Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

Photocatalytic α-Fluoro-β-Phosphonoylation of Unsaturated Amides

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Supporting Information Placeholder

Contents

1. General Information

Unless otherwise specified, Analytical thin layer chromatography (TLC) was performed on HSGF 254 (0.17 mm-0.23 thickness), visualized by irradiation with UV light (254 nm). All reactions were performed with 9 W Semi LEDs lamps (C35L-U-60, λ_{max}=407 nm), the glass reaction tube was placed 2 mm away from LEDs. Column chromatography was performed on silica gel FCP 200-400 using ethyl acetate (EA)/petroleum ether (PE). All reactions were performed in borosilicate glass sealing tubes under nitrogen atmosphere. Acetonitrile was purified by distillation over CaH under a nitrogen atmosphere. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker 400 or JEOL 400 spectrometer. Chemical shifts are reported in δ units relative to $CDCl_3$ [^{1}H δ = 7.260, ^{13}C δ = 77.160]. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), and broad (br). High-resolution mass spectra (HRMS) were measured on Acquity UPLC/XEVO G2-XS QTOF. UV-Vis Absorption Spectrum was recorded on a UV-3600 spectrometer. Fluorescence Spectrum was recorded on an F-4600 spectrometer. **CBZ6** was prepared according to reported procedures. [1,2]

2. General Setup for the Reaction

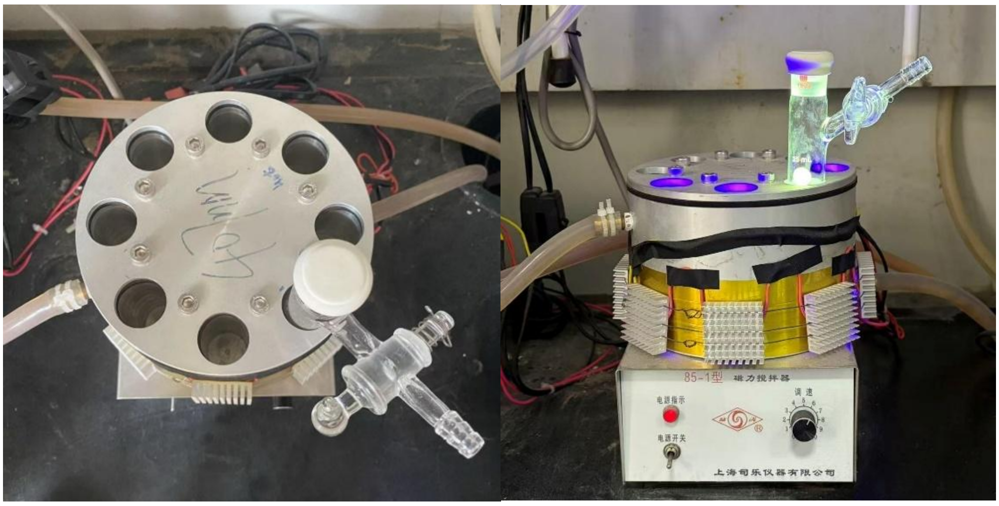
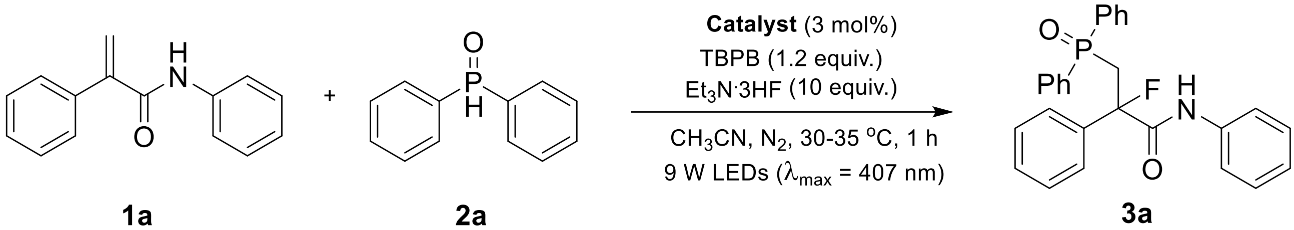


Figure S1. General reaction setup. 9 W LEDs (λ_{max} = 407 nm) lamps were used as the light source.

3. Optimization of Reaction Conditions

Table S1. Variation of catalysts.



Entry	Catalyst	λ/nm	**3a**/%
1	**CBZ6**	407	70
2	Eosin Y	520	0
3	4CzIPN	379	0
4	Michler's ketone	365	0
5	PC-1 (CBZ6-OMe)	407	29
6	PC-2 (CBZ6-CF₃)	407	49

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.), **Catalyst** (3 mol%), $Et_3N·3HF$ (10 equiv.), and CH_3CN (2 mL) at 30-35 °C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for x h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

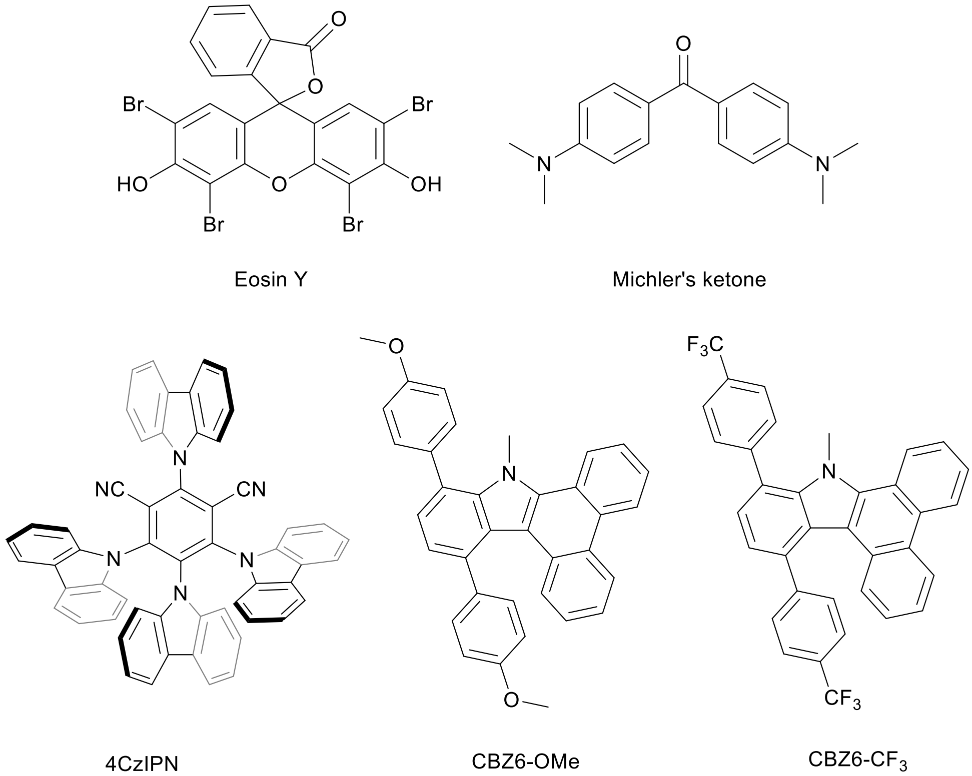
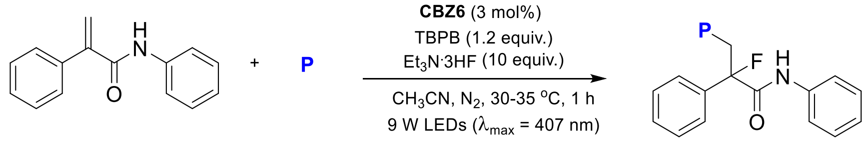
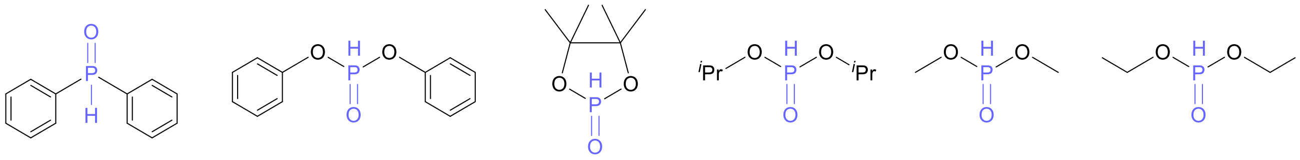


Figure S2. The list of catalysts.

Table S2. Variation of phosphonyl radical precursor.



1a 2 3

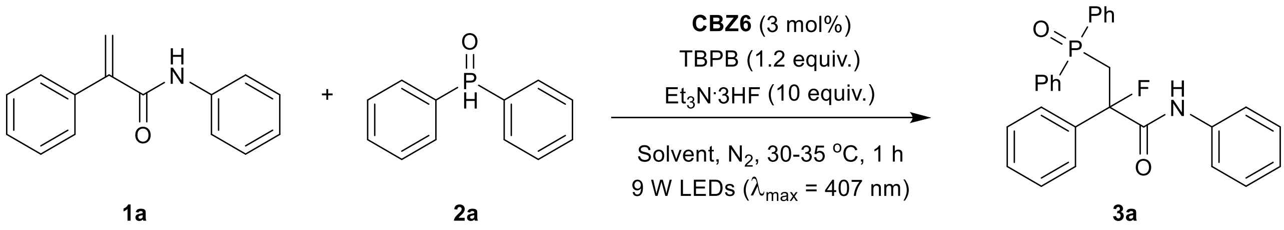


2a, 2b 2c 2d 2e 2f

Entry	P	**3**/%[a]
1	2a	69
2	2b	0
3	2c	0
4	2d	0
5	2e	0
6	2f	0

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.), **CBZ6** (3 mol%), $Et_3N{\cdot}3HF$ (10 equiv.), and CH_3CN (2 mL) at 30-35 °C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for x h. [a] isolated yields.

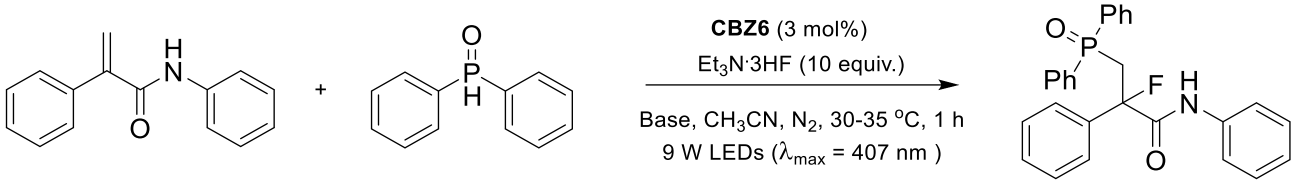
Table S3. Variation of Solvent.



Entry	Solvent	**3a**/%
1	DCM	21
2	CH_3CN	70
3	THF	3
4	1,4-Dioxane	9
5	DMSO	34
6	DMF	0
7	DCE	54

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.) **CBZ6** (3 mol%), $Et_3N{\cdot}3HF$ (10.0 equiv.) and solvent (2 mL) at 30-35 ^{o}C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for 1 h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

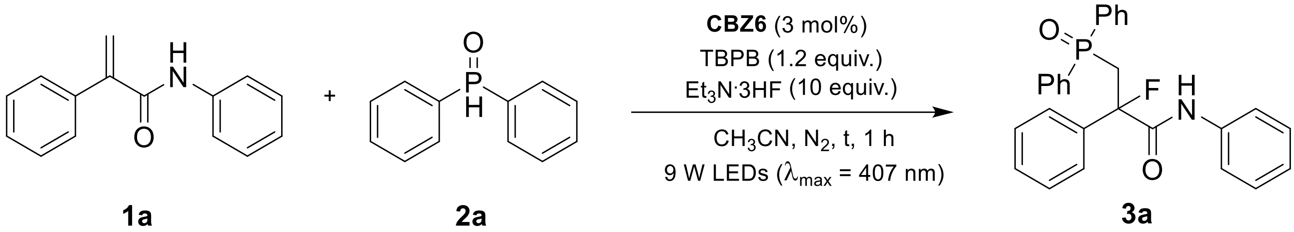
Table S4. Variation of base.



Entry	Base	**3a**/%
1	K_3PO_4	69
2	Na_2CO_3	66
3	DIPEA	60
4	DMAP	29
5	$NaHCO_3$	52
6	KOH	58
7	none	70

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.), **CBZ6** (3 mol%), $Et_3N{\cdot}3HF$ (10.0 equiv.) Base (0.04 mmol, 0.2 equiv.), and CH_3CN (2 mL) at 30-35 ^oC under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for 1 h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

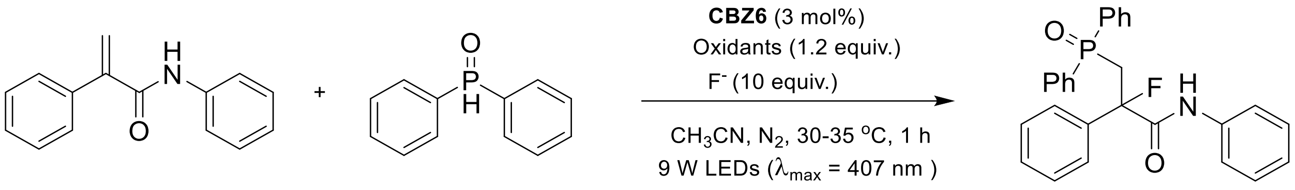
Table S5. Variation of temperature.



Entry	Temperature/^{o}C	**3a/%**
1	13-23	63
2	30-35	70
3	60	52
4	80	21

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.), **CBZ6** (3 mol%), $Et_3N{\cdot}3HF$ (10 equiv.), and CH_3CN (2 mL) at t ^{o}C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for 1 h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

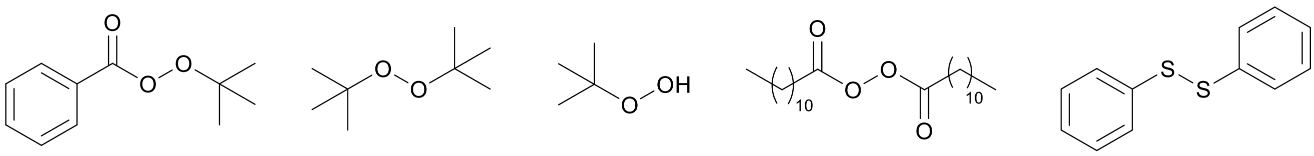
Table S6. Variation of oxidants and fluorine sources.



1a **2a** **3a**

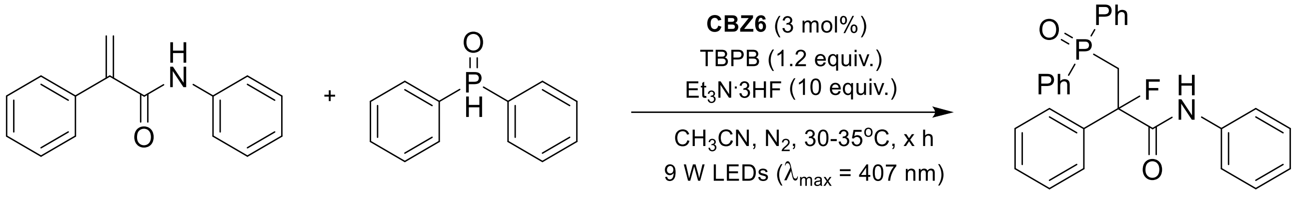
Entry	Oxidants	F^- sources	**3a**/%
1	TBPB	TBAF	0
2	TBPB	Py·HF	0
3	TBPB	CsF	0
4	TBPB	KF+18-Crown-6	0
5	TBPB	Et_3N·3HF	70
6	DTBP	Et_3N·3HF	16
7	TBHP	Et_3N·3HF	0
8	LPO	Et_3N·3HF	23
9	Ph-S-S-Ph	Et_3N·3HF	0

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), Oxidants (0.24 mmol, 1.2 equiv.) **CBZ6** (3 mol%), F^- sources (10.0 equiv.) and CH_3CN (2 mL) at 30-35 °C under nitrogen atmosphere irradiated with a y W LEDs (λ_{max} = 407 nm) for 1 h. ^{31}P NMR yield was reported using PPh_3 as internal standards.



TBPB DTBP TBHP LPO Ph-S-S-Ph

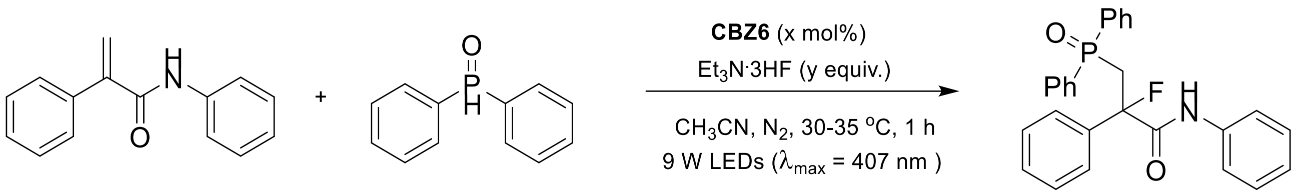
Table S7. Variation of time.



Entry	Time/x h	**3a**/%
1	0.5	13
2	1	55
3	2	55
4	3	55

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.24 mmol, 1.2 equiv.), TBPB (0.24 mmol, 1.2 equiv.), **CBZ6** (0.6 mol%), $Et_3N{\cdot}3HF$ (10 equiv.), and CH_3CN (2 mL) at 30-35 °C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for x h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

Table S8. Variation of feed ratio, triethylamine trihydrofluoride and solvent dosage.



Entry	**1a:2a**	**CBZ6**/x mol%	$Et_3N·3HF$	CH_3CN/mL	**3a**%[b]
1	1 : 1.2	0.6	10	2	55
2	1 : 1.2	1	10	2	43
3	1 : 1.2	3	10	2	70
4	1 : 1.2	5	10	2	57
5	1 : 1.2	3	10	1	62
6	1 : 1	3	10	2	58
7	1 : 2	3	10	2	68
8	1 : 3	3	10	2	61
9	1 : 1.2	3	5	2	54
10	1 : 1.2	3	20	2	62

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **CBZ6** (x mol%), $Et_3N·3HF$ (y equiv.), and CH_3CN (2 mL) at 30-35 °C under a nitrogen atmosphere irradiated with a 9 W LEDs (λ_{max} = 407 nm) for 1 h. ^{31}P NMR yield was reported using PPh_3 as internal standards.

4. Preparation of 1

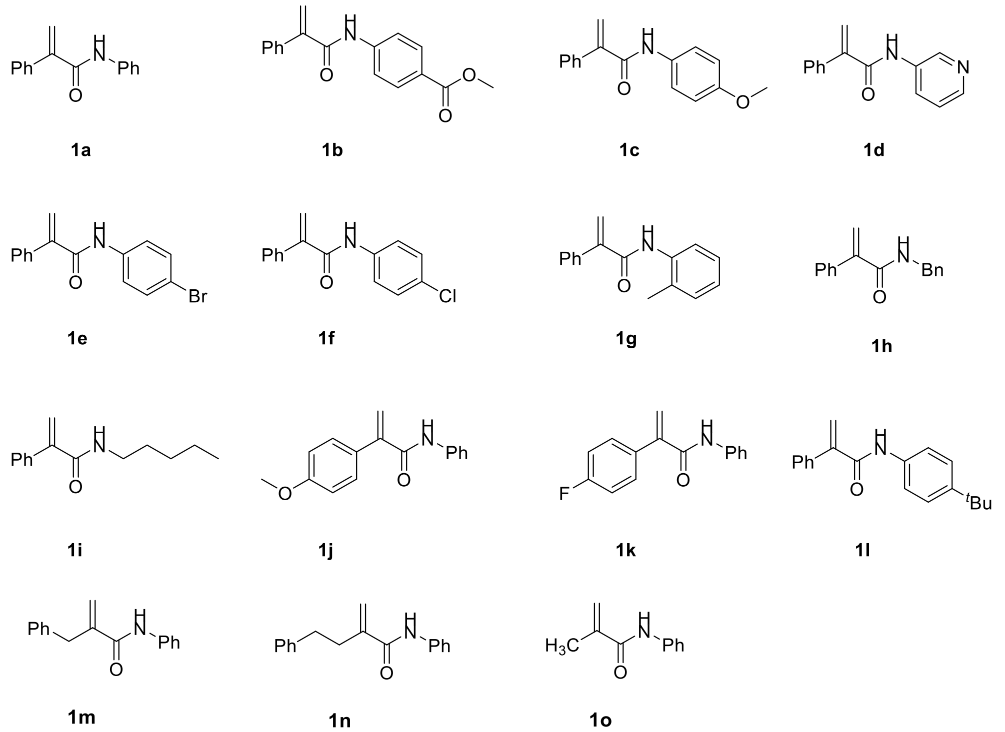
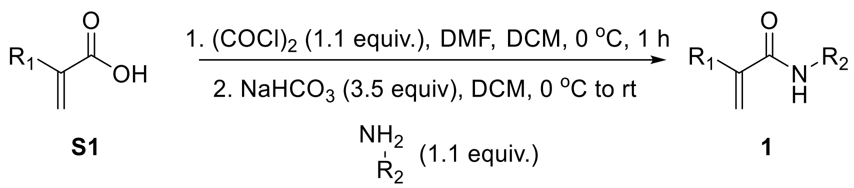


Figure S3. The list of **1.** Compounds **1a-1i** were synthesized according to procedure A. Compounds **1j, 1k,1m** and **1n** were synthesized according to the literature procedure [2-4]. **1o** can be purchased directly.

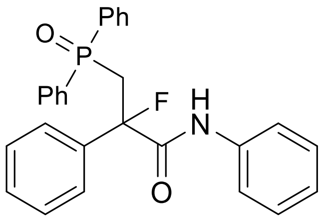
General Procedure A [2]:



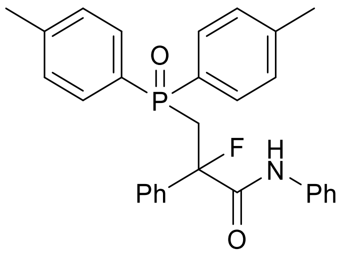
To a 100 mL round-bottom flask was successively charged with acrylic acid **S1** (3 mmol, 1.0 equiv.), two drops of DMF, CH_2Cl_2 (10 mL) and $(COCl)_2$ (3.3 mmol, 1.1 equiv.) at 0 °C. The reaction was stirred at 0 °C for 1 h. Then reaction was diluted with the dichloromethane (15 mL). Amine (3.3 mmol, 1.1 equiv.) and $NaHCO_3$ (10.5 mmol, 3.5 equiv.) were added at 0 °C. The mixture was stirred at room temperature for 3 h and monitored by thin-layer chromatography (TLC). After the reaction was completed, the reaction solution was filtered through funnel and rinsed with dichloromethane. Then organic layers were combined, concentrated under vacuum, and purified by flash column chromatography to afford the product **1**.

5. Preparation of 3

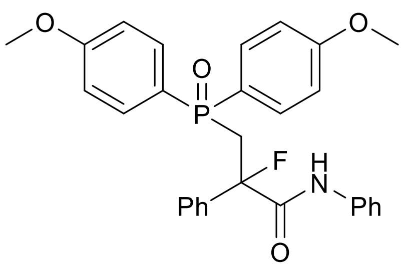
General Procedure B: CBZ6 (2.6 mg, 3 mol%), **1** (0.2 mmol, 1.0 equiv.) and **2** (0.24 mmol, 1.2 equiv.) were weighed directly into a 10 mL dry Schlenk tube and dried under vacuum for 15 min and purged with nitrogen 3 times. Under an atmosphere of nitrogen, dry CH_3CN (1 mL) $Et_3N{\cdot}3HF$ (2 mmol, 10.0 equiv.) and TBPB (0.24 mmol, 1.2 equiv.) were added successively with the addition of another 1 mL of CH_3CN. The resulting reaction mixture was stirred under the irradiation of 9 W LEDs (λ_{max} = 407 nm) and monitored by TLC analysis. For larger-scale reactions, an aqueous basic quench/wash (e.g., $NaHCO_3$) is recommended to remove residual $Et_3N{\cdot}3HF$ prior to purification. After completion, the reaction solvent was removed under reduced pressure. The crude yield was determined by ^{31}P NMR analysis of the crude product. Finally, the crude product was purified by flash chromatography on silica gel to afford the corresponding products.



3-(Diphenylphosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3a) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0619 g, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.13 (d, *J* = 6.1 Hz, 1H), 7.81 – 7.71 (p, *J* = 5.8, 4.9 Hz, 4H), 7.59 – 7.29 (m, 14H), 7.28 – 7.22 (t, *J* = 7.9 Hz, 3H), 7.12 – 7.05 (m, 1H), 3.92 – 3.71 (dt, *J* = 35.3, 13.8 Hz, 1H), 3.28 – 3.16 (dt, *J* = 16.5, 8.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 – 166.4 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 20.4 Hz), 138.3 – 135.4, 132.4 – 131.6 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 7.5 Hz), 131.6 – 130.5 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 24.4, 8.9 Hz), 129.4 – 128.3 (m), 125.4 – 124.8, 124.7 – 124.0 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.2 Hz), 120.7 – 119.7, 33.3 – 24.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -156.5 – -158.5 (dq, *J* = 35.4, 8.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.5 – 26.2 (d, *J* = 8.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}FNO_2P^+$ 444.1523, found 444.1525.

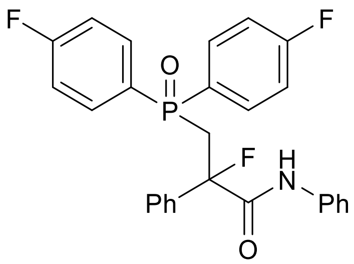


3-(Di-*p*-tolylphosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3b) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA =5/1) as a colorless oil (0.0582 g, 64%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.09 (d, *J* = 6.8 Hz, 1H), 7.69 – 7.59 (ddd, *J* = 11.8, 8.0, 4.9 Hz, 4H), 7.59 – 7.54 (m, 2H), 7.40 – 7.28 (m, 5H), 7.28 – 7.21 (m, 4H), 7.17 – 7.11 (dd, *J* = 8.0, 2.8 Hz, 2H), 7.10 – 7.03 (m, 1H), 3.99 – 3.62 (ddd, *J* = 36.9, 15.4, 11.7 Hz, 1H), 3.33 – 3.03 (ddd, *J* = 15.4, 10.1, 7.4 Hz, 1H), 2.36 – 2.35 (s, 3H), 2.21 – 2.20 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 20.4, 2.2 Hz), 142.7 – 142.3 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 19.9, 2.7 Hz), 139.5 – 139.1 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.7, 8.5 Hz), 137.2 – 136.7, 131.7 – 130.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 43.3, 9.9 Hz), 130.7 – 129.5 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 104.8 Hz), 129.5 – 129.1 (m), 128.9 – 128.4 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 18.3 Hz), 124.8 – 124.7, 124.4 – 124.1 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.7 Hz), 120.3 – 120.0, 98.2 – 95.9 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 195.3, 6.2 Hz), 40.9 – 39.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 66.4, 23.7 Hz), 22.0 – 21.2 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 10.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.2 – -157.6 (dq, *J* = 36.6, 7.6 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 38.7 – 20.8 (d, *J* = 8.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}FNO_2P^+$ 472.1836, found 472.1841.

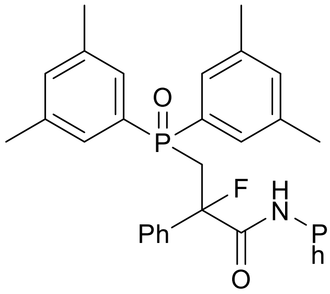


3-(Bis(4-methoxyphenyl)phosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3c) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0725 g, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.02 (d, *J* = 6.8 Hz, 1H), 7.73 – 7.63 (m, 4H), 7.59 – 7.54 (m, 2H), 7.39 – 7.29 (m, 5H), 7.27 – 7.21 (m, 2H), 7.10 – 7.04 (m, 1H), 6.95 – 6.90 (dd, *J* = 8.9, 2.3

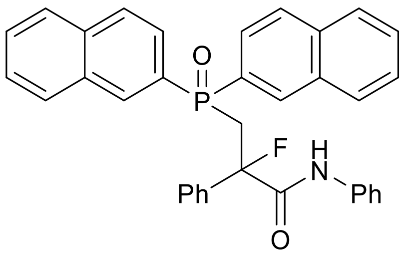
Hz, 2H), 6.84 – 6.78 (m, 2H), 3.85 – 3.67 (m, 1H), 3.81 – 3.63 (d, *J* = 60.4 Hz, 6H), 3.18 – 3.08 (ddd, *J* = 15.4, 10.6, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 20.4, 2.2 Hz), 162.5 – 162.3 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 3.0 Hz), 139.8 – 138.9 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.6, 8.5 Hz), 137.8 – 136.6, 133.5 – 132.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 53.0, 11.1 Hz), 129.0 – 128.3 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 17.2 Hz), 124.8 – 124.7, 124.5 – 124.1 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.7 Hz), 125.6 – 122.6 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 129.0, 108.3 Hz), 120.2 – 119.8, 114.3 – 113.9 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 16.8, 13.0 Hz), 98.2 – 95.9 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 195.0, 5.9 Hz), 55.9 – 54.8 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 17.8 Hz), 41.2 – 39.5 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 67.1, 23.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.6 – -157.8 (dq, *J* = 37.4, 7.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.6 – 26.3 (d, *J* = 8.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{28}FNO_4P^+$ 504.1734, found 504.1735.



3-(Bis(4-fluorophenyl)phosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3d) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0635 g, 67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.07 (d, *J* = 6.6 Hz, 1H), 7.79 – 7.69 (m, 4H), 7.59 – 7.52 (m, 2H), 7.41 – 7.30 (m, 5H), 7.30 – 7.24 (m, 2H), 7.18 – 7.00 (m, 5H), 3.88 – 3.68 (ddd, *J* = 35.0, 15.5, 12.0 Hz, 1H), 3.27 – 3.11 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.0 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 20.5, 3.1 Hz), 166.7 – 163.7 (m), 138.9 – 138.3 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.6, 8.5 Hz), 136.8 – 136.6, 134.1 – 133.1 (ddd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 34.6, 11.0, 9.0 Hz), 129.1 – 128.9 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 7.3 Hz), 128.8 – 128.7, 129.6 – 127.7 (m), 125.3 – 124.8, 124.5 – 124.0 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.6 Hz), 120.7 – 119.8, 116.4 – 115.9 (ddd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 21.6, 13.3, 10.4 Hz), 98.3 – 95.8 ($dd_{(C\text{-}F,\ C\text{-}P)}$, *J* = 195.1, 6.5 Hz), 40.8 – 39.4 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 67.9, 23.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.0 – -106.2 (p, *J* = 8.2 Hz), -106.3 – -106.4 (q, *J* = 7.1 Hz), -156.3 – -159.9 (dq, *J* = 34.6, 7.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.7 – 16.0 (d, *J* = 8.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}FNO_2P^+$ 480.1335, found 480.1337.

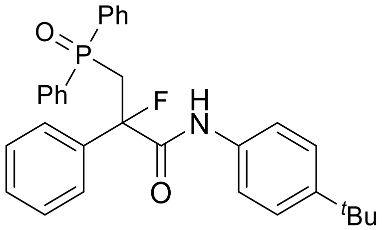


3-(Bis(3,5-dimethylphenyl)phosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3e) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a yellow oil (0.0598 g, 62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.18 (d, *J* = 6.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.43 – 7.28 (m, 9H), 7.28 – 7.22 (m, 2H), 7.12 – 7.05 (m, 2H), 6.95 – 6.92 (m, 1H), 3.88 – 3.63 (ddd, *J* = 34.9, 15.4, 11.6 Hz, 1H), 3.28 – 3.10 (ddd, *J* = 15.4, 10.1, 9.0 Hz, 1H), 2.32 – 2.19 (d, *J* = 37.3 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6 – 167.3 (dd, $J_{(C-F,\ C-P)}$ = 20.8, 2.5 Hz), 139.5 – 138.9 (dd, $J_{(C-F,\ C-P)}$ = 22.9, 8.0 Hz), 138.4 – 138.1 (dd, $J_{(C-F,\ C-P)}$ = 12.6, 7.6 Hz), 137.0 – 136.9, 133.8 – 133.5 (m), 132.72 – 132.5 (d, $J_{(C-F,\ C-P)}$ = 10.2 Hz), 131.6 – 131.5, 128.8 – 128.7, 128.7 – 128.2 (dd, $J_{(C-F,\ C-P)}$ = 27.2, 10.8 Hz), 124.8 – 124.8, 124.5 – 124.21(d, $J_{(C-F,\ C-P)}$ = 9.7 Hz), 120.1 – 120.0, 98.1 – 95.9 (dd, $J_{(C-F,\ C-P)}$ = 195.3, 6.1 Hz), 40.3 – 38.9 (dd, $J_{(C-F,\ C-P)}$ = 65.8, 23.7 Hz), 22.9 – 20.0 (d, $J_{(C-F,\ C-P)}$ = 11.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -156.9 – -157.3 (dq, *J* = 35.2, 8.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.1 – 22.2 (d, *J* = 8.7 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{32}FNO_2P^+$ 500.2149, found 500.2145.

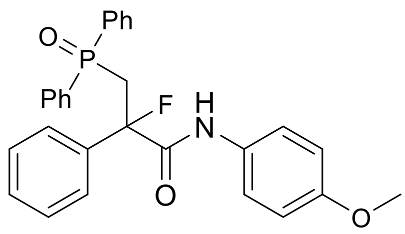


3-(Di(naphthalen-2-yl)phosphoryl)-2-fluoro-*N*,2-diphenylpropanamide (3f) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0609 g, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 – 8.41 (m, 2H), 8.14 – 8.08 (d, *J* = 6.7 Hz, 1H), 7.93 – 7.72 (m, 8H), 7.64 – 7.47 (m, 6H), 7.34 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 7.16 – 7.10 (m, 2H), 7.04 – 6.98 (m, 1H), 4.10 – 3.92 (ddd, *J* = 35.2, 15.5, 11.9 Hz, 1H), 3.47 – 3.36 (ddd, *J* = 15.4, 9.3

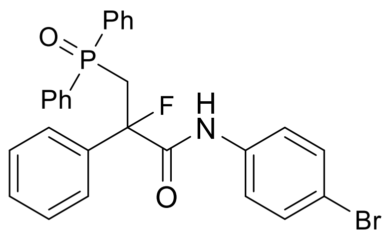
Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.2 (dd, $J_{(C-F, C-P)}$ = 20.3, 2.8 Hz), 139.3 – 138.7 (dd, $J_{(C-F, C-P)}$ = 22.6, 8.2 Hz), 136.8 – 136.5, 134.9 – 134.6 (dd, $J_{(C-F, C-P)}$ = 7.3, 2.4 Hz), 133.4 – 132.8 (dd, $J_{(C-F, C-P)}$ = 32.8, 8.8 Hz), 132.9 – 132.3 (dd, $J_{(C-F, C-P)}$ = 13.0, 9.1 Hz), 131.0 – 129.7 (m), 129.1 – 128.9 (m), 128.8 – 128.7, 128.7 – 128.4 (m), 128.4 – 127.8 (dd, $J_{(C-F, C-P)}$ = 44.0, 5.6 Hz), 127.2 – 126.9 (d, $J_{(C-F, C-P)}$ = 13.4 Hz), 126.1 – 125.5 (dd, $J_{(C-F, C-P)}$ = 24.1, 10.8 Hz), 124.8 – 124.7, 124.5 – 124.2 (d, $J_{(C-F, C-P)}$ = 9.6 Hz), 120.2 – 120.0, 98.4 – 95.7 (dd, $J_{(C-F, C-P)}$ = 195.0, 6.4 Hz), 40.6 – 39.1 (dd, $J_{(C-F, C-P)}$ = 66.9, 23.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.0 – -157.2 (dq, *J* = 35.4, 8.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.5 – 26.3 (d, *J* = 8.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{28}FNO_2P^+$ 544.1836, found 544.1837.



***N*-(4-(Tert-butyl)phenyl)-3-(diphenylphosphoryl)-2-fluoro-2-phenylpropanamide (3g)** was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0747 g, 75%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.10 (d, *J* = 6.5 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.61 – 7.53 (m, 2H), 7.51 – 7.24 (m, 13H), 3.89 – 3.70 (ddd, *J* = 34.5, 15.5, 12.3 Hz, 1H), 3.29 – 3.17 (ddd, *J* = 15.5, 10.0, 8.8 Hz, 1H), 1.32 – 1.22 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6 – 167.0 (dd, $J_{(C-F, C-P)}$ = 20.6, 3.3 Hz), 148.2 – 147.6, 139.3 – 138.7 (dd, $J_{(C-F, C-P)}$ = 22.7, 8.1 Hz), 134.5 – 133.8, 133.9 – 132.2 (dd, $J_{(C-F, C-P)}$ = 101.7, 49.6 Hz), 132.0 – 131.8 (dd, $J_{(C-F, C-P)}$ = 8.2, 2.9 Hz), 131.4 – 130.7 (dd, $J_{(C-F, C-P)}$ = 19.6, 9.7 Hz), 129.0 – 128.8, 128.7 – 128.5 (m), 125.9 – 125.5, 124.7 – 124.2 (d, $J_{(C-F, C-P)}$ = 9.6 Hz), 120.3 – 119.8, 98.2 – 95.7 (dd, $J_{(C-F, C-P)}$ = 195.1, 6.2 Hz), 40.7 – 38.8 (dd, $J_{(C-F, C-P)}$ = 67.0, 23.8 Hz), 35.2 – 34.0, 32.0 – 30.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -156.7 – -157.6 (dq, *J* = 34.5, 8.6 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.9 – 22.4 (d, *J* = 8.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{32}FNO_2P^+$ 500.2149, found 500.2151.

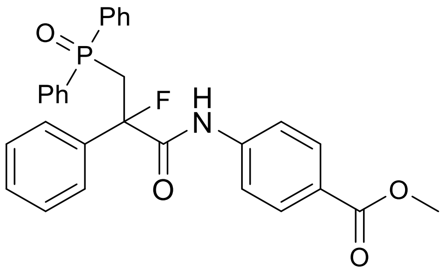


3-(Diphenylphosphoryl)-2-fluoro-*N*-(4-methoxyphenyl)-2-phenylpropanamide (3h) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0649 g, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.05 (d, *J* = 6.5 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.60 – 7.55 (m, 2H), 7.52 – 7.27 (m, 10H), 6.84 – 6.76 (m, 2H), 3.89 – 3.72 (m, 1H), 3.77 – 3.76 (s, 3H), 3.25 – 3.15 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4 – 167.1 (dd, $J_{(C-F, C-P)}$ = 20.4, 3.0 Hz), 156.9 – 156.8, 139.6 – 138.9 (dd, $J_{(C-F, C-P)}$ = 23.0, 8.4 Hz), 134.0 – 132.1 (dd, $J_{(C-F, C-P)}$ = 101.7, 59.7 Hz), 132.1 – 131.8 (dd, $J_{(C-F, C-P)}$ = 8.1, 2.8 Hz), 131.3 – 130.8 (dd, $J_{(C-F, C-P)}$ = 24.8, 9.6 Hz), 130.1 – 130.0, 129.0 – 128.9, 128.8 – 128.5 (m), 124.6 – 124.2 (d, $J_{(C-F, C-P)}$ = 9.7 Hz), 122.5 – 122..0, 114.4 – 113.8, 98.1 – 96.0 (dd, $J_{(C-F, C-P)}$ = 194.9, 6.1 Hz), 55.6 – 55.5, 40.4 – 39.3 (dd, $J_{(C-F, C-P)}$ = 66.9, 23.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -152.8 – -162.7 (dq, *J* = 35.6, 8.6 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.7 – 15.6 (d, *J* = 8.7 Hz). HRMS (ESI) m/z: [M+H]$^{+}$ calcd for $C_{28}H_{26}FNO_3P^{+}$ 474.1629, found 474.1634.

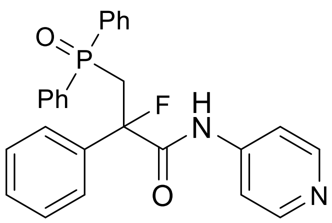


***N*-(4-Bromophenyl)-3-(diphenylphosphoryl)-2-fluoro-2-phenylpropanamide(3i)** was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a yellow oil (0.0580 g, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 – 8.36 (d, *J* = 6.3 Hz, 1H), 7.78 – 7.69 (m, 5H), 7.58 – 7.52 (m, 2H), 7.52 – 7.48 (m, 1H), 7.48 – 7.29 (m, 11H), 3.91 – 3.69 (ddd, *J* = 36.6, 15.5, 12.4 Hz, 1H), 3.25 – 3.13 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9 – 167.4 (dd, $J_{(C-F, C-P)}$ = 21.0, 2.6 Hz), 140.7 – 137.8 (dd, $J_{(C-F, C-P)}$ = 22.1, 8.9 Hz), 136.4 – 135.6, 133.8 – 132.5 (m), 132.13 – 131.99 (m), 131.9 – 131.9, 131.2 – 130.8 (dd, $J_{(C-F, C-P)}$ = 22.1, 9.6 Hz), 129.1 – 129.0, 128.9 – 128.5 (m), 124.5 – 124.2 (d, $J_{(C-F, C-P)}$ = 9.7 Hz), 122.3 – 121.8, 118.0 – 117.4, 41.0 – 39.0

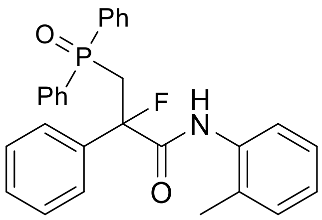
(dd, $J_{(C-F, C-P)}$ = 66.6, 23.9 Hz), 30.0 – 29.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -155.6 – -159.0 (dq, *J* = 36.9, 8.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.4 – 25.6 (d, *J* = 8.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}BrFNO_2P^+$ 522.0628, found 522.0634.



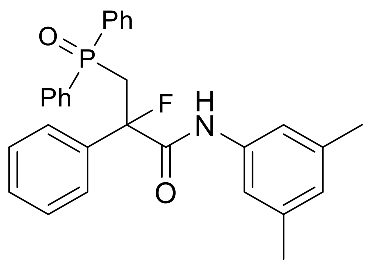
Methyl 4-(3-(diphenylphosphoryl)-2-fluoro-2-phenylpropanamido)benzoate (3j) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0462 g, 46%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 – 8.42 (d, *J* = 6.6 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.79 – 7.70 (m, 4H), 7.58 – 7.42 (m, 7H), 7.40 – 7.30 (m, 5H), 3.89 – 3.88 (s, 3H), 3.87 – 3.71 (m, 1H), 3.24 – 3.15 (ddd, *J* = 15.4, 8.6, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9 – 167.6 (dd, $J_{(C-F, C-P)}$ = 20.8, 2.3 Hz), 166.7 – 166.7, 141.2 – 141.1, 133.7 – 131.8 (dd, $J_{(C-F, C-P)}$ = 102.1, 69.3 Hz), 132.2 – 132.0 (dd, $J_{(C-F, C-P)}$ = 6.8, 2.7 Hz), 131.3 – 131.0 (d, $J_{(C-F, C-P)}$ = 9.8 Hz), 131.0 – 130.8 (d, $J_{(C-F, C-P)}$ = 9.4 Hz), 130.7 – 130.6, 129.2 – 129.1, 129.0 – 128.5 (m), 126.3 – 126.2, 124.6 – 124.2 (d, $J_{(C-F, C-P)}$ = 9.8 Hz), 119.6 – 119.5, 53.8 – 50.4, 40.4 – 39.2 (dd, $J_{(C-F, C-P)}$ = 66.4, 23.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -156.9 – -157.4 (dq, *J* = 36.4, 7.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.6 – 26.3 (d, *J* = 8.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}FNO_4P^+$ 502.1578, found 502.1575.



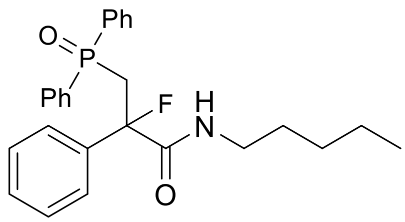
3-(Diphenylphosphoryl)-2-fluoro-2-phenyl-*N*-(pyridin-4-yl)propanamidee (3k) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a yellow oil (0.0446 g, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 – 8.63 (d, *J* = 6.0 Hz, 1H), 8.57 – 8.55 (d, *J* = 2.6 Hz, 1H), 8.34 – 8.29 (m, 1H), 8.04 – 8.00 (ddd, *J* = 8.3, 2.6, 1.5 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.58 – 7.48 (m, 3H), 7.48 – 7.42 (m, 2H), 7.41 – 7.31 (m, 5H), 7.21 – 7.17 (dd, J = 8.4, 4.7 Hz, 1H), 3.92 – 3.70 (ddd, J = 37.5, 15.5, 12.5 Hz, 1H), 3.23 – 3.12 (ddd, J = 15.4, 8.2, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4 – 168.1 (dd, $J_{(C-F,\ C-P)}$ = 20.9, 1.9 Hz), 145.8 – 145.4, 141.9 – 141.7, 139.0 – 138.6 (dd, $J_{(C-F,\ C-P)}$ = 22.8, 8.9 Hz), 134.3 – 132.3 (m), 132.2 – 132.0 (t, $J_{(C-F,\ C-P)}$ = 4.1 Hz), 132.0 – 131.9, 131.2 – 130.7 (dd, $J_{(C-F,\ C-P)}$ = 21.4, 9.8 Hz), 129.2 – 129.0, 128.0 – 128.6 (dd, $J_{(C-F,\ C-P)}$ = 12.7, 7.2 Hz), 127.8 – 127.8, 124.4 – 124.2 (d, $J_{(C-F,\ C-P)}$ = 9.6 Hz), 123.6 – 123.5, 98.1 – 95.8 (dd, $J_{(C-F,\ C-P)}$ = 195.8, 6.2 Hz), 40.3 – 39.2 (dd, $J_{(C-F,\ C-P)}$ = 66.6, 23.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.0 – -157.5 (dq, J = 37.4, 7.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.6 – 24.3 (d, J = 7.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}FN_2O_2P^+$ 445.1476, found 445.1476.



3-(Diphenylphosphoryl)-2-fluoro-2-phenyl-*N*-(o-tolyl)propanamide (3l) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0375 g, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.94 (d, J = 7.0 Hz, 1H), 7.82 – 7.70 (m, 5H), 7.63 – 7.55 (m, 2H), 7.53 – 7.29 (m, 8H), 7.19 – 7.09 (m, 2H), 7.07 – 7.01 (m, 1H), 3.96 – 3.77 (ddd, J = 35.4, 15.4, 12.7 Hz, 1H), 3.27 – 3.17 (ddd, J = 15.5, 9.3, 8.3 Hz, 1H), 2.29 – 2.01 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8 – 167.5 (dd, $J_{(C-F,\ C-P)}$ = 20.2, 2.8 Hz), 139.4 – 139.0 (dd, $J_{(C-F,\ C-P)}$ = 22.6, 8.3 Hz), 134.9 – 134.6, 133.9 – 132.3 (dd, $J_{(C-F,\ C-P)}$ = 101.7, 33.3 Hz), 132.3 – 131.7 (dd, $J_{(C-F,\ C-P)}$ = 11.9, 2.7 Hz), 131.3 – 130.7 (dd, $J_{(C-F,\ C-P)}$ = 17.9, 9.6 Hz), 130.6 – 130.4, 129.3 – 129.2, 129.0 – 128.9, 128.8 – 128.6 (m), 126.8 – 126.7, 125.6 – 125.4, 124.4 – 124.0 (d, $J_{(C-F,\ C-P)}$ = 9.7 Hz), 123.0 – 122.6, 98.5 – 96.3 (dd, $J_{(C-F,\ C-P)}$ = 194.7, 6.3 Hz), 40.4 – 39.0 (dd, $J_{(C-F,\ C-P)}$ = 67.0, 23.5 Hz), 18.4 – 16.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.4 – -157.6 (dq, J = 35.5, 8.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.1 – 19.7 (d, J = 8.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}FNO_2P^+$ 458.1680, found 458.1683.

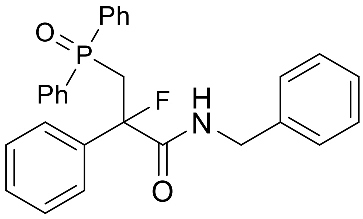


***N*-(3,5-Dimethylphenyl)-3-(diphenylphosphoryl)-2-fluoro-2-phenylpropanamide (3m)** was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil (0.0441 g, 47%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.99 (d, *J* = 6.6 Hz, 1H), 7.84 – 7.67 (m, 3H), 7.58 – 7.53 (m, 2H), 7.52 – 7.46 (m, 1H), 7.46 – 7.27 (m, 6H), 7.04 – 6.99 (s, 1H), 3.93 – 3.70 (ddd, *J* = 34.8, 15.5, 12.2 Hz, 1H), 3.33 – 3.14 (dt, *J* = 15.5, 9.3 Hz, 1H), 2.26 – 2.24 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 20.5, 2.8 Hz), 139.4 – 138.8 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.5, 8.2 Hz), 138.6 – 138.6, 137.1 – 136.4, 134.2 – 132.1 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 101.9, 56.6 Hz), 132.2 – 131.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 6.7, 2.7 Hz), 131.5 – 130.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 24.1, 9.6 Hz), 128.9 – 128.9, 128.8 – 128.5 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 10.7, 7.8 Hz), 126.7 – 126.6, 124.5 – 124.2 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.6 Hz), 118.2 – 117.9, 98.2 – 96.0 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 195.0, 6.3 Hz), 40.4 – 39.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 66.8, 23.9 Hz), 24.1 – 19.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.1 – -157.3 (dq, *J* = 34.6, 8.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.4 – 26.1 (d, *J* = 9.0 Hz). HRMS (ESI) m/z: [M+H]$^+$ calcd for $C_{29}H_{28}FNO_2P^+$ 472.1836, found 472.1836.

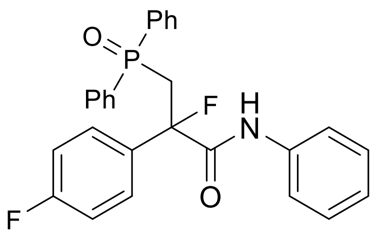


3-(Diphenylphosphoryl)-2-fluoro-*N*-pentyl-2-phenylpropanamide (3n) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0184 g, 21%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.68 (m, 4H), 7.53 – 7.38 (m, 8H), 7.32 – 7.26 (m, 3H), 6.41 – 6.28 (m, 1H), 3.98 – 3.56 (ddd, *J* = 34.0, 15.5, 12.4 Hz, 1H), 3.19 – 3.08 (m, 2H), 3.01 – 2.91 (m, 1H), 1.42 – 1.32 (m, 2H), 1.30 – 1.10 (m, 4H), 0.87 – 0.76 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5 – 169.2 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.1 Hz), 139.8 – 139.4 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.7, 8.8 Hz), 134.0 – 132.4 (m), 132.0

– 131.8 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 17.7, 2.4 Hz), 131.3 – 130.8 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 31.9, 9.6 Hz), 128.8 – 128.4 (m), 41.8 – 37.5 (m), 30.2 – 27.3 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 23.7 Hz), 23.3 – 21.1, 16.0 – 13.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.0 – -160.3 (m). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.6 – 17.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{30}FNO_2P^+$ 438.1993, found 438.1991.

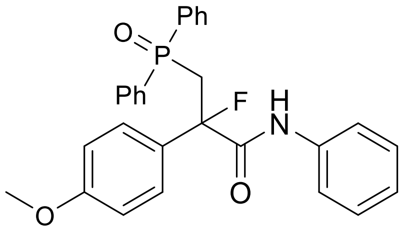


***N*-Benzyl-3-(diphenylphosphoryl)-2-fluoro-2-phenylpropanamide (3o)** was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA= 5/1) as a colorless oil (0.0262 g, 29%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.70 (m, 4H), 7.55 – 7.39 (m, 8H), 7.35 – 7.21 (m, 6H), 7.18 – 7.13 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.72 – 6.66 (q, *J* = 5.3 Hz, 1H), 4.47 – 4.38 (dd, *J* = 14.8, 6.3 Hz, 1H), 4.23 – 4.14 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.90 – 3.70 (ddd, *J* = 34.8, 15.4, 12.9 Hz, 1H), 3.22 – 3.10 (ddd, *J* = 15.4, 9.5, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8 – 169.2 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 21.5, 2.8 Hz), 139.6 – 139.1 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.7, 8.5 Hz), 137.6 – 137.4, 133.9 – 132.5 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 101.6, 9.9 Hz), 132.3 – 131.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 22.1, 2.8 Hz), 131.4 – 130.7 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 21.9, 9.6 Hz), 129.0 – 128.3 (m), 128.1 – 127.8, 127.8 – 127.4, 124.7 – 124.1 (d, $J_{(C\text{-}F,\ C\text{-}P)}$ = 9.6 Hz), 98.3 – 95.8 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 193.4, 6.5 Hz), 44.0 – 43.5, 40.3 – 39.0 (dd, $J_{(C\text{-}F,\ C\text{-}P)}$ = 67.3, 23.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -158.7 – -159.3 (m).^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.6 – 26.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}F_2NO_2P^+$ 458.1680, found 458.1683.

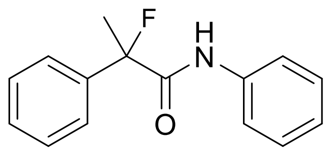


2-Fluoro-4-methyl-*N*,2-diphenylpentanamide (3p) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA=5/1) as a colorless oil

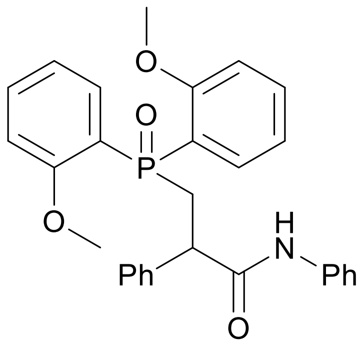
(0.0605 g, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.23 (d, *J* = 6.4 Hz, 1H), 7.77 – 7.69 (dddd, *J* = 9.7, 8.4, 3.6, 1.8 Hz, 3H), 7.57 – 7.33 (m, 10H), 7.29 – 7.23 (m, 3H), 7.12 – 7.07 (m, 1H), 7.01 – 6.94 (m, 2H), 3.82 – 3.65 (ddd, *J* = 33.1, 15.5, 12.0 Hz, 1H), 3.28 – 3.18 (ddd, *J* = 15.5, 11.7, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5 – 167.2 (dd, $J_{(C-F, C-P)}$ = 20.6, 3.4 Hz), 164.4 – 161.5 (d, $J_{(C-F, C-P)}$ = 248.3 Hz), 136.8 – 136.7, 134.8 – 134.3 (ddd, $J_{(C-F, C-P)}$ = 22.8, 7.9, 2.9 Hz), 133.8 – 132.4 (m), 132.2 – 131.9 (dd, $J_{(C-F, C-P)}$ = 10.6, 2.9 Hz), 131.3 – 130.8 (dd, $J_{(C-F, C-P)}$ = 21.9, 9.5 Hz), 129.0 – 128.9, 128.8 – 128.5 (dd, $J_{(C-F, C-P)}$ = 12.1, 5.8 Hz), 126.7 – 126.3 (t, $J_{(C-F, C-P)}$ = 9.1 Hz), 125.1 – 125.0, 120.4 – 120.3, 115.8 – 115.2 (d, $J_{(C-F, C-P)}$ = 21.8 Hz), 98.0 – 95.6 (dd, $J_{(C-F, C-P)}$ = 195.6, 6.1 Hz), 40.4 – 39.3 (dd, $J_{(C-F, C-P)}$ = 67.0, 23.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.8 – -112.9 (m), -156.0 – -156.2 (ddt, *J* = 33.7, 13.4, 7.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.5 – 26.0 (d, *J* = 7.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}F_2NO_2P^+$ 462.1429, found 462.1424.



3-(Diphenylphosphoryl)-2-fluoro-2-(4-methoxyphenyl)-*N*-phenylpropanamide (3q) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0450 g, 48%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.15 (d, *J* = 6.6 Hz, 1H), 7.79 – 7.71 (m, 4H), 7.52 – 7.32 (m, 9H), 7.29 – 7.23 (m, 3H), 7.13 – 7.05 (m, 1H), 6.86 – 6.79 (m, 2H), 3.78 – 3.76 (s, 3H), 3.85 – 3.67 (m, 1H), 3.28 – 3.18 (ddd, *J* = 15.5, 9.9, 9.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9 – 167.4 (dd, $J_{(C-F, C-P)}$ = 20.5, 3.1 Hz), 160.1 – 159.9, 137.0 – 136.8, 134.1 – 132.1 (dd, $J_{(C-F, C-P)}$ = 101.8, 64.7 Hz), 132.2 – 131.8 (dd, $J_{(C-F, C-P)}$ = 9.6, 2.8 Hz), 131.4 – 130.8 (dd, $J_{(C-F, C-P)}$ = 23.8, 9.5 Hz), 128.9 – 128.8, 128.9 – 128.5 (dd, $J_{(C-F, C-P)}$ = 12.0, 7.7 Hz), 126.1 – 125.6 (d, $J_{(C-F, C-P)}$ = 9.3 Hz), 125.1 – 124.6, 120.6 – 120.1, 98.1 – 96.0 (dd, $J_{(C-F, C-P)}$ = 193.9, 6.2 Hz), 56.3 – 54.6, 43.9 – 37.1 (dd, $J_{(C-F, C-P)}$ = 66.9, 24.1 Hz), 31.7 – 28.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -153.5 – -156.1 (dq, *J* = 34.3, 7.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.4 – 21.8 (d, *J* = 8.2 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}FNO_3P^+$ 474.1629, found 474.1629.



2-Fluoro-*N*,2-diphenylpropanamide (7) was prepared according to the **general procedure B (No TBPB)** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0157 g, 32%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.11 (s, 1H), 7.65 – 7.50 (m, 4H), 7.48 – 7.28 (m, 5H), 7.20 – 7.07 (m, 1H), 2.05 – 1.97 (d, *J* = 23.6 Hz, 3H).[2]



3-(Bis(2-methoxyphenyl)phosphoryl)-*N*,2-diphenylpropanamide (8) was prepared according to the **general procedure B** and purified by flash column chromatography (PE/EA = 5/1) as a colorless oil (0.0271 g, 28%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.01 – 8.97 (s, 1H), 7.84 – 7.76 (s, 1H), 7.67 – 7.62 (m, 2H), 7.55 – 7.48 (ddd, *J* = 13.9, 7.6, 1.7 Hz, 1H), 7.45 – 7.28 (m, 5H), 7.24 – 7.19 (m, 2H), 7.15 – 7.00 (m, 4H), 6.96 – 6.91 (ddd, *J* = 8.4, 5.4, 0.8 Hz, 1H), 6.88 – 6.77 (m, 3H), 3.85 – 3.82 (s, 3H), 3.79 – 3.75 (s, 3H), 3.70 – 3.62 (dd, *J* = 15.0, 11.6 Hz, 1H), 3.53 – 3.44 (dd, *J* = 15.0, 11.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1 – 170.8 (d, *J* = 8.2 Hz), 162.2 – 159.8 (dd, *J* = 69.9, 3.5 Hz), 143.8 – 141.9 (d, *J* = 8.3 Hz), 138.0 – 137.5, 134.4 – 133.9 (d, *J* = 25.5 Hz), 133.9 – 133.6 (m), 128.9 – 128.5, 128.0 – 127.7, 127.7 – 127.5, 125.6 – 125.3, 124.3 – 123.7, 121.0 – 120.5 (dd, *J* = 12.1, 7.2 Hz), 119.7 – 119.4, 120.1 – 118.2 (m), 111.5 – 110.6 (dd, *J* = 50.7, 6.7 Hz), 78.3 – 77.9 (d, *J* = 4.8 Hz), 56.1 – 55.3 (d, *J* = 22.2 Hz), 36.3 – 34.8 (d, *J* = 71.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 37.0 – 36.7.

6. Fluorescence quenching effects

Table S9. Test conditions for quenching by **1a** [a]

Entry	**CBZ6**	**1a**	DCM	Total volume
1	0.5 mL (0.025 mM)	0 mL (0 mM)	1.5 mL	2 mL
2	0.5 mL (0.025 mM)	0.2 mL (2.5 mM)	1.3 mL	2 mL
3	0.5 mL (0.025 mM)	0.4 mL (5 mM)	1.1 mL	2 mL
4	0.5 mL (0.025 mM)	0.6 mL (7.5 mM)	0.9 mL	2 mL
5	0.5 mL (0.025 mM)	0.8 mL (10 mM)	0.7 mL	2 mL
5	0.5 mL (0.025 mM)	1.0 mL (12.5 mM)	0.5 mL	2 mL

[a] General information: **1a** (223.4 mg, 1 mmol) dissolved in 40 mL DCM (25 mM), **CBZ6** (4.3 mg, 0.01 mmol) dissolved in 10 mL DCM, then 1 mL of this solution was diluted to 10 mL (0.1 mM). 0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, the corresponding concentration of **1a**, and DCM into a cuvette, maintaining a total volume of 2 mL, Measure the fluorescence intensity at an excitation wavelength of 330 nm. Make and model of fluorescence spectrophotometer: Make: Hitachi High-Technologies Corporation, Tokyo, Japan Model: F-4600.

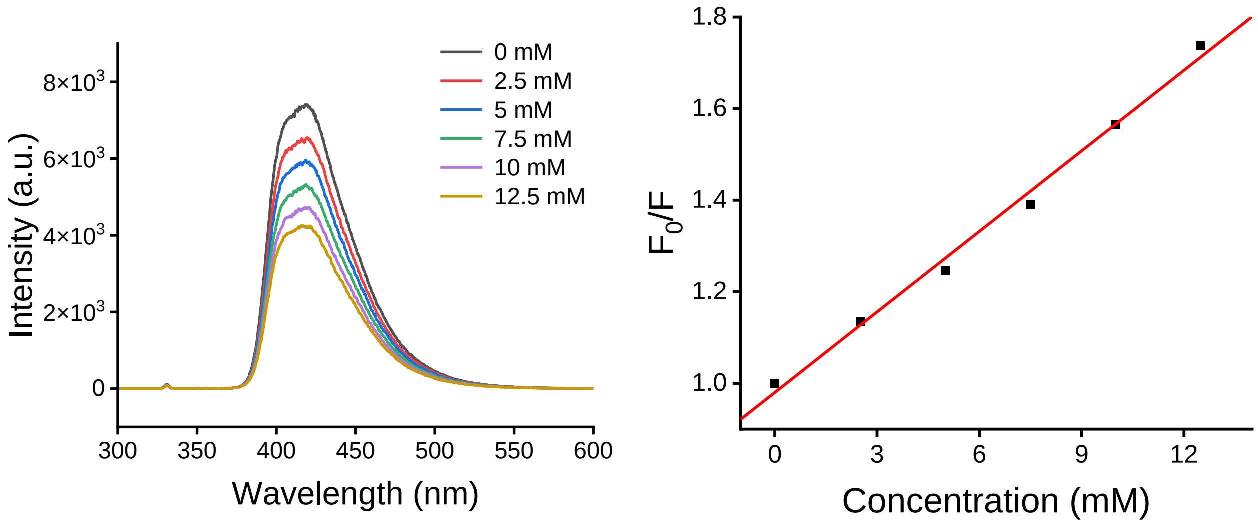


Figure S4. Fluorescence quenching curves (**a**) and Stern-Volmer fitting curve (**b**).

Table S10. Test conditions for quenching by **2a** [a]

Entry	**CBZ6**	**2a**	DCM	Total volume
1	0.5 mL (0.025 mM)	0 mL (0 mM)	1.5 mL	2 mL
2	0.5 mL (0.025 mM)	0.2 mL (10 mM)	1.3 mL	2 mL
3	0.5 mL (0.025 mM)	0.4 mL (20 mM)	1.1 mL	2 mL
4	0.5 mL (0.025 mM)	0.6 mL (30 mM)	0.9 mL	2 mL
5	0.5 mL (0.025 mM)	0.8 mL (40 mM)	0.7 mL	2 mL
6	0.5 mL (0.025 mM)	1.0 mL (50 mM)	0.5 mL	2 mL

[a] General information: **2a** (202.2 mg, 1 mmol) dissolved in 10 mL DCM (100 mM), **CBZ6** (4.3 mg, 0.01 mmol) dissolved in 10 mL DCM, then 1 mL of this solution was diluted to 10 mL (0.1 mM). 0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, the corresponding concentration of **2a**, and DCM into a cuvette, maintaining a total volume of 2 mL, Measure the fluorescence intensity at an excitation wavelength of 330 nm. Make and model of fluorescence spectrophotometer: Make: Hitachi High-Technologies Corporation, Tokyo, Japan Model: F-4600.

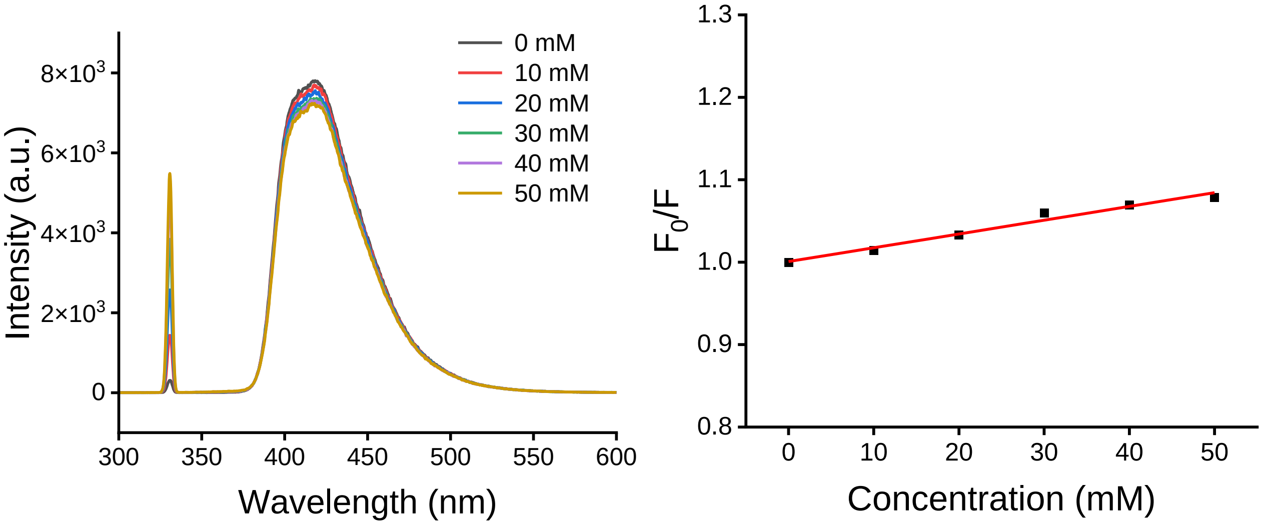


Figure S5. Fluorescence quenching curves (**a**) and Stern-Volmer fitting curve (**b**).

Table S11. Test conditions for quenching by **TBPB** [a]

Entry	**CBZ6**	**TBPB**	DCM	Total volume
1	0.5 mL (0.025 mM)	0 mL (0 mM)	1.5 mL	2 mL
2	0.5 mL (0.025 mM)	0.2 mL (10 mM)	1.3 mL	2 mL
3	0.5 mL (0.025 mM)	0.4 mL (20 mM)	1.1 mL	2 mL
4	0.5 mL (0.025 mM)	0.6 mL (30 mM)	0.9 mL	2 mL
5	0.5 mL (0.025 mM)	0.8 mL (40 mM)	0.7 mL	2 mL
6	0.5 mL (0.025 mM)	1.0 mL (50 mM)	0.5 mL	2 mL

[a] General information: **TBPB** (194.2 mg, 1 mmol) dissolved in 10 mL DCM (100 mM), **CBZ6** (4.3 mg, 0.01 mmol) dissolved in 10 mL DCM, then 1 mL of this solution was diluted to 10 mL (0.1 mM). 0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, the corresponding concentration of **TBPB**, and CH_3CN into a cuvette, maintaining a total volume of 2 mL, Measure the fluorescence intensity at an excitation wavelength of 330 nm. Make and model of fluorescence spectrophotometer: Make: Hitachi High-Technologies Corporation, Tokyo, Japan Model: F-4600

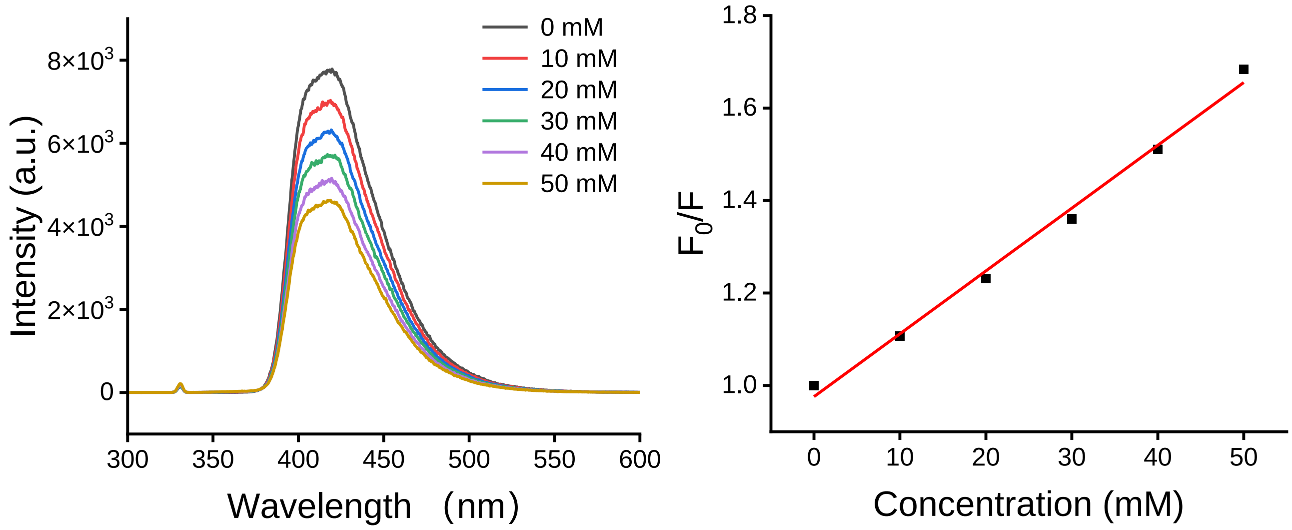


Figure S6. Fluorescence quenching curves (**a**) and Stern-Volmer fitting curve (**b**).

Table S12. Test conditions for quenching by $Et_3N{\cdot}3HF$ [a]

Entry	**CBZ6**	$Et_3N{\cdot}3HF$	CH_3CN	Total volume
1	0.5 mL (2.5×10^{-4} M)	0 mL (0 mM)	1.5 mL	2 mL
2	0.5 mL (2.5×10^{-4} M)	0.25 mL (250 mM)	1.25 mL	2 mL
3	0.5 mL (2.5×10^{-4} M)	0.375 mL (375 mM)	1.125 mL	2 mL
4	0.5 mL (2.5×10^{-4} M)	0.5 mL (500 mM)	1 mL	2 mL
5	0.5 mL (2.5×10^{-4} M)	0.625 mL (625 mM)	0.875 mL	2 mL

[a] General information: $Et_3N{\cdot}3HF$ (1612.1mg, 10 mmol) dissolved in 5 mL CH_3CN (2 M), **CBZ6** (4.3 mg, 0.01 mmol) dissolved in 10 mL CH_3CN (0.001 M), 0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, the corresponding concentration of $Et_3N{\cdot}3HF$, and CH_3CN into a cuvette, maintaining a total volume of 2 mL, Measure the fluorescence intensity at an excitation wavelength of 330nm. Make and model of fluorescence spectrophotometer: Make: Hitachi High-Technologies Corporation, Tokyo, Japan Model: F-4600.

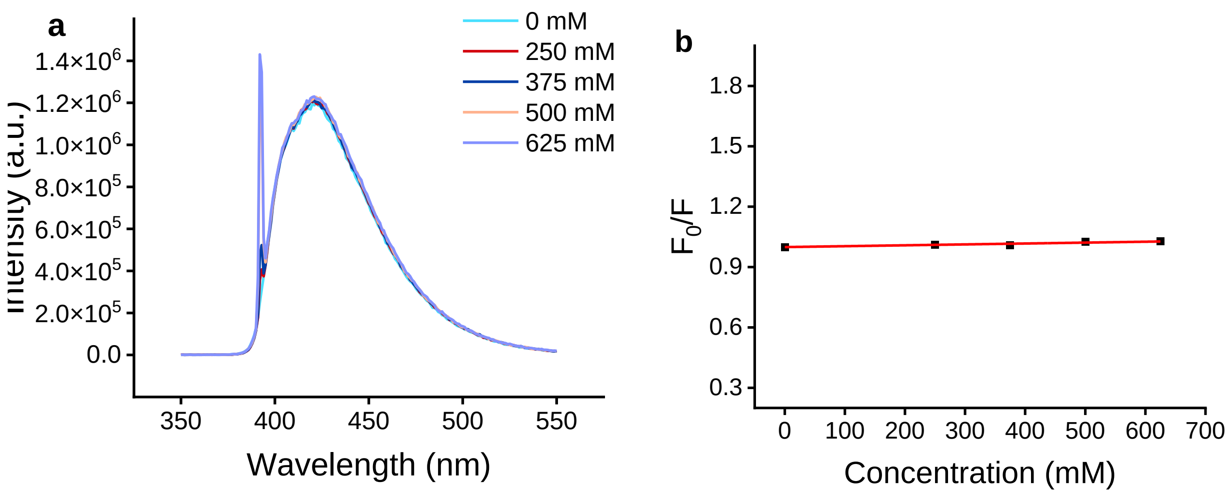


Figure S7. Fluorescence quenching curves (**a**) and Stern-Volmer fitting curve (**b**).

7. Ultraviolet-visible absorption experiments

Table S13. Preparation of solvent for UV-VIS absorption spectrum [a]

Entry	**1a**/mL	**2a**/mL	**CBZ6**/mL	TBPB	$Et_3N{\cdot}3HF$ /mL	Total volume/mL
1	3	0	0	0	0	3
2	0	3	0	0	0	3
3	0	0	3	0	0	3
4	0	0	0	3	0	3
5	0	0	0	0	3	3
6	1.5	1.5	0	0	0	3
7	1.5	0	1.5	0	0	3
8	0	1.5	1.5	0	0	3
9	0	0	1.5	1.5	0	3
10	0	0	1.5	0	1.5	3

[a] General information: **CBZ6** (0.6653 mg) was dissolved in 50 mL of dichloromethane to prepare a solution at a concentration of 0.03 μmol/mL; **1a** (0.6698 mg), **2a** (0.7418 mg), TBPB (0.5826 mg) and $Et_3N{\cdot}3HF$ (4.8363 mg) were then dissolved in 20 mL of methylene chloride, the former being prepared as a solution at a concentration of 0.15 μmol/mL, and the latter as a solution of 1.5 μmol/mL. Keep the total volume at 2 mL, prepared solutions were added as the Table S13.

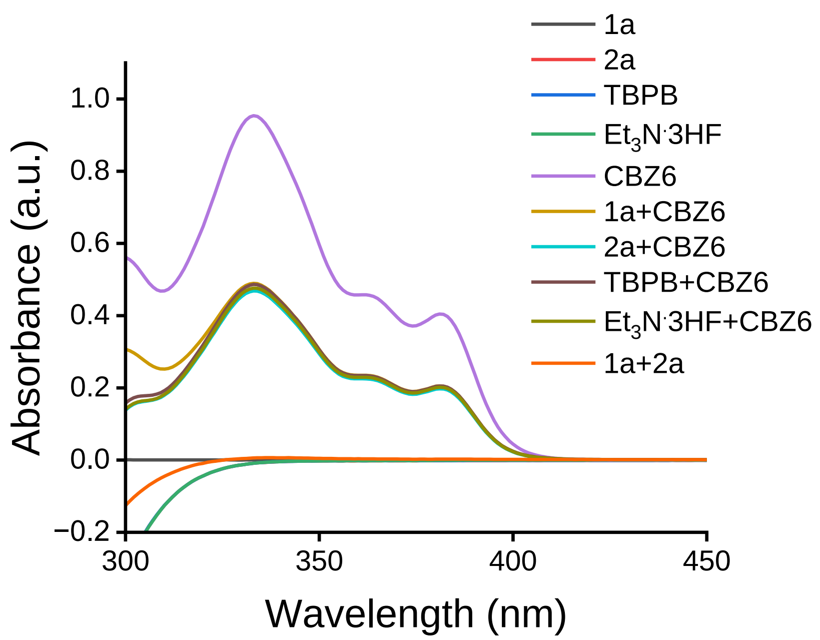


Figure S8. UV-Vis absorption spectra of reactant mixtures

8. The Cyclic Voltammogram

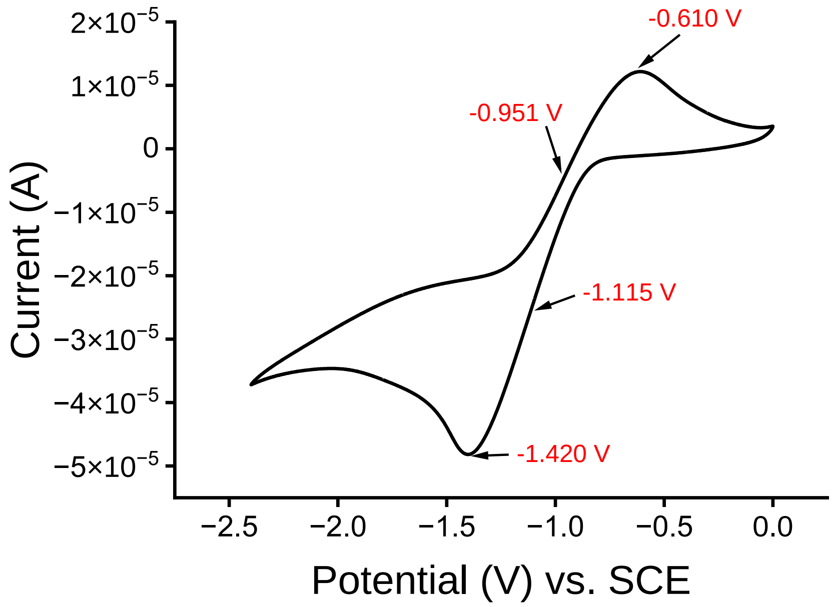


Figure S9. The cyclic voltammogram of the **2a** vs SCE in MeCN.

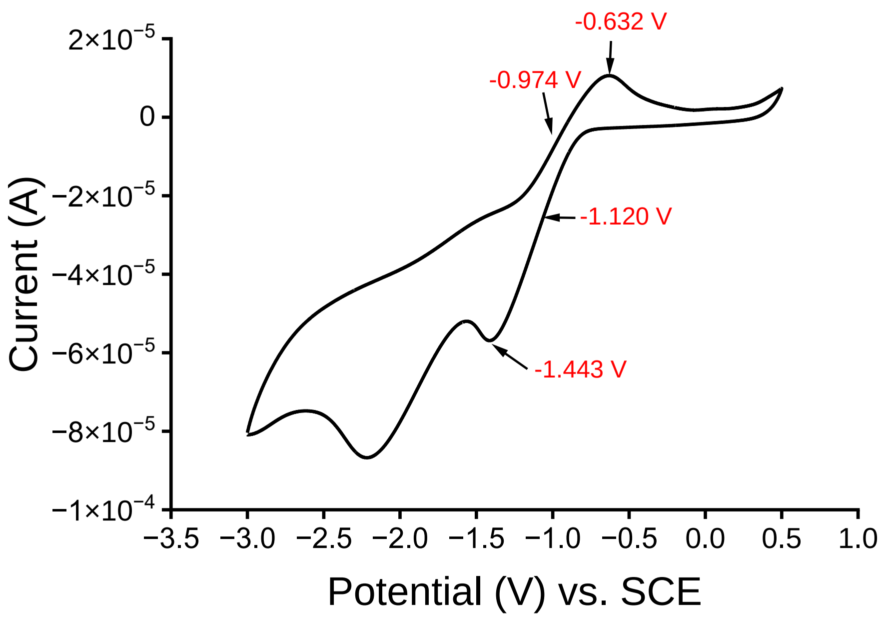


Figure S10. The cyclic voltammogram of the **TBPB** vs SCE in MeCN.

9. References

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4. H.-L. Wang; H.-K. Yuan; X.-Z. Wang; J. Zhao; D.-C. Wei; F. Shi. Synthesis of Amides-Functionalized POPs-Supported Nano-Pd Catalysts for Phosphine Ligand-Free Heterogeneous Hydroaminocarbonylation of Alkynes, *Adv. Synth. Catal.* **2020**, *362*, 2348–2353.

10. Copies of NMR spectra

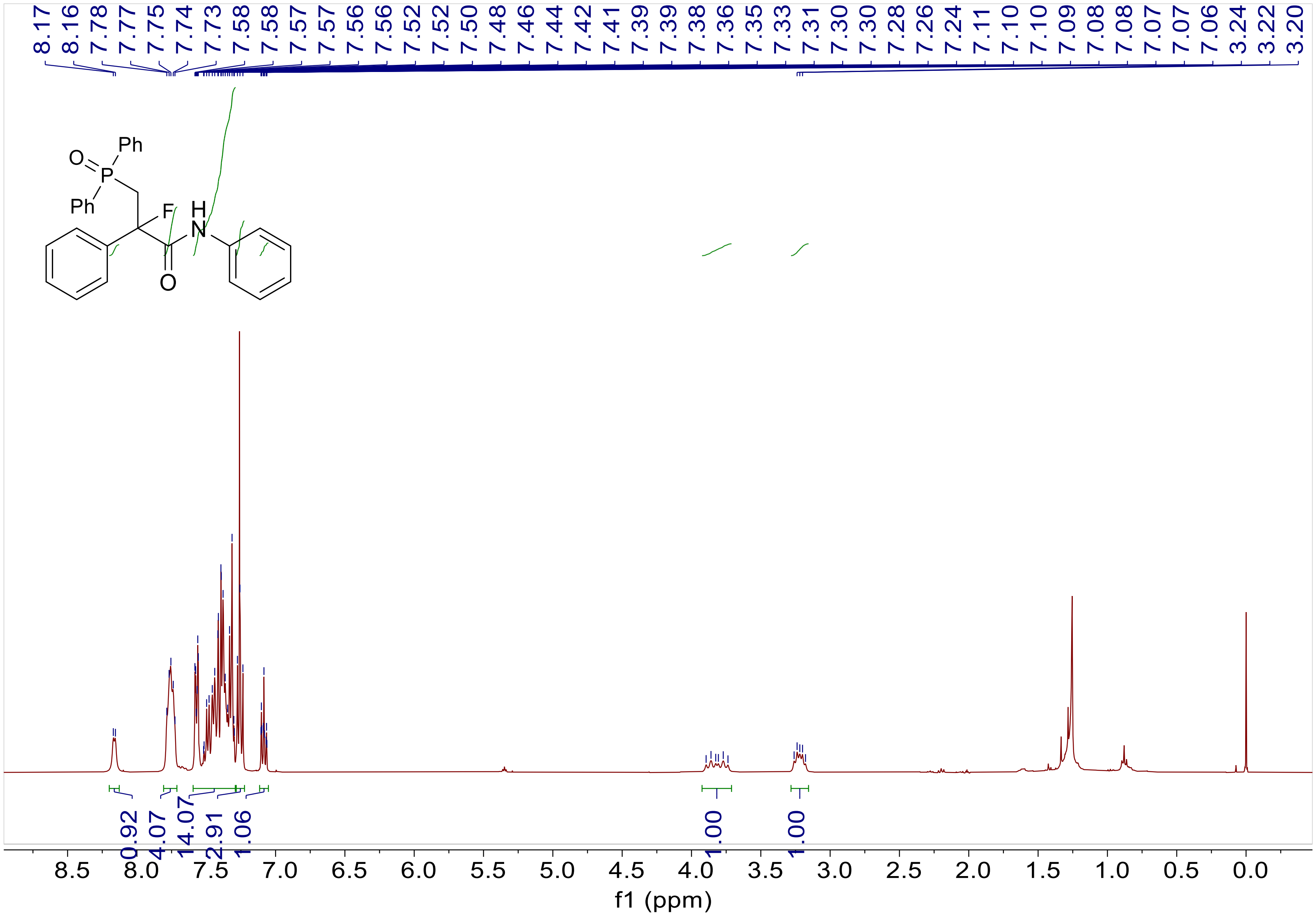


Figure S11. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

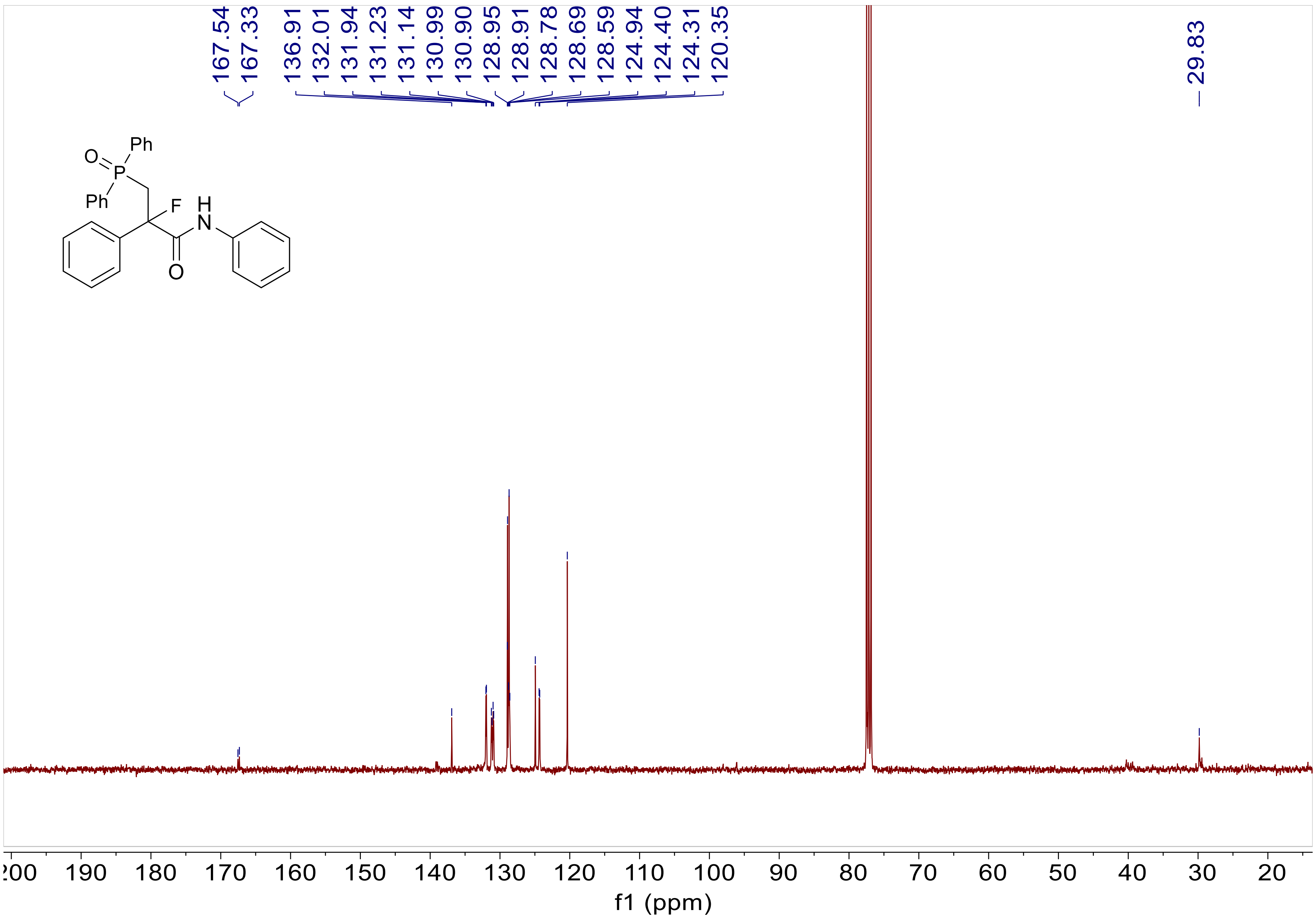


Figure S12. ^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$)

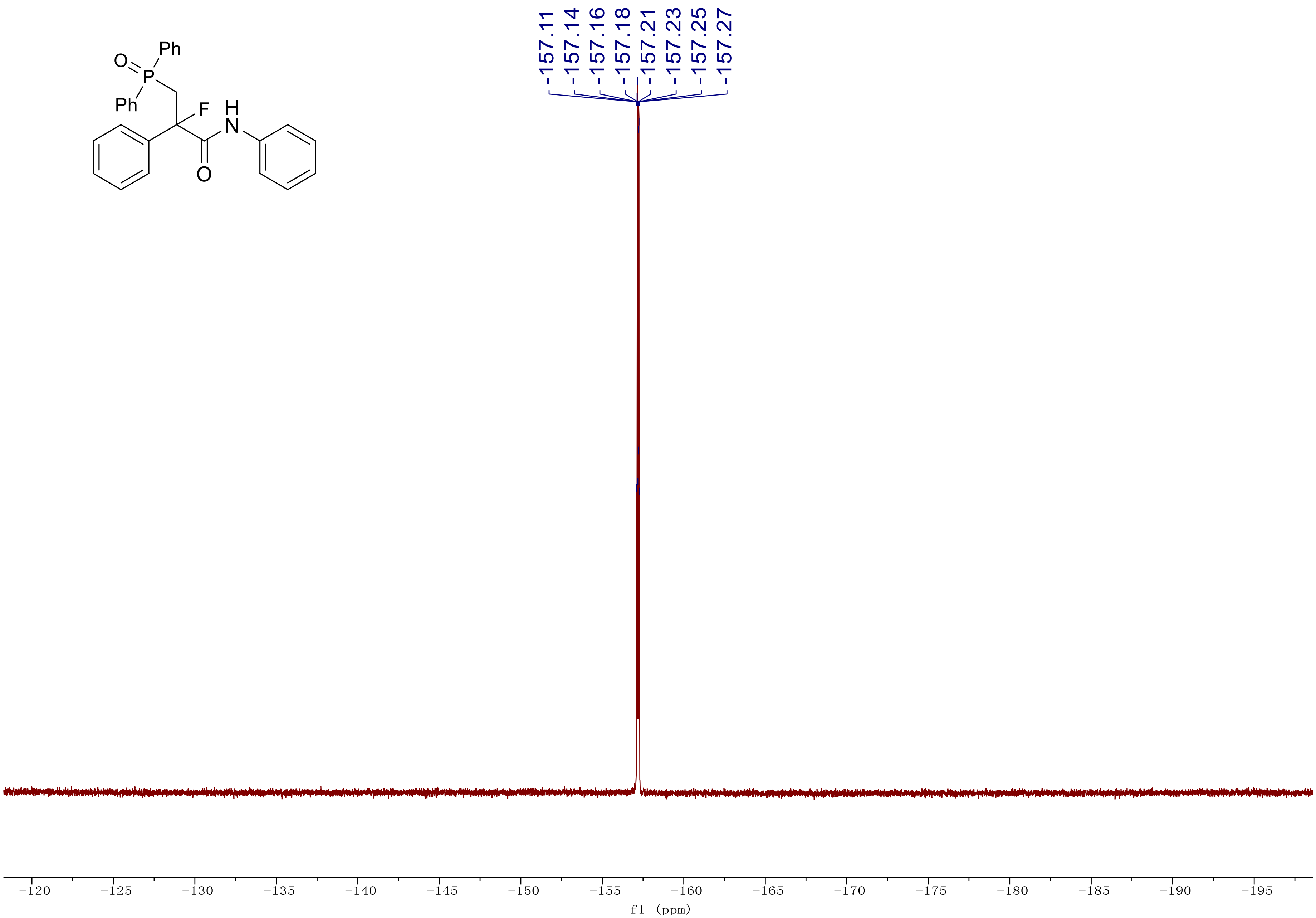
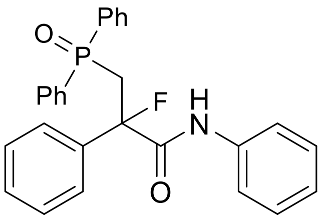


Figure S13. ^{19}F NMR spectrum of **3a** (376 MHz, $CDCl_3$)



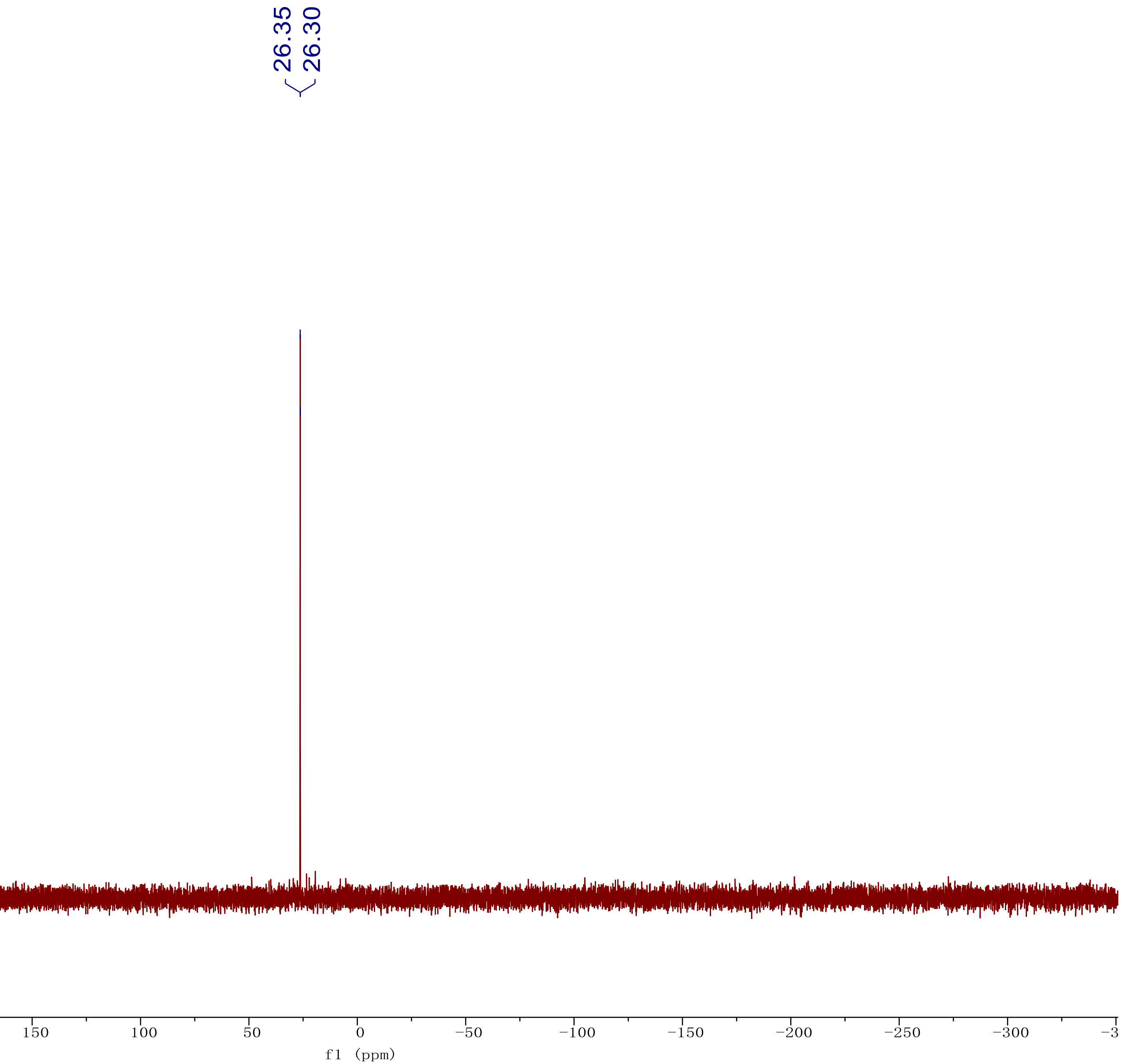


Figure S14. ^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$)

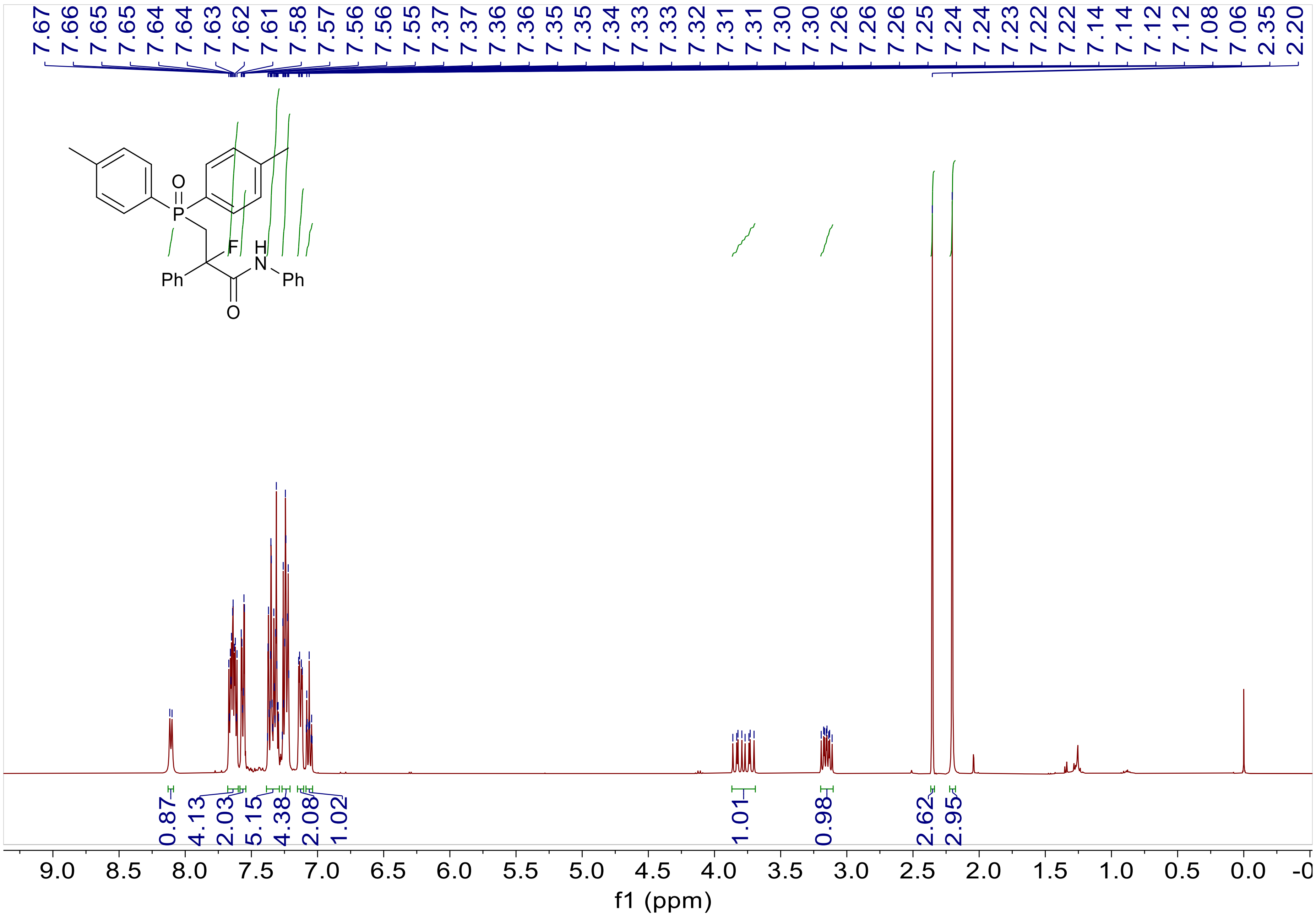


Figure S15. [1]H NMR spectrum of **3b** (400 MHz, $CDCl_3$)

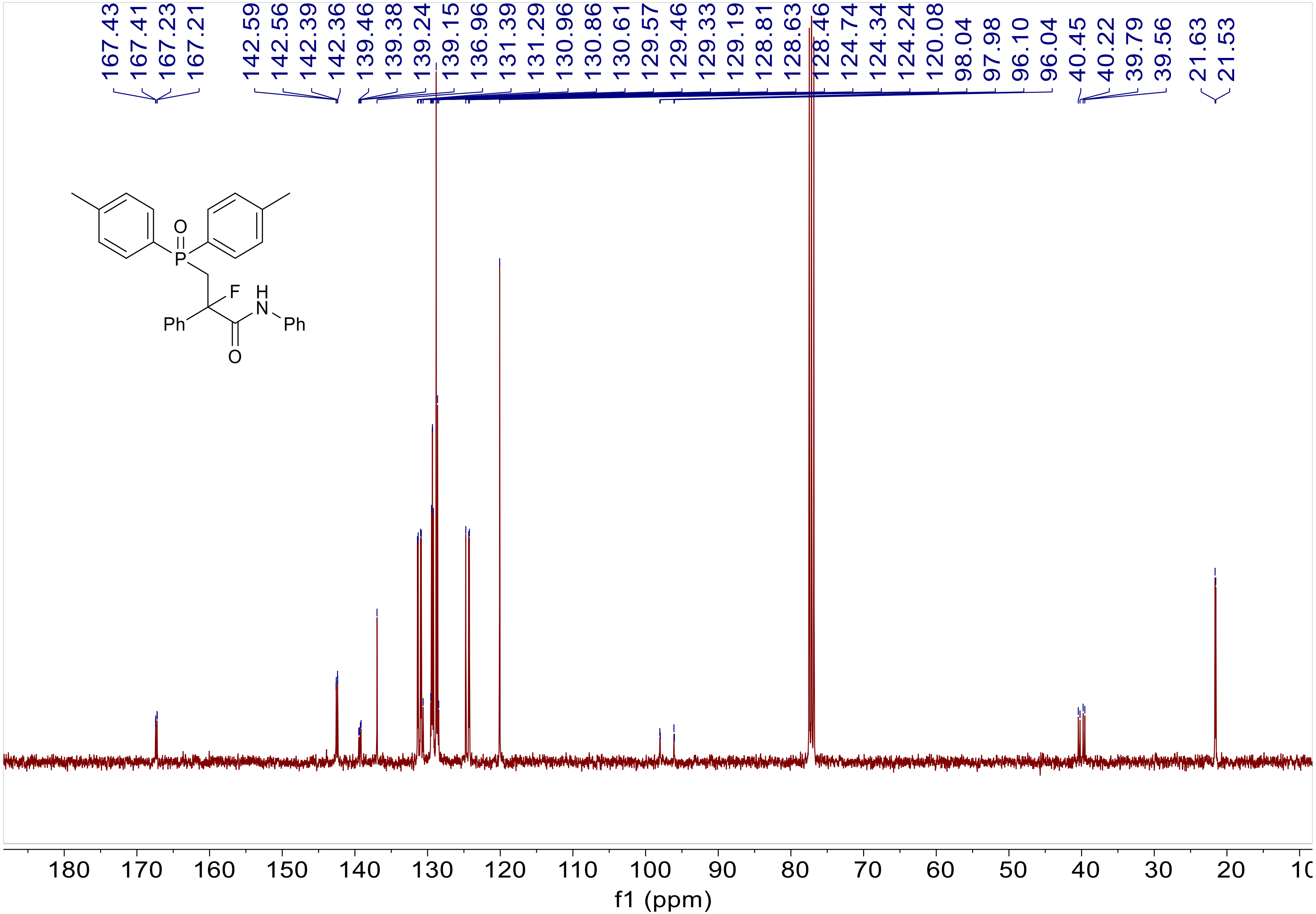


Figure S16. ^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$)

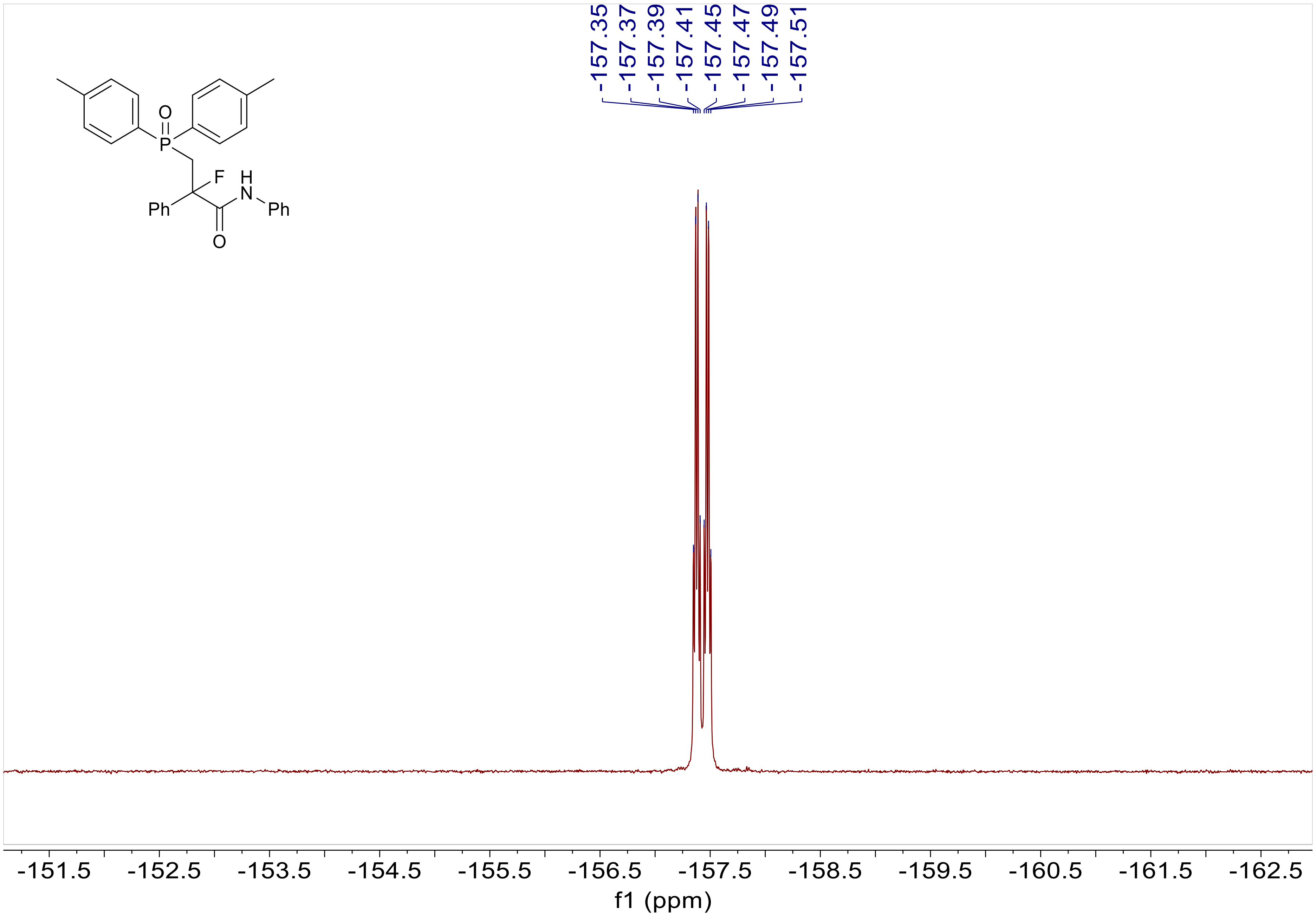


Figure S17. ^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$)

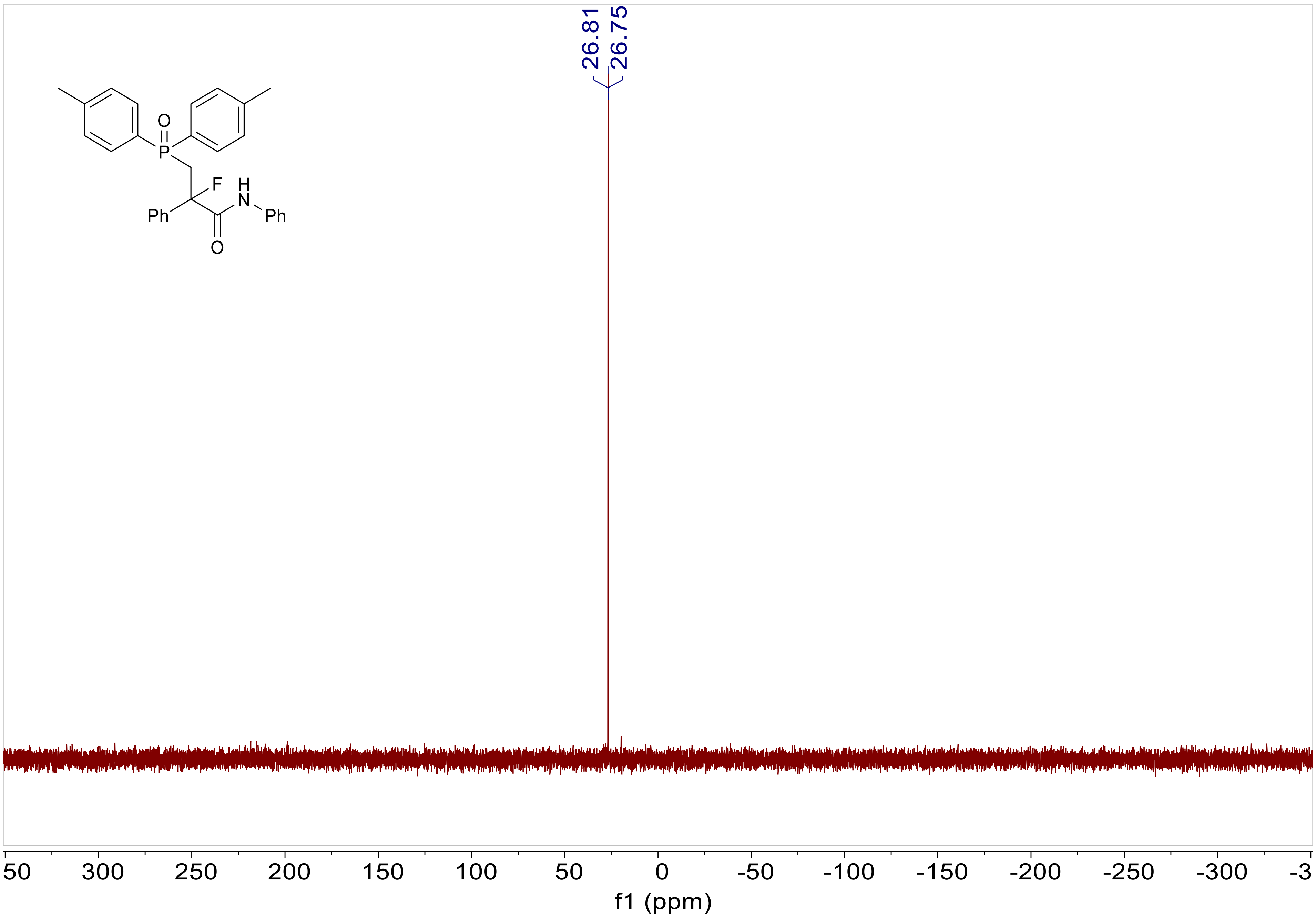


Figure S18. [31]P NMR spectrum of **3b** (162 MHz, $CDCl_3$)

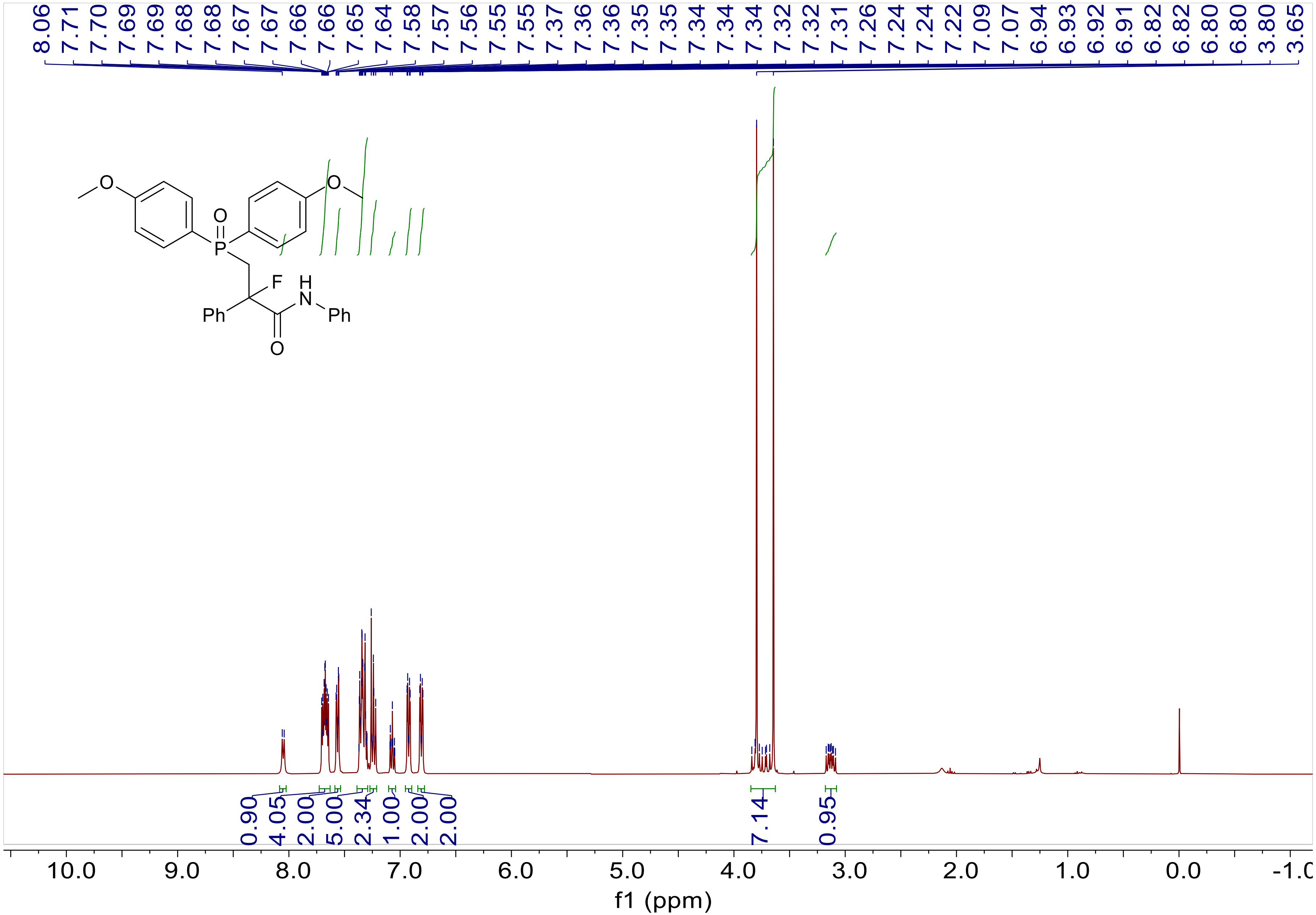


Figure S19. [1]H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

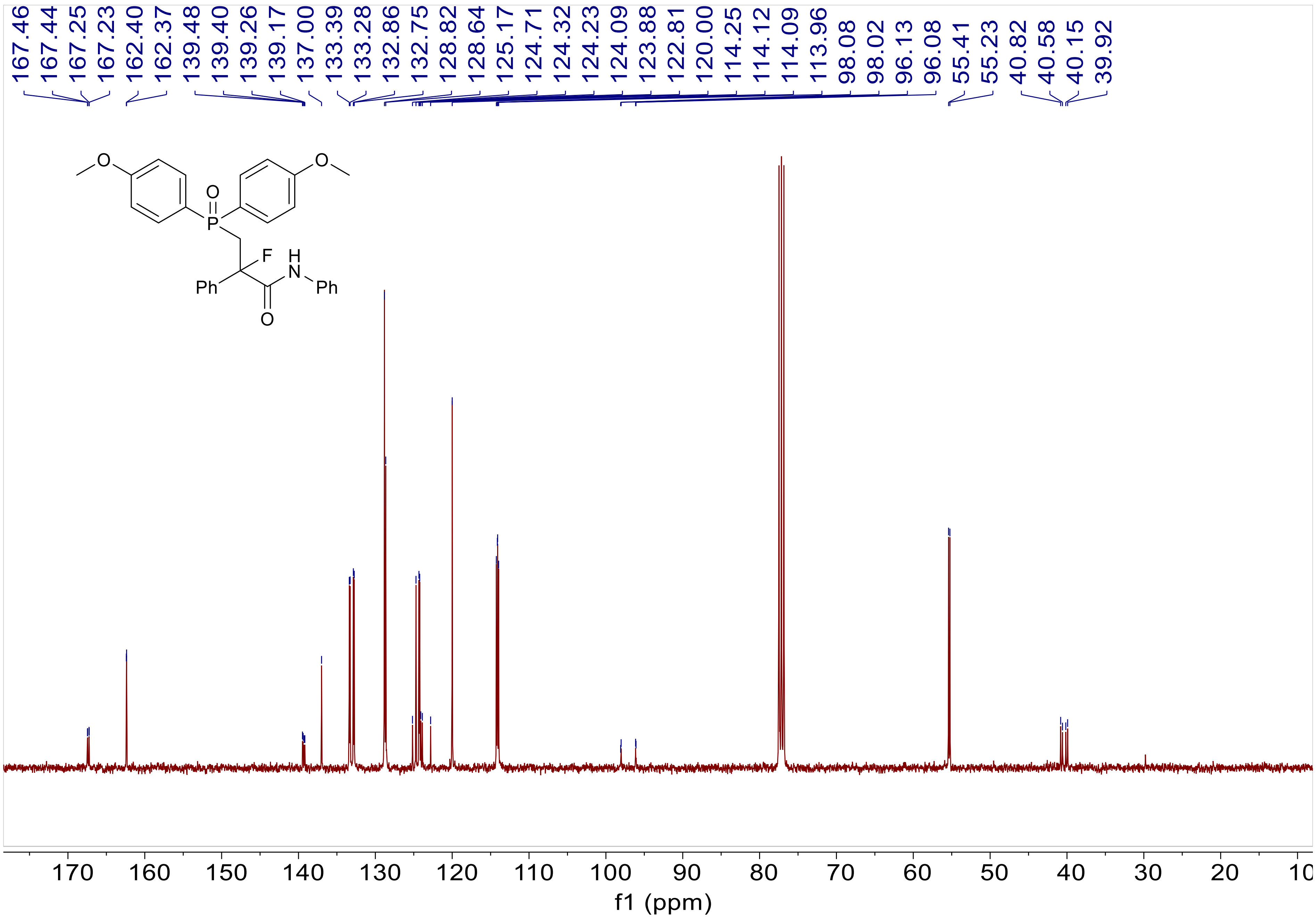


Figure S20. ^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$)

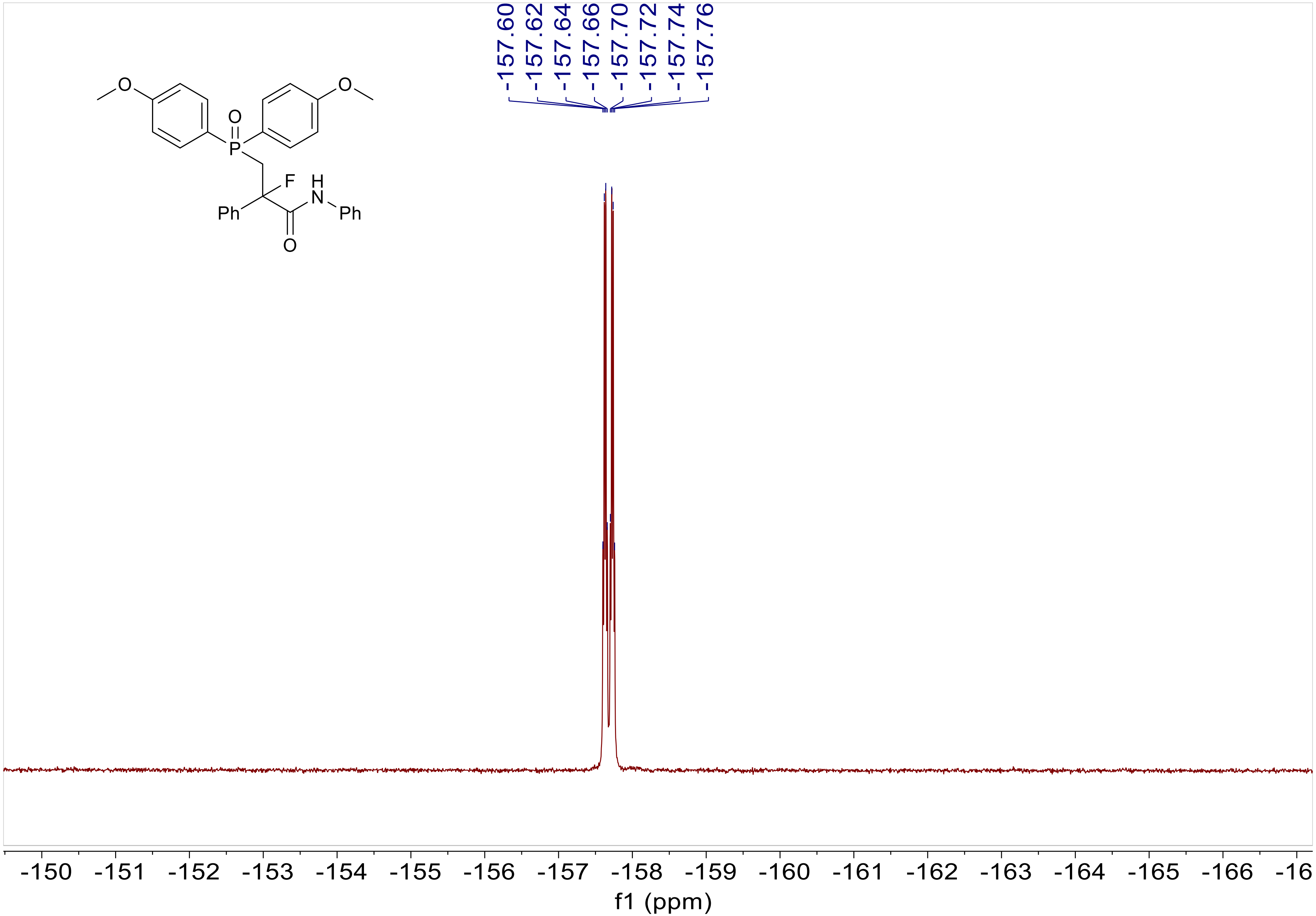


Figure S21. ^{19}F NMR spectrum of **3c** (376 MHz, $CDCl_3$)

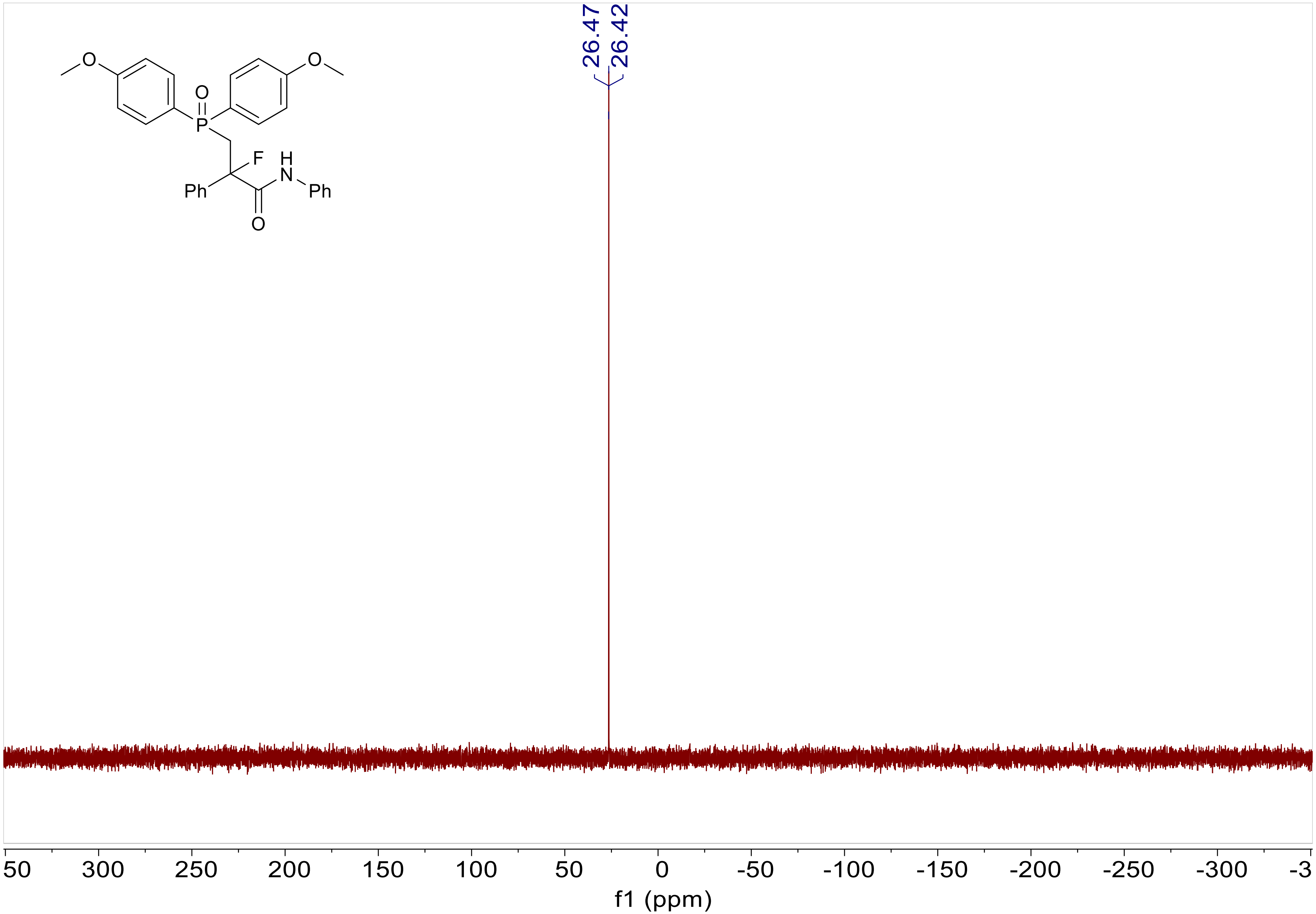


Figure S22. [31]P NMR spectrum of **3c** (162 MHz, $CDCl_3$)

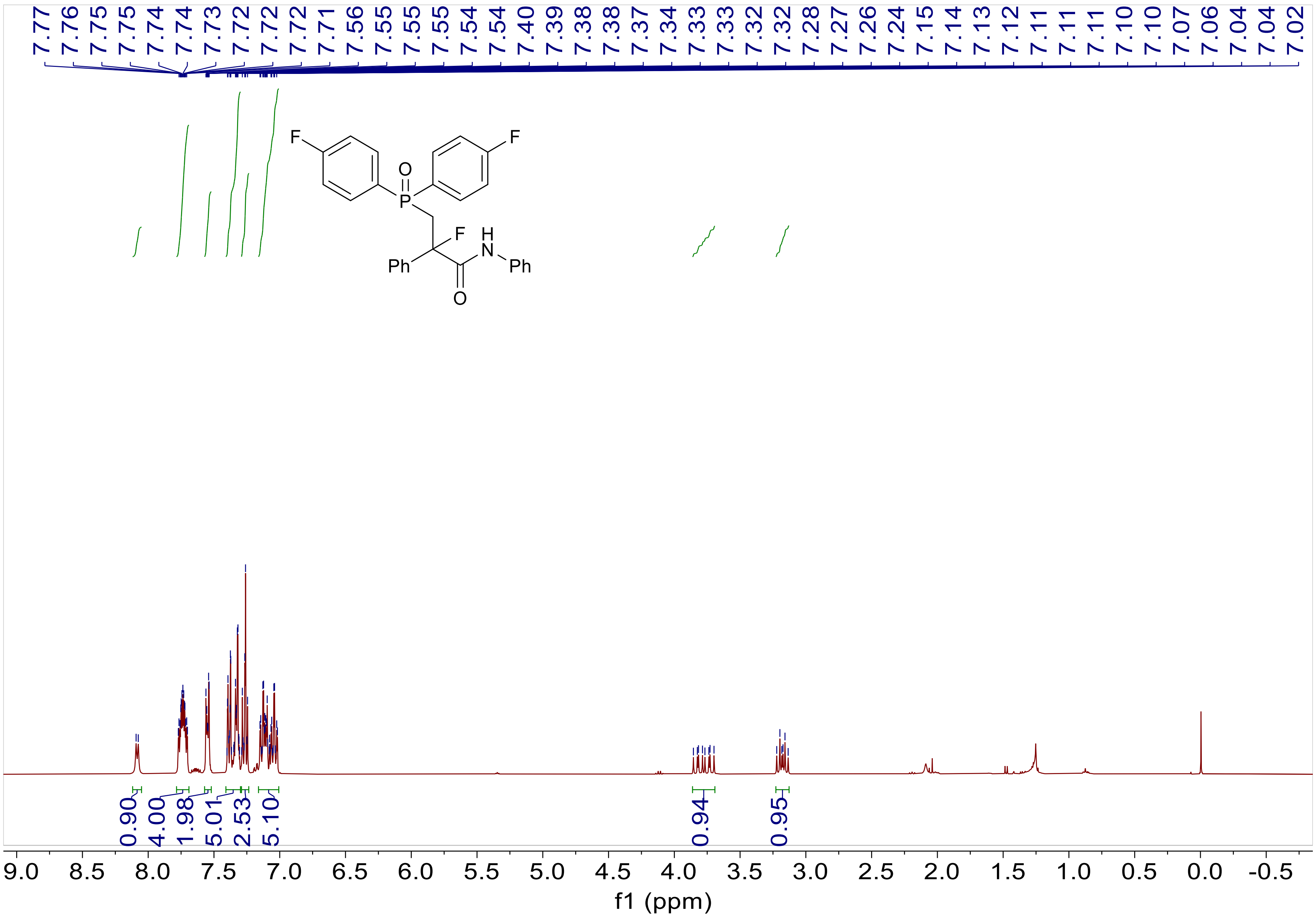


Figure S23. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)

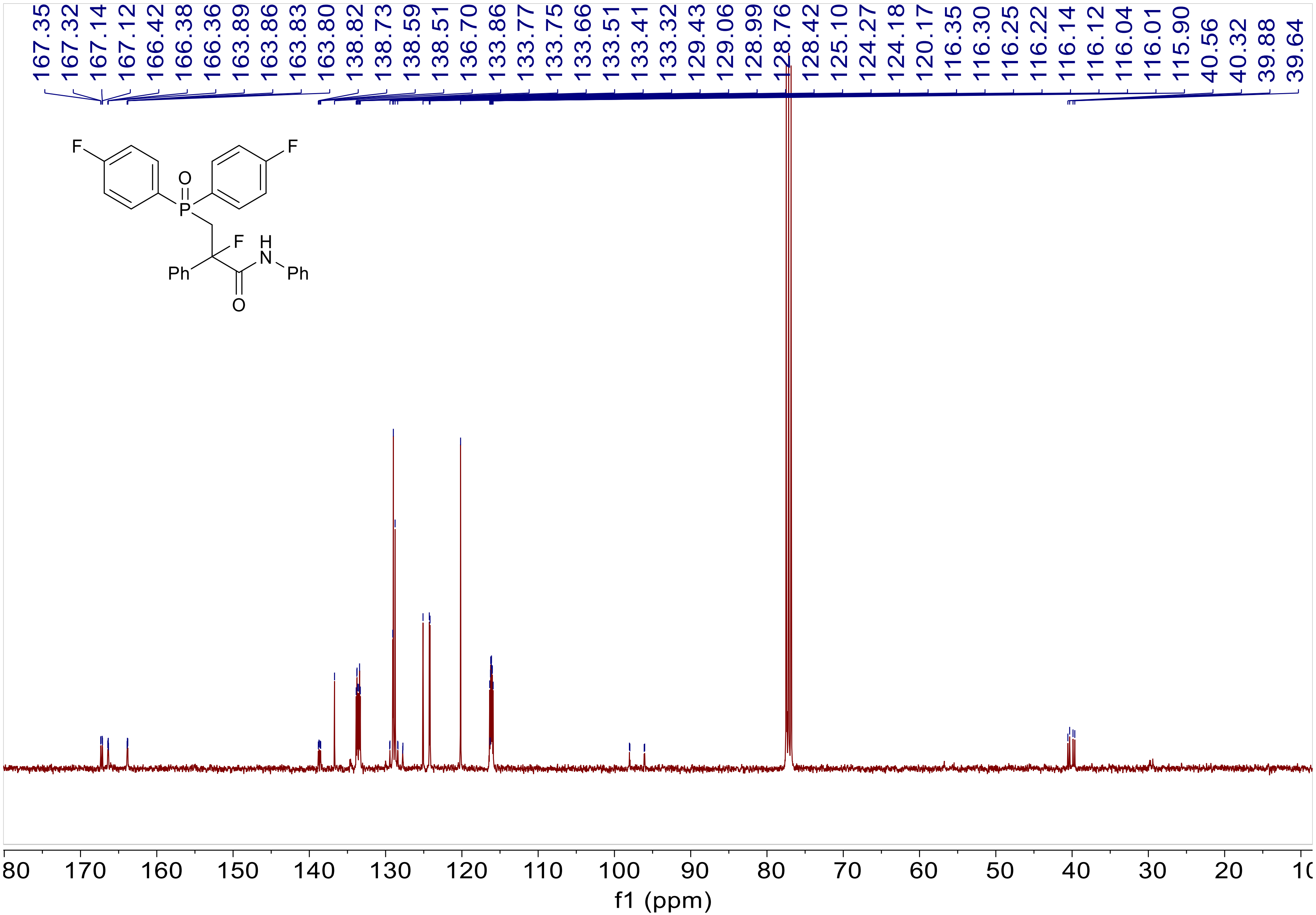


Figure S24. ^{13}C NMR spectrum of **3d** (101 MHz, $CDCl_3$)

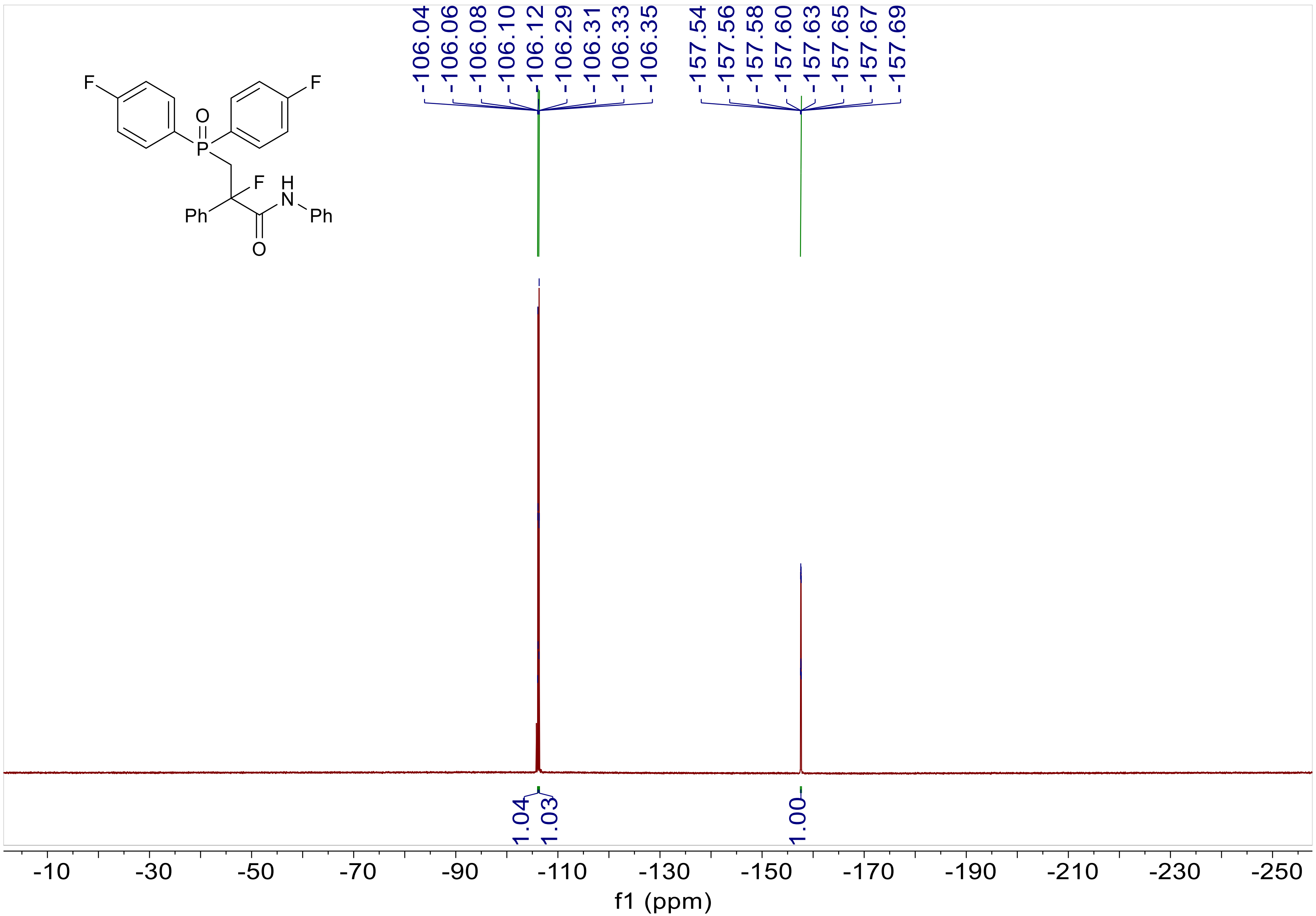


Figure S25. ^{19}F NMR spectrum of **3d** (376 MHz, $CDCl_3$)

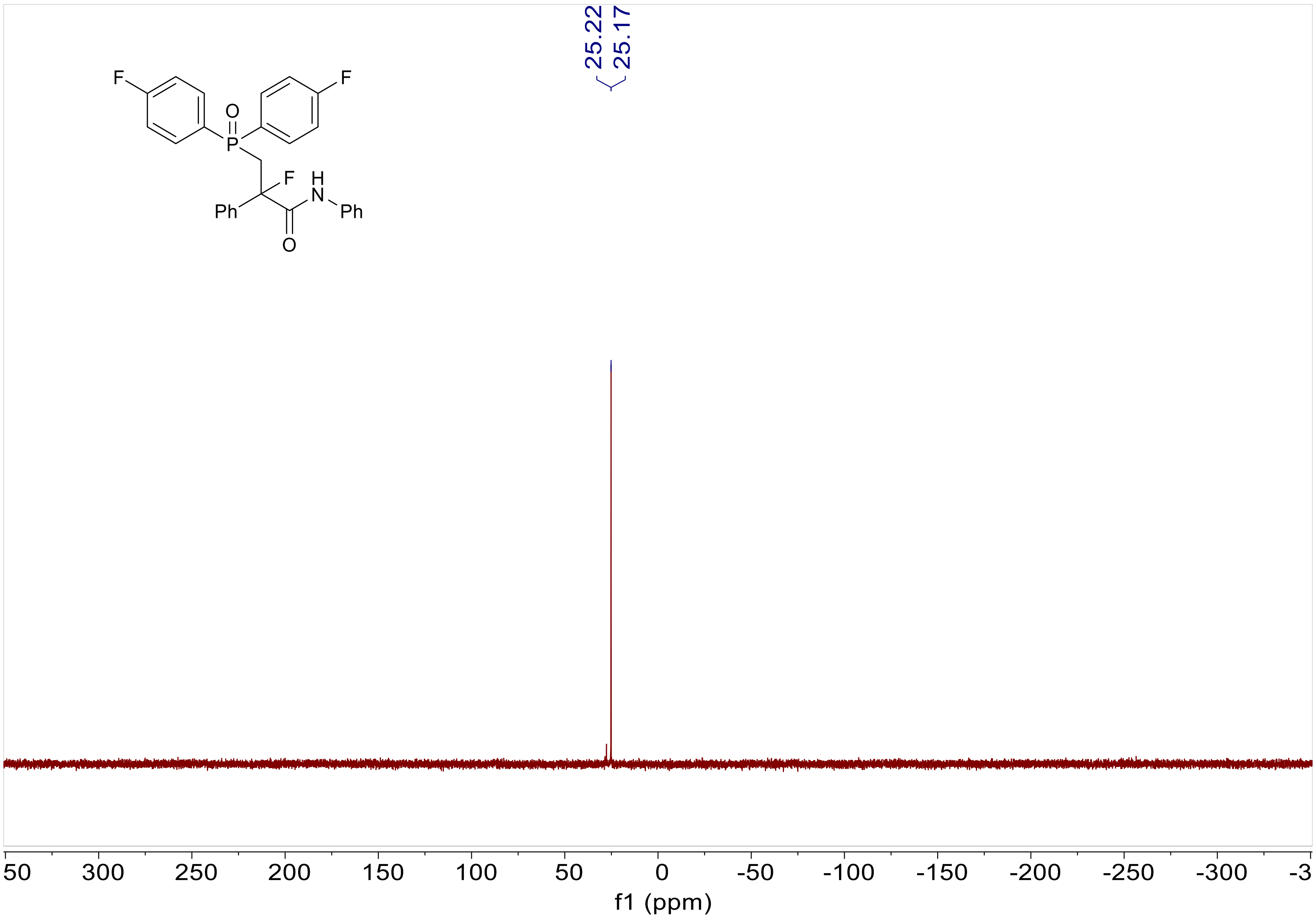


Figure S26. ^{31}P NMR spectrum of **3d** (162 MHz, $CDCl_3$)

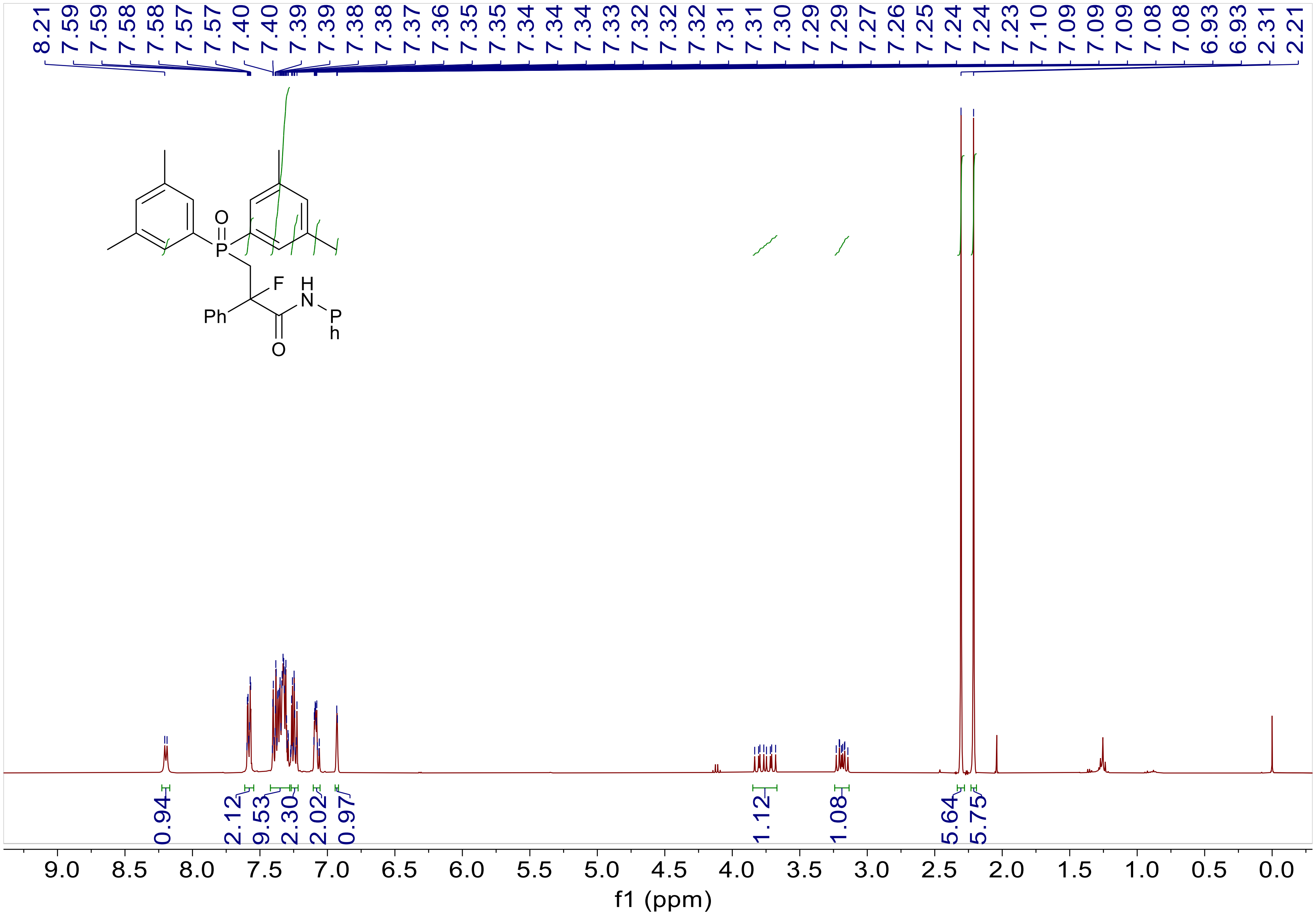


Figure S27. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)

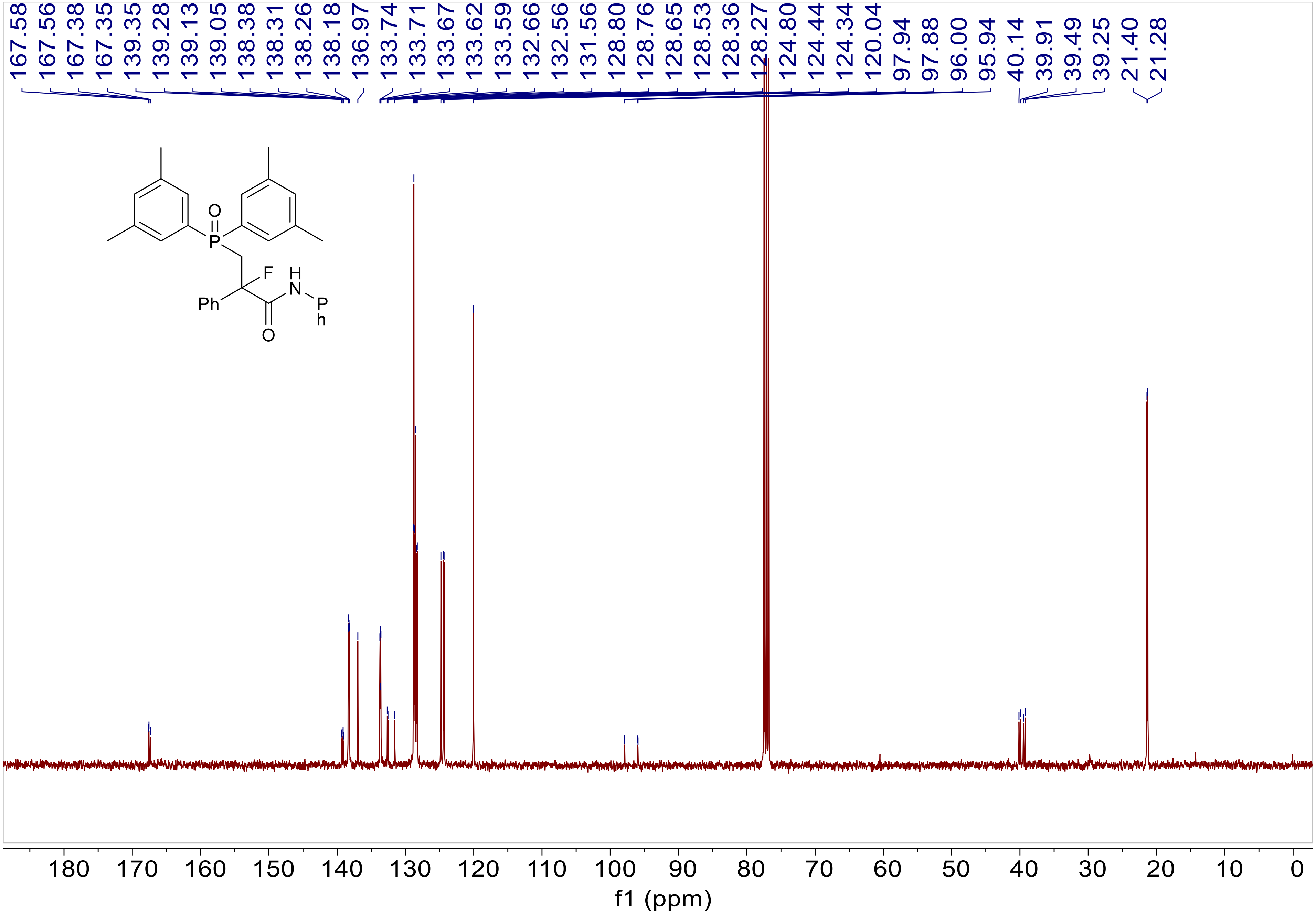


Figure S28. ^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$)

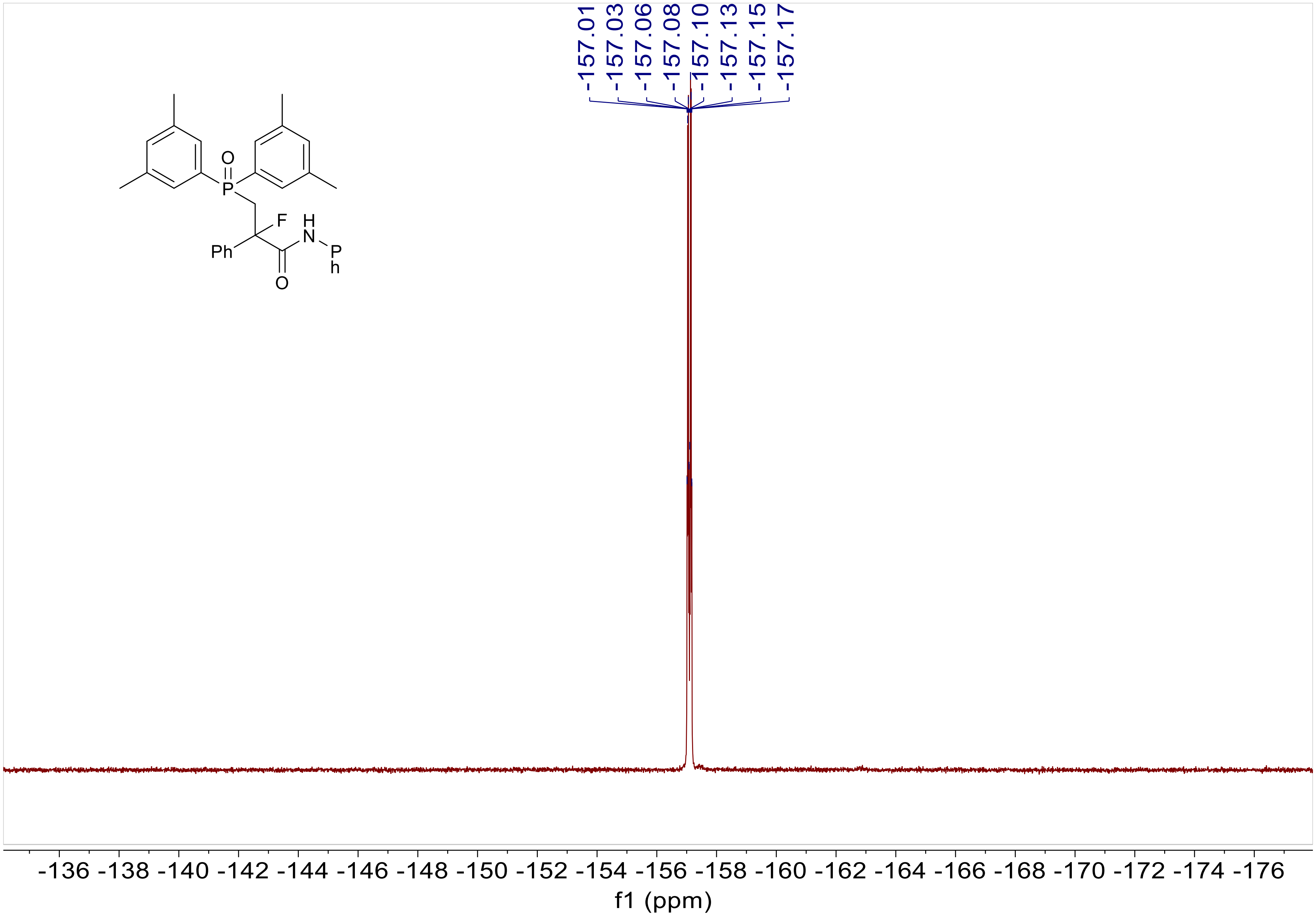


Figure S29. ^{19}F NMR spectrum of **3e** (376 MHz, $CDCl_3$)

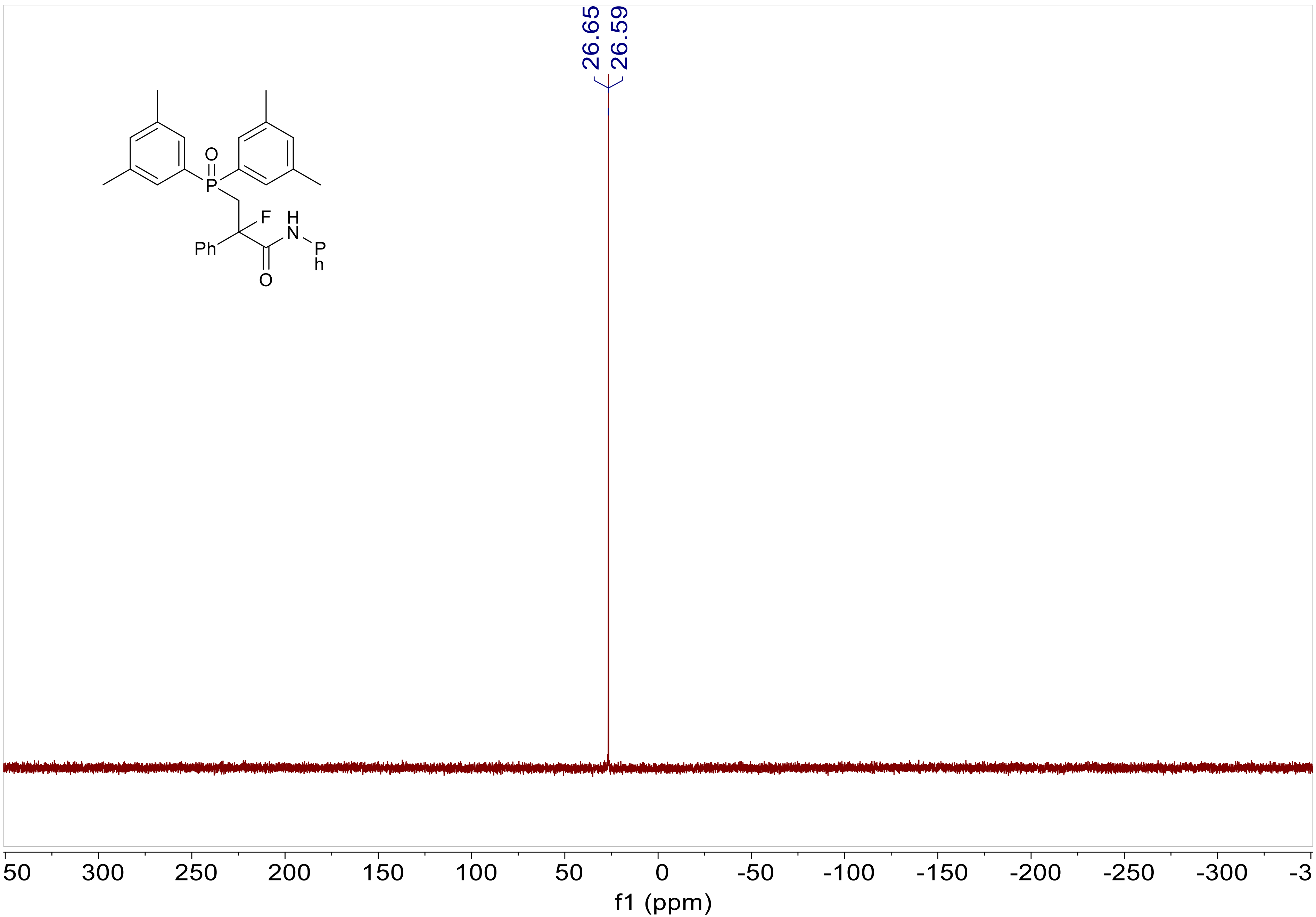


Figure S30. ^{31}P NMR spectrum of **3e** (162 MHz, $CDCl_3$)

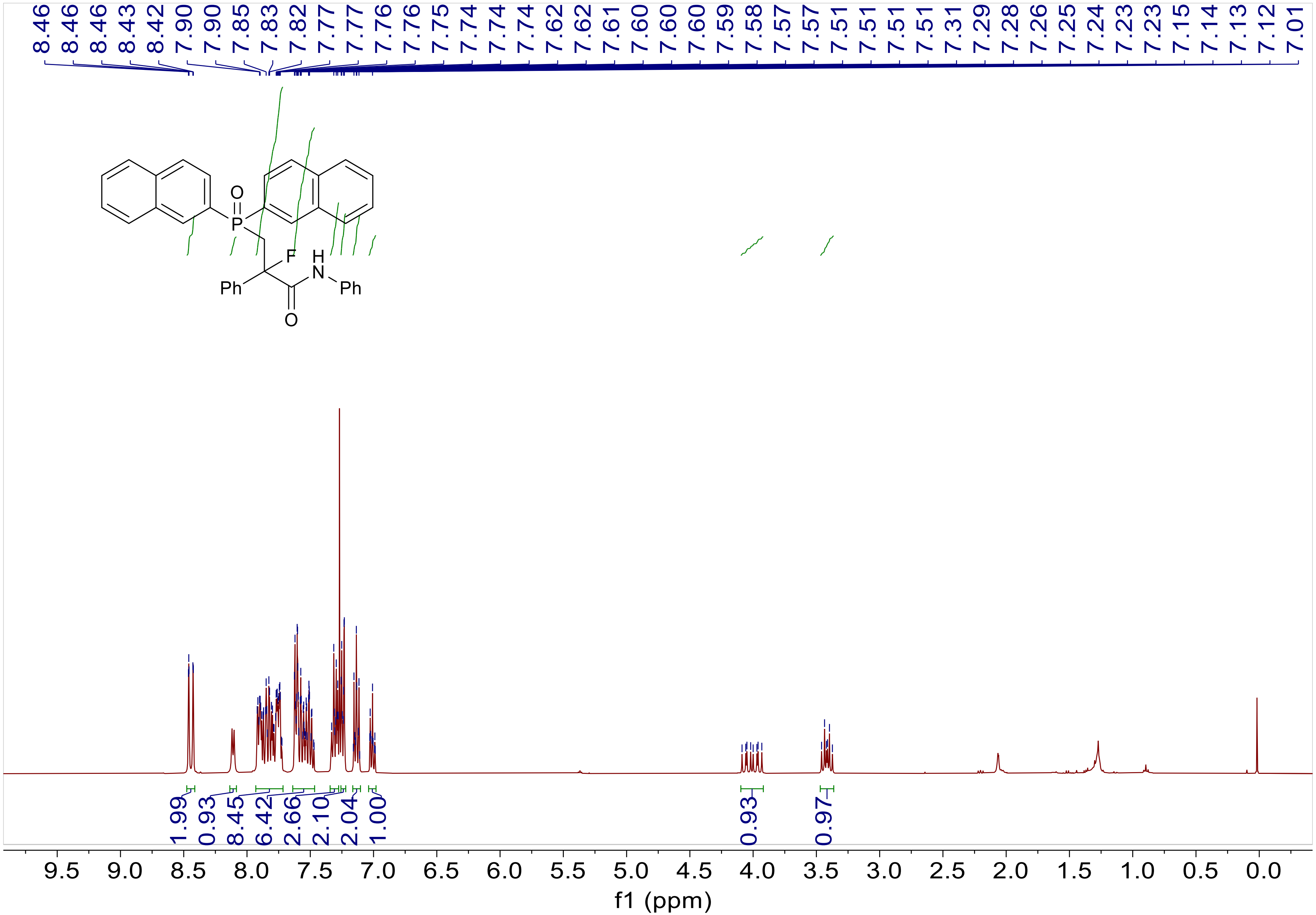


Figure S31. ¹H NMR spectrum of **3f** (400 MHz, $CDCl_3$)

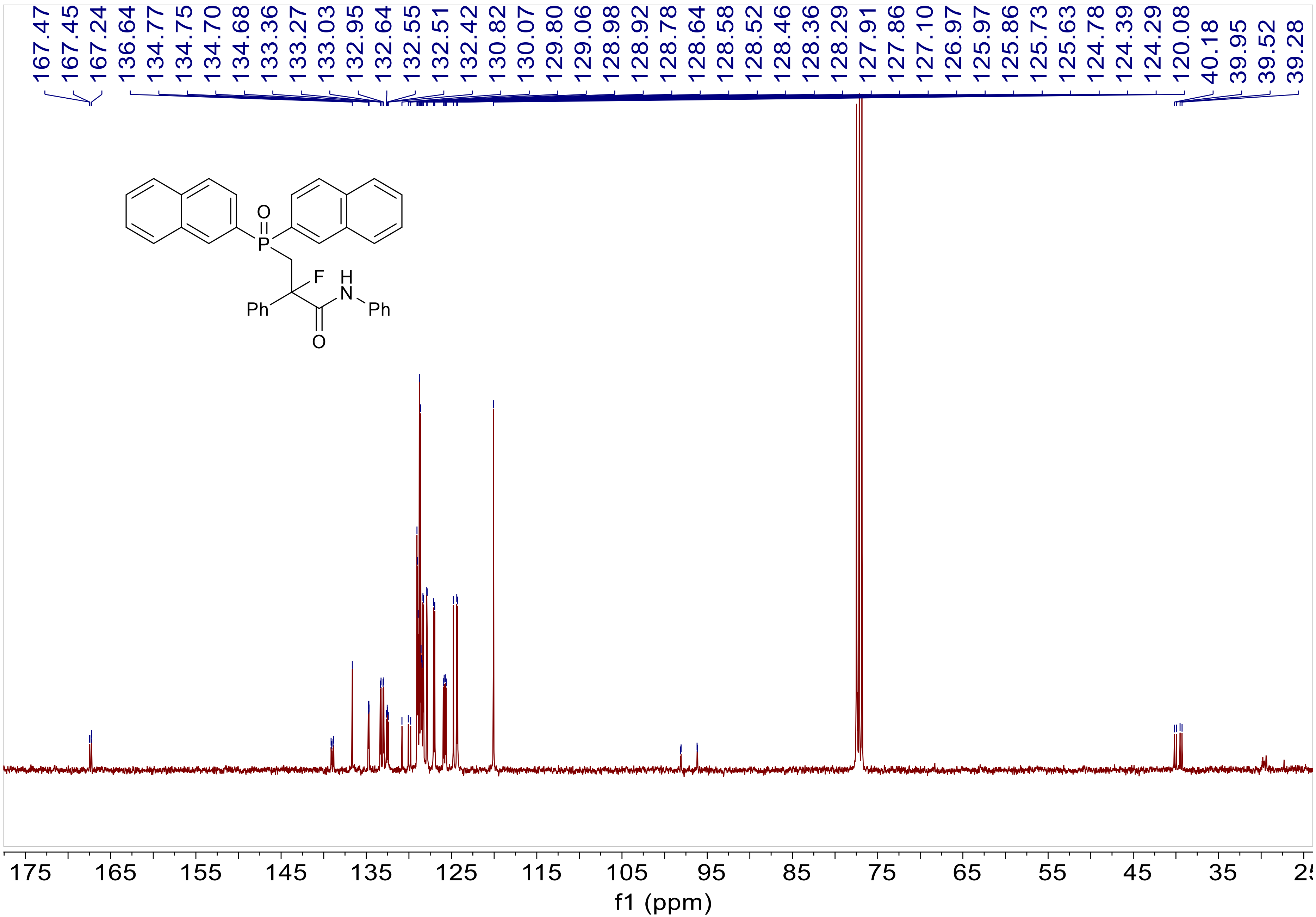


Figure S32. ^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$)

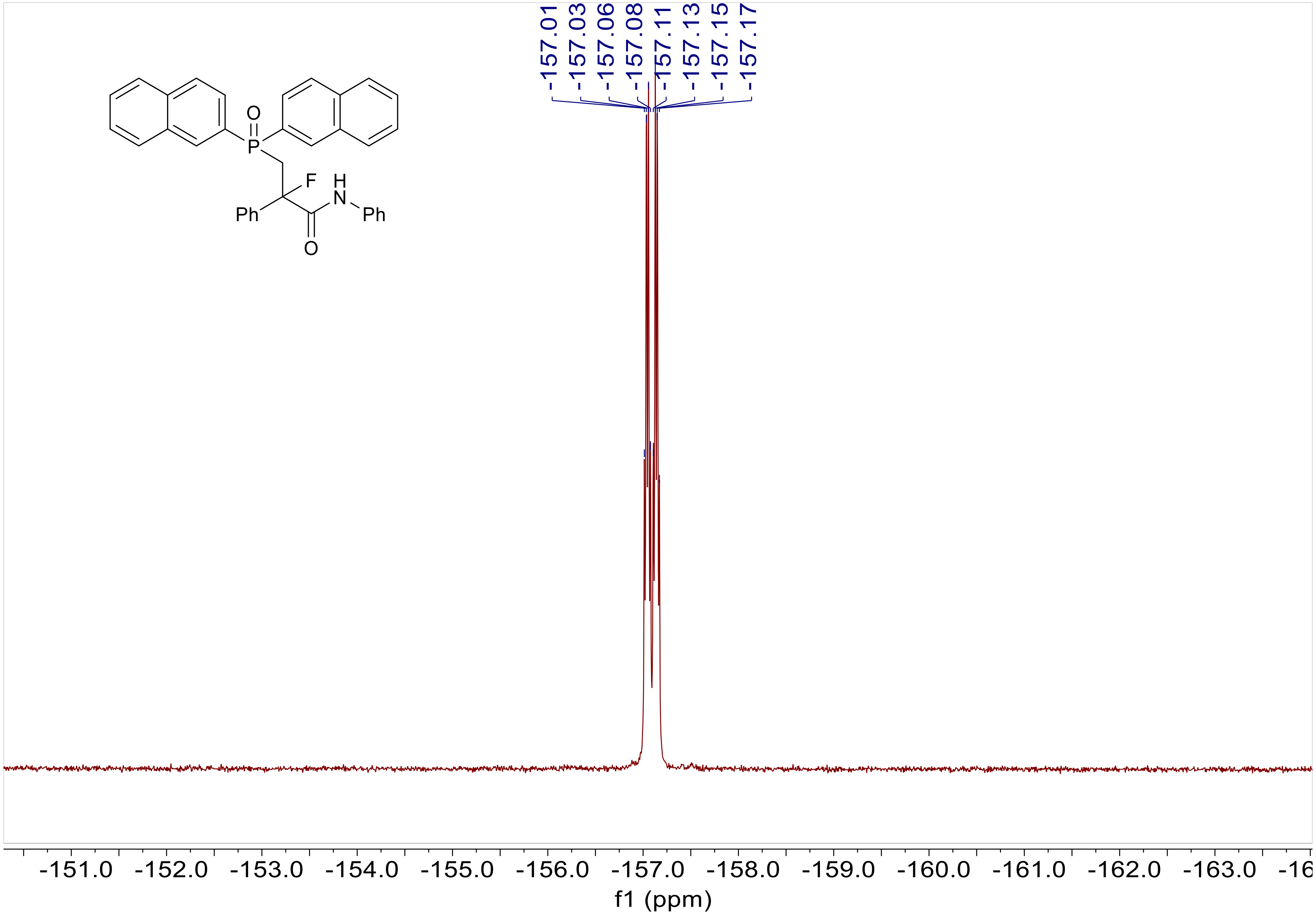


Figure S33. ^{19}F NMR spectrum of **3f** (376 MHz, $CDCl_3$)

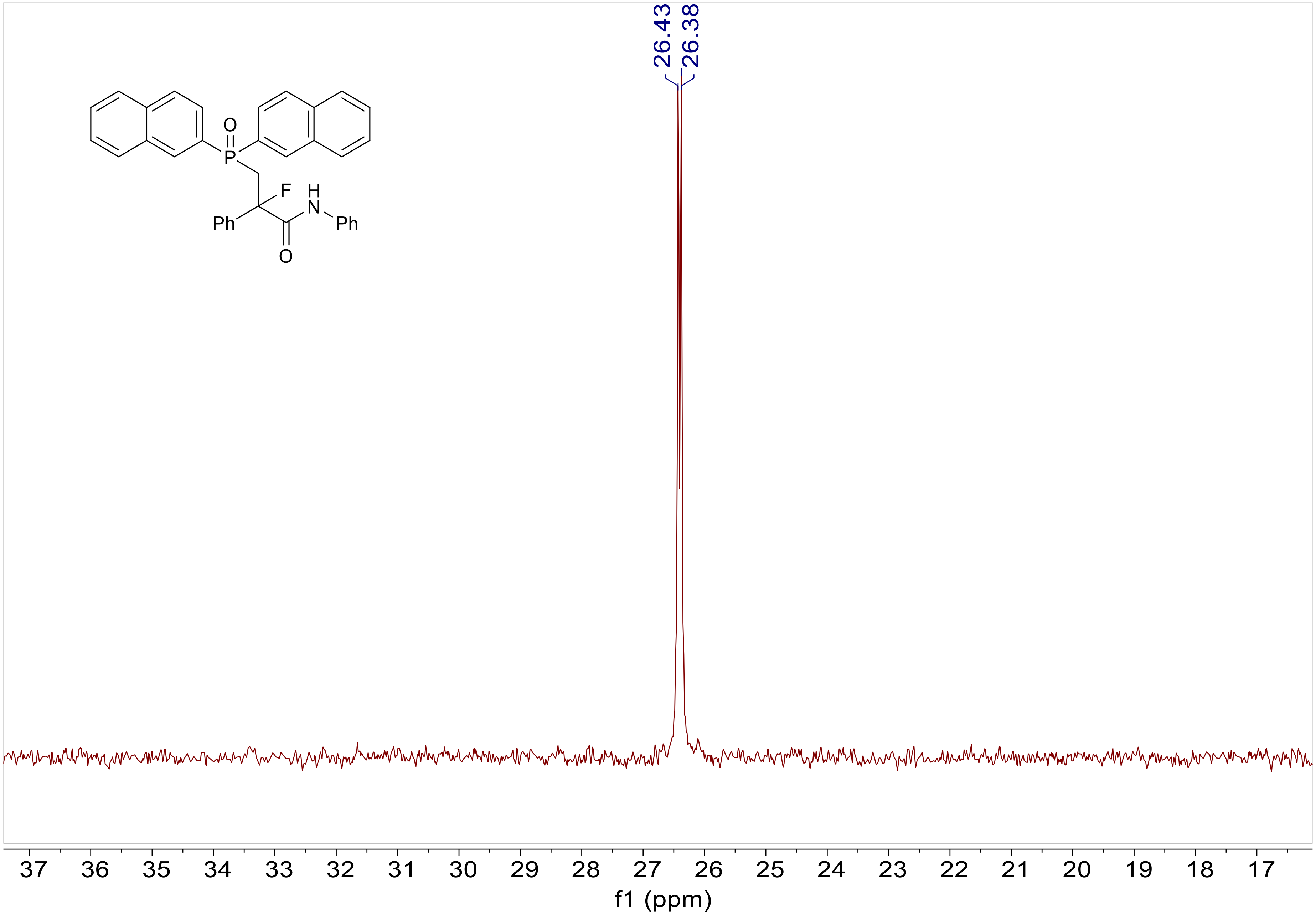


Figure S34. ³¹P NMR spectrum of **3f** (162 MHz, $CDCl_3$)

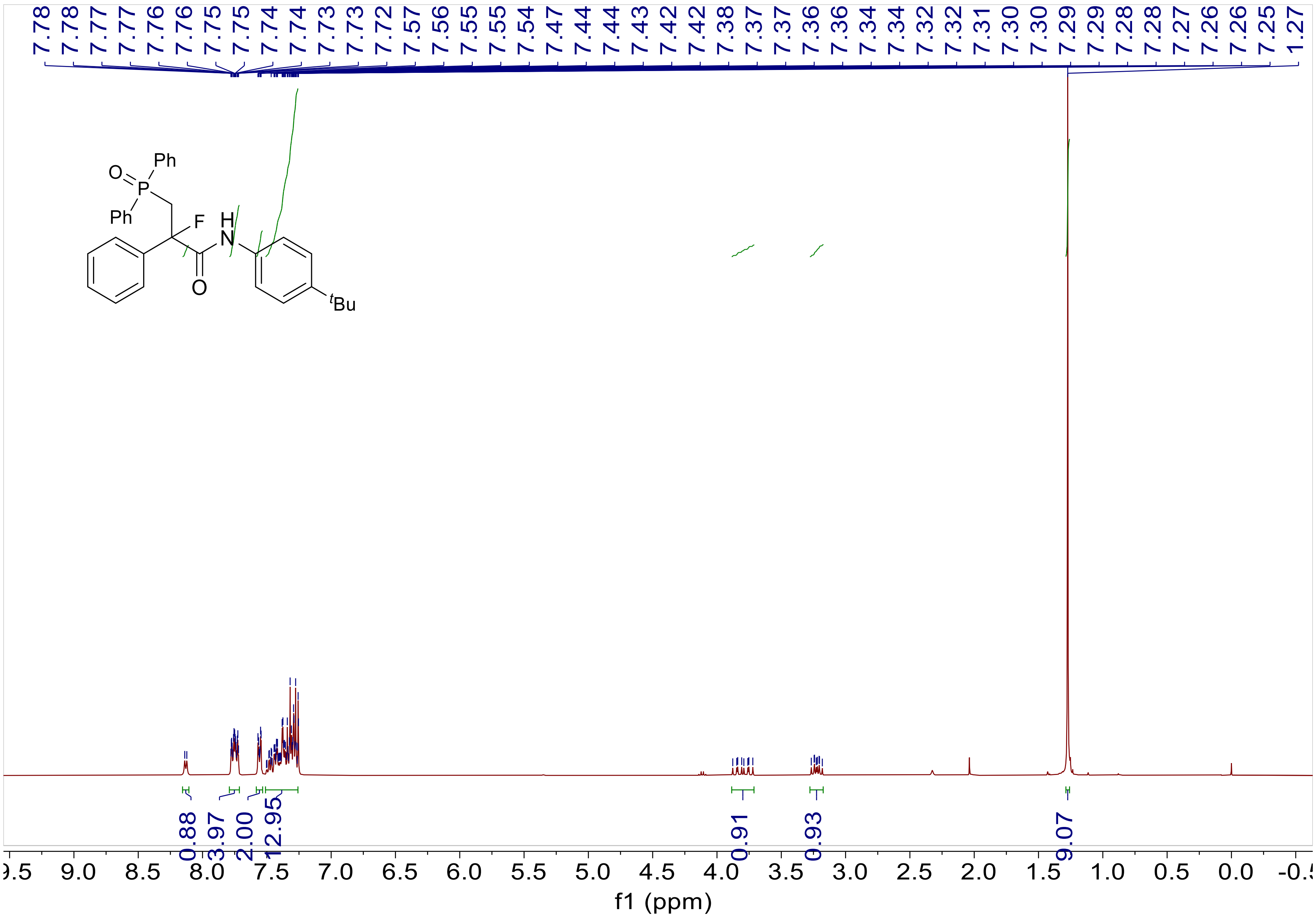


Figure S35. ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)

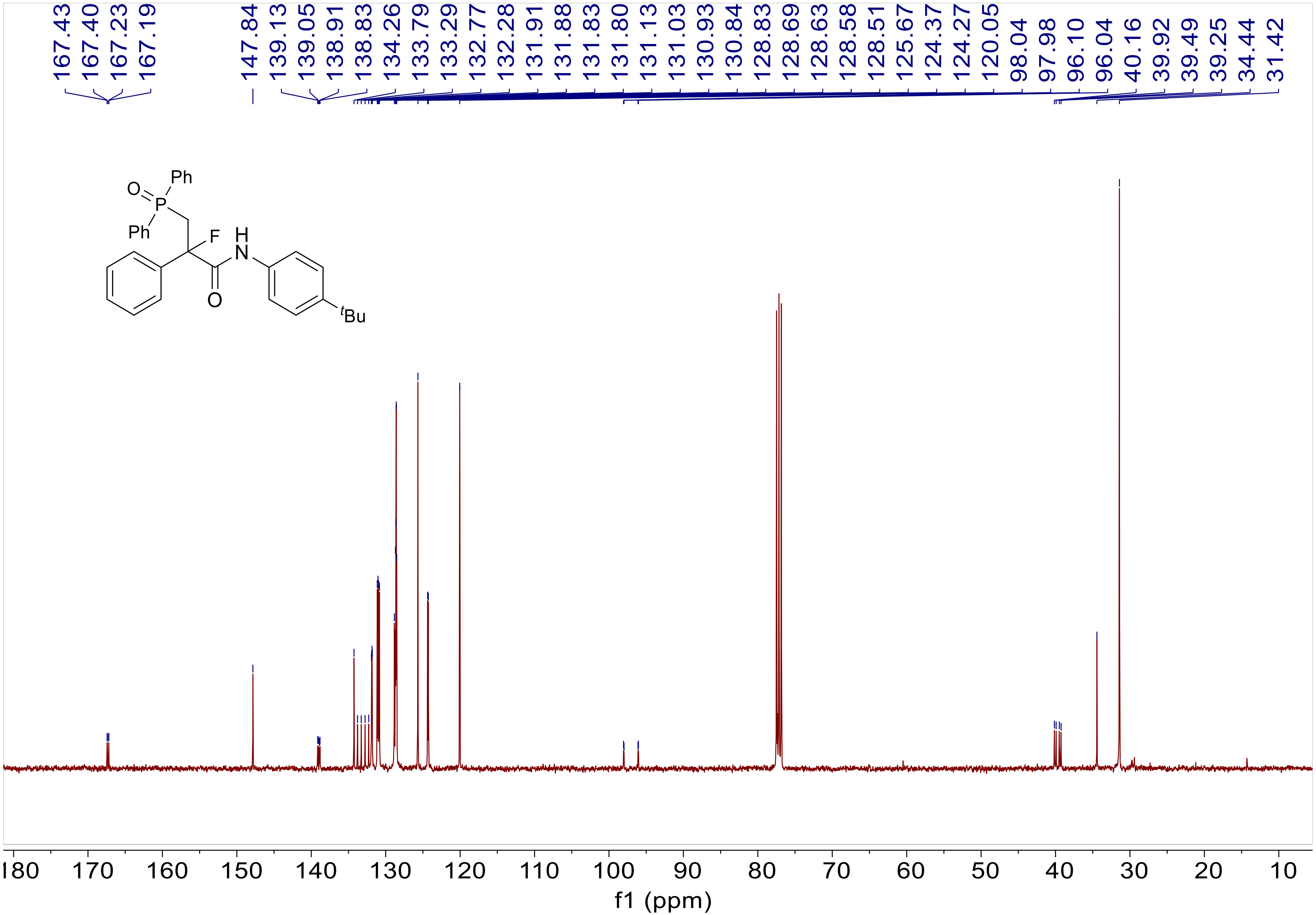


Figure S36. ^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$)

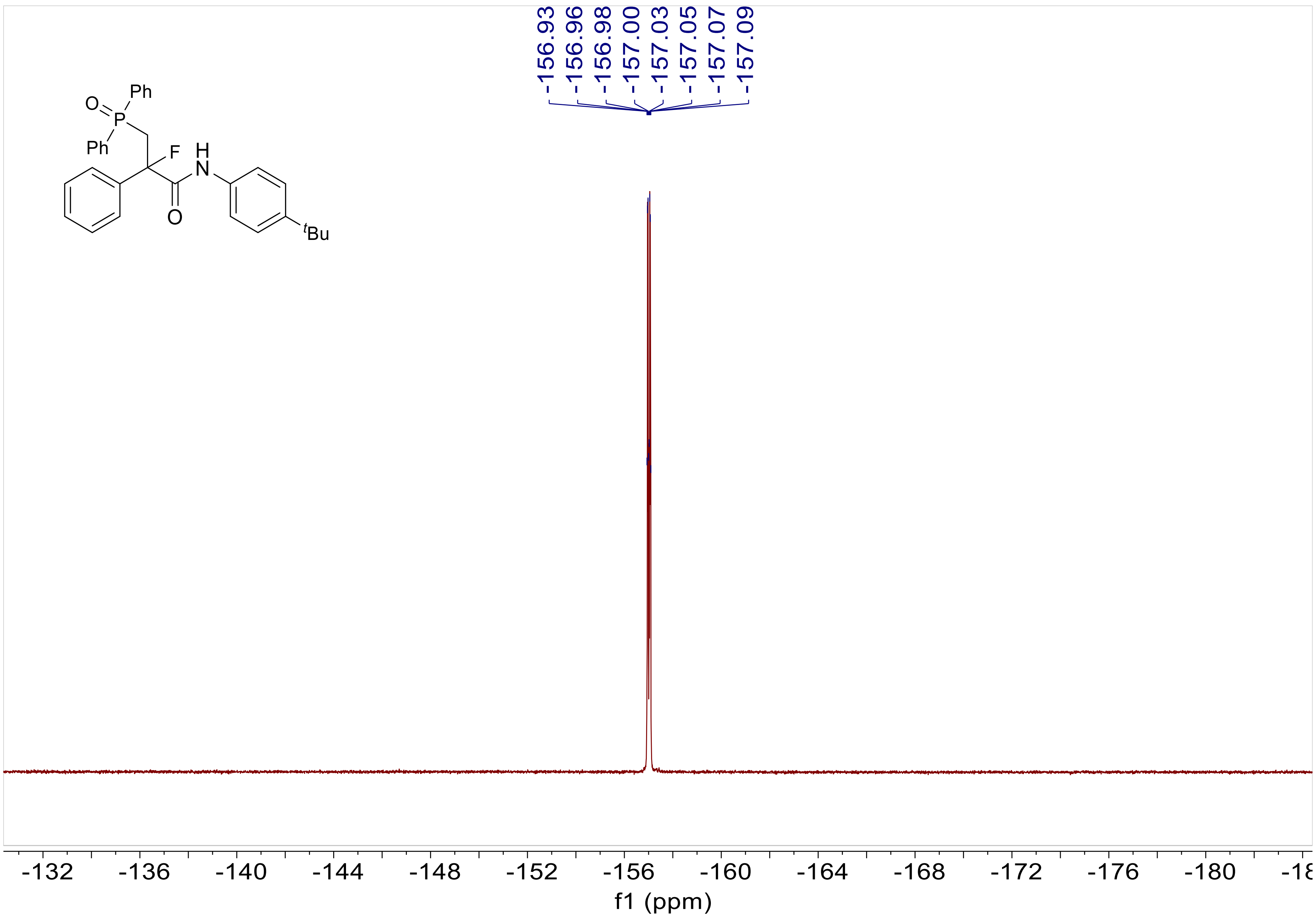


Figure S37. ^{19}F NMR spectrum of **3g** (376 MHz, $CDCl_3$)

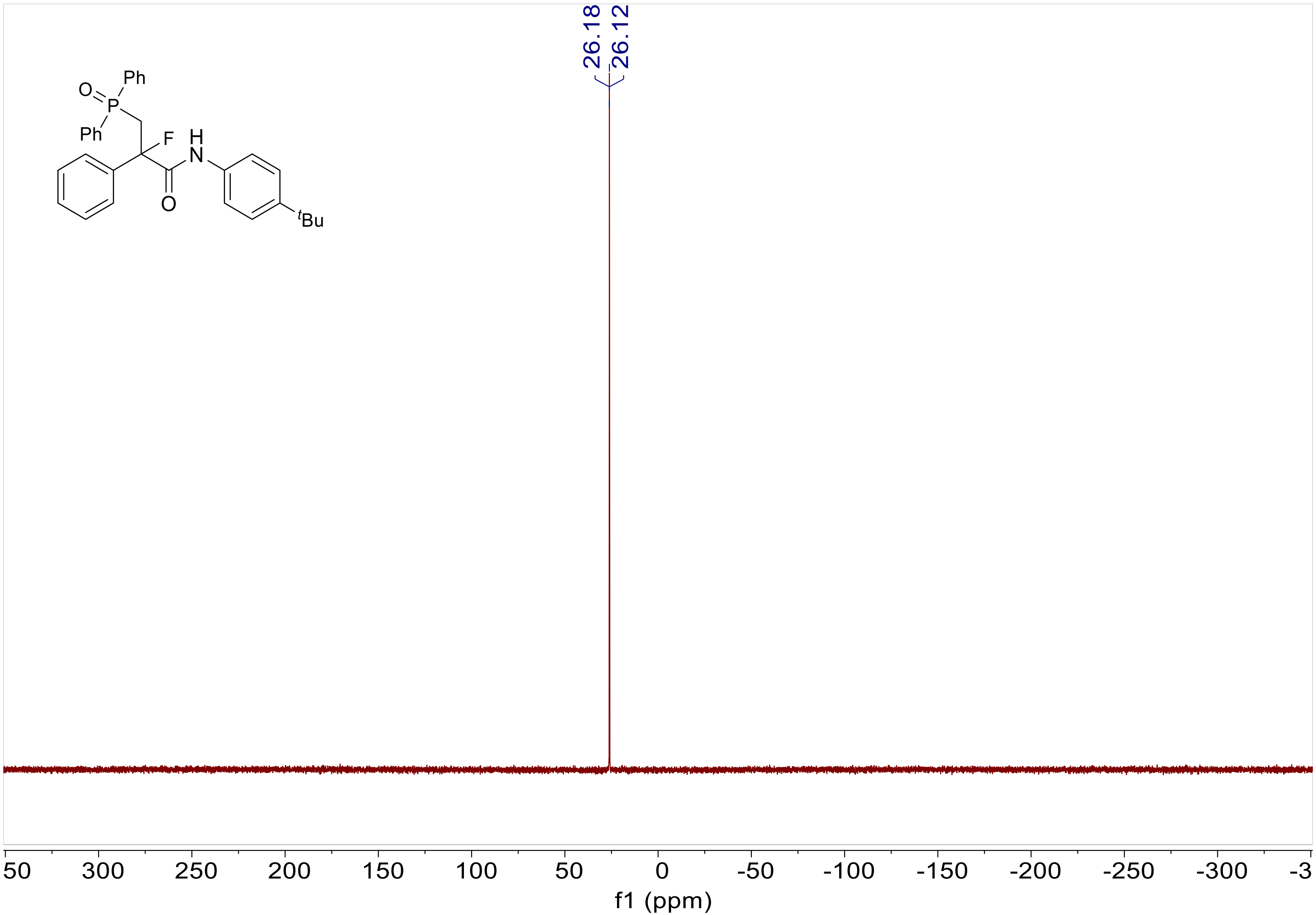


Figure S38. ^{31}P NMR spectrum of **3g** (162 MHz, $CDCl_3$)

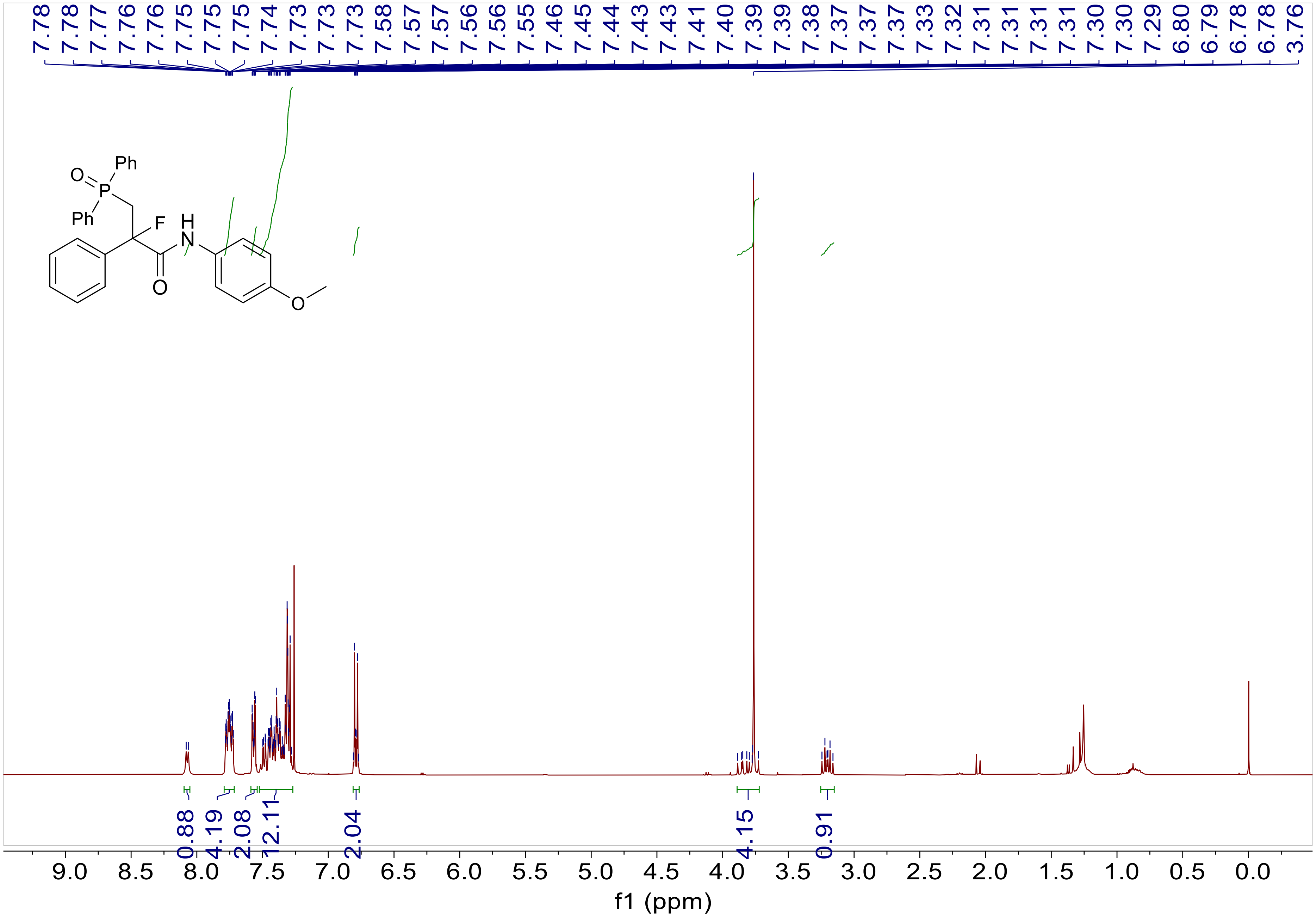


Figure S39. ^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)

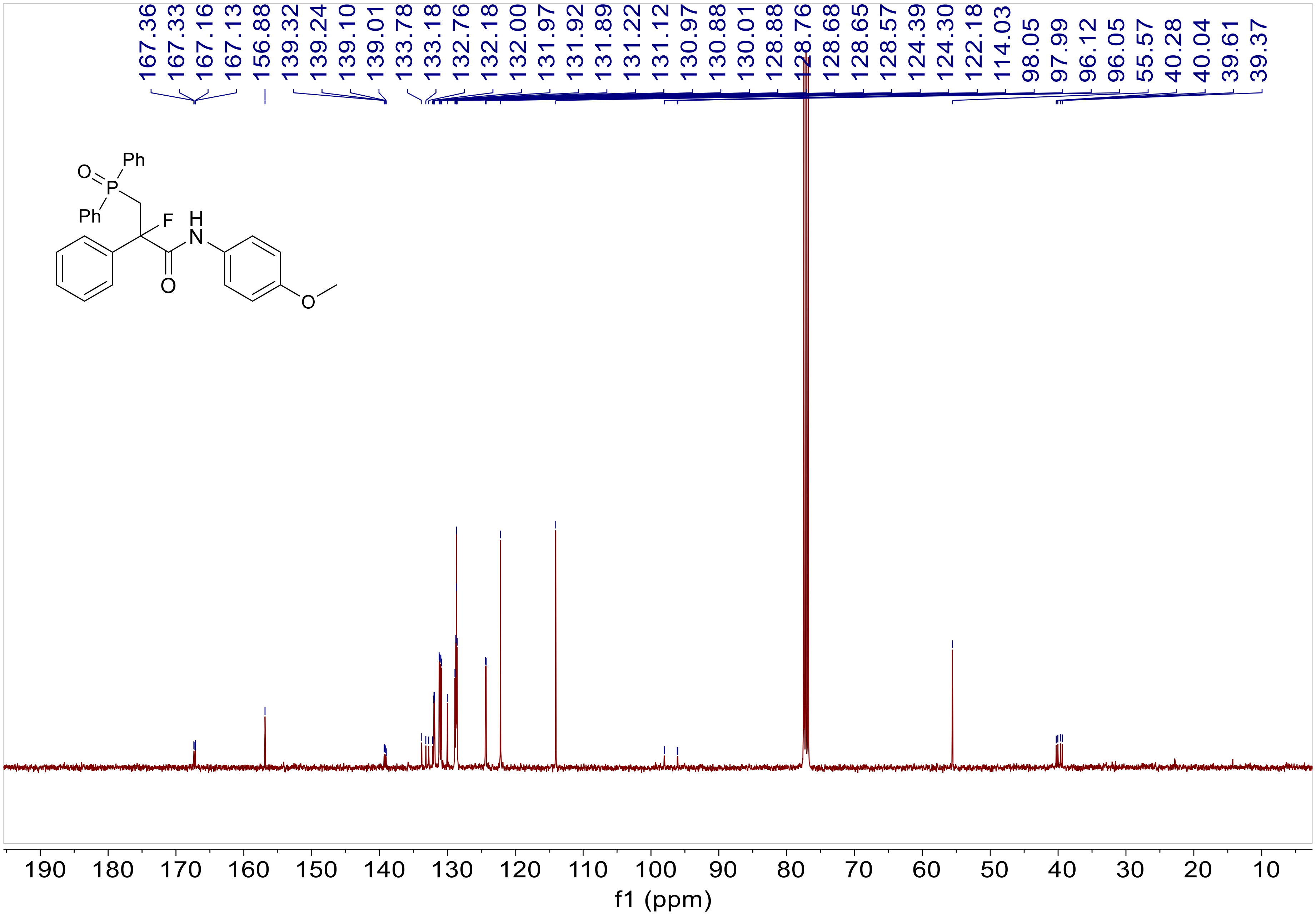


Figure S40. ${}^{13}C$ NMR spectrum of **3h** (101 MHz, $CDCl_3$)

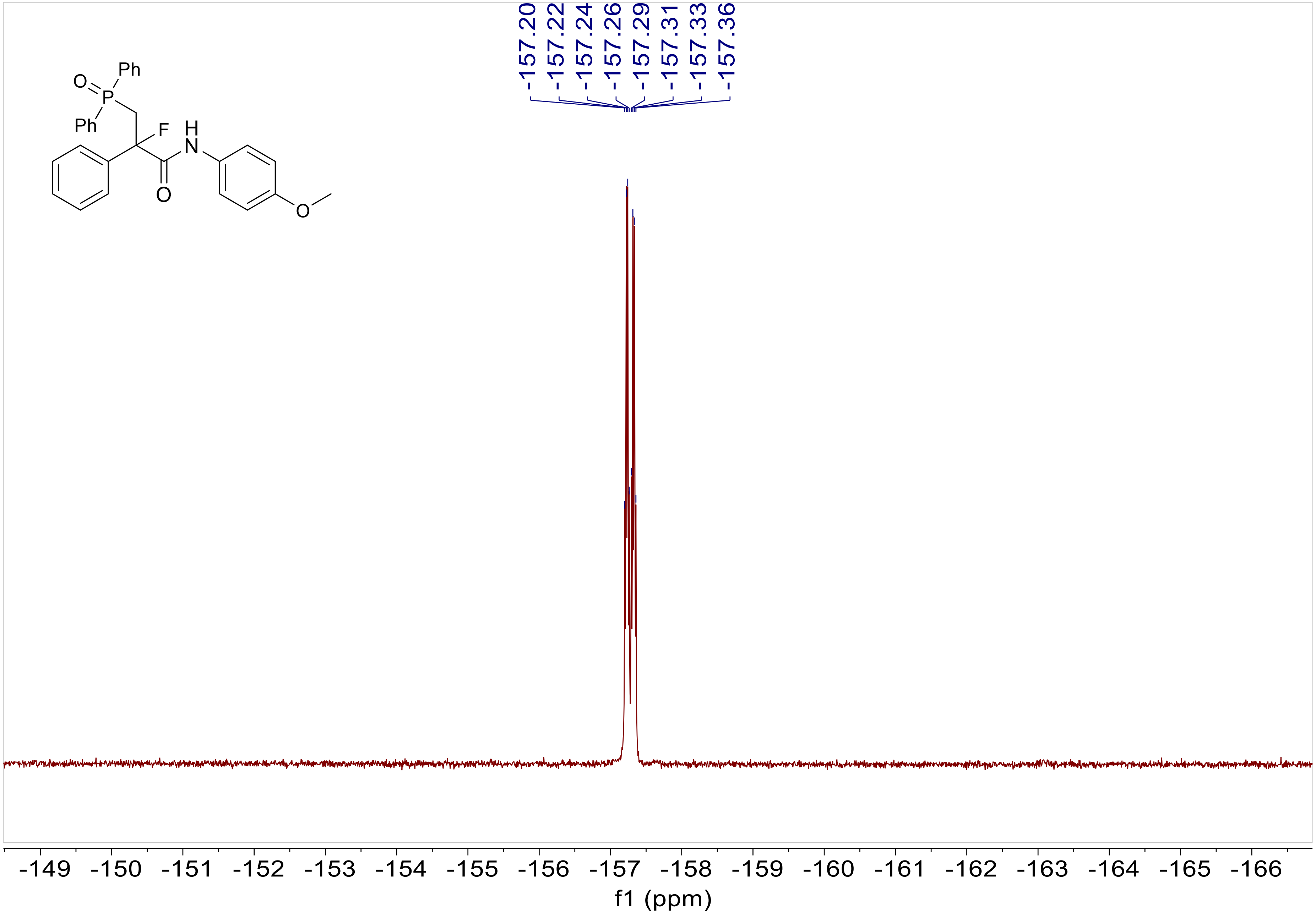


Figure S41. [19]F NMR spectrum of **3h** (376 MHz, $CDCl_3$)

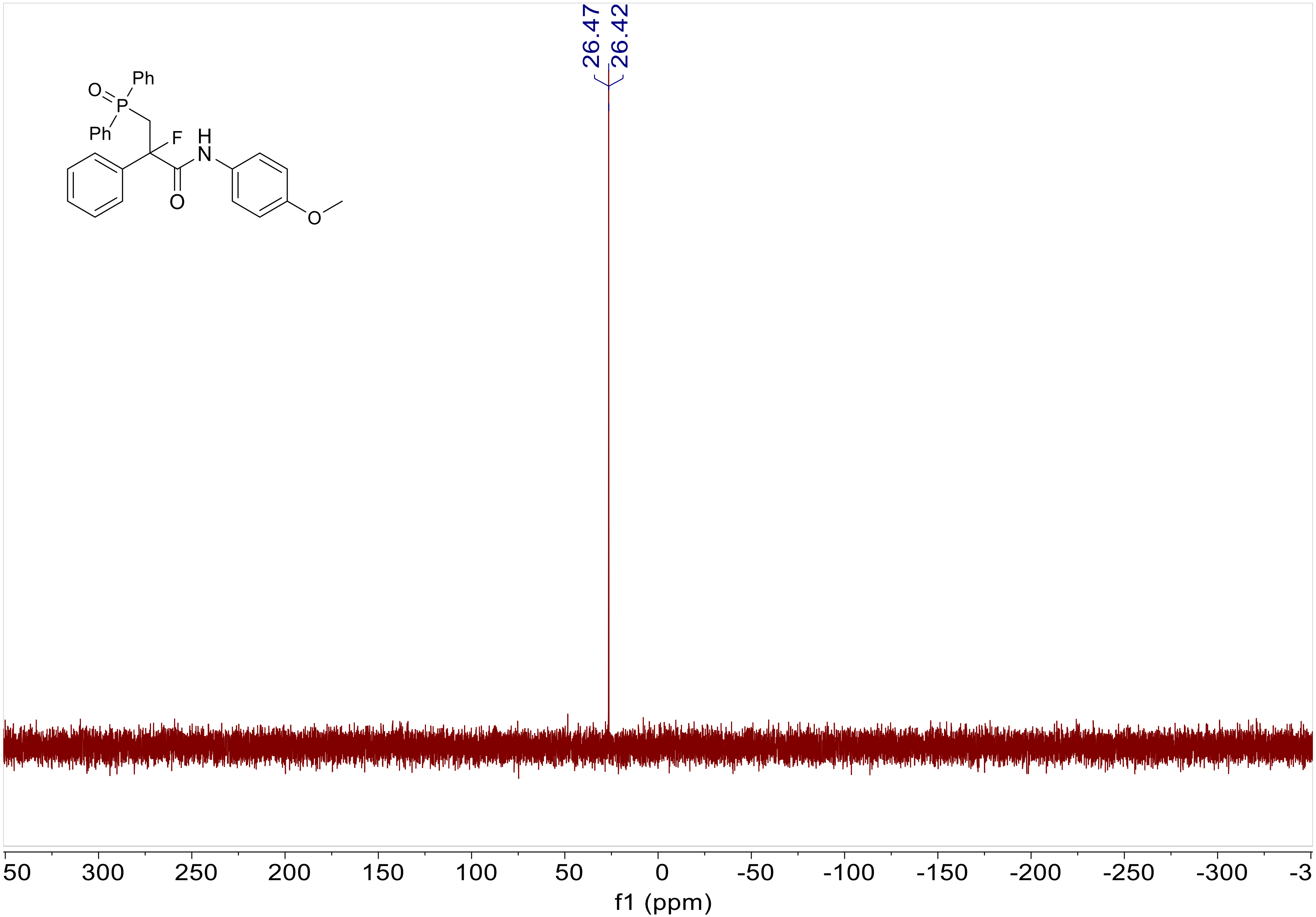


Figure S42. ^{31}P NMR spectrum of **3h** (162 MHz, $CDCl_3$)

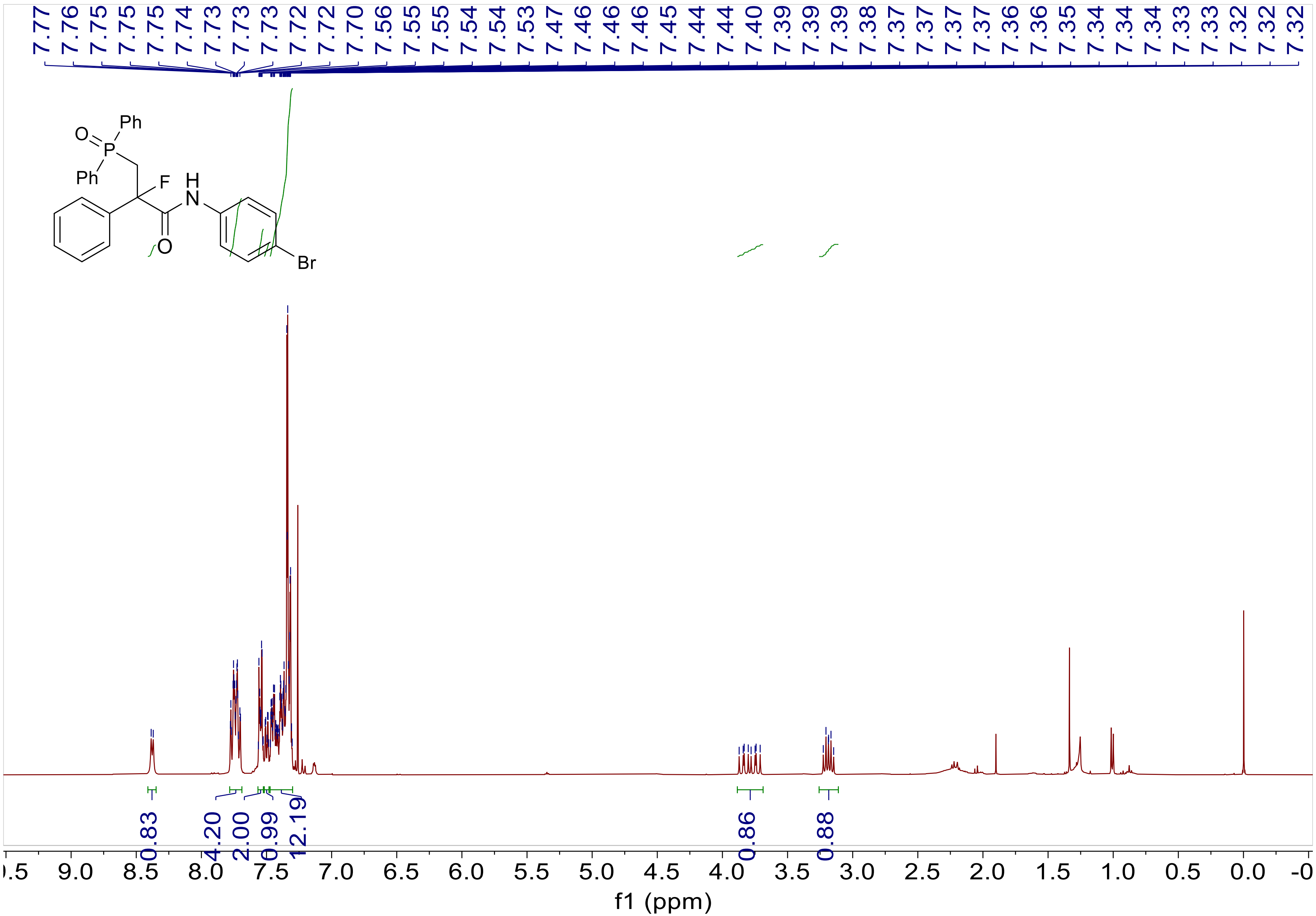


Figure S43. ^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)

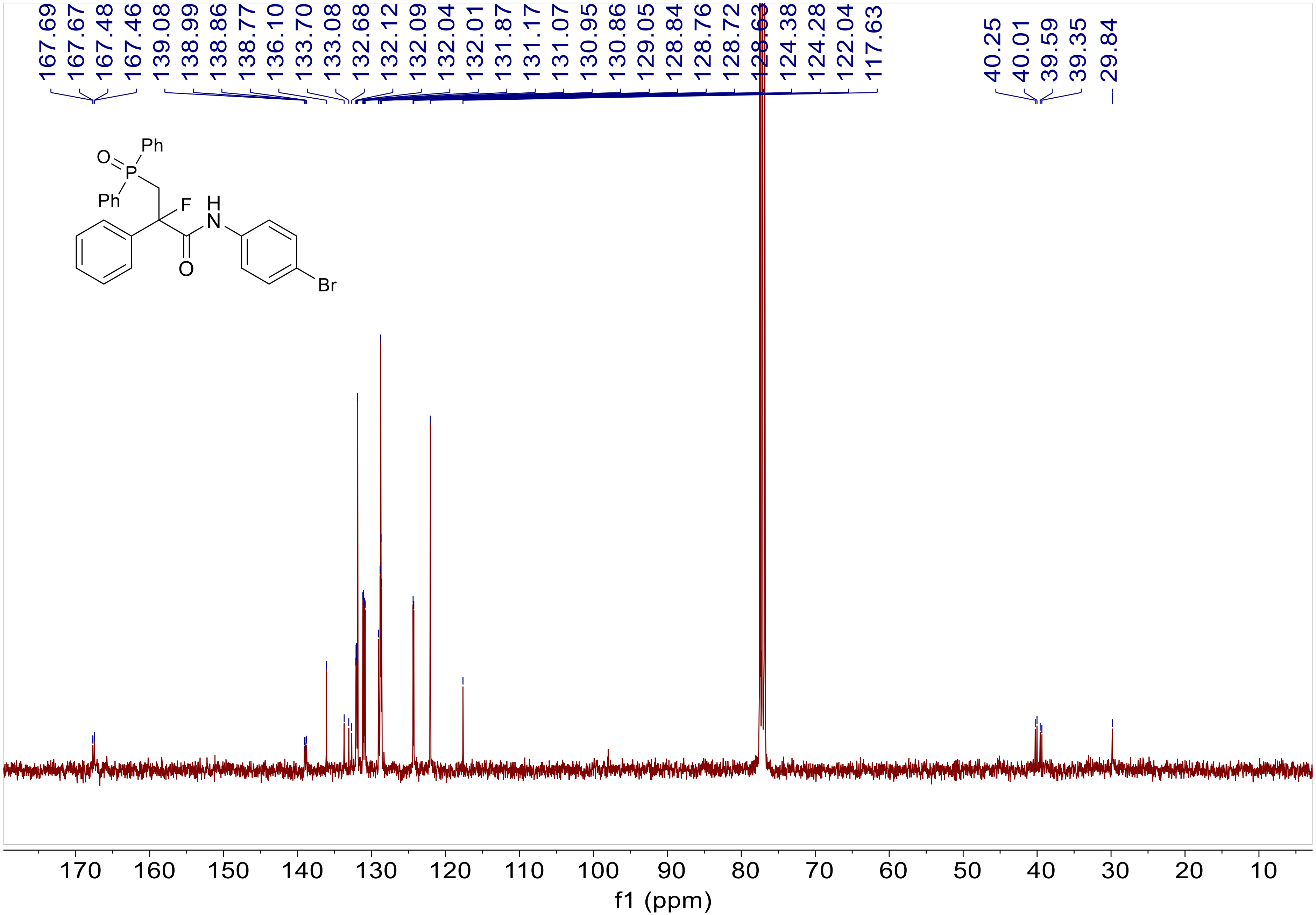


Figure S44. ^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$)

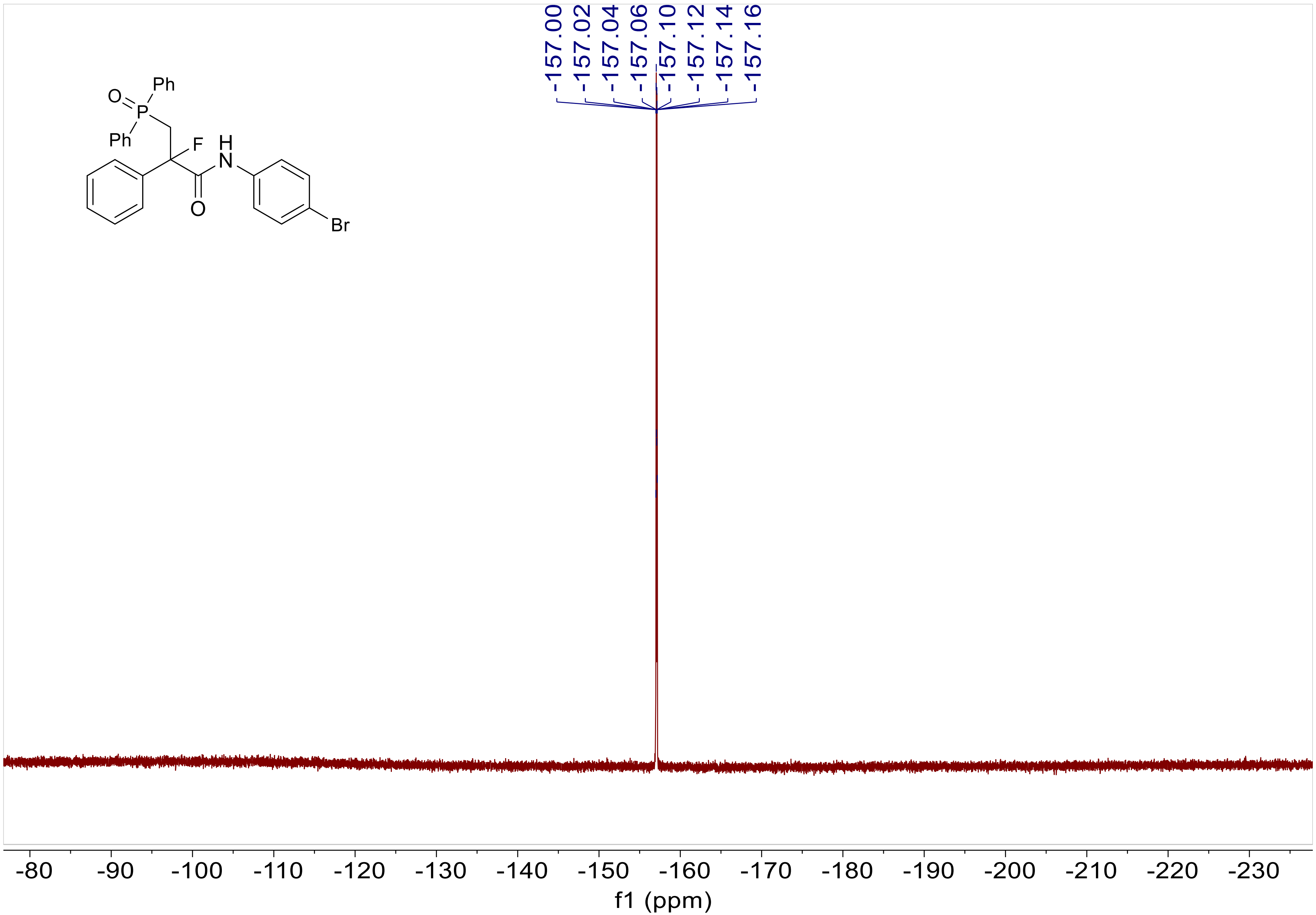


Figure S45. ^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$)

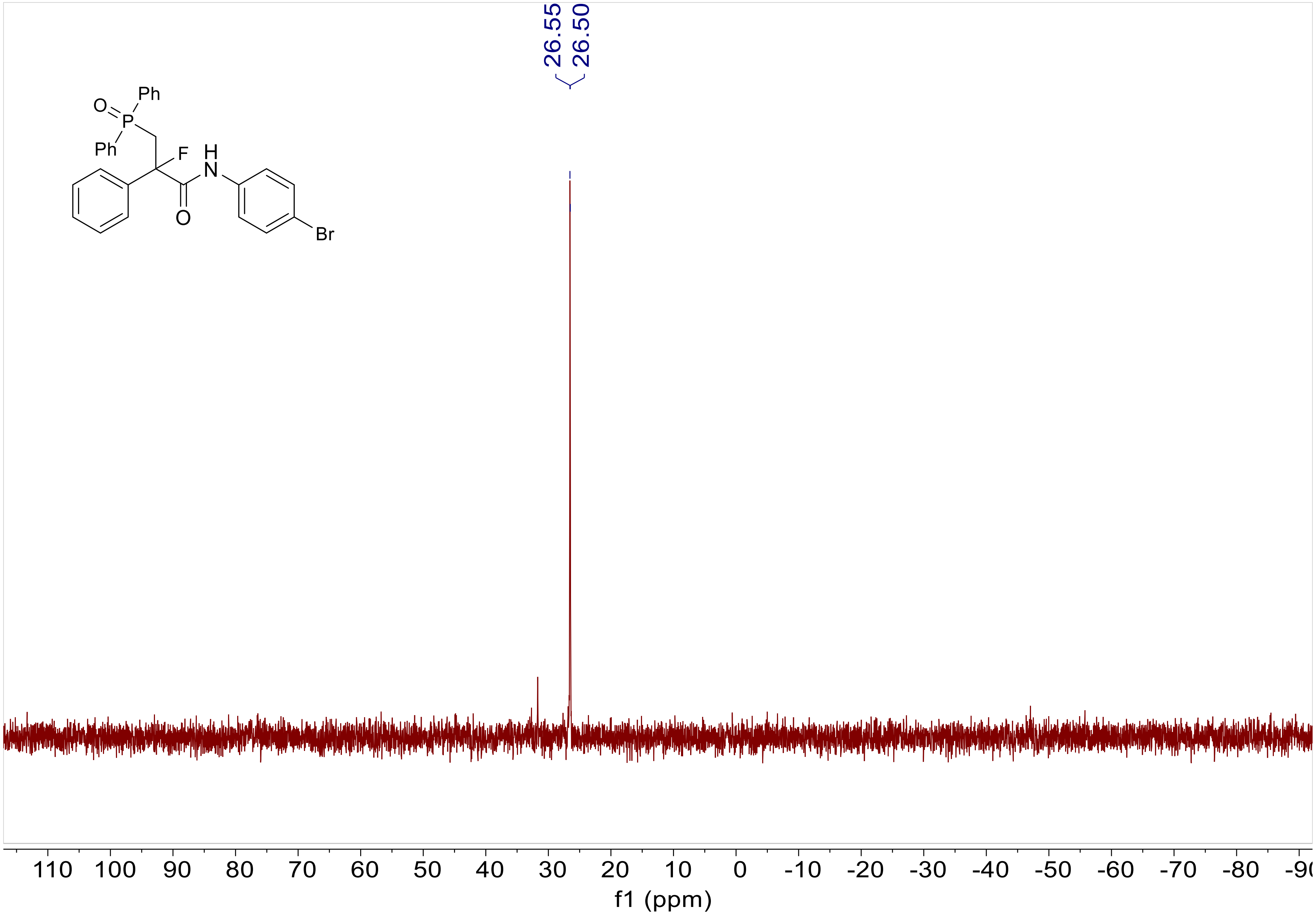


Figure S46. ^{31}P NMR spectrum of **3i** (162 MHz, $CDCl_3$)

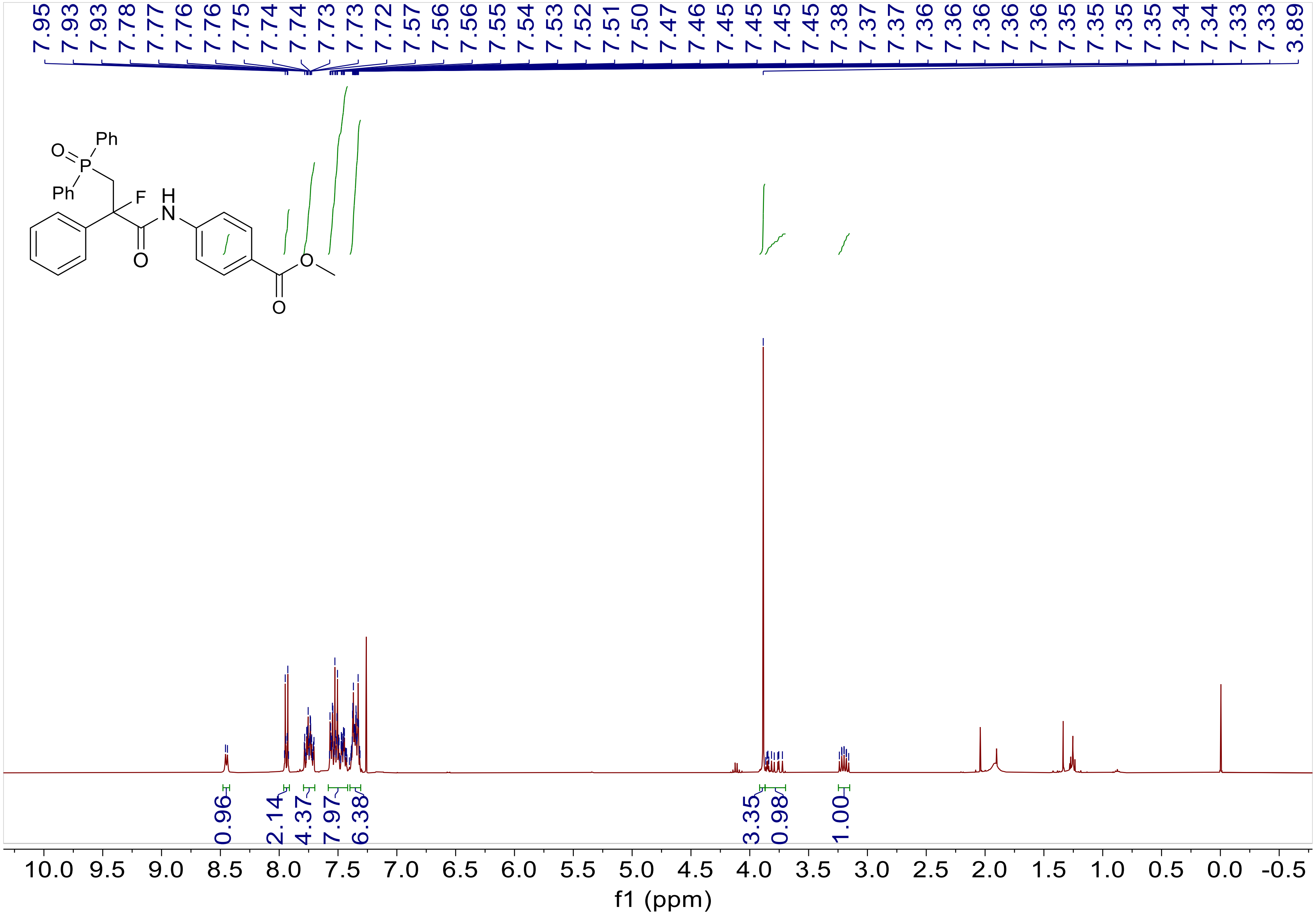


Figure S47. [1]H NMR spectrum of **3j** (400 MHz, $CDCl_3$)

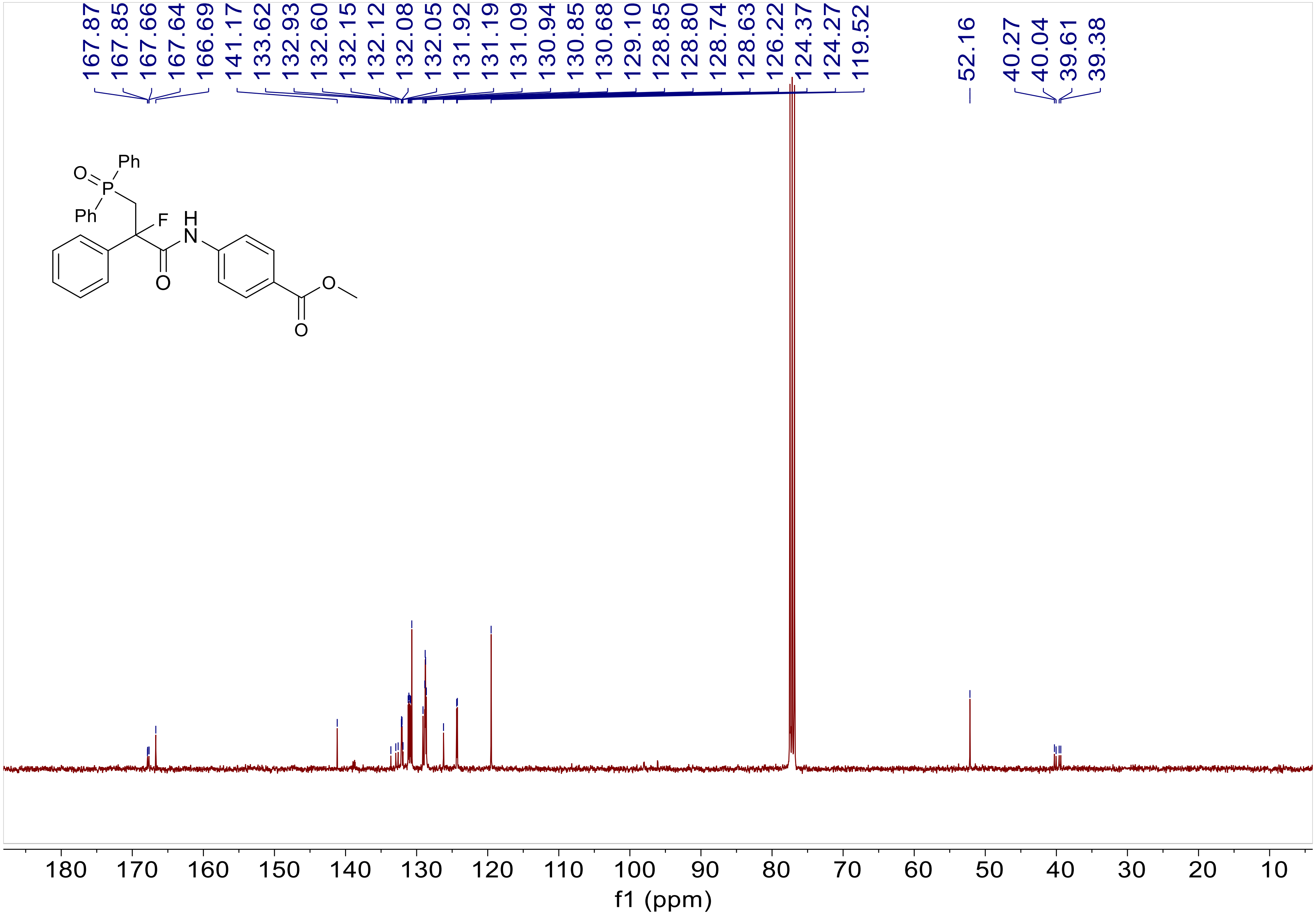


Figure S48. ^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$)

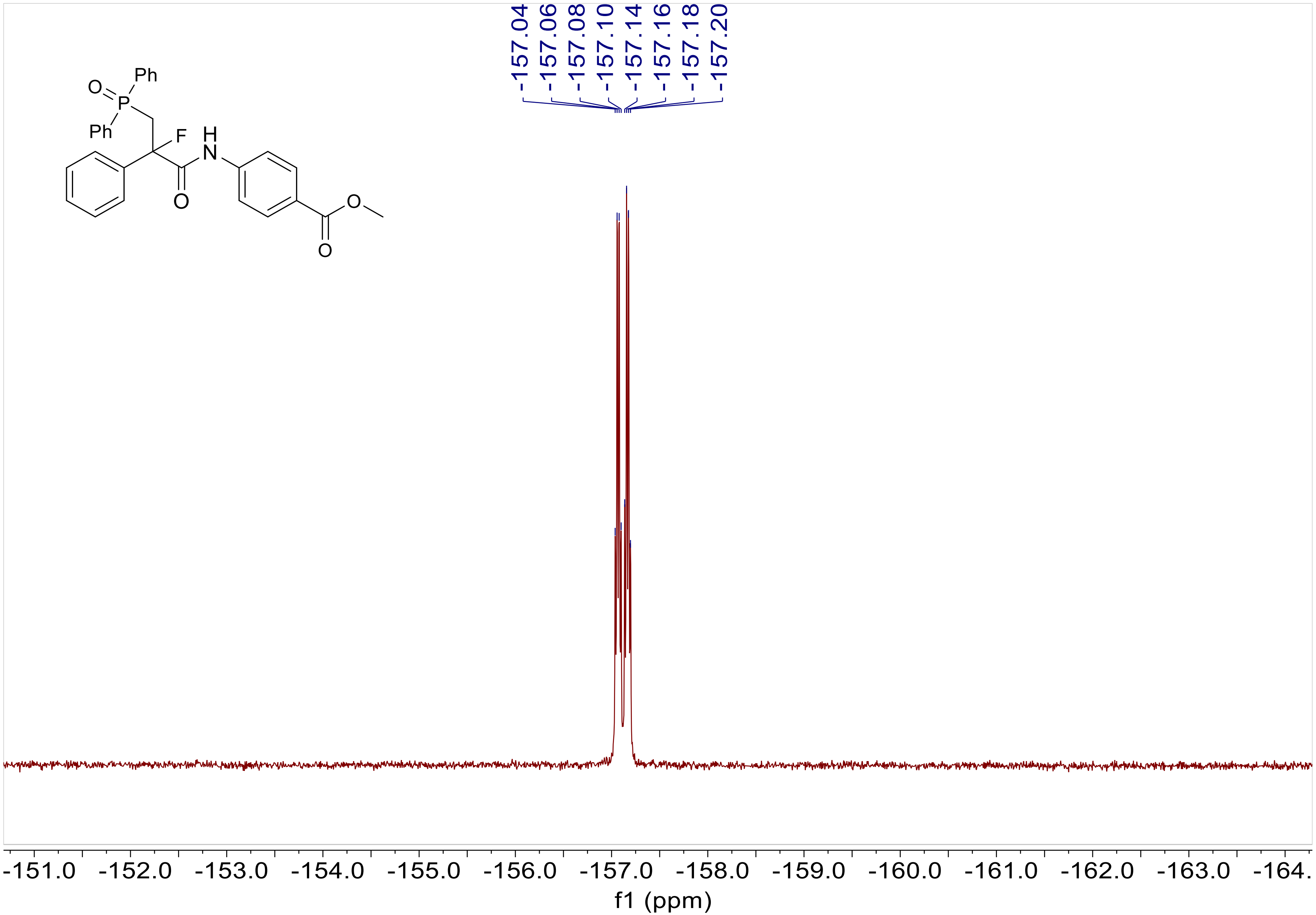


Figure S49. ^{19}F NMR spectrum of **3j** (376 MHz, $CDCl_3$)

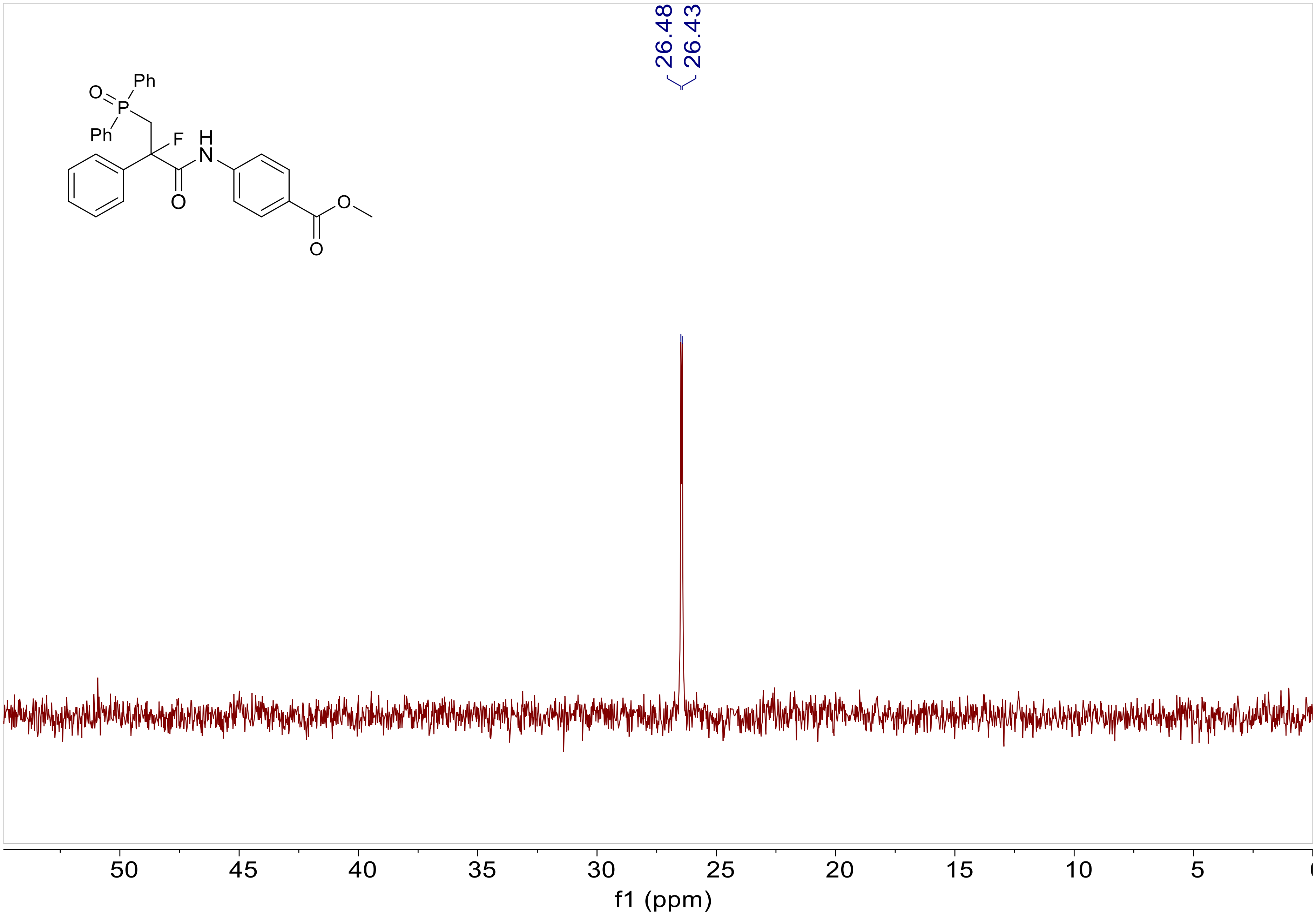


Figure S50. ^{31}P NMR spectrum of **3j** (162 MHz, $CDCl_3$)

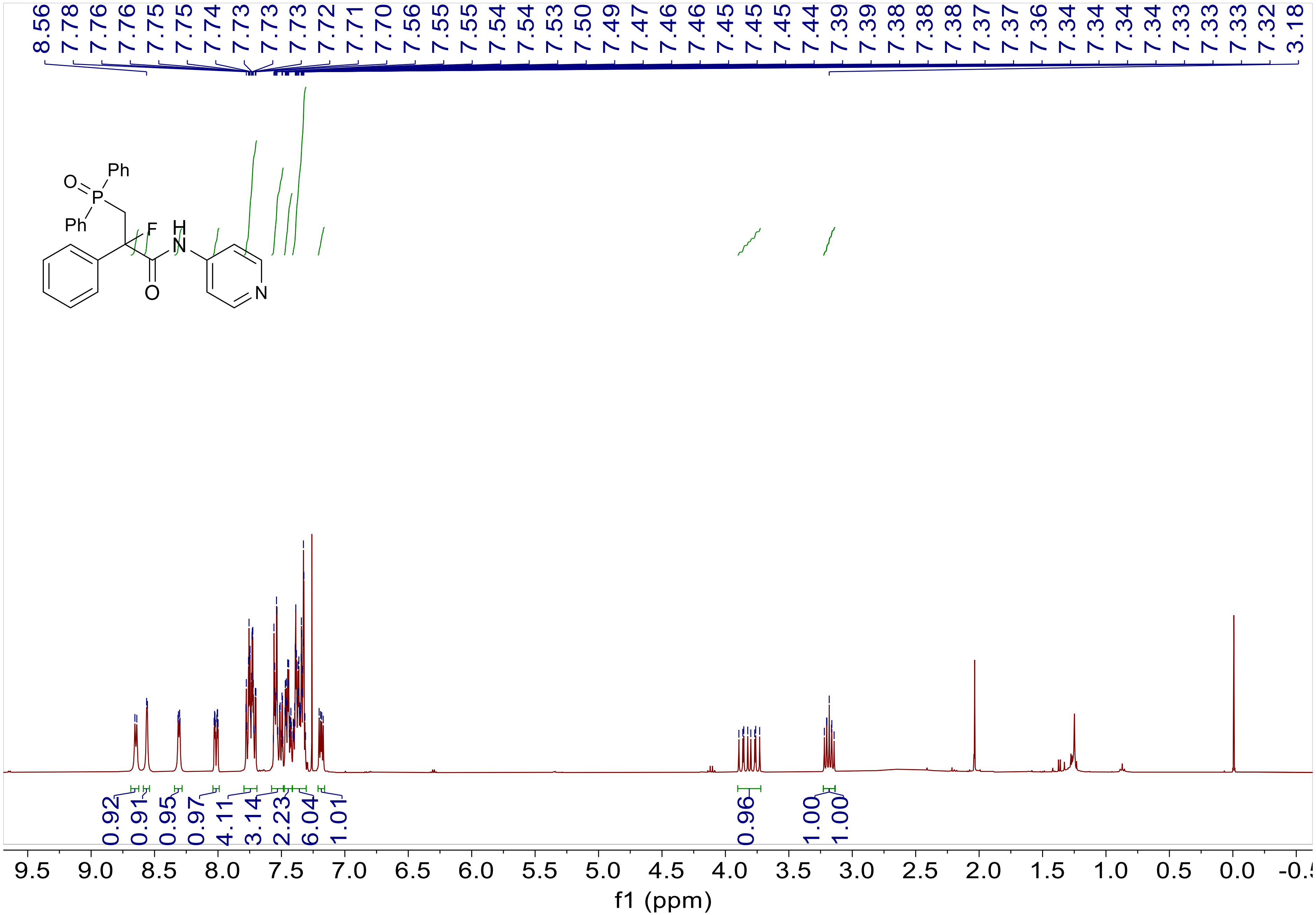


Figure S51. ^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)

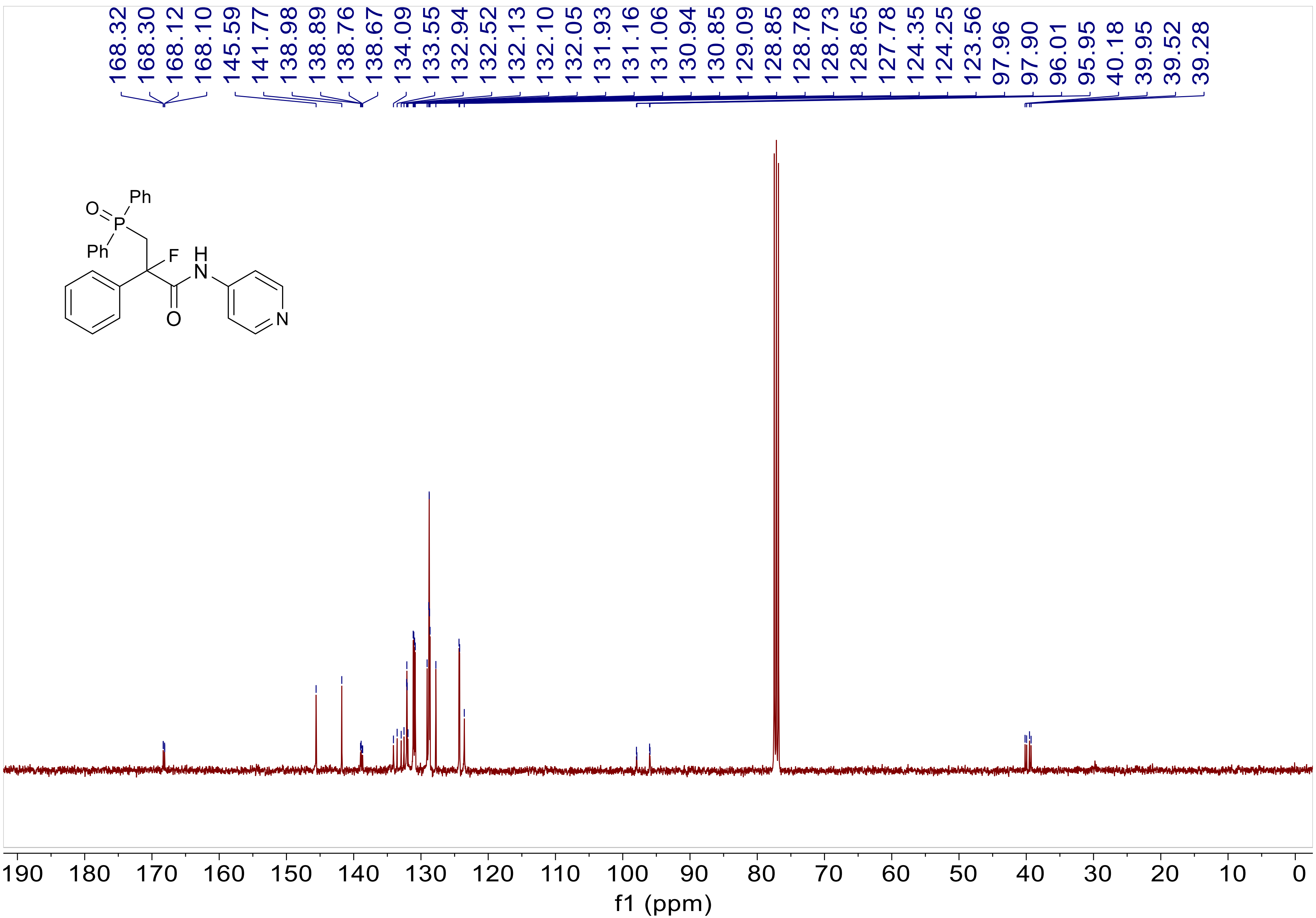


Figure S52. ^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$)

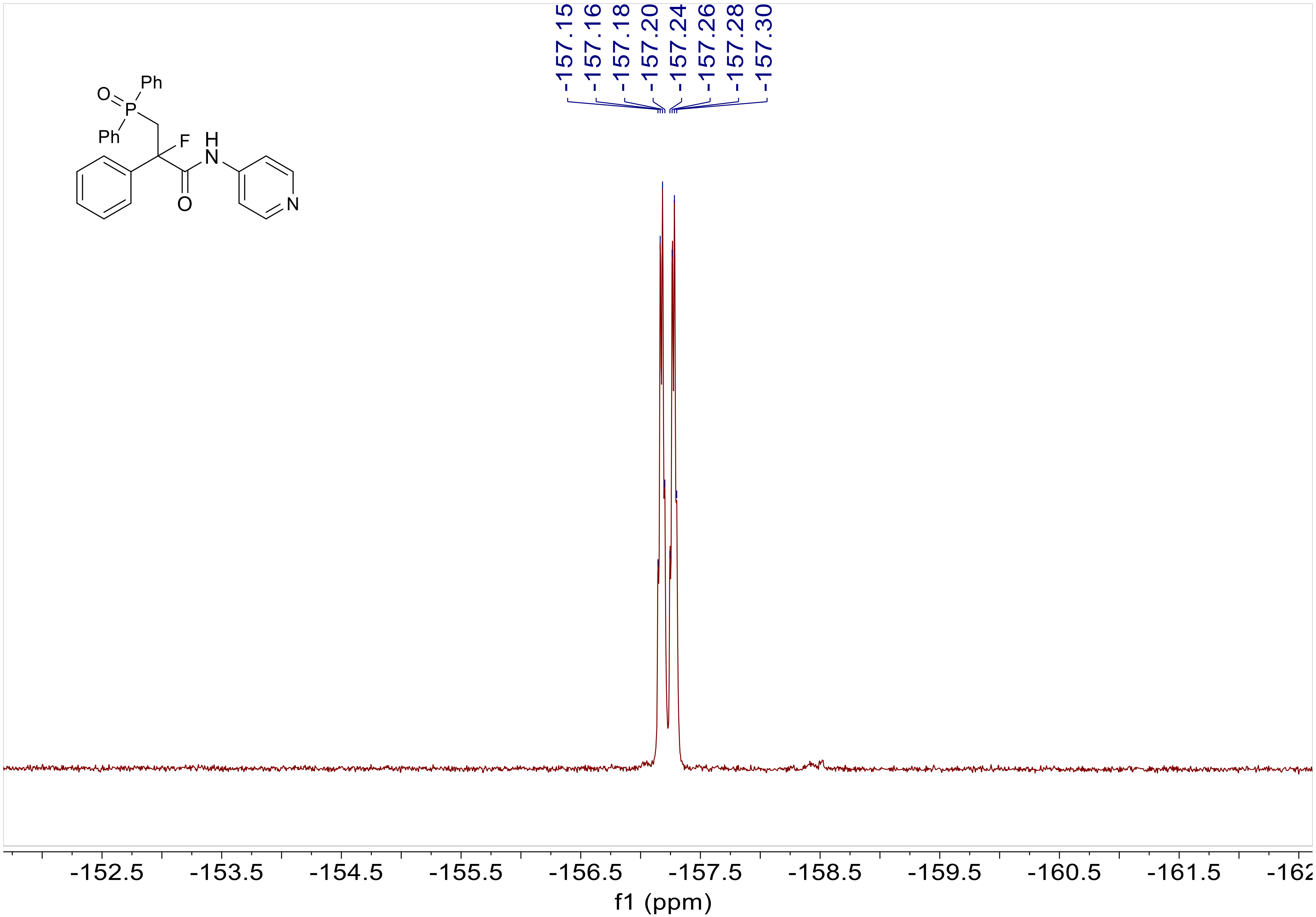


Figure S53. [19]F NMR spectrum of **3k** (376 MHz, $CDCl_3$)

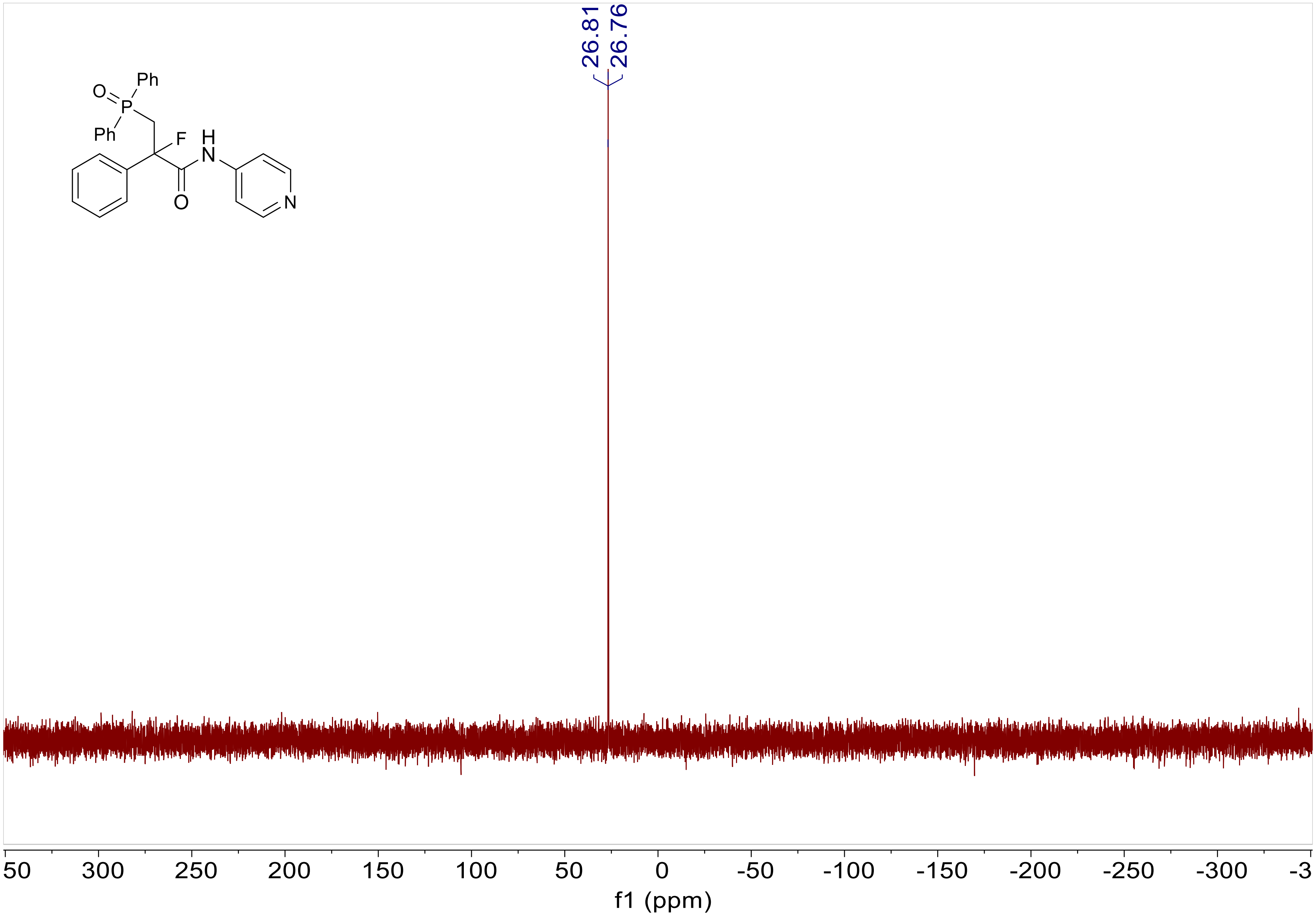


Figure S54. ^{31}P NMR spectrum of **3k** (162 MHz, $CDCl_3$)

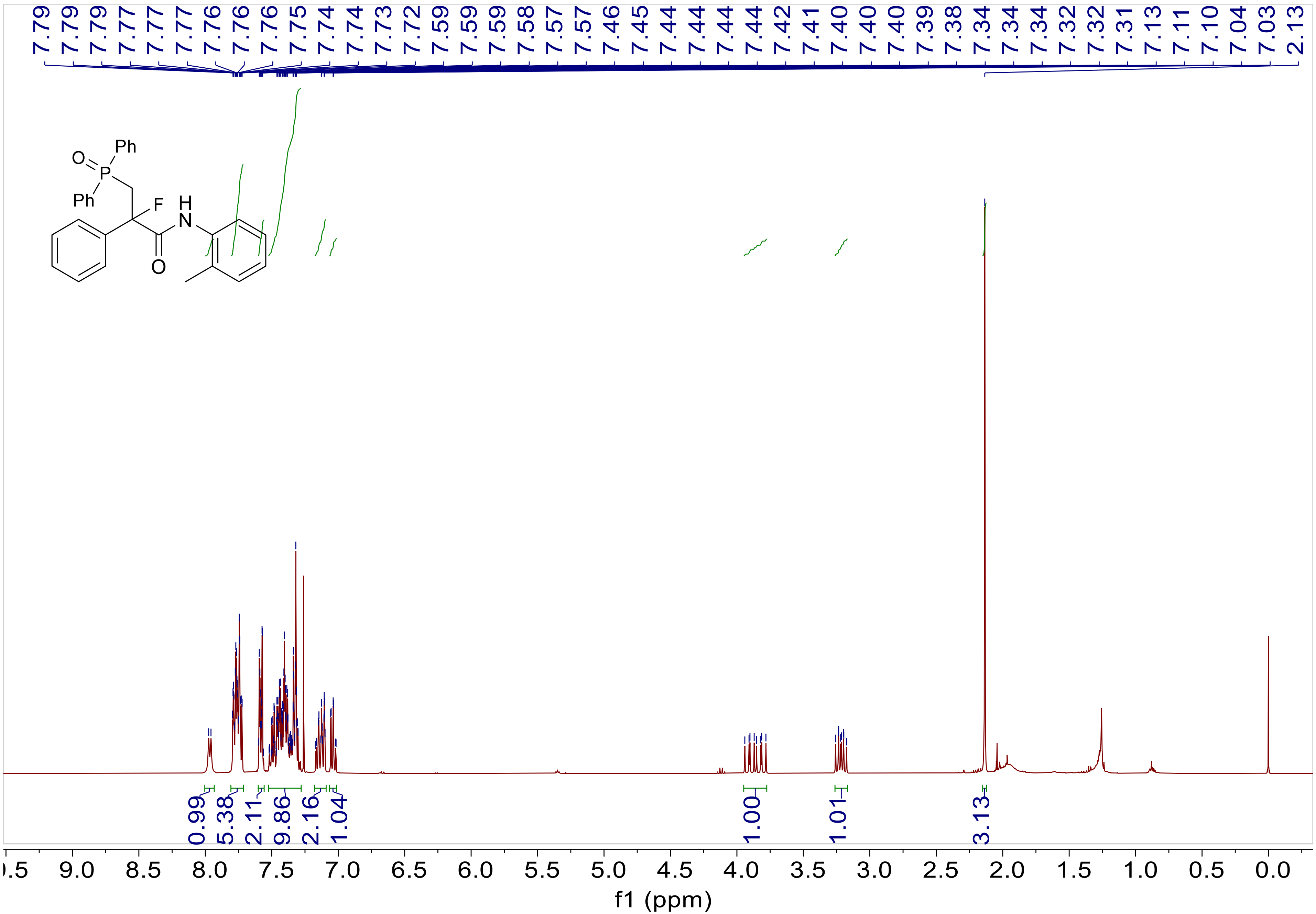


Figure S55. ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)

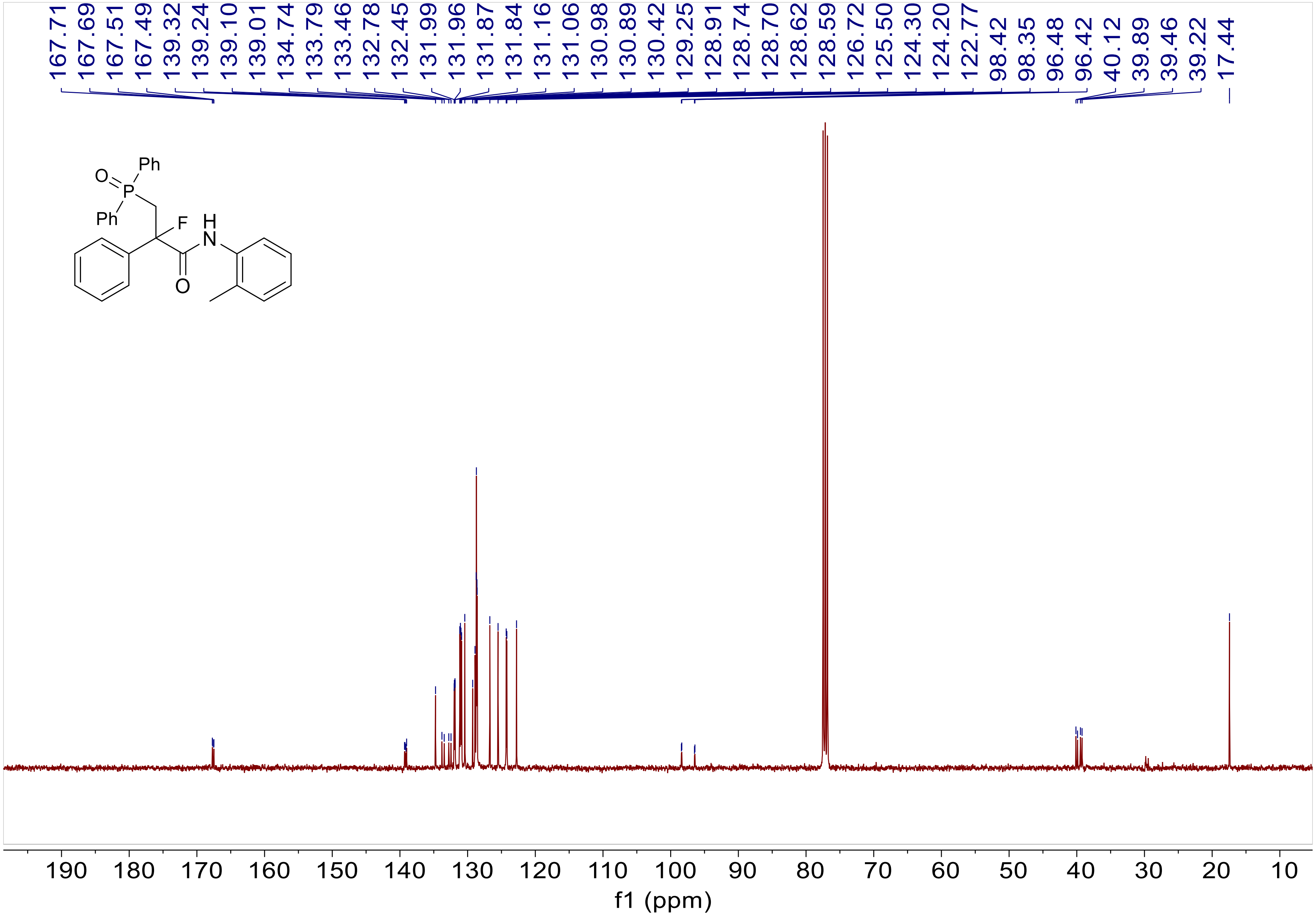


Figure S56. ^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$)

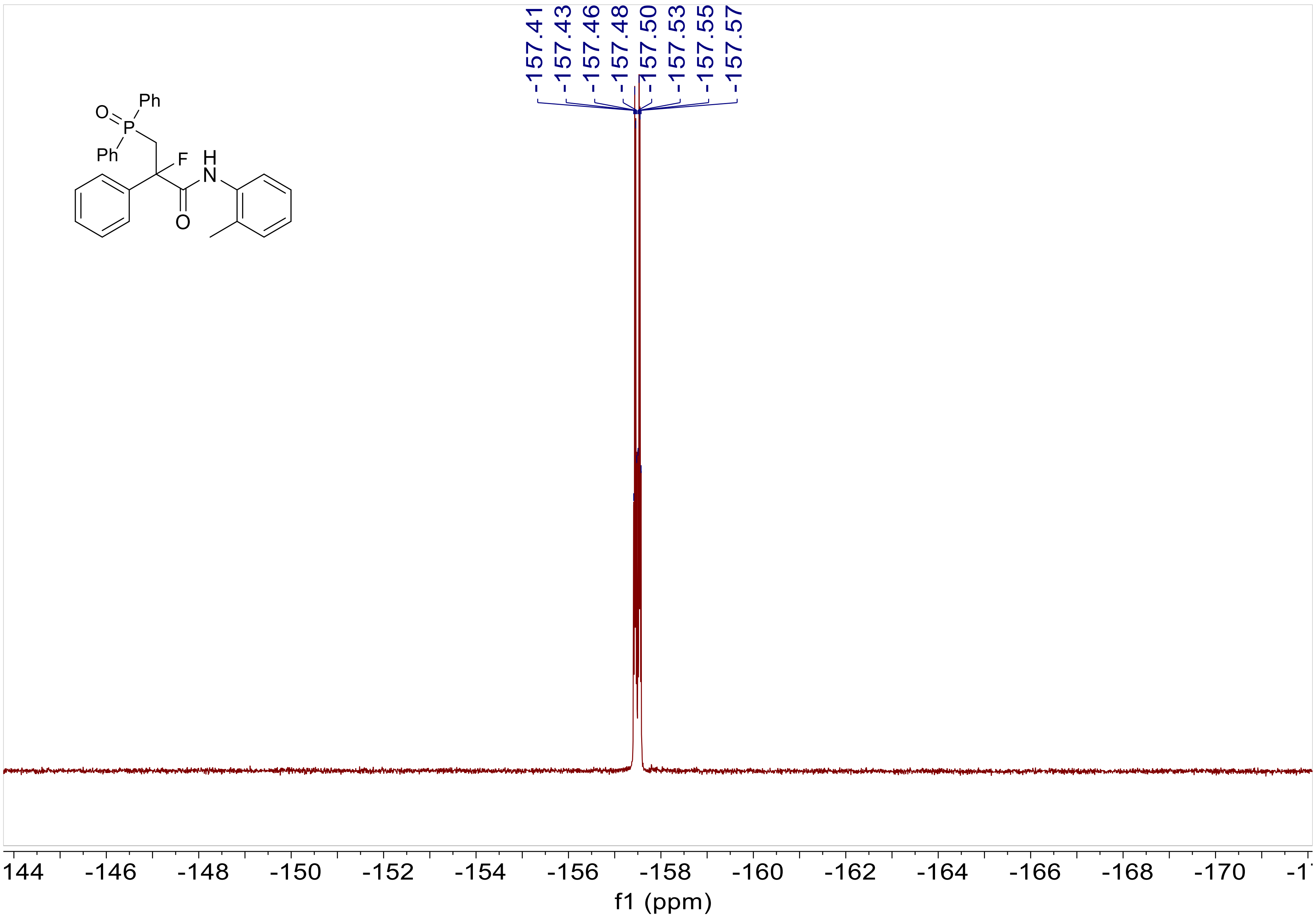


Figure S57. ^{19}F NMR spectrum of **3l** (376 MHz, $CDCl_3$)

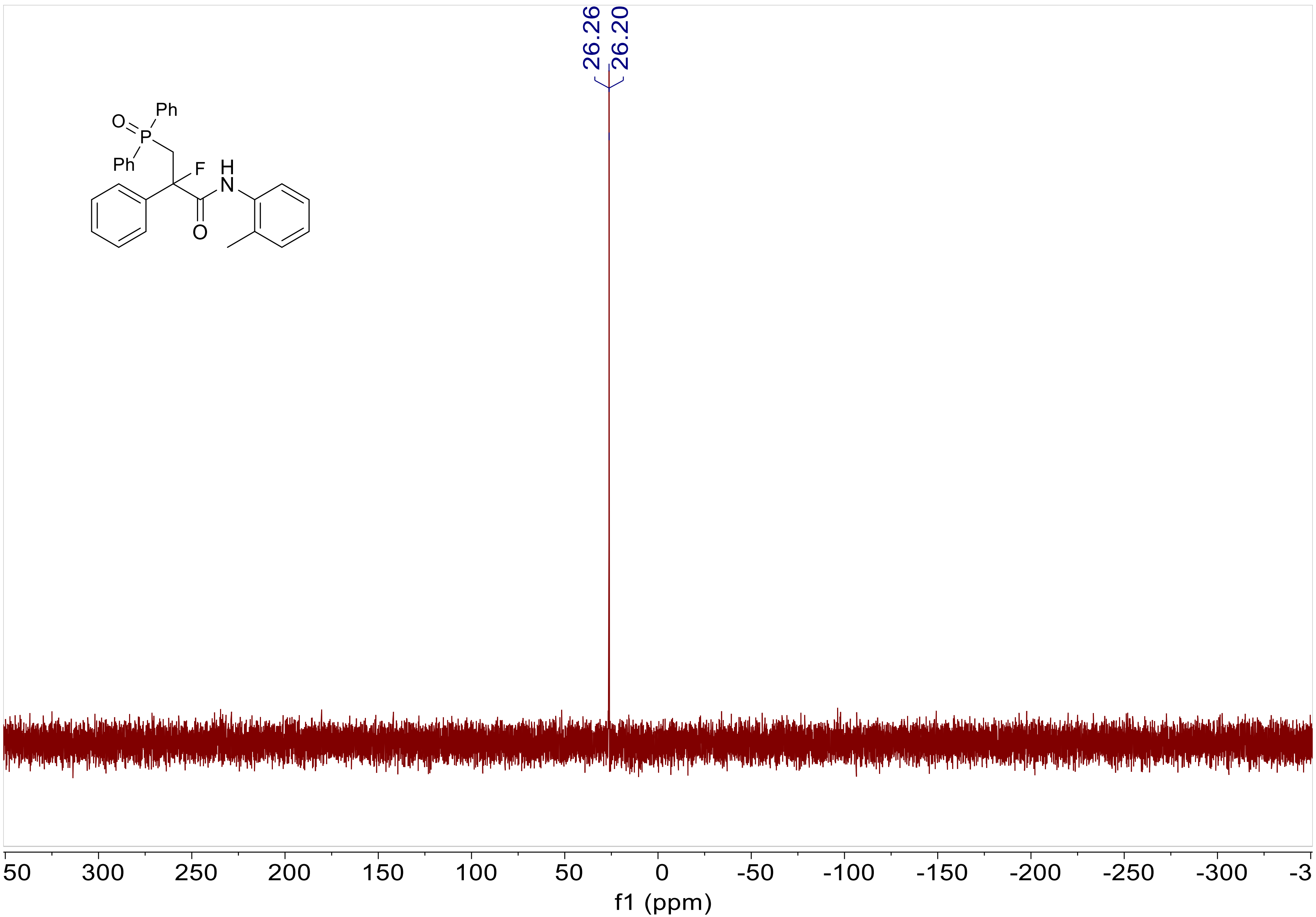


Figure S58. ^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$)

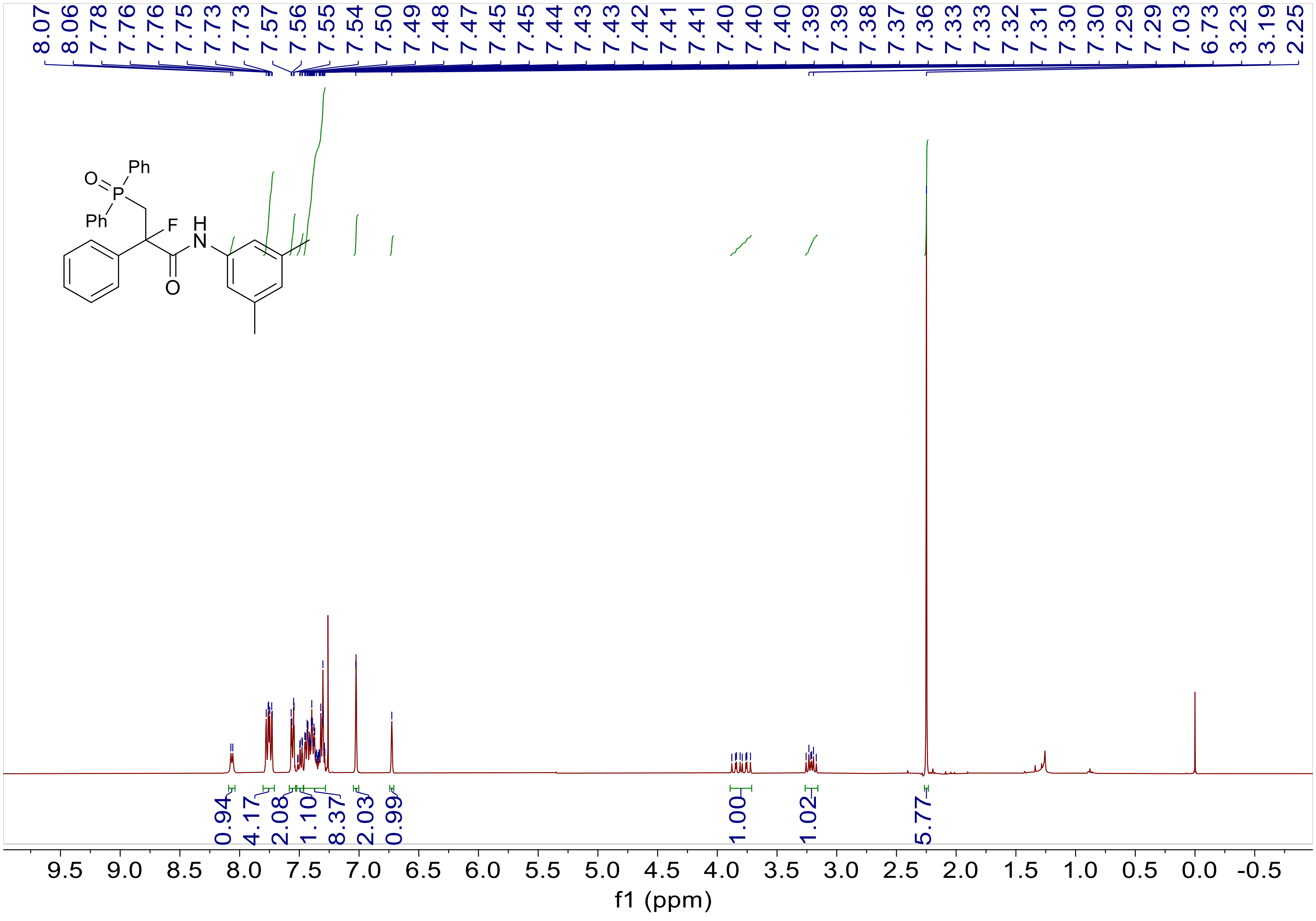


Figure S59. [1]H NMR spectrum of **3m** (400 MHz, $CDCl_3$)

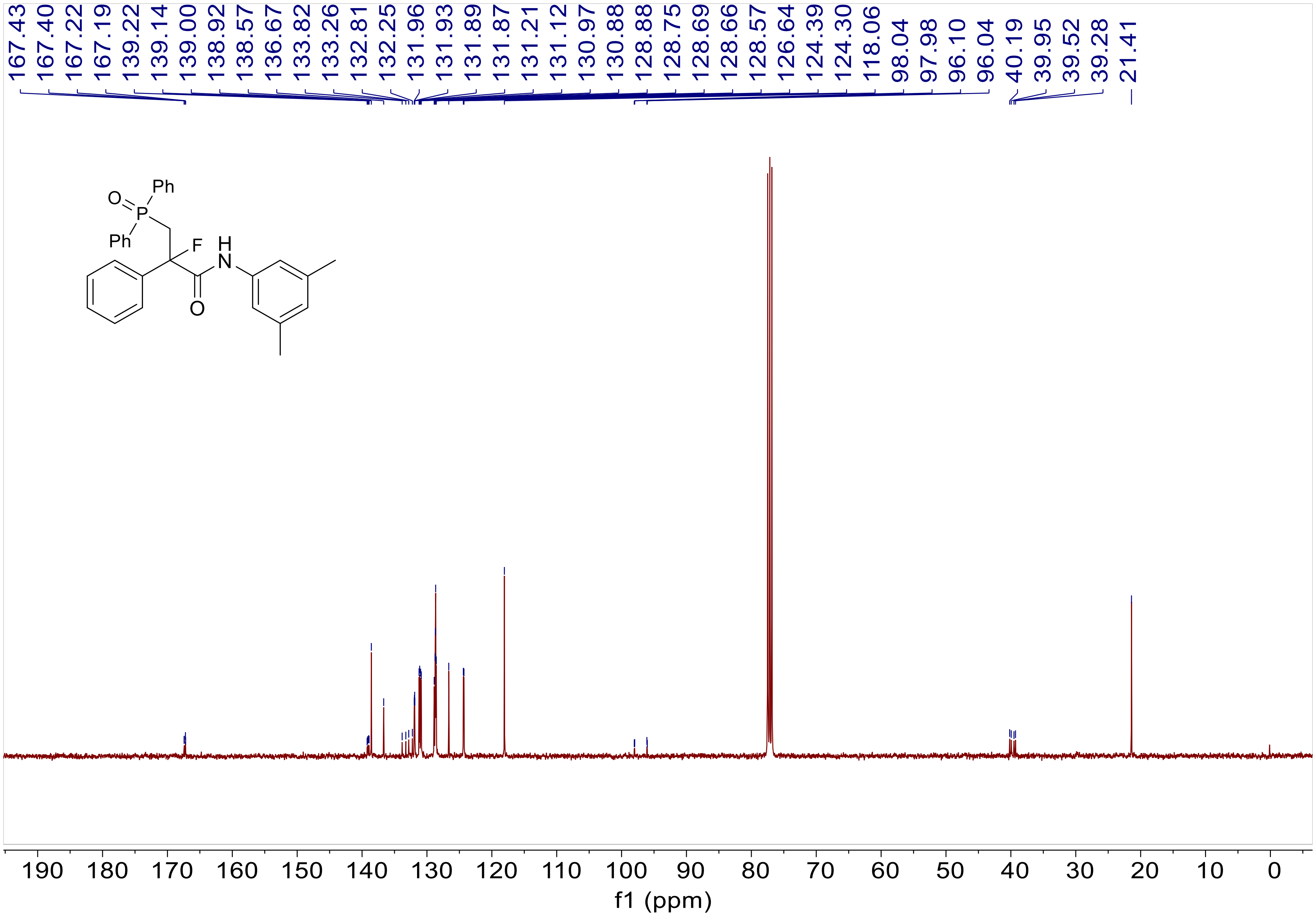


Figure S60. ^{13}C NMR spectrum of **3m** (101 MHz, $CDCl_3$)

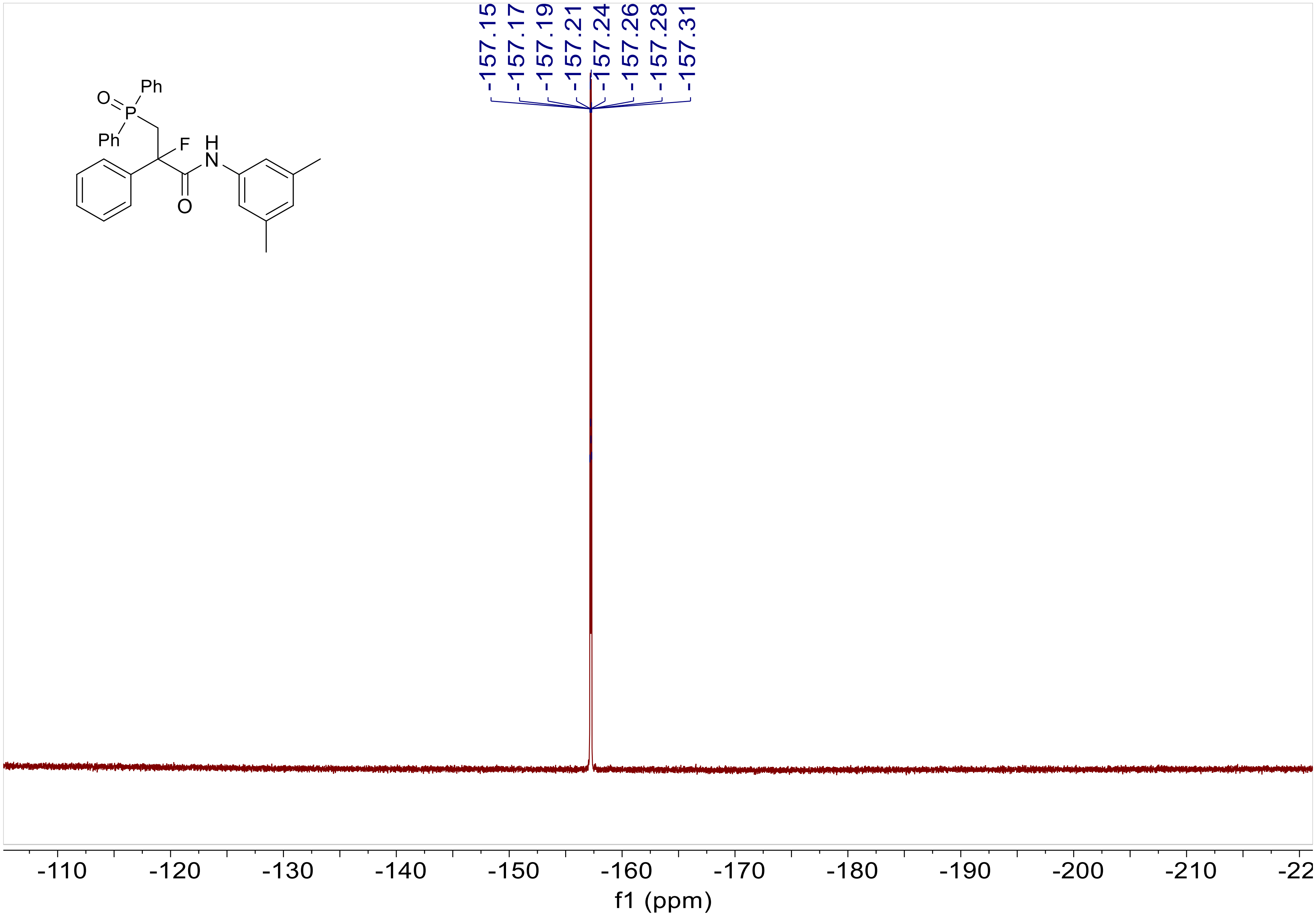


Figure S61. ^{19}F NMR spectrum of **3m** (376 MHz, $CDCl_3$)

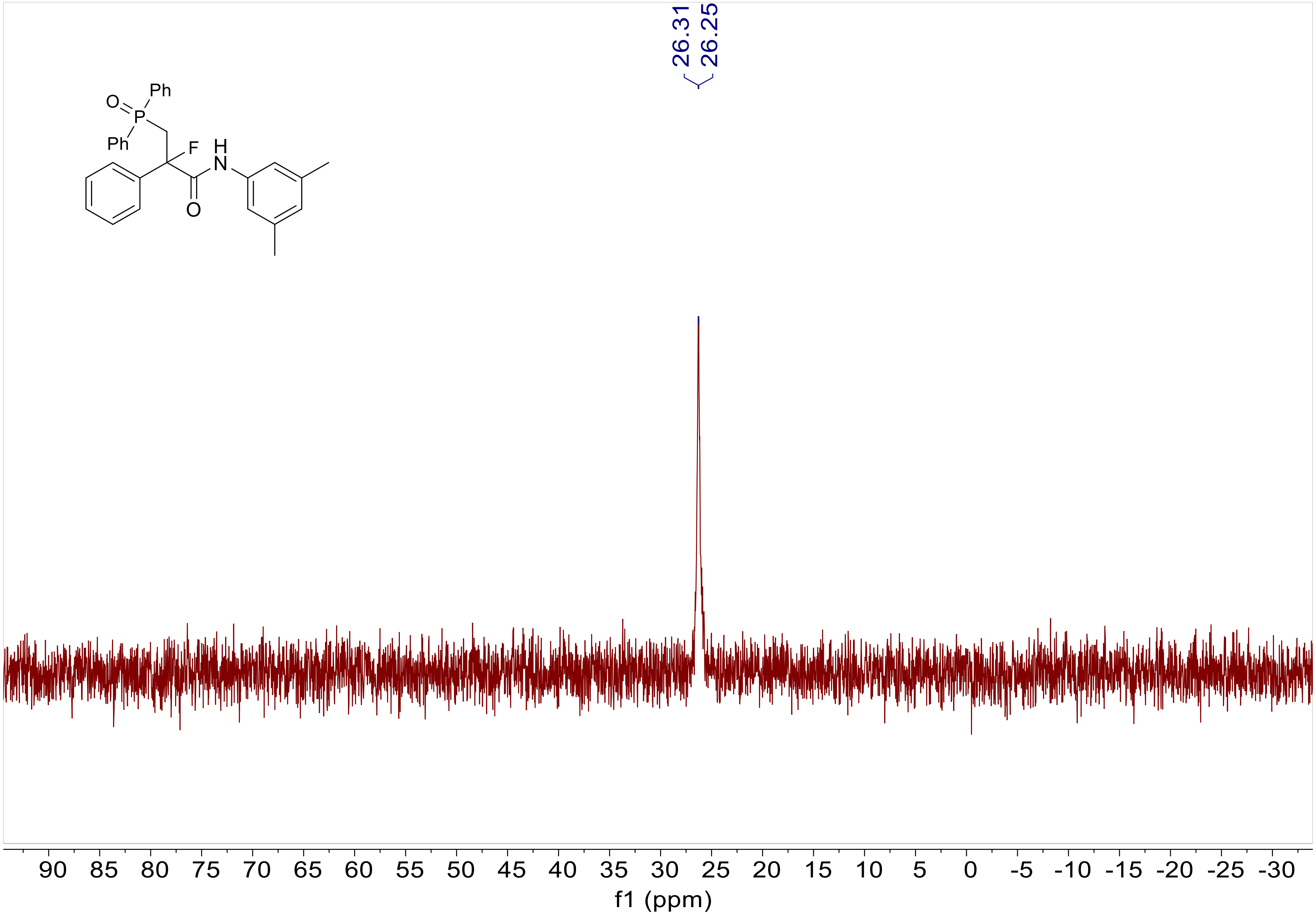


Figure S62. ^{31}P NMR spectrum of **3m** (162 MHz, $CDCl_3$)

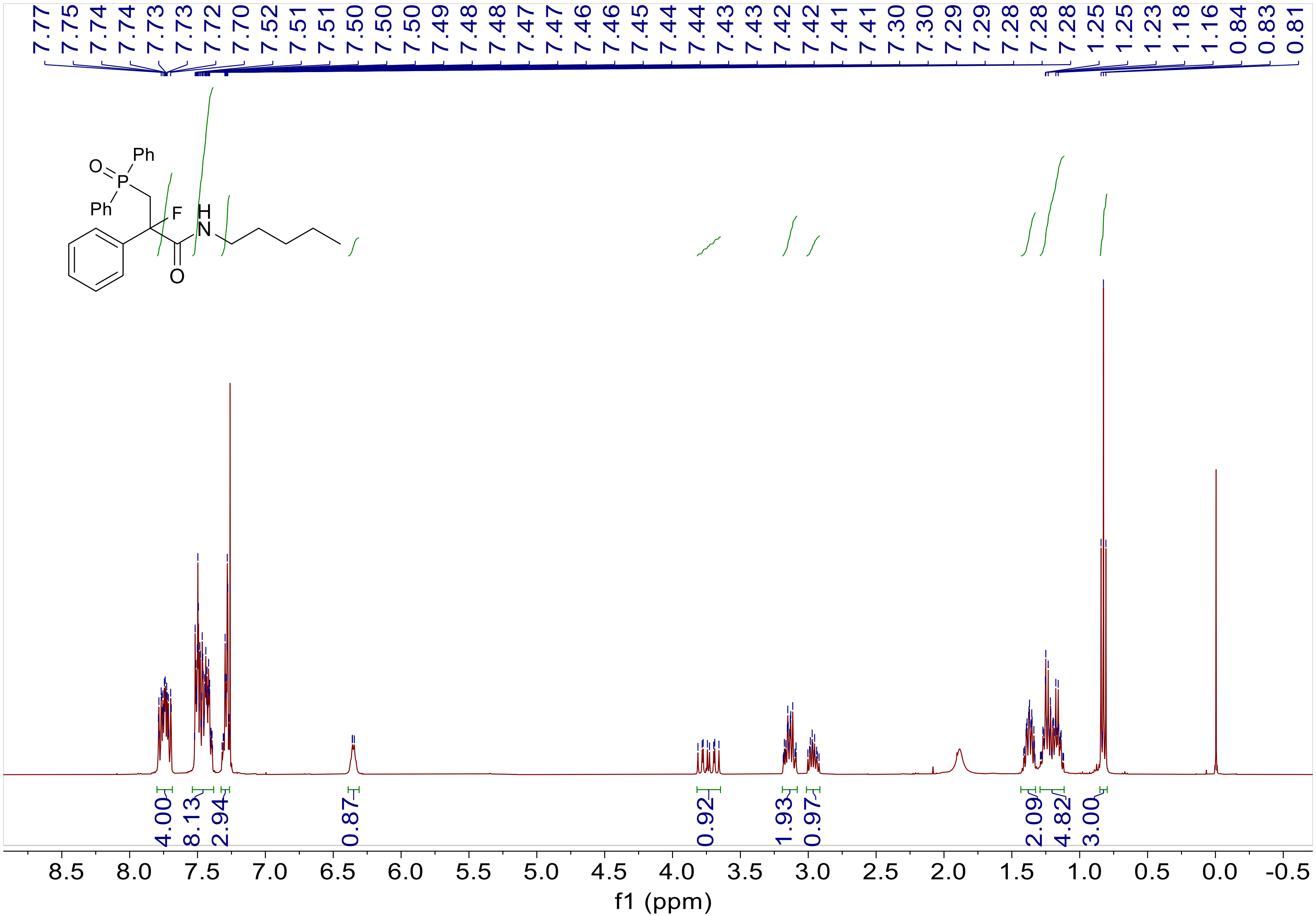


Figure S63. ^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)

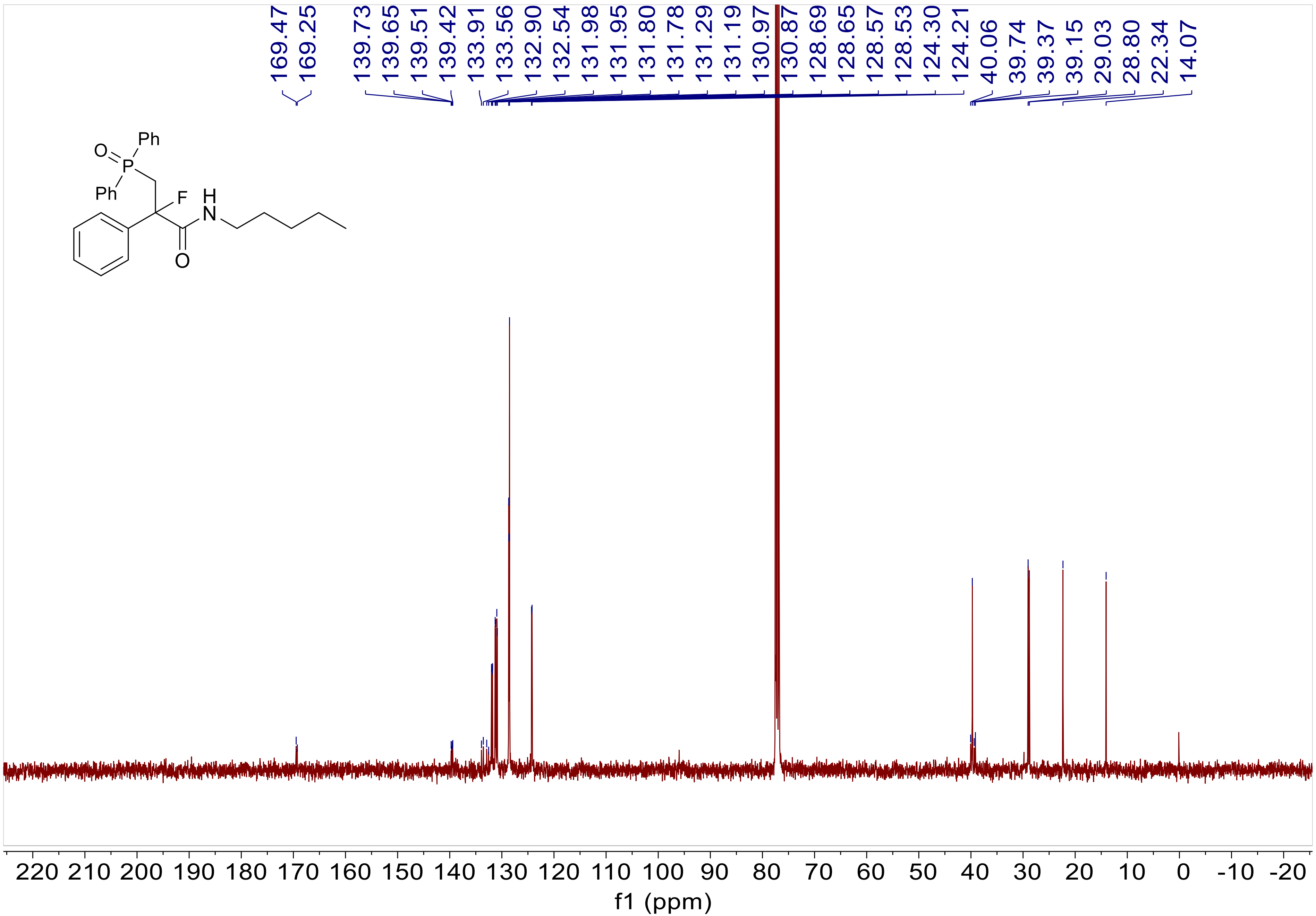


Figure S64. ^{13}C NMR spectrum of **3n** (101 MHz, $CDCl_3$)

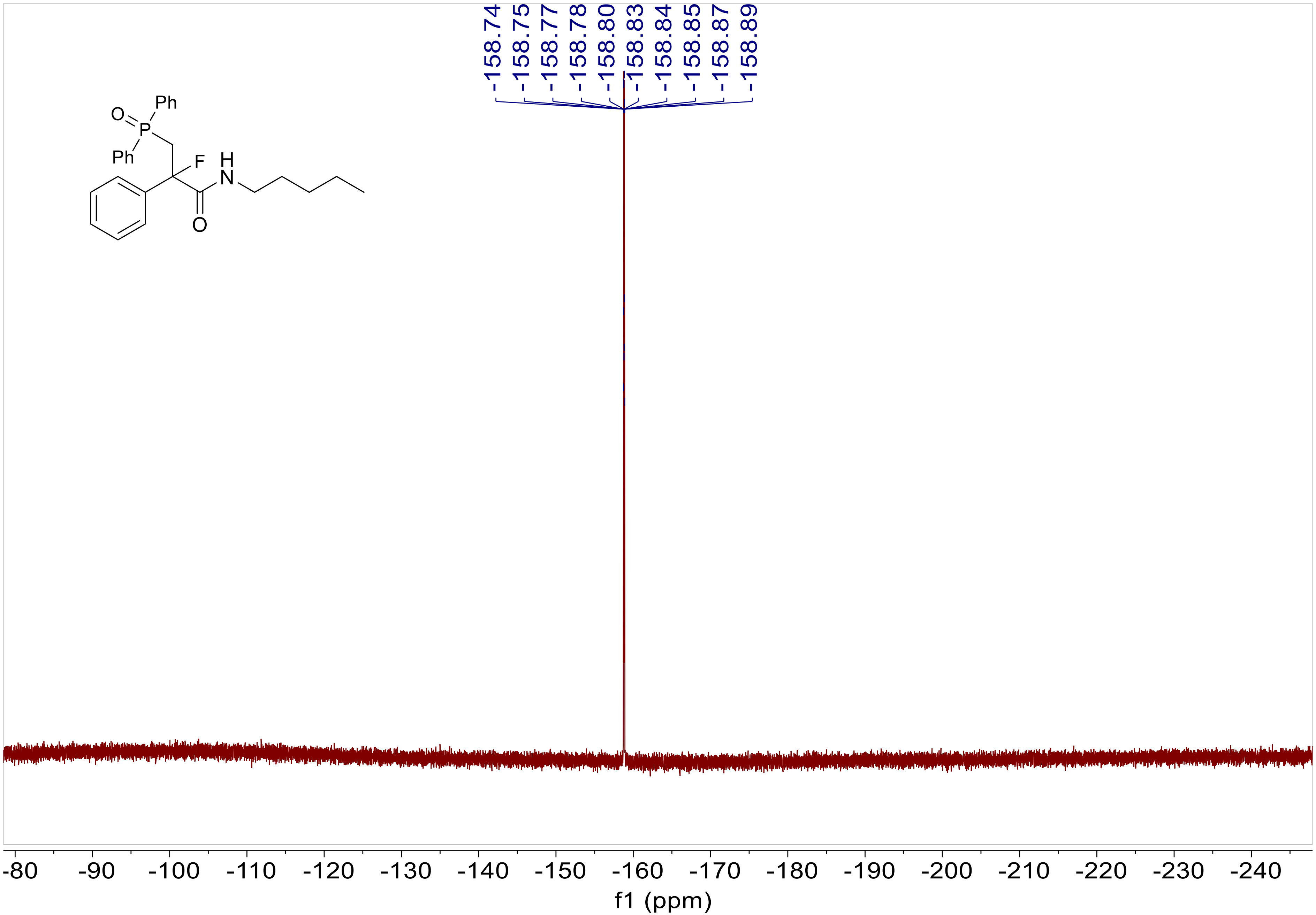


Figure S65. ^{19}F NMR spectrum of **3n** (376 MHz, $CDCl_3$)

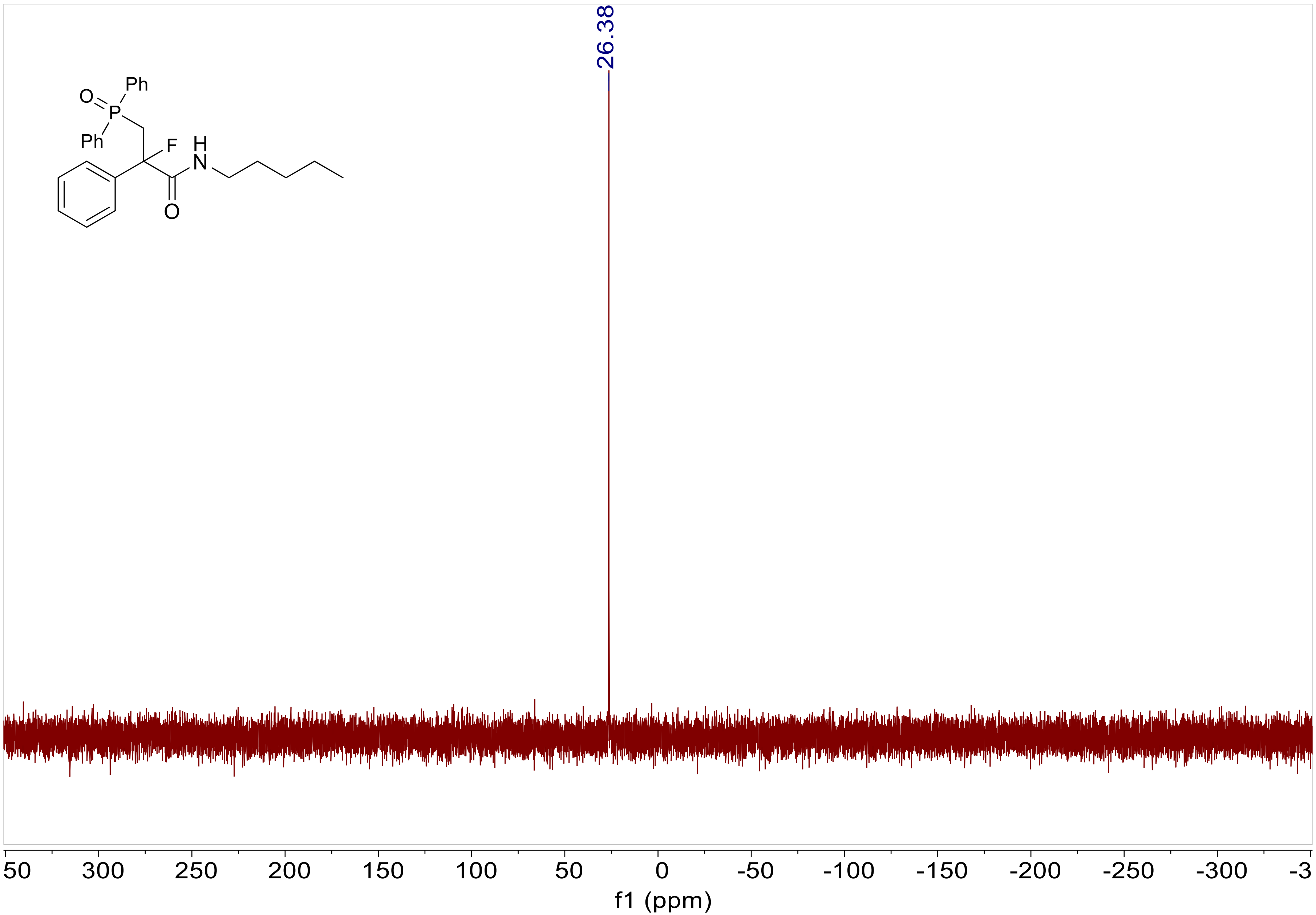


Figure S66. ^{31}P NMR spectrum of **3n** (162 MHz, $CDCl_3$)

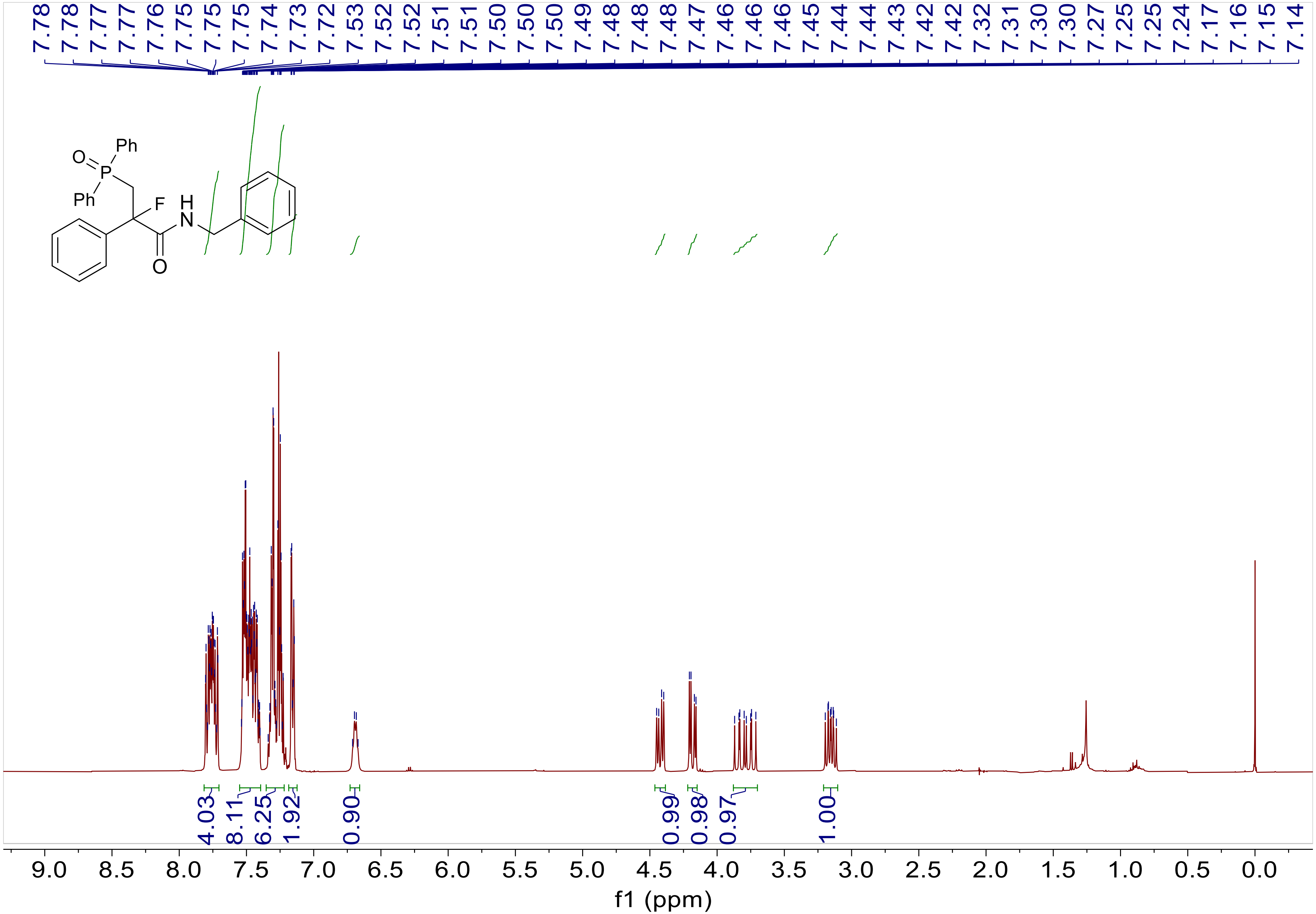


Figure S67. ^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)

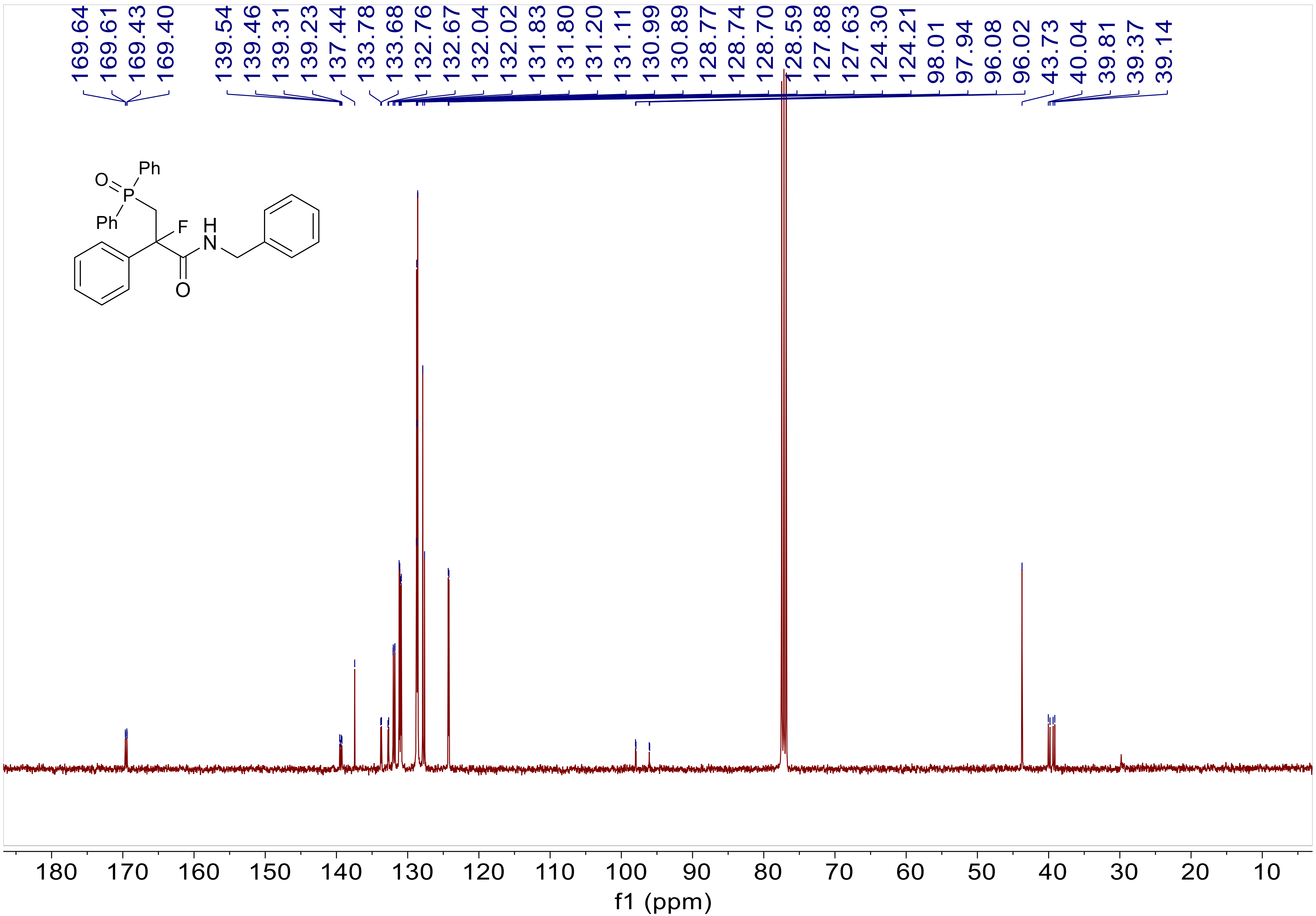


Figure S68. ^{13}C NMR spectrum of **3o** (101 MHz, $CDCl_3$)

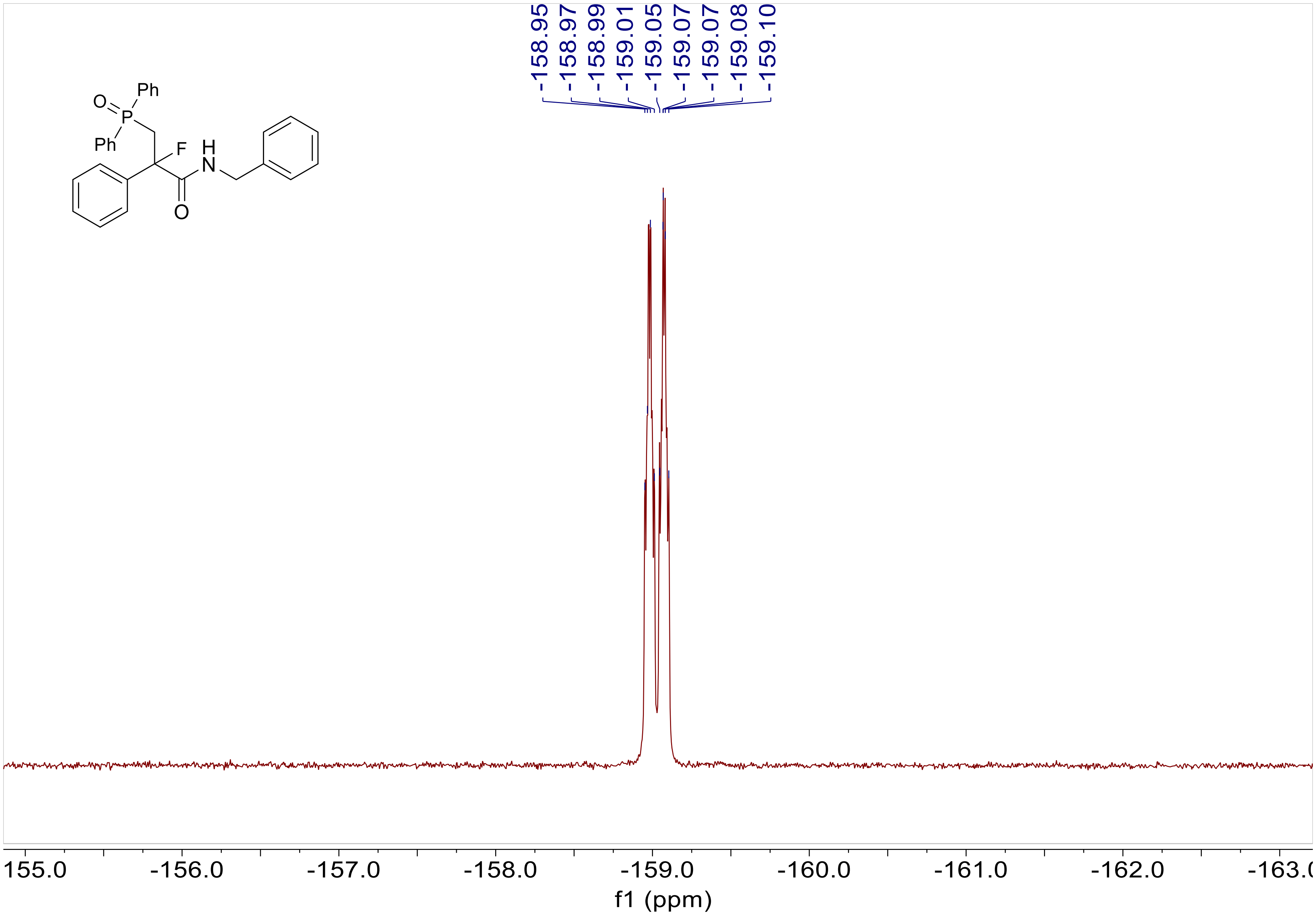


Figure S69. ^{19}F NMR spectrum of **3o** (376 MHz, $CDCl_3$)

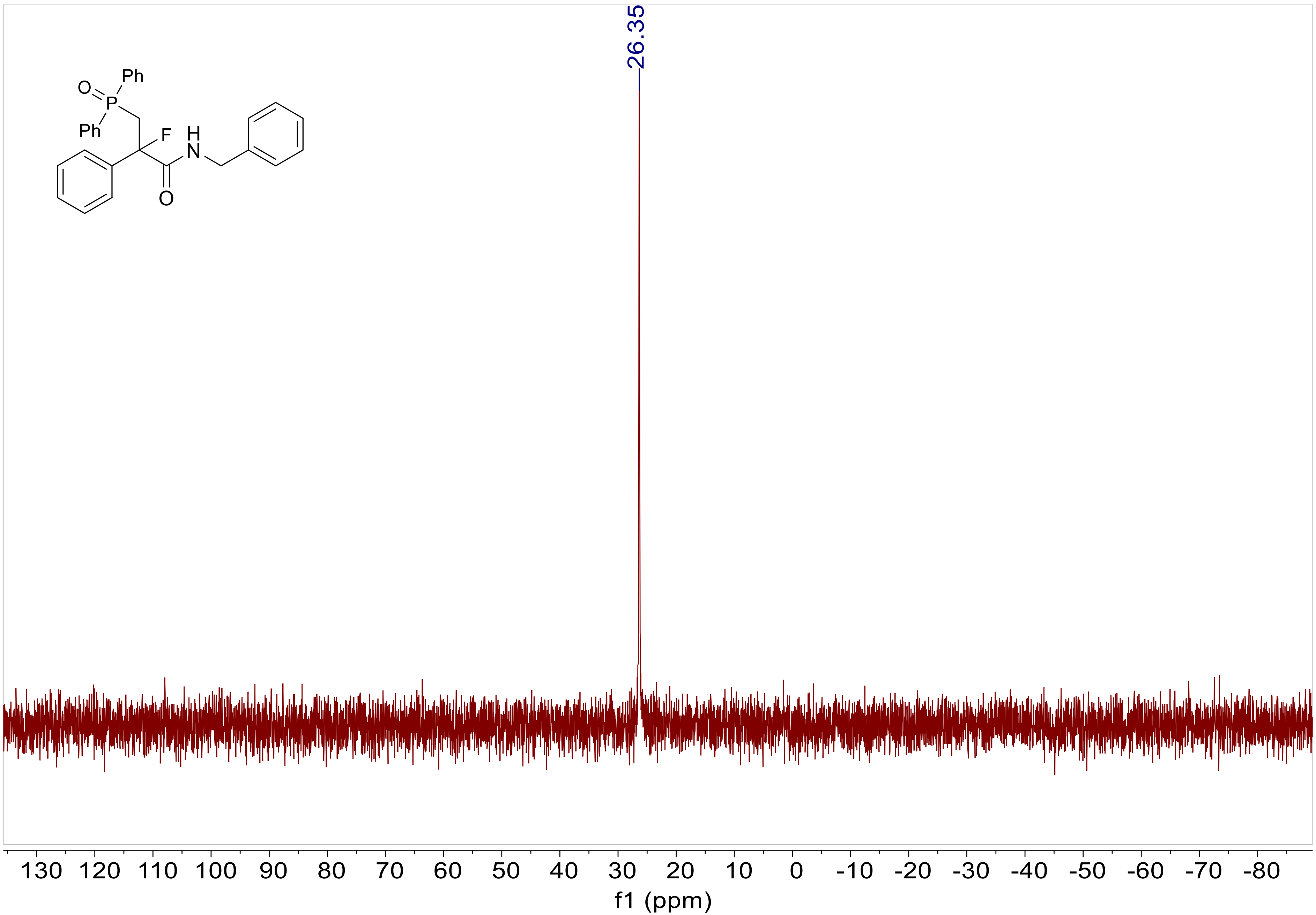


Figure S70. ^{31}P NMR spectrum of **3o** (162 MHz, $CDCl_3$)

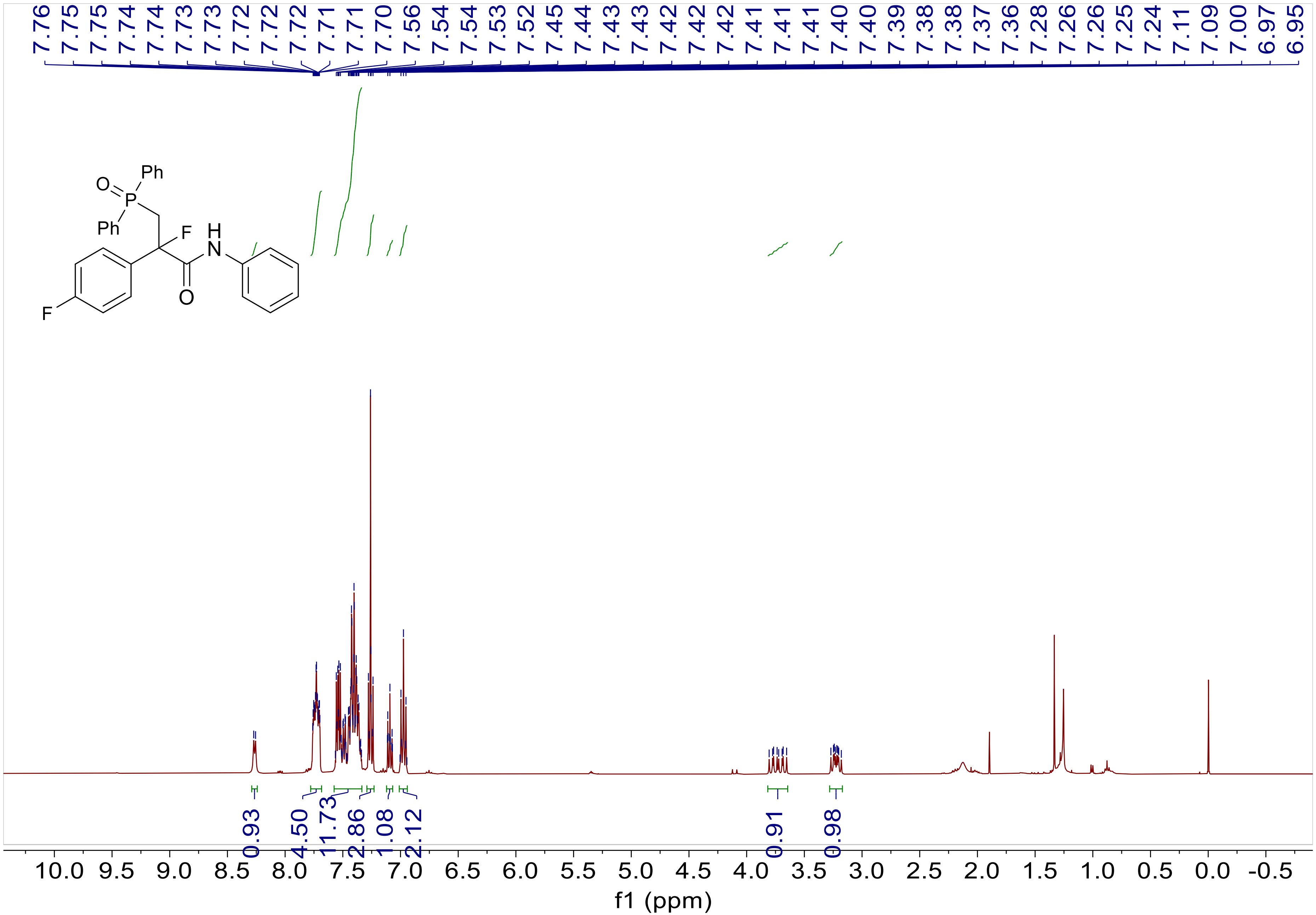


Figure S71. ^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)

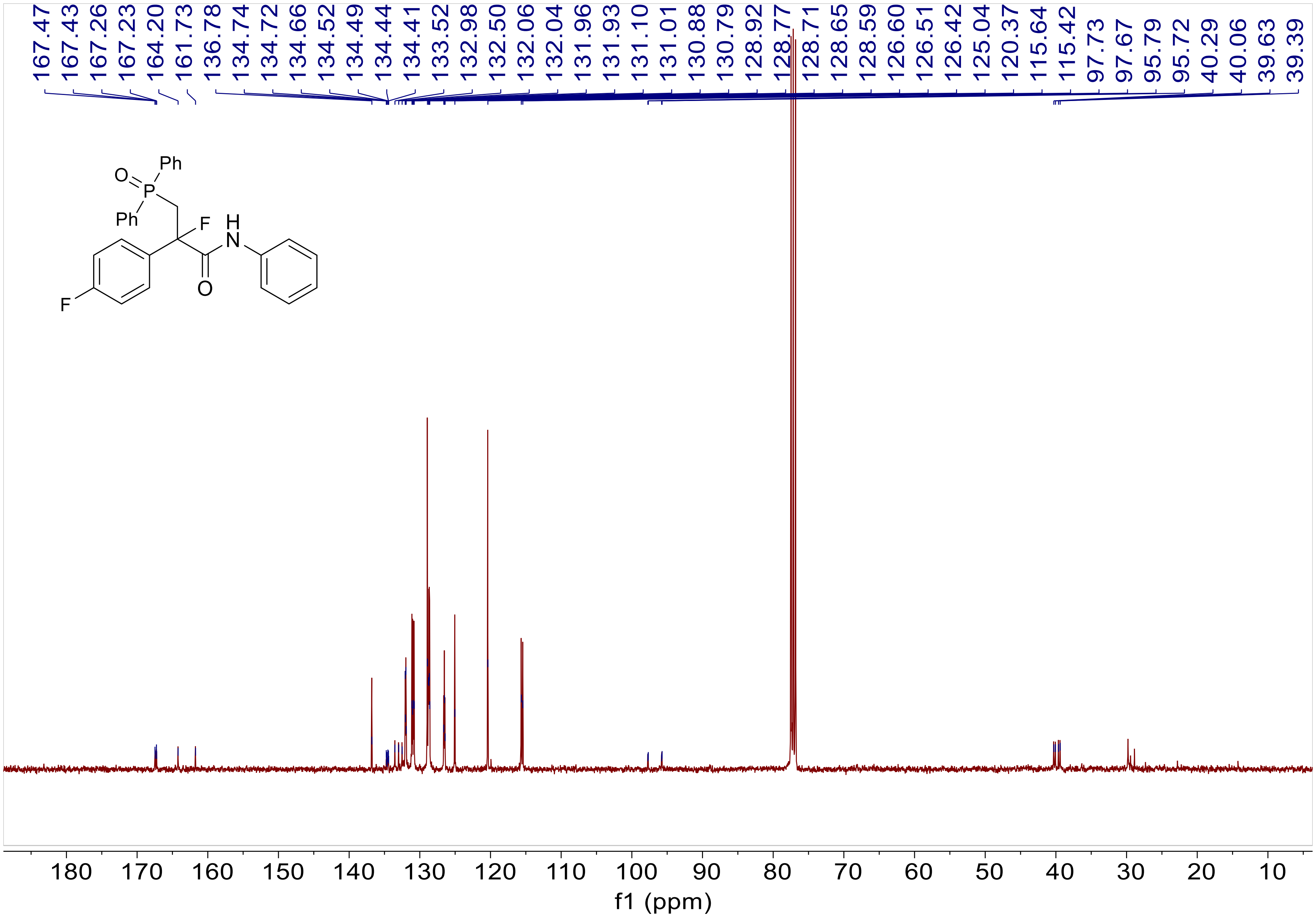


Figure S72. ^{13}C NMR spectrum of **3p** (101 MHz, $CDCl_3$)

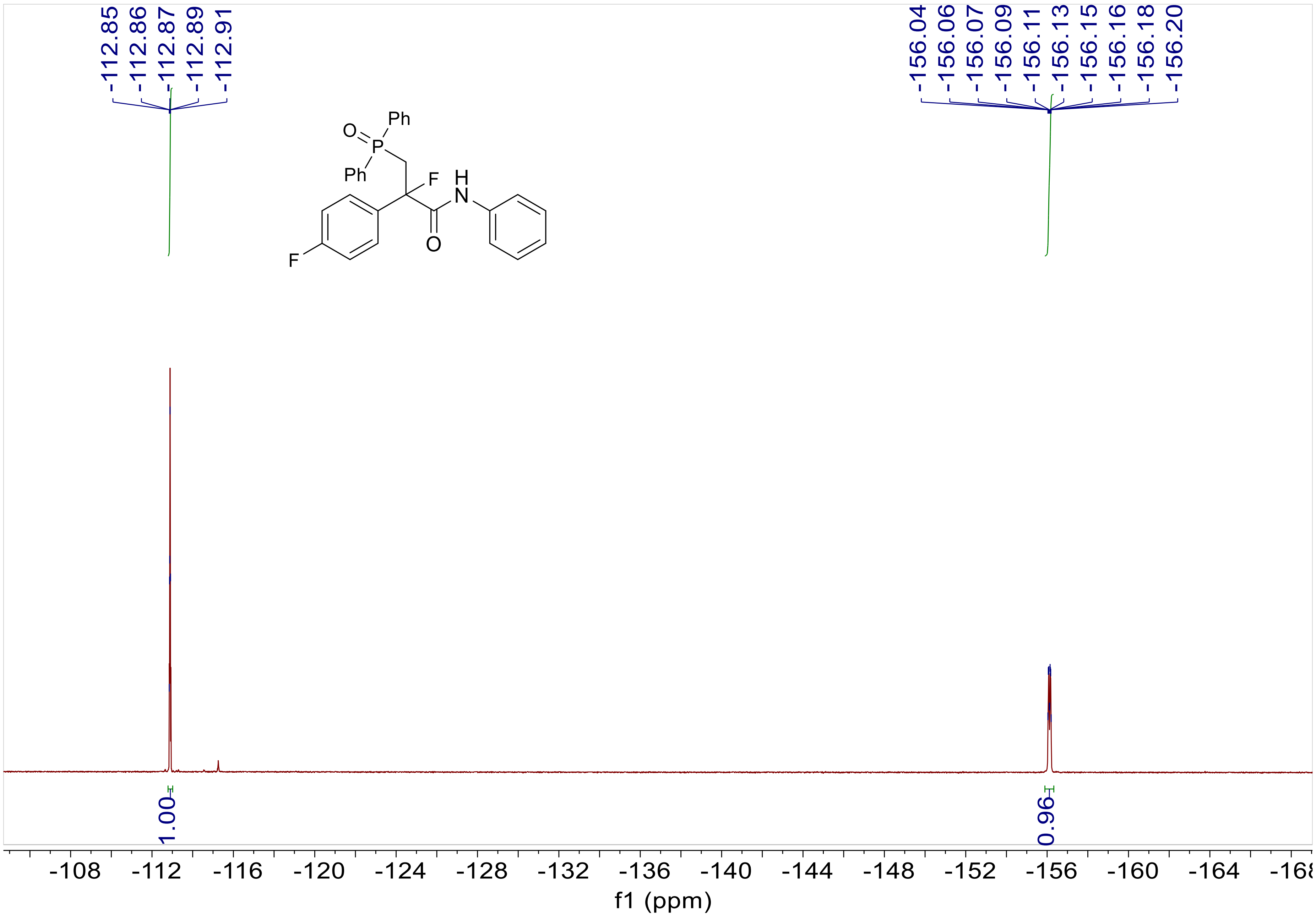


Figure S73. [19]F NMR spectrum of **3p** (376 MHz, $CDCl_3$)

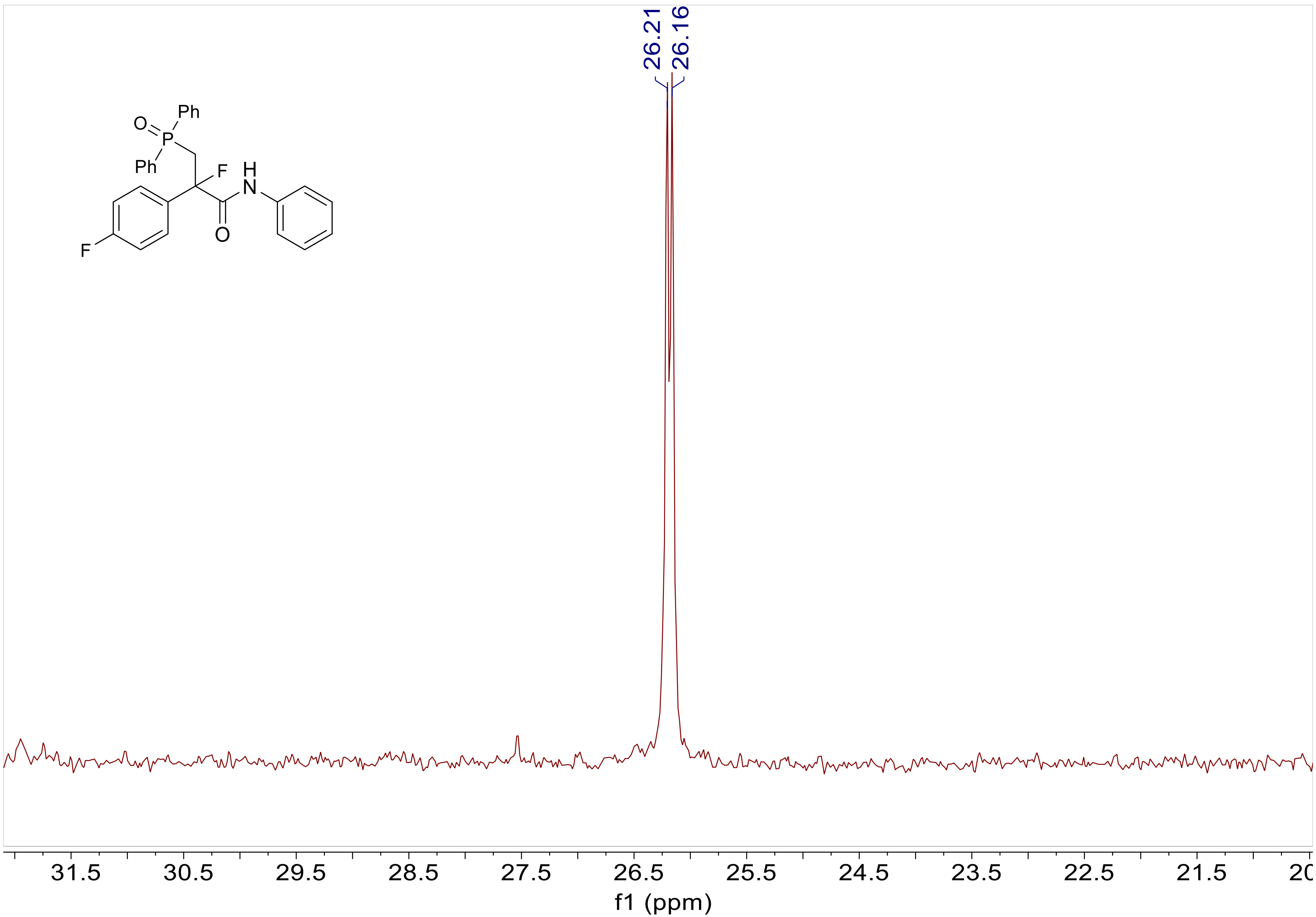


Figure S74. ^{31}P NMR spectrum of **3p** (162 MHz, $CDCl_3$)

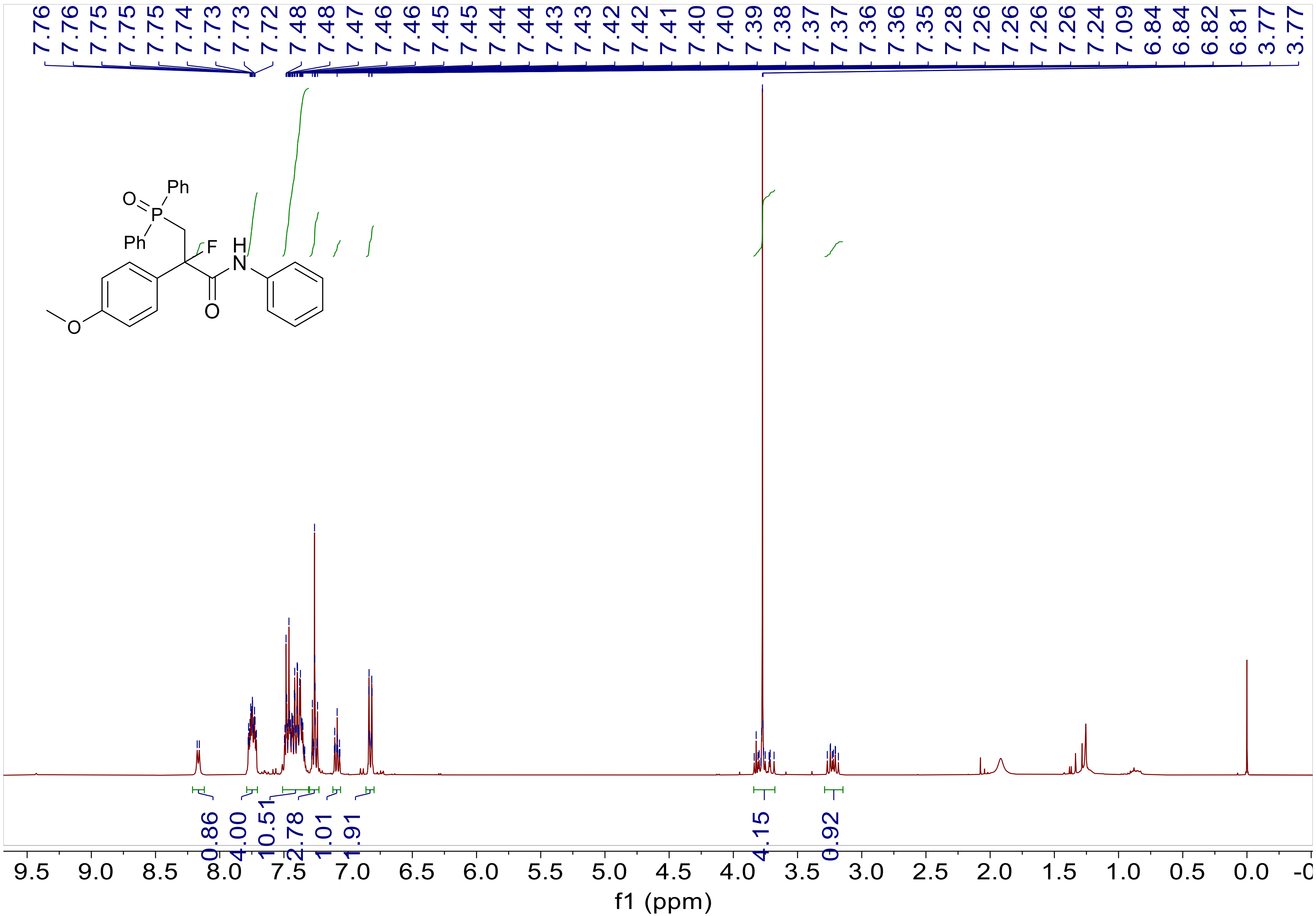


Figure S75. ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)

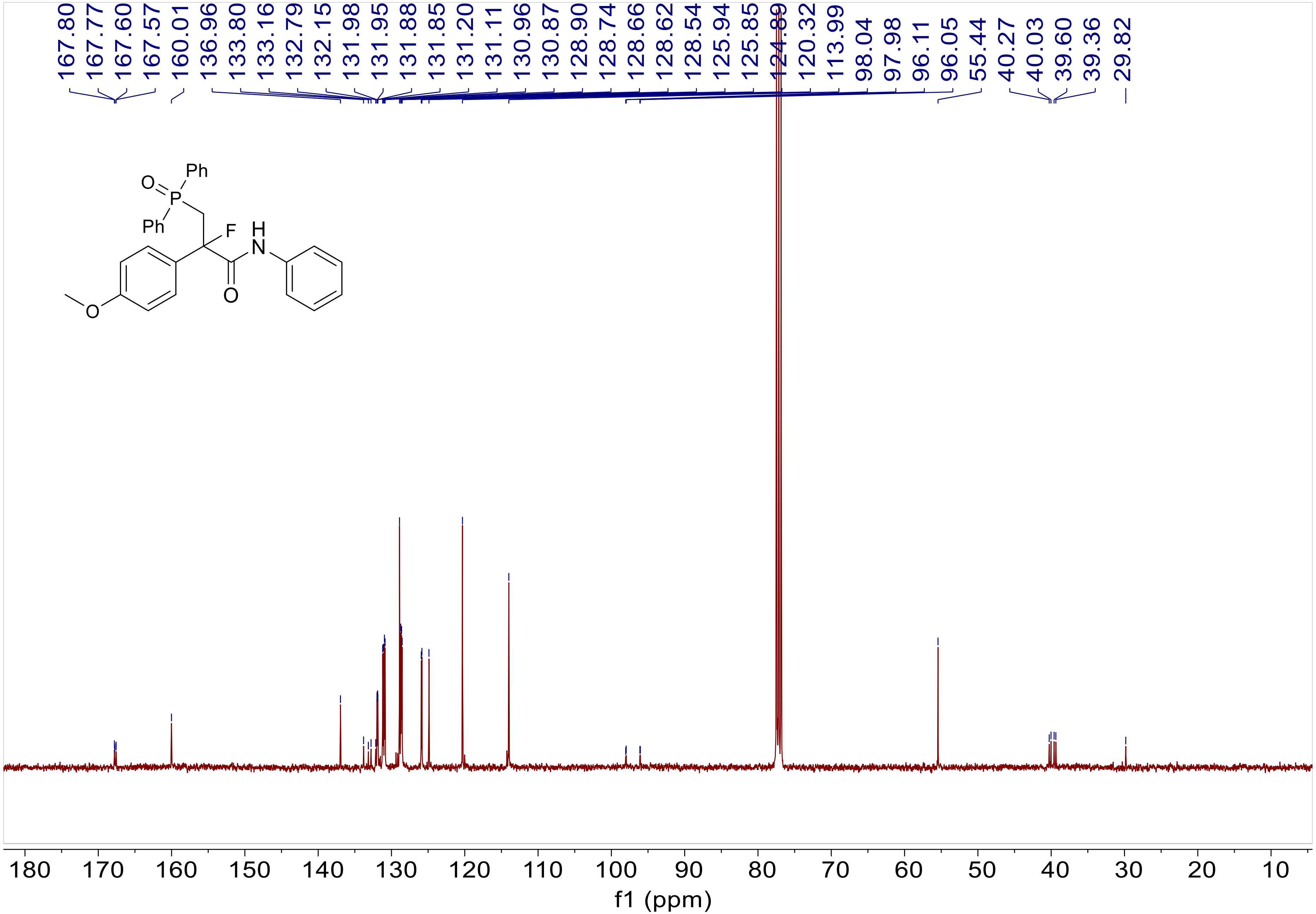


Figure S76. [13]C NMR spectrum of **3q** (101 MHz, $CDCl_3$)

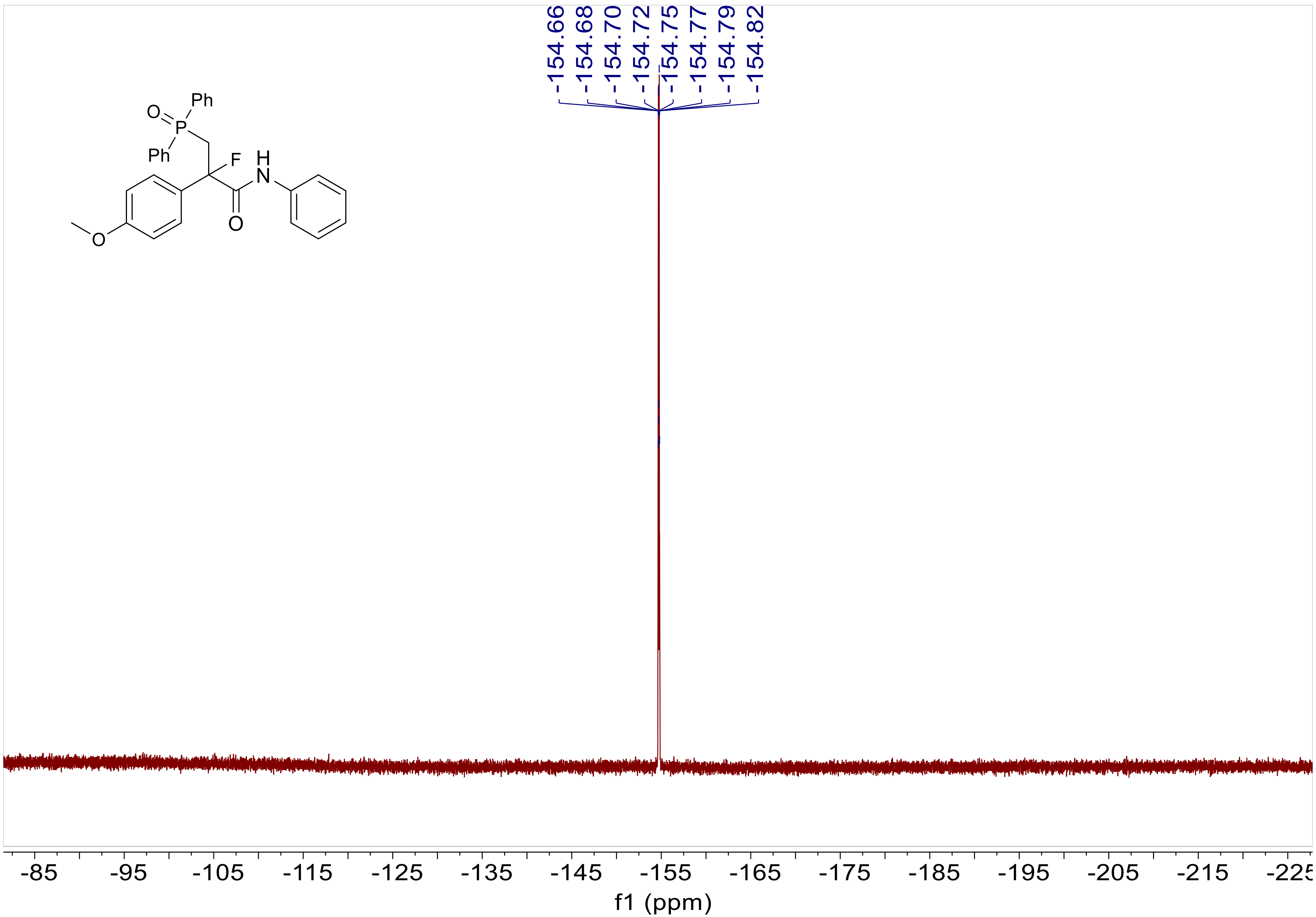


Figure S77. [19]F NMR spectrum of **3q** (376 MHz, $CDCl_3$)

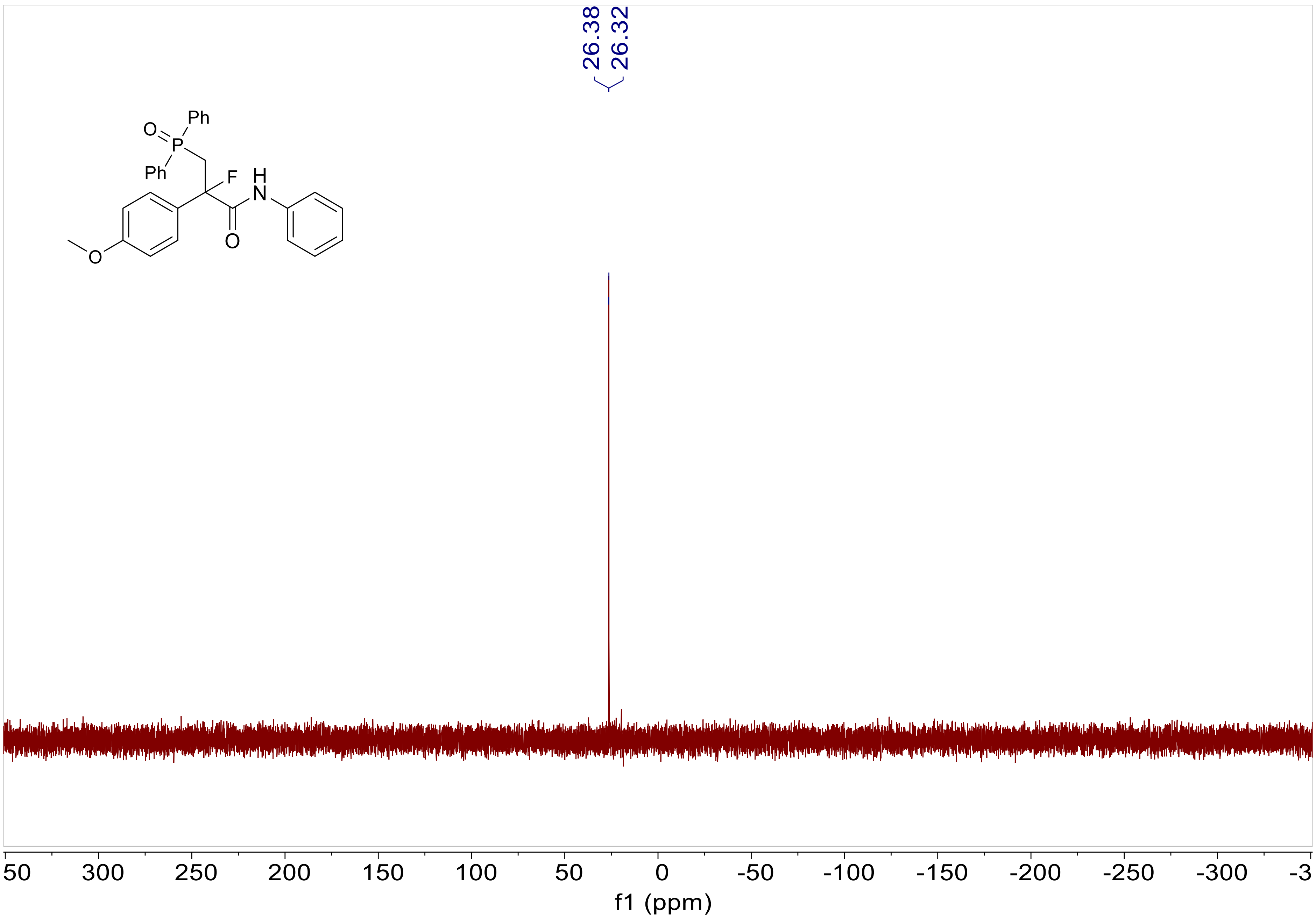


Figure S78. ^{31}P NMR spectrum of **3q** (162 MHz, $CDCl_3$)

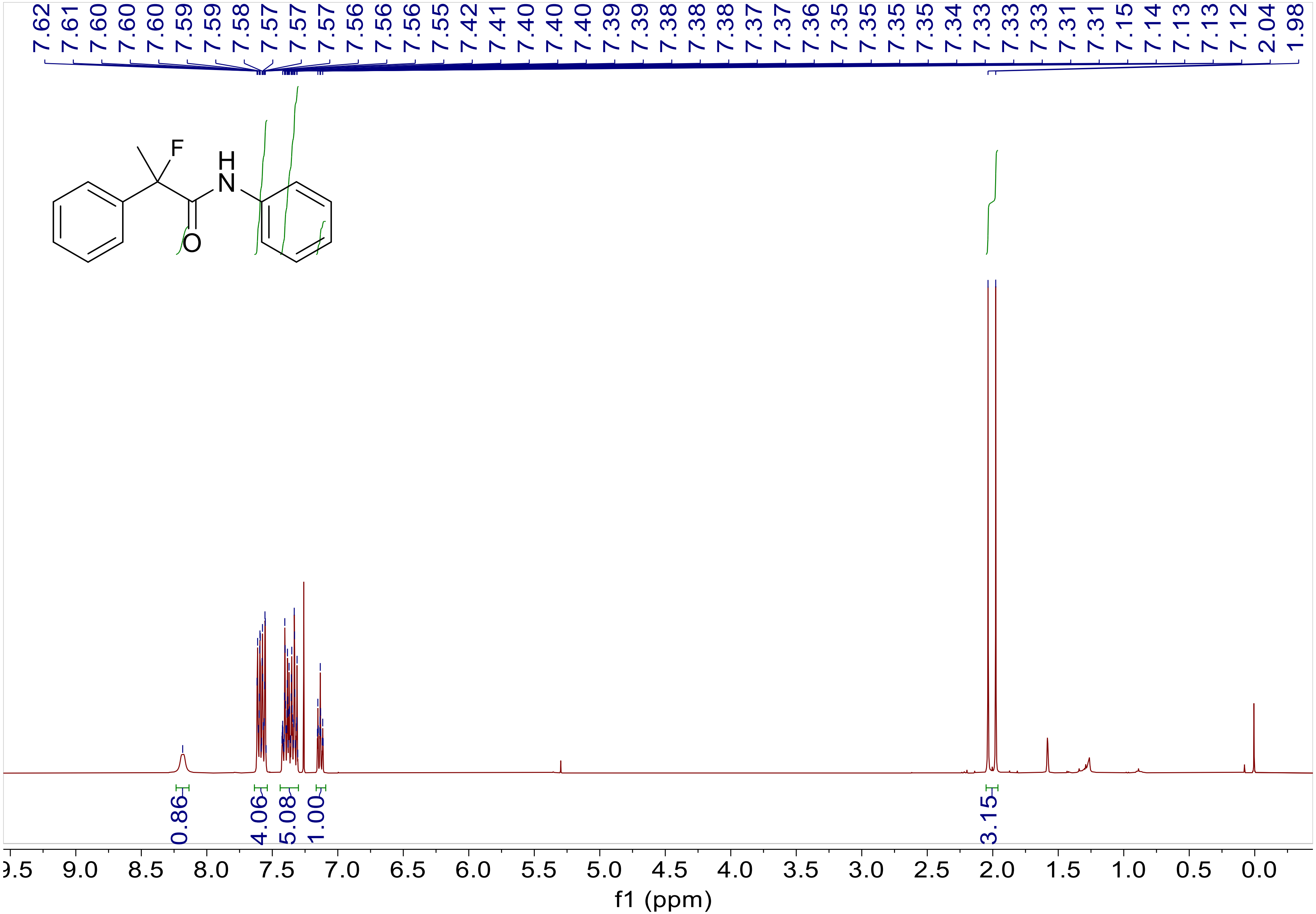


Figure S79. ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)

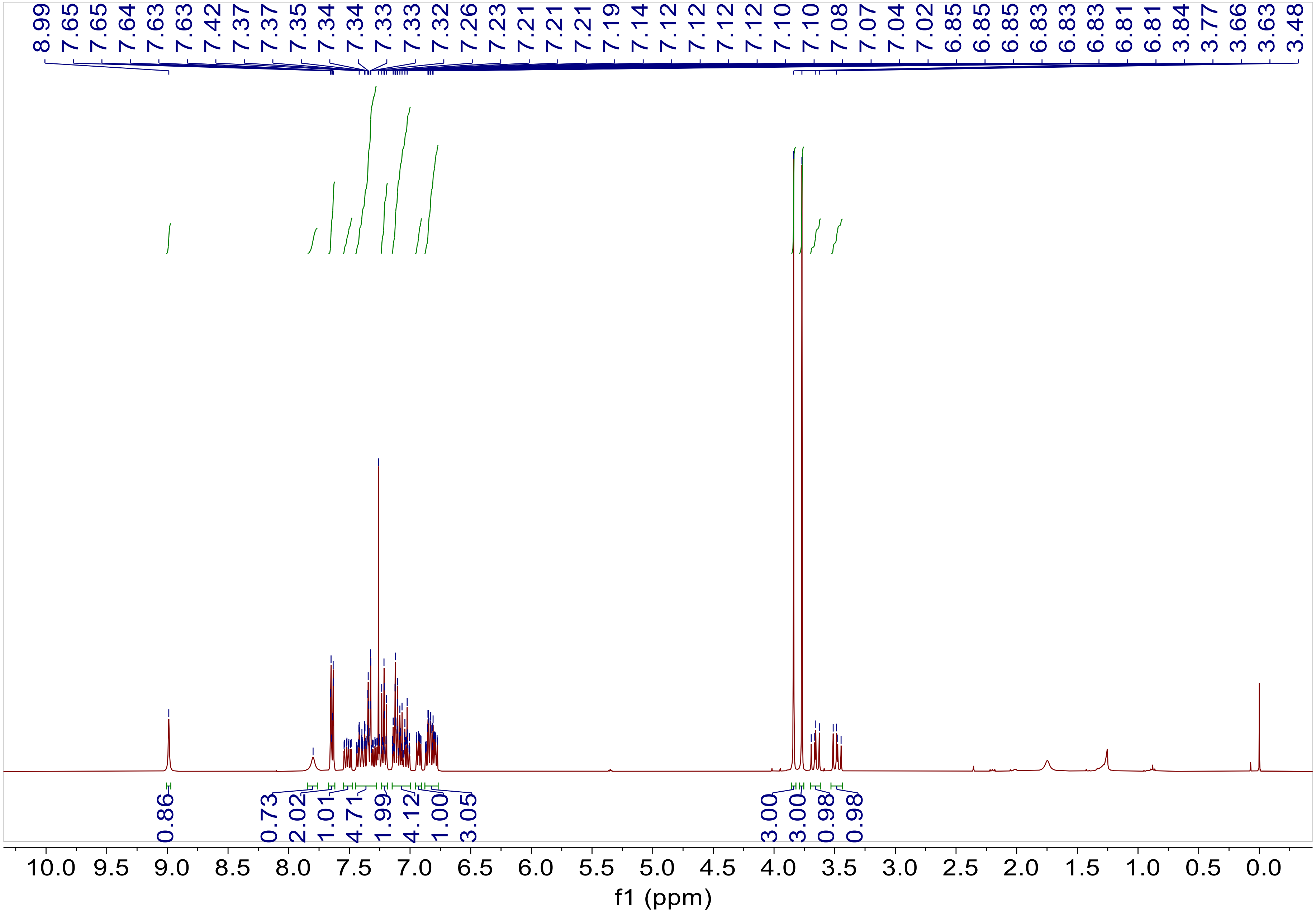


Figure S80. [1]H NMR spectrum of **8** (400 MHz, $CDCl_3$)

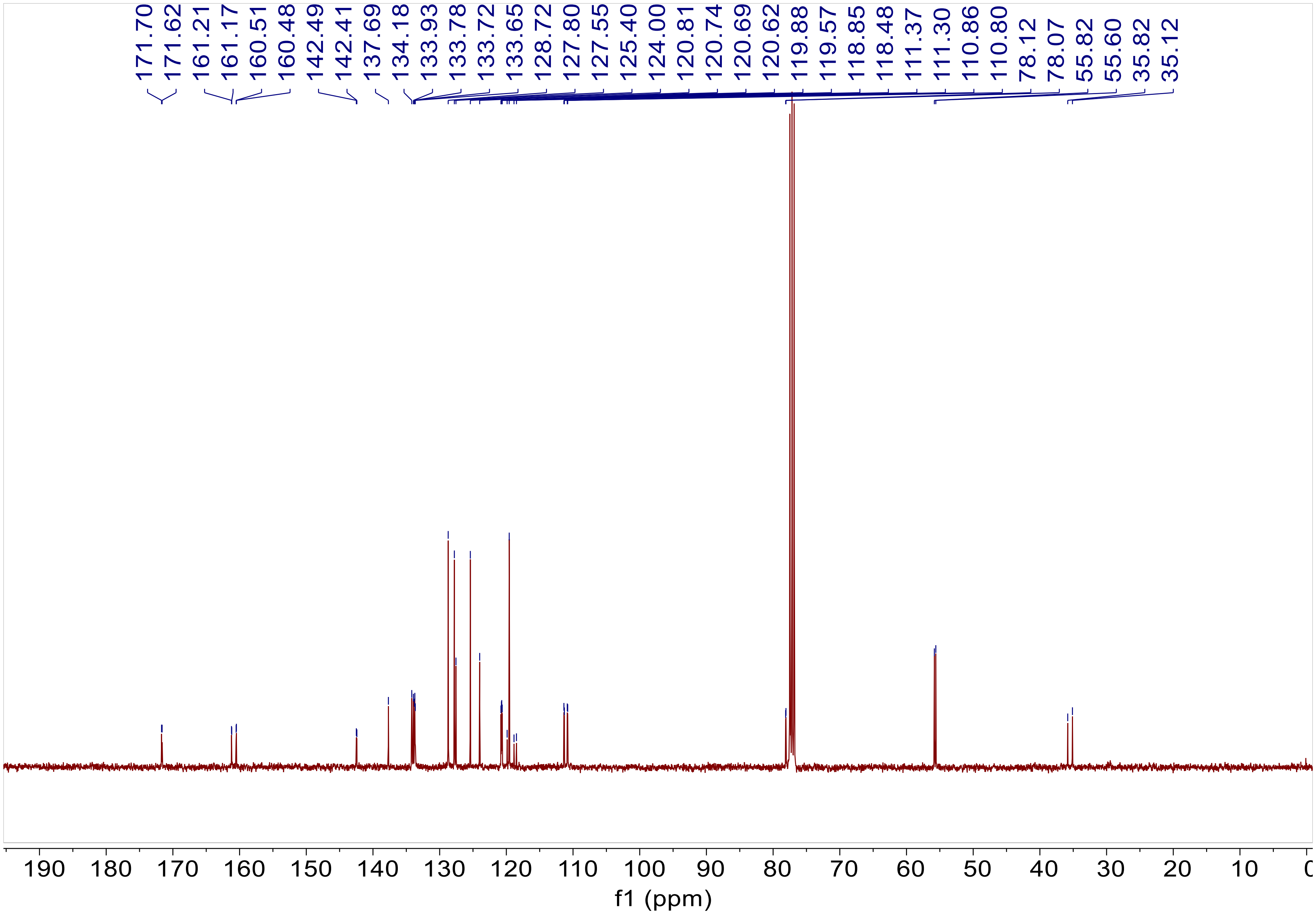


Figure S81. ^{13}C NMR spectrum of **8** (101 MHz, $CDCl_3$)

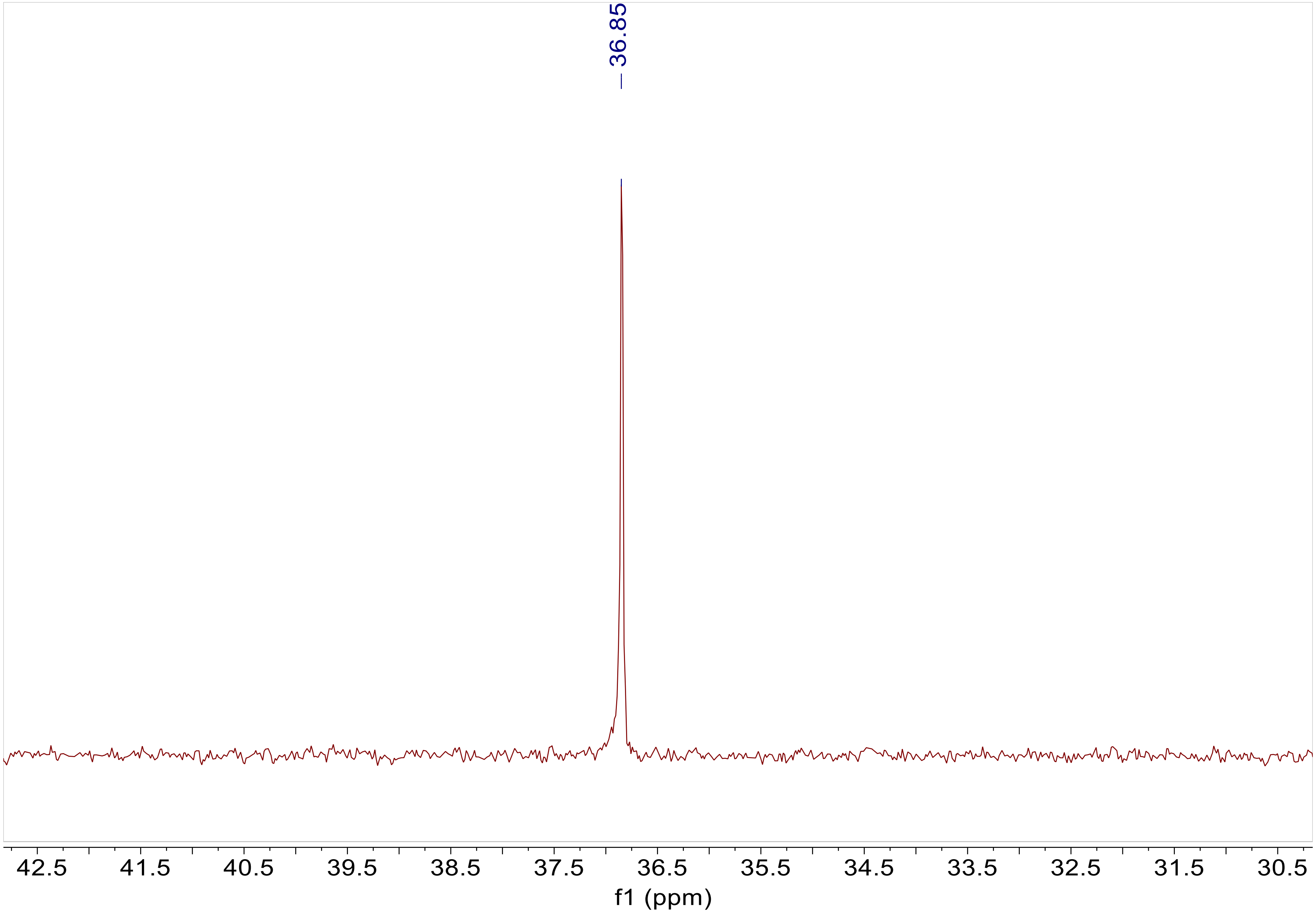


Figure S82. ^{31}P NMR spectrum of **8** (162 MHz, $CDCl_3$)