Electronic Supplementary Material (ESI) for Chemical Communications.


Supporting Information

# Electroreductive formylation of activated alcohols via radical-polar crossover

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## 1. General information

All reactions were conducted under an argon atmosphere unless otherwise noted. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI and Combi Blocks used as received with the following exceptions: *N*,*N*-dimethylformamide (DMF) was distilled over $CaH_2$ and stored in flame-dried Schlenk tube with 3 Å molecular sieves. The electrolyte lithium triflate (LiOTf) was purchased from Alfa Aesar (or Acros) and stored in the glove box. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to ultraviolet light (254 nm or 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). $^{1}H$ NMR (400 or 500 MHz), $^{13}C\{^{1}H\}$ NMR (100 or 126 MHz), and $^{31}P\{^{1}H\}$ NMR (162 MHz or 202 MHz) spectra were recorded on a Bruker Ascend 400 or 500, or a Bruker Avance III HD spectrometer and were reported in ppm, relative to residual solvent peak. All coupling constants (*J* values) were reported in Hertz (Hz). Mass spectra were obtained using a Bruker Daltonik micro TOF-Q II high-resolution mass spectrometer (ESI) at the KAIST Analyst Center for Research Advancement.

Electrolysis experiments were performed using a Biologics VMP3 multichannel potentiostat or a DC power supply. Carbon felt was purchased from Fuel Cell Store. Custom-made 3-hole undivided cells were utilized for electrochemical reactions. The carbon felt was cut into 0.5 x 0.5 x 0.3 $cm^3$ pieces and connected to an electrical feed-through on the Teflon cap of the electrochemical cell via a piece of graphite (4H pencil lead, 2 mm in diameter). Magnesium electrode (Mg, 99.9 % purity) was purchased from Alfa Aesar. The Mg electrode was cut into 2.5 x 0.5 x 0.1 $cm^3$ and was connected to an electrical feed-through on the Teflon cap of the electrochemical cell via a piece of graphite (4H pencil lead, 2 mm in diameter).

## 2. General procedure for electroreductive formylation

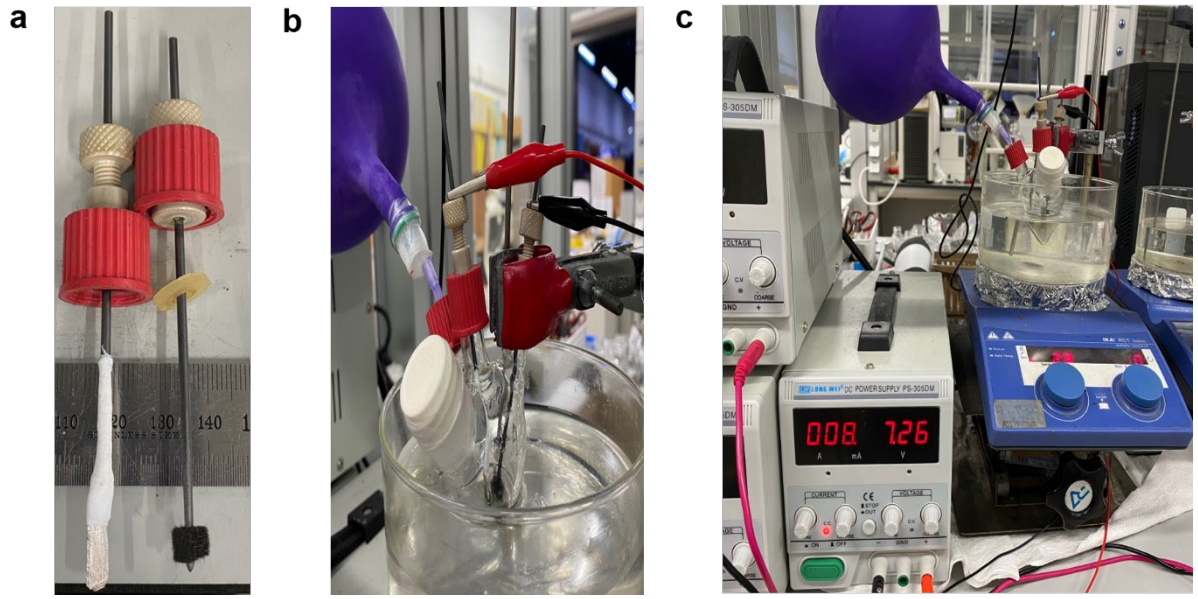
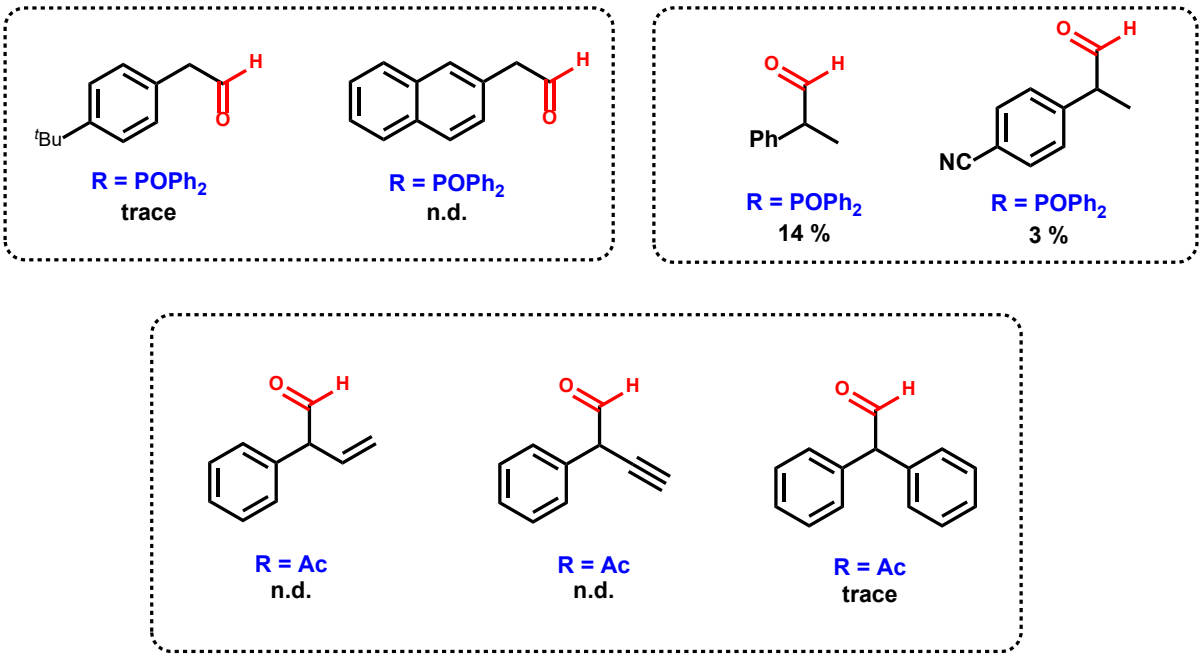



**Figure S1. Set up for 1 mmol scale formylation of activated alcohols.** a) Electrodes; b) Assembled reactor; c) Reaction in progress

An oven-dried, three-hole custom-designed glass electrochemical cell was equipped with a magnetic stir bar, a rubber septum, a magnesium anode (2.5 x 0.5 x 0.1 $cm^3$) and a carbon felt cathode (0.5 x 0.5 x 0.3 $cm^3$) connected to Teflon cap fitted with each separate electrical feed-throughs via 4H pencil leads (2 mm in diameter). This equipped reaction vessel was transferred into Ar-filled glove box. To this reaction vessel, substrate (1 mmol), LiOTf (172 mg, 1.1 mmol), and DMF (5 mL) were added and bring it out of glovebox. Pre-stirring the resulting mixture for 2~3 minutes, and then the reaction mixture was electrolyzed at a constant current of 8 mA electrolysis until passing 3.2 F/mol of a charge at 25 °C under Ar balloon. Then, the crude mixture was further diluted with $Et_2O$ (40 mL). The resulting mixture was washed with saturated $NH_4Cl$ (aq, 30 mL) and $H_2O$ (30 mL x 5 times). The organic layer was dried over with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was subjected to flash column chromatography on silica gel (eluted with *n*-hexane/ethyl acetate) to yield the desired product.

## 3. Unsuccessful substrates




**Detected byprodcts**

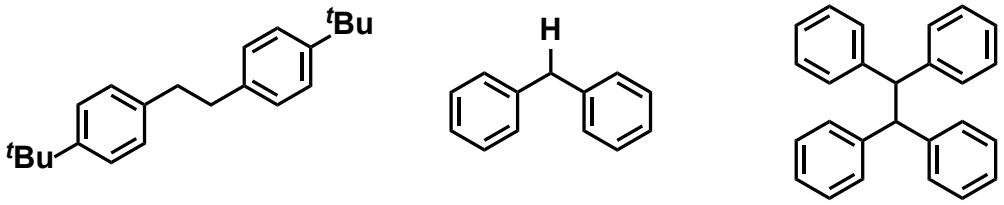



**Figure S2.** Suboptimal and unsuccessful substrates. Yields were determined by $^{1}$H NMR analysis using 0.2 mmol mesitylene as the internal standard. Even though most reactions had a conversion rate of over 90%, the only detected byproducts were protonated or dimerized.

## 4. Cyclic voltammetry (CV) experiments

General information: CV was conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a platinum wire and $Ag/Ag^+$ as counter electrode and reference electrode. The 10 mM substrates in 0.1 M LiOTf in DMA (2 mL) or in 0.1 M LiOTf in DMF (2 mL) solutions were utilized. The solution of interest was sparged with Ar for 5 minutes before data collection. The redox potential of ferrocene/ferrocenium ($Fc^+/Fc$) was measured and used to provide an internal reference. Scan rate is 100 mV/s unless specified.

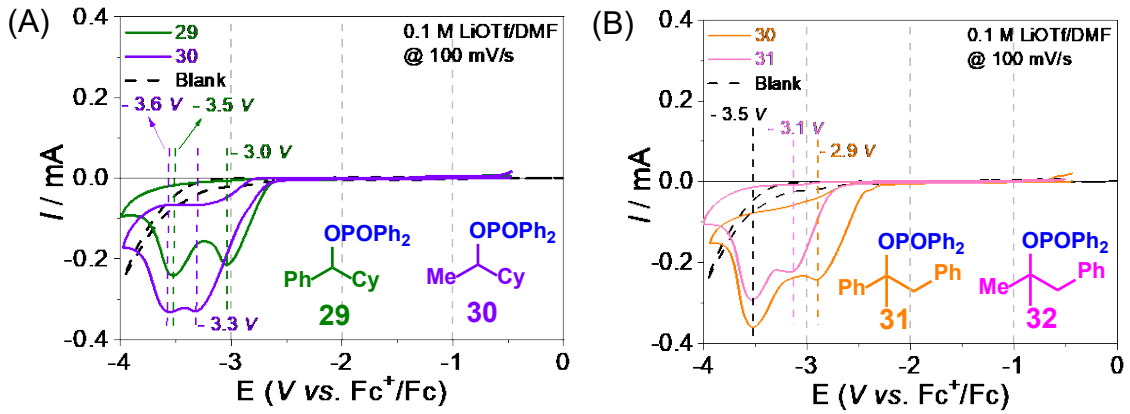



**Figure S3**. Cyclic voltammetry (CV) study of 2,3°-alcohol derivatives in 0.1 M LiOTf/DMF supporting electrolyte. (A) 2°-phosphinates. (B) 3°-phosphinates.

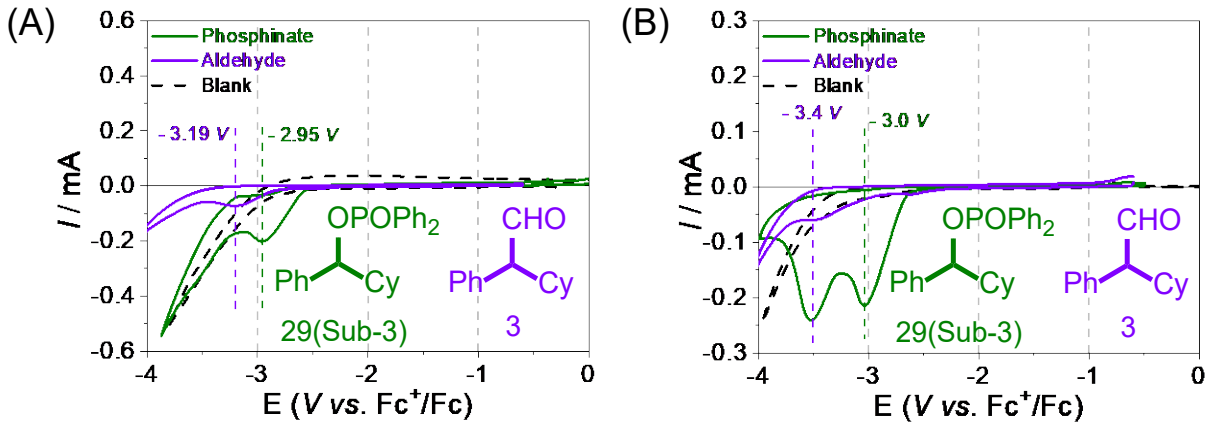



**Figure S4**. CV datas of aldehyde and phosphinate. (A) 0.1 M LiOTf/DMA as supporting electrolyte. (B) 0.1 M LiOTf/DMF as supporting electrolyte.

## 5. Gram-scale synthesis

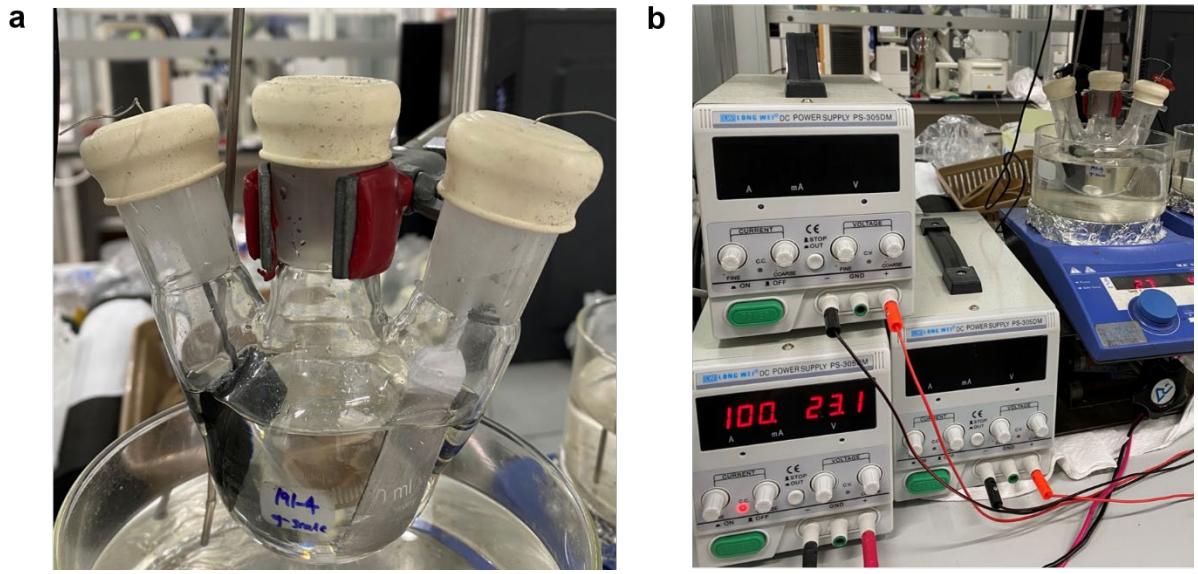
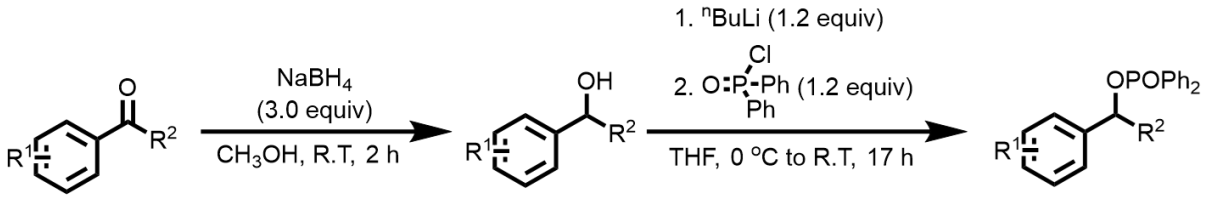



**Figure S5. Set up for 20 mmol scale formylation of activated alcohols.** a) Assembled reactor; b) Reaction in progress

An oven-dried, three-neck 250 mL Round bottom flask (RBF) was equipped with a magnetic stir bar, a rubber septum, a magnesium anode (4 x 1.5 x 0.1 $cm^3$) and a carbon felt cathode (0.3 x 4 x 4 $cm^3$) connected to septum lubber fitted with each separate electrical feed-throughs via 4H pencil leads (2 mm in diameter) and stainless wire (1 mm in diameter). This equipped reaction vessel was transferred into Ar-filled glove box. To this reaction vessel, substrate (20 mmol), LiOTf (3.43 g, 22 mmol), and DMF (100 mL) were added, and bring it was taken out of glovebox. Pre-stirring the resulting mixture for 2~3 minutes, and then the reaction mixture was electrolyzed at a constant current of 100 mA electrolysis was operated at 25 $^oC$ until passing 2.4 F/mol of a charge. Then, the crude mixture was further diluted with $Et_2O$ (40 mL). The resulting mixture was washed with saturated $NH_4Cl$ (aq. 30 mL) and $H_2O$ (30 mL x 5 times). The organic layer was dried over with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was subjected to flash column chromatography on silica gel (eluted with *n*-hexane/ethyl acetate) to give **2** (1.07 g, 33% isolated yield) as a colorless oil.

## 6. Synthesis of starting materials

6.1. General Procedure **A**: Preparation of secondary benzyl alcohol derivatives.

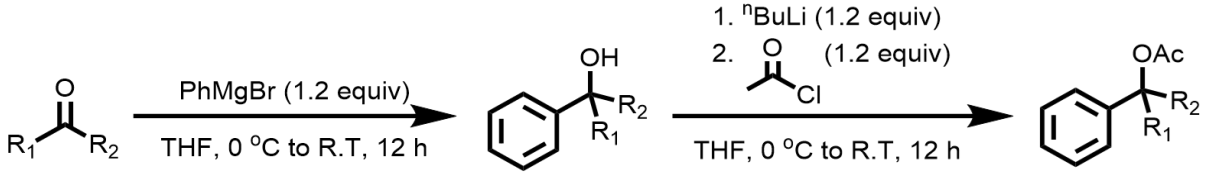



**Scheme S1**. Preparation of secondary benzyl alcohol derivatives.

General Procedure **A:** At 0 °C, to a solution of ketone (5.0 mmol, 1.0 equiv) in 20 mL MeOH was added $NaBH_4$ (567 mg, 3.0 equiv) in 2 portions. The reaction mixture was stirred at 0 °C for 10 min at room temperature for 2 h. Solvent was removed under vacuum. The residue dissolved in EtOAc was washed with water. The organic layers were dried over $MgSO_4$ and evaporated. The crude mixture was used for the next step.

Phosphinates were prepared according to the literature procedure.[1] At 0 °C, $^nBuLi$ (2.0 M in hexane, 1.2 equiv) was added dropwise to a solution of alcohol in 20 mL anhydrous THF under an Ar atmosphere. The resulting mixture was stirred at 0 °C for 1 h, followed by the dropwise addition of diphenyl phosphinic chloride (1.2 equiv). Stirring continued for 1 h at 0 °C and then the reaction was allowed to room temperature and stirred for additional 17 h. The mixture was quenched by sat. aq. $NH_4Cl$ (10 mL). The solvent THF was removed under reduced pressure and the resulting mixture was dissolved in EtOAc. The organic layers were washed with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of pentane and EtOAc as eluent to afford the desired product.

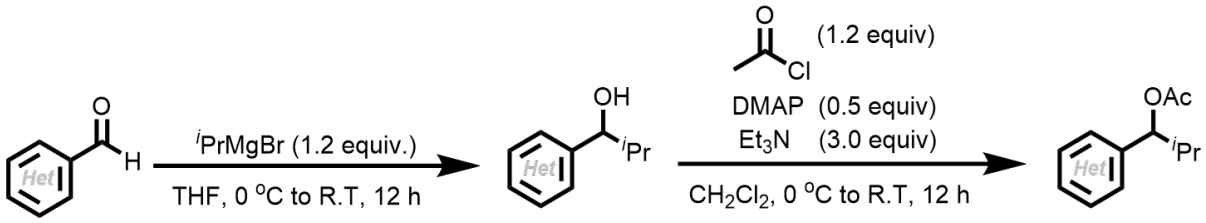
6.2. General Procedure **B**: Preparation of tertiary benzyl alcohol derivatives.




**Scheme S2**. Preparation of tertiary benzyl alcohol derivatives.

General Procedure **B:** At 0 °C, PhMgBr (1.0 M in THF, 1.2 equiv) was added dropwise to a solution of ketone (10.0 mmol, 1.0 equiv) in 20 mL anhydrous THF under an Ar atmosphere. The resulting mixture was stirred at 0 °C for 1 h, and then allowed to at room temperature overnight. The mixture was quenched by sat. aq. $NH_4Cl$ (10 mL). THF was removed under reduced pressure. The resulting mixture was dissolved in EtOAc and washed with water. The organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of *n*-hexane and EtOAc as eluent. $^n$BuLi (2.0 M in hexane, 1.2 equiv) was added dropwise to a solution of isolated alcohol (5.0 mmol) in 20 mL anhydrous THF under an Ar atmosphere. The resulting mixture was stirred at 0 °C for 1 h, followed by the dropwise addition of acetyl chloride (1.2 equiv). Stirring continued for 1 h at 0 °C and then the reaction was allowed to room temperature and stirred for 12 h. The mixture was quenched by sat. aq. $NH_4Cl$ (10 mL). THF was removed under reduced pressure. The resulting mixture was dissolved in EtOAc and washed with water. The organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of *n*-hexane and EtOAc as eluent to afford pure product.

6.3. General Procedure **C**: Preparation of (Hetero)benzyl alcohol derivatives




**Scheme S3**. Preparation of Secondary-(Hetero)benzyl alcohol derivatives.

General Procedure **C**: At 0 °C, $^{i}$PrMgBr (2.0 M in THF, 6.0 mmol, 1.2 equiv) was added dropwise to a solution of aldehyde (5.0 mmol, 1.0 equiv) in 20 mL anhydrous THF under an Ar atmosphere. The resulting mixture was stirred at 0 °C for 1 h, and allowed to room temperature overnight. The mixture was quenched by sat. aq. $NH_4Cl$ (10 mL). THF was removed under reduced pressure. The resulting mixture was dissolved in EtOAc and washed with water. The organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of *n*-hexane and EtOAc as an eluent. At 0 °C, the isolated alcohol (4.0 mmol) was treated with 20 mL $CH_2Cl_2$, $Et_3N$ (12.0 mmol, 3.0 equiv), 4-dimethylaminopyridine (2.0 mmol, 0.5 equiv) and acetyl chloride (4.8 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature overnight. Solvent was removed under vacuum and the residue was purified by flash column chromatography using a mixture of *n*-hexane and EtOAc to give the desired carboxylates.

## 7. Structural determination of 27.

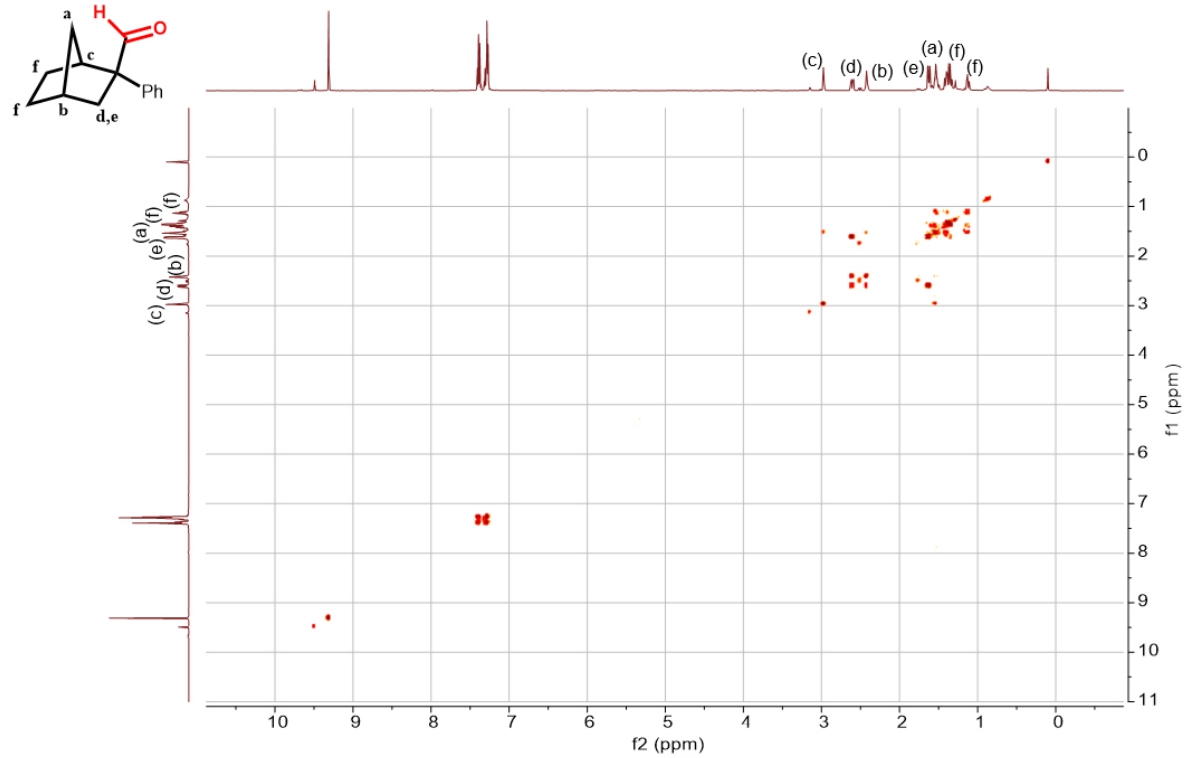



**Figure S6.** 2D-COSY NMR spectrum of **27** (500 MHz, $CDCl_3$).

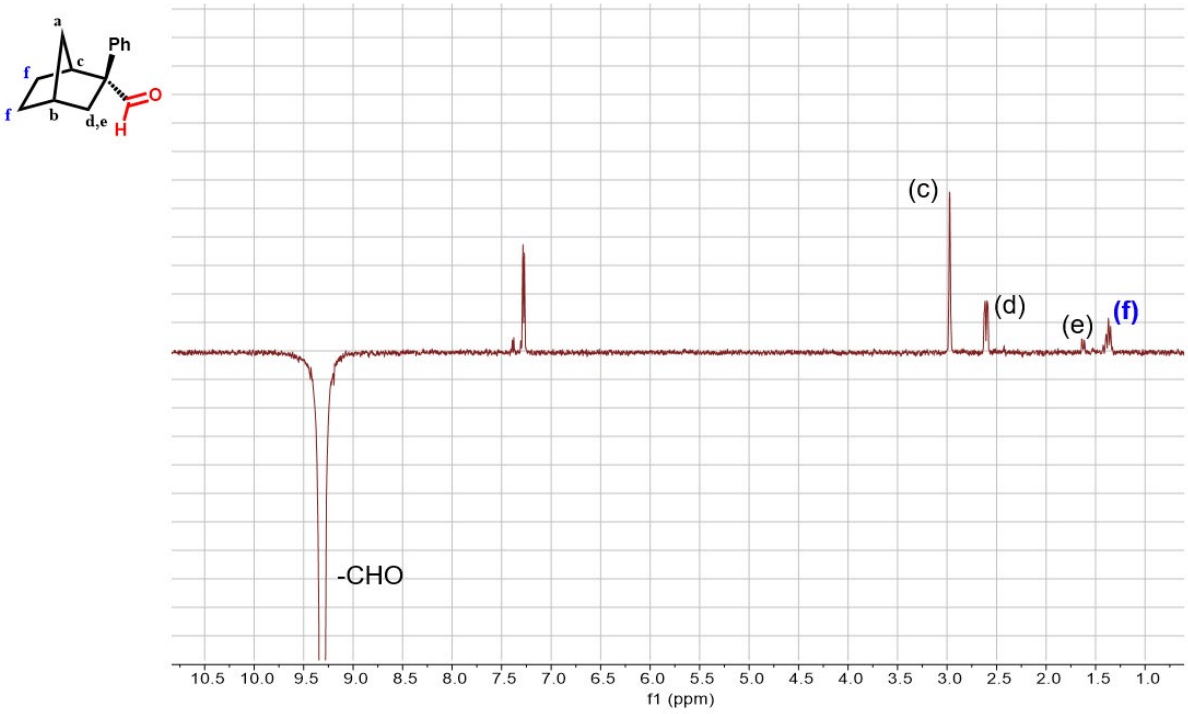
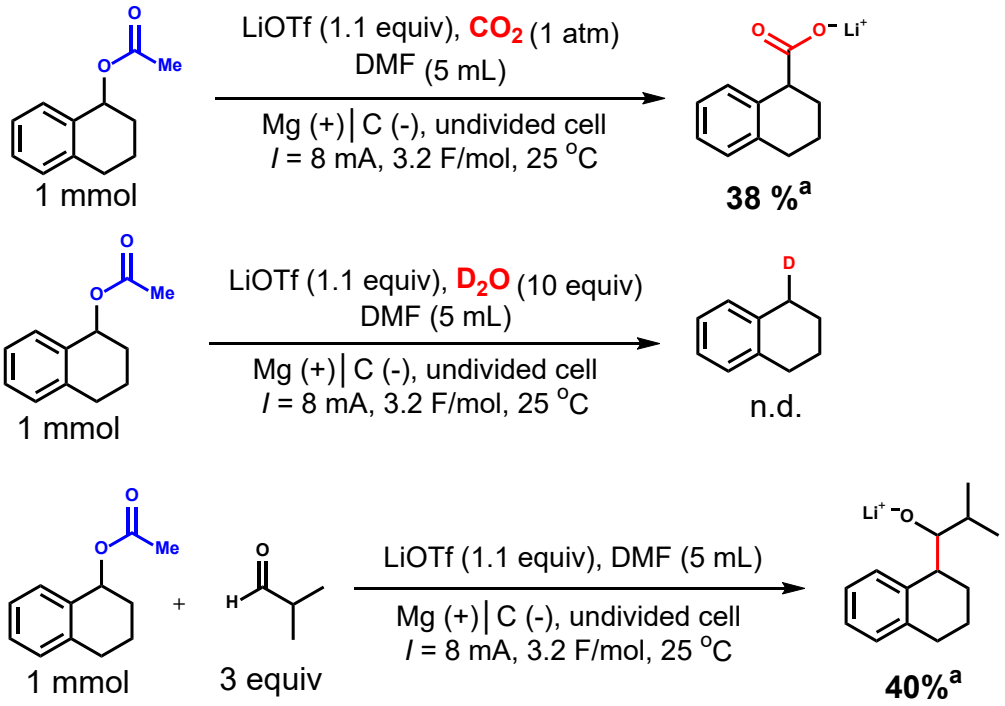



**Figure S7.** $^1$H-1D NOESY NMR spectrum of **27** at 9.310 ppm (500 MHz, $CDCl_3$).

## 8. Reactivity towards other electrophiles

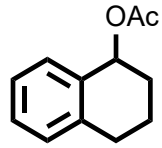



a) $^{1}$H NMR yield using 0.2 mmol mesitylene as internal standard

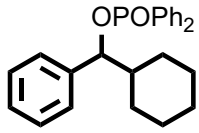
**Scheme S4**. Reactivity towards other electrophiles

## 9. Characterization of compounds

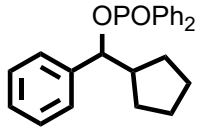
9.1. Starting materials



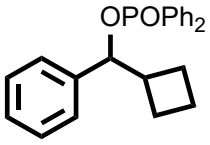

**1 (2-sub)** Colorless liquid. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 3H), 7.14 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.02 (t, *J* = 4.4 Hz, 1H), 2.88 (dt, *J* = 16.3, 4.9 Hz, 1H), 2.76 (ddd, *J* = 16.9, 8.8, 6.2 Hz, 1H), 2.09 (s, 3H), 2.05 – 1.94 (m, 3H), 1.89 – 1.79 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 170.8, 138.0, 134.6, 129.5, 129.1, 128.1, 126.1, 70.0, 29.1, 29.0, 21.5, 18.8. Data are consistent with the literature.[2]




**3-sub** White liquid. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.54 – 7.40 (m, 5H), 7.32 (td, *J* = 7.4, 1.5 Hz, 1H), 7.21 – 7.09 (m, 7H), 5.04 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.06 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.89 (tdt, *J* = 11.2, 7.0, 3.4 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.62 (td, *J* = 14.1, 12.9, 7.2 Hz, 2H), 1.45 – 1.32 (m, 1H), 1.29 – 0.99 (m, 5H), 0.88 (qd, *J* = 12.3, 3.7 Hz, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 139.6, 133.0, 132.0, 132.0, 131.9, 131.9, 131.6, 131.6, 131.5, 131.4, 130.9, 128.5, 128.3, 127.9, 127.9, 127.8, 127.7, 127.3, 82.6, 82.6, 44.4, 44.4, 29.4, 28.5, 26.3, 25.9. **$^{31}$P{$^{1}$H} NMR** (162 MHz, $CDCl_3$) δ 30.7. **HRMS** (ESI) calculated for $C_{25}H_{27}O_2P$ $[M+Na]^+$: 413.1641, Found: 413.1644.

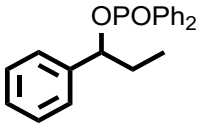



**4-sub** Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88 – 7.73 (m, 2H), 7.57 – 7.39 (m, 5H), 7.32 (td, *J* = 7.4, 1.4 Hz, 1H), 7.19 – 7.12 (m, 7H), 5.13 (t, *J* = 9.1 Hz, 1H), 2.57 – 2.38 (m, 2H), 2.00 – 1.88 (m, 1H), 1.73 – 1.61 (m, 2H), 1.60 – 1.51 (m, 2H), 1.50 – 1.43 (m, 1H), 1.42 – 1.30 (m, 1H), 1.19 – 1.06 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 140.6, 140.5, 132.0, 131.9, 131.9, 131.6, 131.6, 131.4, 131.3, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.1, 82.4, 82.4, 47.2, 47.1, 30.2, 29.0, 25.3. **$^{31}$P{$^{1}$H} NMR** (162 MHz, $CDCl_3$) δ 30.7. **HRMS** (ESI) calculated for $C_{24}H_{25}O_2P$ $[M+Na]^+$: 399.1484, Found: 399.1488.



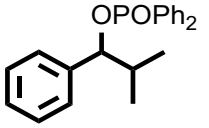

**5-sub**

Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dddd, *J* = 12.3, 8.6, 7.4, 1.4 Hz, 3H), 7.57 – 7.48 (m, 3H), 7.44 (tdd, *J* = 6.6, 3.5, 1.4 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.24 – 7.15 (m, 7H), 5.25 (dd, *J* = 9.6, 8.1 Hz, 1H), 2.91 – 2.78 (m, 1H), 2.18 – 2.07 (m, 1H), 2.06 – 1.98 (m, 1H), 1.83 – 1.68 (m, 4H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 139.5, 139.5, 132.6, 132.6, 132.1, 132.0, 132.0, 131.9, 131.7, 131.7, 131.7, 131.5, 131.4, 131.1, 128.7, 128.6, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 126.8, 81.8, 81.8, 41.7, 41.6, 25.3, 24.1, 17.5. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 31.0. **HRMS** (ESI) calculated for $C_{23}H_{23}O_2P$ [M+Na]$^{+}$: 385.1328, Found: 385.1330.



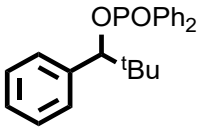

**6-sub**

Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.83 (ddt, *J* = 12.3, 6.9, 1.4 Hz, 2H), 7.58 (ddt, *J* = 12.4, 6.7, 1.4 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.36 (m, 1H), 7.29 – 7.17 (m, 7H), 5.27 (ddd, *J* = 9.4, 7.0, 5.8 Hz, 1H), 2.10 (tt, *J* = 13.6, 7.4 Hz, 1H), 1.95 (dt, *J* = 13.7, 7.3 Hz, 1H), 0.84 (t, *J* = 7.4 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 140.5, 140.4, 133.0, 132.0, 132.0, 132.0, 131.9, 131.8, 131.8, 131.5, 131.4, 131.0, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 127.9, 126.6, 79.6, 79.6, 31.3, 9.5. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 31.0. Data are consistent with the literature.[3]



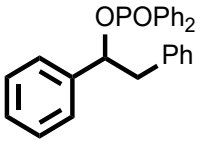

**7-sub**

Colorless oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.56 – 7.41 (m, 5H), 7.35 – 7.31 (m, 1H), 7.23 – 7.11 (m, 7H), 5.07 (dd, *J* = 9.8, 7.1 Hz, 1H), 2.22 (hept, *J* = 6.8 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 139.4, 139.4, 133.0, 132.0, 132.0, 132.0, 131.9, 131.7, 131.6, 131.5, 131.4, 130.9, 128.5, 128.4, 128.0, 127.9, 127.7, 127.2, 83.2, 83.2, 35.1, 35.0, 19.0, 18.1. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 30.9. **HRMS** (ESI) calculated for $C_{22}H_{23}O_2P$ [M+Na]$^{+}$: 373.1328, Found: 373.1329.



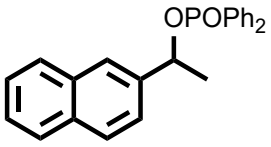

**8-sub**

White solid. (m.p.: 111-115℃) **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.79 (m, 2H), 7.50 – 7.37 (m, 5H), 7.25 – 7.21 (m, 1H), 7.13 – 7.06 (m, 7H), 5.06 (d, *J* = 10.4 Hz, 1H), 0.97 (s, 9H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 138.4, 138.4, 132.8, 132.0, 132.0, 131.9, 131.9, 131.9, 131.7, 131.5, 131.5, 131.4, 130.8, 128.5, 128.4, 128.1, 127.8, 127.7, 127.5, 127.3, 85.3, 85.2, 36.1, 36.0, 26.2. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 30.6. **HRMS** (ESI) calculated for $C_{23}H_{25}O_2P$ [M+Na]$^{+}$: 387.1484, Found: 387.1485.



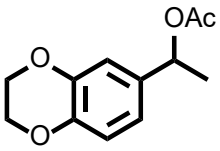

**9-sub**

White solid. (m.p.: 110-114℃) **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.71 – 7.57 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.37 (td, *J* = 7.7, 2.9 Hz, 3H), 7.27 (td, *J* = 7.6, 3.1 Hz, 2H), 7.23 – 7.19 (m, 3H), 7.17 (dd, *J* = 4.7, 2.2 Hz, 5H), 7.01 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.54 (dt, *J* = 8.8, 6.8 Hz, 1H), 3.40 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.22 (dd, *J* = 13.5, 7.1 Hz, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 140.0, 140.0, 136.5, 132.6, 132.1, 132.0, 132.0, 131.9, 131.9, 131.8, 131.6, 131.5, 131.5, 131.1, 130.0, 128.5, 128.4, 128.3, 128.2, 128.0, 126.7, 126.6, 79.0, 79.0, 45.3, 45.3. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 31.4. Data are consistent with the literature.[4]



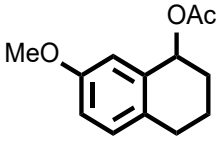

**10-sub**

White soild. (m.p.: 78-81℃) **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.74 (m, 5H), 7.70 – 7.62 (m, 3H), 7.55 – 7.43 (m, 6H), 7.41 – 7.35 (m, 1H), 7.30 – 7.22 (m, 2H), 5.70 (dq, *J* = 9.2, 6.5 Hz, 1H), 1.76 (d, *J* = 6.5 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 139.4, 133.1, 133.1, 132.1, 132.1, 132.0, 132.0, 131.9, 131.8, 131.6, 131.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.7, 126.2, 126.1, 125.0, 123.9, 74.8, 74.8, 25.0, 24.9. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 31.3. **HRMS** (ESI) calculated for $C_{24}H_{21}O_2P$ $[M+Na]^+$: 395.1171, Found: 395.1183.



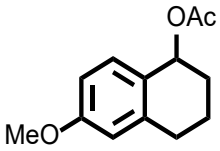

**11-sub**

Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.3 Hz, 1H), 6.82 (d, *J* = 1.4 Hz, 2H), 5.77 (q, *J* = 6.6 Hz, 1H), 4.22 (s, 4 Hz), 2.04 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 170.3, 143.4, 143.2, 135.0, 119.3, 117.2, 115.2, 71.9, 64.3, 64.3, 22.0, 21.3. Data are consistent with the literature.[5]



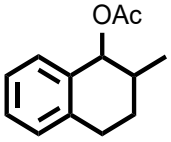

**12-sub**

Yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.06 – 6.97 (m, 2H), 6.18 (t, *J* = 4.4 Hz, 1H), 3.99 (s, 3H), 3.01 (dt, *J* = 15.9, 4.8 Hz, 1H), 2.89 (ddd, *J* = 16.5, 8.8, 5.7 Hz, 1H), 2.31 (s, 3H), 2.23 – 2.11 (m, 3H), 2.03 (ttd, *J* = 15.1, 6.0, 5.2, 2.5 Hz, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 170.9, 157.8, 135.4, 130.1, 130.0, 114.8, 113.7, 70.2, 55.3, 29.1, 28.2, 21.5, 19.0. Data are consistent with the literature.[6]



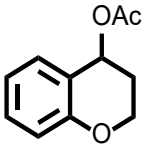

**13-sub**

Yellow oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 1H), 6.77 – 6.71 (m, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 5.96 (t, *J* = 3.8 Hz, 1H), 3.79 (s, 3H), 2.88 – 2.66 (m, 2H), 2.06 (s, 3H), 2.03 – 1.91 (m, 3H), 1.85 – 1.76 (m, 1H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.9, 159.3, 139.5, 131.0, 126.9, 113.4, 112.5, 69.8, 55.2, 29.4, 29.2, 21.6, 18.6. Data are consistent with the literature.[7]



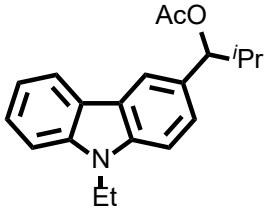

**14-sub**

Colorless soild. (m.p.: 55-57℃) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.20 (qd, *J* = 6.7, 2.0 Hz, 3H), 7.13 (d, *J* = 7.3 Hz, 1H), 5.79 (d, *J* = 6.7 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.15 (s, 3H), 2.06 (dddd, *J* = 22.8, 12.8, 6.5, 3.4 Hz, 2H), 1.64 (dtd, *J* = 13.9, 8.1, 5.9 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 171.2, 137.4, 134.5, 128.8, 128.8, 127.8, 126.1, 75.7, 33.8, 27.1, 26.9, 21.4, 17.3. Data are consistent with the literature.[8]



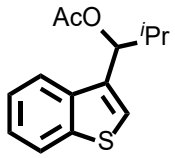

**15-sub**

Colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.23 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.30 (dtd, *J* = 11.1, 4.1, 1.0 Hz, 1H), 4.24 (td, *J* = 11.3, 2.5 Hz, 1H), 2.22 (ddt, *J* = 14.7, 11.6, 4.2 Hz, 1H), 2.14 – 2.03 (m, 4H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 155.2, 130.7, 130.2, 120.6, 120.2, 117.1, 65.2, 62.1, 28.4, 21.4. Data are consistent with the literature.[9]

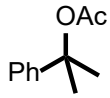



**16-sub**

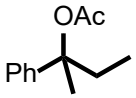
Orange oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.04 (d, *J* = 1.7 Hz, 1H), 7.50 – 7.31 (m, 4H), 7.28 – 7.15 (m, 1H), 5.64 (d, *J* = 8.4 Hz, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 2.24 (dp, *J* = 8.4, 6.7 Hz, 1H), 2.09 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.3, 139.6, 130.4, 125.8, 125.1, 122.9, 122.7, 120.5, 119.4, 118.9, 108.5, 108.1, 82.0, 37.6, 33.9, 21.4, 19.1, 19.0, 13.9. **HRMS** (ESI) calculated for $C_{20}H_{23}NO_2$ $[M+Na]^+$: 332.1621, Found: 332.1619.



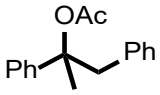

**17-sub** Colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 1H), 7.88 – 7.81 (m, 1H), 7.41 – 7.31 (m, 3H), 5.92 (d, *J* = 7.9 Hz, 1H), 2.38 (dp, *J* = 8.0, 6.6 Hz, 1H), 2.09 (s, 3H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.4, 140.6, 137.5, 135.0, 124.4, 124.1, 124.1, 122.9, 122.7, 76.5, 32.5, 21.1, 19.2, 18.6. **HRMS** (ESI) calculated for $C_{14}H_{16}O_2S$ $[M+Na]^+$: 271.0763, Found: 271.0769.



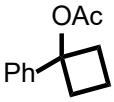

**18-sub** Light yellow liquid. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.27 – 7.22 (m, 1H), 2.04 (s, 3H), 1.77 (s, 6H) **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.8, 145.9, 128.3, 127.0, 124.2, 81.5, 28.7, 22.3. Data are consistent with the literature.



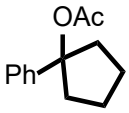

**19-sub** Colorless liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 2.07 (s, 3H), 2.03 (tt, *J* = 7.2, 3.8 Hz, 2H), 1.81 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 144.9, 128.1, 126.8, 124.7, 84.3, 35.1, 24.4, 22.2, 8.1. Data are consistent with the literature.[10]



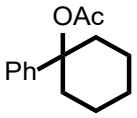

**20-sub** Light yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.19 (m, 6H), 6.98 – 6.90 (m, 2H), 3.31 (d, *J* = 13.5 Hz, 1H), 3.19 (d, *J* = 13.5 Hz, 1H), 2.08 (s, 3H), 1.86 (s, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 144.4, 136.3, 130.8, 128.1, 127.7, 127.0, 126.5, 124.9, 83.7, 49.2, 24.1, 22.3. **HRMS** (ESI) calculated for $C_{17}H_{18}O_2$ $[M+Na]^+$: 277.1199, Found: 277.1201.



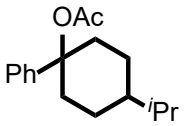

**21-sub** Colorless liquid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.41 – 7.35 (m, 2H), 7.32 – 7.26 (m, 1H), 2.74 – 2.56 (m, 4H), 2.01 (s, 4H), 1.77 (dp, *J* = 11.2, 8.8 Hz, 1H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 142.7, 128.3, 127.3, 125.6, 82.2, 34.9, 21.7, 14.2. Datas are consistent with the literature.[11]



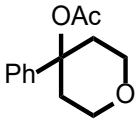

**22-sub** Colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.32 (ddd, *J* = 7.8, 6.7, 1.2 Hz, 2H), 7.26 – 7.20 (m, 1H), 2.44 (dddd, *J* = 12.7, 7.2, 2.9, 1.3 Hz, 2H), 2.19 – 2.05 (m, 2H), 2.00 (s, 3H), 1.93 – 1.69 (m, 4H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.0, 143.6, 128.1, 127.0, 125.2, 91.5, 38.7, 23.4, 22.1. **HRMS** (ESI) calculated for $C_{13}H_{16}O_2$ $[M+Na]^+$: 227.1043, Found: 227.1042.



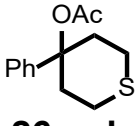

**23-sub** Yellow liquid. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.26 – 7.22 (m, 1H), 2.56 – 2.45 (m, 2H), 2.06 (s, 3H), 1.80 – 1.70 (m, 3H), 1.67 (ddt, *J* = 10.0, 6.5, 3.0 Hz, 4H), 1.31 (dtd, *J* = 12.4, 9.2, 4.7 Hz, 1H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.6, 145.7, 128.3, 127.0, 124.5, 82.5, 36.3, 25.4, 22.1, 22.1. Data are consistent with the literature.[12]




**24-sub** Colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 2.69 – 2.62 (m, 2H), 1.99 – 1.93 (m, 2H), 1.92 (s, 3H), 1.75 (dd, *J* = 10.8, 5.4 Hz, 2H), 1.48 – 1.38 (m, 1H), 1.32 – 1.23 (m, 3H), 0.83 (d, *J* = 6.7 Hz, 6H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.6, 142.1, 128.0, 127.3, 126.7, 83.1, 42.7, 35.0, 30.7, 26.1, 22.4, 20.4. **HRMS** (ESI) calculated for $C_{17}H_{24}O_2$ $[M+Na]^+$: 283.1669, Found: 283.1671.



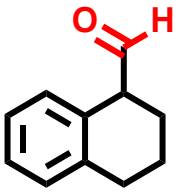

**25-sub** Light yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.28 (ddp, *J* = 8.1, 5.4, 2.6 Hz, 1H), 3.90 (ddd, *J* = 11.6, 5.0, 2.2 Hz, 2H), 3.81 (td, *J* = 11.7, 2.0 Hz, 2H), 2.44 (dq, *J* = 14.5, 2.6 Hz, 2H), 2.14 (ddd, *J* = 13.8, 11.7, 4.9 Hz, 2H), 2.07 (s, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 144.0, 128.5, 127.5, 124.5, 79.7, 63.7, 36.2, 22.1. **HRMS** (ESI) calculated for $C_{13}H_{16}O_3$ $[M+Na]^+$: 243.0992, Found: 243.1003.




**26-sub** White solid. (m.p.: 83-87℃) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 5H), 3.08 (ddd, *J* = 14.2, 12.5, 2.3 Hz, 2H), 2.88 – 2.72 (m, 2H), 2.63 – 2.43 (m, 2H), 2.11 (s, 5H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 169.3, 145.2, 128.6, 127.4, 124.1, 80.9, 37.4, 24.1, 22.0. **HRMS** (ESI) calculated for $C_{13}H_{16}O_2S$ $[M+Na]^+$: 259.0763, Found: 259.0765.

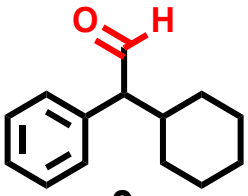

**27-sub** Colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 3.16 (d, *J* = 5.1 Hz, 1H), 2.50 – 2.25 (m, 2H), 1.98 (s, 3H), 1.89 – 1.76 (m, 2H), 1.57 (d, *J* = 9.6 Hz, 2H), 1.45 – 1.25 (m, 3H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 170.1, 145.8, 128.1, 126.7, 125.8, 88.4, 45.8, 45.5, 37.5, 36.6, 29.0, 23.0, 21.8. **HRMS** (ESI) calculated for $C_{15}H_{18}O_2$ $[M+Na]^+$: 253.1199, Found: 253.1206.

9.2. Products



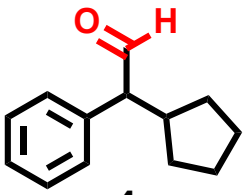

**2**

Light yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.73 (d, *J* = 2.2 Hz, 1H), 7.30 – 7.18 (m, 4H), 3.69 – 3.61 (m, 1H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.34 – 2.24 (m, 1H), 1.99 (dddd, *J* = 13.3, 9.8, 6.4, 3.7 Hz, 1H), 1.86 (dqd, *J* = 13.4, 6.4, 3.4 Hz, 2H). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) δ 202.1, 138.1, 130.9, 129.8, 129.7, 127.2, 126.2, 51.7, 29.2, 23.0, 20.5. **HRMS** (ESI) calculated for $C_{11}H_{12}O$ $[M+Na]^+$: 183.0780, Found: 183.0773.



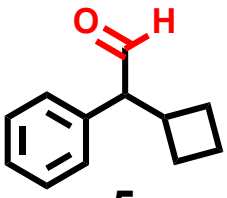

**3**

Colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.70 (d, *J* = 3.5 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 7.20 – 7.16 (m, 2H), 3.25 (dd, *J* = 9.6, 3.5 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.88 – 1.80 (m, 1H), 1.75 (dtd, *J* = 13.1, 3.5, 1.8 Hz, 1H), 1.68 – 1.61 (m, 2H), 1.41 (ddt, *J* = 13.2, 3.7, 2.0 Hz, 1H), 1.36 – 1.00 (m, 5H), 0.84 – 0.75 (m, 1H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 201.2, 135.3, 129.3, 128.9, 127.4, 65.9, 38.2, 31.8, 30.2, 26.3, 26.1, 26.1. **HRMS** (ESI) calculated for $C_{14}H_{18}O$ $[M+Na]^+$: 225.1248, Found: 225.1250.



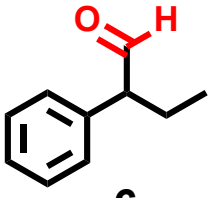

**4**

Colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 3.1 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.25 – 7.21 (m, 2H), 3.32 (dd, *J* = 10.5, 3.1 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.04 – 1.94 (m, 1H), 1.76 – 1.61 (m, 1H), 1.56 – 1.43 (m, 1H), 1.28 (dq, *J* = 12.7, 8.4 Hz, 1H), 1.15 – 1.03 (m, 1H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 200.8, 136.2, 129.1, 128.9, 127.4, 65.3, 40.3, 31.1, 30.8, 25.2, 24.5. **HRMS** (ESI) calculated for $C_{13}H_{16}O$ $[M+Na]^+$: 211.1093, Found: 211.1085.



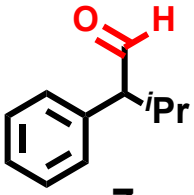
**5**

Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.20 – 7.14 (m, 2H), 3.53 (dd, *J* = 10.5, 2.4 Hz, 1H), 2.98 (dt, *J* = 11.1, 7.4 Hz, 1H), 2.30 – 2.16 (m, 1H), 1.96 – 1.78 (m, 4H), 1.72 – 1.61 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 200.5, 135.1, 129.0, 127.5, 65.7, 35.5, 27.5, 26.5, 18.6. **HRMS** (ESI) calculated for $C_{12}H_{14}O$ $[M+Na]^+$: 197.0937, Found: 197.0930.



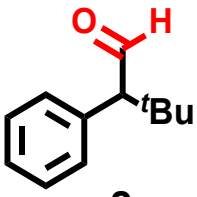
**6**

Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.68 (d, *J* = 2.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 3.41 (t, *J* = 7.5 Hz, 1H), 2.12 (dt, *J* = 14.1, 7.1 Hz, 1H), 1.77 (dt, *J* = 14.5, 7.4 Hz, 1H), 0.91 (t, *J* = 7.4 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 201.1, 136.3, 129.0, 128.8, 127.5, 60.9, 22.3, 11.7. **HRMS** (ESI) calculated for $C_{10}H_{12}O$ $[M+Na]^+$: 197.0937, Found: 197.0930.



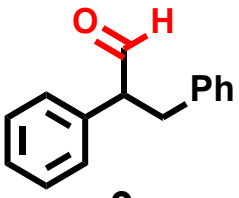
**7**

Colorless oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 3.3 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 7.24 – 7.19 (m, 2H), 3.21 (dd, *J* = 9.5, 3.3 Hz, 1H), 2.44 (dp, *J* = 9.5, 6.7 Hz, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 201.2, 135.5, 129.3, 128.9, 127.5, 66.9, 28.8, 21.2, 20.1. **HRMS** (ESI) calculated for $C_{11}H_{14}O$ $[M+Na]^+$: 185.0937, Found: 185.0938.



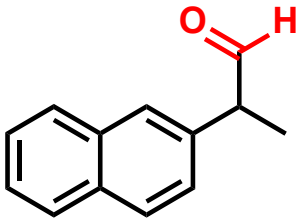
**8**

Colorless oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 3.4 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.25 – 7.20 (m, 2H), 3.29 (d, *J* = 3.4 Hz, 1H), 1.03 (s, 9H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 202.3, 135.3, 130.4, 128.3, 127.3, 68.4, 29.7, 28.2. **HRMS** (ESI) calculated for $C_{12}H_{18}O$ $[MH_2+Na]^+$: 201.1250, Found: 201.1240. HRMS data of the reduced alcohol was obtained.



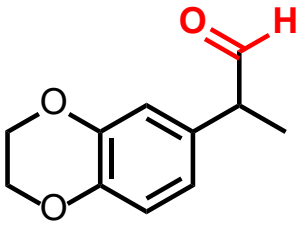

**9**

Yellow solid. (m.p.: 54-57 ℃). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.78 (d, *J* = 1.5 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.26 – 7.14 (m, 5H), 7.10 – 7.06 (m, 2H), 3.86 (ddd, *J* = 8.1, 6.8, 1.5 Hz, 1H), 3.50 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.00 (dd, *J* = 14.0, 7.9 Hz, 1H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 199.9, 138.8, 135.7, 129.1, 128.4, 127.7, 126.3, 61.0, 36.2. **HRMS** (ESI) calculated for $C_{12}H_{18}O$ $[MH_2+Na]^+$: 235.1093, Found: 235.1098. HRMS data of the reduced alcohol was obtained.



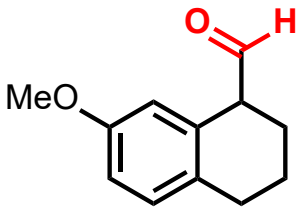

**10**

White solid. (m.p.: 53-58 ℃). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.77 (d, *J* = 1.4 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.81 (dd, *J* = 7.0, 1.4 Hz, 1H), 1.55 (d, *J* = 8.8 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 135.1, 133.6, 128.9, 127.7, 127.2, 126.5, 126.2, 126.1, 53.1, 14.7. Data are consistent with the literature.[13]




**11**

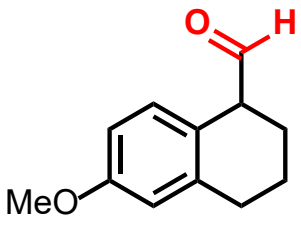
Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.63 (d, *J* = 1.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.71 (s, 1H), 6.67 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.25 (s, 4H), 3.51 (dd, *J* = 7.0, 1.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 201.0, 143.9, 143.0, 130.8, 121.3, 117.8, 117.0, 64.4, 52.2, 31.6, 22.7, 14.5. **HRMS** (ESI) calculated for $C_{11}H_{12}O_3$ $[M+Na]^+$: 215.0684, Found: 205.0679.




**12**

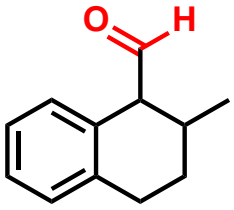
Light yellow oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.3 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.70 (d, *J* = 2.7 Hz, 1H), 3.81 (t, *J* = 0.7 Hz, 3H), 3.60 – 3.52 (m, 1H), 2.74 (t, *J* = 6.3 Hz, 2H), 2.22 (dq, *J* = 13.3, 5.6 Hz, 1H), 1.99

– 1.89 (m, 1H), 1.80 (dq, *J* = 9.2, 5.9 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 202.0, 157.8, 131.8, 130.7, 130.1, 114.2, 113.5, 52.0, 28.3, 23.1, 20.7. **HRMS** (ESI) calculated for $C_{12}H_{14}O_2$ $[M+Na]^+$: 213.0886, Found: 213.0880.



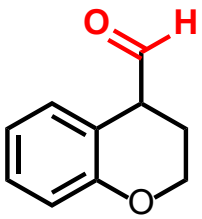

**13**

Light yellow oil. **$^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.3 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.69 (d, *J* = 2.7 Hz, 1H), 3.79 (s, 3H), 3.53 (td, *J* = 5.7, 2.2 Hz, 1H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.23 – 2.15 (m, 1H), 1.92 (tdd, *J* = 13.3, 6.4, 4.1 Hz, 1H), 1.78 (pd, *J* = 6.4, 3.1 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR (**126 MHz, $CDCl_3$) δ 202.3, 158.6, 139.4, 130.6, 122.9, 114.5, 112.5, 55.3, 51.0, 29.5, 23.2, 20.4. **HRMS** (ESI) calculated for $C_{12}H_{14}O_2$ $[M+Na]^+$: 213.0886, Found: 213.0889.



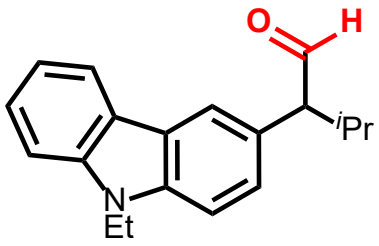

**14**

Light yellow oil. dr=1:1 in crude mixture.**$^{1}H$ NMR** (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 3.9 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.09 – 7.03 (m, 1H), 3.28 (dd, *J* = 8.2, 3.9 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.30 – 2.20 (m, 1H), 1.98 (dtd, *J* = 13.5, 5.2, 3.3 Hz, 1H), 1.59 – 1.51 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 201.6, 130.2, 129.7, 129.5, 127.5, 127.2, 126.3, 59.8, 31.4, 28.9, 28.5, 28.2, 19.9. **HRMS** (ESI) calculated for $C_{12}H_{14}O$ $[M+Na]^+$: 197.0937, Found: 197.0941.



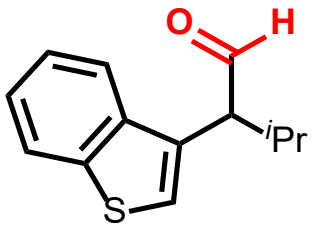

**15**

Light yellow oil. **$^{1}H$ NMR** (400 MHz, $CDCl_3$) 9.74 (t, *J* = 1.2 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.97 (td, *J* = 7.5, 1.3 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.23 (dddd, *J* = 11.2, 4.9, 3.6, 1.1 Hz, 1H), 4.00 (ddd, *J* = 11.2, 10.1, 2.6 Hz, 1H), 3.61 (t, *J* = 5.3 Hz, 1H), 2.44 (dtd, *J* = 14.0, 4.7, 2.7 Hz, 1H), 2.20 – 1.97 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 200.4, 155.3, 129.9, 129.0, 121.0, 117.7, 116.4, 63.8, 47.1, 21.7. **HRMS** (ESI) calculated for $C_{10}H_{10}O_2$ $[M+Na]^+$: 185.0573, Found: 185.0569



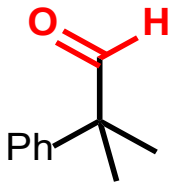

**16**

Yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.82 (d, *J* = 3.2 Hz, 1H), 8.12 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.94 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.34 – 7.23 (m, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.39 (dd, *J* = 9.7, 3.3 Hz, 1H), 2.56 (dhept, *J* = 9.5, 6.6 Hz, 1H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 201.3, 140.3, 139.4, 126.9, 126.0, 125.5, 123.5, 122.6, 121.2, 120.5, 119.0, 108.9, 108.6, 67.0, 37.6, 28.9, 21.4, 20.2, 13.9. **HRMS** (ESI) calculated for $C_{19}H_{21}NO$ $[M+Na]^+$: 197.0337, Found: 197.0941.



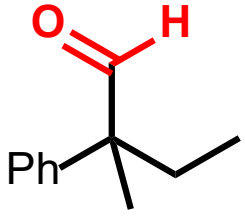

**17**

Yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.69 (d, *J* = 3.3 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.84 – 7.80 (m, 1H), 7.42 (pd, *J* = 7.1, 1.4 Hz, 2H), 7.31 (s, 1H), 3.74 (dd, *J* = 9.3, 3.3 Hz, 1H), 2.60 (dhept, *J* = 9.2, 6.7 Hz, 1H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 199.3, 140.4, 138.8, 130.0, 124.7, 124.4, 124.3, 123.0, 121.8, 59.8, 28.9, 21.3, 20.3. **HRMS** (ESI) calculated for $C_{13}H_{14}OS$ $[M+Na]^+$: 214.0658, Found: 214.0660.




**18**

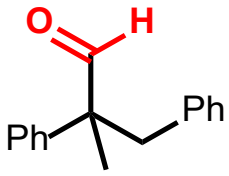
Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.36 (dt, *J* = 48.8, 7.8 Hz, 5H), 1.49 (s, 6H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 202.3, 141.2, 128.9, 127.3, 126.7, 50.5, 22.5.**HRMS** (ESI) calculated for $C_{10}H_{12}O$ $[M+H]^+$: 149.0961, Found: 149.0957.




**19**

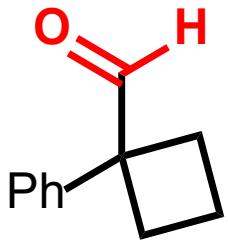
Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.24 (m, 3H), 1.97 (ddt, *J* = 38.1, 14.2, 7.1 Hz, 2H), 1.46 (s, 3H), 0.82 (t, *J* =

7.7 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 202.8, 128.8, 127.2, 127.2, 54.3, 28.6, 18.3, 8.4. **HRMS** (ESI) calculated for $C_{11}H_{14}O$ $[M+H]^+$: 167.1117, Found: 167.1110.



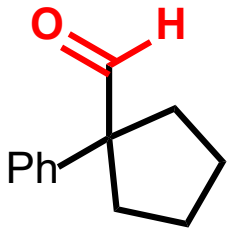

**20**

Yellow oil. **$^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.21 – 7.11 (m, 5H), 6.82 – 6.77 (m, 2H), 3.20 (q, *J* = 13.7 Hz, 2H), 1.38 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 202.0, 139.3, 136.8, 130.4, 128.8, 127.9, 127.6, 127.5, 126.4, 55.1, 42.7, 18.2. **HRMS** (ESI) calculated for $C_{16}H_{16}O$ $[M+Na]^+$: 247.1093, Found: 247.1105.



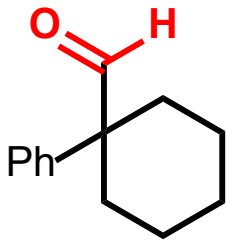

**21**

Colorless oil. **$^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.43 – 7.38 (m, 2H), 7.32 – 7.28 (m, 1H), 7.20 – 7.16 (m, 2H), 2.80 – 2.73 (m, 2H), 2.44 (qd, *J* = 9.3, 2.5 Hz, 2H), 2.10 – 1.90 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 199.5, 141.0, 128.8, 127.0, 126.4, 57.6, 28.4, 15.9. **HRMS** (ESI) calculated for $C_{11}H_{12}O$ $[M+Na]^+$: 183.0780, Found: 183.0778.



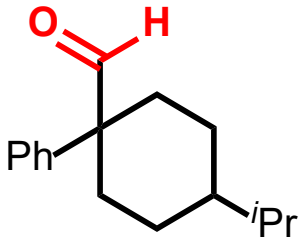

**22**

Colorless oil. **$^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.38 (dd, *J* = 8.7, 6.5 Hz, 2H), 7.33 – 7.26 (m, 3H), 2.56 (ddt, *J* = 15.0, 5.8, 2.2 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.78 (ttq, *J* = 12.7, 8.6, 4.4 Hz, 2H), 1.69 (pd, *J* = 7.5, 3.3 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 200.8, 140.3, 128.8, 127.7, 127.2, 32.4, 24.2. **HRMS** (ESI) calculated for $C_{12}H_{14}O$ $[M+H]^+$: 175.1117, Found: 175.1123.



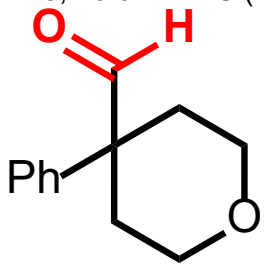

**23**

Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.40 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 2.33 (dt, *J* = 13.7, 4.5 Hz, 2H), 1.88 (ddd, *J* = 14.0, 10.8, 3.7 Hz, 2H), 1.76 – 1.58 (m, 3H), 1.51 (dtt, *J* = 13.6, 10.4, 3.4 Hz, 2H), 1.41 – 1.25 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 202.5, 139.8, 128.88, 127.21, 127.15, 31.29, 25.63, 22.84. **HRMS** (ESI) calculated for $C_{13}H_{16}O$ $[M+Na]^+$: 211.1093, Found: 211.1096.



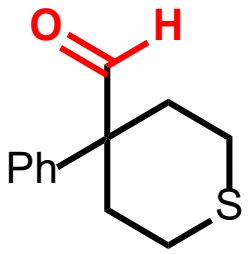

**24**

Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.45 – 7.38 (m, 4H), 7.32 – 7.28 (m, 1H), 2.47 (ddd, *J* = 13.8, 4.2, 2.1 Hz, 2H), 1.82 – 1.68 (m, 4H), 1.35 (hept, *J* = 6.6 Hz, 1H), 1.17 (ddp, *J* = 11.8, 7.7, 4.4, 3.8 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 6H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 202.2, 137.3, 129.0, 128.2, 127.0, 54.6, 43.8, 32.1, 29.5, 24.9, 20.0. **HRMS** (ESI) calculated for $C_{16}H_{22}$ $[M+Na]^+$: 256.1563, Found: 256.1569.



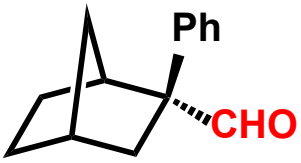

**25**

Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41 (ddd, *J* = 7.9, 6.4, 1.2 Hz, 2H), 7.33 – 7.27 (m, 3H), 3.91 (dt, *J* = 12.0, 4.0 Hz, 2H), 3.60 (ddd, *J* = 11.8, 10.9, 2.5 Hz, 2H), 2.40 (ddt, *J* = 13.7, 4.0, 2.1 Hz, 2H), 2.09 (ddd, *J* = 14.5, 10.8, 4.4 Hz, 2H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 200.9, 129.2, 129.0, 127.8, 126.8, 64.9, 31.1. **HRMS** (ESI) calculated for $C_{12}H_{14}O_2$ $[M+Na]^+$: 213.0886, Found: 213.0891.




**26**

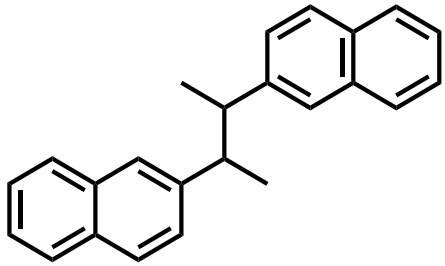
Yellow oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.43 – 7.37 (m, 2H), 7.33 – 7.26 (m, 3H), 2.84 – 2.75 (m, 2H), 2.71 – 2.63 (m, 2H), 2.58 (ddd, *J* = 14.0, 6.5, 2.7 Hz, 2H), 2.29 (ddd, *J* = 13.9, 10.5, 3.2 Hz, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 201.4, 138.6, 129.2, 127.7, 127.0, 53.6, 32.5, 24.8. **HRMS** (ESI) calculated for $C_{12}H_{14}OS$ $[M+H]^+$: 207.0838, Found: 207.0842.




**27**

Colorless oil. dr = 11:1 **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 3H), 2.98 – 2.94 (m, 1H), 2.61 (ddd, *J* = 12.7, 4.9, 2.4 Hz, 1H), 2.42 (d, *J* = 4.5 Hz, 1H), 1.65 – 1.60 (m, 2H), 1.53 (dt, *J* = 9.5, 4.4 Hz, 2H), 1.43 – 1.32 (m, 4H), 1.15 – 1.09 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 199.8, 137.9, 129.3, 128.8, 127.1, 64.6, 41.2, 37.2, 36.7, 35.1, 29.8, 23.4. **HRMS** (ESI) calculated for $C_{14}H_{16}O$ $[M+H]^+$:201.1274, Found: 201.1278.

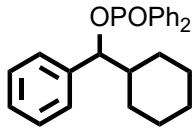
9.3. Mechanistic experiments



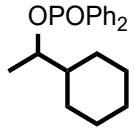
**28**

White solid. (m.p.: 85-88 ℃). *dl* : *meso*=1:1. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 3H), 7.80 – 7.66 (m, 4H), 7.59 – 7.38 (m, 6H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.32 (h, *J* = 7.4 Hz, 1H) (for *dl*), 3.16 (dt, *J* = 7.8, 3.9 Hz, 1H) (for *meso*), 1.44 (d, *J* = 5.8 Hz, 3H), 1.19 (d, *J* = 5.2 Hz, 3H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 144.0, 143.4, 133.7, 133.4, 132.4, 132.1, 128.1, 127.7, 127.7, 127.5, 127.4, 126.8, 126.3, 126.2, 126.1, 126.0, 125.7, 125.3, 125.1, 47.4, 46.3, 21.3, 18.1. Data are consistent with the literatures.[14, 15]

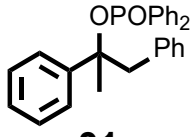
9.4. Substrates for cyclic voltammetry



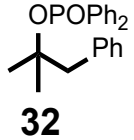

**29(3-sub)** Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.54 – 7.40 (m, 5H), 7.32 (td, *J* = 7.4, 1.5 Hz, 1H), 7.21 – 7.09 (m, 7H), 5.04 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.06 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.89 (tdt, *J* = 11.2, 7.0, 3.4 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.62 (td, *J* = 14.1, 12.9, 7.2 Hz, 2H), 1.45 – 1.32 (m, 1H), 1.29 – 0.99 (m, 5H), 0.88 (qd, *J* = 12.3, 3.7 Hz, 1H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 139.6, 133.0, 132.0, 132.0, 131.9, 131.9, 131.6, 131.6, 131.5, 131.4, 130.9, 128.5, 128.3, 127.9, 127.9, 127.8, 127.7, 127.3, 82.6, 82.6, 44.4, 44.4, 29.4, 28.5, 26.3, 25.9. **$^{31}$P{$^{1}$H} NMR** (162 MHz, $CDCl_3$) δ 30.7. **HRMS** (ESI) calculated for $C_{25}H_{27}O_2P$ [M+Na]$^{+}$: 413.1641, Found: 413.1644.



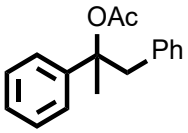

**30** Colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dddd, *J* = 13.7, 12.2, 8.3, 1.4 Hz, 4H), 7.53 – 7.46 (m, 2H), 7.42 (dddt, *J* = 8.4, 6.6, 3.2, 1.5 Hz, 4H), 4.43 – 4.32 (m, 1H), 1.82 – 1.68 (m, 4H), 1.64 (dtt, *J* = 12.3, 3.2, 1.6 Hz, 1H), 1.54 (tdt, *J* = 11.7, 5.2, 3.2 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H), 1.21 – 0.87 (m, 5H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 133.4, 133.0, 132.3, 131.9, 131.9, 131.8, 131.8, 131.7, 131.7, 131.6, 128.4, 128.3, 77.4, 77.4, 44.1, 44.1, 28.5, 28.0, 26.5, 26.1, 26.1, 18.8, 18.8. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 29.3.



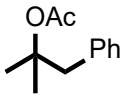

**31** White liquid. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.72 – 7.65 (m, 2H), 7.45 (q, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 7.6, 3.5 Hz, 4H), 7.33 – 7.23 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 7.4 Hz, 2H), 3.52 – 3.40 (m, 2H), 1.89 (s, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 144.4, 144.4, 136.2, 135.0, 134.8, 133.9, 133.7, 131.6, 131.6, 131.6, 131.6, 131.5, 131.3, 131.2, 131.0, 128.4, 128.4, 128.3, 128.3, 128.0, 127.6, 127.4, 126.5, 125.6, 87.6, 87.5, 51.5, 51.5, 26.8, 26.8. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 27.1. **HRMS** (ESI) calculated for $C_{27}H_{25}O_2P$ [M+Na]$^{+}$: 435.1484, Found: 435.1486.




**32** Light yellow oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.46 (td, *J* = 7.3, 1.5 Hz, 2H), 7.38 (ddd, *J* = 8.5, 6.8, 3.5 Hz, 4H), 7.33 – 7.25 (m, 5H), 3.08 (d, *J* = 1.0 Hz, 2H), 1.51 (s, 3H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 137.1, 135.1, 134.0, 131.5, 131.5, 131.3, 131.3, 131.0, 85.3, 85.2, 50.1, 50.1, 28.6, 28.5. **$^{31}$P{$^{1}$H} NMR** (202 MHz, $CDCl_3$) δ 26.5. **HRMS** (ESI) calculated for $C_{25}H_{23}O_2P$ [M+Na]$^{+}$: 373.1328, Found: 373.1327.




**33 (20-sub)** Light yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.19 (m, 6H), 6.98 – 6.90 (m, 2H), 3.31 (d, *J* = 13.5 Hz, 1H), 3.19 (d, *J* = 13.5 Hz, 1H), 2.08 (s, 3H), 1.86 (s, 3H). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 144.4, 136.3, 130.8, 128.1, 127.7, 127.0, 126.5, 124.9, 83.7, 49.2, 24.1, 22.3. **HRMS** (ESI) calculated for $C_{17}H_{18}O_2$ $[M+Na]^+$: 277.1199, Found: 277.1201.

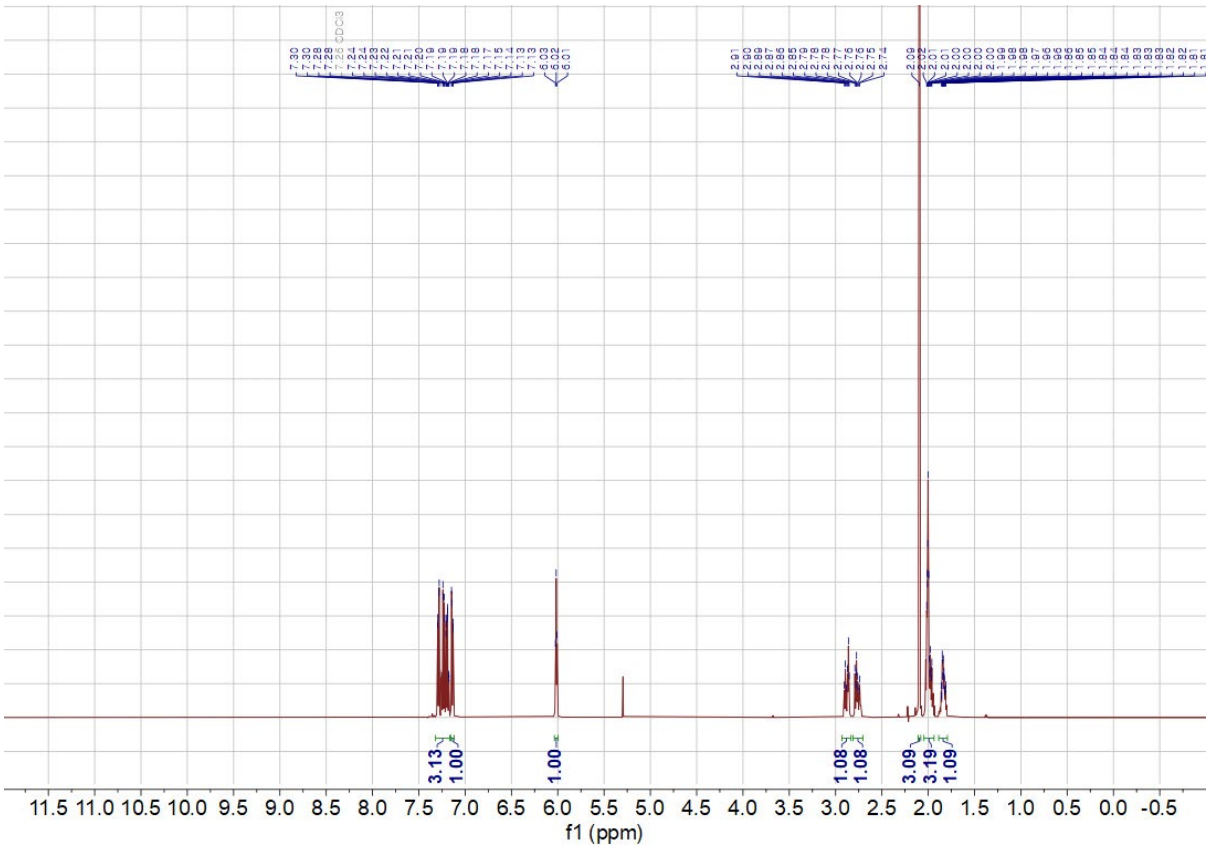



**34** Colorless oil. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.32– 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 3.06 (s, 2H), 1.98 (s, 3H), 1.45 (s, 6H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 170.7, 137.3, 130.6, 128.0, 126.4, 82.1, 46.4, 26.0, 22.6. Data are consistent with the literature.[16]

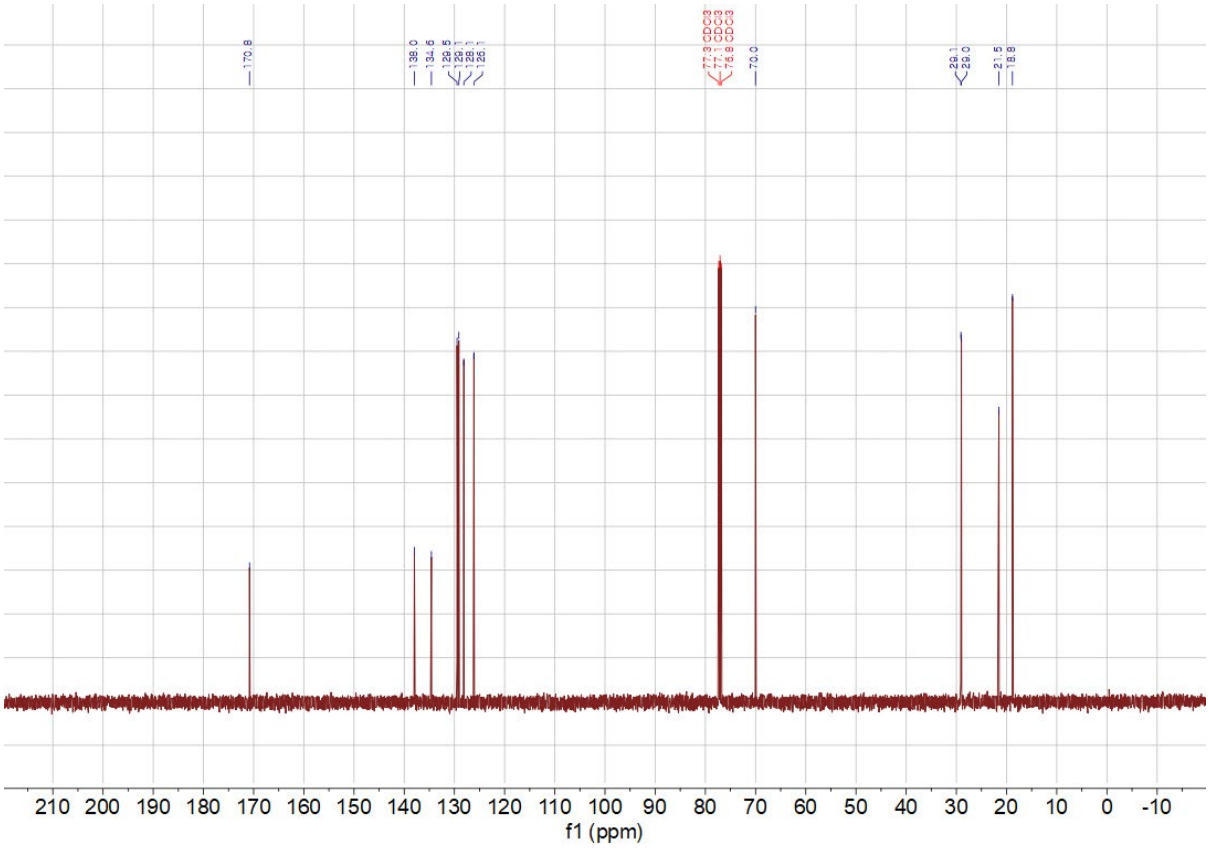
# 10. NMR Spectra

## 10.1. Starting materials

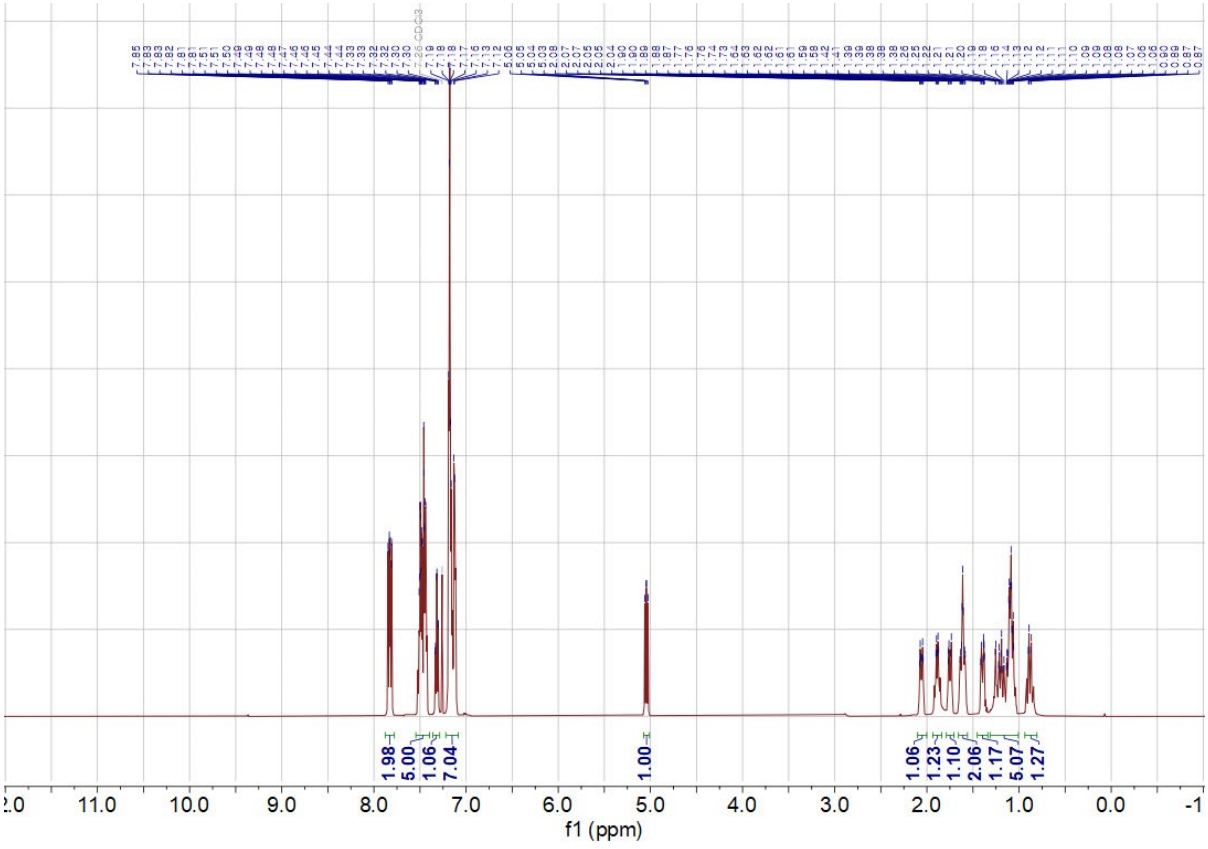
$^1$H NMR spectrum (500 MHz, $CDCl_3$) of **1(2-sub)**



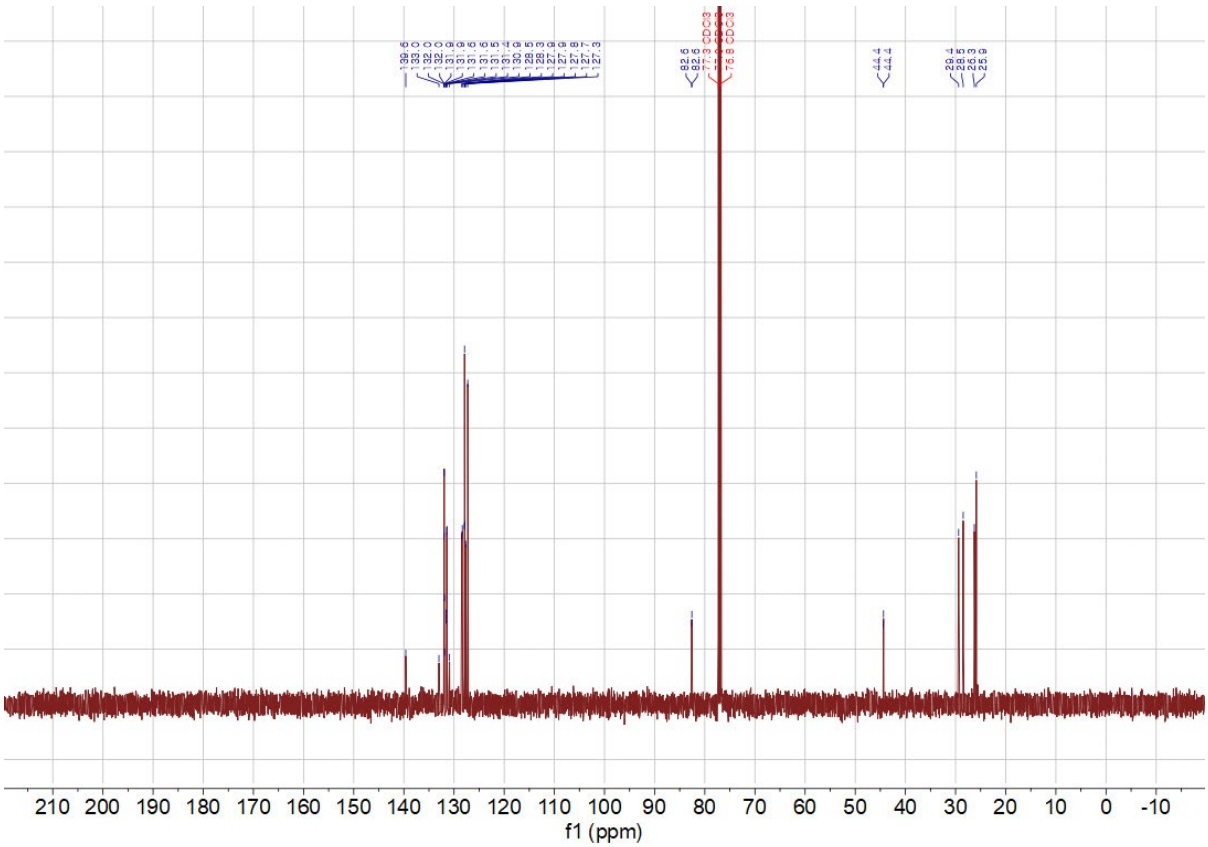
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **1(2-sub)**



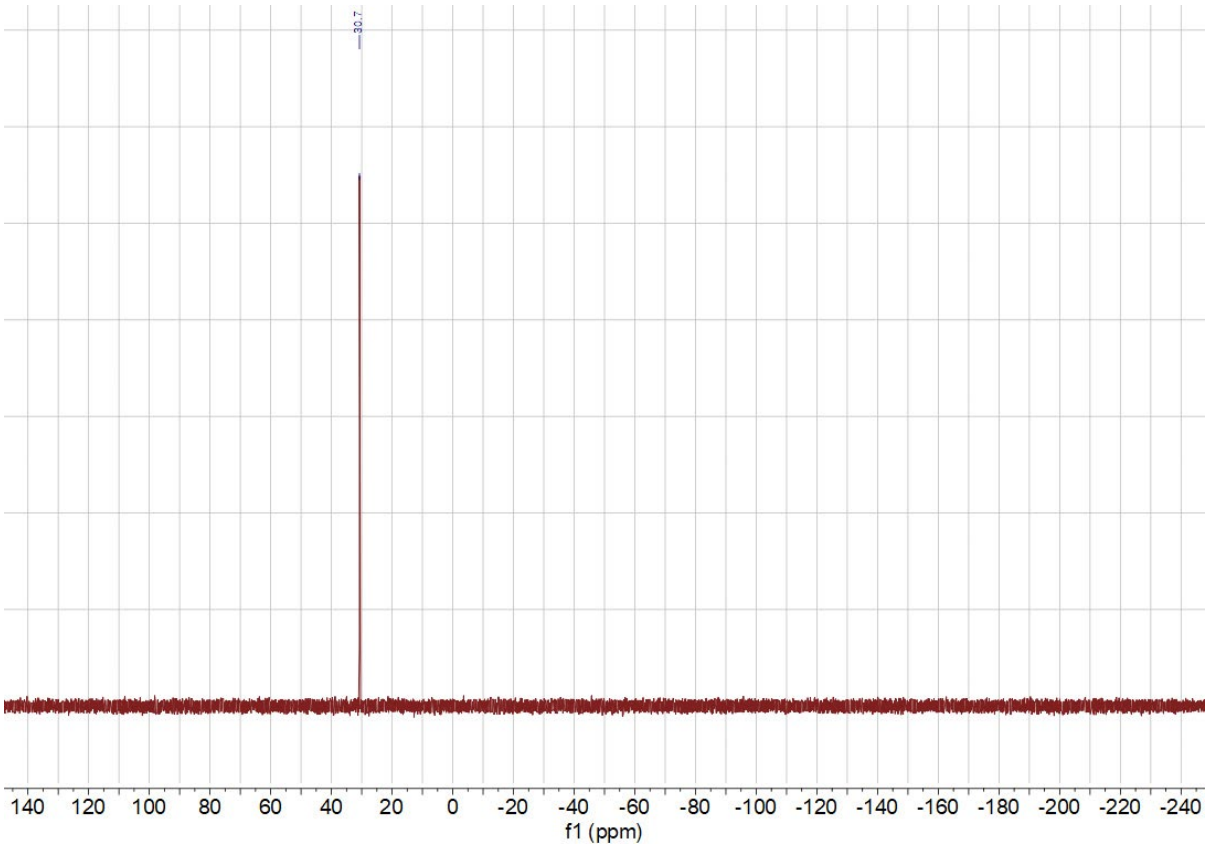

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **3-sub**



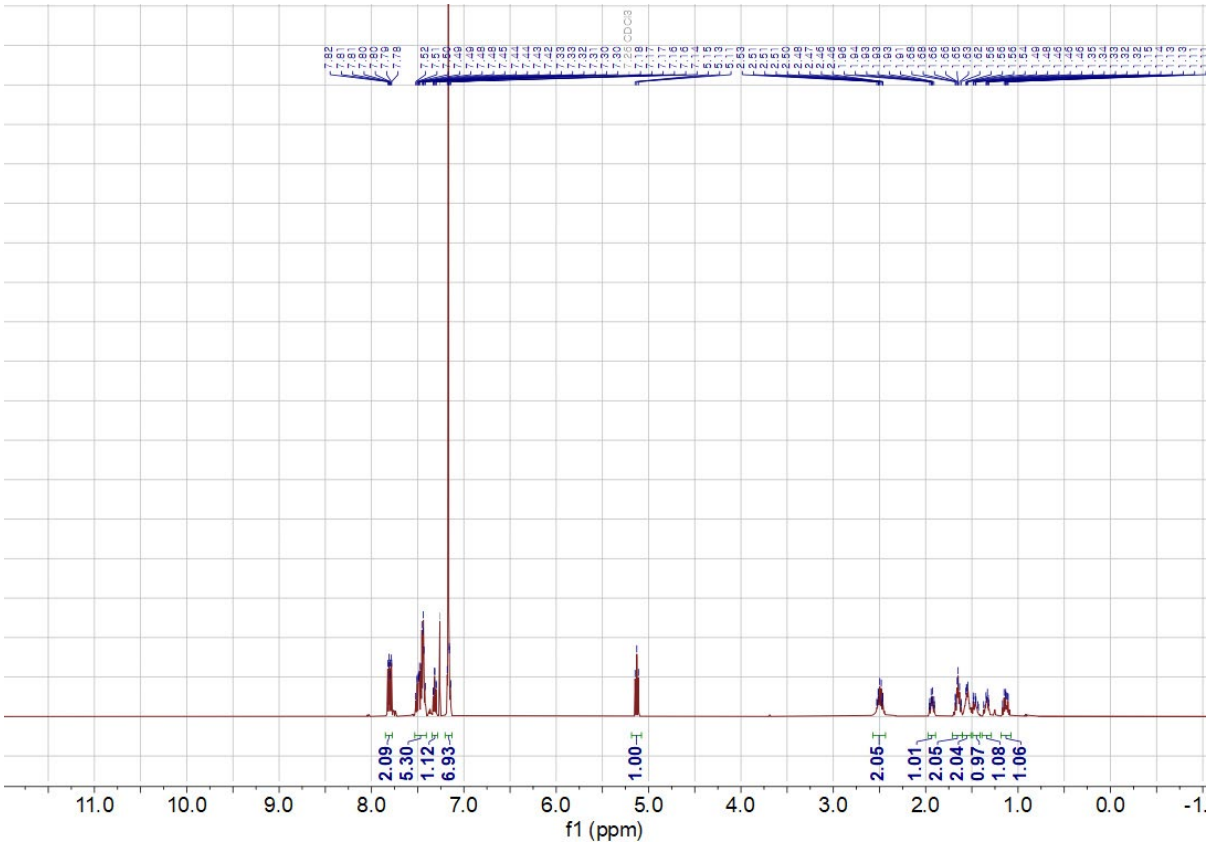
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **3-sub**



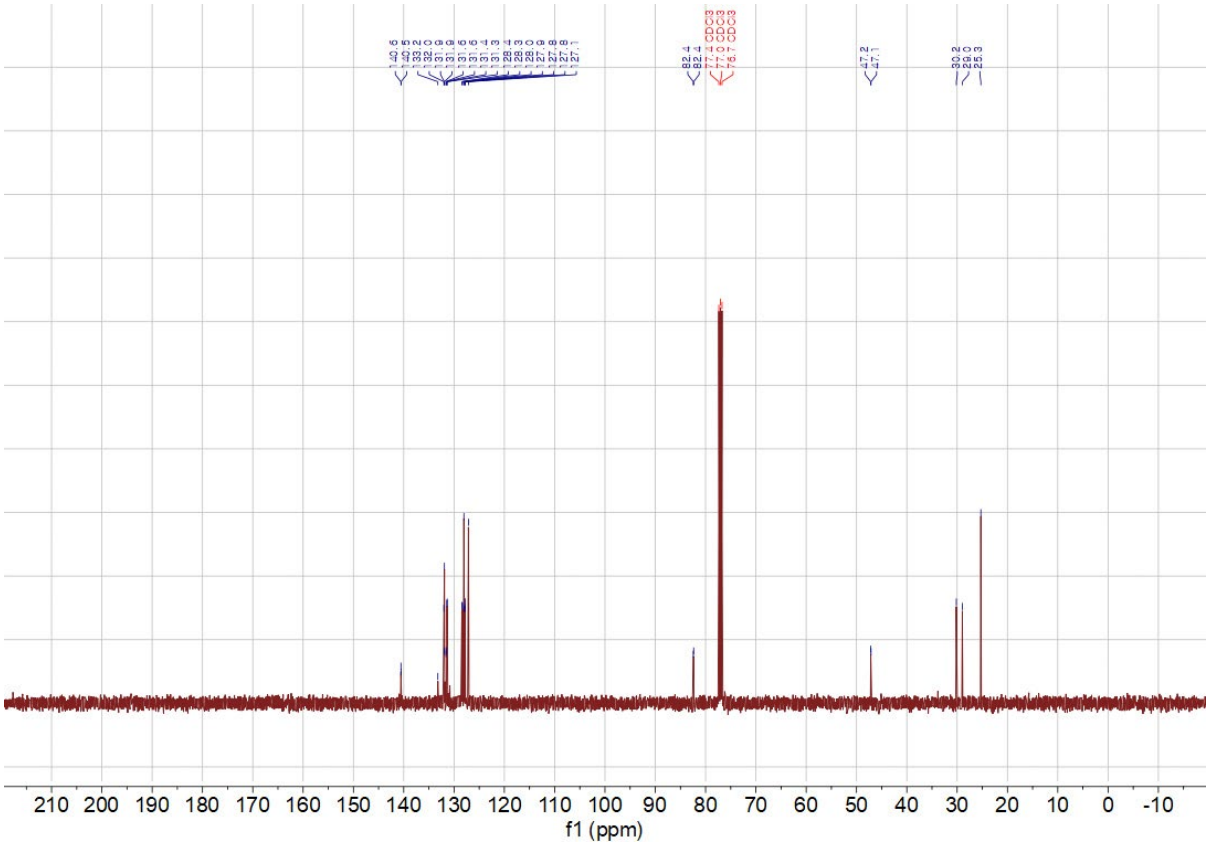

$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3-sub**



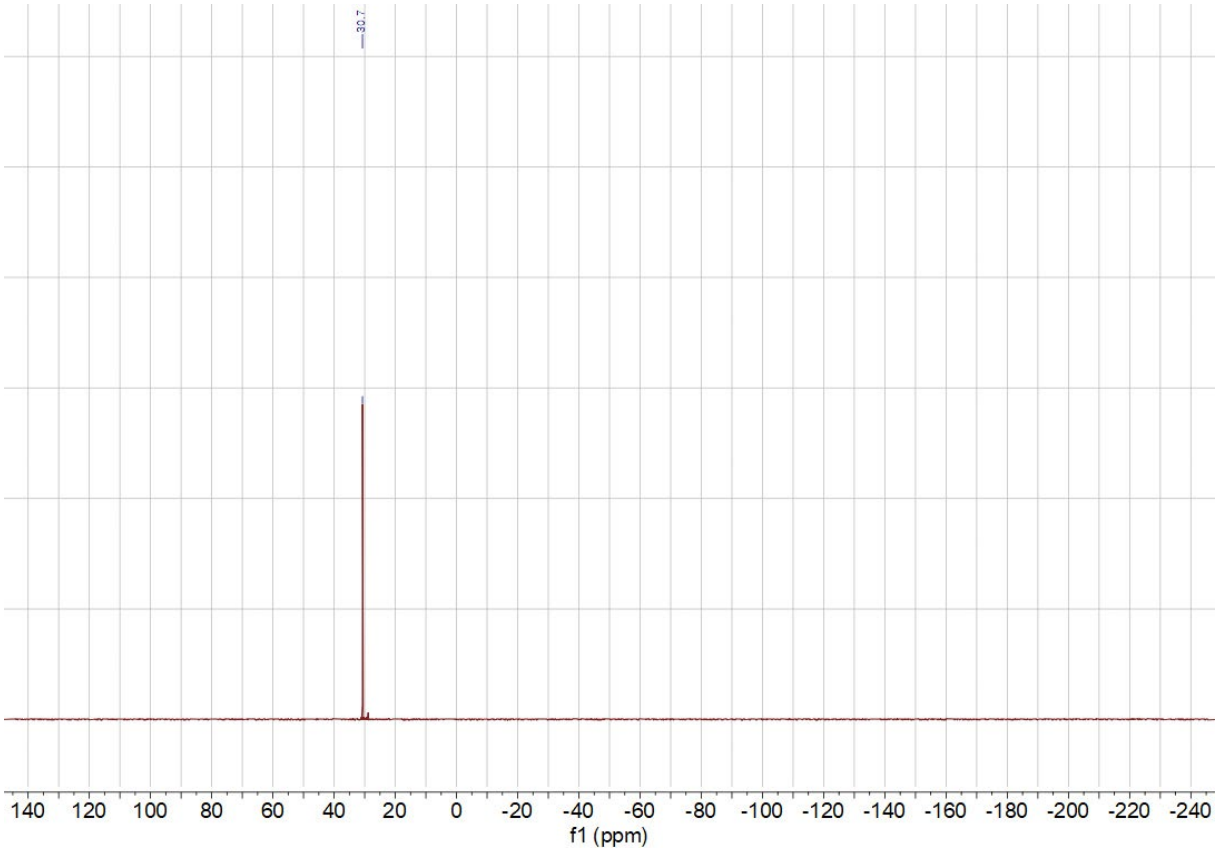
$^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **4-sub**



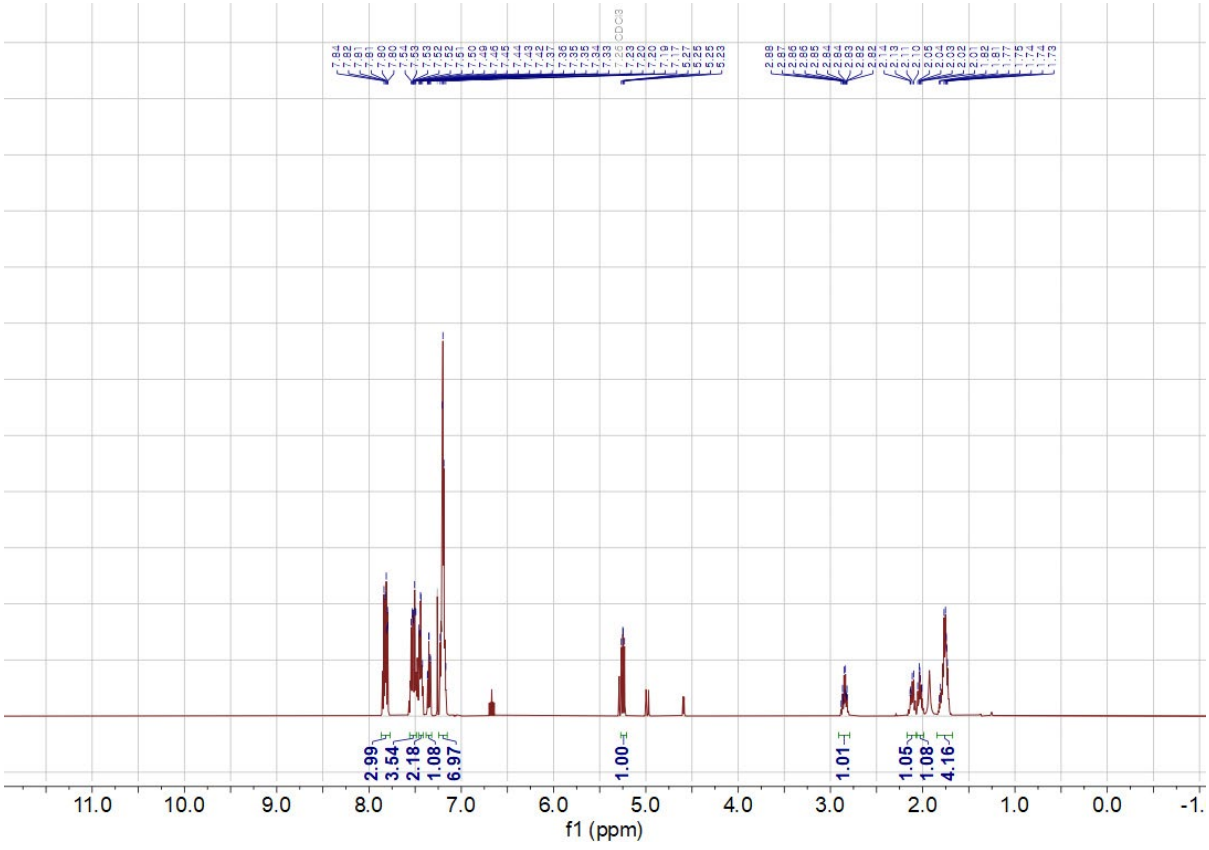

$^{13}$C{$^{1}$H} NMR spectrum (126 MHz, $CDCl_3$) of **4-sub**



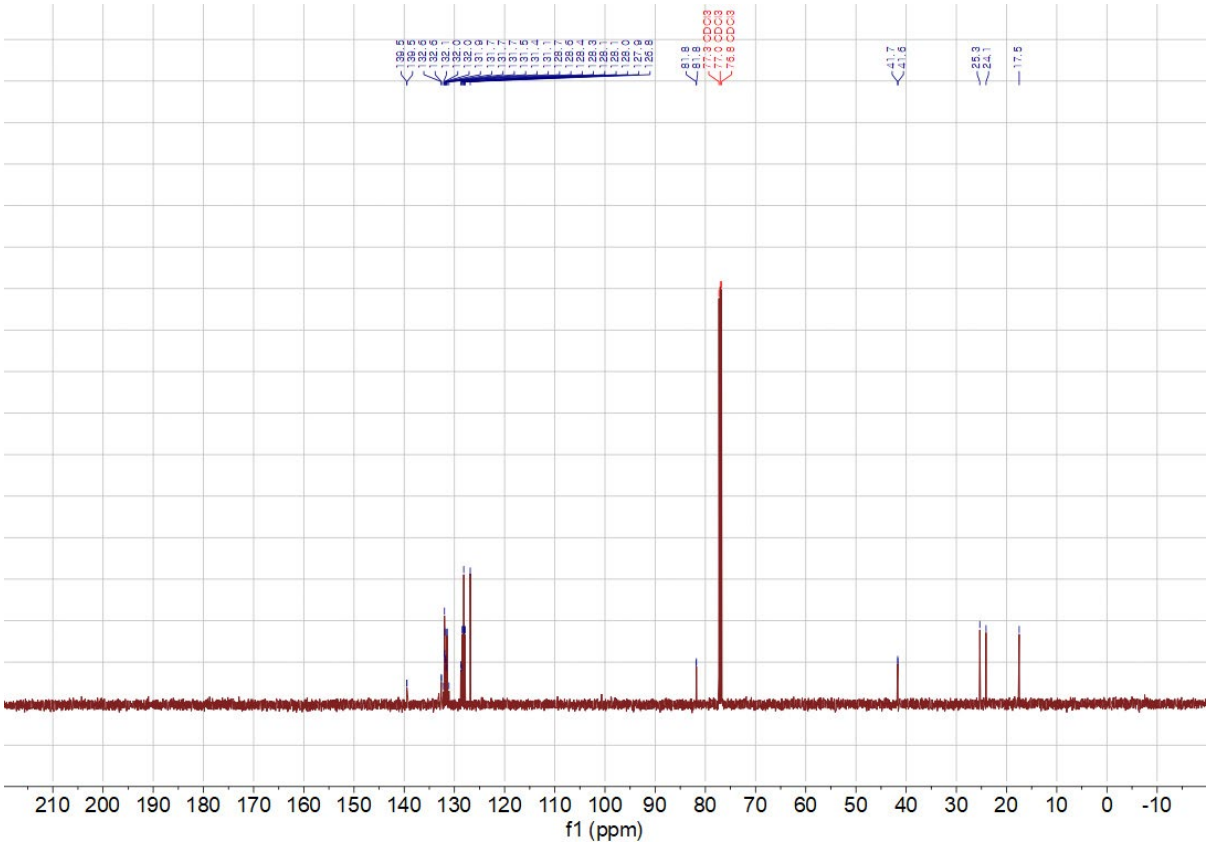
$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4-sub**



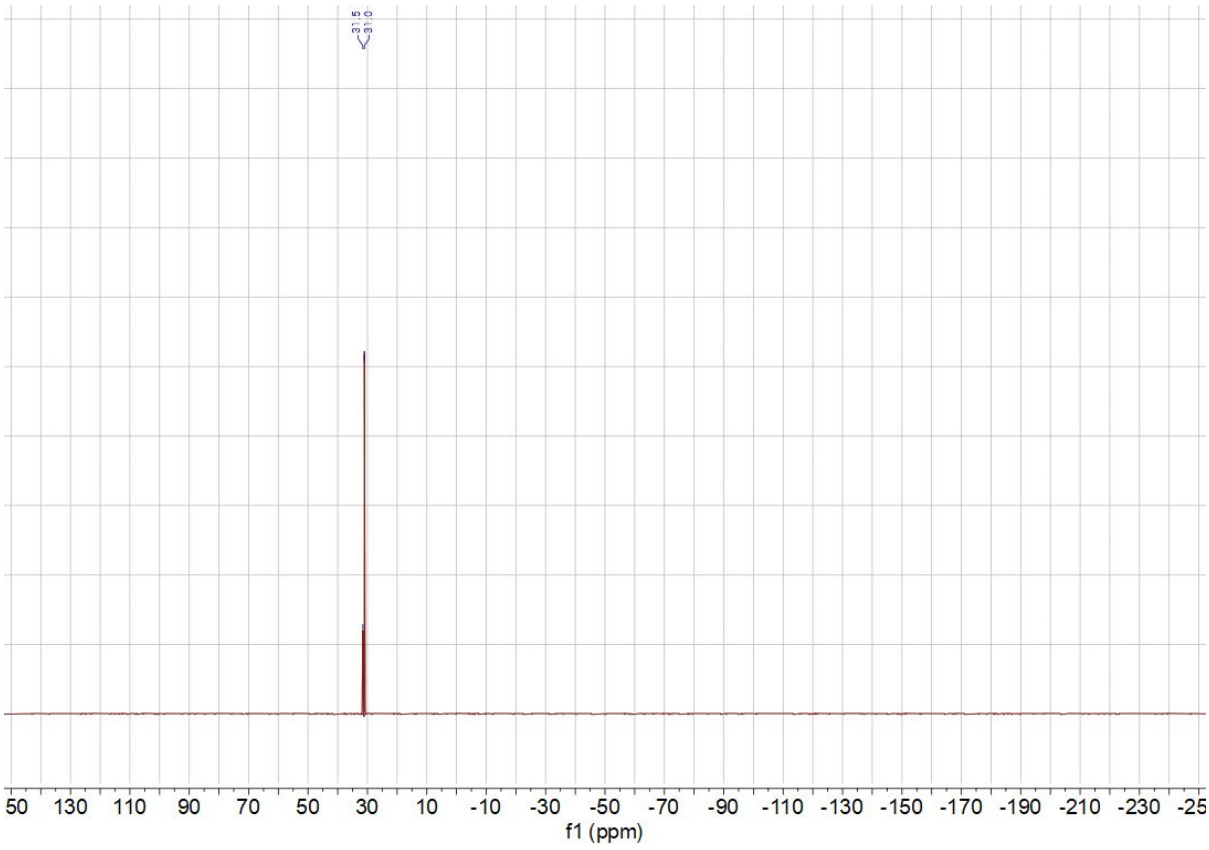

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **5-sub**



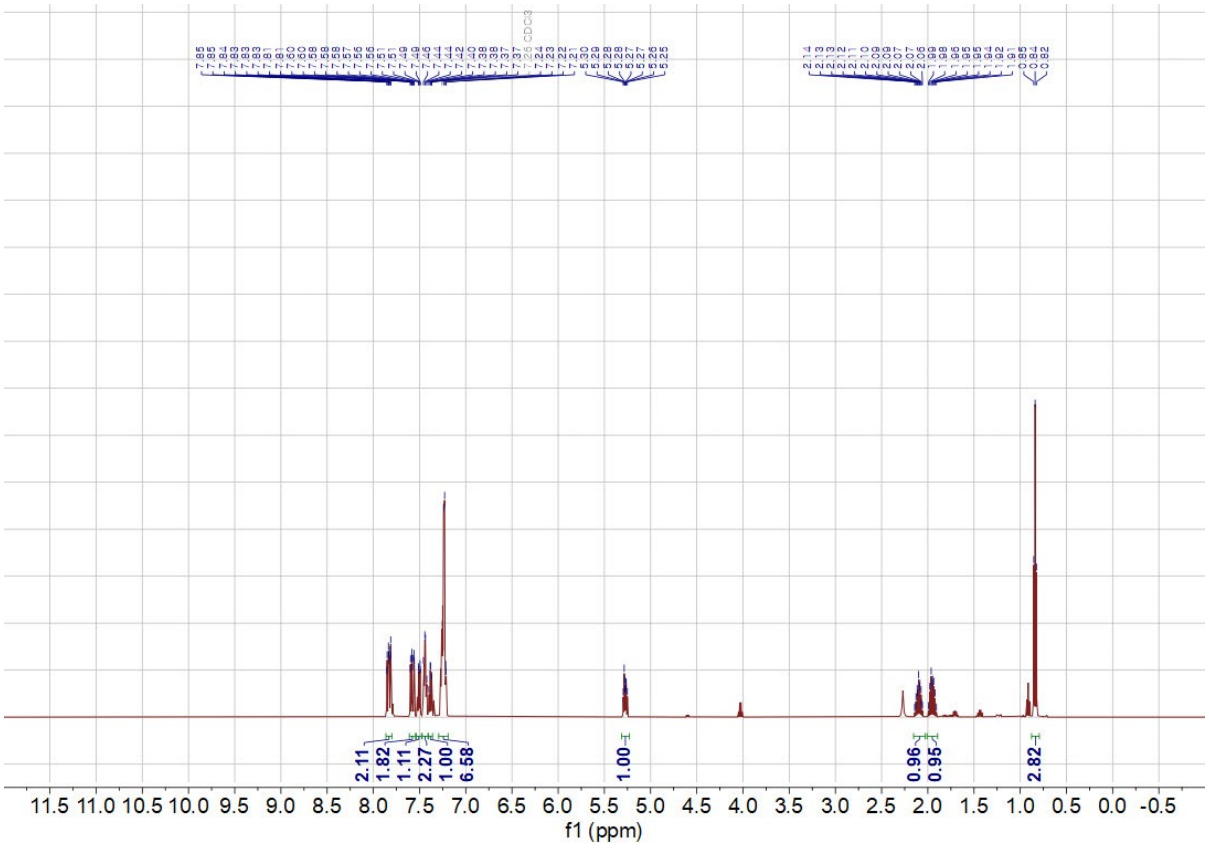
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **5-sub**



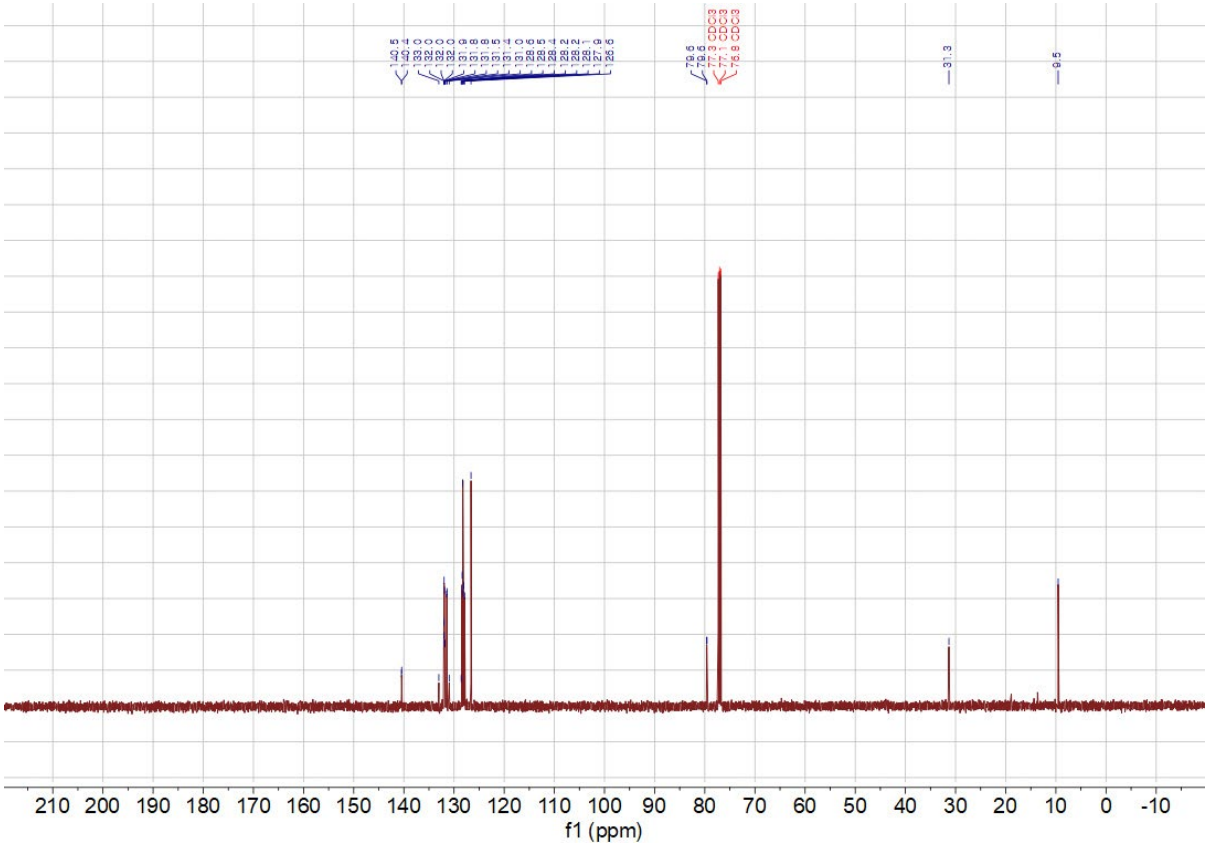

$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **5-sub**



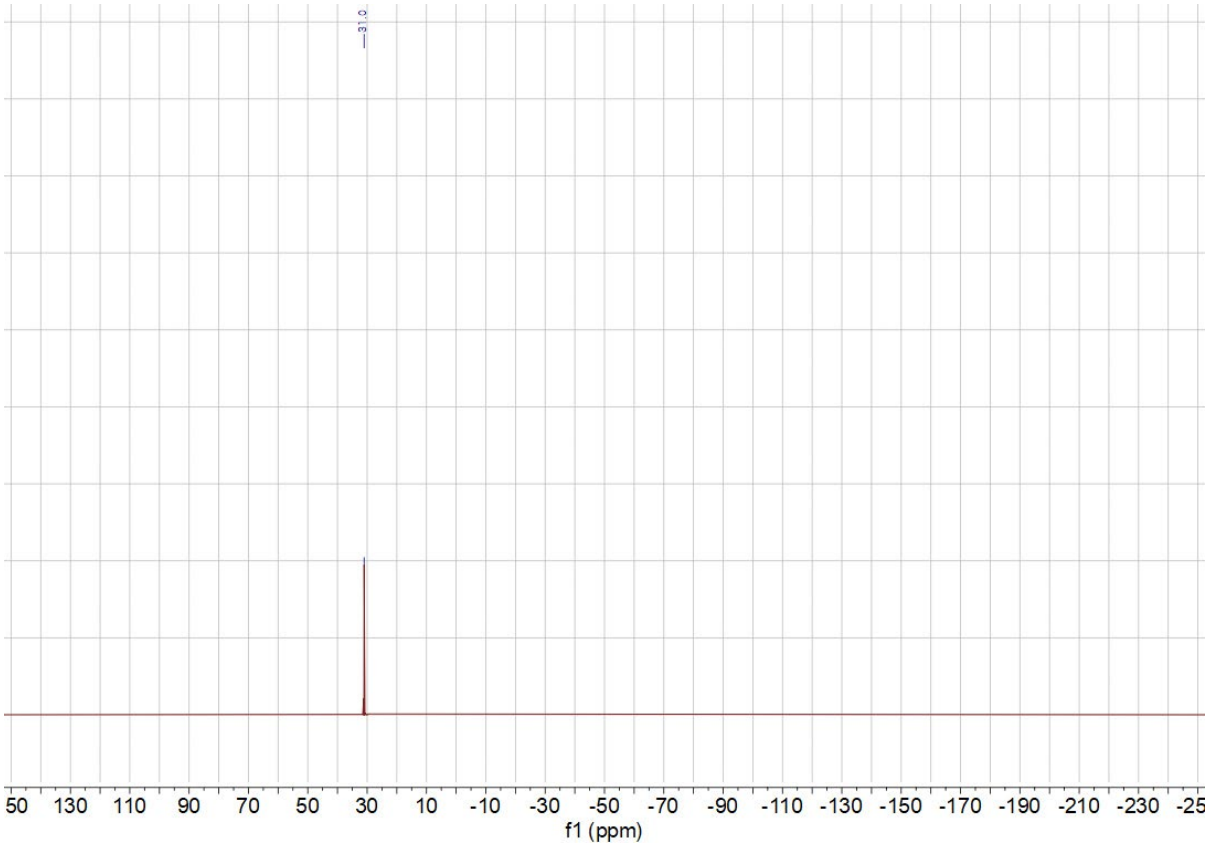
$^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **6-sub**



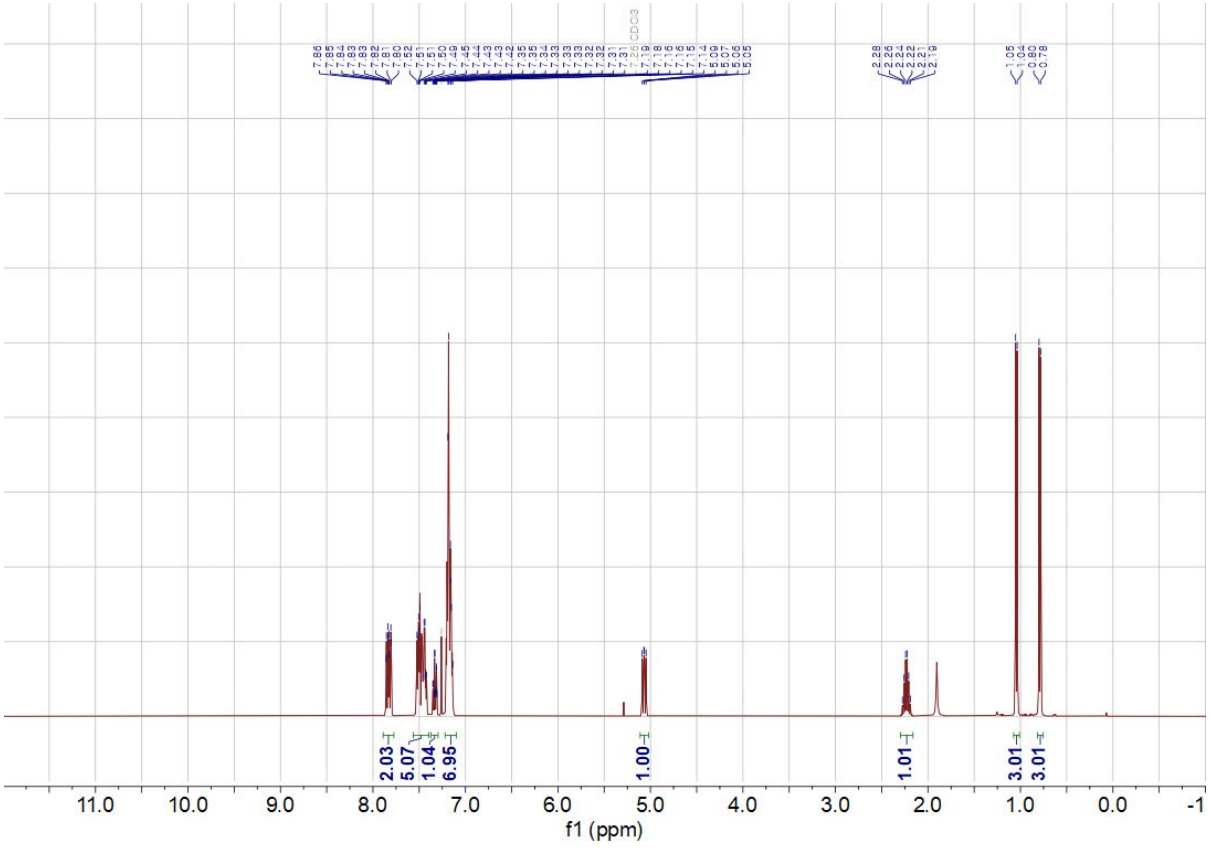

$^{13}$C{$^{1}$H} NMR spectrum (126 MHz, $CDCl_3$) of **6-sub**



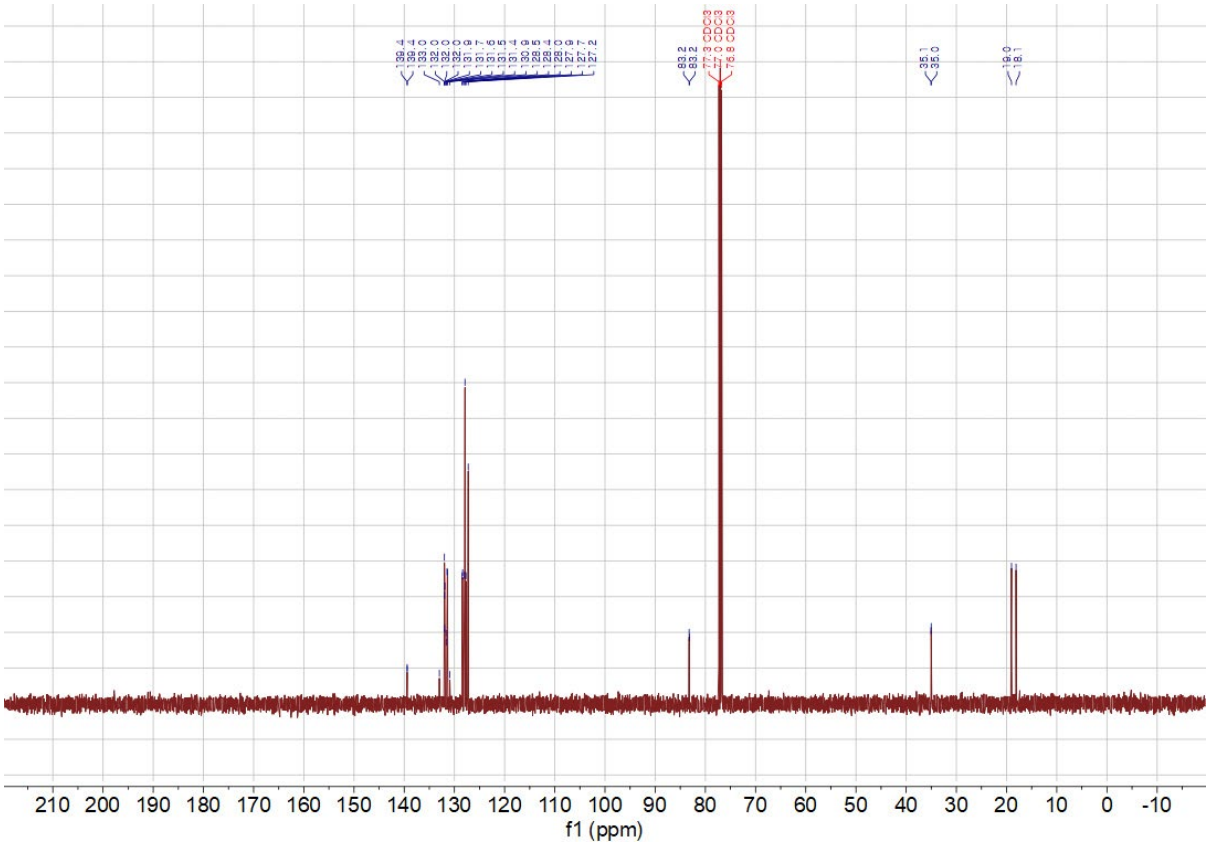
$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **6-sub**



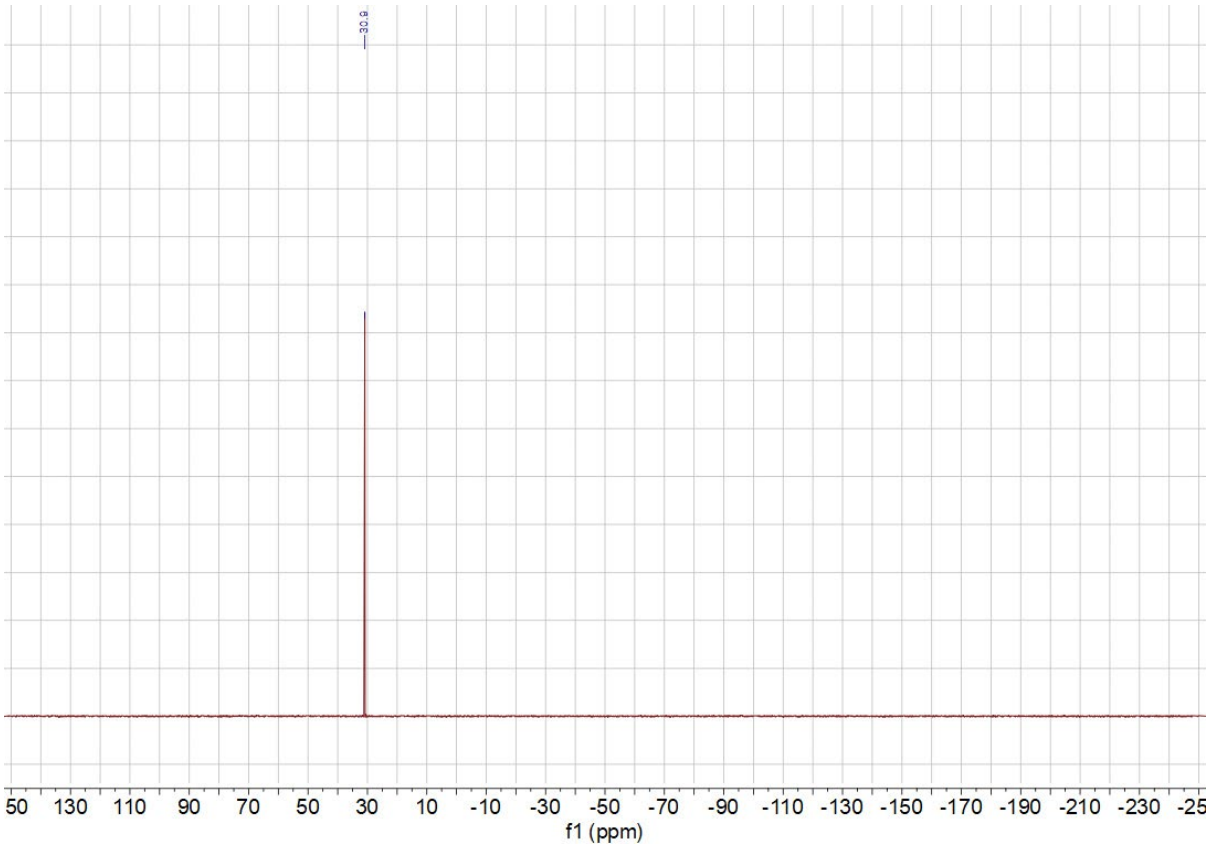

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **7-sub**



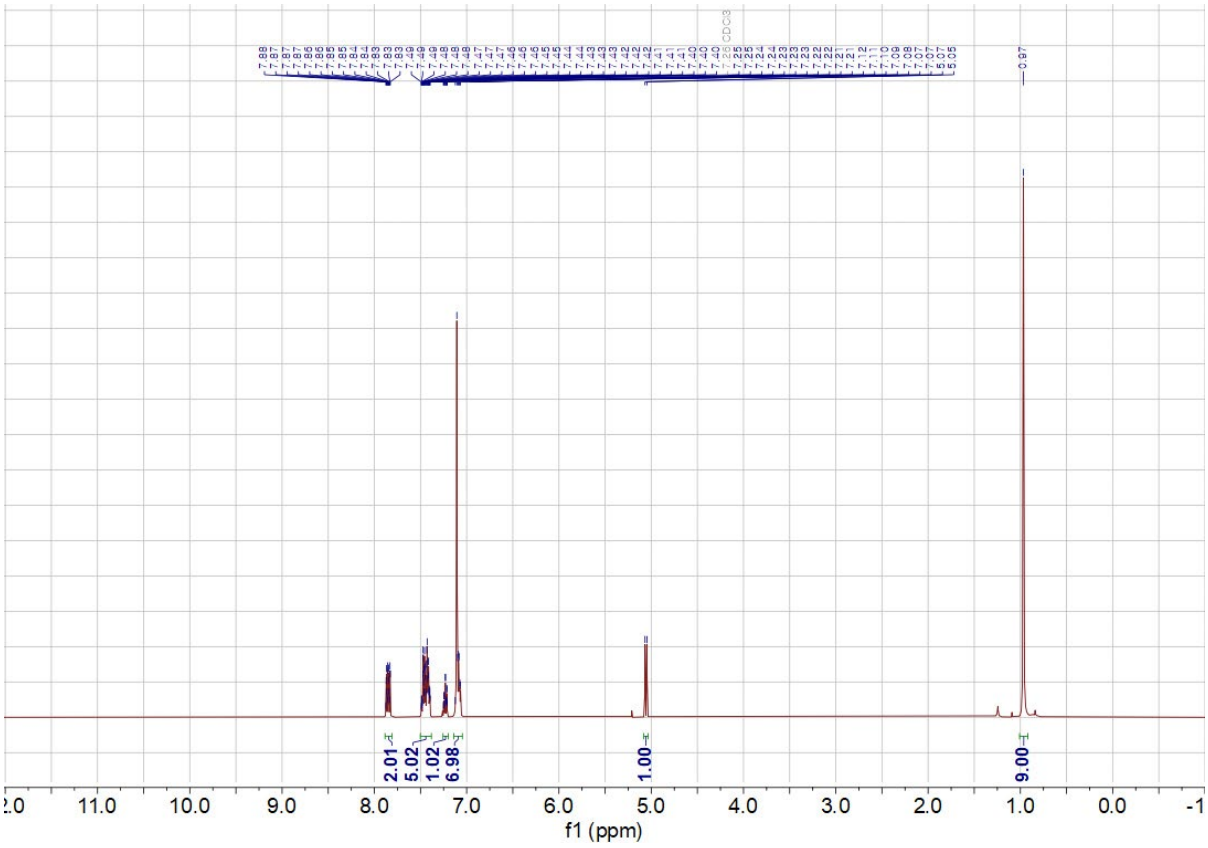
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **7-sub**



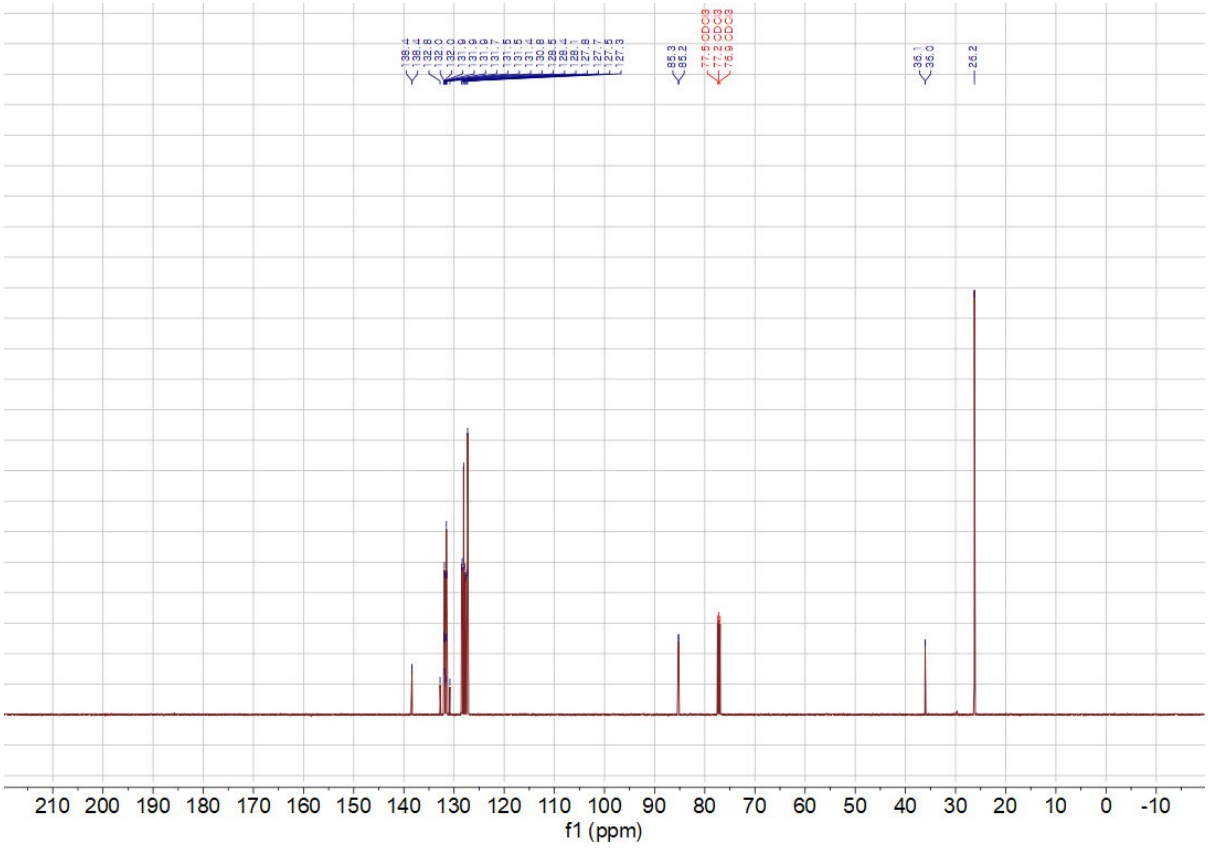

$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **7-sub**



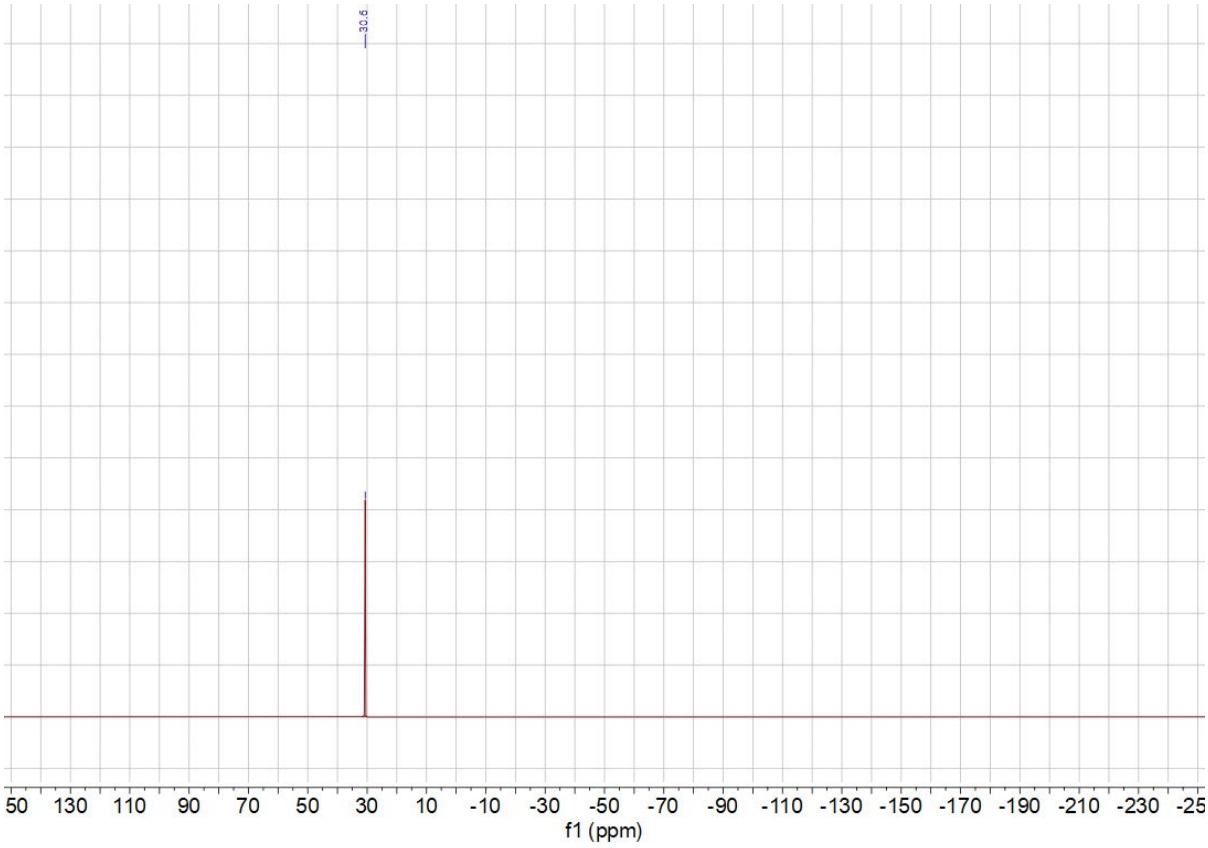
s1H NMR spectrum (500 MHz, $CDCl_3$) of **8-sub**



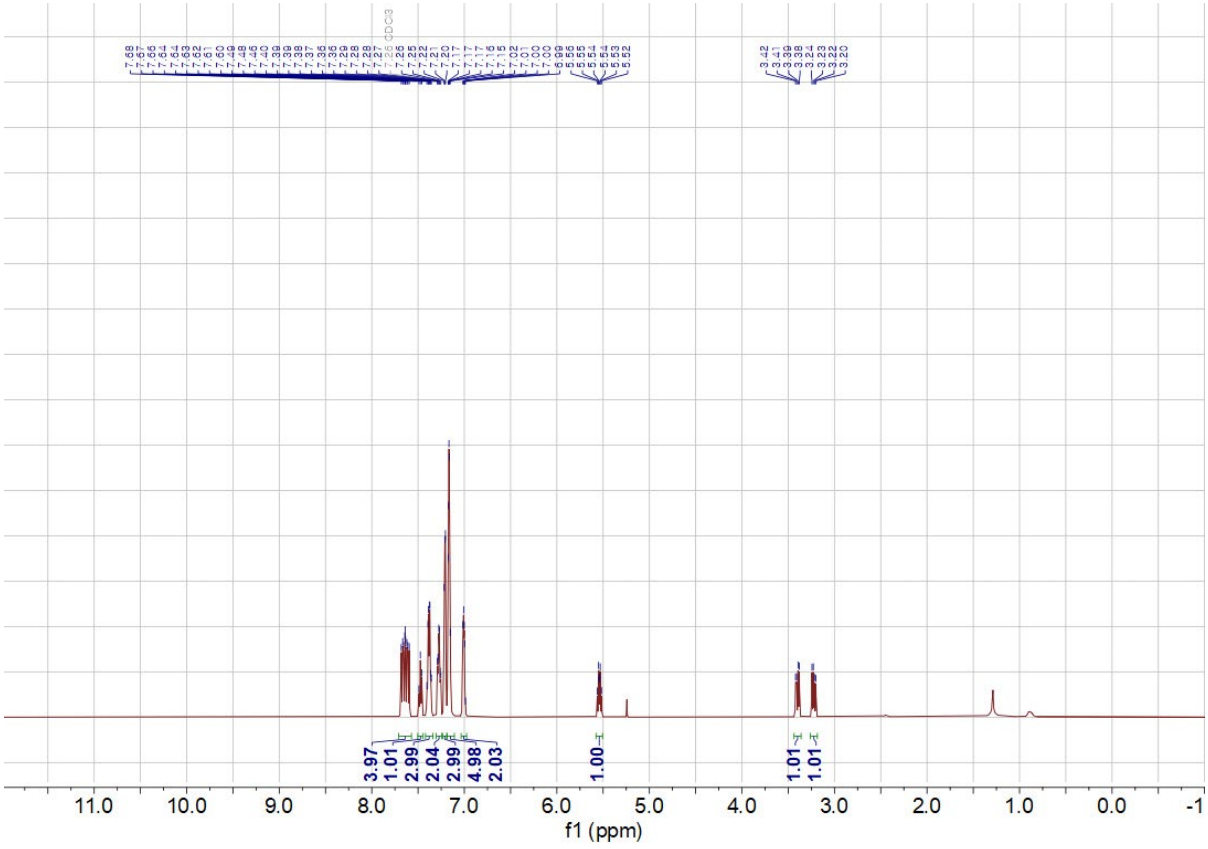

$^{13}C\{^1H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **8-sub**



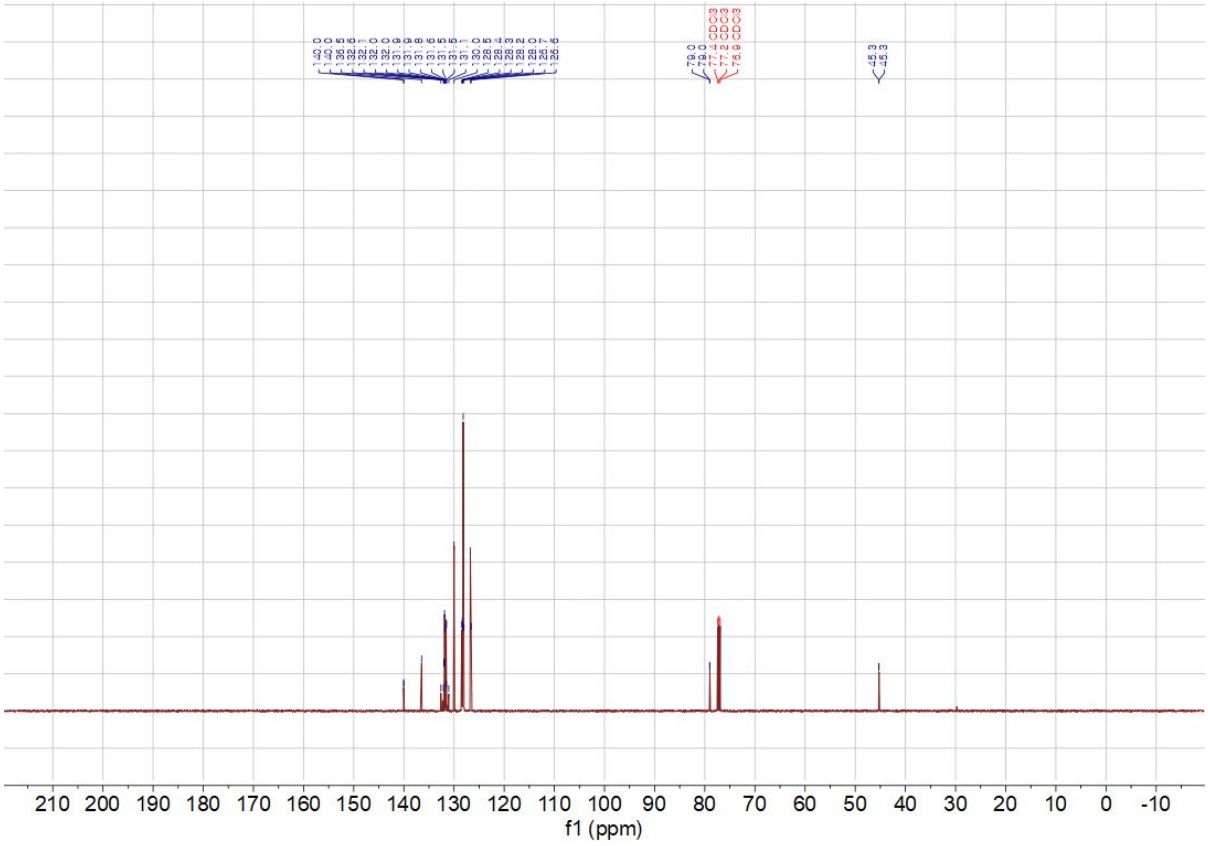
$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **8-sub**



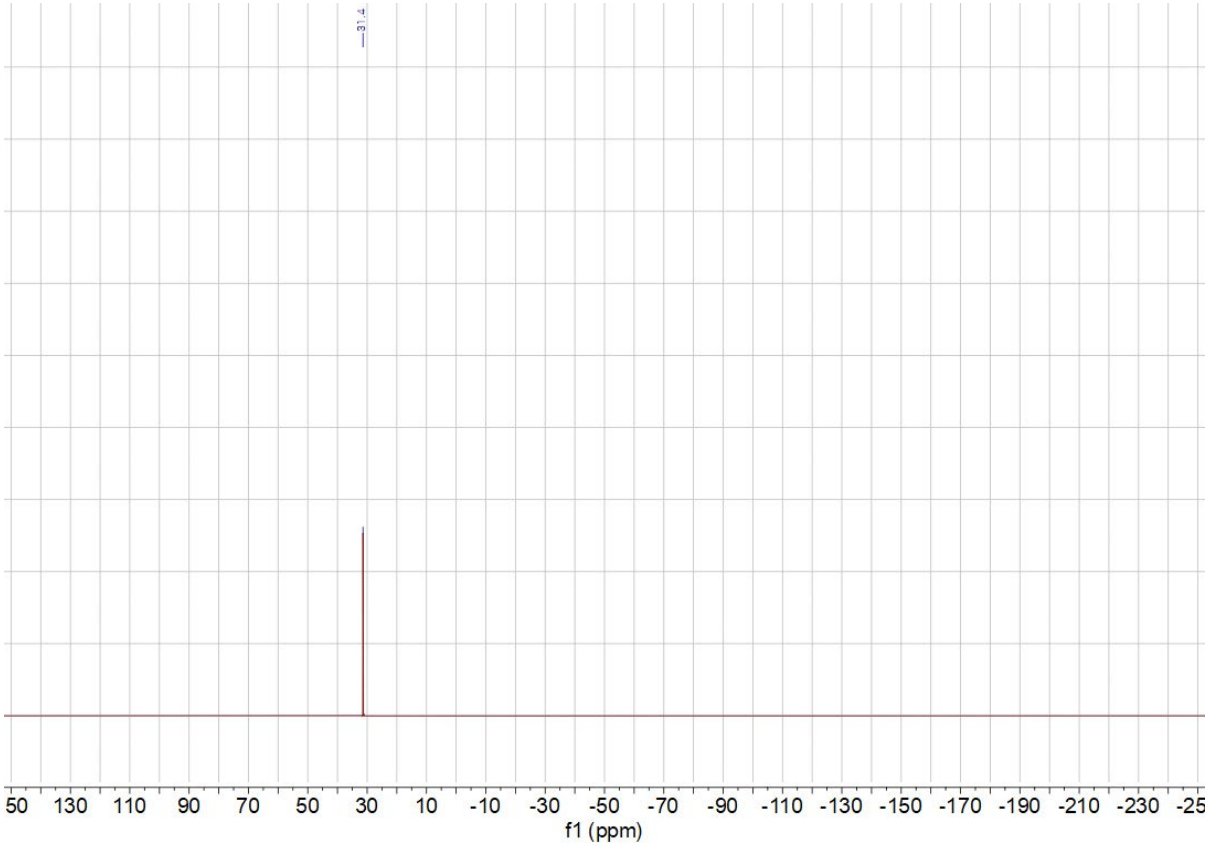

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **9-sub**



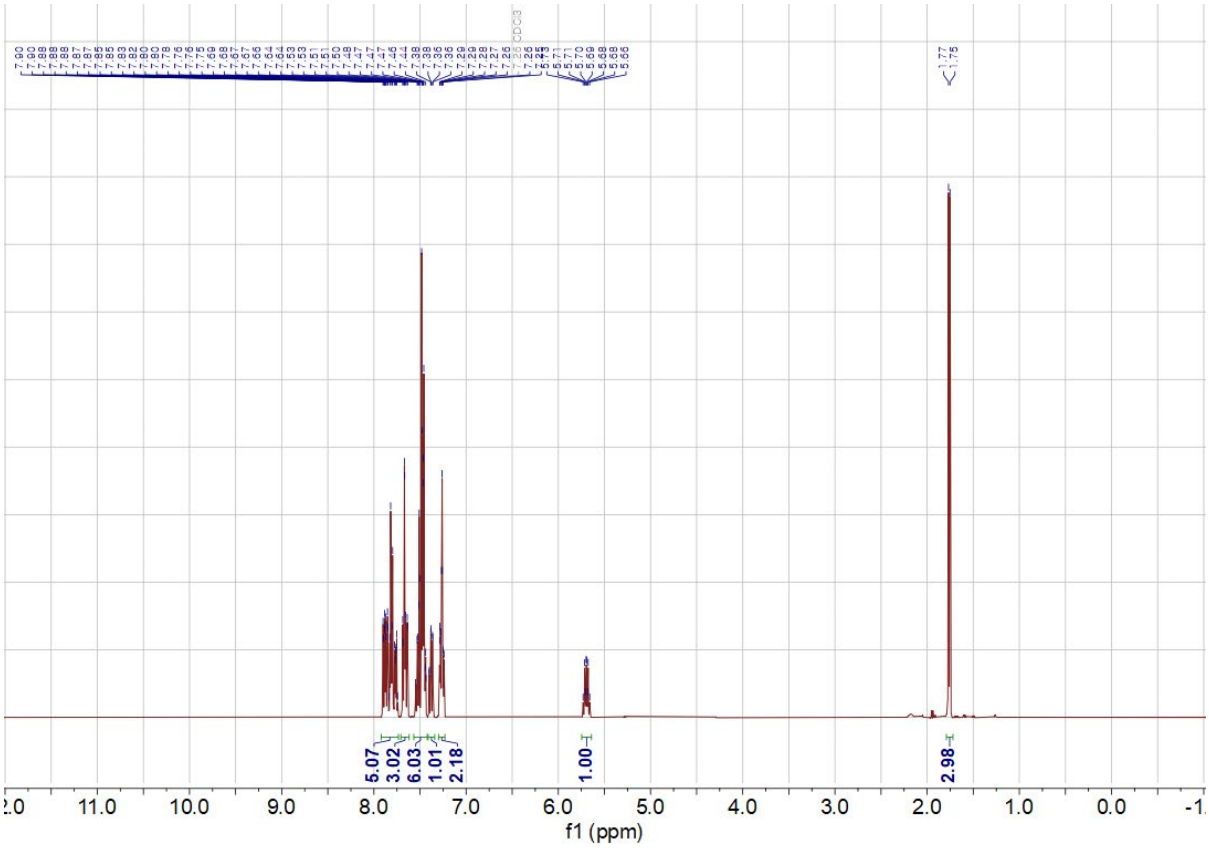
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **9-sub**



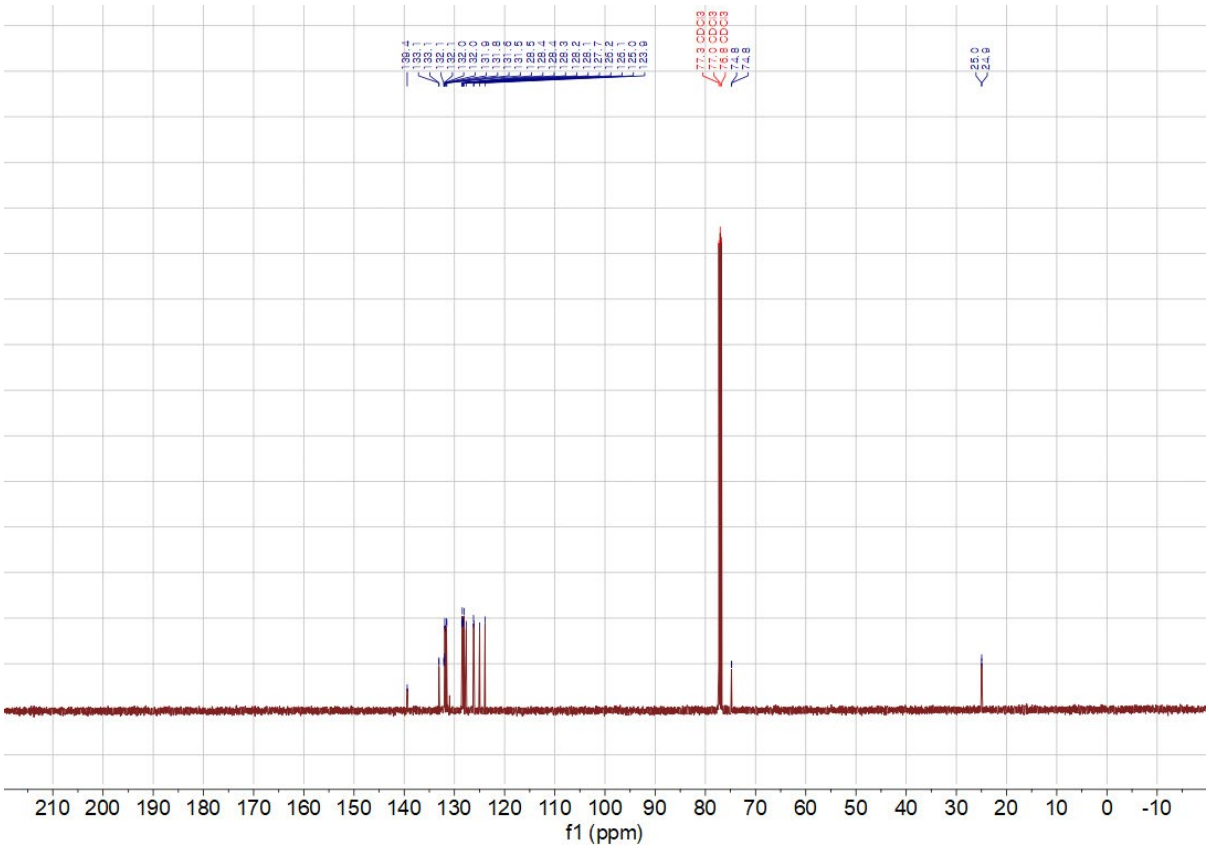

$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **9-sub**



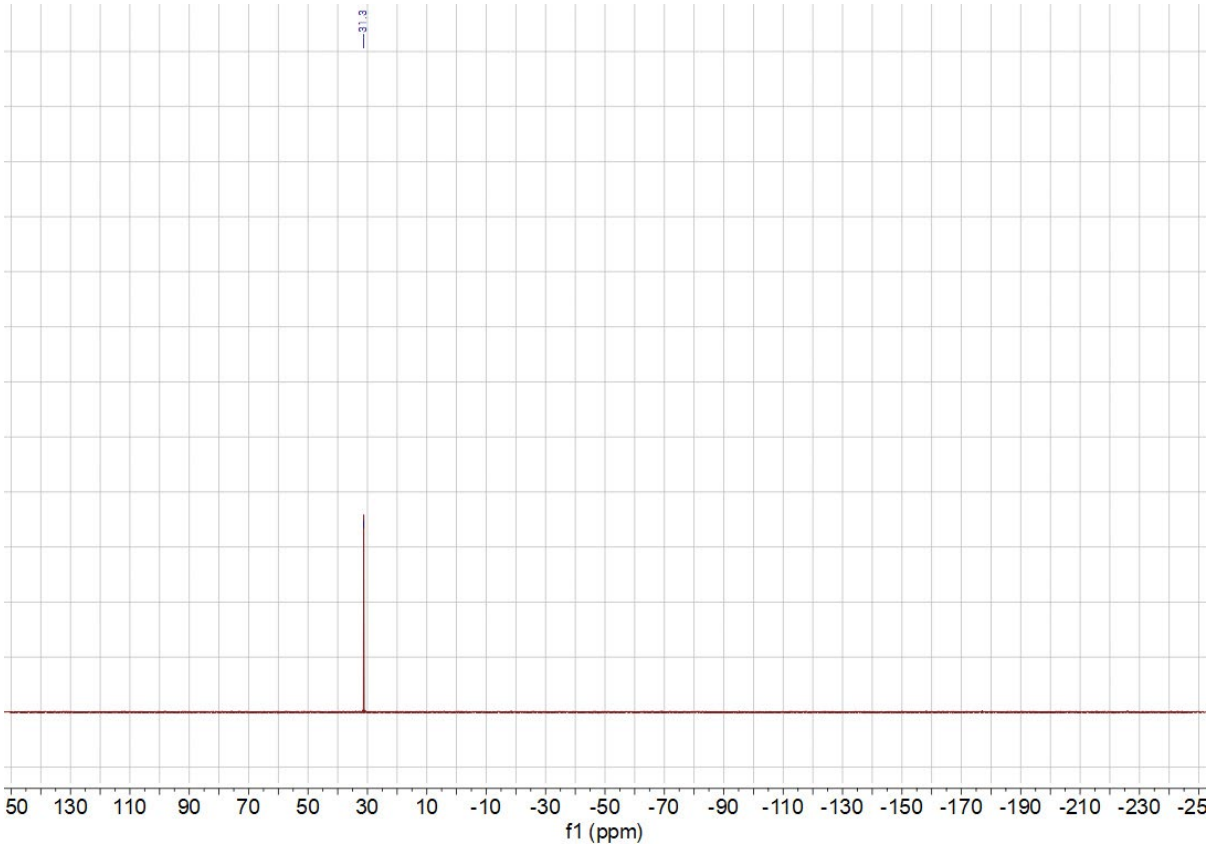
$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **10-sub**



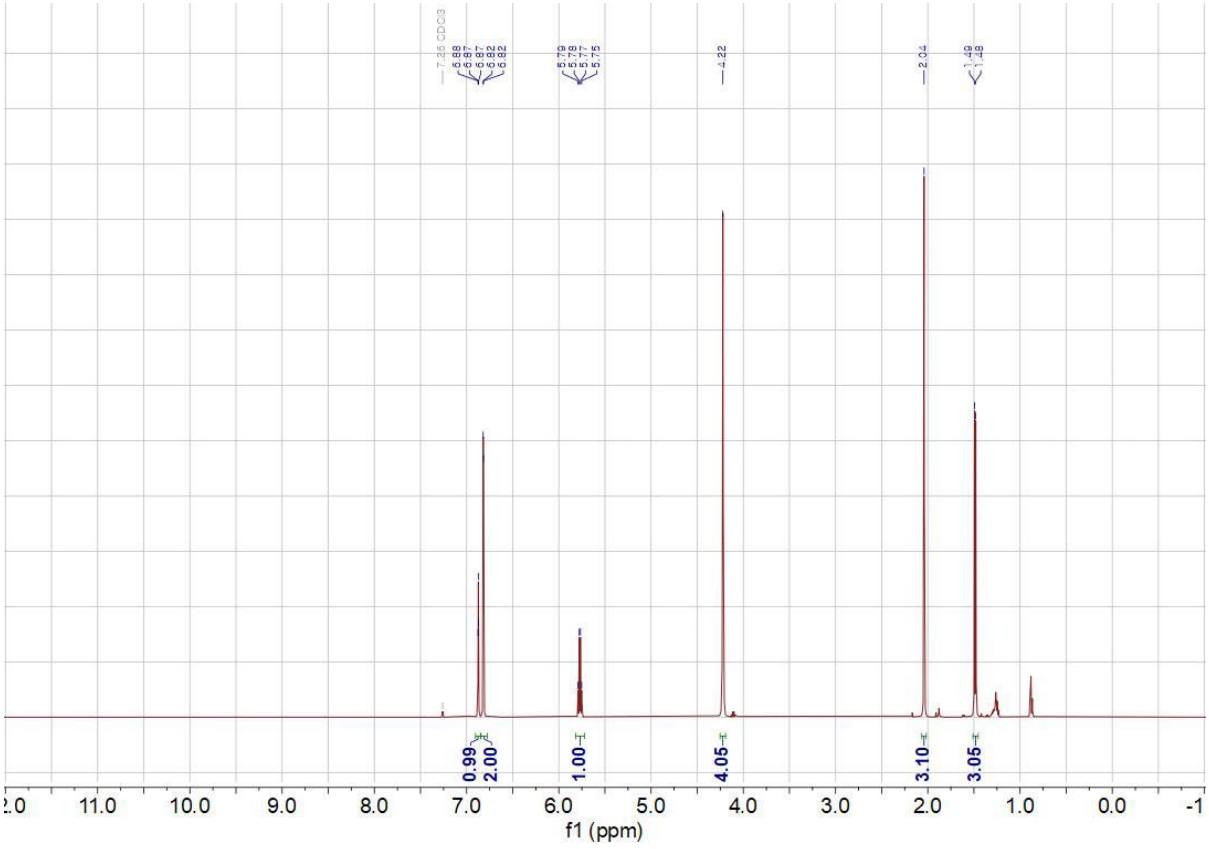

$^{13}$C{$^{1}$H} NMR spectrum (126 MHz, $CDCl_3$) of **10-sub**



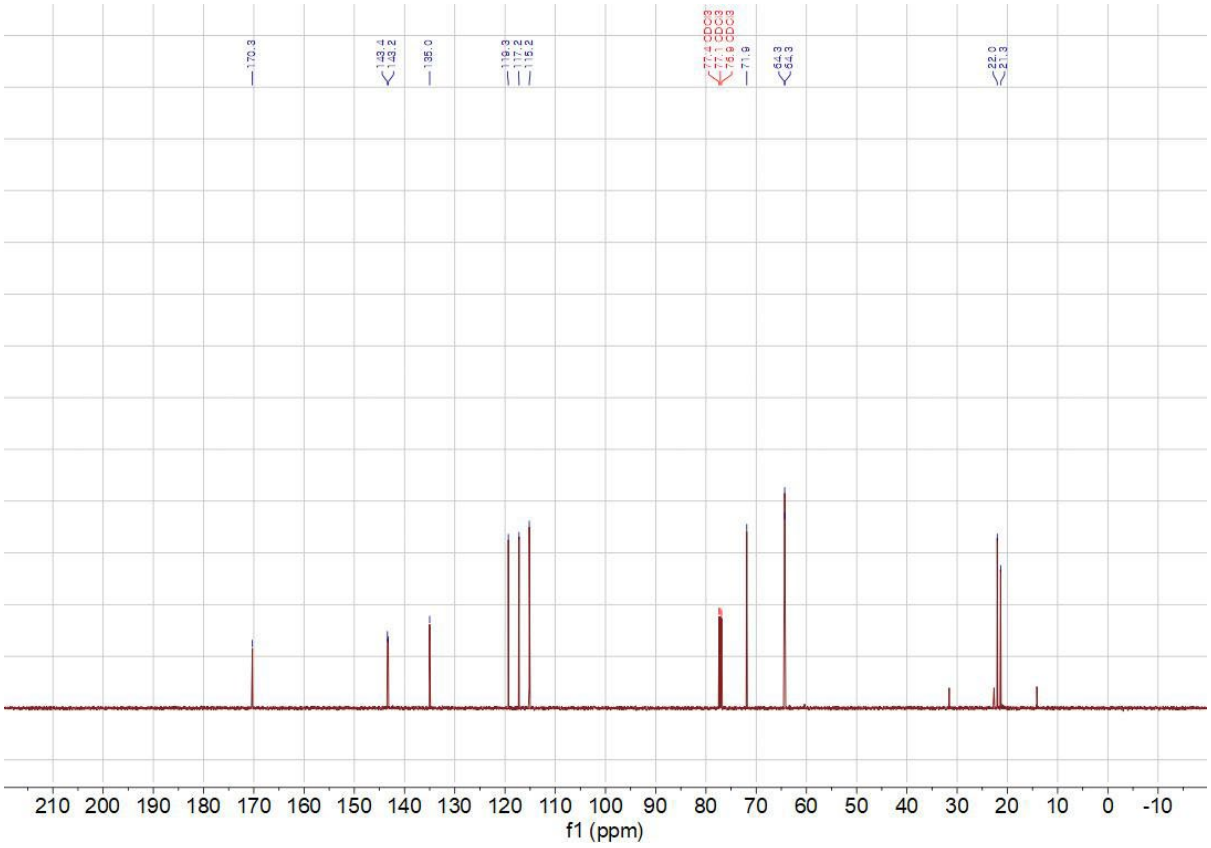
$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **10-sub**



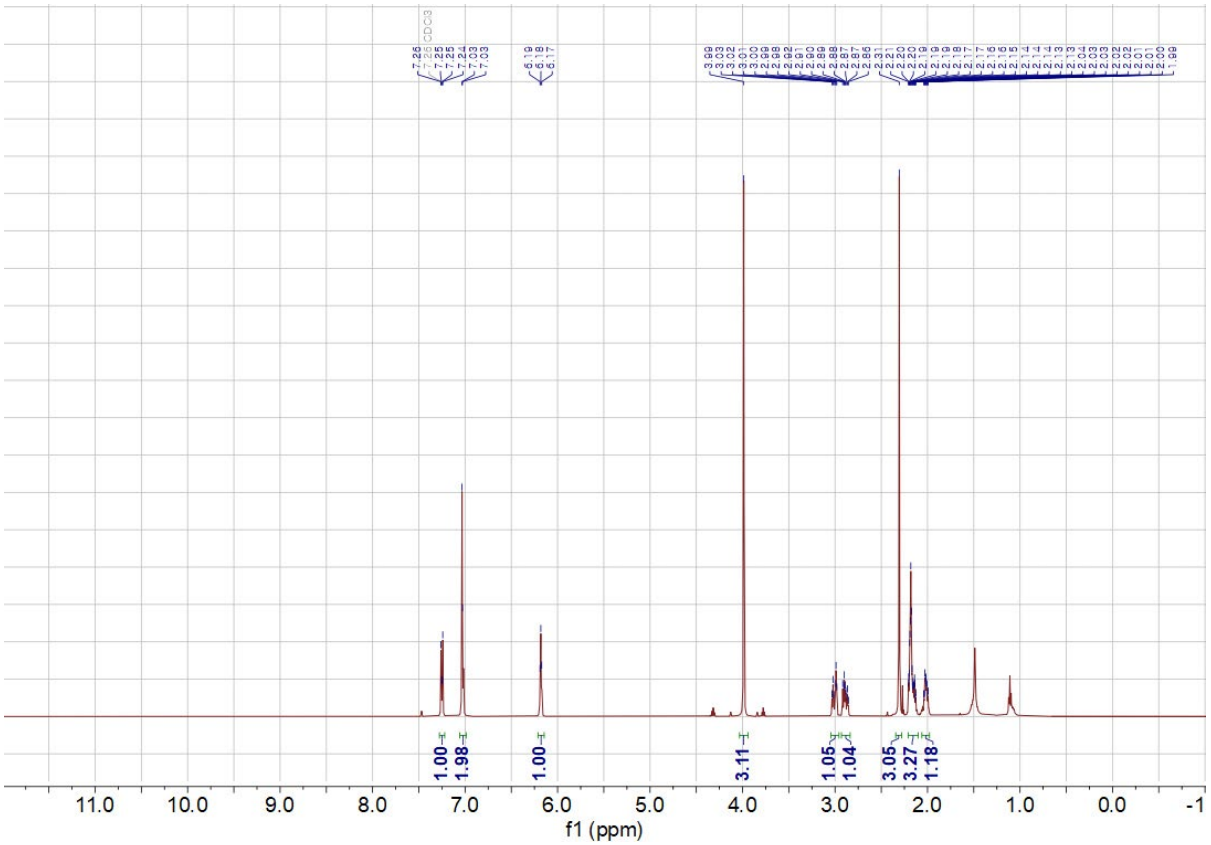

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **11-sub**



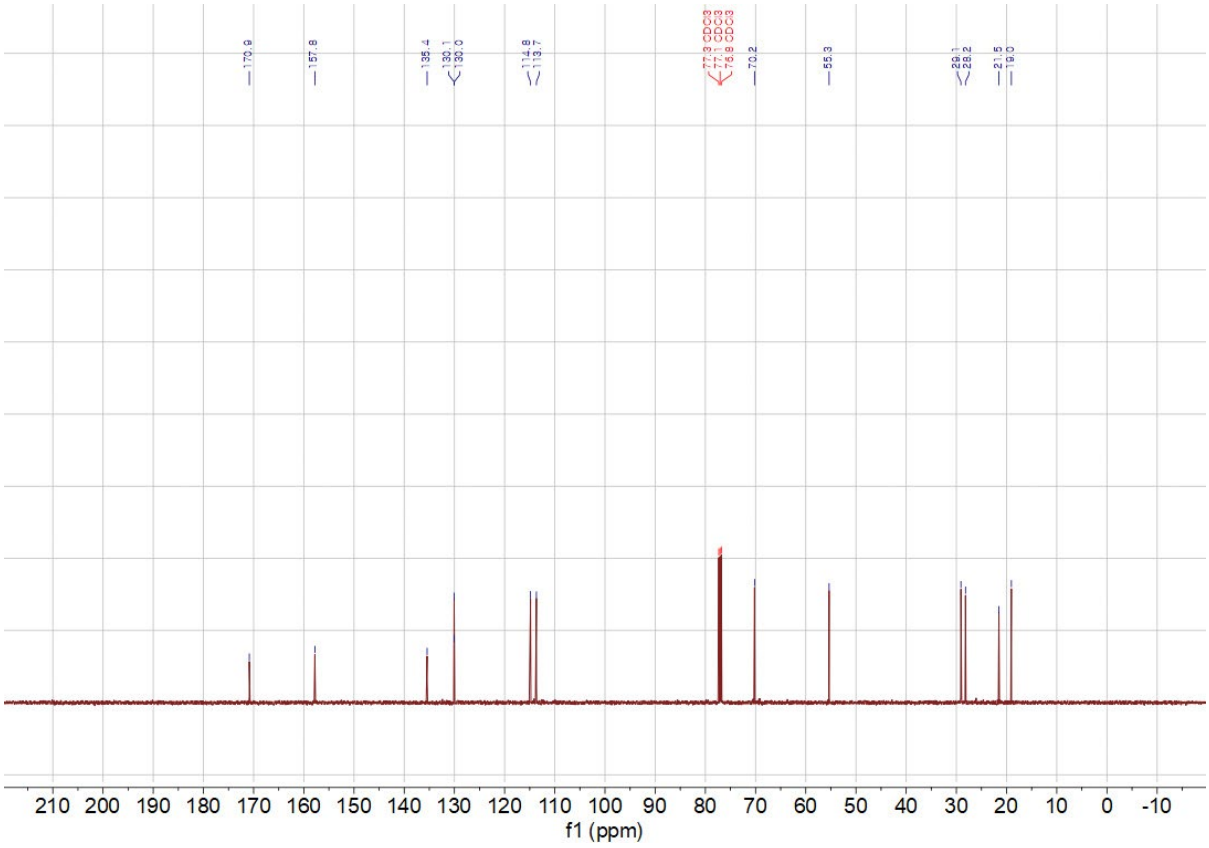
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **11-sub**



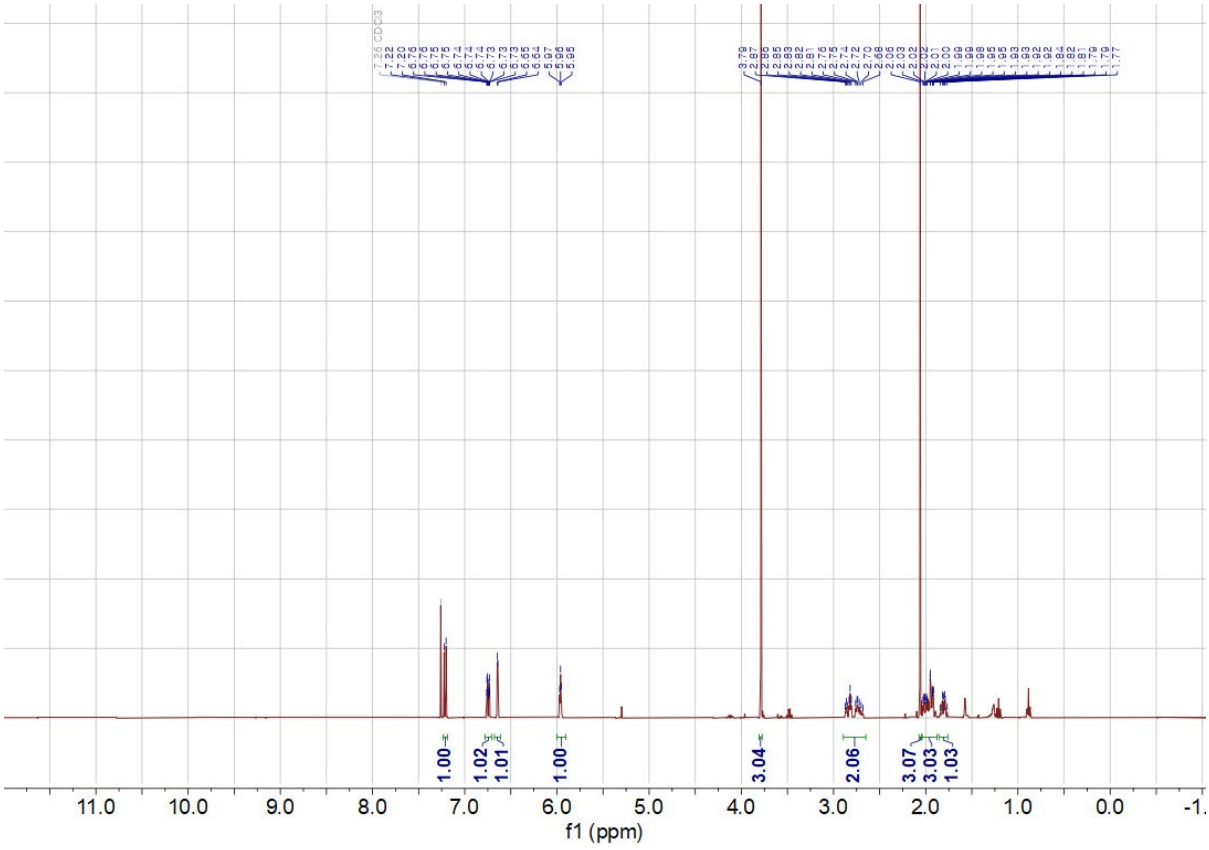

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **12-sub**



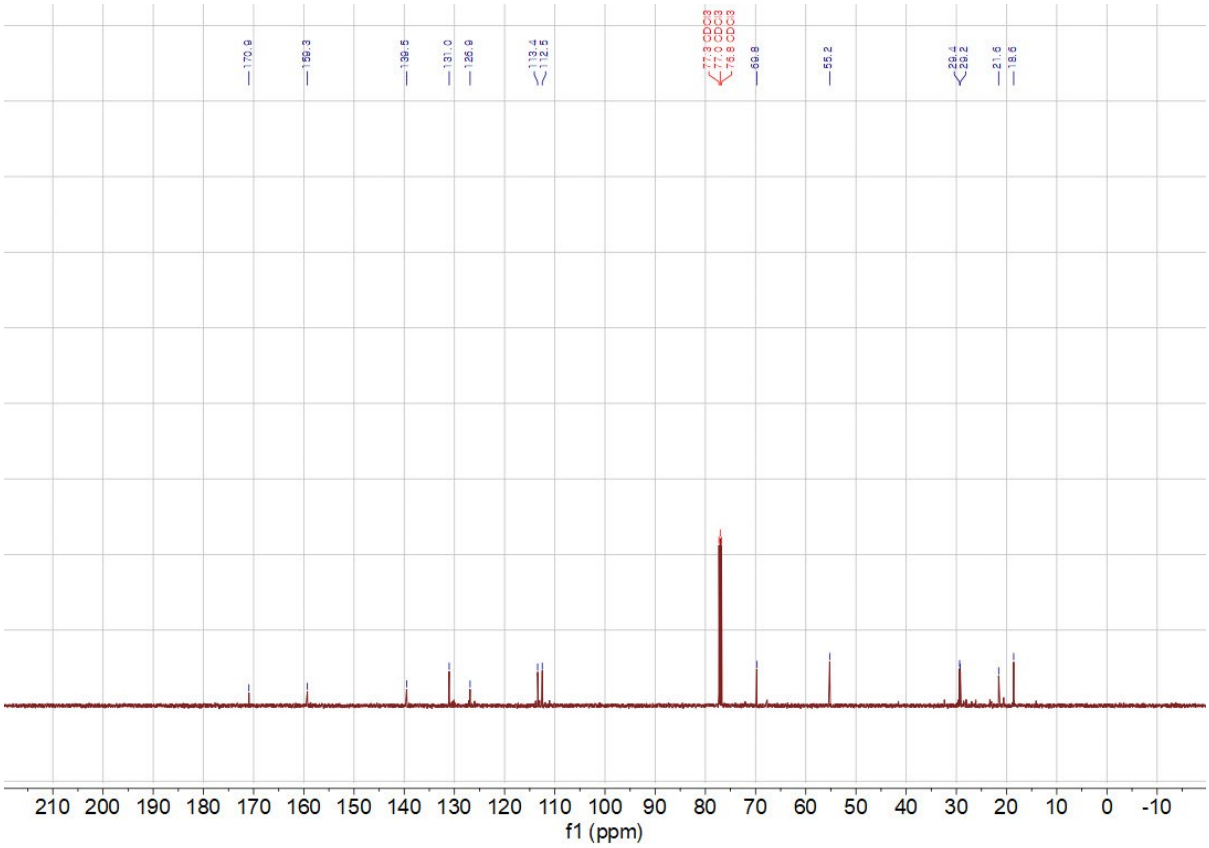
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **12-sub**



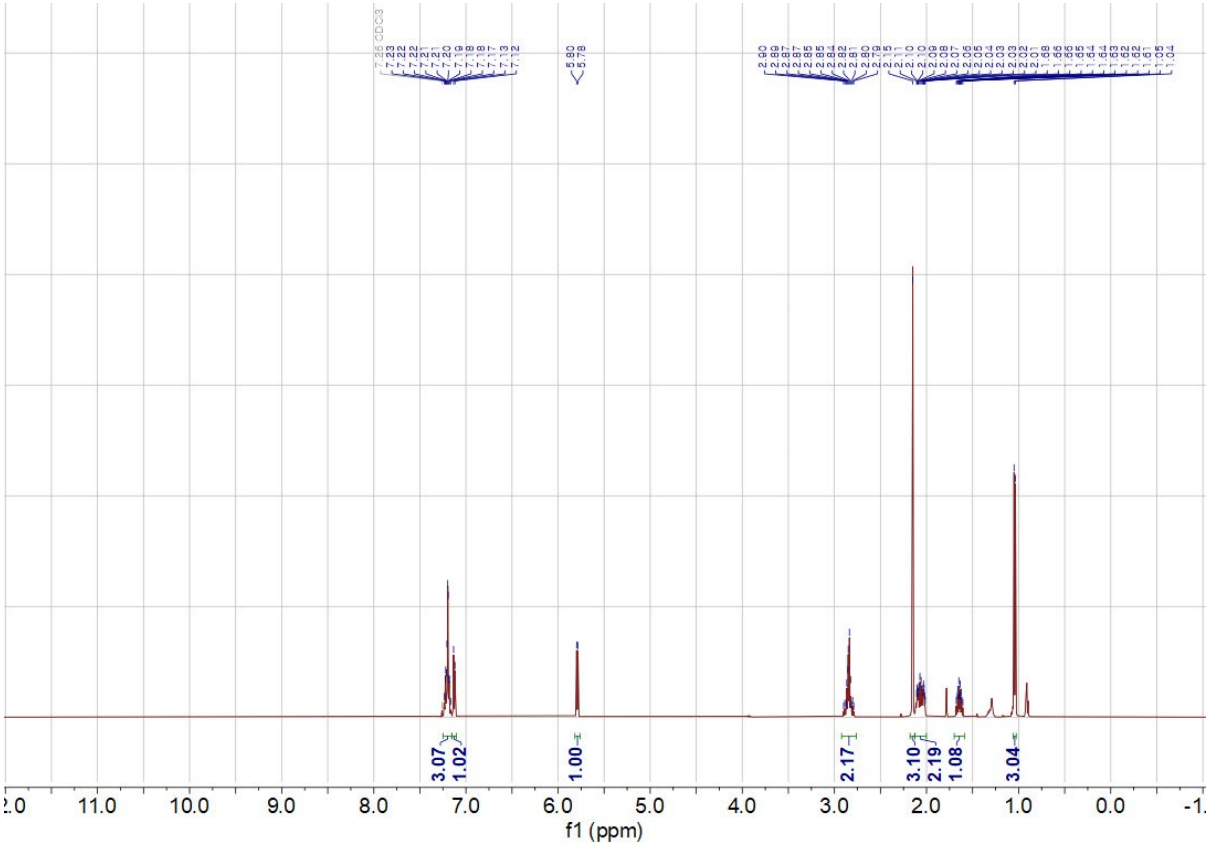

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **13-sub**



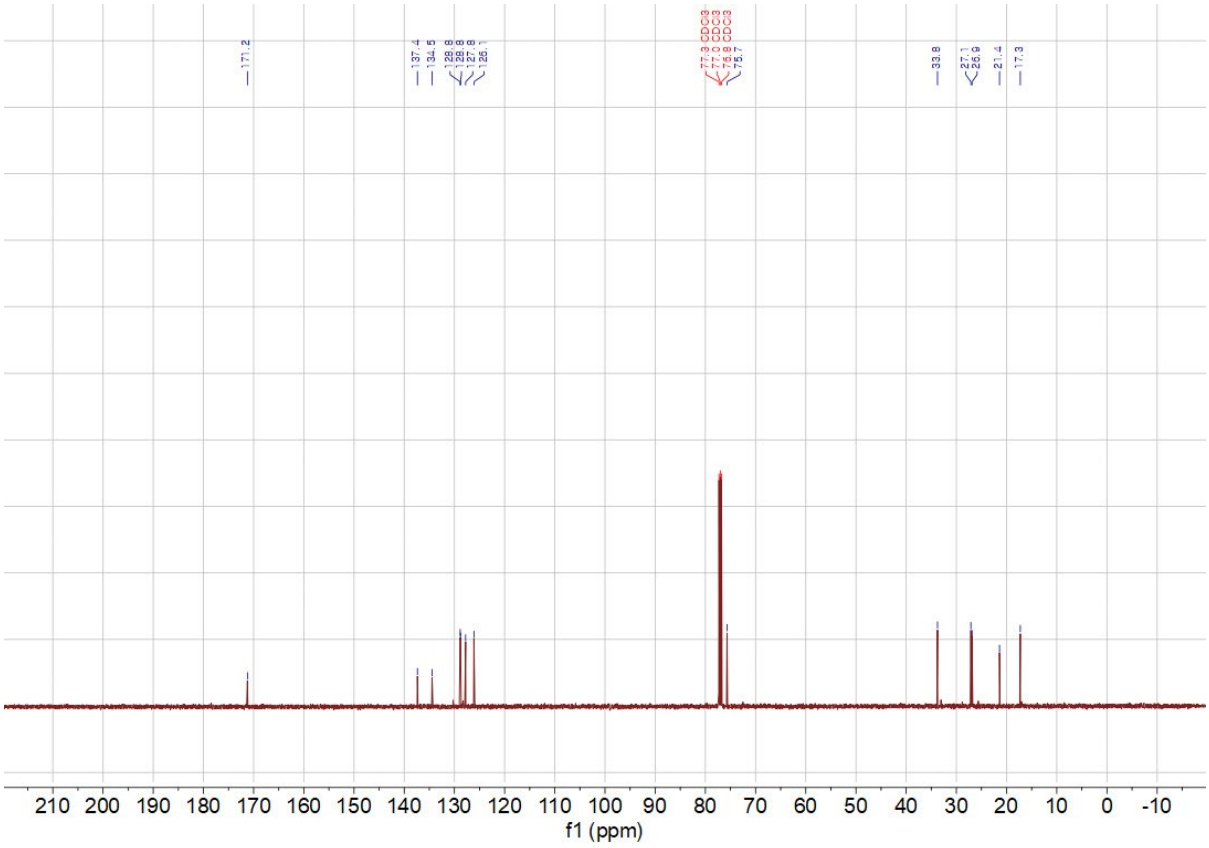
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **13-sub**



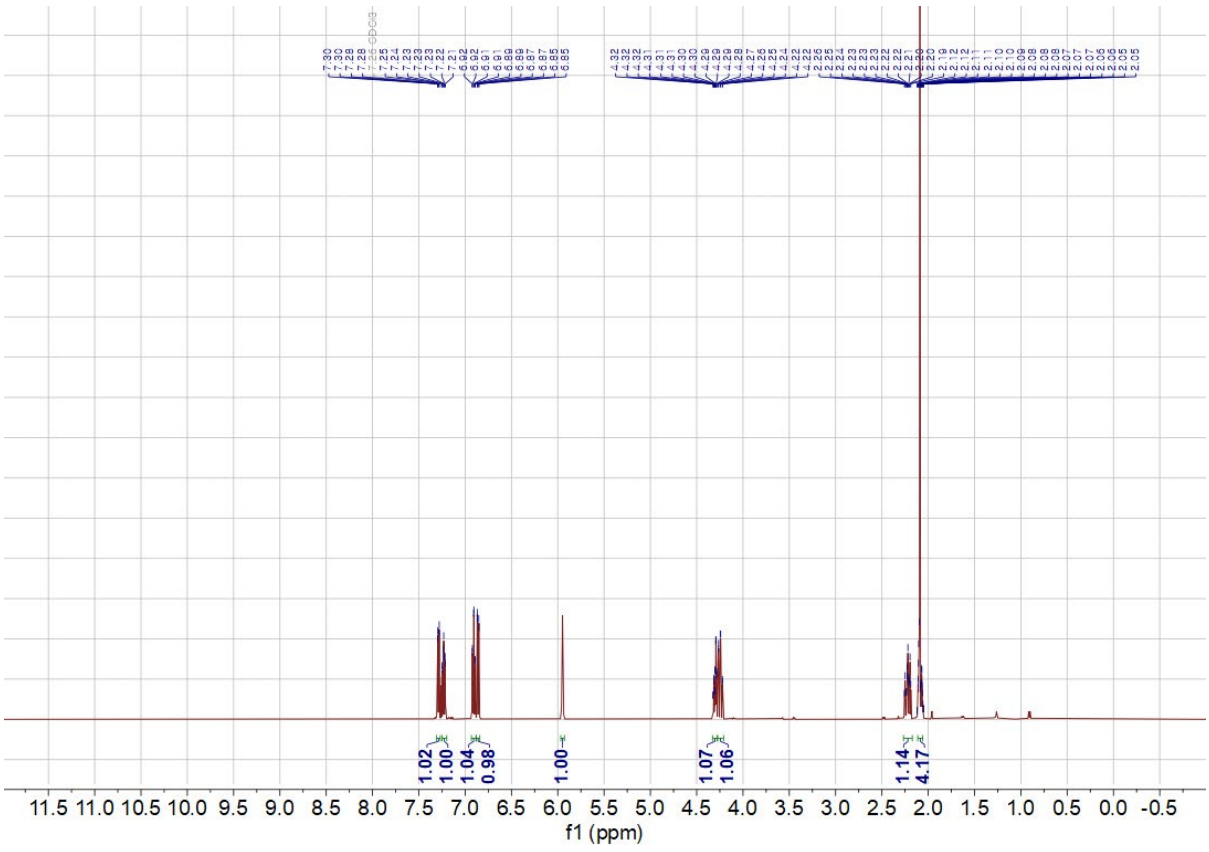

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **14-sub**



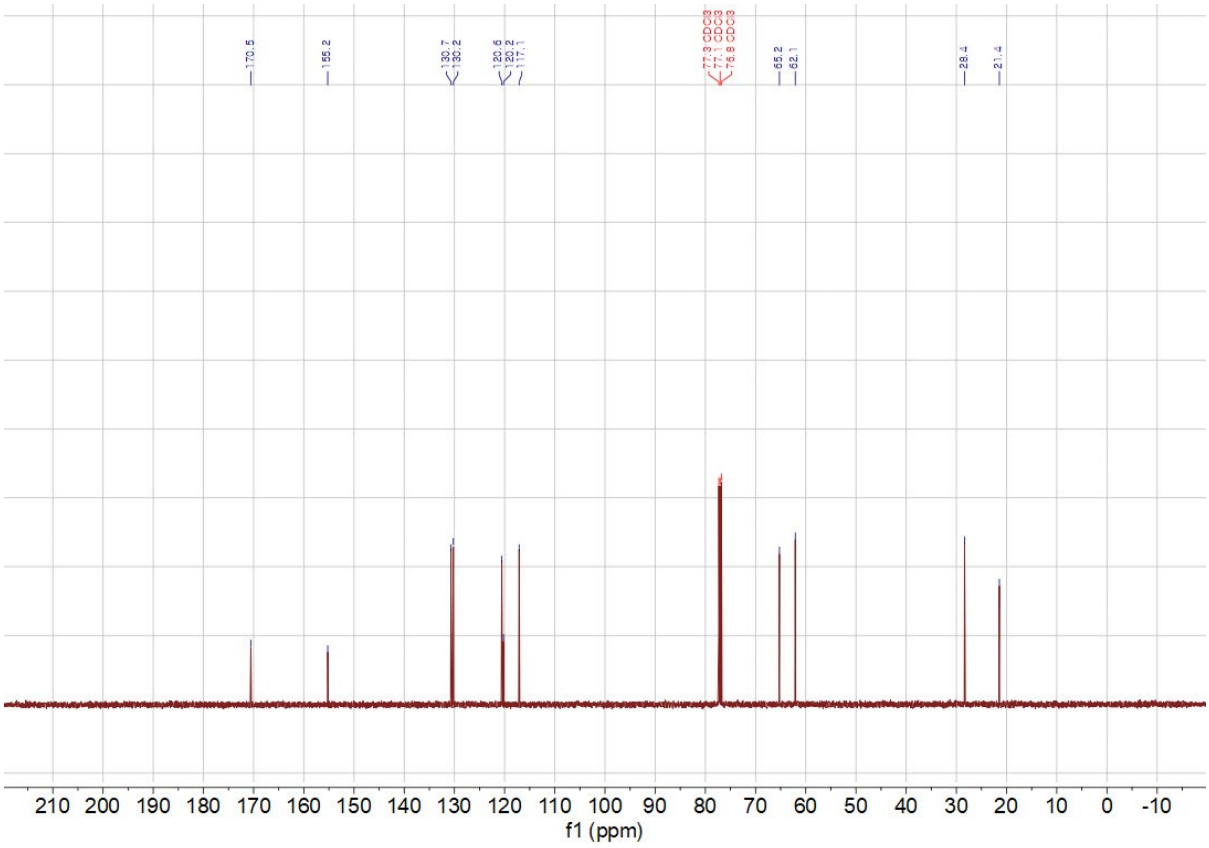
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **14-sub**



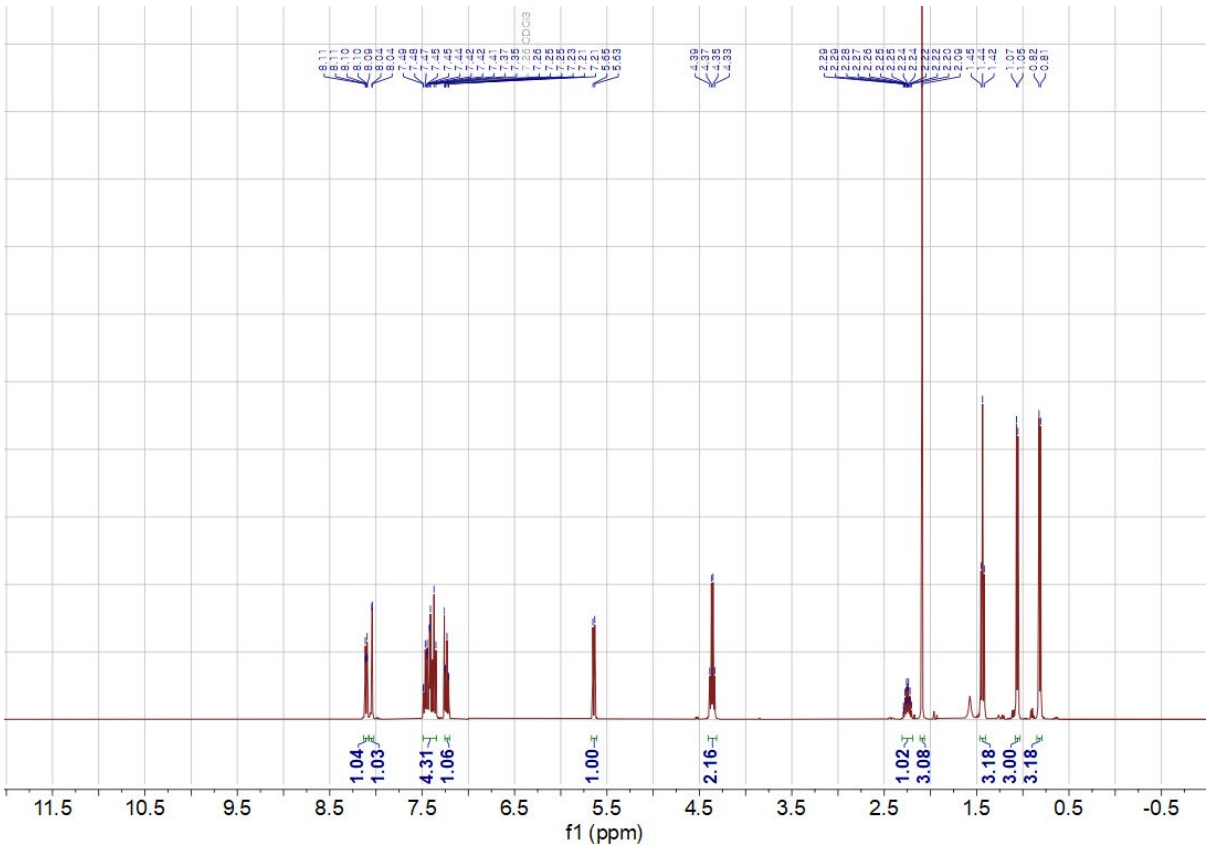

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **15-sub**



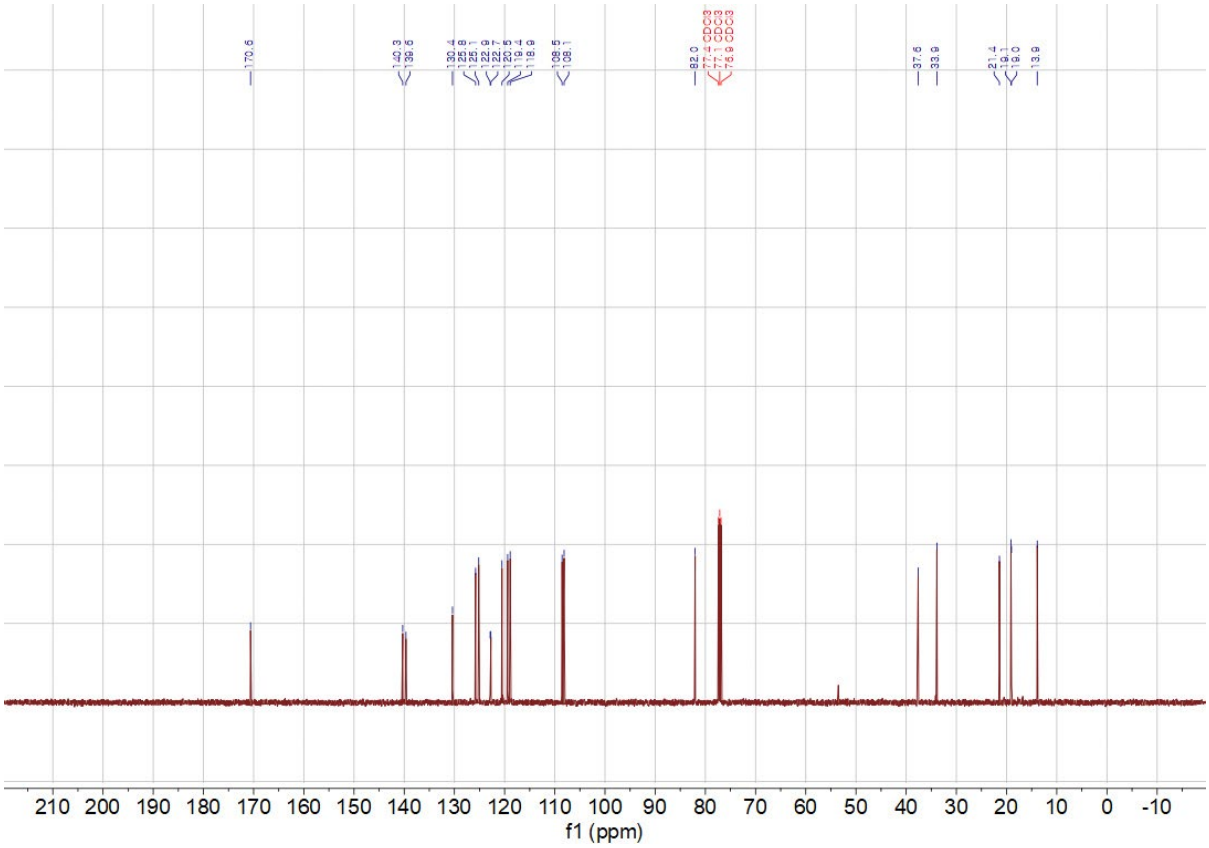
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **15-sub**



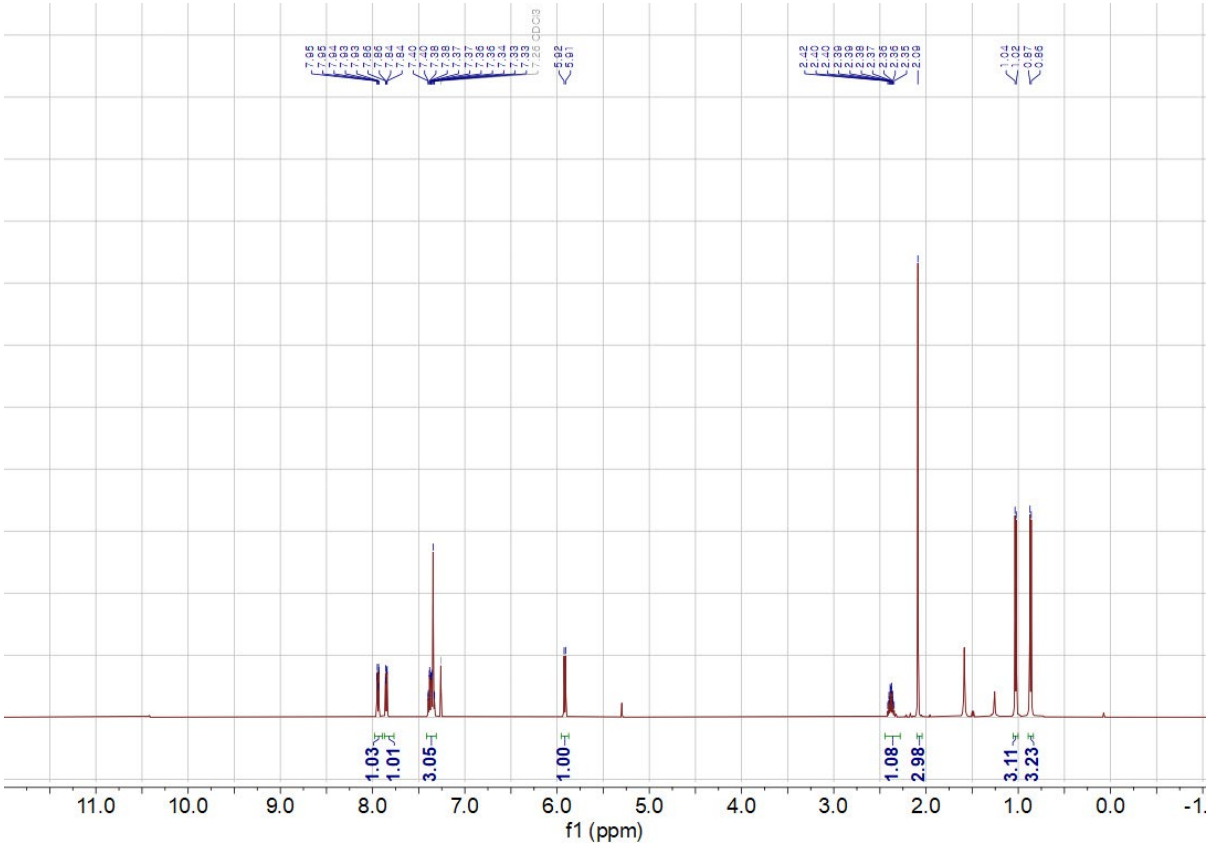

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **16-sub**



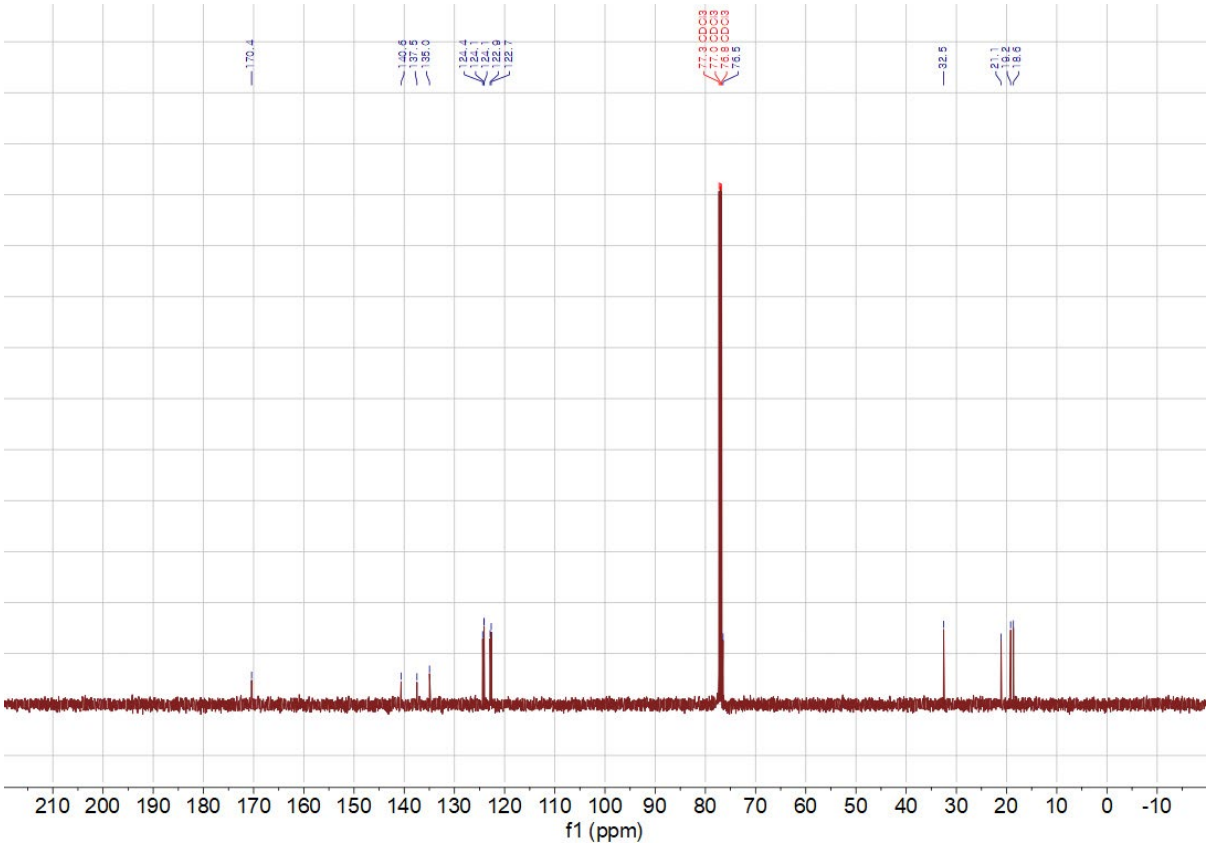
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **16-sub**



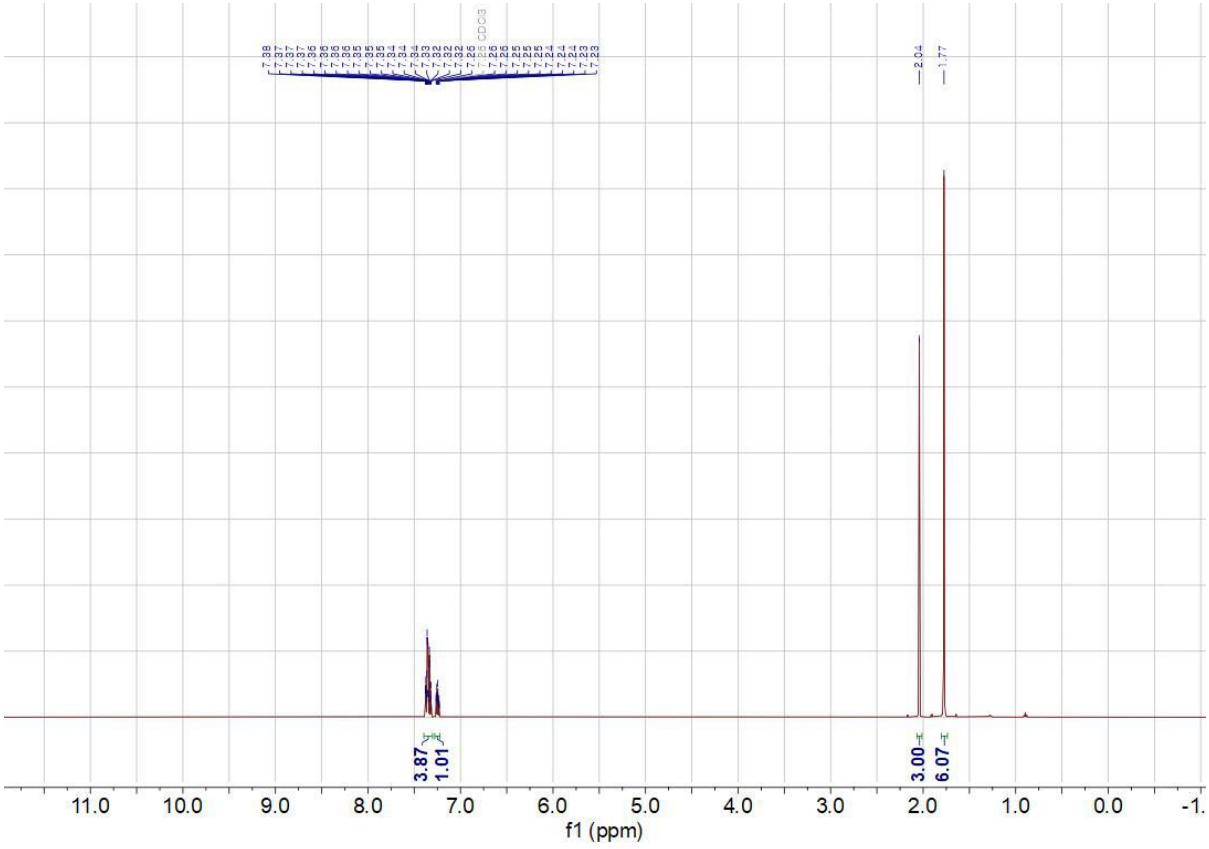

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **17-sub**



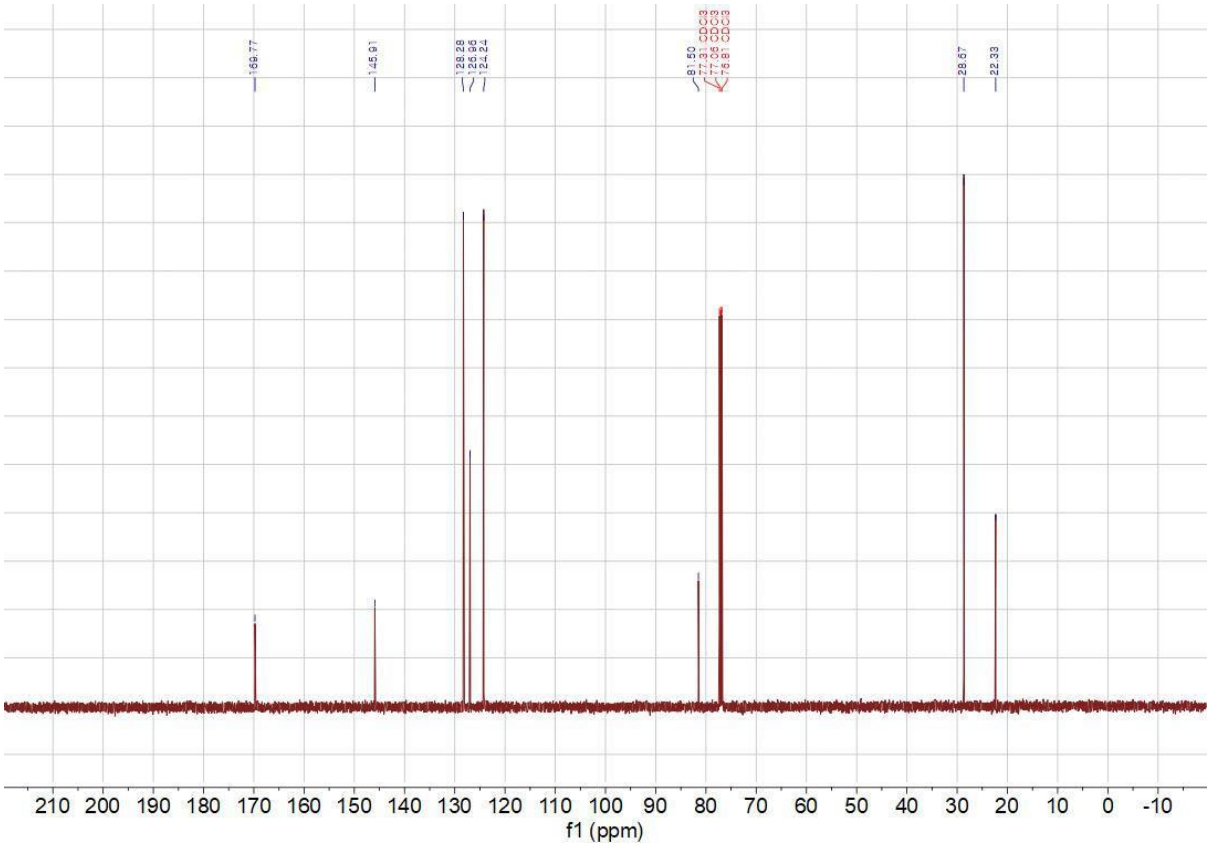
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **17-sub**



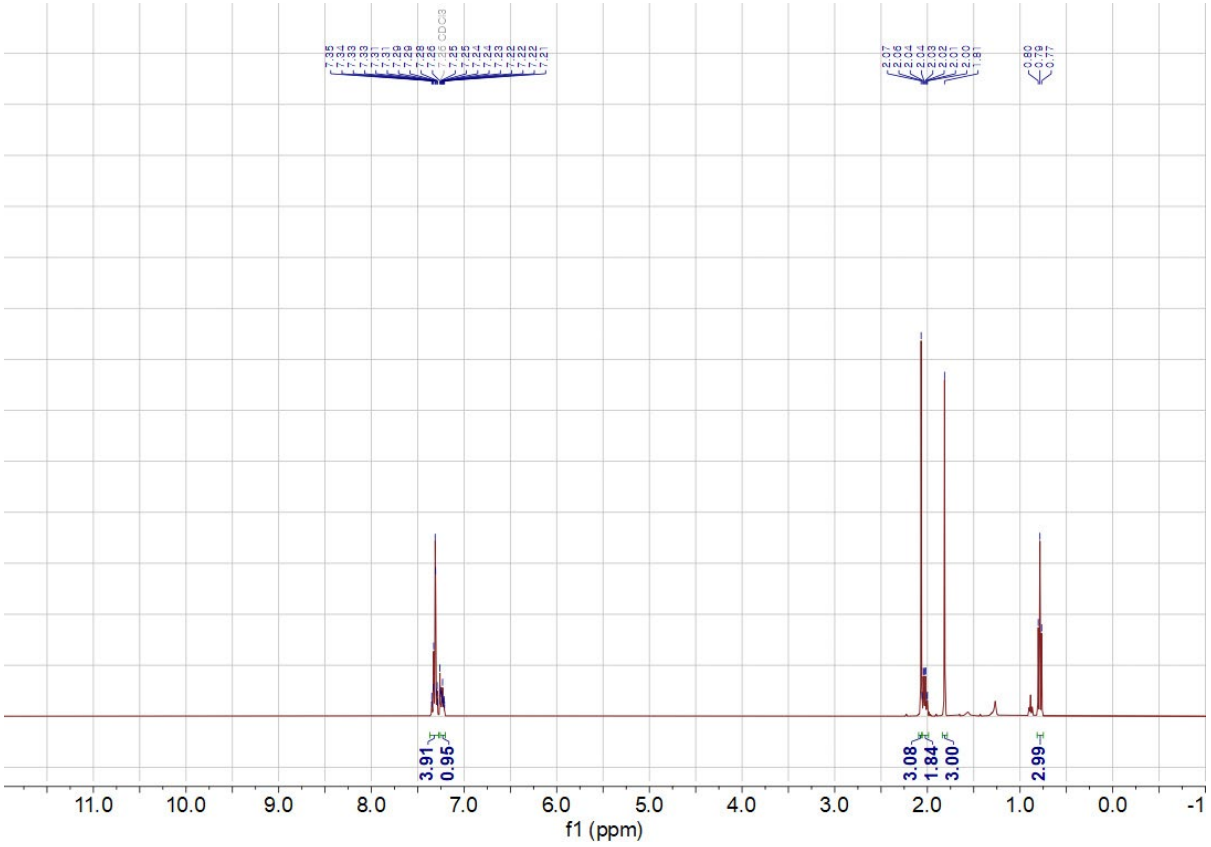

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **18-sub**



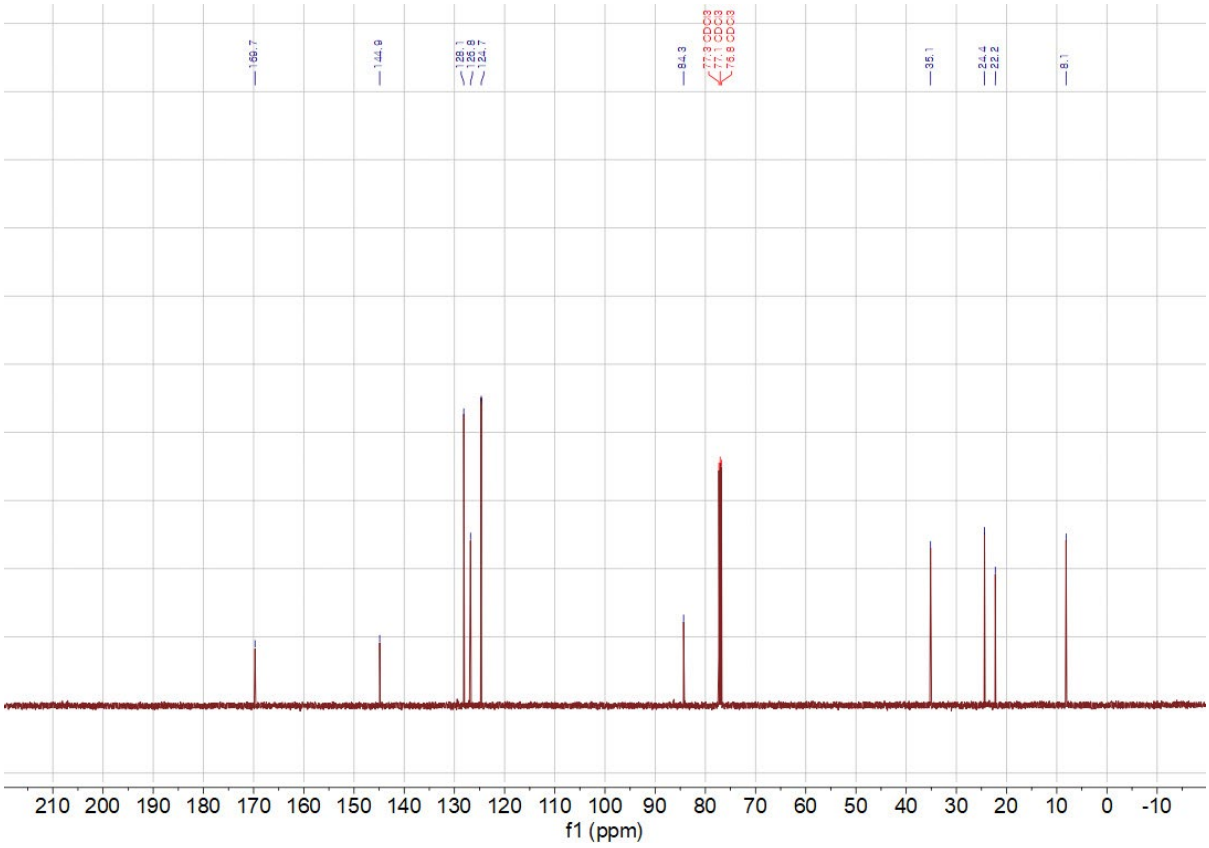
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **18-sub**



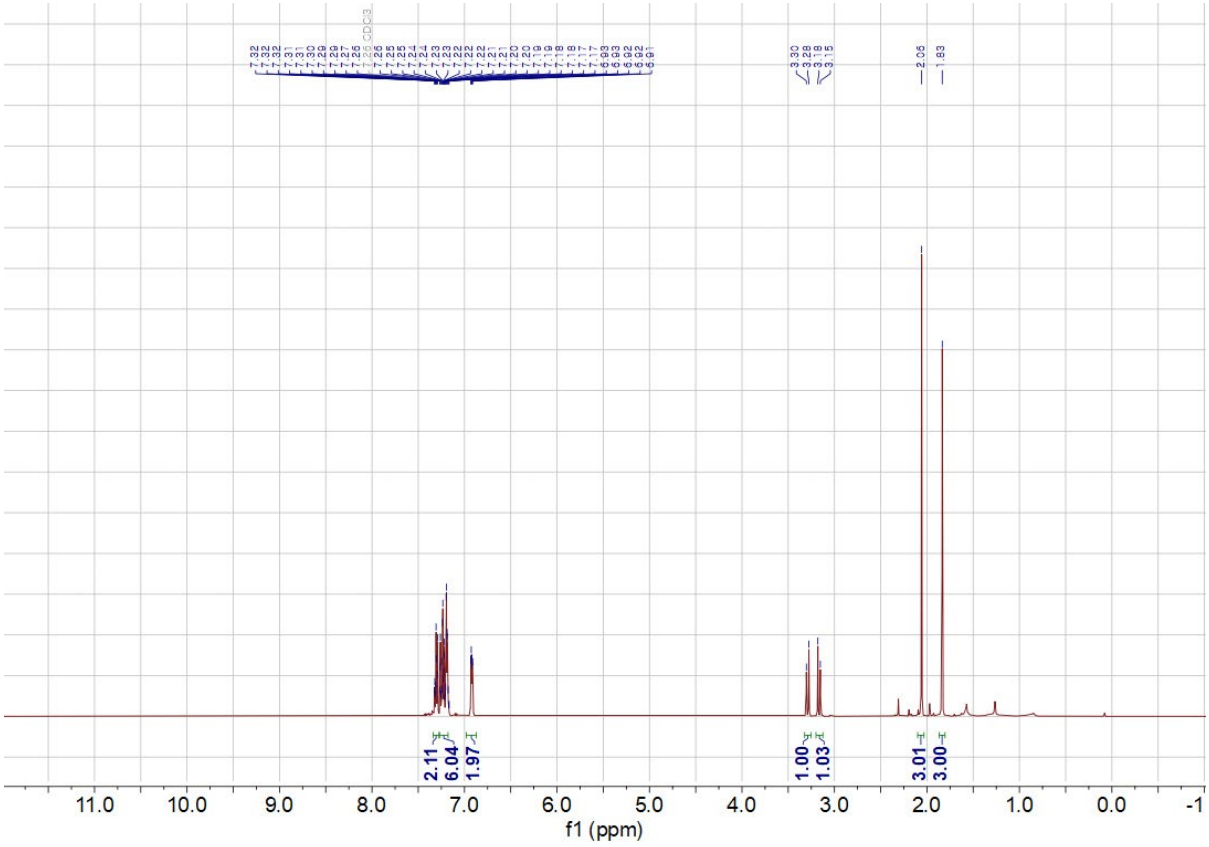

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **19-sub**



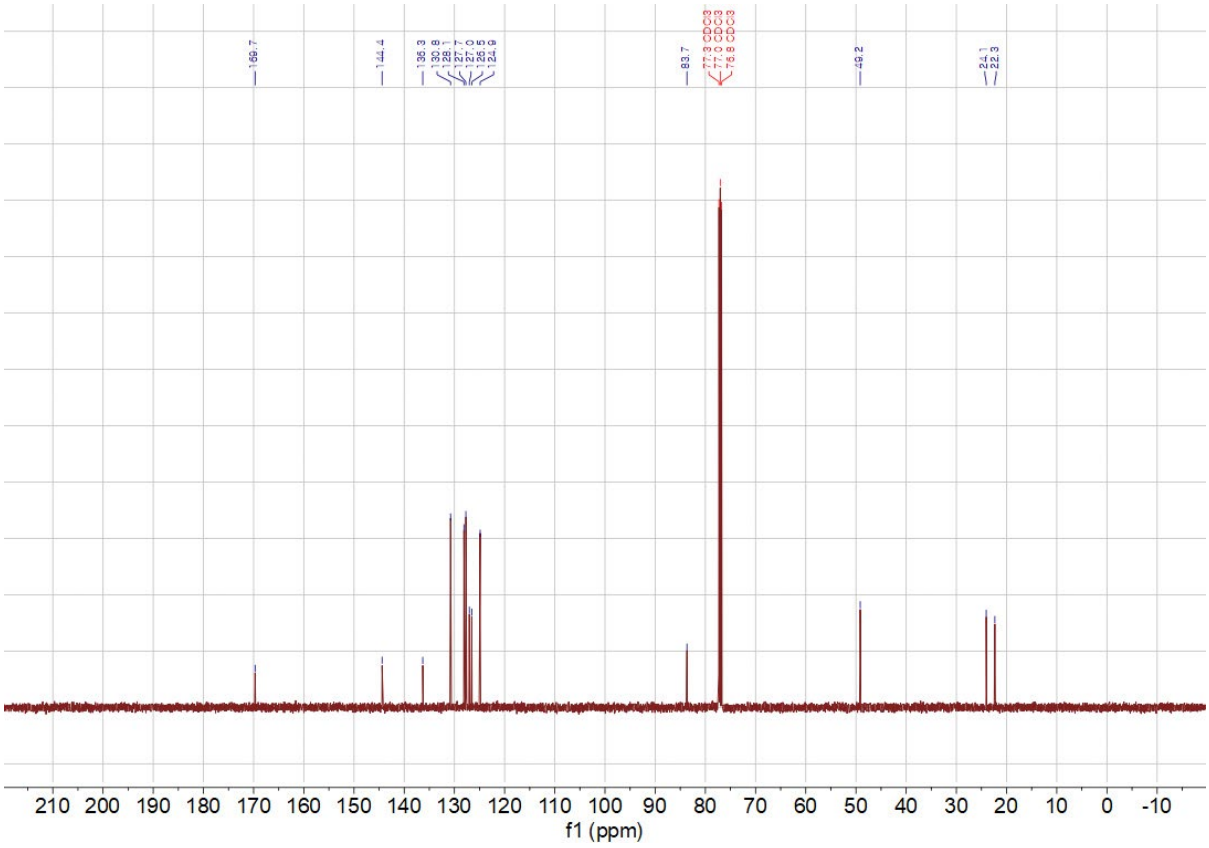
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **19-sub**



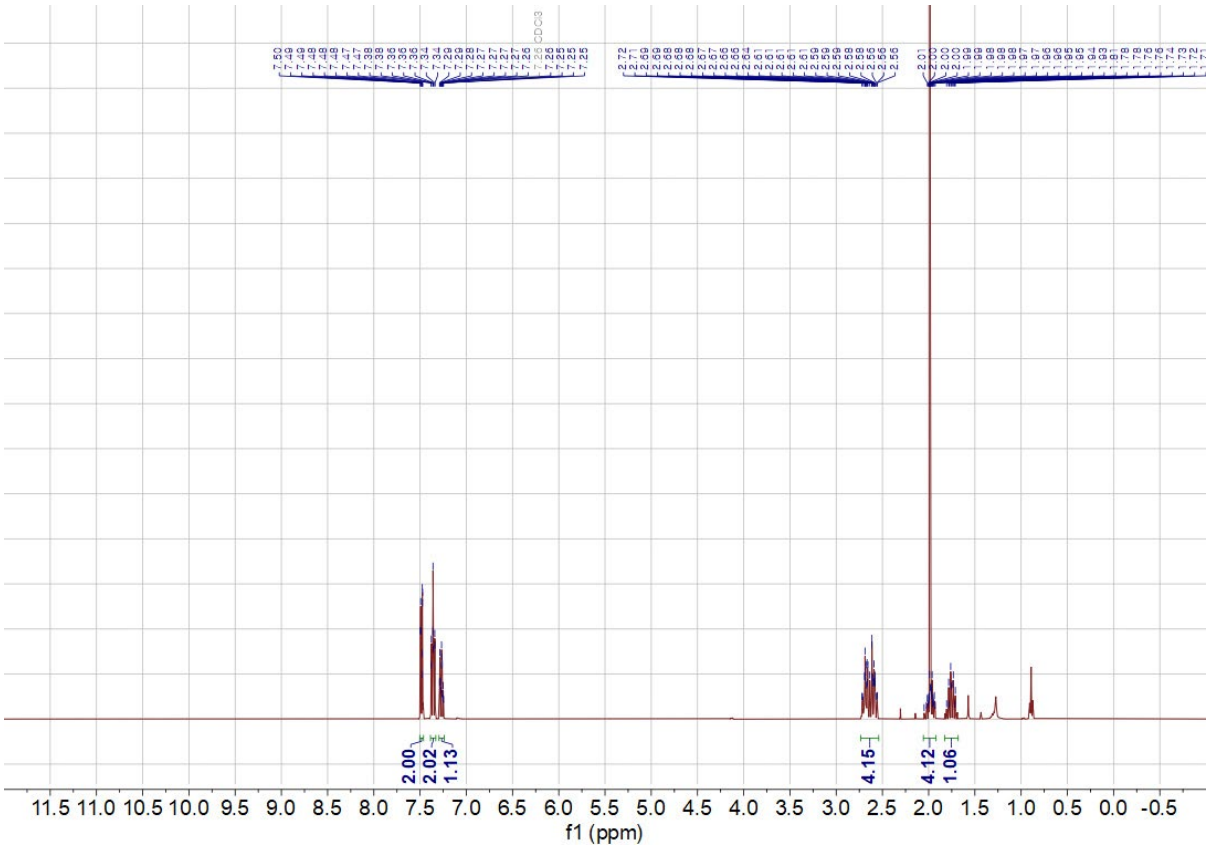

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **20-sub**



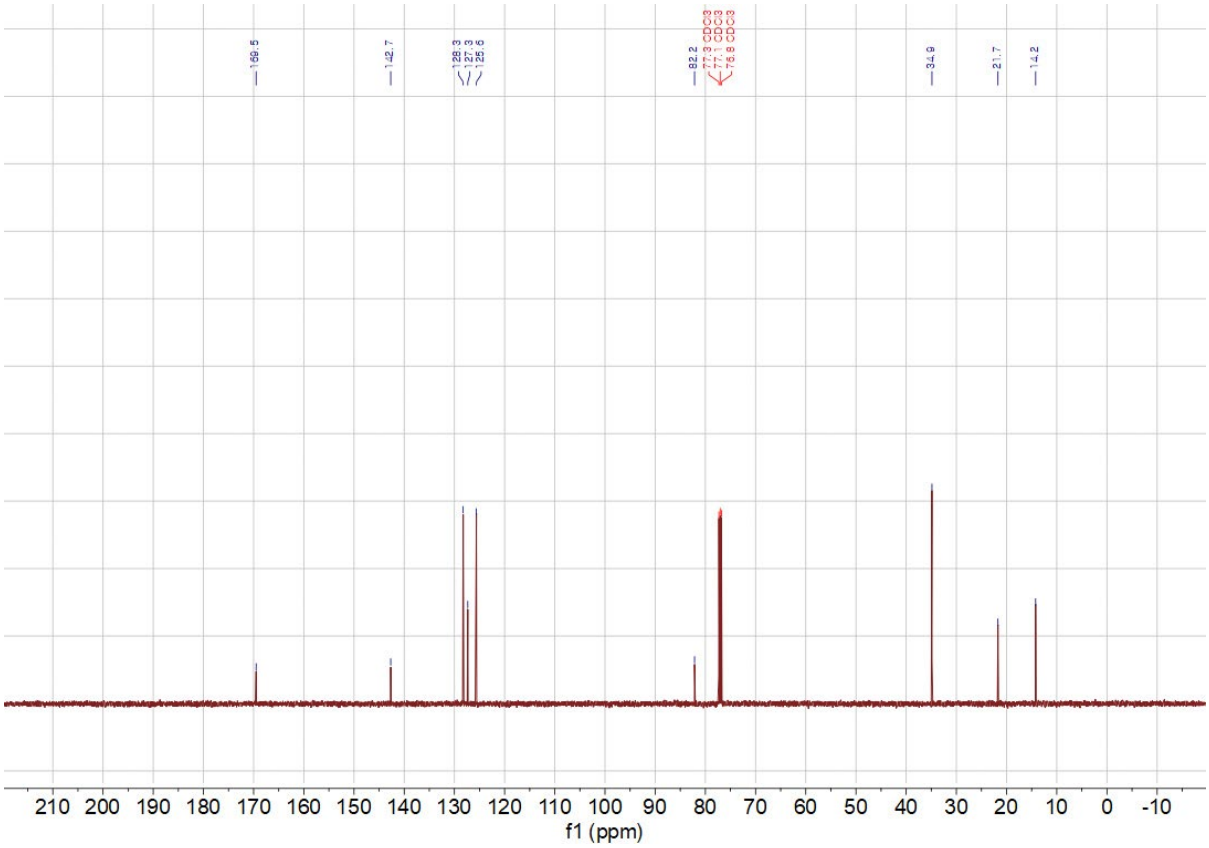
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **20-sub**



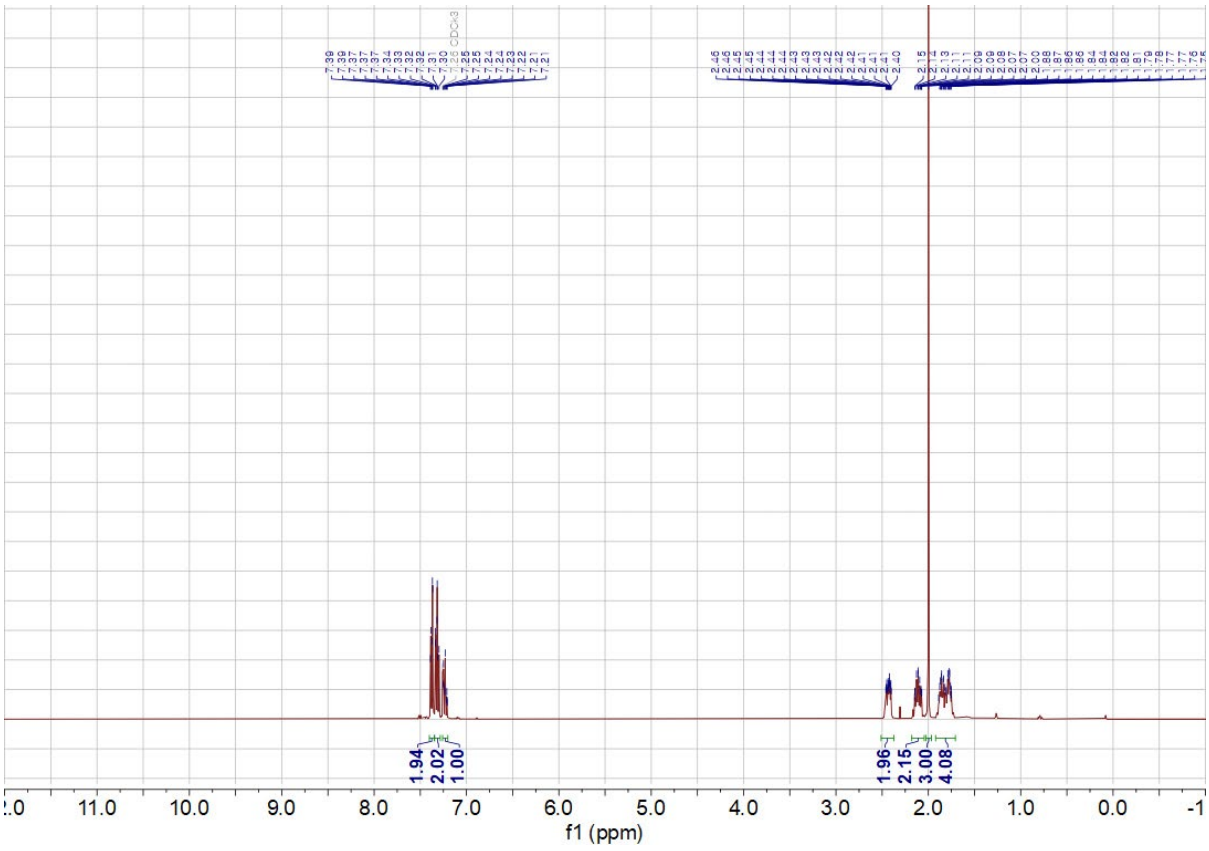

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **21-sub**



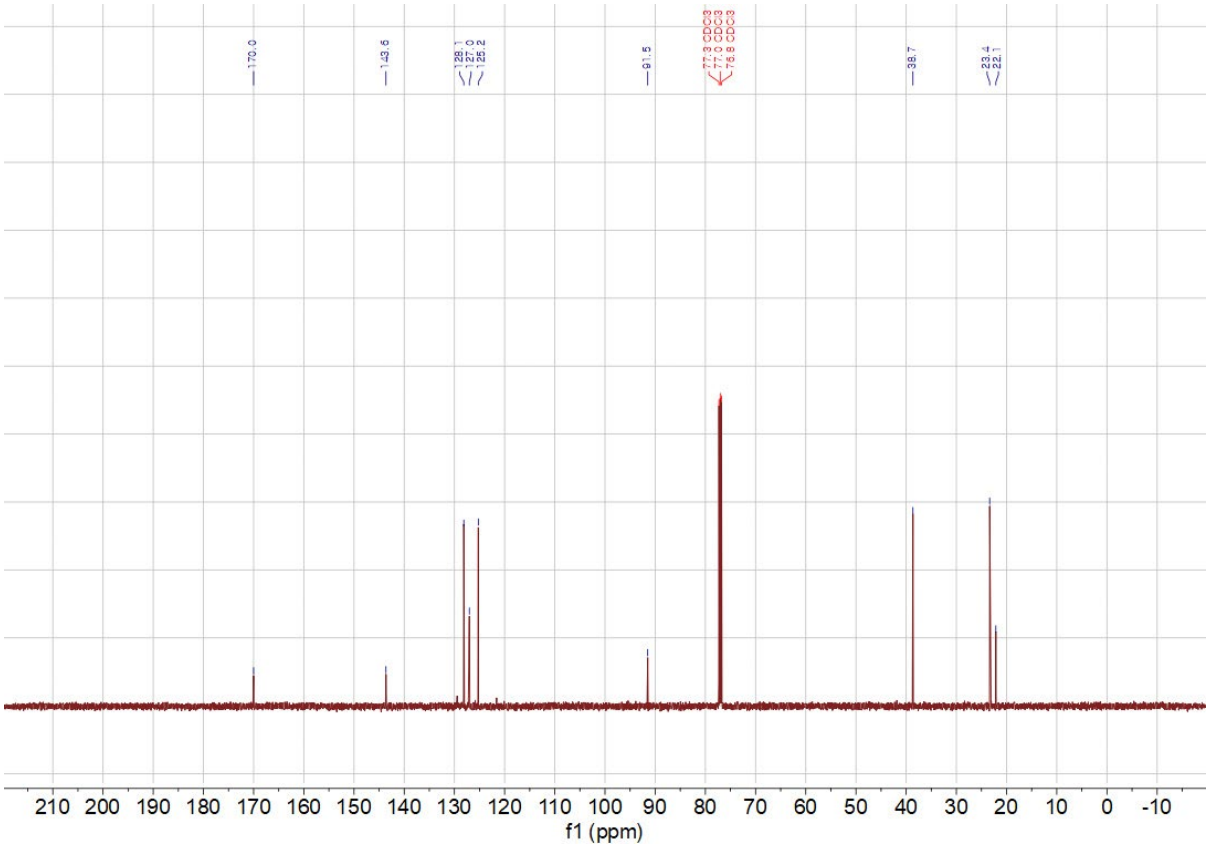
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **21-sub**



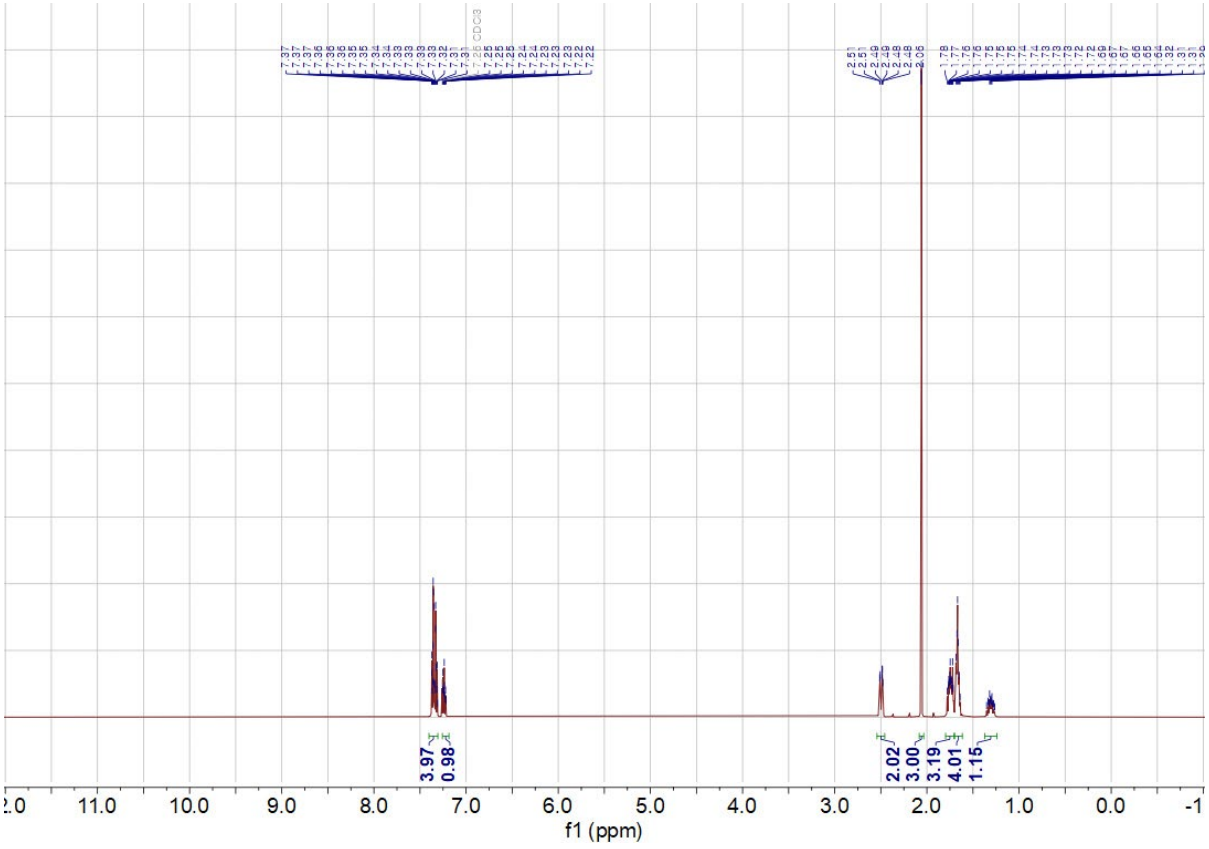

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **22-sub**



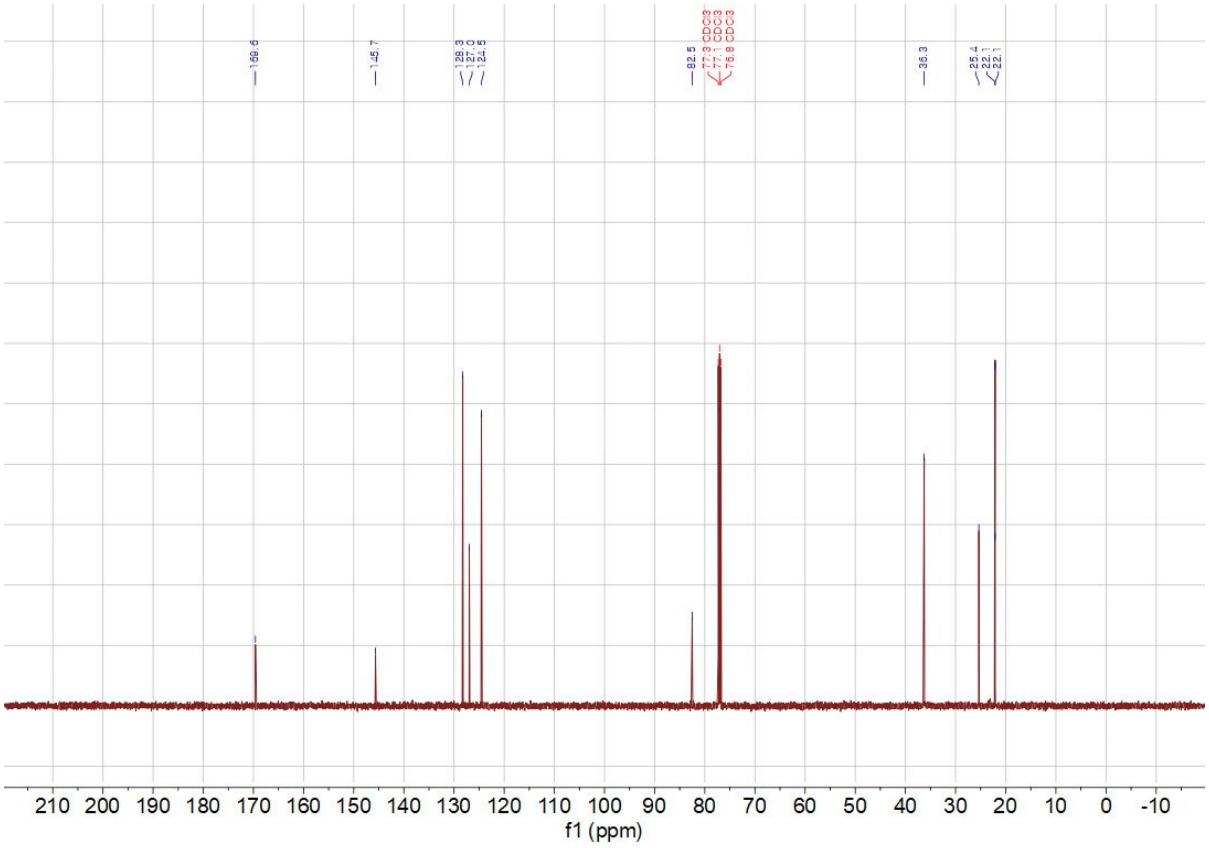
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **22-sub**



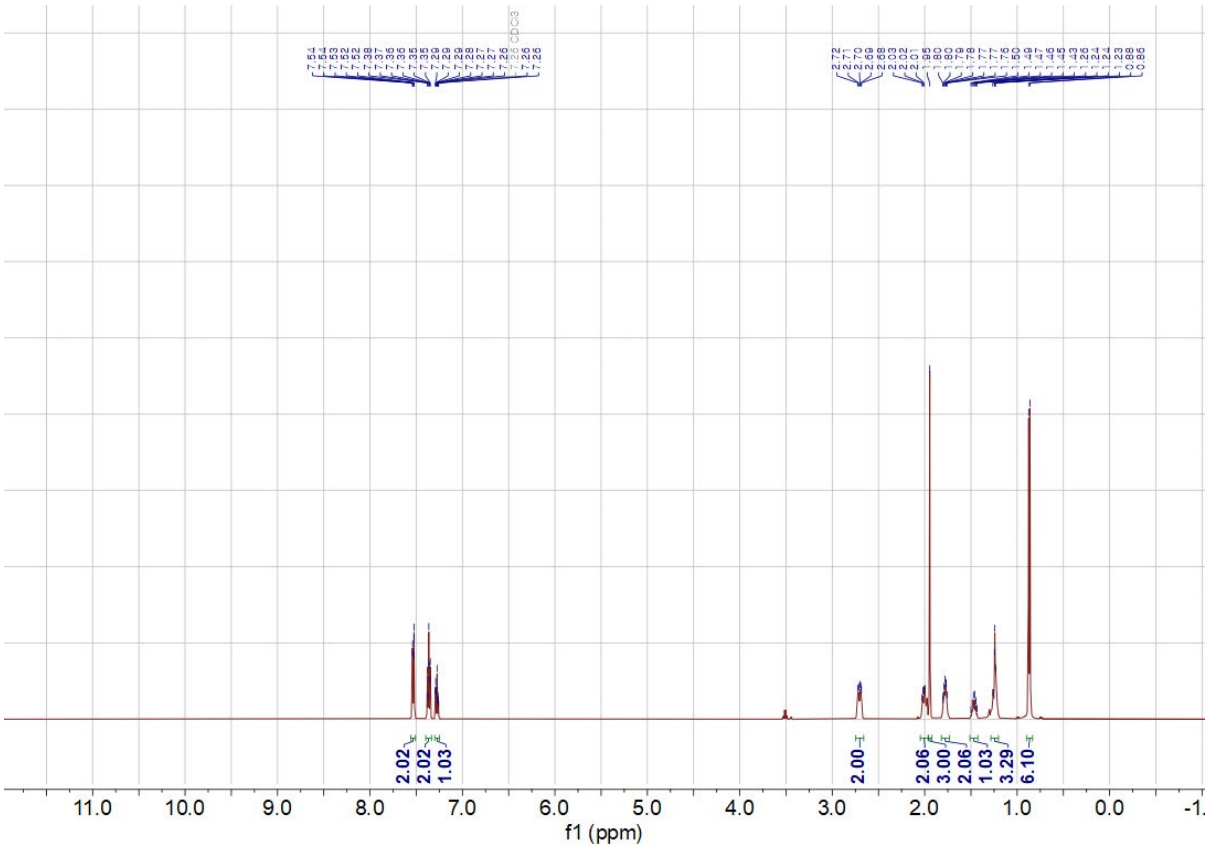

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **23-sub**



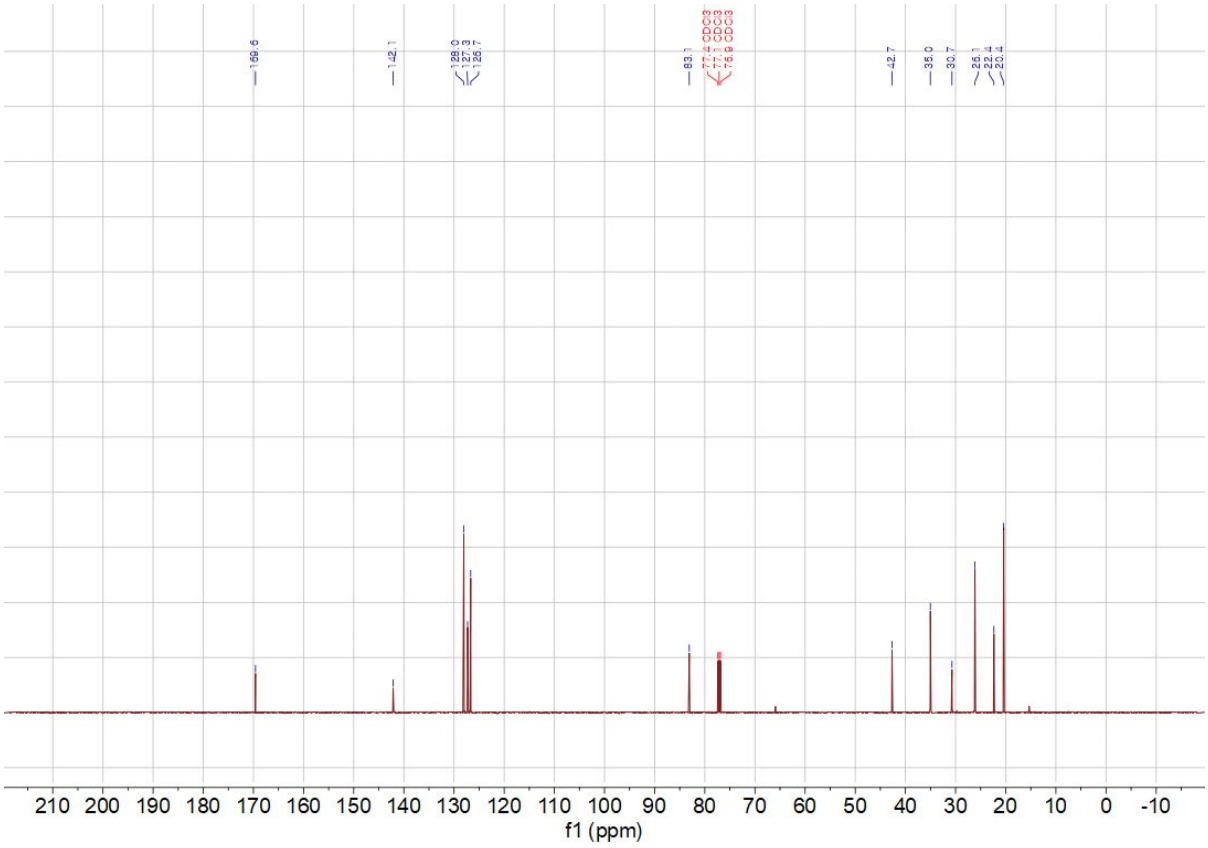
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **23-sub**



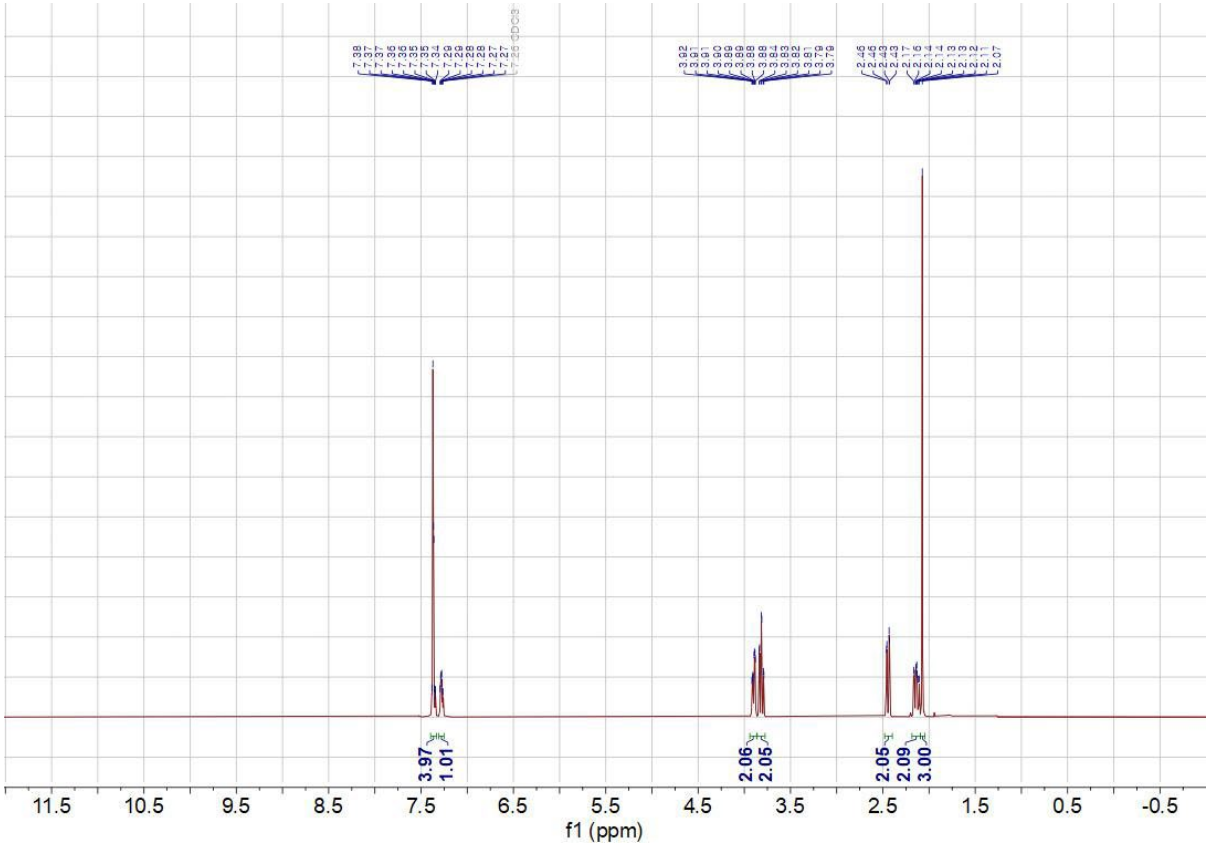

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **24-sub**



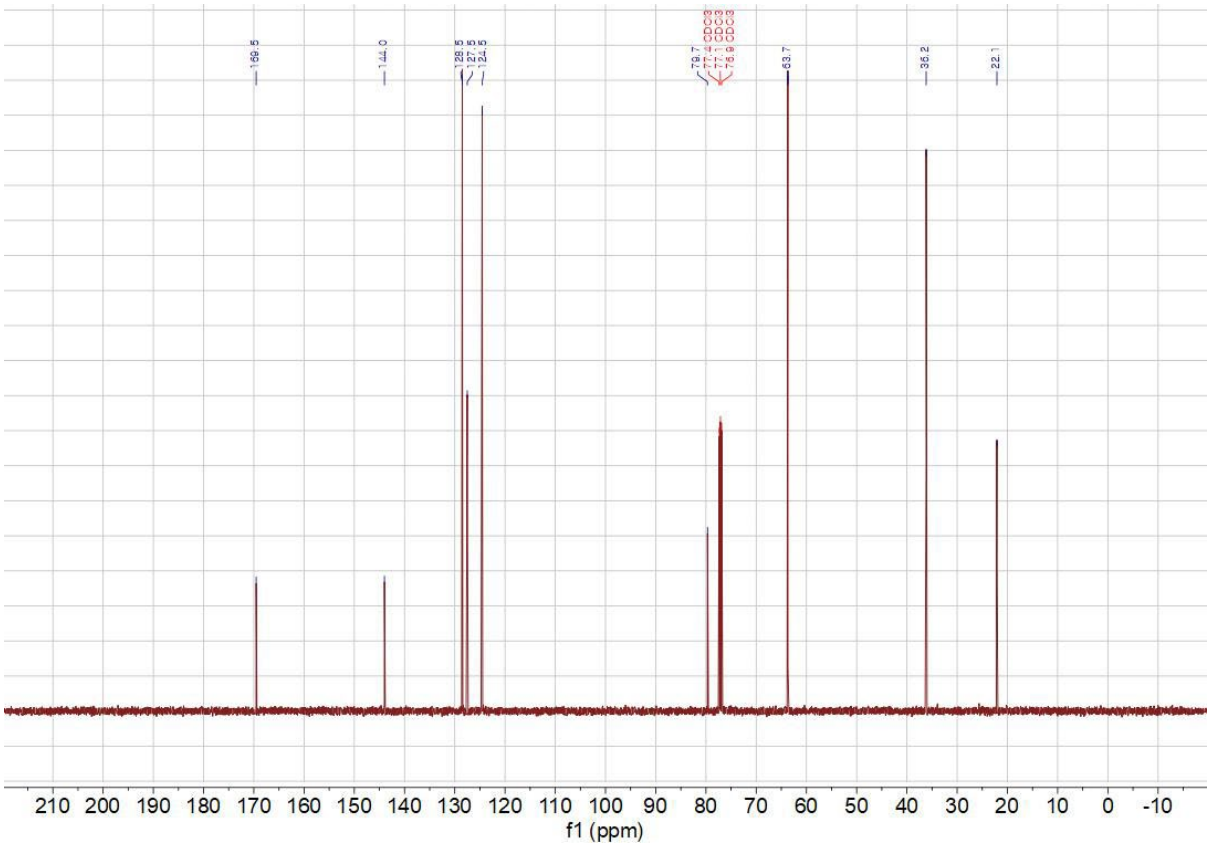
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **24-sub**



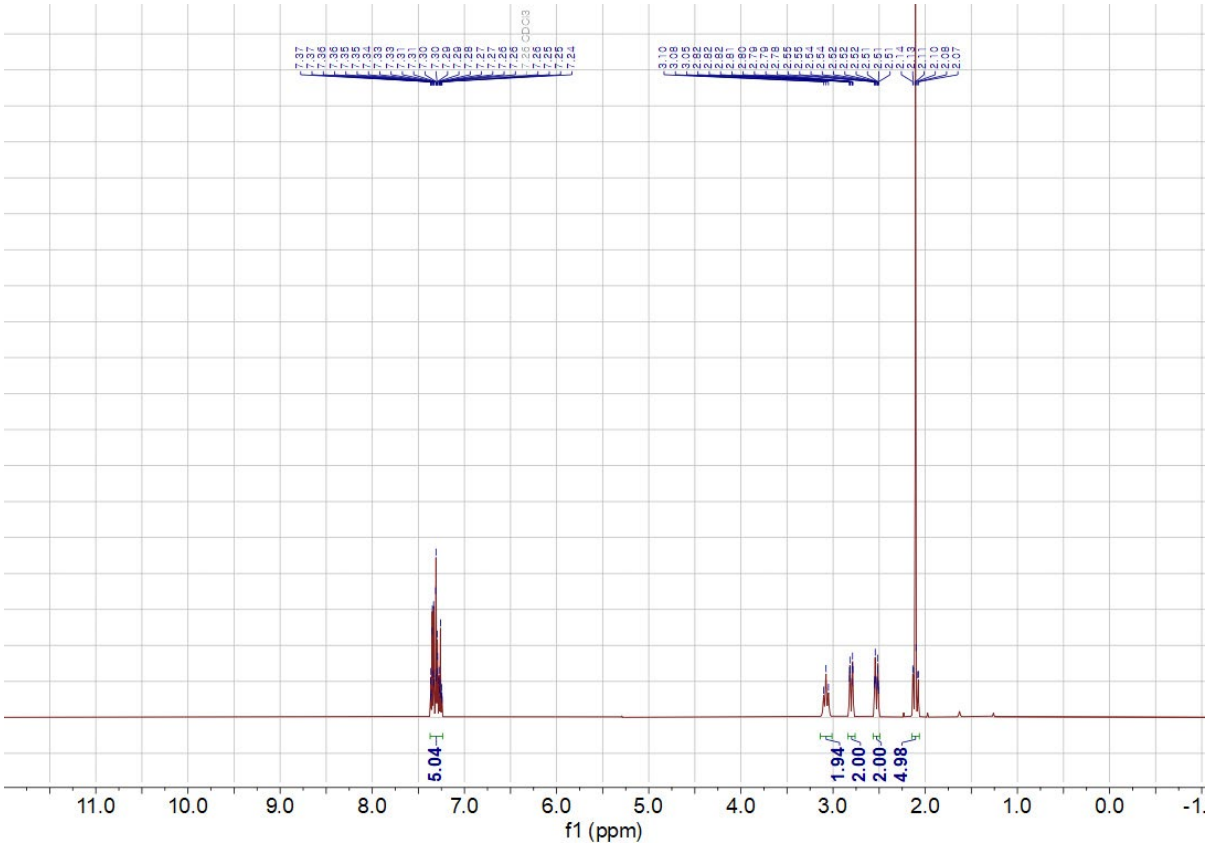

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **25-sub**



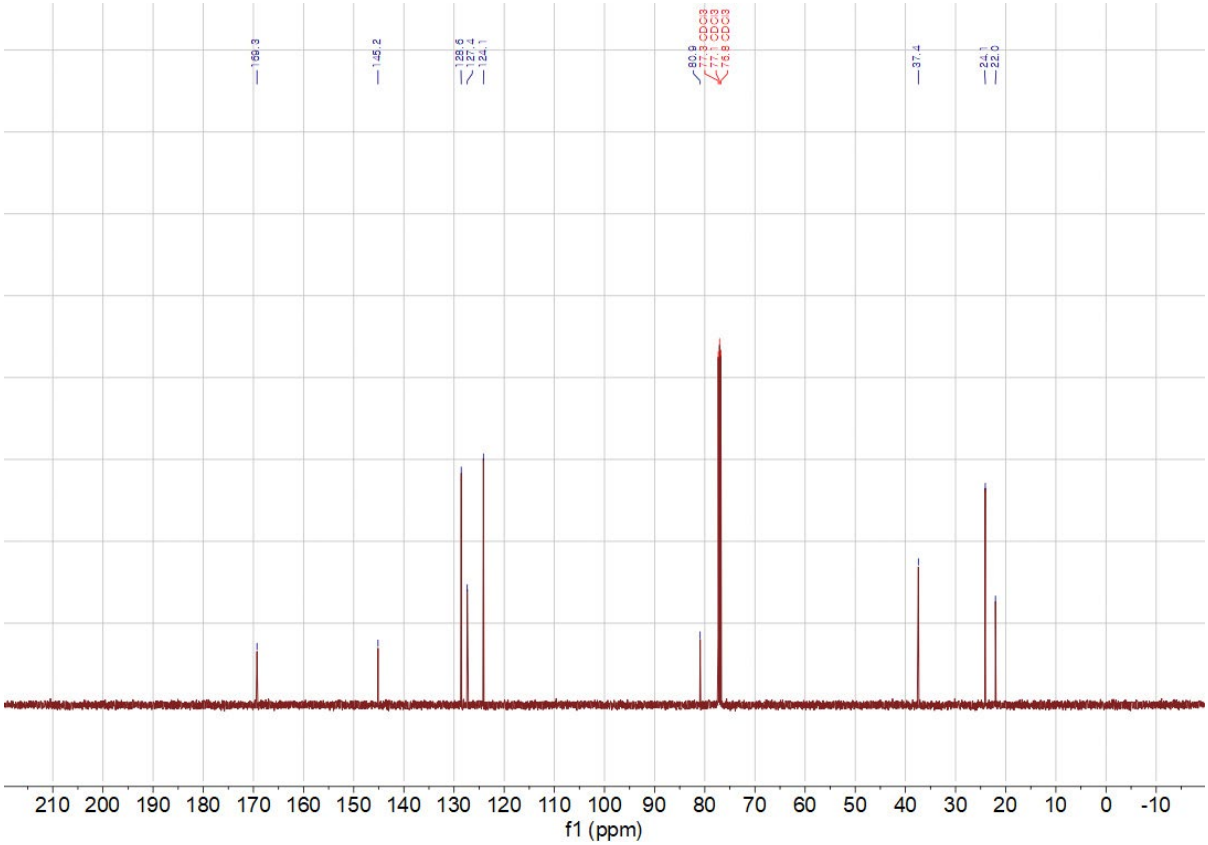
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **25-sub**



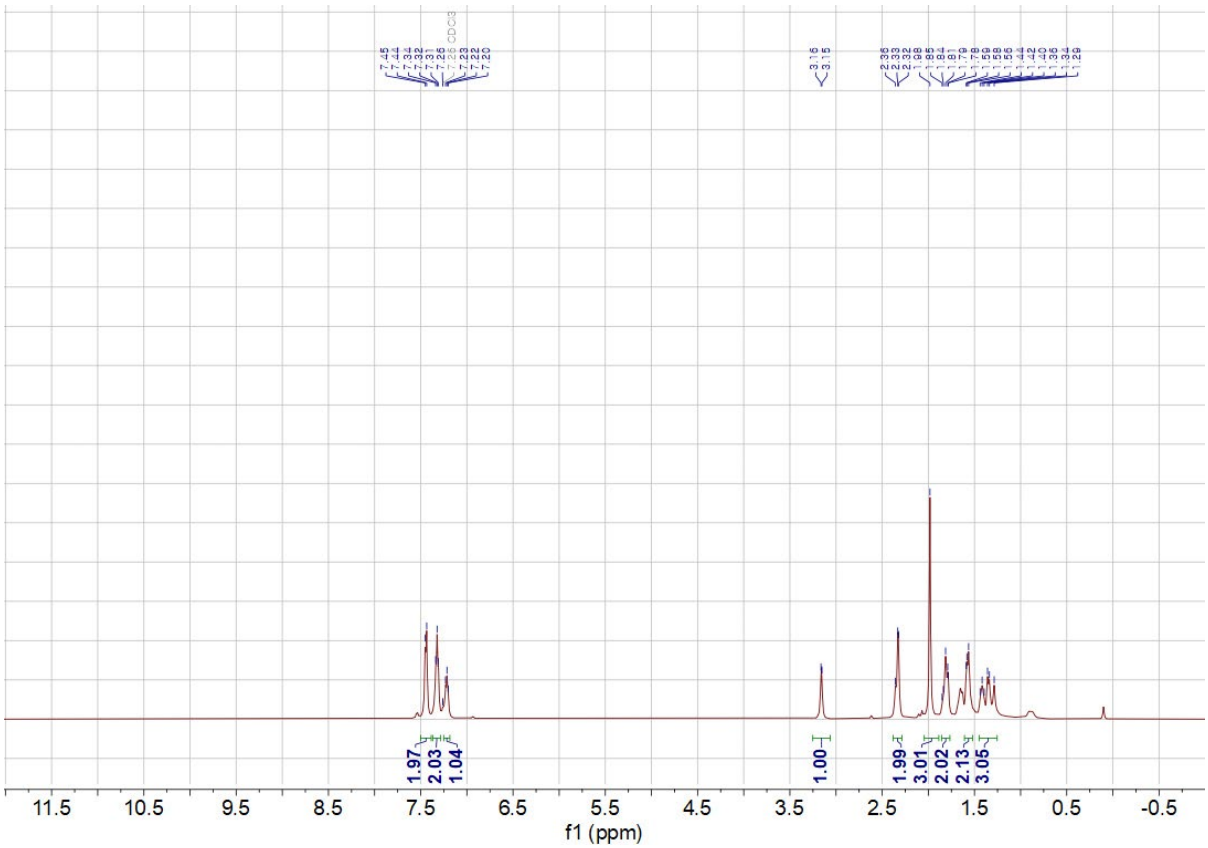

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **26-sub**



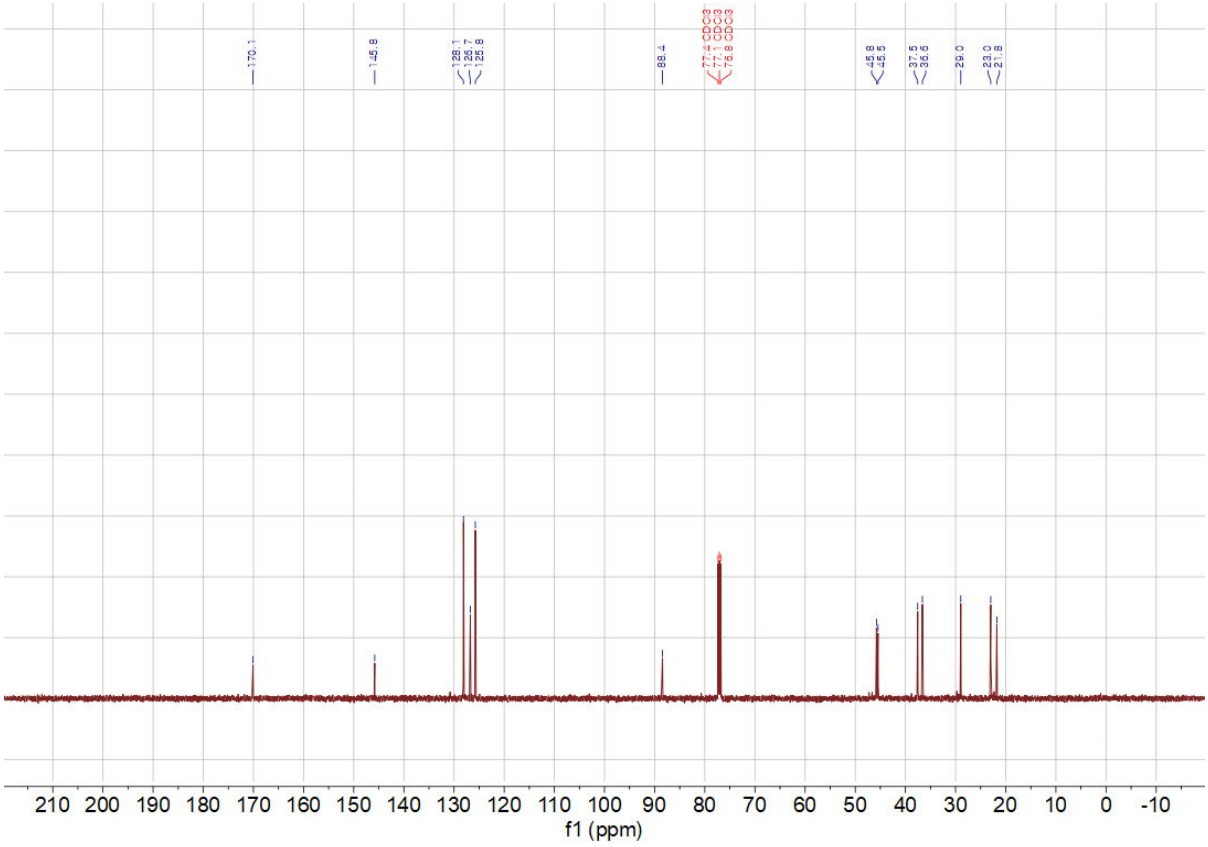
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **26-sub**




$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **27-sub**

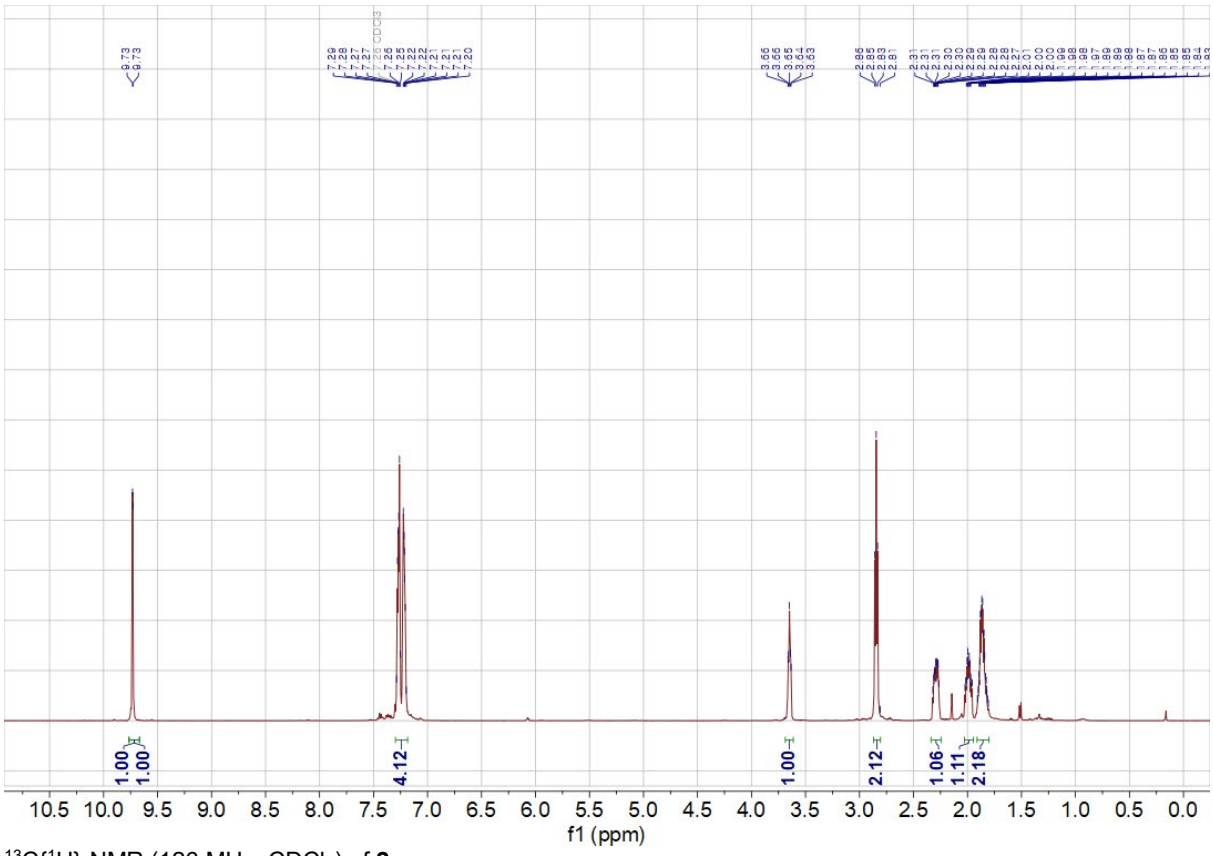


$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **27-sub**

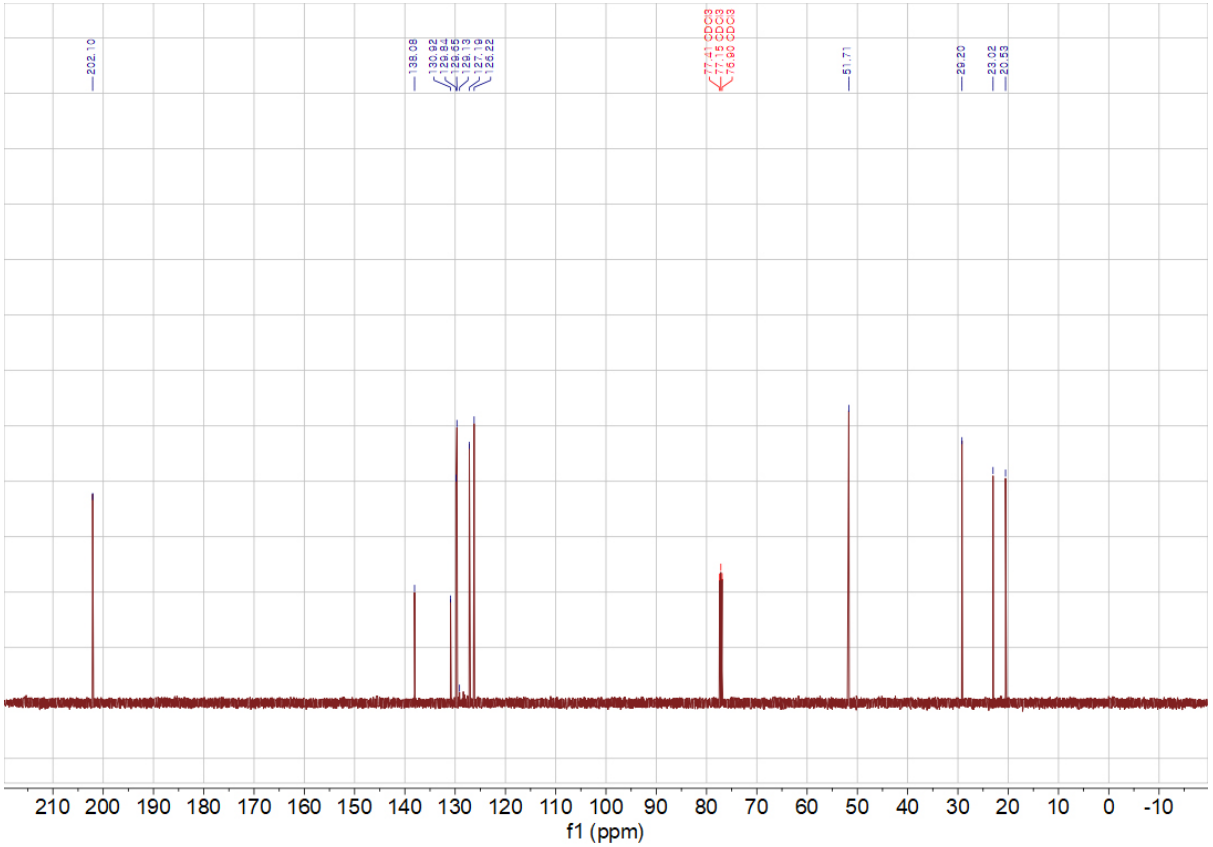


## 10.2. Products

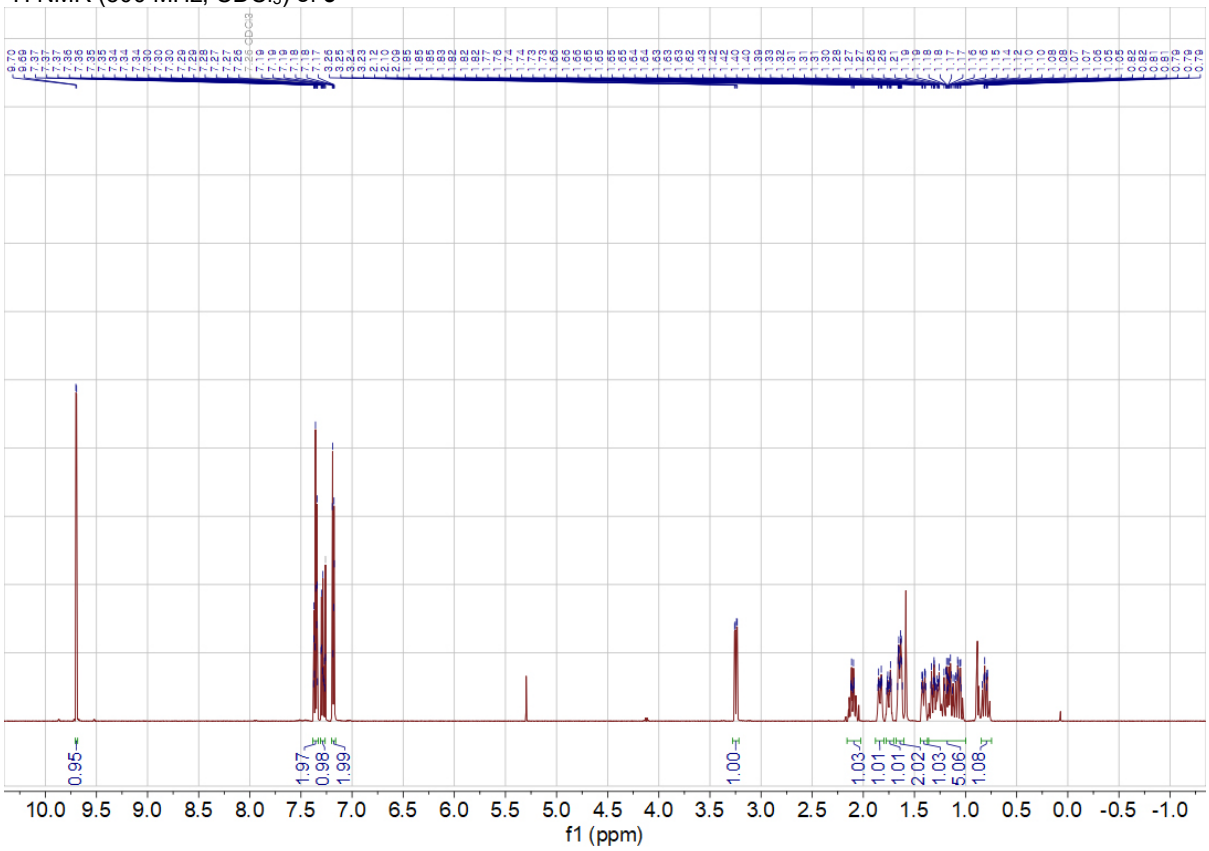
$^{1}$H NMR (500 MHz, $CDCl_3$) of **2**



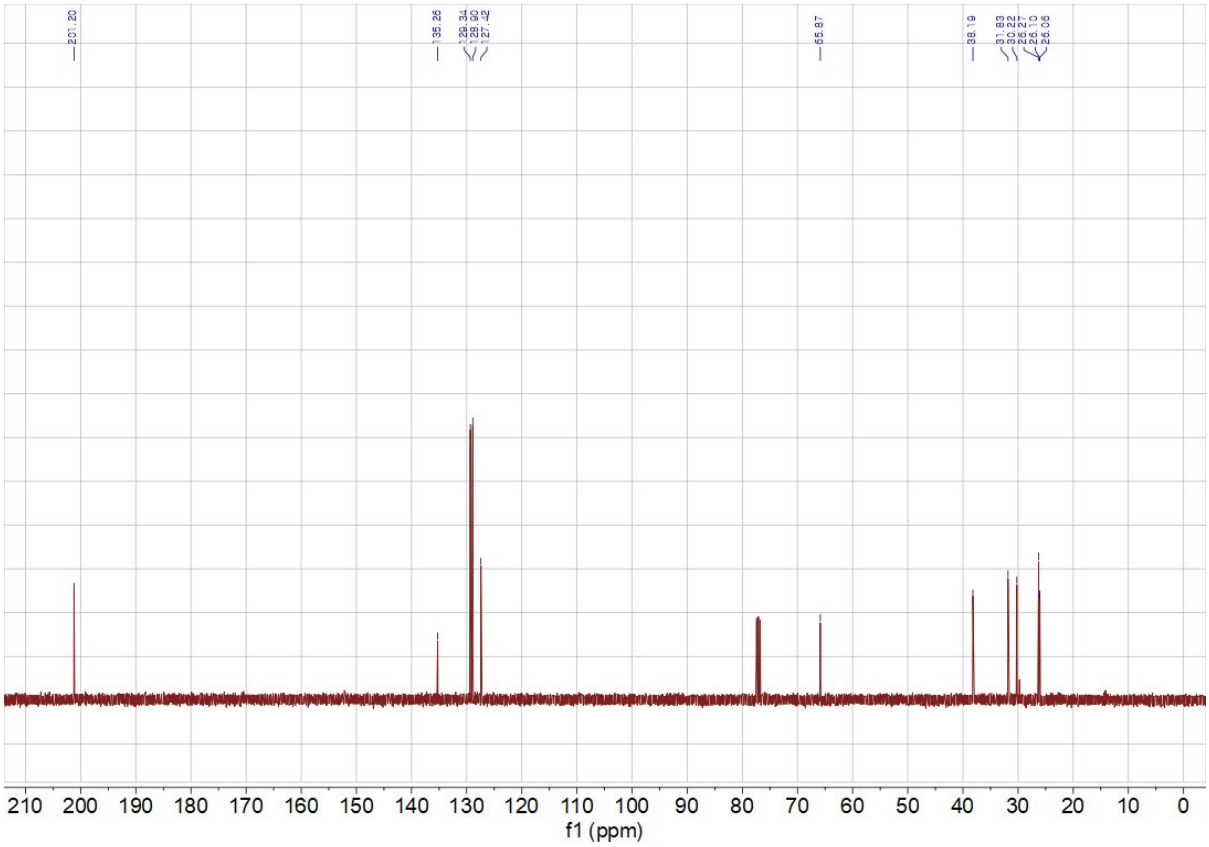

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **2**



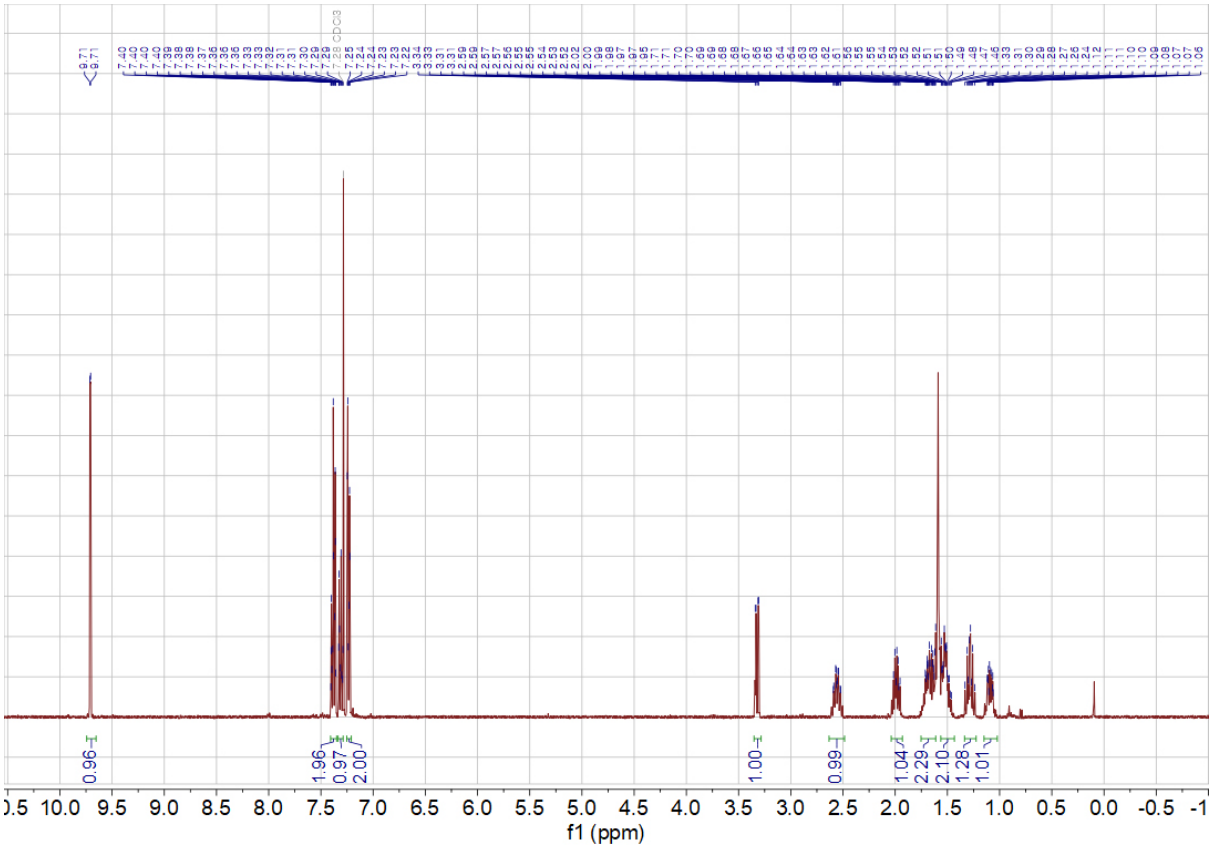
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3**



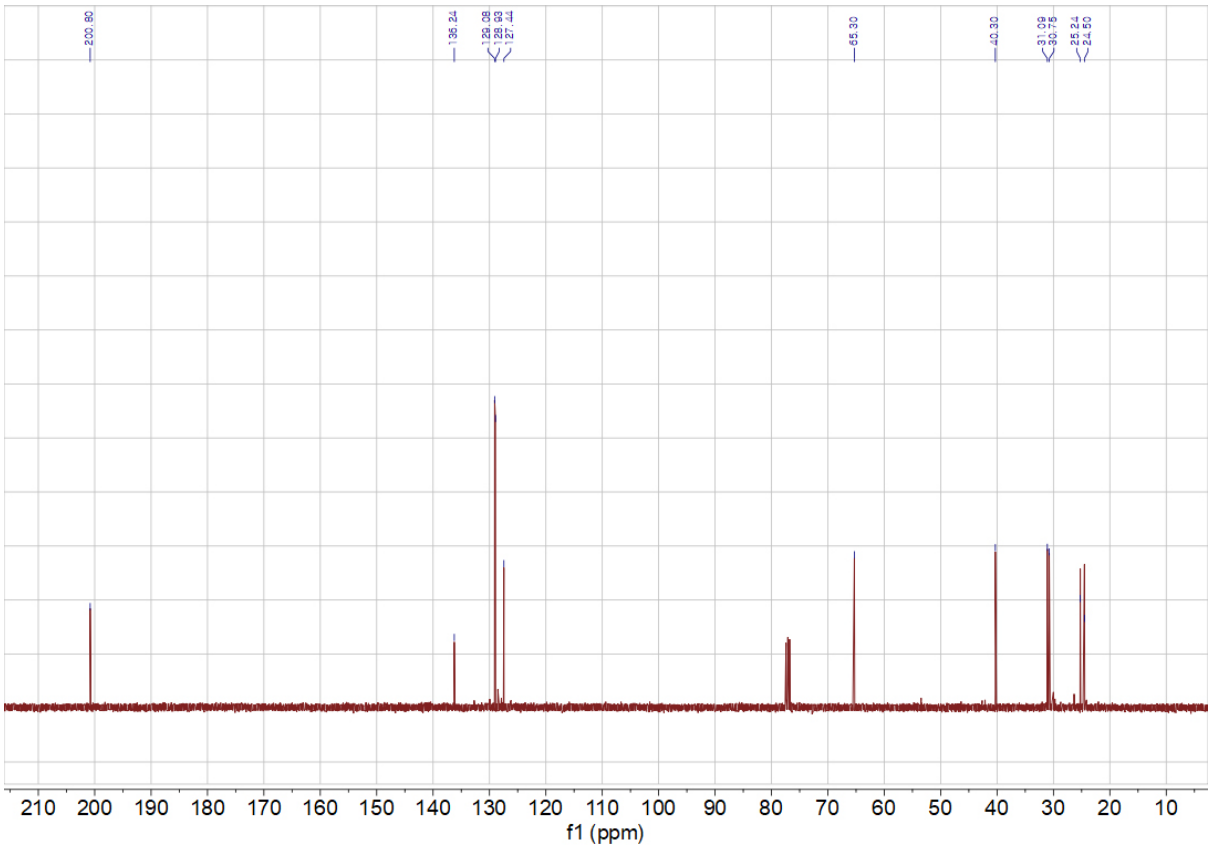

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **3**



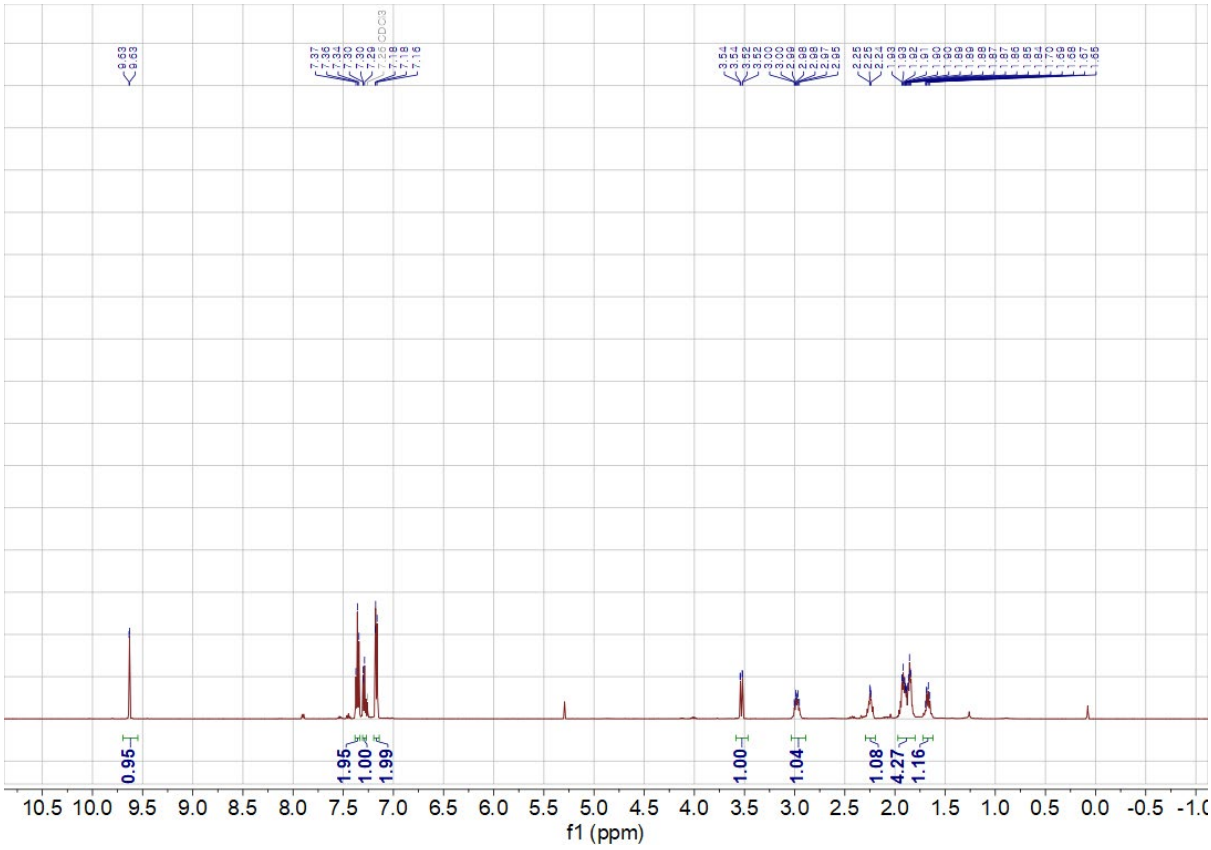
$^{1}$H NMR (400 MHz, $CDCl_3$) of **4**



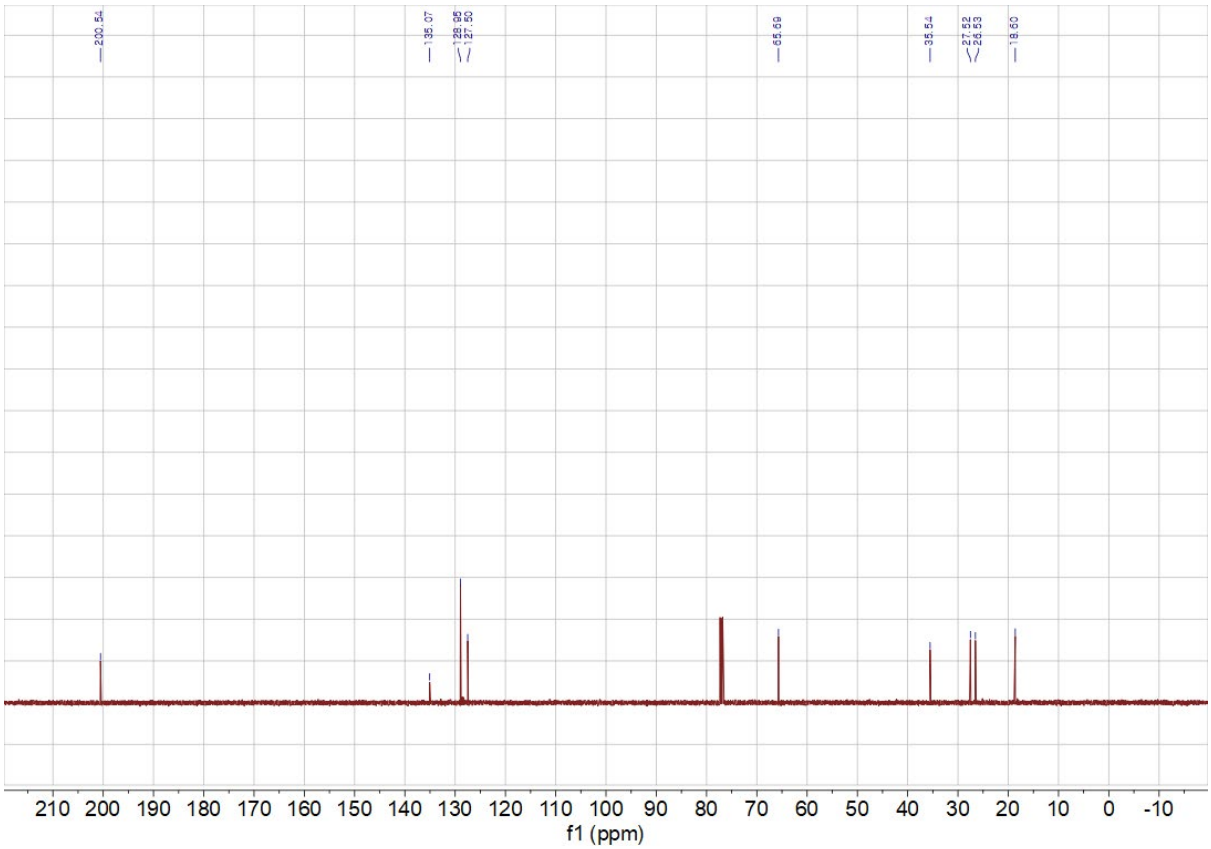

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **4**



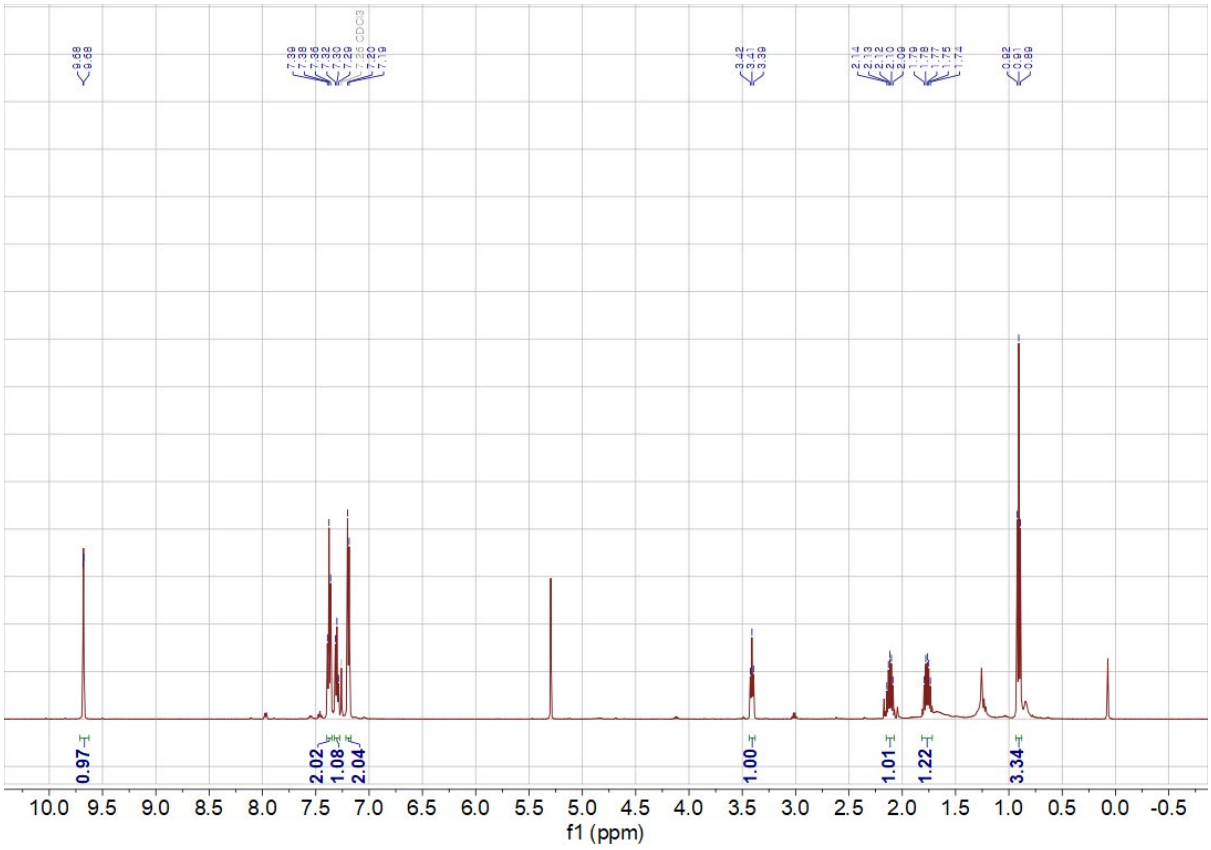
$^{1}$H NMR (500 MHz, $CDCl_3$) of **5**



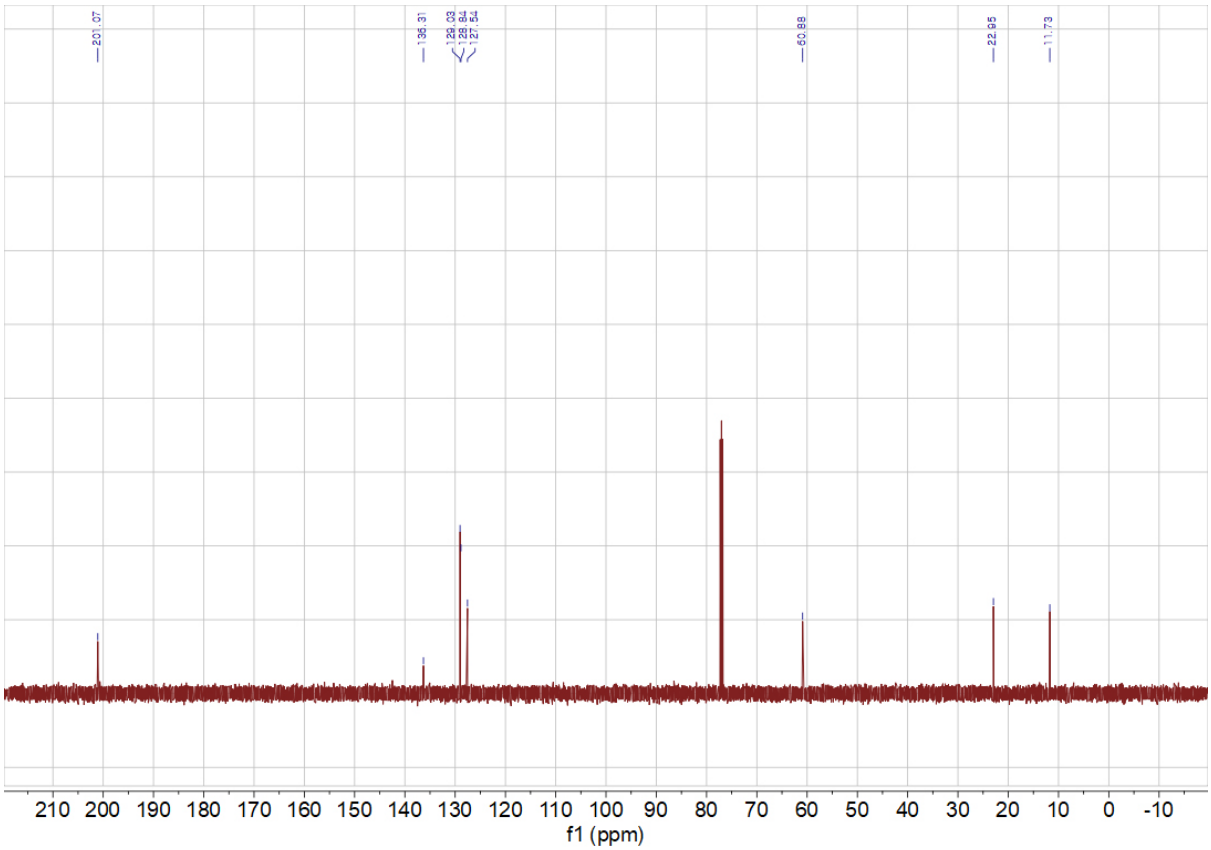

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **5**



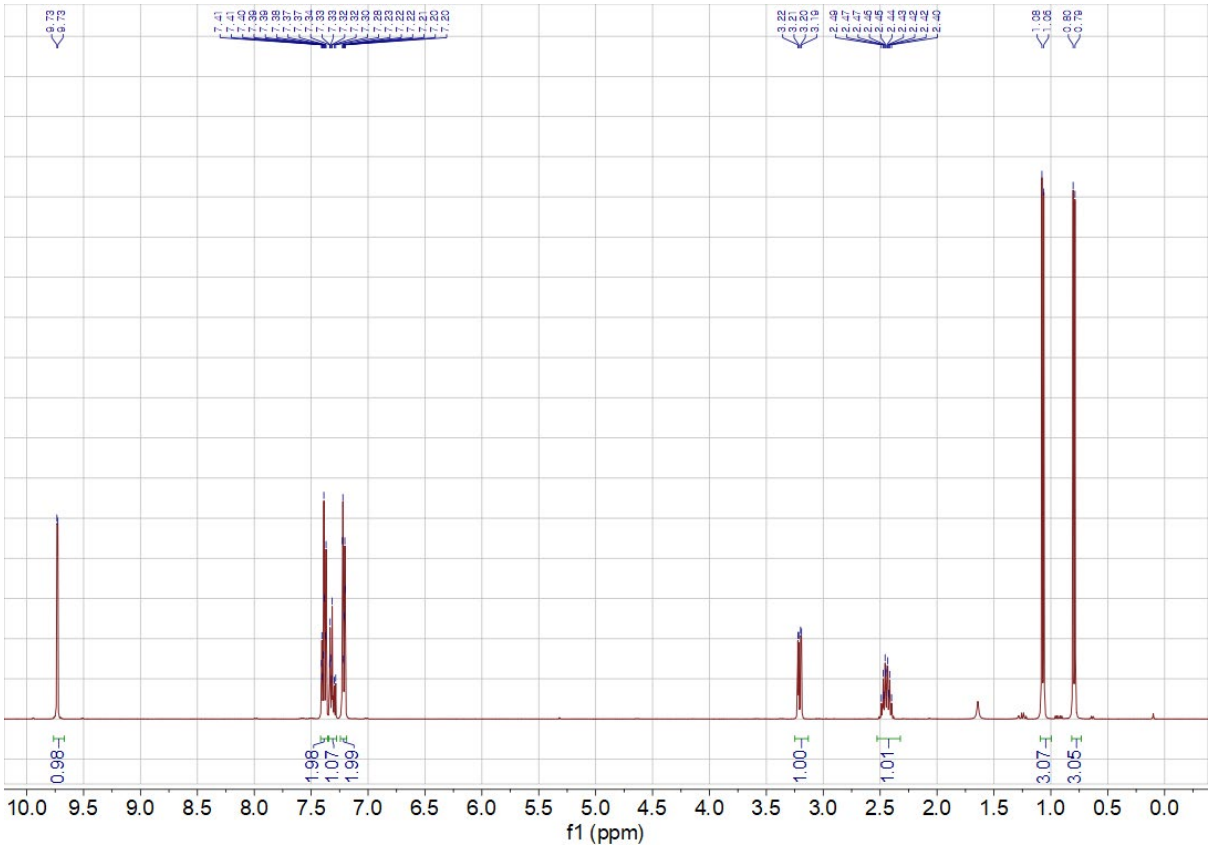
$^{1}$H NMR (500 MHz, $CDCl_3$) of **6**



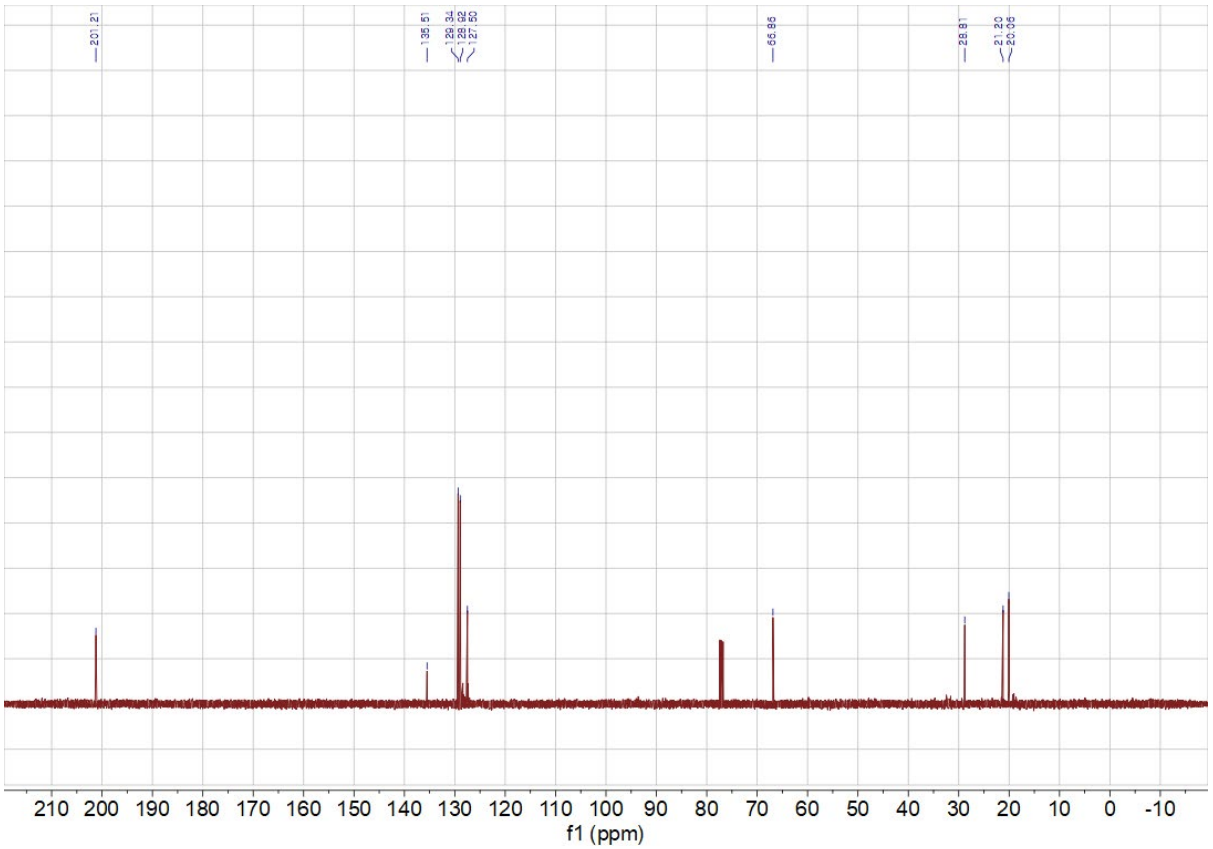

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **6**



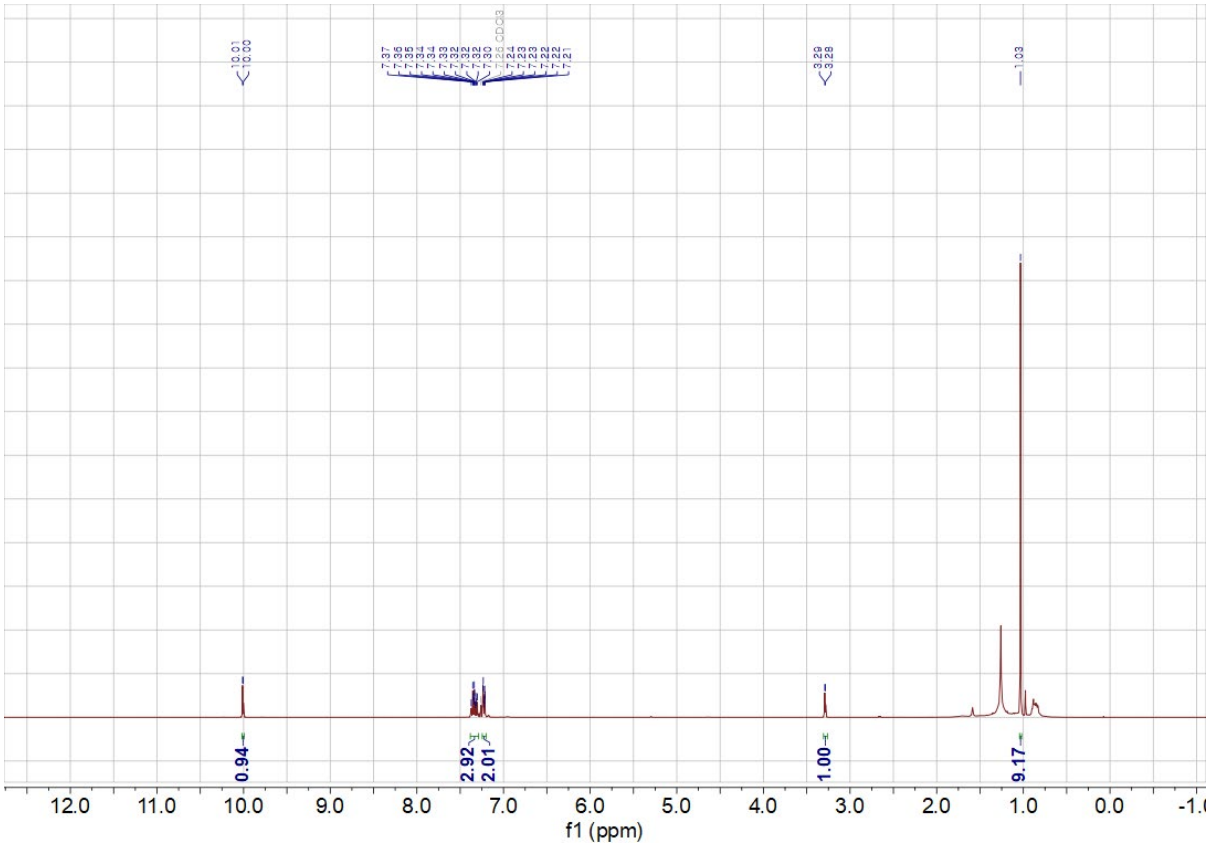
$^{1}$H NMR (400 MHz, $CDCl_3$) of **7**



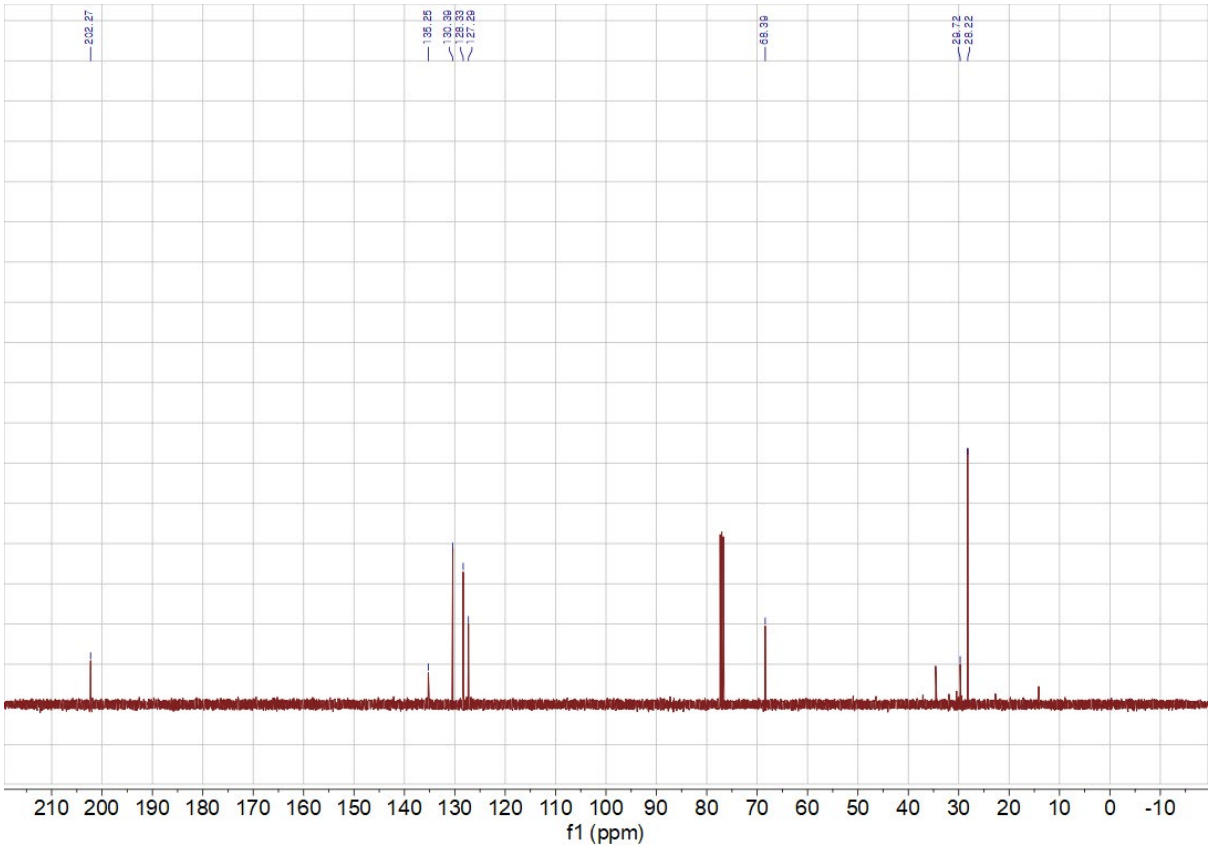

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **7**



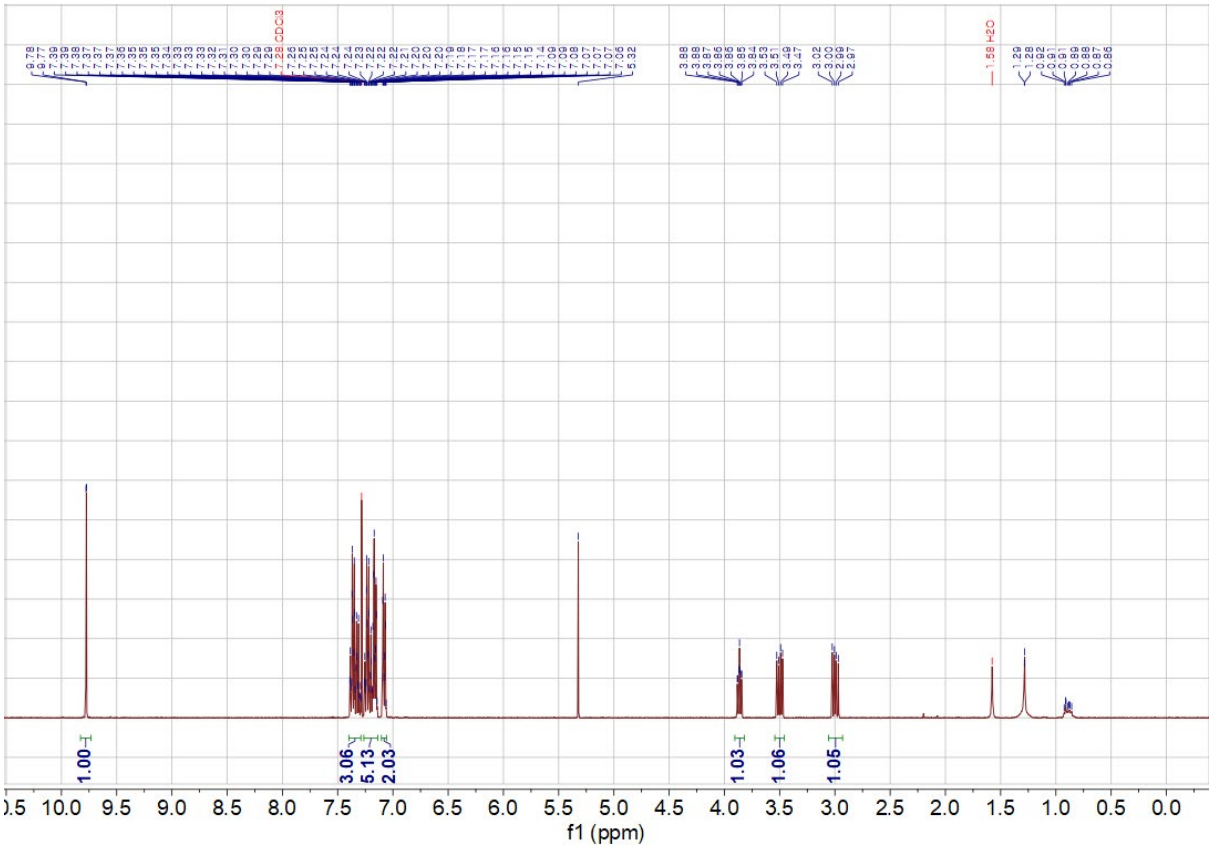
$^{1}$H NMR (400 MHz, $CDCl_3$) of **8**



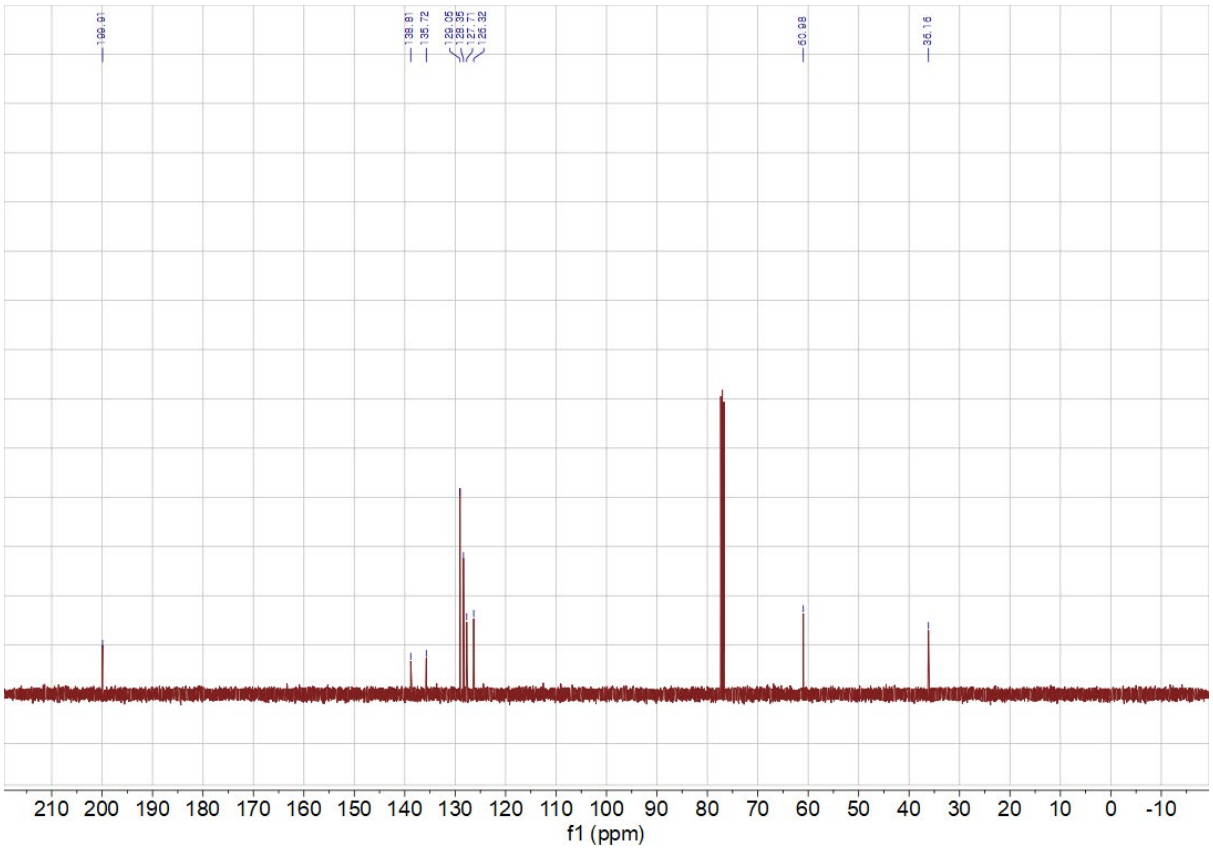

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **8**



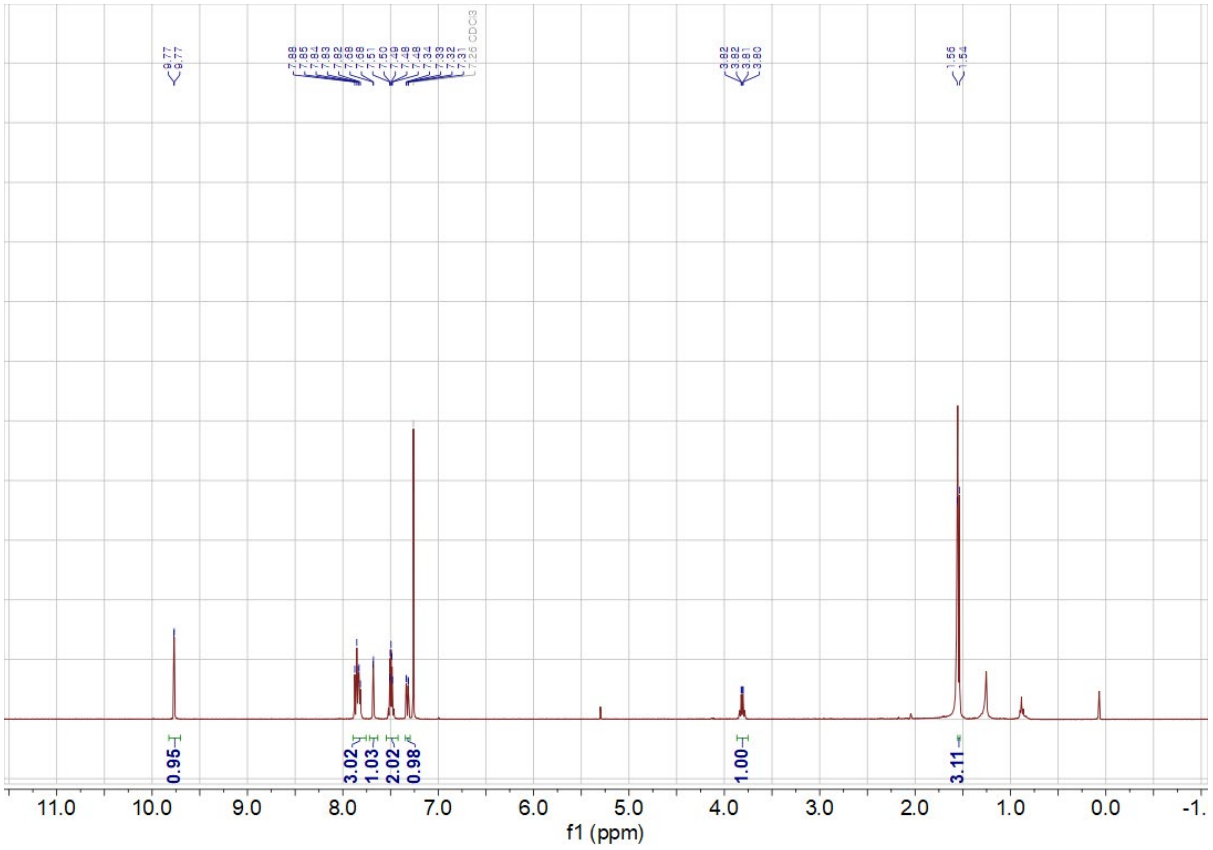
$^{1}$H NMR (400 MHz, $CDCl_3$) of **9**



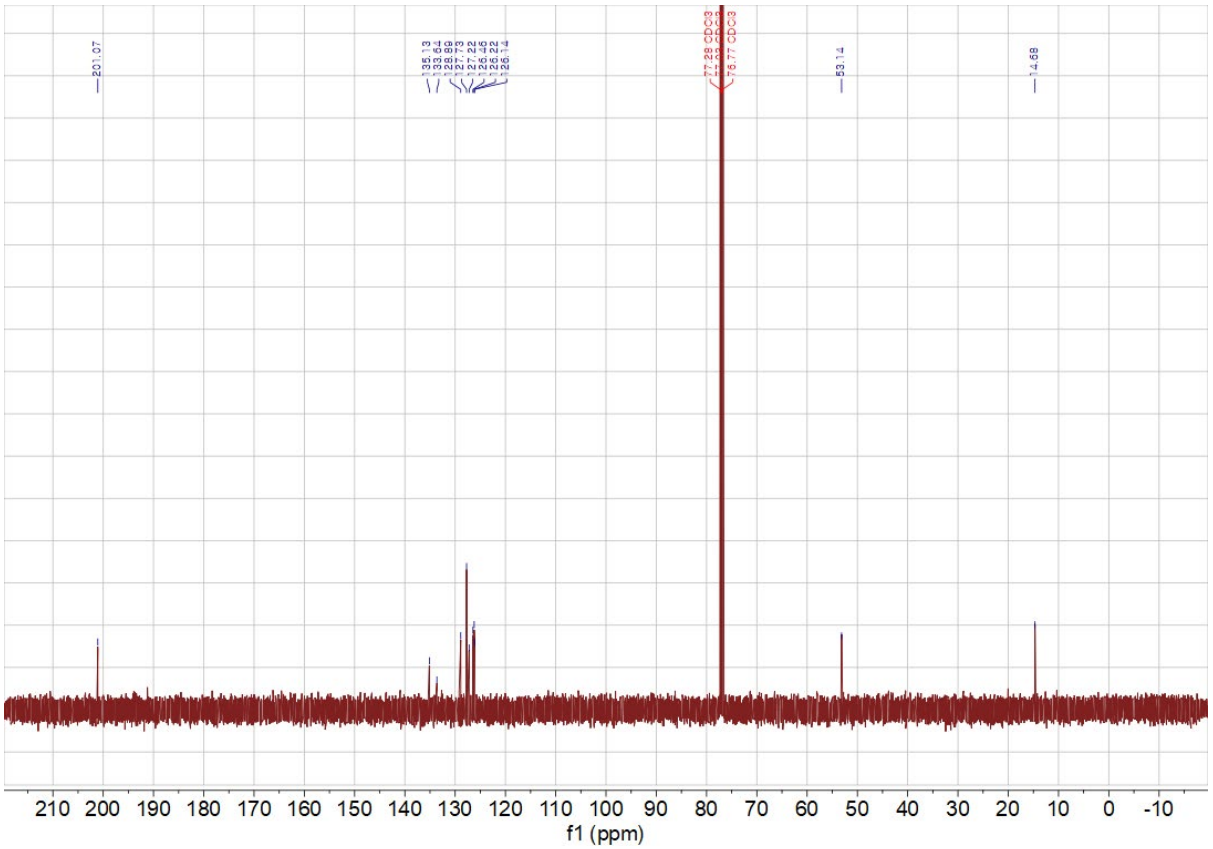

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **9**



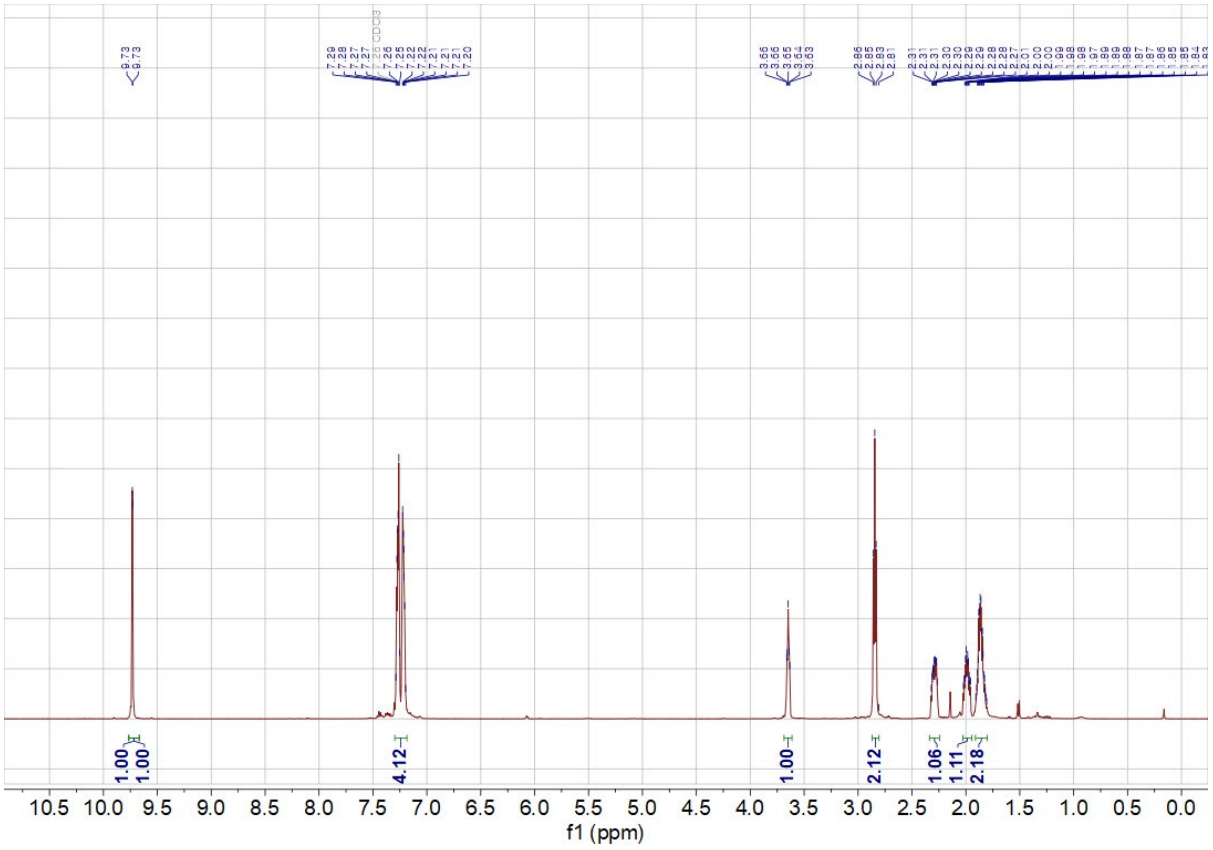
$^{1}$H NMR (400 MHz, $CDCl_3$) of **10**



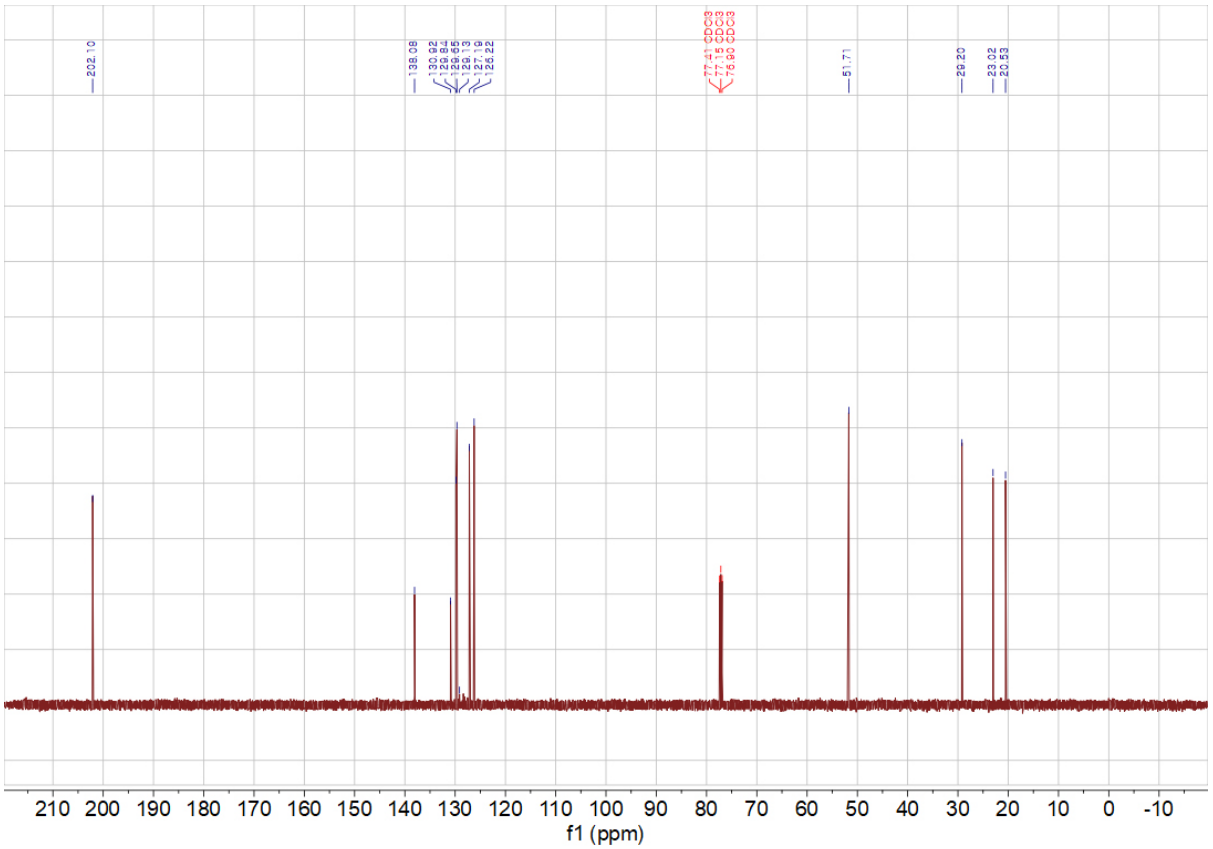

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **10**



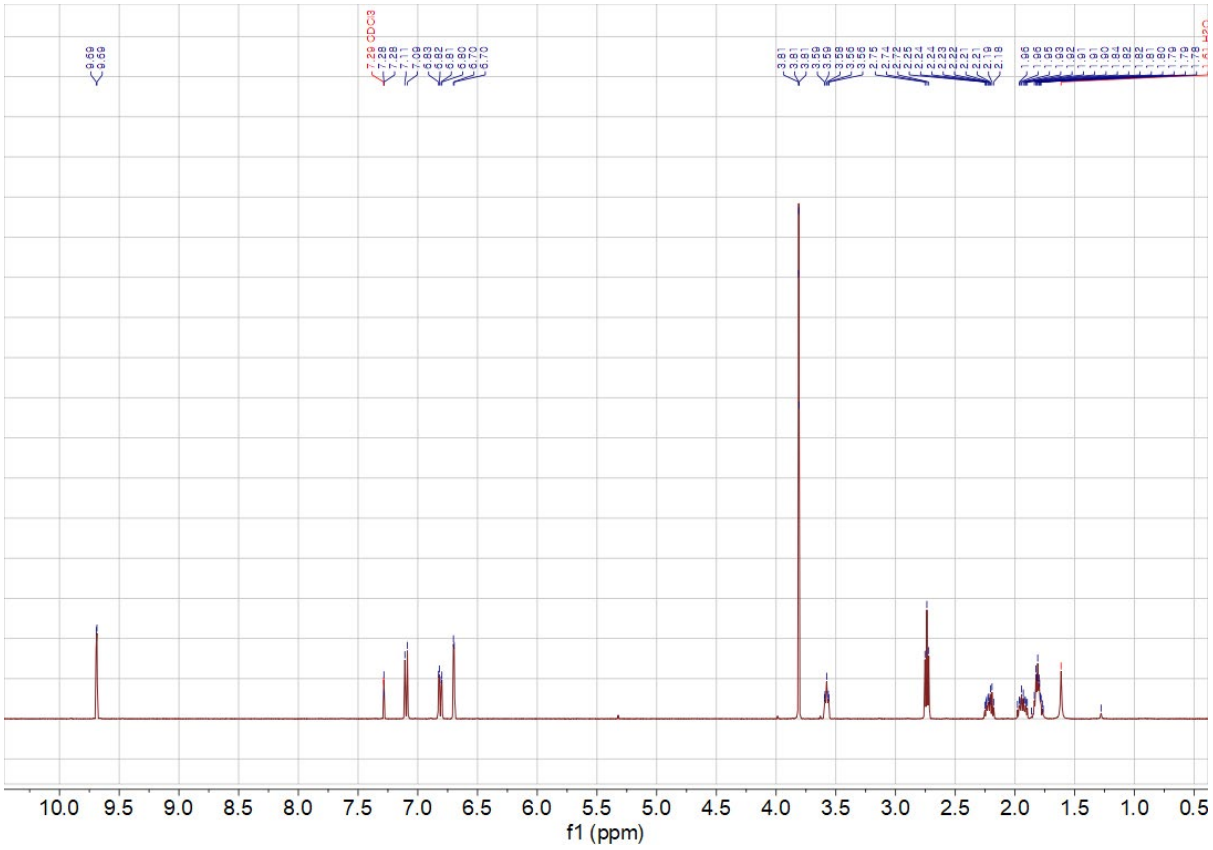
$^{1}$H NMR (500 MHz, $CDCl_3$) of **11**



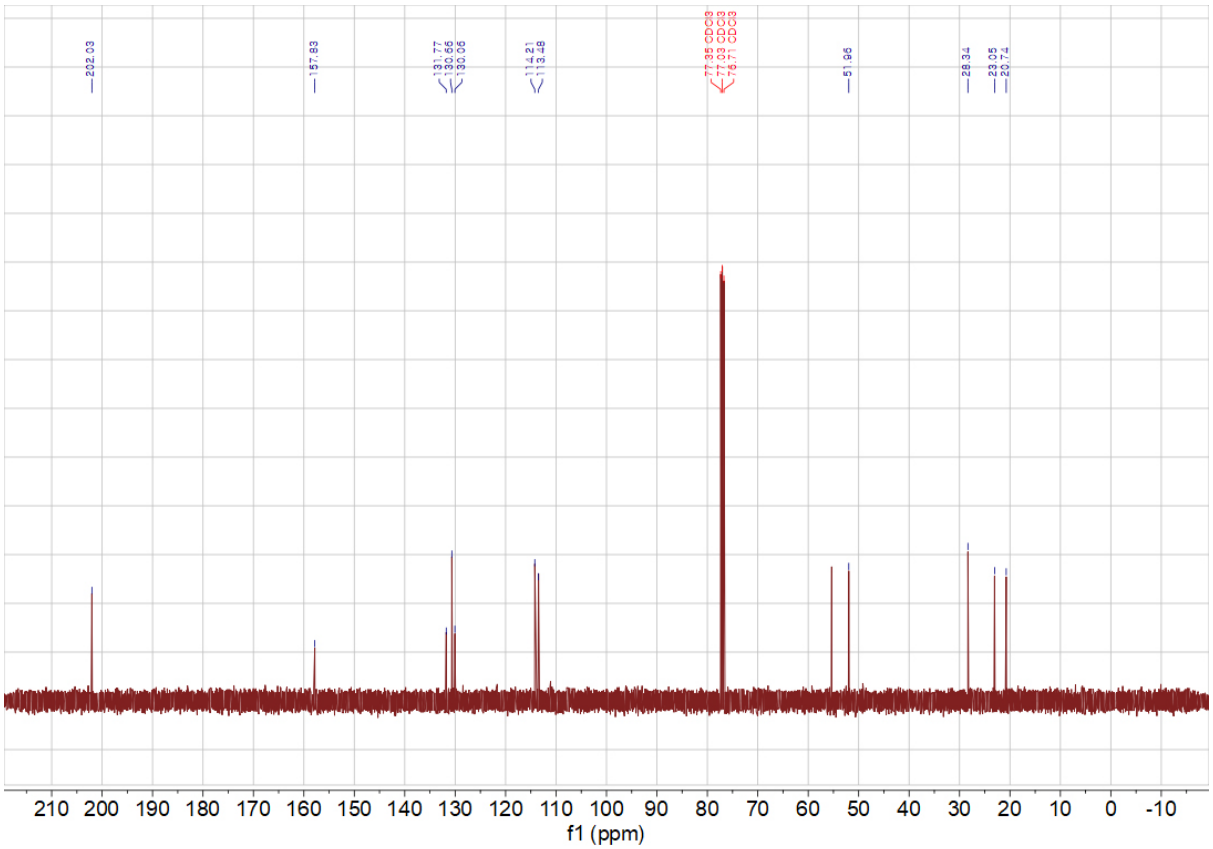

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **11**



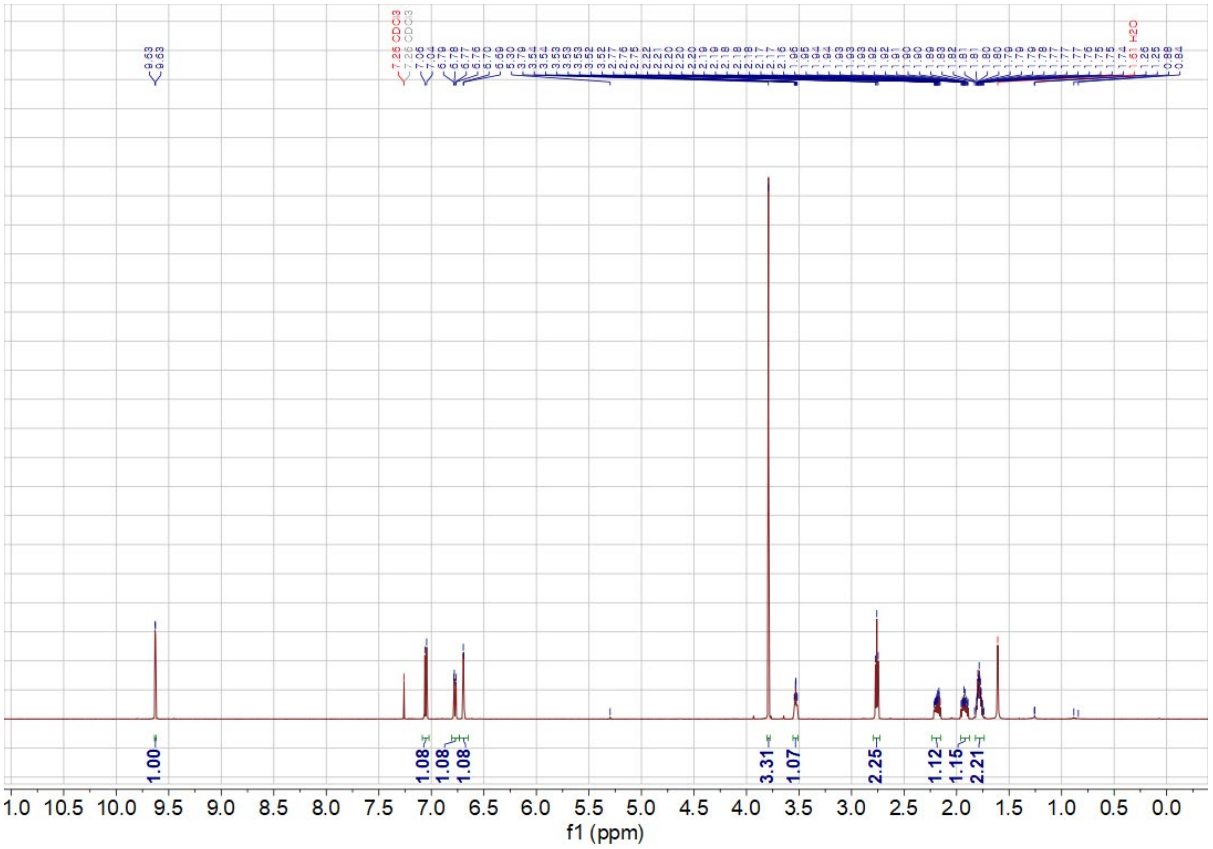
$^{1}$H NMR (400 MHz, $CDCl_3$) of **12**



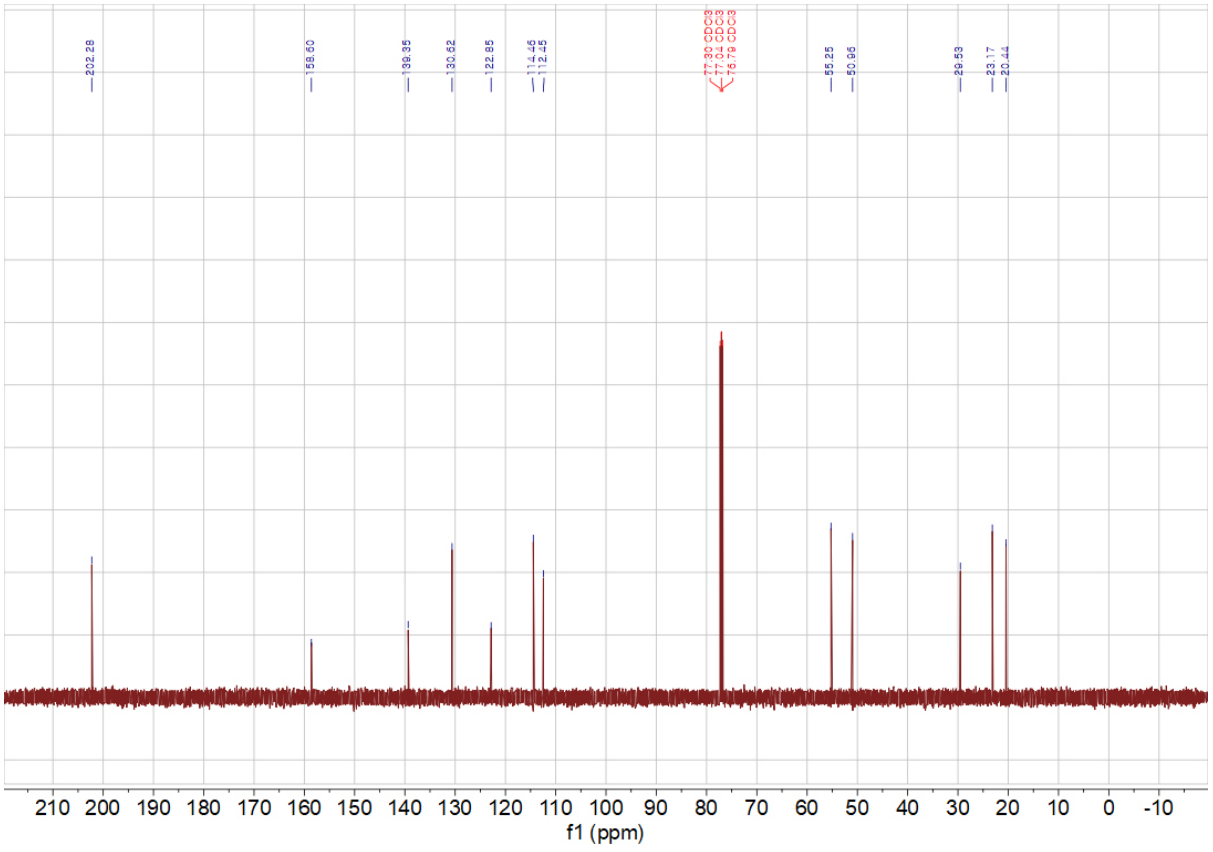

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **12**



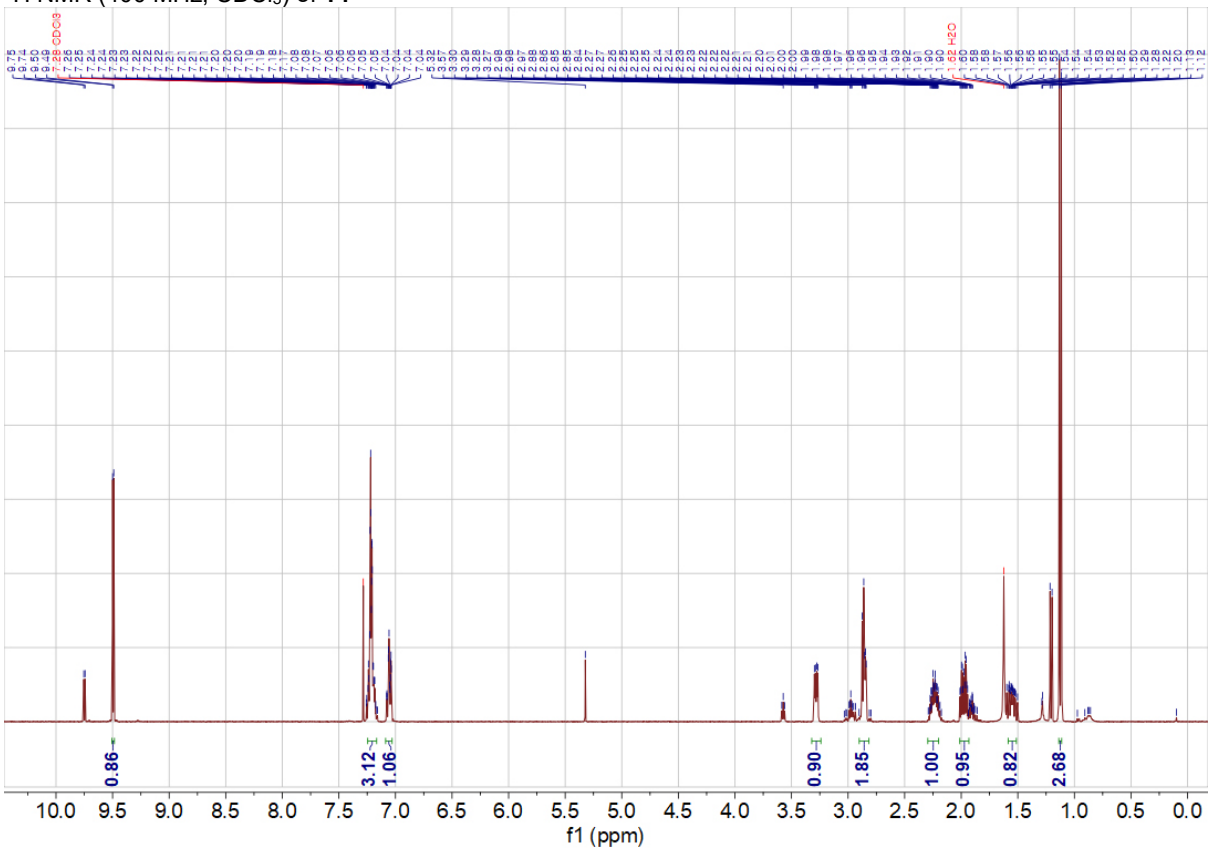
$^{1}$H NMR (500 MHz, $CDCl_3$) of **13**



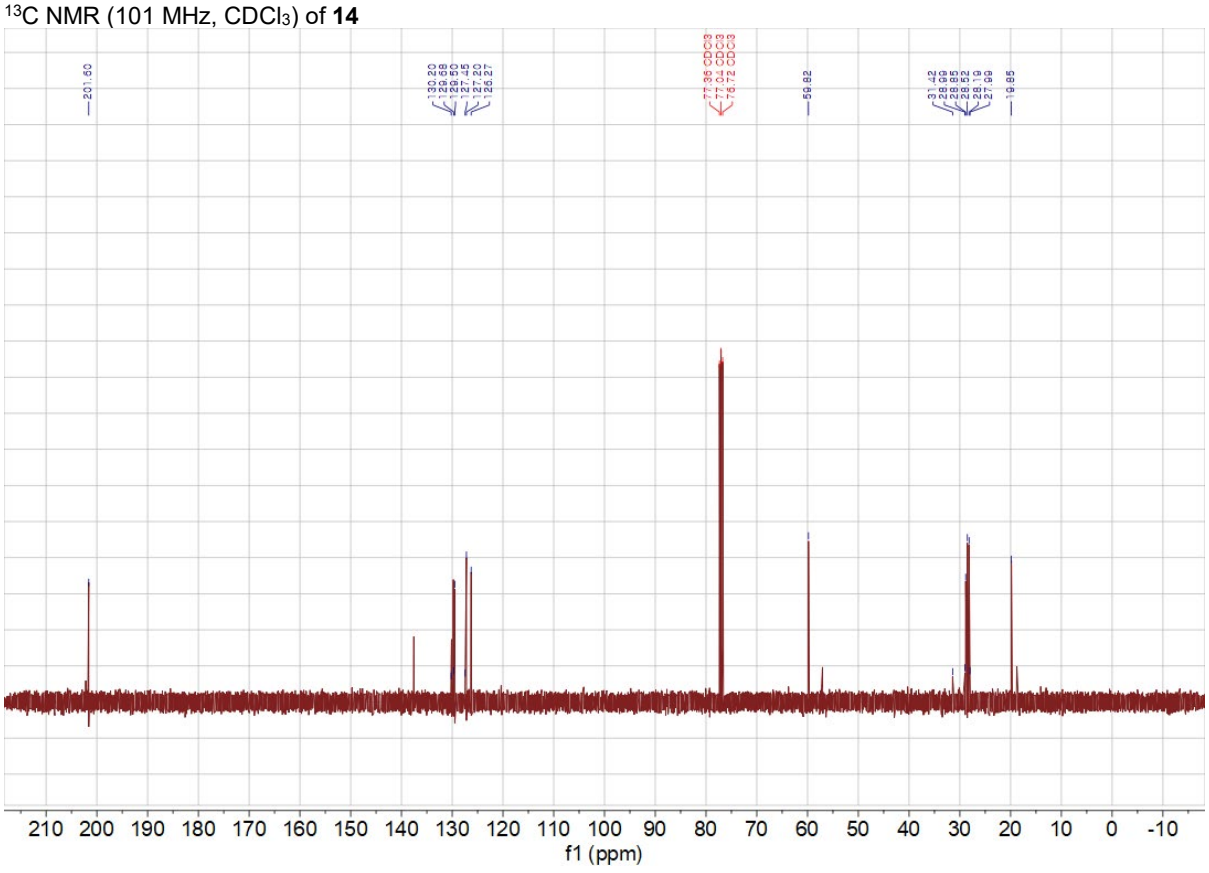

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **13**



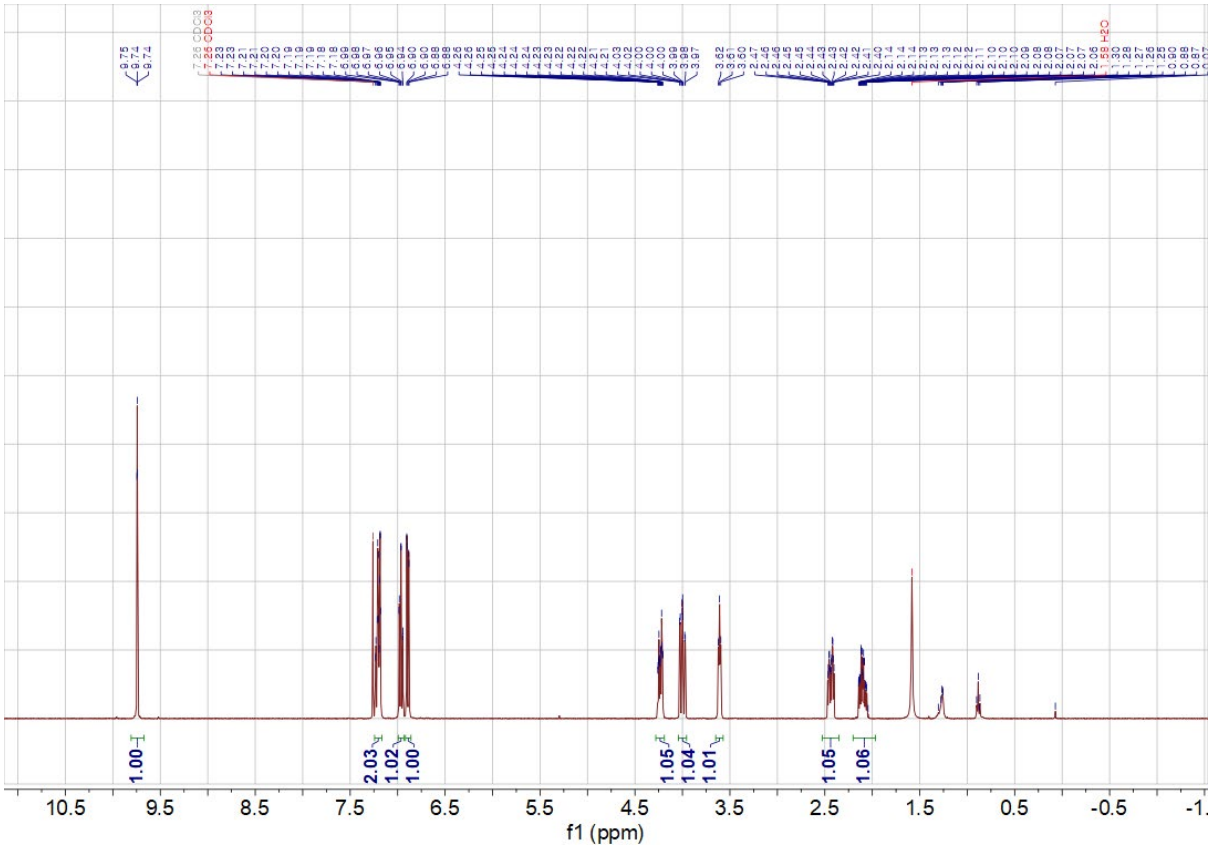
$^{1}$H NMR (400 MHz, $CDCl_3$) of **14**



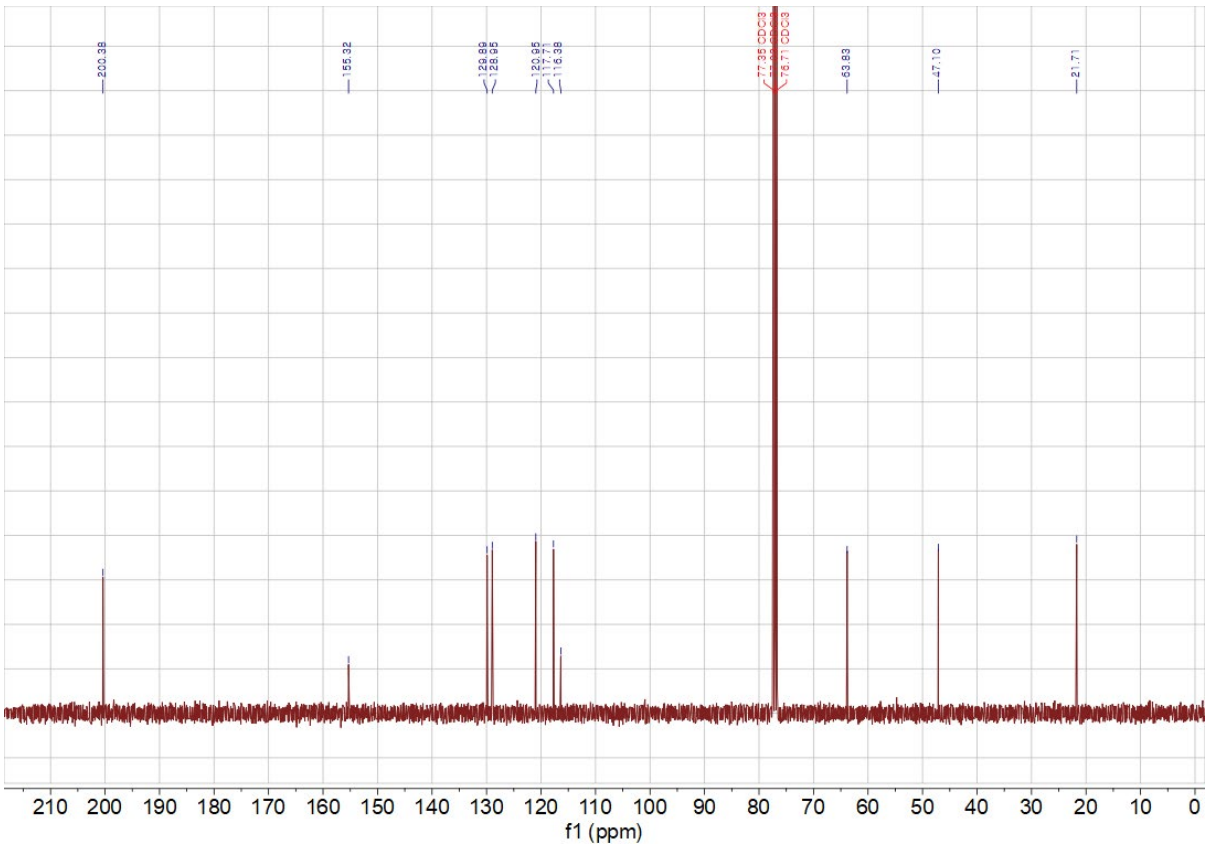

$^{13}$C NMR (101 MHz, $CDCl_3$) of **14**



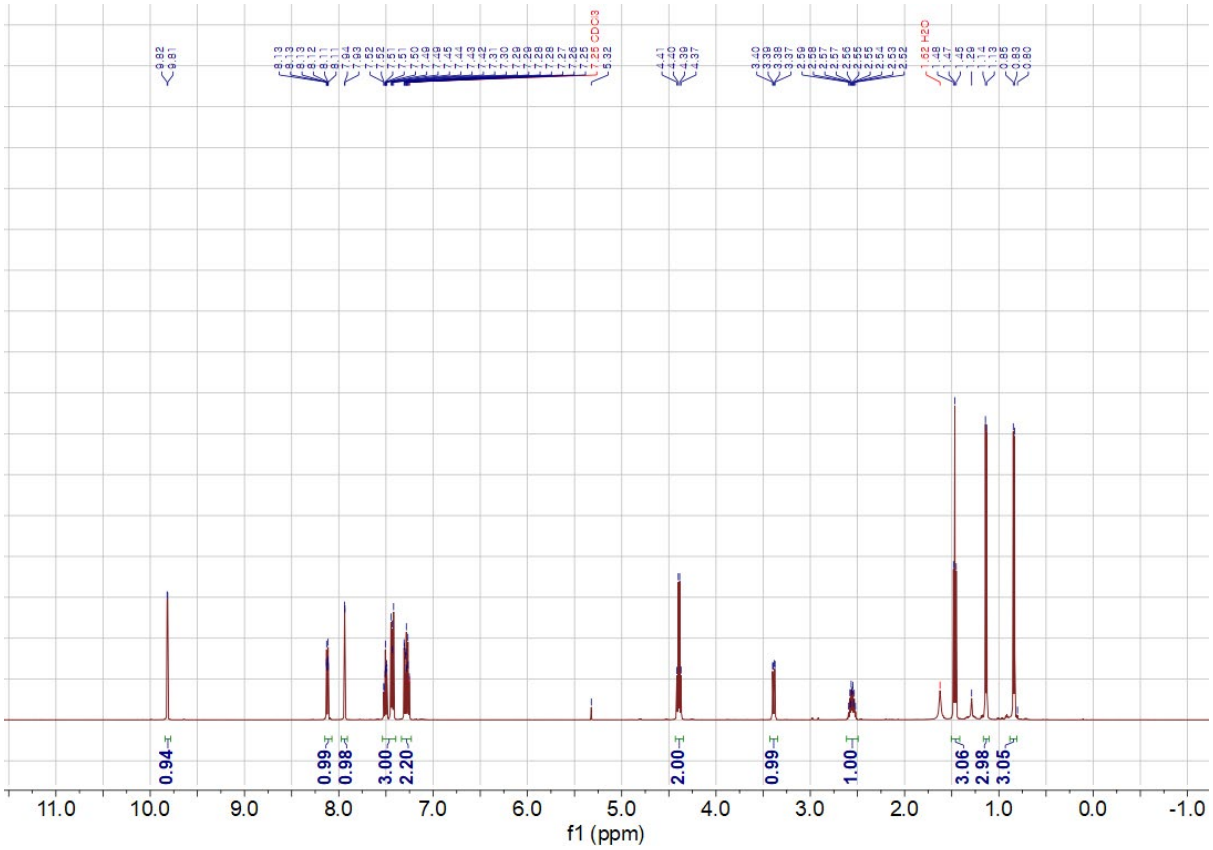
$^{1}$H NMR (400 MHz, $CDCl_3$) of **15**



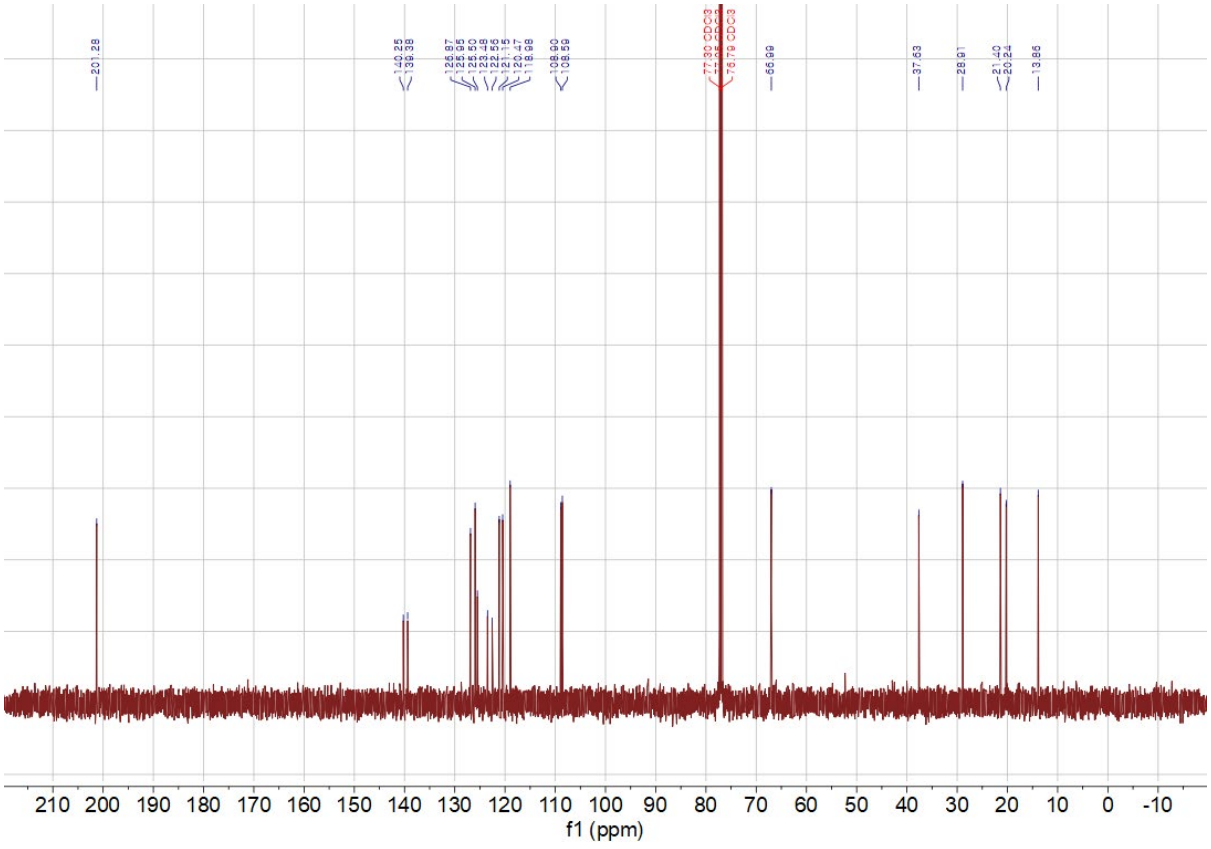

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **15**



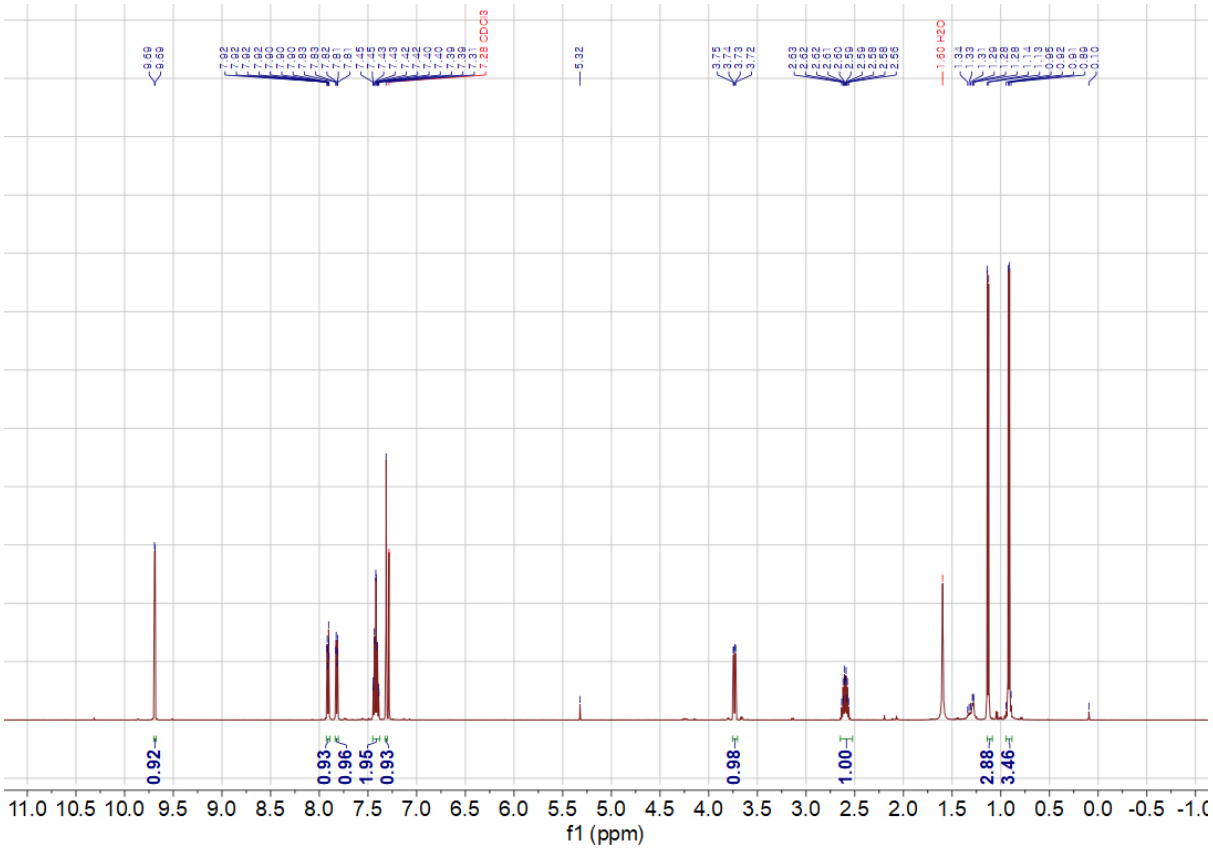
$^{1}$H NMR (500 MHz, $CDCl_3$) of **16**



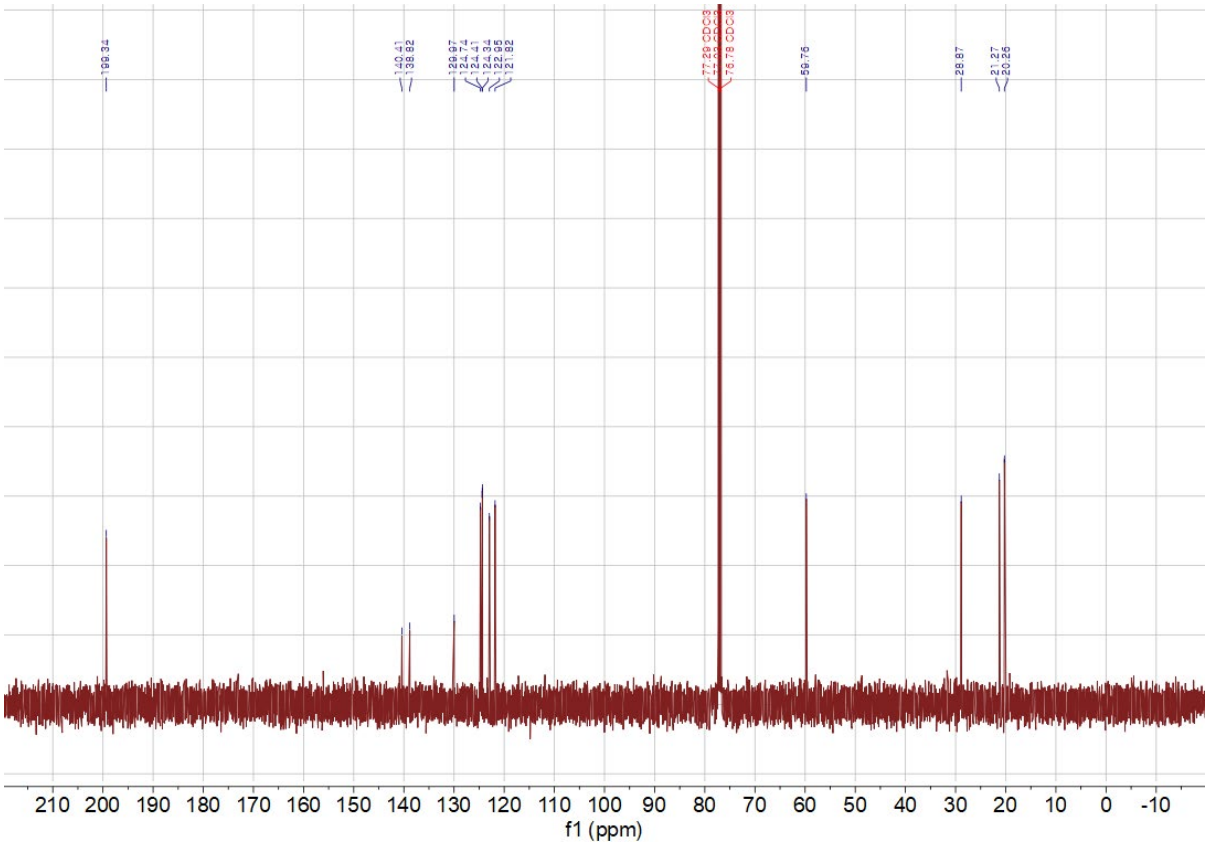

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of **16**



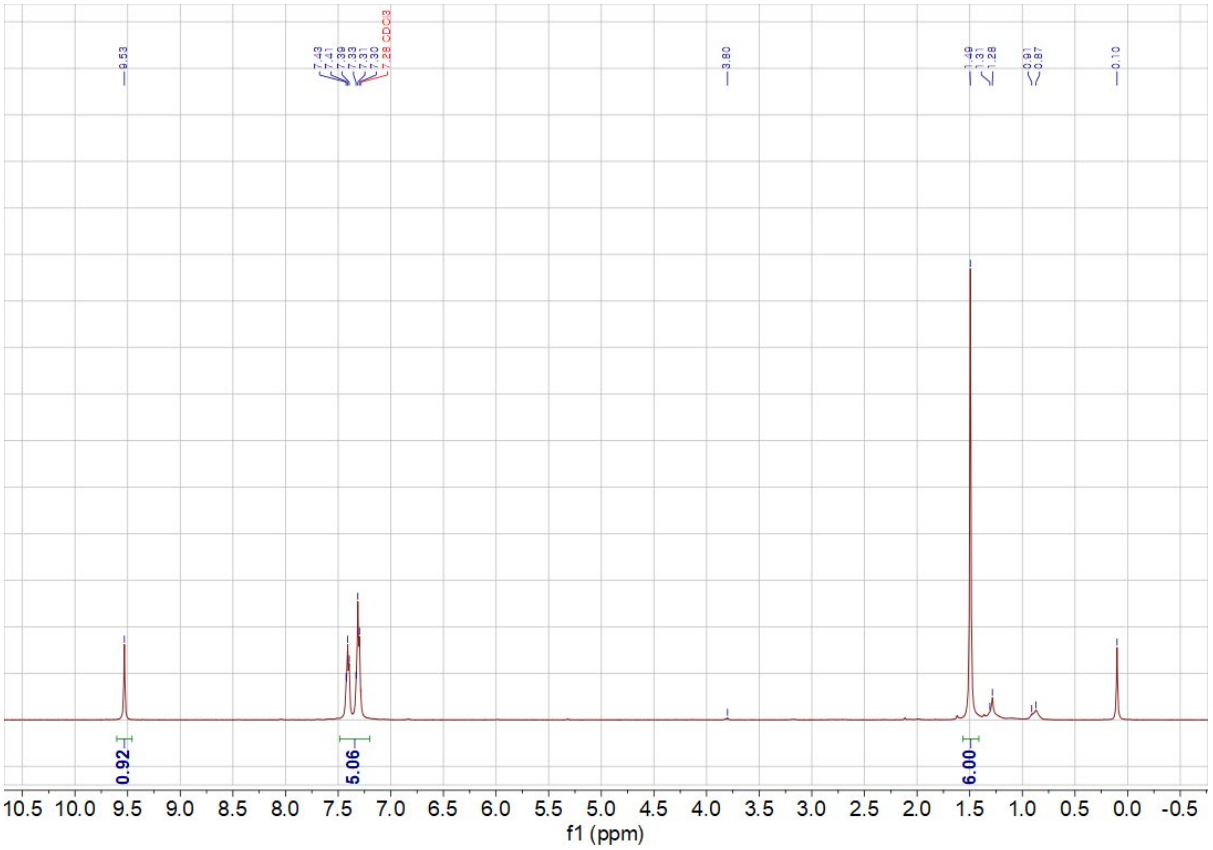
$^{1}$H NMR (500 MHz, $CDCl_3$) of **17**



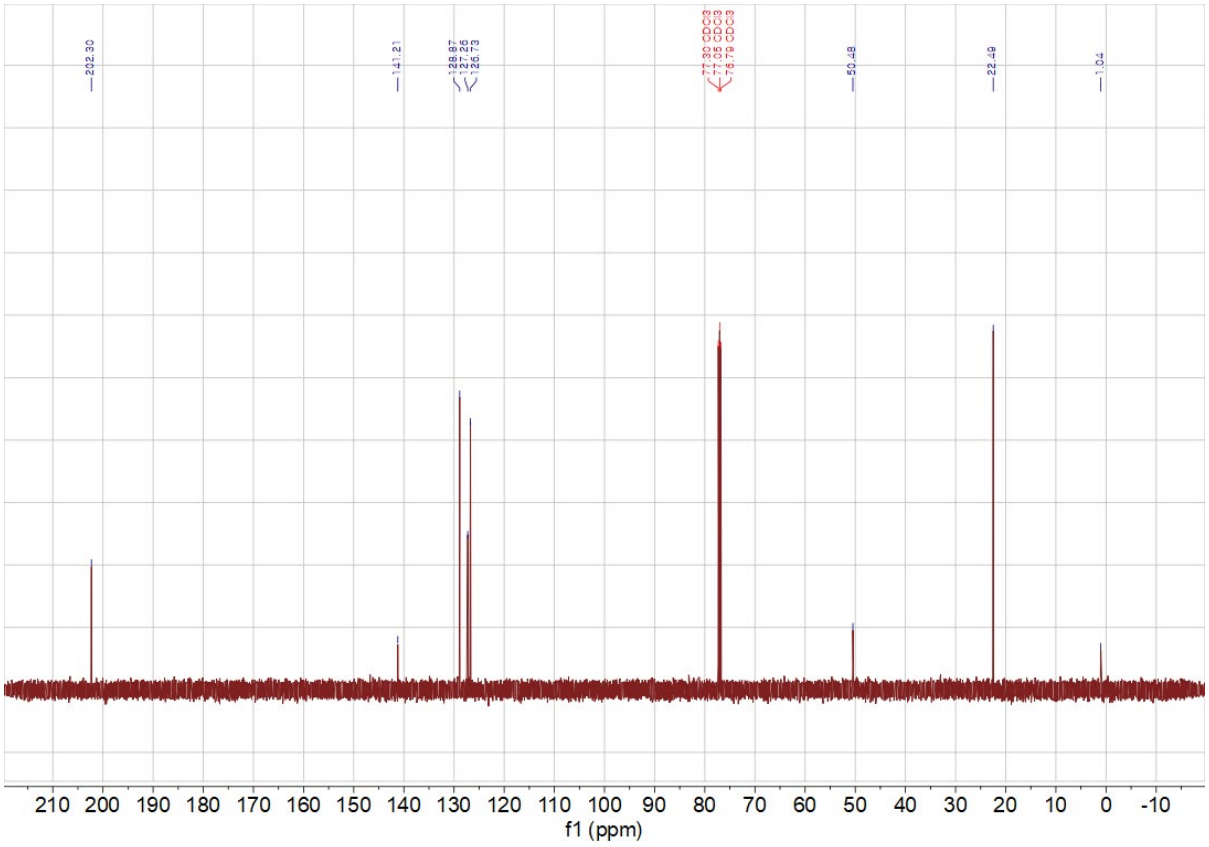

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **17**



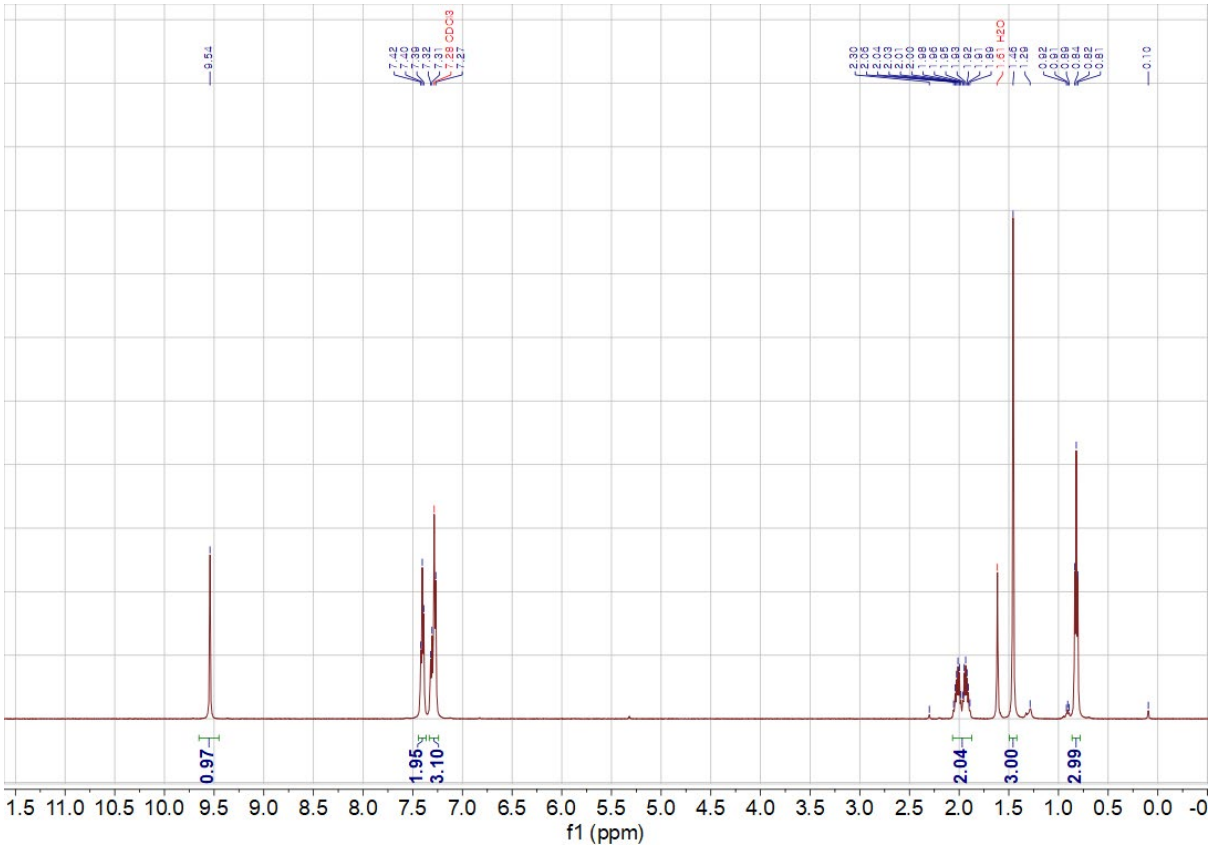
$^{1}$H NMR (500 MHz, $CDCl_3$) of **18**



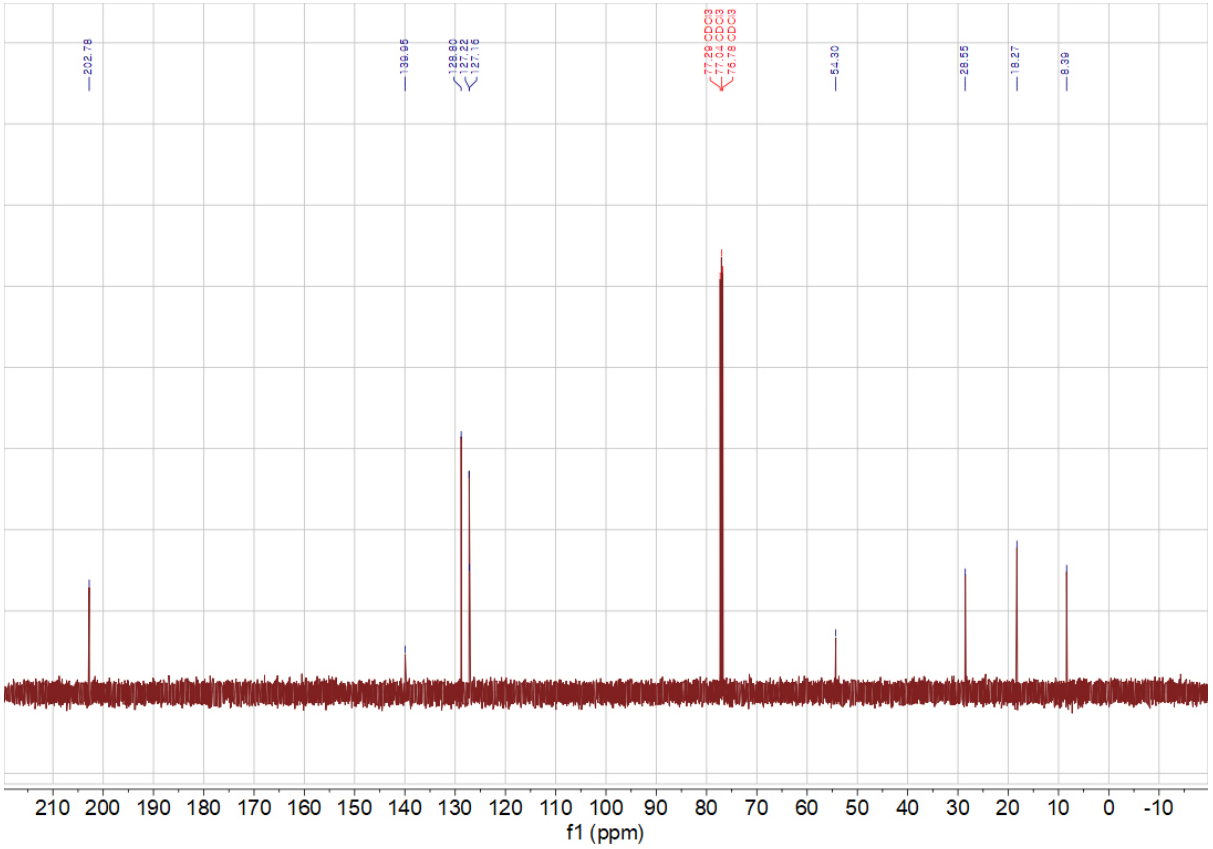

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **18**



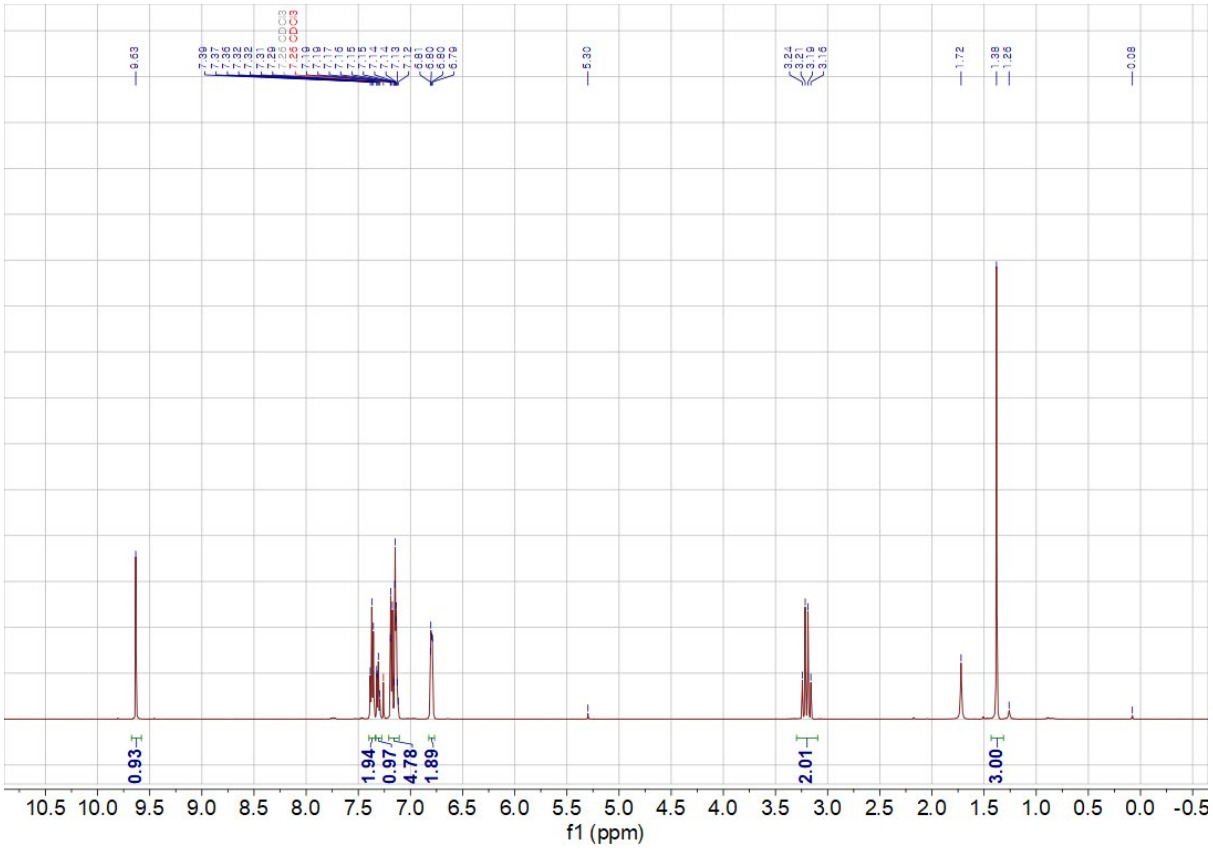
$^{1}$H NMR (500 MHz, $CDCl_3$) of **19**



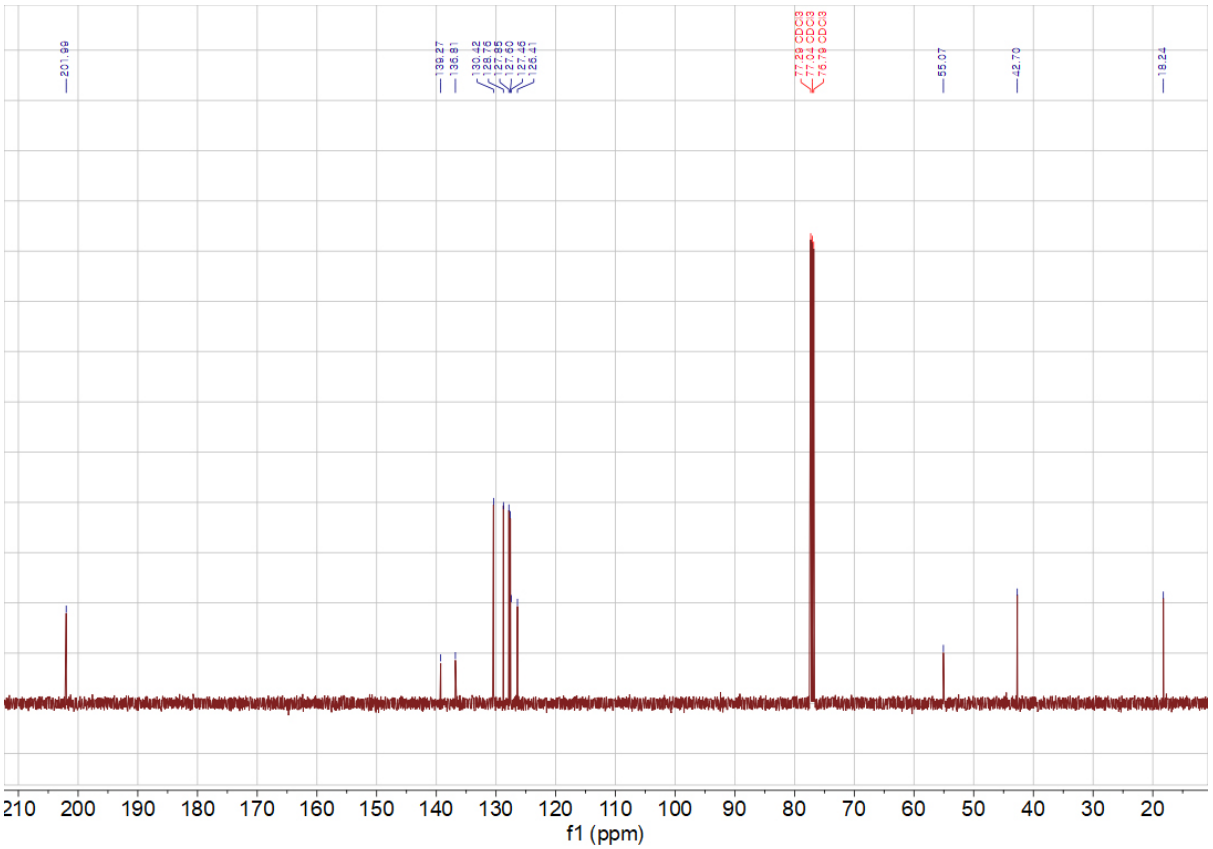

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **19**



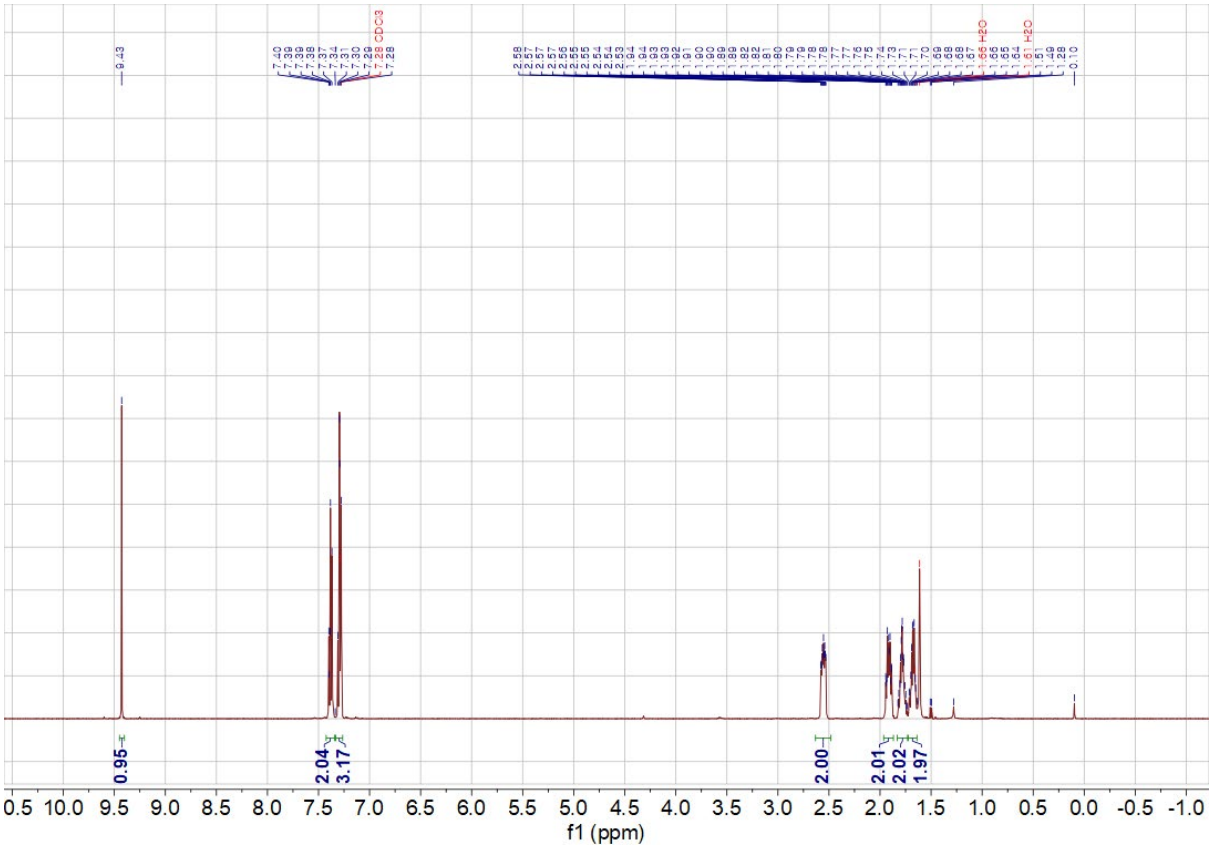
$^{1}$H NMR (500 MHz, $CDCl_3$) of **20**



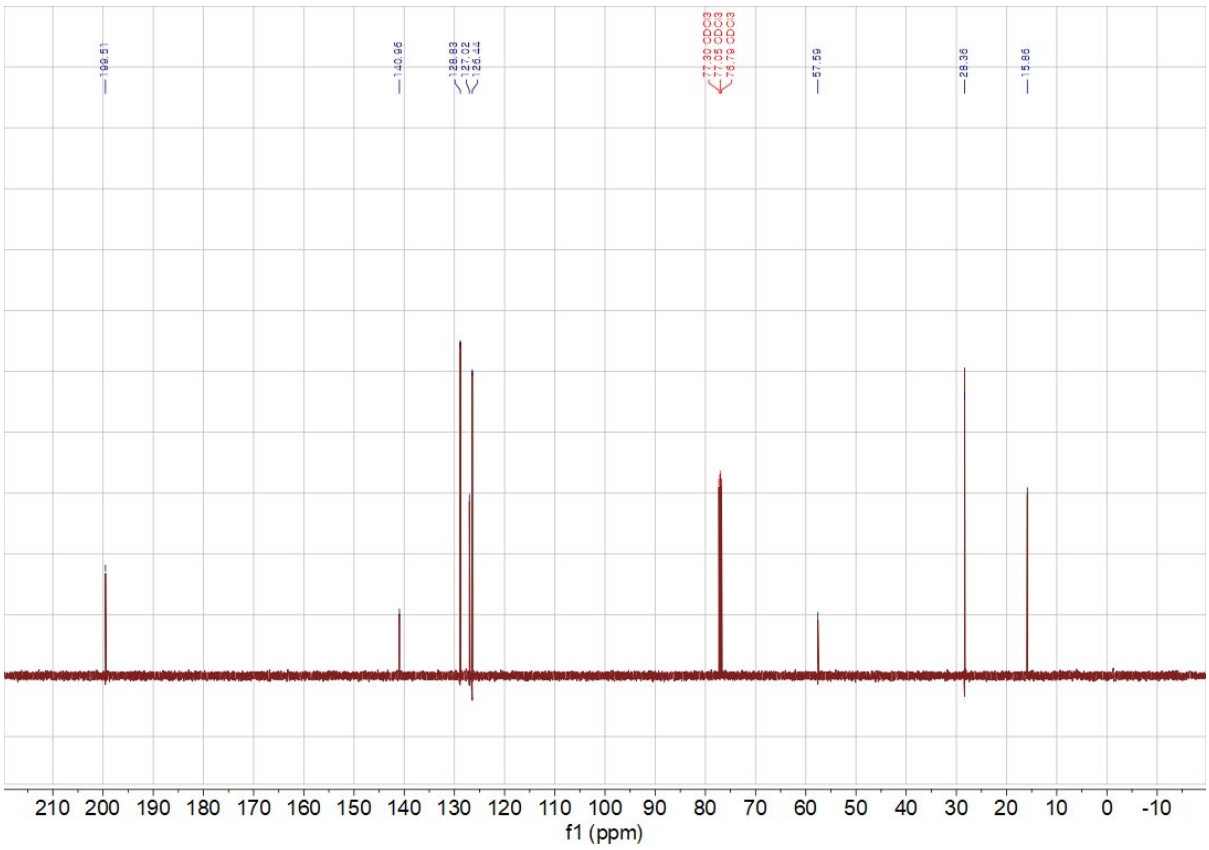

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **20**



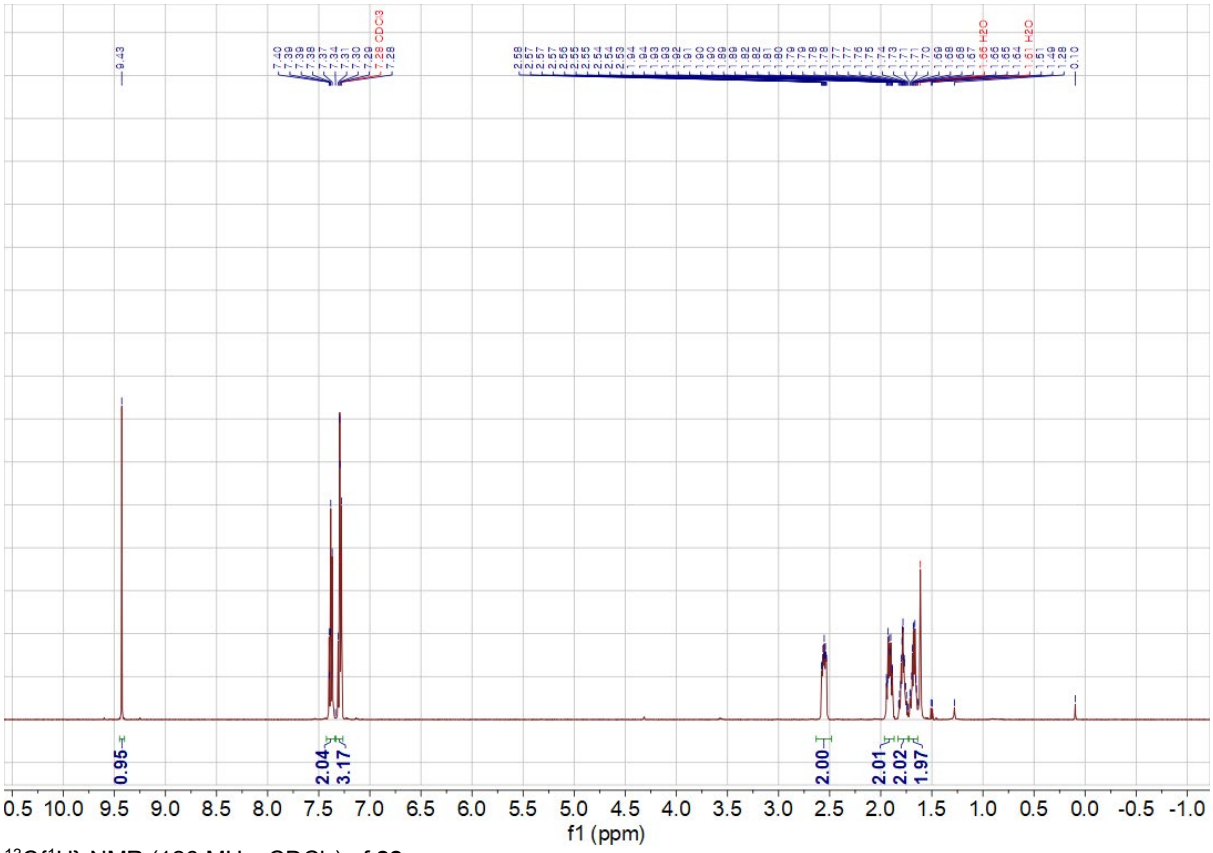
$^{1}$H NMR (500 MHz, $CDCl_3$) of **21**



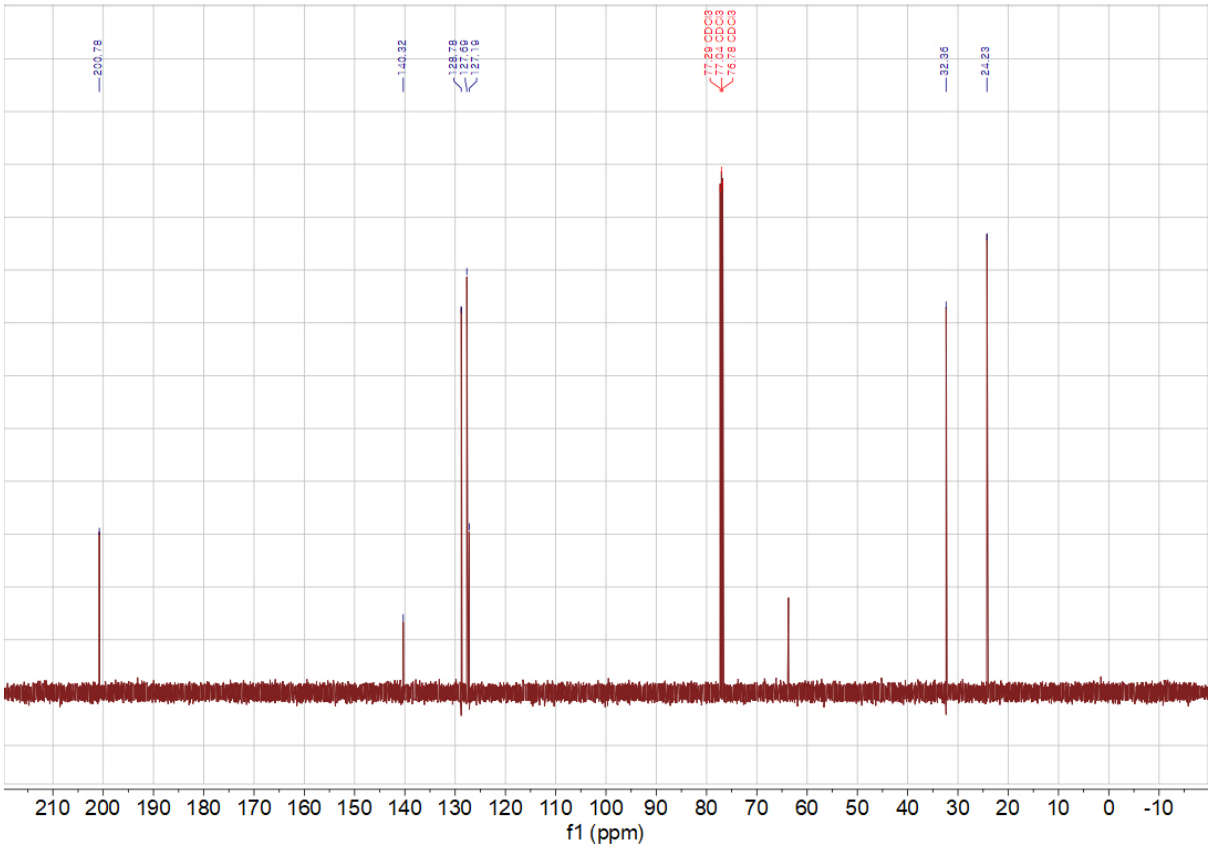

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **21**



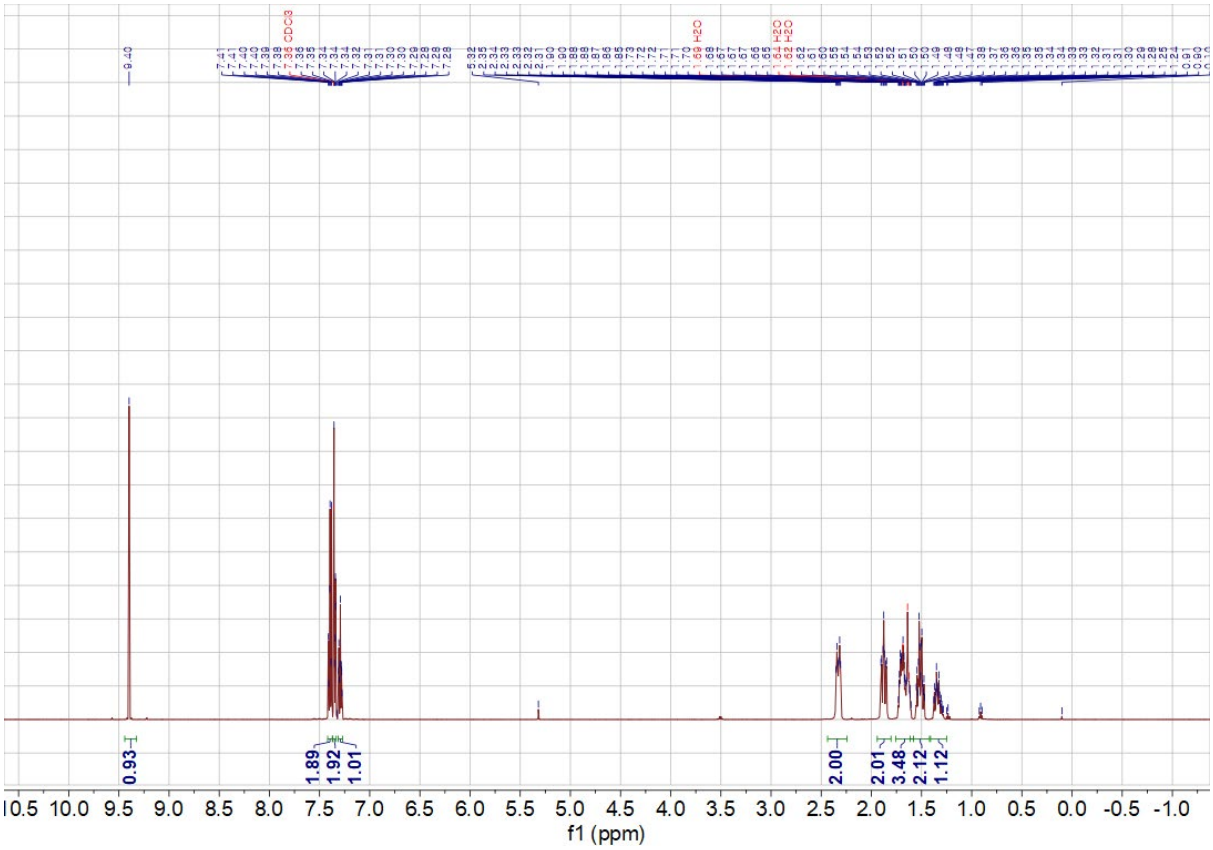
$^{1}$H NMR (500 MHz, $CDCl_3$) of **22**



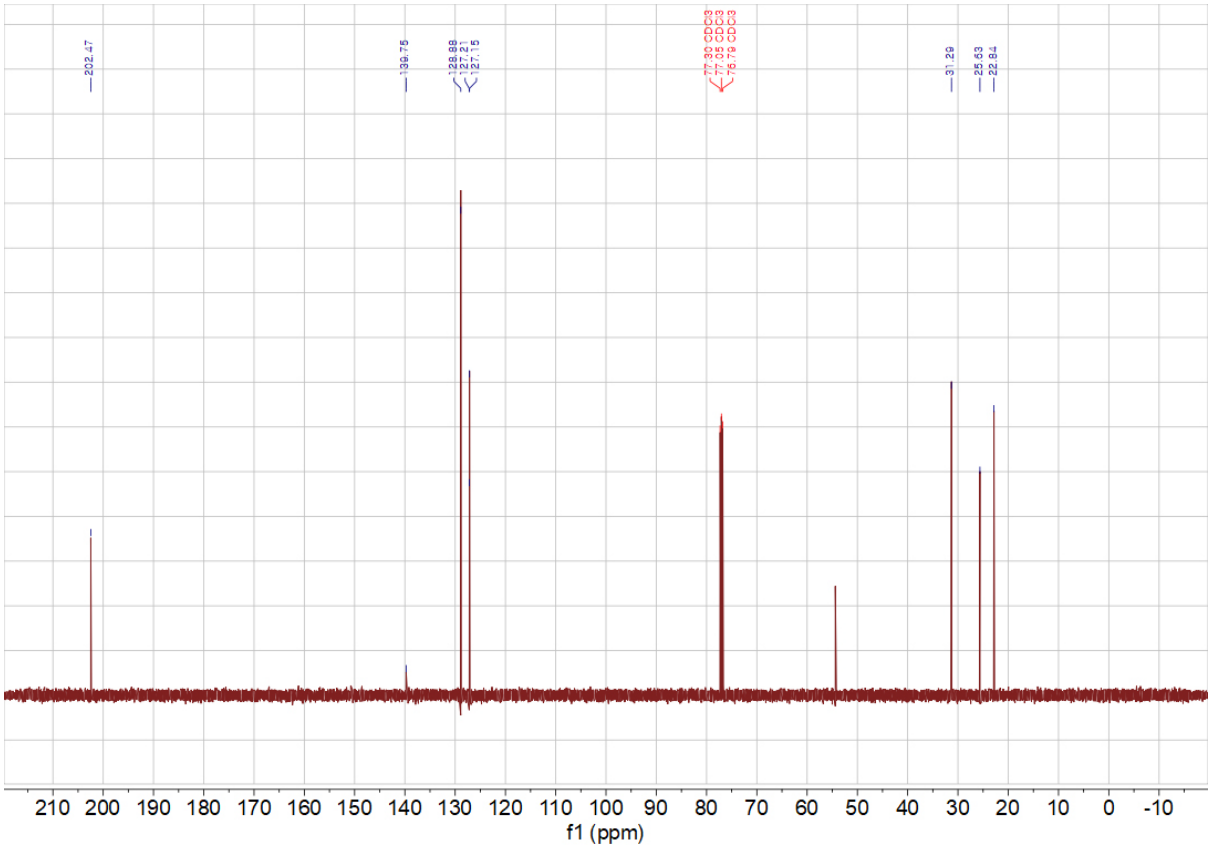

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **22**



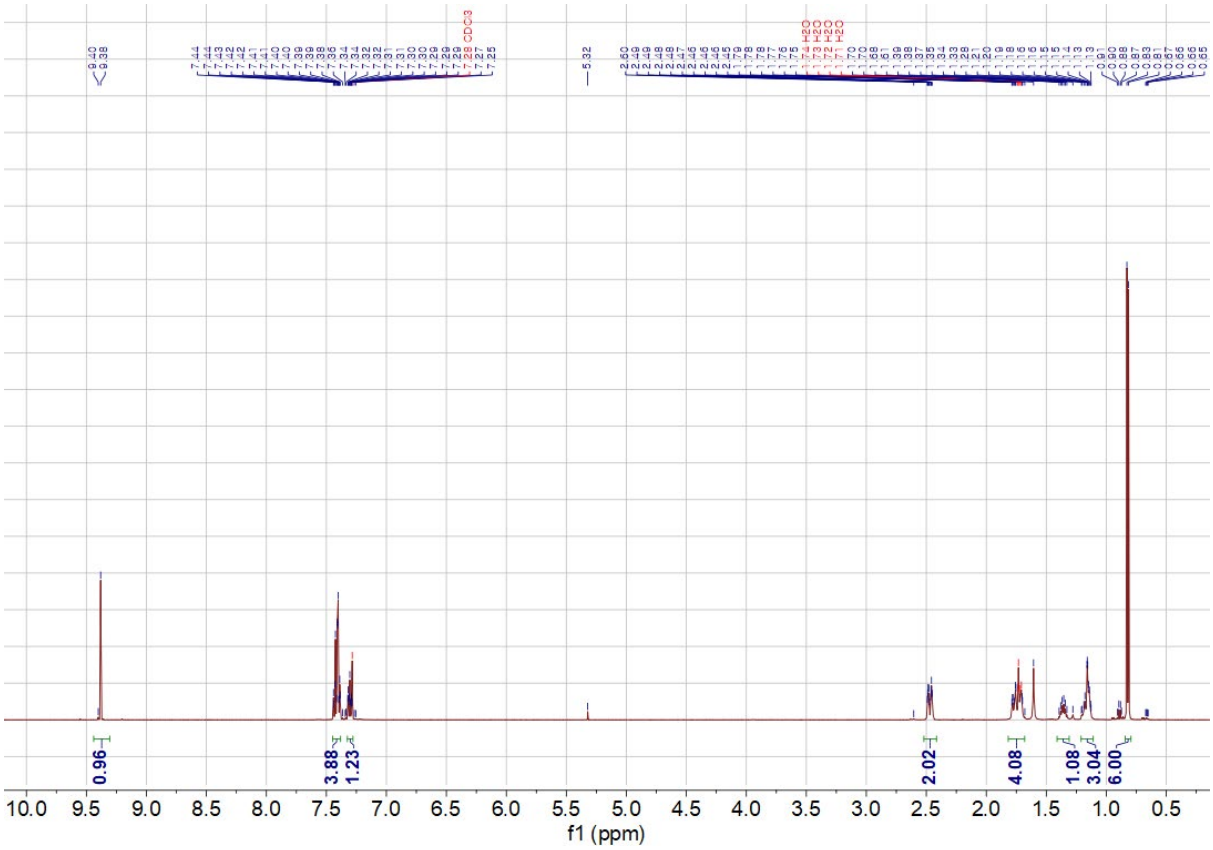
$^{1}$H NMR (500 MHz, $CDCl_3$) of **23**



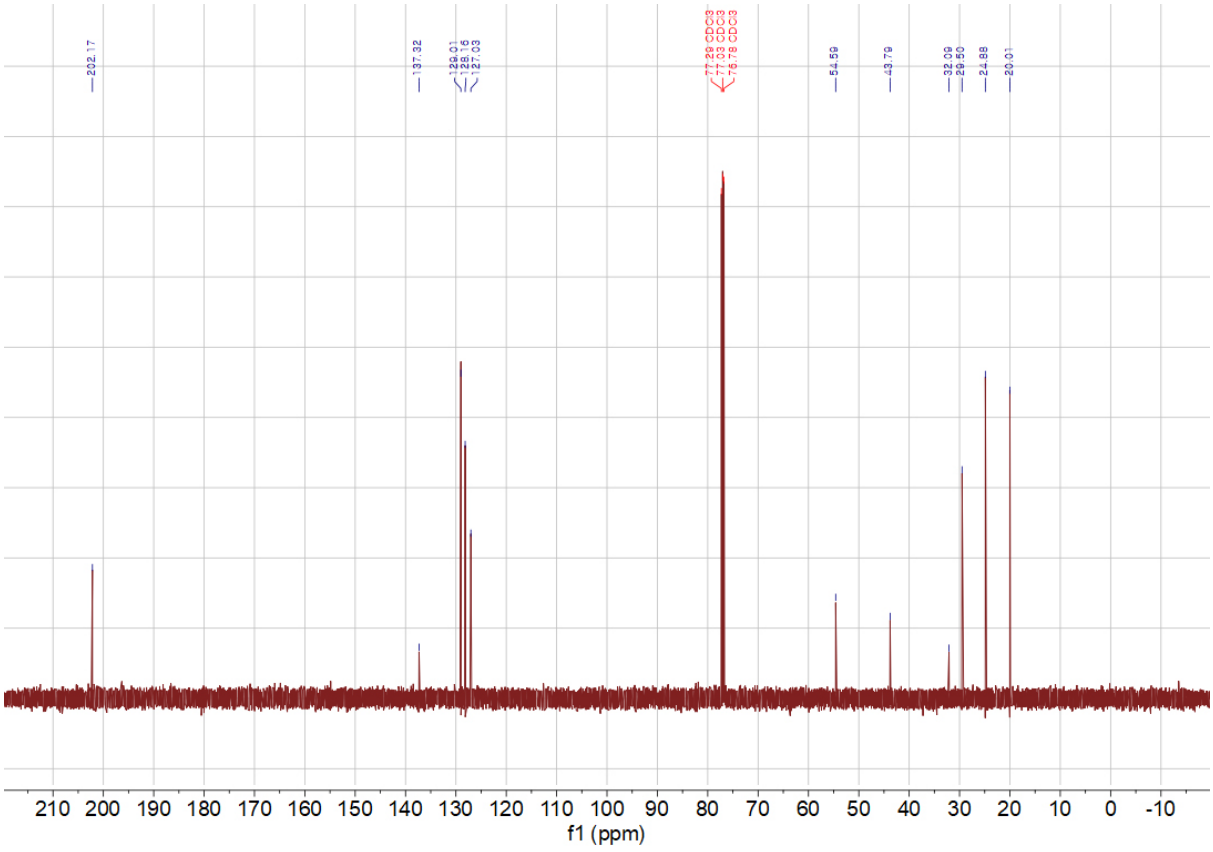

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **23**



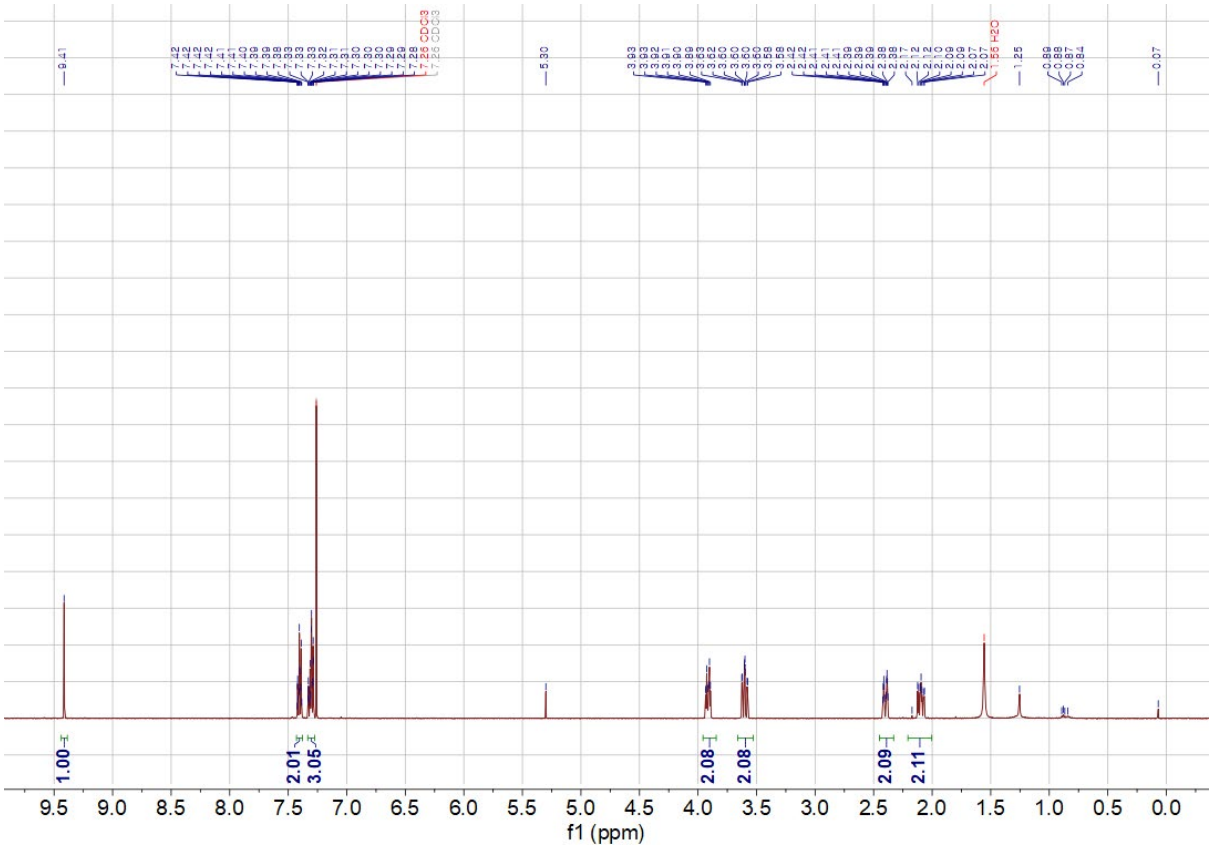
$^{1}$H NMR (500 MHz, $CDCl_3$) of **24**



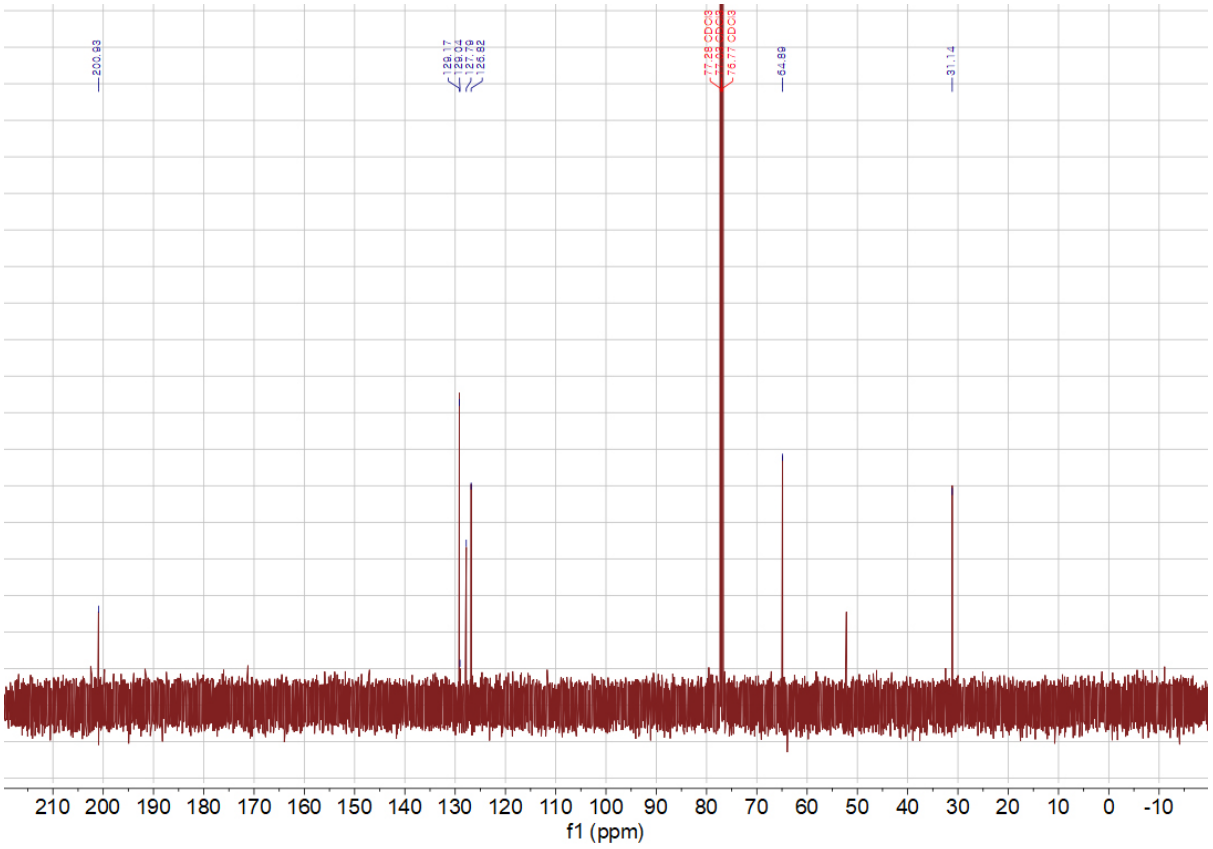

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **24**



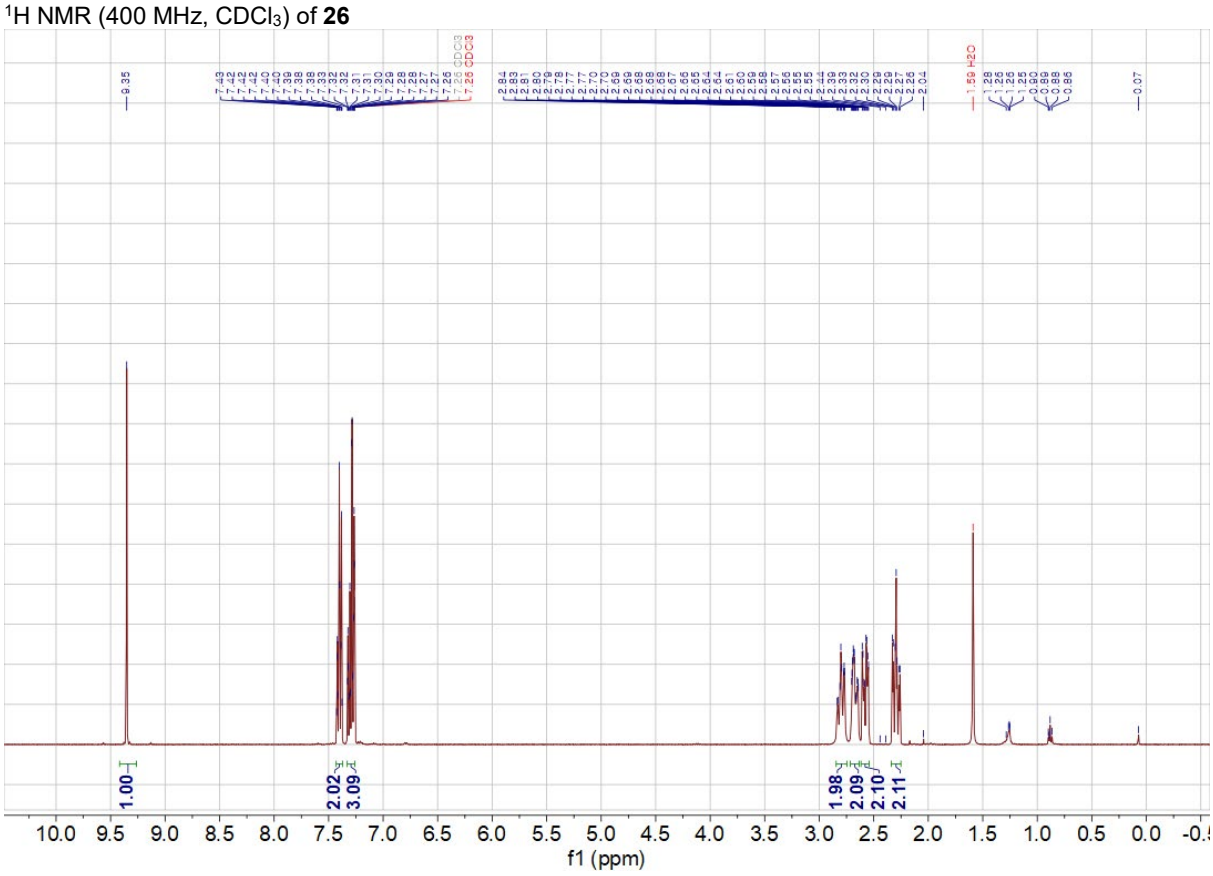
$^{1}$H NMR (500 MHz, $CDCl_3$) of **25**



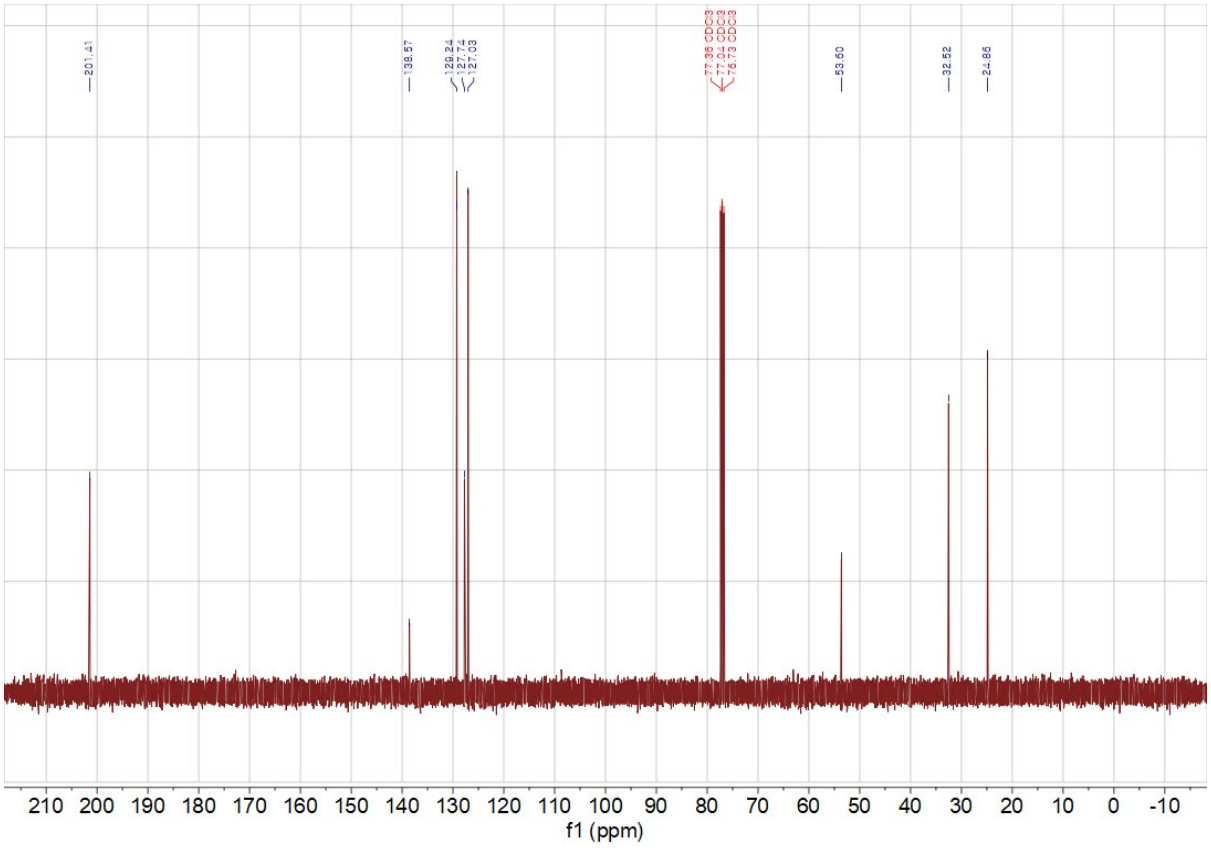

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **25**



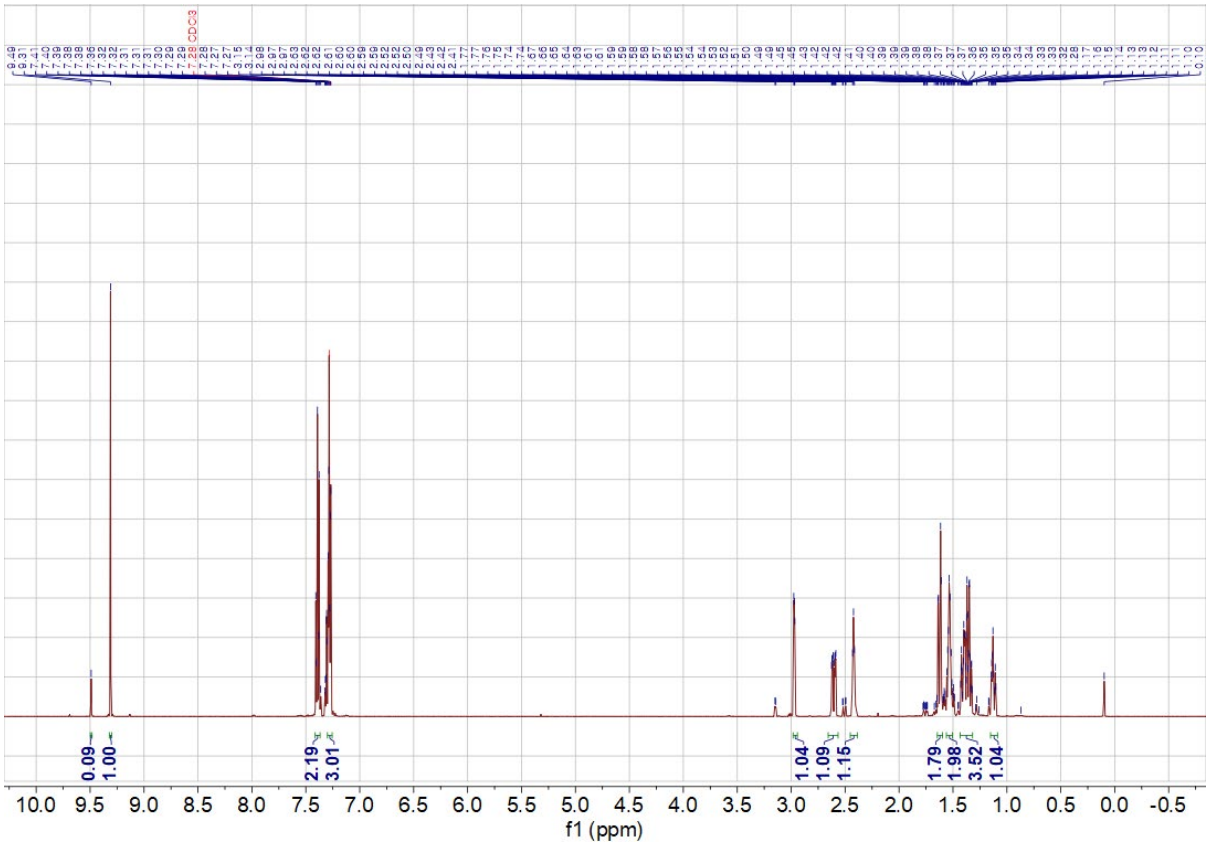
$^{1}$H NMR (400 MHz, $CDCl_3$) of **26**



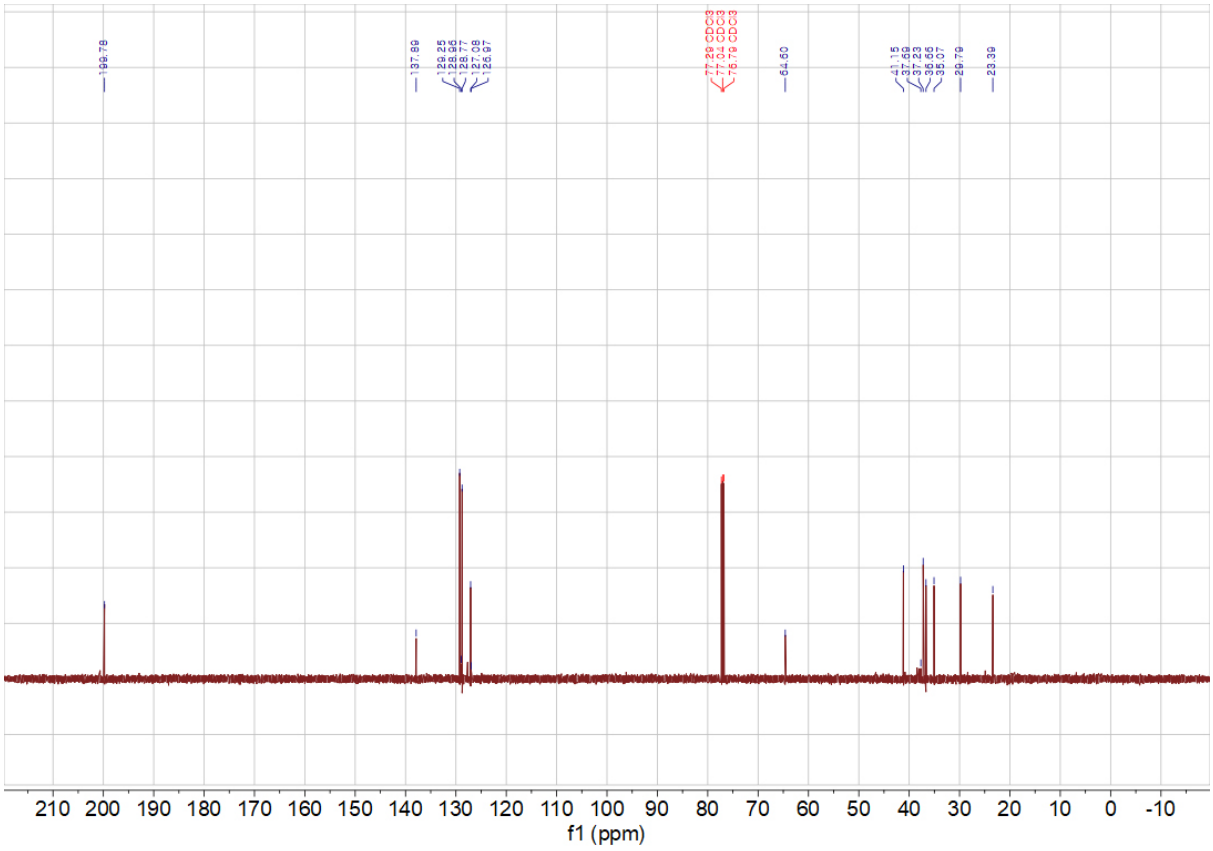

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **26**



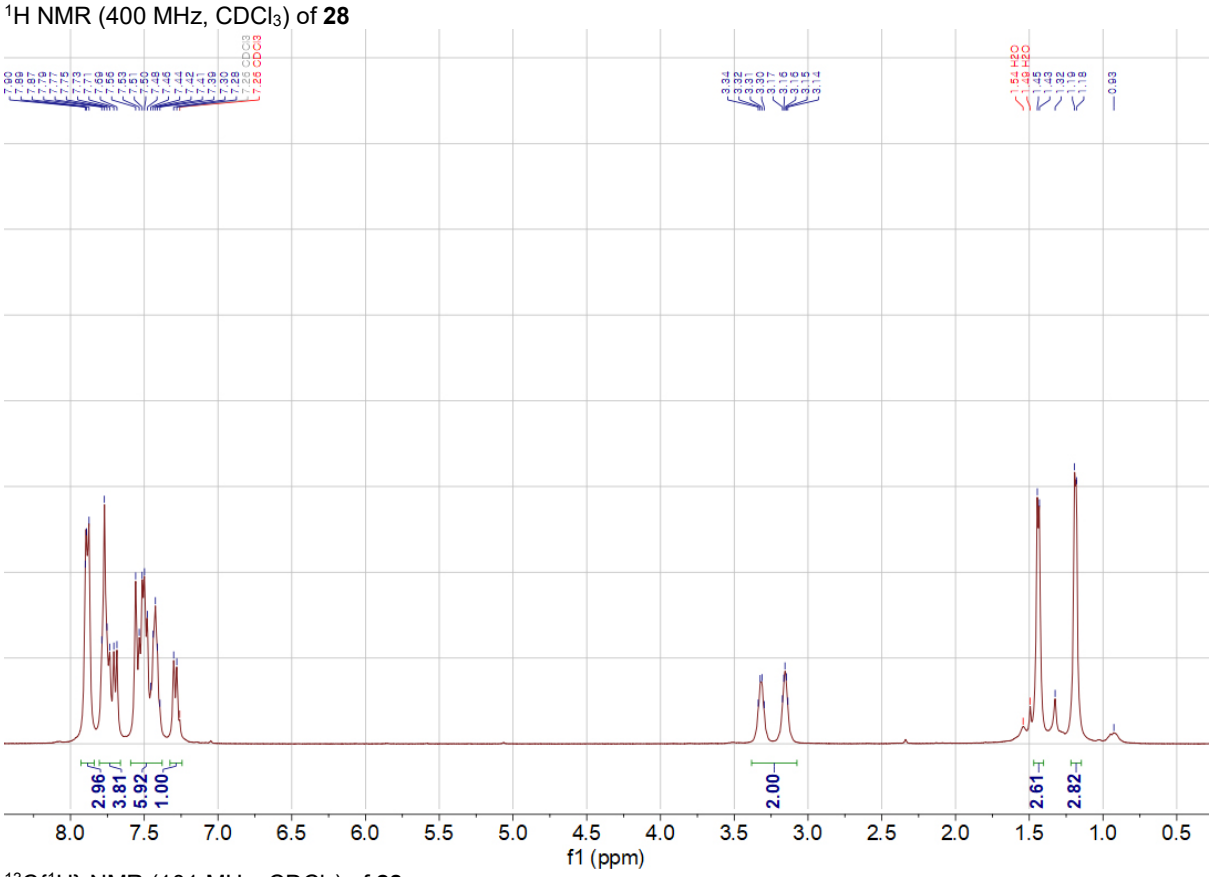
$^{1}$H NMR (500 MHz, $CDCl_3$) of **27**



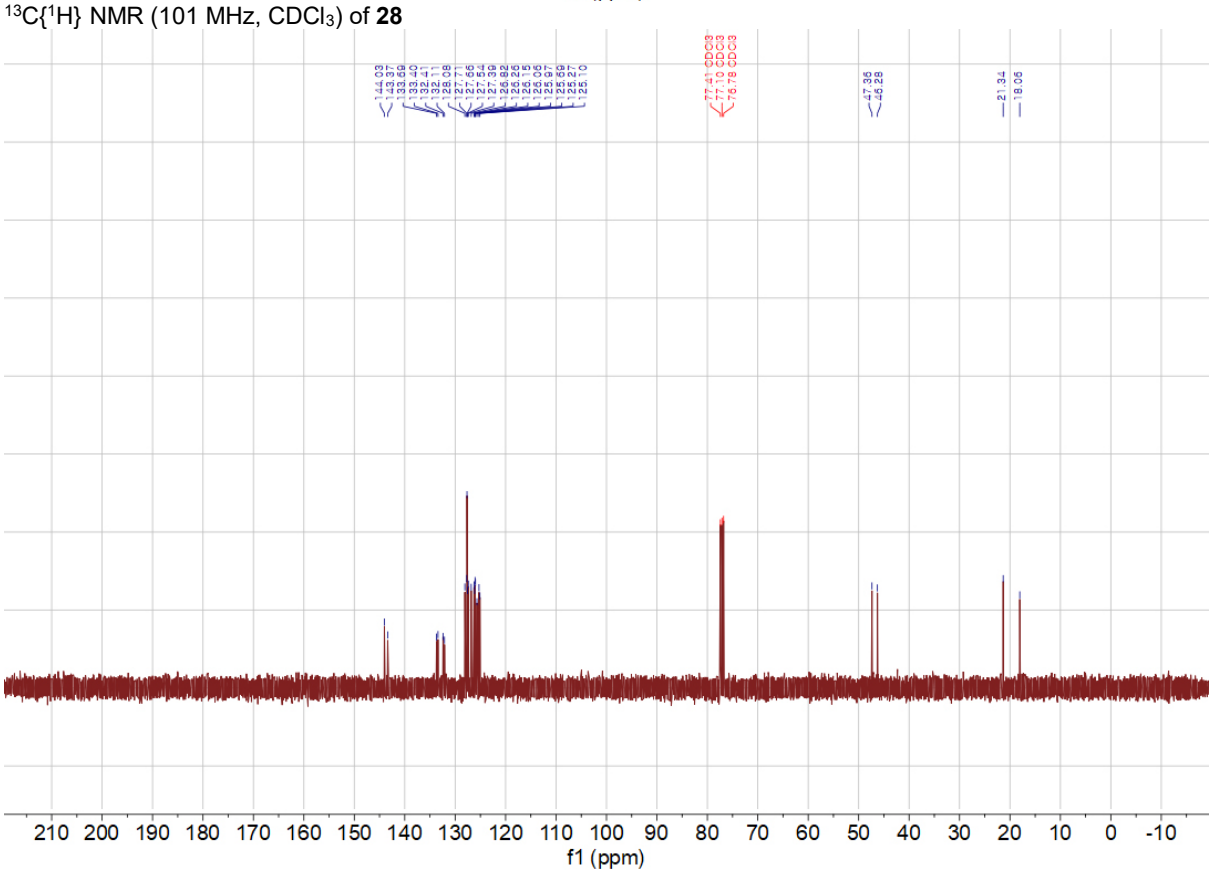

$^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) of **27**



$^{1}$H NMR (400 MHz, $CDCl_3$) of **28**

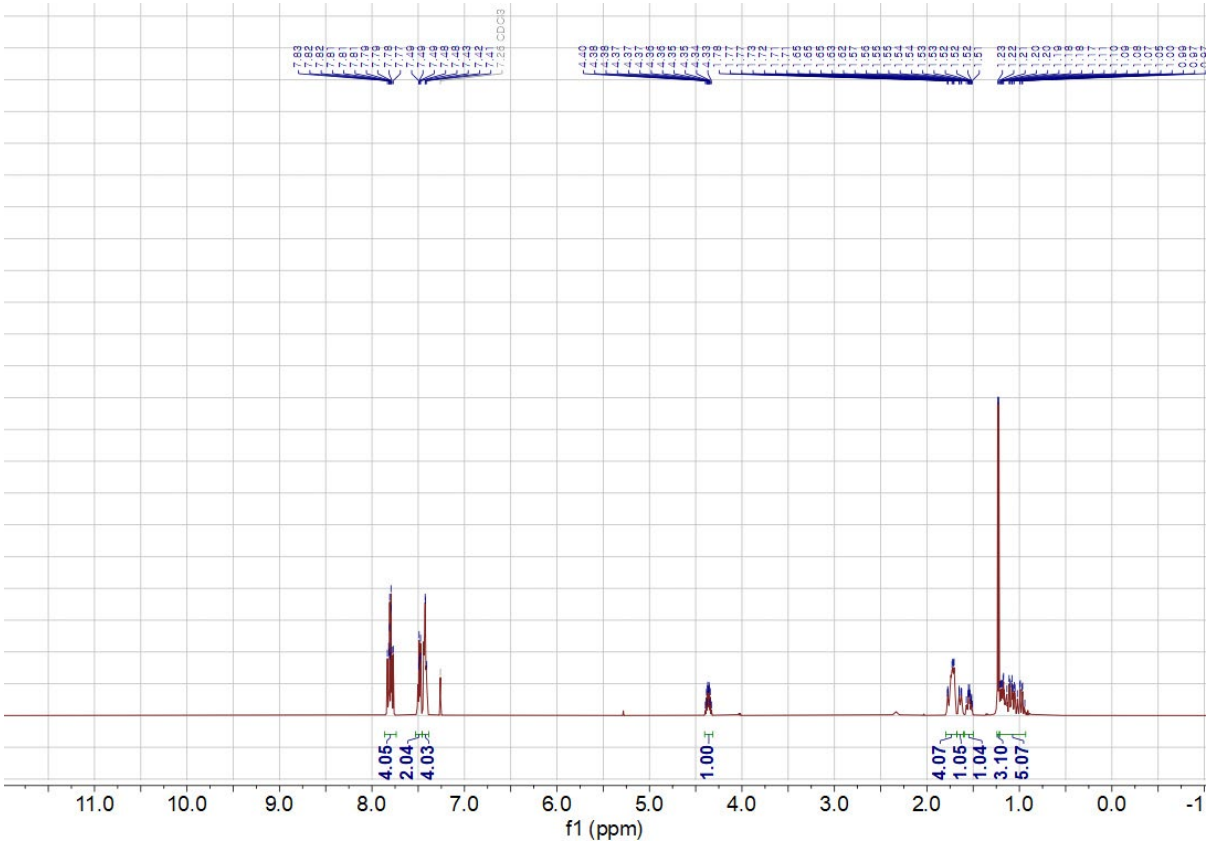



$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of **28**

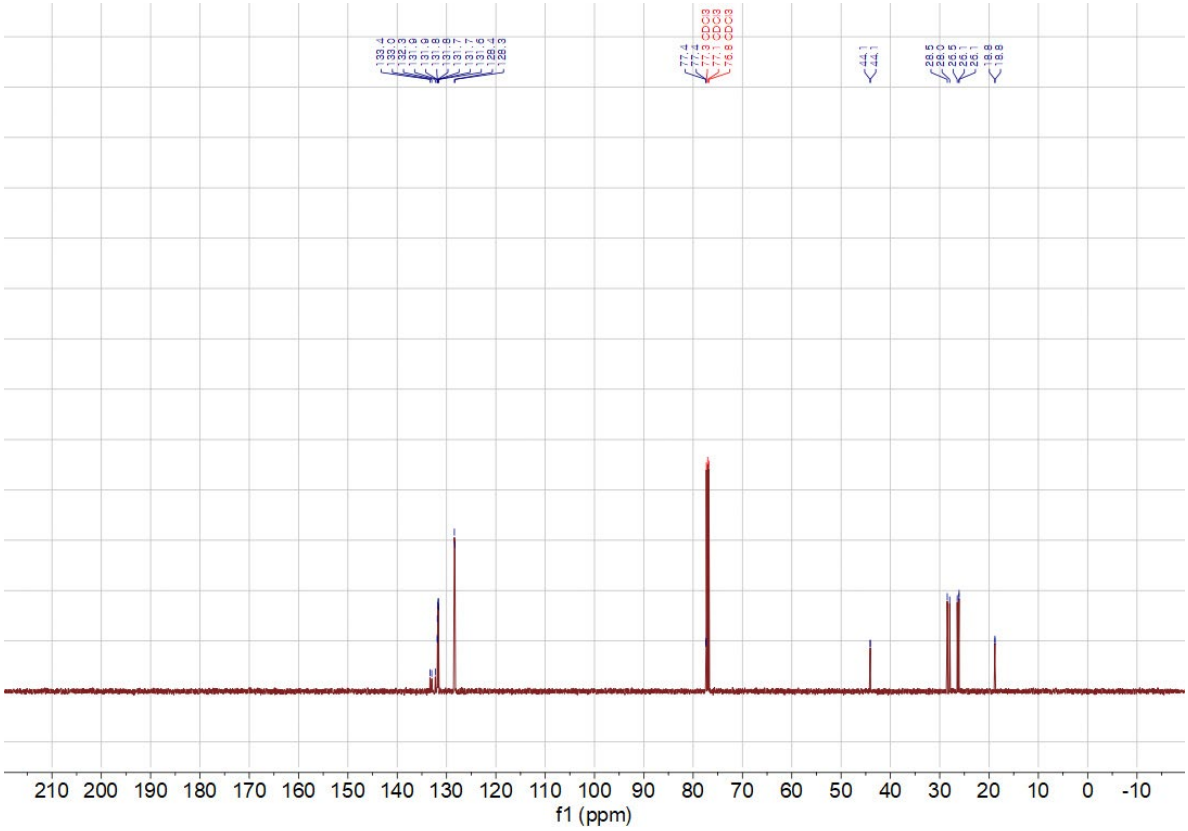


## 10.3. Substrates for cyclic voltammetry

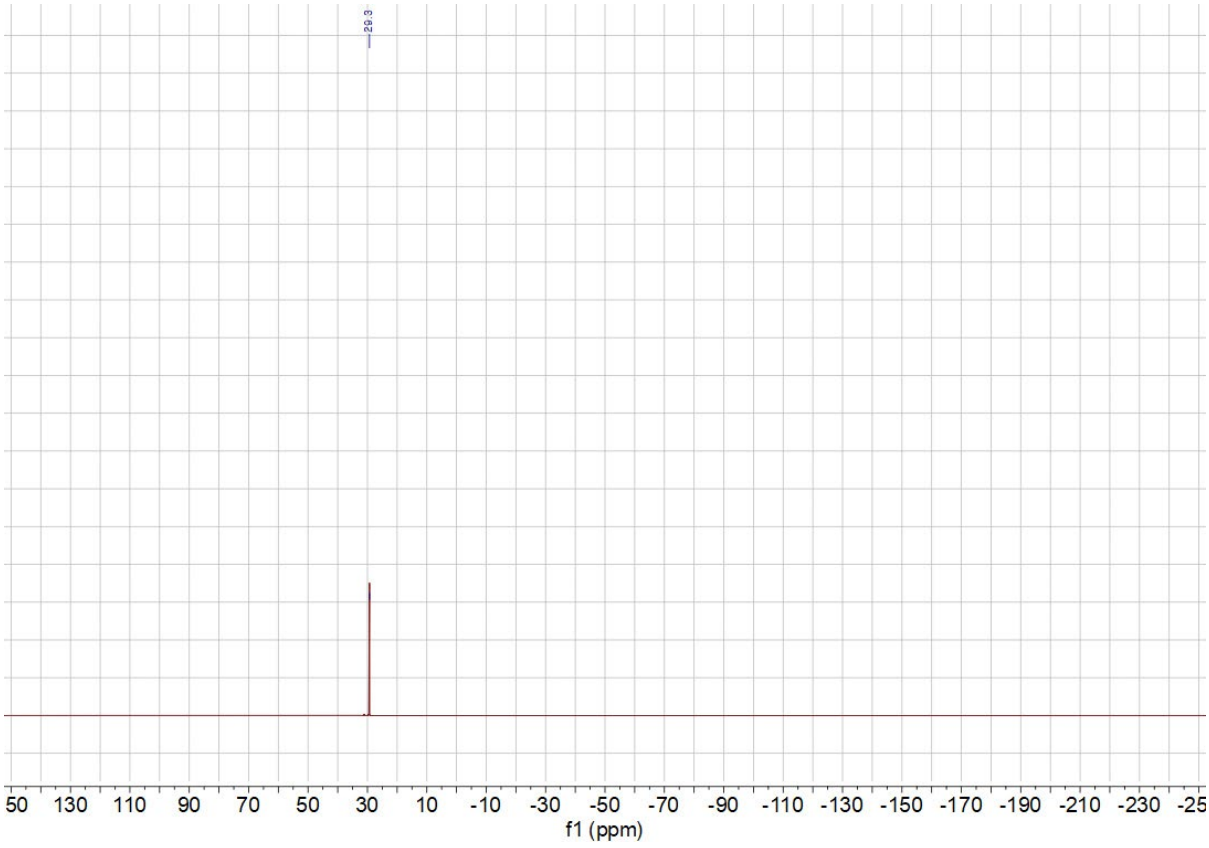
$^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **30**



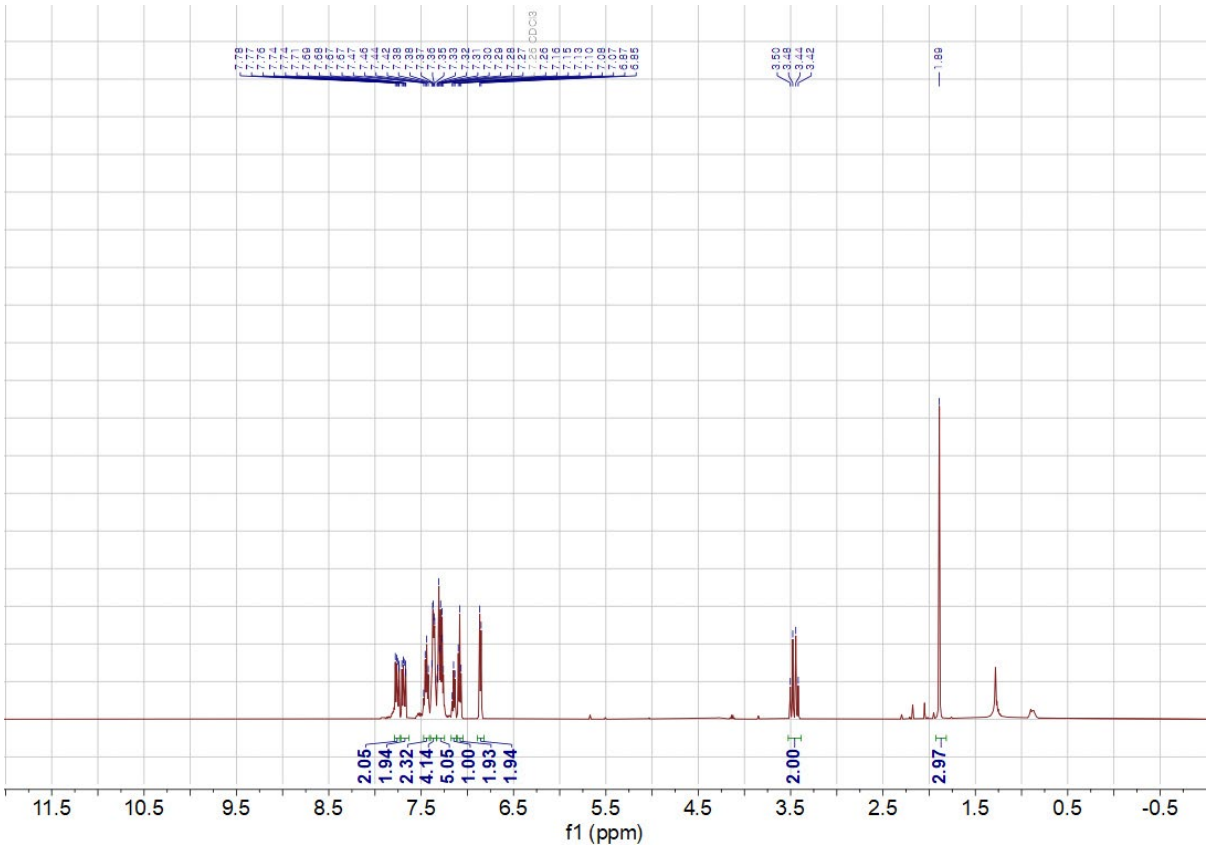

$^{13}$C{$^{1}$H} NMR spectrum (126 MHz, $CDCl_3$) of **30**



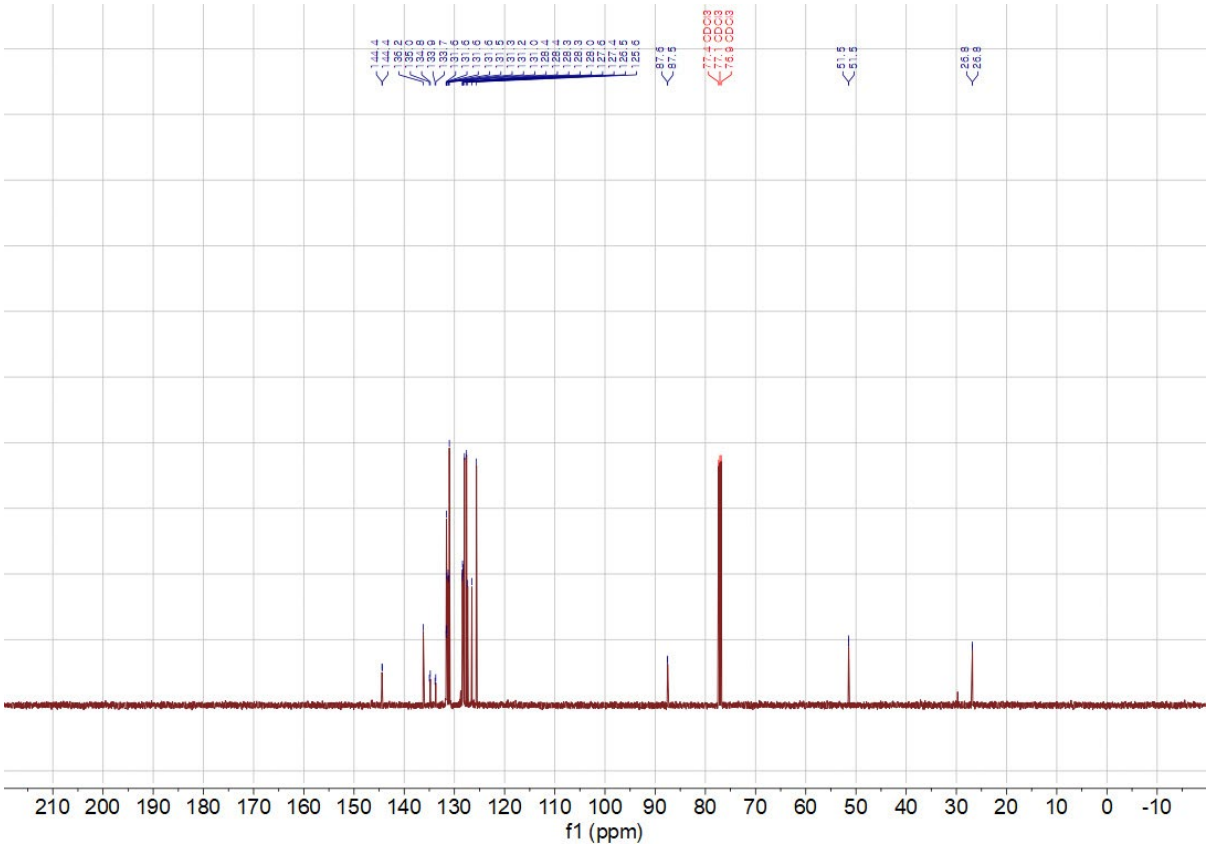
$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **30**



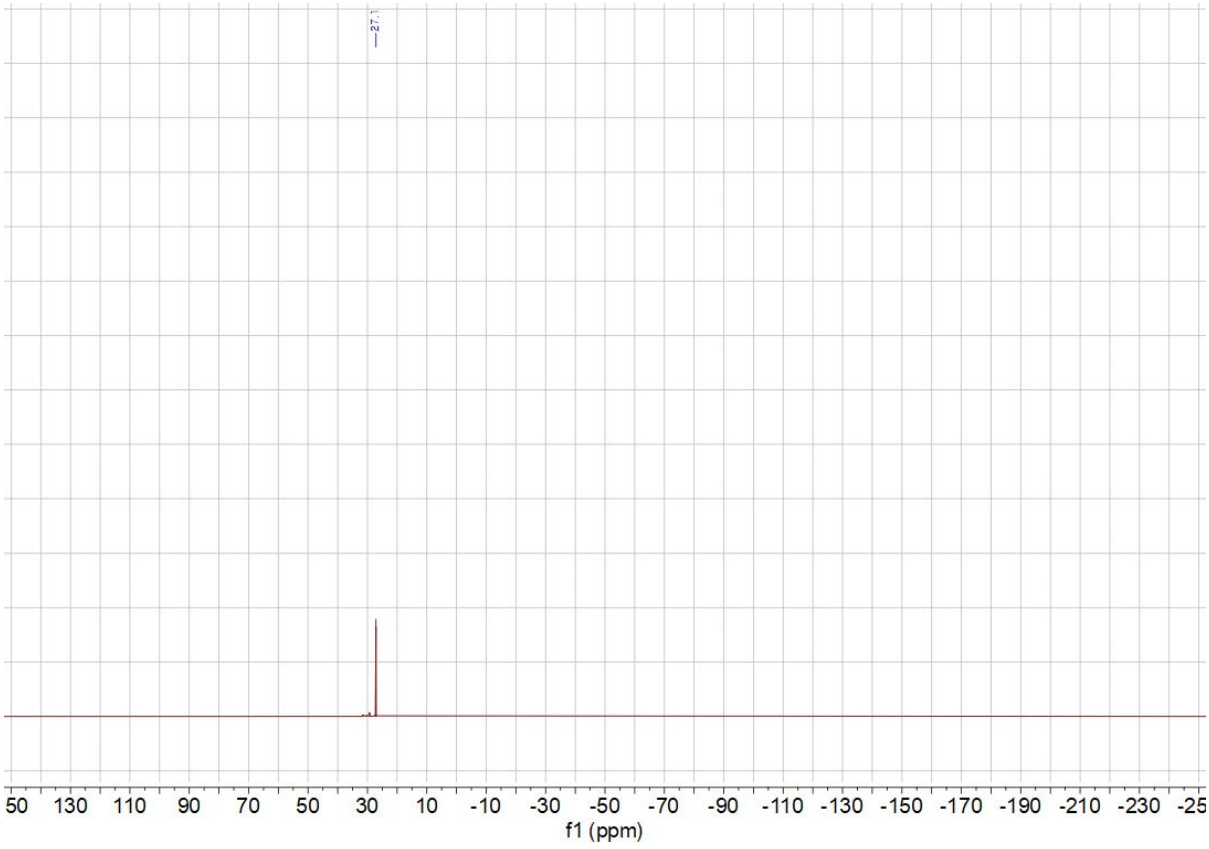

$^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **31**



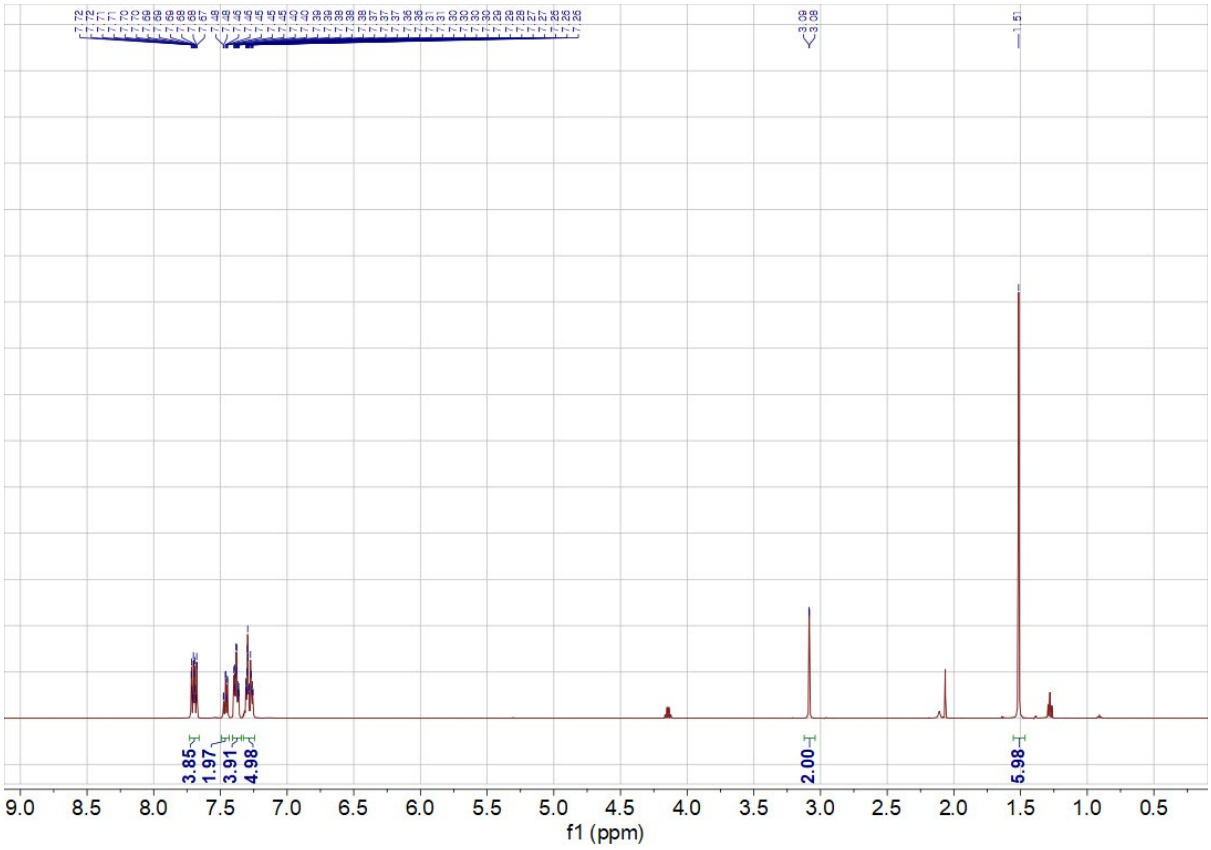
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **31**



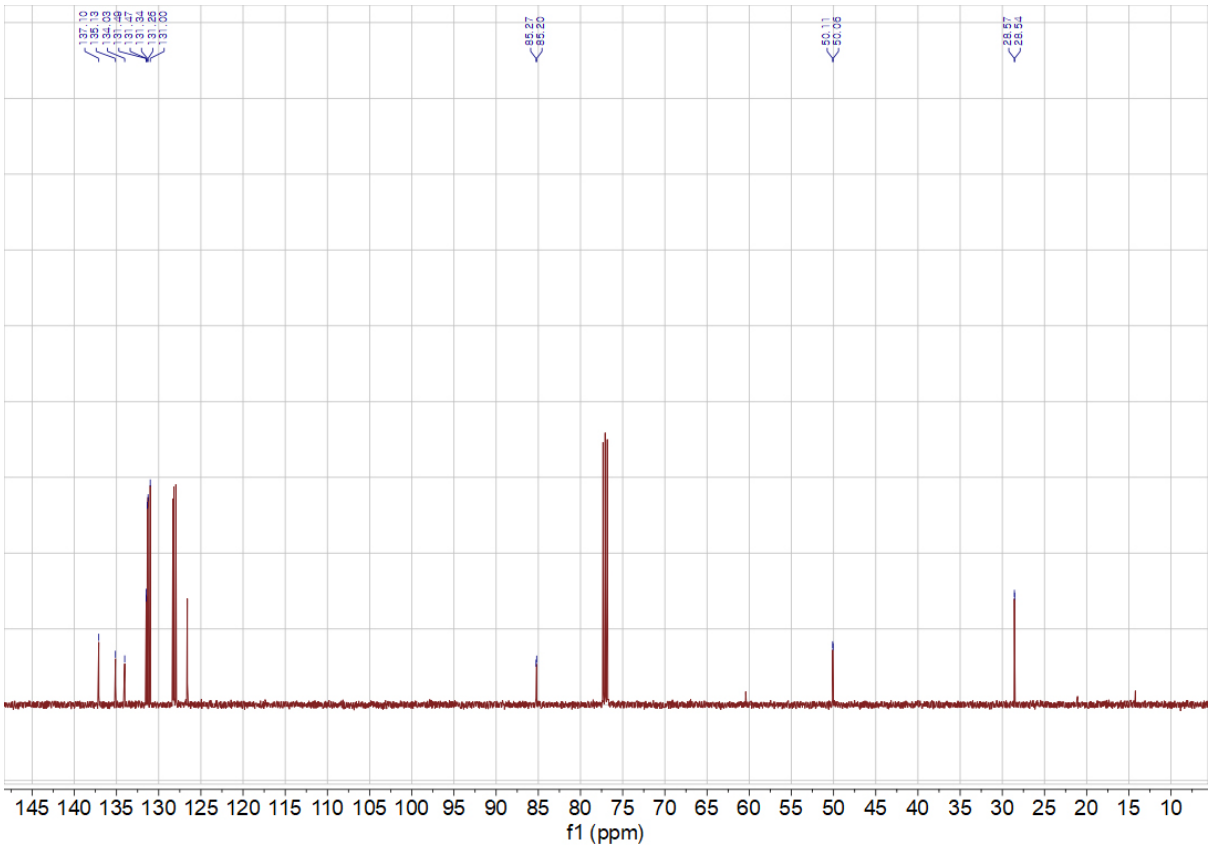

$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$) of **31**



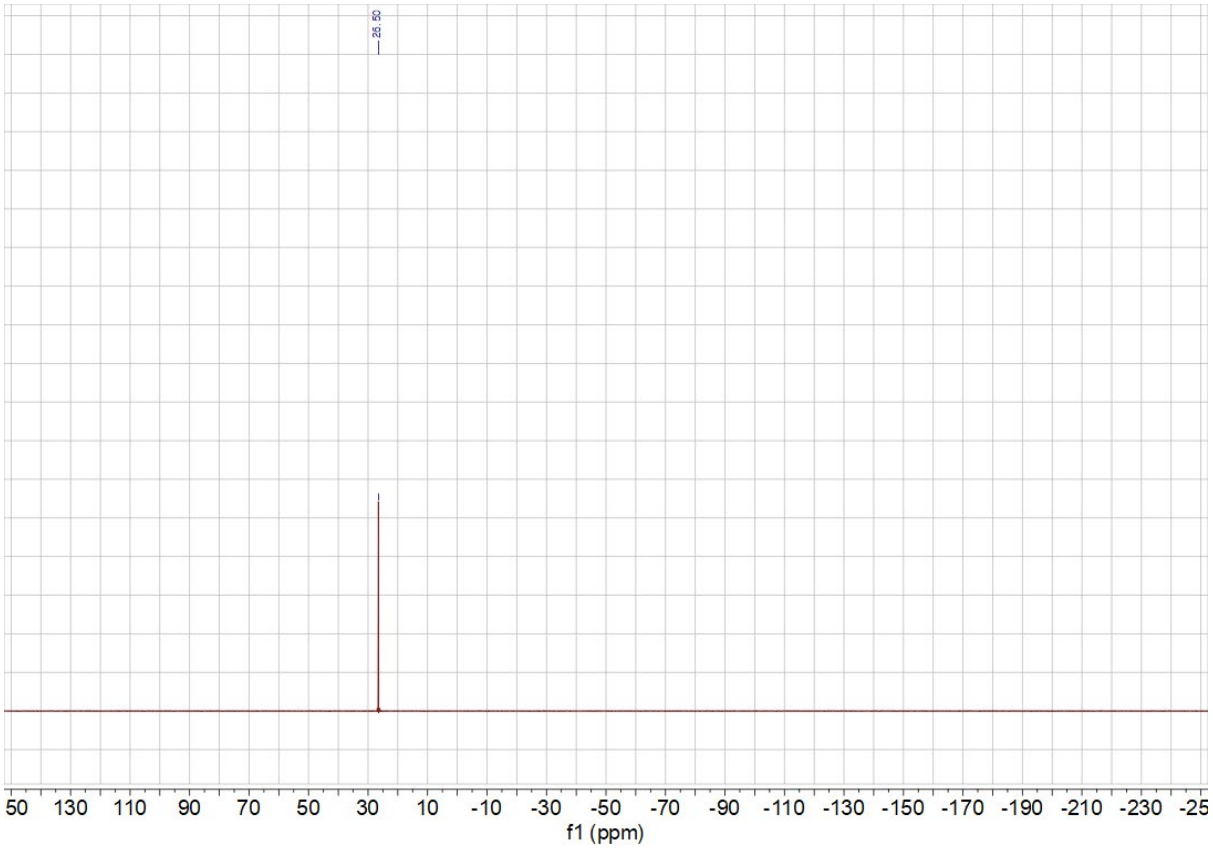
$^{1}$H NMR (400 MHz, $CDCl_3$) of **32**



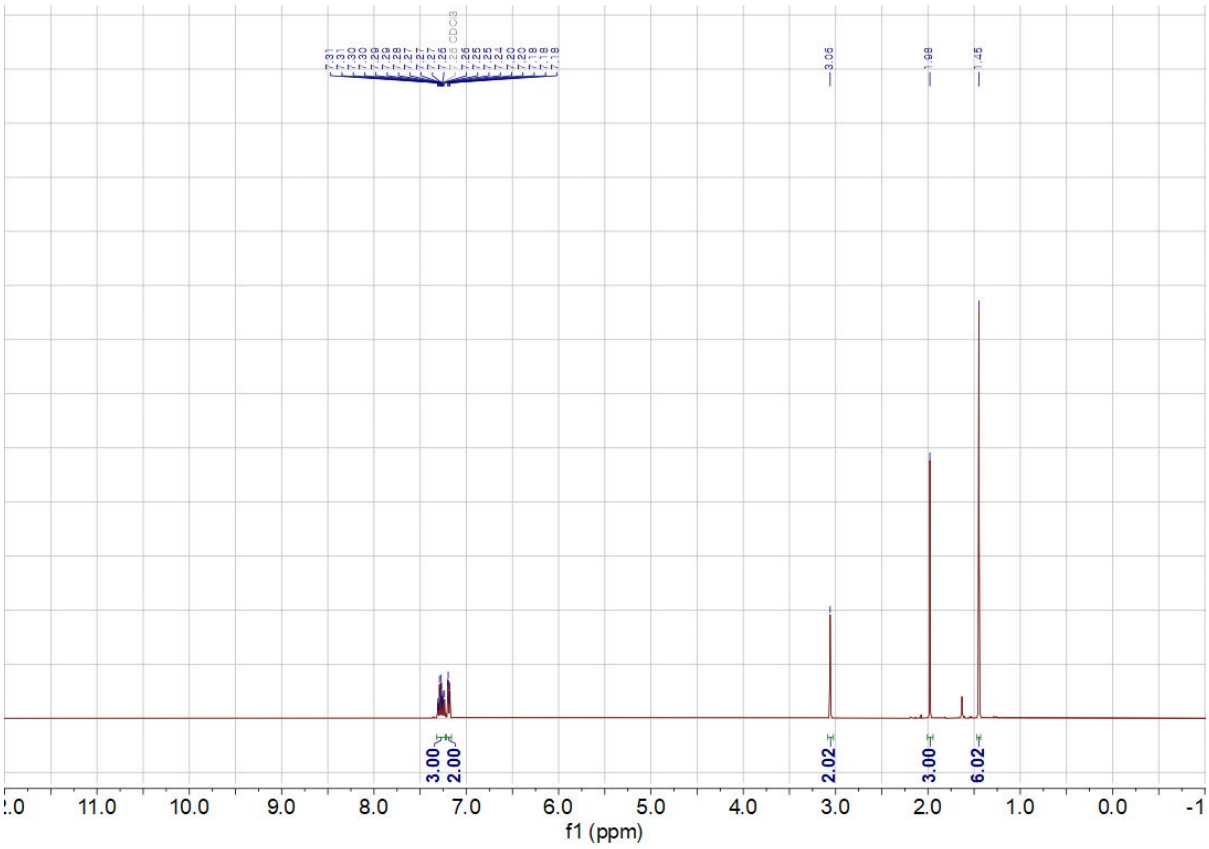

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **32**



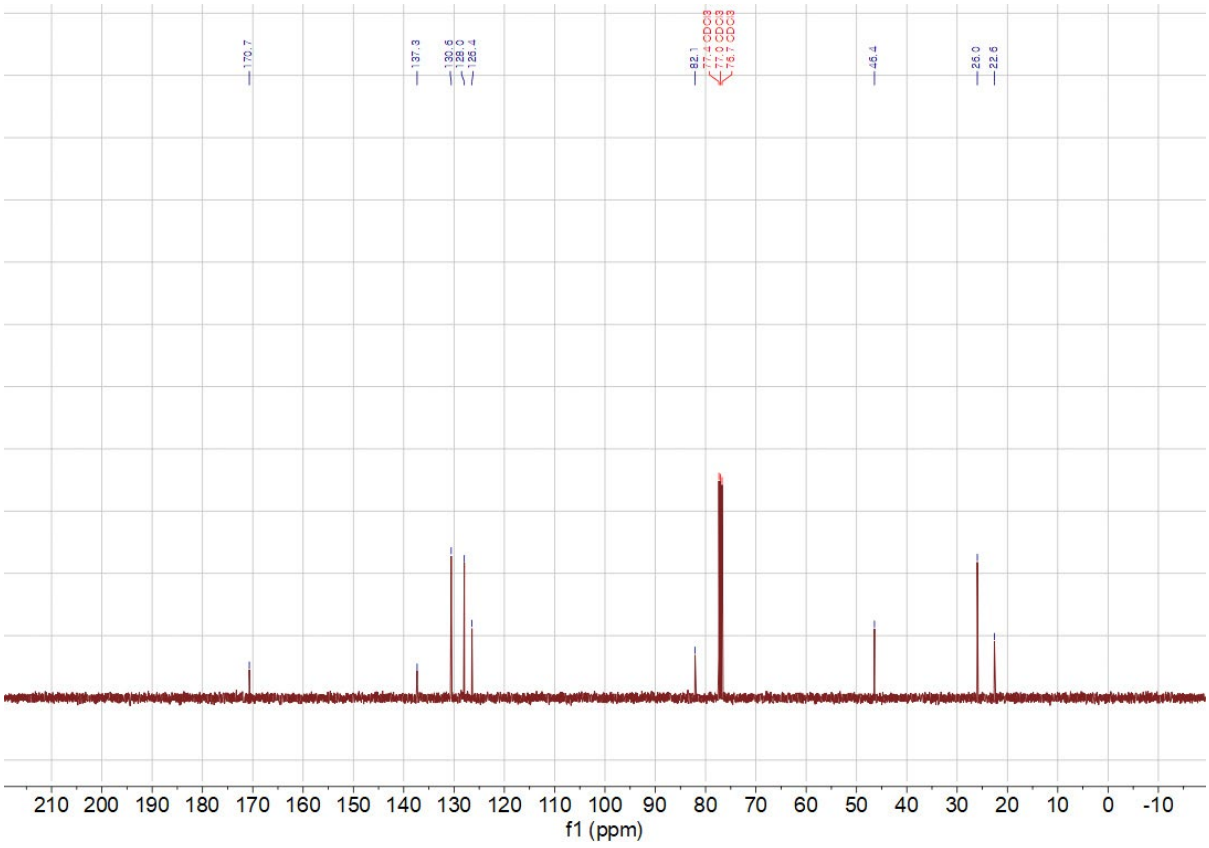
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) of **32**




$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **34**



$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **34**



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