Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


Supporting Information

# A Nickel/Organoboron Catalyzed Metallaphotoredox Platform for C($sp^2$)–P and C($sp^2$)–S Bond Construction

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# Content

# 1. General considerations

**General.** Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

**Structural analysis.** NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts ($\delta$) are reported in parts per million (ppm). $^{1}$H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and $^{13}$C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers ($cm^{-1}$). High resolution mass spectra (HRMS) were acquired on Thermo Scientific LTQ Orbitrap XL with an ESI source.

**Materials.** Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

## 2. The reaction condition screening for the synthesis of triarylphosphine oxides

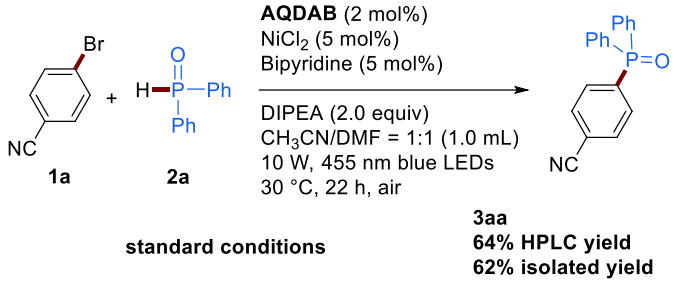
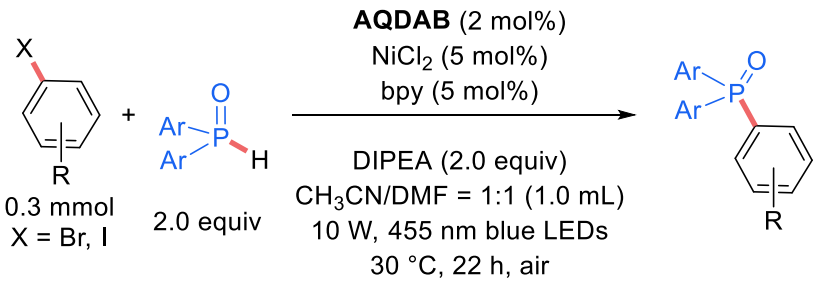



**Table S1** Optimization of the reaction conditions

| Entry | Variations from the 'standard' conditions | HPLC yield (%) |
|---|---|---|
| 1. | none | 64 |
| | *the dosage of AQDAB* | |
| 2. | 5 mol% AQDAB | 64 |
| 3. | 1 mol% AQDAB | 64 |
| 4. | 0.5 mol% AQDAB | 64 |
| 5. | 0.1 mol% AQDAB | 61 |
| 6. | 0.05 mol% AQDAB | 53 |
| | *the dosage of $NiCl_2$ + ligand* | |
| 7. | $NiCl_2$ 10 mol%, bpy 10 mol% | 64 |
| 8. | $NiCl_2$ 20 mol%, bpy 20 mol% | 64 |
| | *Photocatalyst used instead of AQDAB* | |
| 9. | 2 mol% CdS | 37 |
| 10. | 2 mol% $Ir(ppy)_2(dtbbpy)(PF_6)$ | 46 |
| 11. | 2 mol% 4CzIPN | 49 |
| 12. | 2 mol% TXO | 45 |
| | *Ligand used instead of bpy* | |
| 13. | dtbbpy | 43 |
| 14. | 4,4'-dimethyl-2,2'-bipyridine | 52 |
| 15. | 1,10-phenanthroline monohydrate | 51 |
| 16. | 5,5'-dimethyl-2,2'-bipyridine | 53 |
| 17. | triphenylphosphine | 37 |
| | *Base used instead of DIPEA* | |
| 18. | TEA | 52 |
| 19. | DBU | 24 |
| 20. | DABCO | 16 |
| 21. | tBuOK | 25 |

| | | |
|---|---|---|
| 22. | 2,6-lutidine | 24 |
| | *Solvent used* | |
| 23. | Toluene | 22 |
| 24. | Dichloroethane | 38 |
| 25. | THF | 48 |
| 26. | Acetone | 23 |
| | *Other variations* | |
| 27. | Ar atmosphere | 63 |
| 28. | 1.0 equiv DIPEA | 38 |
| 29. | 3.0 equiv DIPEA | 51 |
| 30. | Reaction time 30 hours | 60 |
| 31. | 5.0 equiv diphenylphosphine oxide | 75 |

## 3. The synthesis of triarylphosphine oxides



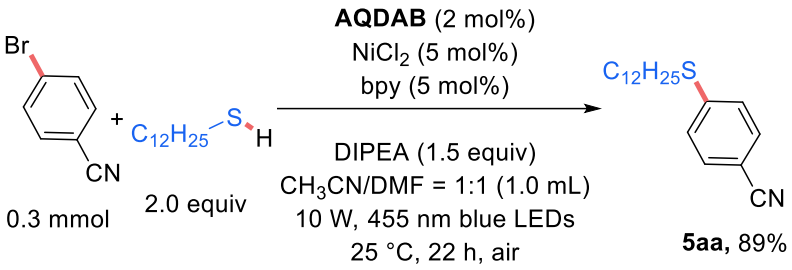

**General Procedure A**: A flame-dried 25 mL quartz column reaction tube was placed with a magnetic stir bar. Then, aryl bromide /aryl iodine (0.3 mmol, 1.0 equiv), diphenylphosphine oxide (120.7 mg, 0.6 mmol, 2.0 equiv), **AQDAB** (2.6 mg, 0.006 mmol, 2 mol%), $NiCl_2$ (1.9 mg, 0.015 mmol, 5 mol%), bpy (2.3 mg, 0.015 mmol, 5 mol%), DIPEA (77.5 mg, 0.6 mmol, 2.0 equiv), and $CH_3CN$/DMF (0.5/0.5 mL) were added. The reaction tube was placed on a photocatalytic parallel reactor with a 455 - 460 nm blue LEDs light source (10 W) at the bottom (**Figure S1)**. Then the reaction mixture was irradiated with the 455 nm blue LEDs (at approximately 0.3 cm away from the light source). After stirring for 22 hours at 25 ℃, the reaction mixture was added 20 mL $H_2O$ and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL), dried over anhydrous $Na_2SO_4$, and concentrated under vacuum to afford the crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the target products.


**Figure S1**. Picture of the reactor

# 4. The synthesis of thioethers

## 3.1 Control experiments for the used reaction conditions in thioether synthesis

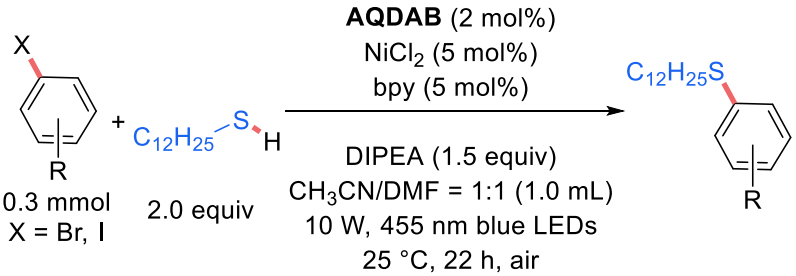
**Table S2.** The control experiments for the thioether synthesis [a]




| Entry | Variations from the 'standard' conditions | Yield (%)[a] |
|---|---|---|
| 1 | no **AQDAB** | 4 |
| 2 | no $NiCl_2$ | 12 |
| 3 | no bpy | 36 |
| 4 | no light | N. D. |
| 5 | no DIPEA | N. D. |

Standard reaction conditions: 4-bromobenzonitrile (0.3 mmol, 1.0 equiv), 1-dodecanethiol (0.6 mmol, 2.0 equiv), **AQDAB** (0.006 mmol, 2 mol%), $NiCl_2$ (0.015 mmol, 5 mol%), bpy (0.015 mmol, 5 mol%), DIPEA (0.45 mmol, 1.5 equiv), and $CH_3CN$/ DMF (0.5/0.5 mL), 10 W 455 nm blue LEDs, 25 °C, air, 22 h. [a] Isolated yield. N.D. = not detected.

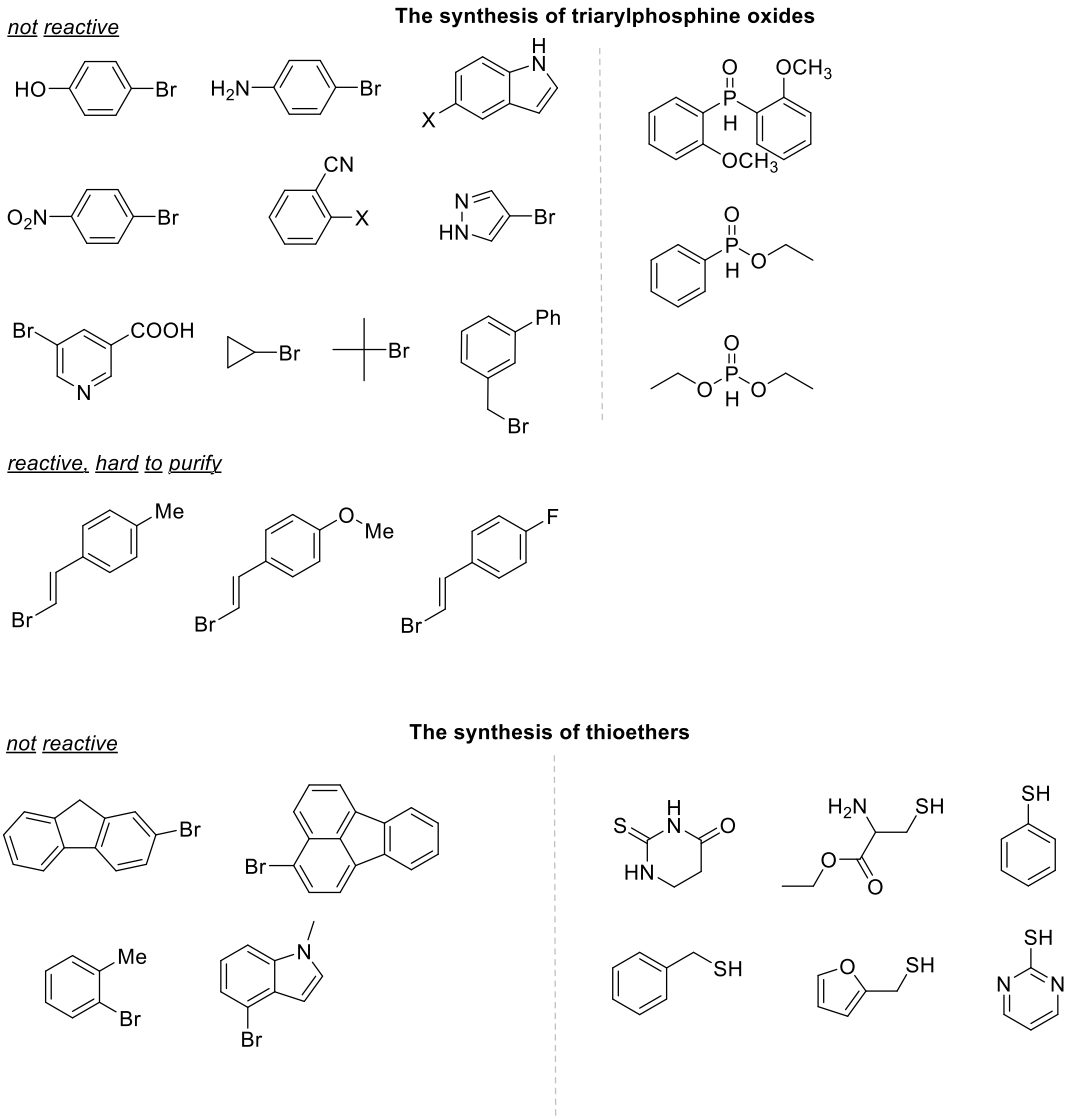
## 3.2 General procedure for the synthesis of thioethers




**General Procedure B**: A flame-dried 25 mL quartz column reaction tube was placed with a magnetic stir bar. Then, aryl bromide /aryl iodine (0.3 mmol, 1.0 equiv), 1-dodecanethiol (121.4 mg, 0.6 mmol, 2.0 equiv), **AQDAB** (2.6 mg, 0.006 mmol, 2 mol%), $NiCl_2$ (1.9 mg, 0.015 mmol, 5 mol%), bpy (2.3 mg, 0.015 mmol, 5 mol%), DIPEA (58.2 mg, 0.45 mmol, 1.5 equiv), and $CH_3CN$/DMF (0.5/0.5 mL) were added. The reaction tube was placed on a photocatalytic parallel reactor with a 455 - 460 nm blue LEDs light source (10 W) at the bottom (**Figure S1)**. Then the reaction mixture was irradiated with the 455 nm blue LEDs (at approximately 0.3 cm away from the light source). After stirring for 22 hours at 25 °C, the reaction mixture was added 20 mL $H_2O$ and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL), dried over anhydrous $Na_2SO_4$, and concentrated

under vacuum to afford the crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the target products.

## 5. A summary of unsuccessful cases




**Scheme S1** A summary of unsuccessful coupling counterparts

## 6. Stern-Volmer experiments

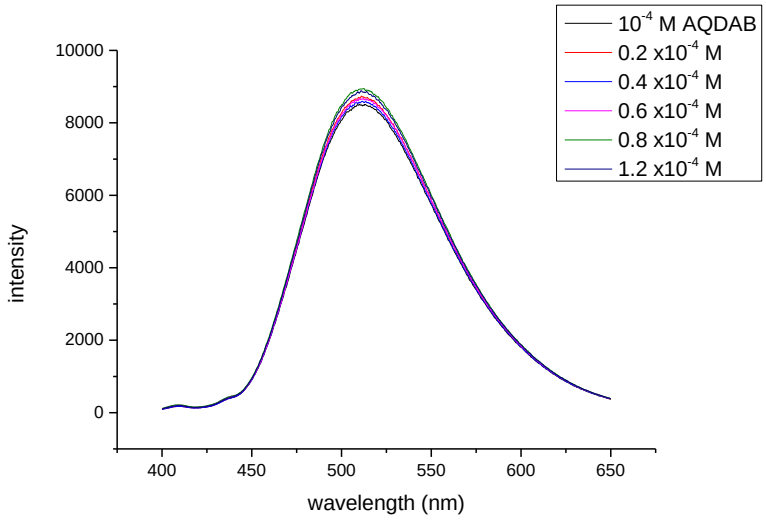



**Figure S2** Fluorescence quenching date with AQDAB (0.1 mM) and variable diphenylphosphine oxide ($10^{-4}$ M)

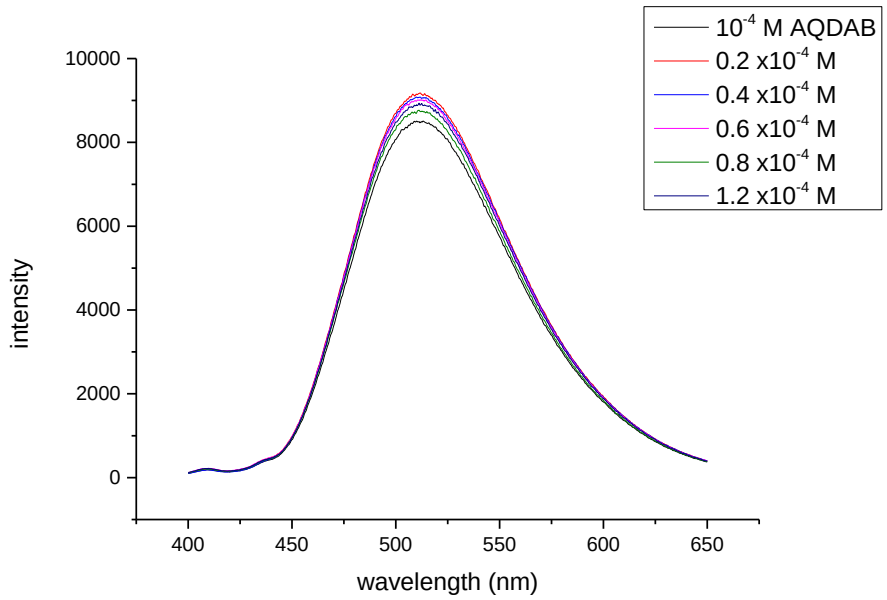



**Figure S3** Fluorescence quenching date with AQDAB (0.1 mM) and variable DIPEA ($10^{-4}$ M)

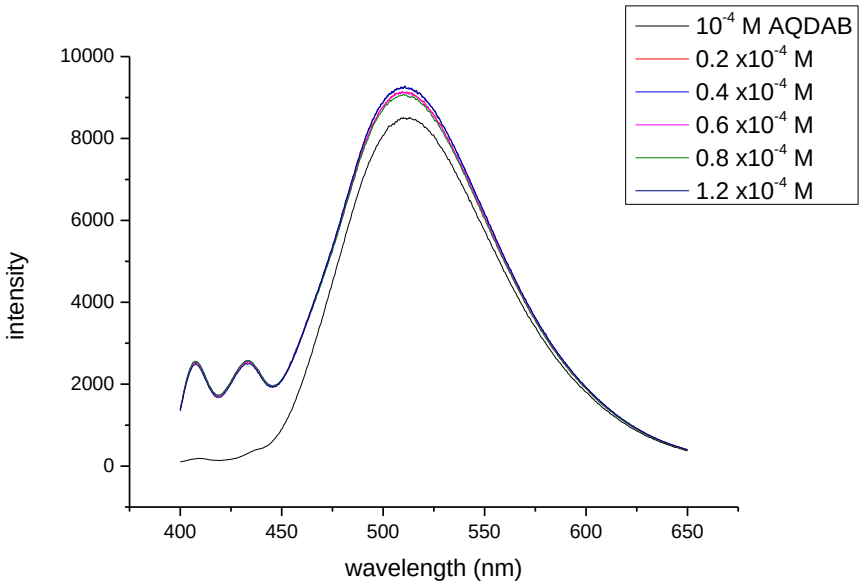



**Figure S4** Fluorescence quenching date with AQDAB (0.1 mM) and variable $C_{12}H_{25}SH$ ($10^{-4}$ M)

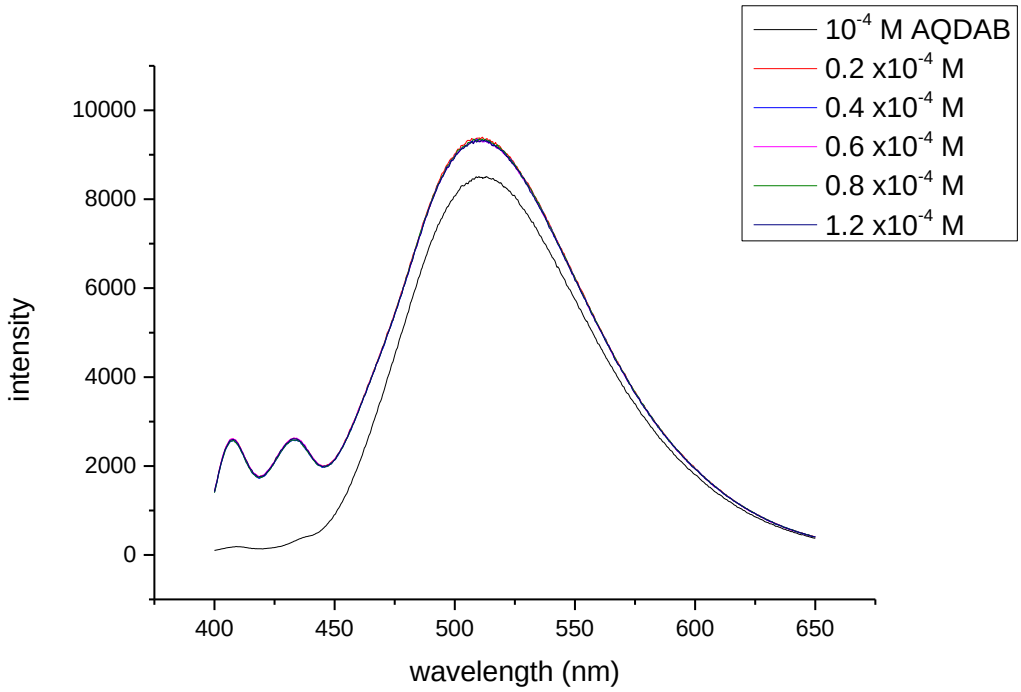



**Figure S5** Fluorescence quenching date with AQDAB (0.1 mM) and variable $NiCl_2$ ($10^{-4}$ M)

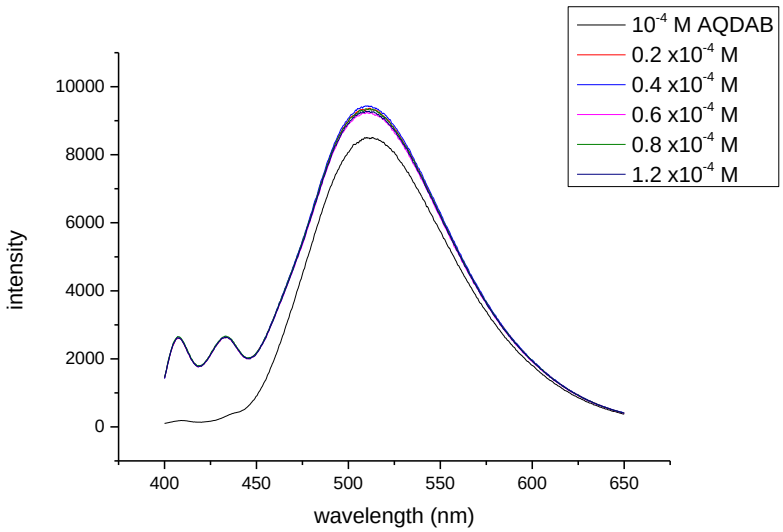



**Figure S6** Fluorescence quenching date with AQDAB (0.1 mM) and variable 4-bromobenzonitrile ($10^{-4}$ M)

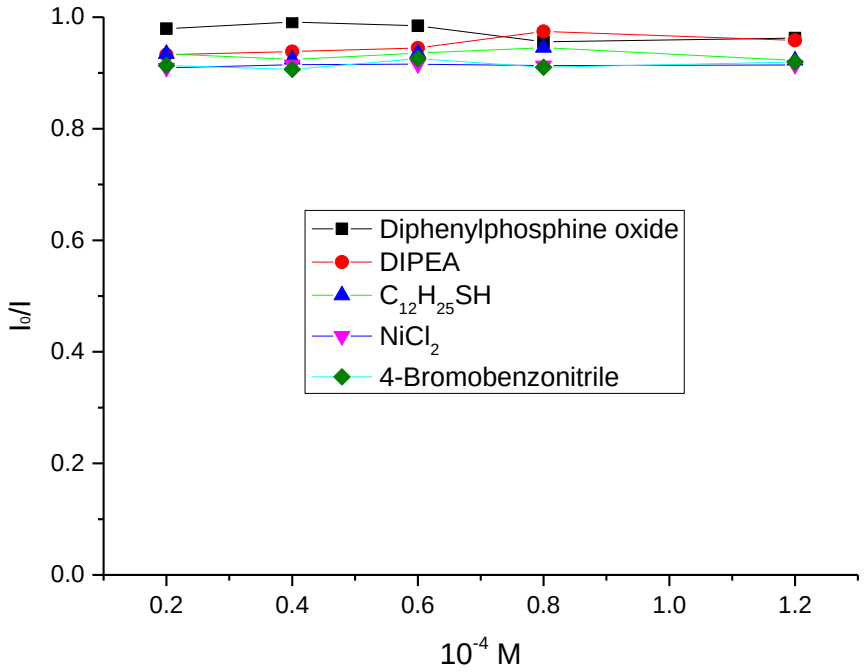



**Figure S7** Stern-Volmer plots of AQDAB (0.1 mM) and five quenchers. $I_0$ and I were luminescence intensities in the absence and presence of the indicated concentrations ($10^{-4}$ M) of the corresponding quencher, respectively. The solutions were irradiated at 387 nm and fluorescence was measured from 300 nm to 650 nm.

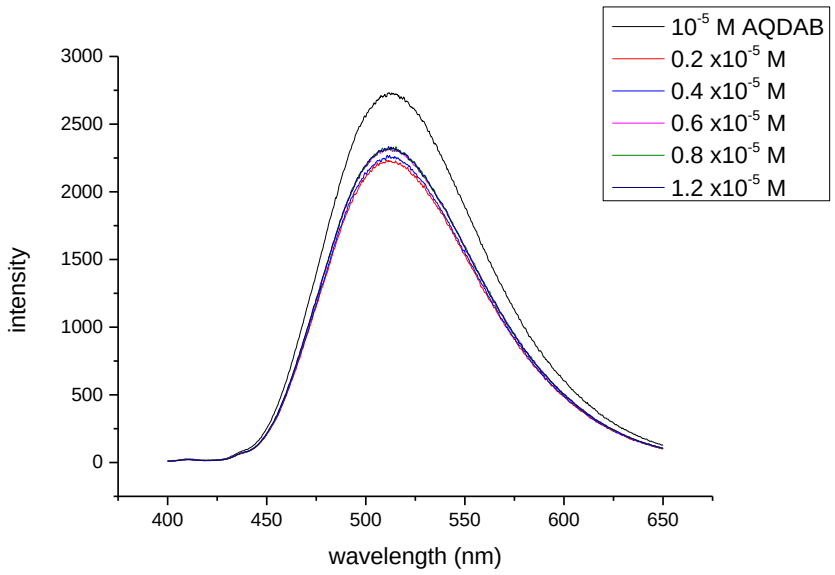



**Figure S8** Fluorescence quenching date with AQDAB (0.01 mM) and variable diphenylphosphine oxide ($10^{-5}$ M)

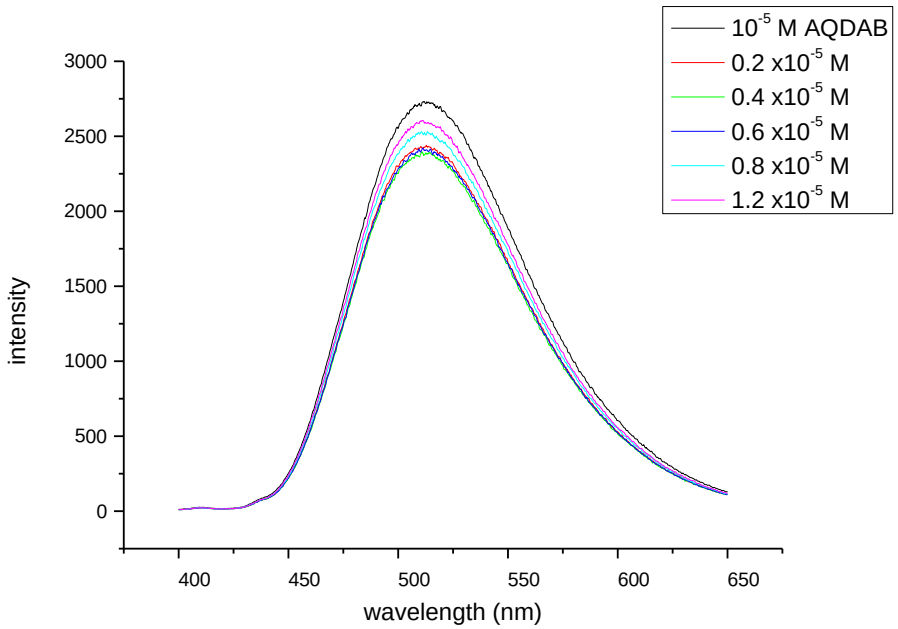



**Figure S9** Fluorescence quenching date with AQDAB (0.01 mM) and variable DIPEA ($10^{-5}$ M)

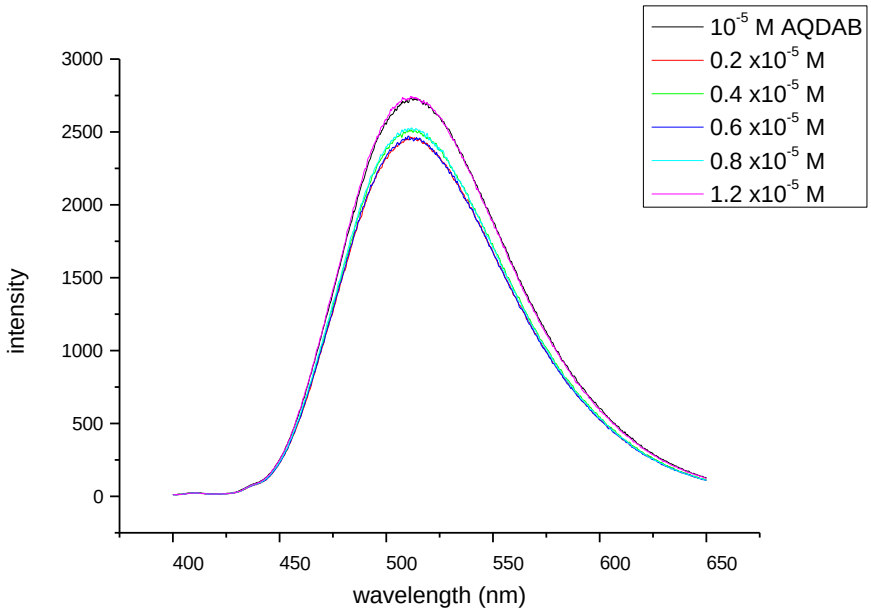



**Figure S10** Fluorescence quenching date with AQDAB (0.01 mM) and variable $C_{12}H_{25}SH$ ($10^{-5}$ M)

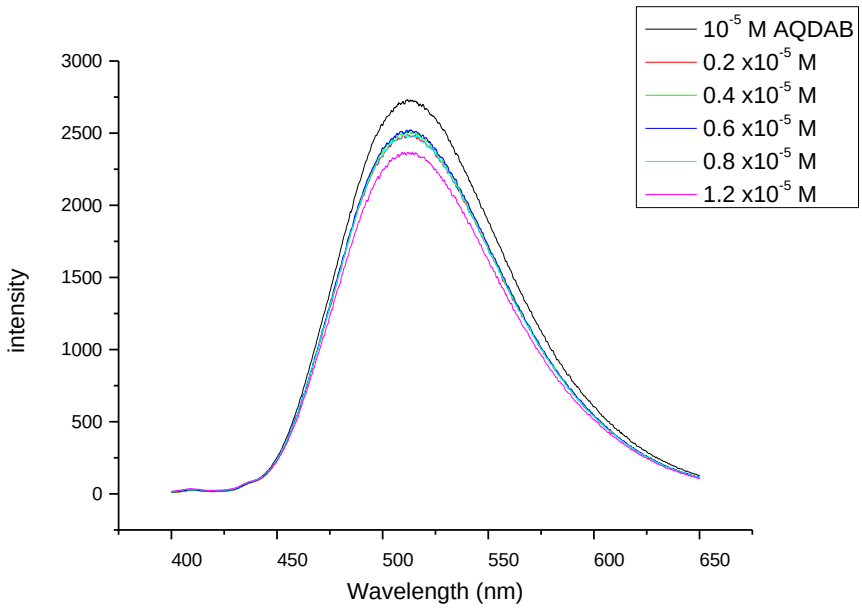



**Figure S11** Fluorescence quenching date with AQDAB (0.01 mM) and variable $NiCl_2$ ($10^{-5}$ M)

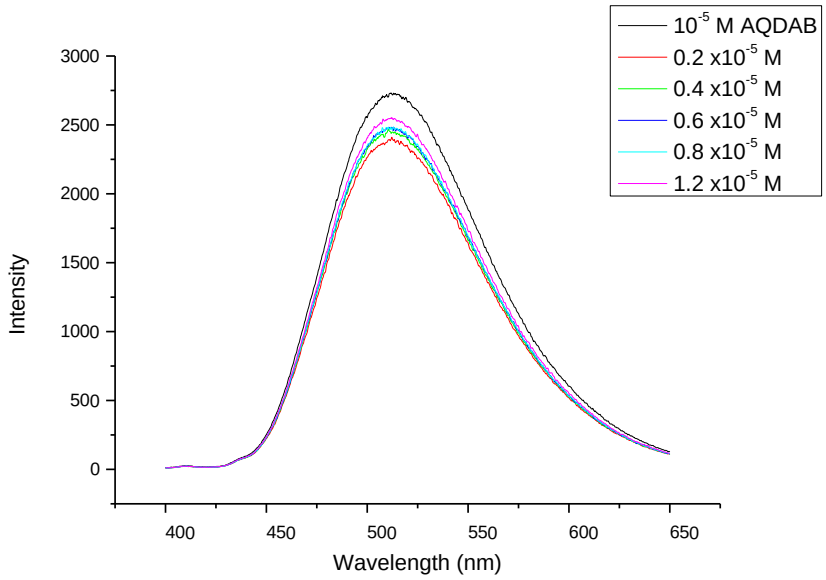



**Figure S12** Fluorescence quenching date with AQDAB (0.01 mM) and variable 4-bromobenzonitrile ($10^{-5}$ M)

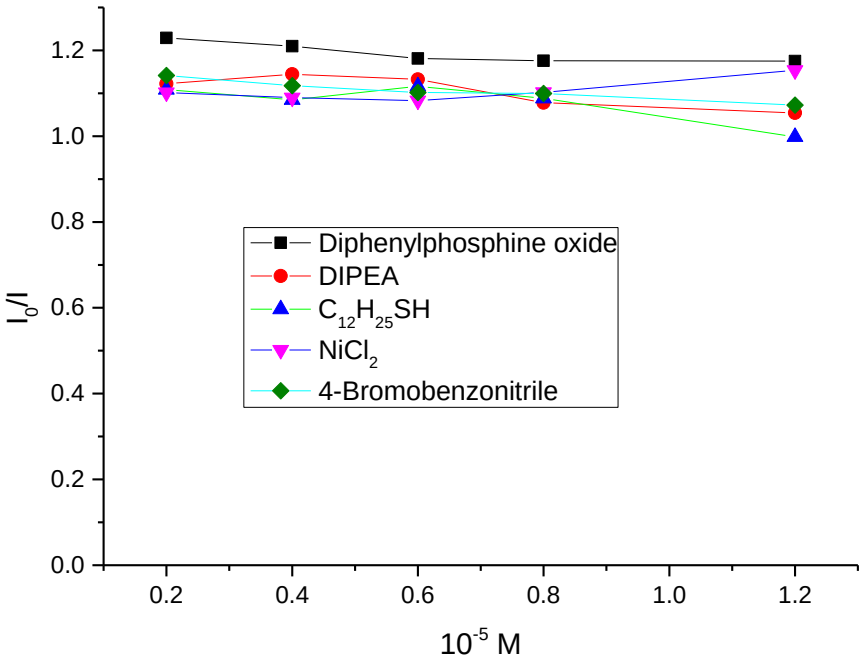



**Figure S13** Stern-Volmer plots of AQDAB (0.01 mM) and five quenchers. $I_0$ and I were luminescence intensities in the absence and presence of the indicated concentrations ($10^{-5}$ M) of the corresponding quencher, respectively. The solutions were irradiated at 387 nm and fluorescence was measured from 300 nm to 650 nm.

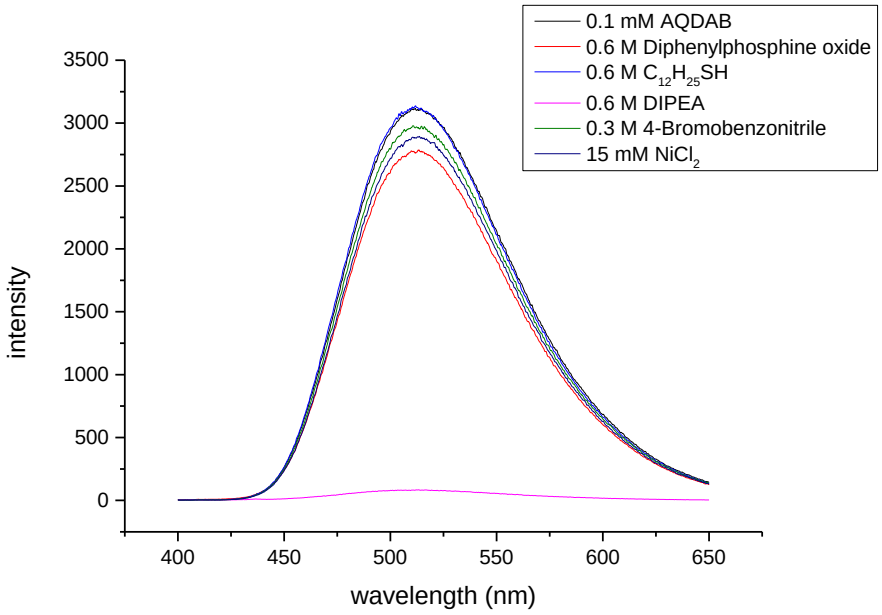



**Figure S14** Fluorescence quenching date with 0.1 mM AQDAB and five quenchers (0.6 M for the diphenylphosphine oxide, $C_{12}H_{25}SH$ and DIPEA, 0.3 M for 4-bromobenzonitrile, and 15 mM for $NiCl_2$).

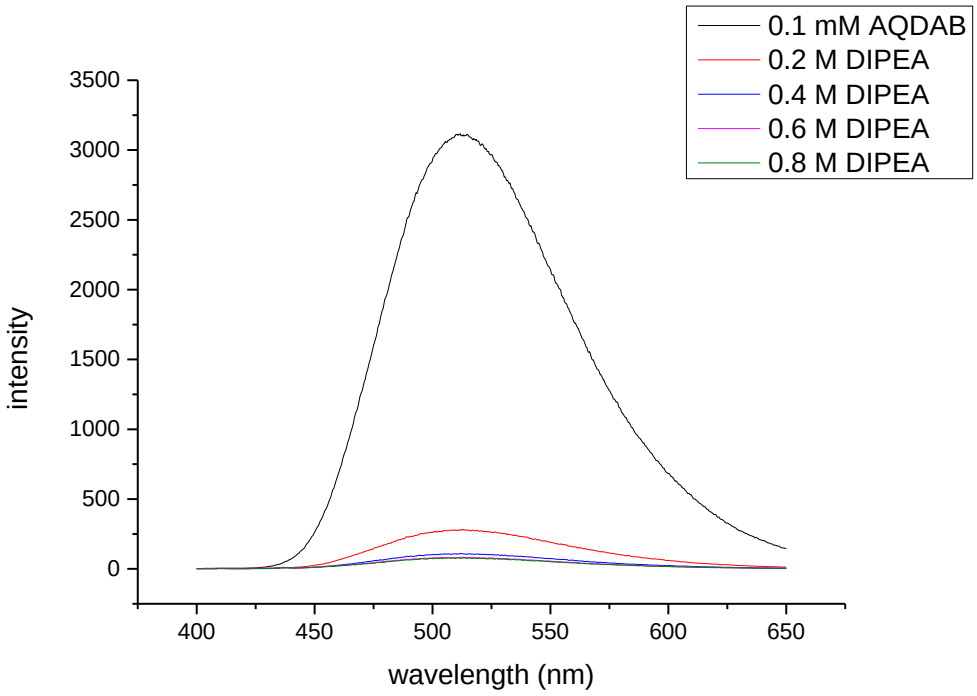



**Figure S15** Fluorescence quenching date with AQDAB (0.1 mM) and variable concentration of DIPEA

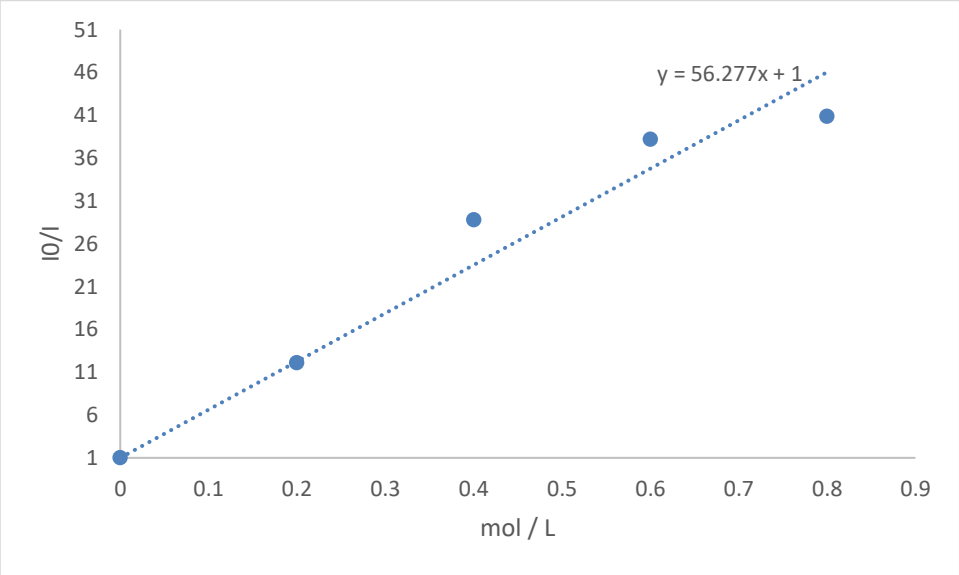
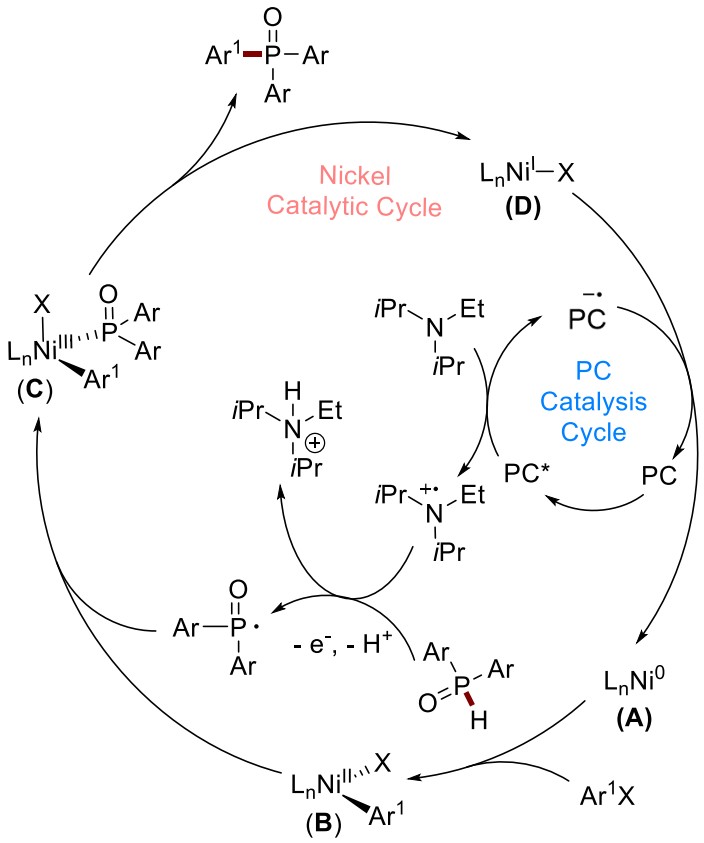



**Figure S16** Stern-Volmer plots of AQDAB (0.1 mM) and DIPEA as the quencher. $I_0$ and I were luminescence intensities in the absence and presence of the indicated concentrations (mol / L) of the corresponding quencher, respectively.

The quenching phenomenon of DIPEA made us reconsider its function. DIPEA might function as a reductive quencher in the transformation. Based on this, an electron-transfer-based catalytic cycle and the corresponding description were shown below (**Scheme S2**).

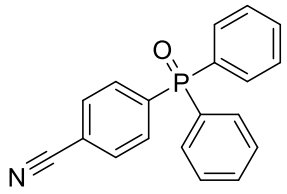
After the photocatalyst (PC) was excited to PC* under light, The excited photocatalyst was reduced by DIPEA, affording free radical cation $DIPEA^{+\bullet}$. The hydrogen of diphenylphosphine oxide was then transferred to $DIPEA^{+\bullet}$, generating the P-based radical. As for the nickel-catalyzed cycle, the oxidative addition of ArX onto the zero-valent $L_nNi0$ (**A**) would generate $L_nNiII(Ar)X$ (**B**). The combination of **B** and the P-radical then occurred to produce the Ni(III) species **C**, whose reductive elimination would form the desired product along with the one-valent nickel species **D**. Further reduction of **D** to **A** was then realized using $PC^{-\bullet}$, completing both the Ni-catalyzed and PC-catalyzed cycles.




**Scheme S2** A possible mechanism via the electron transfer pathway

# 7. Characterization data

**(3aa) 4-(diphenylphosphoryl)benzonitrile (CAS: 5032-54-2)[1]**



4-(diphenylphosphoryl)benzonitrile
Chemical Formula: $C_{19}H_{14}NOP$
Exact Mass: 303.0813
Molecular Weight: 303.3008

Following the General Procedure A with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3aa** was obtained as colorless oil (56.5 mg, 62%).

Following the General Procedure A with 4-iodobenzonitrile (68.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3aa** was obtained as colorless oil (49.3 mg, 54%).

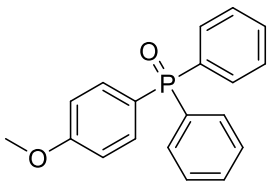
This target product was purified by acidic alumina flash chromatography (PE: EA: MeOH = 1:1:0.1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 – 7.74 (m, 2H), 7.74 – 7.69 (m, 2H), 7.66 – 7.58 (m, 4H), 7.58 – 7.52 (m, 2H), 7.50 – 7.43 (m, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.5 (d, $J$ = 99 Hz), 132.7, 132.6 (d, $J$ = 2 Hz), 132.1 (d, $J$ = 3 Hz), 131.9 (d, $J$ = 1 Hz), 131.2 (d, $J$ = 106 Hz), 128.8 (d, $J$ = 12 Hz), 117.9 (d, $J$ = 1 Hz), 115.6 (d, $J$ = 3 Hz),.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 27.76.

**(3ba) (4-methoxyphenyl)diphenylphosphine oxide (CAS: 795-44-8)[2]**



(4-methoxyphenyl)diphenylphosphine oxide
Chemical Formula: $C_{19}H_{17}O_2P$
Exact Mass: 308.0966
Molecular Weight: 308.3168

Following the General Procedure A with 1-bromo-4-methoxybenzene (56.1 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ba** was obtained as white solid (63.2 mg, 68%).

Following the General Procedure A with 4-iodoanisole (70.2 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ba** was obtained as white solid (70.3 mg, 76%).

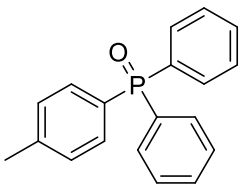
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 – 7.61 (m, 4H), 7.61 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.39 (m, 4H), 6.98 – 6.92 (m, 2H), 3.82 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.5 (d, $J$ = 3 Hz), 134.0 (d, $J$ = 11 Hz), 133.0 (d, $J$ = 105 Hz), 132.1 (d, $J$ = 10 Hz), 131.8 (d, $J$ = 3 Hz), 128.5 (d, $J$ = 12 Hz), 123.6 (d, $J$ = 111 Hz), 114.1 (d, $J$ = 13 Hz), 55.4.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 29.04.

**(3ca) diphenyl(p-tolyl)phosphine oxide (CAS: 6840-28-4)[2]**



diphenyl(*p*-tolyl)phosphine oxide
Chemical Formula: $C_{19}H_{17}OP$
Exact Mass: 292.1017
Molecular Weight: 292.3178

Following the General Procedure A with 4-bromotoluene (51.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ca** was obtained as white solid (50.4 mg, 58%).

Following the General Procedure A with 4-iodotoluene (65.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ca** was obtained as white solid (47.1 mg, 54%).

This target product was purified by acidic alumina flash chromatography (PE: EA: MeOH = 1:1:0.1).

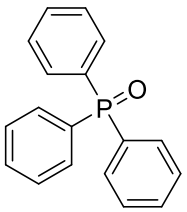
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 – 7.62 (m, 4H), 7.59 – 7.49

(m, 4H), 7.48 - 7.40 (m, 4H), 7.30 – 7.23 (m, 2H), 2.39 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 142.5 (d, $J$ = 3 Hz), 132.8 (d, $J$ = 104 Hz), 132.1 (d, $J$ = 10 Hz), 132.1 (d, $J$ = 10 Hz), 131.8 (d, $J$ = 3 Hz), 129.3 (d, $J$ = 13 Hz), 129.2 (d, $J$ = 107 Hz), 128.5 (d, $J$ = 12 Hz), 21.6 (d, $J$ = 1 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 29.20.

**(3da) triphenylphosphine oxide (CAS: 791-28-6)[2]**



triphenylphosphine oxide
Chemical Formula: $C_{18}H_{15}OP$
Exact Mass: 278.0861
Molecular Weight: 278.2908

Following the General Procedure A with bromobenzene (47.1 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3da** was obtained as white solid (41.9 mg, 50%).

Following the General Procedure A with iodobenzene (61.2 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3da** was obtained as white solid (47.3 mg, 57%).

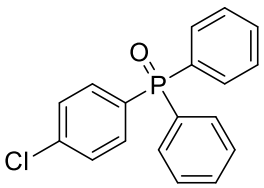
This target product was purified by acidic alumina flash chromatography (PE: EA: MeOH = 1:1:0.1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 – 7.61 (m, 6H), 7.56 – 7.49 (m, 3H), 7.48 - 7.40 (m, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 132.5 (d, $J$ = 104 Hz), 132.1 (d, $J$ = 10 Hz), 131.9 (d, $J$ = 3 Hz), 128.5 (d, $J$ = 12 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 29.08.

**(3ea) (4-chlorophenyl)diphenylphosphine oxid (CAS: 34303-18-9)[2]**



(4-chlorophenyl)diphenylphosphine oxide
Chemical Formula: $C_{18}H_{14}ClOP$
Exact Mass: 312.0471
Molecular Weight: 312.7328

Following the General Procedure A with 1-bromo-4-chlorobenzene (57.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ea** was obtained as white solid (32.9 mg, 35%).

Following the General Procedure A with 1-chloro-4-iodobenzene (71.5 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ea** was obtained as white solid (72.7 mg, 78%).

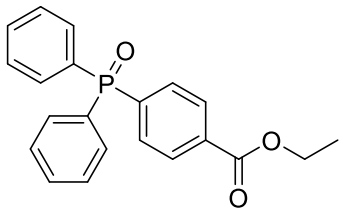
This target product was purified by acidic alumina flash chromatography (PE: EA: MeOH = 1:1:0.1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 – 7.50 (m, 8H), 7.48 – 7.39 (m, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.6 (d, $J$ = 3 Hz), 133.5 (d, $J$ = 11 Hz), 132.2 (d, $J$ = 3 Hz), 132.1 (d, $J$ = 105 Hz), 132.0 (d, $J$ = 10 Hz), 131.2 (d, $J$ = 105 Hz), 128.9 (d, $J$ = 13 Hz), 128.6 (d, $J$ = 12 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 28.41.

**(3fa) ethyl 4-(diphenylphosphoryl)benzoate (CAS: 101630-35-7)[3]**



ethyl 4-(diphenylphosphoryl)benzoate
Chemical Formula: $C_{21}H_{19}O_3P$
Exact Mass: 350.1072
Molecular Weight: 350.3538

Following the General Procedure A with ethyl-4-bromobenzoate (68.7 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3fa** was obtained as colorless oil (67.6 mg, 64%).

Following the General Procedure A with ethyl-4-iodobenzoate (82.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3 /1 a** was obtained as colorless oil (86.3 mg, 82%).

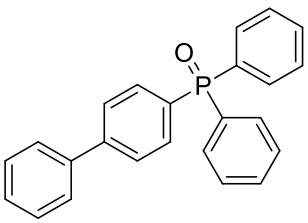
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 – 8.10 (dd, $J$ = 8.4, 2.4 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.71 – 7.63 (m, 4H), 7.60 – 7.53 (m, 2H), 7.51 – 7.44 (m, 4H), 4.39 (q, $J$ = 7.0 Hz, 2H), 1.39 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 165.7, 137.4 (d, $J$ = 101 Hz), 133.6 (d, $J$ = 3 Hz), 132.3 (d, $J$ = 3 Hz), 132.2, 132.0 (d, $J$ = 10 Hz), 131.8 (d, $J$ = 104 Hz), 129.4 (d, $J$ = 12 Hz), 128.7 (d, $J$ = 12 Hz), 61.4, 14.3.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 28.48.

**(3ga) [1,1'-biphenyl]-4-yldiphenylphosphine oxide (CAS: 1942-83-2)[1]**



[1,1'-biphenyl]-4-yldiphenylphosphine oxide
Chemical Formula: $C_{24}H_{19}OP$
Exact Mass: 354.1174
Molecular Weight: 354.3888

Following the General Procedure A with 4-bromobiphenyl (69.9 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ga** was obtained as white solid (79.5 mg, 75%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

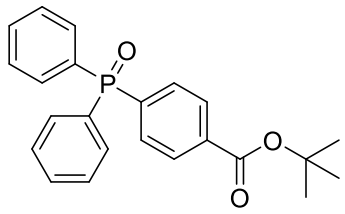
Melting point (°C): 158.3-159.6.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79 – 7.64 (m, 8H), 7.63 - 7.52 (m 4H), 7.51 – 7.41 (m, 6H), 7.38 (t, $J$ = 7.2 Hz, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 144.7 (d, $J$ = 3 Hz), 139.9, 132.6 (d, $J$ = 10 Hz), 132.5 (d, $J$ = 105 Hz), 132.1 (d, $J$ = 10 Hz), 132.09 (d, $J$ = 3 Hz), 131.1 (d, $J$ = 106 Hz), 129.0, 128.6 (d, $J$ = 12 Hz), 127.3, 127.3, 127.1.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 28.97.

**(3ha) tert-butyl 4-(diphenylphosphoryl)benzoate**



*tert*-butyl 4-(diphenylphosphoryl)benzoate
Chemical Formula: $C_{23}H_{23}O_3P$
Exact Mass: 378.1385
Molecular Weight: 378.4078

Following the General Procedure A with tert-butyl 4-bromobenzoate (77.1 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ha** was obtained as white solid (80.6 mg, 71%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (°C): 122.6-125.2.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.06 – 8.01 (m, 2H), 7.71 (dd, $J$ = 11.6, 8.4 Hz, 2H), 7.66 – 7.58 (m, 4H), 7.55 – 7.48 (m, 2H), 7.46 – 7.39 (m, 4H), 1.55 (s, 9H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 164.8, 137.5 (d, $J$ = 101.6 Hz), 135.1 (d, $J$ = 2.8 Hz), 132.0 (d, $J$ = 105.0

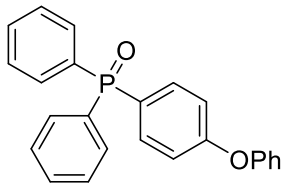
Hz), 132.2 (d, $J$ = 2.8 Hz), 132.0 (d, $J$ = 10.0 Hz), 132.0 (d, $J$ = 10.2 Hz), 129.3 (d, $J$ = 12.2 Hz), 128.6 (d, $J$ = 12.2 Hz), 81.8, 28.1.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.52.

IR ($cm^{-1}$): 3422, 2980, 1710, 1300, 1188, 1110, 718, 547.

HRMS (ESI) m/z calcd for $C_{23}H_{23}O_3PNa^+$ $(M+Na)^+$ 401.12770, found 401.12796.

**(3ia) (4-phenoxyphenyl)diphenylphosphine oxide (CAS: 2412926-10-2)[4]**




(4-phenoxyphenyl)diphenylphosphine oxide
Chemical Formula: $C_{24}H_{19}O_2P$
Exact Mass: 370.1123
Molecular Weight: 370.3878

Following the General Procedure A with 1-bromo-4-phenoxybenzene (74.7 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ia** was obtained as white solid (72.2 mg, 65%).

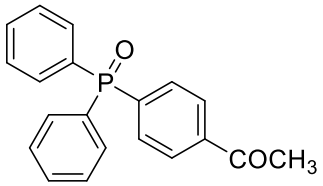
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.39 (m, 4H), 7.38 – 7.31 (m, 2H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.07 – 6.97(m, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, $J$ = 3.0 Hz), 155.5, 134.1 (d, $J$ = 11.2 Hz), 132.7 (d, $J$ = 104.9 Hz), 132.1 (d, $J$ = 10.0 Hz), 131.9 (d, $J$ = 2.8 Hz), 130.1, 128.5 (d, $J$ = 12.1 Hz), 126.0 (d, $J$ = 108.8 Hz), 124.6, 120.2, 117.6 (d, $J$ = 13.1 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.76.

**(3ja) 1-(4-(diphenylphosphoryl)phenyl)ethan-1-one (CAS: 5032-76-8)[4]**




1-(4-(diphenylphosphoryl)phenyl)ethan-1-one
Chemical Formula: $C_{20}H_{17}O_2P$
Exact Mass: 320.0966
Molecular Weight: 320.3278

Following the General Procedure A with 1-(4-bromophenyl)ethan-1-one (59.7 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ja** was obtained as white solid (59.6 mg, 62%).

Following the General Procedure A with 1-(4-iodophenyl)ethan-1-one (73.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ja** was obtained as colorless oil (73.1 mg, 76%).

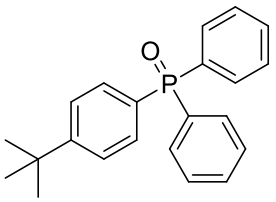
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.80 – 7.74 (m, 2H), 7.68 – 7.60 (m, 4H), 7.58 – 7.52 (m, 2H), 7.49 – 7.43 (m, 4H), 2.61 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 139.5 (d, $J$ = 2.7 Hz), 137.7 (d, $J$ = 101 Hz), 132.4 (d, $J$ = 10.1 Hz), 132.3 (d, $J$ = 3.0 Hz), 132.0 (d, $J$ = 10.0 Hz), 131.2, 128.7 (d, $J$ = 12.2 Hz), 128.1 (d, $J$ = 12.1 Hz), 26.8.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.35.

**(3ka) (4-(tert-butyl)phenyl)diphenylphosphine oxide (CAS: 1448632-01-6)[5]**



(4-(*tert*-butyl)phenyl)diphenylphosphine oxide
Chemical Formula: $C_{22}H_{23}OP$
Exact Mass: 334.1487
Molecular Weight: 334.3988

Following the General Procedure A with 1-(tert-butyl)-4-iodobenzene (78.0 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ka** was obtained as white solid (63.2 mg, 63%).

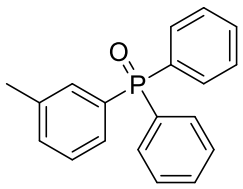
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.61 – 7.54 (m, 2H), 7.53 – 7.40 (m, 8H), 1.30 (s, 9H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.4 (d, *J* = 2.8 Hz), 132.9 (d, *J* = 104.3 Hz), 132.1 (d, *J* = 9.7 Hz), 131.9, 131.8 (d, *J* = 2.7 Hz), 129.2 (d, *J* = 106.9 Hz), 128.4 (d, *J* = 12.1 Hz), 125.5 (d, *J* = 12.4 Hz), 35.0, 31.1.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.93.

**(3la) diphenyl(m-tolyl)phosphine oxide (CAS: 6840-27-3)[6]**



diphenyl(*m*-tolyl)phosphine oxide
Chemical Formula: $C_{19}H_{17}OP$
Exact Mass: 292.1017
Molecular Weight: 292.3178

Following the General Procedure A with 1-bromo-3-methylbenzene (51.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3la** was obtained as white solid (33.3 mg, 38%).

Following the General Procedure A with 1-iodo-3-methylbenzene (65.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3la** was obtained as white solid (48.2 mg, 55%).

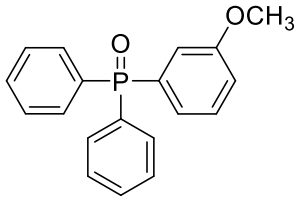
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.60 – 7.50 (m, 3H), 7.48 – 7.42 (m, 4H), 7.40 – 7.31 (m, 3H), 2.35 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.5 (d, *J* = 12.0 Hz), 133.0 (d, *J* = 43.5 Hz), 132.8 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 9.5 Hz), 132.1 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 2.8 Hz), 131.8, 129.2 (d, *J* = 10.3 Hz), 128.5 (d, *J* = 12.1 Hz), 128.3 (d, *J* = 12.9 Hz), 21.4.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 29.27.

**(3ma) (3-methoxyphenyl)diphenylphosphine oxide (CAS: 95278-09-4)[4]**



(3-methoxyphenyl)diphenylphosphine oxide
Chemical Formula: $C_{19}H_{17}O_2P$
Exact Mass: 308.0966
Molecular Weight: 308.3168

Following the General Procedure A with 1-iodo-3-methoxybenzene (70.2 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ma** was obtained as white solid (38.8 mg, 42%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

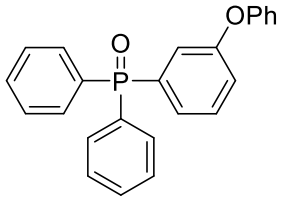
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.57 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.38 – 7.32 (m, 1H), 7.31 – 7.24 (m, 1H), 7.17 – 7.10 (m, 1H), 7.09 – 7.03 (m, 1H), 3.78 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 14.8 Hz), 133.9 (d, *J* = 103.6 Hz), 133.0, 132.1 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 2.8 Hz), 129.7 (d, *J* = 14.4 Hz), 128.5 (d, *J* = 12.2 Hz), 124.4 (d, *J* = 10.0 Hz), 118.2

(d, *J* = 2.6 Hz), 116.8 (d, *J* = 10.7 Hz), 55.4.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 29.37.

**(3na) (3-phenoxyphenyl)diphenylphosphine oxide**




(3-phenoxyphenyl)diphenylphosphine oxide
Chemical Formula: $C_{24}H_{19}O_2P$
Exact Mass: 370.1123
Molecular Weight: 370.3878

Following the General Procedure A with 1-bromo-3-phenoxybenzene (74.7 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3na** was obtained as yellow oil (76.7 mg, 69%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 4H), 7.57 – 7.49 (m, 2H), 7.49 – 7.42 (m, 4H), 7.41 – 7.38 (m, 1H), 7.37 – 7.34 (m, 1H), 7.34 – 7.26 (m, 3H), 7.15 – 7.06 (m, 2H), 7.00 – 6.94 (m, 2H).

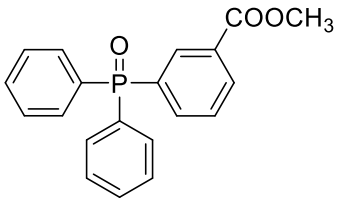
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.6 (d, *J* = 15.5 Hz), 156.3, 134.6 (d, *J* = 103.1 Hz), 132.2 (d, *J* = 104.9 Hz), 132.1, 132.0, 130.1 (d, *J* = 13.9 Hz), 129.9, 128.6 (d, *J* = 12.2 Hz), 126.6 (d, *J* = 9.6 Hz), 123.9, 122.0 (d, *J* = 11.0 Hz), 121.8 (d, *J* = 2.6 Hz), 119.2.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.74.

IR ($cm^{-1}$): 3659, 3055, 1673, 1580, 1482, 1233, 1110, 908, 757, 698, 537.

HRMS (ESI) m/z calcd for $C_{24}H_{19}O_2PNa^+$ $(M+Na)^+$ 393.1015, found 393.1011.

**(3oa) methyl 3-(diphenylphosphoryl)benzoate (CAS: 204930-15-4)[7]**




methyl 3-(diphenylphosphoryl)benzoate
Chemical Formula: $C_{20}H_{17}O_3P$
Exact Mass: 336.0915
Molecular Weight: 336.3268

Following the General Procedure A with methyl 3- bromo benzoate (64.5 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3oa** was obtained as white solid (38.4 mg, 38%).

Following the General Procedure A with methyl 3-iodobenzoate (78.6 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3oa** was obtained as white solid (41.4 mg, 41%).

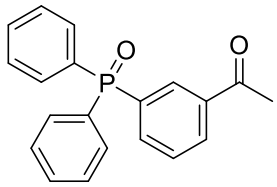
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 12.0, 1.2 Hz, 1H), 8.24 – 8.15 (m, 1H), 7.93 – 7.83 (m, 1H), 7.68 – 7.61 (m, 4H), 7.57 – 7.51 (m, 3H), 7.49 – 7.42 (m, 4H), 3.86 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 136.2 (d, *J* = 9.8 Hz), 133.5 (d, *J* = 103.5 Hz), 133.0 (d, *J* = 14.5 Hz), 132.9, 132.2 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 105.2 Hz), 132.0 (d, *J* = 10.1 Hz), 130.6 (d, *J* = 12.1 Hz), 128.8 (d, *J* = 11.8 Hz), 128.7 (d, *J* = 12.3 Hz), 52.4 .

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.28.

**(3pa) 1-(3-(diphenylphosphoryl)phenyl)ethan-1-one (CAS: 50777-54-3)[8]**



1-(3-(diphenylphosphoryl)phenyl)ethan-1-one
Chemical Formula: $C_{20}H_{17}O_2P$
Exact Mass: 320.0966
Molecular Weight: 320.3278

Following the General Procedure A with 1-(3-bromophenyl)ethan-1-one (59.7 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3pa** was obtained as white solid (44.2 mg, 46%).

Following the General Procedure A with 1-(3-iodophenyl)ethan-1-one (73.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3pa** was obtained as white solid (43.2 mg, 45%).

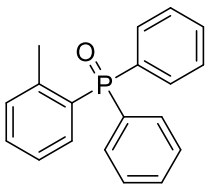
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 12.4 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.70 – 7.60 (m, 4H), 7.58 – 7.51 (m, 3H), 7.49 – 7.43 (m, 4H), 2.56 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.2, 137.2 (d, *J* = 11.0 Hz), 136.3 (d, *J* = 10.1 Hz), 133.6 (d, *J* = 103.1 Hz), 131.9 (d, *J* = 105.3 Hz), 132.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.1 Hz), 131.9 (d, *J* = 10.2 Hz), 131.5 (d, *J* = 2.6 Hz), 128.9 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 12.3 Hz), 26.71.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.51.

**(3qa) diphenyl(o-tolyl)phosphine oxide (CAS: 6840-26-2)[5]**



diphenyl(*o*-tolyl)phosphine oxide
Chemical Formula: $C_{19}H_{17}OP$
Exact Mass: 292.1017
Molecular Weight: 292.3178

Following the General Procedure A with 1-bromo-2-methylbenzene (51.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3qa** was obtained as yellow solid (22.5 mg, 26%).

Following the General Procedure A with 1-iodo-2-methylbenzene (65.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3qa** was obtained as white solid (32.9 mg, 38%).

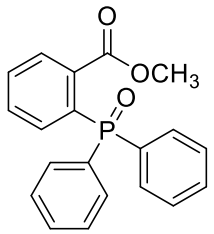
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.38 (m, 5H), 7.30 – 7.25 (m, 1H), 7.16 – 7.08 (m, 1H), 7.02 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.45 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.3 (d, *J* = 8.1 Hz), 133.5 (d, *J* = 12.9 Hz), 132.8 (d, *J* = 103.8 Hz), 132.1 (d, *J* = 2.6 Hz), 132.0, 131.9, 131.8 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 103.3 Hz), 128.6 (d, *J* = 12.1 Hz), 125.2 (d, *J* = 12.9 Hz), 21.7 (d, *J* = 4.7 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 31.66.

**(3ra) methyl 2-(diphenylphosphoryl)benzoate (CAS: 79317-63-8)[7]**



methyl 2-(diphenylphosphoryl)benzoate
Chemical Formula: $C_{20}H_{17}O_3P$
Exact Mass: 336.0915
Molecular Weight: 336.3268

Following the General Procedure A with methyl 2-bromobenzoate (64.5 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ra** was obtained as white solid (35.3 mg, 35%).

Following the General Procedure A with methyl 2-iodobenzoate (78.6 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ra** was obtained as white solid (27.2 mg, 27%).

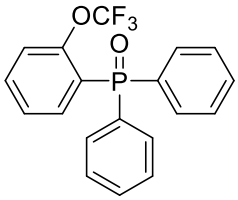
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 1H), 7.71 – 7.58 (m, 5H), 7.57 – 7.40 (m, 8H), 3.48 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.7 (d, *J* = 3.0 Hz), 136.0 (d, *J* = 6.2 Hz), 134.7 (d, *J* = 10.6 Hz), 133.3 (d, *J* = 108.3 Hz), 132.9, 131.8 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 10.0 Hz), 131.6, 130.9 (d, *J* = 11.8 Hz), 130.5 (d, *J* = 8.5 Hz), 128.4 (d, *J* = 12.4 Hz), 52.2.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 30.87.

**(3sa) diphenyl(2-(trifluoromethoxy)phenyl)phosphine oxide (CAS: 2242839-53-6)**



diphenyl(2-(trifluoromethoxy)phenyl)phosphine oxide
Chemical Formula: $C_{19}H_{14}F_3O_2P$
Exact Mass: 362.0684
Molecular Weight: 362.2880

Following the General Procedure A with 1-iodo-2-(trifluoromethoxy)benzene (86.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3sa** was obtained as yellow solid (44.8 mg, 42%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (°C): 113.1-114.5.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 1H), 7.76 – 7.66 (m, 4H), 7.62 – 7.50 (m, 3H), 7.50 – 7.41 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.25 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.6, 135.5 (d, *J* = 6.5 Hz), 134.2 (d, *J* = 1.7 Hz), 131.9 (d, *J* = 108.7 Hz), 132.1 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.3 Hz), 128.5 (d, *J* = 12.6 Hz), 126.0 (d, *J* = 10.8 Hz), 124.3 (d, *J* = 99.6 Hz), 119.9 (d, *J* = 261.6 Hz), 117.8 (dd, *J* = 5.5, 2.4 Hz).

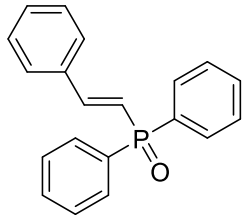
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -56.29.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 25.22.

IR ($cm^{-1}$): 3063, 1588, 1439, 1263, 1210, 1167, 1120, 708, 547.

HRMS (ESI) m/z calcd for $C_{19}H_{14}F_3O_2PNa^+$ $(M+Na)^+$ 385.0576, found 385.0576.

**(3ta) (E)-diphenyl(styryl)phosphine oxide (CAS: 3582-82-9)[9]**



(*E*)-diphenyl(styryl)phosphine oxide
Chemical Formula: $C_{20}H_{17}OP$
Exact Mass: 304.1017
Molecular Weight: 304.3288

Following the General Procedure A with beta-bromostyrene (54.9 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ta** was obtained as white solid (47.0 mg, 52%).

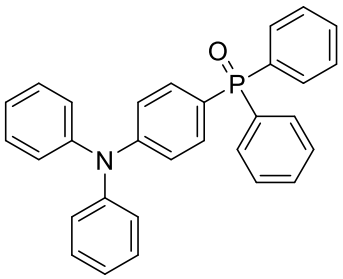
This target product was purified by acidic alumina flash chromatography (PE: EA: MeOH = 1:1:0.1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 – 7.72 (m, 4H), 7.57 – 7.44 (m, 9H), 7.39 – 7.34 (m, 3H), 6.84 (dd, 22.0, 17.6 Hz, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.6 (d, $J$ = 4 Hz), 135.1 (d, $J$ = 18 Hz), 133.0 (d, $J$ = 106 Hz), 131.9 (d, $J$ = 3 Hz), 131.4 (d, $J$ = 10 Hz), 130.1, 128.9, 128.7 (d, $J$ = 12 Hz), 127.8, 119.3 (d, $J$ = 105 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 24.43.

**(3ua) (4-(diphenylamino)phenyl)diphenylphosphine oxide (CAS: 887651-41-4)[2]**



(4-(diphenylamino)phenyl)diphenyl phosphine oxide
Chemical Formula: $C_{30}H_{24}NOP$
Exact Mass: 445.1596
Molecular Weight: 445.5018

Following the General Procedure A with 4-bromotriphenylamine (97.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ua** was obtained as white solid (98.8 mg, 74%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

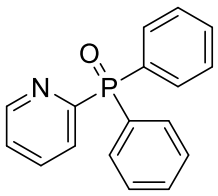
Melting point (°C): 55.2-56.5.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.74 – 7.66 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 6H), 7.27 (t, $J$ = 8.0 Hz, 4H), 7.13 (d, $J$ = 7.6 Hz, 4H), 7.08 (t, $J$ = 7.4 Hz, 2H), 7.01 (dd, $J$ = 8.8, 2.4 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 151.1 (d, $J$ = 3 Hz), 146.6, 133.2 (d, $J$ = 11 Hz), 133.0 (d, $J$ = 105 Hz), 132.1 (d, $J$ = 10 Hz), 131.8 (d, $J$ = 3 Hz), 129.5, 128.4 (d, $J$ = 12 Hz), 125.8, 124.5, 123.1 (d, $J$ = 111 Hz), 120.2 (d, $J$ = 13 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 29.02.

**(3va) diphenyl(pyridin-2-yl)phosphine oxide (CAS: 64741-30-6)[8]**



diphenyl(pyridin-2-yl)phosphine oxide
Chemical Formula: $C_{17}H_{14}NOP$
Exact Mass: 279.0813
Molecular Weight: 279.2788

Following the General Procedure A with 2-bromopyridine (47.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3va** was obtained as white solid (43.5 mg, 52%).

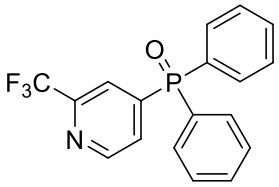
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, $J$ = 4.6 Hz, 1H), 8.33 – 8.25 (m, 1H), 7.92 – 7.80 (m, 5H), 7.52 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.39 – 7.34 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.4 (d, $J$ = 132.4 Hz), 150.2 (d, $J$ = 19.2 Hz), 136.2 (d, $J$ = 9.3 Hz), 132.2 (d, $J$ = 104.5 Hz), 132.1 (d, $J$ = 9.5 Hz), 131.9 (d, $J$ = 2.8 Hz), 128.4 (d, $J$ = 19.9 Hz), 128.4 (d, $J$ = 12.2 Hz), 125.3 (d, $J$ = 3.1 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 20.83.

**(3wa) diphenyl(2-(trifluoromethyl)pyridin-4-yl)phosphine oxide**



diphenyl(2-(trifluoromethyl)pyridin-4-yl)phosphine oxide
Chemical Formula: $C_{18}H_{13}F_3NOP$
Exact Mass: 347.0687
Molecular Weight: 347.2770

Following the General Procedure A with 2-(trifluoromethyl)-4-bromopyridine (67.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3wa** was obtained as white solid (64.7 mg, 62%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (° C): 138.5-140.0.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.83 (t, $J$ = 4.2 Hz, 1H), 7.98 (d, $J$ = 11.6 Hz, 1H), 7.73 – 7.57 (m, 7H), 7.54 – 7.47 (m, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.1 (d, $J$ = 10 Hz), 148.8 (qd, $J$ = 35, 10 Hz), 144.5 (d, $J$ = 94 Hz), 133.0 (d, $J$ = 3 Hz), 131.9 (d, $J$ = 10 Hz), 129.6 (d, $J$ = 107 Hz), 129.1 (d, $J$ = 12 Hz), 128.6 (d, $J$ = 8 Hz), 122.4 (dq, $J$ = 9, 3 Hz), 121.7 (qd, $J$ = 272, 3 Hz).

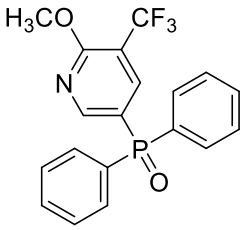
$^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -67.99.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 26.08.

IR ($cm^{-1}$): 3056, 3027, 1436, 1333, 1201, 1136, 683, 533.

HRMS (ESI) m/z calcd for $C_{18}H_{14}F_3NOP^+$ $(M+H)^+$ 348.0760, found 348.0761.

**(3xa) (6-methoxy-5-(trifluoromethyl)pyridin-3-yl)diphenylphosphine oxide**



(6-methoxy-5-(trifluoromethyl)pyridin-3-yl)diphenylphosphine oxide
Chemical Formula: $C_{19}H_{15}F_3NO_2P$
Exact Mass: 377.0792
Molecular Weight: 377.3030

Following the General Procedure A with 5-bromo-2-methoxy-3-(trifluoromethyl)pyridine (78.4 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3xa** was obtained as white solid (60.6 mg, 54%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (° C): 69.9-71.1.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, $J$ = 6.0, 2.0 Hz, 1H), 8.16 (dd, $J$ = 10.4, 1.6 Hz, 1H), 7.70 – 7.61 (m, 4H), 7.60 – 7.53 (m, 2H), 7.52 – 7.43 (m, 4H), 4.05 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.9, 154.5 (d, $J$ = 13.1 Hz), 139.7 (dd, $J$ = 10.1, 4.8 Hz), 132.6 (d, $J$ = 2.8 Hz), 131.9 (d, $J$ = 10.2 Hz), 131.4 (d, $J$ = 107.3 Hz), 128.9 (d, $J$ = 12.4 Hz), 123.8, 121.1, 121.1 (d, $J$ = 106.7 Hz), 54.8.

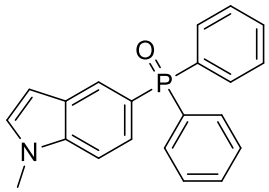
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.09.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 25.80.

IR ($cm^{-1}$): 3412, 3029, 2916, 2229, 1600, 1404, 1186, 1127, 847, 694, 578.

HRMS (ESI) m/z calcd for $C_{19}H_{15}F_3NO_2PNa^+$ $(M+Na)^+$ 400.06847, found 400.06854.

**(3ya) (1-methyl-1H-indol-5-yl)diphenylphosphine oxide**



(1-methyl-1*H*-indol-5-yl)diphenylphosphine oxide
Chemical Formula: $C_{21}H_{18}NOP$
Exact Mass: 331.1126
Molecular Weight: 331.3548

Following the General Procedure A with 5-bromo-1-methyl-1H-indole (63.0 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ya** was obtained as yellow solid (71.0 mg, 71%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:2).

Melting point (°C): 181.2-183.0.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (d, $J$ = 13.2 Hz, 1H), 7.72 – 7.64 (m, 4H), 7.53 – 7.47 (m, 3H), 7.44 – 7.35 (m, 5H), 7.09 (d, $J$ = 3.2 Hz, 1H), 6.48 (d, $J$ = 2.8 Hz, 1H), 3.77 (s, 3H).

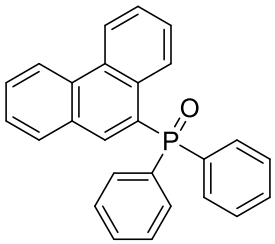
$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.4 (d, $J$ = 3 Hz), 133.5 (d, $J$ = 104 Hz), 132.2 (d, $J$ = 10 Hz), 131.7 (d, $J$ = 3 Hz), 130.3, 128.4 (d, $J$ = 12 Hz), 126.4 (d, $J$ = 12 Hz), 124.6 (d, $J$ = 12 Hz), 121.5 (d, $J$ = 110 Hz), 109.6 (d, $J$ = 14 Hz), 102.2, 33.0.

$^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 31.43.

IR ($cm^{-1}$): 3102, 2914, 1436, 1324, 1173, 1166, 706, 505.

HRMS (ESI) m/z calcd for $C_{21}H_{19}NOP^+$ $(M+H)^+$ 332.1199, found 332.1201.

**(3za) phenanthren-9-yldiphenylphosphine oxide (CAS: 401798-09-2)[10]**



phenanthren-9-yldiphenylphosphine oxide
Chemical Formula: $C_{26}H_{19}OP$
Exact Mass: 378.1174
Molecular Weight: 378.4108

Following the General Procedure A with 9-bromophenanthrene (77.1 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3za** was obtained as white solid (56.8 mg, 50%).

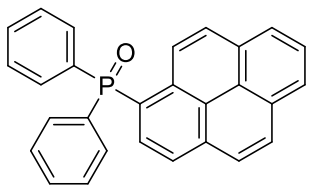
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.60 (m, 3H), 7.79 – 7.43 (m, 16H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.9 (d, $J$ = 11.3 Hz), 133.2, 132.2 (d, $J$ = 9.8 Hz), 132.2, 132.0 (d, $J$ = 2.7 Hz), 131.0 (d, $J$ = 8.4 Hz), 130.8 (d, $J$ = 8.5 Hz), 130.1, 129.70 (d, $J$ = 14.8 Hz), 129.2, 128.8, 128.7, 128.6, 127.9 (d, $J$ = 102.3 Hz), 127.2 (d, $J$ = 5.8 Hz), 127.1, 123.1, 122.7.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 32.64.

**(3zb) diphenyl(pyren-1-yl)phosphine oxide (CAS: 2260821-57-4)[11]**



diphenyl(pyren-1-yl)phosphine oxide
Chemical Formula: $C_{28}H_{19}OP$
Exact Mass: 402.1174
Molecular Weight: 402.4328

Following the General Procedure A with 1-bromopyrene (84.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3zb** was obtained as white solid (66.4 mg, 55%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

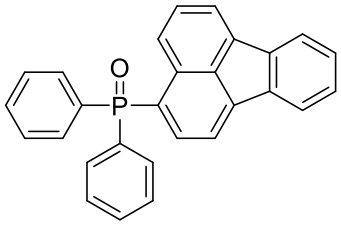
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, $J$ = 9.3 Hz, 1H), 8.23 – 8.11 (m, 3H), 8.09 – 7.97 (m, 4H), 7.79 – 7.68 (m, 5H), 7.58 – 7.51 (m, 2H), 7.50 – 7.42 (m, 4H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.3 (d, $J$ = 2.5 Hz), 134.2 (d, $J$ = 8.1 Hz),133.3 (d, $J$ = 104.7 Hz), 132.2 (d, $J$ = 9.8 Hz), 132.0 (d, $J$ = 2.7 Hz), 131.2 (d, $J$ = 12.3 Hz), 131.0, 130.4, 129.4 (d, $J$ = 95.5 Hz), 128.7 (d, $J$ = 12.2 Hz), 127.1, 126.5, 126.3 (d, $J$ = 6.6 Hz),

126.2, 125.6, 125.1 (d, $J$ = 10.2 Hz), 124.6, 124.2, 123.6 (d, $J$ = 13.7 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 32.85.

**(3zc) fluoranthen-3-yldiphenylphosphine oxide**



fluoranthen-3-yldiphenylphosphine oxide
Chemical Formula: $C_{28}H_{19}OP$
Exact Mass: 402.1174
Molecular Weight: 402.4328

Following the General Procedure A with 3-bromofluoranthene (84.3 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3zc** was obtained as white solid (97.8 mg, 81%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (° C): 87.9-90.3.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, $J$ = 8.4 Hz, 1H), 7.84 – 7.68 (m, 8H), 7.56 – 7.41 (m, 8H), 7.39 – 7.27 (m, 2H).

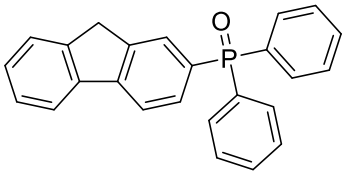
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.5 (d, $J$ = 2.8 Hz), 140.2, 138.3, 137.5 (d, $J$ = 1.5 Hz), 135.3 (d, $J$ = 12.4 Hz), 133.6, 132.9 (d, $J$ = 10.2 Hz), 132.6, 132.1 (d, $J$ = 9.9 Hz), 132.0 (d, $J$ = 2.7), 130.9 (d, $J$ = 8.2 Hz), 128.9 (d, $J$ = 102.4 Hz), 129.3, 128.9, 128.6 (d, $J$ = 12.2 Hz), 127.83, 127.18 (d, $J$ = 3.9 Hz), 121.9 (d, $J$ = 64.4 Hz), 120.8, 118.3 (d, $J$ = 14.1 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 30.69.

IR ($cm^{-1}$): 3429, 3055, 1604, 1439, 1186, 1112, 753, 702, 543.

HRMS (ESI) m/z calcd for $C_{28}H_{19}OPNa^+$ $(M+Na)^+$ 425.1066, found 425.1064.

**(3zd) (9H-fluoren-2-yl)diphenylphosphine oxide**



(9*H*-fluoren-2-yl)diphenylphosphine oxide
Chemical Formula: $C_{25}H_{19}OP$
Exact Mass: 366.1174
Molecular Weight: 366.3998

Following the General Procedure A with 9-bromophenanthrene (73.5 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3zd** was obtained as yellow oil (73.6 mg, 67%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J$ = 11.6 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.75 – 7.66 (m, 4H), 7.62 (dd, $J$ = 11.6, 8.0 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.48 – 7.41 (m, 4H), 7.39 – 7.31 (m, 2H), 3.87 (s, 2H).

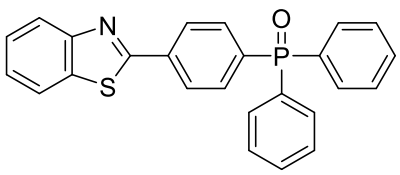
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.5 (d, $J$ = 2.7 Hz), 144.0, 143.3 (d, $J$ = 13.2 Hz), 140.4, 132.8 (d, $J$ = 104.5 Hz), 132.1 (d, $J$ = 9.9 Hz), 131.9 (d, $J$ = 2.7 Hz), 131.0 (d, $J$ = 11.1 Hz), 130.1 (d, $J$ = 105.7 Hz), 128.6 (d, $J$ = 10.3 Hz), 128.5 (d, $J$ = 12.1 Hz), 128.0, 127.0, 125.2, 120.7, 119.8 (d, $J$ = 13.6 Hz), 36.9.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 29.96.

IR ($cm^{-1}$): 3661, 3055, 2884, 1720, 1492, 1435, 1190, 737, 700, 543.

HRMS (ESI) m/z calcd for $C_{25}H_{19}OPNa^+$ $(M+Na)^+$ 389.1066, found 389.1067.

**(3ze) (4-(benzo[d]thiazol-2-yl)phenyl)diphenylphosphine oxide (CAS: 1438435-79-0)[12]**



(4-(benzo[*d*]thiazol-2-yl)phenyl)diphenylphosphine oxide
Chemical Formula: $C_{25}H_{18}NOPS$
Exact Mass: 411.0847
Molecular Weight: 411.4588

Following the General Procedure A with 2-(4-bromophenyl)benzo[d]thiazole (88.8 mg, 0.3 mmol), diphenylphosphine oxide (120.7 mg, 0.6 mmol), **3ze** was obtained as white solid (83.9 mg, 68%).

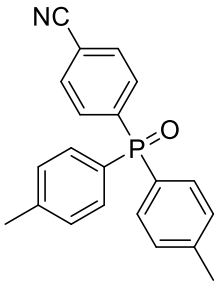
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.79 (dd, *J* = 11.6, 8.4 Hz, 2H), 7.69 (dd, *J* = 12.4, 7.6 Hz, 4H), 7.56 – 7.49 (m, 2H), 7.48 – 7.41 (m, 5H), 7.40 – 7.32 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.4, 154.1, 136.7 (d, *J* = 2.9 Hz), 135.3 (d, *J* = 103.0 Hz), 135.2, 132.8 (d, *J* = 10.1 Hz), 132.1 (d, *J* = 105.1 Hz), 132.2 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 10.0 Hz), 128.7 (d, *J* = 12.2 Hz), 127.4 (d, *J* = 12.3 Hz), 126.6, 125.8, 123.6, 121.8.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.43.

**(3ab) (4-isocyanophenyl)di-p-tolylphosphine oxide**



(4-isocyanophenyl)di-*p*-tolylphosphine oxide
Chemical Formula: $C_{21}H_{18}NOP$
Exact Mass: 331.1126
Molecular Weight: 331.3548

Following the General Procedure A with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), di-p-tolylphosphine oxide (138.2 mg, 0.6 mmol), **3ab** was obtained as white solid (60.6 mg, 61%).

Following the General Procedure A with 4-iodobenzonitrile (68.7 mg, 0.3 mmol), di-p-tolylphosphine oxide (138.2 mg, 0.6 mmol), **3ab** was obtained as white solid (75.5 mg, 76%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (°C): 101.4-103.2.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.53 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.33 – 7.26 (m, 4H), 2.41 (s, 6H).

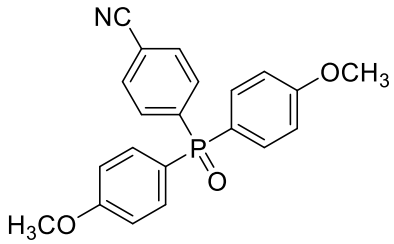
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.1 (d, *J* = 2.8 Hz), 139.1 (d, *J* = 99.4 Hz), 132.6 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 10.4 Hz), 131.8, 129.5 (d, *J* = 12.7 Hz), 128.0 (d, *J* = 108.4 Hz), 118.0 (d, *J* = 1.4 Hz), 115.4 (d, *J* = 3.0 Hz), 21.6 (d, *J* = 1.1 Hz).

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 27.94.

IR ($cm^{-1}$): 3420, 3037, 2922, 2228, 1604, 1398, 1186, 1114, 808, 659, 514.

HRMS (ESI) m/z calcd for $C_{21}H_{18}NOPNa^+$ $(M+Na)^+$ 354.10182, found 354.10211.

**(3ac) 4-(bis(4-methoxyphenyl)phosphoryl)benzonitrile**




4-(bis(4-methoxyphenyl)phosphoryl)benzonitrile
Chemical Formula: $C_{21}H_{18}NO_3P$
Exact Mass: 363.1024
Molecular Weight: 363.3528

Following the General Procedure A with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), bis(4-methoxyphenyl)phosphine oxide (157.2 mg, 0.6 mmol), **3ac** was obtained as white solid (65.3 mg, 60%).

Following the General Procedure A with 4-iodobenzonitrile (68.7 mg, 0.3 mmol), bis(4-methoxyphenyl)phosphine oxide (157.2 mg, 0.6 mmol), **3ac** was obtained as white solid (78.4 mg, 72%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (°C): 69.0-72.1.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.80-7.66 (m, 4H), 7.56 – 7.46 (m, 4H), 6.99 – 6.90 (m, 4H), 3.81 (s, 6H).

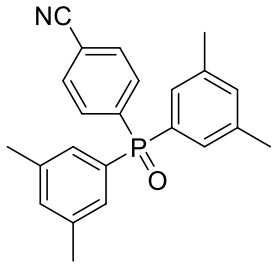
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $J$ = 2.8 Hz), 139.4 (d, $J$ = 100.0 Hz), 133.9 (d, $J$ = 11.4 Hz), 132.5 (d, $J$ = 9.9 Hz), 131.9 (d, $J$ = 11.8 Hz), 125.6 (d, $J$ = 112.7 Hz), 118.0, 115.3 (d, $J$ = 3.0 Hz), 114.4 (d, $J$ = 13.3 Hz), 55.4.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 27.43.

IR ($cm^{-1}$): 3414, 2951, 2805, 2229, 1596, 1500, 1298, 1259, 1178, 1114, 1020, 831.

HRMS (ESI) m/z calcd for $C_{21}H_{18}NO_3PNa^+$ $(M+Na)^+$ 386.09165, found 386.09137.

**(3ad) bis(3,5-dimethylphenyl)(4-isocyanophenyl)phosphine oxide**




bis(3,5-dimethylphenyl)(4-isocyanophenyl)phosphine oxide
Chemical Formula: $C_{23}H_{22}NOP$
Exact Mass: 359.1439
Molecular Weight: 359.4088

Following the General Procedure A with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), bis(3,5-dimethylphenyl)phosphine oxide (155.0 mg, 0.6 mmol), **3ad** was obtained as white solid (67.9 mg, 63%).

Following the General Procedure A with 4-iodobenzonitrile (68.7 mg, 0.3 mmol), bis(3,5-dimethylphenyl)phosphine oxide (155.0 mg, 0.6 mmol), **3ad** was obtained as white solid (89.4 mg, 83%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).

Melting point (°C): 150.6-153.4.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 4H), 7.22 (d, $J$ = 12.6 Hz, 4H), 7.17 (s, 2H), 2.30 (s, 12H).

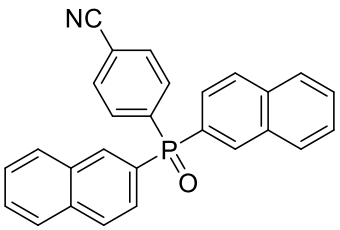
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.5, 138.5 (d, $J$ = 12.9 Hz), 134.2 (d, $J$ = 2.9 Hz), 132.6 (d, $J$ = 9.8 Hz), 131.9 (d, $J$ = 11.8 Hz), 131.0 (d, $J$ = 104.9 Hz), 129.5 (d, $J$ = 10.0 Hz), 118.0 (d, $J$ = 1.4 Hz), 115.4 (d, $J$ = 3.1 Hz), 21.3.

$^{31}$P NMR (162 MHz, $CDCl_3$) δ 28.37.

IR ($cm^{-1}$): 3412, 3031, 2918, 2855, 2229, 1596, 1406, 1186, 1127, 849, 696, 578.

HRMS (ESI) m/z calcd for $C_{23}H_{22}NOPNa^+$ $(M+Na)^+$ 382.13312, found 382.13345.

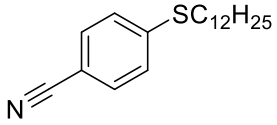
**(3ae) 4-(di(naphthalen-2-yl)phosphoryl)benzonitrile**



4-(di(naphthalen-2-yl)phosphoryl)benzonitrile
Chemical Formula: $C_{27}H_{18}NOP$
Exact Mass: 403.1126
Molecular Weight: 403.4208

Following the General Procedure A with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), di(naphthalen-2-yl)phosphine oxide (181.2 mg, 0.6 mmol), **3ae** was obtained as white solid (87.5 mg, 69%).
Following the General Procedure A with 4-iodobenzonitrile (68.7 mg, 0.3 mmol), di(naphthalen-2-yl)phosphine oxide (181.2 mg, 0.6 mmol), **3ae** was obtained as white solid (101.5 mg, 80%).
This target product was purified by acidic alumina flash chromatography (PE: EA = 1:3).
Melting point (°C): 72.8-74.2.
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 14.2 Hz, 2H), 7.96 – 7.83 (m, 8H), 7.74 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.69 – 7.51 (m, 6H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.6 (d, *J* = 99.8 Hz), 134.9 (d, *J* = 2.3 Hz), 134.3 (d, *J* = 9.6 Hz), 132.8 (d, *J* = 10.0 Hz), 132.5 (d, *J* = 13.6 Hz), 132.1 (d, *J* = 12.0 Hz), 129.0, 128.9, 128.7 (d, *J* = 3.3 Hz), 128.0, 127.7, 127.3, 126.5 (d, *J* = 10.8 Hz), 117.9, 115.7 (d, *J* = 3.1 Hz).
$^{31}$P NMR (162 MHz, $CDCl_3$) δ 27.93.
IR ($cm^{-1}$): 3431, 3055, 2229, 1633, 1388, 1190, 1094, 822, 657.
HRMS (ESI) m/z calcd for $C_{27}H_{18}NOPNa^+$ $(M+Na)^+$ 426.10182, found 426.10172.

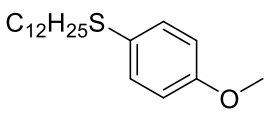
**(5aa) 4-(dodecylthio)benzonitrile (CAS: 26960-82-7)[13]**



4-(dodecylthio)benzonitrile
Chemical Formula: $C_{19}H_{29}NS$
Exact Mass: 303.2021
Molecular Weight: 303.5080

Following the General Procedure B with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5aa** was obtained as yellow solid (80.9 mg, 89%).
Following the General Procedure B with 4-iodobenzonitrile (68.8 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5aa** was obtained as yellow solid (74.4 mg, 82%).
This target product was purified by silica gel flash chromatography (PE: EA = 100:1).
$^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.53 – 7.48 (m, 2H), 7.30 – 7.25 (m, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.69 (pent, *J* = 7.6 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.36 - 1.22 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).
$^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 145.4, 132.2, 126.6, 119.0, 107.84, 31.9, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.1, 28.9, 28.6, 22.7, 14.2.

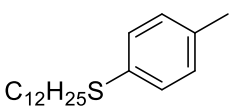
**(5ba) dodecyl(4-methoxyphenyl)sulfane (CAS: 867017-31-0)[13]**



dodecyl(4-methoxyphenyl)sulfane
Chemical Formula: $C_{19}H_{32}OS$
Exact Mass: 308.2174
Molecular Weight: 308.5240

Following the General Procedure B with 4-iodoanisole (70.2 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ba** was obtained as white solid (80.4 mg, 87%).
This target product was purified by silica gel flash chromatography (PE: EA = 200:1).
$^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.36 – 7.31 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.57 (pent, *J* = 7.4 Hz, 2H), 1.42 – 1.34 (m, 2H), 1.31 – 1.21 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).
$^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 158.7, 132.9, 127.0, 114.5, 55.3, 35.84, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 28.7, 22.7, 14.2.

**(5ca) dodecyl(p-tolyl)sulfane (CAS: 94435-76-4)[14]**



dodecyl(*p*-tolyl)sulfane
Chemical Formula: $C_{19}H_{32}S$
Exact Mass: 292.2225
Molecular Weight: 292.5250

Following the General Procedure B with 4 4-bromotoluene (51.3 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ca** was obtained as colorless oil (68.5 mg, 78%).

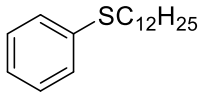
Following the General Procedure B with 4-iodotoluene (65.4 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ca** was obtained as colorless oil (68.4 mg, 78%).

This target product was purified by silica gel flash chromatography (PE: EA = 200:1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 – 7.22 (m, 2H), 7.09 (d, $J$ = 8.0 Hz, 2H), 2.87 (t, $J$ = 7.4 Hz, 2H), 2.31 (s, 3H), 1.61 (pent, $J$ = 7.4 Hz, 2H), 1.1.43 - 1.34 (m, 2H), 1.32 – 1.22 (m, 16H), 0.88 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 135.8, 133.2, 129.7, 129.6, 34.4, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 28.9, 22.7, 21.0, 14.2.

**(5da) dodecyl(phenyl)sulfane (CAS: 56056-49-6)[13]**



dodecyl(phenyl)sulfane
Chemical Formula: $C_{18}H_{30}S$
Exact Mass: 278.2068
Molecular Weight: 278.4980

Following the General Procedure B with bromobenzene (47.1 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5da** was obtained as colorless oil (73.6 mg, 88%).

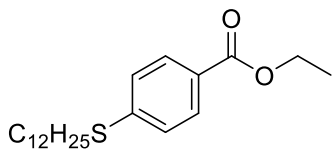
Following the General Procedure B with iodobenzene (61.2 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5da** was obtained as colorless oil (53.8 mg, 64%).

This target product was purified by silica gel flash chromatography (PE: EA = 200:1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 7.19 – 7.12 (m, 1H), 2.91 (t, $J$ = 7.4 Hz, 2H), 1.64 (pent, $J$ = 7.6 Hz, 2H), 1.40 (m, 2H), 1.33 – 1.22 (m, 16H), 0.88 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 137.1, 128.8, 128.8, 125.6, 33.6, 31.93, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 29.2, 28.9, 22.7, 14.1.

**(5ea) ethyl 4-(dodecylthio)benzoate (CAS: 1207539-20-5)[14]**



ethyl 4-(dodecylthio)benzoate
Chemical Formula: $C_{21}H_{34}O_2S$
Exact Mass: 350.2280
Molecular Weight: 350.5610

Following the General Procedure B with ethyl-4-bromobenzoate (68.7 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ea** was obtained as yellow oil (63.8 mg, 61%).

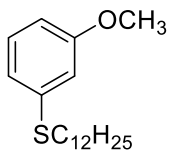
Following the General Procedure B with ethyl-4-iodobenzoate (82.8 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ea** was obtained as yellow oil (86.2 mg, 82%).

This target product was purified by silica gel flash chromatog raphy (PE: EA = 200:1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 – 7.90 (m, 2H), 7.30 – 7.25 (m, 2H), 4.36 (q, $J$ = 7.1 Hz, 2H), 2.97 (t, $J$ = 7.4 Hz, 2H), 1.69 (pent, $J$ = 7.5 Hz, 2H), 1.48 - 1.41 (m, 2H), 1.38 (t, $J$ = 7.2 Hz, 3H), 1.34 -1.22 (m, 16H), 0.88 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 166.4, 144.3, 129.9, 126.9, 126.3, 60.9, 32.1, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 28.9, 28.8, 22.7, 14.4, 14.2.

**(5fa) dodecyl(3-methoxyphenyl)sulfane (CAS: 2126724-71-6)[15]**



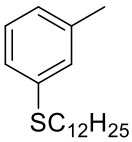
dodecyl(3-methoxyphenyl)sulfane
Chemical Formula: $C_{19}H_{32}OS$
Exact Mass: 308.21739
Molecular Weight: 308.52400

Following the General Procedure B with 1-iodo-3-methoxybenzene (70.2 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5fa** was obtained as colorless oil (70.3 mg, 76%). This target product was purified by acidic alumina flash chromatography (PE: EA = 100:1).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.69 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.78 (s, 3H), 2.95 – 2.85 (m, 2H), 1.69 – 1.60 (m, 2H), 1.45 – 1.37 (m, 2H), 1.26 (s, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.8, 138.6, 129.6, 120.8, 114.0, 111.2, 55.2, 33.4, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 29.2, 28.9, 22.7, 14.2.

**(5ga) dodecyl(m-tolyl)sulfane (CAS: 1450829-03-4)[16]**



dodecyl(*m*-tolyl)sulfane
Chemical Formula: $C_{19}H_{32}S$
Exact Mass: 292.22247
Molecular Weight: 292.52500

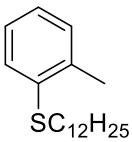
Following the General Procedure B with 1-iodo-3-methylbenzene (65.4 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ga** was obtained as colorless oil (57.0 mg, 65%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 100:1).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.34 (s, 3H), 1.72 – 1.60 (m, 2H), 1.49 – 1.38 (m, 2H), 1.28 (s, 16H), 0.90 (t, *J* = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.5, 136.9, 129.5, 128.7, 126.5, 125.8, 33.6, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 29.2, 28.9, 22.7, 21.4, 14.2.

**(5ha) dodecyl(o-tolyl)sulfane (CAS: 1079988-46-7)[16]**



dodecyl(*o*-tolyl)sulfane
Chemical Formula: $C_{19}H_{32}S$
Exact Mass: 292.22247
Molecular Weight: 292.52500

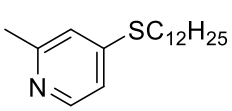
Following the General Procedure B with 1-iodo-2-methylbenzene (65.4 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ha** was obtained as colorless oil (48.3 mg, 55%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 100:1).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 6.6 Hz, 2H), 7.09 – 7.03 (m, 1H), 2.94 – 2.83 (m, 2H), 2.36 (s, 3H), 1.71 – 1.61 (m, 2H), 1.47 – 1.39 (m, 2H), 1.26 (s, 16H), 0.88 (t, *J* = 6.6 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.2, 136.5, 130.0, 127.3, 126.3, 125.2, 32.8, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 29.1, 29.0, 22.7, 20.4, 14.2.

**(5ia) 4-(dodecylthio)-2-methylpyridine**



4-(dodecylthio)-2-methylpyridine
Chemical Formula: $C_{18}H_{31}NS$
Exact Mass: 293.2177
Molecular Weight: 293.5130

Following the General Procedure B with 4-bromo-2-methylpyridine (51.6 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ia** was obtained as colorless oil (29.6 mg, 34%).

This target product was purified by silica gel flash chromatography (PE: EA = 10:1).

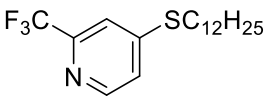
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.26 (d, $J$ = 5.2 Hz, 1H), 6.95 (s, 1H), 6.90 (dd, $J$ = 5.6, 1.6 Hz, 1H), 2.94 (t, $J$ = 7.4 Hz, 2H), 2.48 (s, 3H), 1.75 – 1.64 (m, 2H), 1.49 – 1.39 (m, 2H), 1.28 - 1.22 (m, 16H), 0.87 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 157.9, 149.6, 148.6, 120.0, 117.8, 31.9, 30.6, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 28.5, 24.4, 22.7, 14.1.

IR (cm$^{-1}$): 2961, 2933, 2848, 1578, 1474, 872.

HRMS (ESI) m/z calcd for $C_{18}H_{32}NS^+$ $(M+H)^+$ 294.2250, found 294.2253.

**(5ja) 4-(dodecylthio)-2-(trifluoromethyl)pyridine**



4-(dodecylthio)-2-(trifluoromethyl)pyridine
Chemical Formula: $C_{18}H_{28}F_3NS$
Exact Mass: 347.1895
Molecular Weight: 347.4842

Following the General Procedure B with 2-(trifluoromethyl)-4-bromopyridine (67.8 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ja** was obtained as colorless oil (85.7 mg, 82%).

This target product was purified by silica gel flash chromatography (PE: EA = 10:1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 5.2 Hz, 1H), 7.44 (d, $J$ = 1.6 Hz, 1H), 7.23 (dd, $J$ = 5.4, 1.4 Hz, 1H), 2.99 (t, $J$ = 7.4 Hz, 2H), 1.77 – 1.65 (m, 2H), 1.51 – 1.41 (m, 2H), 1.35 – 1.19 (m, 16H), 0.86 (t, $J$ = 6.8 Hz, 3H).

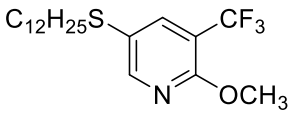
$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 152.4, 149.2, 148.0 (q, $J$ = 34 Hz), 122.5, 121.5 (q, $J$ = 276 Hz), 117.1 (q, $J$ = 3 Hz), 31.9, 30.8, 29.6, 29.5, 29.4, 29.3, 29.1, 28.8, 28.2, 22.7, 14.1.

$^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -68.32.

IR (cm$^{-1}$): 2943, 2848, 1587, 1314, 1145, 721.

HRMS (ESI) m/z calcd for $C_{18}H_{29}F_3NS^+$ $(M+H)^+$ 348.1967, found 348.1968.

**(5ka) 5-(dodecylthio)-2-methoxy-3-(trifluoromethyl)pyridine**



5-(dodecylthio)-2-methoxy-3-(trifluoromethyl)pyridine
Chemical Formula: $C_{19}H_{30}F_3NOS$
Exact Mass: 377.2000
Molecular Weight: 377.5102

Following the General Procedure B with 5-bromo-2-methoxy-3-(trifluoromethyl)pyridine (76.8 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ka** was obtained as colorless oil (76.8 mg, 68%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 10:1).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.40 – 8.27 (m, 1H), 7.90 (dd, $J$ = 20.0, 1.6 Hz, 1H), 4.02 (s, 3H), 2.80 (t, $J$ = 7.2 Hz, 1H), 2.61 – 2.41 (m, 1H), 1.57 (m, 2H), 1.39 (d, $J$ = 11.6 Hz, 2H), 1.25 (s, 16H), 0.87 (t, $J$ = 6.6 Hz, 3H).

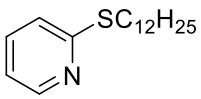
$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 153.1, 151.1, 140.0 (q, $J$ = 4.8 Hz), 138.8 (q, $J$ = 5.0 Hz), 124.3, 110.6, 54.4, 54.2, 36.1, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.5, 22.7, 14.1.

$^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -64.00 (s).

IR (cm$^{-1}$): 2924, 2855, 1718, 1598, 1469, 1324, 1149, 1057, 918, 692.

HRMS (ESI) m/z calcd for $C_{19}H_{31}F_3NOS^+$ $(M+H)^+$ 378.2073, found 378.2071.

**(5la) 2-(dodecylthio)pyridine (CAS: 1079988-48-9)[17]**



2-(dodecylthio)pyridine
Chemical Formula: $C_{17}H_{29}NS$
Exact Mass: 279.2021
Molecular Weight: 279.4860

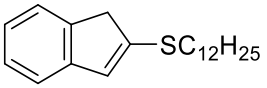
Following the General Procedure B with 2-bromopyridine (47.4 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5la** was obtained as colorless oil (50.3 mg, 60%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 10:1).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, $J$ = 4.4 Hz, 1H), 7.44 (td, $J$ = 8.0, 2.0 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 1H), 6.94 (dd, $J$ = 6.8, 5.2 Hz, 1H), 3.15 (t, $J$ = 7.4 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.49 – 1.39 (m, 2H), 1.25 (s, 16H), 0.87 (t, $J$ = 6.4 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.4, 135.8, 122.1, 119.1, 31.9, 30.1, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 22.7, 14.1.

**(5ma) dodecyl(1H-inden-2-yl)sulfane**



dodecyl(1*H*-inden-2-yl)sulfane
Chemical Formula: $C_{21}H_{32}S$
Exact Mass: 316.2225
Molecular Weight: 316.5470

Following the General Procedure B with 2-bromo-1H-indene (58.5 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5ma** was obtained as white solid (60.3 mg, 64%).

This target product was purified by silica gel flash chromatography (PE: EA = 200:1).

Melting point (°C): 49.8-51.2.

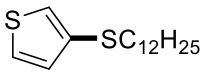
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35 (d, $J$ = 7.2 Hz, 1H), 7.22 (d, $J$ = 4.0 Hz, 2H), 7.12 – 7.04 (m, 1H), 6.50 (s, 1H), 3.49 (s, 2H), 2.93 (t, $J$ = 7.4 Hz, 2H), 1.74 (pent, $J$ = 7.4 Hz, 2H), 1.51 - 1.42 (m, 2H), 1.38 - 1.24 (m, 16H), 0.91 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 145.2, 144.1, 142.2, 126.6, 124.3, 123.4, 123.1, 119.0, 42.1, 32.6, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.1, 29.0, 22.7, 14.2.

IR ($cm^{-1}$): 2961, 2914, 2858, 1465, 834, 721.

HRMS (ESI) m/z calcd for $C_{21}H_{33}S^+$ $(M+H)^+$ 317.2298, found 317.2299.

**(5na) 3-(dodecylthio)thiophene (CAS: 120186-63-2)**



3-(dodecylthio)thiophene
Chemical Formula: $C_{16}H_{28}S_2$
Exact Mass: 284.1632
Molecular Weight: 284.5200

Following the General Procedure B with 3-iodothiophene (63.0 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5na** was obtained as brown solid (72.0 mg, 84%).

This target product was purified by silica gel flash chromatography (PE: EA = 200:1).

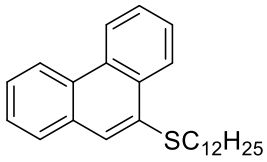
Melting point (°C): 32.5-33.7.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31 (dd, $J$ = 5.0, 3.0 Hz, 1H), 7.11 (dd, $J$ = 2.8, 1.2 Hz, 1H), 7.02 (dd, $J$ = 5.2, 1.2 Hz, 1H), 2.84 (t, $J$ = 7.4 Hz, 2H), 1.62 (pent, $J$ = 7.4 Hz, 2H), 1.45 - 1.36 (m, 2H), 1.35 - 1.19 (m, 16H), 0.89 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 132.4, 129.7, 126.0, 122.8, 35.4, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.2, 28.7, 22.7, 14.2.

HRMS (ESI) m/z calcd for $C_{16}H_{29}S_2^+$ $(M+H)^+$ 285.1705, found 285.1706.

**(5oa) dodecyl(phenanthren-9-yl)sulfane (CAS: 259270-08-1)**



dodecyl(phenanthren-9-yl)sulfane
Chemical Formula: $C_{26}H_{34}S$
Exact Mass: 378.23812
Molecular Weight: 378.61800

Following the General Procedure B with 9-bromophenanthrene (78.7 mg, 0.3 mmol), 1-dodecanethiol (121.4 mg, 0.6 mmol), **5oa** was obtained as white solid (46.1 mg, 41%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 100:1).

Melting point (° C): 60.7-62.0.

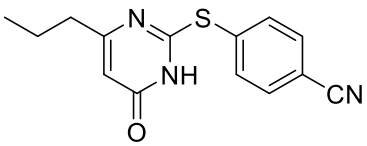
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 6.7, 2.8 Hz, 1H), 8.64 (d, *J* = 7.6 Hz, 1H), 8.53 – 8.47 (m, 1H), 7.84 – 7.79 (m, 1H), 7.78 (s, 1H), 7.70 – 7.65 (m, 2H), 7.64 – 7.56 (m, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.53 – 1.46 (m, 2H), 1.26 (s, 16H), 0.89 (t, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 132.9, 131.9, 131.3, 130.6, 129.4, 127.8, 127.3, 126.9, 126.9, 126.8, 126.4, 125.6, 123.0, 122.6, 33.8, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0, 22.7, 14.2.

IR ($cm^{-1}$): 3059, 2924, 2849, 1716, 1580, 1459, 1365, 941, 753.

HRMS (ESI) m/z calcd for $C_{26}H_{34}SNa^+$ $(M+Na)^+$ 401.2273, found 401.2270

**(5ab) 4-((6-oxo-4-propyl-1,6-dihydropyrimidin-2-yl)thio)benzonitrile (CAS: 1019608-50-4)**



4-((6-oxo-4-propyl-1,6-dihydropyrimidin-2-yl)thio)benzonitrile
Chemical Formula: $C_{14}H_{13}N_3OS$
Exact Mass: 271.0779
Molecular Weight: 271.3380

Following the General Procedure B with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), propylthiouracil (102.1 mg, 0.6 mmol), **5ab** was obtained as white solid (43.2 mg, 53%).

Following the General Procedure B with 4-iodobenzonitrile (68.8 mg, 0.3 mmol), propylthiouracil (102.1 mg, 0.6 mmol), **5ab** was obtained as white solid (40.7 mg, 50%).

This target product was purified by acidic alumina flash chromatography (DCM: EA: MeOH = 1:1:0.1).

Melting point (° C): 182.2-184.1.

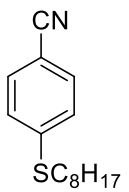
$^1$H NMR (400 MHz, $CDCl_3$) *δ* 13.02 (s, 1H), 7.77 - 7.65 (m, 4H), 6.09 (s, 1H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.60 – 1.49 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 170.0, 165.5, 158.2, 135.2, 133.3, 132.6, 118.1, 113.4, 108.9, 39.3, 20.8, 13.5.

IR ($cm^{-1}$): 2971, 2933, 2227, 1653, 1541, 1173, 975, 834, 533.

HRMS (ESI) m/z calcd for $C_{14}H_{14}N_3OS^+$ $(M+H)^+$ 272.0852, found 272.0856.

**(5ac) 4-(octylthio)benzonitrile (CAS: 153199-19-0)[18]**



4-(octylthio)benzonitrile
Chemical Formula: $C_{15}H_{21}NS$
Exact Mass: 247.13947
Molecular Weight: 247.40000

Following the General Procedure B with 4-bromobenzonitrile (54.6 mg, 0.3 mmol), octane-1-thiol (85.6 mg, 0.6 mmol), **5ac** was obtained as colorless oil (57.9 mg, 78%).

This target product was purified by acidic alumina flash chromatography (PE: EA = 100:1).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 3.02 – 2.92 (m, 2H), 1.73 – 1.64 (m, 2H), 1.49 – 1.40 (m, 2H), 1.28 (s, 8H), 0.89 (t, *J* = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.4, 132.2, 126.6, 119.0, 107.9,

31.9, 31.8, 29.1, 29.1, 28.9, 28.6, 22.6, 14.1.

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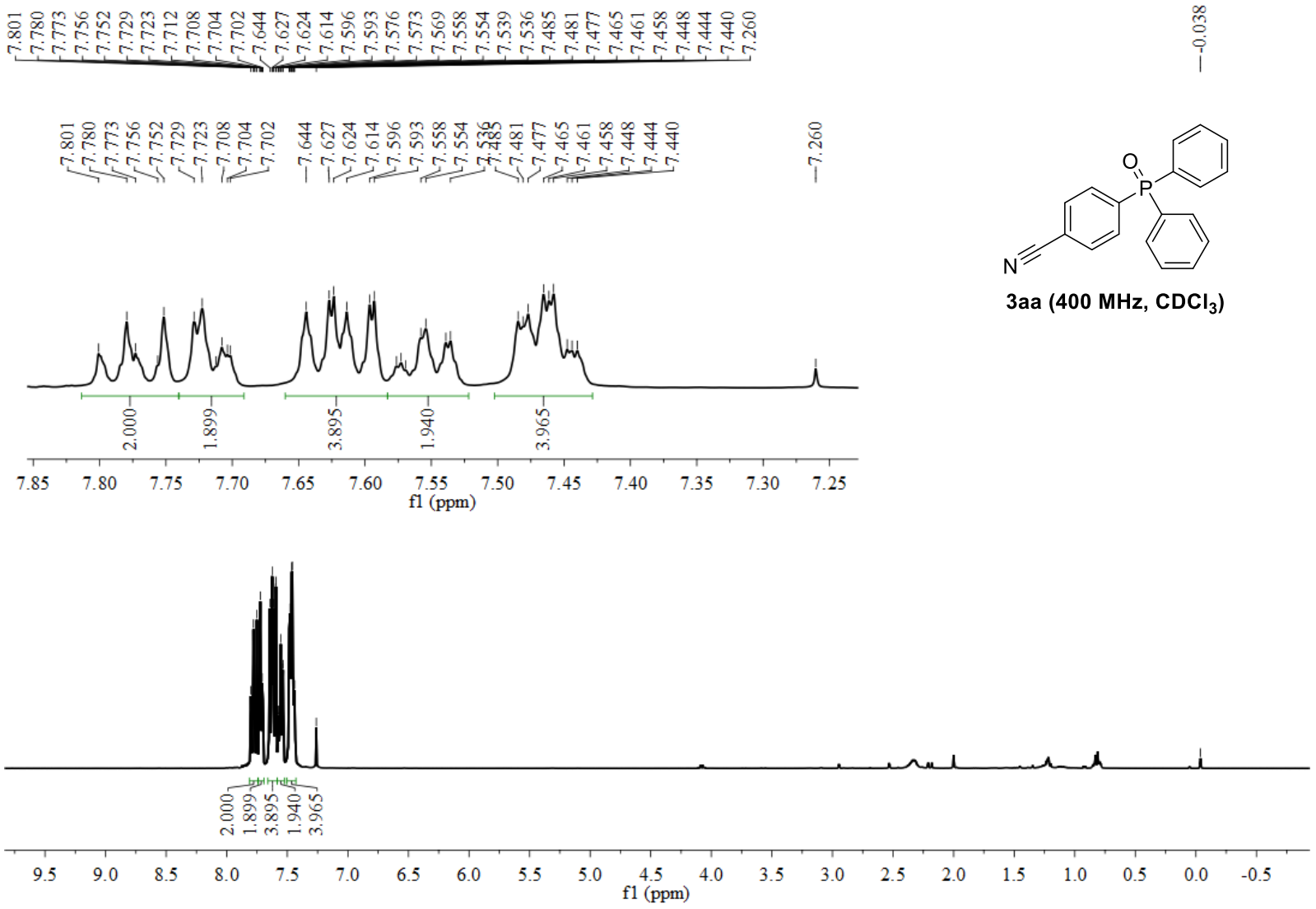
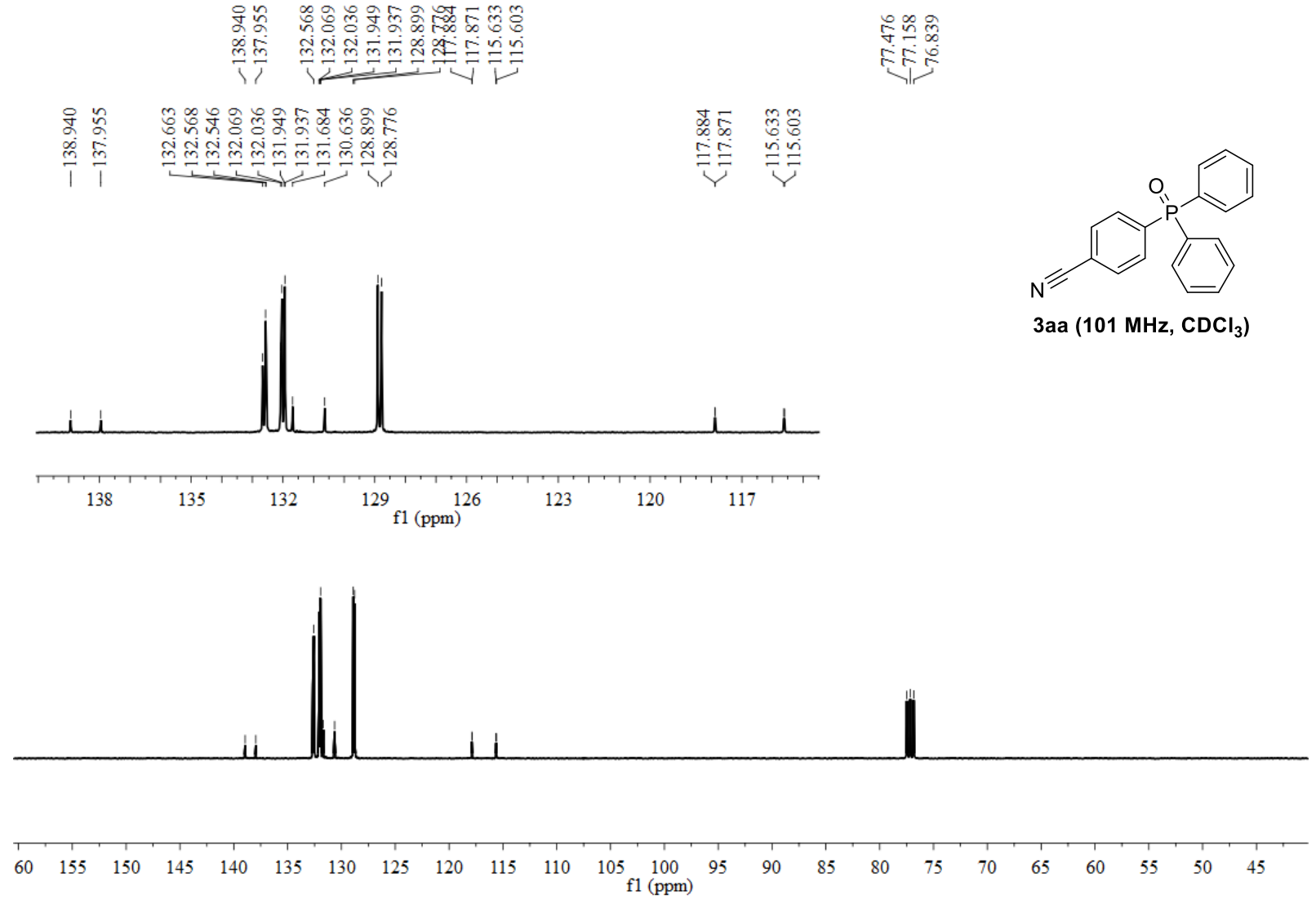
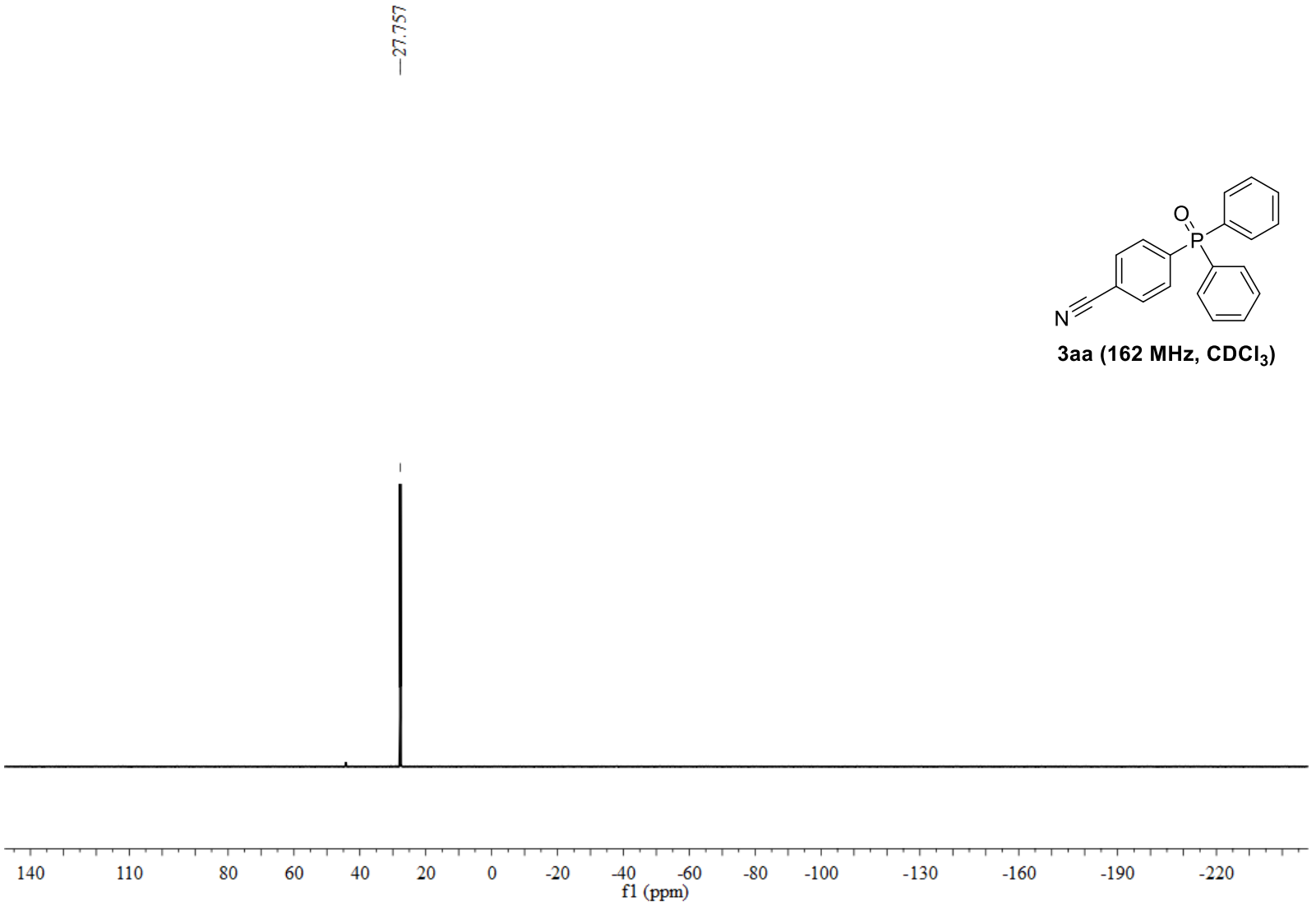
## 9. Copies of NMR spectra




**3aa (400 MHz, $CDCl_3$)**




**3aa (101 MHz, $CDCl_3$)**

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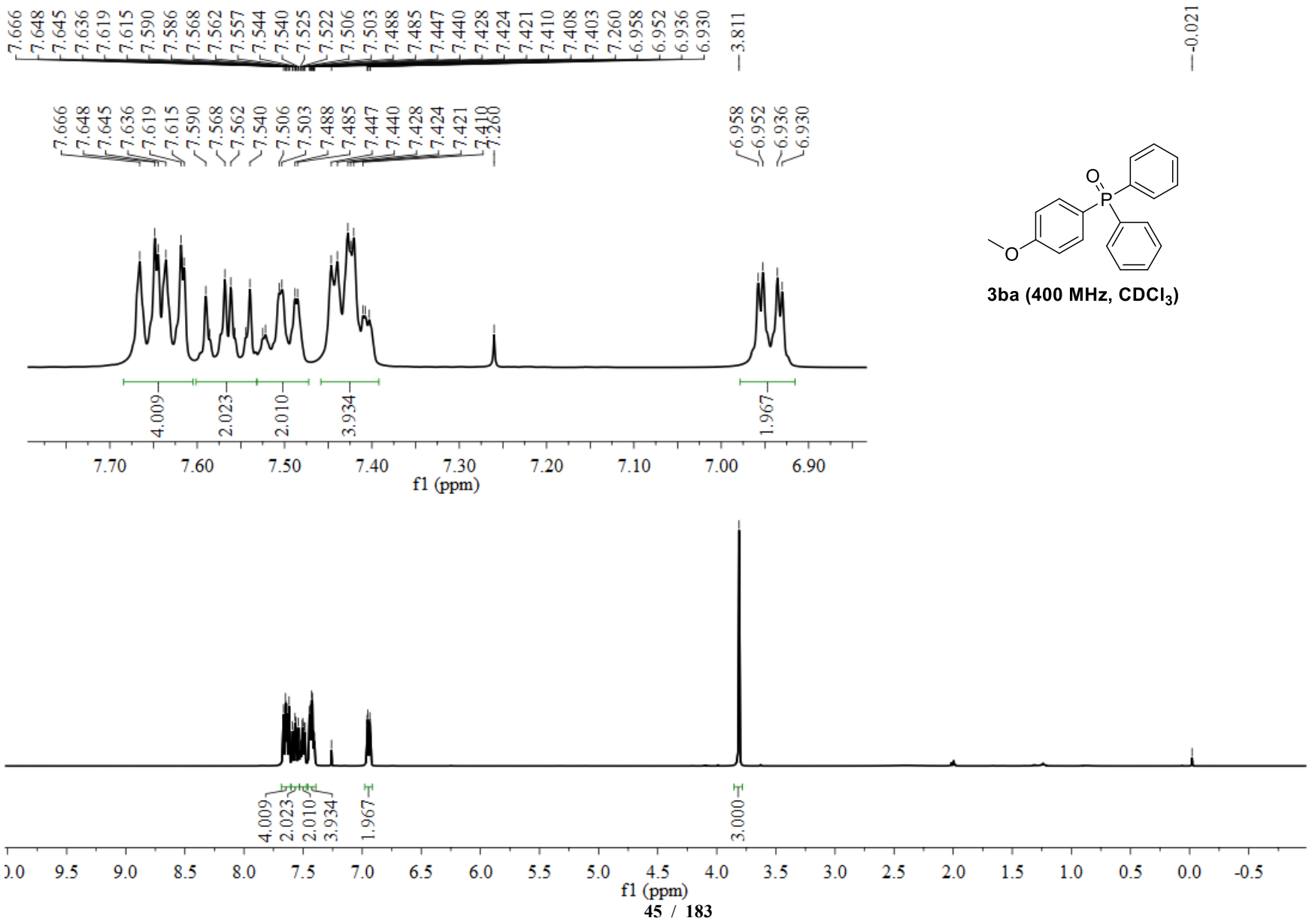




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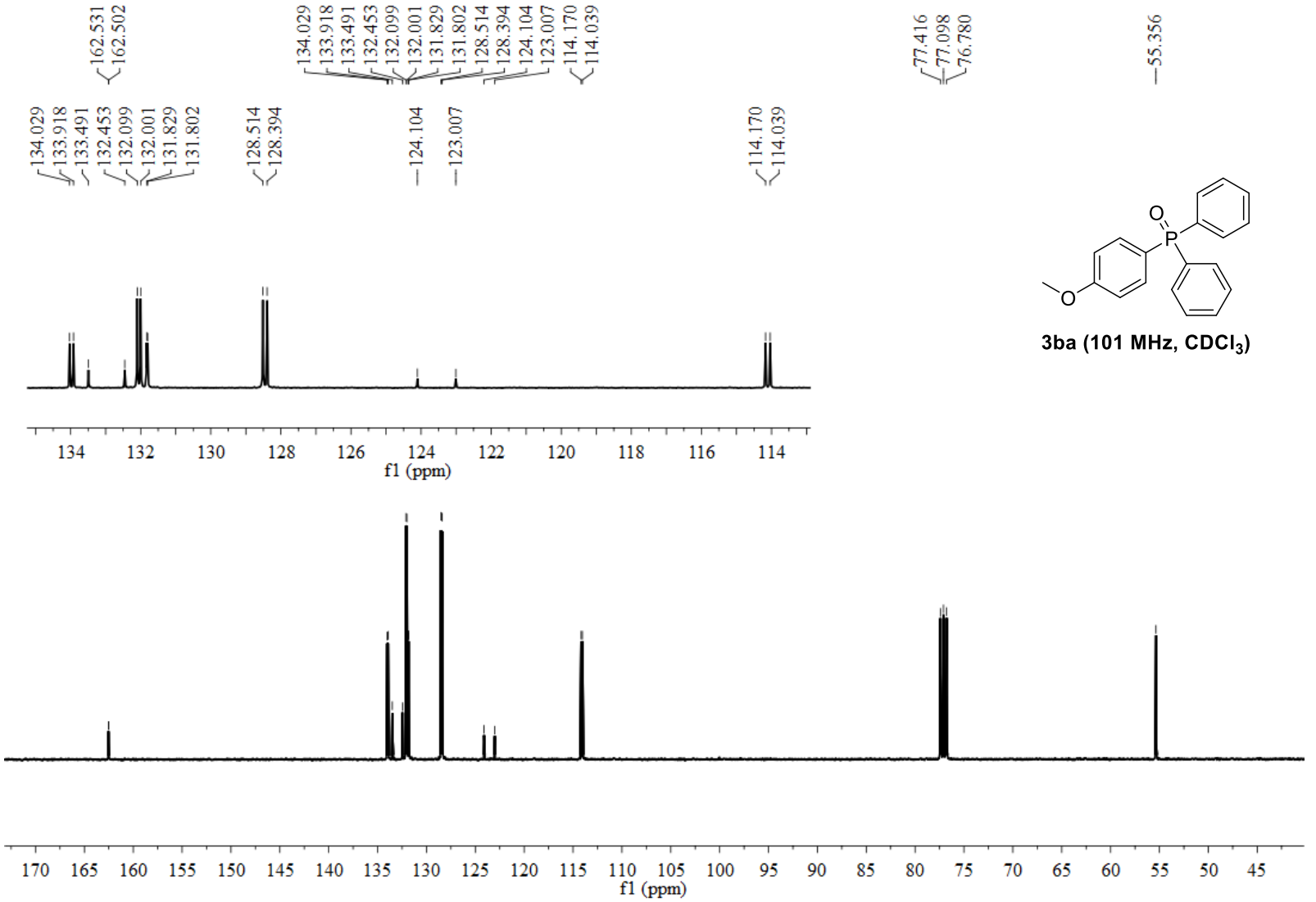
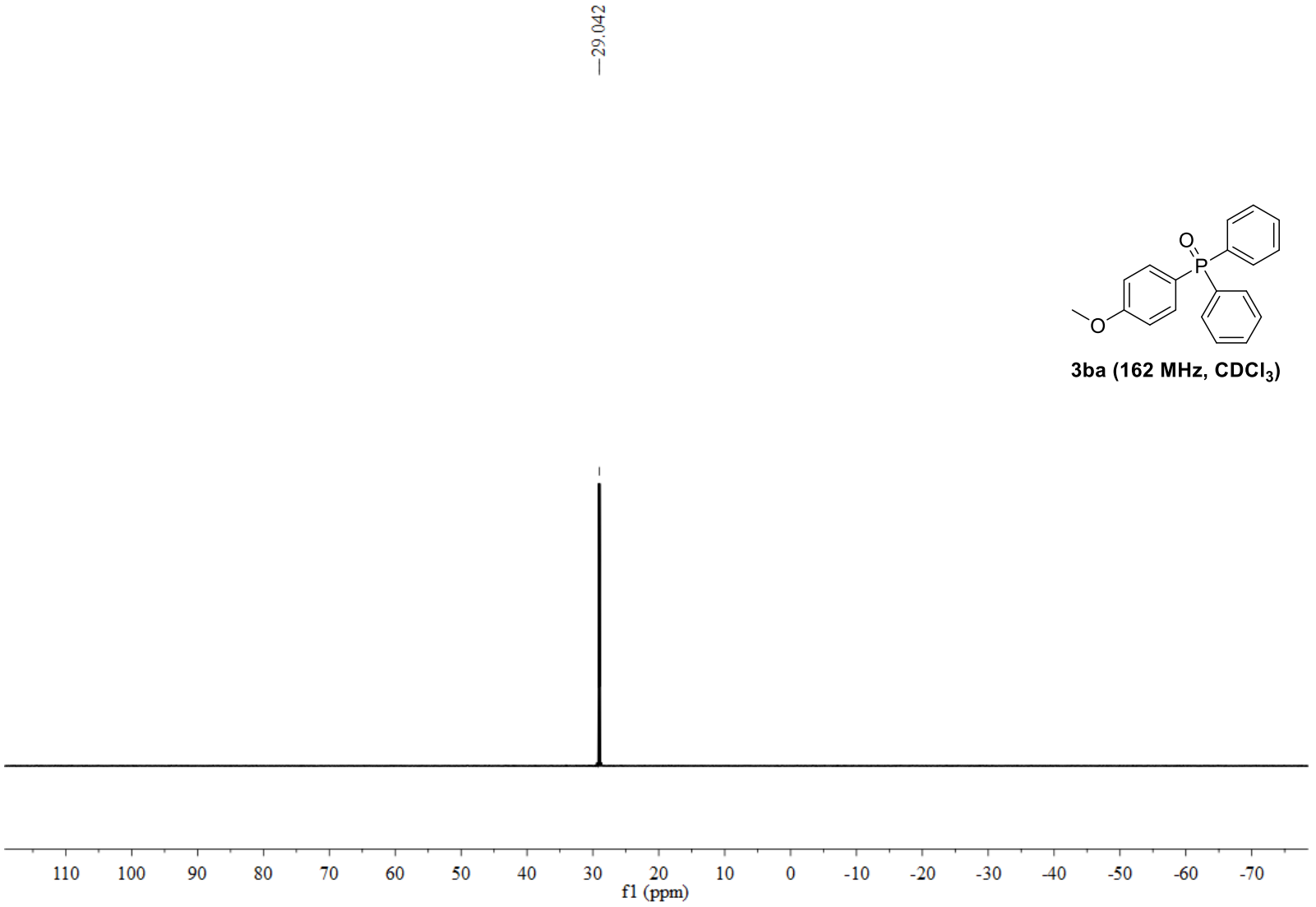
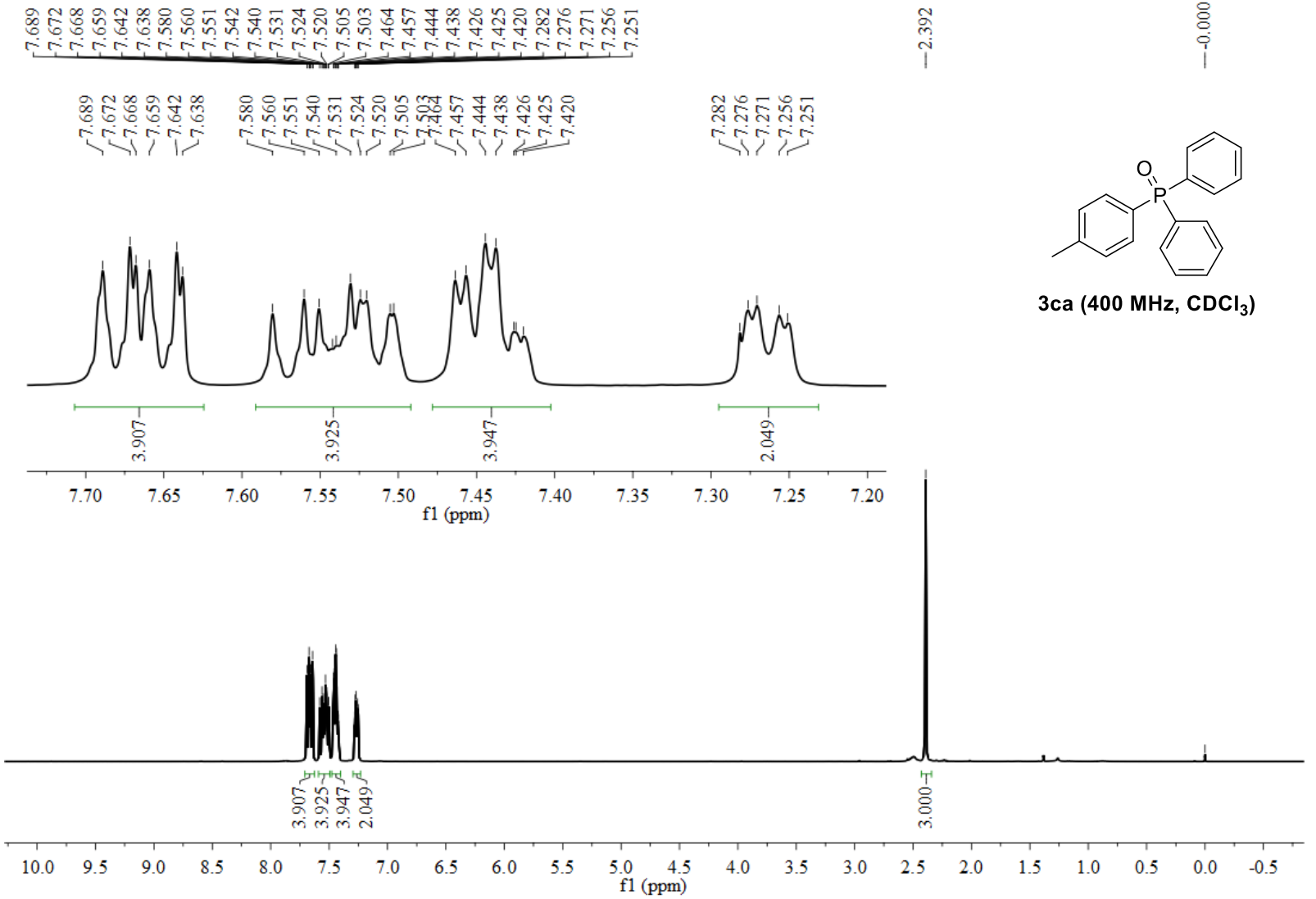
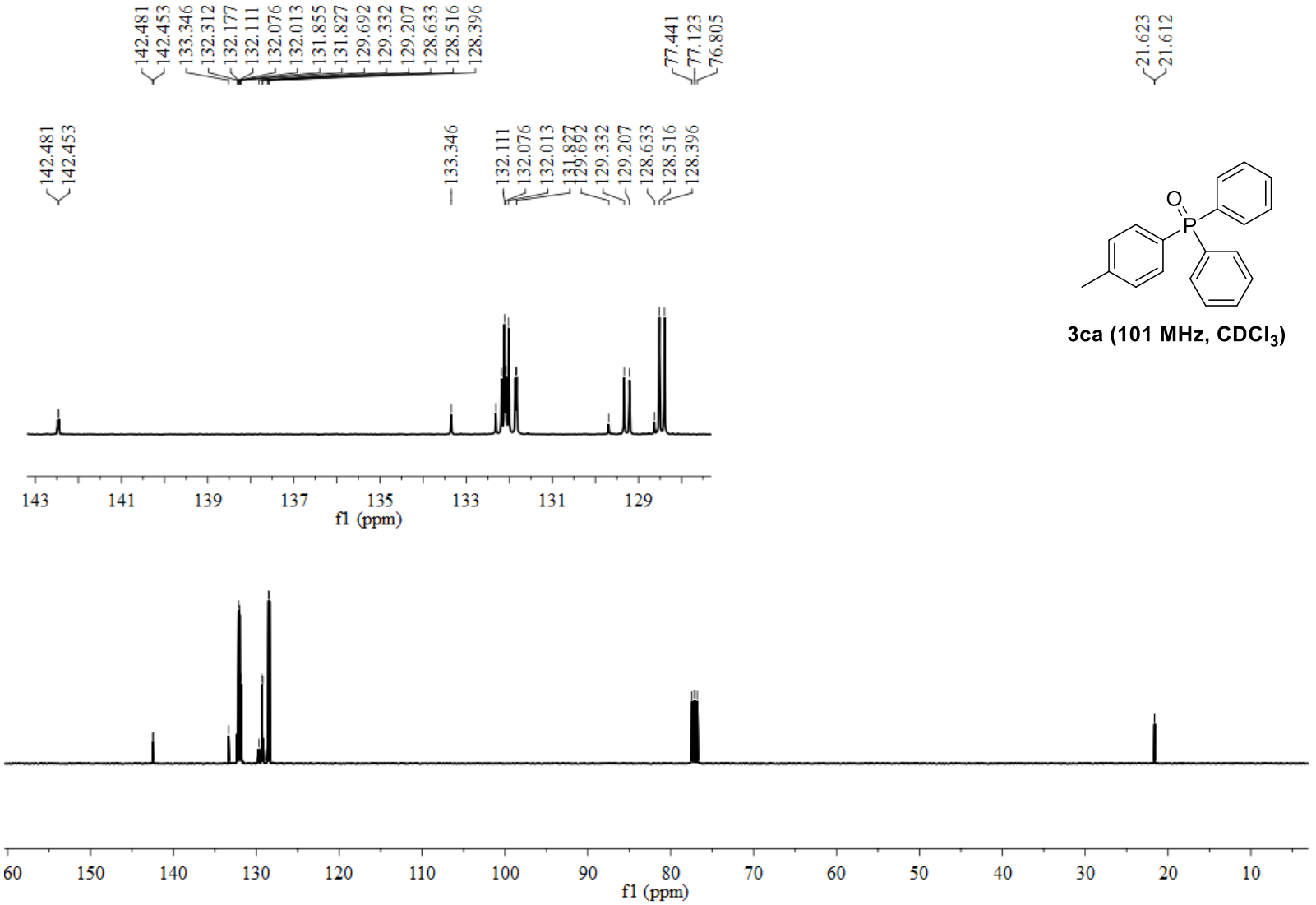



**3ba (101 MHz, $CDCl_3$)**

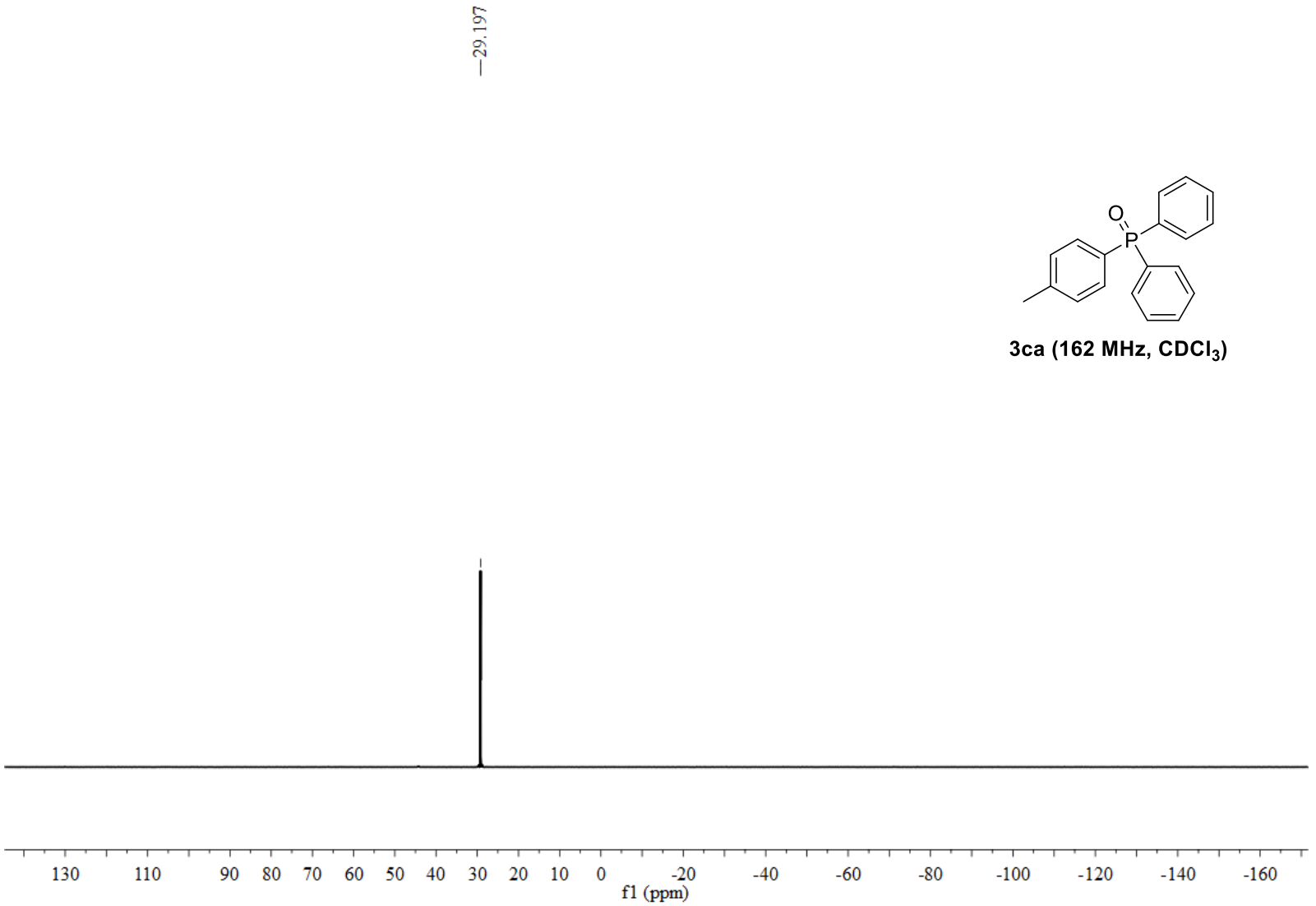



**3ba (162 MHz, $CDCl_3$)**


7.689
7.672
7.668
7.659
7.642
7.638
7.580
7.560
7.551
7.542
7.540
7.531
7.524
7.520
7.505
7.503
7.464
7.457
7.444
7.438
7.426
7.425
7.420
7.282
7.276
7.271
7.256
7.251
2.392
-0.000
3.907
3.925
3.947
2.049
3.000
f1 (ppm)
O
P
3ca (400 MHz, CDCl3)



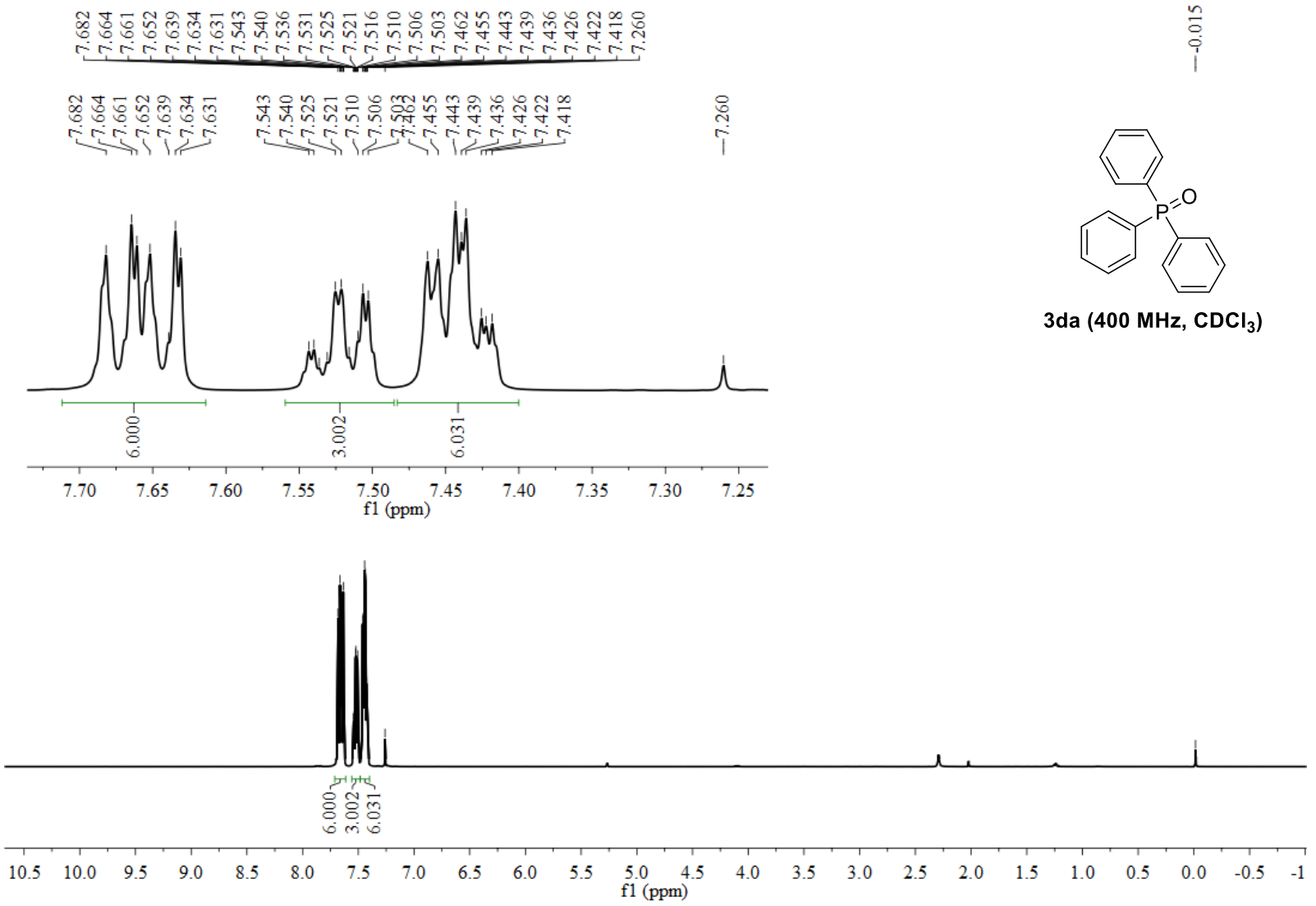

**3ca (101 MHz, $CDCl_3$)**







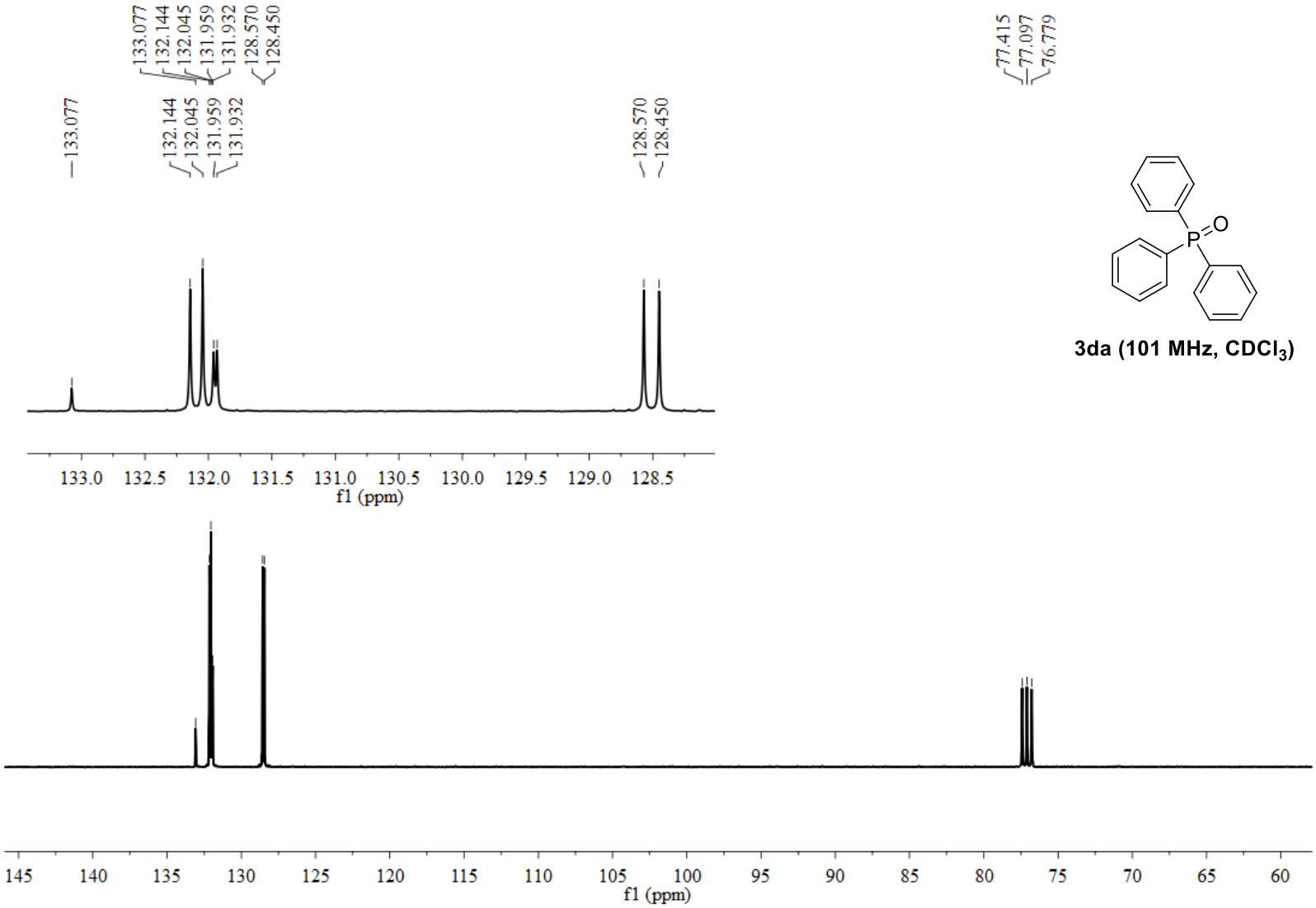
**3ca (162 MHz, $CDCl_3$)**







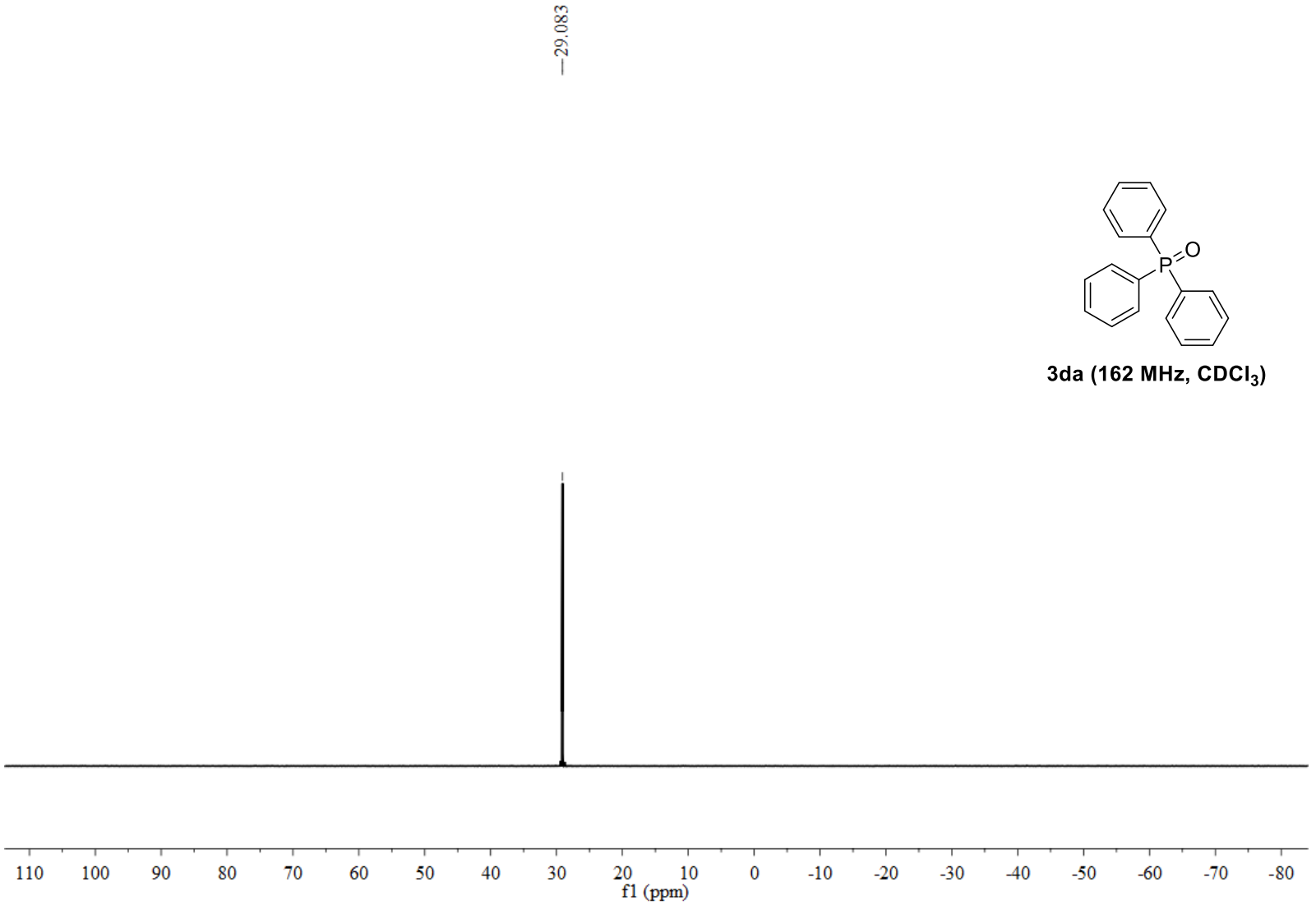
**3da (400 MHz, $CDCl_3$)**



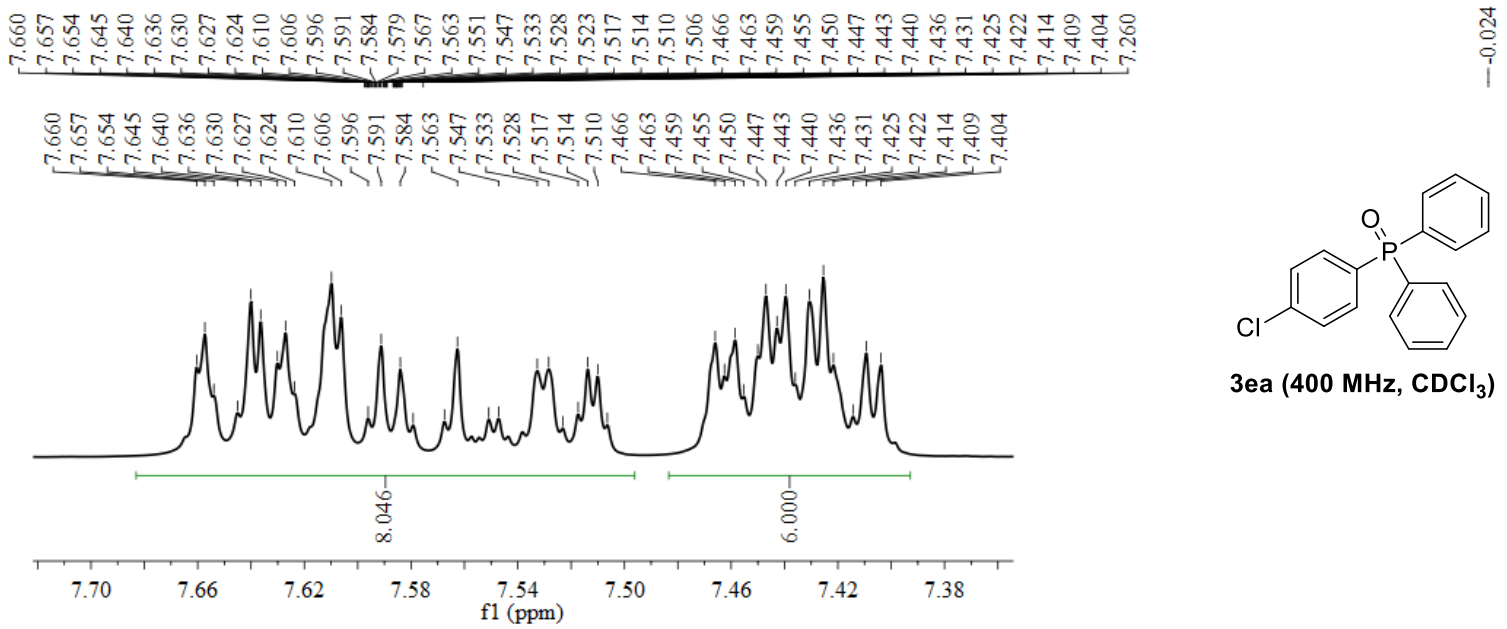




**3da (101 MHz, $CDCl_3$)**



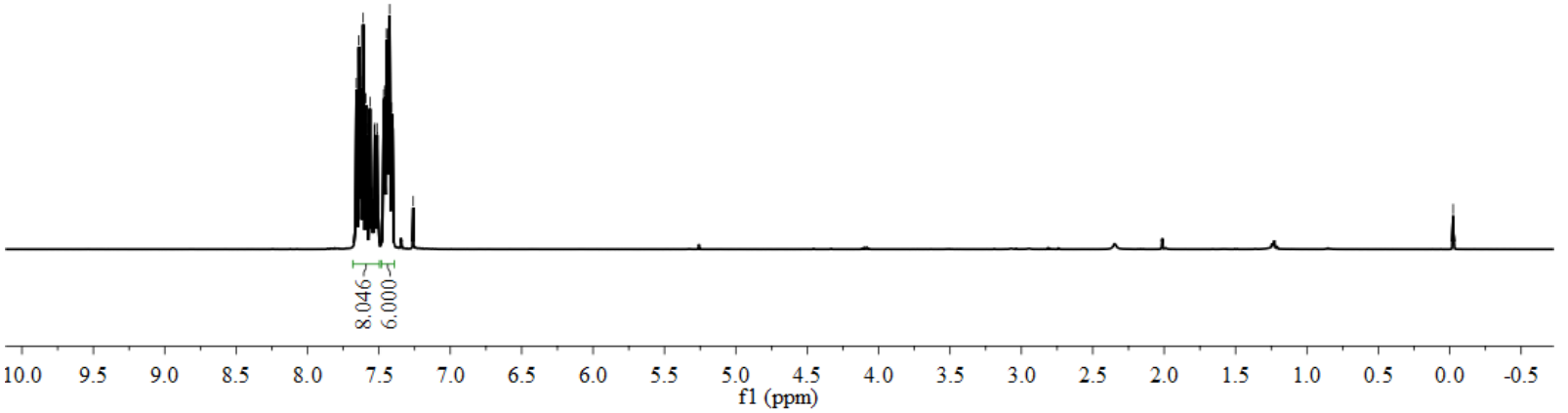

**3da (162 MHz, $CDCl_3$)**

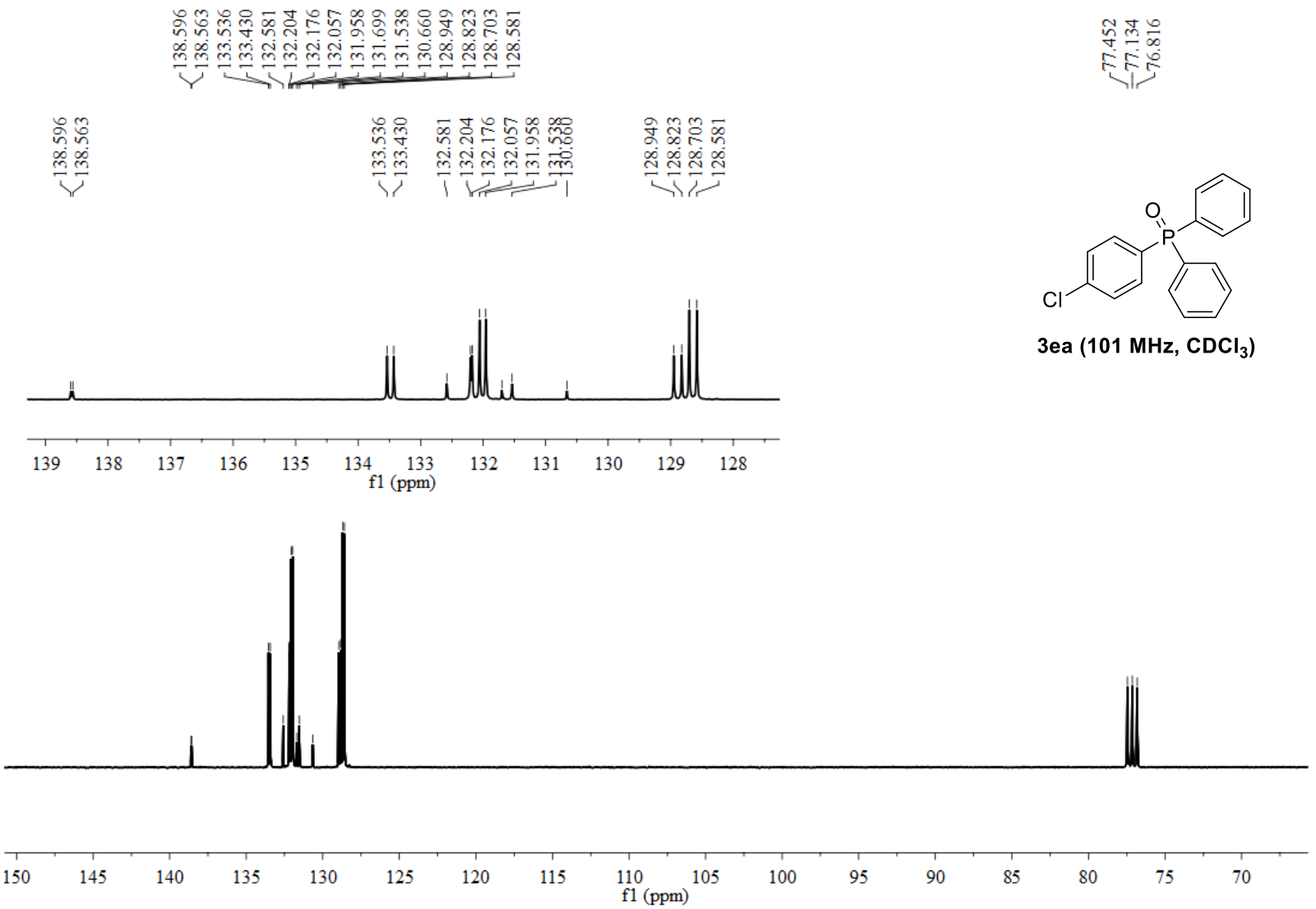




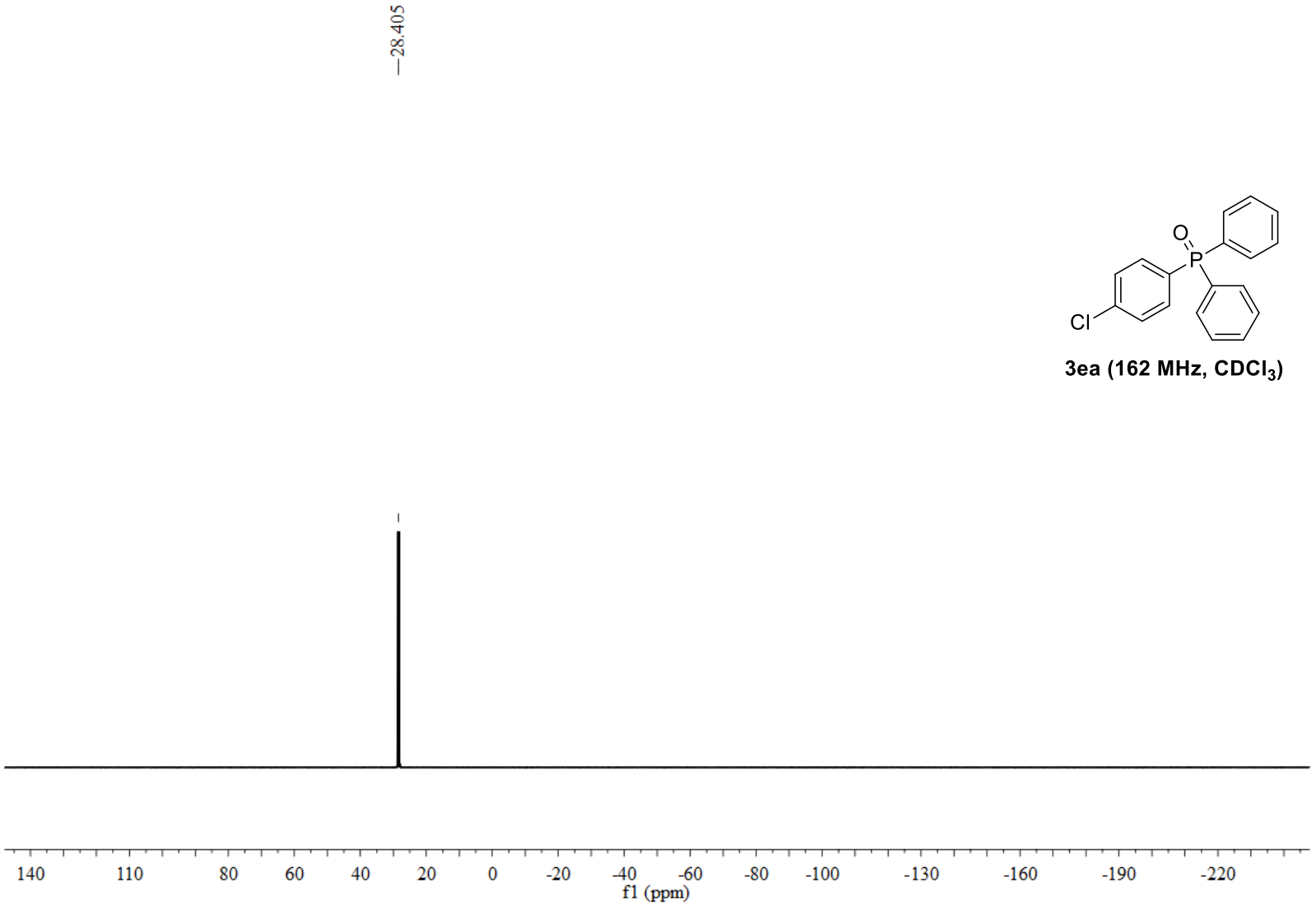


**3ea (400 MHz, $CDCl_3$)**

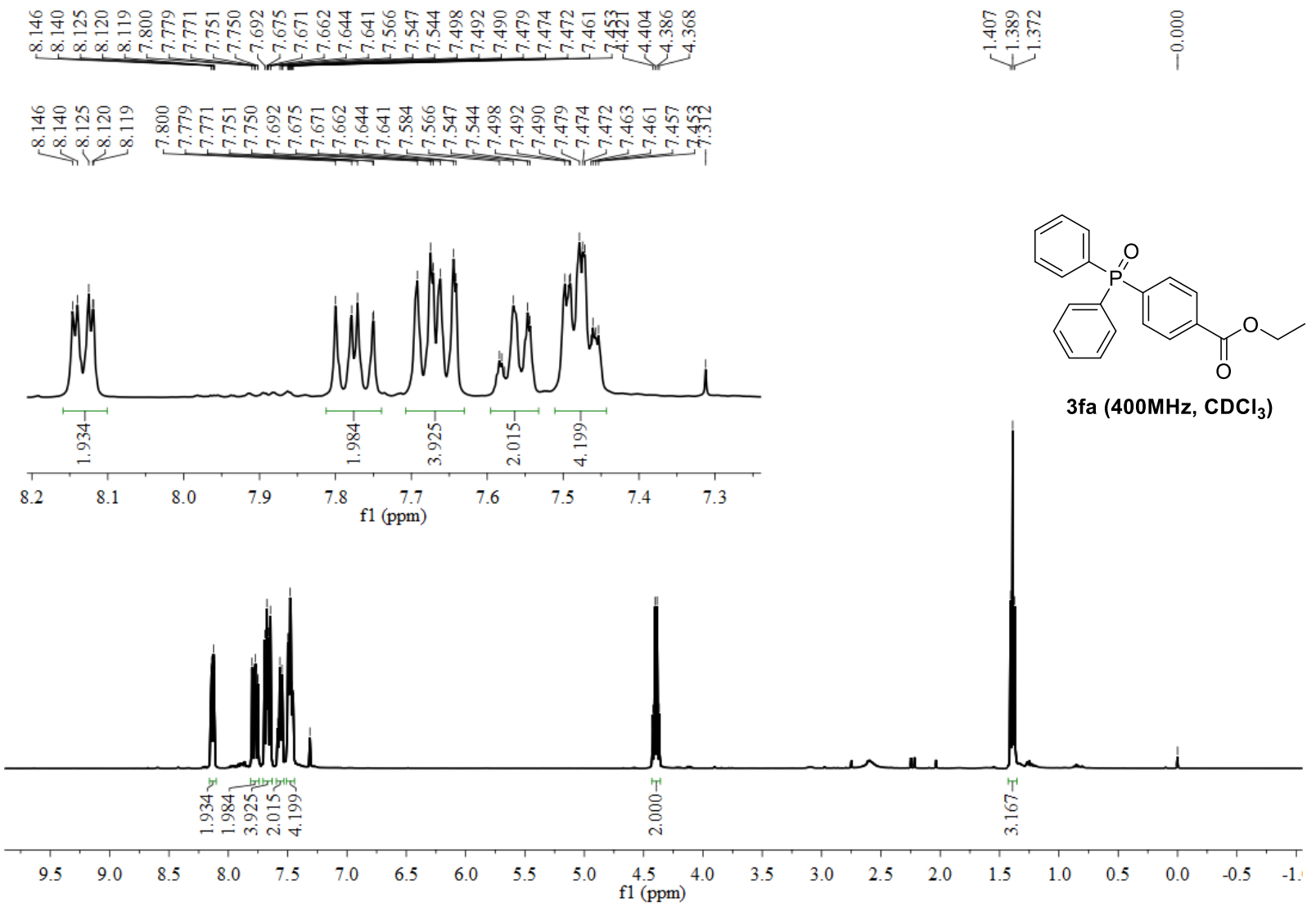





**3ea (101 MHz, $CDCl_3$)**

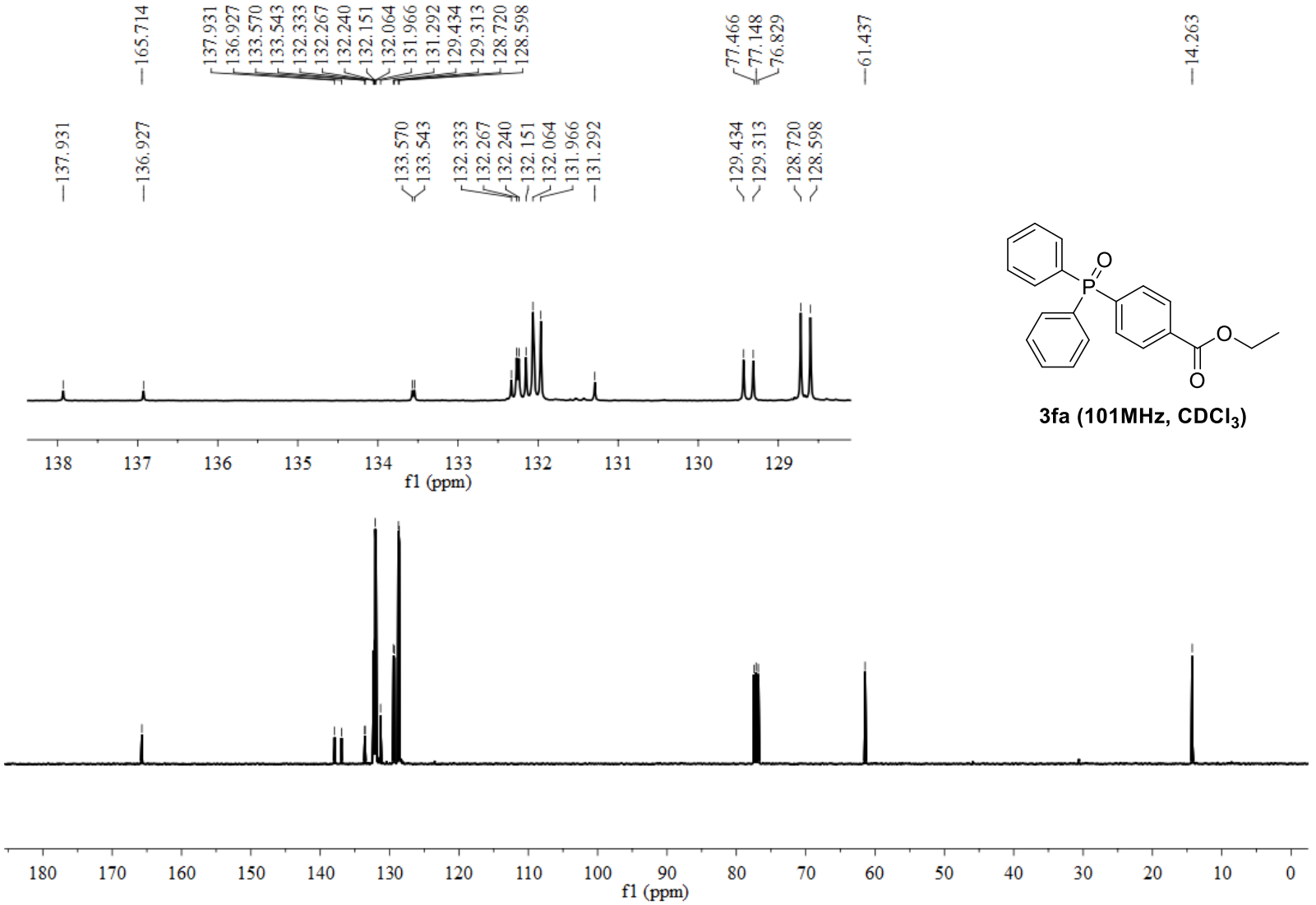



**3ea (162 MHz, $CDCl_3$)**



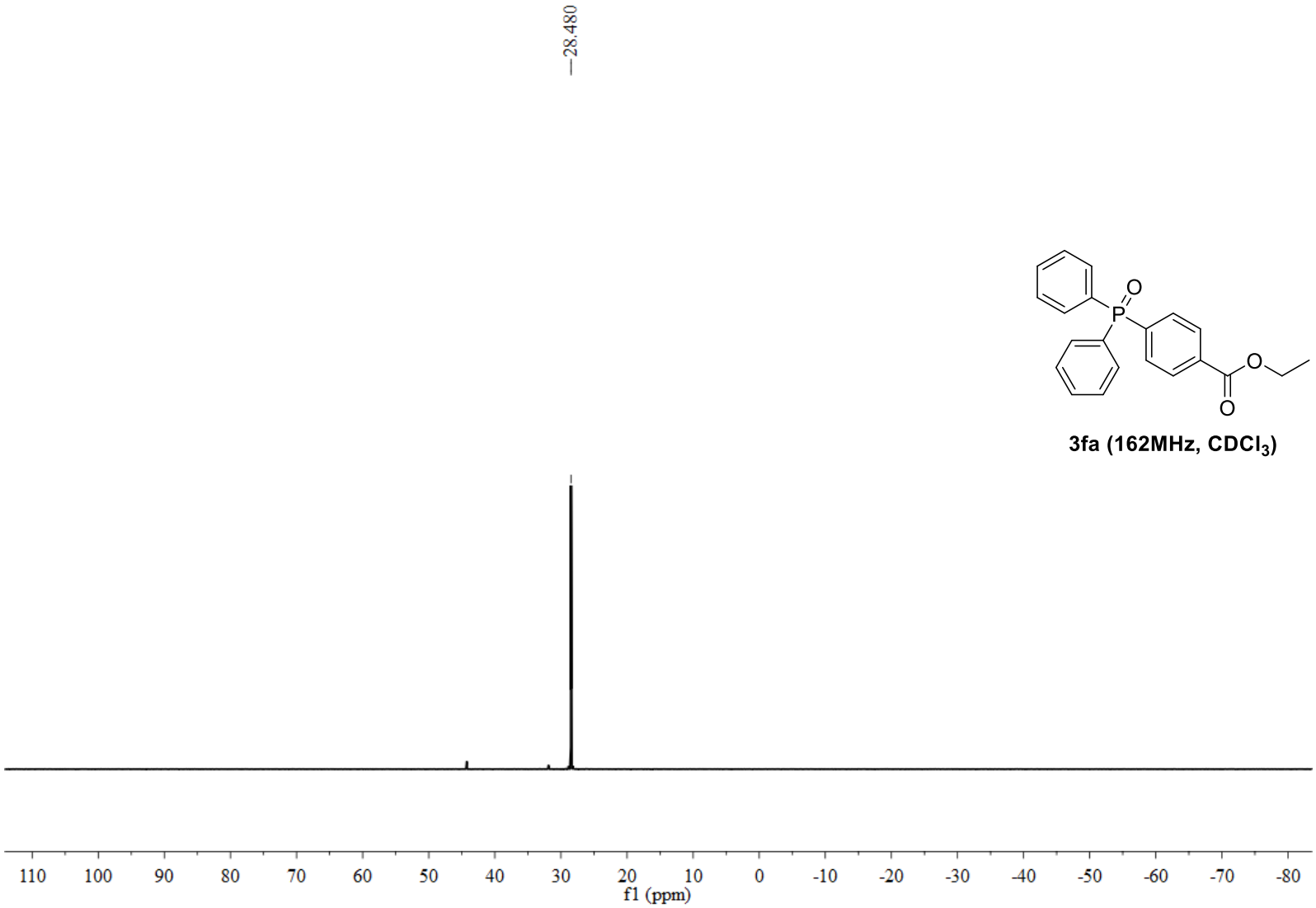



3fa (400MHz, $CDCl_3$)

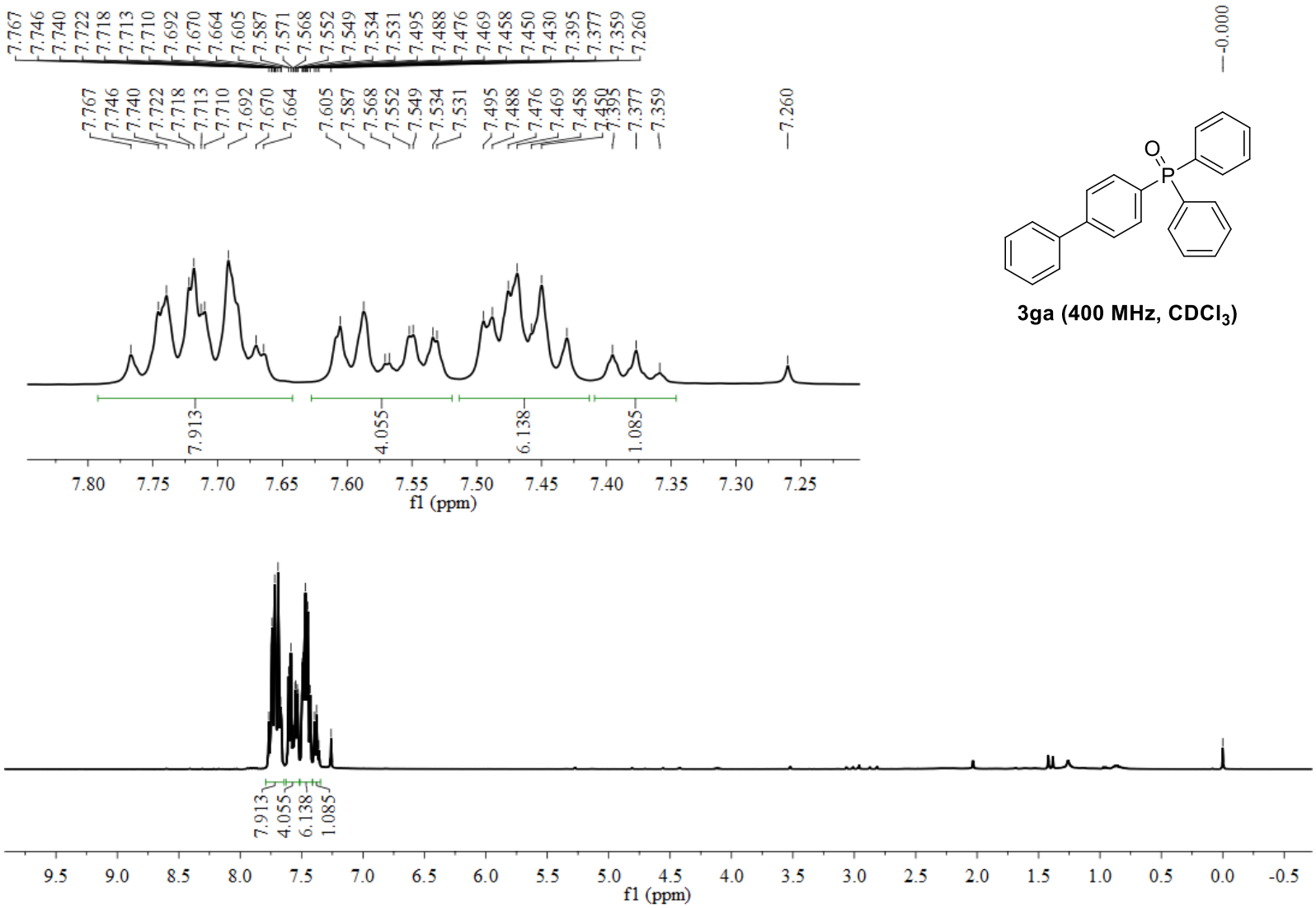





**3fa (101MHz, $CDCl_3$)**



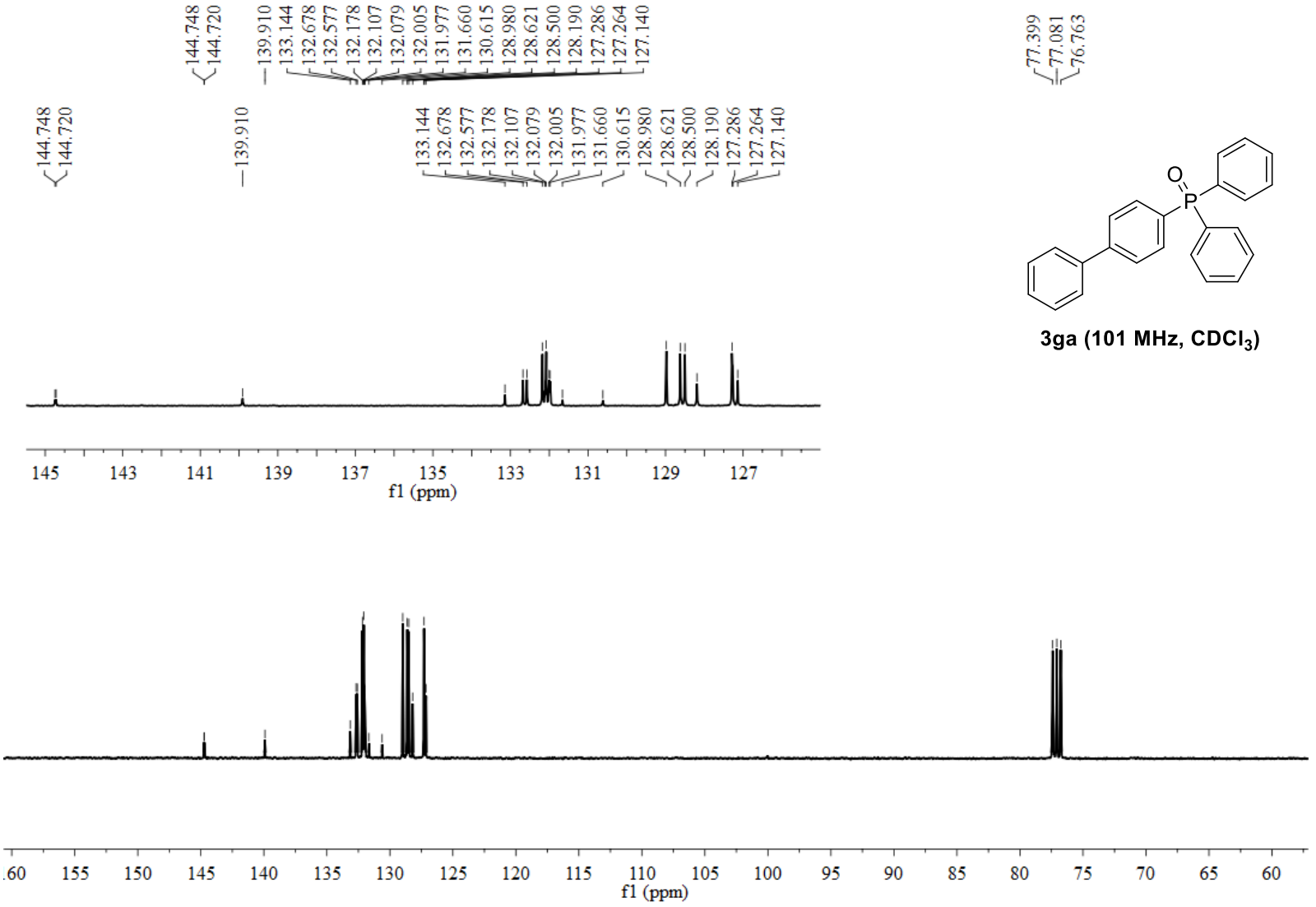

**3fa (162MHz, $CDCl_3$)**



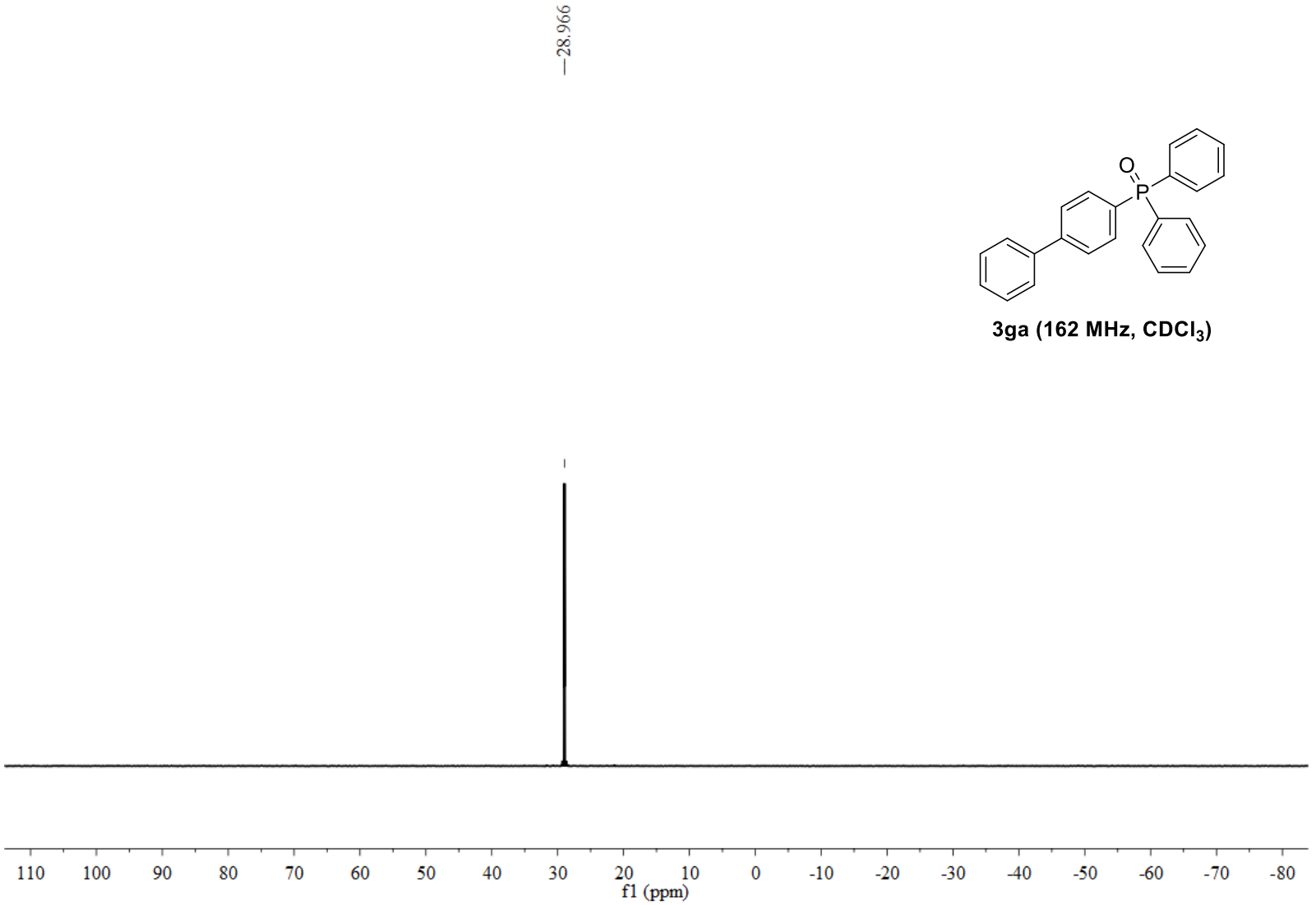




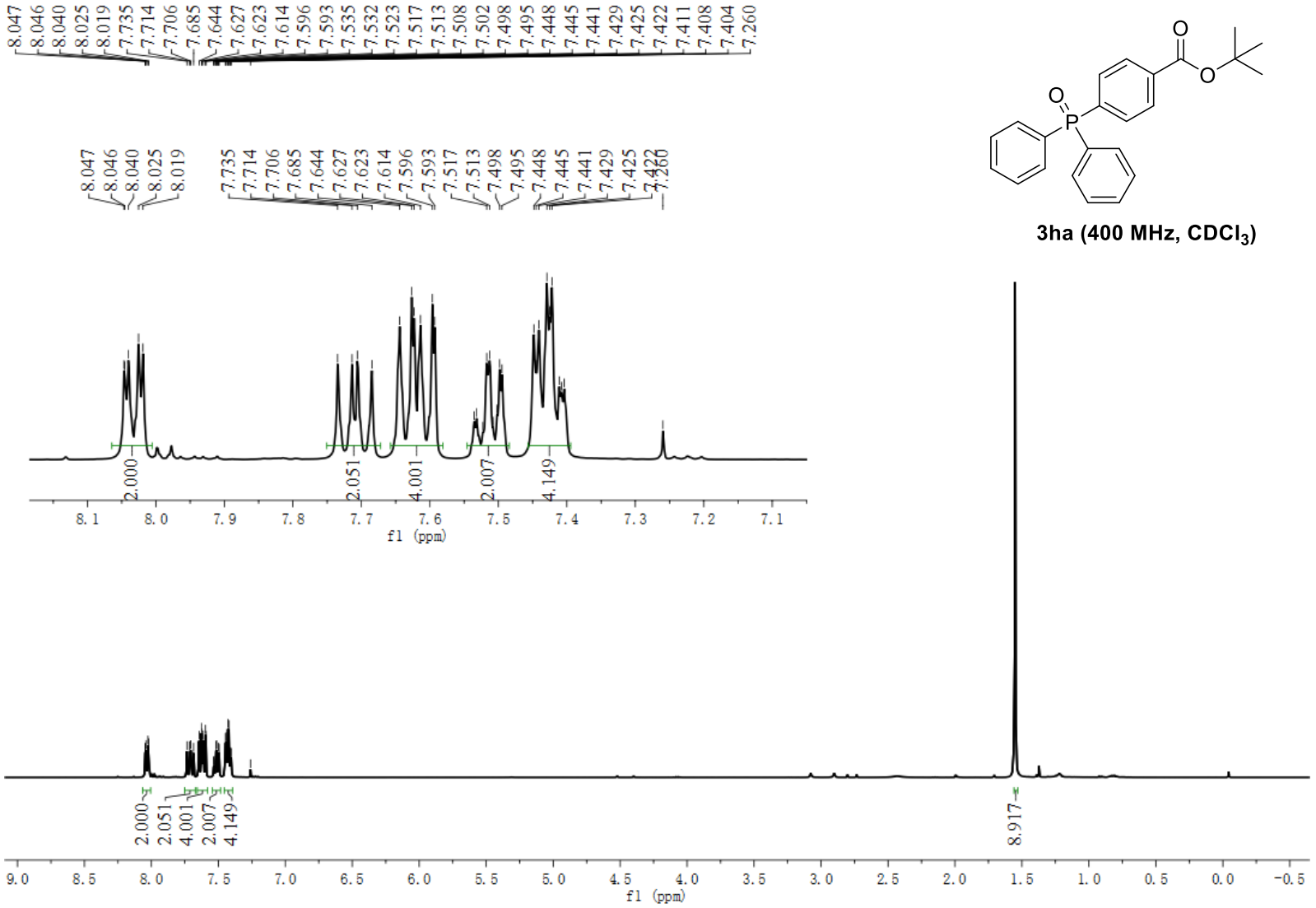
**3ga (400 MHz, $CDCl_3$)**




**3ga (101 MHz, $CDCl_3$)**

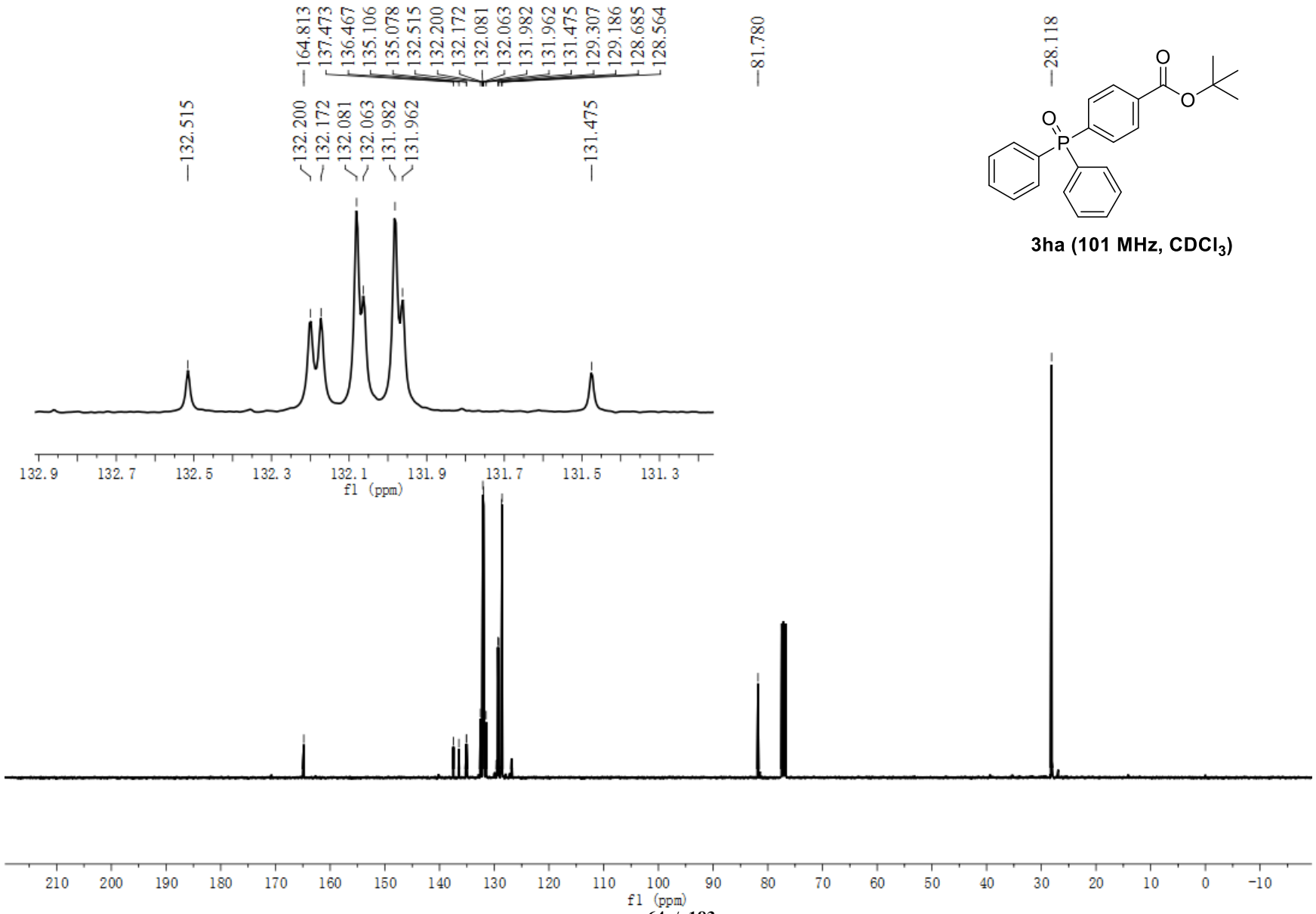



**3ga (162 MHz, $CDCl_3$)**

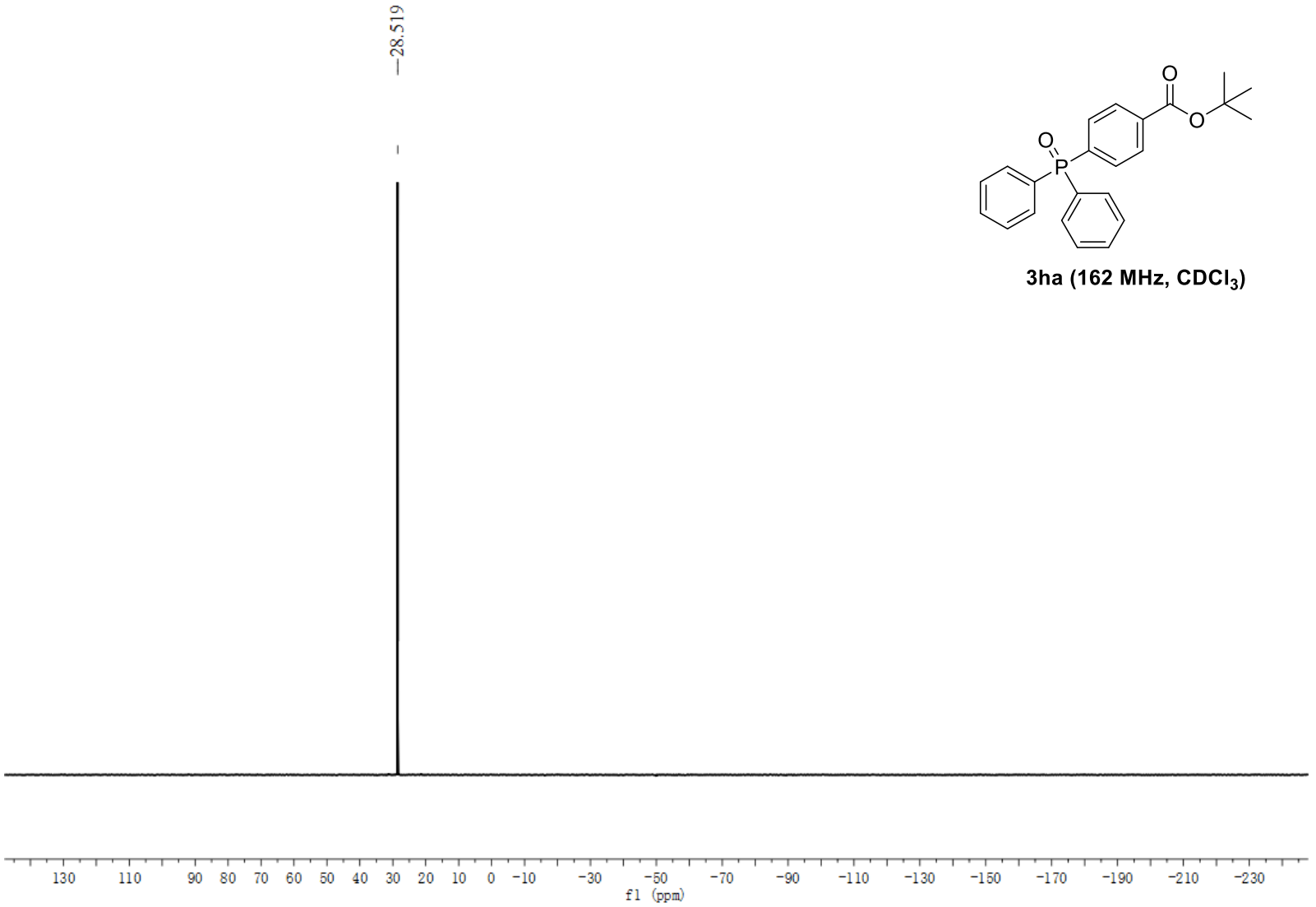





**3ha (400 MHz, $CDCl_3$)**



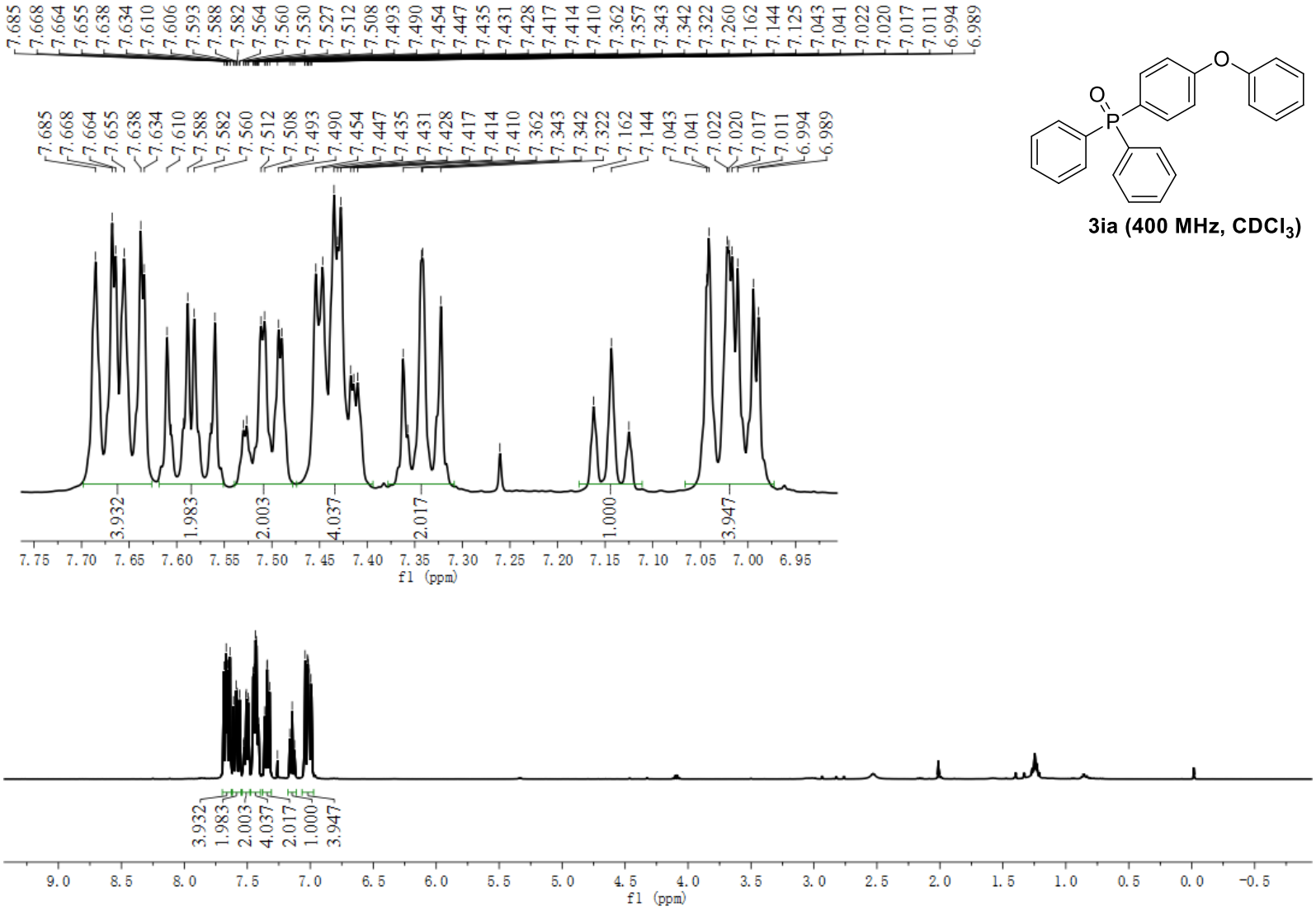

**3ha (101 MHz, $CDCl_3$)**





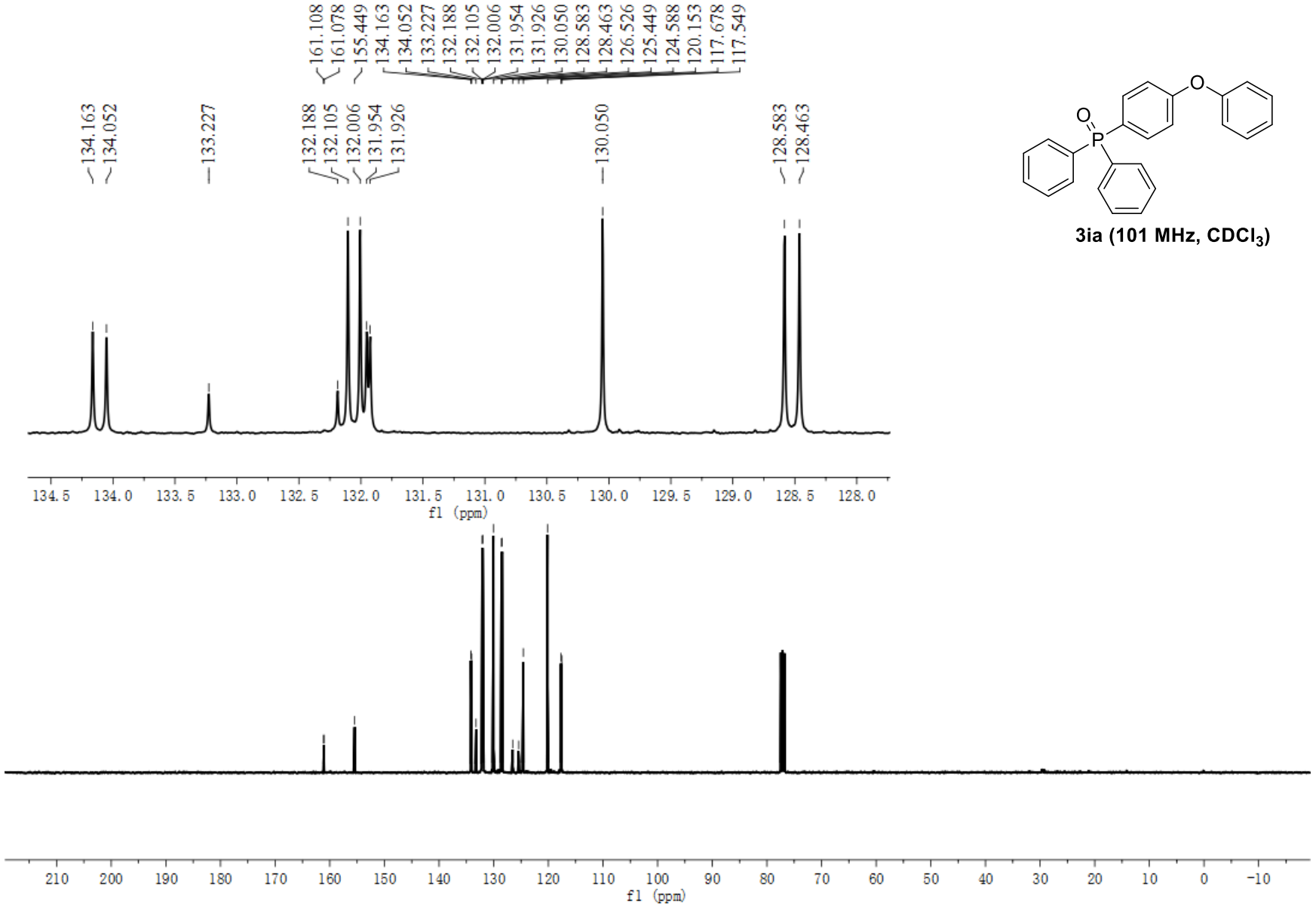


**3ha (162 MHz, $CDCl_3$)**

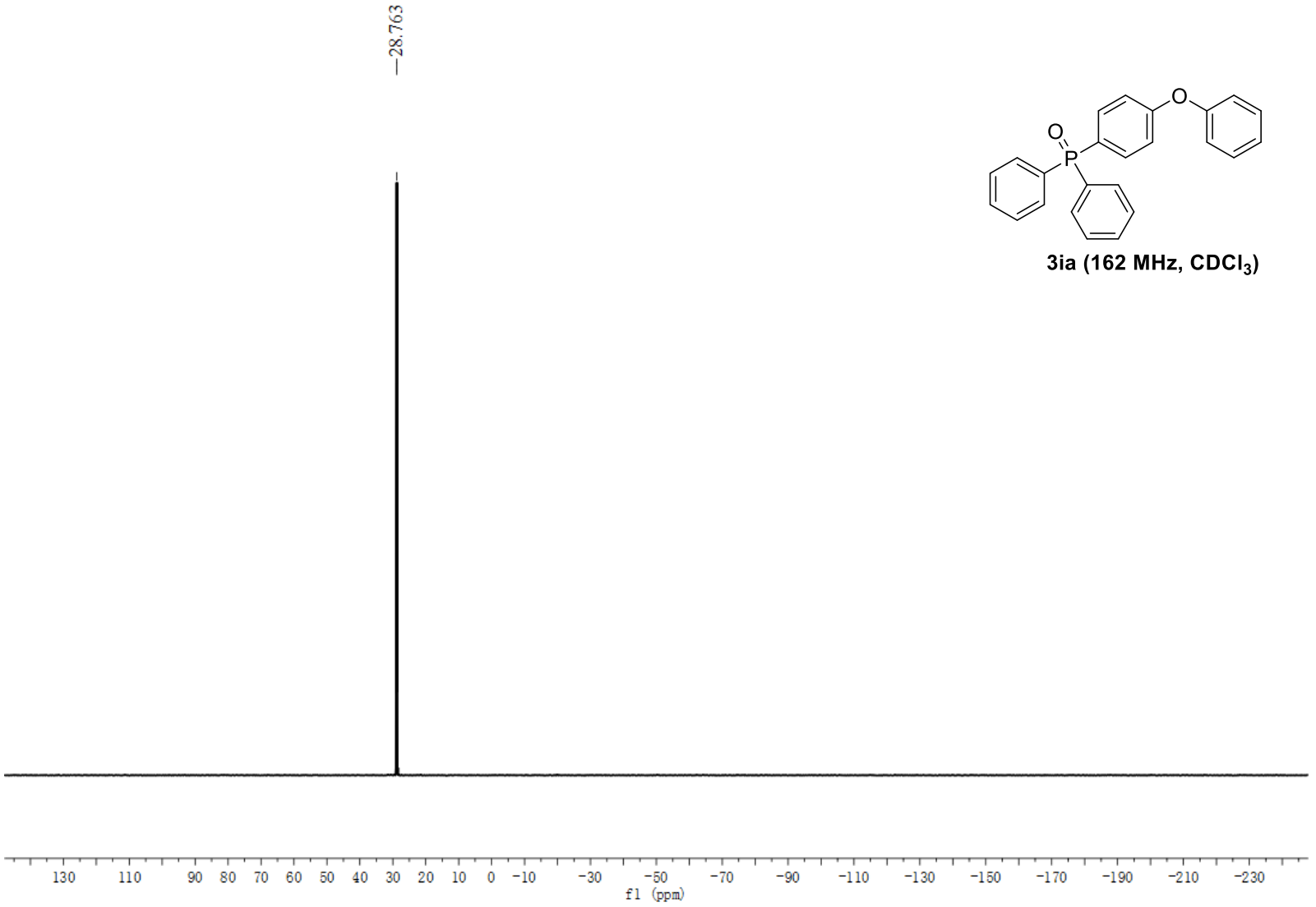




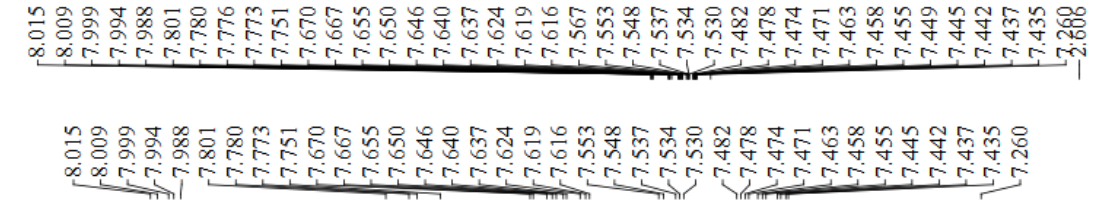

**3ia (400 MHz, $CDCl_3$)**

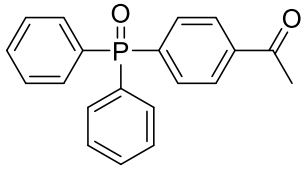



**3ia (101 MHz, $CDCl_3$)**

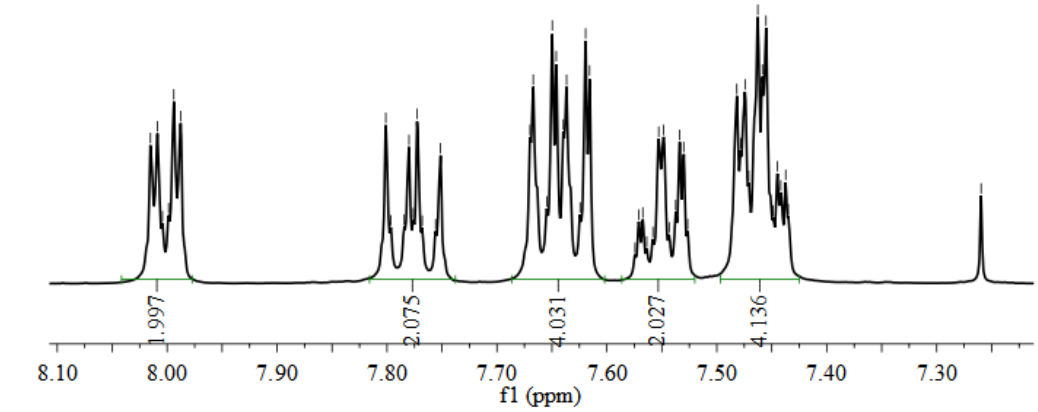


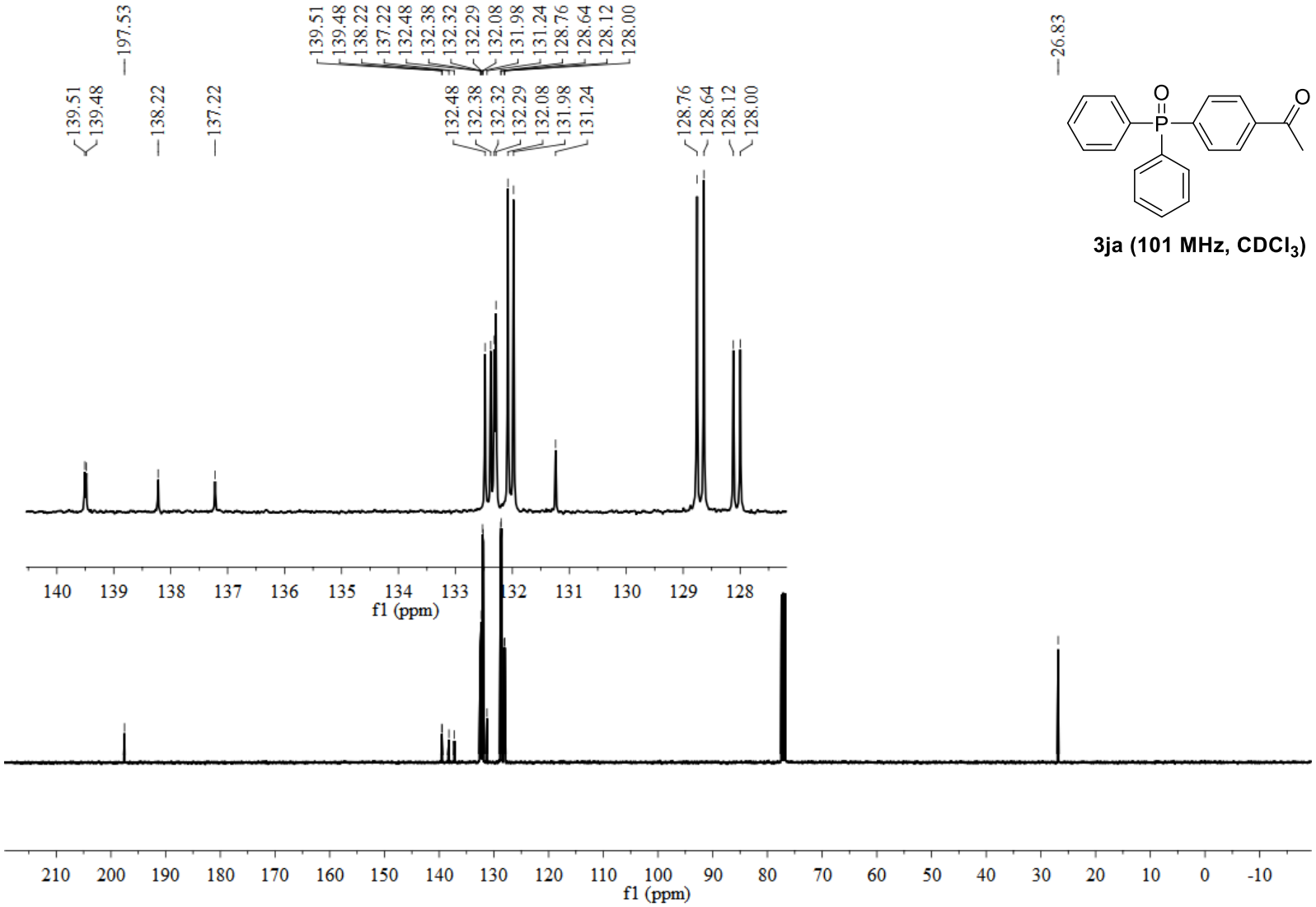

**3ia (162 MHz, $CDCl_3$)**



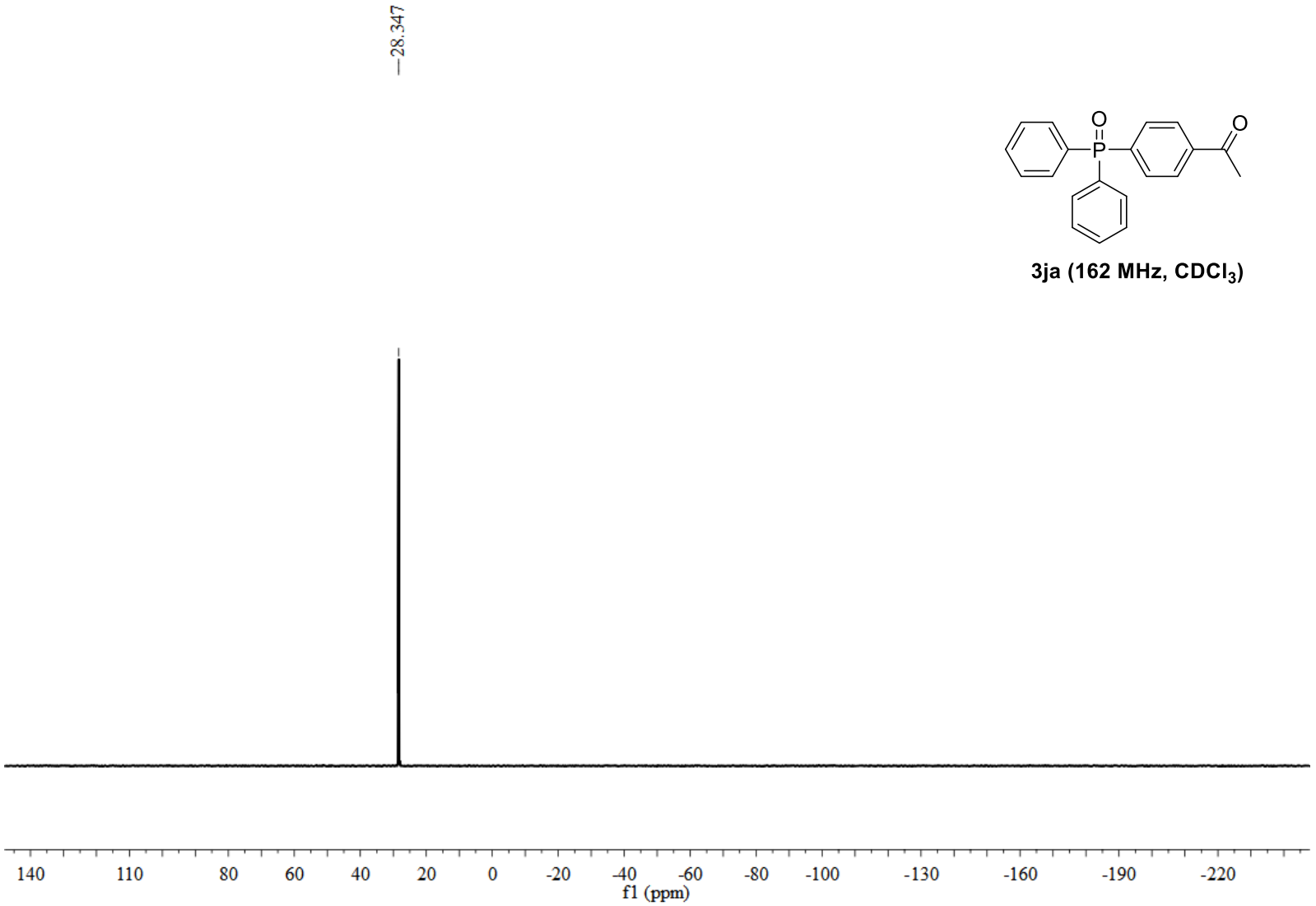



**3ja (400 MHz, $CDCl_3$)**

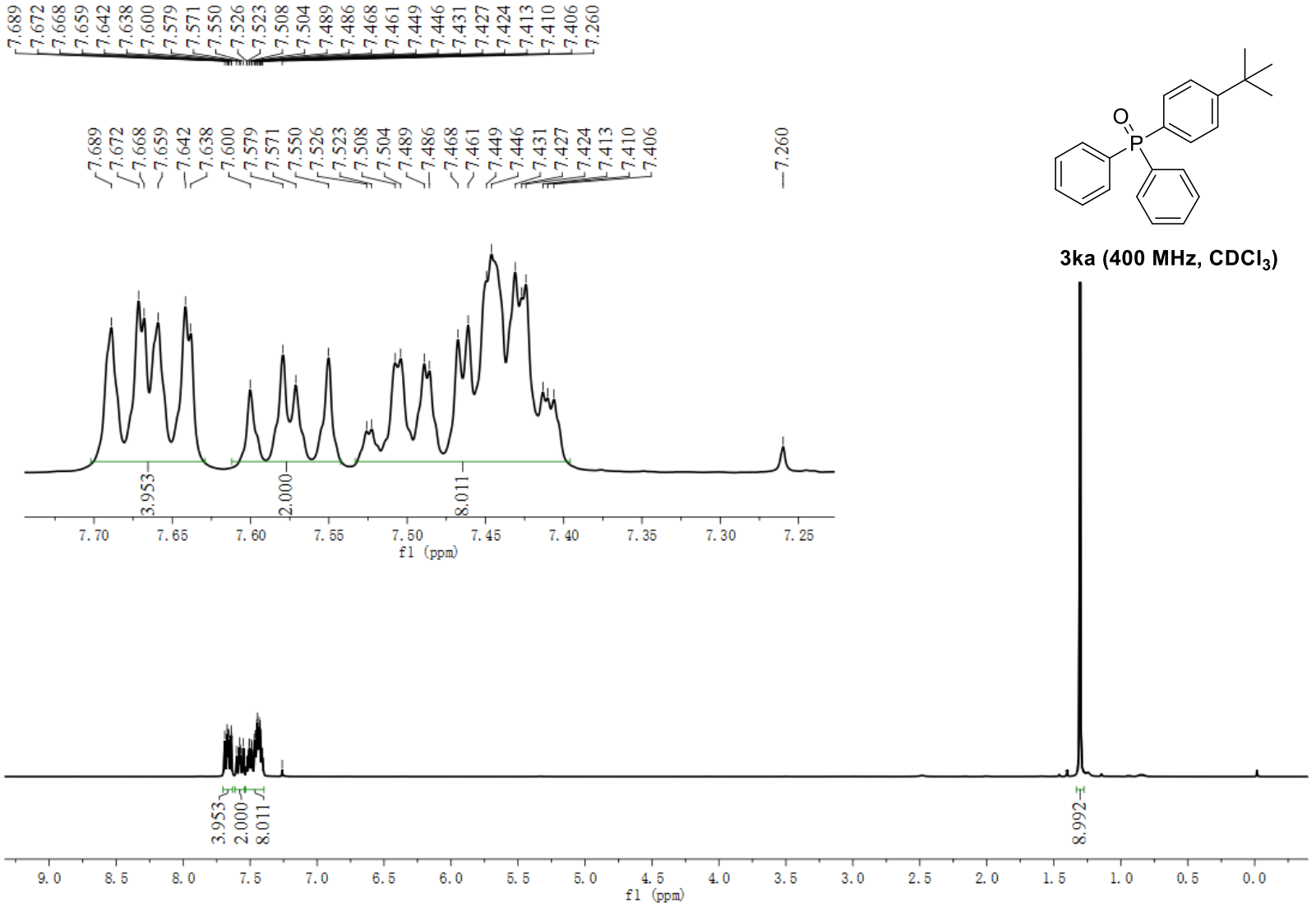


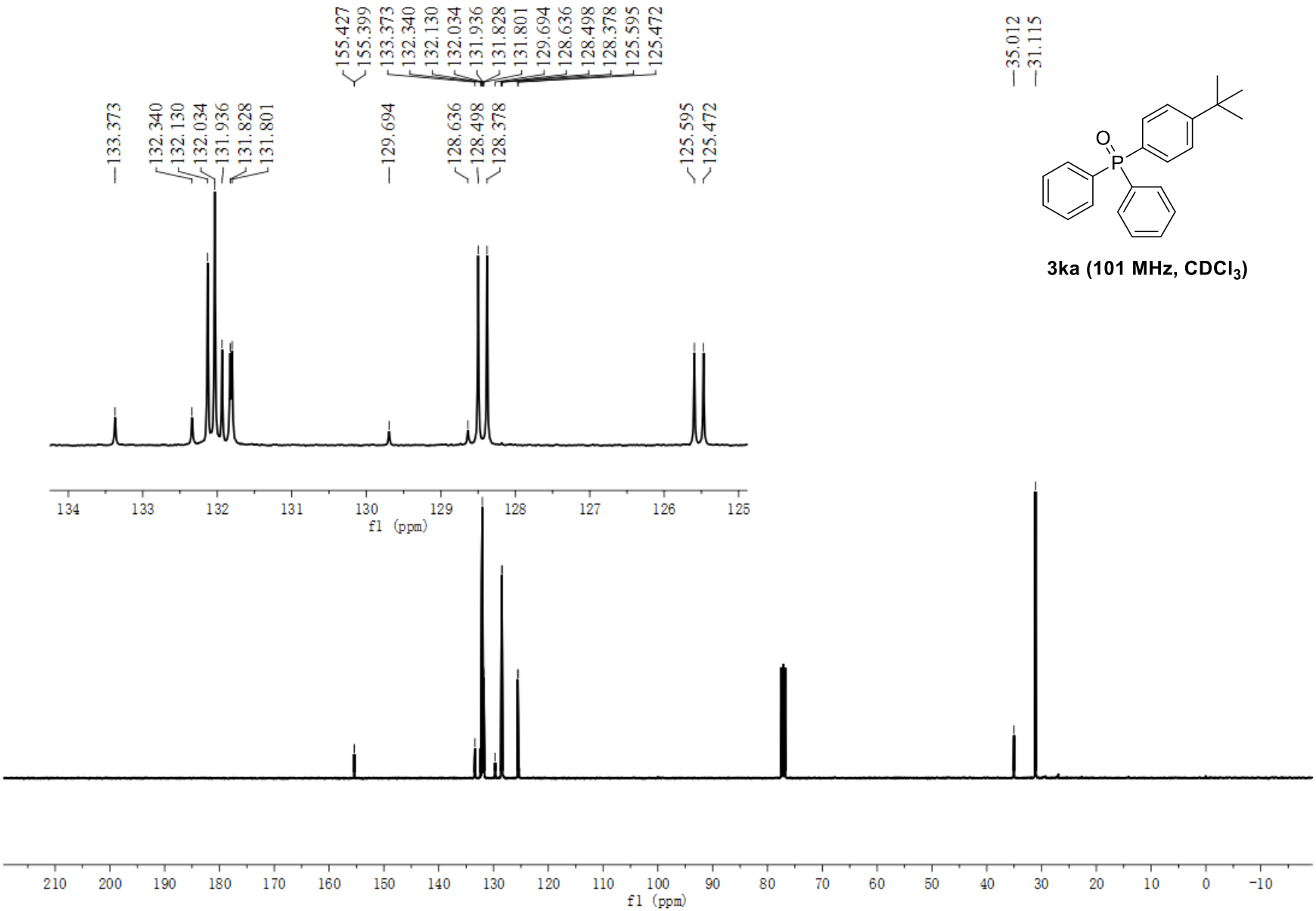



**3ja (101 MHz, $CDCl_3$)**

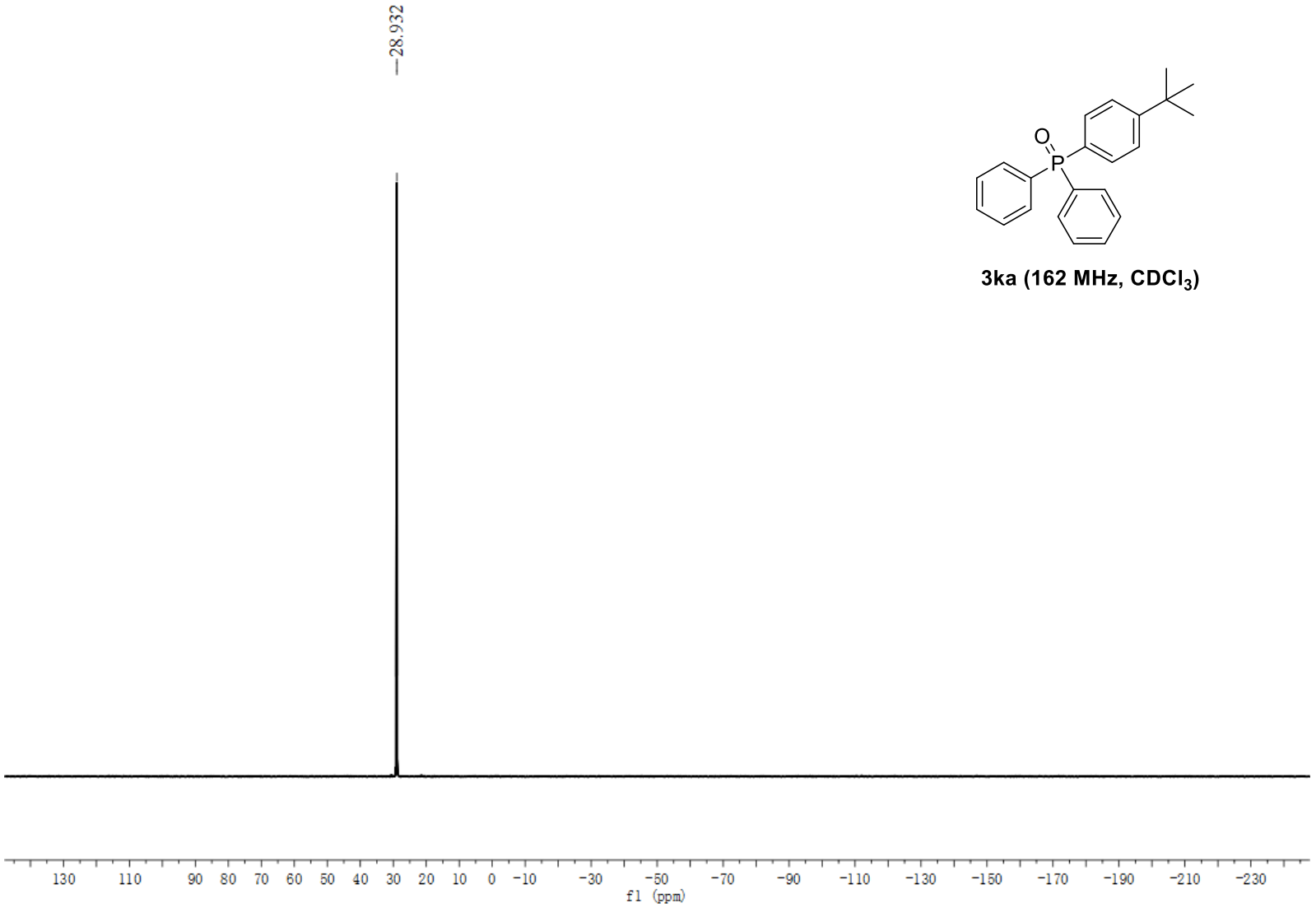



**3ja (162 MHz, $CDCl_3$)**


7.689
7.672
7.668
7.659
7.642
7.638
7.600
7.579
7.571
7.550
7.526
7.523
7.508
7.504
7.489
7.486
7.468
7.461
7.449
7.446
7.431
7.427
7.424
7.413
7.410
7.406
7.260
3.953
2.000
8.011
f1 (ppm)
O
P
3ka (400 MHz, CDCl3)
8.992
f1 (ppm)



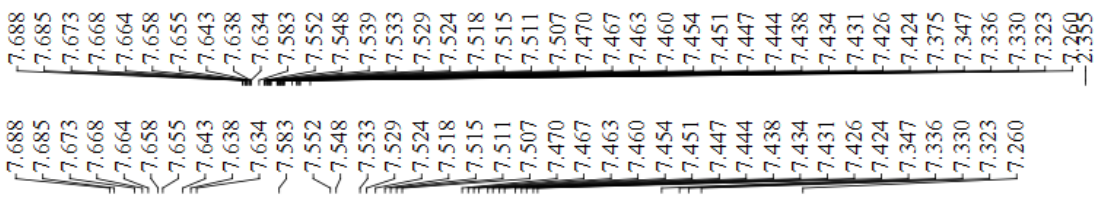

**3ka (101 MHz, $CDCl_3$)**

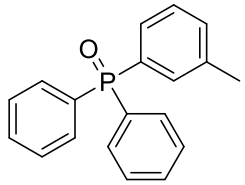




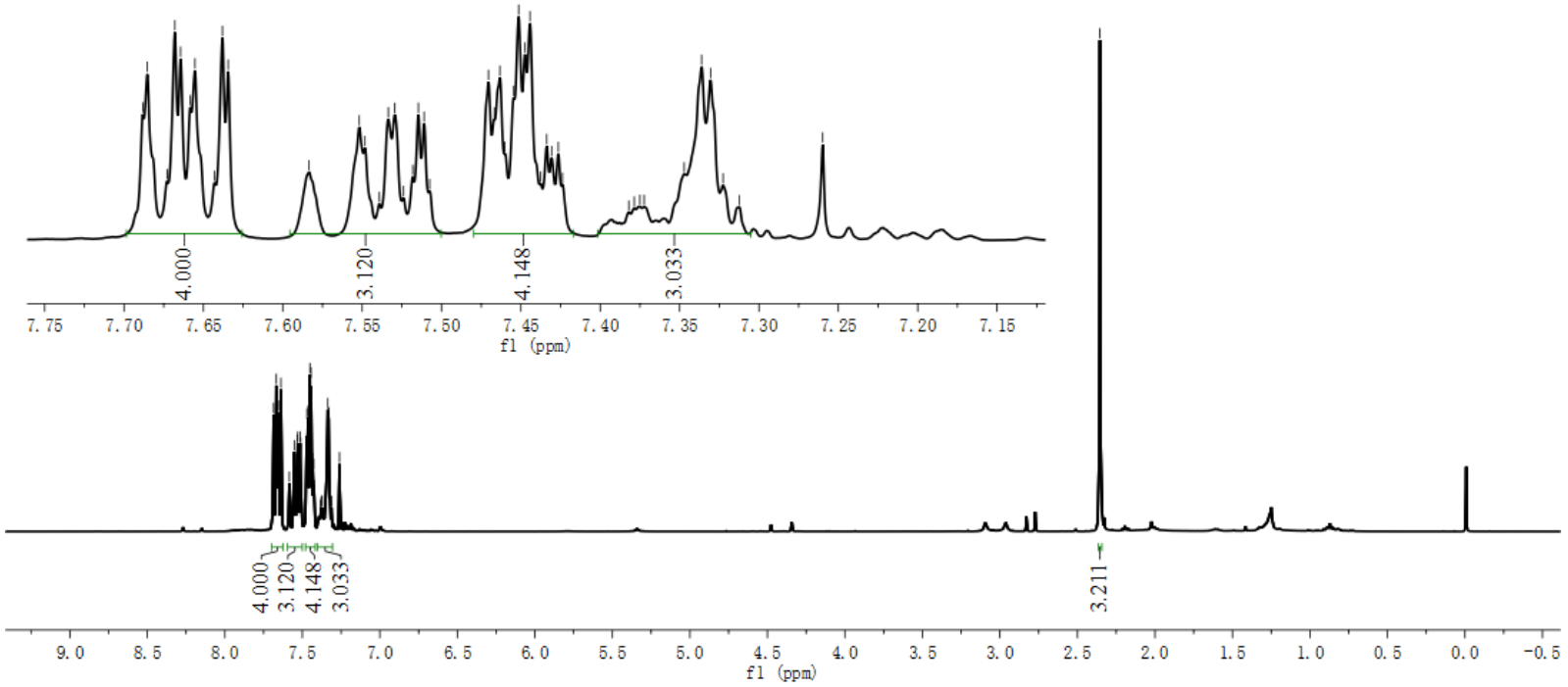


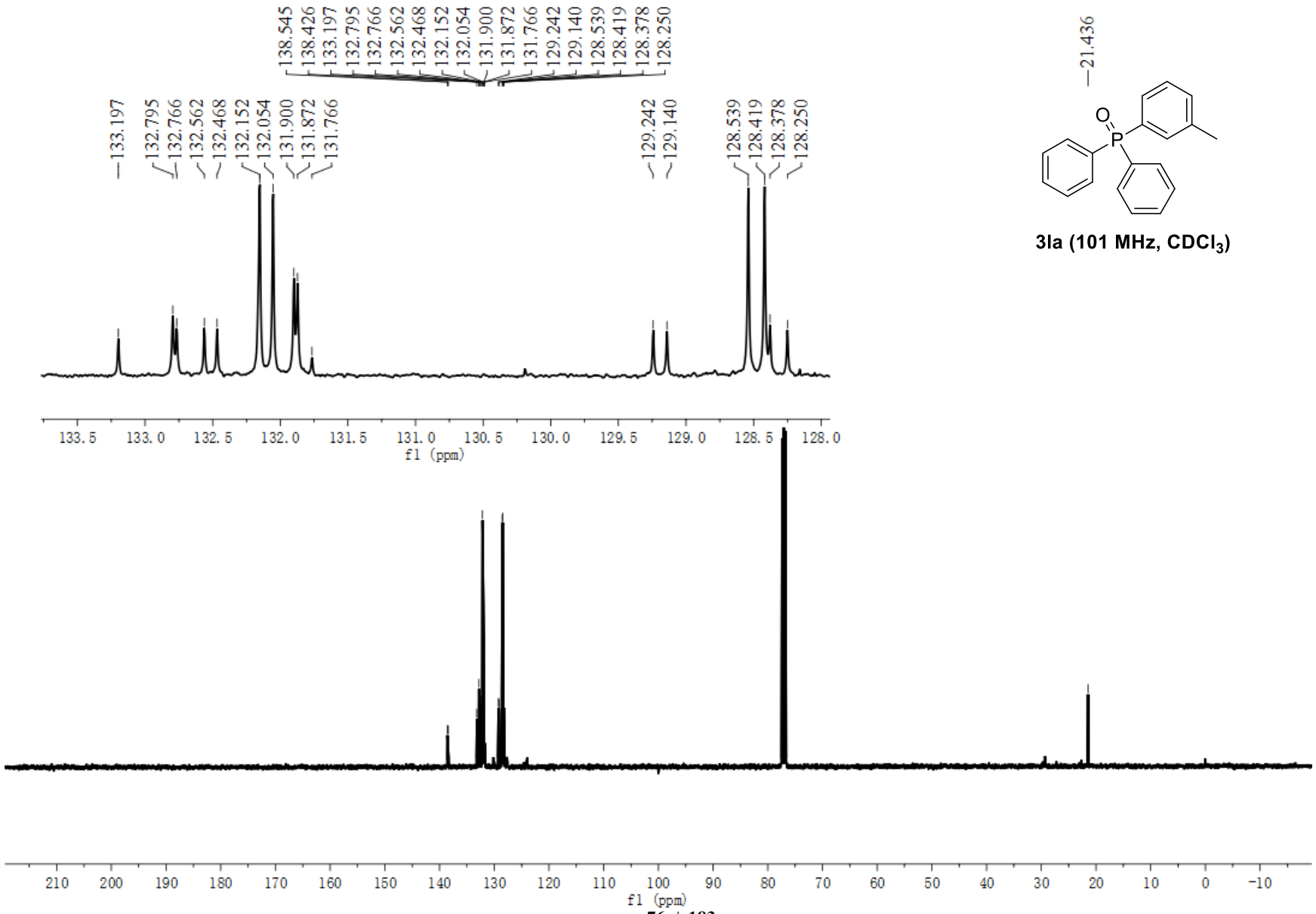
**3ka (162 MHz, $CDCl_3$)**



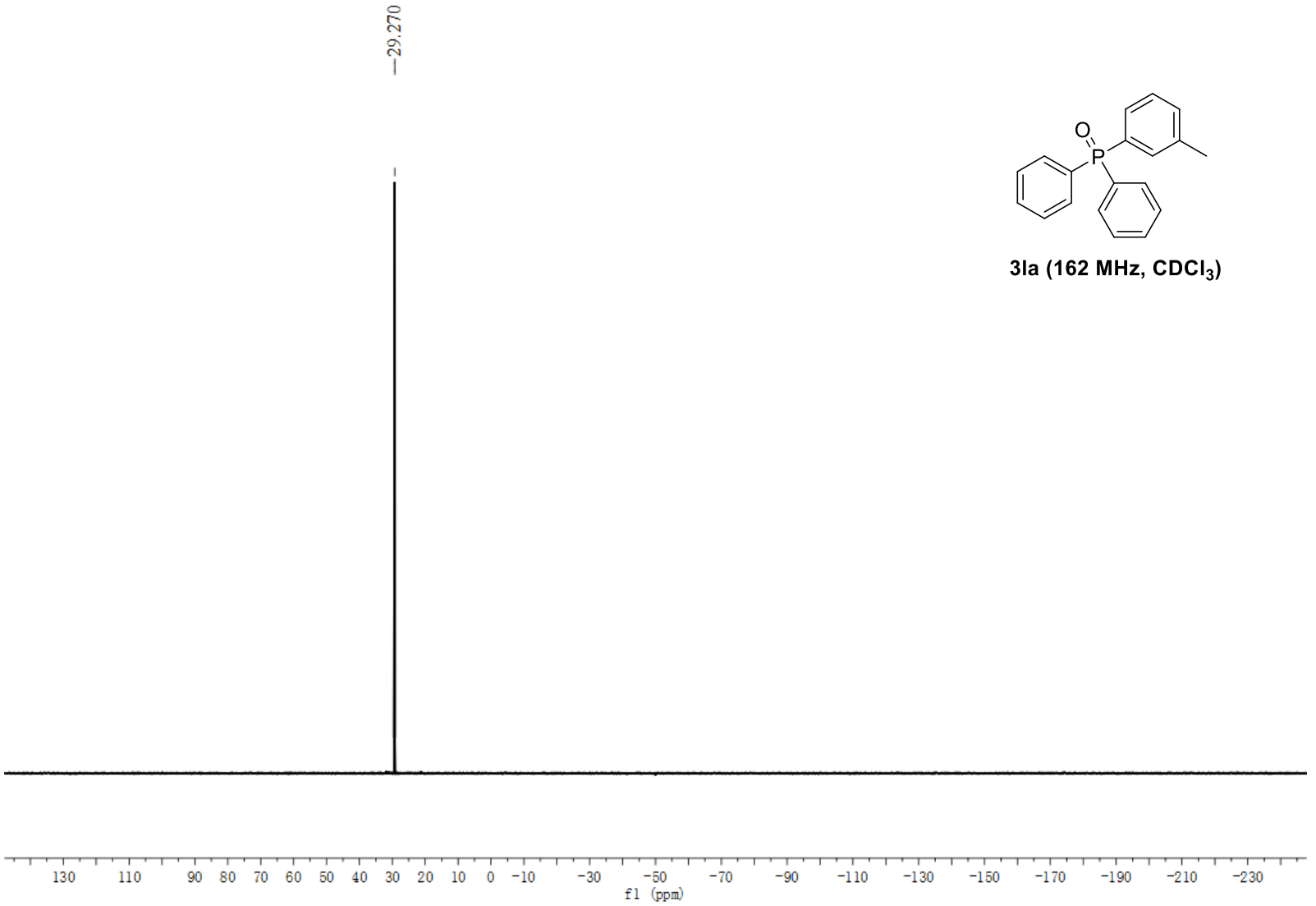



**3la (400 MHz, $CDCl_3$)**





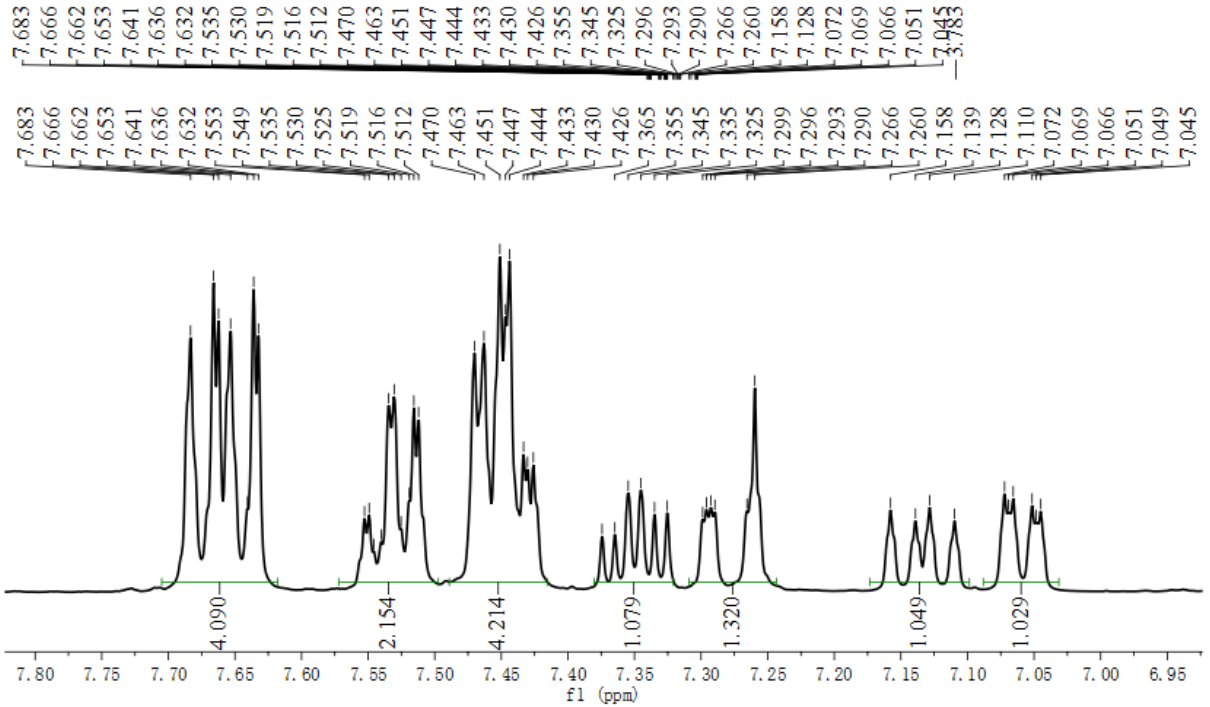

**3la (101 MHz, $CDCl_3$)**

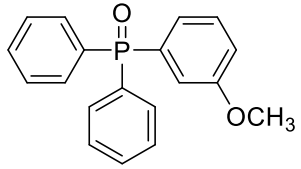




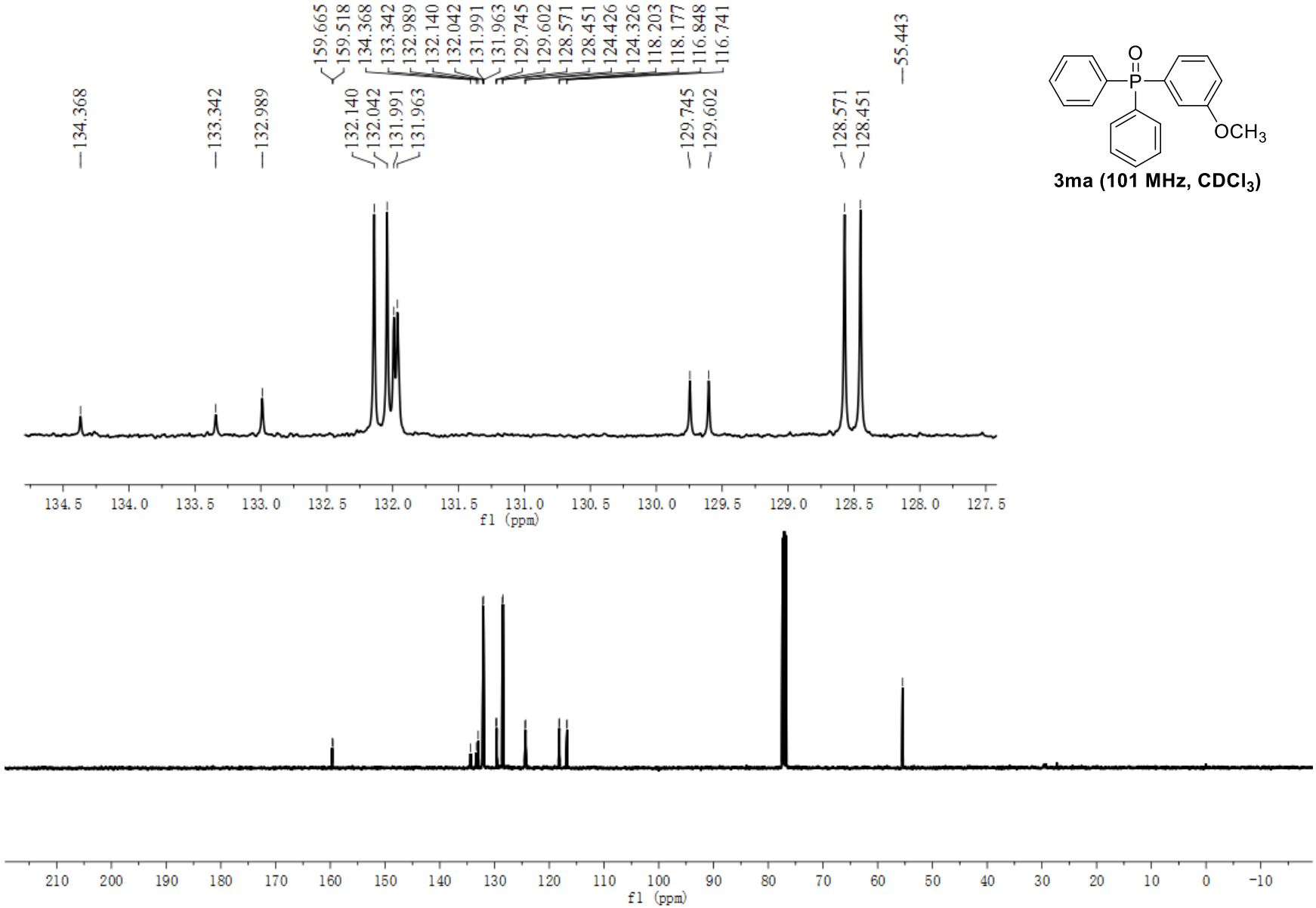


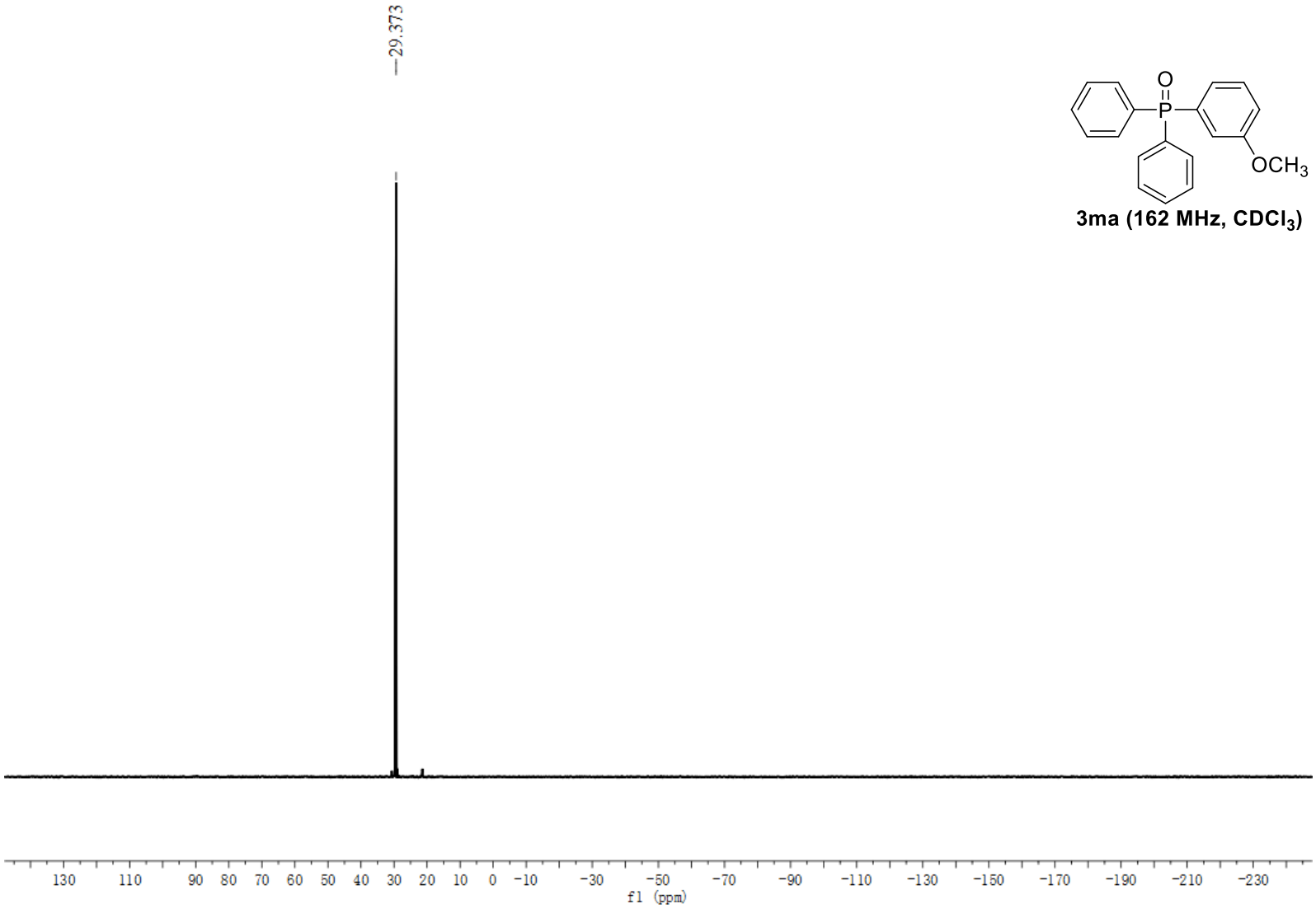
**3la (162 MHz, $CDCl_3$)**



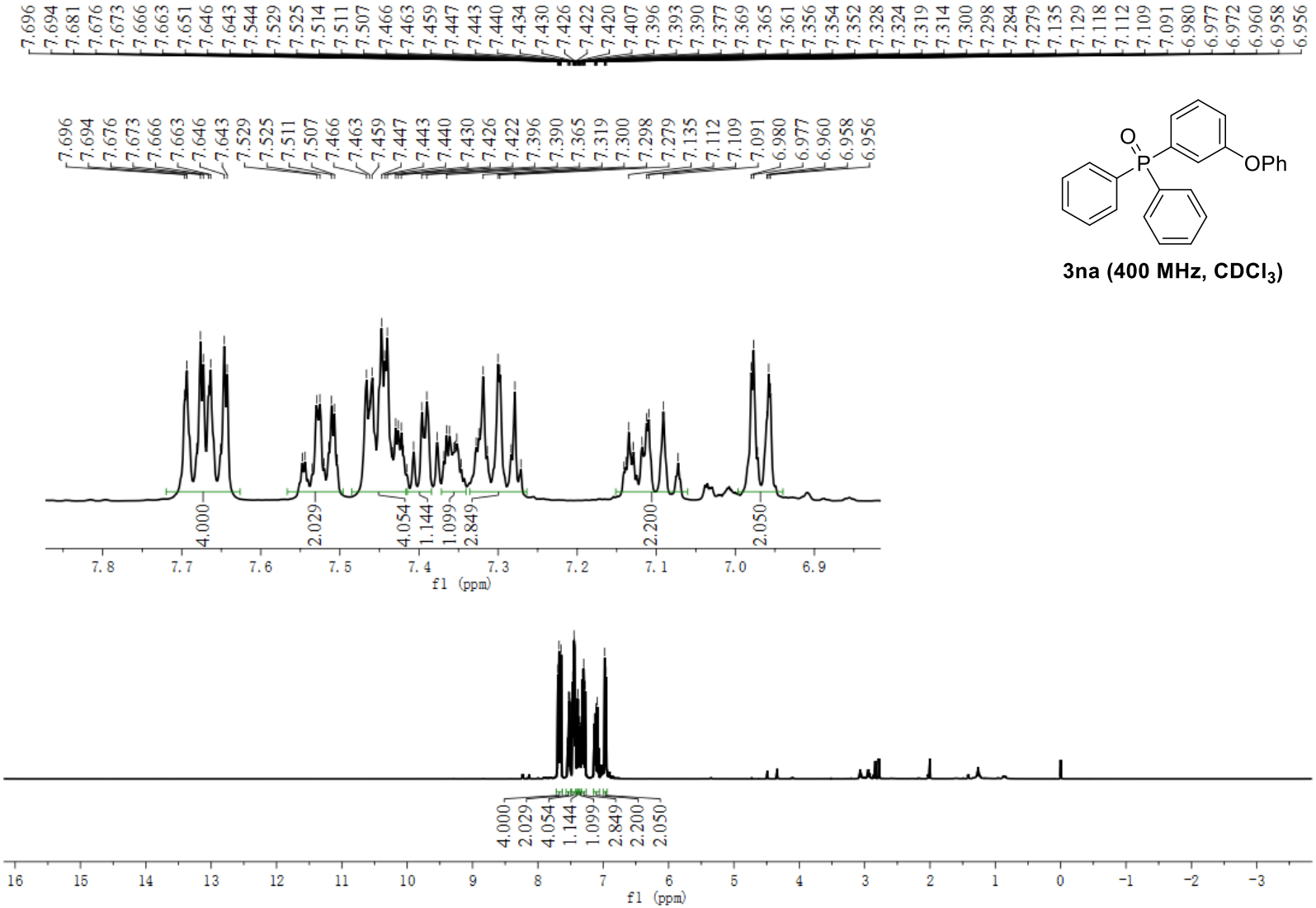




**3ma (400 MHz, $CDCl_3$)**

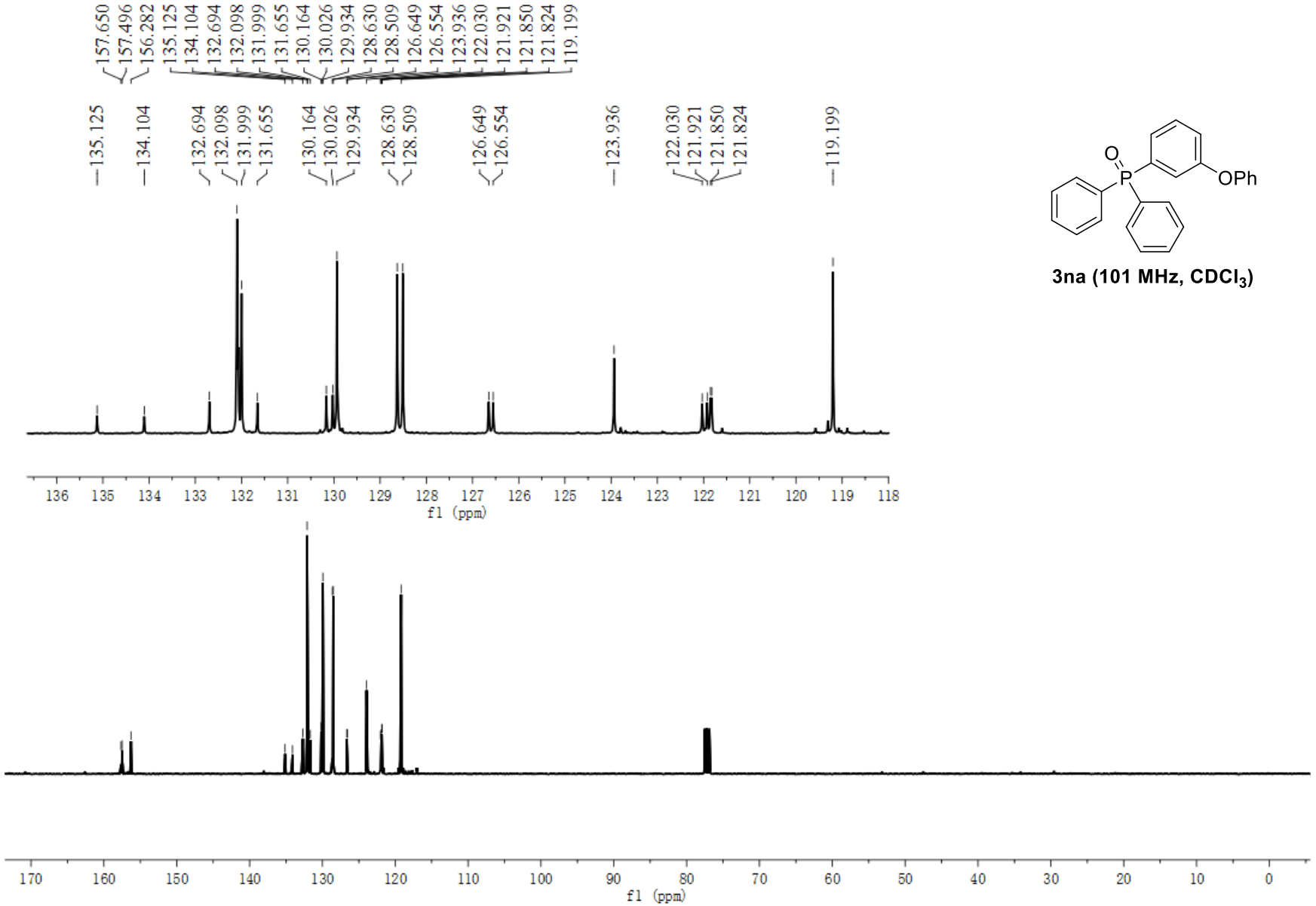

159.665
159.518
134.368
133.342
132.989
132.140
132.042
131.991
131.963
129.745
129.602
128.571
128.451
124.426
124.326
118.203
118.177
116.848
116.741
55.443
134.368
133.342
132.989
132.140
132.042
131.991
131.963
129.745
129.602
128.571
128.451
O
P
OCH3
3ma (101 MHz, CDCl3)
f1 (ppm)
f1 (ppm)




**3ma (162 MHz, $CDCl_3$)**



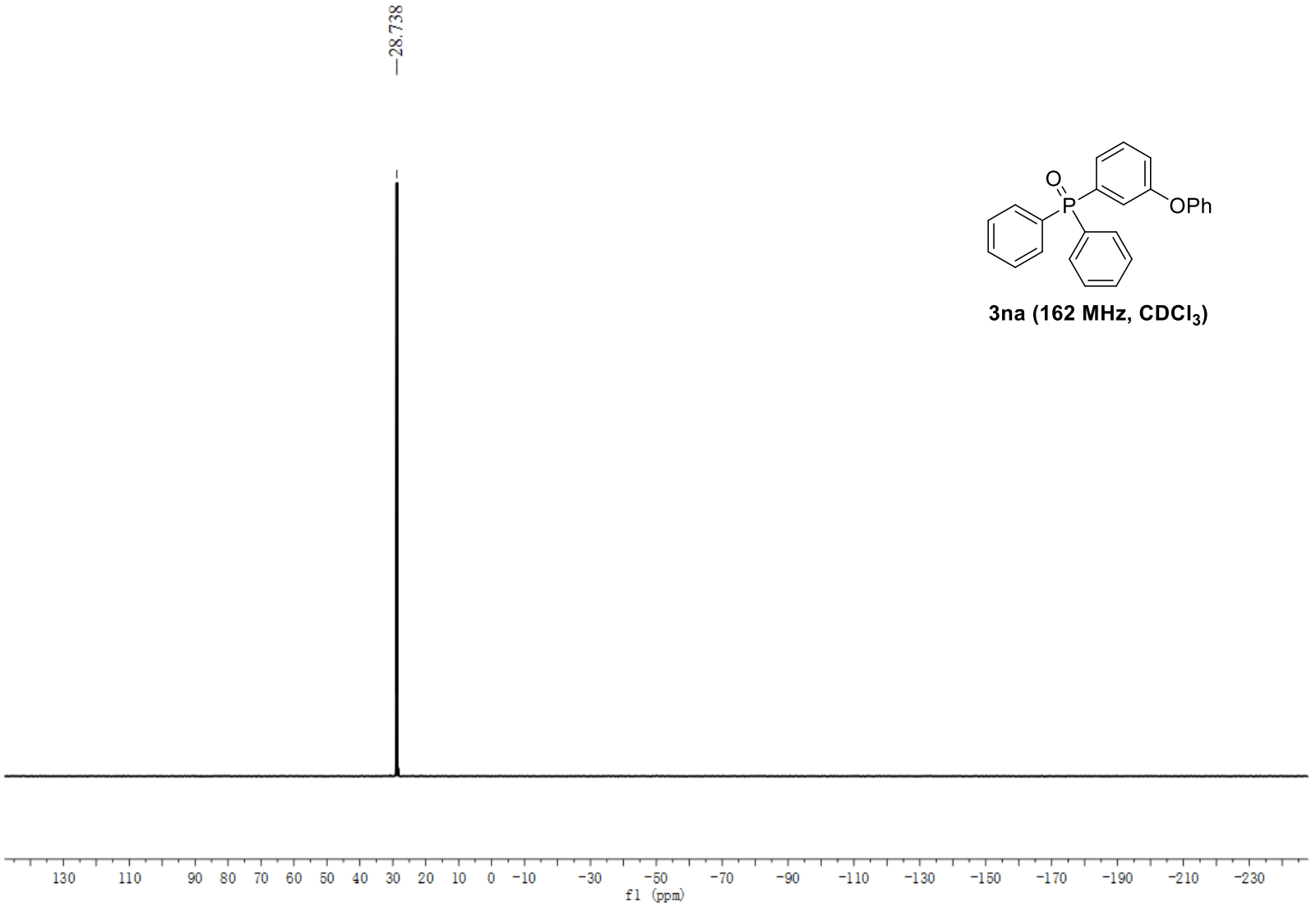

**3na (400 MHz, $CDCl_3$)**



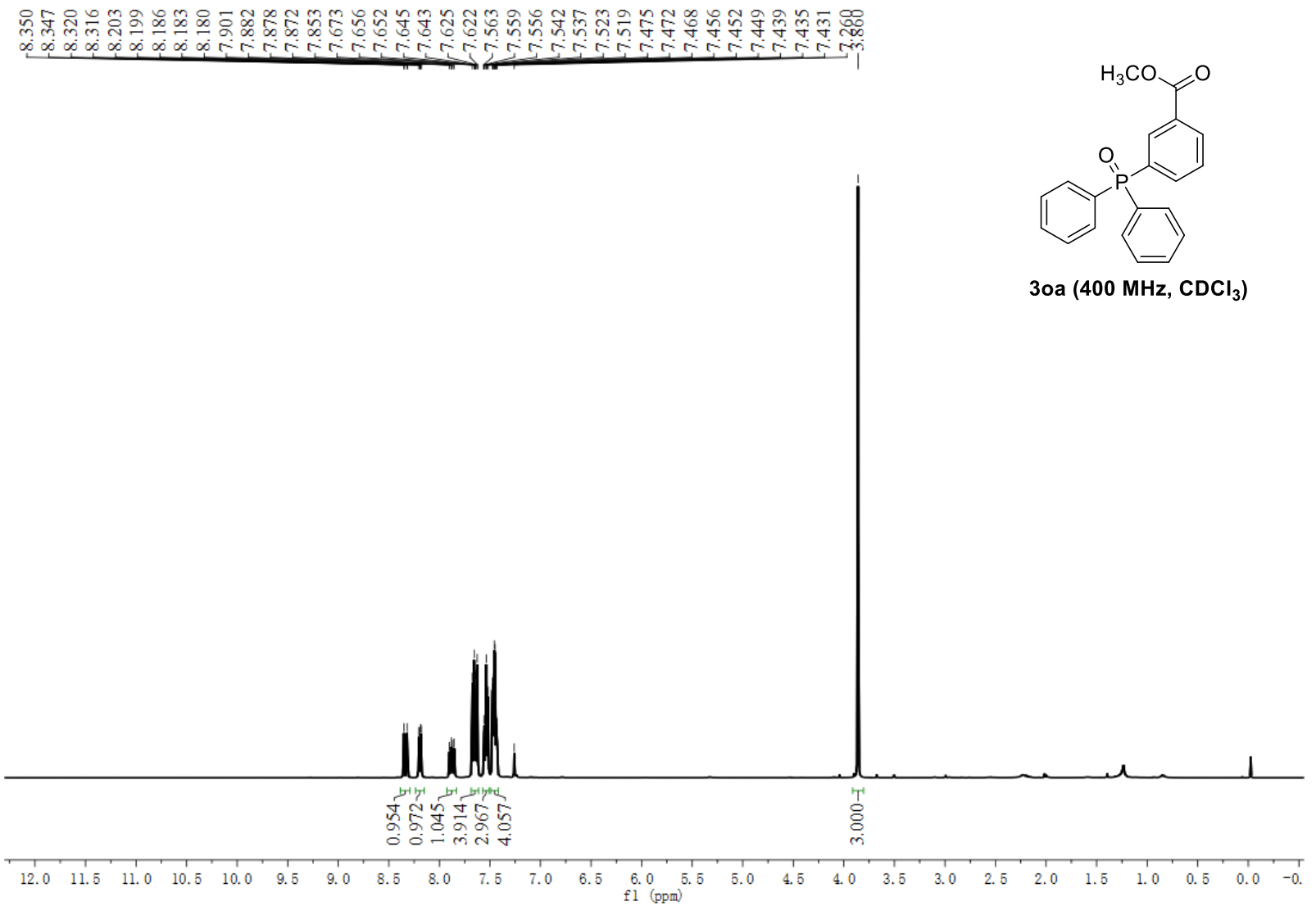




**3na (101 MHz, $CDCl_3$)**



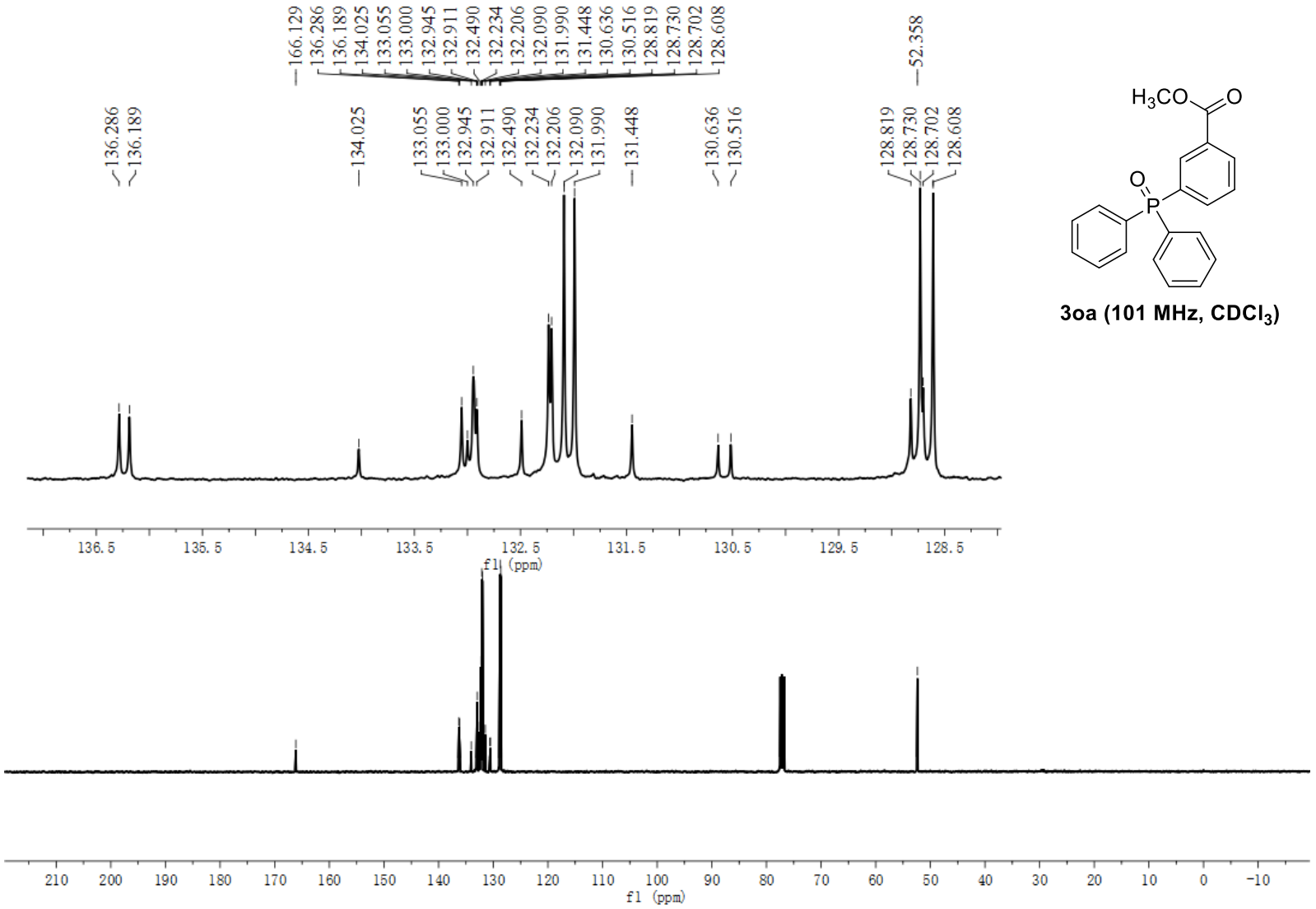

**3na (162 MHz, $CDCl_3$)**







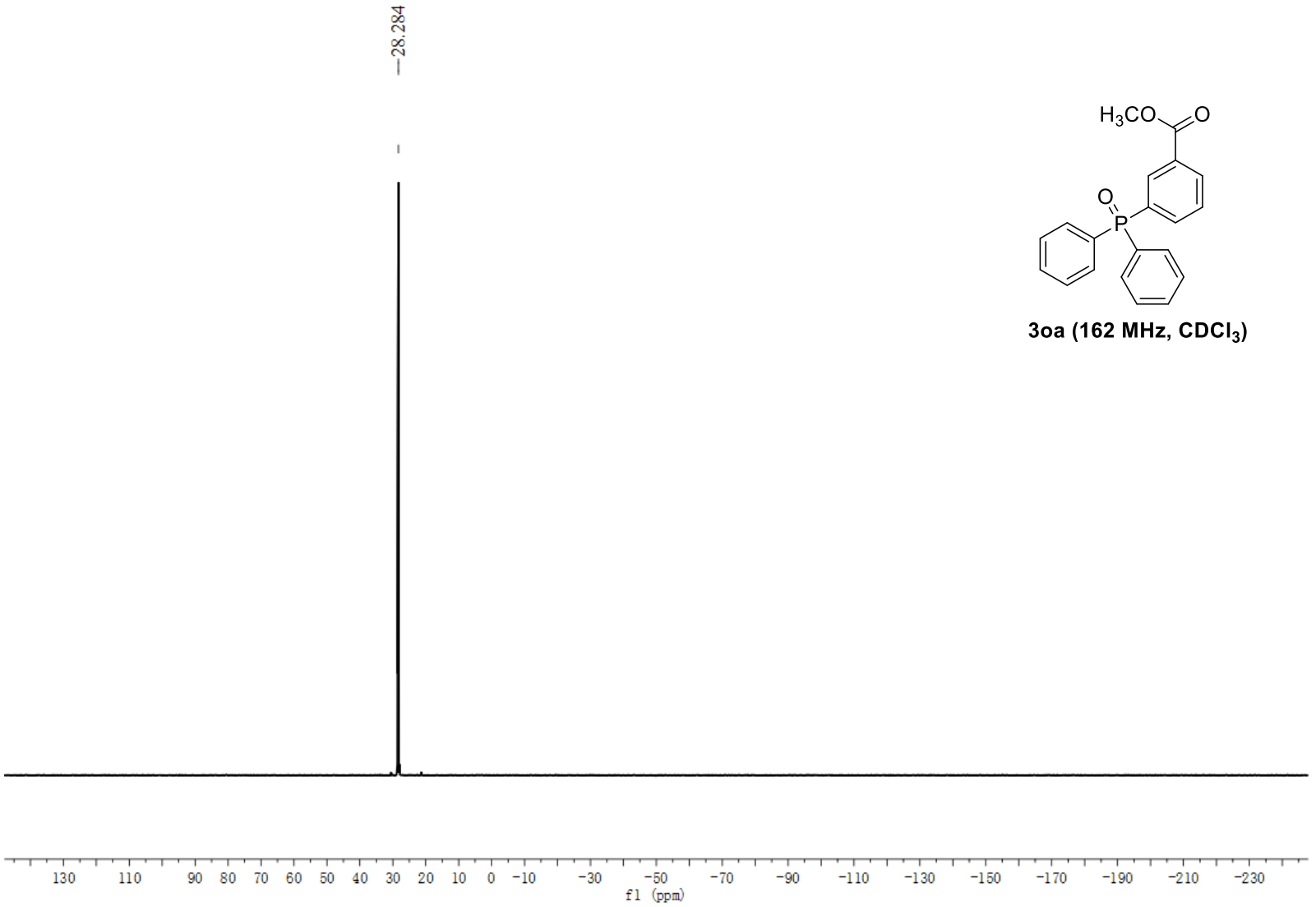
**3oa (400 MHz, $CDCl_3$)**



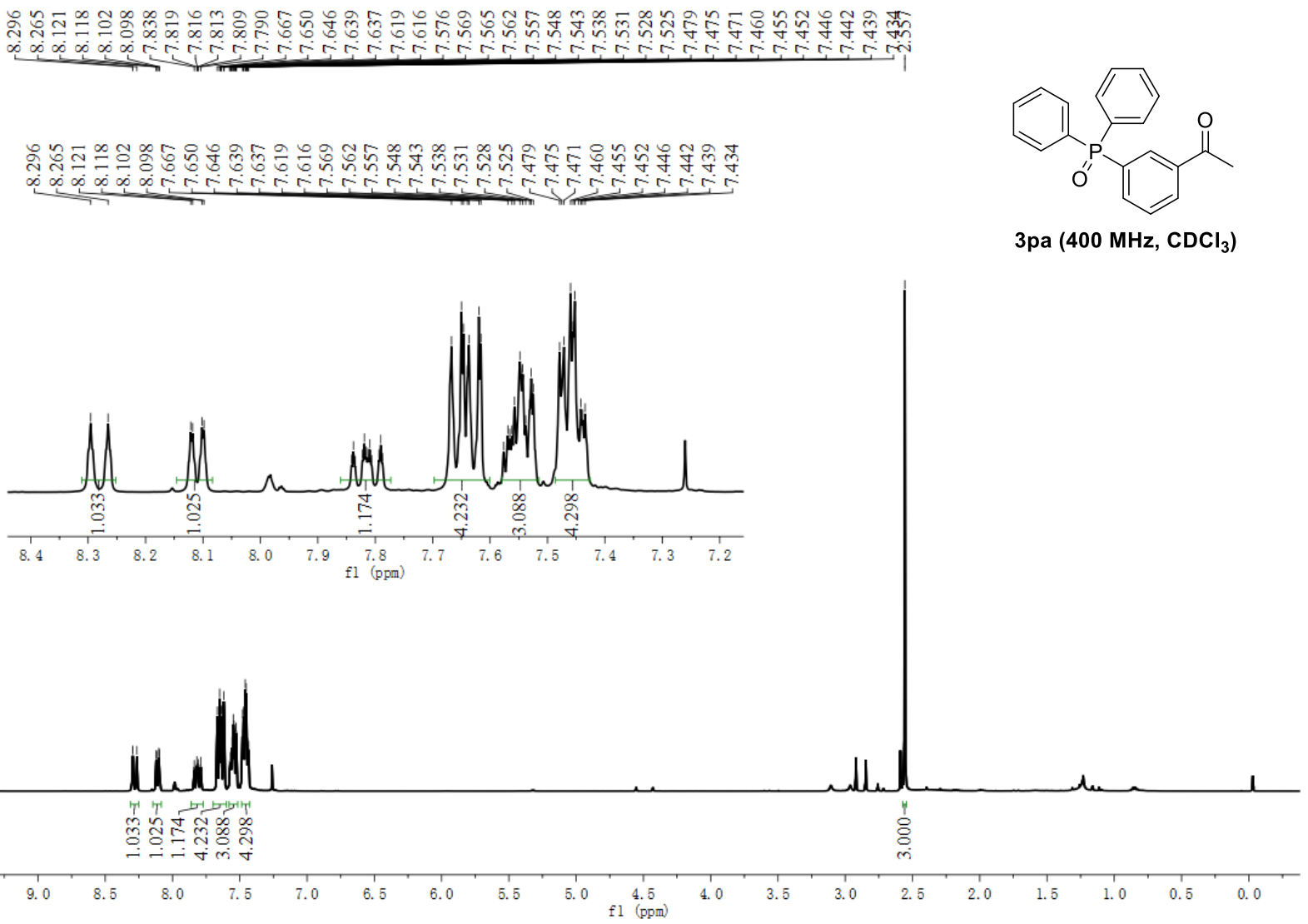




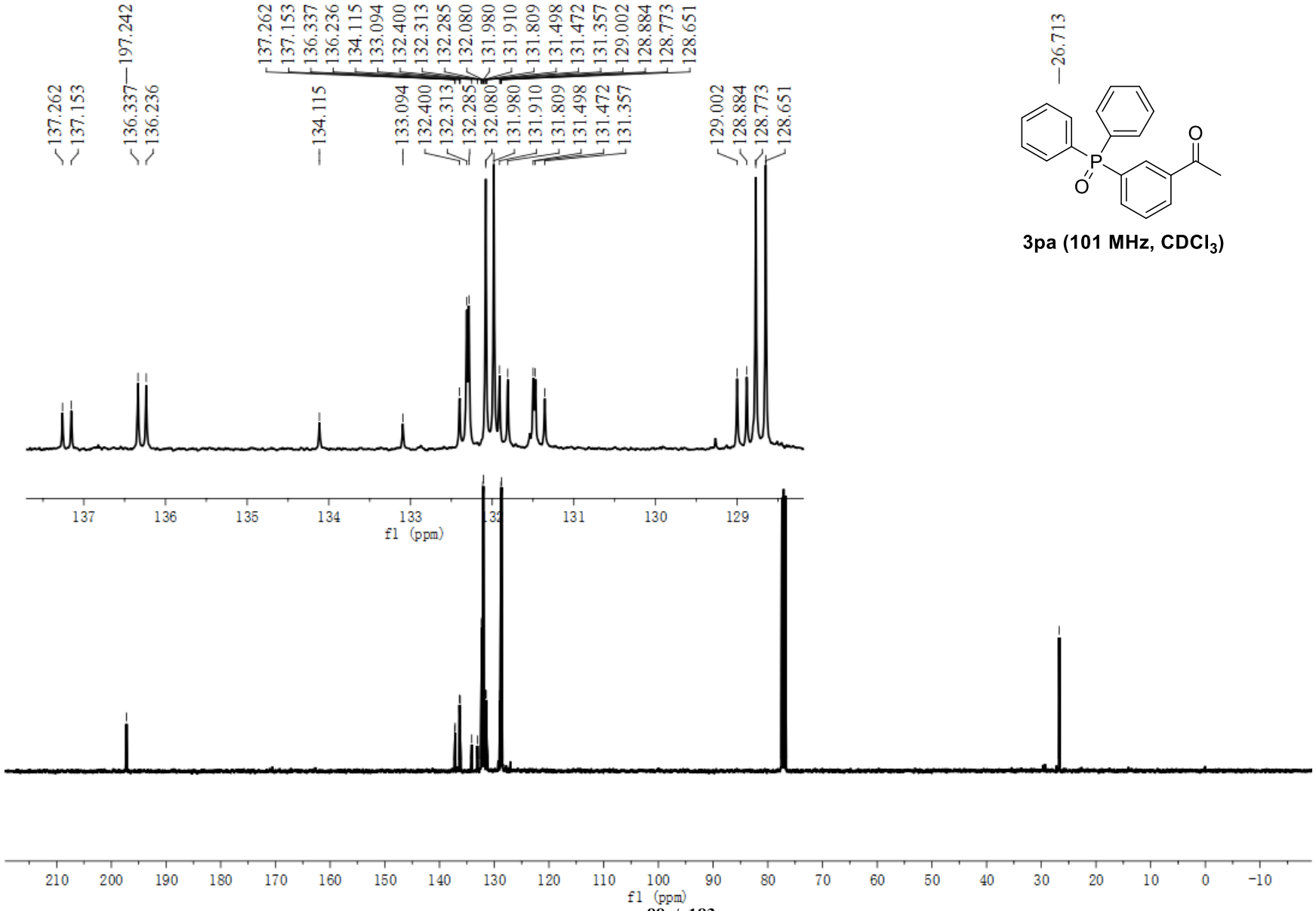
**3oa (101 MHz, $CDCl_3$)**



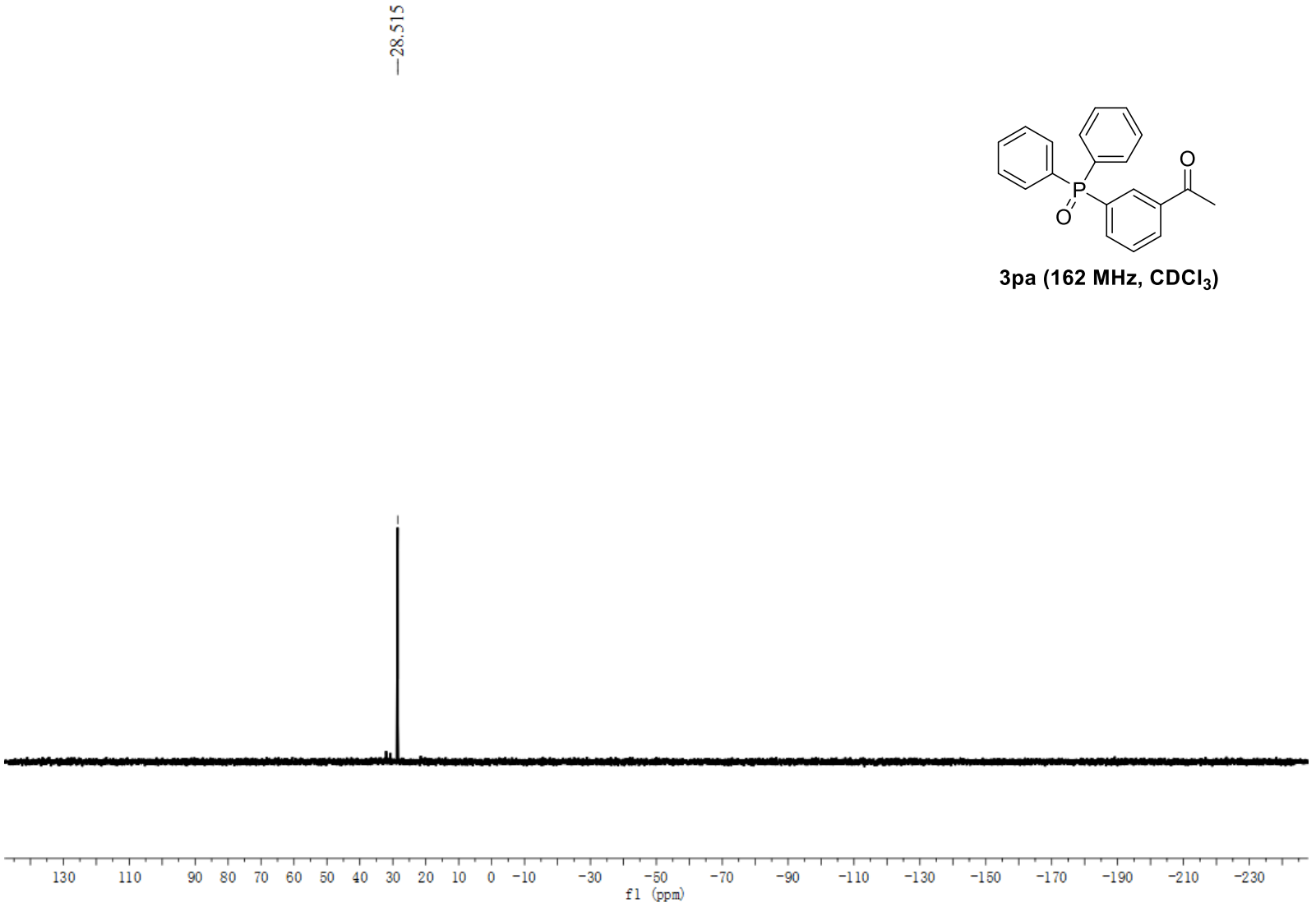

**3oa (162 MHz, $CDCl_3$)**



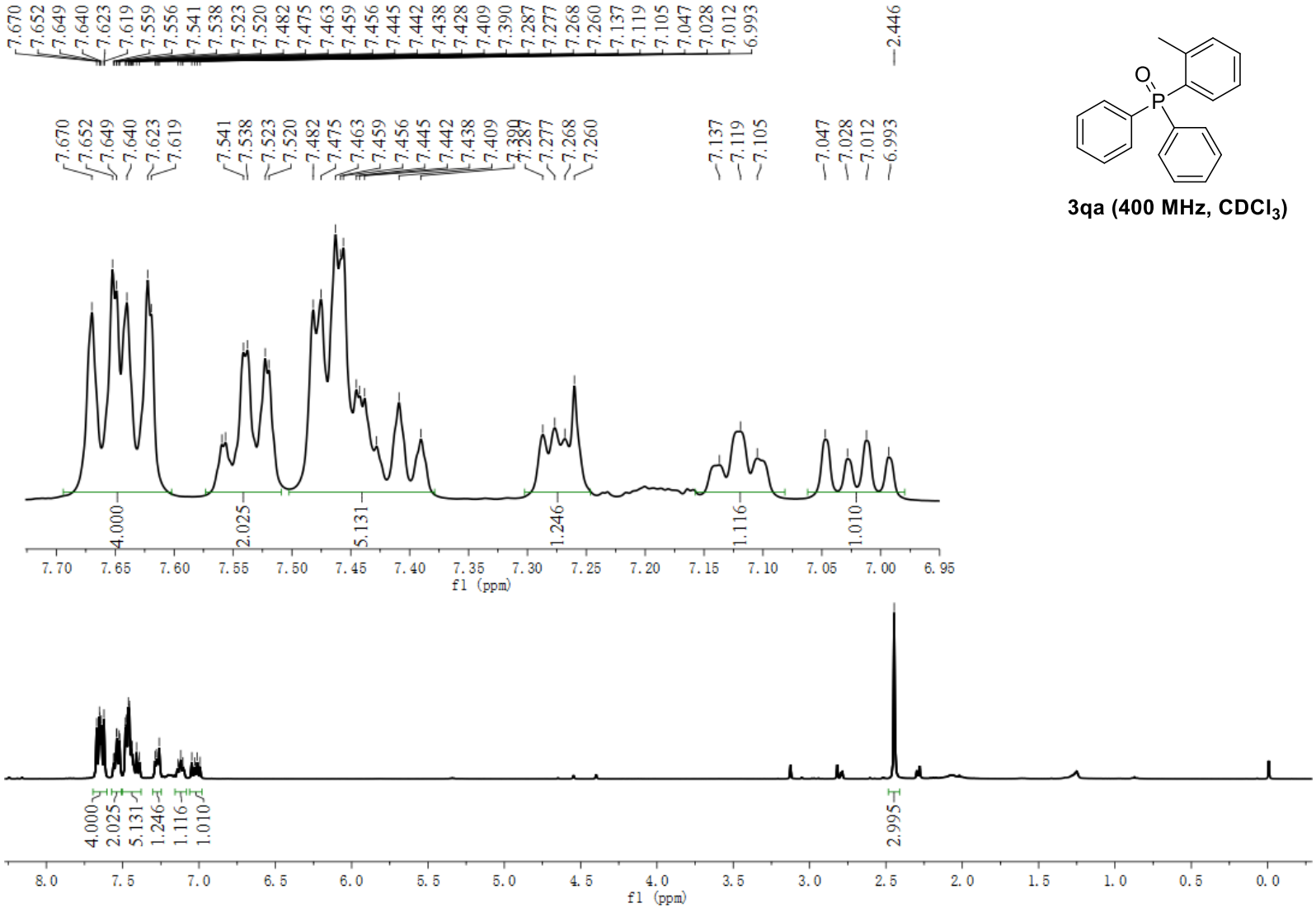

**3pa (400 MHz, $CDCl_3$)**




**3pa (101 MHz, $CDCl_3$)**

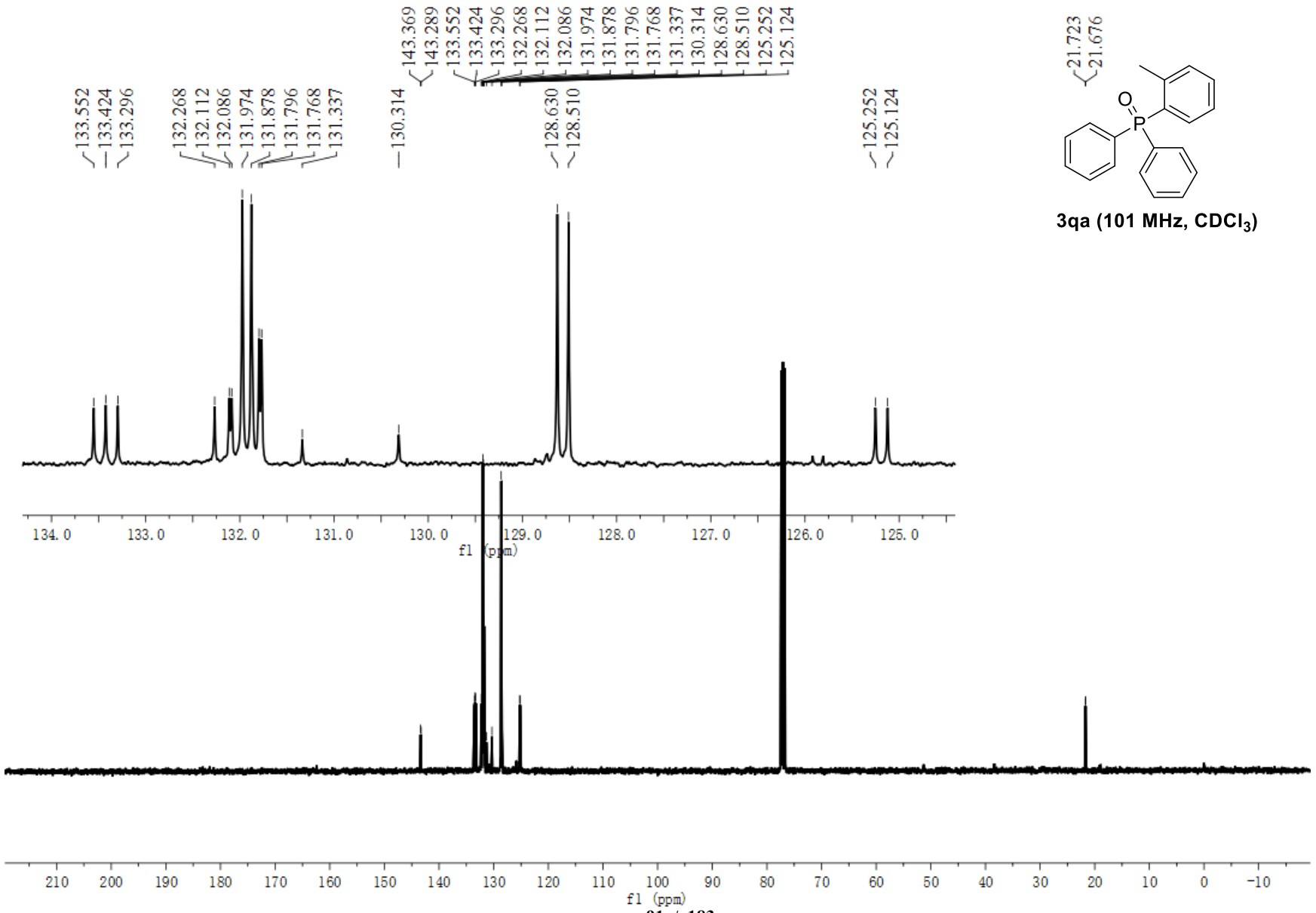



**3pa (162 MHz, $CDCl_3$)**

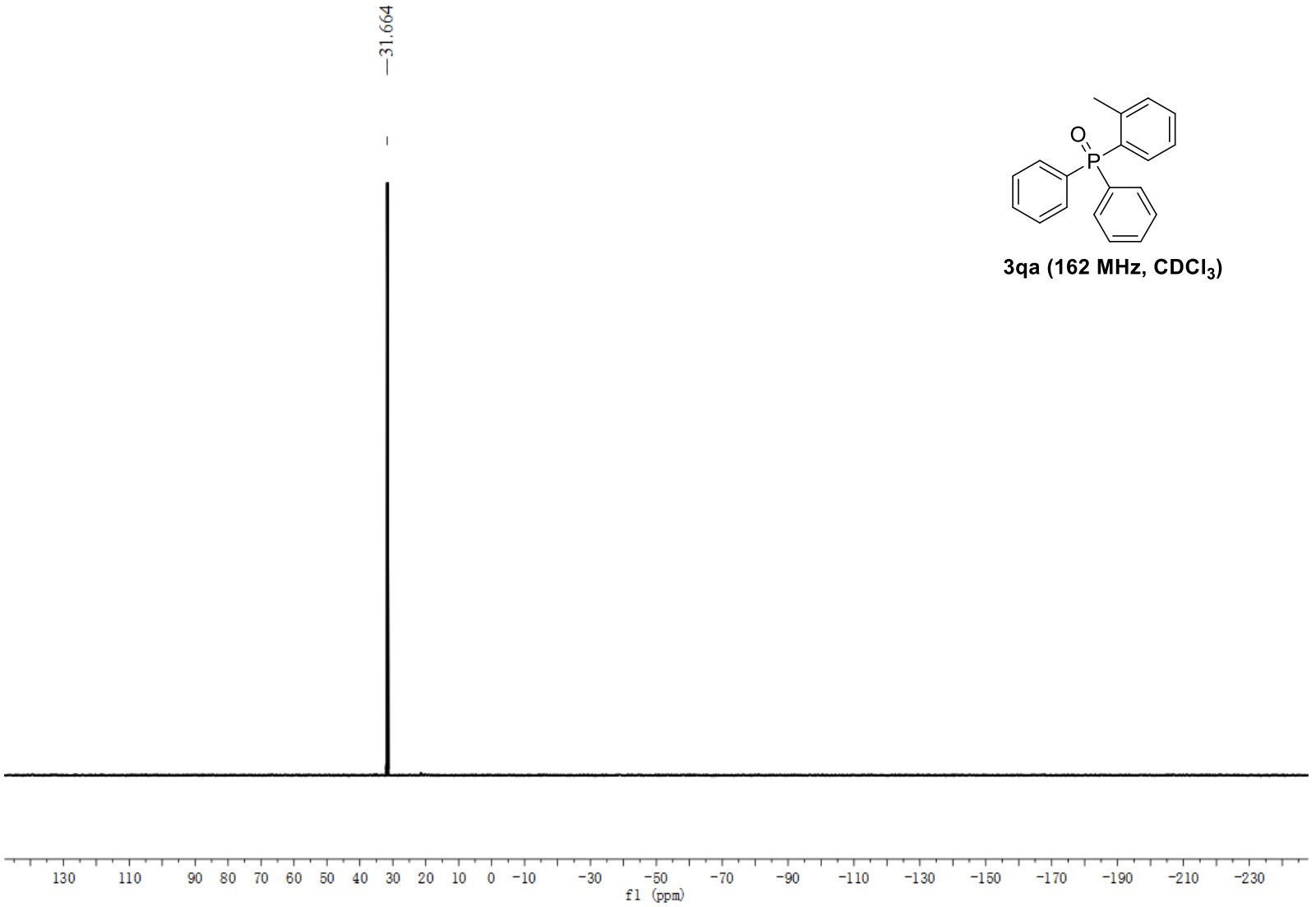





**3qa (400 MHz, $CDCl_3$)**



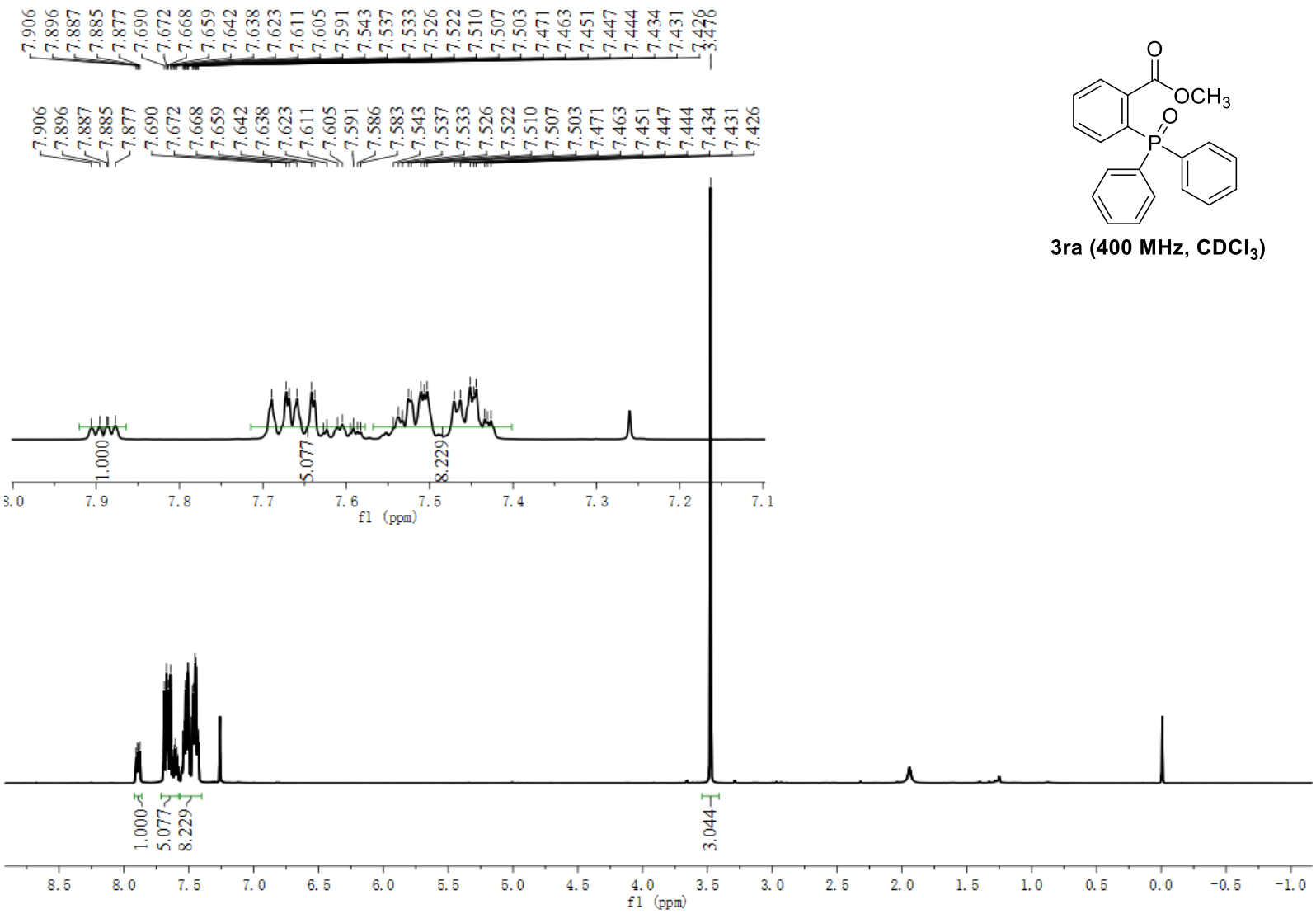

**3qa (101 MHz, $CDCl_3$)**



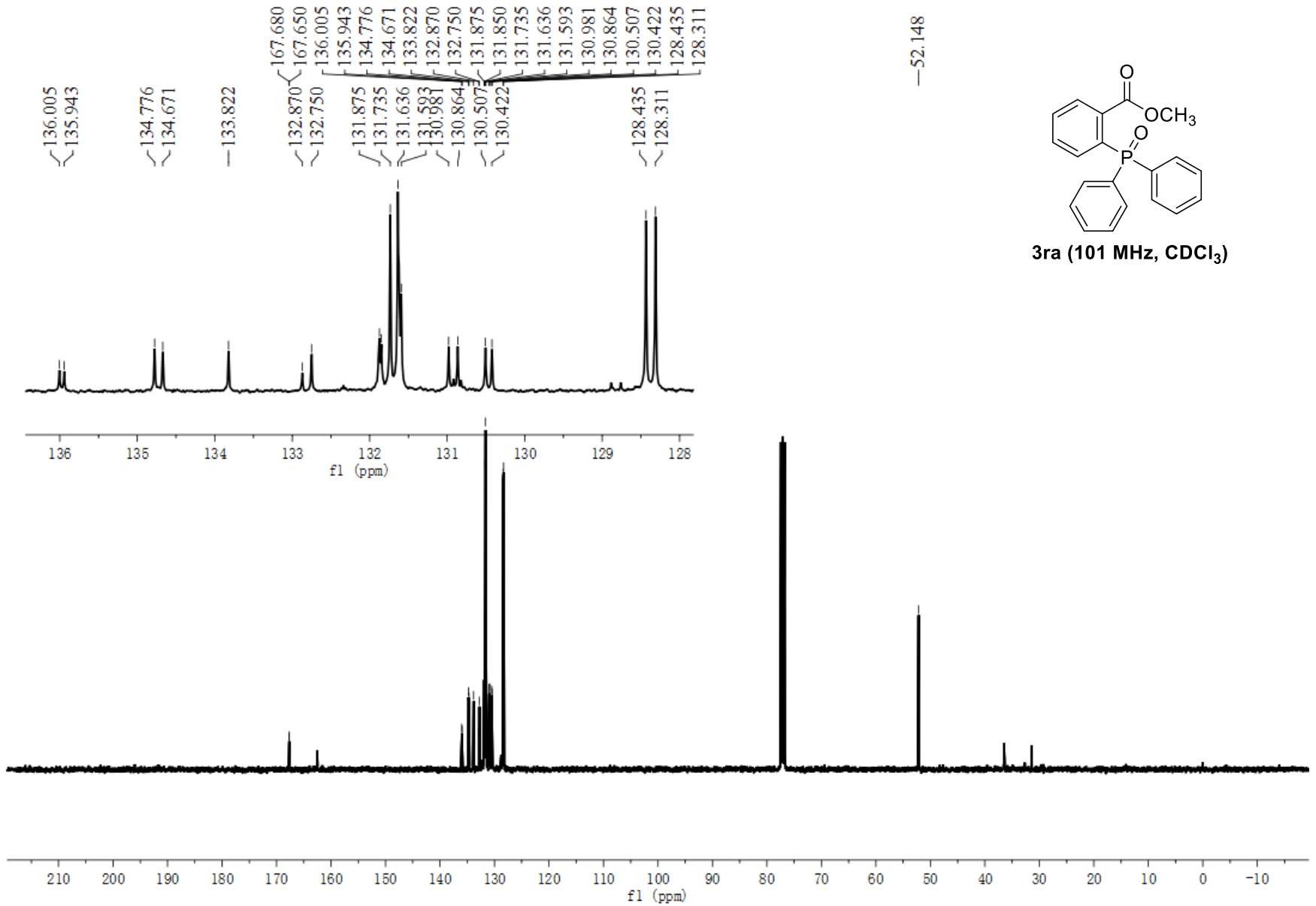




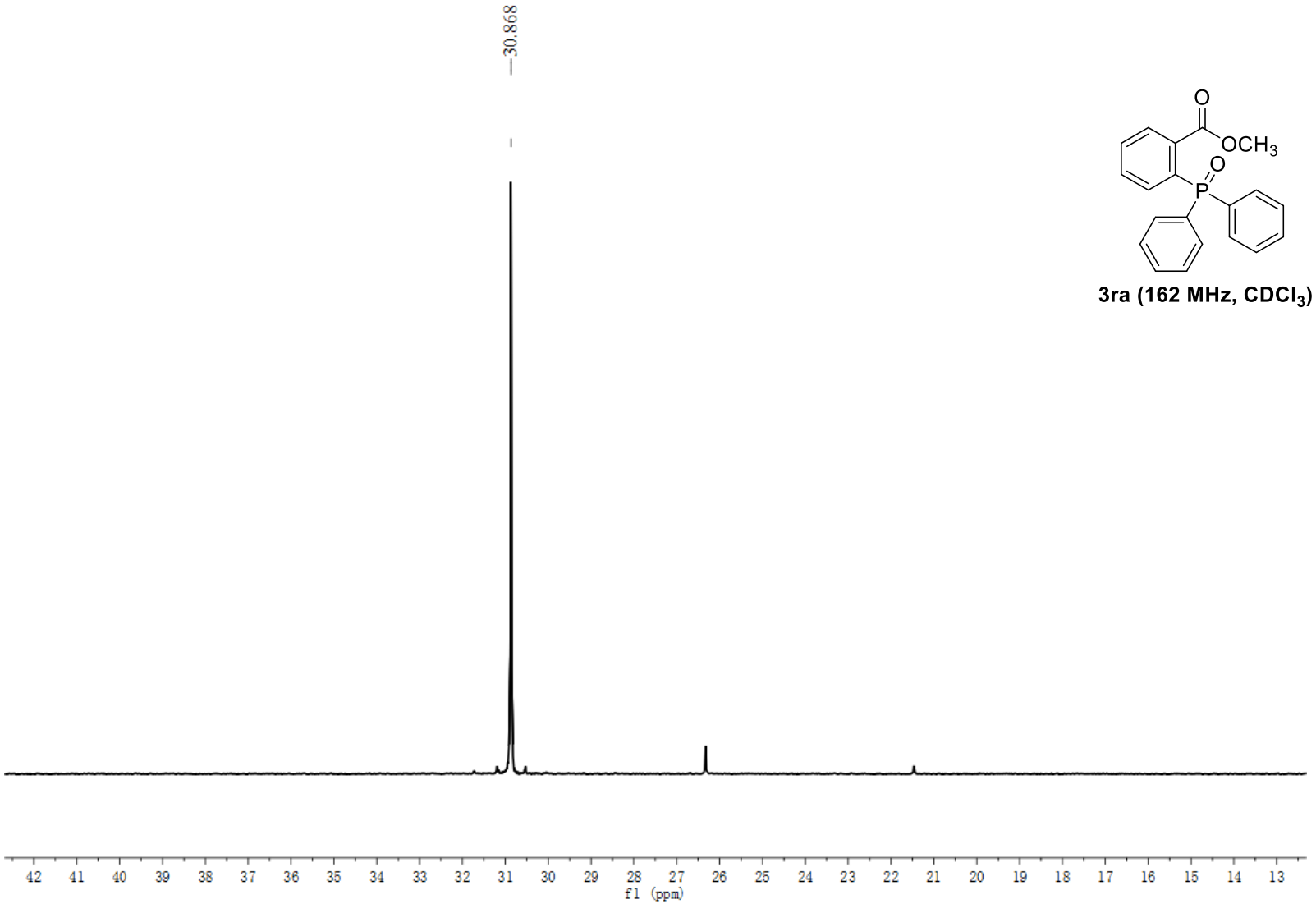
**3qa (162 MHz, $CDCl_3$)**




3ra (400 MHz, $CDCl_3$)



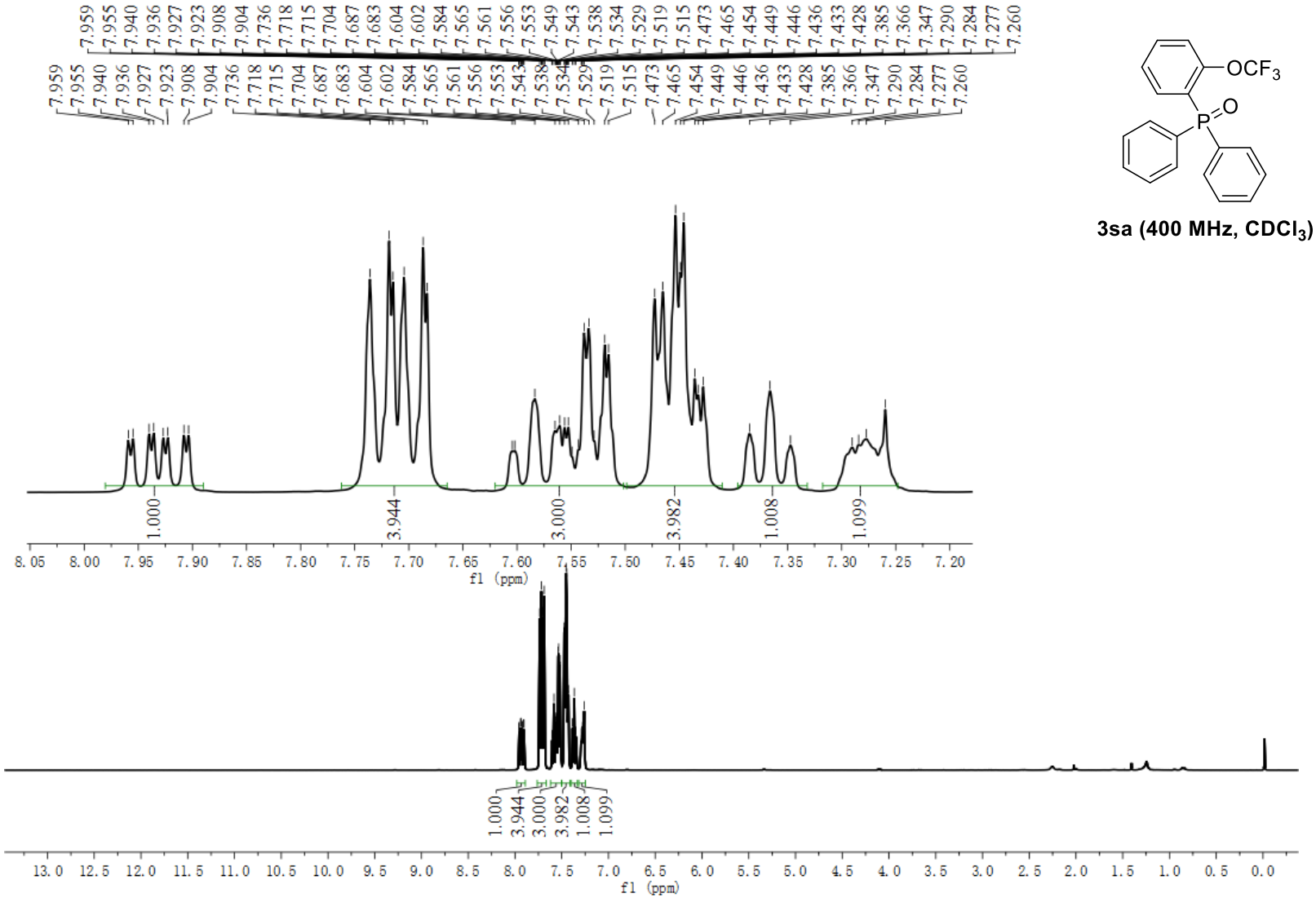

**3ra (101 MHz, $CDCl_3$)**







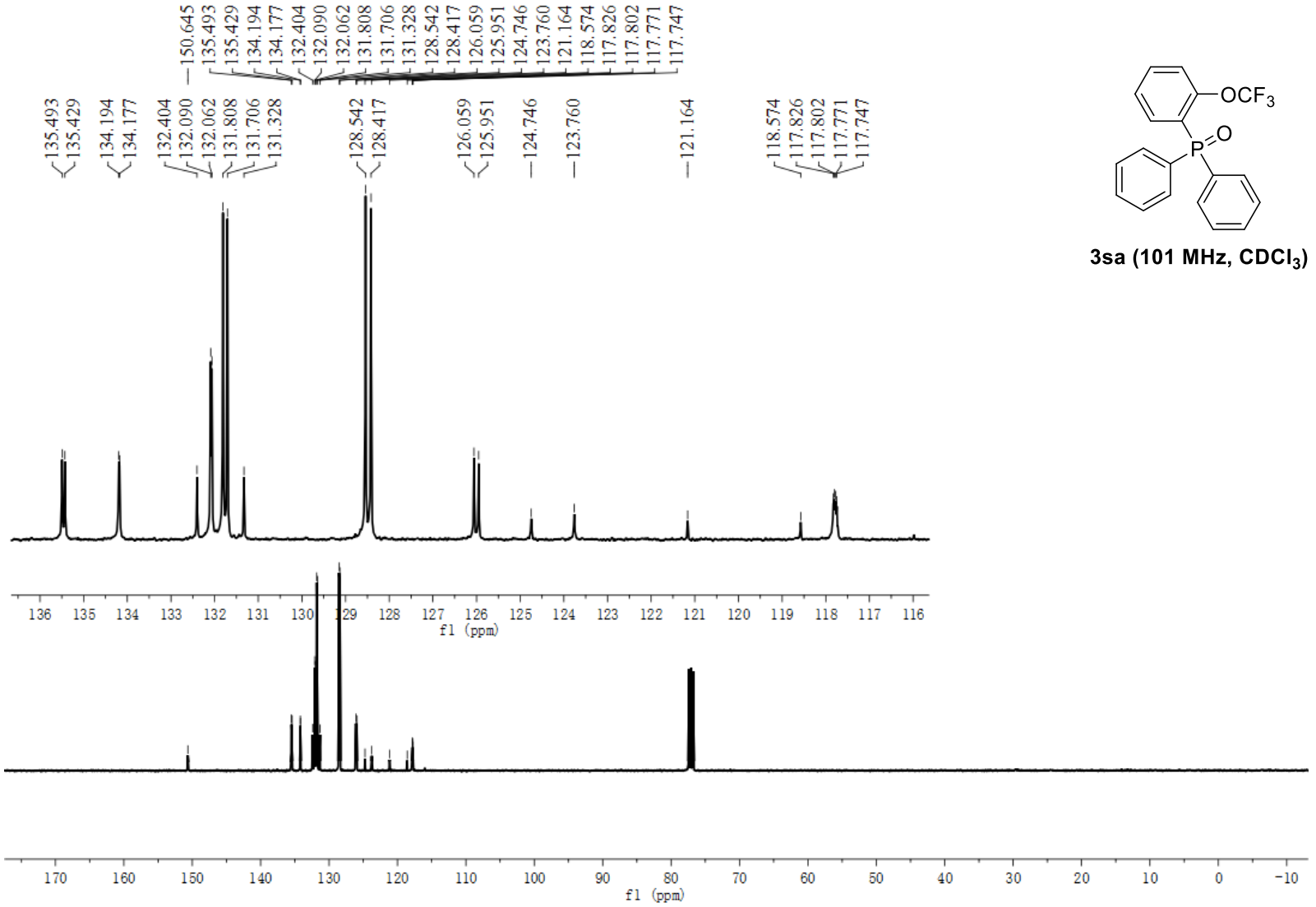
**3ra (162 MHz, $CDCl_3$)**







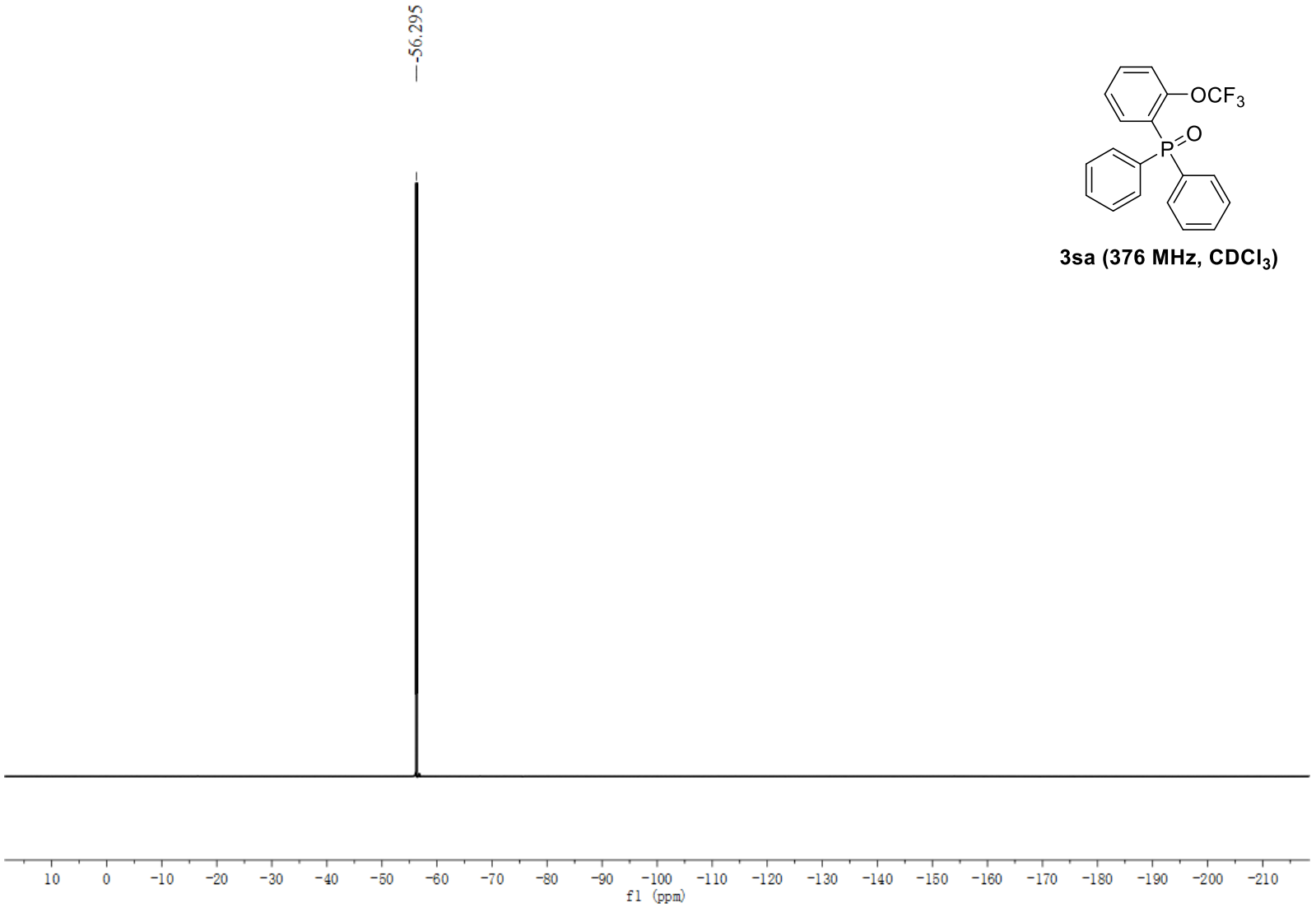
**3sa (400 MHz, $CDCl_3$)**



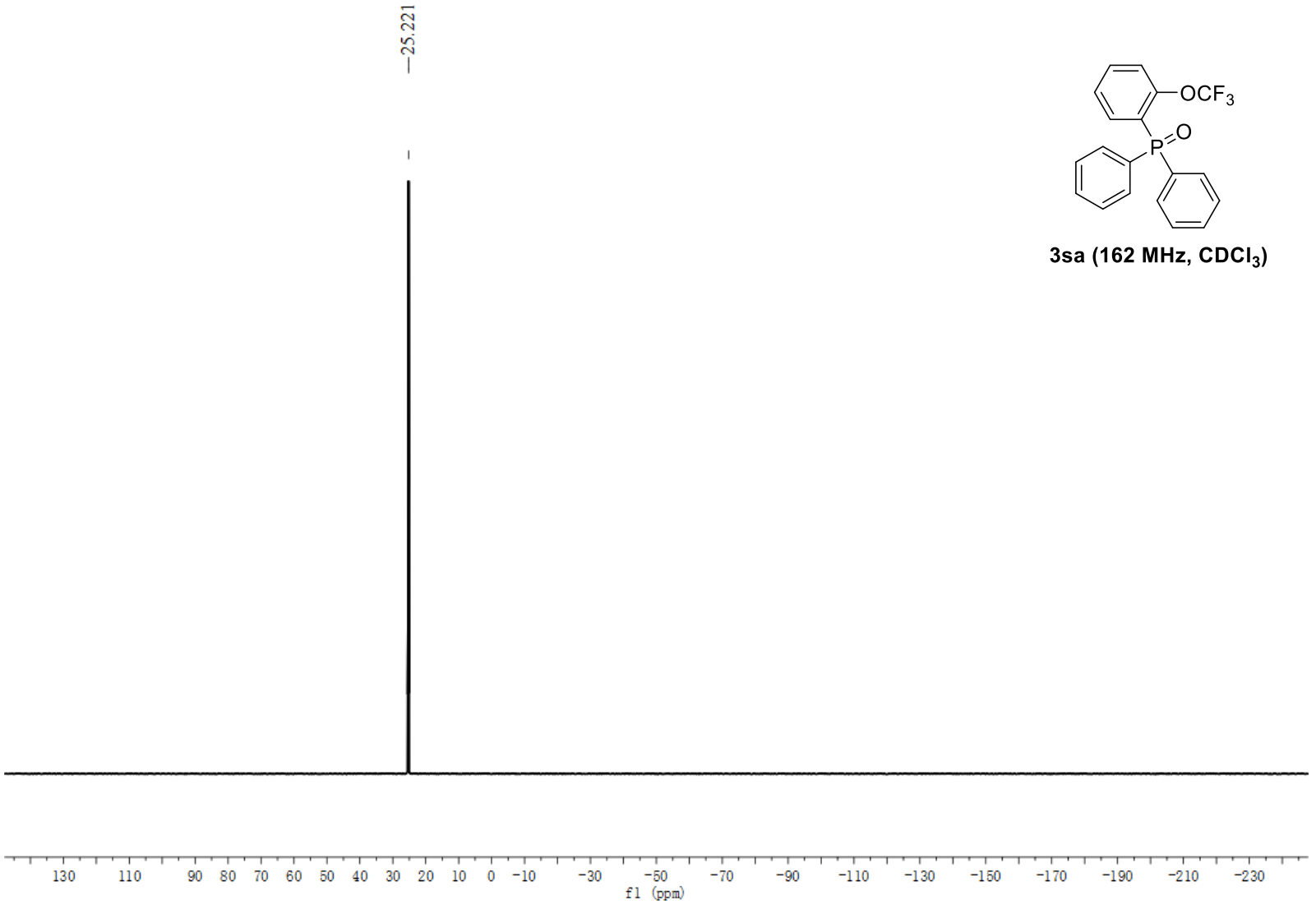




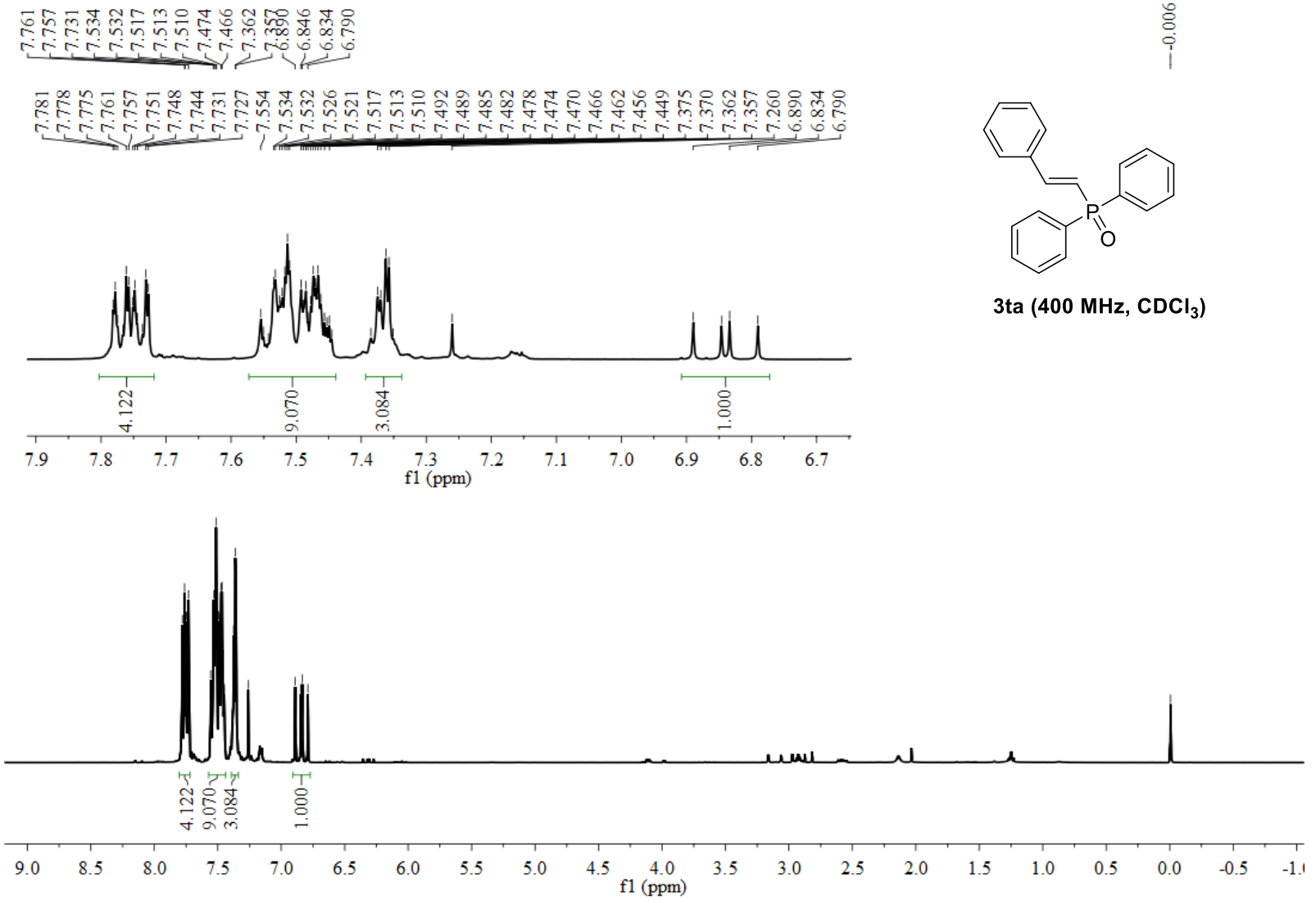
**3sa (101 MHz, $CDCl_3$)**

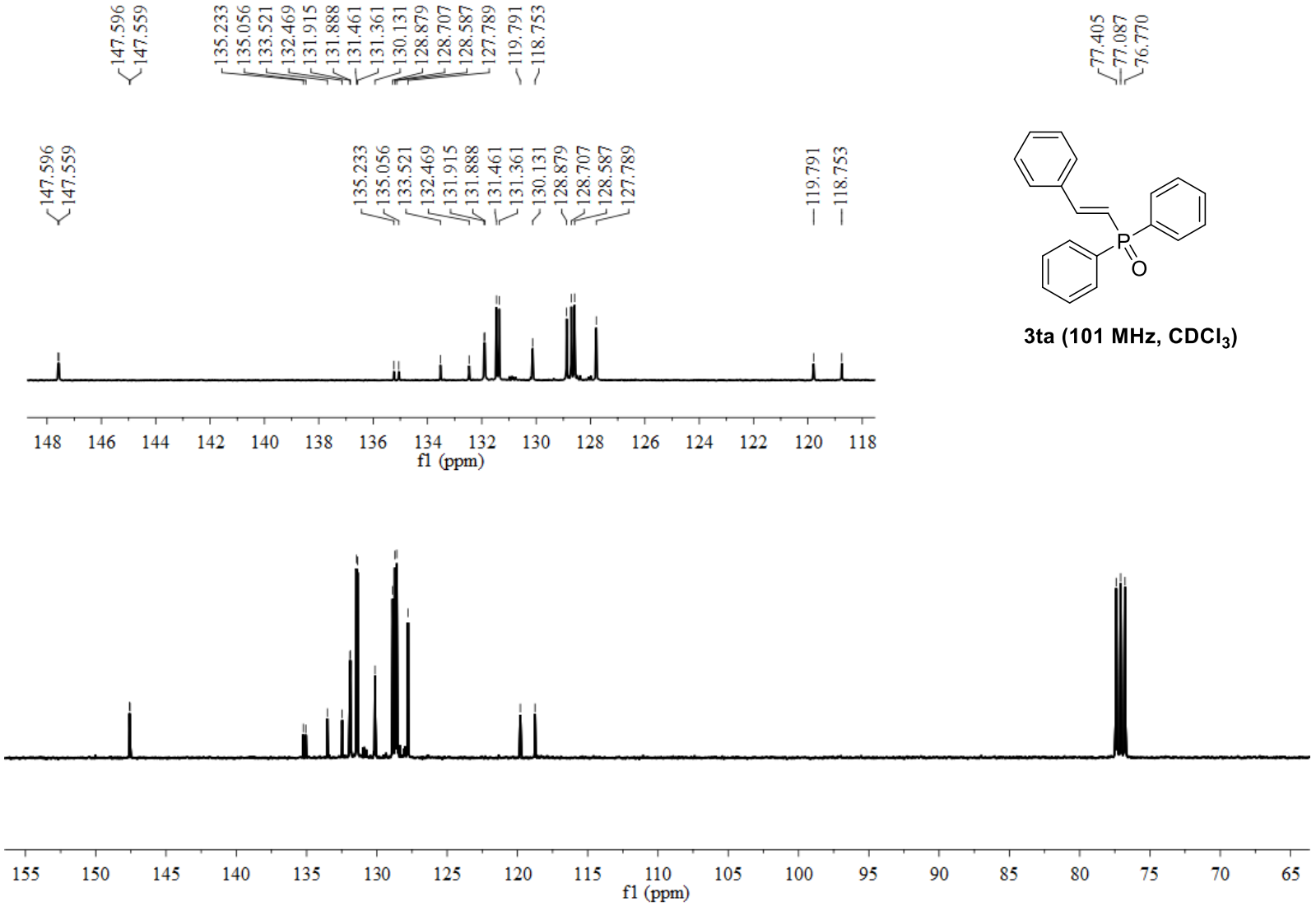



**3sa (376 MHz, $CDCl_3$)**

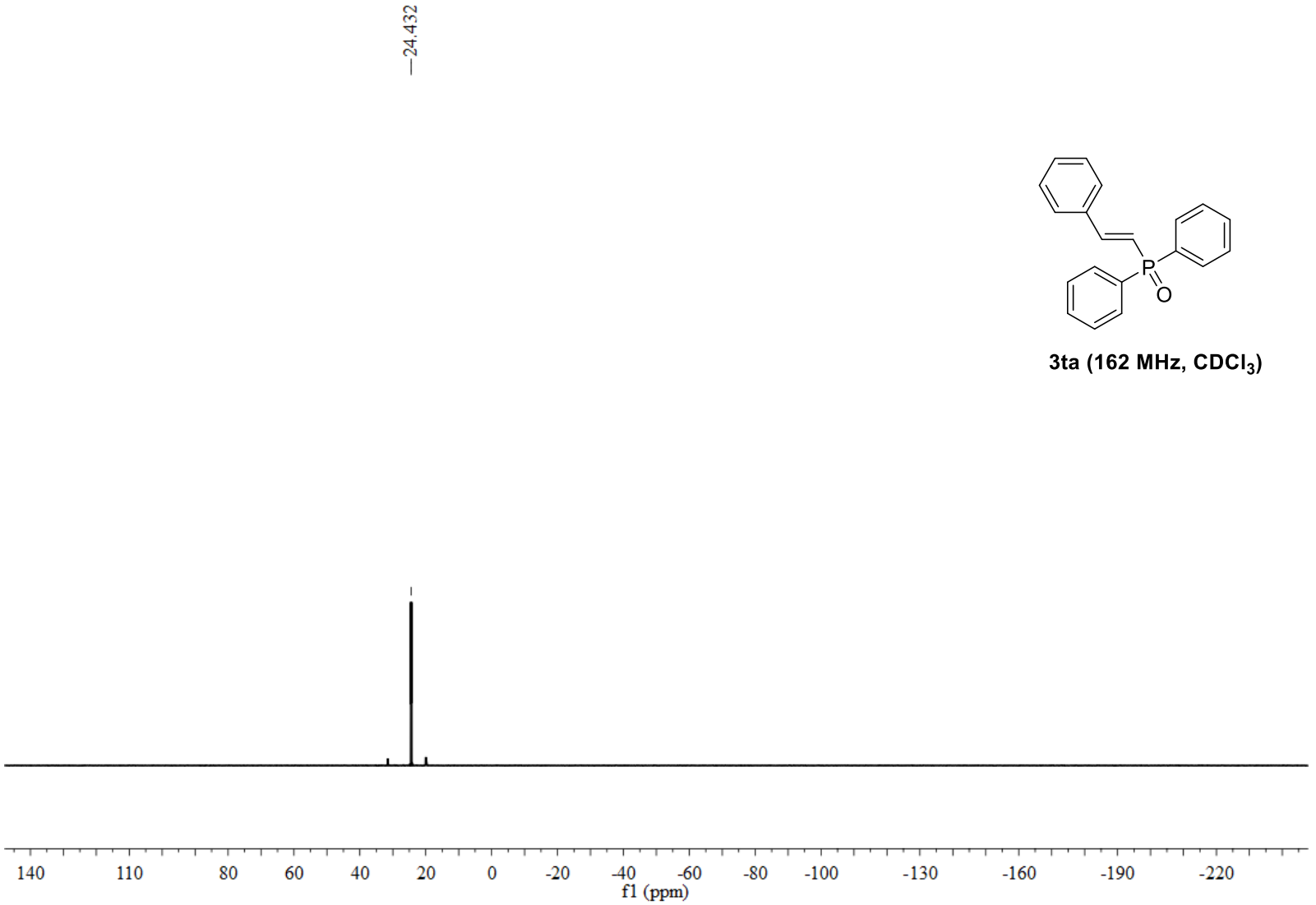



**3sa (162 MHz, $CDCl_3$)**

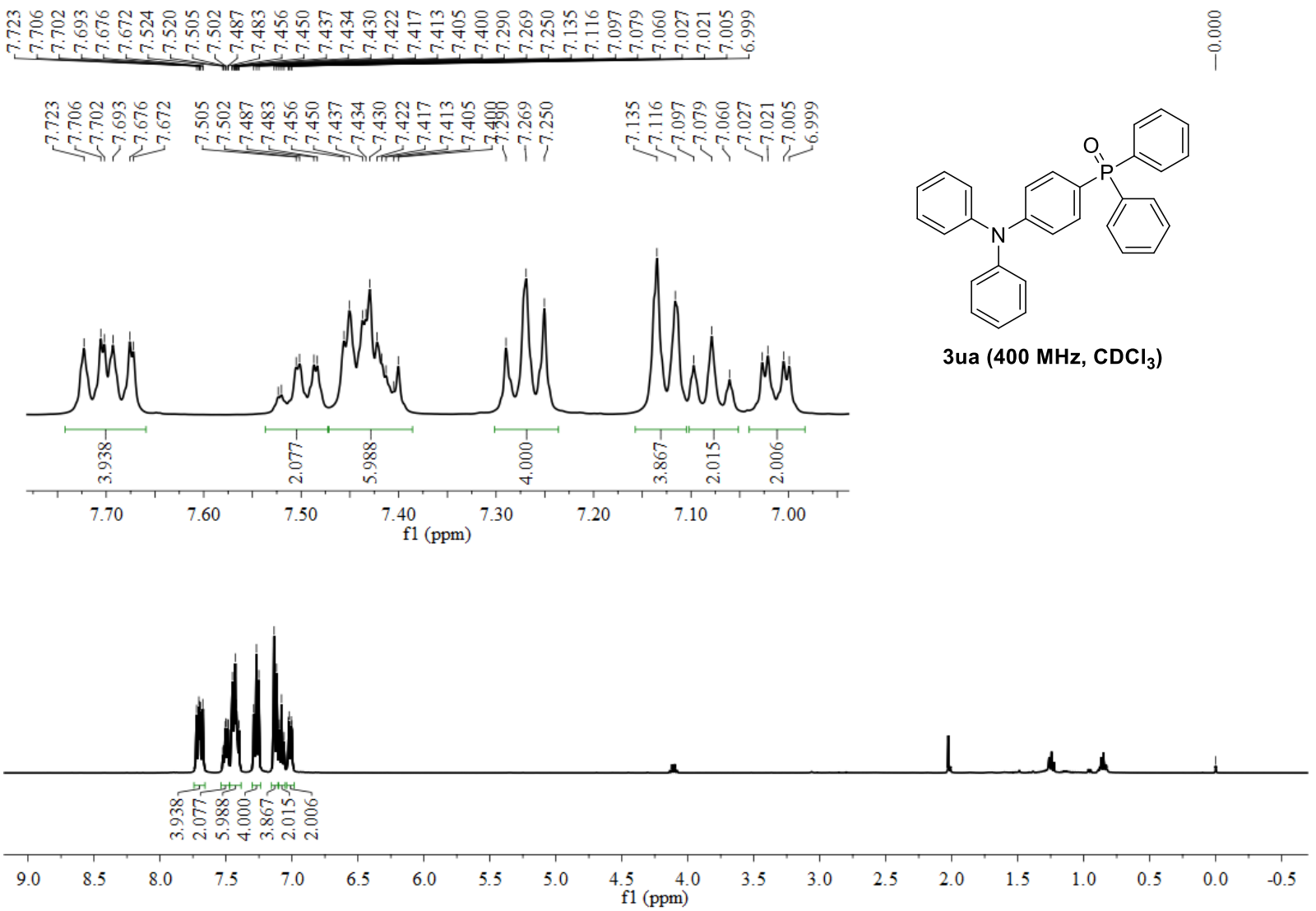

7.761
7.757
7.731
7.534
7.532
7.517
7.513
7.510
7.474
7.466
7.362
7.357
6.890
6.846
6.834
6.790
7.781
7.778
7.775
7.761
7.757
7.751
7.748
7.744
7.731
7.727
7.554
7.534
7.532
7.526
7.521
7.517
7.513
7.510
7.492
7.489
7.485
7.482
7.478
7.474
7.470
7.466
7.462
7.456
7.449
7.375
7.370
7.362
7.357
7.260
6.890
6.834
6.790
-0.006
P
O
3ta (400 MHz, CDCl3)
4.122
9.070
3.084
1.000
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.122
9.070
3.084
1.000
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)




**3ta (101 MHz, $CDCl_3$)**



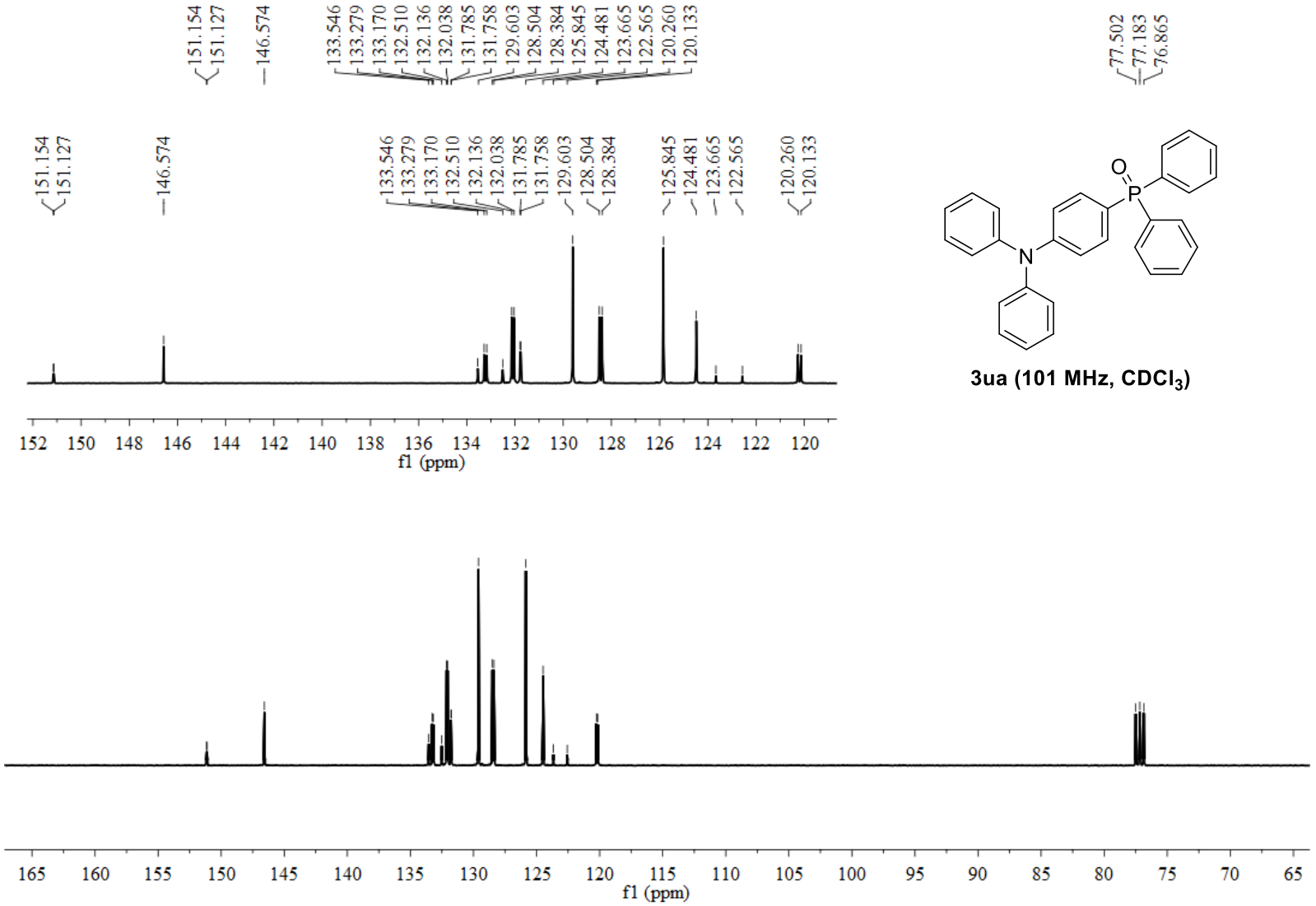

**3ta (162 MHz, $CDCl_3$)**



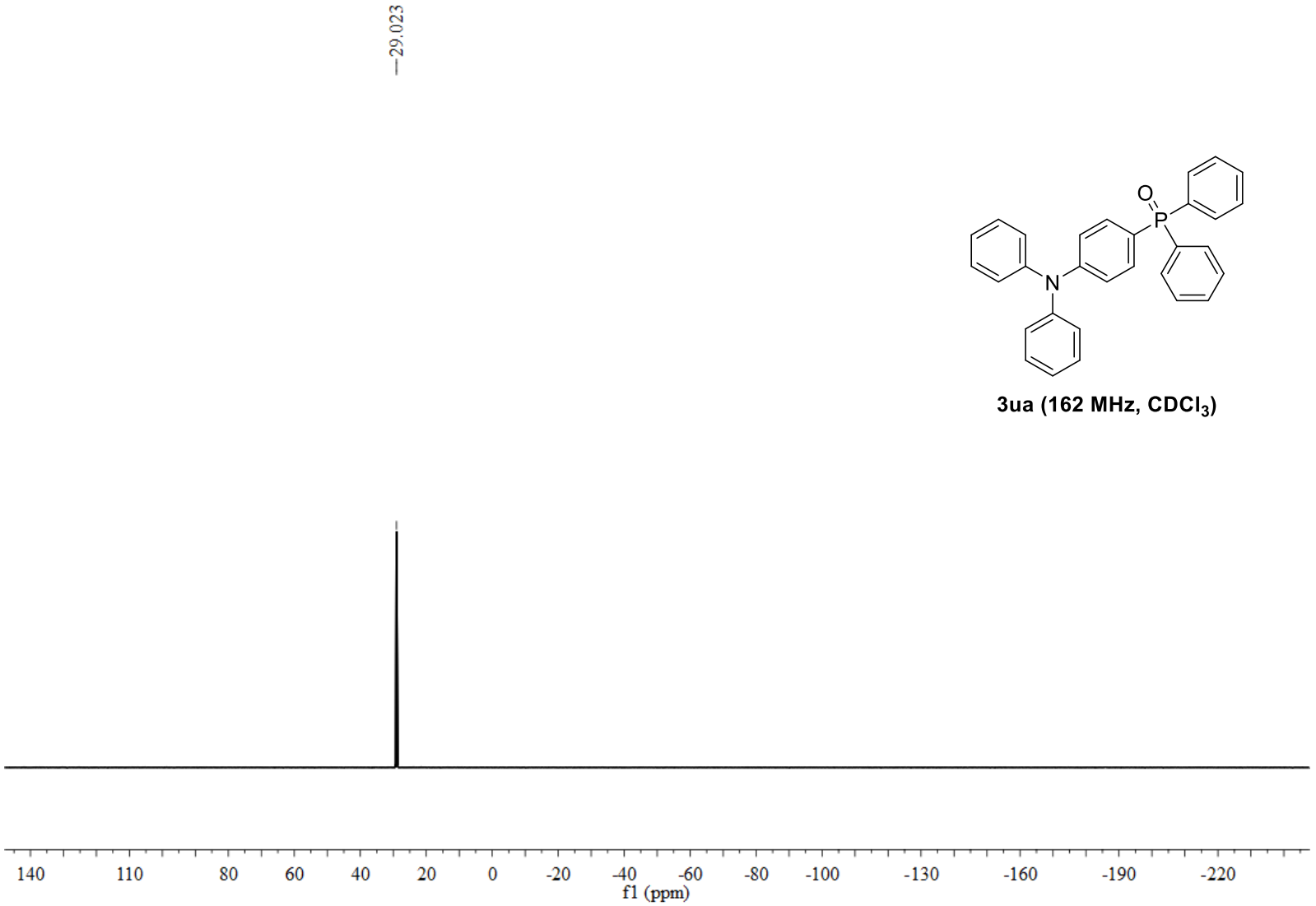




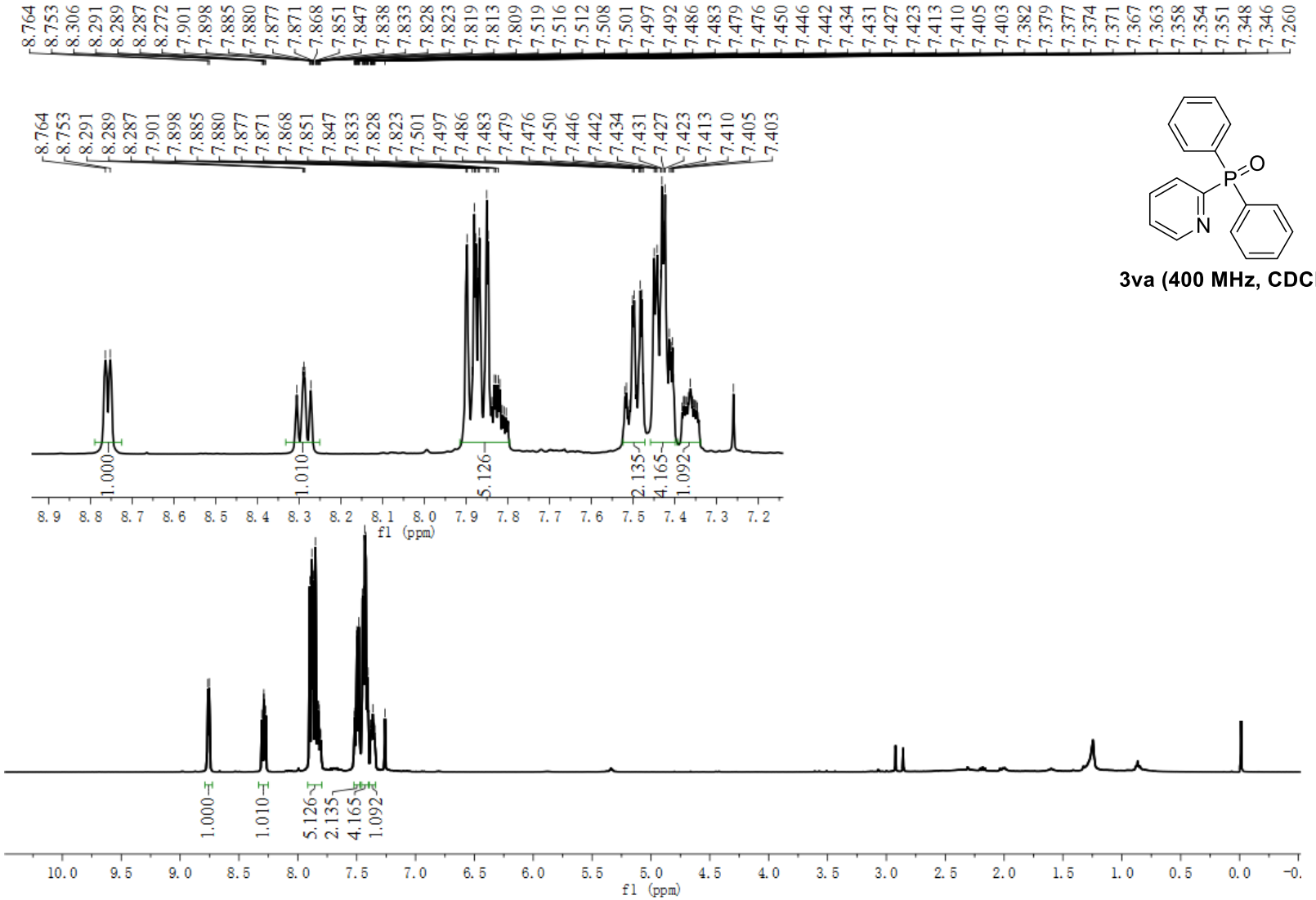
**3ua (400 MHz, $CDCl_3$)**

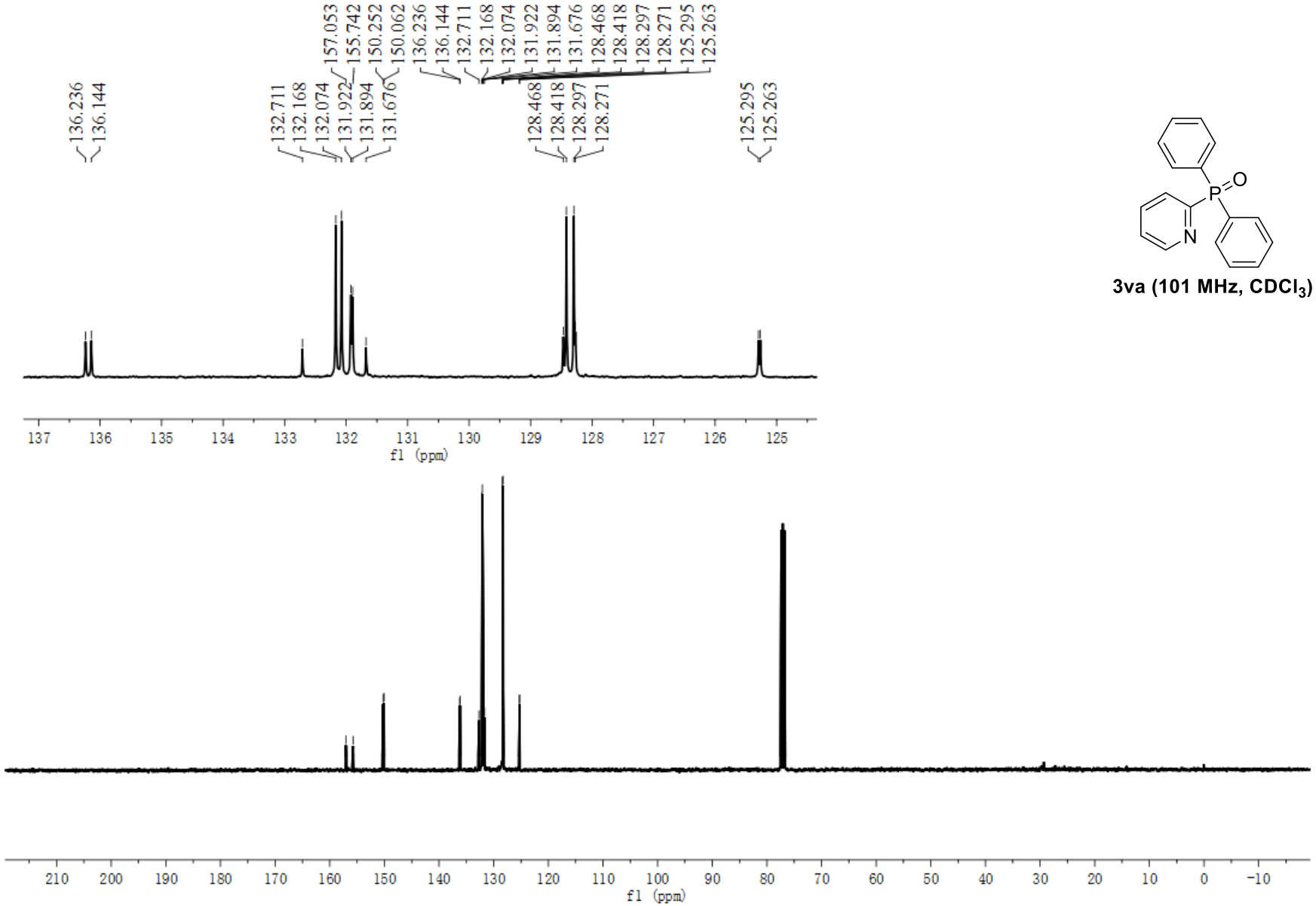



**3ua (101 MHz, $CDCl_3$)**




**3ua (162 MHz, $CDCl_3$)**

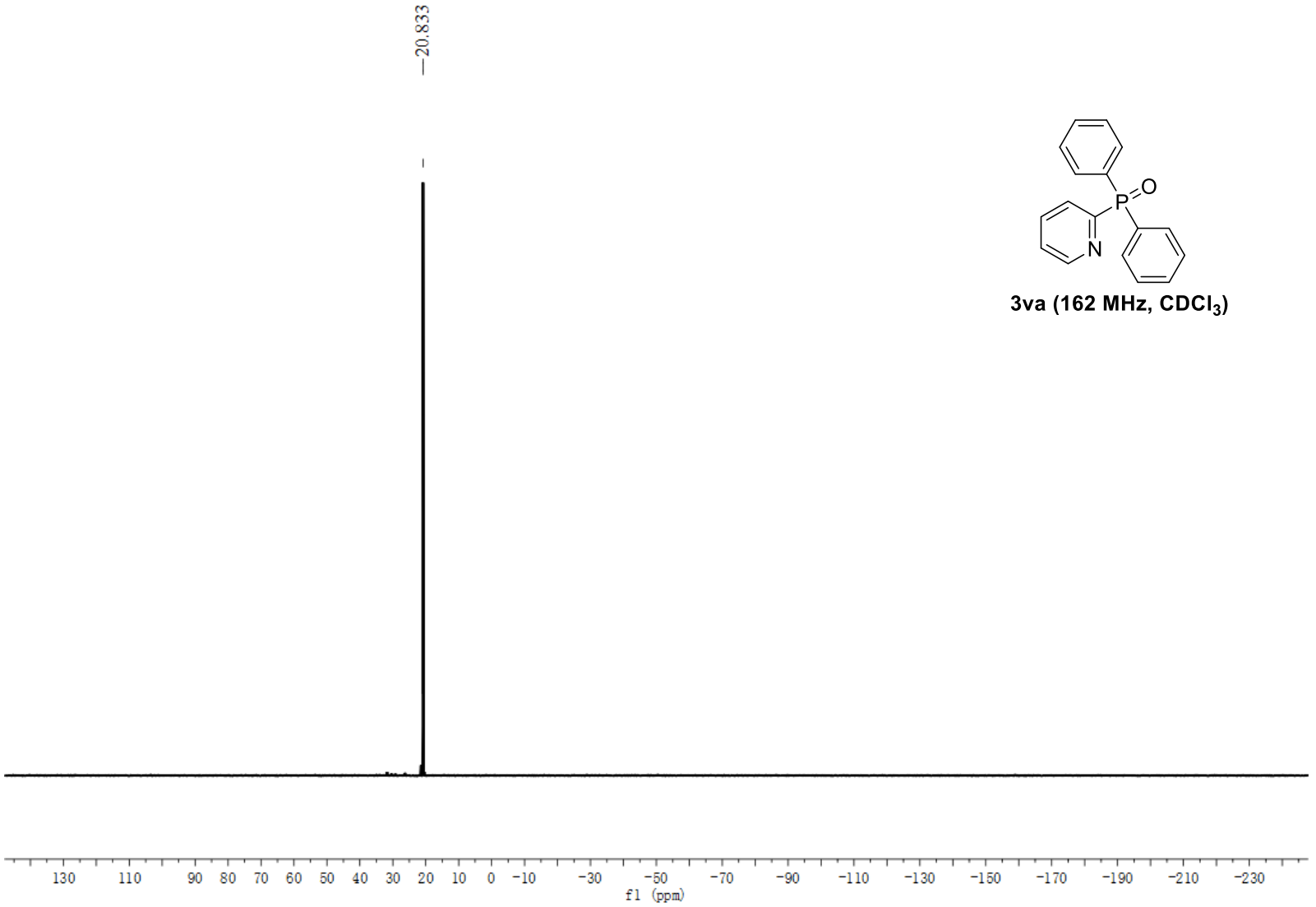

8.764 8.753 8.306 8.291 8.289 8.287 8.272 7.901 7.898 7.885 7.880 7.877 7.871 7.868 7.851 7.847 7.838 7.833 7.828 7.823 7.819 7.813 7.809 7.519 7.516 7.512 7.508 7.501 7.497 7.492 7.486 7.483 7.479 7.476 7.450 7.446 7.442 7.434 7.431 7.427 7.423 7.413 7.410 7.405 7.403 7.382 7.379 7.377 7.374 7.371 7.367 7.363 7.358 7.354 7.351 7.348 7.346 7.260
1.000 1.010 5.126 2.135 4.165 1.092
f1 (ppm)
3va (400 MHz, CDCl3)



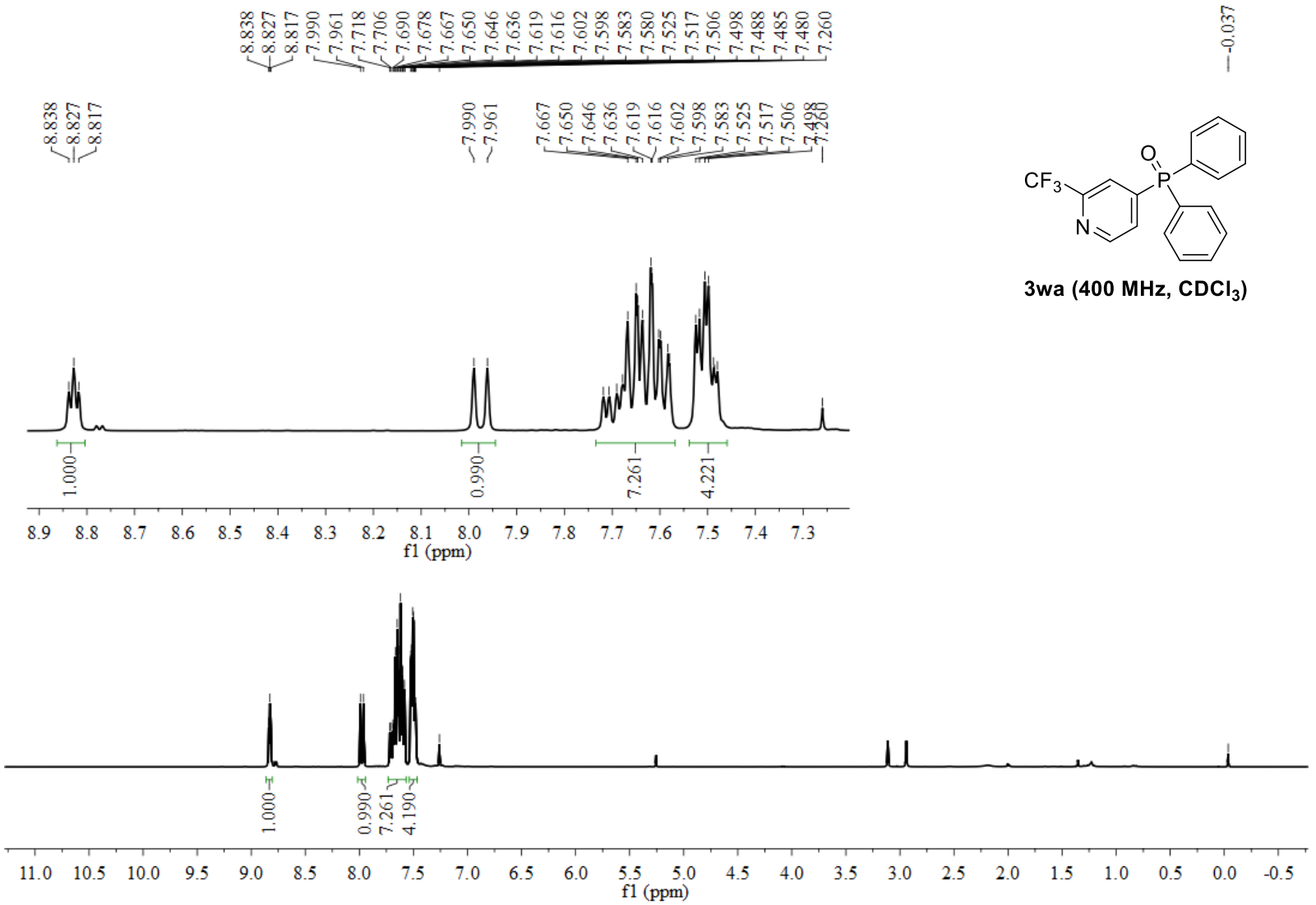




**3va (101 MHz, $CDCl_3$)**



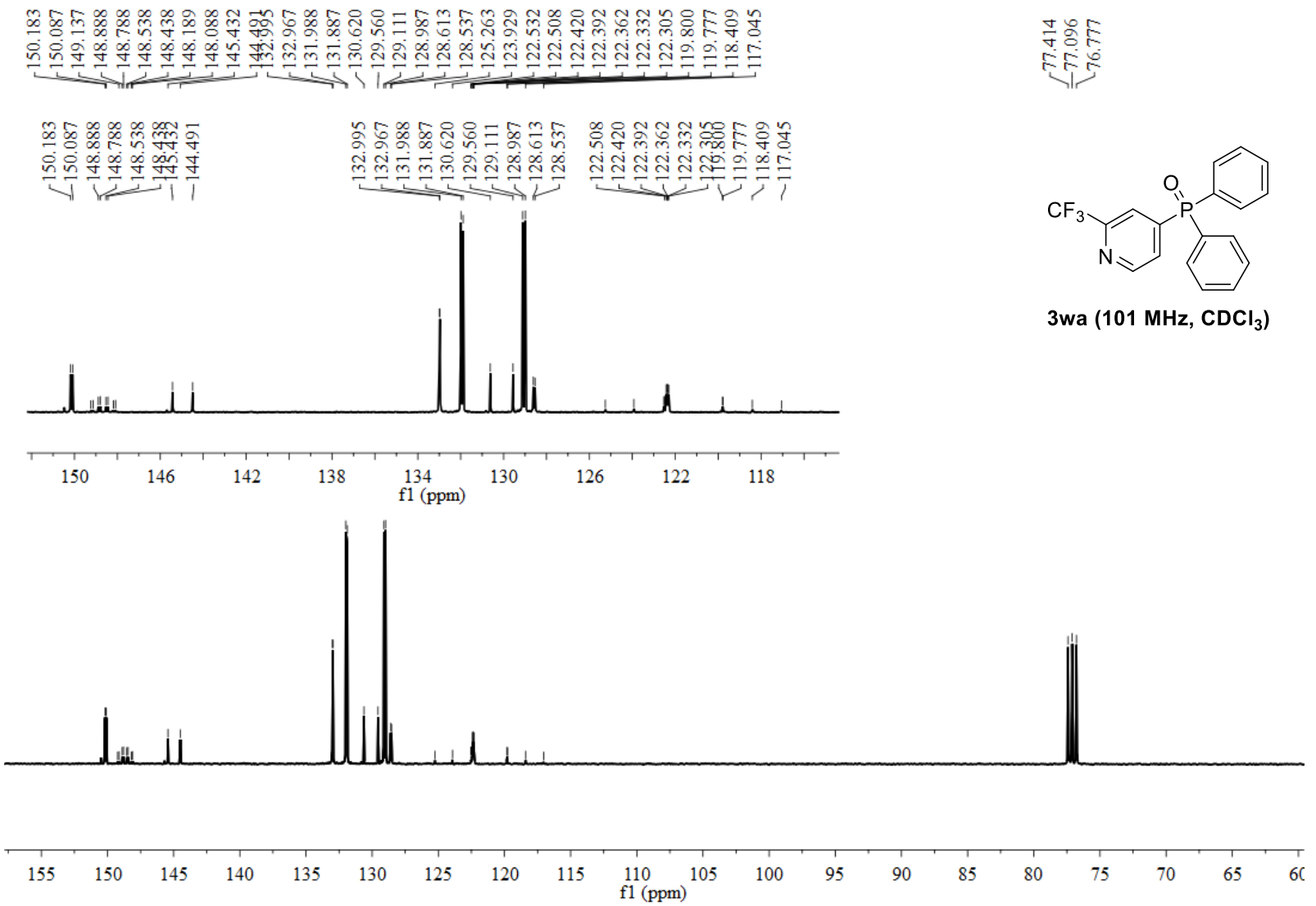

**3va (162 MHz, $CDCl_3$)**



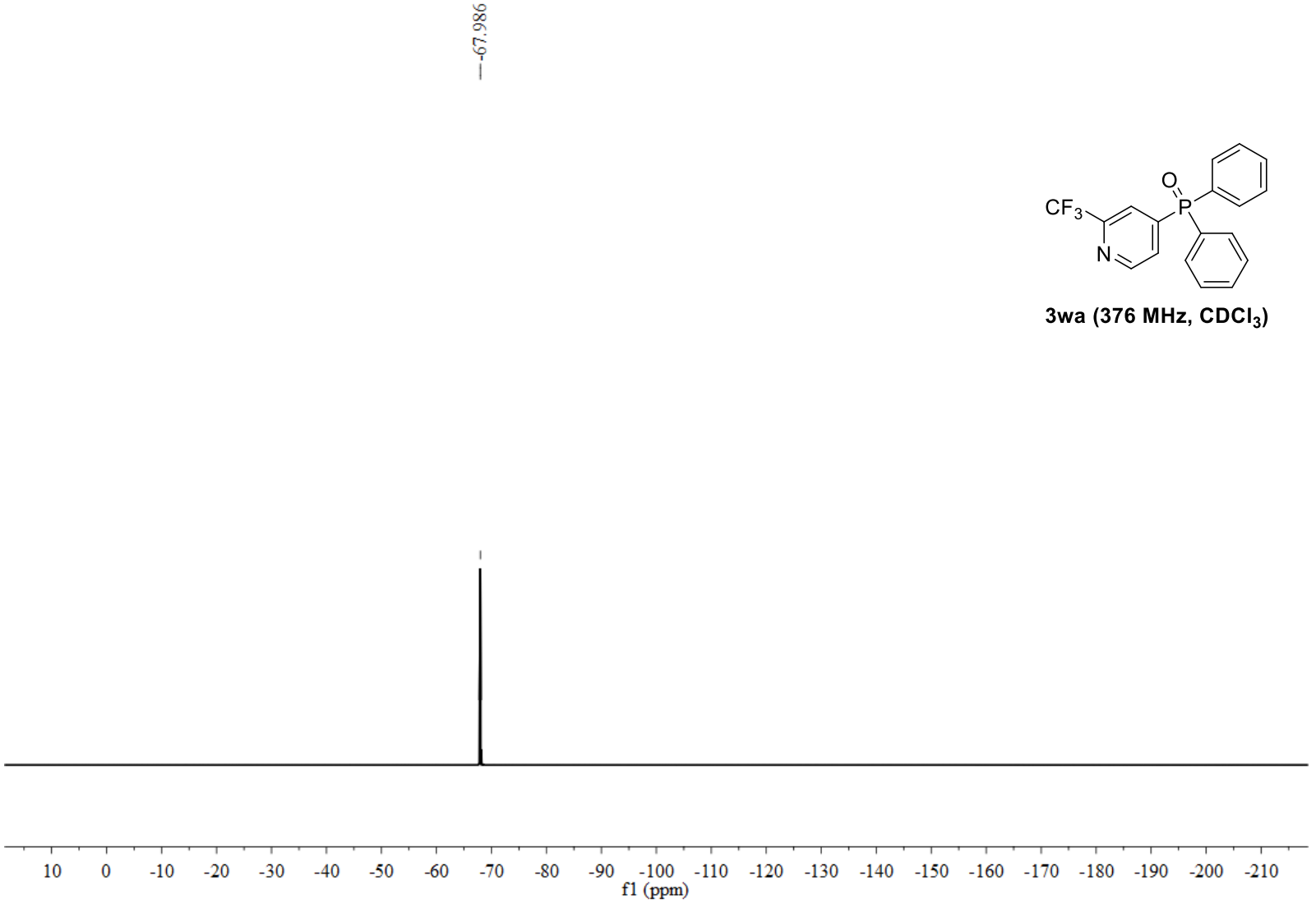




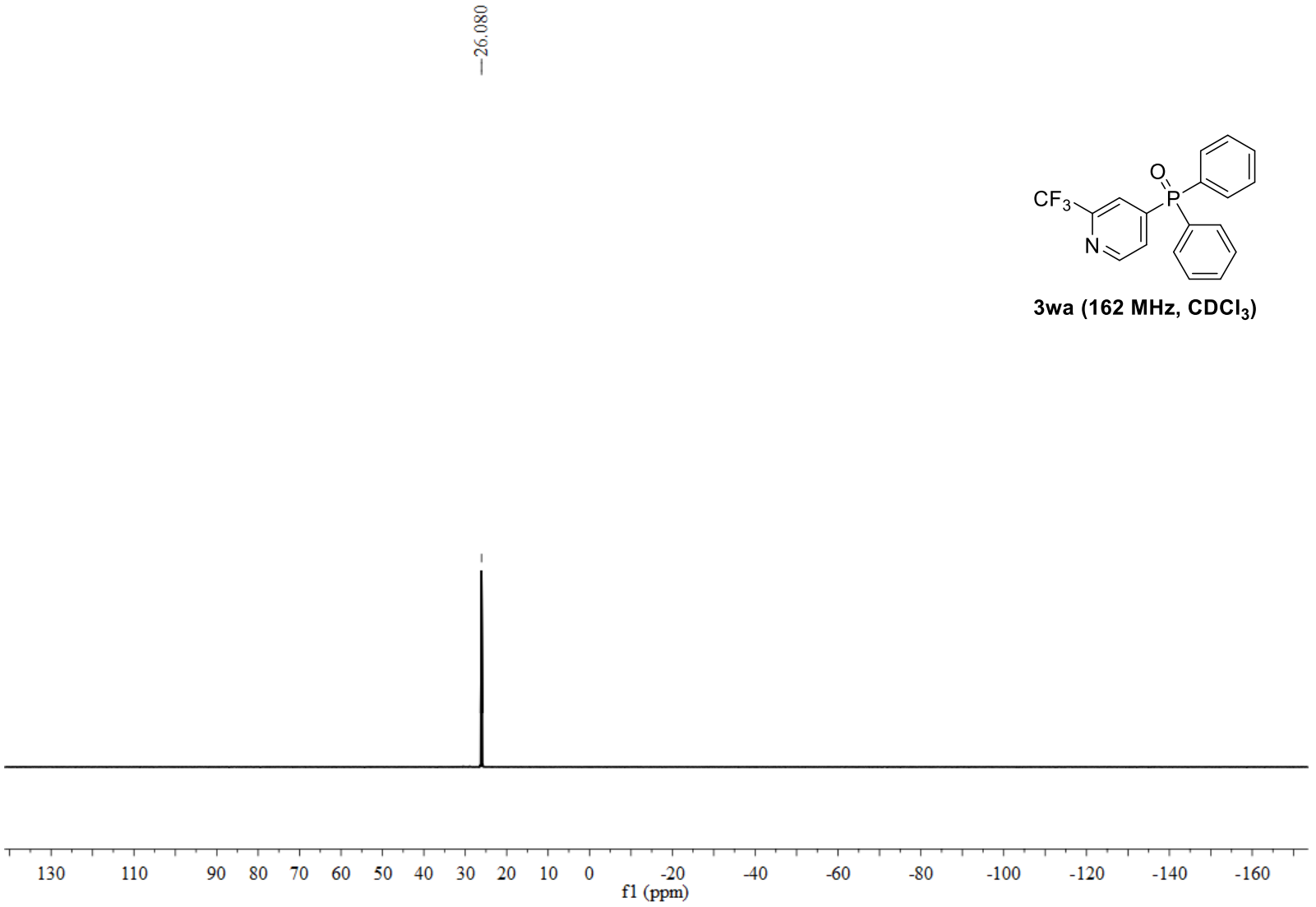
**3wa (400 MHz, $CDCl_3$)**



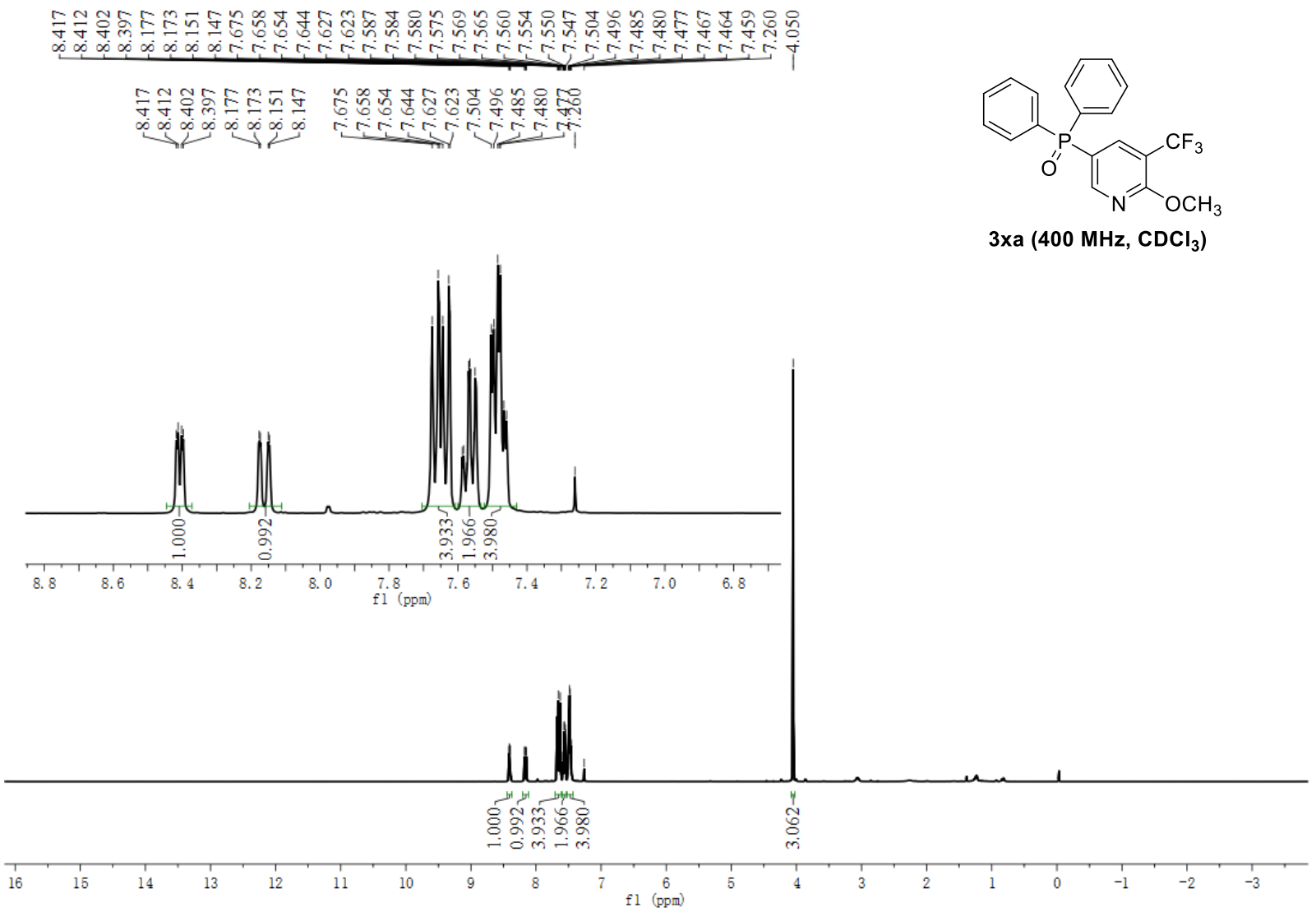

**3wa (101 MHz, $CDCl_3$)**




**3wa (376 MHz, $CDCl_3$)**



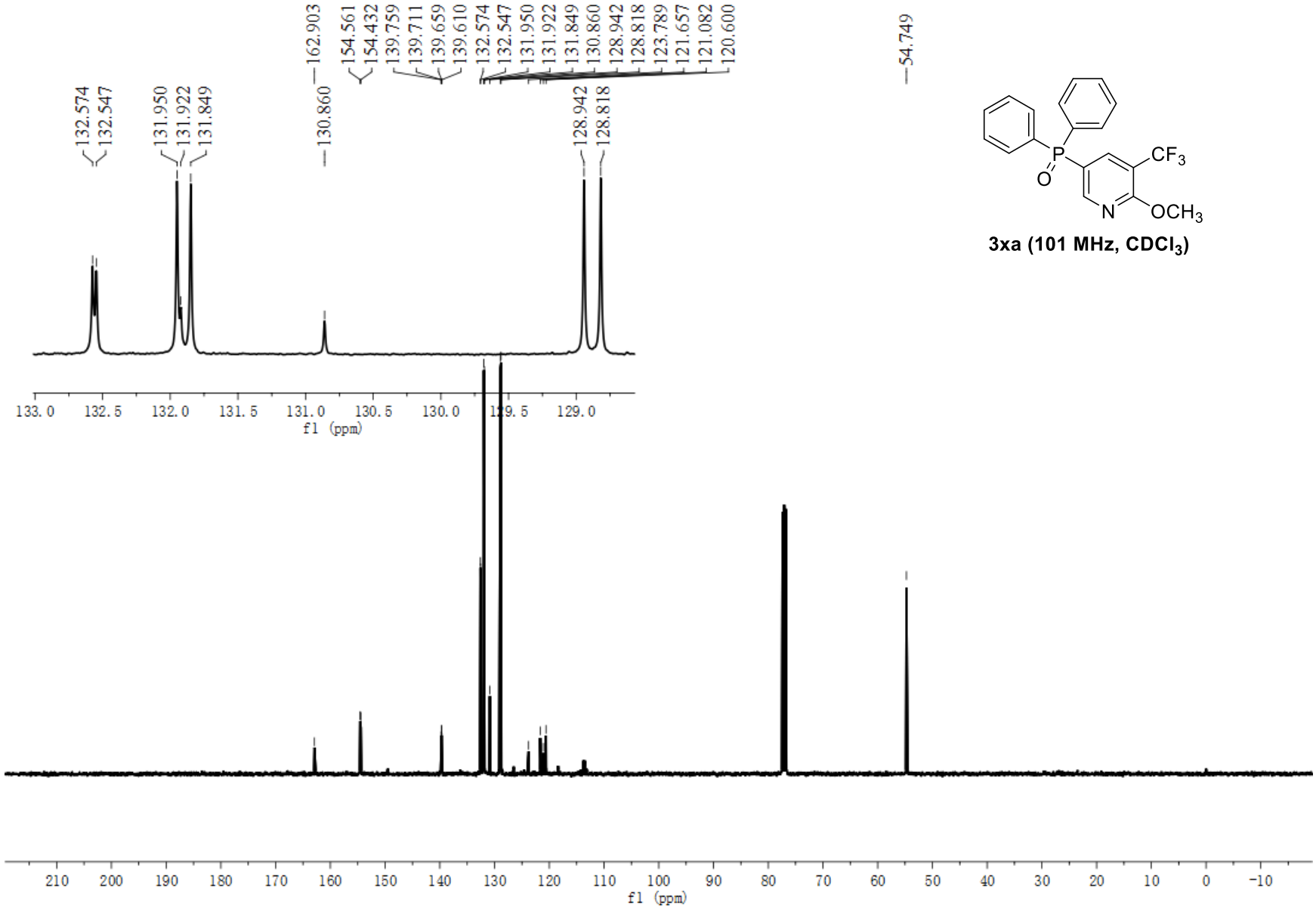

**3wa (162 MHz, $CDCl_3$)**



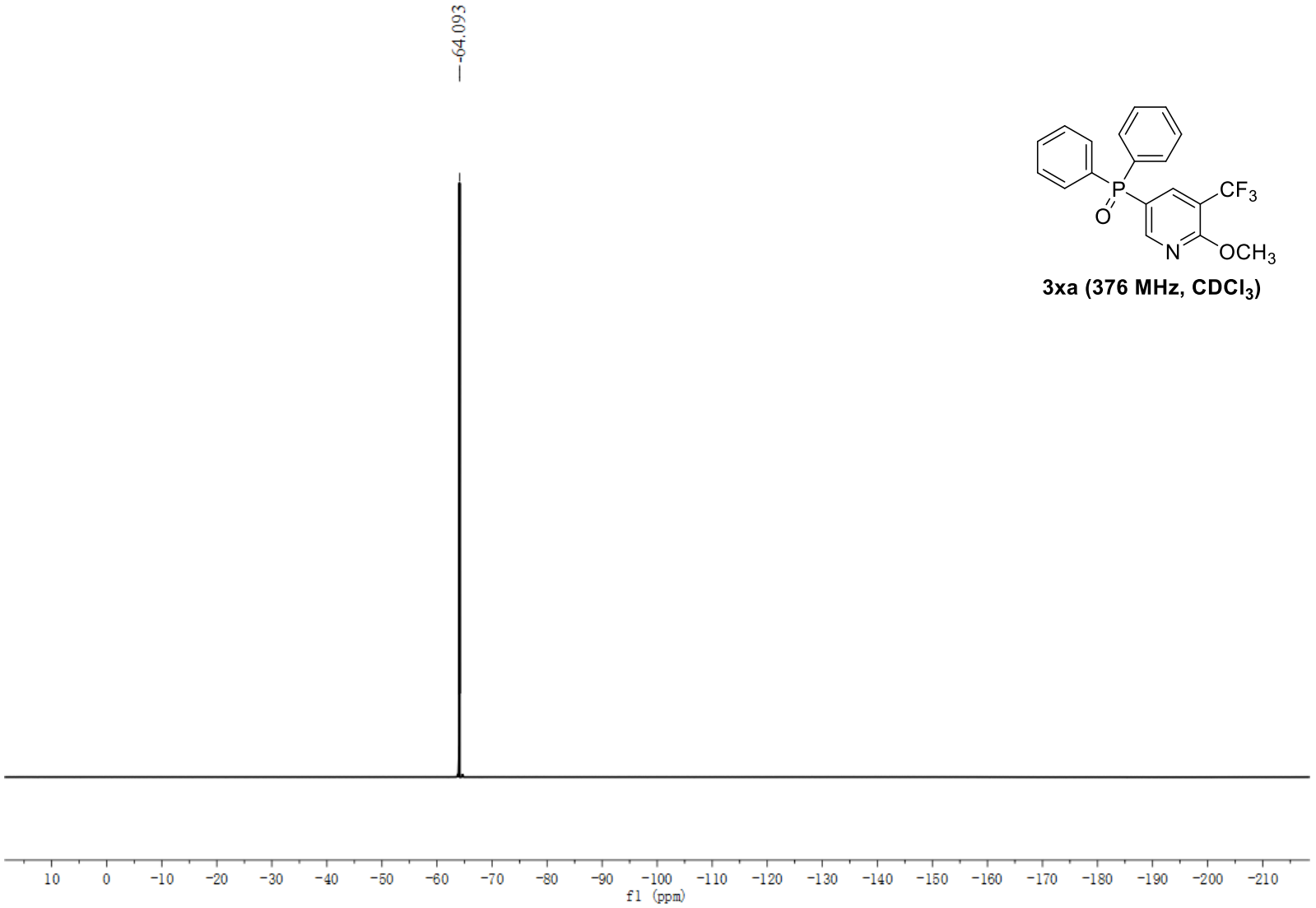




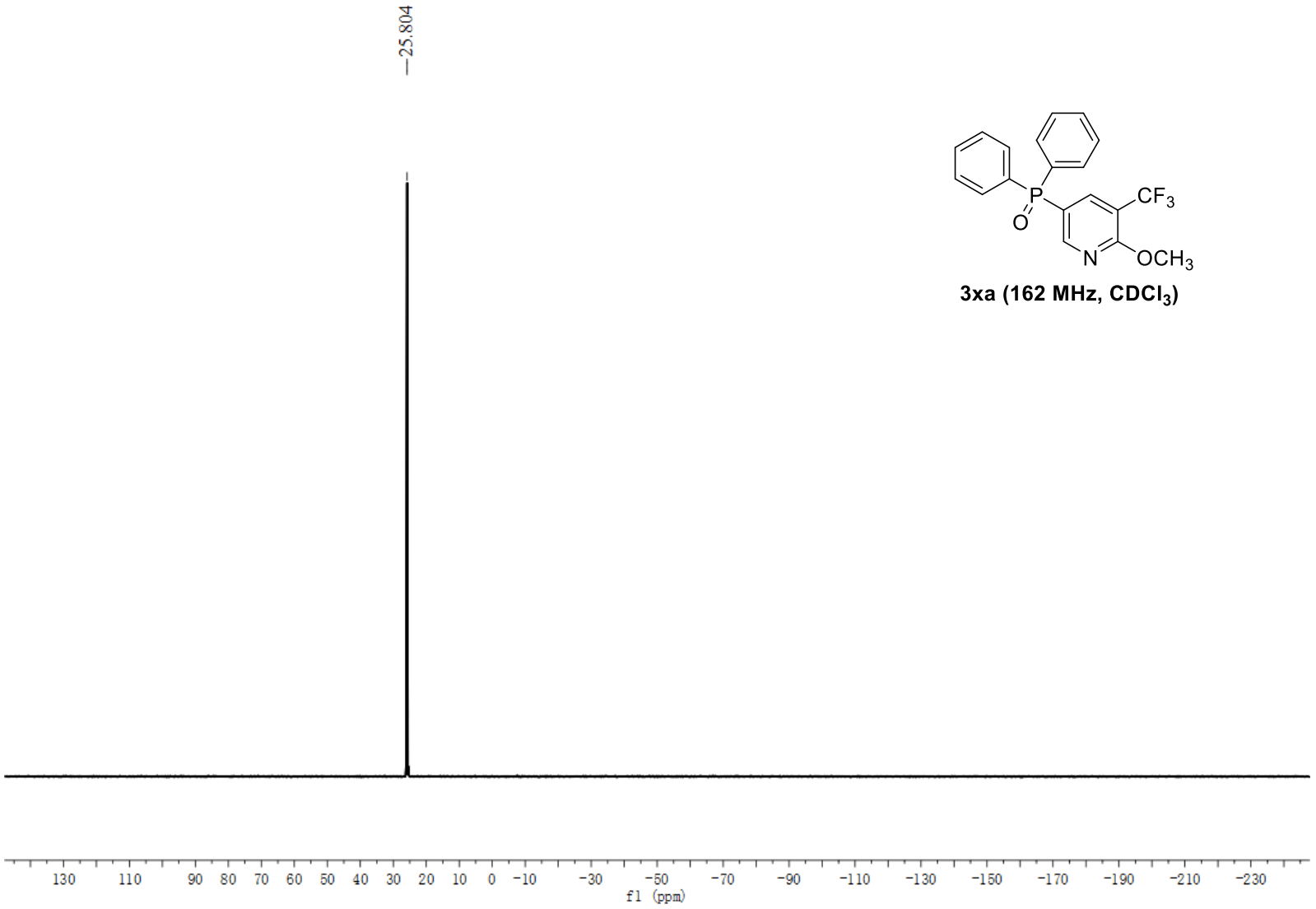
**3xa (400 MHz, $CDCl_3$)**



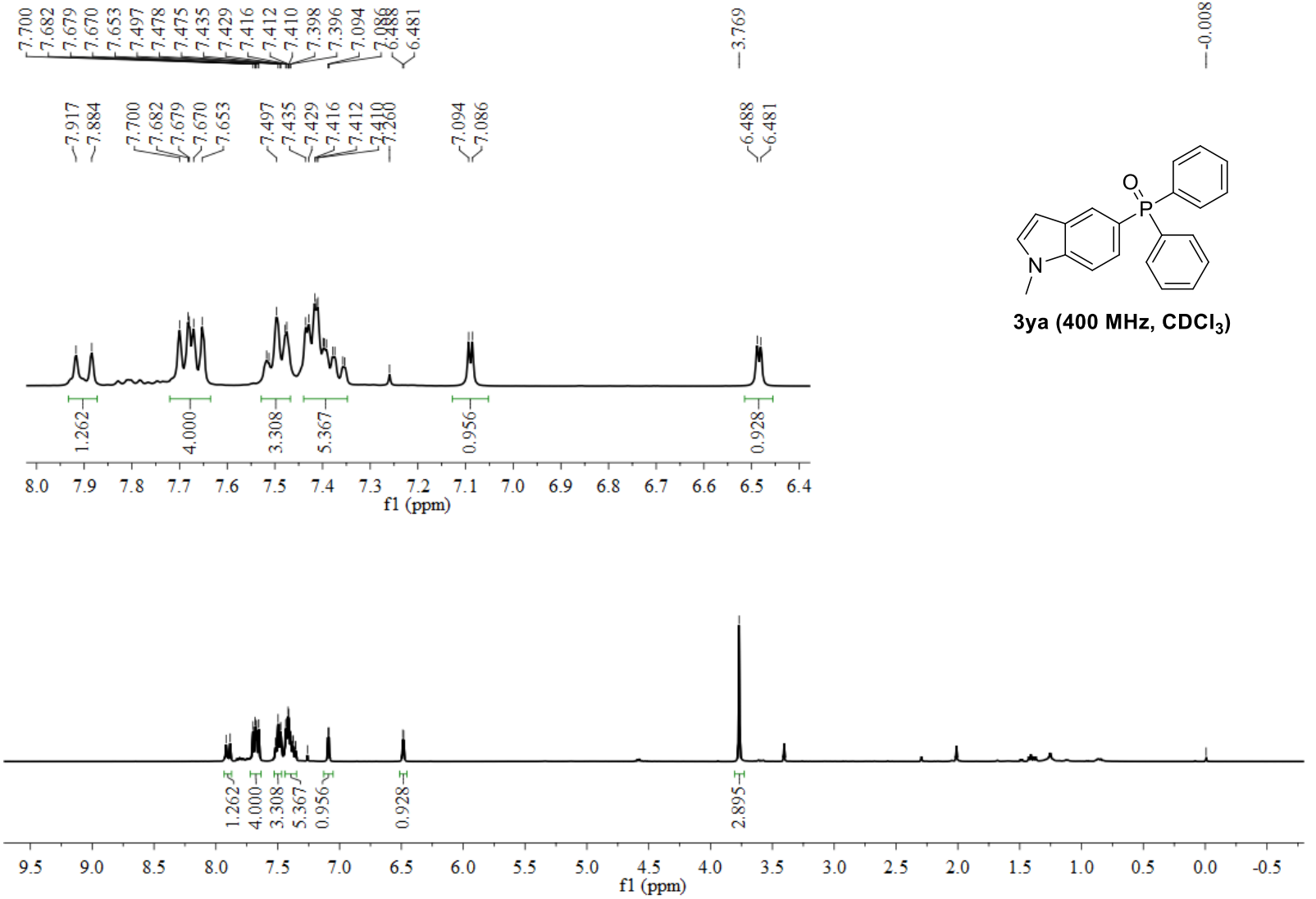

**3xa (101 MHz, $CDCl_3$)**



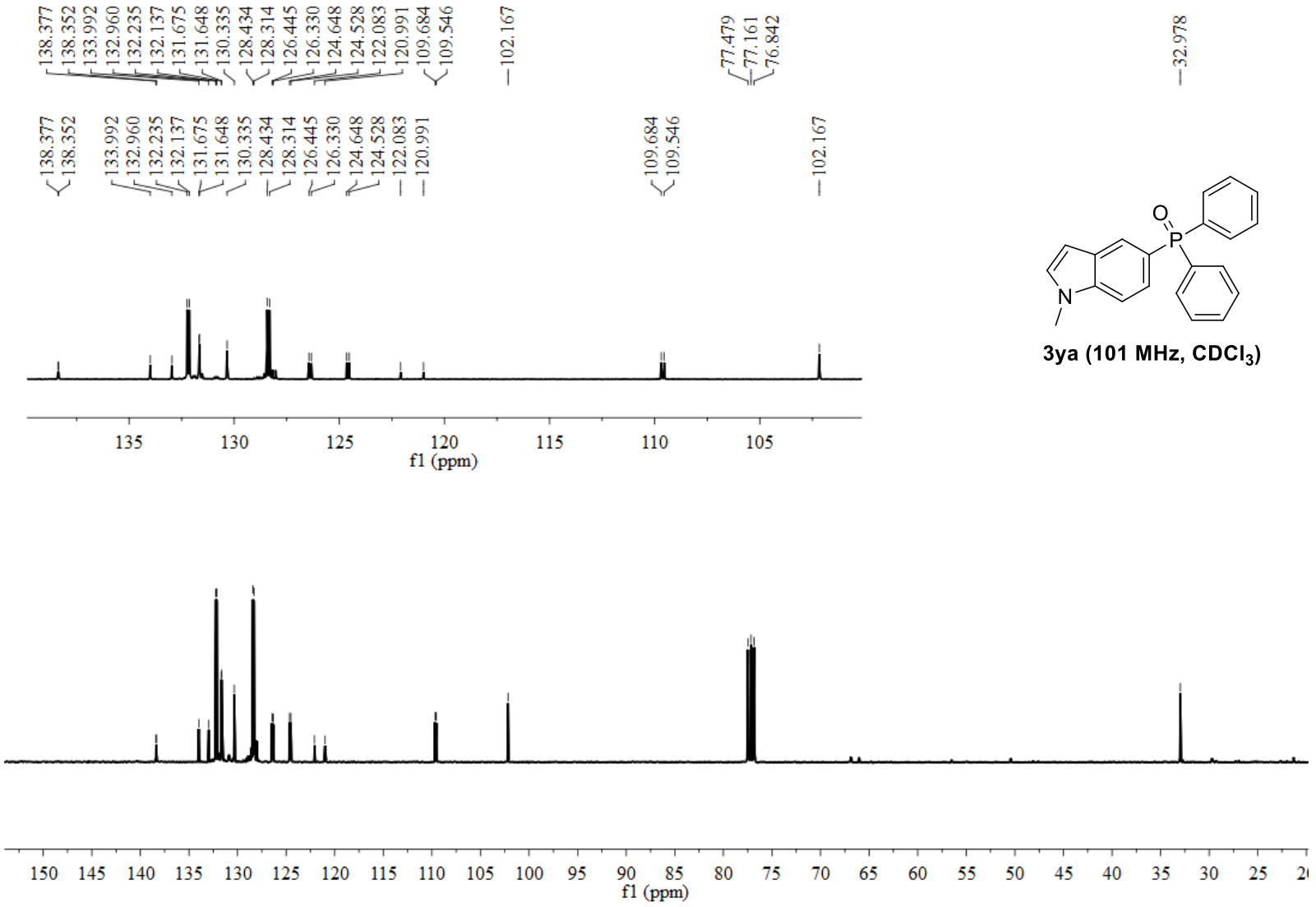

**3xa (376 MHz, $CDCl_3$)**



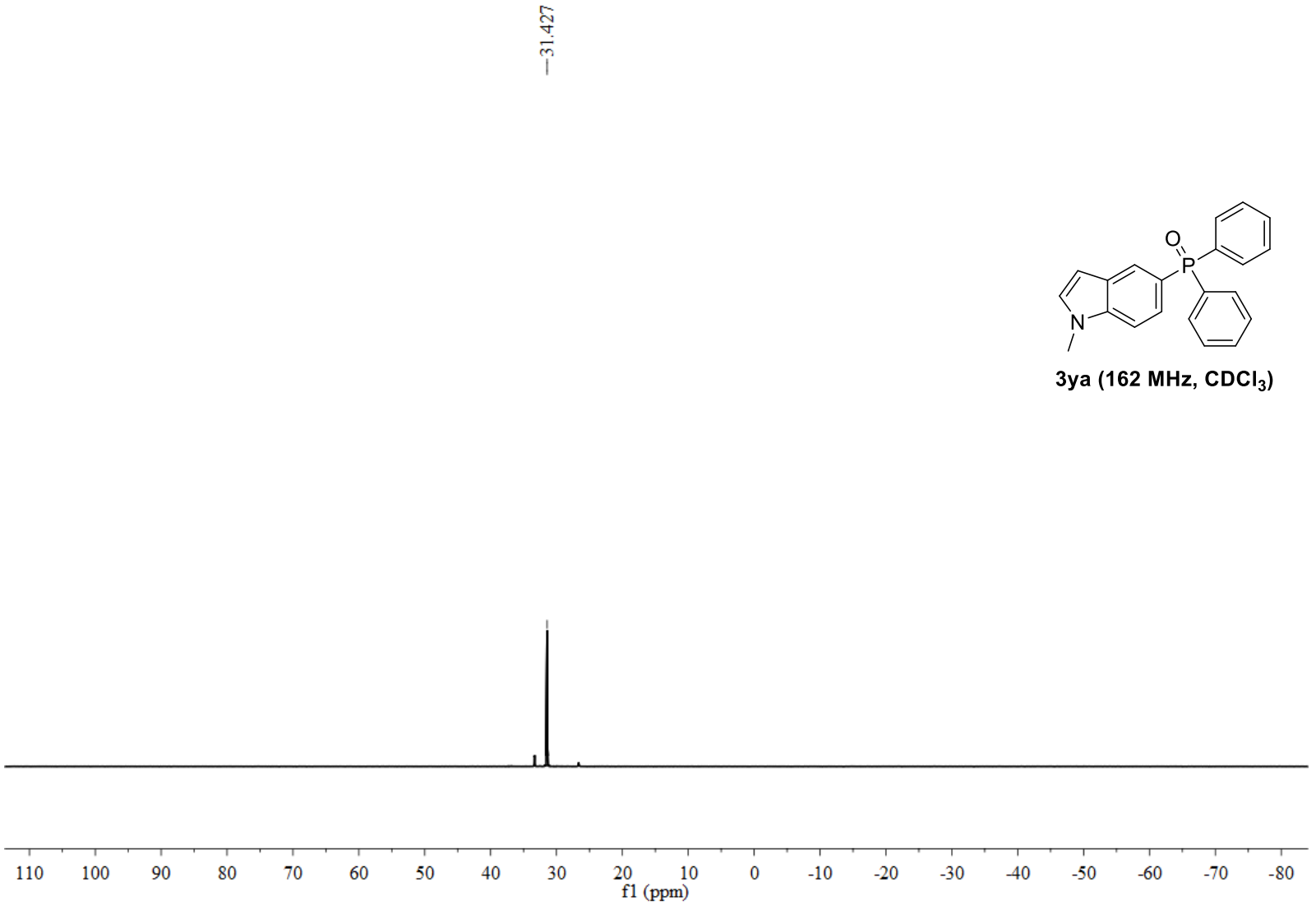

**3xa (162 MHz, $CDCl_3$)**



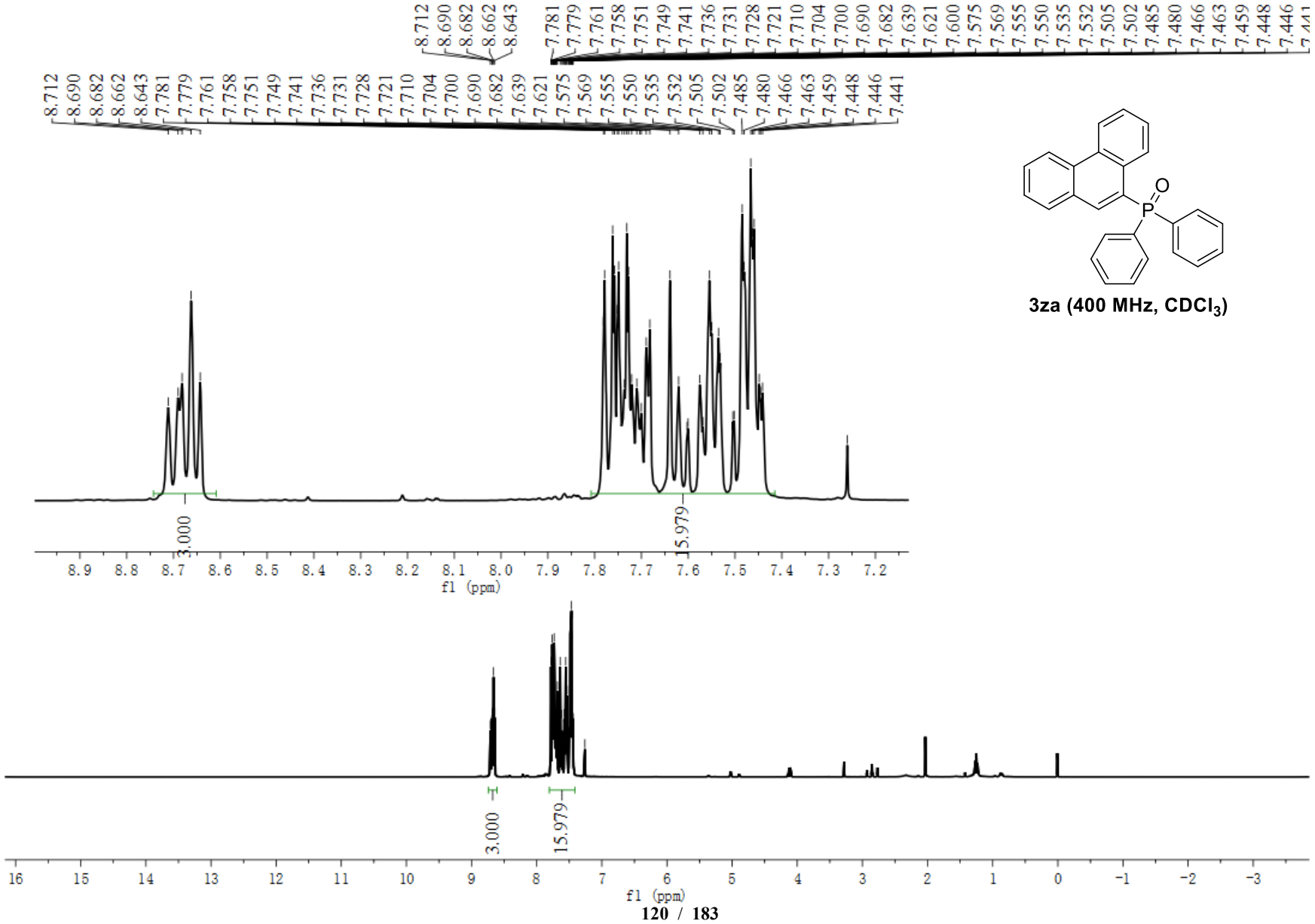

**3ya (400 MHz, $CDCl_3$)**



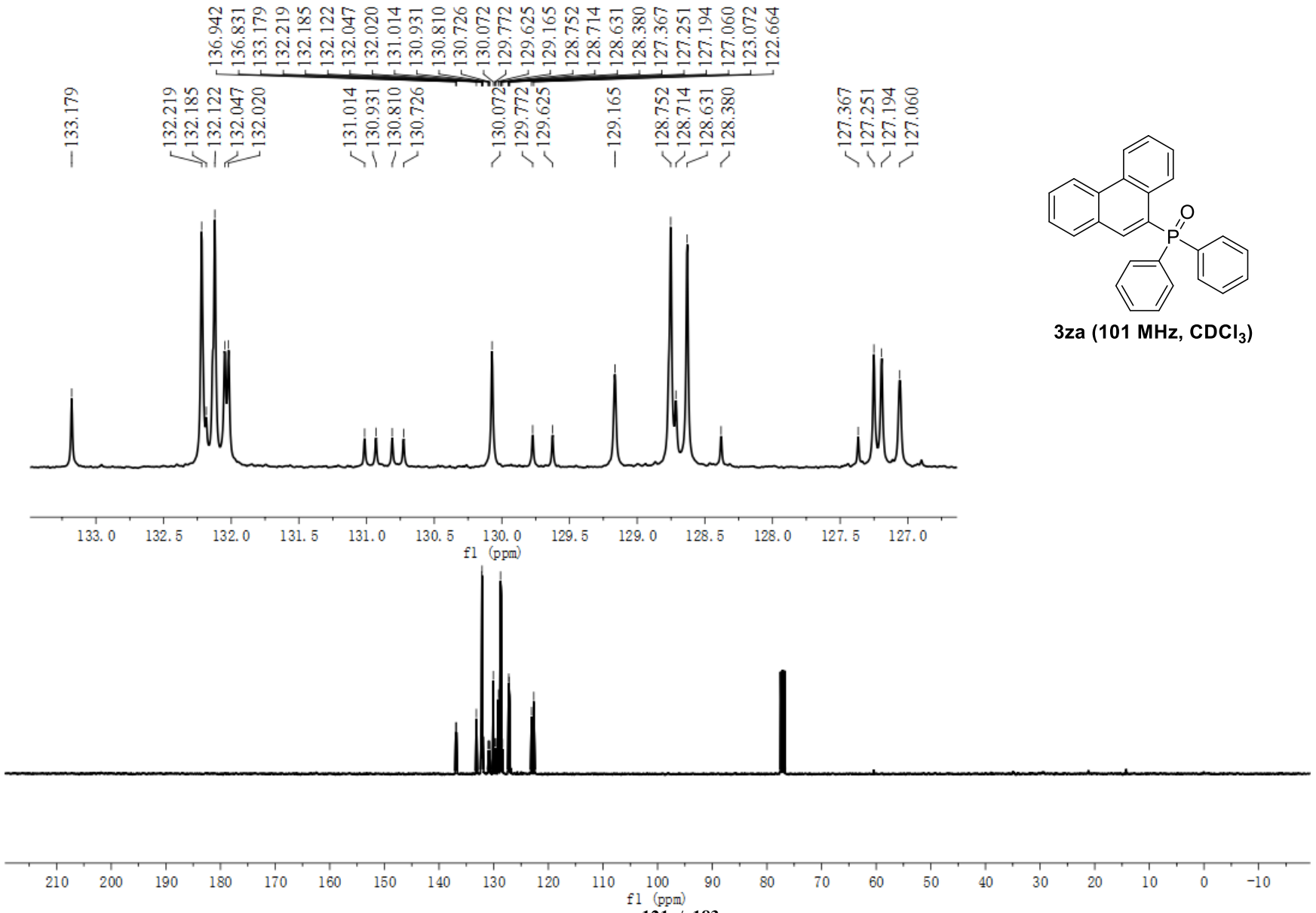

**3ya (101 MHz, $CDCl_3$)**

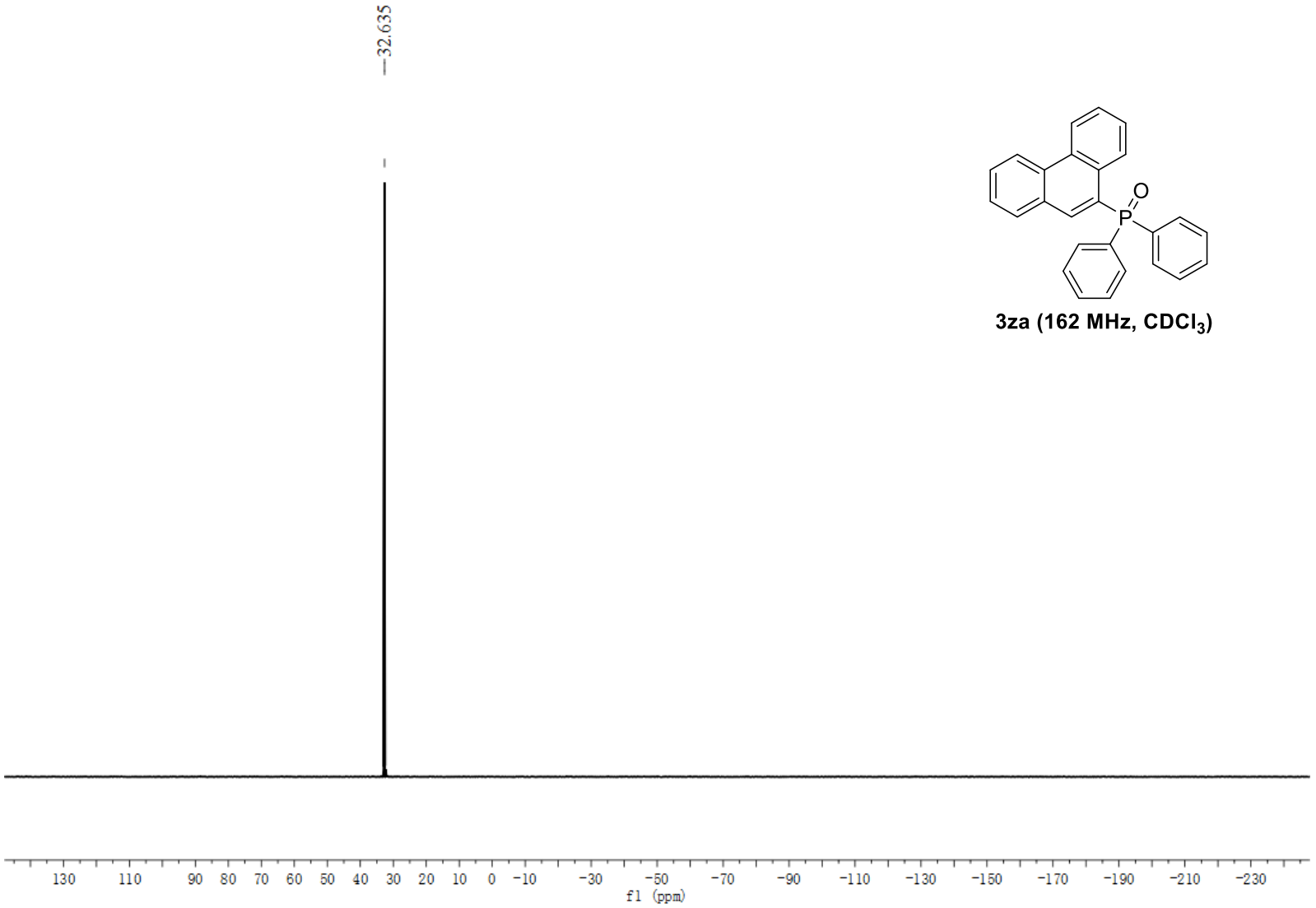



**3ya (162 MHz, $CDCl_3$)**




**3za (400 MHz, $CDCl_3$)**

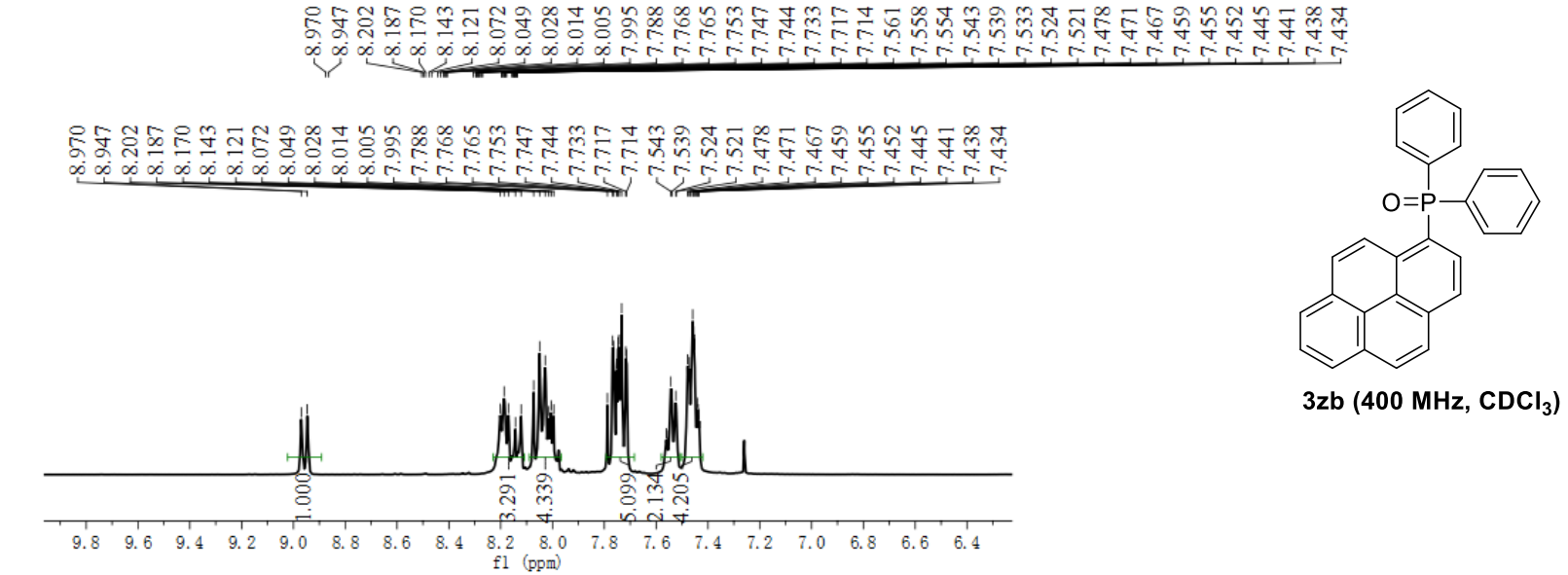

136.942
136.831
133.179
132.219
132.185
132.122
132.047
132.020
131.014
130.931
130.810
130.726
130.072
129.772
129.625
129.165
128.752
128.714
128.631
128.380
127.367
127.251
127.194
127.060
123.072
122.664
133.179
132.219
132.185
132.122
132.047
132.020
131.014
130.931
130.810
130.726
130.072
129.772
129.625
129.165
128.752
128.714
128.631
128.380
127.367
127.251
127.194
127.060
O
P
3za (101 MHz, CDCl3)
133.0
132.5
132.0
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)







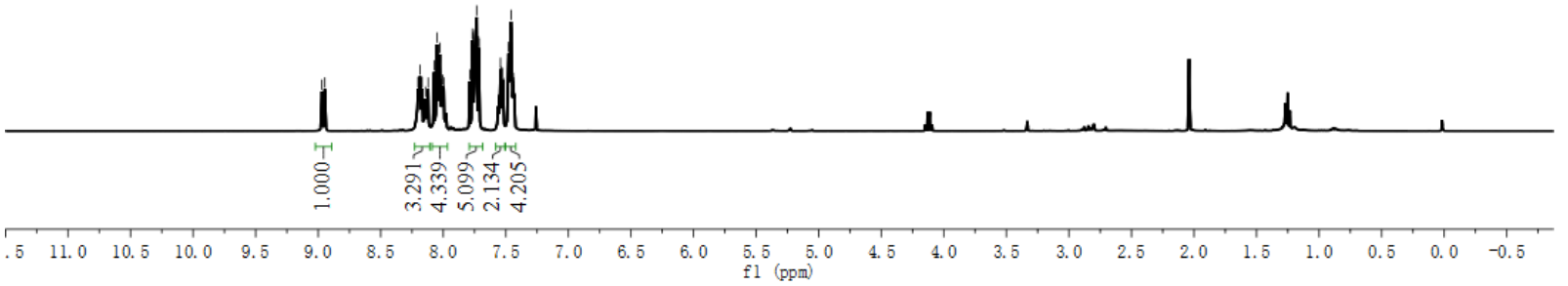
**3za (162 MHz, $CDCl_3$)**

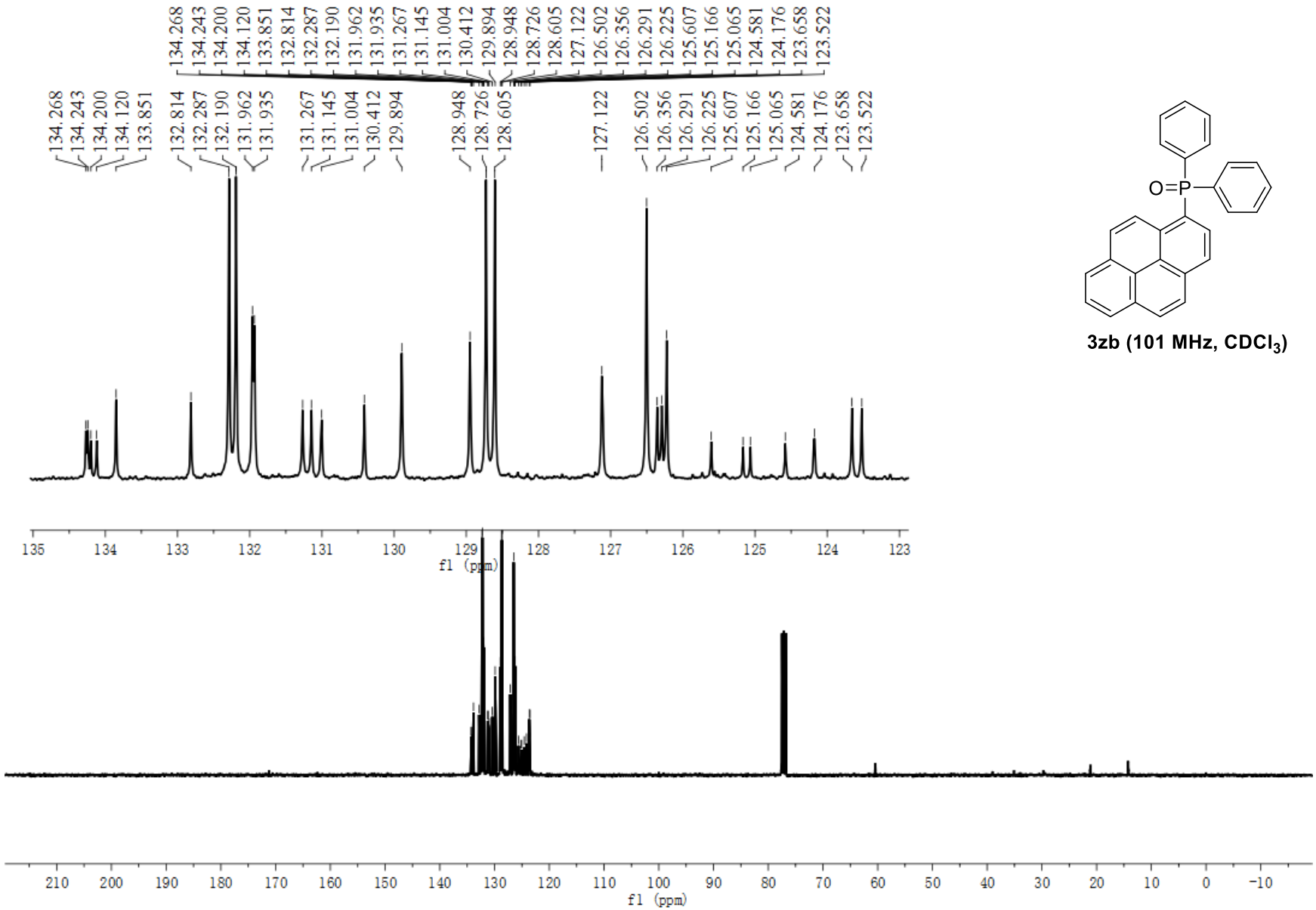






**3zb (400 MHz, $CDCl_3$)**

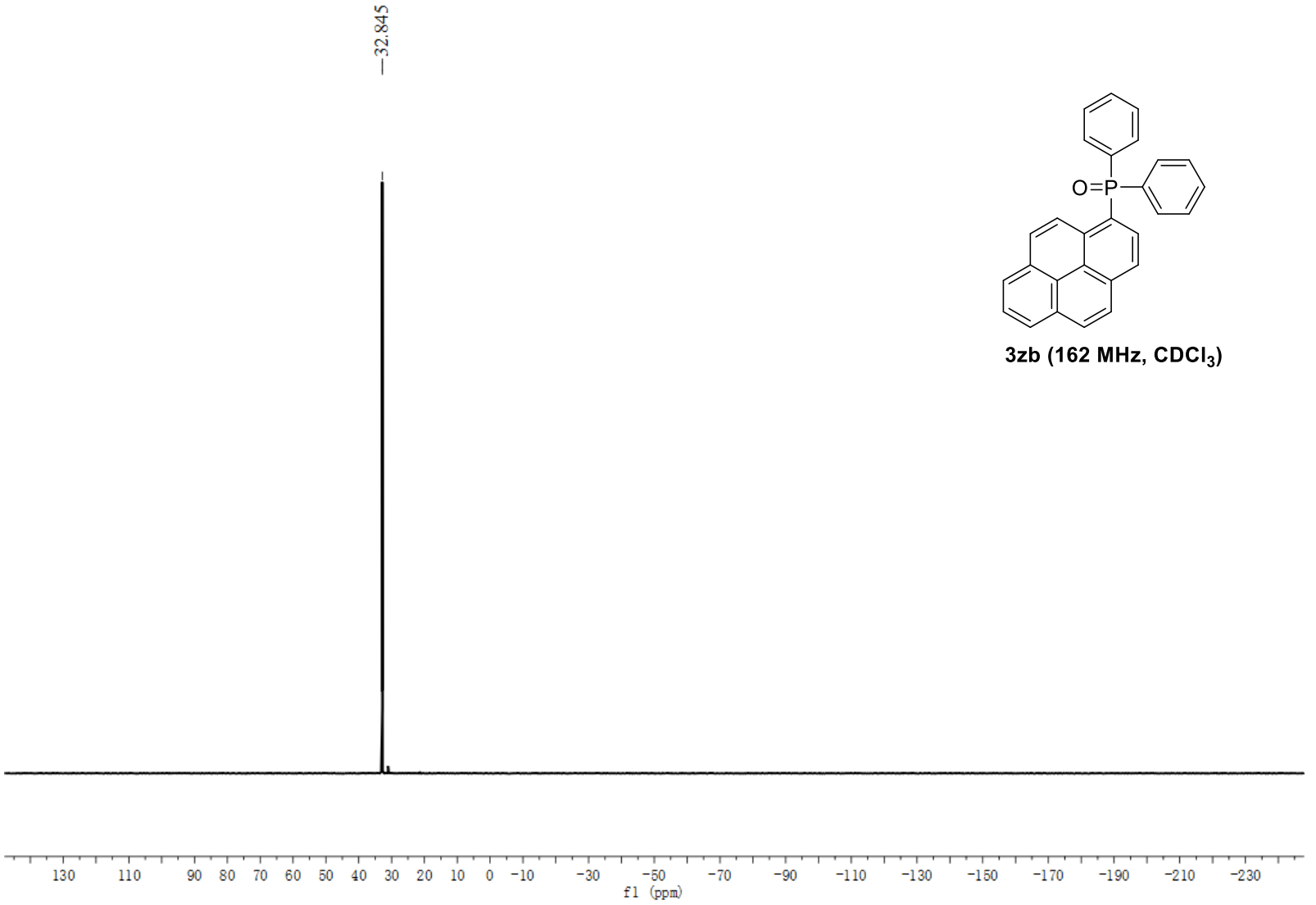




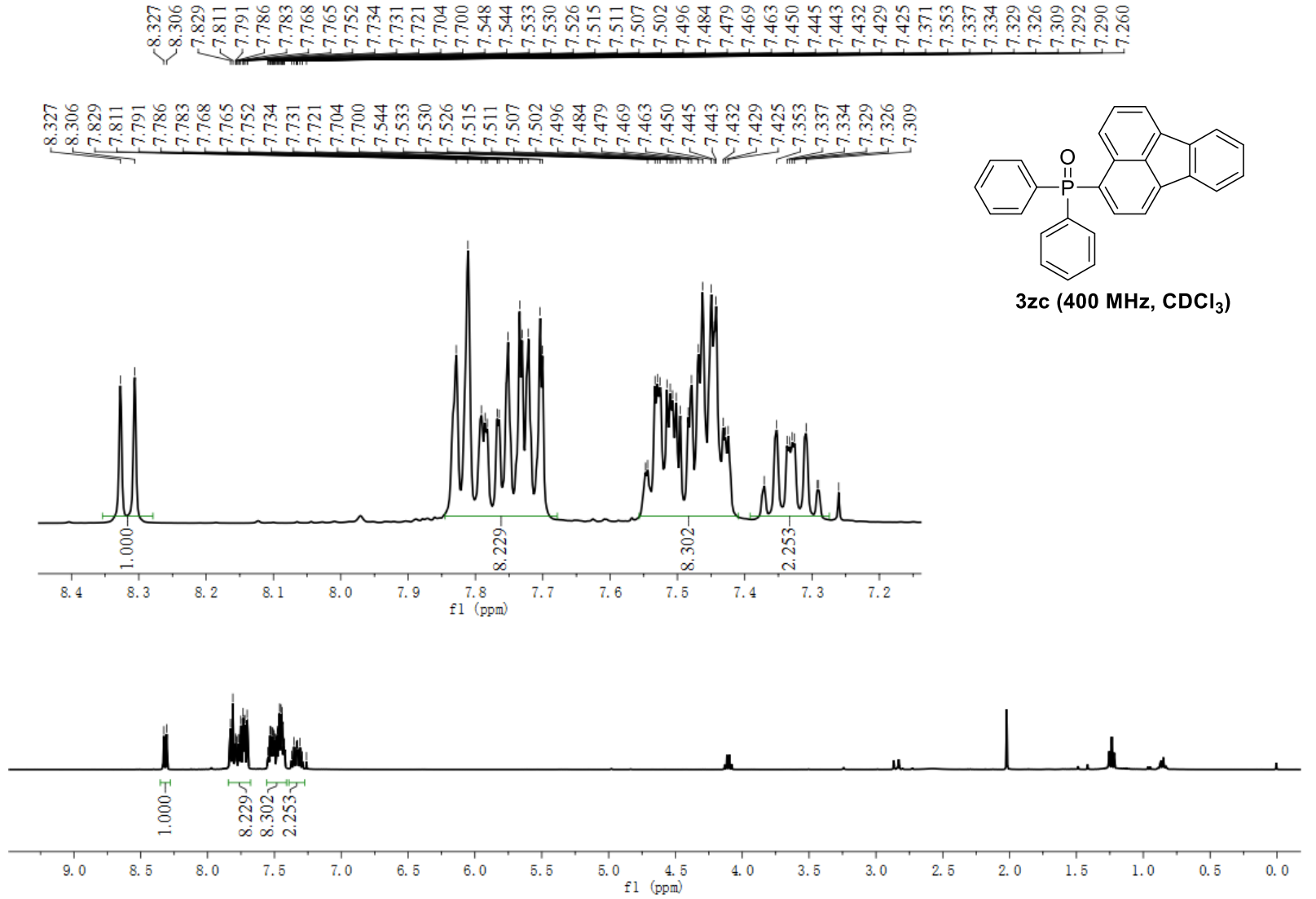




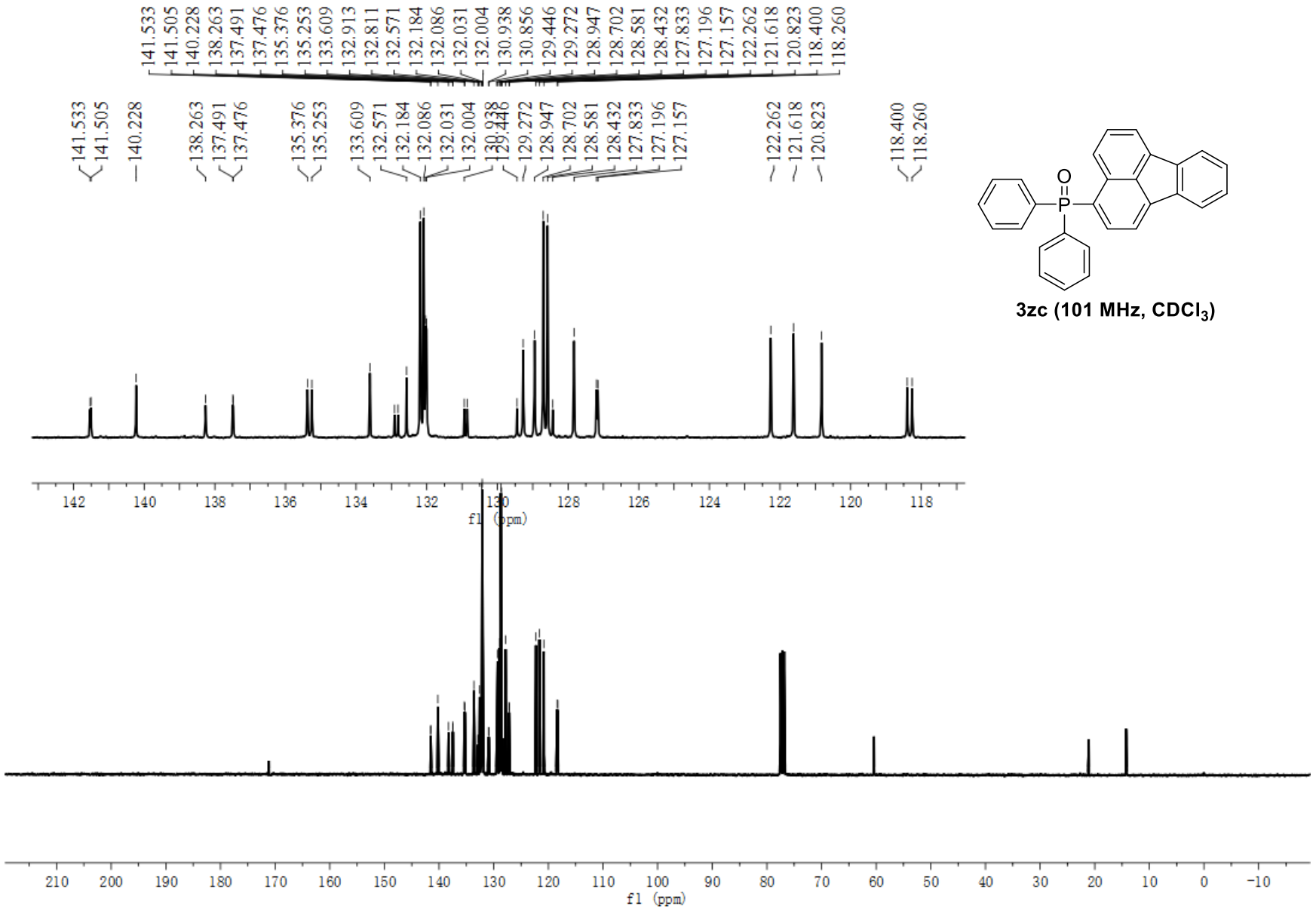
**3zb (101 MHz, $CDCl_3$)**



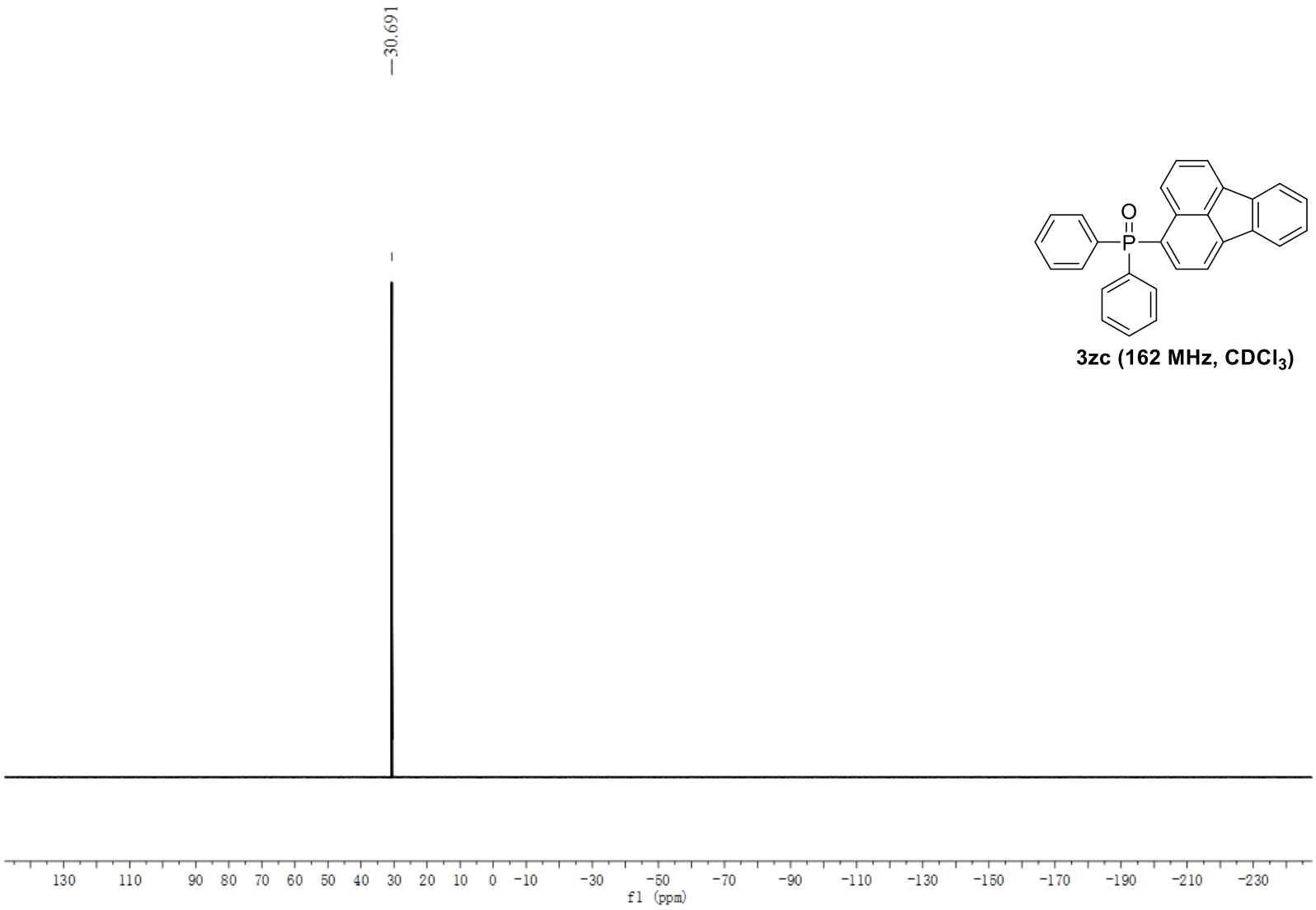

**3zb (162 MHz, $CDCl_3$)**



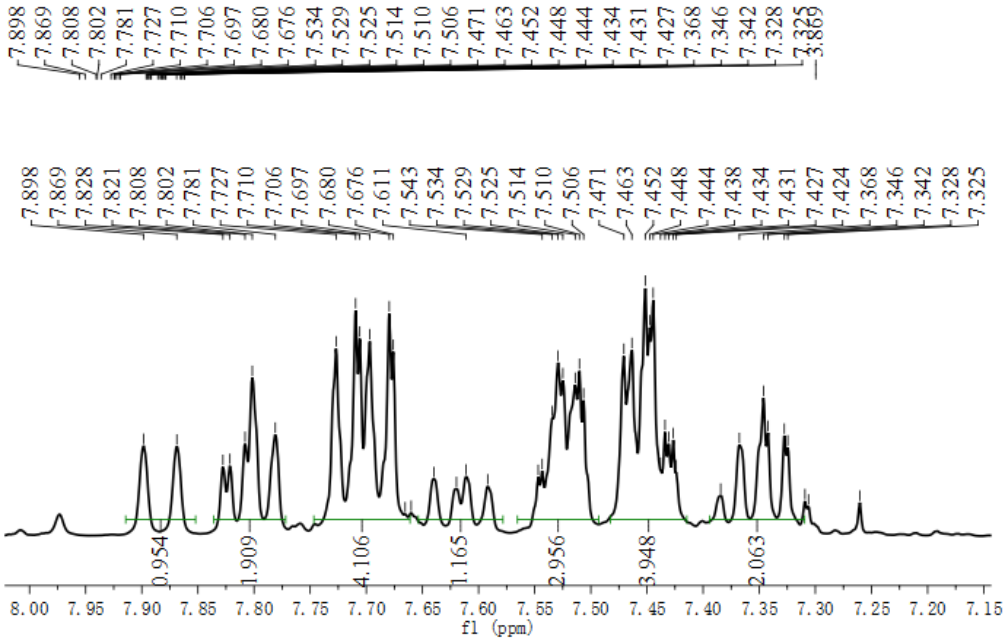

**3zc (400 MHz, $CDCl_3$)**

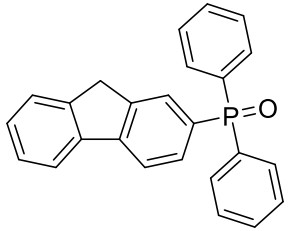



**3zc (101 MHz, $CDCl_3$)**

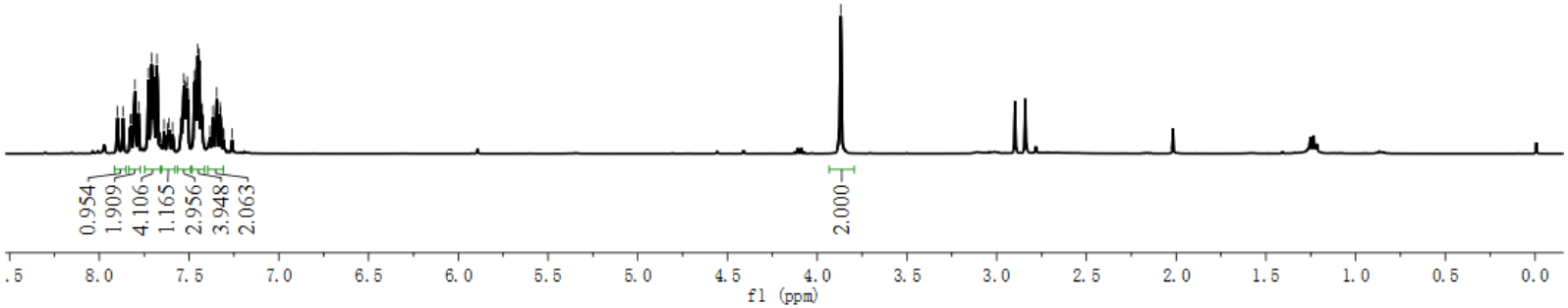


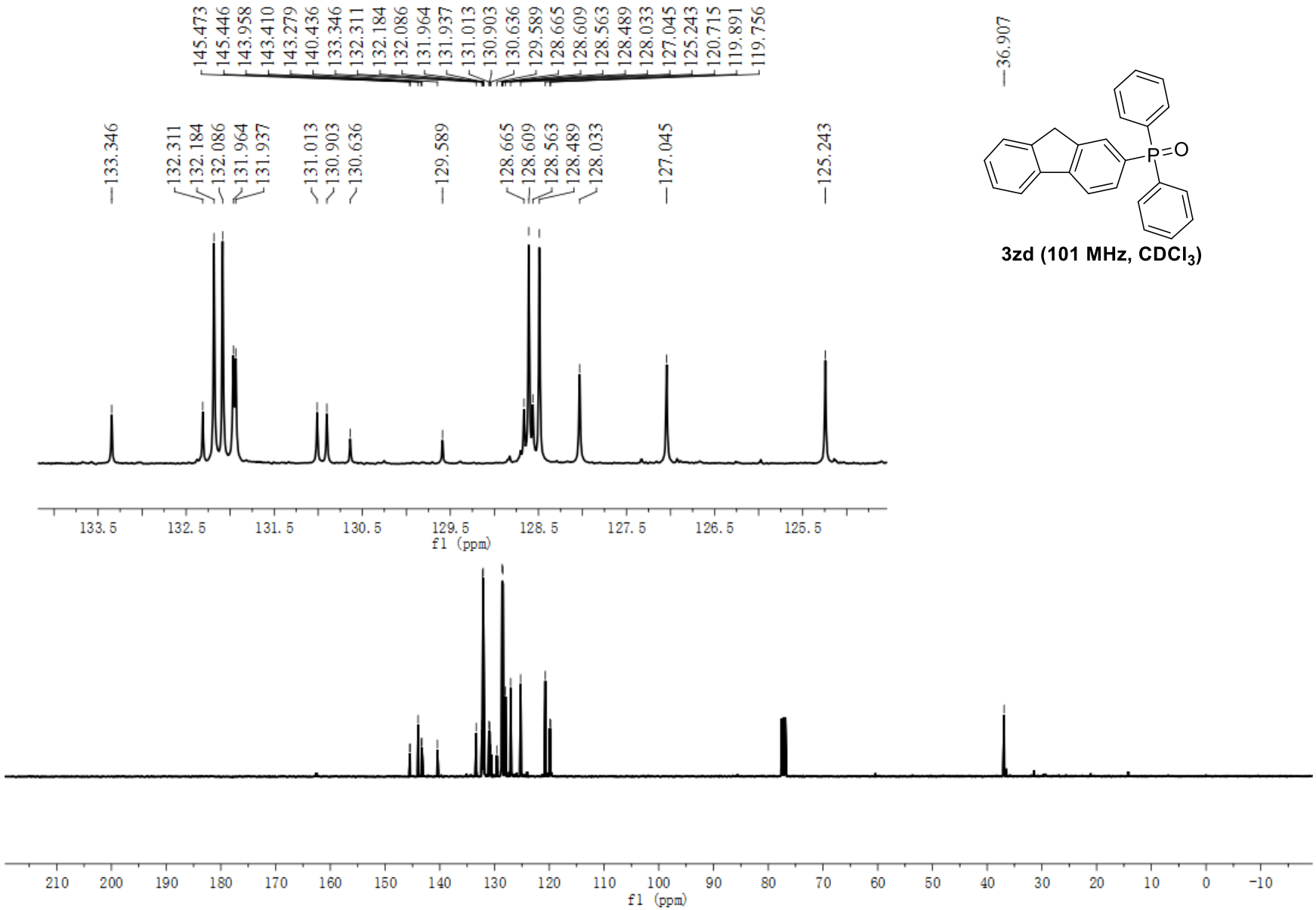

**3zc (162 MHz, $CDCl_3$)**



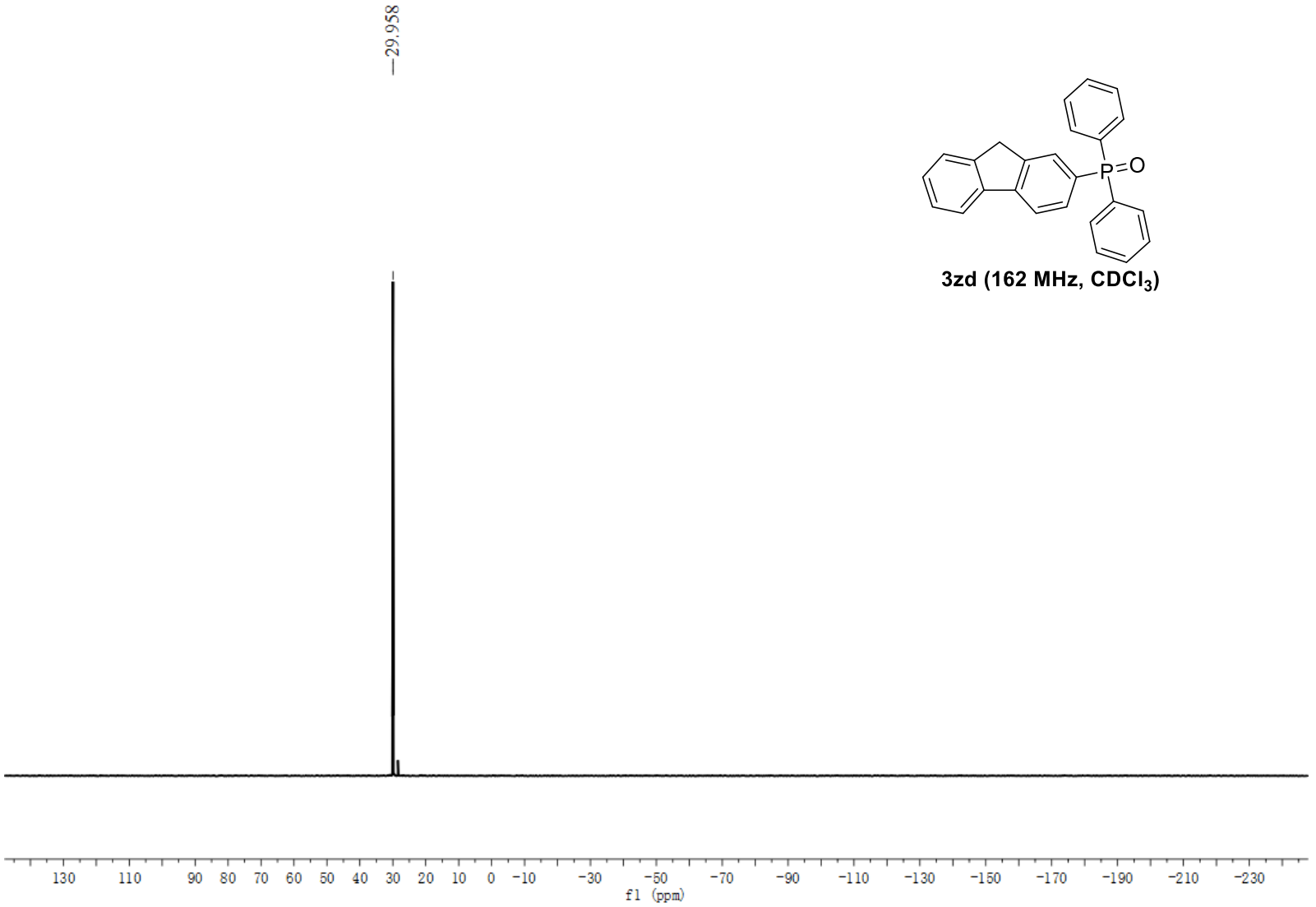




**3zd (400 MHz, $CDCl_3$)**

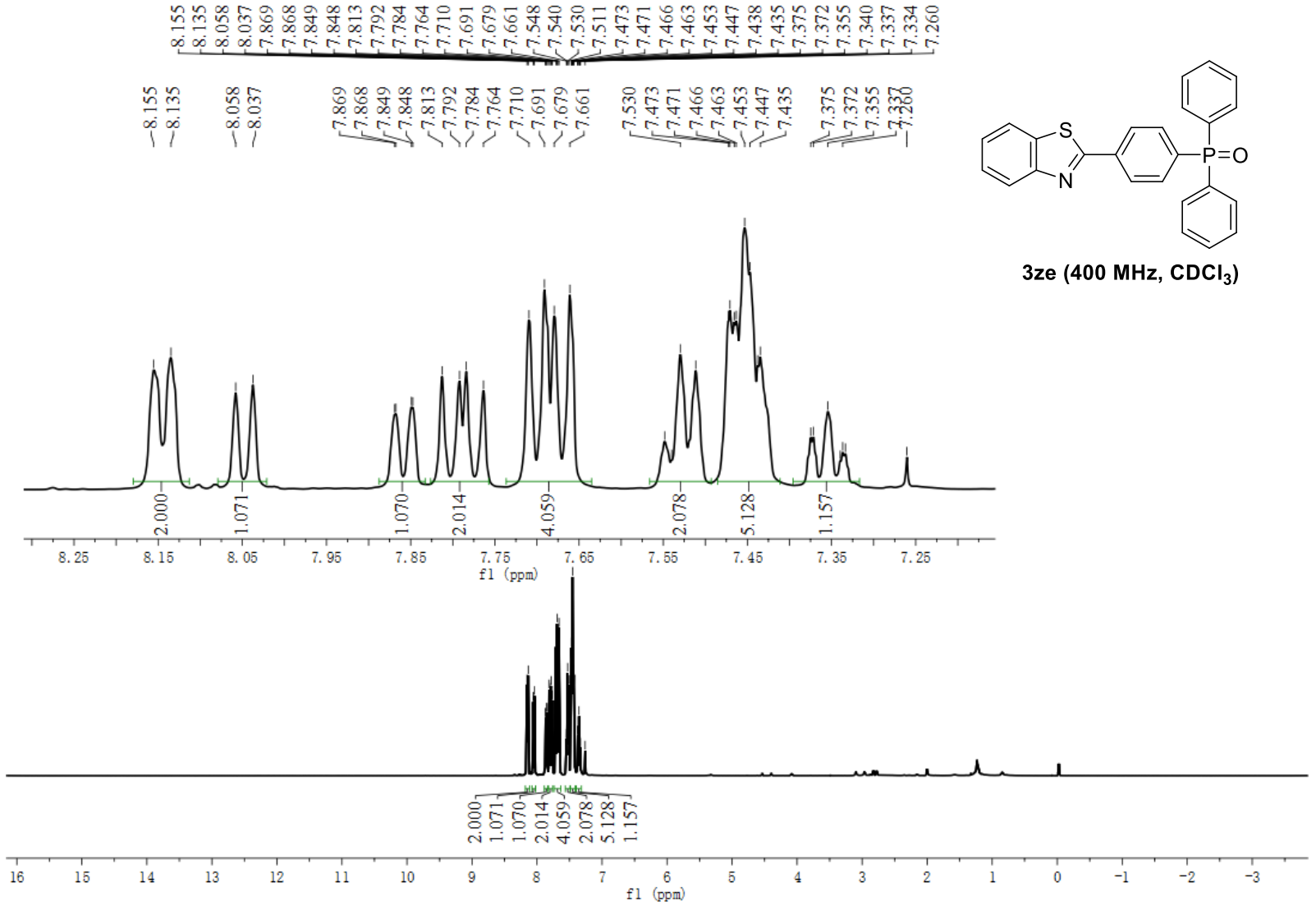




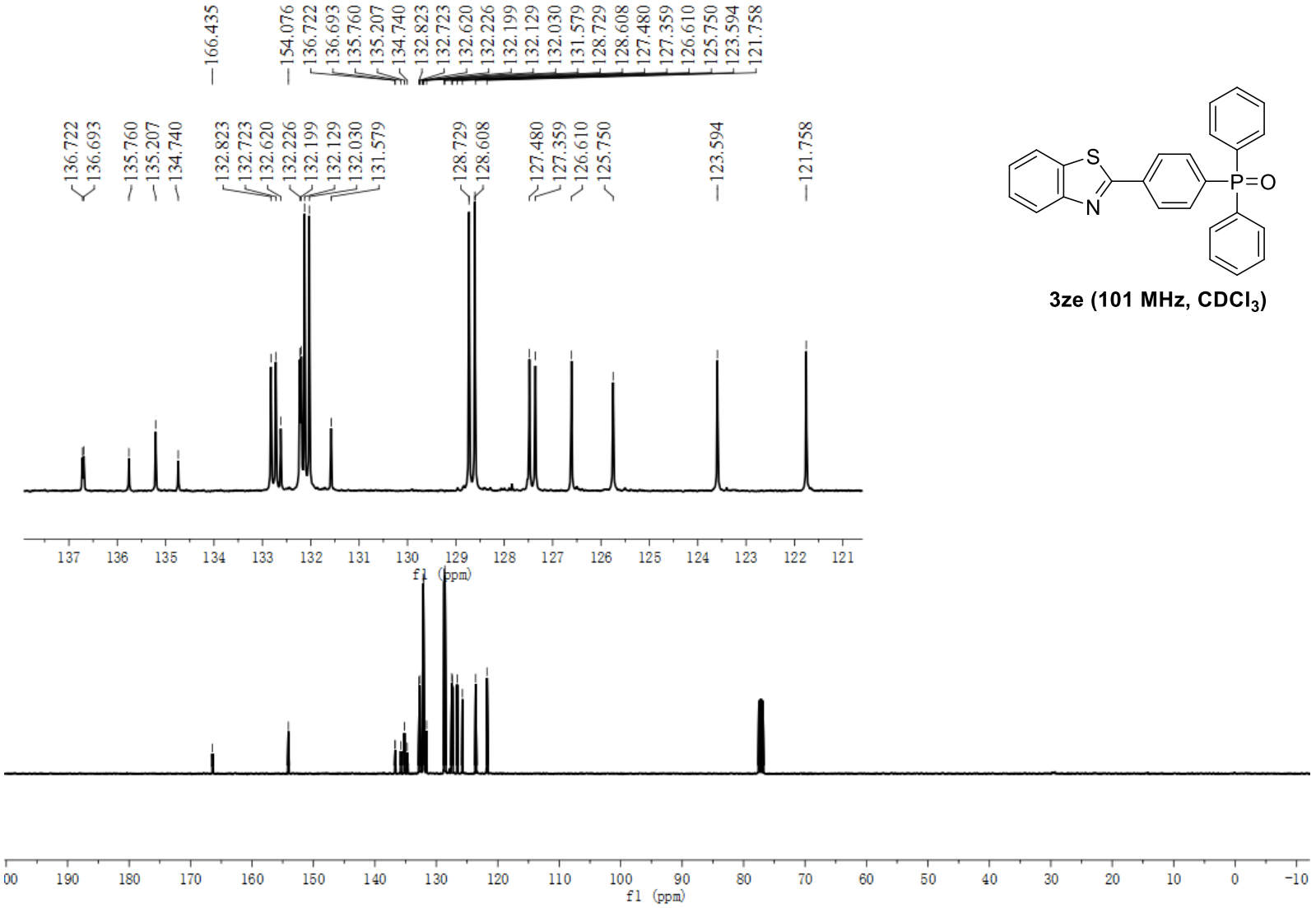

**3zd (101 MHz, $CDCl_3$)**




**3zd (162 MHz, $CDCl_3$)**



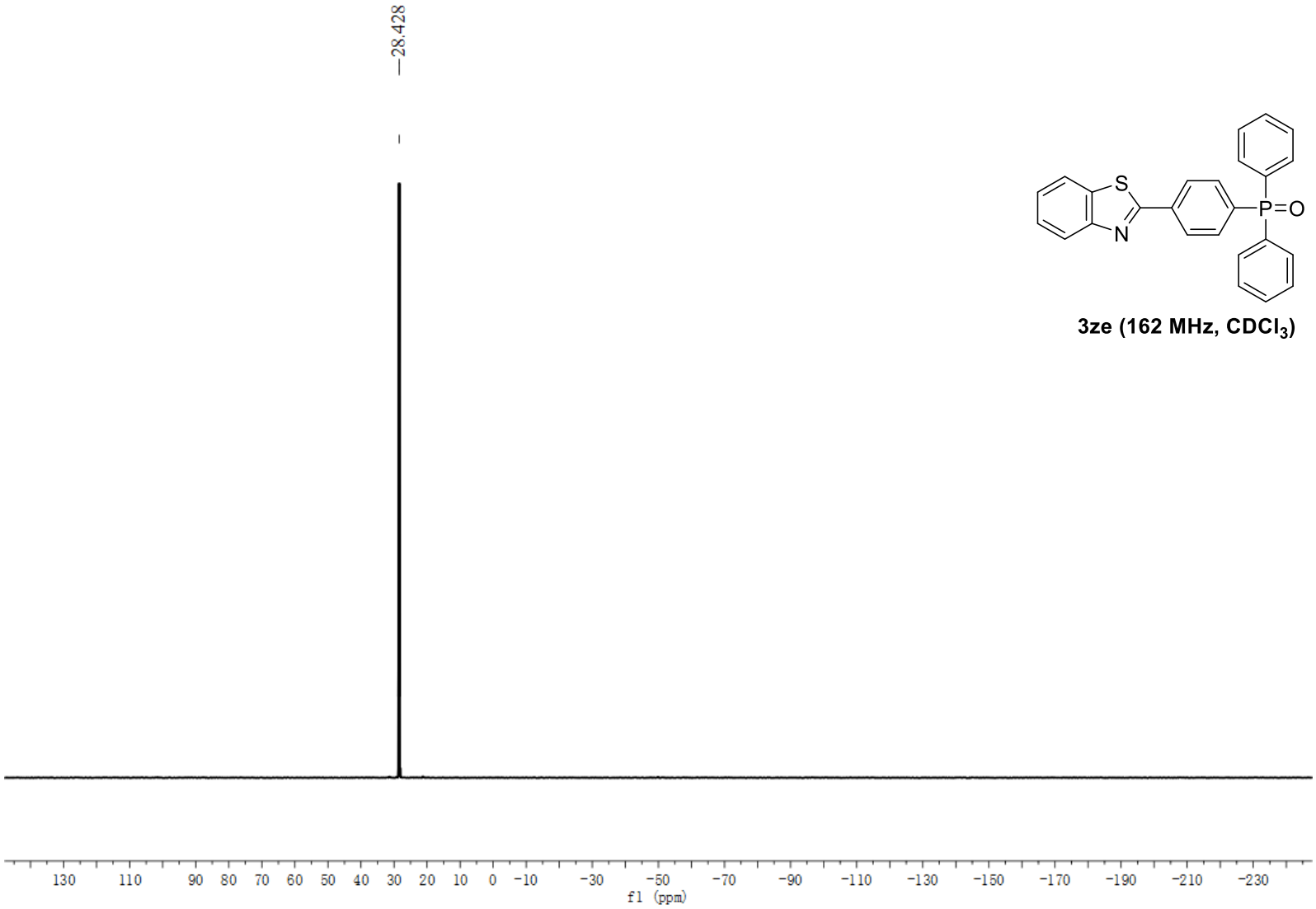

**3ze (400 MHz, $CDCl_3$)**



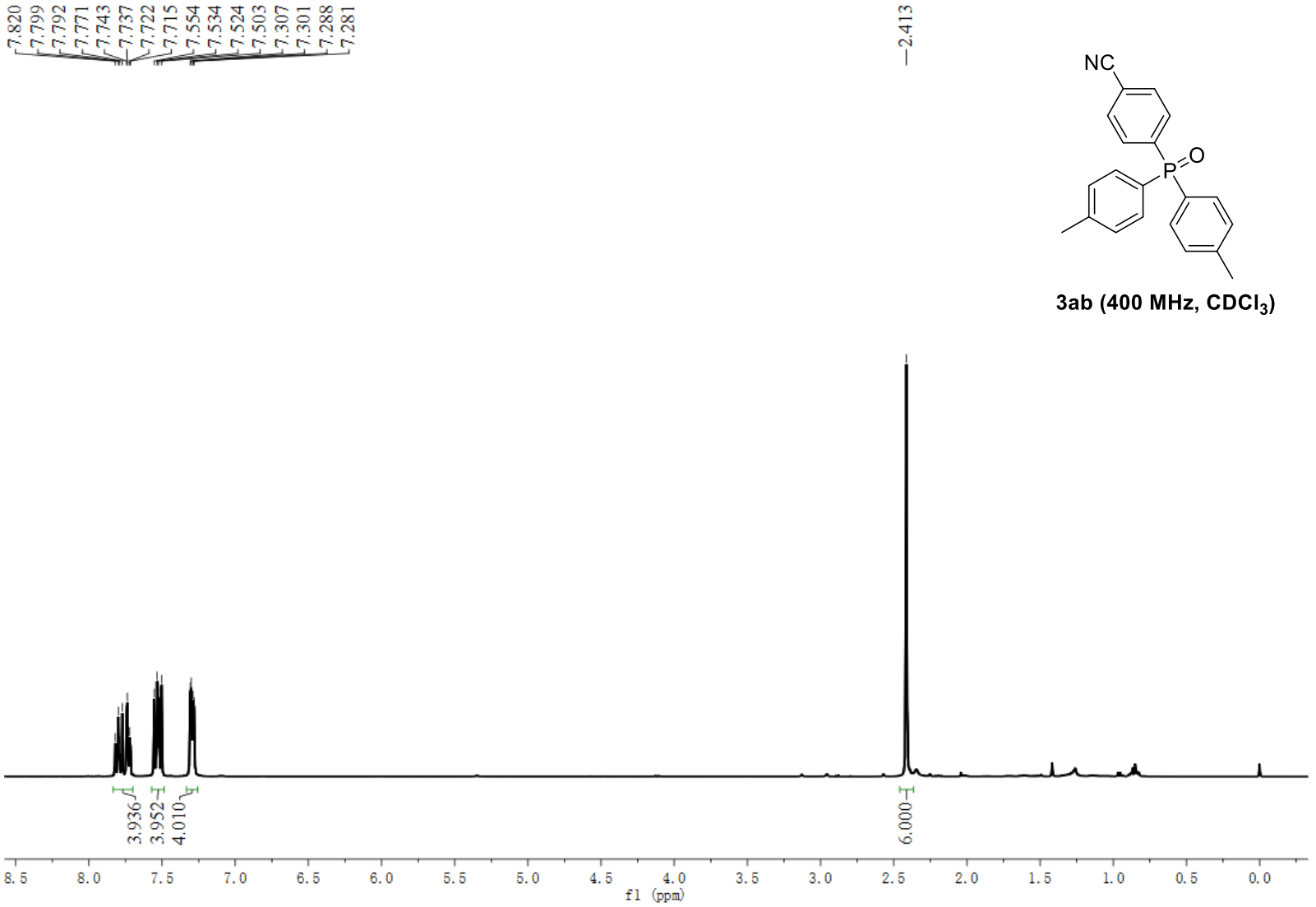




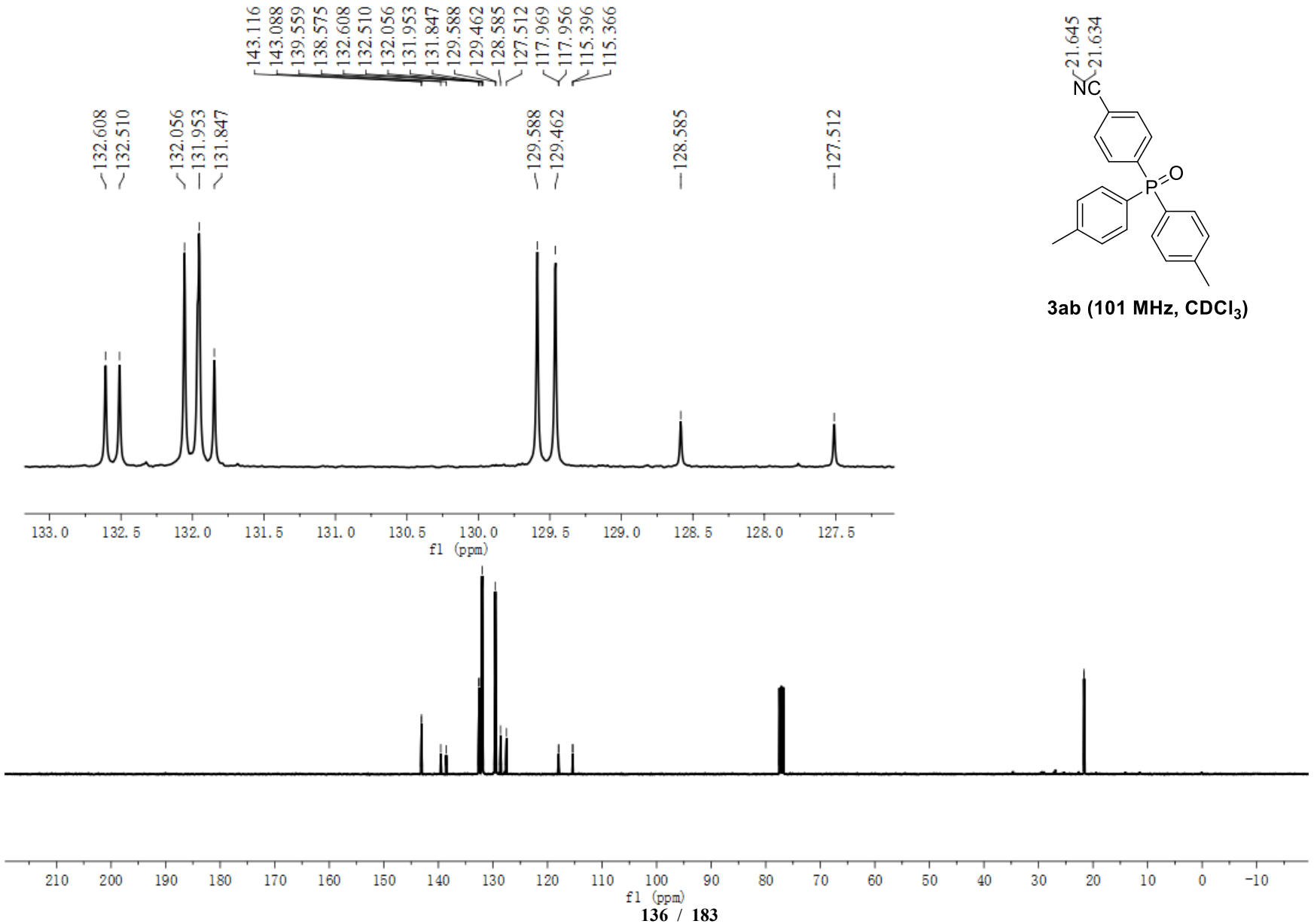
**3ze (101 MHz, $CDCl_3$)**



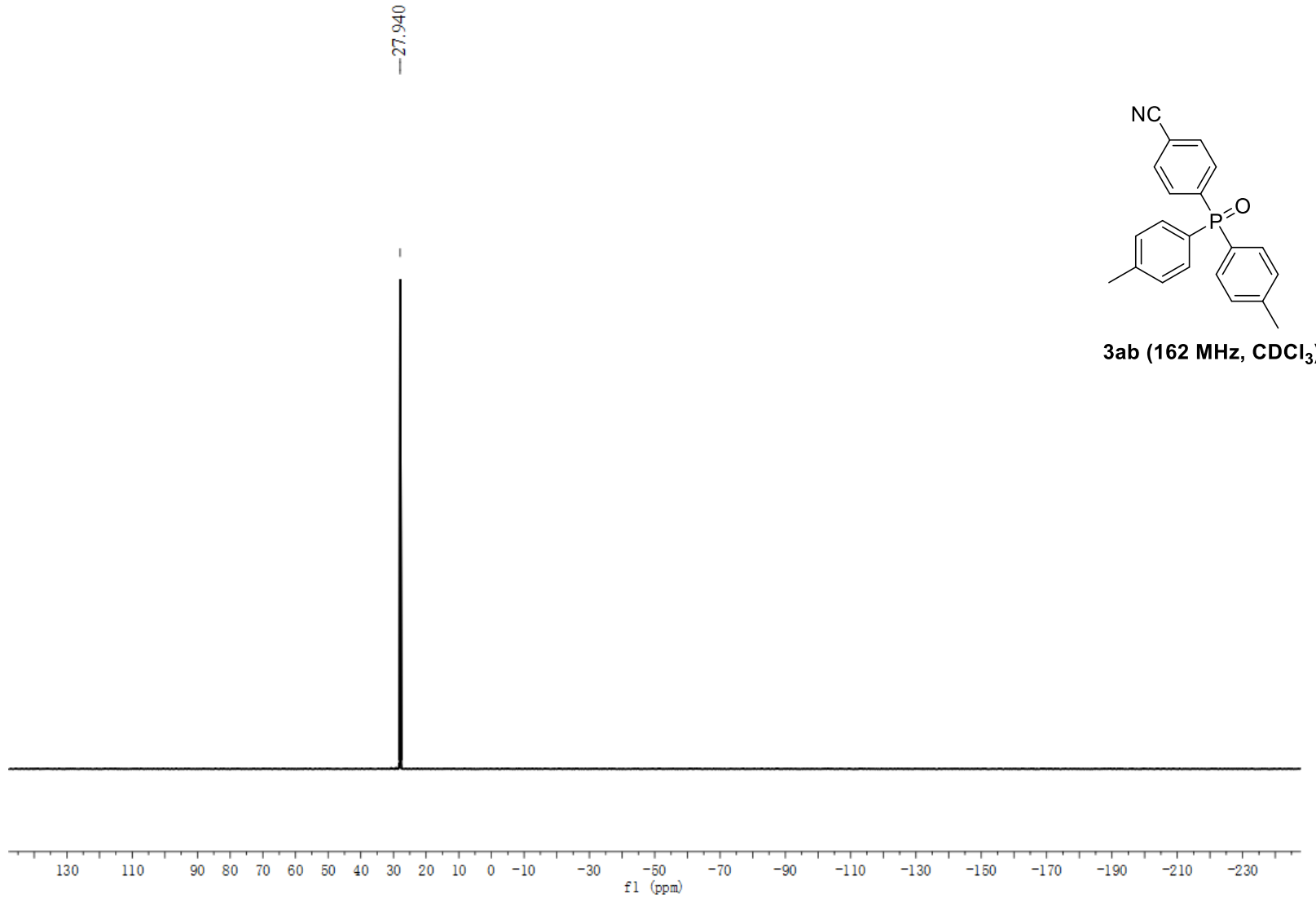

**3ze (162 MHz, $CDCl_3$)**



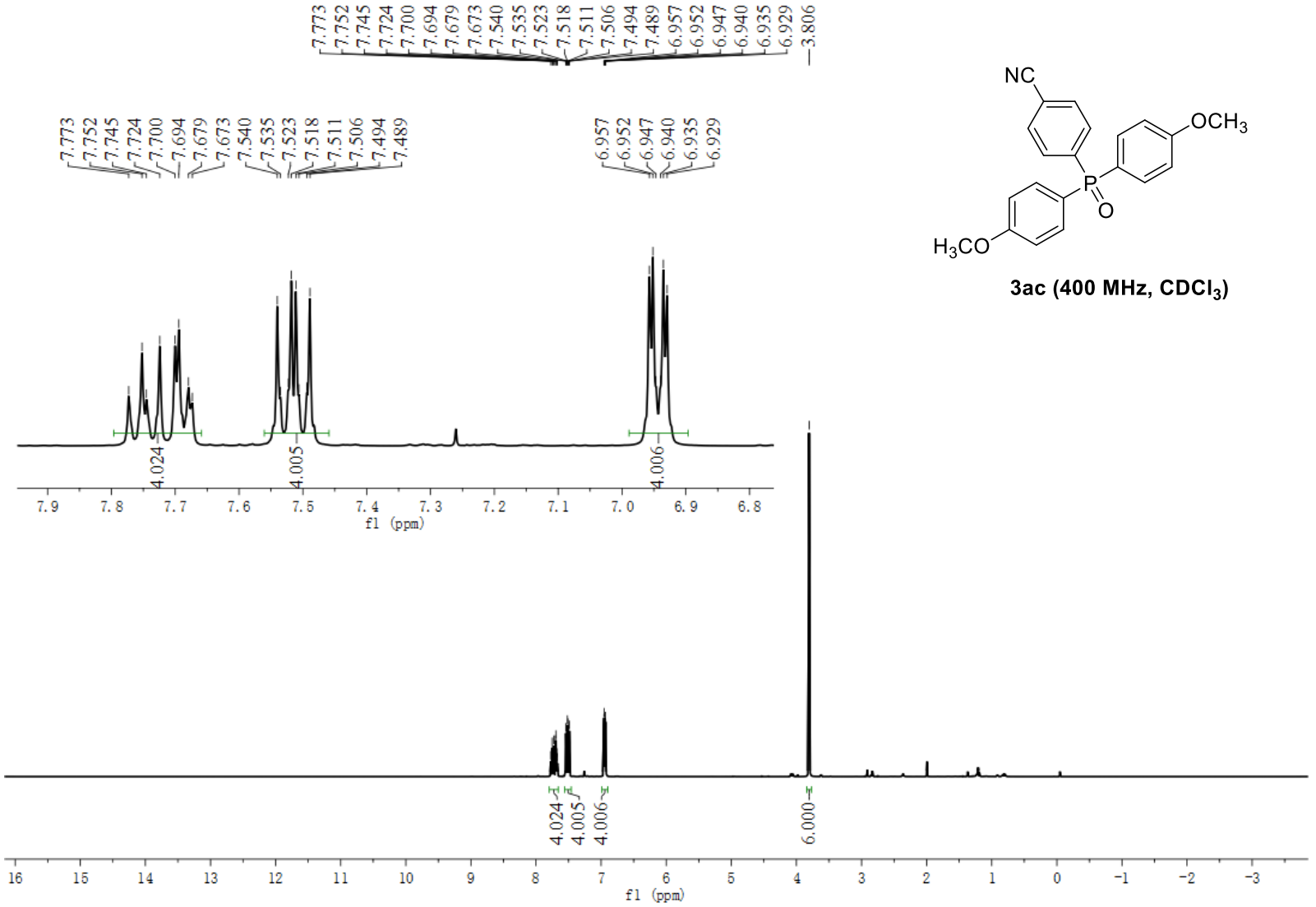

**3ab (400 MHz, $CDCl_3$)**




**3ab (101 MHz, $CDCl_3$)**



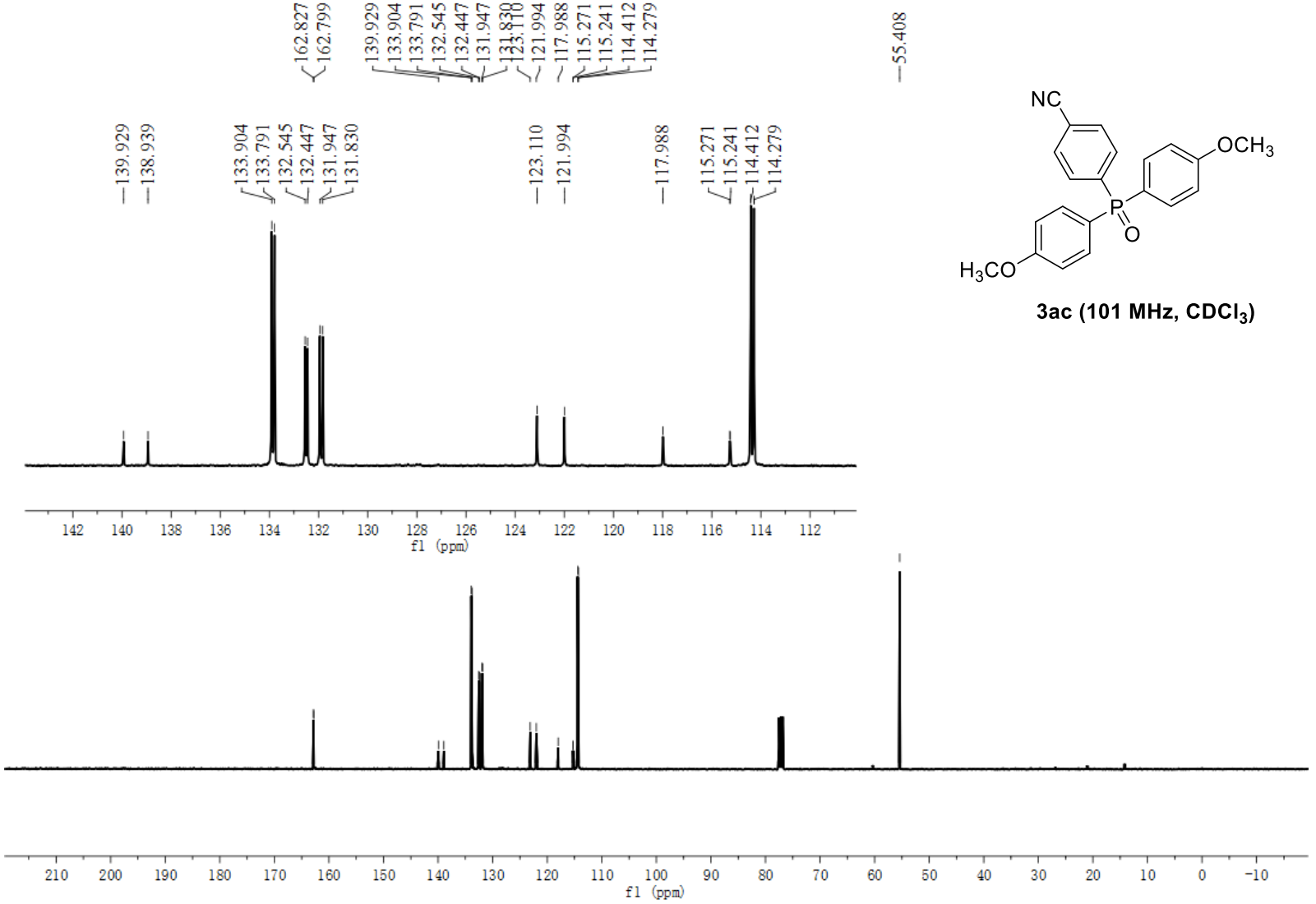

**3ab (162 MHz, $CDCl_3$)**







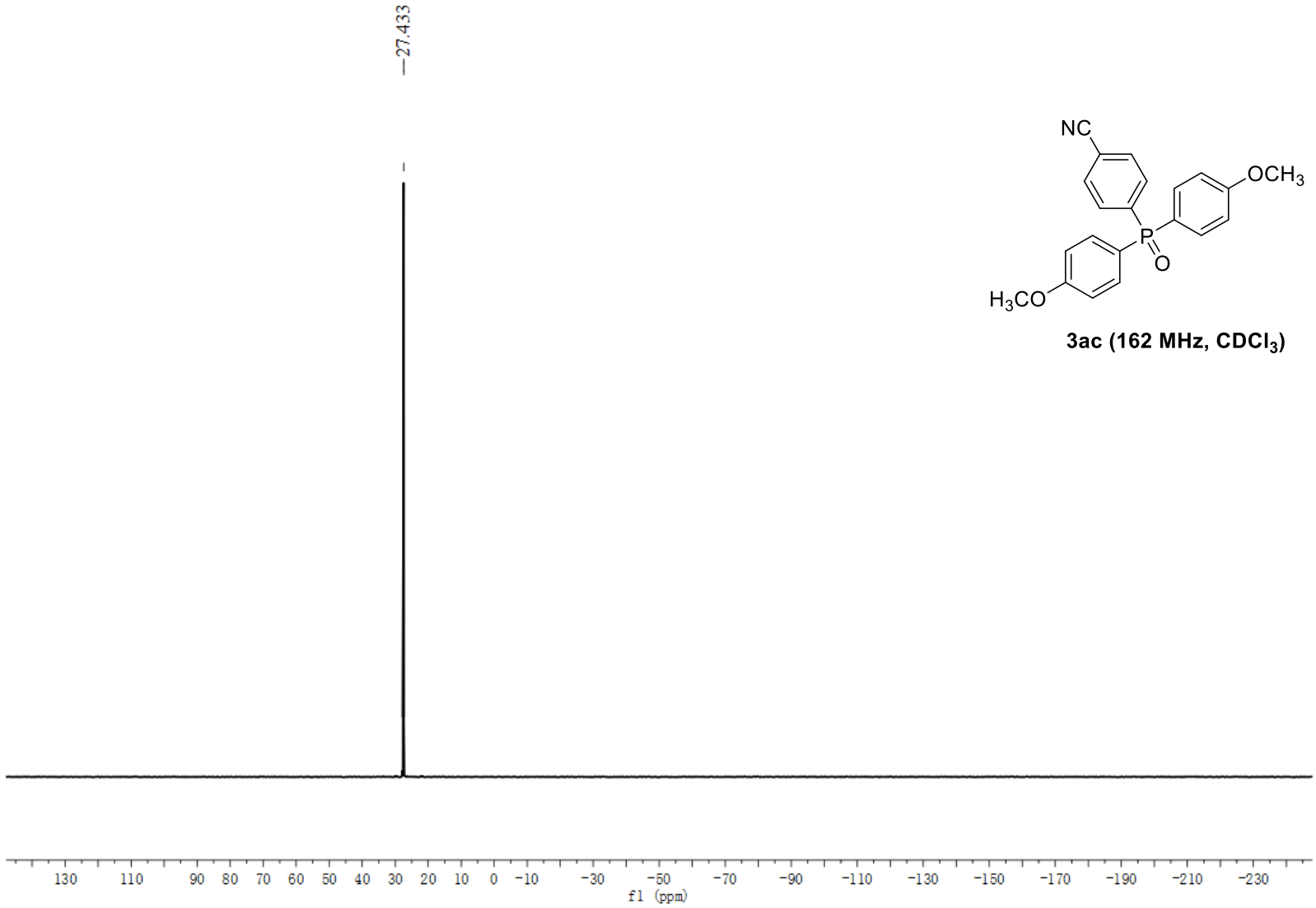
**3ac (400 MHz, $CDCl_3$)**



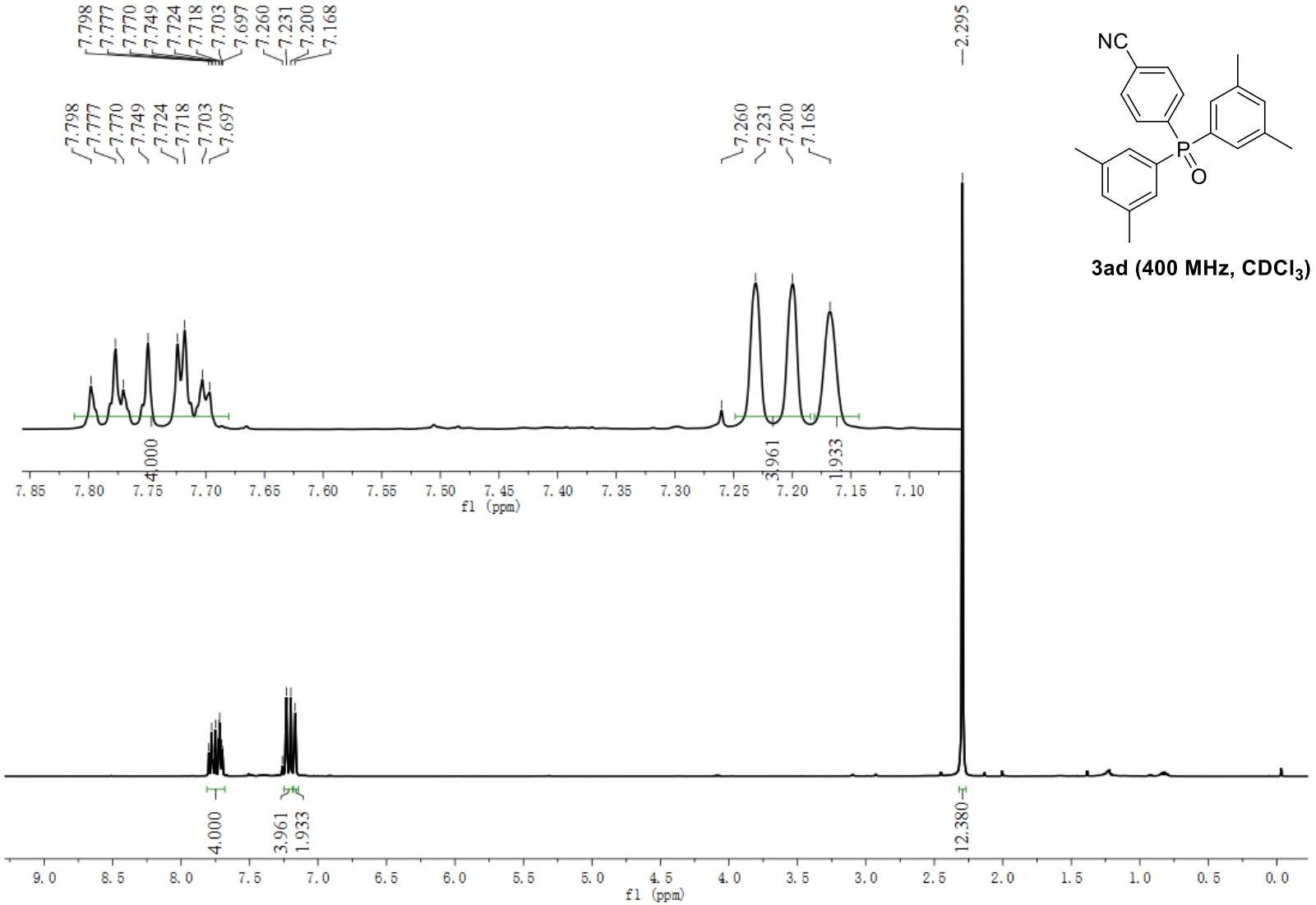




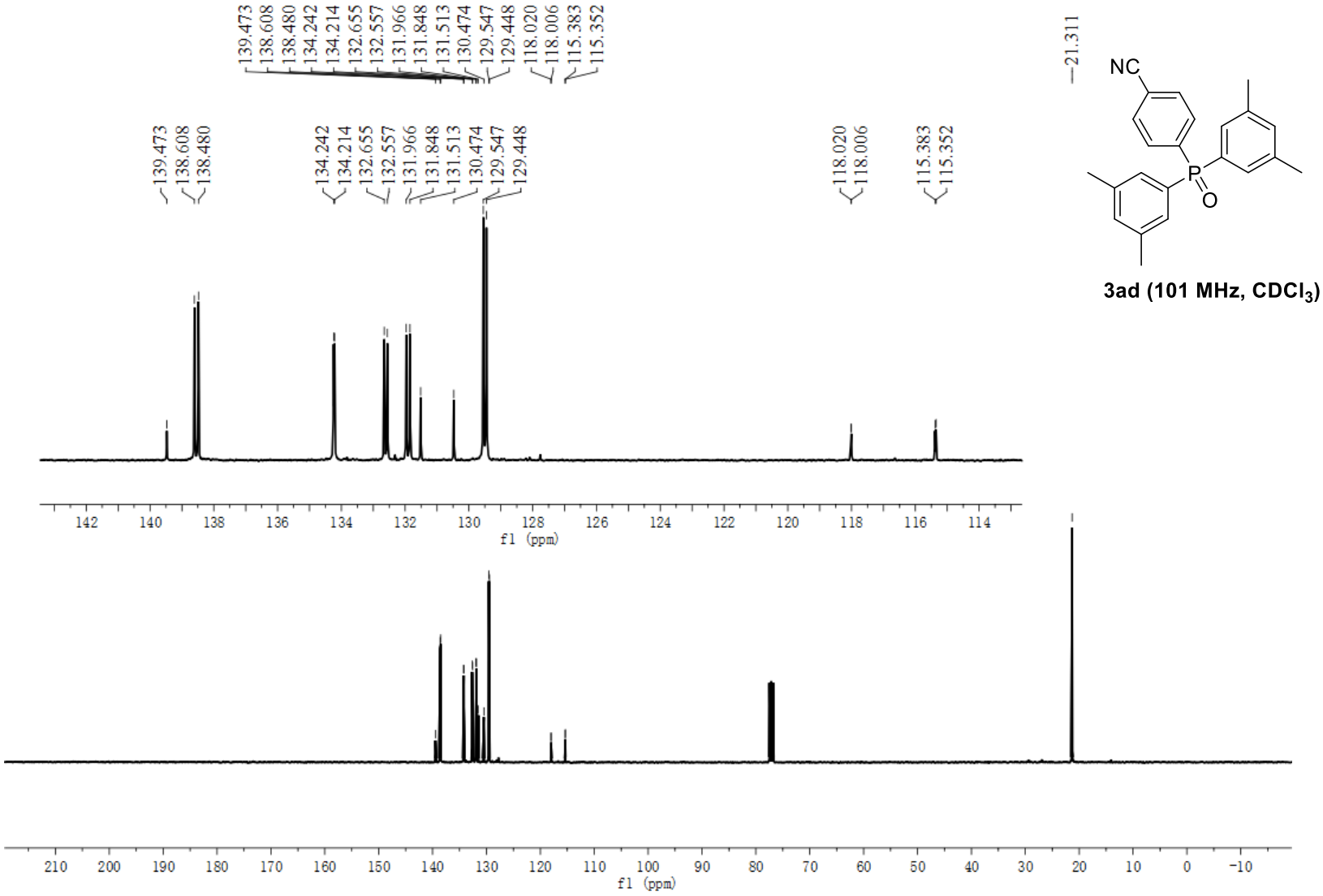
**3ac (101 MHz, $CDCl_3$)**



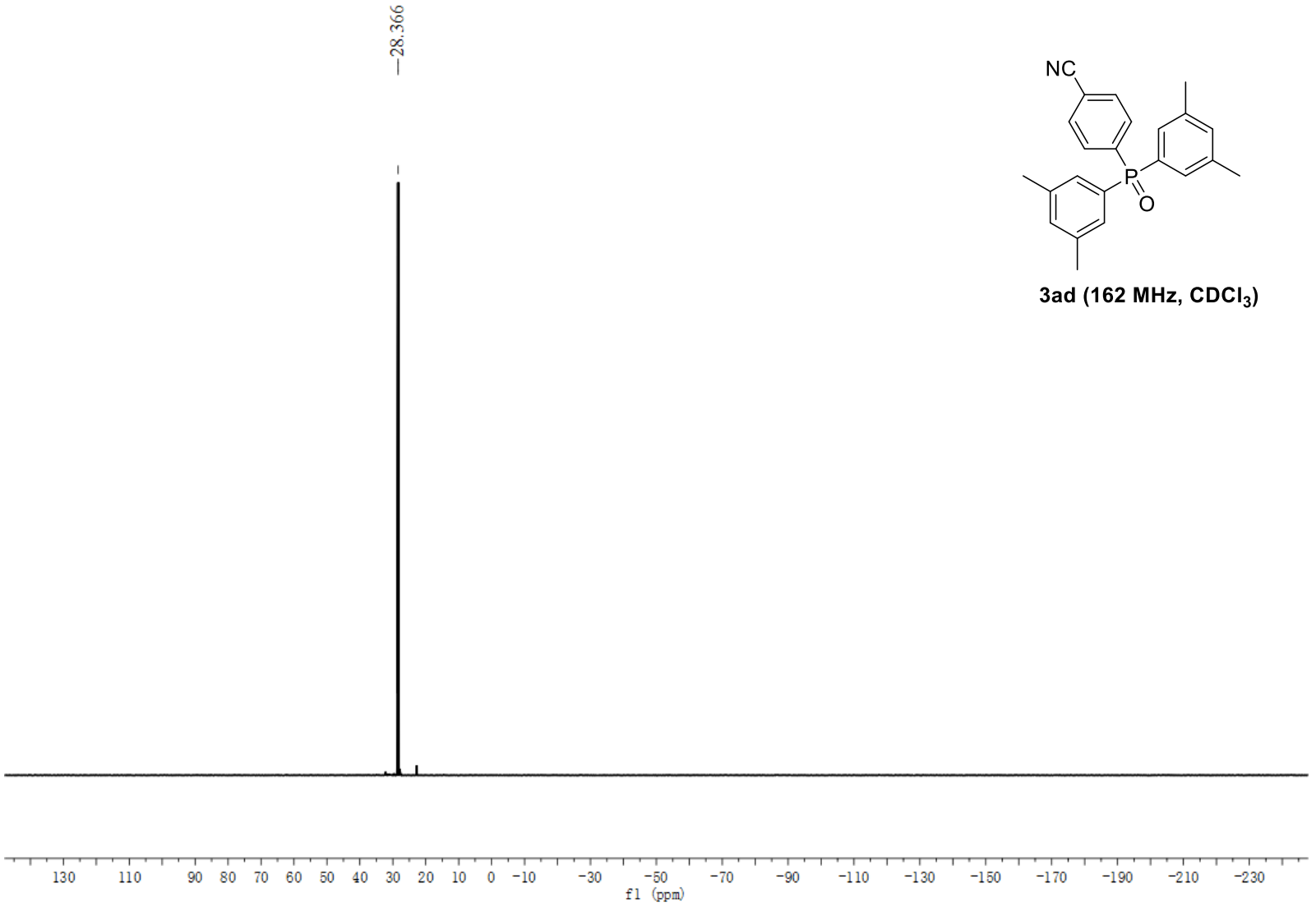

**3ac (162 MHz, $CDCl_3$)**



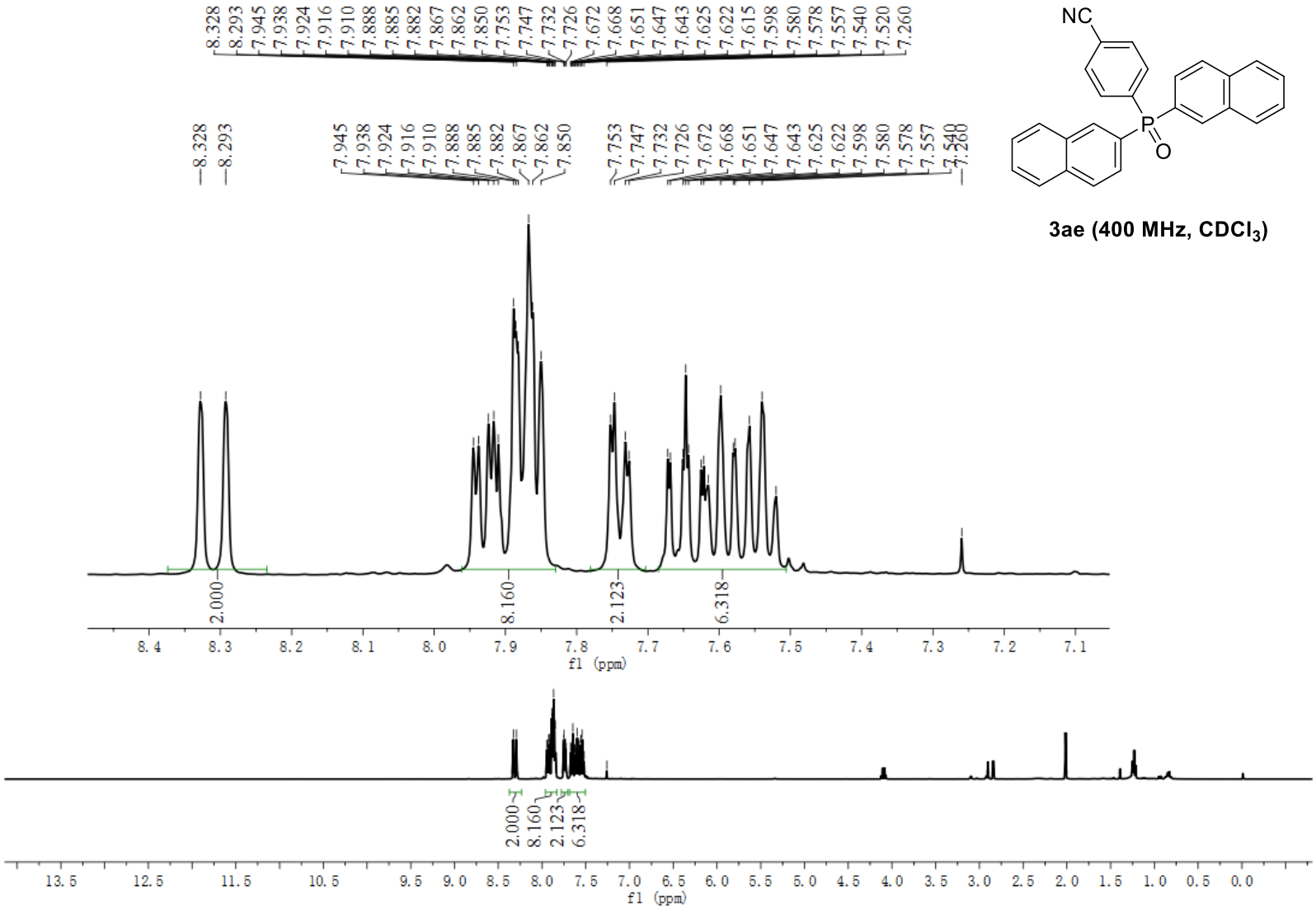

**3ad (400 MHz, $CDCl_3$)**



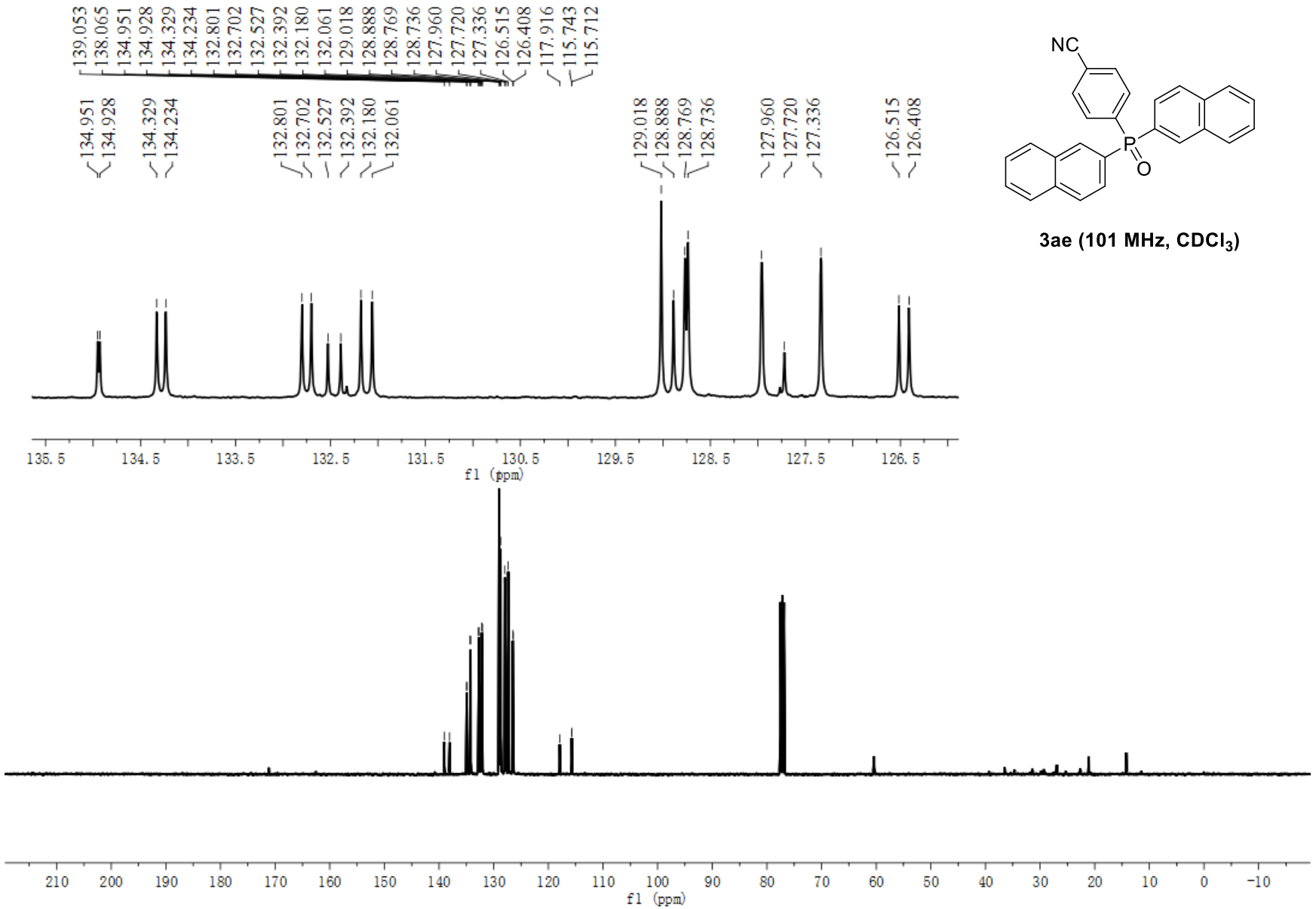

**3ad (101 MHz, $CDCl_3$)**




**3ad (162 MHz, $CDCl_3$)**



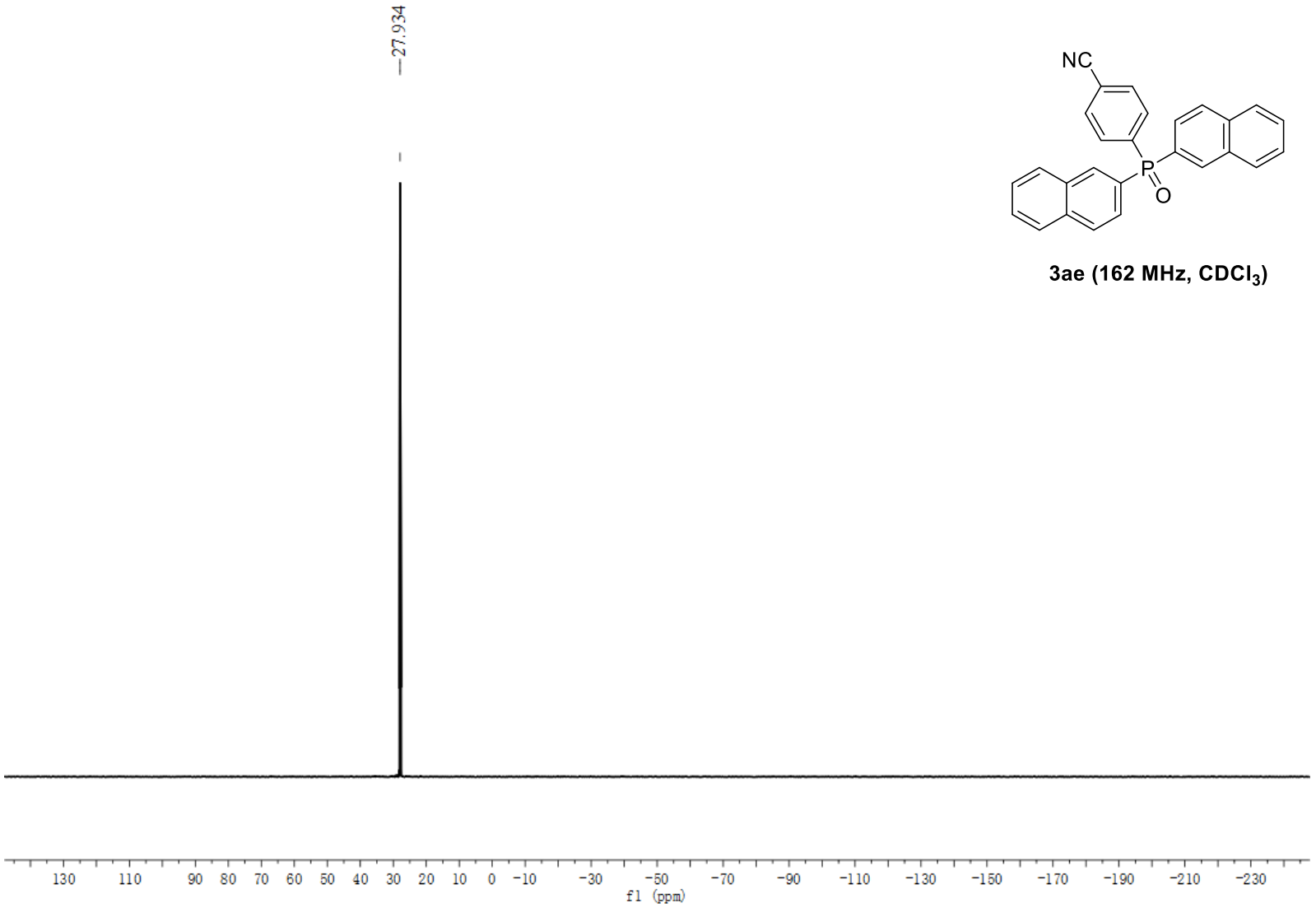

**3ae (400 MHz, $CDCl_3$)**



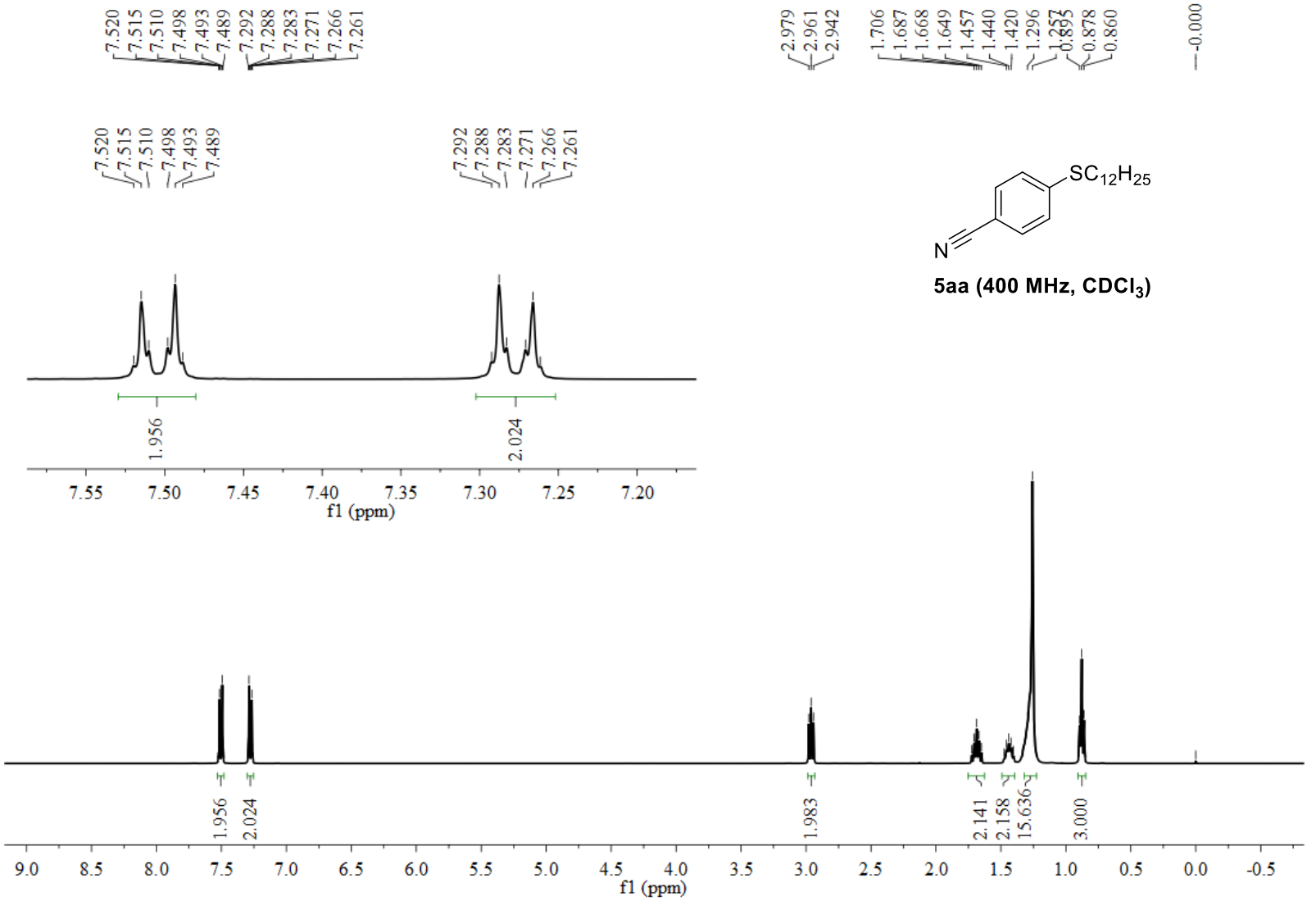




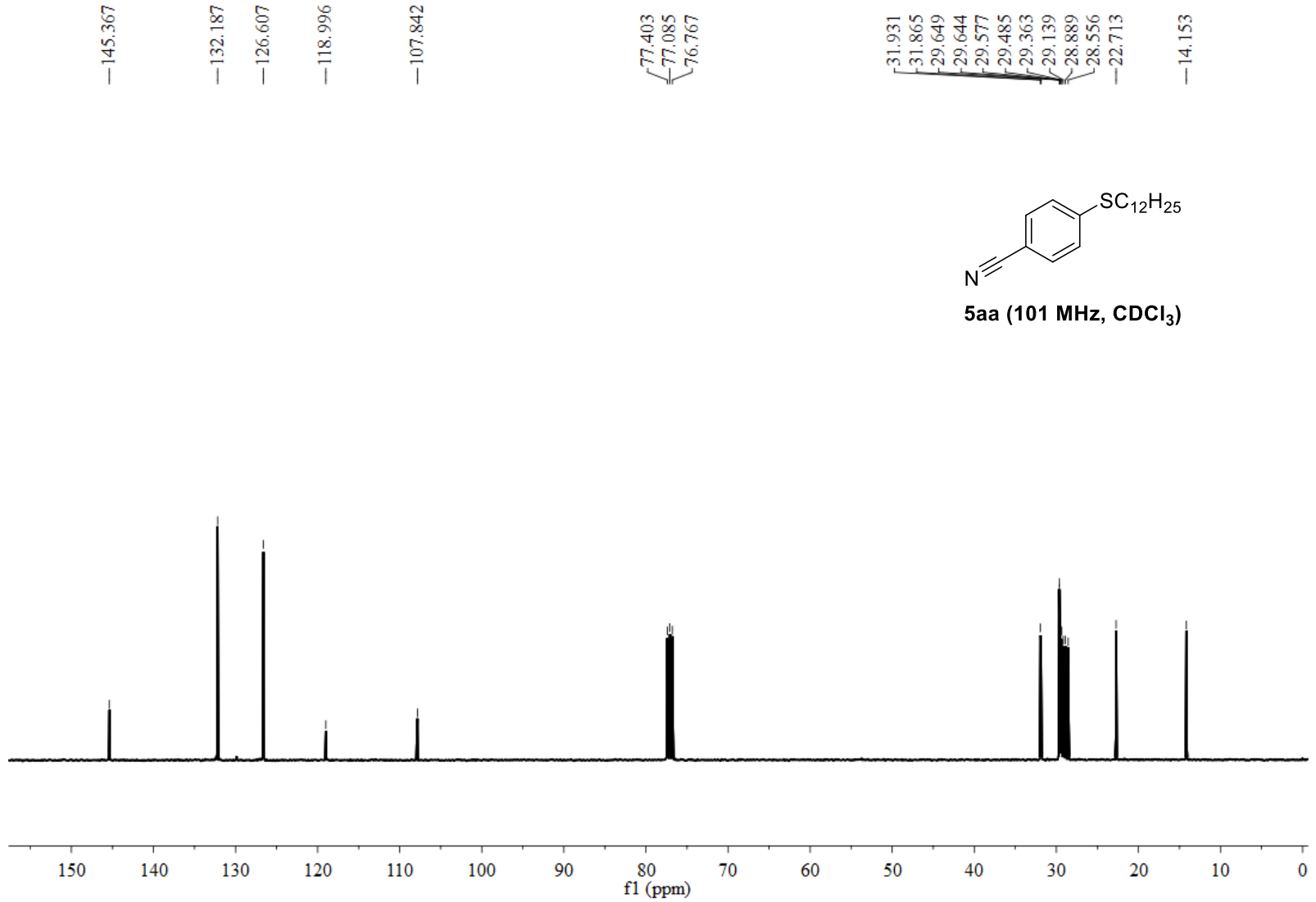
**3ae (101 MHz, $CDCl_3$)**



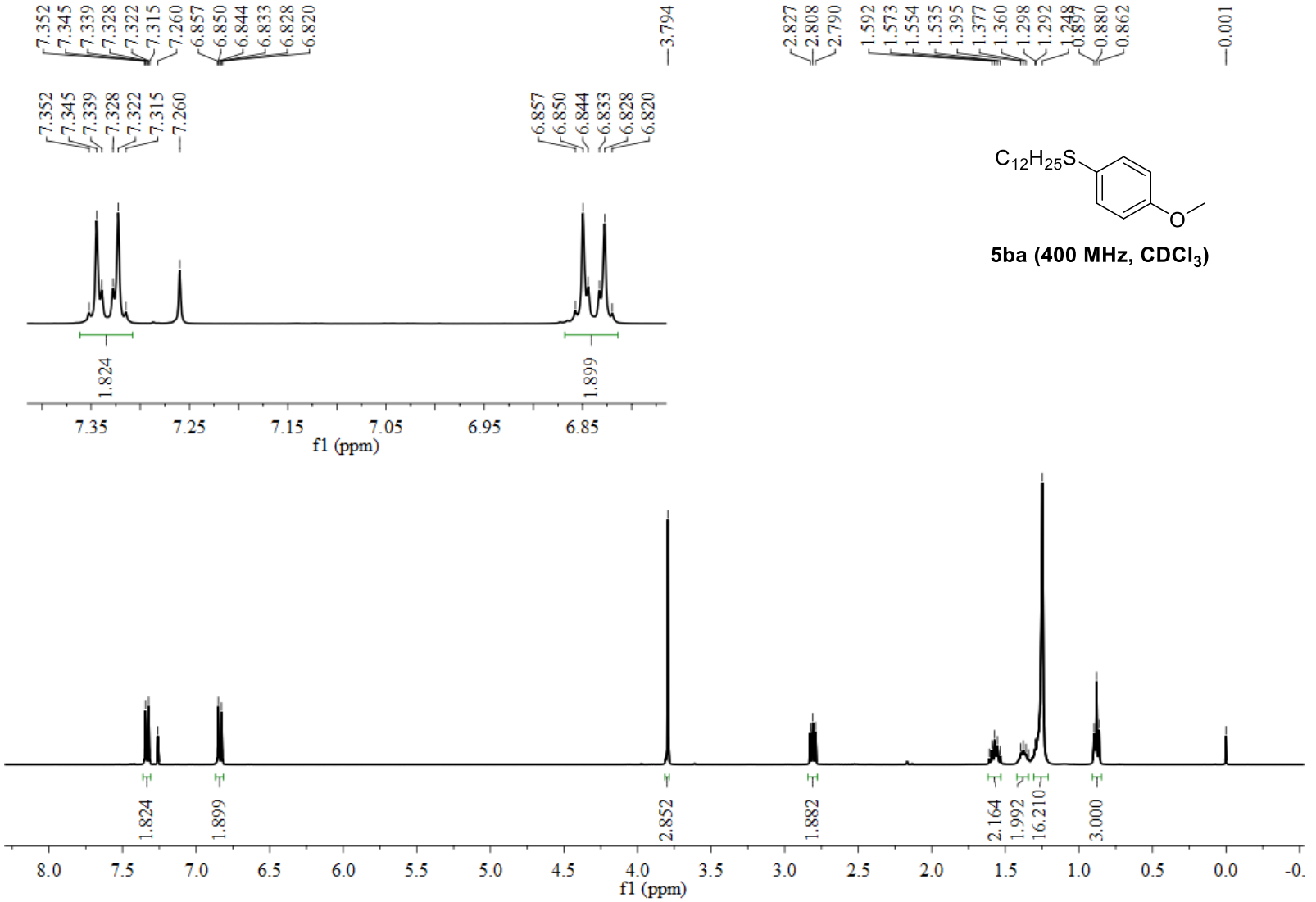

**3ae (162 MHz, $CDCl_3$)**



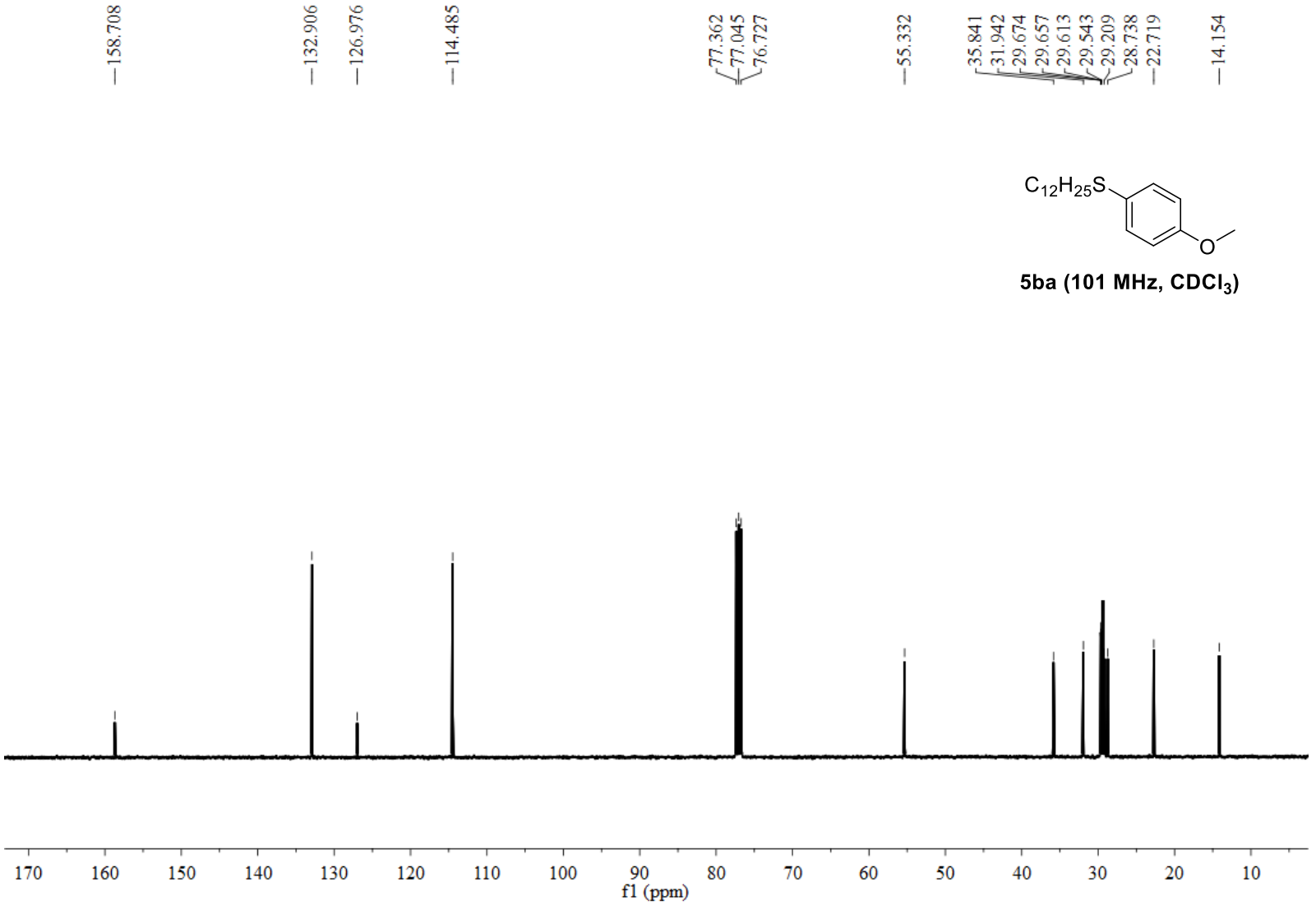

**5aa (400 MHz, $CDCl_3$)**



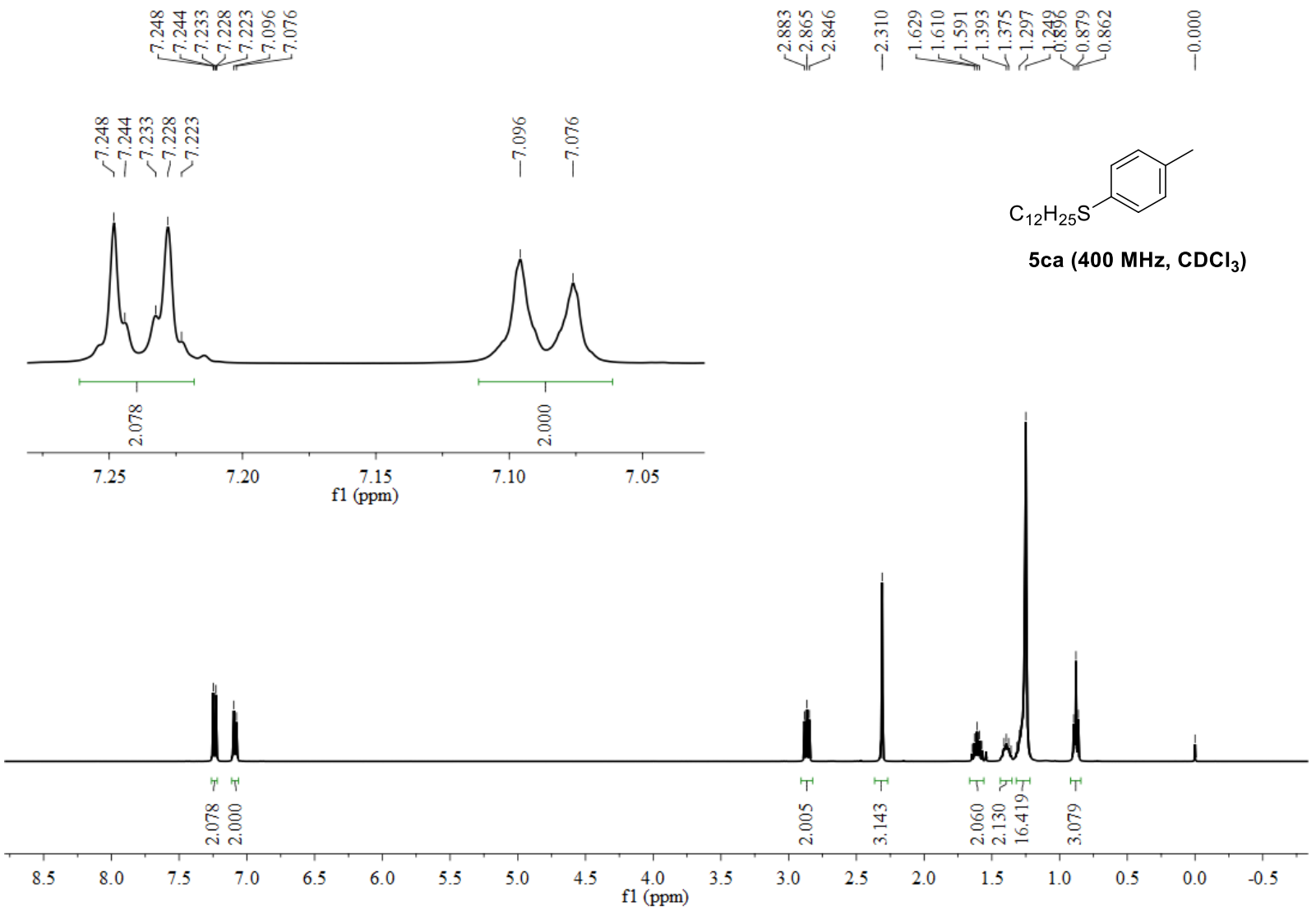

**5aa (101 MHz, $CDCl_3$)**




**5ba (400 MHz, $CDCl_3$)**

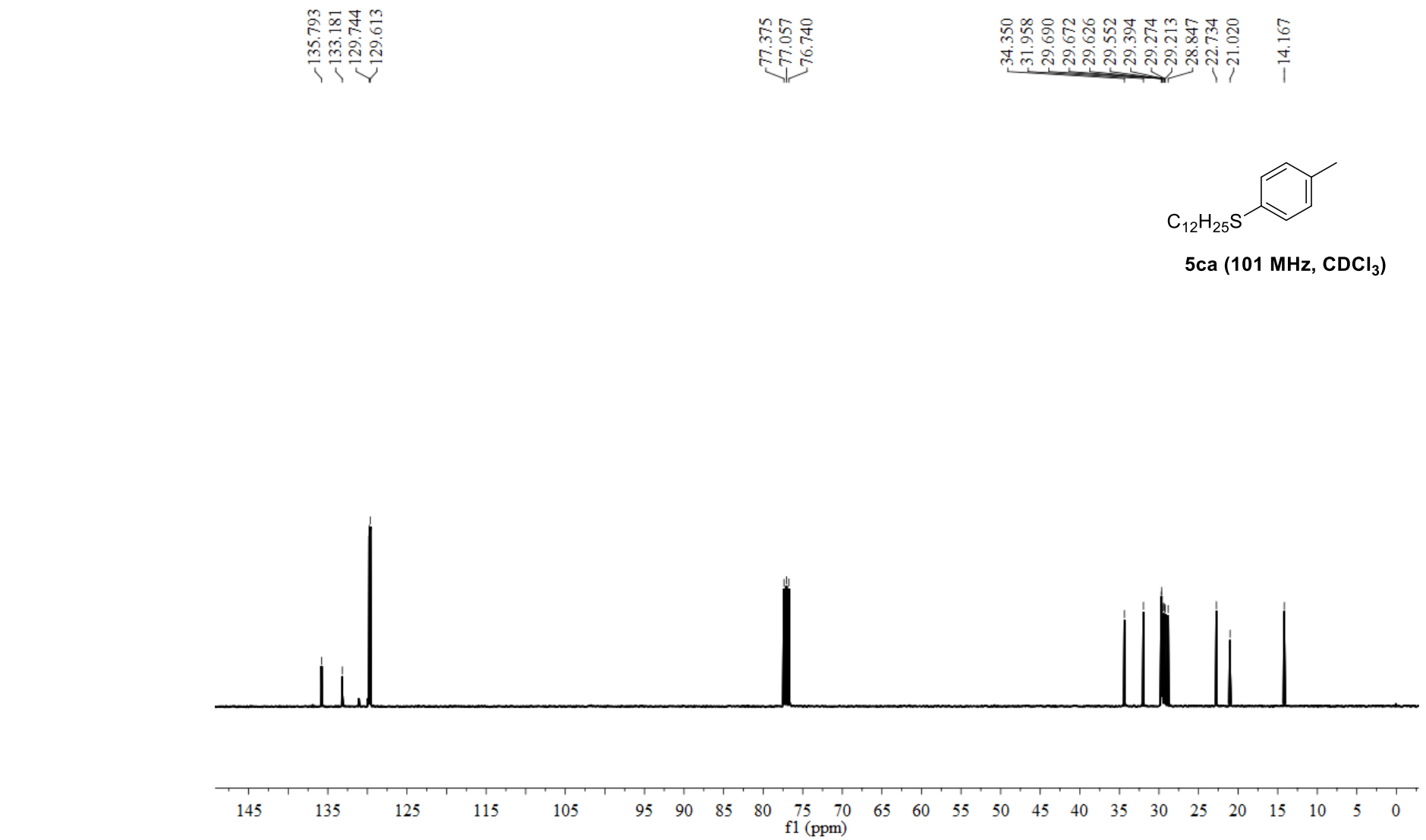



**5ba (101 MHz, $CDCl_3$)**

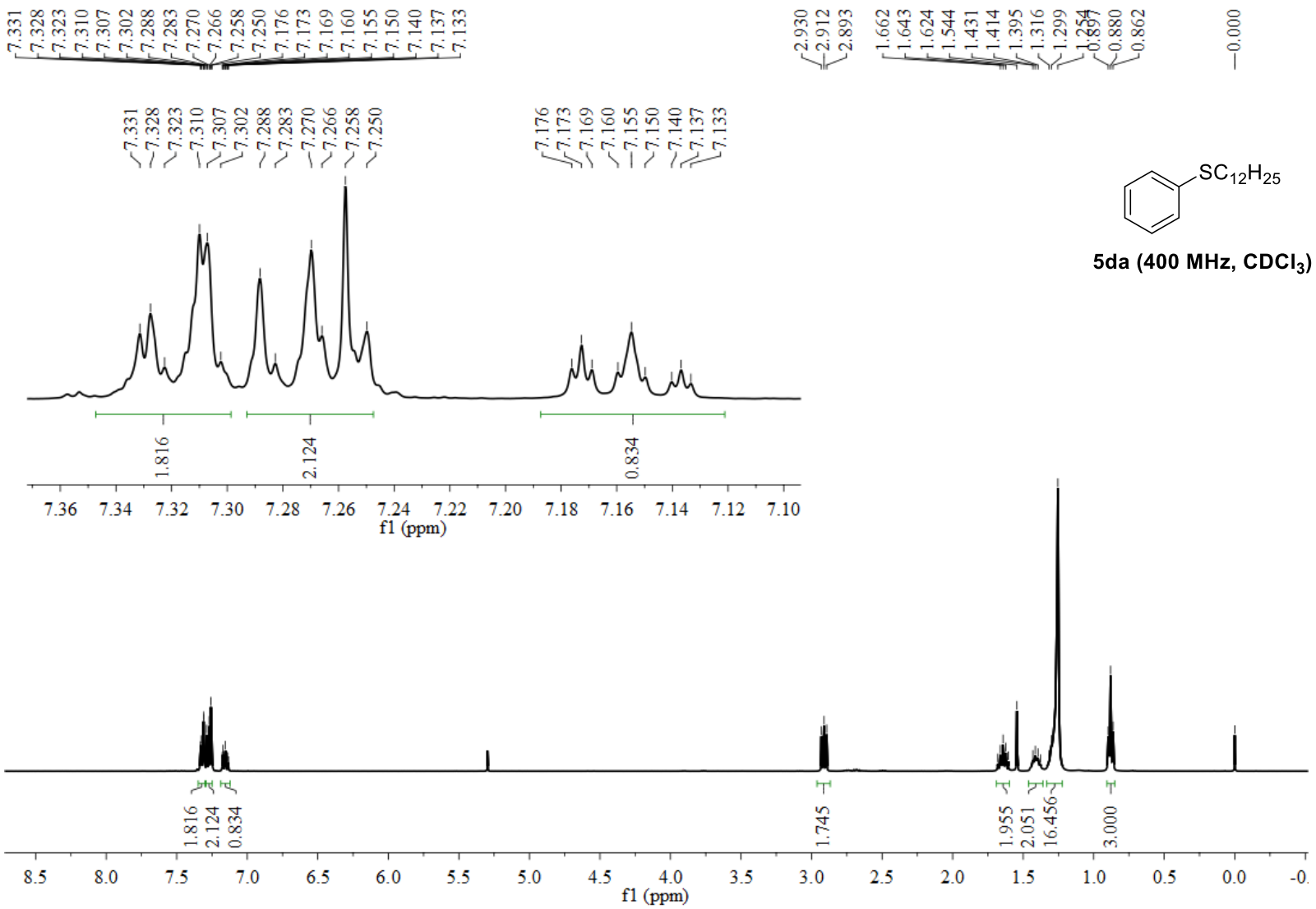


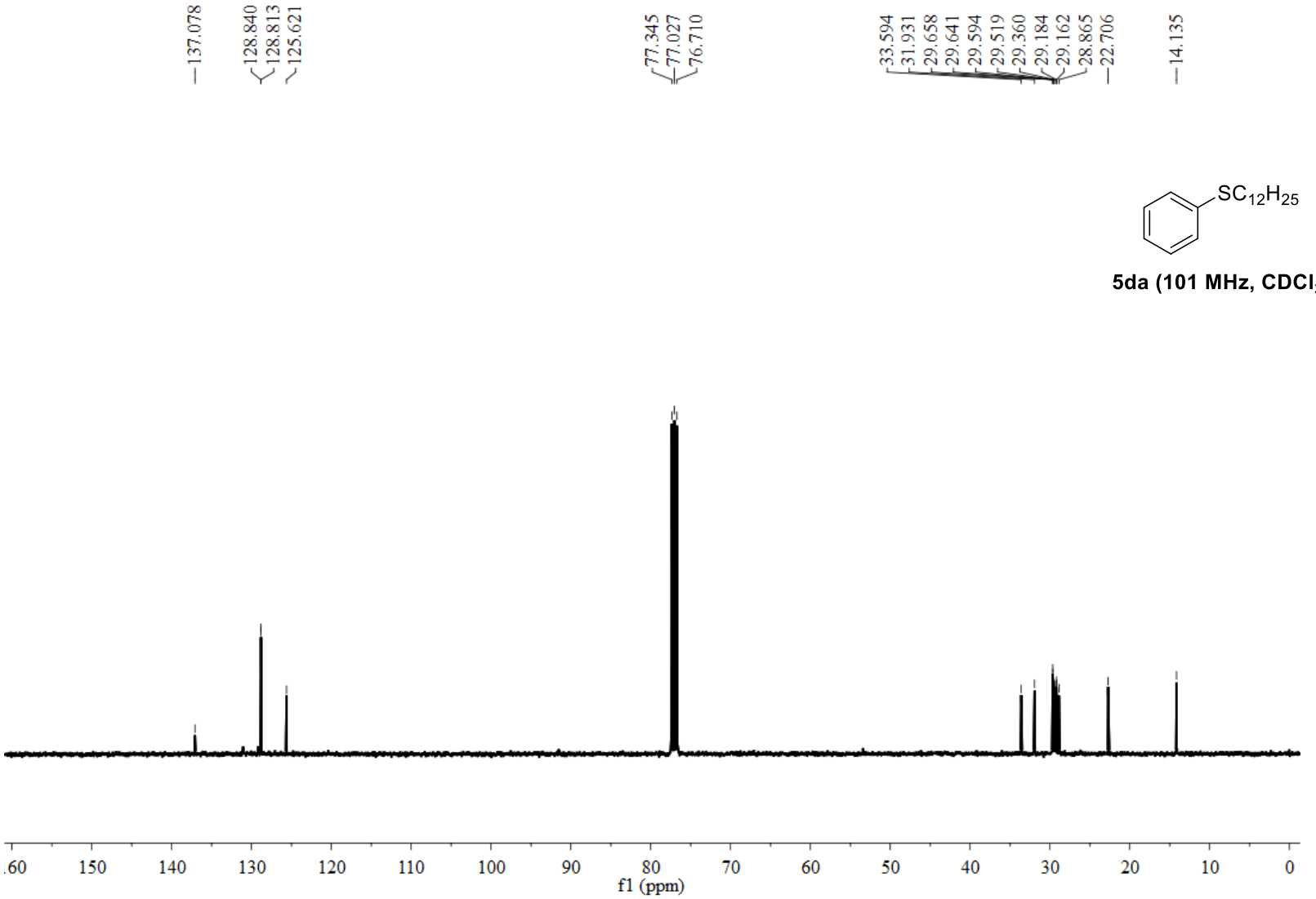

$C_{12}H_{25}S$

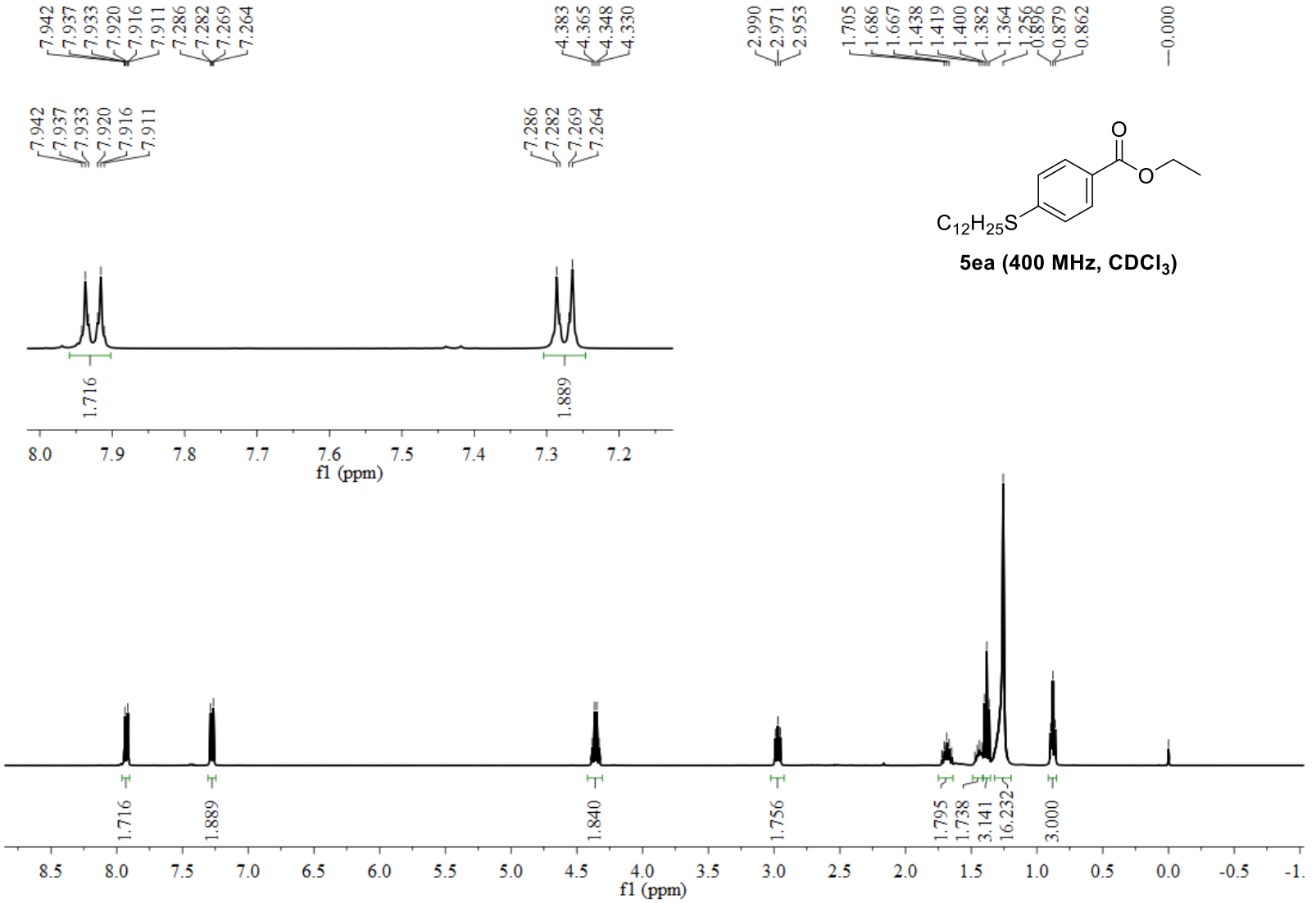
**5ca (400 MHz, $CDCl_3$)**



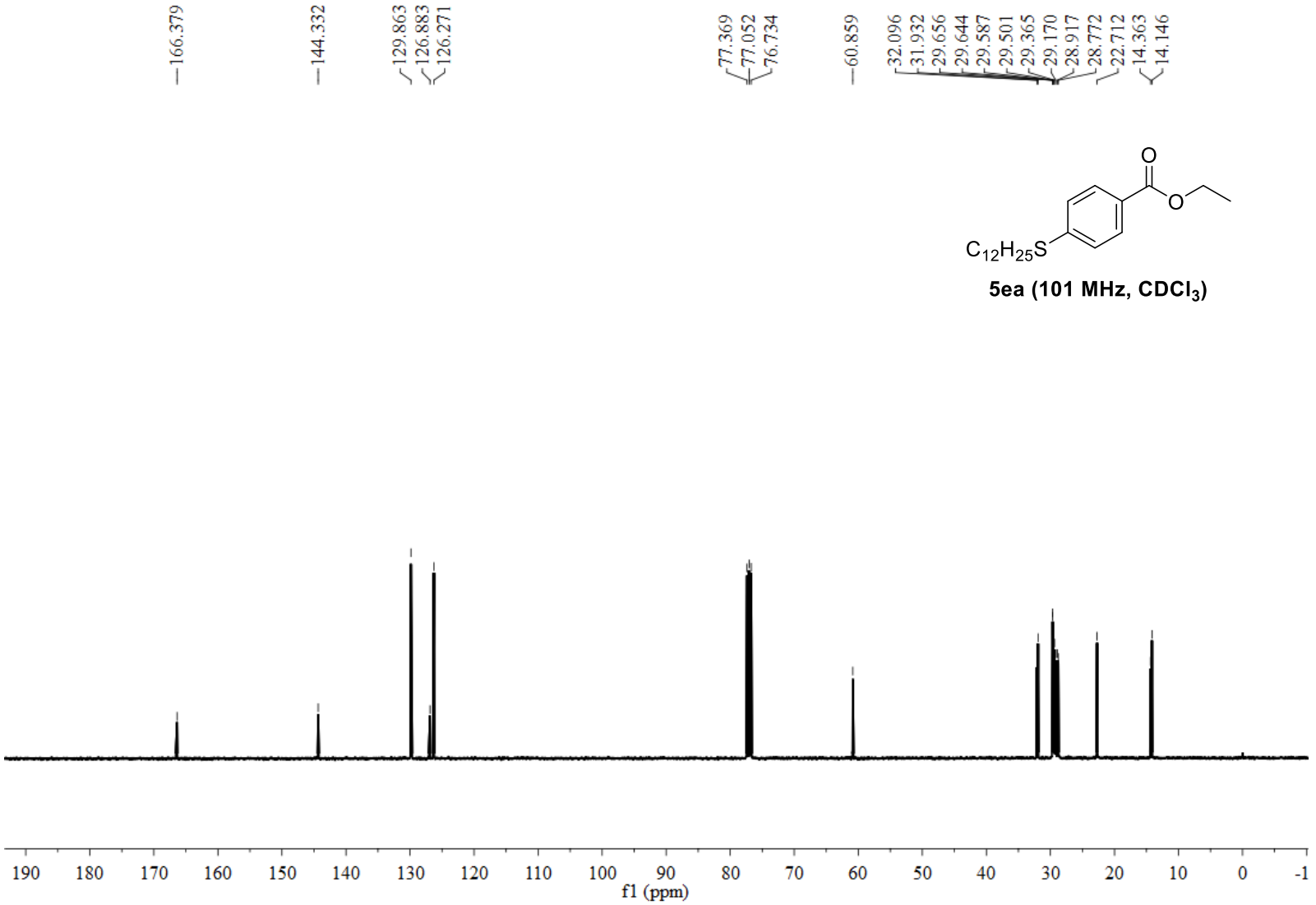

**5ca (101 MHz, $CDCl_3$)**


7.331
7.328
7.323
7.310
7.307
7.302
7.288
7.283
7.270
7.266
7.258
7.250
7.176
7.173
7.169
7.160
7.155
7.150
7.140
7.137
7.133
2.930
2.912
2.893
1.662
1.643
1.624
1.544
1.431
1.414
1.395
1.316
1.299
1.254
0.897
0.880
0.862
0.000
SC12H25
5da (400 MHz, CDCl3)
1.816
2.124
0.834
f1 (ppm)
1.745
1.955
2.051
16.456
3.000

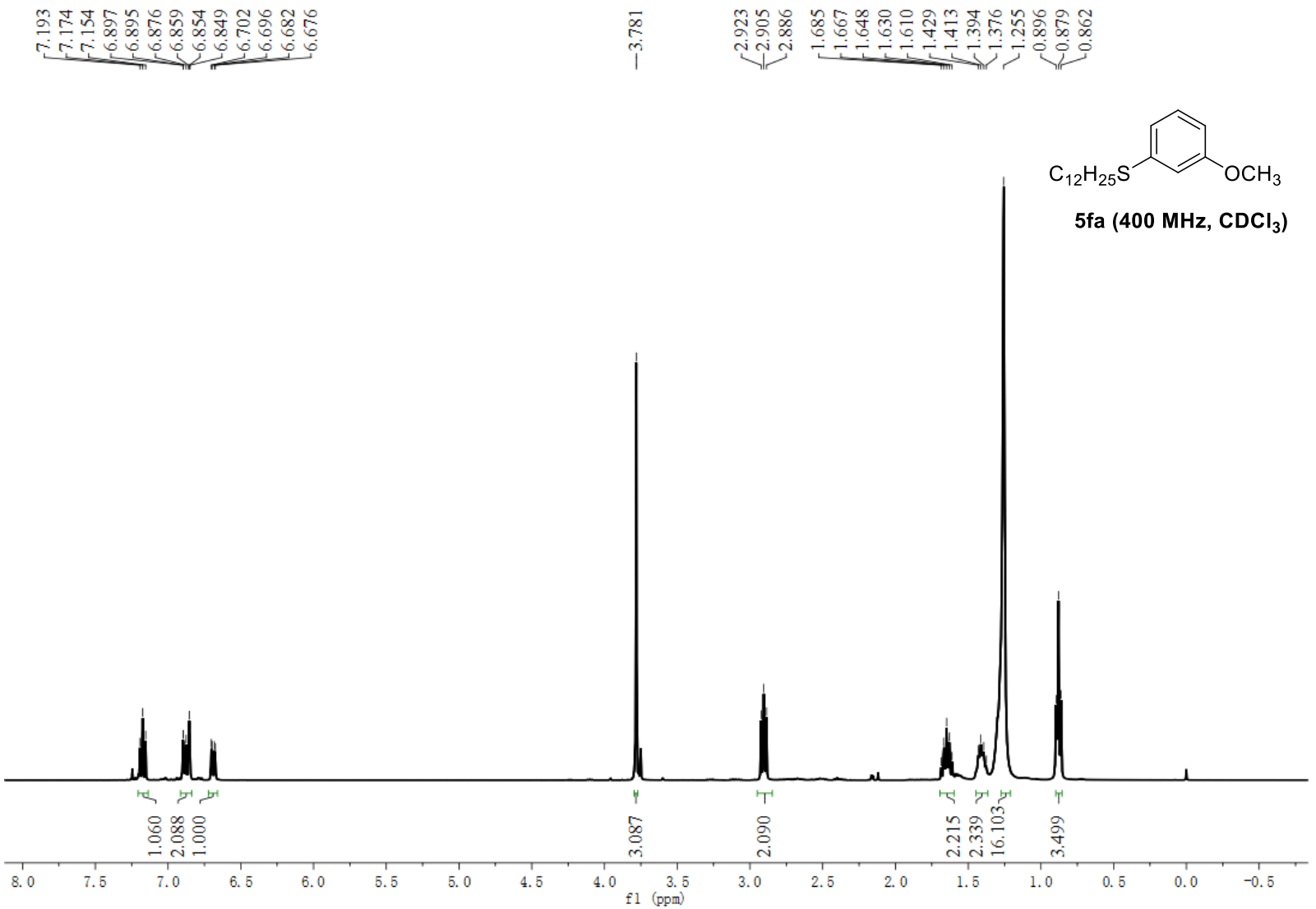

137.078
128.840
128.813
125.621
77.345
77.027
76.710
33.594
31.931
29.658
29.641
29.594
29.519
29.360
29.184
29.162
28.865
22.706
14.135
SC12H25
5da (101 MHz, CDCl3)
f1 (ppm)

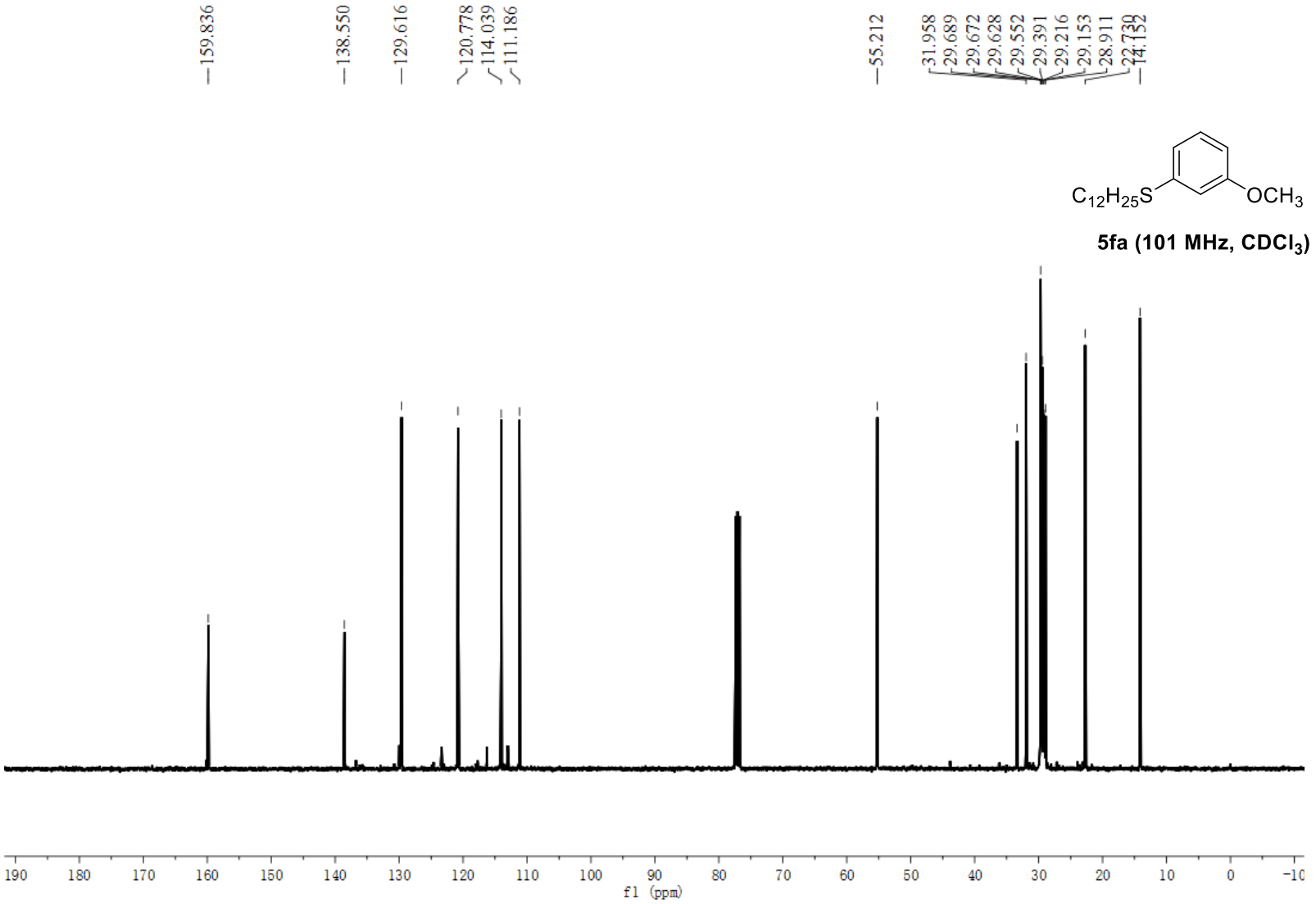


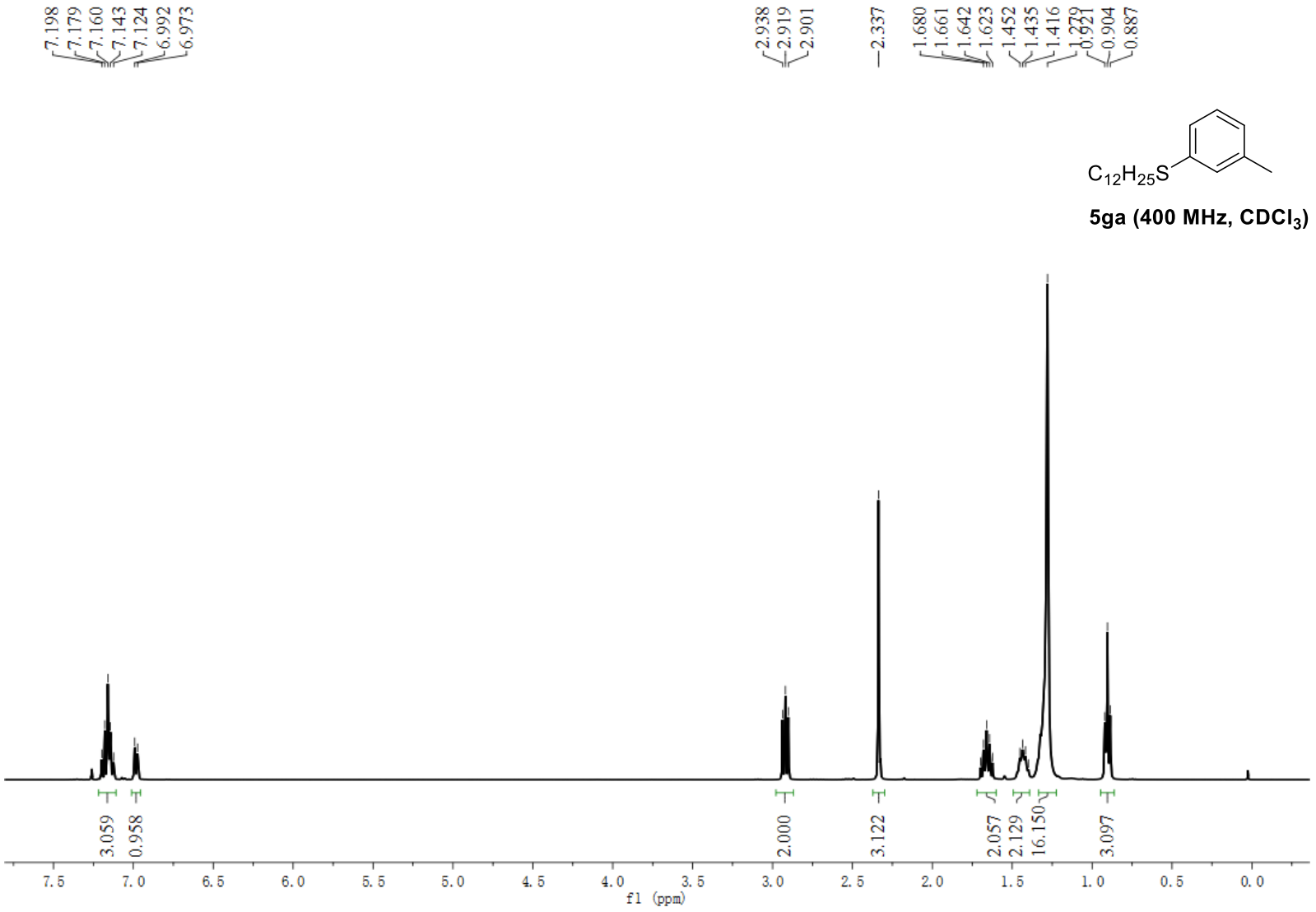

**5ea (400 MHz, $CDCl_3$)**



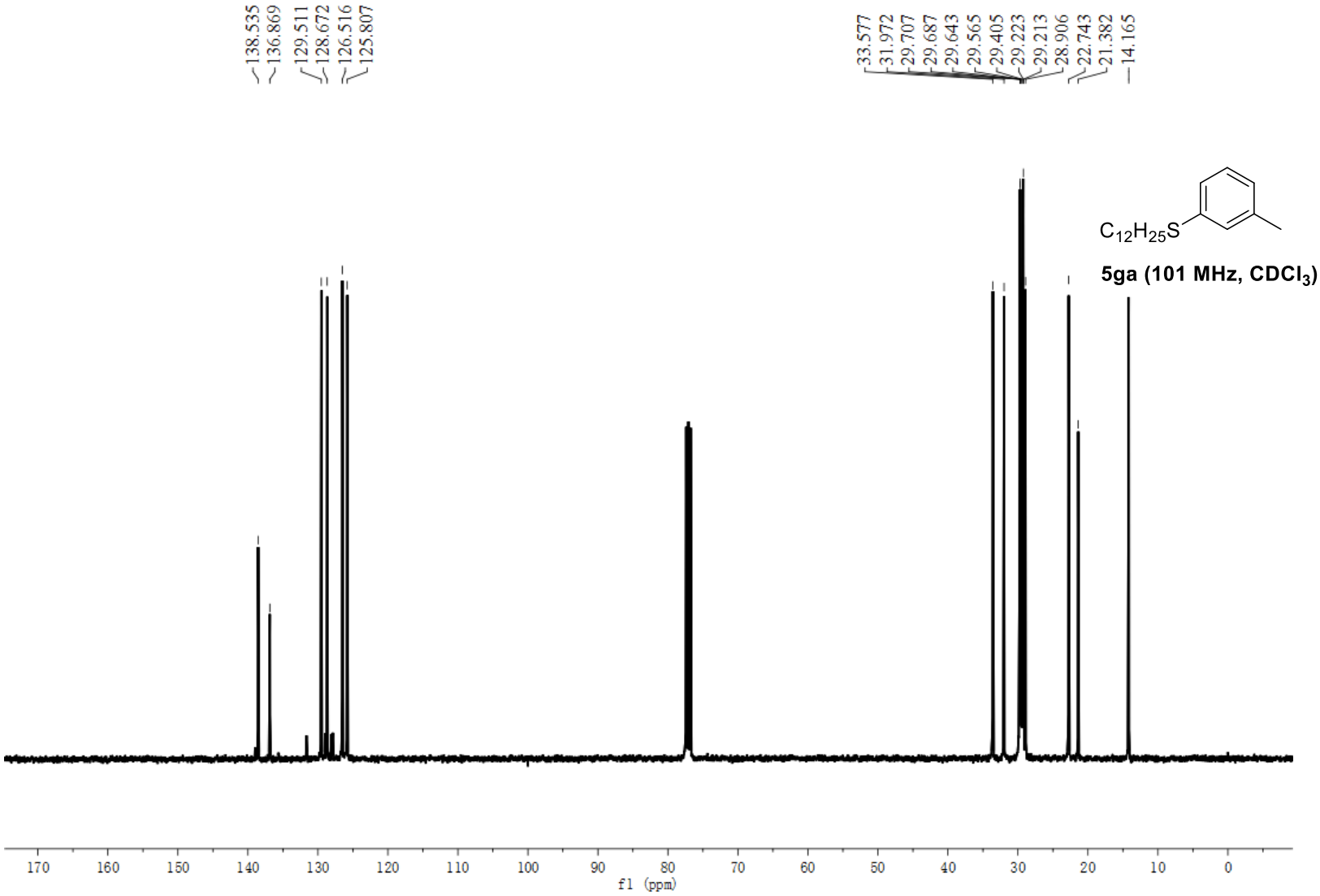

**5ea (101 MHz, $CDCl_3$)**

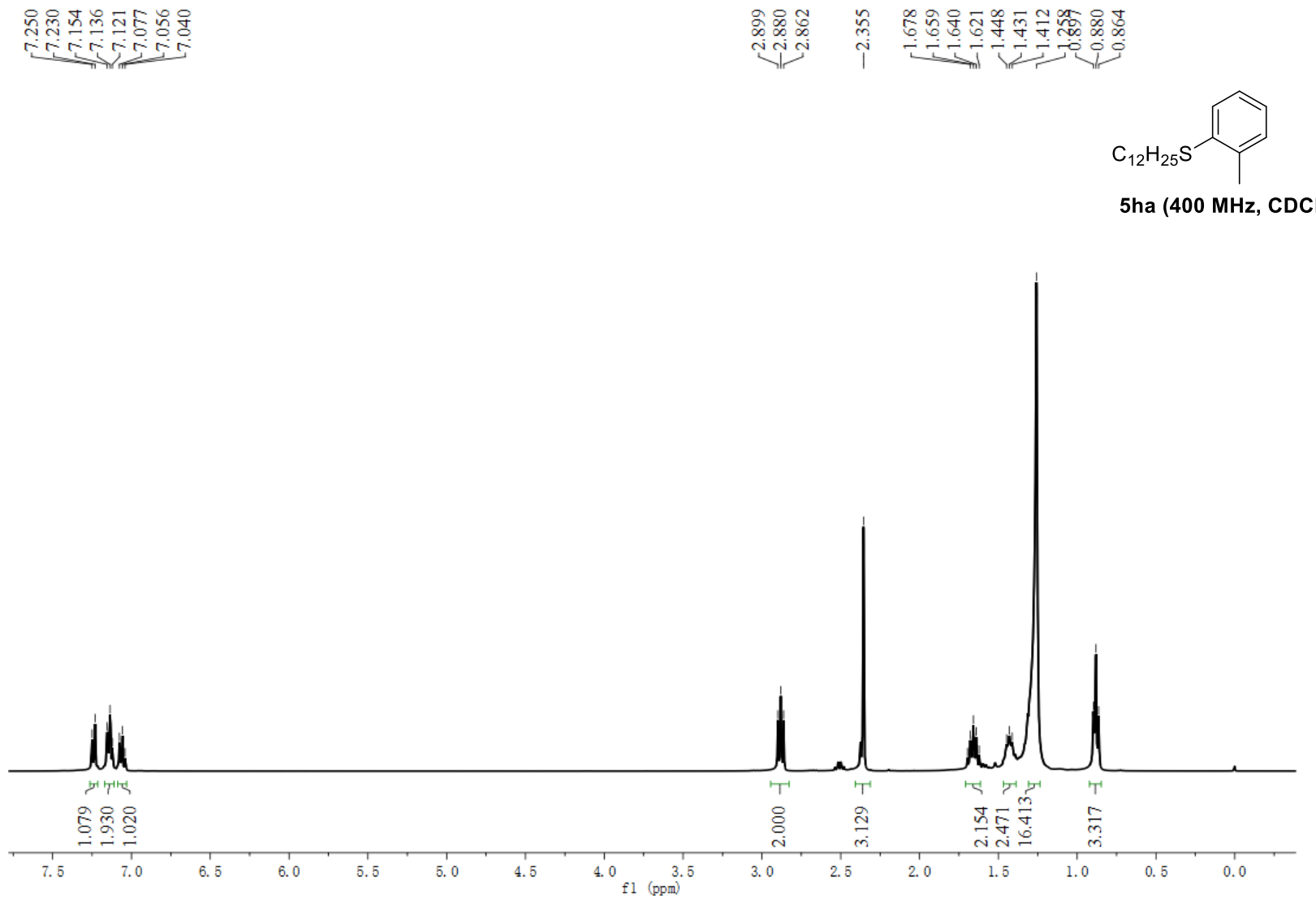

7.193
7.174
7.154
6.897
6.895
6.876
6.859
6.854
6.849
6.702
6.696
6.682
6.676
3.781
2.923
2.905
2.886
1.685
1.667
1.648
1.630
1.610
1.429
1.413
1.394
1.376
1.255
0.896
0.879
0.862
C12H25S
OCH3
5fa (400 MHz, CDCl3)
1.060
2.088
1.000
3.087
2.090
2.215
2.339
16.103
3.499
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.836
138.550
129.616
120.778
114.039
111.186
55.212
31.958
29.689
29.672
29.628
29.552
29.391
29.216
29.153
28.911
22.730
14.132
C12H25S
OCH3
5fa (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

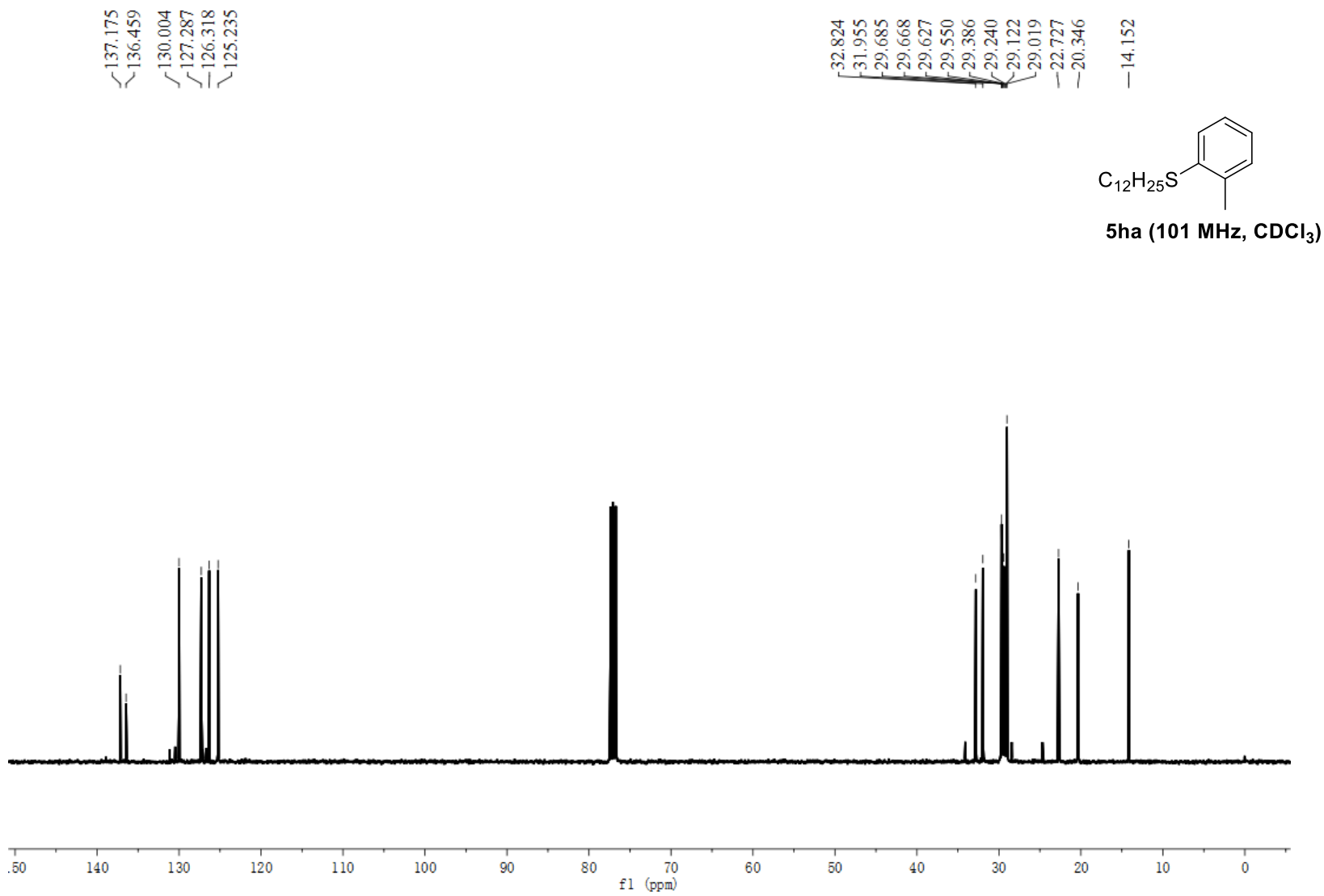



**5ga (400 MHz, $CDCl_3$)**

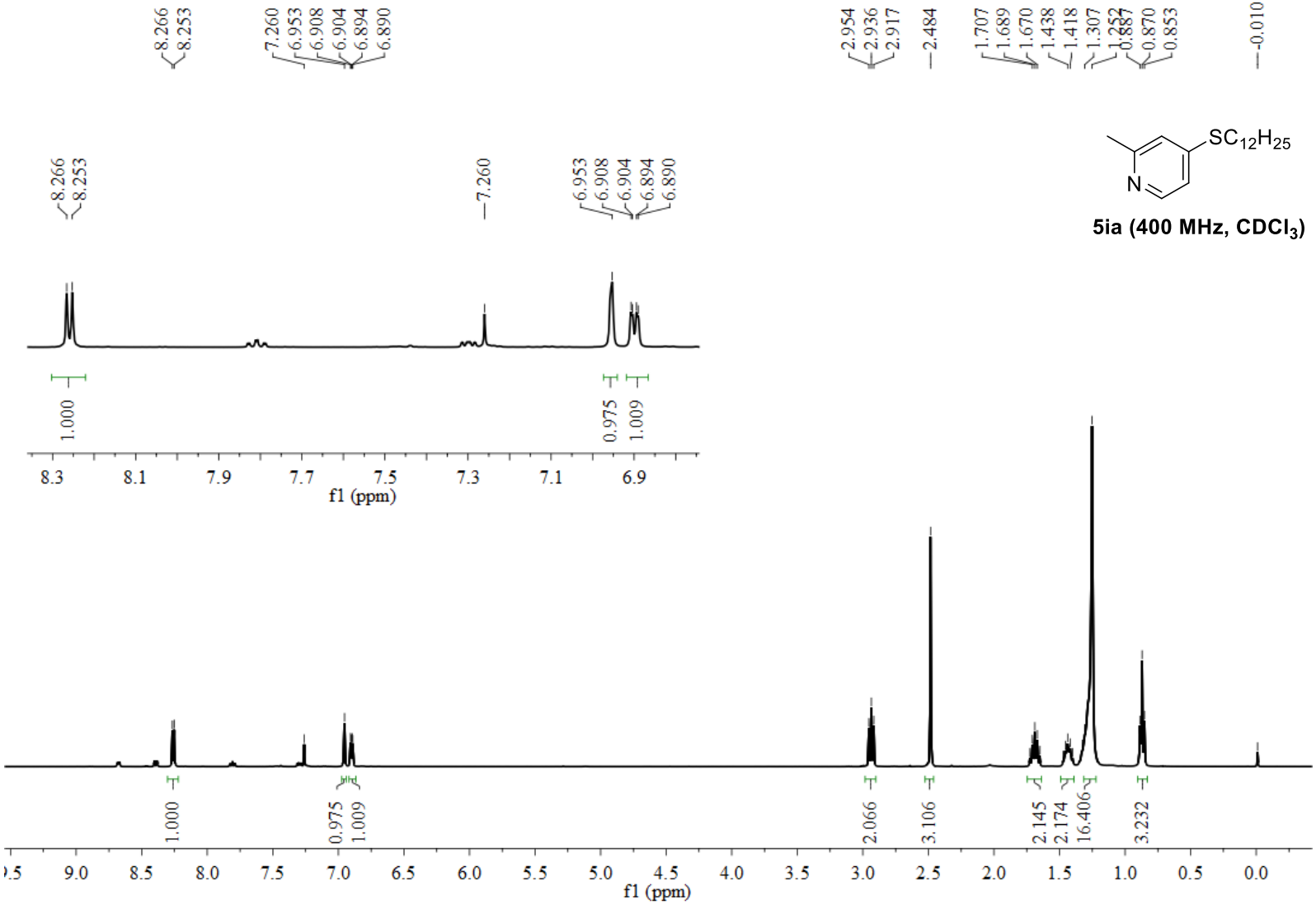

138.535
136.869
129.511
128.672
126.516
125.807
33.577
31.972
29.707
29.687
29.643
29.565
29.405
29.223
29.213
28.906
22.743
21.382
14.165
C12H25S
5ga (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

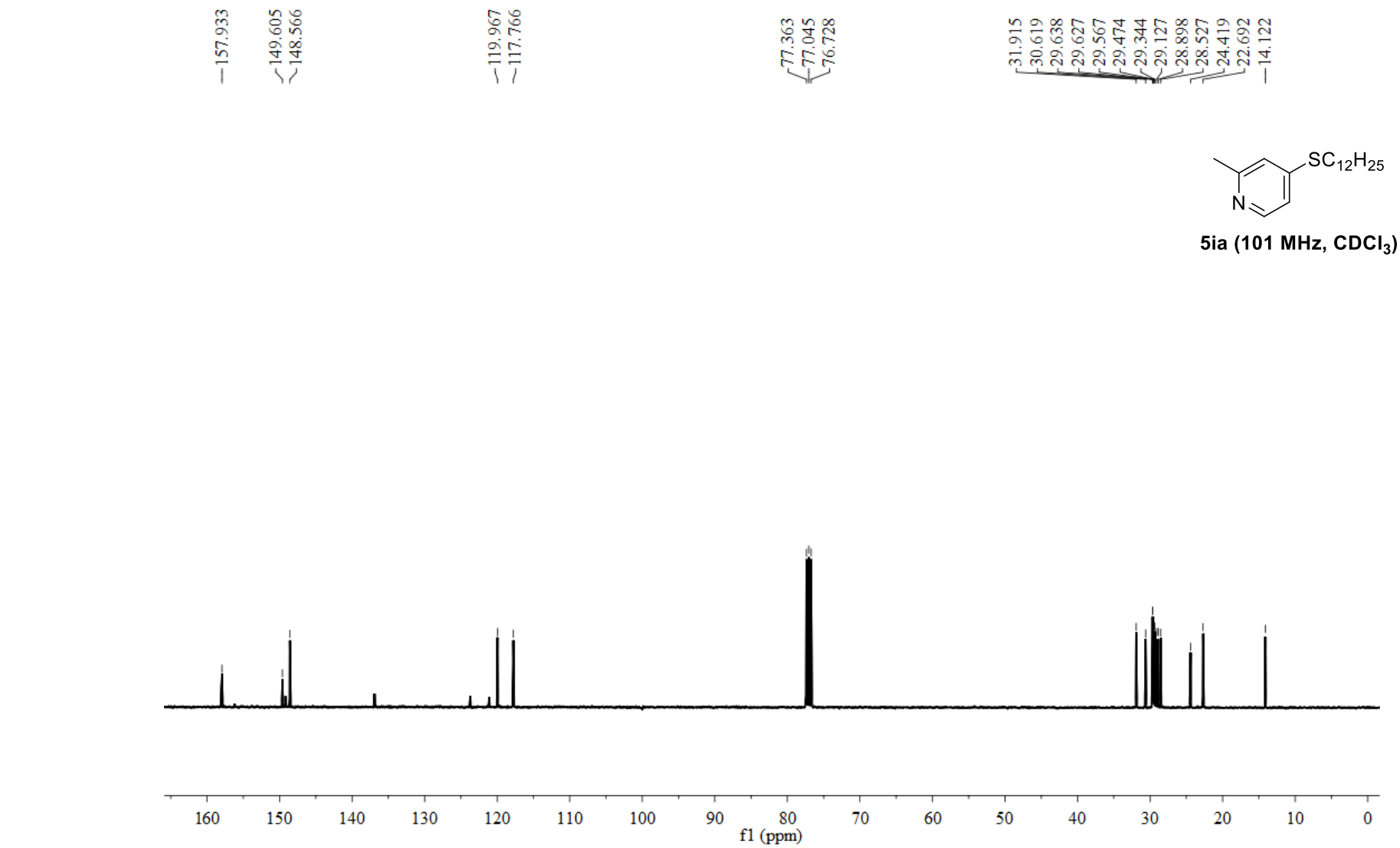



**5ha (400 MHz, $CDCl_3$)**

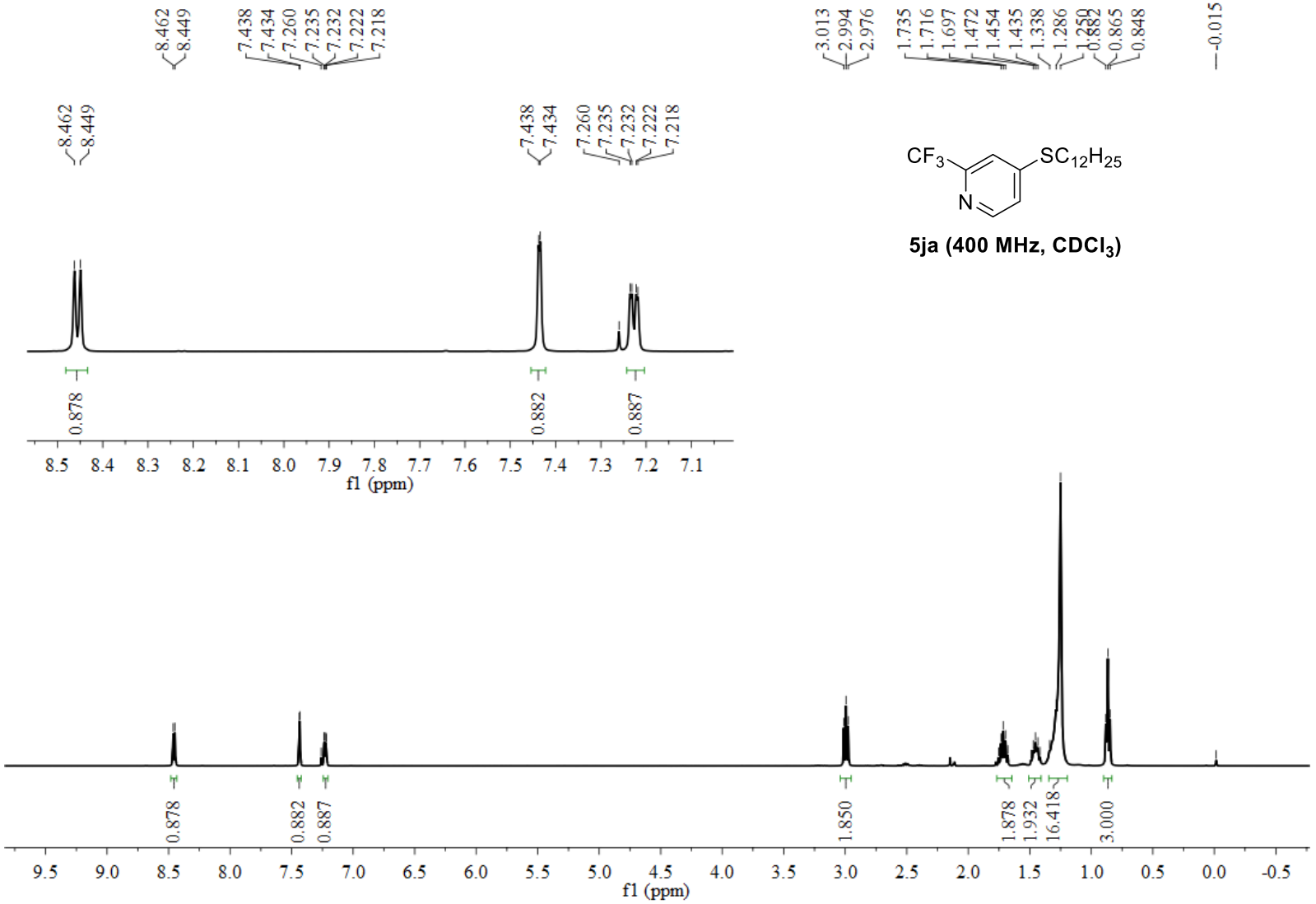



**5ha (101 MHz, $CDCl_3$)**

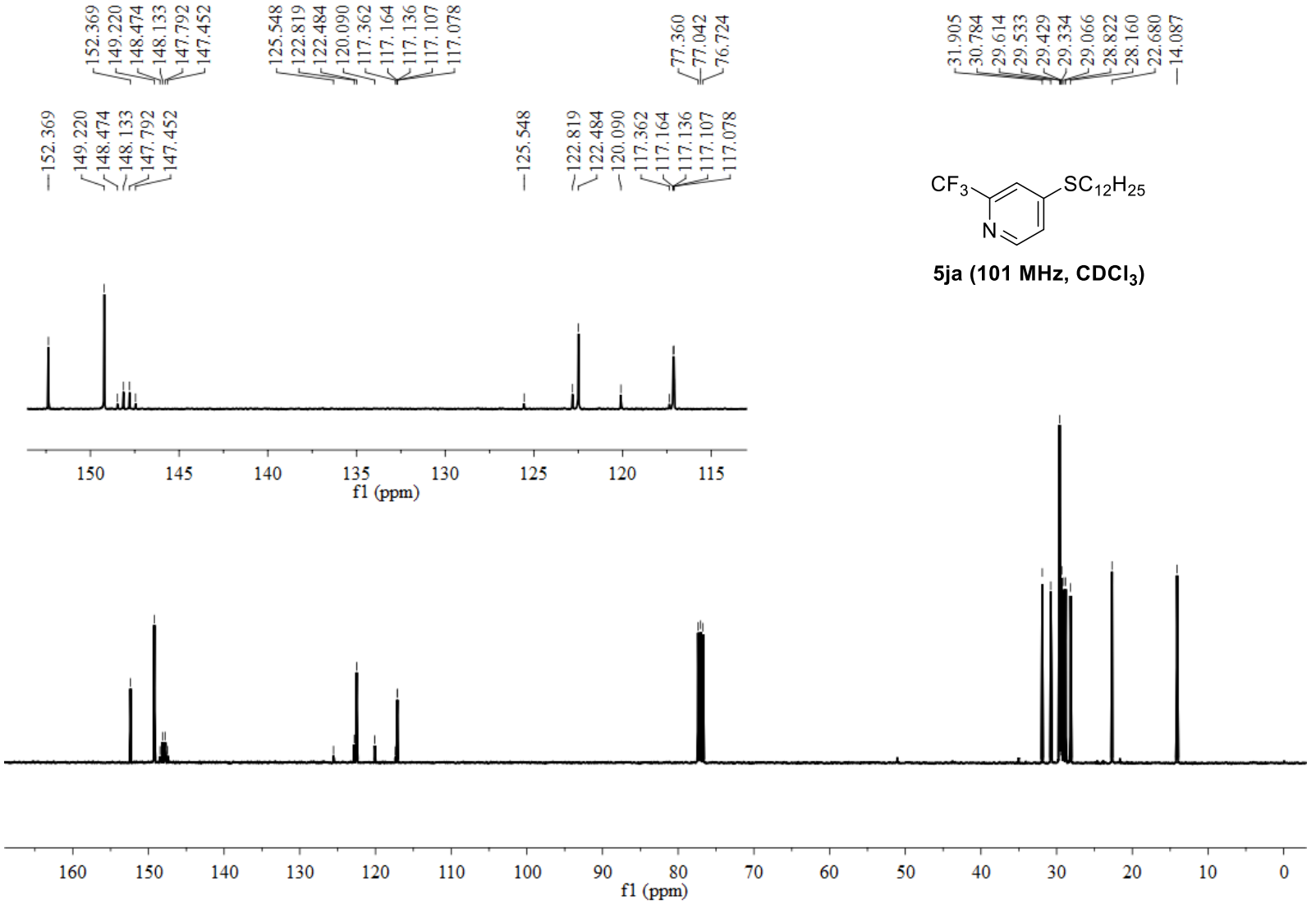

8.266
8.253
7.260
6.953
6.908
6.904
6.894
6.890
2.954
2.936
2.917
2.484
1.707
1.689
1.670
1.438
1.418
1.307
0.887
0.870
0.853
0.010
SC12H25
N
5ia (400 MHz, CDCl3)
1.000
0.975
1.009
f1 (ppm)
2.066
3.106
2.145
2.174
16.406
3.232

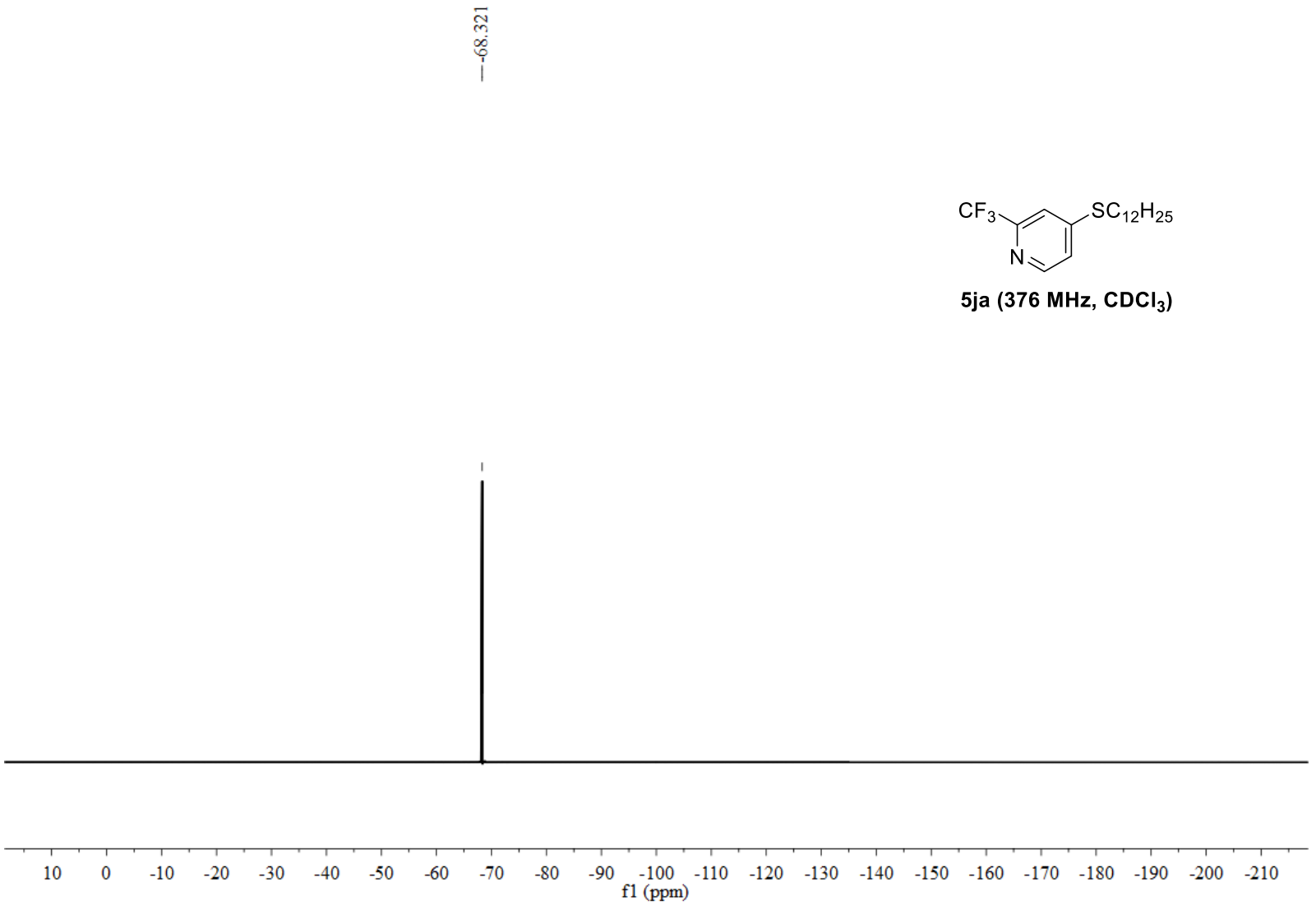



**5ia (101 MHz, $CDCl_3$)**

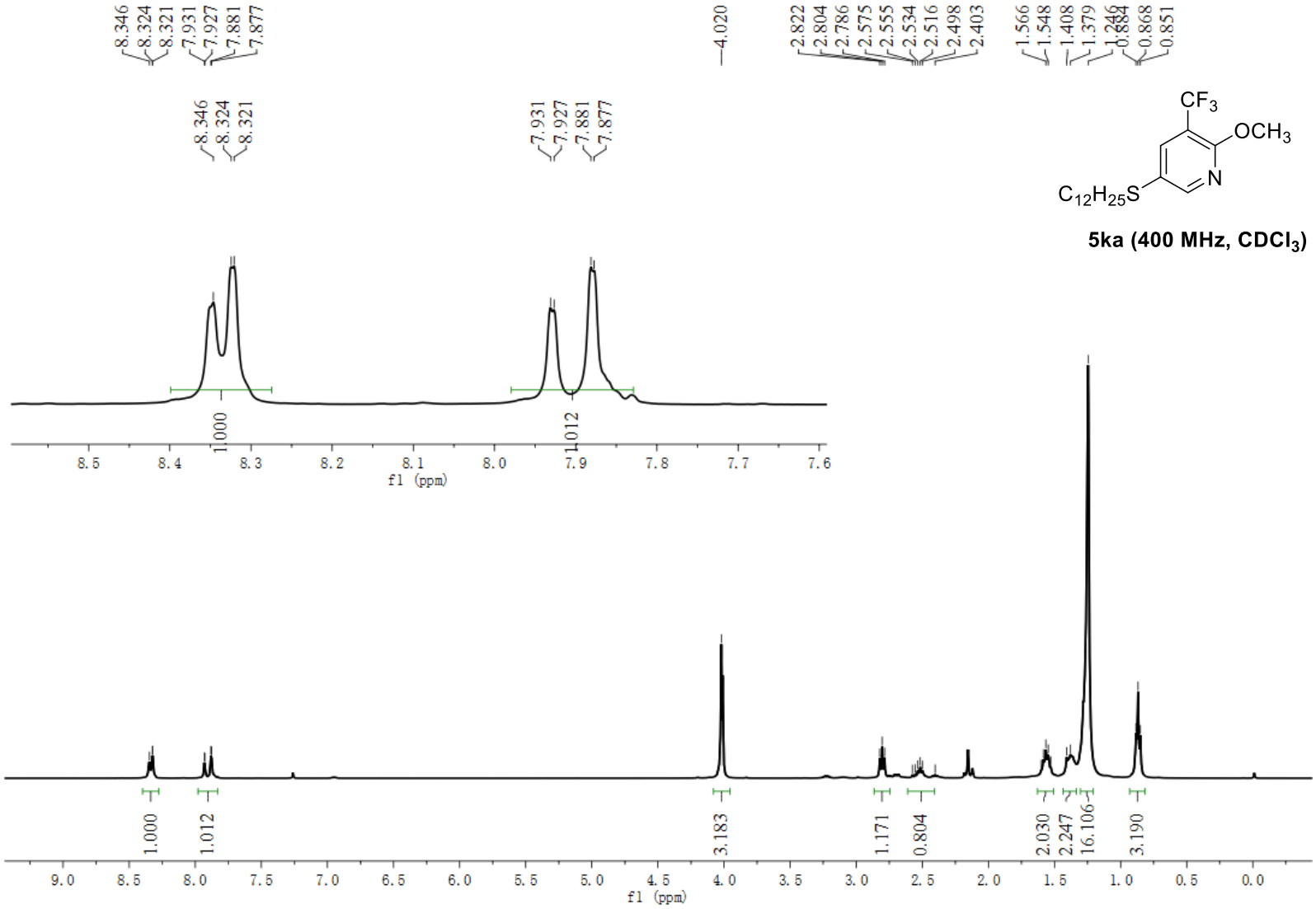



**5ja (400 MHz, $CDCl_3$)**

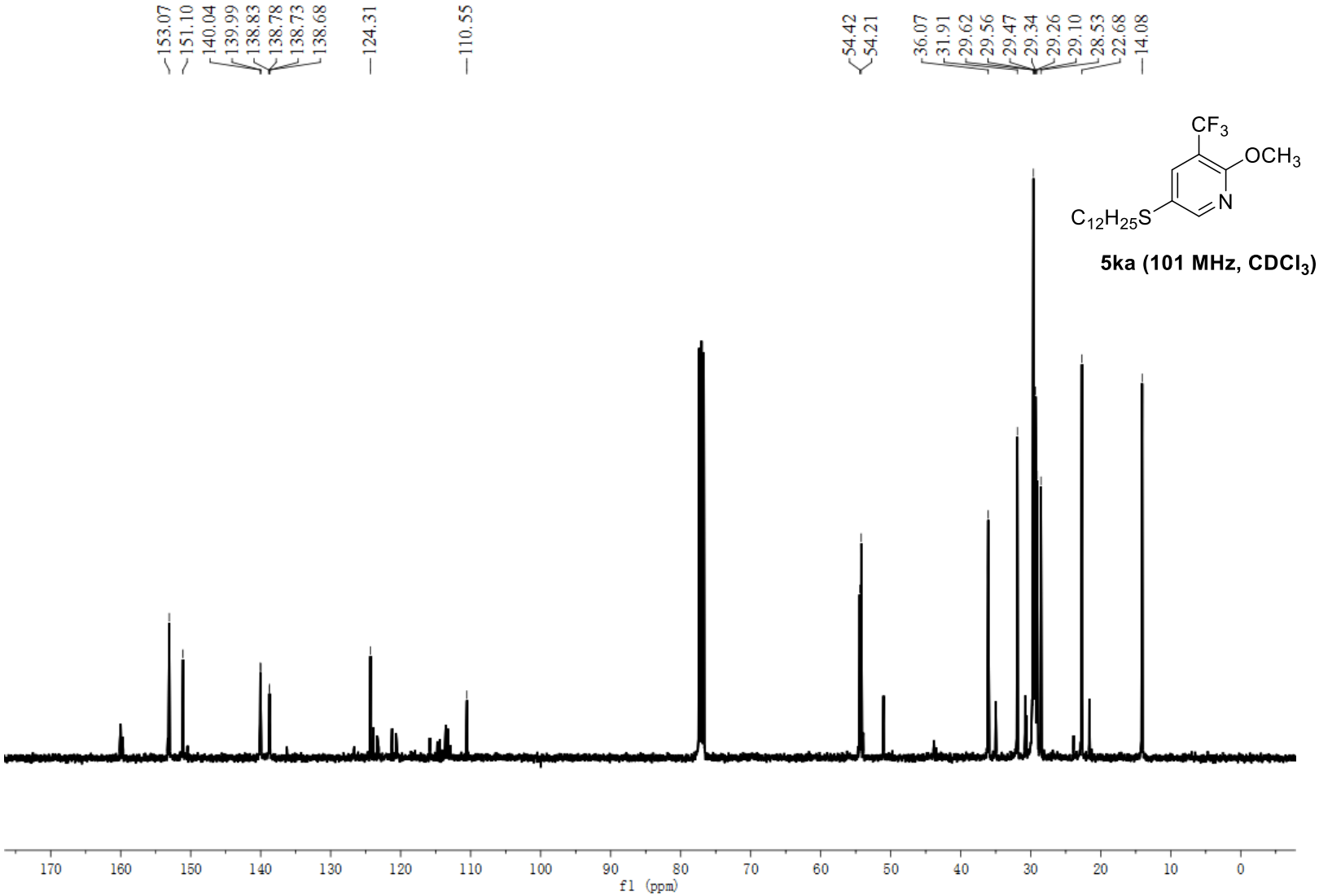

152.369
149.220
148.474
148.133
147.792
147.452
125.548
122.819
122.484
120.090
117.362
117.164
117.136
117.107
117.078
77.360
77.042
76.724
31.905
30.784
29.614
29.533
29.429
29.334
29.066
28.822
28.160
22.680
14.087
CF3
SC12H25
N
5ja (101 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

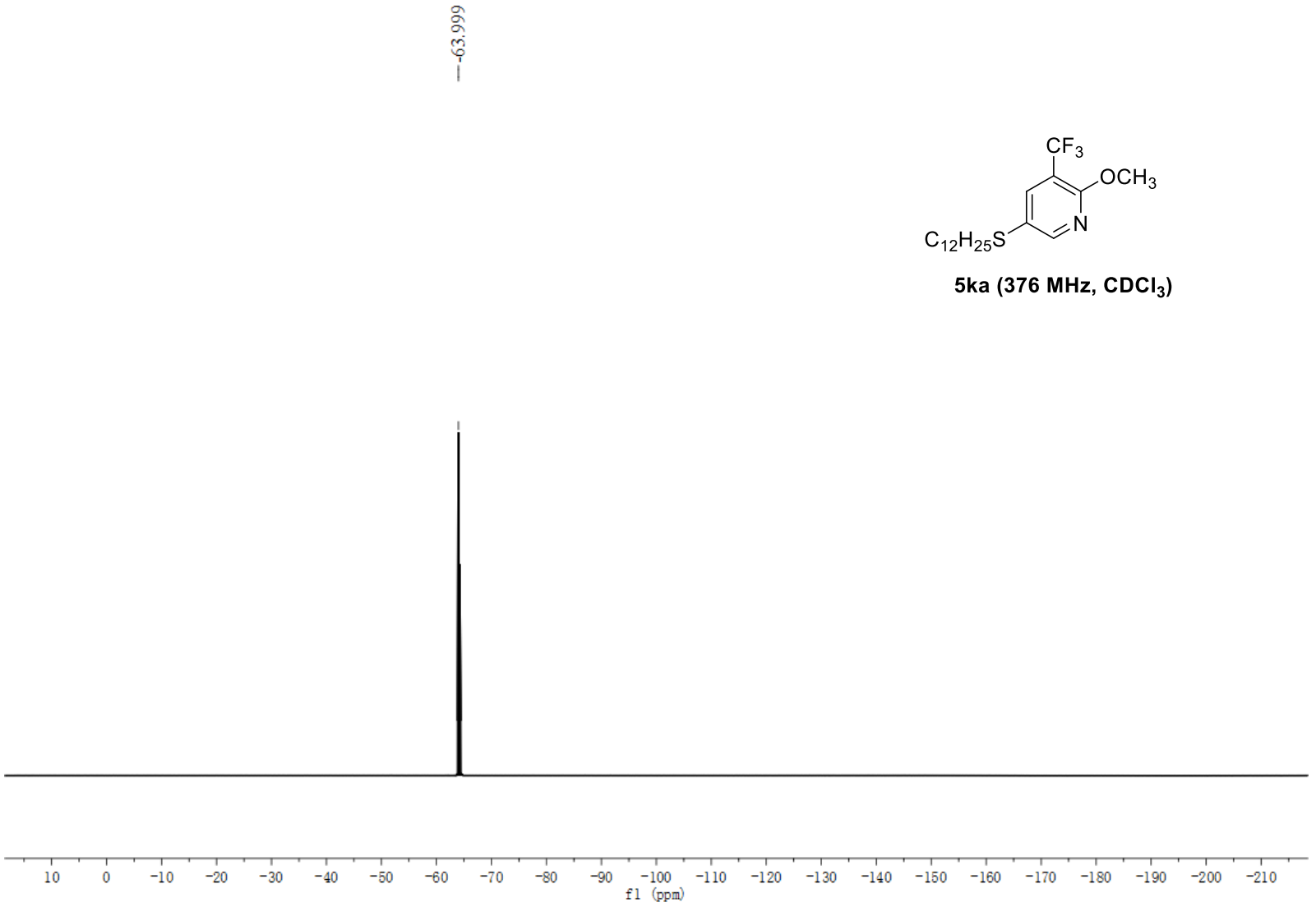



**5ja (376 MHz, $CDCl_3$)**

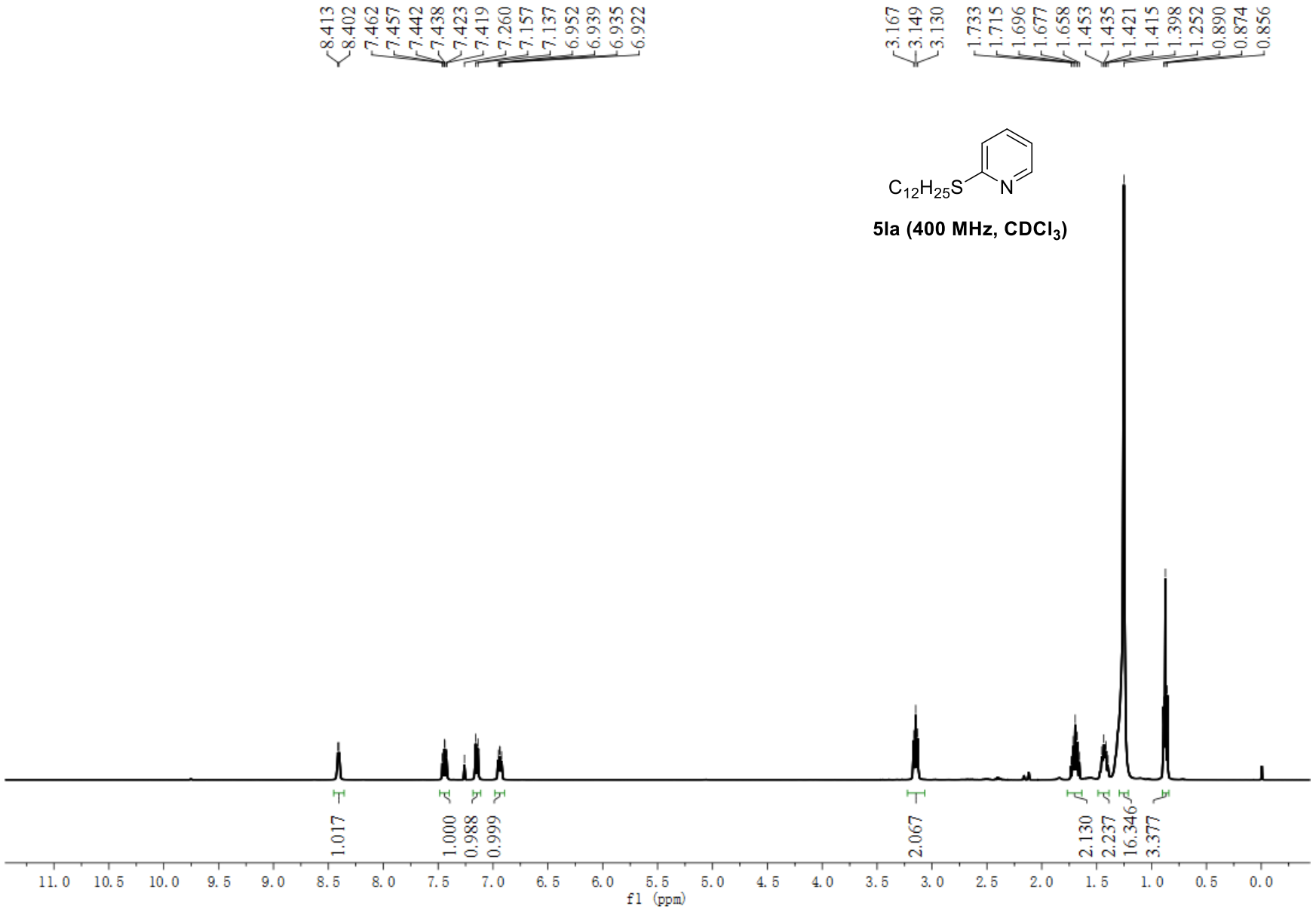



**5ka (400 MHz, $CDCl_3$)**

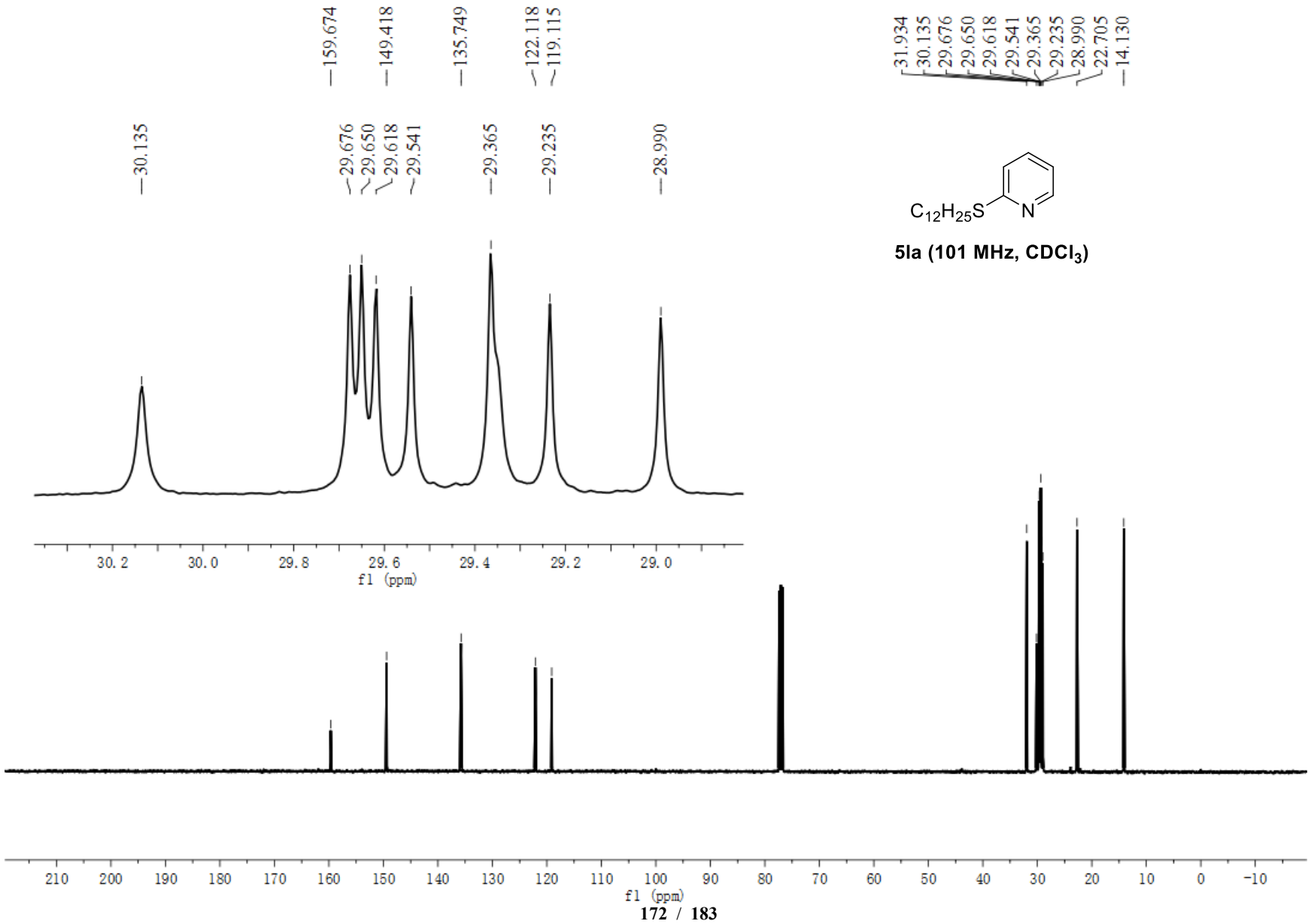

153.07
151.10
140.04
139.99
138.83
138.78
138.73
138.68
124.31
110.55
54.42
54.21
36.07
31.91
29.62
29.56
29.47
29.34
29.26
29.10
28.53
22.68
14.08
CF3
OCH3
N
C12H25S
5ka (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



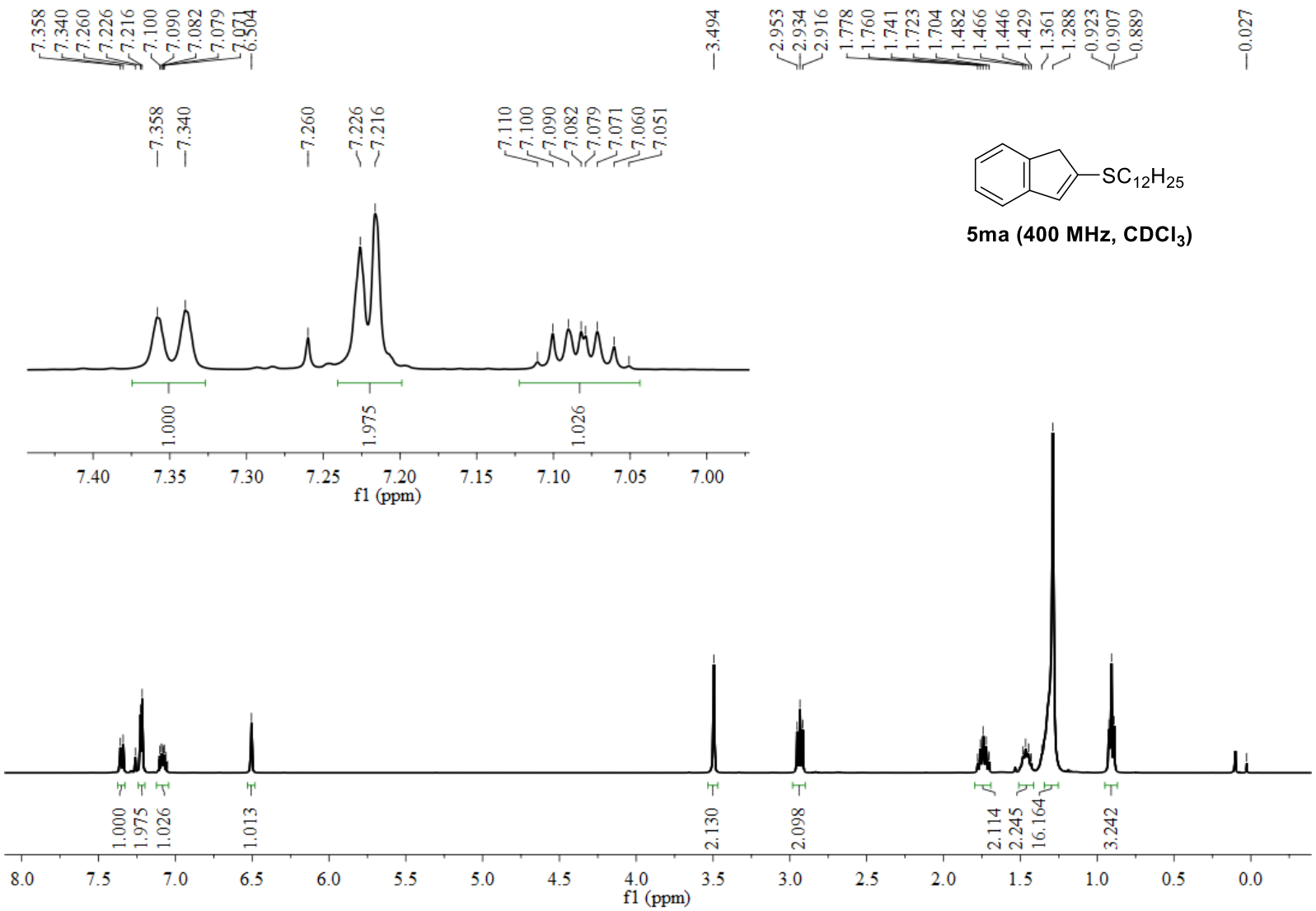

**5ka (376 MHz, $CDCl_3$)**

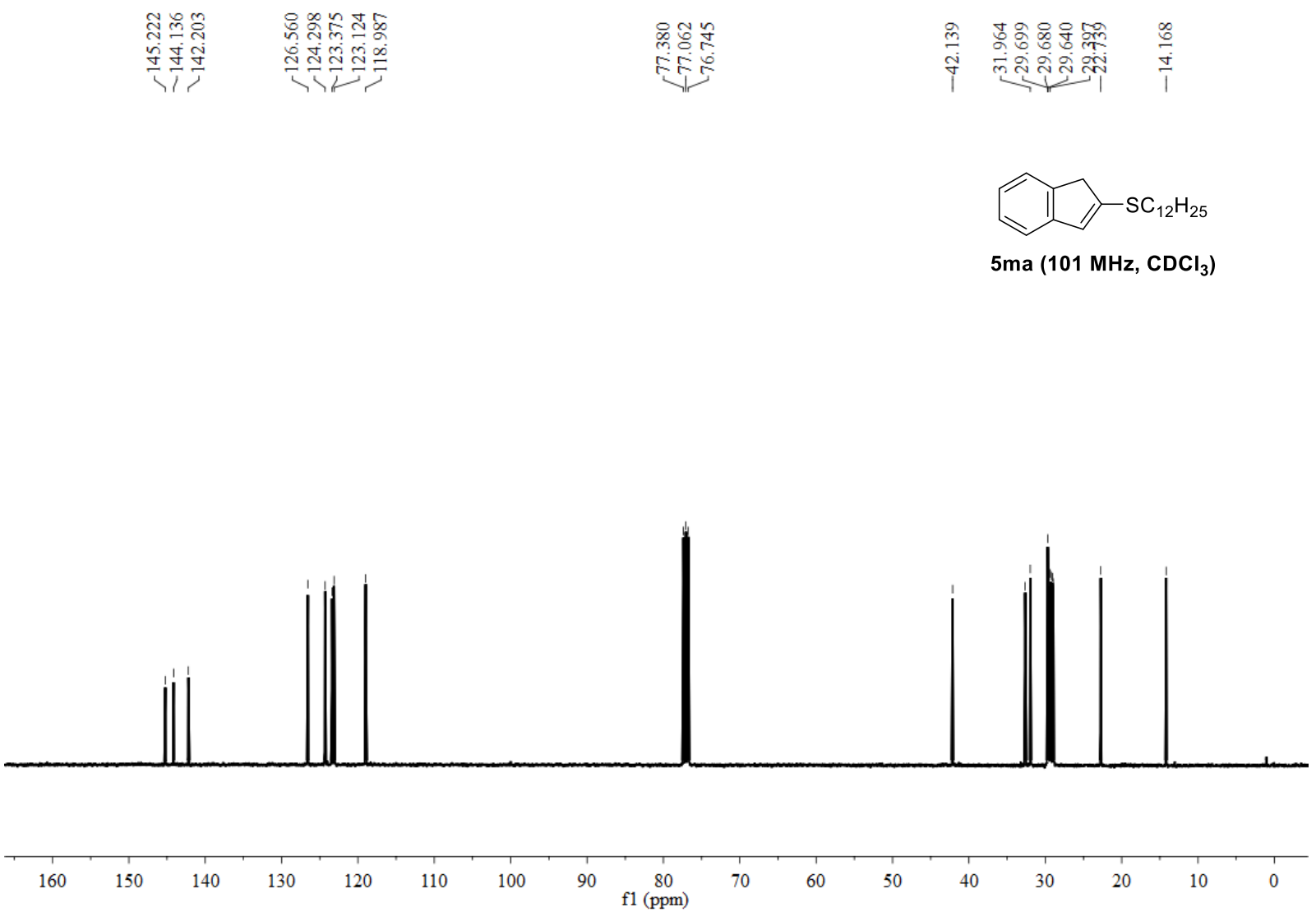



**5la (400 MHz, $CDCl_3$)**

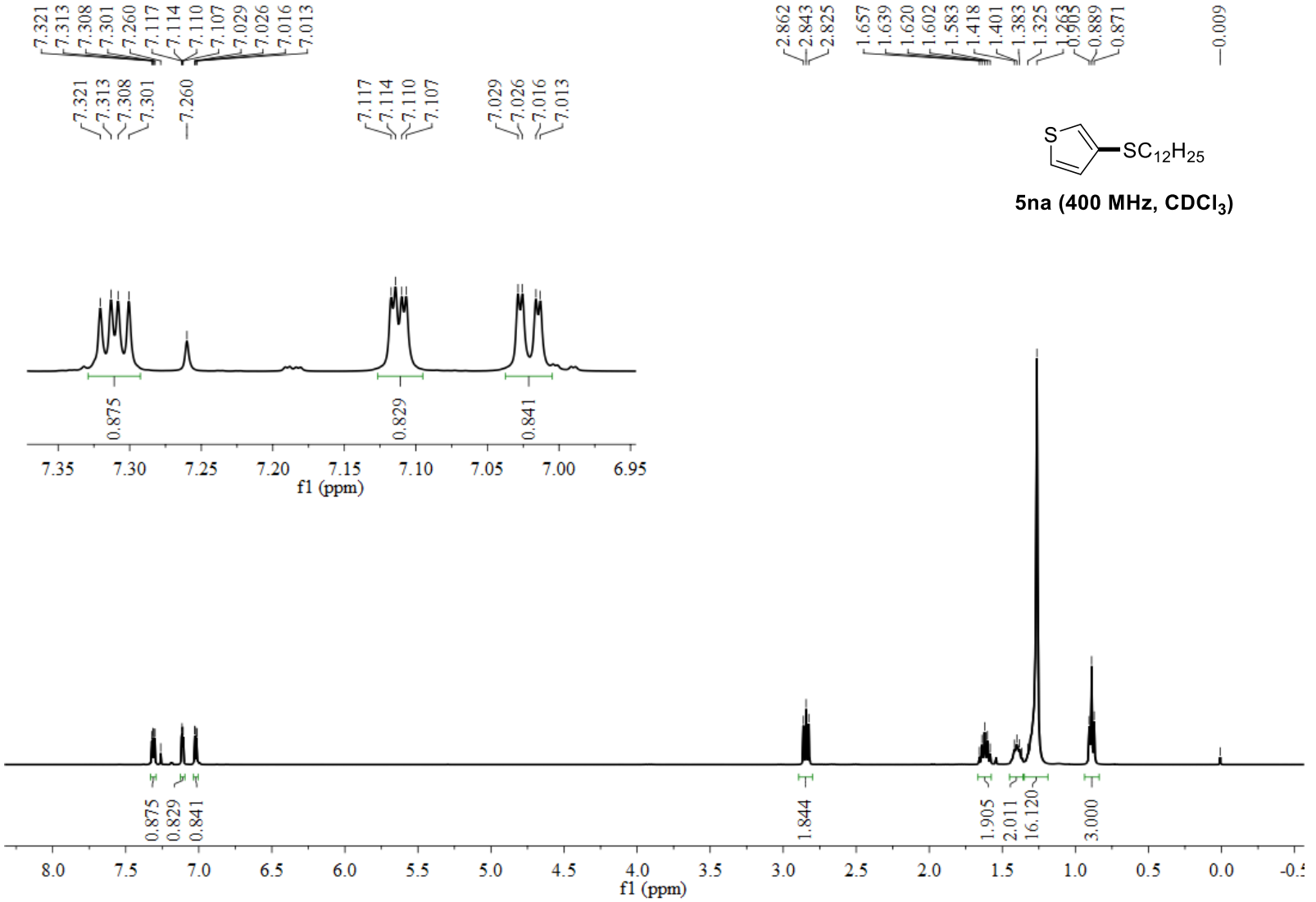



**5la (101 MHz, $CDCl_3$)**

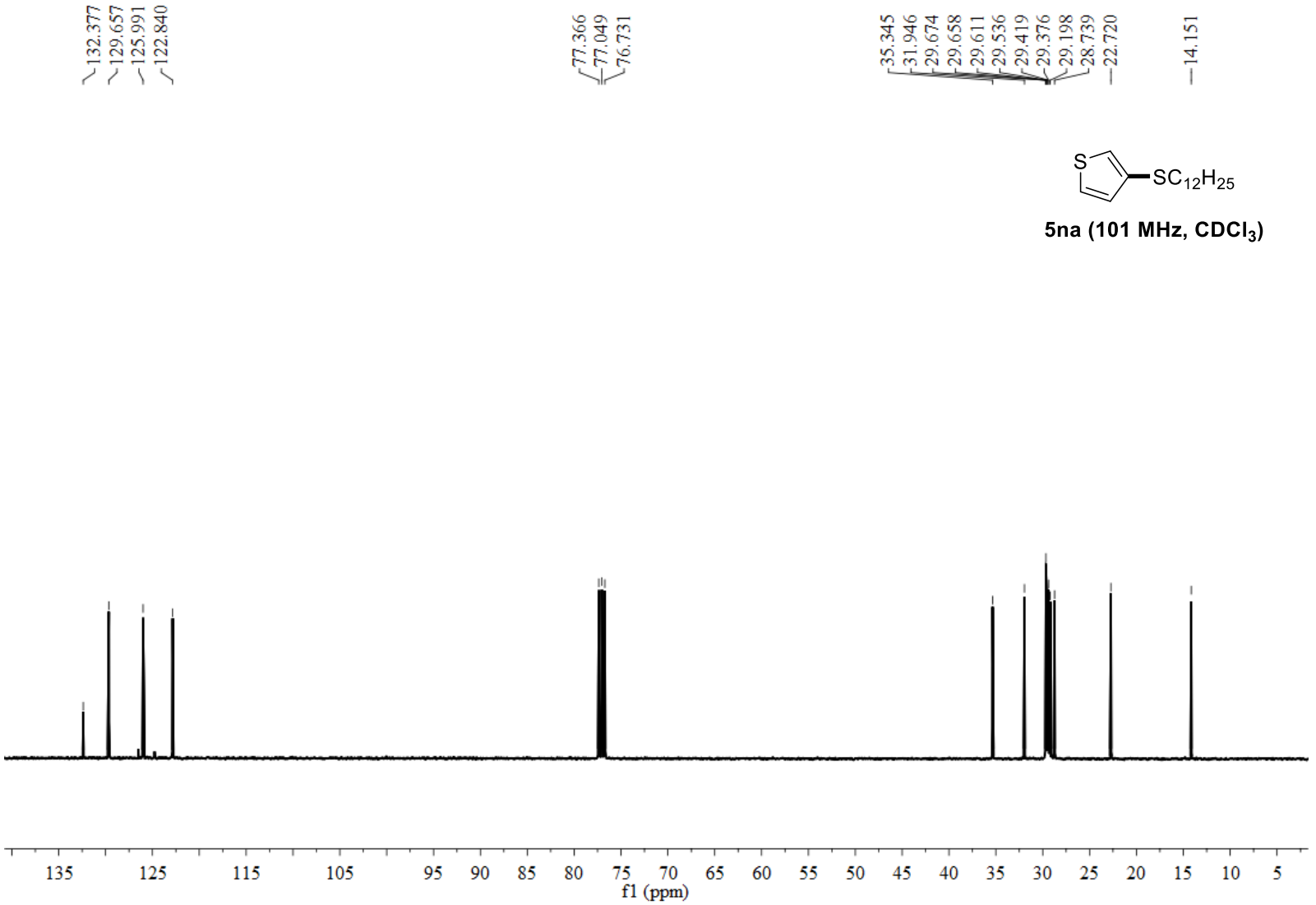

7.358
7.340
7.260
7.226
7.216
7.100
7.090
7.082
7.079
7.071
6.504
3.494
2.953
2.934
2.916
1.778
1.760
1.741
1.723
1.704
1.482
1.466
1.446
1.429
1.361
1.288
0.923
0.907
0.889
0.027
SC12H25
5ma (400 MHz, CDCl3)
1.000
1.975
1.026
1.013
2.130
2.098
2.114
2.245
16.164
3.242
f1 (ppm)



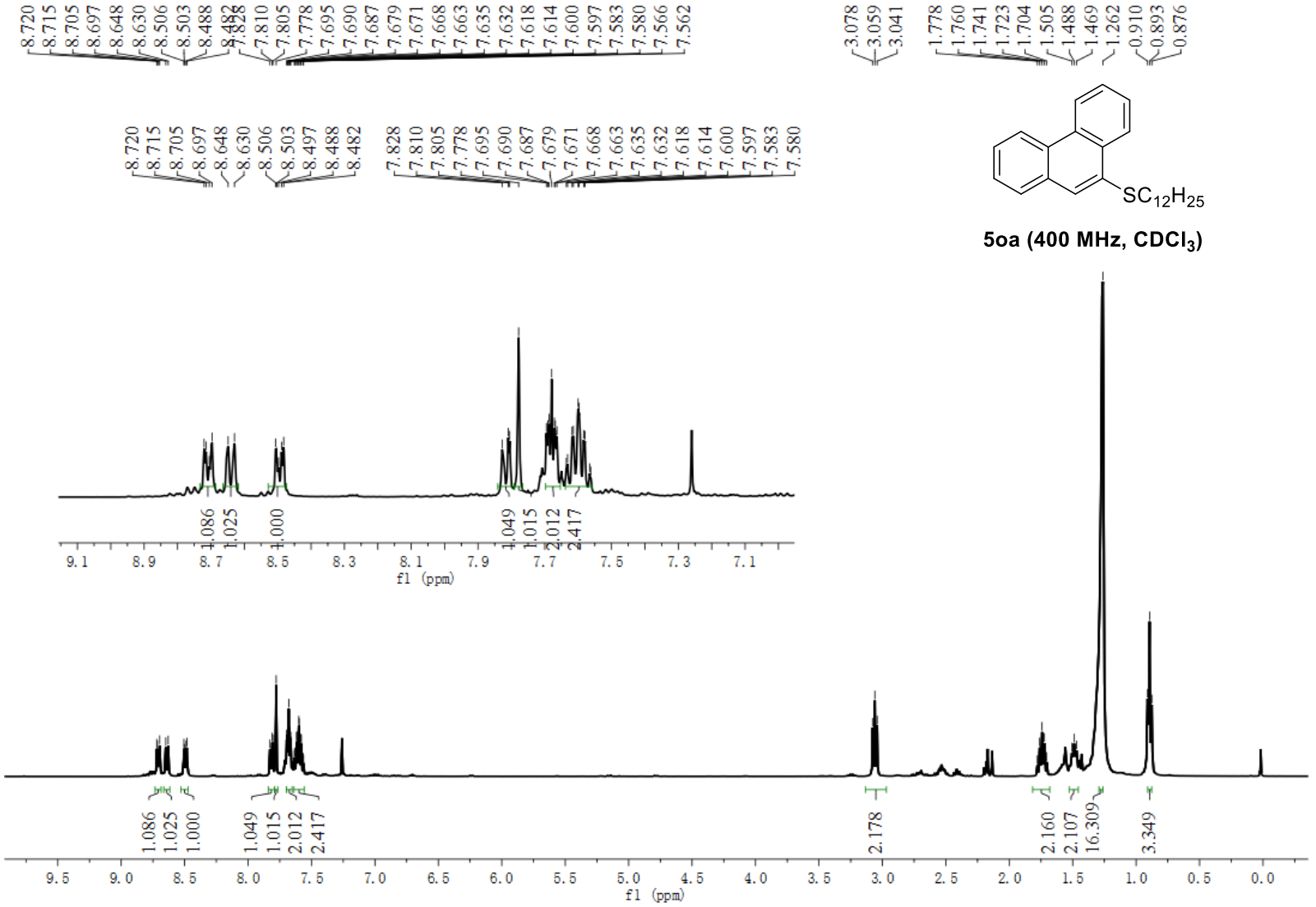

**5ma (101 MHz, $CDCl_3$)**

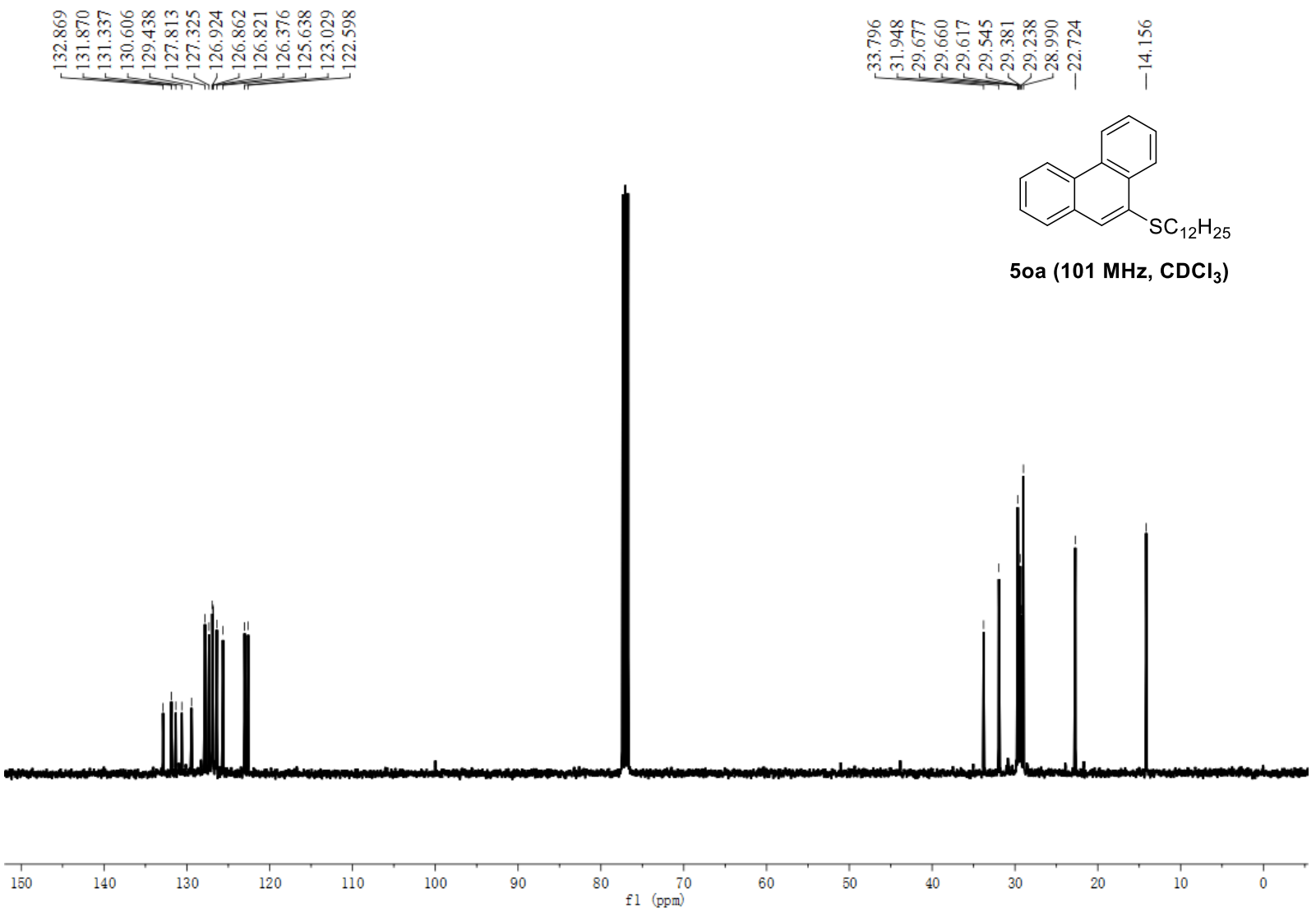



**5na (400 MHz, $CDCl_3$)**

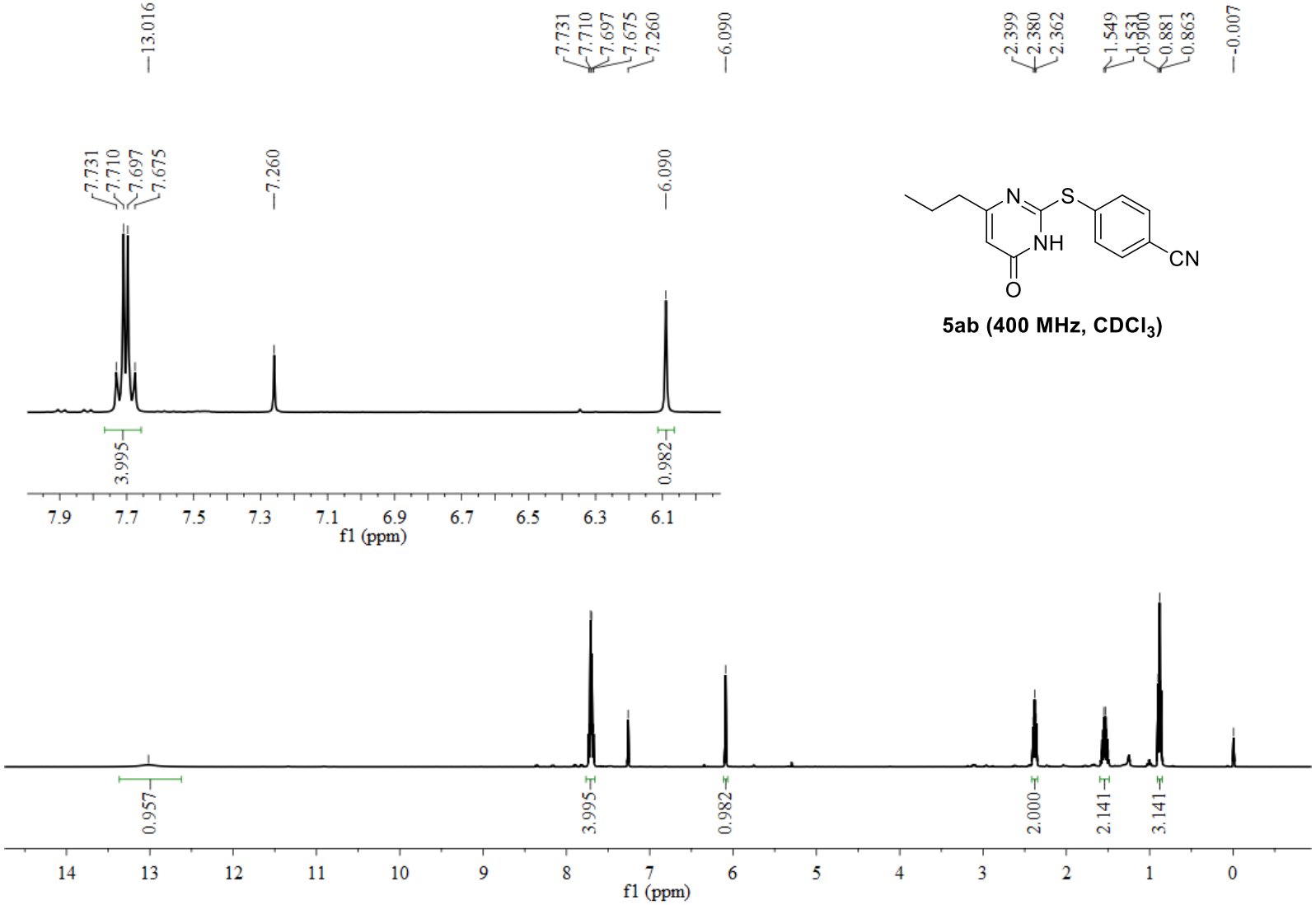



**5na (101 MHz, $CDCl_3$)**

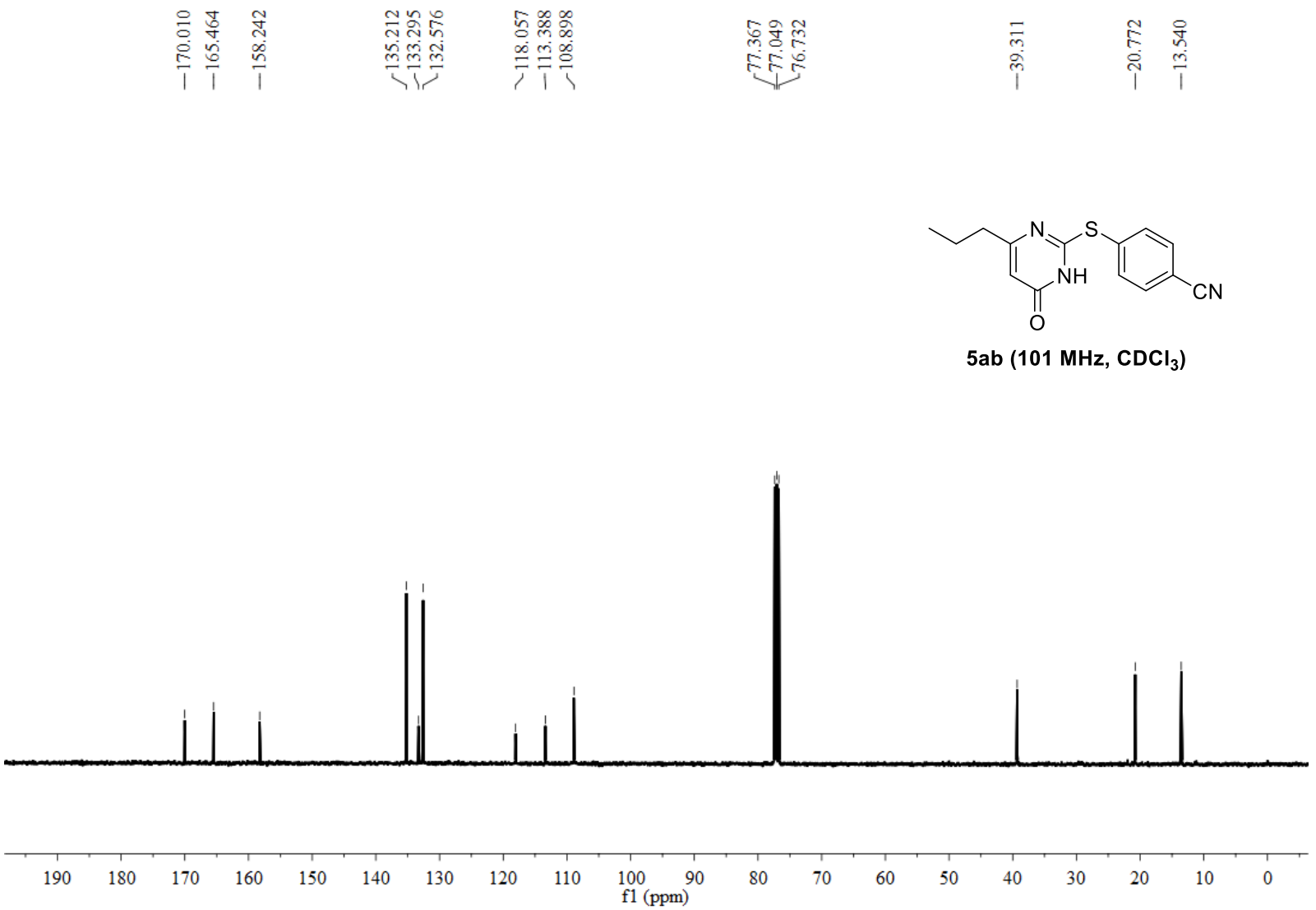

8.720
8.715
8.705
8.697
8.648
8.630
8.506
8.503
8.488
8.482
7.828
7.810
7.805
7.778
7.695
7.690
7.687
7.679
7.671
7.668
7.663
7.635
7.632
7.618
7.614
7.600
7.597
7.583
7.580
7.566
7.562
3.078
3.059
3.041
1.778
1.760
1.741
1.723
1.704
1.505
1.488
1.469
1.262
0.910
0.893
0.876
SC12H25
5oa (400 MHz, CDCl3)
1.086
1.025
1.000
1.049
1.015
2.012
2.417
2.178
2.160
2.107
16.309
3.349
f1 (ppm)



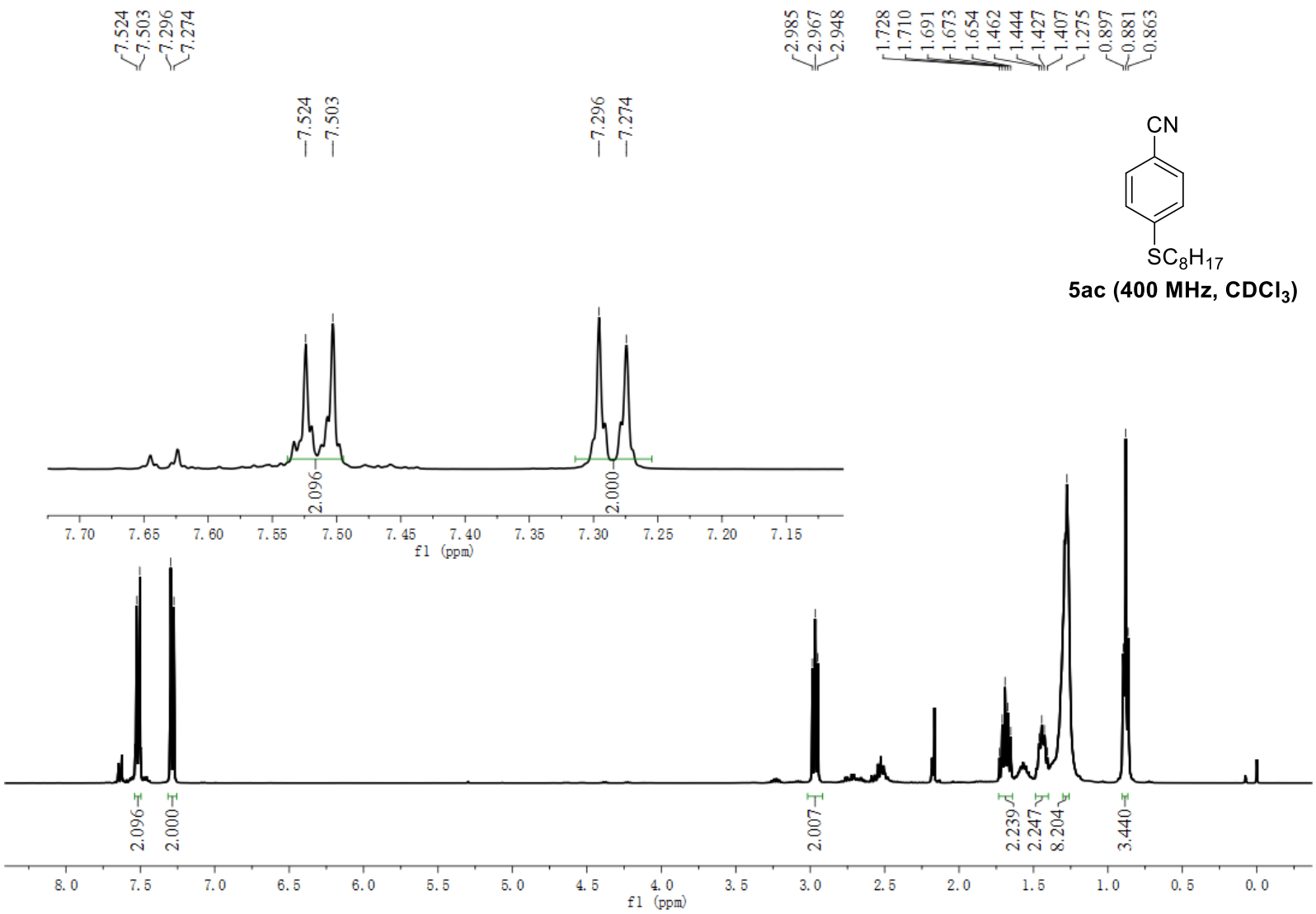

**5oa (101 MHz, $CDCl_3$)**



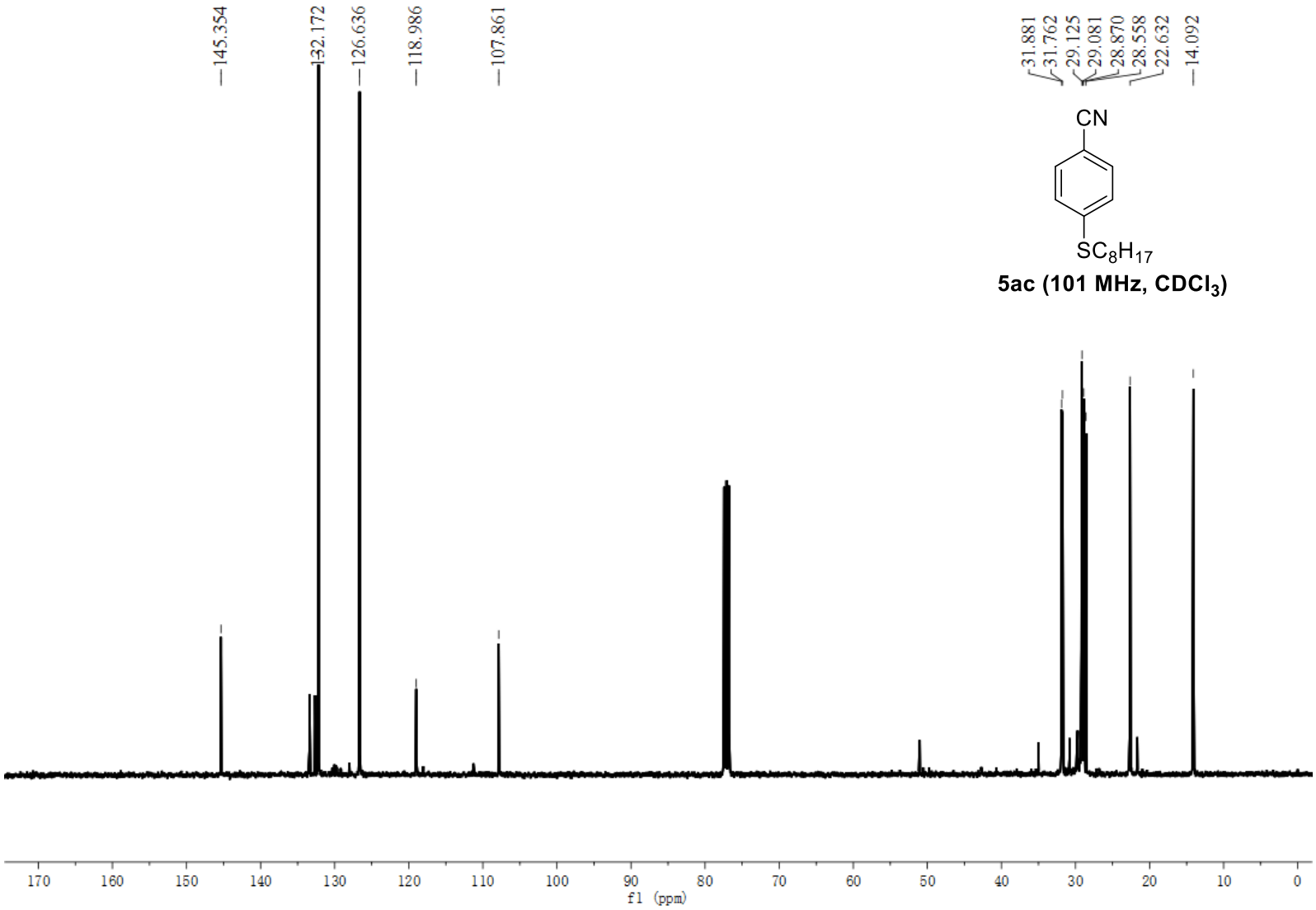

**5ab (400 MHz, $CDCl_3$)**




**5ab (101 MHz, $CDCl_3$)**




**5ac (400 MHz, $CDCl_3$)**


145.354
132.172
126.636
118.986
107.861
31.881
31.762
29.125
29.081
28.870
28.558
22.632
14.092
CN
SC8H17
5ac (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)