Electronic Supplementary Information

Oxidative Esterification of Alcohols by Single-side Organically Decorated Anderson-type Chrome-based Catalyst

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[†] Electronic Supplementary Information (ESI) available: experimental conditions, supplementary table and NMR spectra. See DOI: 10.1039/x0xx00000x

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I. General information.

All reagents obtained from Sigma-Aldrich and Admas-beta were used without further purification. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ or DMSO-d_6 as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). FT-IR spectra were recorded on a Thermo fisher Nicolet 6700. XRD were explored on D/max 2200PC of Janpan. GC mass spectra were recorded on Shimadzu GCMS-QP2010 with a capillary column (0.25 mm× 30 m). Column chromatography was performed using 200-300 mesh base-washed silica gel.

II. Synthesis and characterizations of catalyst

Synthesis of $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]$[1,2]: $(NH_4)_6Mo_7O_{24}\cdot 2H_2O$ (7.41g, 6 mmol) were dissolved in water (100 mL) and mix thoroughly. Nitric acid is then added drop by drop until pH value is up to 3.0-4.0. We need to reflux and stir constantly. After that, a solution that $Cr(NO_3)_3$ (1.66g, 7 mmol) was dissolved in water (15 mL) was slowly added to above solution. Then we need to continue stirring the mixture for about 15 minutes. Finally, the filtrate obtained after filtration was placed at room temperature to crystallize. After a week, by filtering and vacuum drying, the pink crystals were collected.
Synthesis of $[N(C_4H_9)_4]_3[CrMo_6O_{18}(OH)_3C(OCH_2)_3CH_2OH\}]$[3,4]: The compounds $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]$ (1.071g, 1mmol) are dissolved in water (10 mL) under heating conditions. Then pentaerythritol (0.402g, 3mmol) was slowly added to the above solution and reflux about 12 h. Subsequently, tetrabutyl bromide (1.13g, 3.5 mmol) is added to the solution in batches. After stirring for three hours, pink precipitate will form. After filtration and vacuum drying, the target compound can be obtained.

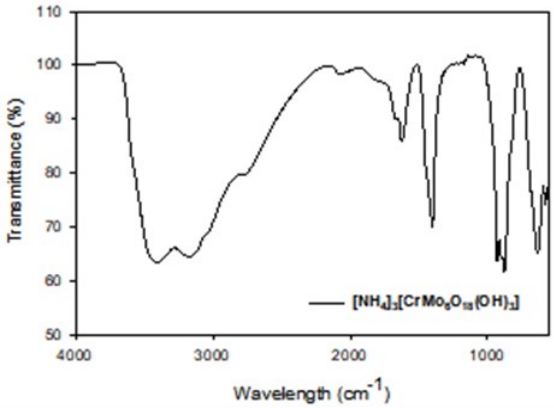


Figure S1. The FT-IR spectra of $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]$.

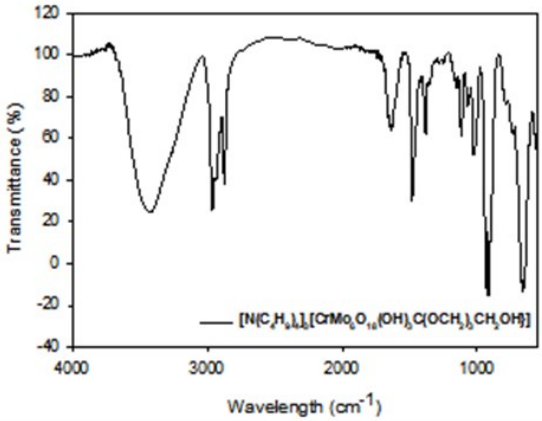


Figure S2. The FT-IR spectra of $[N(C_4H_9)_4]_3[CrMo_6O_{18}(OH)_3C(OCH_2)_3CH_2OH\}]$.

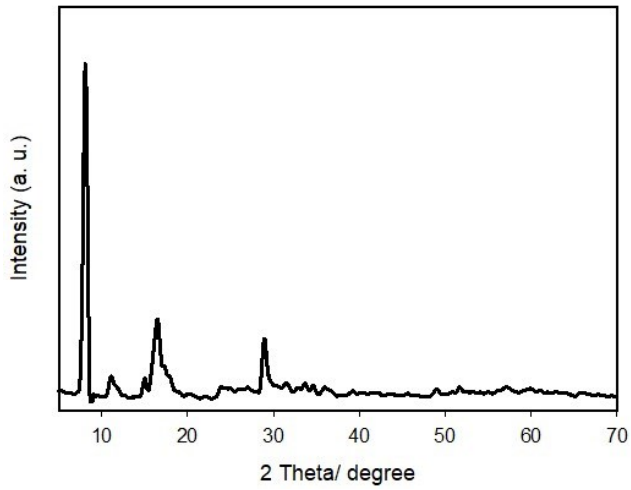


Figure S3. The XRD spectra of $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]$.

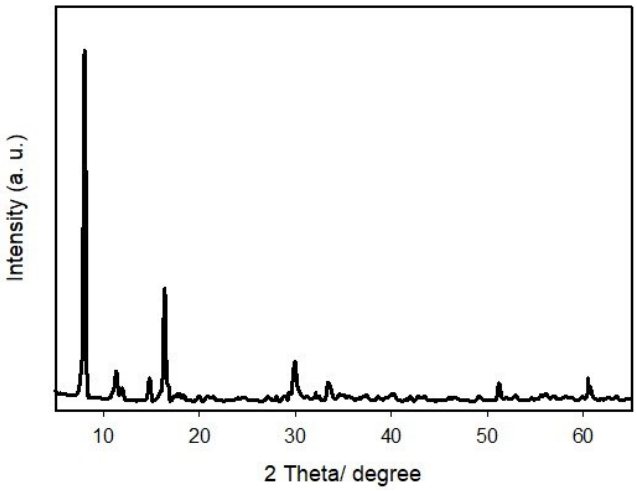
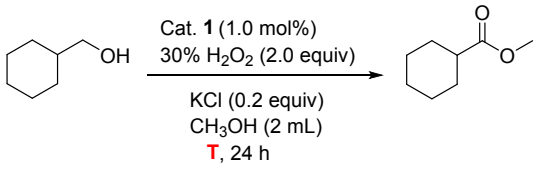
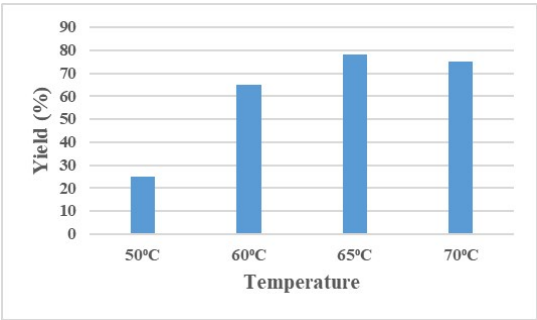


Figure S4. The XRD spectra of $[N(C_4H_9)_4]_3[CrMo_6O_{18}(OH)_3C(OCH_2)_3CH_2OH\}]$.

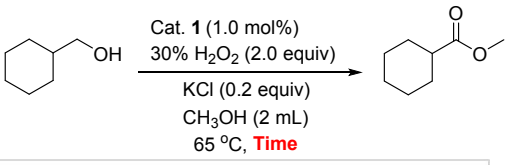
III. Screening of optimal reaction conditions

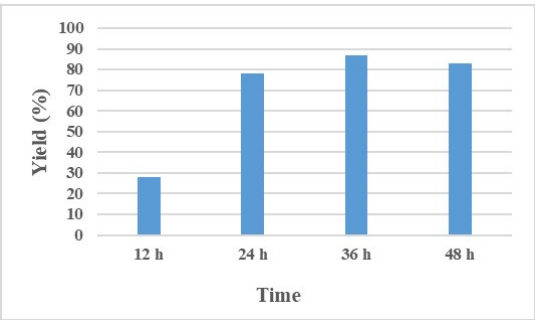
A. Influence of temperature.



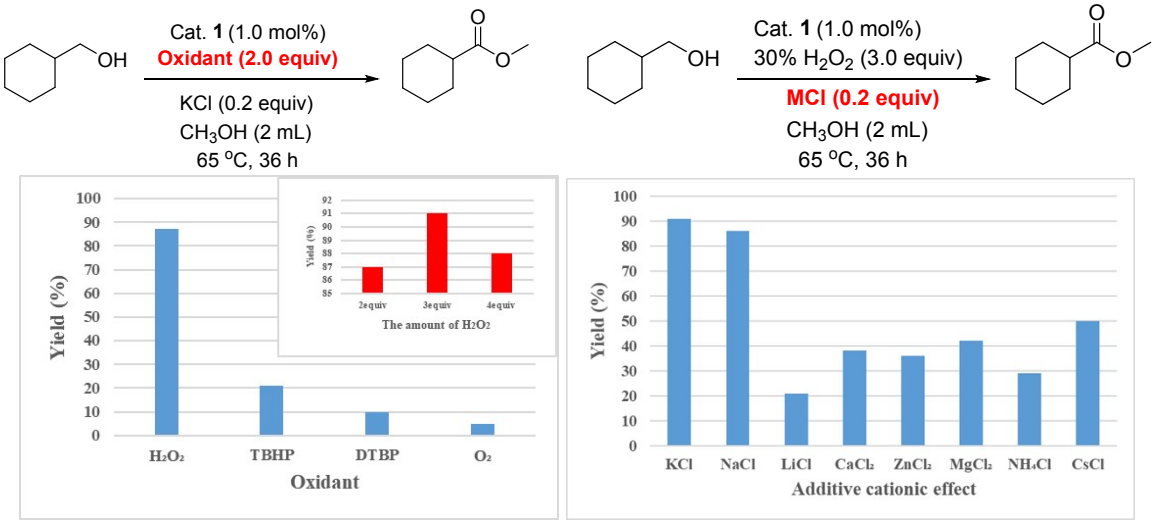


B. Influence of time.





C. Influence of oxidant and the amount of oxidant. **D.** Influence of positive ion of additive.



E. Influence of negative ion of additive.

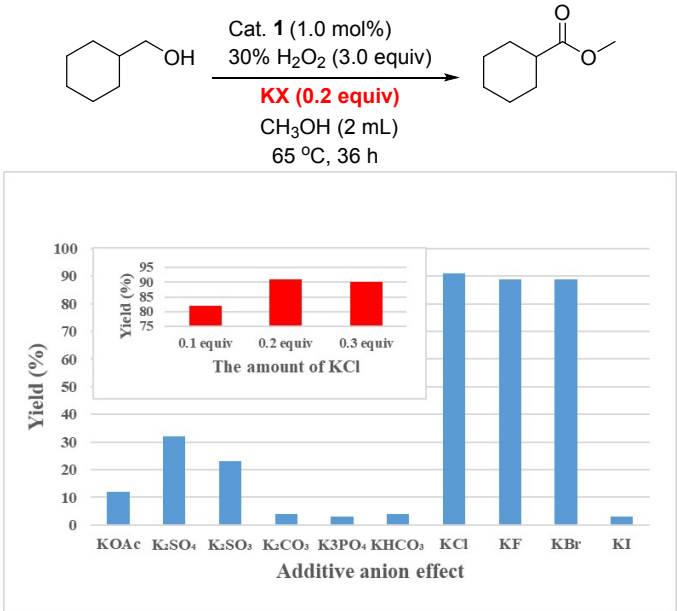


Figure S5. Screening of reaction conditions.

IV. General procedure for the oxidation of alcohols to esters.

General procedure: $[N(C_4H_9)_4]_3[CrMo_6O_{18}(OH)_3C(OCH_2)_3CH_2OH]$ (18.0 mg, 1.0 mol%) and KCl (14.9 mg, 0.2 equiv.) were added in a Shlenck tube. Alcohols (1.0 mmol), 30% hydrogen peroxide (0.34 g, 3.0 equiv.) and methanol (2 mL) were consequently added to the reaction tube. The reaction mixture was stirred at 65 °C for 36 h. After completion, the reaction mixture was cooled to room temperature, diluted with water and extracted by ethyl acetate (3×5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (200-300 mesh base-washed silica gel, petroleum ether/ethyl acetate (20: 1) as the eluent). It should be noticed silicotungstic acid (0.1 mmol) was added at the same time for part of reaction system.

V. Gram-scale experiment and recycling experiments of the catalyst.

We explored the gram scale reaction in oxidative esterification of alcohols (benzyl alcohol, 4-methoxybenzyl alcohol, 4-fluorobenzyl alcohol and 4-nitrobenzyl alcohol). Then, the catalyst of the

reaction with 4-fluorobenzyl alcohol as substrate was used for repeated experiments. After finishing the reaction, the catalyst can be precipitated by adding diethyl ether to the reaction system, and then recovered for reuse. The recovered catalyst was characterized by FT-IR and XRD spectra.

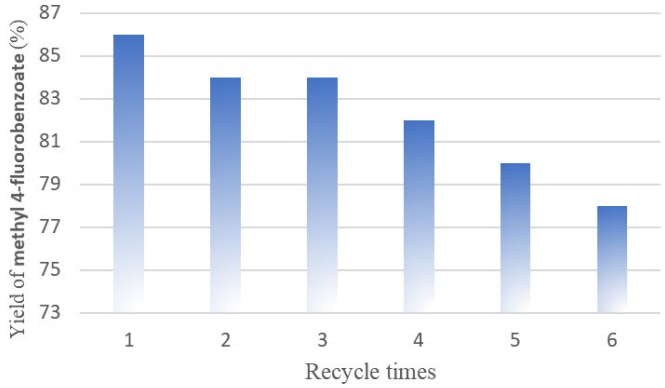


Figure S6. Catalyst recovery experiment in cross esterification of 4-fluorobenzyl alcohol and methyl alcohol.

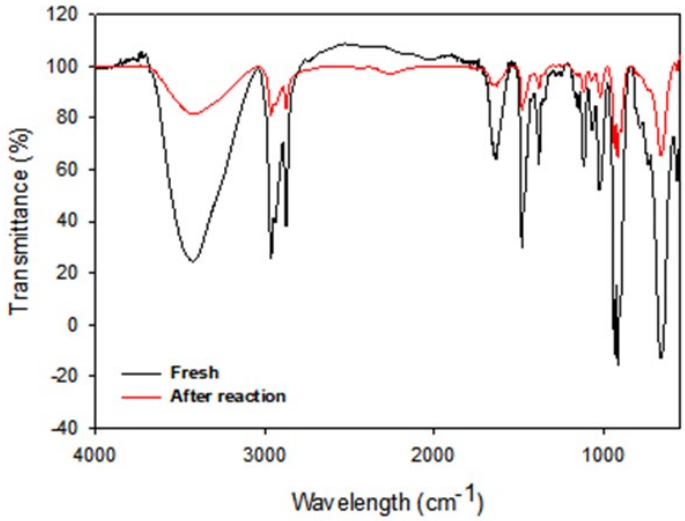


Figure S7. The FT-IR spectra of the catalyst before and after reaction.

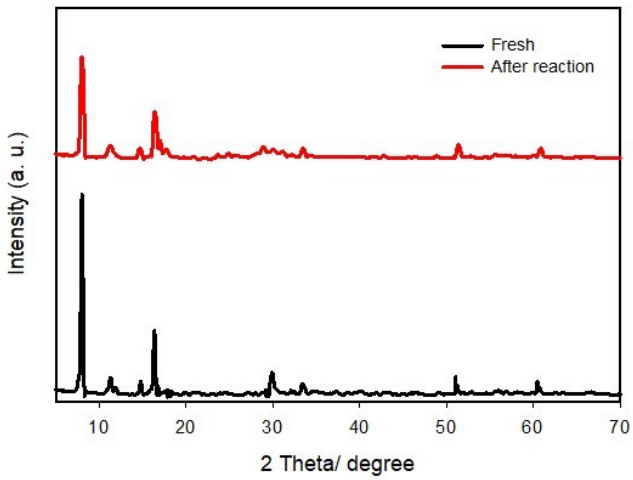


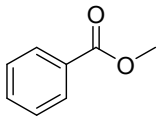
Figure S8. The XRD spectra of the catalyst before and after reaction.

VI. 100 Gram-scale experiment.

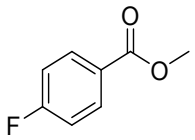
To a 5000 mL three-necked bottle were added benzyl alcohol (108.1 g, 1.0 mol), methanol (2000 mL), Cat.1 (18 g, 10 mmol), KCl (14.9 g, 0.2 mol), and 30% H_2O_2 (340 g, 3.0 mol). The three-necked

bottle was then stirred at 65 °C until completion of the reaction as monitored by TLC (36 h). The methanol 1866 mL (95.2 % recovery) was recovered by distillation, and the layers were separated. Then, ethyl acetate (100 ml) was added to the aqueous phase to recover the catalyst. Methyl benzoate (102 g, 74.9% yield) was obtained from the oil phase by pressure distillation (104-105°C/382Pa).

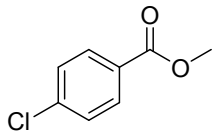
VII. NMR data of products



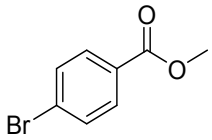
Methyl benzoate (2a)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.06 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.14 (s), 132.94 (s), 130.16 (s), 129.59 (s), 128.38 (s), 52.13 (s).



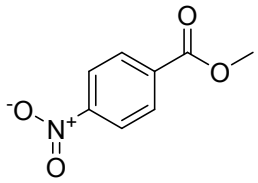
Methyl 4-fluorobenzoate (2b)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.14 – 7.99 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.77 (s), 166.11 (s), 164.75 (s), 132.11 (d, *J* = 9.3 Hz), 126.44 (d, *J* = 0.7 Hz), 115.57 (s), 115.39 (s), 52.13 (s).



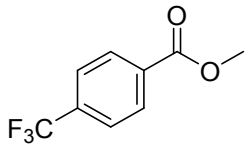
4-Chlorobenzoic acid methyl ester (2c)[5-7]: Light yellow solid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.11 (s), 139.30 (s), 130.93 (s), 128.60 (d, *J* = 13.6 Hz), 52.21 (s).



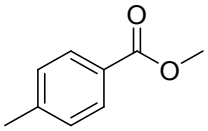
Methyl 4-bromobenzoate (2d)[5-7]: White solid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.29 (s), 131.69 (s), 131.11 (s), 129.01 (s), 128.03 (s), 52.29 (s).



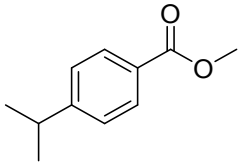
Methyl 4-nitrobenzoate (2e)[5-7]: Yellow solid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.18 (s), 150.53 (s), 135.48 (s), 130.72 (s), 123.55 (s), 52.84 (s).



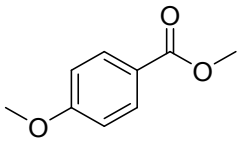
Methyl 4-(trifluoromethyl)benzoate (2f)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.84 (s), 134.60 (s), 133.40 (s), 129.97 (s), 125.40 (s), 122.53 (s), 52.45 (s).



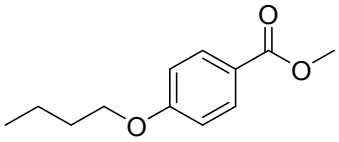
Methyl 4-methylbenzoate (2g)[5-7]: White crystalline solid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.15 (s), 143.54 (s), 129.59 (s), 129.07 (s), 127.41 (s), 51.90 (s), 21.60 (s).



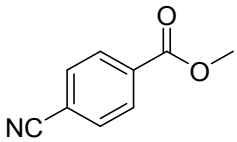
Methyl 4-propan-2-ylbenzoate (2h)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.92 (s, 3H), 2.98 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.19 (s), 154.32 (s), 129.75 (s), 127.78 (s), 126.48 (s), 51.95 (s), 34.26 (s), 23.72 (s).



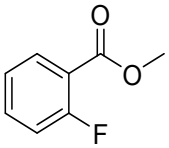
Methyl anisate (2i)[5-7]: White powder. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.79 (s), 163.30 (s), 131.54 (s), 122.51 (s), 113.55 (s), 55.32 (s), 51.78 (s).



Methyl 4-n-butoxybenzoate (2j)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.97 (dd, *J* = 10.6, 6.5 Hz, 2H), 3.84 (s, 3H), 1.75 (s, 2H), 1.47 (dd, *J* = 7.4, 3.8 Hz, 2H), 0.96 – 0.94 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.24 (s), 162.95 (s), 131.52 (s), 122.26 (s), 114.70 (s), 68.05 (s), 51.73 (s), 31.13 (s), 19.17 (s), 13.78 (s).

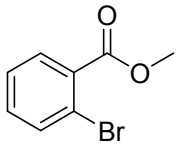


4-cyanobenzoic acid methyl ester (2k)[5-7]: White crystal. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.46 (s), 133.92 (s), 132.26 (s), 130.11 (s), 118.00 (s), 116.38 (s), 52.77 (s).

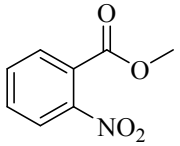


Methyl 2-fluorobenzoate (3a)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.1 Hz, 1H), 7.52 (dd, *J* = 12.5, 6.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 10.2, 9.1 Hz, 1H), 3.94 (s, 3H). ^{13}C

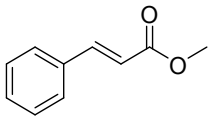
NMR (126 MHz, $CDCl_3$) δ 164.93 (d, *J* = 3.9 Hz), 162.95 (s), 160.89 (s), 134.52 (d, *J* = 9.0 Hz), 132.14 (s), 123.98 (d, *J* = 3.9 Hz), 118.59 (d, *J* = 9.6 Hz), 117.07 (s), 116.89 (s), 52.35 (s).



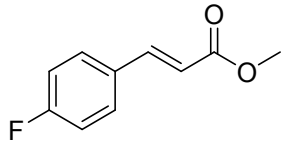
Methyl 2-bromobenzoate (3b)[5-7]: Light yellow liquid; ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 13.9, 7.5 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.38 – 7.30 (m, 2H), 3.93 (d, *J* = 14.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.61 (s), 134.33 (s), 132.59 (s), 131.32 (s), 128.38 (s), 127.18 (s), 121.66 (s), 52.46 (s).



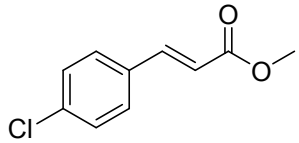
2-Nitrobenzoic acid methyl ester (3c)[5-7]: Yellow solid; ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.37 (m, 3H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.18 (s), 143.42 (s), 136.21 (s), 132.87 (s), 129.21 (d, *J* = 6.9 Hz), 118.38 (s), 51.79 (s).



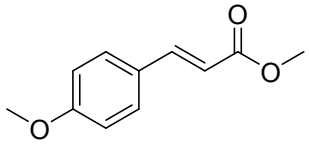
Methyl cinnamate (4a)[5-7]: White crystal. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 3.5 Hz, 2H), 7.45 – 7.36 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.47 (s), 144.91 (s), 134.37 (s), 130.34 (s), 128.92 (s), 128.11 (s), 117.79 (s), 51.74 (s).



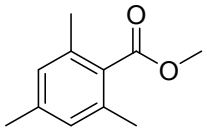
Methyl 4- fluorocinnamate (4b)[5-7]: Light yellow liquid; ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.90 (s), 162.91 (s), 143.56 (s), 130.63 (d, *J* = 3.3 Hz), 129.94 (d, *J* = 8.5 Hz), 117.54 (s), 115.95 (s), 51.73 (s).



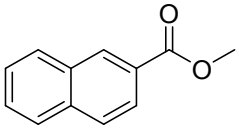
Methyl 4-chlorocinnamate (4c)[5-7]: Light yellow crystals; ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.18 (s), 143.42 (s), 136.21 (s), 132.87 (s), 129.21 (d, *J* = 6.9 Hz), 118.38 (s), 51.81 (s).



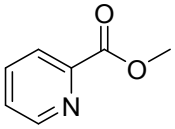
(3-Methoxyphenyl)methyl prop-2-enoate (4d)[5-7]: Light yellow crystal; ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 3.86 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.73 (s), 161.40 (s), 144.51 (s), 129.71 (s), 127.06 (s), 115.22 (s), 114.31 (s), 55.54 (s), 51.52 (s).



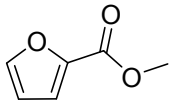
Methyl 2,4,6-trimethylbenzoate (5)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.91 (s, 3H), 2.34 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.64 (s), 143.84 (s), 141.51 (s), 135.18 (s), 128.39 (s), 51.75 (s), 21.48 (s), 20.51 (s).



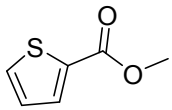
Methyl 2-naphthoate (6)[5-7]: White powder. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.59 (dt, *J* = 14.8, 7.1 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.30 (s), 135.53 (s), 132.51 (s), 131.10 (s), 129.38 (s), 128.23 (d, *J* = 10.7 Hz), 127.79 (s), 127.40 (s), 126.67 (s), 125.25 (s), 52.28 (s).



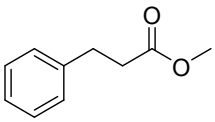
Methyl picolinate (7)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.4 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.45 (m, 1H), 4.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.71 (s), 149.81 (s), 148.00 (s), 137.11 (s), 127.00 (s), 125.17 (s), 52.91 (s).



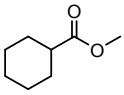
Methyl 2-furoate (8)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.1 Hz, 1H), 7.29 – 7.14 (m, 1H), 6.58 – 6.49 (m, 1H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.15 (s), 146.29 (s), 142.79 (s), 117.93 (s), 111.83 (s), 51.90 (s).



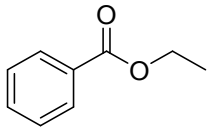
Methyl thiophene-2-carboxylate (9)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.80 (d, *J* = 3.6 Hz, 1H), 7.55 (d, *J* = 4.9 Hz, 1H), 7.13 – 7.05 (m, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.71 (s), 133.52 (d, *J* = 8.2 Hz), 132.39 (s), 127.77 (s), 52.16 (s).



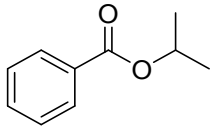
3-Phenylpropionic acid methyl ester (10)[5-7]: White crystal. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 3H), 3.38 (s, 3H), 2.77 – 2.63 (m, 2H), 1.98 (dt, *J* = 7.8, 5.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.34 (s), 141.67 (s), 128.45 (s), 126.31 (s), 125.93 (s), 52.73 (s), 34.14 (s), 30.92 (s).



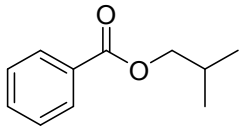
Cyclohexanecarboxylic acid methyl ester (11)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.39 – 2.21 (m, 1H), 1.90 (d, J = 12.8 Hz, 2H), 1.80 – 1.61 (m, 3H), 1.52 – 1.39 (m, 2H), 1.35 – 1.19 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.59 (s), 51.44 (s), 43.11 (s), 29.02 (s), 25.75 (s), 25.45 (s)



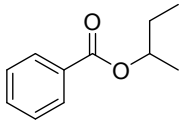
Ethyl benzoate (18)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.65 (s), 132.83 (s), 130.49 (s), 129.54 (s), 128.33 (s), 60.97 (s), 14.35 (s).



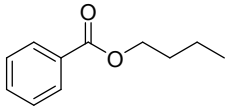
Benzoic acid isopropyl ester (19)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.28 (dt, *J* = 12.5, 6.2 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.12 (s), 132.69 (s), 130.93 (s), 129.51 (s), 128.26 (s), 68.34 (s), 21.96 (s).



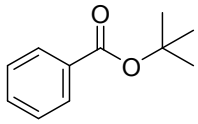
Isobutyl benzoate (20)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.14 (d, J = 6.6 Hz, 2H), 2.12 (td, J = 13.4, 6.7 Hz, 1H), 1.05 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.63 (s), 132.81 (s), 130.56 (s), 129.55 (s), 128.34 (s), 71.01 (s), 27.93 (s), 19.21 (s).



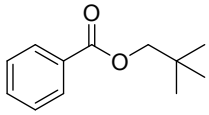
S-Butyl benzoate (21)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.1, 3.7 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.47 (dd, *J* = 7.7, 4.0 Hz, 2H), 5.52 – 4.72 (m, 1H), 1.84 – 1.64 (m, 2H), 1.36 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.28 (s), 133.66 (s), 130.18 (s), 129.51 (s), 128.48 (s), 72.87 (s), 27.93 (s), 19.55 (s), 9.72 (s).



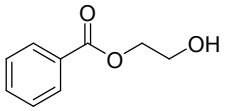
Butyl benzoate (22)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.51 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.73 (s), 132.80 (s), 130.54 (s), 129.54 (s), 128.33 (s), 64.85 (s), 30.79 (s), 19.30 (s), 13.78 (s).



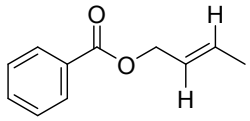
Benzoic acid tert-butyl ester (23)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.46 (s), 133.36 (s), 129.15 (s), 128.65 (s), 128.54 (d, *J* = 25.2 Hz), 84.01 (s), 26.27 (s).



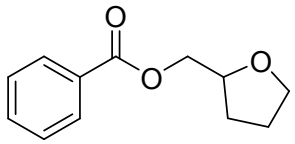
2,2-Dimethylpropyl benzoate (24)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.04 (s, 2H), 1.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.61 (s), 132.84 (s), 130.57 (s), 129.54 (s), 128.37 (s), 74.22 (s), 31.62 (s), 26.60 (s).



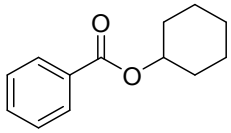
2-Hydroxyethyl benzoate (25)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.52 – 4.36 (m, 2H), 4.05 – 3.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.07 (s), 133.21 (s), 129.99 (s), 129.76 (d, *J* = 16.0 Hz), 128.43 (s), 66.59 (s), 61.12 (s).



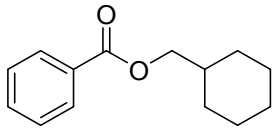
(E)-But-2-en-1-yl benzoate (26)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 6.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.90 (td, *J* = 13.0, 6.4 Hz, 1H), 5.73 (dd, *J* = 14.5, 6.6 Hz, 1H), 4.78 (d, *J* = 6.4 Hz, 2H), 1.78 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46 (s), 132.85 (s), 131.34 (s), 130.43 (s), 129.61 (s), 128.32 (s), 125.20 (s), 65.65 (s), 17.80 (s).



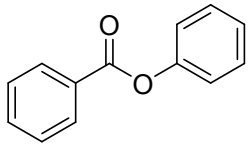
Oxolan-2-ylmethyl benzoate (27)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.09 (d, *J* = 16.6 Hz, 2H), 7.52 (ddd, *J* = 22.9, 15.8, 6.5 Hz, 3H), 4.36 (dd, *J* = 52.1, 14.5 Hz, 3H), 4.01 – 3.79 (m, 2H), 2.03 (d, *J* = 60.6 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.58 (d, *J* = 5.0 Hz), 133.01 (d, *J* = 4.8 Hz), 130.12 (d, *J* = 3.8 Hz), 129.72 (d, *J* = 6.3 Hz), 128.37 (d, *J* = 6.1 Hz), 68.57 (d, *J* = 5.5 Hz), 66.96 (d, *J* = 6.0 Hz), 28.14 (d, *J* = 6.5 Hz), 25.80 (d, *J* = 6.5 Hz).



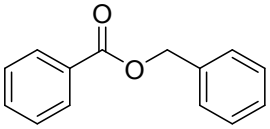
Cyclohexyl benzoate (28)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.24 – 4.88 (m, 1H), 1.97 (d, *J* = 5.4 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.62 (dd, *J* = 18.6, 9.2 Hz, 3H), 1.47 (dt, *J* = 13.1, 9.9 Hz, 2H), 1.42 – 1.34 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.00 (s), 132.67 (s), 131.05 (s), 129.53 (s), 128.26 (s), 73.03 (s), 31.65 (s), 25.50 (s), 23.67 (s).



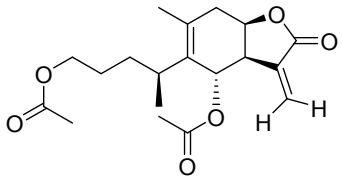
Cyclohexylmethyl benzoate (29)[5-7]: Light yellow liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 4.10 (d, *J* = 6.3 Hz, 2H), 1.81 – 1.64 (m, 6H), 1.27 – 1.15 (m, 3H), 1.03 (dd, *J* = 23.8, 12.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46 (s), 132.70 (s), 130.55 (s), 129.49 (s), 128.25 (s), 69.93 (s), 37.27 (s), 29.74 (s), 26.37 (s), 25.71 (s).



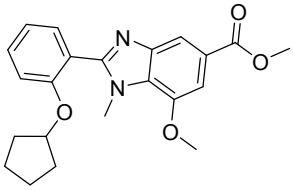
Benzoic acid phenyl ester (30)[5-7]: White crystal powder. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.21 (s), 151.01 (s), 133.60 (s), 130.20 (s), 129.57 (d, *J* = 13.9 Hz), 128.60 (s), 125.91 (s), 121.75 (s).



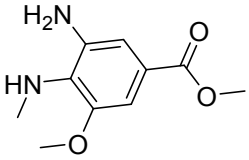
Benzyl benzoate (31)[5-7]: Colorless liquid. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (ddt, *J* = 32.1, 24.6, 7.2 Hz, 7H), 5.41 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.47 (s), 136.11 (s), 133.07 (s), 130.19 (s), 129.75 (s), 128.64 (s), 128.52 – 128.13 (m), 66.73 (s).



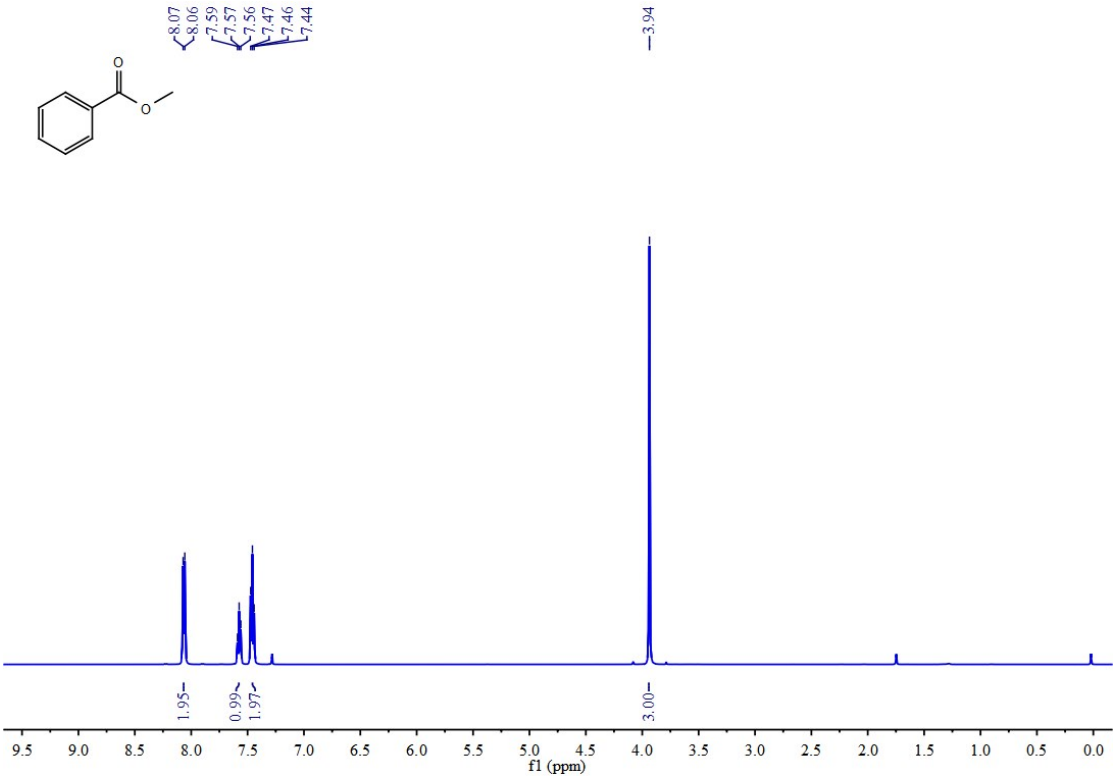
1,6-O,O-diacetylbritannilactone (32): White crystals. ^{1}H NMR (399 MHz, $CDCl_3$) δ 6.38 (d, J = 2.7 Hz, 1H), 5.94 (d, J = 2.3 Hz, 1H), 5.21 (d, J = 1.7 Hz, 1H), 4.99 – 4.90 (m, 1H), 3.93 (qd, J = 11.0, 5.8 Hz, 2H), 3.49 (s, 1H), 2.70 (ddd, J = 10.3, 6.8, 2.5 Hz, 2H), 2.49 (dd, J = 16.1, 2.1 Hz, 1H), 2.05 (d, J = 1.9 Hz, 6H), 1.80 (s, 3H), 1.45 – 1.35 (m, 1H), 1.28 – 1.24 (m, 2H), 1.07 – 0.98 (m, 1H), 0.88 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.25 (s), 170.92 (s), 169.55 (s), 136.28 (s), 133.85 (s), 132.03 (s), 125.06 (s), 74.98 (s), 69.26 (s), 64.26 (s), 42.90 (s), 34.57 (s), 33.09 (s), 31.10 (s), 26.51 (s), 21.32 (s), 21.01 (s), 20.54 (s), 18.46 (s).



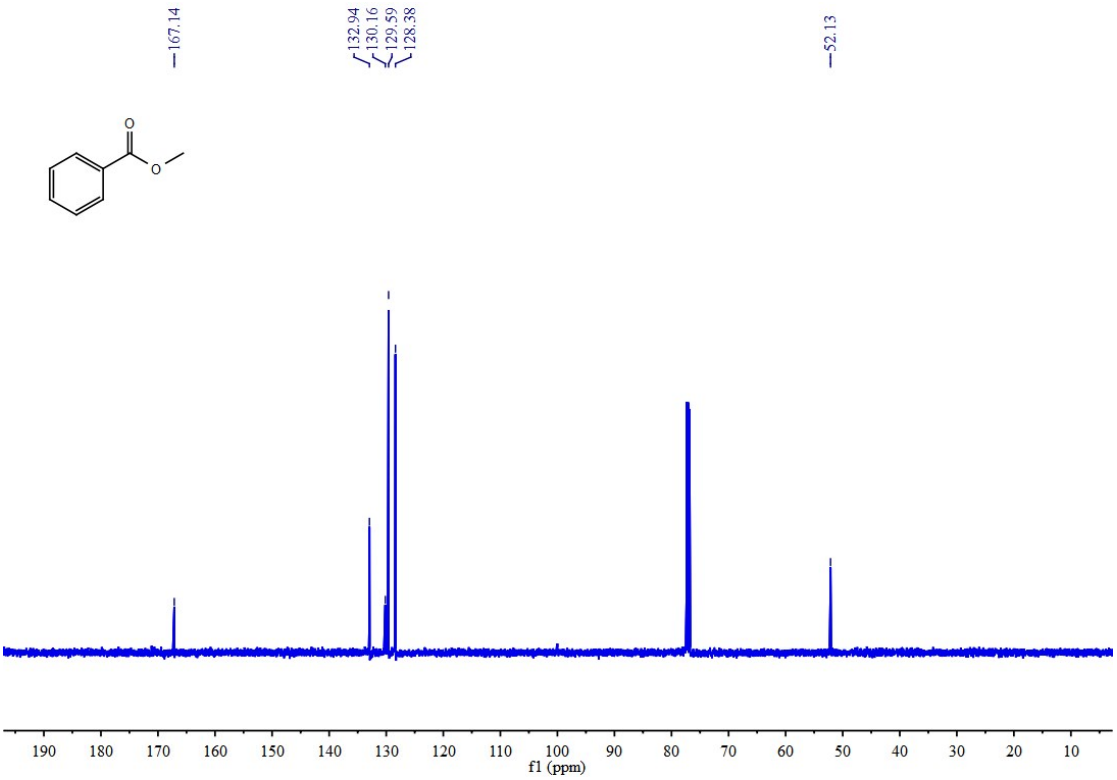
Methyl 2-(2-(cyclopentyloxy)phenyl)-7-methoxy-1-methyl-1H-benzo[d]imidazole-5-carboxylate (33): ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.49 (dd, J = 15.9, 7.8 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 4.81 (s, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H), 1.89 (dd, J = 12.9, 6.2 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.64 – 1.51 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.77 (s), 156.16 (s), 154.14 (s), 146.86 (s), 132.57 (s), 131.62 (s), 128.70 (s), 124.39 (s), 120.71 (s), 119.78 (s), 115.52 (s), 113.59 (s), 104.26 (s), 80.33 (s), 55.84 (s), 52.09 (s), 33.81 (s), 32.87 (s), 23.98 (s)



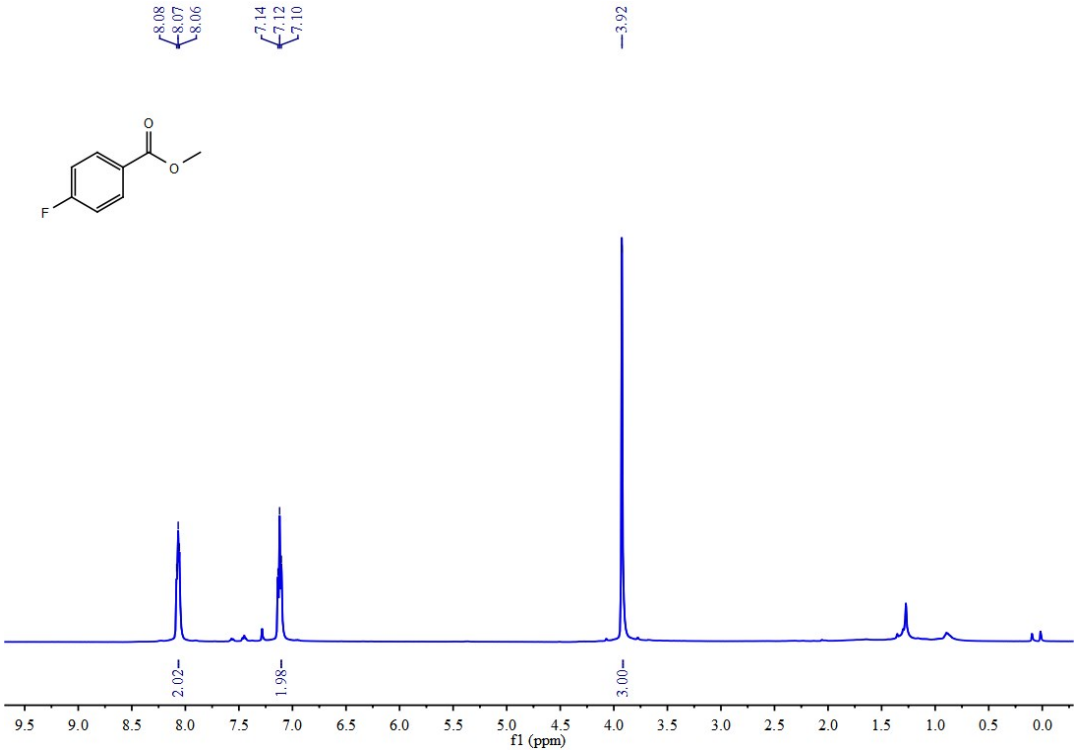
Benzoic acid, 3-amino-5-methoxy-4-(methylamino)-, methyl ester (34): ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.12 (d, J = 0.7 Hz, 1H), 7.05 (s, 1H), 3.89 (s, 6H), 2.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.16 (s), 151.84 (s), 140.08 (s), 124.86 (s), 111.20 (s), 105.81 – 105.65 (m), 102.62 (s), 56.00 (s), 51.96 (s), 33.66 (s).



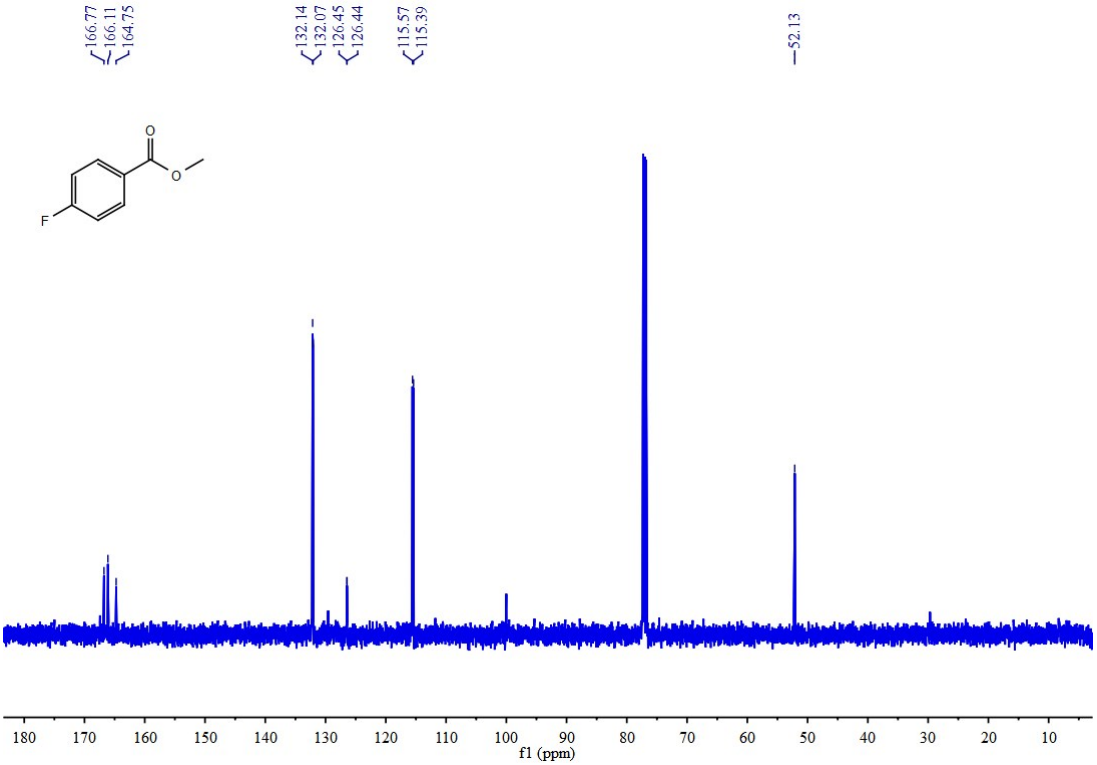
^{1}H NMR spectrum of **2a** (501 MHz, $CDCl_3$).



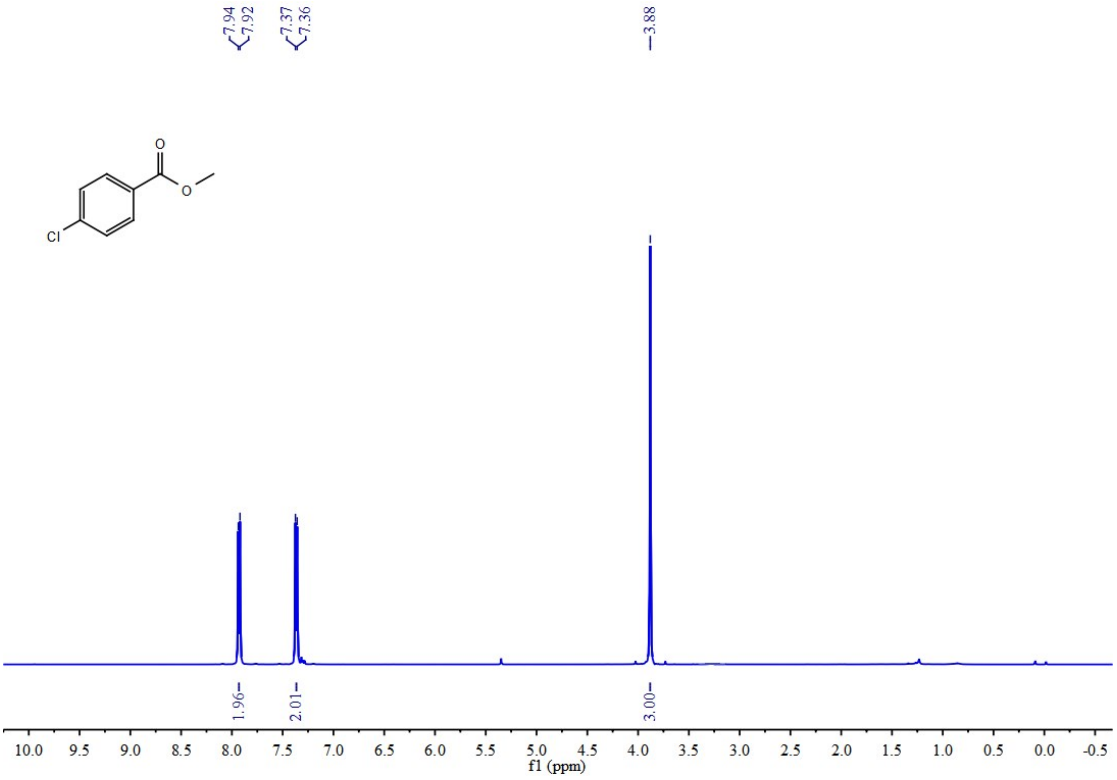
^{13}C NMR spectrum of **2a** (126 MHz, $CDCl_3$).



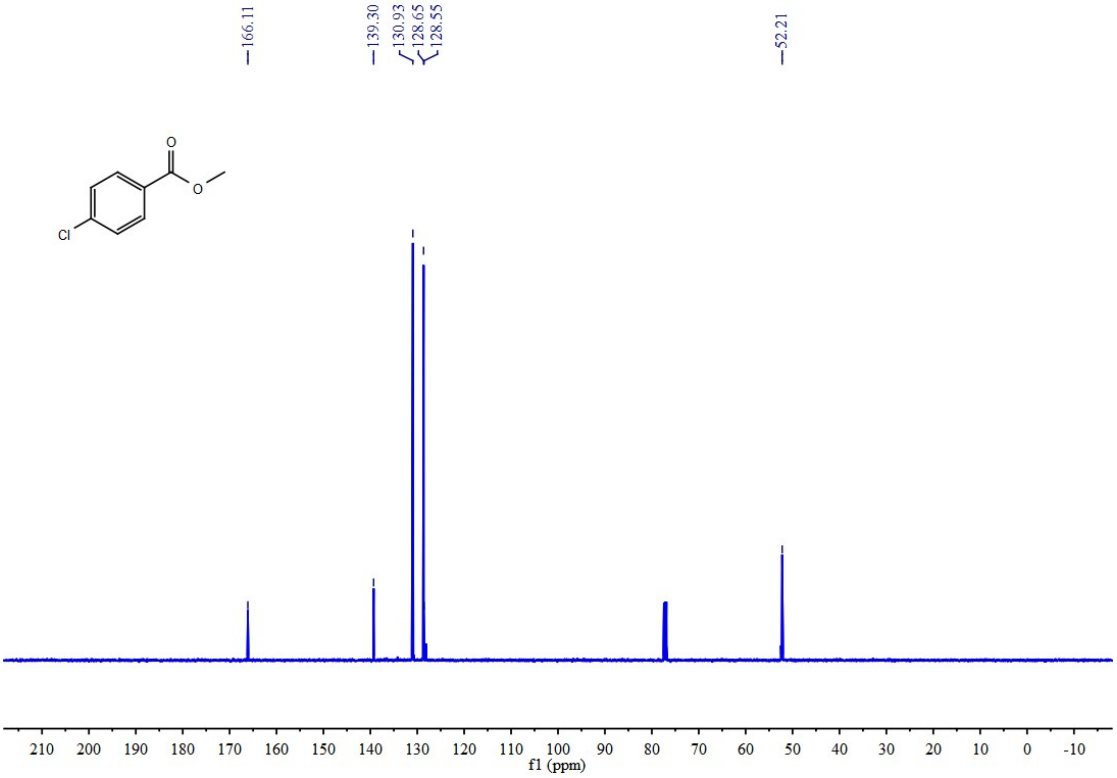
^{1}H NMR spectrum of **2b** (501 MHz, $CDCl_3$).



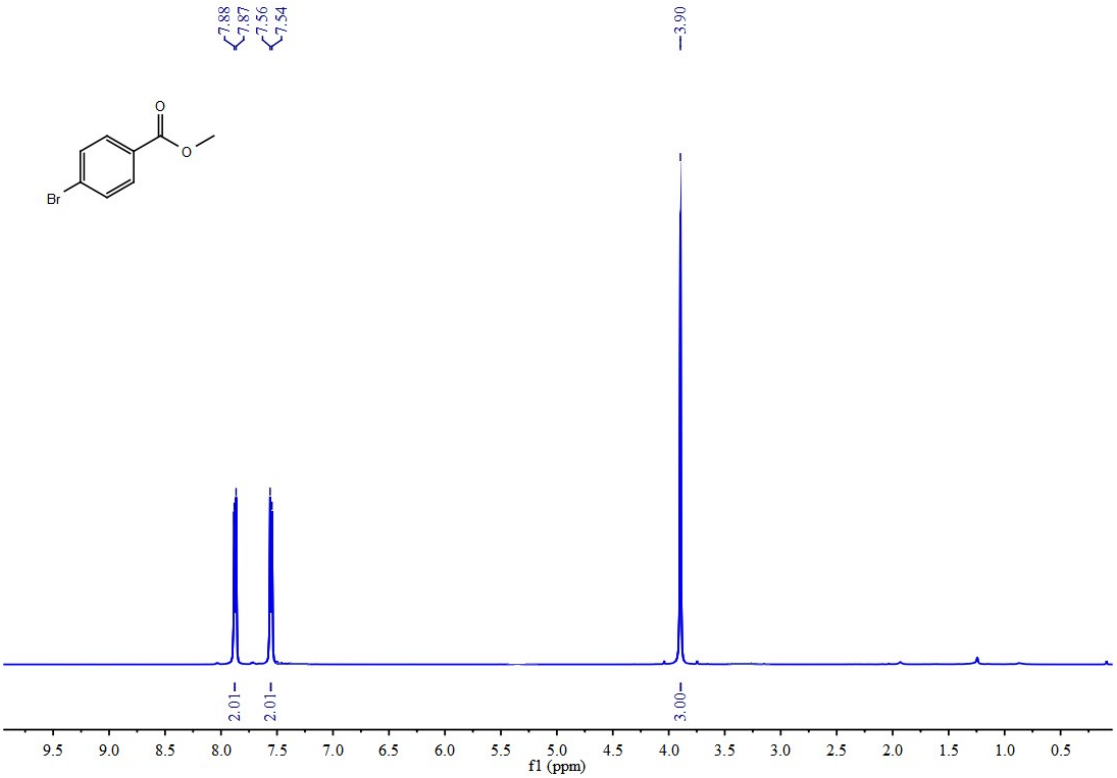
^{13}C NMR spectrum of **2b** (126 MHz, $CDCl_3$).



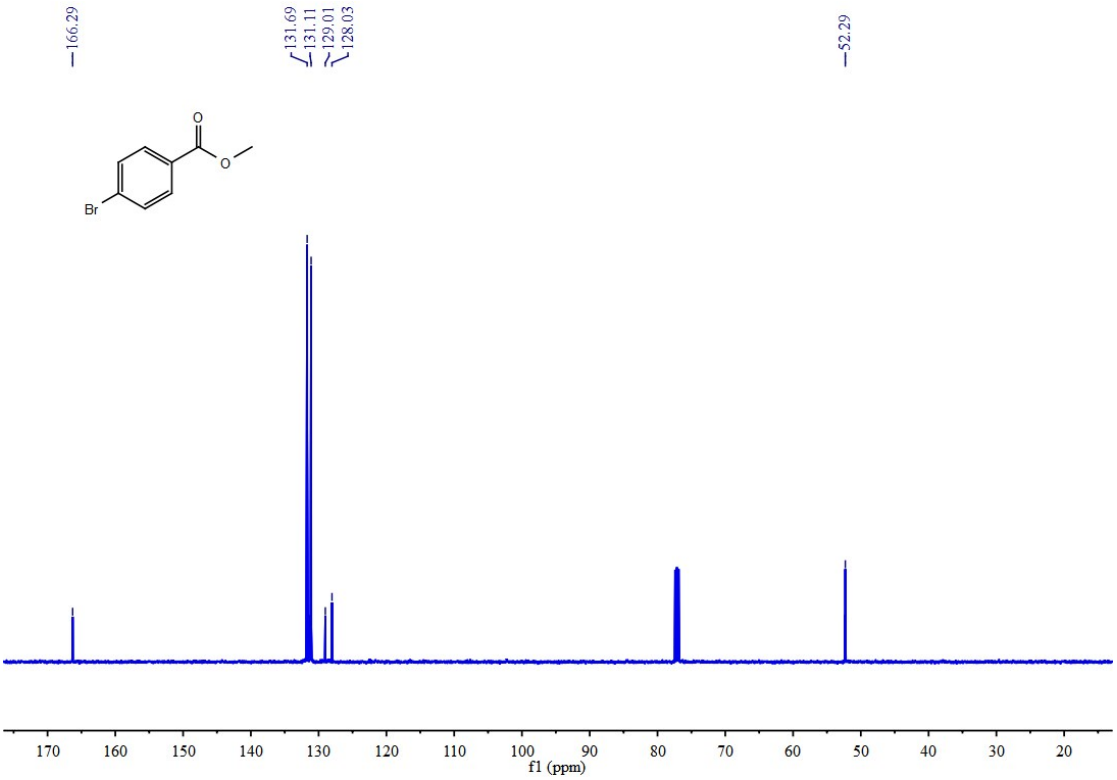
^{1}H NMR spectrum of **2c** (501 MHz, $CDCl_3$).



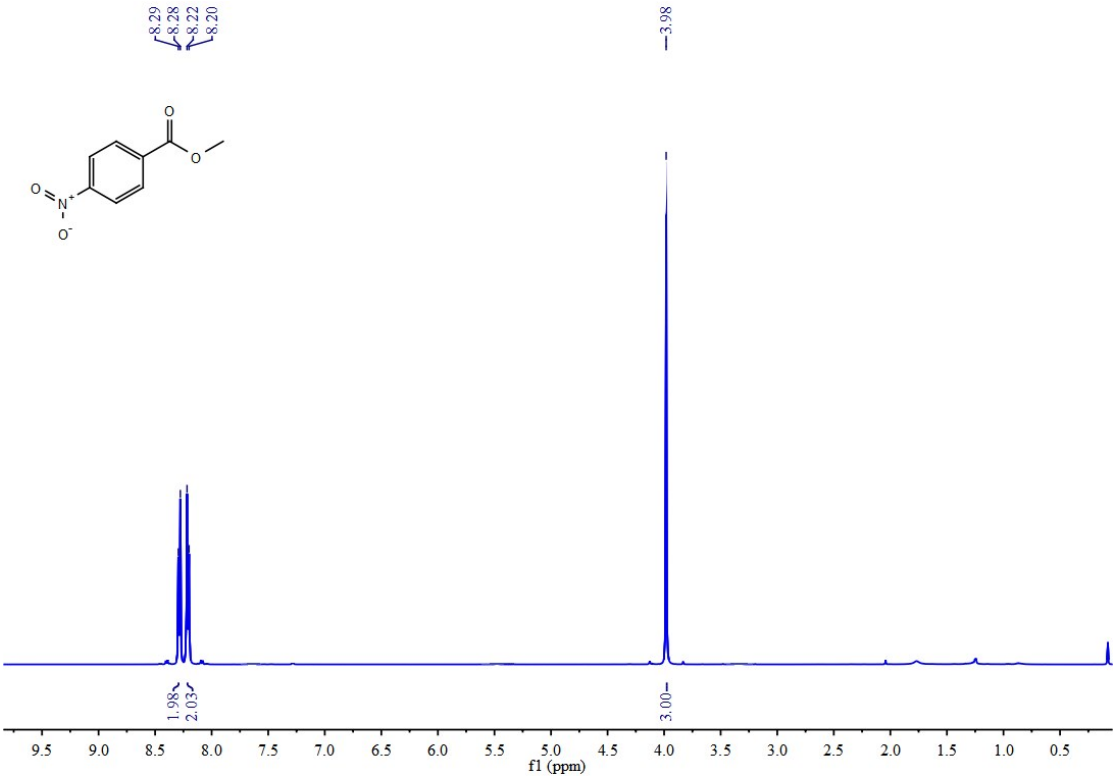
^{13}C NMR spectrum of **2c** (126 MHz, $CDCl_3$).



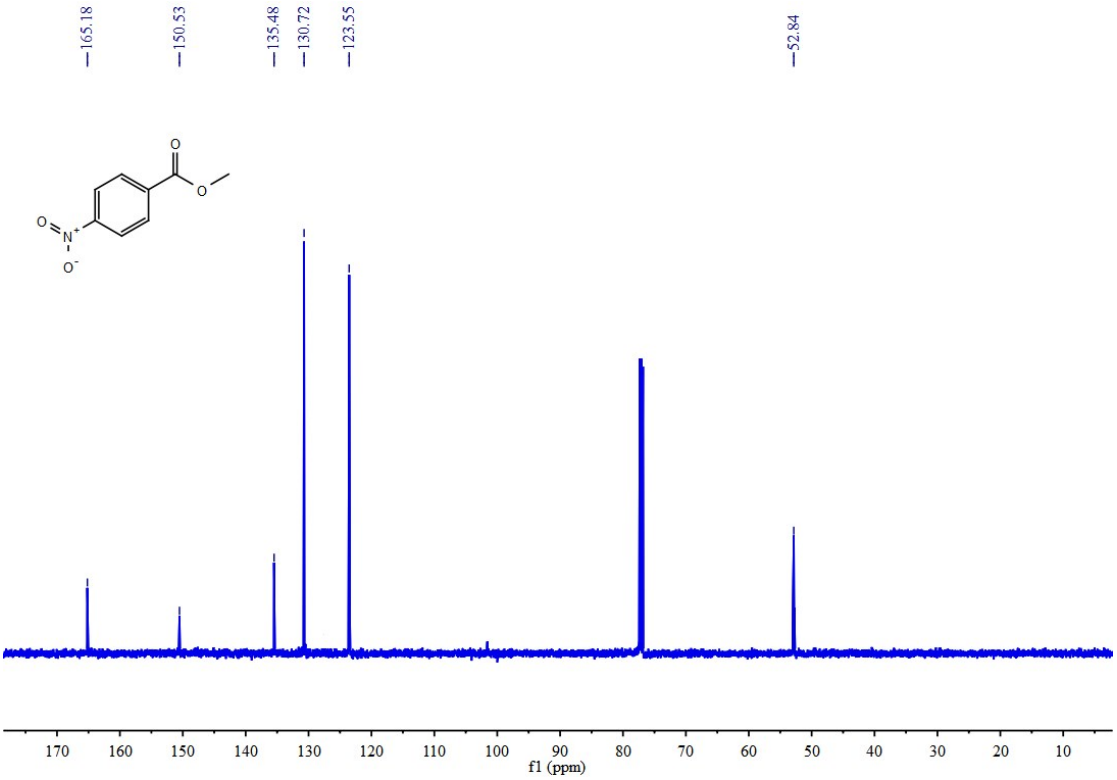
^{1}H NMR spectrum of **2d** (501 MHz, $CDCl_3$).



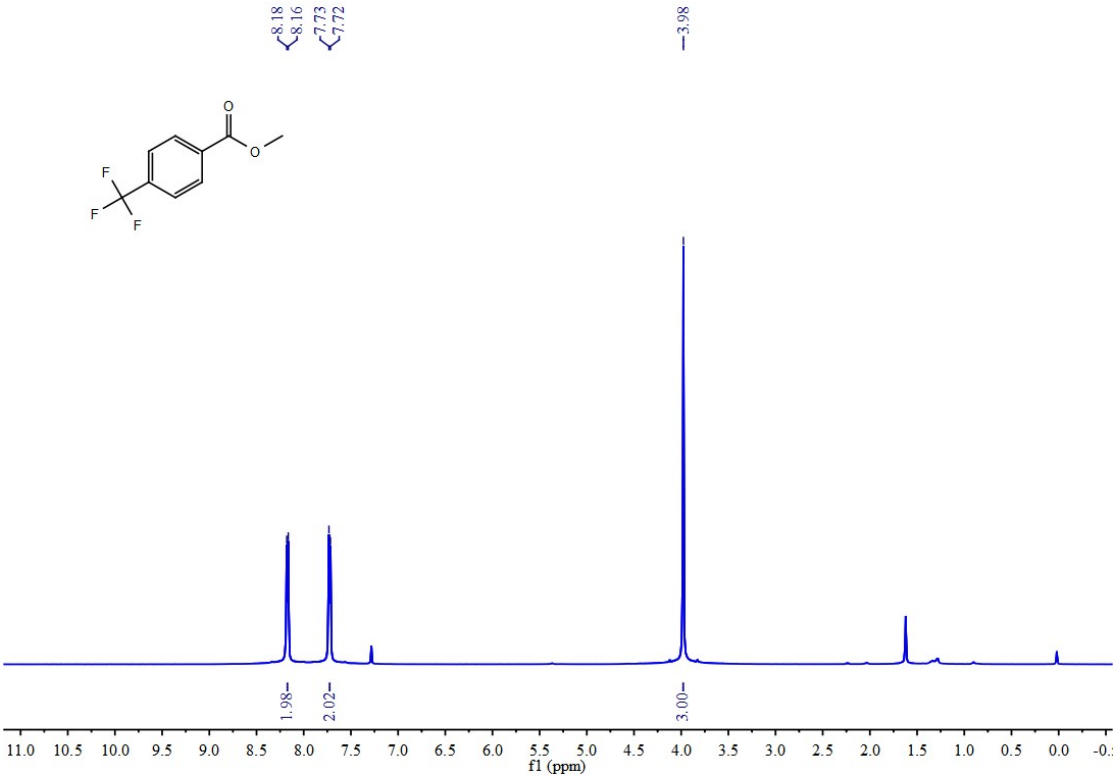
^{13}C NMR spectrum of **2d** (126 MHz, $CDCl_3$).



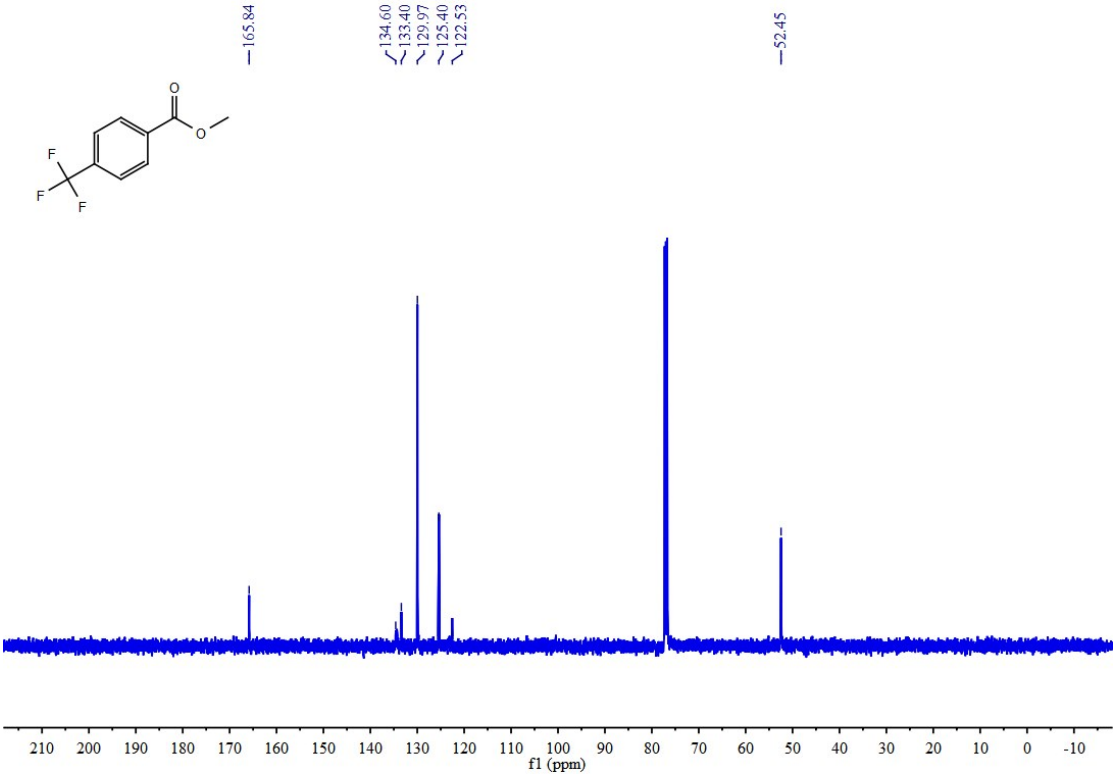
^{1}H NMR spectrum of **2e** (501 MHz, $CDCl_3$).



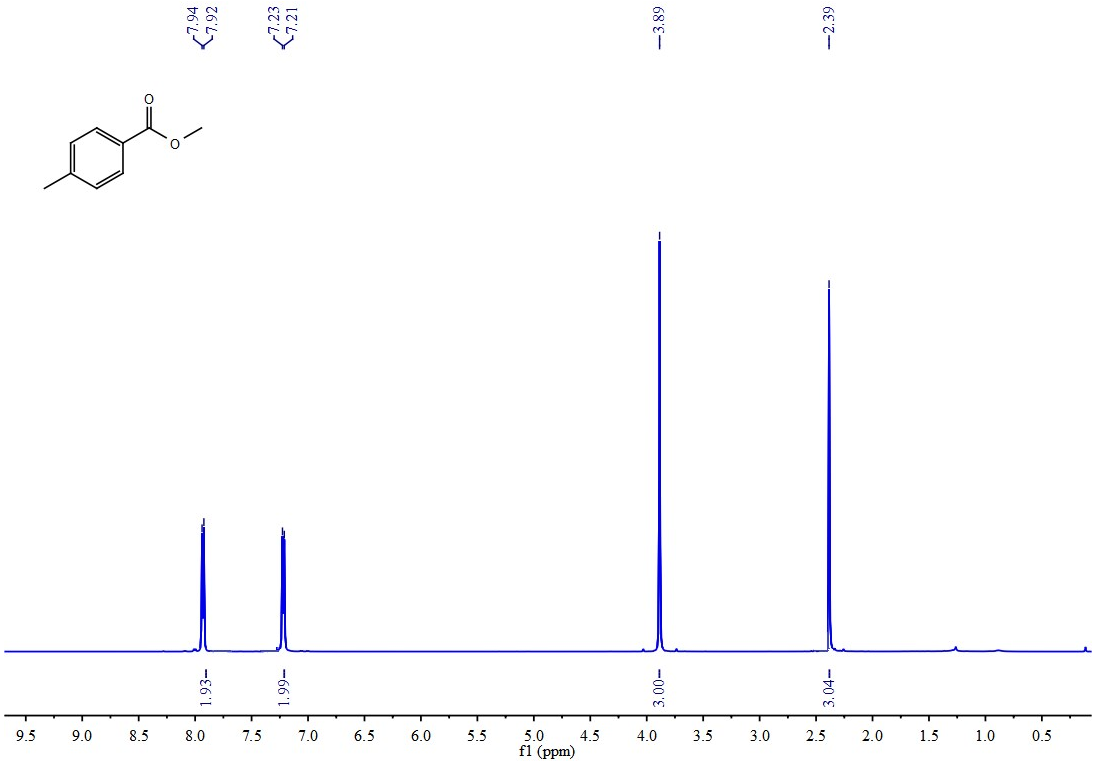
^{13}C NMR spectrum of **2e** (126 MHz, $CDCl_3$).



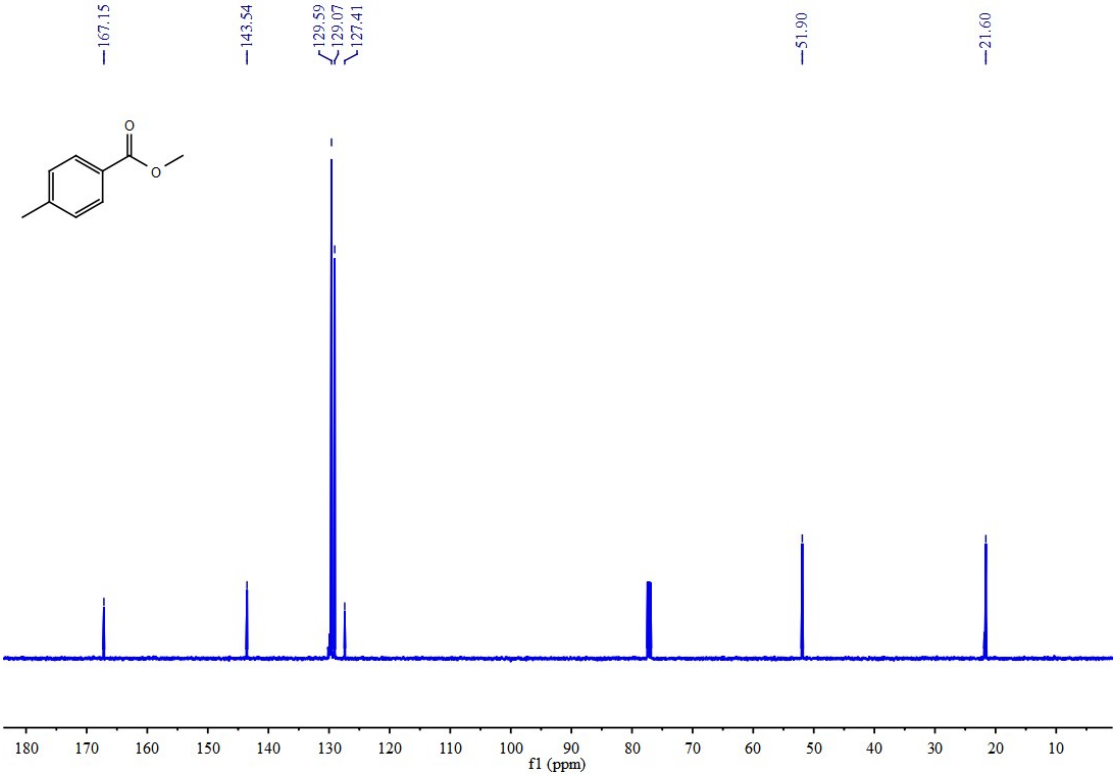
^{1}H NMR spectrum of **2f** (501 MHz, $CDCl_3$).



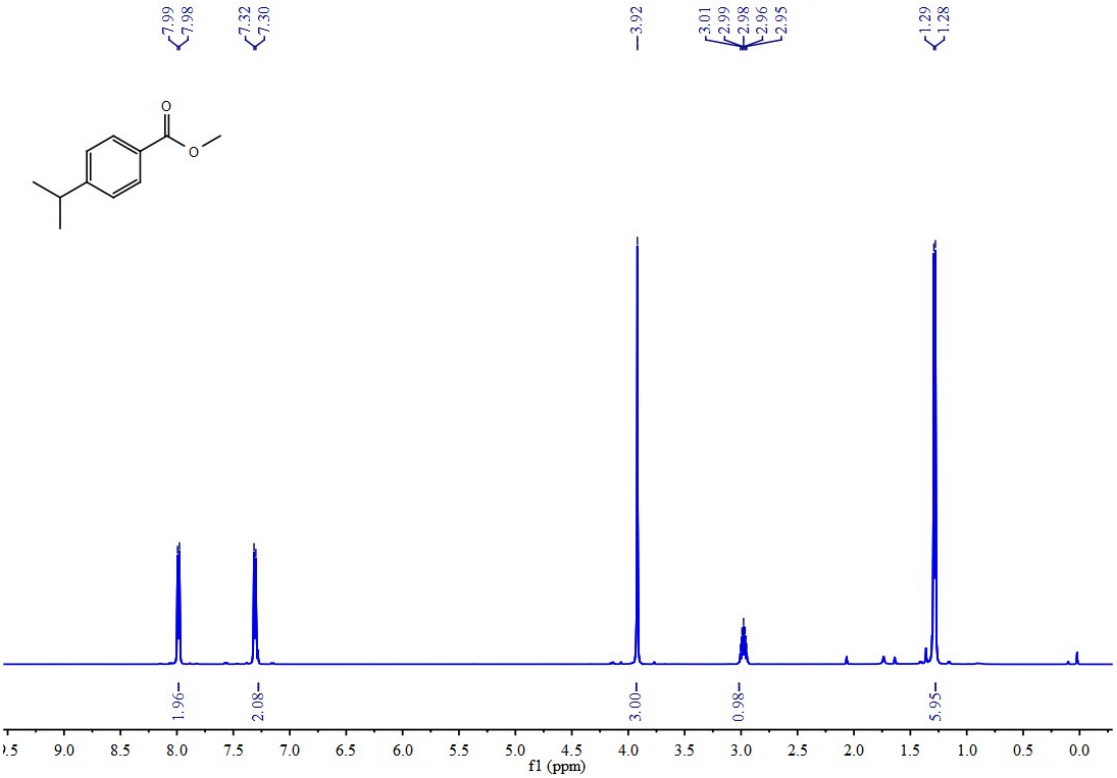
^{13}C NMR spectrum of **2f** (126 MHz, $CDCl_3$).



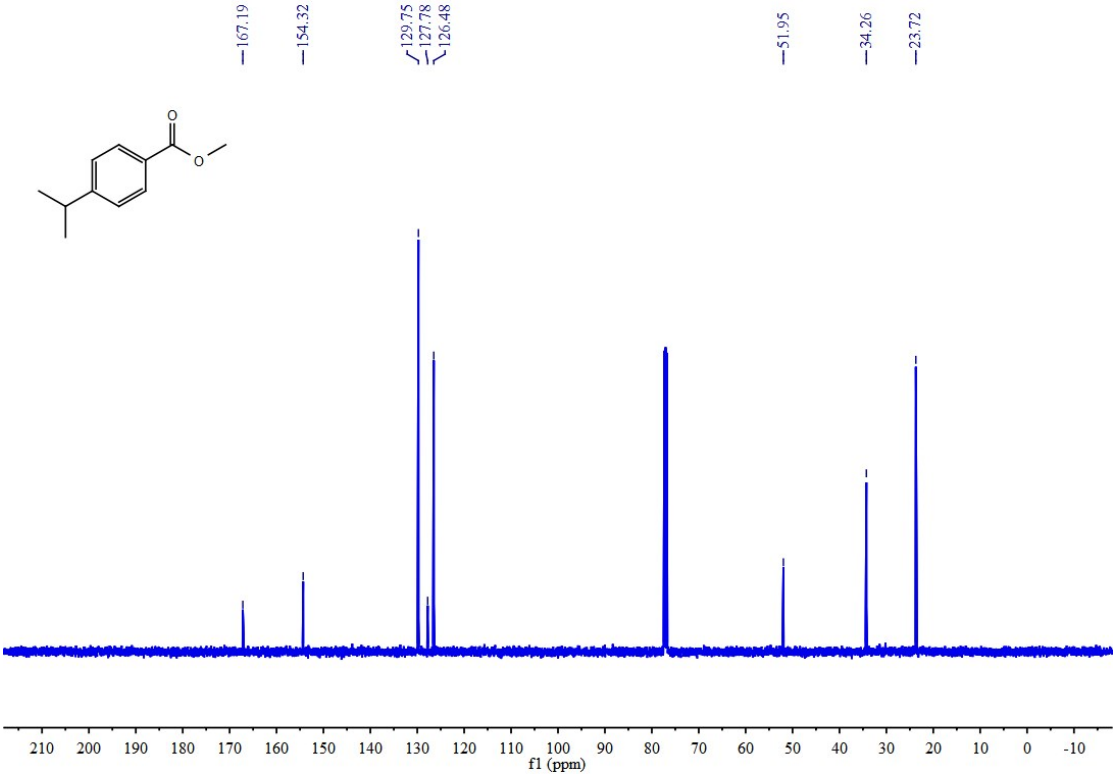
^{1}H NMR spectrum of **2g** (501 MHz, $CDCl_3$).



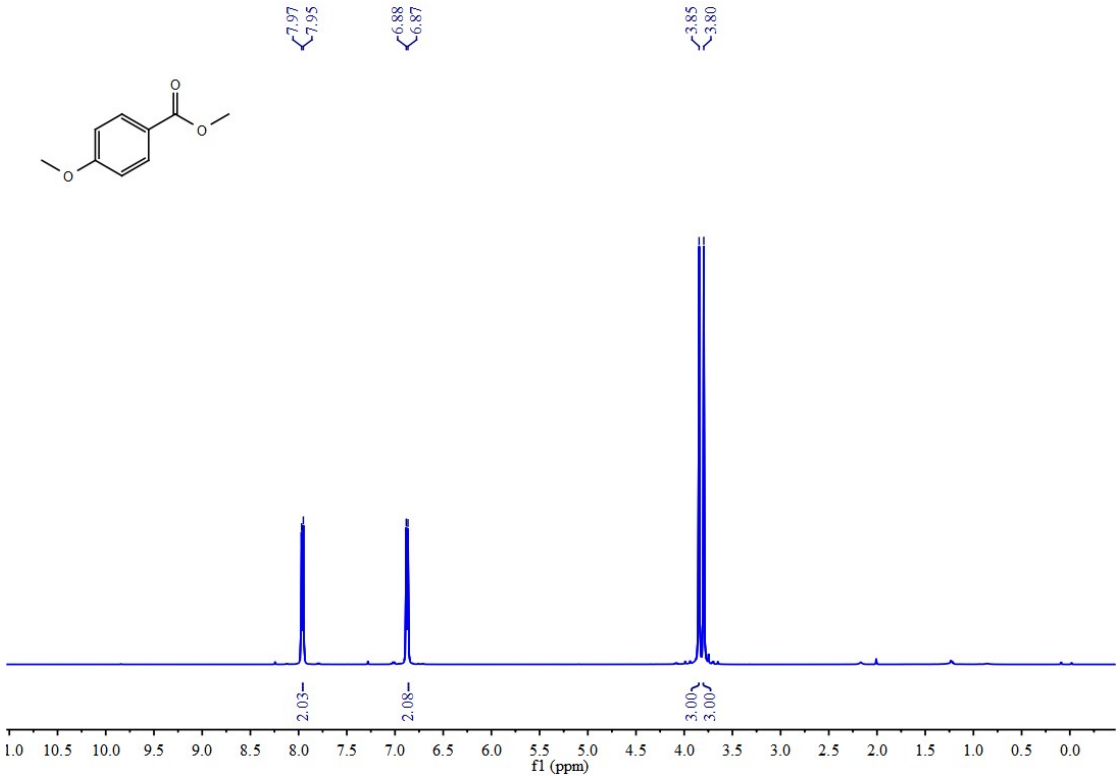
^{13}C NMR spectrum of **2g** (126 MHz, $CDCl_3$).



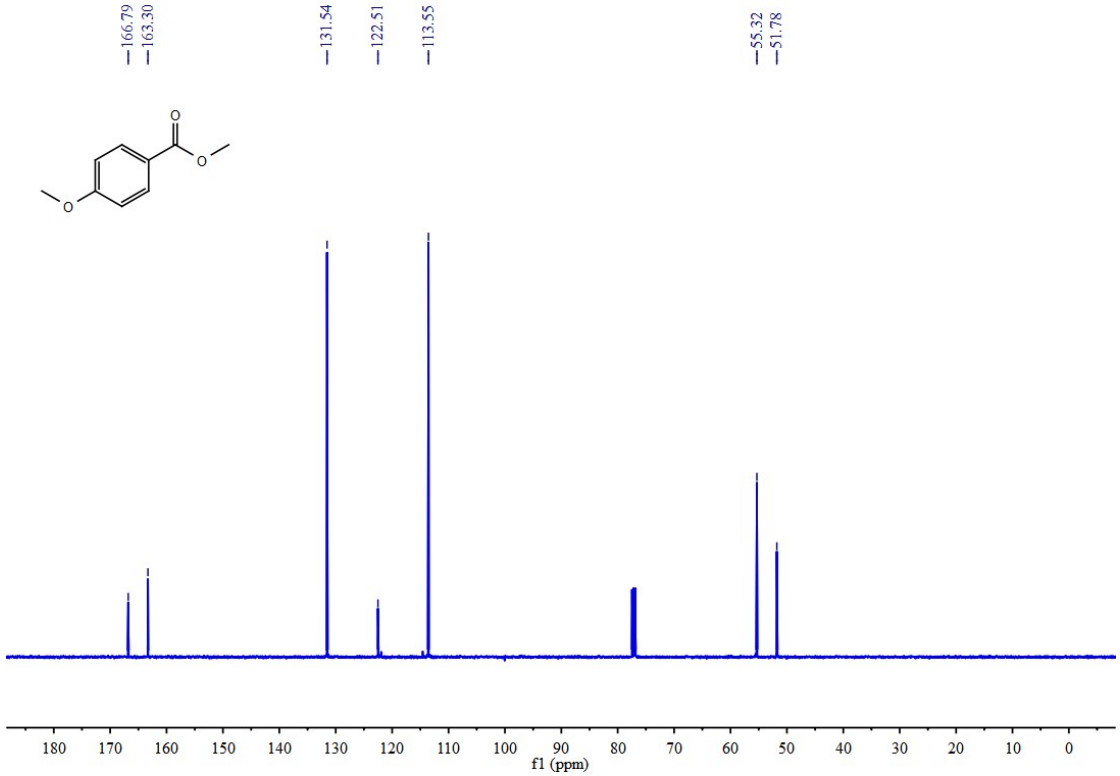
^{1}H NMR spectrum of **2h** (501 MHz, $CDCl_3$).



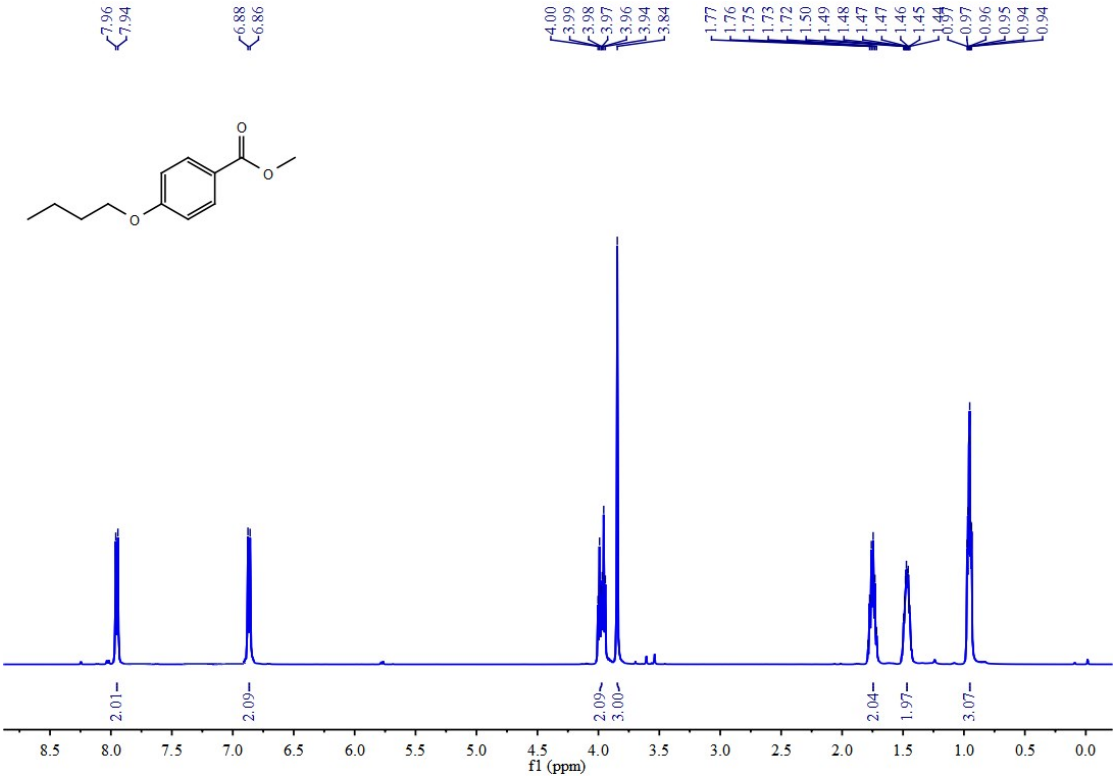
^{13}C NMR spectrum of **2h** (126 MHz, $CDCl_3$).



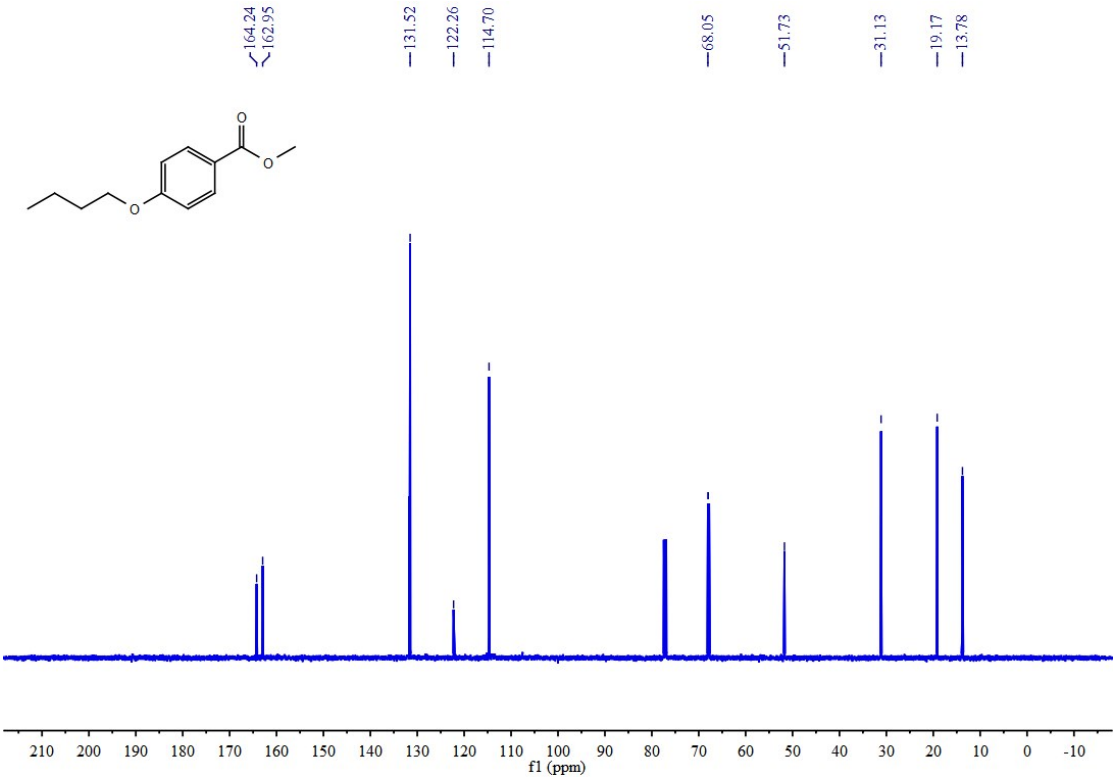
^{1}H NMR spectrum of **2i** (501 MHz, $CDCl_3$).



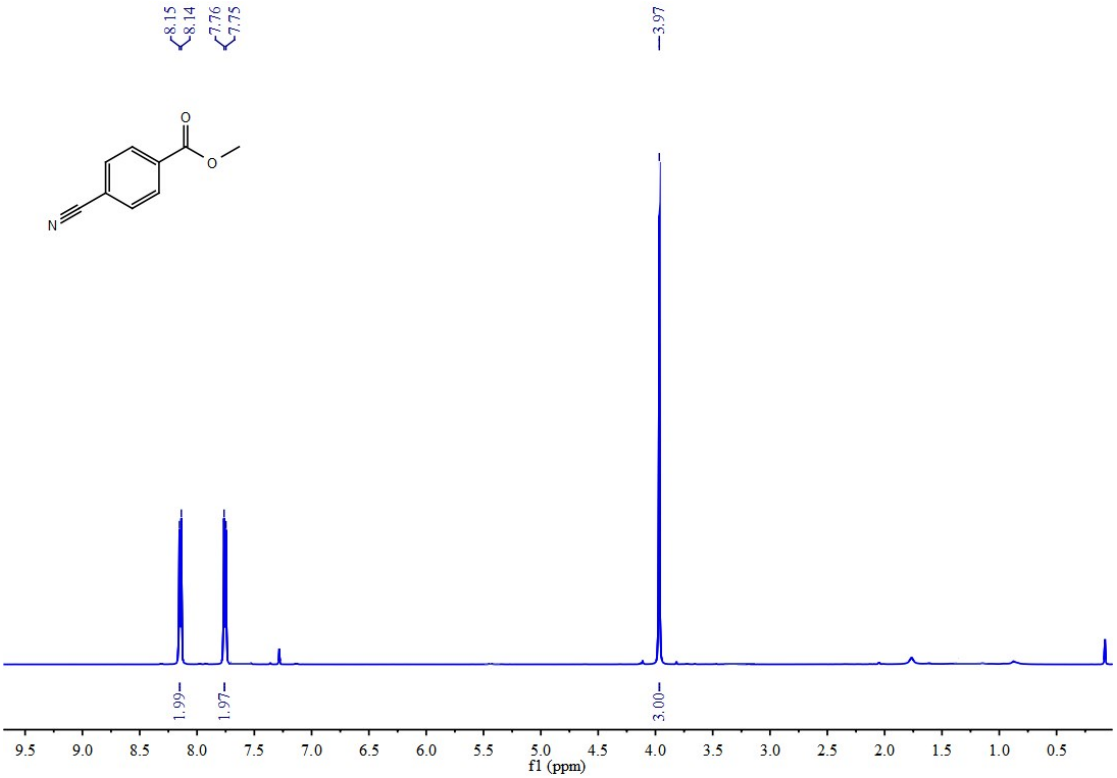
^{13}C NMR spectrum of **2i** (126 MHz, $CDCl_3$).



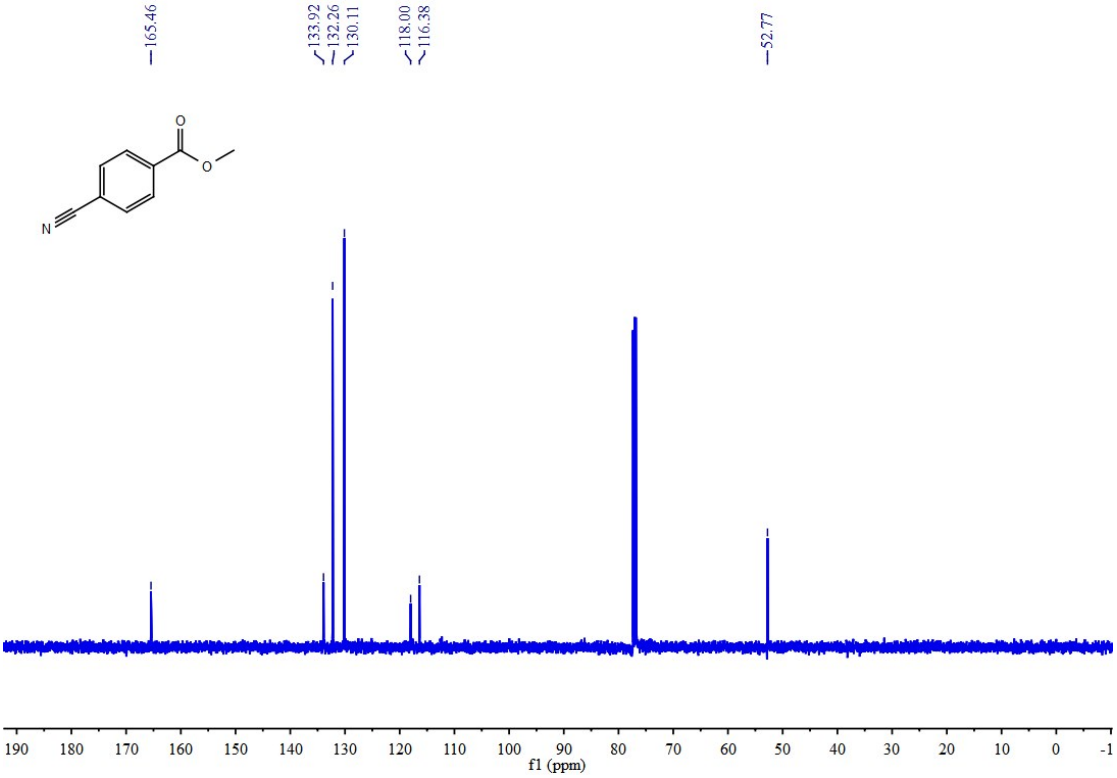
^{1}H NMR spectrum of **2j** (501 MHz, $CDCl_3$).



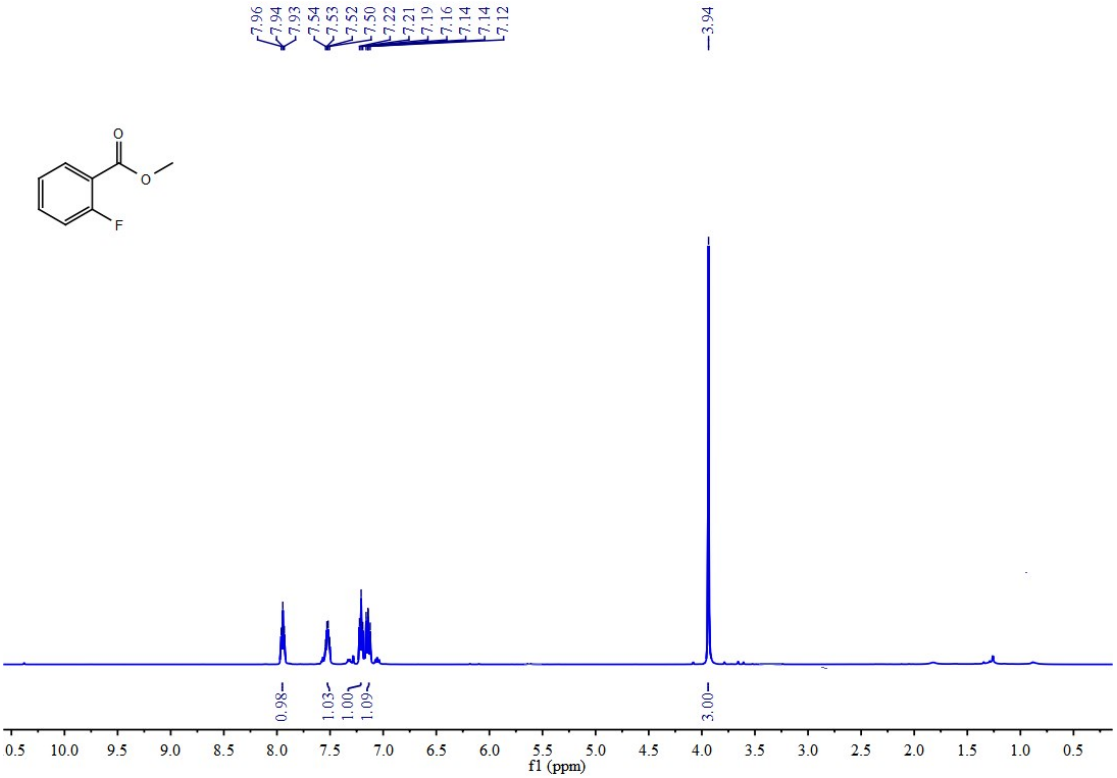
^{13}C NMR spectrum of **2j** (126 MHz, $CDCl_3$).



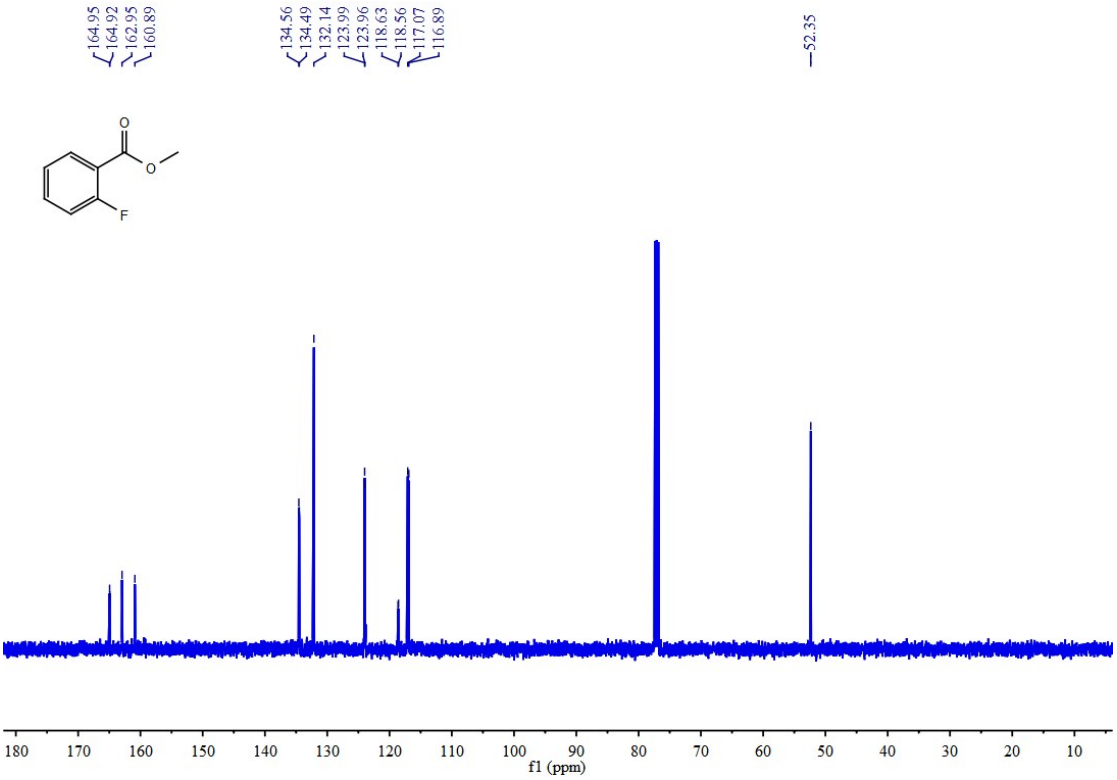
^{1}H NMR spectrum of **2k** (501 MHz, $CDCl_3$).



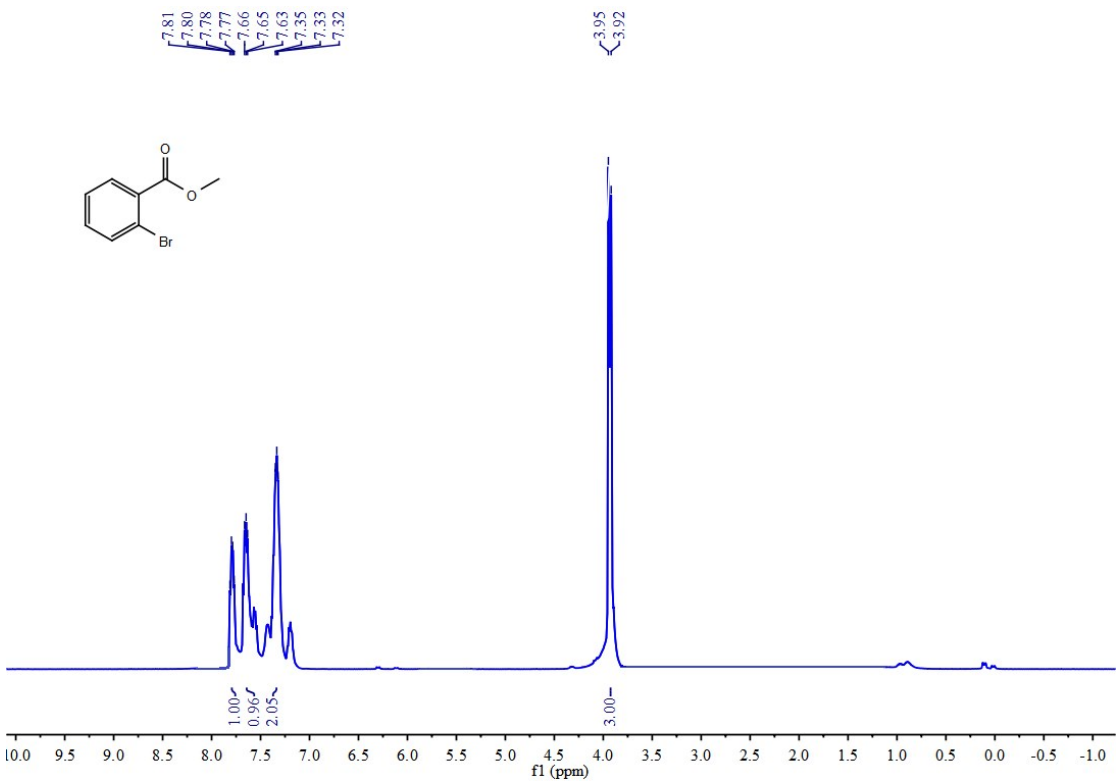
^{13}C NMR spectrum of **2k** (126 MHz, $CDCl_3$).



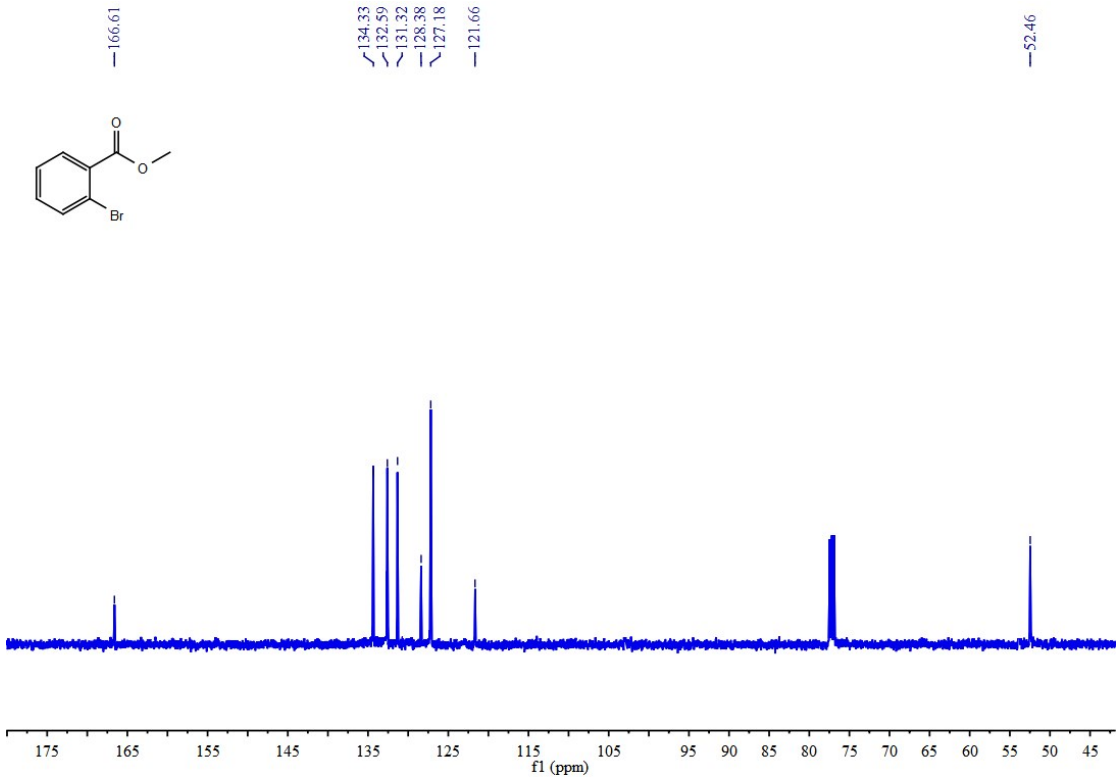
^{1}H NMR spectrum of **3a** (501 MHz, $CDCl_3$).



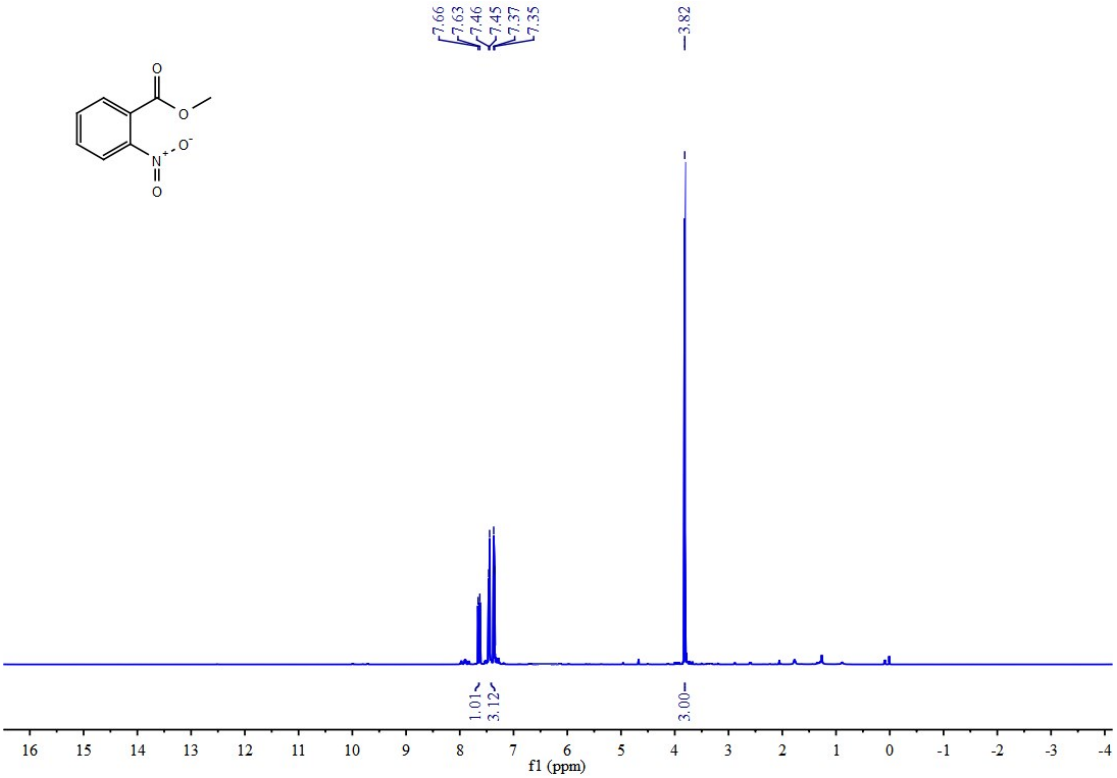
^{13}C NMR spectrum of **3a** (126 MHz, $CDCl_3$).



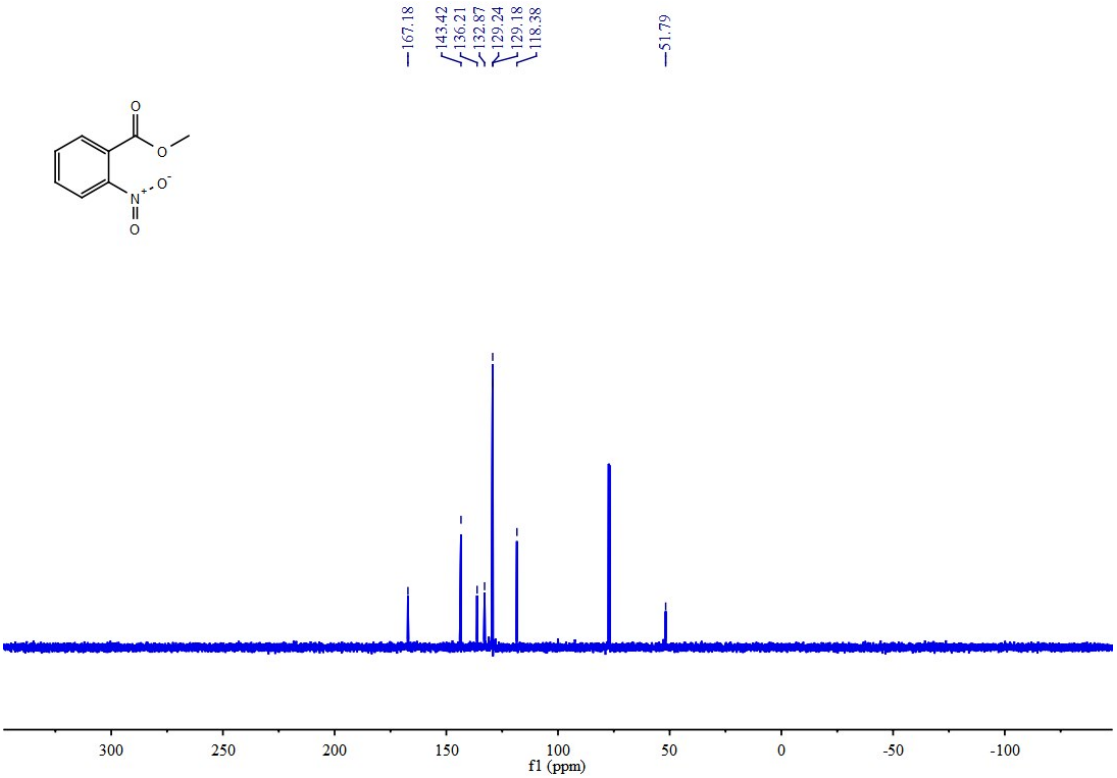
^{1}H NMR spectrum of **3b** (501 MHz, $CDCl_3$).



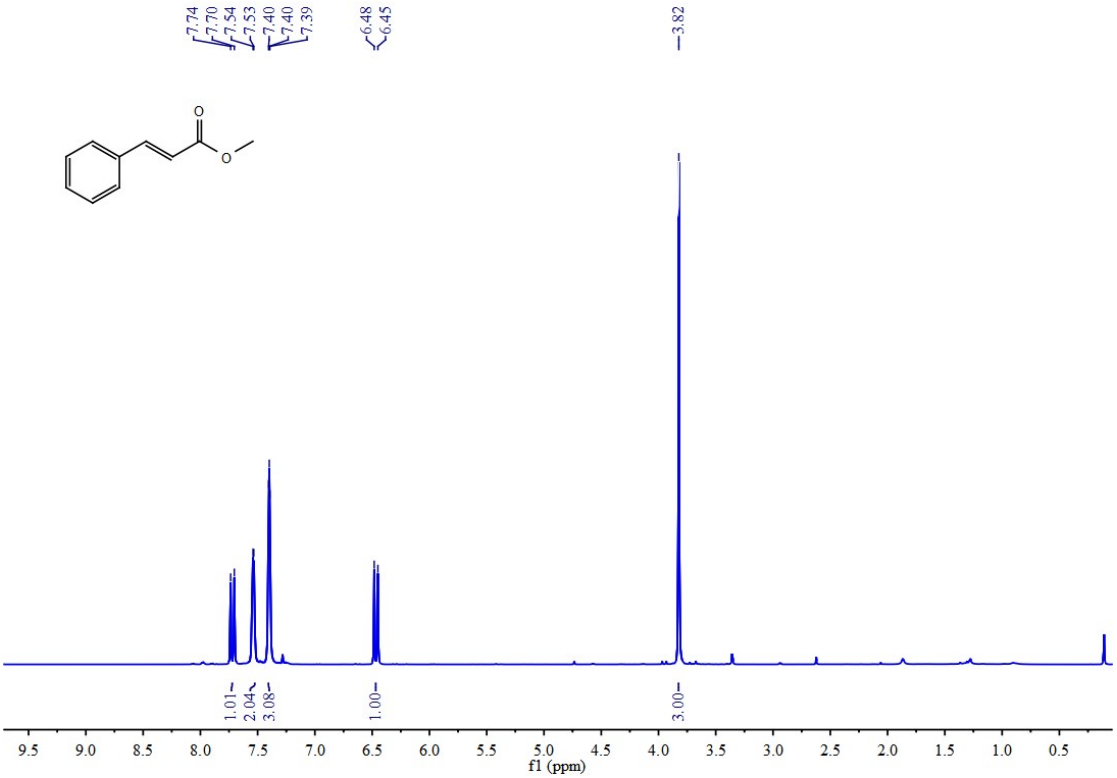
^{13}C NMR spectrum of **3b** (126 MHz, $CDCl_3$).



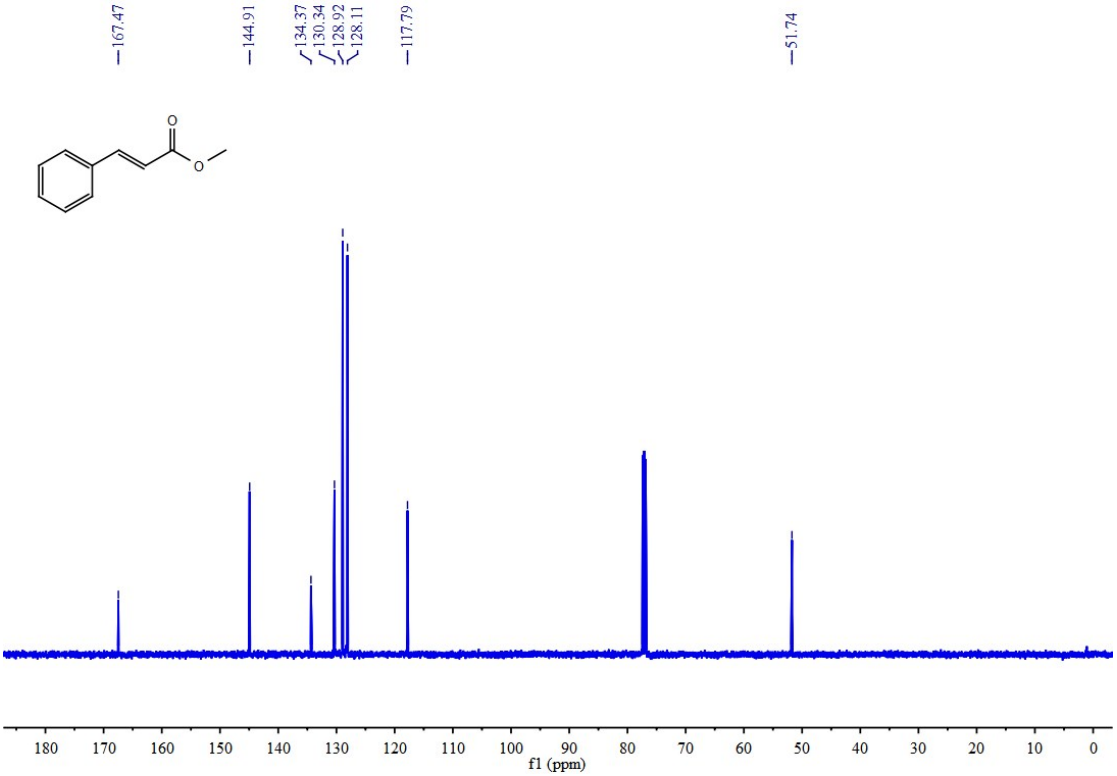
^{1}H NMR spectrum of **3c** (501 MHz, $CDCl_3$).



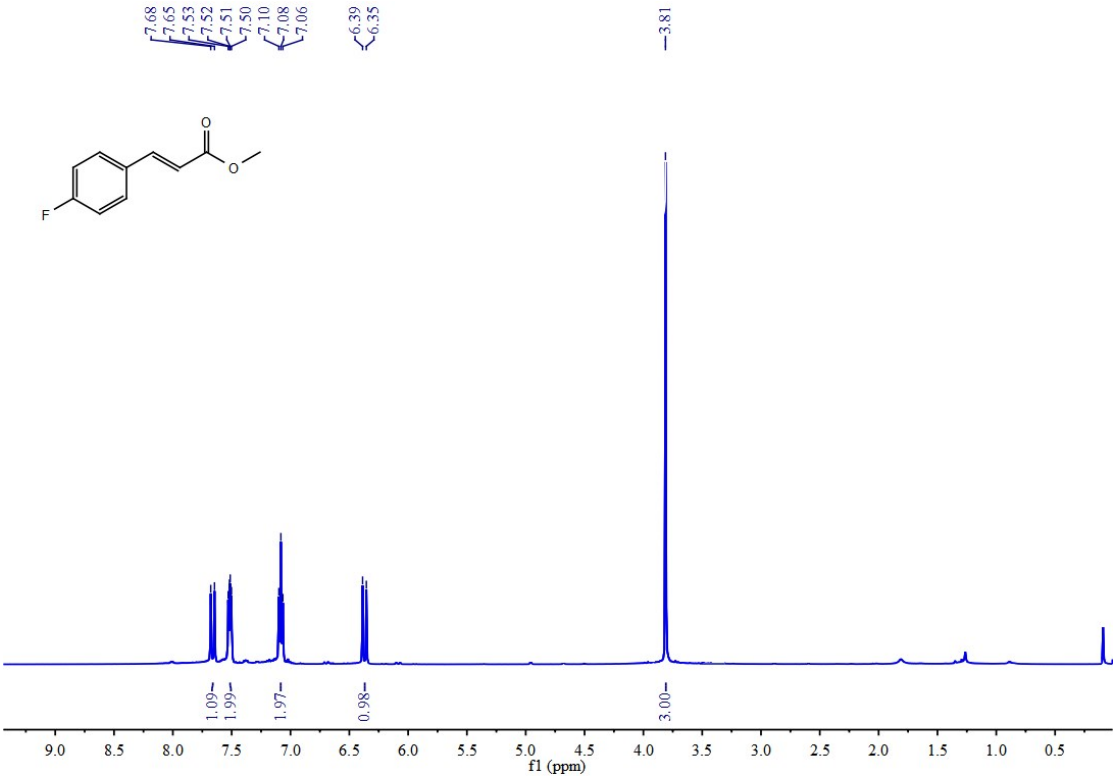
^{13}C NMR spectrum of **3c** (126 MHz, $CDCl_3$).



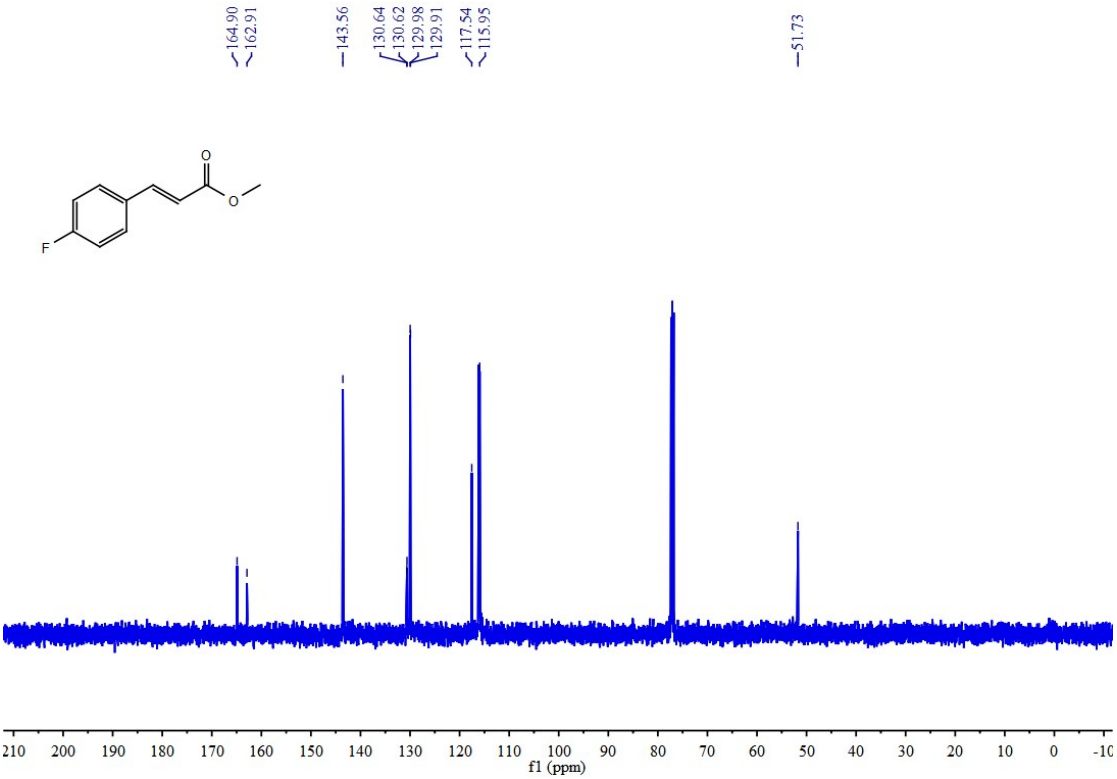
^{1}H NMR spectrum of **4a** (501 MHz, $CDCl_3$).



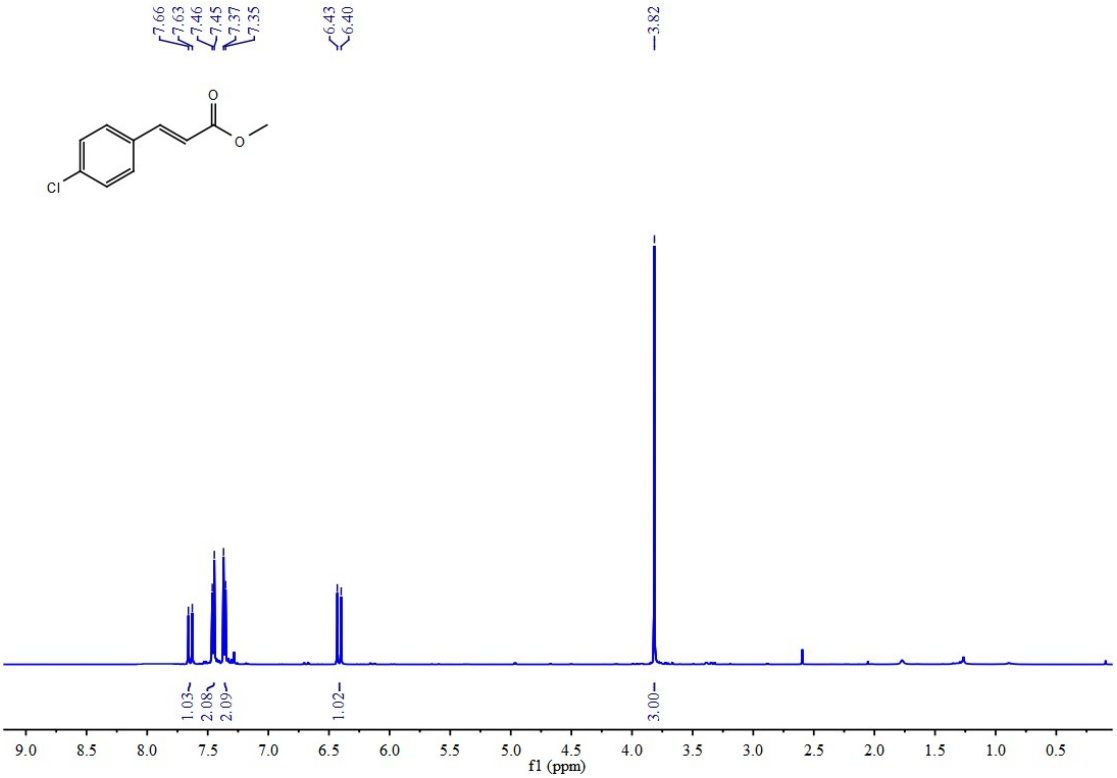
^{13}C NMR spectrum of **4a** (126 MHz, $CDCl_3$).



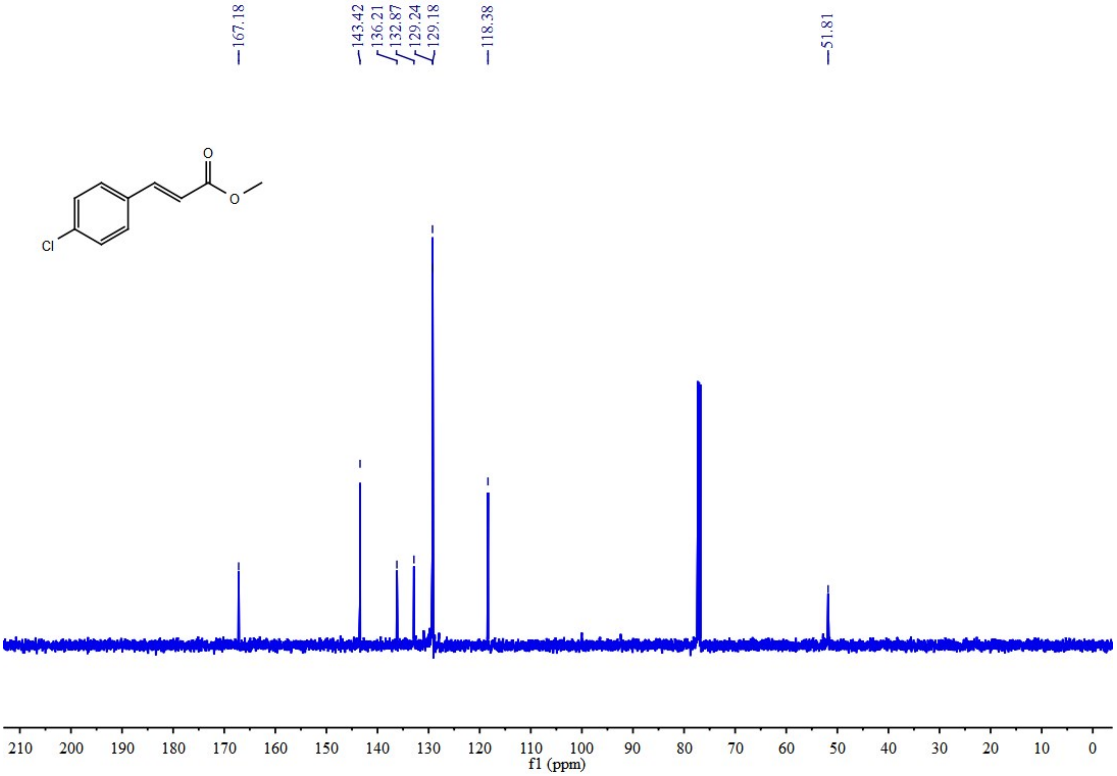
^{1}H NMR spectrum of **4b** (501 MHz, $CDCl_3$).



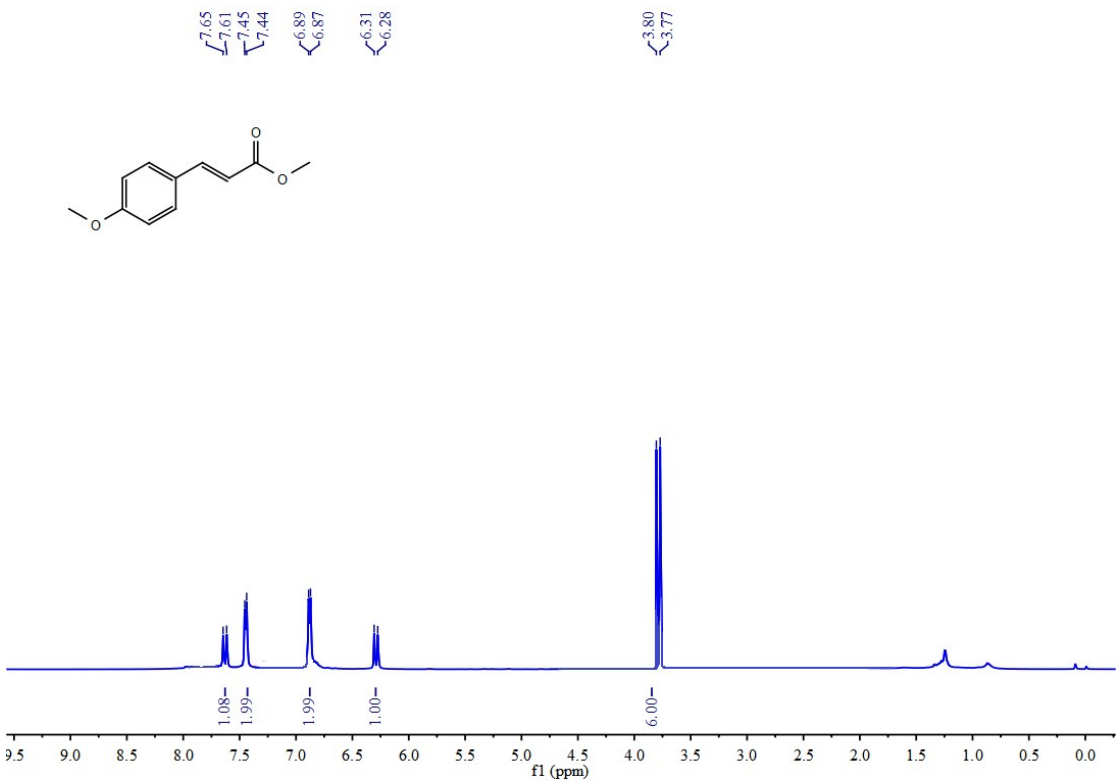
^{13}C NMR spectrum of **4b** (126 MHz, $CDCl_3$).



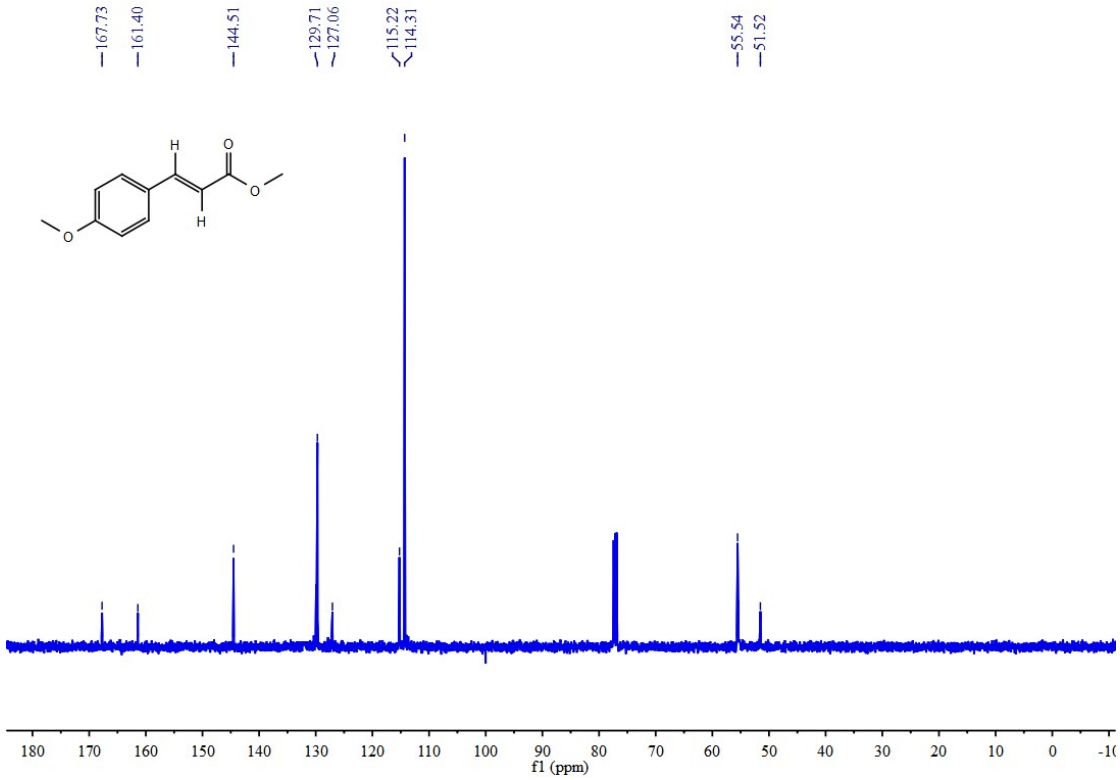
^{1}H NMR spectrum of **4c** (501 MHz, $CDCl_3$).



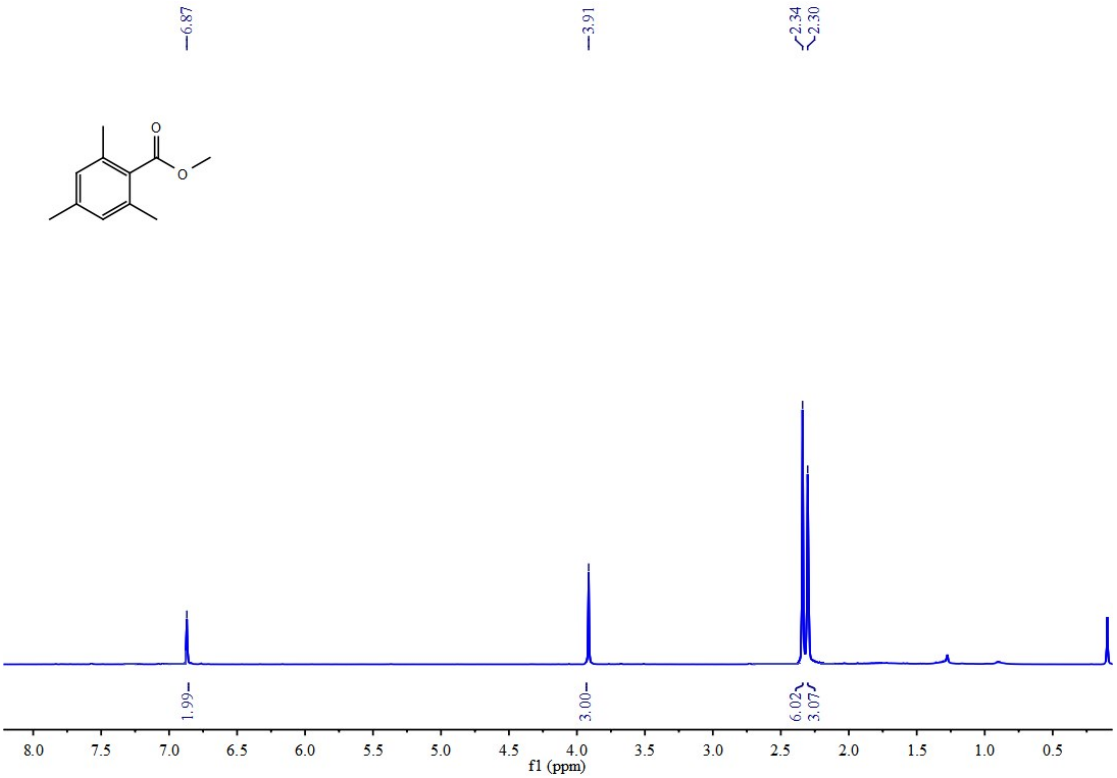
^{13}C NMR spectrum of **4c** (126 MHz, $CDCl_3$).



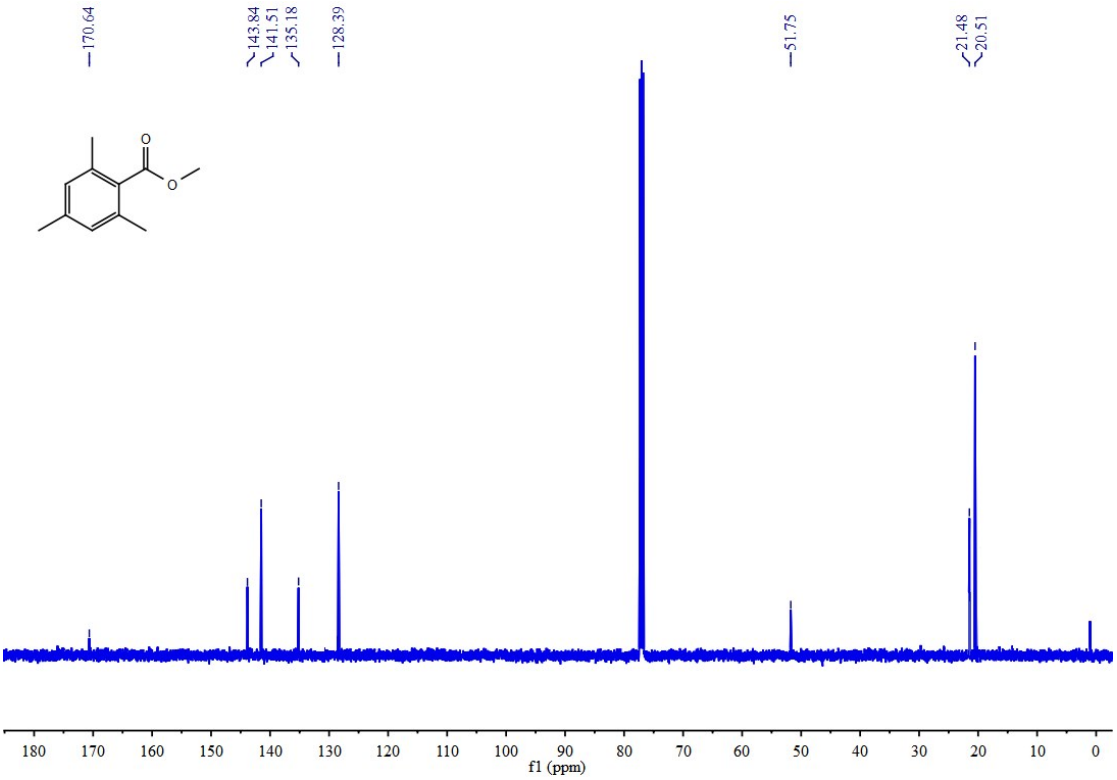
^{1}H NMR spectrum of **4d** (501 MHz, $CDCl_3$).



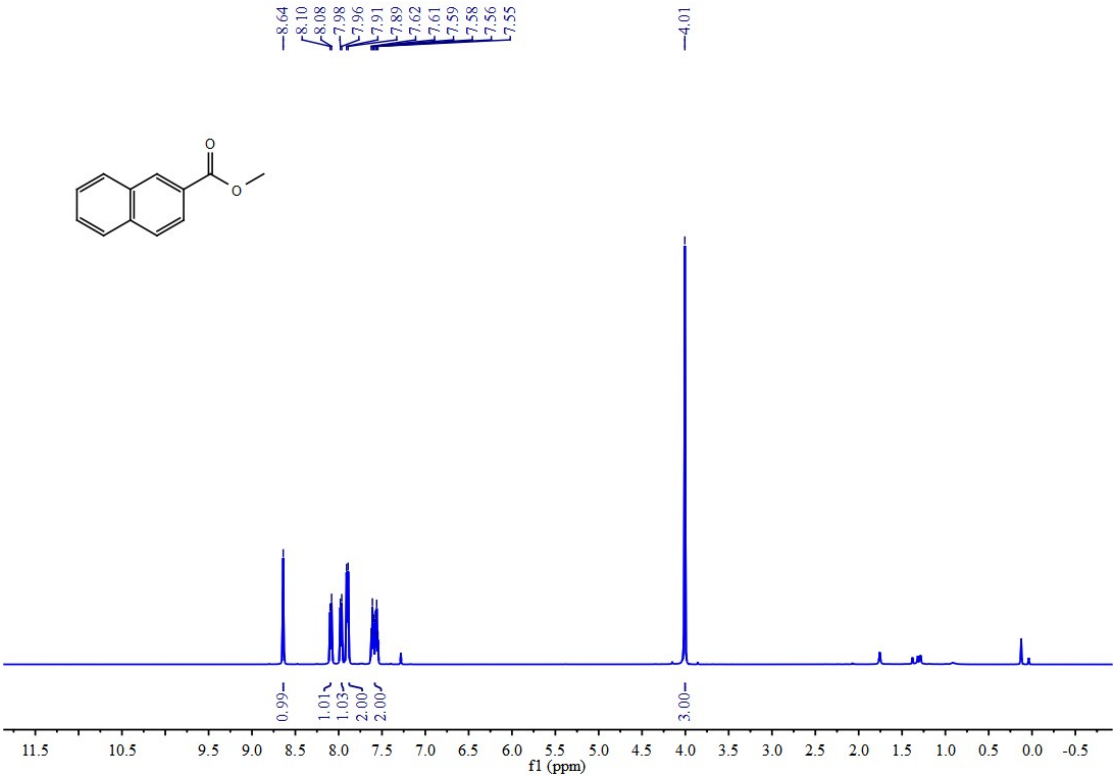
^{13}C NMR spectrum of **4d** (126 MHz, $CDCl_3$).



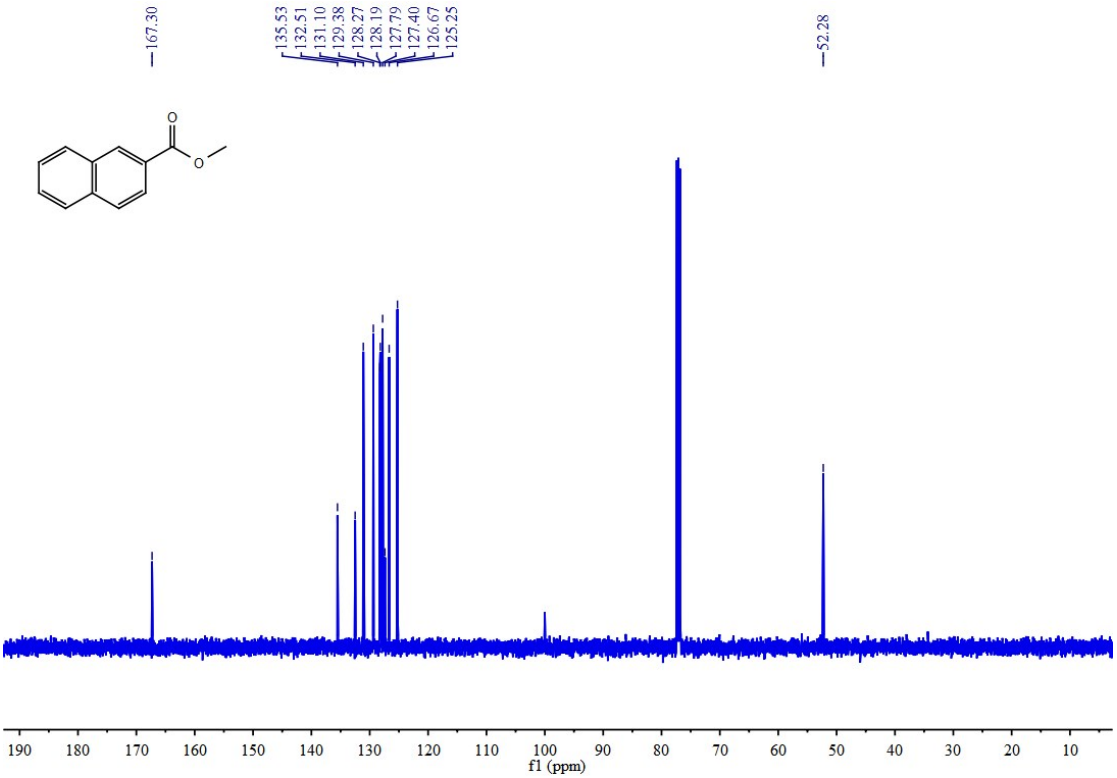
^{1}H NMR spectrum of **5** (501 MHz, $CDCl_3$).



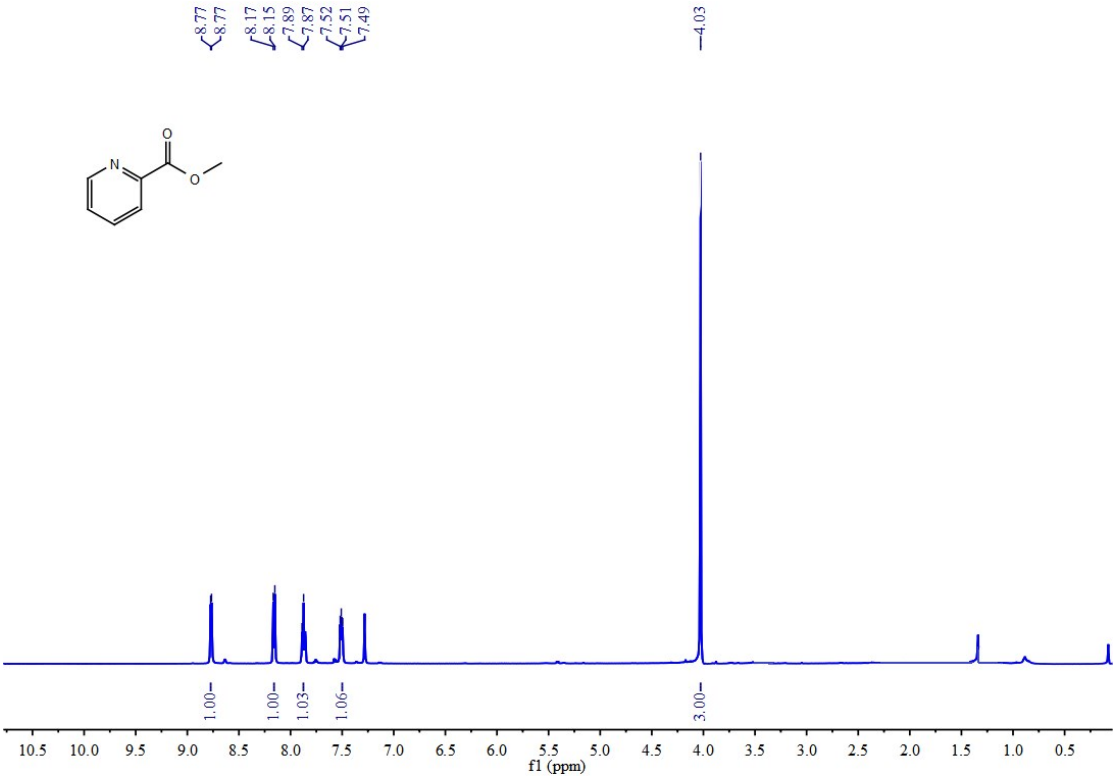
^{13}C NMR spectrum of **5** (126 MHz, $CDCl_3$).



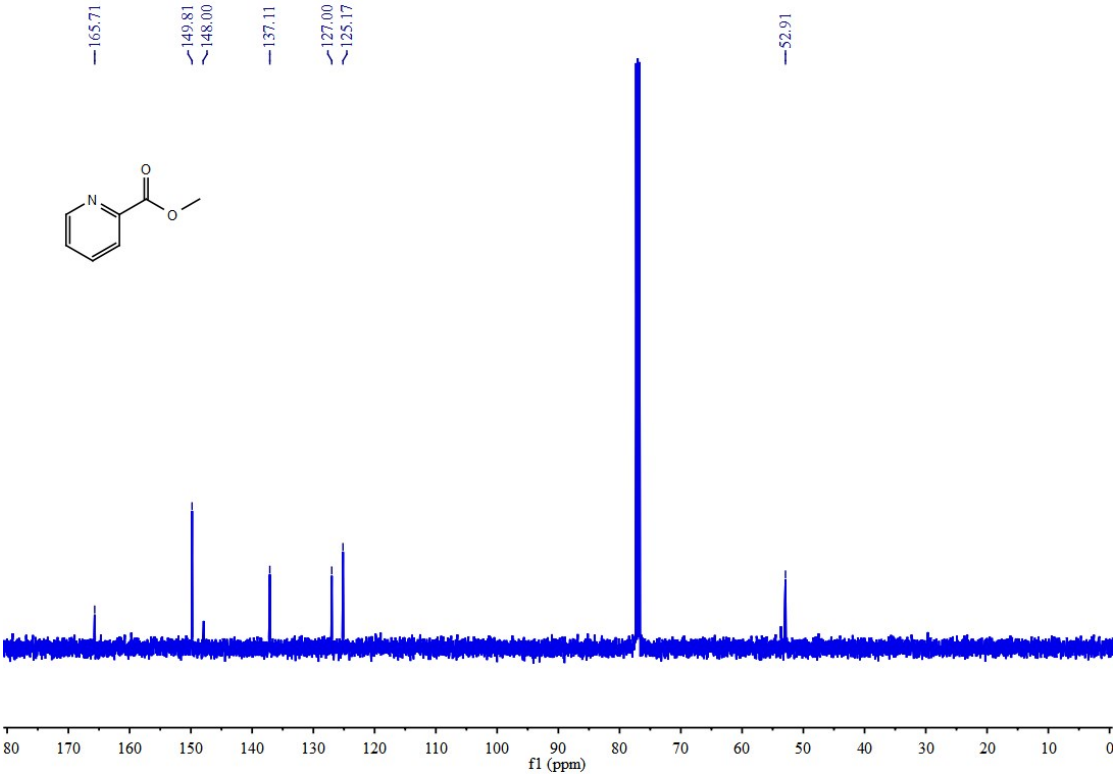
^{1}H NMR spectrum of **6** (501 MHz, $CDCl_3$).



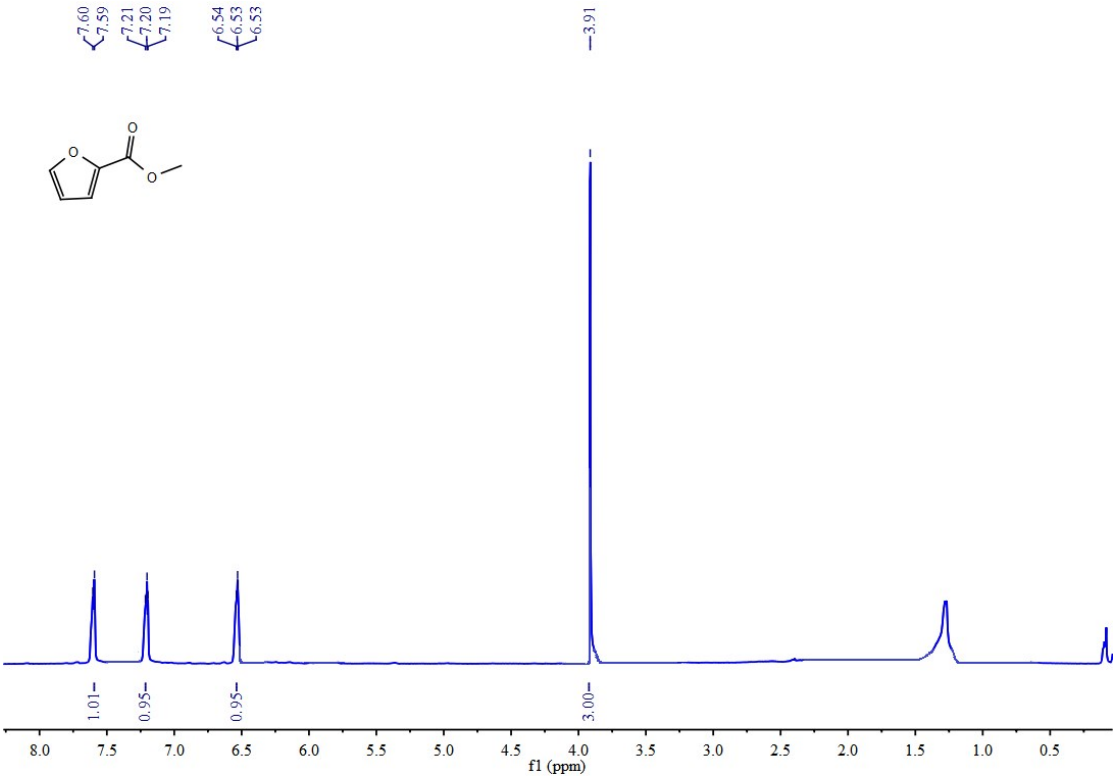
^{13}C NMR spectrum of **6** (126 MHz, $CDCl_3$).



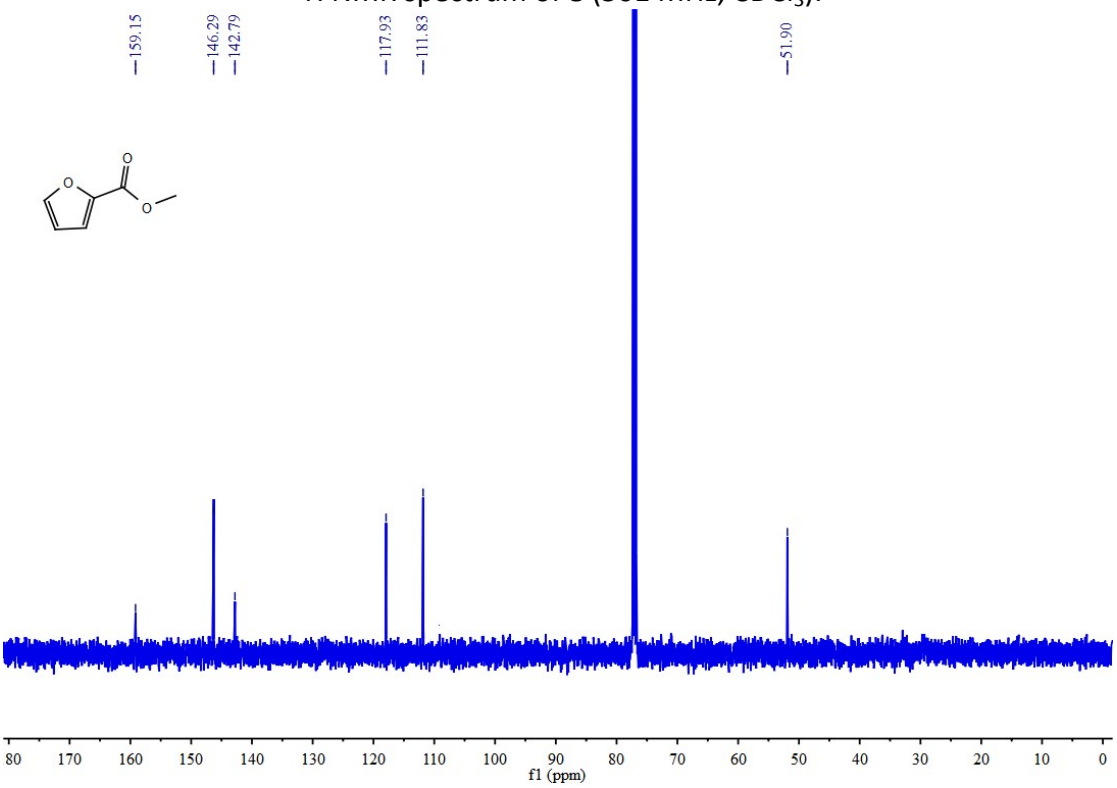
^{1}H NMR spectrum of **7** (501 MHz, $CDCl_3$).



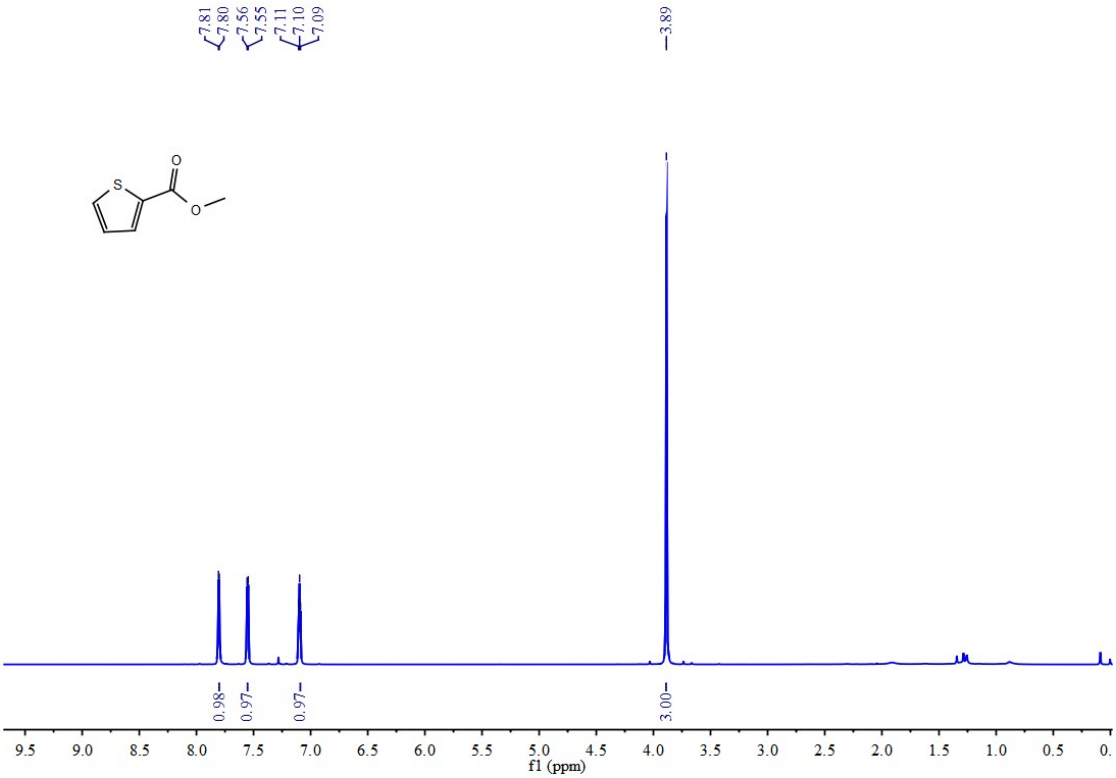
^{13}C NMR spectrum of **7** (126 MHz, $CDCl_3$).



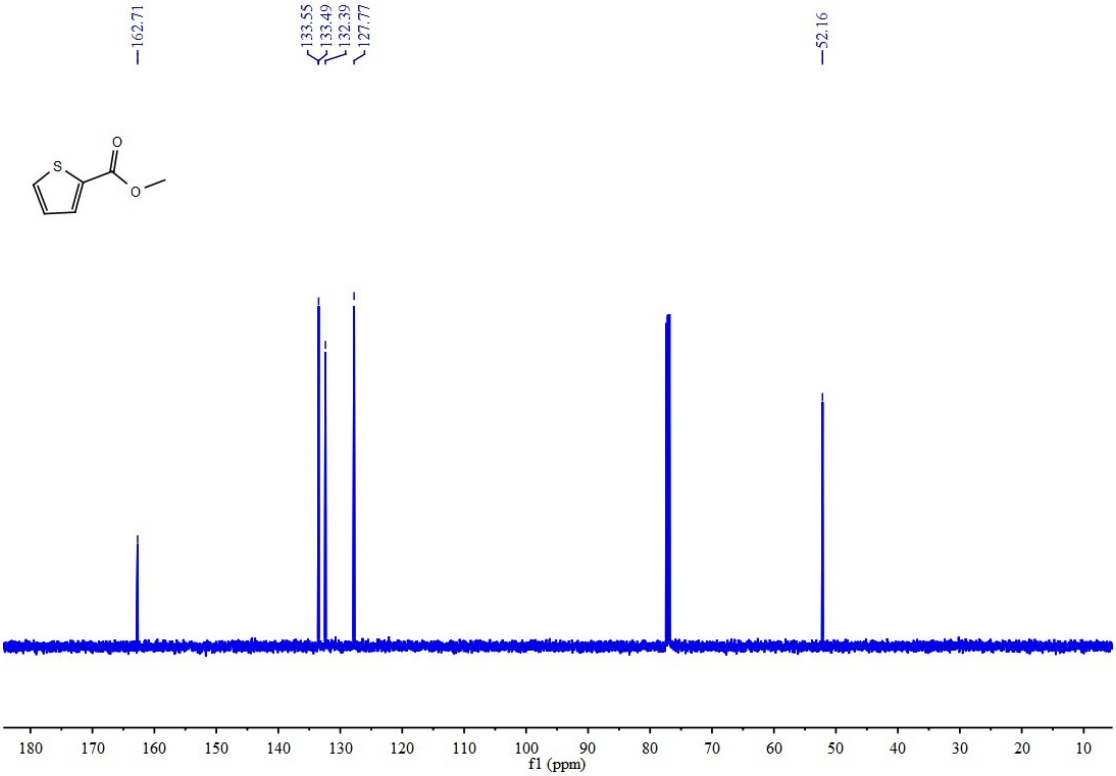
^{1}H NMR spectrum of **8** (501 MHz, $CDCl_3$).



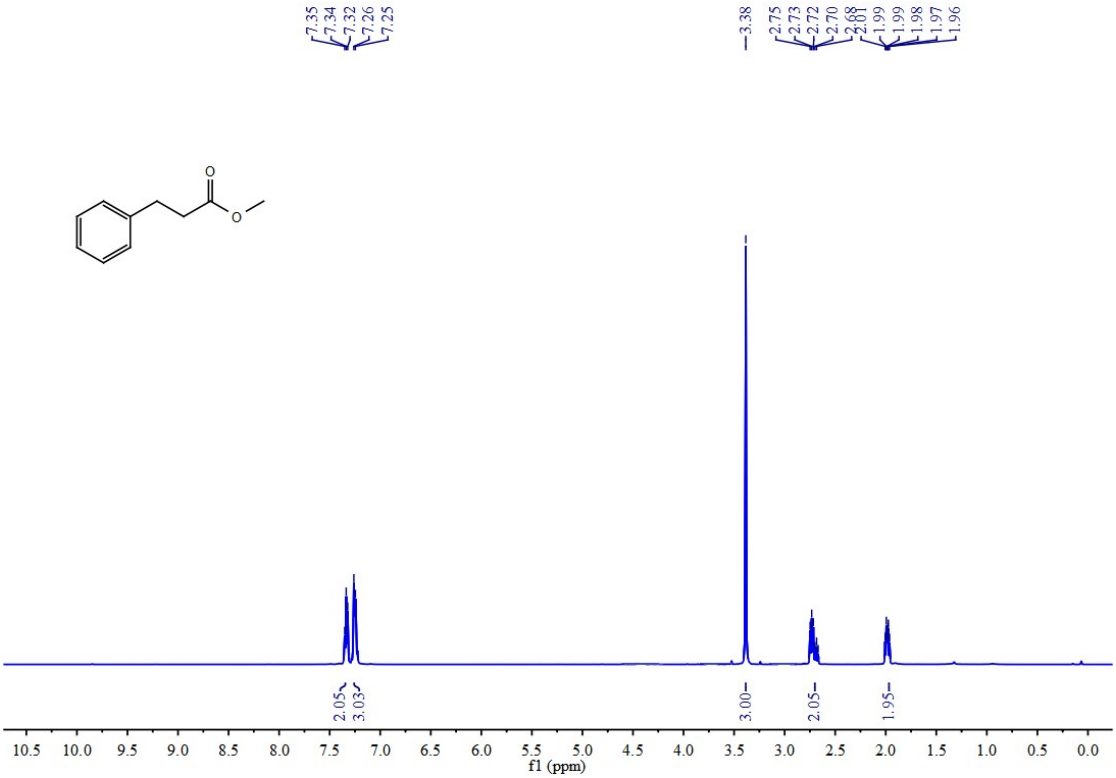
^{13}C NMR spectrum of **8** (126 MHz, $CDCl_3$).



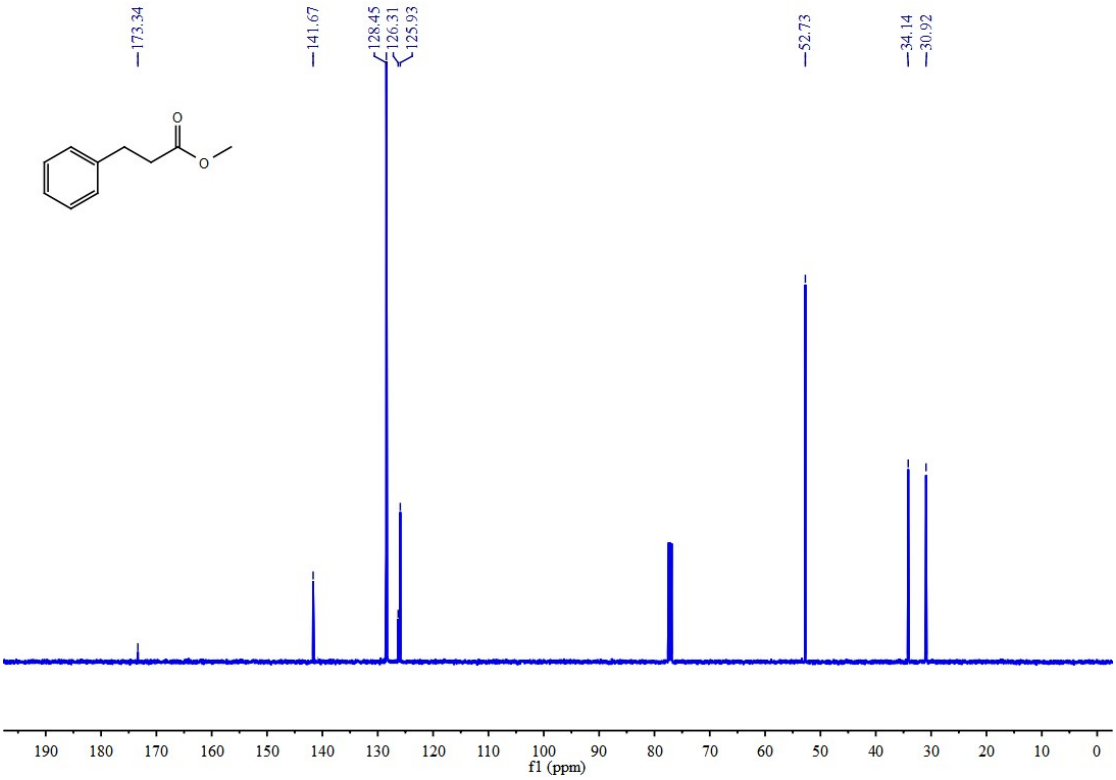
^{1}H NMR spectrum of **9** (501 MHz, $CDCl_3$).



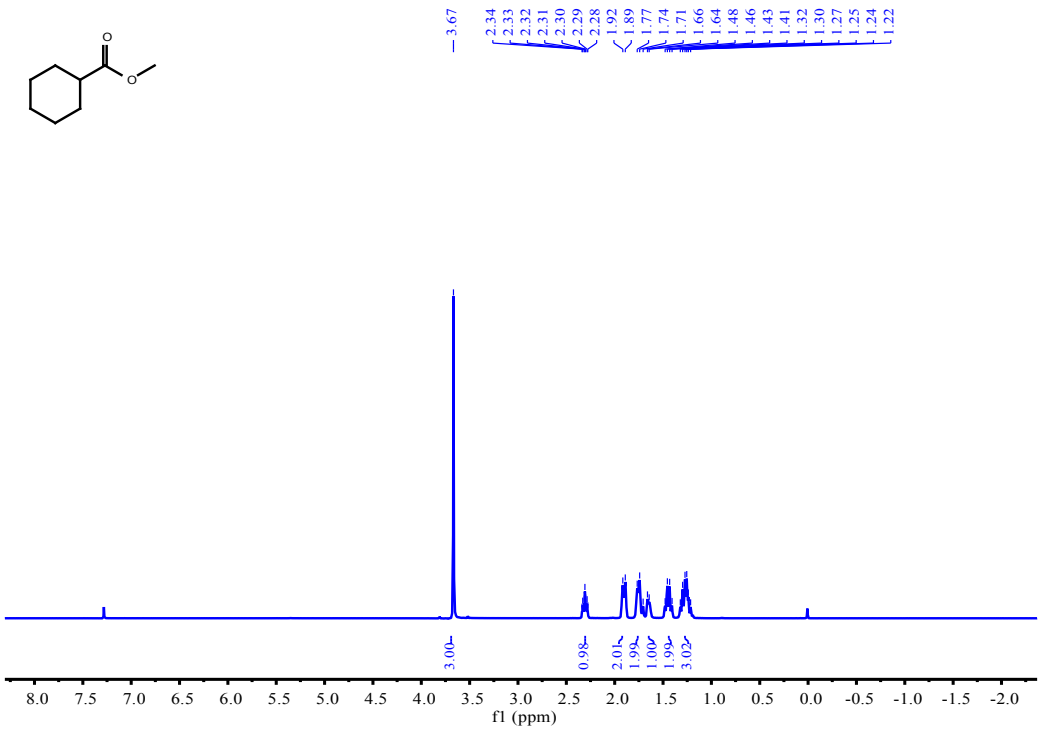
^{13}C NMR spectrum of **9** (126 MHz, $CDCl_3$).



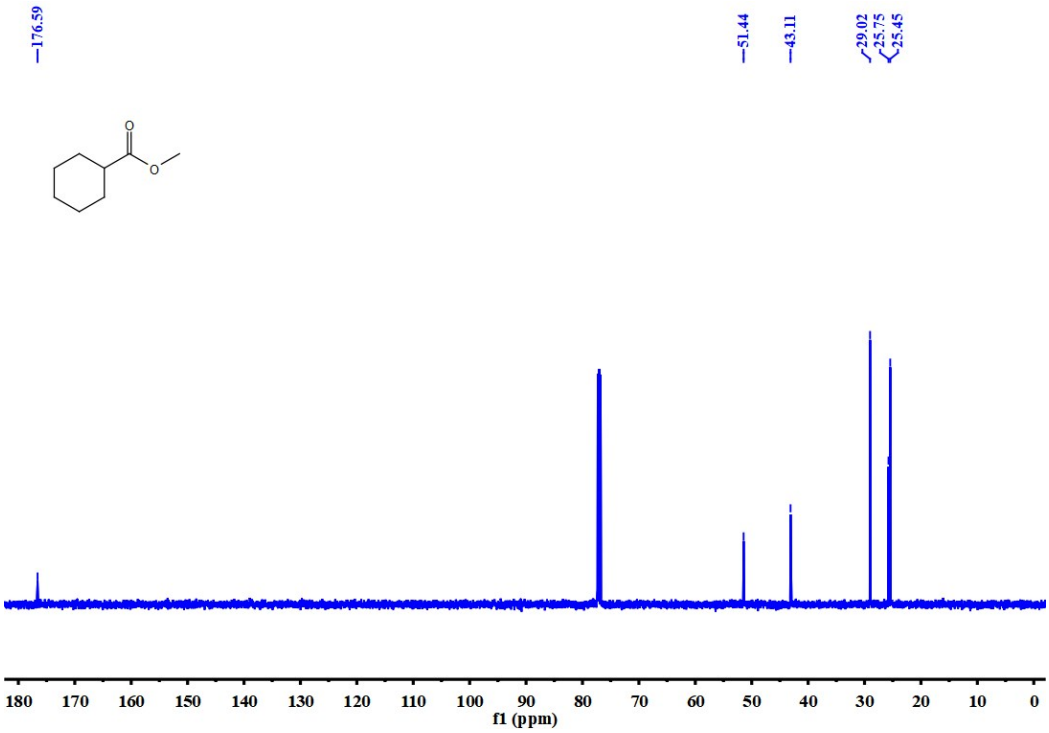
^{1}H NMR spectrum of **10** (501 MHz, $CDCl_3$).



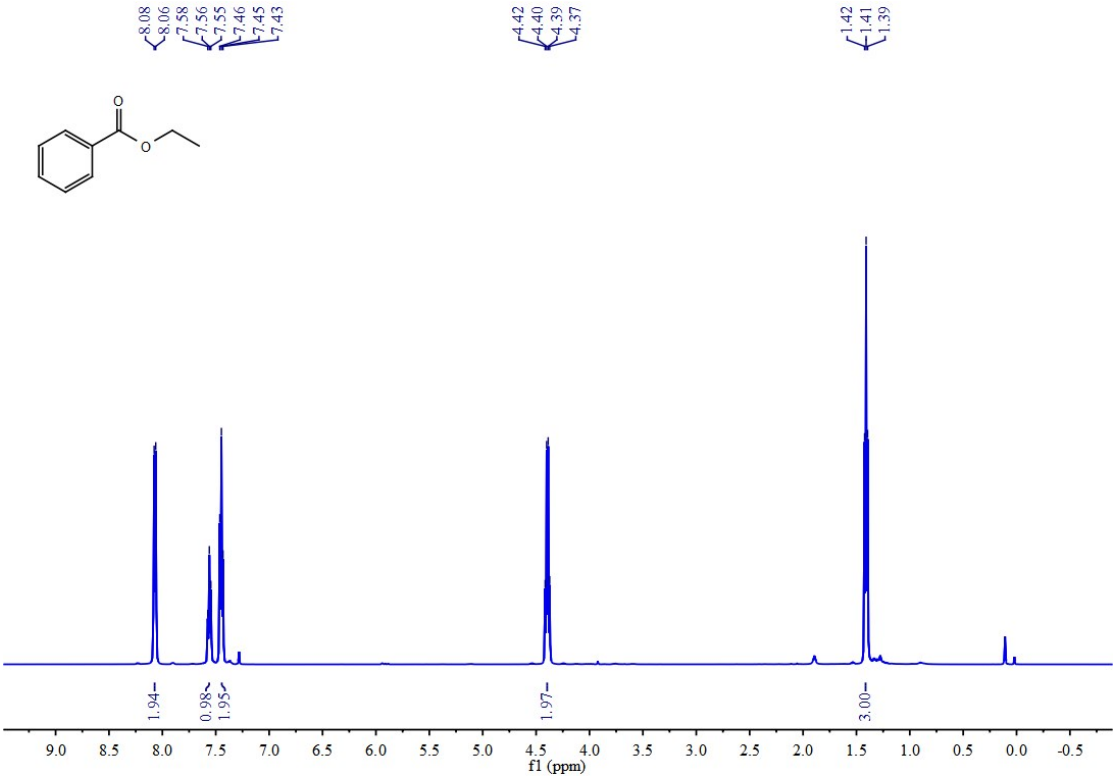
^{13}C NMR spectrum of **10** (126 MHz, $CDCl_3$).



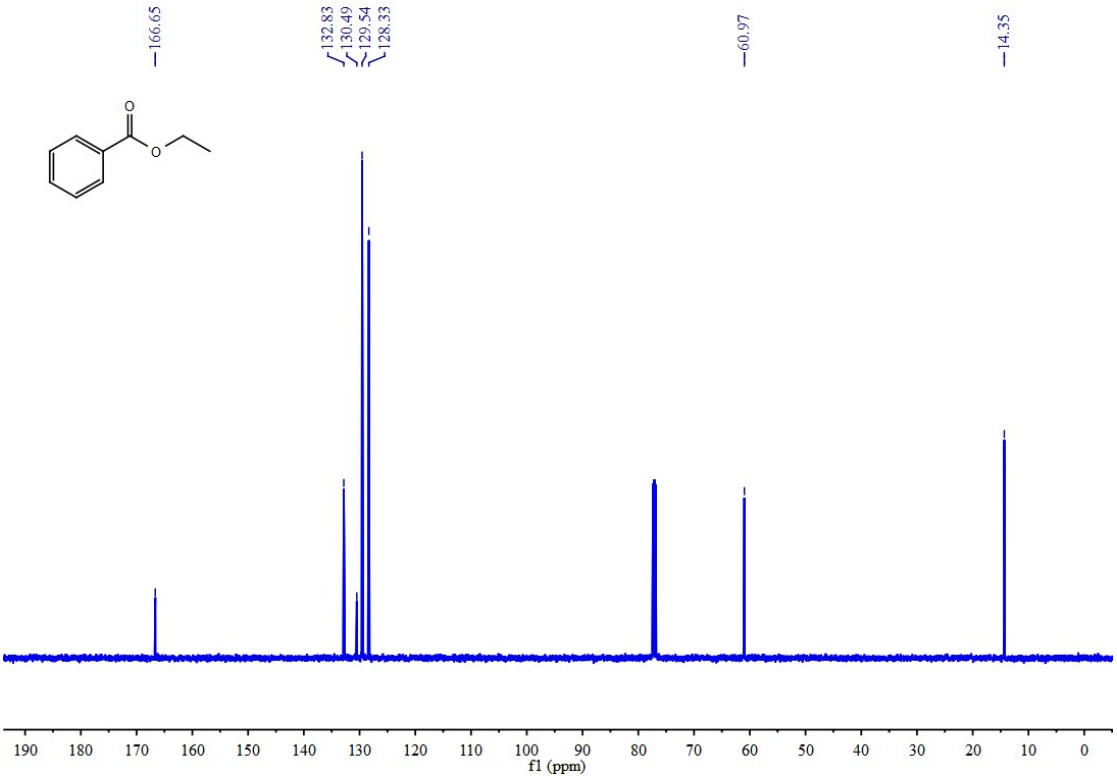
^{1}H NMR spectrum of **11** (501 MHz, $CDCl_3$).



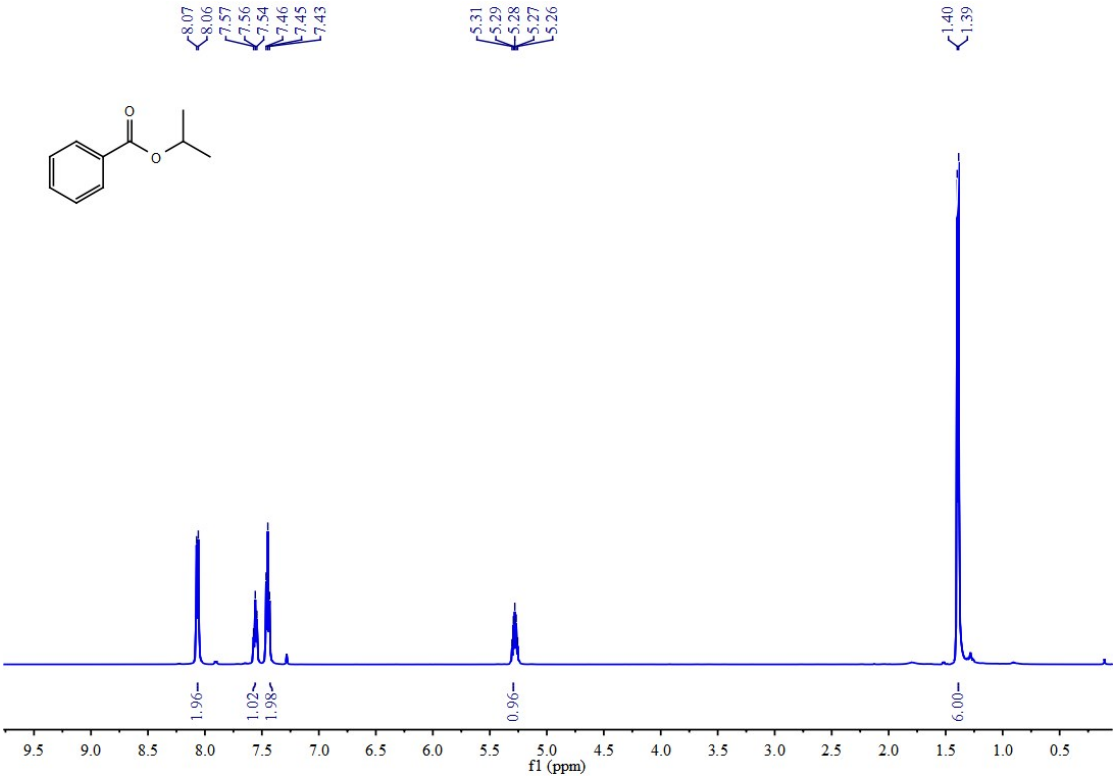
^{13}C NMR spectrum of **11** (126 MHz, $CDCl_3$).



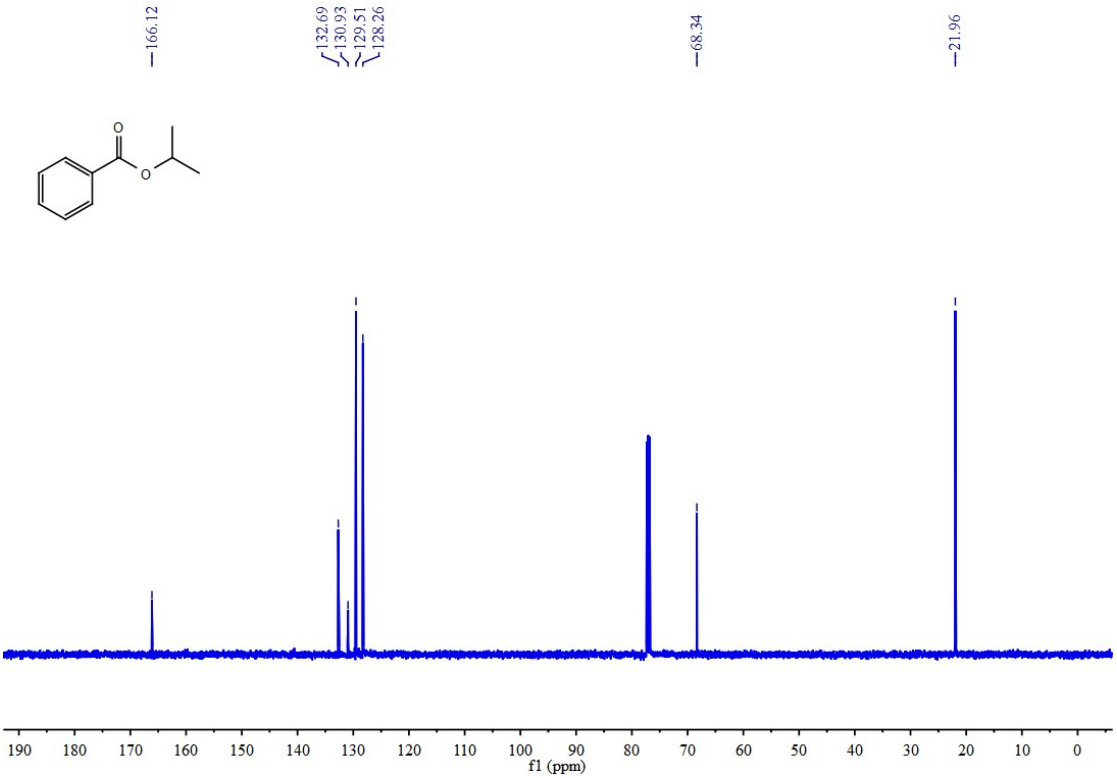
^{1}H NMR spectrum of **18** (501 MHz, $CDCl_3$).



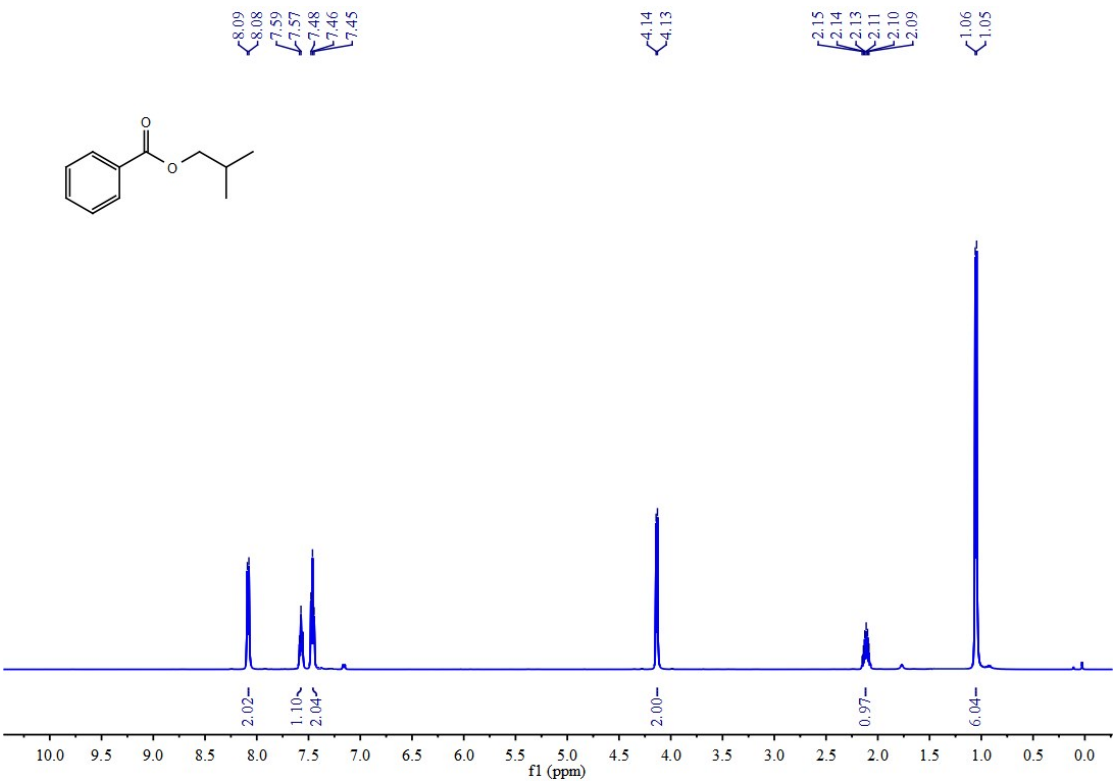
^{13}C NMR spectrum of **18** (126 MHz, $CDCl_3$).



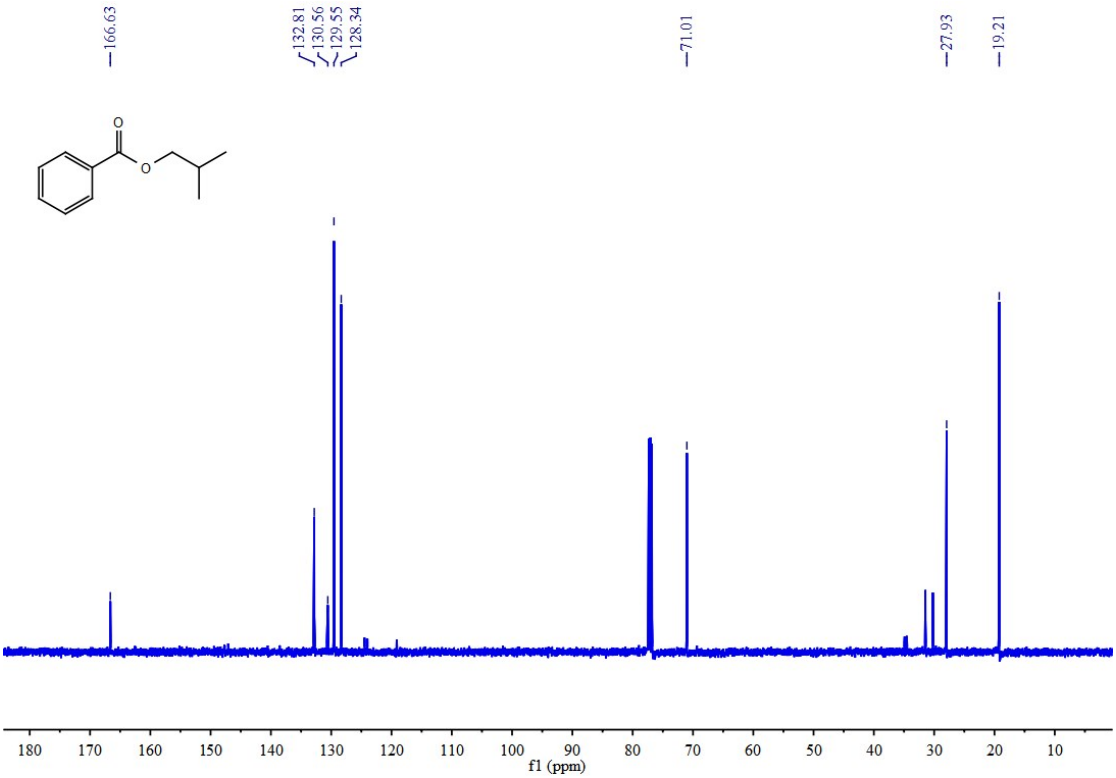
^{1}H NMR spectrum of **19** (501 MHz, $CDCl_3$).



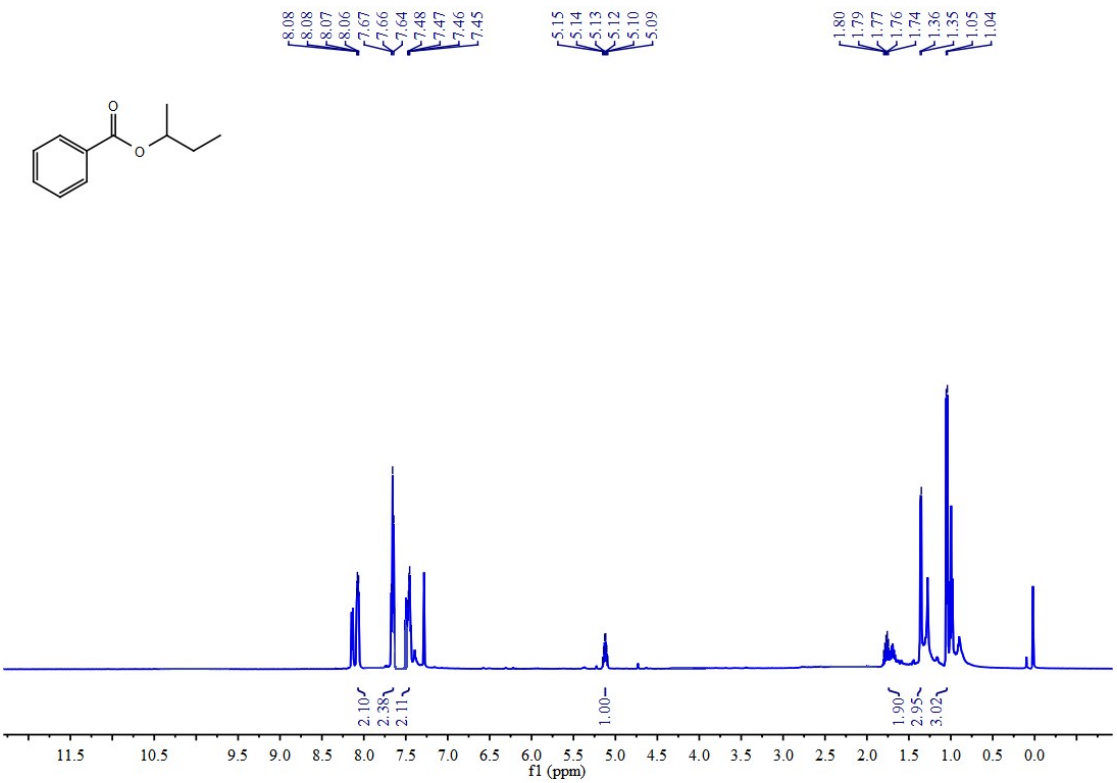
^{13}C NMR spectrum of **19** (126 MHz, $CDCl_3$).



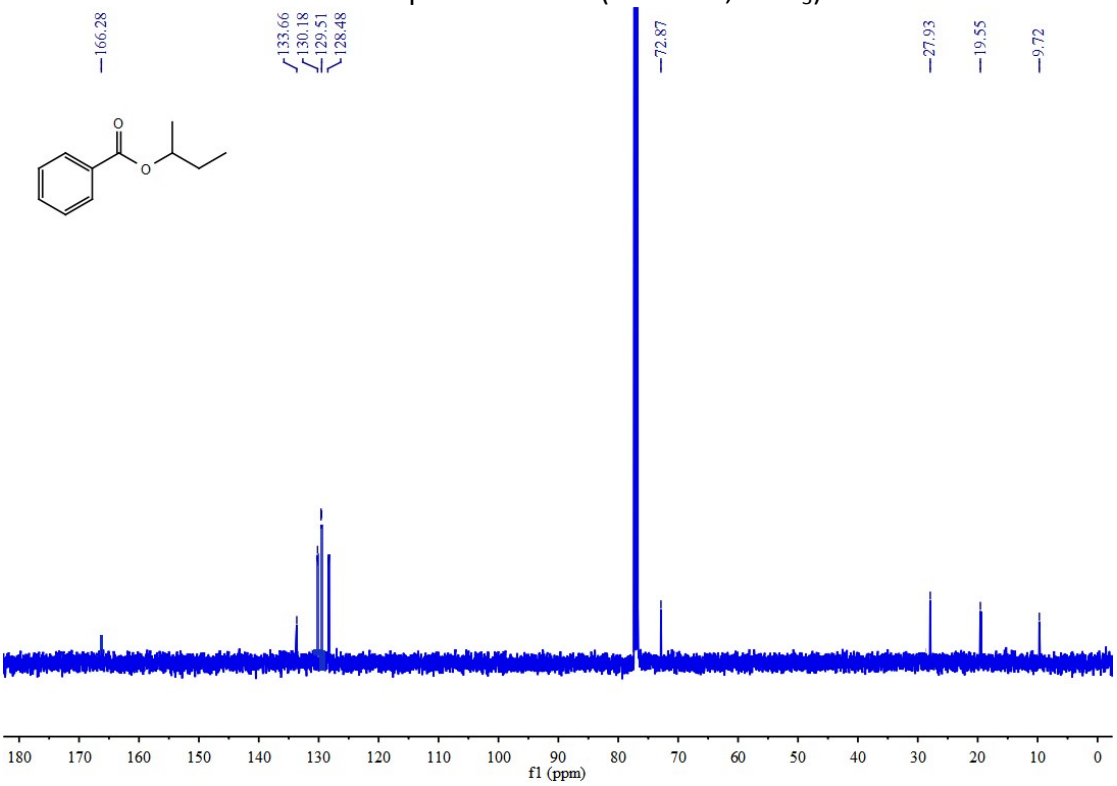
^{1}H NMR spectrum of **20** (501 MHz, $CDCl_3$).



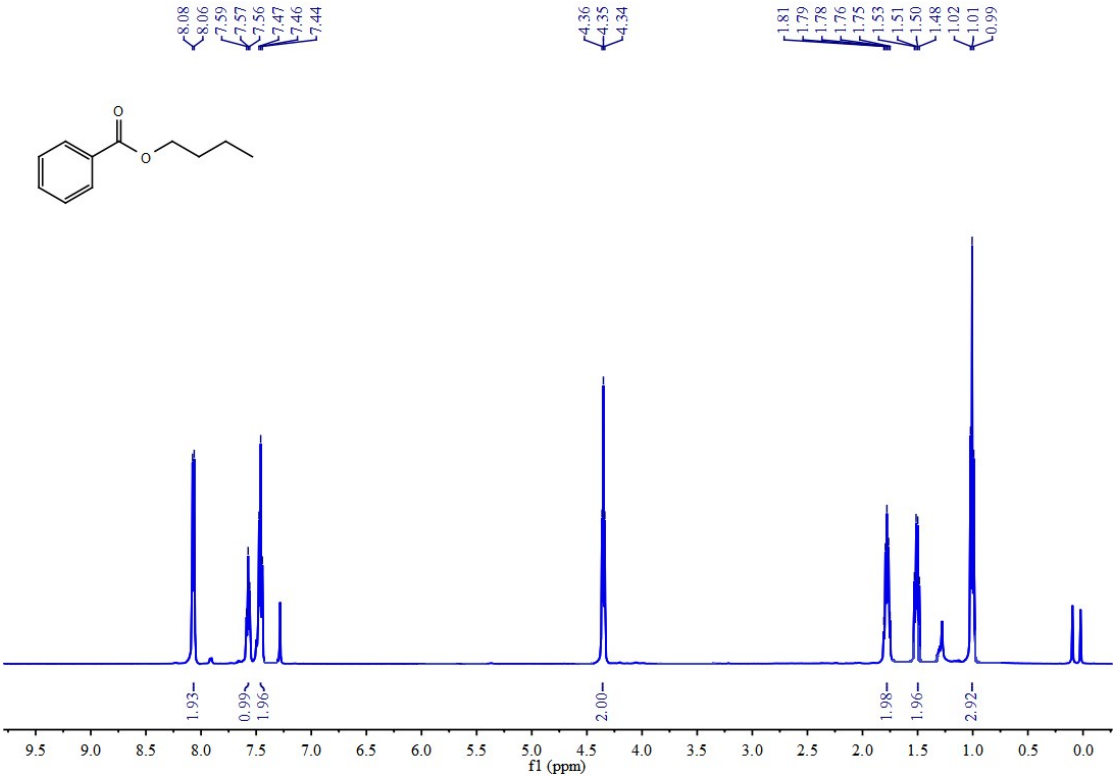
^{13}C NMR spectrum of **20** (126 MHz, $CDCl_3$).



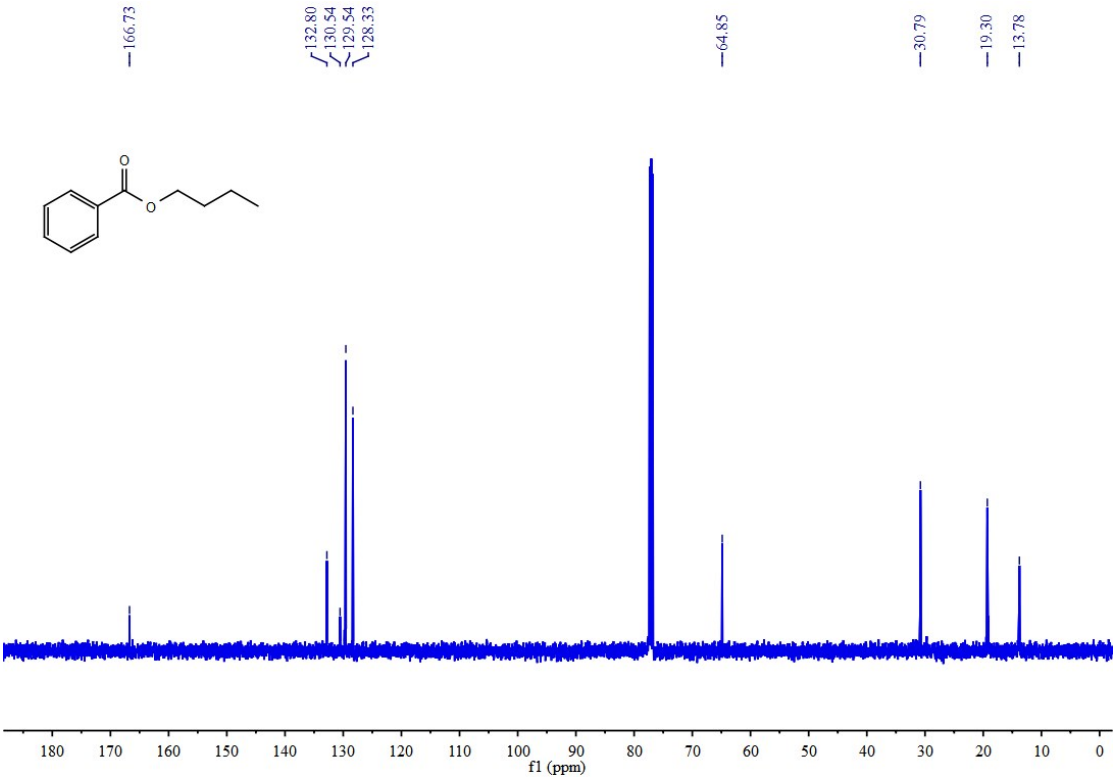
^{1}H NMR spectrum of **21** (501 MHz, $CDCl_3$).



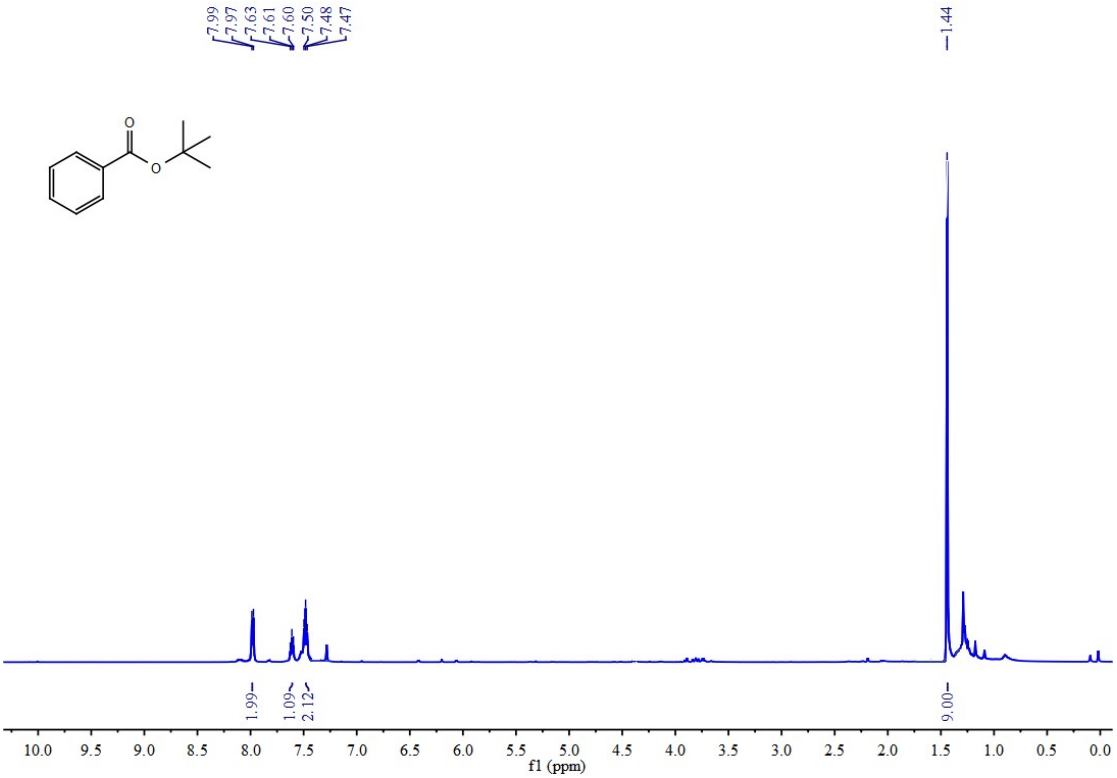
^{13}C NMR spectrum of **21** (126 MHz, $CDCl_3$).



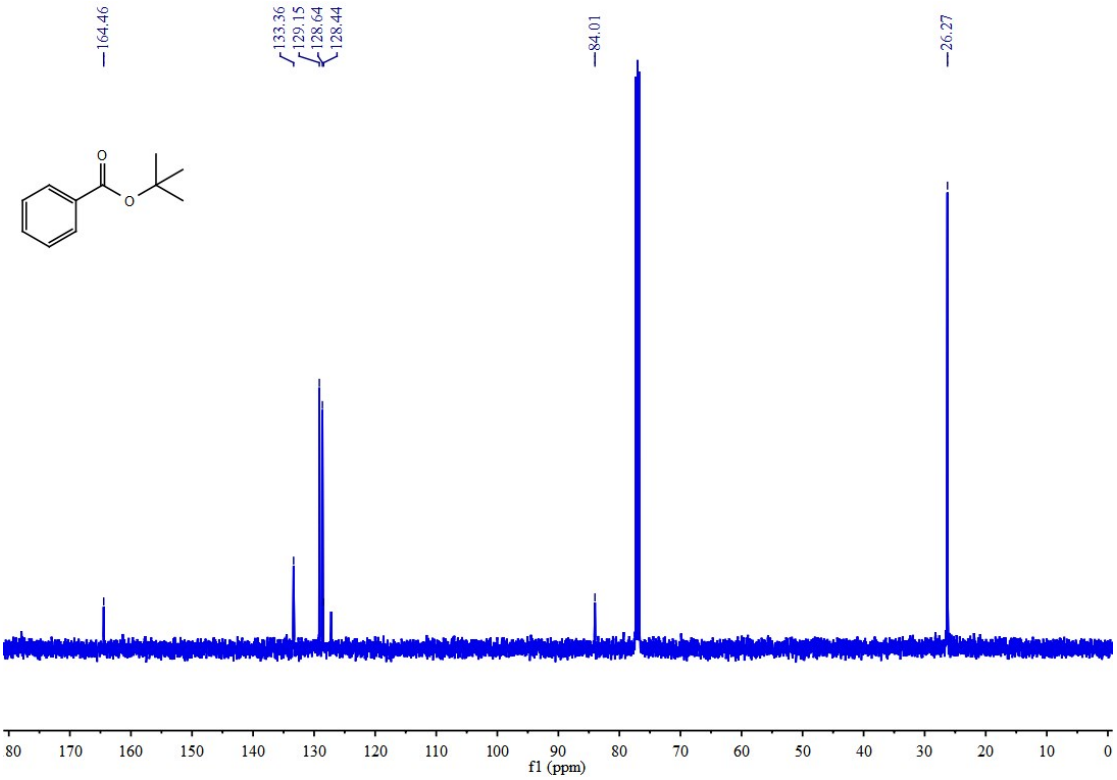
^{1}H NMR spectrum of **22** (501 MHz, $CDCl_3$).



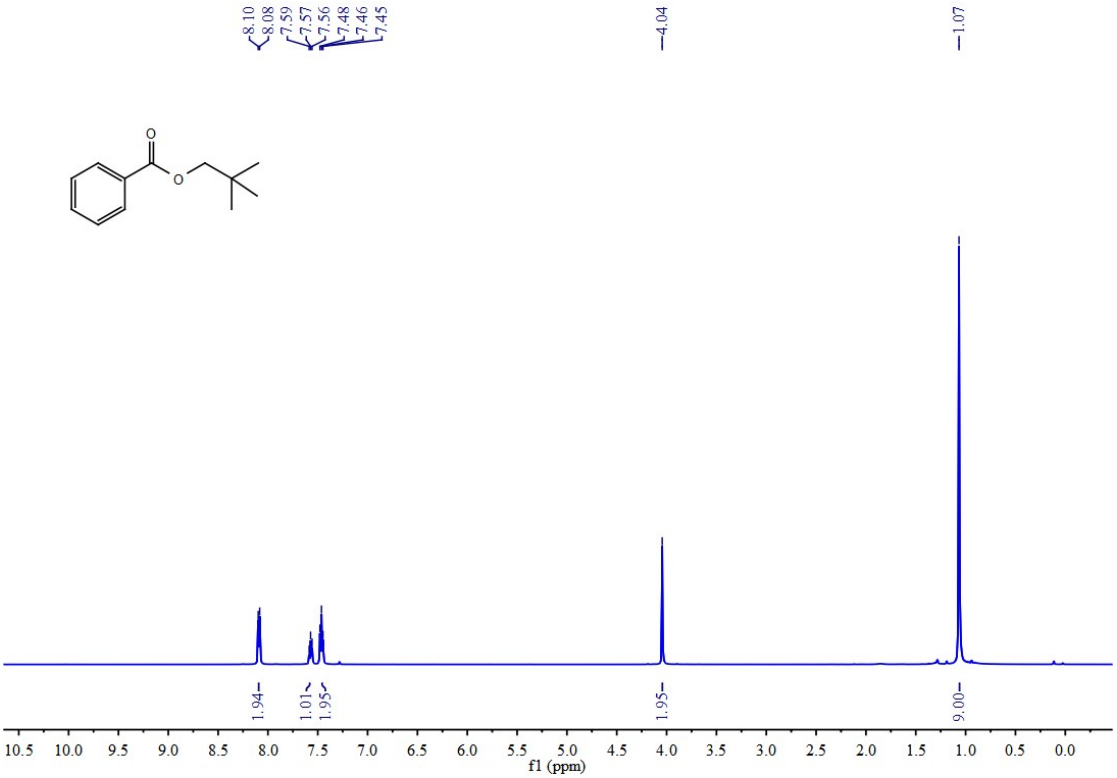
^{13}C NMR spectrum of **22** (126 MHz, $CDCl_3$).



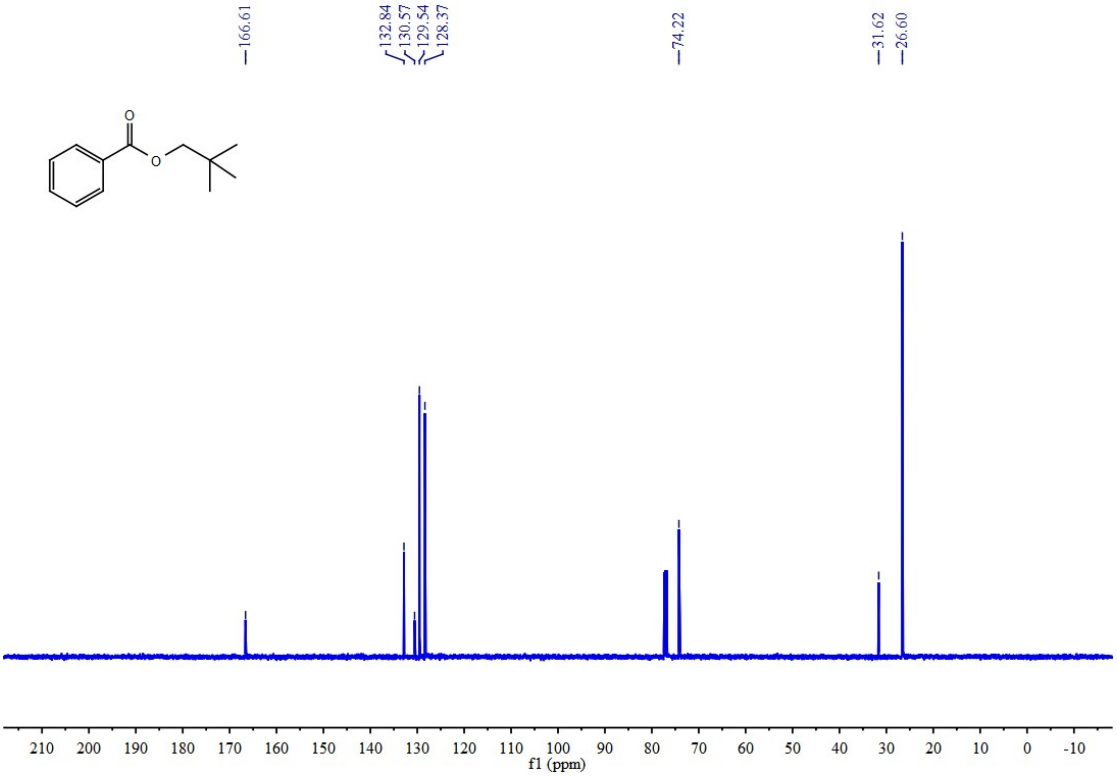
^{1}H NMR spectrum of **23** (501 MHz, $CDCl_3$).



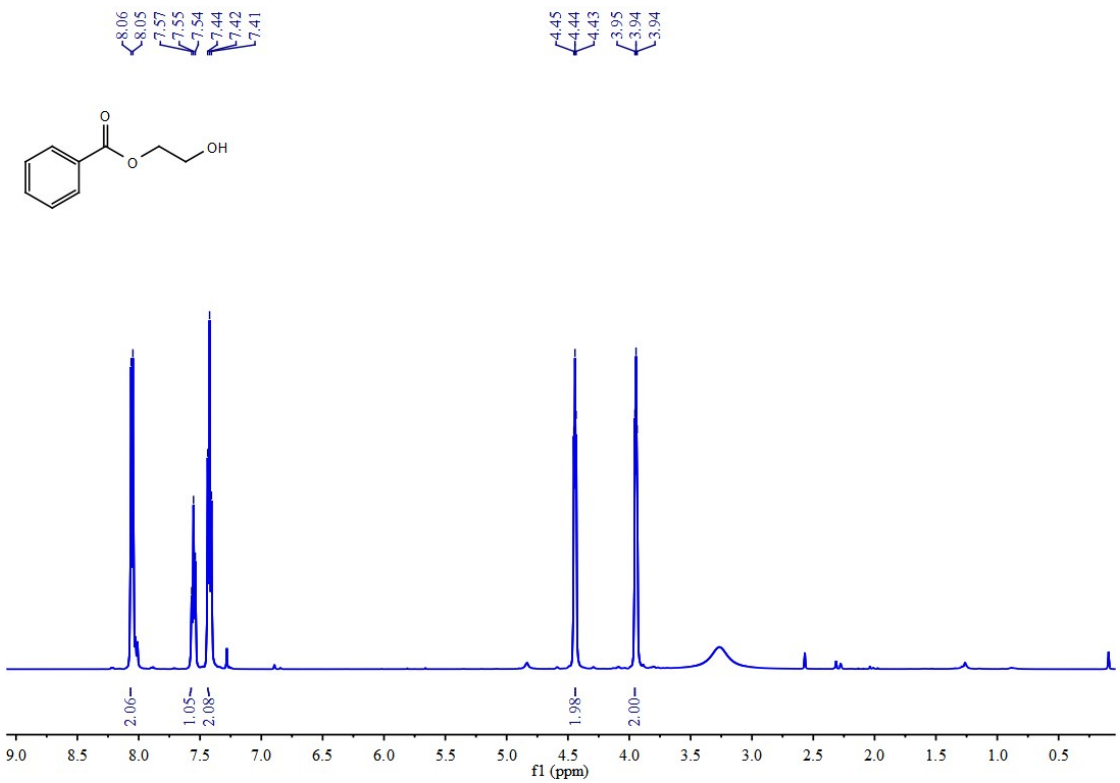
^{13}C NMR spectrum of **23** (126 MHz, $CDCl_3$).



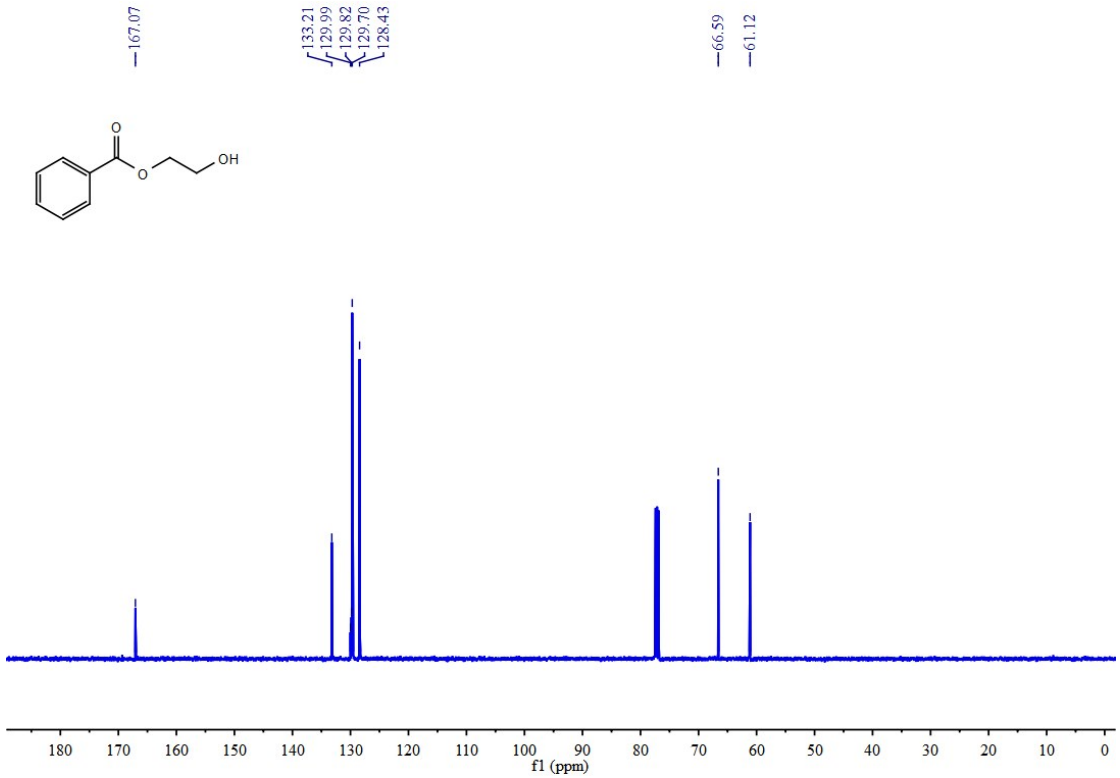
^{1}H NMR spectrum of **24** (501 MHz, $CDCl_3$).



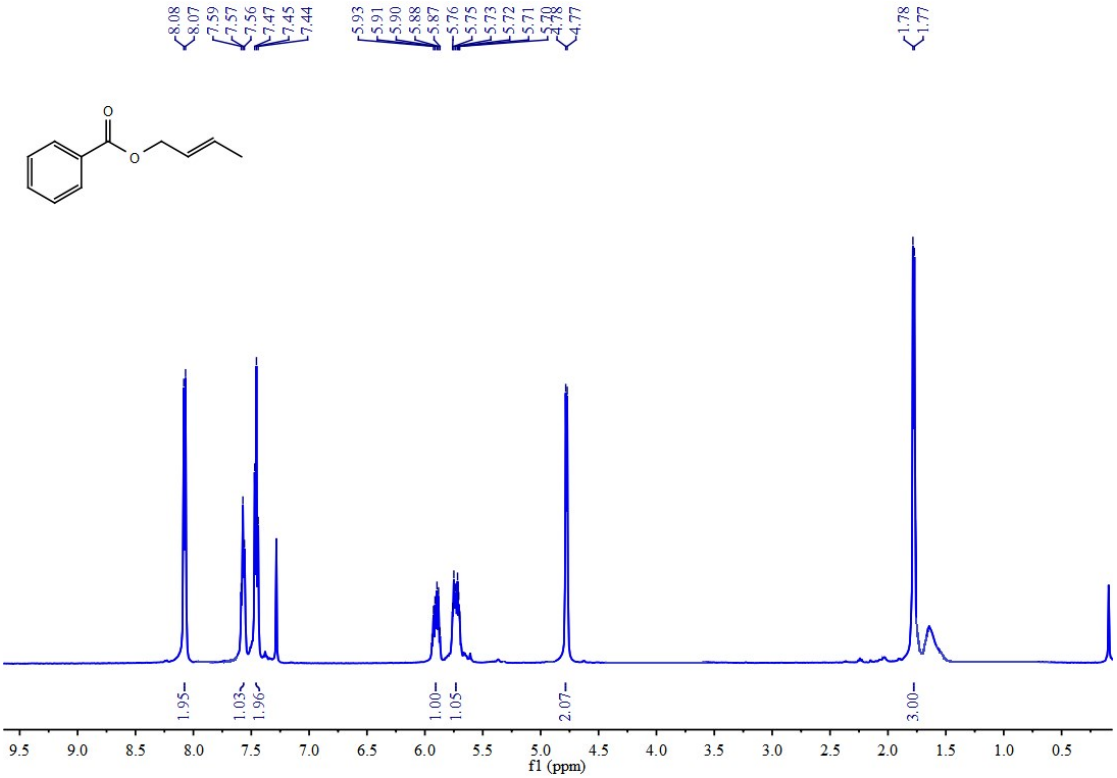
^{13}C NMR spectrum of **24** (126 MHz, $CDCl_3$).



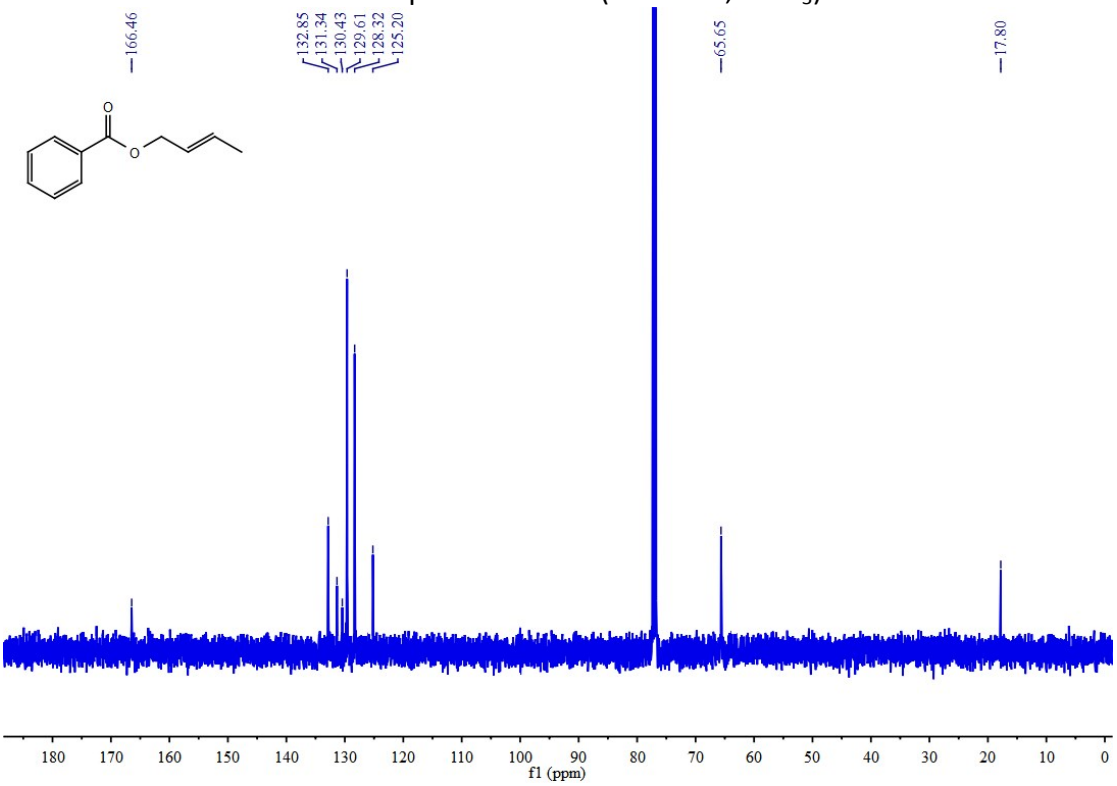
^{1}H NMR spectrum of **25** (501 MHz, $CDCl_3$).



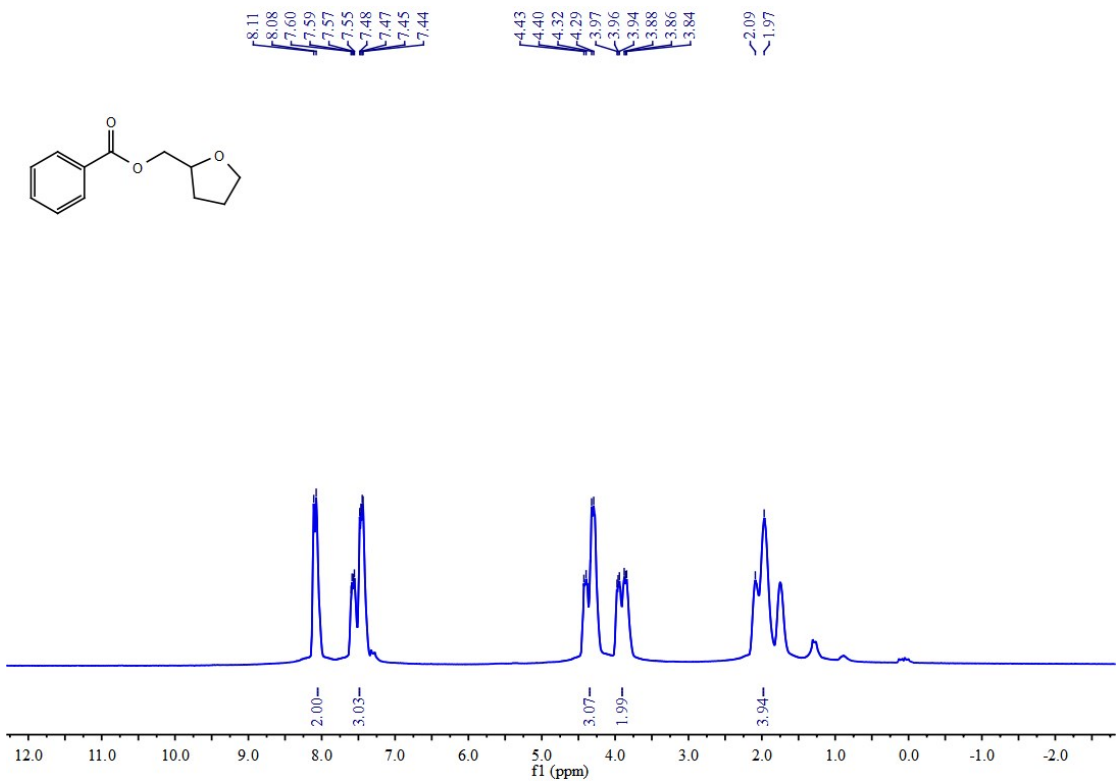
^{13}C NMR spectrum of **25** (126 MHz, $CDCl_3$).



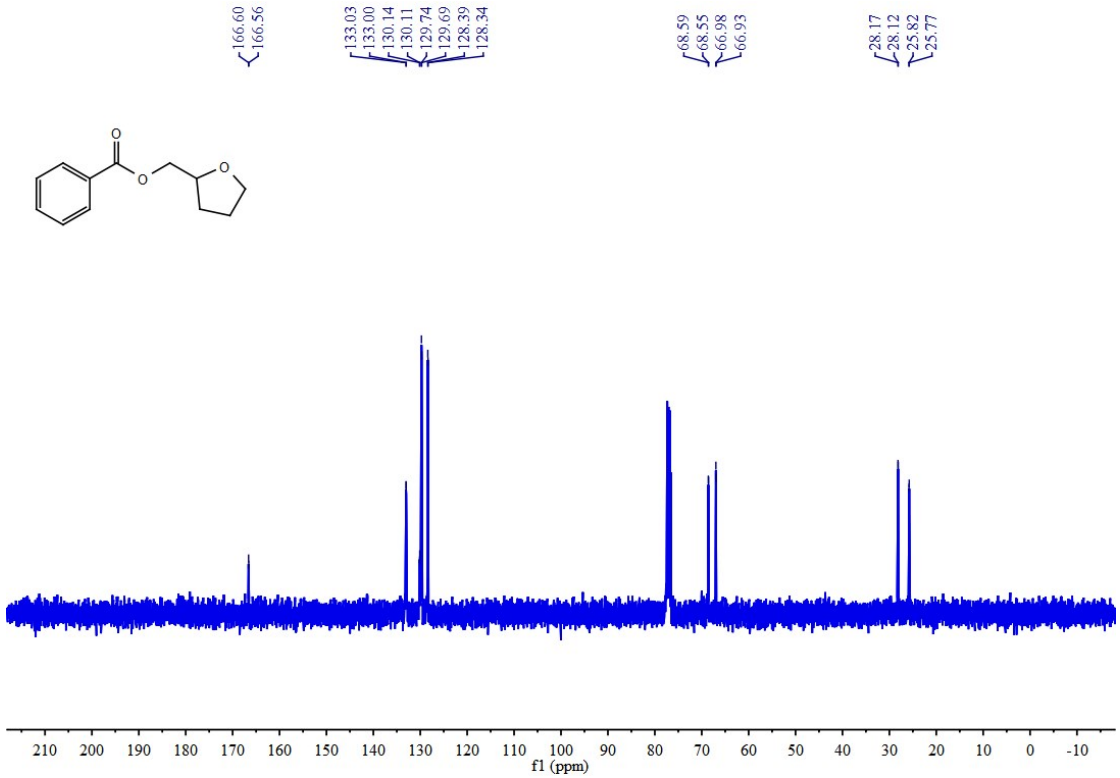
^{1}H NMR spectrum of **26** (501 MHz, $CDCl_3$).



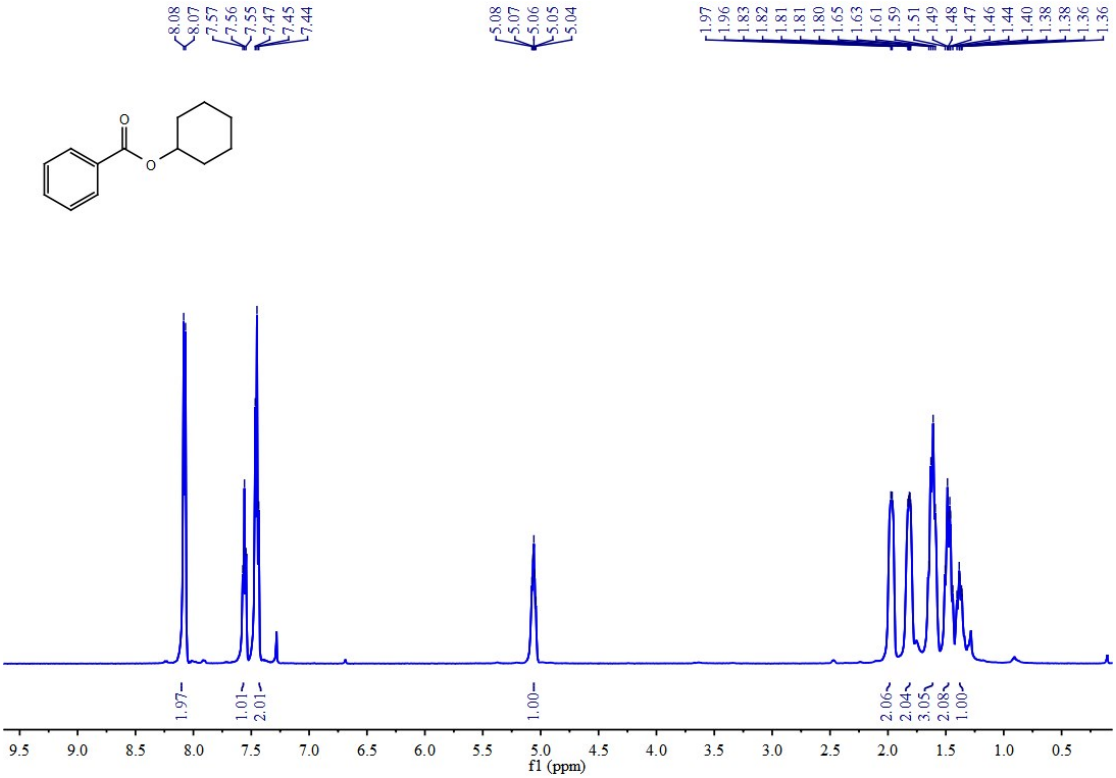
^{13}C NMR spectrum of **26** (126 MHz, $CDCl_3$).



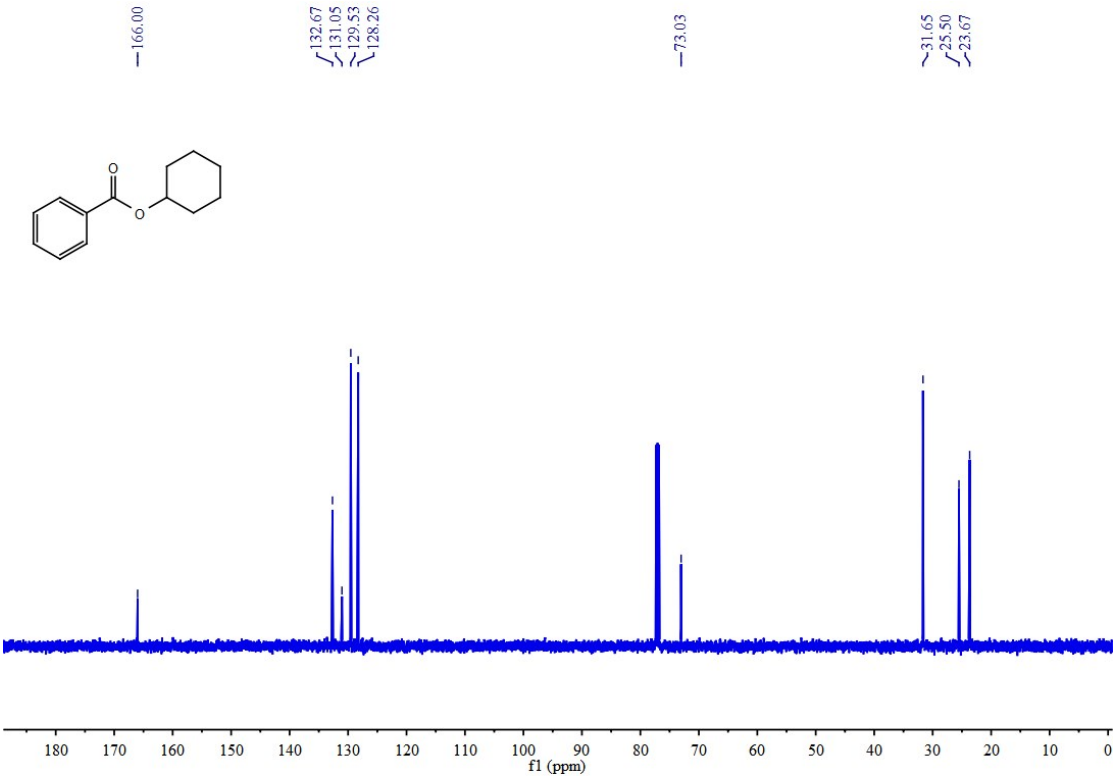
^{1}H NMR spectrum of **27** (501 MHz, $CDCl_3$).



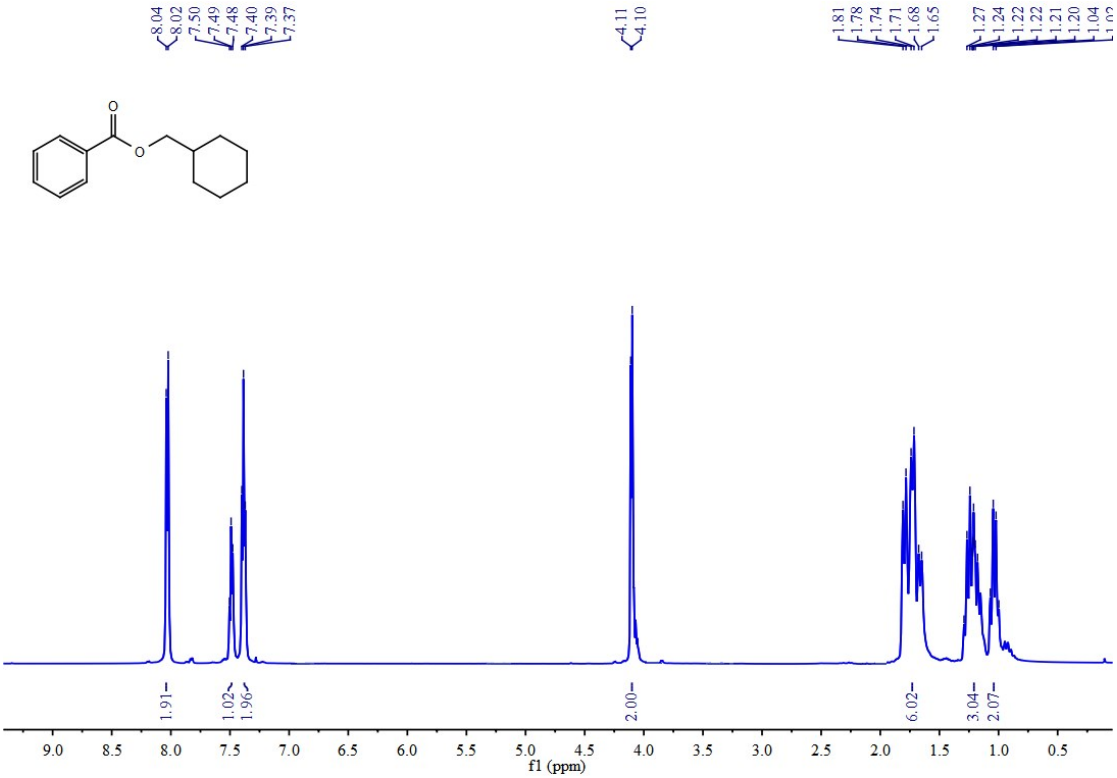
^{13}C NMR spectrum of **27** (126 MHz, $CDCl_3$).



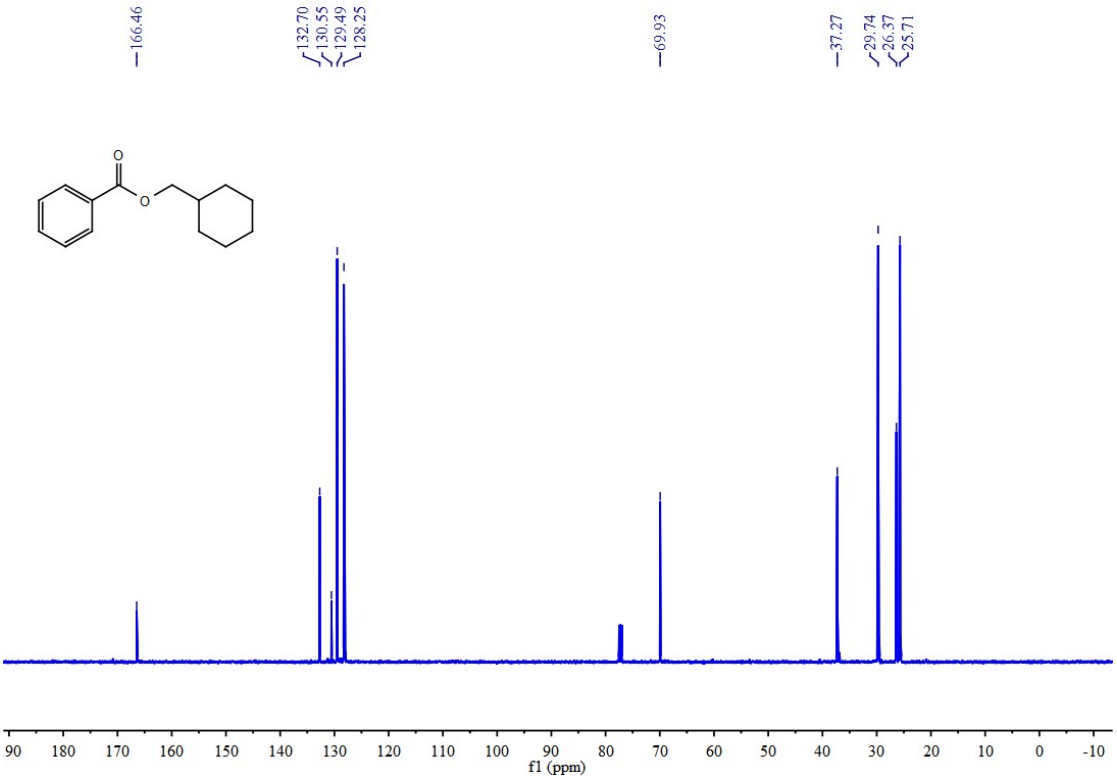
^{1}H NMR spectrum of **28** (501 MHz, $CDCl_3$).



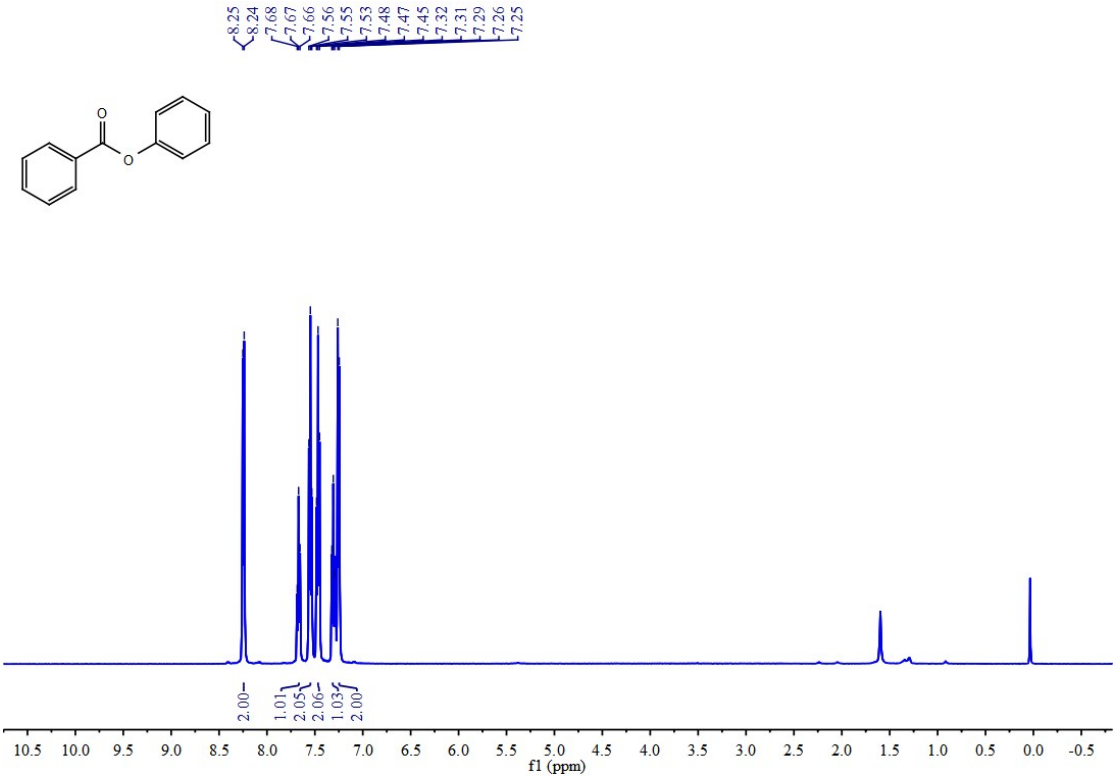
^{13}C NMR spectrum of **28** (126 MHz, $CDCl_3$).



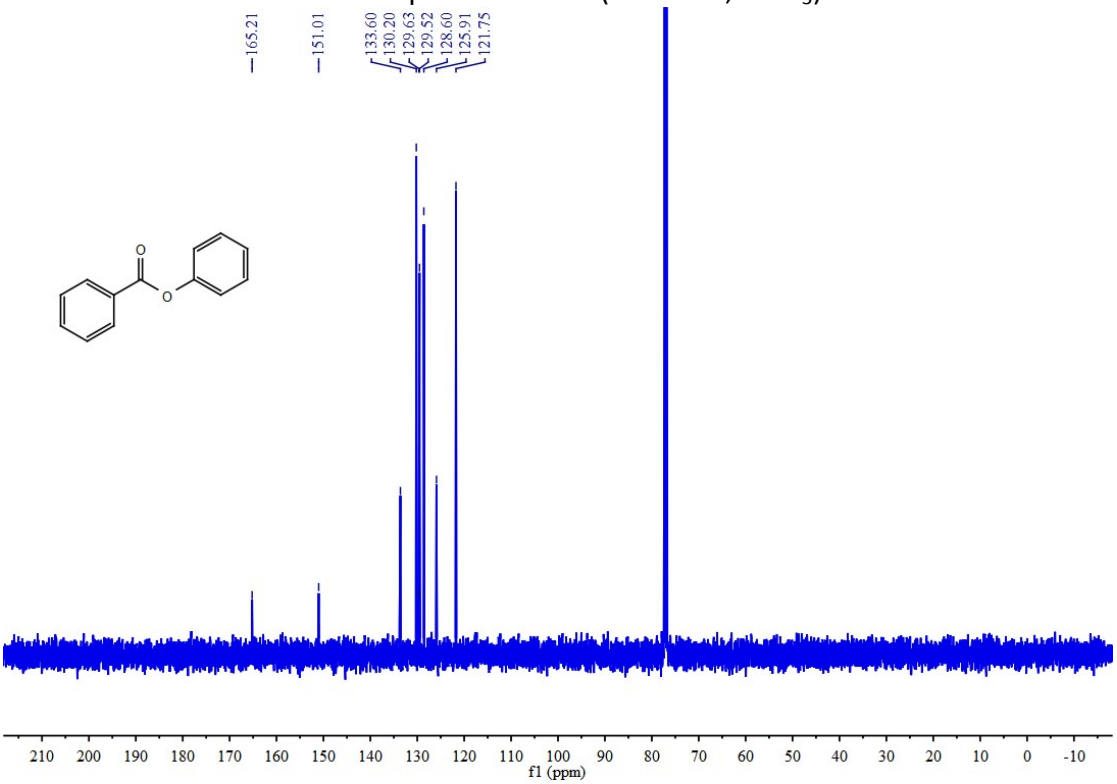
^{1}H NMR spectrum of **29** (501 MHz, $CDCl_3$).



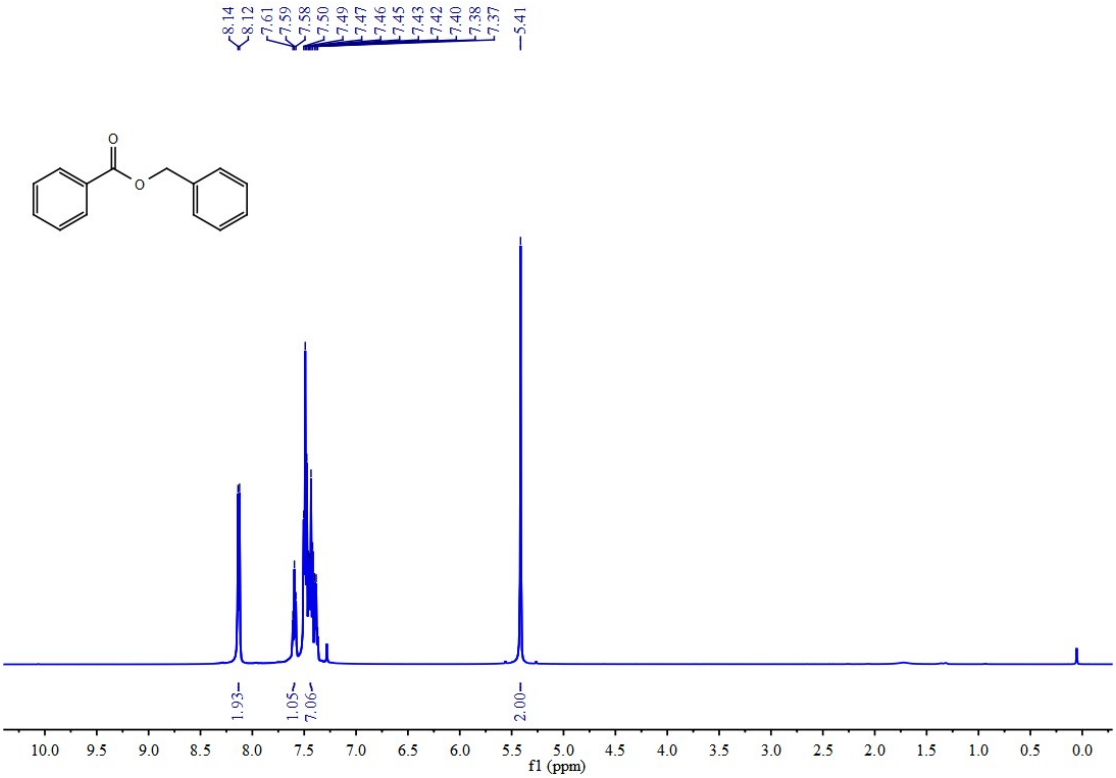
^{13}C NMR spectrum of **29** (126 MHz, $CDCl_3$).



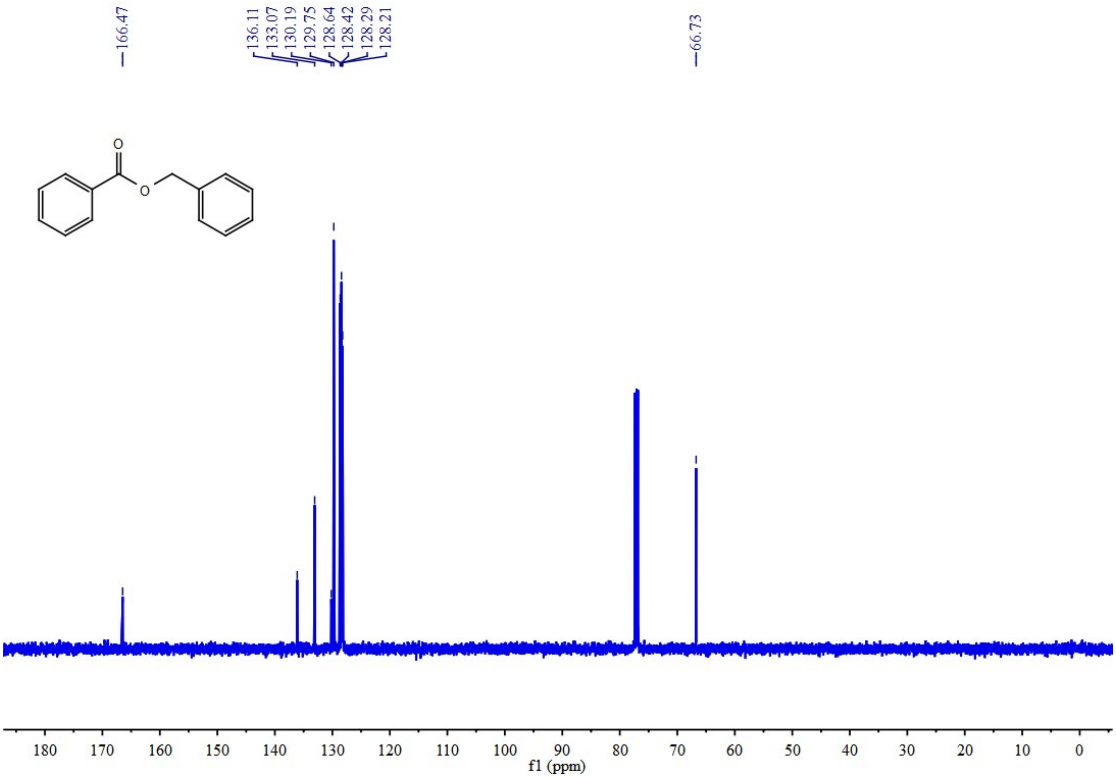
^{1}H NMR spectrum of **30** (501 MHz, $CDCl_3$).



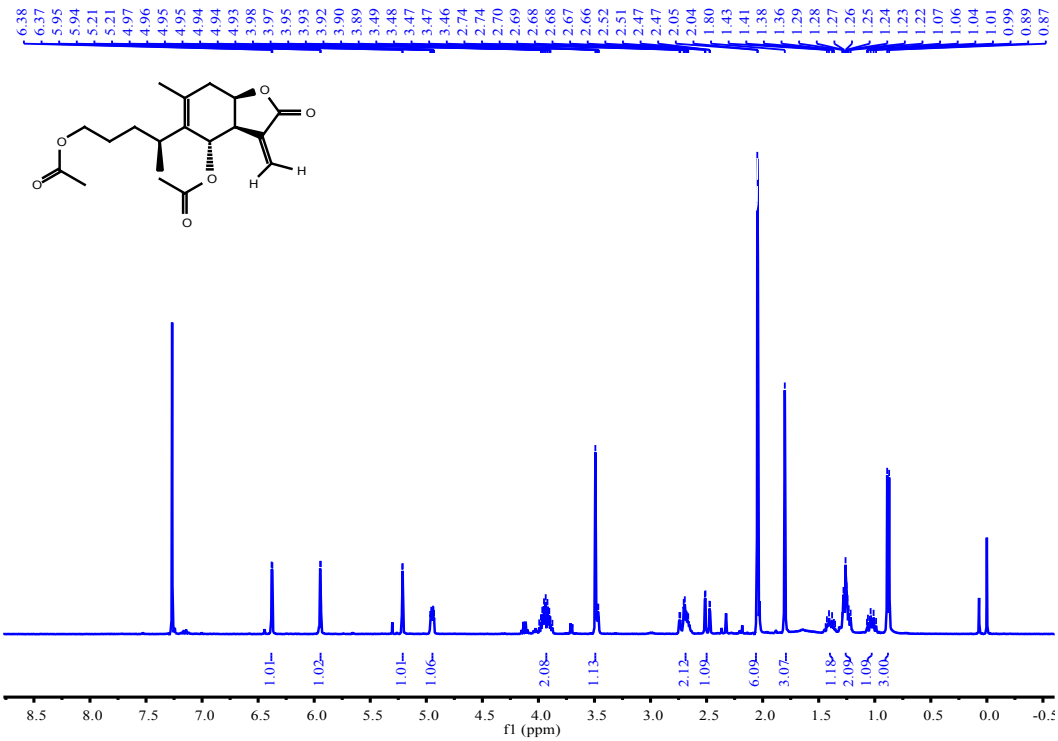
^{13}C NMR spectrum of **30** (126 MHz, $CDCl_3$).



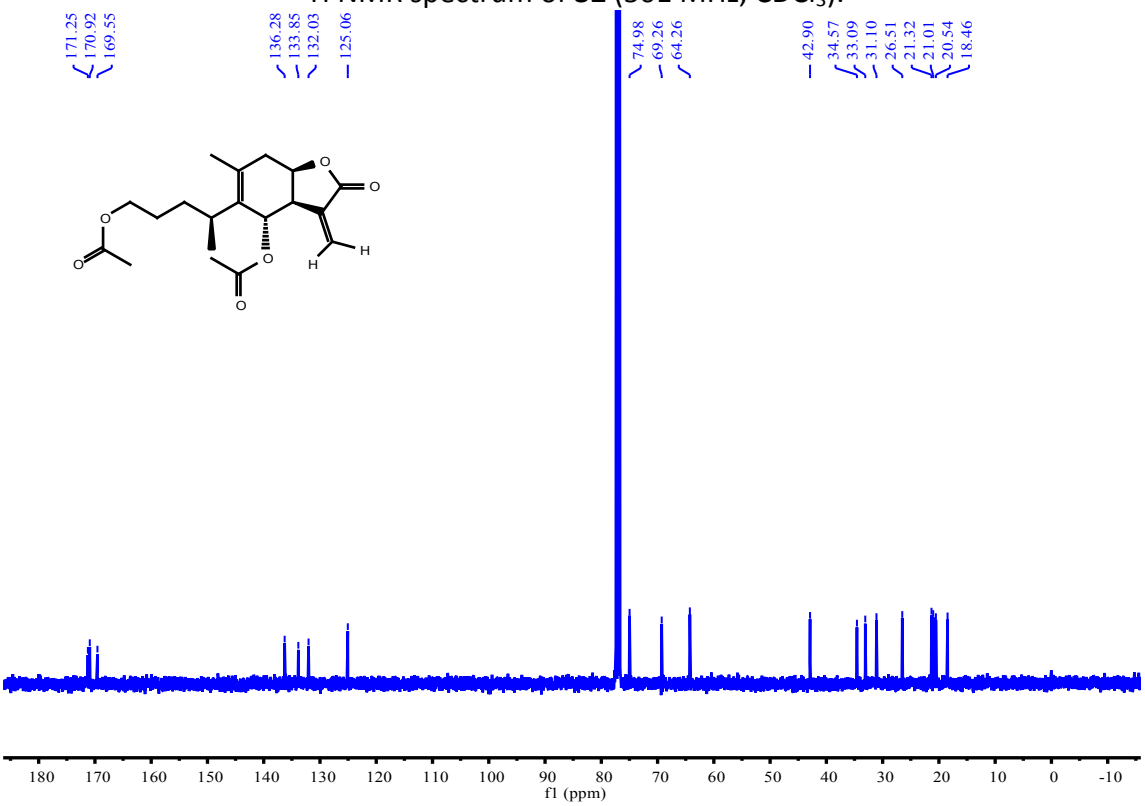
^{1}H NMR spectrum of **31** (501 MHz, $CDCl_3$).



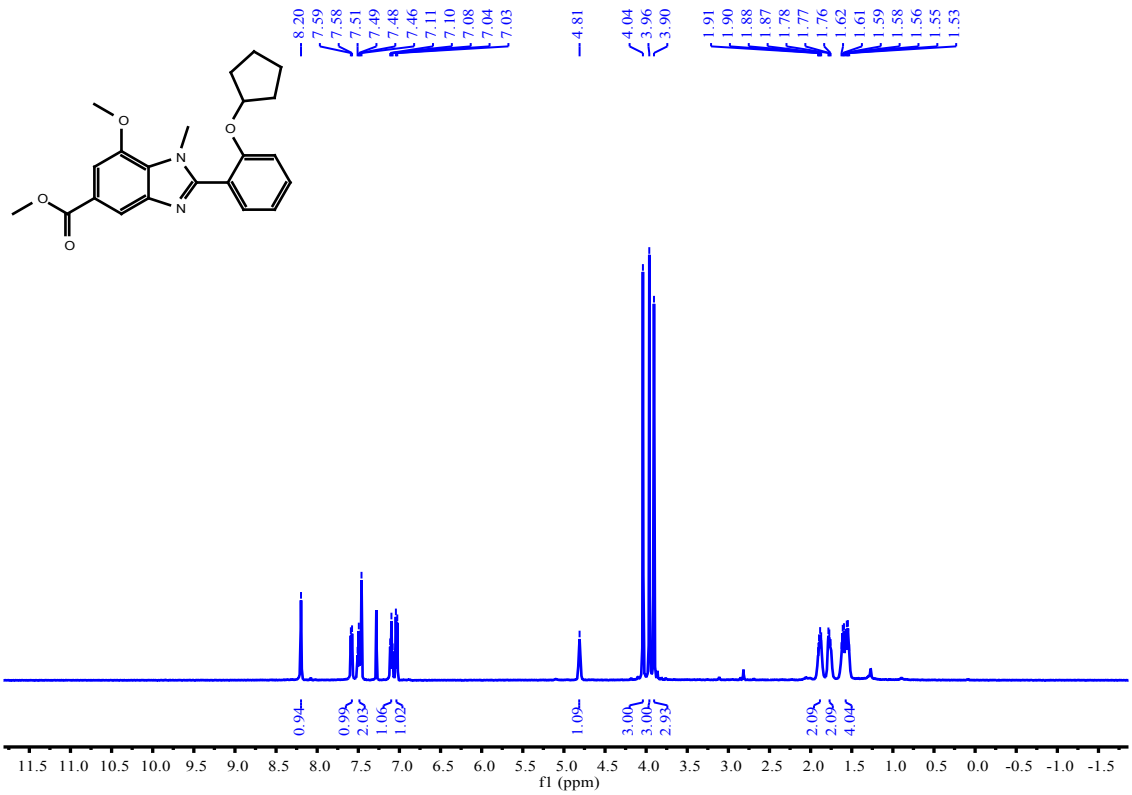
^{13}C NMR spectrum of **31** (126 MHz, $CDCl_3$).



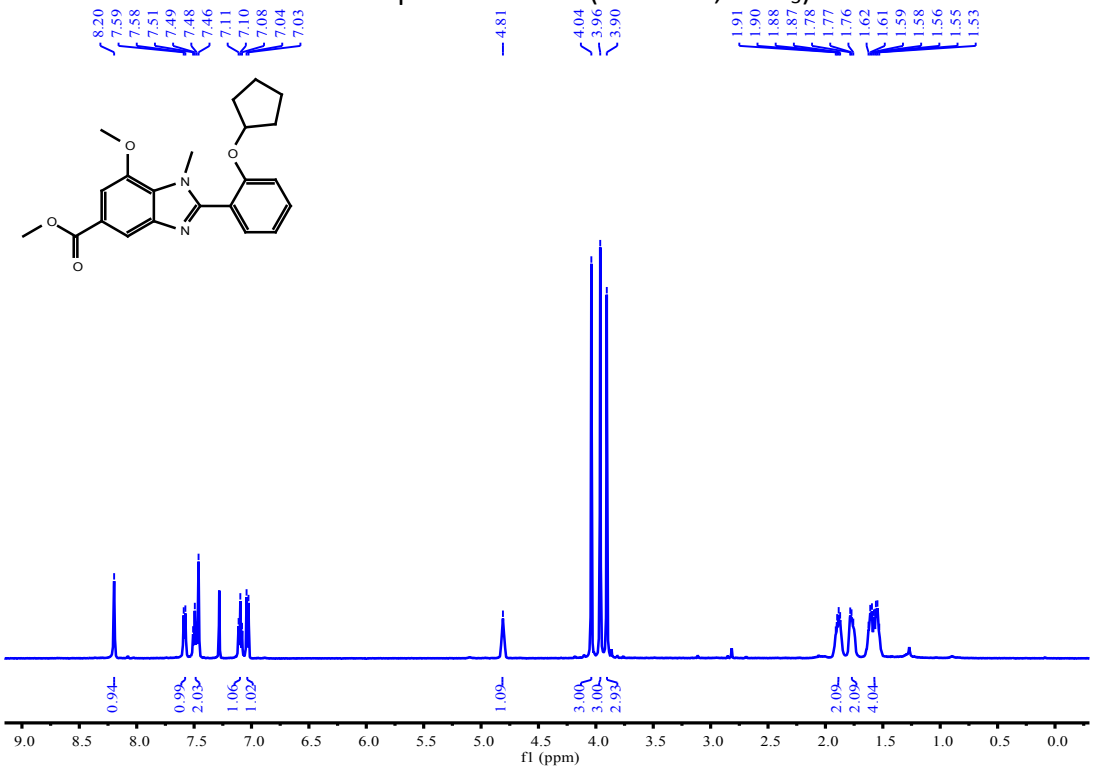
^{1}H NMR spectrum of **32** (501 MHz, $CDCl_3$).



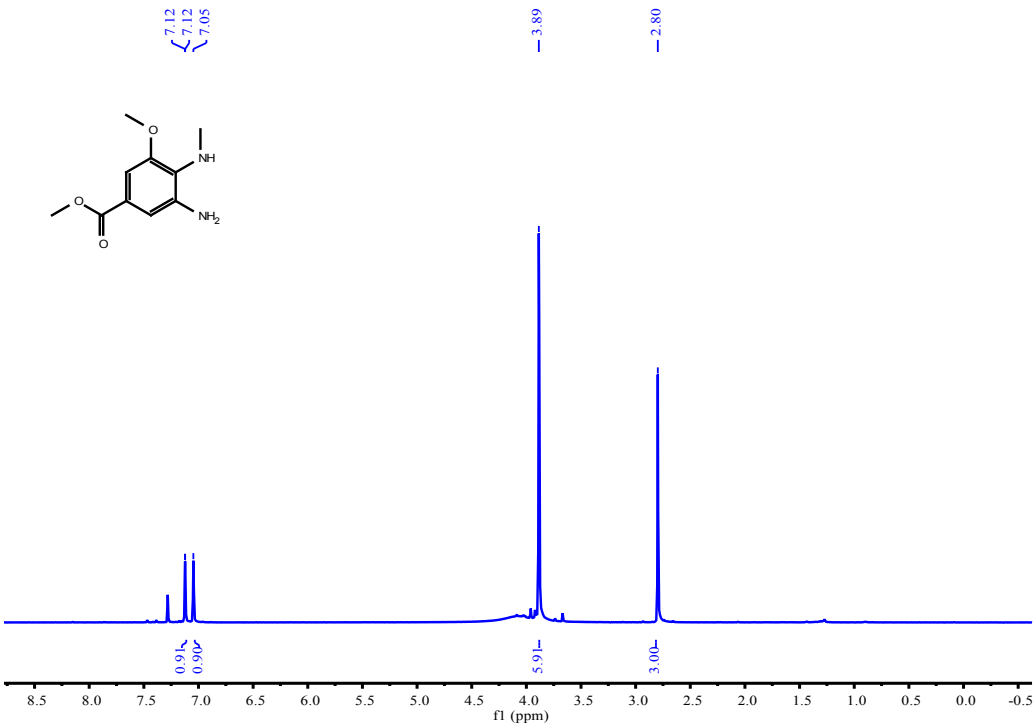
^{13}C NMR spectrum of **32** (126 MHz, $CDCl_3$).



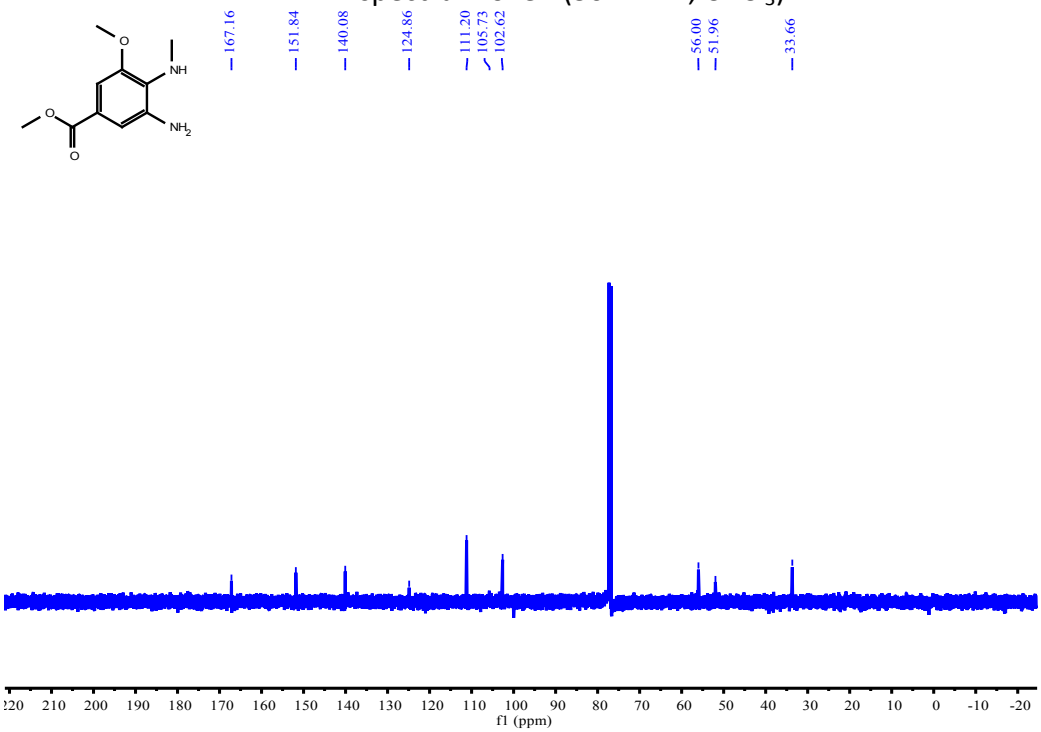
^{1}H NMR spectrum of **33** (501 MHz, $CDCl_3$).



^{13}C NMR spectrum of **33** (126 MHz, $CDCl_3$).



^{1}H NMR spectrum of **34** (501 MHz, $CDCl_3$).



^{13}C NMR spectrum of **34** (126 MHz, $CDCl_3$).

VIII. References

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