Supporting Information

KOH-catalyzed highly efficient aminohalogenation of β-nitrostyrenes with *t*-butyl *N*,*N*-dichlorocarbamate as nitrogen/halogen source

Haibo Mei,[a] Jianlin Han,*[a] Guigen Li[a] and Yi Pan*[a,b]

[a] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China. Fax: 86-25-83593153; Tel: 86-25-83593153; E-mail: hanjl@nju.edu.cn

[b] State of Key Laboratory of Coordination, Nanjing University, Nanjing, 210093, China. E-mail: yipan@nju.edu.cn

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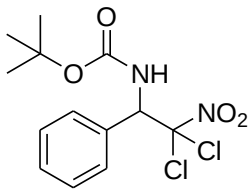
1. General information

All aminohalogenation reactions were performed in oven-dried vials under N_2 atmosphere. Solvent acetonitrile was dried and distilled prior to use. $BocNCl_2$[1] and all the *β*-nitrostyrenes[2] were prepared according to the reported methods. The other chemicals were used as obtained from commercial sources without further purification. Flash chromatography was performed using silica gel 60 (200-300 mesh). Thin layer chromatography was carried out on silica gel 60 F-254 TLC plates of 20 cm × 20 cm. Melting points are uncorrected. IR spectra were collected on Bruker Vector 22 in KBr pellets. ^1H and ^{13}C NMR (TMS used as internal standard) spectra were recorded with a Bruker ARX 300 spectrometer. High resolution mass spectra for all the new compounds were done by Micromass Q-Tof instrument (ESI).

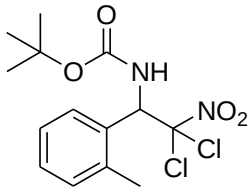
2. Aminohalogenation of *β*-nitrostyrenes with $BocNCl_2$

Into an oven-dried reaction vial flushed with N_2 were taken *β*-nitrostyrenes (0.5 mmol), KOH (0.1 mmol), anhydrous MeCN (5.0 mL) and $BocNCl_2$ (1.25 mmol). The reaction mixture was stirred at room temperature for desired time, and then the reaction was quenched with saturated Na_2SO_3 (3.0 mL). The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by TLC plate (hexane/EtOAc, 8:1).

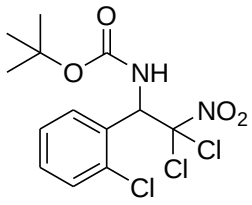


Tert-butyl 2,2-dichloro-2-nitro-1-phenylethylcarbamate (**3a**): white solid, yield 93%, mp 105-107 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42 (s, 5 H), 5.99 (d, *J* = 9.6 Hz, 1 H), 5.57 (d, *J* = 9.9 Hz, 1 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.0, 133.1, 129.7, 128.9, 128.7, 116.0, 81.4, 63.8, 28.2. IR

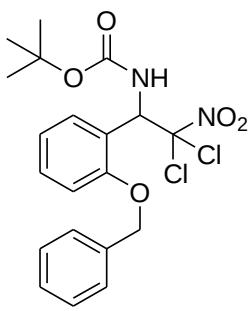
(KBr): ν = 3415, 2971, 1705, 1572, 1510, 1241, 709 cm^{-1}. HRMS [M+Na^+]: calcd for $C_{13}H_{16}N_2O_4Cl_2Na$: 357.0379, found: 357.0387.



Tert-butyl 2,2-dichloro-2-nitro-1-o-tolylethylcarbamate (**3b**): white solid, yield 77%, mp 154-156 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.49 (d, *J* = 6.9 Hz, 1 H), 7.26-7.36 (m, 3 H), 6.39 (d, *J* = 9.9 Hz, 1 H), 5.49 (d, *J* = 9.9 Hz, 1 H), 2.61 (s, 3 H), 1.43 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.0, 138.1, 133.0, 131.1, 129.4, 126.5, 125.4, 116.4, 81.4, 58.6, 28.1, 20.3. IR (KBr): ν = 3260, 2987, 1709, 1585, 1367, 1155, 1019, 740 cm^{-1}. HRMS [M+Na^+]: calcd for $C_{14}H_{18}N_2O_4Cl_2Na$: 371.0536, found: 371.0531.

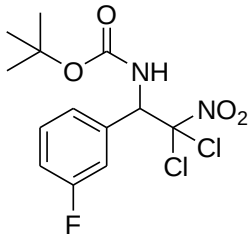


Tert-butyl 2,2-dichloro-1-(2-chlorophenyl)-2-nitroethylcarbamate (**3c**): white solid, yield 75%, mp 167-169 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48-7.51 (m, 2 H), 7.33-7.40 (m, 2 H), 6.75 (d, *J* = 10.2 Hz, 1 H), 5.56 (s, 1 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.6, 135.6, 132.3, 130.7, 130.2, 128.6, 127.3, 115.6, 81.6, 59.2, 28.1. IR (KBr): ν = 3258, 3148, 2992, 1708, 1585, 1367, 1155, 749 cm^{-1}. HRMS [M+Na^+]: calcd for $C_{13}H_{15}N_2O_4Cl_3Na$: 390.9990, found: 390.9992.

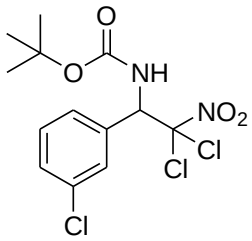


Tert-butyl

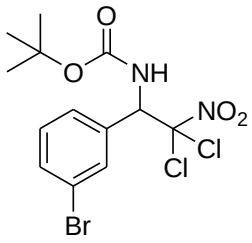
1-(2-(benzyloxy)phenyl)-2,2-dichloro-2-nitroethylcarbamate (**3d**): white solid, yield 76%, mp 113-114 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35-7.51 (m, 7 H), 7.04 (t, *J* = 4.2 Hz, 2 H), 6.36 (d, *J* = 10.2 Hz, 1 H), 6.19 (d, *J* = 10.5 Hz, 1 H), 5.17 (s, 2 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 154.3, 136.2, 131.9, 130.9, 129.8, 128.8, 128.2, 127.4, 121.1, 116.6, 112.8, 80.9, 70.6, 61.1, 28.2. IR (KBr): ν = 3255, 2979, 1711, 1584, 1368, 1254, 749 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{20}H_{22}N_2O_5Cl_2Na$: 463.0798, found: 463.0801.



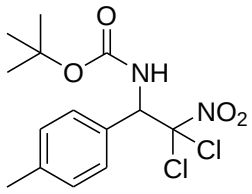
Tert-butyl 2,2-dichloro-1-(3-fluorophenyl)-2-nitroethylcarbamate (**3e**): white solid, yield 93%, mp 116-117 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36-7.43 (m, 1 H), 7.10-7.24 (m, 3 H), 5.99 (d, *J* = 9.9 Hz, 1 H), 5.55 (s, 1 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.2, 160.9, 153.9, 135.5 (d, *J* =6.3 Hz), 130.3 (d, *J* =7.9 Hz), 124.8 (d, *J* =2.8 Hz), 116.9 (d, *J* =20.7 Hz), 116.1 (d, *J* =22.7 Hz), 81.7, 63.3, 28.1. IR (KBr): ν = 3255, 3146, 2987, 1698, 1585, 1368, 1158, 724 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{13}H_{15}N_2O_4Cl_2FNa$: 375.0285, found: 375.0292.



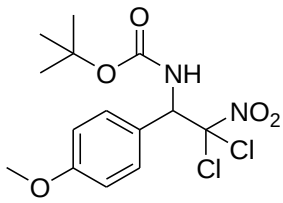
Tert-butyl 2,2-dichloro-1-(3-chlorophenyl)-2-nitroethylcarbamate (**3f**): white solid, yield 92%, mp 136-137 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38-7.44 (m, 2 H), 7.35 (d, *J* = 6.3 Hz, 2 H), 5.98 (d, *J* = 9.9 Hz, 1 H), 5.57 (s, 1H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.9, 135.1, 134.6, 130.9, 129.9, 129.0, 127.3, 115.4, 81.7, 63.2, 28.1. IR (KBr): ν = 3252, 3149, 2985, 1703, 1588, 1370, 1158, 722 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{13}H_{15}N_2O_4Cl_3Na$: 390.9990, found: 390.9989.



Tert-butyl 1-(3-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (**3g**): white solid, yield 90%, mp 153-154 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.54-7.60 (m, 2 H), 7.39 (d, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 7.8 Hz, 1 H), 5.97 (d, *J* = 9.9 Hz, 1 H), 5.59 (d, *J* = 9.6 Hz, 1 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.8, 135.4, 132.8, 131.8, 130.2, 127.7, 122.7, 115.4, 81.8, 63.2, 28.1. IR (KBr): ν = 3250, 3149, 2983, 1702, 1586, 1369, 1158 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{13}H_{15}N_2O_4Cl_2BrNa$: 436.9461, found: 436.9470.

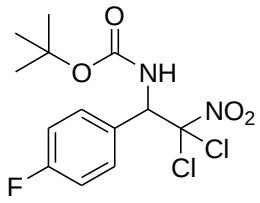


Tert-butyl 2,2-dichloro-2-nitro-1-p-tolylethylcarbamate (**3h**): white solid, yield 99%, mp 108-109 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 5.94 (d, *J* = 9.9 Hz, 1 H), 5.54 (d, *J* = 10.2 Hz, 1 H), 2.38 (s, 3 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.1, 139.7, 130.1, 129.4, 128.7, 116.2, 81.4, 63.6, 28.2, 21.2. IR (KBr): ν = 3260, 3153, 2981, 1707, 1586, 1367, 1155, 775 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{14}H_{18}N_2O_4Cl_2Na$: 371.0536, found: 371.0525.

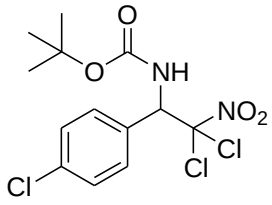


Tert-butyl 2,2-dichloro-1-(4-methoxyphenyl)-2-nitroethylcarbamate (**3i**): white solid, yield 96%, mp 114-115 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (d, *J* = 8.7 Hz, 2 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 5.93 (d, *J* = 9.6 Hz, 1 H), 5.51 (d, *J* = 9.9 Hz, 1 H), 3.83 (s, 3 H), 1.45

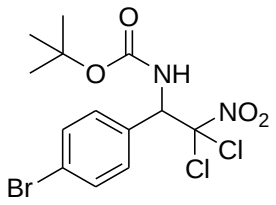
(s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 160.5, 154.0, 130.1, 125.0, 116.2, 114.0, 81.4, 63.4, 55.3, 28.2. IR (KBr): ν = 3310, 2976, 1694, 1510, 1243, 1170, 841 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{14}H_{18}N_2O_5Cl_2Na$: 387.0485, found: 387.0474.



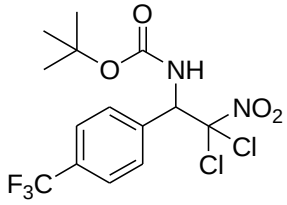
Tert-butyl 2,2-dichloro-1-(4-fluorophenyl)-2-nitroethylcarbamate (**3j**): white solid, yield 93%, mp 109-110 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40-7.45 (m, 2 H), 7.06-7.14 (m, 2 H), 5.98 (d, *J* = 9.6 Hz, 1 H), 5.56 (d, *J* = 8.4 Hz, 1 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.0 (d, *J* = 248.0 Hz), 153.9, 131.8, 130.8 (d, *J* = 8.5 Hz), 129.1, 115.9 (d, *J* = 21.4 Hz), 81.6, 63.1, 28.1. IR (KBr): ν = 3289, 2977, 1687, 1587, 1510, 1164, 839 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{13}H_{15}N_2O_4Cl_2FNa$: 375.0285, found: 375.0290.



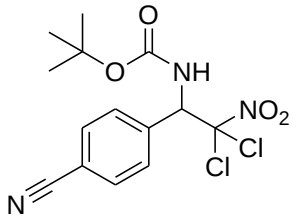
Tert-butyl 2,2-dichloro-1-(4-chlorophenyl)-2-nitroethylcarbamate (**3k**): white solid, yield 95%, mp 101-103 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (s, 4 H), 5.97 (d, *J* = 9.9 Hz, 1 H), 5.56 (s, 1 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.9, 135.9, 131.7, 130.2, 128.9, 115.5, 81.7, 63.2, 28.1. IR (KBr): ν = 3258, 3153, 2982, 1705, 1586, 1368, 1155, 751 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{13}H_{15}N_2O_4Cl_3Na$: 390.9990, found: 390.9998.



Tert-butyl 1-(4-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (**3l**): white solid, yield 94%, mp 106-107 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.56 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 5.96 (d, *J* = 9.6 Hz, 1 H), 5.56 (d, *J* = 8.1 Hz, 1 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.8, 132.2, 131.9, 130.5, 124.1, 115.4, 81.7, 63.2, 28.1. IR (KBr): ν = 3263, 3159, 2987, 1703, 1588, 1368, 1158, 1013 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{13}H_{15}N_2O_4Cl_2BrNa$: 436.9461, found: 436.9465.

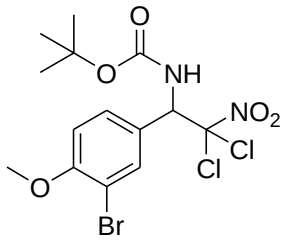


Tert-butyl 2,2-dichloro-2-nitro-1-(4-(trifluoromethyl)phenyl)ethylcarbamate (**3m**): white solid, yield 91%, mp 117-118 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (d, *J* = 7.5 Hz, 2 H), 7.59 (d, *J* = 7.8 Hz, 2 H), 6.05 (d, *J* = 6.9 Hz, 1 H), 5.57 (d, *J* = 8.1 Hz, 1 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.9, 137.1, 132.1 (d, *J* = 32.9 Hz), 129.4, 125.7 (d, *J* = 3.2 Hz), 121.8, 115.1, 81.9, 63.3, 28.1. IR (KBr): ν = 3327, 2982, 1686, 1589, 1327, 1166, 1071 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{14}H_{15}N_2O_4Cl_2F_3Na$: 425.0253, found: 425.0249.

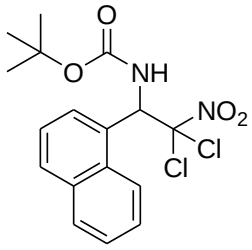


Tert-butyl 2,2-dichloro-1-(4-cyanophenyl)-2-nitroethylcarbamate (**3n**): white solid, yield 74%, mp 129-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.74 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J*

= 8.1 Hz, 2 H), 6.05 (d, *J* = 10.2 Hz, 1 H), 5.58 (d, *J* = 9.3 Hz, 1 H), 1.44 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.8, 138.3, 132.3, 129.9, 118.0, 114.9, 113.7, 82.0, 63.3, 28.1. IR (KBr): ν = 3368, 3328, 2974, 2235, 1707, 1592, 1504, 1246, 1167, 838 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{14}H_{15}N_3O_4Cl_2Na$: 382.0332, found: 382.0330.



Tert-butyl 1-(3-bromo-4-methoxyphenyl)-2,2-dichloro-2-nitroethylcarbamate (**3o**): white solid, yield 79%, mp 169-171 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62 (d, *J* = 2.4 Hz, 1 H), 7.35 (dd, *J* = 2.4, 8.4 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 5.91 (d, *J* = 9.3 Hz, 1 H), 5.50 (d, *J* = 9.3 Hz, 1 H), 3.93 (s, 3 H), 1.45 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 153.9, 133.4, 129.5, 126.5, 115.7, 111.9, 111.6, 81.7, 62.8, 56.3, 28.1. IR (KBr): ν = 3271, 2984, 1698, 1585, 1367, 1163, 1020, 901, 775 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{14}H_{17}N_2O_5Cl_2BrNa$: 466.9567, found: 466.9562.



Tert-butyl 2,2-dichloro-1-(naphthalen-1-yl)-2-nitroethylcarbamate (**3p**): white solid, yield 56%, mp 197-199 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.41 (d, *J* = 7.8 Hz, 1 H), 7.91-7.97 (m, 2 H), 7.64-7.73 (m, 2 H), 7.52-7.60 (m, 2 H), 7.06 (d, *J* = 9.9 Hz, 1 H), 5.69 (d, *J* = 9.0 Hz, 1 H), 1.42 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.1, 133.7, 132.0, 130.7, 130.4, 129.0, 127.3, 126.3, 125.3, 125.0, 123.3, 116.4, 81.5, 57.5, 28.1. IR (KBr): ν = 3242, 3137, 2974, 1694, 1585, 1364, 1156, 776 cm^{-1}. HRMS [M+Na$^+$]: calcd for $C_{17}H_{18}N_2O_4Cl_2Na$: 407.0536, found: 407.0525.

3. X-ray crystal structure of compound 3a

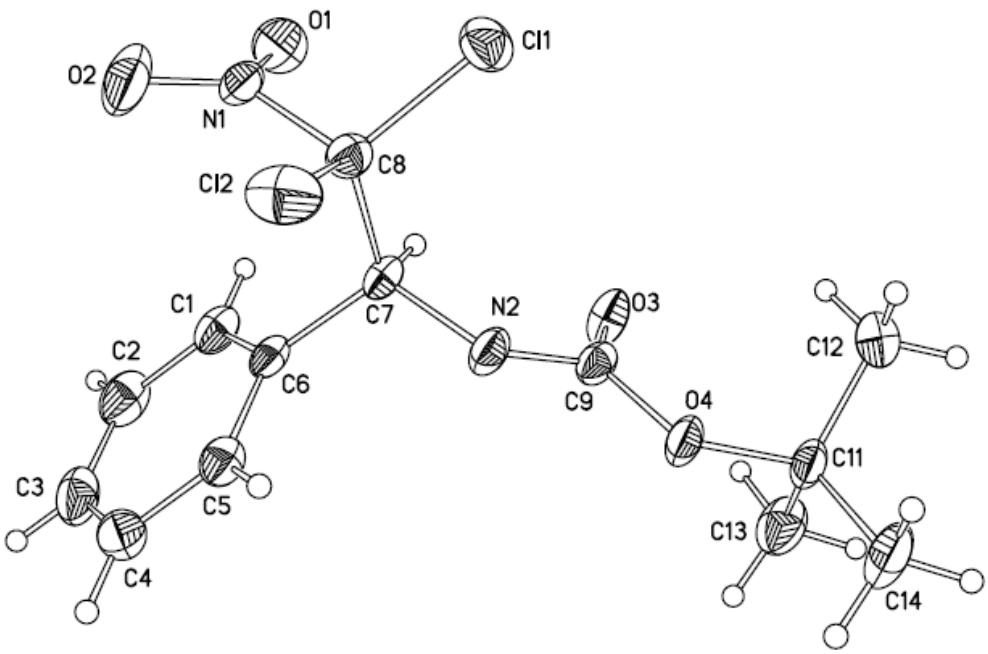


Figure 1 X-ray crystal structure of compound **3a** (CCDC number 820793)

4. Aminohalogenation of *β*-nitrostyrene with $BocNH_2$ and NCS

Into an oven-dried reaction vial flushed with N_2 were taken *β*-nitrostyrenes (0.5 mmol), K_2CO_3 (0.1 mmol), $BocNCl_2$ (1.5 mmol), NCS (1.5 mmol) and anhydrous MeCN (5.0 mL). The reaction mixture was stirred at room temperature for 12 h, and then the reaction was quenched with saturated Na_2SO_3 (3.0 mL). The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by TLC plate (hexane/EtOAc, 8:1).

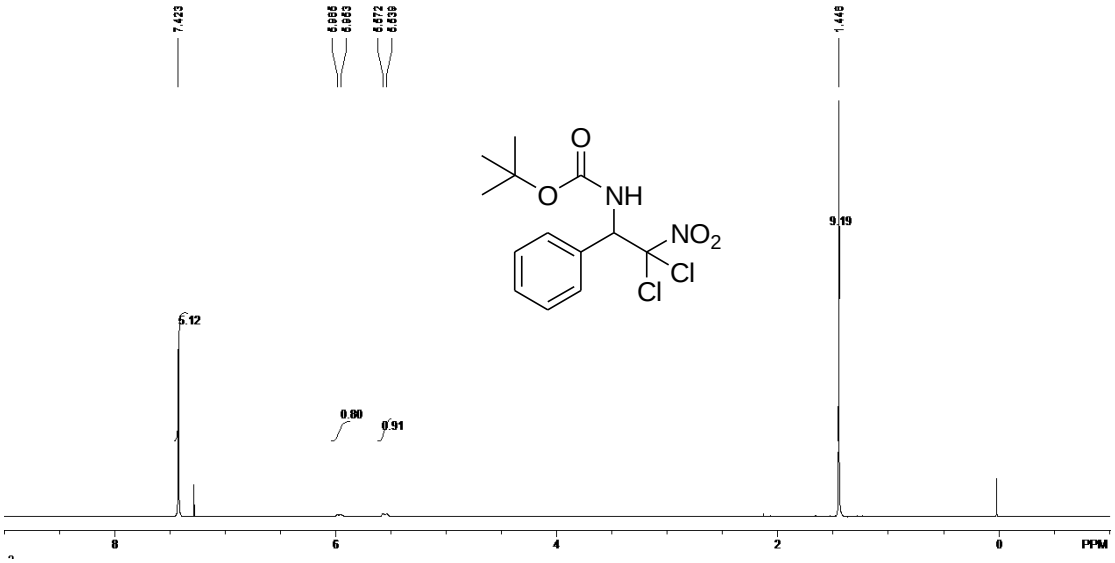
Reference

[1] White, R. E.; Kovacic, P.; *J. Am. Chem. Soc.* **1975**, 1180.

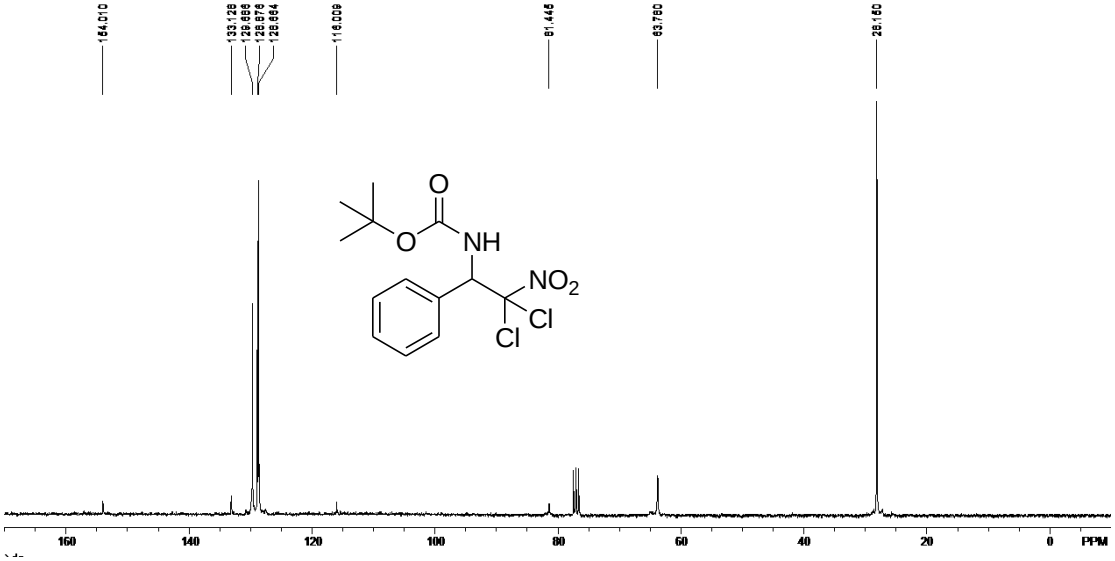
[2] Bowman, R. K.; Johnson, J. S. *J. Org. Chem.* **2004**, *69*, 8537.

5. ^{1}H and ^{13}C NMR spectra for compound 3

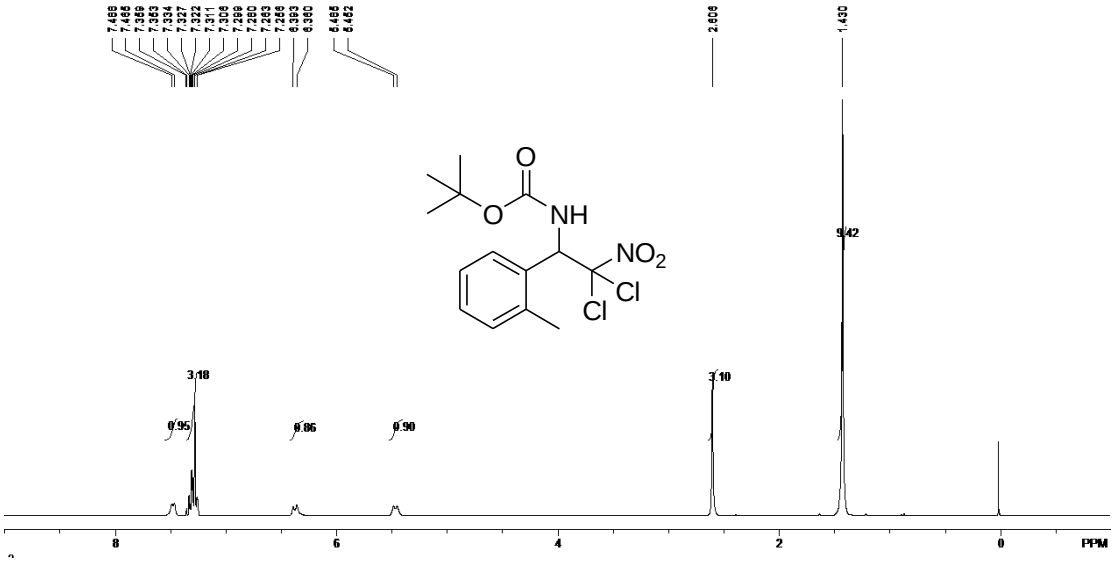
^{1}H NMR of **3a** ($CDCl_3$, 300 MHz)



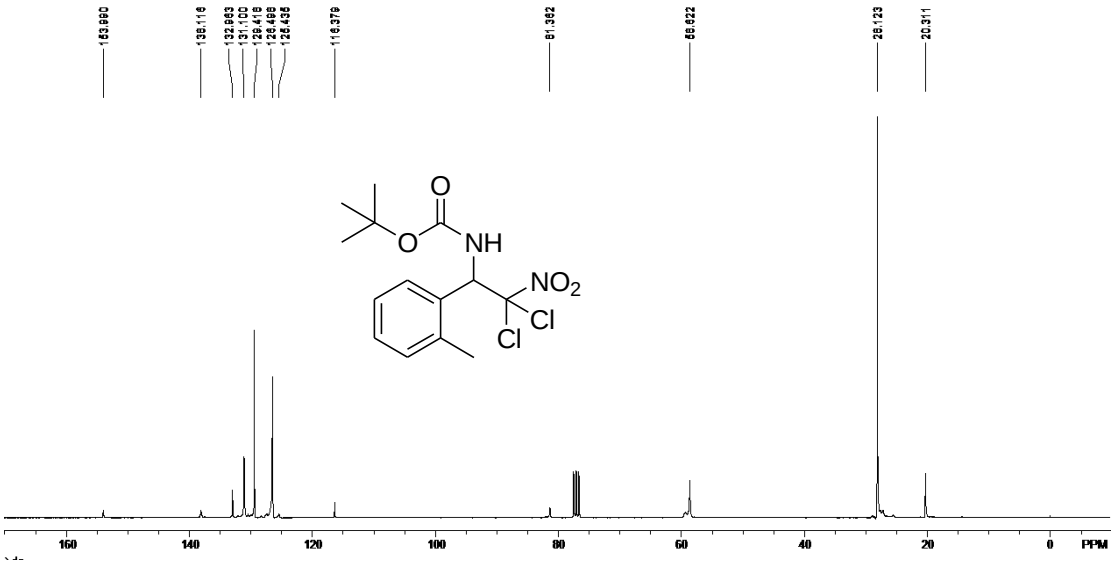
^{13}C NMR of **3a** ($CDCl_3$, 75 MHz)



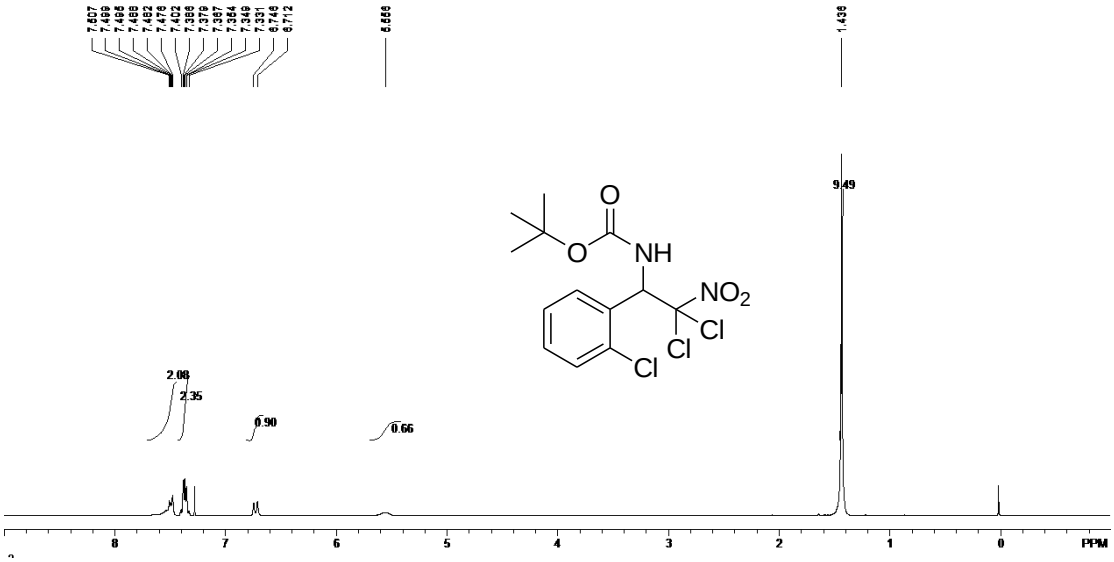
^{1}H NMR of **3b** ($CDCl_3$, 300 MHz)



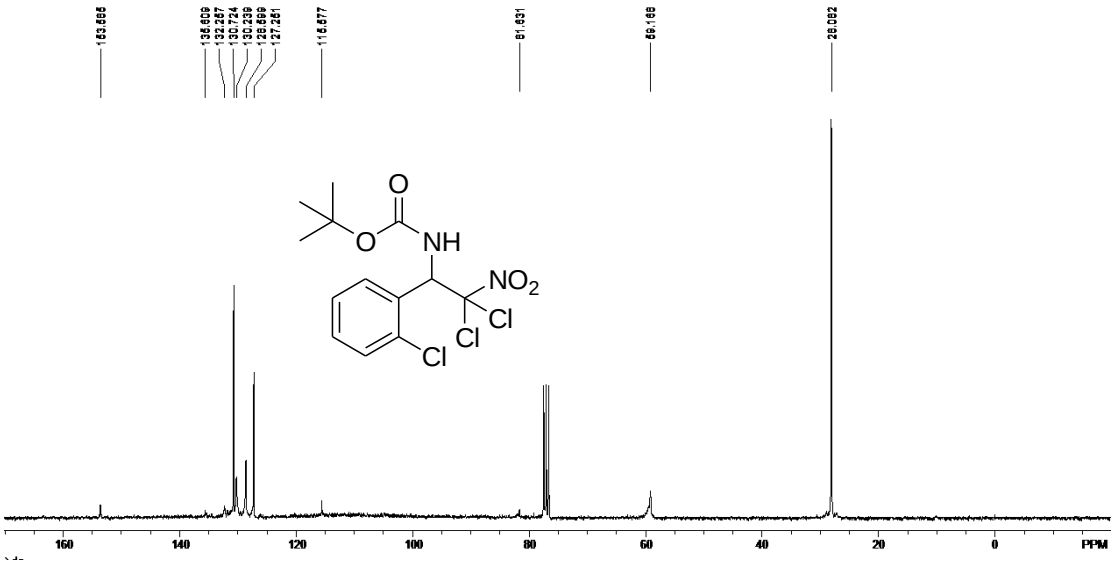
^{13}C NMR of **3b** ($CDCl_3$, 75 MHz)



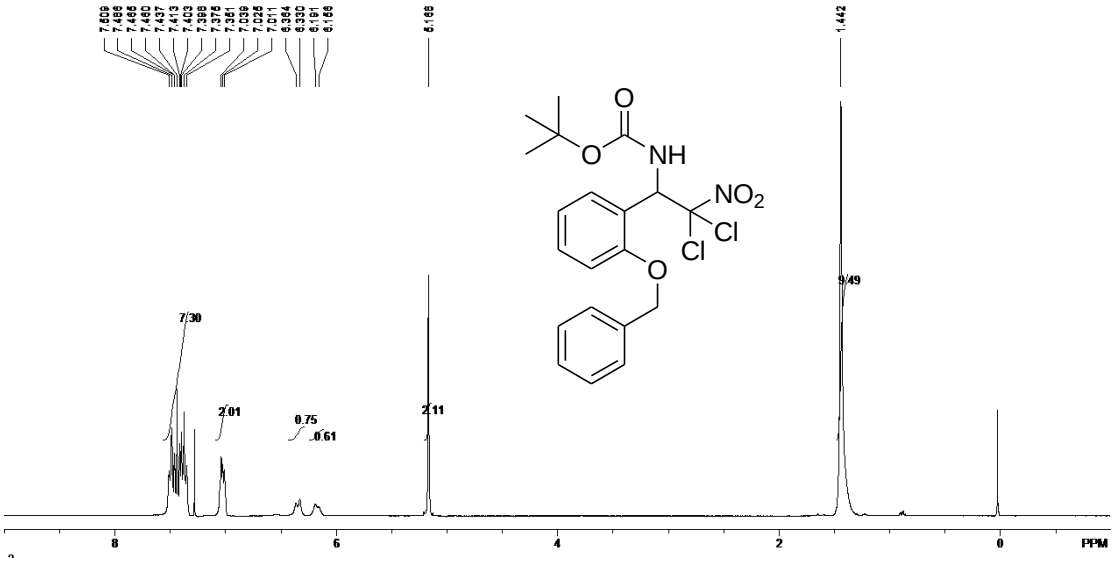
^{1}H NMR of **3c** ($CDCl_3$, 300 MHz)



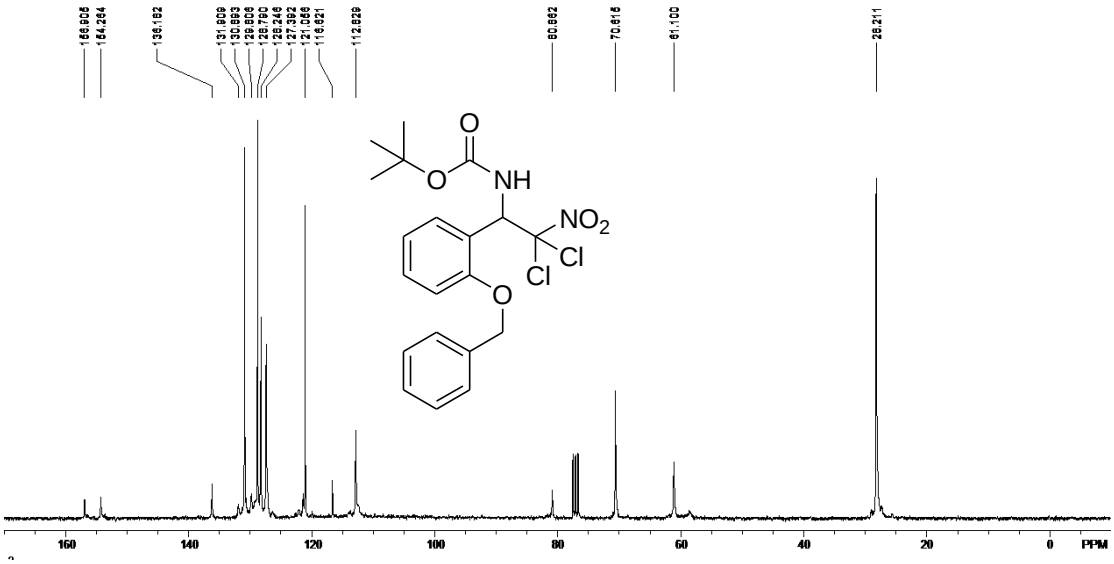
^{13}C NMR of **3c** ($CDCl_3$, 75 MHz)



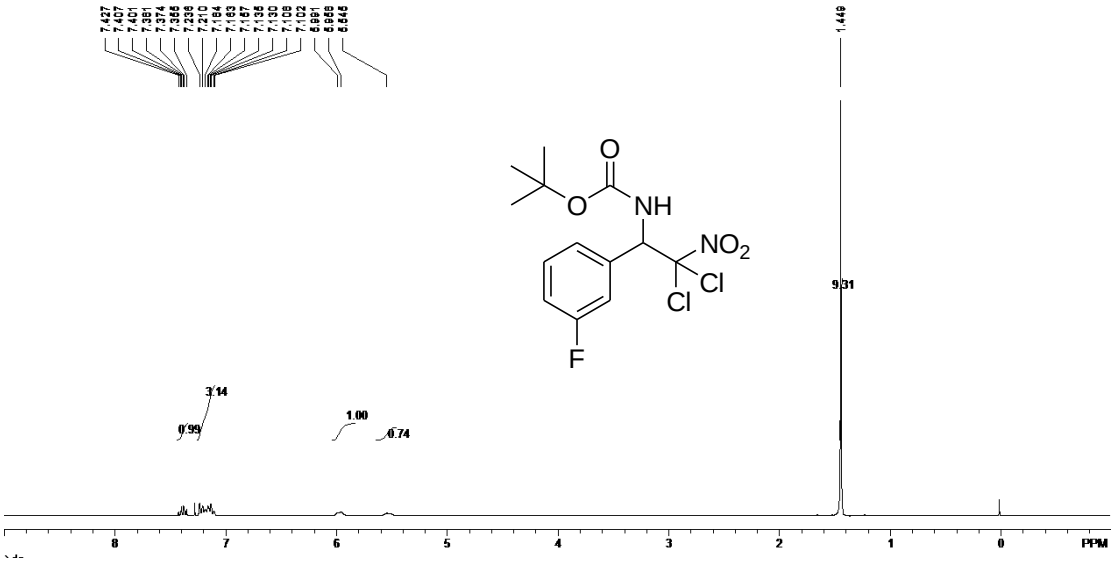
^{1}H NMR of **3d** ($CDCl_3$, 300 MHz)



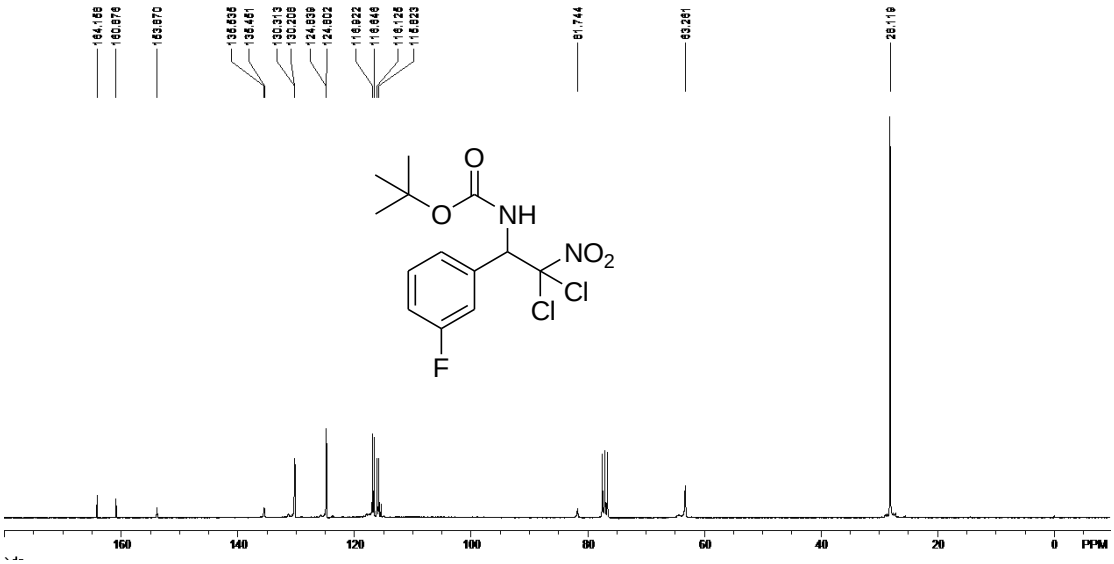
^{13}C NMR of **3d** ($CDCl_3$, 75 MHz)



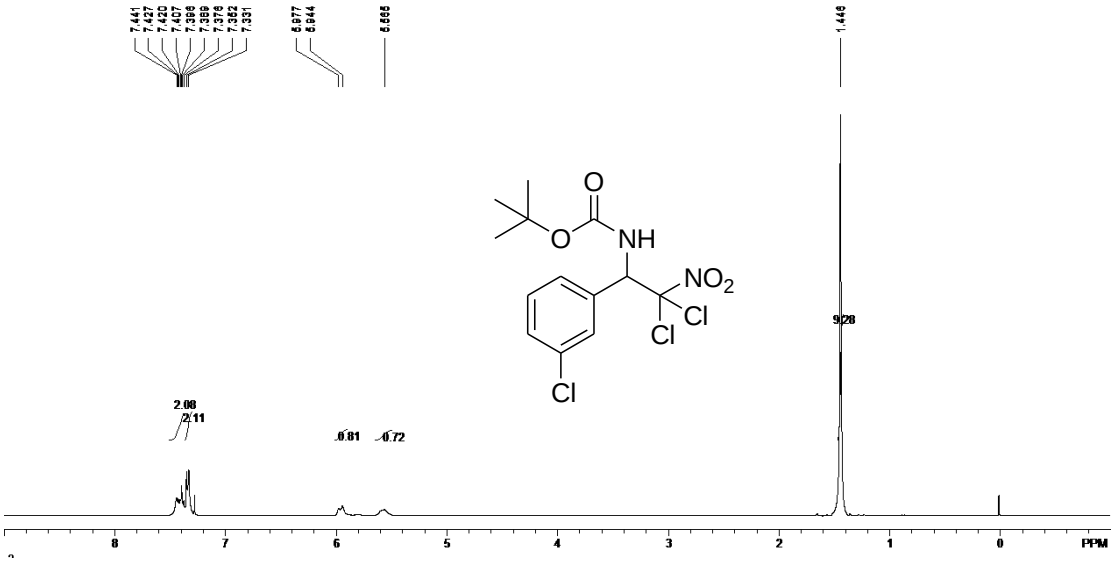
^{1}H NMR of **3e** ($CDCl_3$, 300 MHz)



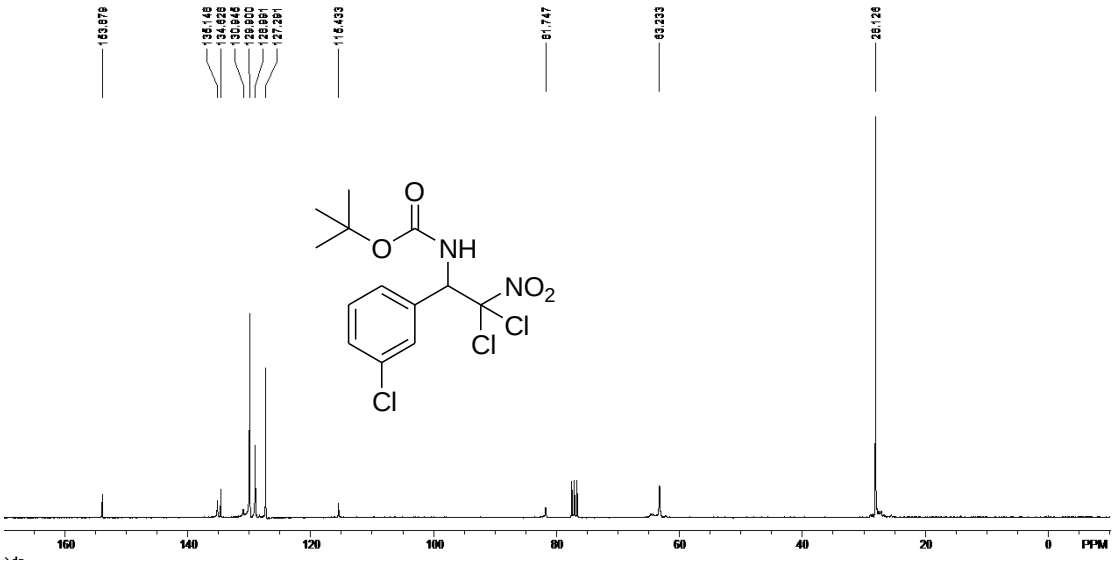
^{13}C NMR of **3e** ($CDCl_3$, 75 MHz)



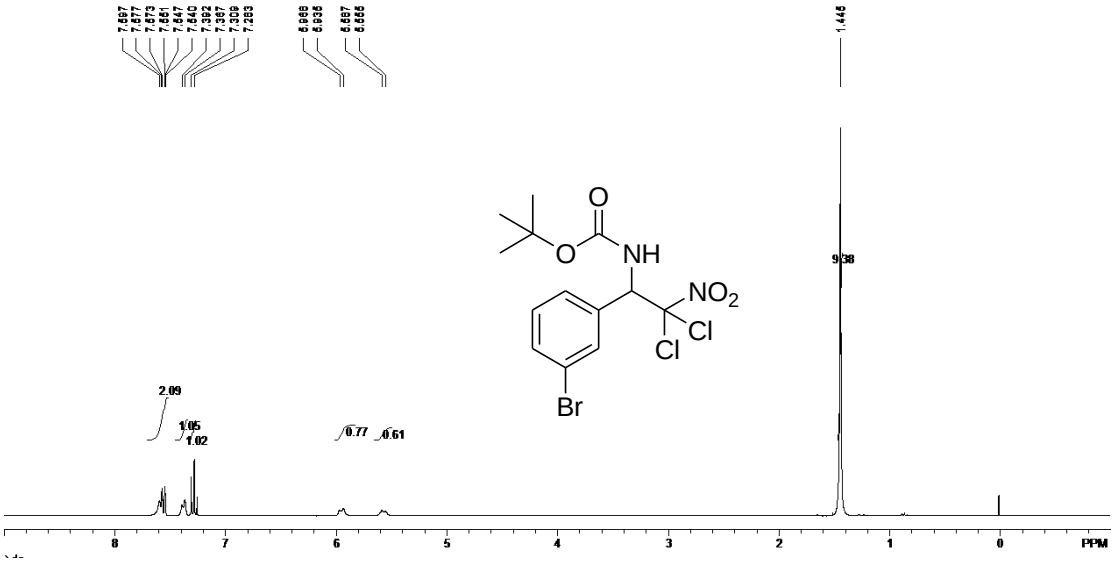
^{1}H NMR of **3f** ($CDCl_3$, 300 MHz)



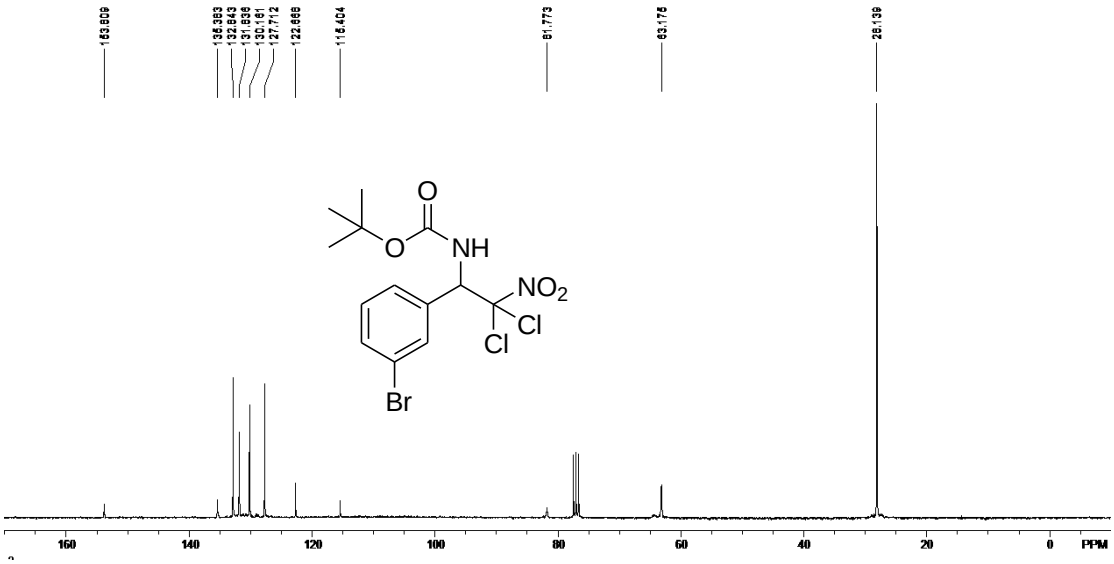
^{13}C NMR of **3f** ($CDCl_3$, 75 MHz)



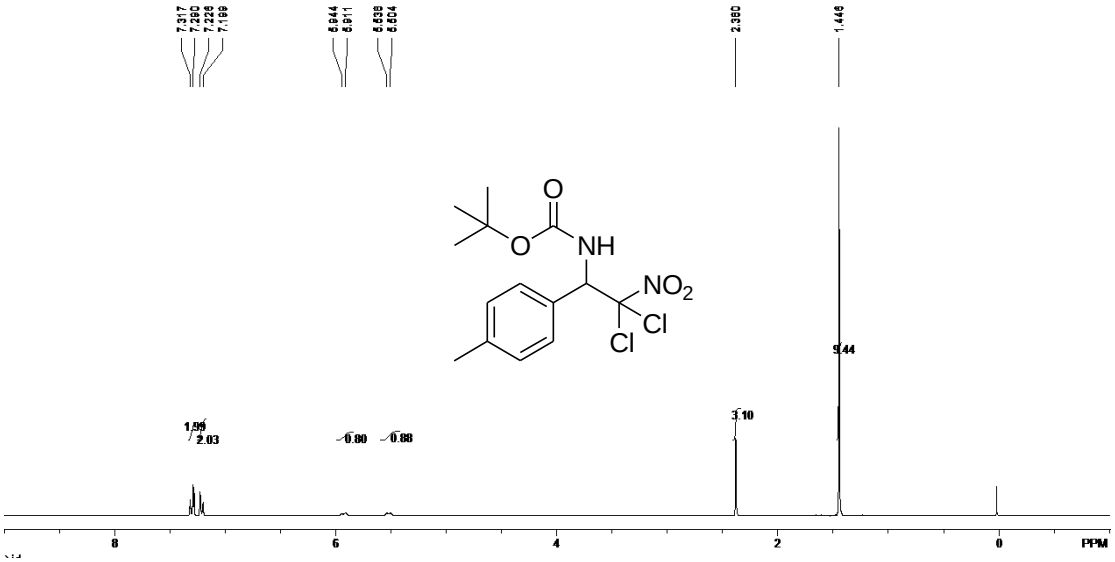
^{1}H NMR of **3g** ($CDCl_3$, 300 MHz)



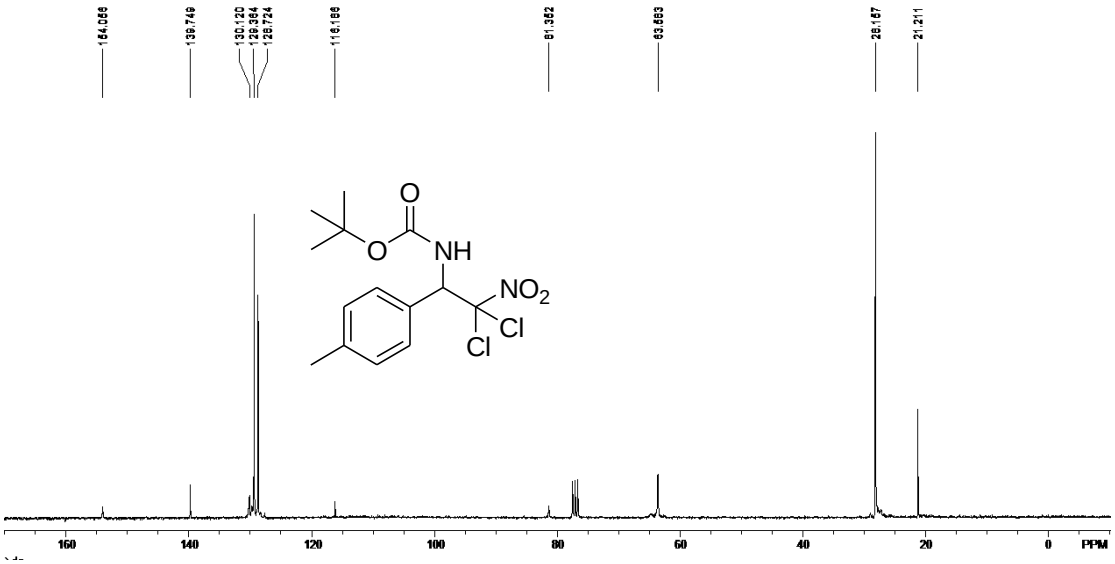
^{13}C NMR of **3g** ($CDCl_3$, 75 MHz)



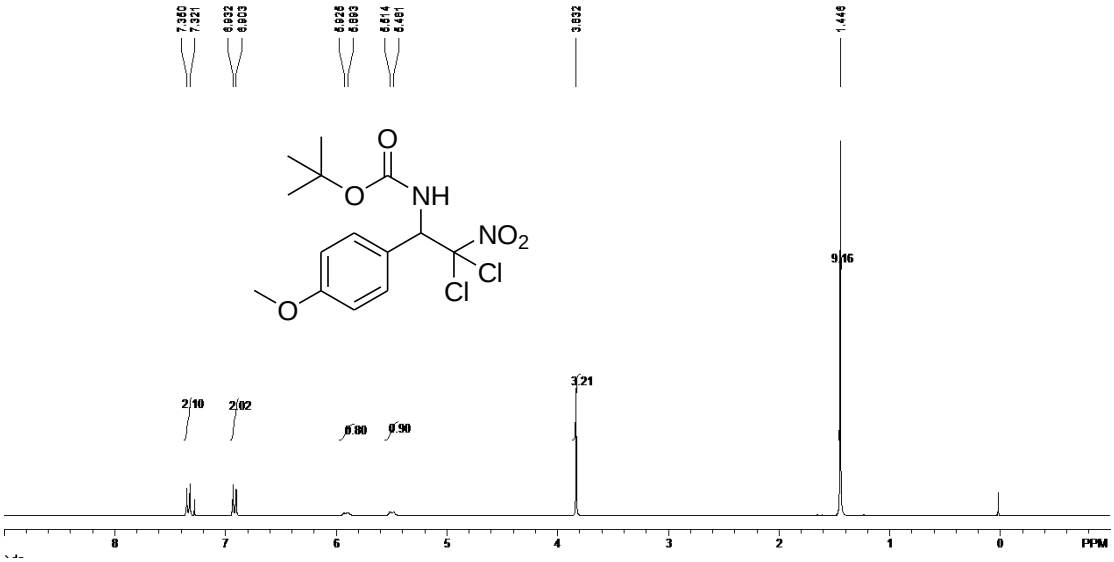
^{1}H NMR of **3h** ($CDCl_3$, 300 MHz)



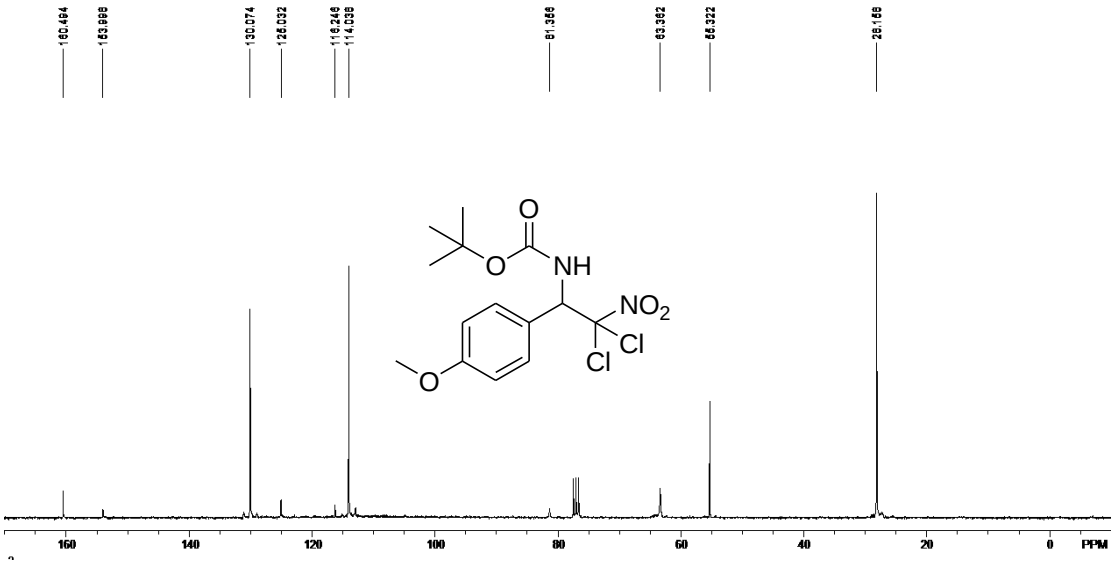
^{13}C NMR of **3h** ($CDCl_3$, 75 MHz)



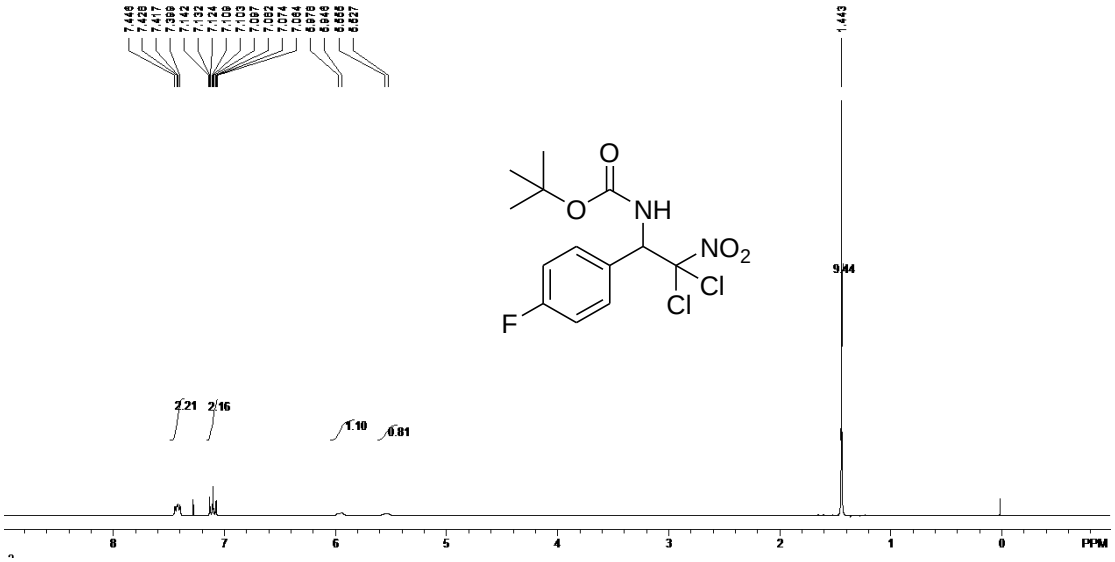
^{1}H NMR of **3i** ($CDCl_3$, 300 MHz)



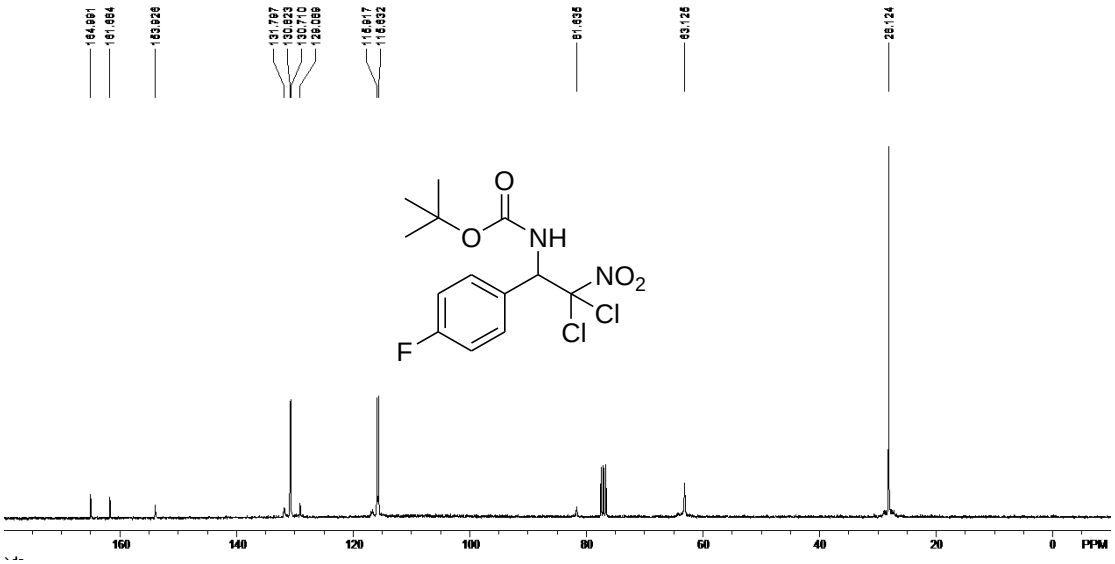
^{13}C NMR of **3i** ($CDCl_3$, 75 MHz)



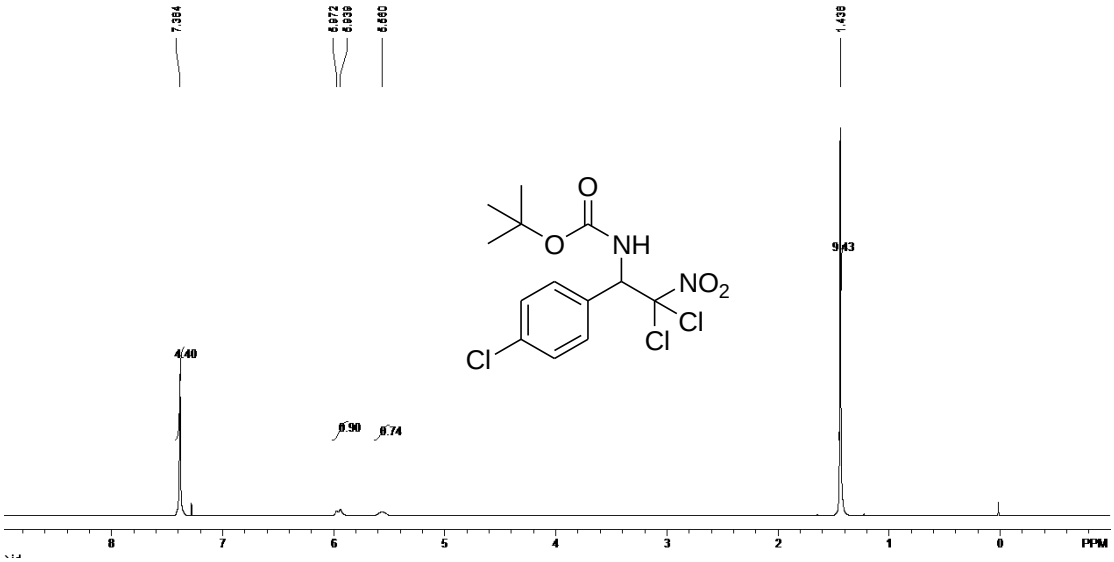
^{1}H NMR of **3j** ($CDCl_3$, 300 MHz)



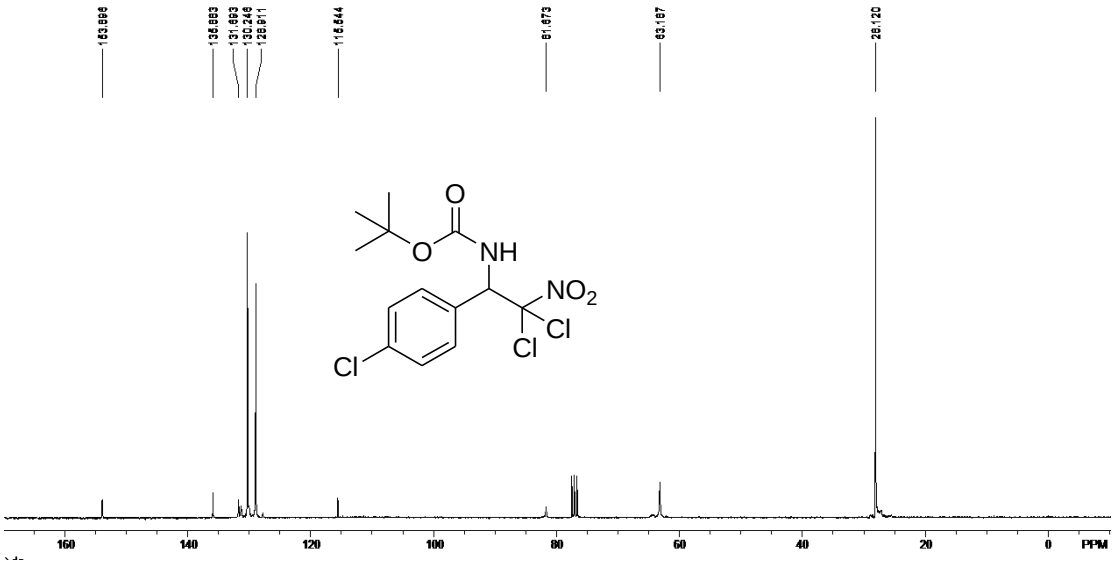
^{13}C NMR of **3j** ($CDCl_3$, 75 MHz)



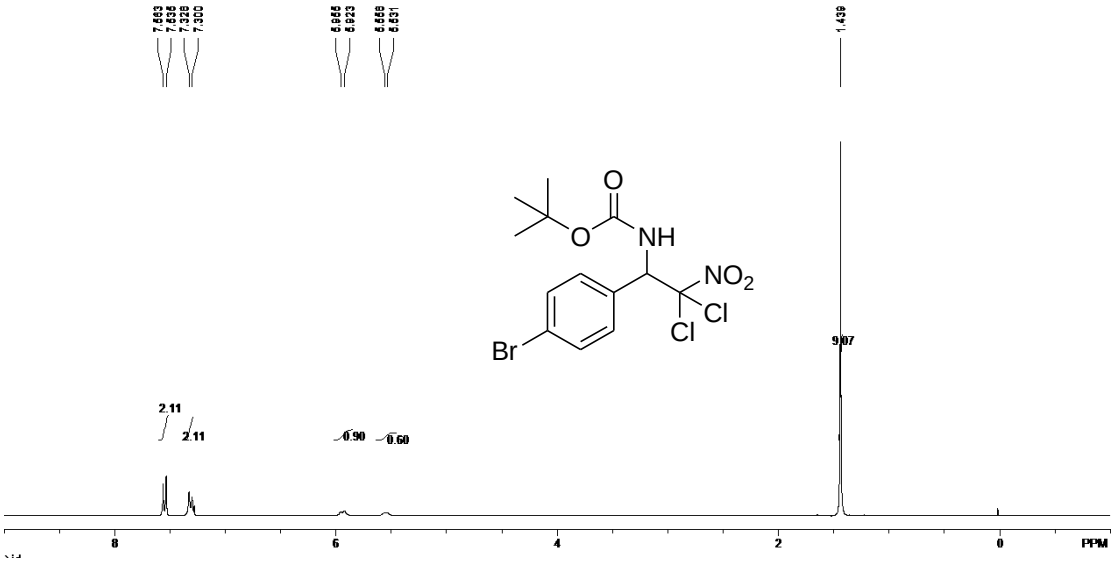
^{1}H NMR of **3k** ($CDCl_3$, 300 MHz)



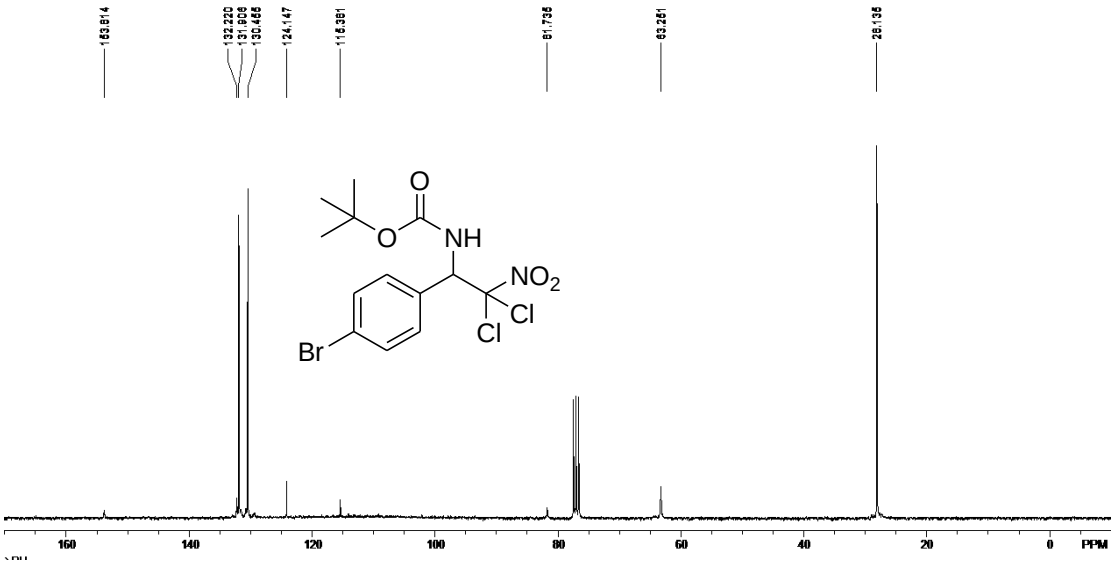
^{13}C NMR of **3k** ($CDCl_3$, 75 MHz)



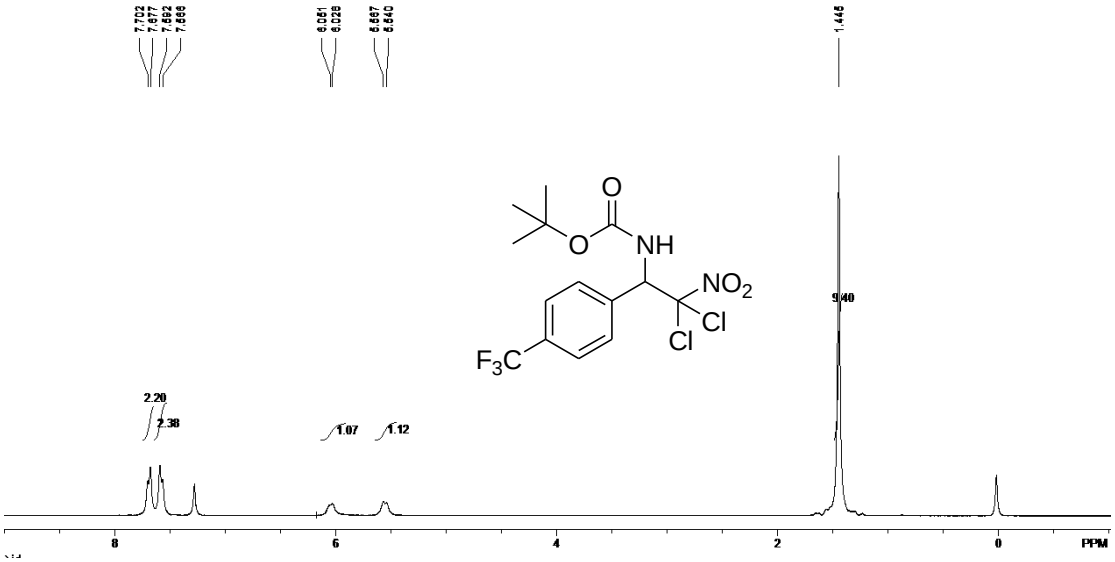
^{1}H NMR of **3l** ($CDCl_3$, 300 MHz)



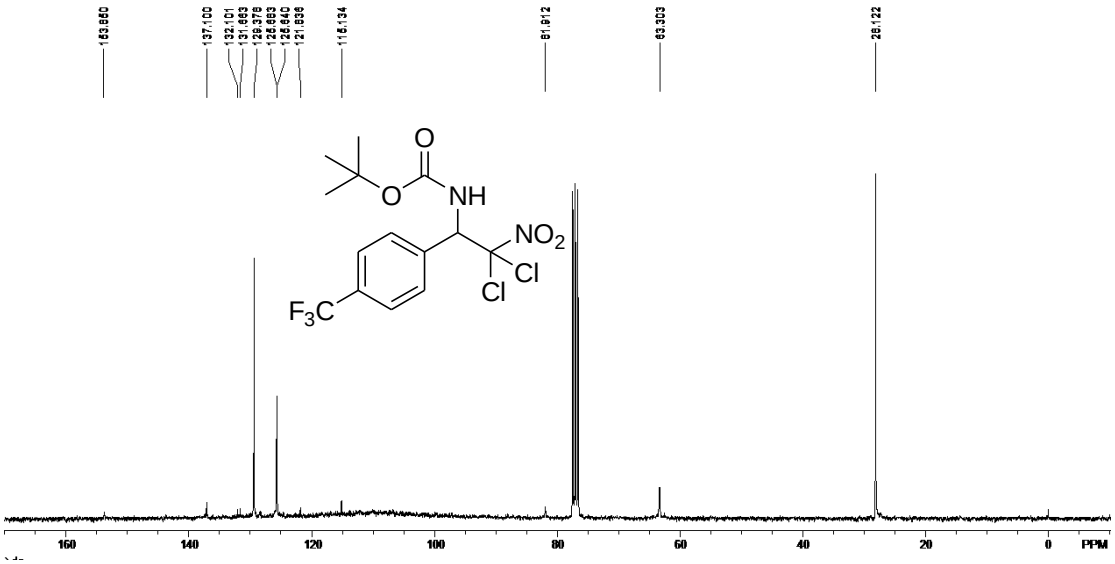
^{13}C NMR of **3l** ($CDCl_3$, 75 MHz)



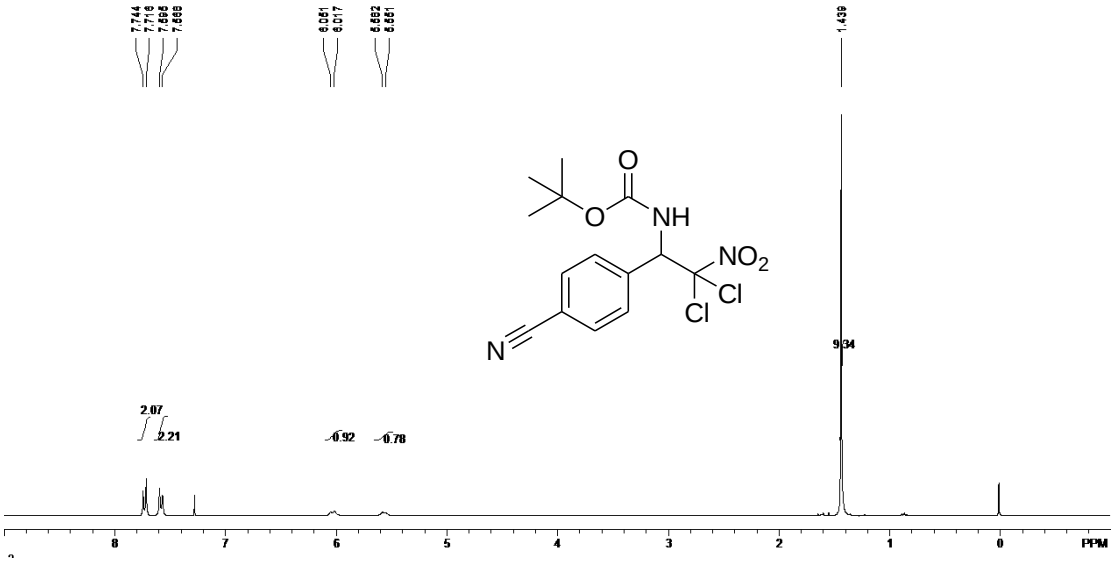
^{1}H NMR of **3m** ($CDCl_3$, 300 MHz)



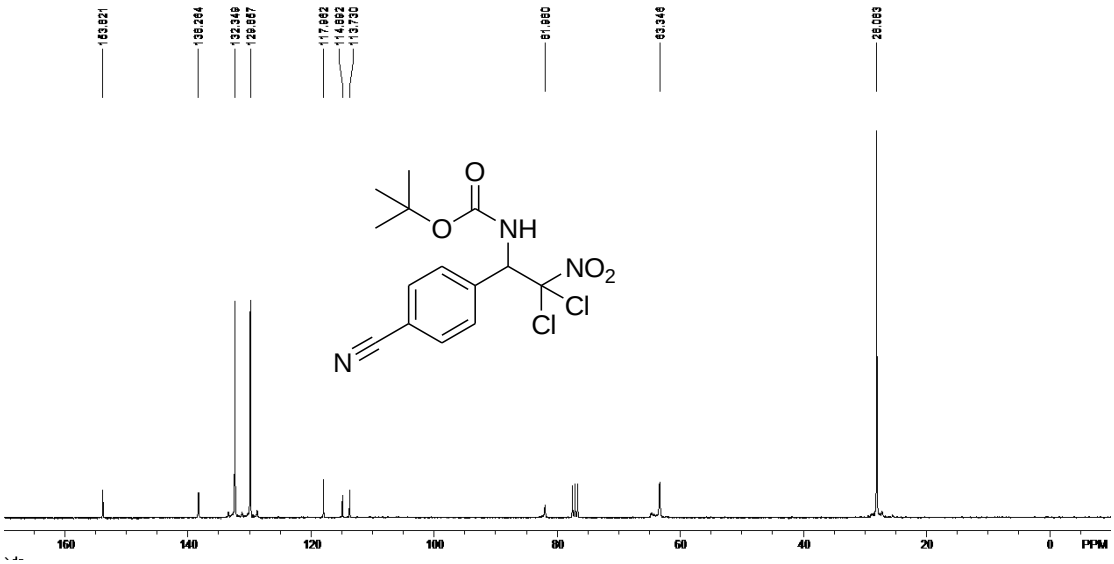
^{13}C NMR of **3m** ($CDCl_3$, 75 MHz)



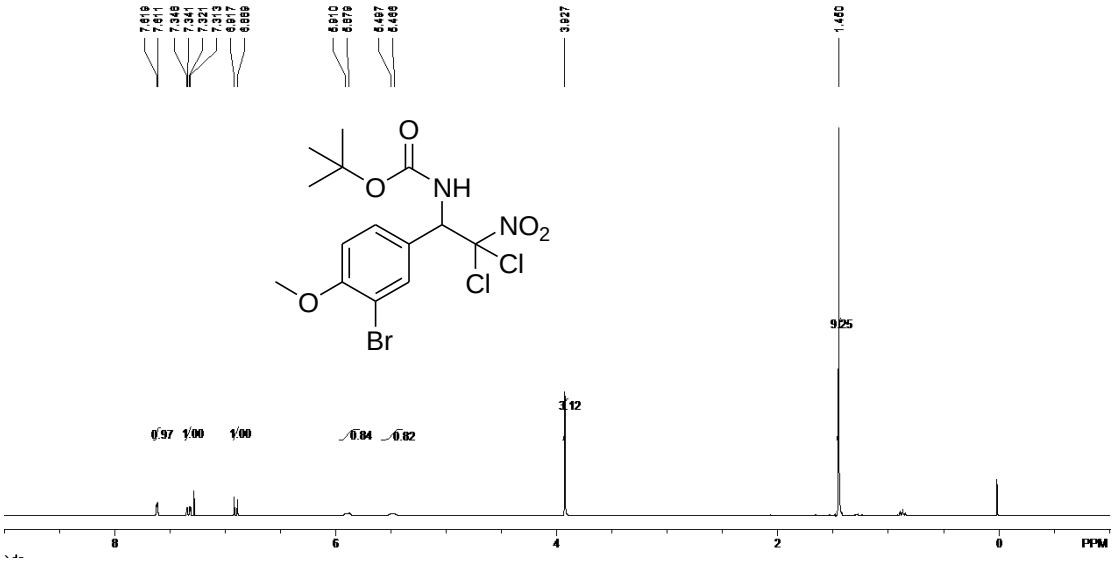
^{1}H NMR of **3n** ($CDCl_3$, 300 MHz)



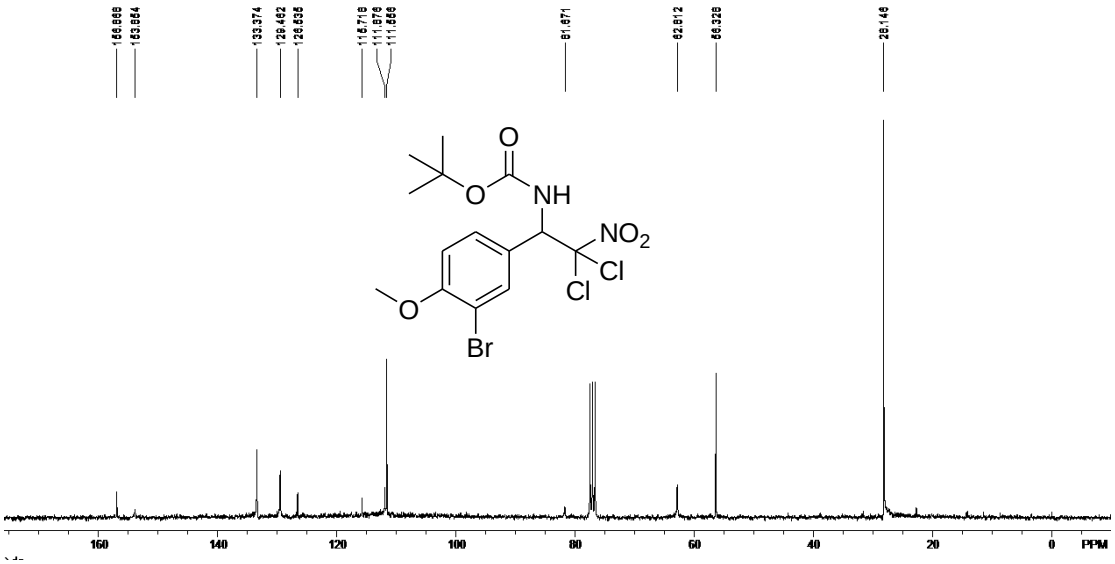
^{13}C NMR of **3n** ($CDCl_3$, 75 MHz)



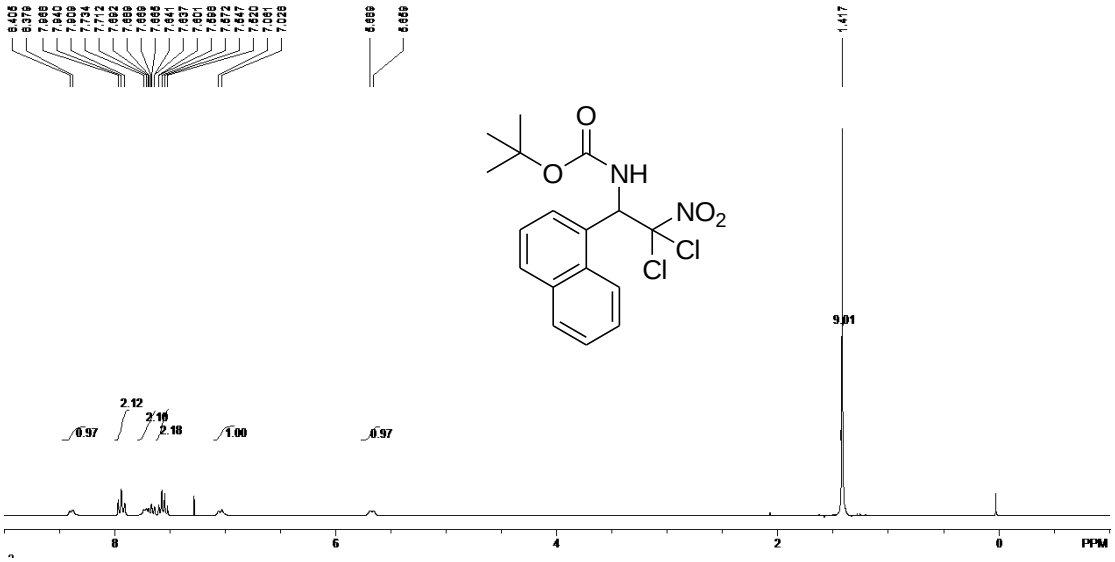
^{1}H NMR of **3o** ($CDCl_3$, 300 MHz)



^{13}C NMR of **3o** ($CDCl_3$, 75 MHz)



^{1}H NMR of **3p** ($CDCl_3$, 300 MHz)



^{13}C NMR of **3p** ($CDCl_3$, 75 MHz)