Supplementary Information (SI) for ChemComm.

Supporting Information

for

1,4-Dihydropyridine Compounds as Versatile Dehalogenation Reagents under Visible-Light Irradiation

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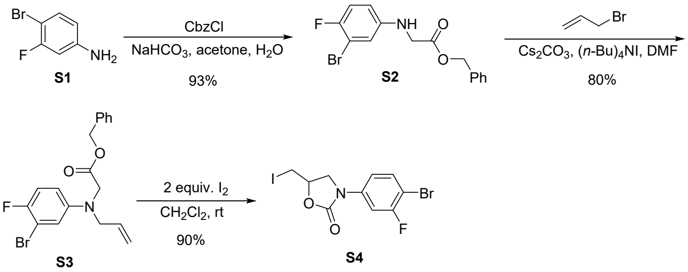
1. General information

All reagents and solvents were purchased from Adamas Reagent, Chendu Huaxia Chemical Reagent, Energy chemical, Alfa Aesa chemical company, Aladin Industrial Crporation, Macklin Biochemical Company, Acros Organics, Bide Pharmatech Ltd, and so forth. All chemicals are without purified unless otherwise stated. Petroleum ether (PE) and ethyl acetate (EA) for flash column chromatography were distilled before use. Thin layer chromatography (TLC) for analysis was performed on Schleicher & Schuell F1400/LS 254 silica gel plates, and observation under UV light (λ = 254 nm). ^{1}H NMR spectra recorded at 600 MHz, and ^{13}C NMR were recorded at 151 MHz. Use $CDCl_3$ as solvent and tetramethyl silane as internal standard (0.00 ppm) unless otherwise stated. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz). Flash chromatography was performed with Qingdao Haiyang flash silica gel (300–400 mesh). The substrates amine could be prepared according to literature.[1,2] Benzyl bromide could be easily prepared according to literature.[3]

Abbreviated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); THF (Tetrahydrofuran); DMF (Dimethylformamide); SDS (Sodium dodecyl sulfonate); CE (current efficiency).

2. Synthetic routes for alkyl halide[1]

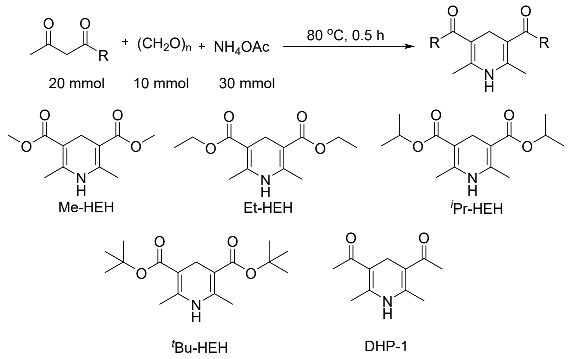


A mixture of the aryl amine **S1** (30.00 mmol) and $NaHCO_3$ (5 g, 60 mmol) in water (60 mL) and acetone (150 mL) was cooled to 0 °C and then treated with benzyl chloroformate (6 g, 5 mL, 36 mmol) over 10 min. The mixture was stirred for 1 h at 0 °C, and then the cooling bath was removed. Stirring continued at an ambient temperature overnight. Most of the acetone was then removed by rotary evaporation under reduced pressure, and the remaining mixture was poured into water (200 mL) and extracted with EtOAc. The combined organic extracts were washed with saturated aq. $NaHCO_3$, followed by brine, dried over with Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was then purified by recrystallization or silica gel chromatography to provide the **S2** (9.4 g) in a 93% yield.

To a solution of the **S2** (20 mmol) in dry DMF (200 mL) under N_2 were added $CsCO_3$ (26 g, 80 mmol), *n*-Bu_4NI (1g, 2.8 mmol), and then allyl bromide (10 g, 7 mL, 80 mmol). The resultant mixture was warmed to 40 °C and stirred under N_2 until TLC analysis (hexane/EtOAc) revealed the reaction to be complete. The reaction mixture was cooled to an ambient temperature, treated with H_2O (200 mL), and then extracted with 1:1 hexane/Et_2O (3×200 mL). The combined organic extracts were washed once with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the crude allylated product. Chromatography on silica gel, eluting with hexane/ EtOAc, afforded, after combining appropriate fractions and concentration under reduced pressure, 80% yields of **S3** were obtained.

To a solution of the **S3** (10 mmol) in CH_2Cl_2 (150 mL) under N_2 was added I_2 (5 g, 20 mmol). The dark brown solution was then stirred at an ambient temperature under N_2, and the reaction progress was monitored by TLC (hexane/EtOAc). When the reaction was complete, the mixture was diluted with CH_2Cl_2, poured into 10% aqueous $Na_2S_2O_3$, and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the crude product. Chromatography over silica gel, eluting with hexane/EtOAc, afforded, after combining appropriate fractions and concentration under reduced pressure, 90% yields of the targeted **S4** (3.2 g) products.

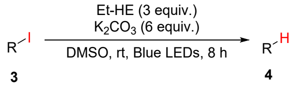
3. Synthetic routes for 1,4-dihydropyridine compounds[2]



In a 100 mL round bottom flask equipped with a magnetic bar and condenser, a mixture of paraformaldehyde (10 mmol), β-ketoester (20 mmol), ammonium acetate (40 mmol). The resulting mixture was stirred at 80 °C for 0.5 hour. After completion of the reaction, a substantial amount of yellow solid precipitated at the bottom of the reaction flask. Subsequently, 10 mL of cold water was added to the flask, and the resulting mixture was stirred for 5 min. The separated crystals were filtered off, washed with cold water three times to afford the crude product. For further purification, the crude product was recrystallized from methanol. After recrystallization, the mixture was filtered again, and the obtained solid was rinsed with methanol three times and dried at 60 °C in oven for 1 h. The final solid thus collected was confirmed as the target product.

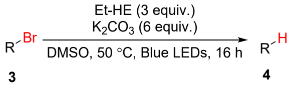
4. General procedure of dehalogenative hydrogenation reaction

4.1 Deiodination reaction-CP1



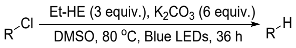
A dry tube filled with N_2 and equipped with a stirring bar was charged with the iodine-containing compounds (0.10 mmol, 1.0 equiv.), Et-EHE (0.30 mmol, 3.0 equiv.), the K_2CO_3 (0.6 mol, 6.0 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at room temperature under blue LEDs irradiation for 8 h. After the reaction is completed, the reaction mixture was treated with saturated aq. NH_4Cl (100 mL) and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained. Or the reaction was carried out in deuterated dimethyl sulfoxide (DMSO-*d*₆), followed by the addition of an internal standard (**4f**,**4h**,**4j**, and **4l** use 0.1 mmol dimethyl terephthalate as internal standard; **3i**, **3k**, and **3ah** use 0.1 mmol 1,3,5-trimethoxybenzene as internal standard) and ^{1}H NMR analysis to determine the yield.

4.2 Debromination reaction-GP2



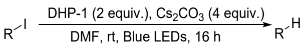
A dry tube filled with N_2 and equipped with a stirring bar was charged with the bromine-containing compounds (0.10 mmol, 1.0 equiv.), Et-EHE (0.30 mmol, 3.0 equiv.), the K_2CO_3 (0.6 mol, 6.0 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at 50 °C under blue LEDs irradiation for 16 h. After the reaction is completed, the reaction mixture was cooled to rt, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained. Or the reaction was carried out in deuterated dimethyl sulfoxide (DMSO-*d*₆), followed by the addition of an internal standard (**4ah** use 0.1 mmol 1,3,5-trimethoxybenzene as internal standard, others use 0.05 mmol 1,3,5-trimethoxybenzene as internal standard) and ^{1}H NMR analysis to determine the yield.

4.3 Dichlorination reaction-GP3



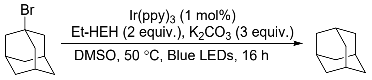
A dry tube filled with N_2 and equipped with a stirring bar was charged with the chlorine-containing compounds (0.10 mmol, 1.0 equiv.), Et-EHE (0.30 mmol, 3.0 equiv.), the K_2CO_3 (0.6 mol, 6.0 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at 80 °C under blue LEDs irradiation for 36 h. After the reaction is completed, the reaction mixture was cooled to rt, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained. Or the reaction was carried out in deuterated dimethyl sulfoxide (DMSO-*d*₆), followed by the addition of an internal standard (0.05 mmol 1,3,5-trimethoxybenzene) and ^{1}H NMR analysis to determine the yield.

4.4 Selective deiodination reaction of polyhalogenated aromatic systems-GP4



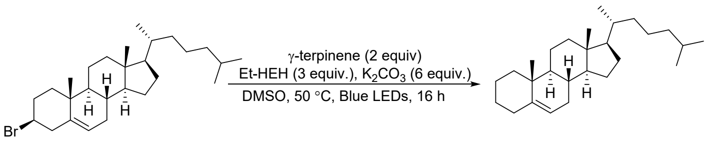
A dry tube filled with N_2 and equipped with a stirring bar was charged with polyhalogenated aromatic compounds (0.10 mmol, 1.0 equiv.), DHP-1 (0.20 mmol, 2.0 equiv.), the Cs_2CO_3 (0.4 mol, 4.0 equiv.) and degassed DMF (1 mL, 0.1 M). The reaction was stirred at room temperature under blue LEDs irradiation for 16 h. After the reaction is completed, the reaction mixture was treated with saturated aq. NH_4Cl (100 mL) and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained. Alternatively, an internal standard (0.05 mmol 1,3,5-trimethoxybenzene) was added to the crude product, and the yield was determined by ^1H NMR spectroscopy.

4.5 Selective deiodination reaction of polyhalogenated aromatic systems-GP5



A dry tube filled with N_2 and equipped with a stirring bar was charged with the starting material (0.10 mmol, 1.0 equiv.), Et-EHE (0.20 mmol, 3.0 equiv.), K_2CO_3 (0.6 mol, 6.0 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at 50 ^oC under blue LEDs irradiation for 16 h. After the reaction is completed, the reaction mixture was cooled to rt, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane, after combining appropriate fractions and concentration under reduced pressure, target products were obtained.

4.6 Selective deiodination reaction of polyhalogenated aromatic systems-GP6

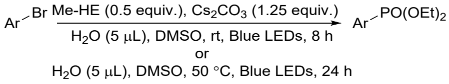


A dry tube filled with N_2 and equipped with a stirring bar was charged with the starting material (0.10 mmol, 1.0 equiv.), Et-EHE (0.30 mmol, 3.0 equiv.), K_2CO_3 (0.6 mol, 6.0 equiv.), γ-terpinene (0.20 mmol, 2.0 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at 50 ^oC under blue LEDs irradiation for 16 h. After the reaction is completed, the reaction mixture was cooled to rt, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane, after combining appropriate fractions and concentration under reduced pressure, target products were obtained.

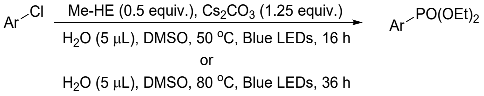
5. General procedure of dehalogenative functionalization reaction-GP7

$$\mathrm{Ar{-}I} \xrightarrow[\text{DMSO, rt, Blue LEDs, 8 h}]{\text{Me-HE (0.5 equiv.), NaOH (1.25 equiv.)}} \mathrm{Ar{-}PO(OEt)_2}$$

A dry tube filled with N_2 and equipped with a stirring bar was charged with the starting material (0.10 mmol, 1.0 equiv.), Me-HEH (0.05 mmol, 0.5 equiv.), NaOH (0.125 mol, 1.25 equiv.) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at rt under blue LEDs irradiation for 8 h. After the reaction is completed, the reaction mixture was cooled to an ambient temperature, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained.



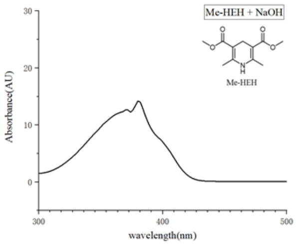
A dry tube filled with N_2 and equipped with a stirring bar was charged with the starting material (0.10 mmol, 1.0 equiv.), Me-HEH (0.05 mmol, 0.5 equiv.), the Cs_2CO_3 (0.125 mol, 1.25 equiv.), H_2O (5 μL) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at rt or 50 ^{o}C under blue LEDs irradiation for 8 or 16 h. After the reaction is completed, the reaction mixture was cooled to an ambient temperature, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained.

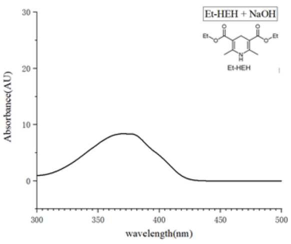


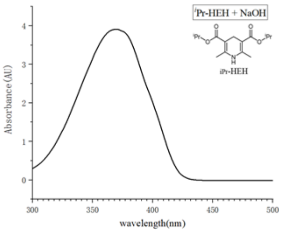
A dry tube filled with N_2 and equipped with a stirring bar was charged with the starting material (0.10 mmol, 1.0 equiv.), Me-HEH (0.05 mmol, 0.5 equiv.), the Cs_2CO_3 (0.125 mol, 1.25 equiv.), H_2O (5 μL) and degassed DMSO (1 mL, 0.1 M). The reaction was stirred at 50 ^{o}C or 80 ^{o}C under blue LEDs irradiation for 16 or 36 h. After the reaction is completed, the reaction mixture was cooled to an ambient temperature, treated with saturated aq. NH_4Cl (100 mL), and then extracted with EA (3×100 mL). The combined organic extracts were washed once with H_2O and brine, dried over with Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. Chromatography on silica gel, eluting with hexane/EtOAc, after combining appropriate fractions and concentration under reduced pressure, target products were obtained.

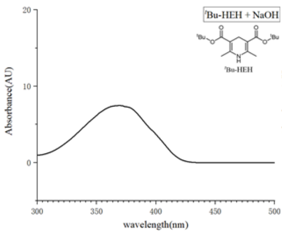
6. Mechanistic studies

6.1 UV-Vis studies









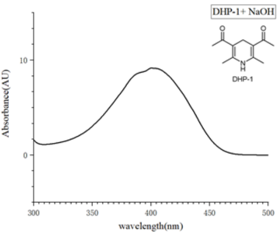


Fig. 1 **Me-HEH + NaOH**: Me-HEH (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL); **Et-HEH + NaOH**: Et-HEH (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL); ***ⁱ*Pr-HEH + NaOH**: *ⁱ*Pr-HEH (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL); ***ᵗ*Bu -HEH + NaOH**: *ᵗ*Bu -HEH (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL); **DHP-1 + NaOH**: DHP-1 (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL);

6.2 EDA complexation studies

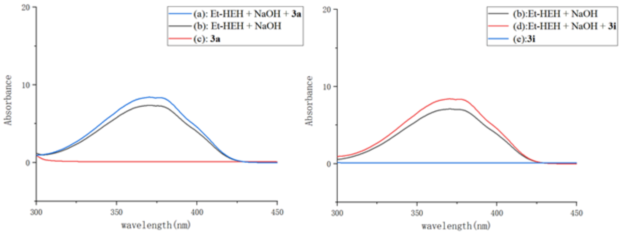


Fig. 2 (a): Et-HEH (0.1 mmol), NaOH (0.1 mmol), 3a (0.1 mmol), DMSO (10 mL); (b): Et-HEH (0.1 mmol), NaOH (0.1 mmol), DMSO (10 mL); (c): **3a** (0.1 mmol), DMSO (10 mL);(d): Et-HEH (0.1 mmol), NaOH (0.1 mmol), **3i** (0.1 mmol), DMSO (10 mL); (e): **3i** (0.1 mmol), DMSO (10 mL);

6.3 Fluorescence studies

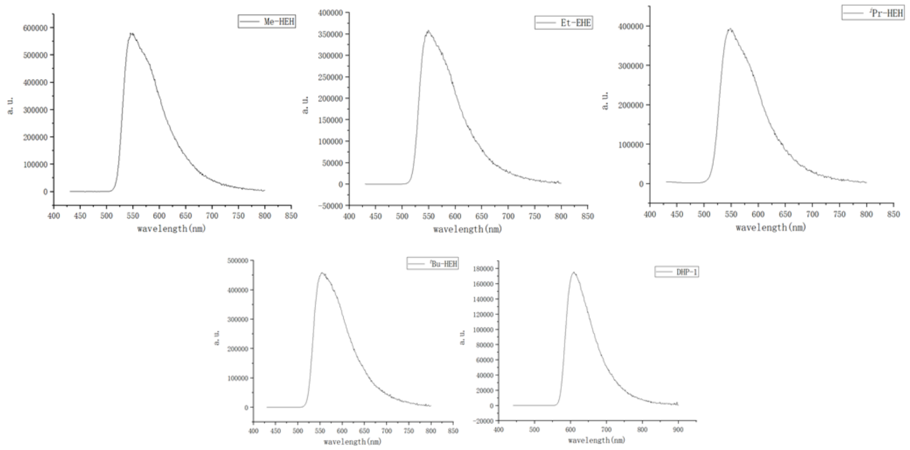
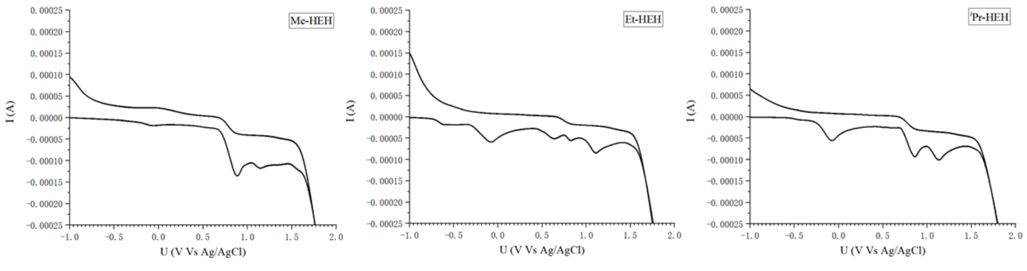


Fig. 3 **Me-HEH**: Me-HEH (0.025 mmol), NaOH (0.025 mmol), DMSO (10 mL); **Et-HEH**: Et-HEH (0.025 mmol), NaOH (0.025 mmol), DMSO (10 mL); ***ⁱ*Pr-HEH**: *ⁱ*Pr-HEH (0.025 mmol), NaOH (0.025mmol), DMSO (10 mL); ***ᵗ*Bu -HEH**: *ᵗ*Bu -HEH (0.025 mmol), NaOH (0.025 mmol), DMSO (10 mL); **DHP-1**: DHP-1 (0.025 mmol), NaOH (0.025 mmol), DMSO (10 mL);

7. Electrochemical measurements



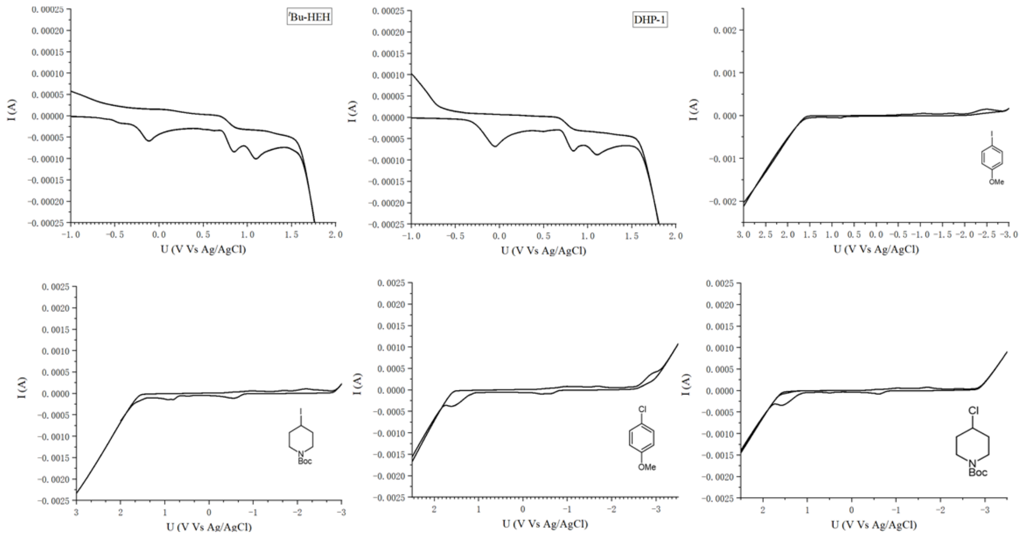


Fig. 4 Cyclic voltammograms of substrates in 10 mL DMSO (0.1 M ^{n}Bu$_4$NBF$_4$) using a glassy carbon as working electrode, Pt wire as counter and Ag/AgCl as reference electrodes, scan rate: 100 mV/s; **Me-HEH:** Me-HEH (0.1 mmol), NaOH (0.1 mmol); **Et-HEH:** Et-HEH (0.1 mmol), NaOH (0.1 mmol); **^{i}Pr-HEH:** ^{i}Pr-HEH (0.1 mmol), NaOH (0.1 mmol); **^{t}Bu-HEH:** ^{t}Bu-HEH (0.1 mmol), NaOH (0.1 mmol); **DHP-1: DHP-1** (0.1 mmol), NaOH (0.1 mmol); **3-9i: 3-9i** (0.1 mmol), NaOH (0.1 mmol); **3-5: 3-5** (0.1 mmol), NaOH (0.1 mmol); **3-9at: 3-9at** (0.1 mmol), NaOH (0.1 mmol); **3-1: 3-1** (0.1 mmol), NaOH (0.1 mmol)。

8. The redox potential of photosensitizers and some substrates

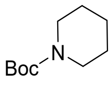
Table S1 The redox potential of photosensitizers and some substrates

	Me-HEH	Et-HEH	^{i}Pr-HEH	^{t}Bu-HEH	DHP-1	**3-9h**	**3-5**	**3-9aq**	**3-1**
$E_{0,0}$	2.76 eV	2.76 eV	2.76 eV	2.76 eV	2.54 eV	--	--	--	--
$E_{ox}{}^a$	-0.08 V	-0.08 V	-0.08 V	-0.12 V	-0.05 V	--	--	--	--
$E^*_{ox}{}^a$	-2.84 V	-2.84V	-2.84 V	-2.88 V	-2.59 V	--	--	--	--
$E_{re}{}^a$	--	--	--	--	--	-2.17 V	-2.48V	-2.87 V	--

^{a} Vs Ag/AgCl, $E^*_{ox} = E_{ox} - E_{0,0}$, $E_{0,0} = (1240/\lambda_{c,abs} + 1240/\lambda_{c,em})/2$ ($\lambda_{c,abs}$ are the centroid wavelength of the Vis absorption spectrum and $\lambda_{c,em}$ is that of the fluorescence emission spectrum)

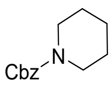
9. Characterization of products

tert-Butyl piperidine-1-carboxylate (4a)[3]



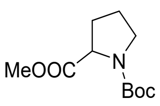
Target compound was obtained according to **GP1** giving pure product (17.0 mg, 92% yield) and **GP2** giving pure product (17.5 mg, 95% yield) and **GP3** giving pure product (15.1 mg, 82% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R$_f$: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, CDCl$_3$) δ 3.29 (t, J = 5.5 Hz, 4H), 1.50 (s, 2H), 1.43 (q, J = 5.7 Hz, 4H), 1.39 (s, 9H). Data in accordance with the literature.

Benzyl piperidine-1-carboxylate (4b)[4]



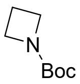
Target compound was obtained according to **GP1** giving pure product (20.6 mg, 94% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R$_f$: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.35 (d, J = 4.3 Hz, 4H), 7.32–7.28 (m, 1H), 5.12 (s, 2H), 3.44 (t, *J* = 5.5 Hz, 4H), 1.62–1.48 (m, 6H). Data in accordance with the literature.

1-(*tert*-Butyl) 2-methyl pyrrolidine-1,2-dicarboxylate (4c)[3]



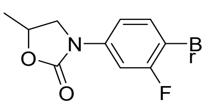
Target compound was obtained according to **GP1** giving pure product (21.3 mg, 93% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 (dd, *J* = 8.4, 3.6 Hz, 0.43H), 4.22 (dd, *J* = 8.6, 4.2 Hz, 0.57H), 3.72 (d, *J* = 3.1 Hz, 3H), 3.61–3.54 (m, 0.57H), 3.51 (s, 0.43H), 3.46 (dt, *J* = 10.0, 6.6 Hz, 0.57H), 3.42–3.35 (m, 0.43H), 2.27–2.20 (m, 0.57H), 2.16 (d, *J* = 8.7 Hz, 0.43H), 2.00–1.85 (m, 3H), 1.46 (s, 3.87H), 1.41 (s, 5.14H). Data in accordance with the literature.

***tert*-Butyl azetidine-1-carboxylate (4d)**[3]



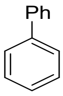
Target compound was obtained according to **GP1** giving pure product (15.5 mg, 96% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.94 (t, *J* = 7.7 Hz, 4H), 2.17 (p, *J* = 7.7 Hz, 2H), 1.44 (s, 9H). Data in accordance with the literature.

3-(4-Bromo-3-fluorophenyl)-5-methyloxazolidin-2-one (4e)[5]



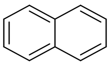
Target compound was obtained according to **GP1** giving pure product (25.7 mg, 94% yield), purification by flash chromatography on silica gel (PE : EA = 5 : 1); white solid; R_f: 0.3 (PE : EA = 3 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 0H), 4.81 (h, *J* = 7.9, 7.2 Hz, 1H), 4.08 (t, *J* = 8.4 Hz, 1H), 3.58 (dd, *J* = 8.6, 7.0 Hz, 1H), 1.55 (d, *J* = 6.2 Hz, 3H). Data in accordance with the literature.

1,1'-Biphenyl (4f)[6]



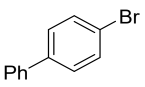
Target compound was obtained according to **GP1** giving pure product (15.2 mg, 99% yield) or general procedure **B** giving pure product (14.8 mg, 96% yield) or general procedure **C** giving pure product (15.0 mg, 98% yield), purification by flash chromatography on silica gel (PE); white solid; R_f: 0.7 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 2H). Data in accordance with the literature.

Naphthalene (4m)[3]



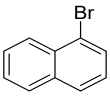
Target compound was obtained according to **GP1** giving pure product (12.2 mg, 95% yield) or general procedure **B** giving pure product (120.0 mg, 94% yield) or general procedure **C** giving pure product (11.1 mg, 87% yield), purification by flash chromatography on silica gel (PE); white solid; R_f: 0.7 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.47 (dd, *J* = 6.3, 3.3 Hz, 1H). Data in accordance with the literature.

4-Bromo-1,1'-biphenyl (4n)[7]



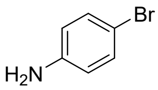
Target compound was obtained according to **GP4** giving pure product (23 mg, 98% yield), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.8 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60–7.52 (m, 4H), 7.44 (dd, *J* = 14.6, 7.2 Hz, 4H), 7.39–7.34 (m, 1H). Data in accordance with the literature.

1-Bromonaphthalene (4p)[8]



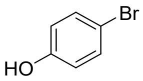
Target compound was obtained according to **GP4** giving pure product (19.5 mg, 95% yield), purification by flash chromatography on silica gel (PE); colorless liquid; R_f: 0.8 (PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 1H), 7.85–7.75 (m, 3H), 7.61–7.56 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H). Data in accordance with the literature.

4-Bromoaniline (4q) [9]



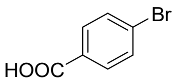
Target compound was obtained according to **GP4** giving pure product (15.4 mg, 90% yield), purification by flash chromatography on silica gel (PE : EA = 10 : 1); white solid; R_f: 0.4 (PE : EA = 5 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20–7.09 (m, 2H), 6.54–6.41 (m, 2H), 3.54 (s, 2H). Data in accordance with the literature.

4-Bromophenol (4r) [10]



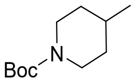
Target compound was obtained according to **GP4** giving pure product (11.0 mg, 64% yield), purification by flash chromatography on silica gel (PE : EA = 5 : 1); white solid; R_f: 0.4 (PE : EA = 3 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H). Data in accordance with the literature.

4-bromobenzoic acid (4s)[11]



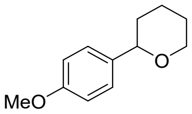
Target compound was obtained according to **GP4** giving pure product (19.4 mg, 97% yield), purification by flash chromatography on silica gel (DCM : MeOH = 70 : 1); white solid; R_f: 0.4 (DCM : MeOH = 30 : 1). ^{1}H NMR (600 MHz, CD_3OD) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H). Data in accordance with the literature.

***tert*-Butyl 4-methylpiperidine-1-carboxylate (4u)** [3]



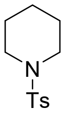
Target compound was obtained according to **GP2** giving pure product (18.9 mg, 95% yield) or general procedure **GP3** giving pure product (18.9 mg, 95% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.04 (s, 2H), 2.68 (t, *J* = 13.0 Hz, 2H), 1.59 (d, *J* = 13.3 Hz, 2H), 1.53–1.47 (m, 1H), 1.45 (s, 9H), 1.08 (qd, *J* = 12.6, 4.3 Hz, 2H), 0.93 (d, *J* = 6.6 Hz, 3H). Data in accordance with the literature.

2-(4-Methoxyphenyl)tetrahydro-2H-pyran (4v)[12]



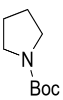
Target compound was obtained according to **GP2** giving pure product (17.2 mg, 90% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.20 (d, *J* = 11.3 Hz, 1H), 4.04 (d, *J* = 15.1 Hz, 1H), 3.72 (s, 3H), 3.59–3.46 (m, 1H), 1.86 (d, *J* = 11.5 Hz, 1H), 1.72 (d, *J* = 11.9 Hz, 1H), 1.55 (ddd, *J* = 47.5, 23.7, 12.9 Hz, 4H). Data in accordance with the literature.

1-Tosylpiperidine (4w)[13]



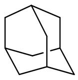
Target compound was obtained according to **GP2** giving pure product (22.0 mg, 92% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); white solid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.97 (t, *J* = 5.4 Hz, 4H), 2.43 (s, 3H), 1.64 (p, *J* = 5.7 Hz, 4H), 1.41 (p, *J* = 5.8 Hz, 2H). Data in accordance with the literature.

***tert*-Butyl pyrrolidine-1-carboxylate (4x)**[14]



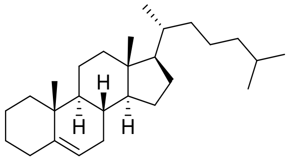
Target compound was obtained according to **GP2** giving pure product (16.9 mg, 99% yield), purification by flash chromatography on silica gel (PE : EA = 50 : 1); colorless liquid; R_f: 0.4 (PE : EA = 10 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.23 (dt, *J* = 31.8, 6.5 Hz, 4H), 1.86–1.70 (m, 4H), 1.39 (s, 9H). Data in accordance with the literature.

Adamantane (4aa)[3]



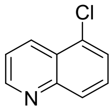
Target compound was obtained according to **GP5** and giving pure product (16.9 mg, 99% yield), purification by flash chromatography on silica gel (PE); colorless solide; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.73–1.76 (m, 12H), 1.90–1.85 (4H, m). Data in accordance with the literature.

Cholest-5-ene (4ab)[3]



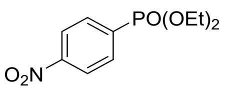
Target compound was obtained according to **GP6** and giving pure product (16.9 mg, 99% yield), purification by flash chromatography on silica gel (PE); colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27 (dt, *J* = 4.8, 2.2 Hz, 1H), 2.24 (t, *J* = 15.3 Hz, 1H), 2.03–1.92 (m, 3H), 1.86–1.78 (m, 2H), 1.72 (d, *J* = 12.8 Hz, 1H), 1.53–1.01 (m, 23H), 1.00 (3H, s), 0.98 – 0.88 (m, 6H), 0.68 (3H, s). Data in accordance with the literature.

5-Chloroquinoline (al)[15]



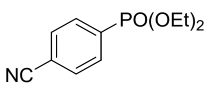
Target compound was obtained according to **GP2** giving pure product (13.4 mg, 82% yield), purification by flash chromatography on silica gel (PE : EA = 10 : 1); white solid; R_f: 0.4 (PE : EA = 5 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.3 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.10–8.04 (m, 1H), 7.65 (d, *J* = 3.6 Hz, 2H), 7.53 (dd, *J* = 8.6, 4.2 Hz, 1H). Data in accordance with the literature.

Diethyl (4-nitrophenyl)phosphonate (5a)[16]



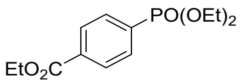
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; R_f: 0.4 (PE : EA = 3 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.6, 3.1 Hz, 2H), 8.01 (dd, *J* = 12.7, 8.5 Hz, 2H), 4.24–4.10 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). Data in accordance with the literature.

Diethyl (4-cyanophenyl)phosphonate (5b)[17]



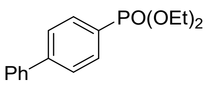
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; R_f: 0.4 (PE : EA = 3 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 13.1, 7.9 Hz, 2H), 7.76 (dd, *J* = 8.2, 3.5 Hz, 2H), 4.23–4.08 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). Data in accordance with the literature.

Ethyl 4-(diethoxyphosphoryl)benzoate (5c)[18]



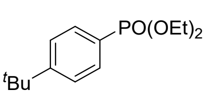
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; R_f: 0.4 (PE : EA = 3 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.2, 3.7 Hz, 2H), 7.82 (q, *J* = 7.4, 6.6 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.15–3.97 (m, 6H), 1.34 (d, *J* = 14.3 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 9H). Data in accordance with the literature.

Diethyl [1,1'-biphenyl]-4-ylphosphonate (5d) [18]



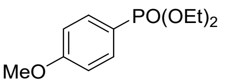
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 13.1, 7.9 Hz, 2H), 7.60 (dd, *J* = 8.2, 3.8 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 4.10 (dq, *J* = 10.1, 7.2 Hz, 2H), 4.06–3.99 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 9H). Data in accordance with the literature.

Diethyl (4-(*tert*-butyl)phenyl)phosphonate (5e) [18]



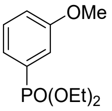
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67 (dd, J = 12.7, 8.0 Hz, 2H), 7.41 (d, J = 5.2 Hz, 2H), 4.15–3.97 (m, 4H), 1.26 (d, J = 4.3 Hz, 15H). Data in accordance with the literature.

Diethyl (4-methoxyphenyl)phosphonate (5f) [18]



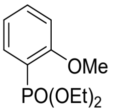
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.68 (dd, J = 12.7, 8.4 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 4.12–3.93 (m, 4H), 3.78 (s, 3H), 1.24 (t, J = 7.0 Hz, 6H). Data in accordance with the literature.

Diethyl (3-methoxyphenyl)phosphonate (5h) [18]



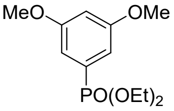
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41–7.36 (m, 2H), 7.34 (d, J = 16.2 Hz, 1H), 7.08 (t, J = 6.0 Hz, 1H), 4.11 (ddd, J = 32.6, 15.9, 8.6 Hz, 4H), 3.85 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H). Data in accordance with the literature.

Diethyl (2-methoxyphenyl)phosphonate (5i) [18]



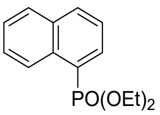
Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.75 (ddd, J = 14.8, 7.5, 1.8 Hz, 1H), 7.43 (d, J = 7.0 Hz, 1H), 6.94 (td, J = 7.4, 3.5 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 4.14 – 4.03 (m, 4H), 3.84 (s, 3H), 1.27 (t, J = 7.1 Hz, 6H). Data in accordance with the literature.

Diethyl (3,5-dimethoxyphenyl)phosphonate (5g) [18]



Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.94 (dd, J = 14.8, 2.3 Hz, 2H), 6.62 (t, J = 2.2 Hz, 1H), 4.21–4.03 (m, 4H), 3.83 (d, J = 1.5 Hz, 6H), 1.33 (t, J = 7.0 Hz, 6H). Data in accordance with the literature.

Diethyl naphthalen-1-ylphosphonate (5j) [18]



Target compound was obtained according to **GP7** giving pure product, purification by flash chromatography on silica gel (PE : EA = 5 : 1); colorless liquid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.45 (d, J = 8.6 Hz, 1H), 8.23–8.13 (m, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.60–7.52 (m, 1H), 7.52–7.44 (m, 2H), 4.19–4.08 (m, 2H), 4.02 (h, J = 7.2 Hz, 2H), 1.24 (t, J = 7.1 Hz, 6H). Data in accordance with the literature.

10. References

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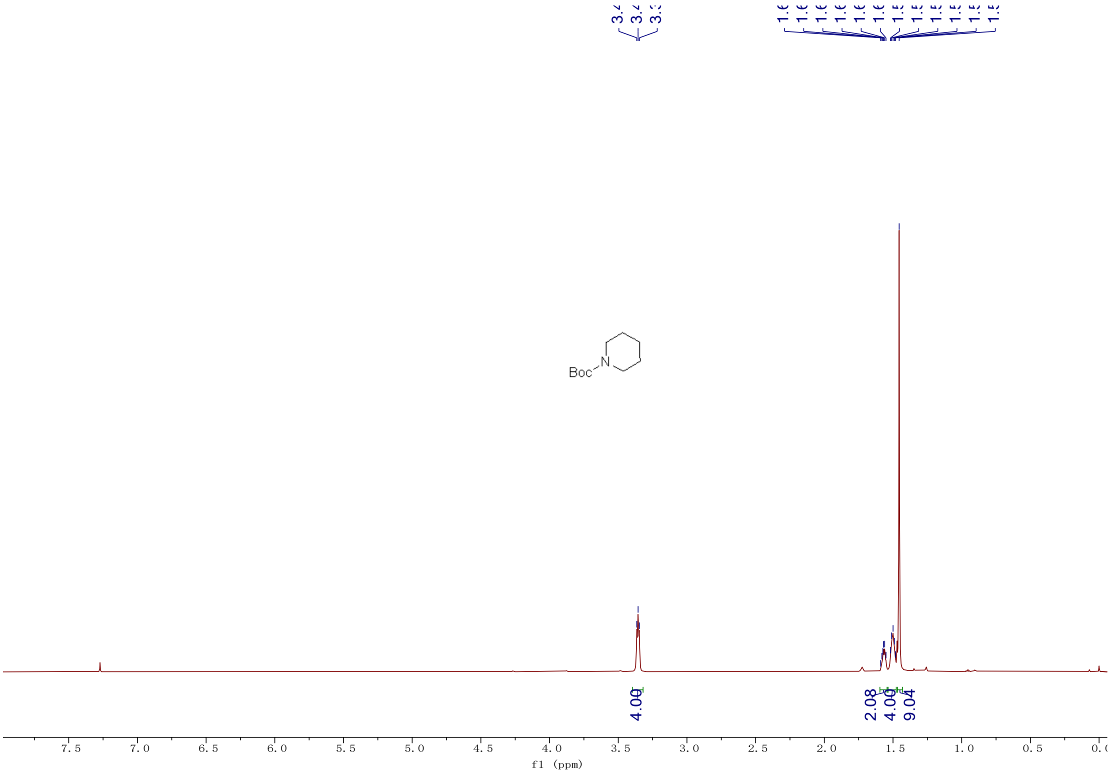
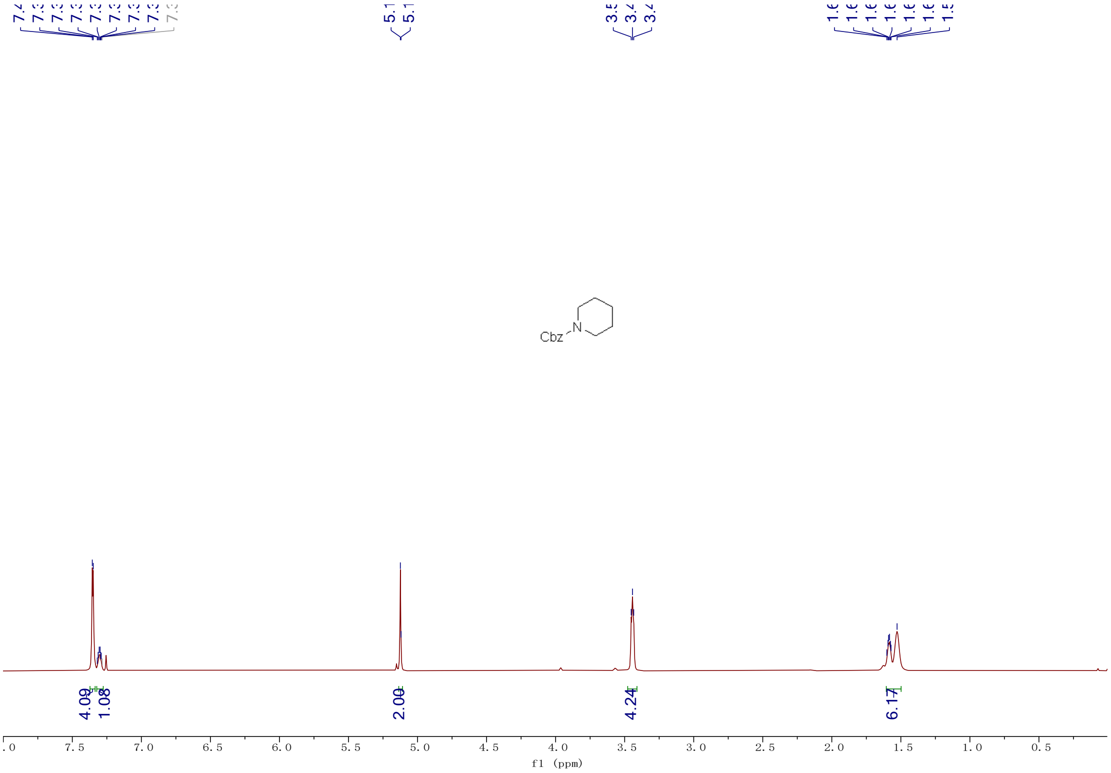
11. The spectra of NMR

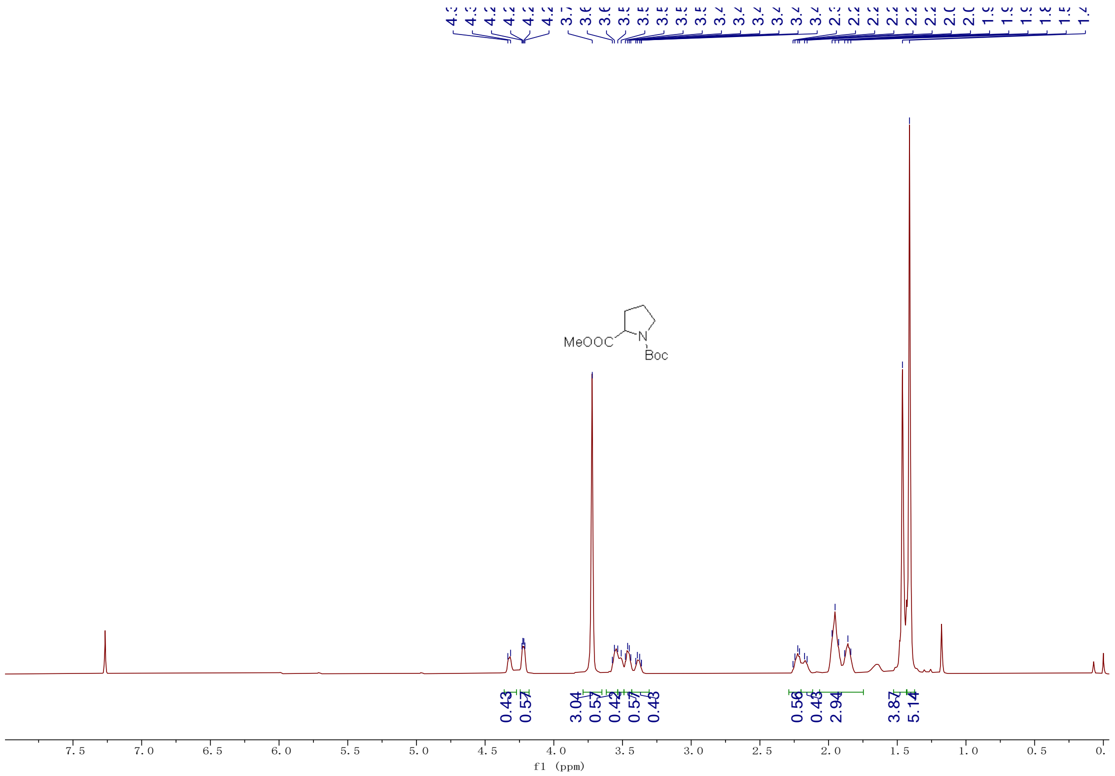
tert-Butyl piperidine-1-carboxylate (4a)



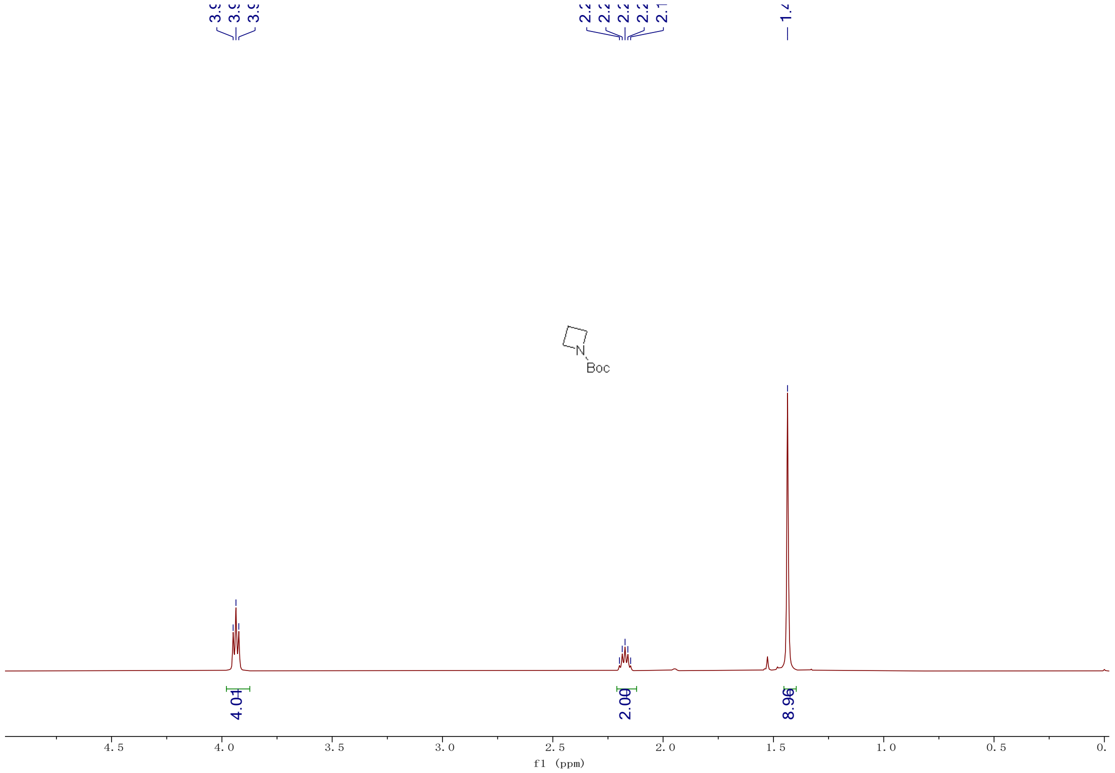
Benzyl piperidine-1-carboxylate (4b)



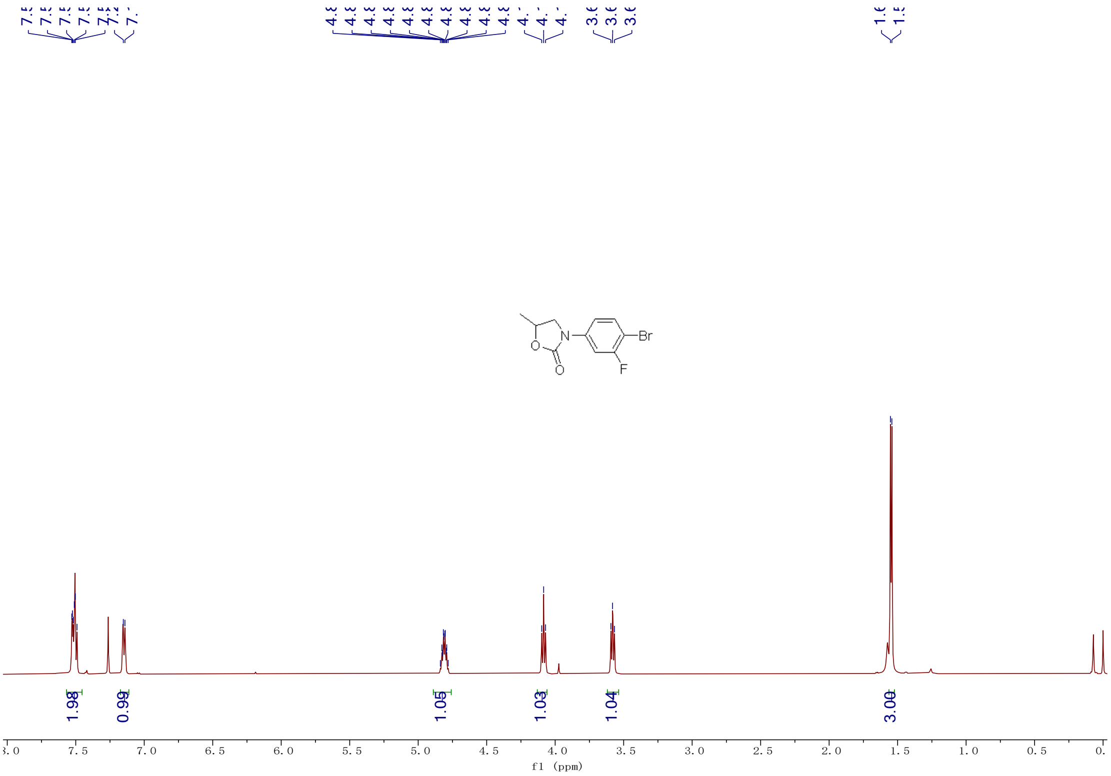
1-(*tert*-Butyl) 2-methyl pyrrolidine-1,2-dicarboxylate (4c)



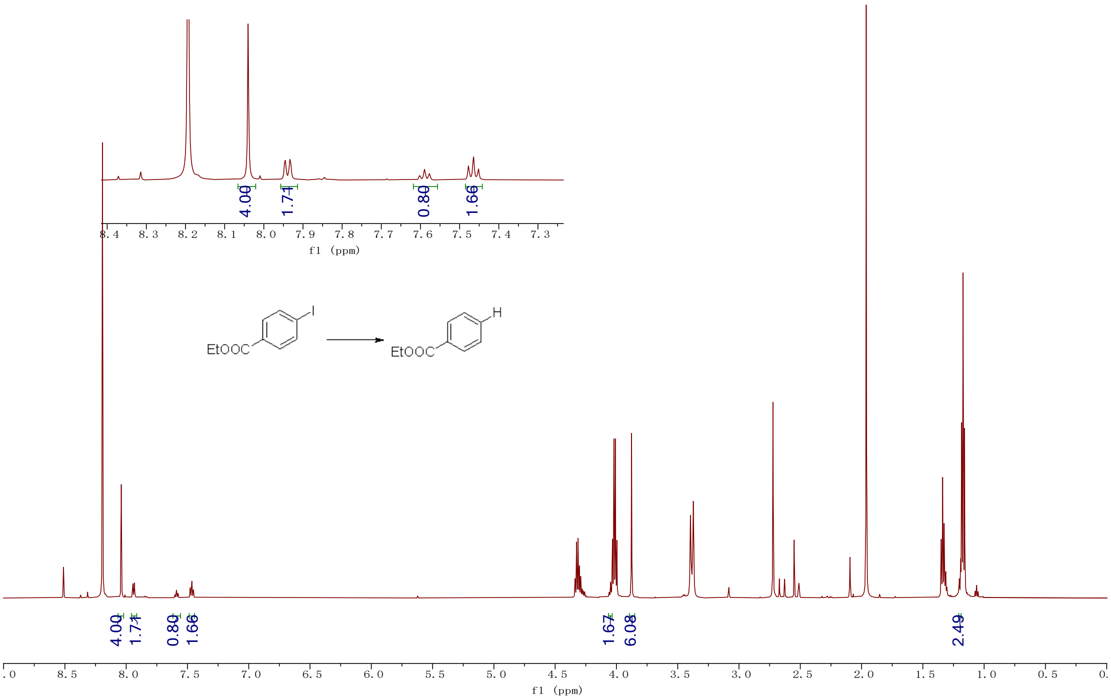
tert-butyl azetidine-1-carboxylate (4d)



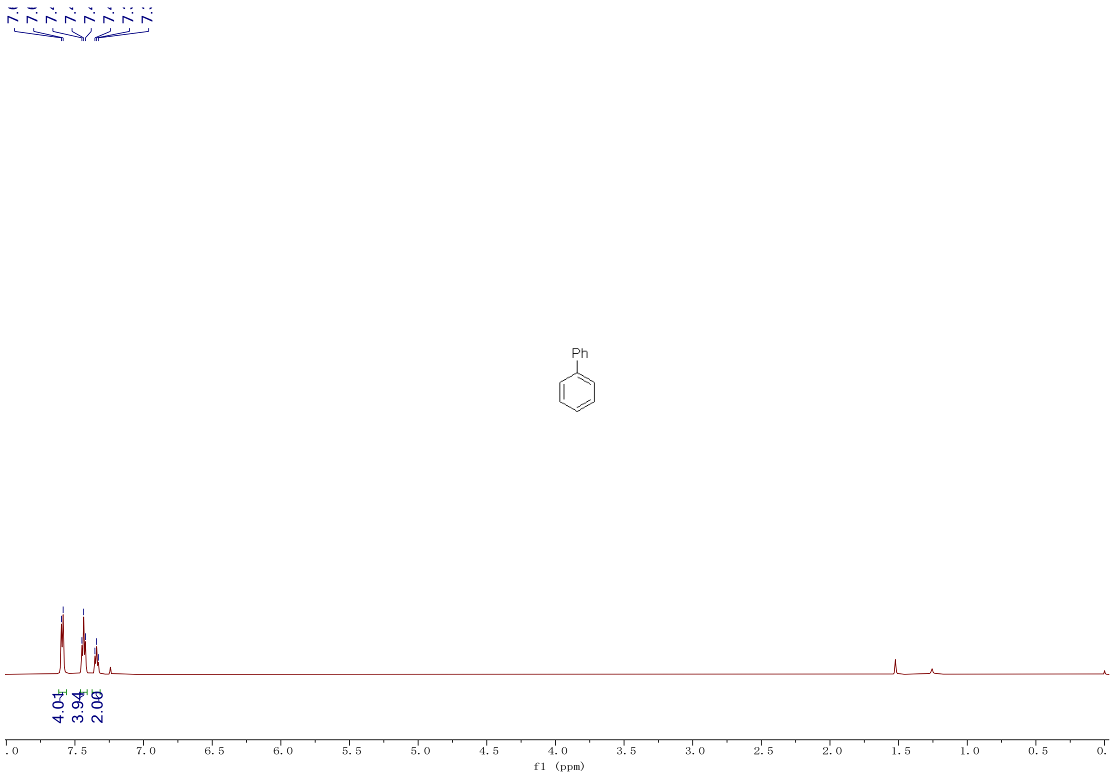
3-(4-bromo-3-fluorophenyl)-5-methyloxazolidin-2-one (4e)



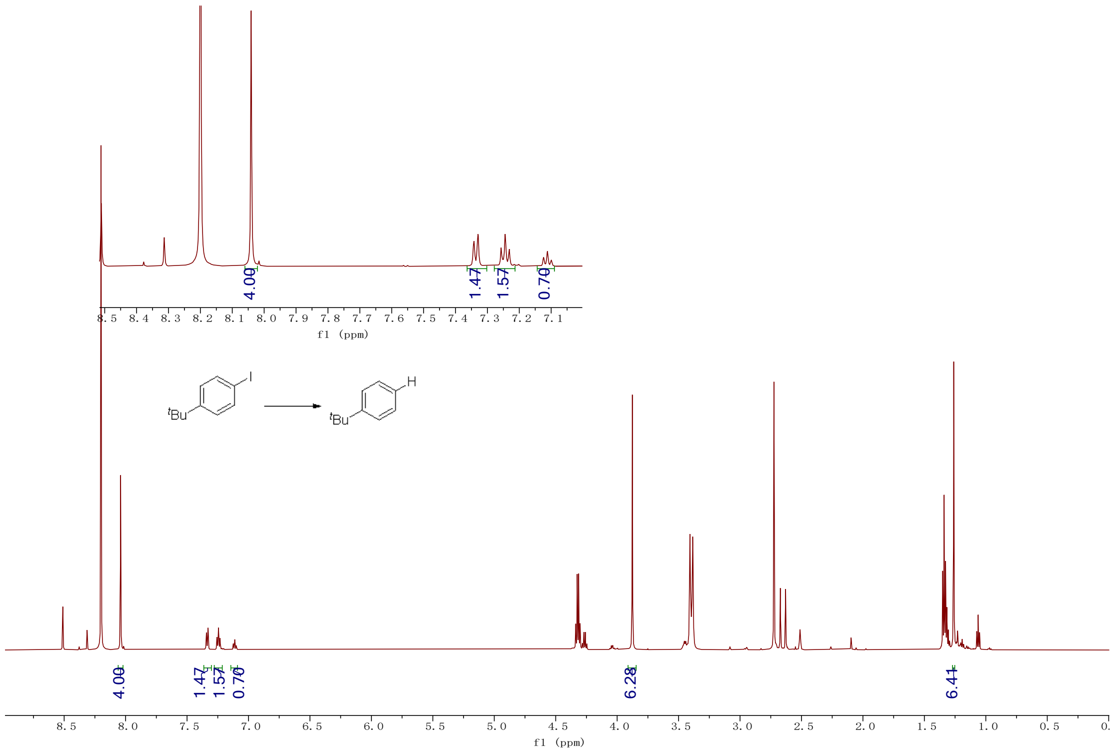
Ethyl 4-iodobenzoate (3f)



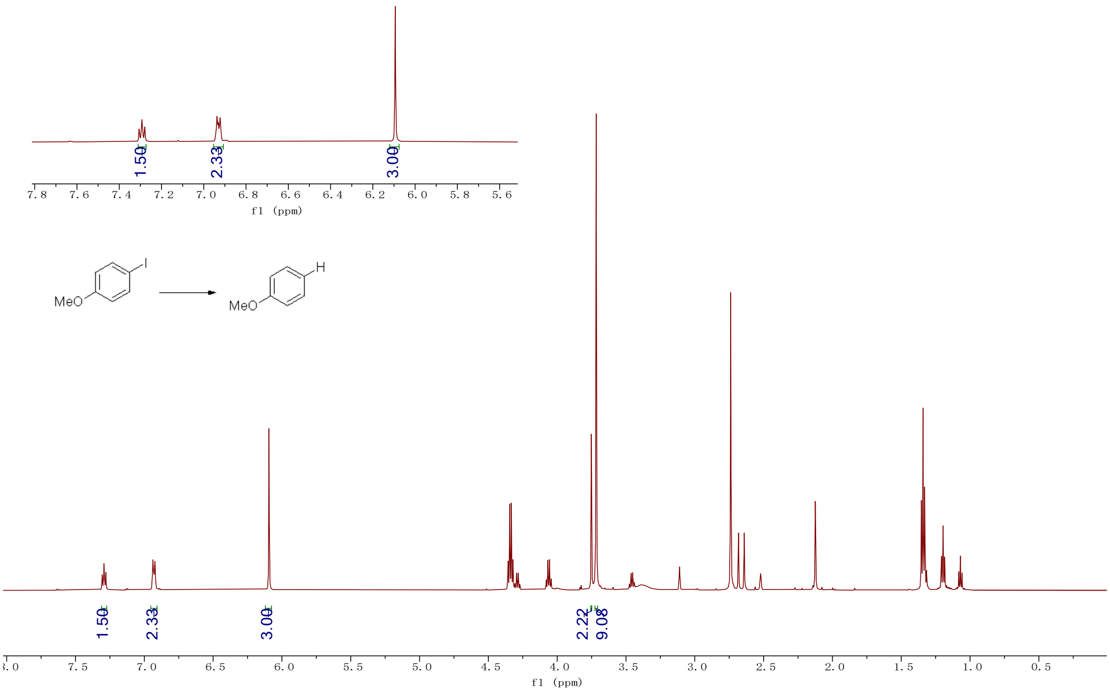
1,1'-Biphenyl (4g)



1-(*tert*-Butyl)-4-iodobenzene (4h)



1-Iodo-4-methoxybenzene (4i)



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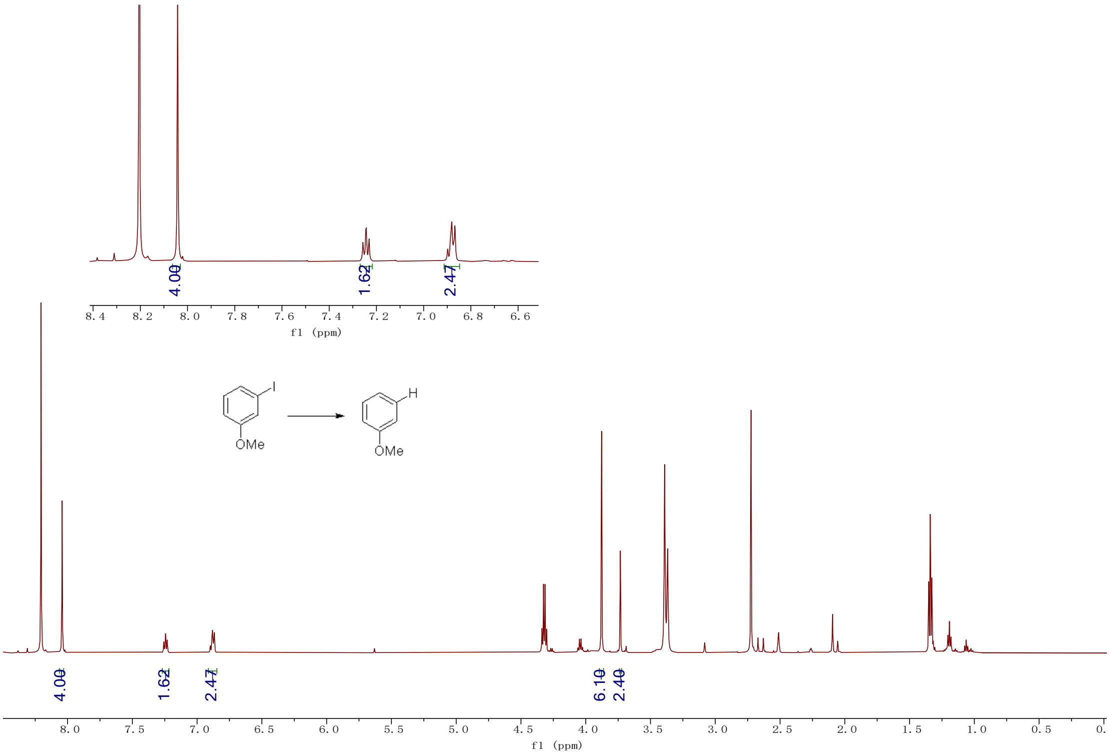
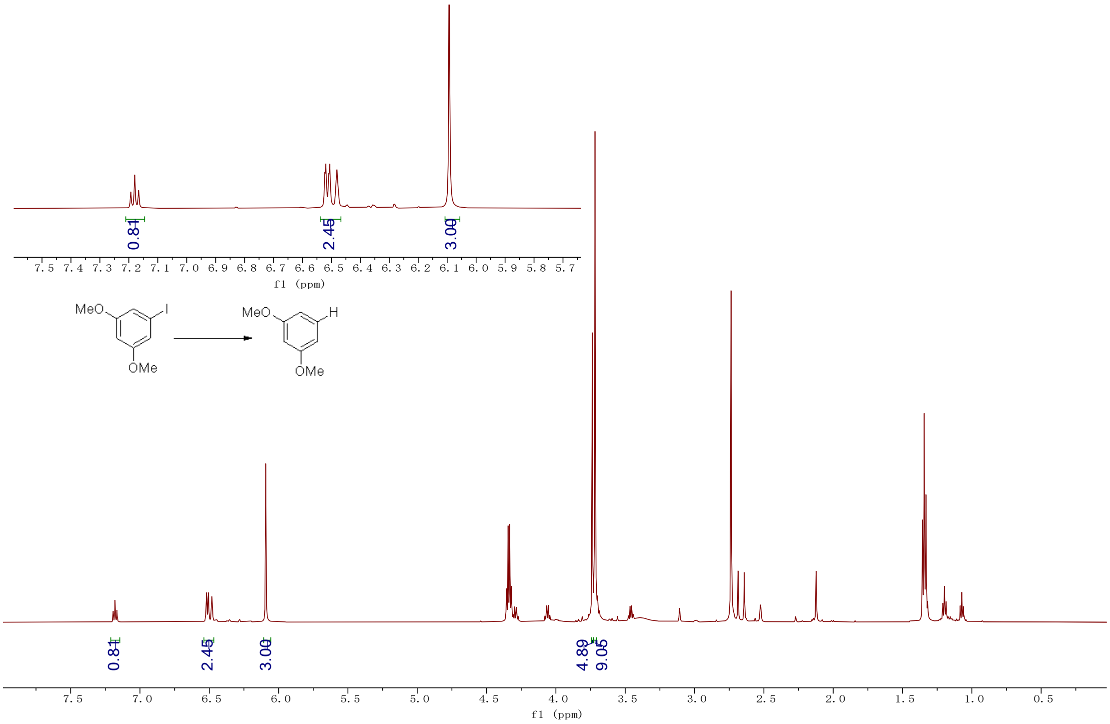
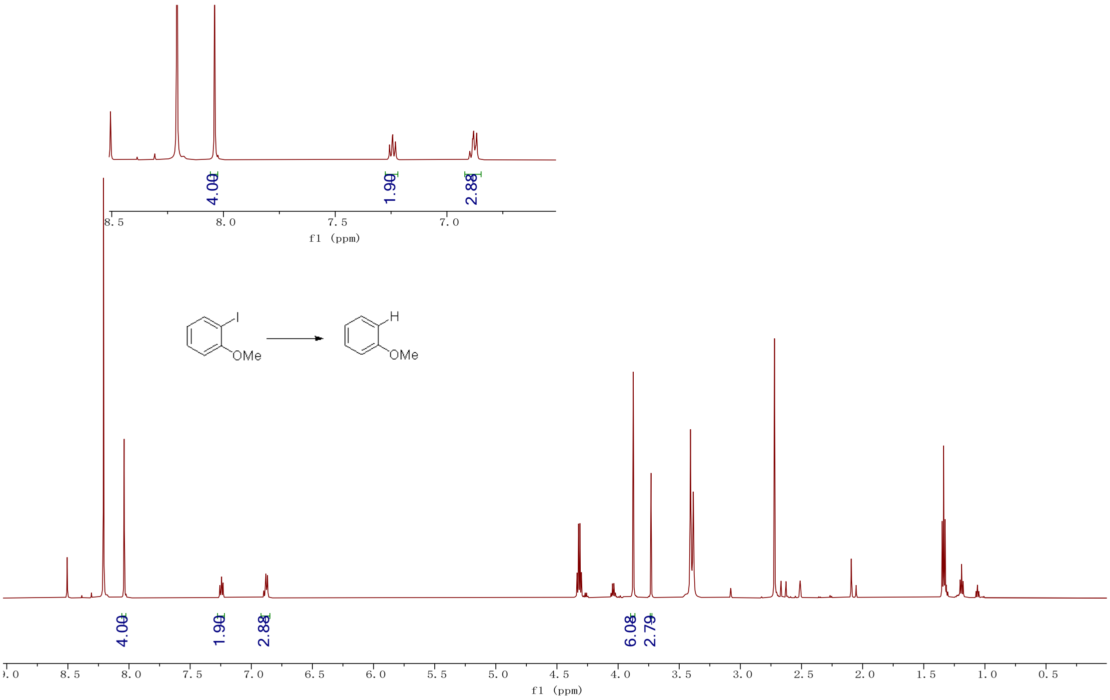


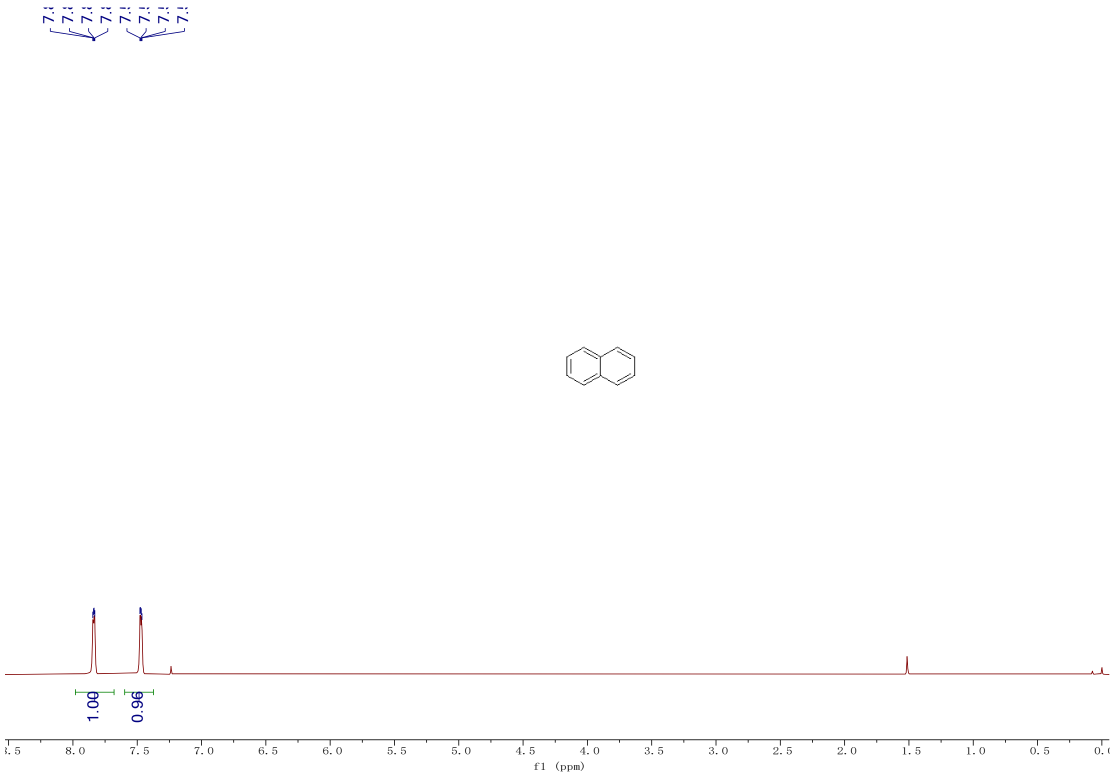
1-Iodo-3,5-dimethoxybenzene (4k)



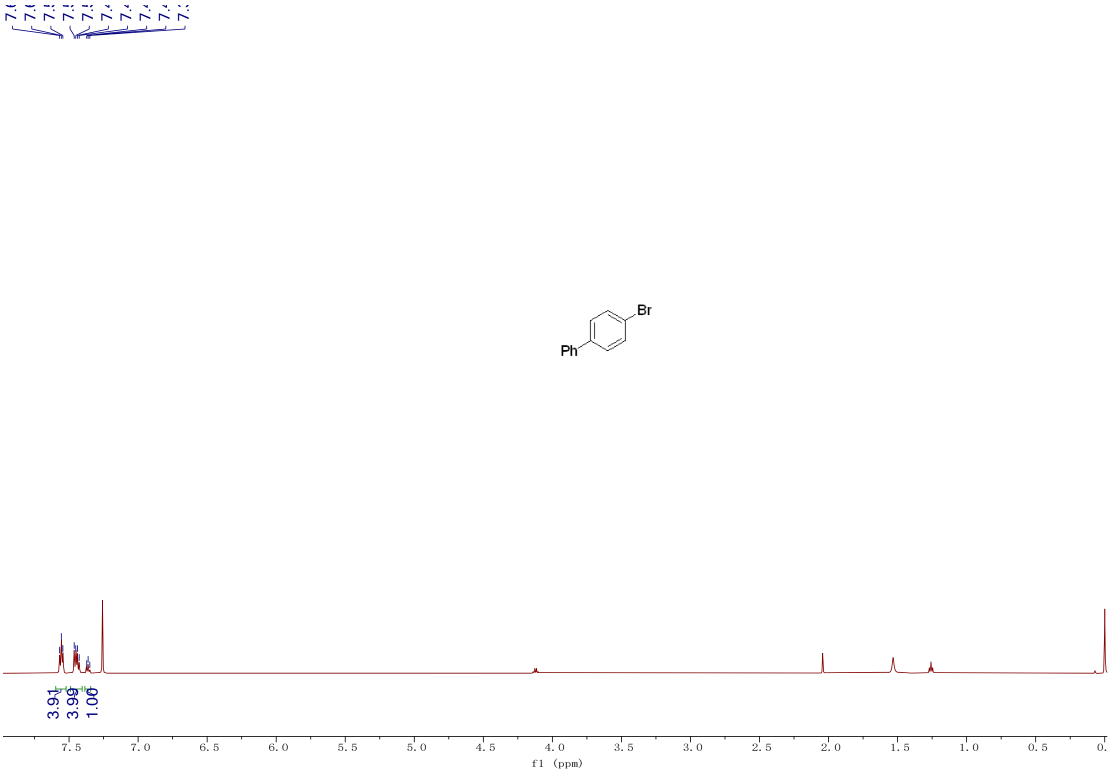
1-Iodo-2-methoxybenzene (4i)



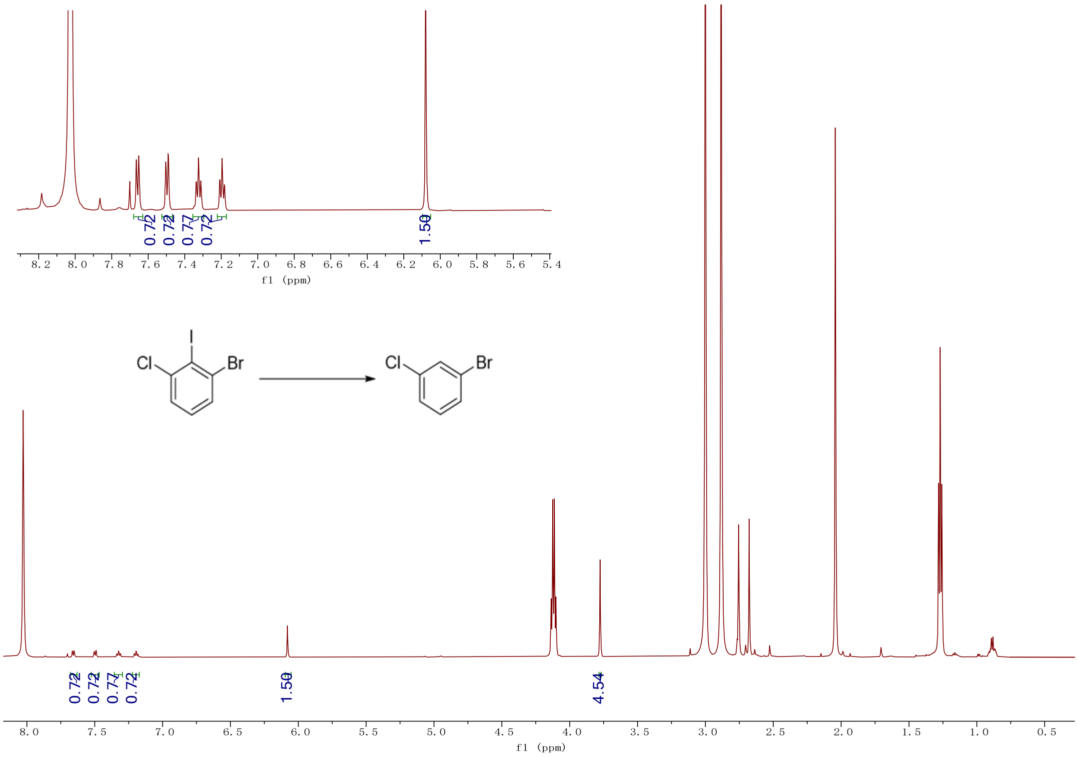
Naphthalene (4m)



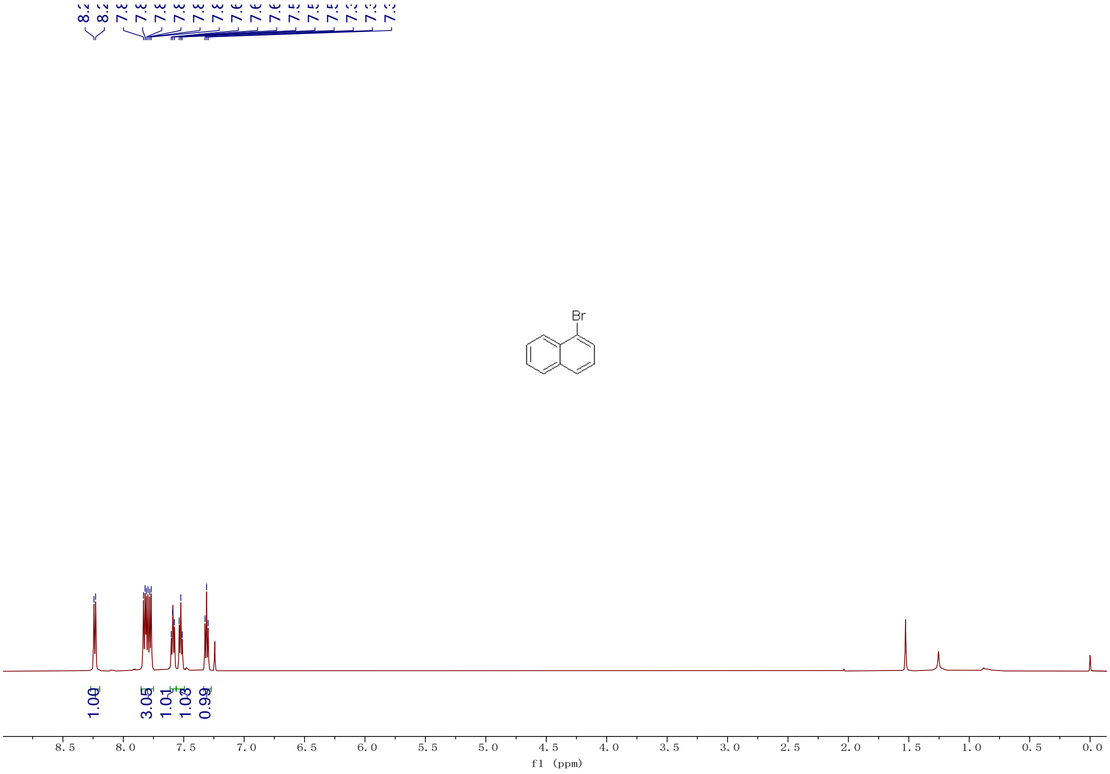
4-Bromo-1,1'-biphenyl (4n)



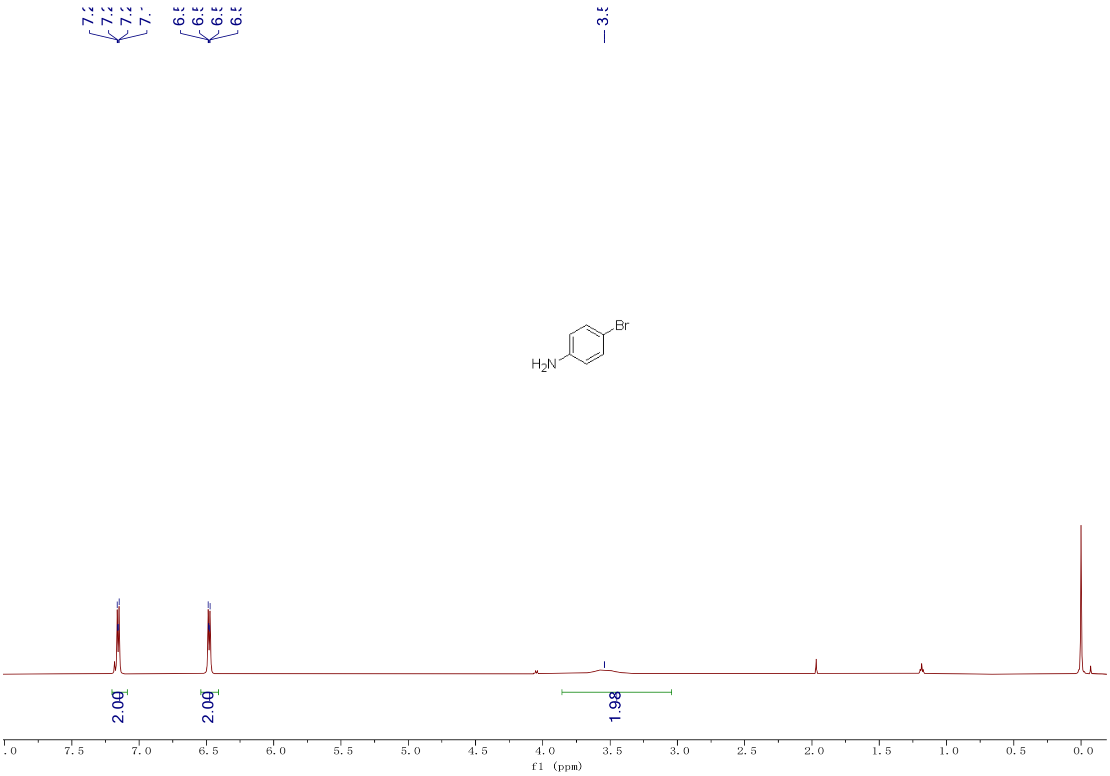
2-Bromo-1-chloro-3-iodobenzene (4o)



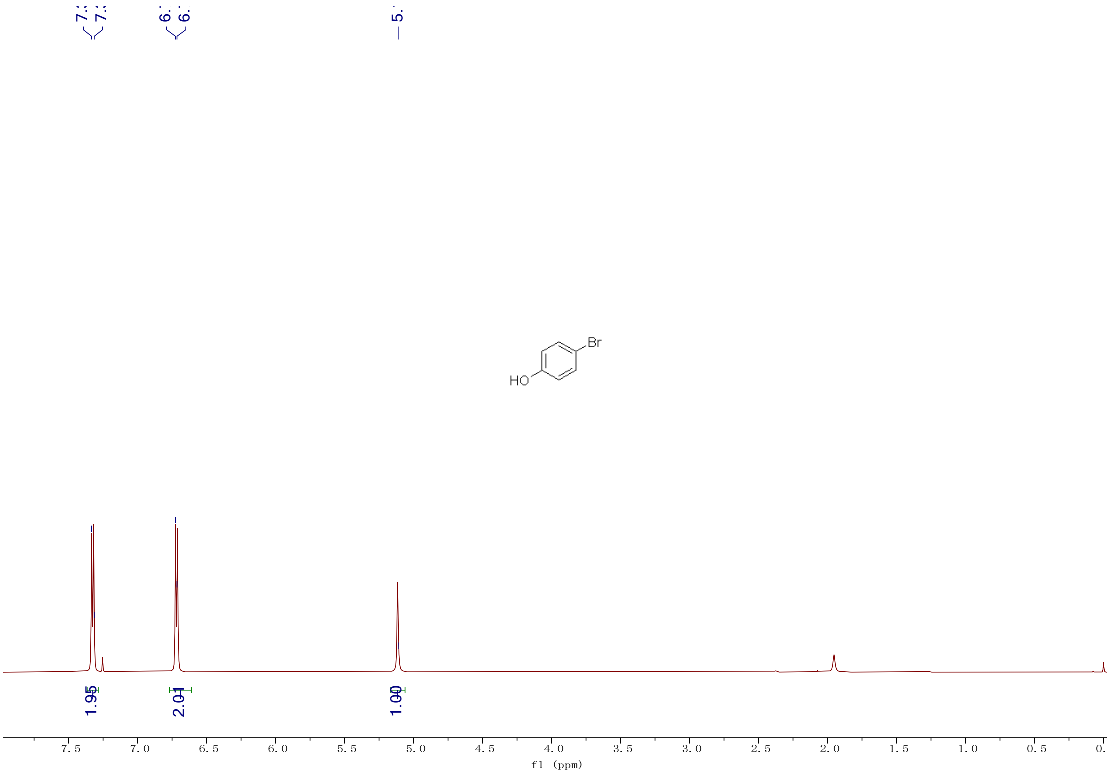
1-Bromonaphthalene (4p)



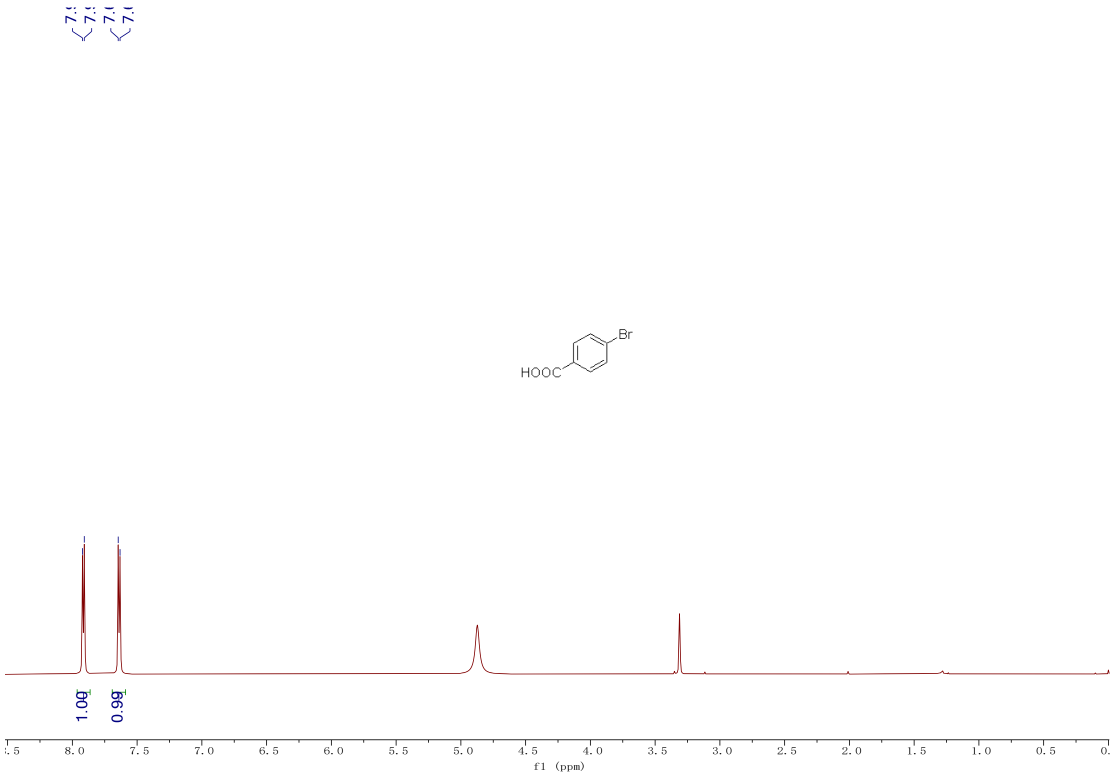
4-Bromoaniline (4q)



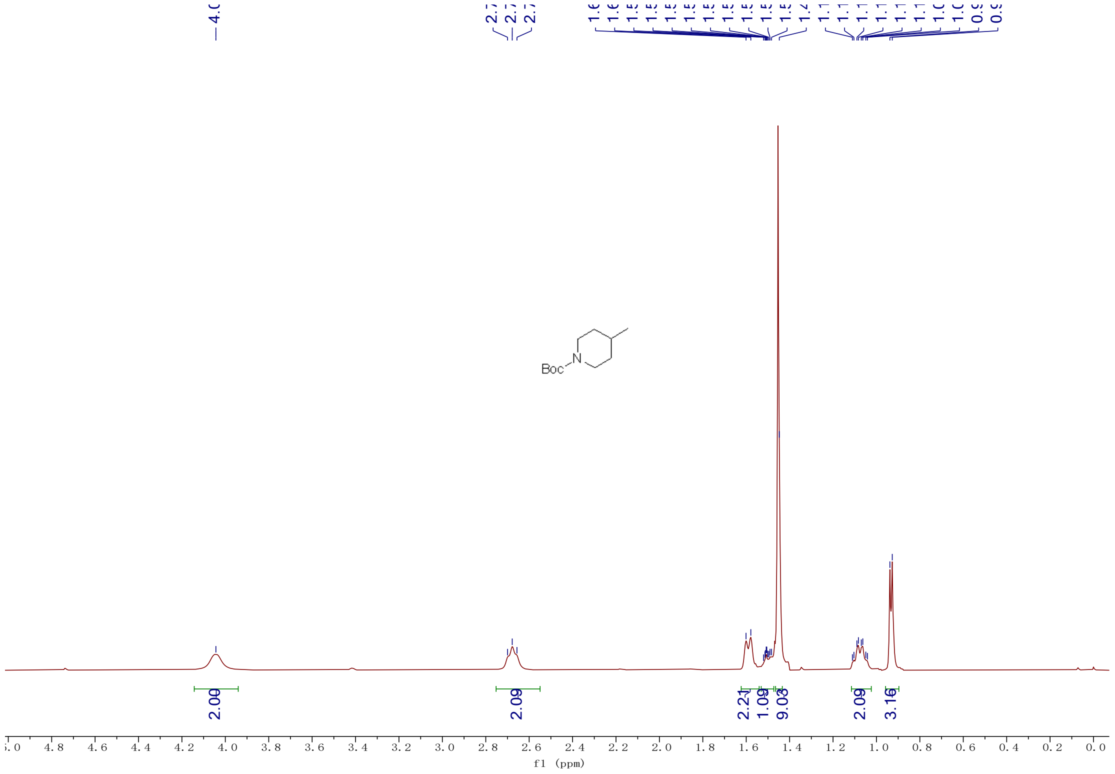
4-Bromophenol (4r)



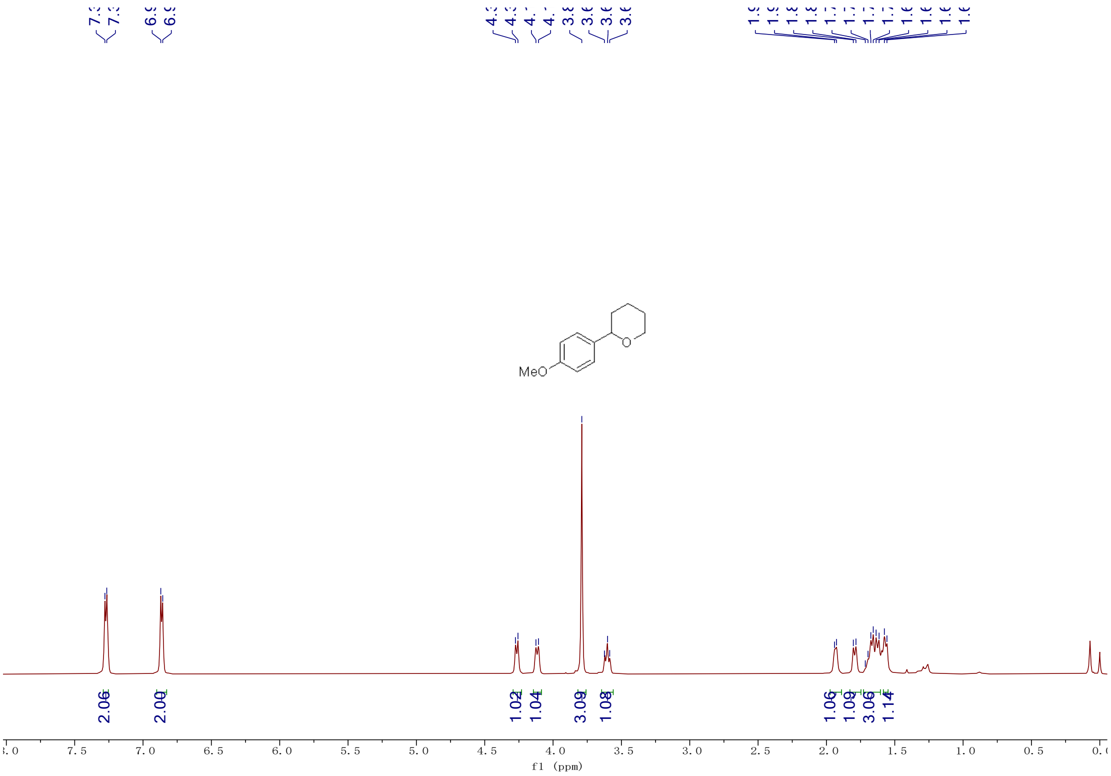
4-Bromobenzoic acid (4s)



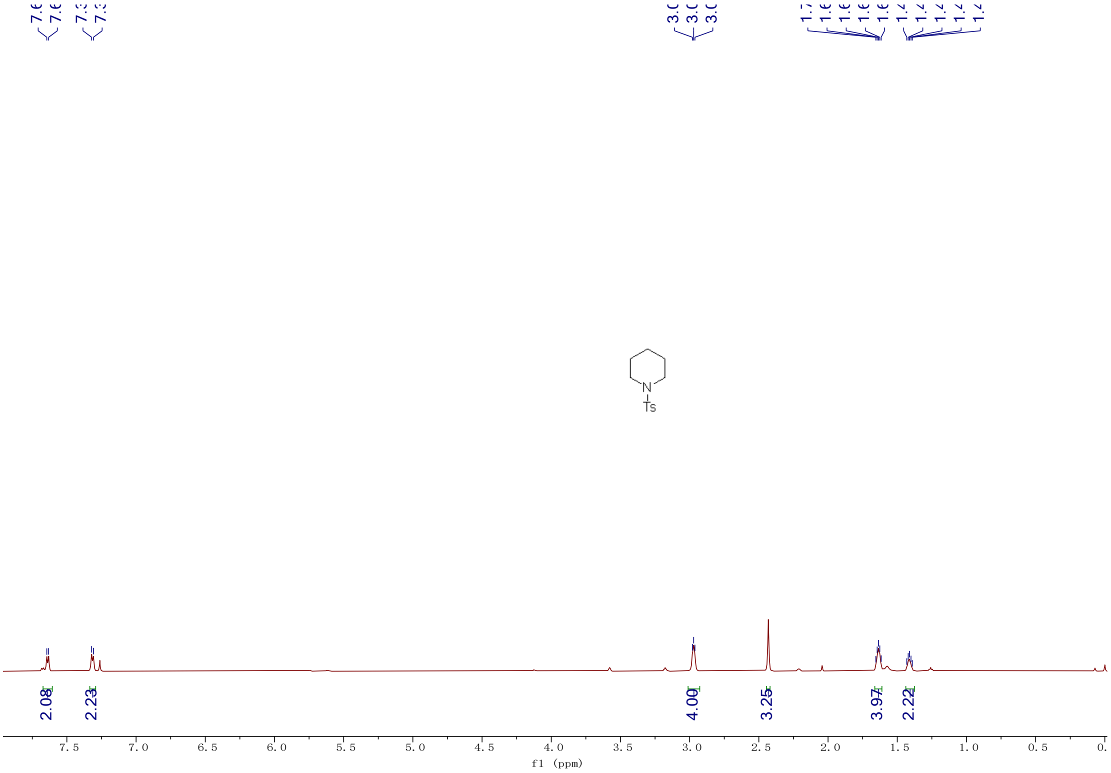
tert-Butyl 4-methylpiperidine-1-carboxylate (4u)



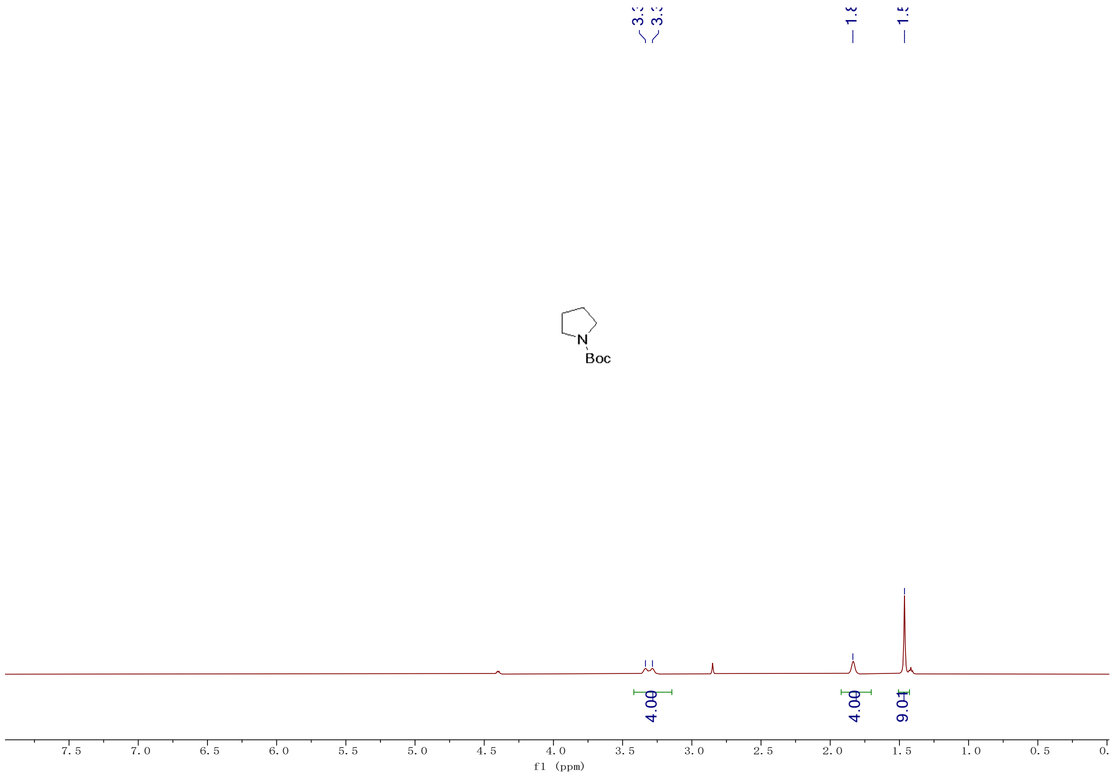
2-(4-Methoxyphenyl)tetrahydro-2H-pyran (4v)



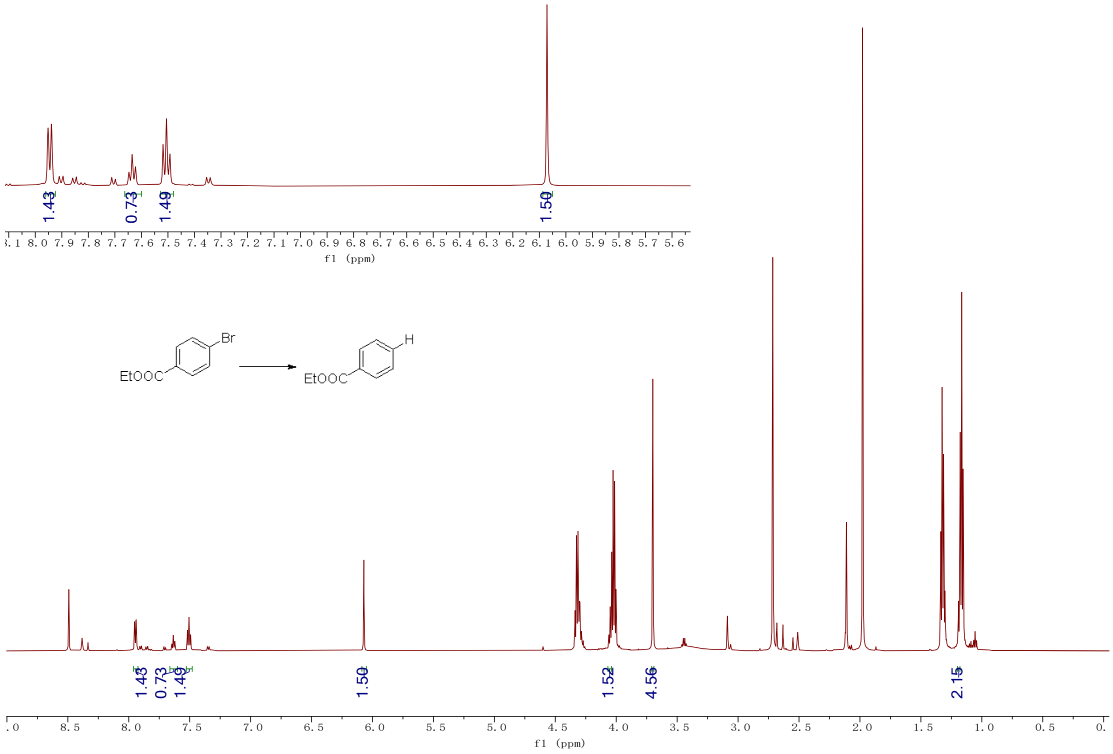
1-Tosylpiperidine (4w)



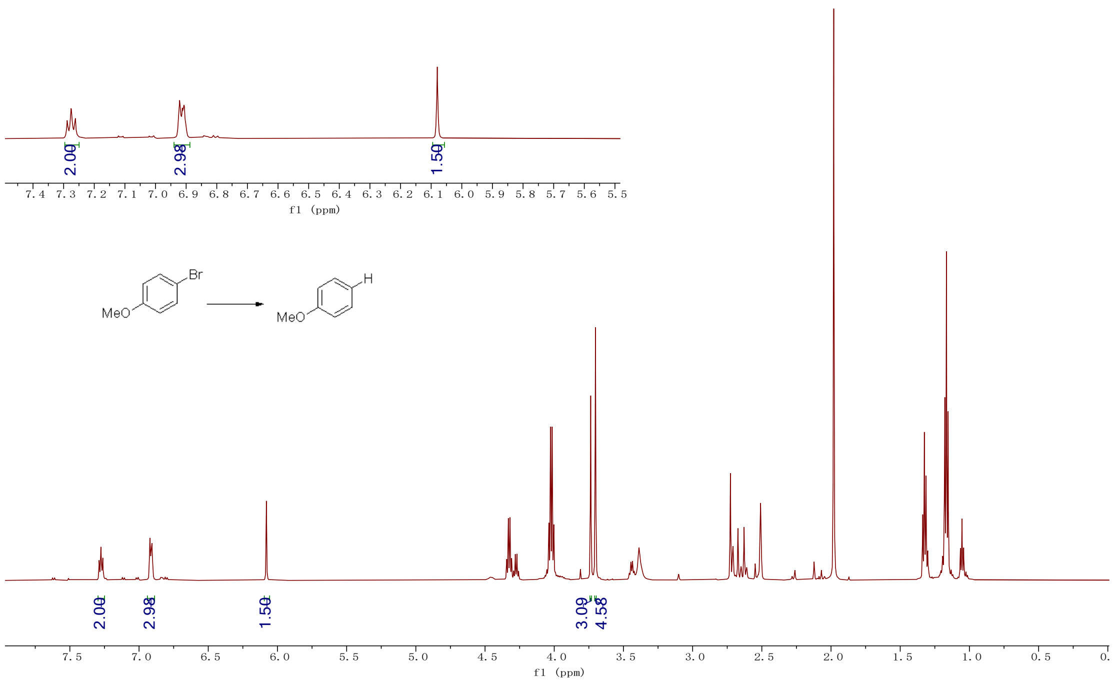
tert-Butyl pyrrolidine-1-carboxylate (4x)



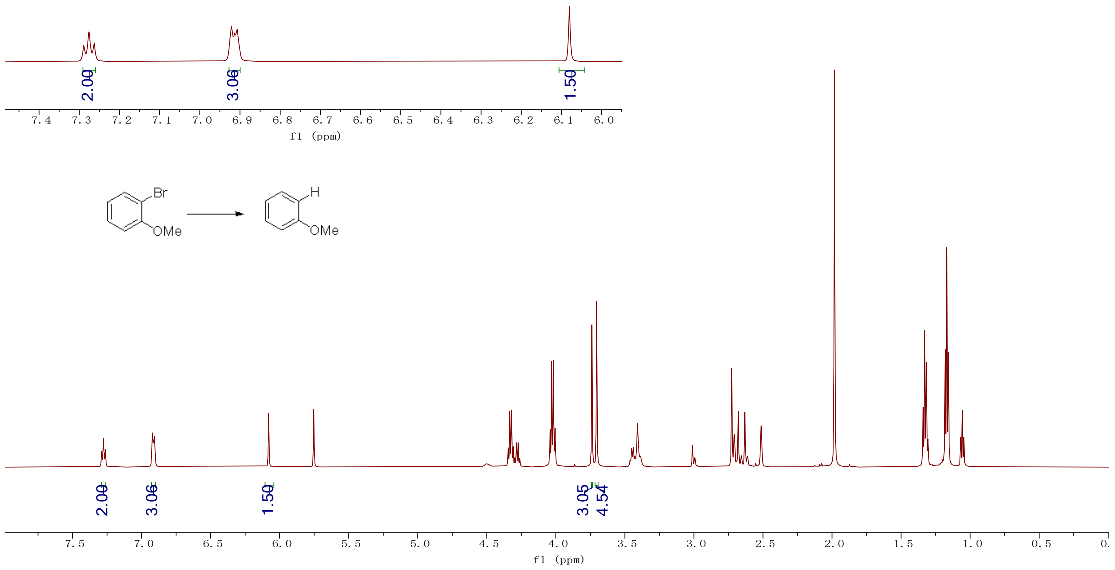
Ethyl 4-bromobenzoate (4ae)



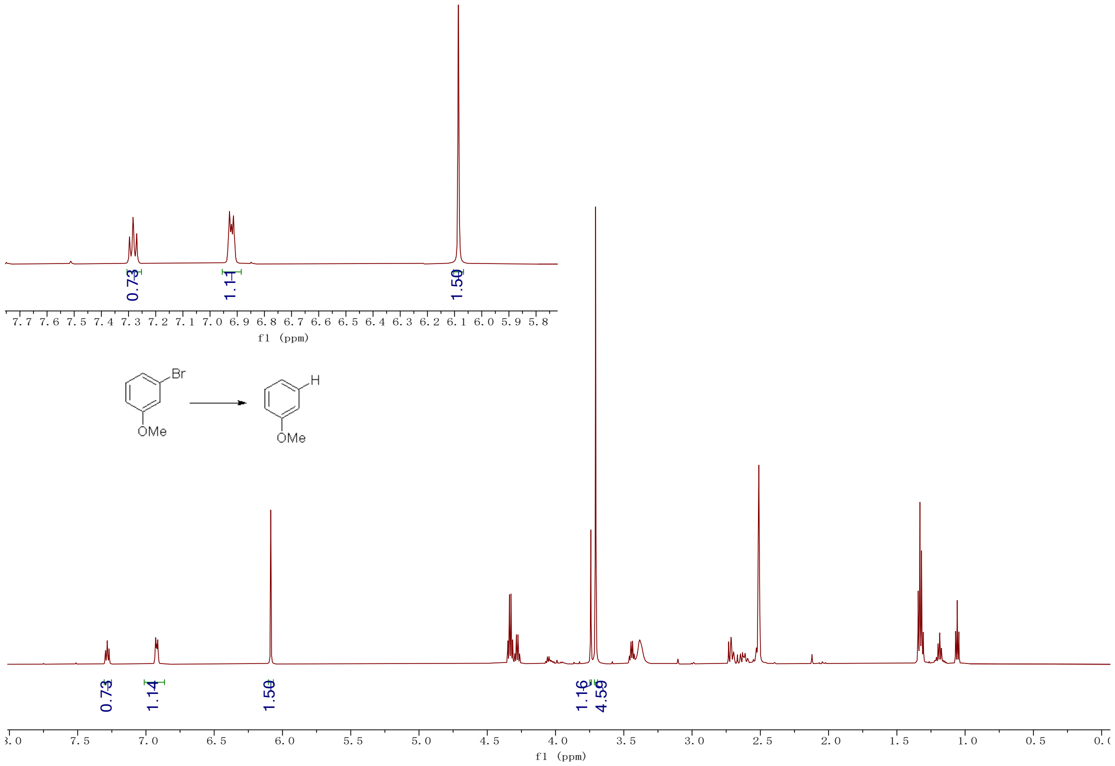
1-Bromo-4-methoxybenzene (4ae)



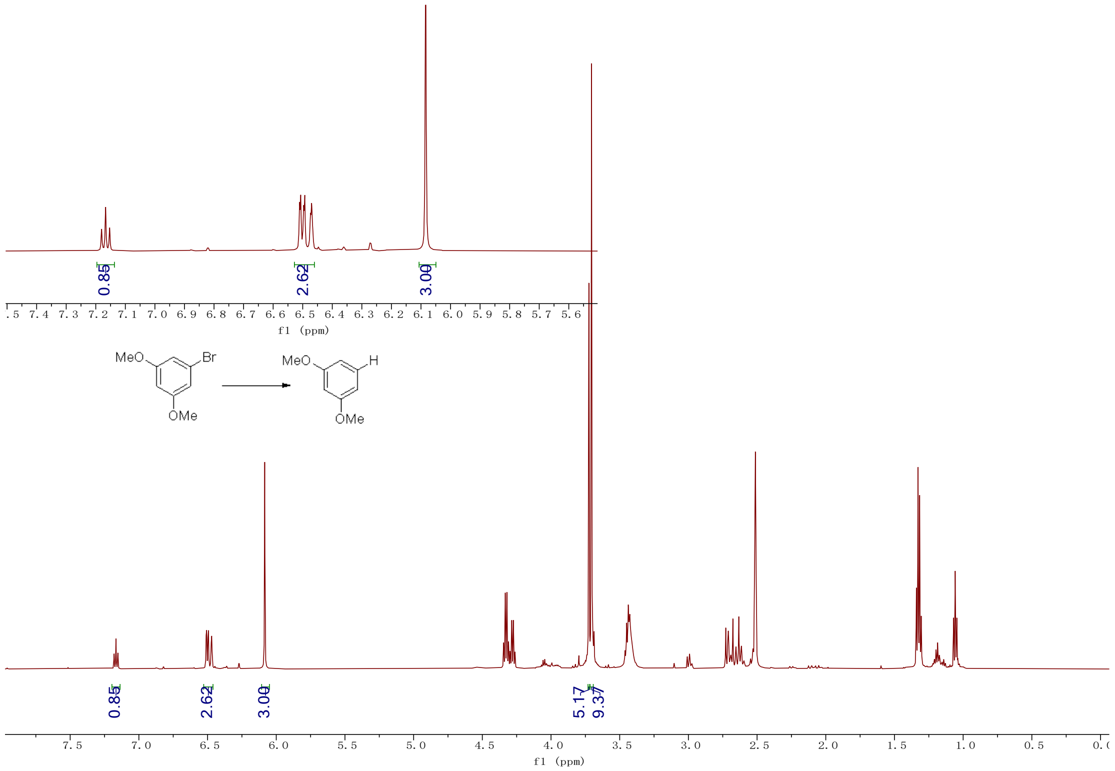
1-Bromo-2-methoxybenzene (4af)



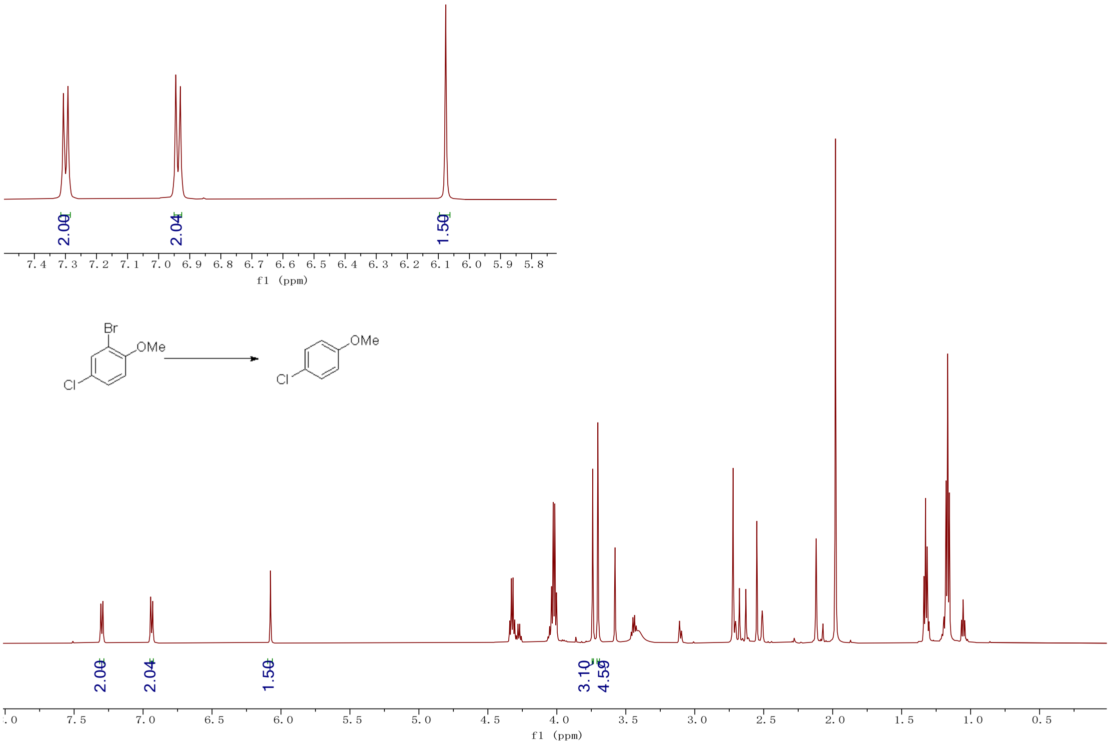
1-Bromo-3-methoxybenzene (4ag)



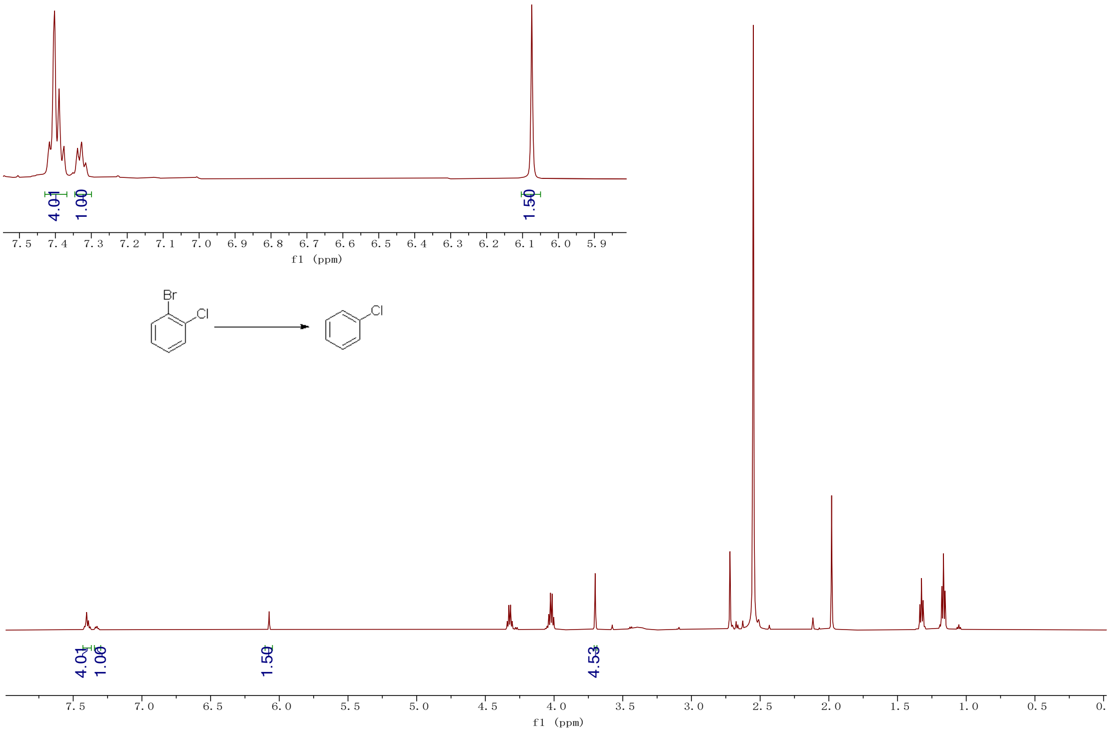
1-Bromo-3,5-dimethoxybenzene (4ah)



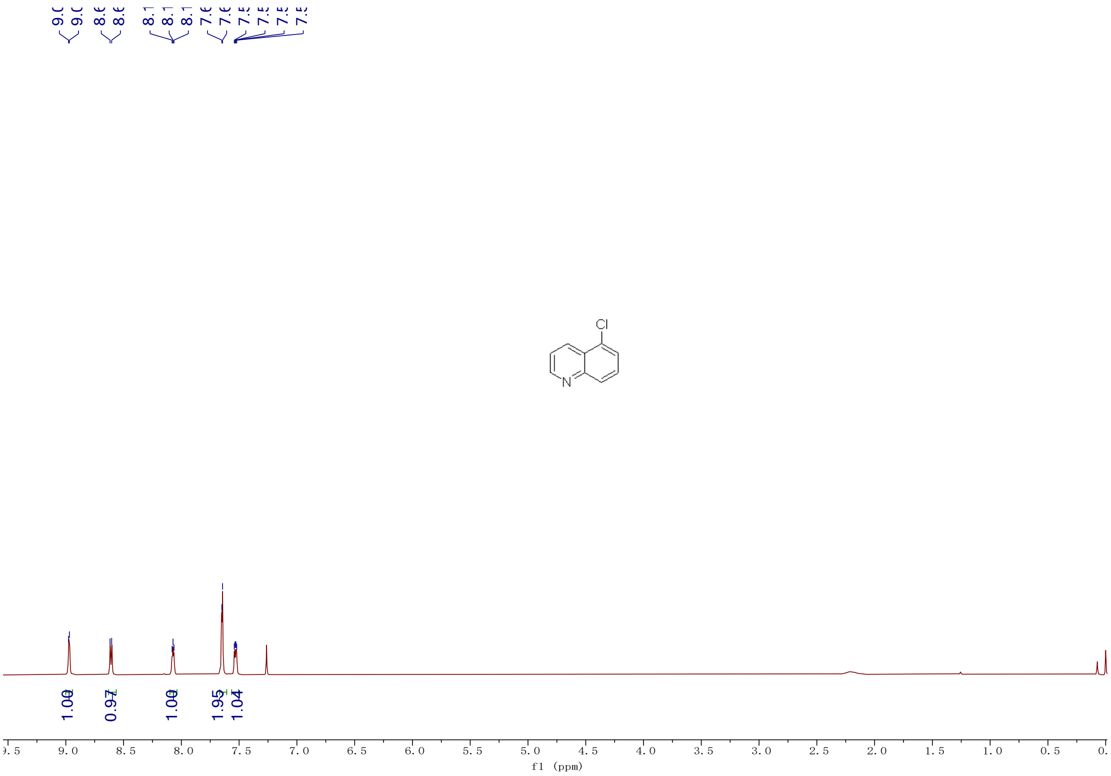
2-Bromo-4-chloro-1-methoxybenzene (4aj)



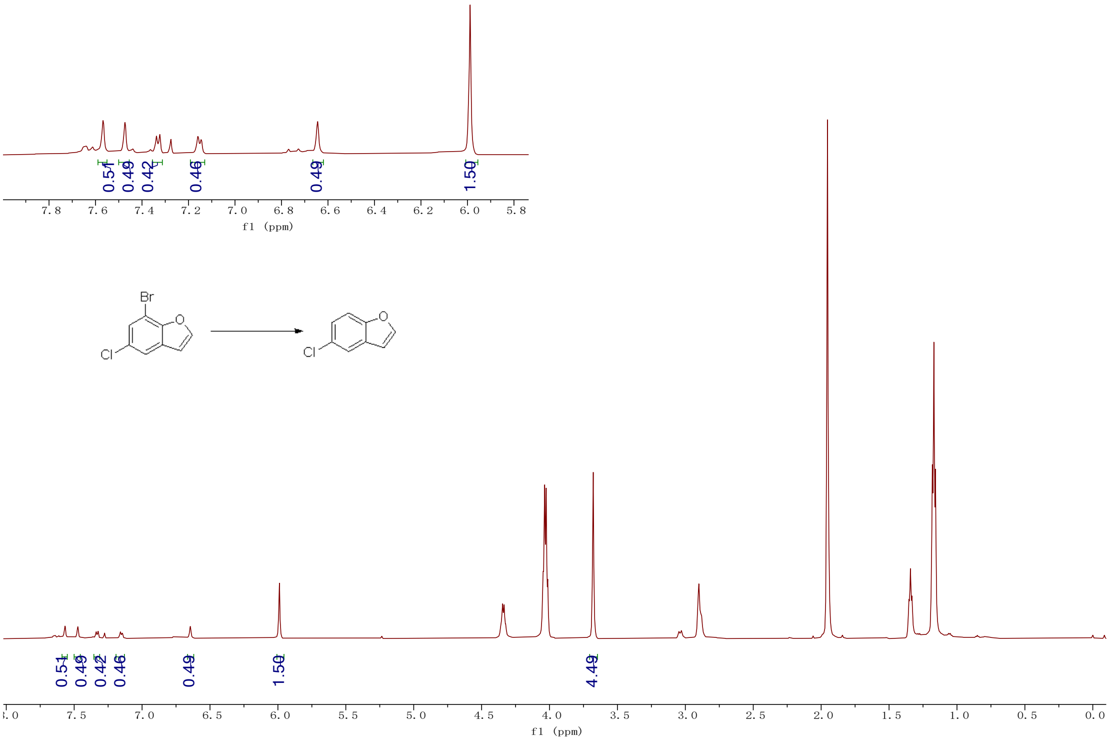
1-Bromo-2-chlorobenzene (4ak)



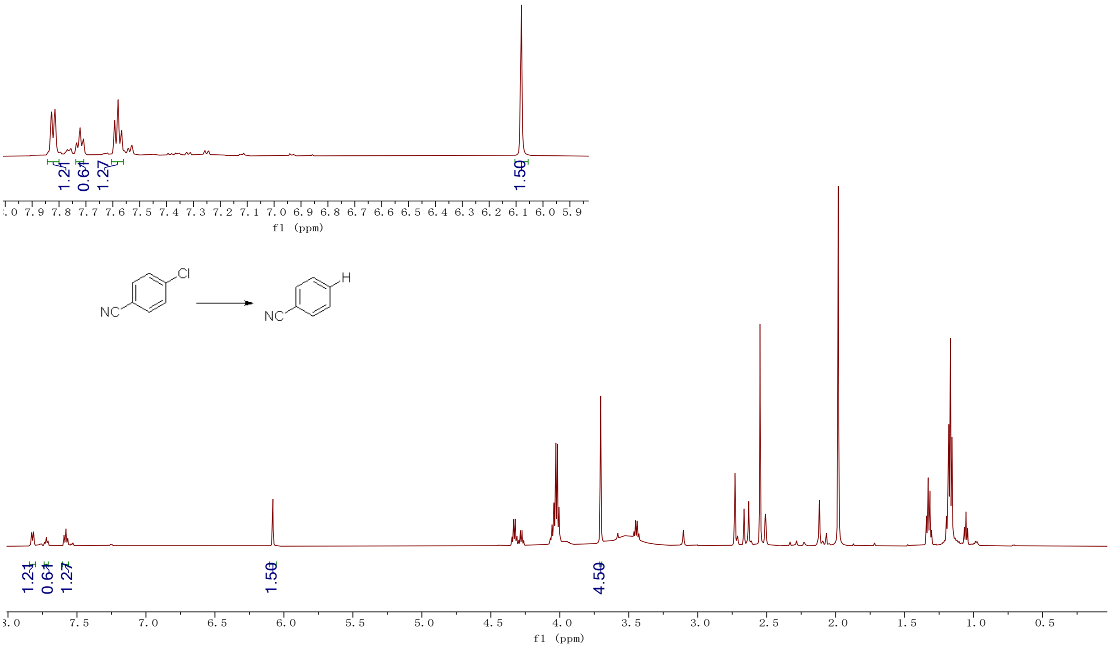
5-Chloroquinoline (4al)



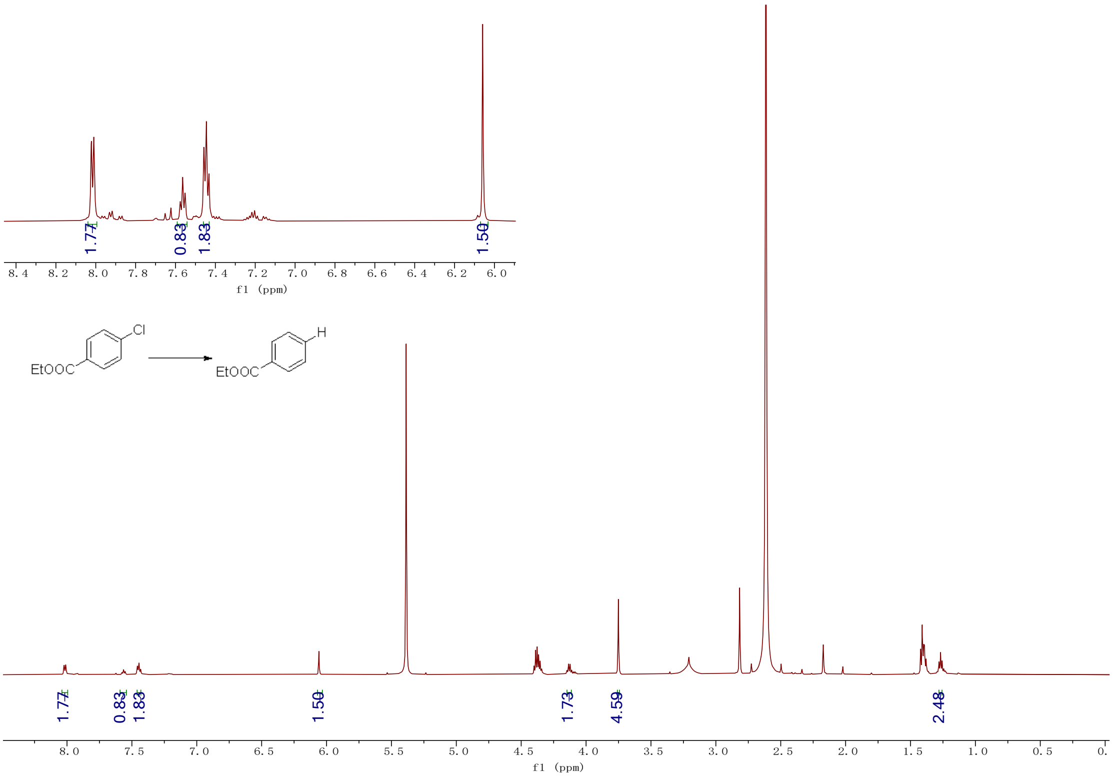
7-Bromo-5-chlorobenzofuran (4am)



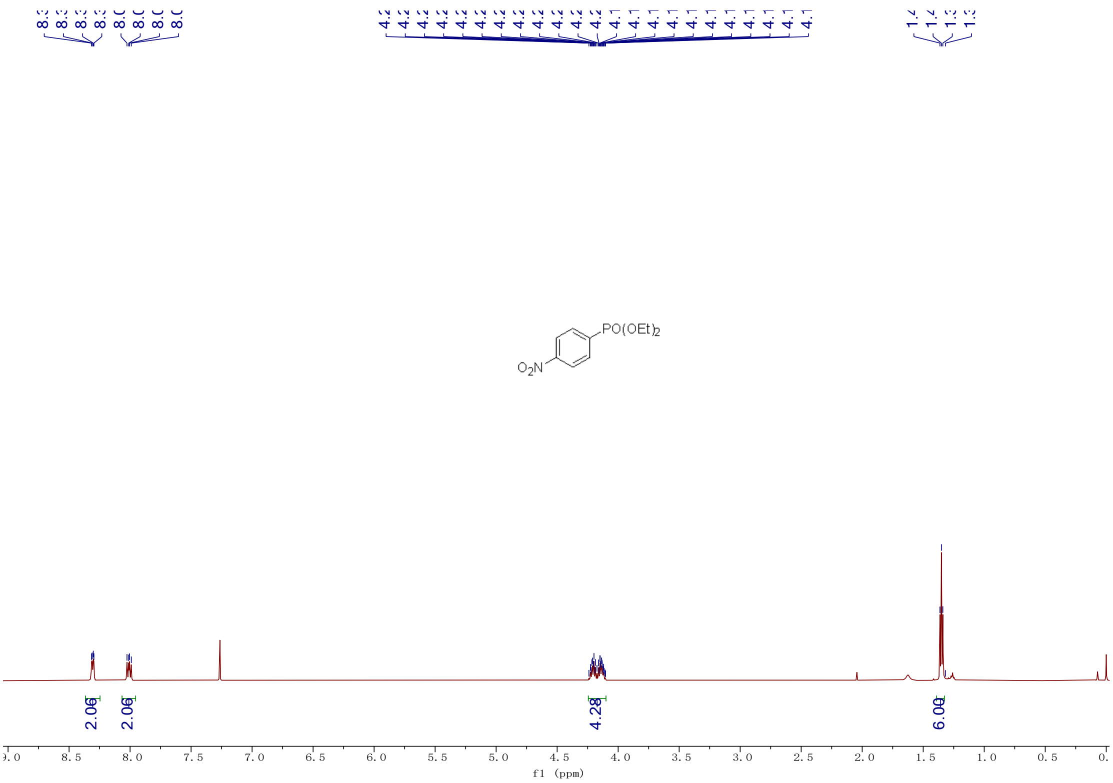
4-Chlorobenzonitrile (4ap)



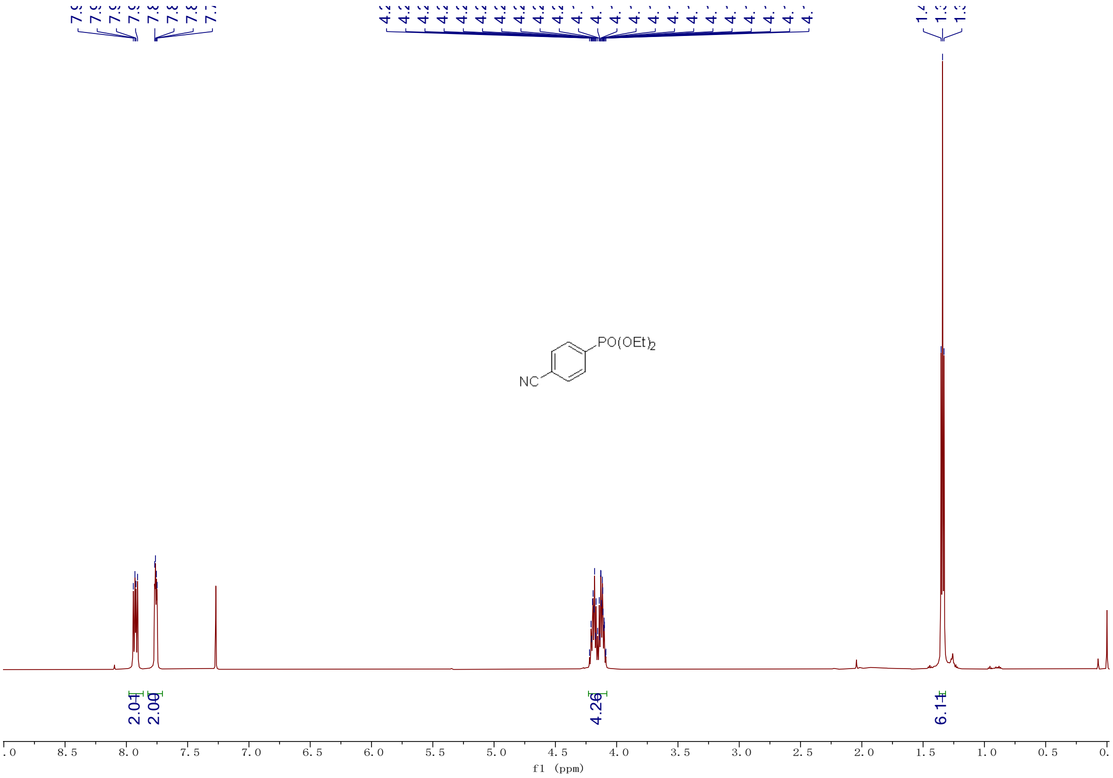
Ethyl 4-chlorobenzoate (4aq)



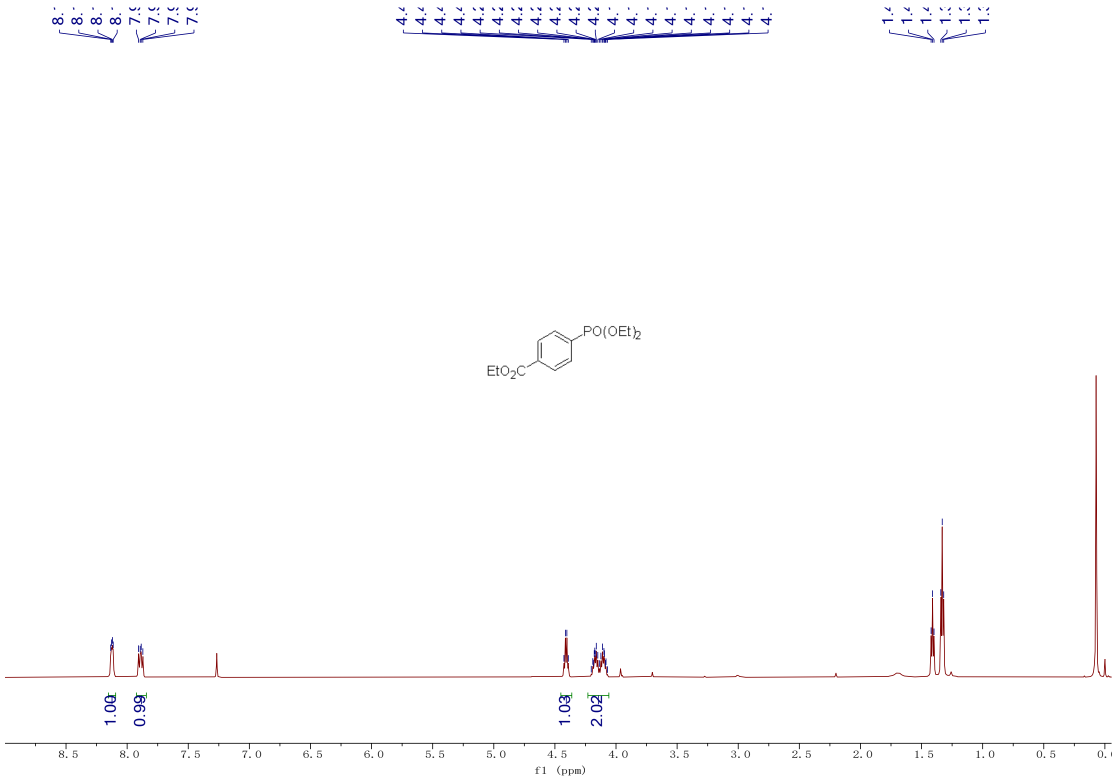
Diethyl (4-nitrophenyl)phosphonate (5a)



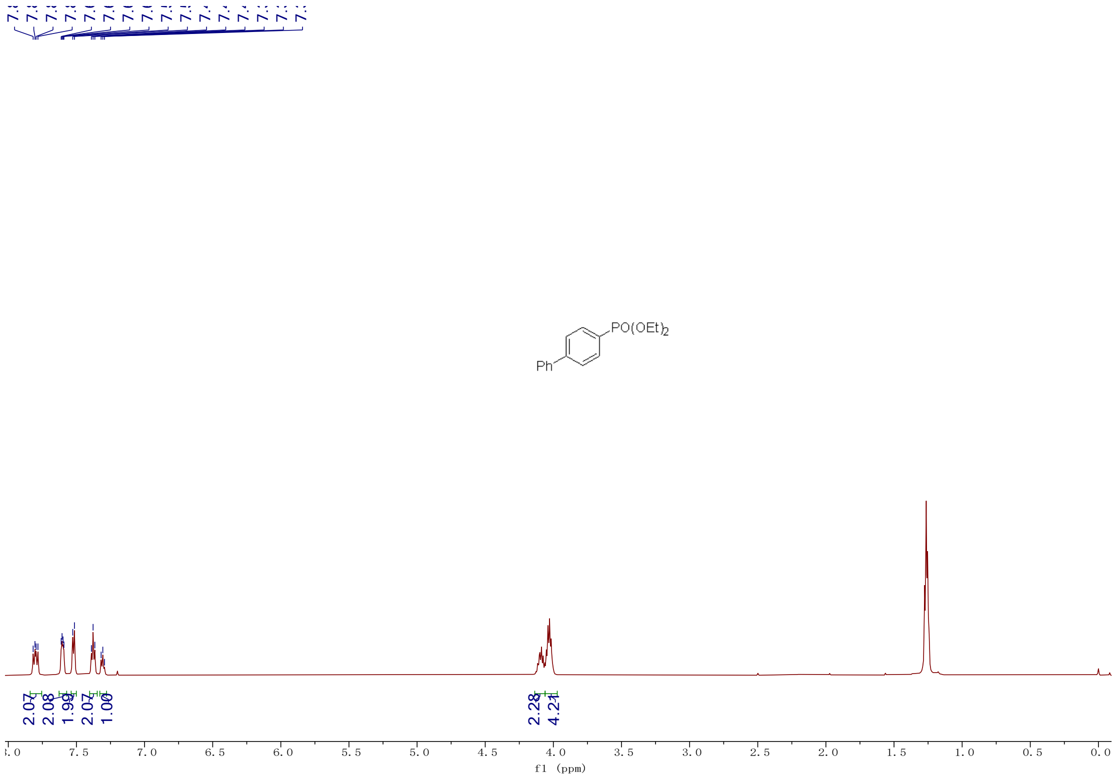
Diethyl (4-cyanophenyl)phosphonate (5b)



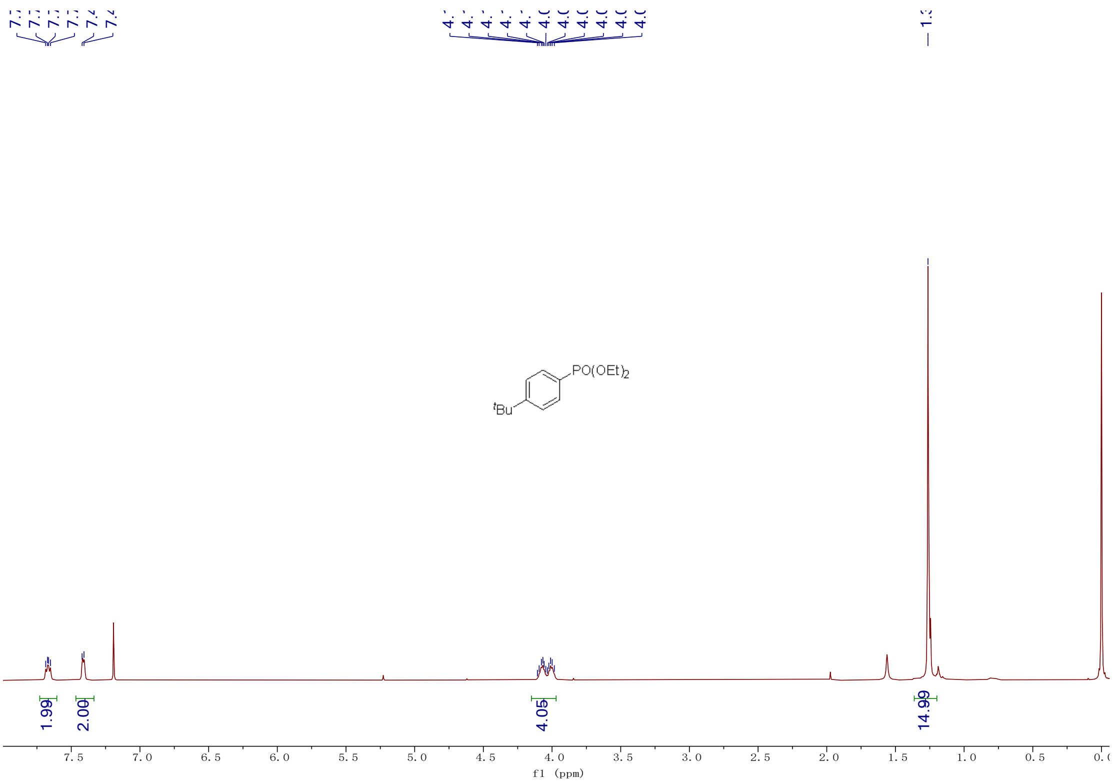
Ethyl 4-(diethoxyphosphoryl)benzoate (5c)



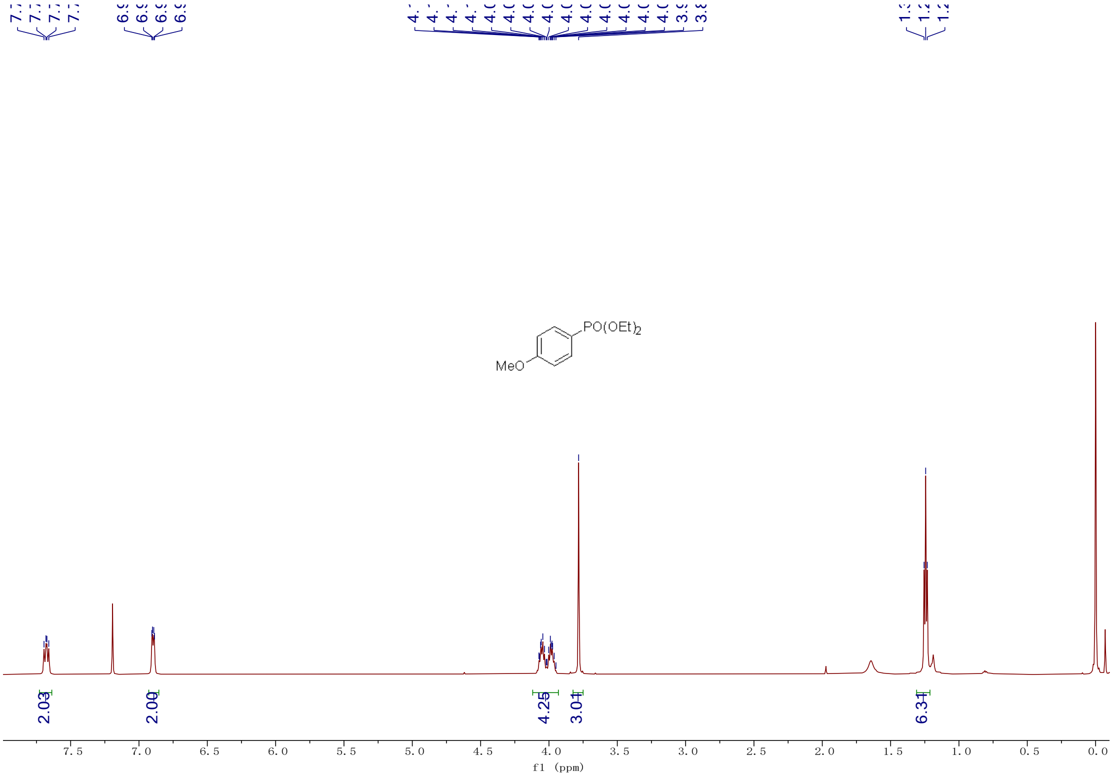
Diethyl [1,1'-biphenyl]-4-ylphosphonate (5d)



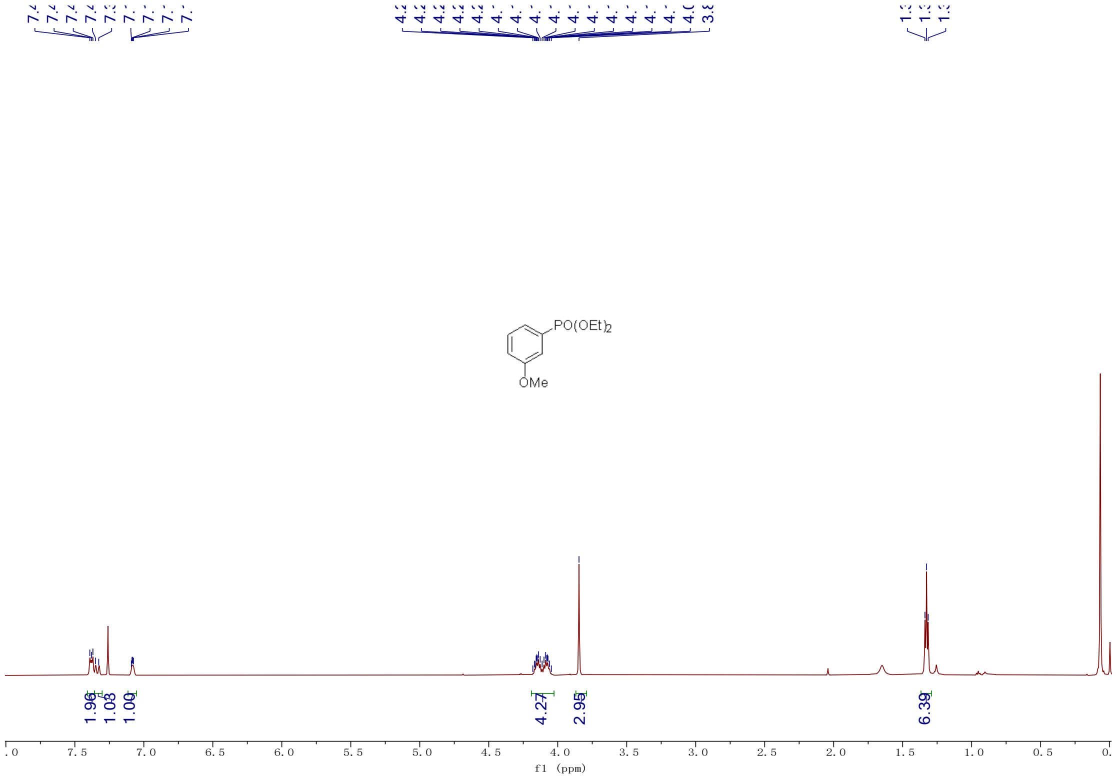
Diethyl (4-(*tert*-butyl)phenyl)phosphonate (5e)



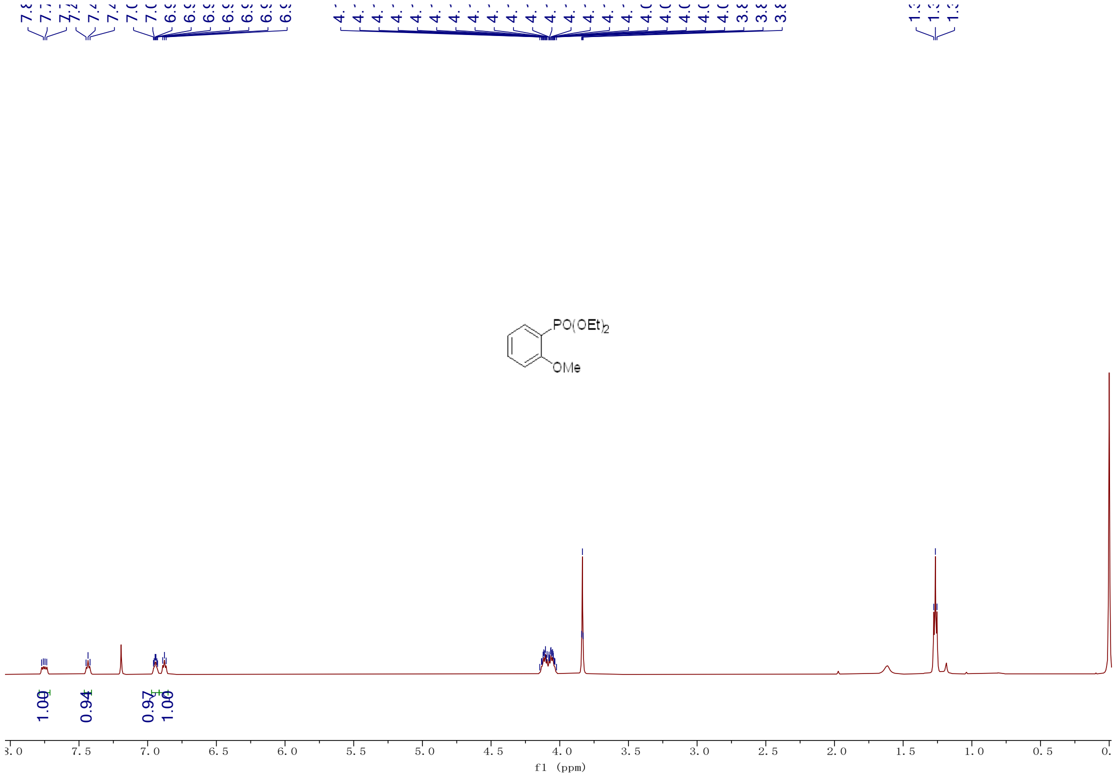
Diethyl (4-methoxyphenyl)phosphonate (5f)



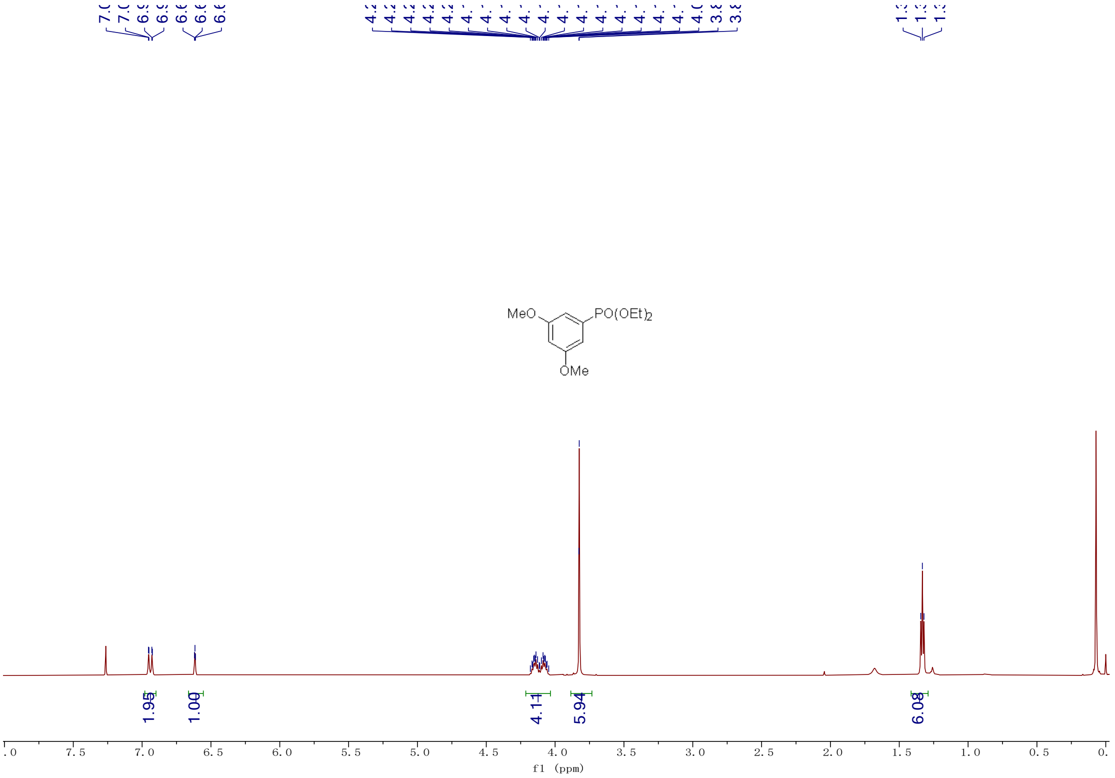
Diethyl (3-methoxyphenyl)phosphonate (5g)



Diethyl (2-methoxyphenyl)phosphonate (5h)



Diethyl (3,5-dimethoxyphenyl)phosphonate (5i)



Diethyl naphthalen-1-ylphosphonate (5j)