Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary information

Organic amines-mediated free-radical carbocyclization reactions of 2,2,2-trihalogeno substituted *N*-(2-alkynylphenyl)acetamides

Tsung-Han Chuang and Che-Ping Chuang*

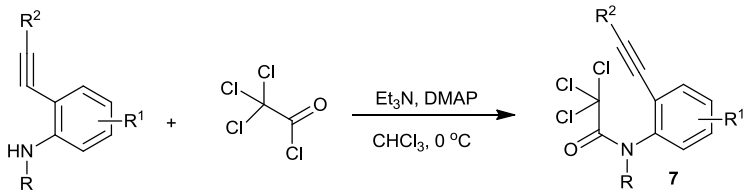
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China.
Fax: +886-6-2740552; E-mail: cpchuang@mail.ncku.edu.tw

Contents

Experimental Section

General considerations: Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the ^{13}C NMR signals was determined by means of DEPT 135 experiments. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102A mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh).

1) Experimental details and characterization data of starting *N*-(2-alkynylphenyl)-2,2,2-trichloroacetamides 7.



Typical procedure for the preparation of *N*-(alkynylphenyl)-2,2,2-trichloroacetamides 7:

A solution of *N*-benzyl-2-(phenylethynyl)phenylamine (1.08 g, 3.81 mmol), 2,2,2-trichloroacetylchloride (1.06 g, 5.83 mmol), triethylamine (603 mg, 5.96 mmol) and DMAP (49 mg, 0.40 mmol) in chloroform (20 mL) was stirred in an ice-water bath for 15 min. The reaction mixture was then diluted with 100 mL of ethyl acetate washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1:20 ethyl acetate–hexanes) to give 1.41 g (86%) of **7a**.

Based on ^{1}H NMR spectra, trichloroacetamides **7a,7b, 7d-p** exist as a mixture of two rotamers, which do not interconvert easily at room temperature.

***N*-Benzyl-2,2,2-trichloro-*N*-[2-(phenylethynyl)phenyl]acetamide 7a.** Colorless crystals; mp 123–124 °C (from ethyl acetate–hexanes); yield: 86 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.30 (d, J = 12.4 Hz, 1H, NCH), 5.81 (d, J = 12.4 Hz, 1H, NCH), 6.97 (d, J = 7.9 Hz, 1H, ArH), 7.16 (td, J = 7.9, 1.3 Hz, 1H, ArH), 7.20–7.35 (m, 6H, ArH), 7.36–7.41 (m, 3H, ArH), 7.51–7.56 (m, 2H, ArH), 7.58 (dd, J = 7.9, 1.3 Hz, 1H, ArH); IR (KBr): 2950, 1670, 1590, 1450, 1245 cm^{-1}; HRMS(EI) calcd for $C_{23}H_{16}Cl_3NO$: m/z 427.0297 $[M]^+$, found: m/z 427.0297.

2,2,2-Trichloro-*N*-ethyl-*N*-[2-(phenylethynyl)phenyl]acetamide 7b. Yellow oils; yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, J = 6.8 Hz, 3H, CH_3), 3.45 (brs, 1H, NCH), 4.37 (brs, 1H, NCH), 7.31–7.42 (m, 6H, ArH), 7.46–7.52 (m, 2H, ArH), 7.61 (brs, 1H, ArH); IR (neat): 2935, 1680, 1600, 1450, 1280 cm^{-1}; HRMS(ESI) calcd for $C_{18}H_{15}Cl_3NO$: m/z 366.0213 $[MH]^+$, found: m/z 366.0203.

2,2,2-Trichloro-*N*-[2-(phenylethynyl)phenyl]acetamide 7c. Colorless crystals; mp 104–105 °C (from ethyl acetate–hexanes); yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, J = 7.9 Hz, 1H, ArH), 7.35–7.46 (m, 4H, ArH), 7.51–7.55 (m, 2H, ArH), 7.57 (d, J = 7.9 Hz, 1H, ArH), 8.38 (d, J = 7.9 Hz, 1H, ArH), 9.45 (s, 1H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 83.3 (s), 93.0 (s), 97.7 (s), 113.6 (s), 119.0 (d), 121.9 (s), 125.1 (d), 128.6 (2 × d), 129.2 (d), 129.9 (d), 131.5 (2 × d), 131.7 (d),137.1 (s), 159.0 (s); IR (KBr): ν = 3360, 1720, 1580, 1450, 755 cm^{-1}; HRMS(EI) calcd for $C_{16}H_{10}Cl_3NO$: m/z 336.9828 $[M]^+$, found: m/z 336.9828.

***N*-Benzyl-2,2,2-trichloro-*N*-[4-methyl-2-(phenylethynyl)phenyl]acetamide 7d.** Colorless crystals; mp 74–75 °C (from ethyl acetate–hexanes); yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 4.26 (d, J = 14.0 Hz, 1H, NCH), 5.79 (d, J = 14.0 Hz, 1H, NCH), 6.84 (d, J = 8.2 Hz, 1H, ArH), 6.96 (dd, J = 8.2, 1.6 Hz, 1H, ArH), 7.20–7.30 (m, 5H, ArH), 7.34–7.42 (m, 4H, ArH), 7.49–7.56 (m, 2H, ArH); IR (KBr): 2950, 1670, 1600, 1245, 835 cm^{-1}; HRMS(EI) calcd for $C_{24}H_{18}Cl_3NO$: m/z 441.0454 $[M]^+$, found: m/z 441.0456.

***N*-Benzyl-2,2,2-trichloro-*N*-[4,5-dimethyl-2-(phenylethynyl)phenyl]acetamide 7e.** Yellow oils; yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.28 (d, J = 13.8 Hz, 1H, NCH), 5.74 (d, J = 13.8 Hz, 1H, NCH), 6.73 (s, 1H, ArH), 7.20–7.30 (m, 5H, ArH), 7.32–7.40 (m, 4H, ArH), 7.48–7.53 (m, 2H, ArH); IR (neat): 2920, 1680, 1595, 1455, 1245 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{20}Cl_3NO$: m/z 455.061 $[M]^+$, found: m/z 455.0616.

***N*-Benzyl-2,2,2-trichloro-*N*-[4-chloro-2-(phenylethynyl)phenyl]acetamide 7f.** Yellow oils; yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 (brs, 1H, NCH), 5.81 (d, J = 14.4 Hz, 1H, NCH), 6.86 (d, J = 8.6 Hz, 1H, ArH), 7.11 (dd, J = 8.6, 2.4 Hz, 1H, ArH), 7.18–7.23 (m, 2H, ArH), 7.24–7.30 (m, 3H, ArH), 7.36–7.43 (m, 3H, ArH), 7.50–7.56 (m, 2H,

ArH), 7.57 (d, *J* = 2.4 Hz, 1H, ArH); IR (neat): 3035, 1685, 1480, 1240, 830 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{16}Cl_4NO$: *m/z* 461.9981 $[MH]^+$, found: *m/z* 461.9972.

***N*-Benzyl-*N*-[4-bromo-2-(phenylethynyl)phenyl]-2,2,2-trichloroacetamide 7g.** Yellow oils; yield: 93%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.26 (brs, 1H, NCH), 5.80 (d, *J* = 14.0 Hz, 1H, NCH), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 7.16–7.23 (m, 2H, ArH), 7.24–7.30 (m, 5H, ArH), 7.35–7.42 (m, 3H, ArH), 7.50–7.55 (m, 2H, ArH), 7.73 (d, *J* = 2.4 Hz, 1H, ArH); IR (neat): 3030, 1680, 1600, 1495, 1240 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{15}BrCl_3NO$: *m/z* 504.9403 $[M]^+$, found: *m/z* 504.9406.

***N*-Benzyl-2,2,2-trichloro-*N*-{2-[(4-methoxycarbonylphenyl)ethynyl]phenyl}acetamide 7h.** Yellow oils; yield: 85%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 3.93 (s, 3H, OCH_3), 4.31 (brs, 1H, NCH), 5.83 (d, *J* = 14.0 Hz, 1H, NCH), 7.02 (d, *J* = 8.3 Hz, 1H, ArH), 7.18–7.29 (m, 5H, ArH), 7.35–7.42 (m, 3H, ArH), 7.52–7.59 (m, 2H, ArH), 7.80 (dd, *J* = 8.3, 1.7 Hz, 1H, ArH), 8.26 (d, *J* = 1.7 Hz, 1H, ArH); IR (neat): 2950, 1725, 1685, 1600, 1255 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}Cl_3NO_3$: *m/z* 486.0425 $[MH]^+$, found: *m/z* 486.0414.

***N*-Benzyl-2,2,2-trichloro-*N*-{2-[(4-methylphenyl)ethynyl]phenyl}acetamide 7i.** Colorless crystals; mp 95–96 °C (from ethyl acetate–hexanes); yield: 92%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.37 (s, 3H, CH_3), 4.30 (brs, 1H, NCH), 5.81 (d, *J* = 14.4 Hz, 1H, NCH), 6.95 (d, *J* = 7.8 Hz, 1H, ArH), 7.09–7.33 (m, 9H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.59 (d, *J* = 7.8 Hz, 1H, ArH); IR (KBr): 3030, 1680, 1605, 1455, 1240 cm^{-1}; HRMS(EI) calcd for $C_{24}H_{18}Cl_3NO$: *m/z* 441.0454 $[M]^+$, found: *m/z* 441.0454.

***N*-Benzyl-2,2,2-trichloro-*N*-{2-[(4-methoxyphenyl)ethynyl]phenyl}acetamide 7j.** Yellow oils; yield: 90%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 3.84 (s, 3H, OCH_3), 4.29 (d, *J* = 13.6 Hz, 1H, NCH), 5.80 (d, *J* = 13.6 Hz, 1H, NCH), 6.90 (d, *J* = 9.4 Hz, 2H, ArH), 6.95 (d, *J* = 7.8 Hz, 1H, ArH), 7.13 (td, *J* = 7.8, 1.4 Hz, 1H, ArH), 7.21–7.32 (m, 6H, ArH), 7.48 (d, *J* = 9.4 Hz, 2H, ArH), 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H, ArH); IR (neat): 2935, 1680, 1600, 1450, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}Cl_3NO_2$: *m/z* 458.0476 $[MH]^+$, found: *m/z* 458.0465.

***N*-Benzyl-2,2,2-trichloro-*N*-{2-[(4-chlorophenyl)ethynyl]phenyl}acetamide 7k.** Colorless crystals; mp 84–85 °C (from ethyl acetate–hexanes); yield: 87%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.30 (brs, 1H, NCH), 5.77 (d, *J* = 14.0 Hz, 1H, NCH), 6.97 (d, *J* = 7.4 Hz, 1H, ArH), 7.14–7.23 (m, 3H, ArH), 7.24–7.33 (m, 4H, ArH), 7.35 (d, *J* = 8.6 Hz, 2H, ArH), 7.46 (d, *J* = 8.6 Hz, 2H, ArH), 7.57 (d, *J* = 7.4 Hz, 1H, ArH); IR (KBr): 2950, 1670, 1450, 1245, 815 cm^{-1}; HRMS(EI) calcd for $C_{23}H_{15}Cl_4NO$: *m/z* 460.9908 $[M]^+$, found: *m/z* 460.9910.

***N*-Benzyl-*N*-{2-[(4-bromophenyl)ethynyl]phenyl}-2,2,2-trichloroacetamide 7l.** Yellow oils; yield: 85%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.30 (brs, 1H, NCH), 5.76 (d, *J* = 13.6 Hz, 1H, NCH), 6.97 (d, *J* = 7.1 Hz, 1H, ArH), 7.14–7.35 (m, 7H, ArH), 7.38 (d, *J* = 8.4 Hz, 2H, ArH), 7.51 (d, *J* = 8.4 Hz, 2H, ArH), 7.57 (dd, *J* = 7.1, 1.2 Hz, 1H, ArH); IR (neat): 3030, 1680, 1450, 1245, 825 cm^{-1}; HRMS(ESI) calcd for $C_{23}H_{16}BrCl_3NO$: *m/z* 505.9475 $[MH]^+$, found: *m/z* 505.9469.

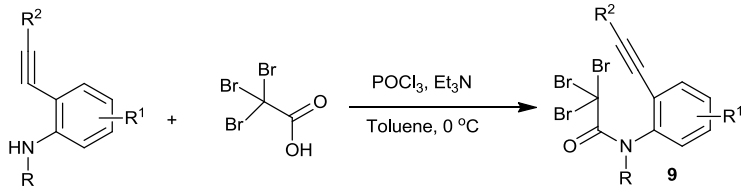
***N*-Benzyl-2,2,2-trichloro-*N*-{2-[(3-methoxyphenyl)ethynyl]phenyl}acetamide 7m.** Yellow oils; yield: 94%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 3.85 (s, 3H, OCH_3), 4.30 (brs, 1H, NCH), 5.81 (d, *J* = 13.6 Hz, 1H, NCH), 6.91–7.01 (m, 2H, ArH), 7.03–7.09 (m, 1H, ArH), 7.12–7.19 (m, 2H, ArH), 7.19–7.35 (m, 7H, ArH), 7.58 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH); IR (neat): 2940, 1680, 1595, 1455, 1235 cm^{-1}; HRMS(EI) calcd for $C_{24}H_{19}Cl_3NO_2$: *m/z* 457.0403 $[M]^+$, found: *m/z* 457.0399.

***N*-Benzyl-2,2,2-trichloro-*N*-[2-(hex-1-yn-1-yl)phenyl]acetamide 7n.** Yellow oils; yield: 99%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 0.96 (t, *J* = 7.8 Hz, 3H, CH_3), 1.49 (sextet, *J* = 7.8 Hz, 2H, CH_2), 1.61 (quintet, *J* = 7.8 Hz, 2H, CH_2), 2.46 (t, *J* = 7.8 Hz, 2H, CH_2), 4.20 (d, *J* = 14.0 Hz, 1H, NCH), 5.74 (d, *J* = 14.0 Hz, 1H, NCH), 6.88 (d, *J* = 7.4 Hz, 1H, ArH), 7.07 (t, *J* = 7.4 Hz, 1H, ArH), 7.15–7.32 (m, 6H, ArH), 7.44 (dd, *J* = 7.4, 0.8 Hz, 1H, ArH); IR (neat): 2935, 1680, 1455, 1260, 835 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}Cl_3NO_2$: *m/z* 408.0683 $[MH]^+$, found: *m/z* 408.0673.

***N*-Benzyl-2,2,2-trichloro-*N*-[2-(cyclohexylethynyl)phenyl]acetamide 7o.** Yellow oils; yield: 96%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.37–1.43 (m, 3H, 3 × CH), 1.52–1.82 (m, 4H, 4 × CH), 1.84–1.93 (m, 2H, 2 × CH), 2.00–2.18 (m, 1H, CH), 2.59–2.73 (m, 1H, CH), 4.17 (d, *J* = 13.6 Hz, 1H, NCH), 5.77 (d, *J* = 13.6 Hz, 1H, NCH), 6.87 (d, *J* = 7.8 Hz, 1H, ArH), 7.07 (td, *J* = 7.8, 1.4 Hz, 1H, ArH), 7.15–7.31 (m, 8H, ArH), 7.44 (dd, *J* = 7.8, 1.4 Hz, 1H, ArH); IR (neat): 2930, 1685, 1595, 1450, 1255 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}Cl_3NO$: *m/z* 437.0767 $[MH]^+$, found: *m/z* 437.0769.

***N*-Benzyl-2,2,2-trichloro-*N*-[2-(thiophen-3-ylethynyl)phenyl]acetamide 7p.** Colorless crystals; mp 121–122 °C (from ethyl acetate–hexanes); yield: 83%; ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.28 (d, *J* = 12.2 Hz, 1H, NCH), 5.78 (d, *J* = 12.2 Hz, 1H, NCH), 6.96 (d, *J* = 7.4 Hz, 1H, ArH), 7.15 (td, *J* = 7.4, 1.2 Hz, 1H, ArH), 7.18–7.35 (m, 8H, ArH), 7.56 (d, *J* = 7.4 Hz, 1H, ArH), 7.57 (s, 1H, ArH); IR (KBr): 2950, 1670, 1595, 1455, 1245 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{14}Cl_3NOS$: *m/z* 432.9862 $[M]^+$, found: *m/z* 432.9861.

2) Experimental details and characterization data of starting *N*-(2-alkynylphenyl)-2,2,2-tribromoacetamides 9.



Typical procedure for the preparation of *N*-(alkynylphenyl)-2,2,2-tribromoacetamides 9:

A solution of 2,2,2-tribromoacetic acid (1.11 g, 3.74 mmol) and phosphorus oxychloride (571 mg, 3.74 mol) in toluene (20 mL) was stirred in an ice-water bath. After stirred for 1 h, *N*-benzyl-2-(phenylethynyl)phenylamine (703 mg, 2.48 mmol) and triethylamine (525 mg, 5.19 mmol) was added. The resulting solution was stirred in an ice-water bath for another 5 h. The reaction mixture was then diluted with 100 mL of ethyl acetate, washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1:20 ethyl acetate–hexanes) to give 1.28 g (92%) of **9a**.

Based on ^{1}H NMR spectra, tribromoacetamides **9a-i** exist as a mixture of two rotamers, which do not interconvert easily at room temperature.

***N*-Benzyl-2,2,2-tribromo-*N*-[2-(phenylethynyl)phenyl]acetamide 9a.** White solids; mp 91–92 ^{o}C (from ethyl acetate–hexanes); yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.32 (brs, 1H, NCH), 5.85 (d, *J* = 14.4 Hz, 1H, NCH), 7.10 (brs, 1H, ArH), 7.17 (td, *J* = 7.7, 1.2 Hz, 1H, ArH), 7.21–7.33 (m, 6H, ArH), 7.34–7.42 (m, 3H, ArH), 7.52–7.62 (m, 3H, ArH); IR (KBr): *v* = 3060, 1650, 1450, 1240, 760 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{17}Br_3NO$: *m/z* 559.8855 $[MH]^+$, found: *m/z* 559.8860.

***N*-Benzyl-2,2,2-tribromo-*N*-[4-methyl-2-(phenylethynyl)phenyl]acetamide 9b.** Colorless oils; yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 4.28 (brs, 1H, NCH), 5.84 (d, *J* = 14.4 Hz, 1H, NCH), 6.89–7.05 (m, 2H, ArH), 7.22–7.32 (m, 5H, ArH), 7.35–7.43 (m, 4H, ArH), 7.52–7.60 (m, 2H, ArH); IR (neat): 2920, 1670, 1600, 1495, 1240 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}Br_3NO$: *m/z* 573.9011 $[MH]^+$, found : *m/z* 573.9014.

***N*-Benzyl-2,2,2-tribromo-*N*-[4-chloro-2-(phenylethynyl)phenyl]acetamide 9c.** Yellow oils; yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.31 (brs, 1H, NCH), 5.85 (d, *J* = 14.4 Hz, 1H, NCH), 6.99 (brs, 1H, ArH), 7.12 (dd, *J* = 8.4, 2.4 Hz, 1H, ArH), 7.20–7.33 (m, 5H, ArH), 7.36–7.41 (m, 3H, ArH), 7.52–7.58 (m, 3H, ArH); IR (neat): 2950, 1670, 1600, 1495, 1235 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{16}Br_3ClNO$: *m/z* 593.8465 $[MH]^+$, found: *m/z* 593.8466.

***N*-Benzyl-2,2,2-tribromo-*N*-[4-bromo-2-(phenylethynyl)phenyl]acetamide 9d.** Yellow oils; yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.35 (brs, 1H, NCH), 5.84 (d, *J* = 14.4 Hz, 1H, NCH), 6.91 (d, *J* = 7.6 Hz, 1H, ArH), 7.22–7.30 (m, 6H, ArH), 7.34–7.42 (m, 3H, ArH), 7.52–7.58 (m, 2H, ArH), 7.71 (d, *J* = 2.0 Hz, 1H, ArH); IR (neat): 3030, 1670, 1600, 1495, 1235 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{16}Br_4NO$: *m/z* 637.7960 $[MH]^+$, found: *m/z* 637.7952.

***N*-Benzyl-2,2,2-tribromo-*N*-[4-methoxycarbonyl-2-(phenylethynyl)phenyl]acetamide 9e.** Colorless oils; yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H, OCH_3), 4.46 (brs, 1H, NCH), 5.86 (d, *J* = 14.0 Hz, 1H, NCH), 7.14 (d, *J* = 7.8 Hz, 1H, ArH), 7.21–7.29 (m, 5H, ArH), 7.36–7.43 (m, 3H, ArH), 7.54–7.61 (m, 2H, ArH), 7.81 (dd, *J* = 7.8, 1.9 Hz, 1H, ArH), 8.25 (d, *J* = 1.9 Hz, 1H, ArH); IR (neat): 2950, 1725, 1670, 1600, 1255 cm^{-1}; HRMS(ESI) calcd for $C_{25}H_{19}Br_3NO_3$: *m/z* 617.8909 $[MH]^+$, found: *m/z* 617.8898.

***N*-Benzyl-2,2,2-tribromo-*N*-{2-[(4-methylphenyl)ethynyl]phenyl}acetamide 9f.** Colorless oils; yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3), 4.34 (brs, 1H, NCH), 5.85 (d, *J* = 14.4 Hz, 1H, NCH), 7.09 (brs, 1H, ArH), 7.15 (t, *J* = 7.4 Hz, 1H, ArH), 7.19 (d, *J* = 8.0 Hz, 2H, ArH), 7.22–7.33 (m, 6H, ArH), 7.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.56 (d, *J* = 7.4 Hz, 1H, ArH); IR (neat): 2920, 1670, 1450, 1240, 815 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}Br_3NO$: *m/z* 573.9011 $[MH]^+$, found: *m/z* 573.9005.

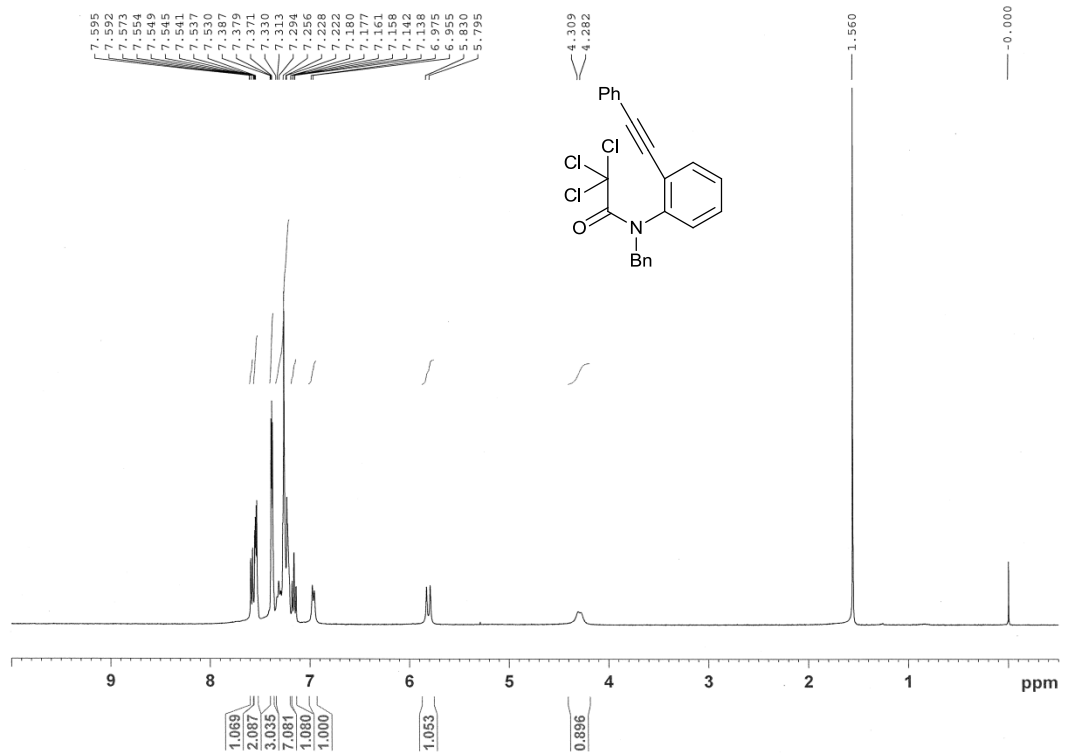
***N*-Benzyl-2,2,2-tribromo-*N*-{2-[(4-methoxyphenyl)ethynyl]phenyl}acetamide 9g.** Colorless oils; yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, OCH_3), 4.34 (brs, 1H, NCH), 5.84 (d, *J* = 14.0 Hz, 1H, NCH), 6.90 (d, *J* = 8.8 Hz, 2H, ArH), 7.08 (brs, 1H, ArH), 7.13 (t, *J* = 7.6 Hz, 1H, ArH), 7.19–7.30 (m, 6H, ArH), 7.50 (d, *J* = 8.8 Hz, 2H, ArH), 7.54 (d, *J* = 7.6 Hz, 1H, ArH); IR (neat): 2935, 1660, 1605, 1455, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}Br_3NO_2$: *m/z* 589.8960 $[MH]^+$, found: *m/z* 589.8944.

***N*-Benzyl-2,2,2-tribromo-*N*-{2-[(4-chlorophenyl)ethynyl]phenyl}acetamide 9h.** Brown oils; yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.36 (brs, 1H, NCH), 5.80 (d, *J* = 14.0 Hz, 1H, NCH), 7.09 (brs, 1H, ArH), 7.17 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 7.21–7.31 (m, 6H, ArH), 7.34 (d, *J* = 8.4 Hz, 2H, ArH), 7.48 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (d, *J* = 7.5 Hz, 1H, ArH); IR (neat): *v* 3030, 1670, 1595, 1450, 1240 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{16}Br_3ClNO$: *m/z* 593.8465 $[MH]^+$, found: *m/z* 593.8460.

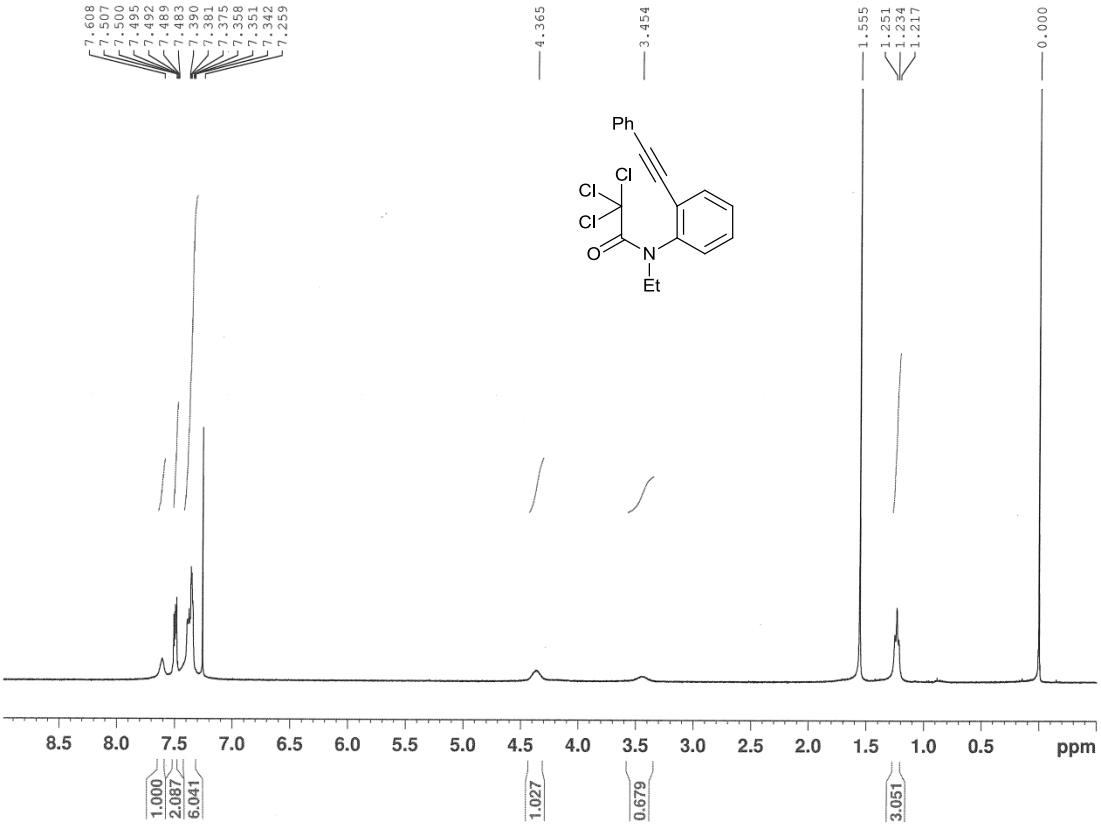
***N*-Benzyl-2,2,2-tribromo-*N*-{2-[(4-bromophenyl)ethynyl]phenyl}acetamide 9i.** Brown oils; yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.32 (brs, 1H, NCH), 5.81 (d, J = 14.0 Hz, 1H, NCH), 7.10 (brs, 1H, ArH), 7.19 (t, J = 7.5 Hz, 1H, ArH), 7.22–7.34 (m, 6H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.56 (d, J = 7.5 Hz, 1H, ArH); IR (neat): 3030, 1670, 1595, 1495, 1240 cm^{-1}; HRMS(ESI) calcd for $C_{23}H_{16}Br_4NO$: *m/z* 637.7960 $[MH]^+$, found: *m/z* 637.7949.

3) Copies of ^{1}H and ^{13}C NMR spectra for the starting *N*-(2-alkynylphenyl) trichloroacetamides 7 *N*-(2-alkynylphenyl) tribromooacetamides 9.

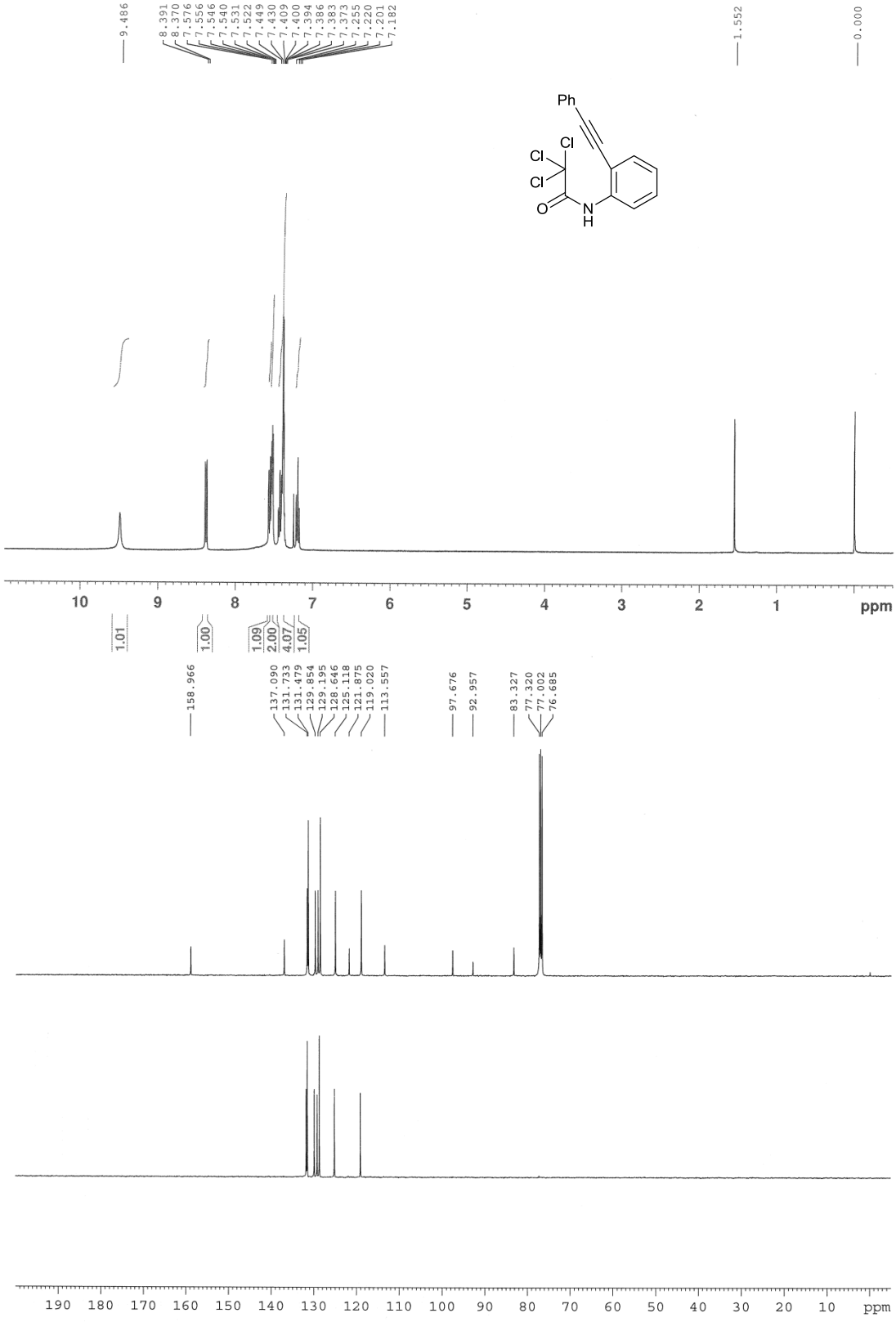
^{1}H NMR spectra of **7a**



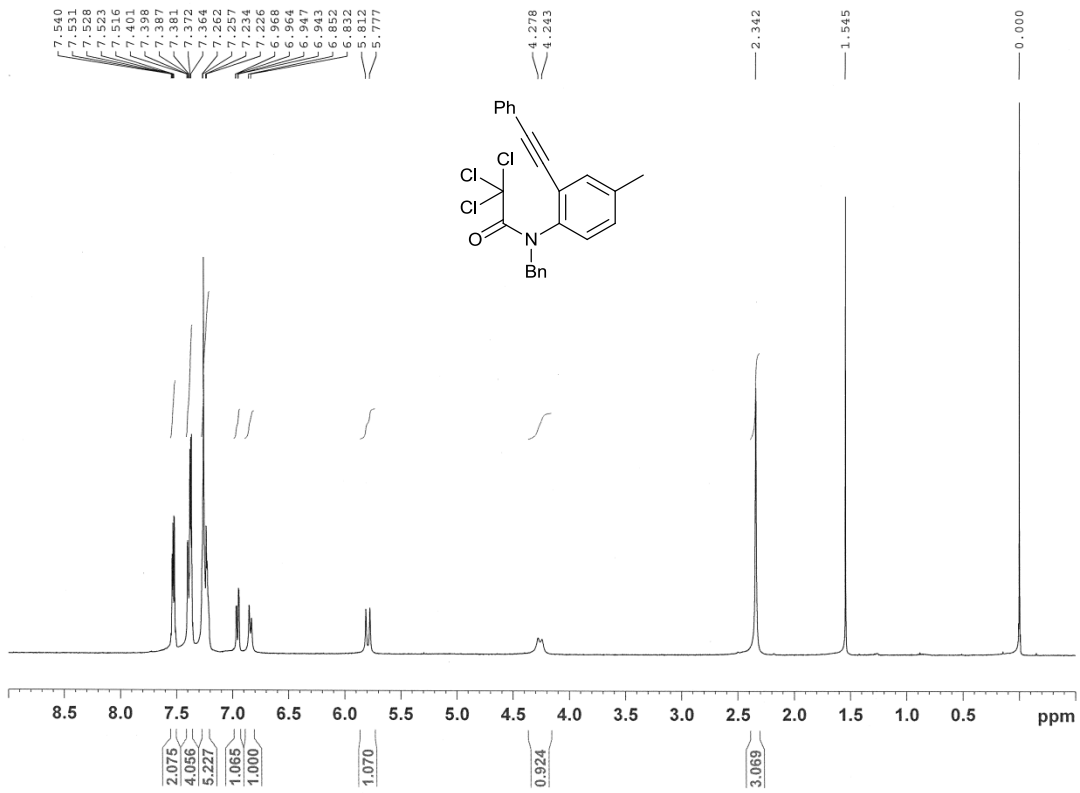
^{1}H NMR spectra of **7b**



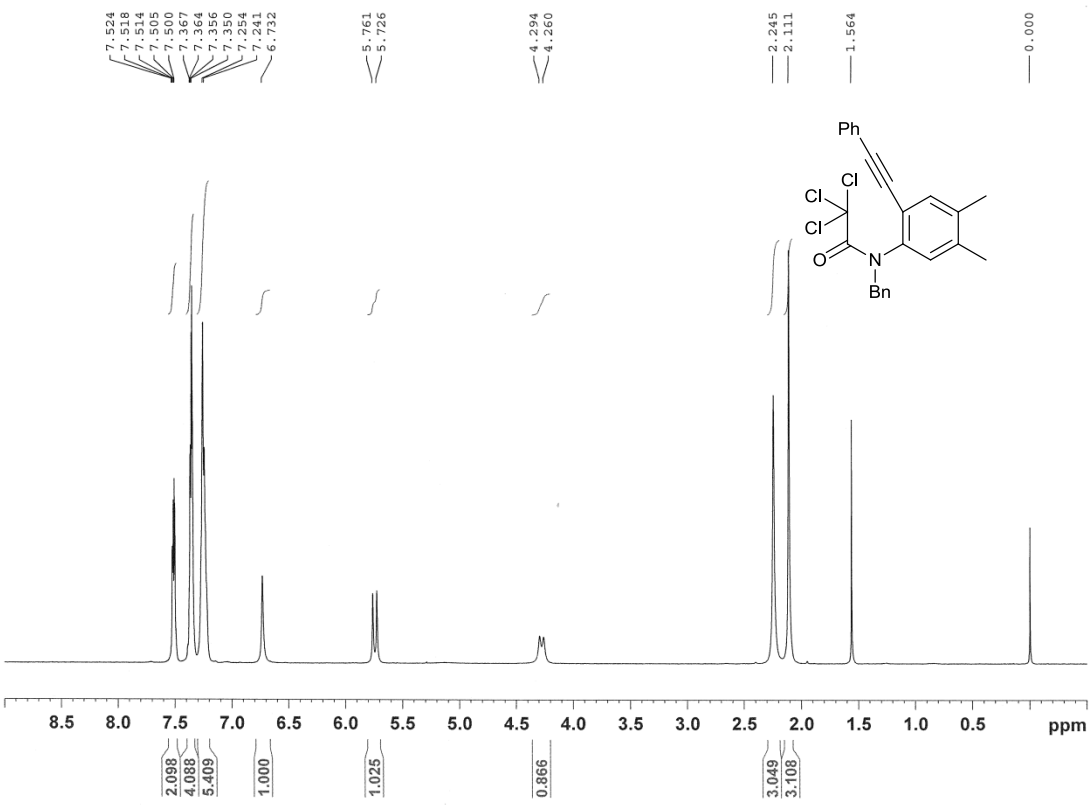
^{1}H & ^{13}C NMR spectra of **7c**



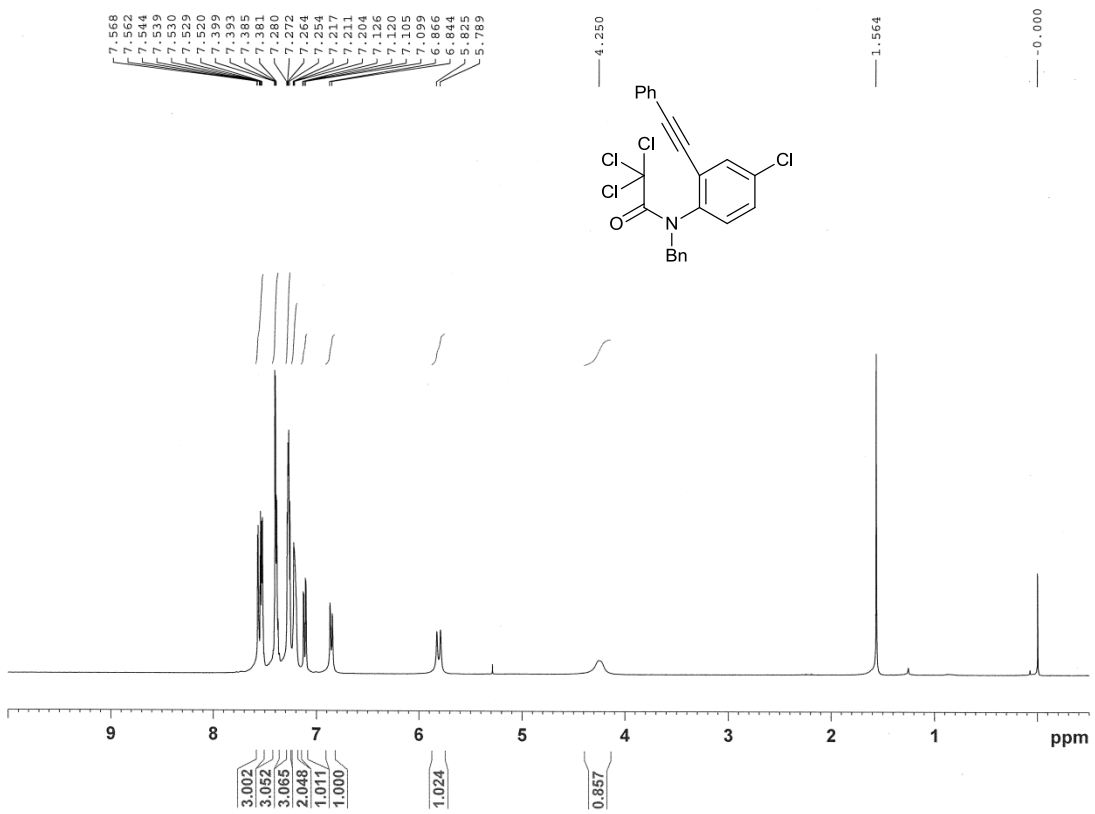
^{1}H NMR spectra of **7d**



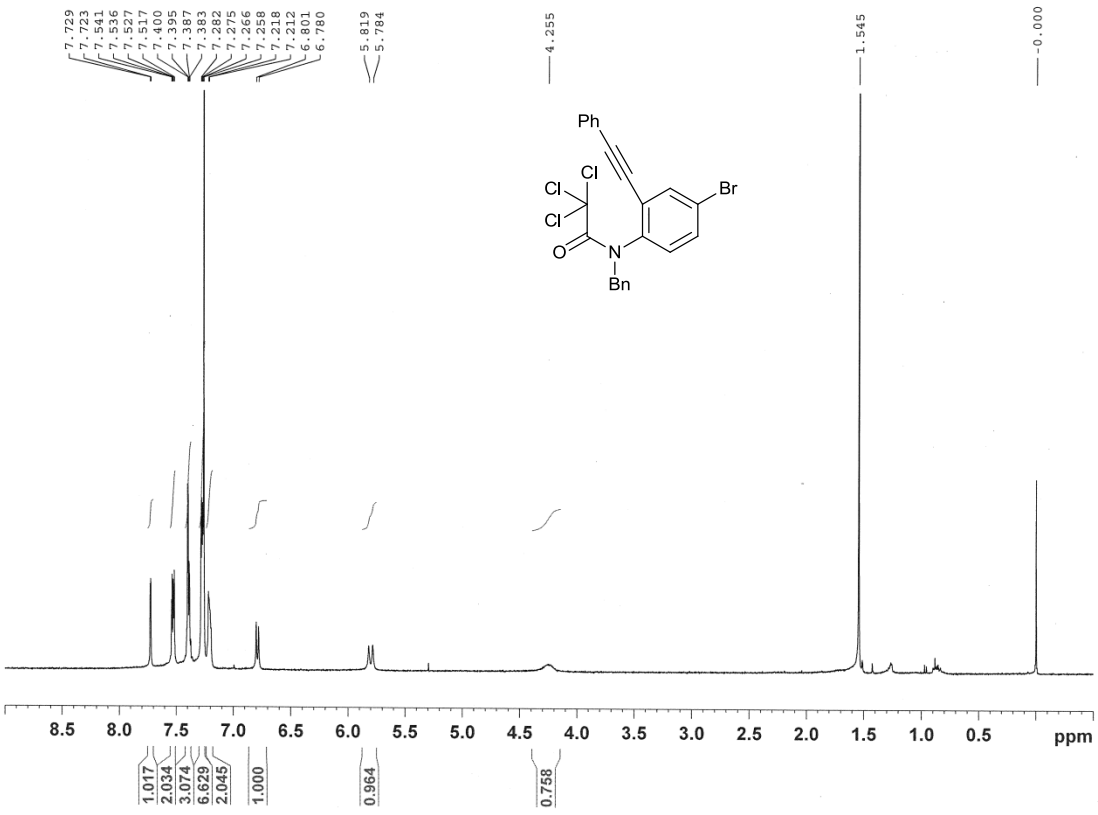
^{1}H NMR spectra of **7e**



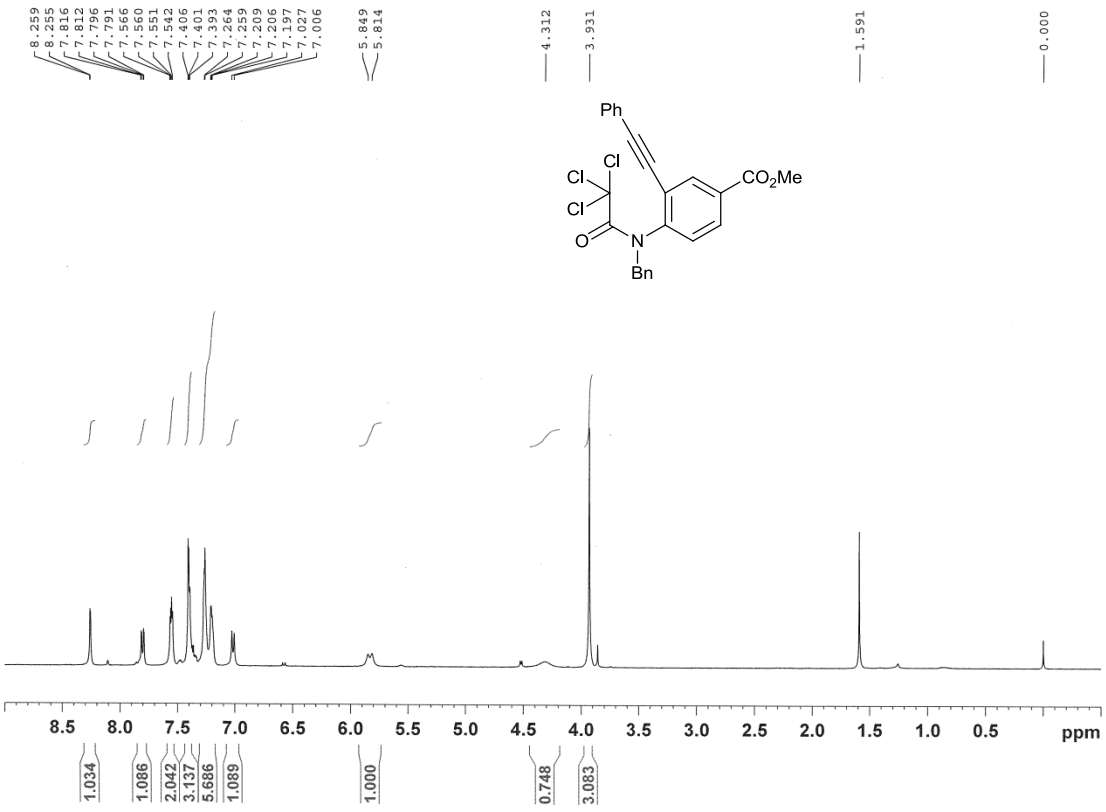
^{1}H NMR spectra of **7f**



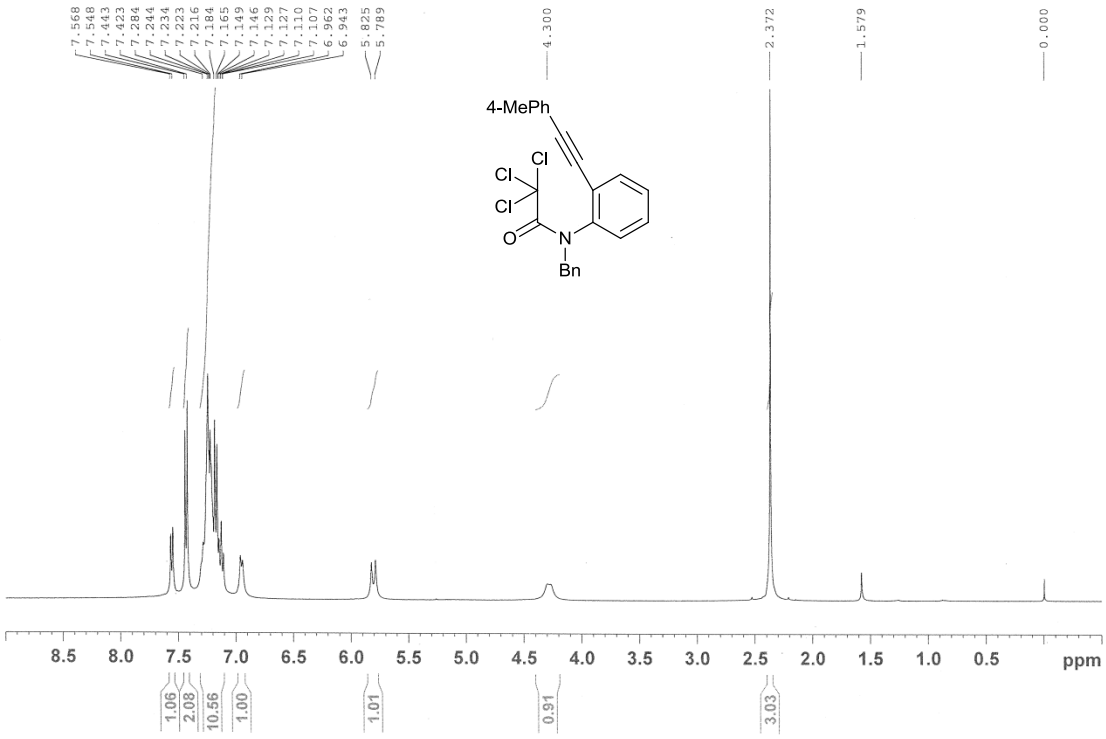
^{1}H NMR spectra of **7g**



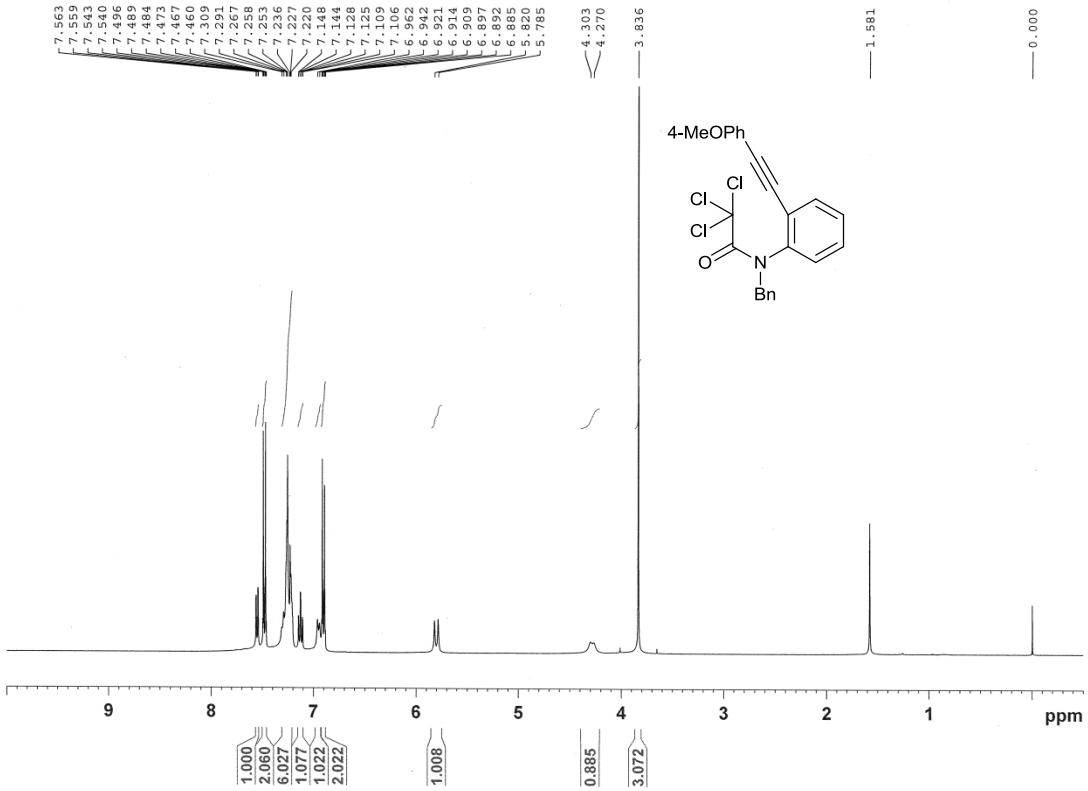
^{1}H NMR spectra of **7h**



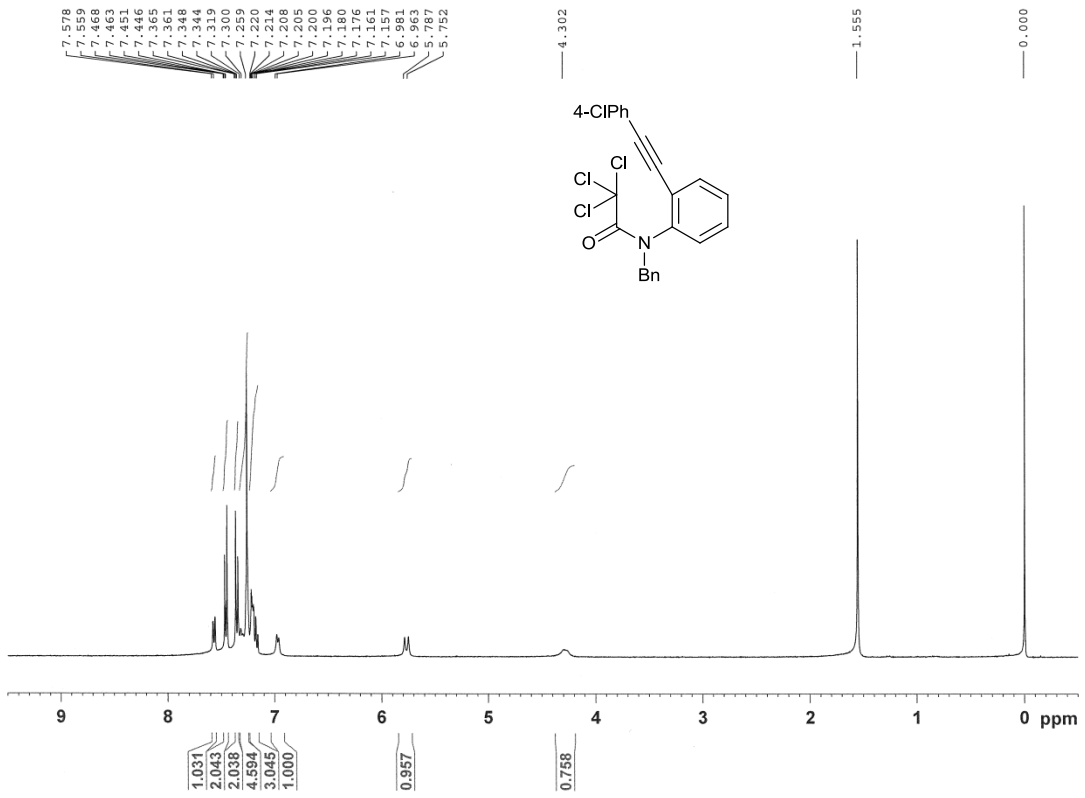
^{1}H NMR spectra of **7i**



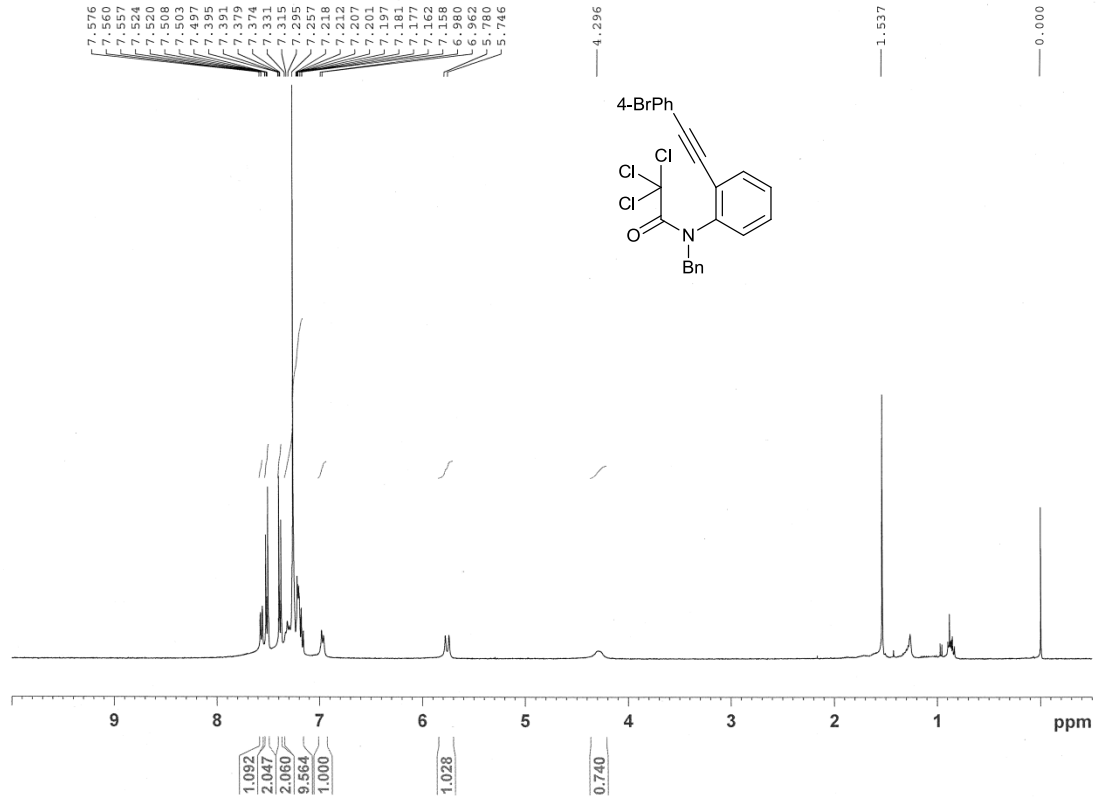
^{1}H NMR spectra of **7j**



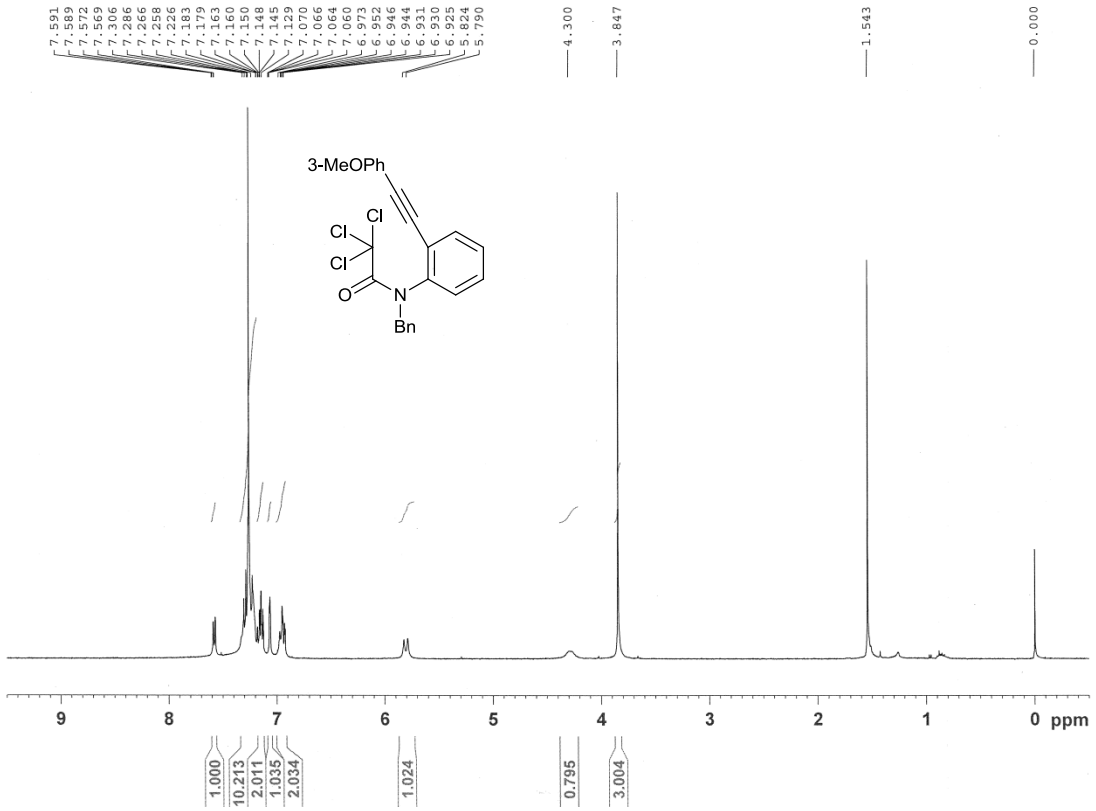
^{1}H NMR spectra of **7k**



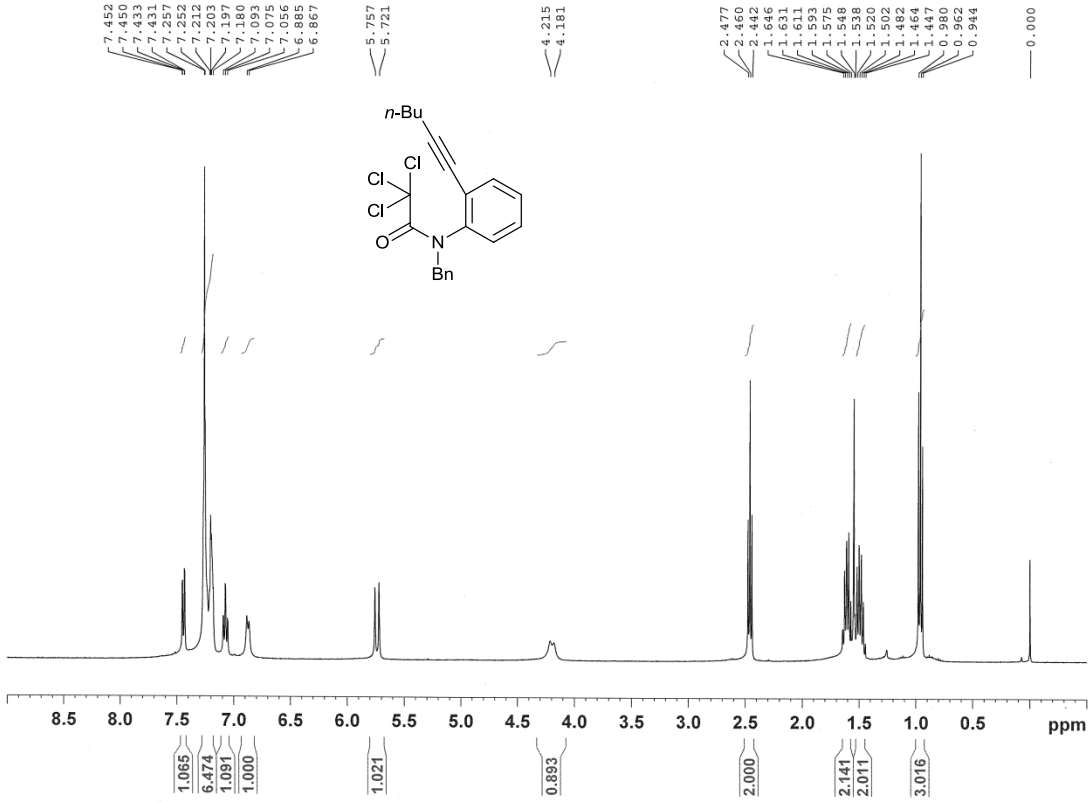
^{1}H NMR spectra of **7l**



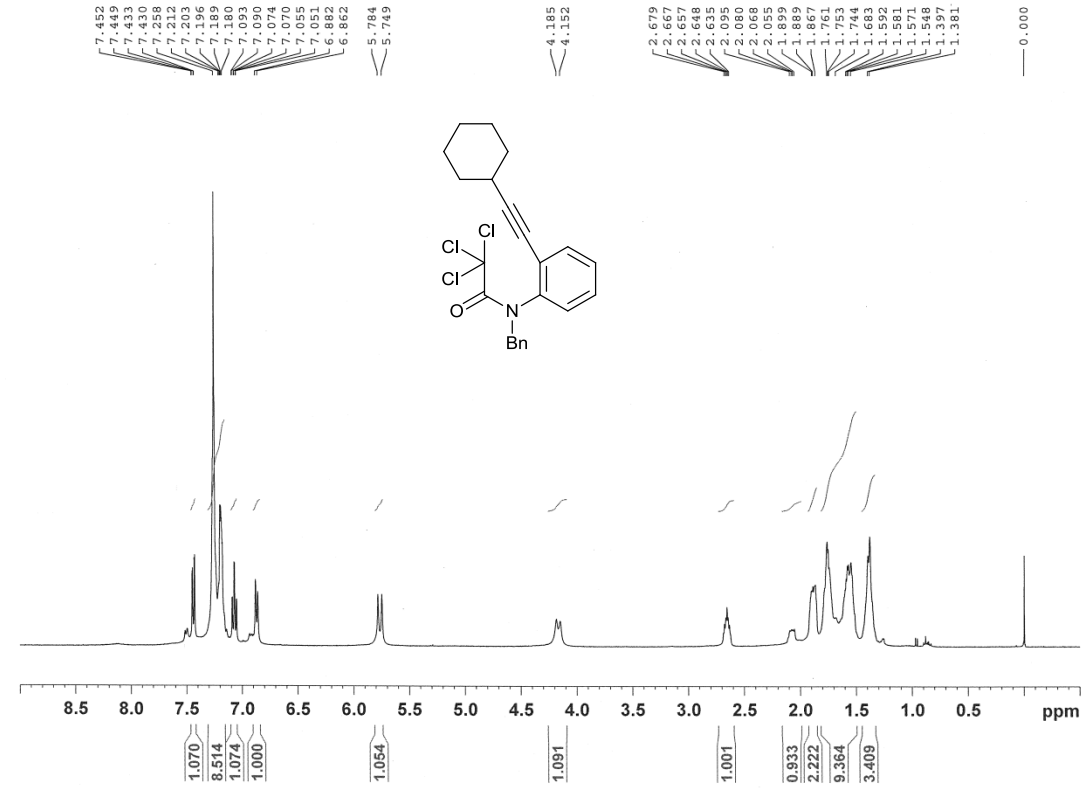
^{1}H NMR spectra of **7m**



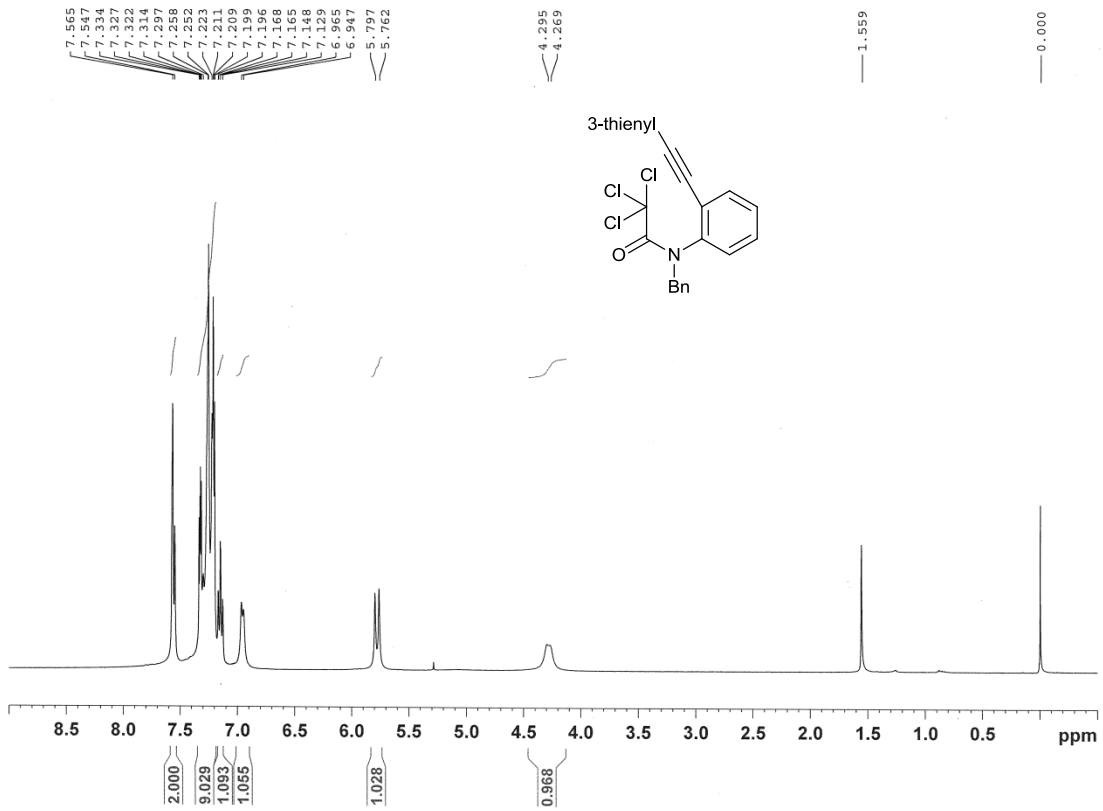
^{1}H NMR spectra of **7n**



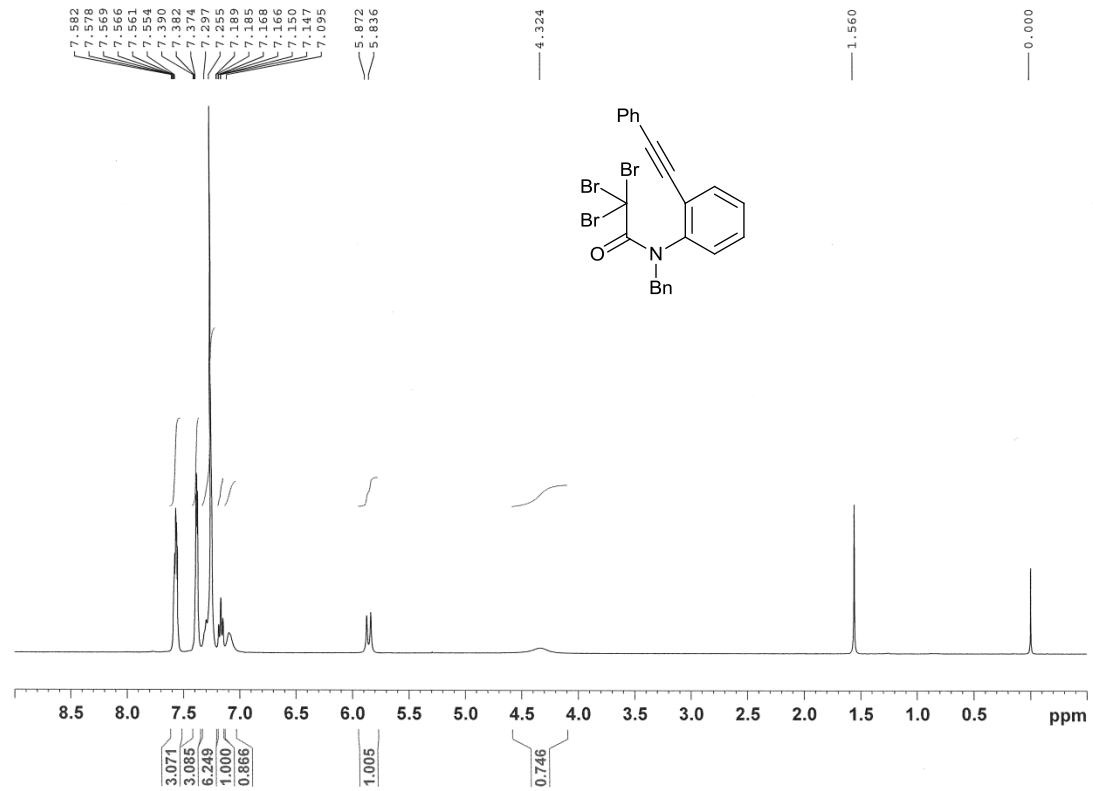
^{1}H NMR spectra of **7o**



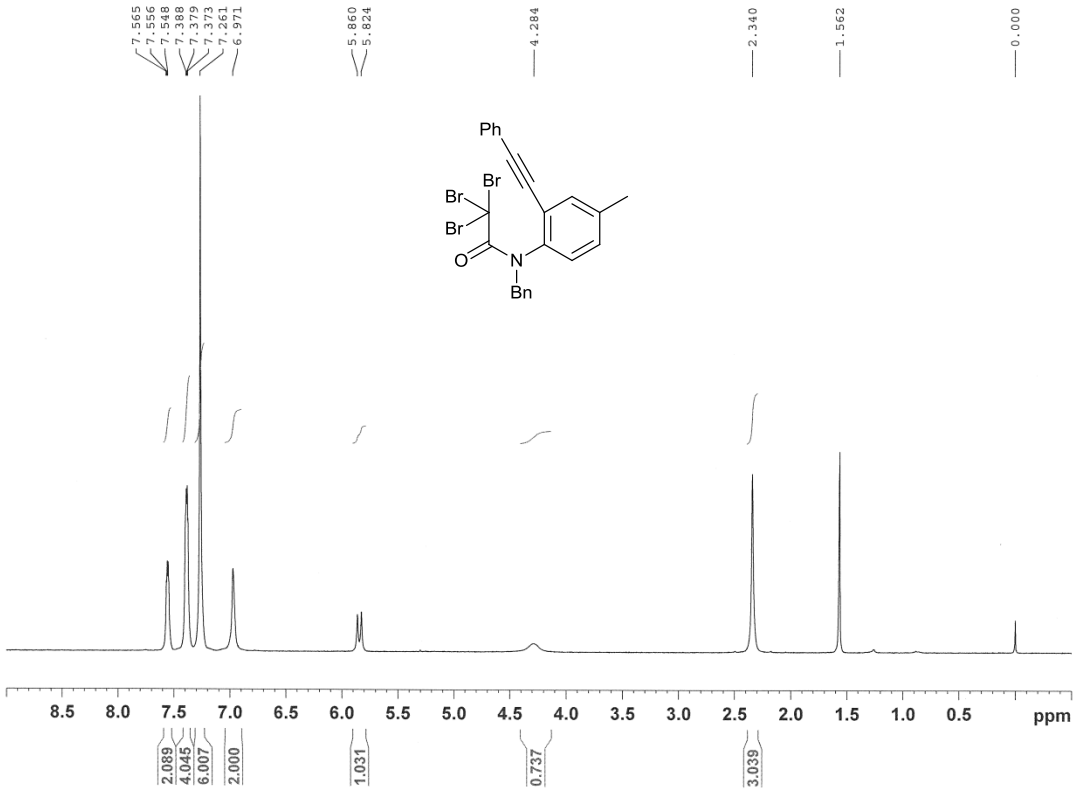
^{1}H NMR spectra of **7p**



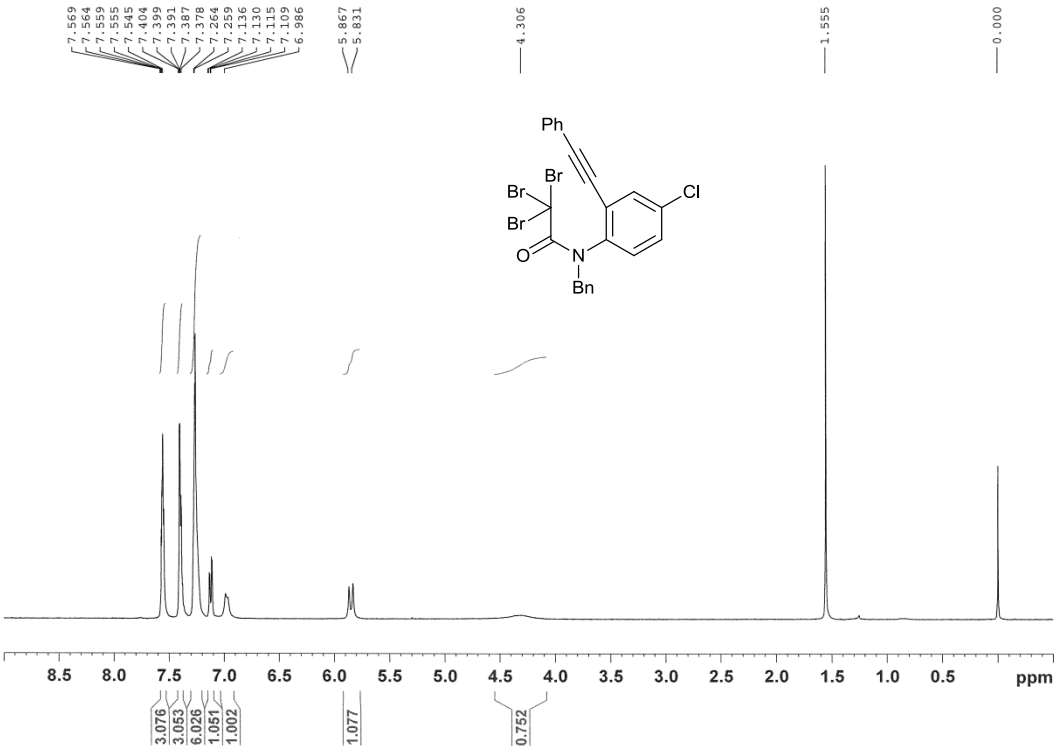
^{1}H NMR spectra of **9a**



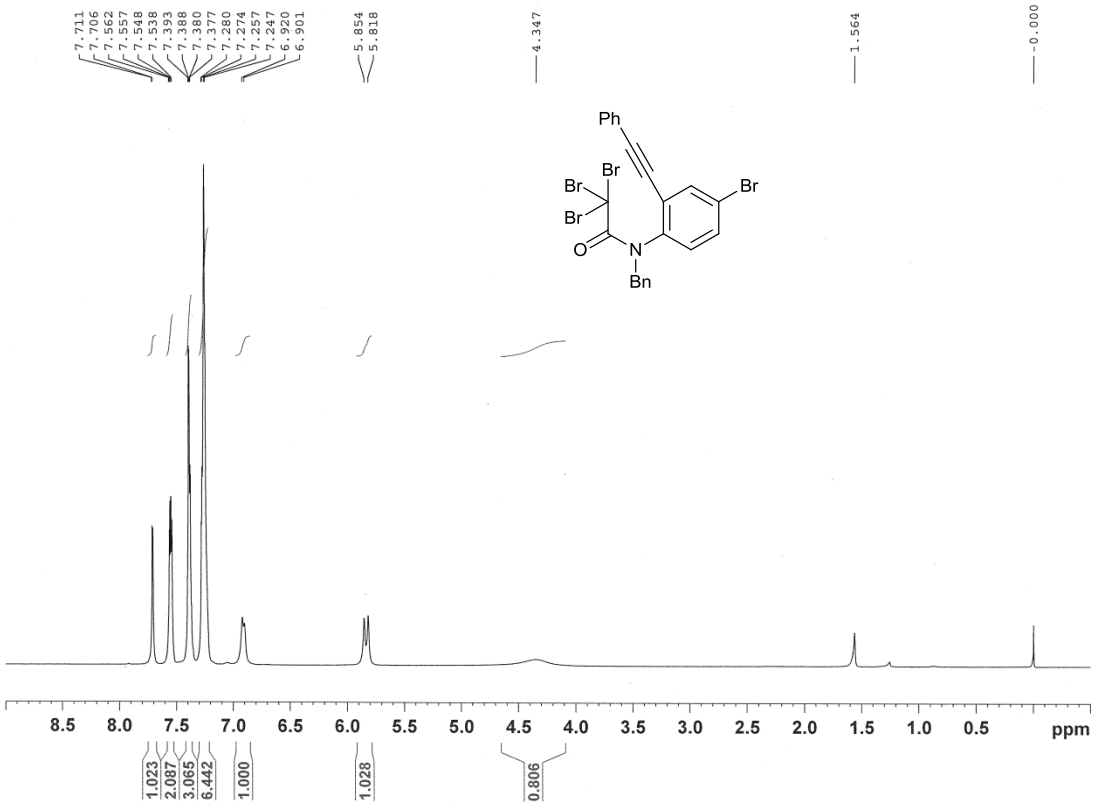
^{1}H NMR spectra of **9b**



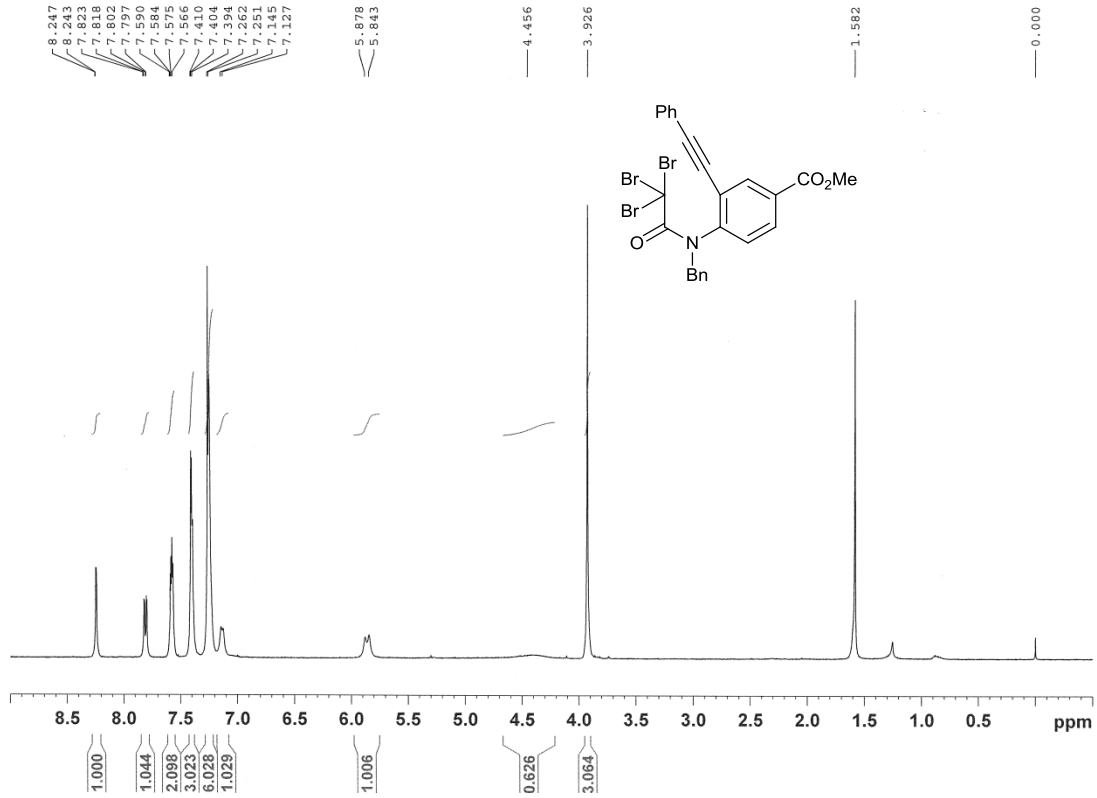
^{1}H NMR spectra of **9c**



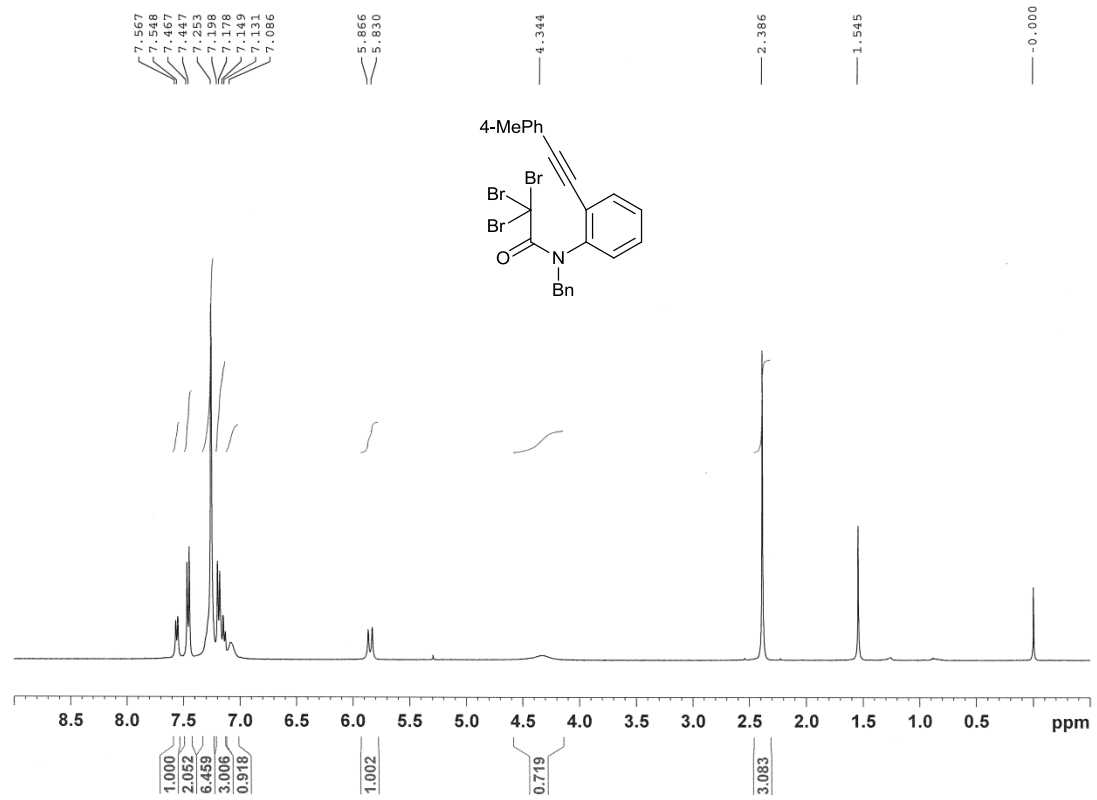
^{1}H NMR spectra of **9d**



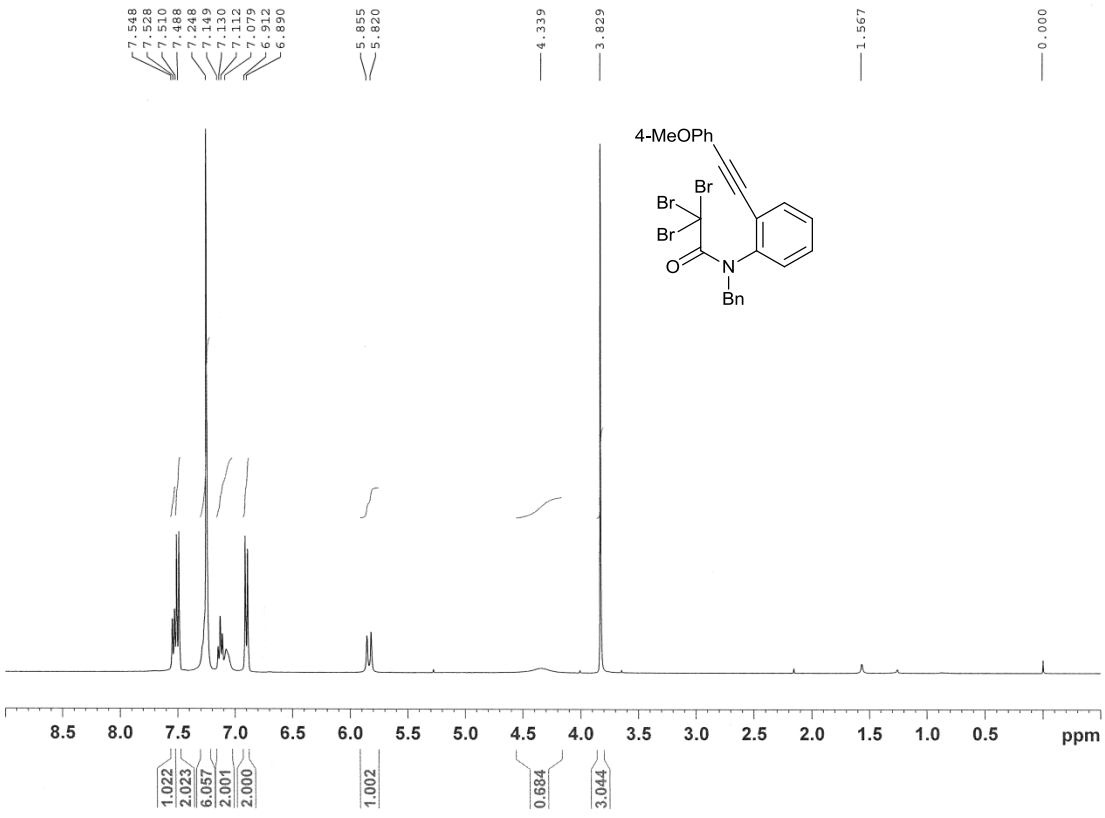
^{1}H NMR spectra of **9e**



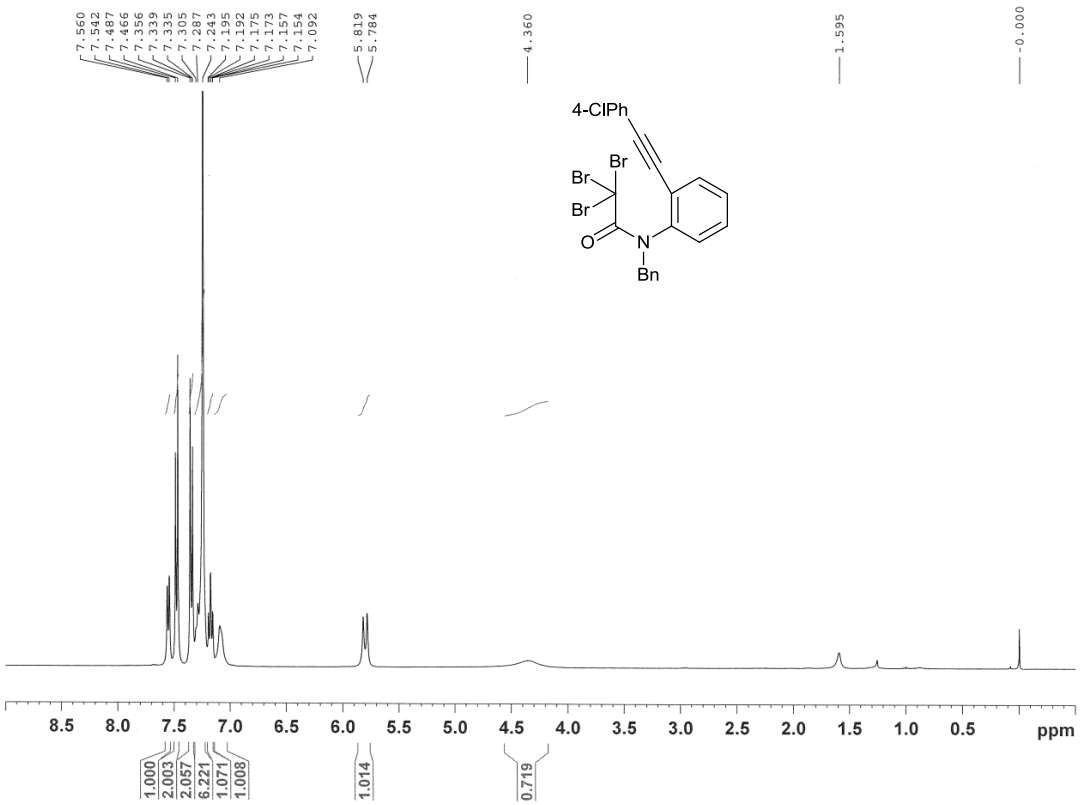
^{1}H NMR spectra of **9f**



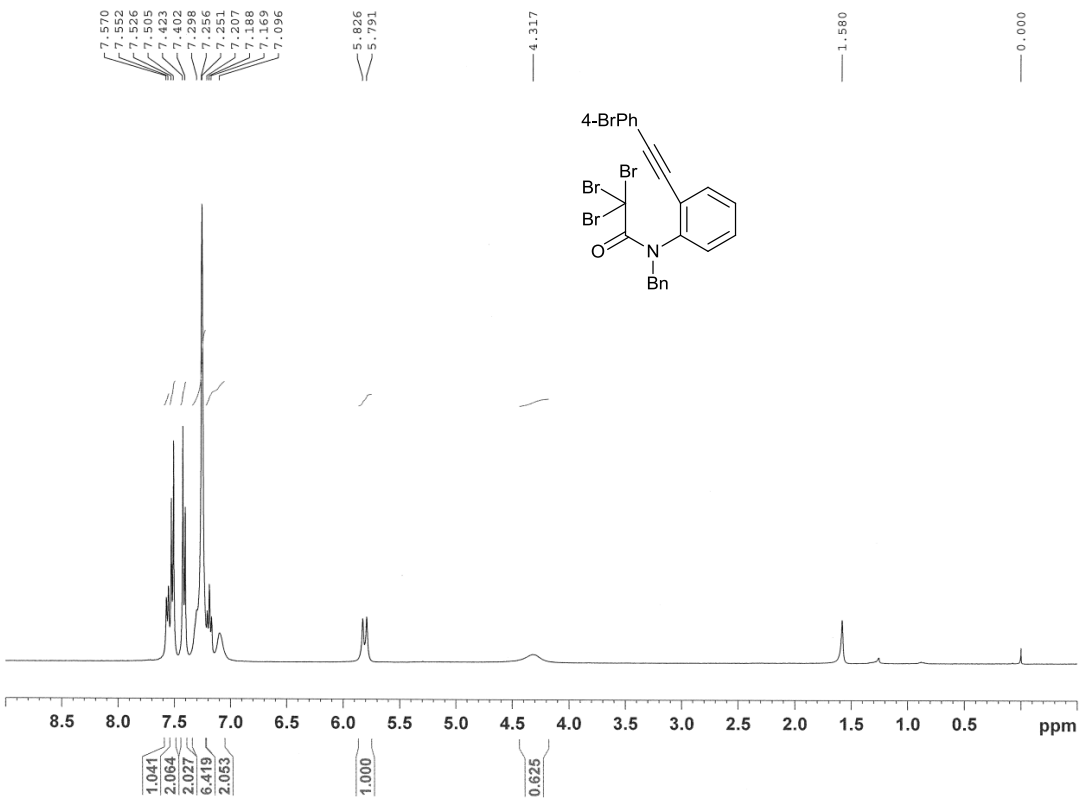
^{1}H NMR spectra of **9g**



^{1}H NMR spectra of **9h**

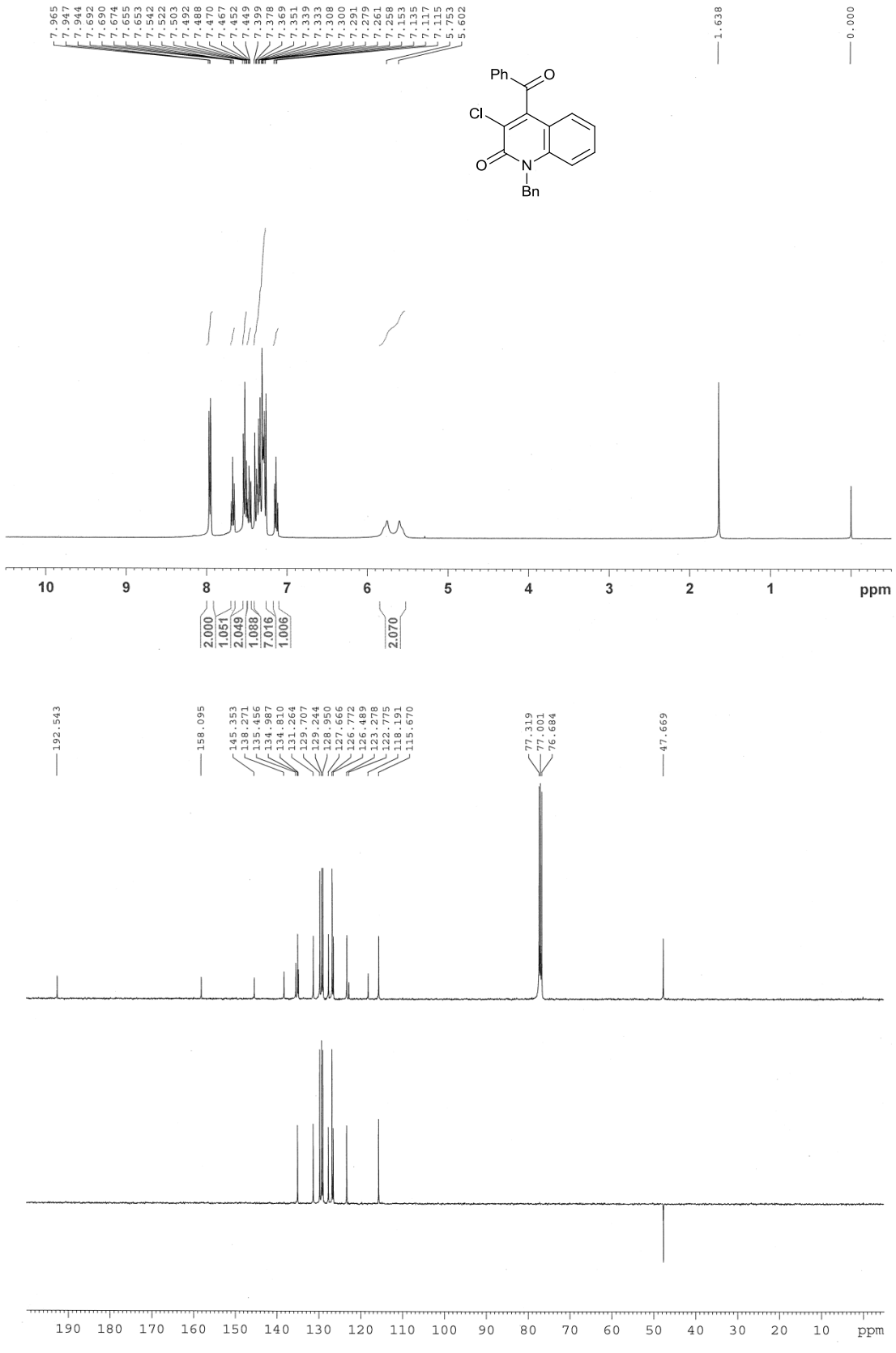


^{1}H NMR spectra of **9i**

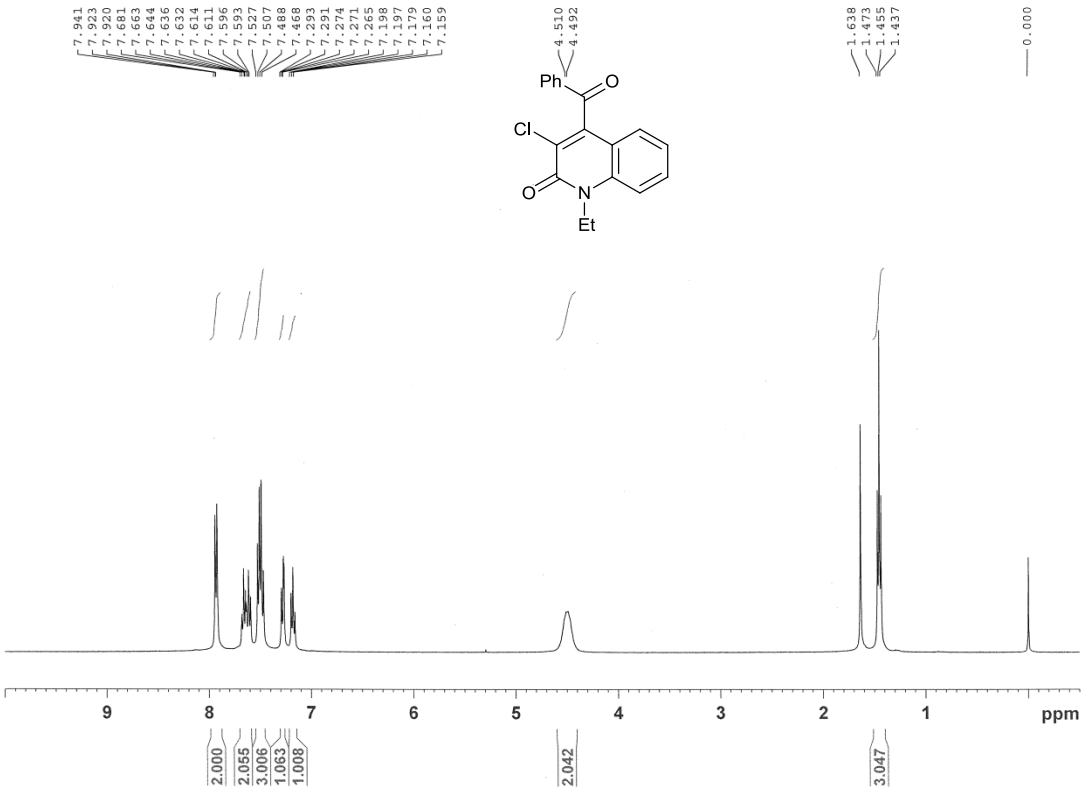


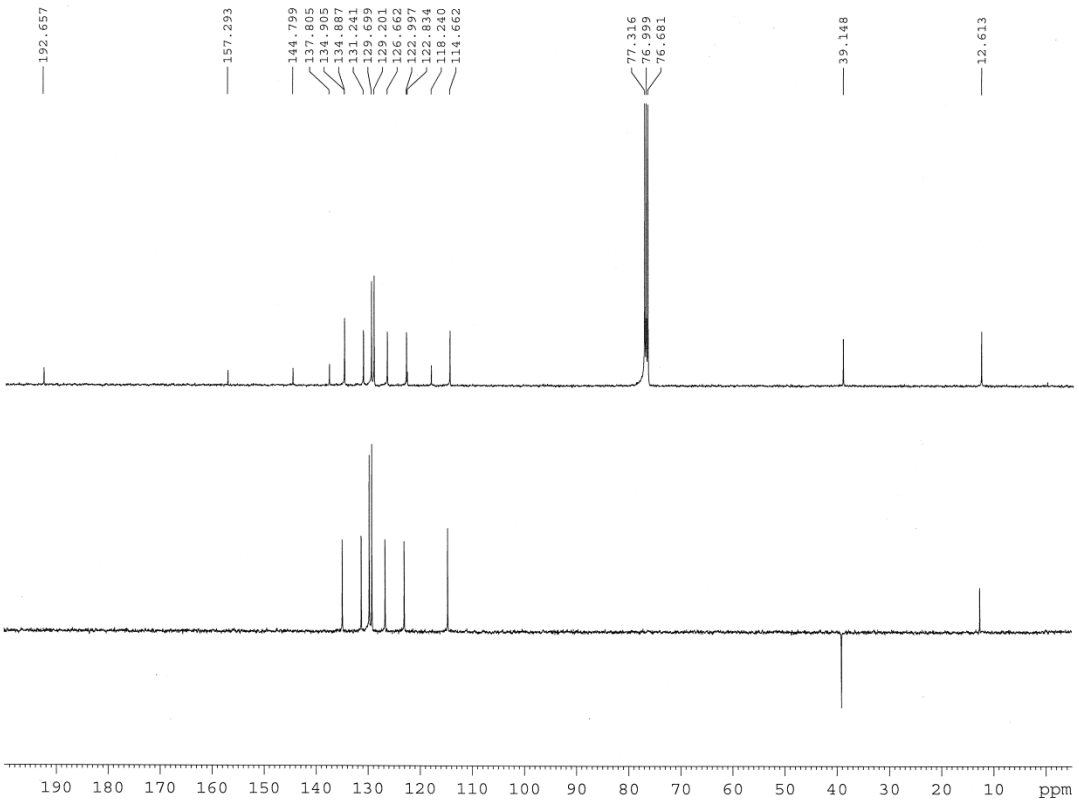
4) **Copies of ^{1}H and ^{13}C NMR spectra for 4-benzoylquinolin-2(1*H*)-ones 8 and 10.**

^{1}H & ^{13}C NMR spectra of **8a**

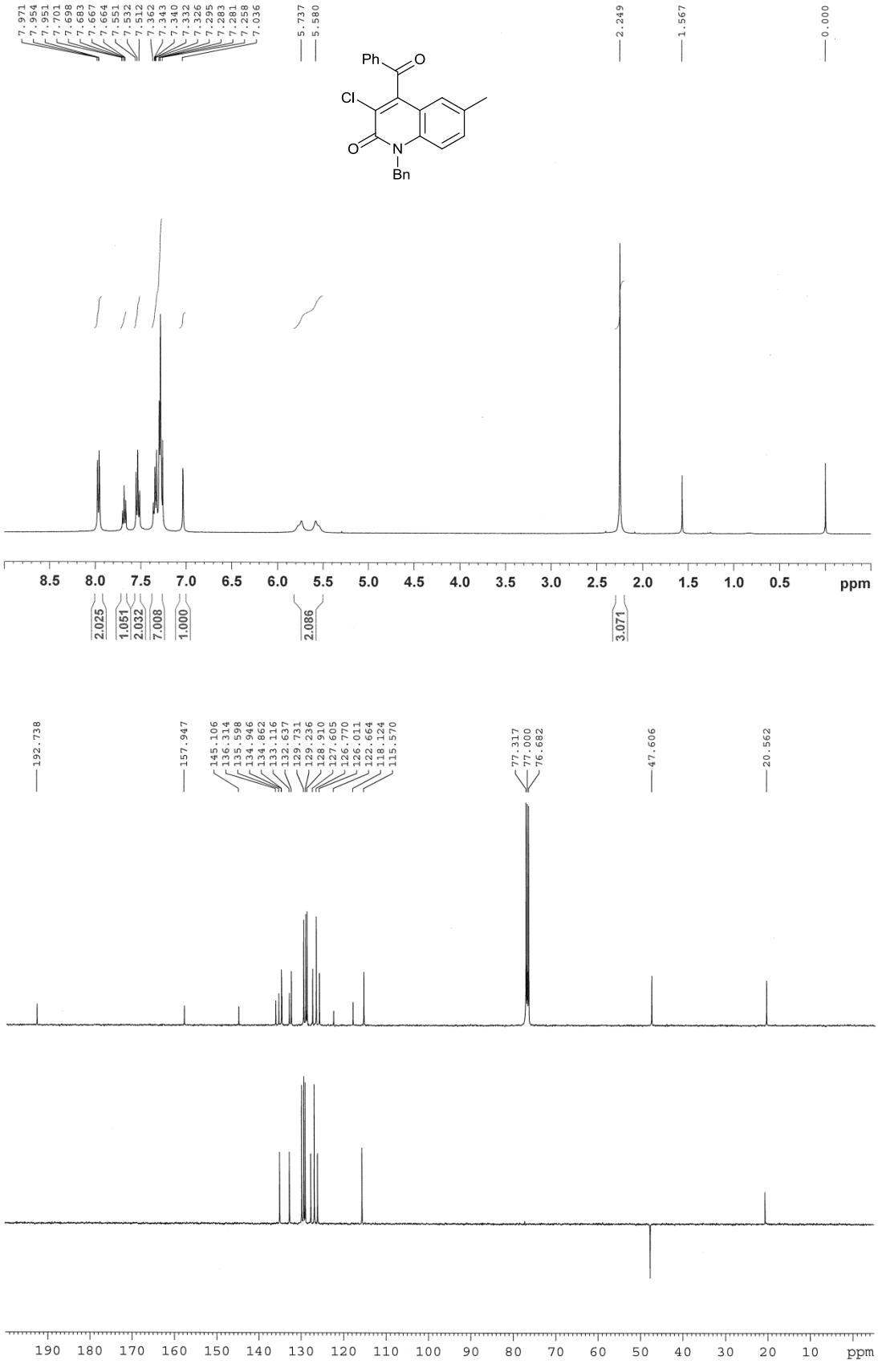


^{1}H & ^{13}C NMR spectra of **8b**

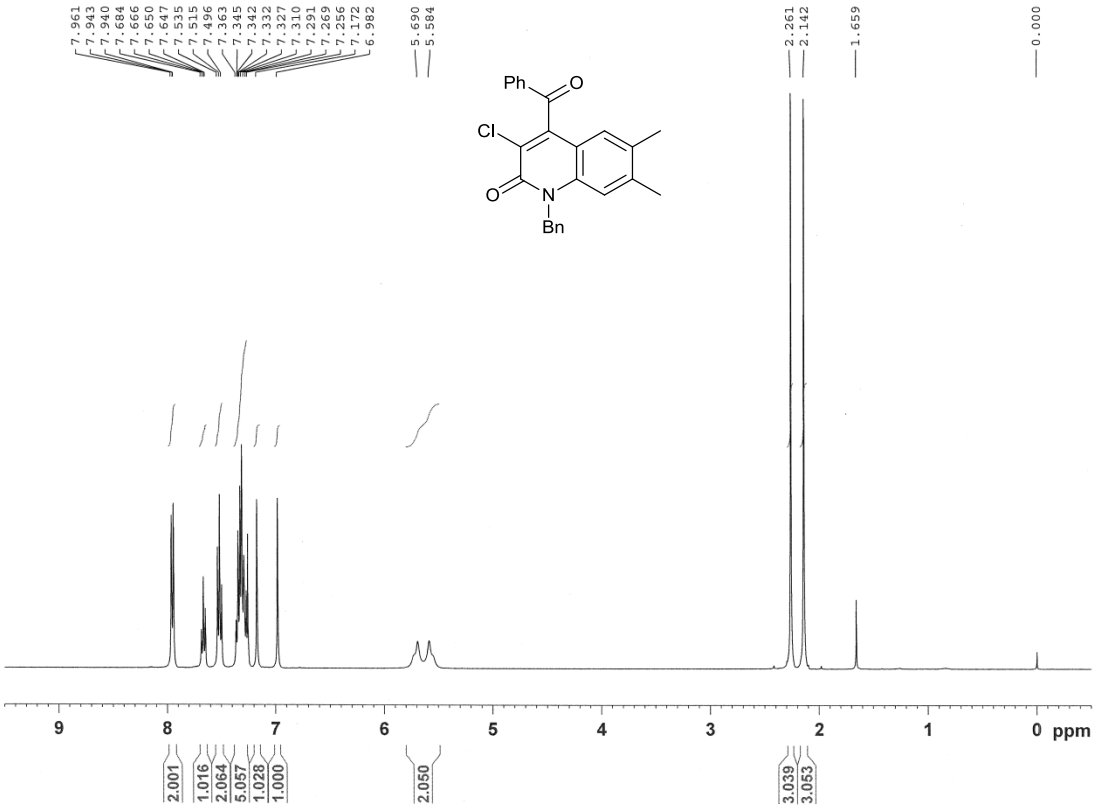


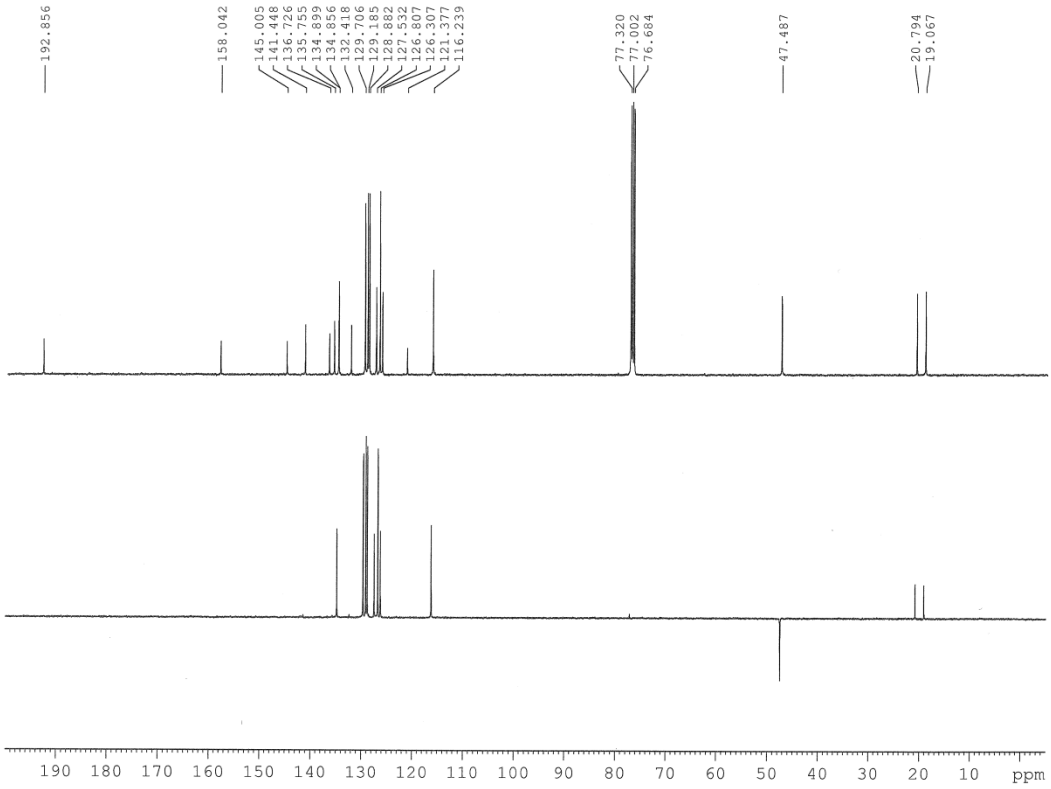


^{1}H & ^{13}C NMR spectra of **8d**

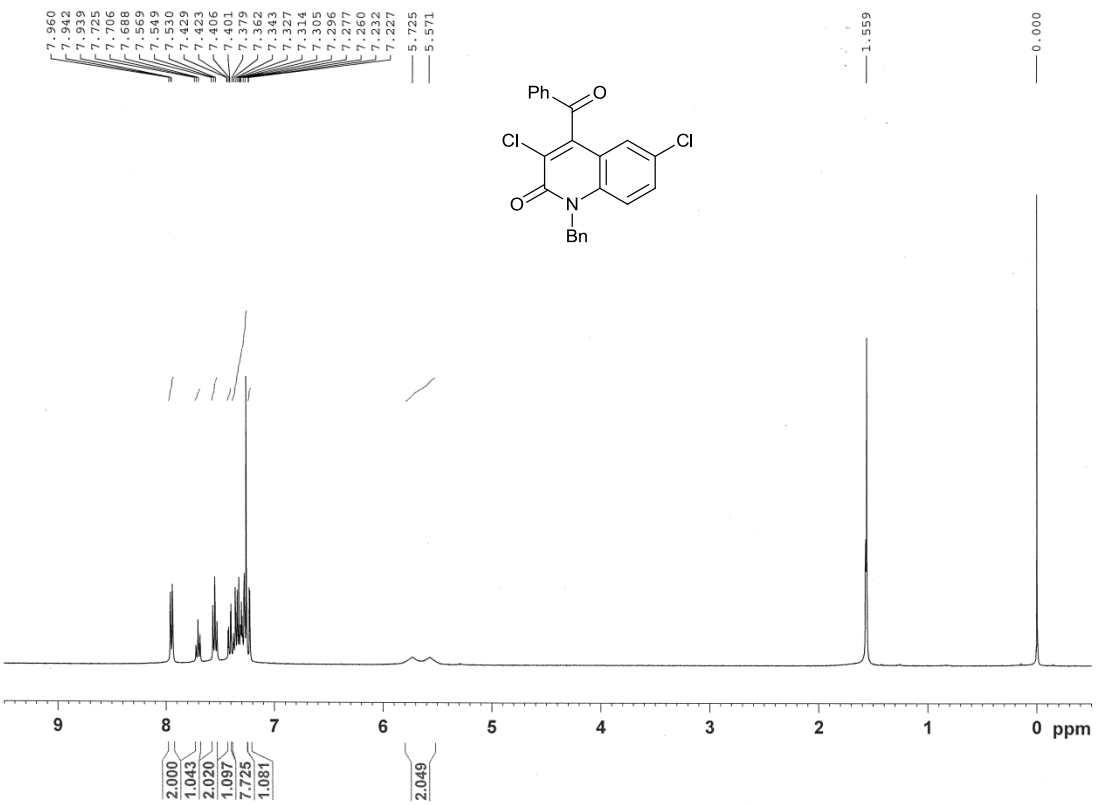


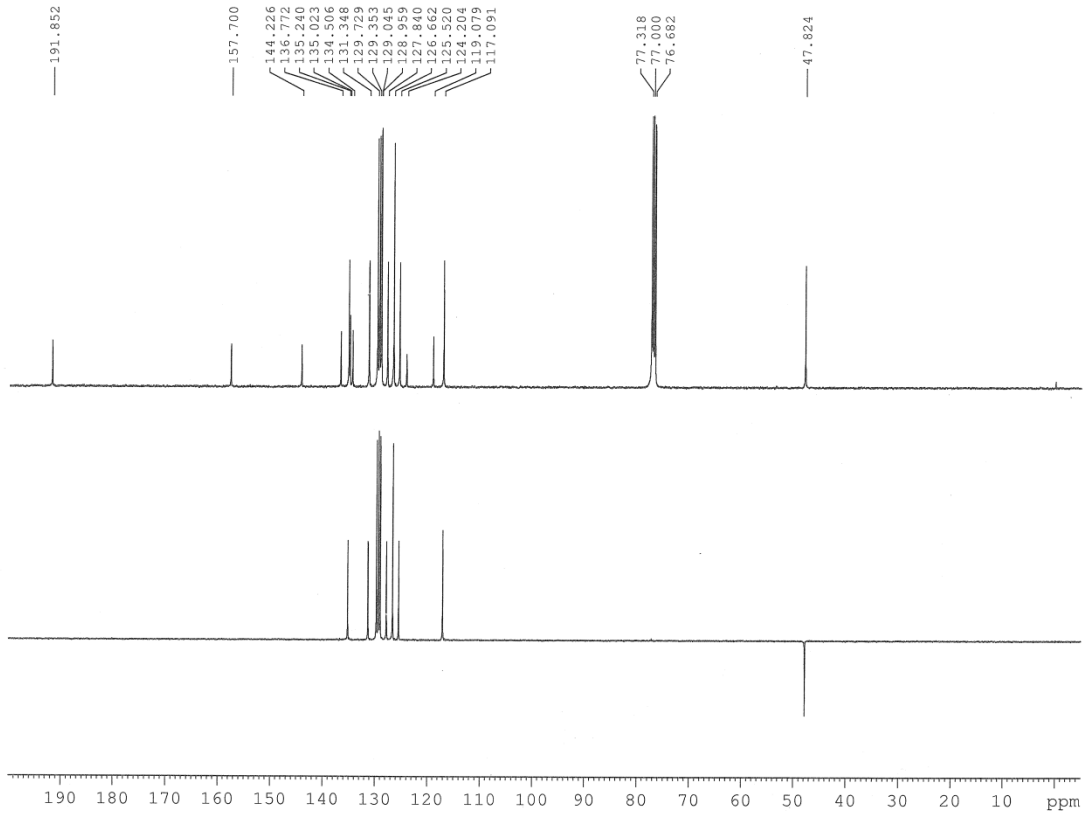
^{1}H & ^{13}C NMR spectra of **8e**



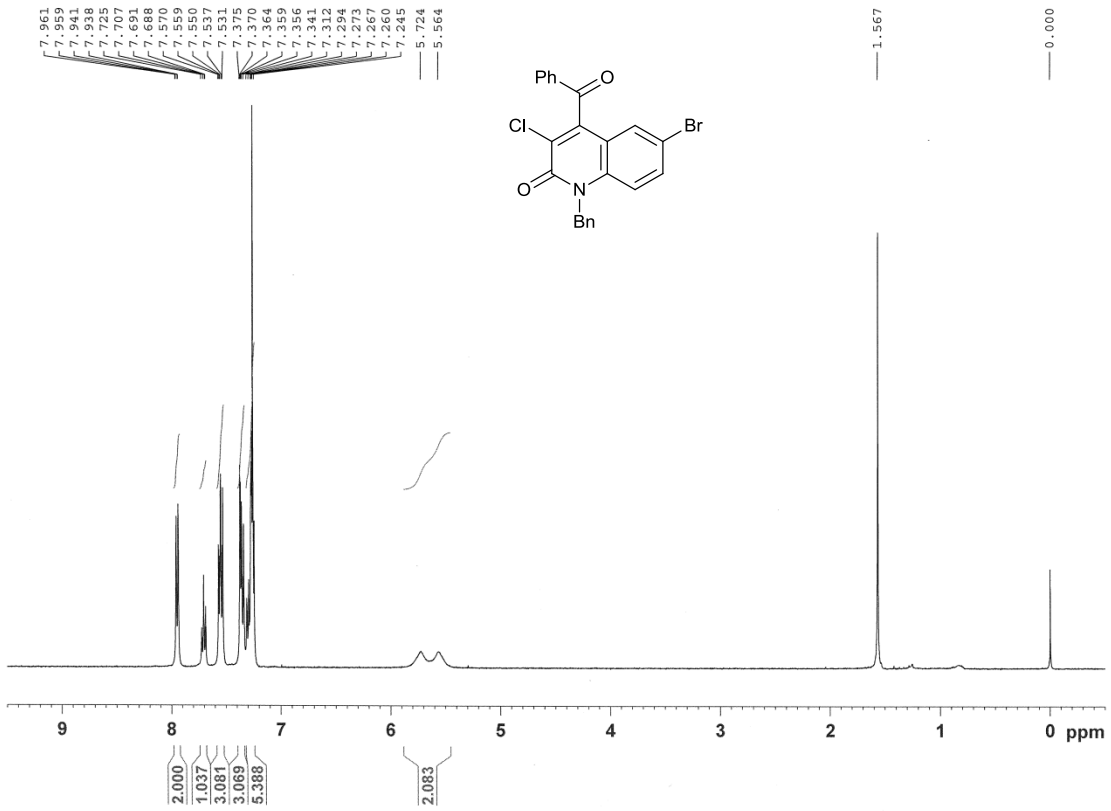


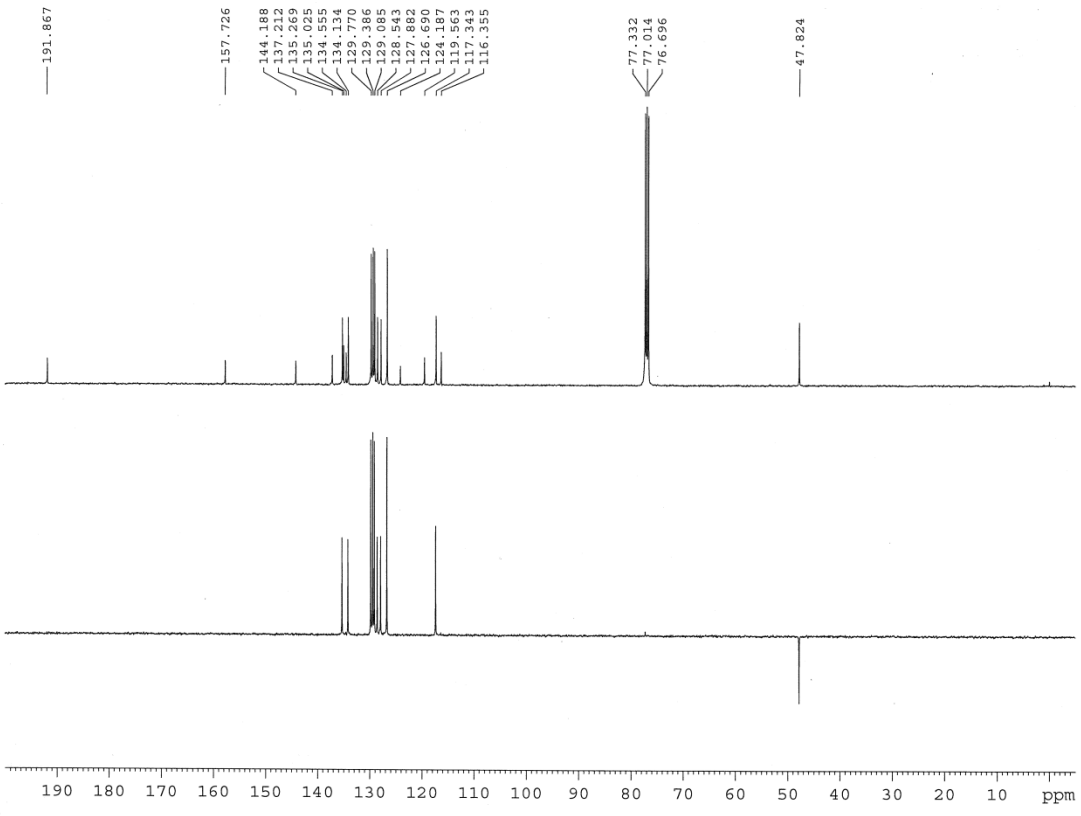
^{1}H & ^{13}C NMR spectra of **8f**



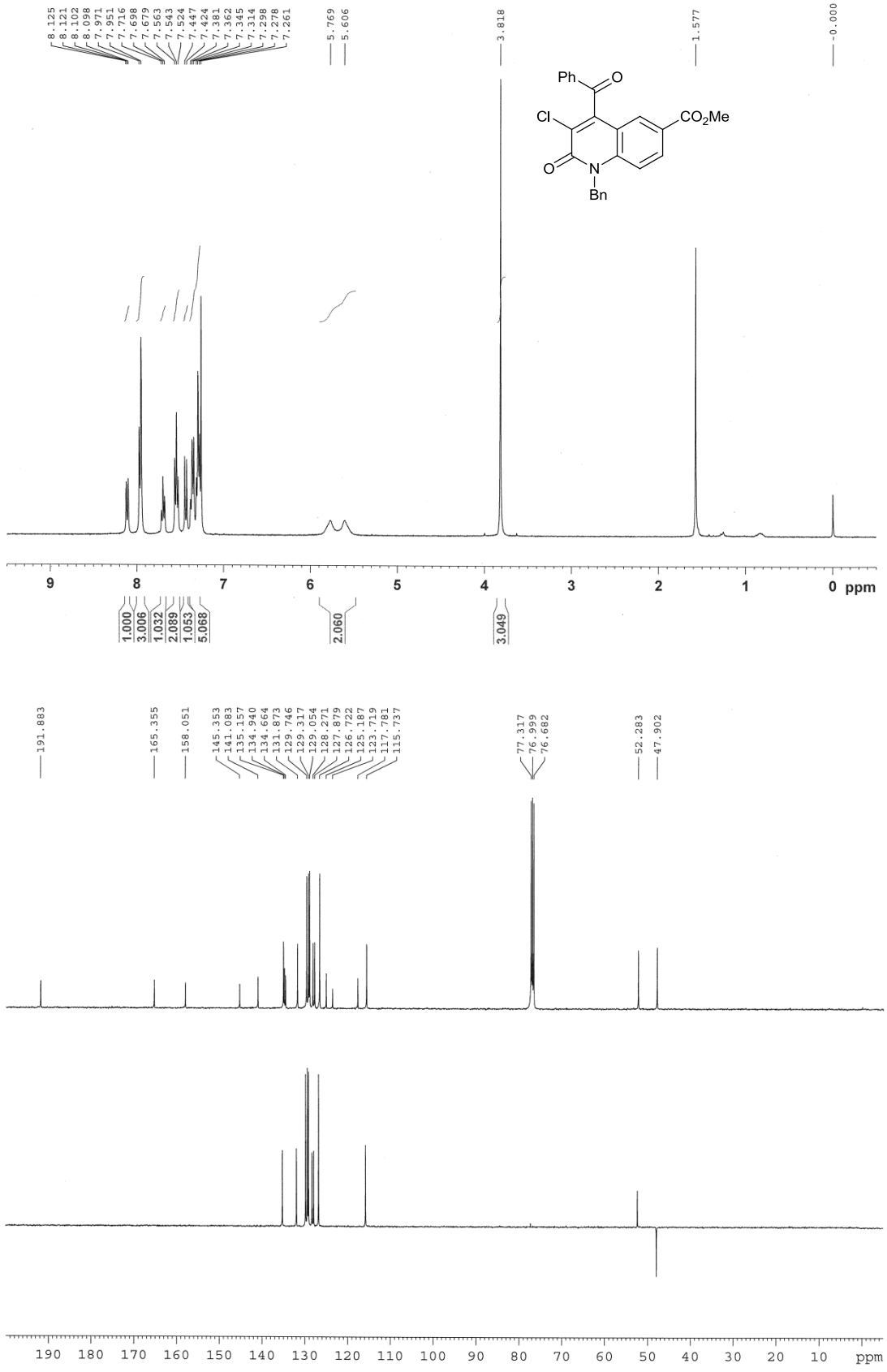


^{1}H & ^{13}C NMR spectra of **8g**

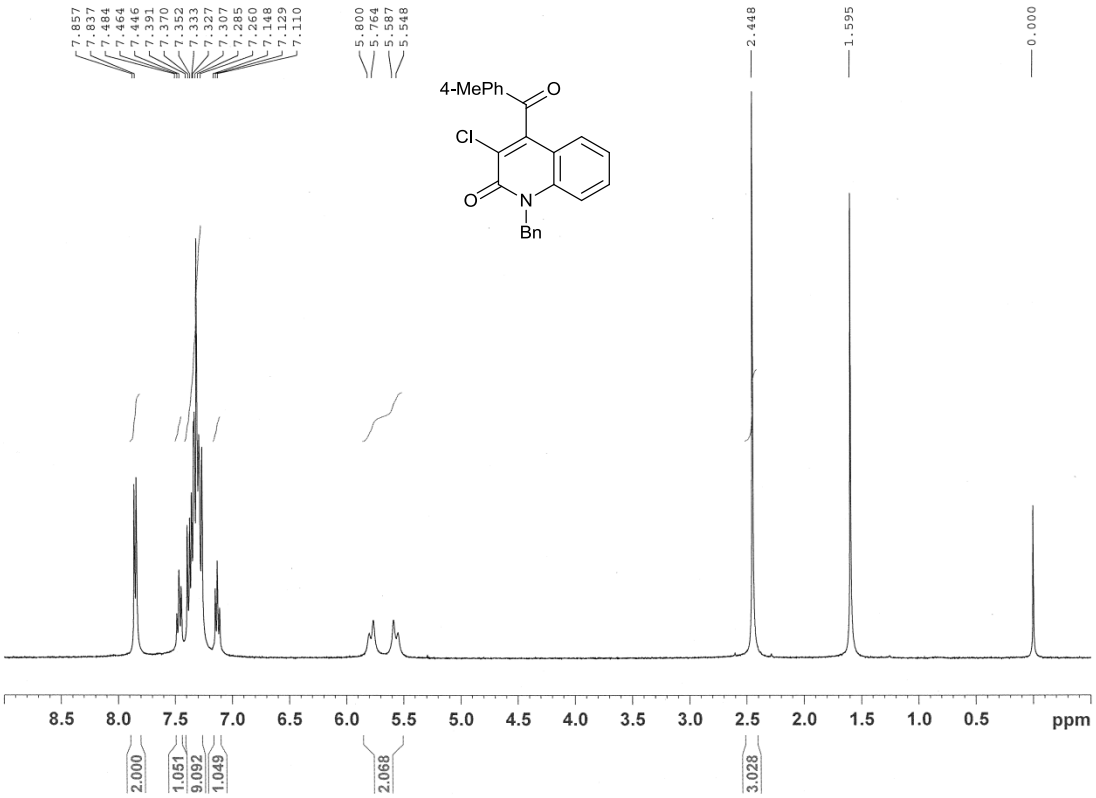


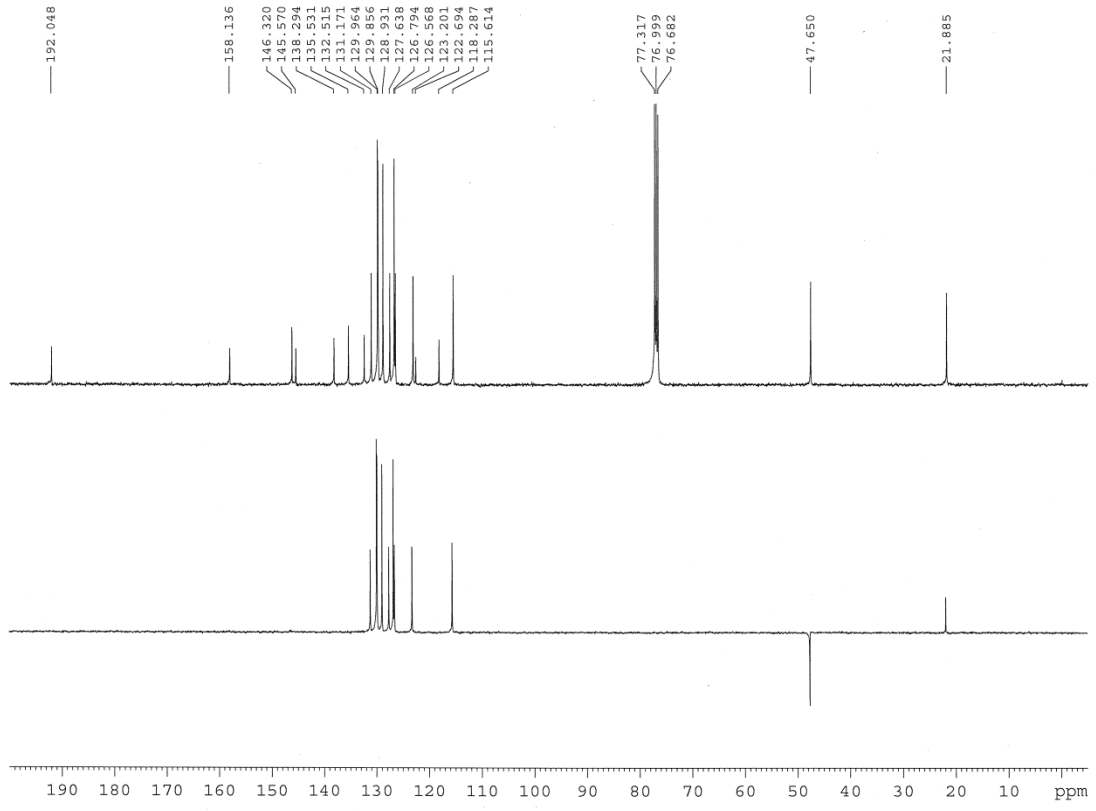


^{1}H & ^{13}C NMR spectra of **8h**

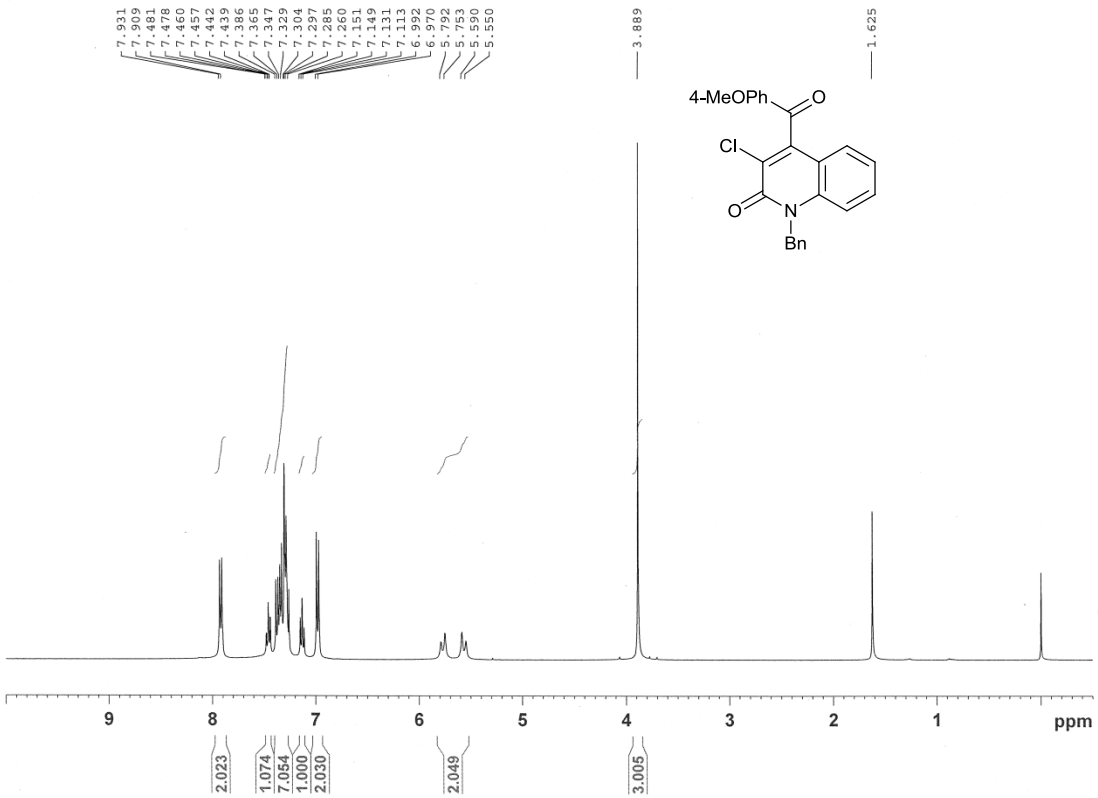


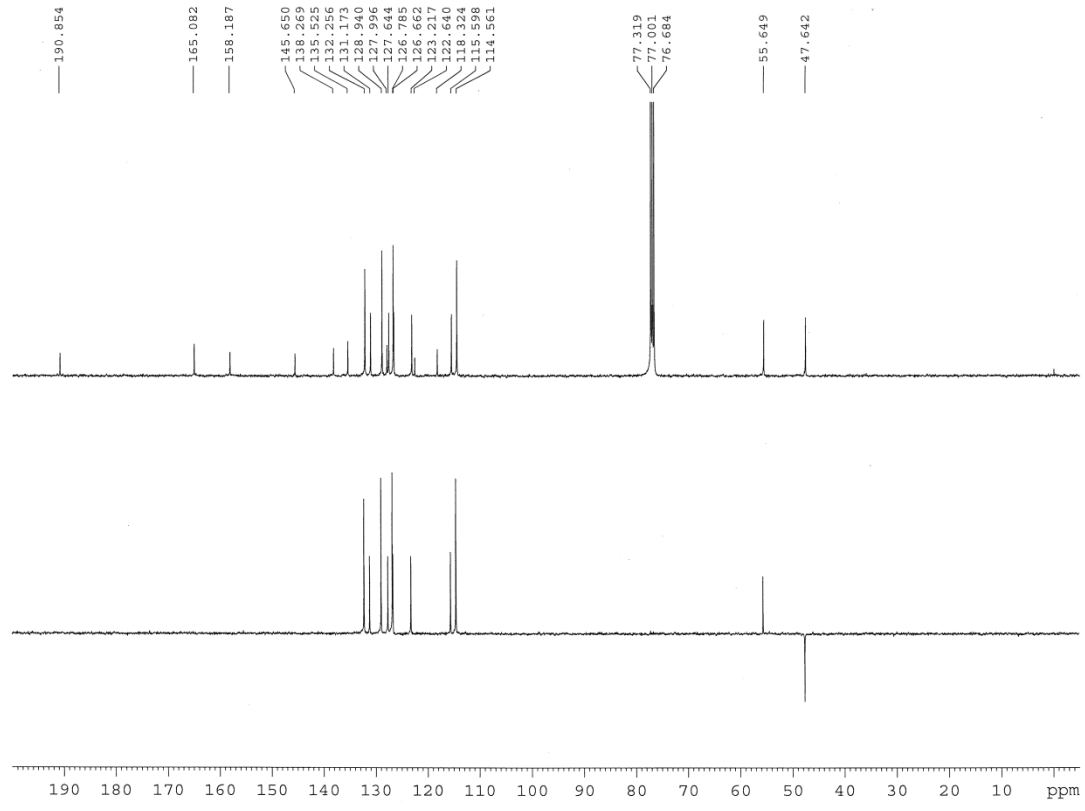
^{1}H & ^{13}C NMR spectra of **8i**



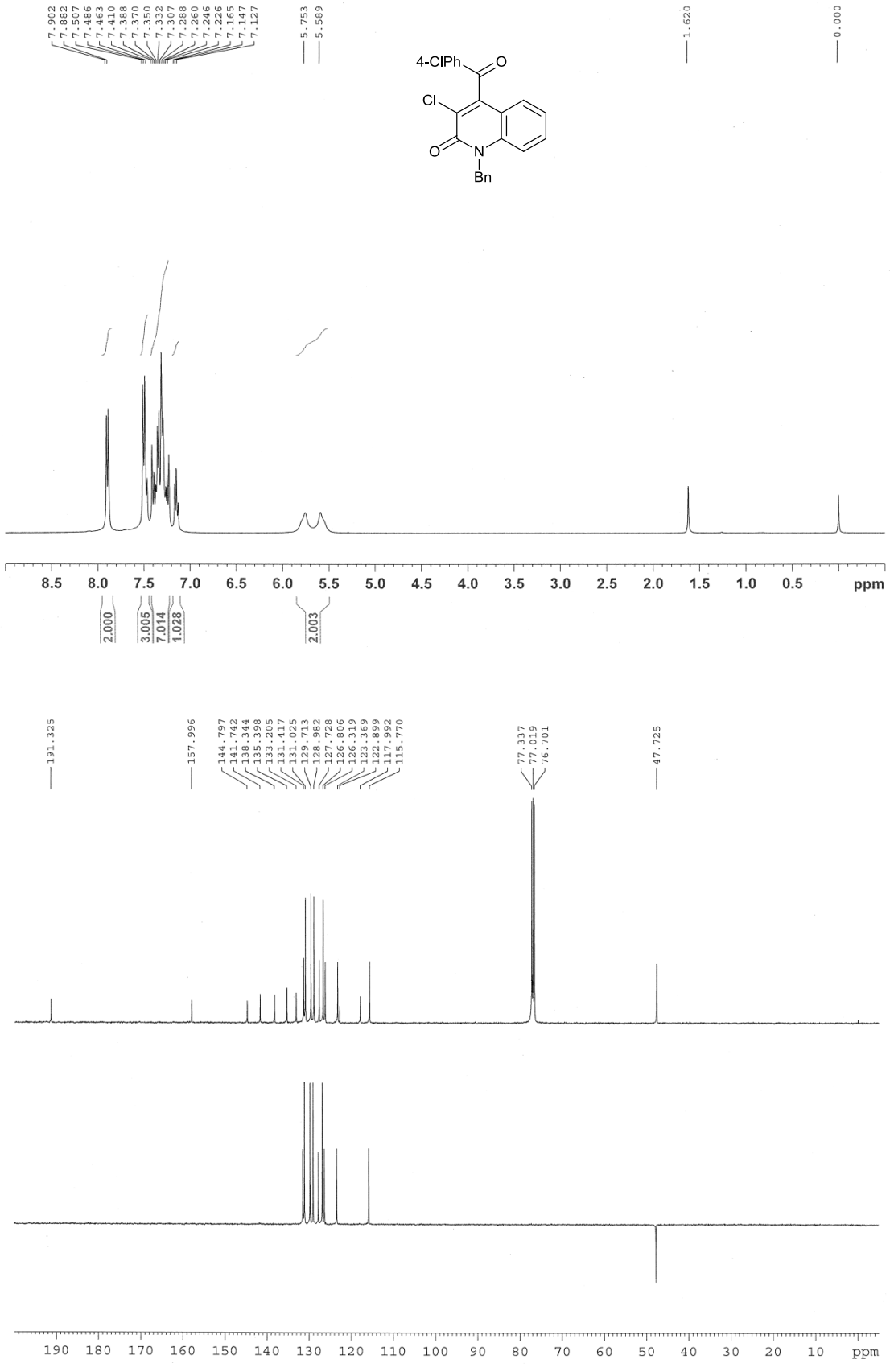


^{1}H & ^{13}C NMR spectra of **8j**

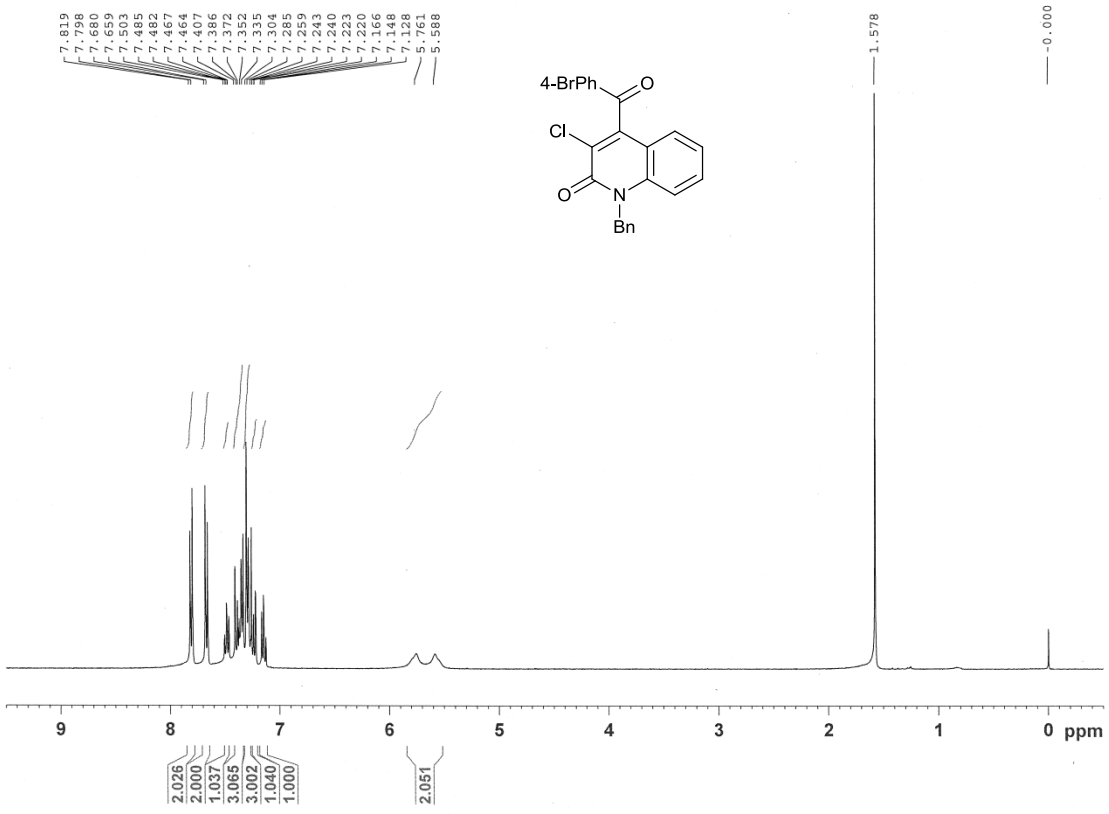


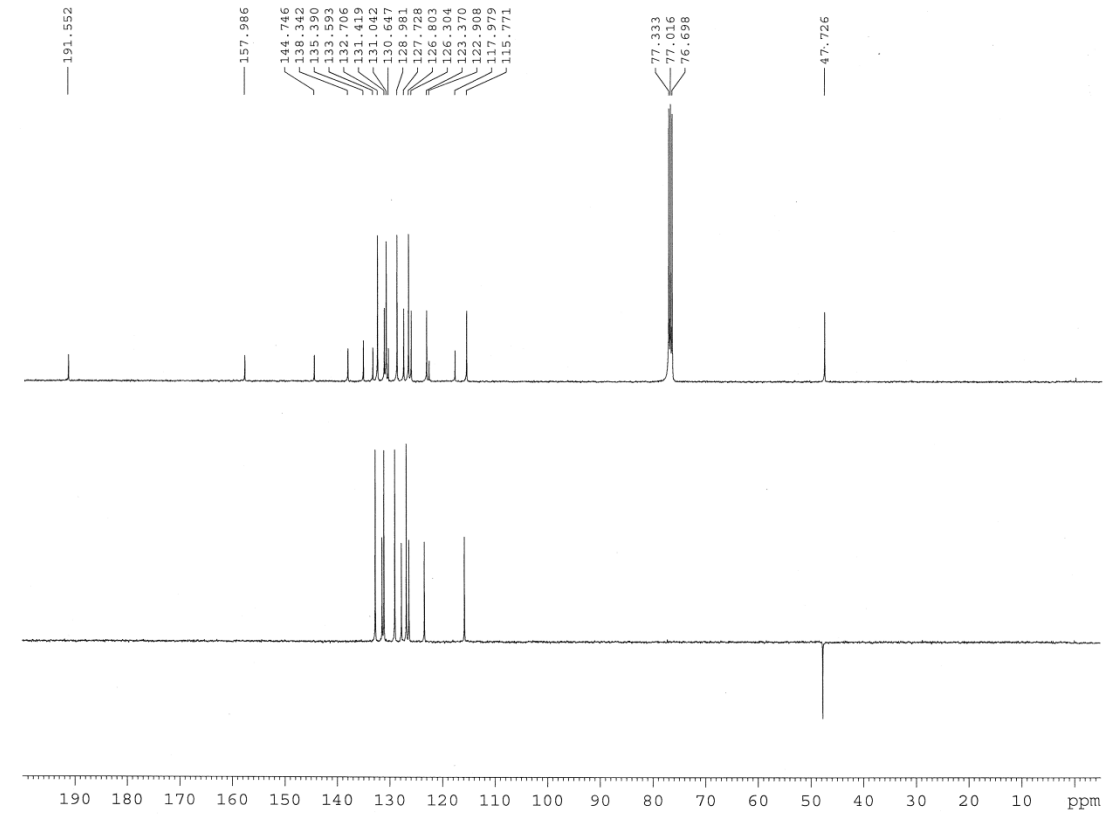


^{1}H & ^{13}C NMR spectra of **8k**

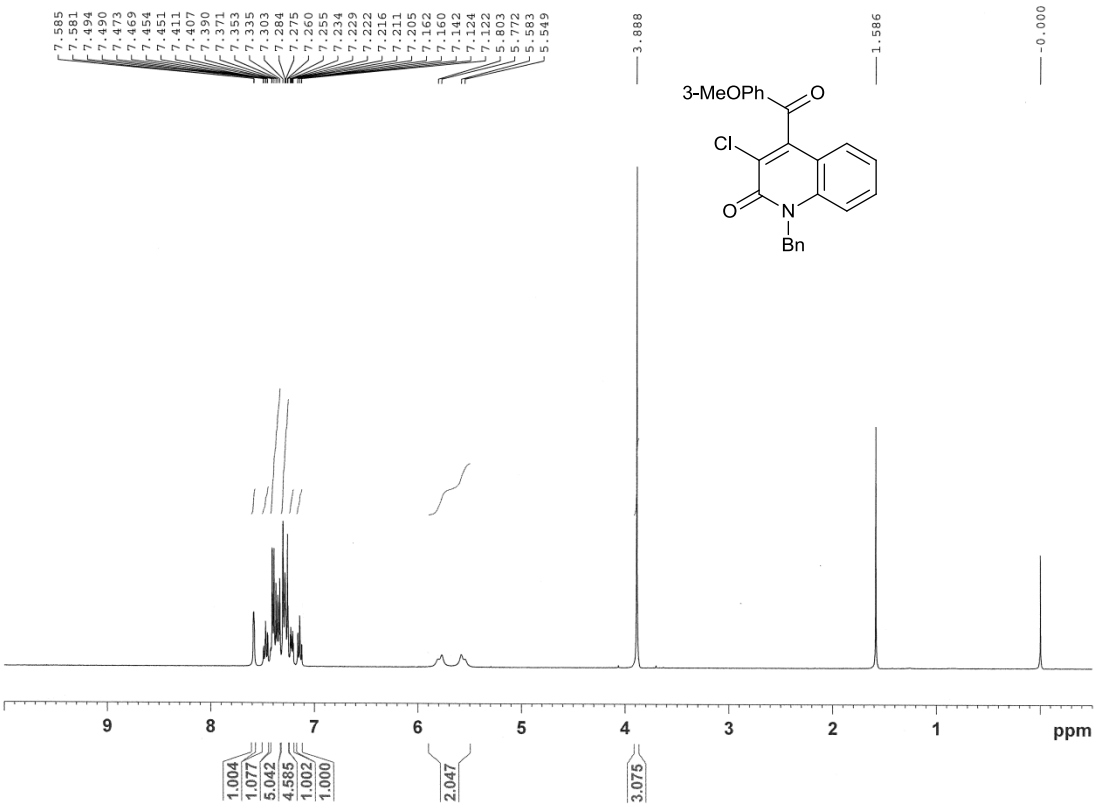


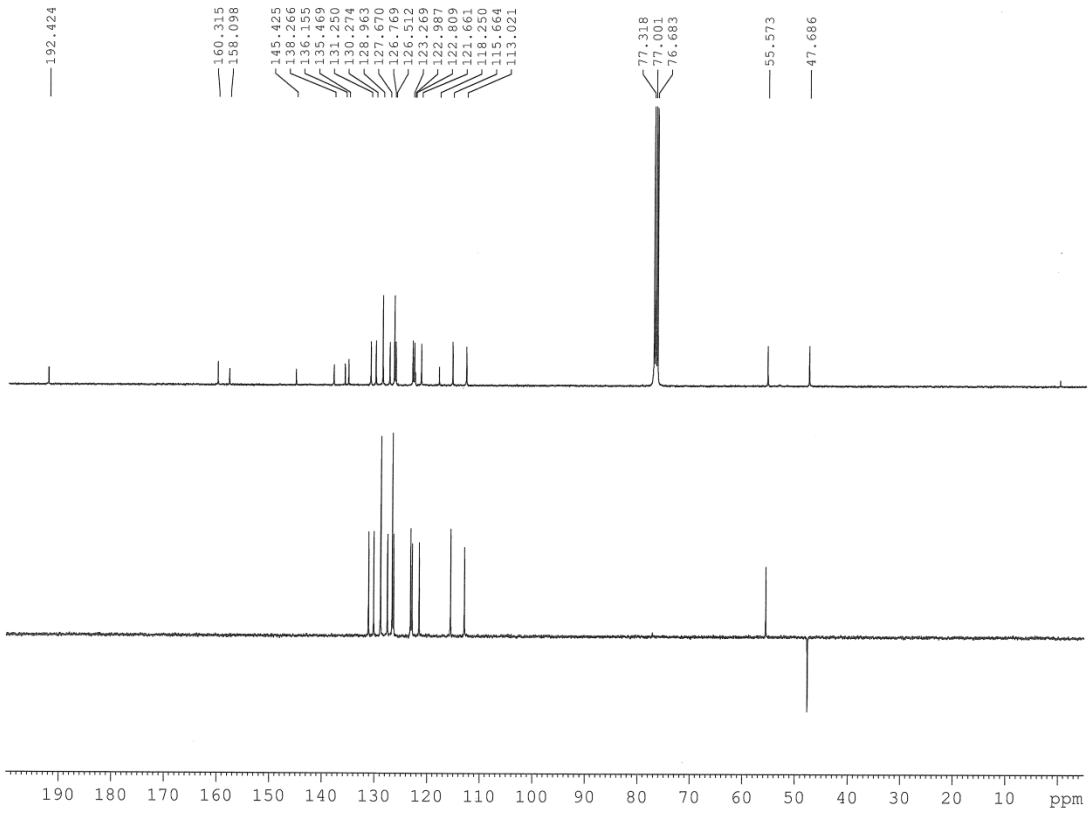
^{1}H & ^{13}C NMR spectra of **8l**



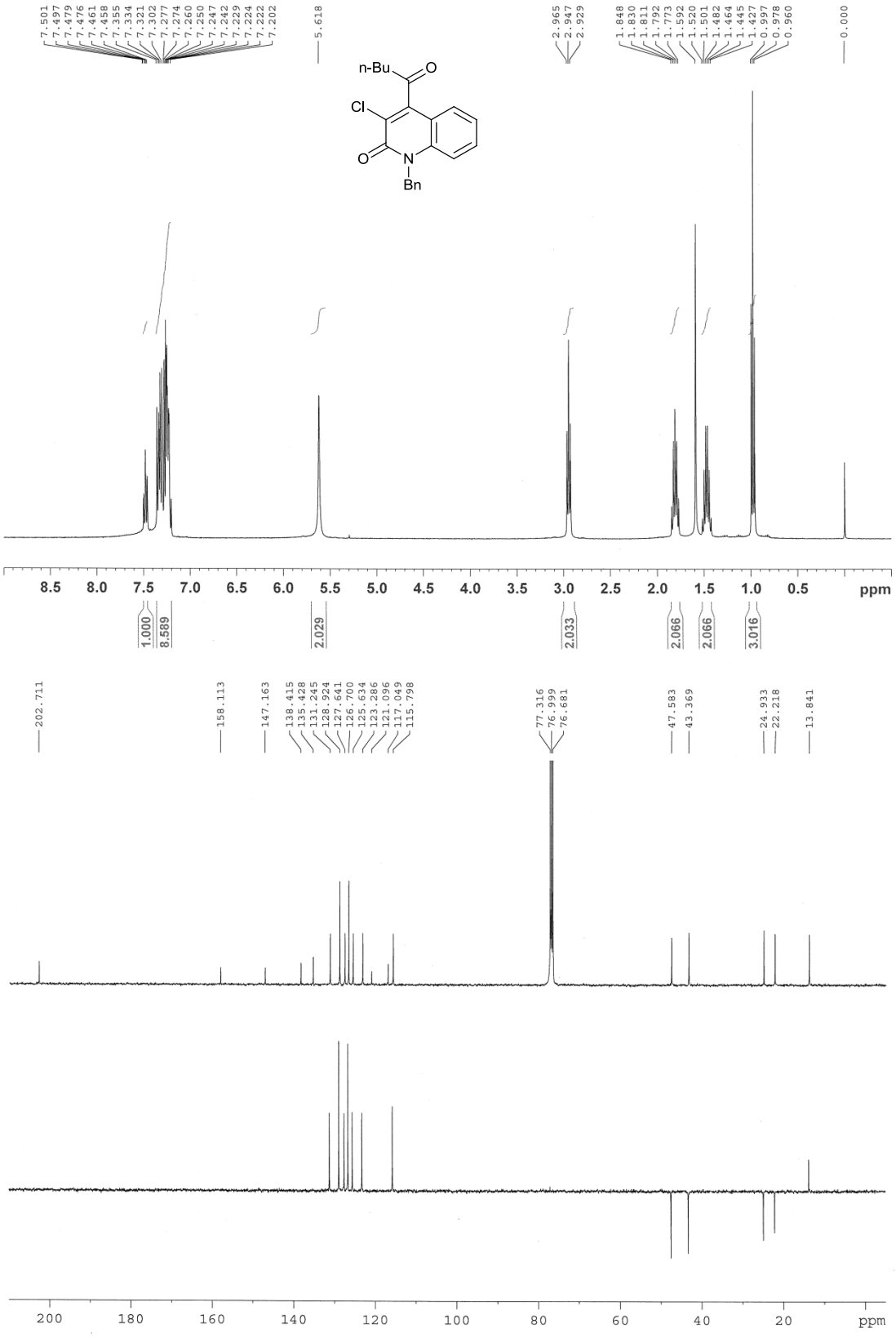


^{1}H & ^{13}C NMR spectra of **8m**

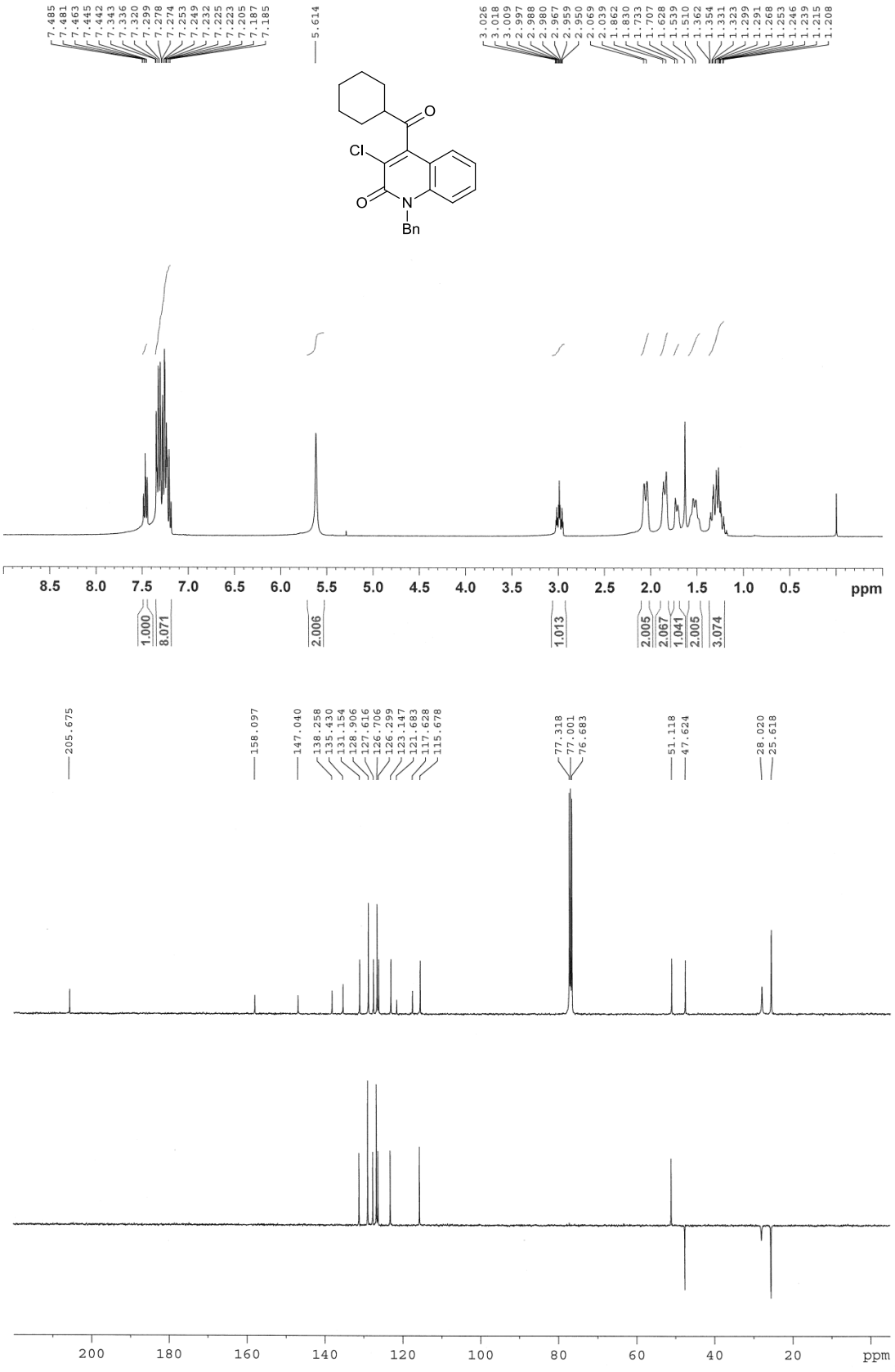




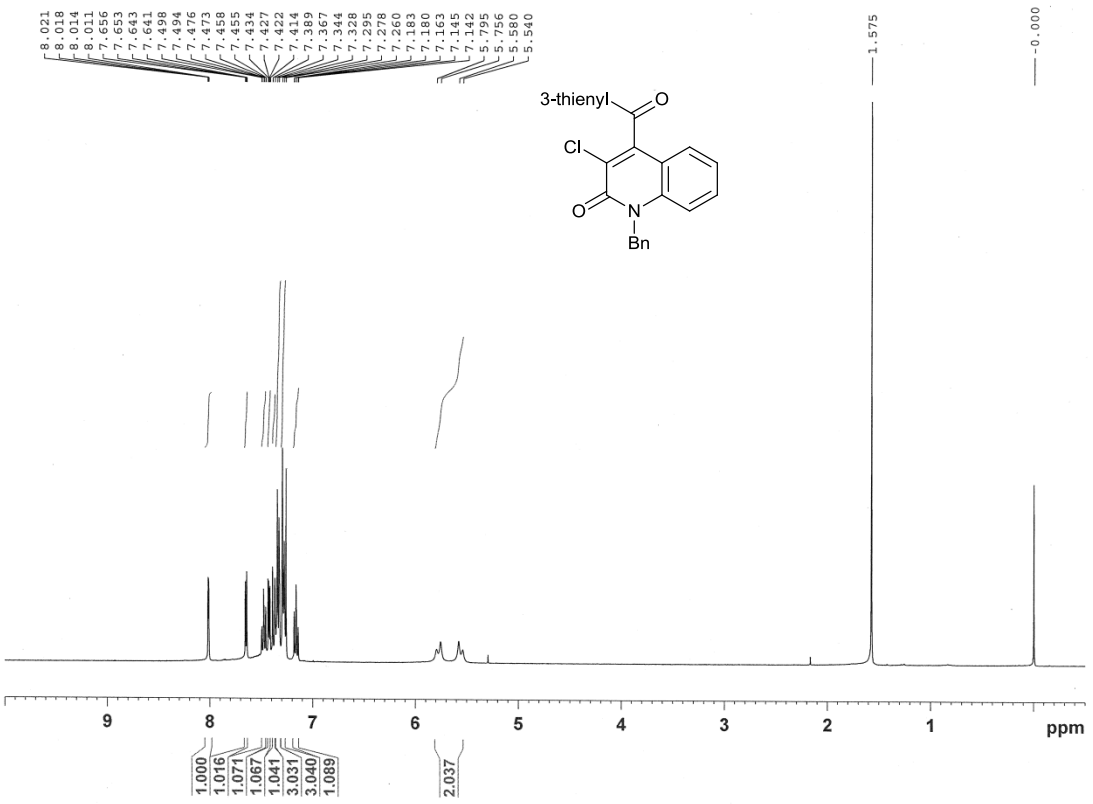
^{1}H & ^{13}C NMR spectra of **8n**

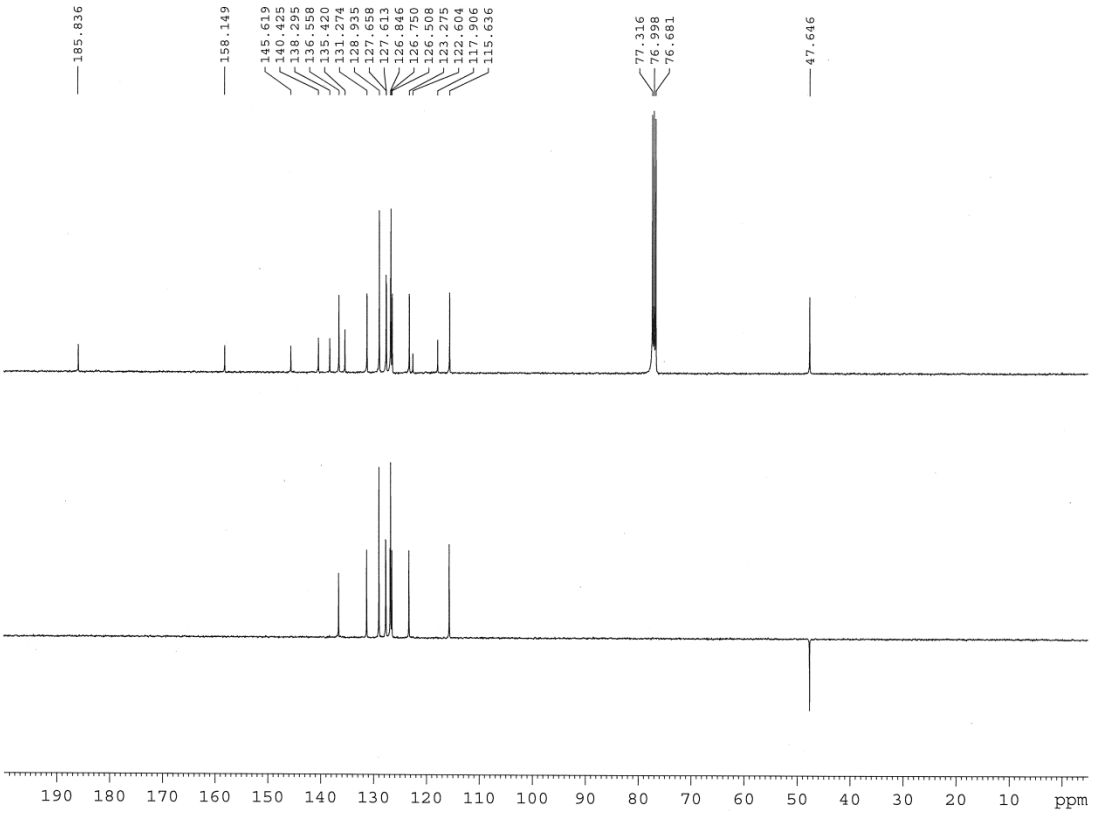


^{1}H & ^{13}C NMR spectra of **8o**

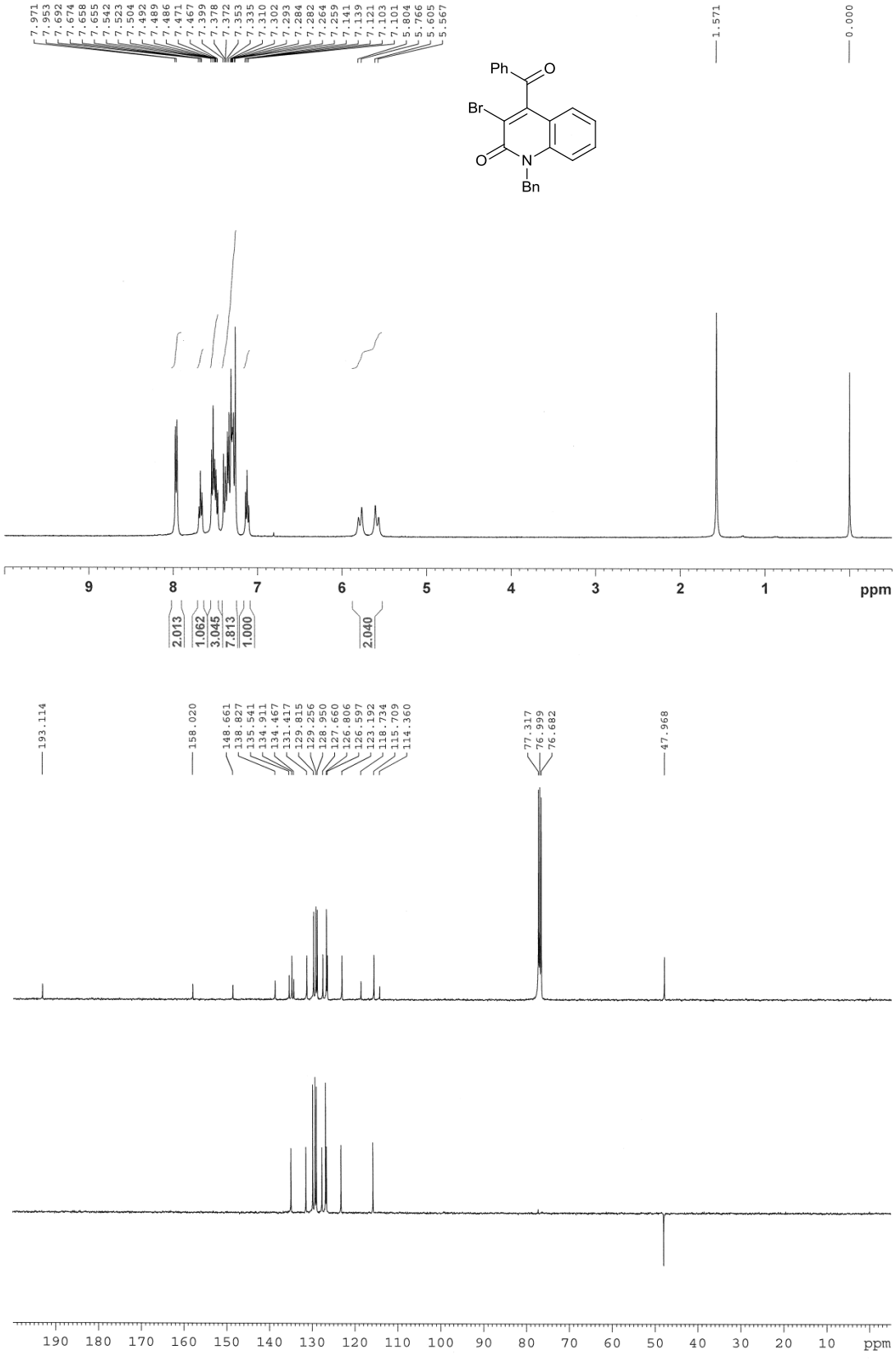


^{1}H & ^{13}C NMR spectra of **8p**

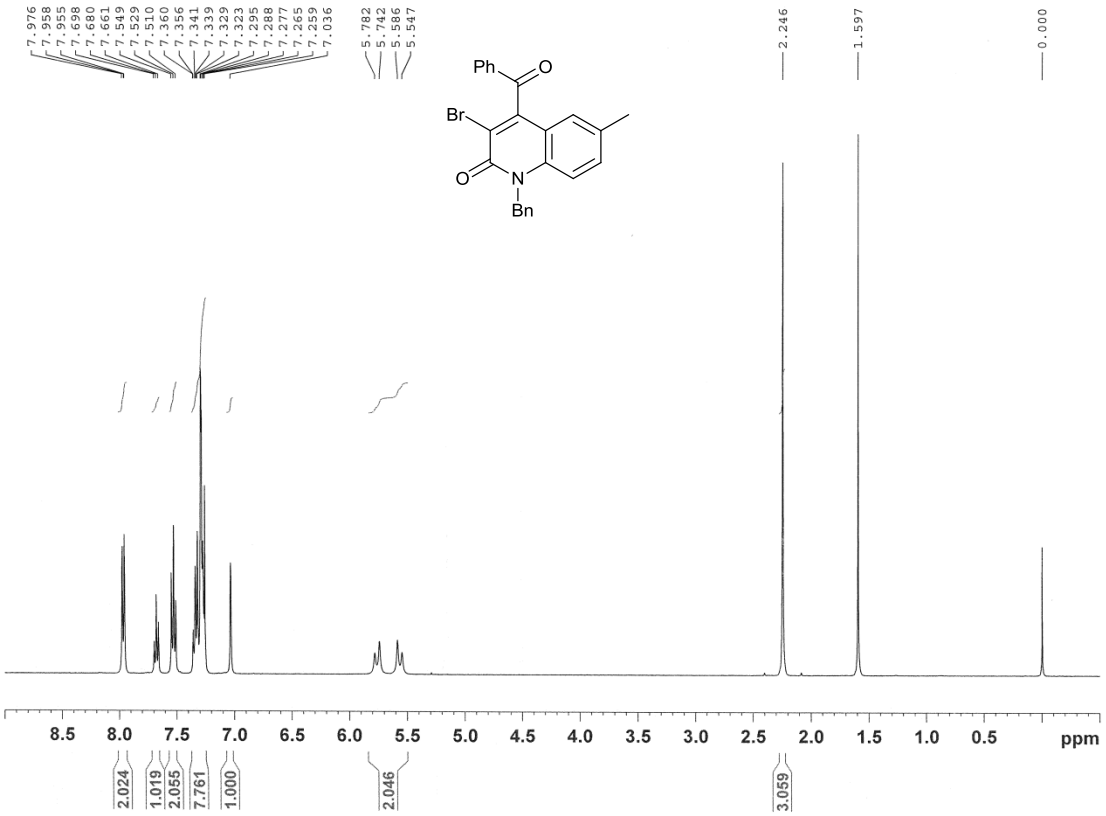


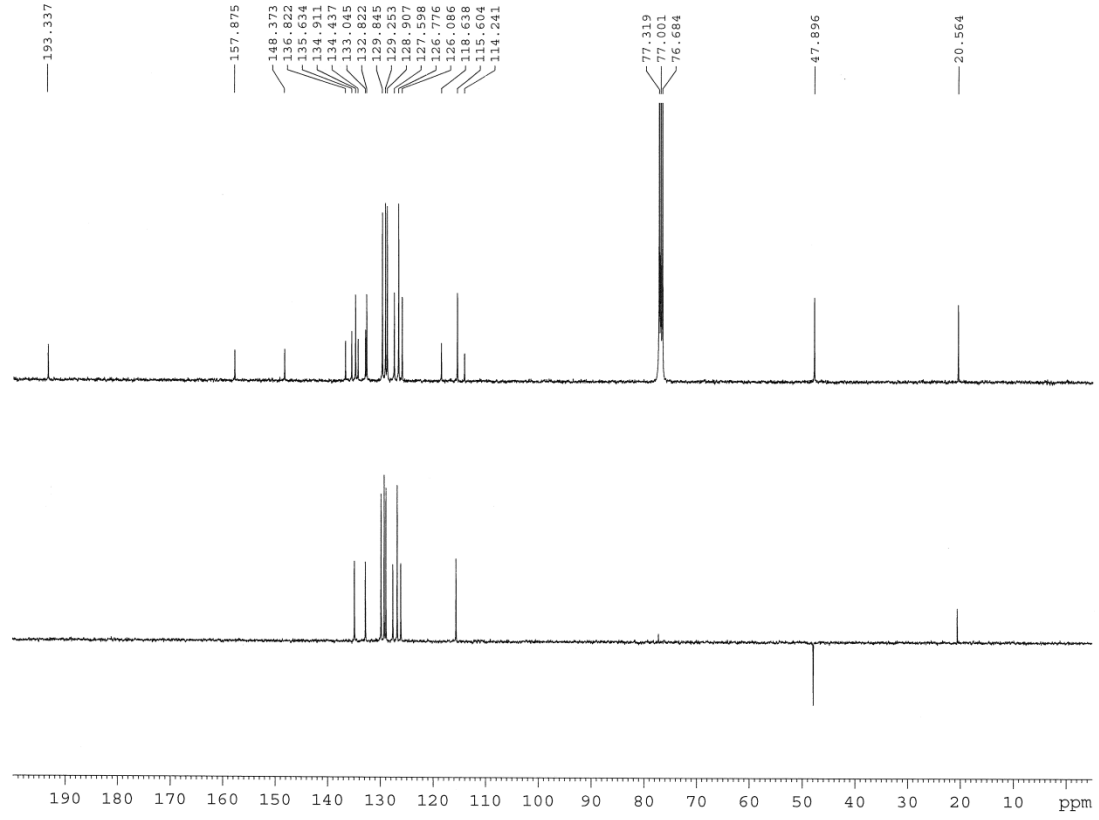


^{1}H & ^{13}C NMR spectra of **10a**

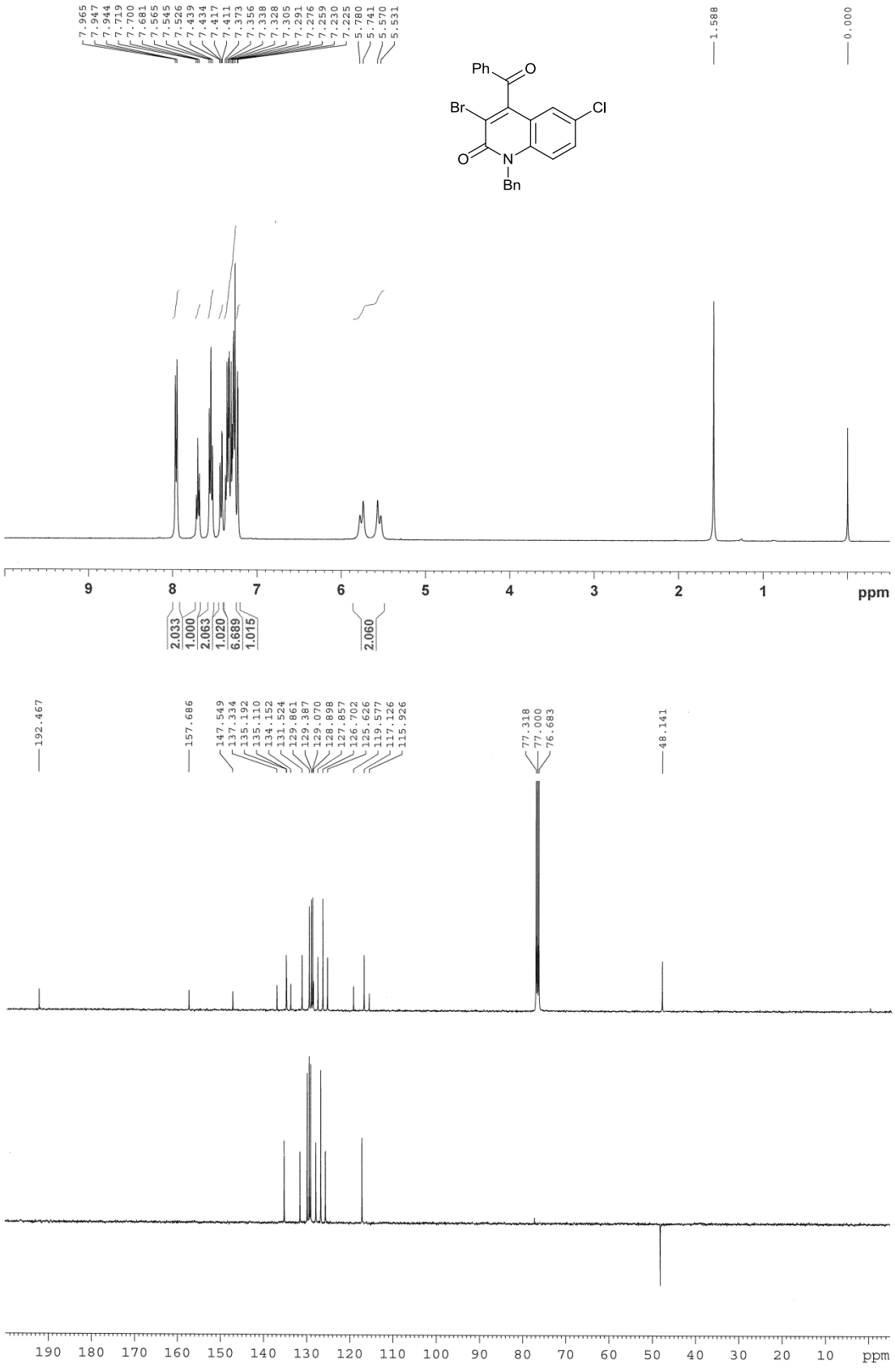


^{1}H & ^{13}C NMR spectra of **10b**

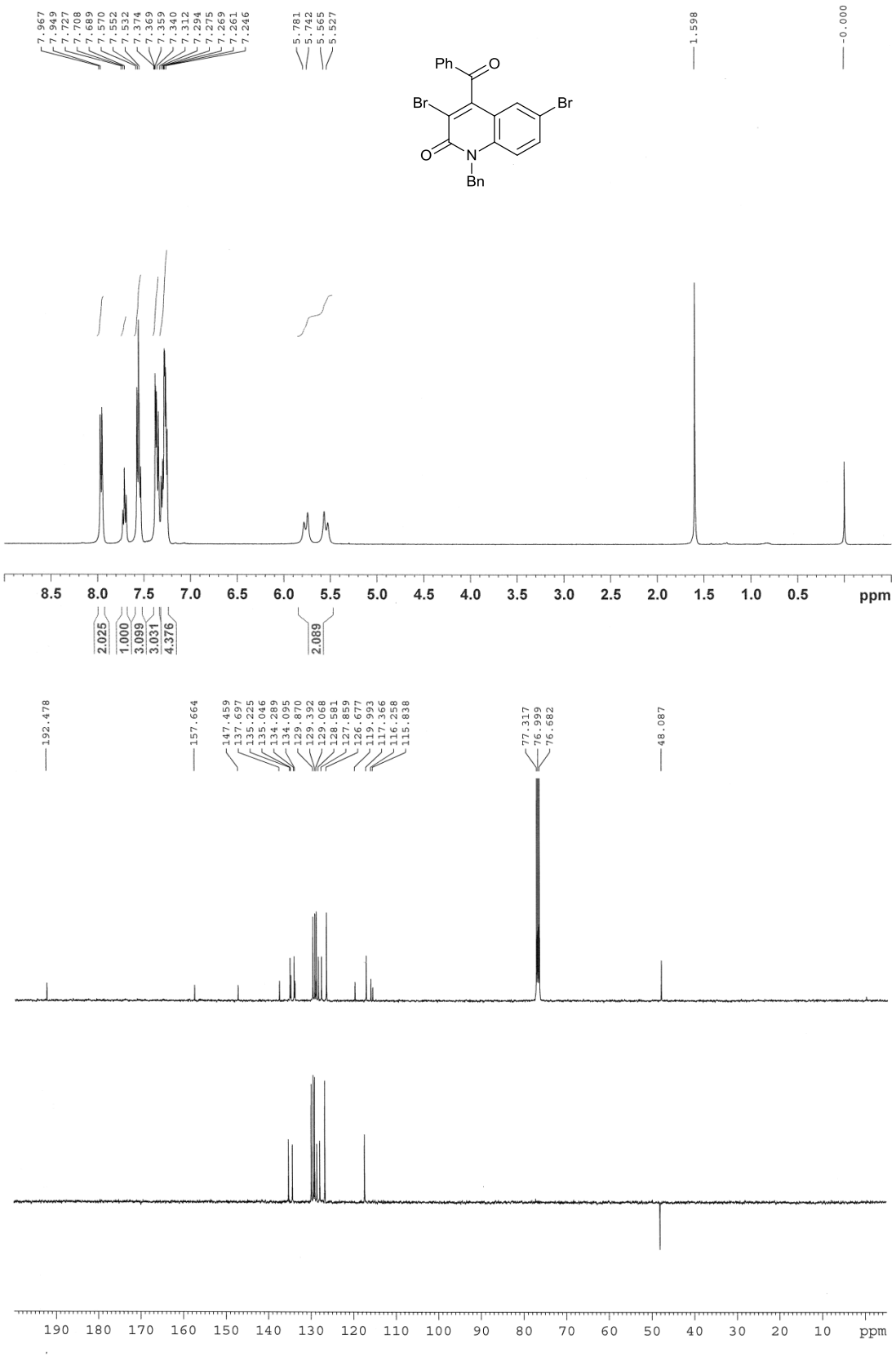




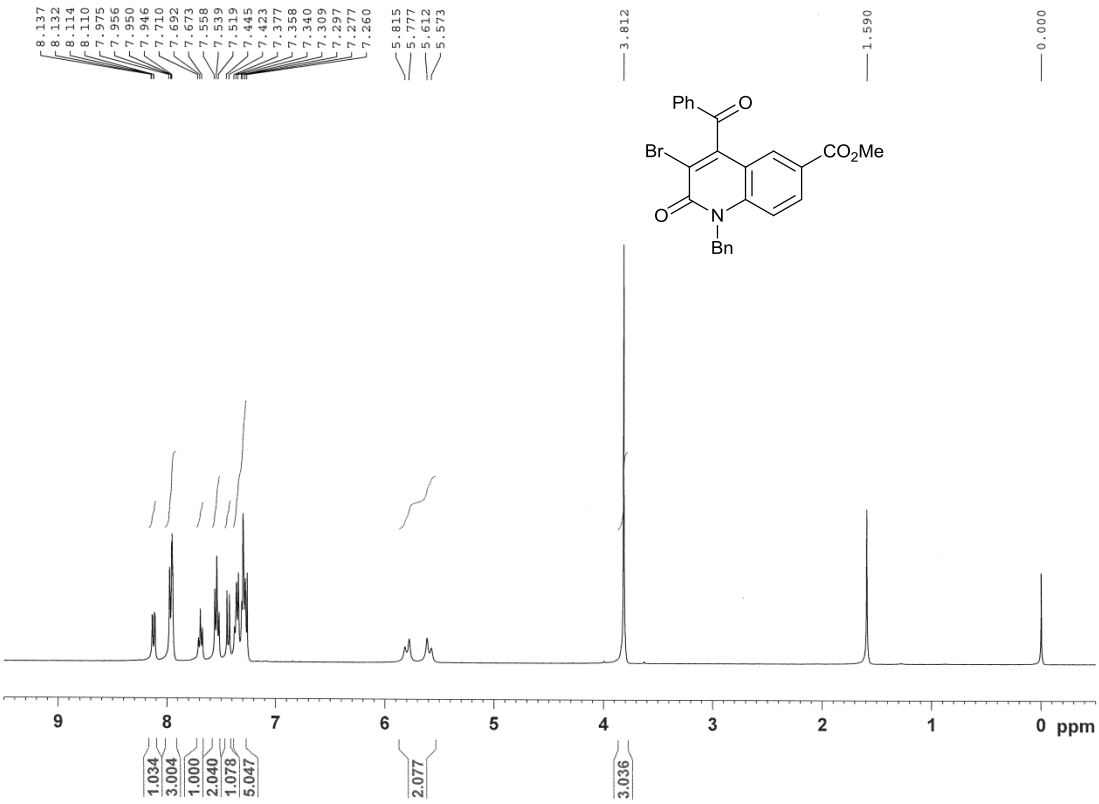
^{1}H & ^{13}C NMR spectra of **10c**

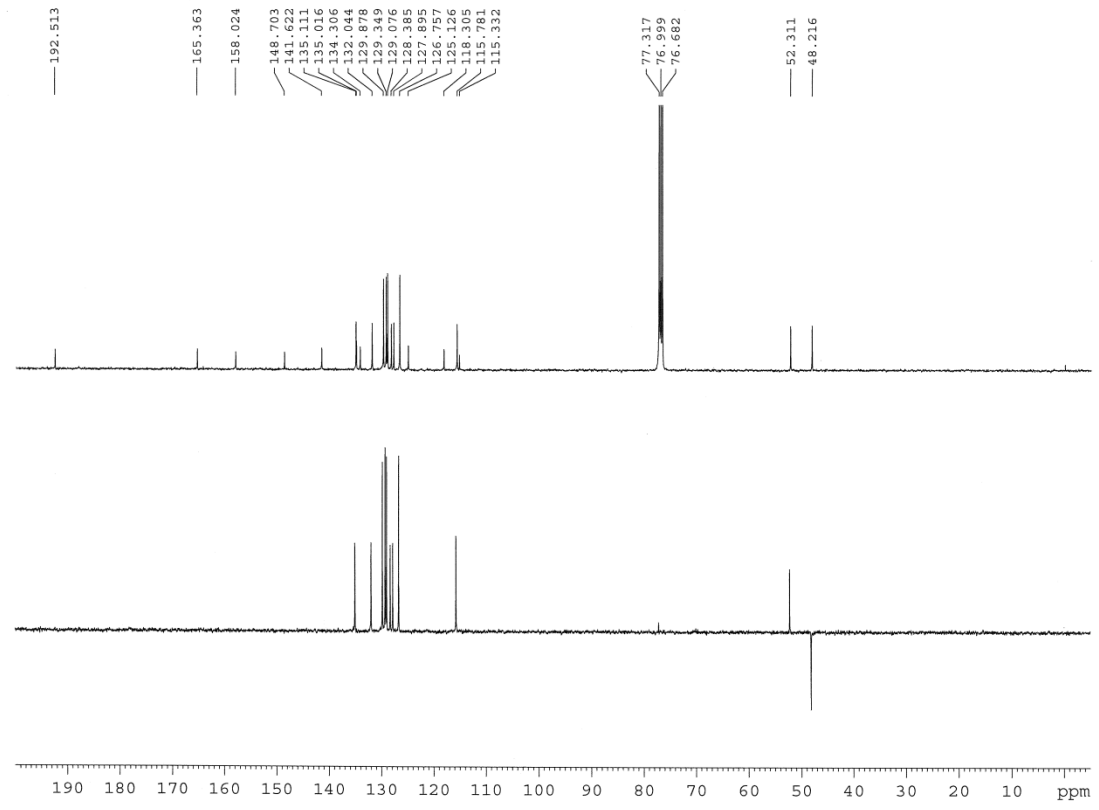


^{1}H & ^{13}C NMR spectra of **10d**

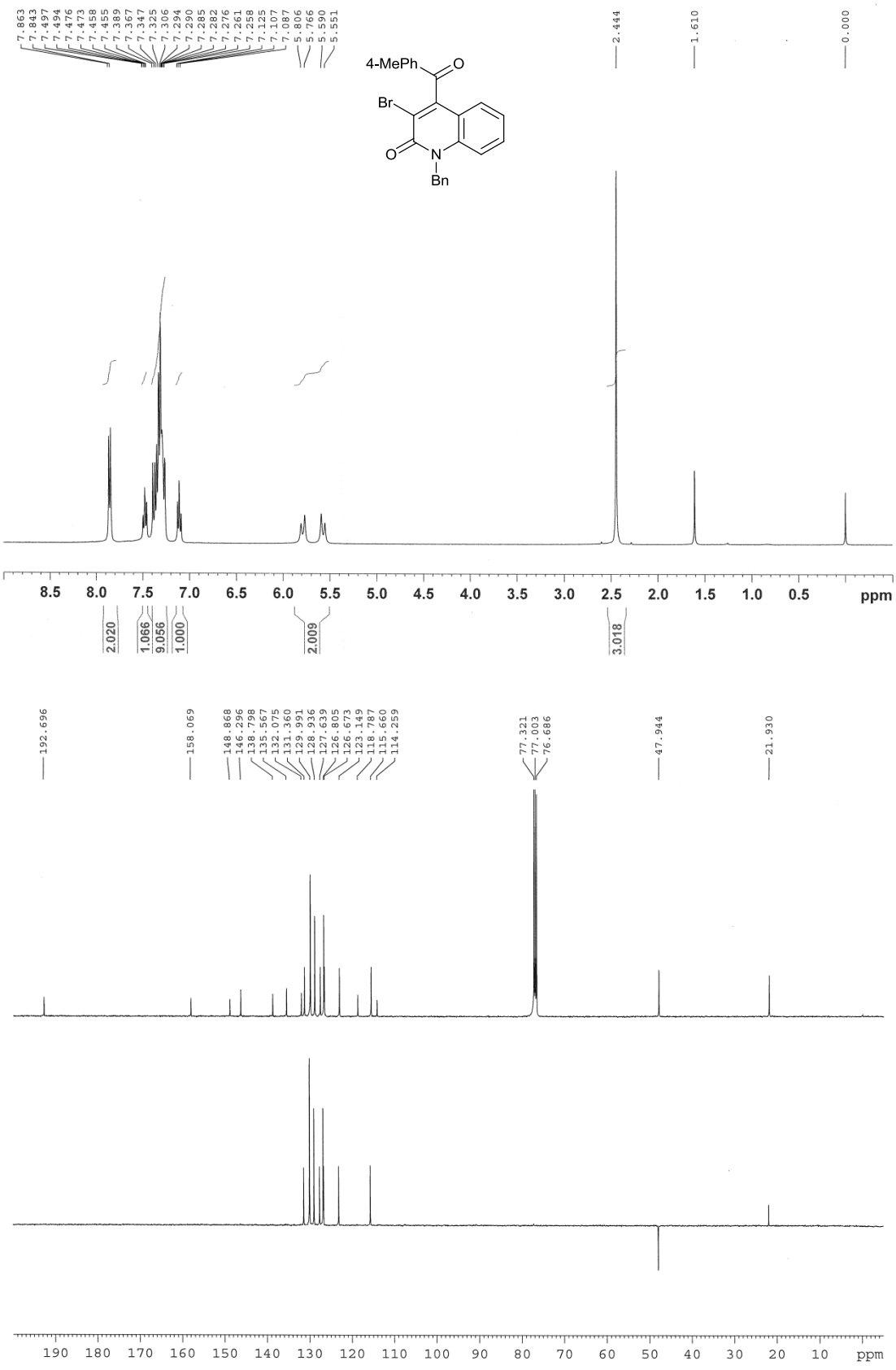


^{1}H & ^{13}C NMR spectra of **10e**

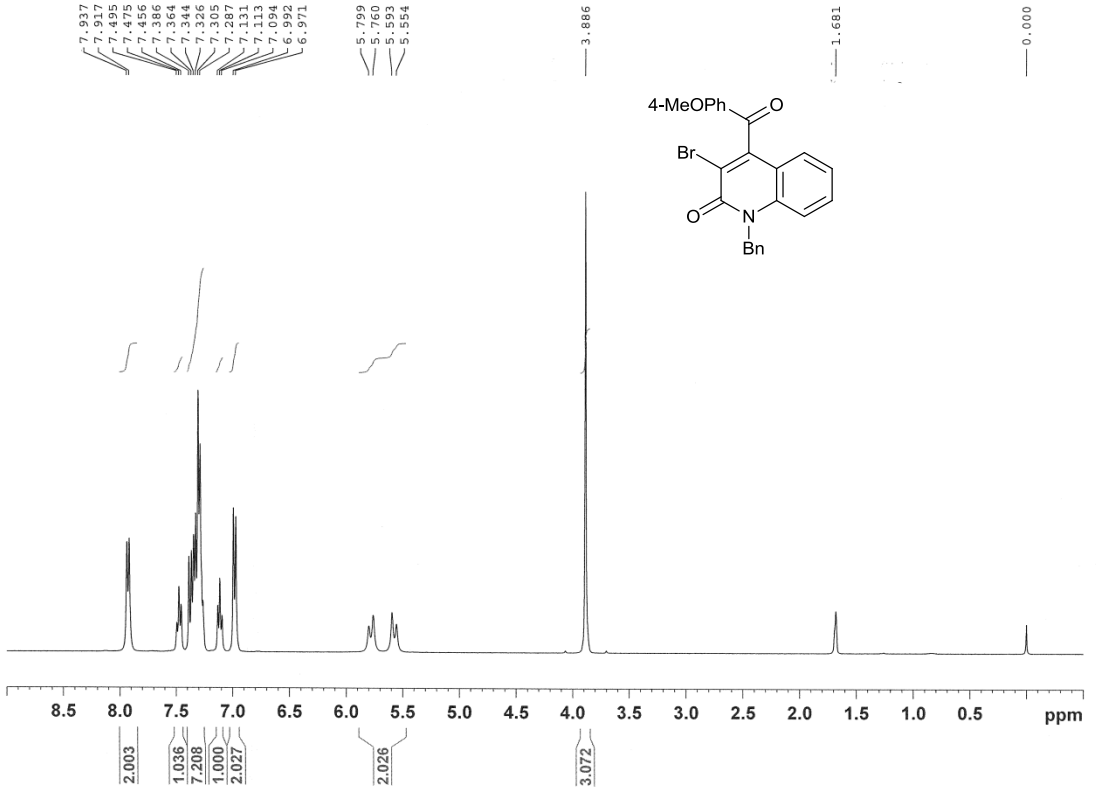


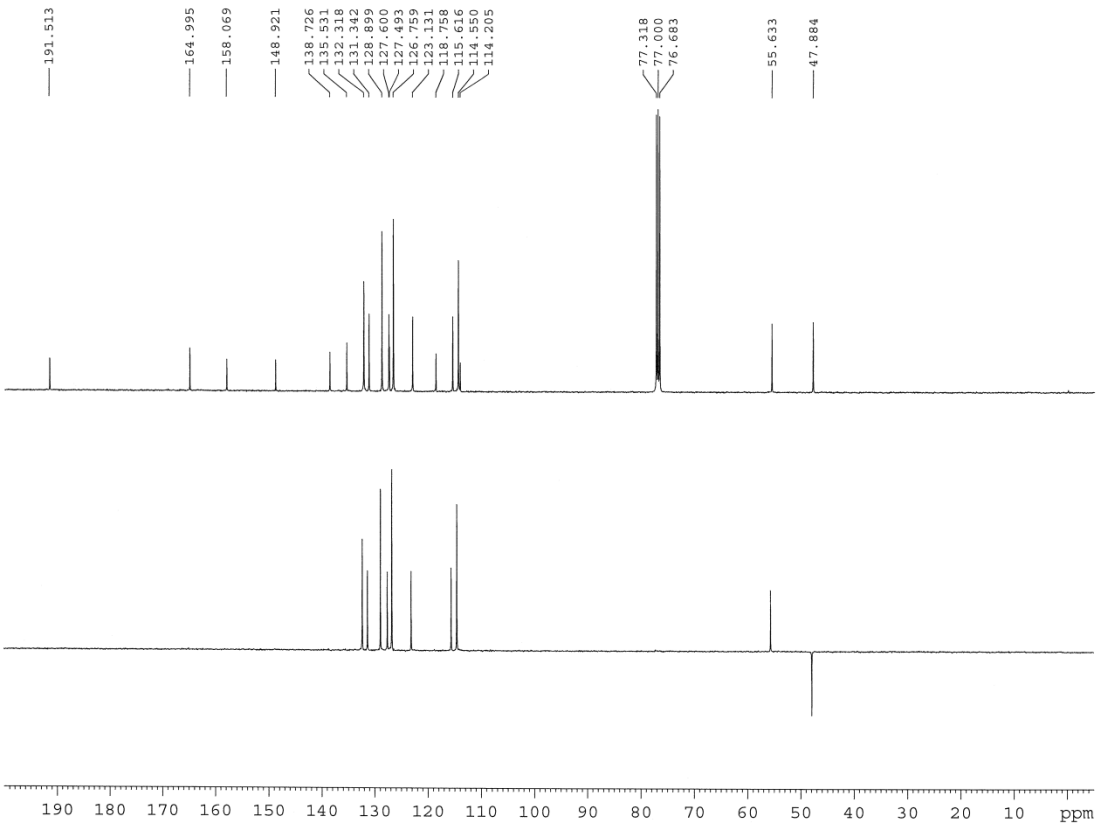


^{1}H & ^{13}C NMR spectra of **10f**

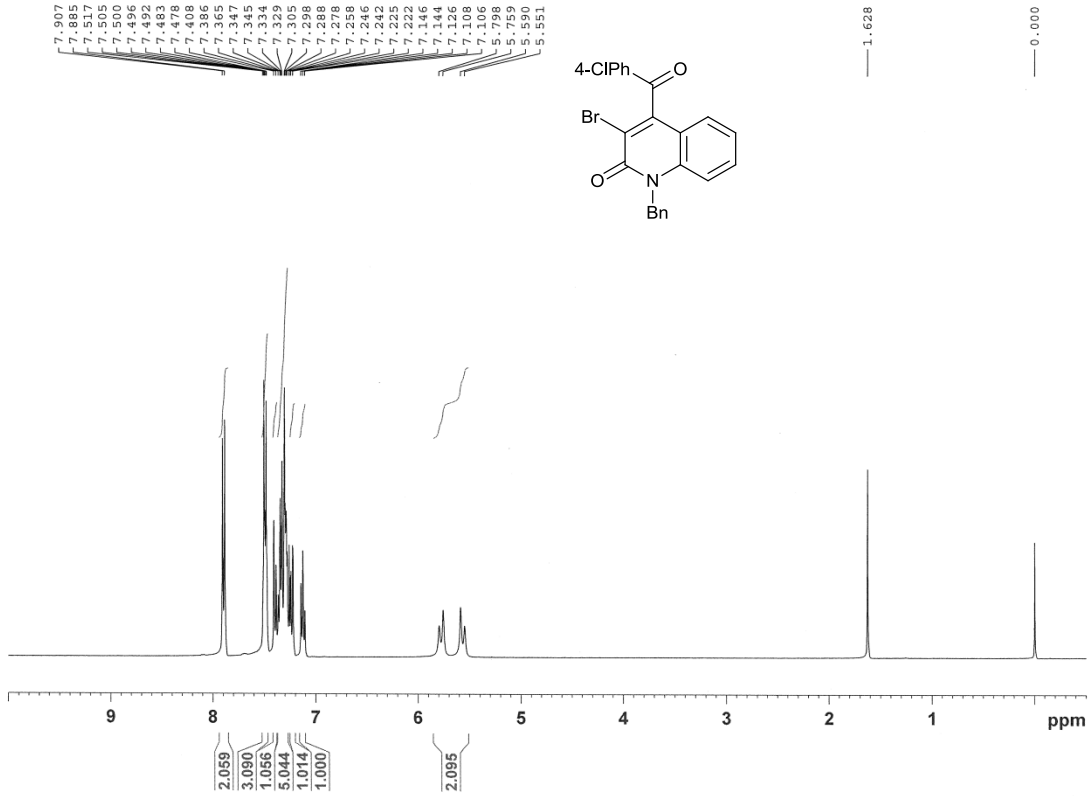


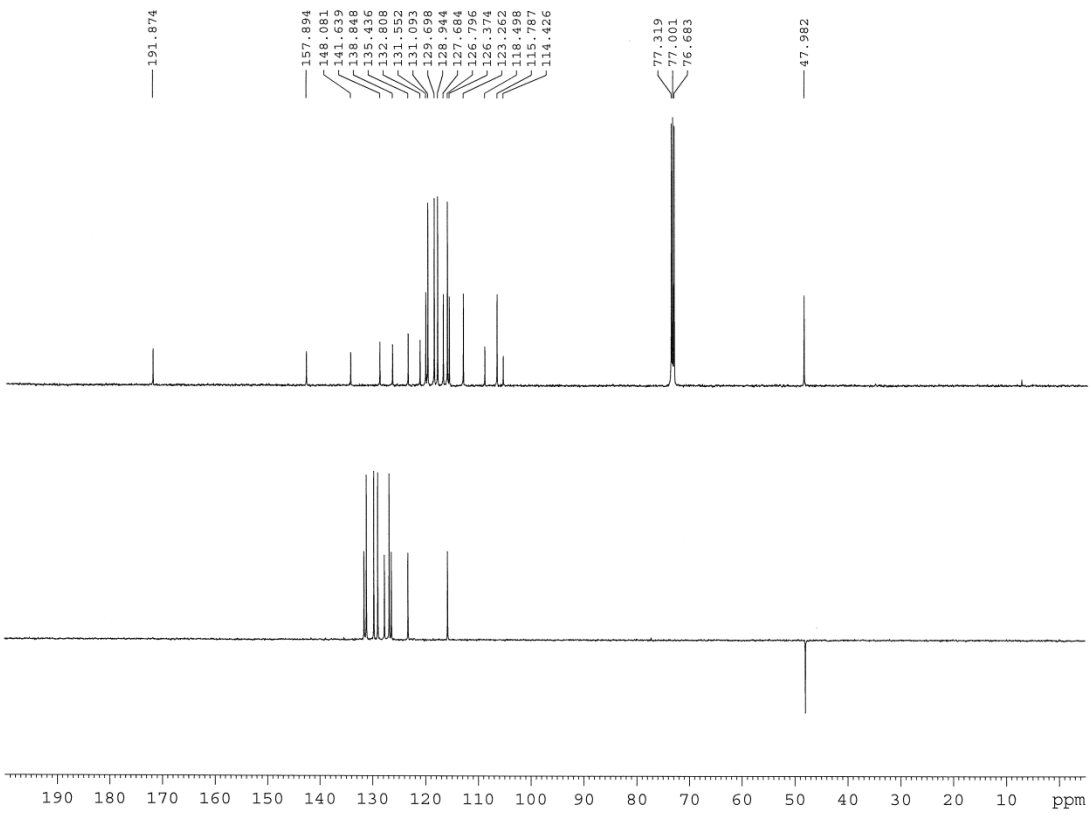
^{1}H & ^{13}C NMR spectra of **10g**





^{1} H & ^{13}C NMR spectra of **10h**





^{1}H & ^{13}C NMR spectra of **10i**