Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Na_3PO_4-catalyzed aminochlorination reaction of β-nitrostyrenes in water

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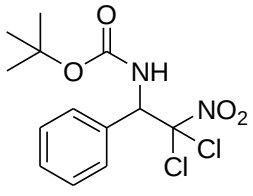
1. General information

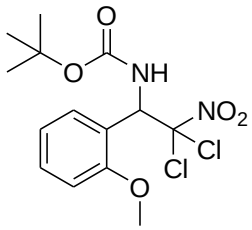
All aminohalogenation reactions were performed in vials at room temperature without protection of inert gases. $BocNCl_2$[1] was prepared according to the reported methods. The other chemicals were used as obtained from commercial sources without further purification. Flash chromatography was performed 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. Aminochlorination of β-nitrostyrenes with $BocNCl_2$

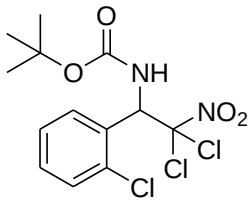
Into a reaction vial were taken β-nitrostyrenes (0.5 mmol), $Na_3PO_4 \cdot 12H_2O$ (0.1 mmol), $BocNCl_2$ (1.25 mmol), MeCN (1.6 mL) and H_2O (3.2 mL). The reaction mixture was stirred at room temperature for 12 min, and then the reaction was quenched with saturated Na_2SO_3 (3.0 mL). The organic layer 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).



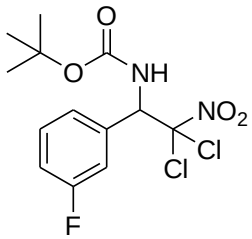
Tert-butyl 2,2-dichloro-2-nitro-1-phenylethylcarbamate (**3a**): white solid, yield 88%, mp 105-106 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42 (s, 5 H), 5.99 (d, *J* = 10.5 Hz, 1 H), 5.56 (d, *J* = 10.5 Hz, 1 H), 1.45 (s, 9 H).



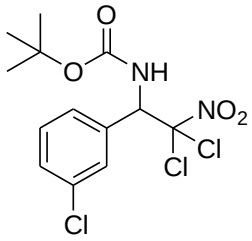
Tert-butyl 2,2-dichloro-1-(2-methoxyphenyl)-2-nitroethylcarbamate (**3b**): white solid, yield 97%, mp 152-154 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33-7.42 (m, 2 H), 6.94-7.03 (m, 2 H), 6.28 (d, *J* = 10.5 Hz, 1 H), 6.08 (d, *J* = 9.6 Hz, 1 H), 3.88 (s, 3 H)， 1.46 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.7, 154.3, 130.9, 130.6, 120.8, 116.5, 112.8, 111.6, 81.0, 61.0, 55.6, 28.2. IR (KBr): ν = 3253, 3142, 2978, 1697, 1585, 1365, 1249, 1160, 756 cm^{-1}. HRMS [M+Na^{+}]: calcd for $C_{14}H_{18}N_2O_5Cl_2Na$: 387.0485, found: 387.0490.



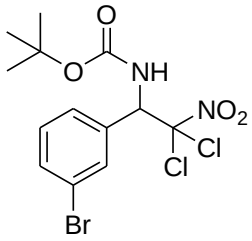
Tert-butyl 2,2-dichloro-1-(2-chlorophenyl)-2-nitroethylcarbamate (**3c**): white solid, yield 98%, mp 168-170 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48-7.51 (m, 2 H), 7.33-7.40 (m, 2 H), 6.75 (d, *J* = 10.2 Hz, 1 H), 5.58 (d, *J* = 10.2 Hz, 1 H), 1.44 (s, 9 H).



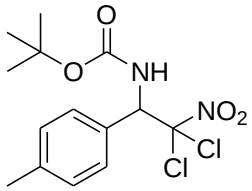
Tert-butyl 2,2-dichloro-1-(3-fluorophenyl)-2-nitroethylcarbamate (**3d**): white solid, yield 87%, mp 115-117 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35-7.43 (m, 1 H), 7.10-7.24 (m, 3 H), 5.99 (d, *J* = 8.7 Hz, 1 H), 5.55 (s, 1 H), 1.45 (s, 9 H).



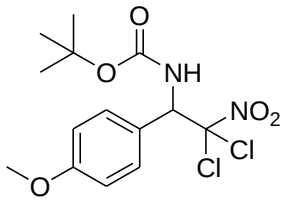
Tert-butyl 2,2-dichloro-1-(3-chlorophenyl)-2-nitroethylcarbamate (**3e**): white solid, yield 73%, mp 136-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33-7.45 (m, 4 H), 5.97 (d, *J* = 9.3 Hz, 1 H), 5.58 (s, 1H), 1.45 (s, 9 H).



Tert-butyl 1-(3-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (**3f**): white solid, yield 86%, mp 152-154 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55-7.60 (m, 2 H), 7.39 (d, *J* = 7.2 Hz, 1 H), 7.31 (d, *J* = 7.8 Hz, 1 H), 5.96 (d, *J* = 9.0 Hz, 1 H), 5.57 (d, *J* = 8.7 Hz, 1 H), 1.45 (s, 9 H).

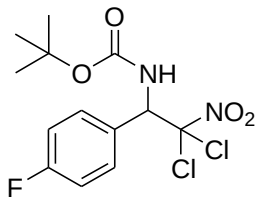


Tert-butyl 2,2-dichloro-2-nitro-1-p-tolylethylcarbamate (**3g**): white solid, yield 83%, mp 108-110 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (d, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 5.95 (d, *J* = 9.9 Hz, 1 H), 5.58 (d, *J* = 9.0 Hz, 1 H), 2.38 (s, 3 H), 1.45 (s, 9 H).

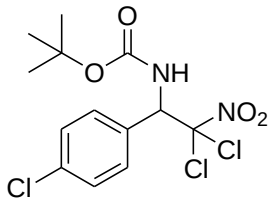


Tert-butyl 2,2-dichloro-1-(4-methoxyphenyl)-2-nitroethylcarbamate (**3h**): white solid,

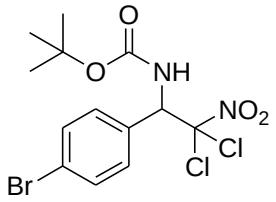
yield 77%, mp 113-114 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (d, *J* = 8.7 Hz, 2 H), 6.93 (d, *J* = 9.0 Hz, 2 H), 5.93 (d, *J* = 9.3 Hz, 1 H), 5.54 (d, *J* = 9.9 Hz, 1 H), 3.83 (s, 3 H), 1.45 (s, 9 H).



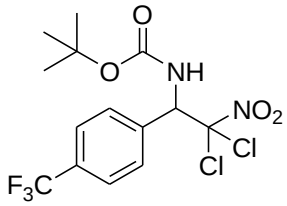
Tert-butyl 2,2-dichloro-1-(4-fluorophenyl)-2-nitroethylcarbamate (**3i**): white solid, yield 85%, mp 109-110 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40-7.44 (m, 2 H), 7.08-7.13 (m, 2 H), 5.97 (d, *J* = 9.6 Hz, 1 H), 5.55 (d, *J* = 9.9 Hz, 1 H), 1.44 (s, 9 H).



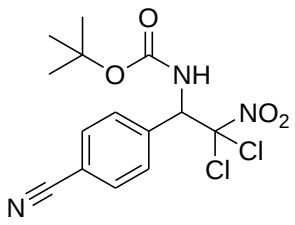
Tert-butyl 2,2-dichloro-1-(4-chlorophenyl)-2-nitroethylcarbamate (**3j**): white solid, yield 94%, mp 101-102 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (s, 4 H), 5.96 (d, *J* = 8.7 Hz, 1 H), 5.54 (s, 1 H), 1.44 (s, 9 H).



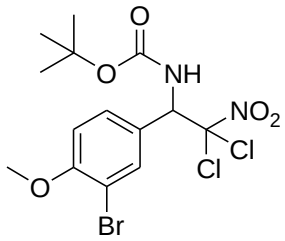
Tert-butyl 1-(4-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (**3k**): white solid, yield 78%, mp 106-107 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 5.95 (d, *J* = 9.9 Hz, 1 H), 5.52 (s, 1 H), 1.44 (s, 9 H).



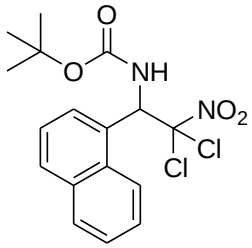
Tert-butyl 2,2-dichloro-2-nitro-1-(4-(trifluoromethyl)phenyl)ethylcarbamate (**3l**): white solid, yield 84%, mp 118-119 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 6.06 (d, *J* = 9.0 Hz, 1 H), 5.60 (d, *J* = 9.3 Hz, 1 H), 1.44 (s, 9 H).



Tert-butyl 2,2-dichloro-1-(4-cyanophenyl)-2-nitroethylcarbamate (**3m**): white solid, yield 96%, mp 129-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.74 (d, *J* = 7.5 Hz, 2 H), 7.60 (d, *J* = 5.7 Hz, 2 H), 6.04 (d, *J* = 5.1 Hz, 1 H), 5.63 (d, *J* = 4.8 Hz, 1 H), 1.43 (s, 9 H).



Tert-butyl 1-(3-bromo-4-methoxyphenyl)-2,2-dichloro-2-nitroethylcarbamate (**3n**): white solid, yield 90%, mp 169-171 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62 (s, 1 H), 7.34 (d, *J* = 7.2 Hz, 1 H), 6.92 (d, *J* = 8.7 Hz, 1 H), 5.91 (d, *J* = 7.8 Hz, 1 H), 5.51 (d, *J* = 7.8 Hz, 1 H), 3.92 (s, 3 H), 1.45 (s, 9 H).



Tert-butyl 2,2-dichloro-1-(naphthalen-1-yl)-2-nitroethylcarbamate (**3o**): white solid, yield 61%, mp 198-199 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.40 (d, *J* = 6.6 Hz, 1 H),

7.97 (t, *J* = 8.4 Hz, 2 H), 7.64-7.72 (m, 2 H), 7.52-7.60 (m, 2 H), 7.06 (d, *J* = 8.7 Hz, 1 H), 5.70 (d, *J* = 9.0 Hz, 1 H), 1.42 (s, 9 H).

3. Aminochlorination of β-nitrostyrene with $BocNH_2$ and NCS

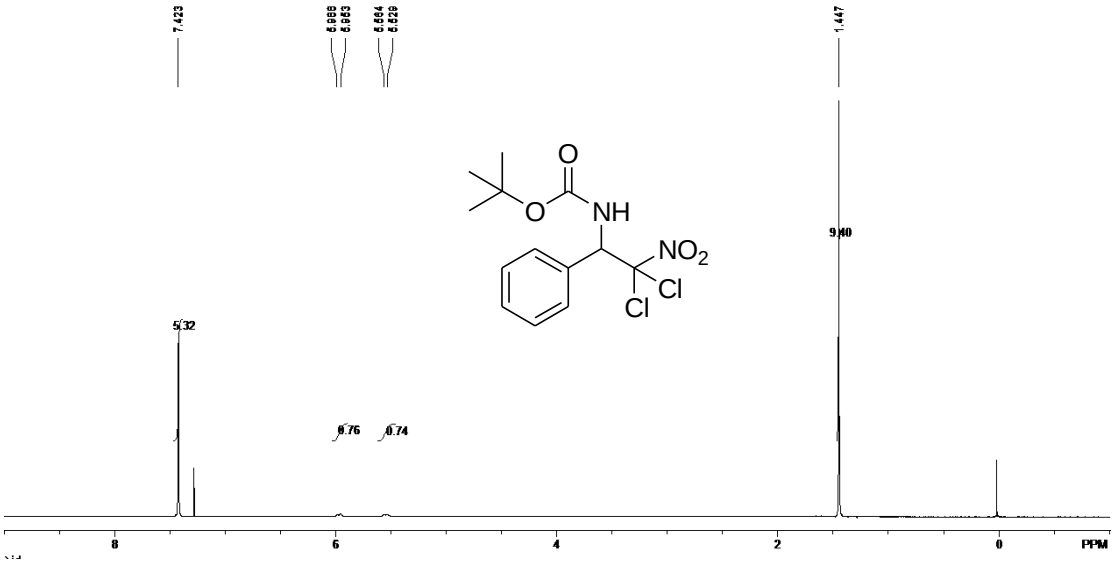
Into a reaction vial were taken β-nitrostyrenes (0.5 mmol), $Na_3PO_4 \cdot 12H_2O$ (0.1 mmol), $BocNH_2$ (1.5 mmol), NCS (1.5 mmol), MeCN (1.6 mL) and H_2O (3.2 mL). The reaction mixture was stirred at room temperature for 48 h, and then the reaction was quenched with saturated Na_2SO_3 (3.0 mL). The 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

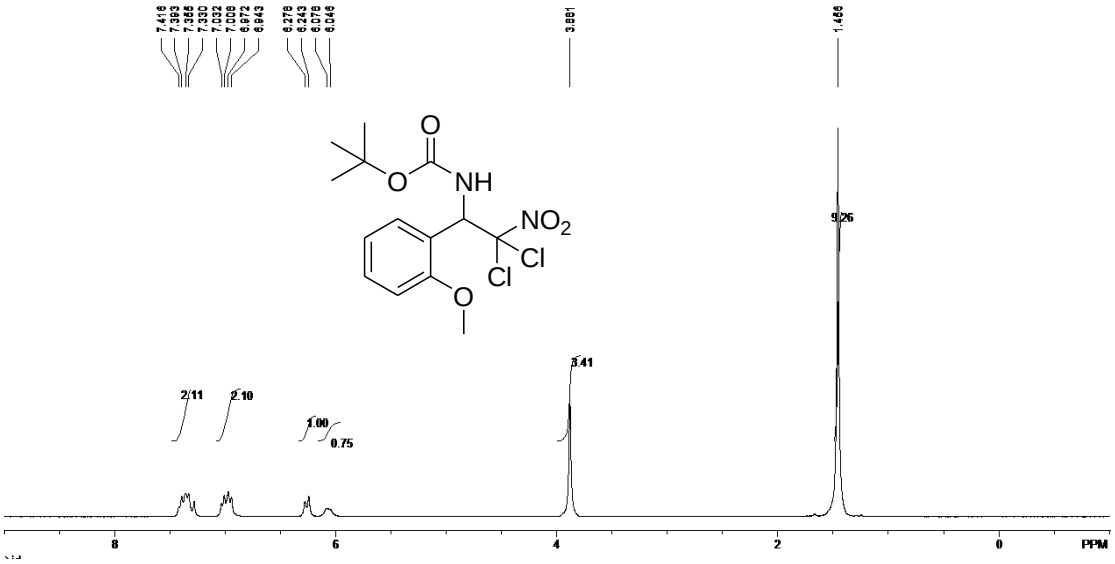
1 R. E. White and P. Kovacic, *J. Am. Chem. Soc.*, 1975, **97**, 1180.

4. ^{1}H and ^{13}C NMR spectra for compound 3

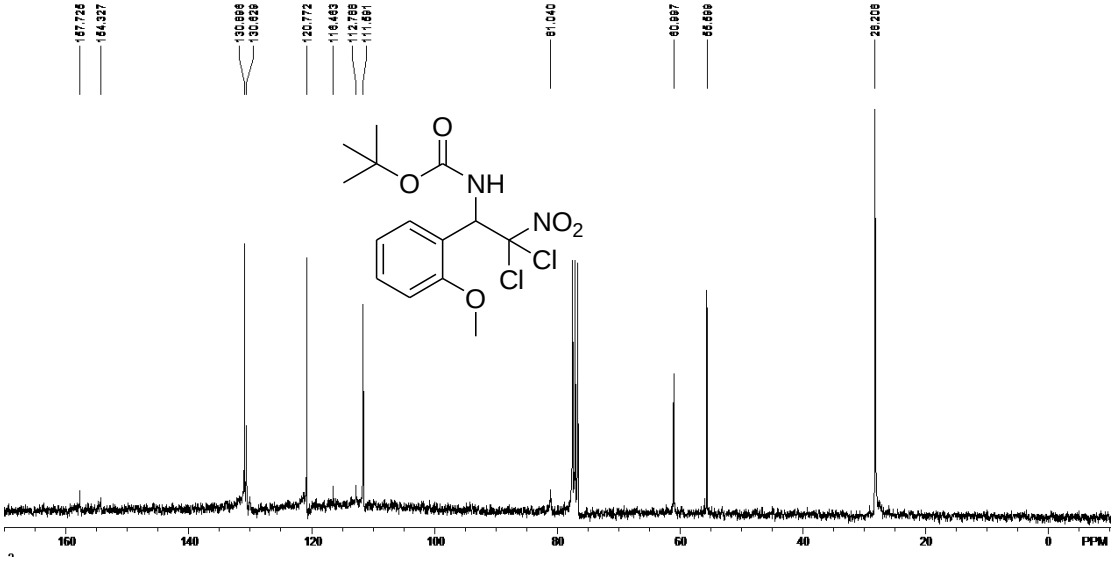
^{1}H NMR of **3a**



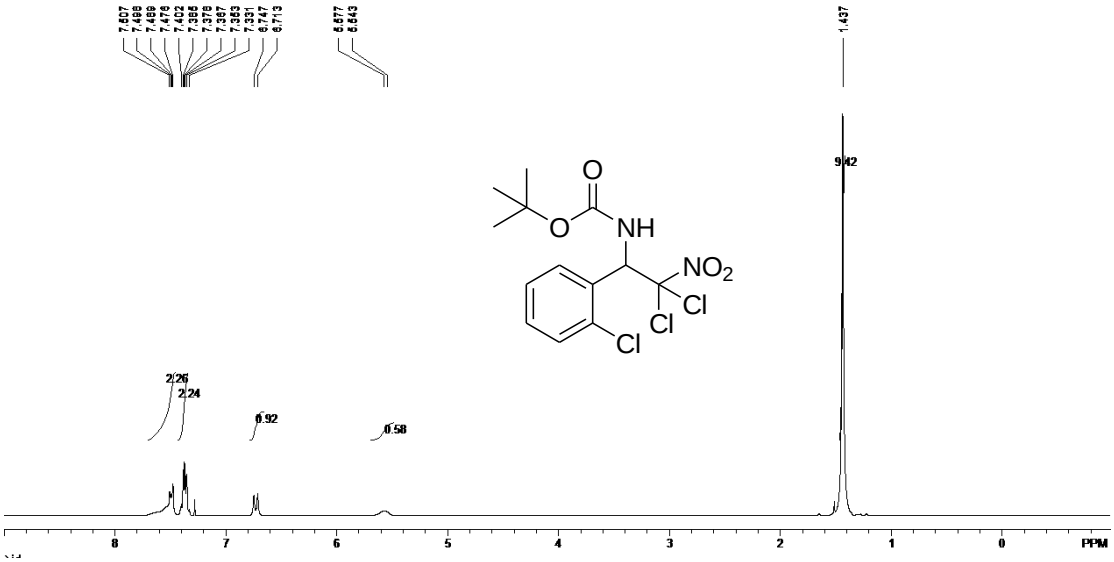
^{1}H NMR of **3b**



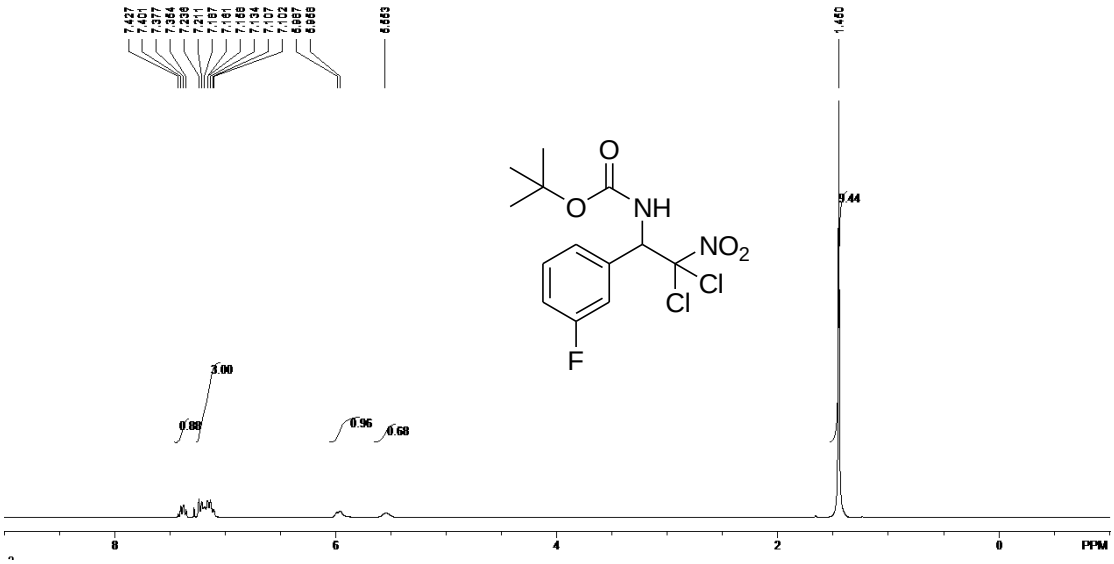
^{13}C NMR of **3b**



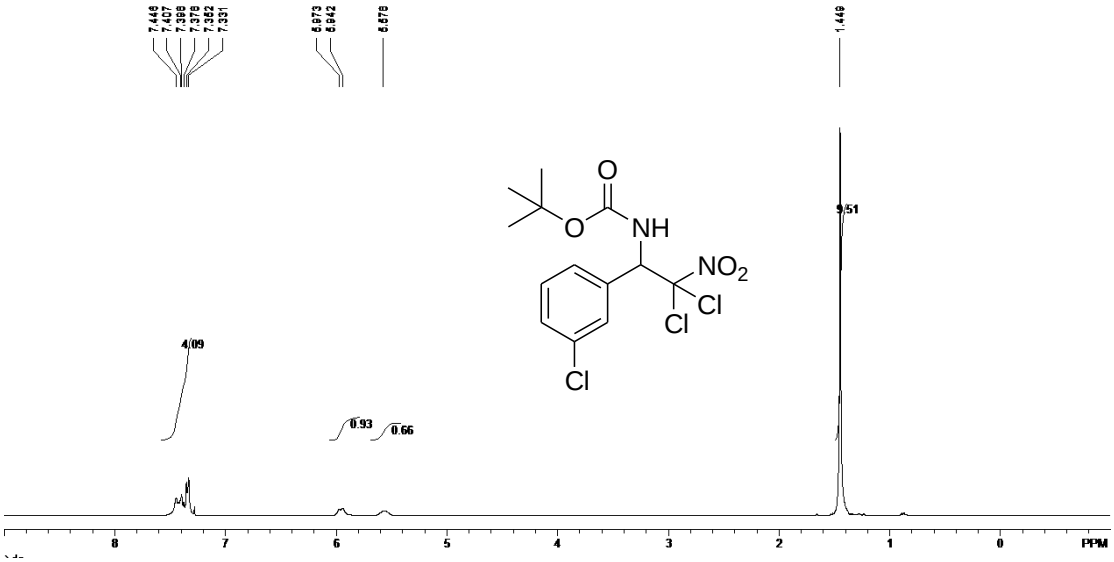
^{1}H NMR of **3c**



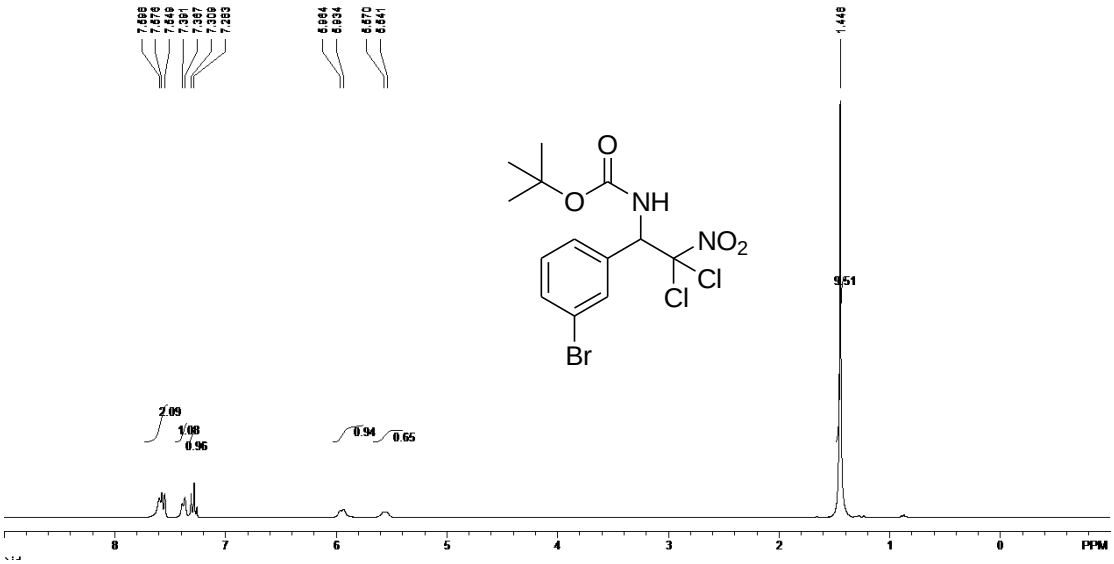
^{1}H NMR of **3d**



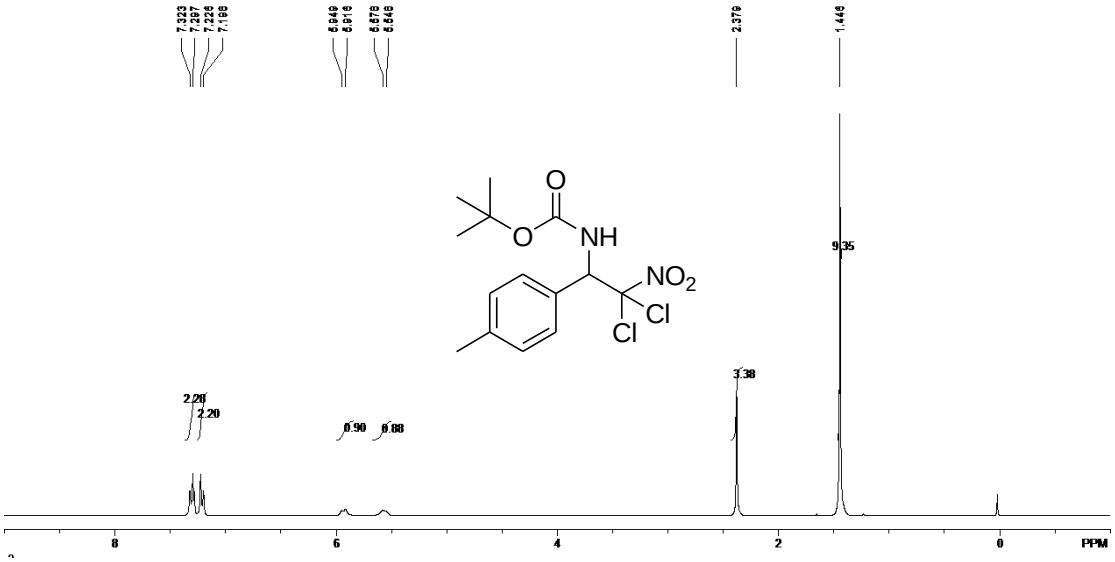
^{1}H NMR of **3e**



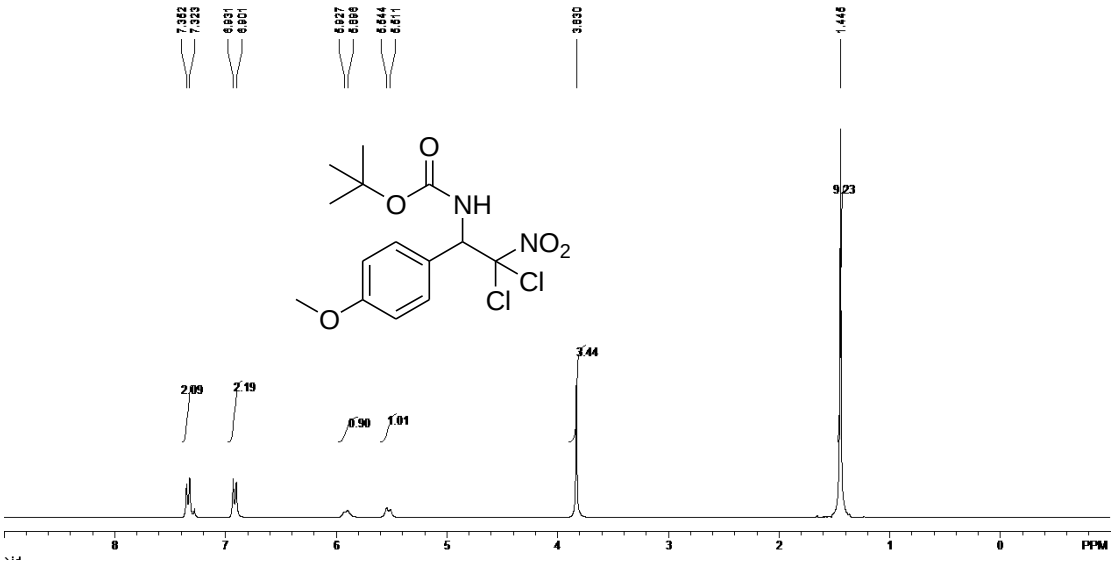
^{1}H NMR of **3f**



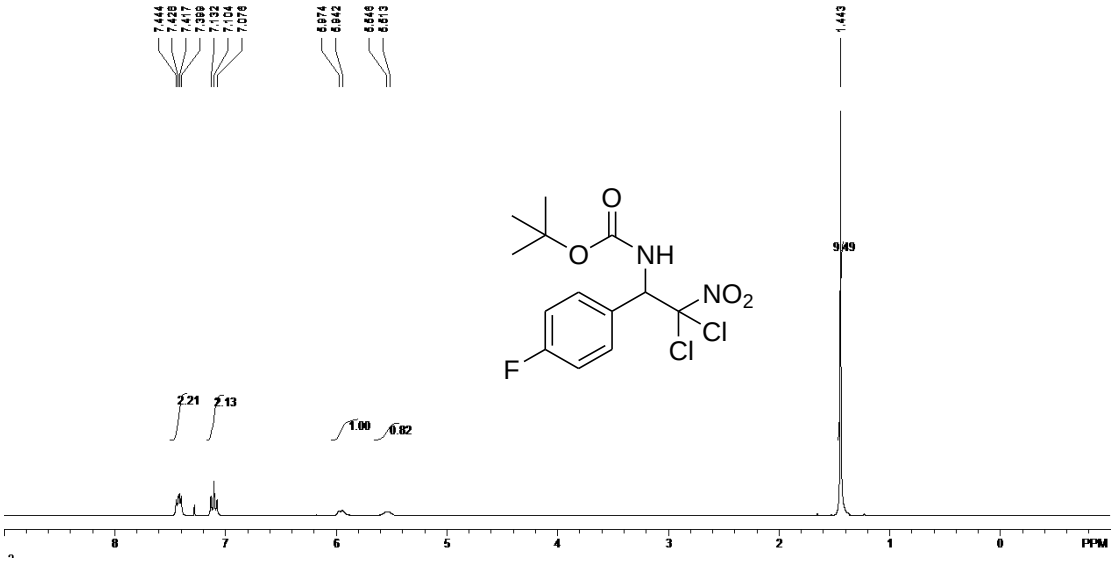
^{1}H NMR of **3g**



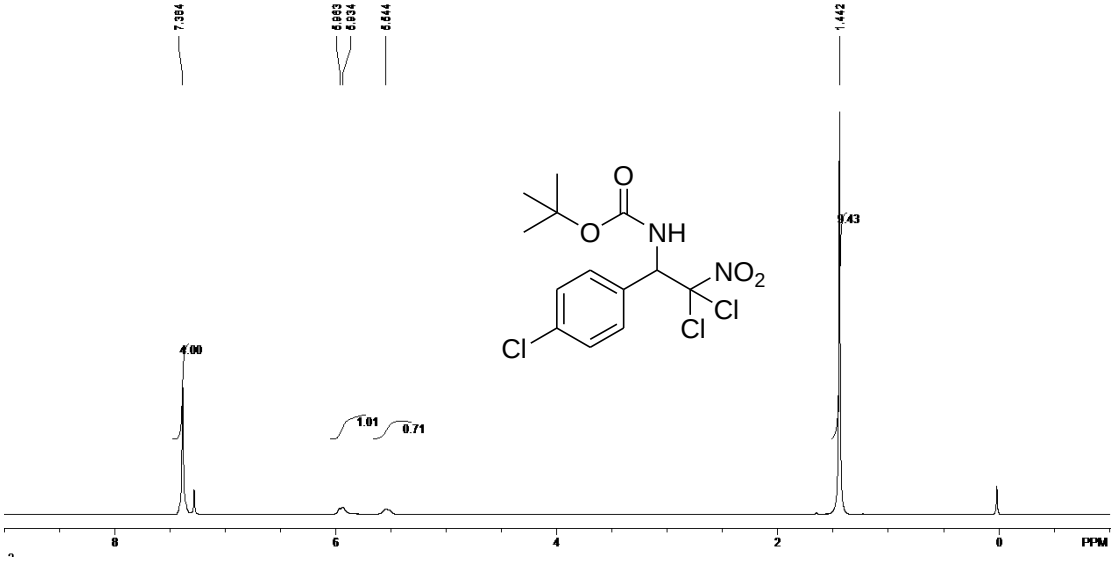
^{1}H NMR of **3h**



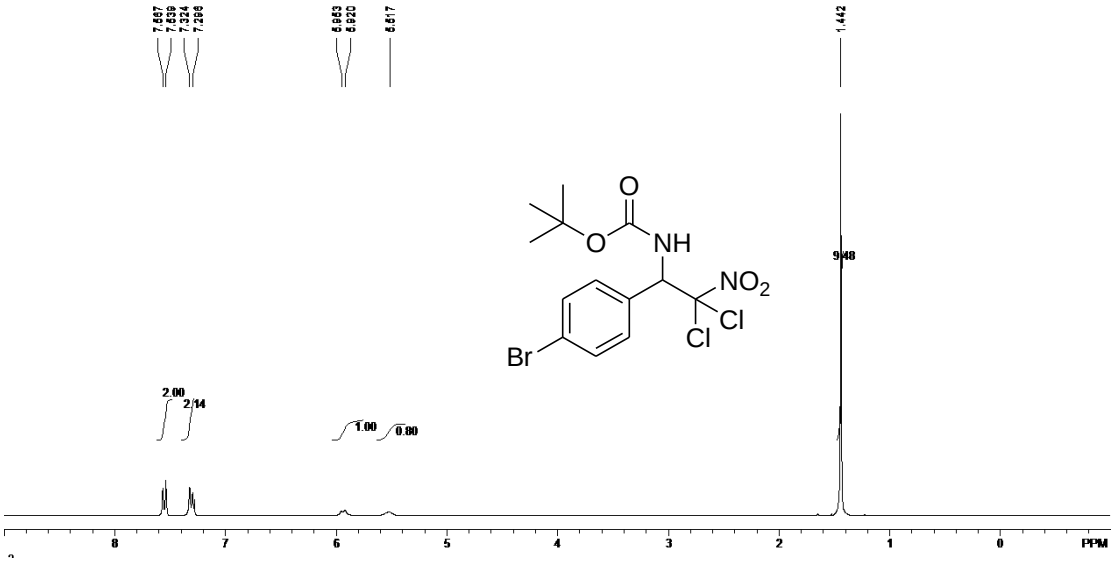
^{1}H NMR of **3i**



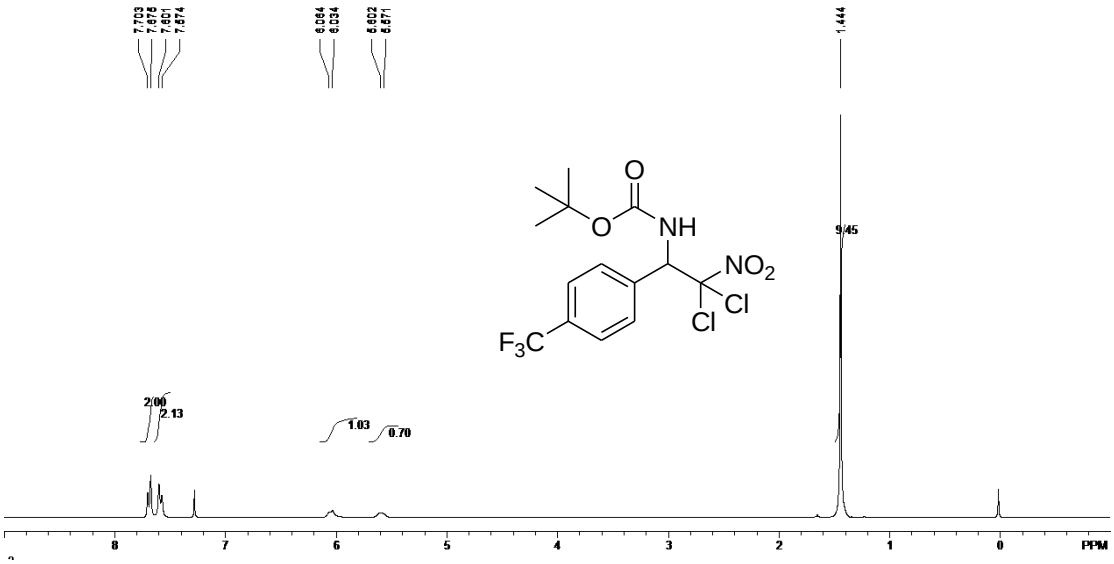
^{1}H NMR of **3j**



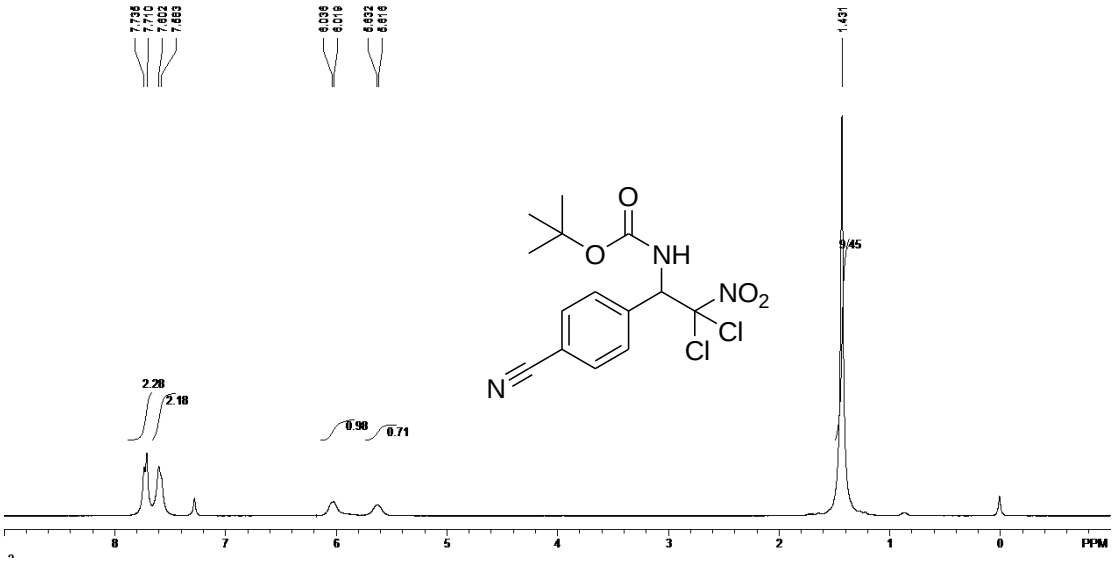
^{1}H NMR of **3k**



^{1}H NMR of **3l**



^{1}H NMR of **3m**



^{1}H NMR of **3n**