, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_2N_2O_5$ ($[M+H]^+$) 525.0979, found 525.0983.

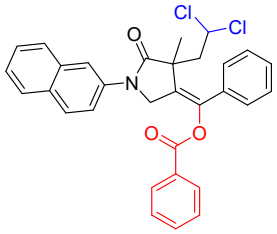


(1-(3-Chlorophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4p). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow solid (0.0831 g, 81% yield, *Z*/*E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 2H), 7.73 (t, J = 2.0 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.55-7.52 (m, 3H), 7.49 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 3.5 Hz, 3H), 7.28 (t, J = 8.0 Hz, 1H), 7.15-7.13 (m, 1H), 6.21-6.18 (m, 1H), 4.61 (d, J = 14.5 Hz, 1H), 4.48 (d, J = 14.5 Hz, 1H), 2.85-2.80 (m, 1H), 2.17-2.14 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.2, 164.2, 144.0, 139.6, 134.7, 134.0, 133.5, 130.2, 130.0, 129.9, 129.7, 128.7 (2), 128.6, 125.2, 125.0, 120.3, 118.2, 70.2, 50.2, 49.5, 47.7, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_3NO_3$ ($[M+H]^+$) 514.0738, found 514.0742.

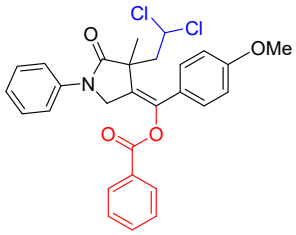


(4-(2,2-Dichloroethyl)-1-(3,4-dimethylphenyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4q). The

product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0821 g, 81% yied, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.11-8.09 (m, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.56-7.54 (m, 2H), 7.50-7.44 (m, 7H), 7.10 (d, J = 8.5 Hz, 1H), 6.20-6.17 (m, 1H), 4.59 (d, J = 14.5 Hz, 1H), 4.48 (d, J = 14.5 Hz, 1H), 2.84-2.79 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 2.17-2.13 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 174.6, 164.3, 143.6, 137.4, 136.2, 134.0, 133.9, 133.7, 130.2, 130.0, 129.9, 129.8, 128.9, 128.7, 128.6, 125.8, 122.1, 118.2, 70.4, 50.1, 50.0, 47.6, 26.8, 20.0, 19.3; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}Cl_2NO_3$ ($[M+H]^+$) 508.1441, found 508.1443.

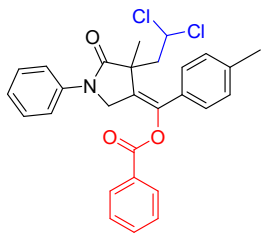


(4-(2,2-Dichloroethyl)-4-methyl-1-(naphthalen-2-yl)-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4r). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0762 g, 72% yield, *Z/E* >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02-7.99 (m, 2H), 7.89-7.83 (m, 2H), 7.79-7.76 (m, 1H), 7.65-7.63 (m, 2H), 7.56-7.47 (m, 7H), 7.42-7.37 (m, 3H), 6.32-6.29 (m, 1H), 4.62-4.54 (m, 2H), 2.87-2.83 (m, 1H), 2.26-2.22 (m, 1H), 1.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.8, 164.2, 143.5, 134.5, 134.4, 133.8, 133.6, 130.0, 129.9 (2), 129.7, 128.8, 128.6 (3), 128.5, 128.4, 127.0, 126.8, 126.4, 125.7, 122.2, 70.6, 52.6, 49.3, 46.8, 27.6; HRMS *m/z* (ESI) calcd for $C_{31}H_{26}Cl_2NO_3$ ($[M+H]^+$) 530.1284, found 530.1280.

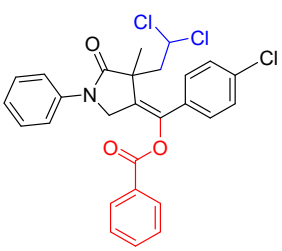


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(4-methoxyphenyl)methyl benzoate (4t). The product was purified by silica gel column

chromatography with petroleum ether/ethyl acetate (6:1, v/v). Yellow oil (0.0815 g, 80% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.09 (m, 3H), 7.63-7.60 (m, 3H), 7.50-7.45 (m, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 6.96-6.93 (m, 2H), 6.21-6.18 (m, 1H), 4.62 (d, J = 14.8 Hz, 1H), 4.49 (d, J = 14.8 Hz, 1H), 3.83 (s, 3H), 2.87-2.81 (m, 1H), 2.21-2.16 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.0, 164.3, 160.6, 143.7, 138.5, 133.9, 133.6, 131.2, 130.1, 129.0, 128.6, 128.4, 125.8, 125.3, 120.6, 113.9, 70.4, 55.3, 50.0, 49.8, 47.7, 26.7; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_4$ ([M+H]$^+$) 510.1233, found 510.1237.

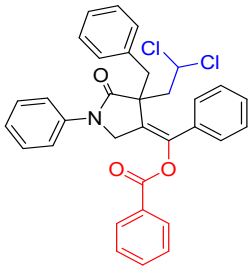


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(p-tolyl)methyl benzoate (4u). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0809 g, 82% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11-8.07 (m, 2H), 7.64-7.60 (m, 3H), 7.50-7.43 (m, 4H), 7.36 (t, J = 7.6 Hz, 2H), 7.27-7.23 (m, 2H), 7.19-7.13 (m, 1H), 6.23-6.17 (m, 1H), 4.63 (d, J = 18.0 Hz, 1H), 4.49 (d, J = 14.4 Hz, 1H), 2.87-2.80 (m, 1H), 2.38 (s, 3H), 2.20-2.14 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 164.2, 143.8, 140.0, 138.4, 133.9, 130.6, 130.1, 129.5, 129.2, 128.9, 128.7, 128.6, 125.3, 125.1, 120.5, 70.4, 50.0, 49.7, 47.6, 26.7, 21.4; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}Cl_2NO_3$ ([M+H]$^+$) 494.1284, found 494.1280.

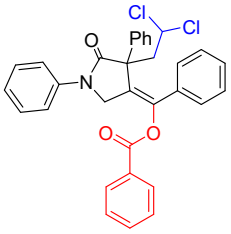


(4-Chlorophenyl)(4-(2,2-dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl benzoate (4v). The product was purified by silica gel column chromatography

with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0790 g, 77% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10-8.07 (m, 2H), 7.65-7.60 (m, 3H), 7.52-7.47 (m, 4H), 7.45-7.42 (m, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 6.16-6.13 (m, 1H), 4.62 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 2.87-2.81 (m, 1H), 2.20-2.15 (m, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.5, 146.2, 142.5, 138.3, 136.1, 134.1, 132.0, 131.2, 130.1, 129.0 (2), 128.7, 128.5, 126.5, 125.4, 120.5, 70.1, 50.2, 49.7, 47.6, 26.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_3NO_3$ ($[M+H]^+$) 514.0738, found 514.0744.

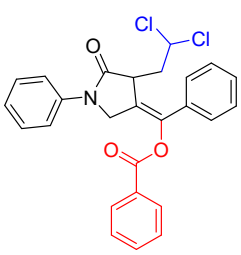


(4-Benzyl-4-(2,2-dichloroethyl)-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4w). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0988 g, 89% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 6.0 Hz, 2H), 7.60 (t, J = 6.8 Hz, 1H), 7.54-7.44 (m, 9H), 7.29-7.25 (m, 2H), 7.15-7.08 (m, 4H), 6.08-6.04 (m, 1H), 4.25 (d, J = 14.4 Hz, 1H), 3.55 (d, J = 14.8 Hz, 1H), 3.12 (d, J = 12.8 Hz, 1H), 3.04 (d, J = 12.8 Hz, 1H), 2.98-2.91 (m, 1H), 2.24-2.19 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.7, 164.1, 143.2, 137.8, 134.8, 133.9, 133.8, 130.1, 130.0 (2), 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 127.3, 125.6, 124.2, 121.4, 70.1, 53.9, 50.5, 47.1, 46.5; HRMS *m/z* (ESI) calcd for $C_{33}H_{28}Cl_2NO_3$ ($[M+H]^+$) 556.1441, found 556.1447.

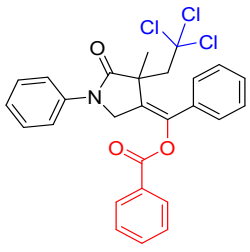


(4-(2,2-Dichloroethyl)-5-oxo-1,4-diphenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4x). The product was purified

by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (0.0909 g, 84% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.17 (m, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.60-7.54 (m, 5H), 7.44 (t, J =8.0 Hz, 3H), 7.36-7.30 (m, 5H), 7.19-7.16 (m, 4H), 5.91-5.87 (m, 1H), 4.80-4.73 (m, 2H), 3.63-3.57 (m, 1H), 2.60-2.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.8, 164.4, 144.1, 142.6, 138.6, 134.1, 133.3, 130.2, 129.8, 129.1, 128.9, 128.8, 128.6, 128.5, 127.9 (2), 126.4, 125.3, 124.4, 120.4, 70.3, 55.6, 50.6, 45.3; HRMS *m/z* (ESI) calcd for $C_{32}H_{26}Cl_2NO_3$ ($[M+H]^+$) 542.1284, found 542.1288.

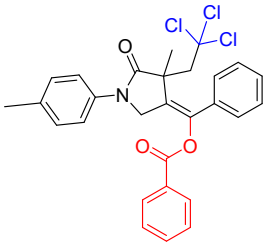


(4-(2,2-Dichloroethyl)-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4y). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0660 g, 71% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.56-7.51 (m, 4H), 7.46-7.41 (m, 3H), 7.37 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 6.26-6.23 (m, 1H), 4.66 (d, J = 12.8 Hz, 1H), 4.54 (d, J = 14.4 Hz, 1H), 4.12-4.07 (m, 1H), 2.60-2.54 (m, 1H), 2.44-2.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4 , 164.1, 142.9, 138.2, 134.1, 133.3, 130.2, 129.7 (2), 129.0, 128.8, 128.6, 127.4, 125.5, 120.5, 120.0, 70.5, 50.8, 43.2, 43.0; HRMS *m/z* (ESI) calcd for $C_{26}H_{22}Cl_2NO_3$ ($[M+H]^+$) 466.0971, found 466.0975.

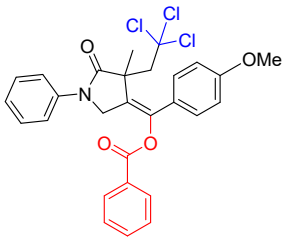


(4-Methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4z). The product was purified by silica gel column chromatography with petroleum

ether/ethyl acetate (10:1, v/v). Yellow oil (0.0821 g, 80% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09-8.06 (m, 2H), 7.71-7.65 (m, 4H), 7.61 (t, J = 7.6 Hz, 1H), 7.49-7.43 (m, 5H), 7.37 (t, J = 8.0 Hz, 2H), 7.17 (t, J = 7.6, 1H), 4.72-4.62 (m, 2H), 3.38 (d, J = 15.2 Hz, 1H), 3.01 (d, J = 15.2 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.7, 164.0, 144.0, 138.6, 134.4, 133.7, 130.0, 129.6 (2), 129.0 (2), 128.6, 128.5, 125.3, 124.9, 119.8, 96.4, 50.1, 49.1, 48.1, 26.1; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}Cl_3NO_3$ ([M+H]$^+$) 514.0738, found 514.0744.

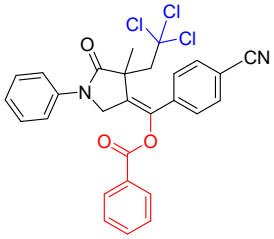


(4-Methyl-5-oxo-1-(*p*-tolyl)-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4aa). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Yellow oil (0.0822 g, 78% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63-7.60 (m, 3H), 7.49-7.34 (m, 8H), 7.23-7.20 (m, 3H), 4.73-4.59 (m, 2H), 3.25-3.18 (m, 1H), 2.94-2.85 (m, 1H), 2.36 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.1, 160.7, 142.6, 140.2, 137.4, 136.0, 135.1, 132.5, 129.6 (2), 129.5, 128.8, 128.7, 128.5, 120.2, 120.1, 96.4, 53.1, 51.4, 49.8, 26.0, 20.9; HRMS *m/z* (ESI) calcd for $C_{28}H_{25}Cl_3NO_3$ ([M+H]$^+$) 528.0895, found 528.0891.



(4-Methoxyphenyl)(4-methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)methyl benzoate (4ab). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (0.0771 g, 71% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J = 8.0 Hz,

3H), 7.44-7.41 (m, 6H), 7.22 (t, J = 7.2 Hz, 2H), 6.98-6.91 (m, 3H), 4.72 (d, J = 14.8, 1H), 4.61 (d, J = 14.8 Hz, 1H), 3.86 (s, 3H), 3.24 (d, J = 14.8 Hz, 1H), 2.89 (d, J = 15.2 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.8, 160.2, 159.6, 138.5, 132.3, 130.3, 129.5, 129.1 (2), 129.0, 125.4, 125.3, 120.2, 120.1, 114.0, 113.8, 96.4, 60.7, 55.3, 53.0, 49.9, 26.2; HRMS *m/z* (ESI) calcd for $C_{28}H_{25}Cl_3NO_4$ ($[M+H]^+$) 544.0844, found 544.0840.



(4-Cyanophenyl)(4-methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)methyl benzoate (4ac). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Yellow oil (0.0882 g, 82% yield, *Z/E* >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14-8.11 (m, 2H), 7.80-7.72 (m, 4H), 7.65-7.60 (m, 3H), 7.49 (d, J = 7.6 Hz, 2H), 7.47-7.41 (m, 2H), 7.23 (t, J = 7.2 Hz, 1H), 4.77-4.63 (m, 2H), 3.34-3.26 (m, 1H), 2.82-2.75 (m, 1H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.7, 171.7, 141.7, 138.2, 134.3, 133.7, 132.6, 132.4, 130.2, 129.7, 129.2, 128.5, 126.3, 125.6, 120.2, 117.9, 113.6, 96.0, 61.0, 53.0, 49.8, 26.2; HRMS *m/z* (ESI) calcd for $C_{28}H_{22}Cl_3N_2O_3$ ($[M+H]^+$) 539.0691, found 539.0697.

(E) Reference

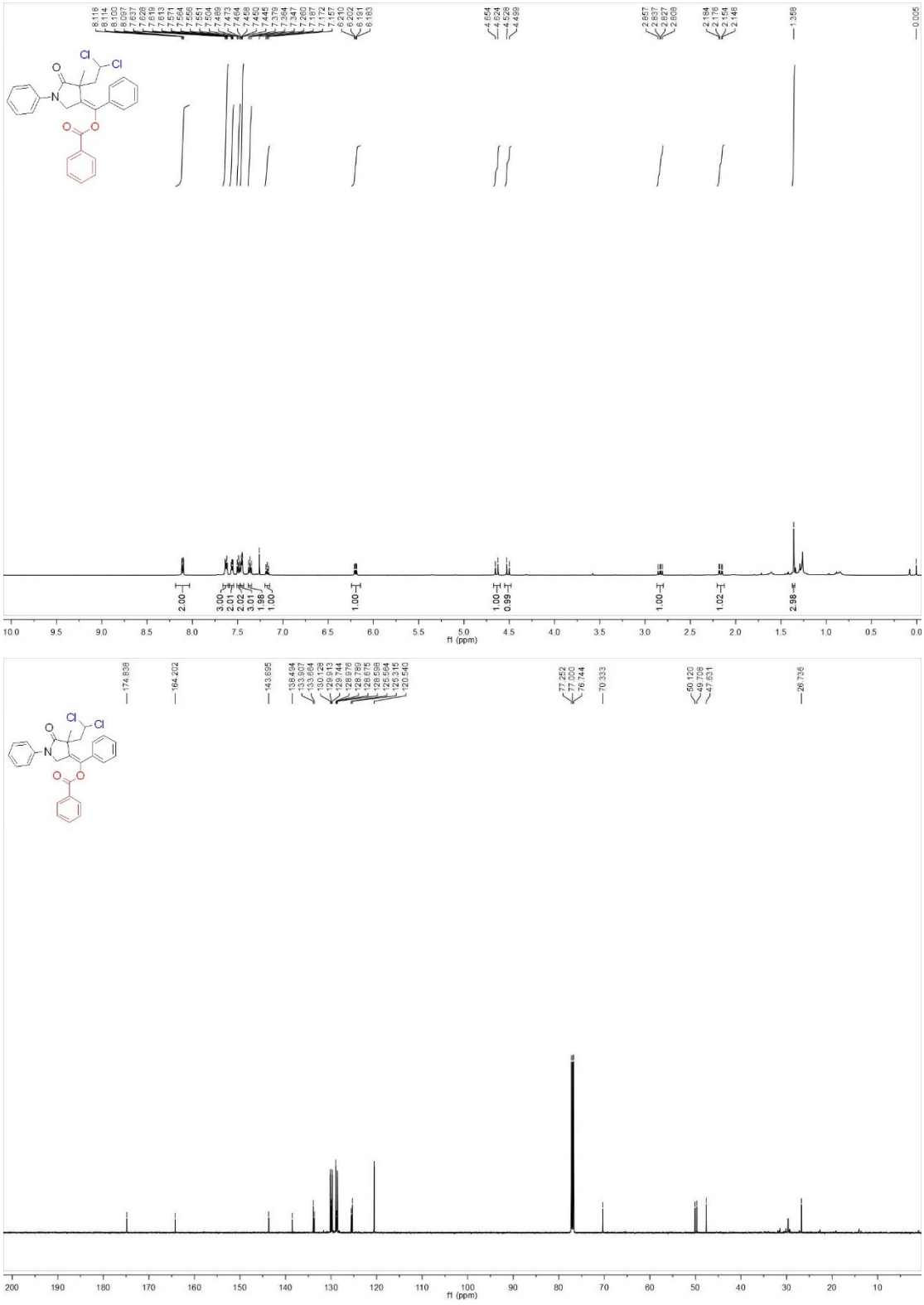
[1] W.-Y. Yu, W. N. Sit, Z. Zhou and A. S.-C. Chan, *Org. Lett.* 2009, **11**, 3174-3177.

[2] J. Christoffers, T. Kauf, T. Werner and M. Rössle, *Eur. J. Org. Chem.* 2006, **2006**, 2601-2608.

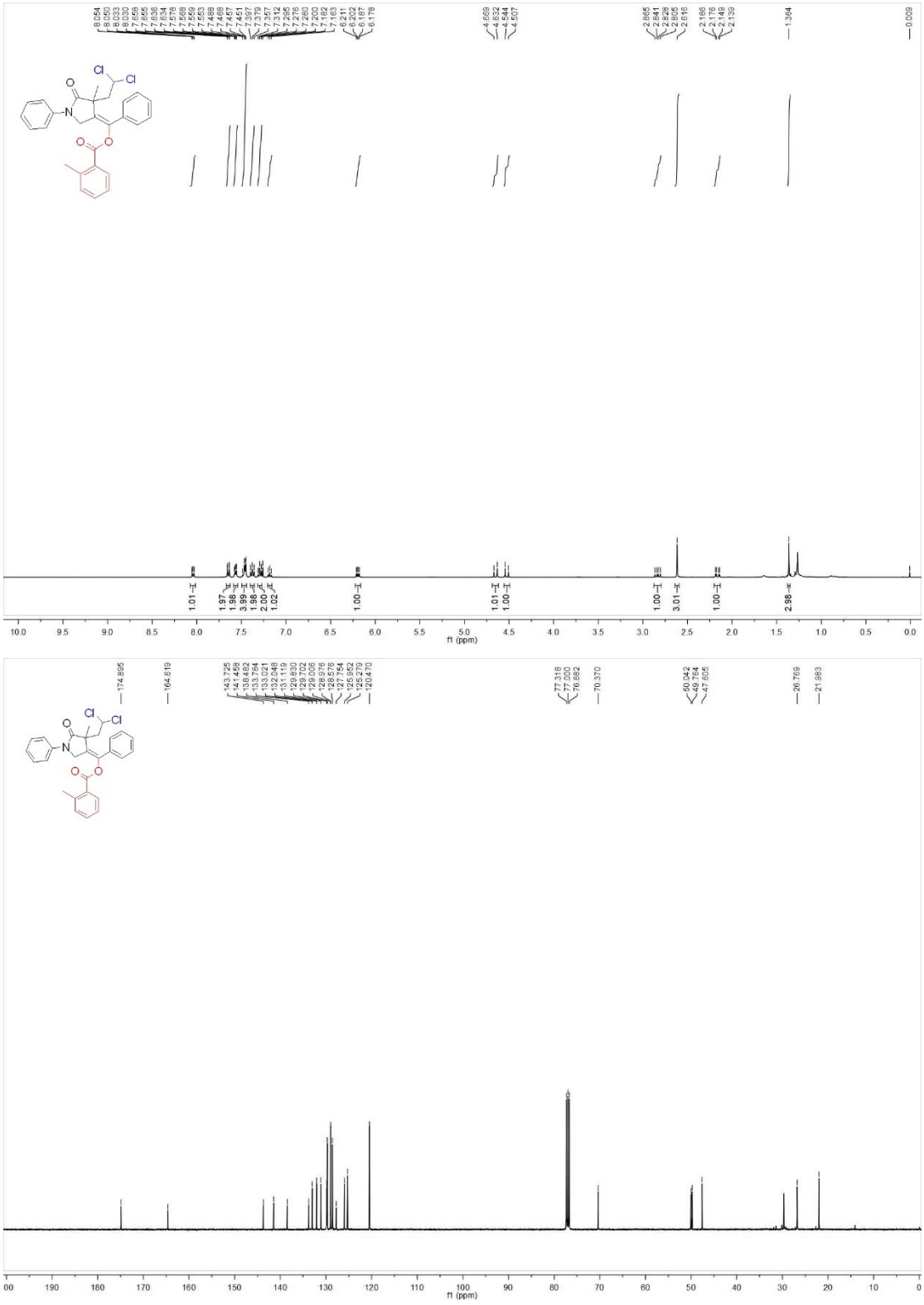
[3] Y.-T. Lee, Y.-J. Jang, S.-E. Syu, S.-C. Chou, C.-J. Lee and W. Lin, *Chem. Commun.* 2012, **48**, 8135-8137.

(F) Spectra

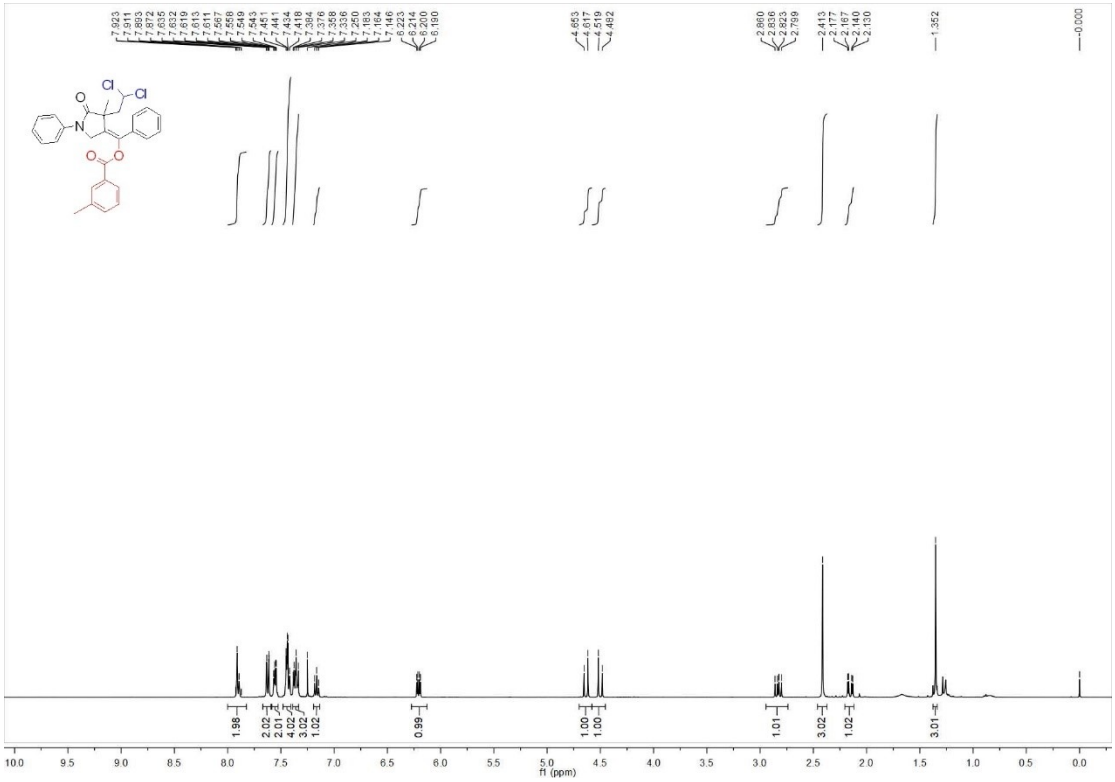
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4a)

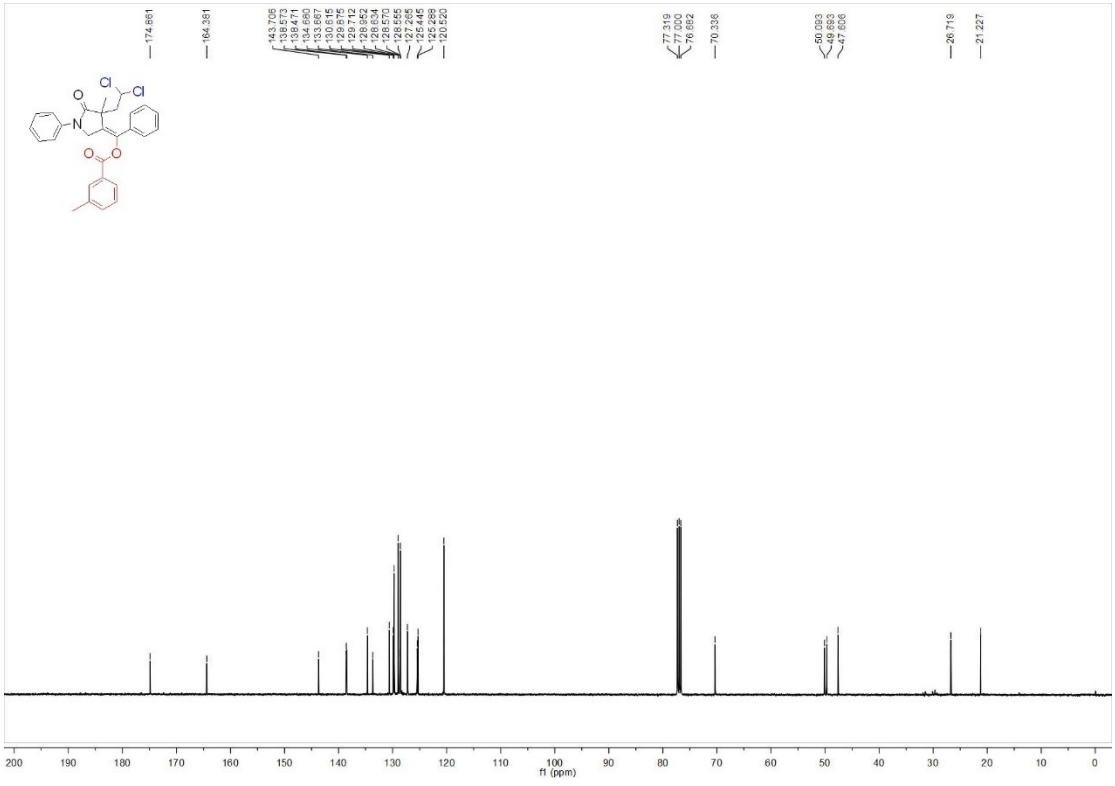


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 2-methylbenzoate (4b)

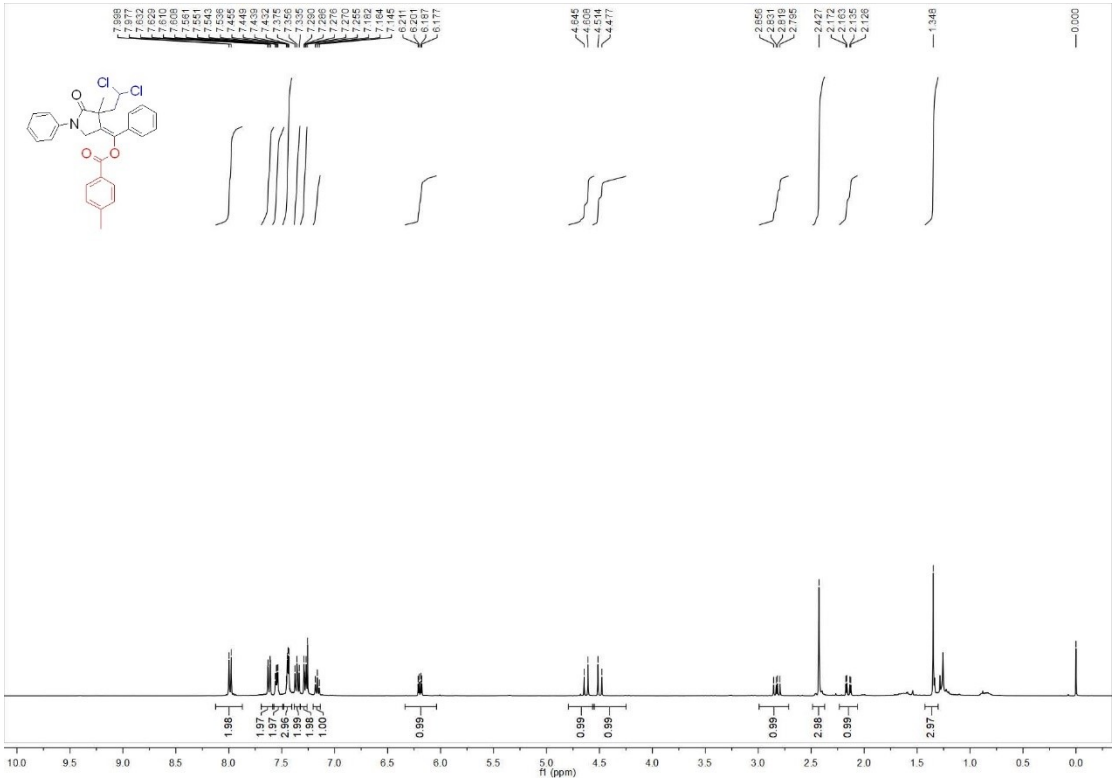


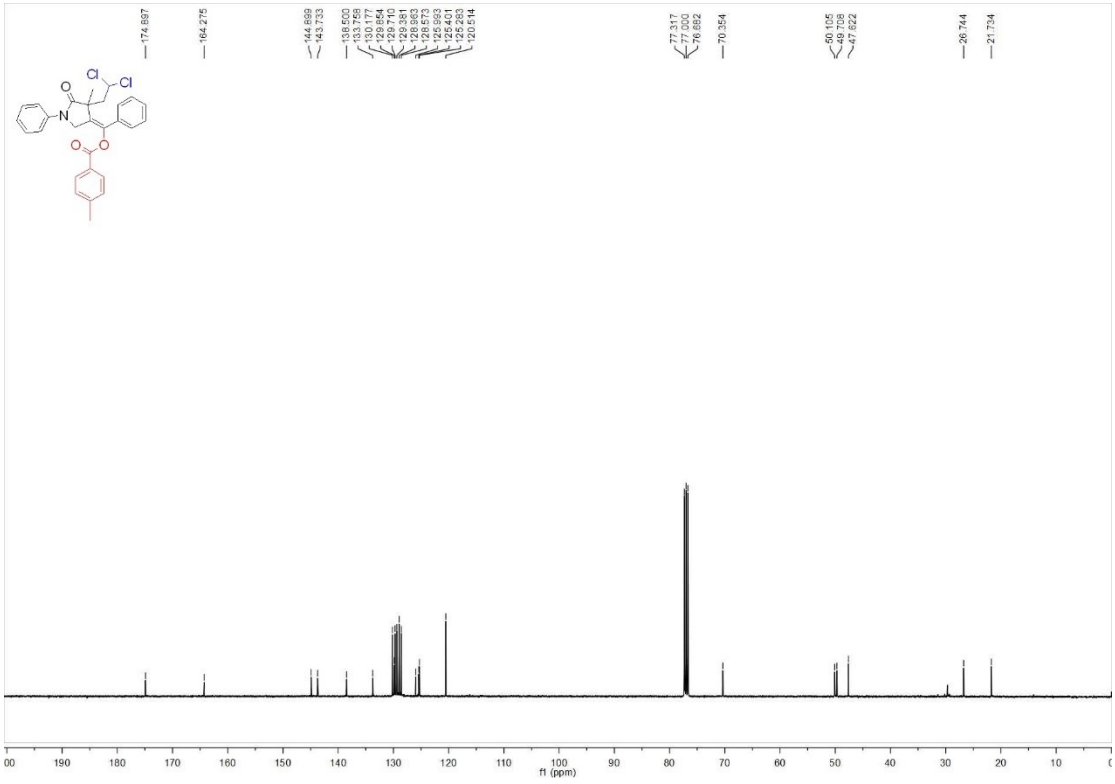
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 3-methylbenzoate (4c)



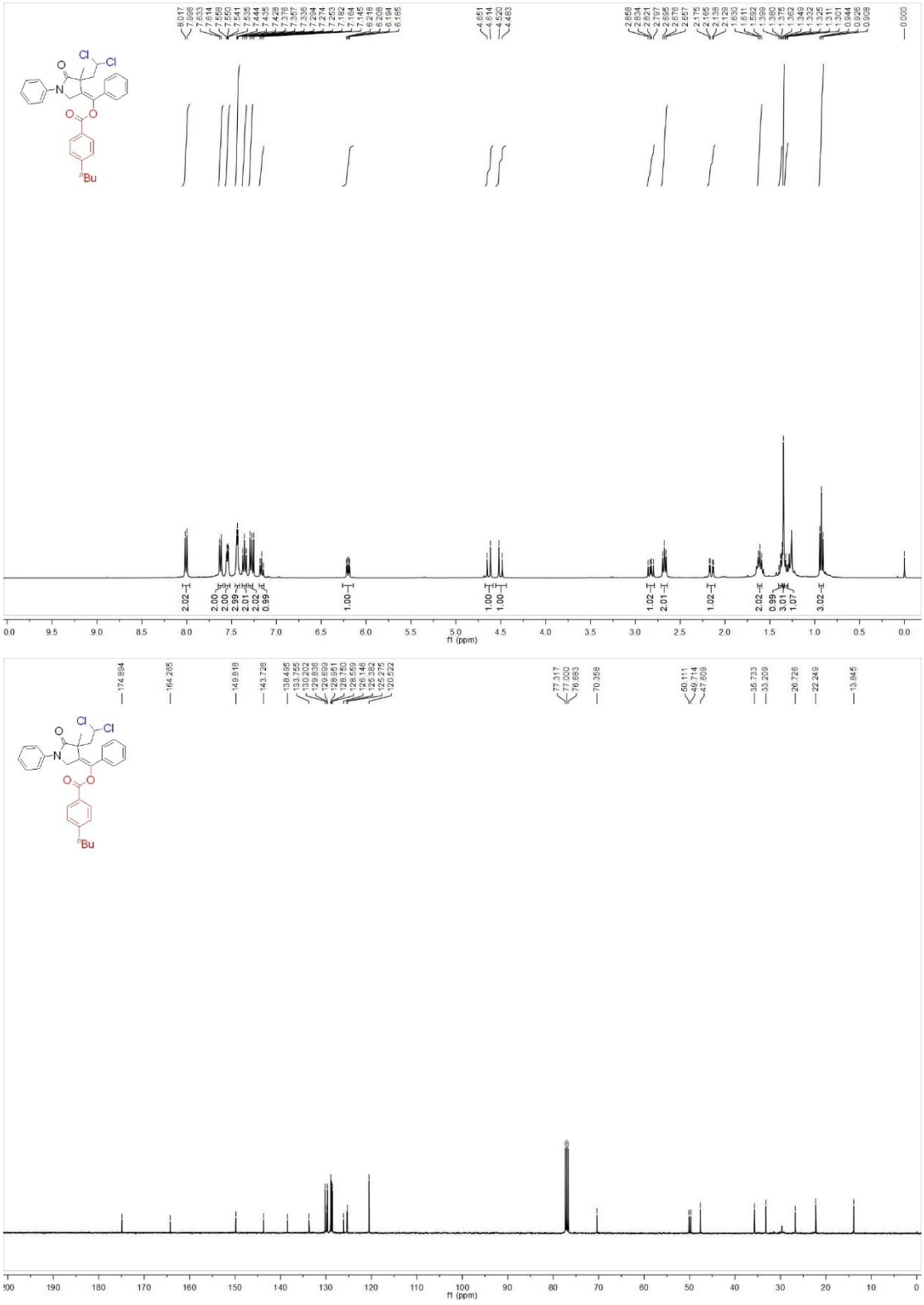


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-methylbenzoate (4d)

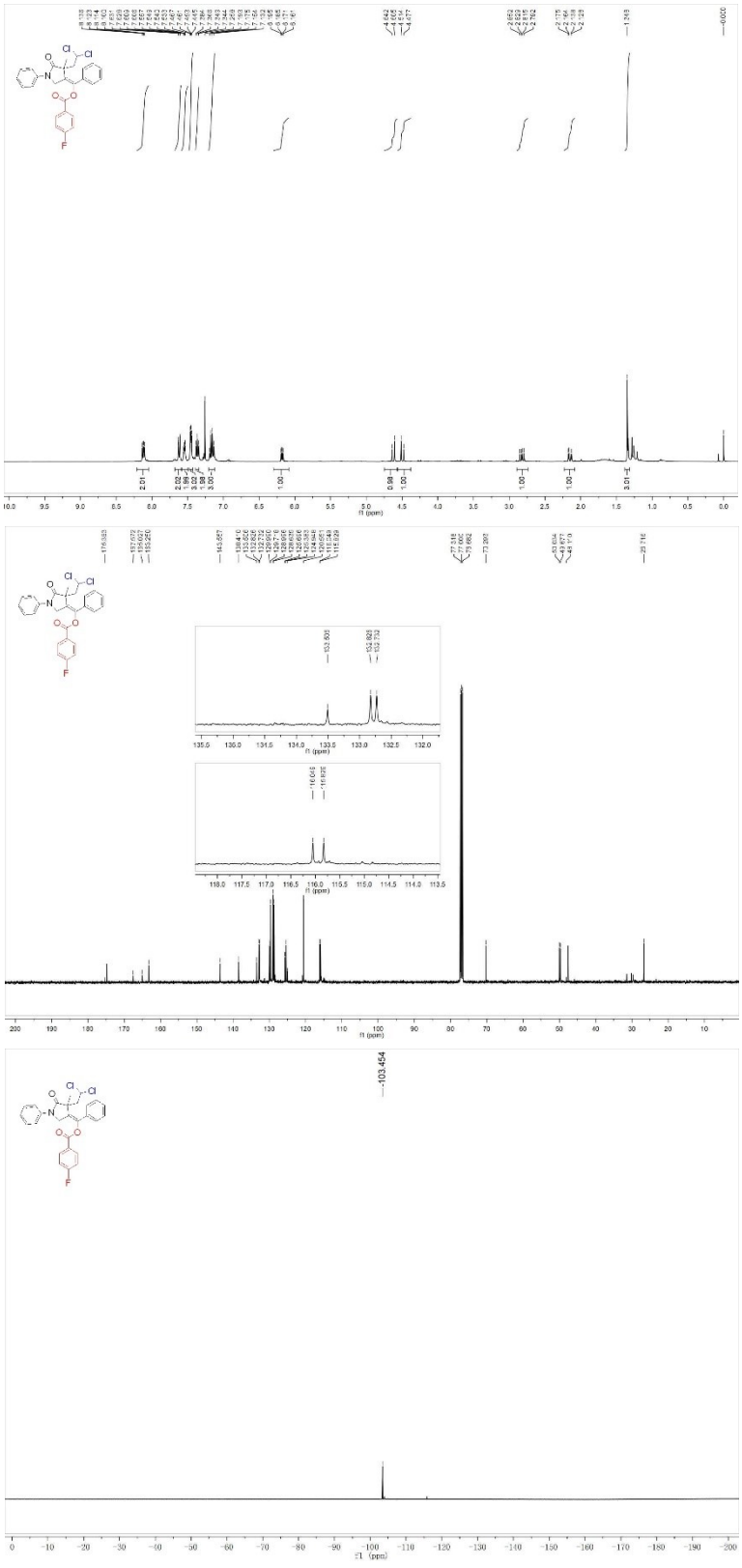




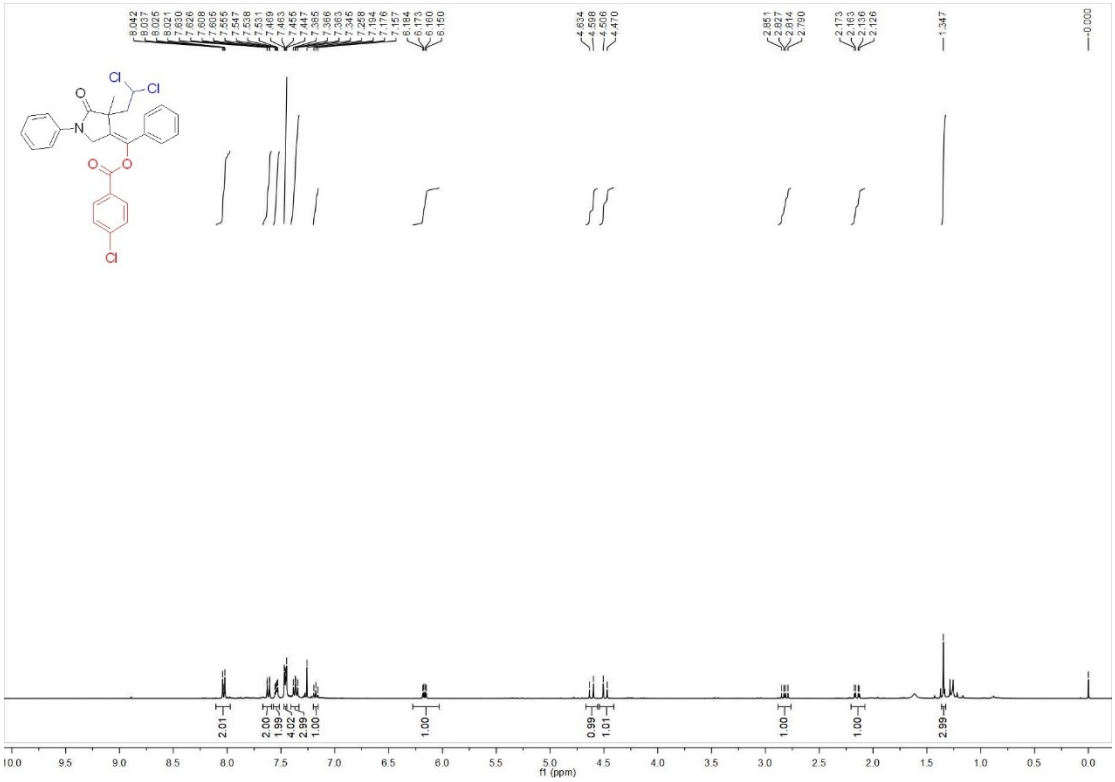
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-butylbenzoate (4e)

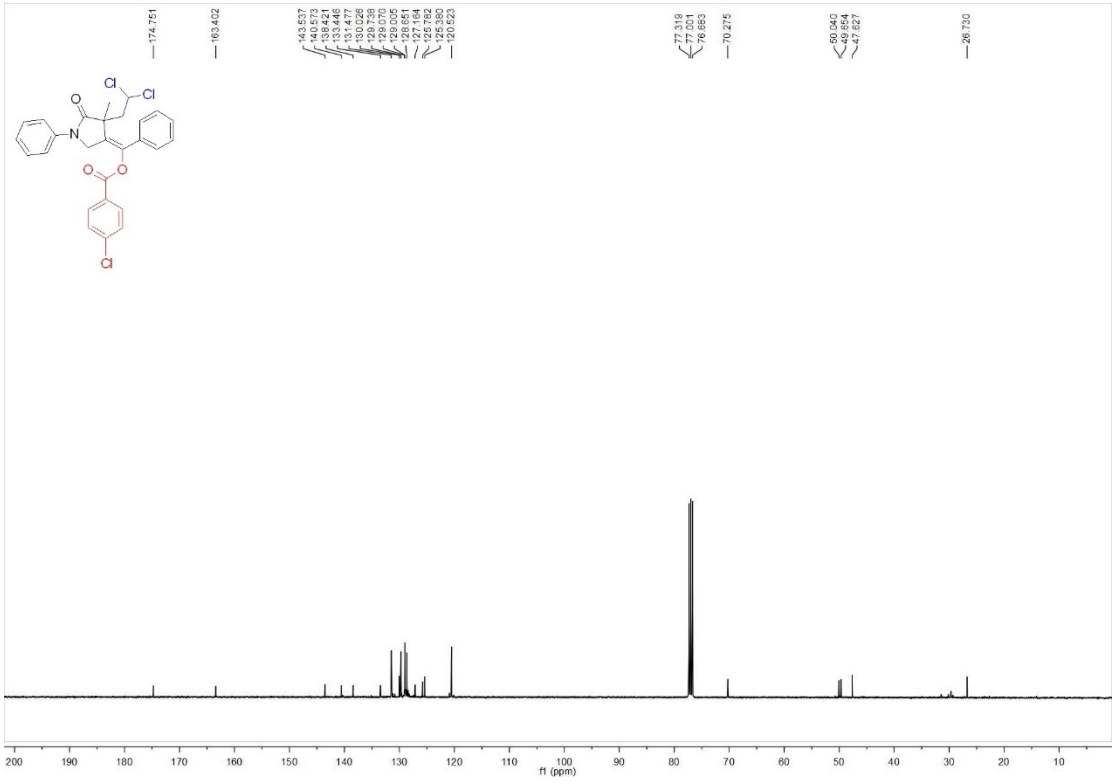


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-fluorobenzoate (4f)

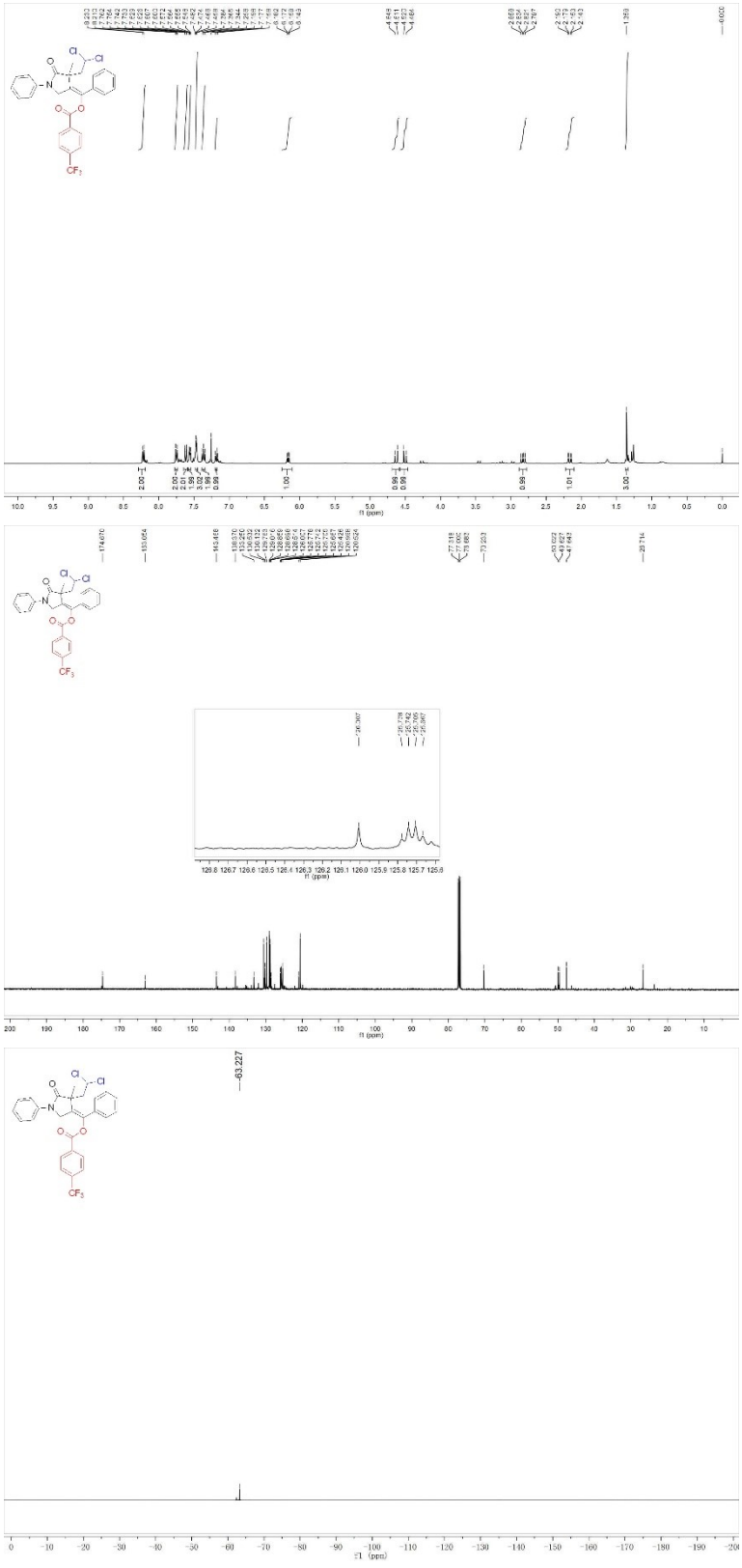


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-chlorobenzoate (4g)

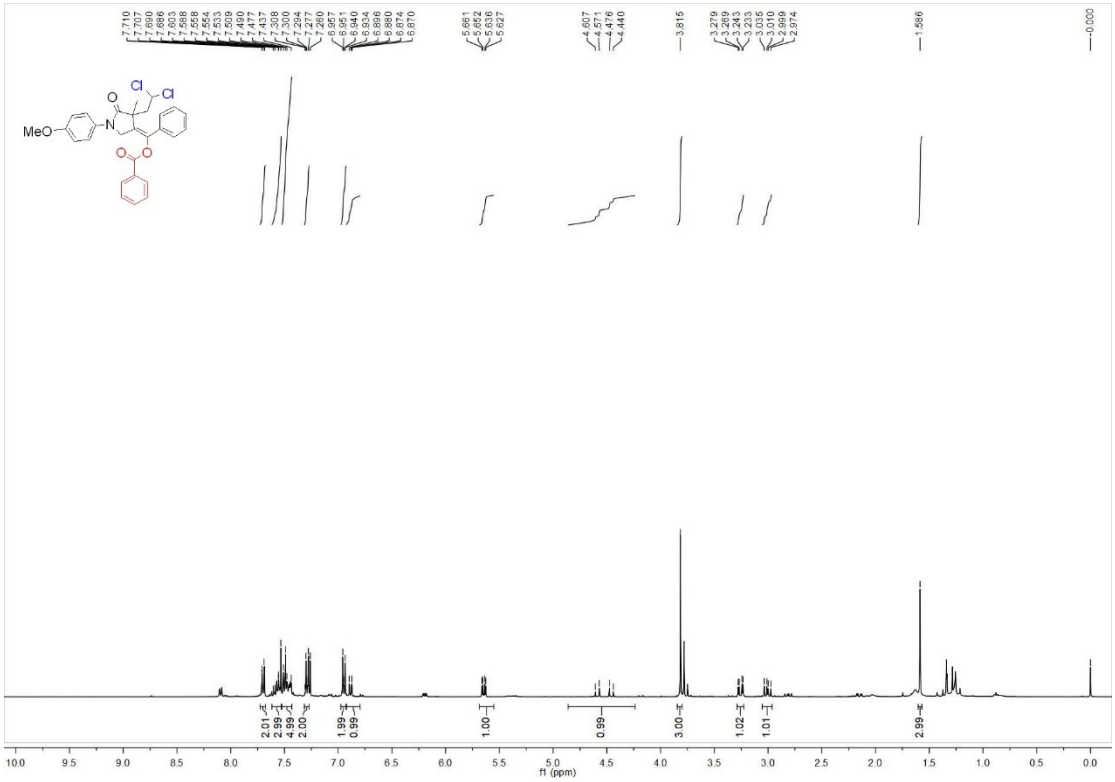


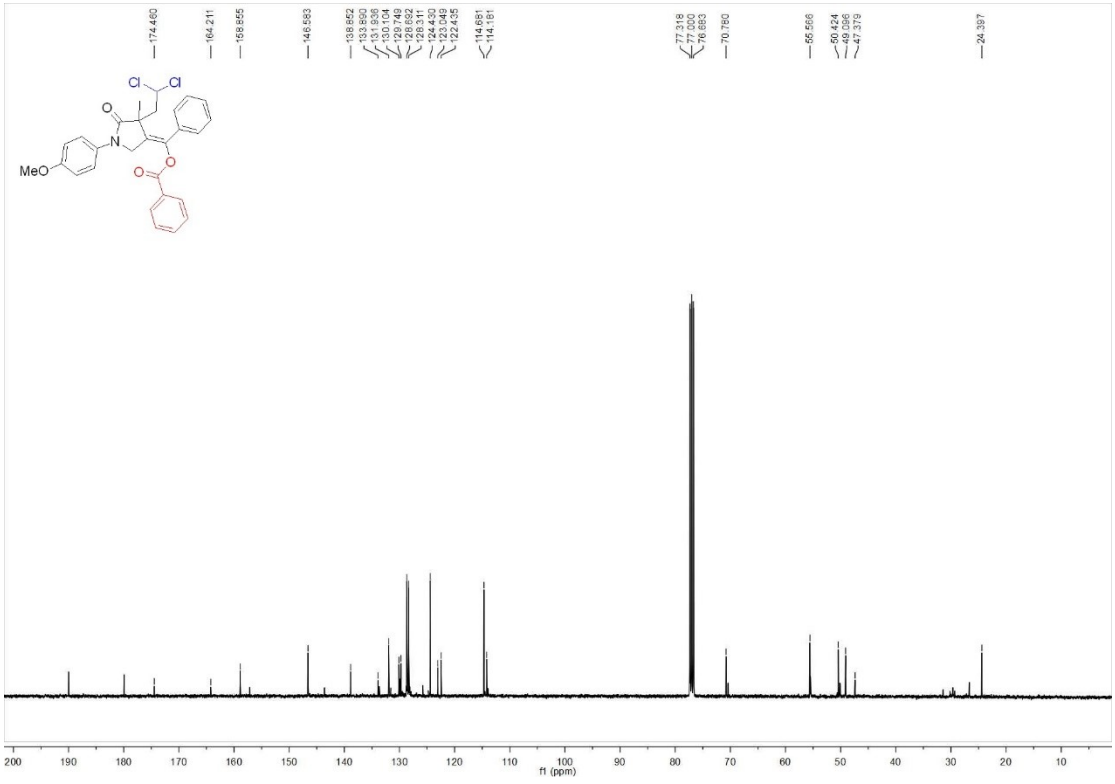


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl 4-(trifluoromethyl)benzoate (4h)

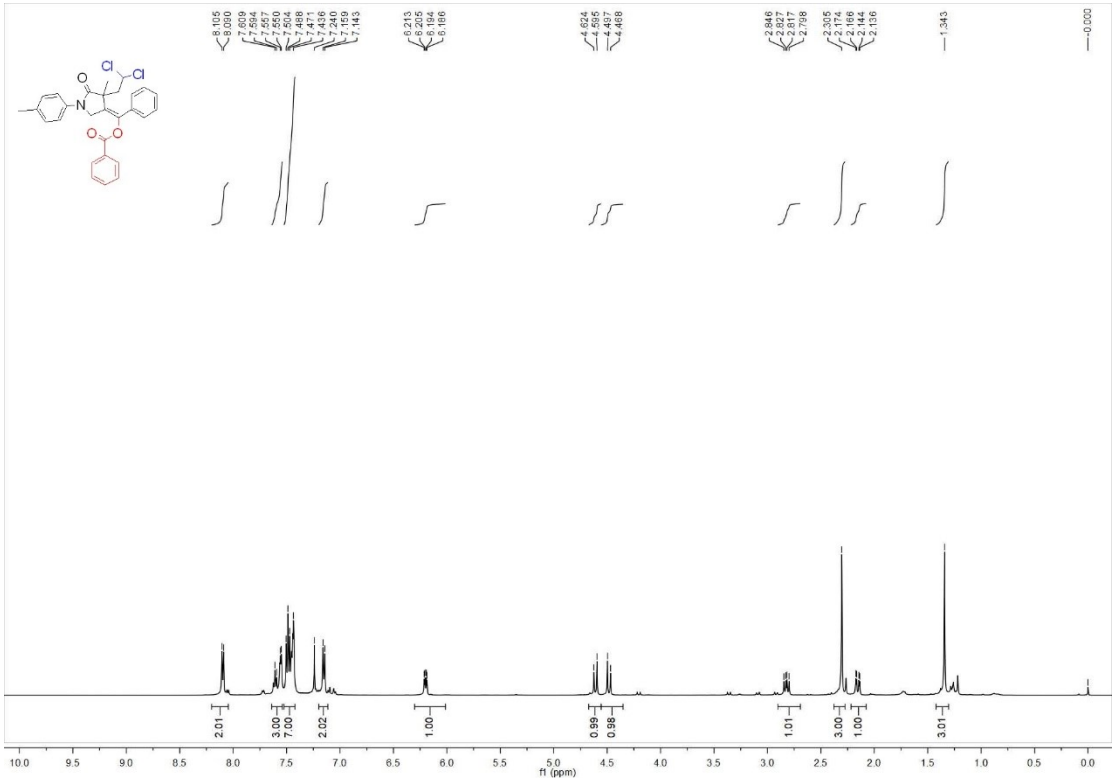


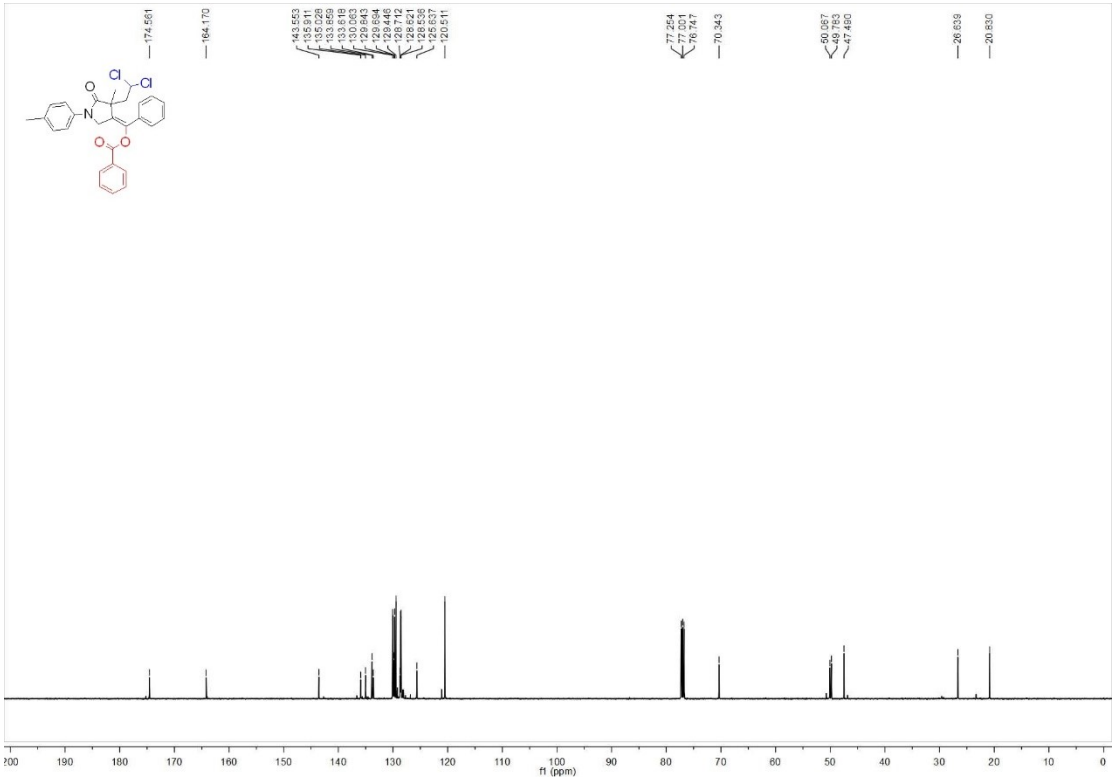
(4-(2,2-Dichloroethyl)-1-(4-methoxyphenyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4j)



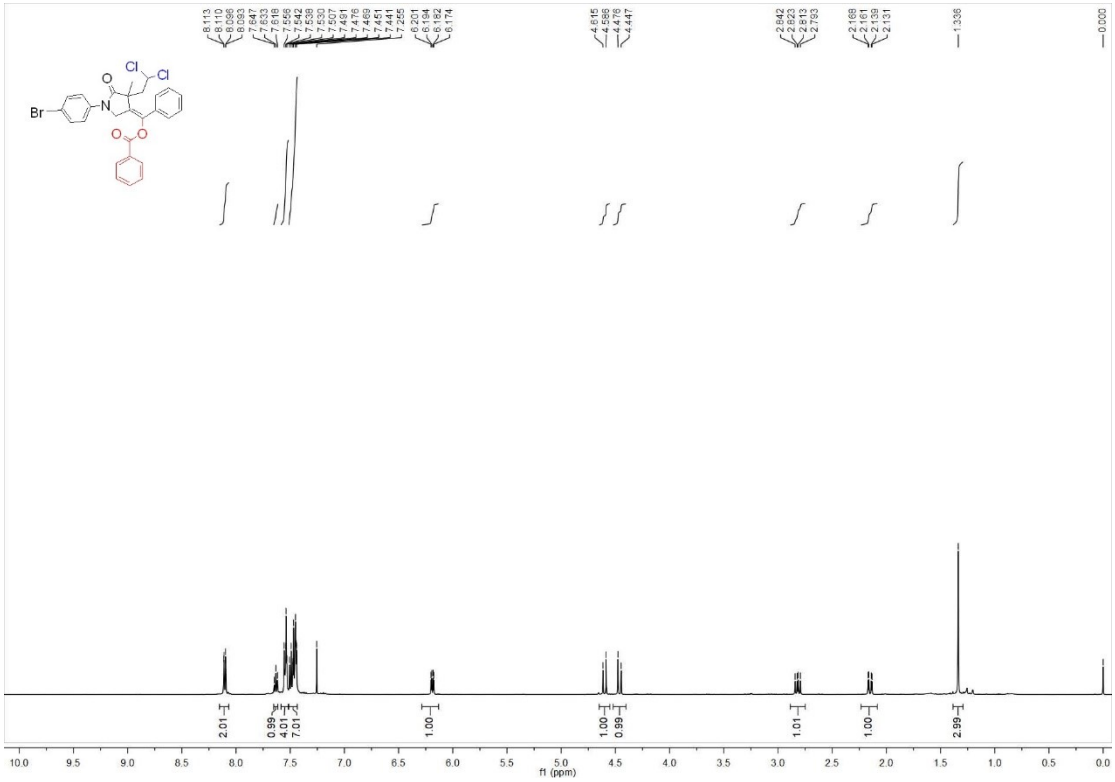


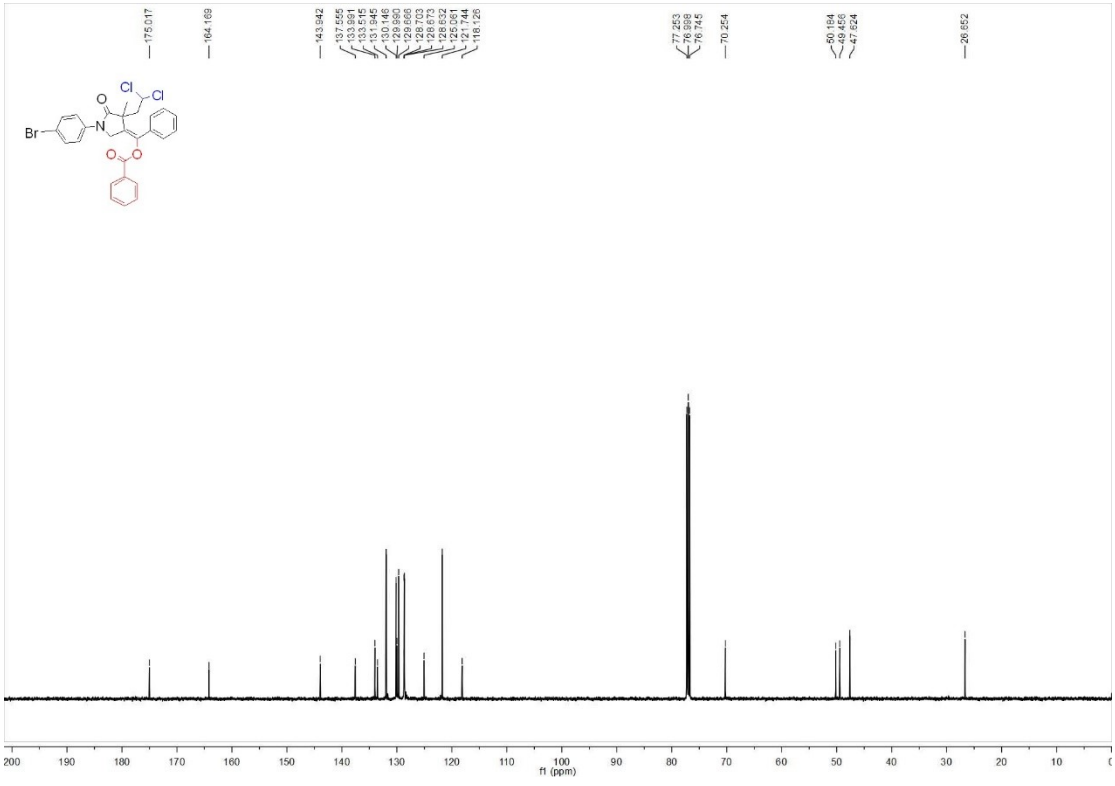
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-(*p*-tolyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4k)



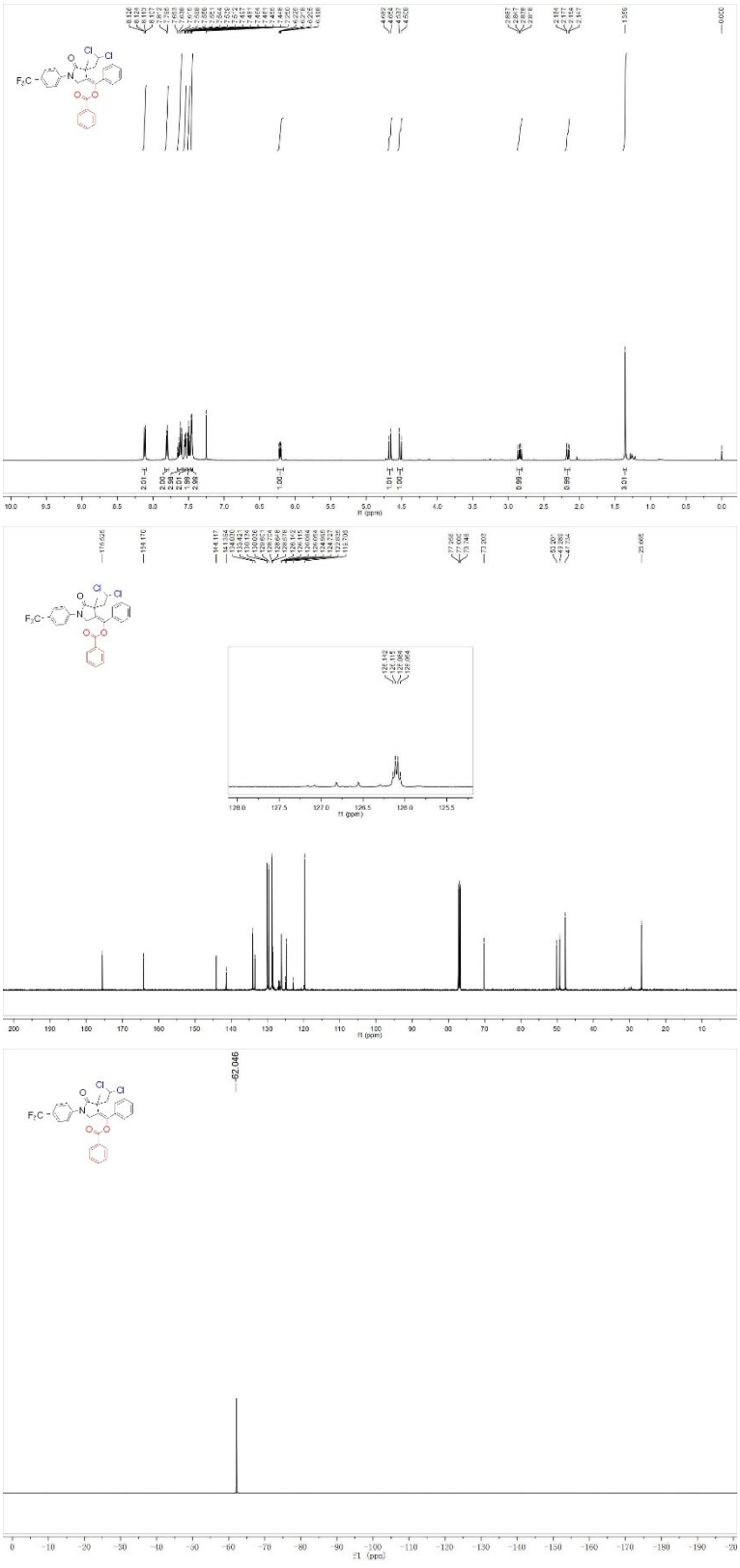


(1-(4-Bromophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4l)

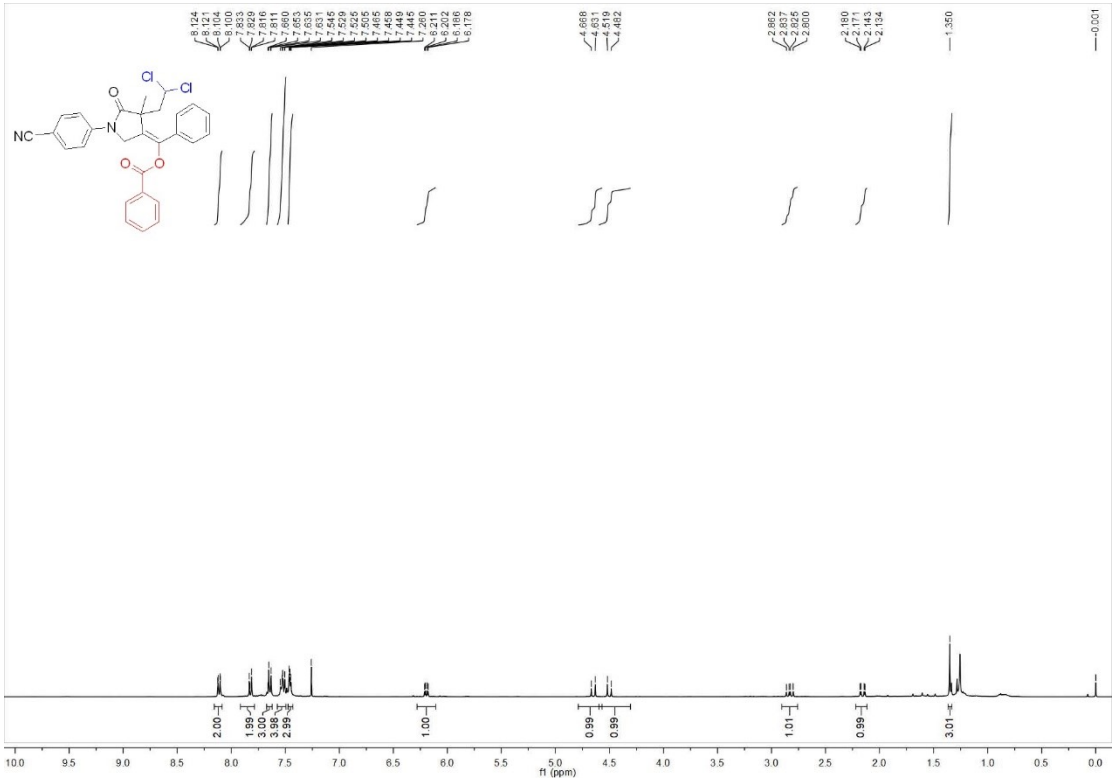


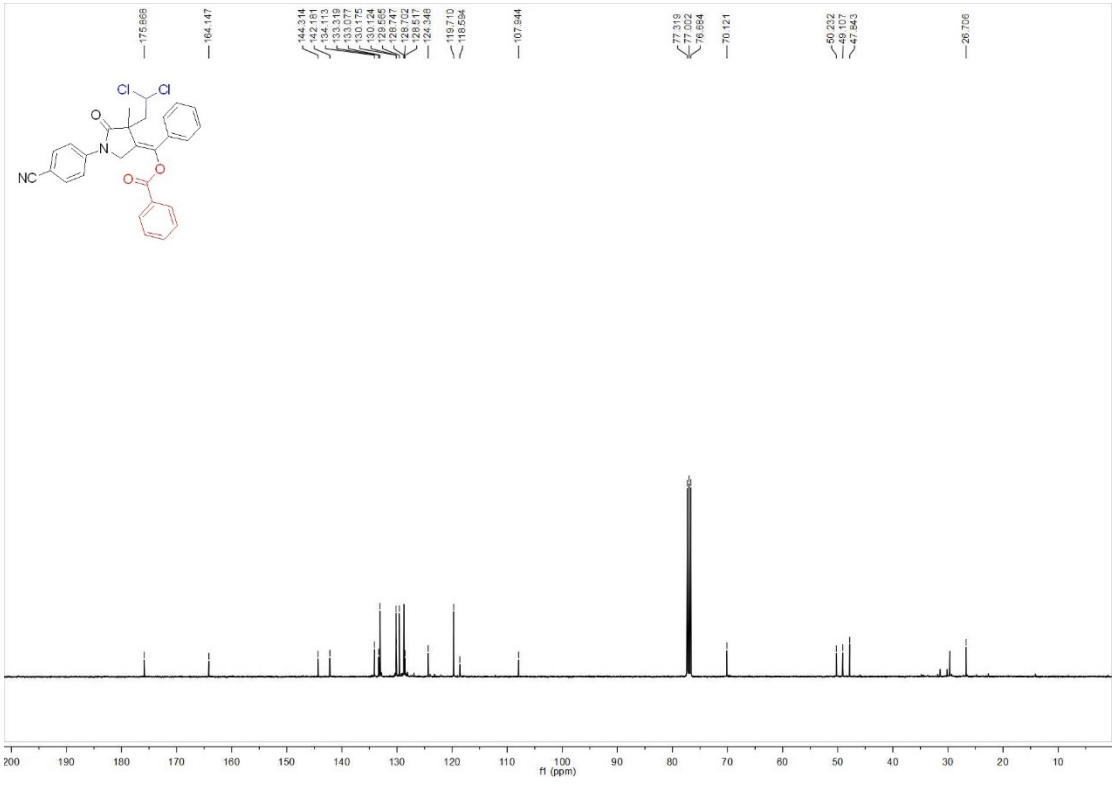


(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4m)

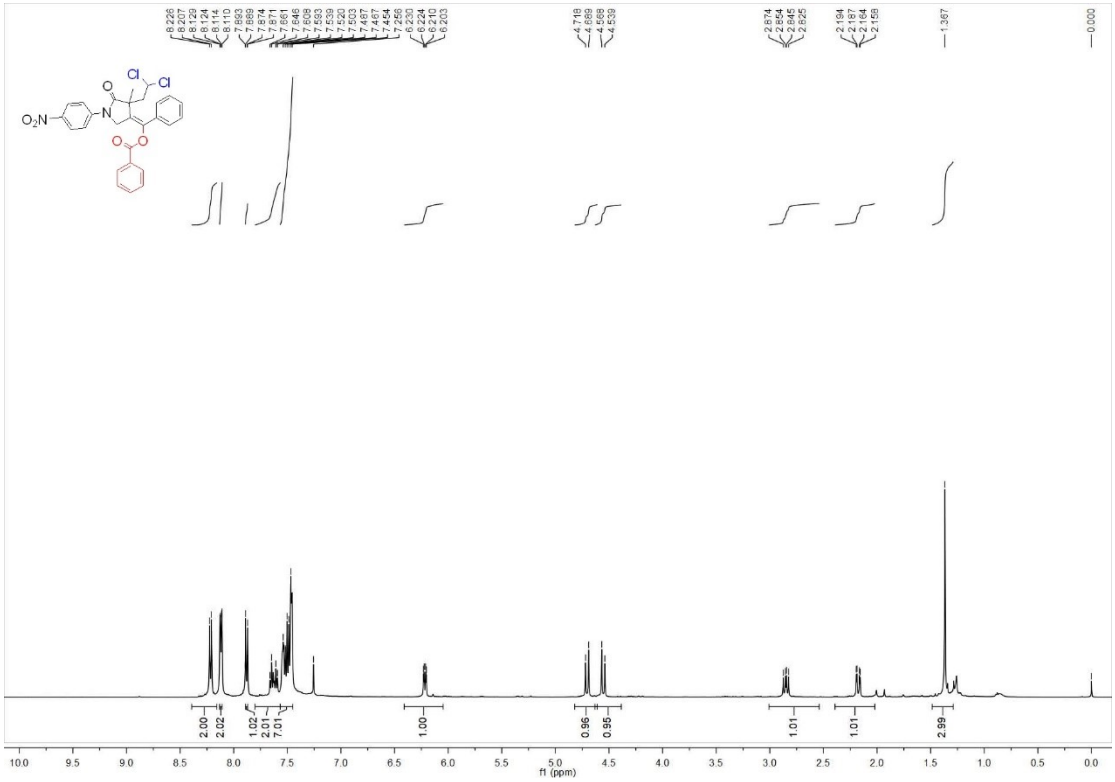


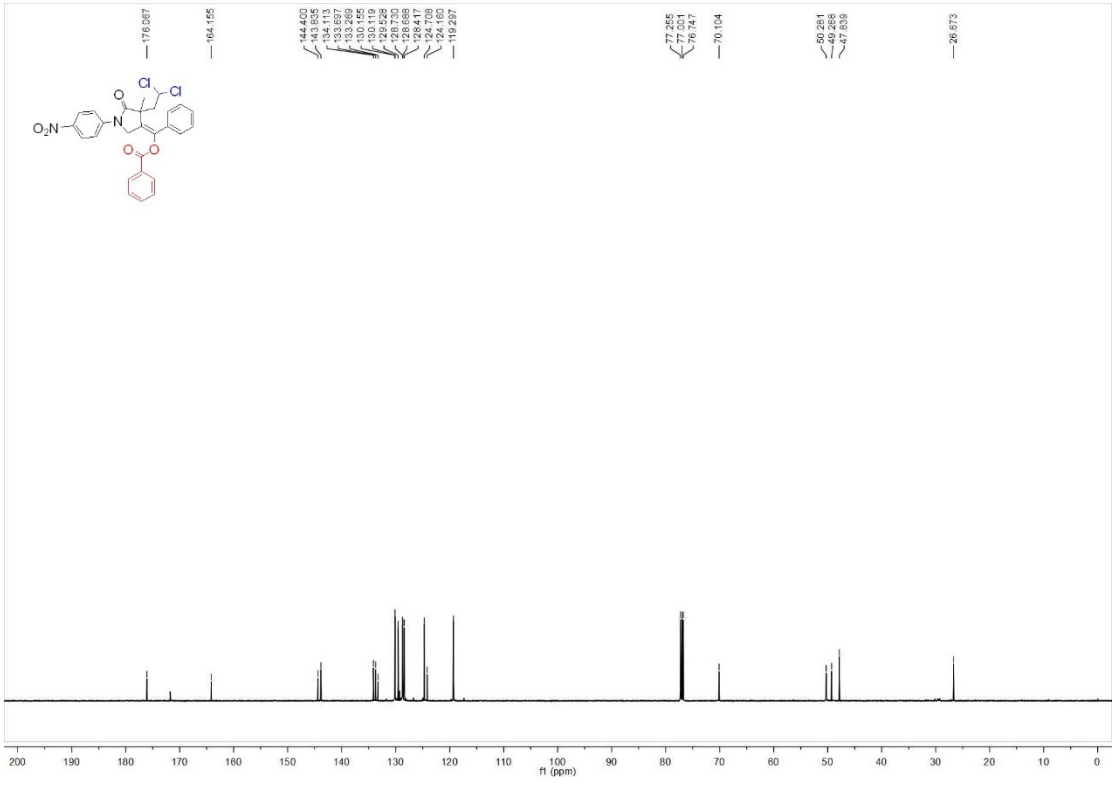
(1-(4-Cyanophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4n)



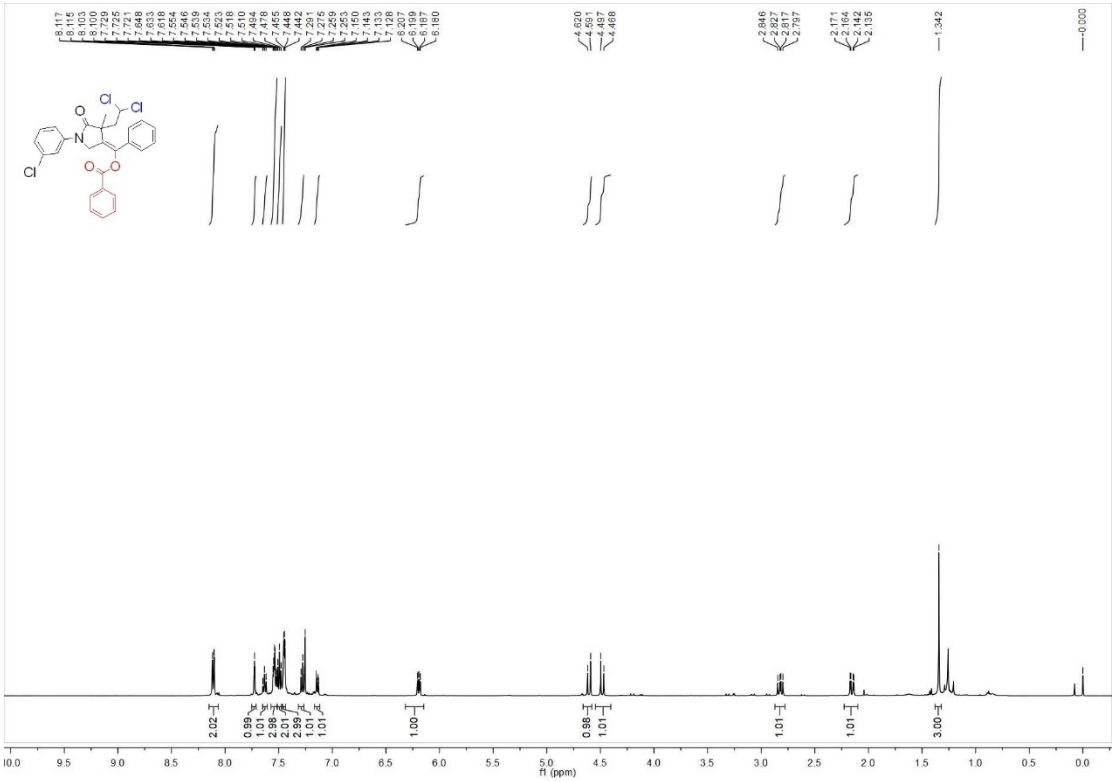


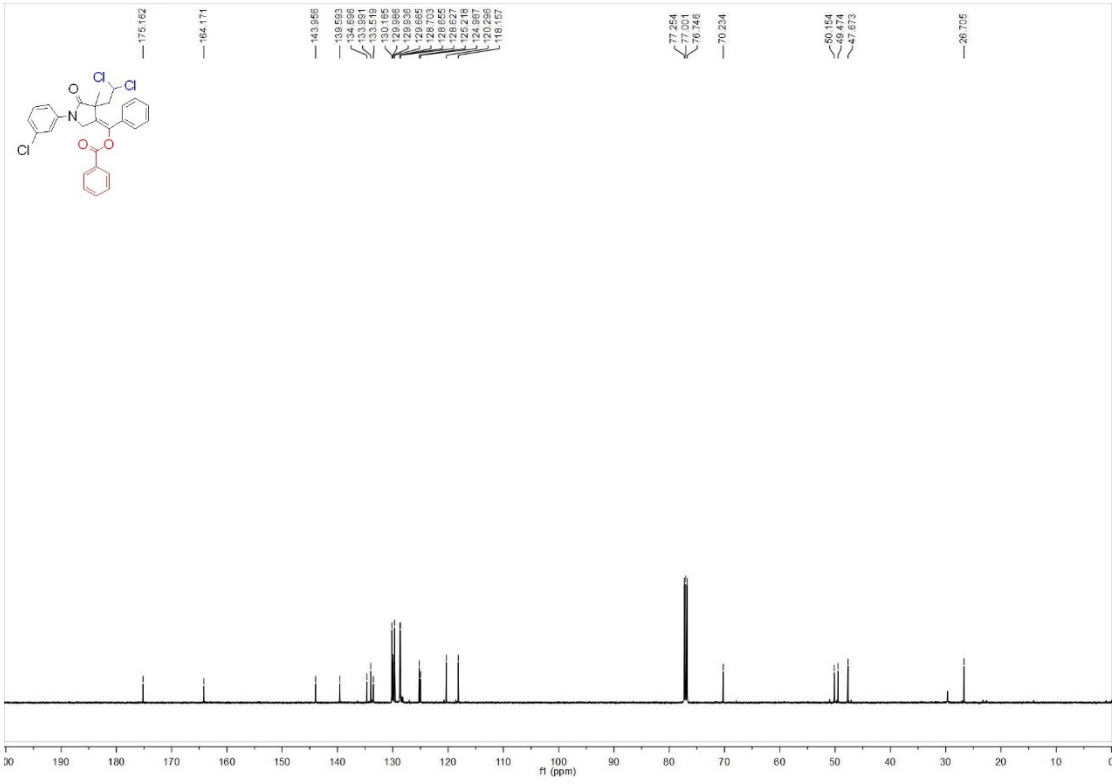
(4-(2,2-Dichloroethyl)-4-methyl-1-(4-nitrophenyl)-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4o)



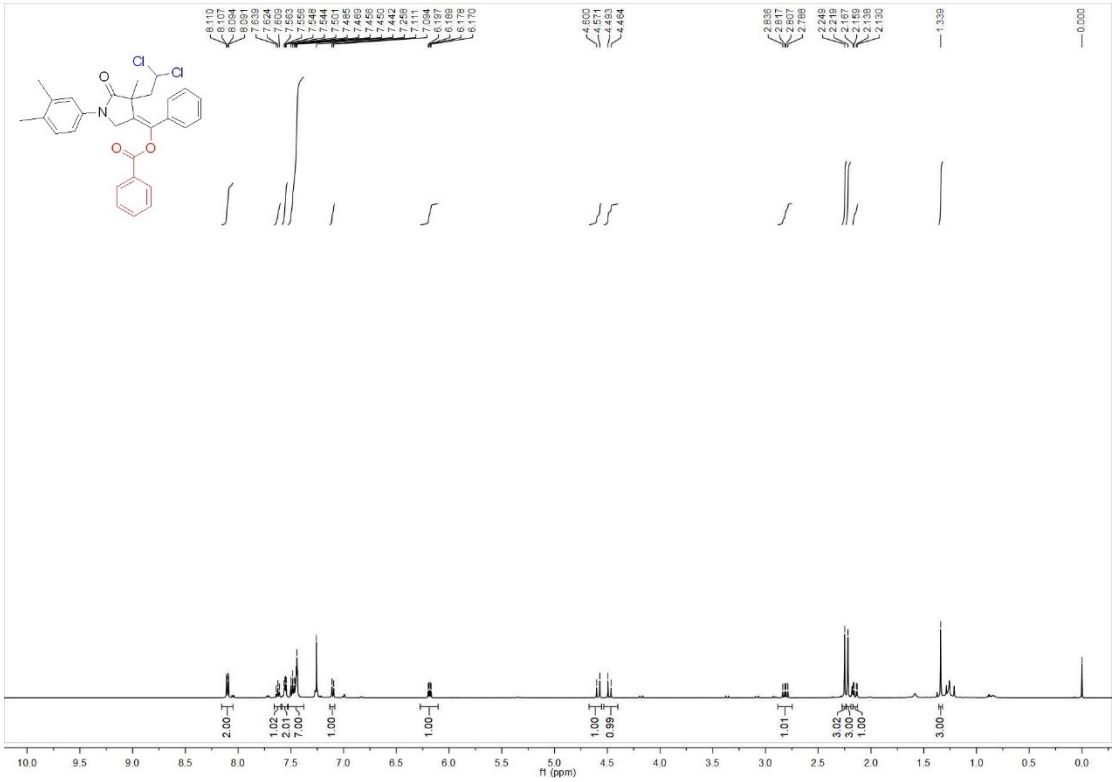


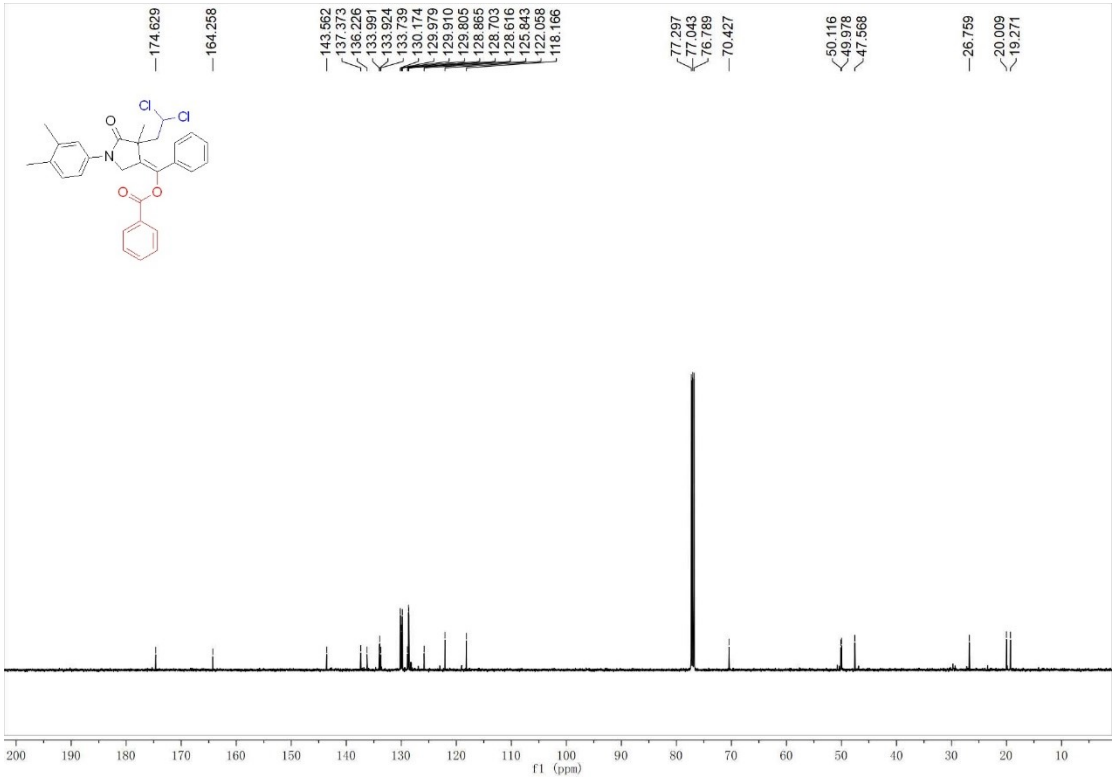
(1-(3-Chlorophenyl)-4-(2,2-dichloroethyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4p)



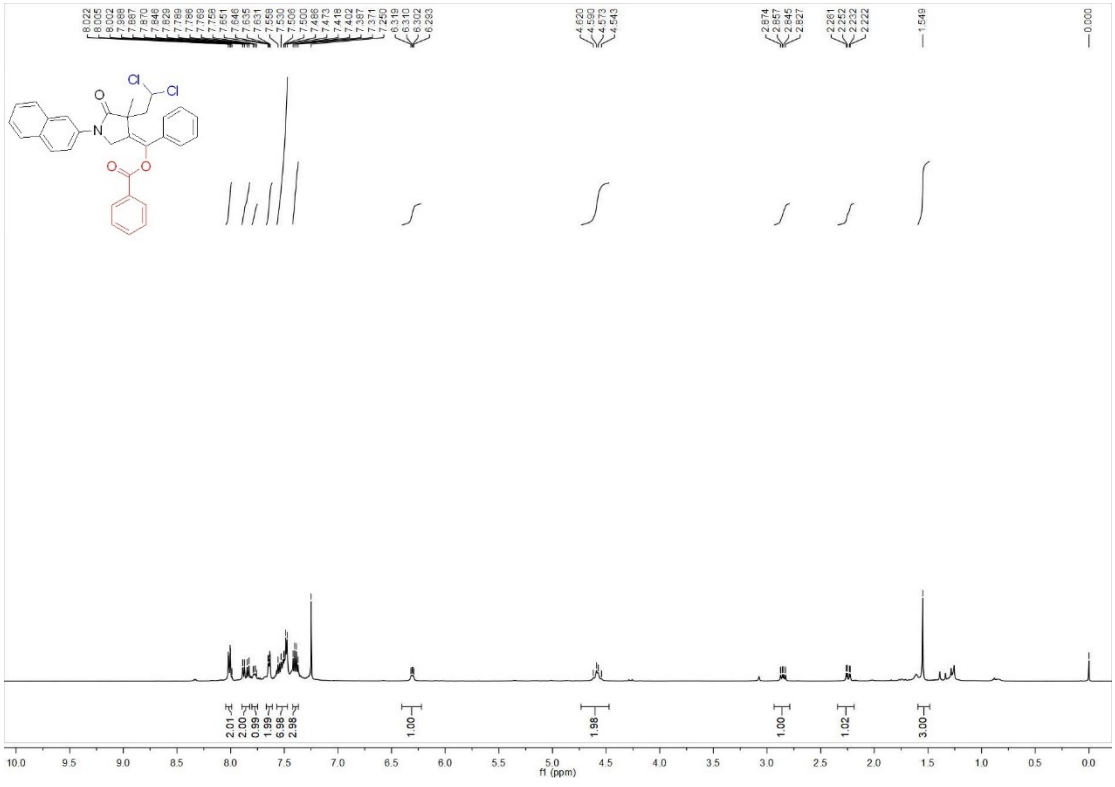


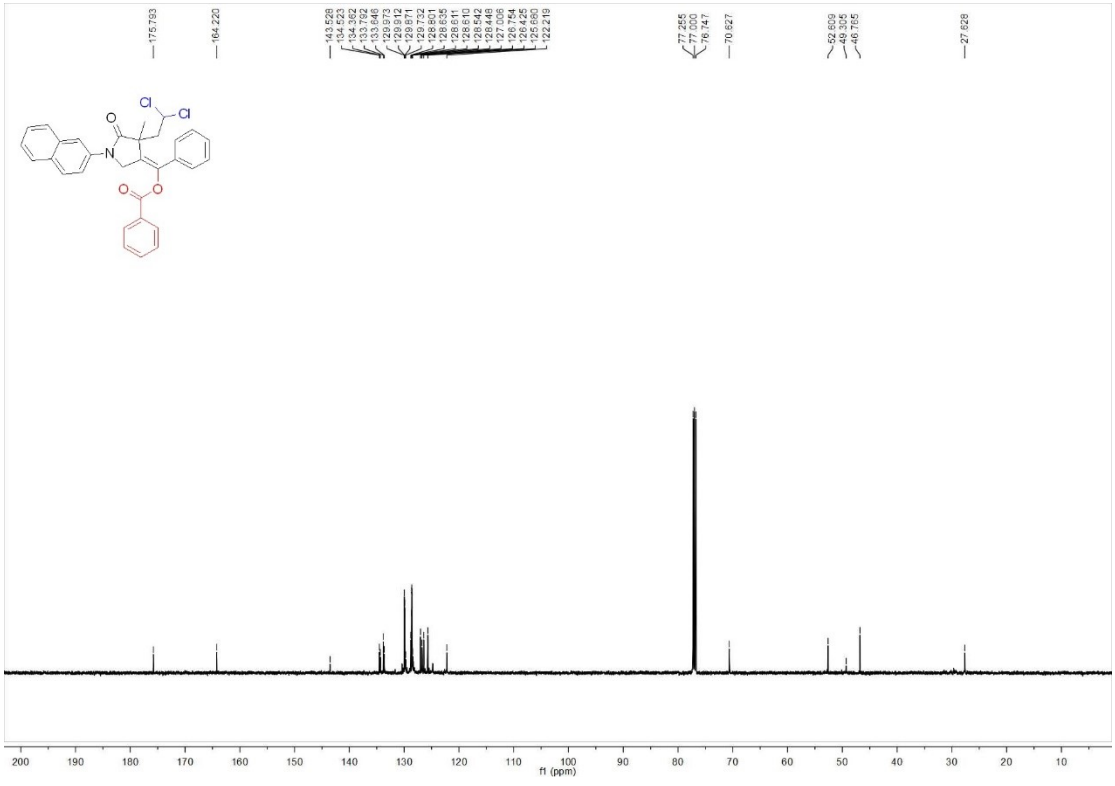
(4-(2,2-Dichloroethyl)-1-(3,4-dimethylphenyl)-4-methyl-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4q)



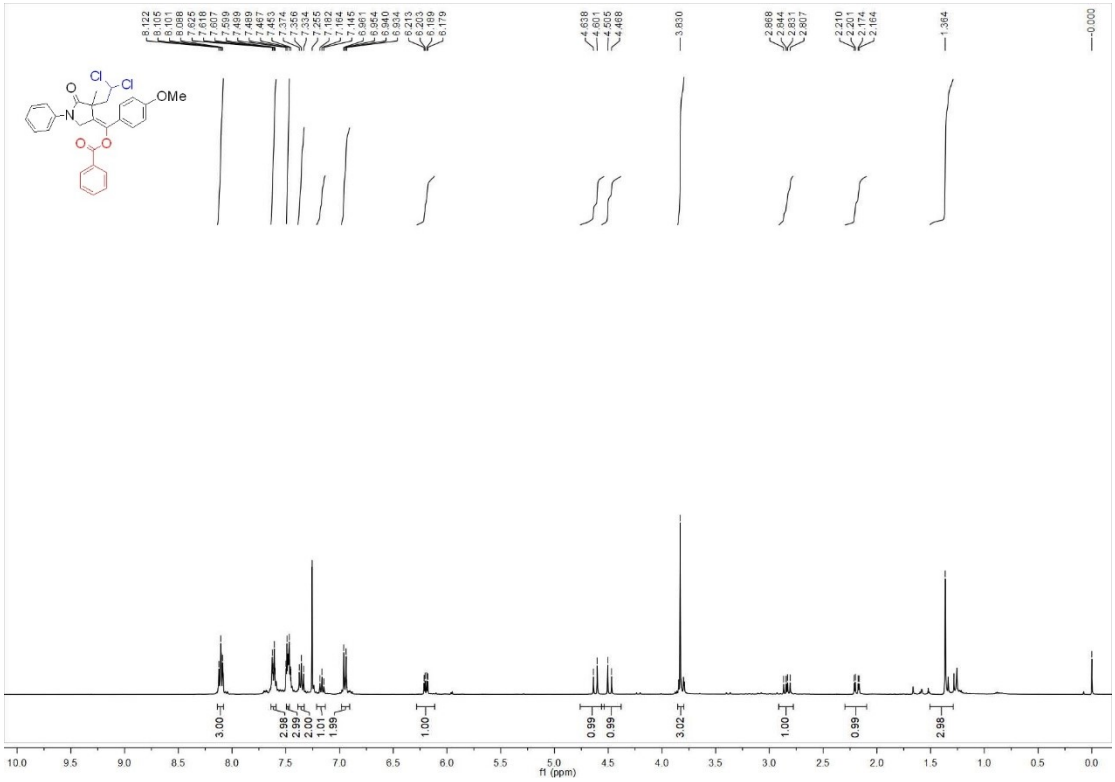


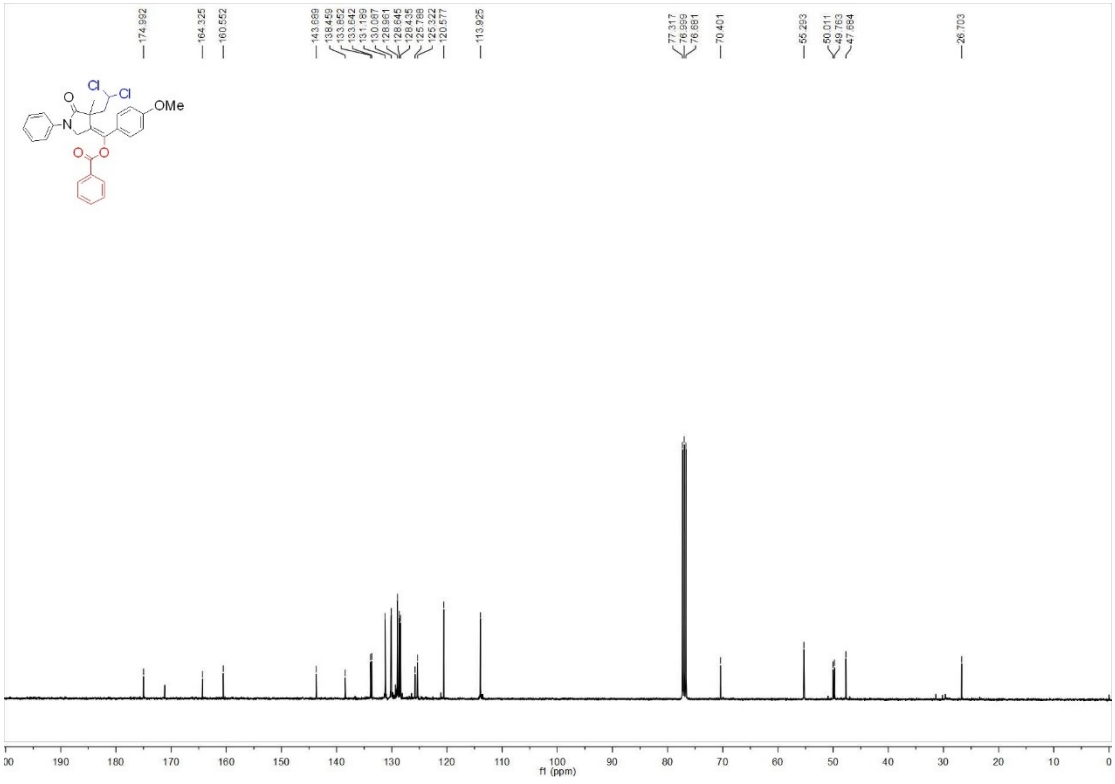
(4-(2,2-Dichloroethyl)-4-methyl-1-(naphthalen-2-yl)-5-oxopyrrolidin-3-ylidene)(phenyl)methyl benzoate (4r)



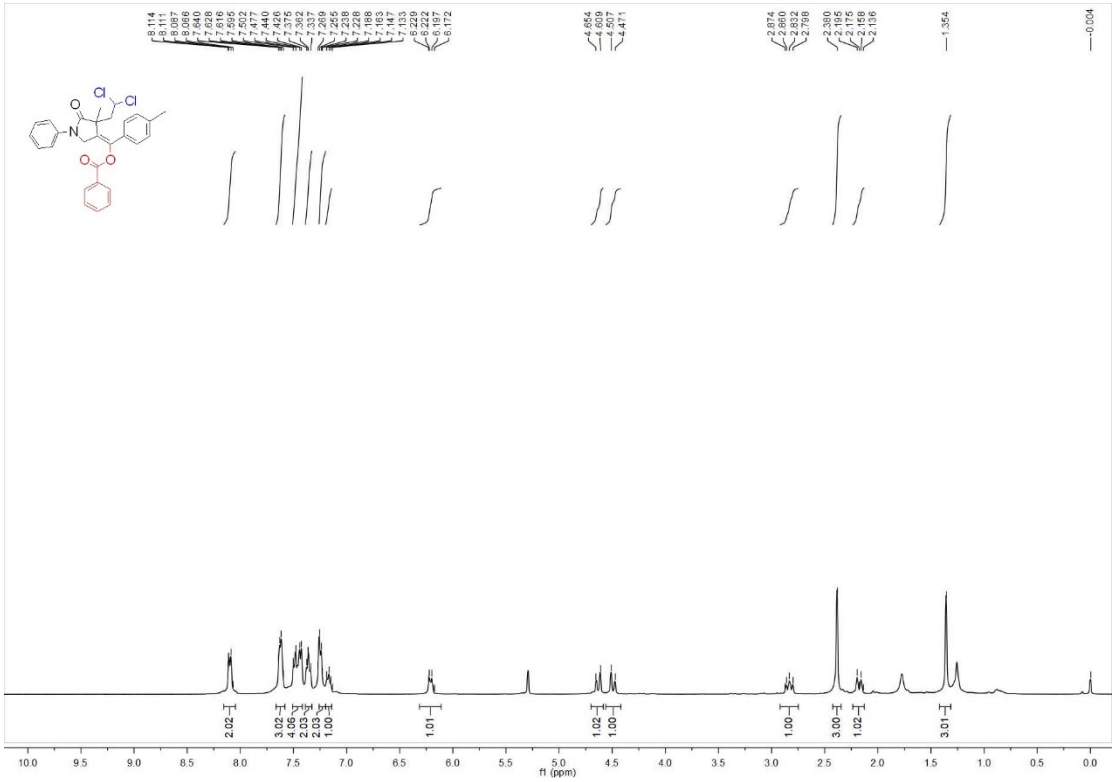


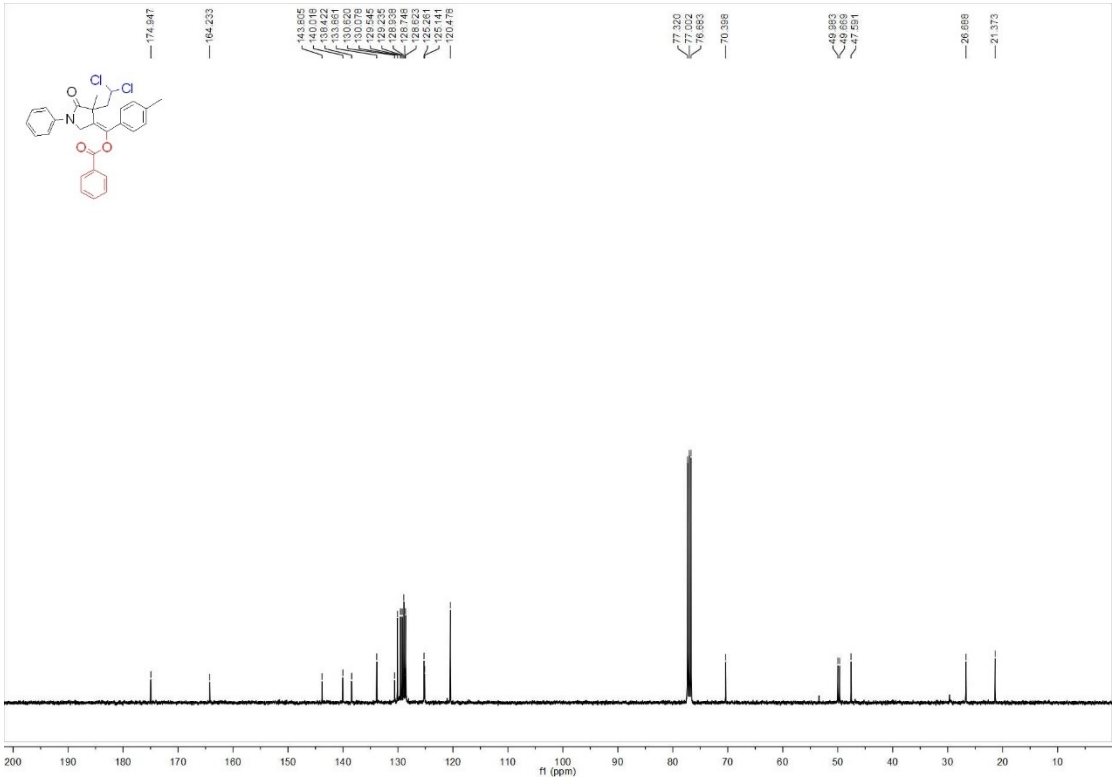
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(4-methoxyphenyl)methyl benzoate (4t)



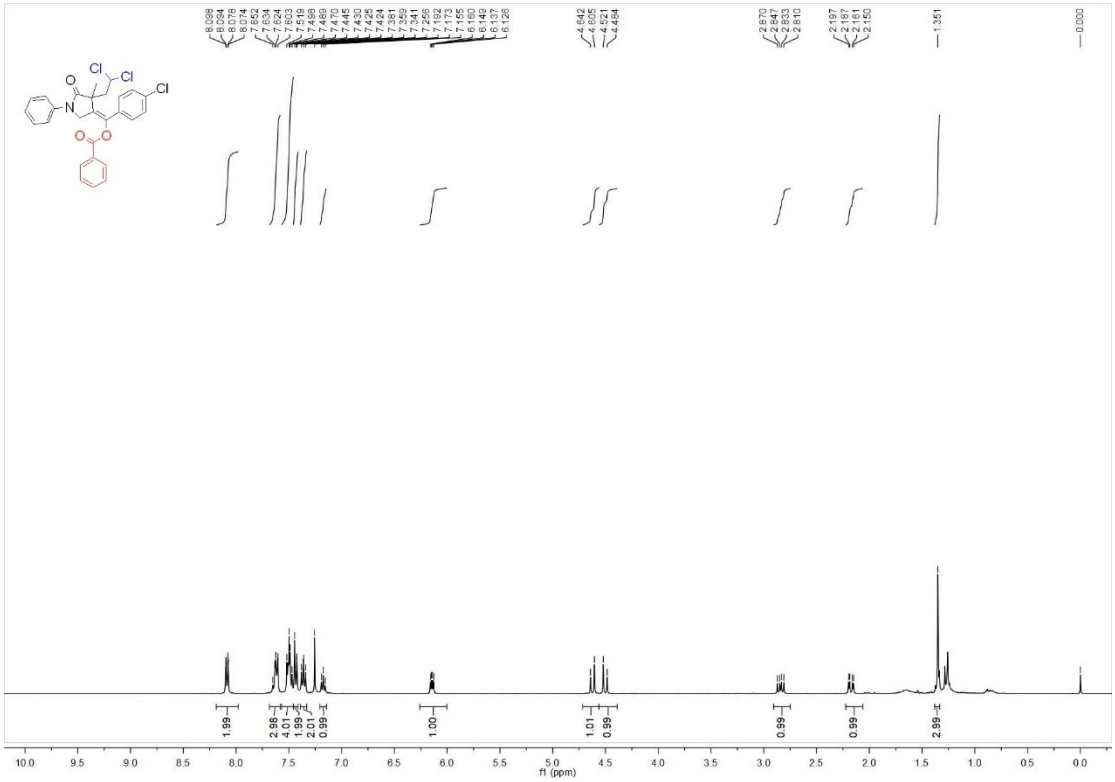


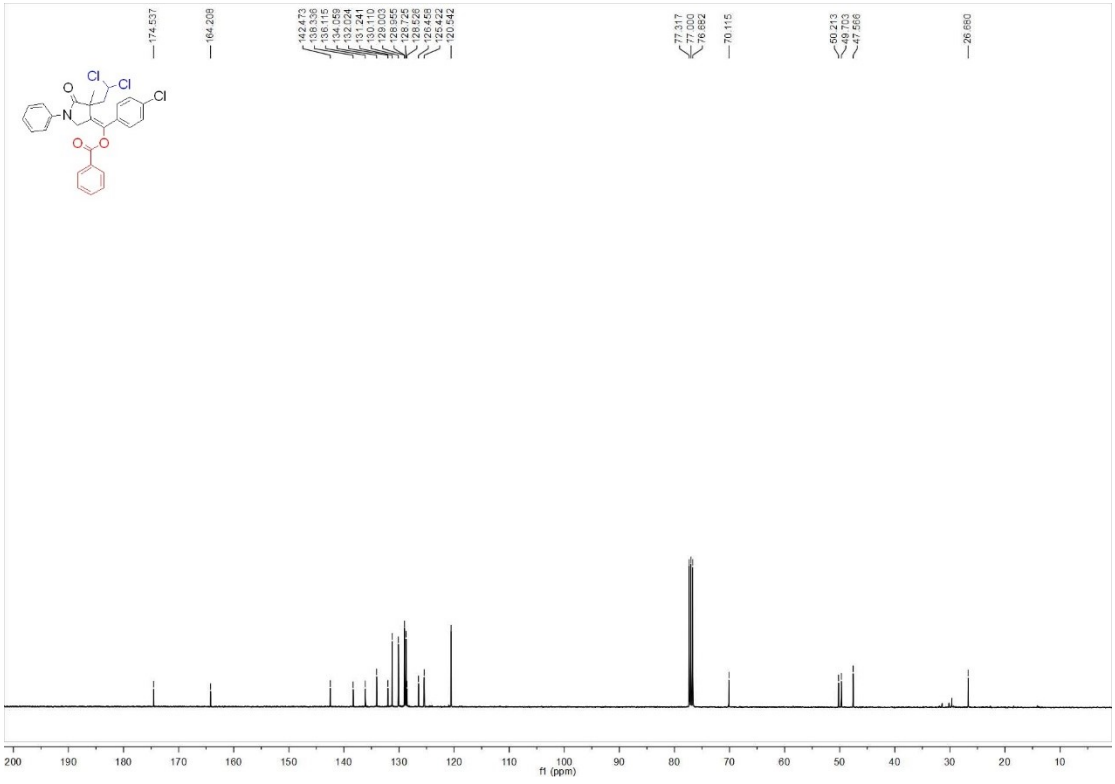
(4-(2,2-Dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)(*p*-tolyl)methyl benzoate (4u)



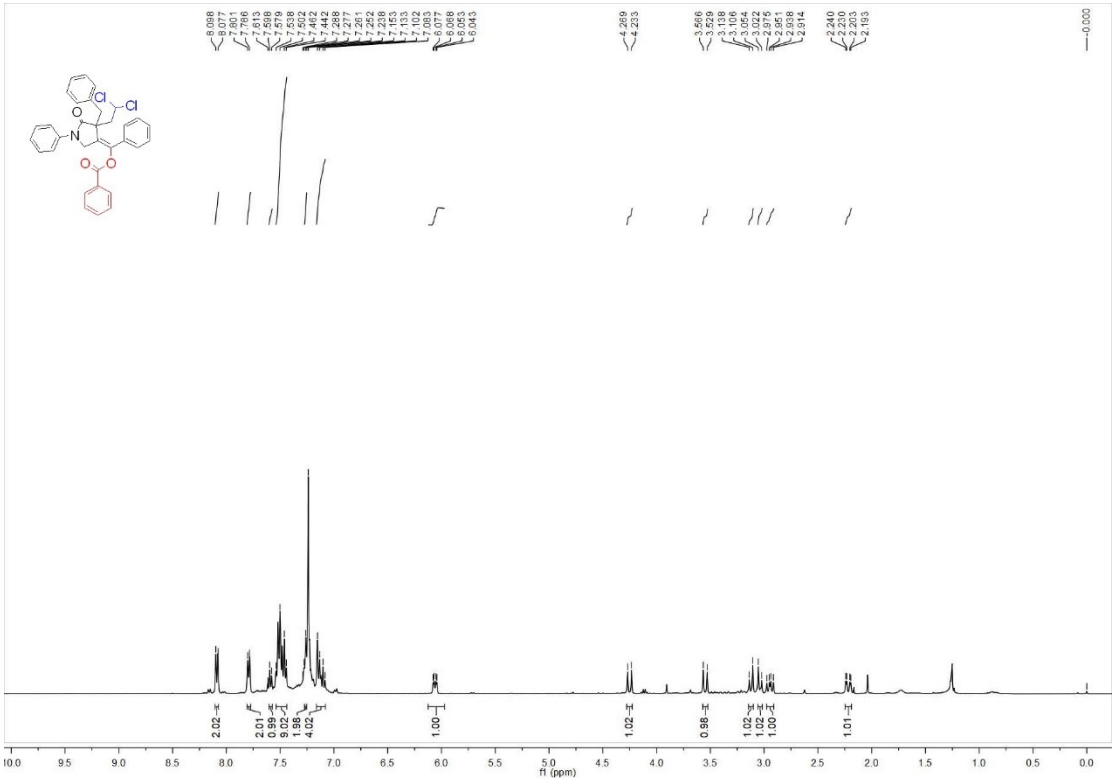


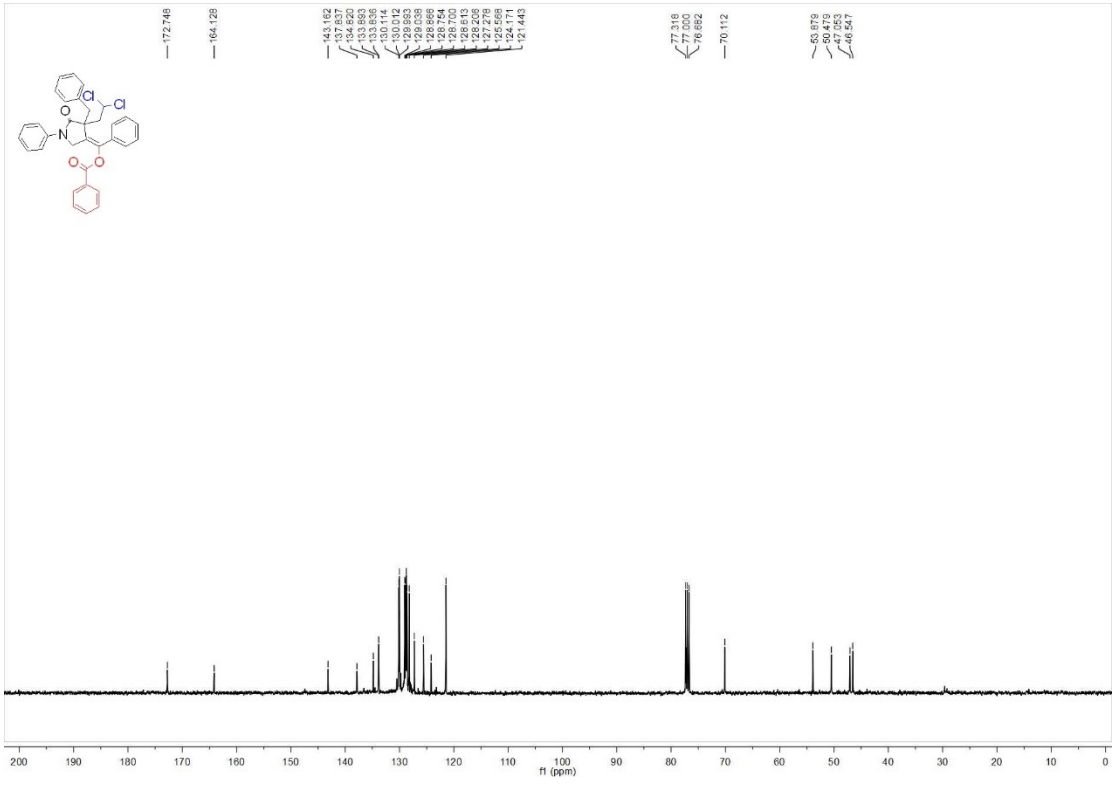
(4-Chlorophenyl)(4-(2,2-dichloroethyl)-4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl benzoate (4v)



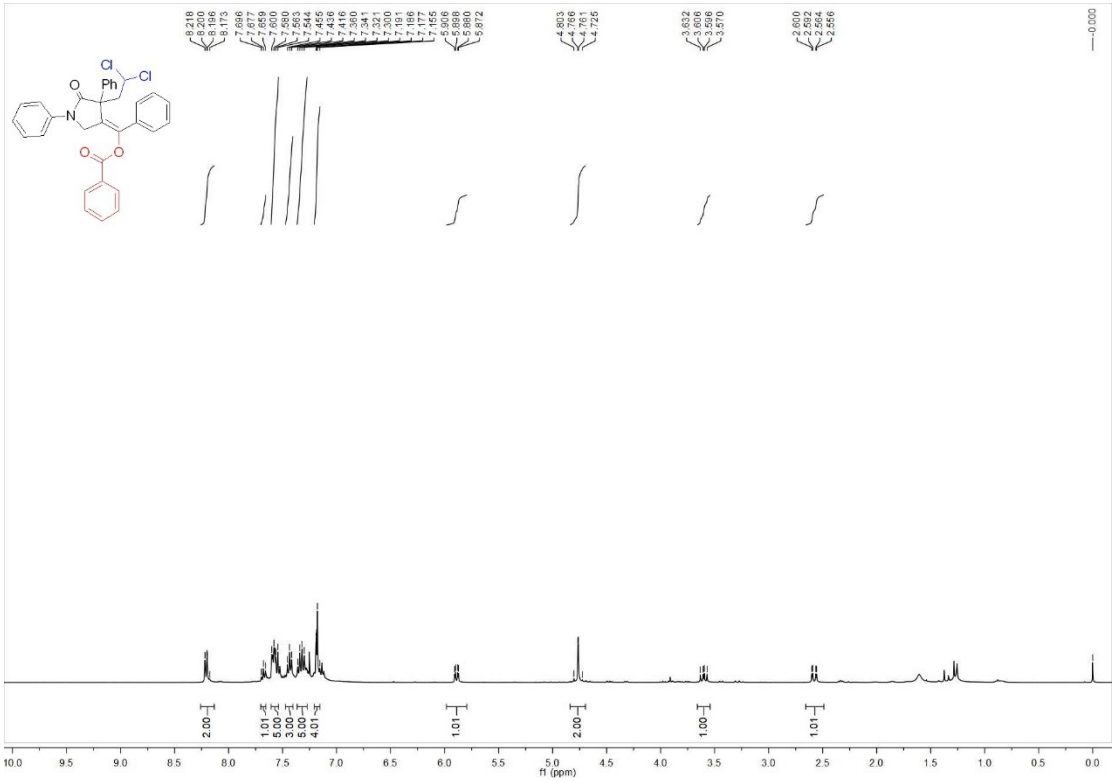


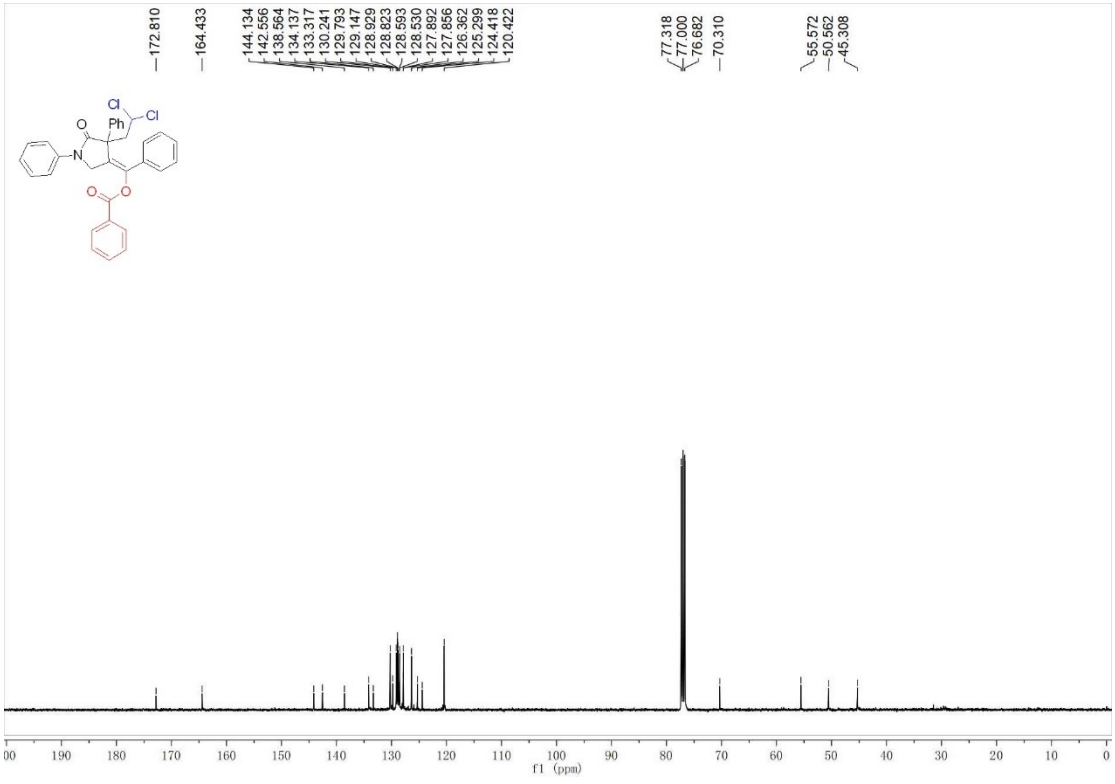
(4-Benzyl-4-(2,2-dichloroethyl)-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4w)



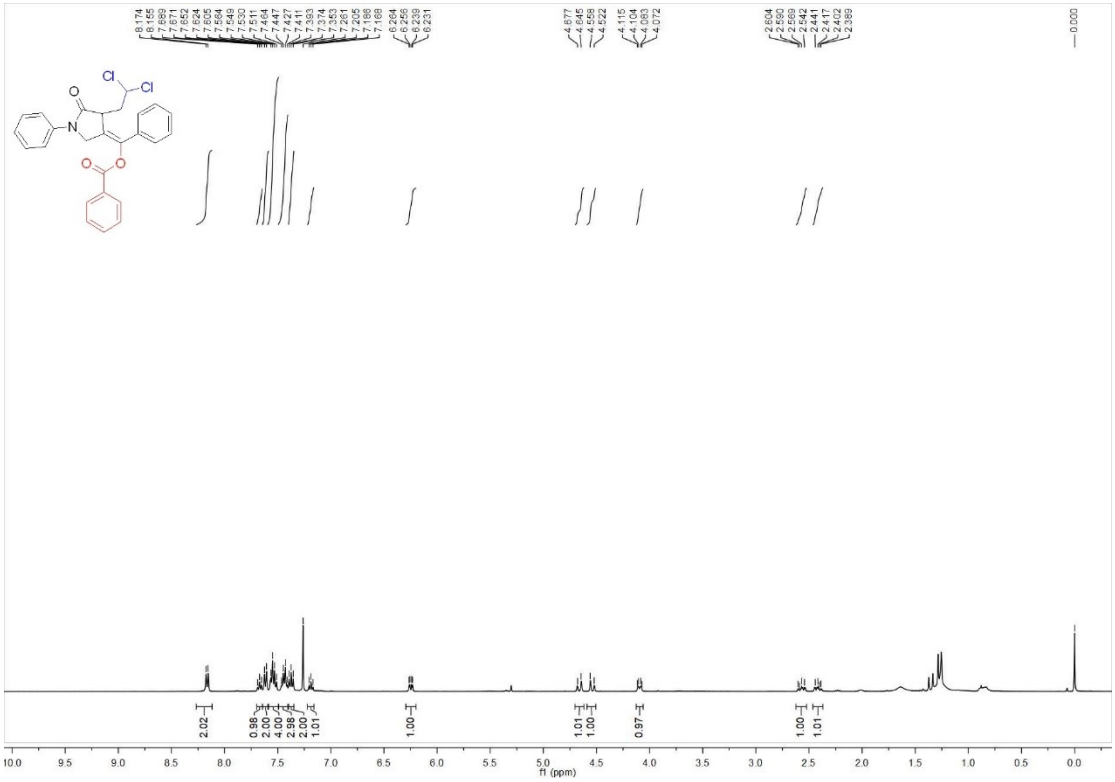


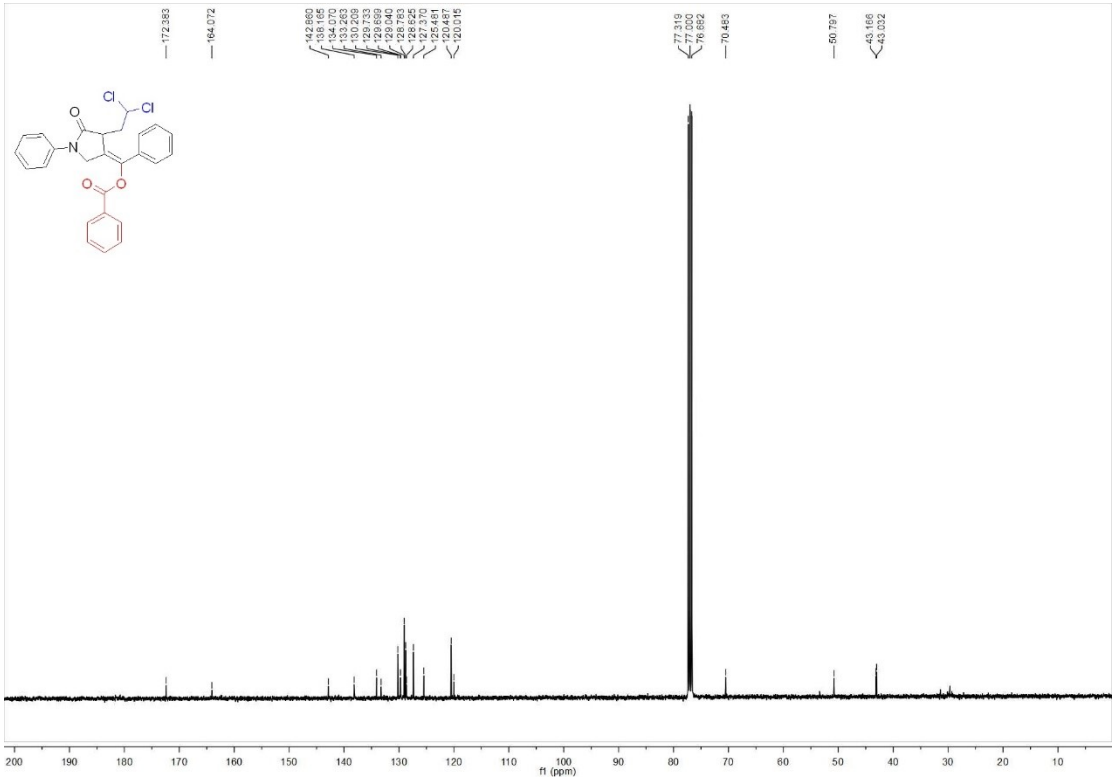
(4-(2,2-Dichloroethyl)-5-oxo-1,4-diphenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4x)



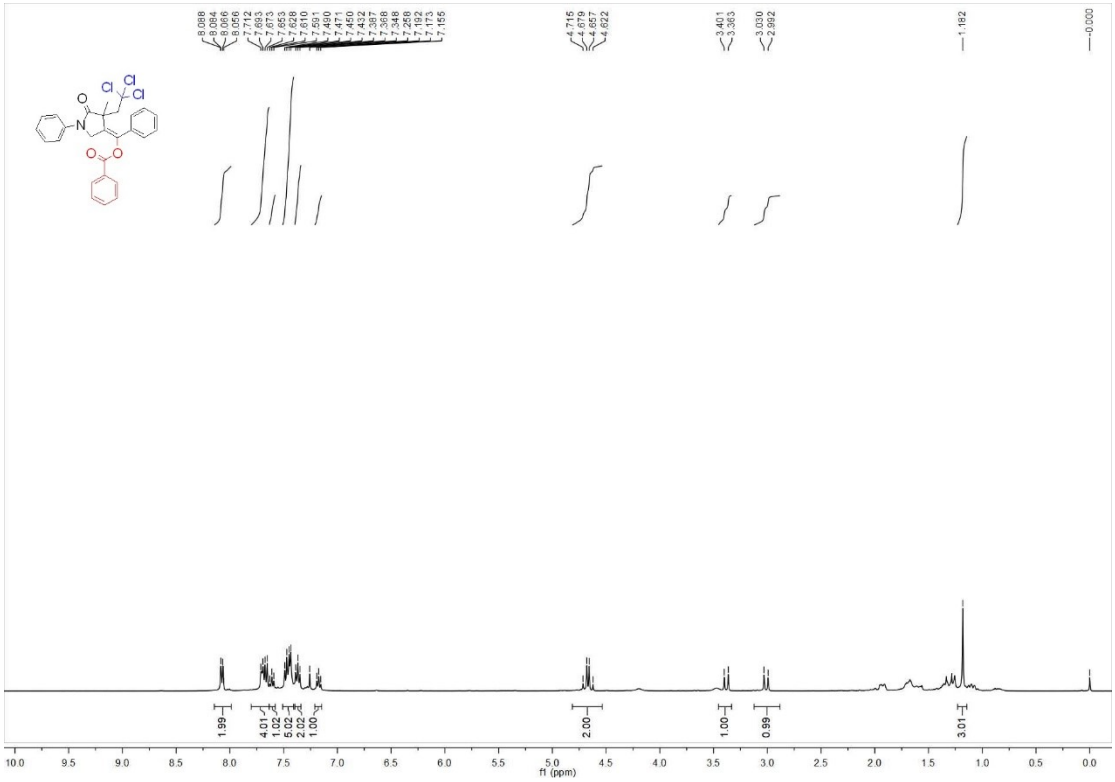


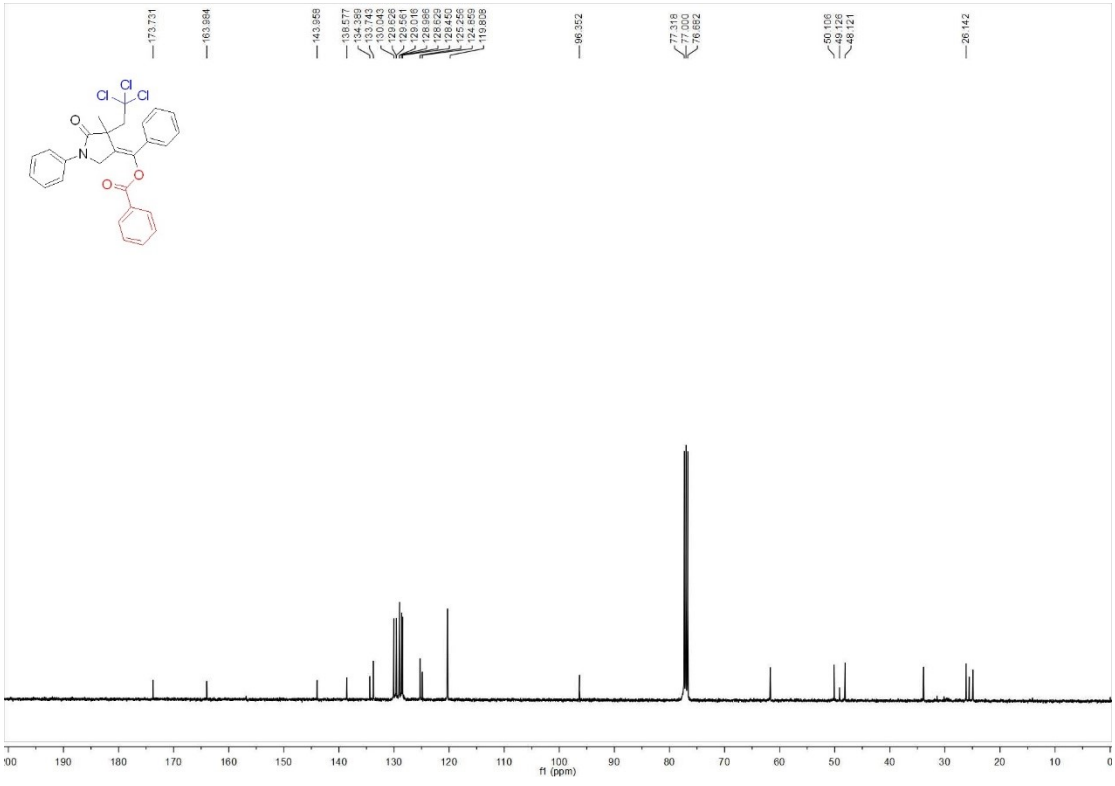
(4-(2,2-Dichloroethyl)-5-oxo-1-phenylpyrrolidin-3-ylidene)(phenyl)methyl benzoate (4y)



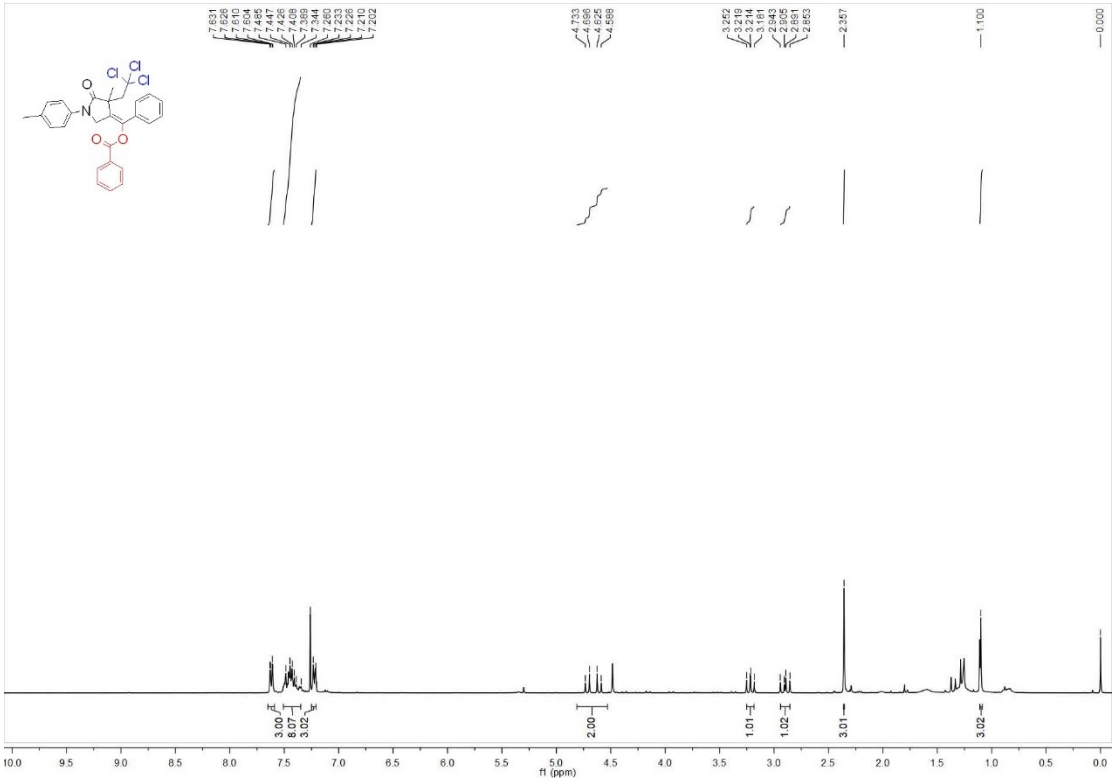


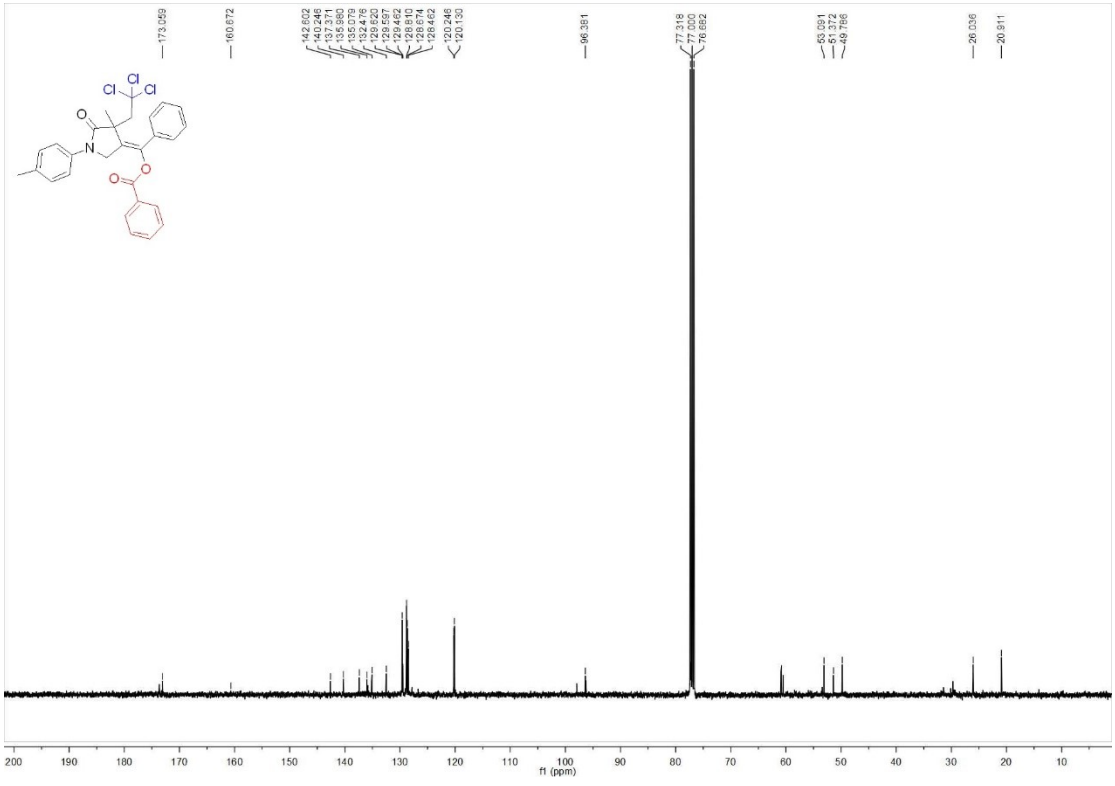
(4-Methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4z)



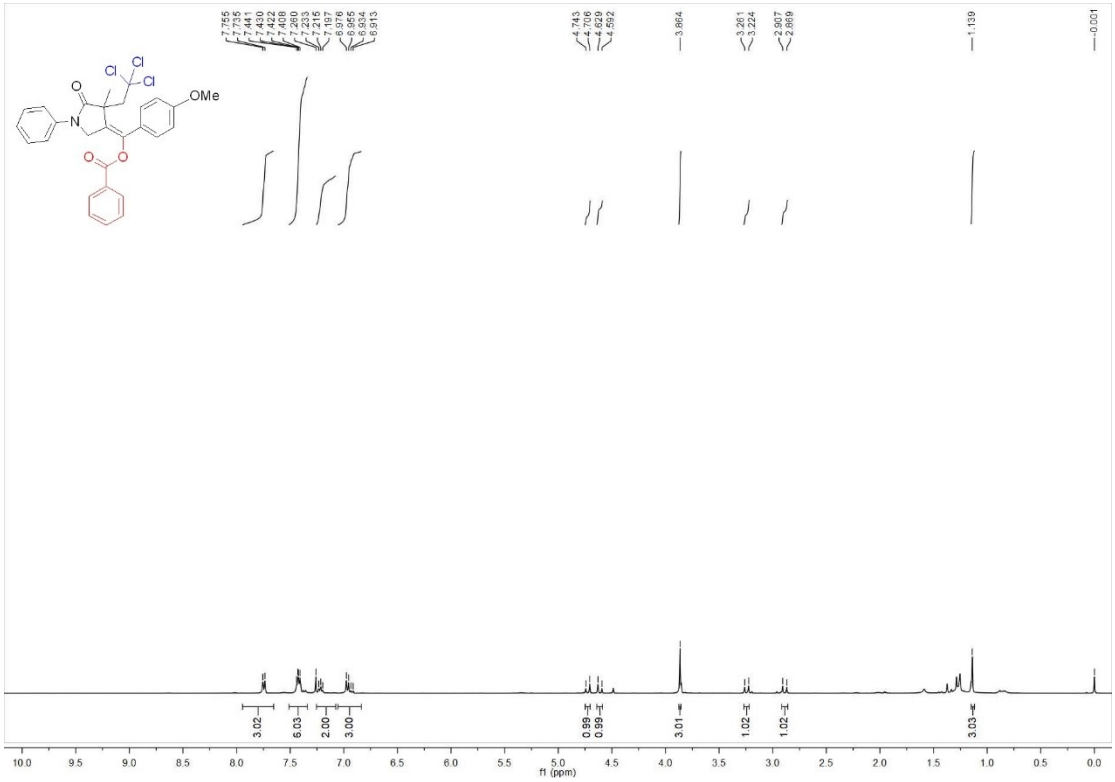


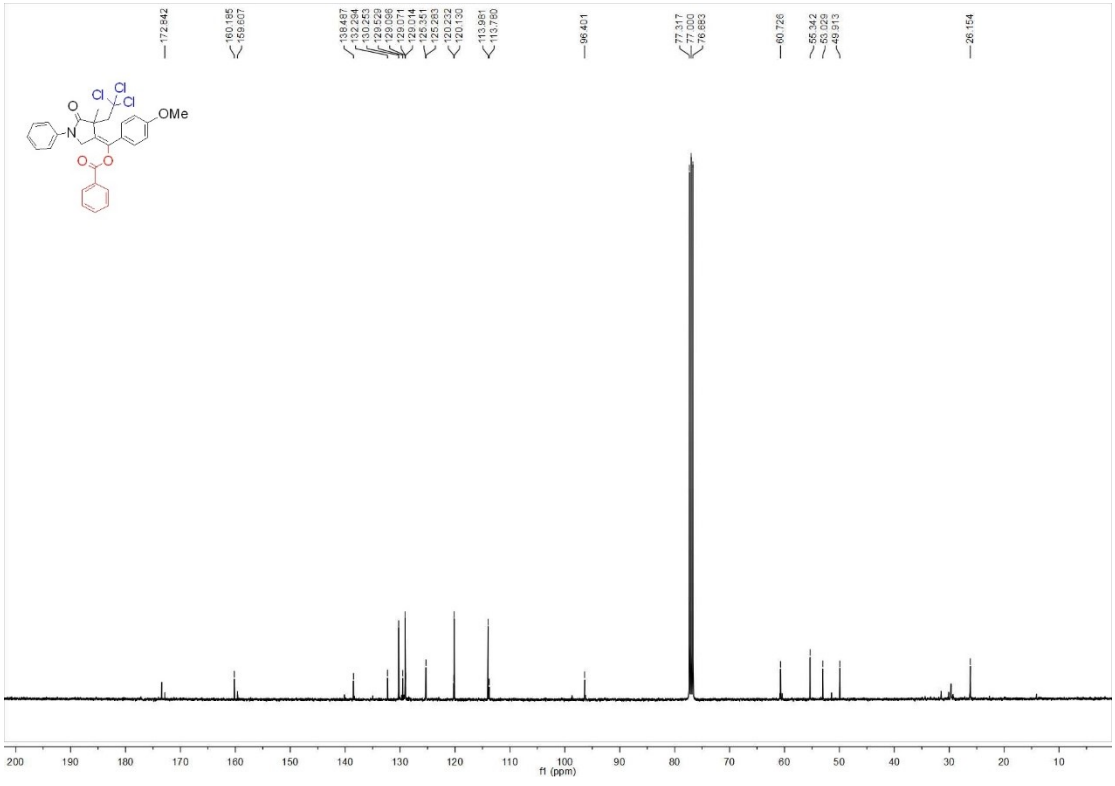
(4-Methyl-5-oxo-1-(*p*-tolyl)-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)(phenyl)methyl benzoate (4aa)



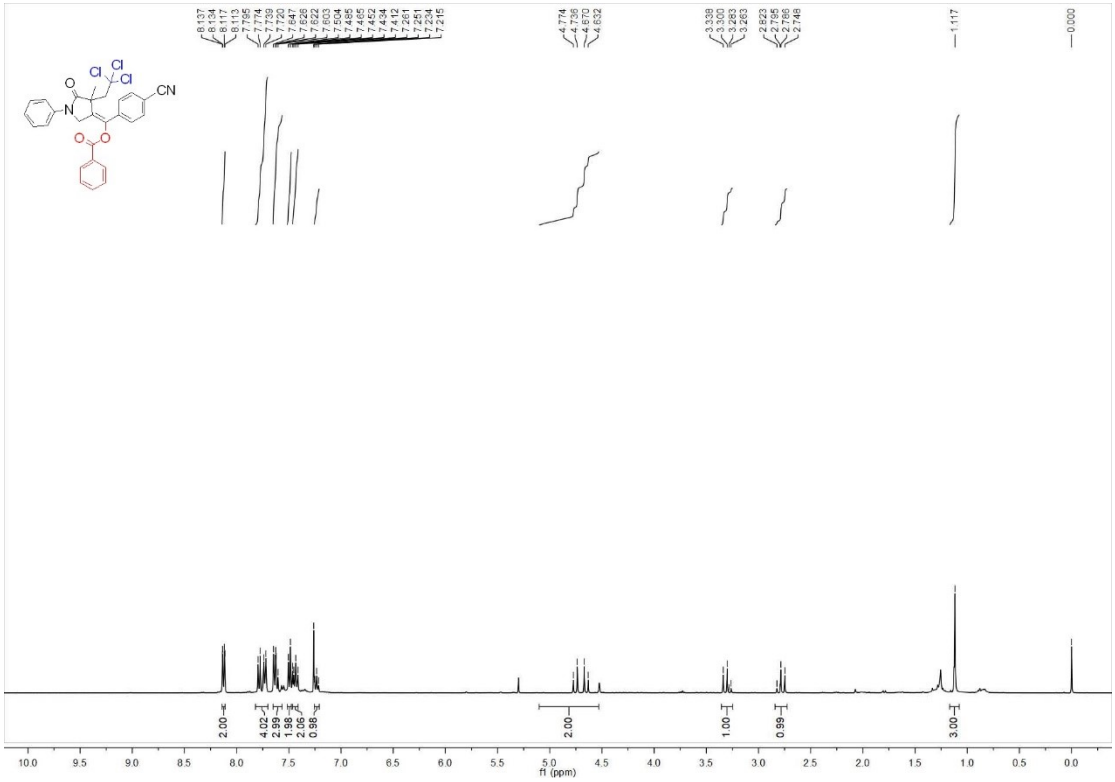


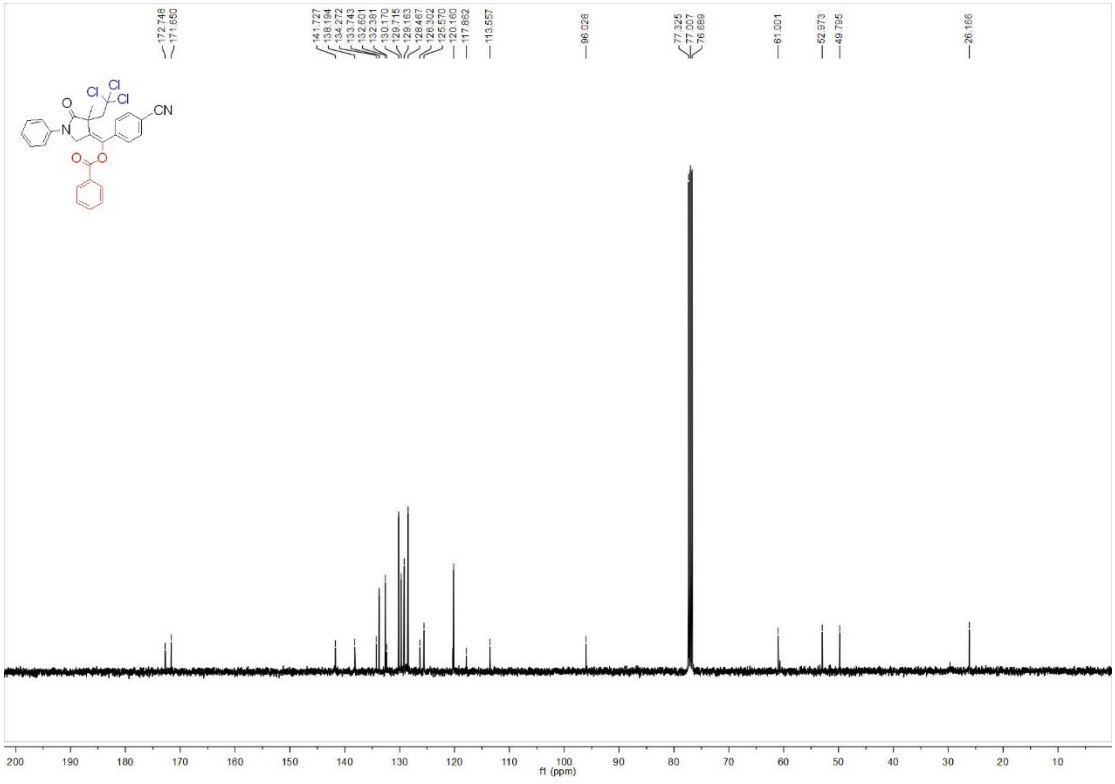
(4-Methoxyphenyl)(4-methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)methyl benzoate (4ab)



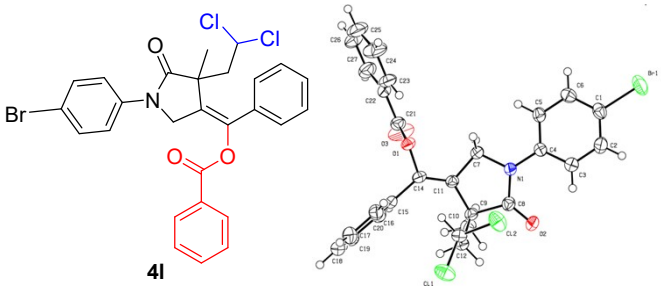


(4-Cyanophenyl)(4-methyl-5-oxo-1-phenyl-4-(2,2,2-trichloroethyl)pyrrolidin-3-ylidene)methyl benzoate (4ac)





(G) The X-ray single-crystal diffraction analysis of product 4l



4l

Table 1 Crystal data and structure refinement for 4l.

Identification code	**4l**
Empirical formula	$C_{27}H_{22}BrCl_2NO_3$
Formula weight	559.26
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3719(9)
b/Å	11.0520(9)
c/Å	18.6624(14)
α/°	90
β/°	103.575(2)
γ/°	90
Volume/Å^3	2480.5(3)
Z	4
ρ_{calc}g/cm^3	1.498
μ/mm^{-1}	1.902
F(000)	1136.0
Crystal size/mm^3	0.15 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.316 to 52.84
Index ranges	-15 ≤ h ≤ 15, -13 ≤ k ≤ 13, -23 ≤ l ≤ 22
Reflections collected	18682
Independent reflections	5012 [R_{int} = 0.0550, R_{sigma} = 0.0607]
Data/restraints/parameters	5012/0/308
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0934, wR_2 = 0.0973
Largest diff. peak/hole / e Å^{-3}	0.39/-0.52

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4l.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	9528.6(3)	7715.5(4)	8091.6(2)	56.71(15)
Cl2	6024.2(8)	1364.1(8)	7492.4(5)	50.6(3)
Cl1	4840.6(9)	-793.2(8)	6869.6(5)	50.6(3)
O1	2825.1(16)	3841.9(17)	5826.3(11)	29.4(5)
O2	7484.7(17)	2399.7(19)	6356.5(13)	39.3(6)
N1	6281.2(19)	3954(2)	6471.3(14)	26.3(6)
O3	2759(2)	4762(2)	4749.5(15)	60.8(8)
C4	7029(2)	4808(3)	6872.8(17)	26.6(7)
C8	6564(3)	2841(3)	6237.0(17)	30.3(7)
C14	3514(2)	2930(3)	5632.7(16)	27.0(7)
C15	2872(2)	1878(3)	5266.8(17)	27.9(7)
C11	4601(2)	3109(3)	5822.1(16)	26.2(7)
C12	5396(3)	935(3)	6001.5(17)	30.0(7)
C5	6701(3)	6006(3)	6896.6(17)	31.8(7)
C9	5523(2)	2251(3)	5754.0(17)	27.5(7)
C7	5118(2)	4264(3)	6157.5(17)	28.9(7)
C3	8093(3)	4477(3)	7260.1(19)	37.9(8)
C22	1663(2)	5547(3)	5543.1(19)	32.8(8)
C20	2747(3)	1683(3)	4520.0(19)	35.5(8)
C13	5055(3)	772(3)	6727.9(17)	31.8(7)
C1	8504(3)	6532(3)	7616.2(18)	35.8(8)
C6	7431(3)	6868(3)	7271.1(18)	35.0(8)
C21	2450(3)	4709(3)	5307.9(19)	33.4(8)
C10	5713(3)	2227(3)	4966.0(17)	35.3(8)
C16	2347(3)	1093(3)	5659.2(19)	36.6(8)
C19	2122(3)	704(3)	4174(2)	41.9(9)
C2	8820(3)	5346(3)	7620(2)	42.5(9)
C23	1525(3)	5544(3)	6256(2)	41.1(9)
C18	1636(3)	-80(3)	4577(2)	46.0(10)
C17	1744(3)	119(3)	5320(2)	44.8(9)
C27	1059(3)	6338(3)	5028(2)	49.2(10)
C26	309(3)	7111(3)	5234(3)	62.5(12)
C24	795(4)	6343(4)	6459(3)	64.8(13)
C25	177(4)	7110(4)	5938(3)	66.7(13)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4l.

The Anisotropic displacement factor exponent takes the form: -

$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	46.2(2)	61.8(3)	62.1(3)	-23.7(2)	12.64(19)	-22.7(2)
Cl2	62.5(6)	55.0(6)	31.0(5)	-0.9(4)	4.2(4)	-14.1(5)
Cl1	74.6(7)	35.5(5)	44.5(6)	0.0(4)	19.4(5)	-7.3(4)
O1	28.6(12)	30.7(12)	29.3(13)	-1.5(10)	7.6(10)	7.0(9)
O2	23.3(12)	42.9(14)	49.9(16)	-9.8(11)	5.0(10)	4.5(10)
N1	23.7(13)	27.7(14)	27.1(15)	-3.7(11)	4.9(11)	0.4(11)
O3	88(2)	61.7(17)	42.7(17)	19.4(13)	34.5(16)	34.4(15)
C4	26.6(16)	28.6(17)	25.2(18)	-1.7(13)	7.6(13)	-2.5(13)
C8	27.3(17)	34.8(18)	28.9(19)	-2.5(14)	6.7(14)	1.0(14)
C14	29.3(17)	26.6(17)	25.1(17)	-0.2(13)	6.2(13)	7.4(13)
C15	21.1(15)	29.1(17)	32.0(19)	-2.9(14)	3.3(13)	3.9(13)
C11	27.1(16)	27.3(17)	23.8(17)	-3.0(13)	5.2(13)	3.8(13)
C12	28.3(17)	29.0(17)	32.1(19)	-4.1(14)	5.9(14)	3.7(13)
C5	29.4(17)	35.4(19)	28.0(19)	-2.7(14)	1.4(14)	-1.0(14)
C9	26.2(16)	28.8(16)	27.4(18)	-3.2(13)	6.1(13)	3.5(13)
C7	25.8(16)	28.9(17)	31.0(19)	-1.7(14)	5.1(14)	3.8(13)
C3	31.7(19)	34.4(19)	45(2)	-6.3(16)	3.9(16)	1.6(15)
C22	25.5(17)	29.4(17)	41(2)	-0.1(15)	3.8(15)	3.1(14)
C20	30.0(18)	41(2)	35(2)	-3.0(15)	6.5(15)	2.5(15)
C13	37.2(18)	27.1(17)	32.2(19)	-2.3(14)	10.3(15)	1.9(14)
C1	33.8(19)	42(2)	34(2)	-8.3(15)	12.9(15)	-10.0(15)
C6	41(2)	30.5(18)	35(2)	-0.7(15)	12.3(16)	-3.7(15)
C21	35.7(19)	28.9(18)	34(2)	2.7(15)	4.9(16)	4.9(14)
C10	36.4(18)	39.7(19)	32(2)	-4.5(15)	11.5(15)	5.4(15)
C16	33.1(18)	39(2)	37(2)	-2.9(16)	8.2(15)	-2.2(16)
C19	32.1(19)	50(2)	40(2)	-16.3(18)	2.4(16)	6.4(17)
C2	28.6(18)	50(2)	47(2)	-9.3(17)	4.2(16)	0.8(16)
C23	40(2)	32.6(19)	55(3)	2.6(17)	19.7(18)	11.0(16)
C18	32(2)	38(2)	64(3)	-15.7(19)	3.4(18)	2.2(16)
C17	33(2)	45(2)	57(3)	-1.3(19)	11.6(18)	-5.4(16)
C27	46(2)	47(2)	50(3)	3.7(18)	1.2(18)	15.3(18)
C26	45(2)	44(2)	92(4)	11(2)	3(2)	17.2(19)
C24	72(3)	55(3)	81(3)	-1(2)	47(3)	19(2)
C25	52(3)	46(2)	111(4)	-2(3)	36(3)	17(2)

Table 4 Bond Lengths for 4l.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Br1	C1	1.891(3)	C12	C9	1.544(4)
Cl2	C13	1.760(3)	C12	C13	1.522(4)
Cl1	C13	1.779(3)	C5	C6	1.385(4)
O1	C14	1.420(3)	C9	C10	1.543(4)
O1	C21	1.363(4)	C3	C2	1.378(4)
O2	C8	1.211(3)	C22	C21	1.483(4)
N1	C4	1.408(4)	C22	C23	1.380(5)
N1	C8	1.378(4)	C22	C27	1.382(5)
N1	C7	1.461(4)	C20	C19	1.397(5)
O3	C21	1.193(4)	C1	C6	1.383(5)
C4	C5	1.388(4)	C1	C2	1.368(5)
C4	C3	1.393(4)	C16	C17	1.377(5)
C8	C9	1.533(4)	C19	C18	1.374(5)
C14	C15	1.481(4)	C23	C24	1.379(5)
C14	C11	1.323(4)	C18	C17	1.379(5)
C15	C20	1.383(4)	C27	C26	1.381(5)
C15	C16	1.391(4)	C26	C25	1.363(6)
C11	C9	1.512(4)	C24	C25	1.378(6)
C11	C7	1.498(4)			

Table 5 Bond Angles for 4l.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	O1	C14	116.3(2)	N1	C7	C11	104.6(2)
C4	N1	C7	121.3(2)	C2	C3	C4	119.9(3)
C8	N1	C4	125.7(2)	C23	C22	C21	121.5(3)
C8	N1	C7	112.4(2)	C23	C22	C27	120.2(3)
C5	C4	N1	119.7(3)	C27	C22	C21	118.3(3)
C5	C4	C3	118.8(3)	C15	C20	C19	120.4(3)
C3	C4	N1	121.5(3)	Cl2	C13	Cl1	109.77(18)
O2	C8	N1	126.8(3)	C12	C13	Cl2	113.5(2)
O2	C8	C9	124.1(3)	C12	C13	Cl1	109.3(2)
N1	C8	C9	109.0(2)	C6	C1	Br1	119.8(2)
O1	C14	C15	112.7(2)	C2	C1	Br1	120.1(3)
C11	C14	O1	117.3(3)	C2	C1	C6	120.1(3)
C11	C14	C15	129.9(3)	C1	C6	C5	119.4(3)
C20	C15	C14	120.6(3)	O1	C21	C22	111.5(3)
C20	C15	C16	118.5(3)	O3	C21	O1	122.0(3)
C16	C15	C14	120.8(3)	O3	C21	C22	126.5(3)
C14	C11	C9	128.6(3)	C17	C16	C15	121.0(3)
C14	C11	C7	123.1(3)	C18	C19	C20	120.0(3)
C7	C11	C9	108.2(2)	C1	C2	C3	120.8(3)
C13	C12	C9	116.6(2)	C24	C23	C22	120.1(3)
C6	C5	C4	120.8(3)	C19	C18	C17	119.9(3)
C8	C9	C12	110.8(3)	C16	C17	C18	120.1(3)
C8	C9	C10	105.8(2)	C26	C27	C22	119.1(4)
C11	C9	C8	103.3(2)	C25	C26	C27	120.6(4)
C11	C9	C12	115.7(2)	C25	C24	C23	119.4(4)
C11	C9	C10	112.2(2)	C26	C25	C24	120.5(4)
C10	C9	C12	108.6(2)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement

Parameters ($Å^2×10^3$) for 4l.

Atom	*x*	*y*	*z*	U(eq)
H12A	4836.49	526.4	5609.77	36
H12B	6113.33	513.95	6039.41	36
H5	5966.68	6235.72	6653.15	38
H7A	5057.59	4902.41	5778.13	35
H7B	4754.51	4550.65	6545.5	35
H3	8316.66	3653.15	7275.87	45
H20	3088.42	2217.16	4240.62	43
H13	4332	1200.65	6689.3	38
H6	7197.29	7683.93	7290.82	42
H10A	5845.76	3052.21	4814.18	53
H10B	5053.89	1893.65	4626.16	53
H10C	6360.15	1721	4957.14	53
H16	2404.88	1231.84	6169.27	44
H19	2031.72	579.38	3659.48	50
H2	9549.62	5118.04	7874.41	51
H23	1934.54	4991.58	6606.56	49
H18	1227.04	-757.59	4344.38	55
H17	1401.74	-416.96	5597.85	54
H27	1158.89	6349.51	4538.31	59
H26	-118	7648.98	4880.86	75
H24	717.59	6363.86	6953.29	78
H25	-345.97	7643.34	6071.67	80