Electronic Supplementary Information

Aldehydes as Potential Acylating Reagents for the Oxidative Esterification by Inorganic Ligand-Supported Iron Catalysis

Han Yu, [ab†] Jingjing Wang,[b†] Zhikang Wu,[b] Qixin Zhao,[b] Demin Dan,[b] Sheng Han,[b*] Jiangjiang Tang[c*] and Yongge Wei[ad*]

[a] Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China.

[b] School of Chemical and Environmental Engineering Shanghai Institute of Technology,No. 100 Haiquan Road, Shanghai 201418 (P.R. China)

[c] Shaanxi Engineering Center of Bioresource Chemistry & Sustainable Utilization, College of Science, Northwest A&F University, Yangling 712100 (P.R. China)

[d] State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191 (P. R. China)

[†] These authors contributed equally to this work.

[*] E-mail: yonggewei@ tsinghua.edu.cn, hansheng654321@sina.com, tangjiang11@nwsuaf.edu.cn

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I. General information.

The catalyst was prepared according to published literature methods. All reagents were purchased from Sigma-Aldrich and Adamas-beta, which were used without further purification. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton, 125MHz for carbon) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ 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 analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a Stabil wax capillary column (internal diameter = 0.25 mm, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 with RTX-5MS column (0.25 mm× 30 m). Column chromatography was performed using 200-300 mesh silica gel.

II. The preparation of iron-catalyst

$(NH_4)_3[FeMo_6O_{18}(OH)_6]$ was synthesized according to the previously reported literature[1,2]: First of all, $(NH_4)_6Mo_7O_{24}\times 4H_2O$ (5.3 g, 4.2 mmol) was dissolved in water (80 mL) and put it in an oil bath and heat it to reflux. Then, $Fe_2(SO_4)_3$ (1.2 g, 3.0 mmol) dissolved in 80mL of water was added dropwise to the above solution. Notely, the pH of the solution needs to be controlled at around 2.5 in this process. After the dropwise is completed, the mixed solution is further stirred at a constant temperature for 1 h. Following by, the solution is filtered while hot. The obtained red-brown liquid was left at room temperature for 12 h and precipitated the white crystals. After recrystallized, filtered and vacuum dried, the white crystals (4.9 g) was deposited and collected. IR: 3208.24 (ν_{as}NH, m), 1638.98 (δOH m), 1401.73 (δNH, s), 945.18(ν Mo=O, vs), 892.11 (ν Mo=O, vs), 648.03 (ν Mo-O-Mo, vs), 573.00 (ν M-O-Mo, w) cm^{-1}.

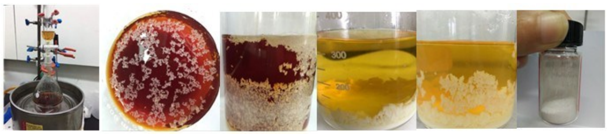


Figure S1. Preparation of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

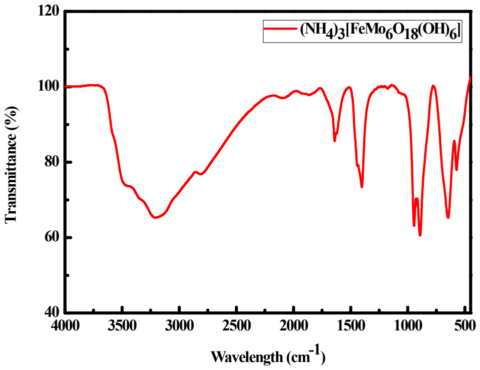


Figure S2. The FT-IR spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

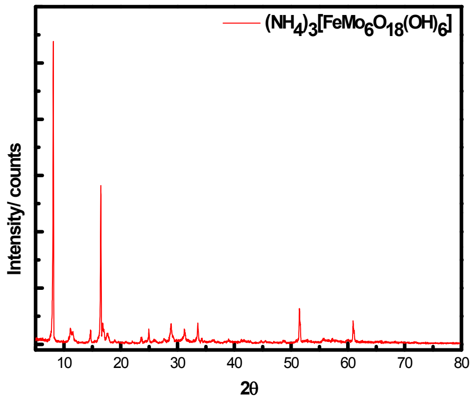
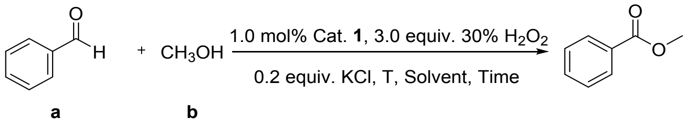


Figure S3. The XRD spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

III. Optimization studies

Table S1. Effect of temperature, solvent and time on oxidative coupling of benzaldehyde with methanol[a]



Entry	Temperature [°C]	Solvent (2 mL)	Time [h]	Yield [%][c]
1	40	CH_3OH	24	36
2	50	CH_3OH	24	53
3	60	CH_3OH	24	72
4	**65**	**CH_3OH**	**24**	**90**
5	70	CH_3OH	24	56
6	65	CH_3OH	12	76
7	65	CH_3OH	36	89
8	65	CH_3OH(1 mL)	24	43
9[b]	65	1,4-dioxane	24	Trace
10[b]	65	THF	24	15
11[b]	65	MeCN	24	Trace
12[b]	65	Toluene	24	Trace
13[b]	65	DMF	24	Trace

[a]Reaction conditions: Cat. **1** (1.0 mol%), benzaldehyde (1.0 mmol), 30%H_2O_2 (3.0 equiv.), CH_3OH (2 mL), KCl (0.2 equiv.). [b]Reaction conditions: Cat. **1** (1.0 mol%), benzaldehyde (1.0 mmol), a:b=1:3, 30% H_2O_2 (3.0 equiv.), KCl (0.2 equiv.), 65 °C, 24 h. [c]Substrate conversion and yield were determined by GC-MS analysis.

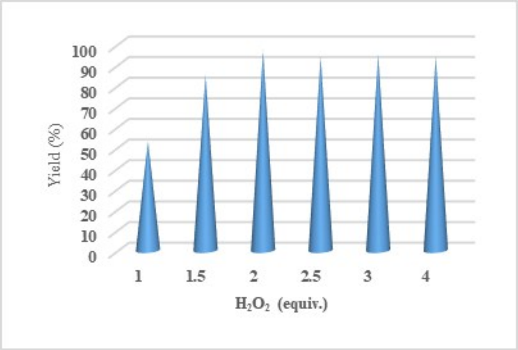


Figure S4. Effect of the amount of H_2O_2 on oxidative coupling of aldehydes with alcohols.

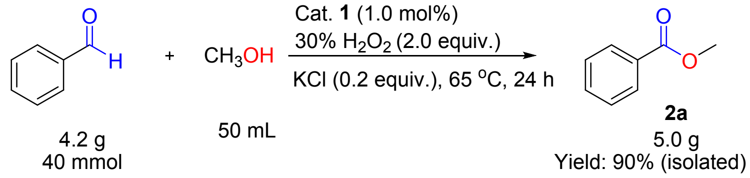


Figure S5. Gram-scale reaction of oxidative esterification.

IV. Experimental Section

General procedure (Method A): $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%) and KCl (14.9 mg, 0.2 equiv.) were placed in a Shlenck tube. Aldehyde (1.0 mmol), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and alcohol (2 mL) were consequently added to the reaction tube. The reaction mixture was stirred at 65 °C for 24 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3×5 mL), the organic layers were combined, and dried over sodium sulphate. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate). Conversion = (number of moles of material of the converted aldehyde / number of moles of starting aldehyde)X 100%, Yield = (mass of the actually obtained ester / theoretical mass of the ester) x 100%.

General procedure (Method B): $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%) and KCl (14.9 mg, 0.2 equiv.) were placed in a Shlenck tube. Aldehyde (1.0 mmol), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and alcohol (2 mL) were consequently added to the reaction tube adding two drops of nitric acid to the system. The reaction mixture was stirred at 65 °C for 24 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3×5 mL), the organic layers were combined, and dried over sodium sulphate. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate). Conversion = (number of moles of material of the converted aldehyde / number of moles of starting aldehyde)X 100%, Yield = (mass of the actually obtained ester / theoretical mass of the ester) x 100%.

General procedure (Method C): $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%) and KCl (14.9 mg, 0.2 equiv.) were placed in a Shlenck tube. Aldehyde (1.0 mmol), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and alcohol (2.0 mmol) were consequently added to the reaction tube adding two drops of nitric acid to the system. The reaction mixture was stirred at 65 °C for 24 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3×5 mL), the organic layers were combined, and dried over sodium sulphate. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate). Conversion = (number of moles of material of the converted aldehyde / number of moles of starting aldehyde)X 100%, Yield = (mass of the actually obtained ester / theoretical mass of the ester) x 100%.

V. Recycling experiments of catalyst for aldehydes to esters

The $Fe^{III}Mo_6$ catalyst was precipitated by adding ethyl acetate or anhydrous ether to the reaction system after the oxidative coupling experiments, and then recovered for reuse. The recovered catalyst was characterized by FT-IR and XRD.

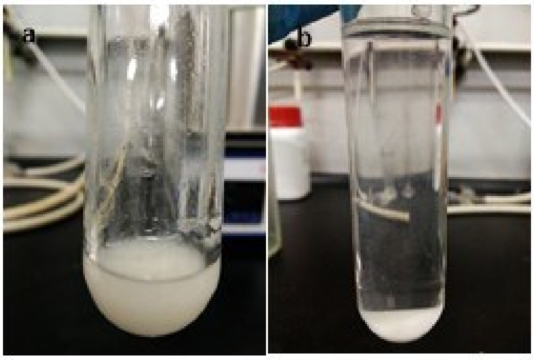


Figure S6. The catalyst recovery

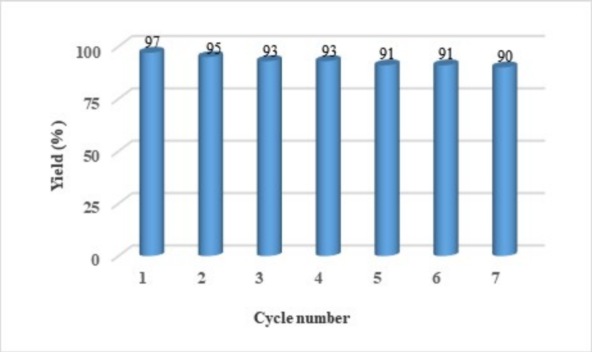


Figure S7. Recycling experiments of the catalyst. conditions: Cat. **1** (1.0 mol%), benzaldehyde (1.0 mmol), 30% H_2O_2 (2.0 equiv.), KCl (0.2 equiv.), and CH_3OH (2 mL) at 65 °C for 24 h.

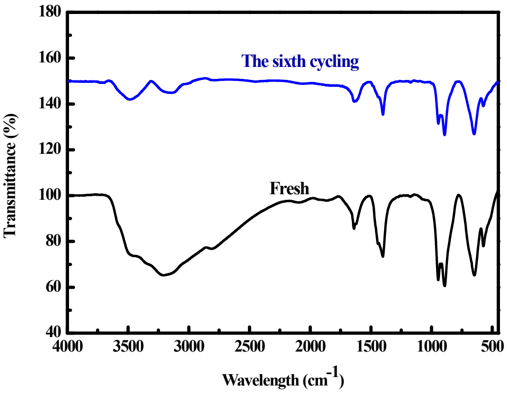


Figure S8. The FT-IR spectra of the catalyst before and after reaction.

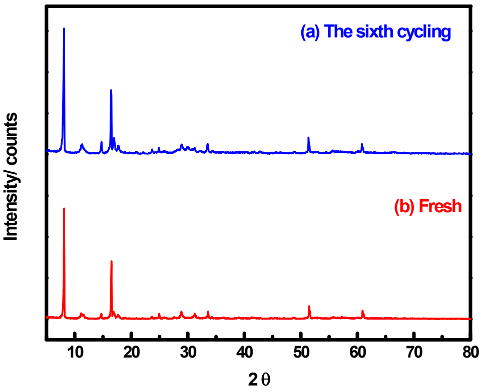


Figure S9. The XRD spectrum of the catalyst before and after reaction.

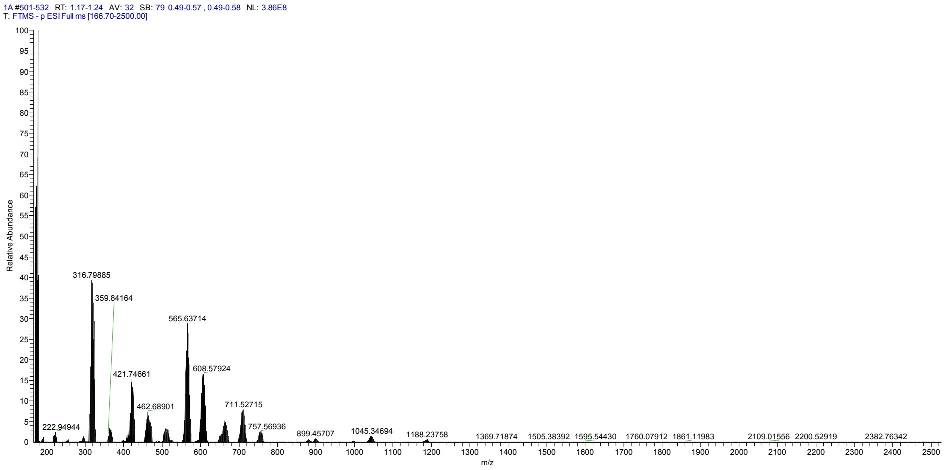


Figure S10. ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

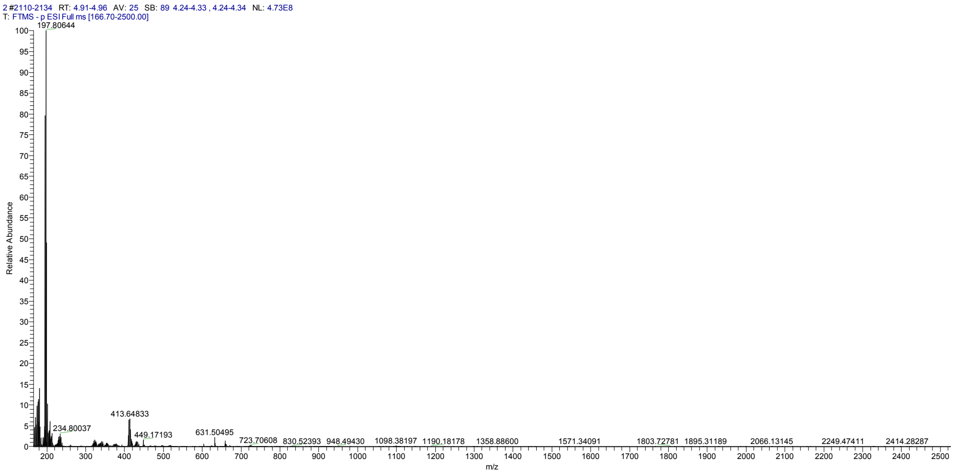


Figure S11. ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ + H_2O_2.

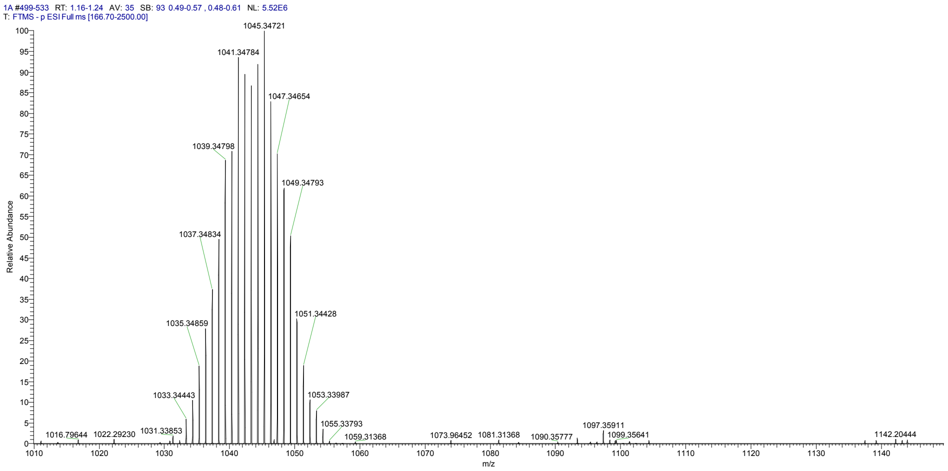


Figure S12. Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$, (m/z = 1010-1500, $\{NH_4H[FeMo_6O_{24}H_6]\}^{1-}$ = 1043.34 g/mol).

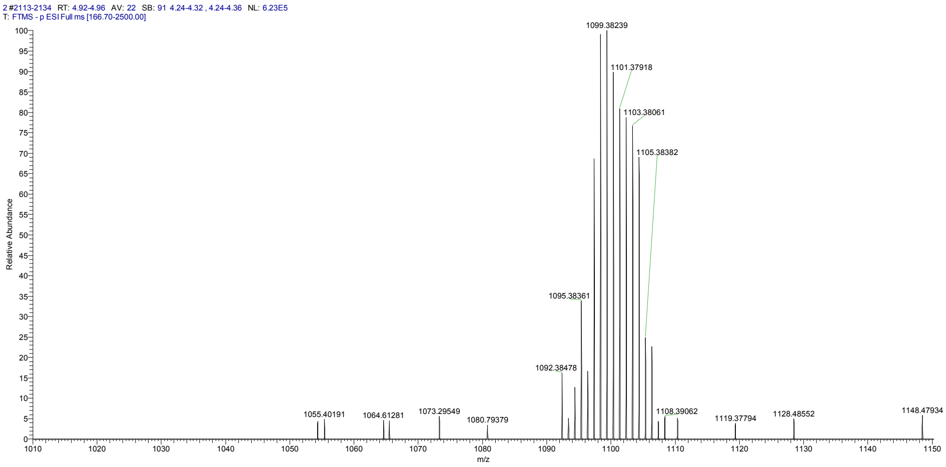
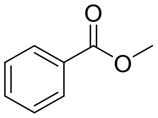
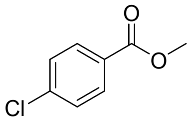


Figure S13. Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]+H_2O_2$, (m/z = 1010-1500, $\{Na_2[FeMo_6O_{24}H_6]+O\}^{1-}\cdot H_2O$ = 1100.61 g/mol).

VI. NMR data of products

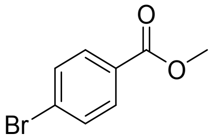


Methyl benzoate (2a)[3-5]: Colorless liquid. Method A was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.13 g, 97%). ^{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), 130.21 (s), 129.59 (s), 128.38 (s), 52.13 (s).

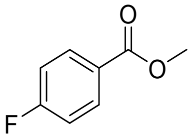


4-Chlorobenzoic acid methyl ester (2b)[3-5]: Light yellow solid. Method A was followed using 4-chlorobenzaldehyde (0.141 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.16 g, 92%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6

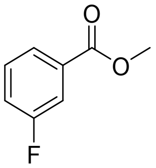
Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.11 (s), 139.30 (s), 130.93 (s), 128.60 (d, J = 13.6 Hz), 52.21 (s).



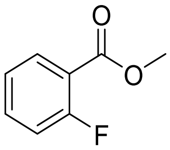
Methyl 4-bromobenzoate (2c)[3-5]: White solid. Method A was followed using 4-bromobenzaldehyde (0.185 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.21 g, 97%). ^{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).



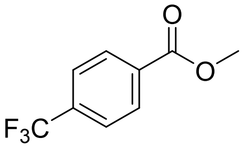
Methyl 4-fluorobenzoate (2d)[3-5]: Colorless liquid. Method A was followed using 4-fluorobenzaldehyde (0.124 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.15 g, 97%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.31 – 7.55 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 3.93 (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), 126.45 (s), 115.44 (d, J = 11.0 Hz), 52.13 (s).



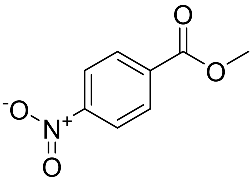
Methyl 3-fluorobenzoate (2e)[3-5]: Colorless liquid. Method A was followed using 3-fluorobenzaldehyde (0.124 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.14 g, 91%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 9.2 Hz, 1H), 7.44 (dd, J = 13.6, 7.9 Hz, 1H), 7.28 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.98 (d, J = 2.5 Hz), 163.55 (s), 161.59 (s), 132.34 (d, J = 7.5 Hz), 129.99 (d, J = 7.8 Hz), 125.31 (d, J = 3.0 Hz), 120.07 (s), 119.90 (s), 116.60 (s), 116.42 (s), 52.36 (s).



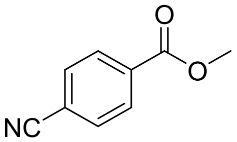
Methyl 2-fluorobenzoate (2f)[3-5]: Colorless liquid. Method A was followed using 2-fluorobenzaldehyde (0.124 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.14 g, 90%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.95 (t, J = 7.1 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.16 – 7.12 (m, 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).



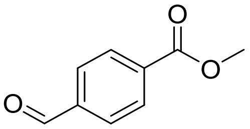
Methyl 4-(trifluoromethyl)benzoate (2g)[3-5]: Colorless liquid. Method A was followed using 4-(trifluoromethyl)benzaldehyde (0.174 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.18 g, 86%). ^{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), 125.39 (d, *J* = 3.7 Hz), 122.55 (s), 52.45 (s).



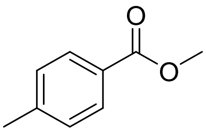
Methyl 4-nitrobenzoate (2h)[3-5]: Yellow solid. Method A was followed using 4-nitrobenzaldehyde (0.151 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.17 g, 92%). ^{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), 150.48 (s), 135.48 (s), 130.72 (s), 123.55 (s), 52.84 (s).



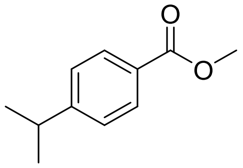
4-cyanobenzoic acid methyl ester (2i)[3-5]: White crystal. Method A was followed using 4-cyanobenzaldehyde (0.131 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.13 g, 80%). ^{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).



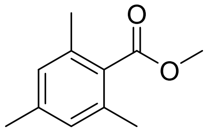
Methyl 4-formylbenzoate (2j)[3-5]: White crystal powder. Method A was followed using terephthalaldehyde (0.134 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.12 g, 74%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.13 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.64 (s), 166.08 (s), 139.16 (s), 135.11 (s), 130.21 (s), 129.53 (s), 52.59 (s).



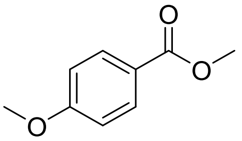
Methyl 4-methylbenzoate (2k)[3-5]: White crystalline solid. Method A was followed using p-tolualdehyde (0.120 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.13 g, 89%). ^{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 167.20 (s), 143.54 (s), 129.59 (s), 129.07 (s), 127.41 (s), 51.90 (s), 21.60 (s).



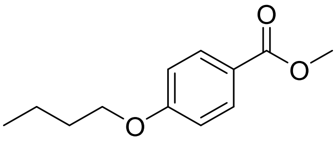
Methyl 4-propan-2-ylbenzoate (2l)[3-5]: Light yellow liquid. Method A was followed using 4-isopropylbenzaldehyde (0.148 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.15 g, 83%). ^{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 (hept, J = 6.8 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).



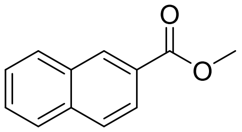
Methyl 2,4,6-trimethylbenzoate (2m)[3-5]: Light yellow liquid. Method A was followed using 2,4,6-trimethylbenzaldehyde (0.148 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.13 g, 72%). ^{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), 141.51 (s), 135.18 (s), 130.54 (s), 128.39 (s), 51.75 (s), 21.48 (s), 20.51 (s).



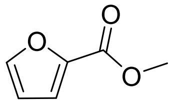
Methyl anisate (2n)[3-5]: White powder. Method A was followed using 4-methoxybenzaldehyde (0.136 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.13 g, 81%). ^{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).



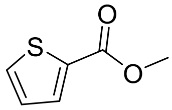
Methyl 4-n-butoxybenzoate (2o)[3-5]: Colorless liquid. Method A was followed using 4-N-butoxybenzaldehyde (0.178 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.15 g, 70%). ^{1}H NMR (501 MHz, CDCl$_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.84 (s, 3H), 1.75 (d, J = 7.4 Hz, 2H), 1.48 (dd, J = 7.4, 3.6 Hz, 2H), 0.95 (d, J = 3.9 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.24 (s), 162.95 (s), 131.52 (s), 122.26 (s), 114.01 (s), 67.82 (s), 51.73 (s), 31.13 (s), 19.17 (s), 13.78 (s).



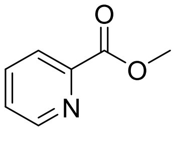
Methyl 2-naphthoate (2p)[3-5]: White powder. Method A was followed using 2-naphthaldehyde (0.156 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.16 g, 86%). ^1H 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), 7.61 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 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).



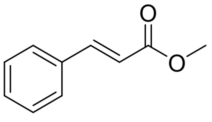
Methyl 2-furoate (2q)[3-5]: Light yellow liquid. Method A was followed using 2-furaldehyde (0.096 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.12 g, 93%). ^1H NMR (501 MHz, $CDCl_3$) δ 7.78 – 7.44 (m, 1H), 7.31 – 7.07 (m, 1H), 6.64 – 6.47 (m, 1H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.17 (s), 146.29 (s), 144.63 (s), 117.95 (s), 111.85 (s), 51.90 (s).



Methyl thiophene-2-carboxylate (2r)[3-5]: Light yellow liquid. Method A was followed using 2-thiophenecarboxaldehyde (0.112 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.13 g, 89%). ^1H NMR (501 MHz, $CDCl_3$) δ 7.80 (d, J = 3.6 Hz, 1H), 7.55 (d, J = 4.9 Hz, 1H), 7.13 – 7.03 (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).

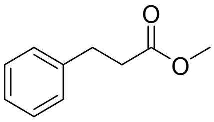


Methyl picolinate (2s)[3-5]: Colorless liquid. Method A was followed using 2-pyridinecarboxaldehyde (0.107 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (ethyl acetate) to afford the corresponding ester (0.12 g, 90%). ^1H NMR (501 MHz, $CDCl_3$) δ 8.77 (d, J = 4.4 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 7.7 Hz, 1H), 7.58 – 7.41 (m, 1H), 4.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.71 (s), 149.81 (s), 147.90 (s), 137.11 (s), 127.00 (s), 125.17 (s), 52.91 (s).

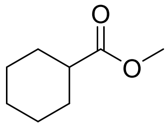


Methyl cinnamate (2t)[3-5]: White crystal. Method A was followed using cinnamaldehyde (0.132 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 10:1) to afford the corresponding ester (0.14 g, 87%). ^1H NMR

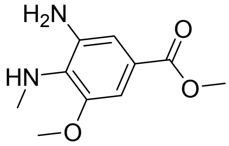
(501 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.54 (d, J = 3.5 Hz, 2H), 7.47 – 7.33 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.47 (s), 144.91 (s), 134.37 (s), 130.34 (s), 128.92 (s), 128.11 (s), 117.79 (s), 51.74 (s).



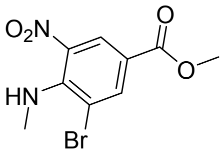
3-Phenylpropionic acid methyl ester (2u)[3-5]: White crystal. Method A was followed using hydrocinnamaldehyde (0.134 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.14 g, 83%). ^1H 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), 2.79 – 2.69 (m, 2H), 2.28 – 1.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.34 (s), 141.67 (s), 128.65 – 128.22 (m), 125.93 (s), 52.73 (s), 34.14 (s), 30.92 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.34 (s), 141.67 (s), 128.65 – 128.22 (m), 126.31 (s), 125.93 (s), 52.73 (s), 34.14 (s), 30.92 (s).



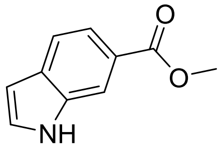
Cyclohexanecarboxylic acid methyl ester (2w)[3-5]: Light yellow liquid. Method A was followed using cyclohexanecarboxaldehyde (0.112 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.11 g, 80%). ^1H NMR (501 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.42 – 2.20 (m, 1H), 1.90 (d, J = 12.8 Hz, 2H), 1.75 (d, J = 12.6 Hz, 2H), 1.65 (d, J = 8.9 Hz, 1H), 1.50 – 1.38 (m, 2H), 1.35 – 1.20 (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).



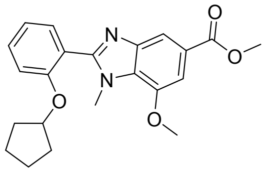
Benzoic acid, 3-amino-5-methoxy-4-(methylamino)-, methyl ester (2aa): Light yellow solid. Method A was followed using 3-amino-5-methoxy-4-(methylamino)benzaldehyde (0.180 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.09 g, 43%). ^1H 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).



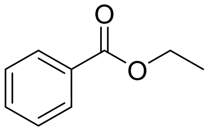
Methyl 3-bromo-4-(methylamino)-5-nitrobenzoate (2ab): Yellow solid. Method A was followed using 3-bromo-4-(methylamino)-5-nitrobenzaldehyde (0.259 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.156 g, 54%). ^1H NMR (501 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.29 (s, 1H), 3.92 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.41 (s), 145.39 (s), 138.55 (s), 128.20 (s), 125.65 (s), 118.74 (s), 111.45 (s), 52.45 (s), 33.83 (s).



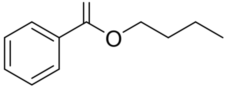
Methyl 1H-indole-6-carboxylate (2ac): Light yellow solid. Method A was followed using 1*H*-indole-6-carbaldehyde (0.145 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.107 g, 61%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.39 (s, 1H), 6.63 (s, 1H), 3.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.31 (s), 135.15 (s), 131.60 (s), 127.60 (s), 123.65 (s), 120.84 (s), 120.30 (s), 113.53 (s), 102.98 (s), 51.99 (s).



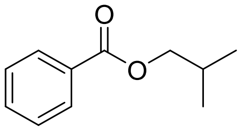
Methyl 2-(2-(cyclopentyloxy)phenyl)-7-methoxy-1-methyl-1H-benzo[d]imidazole-5-carboxylate (2ad): Light brown solid. Method A was followed using 2-(2-(cyclopentyloxy)phenyl)-7-methoxy-1-methyl-1H-benzo[d]imidazole-5-carbaldehyde (0.350 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266g, 2.0 equiv.) in methanol (2 mL) for 24 h and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.137 g, 36%). ^{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, CDCl3) 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).



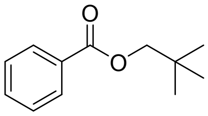
Ethyl benzoate (4a)[3-5]: Light yellow liquid. Method B was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in ethanol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 10:1) to afford the corresponding ester (0.14 g, 91%). ^{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).



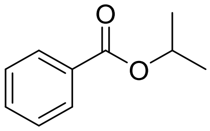
Butyl benzoate (4b)[3-5]: Colorless liquid. Method B was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in 1-butanol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.13 g, 71%). ^{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), 1.83 – 1.73 (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).



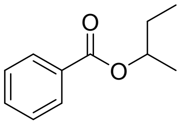
Isobutyl benzoate (4c)[3-5]: Colorless liquid. Method B was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in isobutyl alcohol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.13 g, 73%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.14 (d, J = 6.6 Hz, 2H), 2.11 (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).



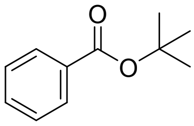
2,2-Dimethylpropyl benzoate (4d)[3-5]: Light yellow liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and neopentyl alcohol (0.176 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.13 g, 68%). ^{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).



Benzoic acid isopropyl ester (4e)[3-5]: Colorless liquid. Method B was followed using benzaldehyde (0.106g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv) and 30% hydrogen peroxide (0.2266g, 2.0 equiv) in 2-propanol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.12 g, 71%). ^{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).

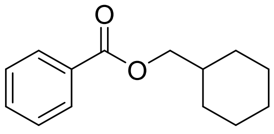


S-Butyl benzoate (4f)[3-5]: Colorless liquid. Method B was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) in 2-butanol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 20:1) to afford the corresponding ester (0.13 g, 74%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 5.37 – 4.86 (m, 1H), 1.81 – 1.66 (m, 2H), 1.36 (d, J = 6.3 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.07 (s), 133.66 (s), 130.18 (s), 129.53 (d, J = 4.0 Hz), 128.48 (s), 72.90 (s), 28.96 (s), 19.20 (s), 9.72 (s).

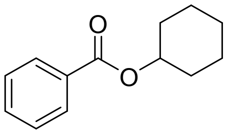


Benzoic acid tert-butyl ester (4g)[3-5]: Colorless liquid. Method B was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.) and 30%

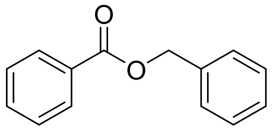
hydrogen peroxide (0.2266 g, 2.0 equiv.) in tert-butanol (2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 40:1) to afford the corresponding ester (0.10 g, 57%). ^{1}H NMR (501 MHz, CDCl$_3$) δ 7.98 (d, J = 7.4 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), 129.89 (s), 129.15 (s), 128.64 (s), 84.01 (s), 26.27 (s).



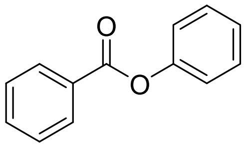
Cyclohexylmethyl benzoate (4h)[3-5]: Light yellow liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and cyclohexanemethanol (0.228 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.16 g, 73%). ^{1}H NMR (501 MHz, CDCl$_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 6.9 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H), 4.10 (d, J = 6.3 Hz, 2H), 1.84 – 1.58 (m, 6H), 1.29 – 1.14 (m, 3H), 1.09 – 0.95 (m, 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).



Cyclohexyl benzoate (4i)[3-5]: Colorless liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and cyclohexanol (0.200 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 50:1) to afford the corresponding ester (0.15 g, 74%). ^{1}H NMR (501 MHz, CDCl$_3$) δ 8.08 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 5.25 – 4.88 (m, 1H), 1.97 (d, J = 5.8 Hz, 2H), 1.82 (dd, J = 7.6, 4.4 Hz, 2H), 1.62 (dd, J = 20.5, 11.1 Hz, 3H), 1.55 – 1.43 (m, 2H), 1.41 – 1.33 (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).

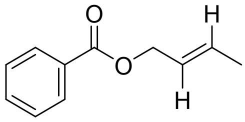


Benzyl benzoate (4j)[3-5]: Colorless liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and benzyl alcohol (0.216 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.14 g, 64%). ^{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).

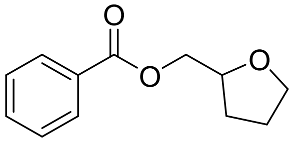


Benzoic acid phenyl ester (4k)[3-5]: White crystal powder. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and phenol (0.128 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.10 g, 52%). ^{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), 7.30 (dd, J = 13.9, 6.4

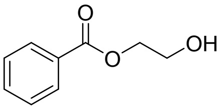
Hz, 1H), 7.25 (d, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.22 (s), 151.01 (s), 133.60 (s), 130.20 (s), 129.57 (d, J = 13.9 Hz), 128.60 (s), 125.91 (s), 121.75 (s).



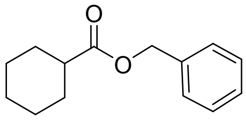
(E)-But-2-en-1-yl benzoate (4l)[3-5]: Light yellow liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and crotyl alcohol (0.144 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.12 g, 71%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 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), 132.87 (d, J = 5.2 Hz), 131.35 (s), 129.61 (s), 128.32 (s), 125.18 (s), 65.65 (s), 17.80 (s).



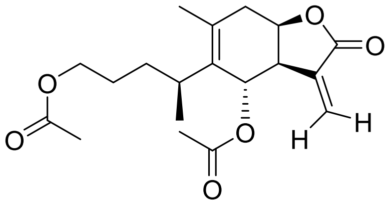
Oxolan-2-ylmethyl benzoate (4m)[3-5]: Light yellow liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and tetrahydrofurfuryl alcohol (0.204 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.19 g, 91%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.09 (d, J = 16.6 Hz, 2H), 7.65 – 7.52 (m, 1H), 7.46 (dd, J = 15.9, 7.0 Hz, 2H), 4.34 (ddd, J = 22.4, 18.5, 11.5 Hz, 3H), 4.05 – 3.73 (m, 2H), 2.02 (dd, J = 58.4, 8.9 Hz, 3H), 1.76 (s, 1H). ^{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), 77.36 (d, J = 4.7 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).



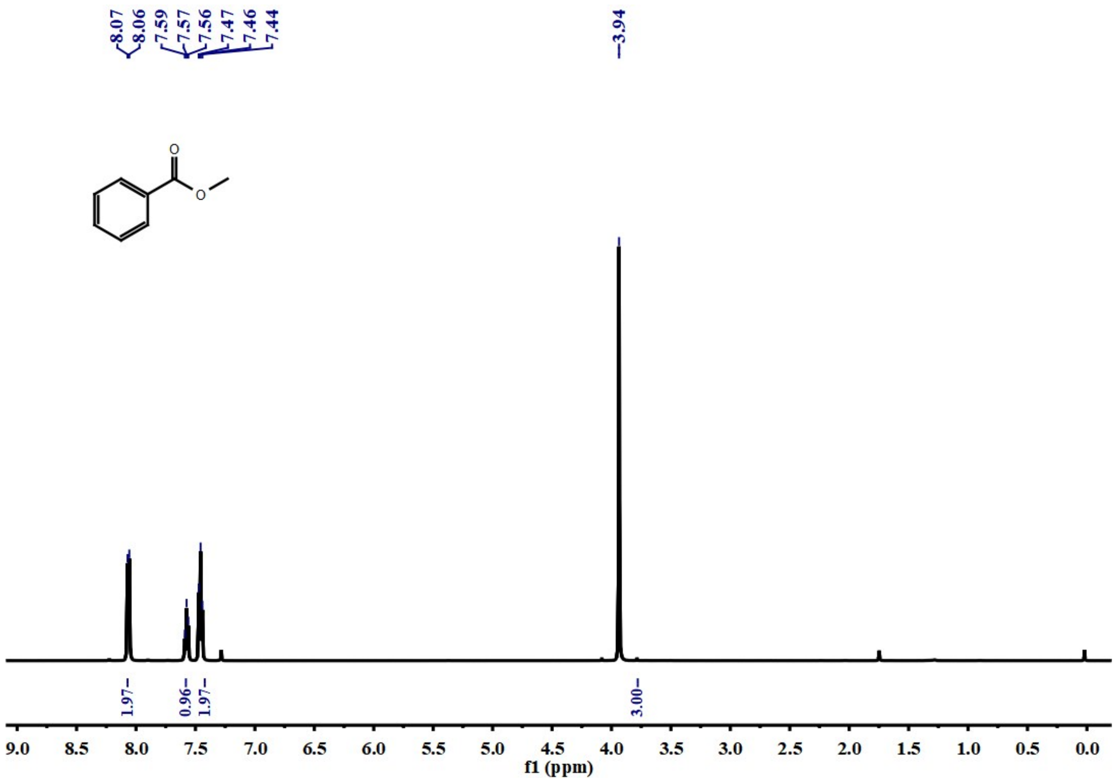
2-Hydroxyethyl benzoate (4n)[3-5]: Light yellow liquid. Method C was followed using benzaldehyde (0.106 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and ethylene glycol (0.124 g, 2 mL) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.14 g, 85%). ^{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), 4.53 – 4.25 (m, 2H), 4.12 – 3.79 (m, 2H), 3.25 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.07 (s), 133.21 (s), 129.99 (s), 129.70 (s), 128.43 (s), 66.59 (s), 61.12 (s).



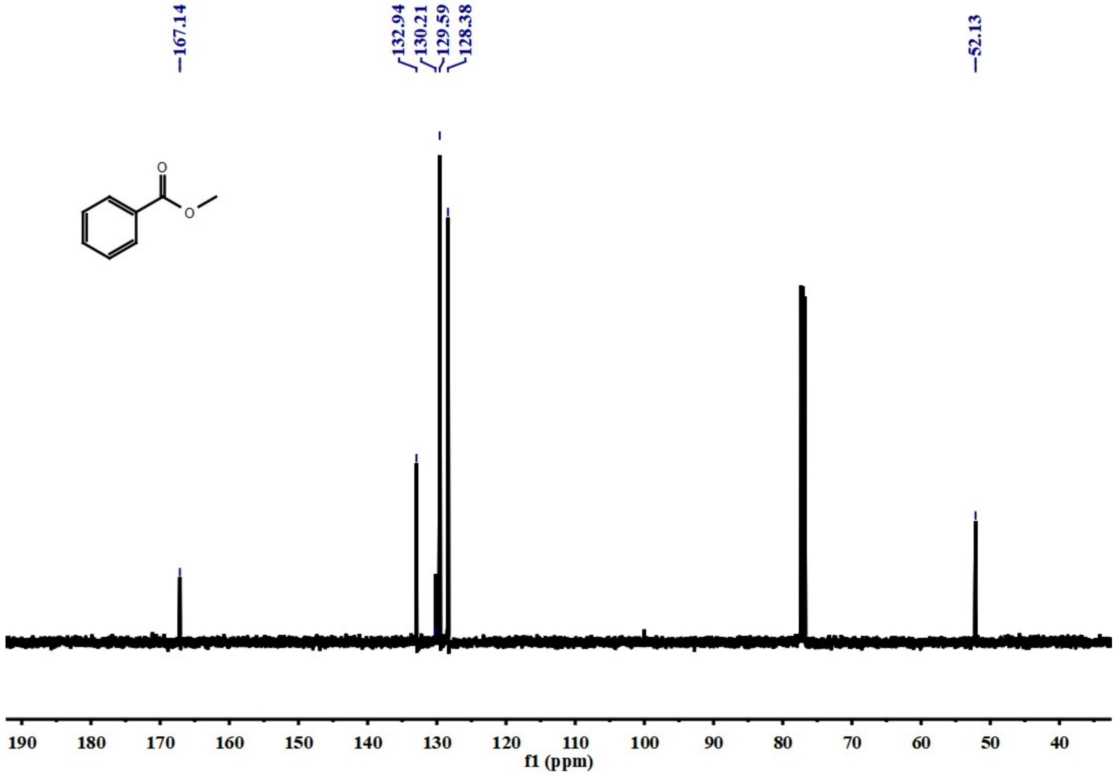
Benzyl cyclohexanecarboxylate (4o)[3-5]: Light yellow liquid. Method C was followed using cyclohexanecarboxaldehyde (0.112 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and benzyl alcohol (0.216 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 30:1) to afford the corresponding ester (0.16 g, 74%). ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 5H), 5.16 (s, 2H), 2.40 (tt, J = 11.3, 3.5 Hz, 1H), 1.99 (d, J = 12.7 Hz, 2H), 1.80 (d, J = 12.2 Hz, 2H), 1.69 (d, J = 8.6 Hz, 1H), 1.53 (dd, J = 22.2, 10.5 Hz, 2H), 1.37 – 1.25 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.84 (s), 136.42 (s), 128.55 (s), 128.04 (d, J = 12.2 Hz), 65.90 (s), 43.23 (s), 29.07 (s), 25.81 (s), 25.49 (s).



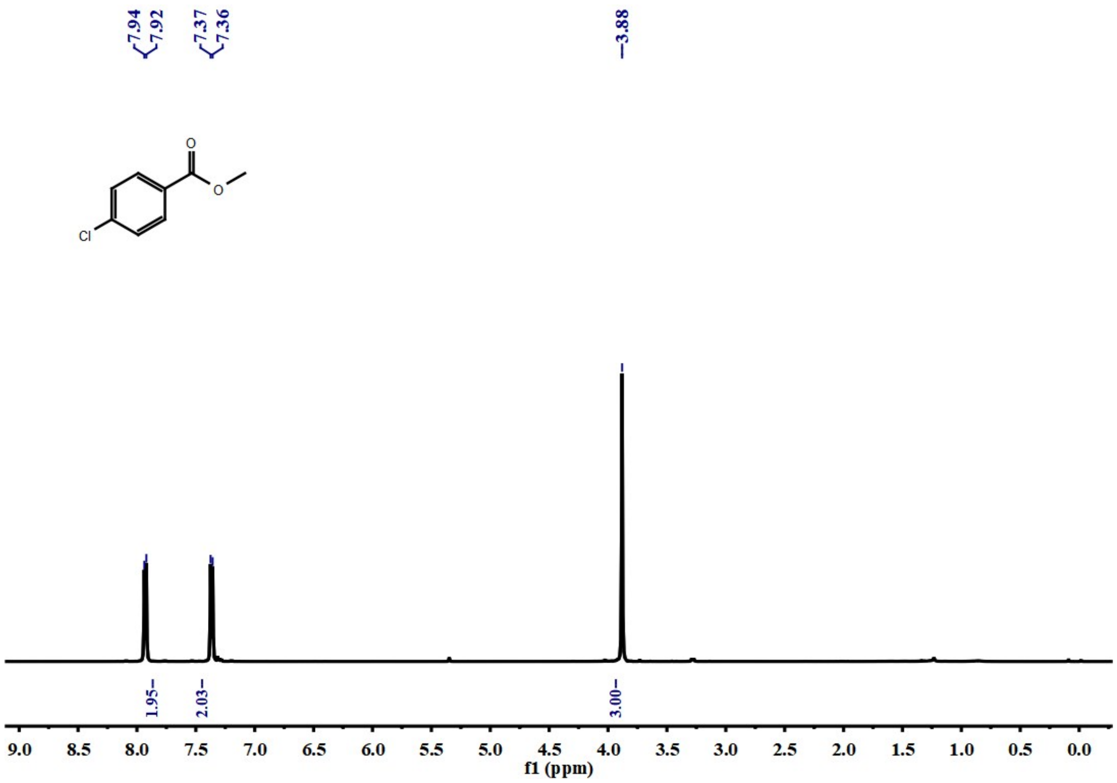
1,6-O,O-diacetylbritannilactone (4p)[6]**:** White crystals. Method C was followed using cyclohexanecarboxaldehyde (0.112 g, 1.0 mmol), $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (12.0 mg, 1.0 mol%), KCl (14.9 mg, 0.2 equiv.), 30% hydrogen peroxide (0.2266 g, 2.0 equiv.) and benzyl alcohol (0.216 g, 2.0 mmol) for 24 h adding two drops of nitric acid to the system and flash column chromatography on silica gel (petroleum ether : ethyl acetate, 10:1) to afford the corresponding ester (0.20 g, 58%).^{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).



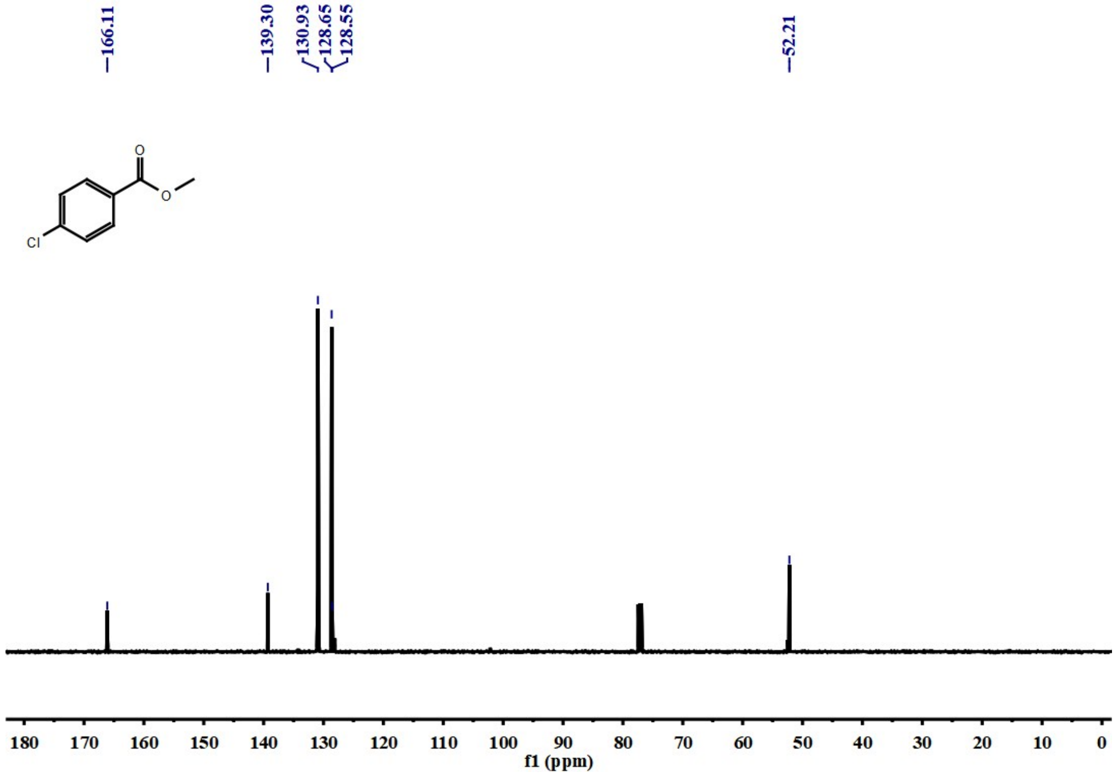
^{1}H NMR spectra of 2a (500 MHz, $CDCl_3$)



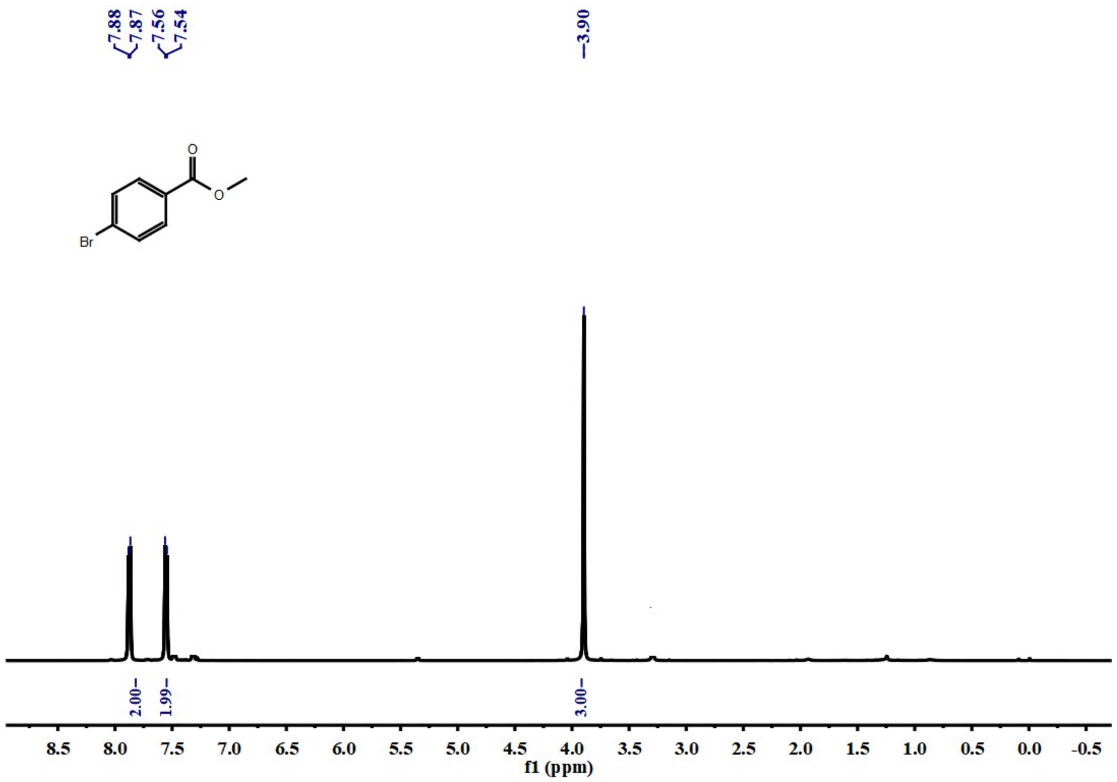
^{13}C NMR spectra of 2a (125 MHz, $CDCl_3$)



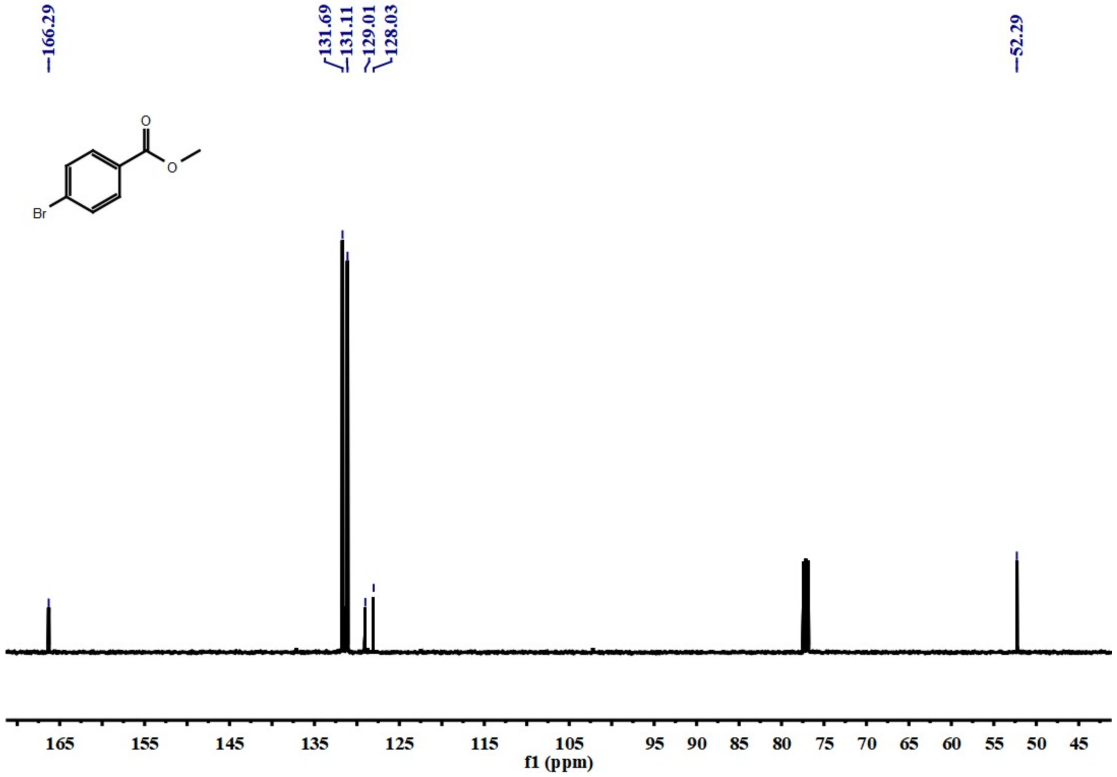
^{1}H NMR spectra of 2b (500 MHz, $CDCl_3$)



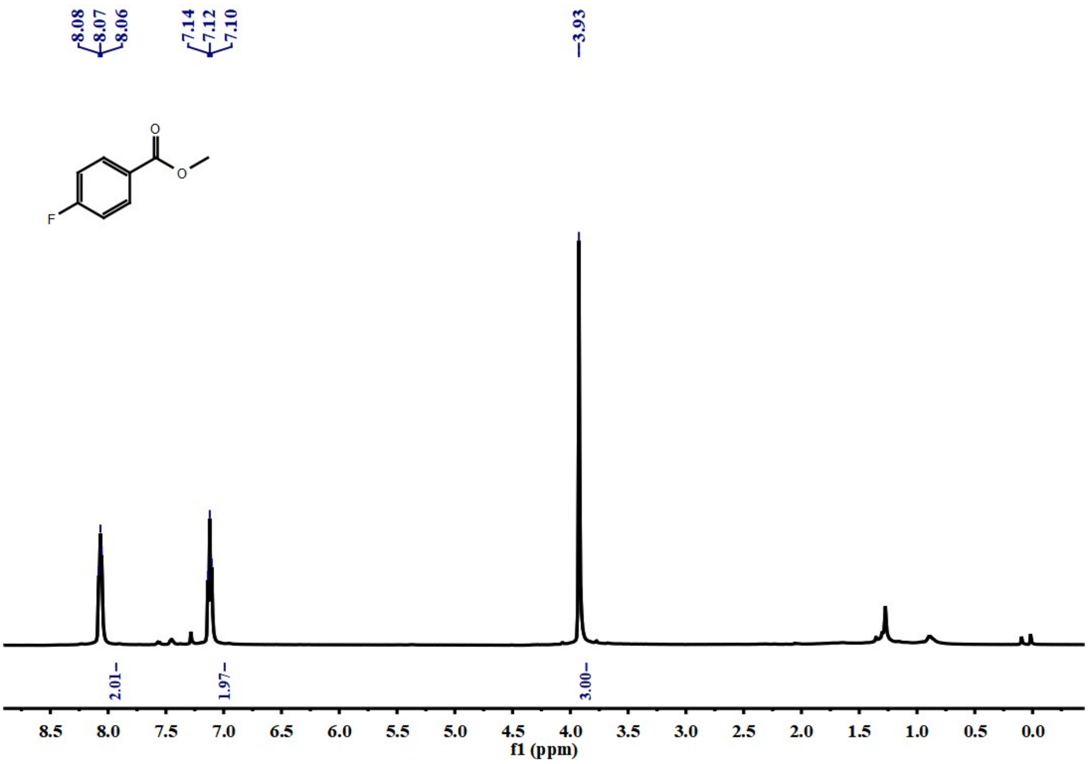
^{13}C NMR spectra of 2b (125 MHz, $CDCl_3$)



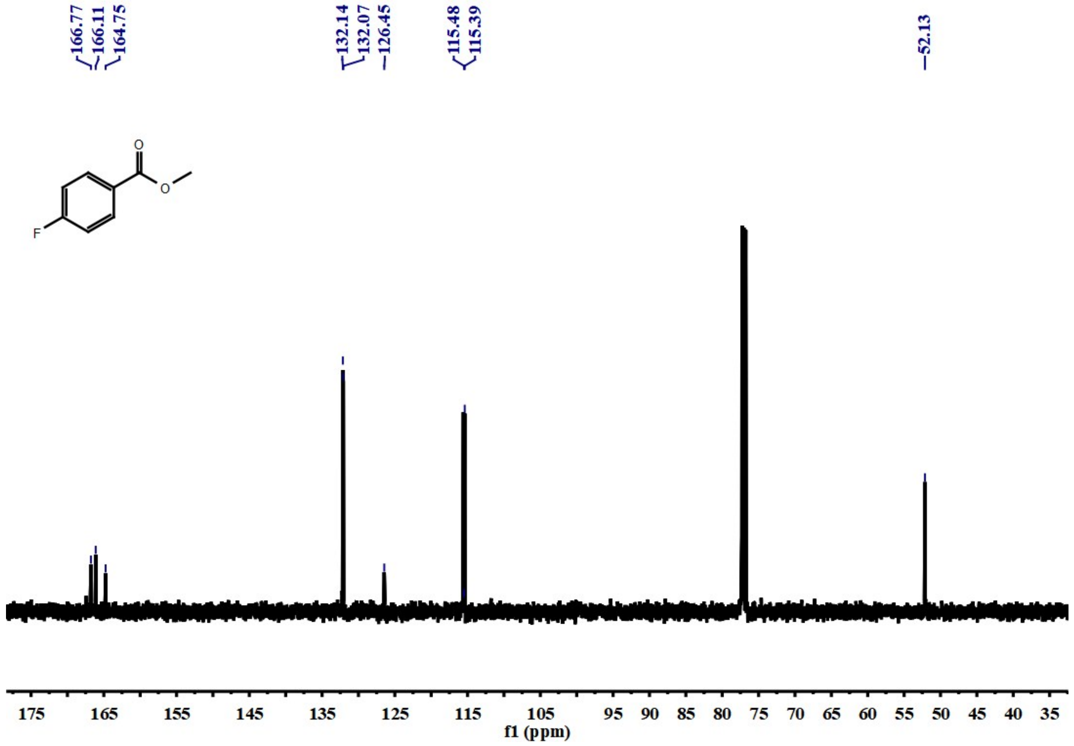
^{1}H NMR spectra of 2c (500 MHz, $CDCl_3$)



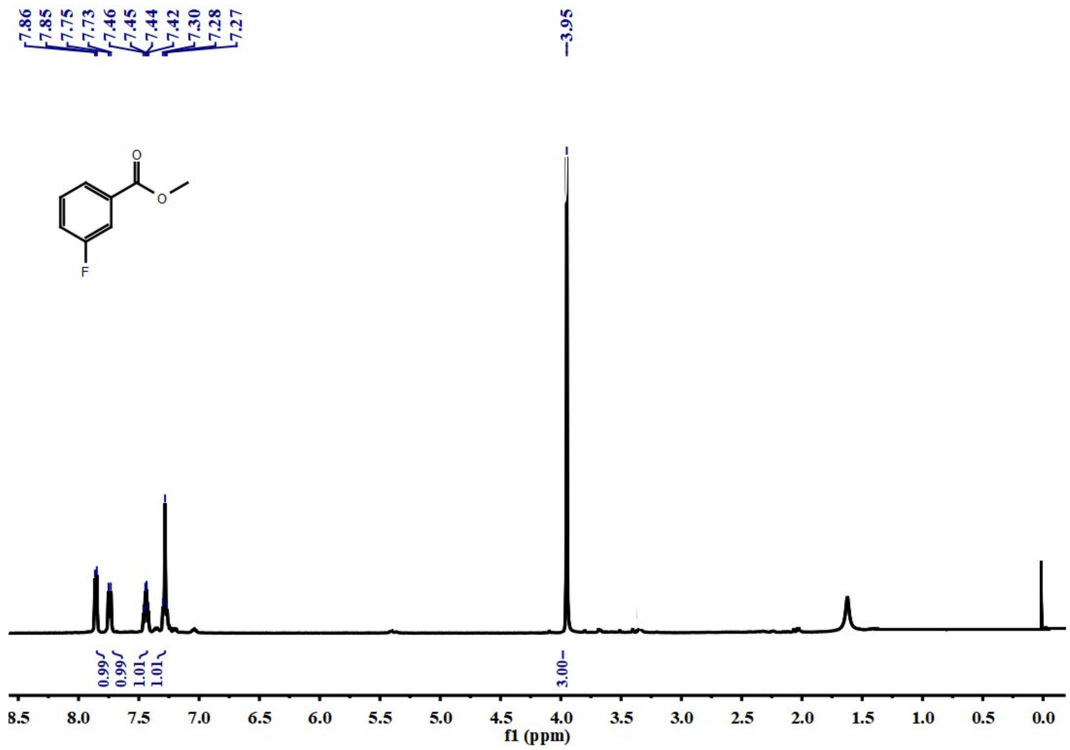
^{13}C NMR spectra of 2c (125 MHz, $CDCl_3$)



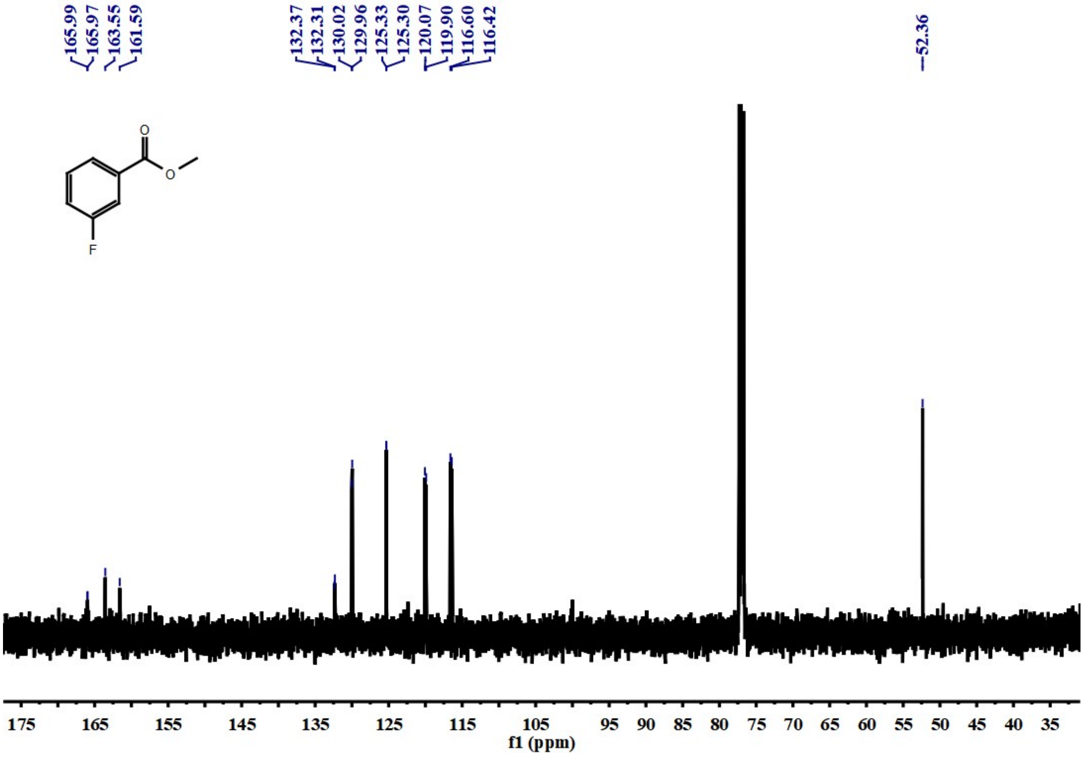
^{1}H NMR spectra of 2d (500 MHz, $CDCl_3$)



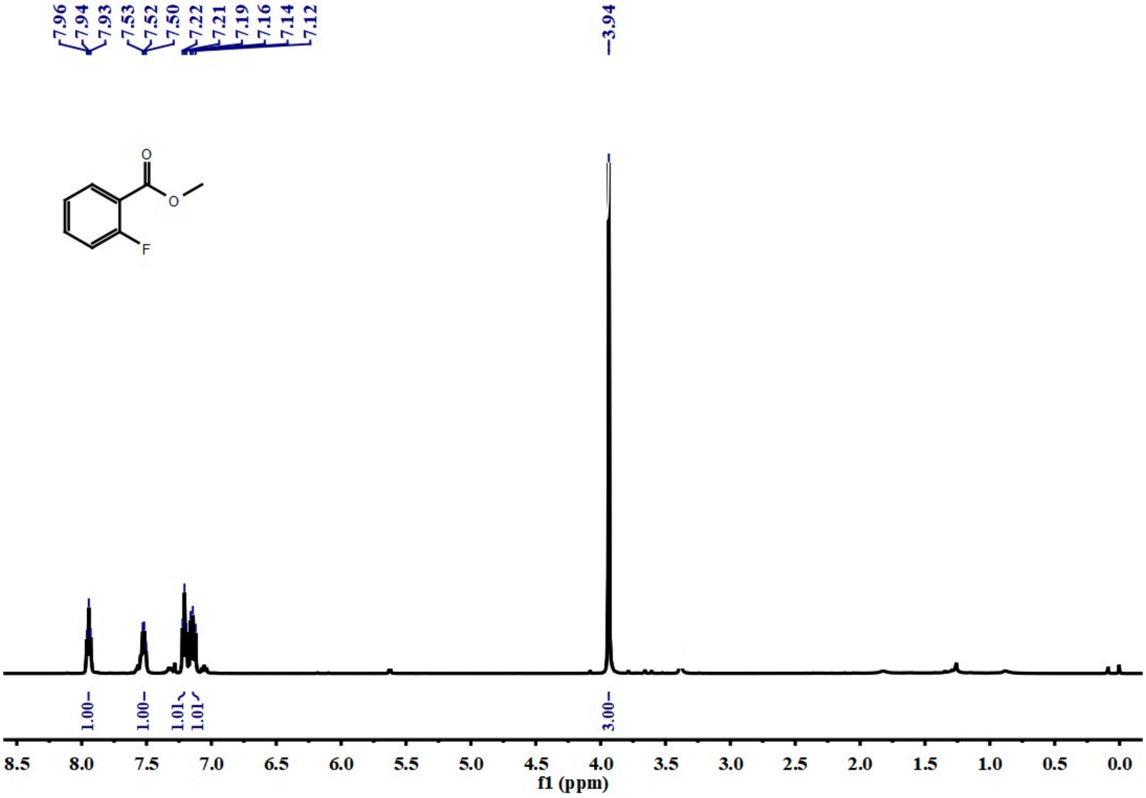
^{13}C NMR spectra of 2d (125 MHz, $CDCl_3$)



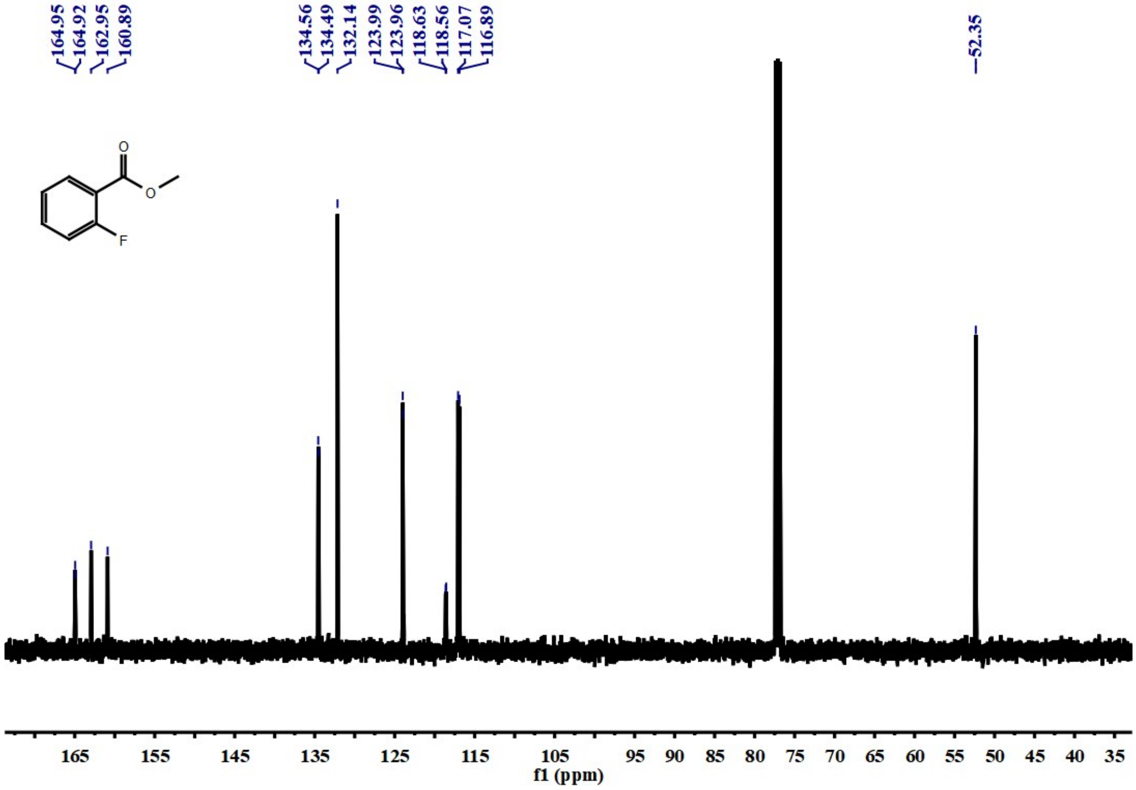
^{1}H NMR spectra of 2e (500 MHz, $CDCl_3$)



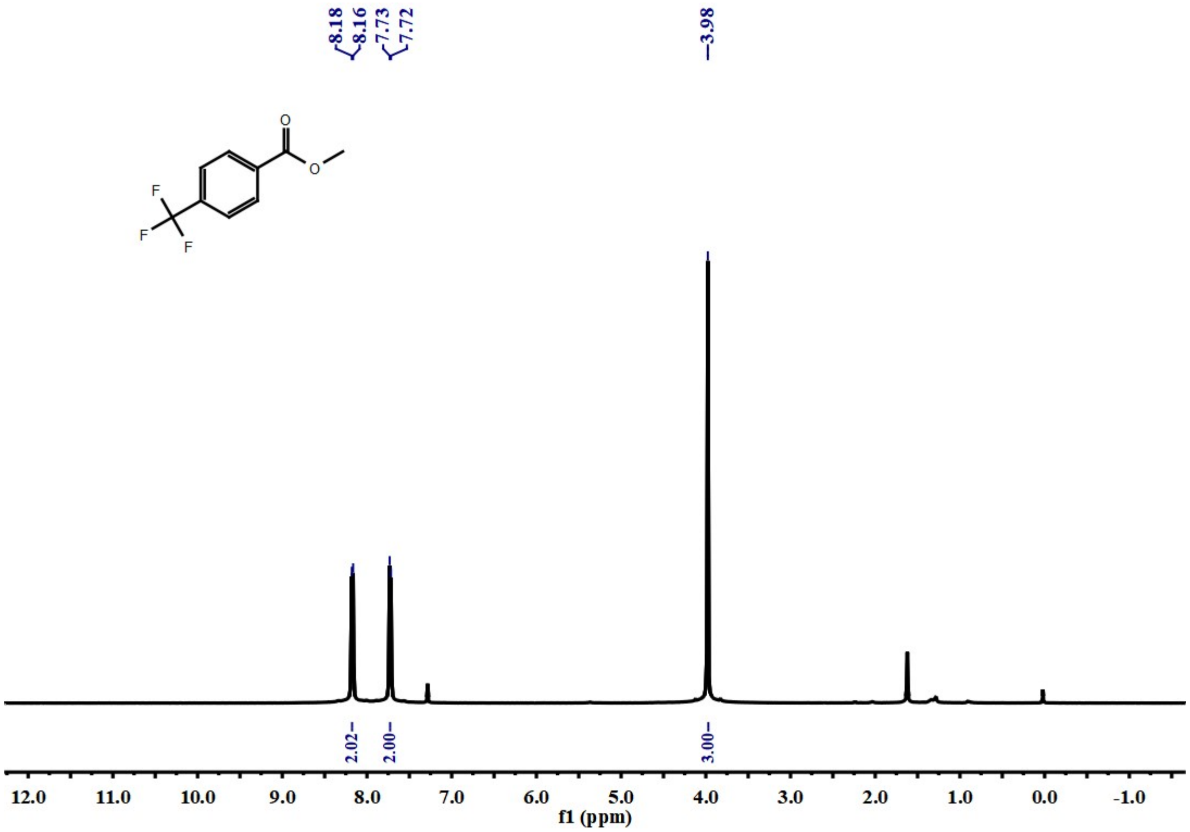
^{13}C NMR spectra of 2e (125 MHz, $CDCl_3$)



^{1}H NMR spectra of 2f (500 MHz, CDCl$_3$)



^{13}C NMR spectra of 2f (125 MHz, CDCl$_3$)



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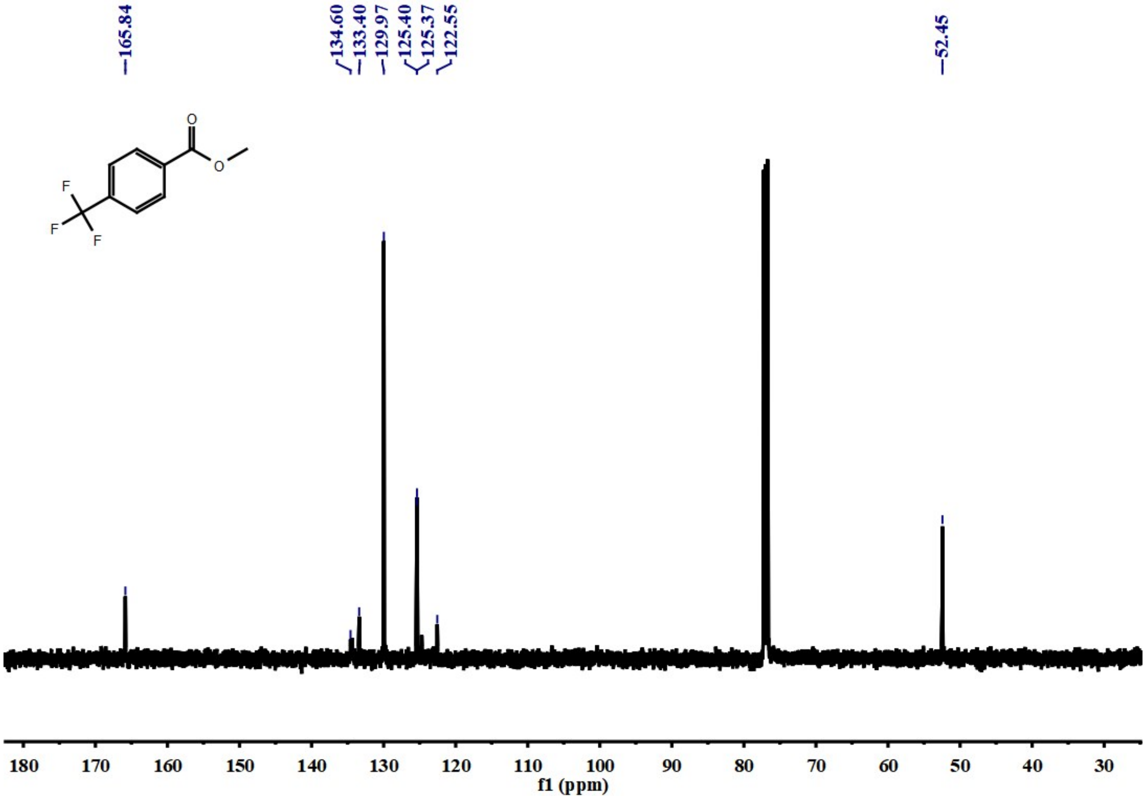
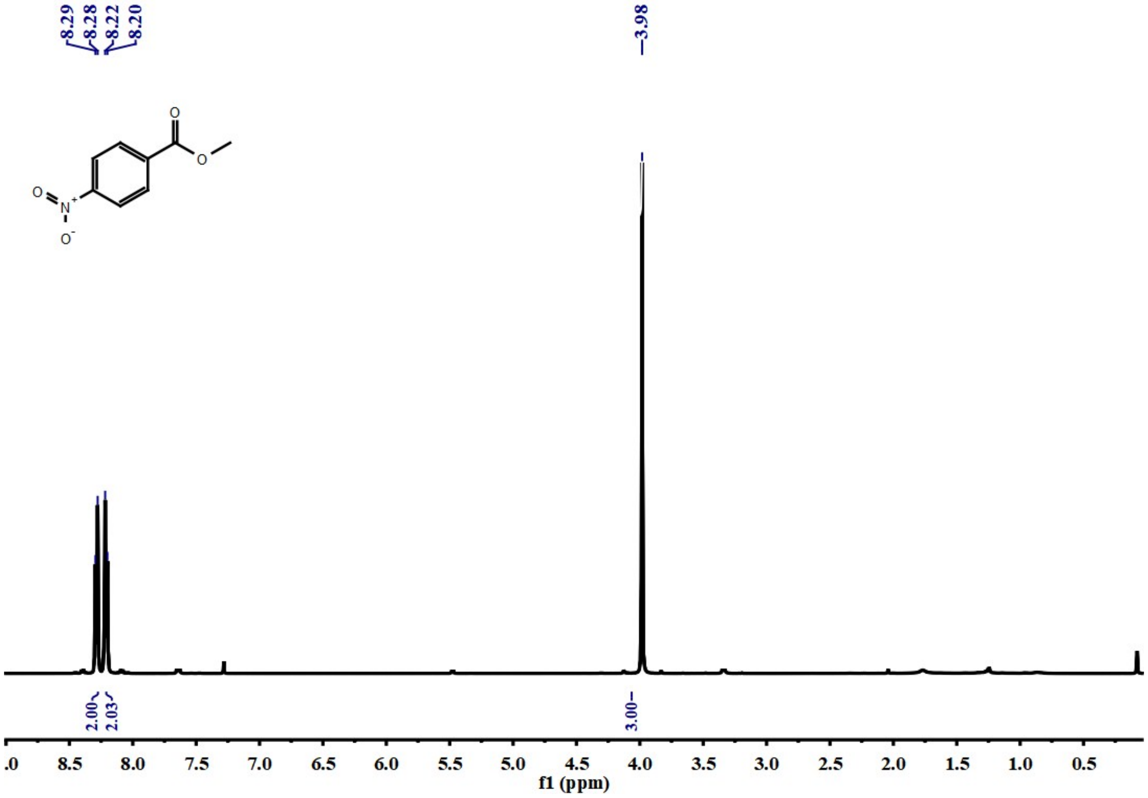


^{13}C NMR spectra of 2g (125 MHz, $CDCl_3$)



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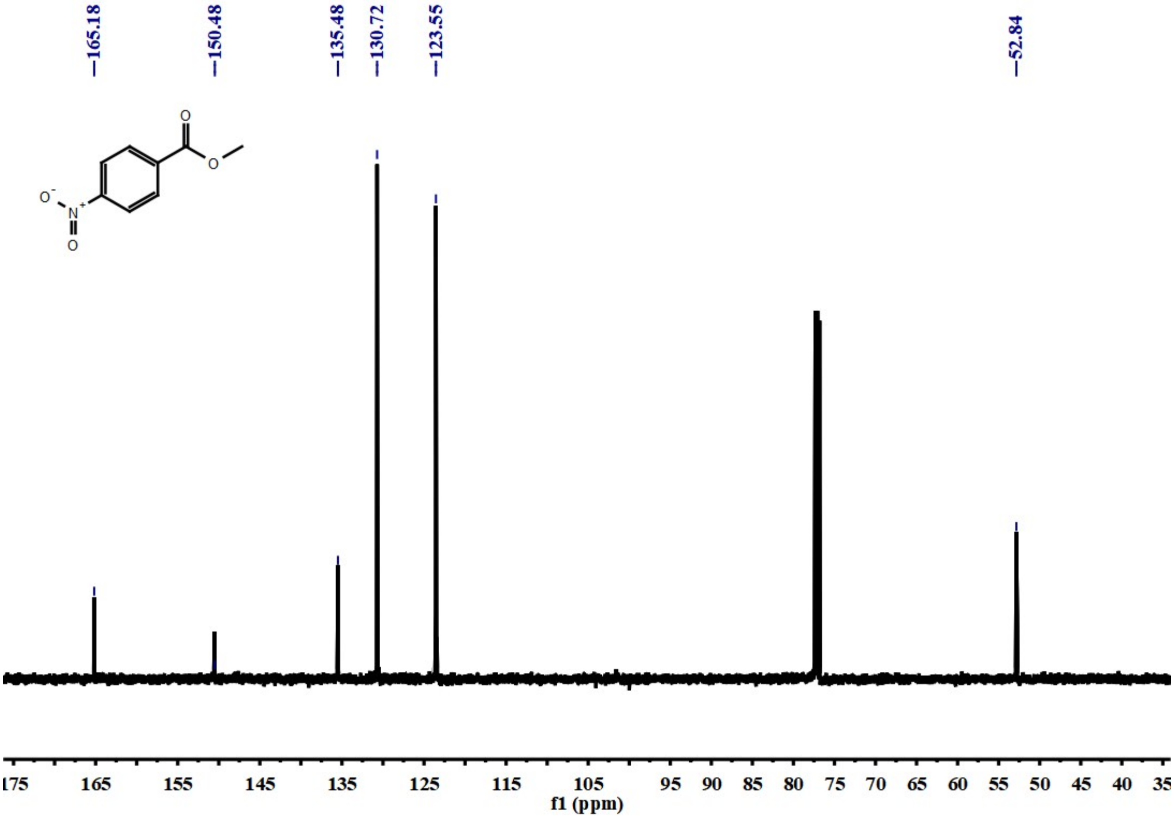
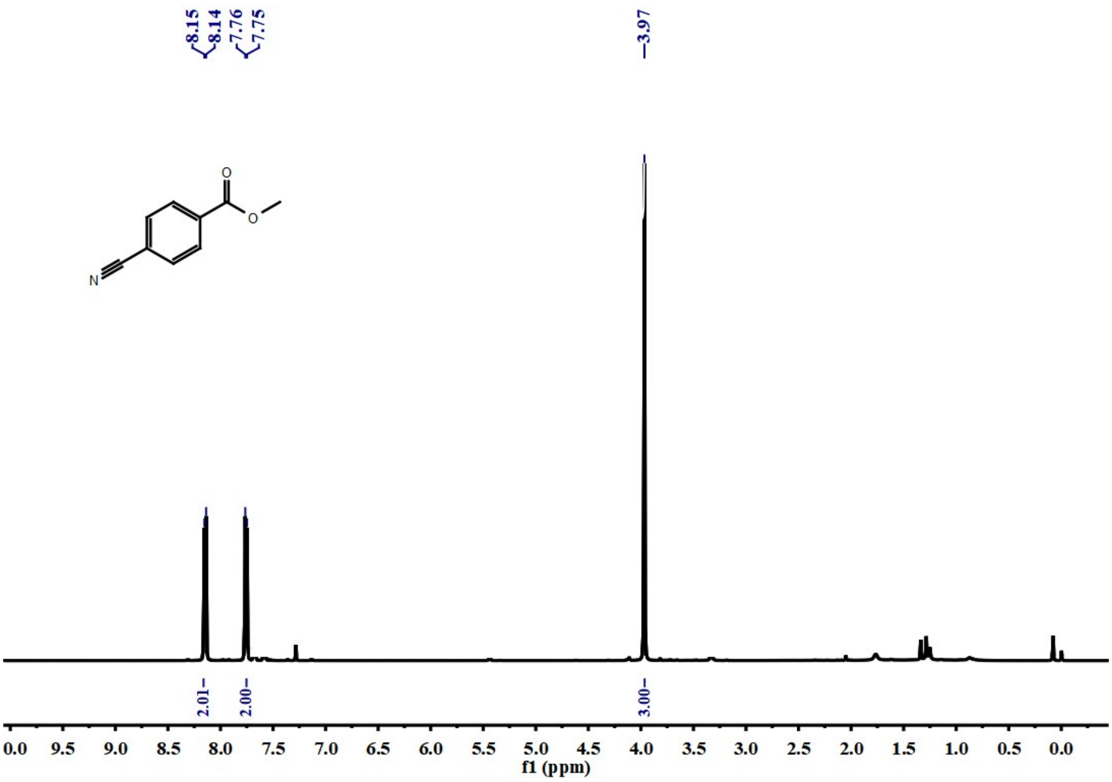
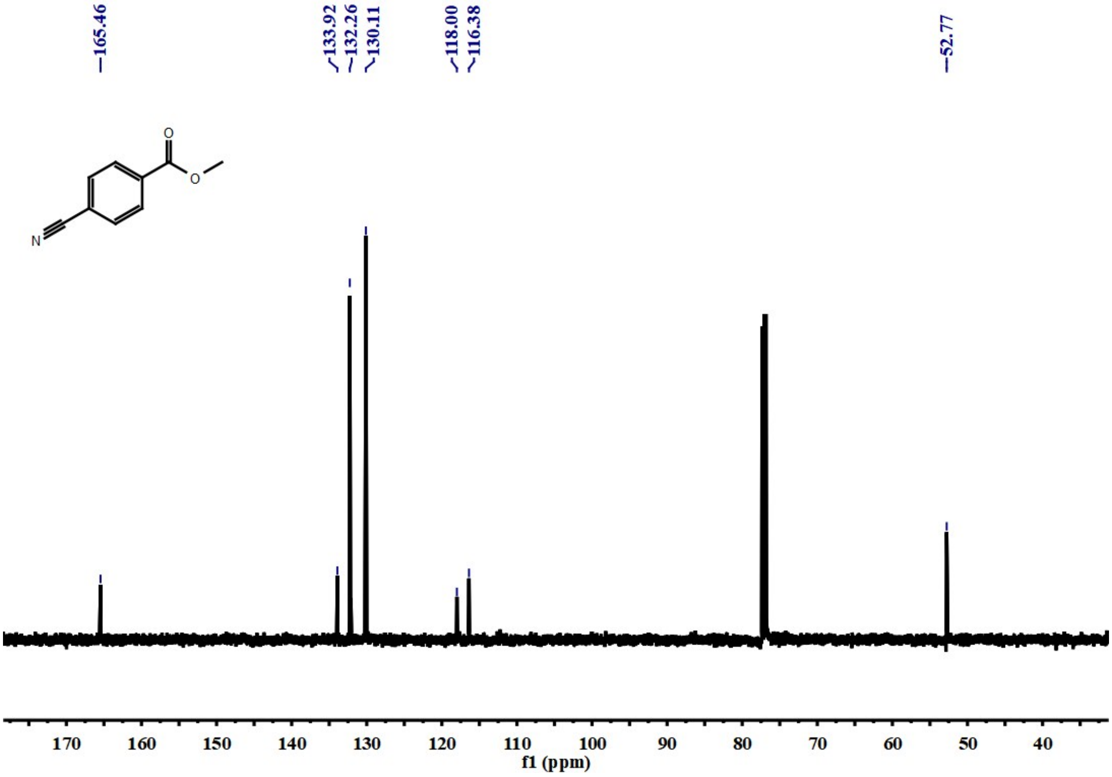


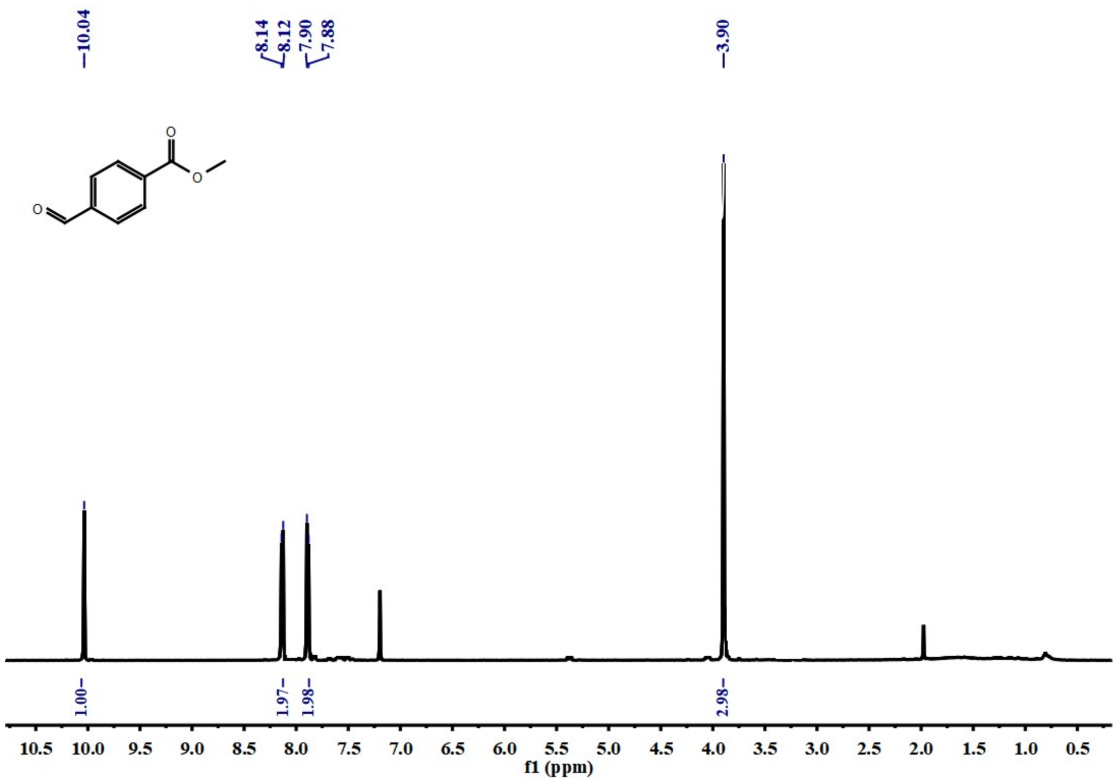
^{13}C NMR spectra of 2h (125 MHz, CDCl$_3$)



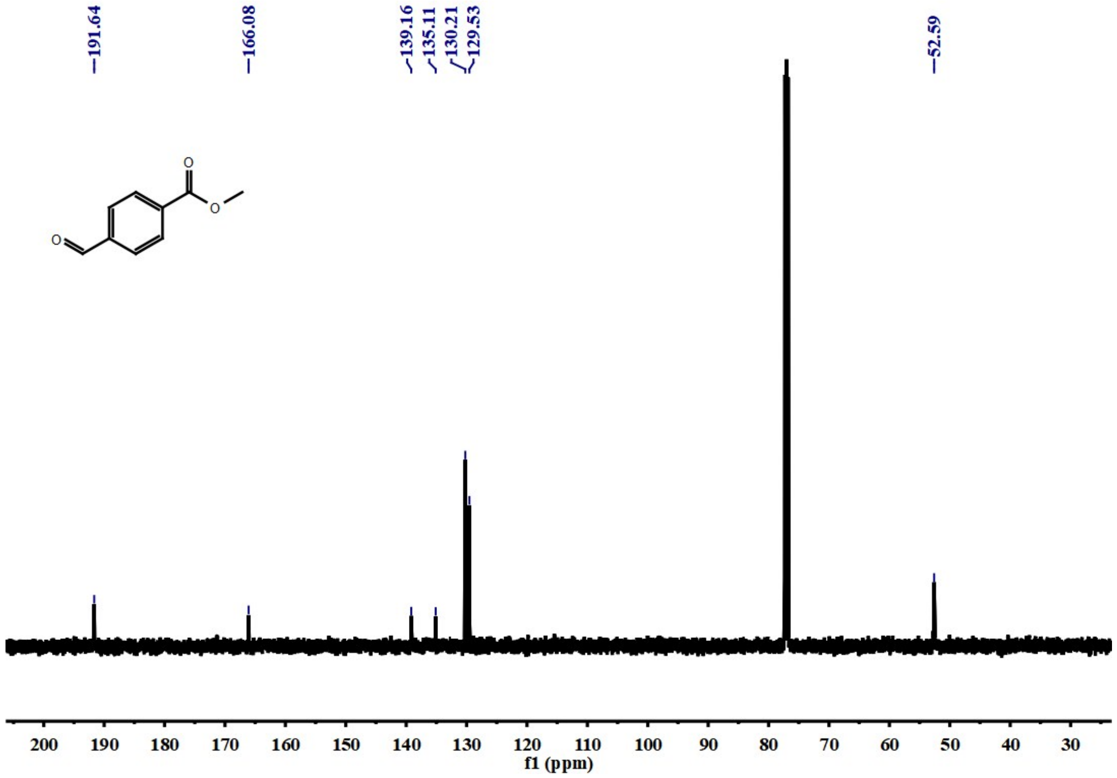
^{1}H NMR spectra of 2i (500 MHz, CDCl$_3$)



^{13}C NMR spectra of 2i (125 MHz, CDCl$_3$)



^{1}H NMR spectra of 2j (500 MHz, CDCl$_3$)



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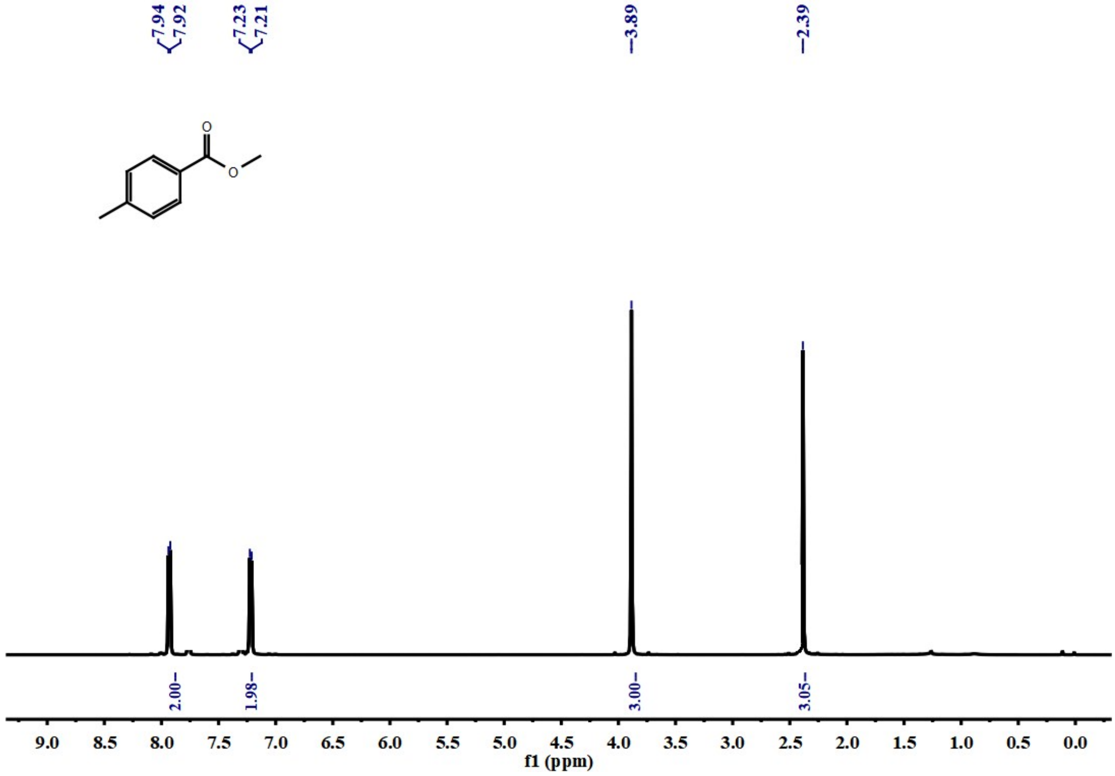
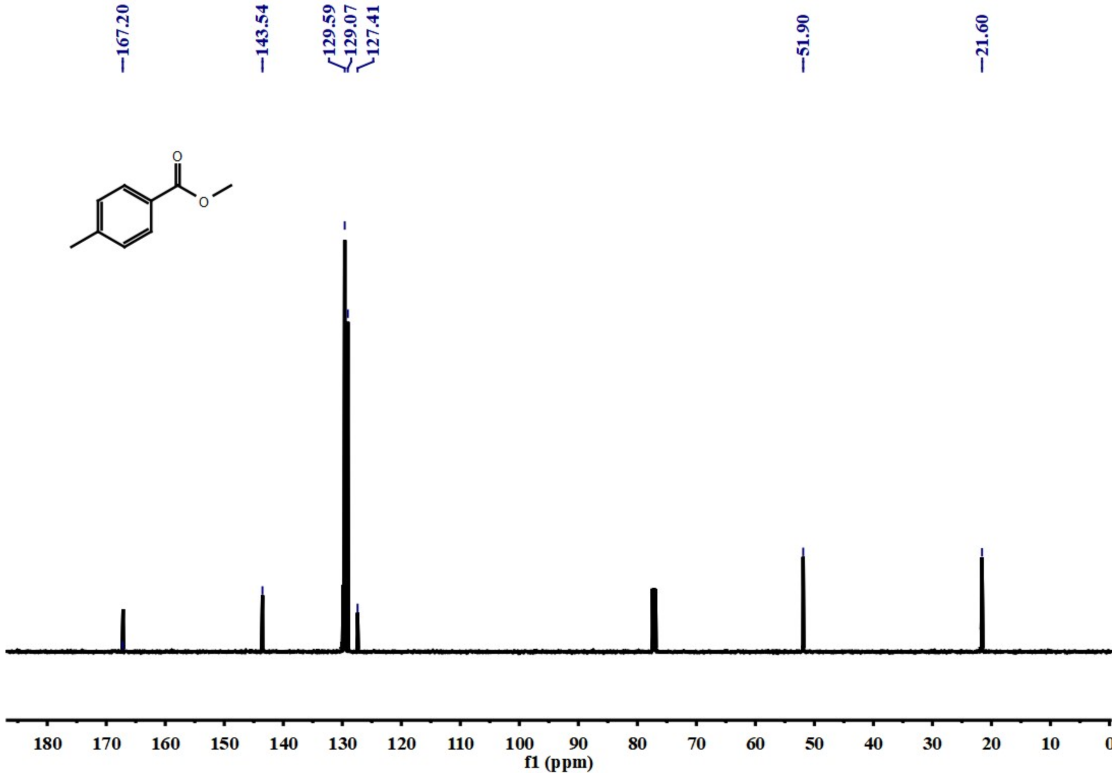
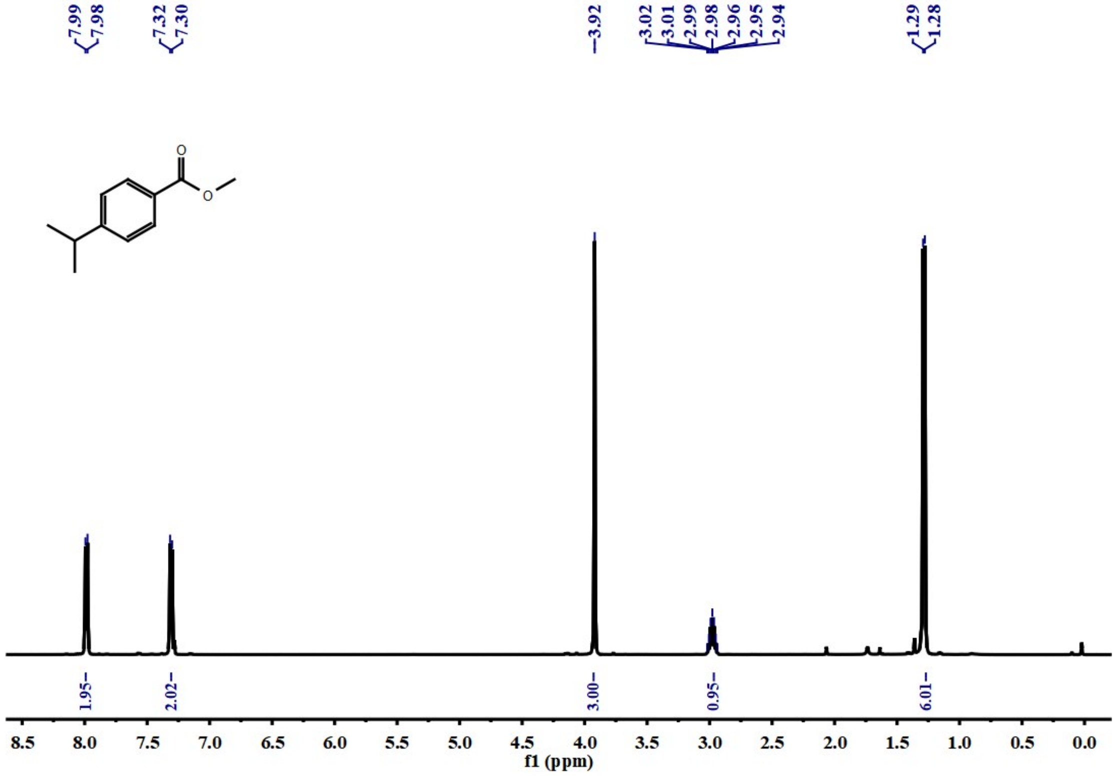


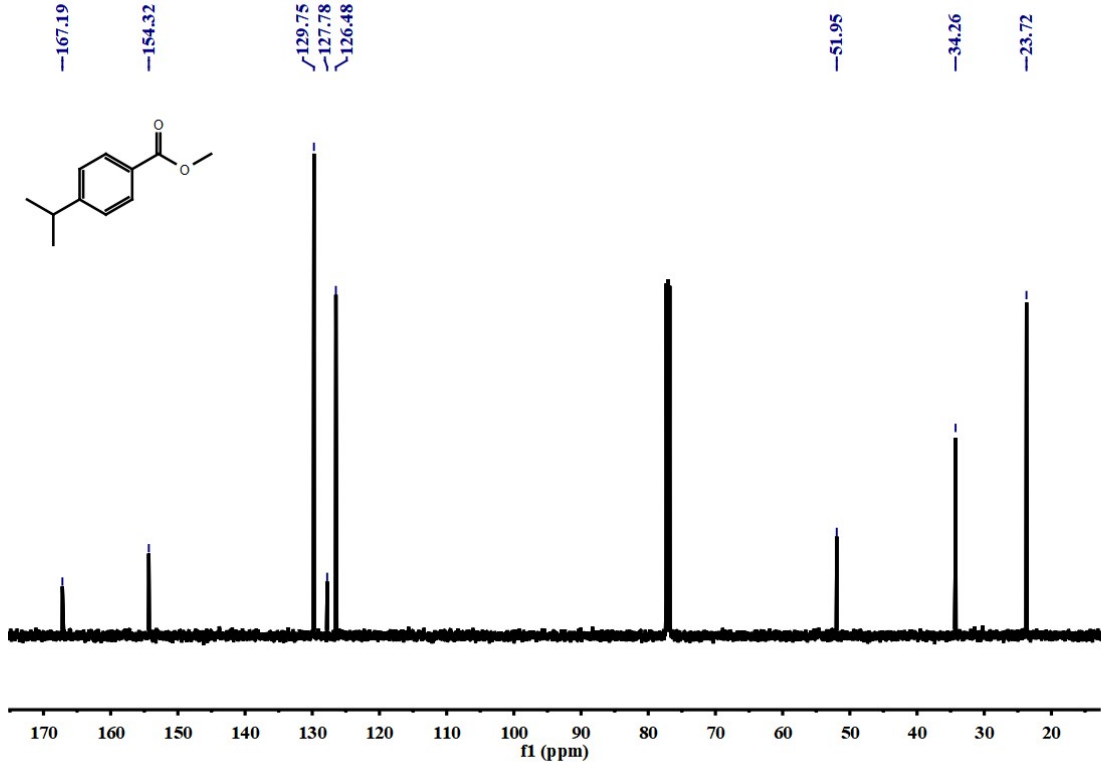
^{1}H NMR spectra of 2k (500 MHz, CDCl$_3$)



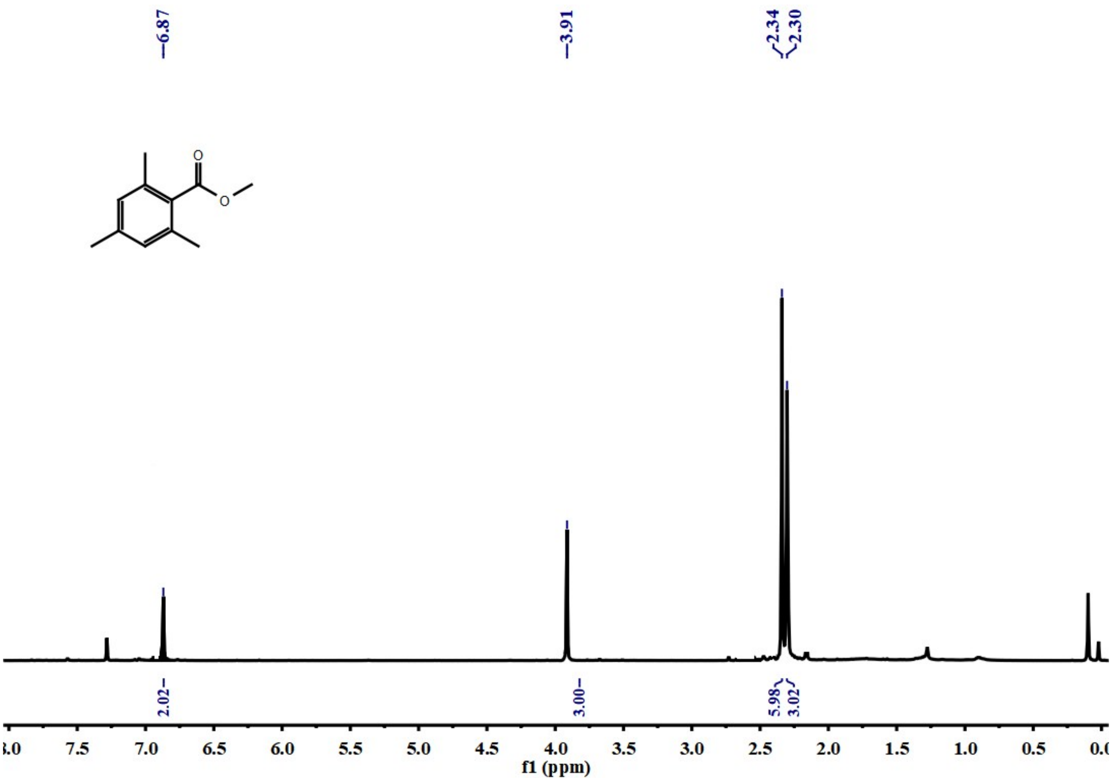
^{13}C NMR spectra of 2k (125 MHz, CDCl$_3$)



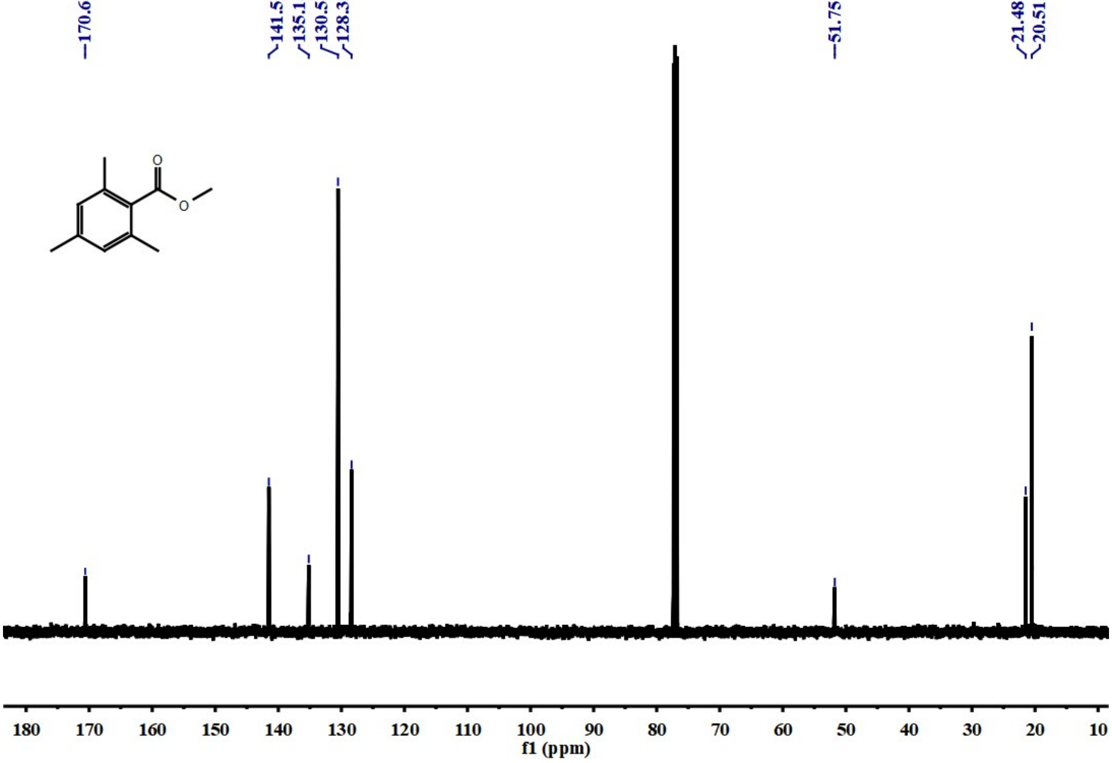
^{1}H NMR spectra of 2l (500 MHz, $CDCl_3$)



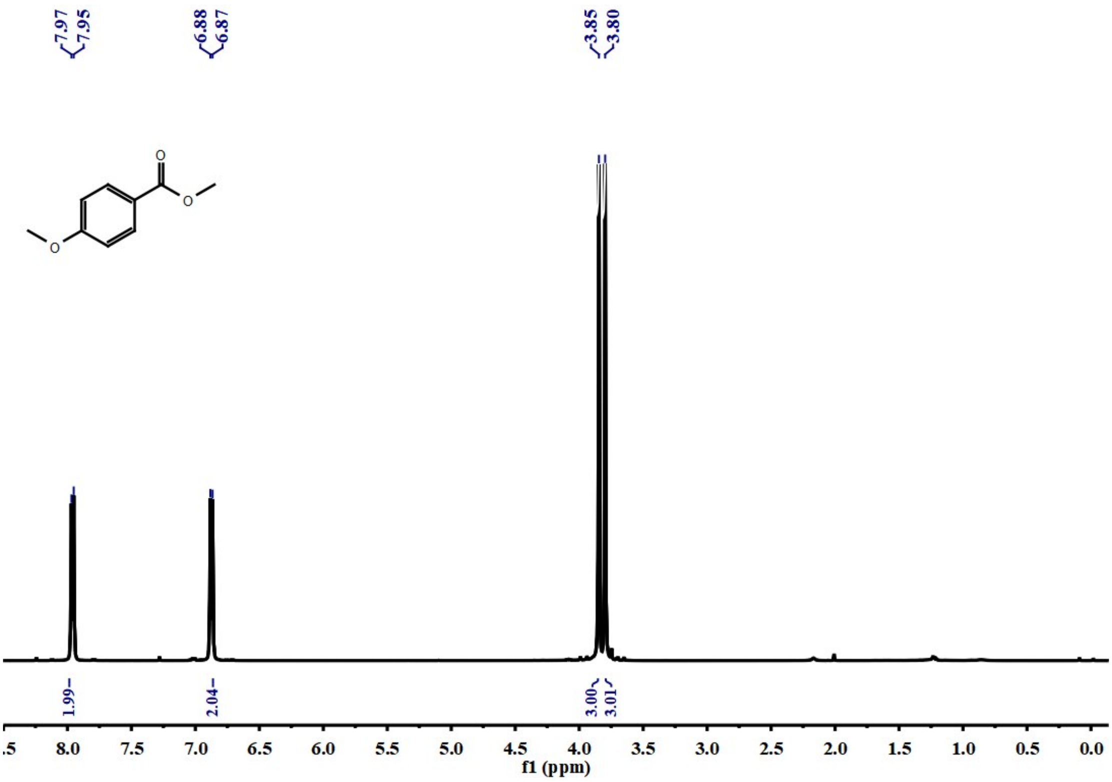
^{13}C NMR spectra of 2l (125 MHz, $CDCl_3$)



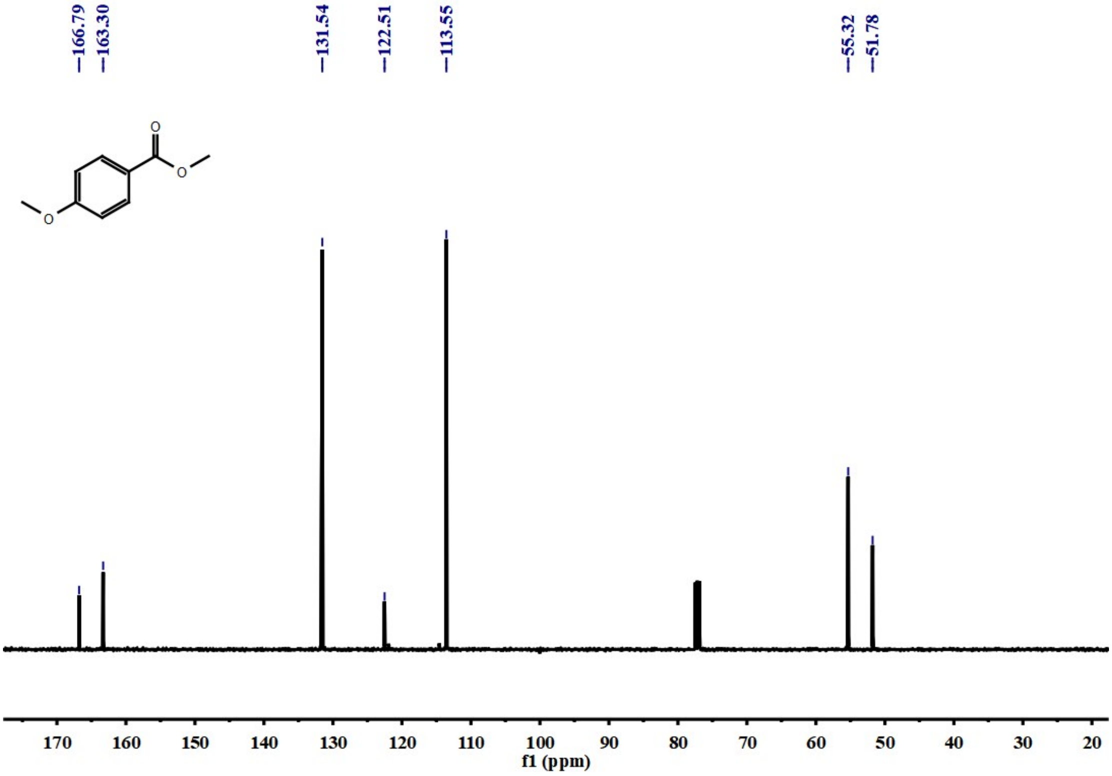
^{1}H NMR spectra of 2m (500 MHz, $CDCl_3$)



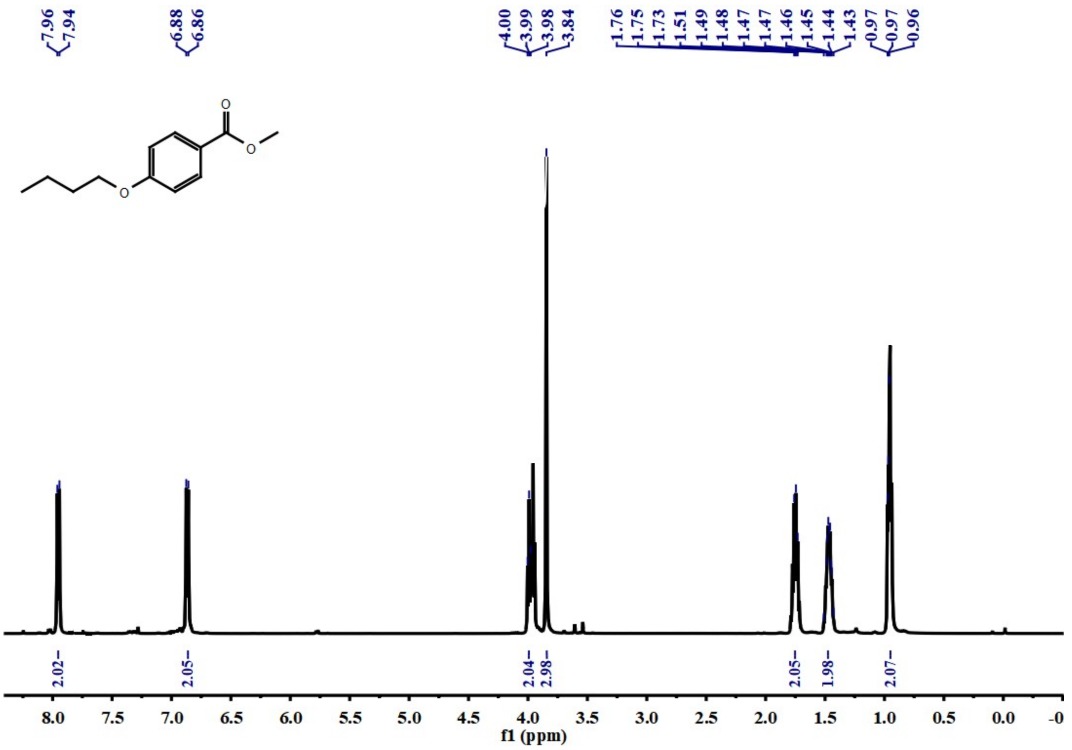
^{13}C NMR spectra of 2m (125 MHz, $CDCl_3$)



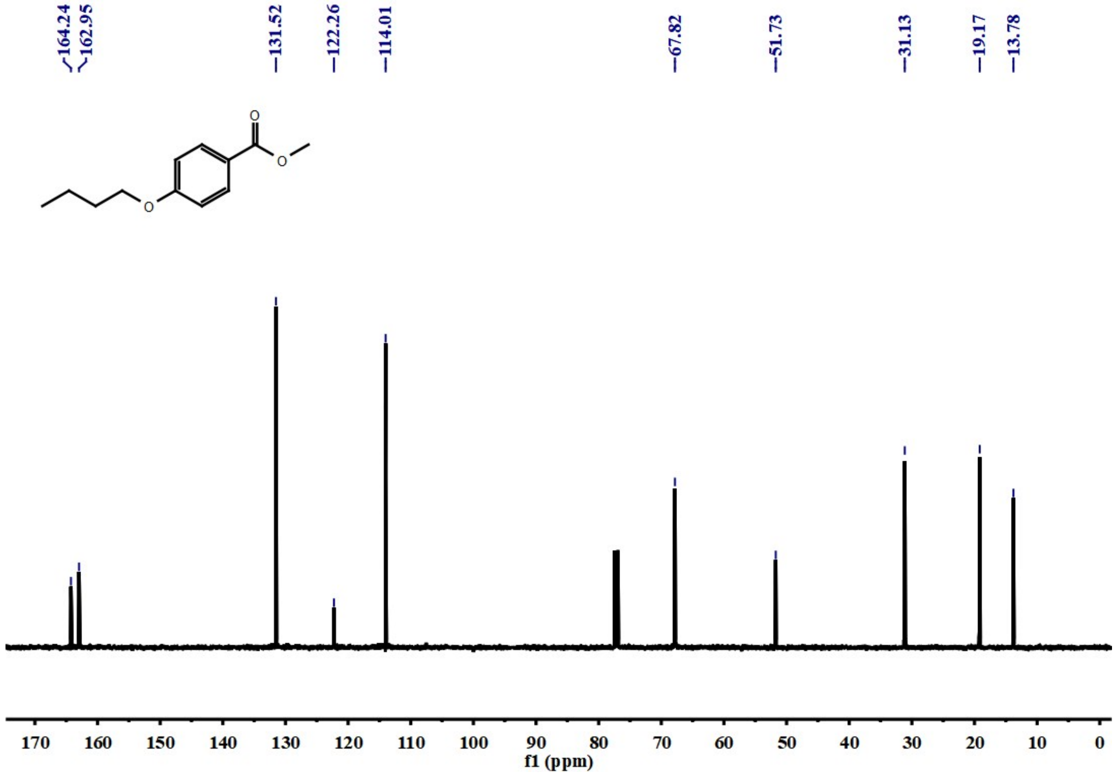
^{1}H NMR spectra of 2n (500 MHz, $CDCl_3$)



^{13}C NMR spectra of 2n (125 MHz, $CDCl_3$)



^{1}H NMR spectra of 2o (500 MHz, CDCl$_3$)



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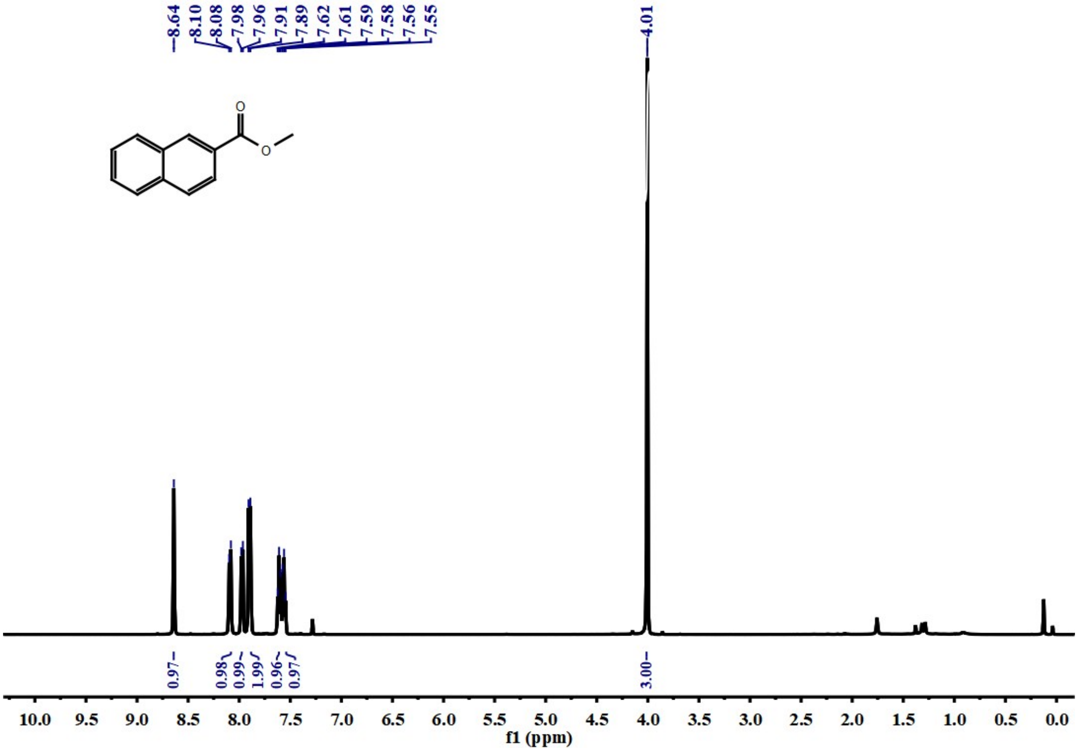
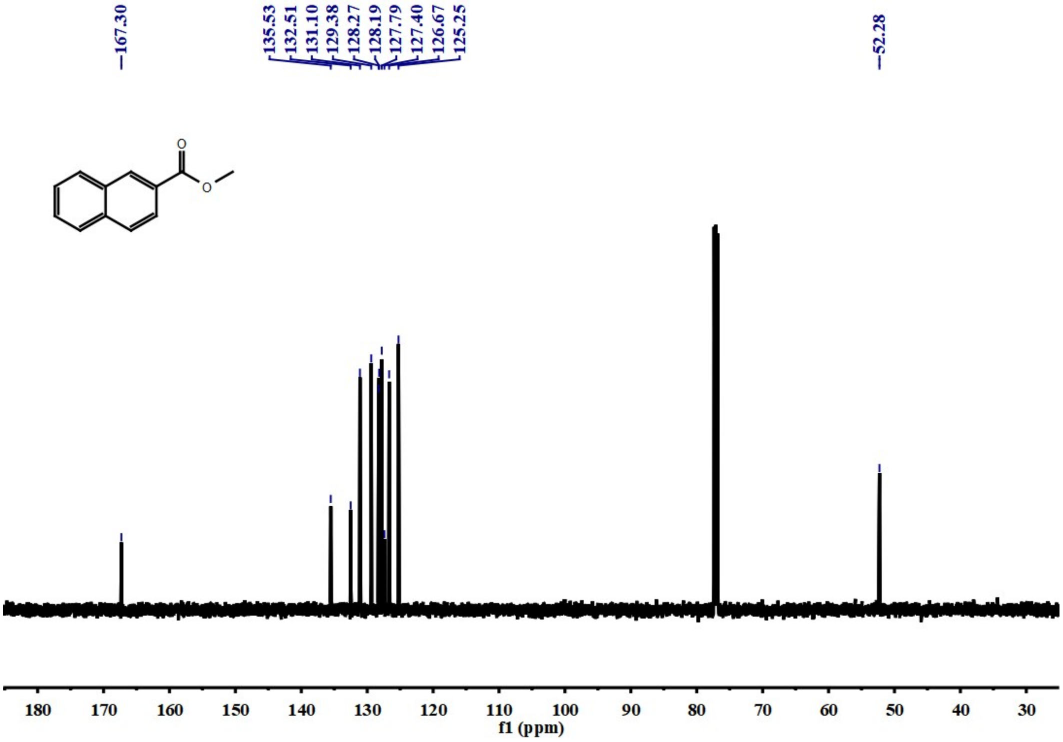
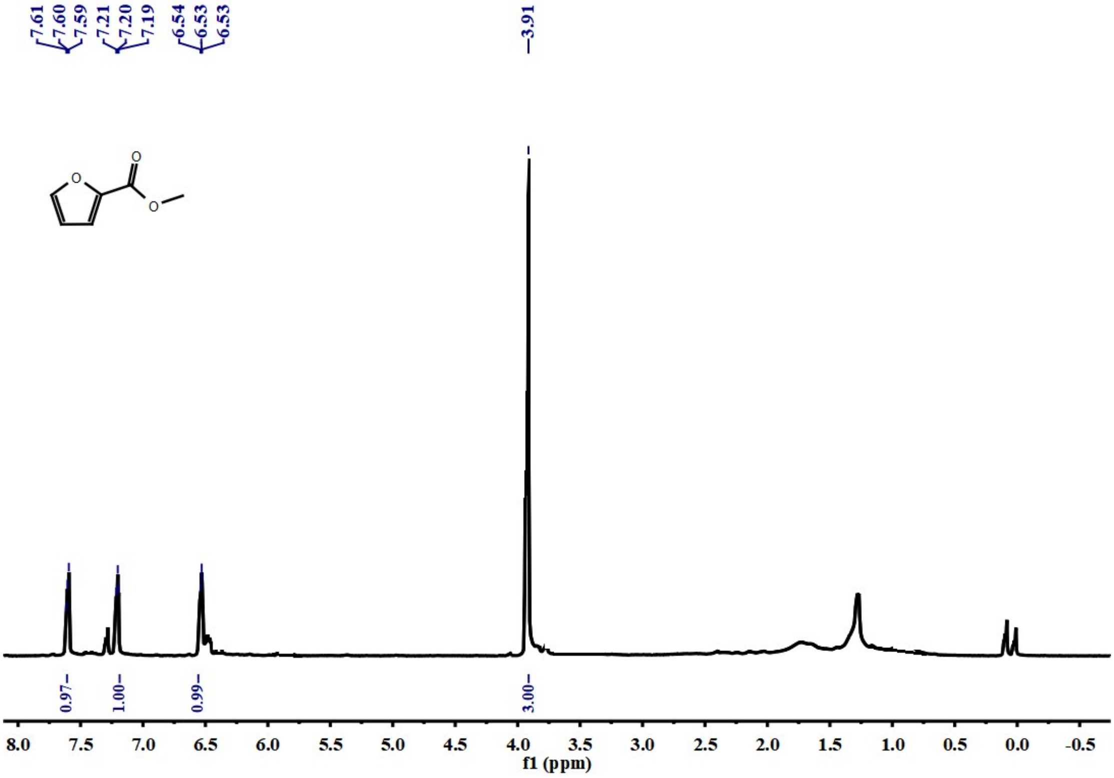


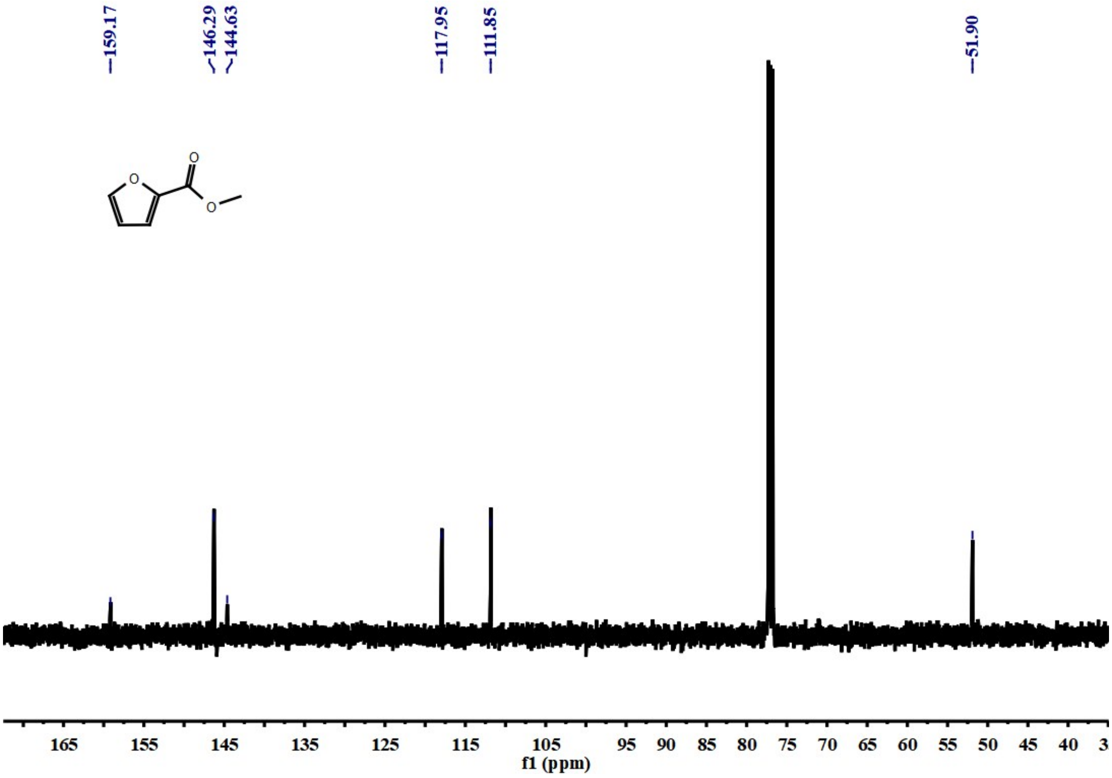
^{1}H NMR spectra of 2p (500 MHz, CDCl$_3$)



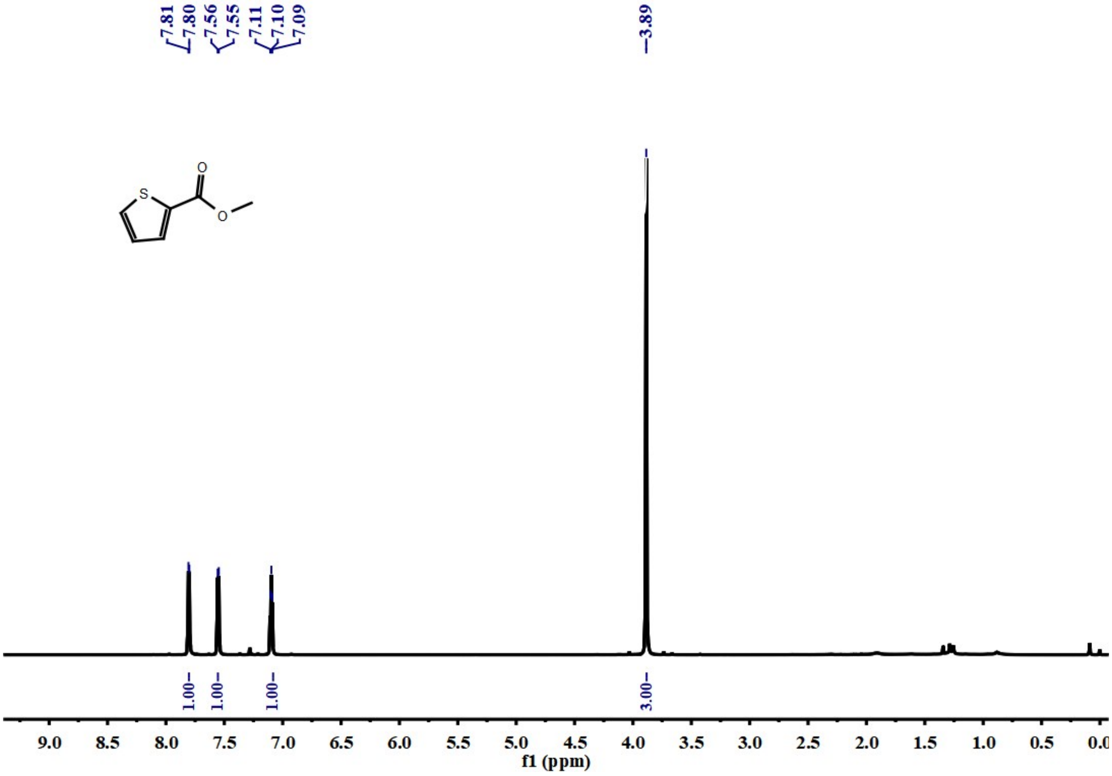
^{13}C NMR spectra of 2p (125 MHz, CDCl$_3$)



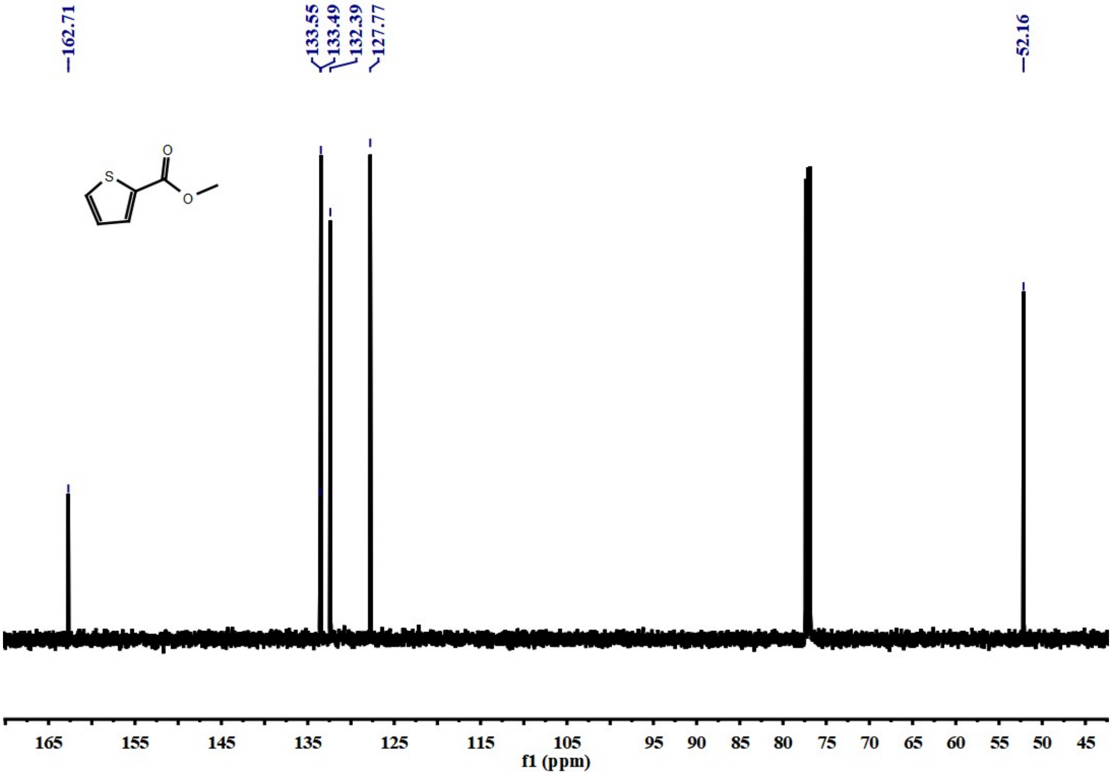
^{1}H NMR spectra of 2q (500 MHz, CDCl$_3$)



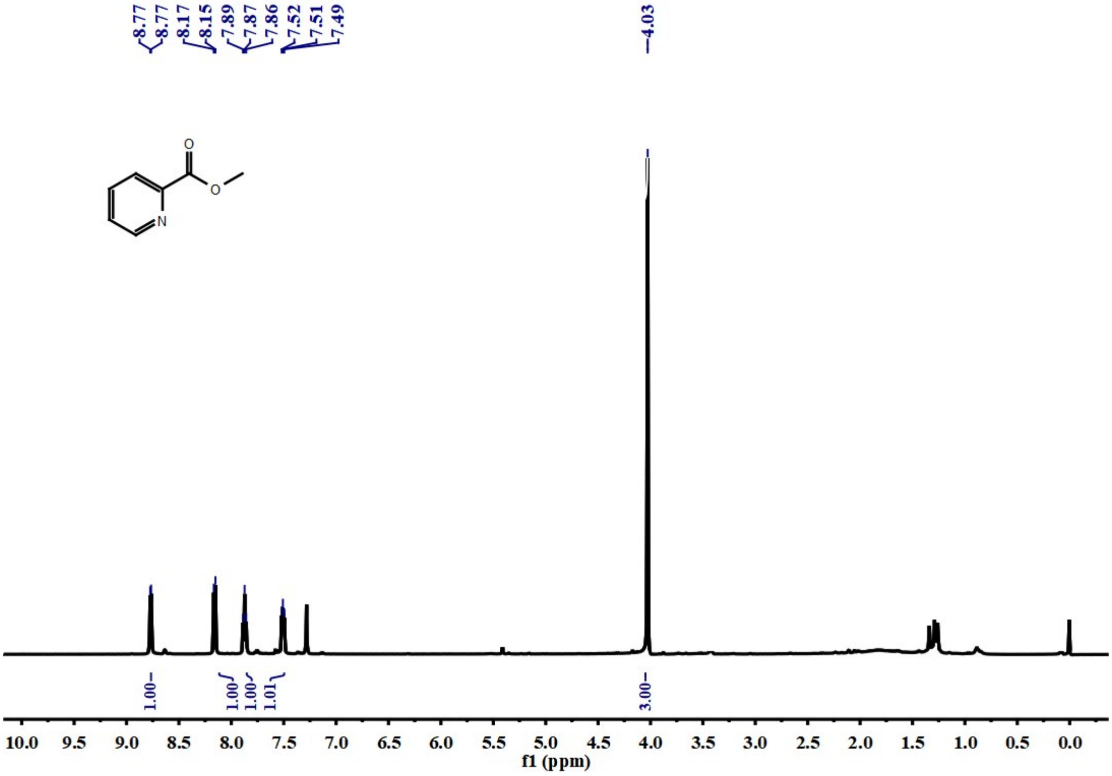
^{13}C NMR spectra of 2q (125 MHz, CDCl$_3$)



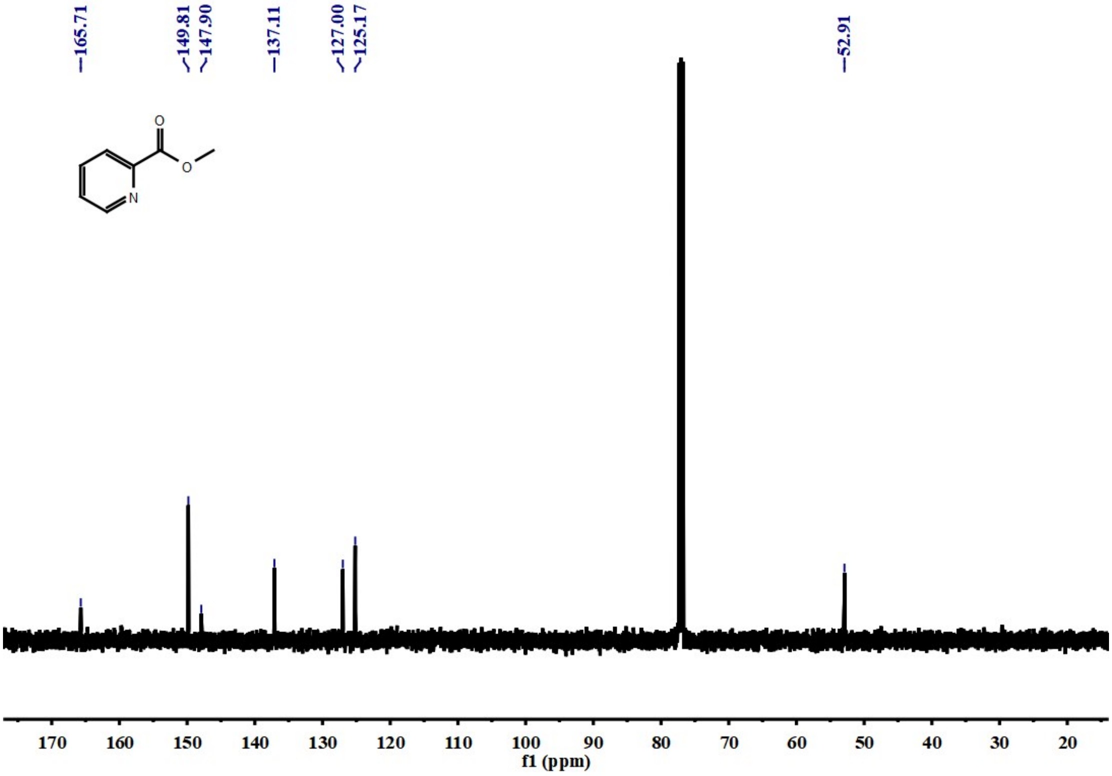
^{1}H NMR spectra of 2r (500 MHz, $CDCl_3$)



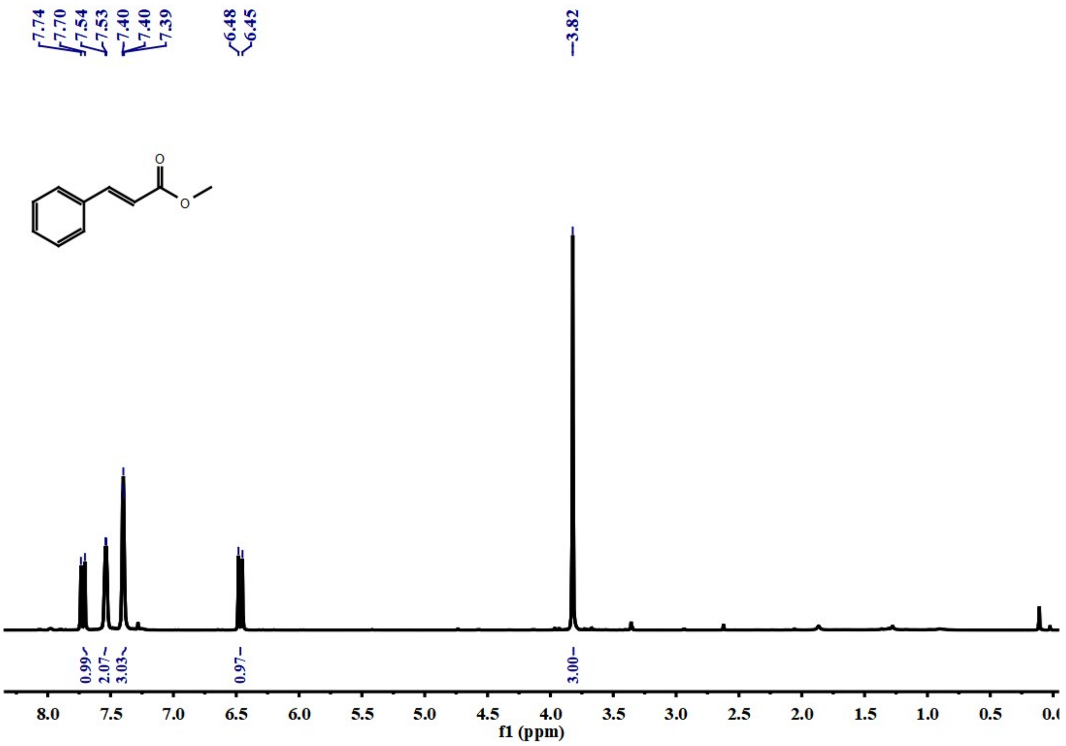
^{13}C NMR spectra of 2r (125 MHz, $CDCl_3$)



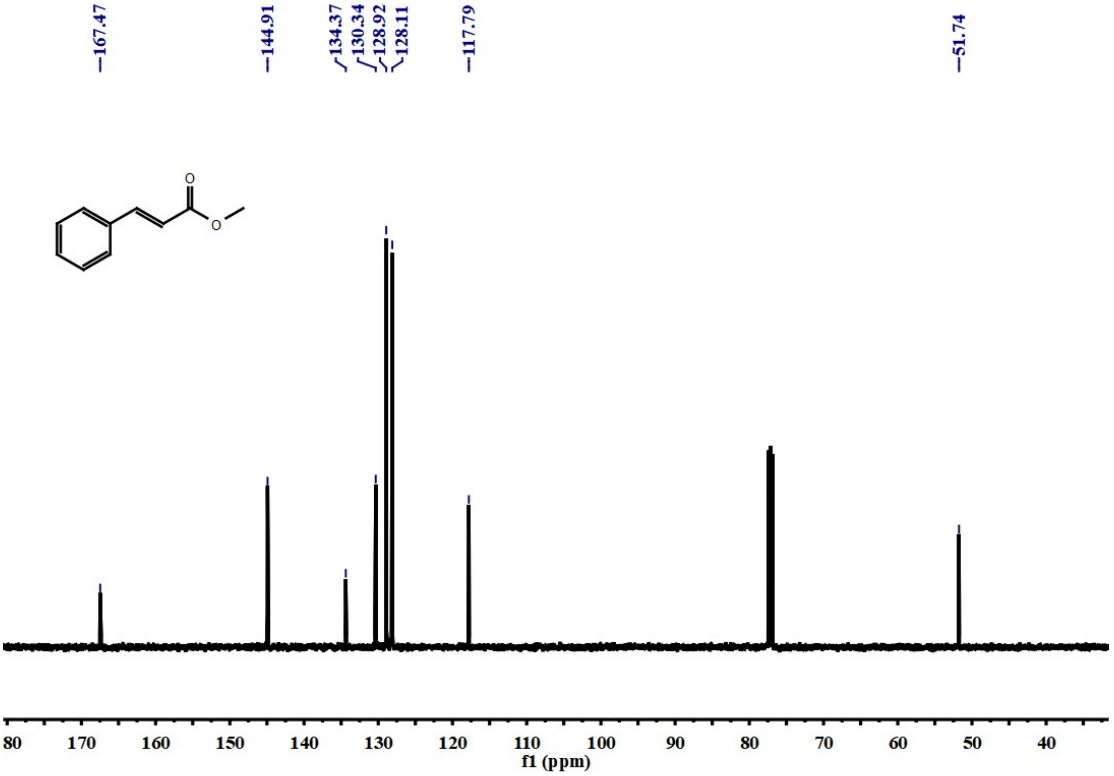
^{1}H NMR spectra of 2s (500 MHz, $CDCl_3$)



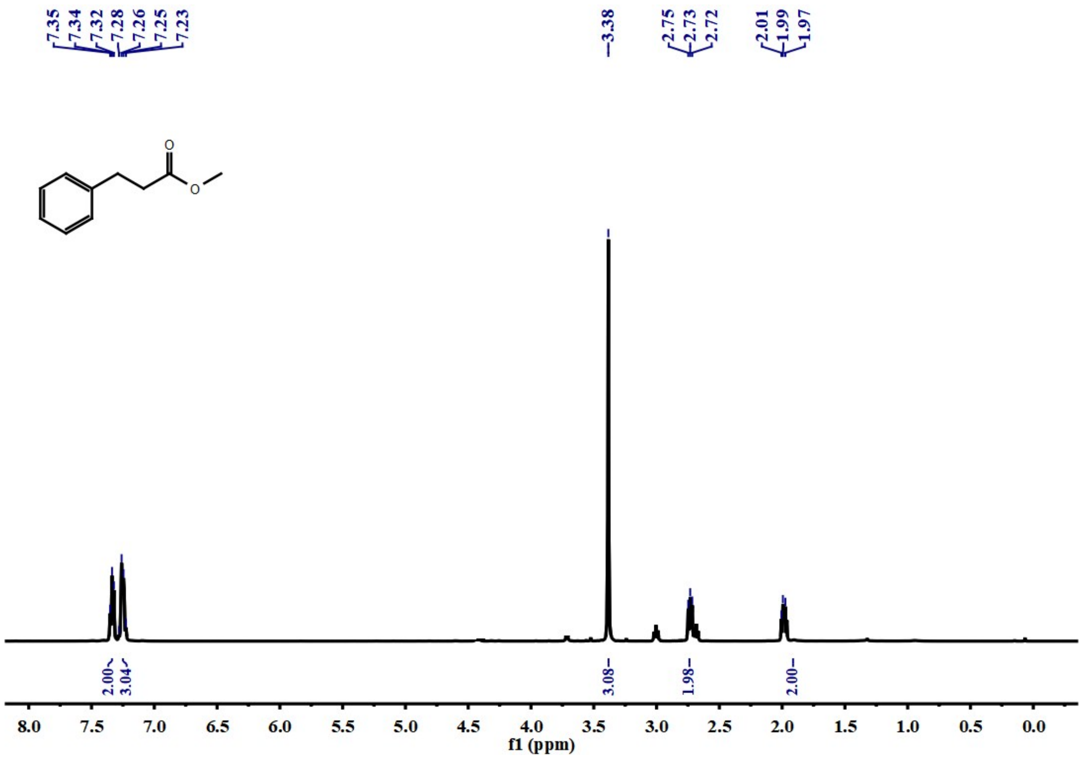
^{13}C NMR spectra of 2s (125 MHz, $CDCl_3$)



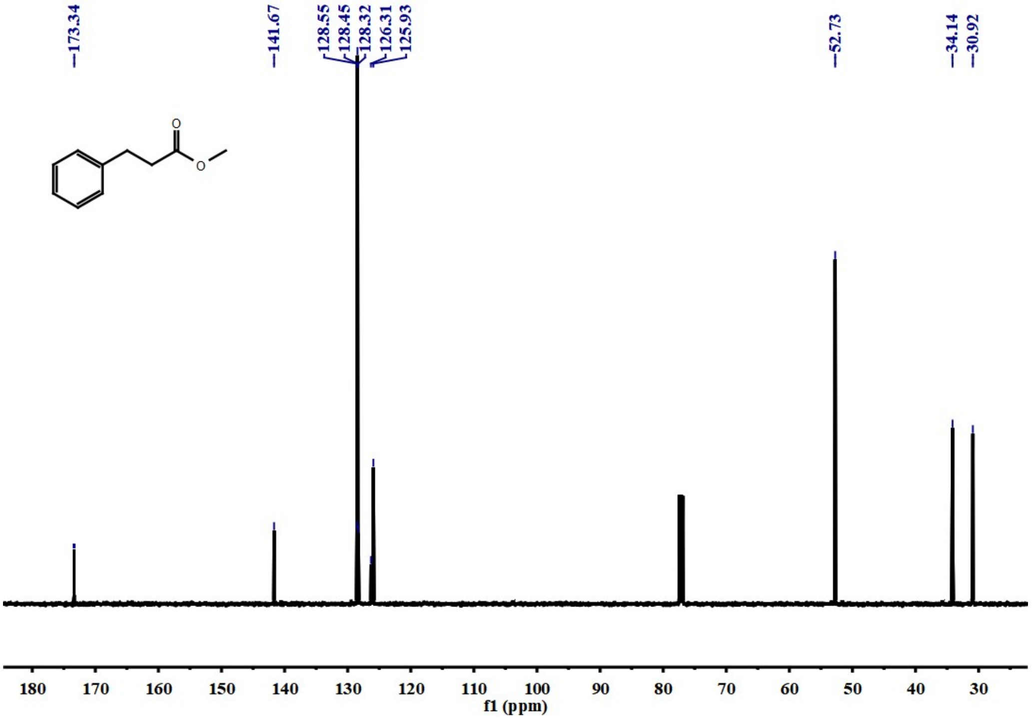
^{1}H NMR spectra of 2t (500 MHz, $CDCl_3$)



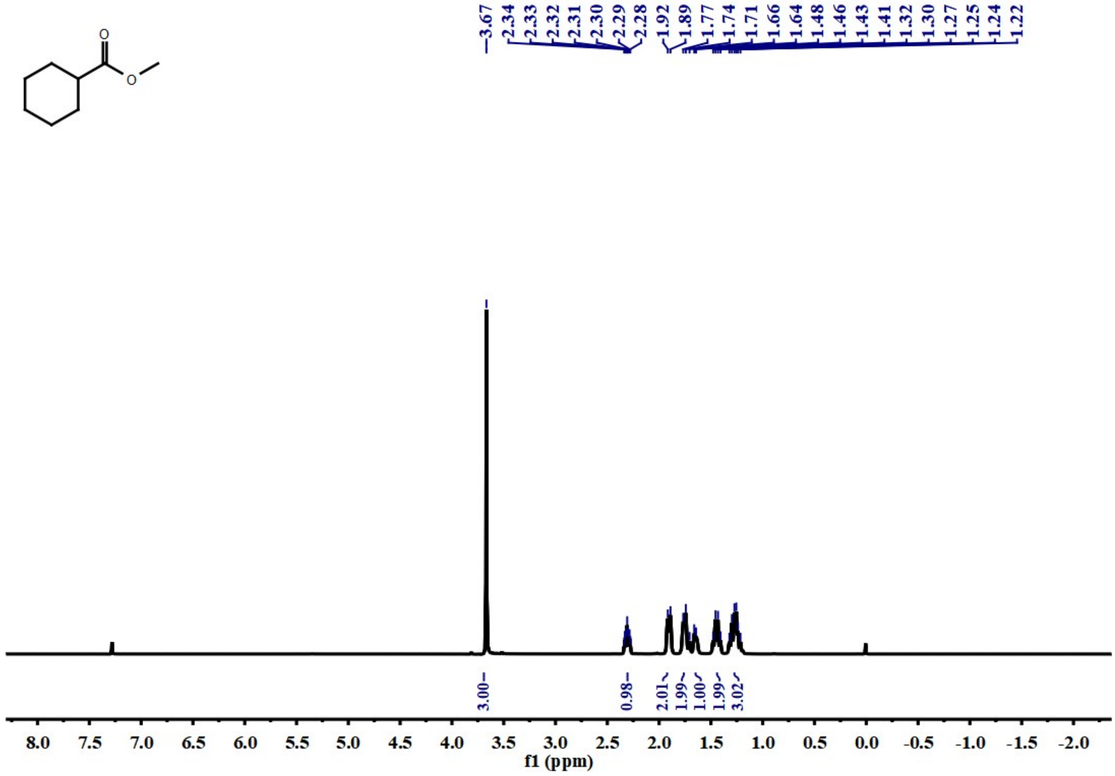
^{13}C NMR spectra of 2t (125 MHz, $CDCl_3$)



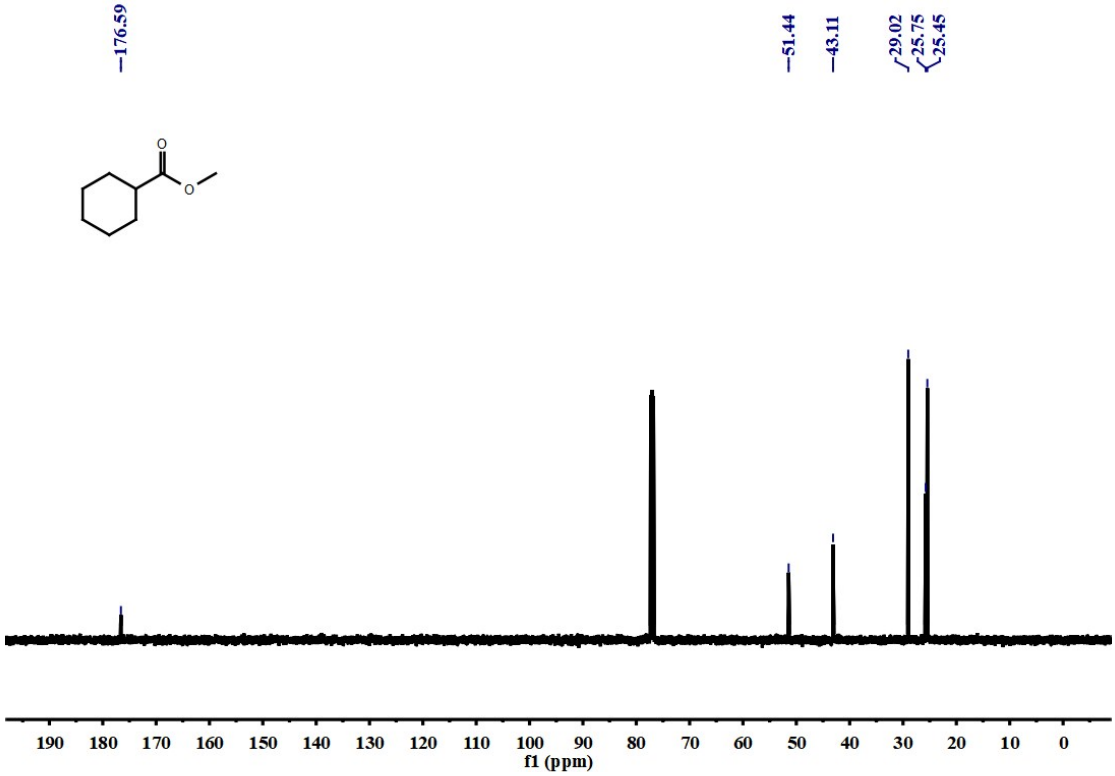
^{1}H NMR spectra of 2u (500 MHz, CDCl$_3$)



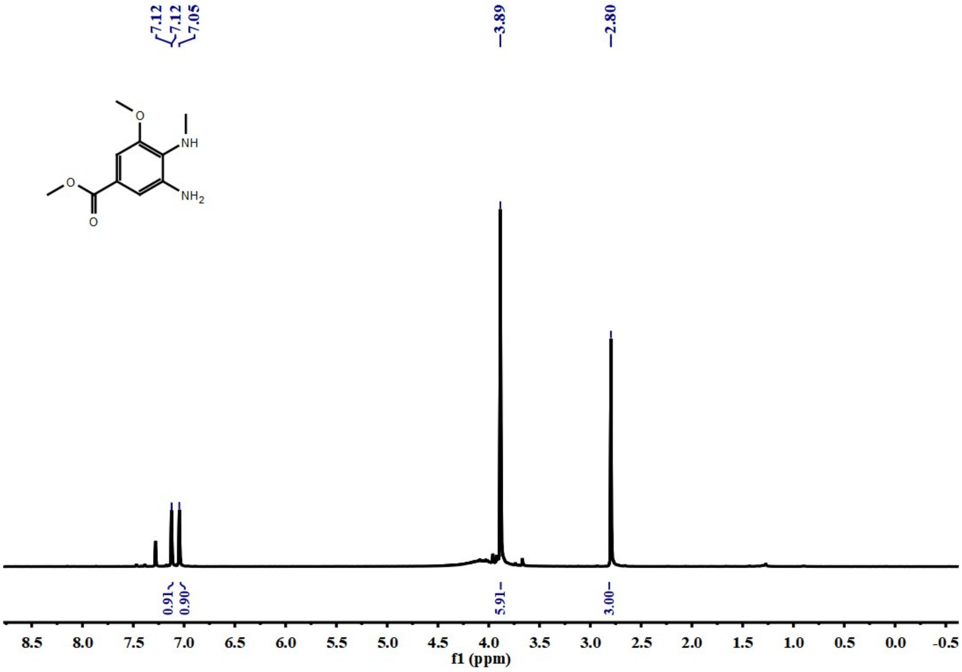
^{13}C NMR spectra of 2u (125 MHz, CDCl$_3$)



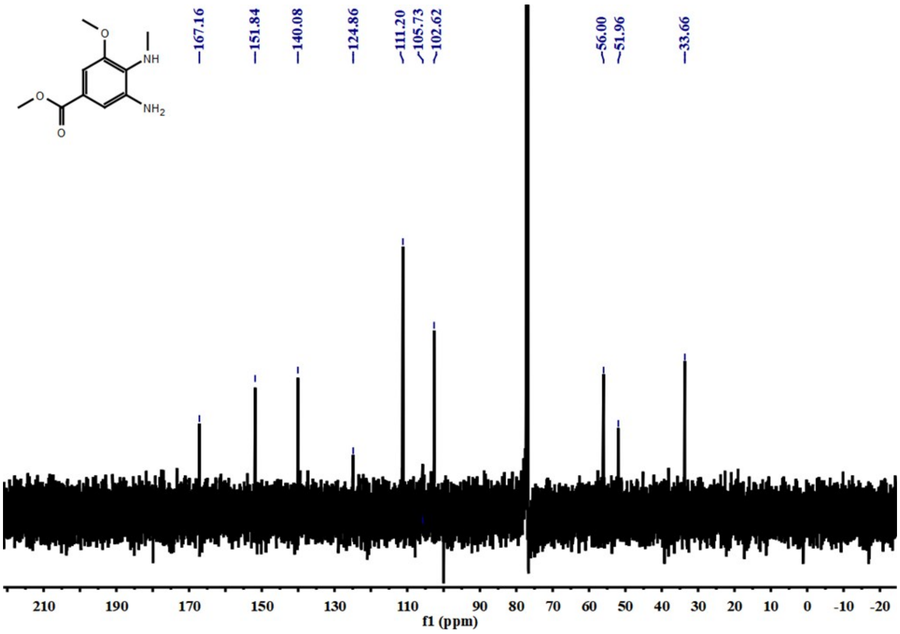
^{1}H NMR spectra of 2w (500 MHz, $CDCl_3$)



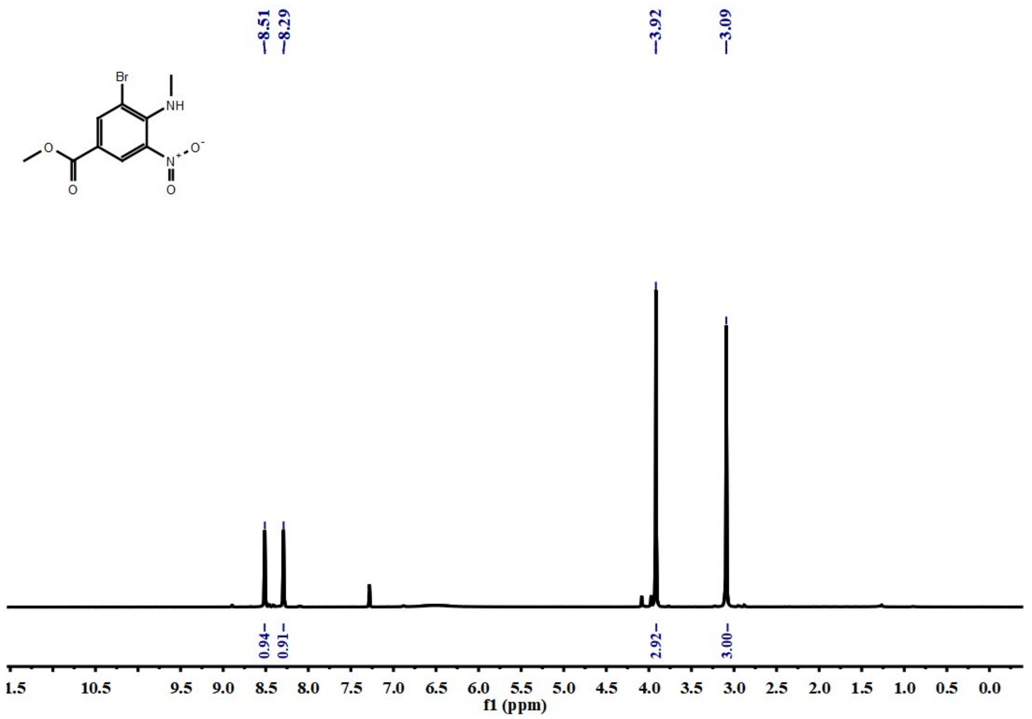
^{13}C NMR spectra of 2w (125 MHz, $CDCl_3$)



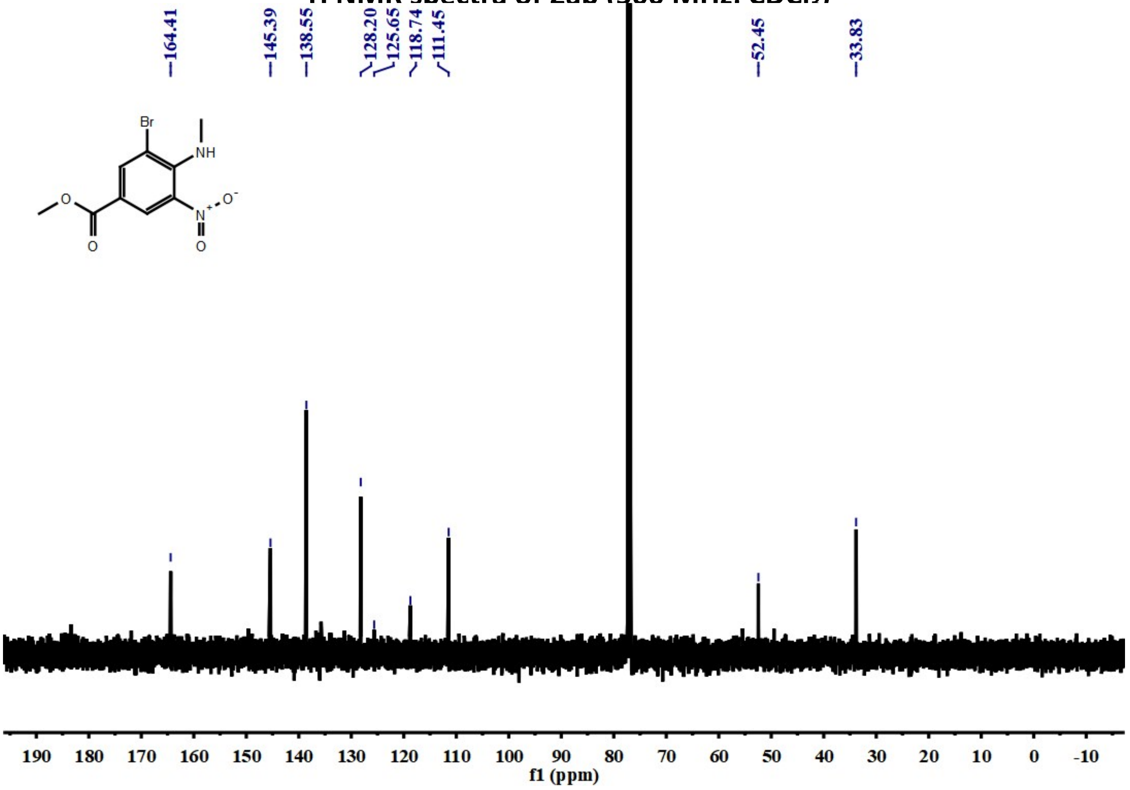
^{1}H NMR spectra of 2aa (500 MHz, $CDCl_3$)



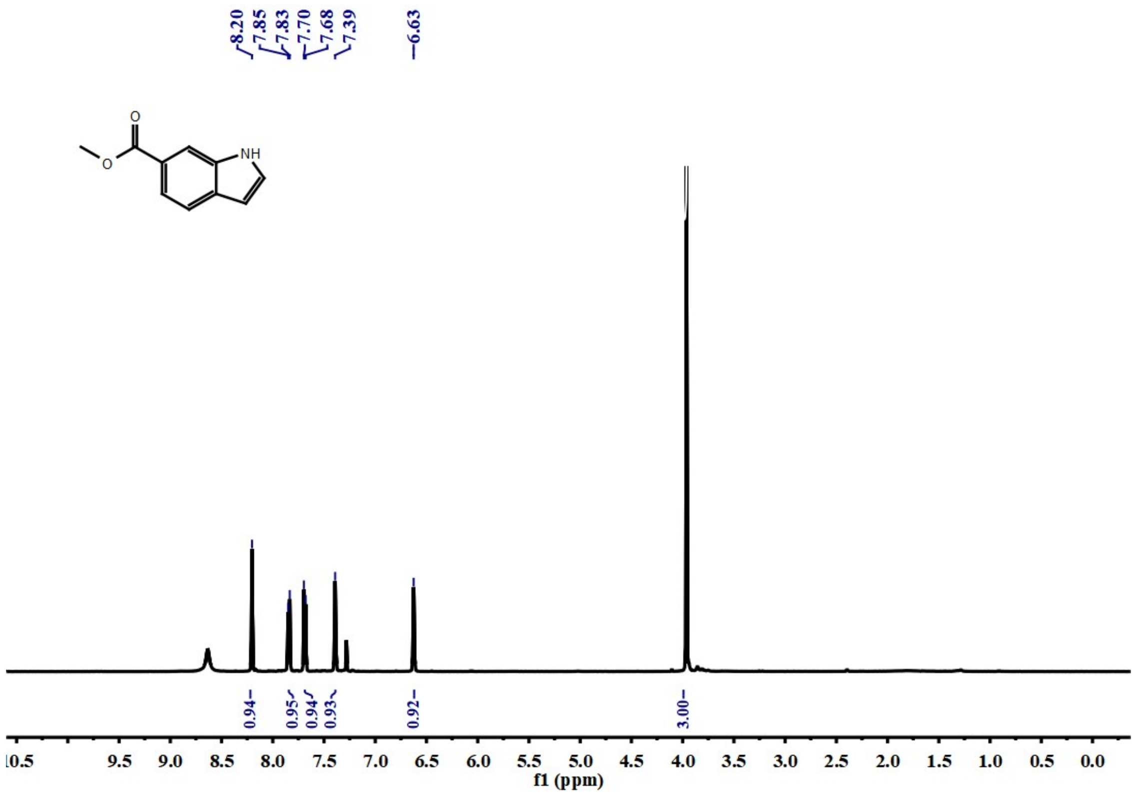
^{13}C NMR spectra of 2aa (125 MHz, $CDCl_3$)



^{1}H NMR spectra of 2ab (500 MHz, CDCl$_3$)



^{13}C NMR spectra of 2ab (125 MHz, CDCl$_3$)



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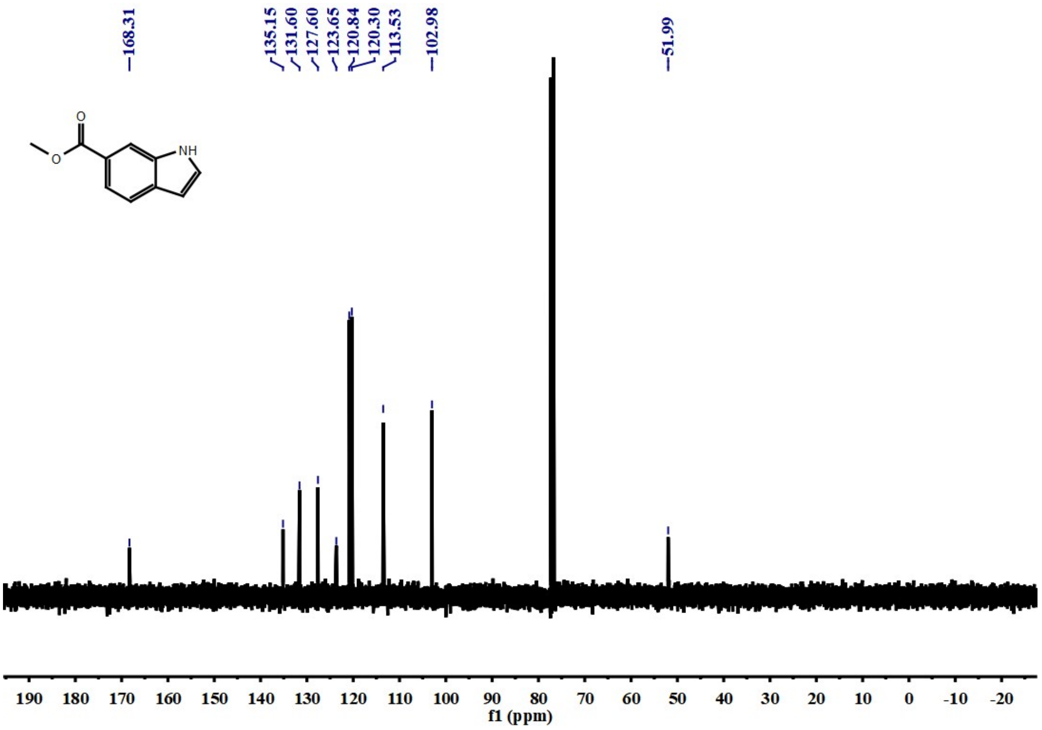

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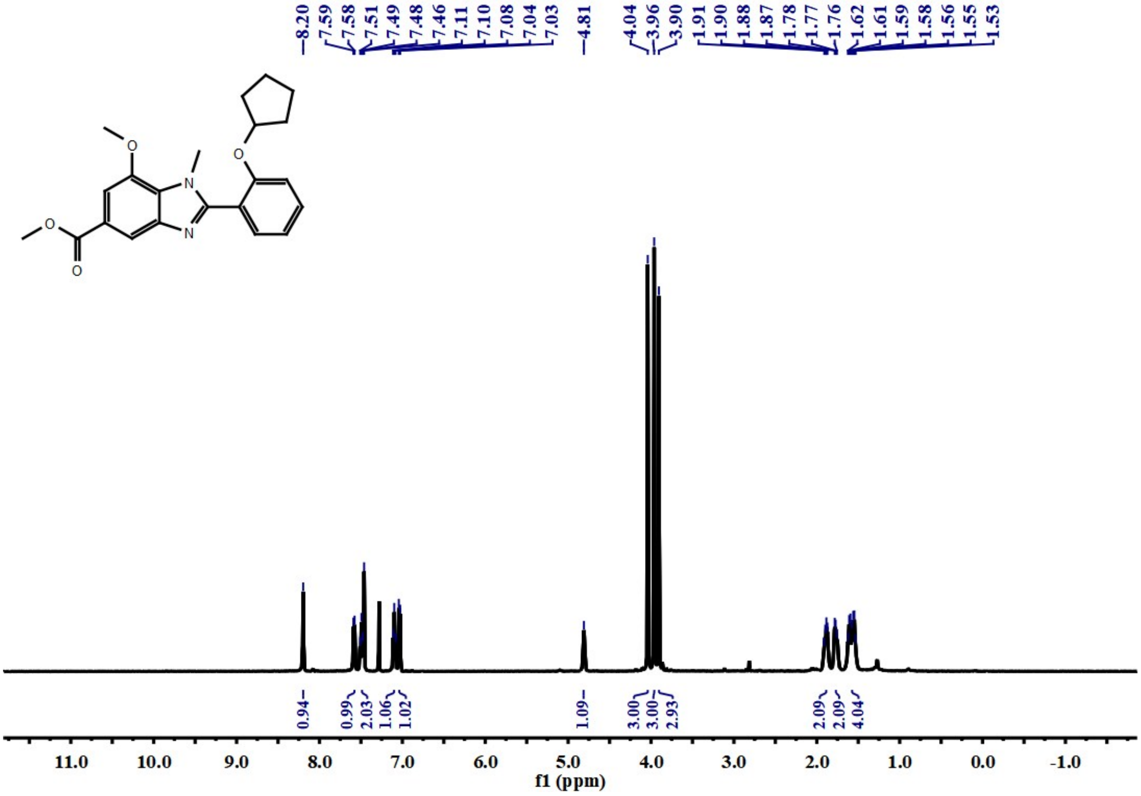
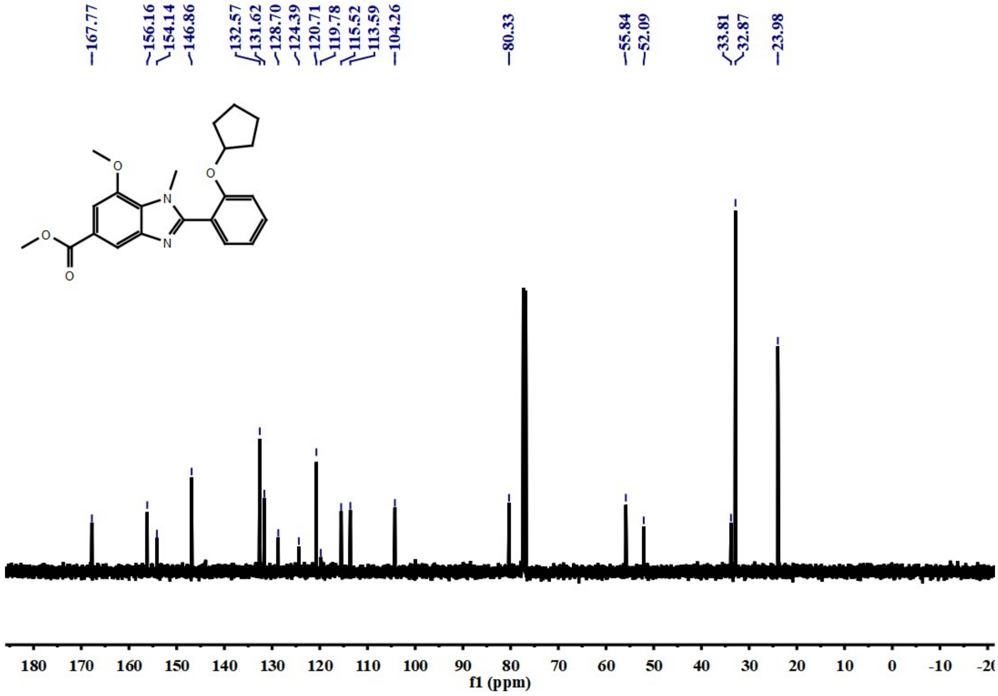
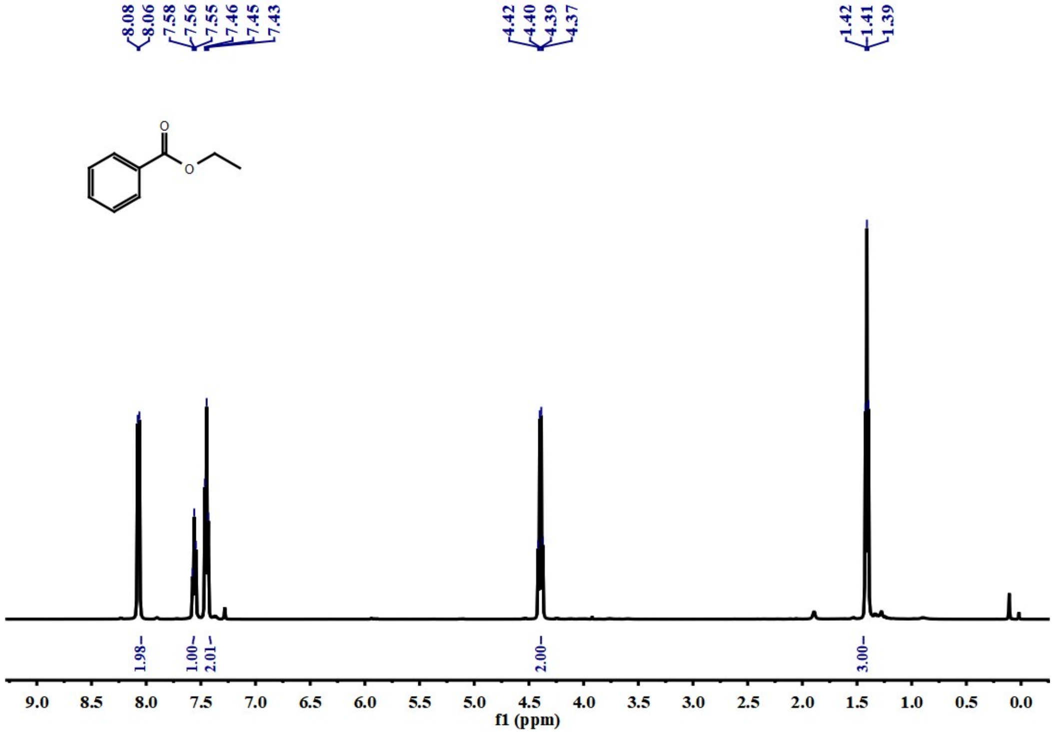


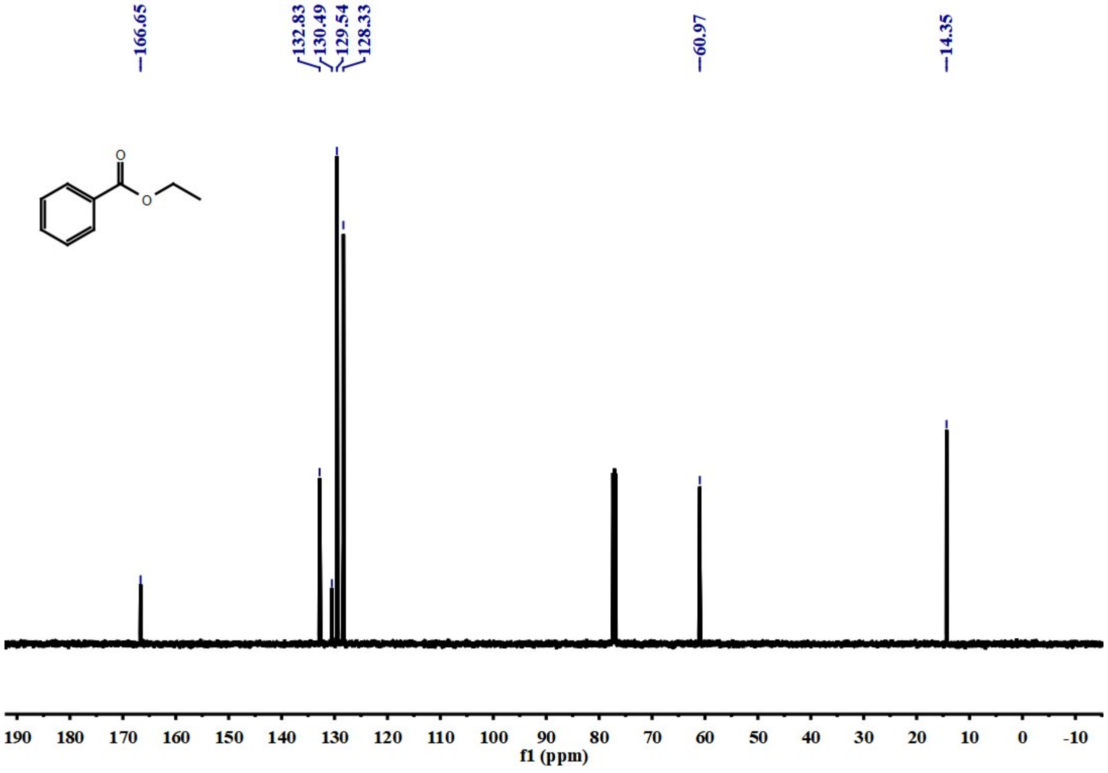
^{1}H NMR spectra of 2ad (500 MHz, CDCl$_3$)



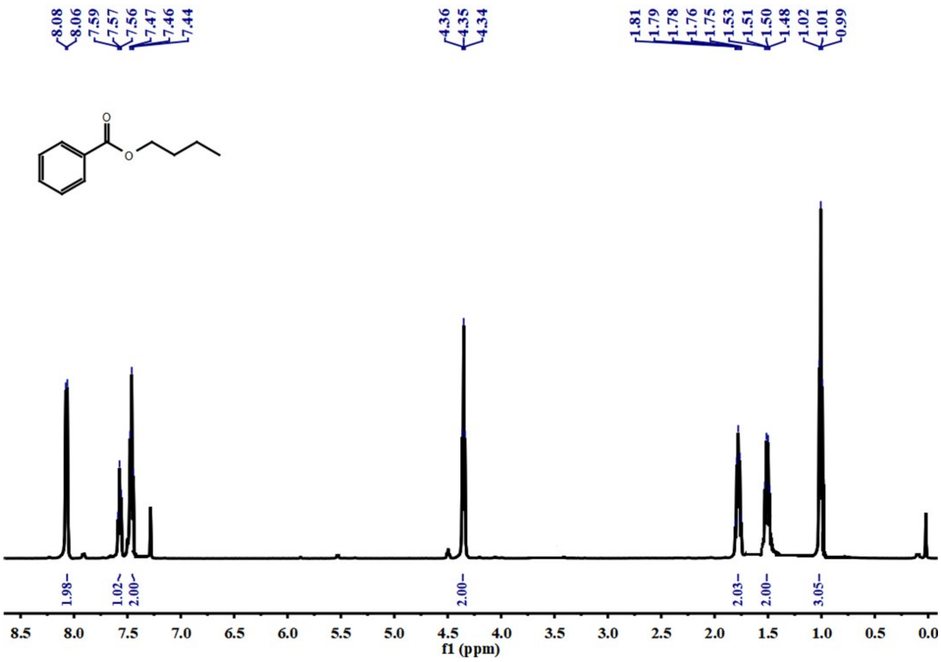
^{13}C NMR spectra of 2ad (125 MHz, CDCl$_3$)



^{1}H NMR spectra of 4a (500 MHz, CDCl$_3$)



^{13}C NMR spectra of 4a (125 MHz, CDCl$_3$)



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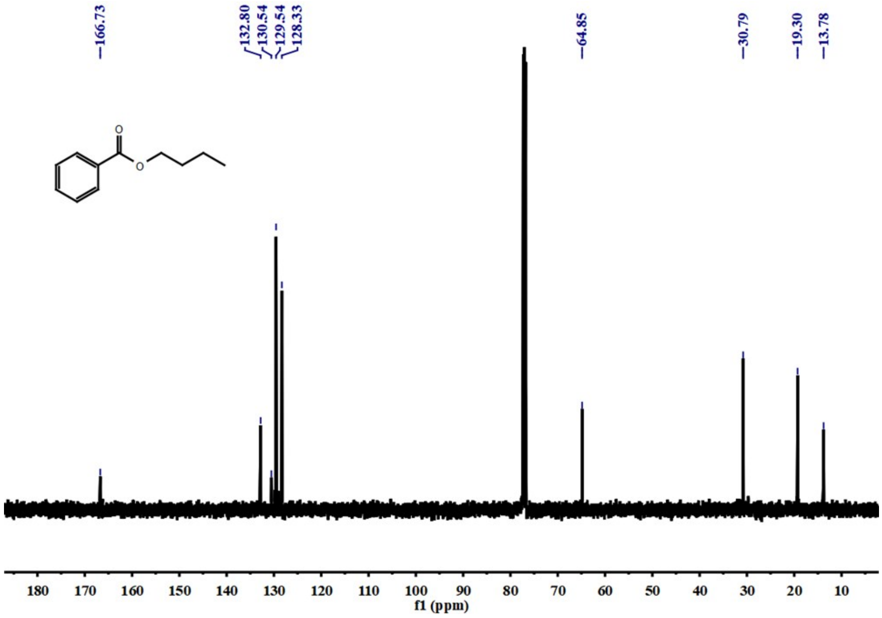

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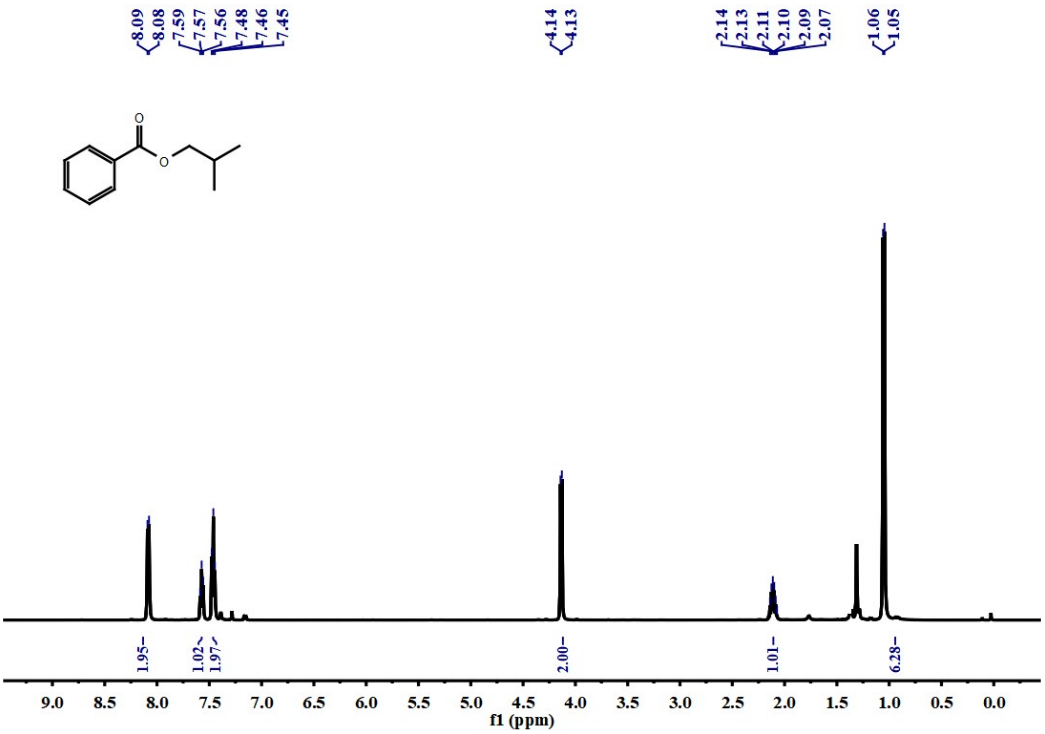

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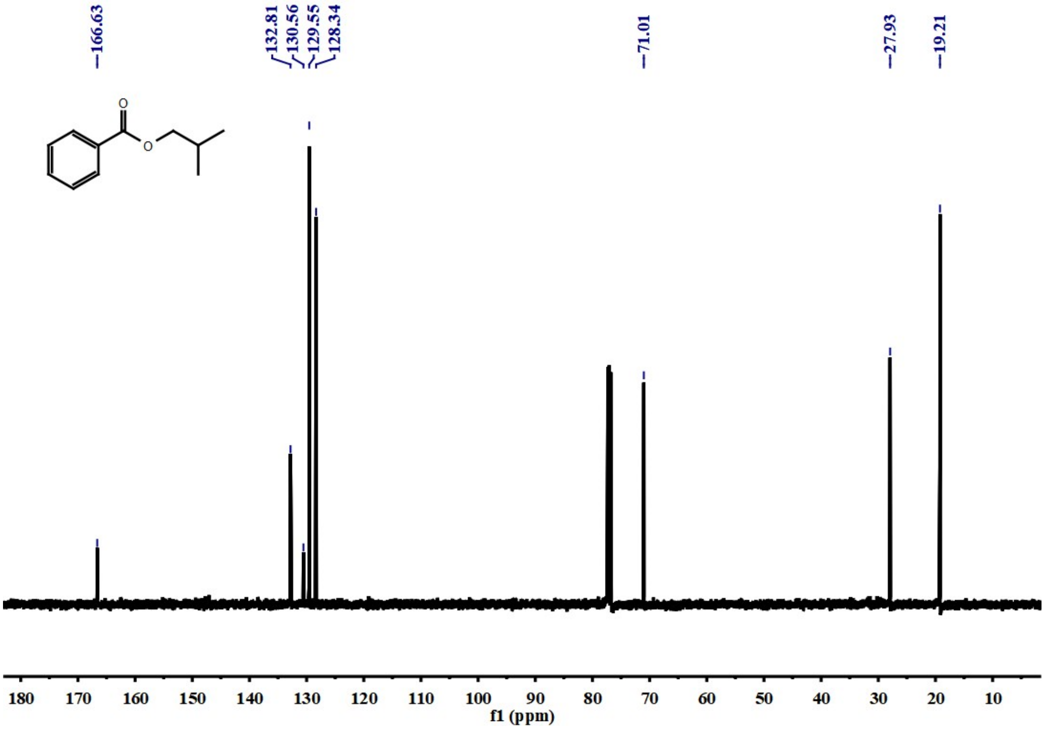

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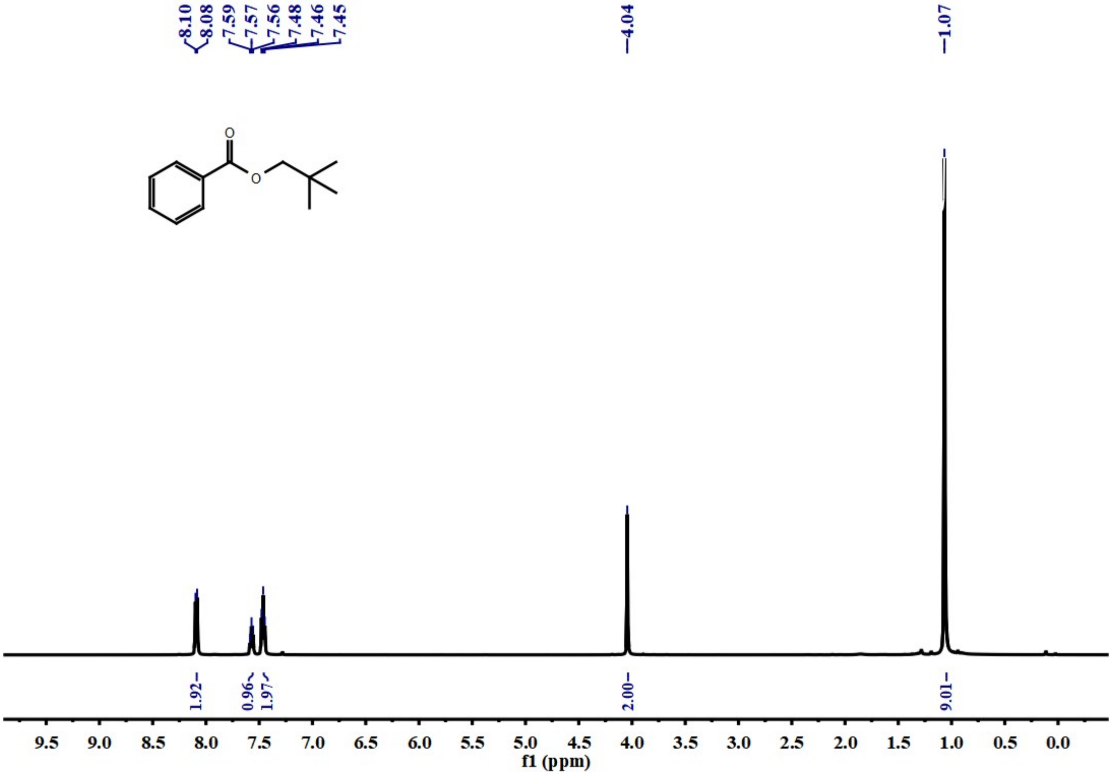

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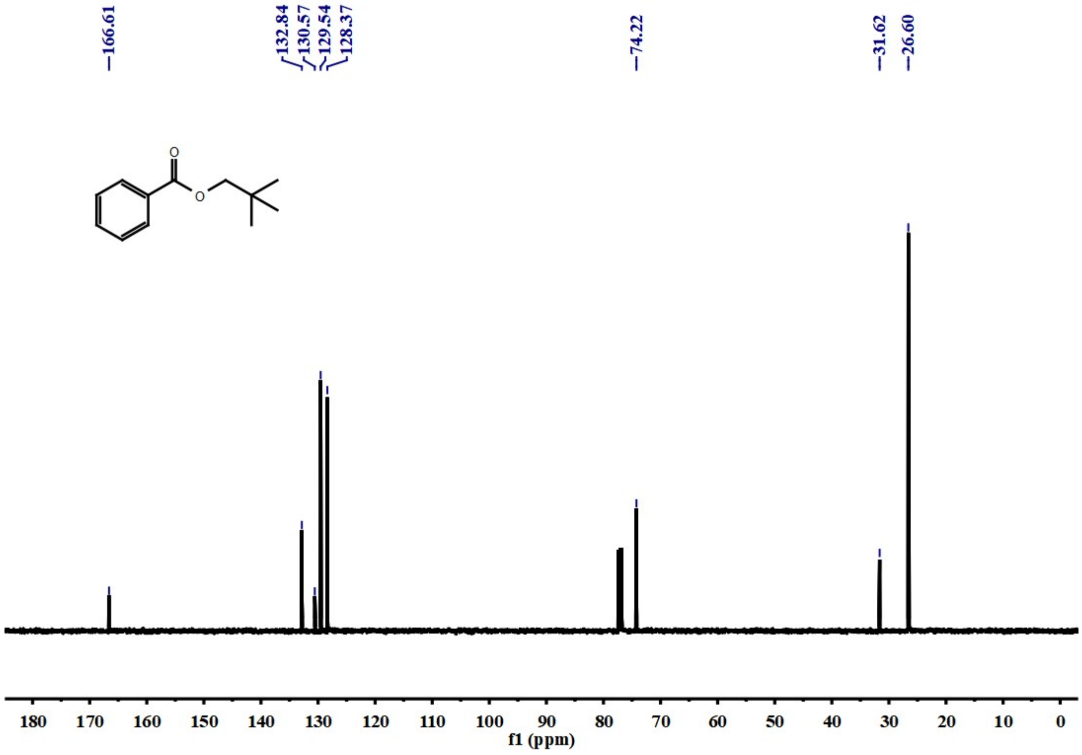

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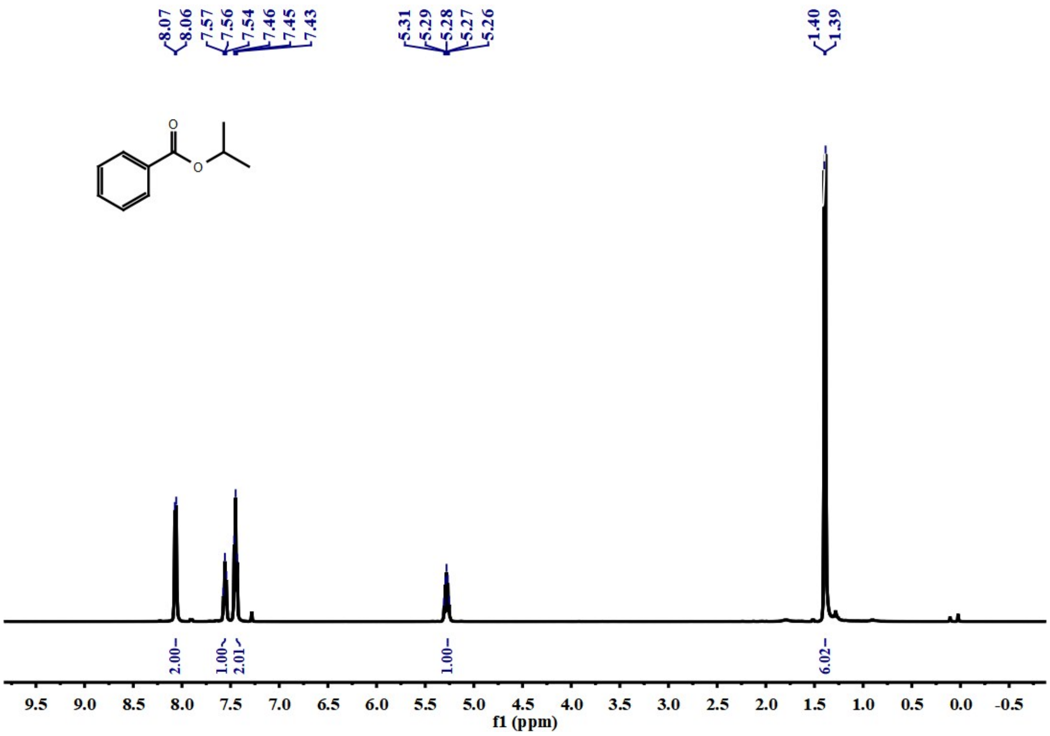

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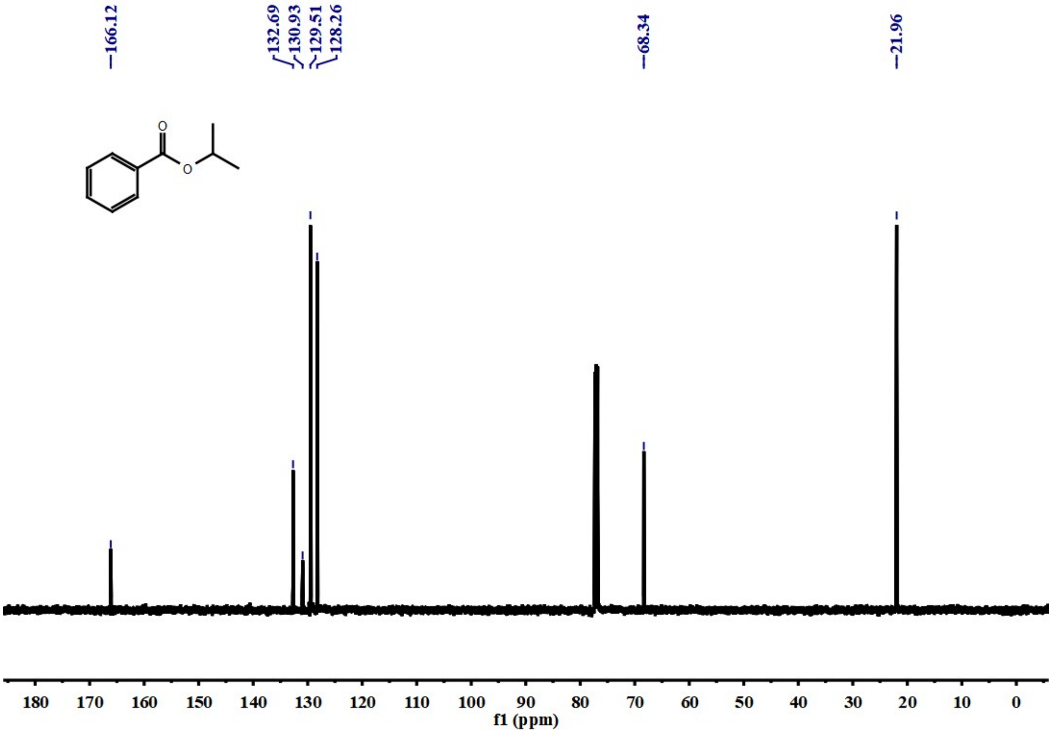

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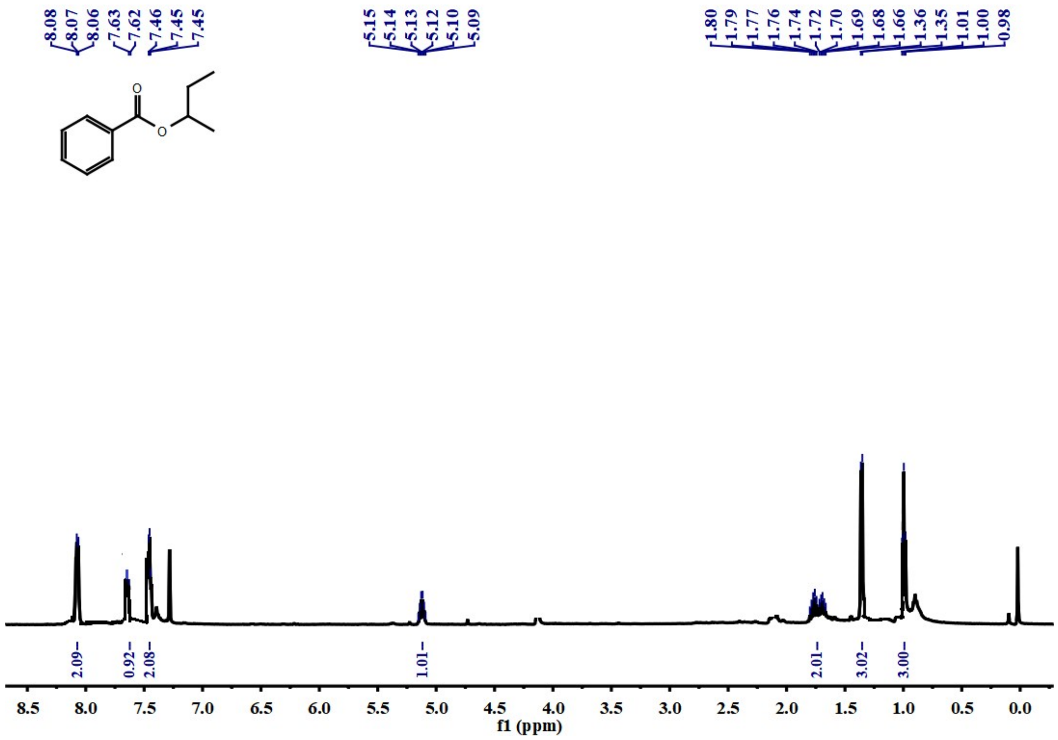

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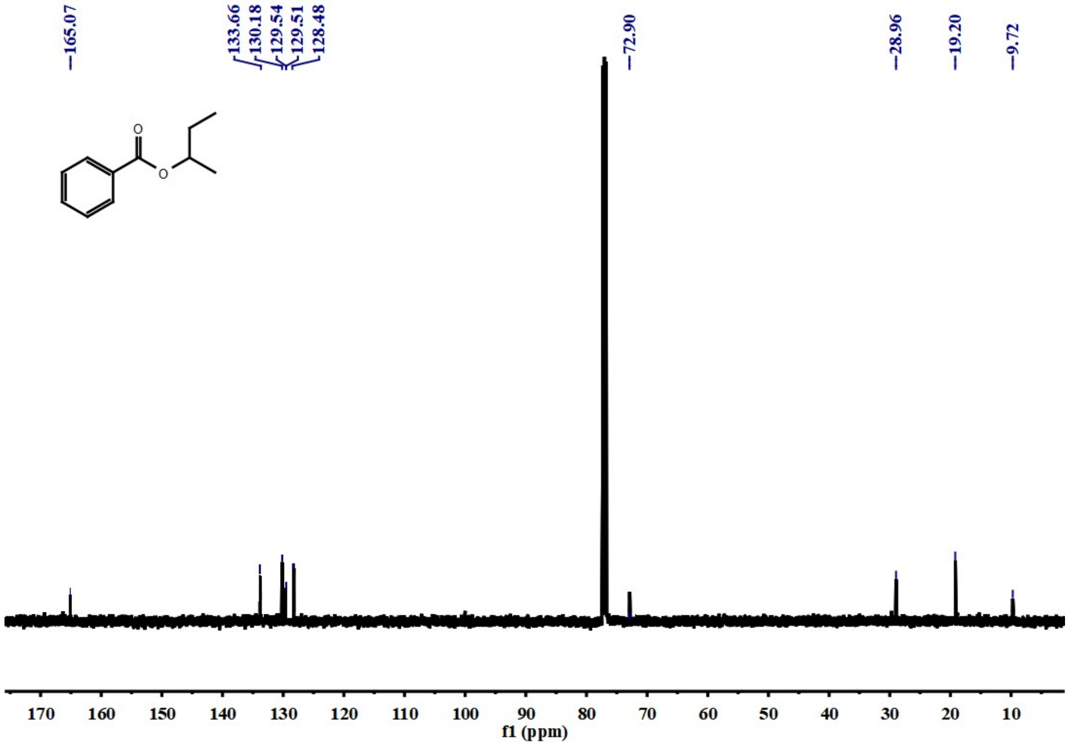

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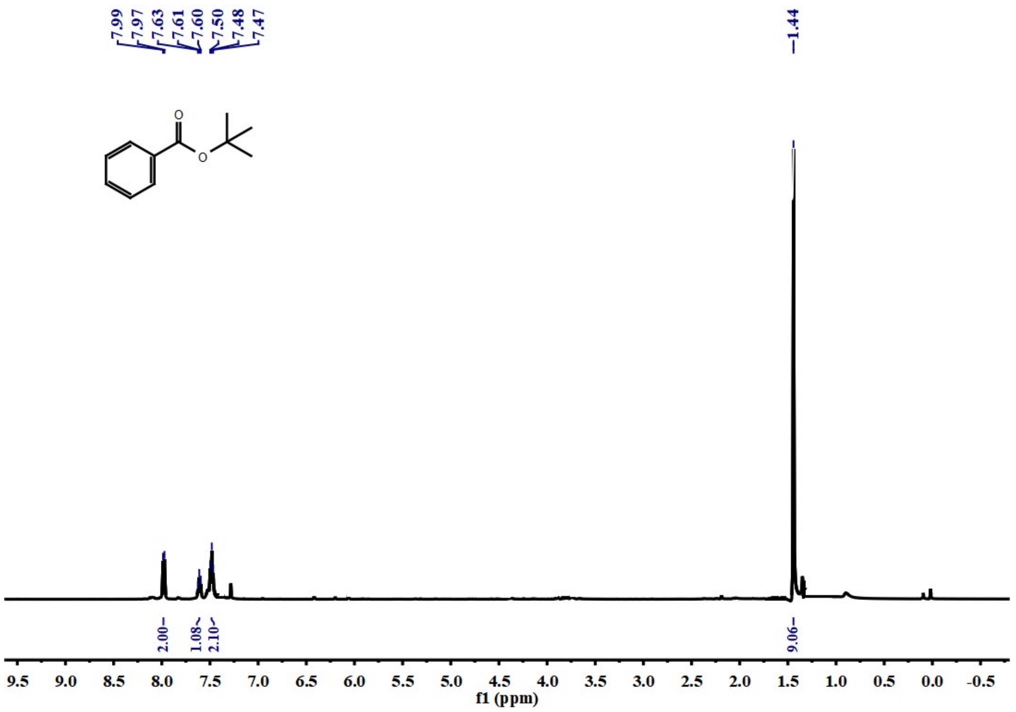
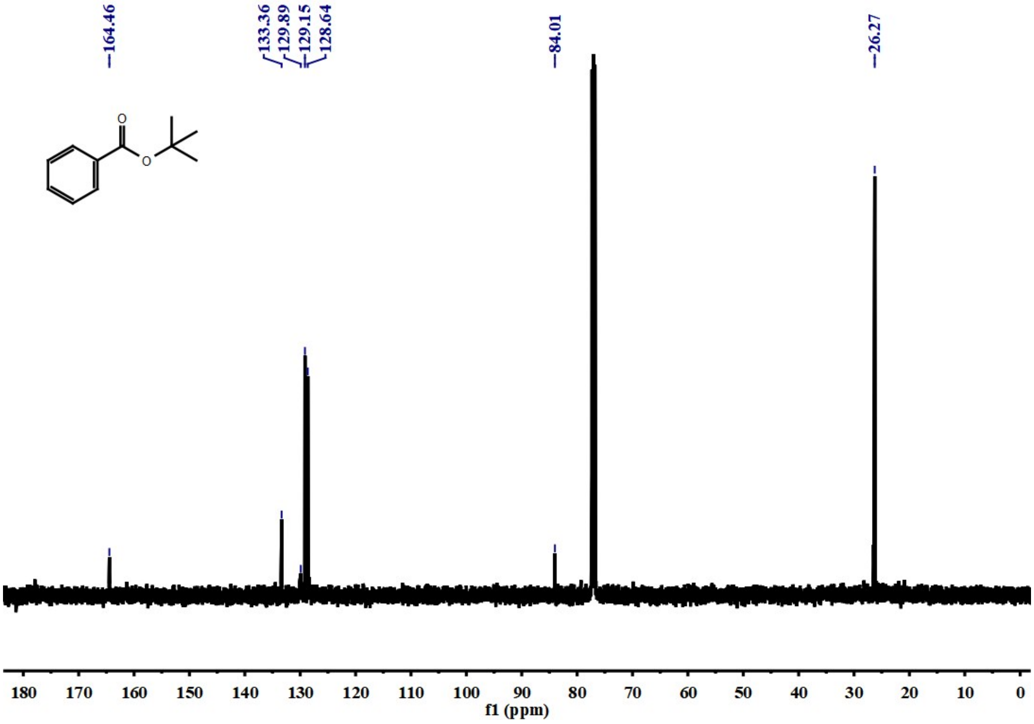


^{1}H NMR spectra of 4g (500 MHz, CDCl$_3$)



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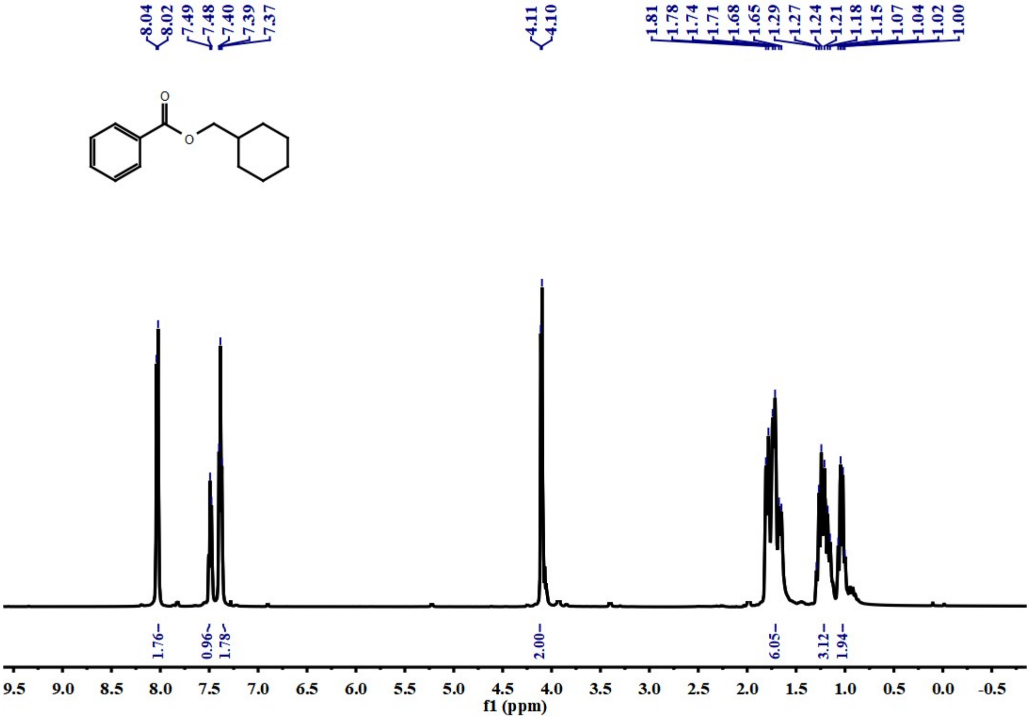

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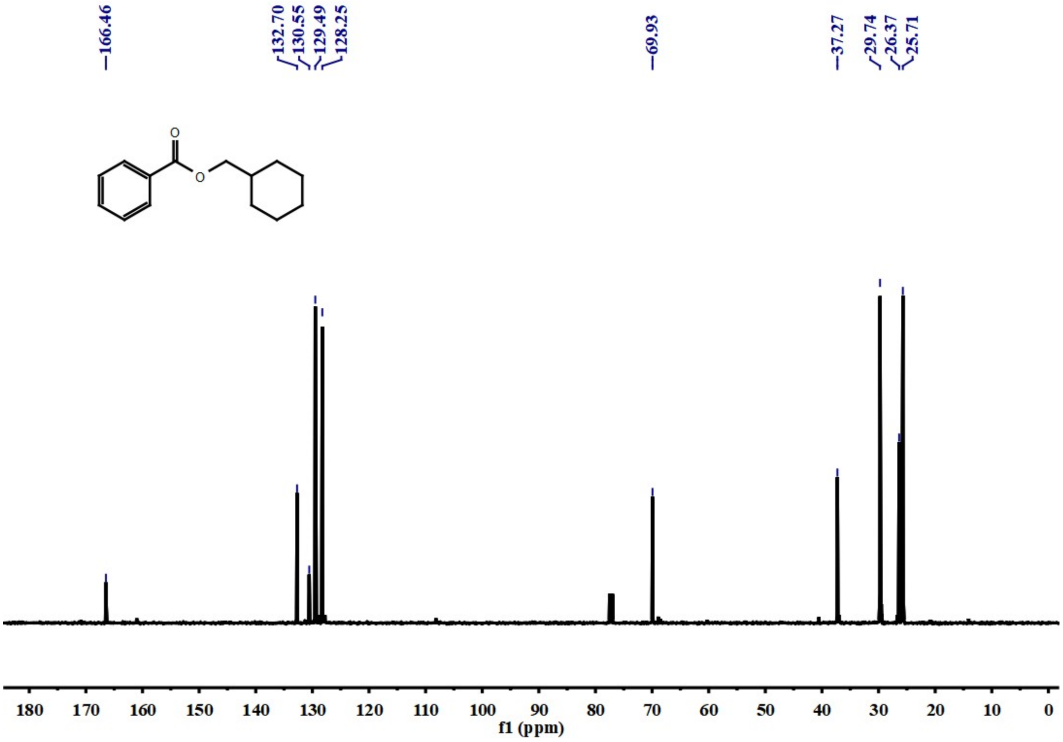

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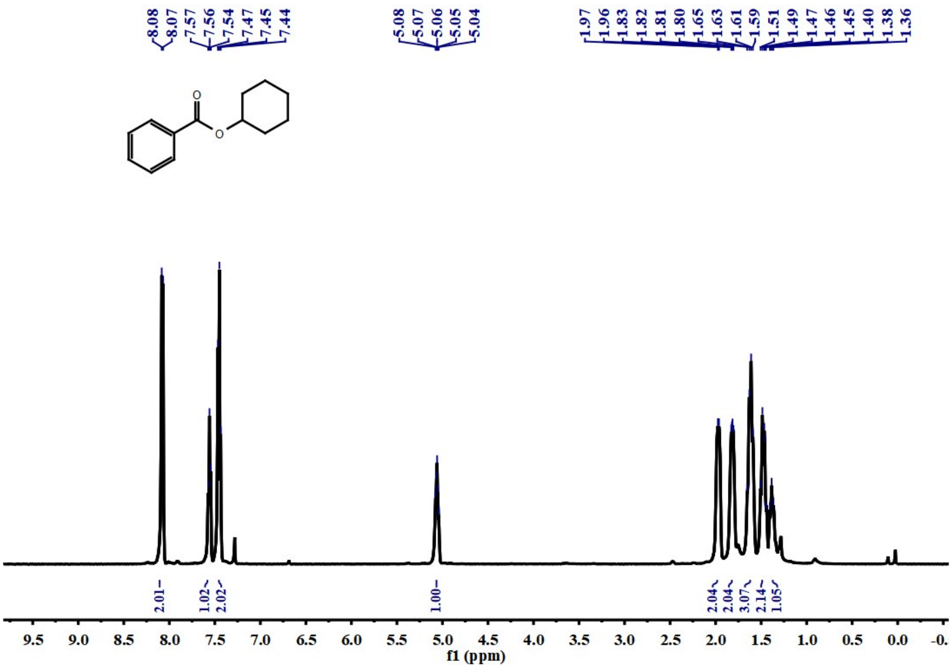

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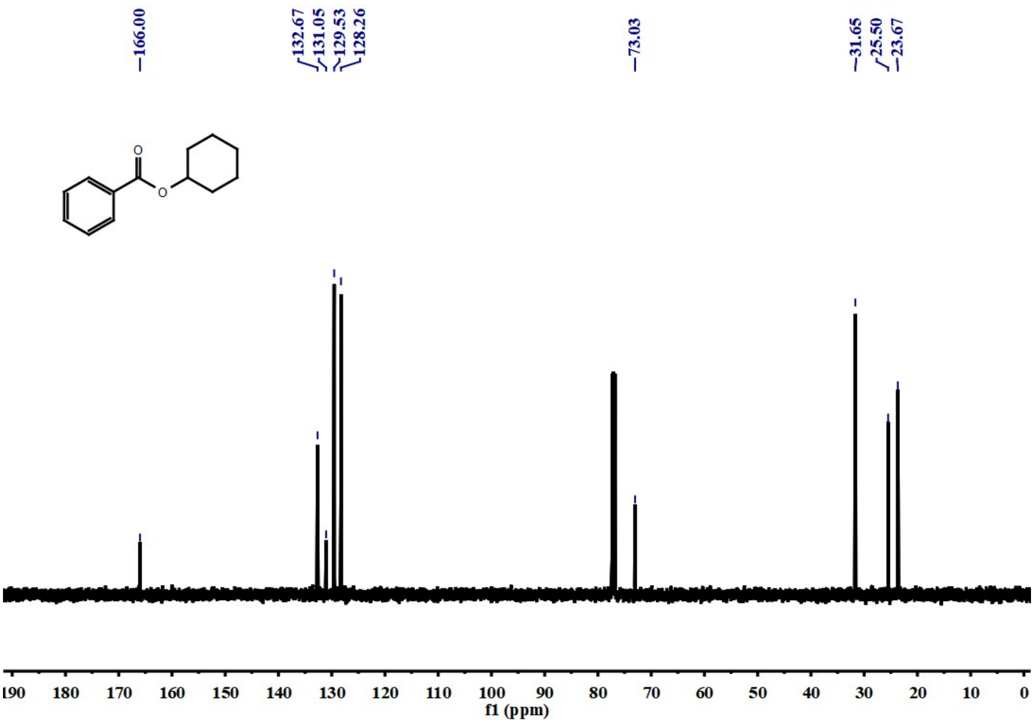

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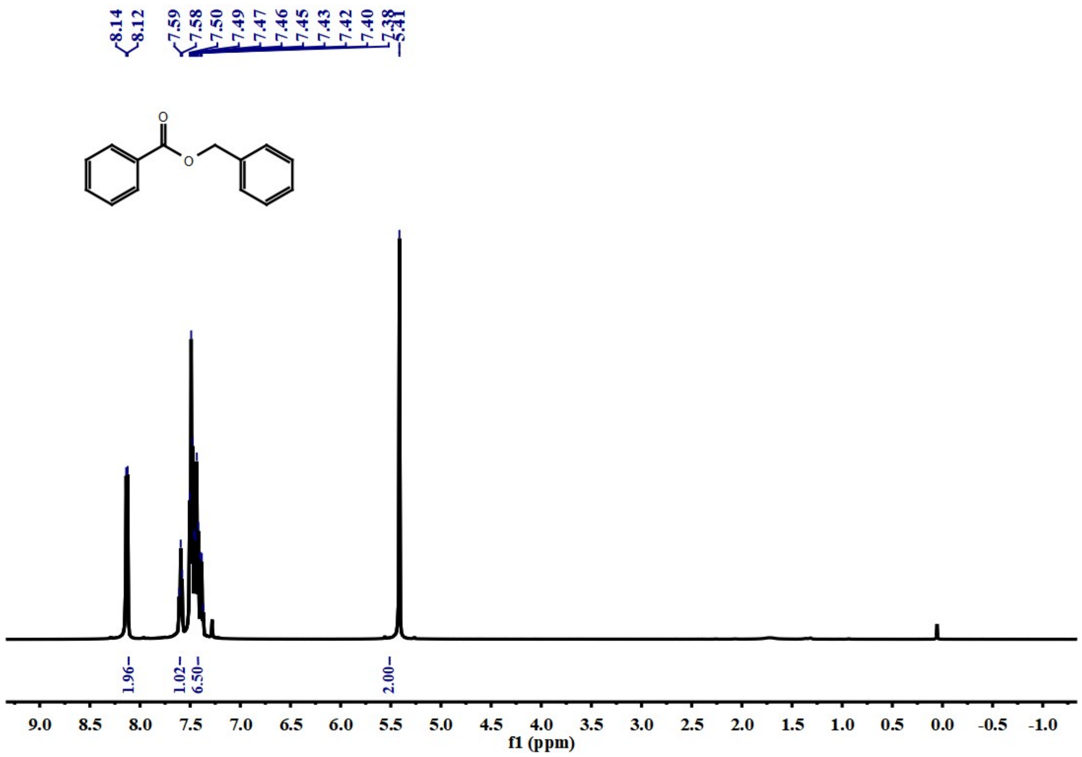

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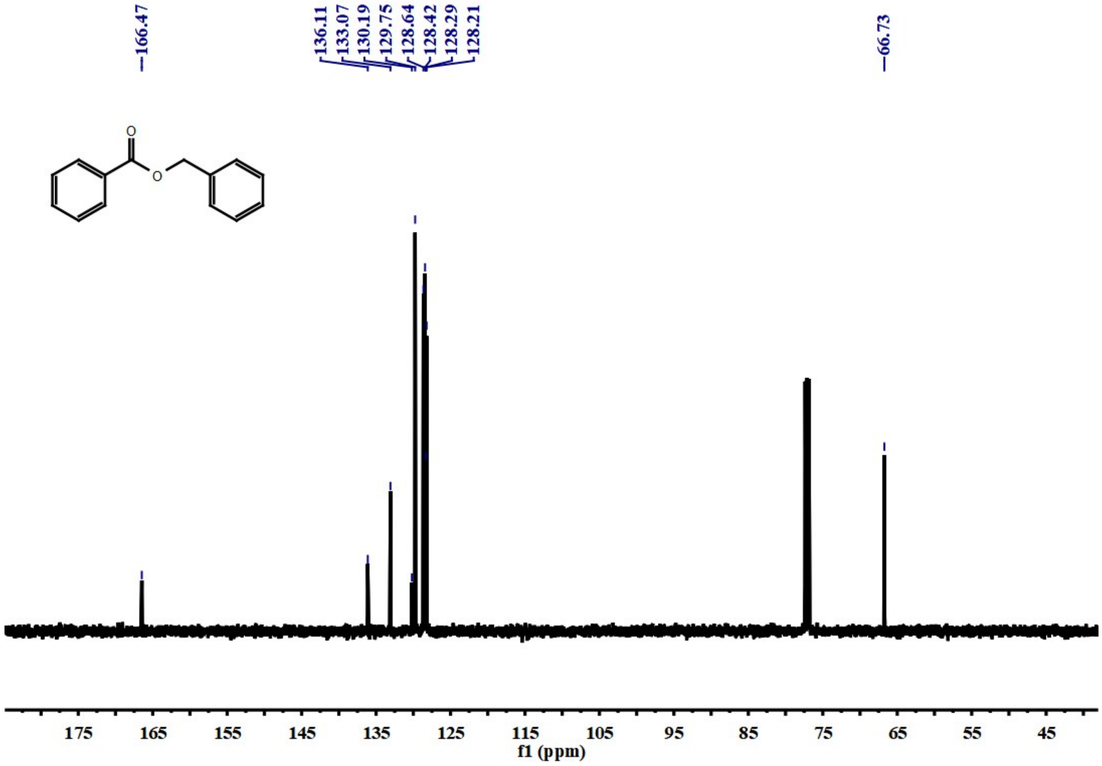

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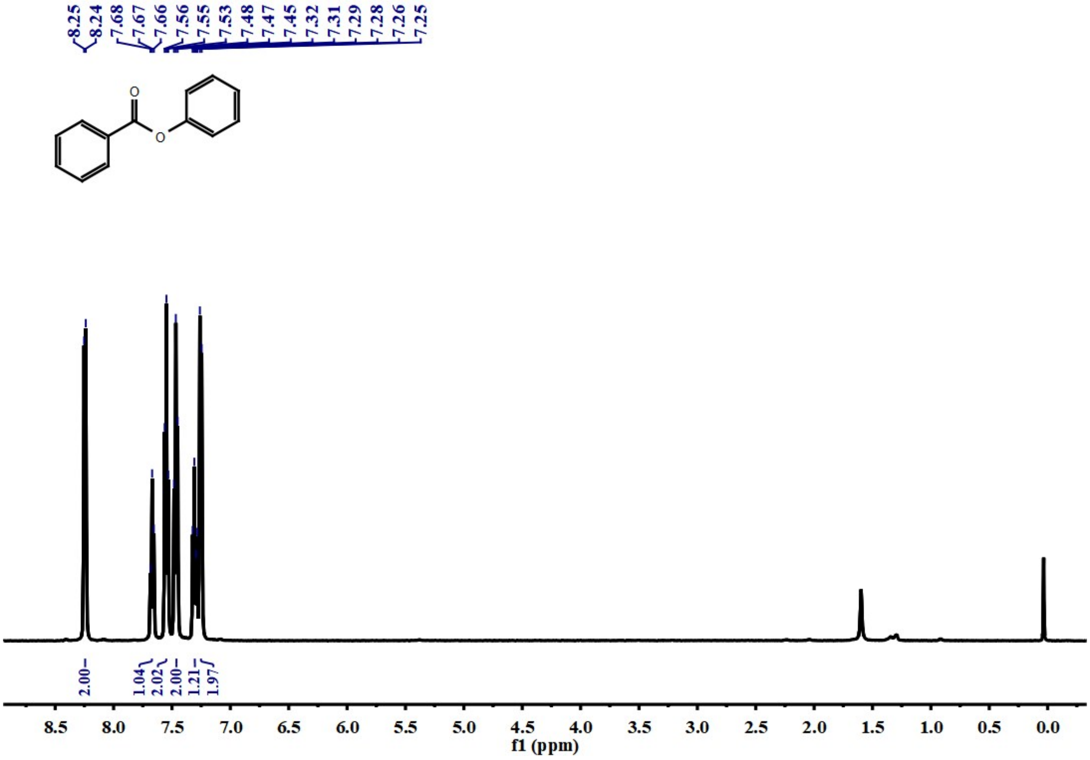

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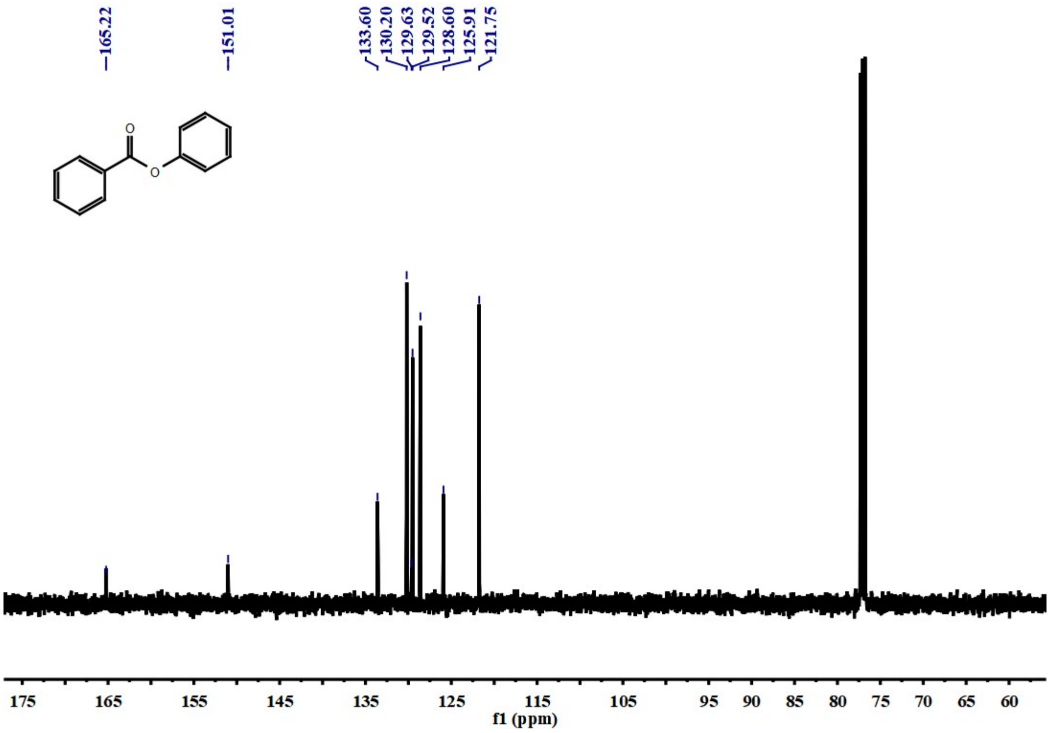
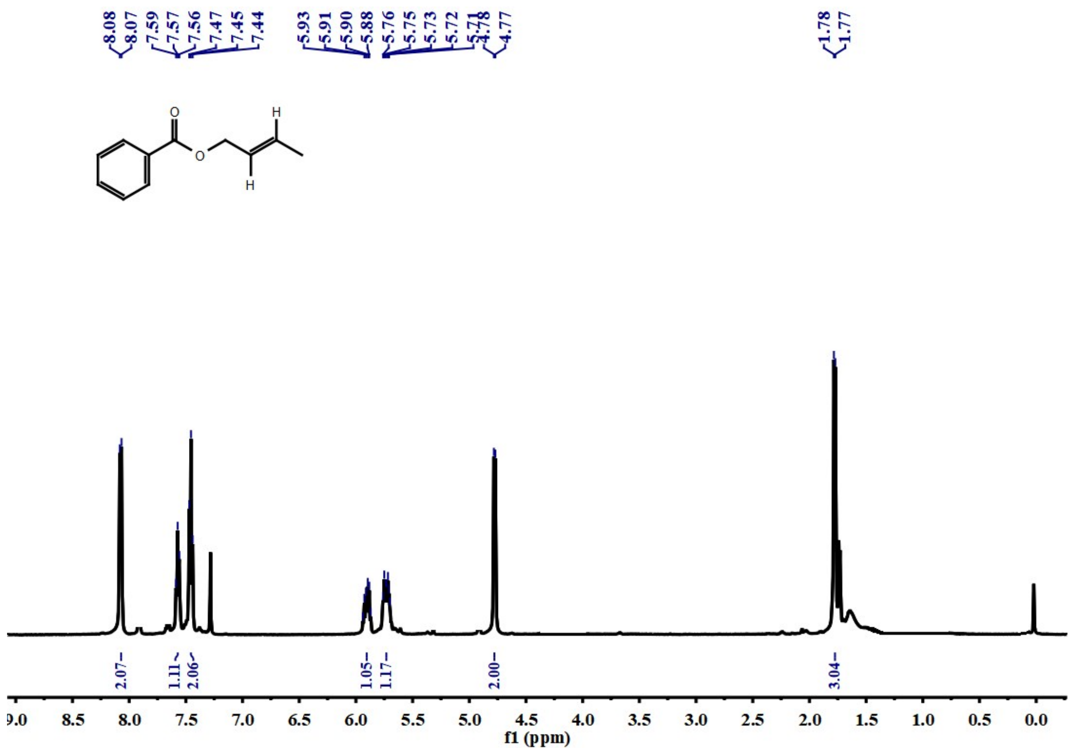
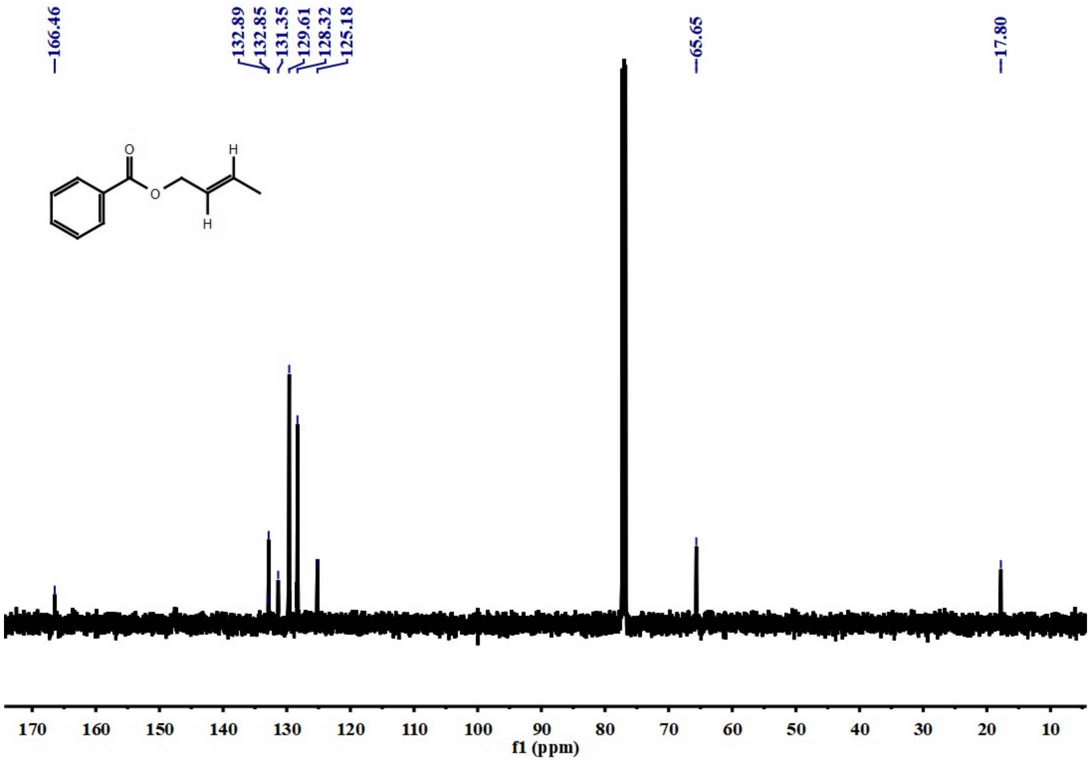


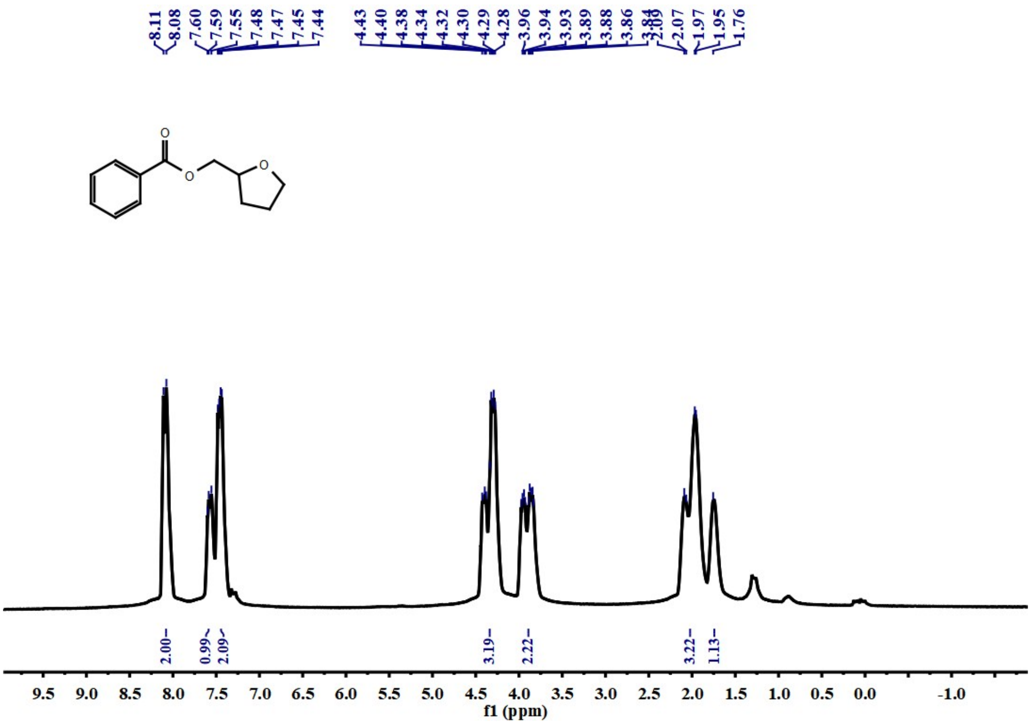
^{13}C NMR spectra of 4k (125 MHz, $CDCl_3$)



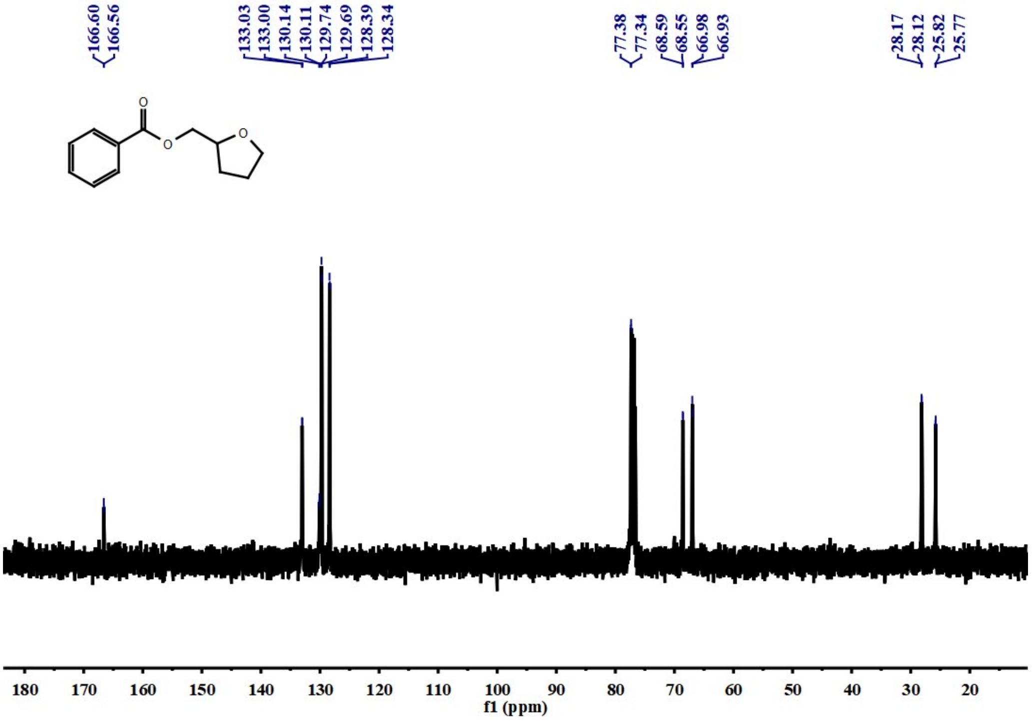
^{1}H NMR spectra of 4l (500 MHz, CDCl$_3$)



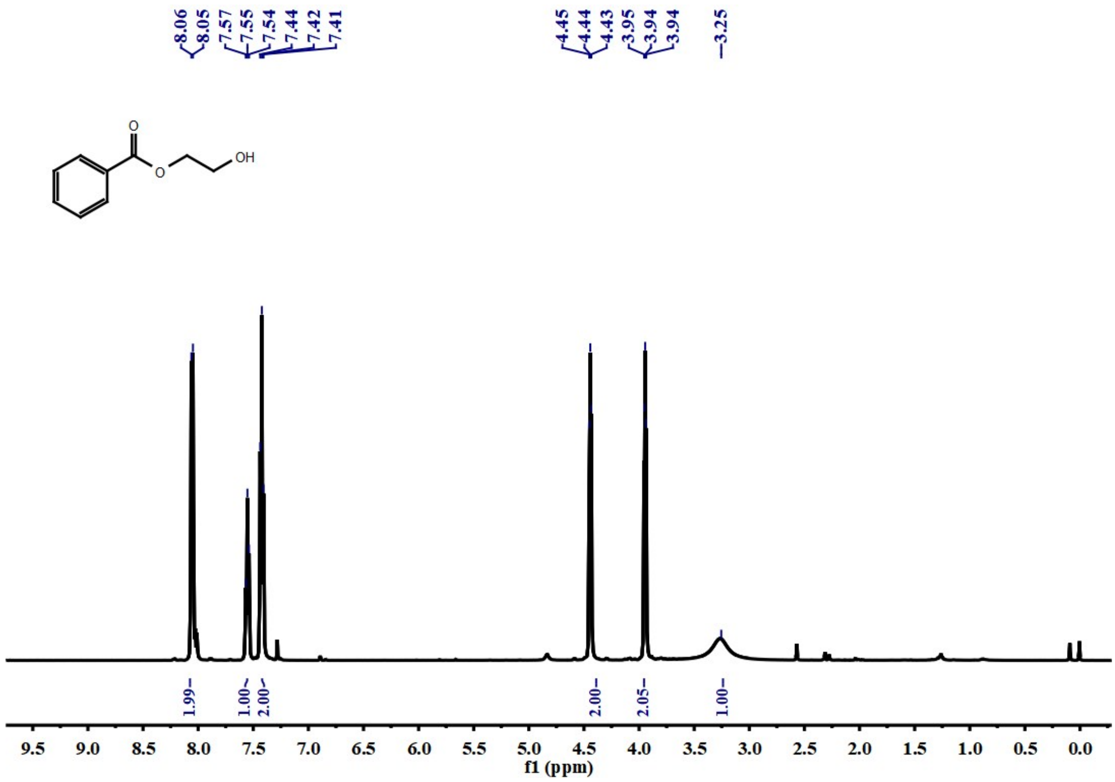
^{13}C NMR spectra of 4l (125 MHz, CDCl$_3$)



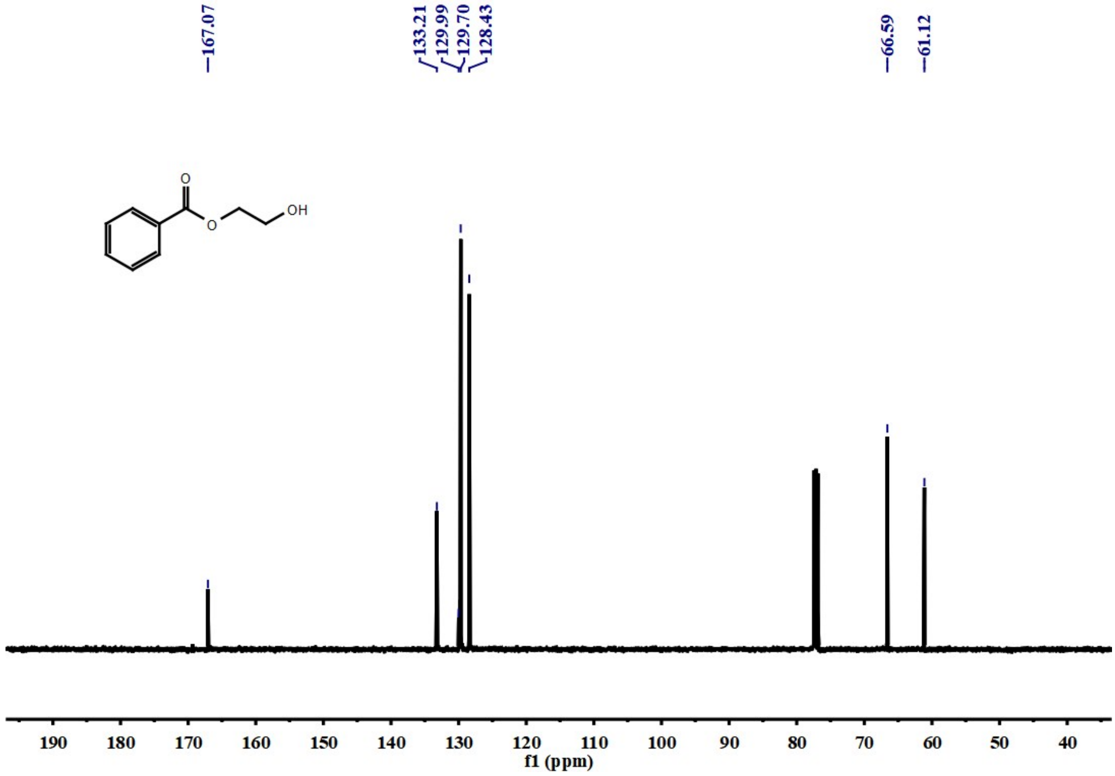
^{1}H NMR spectra of 4m (500 MHz, CDCl$_3$)



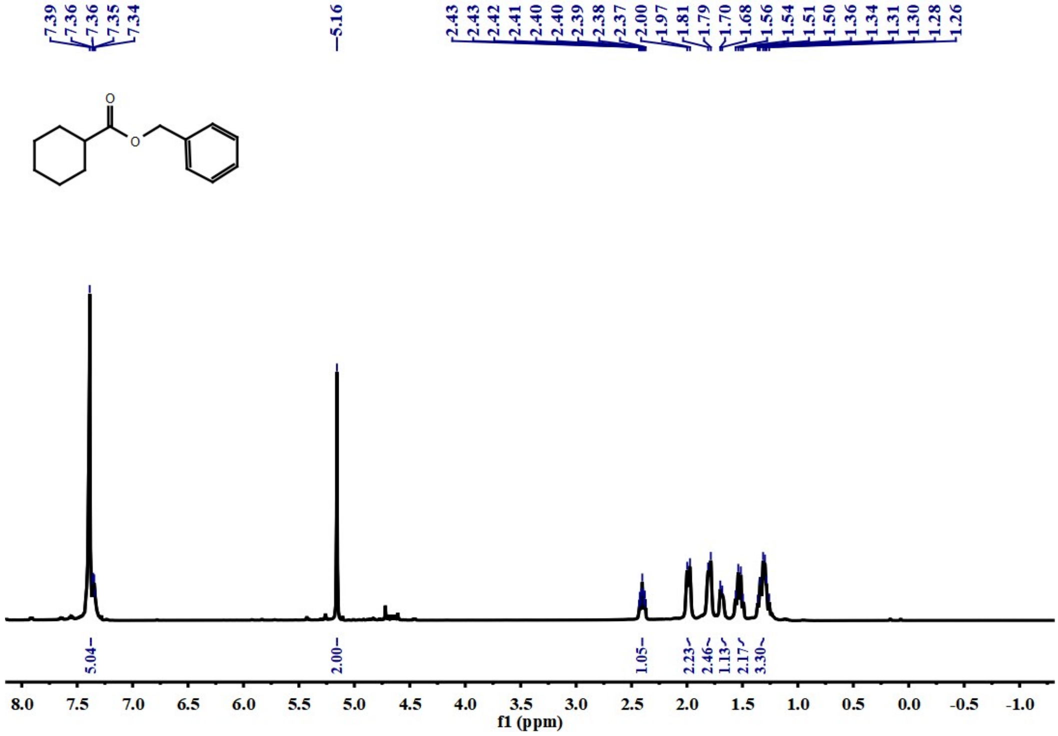
^{13}C NMR spectra of 4m (125 MHz, CDCl$_3$)



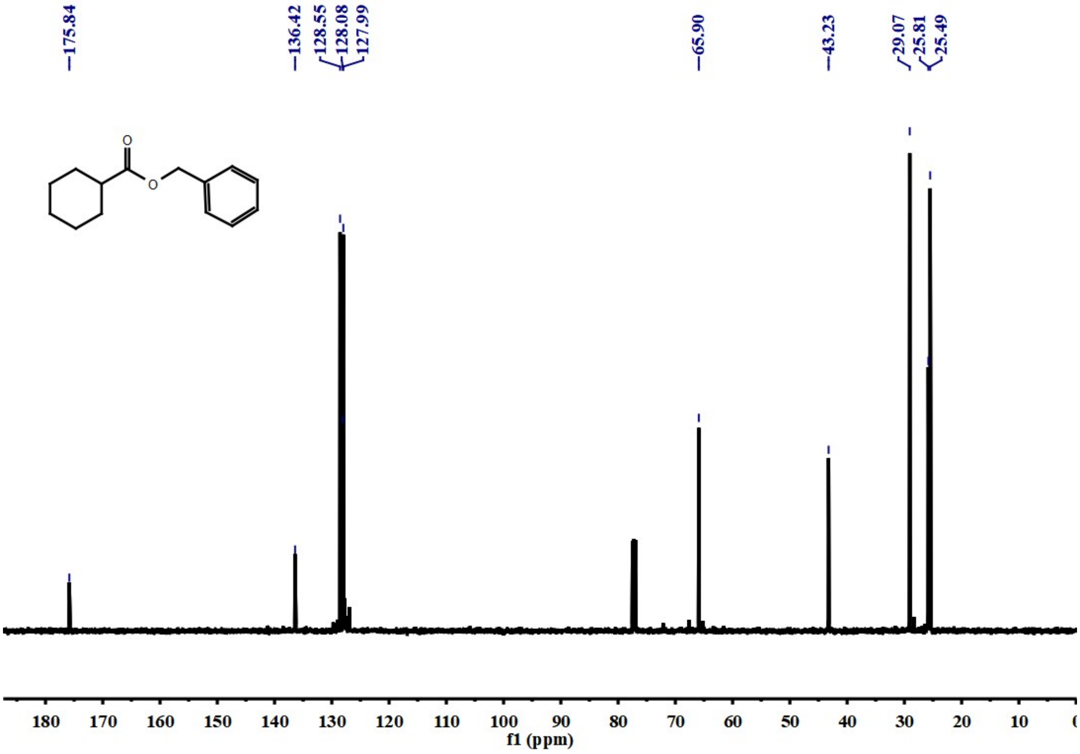
^{1}H NMR spectra of 4n (500 MHz, CDCl$_3$)



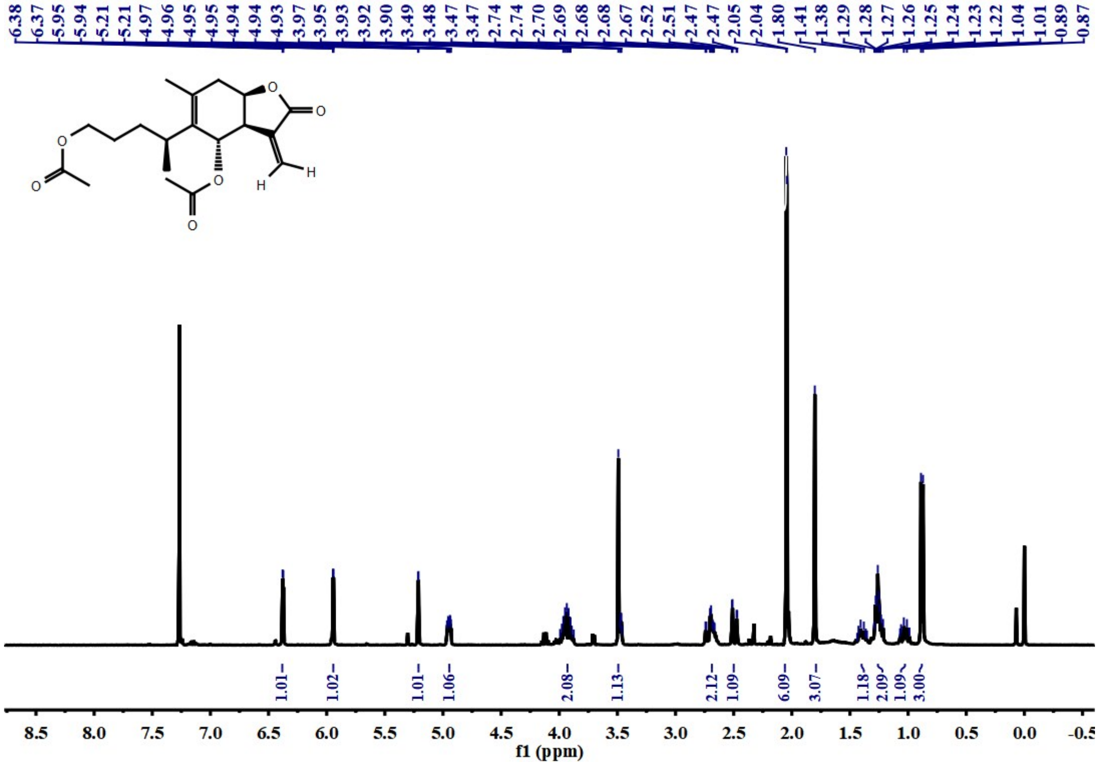
^{13}C NMR spectra of 4n (125 MHz, CDCl$_3$)



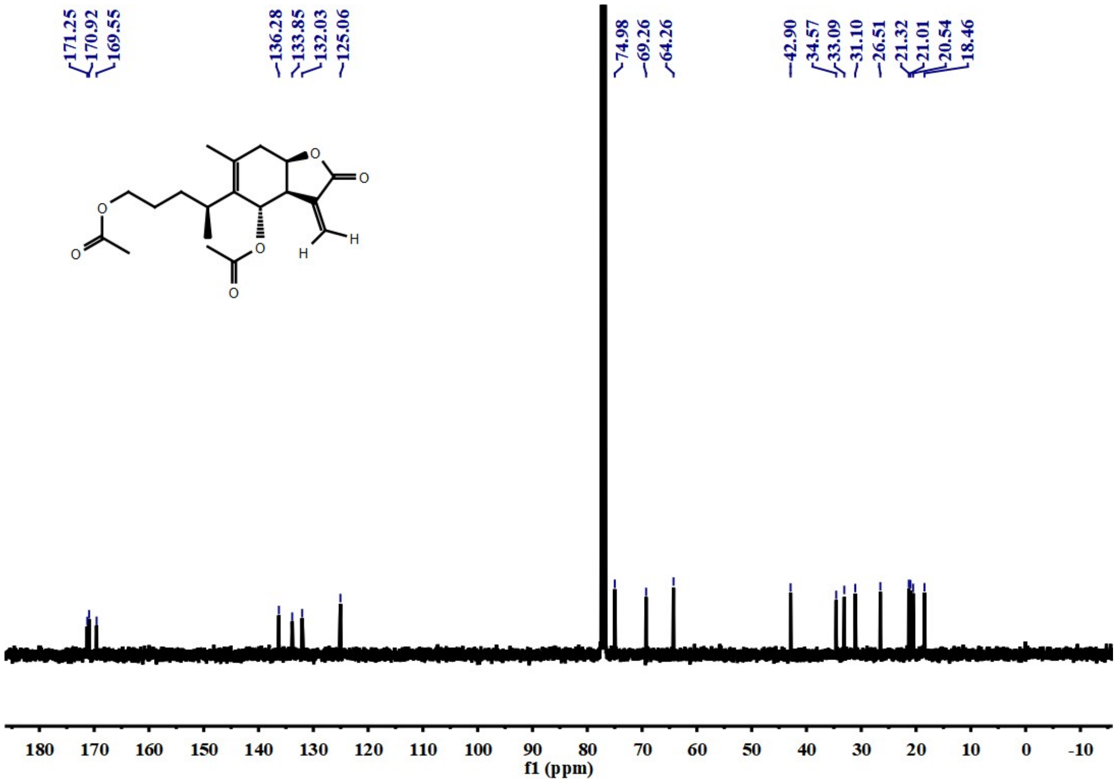
^{1}H NMR spectra of 4o (500 MHz, CDCl$_3$)



^{13}C NMR spectra of 4o (125 MHz, CDCl$_3$)



^{1}H NMR spectra of 4p (400 MHz, CDCl$_3$)



^{13}C NMR spectra of 4p (100 MHz, CDCl$_3$)

VII. References

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