Supporting Information

Three-Component Addition of Terminal Alkynes, Carboxylic Acids, and *tert*-Butyl Hypochlorite

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Table of Contents

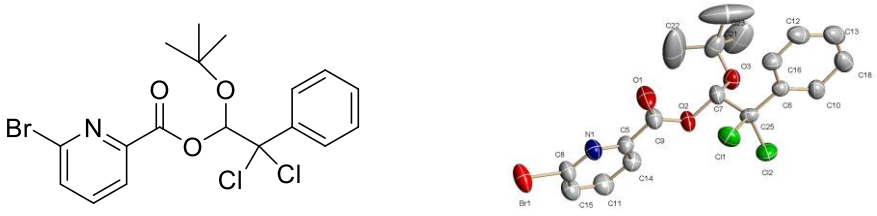
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ was used as a solvent, while TMS was used as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth). GC-MS analysis was performed on an Agilent 7890A GC interfaced to an Agilent 5975C mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. All reactions were carried out under nitrogen atmospheric pressure. The starting materials were purchased from Energy Chemicals Co. Ltd.

2. General Experimental Procedures

Representative Procedure: A reaction flask was charged with a mixture of benzoic acid (36.6 mg, 0.3 mmol), phenyl acetylene (99 uL, 0.9 mmol), *t*-BuOCl (136 uL, 1.2 mmol), CCl_4 (0.5 mL) under N_2 atmosphere. The reaction mixture was stirred at 30 °C for 2 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate: petroleum ether = 1 : 50) to afford corresponding product **3aa** in 90% yield (99.2 mg).

3. X-ray Analysis of 3ta



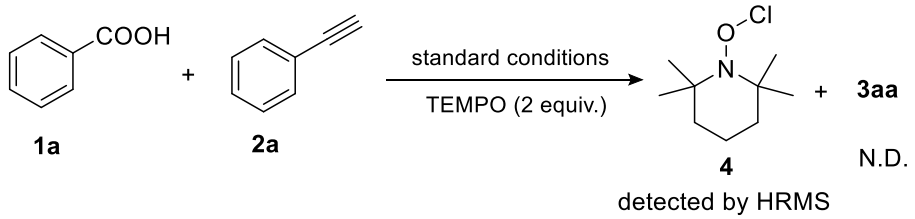
ORTEP Diagram of **3ta** Ellipsoids displayed at 30% probability

Complex	**3ta**
CCDC number	1855890
Temperature, K	298

Formula	$C_{18}H_{18}Cl_2BrNO_3$
Fw	447.14
Crystal system	monoclinic
Space group	*P 21/n*
a, Å	6.2949(3)
b, Å	22.9315(13)
c, Å	13.8808(8)
α, °	90
β, °	97.214(4)
γ, °	90
V, Å^3	1987.85(19)
Z	4
GOF	0.981
*R*1, [I≥2σ(I)]	0.0538
*wR*2, [I≥2σ(I)]	0.1320

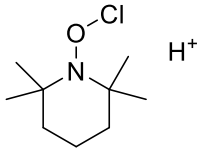
4. TEMPO-trapping Experiment

According to the general procedure, TEMPO (2.0 equiv) was added to the schlenk tube before the solvent. The reaction mixture was stirred at 30 °C for 2 h, and then a small aliquot was removed and submitted to ESI high-resolution mass spectrometry.



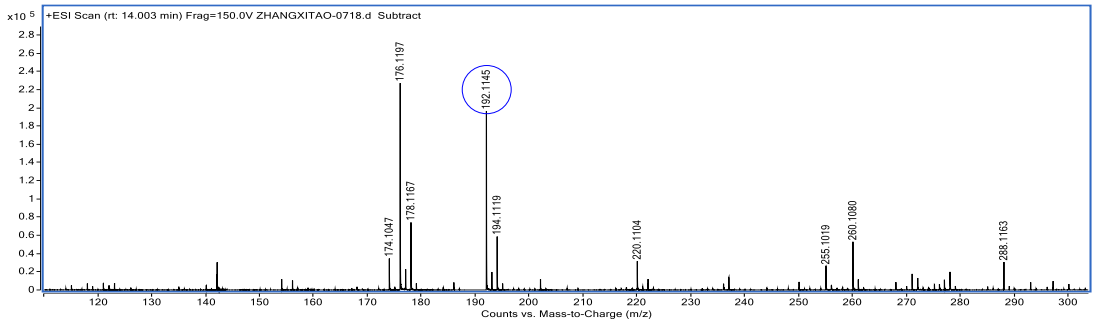
The mass spectrum proves the formation of TEMPO adduct **4** with the chlorine radical.

$[M+H]^+$, calcd. 192.1150, found 192.1145.



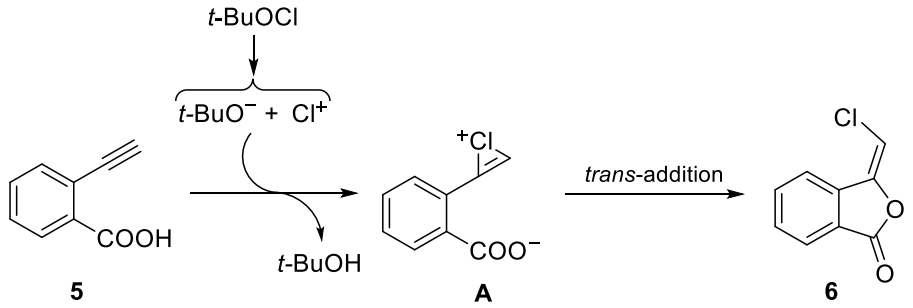
$C_9H_{19}ClNO^+$

Exact Mass: 192.1150

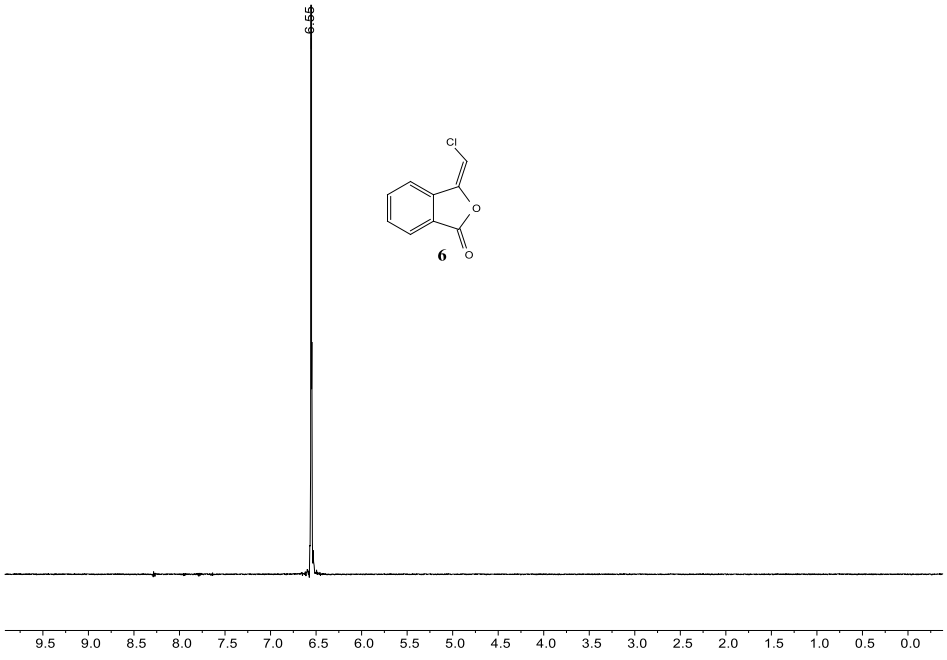


5. Mechanism for Product 6 Generation and Its Structure Confirmation

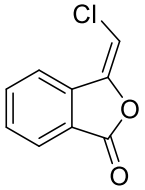
Mechanism:



NOE (400 MHz, $CDCl_3$): No NOE cross peaks between vinylic proton (δ 6.56) and aromatic proton were observed in the NOE spectrum indicating that the trans configuration for product **6**.



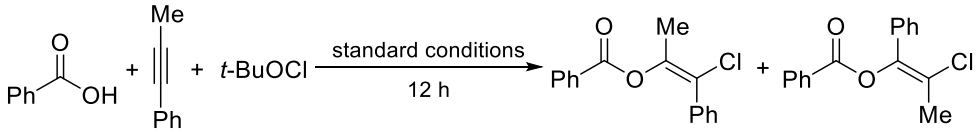
(*E*)-3-(chloromethylene)isobenzofuran-1(3H)-one (6)



White solid (34.8 mg, 66%), mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 7.8 Hz, 1H), 7.95 (dd, J = 7.8, 0.8 Hz, 1H), 7.79 (ddd, J = 7.8, 7.8, 0.8 Hz, 1H), 7.64 (td, J = 7.8, 7.8, 0.8 Hz, 1H), 6.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 147.1, 136.8, 134.9, 131.0, 125.7, 125.5, 124.6, 104.2. IR (KBr): ν 3060, 3035, 2966, 1723, 1601, 1493, 1452, 1270, 1177, 764, 697, 617 cm^{-1}. HRMS (ESI) calcd for [$C_9H_6ClO_2$, M+H]$^+$: 181.0051, found: 181.0050.

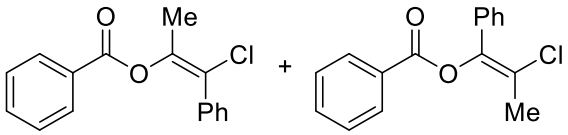
6. Formation and Structure Confirmation of Alkene Derivatives 8 and 8′

Formation:



1a **7** **8** : **8'** = 1.6 : 1 (64% total yield)

Mixture of (*E*)-1-chloro-1-phenylprop-1-en-2-yl benzoate and (*E*)-2-chloro-1-phenylprop-1-en-1-yl benzoate (**8** and **8′**) was obtained in 64% total yield when the internal alkyne, 1-phenyl-1-propyne (**7**), was tested under the standard conditions. The structures of **8** and **8′** were not distinguished at present.

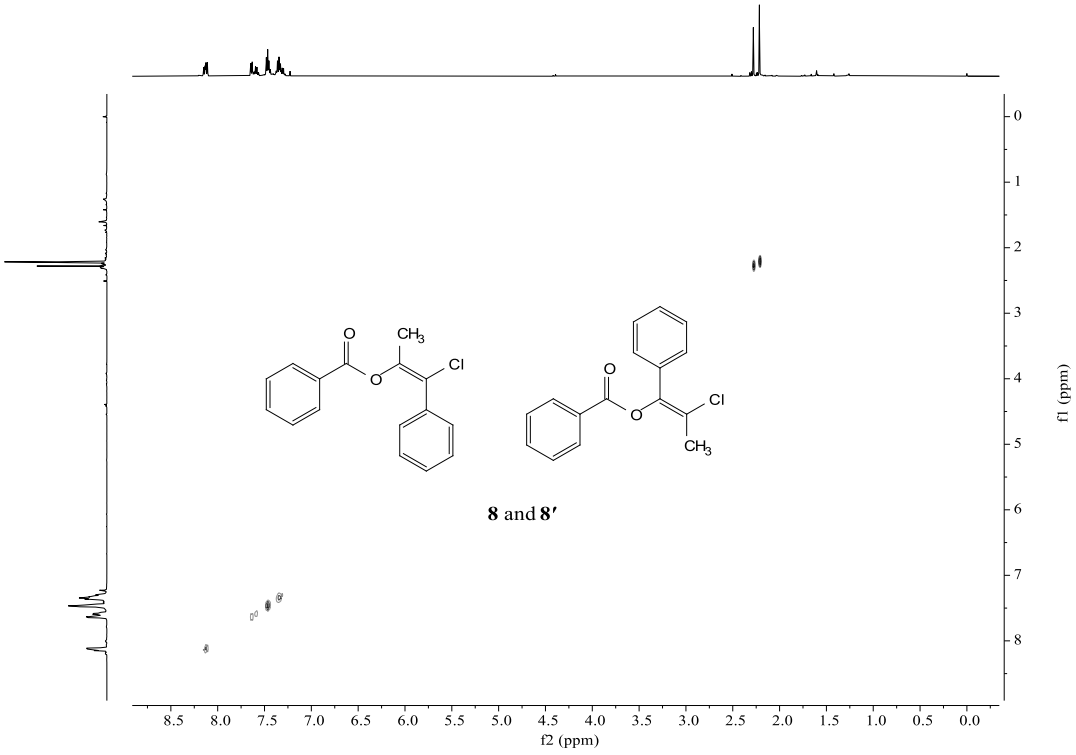


8 and **8'**

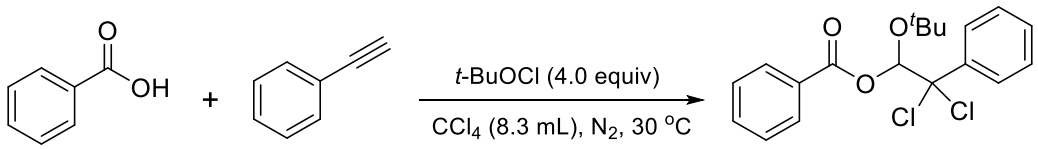
Colorless oil (52.4 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 2H), 7.66–7.60 (m, 2 H), 7.51–7.46 (m, 3H), 7.38–7.31 (m, 2H), 2.30–2.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 164.0, 142.8, 142.8, 133.9, 133.8, 133.8, 133.6, 130.2, 130.2, 129.2, 128.7, 128.7,128.7, 128.6, 128.4, 128.1, 122.8, 122.3, 22.0, 21.2. MS (EI): (8.656 min) 237.1, 115.1, 105.1, 77.1, 51.1; MS (EI): (8.749 min) 237.1, 115.1, 105.0, 77.1, 51.1.

^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$): No NOE cross peaks between methyl protons (δ 2.30–2.23) and phenyl protons were observed in the ^{1}H-^{1}H NOESY

spectrum indicating that the methyl and the phenyl groups are in the *trans*-positions in the structures of products **8** and **8′**.

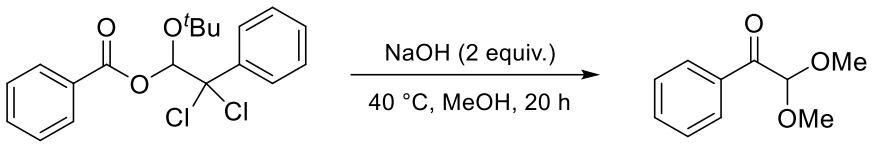


7. Procedure for Gram-Scale Synthesis and Further Transformations



1a, 5.0 mmol **2a**, 15.0 mmol **3aa**, 1.56 g, 85%

A reaction flask was charged with a mixture of benzoic acid (610 mg, 5 mmol), phenyl acetylene (1650 uL, 15 mmol), *t*-BuOCl (2267 uL, 20 mmol), CCl_4 (8.3 mL) under N_2 atmosphere. The reaction mixture was stirred at 30 °C for 2 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate : petroleum ether = 1 : 50) to afford corresponding product (**3aa**) as a white solid (1.56 g, 85%).



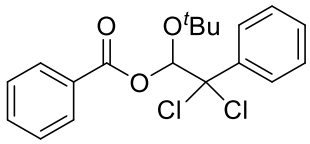
1a **11** (88%)

A reaction flask was charged with a mixture of **1a** (110.2 mg, 0.3 mmol), NaOH (24 mg, 0.6 mmol), and methanol (2 mL). The reaction mixture was stirred at 40 °C for 20 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate : petroleum ether = 1 : 10) to afford corresponding product **11** as a colorless oil (47.5 mg, 88% yield).

8. The Characterization of Products

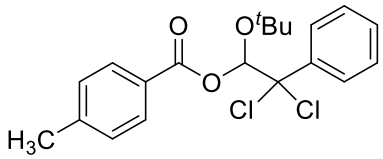
The spectroscopic data of all the products are presented.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl benzoate (3aa)



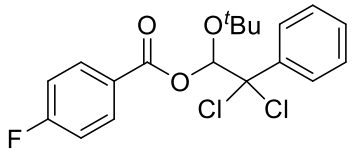
White solid (99.2 mg, 90%), mp 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–8.07 (m, 2H), 7.85–7.83 (m, 2H), 7.57 (dd, J = 7.6, 7.6 Hz, 1H), 7.46–7.42 (m, 2H), 7.40–7.35 (m, 3H), 6.62 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 133.6, 130.1, 129.5, 129.4, 128.5, 127.8, 94.8, 92.2, 78.0, 27.8. IR (KBr): ν 3062, 2980, 1727, 1601, 1492, 1370, 1267, 1144, 1086, 1025, 974, 748, 710, 658 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{20}Cl_2NaO_3$, M+Na$]^+$: 389.0687, found: 389.0678.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 4-methylbenzoate (3ba)



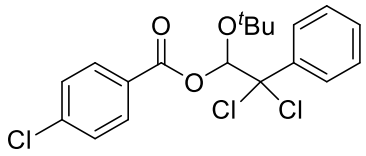
Colorless oil (70.9 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.75–7.73 (m, 2H), 7.28–7.25 (m, 3H), 7.15–7.13 (m, 2H), 6.51 (s, 1H), 2.30 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 144.4, 138.4, 130.2, 129.3, 129.3，128.5, 127.7, 126.8, 94.6, 92.3, 77.9, 27.8, 21.8. IR (KBr): ν 3061, 2980, 1724, 1612, 1493, 1370, 1268, 1118, 1081, 974, 820, 750, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{22}Cl_2NaO_3$, M+Na$]^+$: 403.0844, found: 403.0834.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 4-fluorobenzoate (3ca)



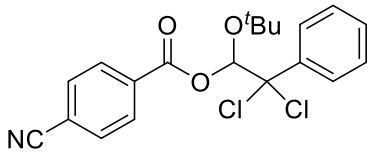
Colorless oil (84.4 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.08 (m, 2H), 7.84–7.82 (m, 2H), 7.39–7.36 (m, 3H), 7.13–7.09 (m, 2H), 6.59 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (d, $^{1}J_{C\text{-}F}$ = 253 Hz), 164.4, 138.3, 132.7(d, $^{3}J_{C\text{-}F}$ = 10 Hz), 129.4, 128.5, 127.8, 125.8 ($^{4}J_{C\text{-}F}$ = 3 Hz), 115.7 ($^{2}J_{C\text{-}F}$ = 22 Hz), 94.9, 92.2, 78.0, 27.8. IR (KBr): ν 3061, 2981, 1728, 1604, 1508, 1268, 1155, 1078, 974, 853, 764, 695 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_2FNaO_3$, M+Na]$^{+}$: 407.0593, found: 407.0570.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 4-chlorobenzoate (3da)



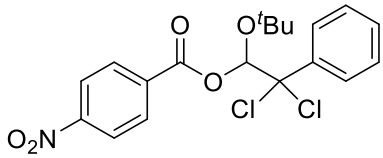
Colorless oil (88.0 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.99 (m, 2H), 7.83–7.81 (m, 2H), 7.43–7.41 (m, 2H), 7.38–7.36 (m, 3H), 6.58 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 140.1, 138.2, 131.5, 129.4, 128.9, 128.5, 127.9, 127.8, 95.0, 92.1, 78.1, 27.8. IR (KBr): ν 3062, 2980, 1729, 1594, 1489, 1370, 1264, 1081, 972, 848, 756, 696 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_3NaO_3$, M+Na]$^{+}$: 423.0297, found: 423.0278.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 4-cyanobenzoate (3ea)



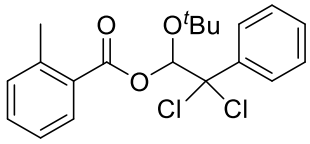
Light yellow solid (82.4 mg, 70%), mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–8.16 (m, 2H), 7.83–7.80 (m, 2H), 7.77–7.75 (m, 2H), 7.41–7.37 (m, 3H), 6.59 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 140.1, 138.0, 133.3, 132.4, 130.5, 129.5, 128.4, 117.9, 117.0, 95.5, 91.9, 78.4, 27.7. IR (KBr): ν 3060, 2981, 2232, 1732, 1610, 1492, 1370, 1267, 1146, 1049, 963, 819, 736, 696 cm^{-1}. HRMS (ESI) calcd for [$C_{20}H_{19}Cl_2NNaO_3$, M+Na]$^{+}$: 414.0640, found: 414.0636.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 4-nitrobenzoate (3fa)



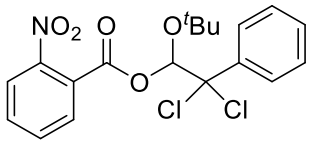
White solid (107.6 mg, 87%), mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31–8.29 (m, 2H), 8.25–8.23 (m, 2H), 7.83–7.81 (m, 2H), 7.41–7.38 (m, 3H), 6.60 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 150.9, 137.9, 134.8, 131.2, 129.6, 128.4, 127.9, 123.7, 95.6, 91.9, 78.4, 27.7. IR (KBr): ν 3058, 2981, 1732, 1608, 1529, 1370, 1266, 1147, 1088, 963, 819, 748, 735, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_2NNaO_5, M+Na]^+$: 434.0538, found: 434.0533.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 2-methylbenzoate (3ga)



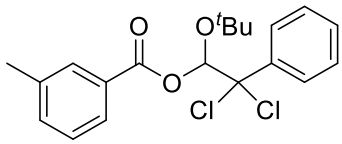
Colorless oil (72.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 1H), 7.85–7.83 (m, 2H), 7.41–7.36 (m, 4H), 7.27–7.23 (m, 2H), 6.60 (s, 1H), 1.10 (s, 9H)；^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 140.9, 138.5, 132.5, 131.7, 131.0, 128.8, 127.8, 125.9, 94.4, 92.3, 77.8, 27.8, 21.7. IR (KBr): ν 3062, 2979, 1728, 1602, 1490, 1370, 1250, 1150, 1057, 974, 738, 735, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{22}Cl_2NaO_3$, M+Na]$^+$: 403.0844, found: 403.0834.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 2-nitrobenzoate (3ha)



White solid (76.7 mg, 62%), mp 107–109. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.85 (m, 1H), 7.84–7.81 (m, 3H), 7.68–7.64 (m, 2H), 7.42–7.38 (m, 3H), 6.59 (s, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 149.0, 138.1, 132.5, 132.5, 128.4, 127.9, 126.2, 124.0, 95.8, 92.1, 78.8, 27.7. IR (KBr): ν 3064, 2980, 1739, 1607, 1540, 1485, 1371, 1354, 1262, 1153, 1064, 959, 748, 731, 695 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_2NNaO_5, M+Na]^+$: 434.0538, found: 434.0533.

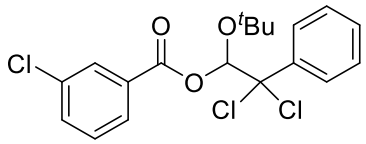
1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 3-methylbenzoate (3ia)



Light yellow oil (74.4 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.87 (m, 2H), 7.85–7.83 (m, 2H), 7.39–7.33 (m, 5H), 6.61 (s, 1H), 2.39 (s, 3H) 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 138.4, 138.3, 134.4, 130.6, 129.4, 129.4, 128.6, 128.4, 127.7, 127.3 94.7, 92.2, 77.9, 27.8, 21.3. IR (KBr): ν 3060, 2980, 1726, 1609,

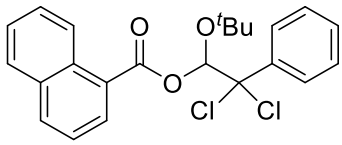
1490, 1273, 1138, 1070, 975, 898, 795, 742, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{22}Cl_2NaO_3, M+Na]^+$: 403.0844, found: 403.0841.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 3-chlorobenzoate (3ja)



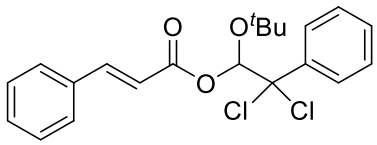
Colorless oil (90.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 2.0, 2.0 Hz, 1H), 7.96 (ddd, J = 7.6, 1.2, 1.2 Hz, 1H), 7.84–7.81 (m, 2H), 7.56–7.63 (m, 1H), 7.40–7.36 (m, 4H), 6.59 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 138.1, 133.6, 131.3, 130.1, 129.9, 129.5, 128.5, 128.2, 127.8, 95.1, 92.0, 78.2, 27.8. IR (KBr): ν 3071, 2980, 1732, 1597, 1492, 1370, 1251, 1149, 1026, 971, 889, 795, 746, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_3NaO_3, M+Na]^+$: 423.0297, found: 423.0281.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 1-naphthoate (3ka)



White solid (78.9 mg, 63%), mp 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (dd, J = 8.8, 0.8 Hz, 1H), 8.36 (dd, J = 7.2, 1.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.93–7.89 (m, 3H), 7.67–7.63 (m, 1H), 7.58–7.52 (m, 2H), 7.45–7.40 (m, 3H), 6.80 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 138.5, 134.1, 133.9, 131.6, 131.1, 129.4, 128.5, 128.0, 127.9, 126.4, 126.1, 125.7, 124.7, 94.7, 92.4, 78.0, 27.9. IR (KBr): ν 3059, 2979, 1720, 1594, 1490, 1369, 1241, 1150, 1077, 973, 781, 756, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{22}Cl_2NaO_3, M+Na]^+$: 439.0844, found: 439.0841.

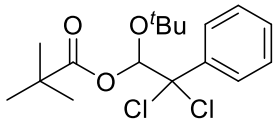
1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl cinnamate (3la)



White solid (83.6 mg, 70%), mp 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.82 (m, 2H), 7.74 (d, J = 16 Hz, 1H), 7.53–7.52 (m, 2H), 7.39–7.37 (m, 6H), 6.49 (s, 1H), 6.44 (d, J = 16 Hz), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 146.5, 138.4, 134.1, 130.7, 129.4, 129.0, 128.5, 128.3, 127.7, 117.3, 94.2, 92.2, 77.9, 27.8. IR (KBr): ν 3059, 2980, 1717, 1635, 1490, 1448, 1369, 1247, 1113, 1057, 977,

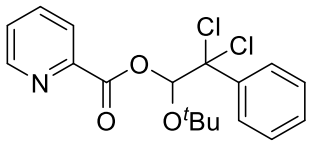
766, 695 cm^{-1}. HRMS (ESI) calcd for $[C_{21}H_{22}Cl_2NaO_3, M+Na]^+$: 415.0844, found: 415.0845.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl pivalate (3ma)



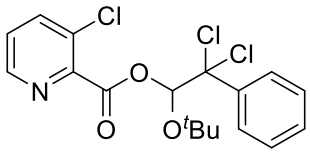
Colorless oil (83.7 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.26–7.24 (m, 3H), 6.28 (d, J = 1.2 Hz, 1H), 1.07 (d, J = 0.8 Hz, 9H), 0.94 (d, J = 0.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 138.5, 129.2, 128.4, 127.7, 93.8, 92.2, 77.5, 38.9, 27.8, 26.8. IR (KBr): ν 3061, 2980, 1739, 1480, 1369, 1276, 1167, 1106, 982, 822, 747, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{17}H_{24}Cl_2NaO_3, M+Na]^+$: 369.1000, found: 369.0993.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl picolinate (3na)



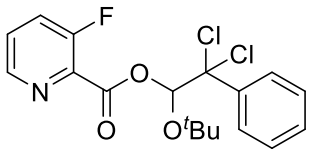
Colorless oil (83.7 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, J = 8.4 Hz, 1H), 8.13 (dd, J = 8, 0.8 Hz, 1H), 7.86–7.82 (m, 3H), 7.50–7.47 (m, 1H), 7.40–7.36 (m, 3H), 6.66 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 150.4, 147.4, 138.1, 137.0, 129.4, 128.5, 127.8, 127.2, 125.6, 95.5, 92.0, 78.3, 27.7. IR (KBr): ν 3060, 2982, 1744, 1588, 1453, 1368, 1241, 1147, 1106, 963, 747, 693 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{19}Cl_2NNaO_3, M+Na]^+$: 390.0640, found: 390.0654.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 3-chloropicolinate (3oa)



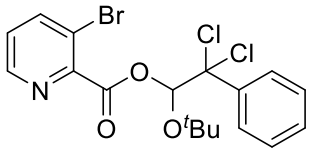
Colorless solid (97.9 mg, 81%), mp 78–80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (dd, J = 4.8, 1.6 Hz, 1H), 7.89–7.86 (m, 2H), 7.77 (dd, J = 8.0, 1.6 Hz, 1H), 7.40–7.35 (m, 4H), 6.68 (s, 1H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 147.5, 147.3, 138.6, 138.1, 131.0, 129.4, 128.6, 127.8, 126.5, 95.8, 91.6, 78.5, 27.8. IR (KBr): ν 3060, 2980, 1746, 1571, 1475, 1371, 1287, 1205, 1110, 1038, 1025, 959, 753, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{18}Cl_3NNaO_3, M+Na]^+$: 424.0250, found: 424.0251.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 3-fluoropicolinate (3pa)



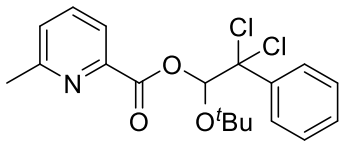
Light yellow solid (71.8 mg, 62%), mp 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58–8.56 (m, 1H), 7.89–7.86 (m, 2H), 7.57–7.47 (m, 2H), 7.41–7.36 (m, 3H), 6.70 (s, 1H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^{3}J_{C\text{-}F}$ = 6 Hz), 159.5 (d, $^{1}J_{C\text{-}F}$ = 270 Hz), 145.7, 145.7, 138.0, 136.3 (d, $^{2}J_{C\text{-}F}$ = = 9 Hz), 129.4, 128.6, 127.7, 125.6, 125.4, 95.7, 91.7, 78.4, 27.8. IR (KBr): ν 3064, 2980, 1740, 1589, 1492, 1447, 1371, 1294, 1203, 1148, 1078, 960, 810, 748, 698 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{18}Cl_2FNNaO_3$: 408.0545 $[M+Na]^+$; found: 408.0548.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 3-bromopicolinate (3qa)



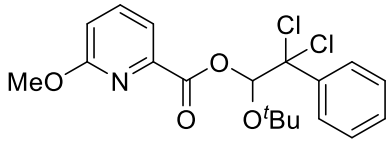
Light yellow solid (107.3 mg, 80%), mp 91–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J = 8.4, 1.6 Hz, 1H), 7.96 (dd, J = 8.0, 1.2 Hz, 1H), 7.89–7.86 (m, 2H), 7.38–7.36 (m, 3H), 7.27 (dd, J = 4.0, 1.6 Hz, 1H), 6.67 (s, 1H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 147.5, 148.8, 147.9, 141.7, 138.1, 129.4, 128.7, 127.8, 126.5, 118.9, 95.8, 91.6, 78.5, 27.8. IR (KBr): ν 3060, 2980, 1746, 1569, 1475, 1371, 1286, 1204, 1106, 1057, 958, 750, 697, 589 cm^{-1}. HRMS (ESI) calcd for [$C_{18}H_{18}Cl_2BrNNaO_3$, $M+Na]^+$: 467.9745, found: 467.9737; [$C_{18}H_{18}Cl_2BrNNaO_3$, $M+2+Na]^+$: 469.9724, found: 469.9716.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 6-methylpicolinate (3ra)



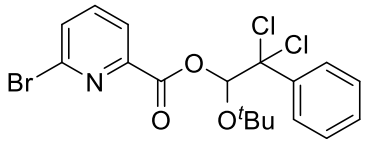
Colorless oil (56.2 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.6 Hz, 1H), 7.81–7.84 (m, 2H), 7.71 (t, J = 8.0 Hz, 1H), 7.42–7.33 (m, 4H), 6.66 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 159.6, 148.5, 146.7, 138.1, 137.1, 129.4, 128.5, 127.7, 127.2, 122.9, 95.3, 92.1, 78.3, 27.8. IR (KBr): ν 3059, 2980, 1748, 1591, 1448, 1370, 1257, 1152, 1110, 1083, 967, 821, 756, 697 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{21}Cl_2NNaO_3$, $M+Na]^+$: 404.0796, found: 404.0795.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 6-methoxypicolinate (3sa)



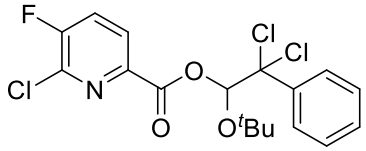
Light yellow solid (98.0 mg, 82%), mp 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.85 (m, 2H), 7.73 (dd, J = 7.2, 0.8 Hz, 1H), 7.68 (dd, J = 8.0, 8.0 Hz, 1H), 7.38–7.35 (m, 3H), 6.93 (dd, J = 8.4, 0.8 Hz, 1H), 6.64 (s, 1H), 4.02 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 163.8, 144.7, 139.0, 138.2, 129.4, 128.6, 127.7, 119.2, 115.9, 95.4, 92.0, 78.1, 53.1, 27.8. IR (KBr): ν 3061, 2981, 1747, 1597, 1467, 1369, 1261, 1243, 1158, 1109, 1026, 970, 938, 850, 767, 698 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{21}Cl_2NNaO_4, M+Na]^+$: 420.0745, found: 420.0742.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 6-bromopicolinate (3ta)



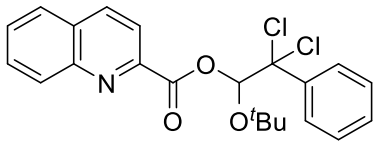
White solid (83.2 mg, 62%), mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, J = 6.8, 1.6 Hz, 1H), 7.87–7.84 (m, 2H), 7.73–7.67 (m, 2H), 7.42–7.37 (m, 3H), 6.63 (s, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 148.0, 142.7, 139.3, 137.9, 130.2, 129.5, 128.6, 127.8, 124.5, 95.8, 91.9, 78.5, 27.8. IR (KBr): ν 3061, 2981, 1748, 1557, 1492, 1370, 1242, 1129, 1027, 984, 906, 819, 757, 697, 513 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{18}Cl_2BrNNaO_3, M+Na]^+$: 467.9745, found: 467.9743; $[C_{18}H_{18}Cl_2BrNNaO_3, M+2+Na]^+$: 469.9724, found: 469.9722.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl 6-chloro-5-fluoropicolinate (3ua)



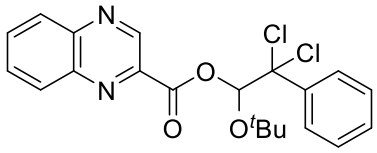
White solid (60.6 mg, 48%), mp 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 8.4, 3.6 Hz, 1H), 7.86–7.83 (m, 2H), 7.61 (dd, J = 8.4, 7.2, 1H), 7.41–7.37 (m, 3H), 6.61 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 157.1 (d, $^{1}J_{C\text{-}F}$ = 268 Hz), 142.7 (d, $^{3}J_{C\text{-}F}$ = 5 Hz), 140.1 (d, $^{2}J_{C\text{-}F}$ = 20 Hz), 137.8, 129.6, 128.5, 127.8, 126.5 (d, $^{4}J_{C\text{-}F}$ = 5 Hz), 125.0 (d, $^{2}J_{C\text{-}F}$ = 19.4 Hz), 124.9, 95.9, 91.9, 78.5, 27.7. IR (KBr): ν 3061, 2981, 1751, 1579, 1457, 1396, 1375, 1252, 1160, 1104, 964, 853, 748, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{17}Cl_3FNKO_3, M+K]^+$: 457.9895, found: 459.9896.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl quinoline-2-carboxylate (3va)



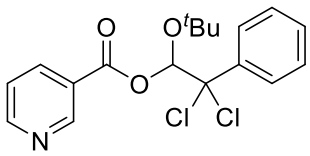
Yellow solid (107.9 mg, 86%), mp 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 7.91–7.88 (m, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.79–7.74 (m, 1H), 7.62 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.42–7.37 (m, 3H), 6.75 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 147.9, 147.2, 138.1, 137.4, 131.0, 130.3, 129.5, 129.4, 128.9, 128.8, 128.6, 127.8, 127.5, 121.2, 95.7, 92.1, 78.4, 27.8. IR (KBr): ν 3063, 2960, 1747, 1592, 1503, 1378, 1240, 1211, 1133, 1105, 1002, 909, 844, 777, 698 cm^{-1}. HRMS (ESI) calcd for $[C_{22}H_{21}Cl_2NNaO_3, M+Na]^+$: 440.0796, found: 440.0792.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl quinoxaline-2-carboxylate (3wa)



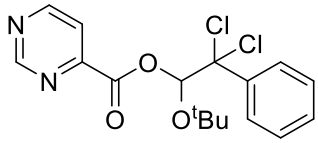
Light yellow solid (80.5 mg, 64%), mp 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.34 (dd, J = 8.0, 1.6 Hz, 1H), 8.20 (dd, J = 8.4, 1.2 Hz, 1H), 7.93–7.87 (m, 4H), 7.42–7.39 (m, 3H), 6.76 (s, 1H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 145.1, 143.8, 142.0, 141.9, 137.8, 132.6, 131.0, 129.6, 129.3, 128.6, 127.9, 96.2, 91.8, 78.7, 27.8. IR (KBr): ν 3061, 2960, 1754, 1578, 1492, 1369, 1264, 1162, 1135, 1087, 957, 804, 775, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{21}H_{20}Cl_2N_2NaO_3, M+Na]^+$: 441.0749, found: 441.0743.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl nicotinate (3xa)



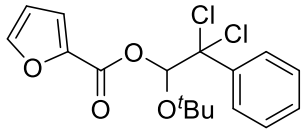
Colorless oil (87.3, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (d, J = 1.6 Hz, 1H), 8.80 (dd, J = 4.8, 1.2 Hz, 1H), 8.32 (ddd, J = 8.0, 1.6, 1.6 Hz, 1H), 7.84–7.82 (m, 2H), 7.42–7.38 (m, 4H), 6.62 (s, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 154.0, 151.3, 138.0, 137.4, 129.4, 128.4, 127.8, 125.4, 123.4, 95.1, 91.9, 78.3, 27.7. IR (KBr): ν 3059, 2980, 1732, 1591, 1492, 1370, 1275, 1150, 1093, 1025, 963, 819, 737, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{19}Cl_2NNaO_3, M+H]^+$: 368.0820, found: 368.0807.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl pyrimidine-4-carboxylate (3ya)



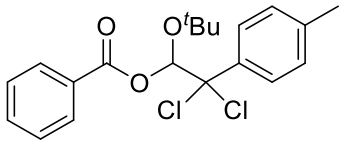
Colorless oil (67.6 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (d, *J* = 1.6 Hz, 1H), 9.02 (d, *J* = 4.8 Hz, 1H), 8.01 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.85–7.82 (m, 2H), 7.42–7.38 (m, 3H), 6.63 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 159.6, 159.3, 154.1, 137.6, 129.6, 128.4, 127.9, 121.2, 96.2, 91.7, 78.7, 27.7. IR (KBr): ν 3061, 2981, 1758, 1572, 1492, 1447, 1269, 1153, 1107, 963, 820, 749, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{17}H_{18}Cl_2N_2NaO_3, M+Na]^+$: 391.0592, found: 391.0588.

1-(*tert*-butoxy)-2,2-dichloro-2-phenylethyl furan-2-carboxylate (3za)



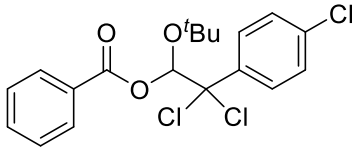
Colorless oil (72.9 mg, 68%). ^{1}H NMR (400 MHz, CDCl3): *δ* 7.83–7.80 (m, 2H), 7.62 (dd, *J* = 1.2, 0.4 Hz, 1H), 7.25 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.54 (s, 1H), 6.53 (dd, *J* = 3.6, 1.6 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 157.3, 147.2, 143.9, 138.1, 129.4, 128.5, 127.7, 119.3, 112.0, 94.6, 91.9, 78.2, 27.8. IR (KBr): ν 2980, 1731, 1578, 1472, 1395, 1370, 1291, 1180, 1089, 971, 935, 758, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{17}H_{18}Cl_2NaO_4, M+Na]^+$: 379.0480, found: 379.0478.

1-(*tert*-butoxy)-2,2-dichloro-2-(p-tolyl)ethyl benzoate (3ab)



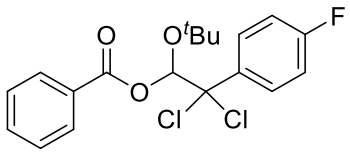
Colorless oil (60.6 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.09–8.07 (m, 2H), 7.72–7.70 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 7.19–7.17 (m, 2H), 6.60 (s, 1H), 2.37 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 165.5, 139.4, 135.4, 133.5, 130.1, 129.6, 128.5, 128.4, 128.4, 94.8, 92.3, 77.9, 27.8, 21.1. IR (KBr): ν 3055, 2978, 1726, 1598, 1504, 1451, 1370, 1266, 1143, 1086, 1025, 971, 796, 747, 710 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{22}Cl_2NaO_3, M+Na]^+$: 403.0844, found: 403.0839.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-chlorophenyl)ethyl benzoate (3ac)



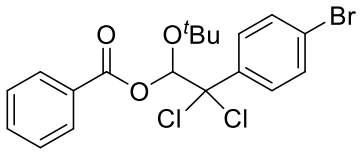
Colorless oil (90.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H), 7.78–7.76 (m, 2H), 7.61–7.58 (m, 1H), 7.48–7.44 (m, 2H), 7.37–7.35 (m, 2H), 6.62 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 136.9, 135.5, 133.6, 130.1, 130.0, 129.4, 128.6, 127.8, 94.6, 91.1, 78.1, 27.9. IR (KBr): ν 3070, 2980, 1727, 1594, 1490, 1370, 1265, 1143, 1085, 1025, 971, 835, 748, 710 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_3NaO_3$, M+Na]$^{+}$: 423.0297, found: 423.0298.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-fluorophenyl)ethyl benzoate (3ad)



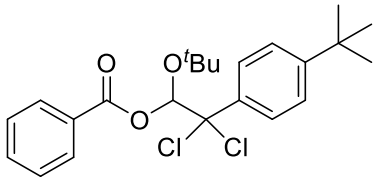
Colorless oil (104.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.05 (m, 2H), 7.84–7.80 (m, 2H), 7.61–7.57 (m, 1H), 7.47–7.44 (m, 2H), 7.09–7.04 (m, 2H), 6.60 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 163.2 (d, $^{1}J_{C\text{-}F}$ = 248 Hz), 134.2 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 133.6, 130.7 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 130.0, 129.4, 128.5, 114.6 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 94.7, 91.3, 78.1, 27.9. IR (KBr): ν 3077, 2980, 1731, 1600, 1508, 1370, 1265, 1143, 1085, 1025, 971, 840, 710 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_2FNaO_3$, M+Na]$^{+}$: 407.0593, found: 407.0599.

2-(4-bromophenyl)-1-(*tert*-butoxy)-2,2-dichloroethyl benzoate (3ae)



Colorless oil (104.4 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H), 7.71–7.69 (m, 2H), 7.61–7.57 (m, 1H), 7.53–7.51 (m, 2H), 7.47–7.44 (m, 2H), 6.62 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 137.4, 133.7, 130.8, 130.4, 130.1, 129.4, 128.6, 123.7, 94.6, 91.2, 78.1, 27.9. IR (KBr): ν 3070, 2980, 1727, 1601, 1586, 1486, 1451, 1369, 1267, 1143, 1084, 1025, 971, 809, 762, 710, 654 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_2BrNaO_3$, M+Na]$^{+}$: 466.9792, found: 466.9783; [$C_{19}H_{19}Cl_2BrNaO_3$, M+2+Na]$^{+}$: 468.9772, found: 468.9763.

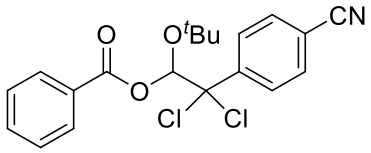
1-(*tert*-butoxy)-2,2-dichloro-2-(4-chlorophenyl)ethyl benzoate (3af)



Colorless oil (120.7 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.08 (m, 2H), 7.77–7.75 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 7.40–7.38 (m, 2H), 6.61 (s,

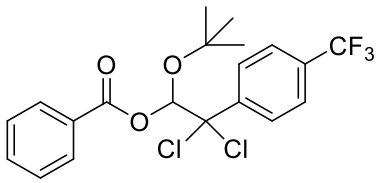
1H), 1.33 (s, 9H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 152.6, 135.5, 133.5, 130.1, 129.6, 128.5, 128.2, 124.6, 94.9, 92.3, 77.9, 34.6, 31.2, 27.8. IR (KBr): ν 3070, 2966, 1727, 1602, 1474, 1370, 1267, 1144, 1086, 1025, 974, 809, 710 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{28}Cl_2NaO_3, M+Na]^+$: 445.1313, found: 445.1314.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-cyanophenyl)ethyl benzoate (3ag)



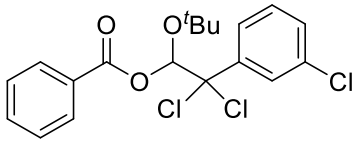
White solid (57.7 mg, 49%), mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–8.00 (m, 2H), 7.98–7.96 (m, 2H), 7.71–7.69 (m, 2H), 7.63–7.59 (m, 1H), 7.48–7.45 (m, 2H), 6.67 (s, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 142.9, 133.8, 137.4, 130.0, 129.6, 129.1, 128.6, 118.2, 113.3, 94.5, 90.2, 78.4, 27.9. IR (KBr): ν 3069, 2980, 2232, 1727, 1602, 1451, 1370, 1263, 1142, 1083, 1024, 972, 814, 710 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{19}Cl_2NNaO_3, M+Na]^+$: 414.0640, found: 414.0640.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-(trifluoromethyl)phenyl)ethyl benzoate (3ah)



White solid (88.8 mg, 68%), mp 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 2H), 7.99–7.96 (m, 2H), 7.67–7.65 (m, 2H), 7.61–7.58 (m, 1H), 7.48–7.44 (m, 2H), 6.68 (s, 1H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 141.9, 133.72, 131.4 (q, J = 33 Hz), 130.0, 129.3, 128.6, 125.2, 124.6 (q, J = 4 Hz), 94.59, 90.64, 78.26, 27.83. IR (KBr): ν 3068, 2987, 1728, 1597, 1450, 1327, 1264, 1136, 1085, 1018, 974, 837, 711 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{19}Cl_2F_3NaO_3, M+Na]^+$: 457.0561, found: 457.0566.

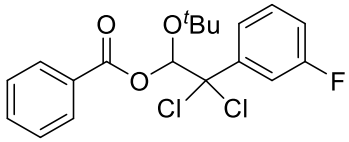
1-(*tert*-butoxy)-2,2-dichloro-2-(3-chlorophenyl)ethyl benzoate (3ai)



Colorless oil (90.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 2H), 7.86–7.85 (m, 1H), 7.72 (ddd, J = 7.6, 1.2, 1.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 7.37–7.30 (m, 2H), 6.61 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 140.1, 133.8, 130.1, 129.1, 128.9, 126.8, 94.6, 90.7, 78.2, 27.9. IR (KBr): ν

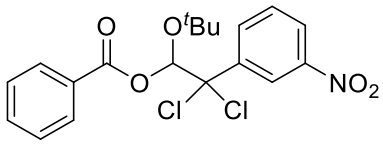
3070, 2980, 1728, 1598, 1476, 1370, 1264, 1144, 1085, 1025, 969, 878, 768, 710 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_3NaO_3, M+Na]^+$: 423.0297, found: 423.0295.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-chlorophenyl)ethyl benzoate (3aj)



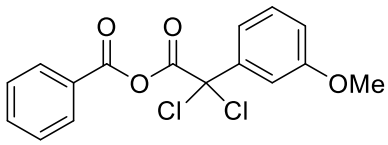
Colorless oil (86.7 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 2H), 7.63–7.56 (m, 3H), 7.47–7.43 (m, 1H), 7.34 (dd, J = 14, 8.0 Hz, 1H), 7.08 (td, J = 8.0, 1.2 Hz, 1H), 6.62 (s, 1H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 162.0 (d, $^1J_{C\text{-}F}$ = 245 Hz), 140.8 (d, $^3J_{C\text{-}F}$ = 7 Hz), 133.6, 130.1, 129.4, 129.2 (d, $^3J_{C\text{-}F}$ = 8 Hz), 128.6, 124.3 (d, $^4J_{C\text{-}F}$ = 3 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 21 Hz), 116.2 (d, $^2J_{C\text{-}F}$ = 24 Hz), 94.6, 90.8, 78.1, 27.8. IR (KBr): ν 3077, 2981, 1728, 1590, 1486, 1370, 1265, 1144, 1085, 1025, 986, 882, 782, 711 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_2FNaO_3, M+Na]^+$: 407.0593, found: 407.0591.

1-(*tert*-butoxy)-2,2-dichloro-2-(3-nitrophenyl)ethyl benzoate (3ak)



Colorless oil (77.9 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76–8.75 (m, 1H), 8.29–8.27 (m, 1H), 8.19–8.17 (m, 1H), 8.03–8.01 (m, 2H), 7.62–7.59 (m, 2H), 7.48–7.45 (m, 2H), 6.71 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 137.4, 133.7, 130.8, 130.1, 129.4, 128.6, 123.9, 94.6, 91.2, 78.1, 27.9. IR (KBr): ν 3090, 2981, 1728, 1601, 1533, 1475, 1351, 1262, 1143, 1065, 1024, 971, 896, 803, 736, 711, 683 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{19}Cl_2NNaO_5, M+Na]^+$: 434.0538, found: 434.0535.

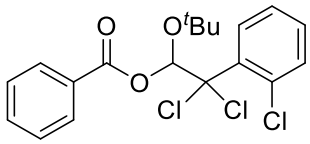
1-(*tert*-butoxy)-2,2-dichloro-2-(2-methoxyphenyl)ethyl benzoate (3al)



Colorless oil (84.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.04 (m, 2H), 7.60–7.57 (m, 1H), 7.48–7.41 (m, 3H), 7.40–7.38 (m, 1H), 7.31–7.27 (m, 1H), 6.94–6.87 (m, 1H), 6.61 (s, 1H), 3.80 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 159.0, 139.8, 133.5, 130.1, 129.5, 128.7, 128.5, 120.9, 115.1, 114.5, 94.8, 91.9, 78.0, 55.4, 27.8. IR (KBr): ν 3077, 2980, 1727, 1601, 1590, 1452, 1262,

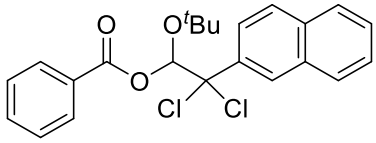
1145, 1086, 1025, 980, 746, 712 cm^{-1}. HRMS (ESI) calcd for [$C_{20}H_{22}Cl_2NaO_4$, M+Na]$^+$: 419.0793, found: 419.0798.

1-(*tert*-butoxy)-2,2-dichloro-2-(2-chlorophenyl)ethyl benzoate (3am)



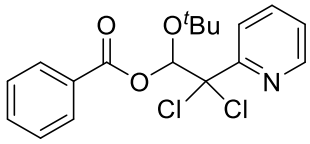
Colorless oil (85.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.18 (m, 1H), 8.10–8.08 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.42 (m, 4H), 7.29–7.27 (m, 2H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 135.0, 133.5, 132.7, 132.2, 131.2, 130.8, 130.1, 129.5, 128.5, 126.6, 92.0, 91.3, 78.1, 28.0. IR (KBr): ν 3068, 2980, 1727, 1601, 1445, 1369, 1267, 1141, 1086, 1066, 977, 755, 710 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{19}Cl_3NaO_3$, M+Na]$^+$: 423.0297, found: 423.0292.

1-(*tert*-butoxy)-2,2-dichloro-2-(naphthalen-2-yl)ethyl benzoate (3an)



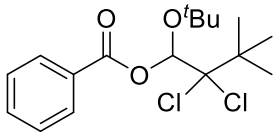
Colorless oil (80.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (m, 1H), 8.15–8.13 (m, 2H), 7.97–7.93 (m, 2H), 7.91–7.89 (m, 2H), 7.64–7.56 (m, 3H), 7.51–7.47 (m, 2H), 6.81 (s, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 135.6, 133.6, 133.2, 132.3, 130.1, 129.6, 128.9, 128.5, 128.4, 127.5, 127.4, 127.3, 126.6, 125.9, 94.9, 92.3, 78.1, 27.9. IR (KBr): ν 3054, 2980, 1725, 1598, 1508, 1449, 1369, 1267, 1143, 1086, 1025, 981, 747, 710 cm^{-1}. HRMS (ESI) calcd for [$C_{23}H_{22}Cl_2NaO_3$, M+Na]$^+$: 439.0844, found: 439.0837.

1-(*tert*-butoxy)-2,2-dichloro-2-(pyridin-2-yl)ethyl benzoate (3ao)



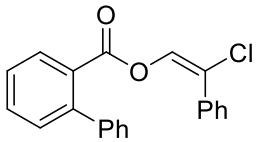
Colorless oil (60.6 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (ddd, J = 3.6, 0.8, 0.8 Hz, 1H), 8.12–8.10 (m, 2H), 8.10 (d, J = 2.4 Hz, 1H), 7.74 (ddd, J = 6.4, 6.4, 1.6 Hz, 1H), 7.59–7.55 (m, 1H), 7.46–7.43 (m, 2H), 7.28–7.25 (m, 1H), 7.14 (s, 1H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 156.7, 148.7, 136.8, 133.4, 130.1, 129.7, 128.5, 123.8, 122.4, 94.0, 90.8, 78.0, 28.0. IR (KBr): ν 3060, 2980, 1726, 1601, 1585, 1461, 1369, 1268, 1143, 1086, 1025, 978, 899, 770, 745, 711 cm^{-1}. HRMS (ESI) calcd for [$C_{18}H_{19}Cl_2NNaO_3$, M+Na]$^+$: 390.0640, found: 390.0636.

1-(*tert*-butoxy)-2,2-dichloro-2-(4-chlorophenyl)ethyl benzoate (3ap)



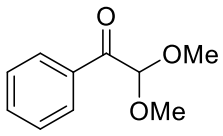
Colorless oil (29.2 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 7.2 Hz, 2H), 7.61–7.58 (m, 1H), 7.49–7.45 (m, 2H), 6.74 (s, 1H), 1.35 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 133.5, 130.1, 129.9, 128.5, 102.6, 94.2, 78.1, 78.0, 44.0, 28.4, 27.6. IR (KBr): ν 3062, 2980, 1726, 1602, 1451, 1368, 1270, 1179, 1146, 1088, 1025, 970, 736, 710 cm^{-1}. HRMS (ESI) calcd for [$C_{17}H_{24}Cl_2NaO_3$, M+Na]$^+$: 369.1000, found: 369.0994.

(*E*)-2-chloro-2-phenylvinyl [1,1'-biphenyl]-2-carboxylate (10)



Colorless oil (35.2 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 7.6, 7.6 Hz, 1H), 7.48 (dd, J = 8.0, 7.2 Hz, 1H), 7.42–7.32 (m, 7H), 7.30–7.27 (m, 3 H), 7.24–7.21 (m, 2H), 6.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 148.6, 143.6, 140.8, 132.8, 132.1, 131.3, 130.4, 129.3, 129.2, 128.7, 128.2, 127.5, 127.4, 124.9, 108.2. IR (KBr): ν 3089, 3060, 3027, 1755, 1624, 1596, 1493, 1477, 1228, 1067, 747, 699 cm^{-1}. HRMS (ESI) calcd for [$C_{21}H_{15}ClNaO_2$, M+Na]$^+$: 335.0839, found: 335.0832.

2,2-dimethoxy-1-phenylethan-1-one (11)[1]



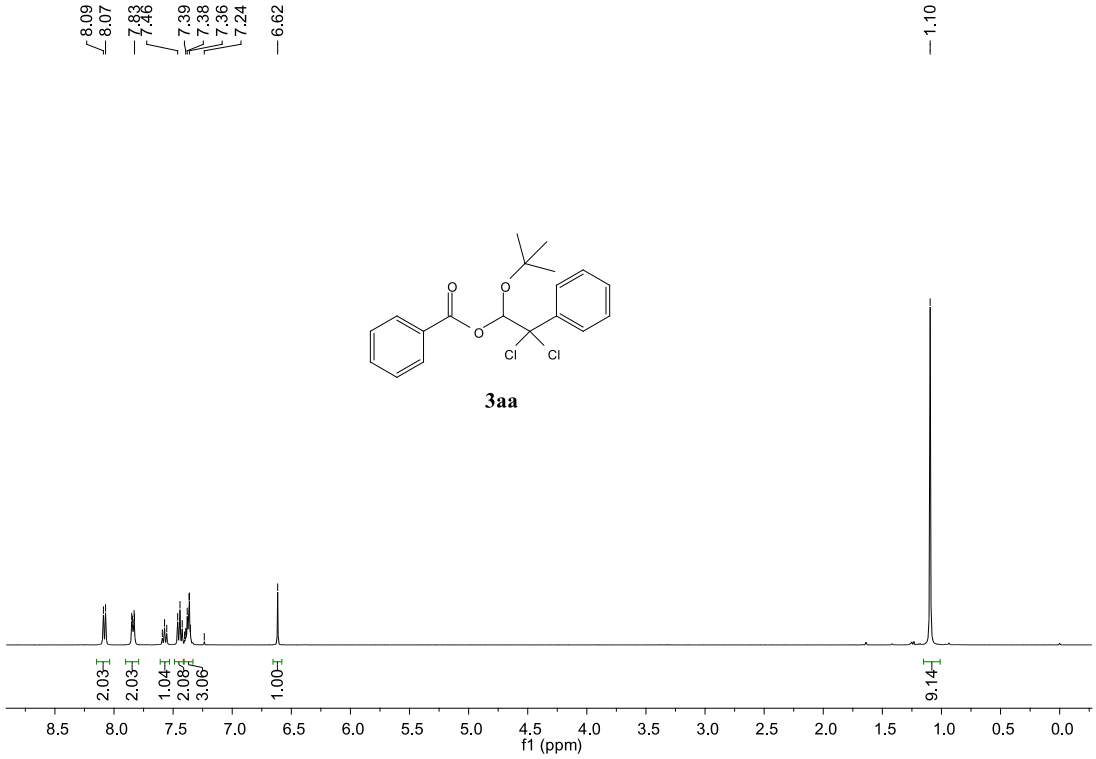
Colorless oil (47.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 7.6 Hz, 2H), 7.56 (dd, J = 7.6, 7.6 Hz, 1H), 7.44 (d, J = 7.6, 7.6 Hz, 2H), 5.21 (s, 1H), 3.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 133.8, 133.7, 129.5, 128.5, 103.3, 54.6.

9. Reference

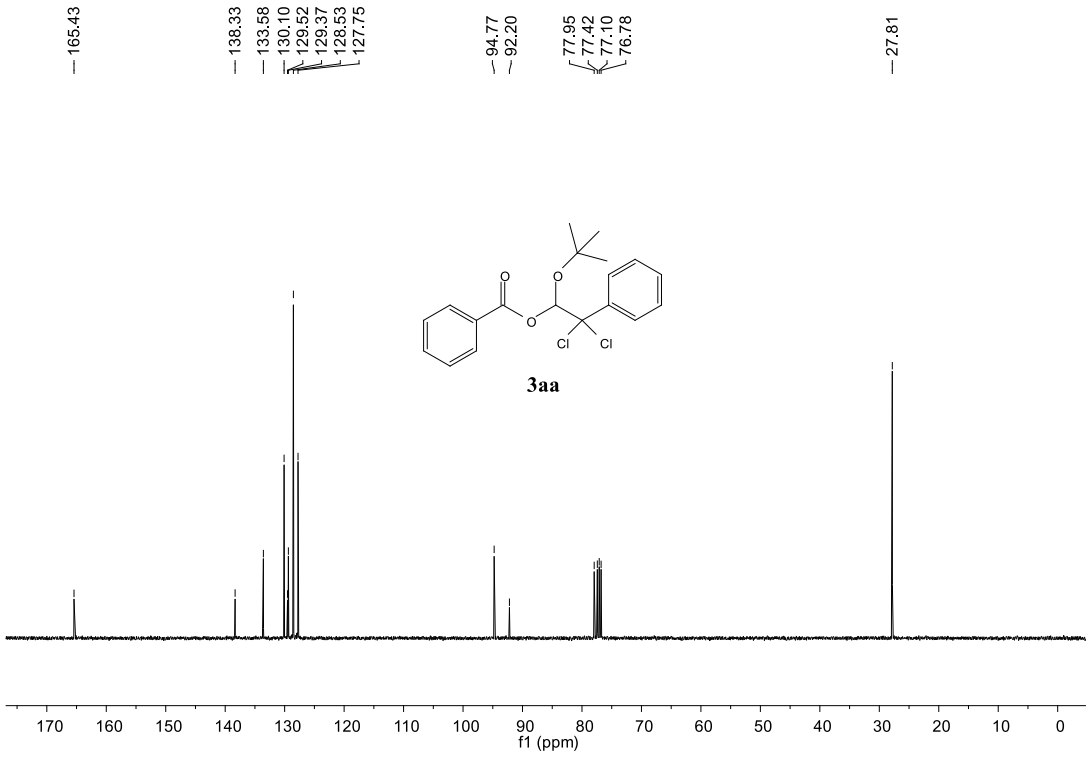
[1] Zhu, C.; Zhang, Y.; Zhao, H.; Huang, S.; Zhang, M.; Su, W. *Adv. Synth. Catal.* **2015**, *357*, 331.

10. Copies of ^{1}H and ^{13}C NMR Spectra of Products

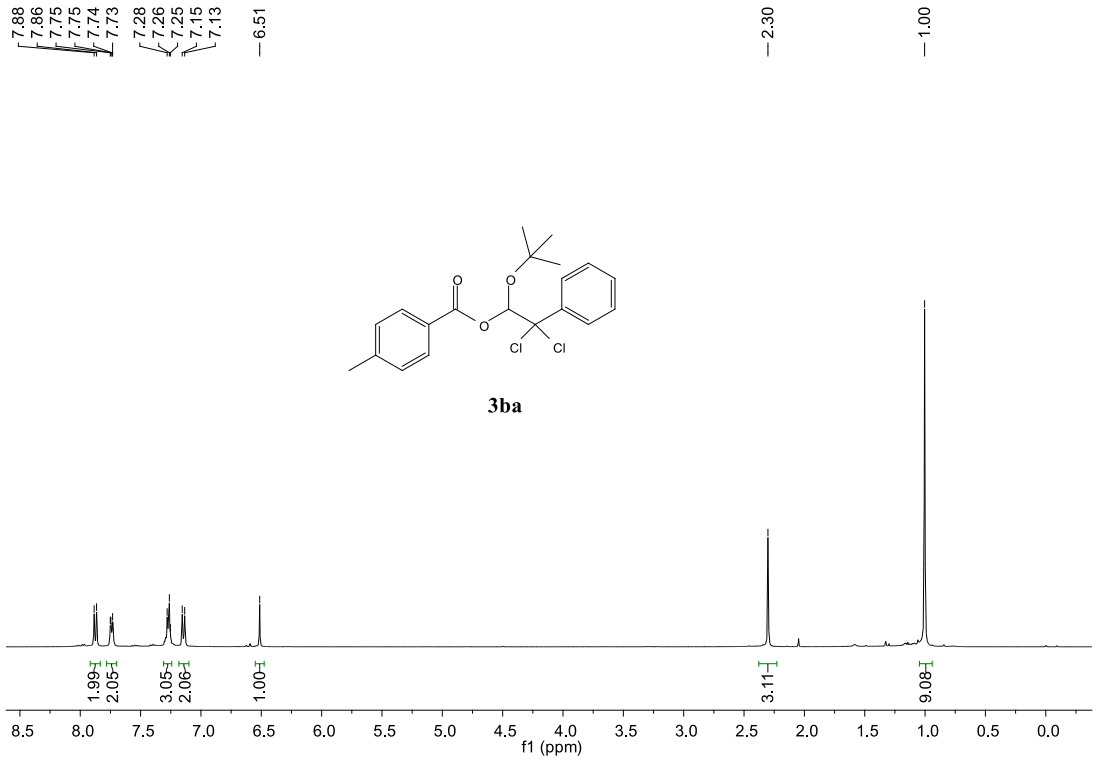
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$

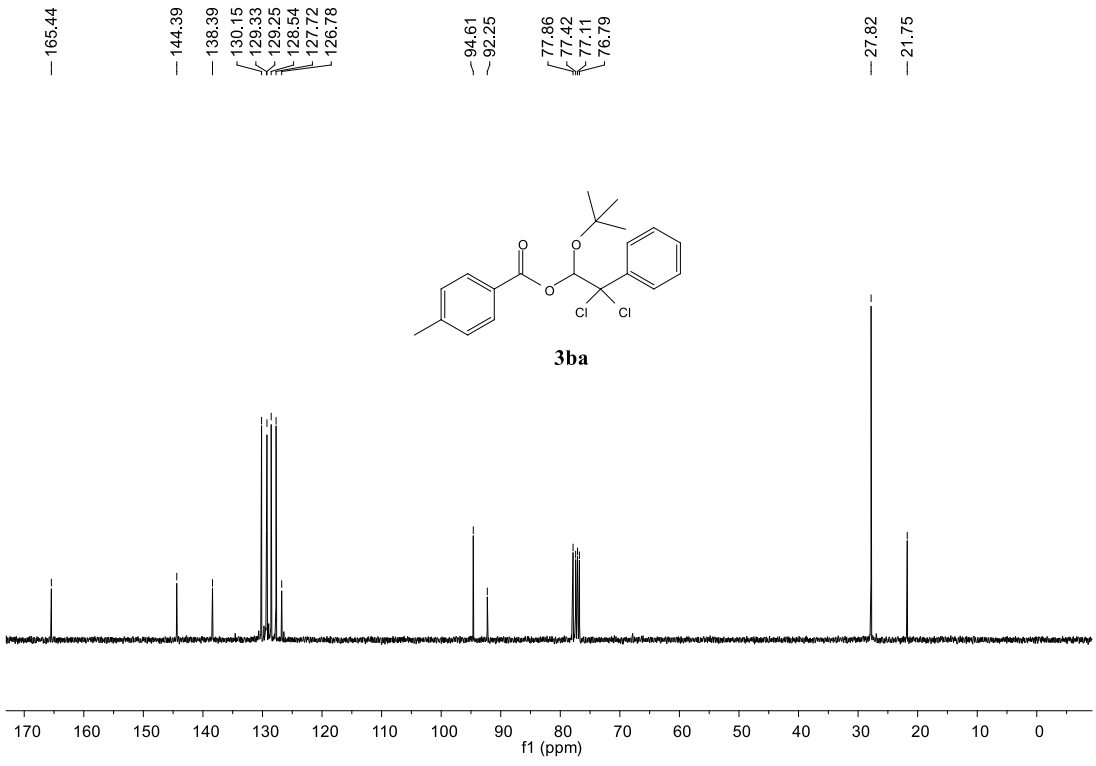


^{1}H NMR, 400 MHz, $CDCl_3$



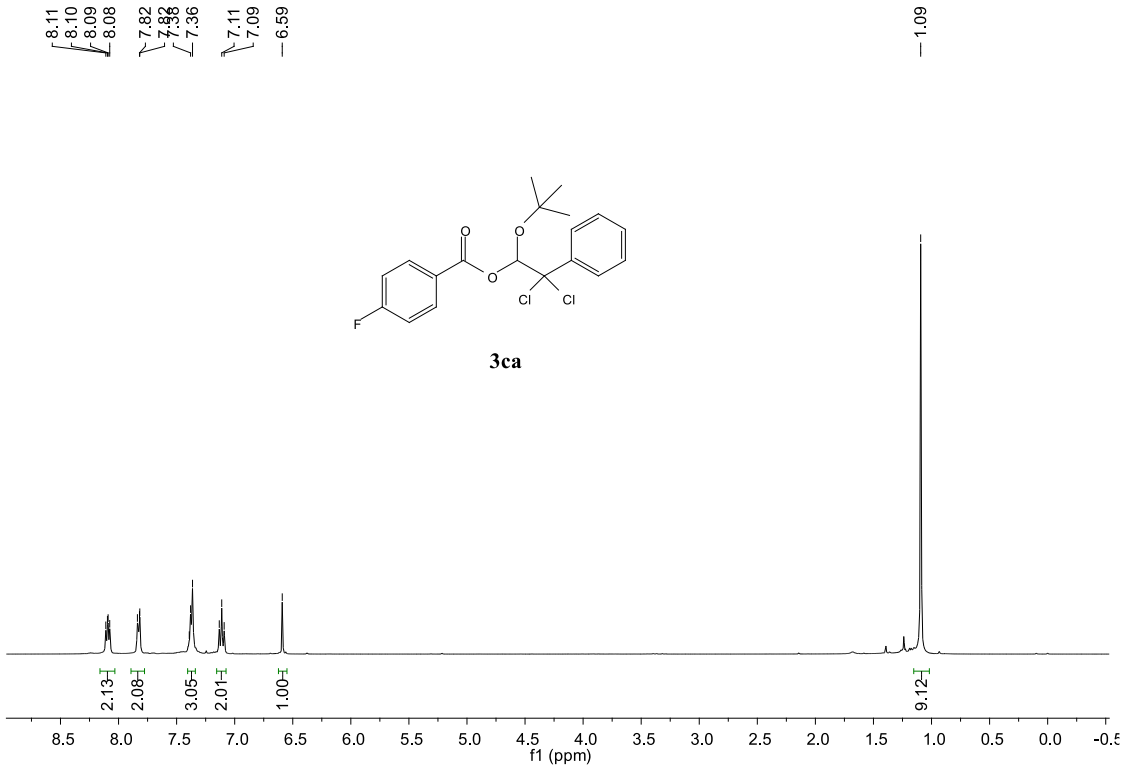
3ba

^{13}C NMR, 100 MHz, $CDCl_3$



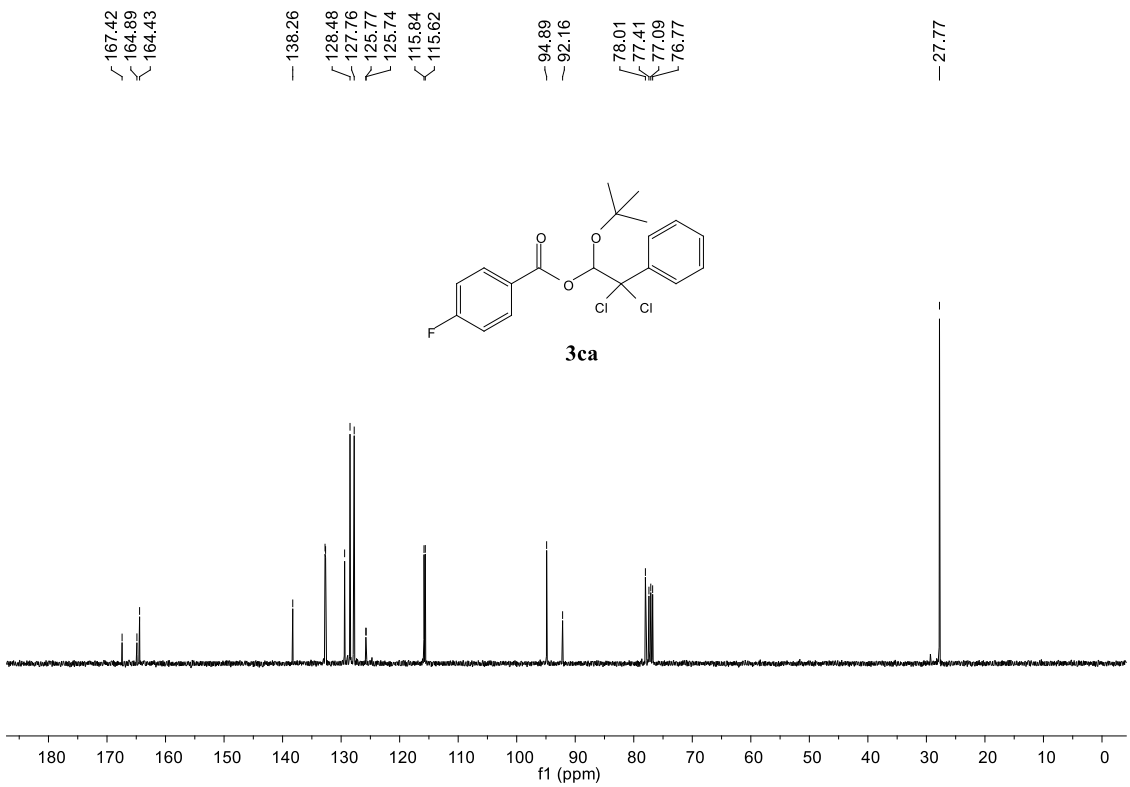
3ba

^{1}H NMR, 400 MHz, $CDCl_3$



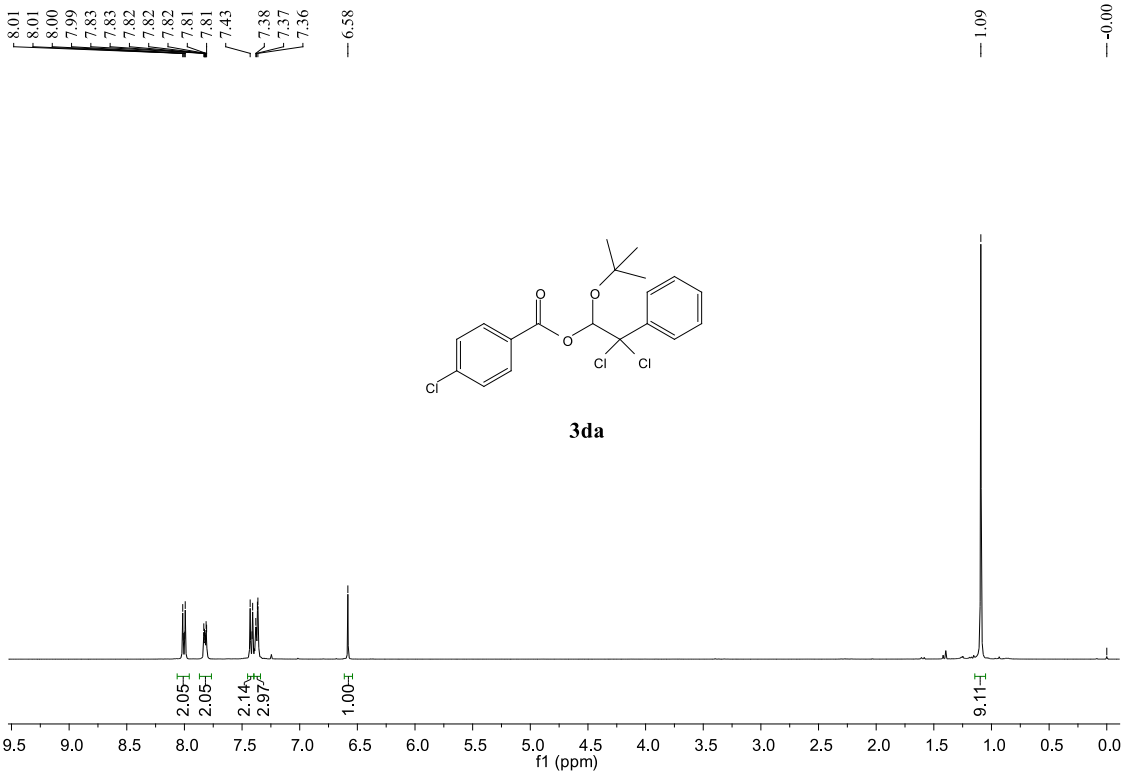
3ca

^{13}C NMR, 100 MHz, $CDCl_3$

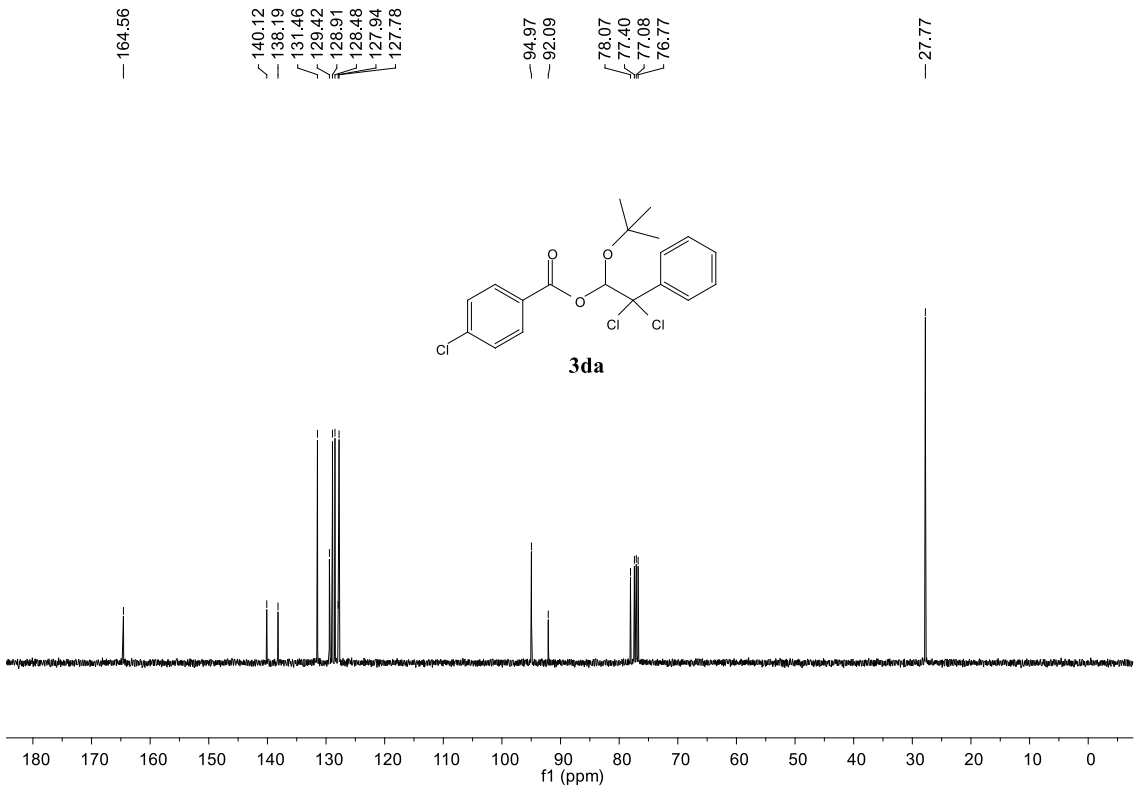


3ca

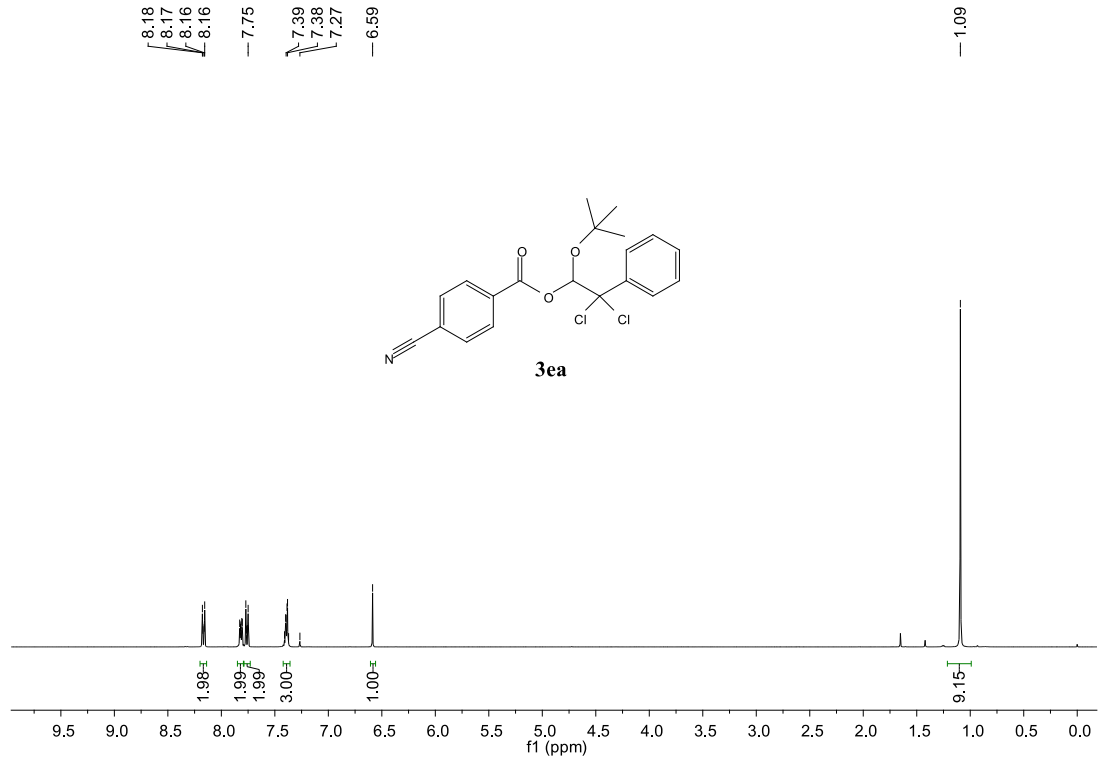
^{1}H NMR, 400 MHz, $CDCl_3$



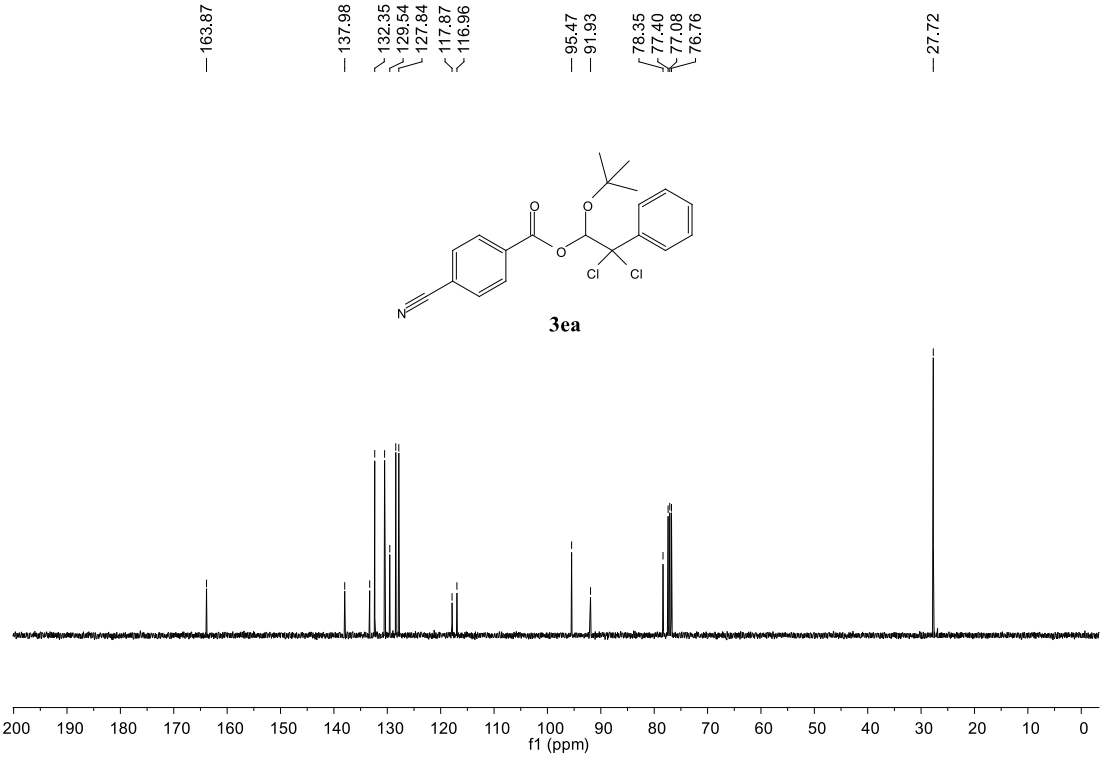
^{13}C NMR, 100 MHz, $CDCl_3$



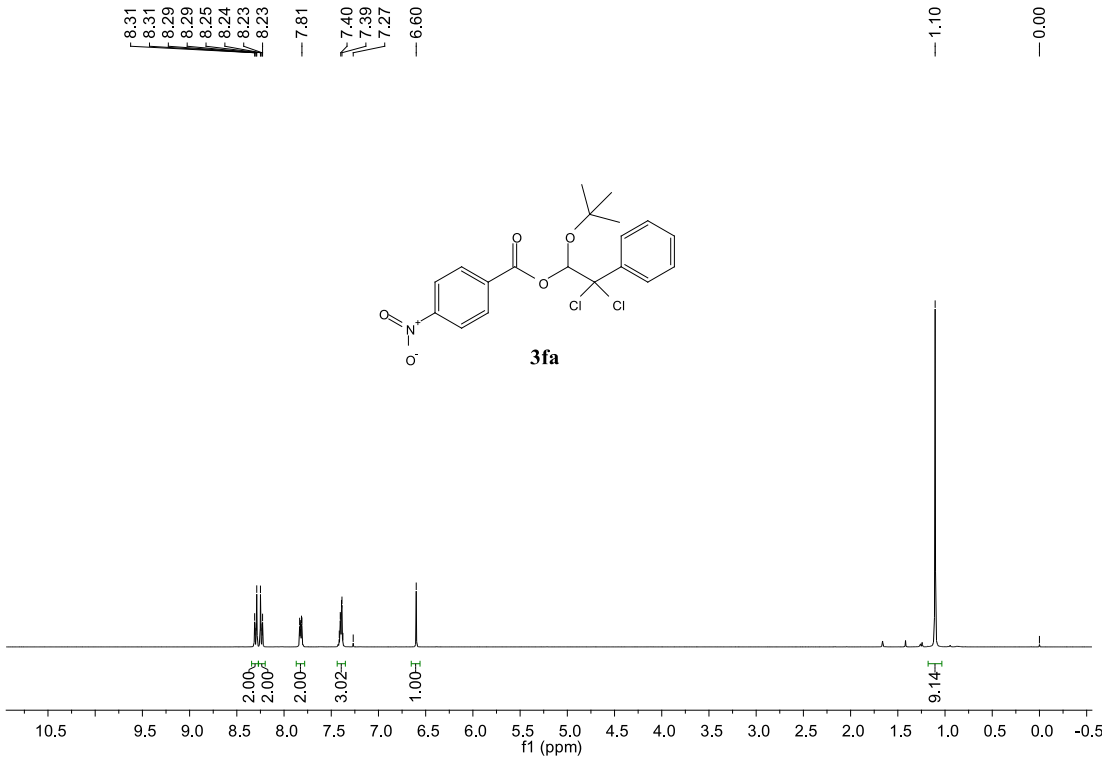
^{1}H NMR, 400 MHz, $CDCl_3$



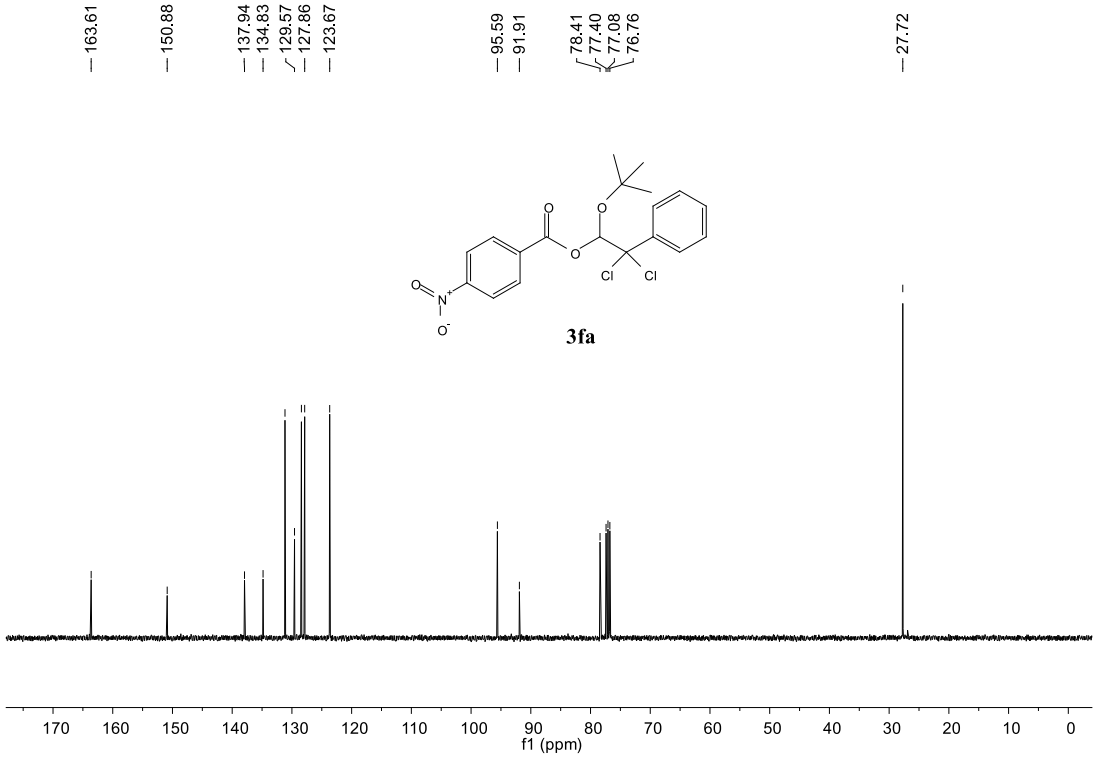
^{13}C NMR, 100 MHz, $CDCl_3$



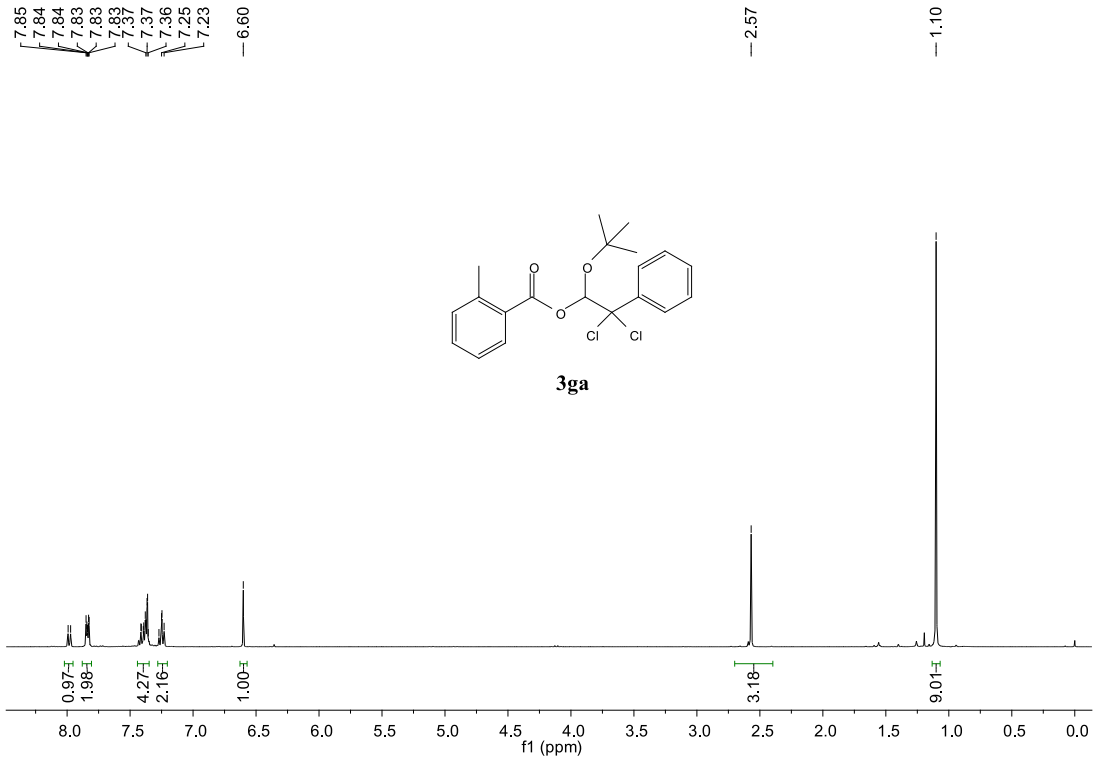
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$

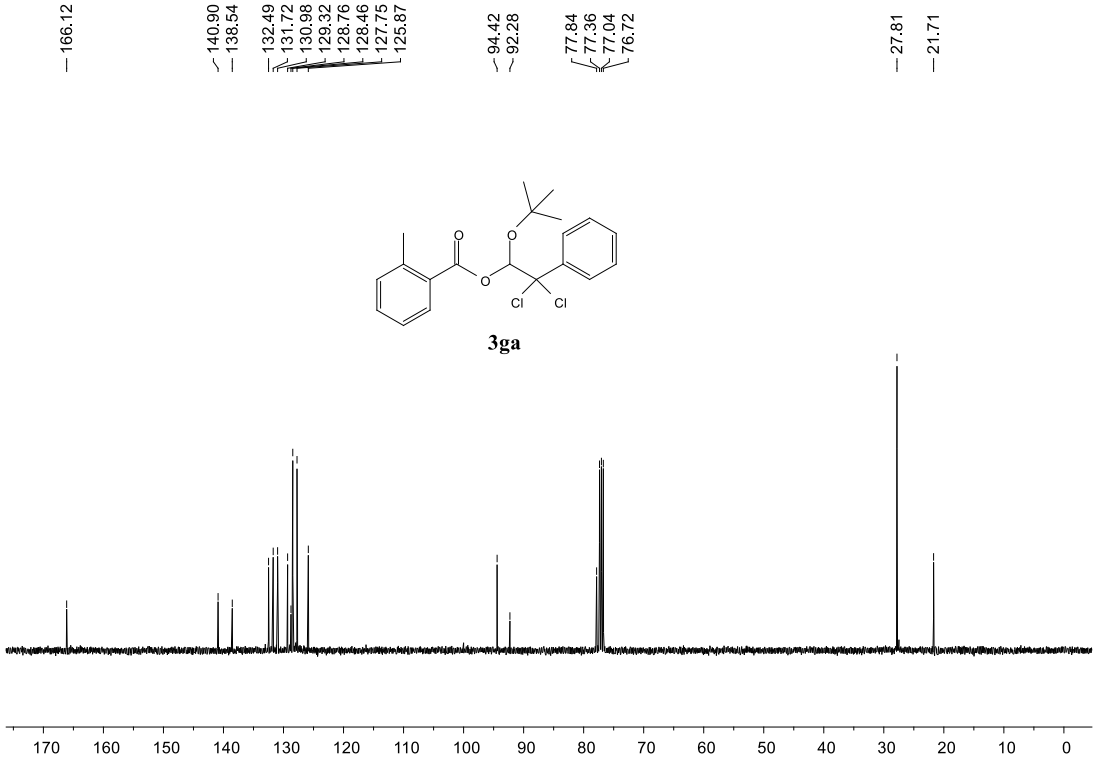


^{1}H NMR, 400 MHz, $CDCl_3$



3ga

^{13}C NMR, 100 MHz, $CDCl_3$



3ga

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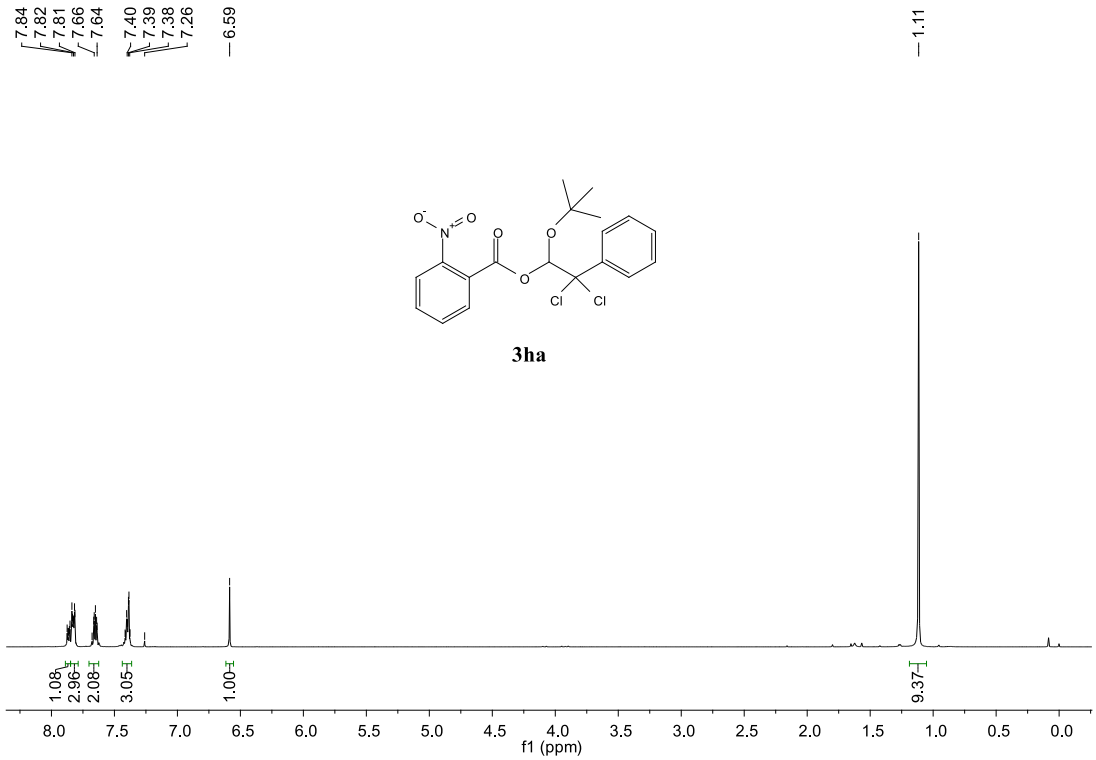
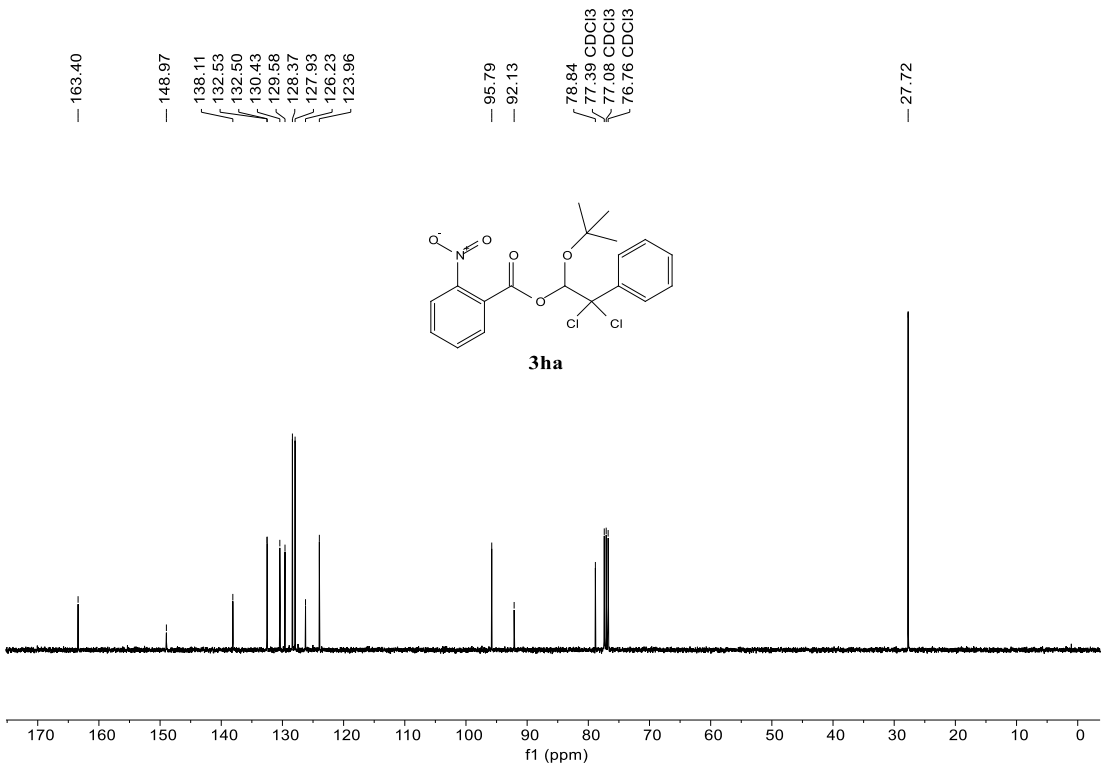
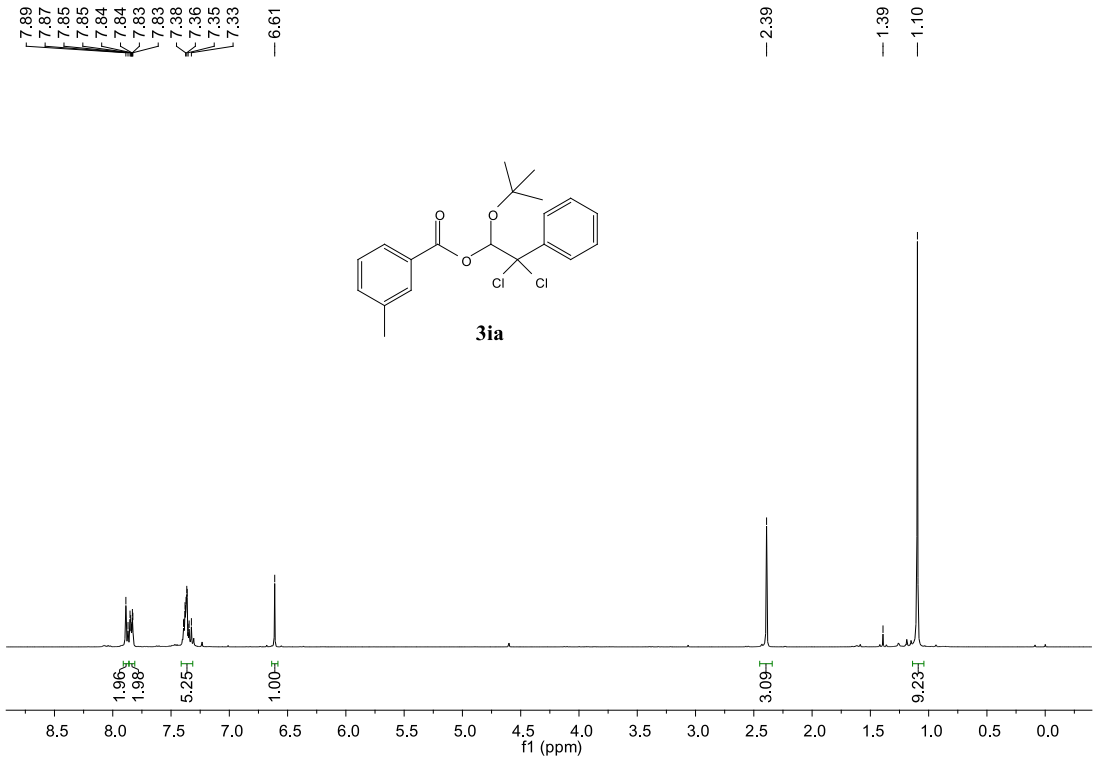


^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



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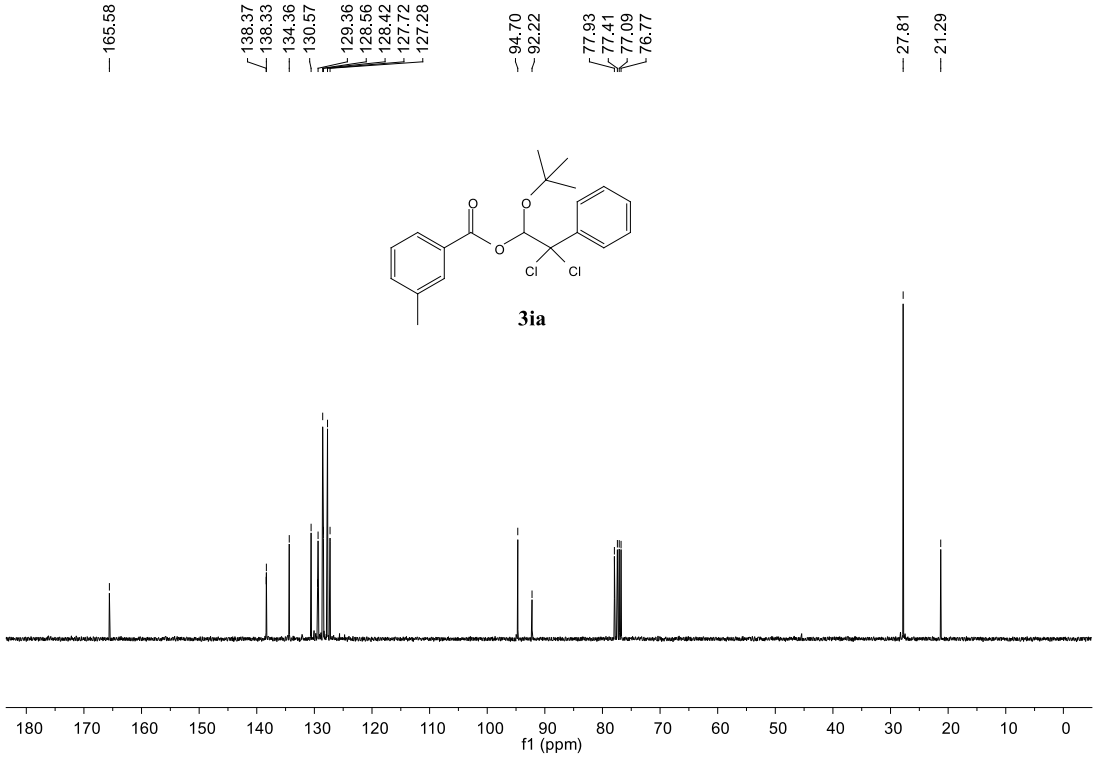

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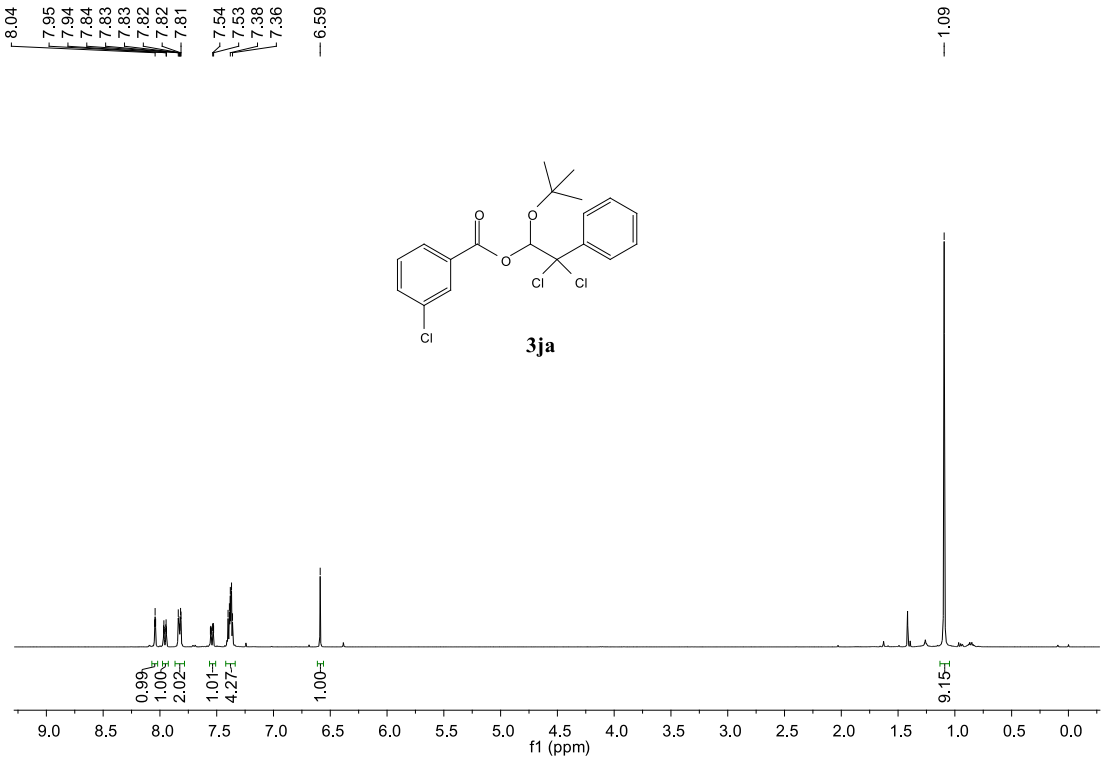

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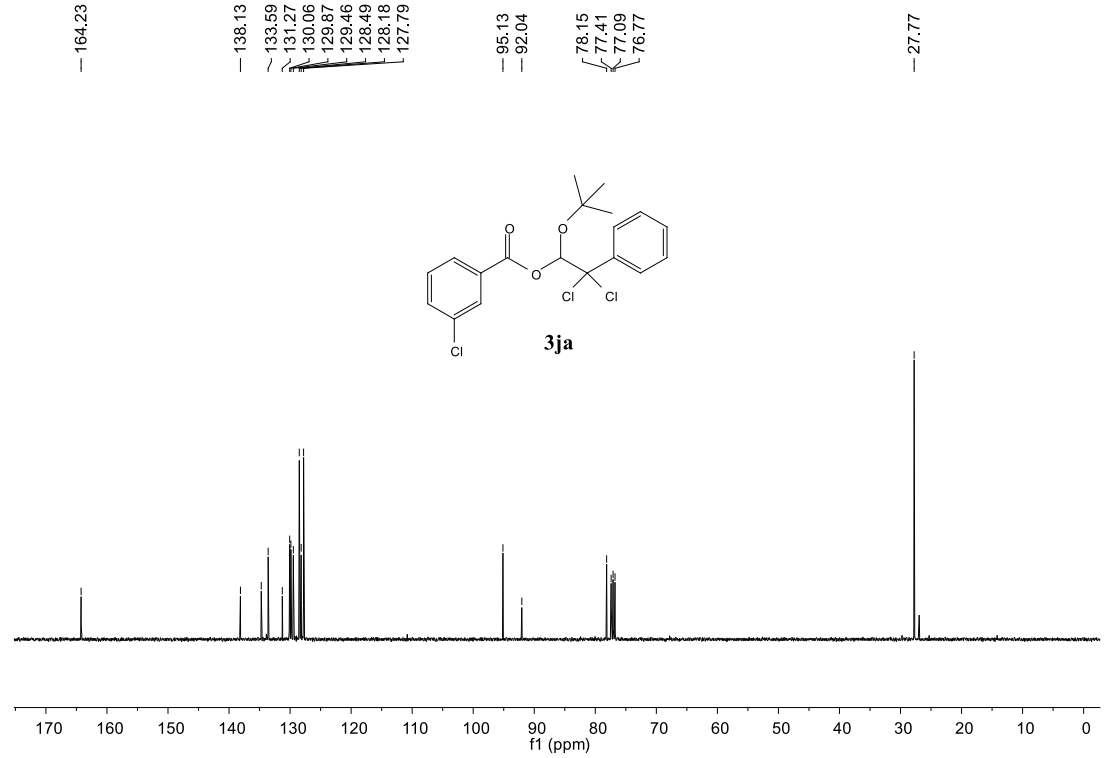

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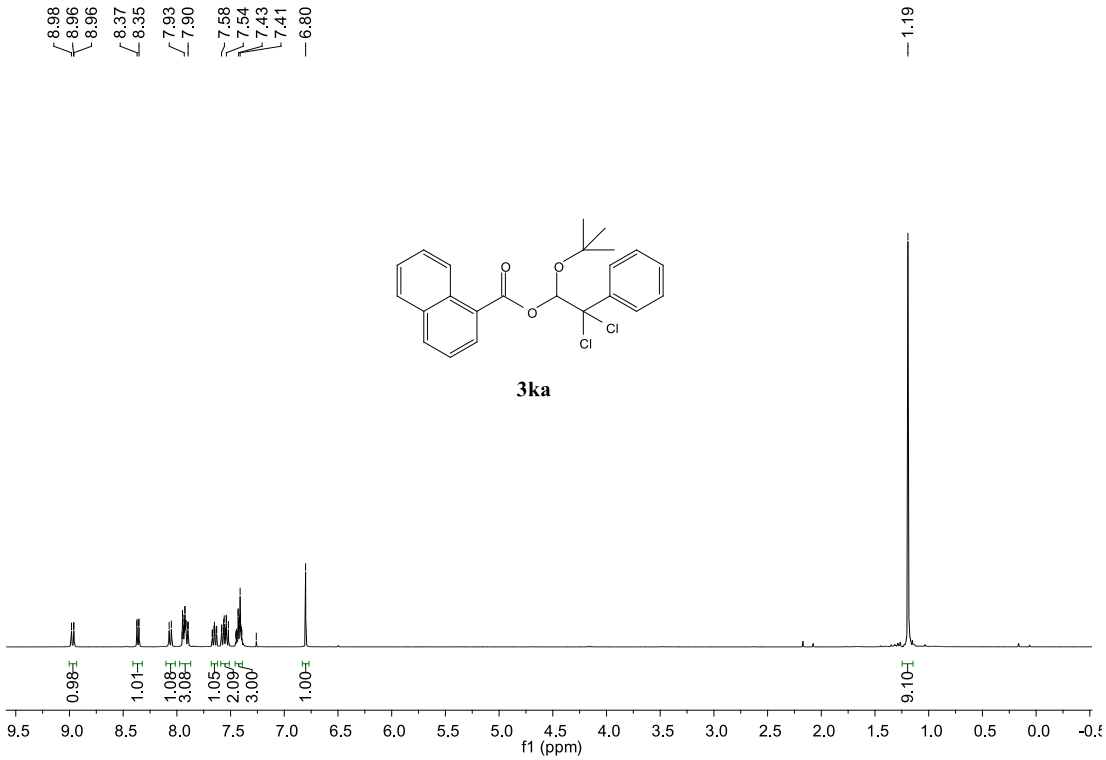
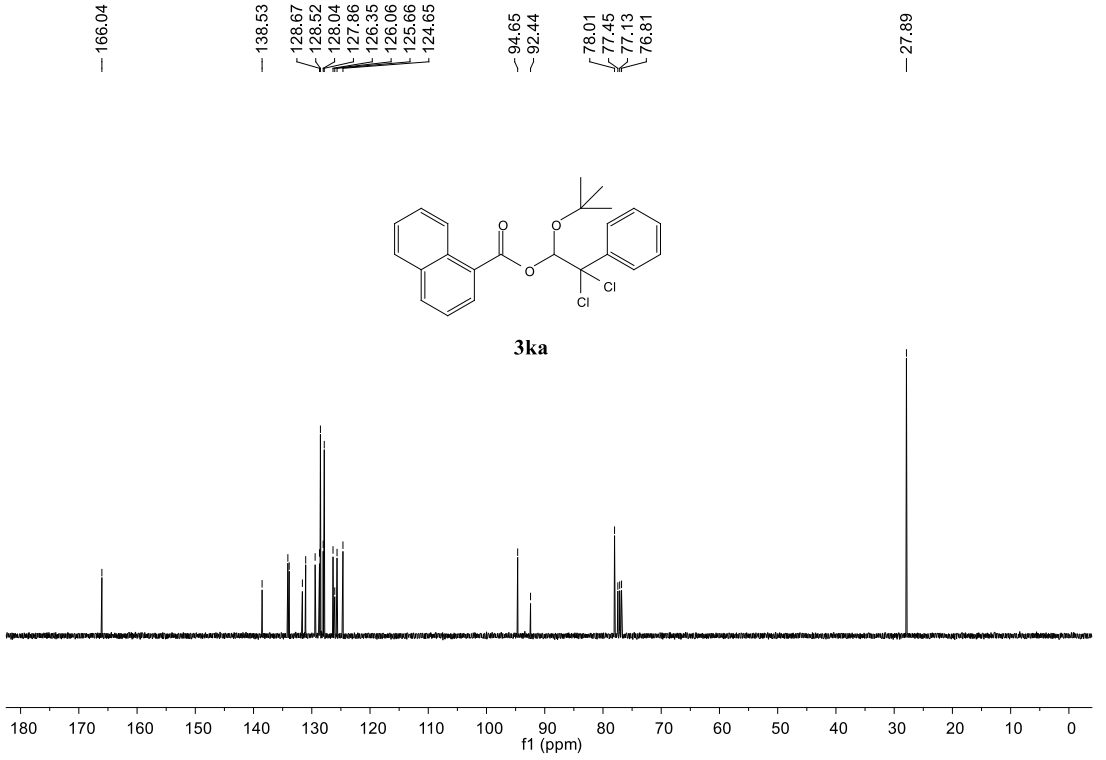
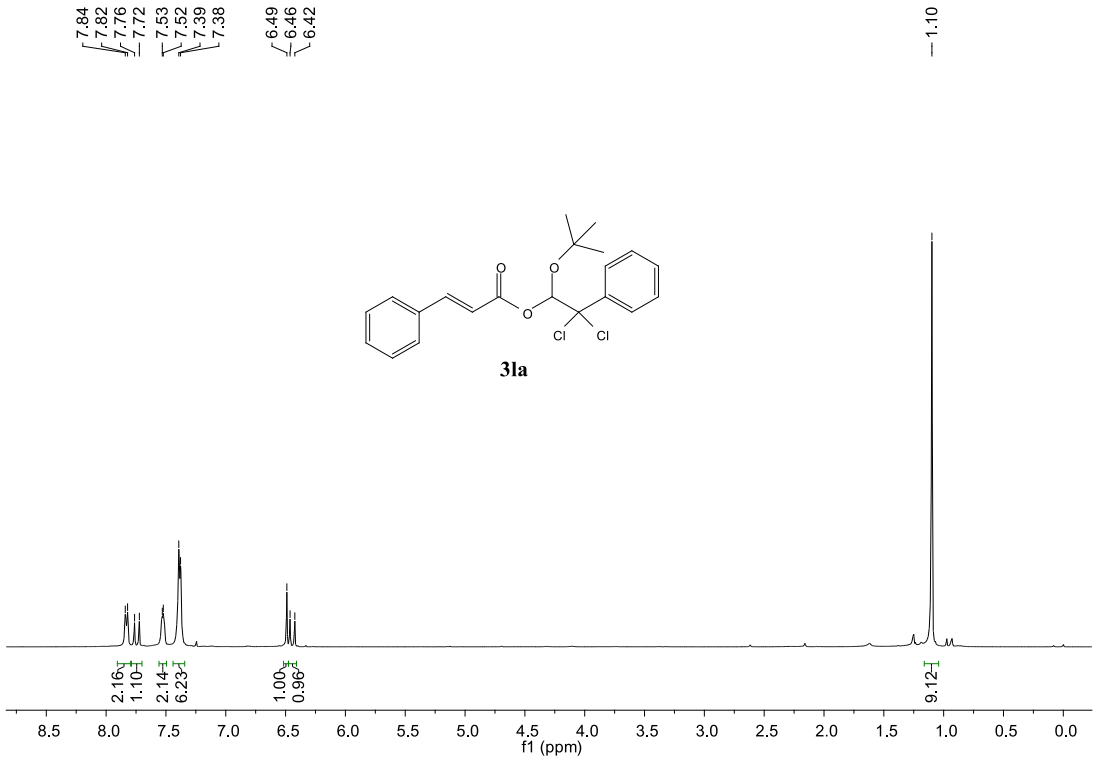


^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



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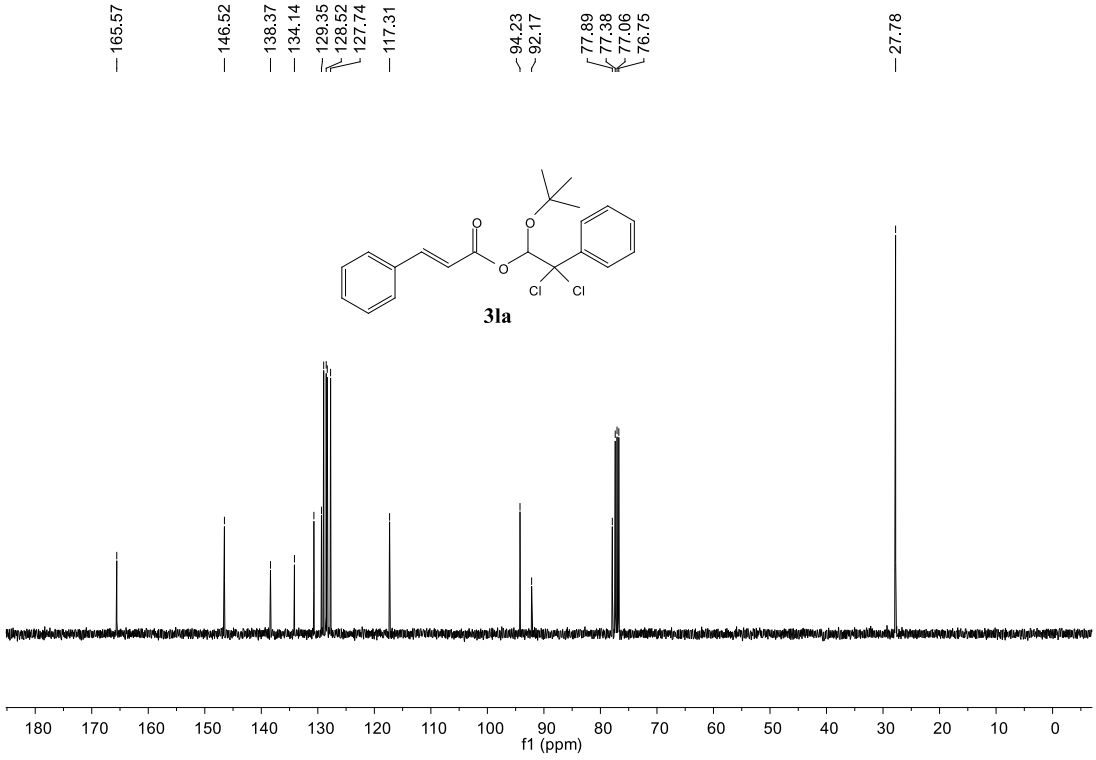

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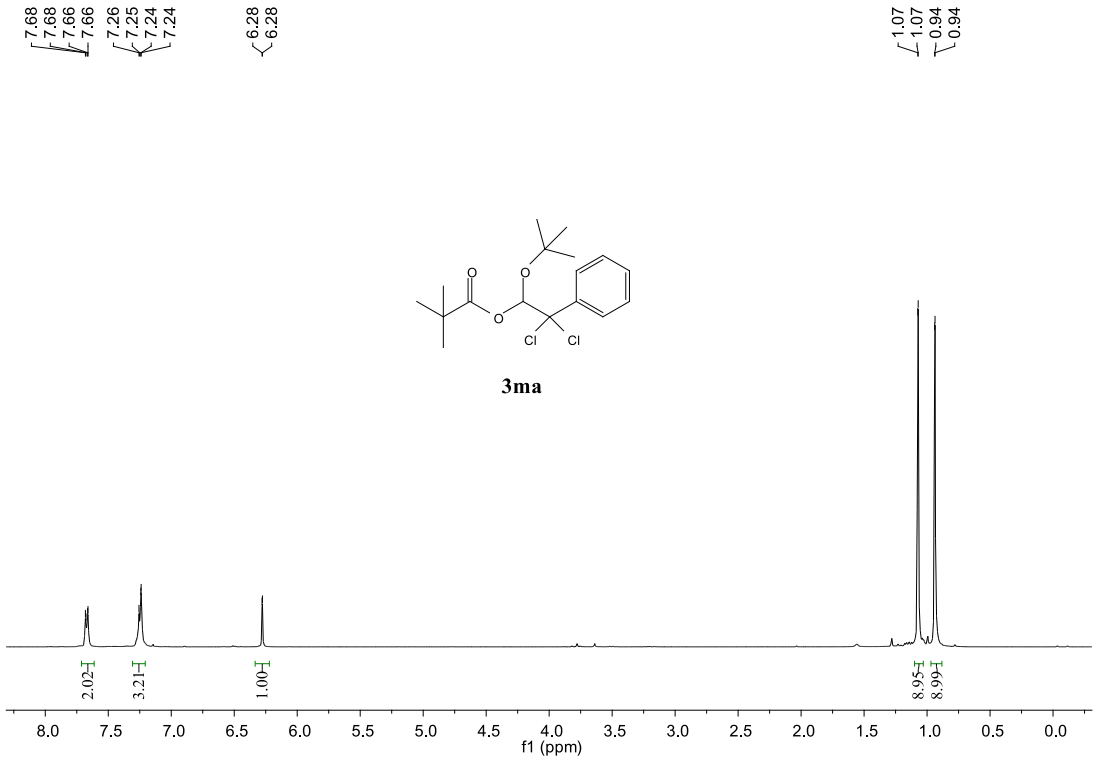
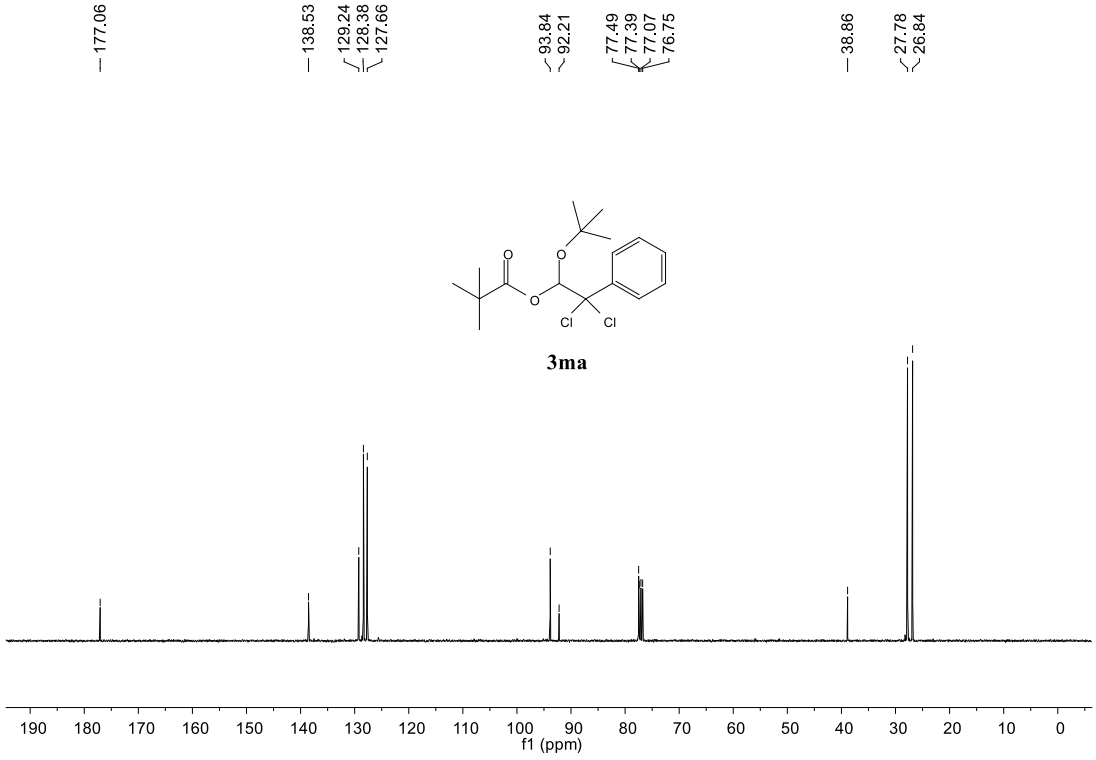


3ma

^{13}C NMR, 100 MHz, $CDCl_3$



3ma

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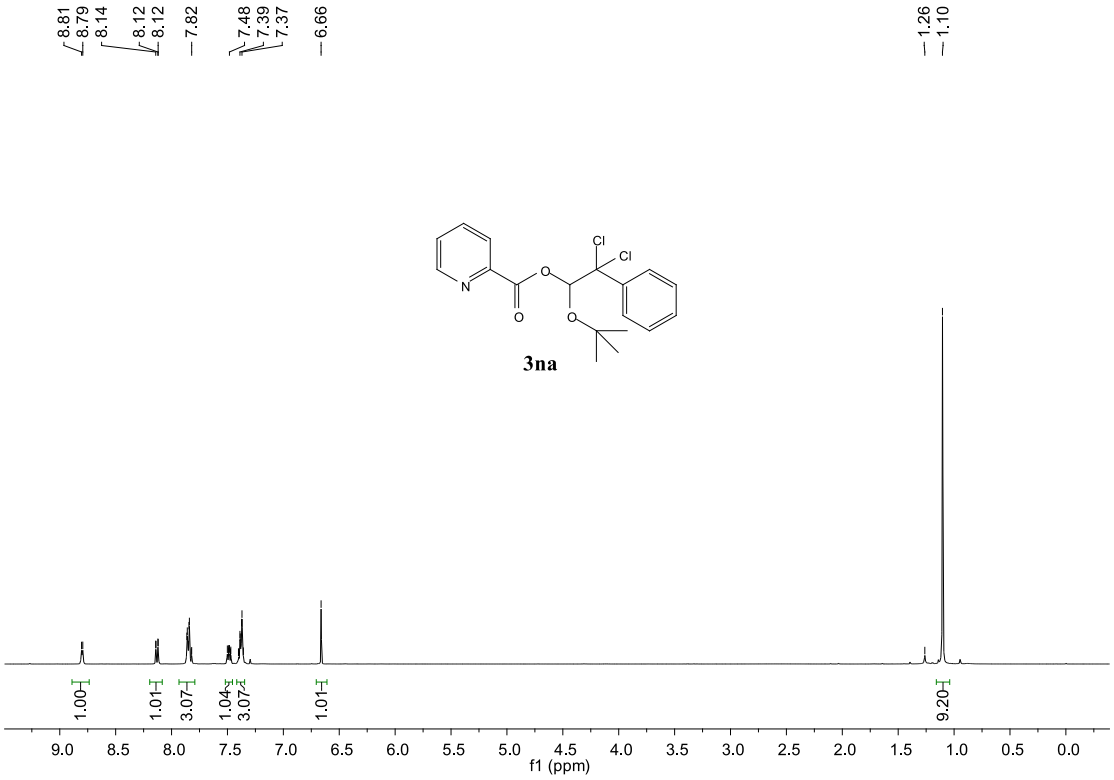
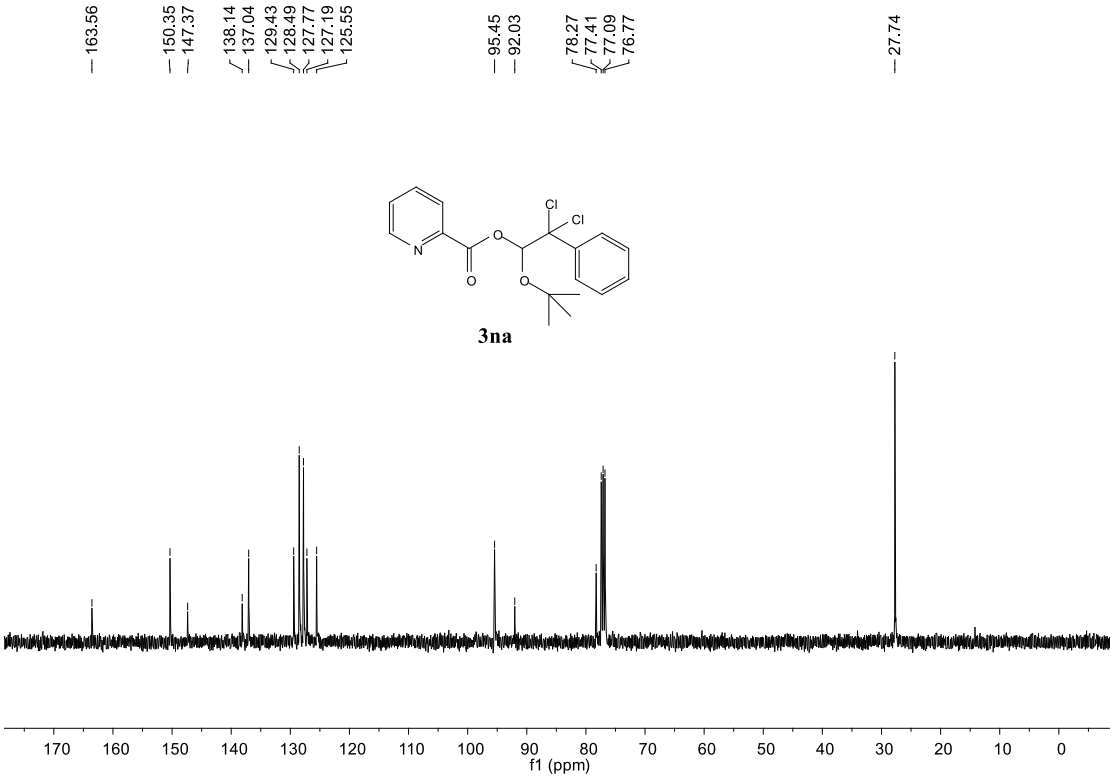


^{13}C NMR, 100 MHz, $CDCl_3$



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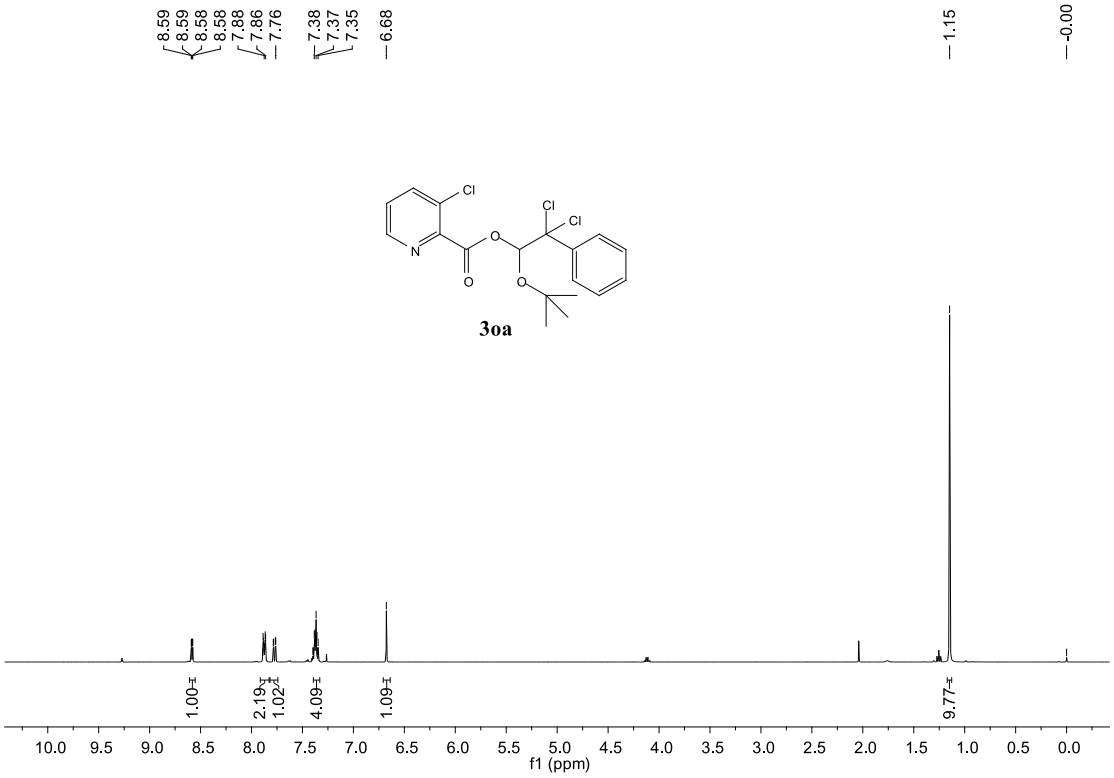

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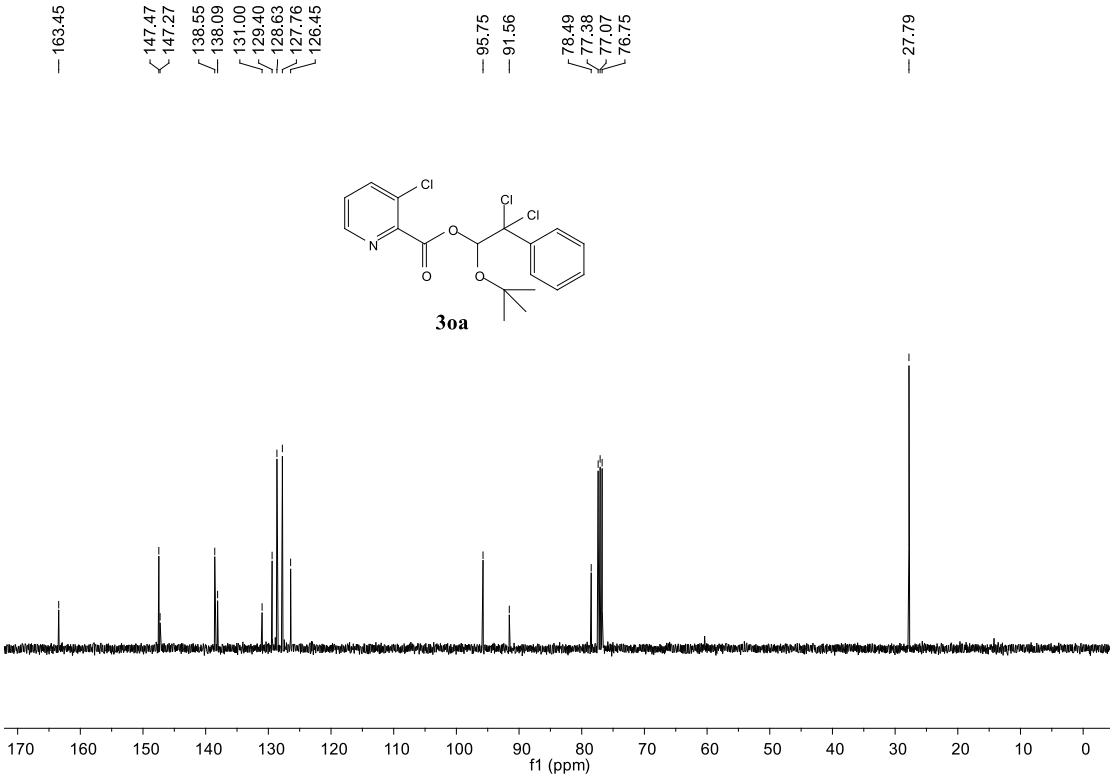
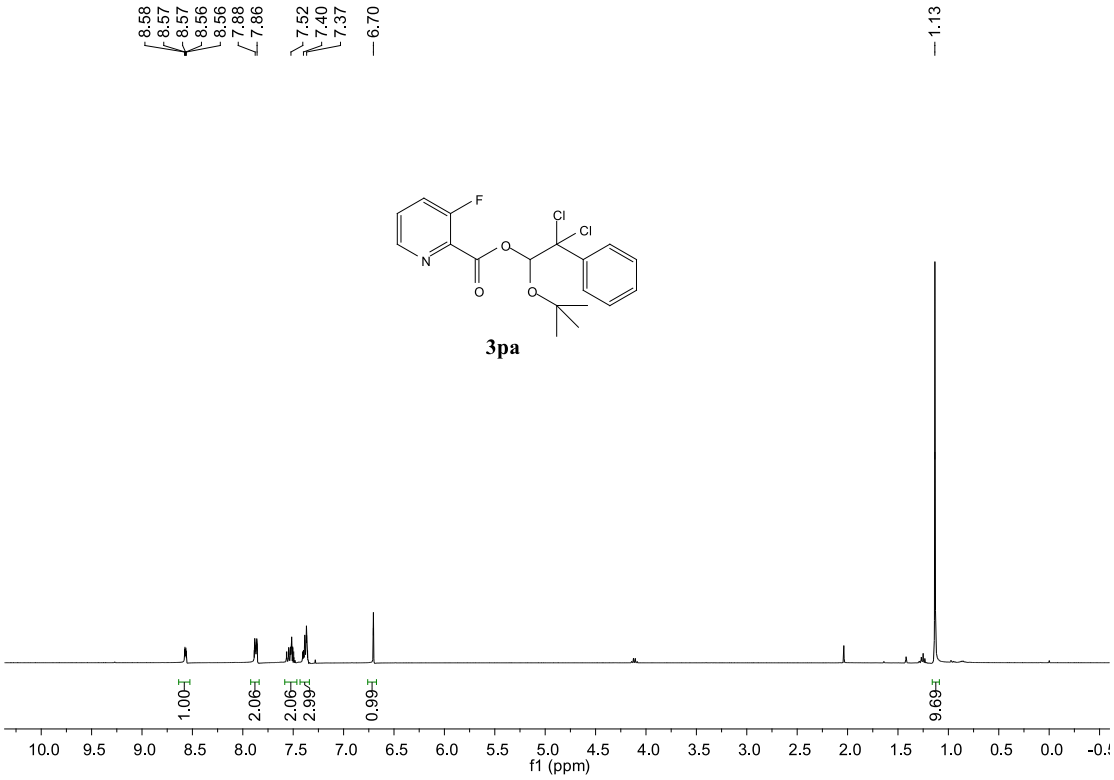
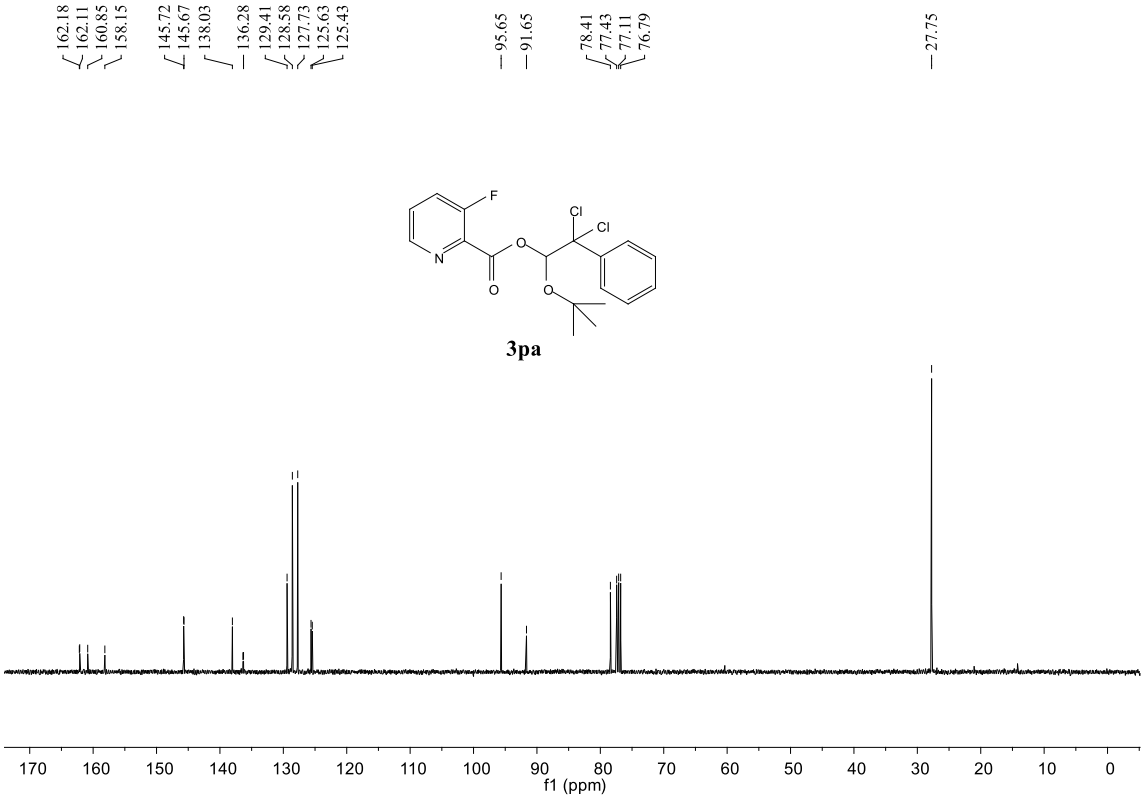


^{1}H NMR, 400 MHz, $CDCl_3$



3pa

^{13}C NMR, 100 MHz, $CDCl_3$



3pa

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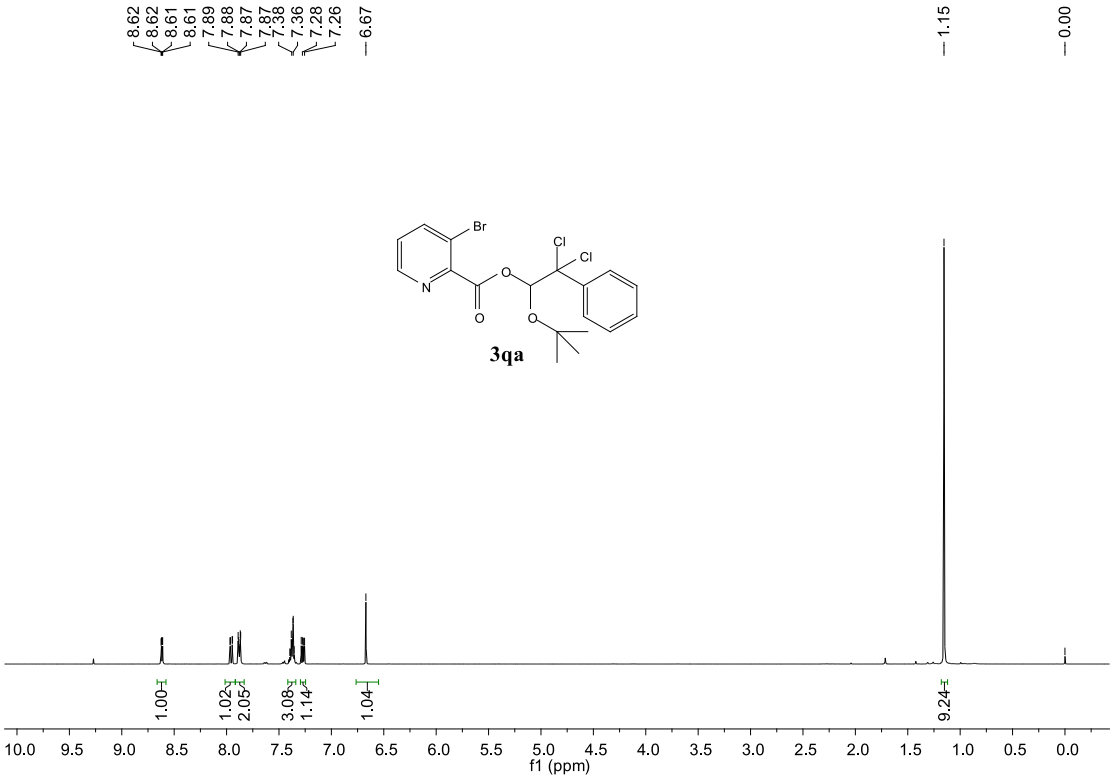
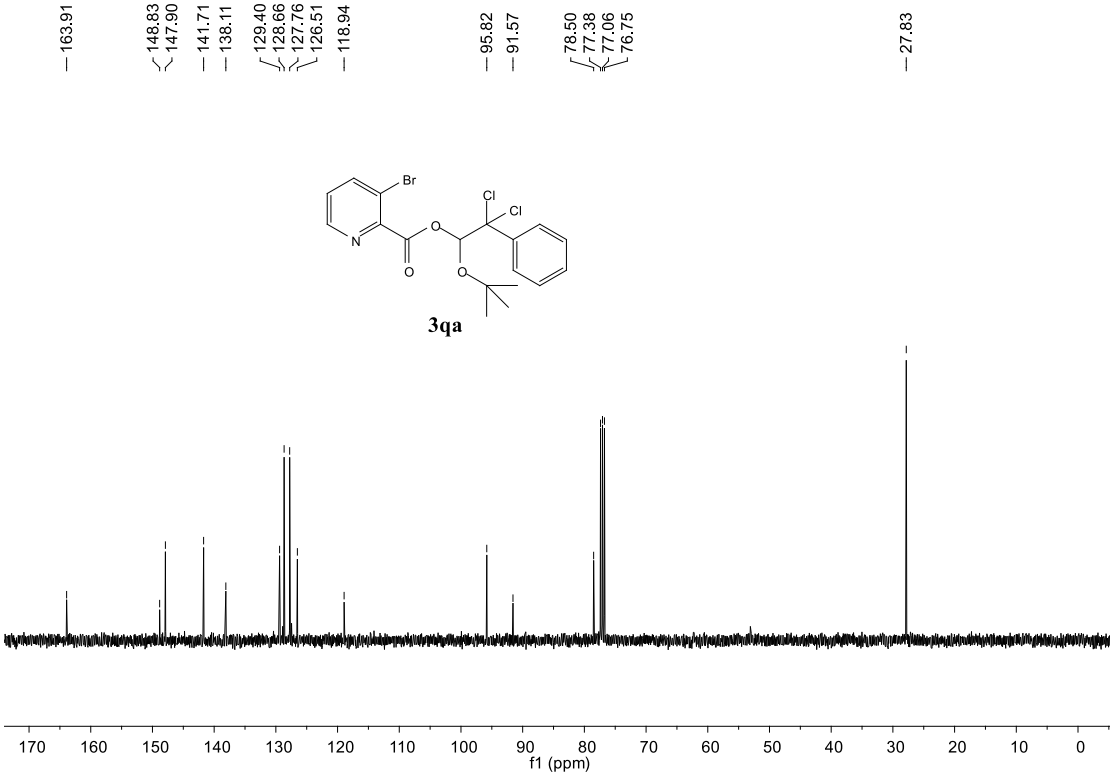
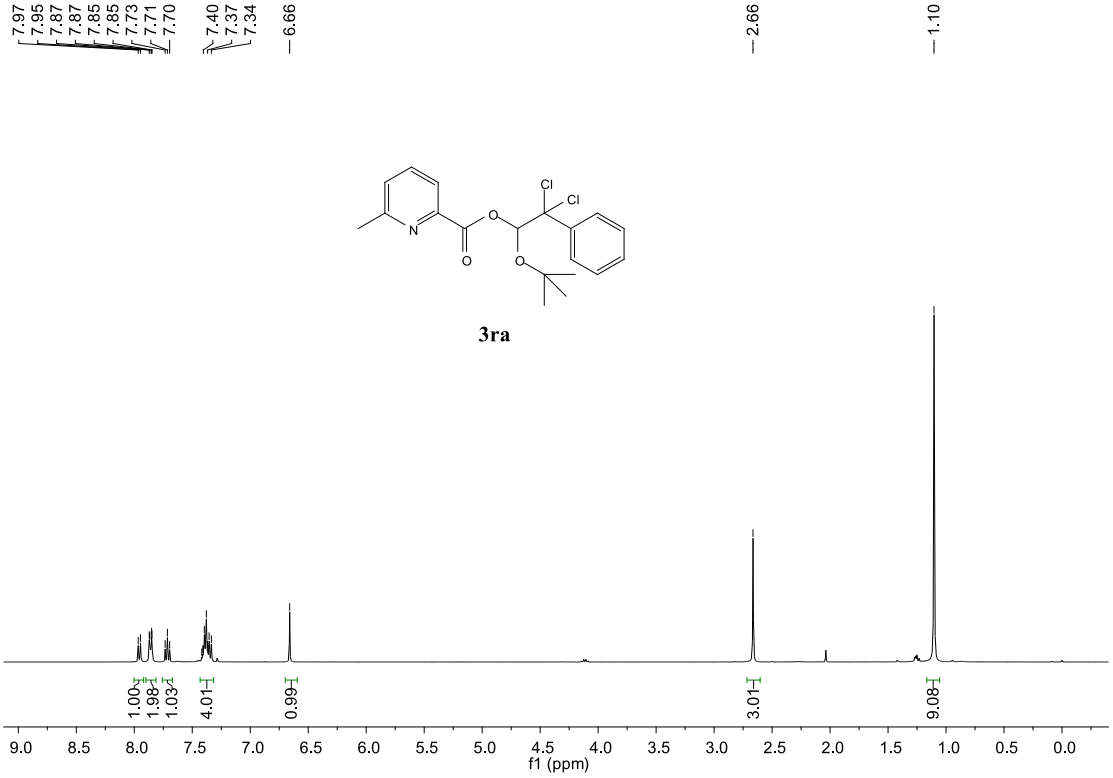


^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



3ra

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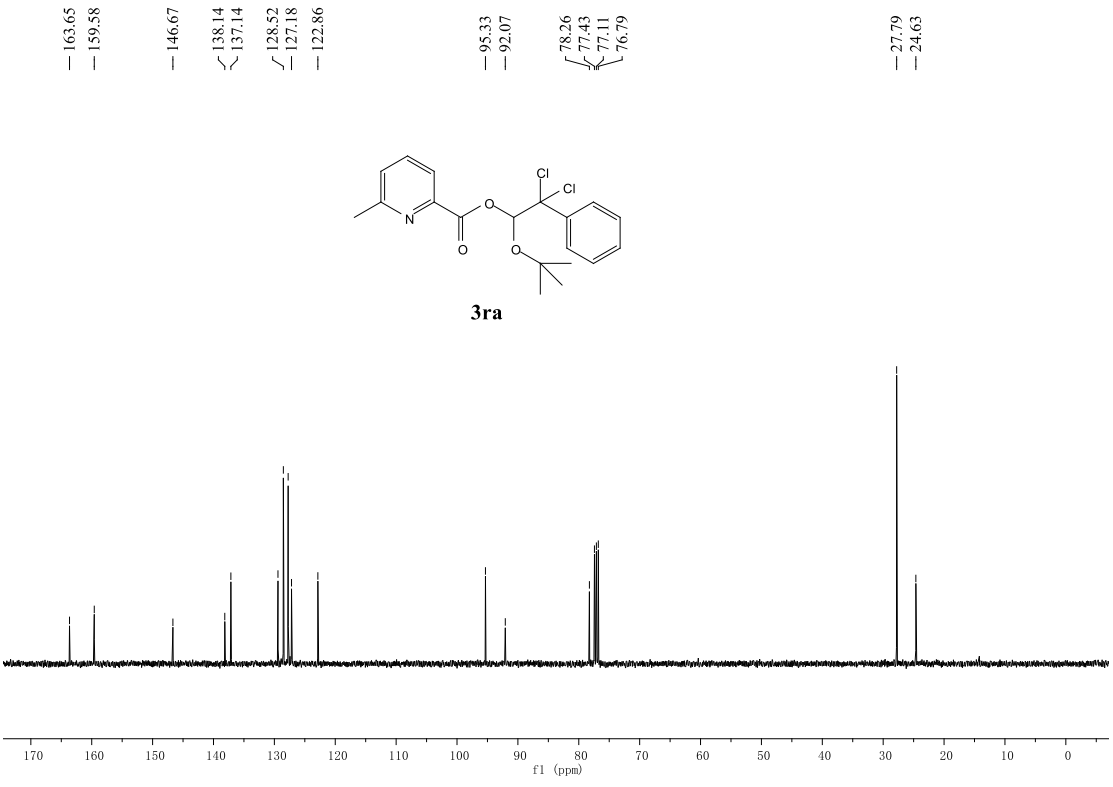
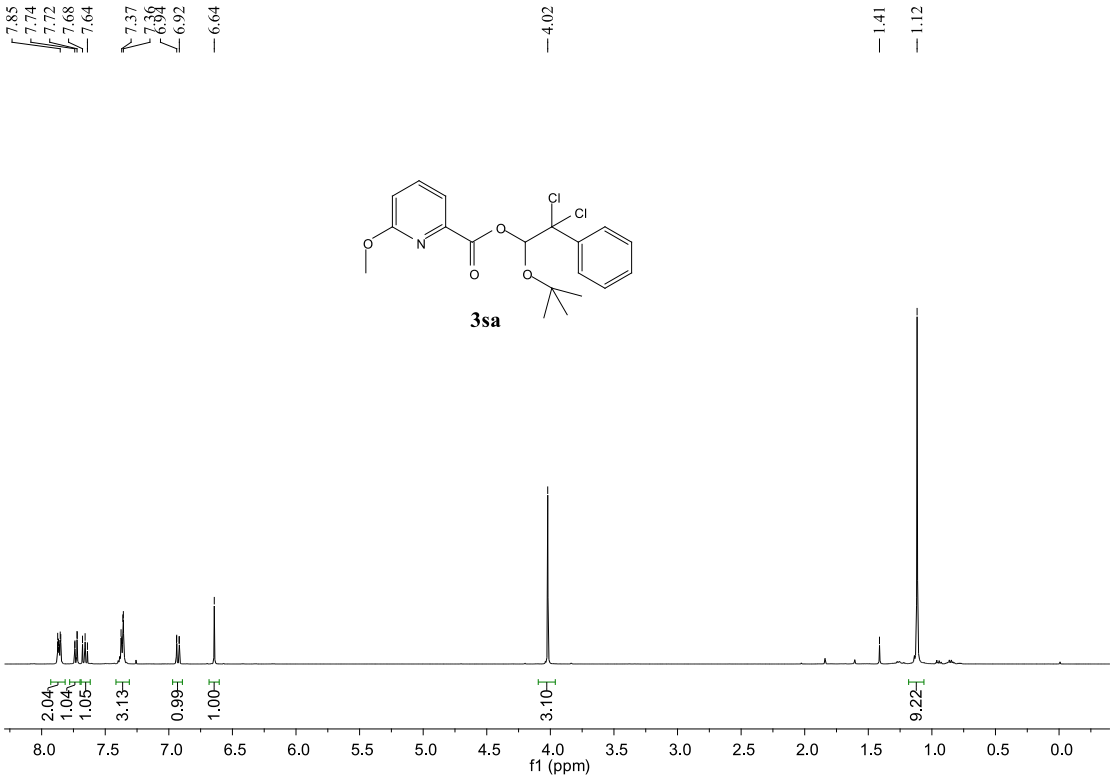
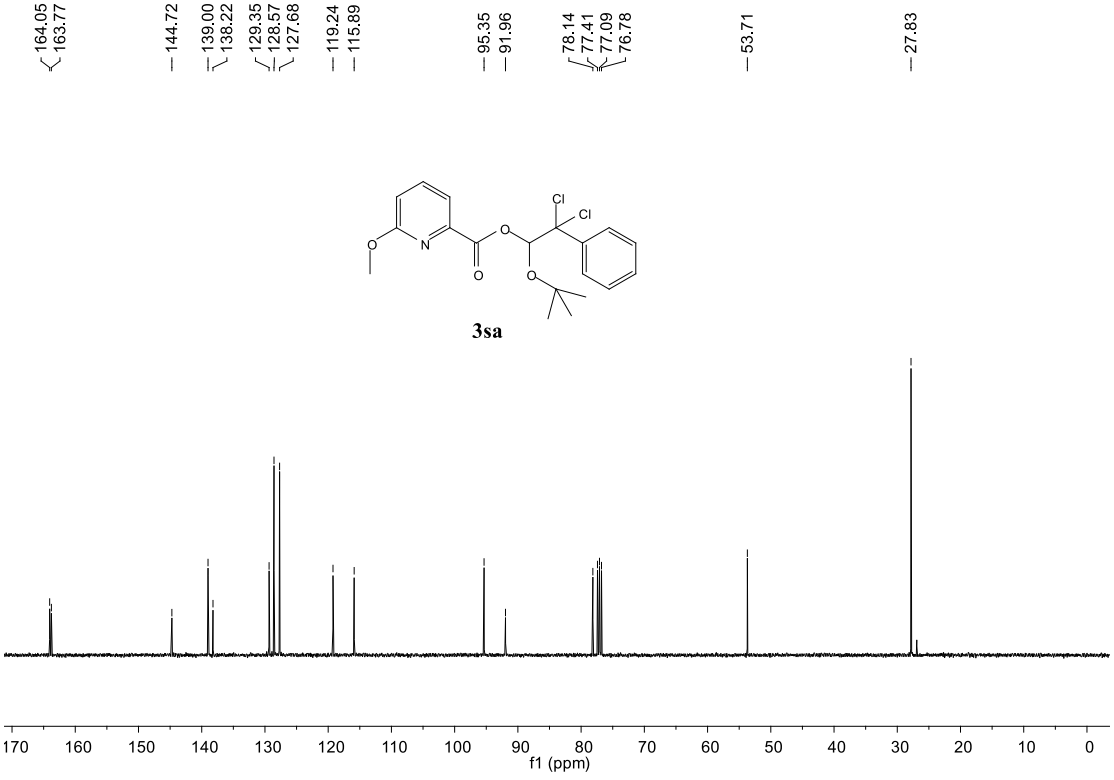


3ra

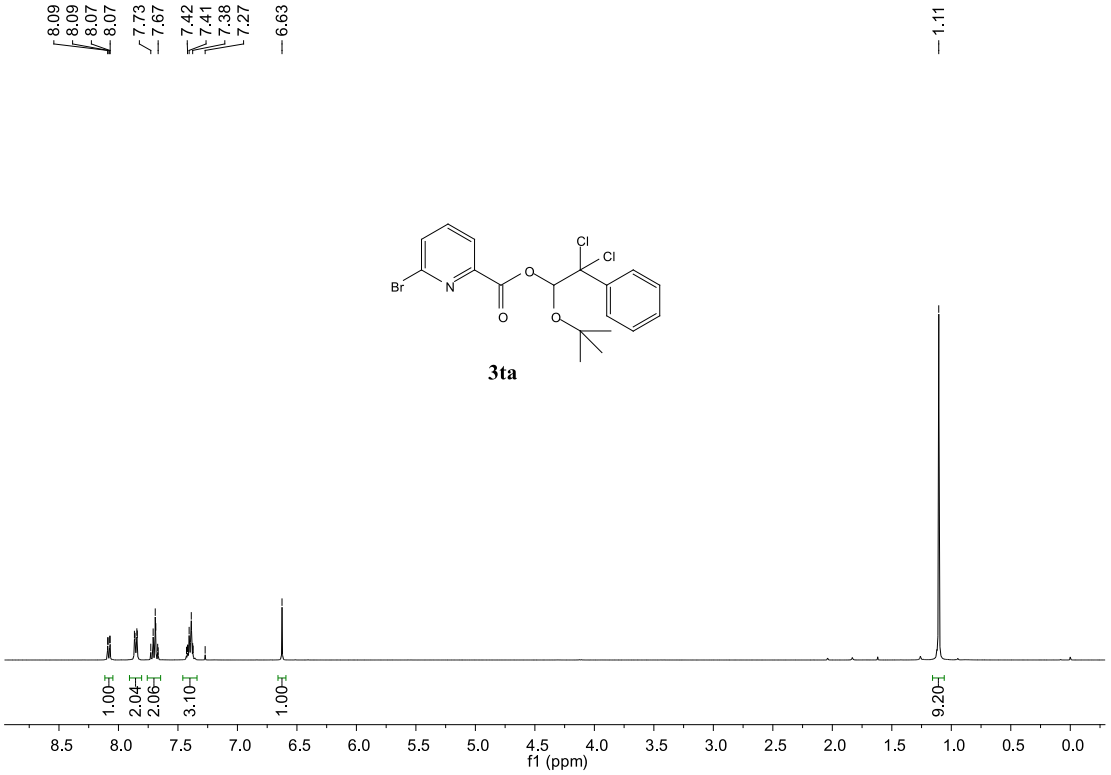
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



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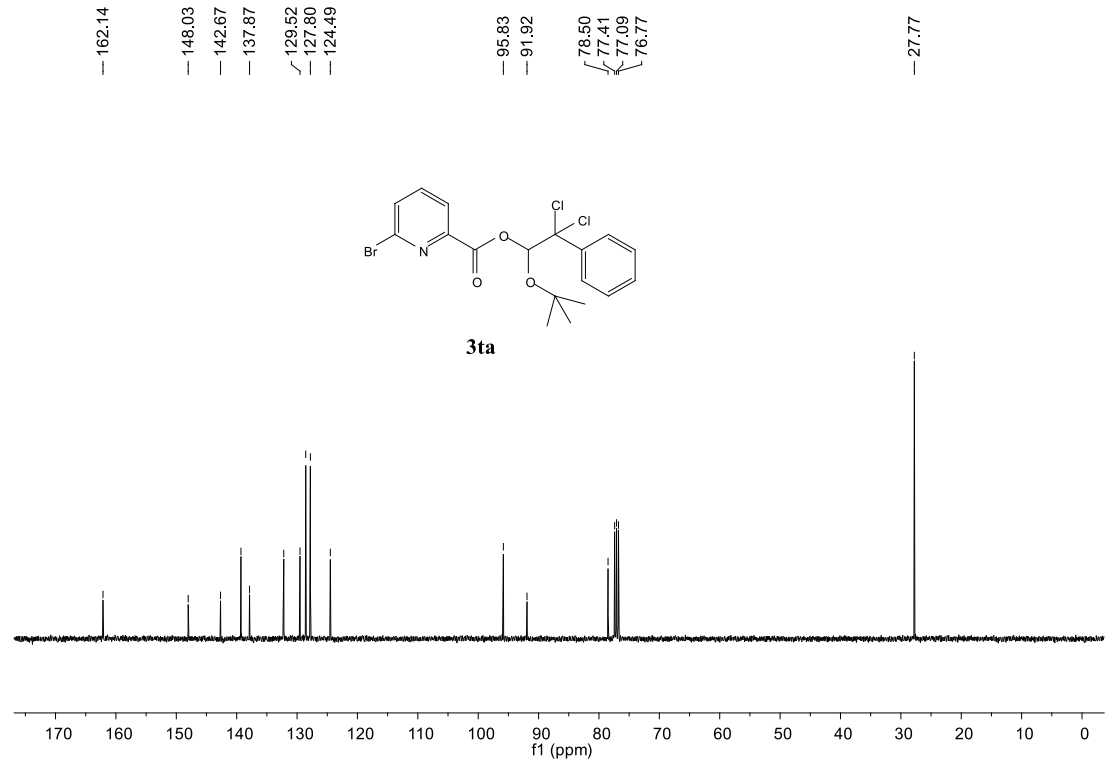

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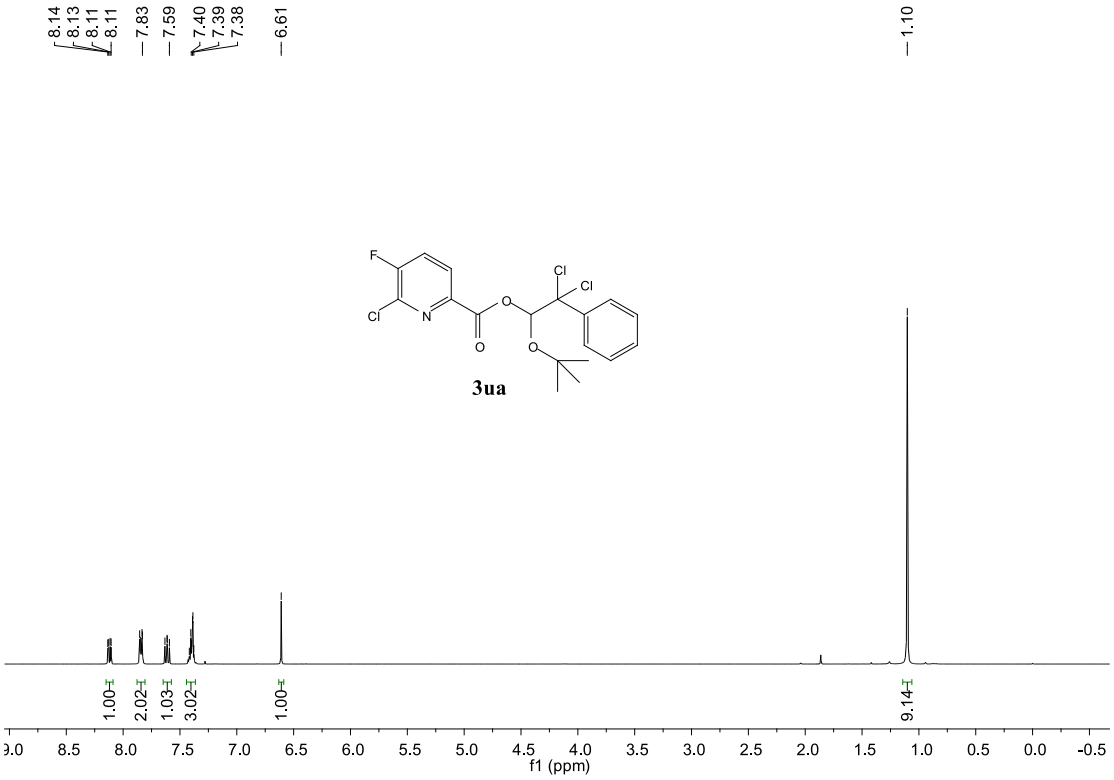

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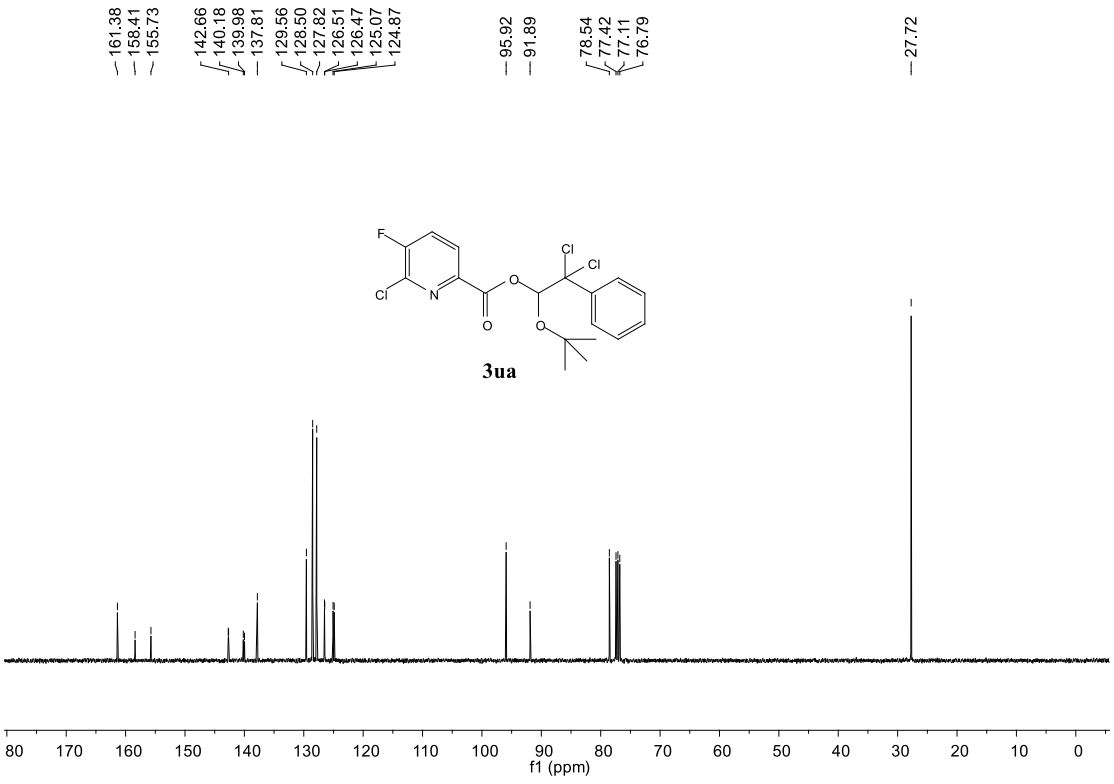

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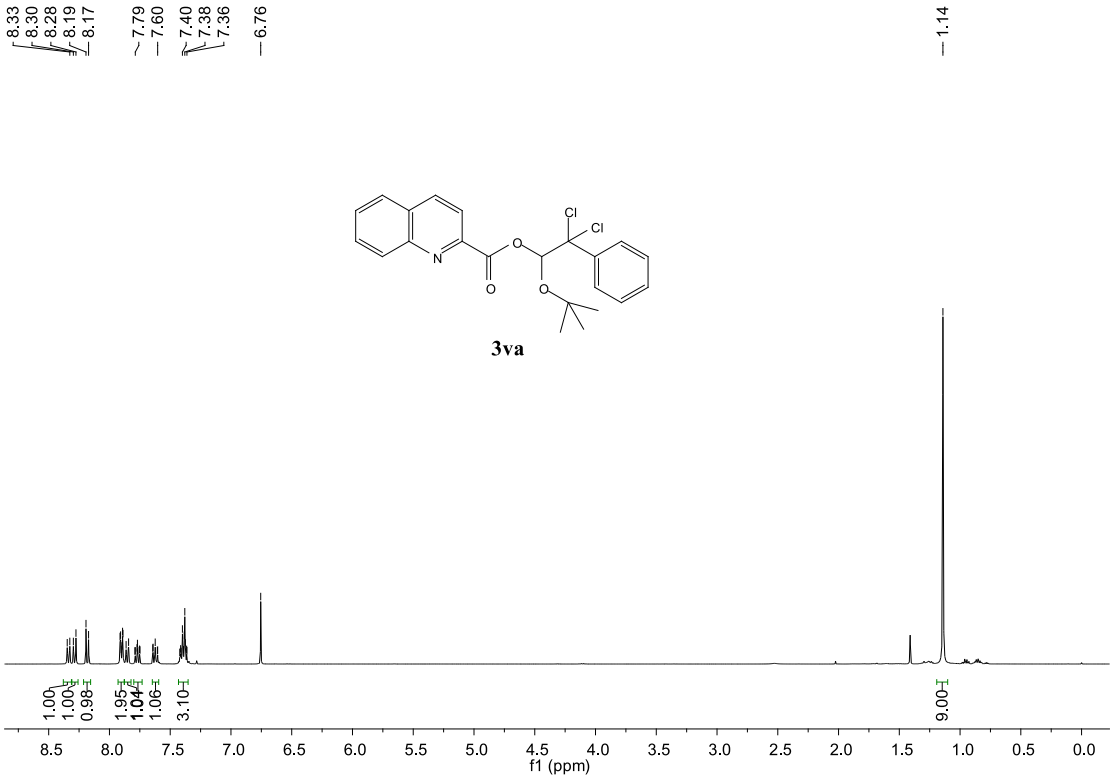
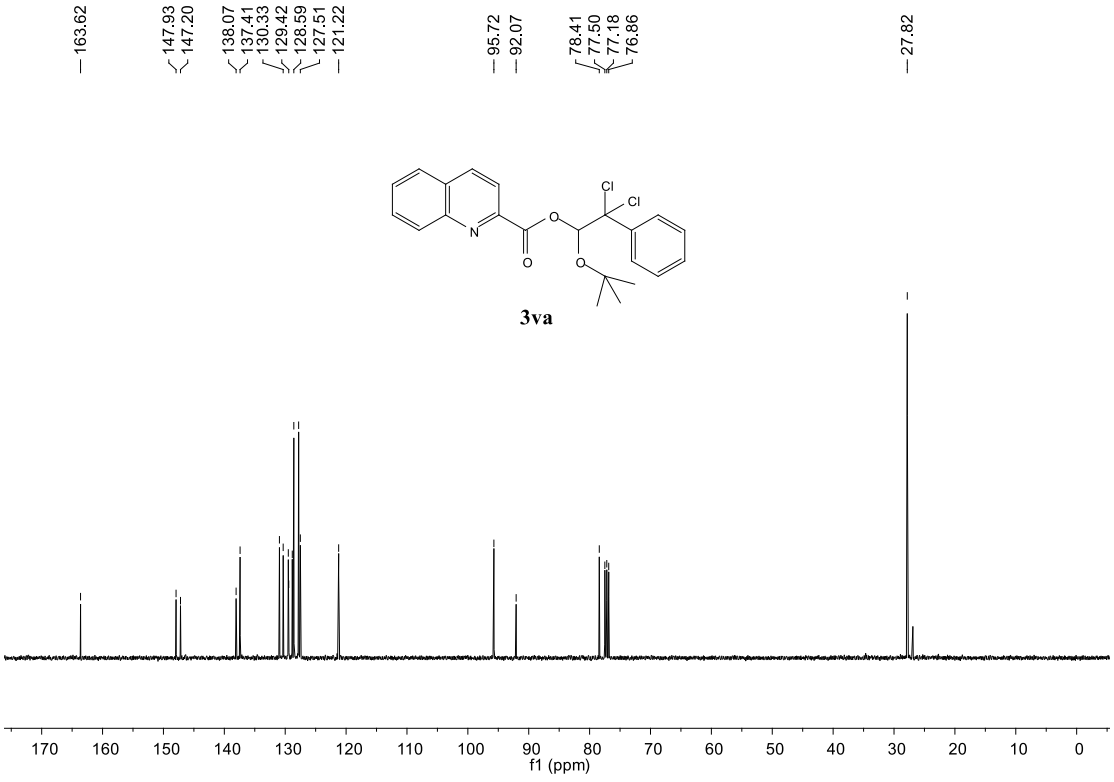
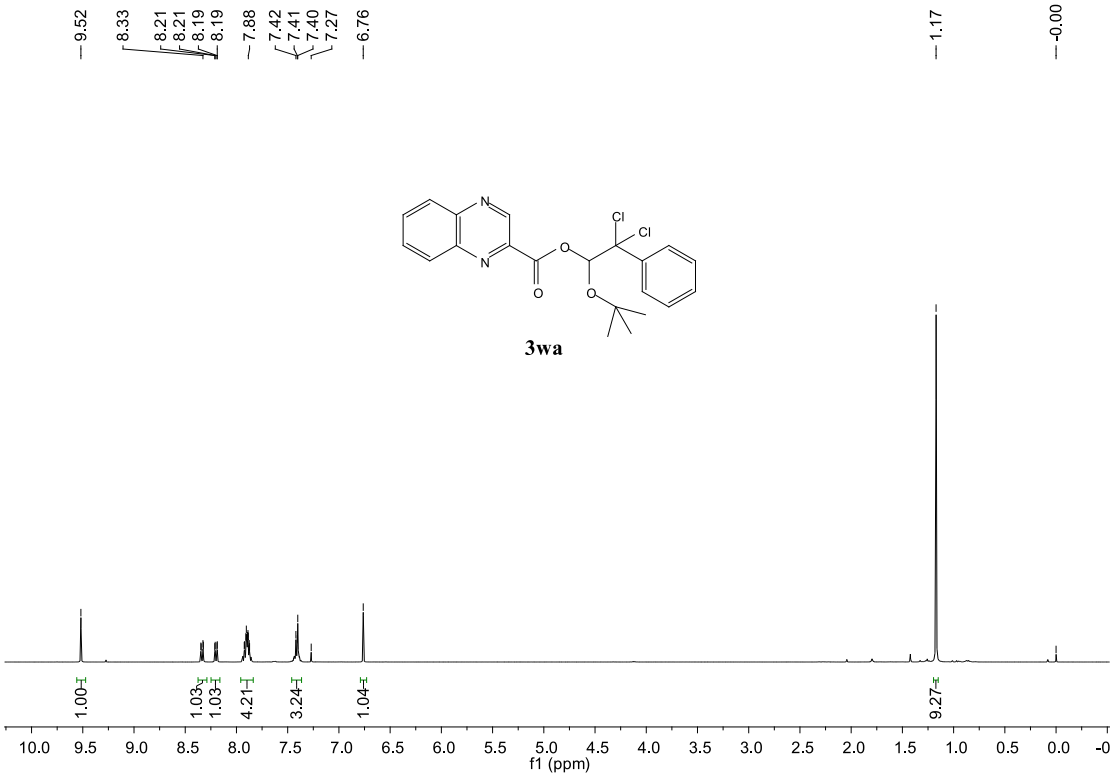


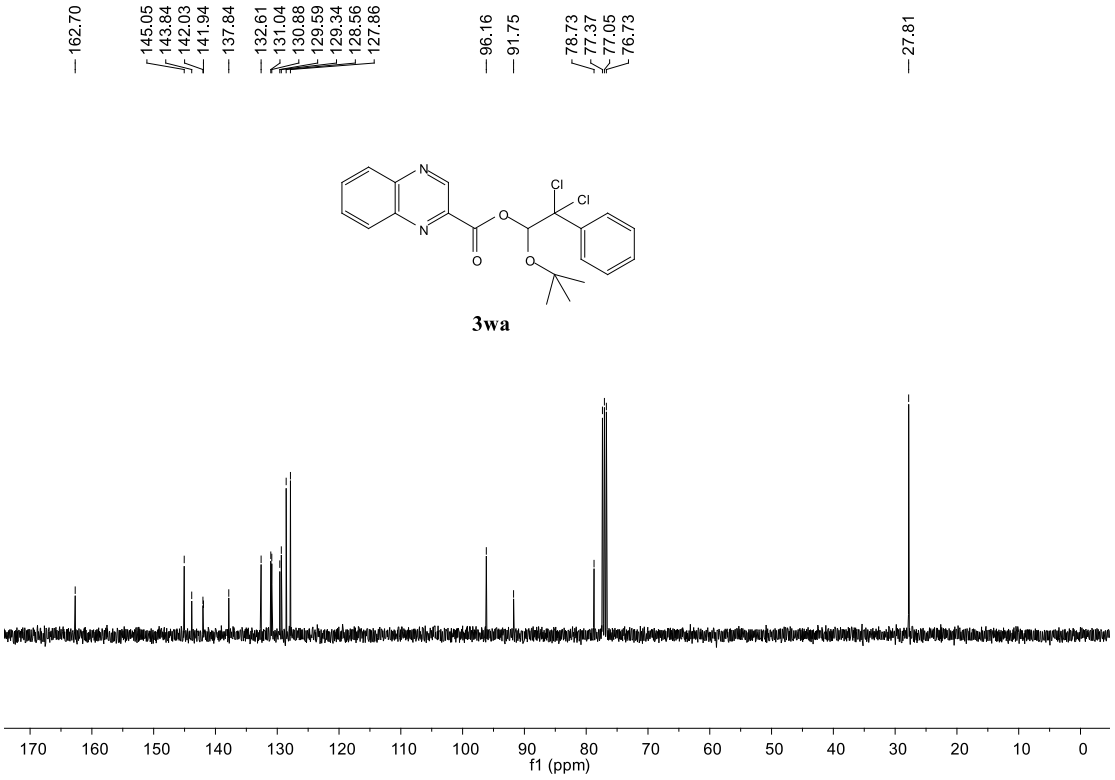
^{13}C NMR, 100 MHz, $CDCl_3$



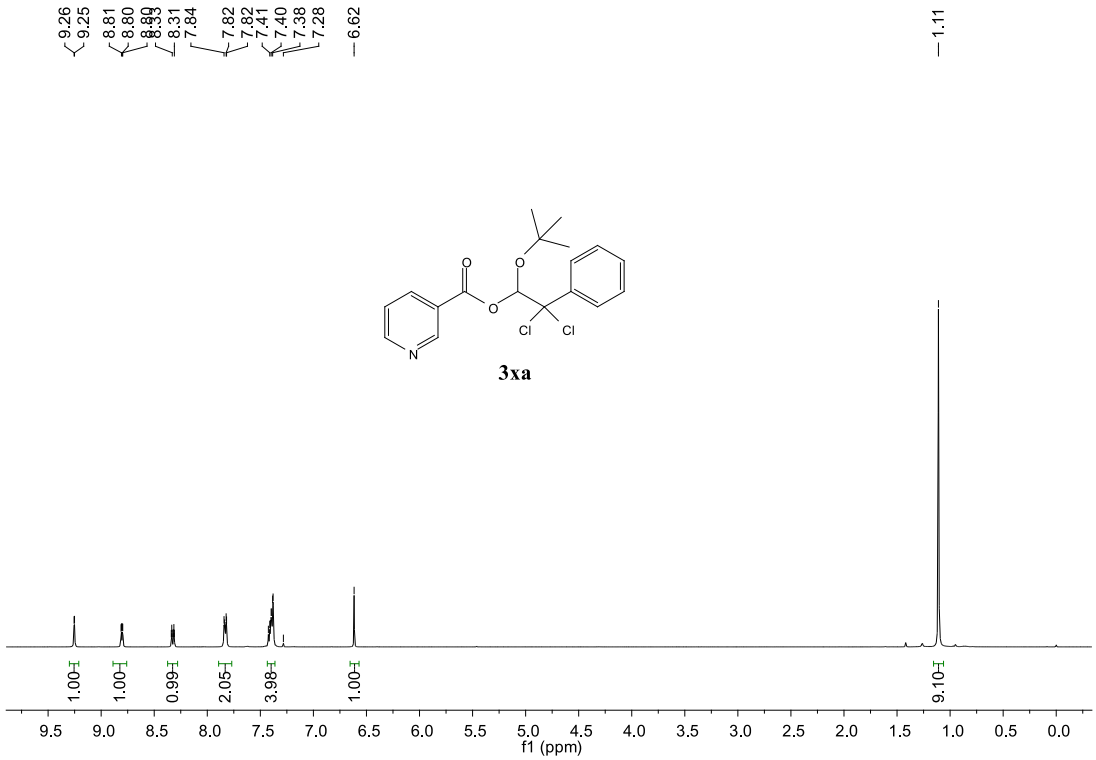
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



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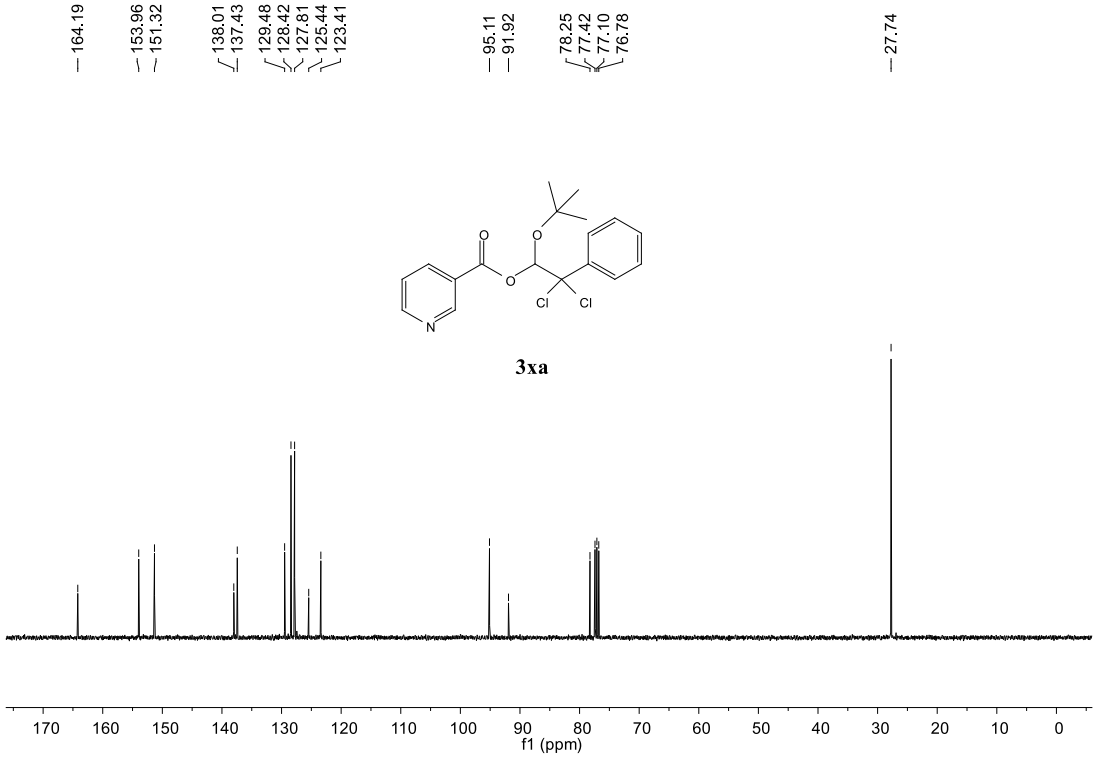

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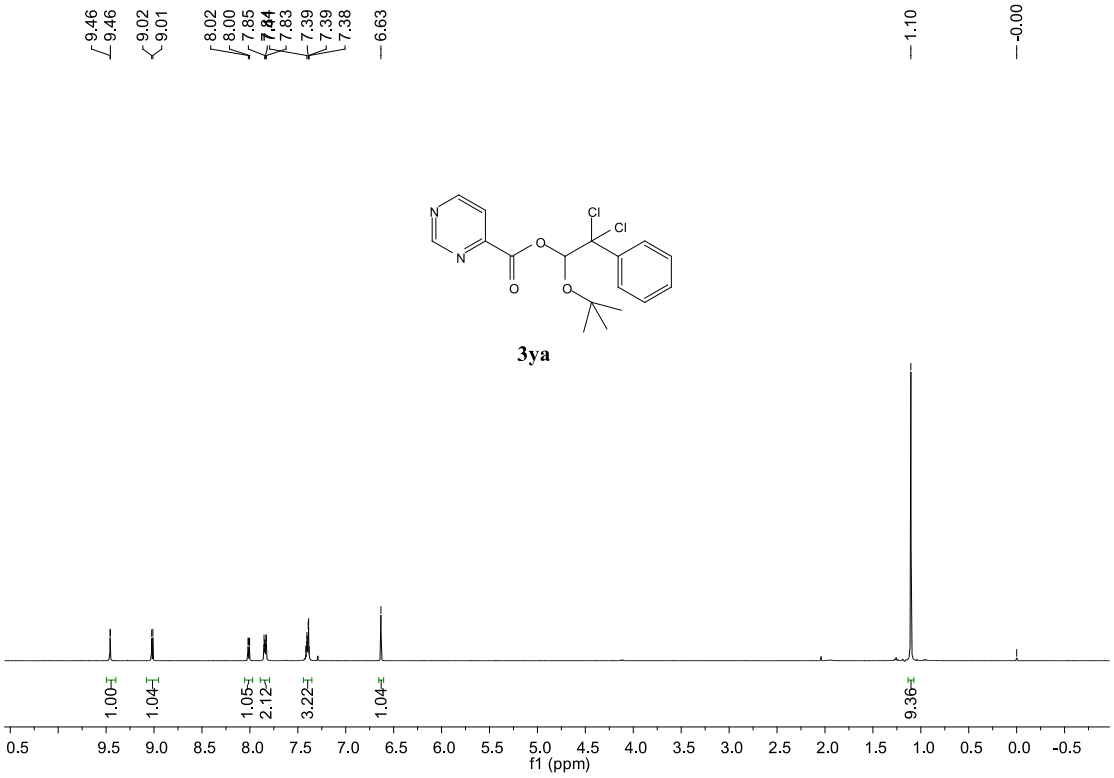
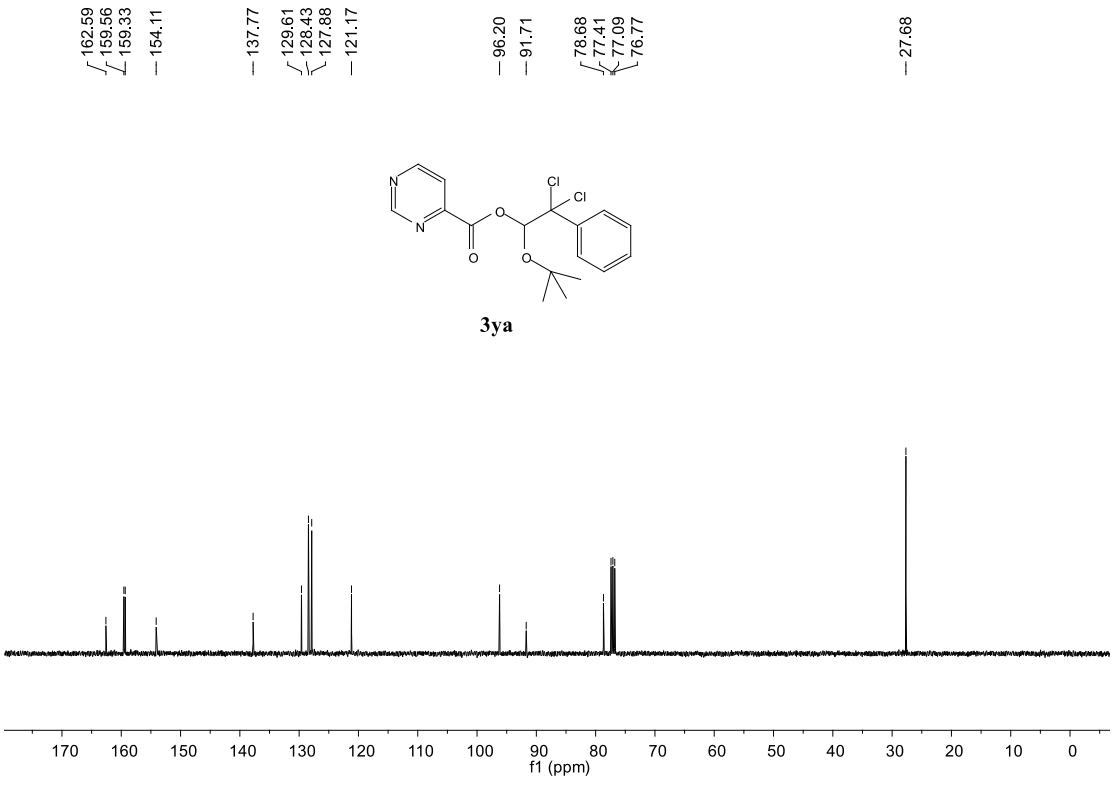


3ya

^{13}C NMR, 100 MHz, $CDCl_3$



3ya

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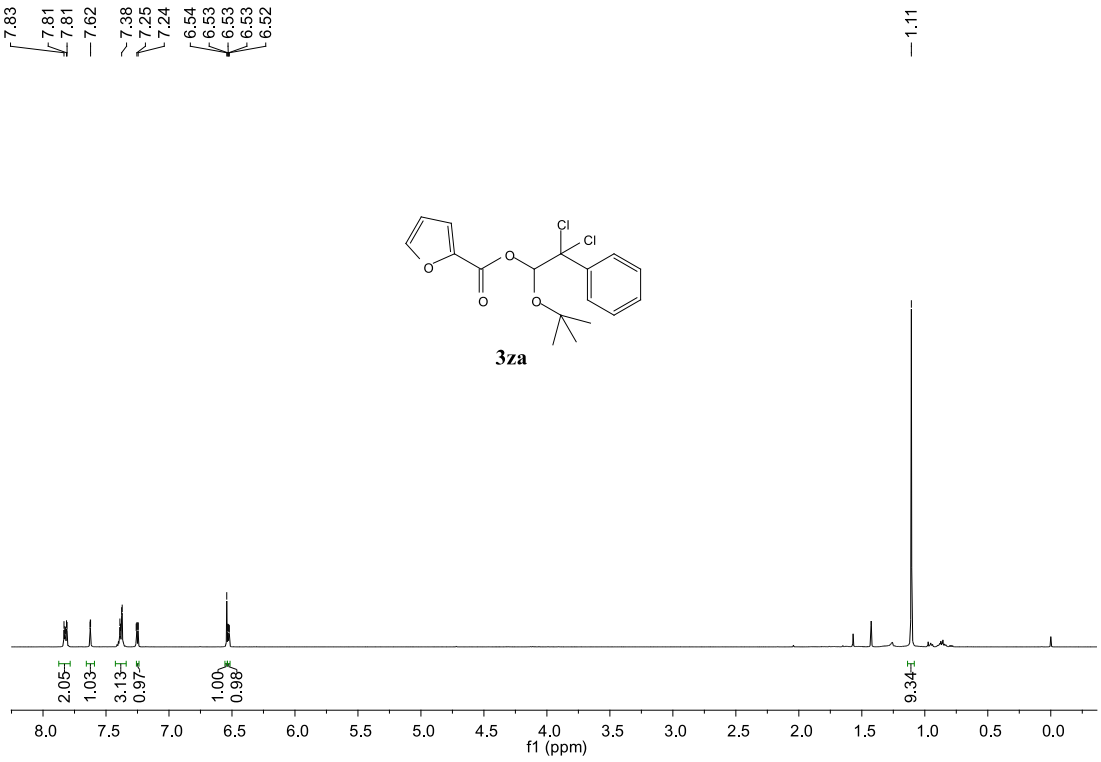
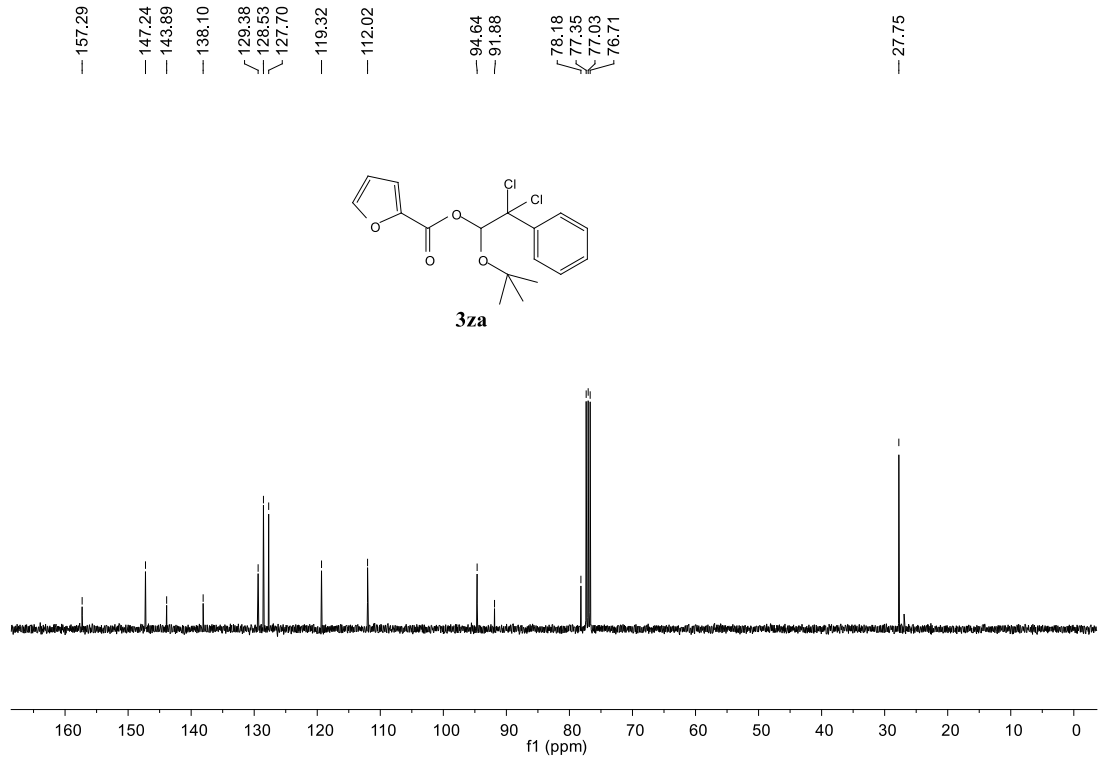
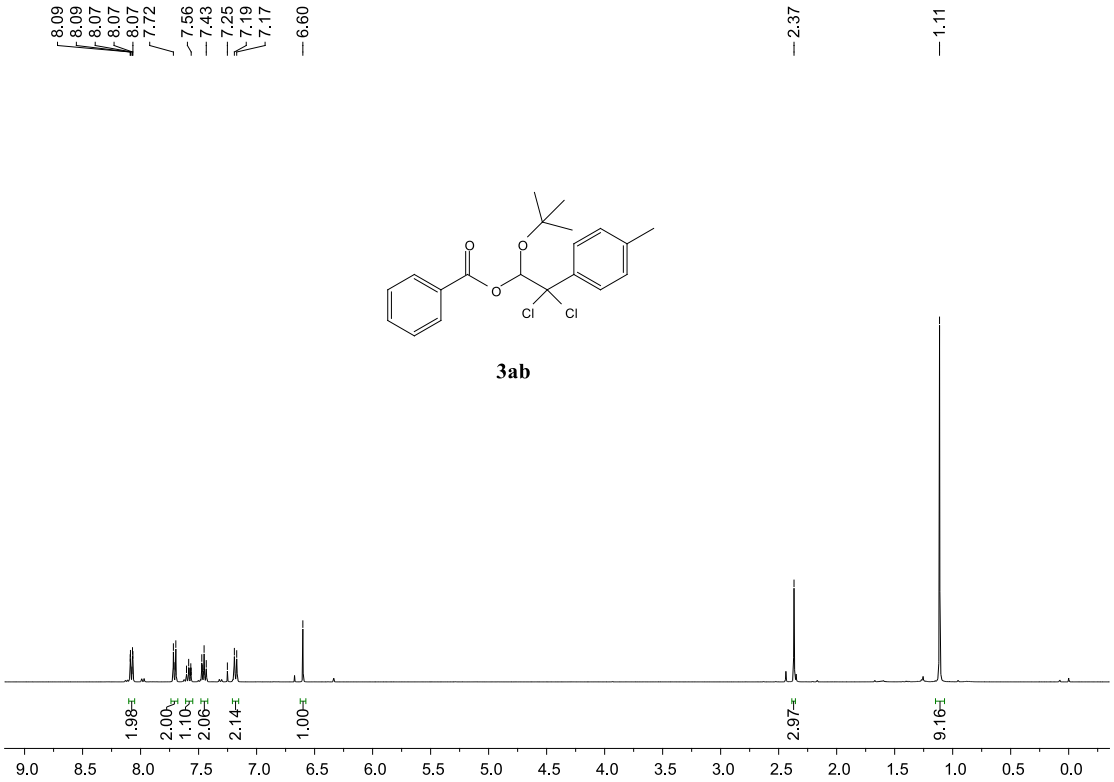


^{13}C NMR, 100 MHz, $CDCl_3$

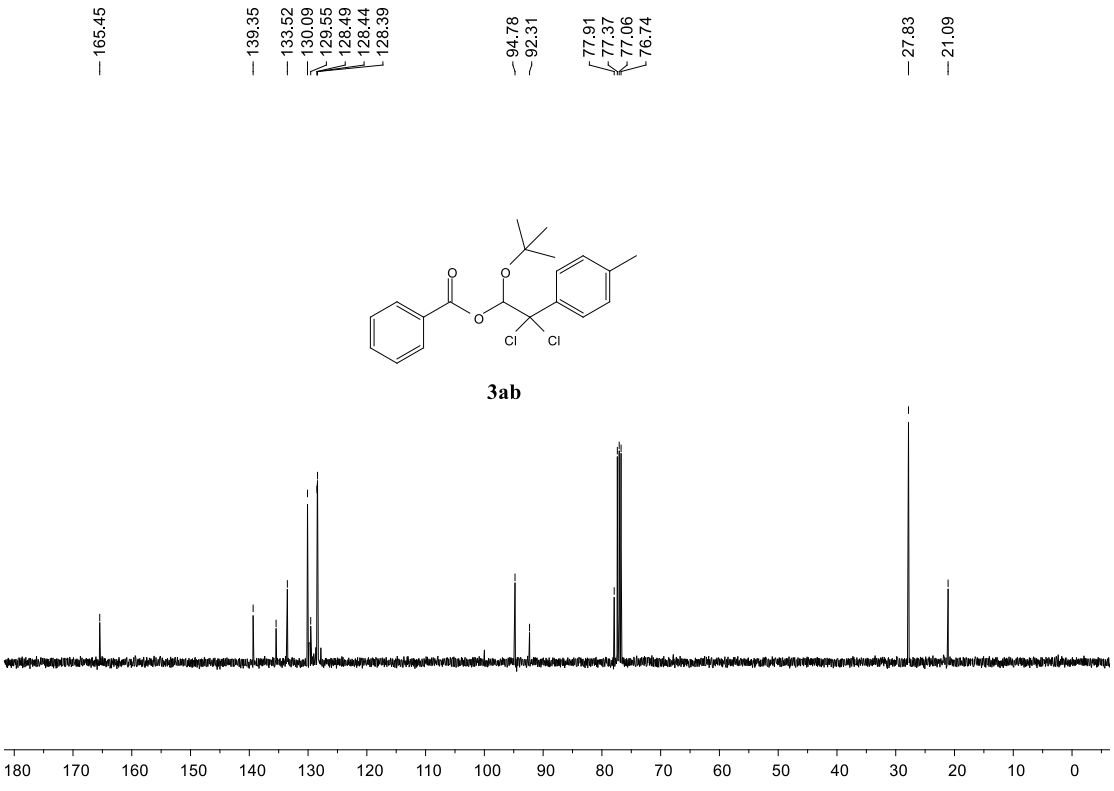


^{1}H NMR, 400 MHz, $CDCl_3$



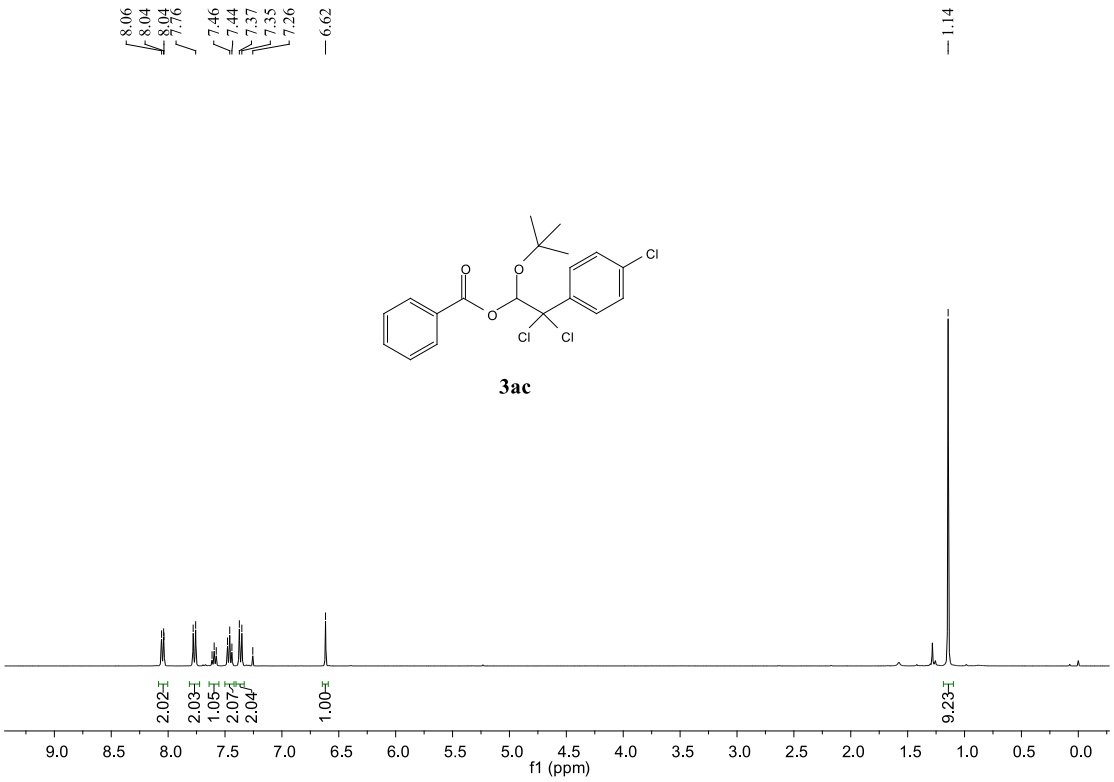
3ab

^{13}C NMR, 100 MHz, $CDCl_3$



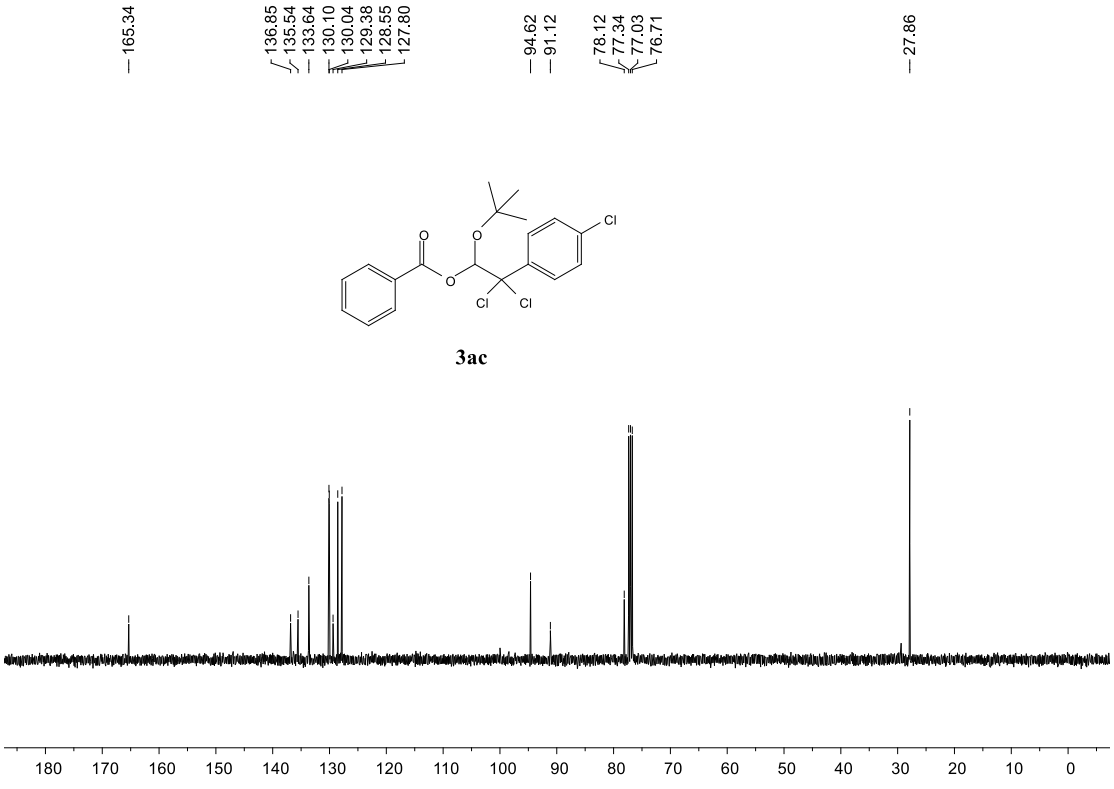
3ab

^{1}H NMR, 400 MHz, $CDCl_3$



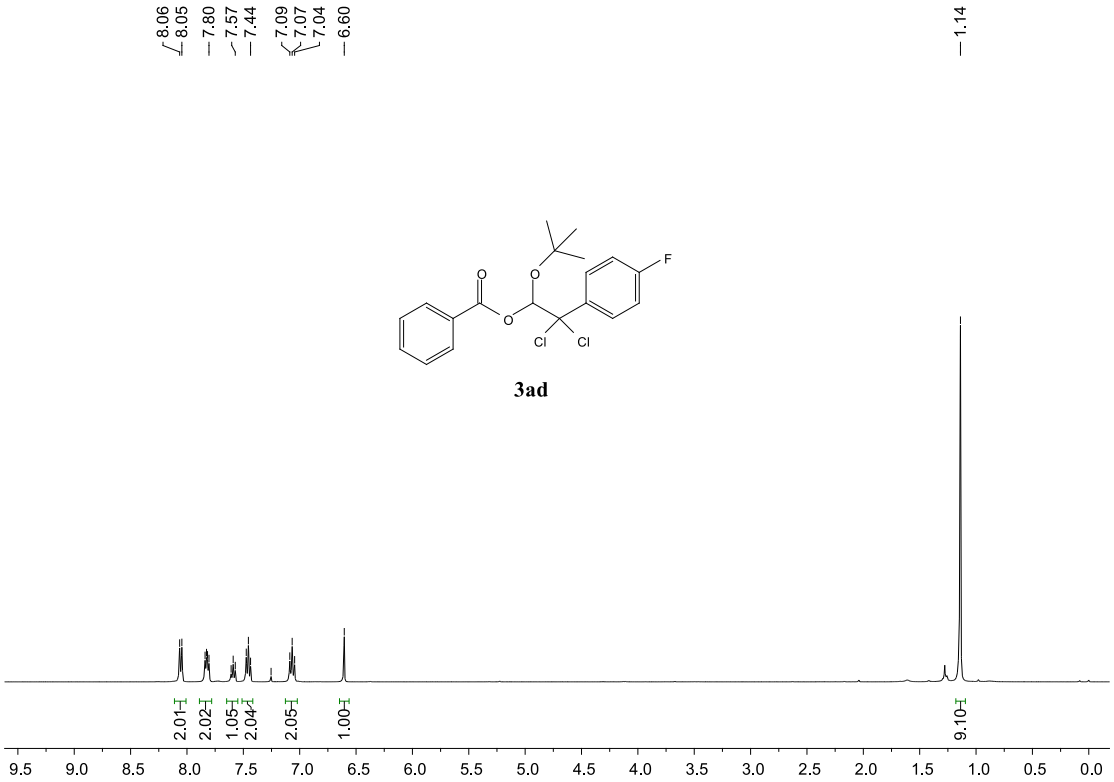
3ac

^{13}C NMR, 100 MHz, $CDCl_3$



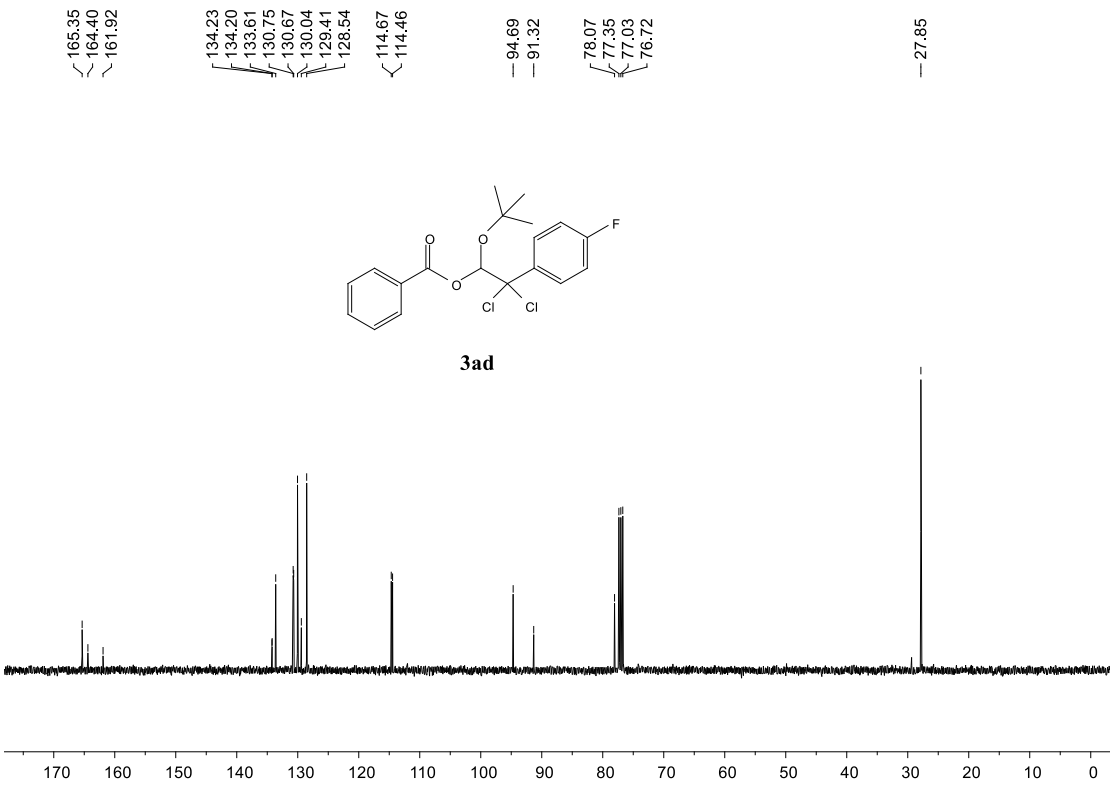
3ac

^{1}H NMR, 400 MHz, $CDCl_3$



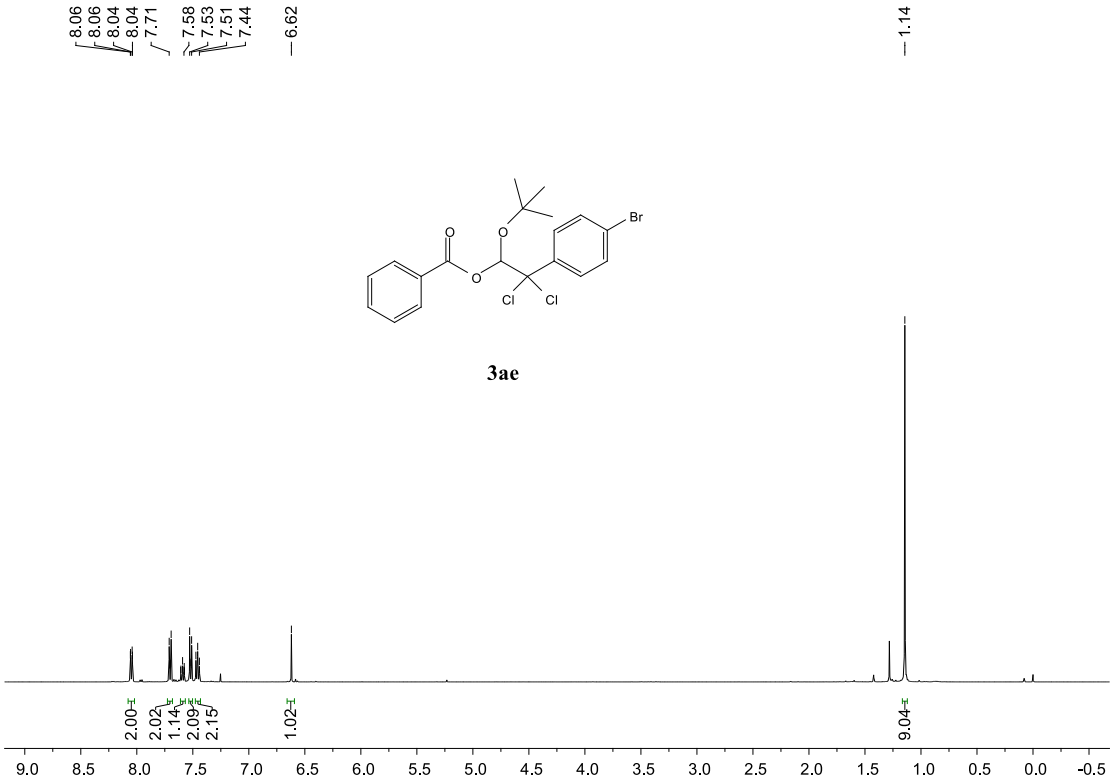
3ad

^{13}C NMR, 100 MHz, $CDCl_3$



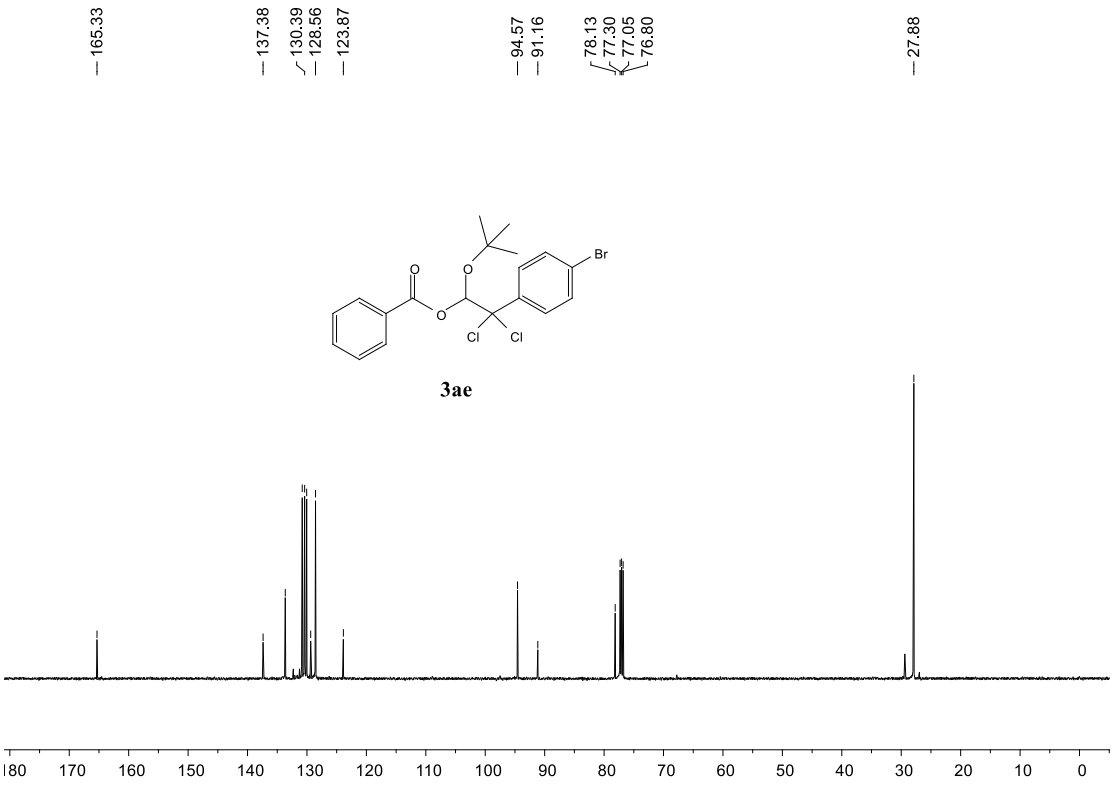
3ad

^{1}H NMR, 400 MHz, $CDCl_3$



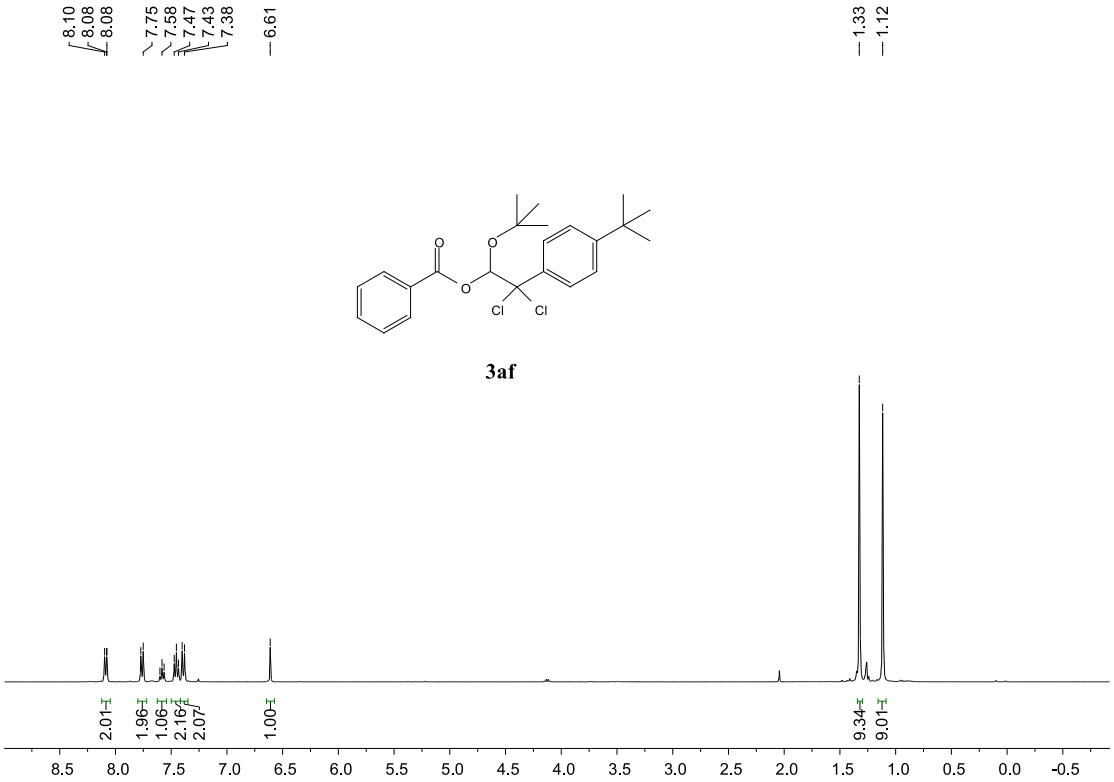
3ae

^{13}C NMR, 100 MHz, $CDCl_3$



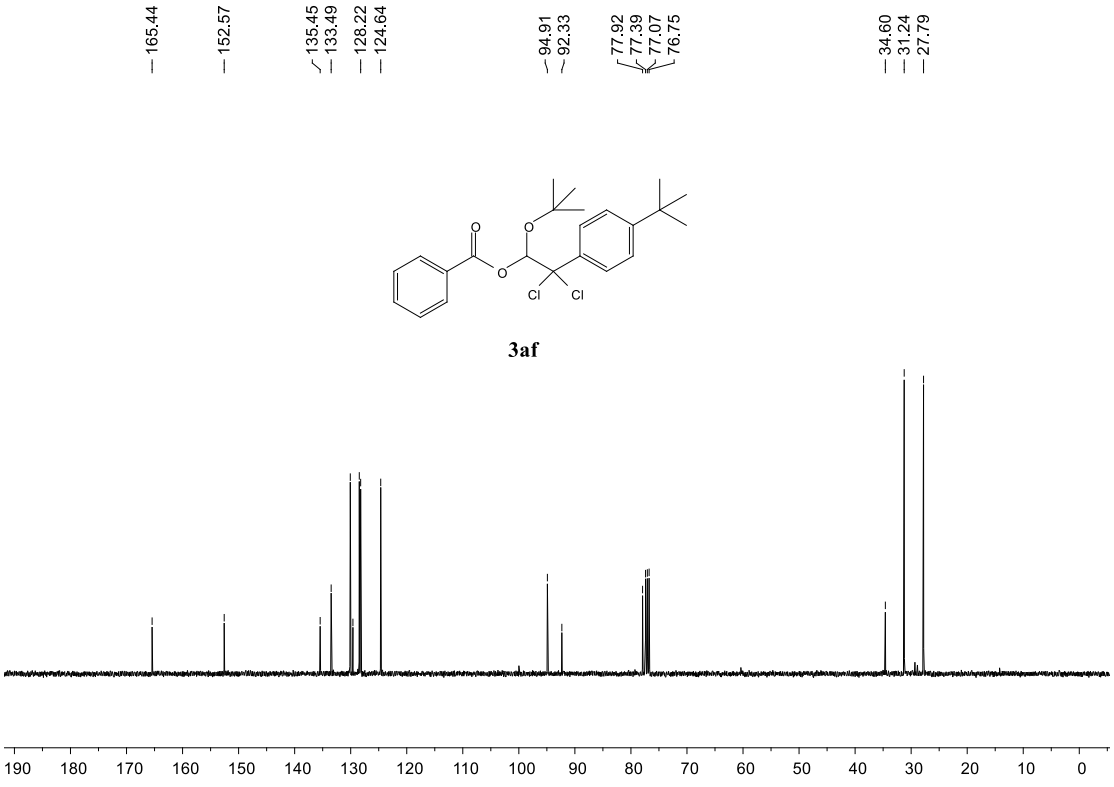
3ae

^{1}H NMR, 400 MHz, $CDCl_3$



3af

^{13}C NMR, 100 MHz, $CDCl_3$



3af

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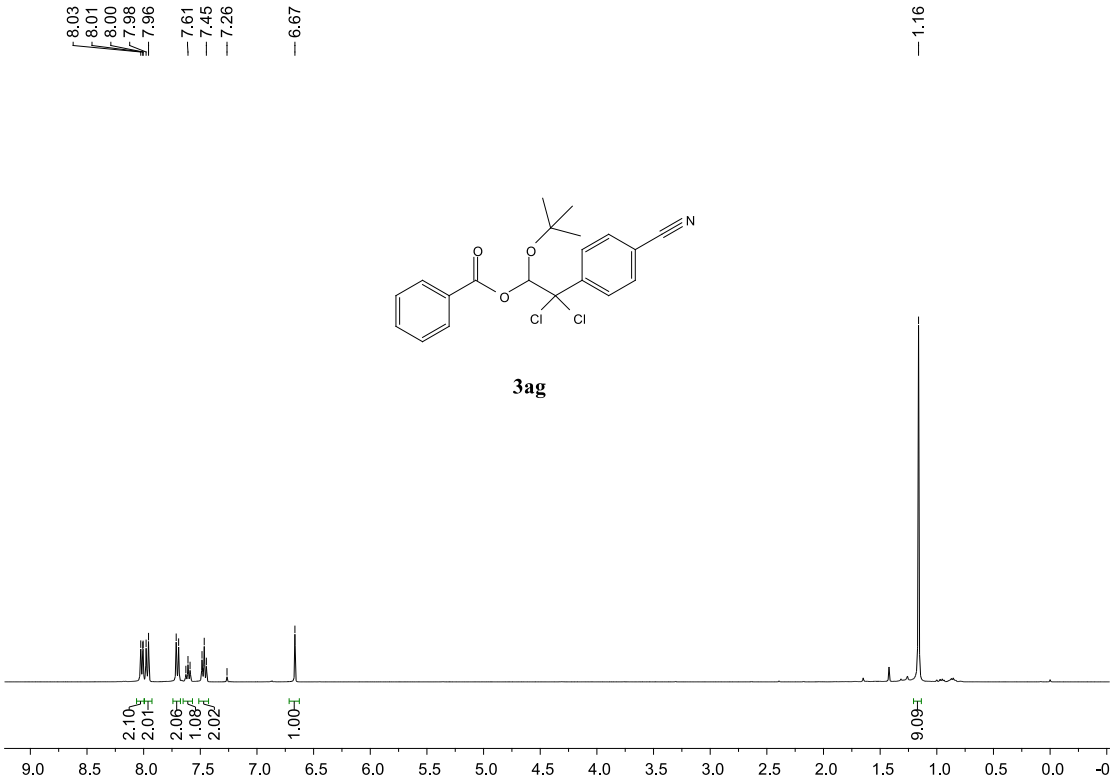
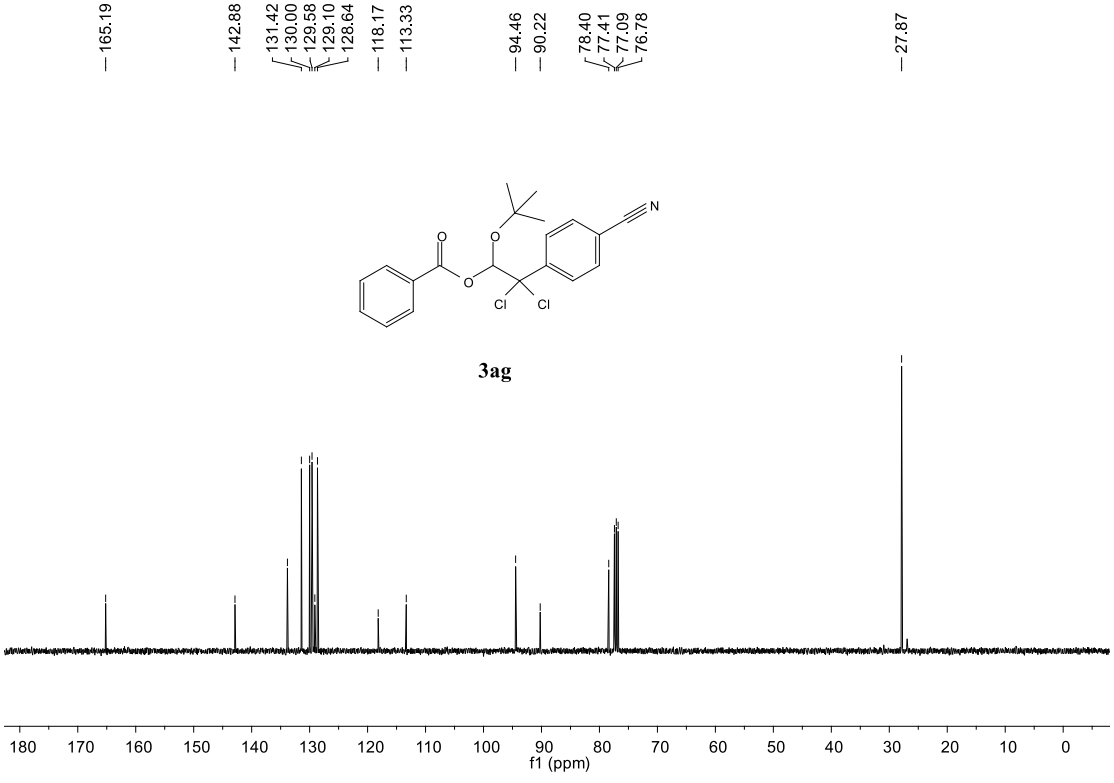


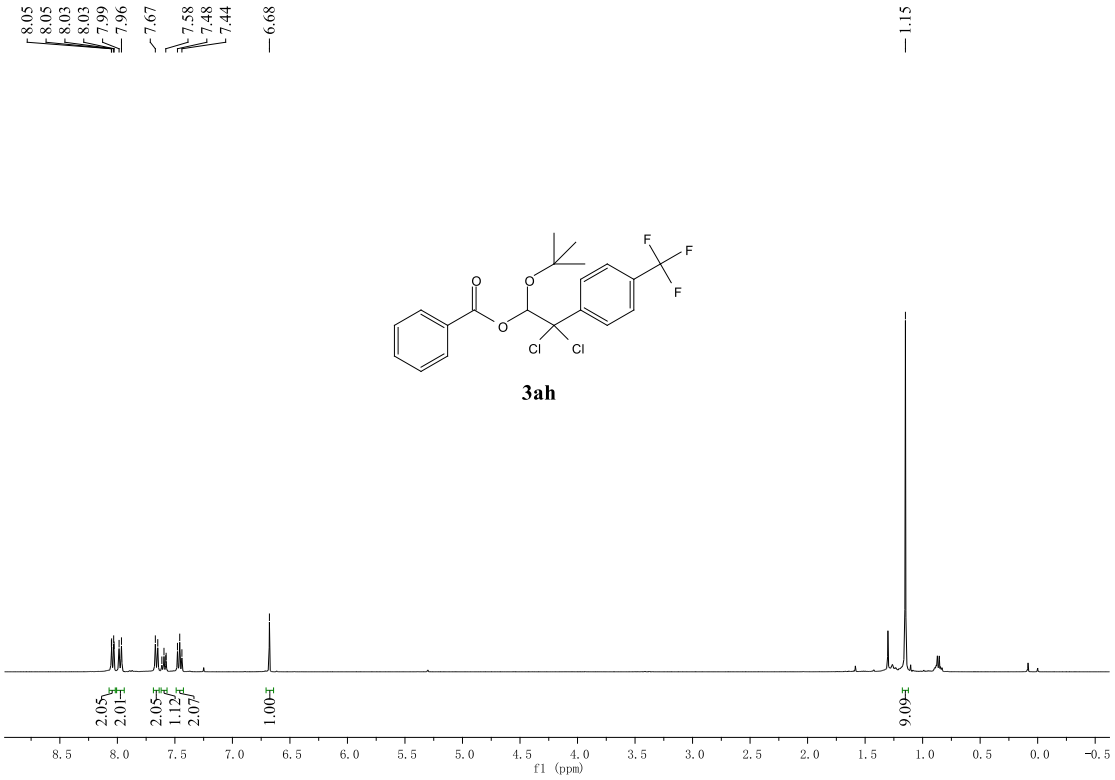
3ag

^{13}C NMR, 100 MHz, $CDCl_3$

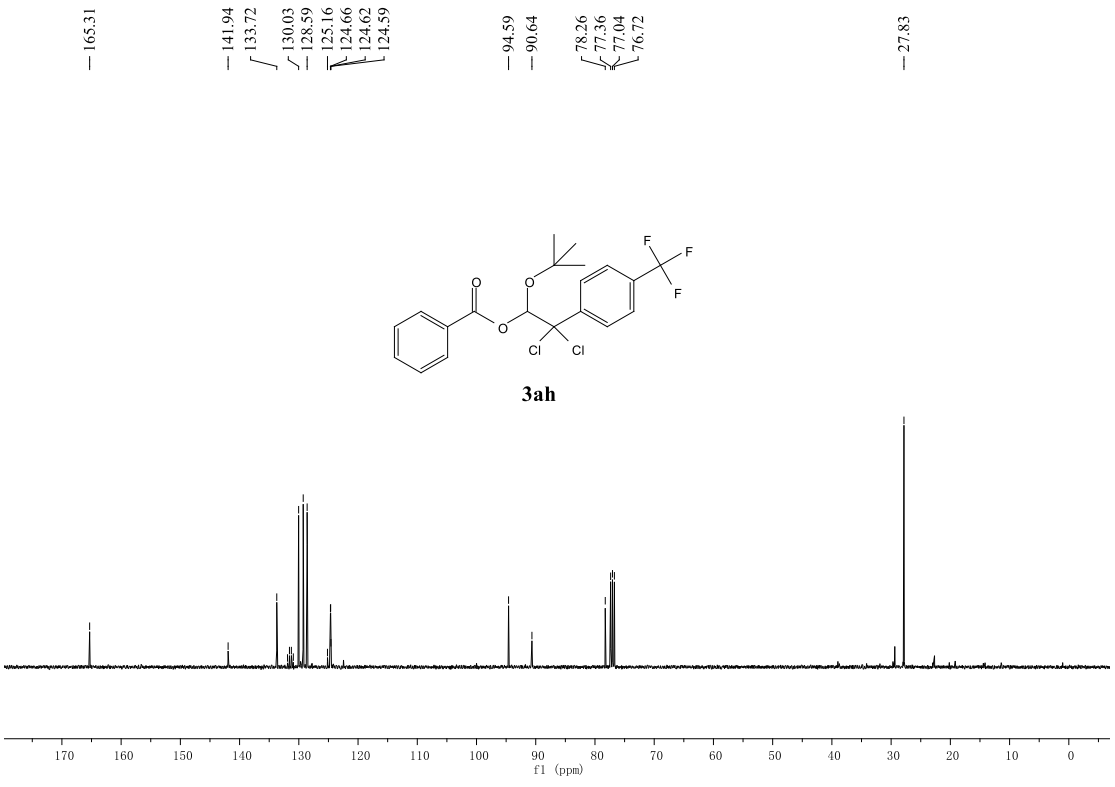


3ag

^{1}H NMR, 400 MHz, $CDCl_3$



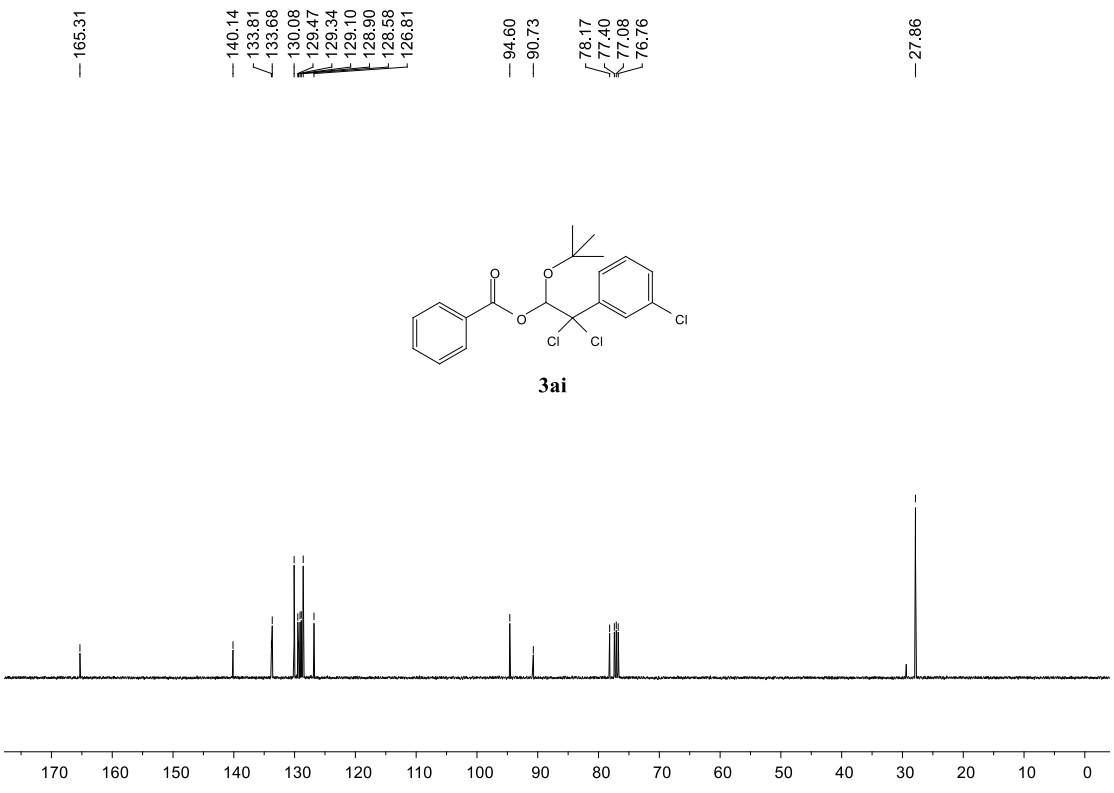
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

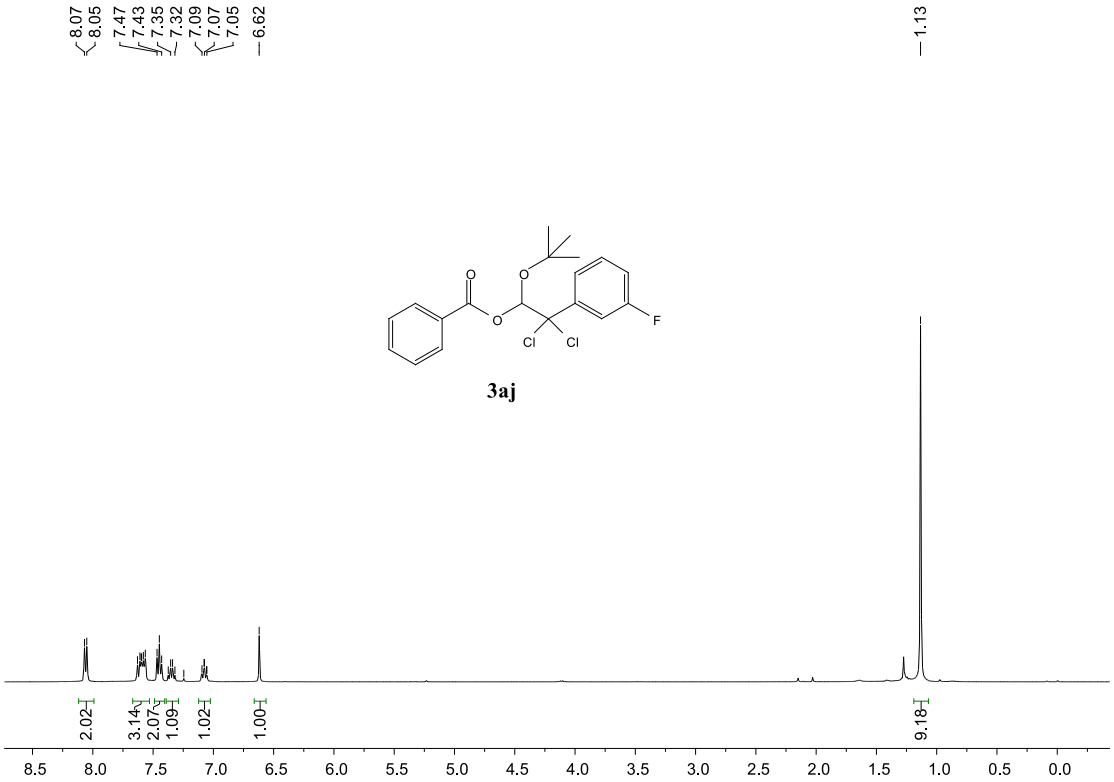
3ai

^{13}C NMR, 100 MHz, $CDCl_3$



3ai

^{1}H NMR, 400 MHz, $CDCl_3$



3aj

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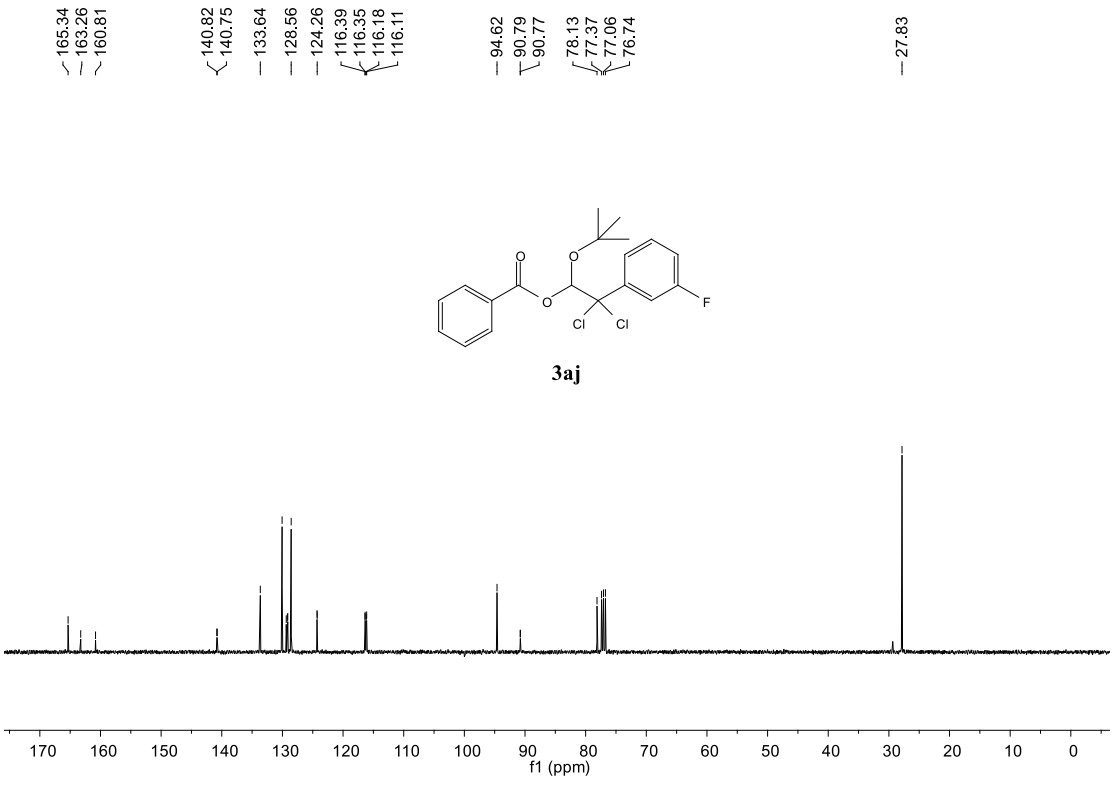

3aj

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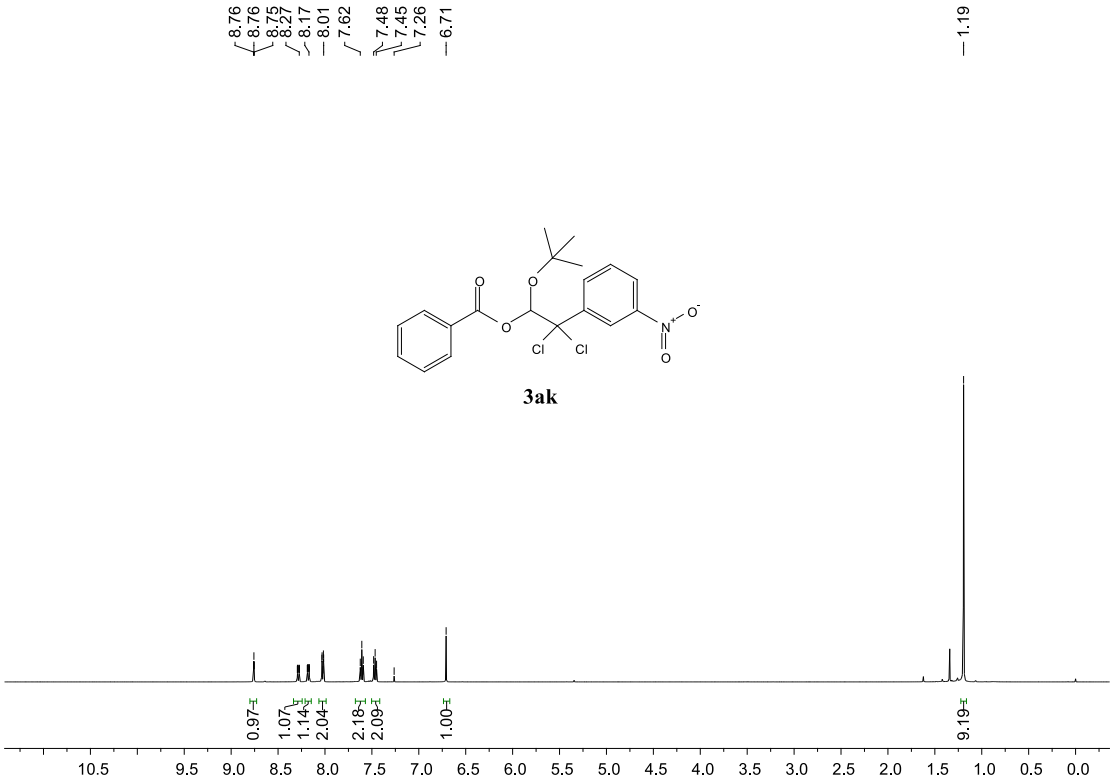

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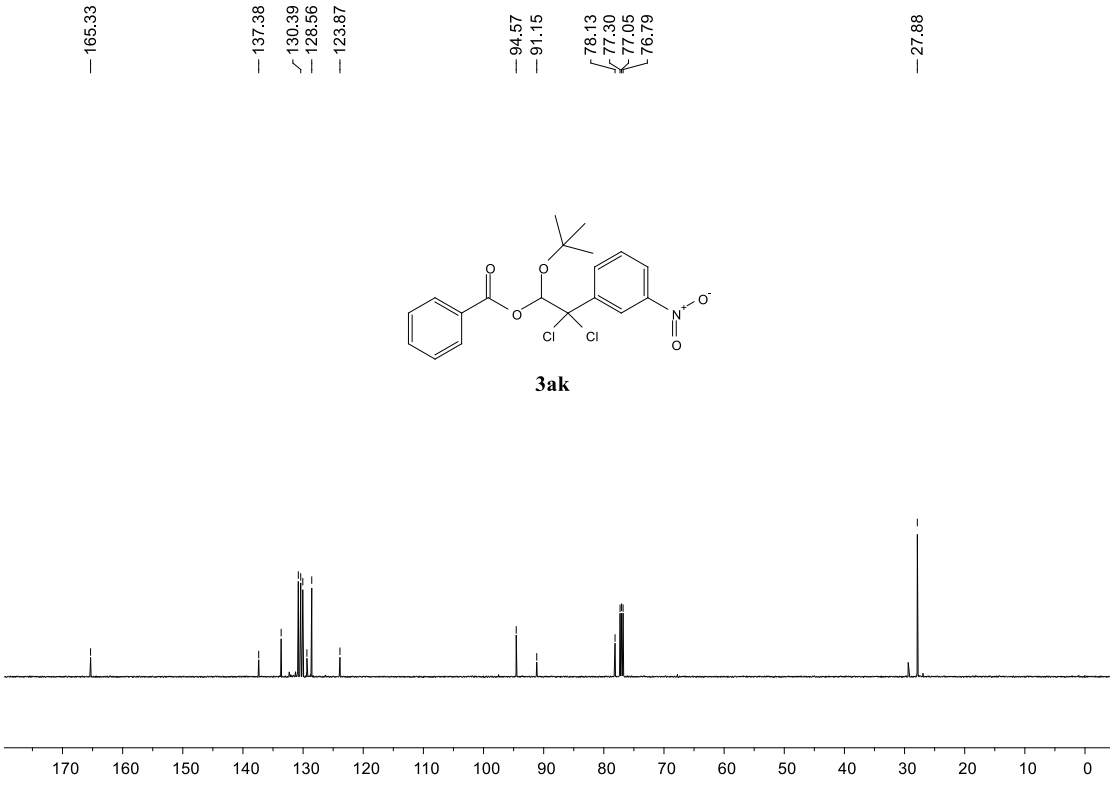

3ak

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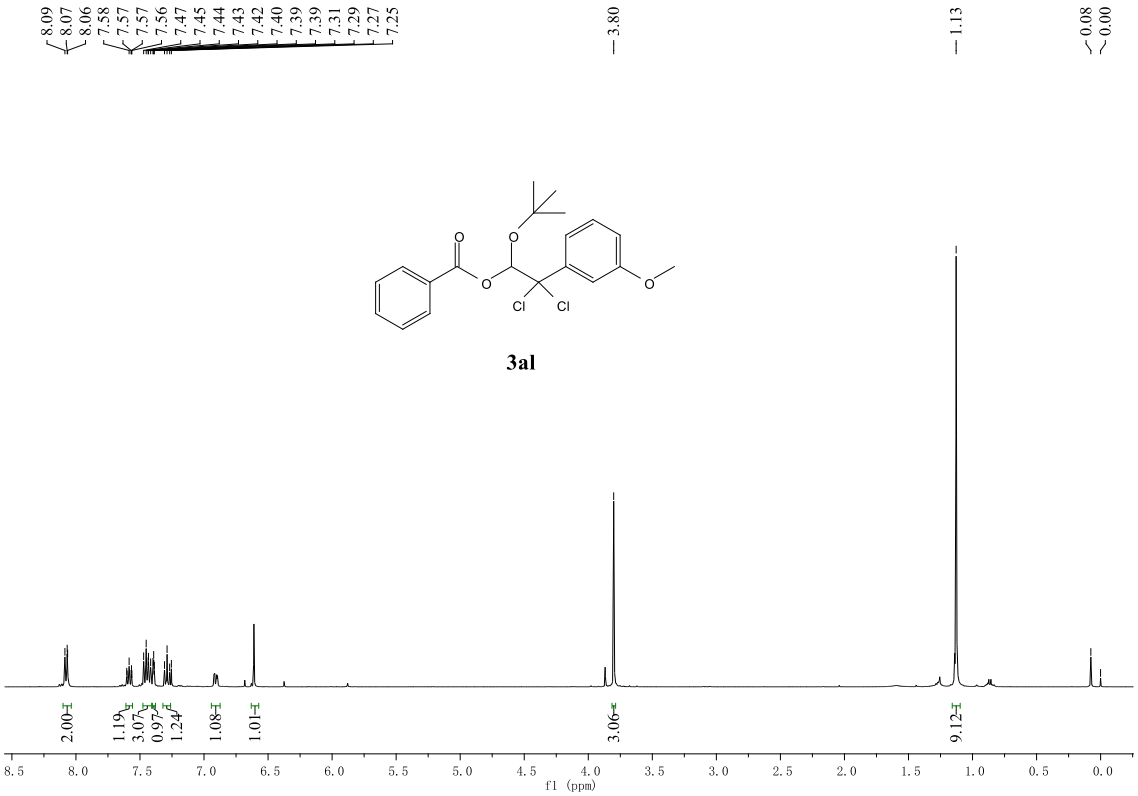
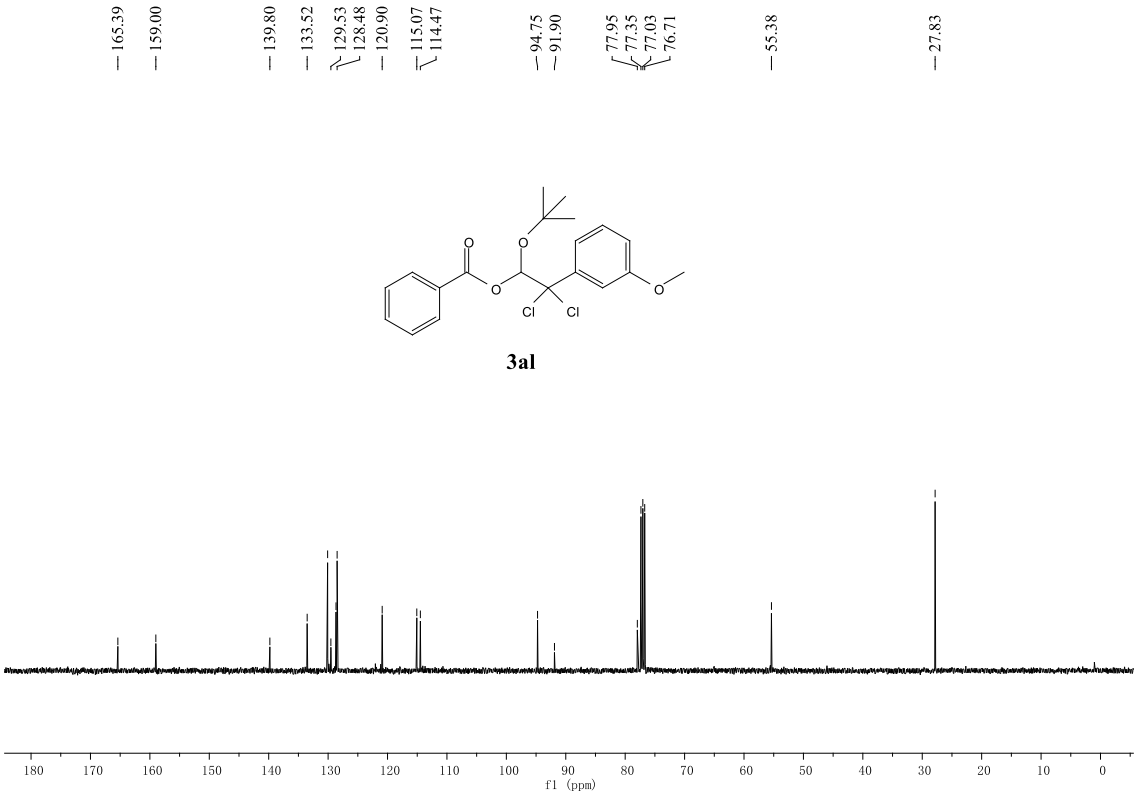


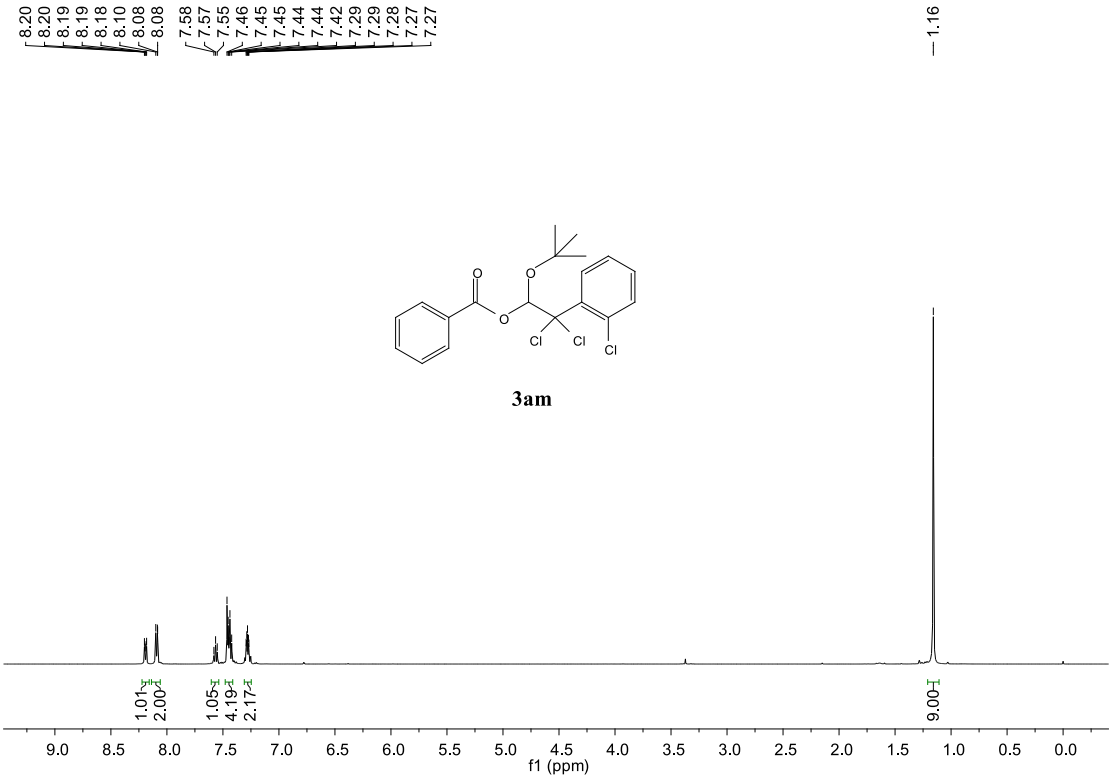
3al

^{13}C NMR, 100 MHz, $CDCl_3$



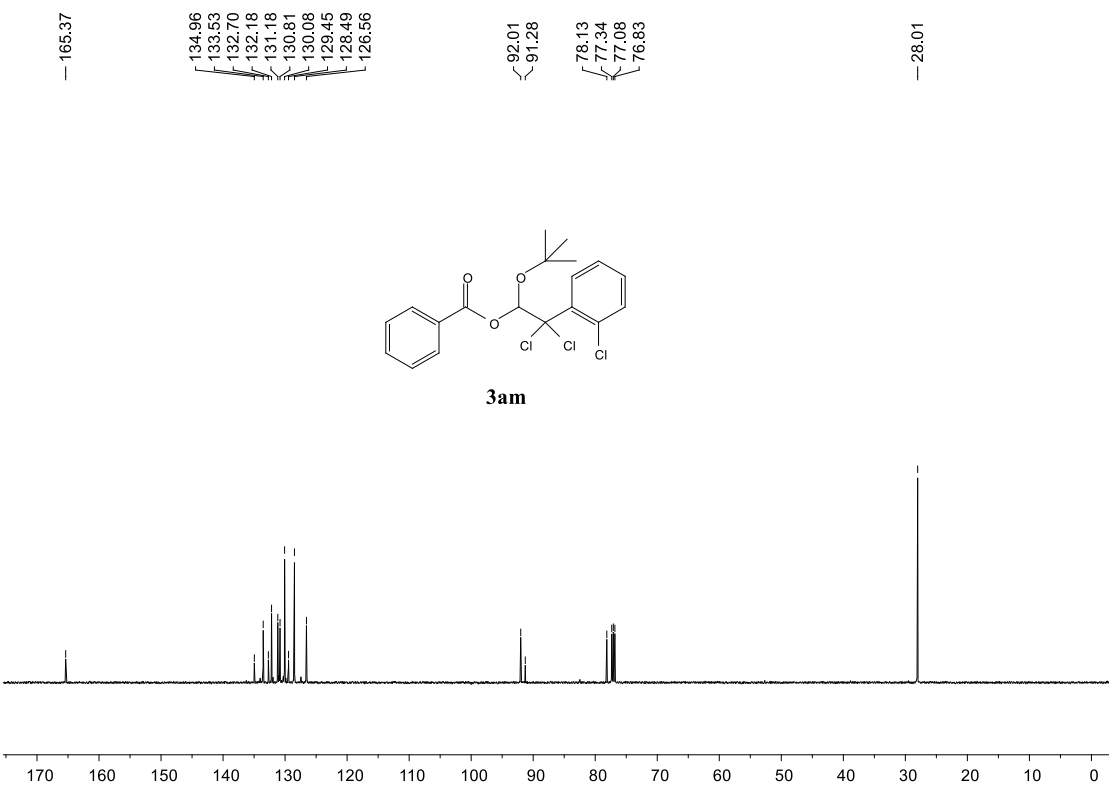
3al

^{1}H NMR, 400 MHz, $CDCl_3$



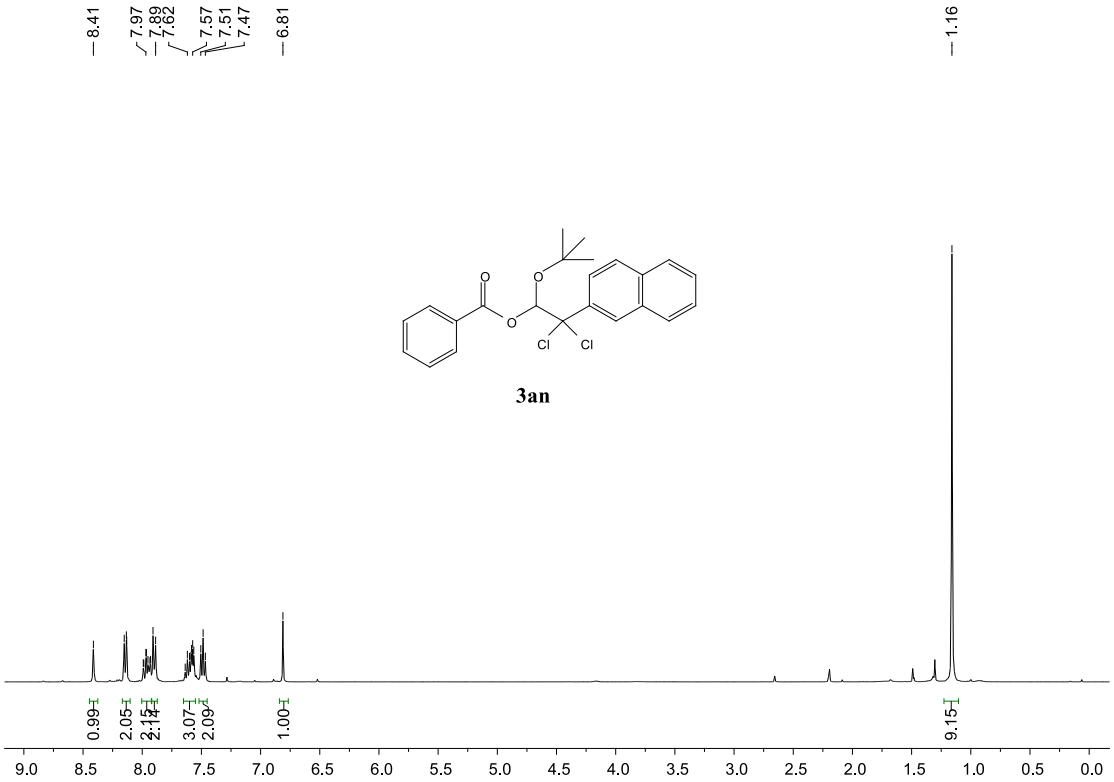
3am

^{13}C NMR, 100 MHz, $CDCl_3$



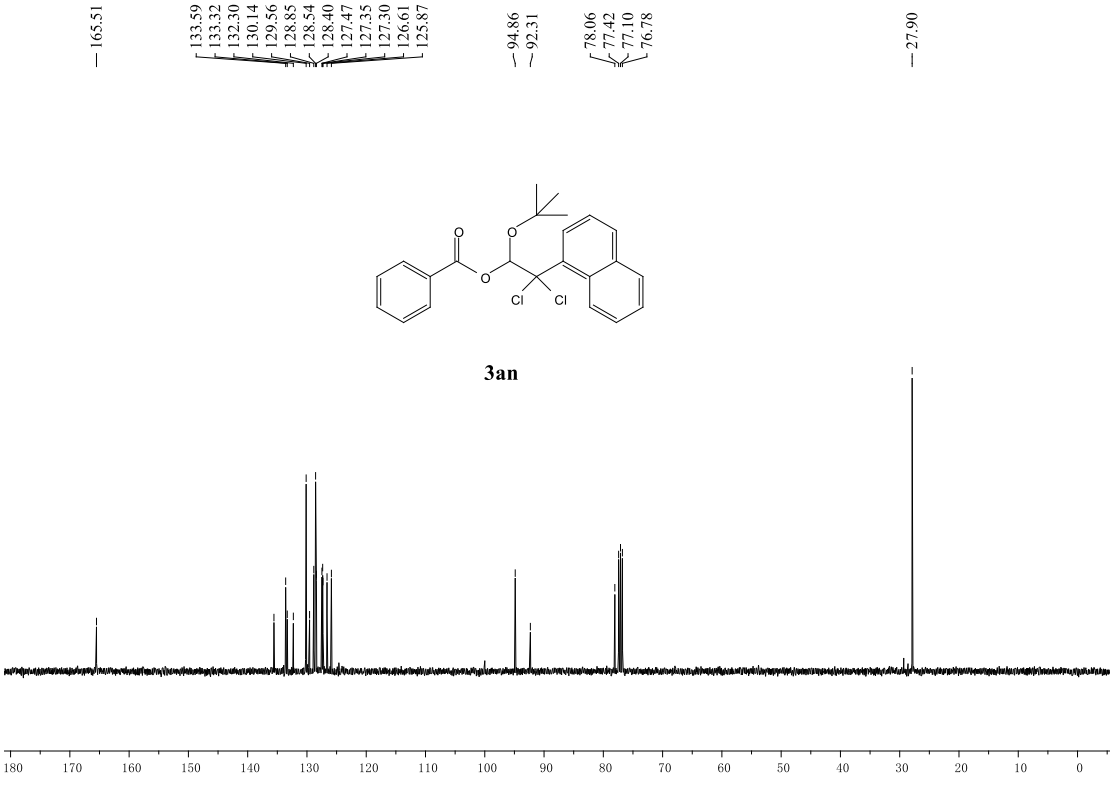
3am

^{1}H NMR, 400 MHz, $CDCl_3$



3an

^{13}C NMR, 100 MHz, $CDCl_3$



3an

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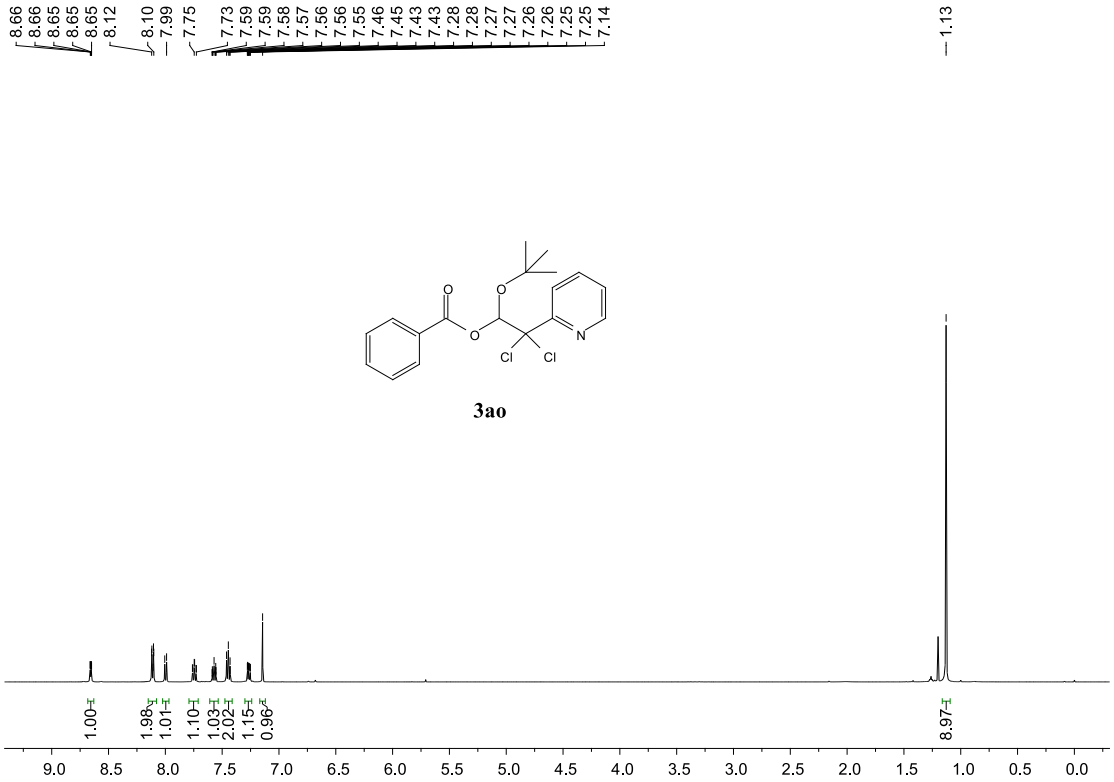
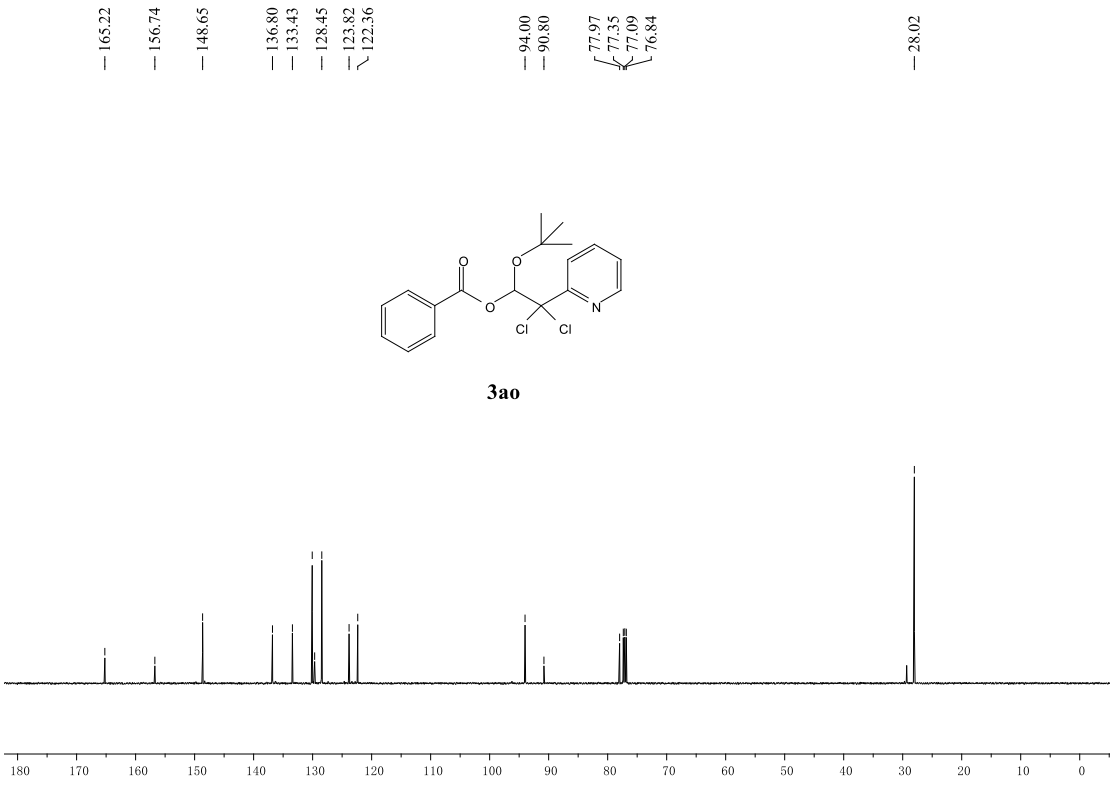


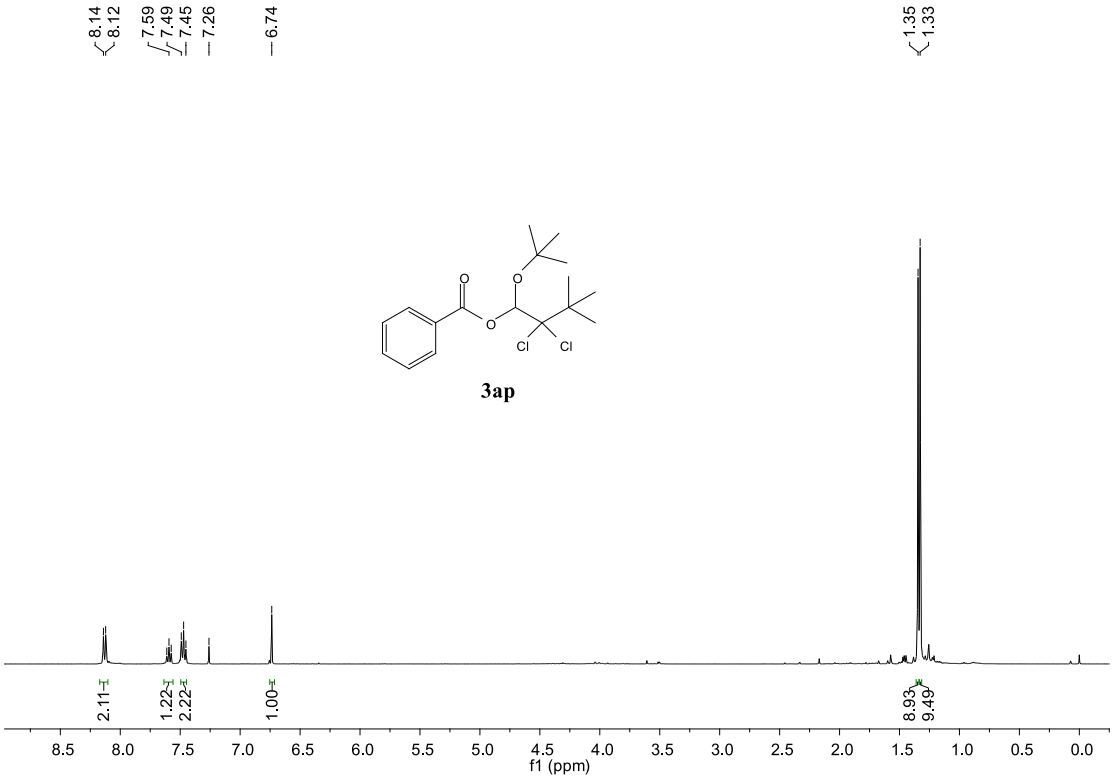
3ao

^{13}C NMR, 100 MHz, $CDCl_3$



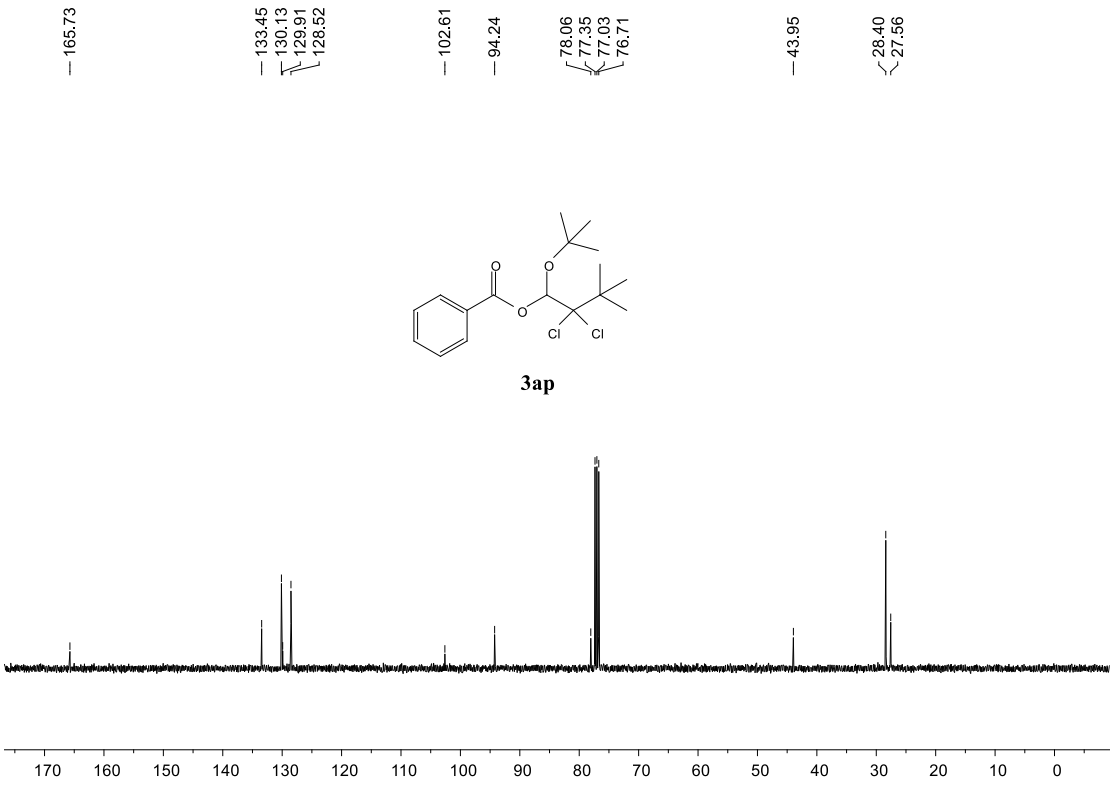
3ao

^{1}H NMR, 400 MHz, $CDCl_3$



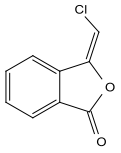
3ap

^{13}C NMR, 100 MHz, $CDCl_3$

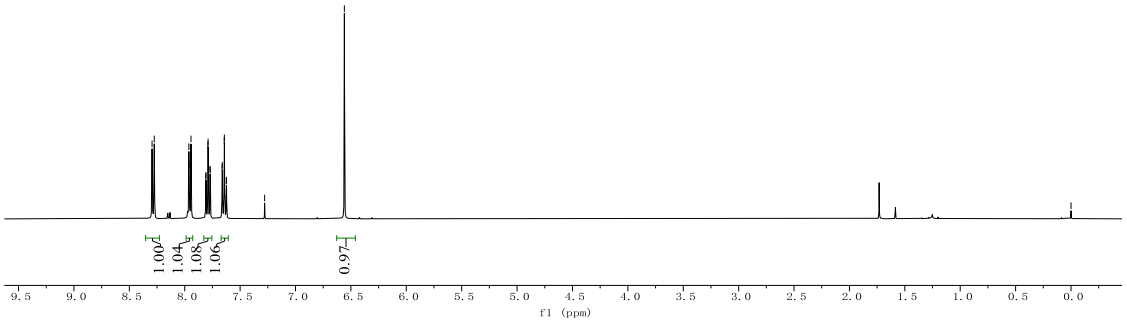


3ap

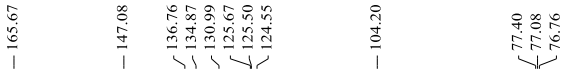
^{1}H NMR, 400 MHz, $CDCl_3$

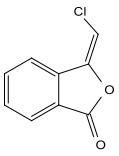


6



^{13}C NMR, 100 MHz, $CDCl_3$





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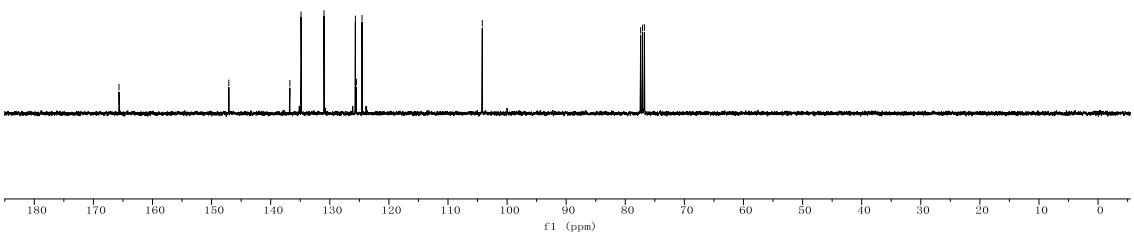
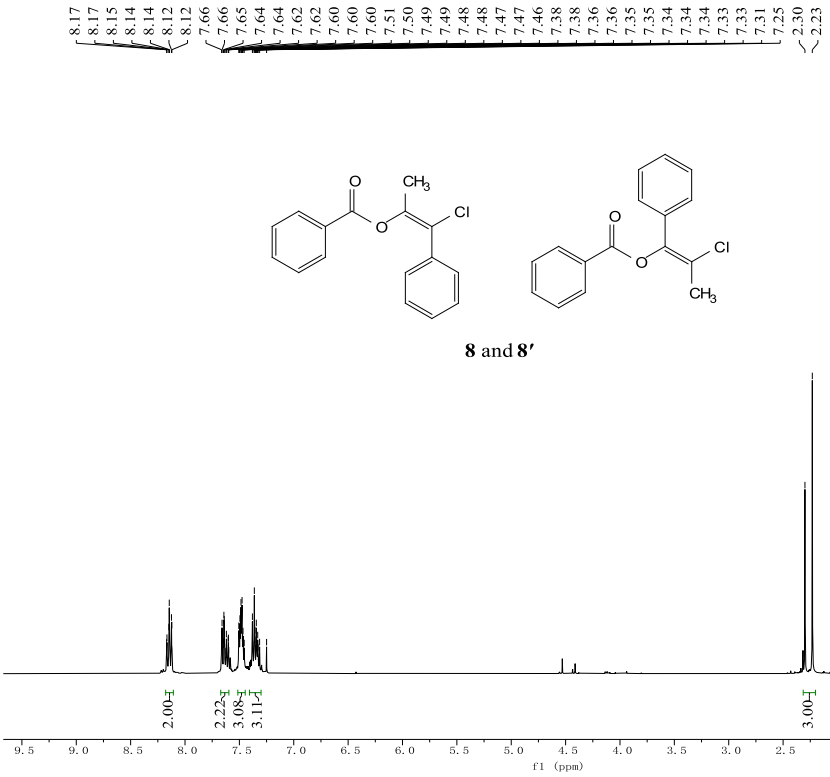
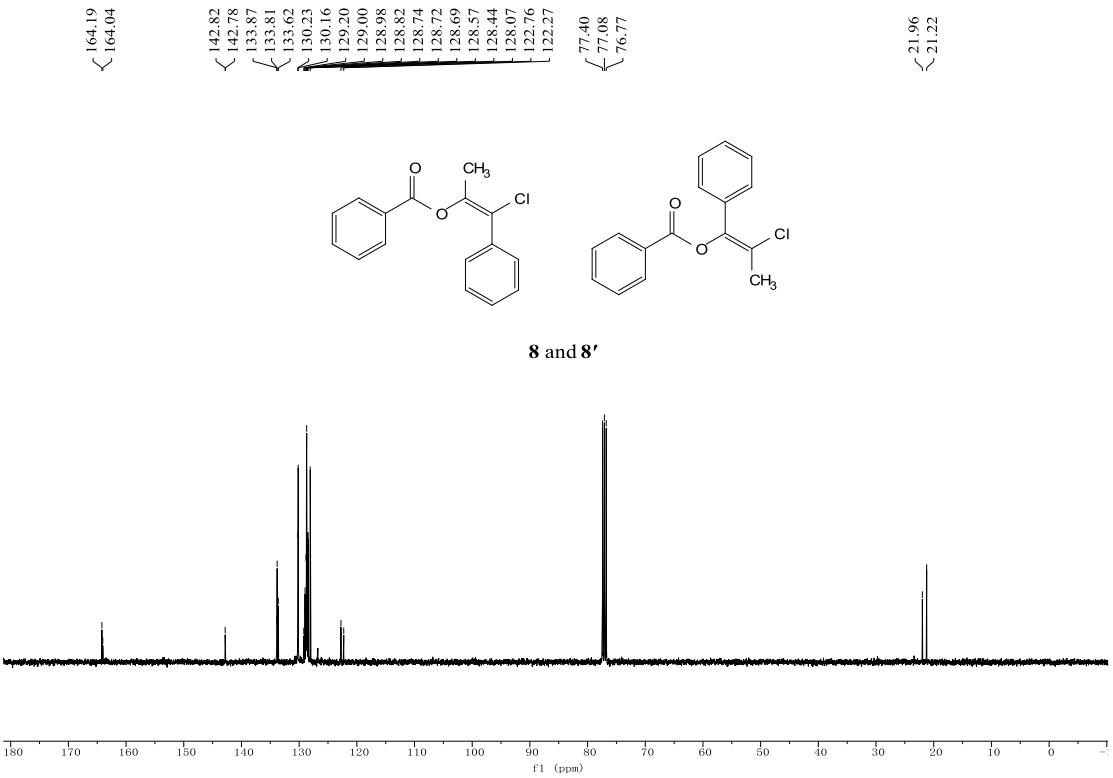


^{1}H NMR, 400 MHz, $CDCl_3$



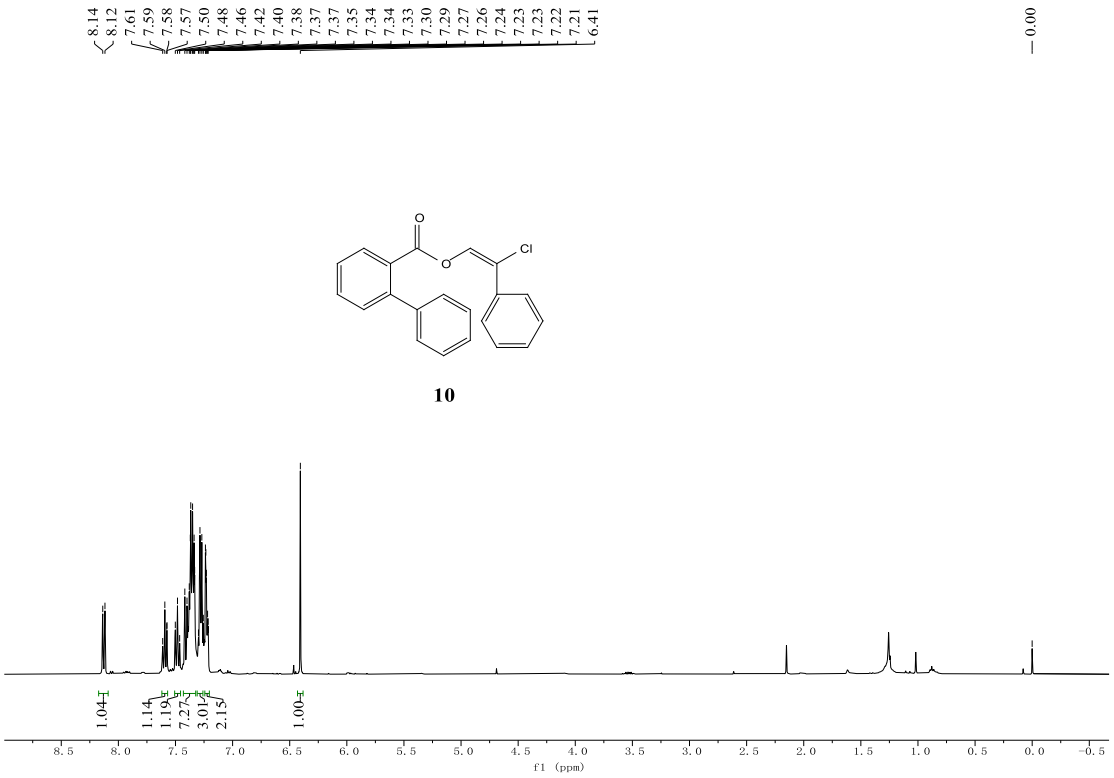
8 and **8′**

^{13}C NMR, 100 MHz, $CDCl_3$



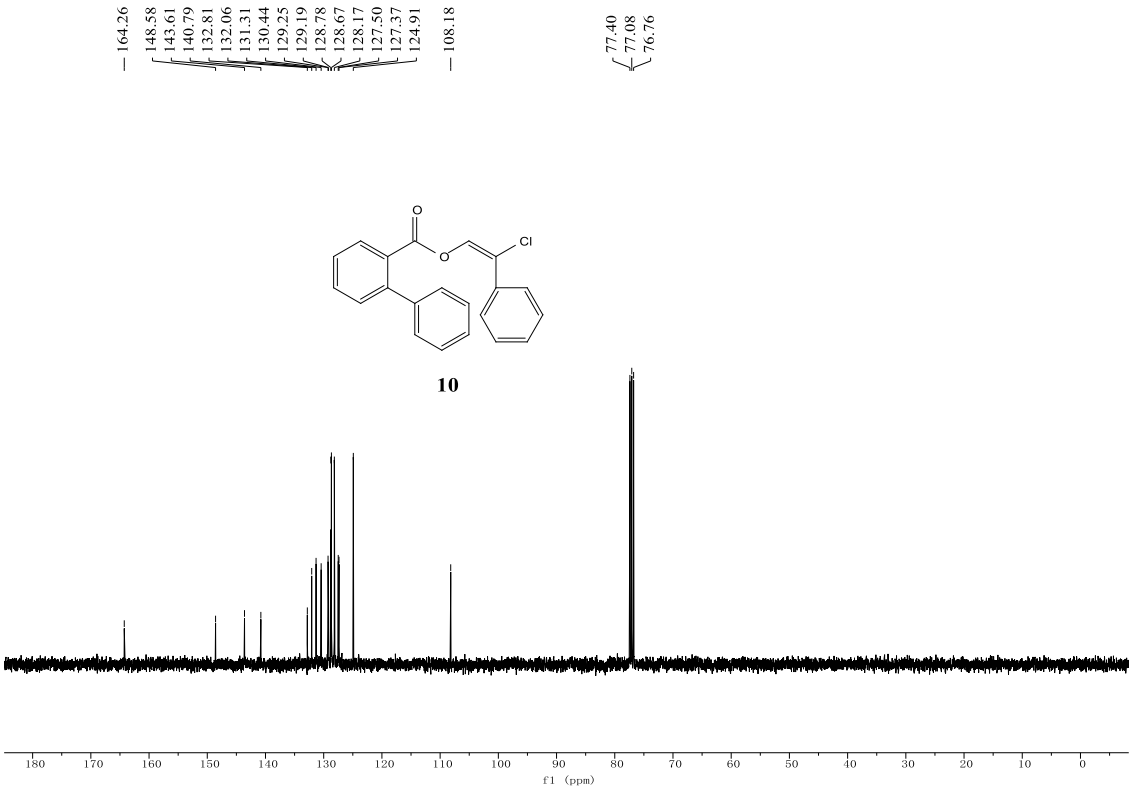
8 and **8′**

^{1}H NMR, 400 MHz, $CDCl_3$



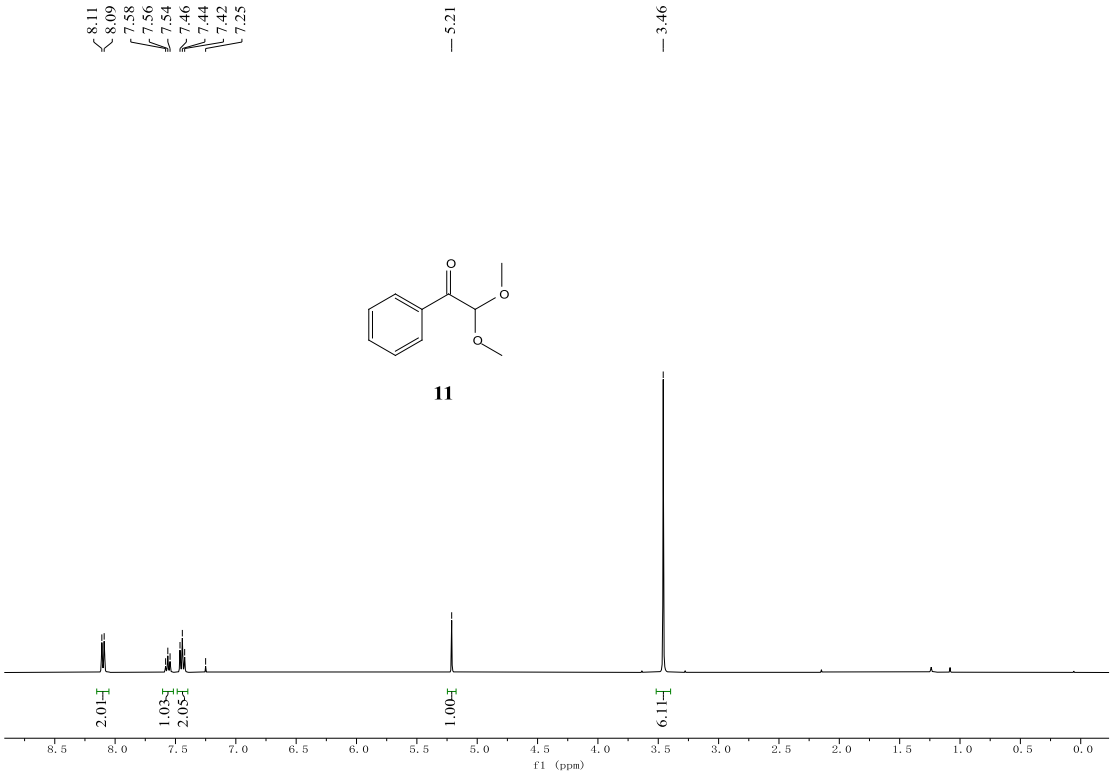
10

^{13}C NMR, 100 MHz, $CDCl_3$



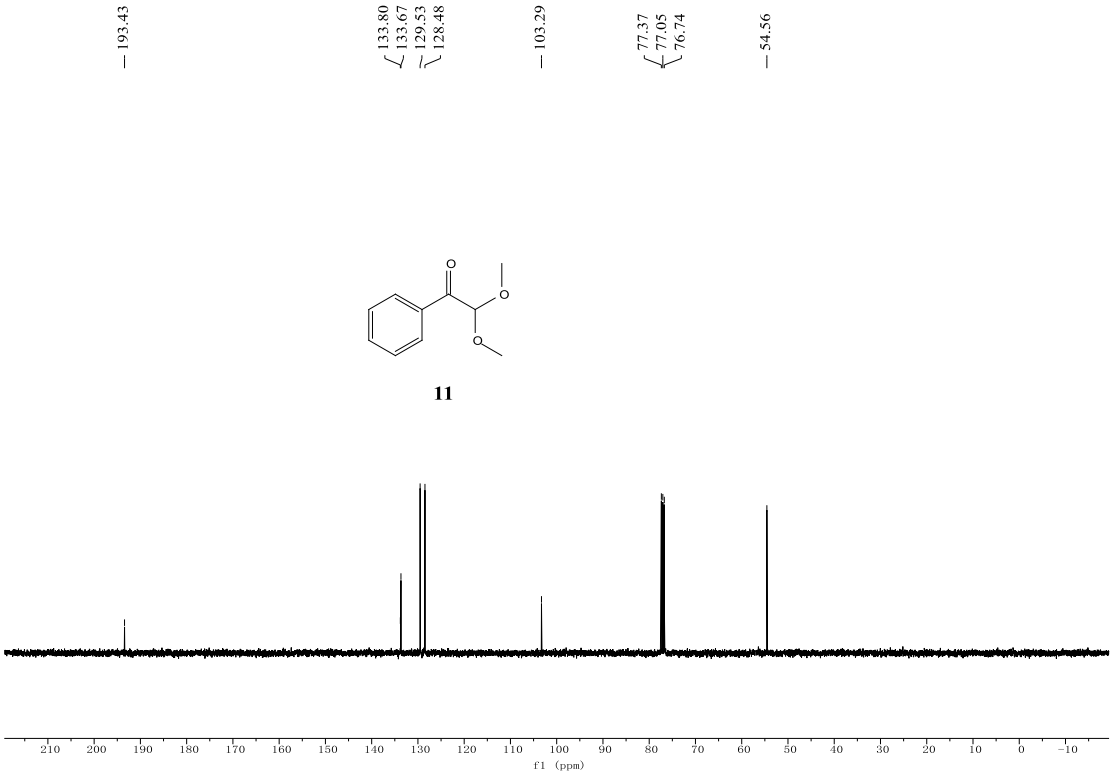
10

^{1}H NMR, 400 MHz, $CDCl_3$



11

^{13}C NMR, 100 MHz, $CDCl_3$



11