Electronic Supporting Information (ESI)

for

An epoxide-opening cyclization/double Smiles rearrangement cascade approach to *N*-aryl-1,4-benzoxazines and *N*-arylindolines

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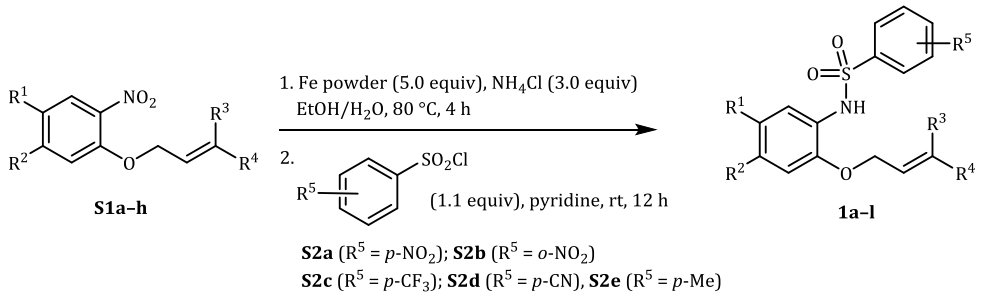
1. General information

All of the reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware. Commercial reagents were used without further purification unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates with UV light (254 nm) as the visualizing agent. Column chromatography was performed over silica gel (60–120 mesh) procured from Merck using freshly distilled solvents. A Perkin Elmer 20 analyzer was utilized for elemental analysis of all compounds. ^{1}H NMR and ^{13}C NMR spectra were run on a JEOL 400 MHz spectrometer using $CDCl_3$ as solvent. All spectra were recorded at 25 °C. Chemical shifts for ^{1}H NMR spectra were recorded in parts per million (ppm) on the δ scale relative to an internal standard of residual chloroform (δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, dt = doublet of triplets, tt = triplet of triplets, dq = doublet of quartets, and m = multiplet), coupling constant (*J*) in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million using the central peak of $CDCl_3$ (δ 77.00 ppm) as the internal standard.

2. Preparation of epoxide substrates 2a–l

2.1. Preparation of alkene-tethered sulfonamides 1a–l

A set of eight known 2-allyloxynitrobenzenes **S1a–h** were employed in the synthesis (Scheme ESI-1). Reduction of the nitro group of **S1a–h** with Fe powder and NH_4Cl in a mixture of EtOH and H_2O (3:1) furnished the corresponding anilines which, without chromatographic purification, were treated with *p*-NO_2-, *o*-NO_2-, *p*-CF_3-, *p*-CN and *p*-Me-substituted benzenesulfonyl chlorides **S2a–e** in pyridine to obtain sulfonamides **1a–k** (Scheme ESI-1).

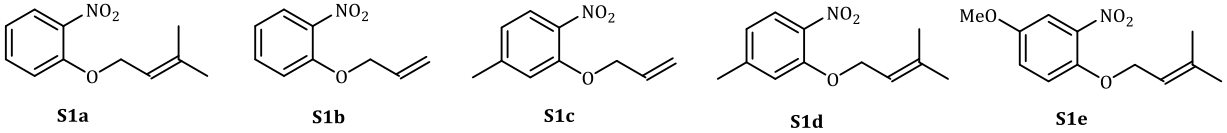


S1a–h

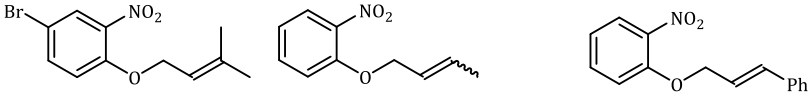
1a–l

S2a (R^5 = *p*-NO_2); **S2b** (R^5 = *o*-NO_2)
S2c (R^5 = *p*-CF_3); **S2d** (R^5 = *p*-CN), **S2e** (R^5 = *p*-Me)

Structures of 2-allyloxynitrobenzenes **S1a–k** used in the reaction:

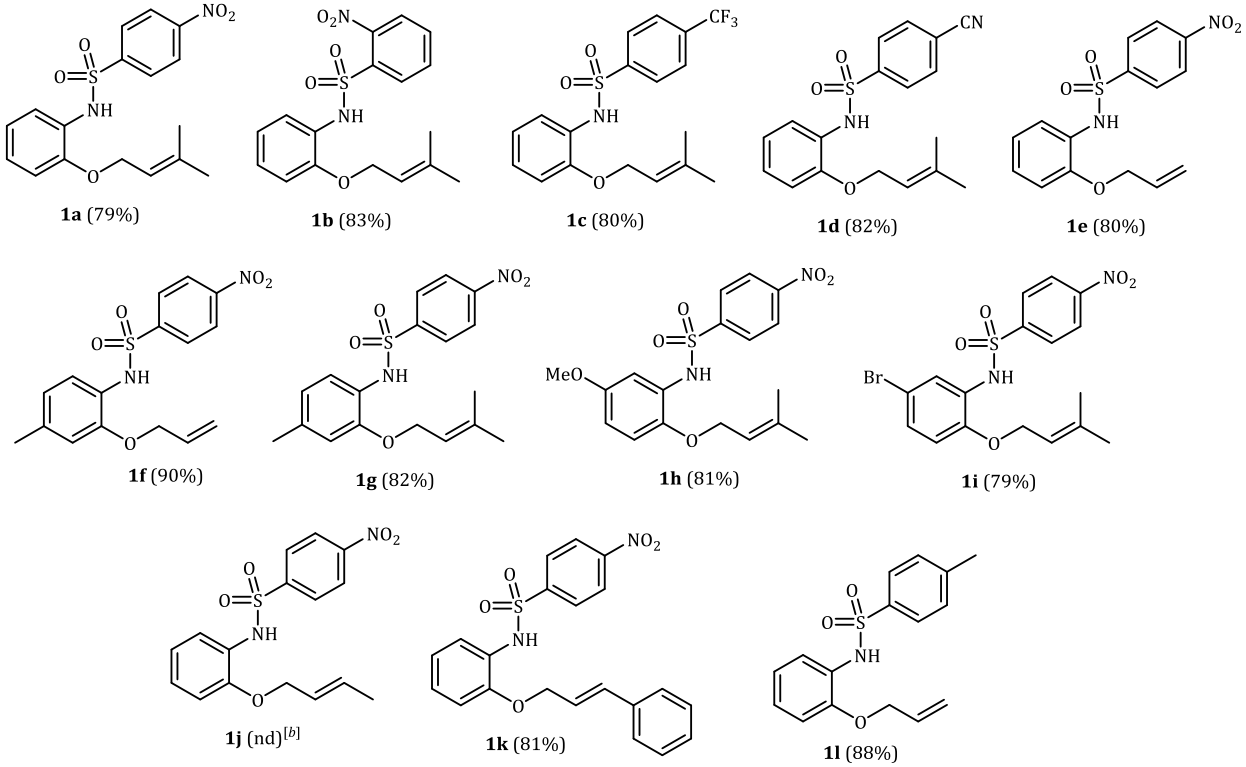


S1a **S1b** **S1c** **S1d** **S1e**



S1f **S1g** (contains minor proportion of the corresponding *cis*-isomer) **S1g**

Structures of alkene-tethered sulfonamides **1a–k:**



1a (79%) **1b** (83%) **1c** (80%) **1d** (82%) **1e** (80%)

1f (90%) **1g** (82%) **1h** (81%) **1i** (79%)

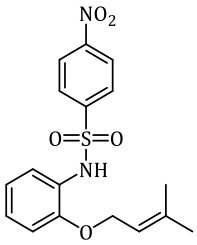
1j (nd)[b] **1k** (81%) **1l** (88%)

Scheme ESI-1. Synthesis of alkene-tethered sulfonamides **1a–l**.

General Procedure A

Fe (223 mg, 4.0 mmol, 5.0 equiv) powder was added to a solution of **S1a–h** (0.8 mmol, 1.0 equiv) and NH_4Cl (128 mg, 2.4 mmol, 3.0 equiv) in EtOH (9 mL) and H_2O (3 mL) and the resulting mixture was heated at 80 ^oC for 4 h under nitrogen atmosphere. After cooling to rt, the reaction mixture was filtered through a short pad of celite and the residue was washed by ethyl acetate (10 mL). The combined filtrate was concentrated under reduced pressure to get a yellow residue which was re-dissolved in ethyl acetate (20 mL) and H_2O (10 mL). The organic layer was separated, washed by brine (10 mL), dried ($MgSO_4$), and filtered. Evaporation of the filtrate under reduced pressure provided the corresponding crude aniline which was immediate used for the next step without further purification and characterization. The crude product thus obtained was dissolved in pyridine (5 mL) at 0 °C. A solution of appropriate arenesulfonyl chloride **S2a–d** (0.88 mmol, 1.1 equiv) in pyridine (3 mL) was then added slowly at 0 °C. The mixture was stirred for 12 h at room temperature. The reaction was quenched by adding 2N HCl solution at 0 °C. The mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel, using hexanes/ethyl acetate mixtures as eluent.

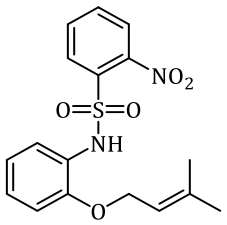
***N*-(2-((3-Methylbut-2-en-1-yl)oxy)phenyl)-4-Nitrobenzenesulfonamide (1a)**



1a

The title compound was prepared from **S1a**[1,2] (166 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 115–117 °C); Yield: 79% (229 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 9.1 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.56 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.10–7.07 (m, 2H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.18–5.14 (m, 1H), 4.30 (d, *J* = 6.8 Hz, 2H), 1.77 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 149.2, 144.8, 139.0, 128.5, 126.6, 124.7, 123.8, 122.6, 121.1, 118.5, 111.6, 65.2, 25.7, 18.1. Anal. calcd. for $C_{17}H_{18}N_2O_5S$: C, 56.34; H, 5.01; N, 7.73; found: C, 56.49; H, 5.05; N, 7.79.

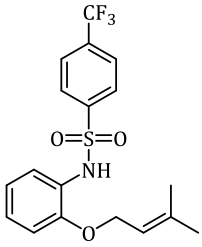
***N*-(2-((3-Methylbut-2-en-1-yl)oxy)phenyl)-2-nitrobenzenesulfonamide (1b)**



1b

The title compound was prepared from **S1a** (166 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 120–122 °C); Yield: 83% (241 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.87 (t, *J* = 7.8 Hz, 2H), 7.70–7.56 (m, 3H), 7.11 (td, *J* = 7.8, 1.3 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 5.16–5.12 (m, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 1.74 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 147.7, 138.3, 133.5, 133.3, 132.5, 131.2, 126.5, 125.4, 125.0, 123.8, 120.8, 118.7, 111.6, 65.1, 25.7, 18.1. Anal. calcd. for $C_{17}H_{18}N_2O_5S$: C, 56.34; H, 5.01; N, 7.73; found: C, 56.48; H, 5.07; N, 7.68.

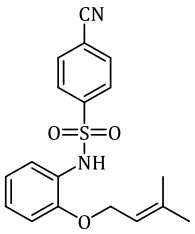
***N*-(2-((3-Methylbut-2-en-1-yl)oxy)phenyl)-4 (trifluoromethyl)benzene sulfonamide (1c)**



1c

The title compound was prepared from **S1a** (166 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 114–116 °C); Yield: 80% (247 mg^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.12 – 7.02 (m, 2H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.16 (t, *J* = 6.7 Hz, 1H), 4.28 (d, *J* = 6.7 Hz, 2H), 1.77 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 142.8, 138.8, 134.4 (q, *J* = 33.0 Hz), 127.8, 126.2, 125.8 (q, *J* = 3.7 Hz), 125.2, 123.2 (q, *J* = 271.2 Hz), 122.3, 121.0, 118.7, 111.7, 65.3, 25.7, 18.1.; Anal. calcd. for $C_{18}H_{18}F_3NO_3S$: C, 56.10; H, 4.71; F, 14.79; N, 3.63; found: C, 56.19; H, 4.66; N, 3.68.

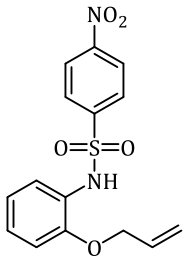
4-Cyano-*N*-(2-((3-methylbut-2-en-1-yl)oxy)phenyl)benzenesulfonamide (1d)



1d

The title compound was prepared from **S1a** (166 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 122–124 °C); Yield: 82% (225 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.11–7.06 (m, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.16 (t, *J* = 6.8 Hz, 1H), 4.29 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 143.3, 138.9, 132.4, 127.8, 126.5, 124.8, 122.4, 121.0, 118.6, 117.2, 116.3, 111.6, 65.2, 25.7, 18.1. Anal. calcd. for $C_{18}H_{18}N_2O_3S$: C, 63.14; H, 5.30; N, 8.18; found: C, 63.07; H, 5.39; N, 8.26.

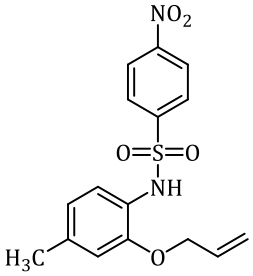
***N*-(2-(Allyloxy)phenyl)-4-nitrobenzenesulfonamide (1e)**



1e

The title compound was prepared from **S1b**[3] (143 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 109–111 °C); Yield: 80% (214 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 9.1 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.58 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.12–7.08 (m, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.86–5.76 (m, 1H), 5.26–5.16 (m, 2H), 4.32 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 149.0, 144.8, 132.0, 128.5, 126.7, 124.6, 123.9, 122.9, 121.4, 118.6, 111.8, 69.2. Anal. calcd. for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38; O, 23.93; S, 9.59; found: C, 53.07; H, 4.30; N, 8.31.

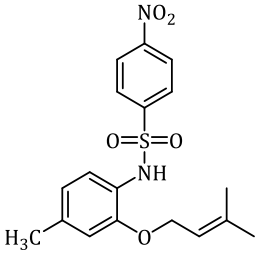
***N*-(2-(Allyloxy)-4-methylphenyl)-4-nitrobenzenesulfonamide (1f)**



1f

The title compound was prepared from **S1c**[4] (154 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 105–107 °C); Yield: 80% (223 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 6.92 (br s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 5.83–5.74 (m, 1H), 5.24–5.14 (m, 2H), 4.26 (d, *J* = 5.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 149.2, 144.8, 137.3, 132.1, 128.5, 123.8, 123.5, 121.9, 121.8, 118.5, 112.6, 69.1, 21.4. Anal. calcd. for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63; N, 8.04; found: C, 55.31; H, 4.68; N, 8.09.

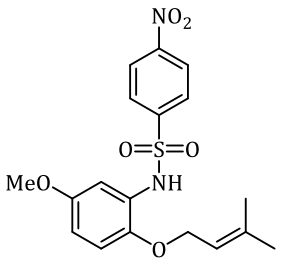
***N*-(4-Methyl-2-((3-methylbut-2-en-1-yl)oxy)phenyl)-4-nitrobenzene sulfonamide (1g)**



1g

The title compound was prepared from **S1d**[1] (177 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 112–114 °C); Yield: 82% (247 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.53 (s, 1H), 5.12 (t, *J* = 5.5 Hz, 1H), 4.23 (t, *J* = 6.4 Hz, 2H), 2.27 (s, 3H), 1.75 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 149.4, 144.8, 138.4, 137.0, 128.5, 123.6, 123.2, 121.7, 121.4, 118.6, 112.4, 64.9, 25.5, 21.3, 17.9. Anal. calcd. for $C_{18}H_{20}N_2O_5S$: C, 57.43; H, 5.36; N, 7.44; found: C, 57.54; H, 5.31; N, 7.37.

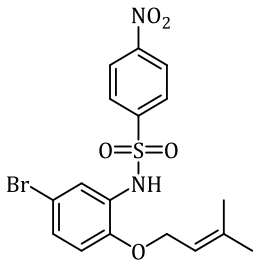
***N*-(5-Methoxy-2-((3-methylbut-2-en-1-yl)oxy)phenyl)-4-nitrobenzene sulfonamide (19h)**



1h

The title compound was prepared from **S1e**[1] (190 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 125–127 °C); Yield: 81% (254 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 2.7 Hz, 1H), 7.12 (s, 1H), 6.67 (d, *J* = 9.1 Hz, 1H), 6.60 (dd, *J* = 9.1, 3.2 Hz, 1H), 5.19–5.16 (m, 1H), 4.26 (d, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 1.77 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 150.1, 144.7, 143.1, 138.9, 128.5, 125.5, 123.9, 112.7, 110.8, 108.2, 99.9, 65.8, 55.7, 25.7, 18.1. Anal. calcd. for $C_{18}H_{20}N_2O_6S$: C, 55.09; H, 5.14; N, 7.14; found: C, 55.28; H, 5.19; N, 7.10.

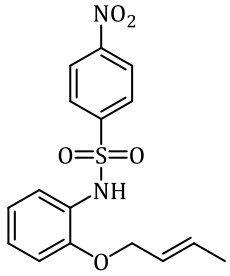
***N*-(5-Bromo-2-((3-methylbut-2-en-1-yl)oxy)phenyl)-4-nitrobenzene sulfonamide (1i)**



1i

The title compound was prepared from **S1f**[1] (229 g, 0.8 mmol) following the **General Procedure A**. White solid (mp: 121–123 °C); Yield: 79% (279 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.11 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.19 – 5.11 (m, 1H), 4.31 (d, *J* = 6.8 Hz, 2H), 1.76 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 148.1, 144.6, 139.6, 129.0, 128.6, 126.2, 124.7, 124.09, 118.1, 113.2, 113.1, 65.7, 25.8, 18.2. Anal. calcd. for $C_{17}H_{17}BrN_2O_5S$: C, 46.27; H, 3.88; N, 6.35; found: C, 46.38; H, 3.92; N, 6.31.

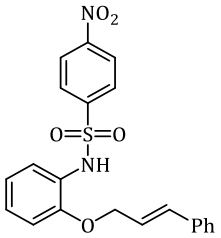
(*E*)-*N*-(2-(But-2-en-1-yloxy)phenyl)-4-nitrobenzenesulfonamide (1j)



1j

The title compound was prepared from **S1g**[1,2] (154 mg, 0.8 mmol) following the **General Procedure A**. Analysis of the ^{1}H and ^{13}C NMR spectra of **19j** revealed that the compound was isolated as an inseparable mixture of the *cis* (minor) and *trans* (major) isomers. Since the sample was not in pure form, NMR data are not provided here. This compound was used for the next step in the impure form.

***N*-(2-(Cinnamyloxy)phenyl)-4-nitrobenzenesulfonamide (1k)**



1k

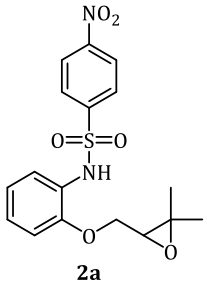
The title compound was prepared from **S1h**[5,6] (204 mg, 0.8 mmol) following the **General Procedure A**. White solid (mp: 160–162 °C); Yield: 81% (266 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 1.2 Hz, 1H), 7.41 – 7.28 (m, 5H), 7.12 – 7.09 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.1, 144.9, 135.6, 134.5, 128.8, 128.6, 128.5, 126.8, 126.6, 124.8, 123.9, 123.0, 122.7, 121.5, 111.9, 69.3. Anal. calcd. for $C_{21}H_{18}N_2O_5S$: C, 61.45; H, 4.42; N, 6.83; found: C, 61.37; H, 4.45; N, 6.79.

2.2. Epoxidation of alkene-tethered sulfonamides 1a–l

General Procedure B

To a stirred solution of appropriate *N*-(2-(allyloxy)aryl)-4-nitrobenzene sulfonamide **1** (0.5 mmol, 1.0 equiv) in DCE (5 mL) was added *m*-CPBA (232 mg, 1.0 mmol, 75%, 2.5 equiv) and the resulting solution mixture heated at 80 ^{o}C for 12 h. The mixture was diluted with CH_2Cl_2 (20 mL) and then washed successively with saturated aq. solutions of Na_2SO_3 (5 mL) and $NaHCO_3$ (5 mL). The organic layer was separated, washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using hexanes/ethyl acetate mixtures as eluent.

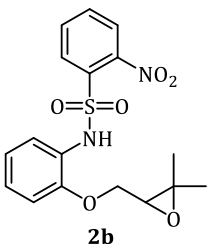
2,2-Dimethyl-3-((2-(((4-nitrophenyl)sulfonyl)methyl)phenoxy)methyl) oxirane (2a)



2a

The title compound was prepared from **1a** (181 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 111–113 °C); Yield: 71% (134 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 9.1 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.38 (br s, 1H), 7.11–7.07 (m, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.15 (dd, *J* = 11.0, 2.7 Hz, 1H), 3.67 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.90 (dd, *J* = 7.3, 3.2 Hz, 1H), 1.36 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 149.1, 144.8, 128.5, 126.7, 124.8, 123.9, 123.1, 121.8, 111.9, 68.0, 60.7, 58.2, 24.5, 19.0. Anal. calcd. for $C_{17}H_{18}N_2O_6S$: C, 53.96; H, 4.79; N, 7.40; found: C, 54.14; H, 4.74; N, 7.45.

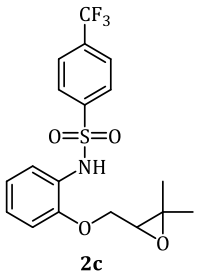
N-(2-((3,3-Dimethyloxiran-2-yl)methoxy)phenyl)-2-nitrobenzenesulfonamide (2b)



2b

The title compound was prepared from **1b** (181 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 120–122 °C); Yield: 79% (149 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (br s, 1H), 7.89 (t, *J* = 7.3 Hz, 2H), 7.70–7.65 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.00 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.84 (dd, *J* = 10.5, 5.9 Hz, 1H), 2.89 (t, *J* = 4.5 Hz, 1H), 1.36 (s, 3H), 1.25 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 149.5, 147.9, 133.6, 133.0, 132.4, 131.2, 126.6, 125.6, 125.1, 123.5, 121.7, 111.6, 67.7, 60.7, 58.1, 24.5, 18.9. Anal. calcd. for $C_{17}H_{18}N_2O_6S$: C, 53.96; H, 4.79; N, 7.40; found: C, 54.22; H, 4.85; N, 7.44.

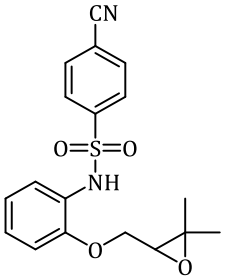
N-(2-((3,3-Dimethyloxiran-2-yl)methoxy)phenyl)-4-(trifluoromethyl) benzenesulfonamide (2c)



2c

The title compound was prepared from **1c** (192 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 120–122 °C); Yield: 75% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.07 (dd, *J* = 11.1, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.1, 6.8 Hz, 1H), 2.85 (dd, *J* = 6.8, 3.3 Hz, 1H), 1.36 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 142.7, 134.4 (q, *J* = 33.0 Hz), 129.1 (q, *J* = 154 Hz), 127.8, 126.5, 125.9 (q, *J* = 3.7 Hz), 125.3, 122.8, 121.8, 111.9 68.0, 60.8, 58.2, 24.5, 19.0. Anal. calcd. for $C_{18}H_{18}F_3NO_4S$: C, 53.86; H, 4.52; N, 3.49; found: C, 54.09; H, 4.59; N, 3.39.

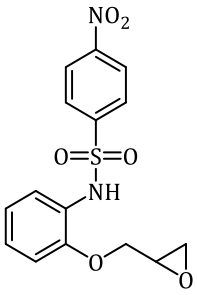
4-Cyano-*N*-(2-((3,3-dimethyloxiran-2-yl)methoxy)phenyl)benzene sulfonamide (2d)



2d

The title compound was prepared from **1d** (171 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 125–127 °C); Yield: 77% (138 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.54 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.48 (br s, 1H), 7.11–7.07 (m, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.15 (dd, *J* = 11.0, 2.7 Hz, 1H), 3.68 (dd, *J* = 11.0, 6.8 Hz, 1H), 2.92 (dd, *J* = 7.3, 3.2 Hz, 1H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): 149.1, 143.2, 132.5, 127.8, 126.5, 124.8, 123.0, 121.6, 117.2, 116.2, 111.8, 67.8, 60.7, 58.2, 24.2, 18.9. Anal. calcd. for $C_{18}H_{18}N_2O_4S$: C, 60.32; H, 5.06; N, 7.82; found: C, 60.45; H, 5.02; N, 7.88.

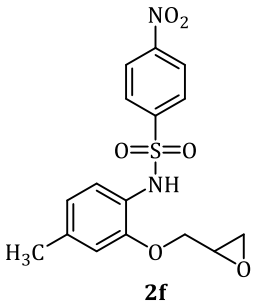
4-Nitro-*N*-(2-(oxiran-2-ylmethoxy)phenyl)benzenesulfonamide (2e)



2e

The title compound was prepared from **1e** (167 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 122–124 °C); Yield: 73% (128 mg). This compound was also prepared in larger scale using 1.67 g (5.0 mmol) of **1e** to afford **2e** in 71% (1.24 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 9.1 Hz, 2H), 7.56–7.50 (m, 2H), 7.09–7.05 (m, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.15 (dd, *J* = 11.0, 2.3 Hz, 1H), 3.61 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.23–3.19 (m, 1H), 2.89 (t, *J* = 4.1 Hz, 1H), 2.64–2.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 149.1, 144.7, 128.5, 126.7, 124.8, 123.9, 123.1, 121.9, 112.1, 69.6, 49.6, 44.3. Anal. calcd. for $C_{15}H_{14}N_2O_6S$: C, 51.43; H, 4.03; N, 8.00; found: C, 51.66; H, 4.10; N, 8.08.

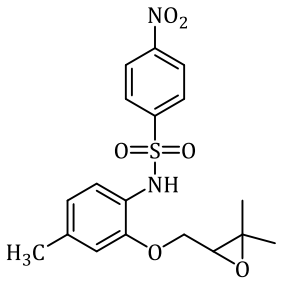
***N*-(4-Methyl-2-(oxiran-2-ylmethoxy)phenyl)-4-nitrobenzenesulfonamide (2f)**



2f

The title compound was prepared from **1f** (174 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 130–132 °C); Yield: 72% (131 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.27 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 4.10 (dd, *J* = 11.0, 1.8 Hz, 1H), 3.55 (dd, *J* = 11.0, 6.4 Hz, 1H), 3.18–3.14 (m, 1H), 2.87 (t, *J* = 4.1 Hz, 1H), 2.60 (dd, *J* = 4.5, 2.7 Hz, 1H), 2.26 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 150.0, 149.2, 144.8, 137.2, 128.5, 123.9, 123.6, 122.4, 122.0, 112.9, 69.6, 49.6, 44.2, 21.3. Anal. calcd. for $C_{15}H_{14}N_2O_6S$: C, 51.43; H, 4.03; N, 8.00; found: C, 51.66; H, 4.10; N, 8.08.

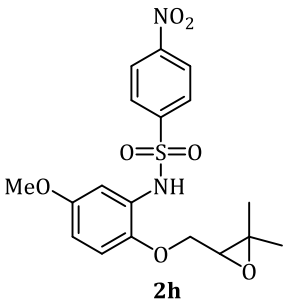
N-(2-((3,3-Dimethyloxiran-2-yl)methoxy)-4-methylphenyl)-4-nitrobenzene sulfonamide (2g)



2g

The title compound was prepared from **1g** (188 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 132–134 °C); Yield: 77% (151 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 9.1 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.12 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 4.10 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.61 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.85 (dd, *J* = 6.8, 2.7 Hz, 1H), 2.28 (s, 3H), 1.36 (s, 3H), 1.28 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 150.0, 149.2, 144.8, 137.2, 128.6, 123.9, 123.9, 123.5, 122.3, 122.0, 112.7, 67.8, 60.8, 58.1, 24.5, 21.4, 19.0. Anal. calcd. for $C_{15}H_{14}N_2O_6S$: C, 51.43; H, 4.03; N, 8.00; found: C, 51.66; H, 4.10; N, 8.08.

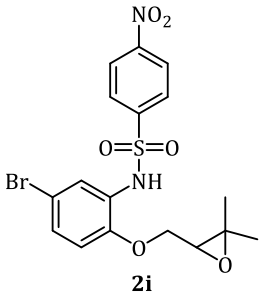
N-(2-((3,3-Dimethyloxiran-2-yl)methoxy)-5-methoxyphenyl)-4-nitrobenzene sulfonamide (2h)



2h

The title compound was prepared from **1h** (196 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 141–143 °C); Yield: 74% (151 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 9.1 Hz, 2H), 7.97 (d, *J* = 9.1 Hz, 2H), 7.35 (s, 1H), 7.18 (d, *J* = 2.7 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 6.60 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.13 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.76 (s, 3H), 3.62 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.89 (dd, *J* = 7.3, 3.2 Hz, 1H), 1.36 (s, 3H), 1.28 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 154.4, 150.1, 144.7, 142.9, 128.6, 125.8, 124.0, 113.3, 110.9, 108.5, 68.8, 60.9, 58.3, 55.7, 24.5, 19.0. Anal. calcd. for $C_{15}H_{14}N_2O_6S$: C, 51.43; H, 4.03; N, 8.00; found: C, 51.66; H, 4.10; N, 8.08.

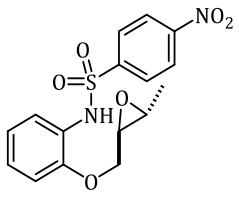
N-(5-Bromo-2-((3,3-dimethyloxiran-2-yl)methoxy)phenyl)-4-nitrobenzene sulfonamide (2i)



2i

The title compound was prepared from **1i** (220 mg, 0.5 mmol) following the **General Procedure B**. White solid (mp: 139–141 °C); Yield: 71% (162 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.24 (s, 1H), 7.19 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 4.19 (dd, *J* = 11.1, 2.9 Hz, 1H), 3.66 (dd, *J* = 11.1, 7.3 Hz, 1H), 2.88 (dd, *J* = 7.3, 2.8 Hz, 1H), 1.37 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 147.9, 144.6, 129.2, 128.6, 126.4, 125.1, 124.2, 114.0, 113.6, 68.6, 60.6, 58.4, 24.6, 19.1; Anal. calcd. for $C_{17}H_{17}BrN_2O_6S$: C, 44.65; H, 3.75; N, 6.13; found: C, 44.90; H, 3.70; N, 6.21.

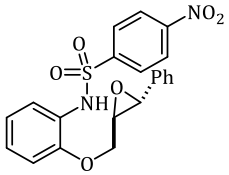
***N*-(2-(((2*R**,3*R**)-3-Methyloxiran-2-yl)methoxy)phenyl)-4-nitrobenzene sulfonamide (2j)**



2j

The title compound was prepared from **1j** (174 mg, 0.5 mmol) following the **General Procedure B**. This compound could not be purified completely due to the presence of *trans* (major) and *cis* (minor) isomeric compounds and was used for the next step in the impure form.

4-Nitro-*N*-(2-(((*2R,*3R**)-3-phenyloxiran-2-yl)methoxy)phenyl)benzene sulfonamide (2k)**



2k

The title compound was prepared from **1k** (205 mg, 0.5 mmol) following the **General Procedure B**. white solid; (mp: 157–158 °C); Yield: 74% (158 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.27 – 7.19 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 4.24 (dd, *J* = 11.3, 2.2 Hz, 1H), 3.81 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.73 (d, *J* = 1.7 Hz, 1H), 3.26 – 3.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 149.0, 144.8, 135.6, 128.6, 126.7, 125.7, 125.5, 125.1, 124.01, 123.0, 122.9, 122.1, 112.3, 68.9, 59.5, 56.2. Anal. calcd. for $C_{21}H_{18}N_2O_6S$: C, 59.15; H, 4.25; N, 6.57; found: C, 59.30; H, 4.32; N, 6.50.

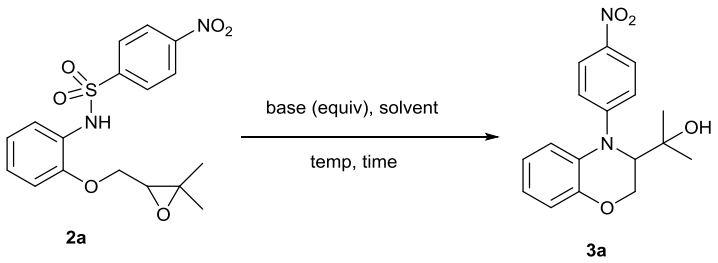
3. Synthesis of *N*-aryl-1,4-benzoxazines, *N*-arylindolines and *N*-arylpyrrolidines

3.1. Optimization of reaction conditions:

We began the studies for the optimization of reaction conditions by investigating the cyclization of **2a** as a model reaction. The results are summarized in Table ESI-1. Since, both

base-mediated heteronucleophilic epoxide-opening reaction and anionic Smiles rearrangement are usually performed in polar solvent under heating conditions, we decided to employ such reaction conditions for the cyclization of **2a**. In our first experiments, we found that the treatment of **2a** with NaH (1.5 equiv) in DMF at 70 °C for 1.5 h resulted in the formation of *N*-(*p*-nitrophenyl)benzo[1,4]oxazine **3a** in moderate yield of 60% (Table ESI-1, entry 1).

Table ESI-1. Screening of reaction conditions[a]



entry	base (equiv)	solvent	temp (°C)	time (h)	yield[b] (%)
1	NaH (1.5)	DMF	70	1.5	60
2	KH (1.5)	DMF	70	1.5	61
3	Et_3N (2.0)	DMF	70	5	0
4	NaH (1.0) + K_2CO_3 (1.0)	DMF	80	1.5	79
5	K_2CO_3 (2.0)	DMF	80	2	84
6	Cs_2CO_3 (2.0	DMF	80	2	82
7	K_2CO_3 (2.0)	DMA	80	2	84
8	K_2CO_3 (2.0)	MeCN	reflux	2	80
9	K_2CO_3 (2.0)	dioxane	80	8	67
10	K_2CO_3 (2.0)	THF	reflux	8	65
11	K_2CO_3 (2.0)	DMSO	reflux	2	92
12	K_2CO_3 (1.0)	DMSO	80	4	74

[a]Reaction conditions: All reactions were conducted with 0.5 mmol of 15a in 4.0 mL of solvent. [b]Isolated yields after silica gel column chromatography.

Alternatively, the use of KH (1.5 equiv) also provided **3a** in similar yield, whilst Et_3N (5 mol %) turned out to be ineffective (entries 2 and 3, respectively). We were delighted to observe that when the reaction was conducted using a combination of NaH (1.0) and K_2CO_3 (1.0 equiv) at 80 °C, product **3a** was obtained in significantly higher yield of 79% (entry 4). Intriguingly, K_2CO_3 (2.0 equiv) alone in DMF at 80 °C could also drive the transformation,

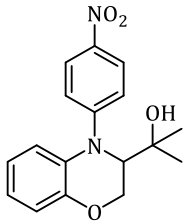
affording **3a** in 84% yield (entry 5). Use of Cs_2CO_3 (2.0 equiv) instead of K_2CO_3 (2.0 equiv) in DMF at 80 °C resulted in the formation of **3a** in 82% yield (entry 6). Using K_2CO_3 (2.0 equiv) as the base, the cascade reaction was then studied in other polar aprotic solvents. In this endeavor, we found that DMSO to be the most effective solvent as DMA, CH_3CN, 1,4-dioxane, and THF delivered inferior results (entries 7–11). Decreasing the equivalents of K_2CO_3 from 2.0 to 1.0 equiv resulted in significantly reduced yield (74%) (entry 12).

3.2. Synthesis of benzo[*b*][1,4]oxazines 3a–k (lower panel, Table 1, main manuscript):

General Procedure C

To a stirred solution of an appropriate epoxide substrate **2** (0.2 mmol, 1 equiv) in DMSO (2 mL) was added K_2CO_3 (0.4 mmol, 2 equiv). The resulting mixture was heated at 80 °C on for 2 h. After the completion of the reaction, the reaction mixture was then diluted with EtOAc (10 ml) and H_2O (10 mL). The mixture was then stirred vigorously for 5 min. The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was further purified by silica gel chromatography.

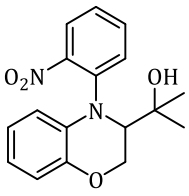
2-(4-(4-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)propan-2-ol (3a)



3a

The title compound was prepared from **2a** (75 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 80–81 °C); Yield: 92% (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.12, 2H), 7.49 (d, *J* = 9.1 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.02–6.98 (m, 1H), 6.93–6.86 (m, 2H), 4.54 (d, *J* = 11.4 Hz, 1H), 4.10 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.68 (d, *J* = 2.7 Hz, 1H), 1.41 (s, 3H), 2.06 (s, 1H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 147.1, 141.6, 127.7, 125.4, 124.4, 123.1, 121.2, 119.6, 117.8, 73.4, 66.7, 63.4, 27.4, 27.1. Anal. calcd. for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91; found: C, 65.14; H, 5.86; N, 8.99.

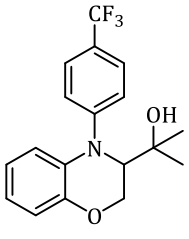
2-(4-(2-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)propan-2-ol (3b)



3b

The title compound was prepared from **2b** (75 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 81–83 °C); Yield: 68% (43 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.90–6.87 (m, 1H), 6.81-6.66 (m, 3H), 6.44 (d, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.27–4.12 (m, 1H), 3.65 (s, 1H), 1.32 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 143.9, 133.6, 125.7, 121.7, 121.6, 120.1, 118.9, 117.3, 116.5, 115.8, 115.0, 74.8, 65.8, 63.7, 27.3, 24.4. Anal. calcd. for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91; found: C, 65.08; H, 5.74; N, 8.85.

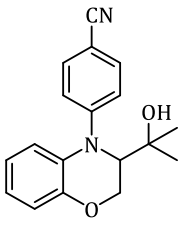
2-(4-(4-(Trifluoromethyl)phenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)propan-2-ol (3c)



3c

The title compound was prepared from **2c** (80 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 85–86 °C); Yield: 83% (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.68 (s, 4H), 7.09 (td, *J* = 7.8, 1.5 Hz, 1H), 6.98 (td, *J* = 7.9, 7.4, 1.5 Hz, 1H), 6.75 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.39 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.09 (dd, *J* = 4.5, 1.6 Hz, 1H), 3.20 (dd, *J* = 12.0, 4.5 Hz, 1H), 1.90 (br. s, 1H), 1.31 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 141.1, 135.0 (*J* = 33 Hz),127.9, 127.1, 126.3, 125.6 123.0 (*J* = 272 Hz), 122.9, 121.6, 119.0, 117.4, 73.0, 62.0, 60.1, 27.8, 26.6. Anal. calcd. for $C_{18}H_{18}F_3NO_2$: C, 64.09; H, 5.38; N, 4.15; found: C, 64.32; H, 5.45; N, 4.04.

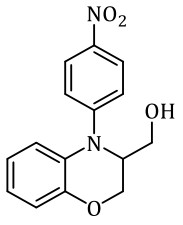
4-(3-(2-Hydroxypropan-2-yl)-2,3-Dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)benzonitrile (3d)



3d

The title compound was prepared from **2d** (71 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 94–95 °C); Yield: 89% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$): ⍰⍰7.50 (q, *J* = 10.3 Hz, 4H), 7.11–7.09 (m, 1H), 6.98–6.83 (m, 3H), 4.51 (d, *J* = 11.9, 1H), 4.05 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.59 (d, *J* = 2.7 Hz, 1H), 2.23 (br s, 1H), 1.38 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 147.2, 133.5, 128.1, 124.1, 123.1, 121.2, 120.9, 119.4, 117.8, 104.5, 73.4, 67.1, 63.1, 27.4, 27.1. Anal. calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52; found: C, 73.34; H, 6.21; N, 9.47.

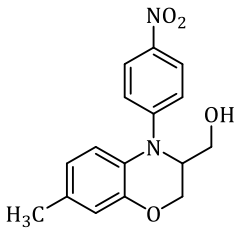
(4-(4-Nitrophenyl)-3,4-Dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)methanol (3e)



3e

The title compound was prepared from **2e** (70 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 103–104 °C); Yield: 84% (48 mg). This compound was also prepared in larger scale using 1.20 g (3.42 mmol) of **2e** to afford **3e** in 80% (784 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 9.1 Hz, 2H), 7.38 (d, *J* = 9.1 Hz, 2H), 7.19–7.17 (m, 1H), 6.98-6.91 (m, 2H), 6.87–6.83 (m, 1H), 4.41 (d, *J* = 10.0 Hz, 1H), 4.13–4.06 (m, 2H), 3.87–3.74 (m, 2H), 2.69 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 145.5, 141.1, 125.9, 125.5, 123.8, 121.2, 121.1, 119.2, 117.8, 63.9, 60.1, 59.0. Anal. calcd. for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79; found: C, 62.80; H, 4.99; N, 9.72.

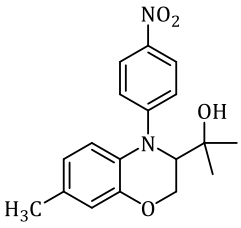
(7-Methyl-4-(4-nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)methanol (3f)



3f

The title compound was prepared from **2f** (73 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 105–106 °C); Yield: 87% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 9.1 Hz, 2H), 7.36 (d, *J* = 9.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.76 (s, 1H), 6.71–6.68 (m, 1H), 4.37 (d, *J* = 10.0 Hz, 1H), 4.13–4.06 (m, 2H), 3.88–3.75 (m, 2H), 2.30 (s, 3H), 1.80–1.71 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 145.5, 141.1, 134.2, 125.6, 123.1, 122.1, 121.5, 119.0, 118.1, 63.9, 60.2, 59.2, 20.8. Anal. calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33; found: C, 64.18; H, 5.32; N, 9.39.

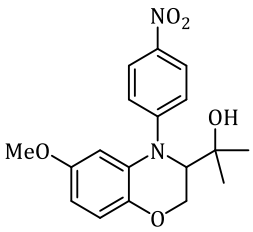
2-(7-Methyl-4-(4-nitrophenyl)-3,4-Dihydro-2H-benzo[b][1,4]oxazin-3-yl) propan-2-ol (3g)



3g

The title compound was prepared from **2g** (78 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 96–97 °C); Yield: 94% (62 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 9.6 Hz, 2H), 7.43 (d, *J* = 9.1 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.72–6.68 (m, 2H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.07 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.68 (d, *J* = 2.7 Hz, 1H), 2.29 (s, 4H), 1.39 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 146.8, 141.0, 134.5, 125.3, 124.7, 122.9, 122.0, 119.1, 117.9, 73.3, 66.4, 63.3, 27.3, 27.0, 20.8. Anal. calcd. for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53; found: C, 65.98; H, 6.18; N, 8.47.

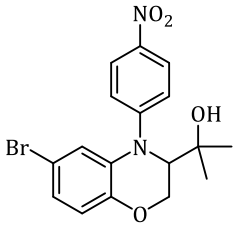
2-(6-Methoxy-4-(4-nitrophenyl)-3,4-Dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl) propan-2-ol (3h)



3h

The title compound was prepared from **2h** (81 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 145–147 °C); Yield: 90% (62 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 9.1 Hz, 2H), 7.53 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 6.58 (dd, *J* = 9.1, 3.2 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.04 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.70 (s, 3H), 3.64 (d, *J* = 2.2 Hz, 1H), 2.11 (br s, 1H), 1.40 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 153.8, 141.7, 141.2, 127.9, 125.4, 120.1, 118.2, 110.7, 107.5, 73.5, 66.8, 63.2, 55.6, 27.4, 27.1. Anal. calcd. for $C_{18}H_{20}N_2O_5$: C, 62.78; H, 5.85; N, 8.13; found: C, 62.96; H, 5.94; N, 8.19.

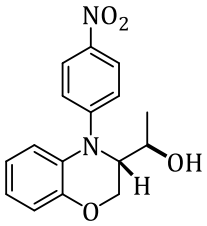
2-(6-Bromo-4-(4-nitrophenyl)-3,4-Dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)propan-2-ol (3i)



3i

The title compound was prepared from **2i** (91 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 149–151°C); Yield: 85% (67 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 9.1 Hz, 2H), 7.51 (d, *J* = 9.1 Hz, 2H), 7.27 (s, 1H), 7.07 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.05 (dd, *J* = 11.9, 3.6 Hz, 1H), 3.65 (d, *J* = 3.2 Hz, 1H), 2.05 (br s, 1H), 1.40 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 146.1, 142.2, 129.4, 126.9, 125.5, 125.1, 120.3, 119.2, 112.9, 73.4, 66.6, 63.3, 27.5, 27.1. Anal. calcd. for $C_{17}H_{17}BrN_2O_4$: C, 51.92; H, 4.36; N, 7.12; found: C, 51.82; H, 4.41; N, 7.17.

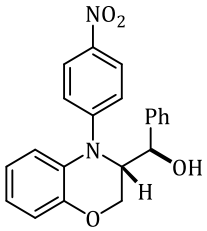
(*R)-1-((*S**)-4-(4-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)ethan-1-ol (3j)**



3j

The title compound was prepared from **2j** following the **General Procedure C**. Orange solid (mp: 170–172 °C); Yield: 68% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 9.1 Hz, 2H), 7.26 (d, *J* = 9.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.02–6.94 (m, 2H), 6.88–6.84 (m, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.01–3.92 (m, 2H), 3.73 (d, *J* = 9.6 Hz, 1H), 1.98 (br s, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 146.9, 141.1, 126.2, 125.7, 124.6, 122.9, 121.0, 118.5, 117.9, 64.7, 63.5, 62.7, 21.1. Anal. calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33; found: C, 64.12; H, 5.32; N, 9.39.

(*R)-((*S**)-4-(4-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl)(phenyl)methanol (3k)**



3k

The title compound was prepared from **2k** (85 mg, 0.2 mmol) following the **General Procedure C**. Orange solid (mp: 187–188 °C);; Yield: 90% (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 9.1 Hz, 2H), 7.40–7.33 (m, 5H), 7.06 (dd, *J* = 14.2, 8.2 Hz, 3H), 6.95–6.90 (m, 1H), 6.54 (d, *J* = 9.1 Hz, 2H), 4.90 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.77 (d, *J* = 9.6 Hz, 1H), 4.08 (dd, *J* = 11.0, 2.3 Hz, 1H), 3.83 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 146.7, 141.7, 141.2, 128.7, 128.5, 126.6, 126.1, 125.3, 124.2, 122.3, 121.3, 118.5, 117.9, 69.8, 69.7, 63.7. Anal. calcd. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73; found: C, 69.79; H, 5.11; N, 7.70.

3.3. Synthesis of benzo[*b*][1,4]oxazines 3m–p (Scheme 2, main manuscript):

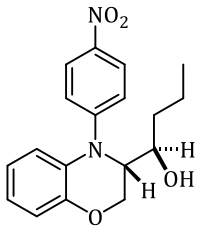
General Procedure D:

A mixture of of 2-nitrophenols **4a–c** (1.0 mmol), K_2CO_3 (1.5 mmol, 1.5 equiv), and *trans*- (**5a**) or *cis*-epoxytosylate (**5b**) (270 mg, 1.0 mmol) in acetone (10 mL) was refluxed for

12 h at 65 °C. After completion of the reaction, solvent was evaporated under reduced pressure. The resulting residue was dissolved in ethyl acetate (15 mL) and water (10 mL). The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure.

To a stirred solution of these crude products in MeOH (3 mL) were added 10% Pd-C (25 mg) and triethylsilane (0.402 mL, 2.52 mmol) under a nitrogen-filled balloon. After 30 min, the mixture was filtered through celite and the solvent was removed in vacuo. The crude products thus obtained were dissolved in pyridine (3 mL) at 0 °C. A solution of 4-nitrobenzenesulfonyl chloride (163 mg, 0.84 mmol) was then added. The mixture was stirred for 12 h at room temperature. The reaction was quenched by adding 5N HCl solution at 0 °C. The mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The resulting crude nosyl amides were then converted into products **3m–p** following **General Procedure C**.

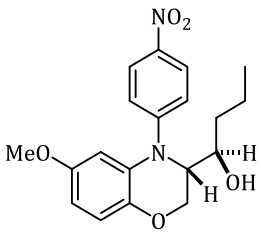
(*R)-1-((*S**)-4-(4-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl) butan-1-ol (3m)**



3m

The title compound was prepared starting from 2-nitrophenol **4a** and epoxy tosylate **5a** following the **General Procedure D**. Orange solid (mp: 181–182 °C); yield: 52% over four steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.3 Hz, 2H), 7.23 (d, *J* = 9.3 Hz, 2H), 7.13 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.04 – 6.93 (m, 2H), 6.91 – 6.84 (m, 1H), 4.71 (d, *J* = 10.9 Hz, 1H), 3.99 (dd, *J* = 10.9, 2.1 Hz, 1H), 3.83 – 3.65 (m, 2H), 2.22 (s, 1H), 1.87 – 1.75 (m, 1H), 1.65 – 1.55 (m, 2H), 1.37 – 1.29 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 147.0, 141.1, 126.2, 125.7, 124.7, 123.0, 121.0, 118.5, 117.9, 68.1, 63.7, 62.1, 36.7, 19.3, 14.0. Anal. calcd. for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53; found: C, 66.11; H, 6.22; N, 8.46.

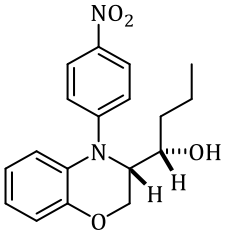
(*R)-1-((*S**)-6-Methoxy-4-(4-nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl) butan-1-ol (3n)**



3n

The title compound was prepared starting from 2-nitrophenol **4b** and epoxy tosylate **5a** following the **General Procedure D**. Orange solid (mp: 168–169 °C); yield: 54% over four steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.3 Hz, 2H), 7.30 – 7.22 (m, 2H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.65 – 6.56 (m, 2H), 4.64 (dd, *J* = 10.9, 1.3 Hz, 1H), 3.93 (dd, *J* = 10.9, 2.1 Hz, 1H), 3.74 – 3.65 (m, 5H), 1.84 – 1.75 (m, 2H), 1.61 – 1.57 (m, 2H), 1.33 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 153.5, 143.4, 141.1, 128.5, 125.7, 119.0, 118.2 110.9, 108.1, 68.24, 63.5, 62.37, 55.7, 36.7, 19.3, 14.0

(*S)-1-((*S**)-4-(4-Nitrophenyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-3-yl) butan-1-ol (3o)**



3o

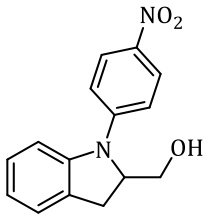
The title compound was prepared starting from 2-nitrophenol **4a** and epoxy tosylate **5b** following the **General Procedure D**. White solid (mp: 162–163 °C); yield: 50% over four steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 9.1 Hz, 2H), 7.42 (d, *J* = 9.1 Hz, 2H), 7.19 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.03–6.94 (m, 2H), 6.91–6.87 (m, 1H), 4.41 (d, *J* = 11.0, 1H), 4.06 (dd, *J* = 11.4, 1.8 Hz, 1H), 3.83–3.72 (m, 2H), 2.28 (br s, 1H), 1.70–1.42 (m, 4H), 0.98 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 146.4, 141.5, 125.9, 125.5, 124.3, 122.3, 121.3, 119.7, 117.9, 67.6, 64.0, 63.7, 35.0, 18.7, 14.1. Anal. calcd. for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53; found: C, 66.07; H, 6.07; N, 8.62.

3.4. Synthesis of *N*-arylindolines 7a–d (Scheme 3, main manuscript):

General Procedure E:

To a solution of **6a–d** (133 mg, 1.0 mmol, 1.0 equiv) in pyridine (5 mL) at 0 °C was added 4-nitrobenzenesulfonyl chloride (244 mg, 1.1 mmol, 1.1 equiv). The mixture was stirred for 12 h at room temperature. The reaction was quenched by adding 2N HCl solution at 0 °C. The mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude products were converted into **7a–d** following **General Procedures B** and **C**.

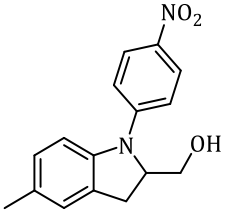
(1-(4-Nitrophenyl)indolin-2-yl)methanol (7a)



7a

First, compound **26a** was subjected to the epoxidation step of **General Procedure B** and then, the resulting crude product was converted into product **7a** following the **General Procedure C**. Orange solid (mp: 75–76 °C); yield: 78% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.2 Hz, 2H), 7.40 (d, *J* = 9.2 Hz, 2H), 7.30–7.27 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 4.55–4.49 (m, 1H), 3.83 (dd, *J* = 11.3, 6.2 Hz, 1H), 3.71 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.40 (dd, *J* = 15.9, 8.8 Hz, 1H), 2.91 (dd, *J* = 15.9, 2.3 Hz, 1H), 2.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 143.6, 140.0, 132.0, 127.2, 125.9, 125.8, 122.7, 115.1, 113.8, 65.8, 63.6, 31.8. Anal. calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36; found: C, 66.83; H, 5.28; N, 10.30.

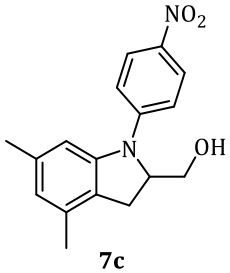
(5-Methyl-1-(4-nitrophenyl)indolin-2-yl)methanol (7b)



7b

First, compound **26b** was subjected to the epoxidation step of **General Procedure B** and then, the resulting crude product was converted into product **7b** following the **General Procedure C**. Orange solid (mp: 82–83 °C); yield: 80% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.3 Hz, 2H), 7.35 (d, *J* = 9.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.09 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 4.52–4.46 (m, 1H), 3.80 (dd, *J* = 11.3, 6.5 Hz, 1H), 3.70 (dd, *J* = 11.3, 5.9 Hz, 1H), 3.36 (dd, *J* = 15.9, 8.8 Hz, 1H), 2.82 (d, *J* = 16.0, 1H), 2.33 (s, 3H), 1.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 141.1, 139.7, 132.6, 132.2, 127.6, 126.7, 125.9, 114.6, 114.0, 66.0, 63.9, 31.88, 21.1. Anal. calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; found: C, 67.85; H, 5.62; N, 9.92.

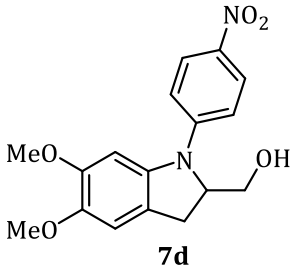
(4,6-Dimethyl-1-(4-nitrophenyl)indolin-2-yl)methanol (7c)



7c

First, compound **26c** was subjected to the epoxidation step of **General Procedure C** and then, the resulting crude product was converted into product **27c** following the **General Procedure D**. Orange solid (mp: 92–93 °C); yield: 75% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 9.6 Hz, 2H), 7.39 (d, *J* = 9.6 Hz, 2H), 6.96 (s, 1H), 6.67 (s, 1H), 4.57–4.51 (m, 1H), 3.83 (dd, *J* = 11.3, 6 Hz, 1H), 3.72 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.24 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.82 (dd, *J* = 15.8, 2.3 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 143.5, 139.8, 137.2, 135.1, 127.6, 125.8, 124.7, 115.2, 112.1, 65.9, 63.9, 30.3, 21.6, 18.7. ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 148.3, 145.4, 139.8, 136.7, 125.9, 123.4, 114.5, 109.7, 100.4, 67.2, 64.1, 56.5, 31.9. Anal. calcd. for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39; found: C, 68.60; H, 6.12; N, 9.43.

(5,6-Dimethoxy-1-(4-nitrophenyl)indolin-2-yl)methanol (7d)

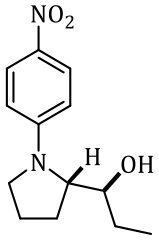


7d

First compound **26d** was subjected to the epoxidation step of **General Procedure C** and then, the resulting crude product was converted into product **7d** following the **General Procedure D**. Orange solid (mp: 106–107 °C); yield: 77% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 9.6 Hz, 2H), 7.35 (d, *J* = 9.1 Hz, 2H), 6.89 (s, 1H), 6.85 (s, 1H), 4.51–4.46 (m, 1H), 3.88 (s, 6H), 3.82 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.71 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.38 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.74 (d, *J* = 15.1, 1H), 1.65 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 148.3, 145.4, 139.8, 136.7, 125.9, 123.4, 114.5, 109.7, 100.4, 67.2, 64.1, 56.5, 31.9. Anal. calcd. for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48; found: C, 61.75; H, 5.57; N, 8.52.

3.5. Synthesis of *N*-arylpyrrolidines 9a and 9b (Scheme 4, main manuscript):

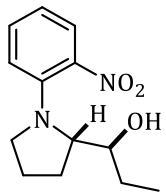
(*S**)-1-((*S**)-1-(4-Nitrophenyl)pyrrolidin-2-yl)propan-1-ol (9a)



9a

A mixture of *p*-$NsNH_2$ (202 mg, 1.0 mmol), tosylate **8** (268 mg, 1.0 mmol), and K_2CO_3 (207 mg, 1.5 mmol) in MeCN was heated for 8 h at 70 °C. Then the mixture was concentrated under reduced pressure. The resulting residue was dissolved in DCE and H_2O. The organic layer was separated and then *m*-CPBA (232 mg, 1.0 mmol, 75%) was added to this solution. The resulting mixture was heated for 12 h at 80 °C. The mixture was diluted with CH_2Cl_2 (20 mL) and then washed successively with saturated aq. solutions of Na_2SO_3 (5 mL) and $NaHCO_3$ (5 mL). The organic layer was separated, washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was converted into **9a** following the **General Procedure C**. Orange solid (mp: 85–86 °C); yield: 60% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 9.6 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 3.96–3.92 (m, 1H), 3.62–3.56 (m, 2H), 3.30 (q, *J* = 8.7 Hz, 1H), 2.13–1.89 (m, 5H), 1.66–1.44 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 153.4, 137.3, 125.9, 111.9, 74.8, 64.0, 49.5, 27.6, 26.4, 23.5, 10.4. Anal. calcd. for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19; found: C, 62.55; H, 7.21; N, 11.27.

***(S*)-1-((S*)-1-(2-Nitrophenyl)pyrrolidin-2-yl)propan-1-ol (9b)**



9b

The title compound was prepared starting from *o*-$NsNH_2$ (202 mg, 1.0 mmol) and tosylate **8** in the same procedure that was used for the preparation of **9a**. White solid (mp: 72–73 °C); yield: 50% over three steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.75 (m, 1H), 7.38–7.34 (m, 1H), 7.27–7.25 (m, 1H), 6.81 (t, *J* = 8.2 Hz, 1H), 4.16 (q, *J* = 5.9 Hz, 1H), 3.55–3.44 (m, 2H), 2.70–2.66 (m, 1H), 2.19–2.12 (m, 1H), 1.97–1.92 (m, 1H), 1.87–1.72 (m, 2H), 1.57–1.50 (m, 1H), 1.43–1.34 (m, 1H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.8, 132.8, 126.4, 118.6, 117.9, 75.9, 62.7, 54.1, 27.7, 26.6, 25.3, 10.5. Anal. calcd. for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48; found: C, 61.93; H, 5.55; N, 8.44.

4. X-Ray crystallography

Compound **3k** was crystallized in Tetragonal space group *P-1*. X-ray reflections were collected on a Bruker APEX-II, CCD diffractometer using Mo Kα (λ = 0.71073 Å) radiation. Data reduction was performed using Bruker SAINT Software.[7] Intensities for absorption were corrected using SADABS. Structures were solved and refined using SHELXL-2014 with anisotropic displacement parameters for non-H atoms. Hydrogen atom on O was experimentally located in the crystal structure. All C–H atoms were fixed geometrically using the HFIX command in SHELX-TL.[8] A check of the final CIF file using PLATON did not show any missed symmetry.[9,10] The ORTEP diagram of **3k** with 40% probability ellipsoid is shown in Figure 1. The crystallographic parameters for **3k** are summarized in Table ESI-2.

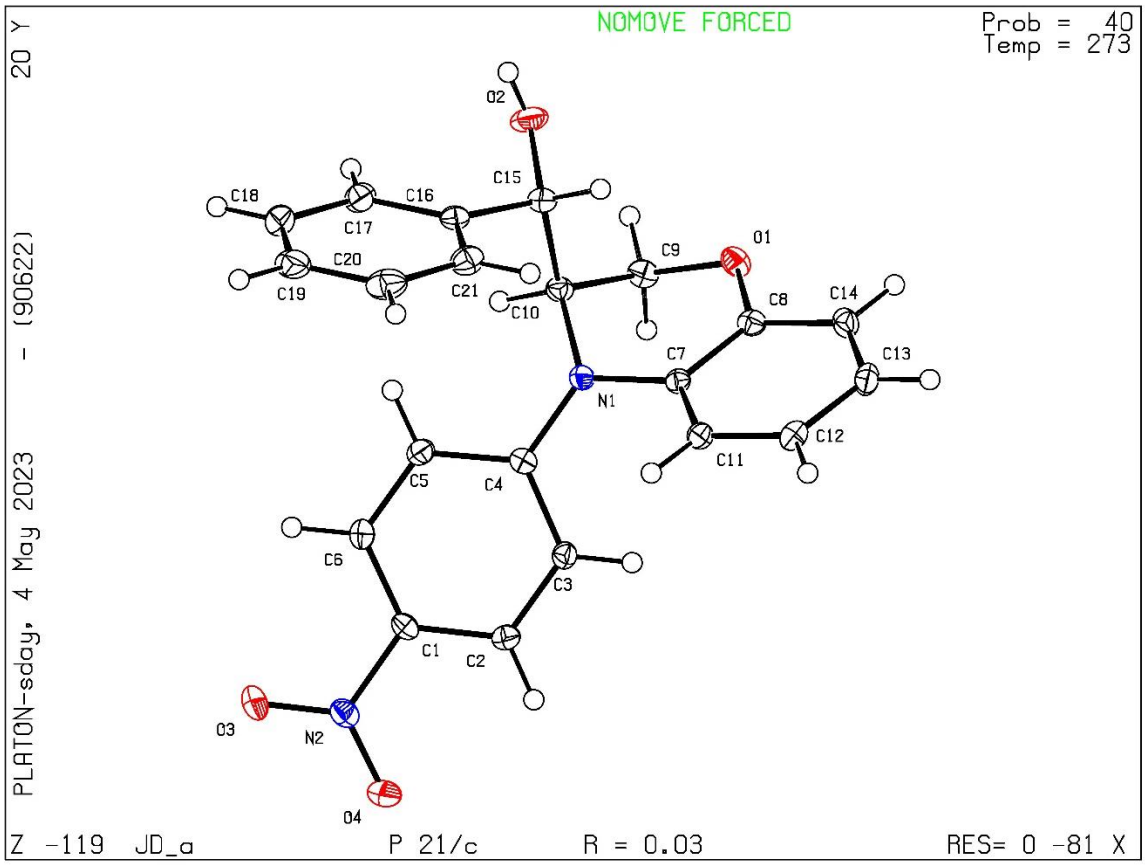


Figure ESI-2. ORTEP diagram of **3k** with 40% probability ellipsoid.

Table ESI1. Crystallographic parameters of **3k**.

Crystal Data	
Formula unit	$C_{21}\ H_{18}\ N_2\ O_4$
Formula wt.	362.37
Crystal system	monoclinic
T [K]	273
a [Å]	10.0642(7)
b [Å]	7.3128(5)
c [Å]	23.5961(16)
α [°]	90
β [°]	97.735(2)

γ [°]	90
Volume [Å^3]	1720.8(2
Space group	P 21/c
Z	4
D_{calc} [mg/m^3]	1.399
μ/mm^{-1}	0.098
Reflns. Collected	70401
Unique reflns.	3439
Observed reflns.	3948
R_1 [I>2σ(I)], wR_2	0.0343, 0.0868
GOF	0.989
Instrument	Bruker APEX-II
X-ray	MoK\α;λ=0.71073
CCDC Reference No.	2149550

5. References

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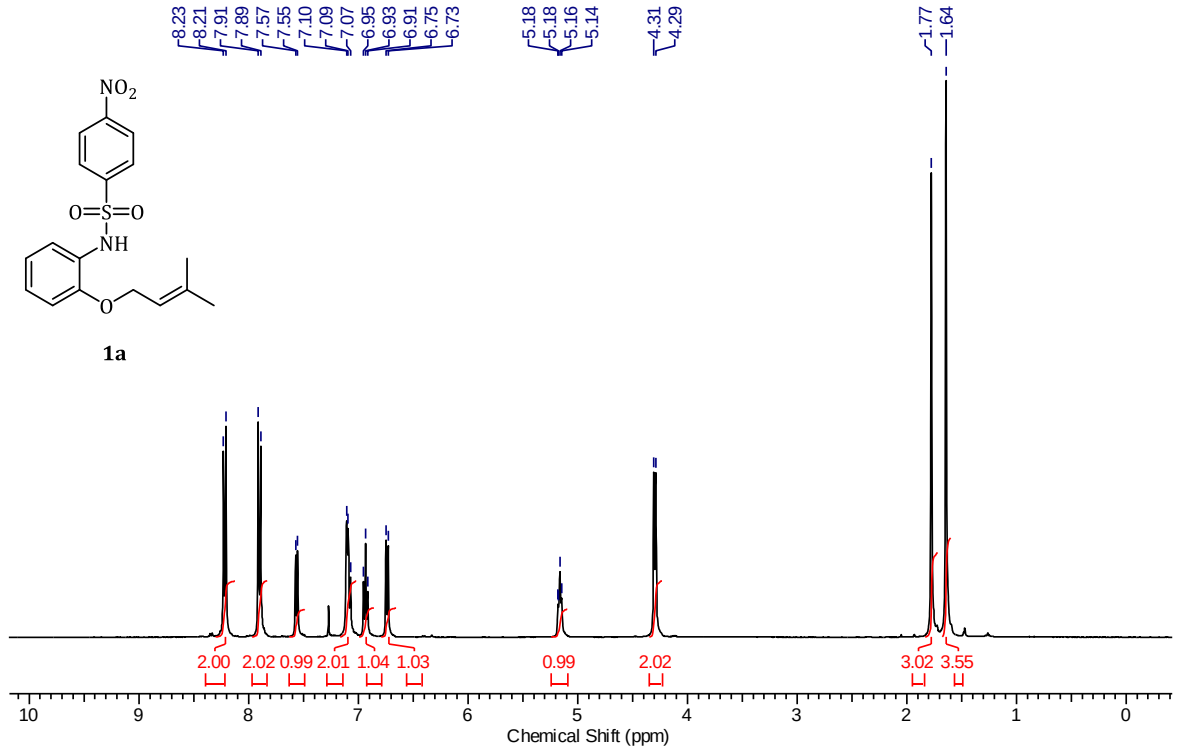
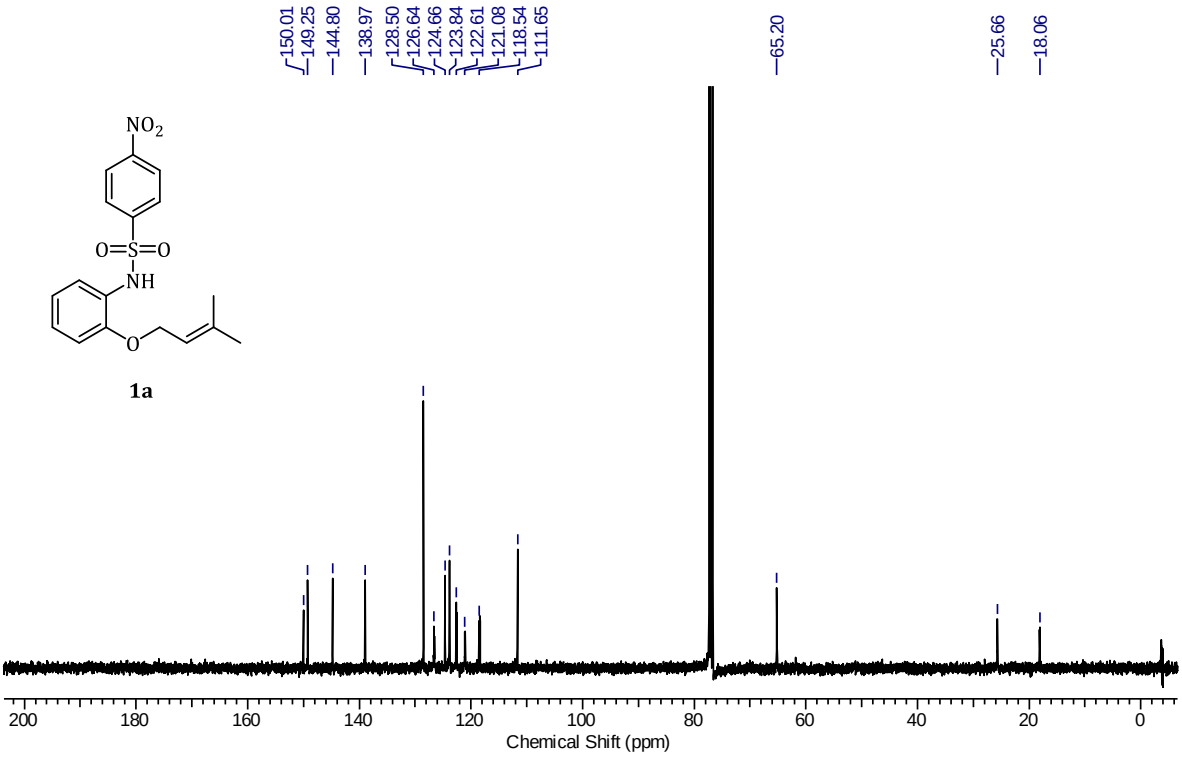
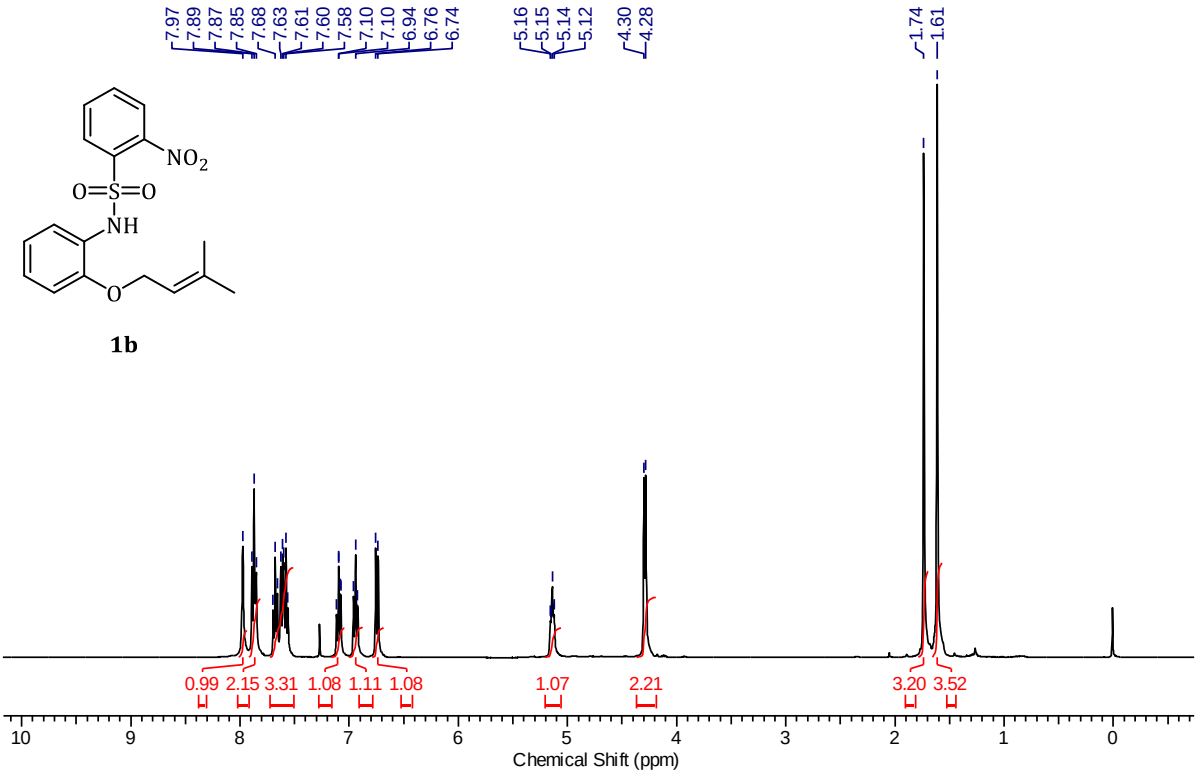
6. NMR Spectra of Compounds



^{1}H NMR (400 MHz, $CDCl_3$) of compound **1a**.

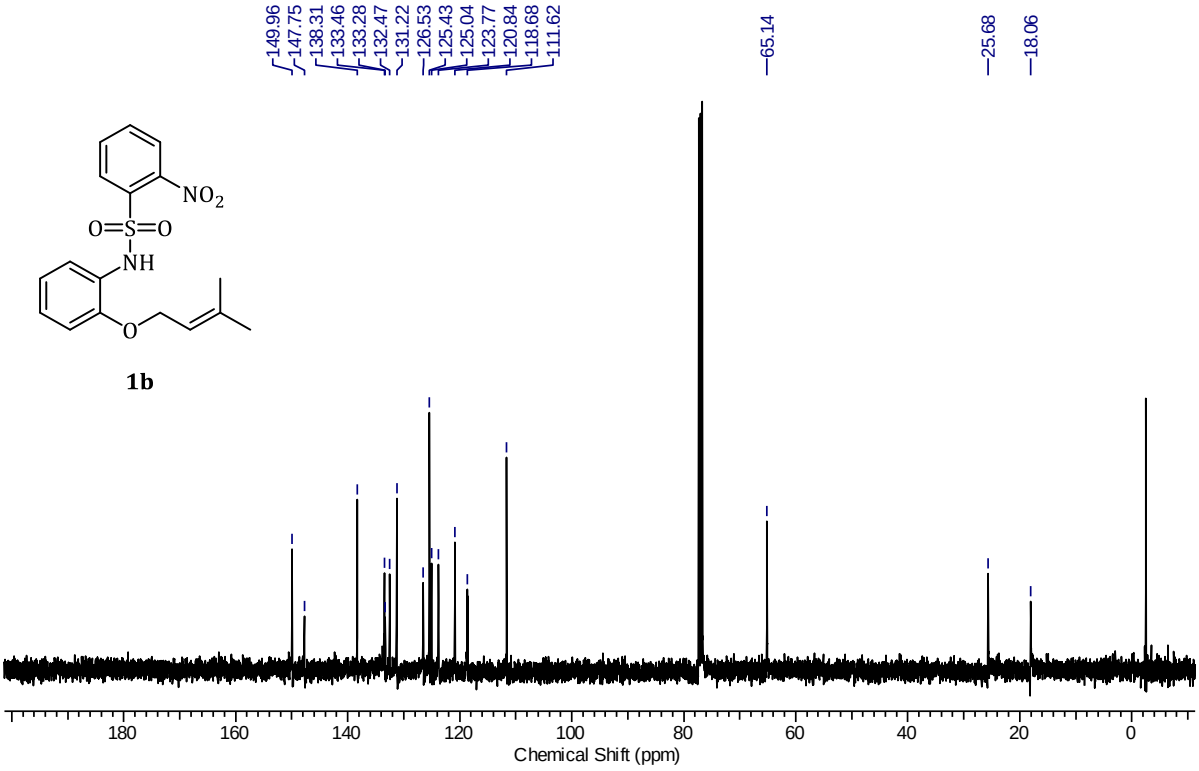


^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a.**



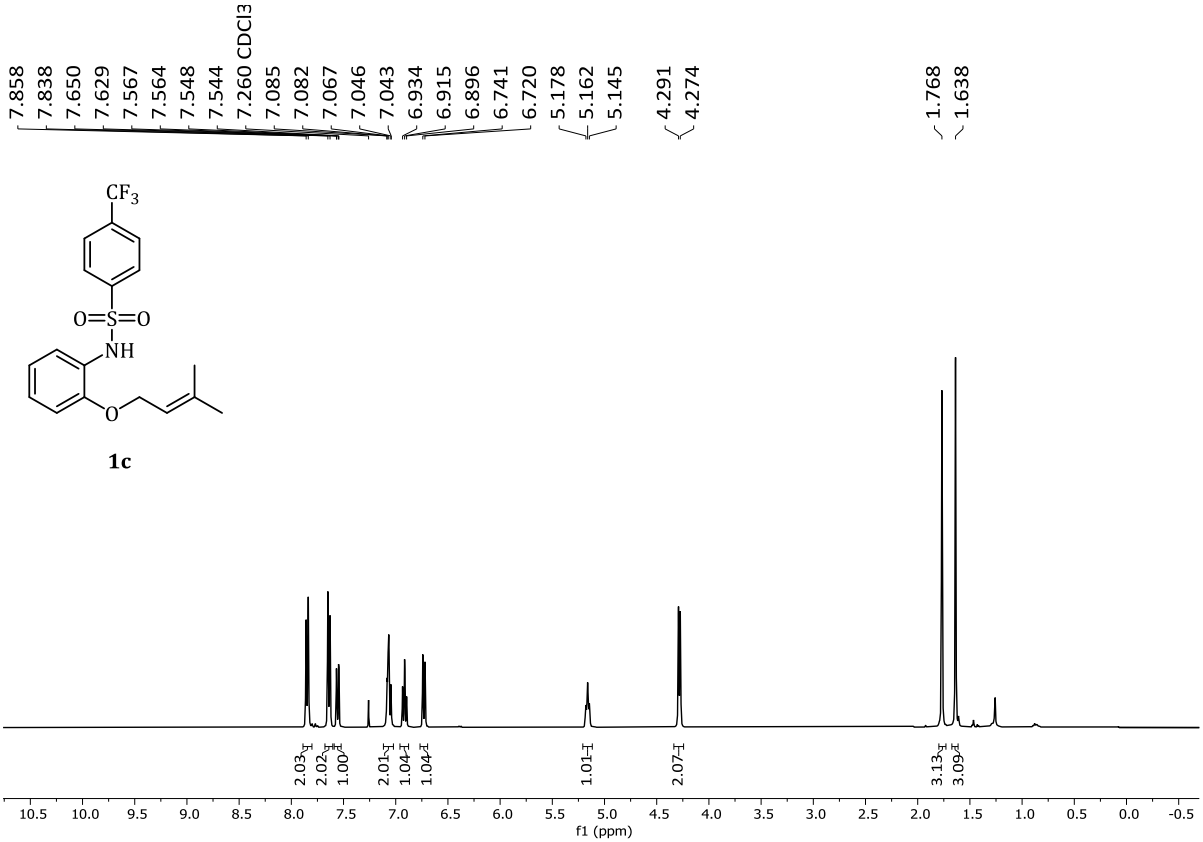
1b

^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b.**

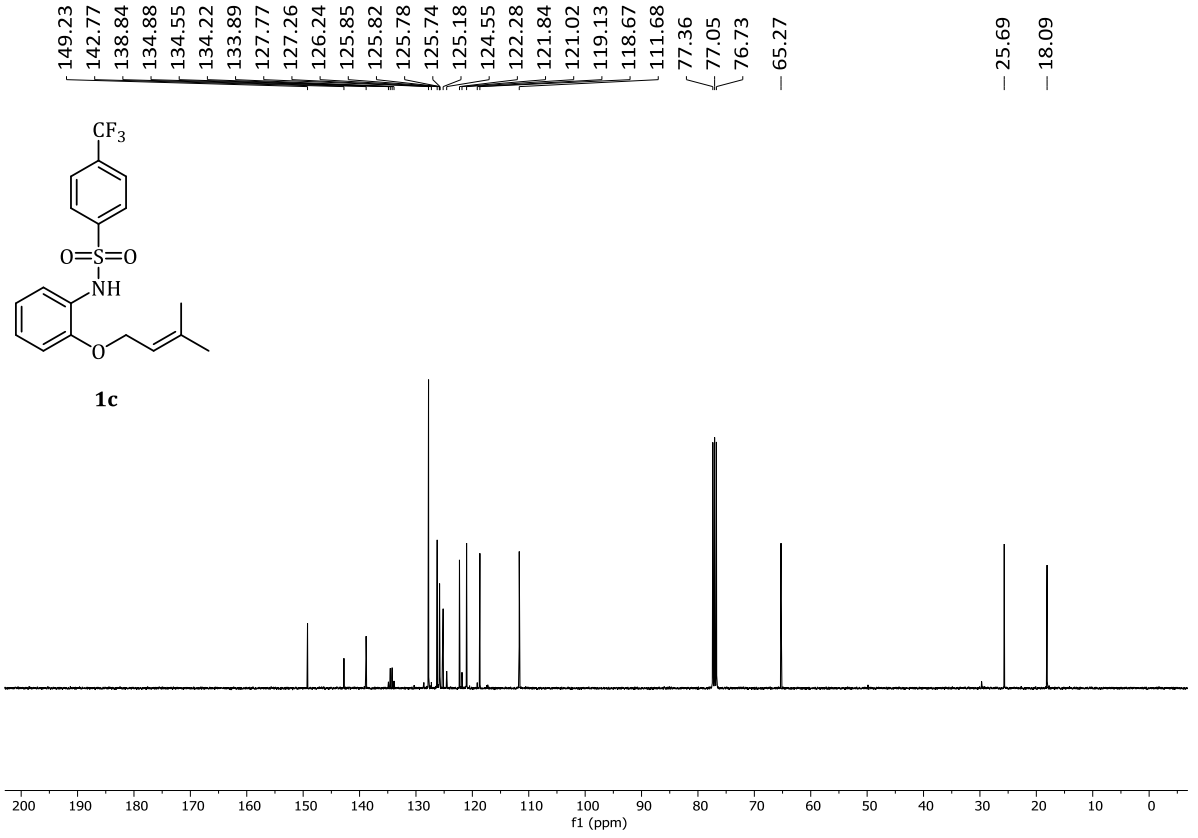


1b

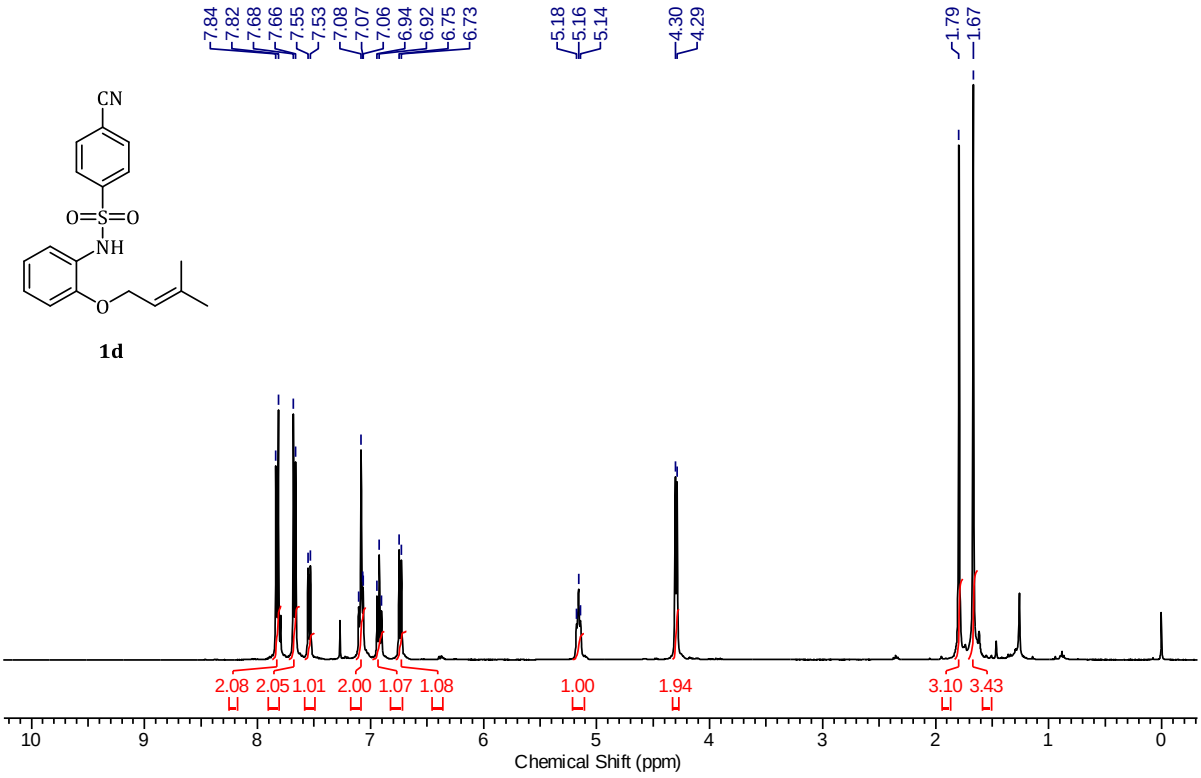
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b.**



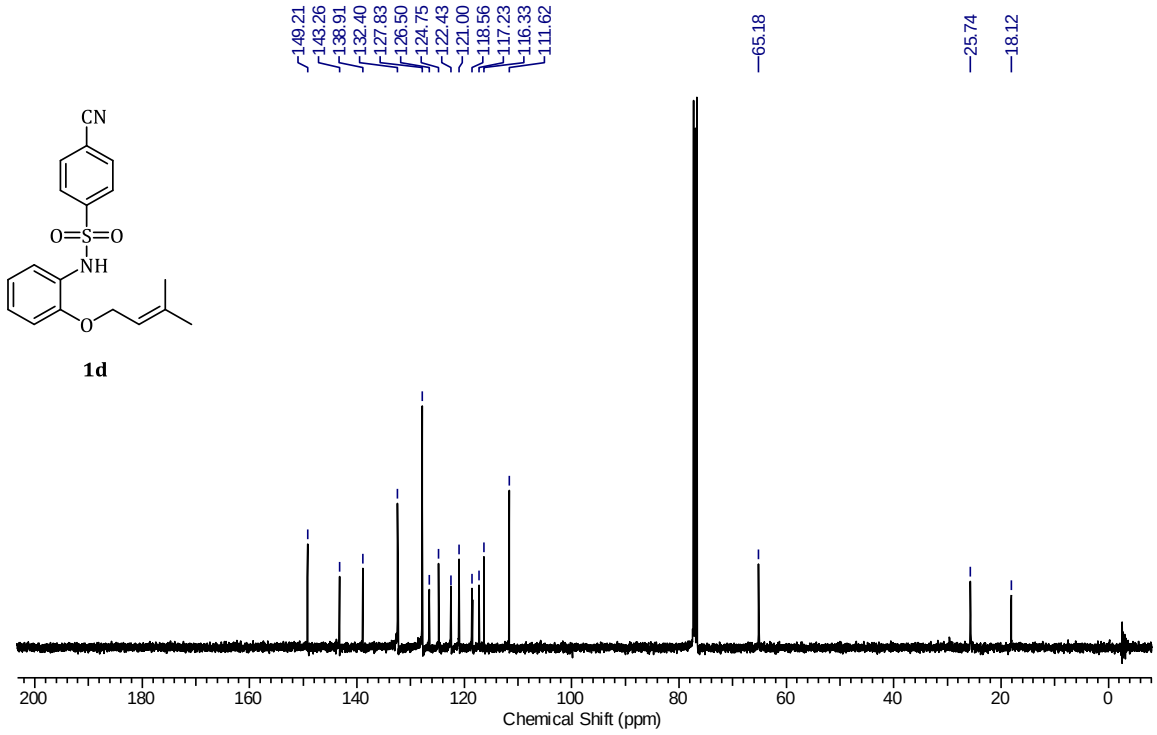
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1c.**



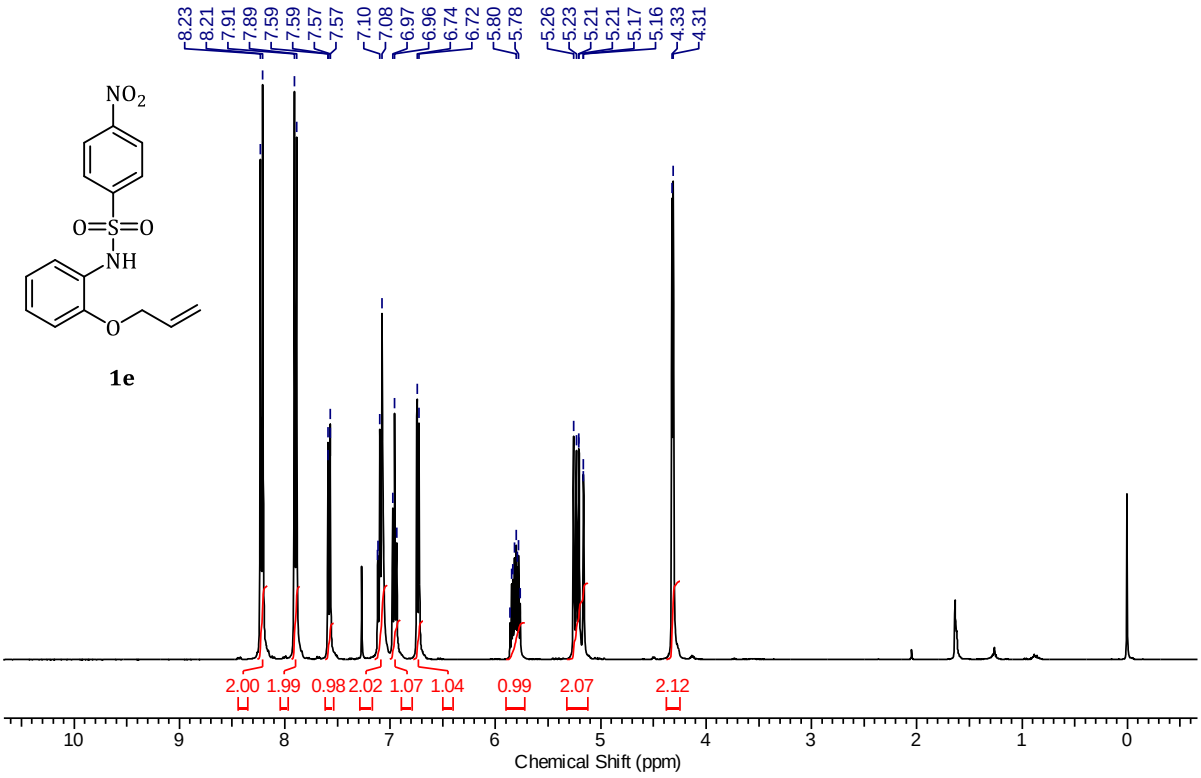
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1c.**



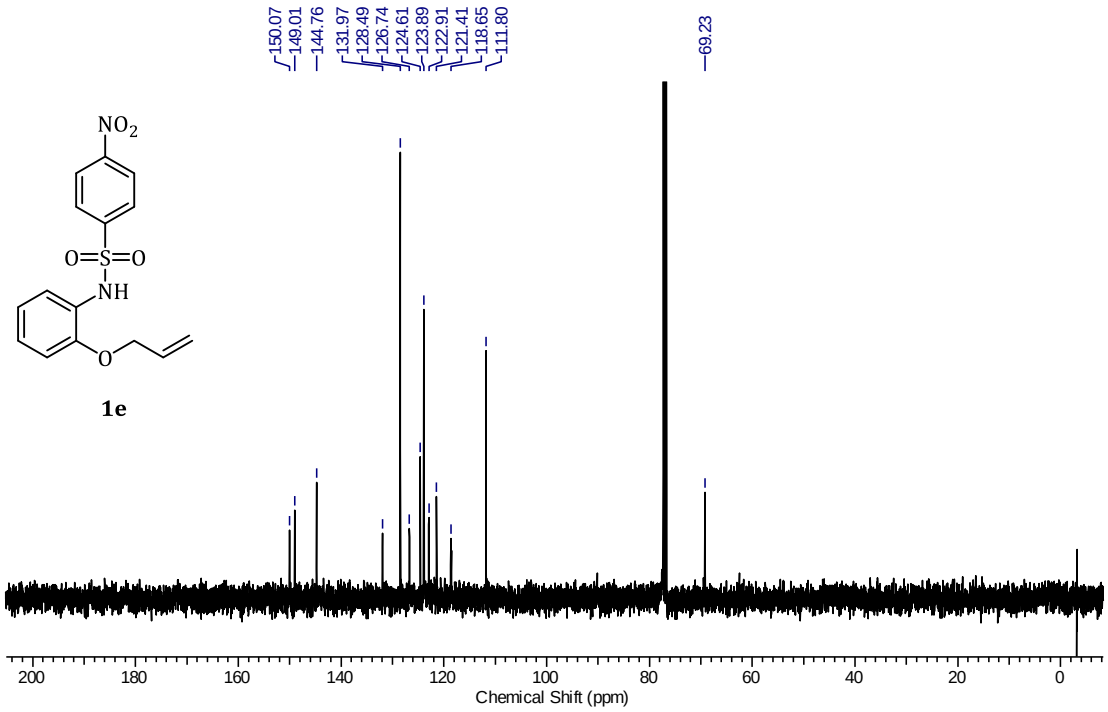
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1d.**



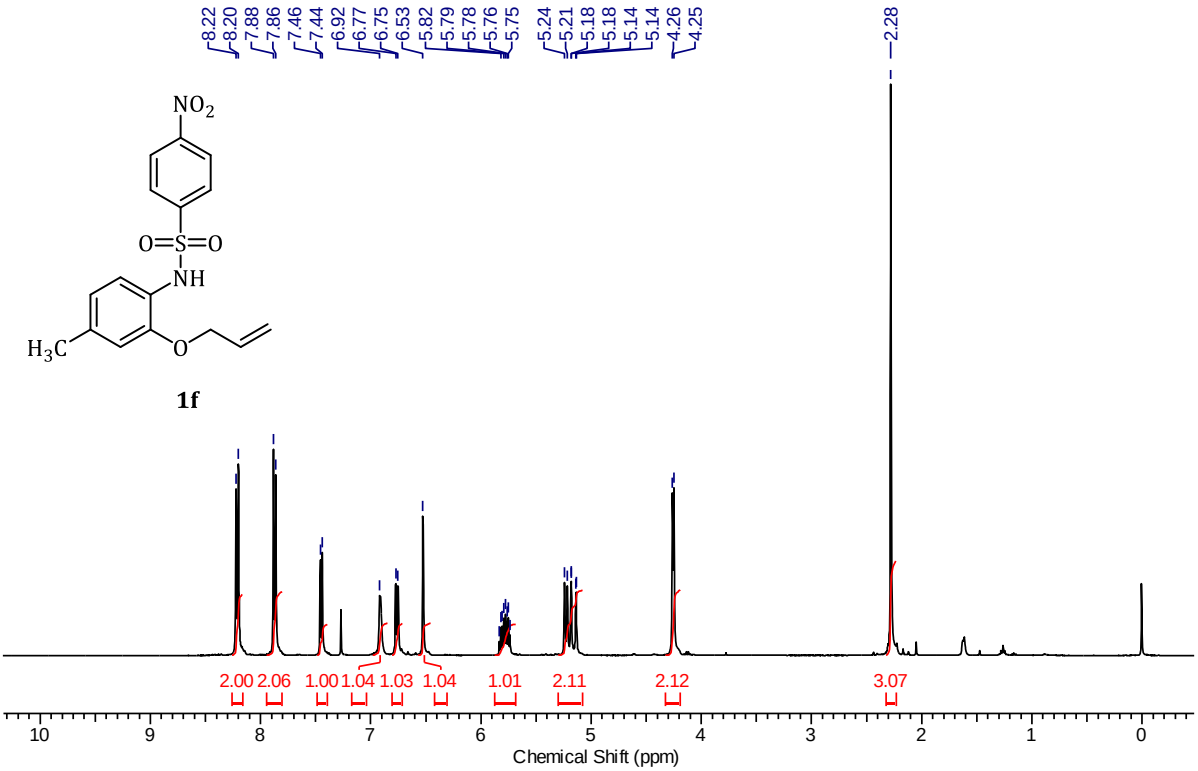
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d.**



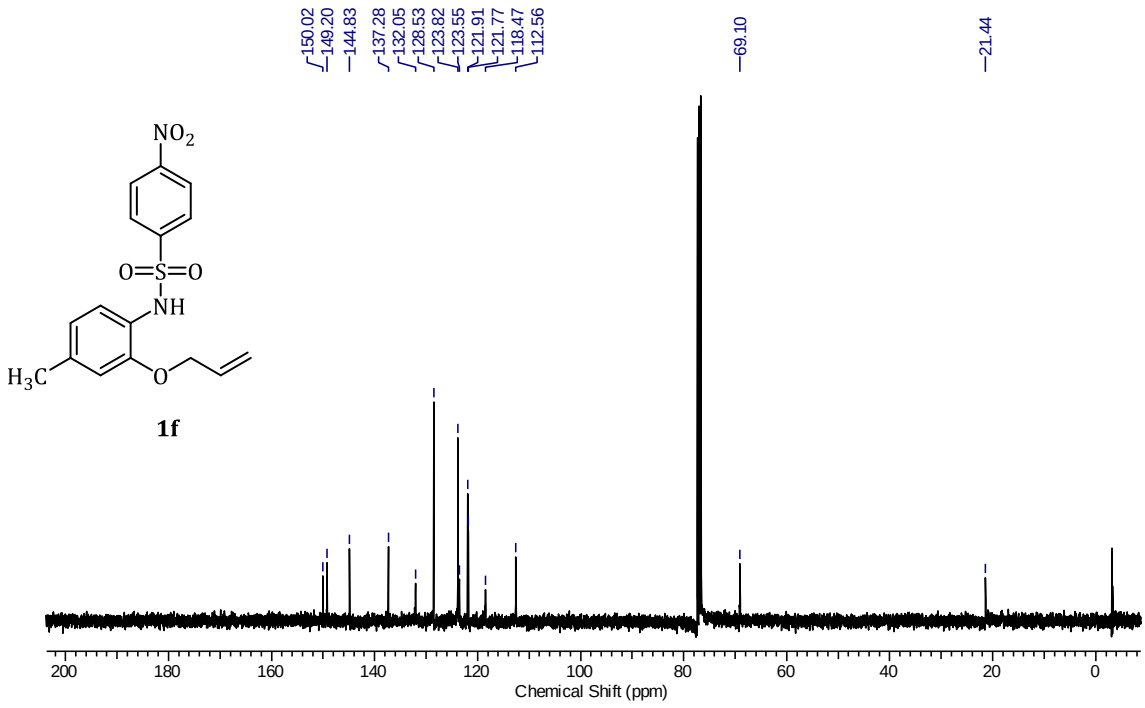
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1e.**



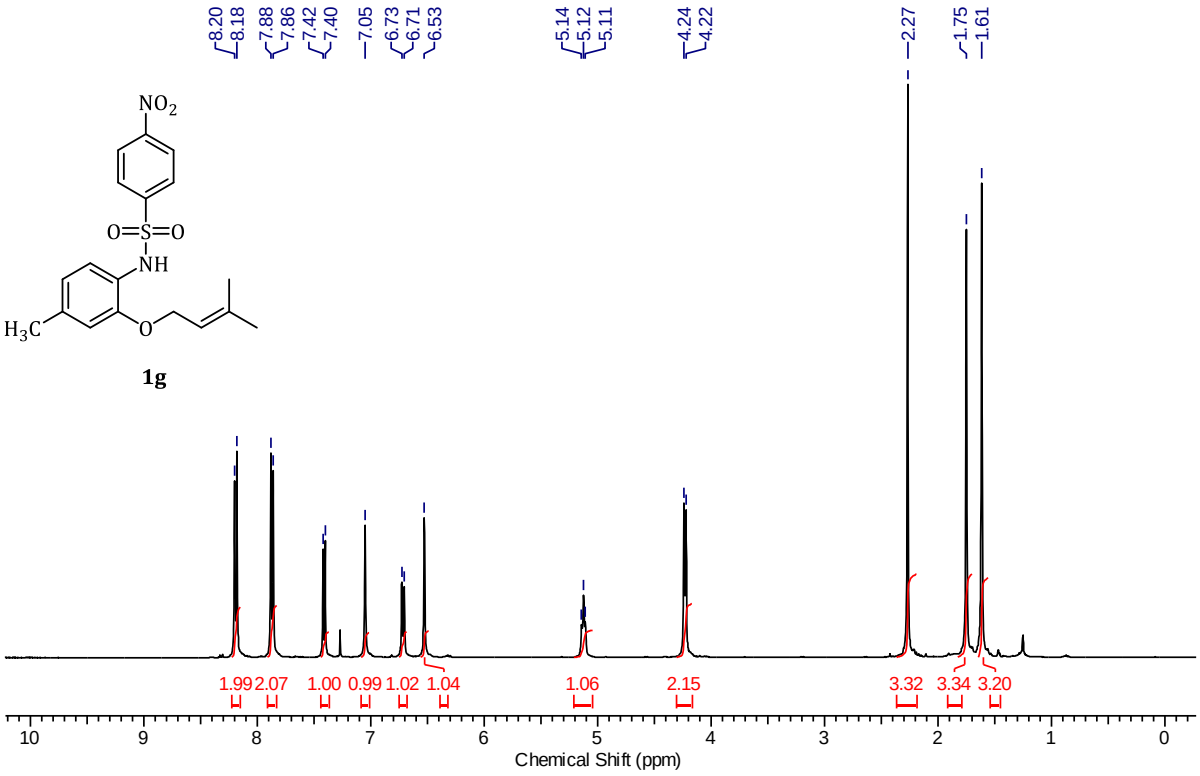
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e.**



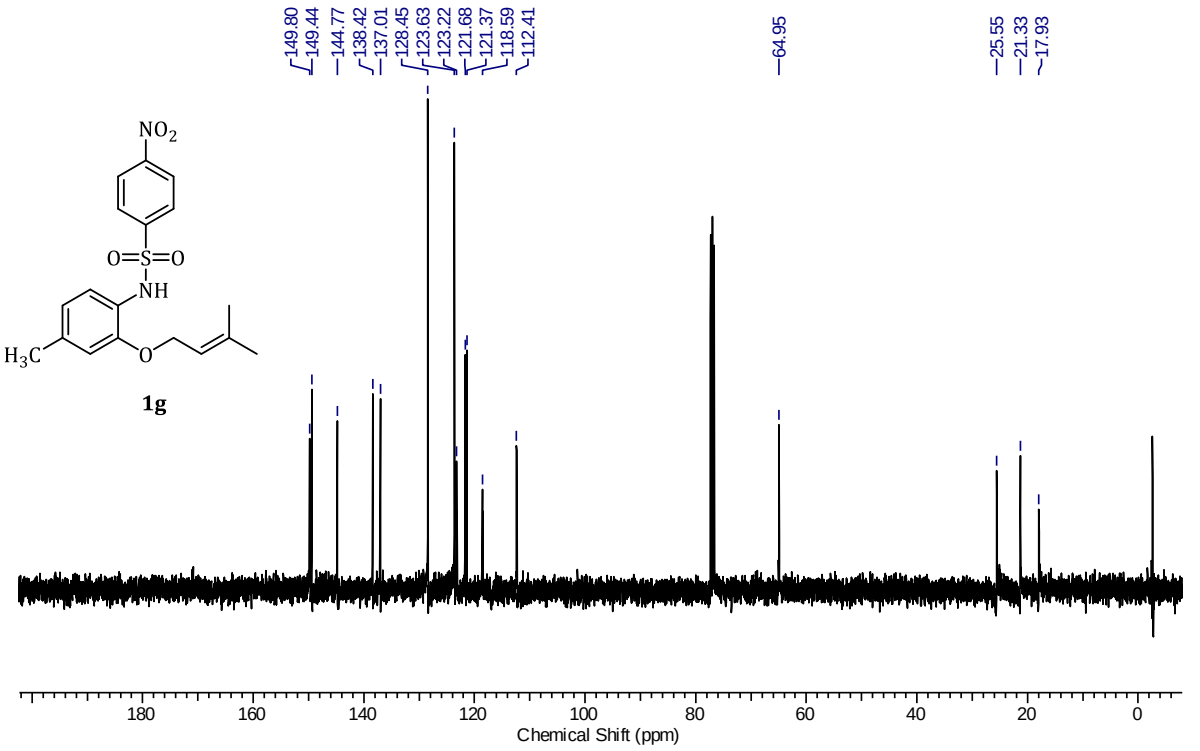
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1f.**



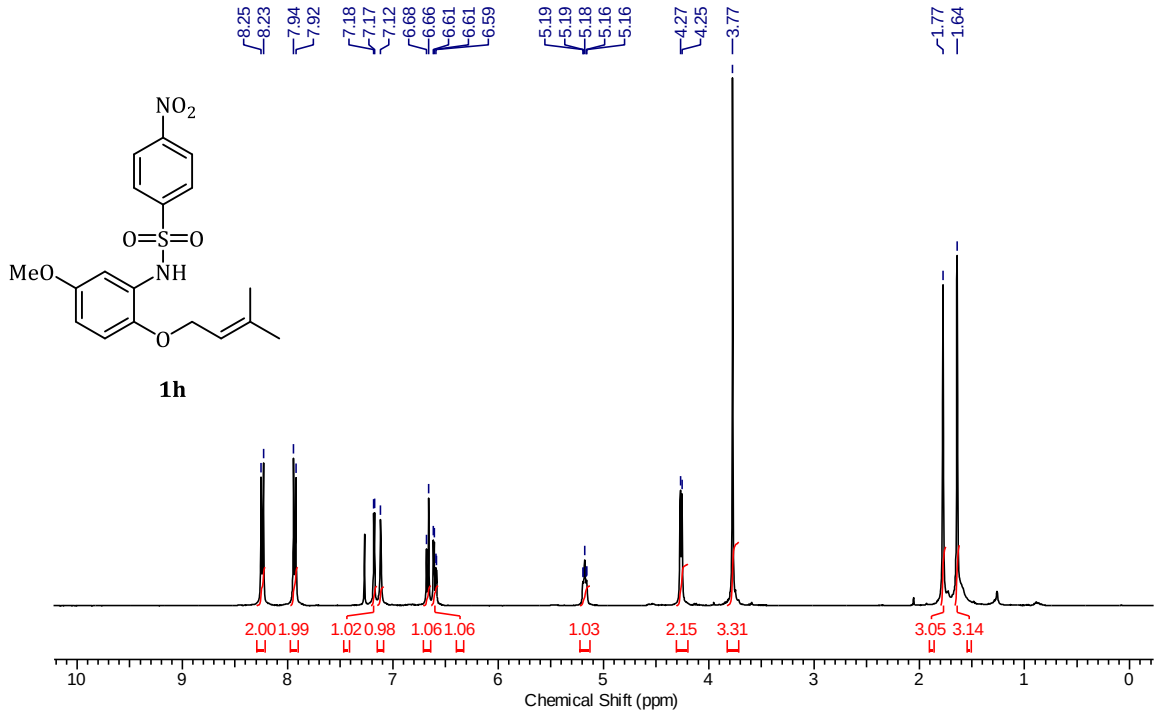
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1f.**



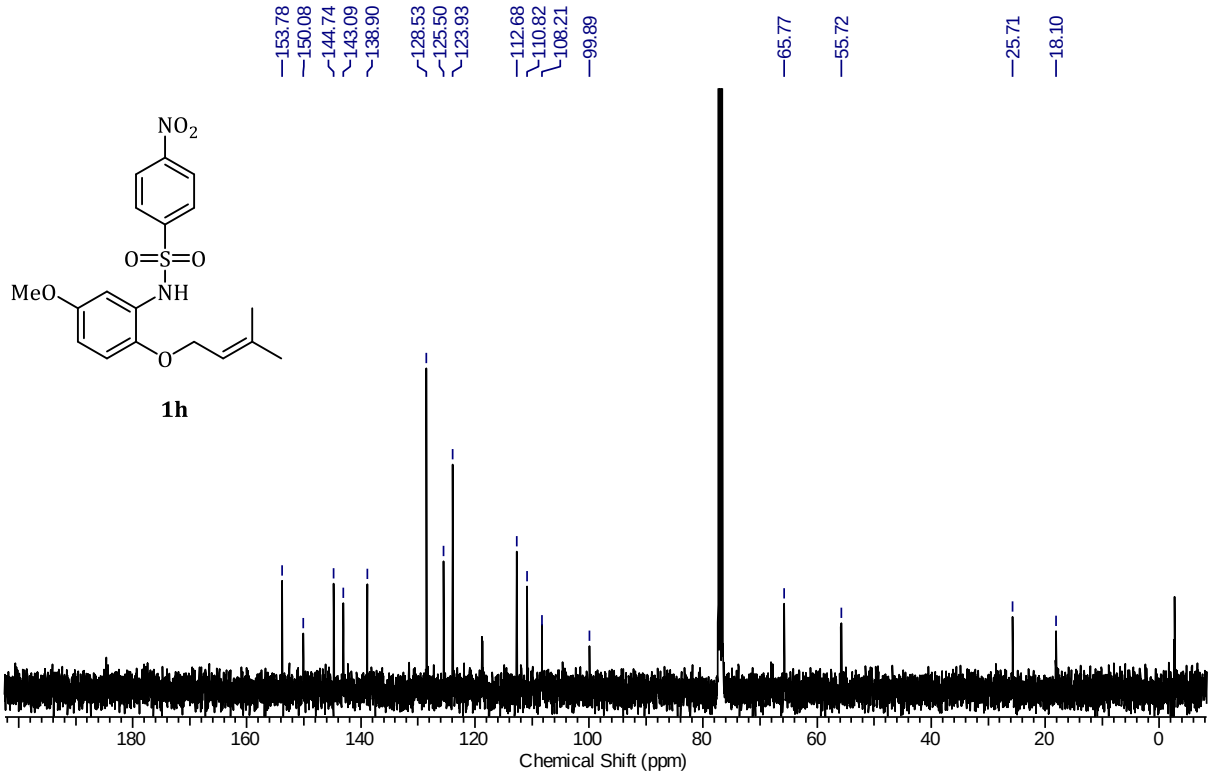
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1g.**



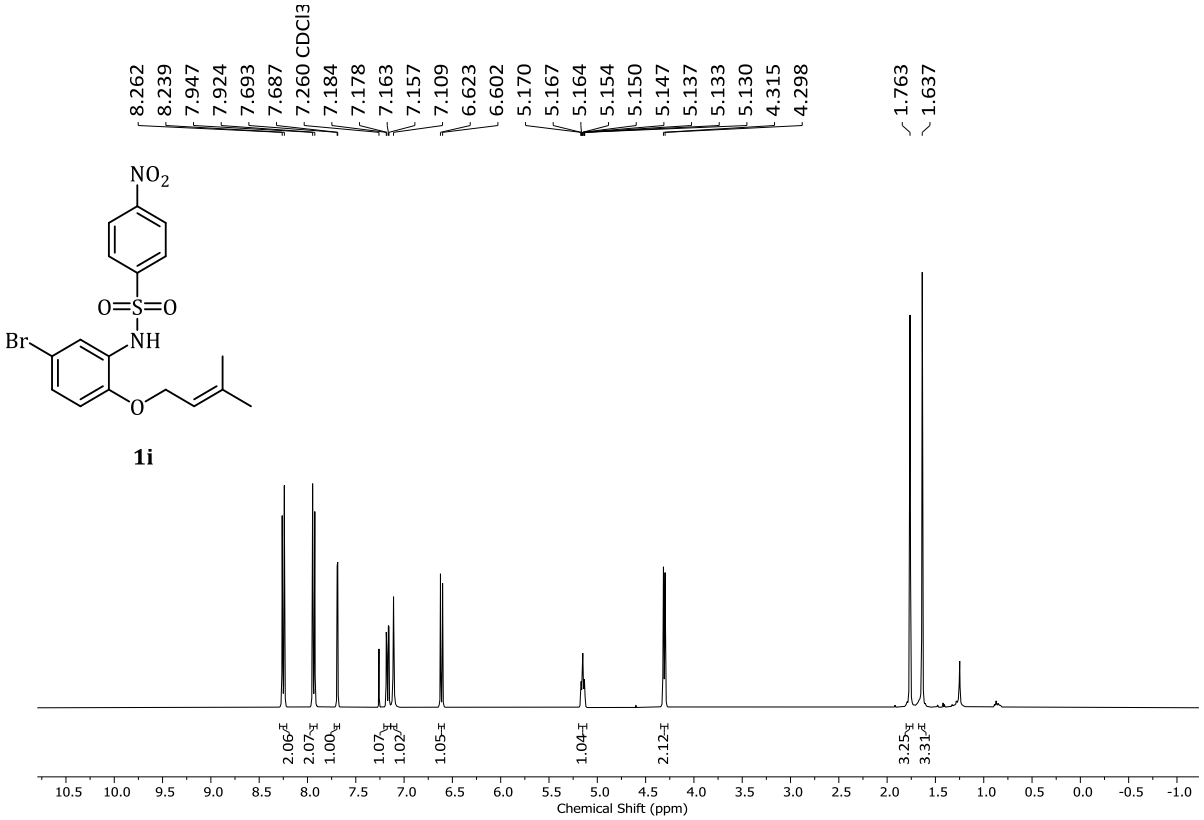
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1g.**



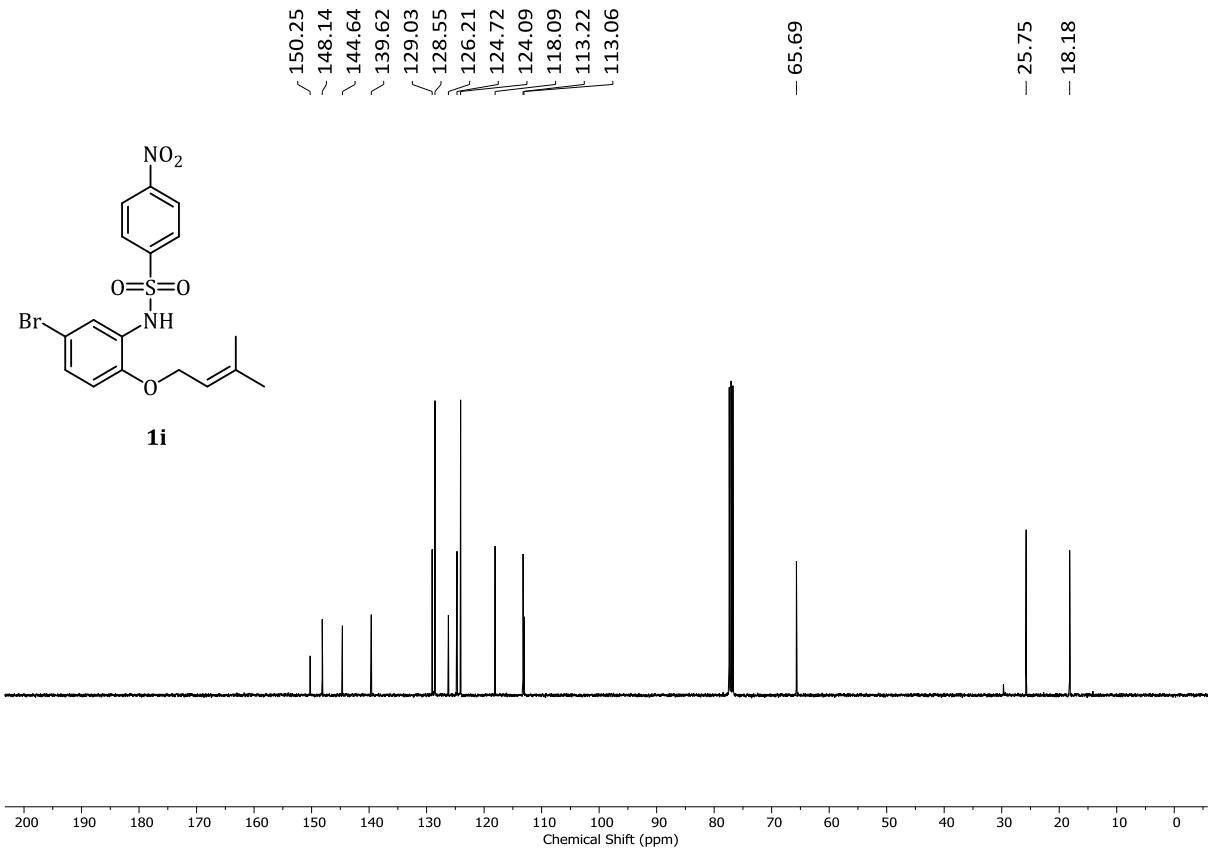
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1h.**



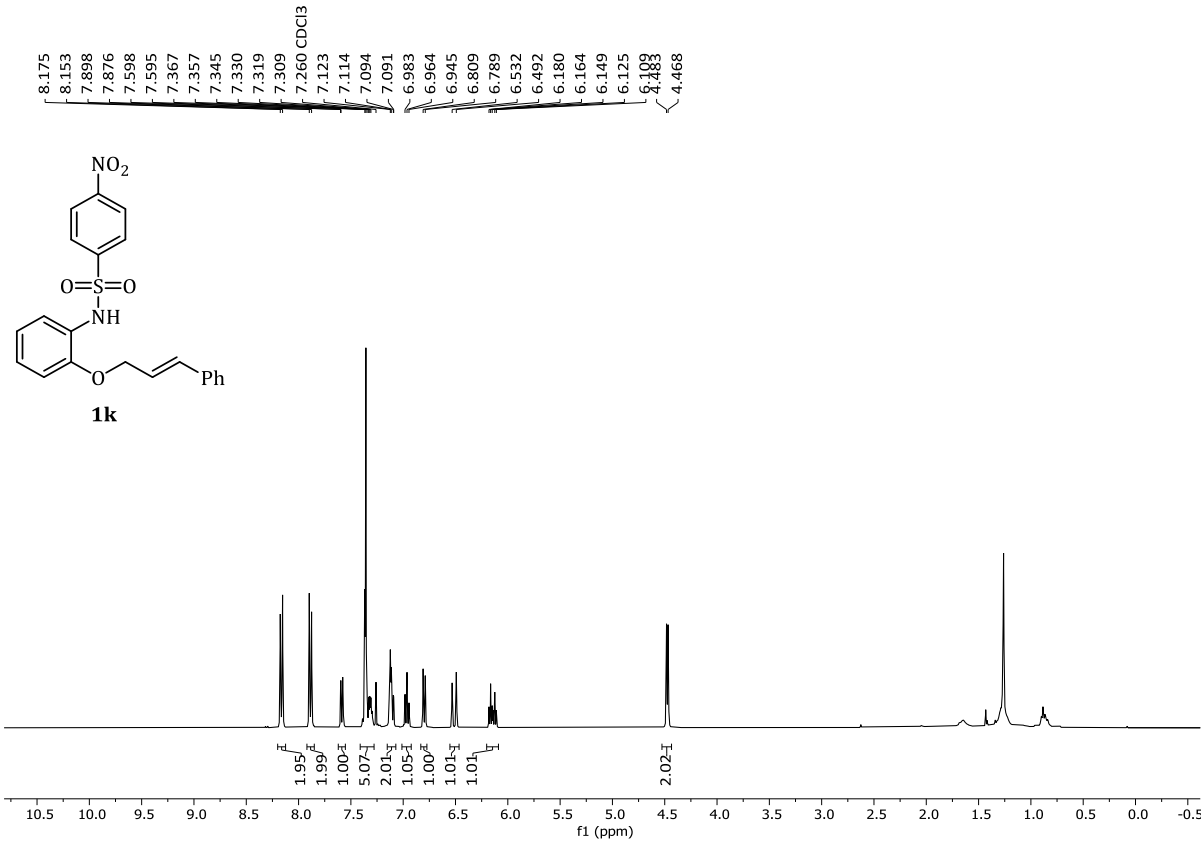
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1h.**



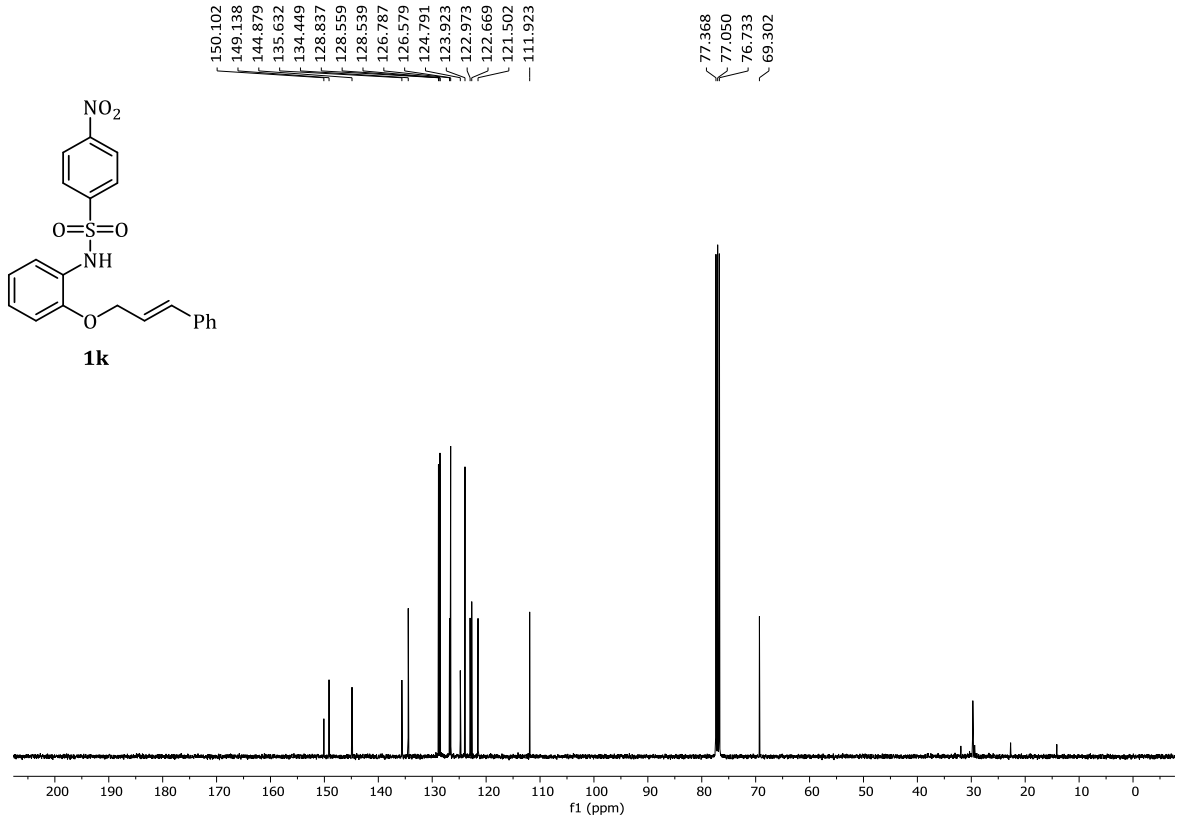
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1i.**



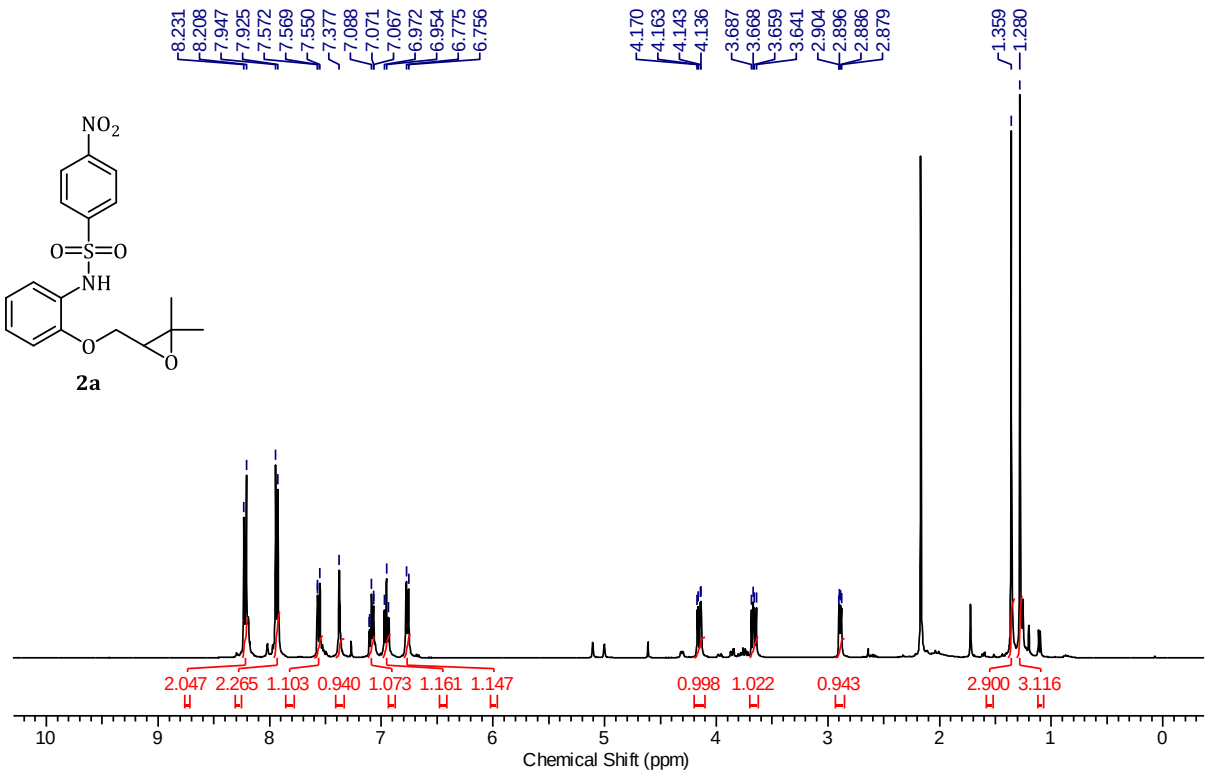
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1i.**



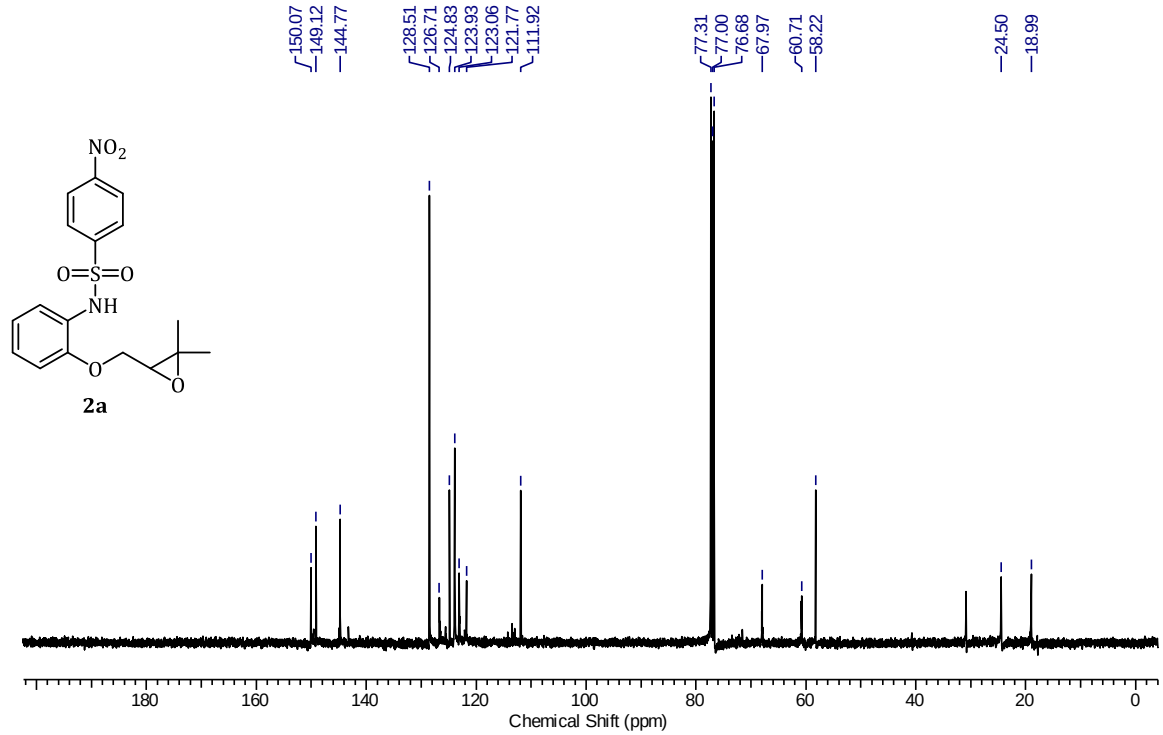
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1k.**



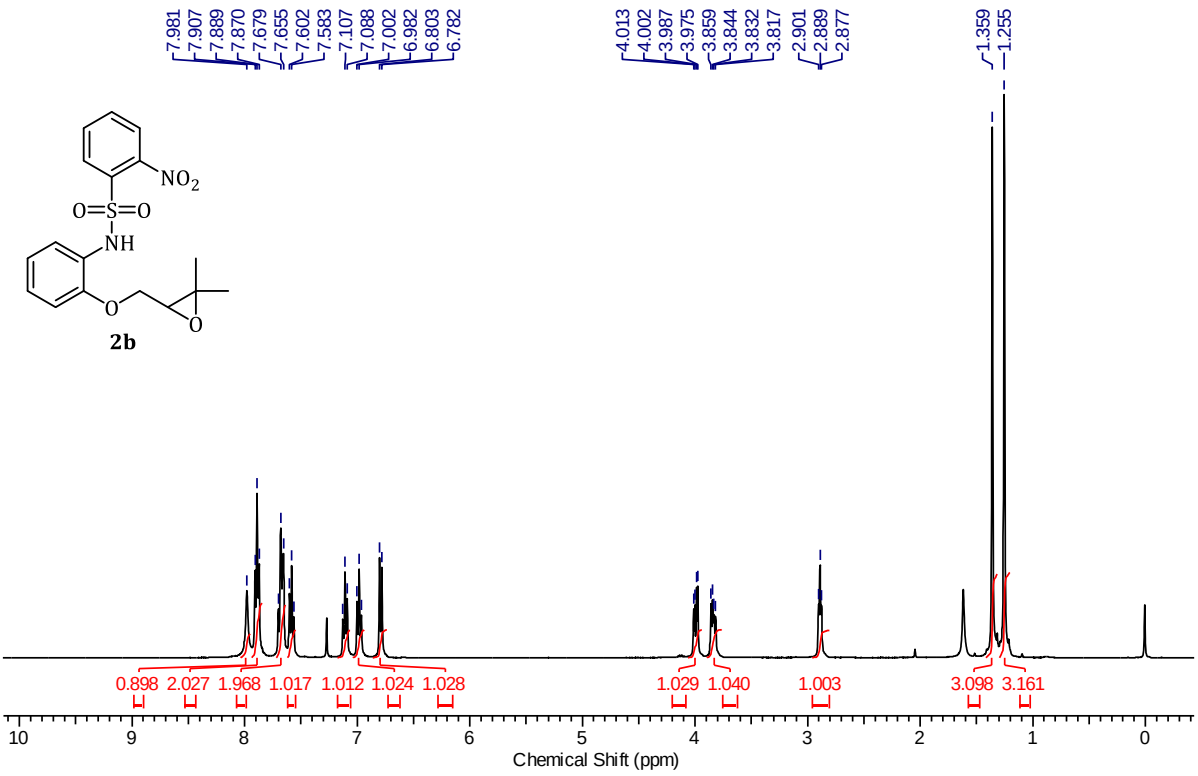
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1k.**



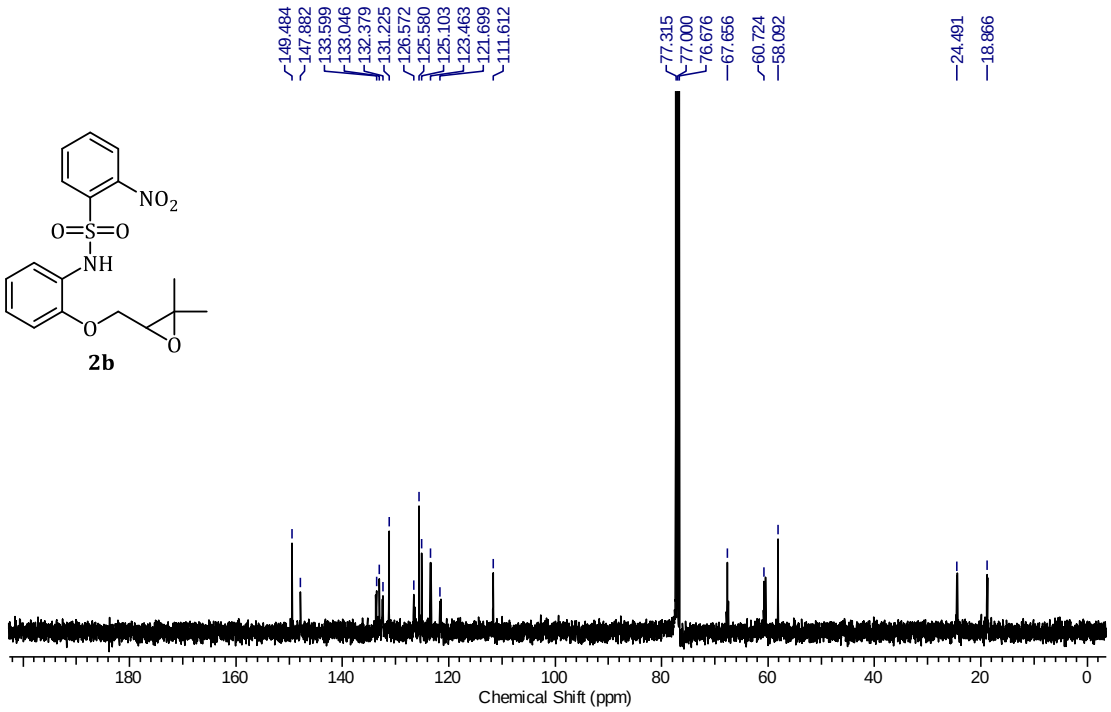
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



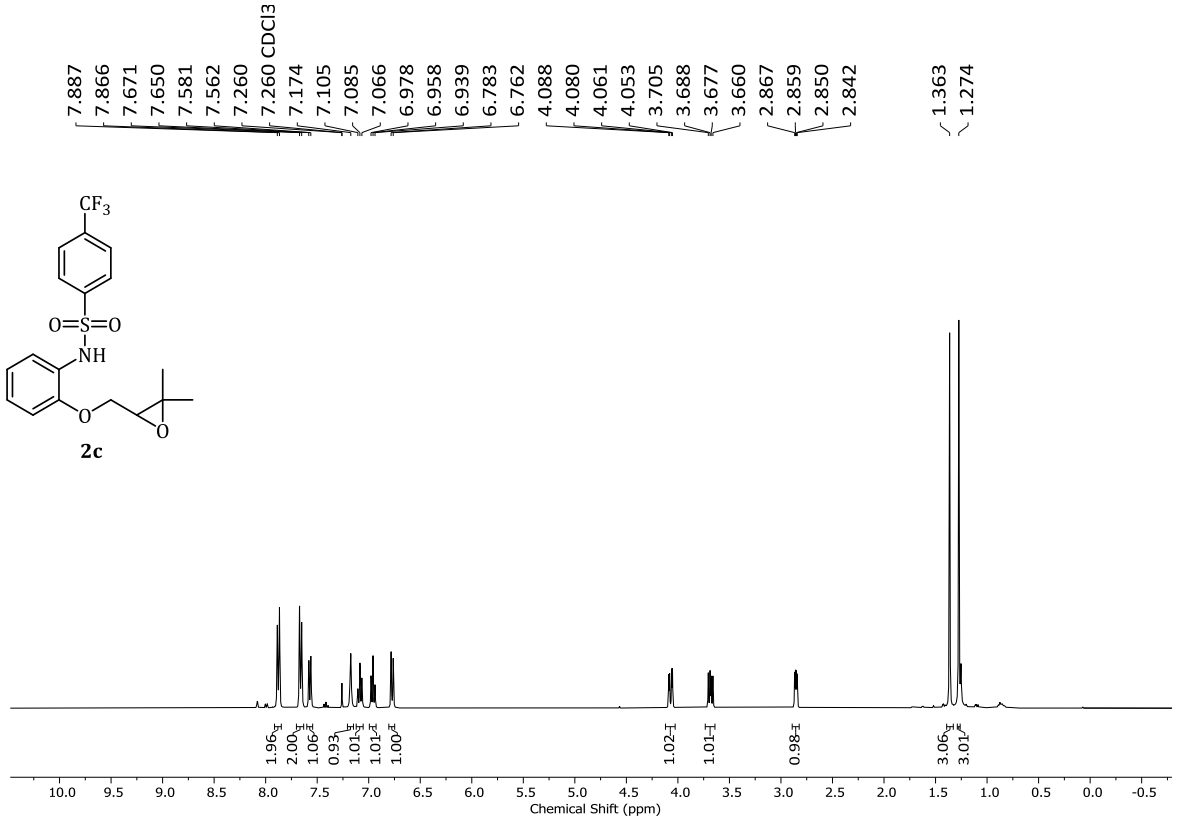
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



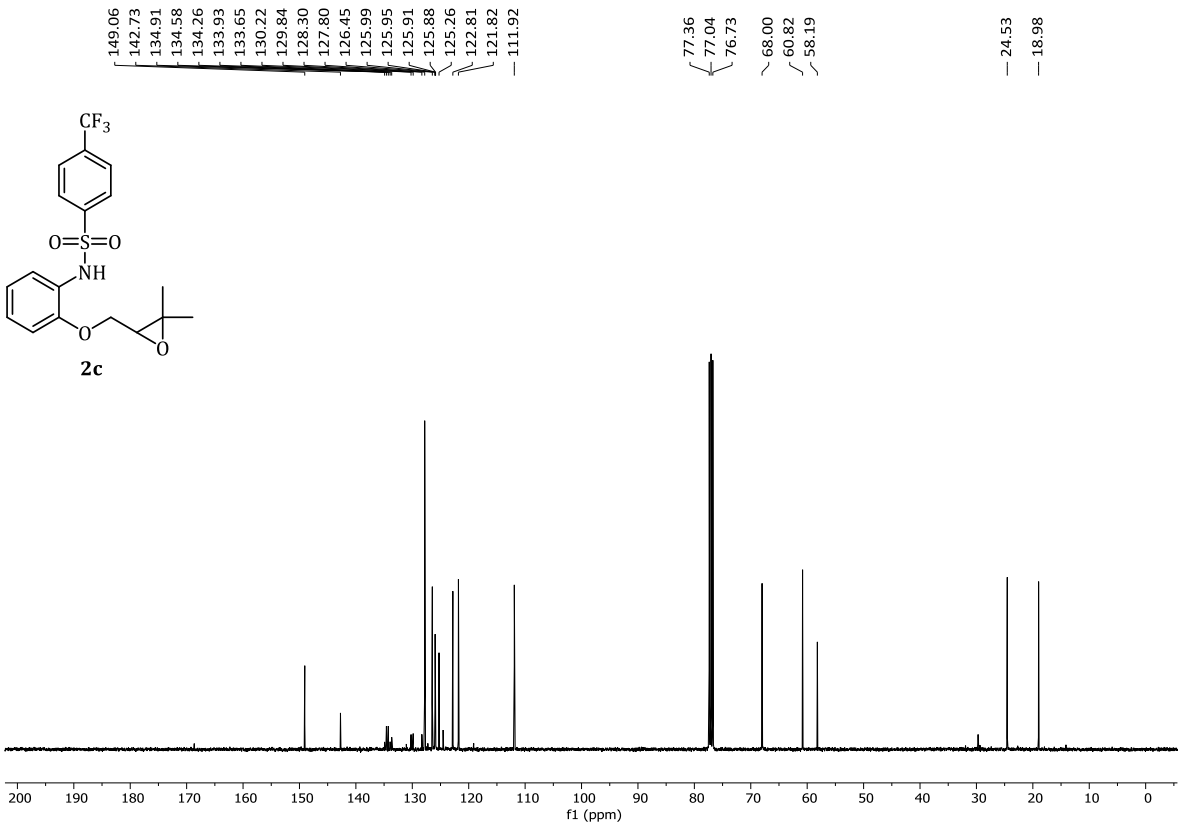
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b.**



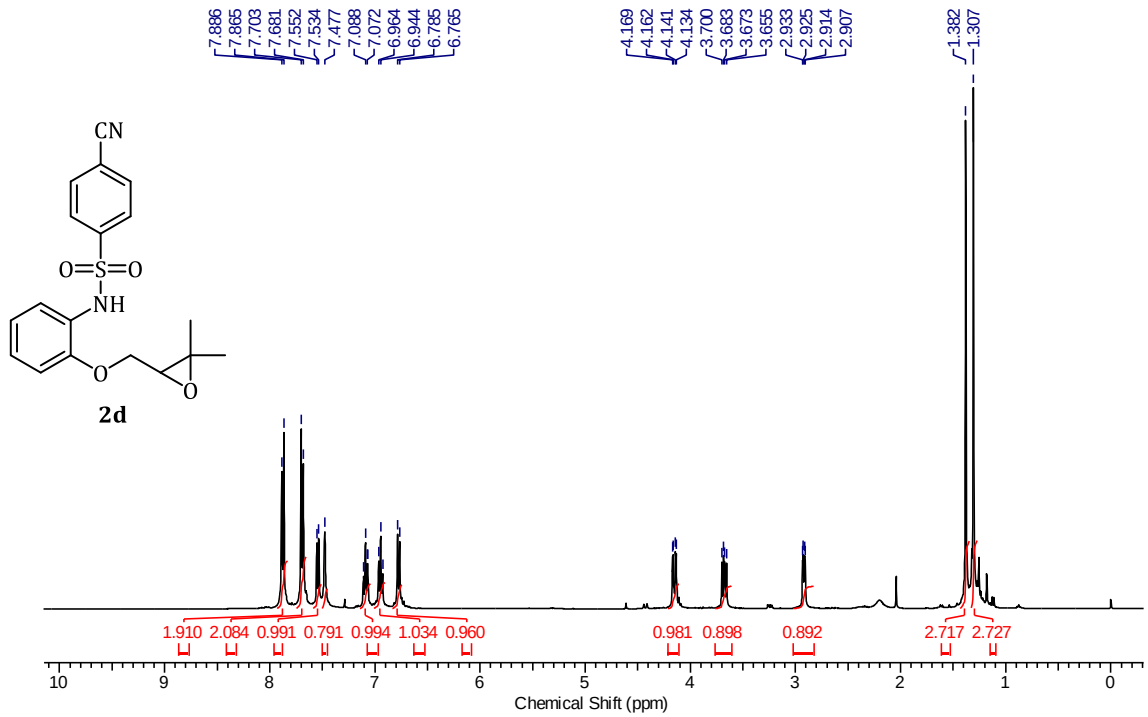
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b.**



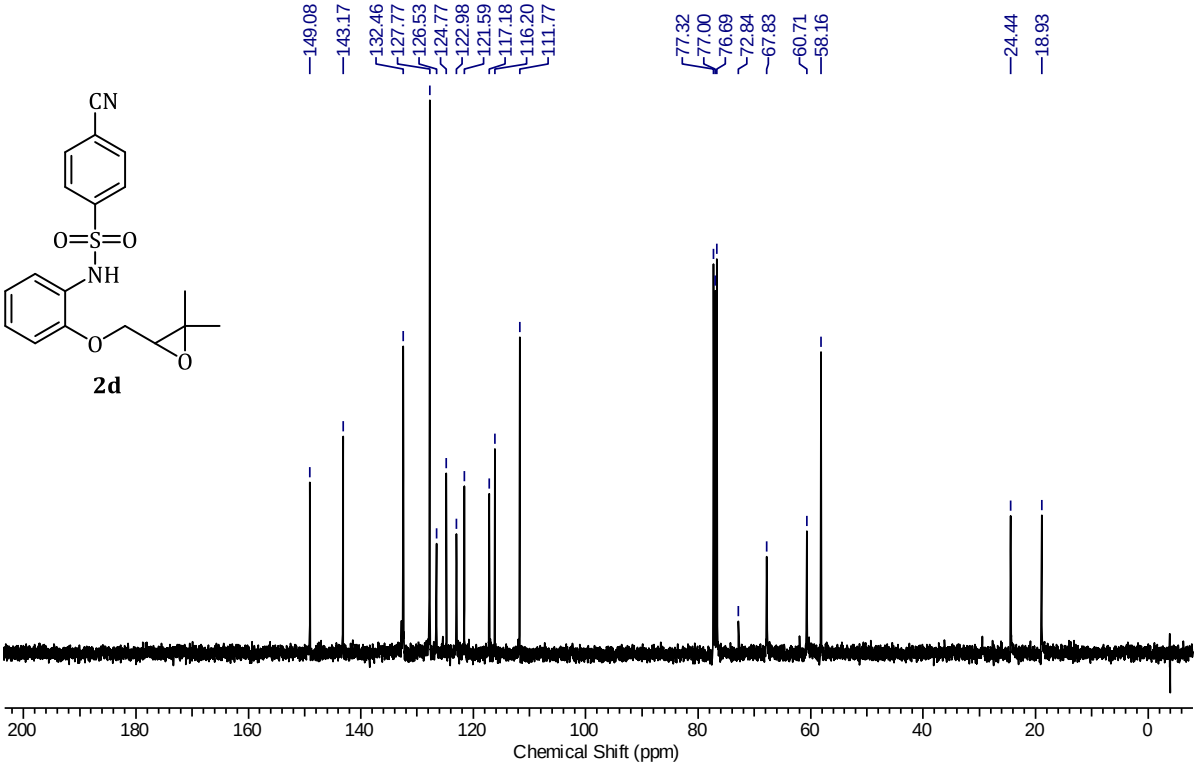
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c.**



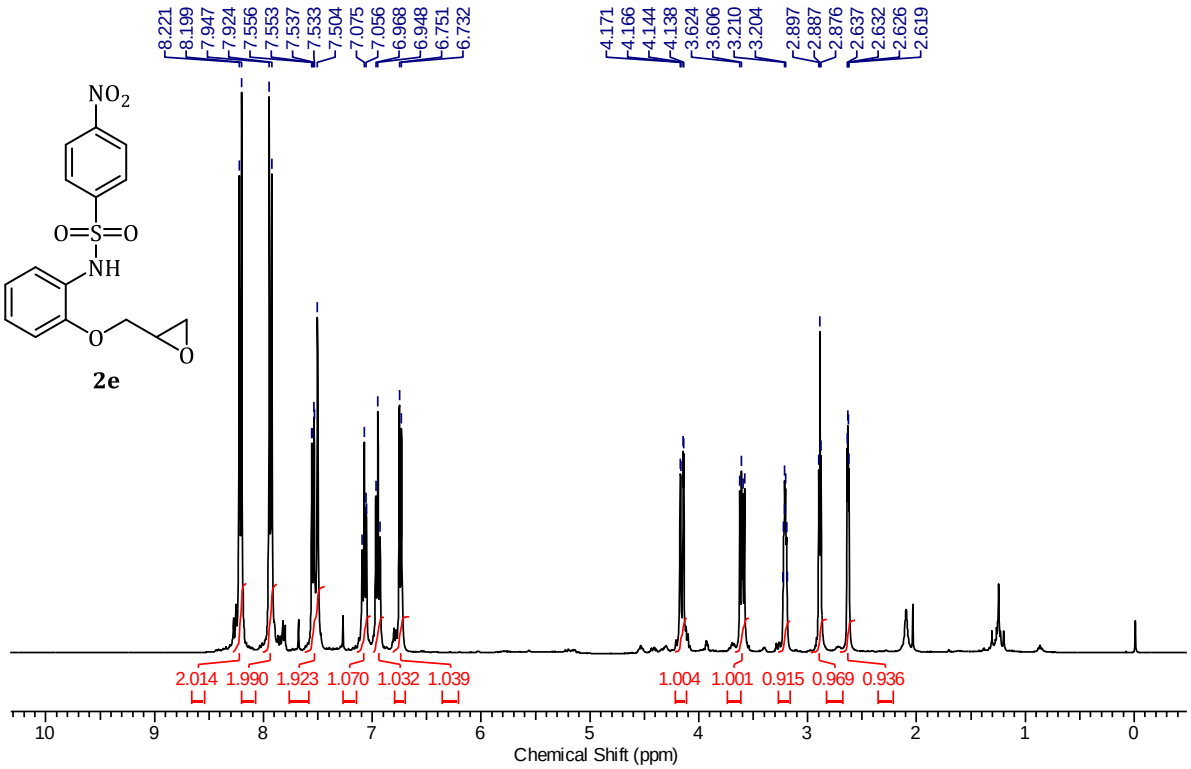
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c.**



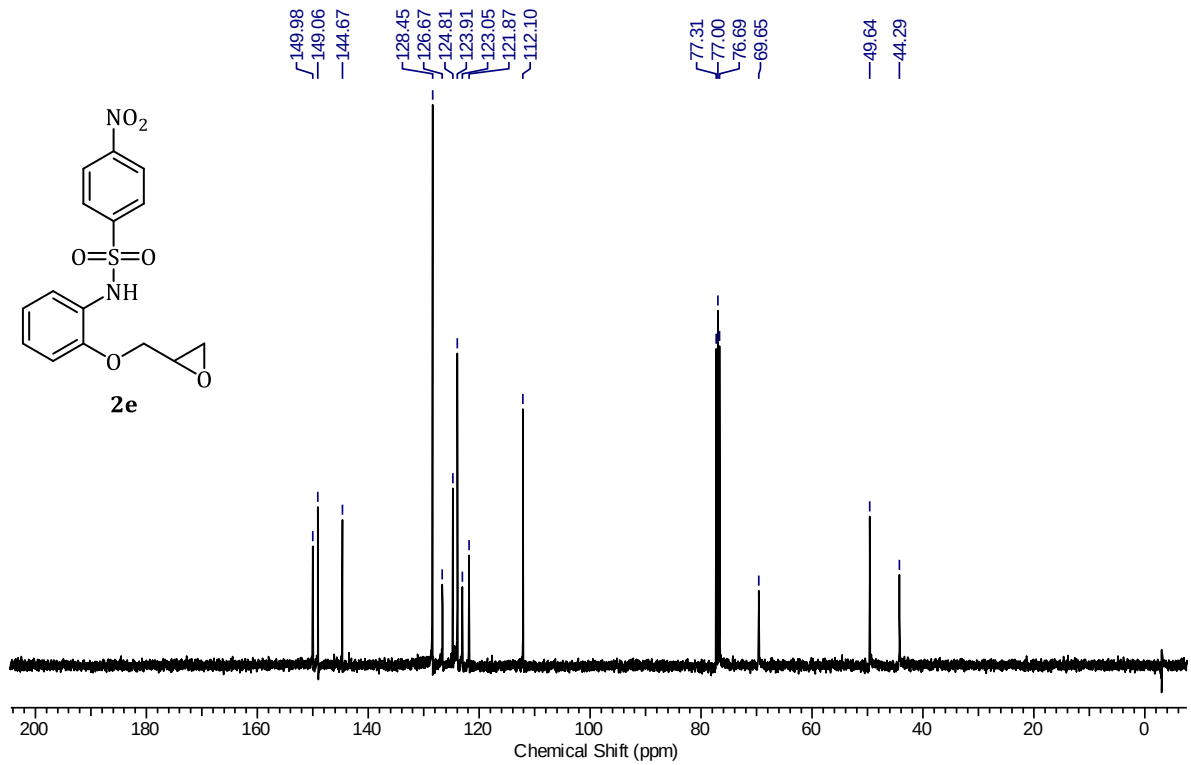
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d.**



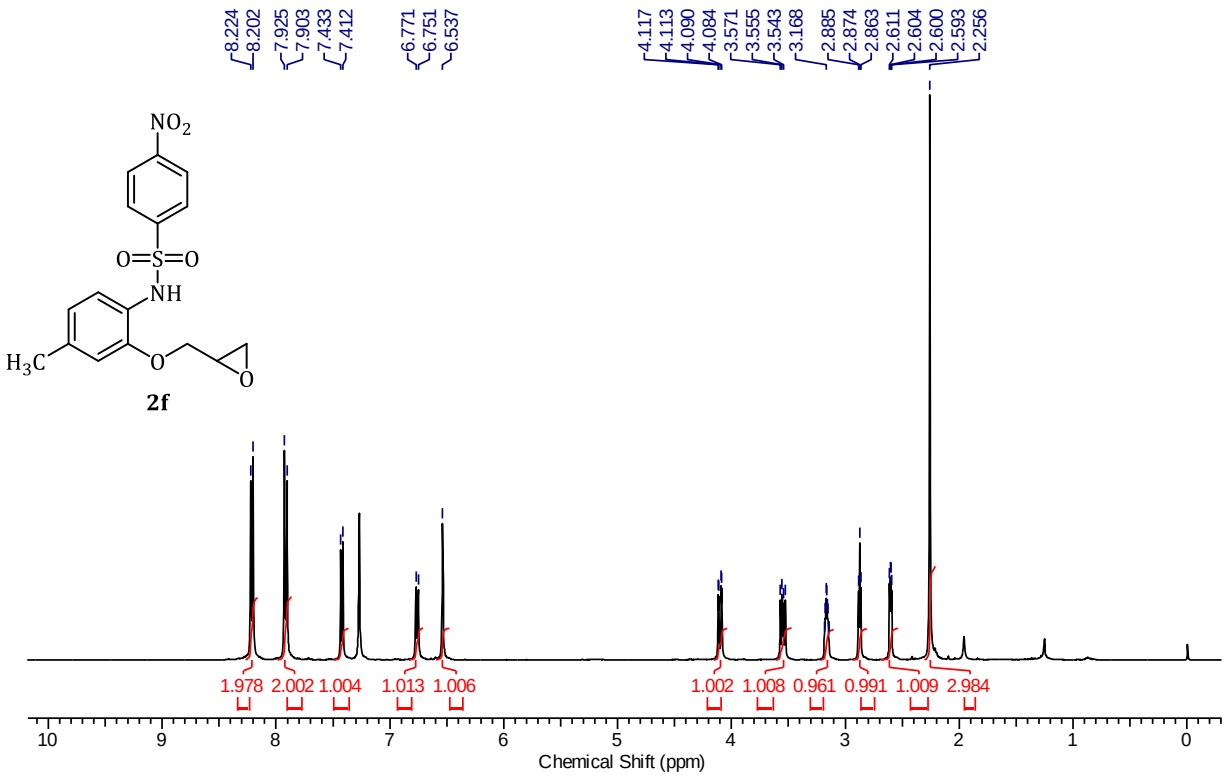
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d.**



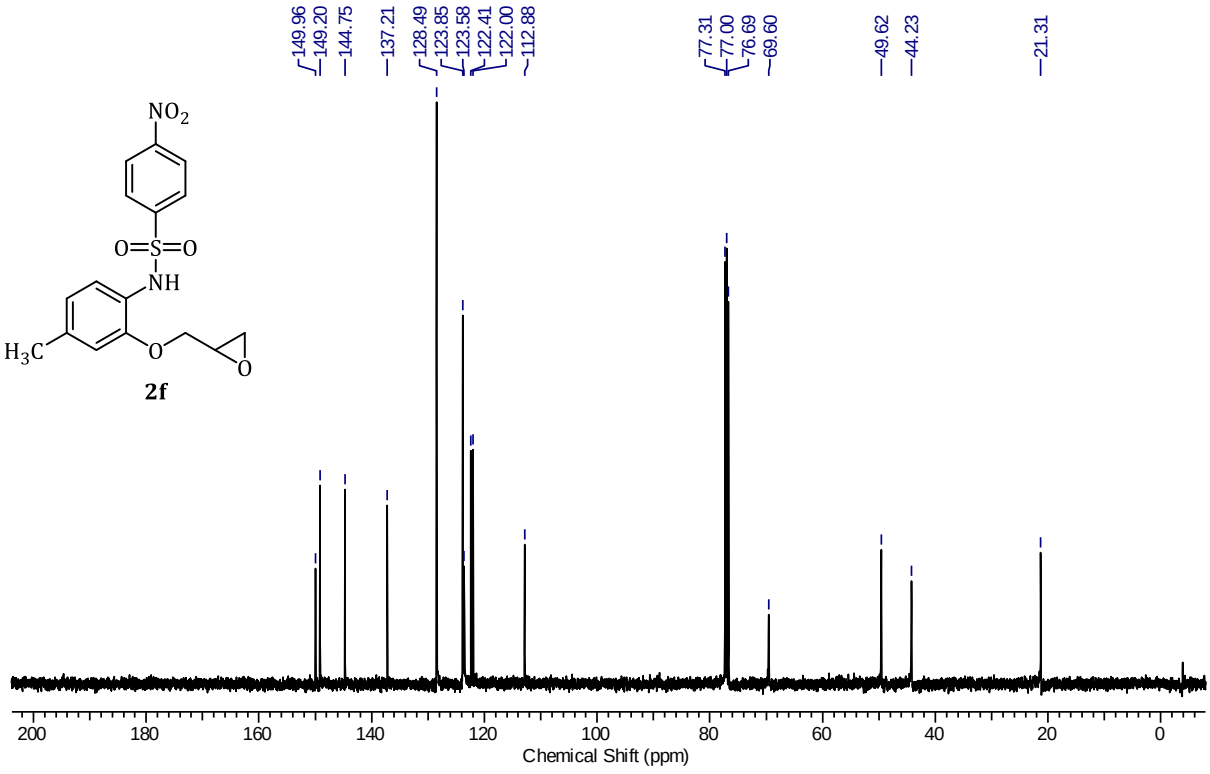
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e.**



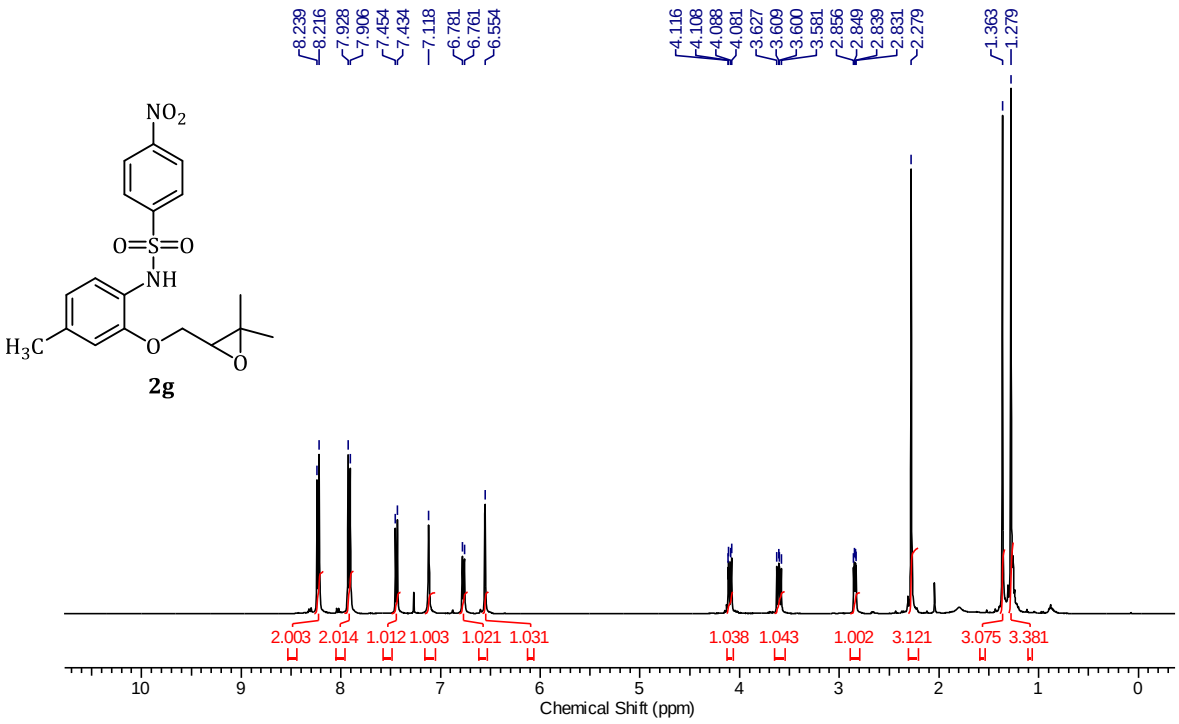
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e.**



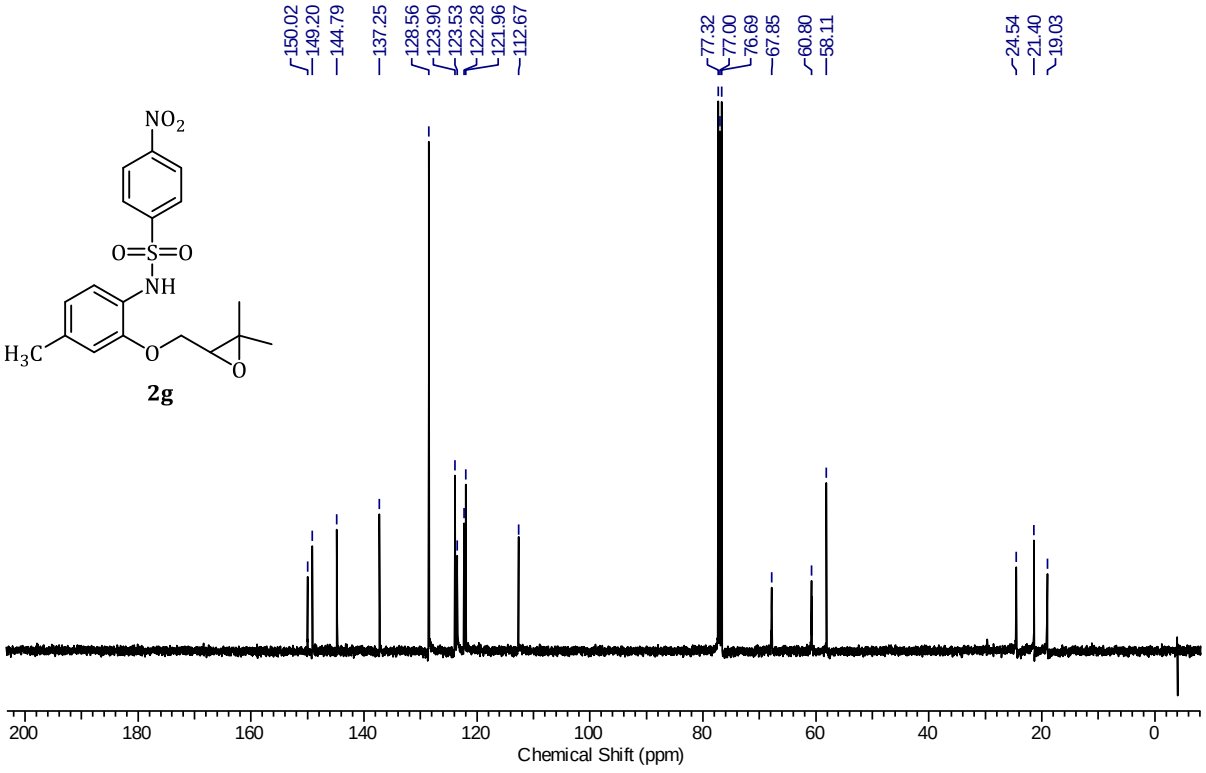
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f.**



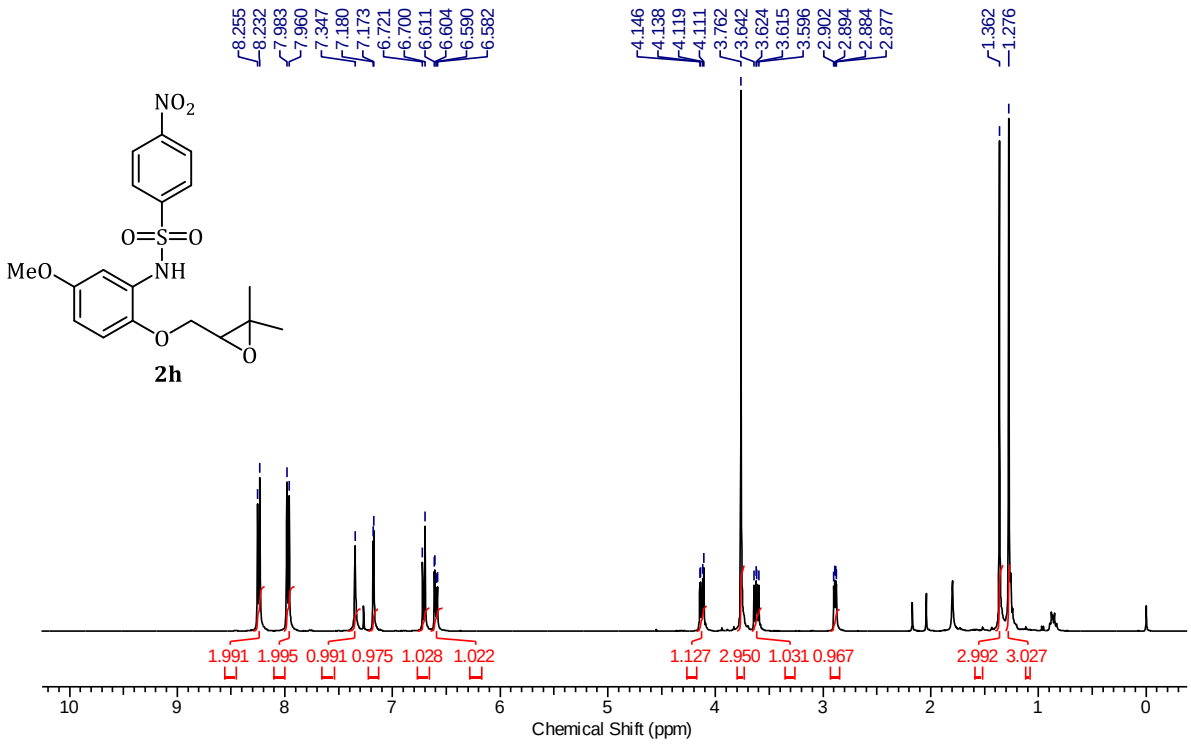
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f.**



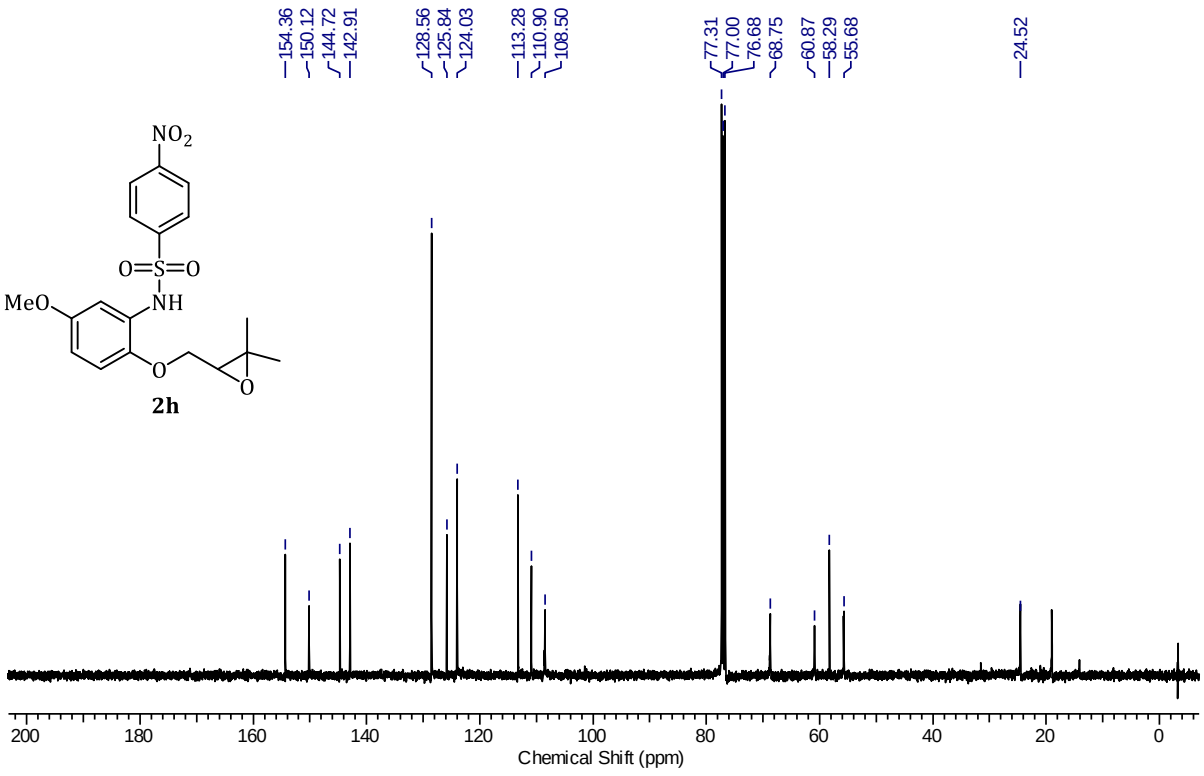
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g.**



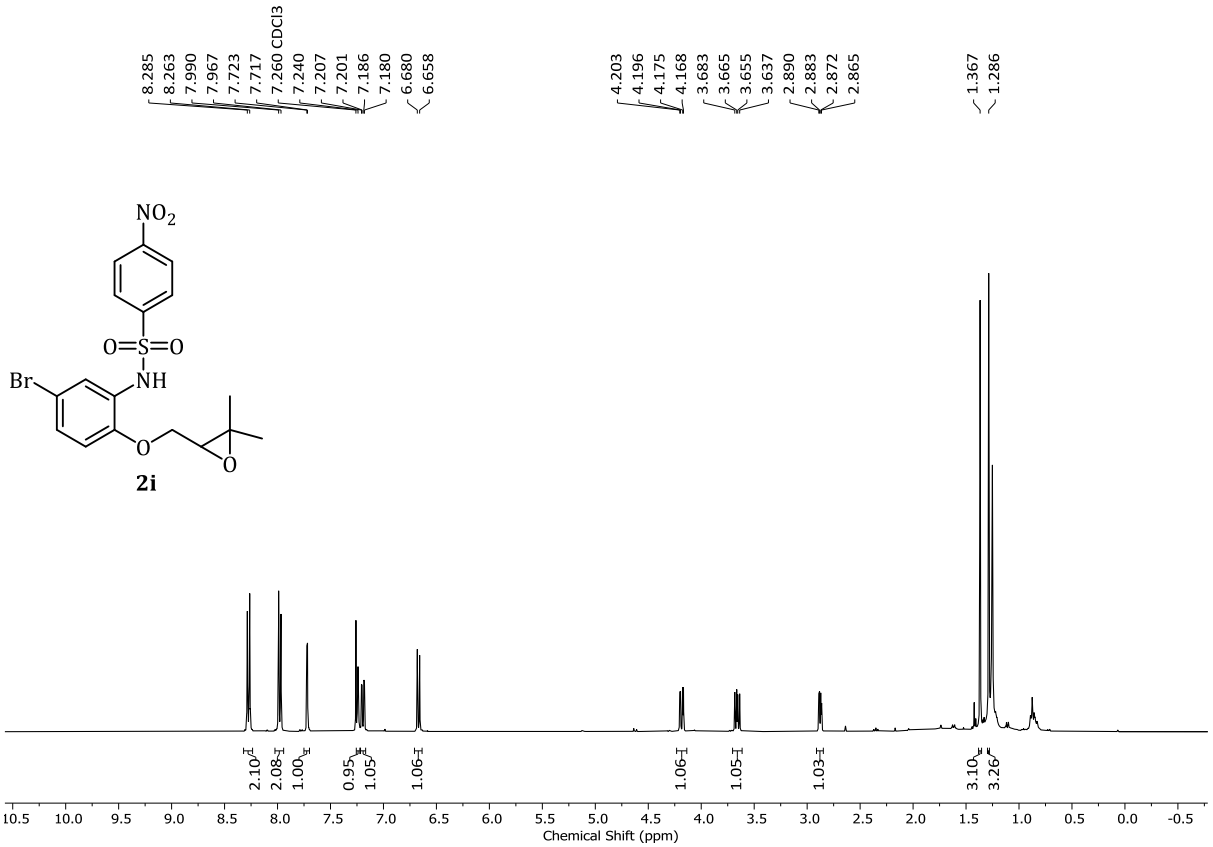
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g.**



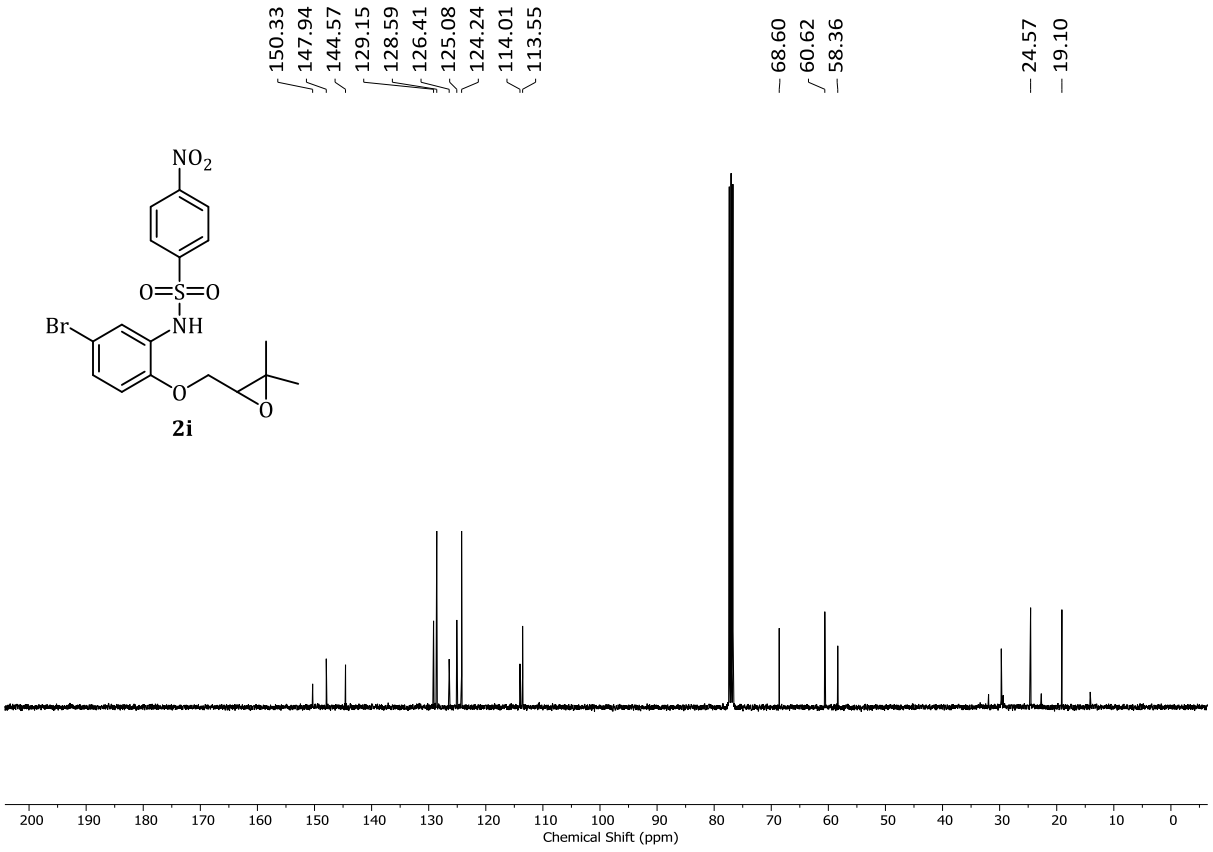
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h.**



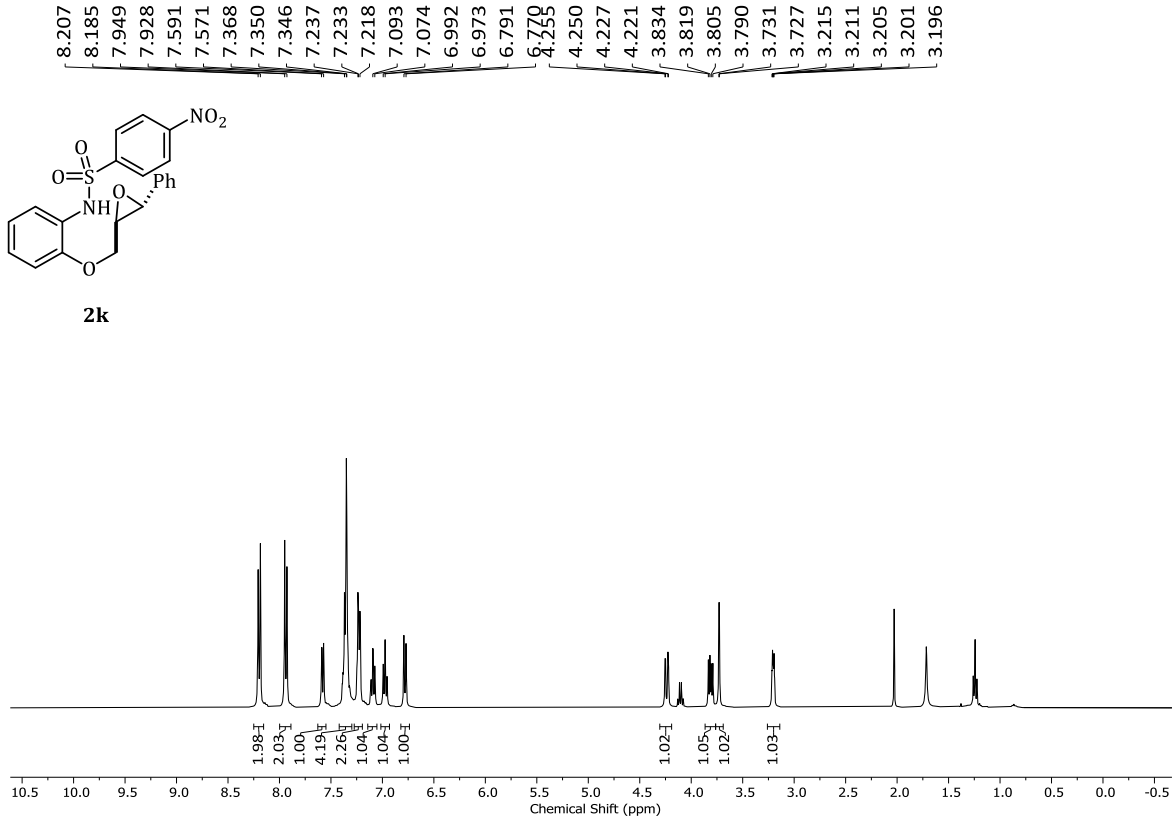
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h.**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i.**

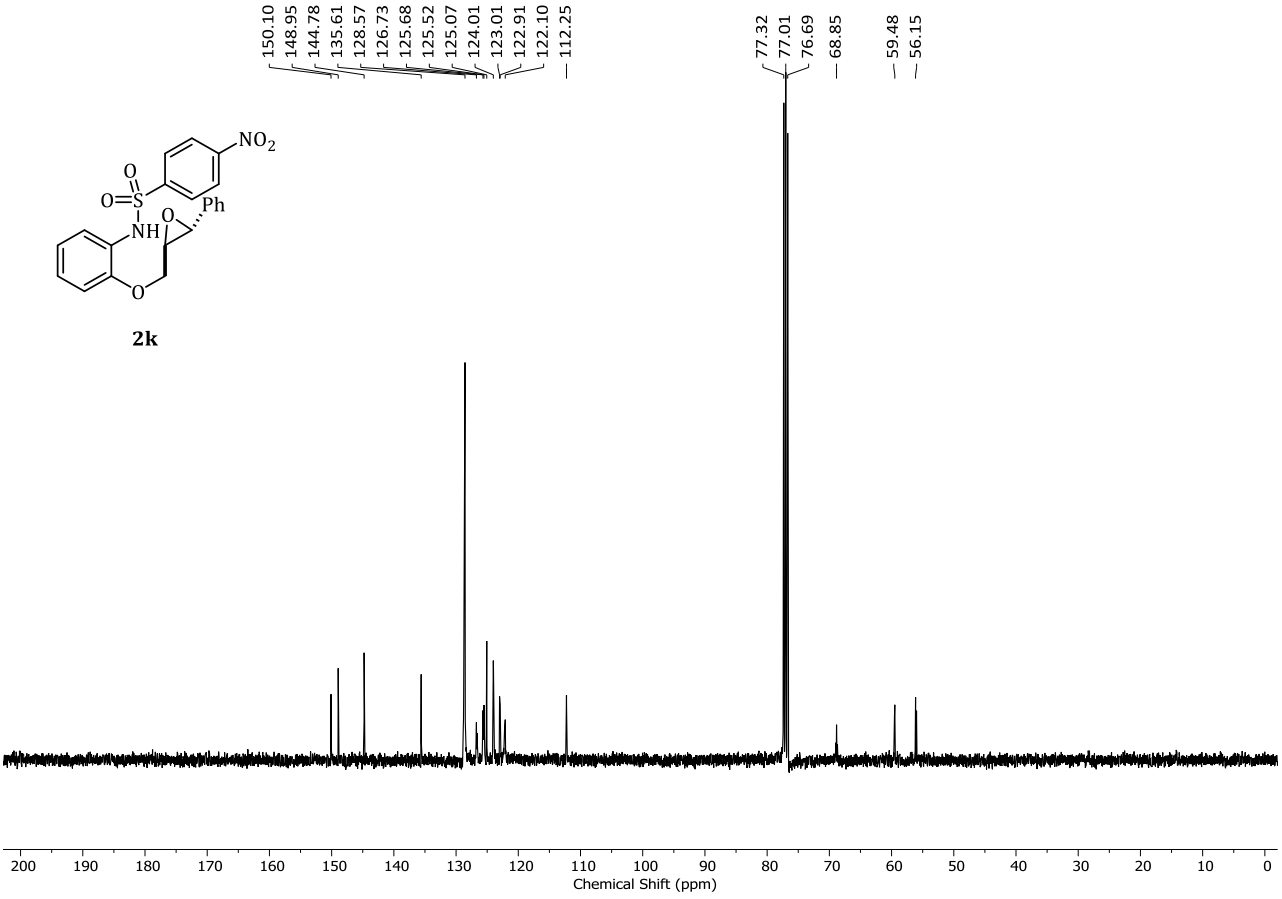


^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



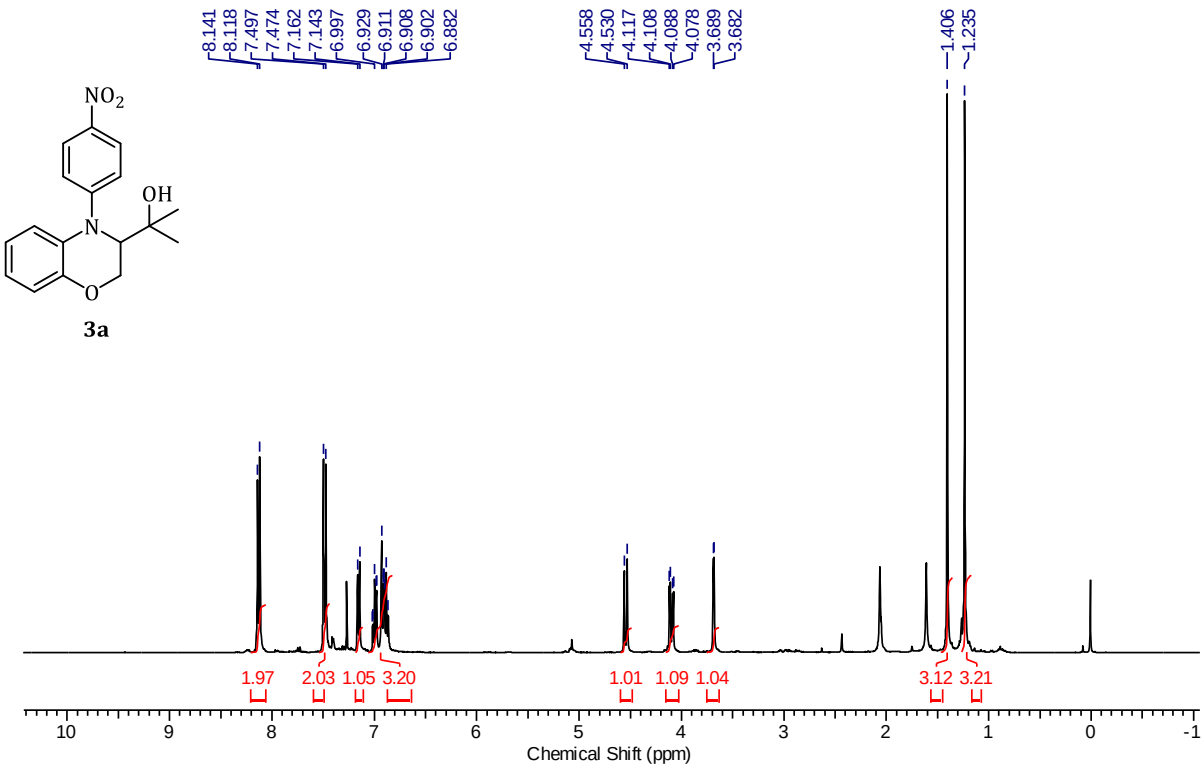
2k

^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k.**

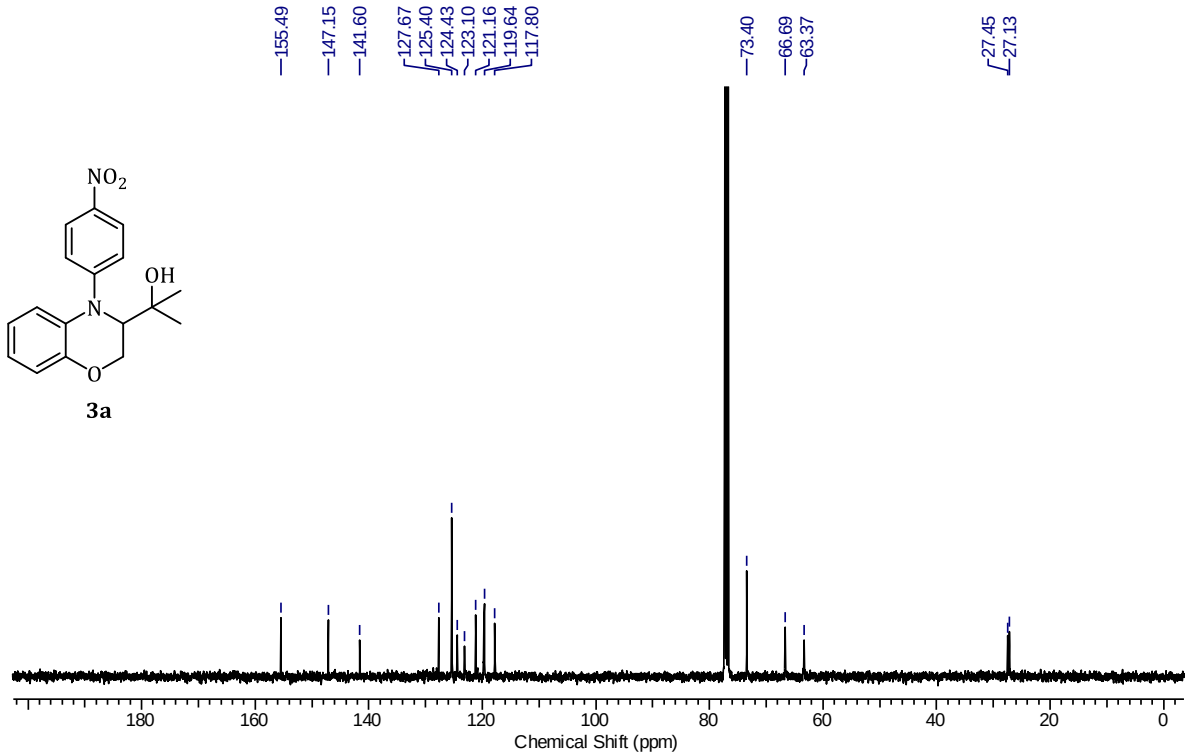


2k

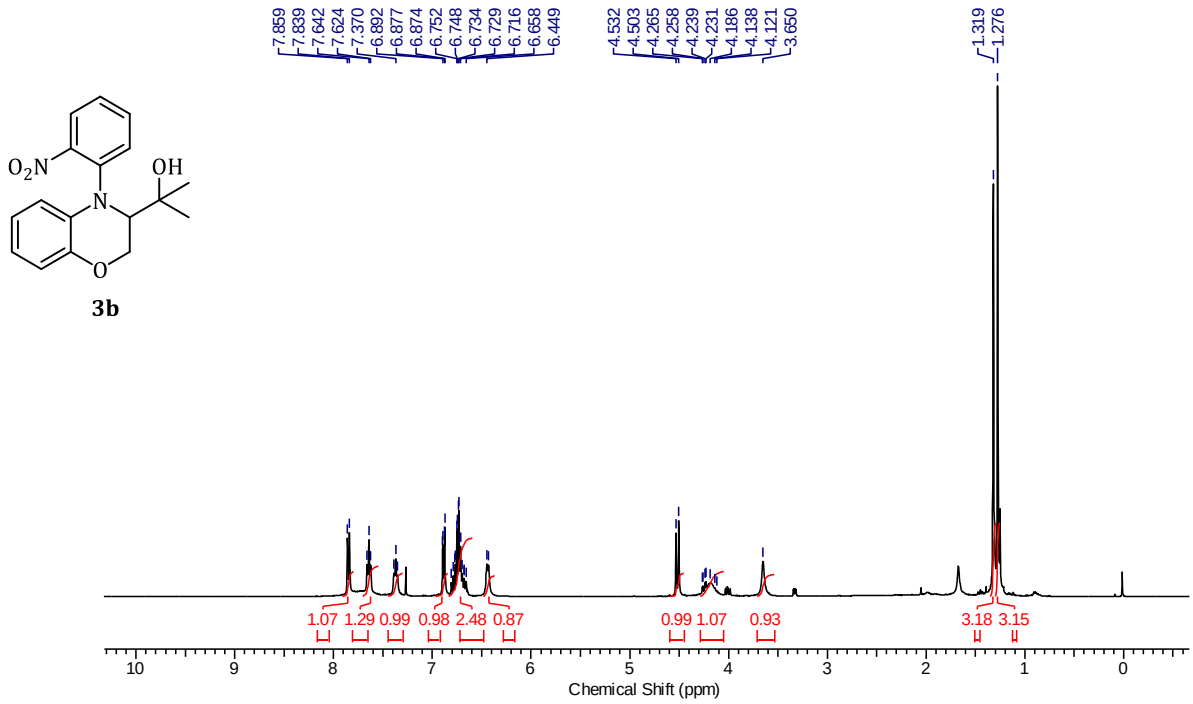
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2k**.



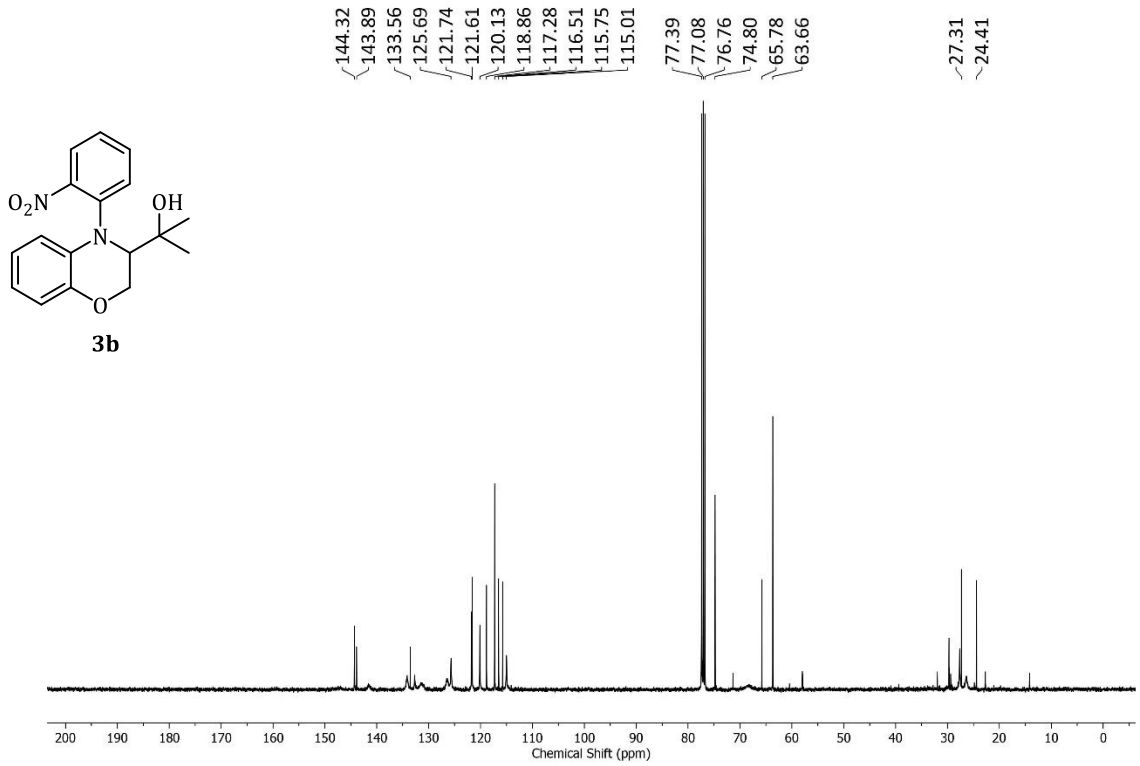
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.



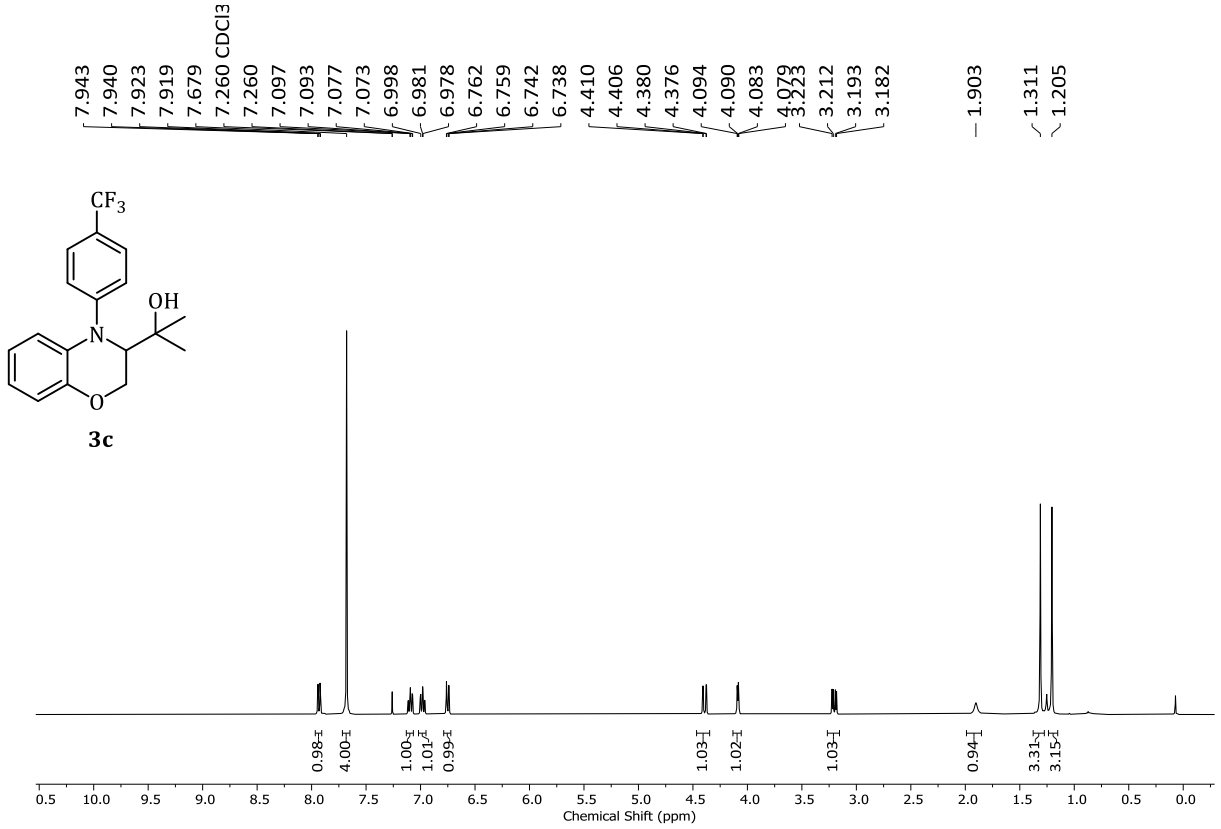
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**.



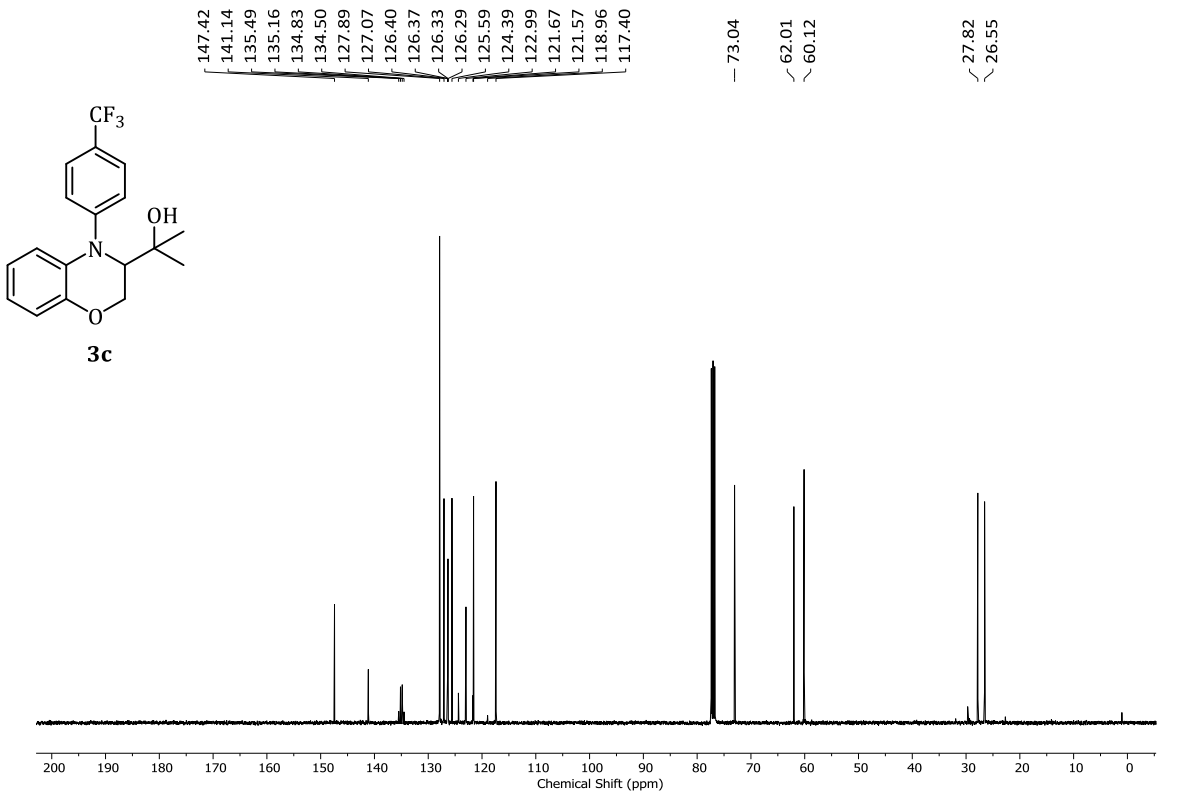
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.



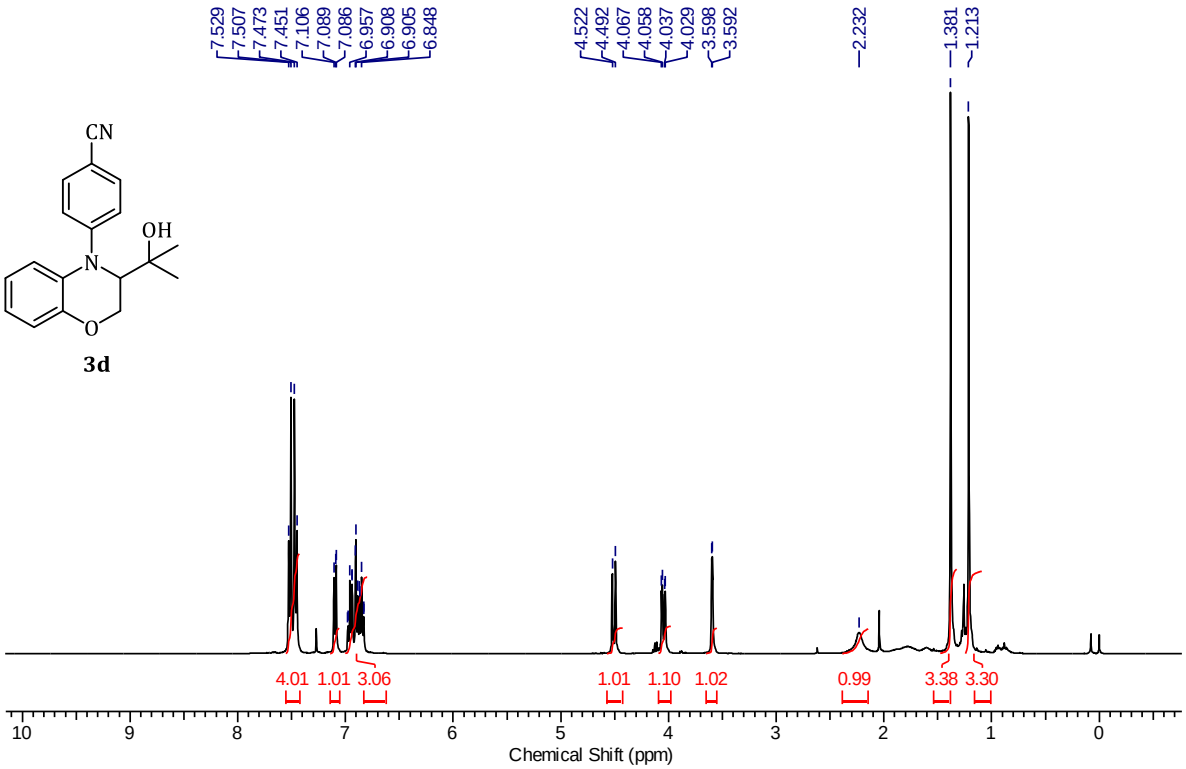
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**.



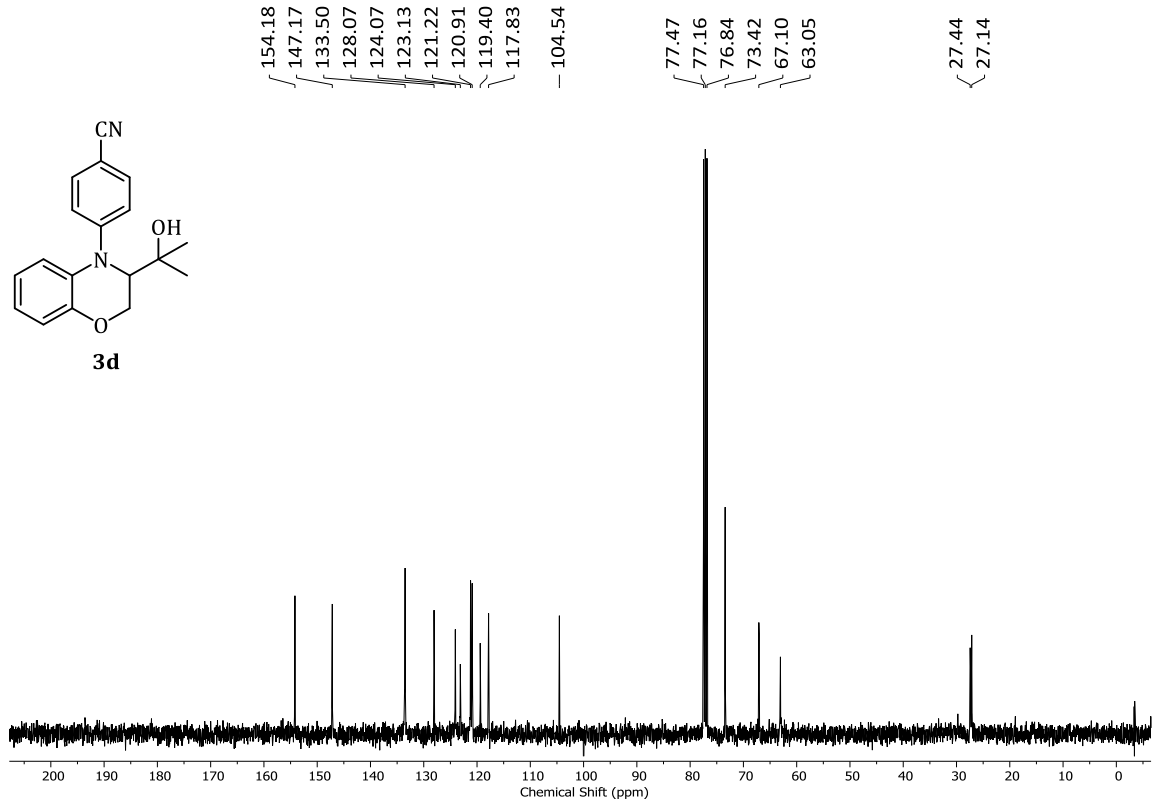
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**.



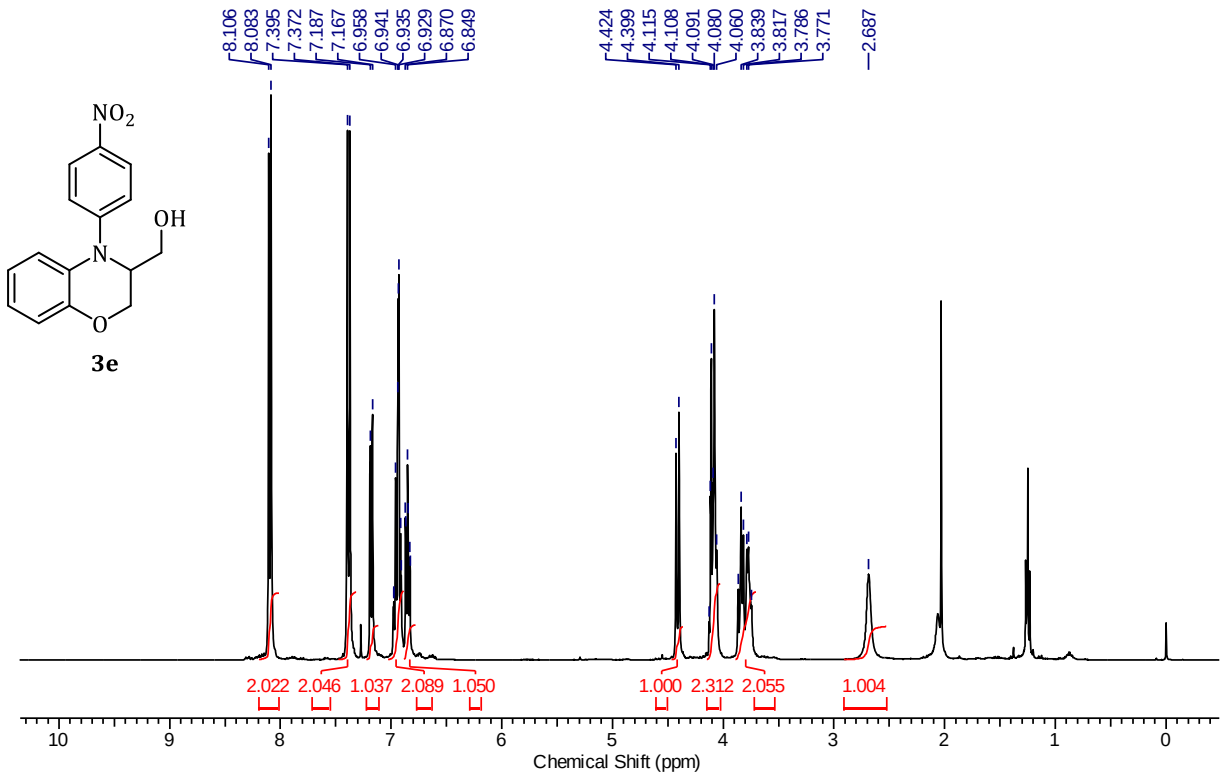
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**.



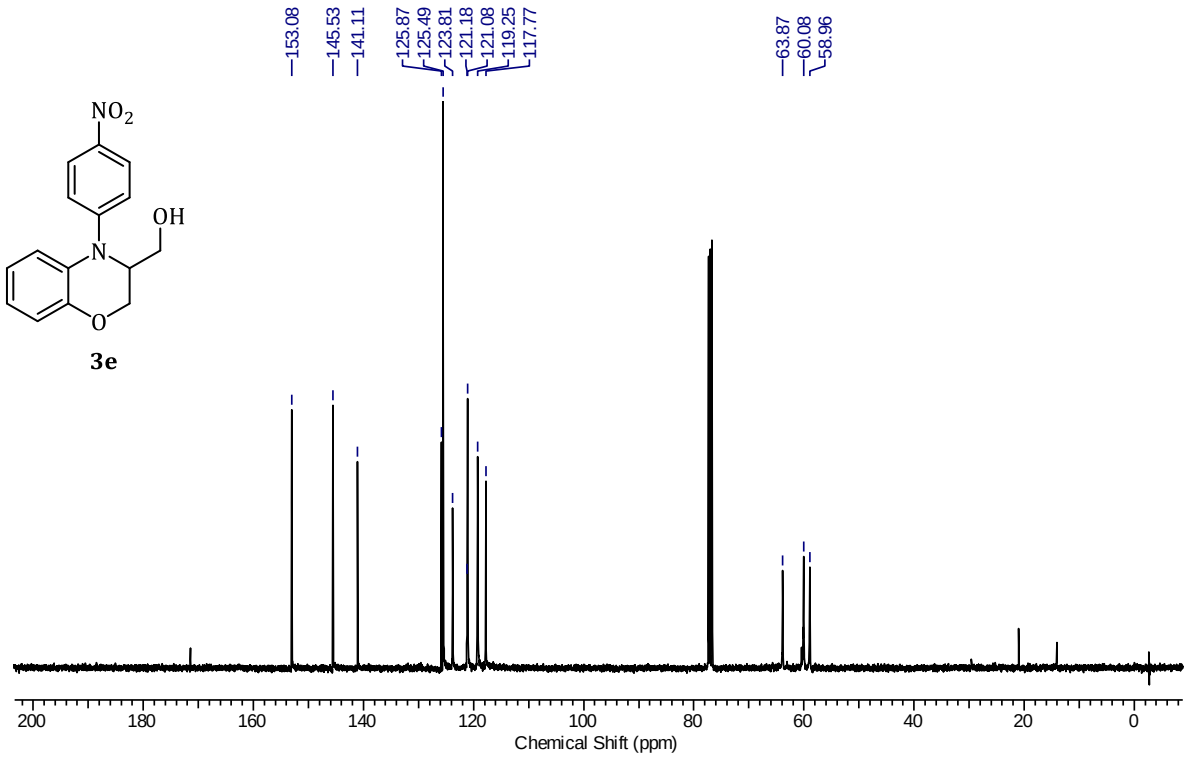
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**.



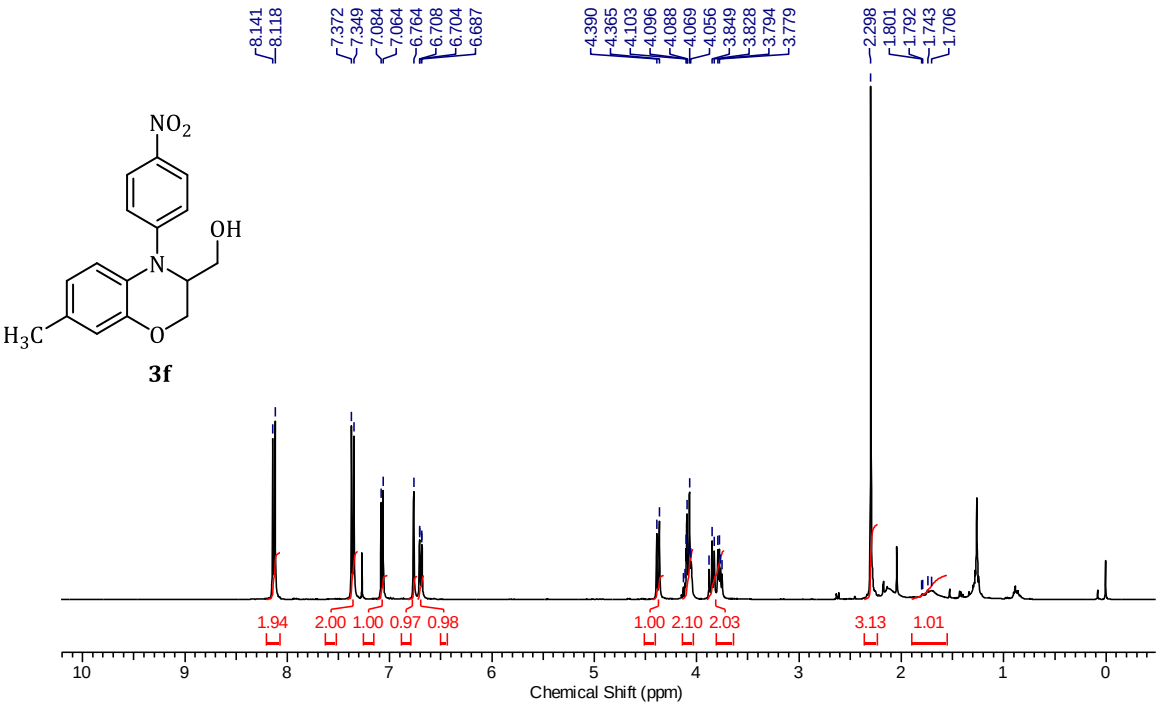
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**.



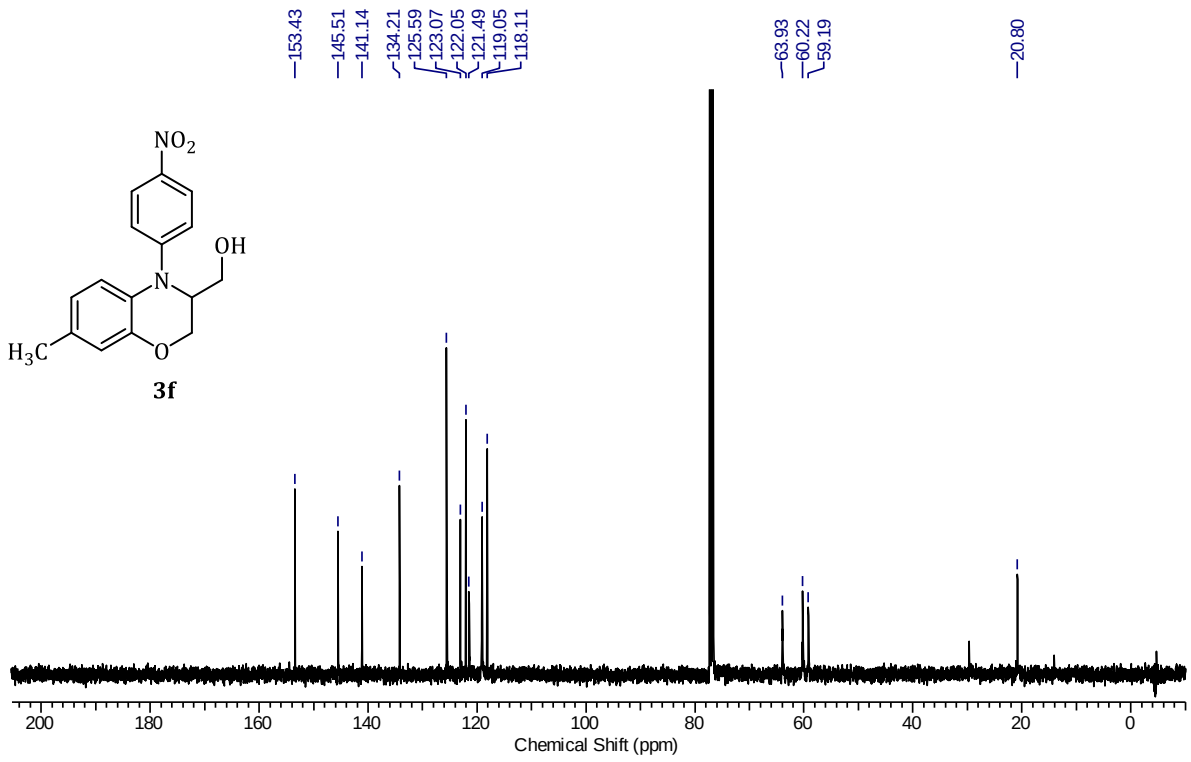
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**.



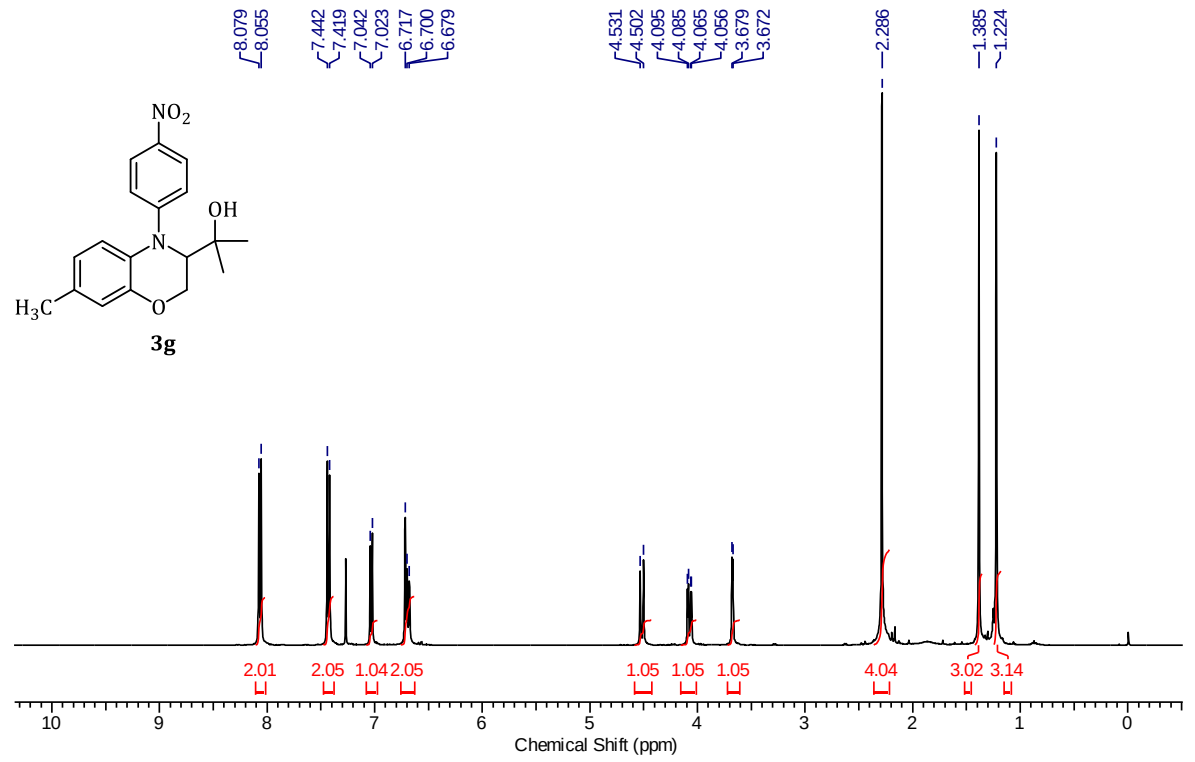
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e.**



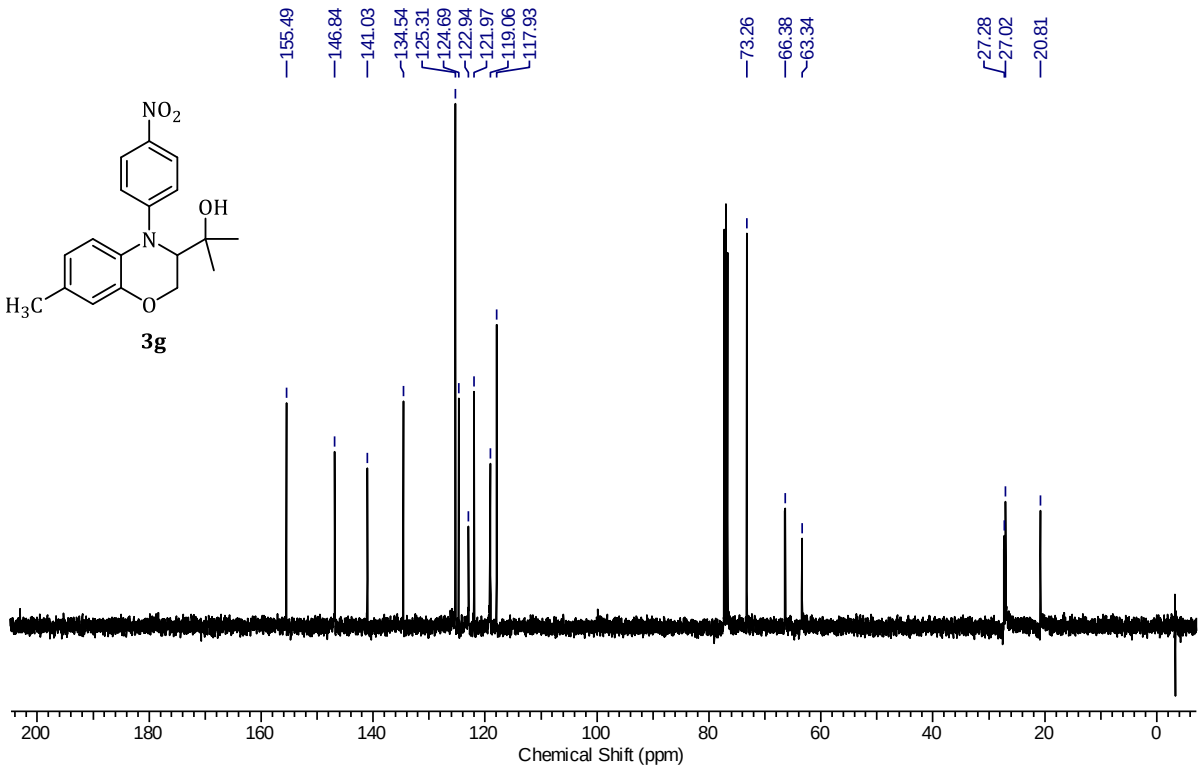
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f.**



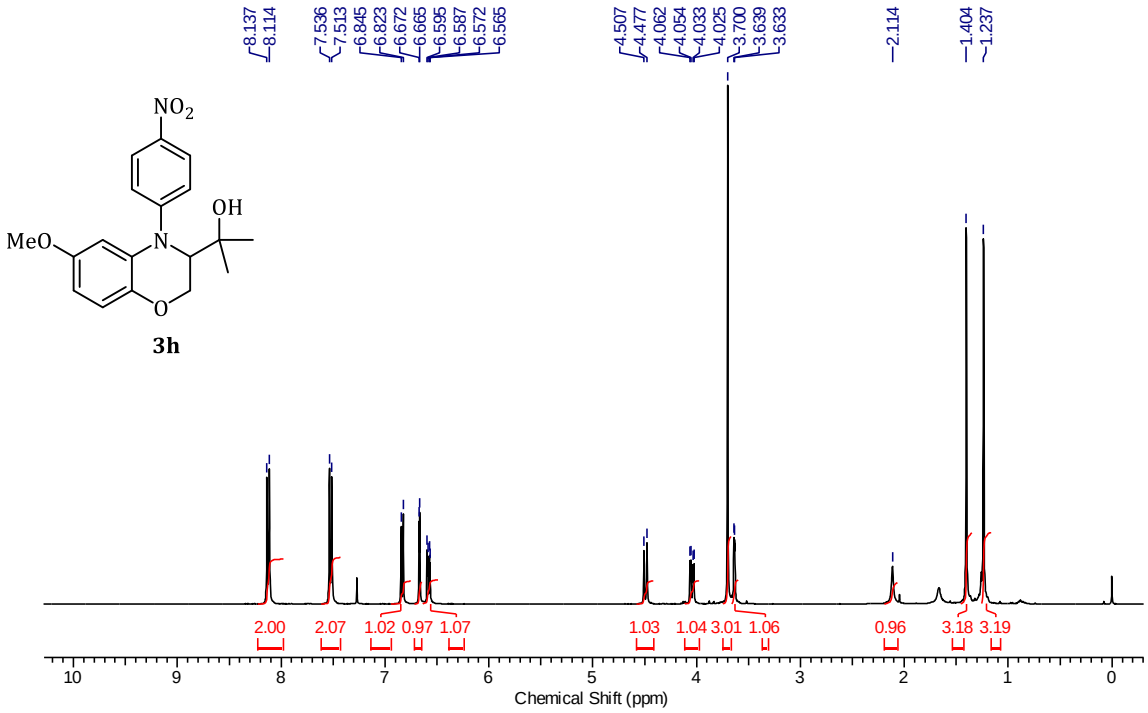
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f.**



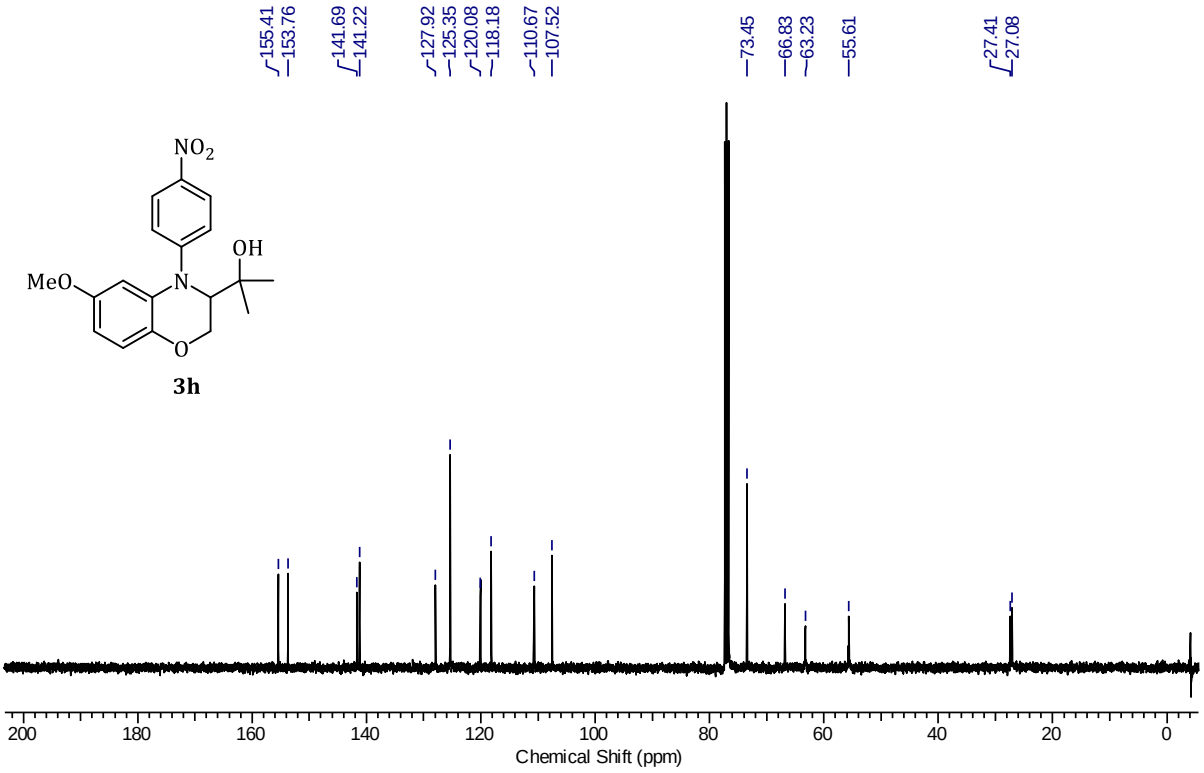
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g.**



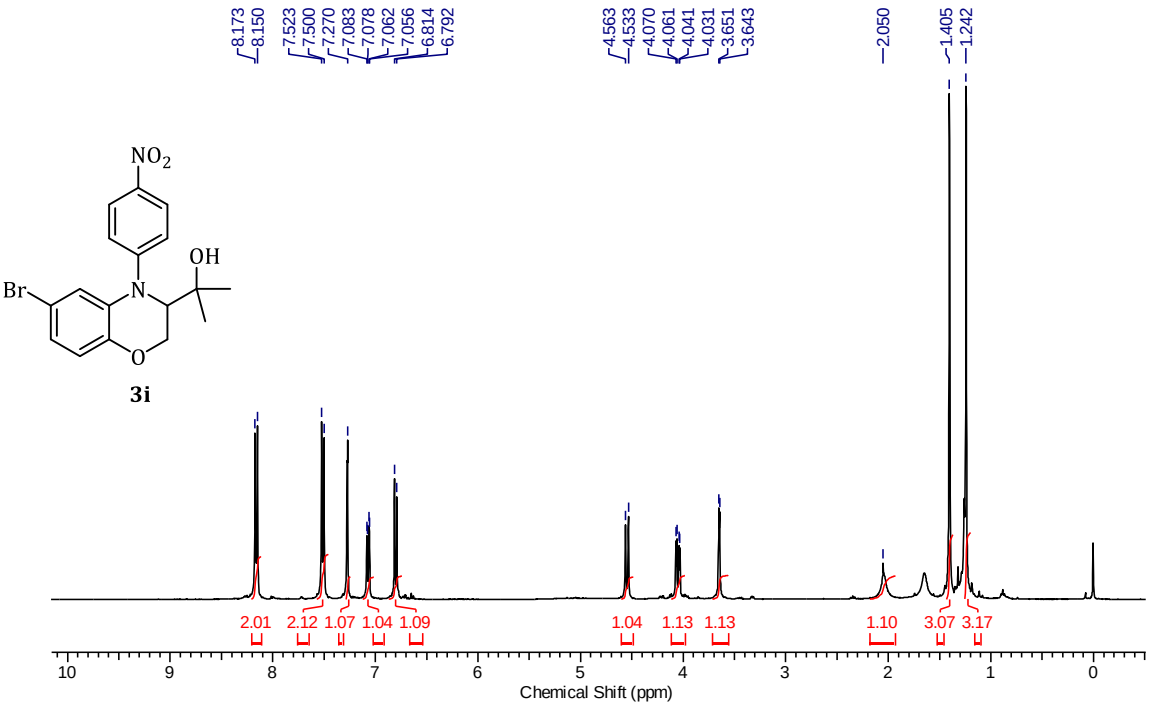
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g.**



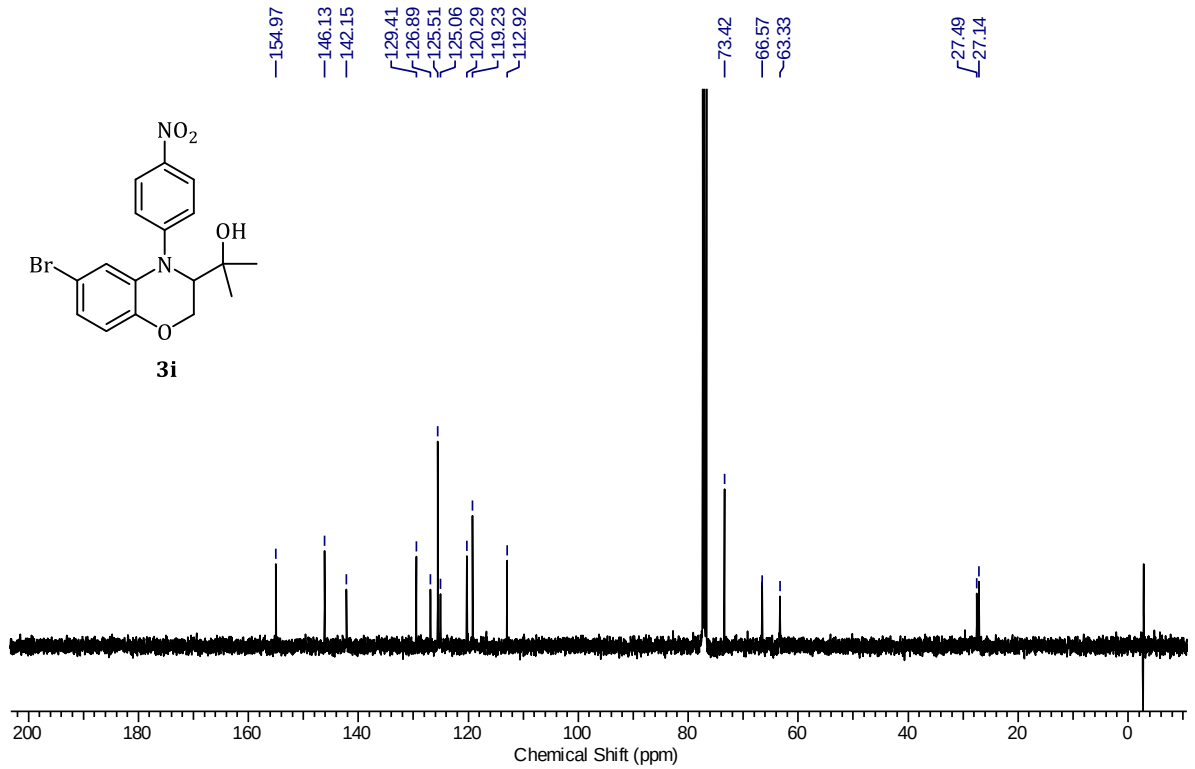
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h.**



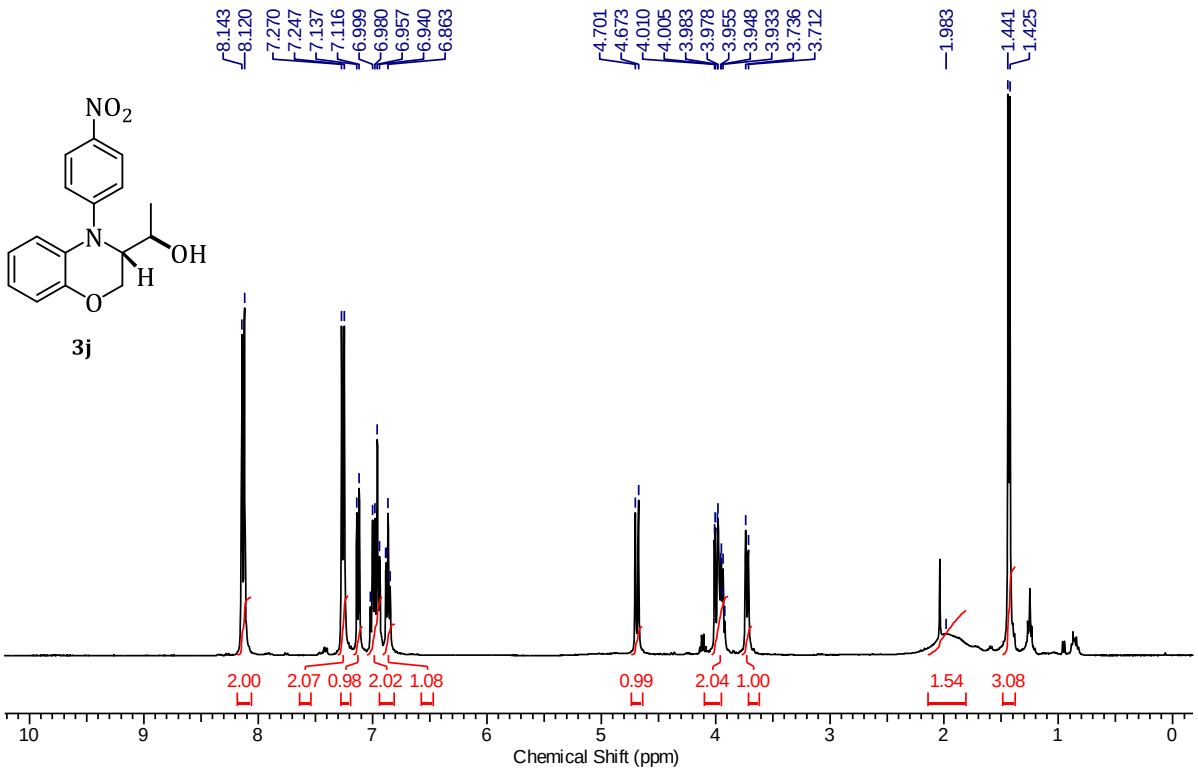
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h.**



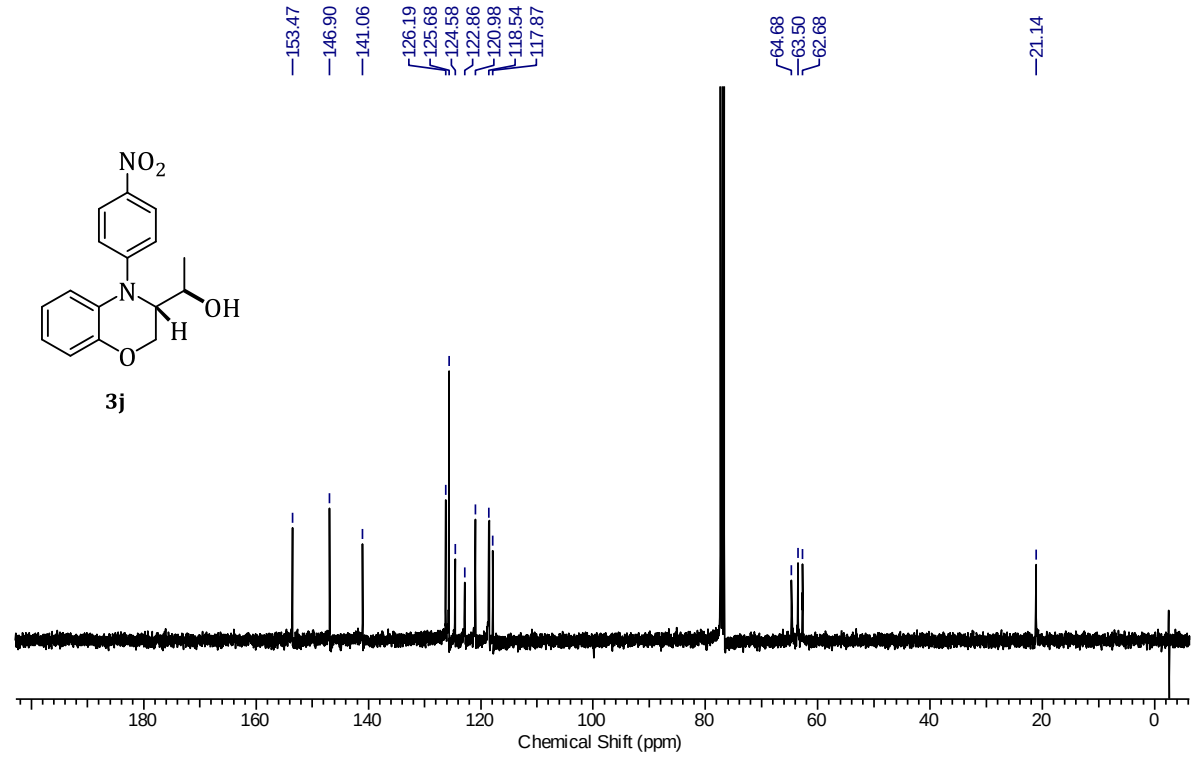
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i.**



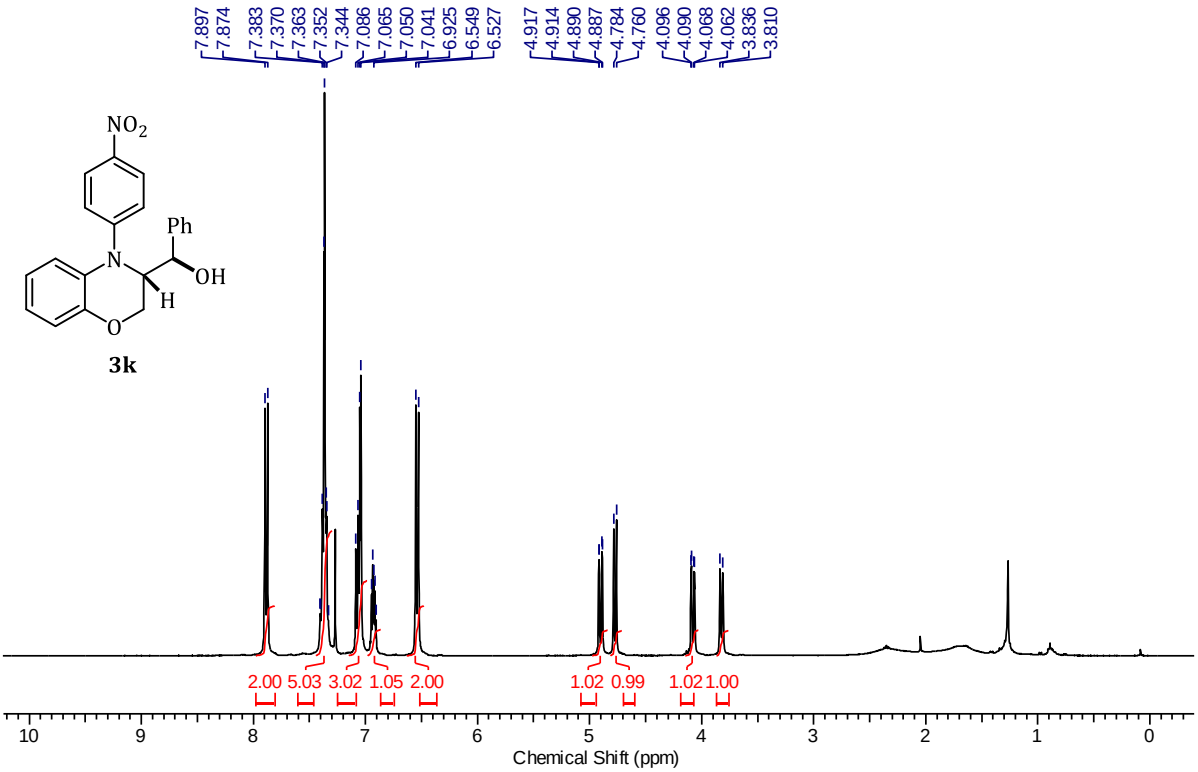
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i.**



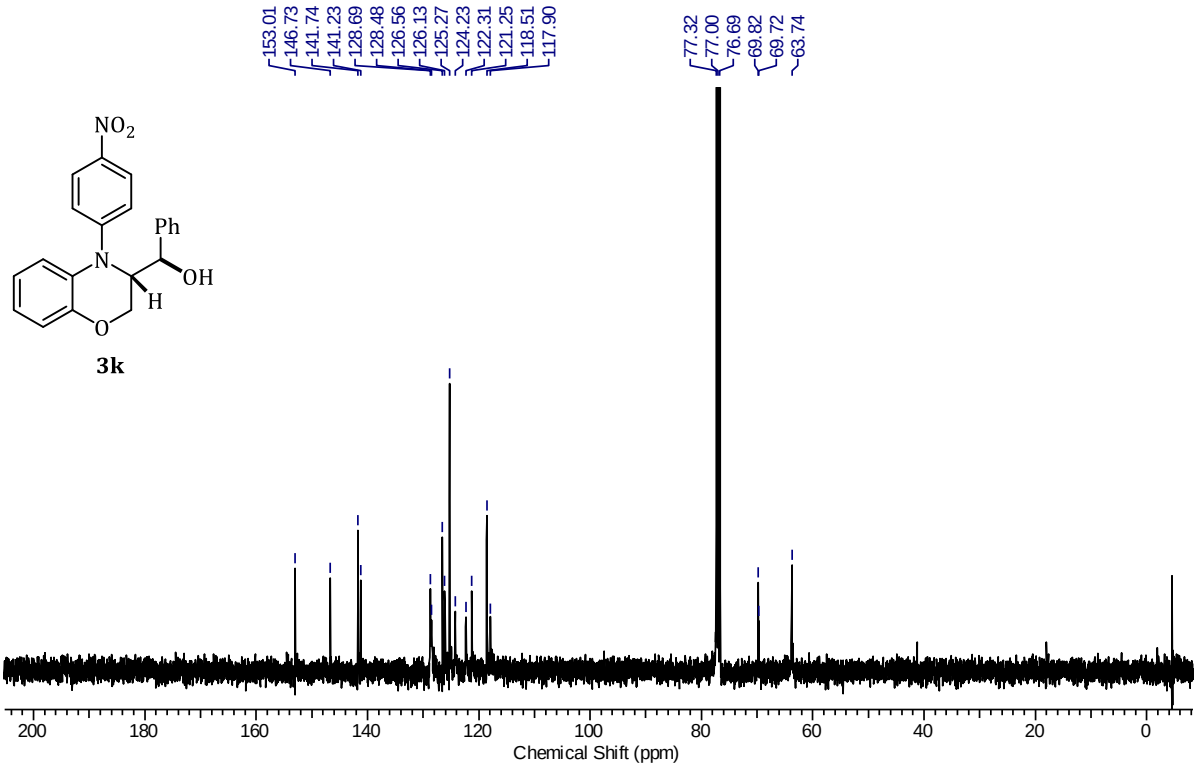
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j.**



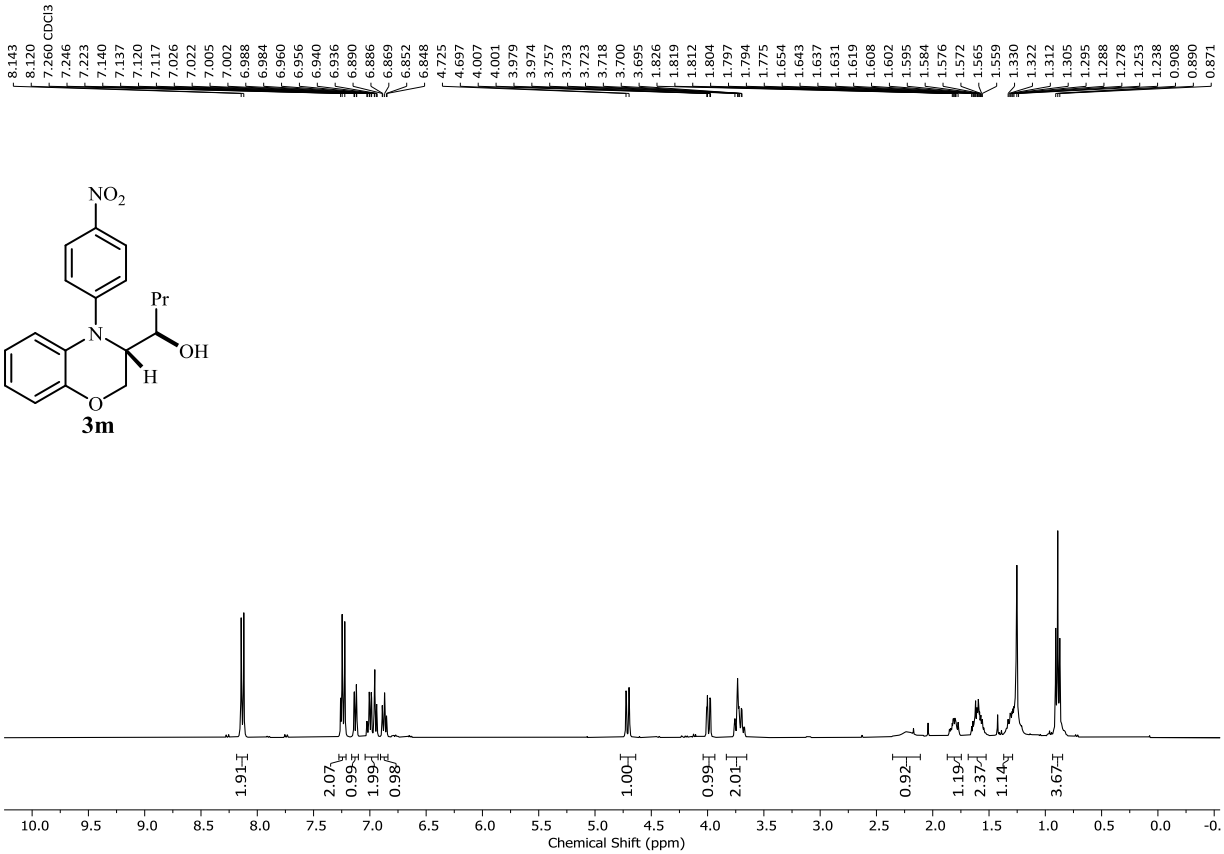
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j.**



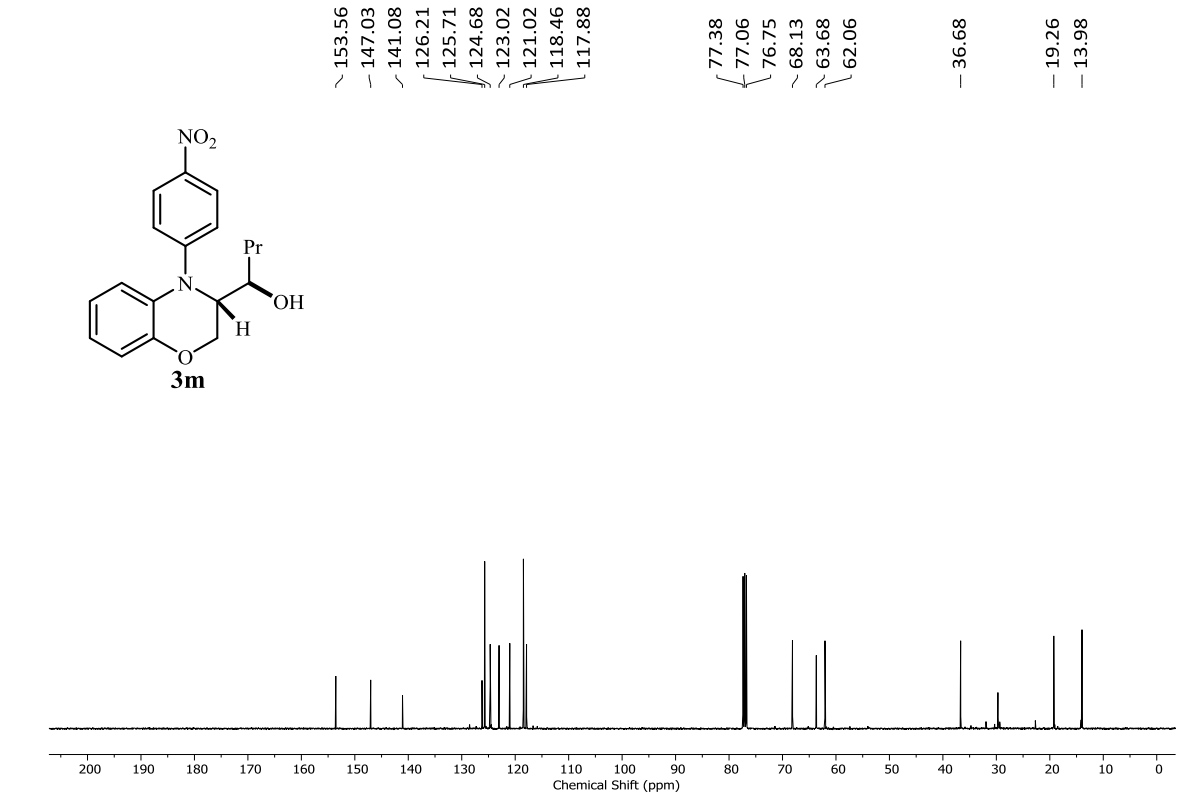
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k.**



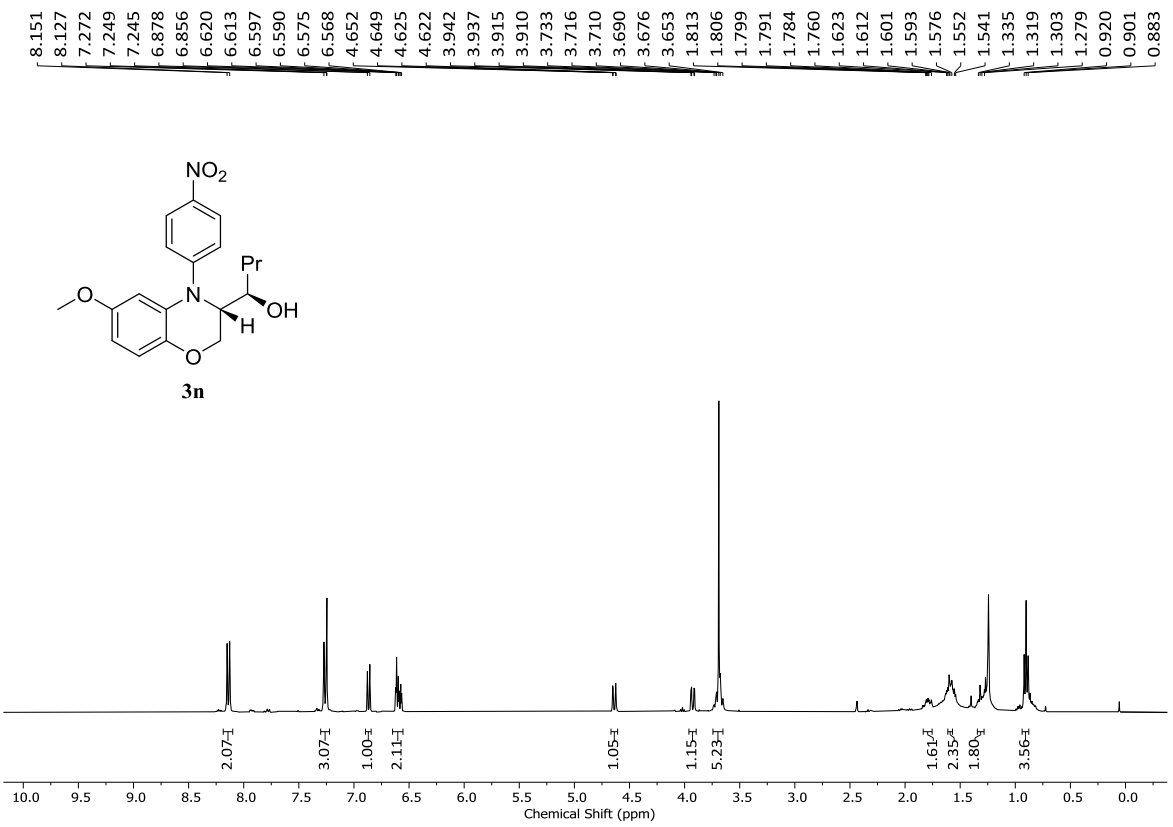
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k.**



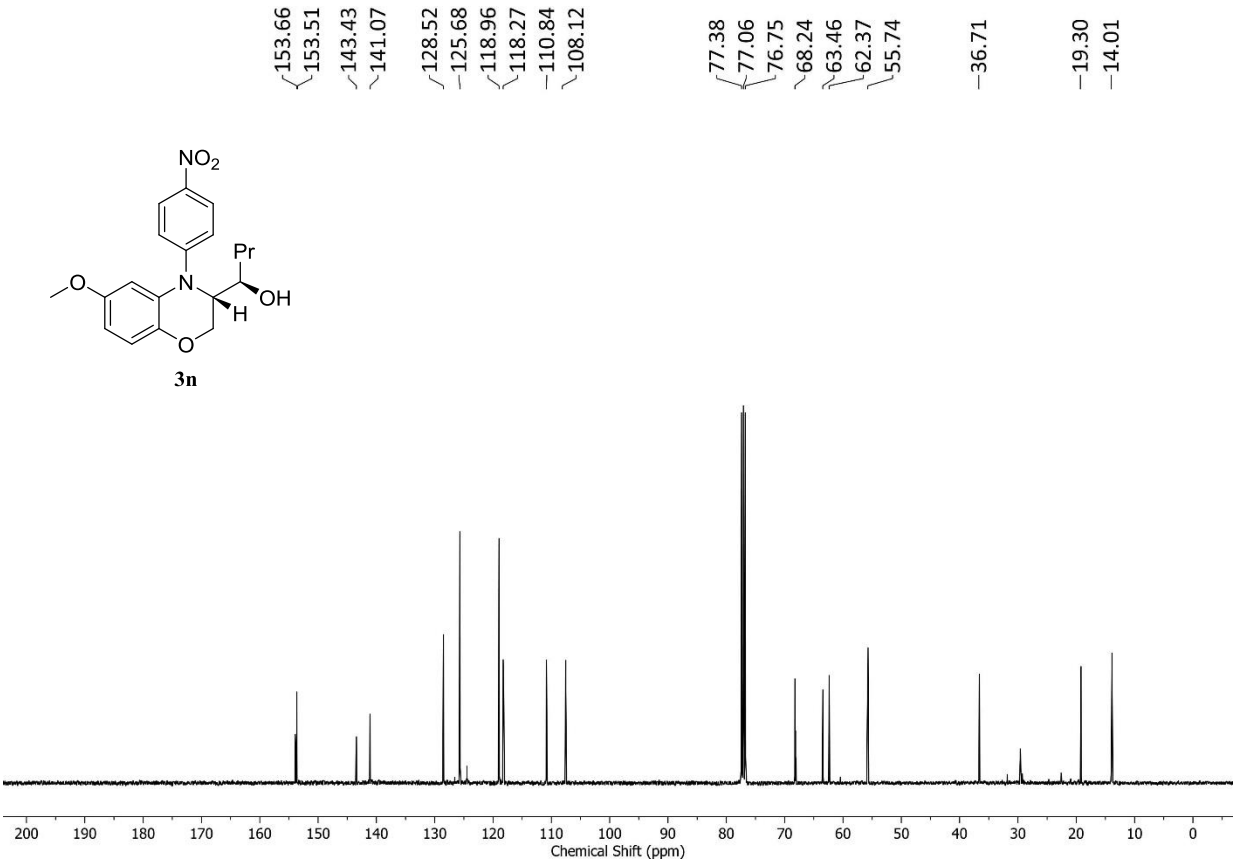
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**



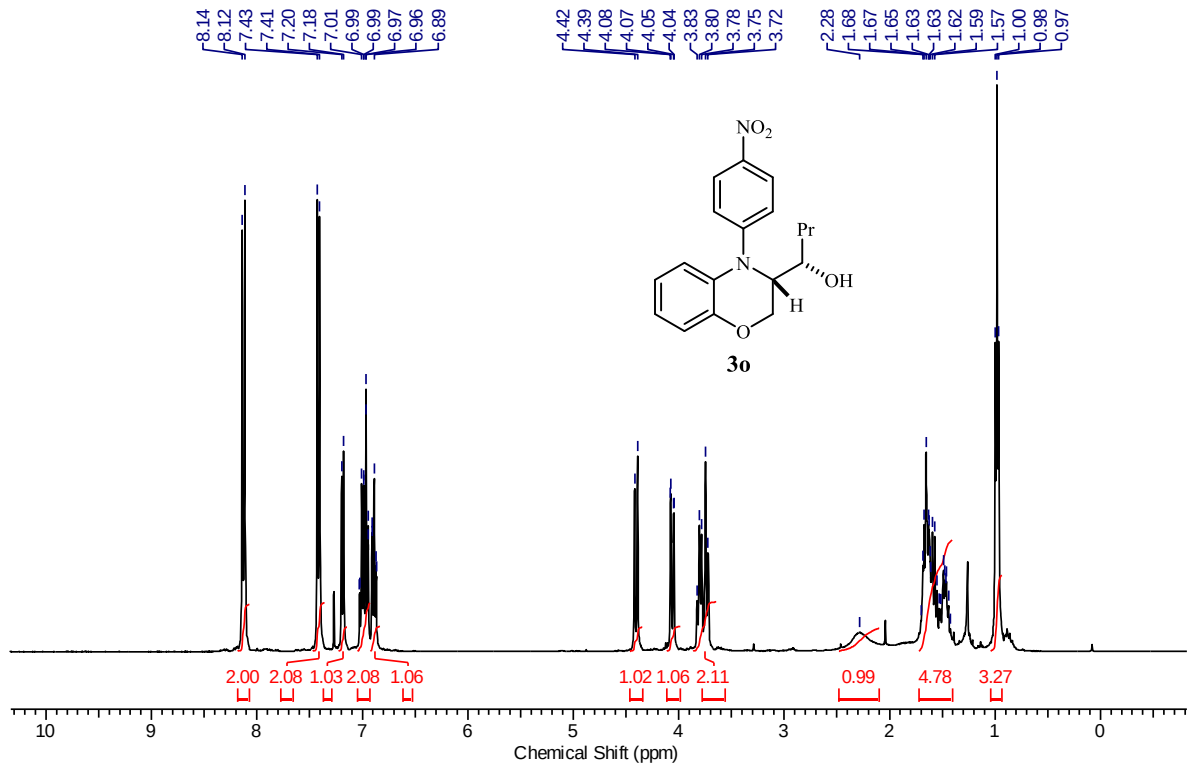
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3m**



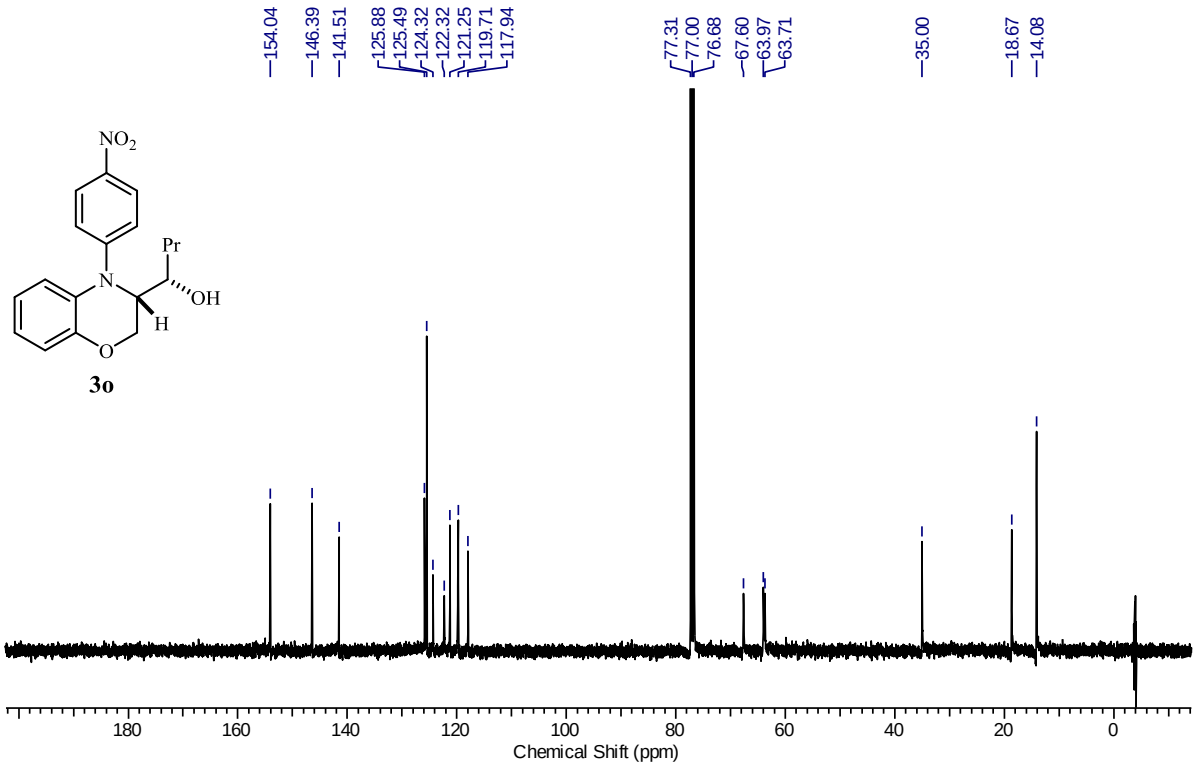
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



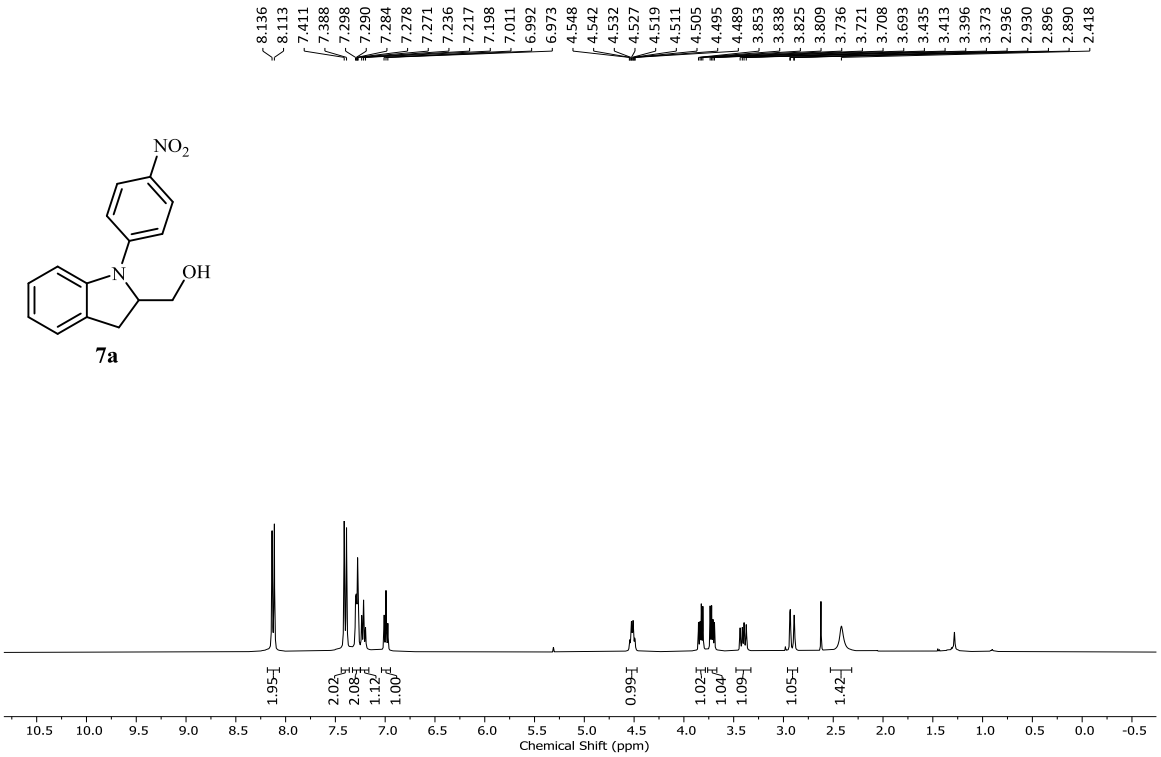
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3n**



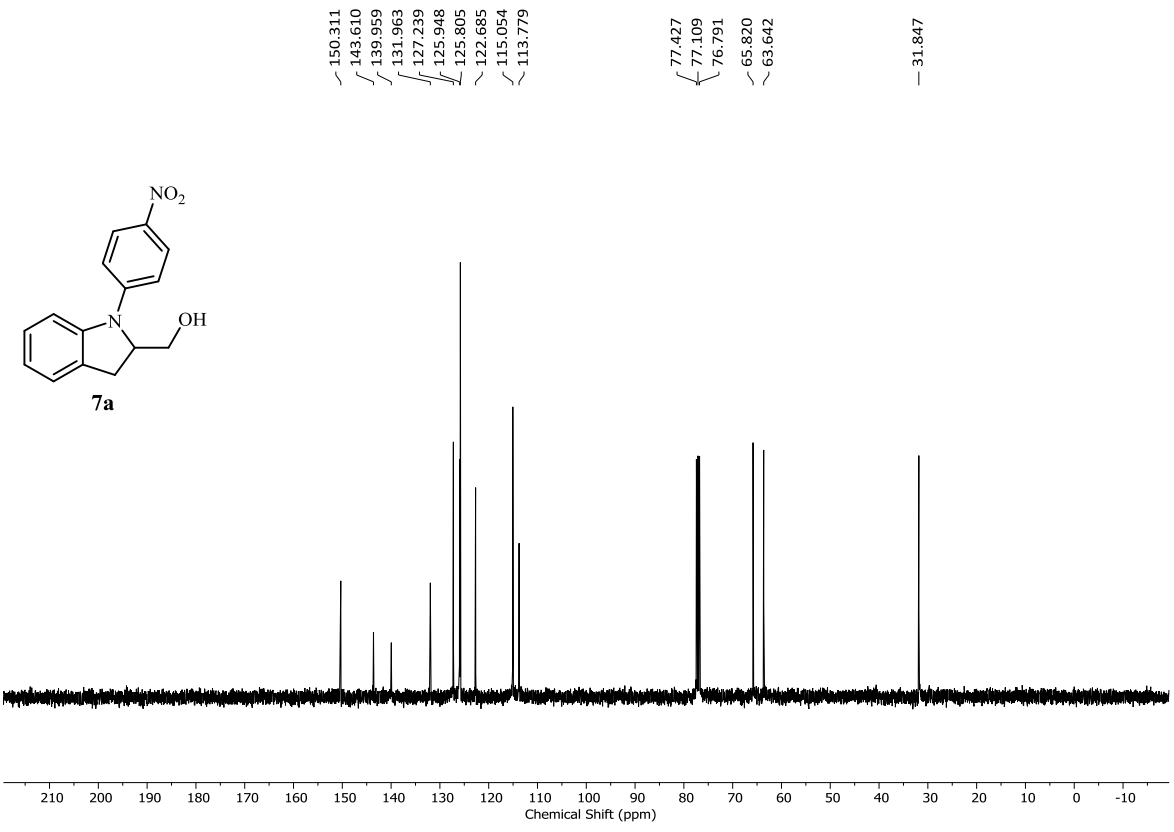
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



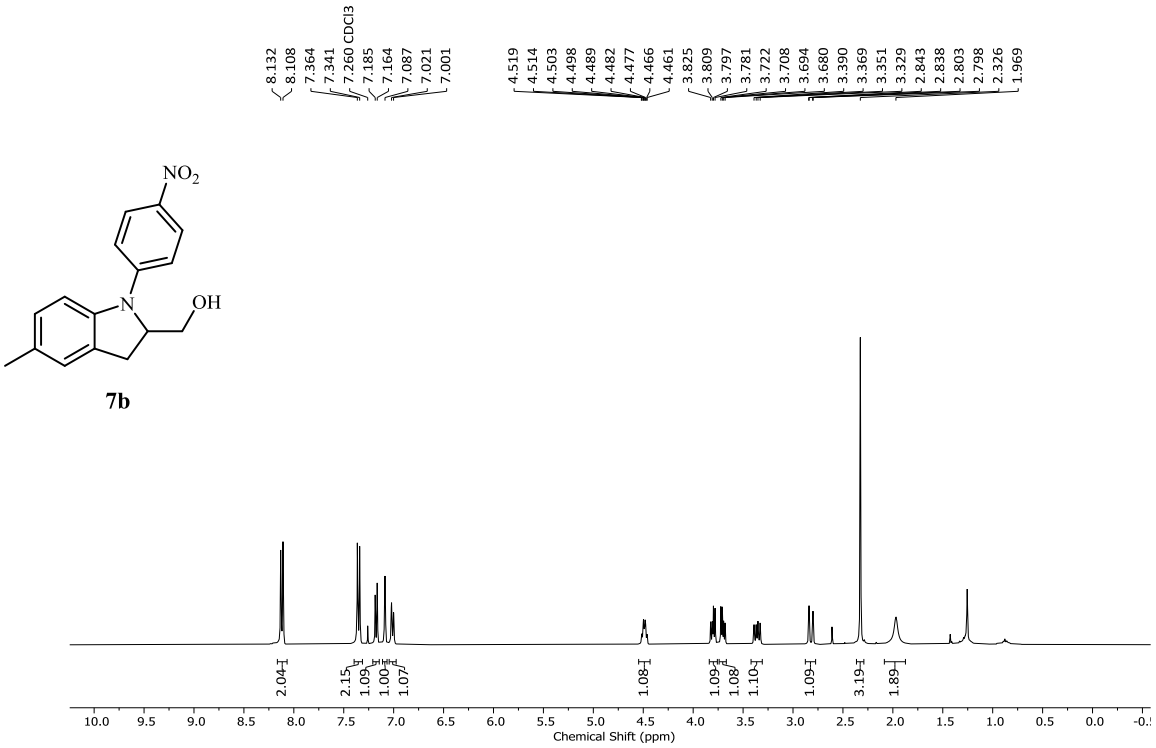
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**



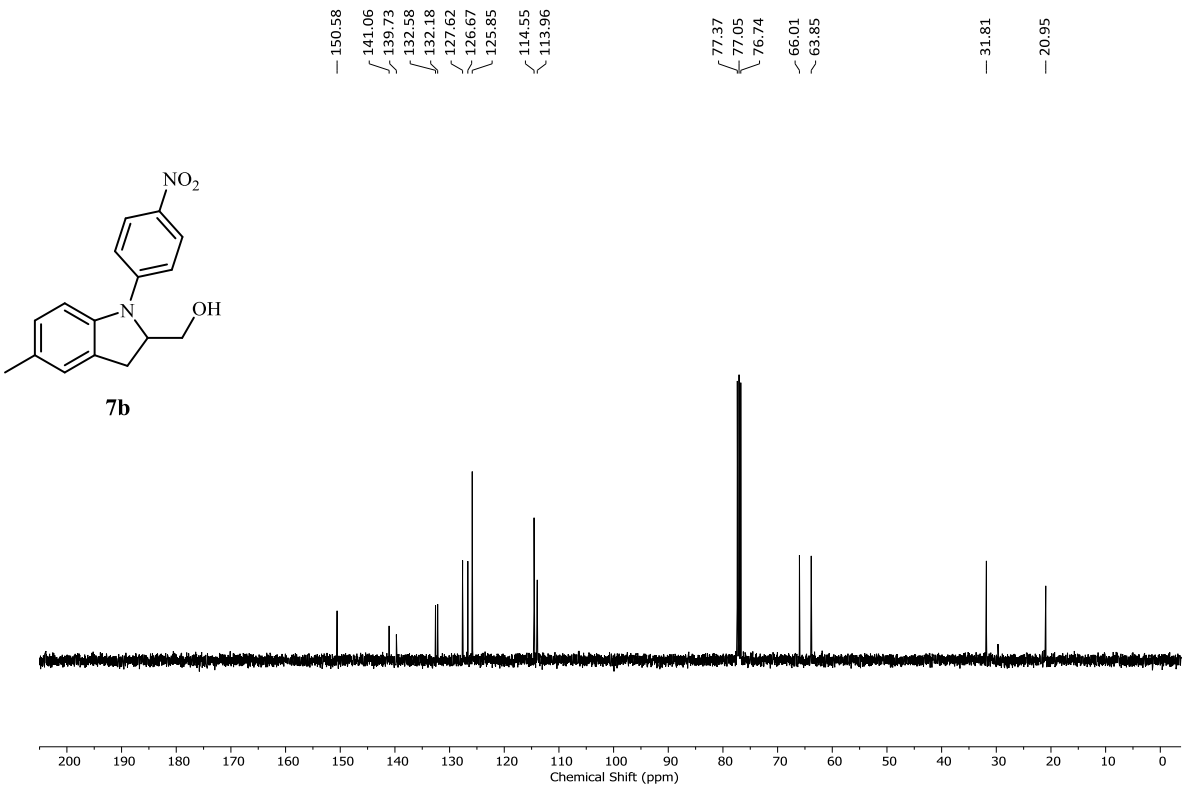
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7a.**



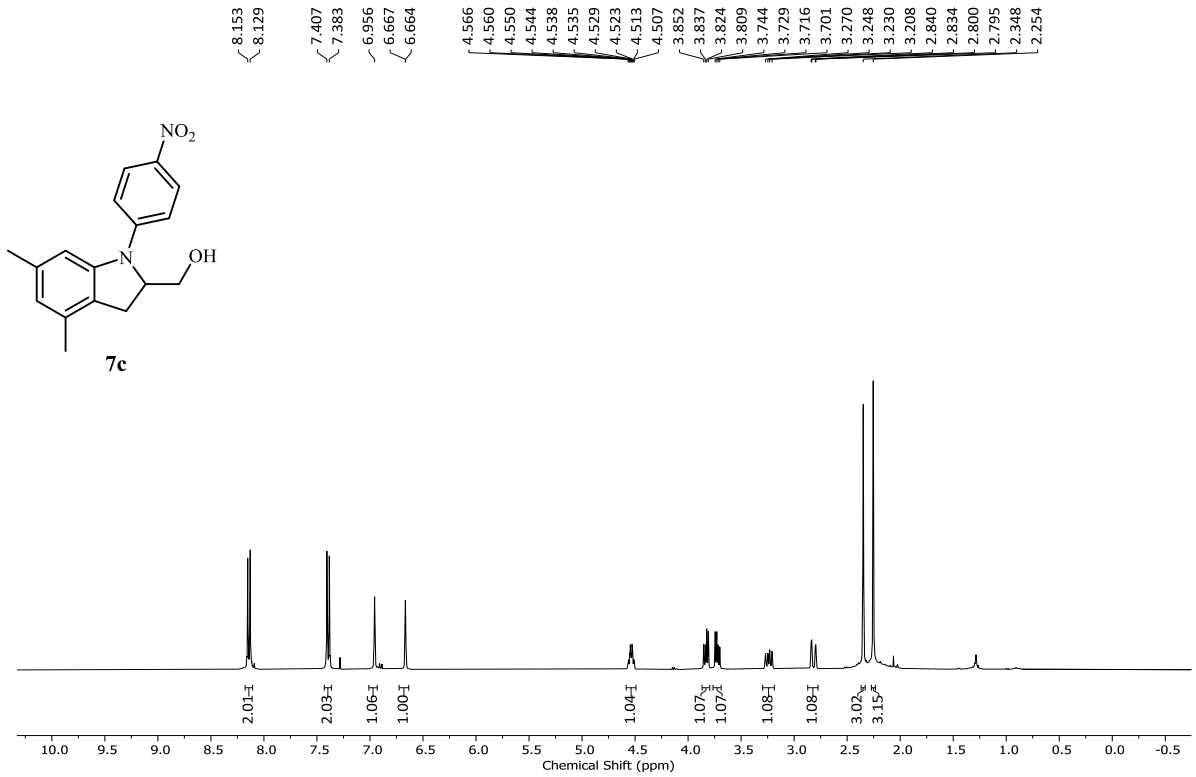
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7a.**



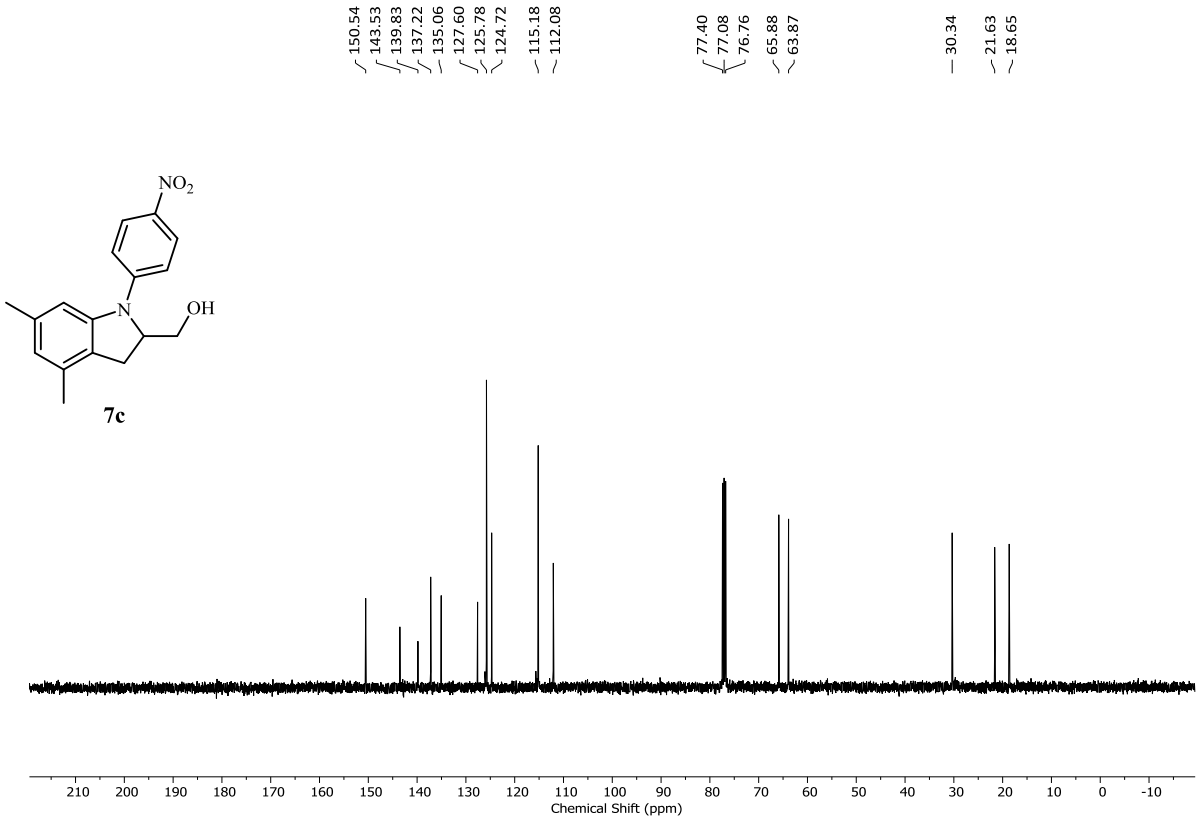
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7b.**



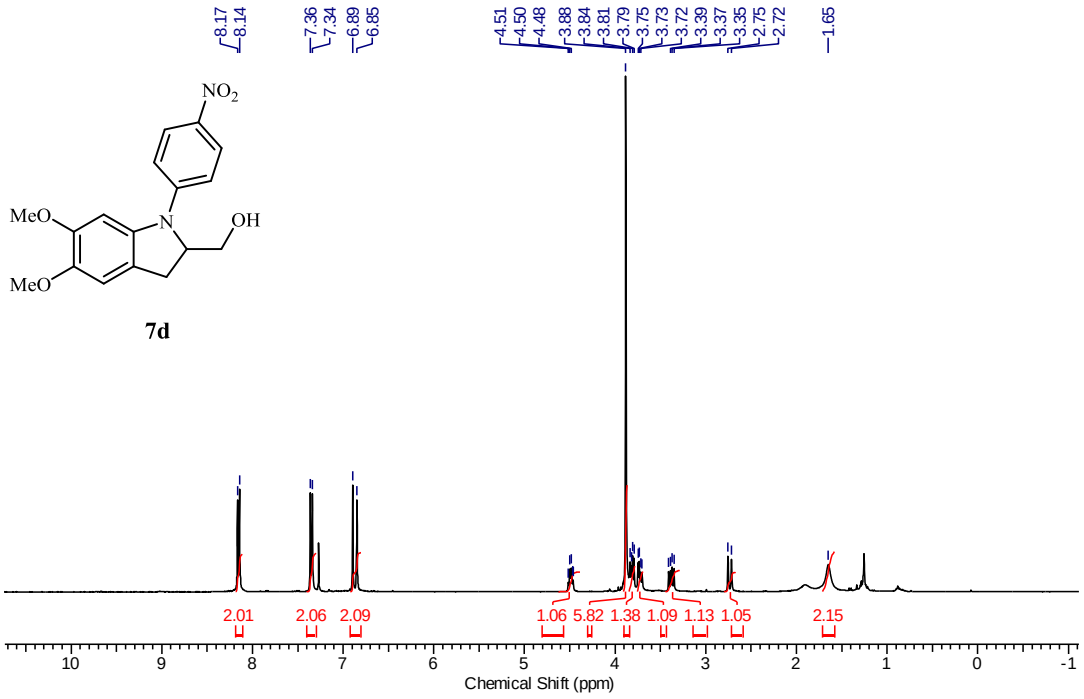
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7b.**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **7c.**

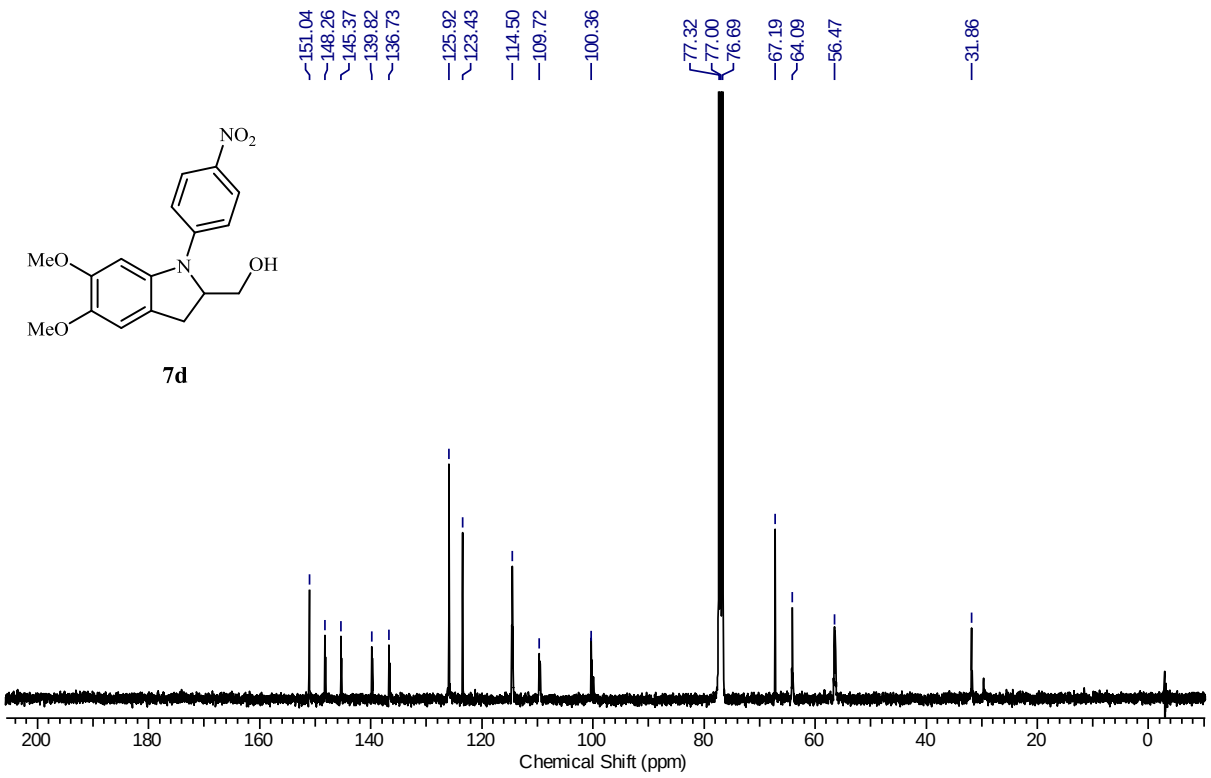


^{13}C NMR (100 MHz, $CDCl_3$) of compound **7c.**



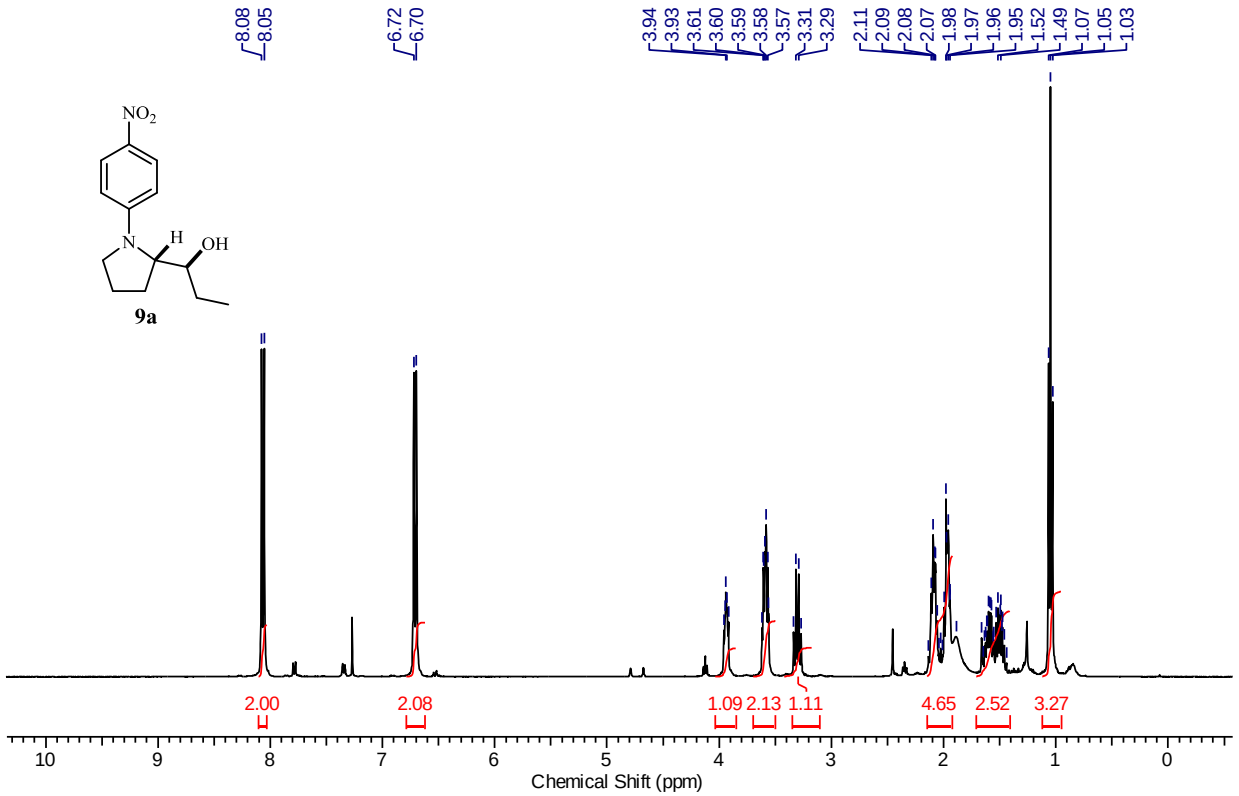
7d

^{1}H NMR (400 MHz, $CDCl_3$) of compound **7d.**

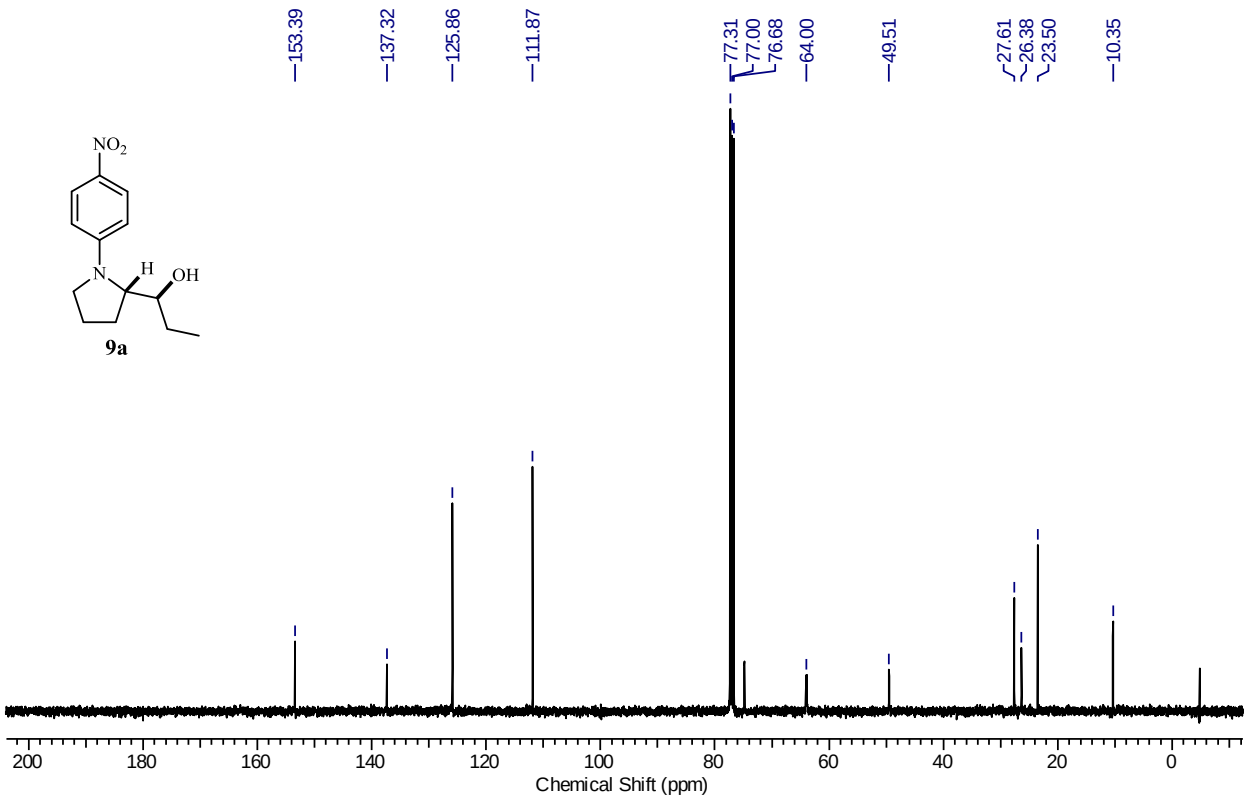


7d

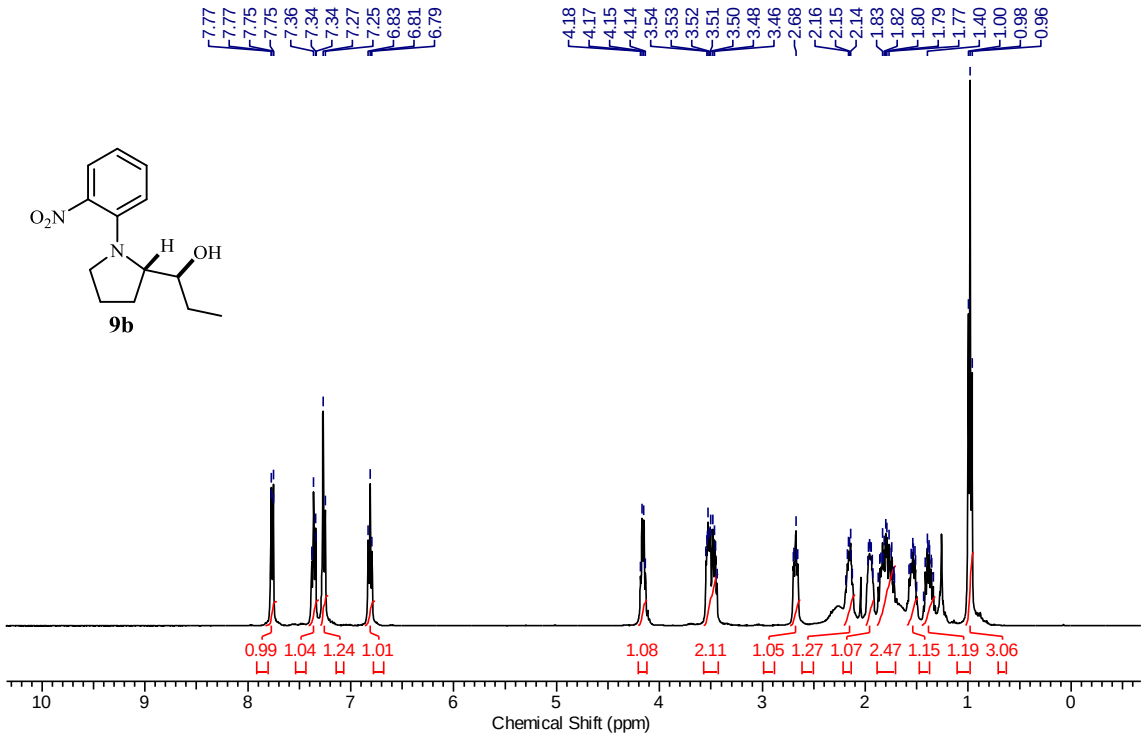
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7d.**



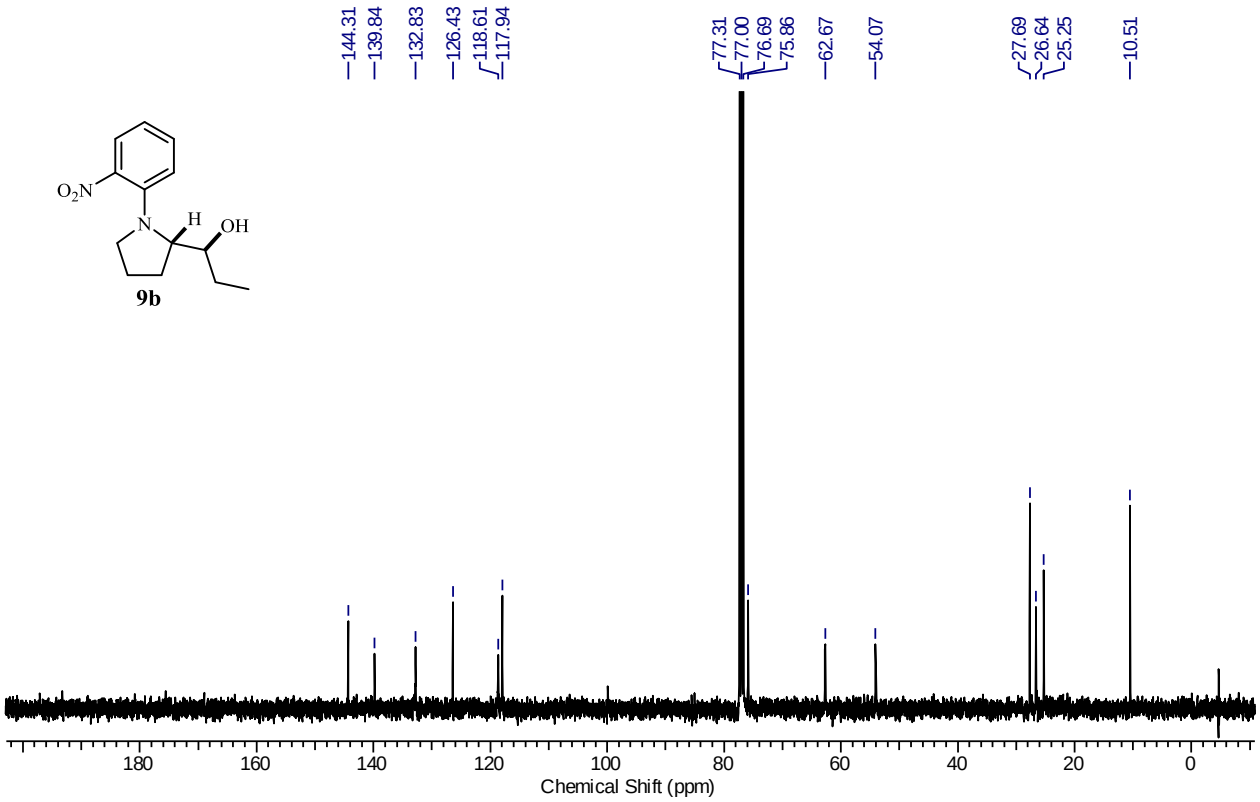
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9a.**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **9a.**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **9b.**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **9b.**