Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ru(II)-catalyzed P(III)-assisted C8-alkylation of naphthphosphines

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Contents

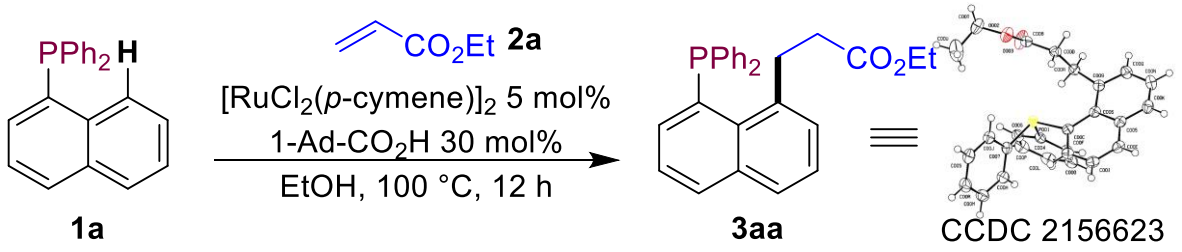
1. General Information

Unless otherwise noted, all reactions were carried out in a flamedried, sealed Schlenk reaction tube under an atmosphere of argon. Unless otherwise noted, materials were purchased from Alfa-Aesar and J&K Scientific Ltd. and used as received. All the solvents were purchased from commercial suppliers and purified by standard procedures as specified in *Purification of Laboratory Chemicals*, 4th Ed (W. L. F. Armarego, D. D. Perrin, Butterworth-Heinemann: 1997). Analytical thin layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash column chromatography was carried out using silica gel (200-300 mesh) at increased pressure. The ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{31}P are reported relative to an external 85% H_3PO_4 standard. ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets). The diffraction data of crystals were collected on a Rigaku XtaLAB Synergy CCD diffractometer with graphite monochromated Cu-Ka radiation (λ = 1.54056 Å) at 293 or 100 K. Absorption corrections were applied by SADABS. All the structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using SHELXTL-2014. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the ligand were generated geometrically. High resolution mass spectra (HRMS) were recorded on the Thermo Scientific Exactive Plus equipped with ESI ionization source.

2. Experimental Procedures

2.1 Optimization of the reaction conditions

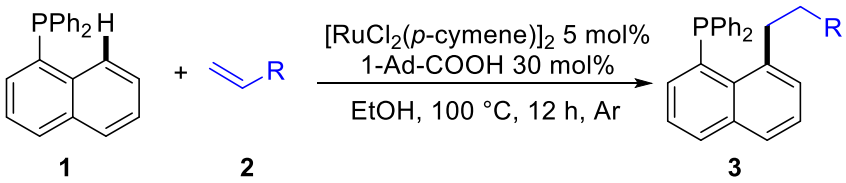
Table 1 Reaction conditions[a]



Entry	Change from standard conditions	Yield
1	none	87%[b]
2	Add NaOAc 2 eq.	68%
3	$MesCO_2H$ instead of $1\text{-}AdCO_2H$	48%
4	toluene instead of EtOH	11%
5	1,4-dioxane instead of EtOH	5%
6	without $1\text{-}Ad\text{-}CO_2H$	0%
7	without $[RuCl_2(p\text{-cymene})]_2$	0%
8	80°C instand of 100 °C	64%

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%) and $1\text{-}Ad\text{-}CO_2H$ (30 mol%) in 1 mL EtOH at 100 °C under argon, 12 h. Yields determined by ^{31}P NMR using triphenylphosphine as an internal standard. [b]Isolated yield.

2.2 General procedure for Ru(II)-catalyzed direct alkylation



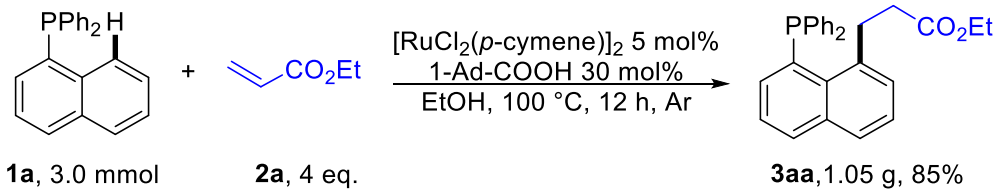
Scheme 1

To a 25 mL Schlenk tube was added 1-naphthalenyldiphenylphosphane **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.8 mmol, 4.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg 5.0 mol%),1-Ad-COOH (10.8 mg, 30 mol%). The tube was purged with Ar three times, followed by addition of EtOH (1 mL). The mixture was stirred at 100 °C for 12 h. The solution was then cooled to room temperature and the solvent was removed under

vacuum directly. The crude product was purified by prepared column chromatography affording the alkylation product **3**.

2.3 General procedures for Synthetic Applications

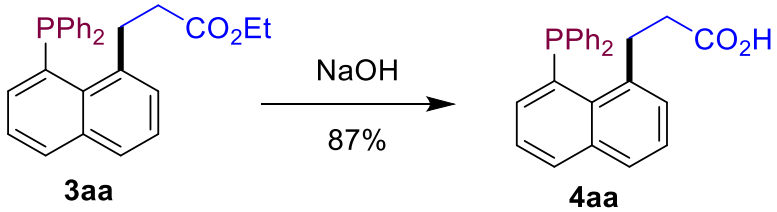
a) Gram-scale reaction



1a, 3.0 mmol **2a**, 4 eq. **3aa**,1.05 g, 85%

Scheme 2

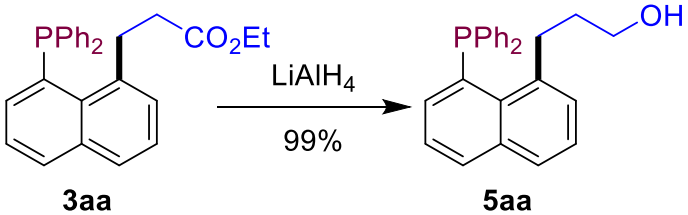
To a 50 mL Schlenk tube was added 1-naphthalenyldiphenylphosphane **1a** (3 mmol, 1.0 equiv), Ethyl Acrylate **2a** (12 mmol, 4.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (91.8 mg, 5.0 mol%), 1-Ad-COOH (162 mg, 30 mol%). The tube was purged with Ar three times, followed by addition of EtOH (5 mL). The mixture was stirred at 100 °C for 24 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.4, EA/hexane = 1/25) affording the alkylation product **3aa** (white solid, 1.05 g, 85% yield).



3aa **4aa**

Scheme 3

To a 50 mL Schlenk tube was added 1-naphthalenyldiphenylphosphane **1a** (3 mmol, 1.0 equiv), Ethyl Acrylate **2a** (12 mmol, 4.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (91.8 mg, 5.0 mol%), 1-Ad-COOH (162 mg, 30 mol%). The tube was purged with Ar three times, followed by addition of EtOH (5 mL). The mixture was stirred at 100 °C for 24 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.4, EA/hexane = 1/25) affording the alkylation product **3aa** (white solid, 1.05 g, 85% yield).

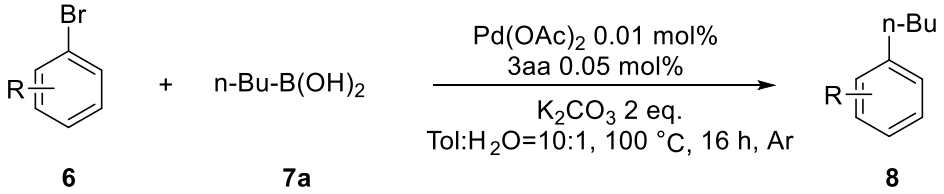


3aa **5aa**

Scheme 4

To a 50 mL Schlenk tube was added 1-naphthalenyldiphenylphosphane **1a** (3 mmol, 1.0 equiv), Ethyl Acrylate **2a** (12 mmol, 4.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (91.8 mg, 5.0 mol%), 1-Ad-COOH (162 mg, 30 mol%). The tube was purged with Ar three times, followed by addition of EtOH (5 mL). The mixture was stirred at 100 °C for 24 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (R_f = 0.4, EA/hexane = 1/25) affording the alkylation product **3aa** (white solid, 1.05 g, 85% yield).

2.4 General procedures for Phosphine-Promoted Pd-catalyzed Suzuki-Miyaura Coupling

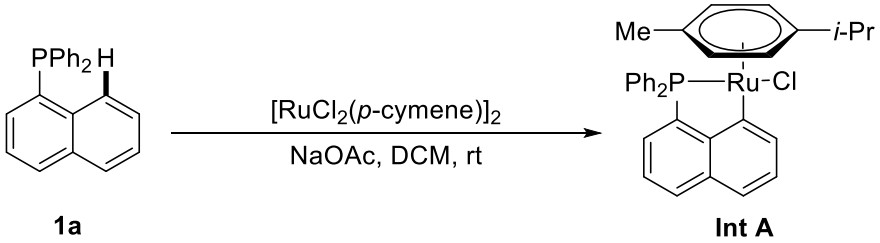


Scheme 5

First, catalyst stock solutions were prepared by dissolving $Pd(OAc)_2$ (2.3 mg) and **3aa** (20.6 mg) in DCM (10 mL) under nitrogen atmosphere at room temperature with continuous stirring for 5 min. Add 0.1 mL of the stock solution to a 25 mL Schlenk tube and remove the solvent under vacuum. Aryl bromide **6** (1 mmol, 1.0 equiv), n-butylboronic acid **7a** (1.3 mmol, 1.3 equiv), K_2CO_3 (276.0 mg, 2 equiv) were added to a Schlenk tube. The tube was then purged 3 times with Ar followed by addition of toluene and water (10:1, 2 mL). The mixture was stirred at 100 °C for 16 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly.

2.5 General procedures for mechanistic experiments

a) Synthesis of ruthenium(II) **Int A**

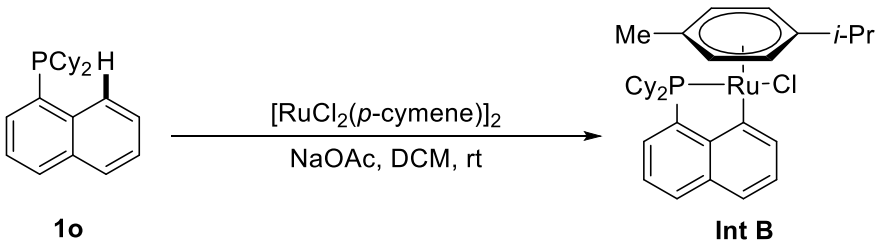


Scheme 6

To a 50 mL Schlenk flask was added 1-naphthalenyldiphenylphosphane **1a** (2 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (1 mmol, 50 mol%), NaOAc (4 mmol, 2.0 equiv). The tube was purged with Ar three times, followed by addition of 10 mL DCM. The mixture was stirred at room temperature for 24 h. The solvent was then removed under vacuum directly. The crude product was purified by neutral alumina

(Al_2O_3) column chromatography (R_f = 0.6, EA/hexane = 5/1) affording the product **Int A** (0.81g, 68% yield) as red powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.30 (m, 1H), 8.13-8.07 (m, 2H), 7.87-7.84 (m, 1H), 7.67-7.63 (m, 1H), 7.49-7.46 (m, 1H), 7.45-7.40 (m, 4H), 7.37-7.29 (m, 4H), 7.21-7.16 (m, 2H), 5.82 (t, *J* = 6.9 Hz, 2H), 4.56 (d, *J* = 6.2 Hz, 1H), 4.46 (d, *J* = 6.1 Hz, 1H), 2.45-2.38 (m, 1H), 1.93 (s, 3H), 1.26 (s, 2H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H).

b) Synthesis of ruthenium(II) **Int B**

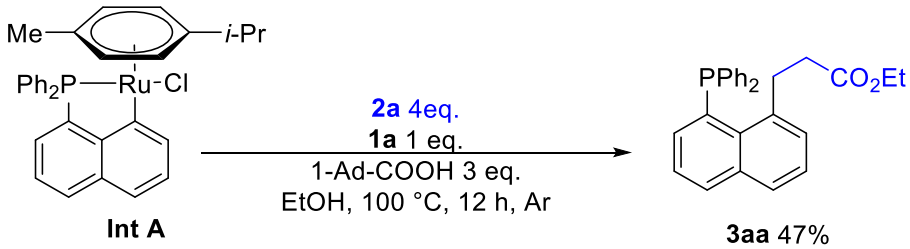


Scheme 7

To a 50 mL Schlenk flask was added dicyclohexyl(naphthalen-1-yl)phosphane **1o** (1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol, 50 mol%), NaOAc (2 mmol, 2.0 equiv). The tube was purged with Ar three times, followed by addition of 10 mL DCM. The mixture was stirred at room temperature for 24 h. The solvent was then removed under vacuum directly. The crude product was purified by neutral alumina (Al_2O_3) column chromatography (R_f = 0.4, EA/hexane = 5/1) affording the product **Int B** (0.45g, 74% yield) as red powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ170.8 (d, *J* = 12.5 Hz), 149.4 (d, *J* = 31.1 Hz), 135.4 (d, *J* = 42.9 Hz), 133.1 (d, *J* = 13.9 Hz), 130.2 (d, *J* = 2.4 Hz), 126.9 (d, *J* = 11.0 Hz), 123.6 (d, *J* = 7.1 Hz), 121.2, 110.6, 96.6 (d, *J* = 5.8 Hz), 95.3, 90.3 (d, *J* = 3.2 Hz), 89.6, 83.8, 39.3 (d, *J* = 24.0 Hz), 35.3 (d, *J* = 23.8 Hz), 30.5, 29.7, 28.9 (d, *J* = 2.8 Hz), 27.7, 27.6 (d, *J* = 2.6 Hz), 27.5, 27.2 (d, *J* = 9.0 Hz), 27.0 (d, *J* = 7.6 Hz), 26.9 (d, *J* = 8.0 Hz), 26.2, 23.0, 22.2, 18.0.^{31}P NMR (162 MHz, $CDCl_3$) δ 71.52.

c) Cyclometalated complex **Int A** as substrate

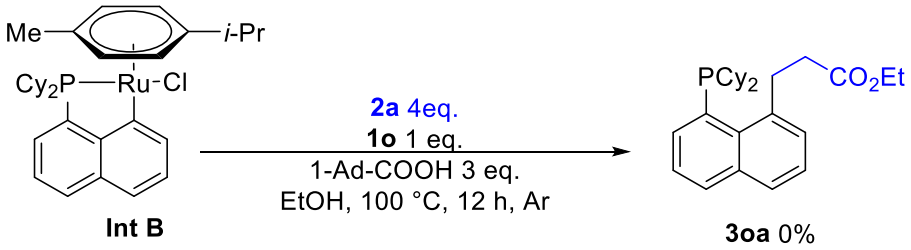


Scheme 8

To a 25 mL Schlenk tube was added **Int A** (0.1 mmol, 1.0 equiv), naphthalen-1-yldiphenylphosphane **1a**, ethyl acrylate **2a** (0.4 mmol, 4.0 equiv), 1-Ad-COOH (54 mg, 3.0 equiv). The tube was purged with Ar three times, followed by addition of EtOH (1 mL).The mixture was stirred at 100 °C for 12 h. The

solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by prepared column chromatography (R_f = 0.4, EA/hexane = 1/25) affording the alkylation product **3aa** (47% yield).

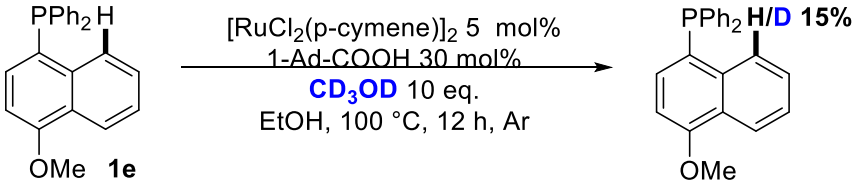
d) Cyclometalated complex **Int B** as substrate



Scheme 9

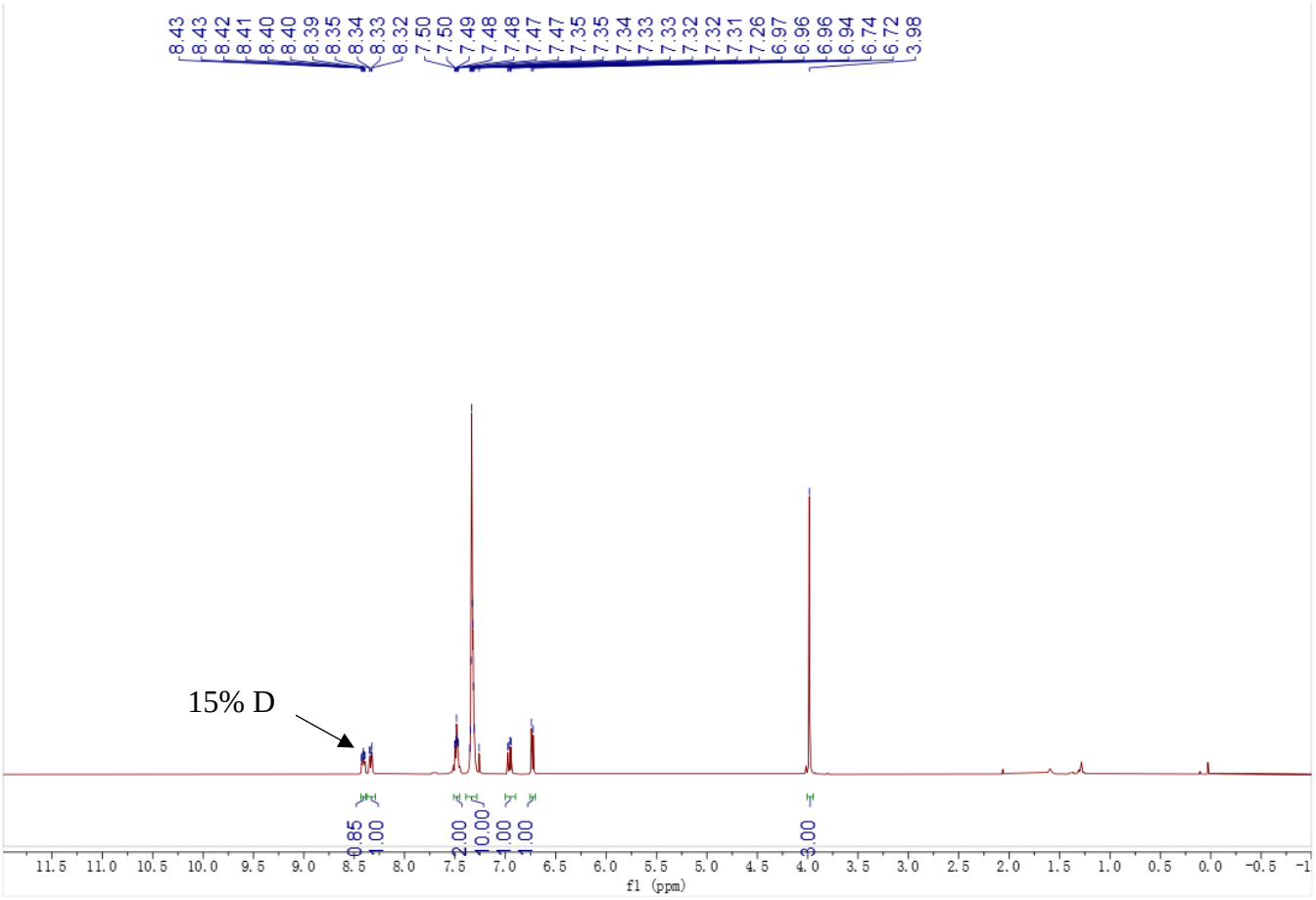
To a 25 mL Schlenk tube was added **Int B** (0.1 mmol, 1.0 equiv), dicyclohexyl(naphthalen-1-yl)phosphane **1o**, Ethyl Acrylate **2a** (0.4 mmol, 4.0 equiv), 1-Ad-COOH (54 mg, 3.0 equiv). The tube was purged with Ar three times, followed by addition of EtOH (1 mL).The mixture was stirred at 100 °C for 12 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. Failed to generate the alkylated product **3oa**.

e) Intermolecular H/D exchange



Scheme 10

To a 25 mL Schlenk tube was added (4-methoxynaphthalen-1-yl)diphenylphosphane **1e** (0.2 mmol, 1.0 equiv), [$RuCl_2$(*p*-cymene)]$_2$ (5.0 mol%), 1-Ad-COOH (10.8 mg, 30 mol%), CD_3OD (10.0 equiv). The tube was purged with Ar three times, followed by addition of EtOH (1.0 mL). The mixture was stirred at 100 °C for 12 h. The solution was then cooled to room temperature and the solvent was removed under vacuum directly. The crude product was purified by prepared column chromatography (R_f = 0.7, EA/hexane = 1/50) affording the mixture products, which was analyzed by ^{1}H NMR spectroscopy.



f) Parallel experiments KIE measurement

Kinetic isotopic effect was determined by performing two independent experiments of naphthalen-1-yldiphenylphosphane **1a** or deuterated naphthalen-1-yldiphenylphosphane **1a-d8** and Ethyl Acrylate **2a** as a coupling partner. Yields determined by 1H NMR using CH_2Br_2 as the internal standard were recorded at predetermined time intervals for 2 h to evaluate the yield of the reaction. The yield of alkylated product using starting material **1a** was 37%, The yield of alkylated product using starting material **1a-d8** was 33%. The kH/kD ratio of 1.1 was obtained.

3. Reference

(1) X. Luo, J. Yuan, C.-D. Yue, Z.-Y. Zhang, J. Chen, G.-A. Yu and C.-M. Che, *Org. Lett.*, 2018, **20**, 1810-1814.

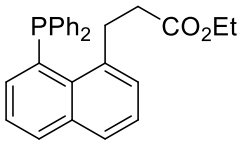
(2) J.-W. Li, L.-N. Wang, M. Li, P.-T. Tang, N.-J. Zhang, T. Li, Y.-J. Liu and M.-H. Zeng, *Org. Lett.*, 2020, **22** , 1331-1335.

(3) Y.-L.-T. Fu, C.-H. Chen, M.-G. Huang, J.-Y. Tao, X. Peng, H.-B. Xu, Y.-J. Liu and M.-H. Zeng ACS Catal., DOI: 10.1021/acscatal.2c00839

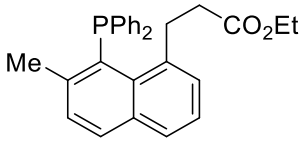
(4) J.-W. Li, L.-N. Wang, M. Li, P.-T. Tang, X.-P. Luo, M. Kurmoo, Y.-J. Liu and M.-H. Zeng, *Org. Lett*., 2019, **21**, 2885-2889

(5) H. Li; Y.-L. Zhong, C.-Y. Chen, A.-E. Ferraro and Wang D., *Org. Lett*., 2015, **17** , 3616-3619.

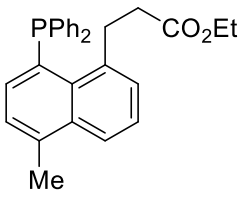
4. Characterization Data



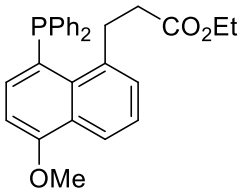
ethyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3aa): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Ethyl Acrylate **2a** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3aa** (71.7 mg, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78-7.71 (m, 1H), 7.41-7.35 (m, 2H), 7.32-7.28 (m, 7H), 7.25-7.19 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.82-3.73 (m, 2H), 2.85-2.78 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 138.6 (d, *J* = 1.9 Hz), 137.9 (d, *J* = 12.8 Hz), 136.3, 135.6 (d, *J* = 5.5 Hz), 134.9 (d, *J* = 20.3 Hz), 134.0 (d, *J* = 20.3 Hz), 133.7 (d, *J* = 28.6 Hz), 131.4, 128.9 (d, *J* = 1.8 Hz), 128.6, 128.6 (d, *J* = 10.6 Hz), 125.4, 124.7, 60.1, 37.6 (d, *J* = 15.6 Hz), 32.9 (d, *J* = 28.2 Hz), 14.2.^{31}P NMR (162 MHz, $CDCl_3$) δ -2.50. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{27}H_{26}O_2P$): 413.1665, found: 413.1665.



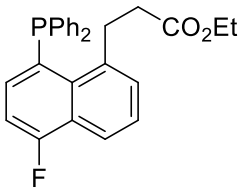
ethyl 3-(8-(diphenylphosphaneyl)-7-methylnaphthalen-1-yl)propanoate (3ba): The representative procedure **2.1** was followed, using (2-methylnaphthalen-1-yl)diphenylphosphane **1b** (85.2 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ba** (31.5 mg, 37%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.72-7.68 (m, 1H), 7.43-7.33 (m, 6H), 7.32-7.26 (m, 5H), 7.25-7.22 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.60-3.47 (m, 2H), 2.86-2.76 (m, 2H), 1.93 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 146.6 (d, *J* = 3.1 Hz), 139.5 (d, *J* = 32.1 Hz), 138.7 (d, *J* = 3.4 Hz), 137.1 (d, *J* = 16.6 Hz), 133.3, 133.2, 131.9 (d, *J* = 1.8 Hz), 131.5 (d, *J* = 18.1 Hz), 130.0, 129.7 (d, *J* = 1.5 Hz), 128.4, 128.3 (d, *J* = 5.0 Hz), 128.2, 127.7 (d, *J* = 1.6 Hz), 127.4, 124.8, 60.0, 37.5 (d, *J* = 14.2 Hz), 32.9 (d, *J* = 29.1 Hz), 24.9 (d, *J* = 1.9 Hz), 14.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ -5.95. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{28}O_2P$): 427.1821, found: 427.1821.



ethyl 3-(8-(diphenylphosphaneyl)-5-methylnaphthalen-1-yl)propanoate (3da): The representative procedure **2.1** was followed, using (4-methylnaphthalen-1-yl)diphenylphosphane **1d** (85.2 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3da** (49.1 mg, 58%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.48-7.37 (m, 2H), 7.34-7.27 (m, 6H), 7.27-7.18 (m, 6H), 7.20-7.08 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), , 3.83-3.72 (m, 2H), 2.86-2.77 (m, 2H), 2.69 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 139.2 (d, *J* = 2.1 Hz), 138.2 (d, *J* = 13.1 Hz), 136.9, 136.2, 135.1 (d, *J* = 20.4 Hz), 134.6 (d, *J* = 5.5 Hz), 133.9 (d, *J* = 20.2 Hz), 131.4 (d, *J* = 27.6 Hz), 130.0, 128.5, 128.5 (d, *J* = 6.8 Hz), 126.2, 125.3, 124.2, 60.2, 37.6 (d, *J* = 16.0 Hz), 33.1 (d, *J* = 29.1 Hz), 20.8, 14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.19. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{28}O_2P$): 427.1821, found: 427.1820.

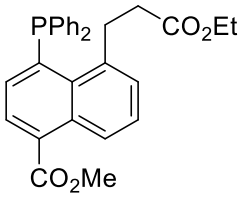


ethyl 3-(8-(diphenylphosphaneyl)-5-methoxynaphthalen-1-yl)propanoate (3ea): The representative procedure **2.1** was followed, using (4-methoxynaphthalen-1-yl)diphenylphosphane **1e** (88.4 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ea** (61.9 mg, 70 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.27 (m, 1H), 7.42-7.37 (m, 2H), 7.35-7.27 (m, 6H), 7.26-7.21 (m, 4H), 7.15 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.97 (s, 3H), 3.83-3.72 (m, 2H), 2.87-2.75 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 156.9, 138.5 (d, *J* = 13.4 Hz), 138.4, 137.1, 135.8, 133.8 (d, *J* = 20.2 Hz), 130.8, 128.5 (d, *J* = 8.8 Hz), 128.4, 127.6 (d, *J* = 6.0 Hz), 124.8, 124.1, 123.8, 121.7, 103.4, 60.1, 55.5, 37.6 (d, *J* = 16.0 Hz), 32.9 (d, *J* = 29.0 Hz), 29.7, 14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.47. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{28}O_3P$): 443.1771, found: 443.1771.

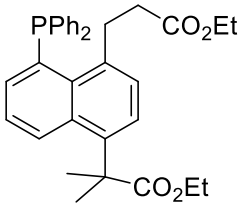


ethyl 3-(8-(diphenylphosphaneyl)-5-fluoronaphthalen-1-yl)propanoate (3fa): The representative procedure **2.1** was followed, using (4-fluoronaphthalen-1-yl)diphenylphosphane **1f** (66.0 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3fa** (38.7 mg, 45 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.50-7.41 (m, 2H), 7.35-7.29 (m, 6H), 7.25-7.13 (m, 5H), 7.02-6.97 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.83-3.72 (m, 2H), 2.86-2.76 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9,

161.4, 158.8, 138.8, 138.8 (d, *J* = 4.9 Hz), 137.7 (d, *J* = 13.0 Hz), 136.4 (dd), 136.2 (d, *J* = 8.9 Hz), 133.9 (d, *J* = 20.4 Hz), 131.2, 129.3 (dd, *J* = 28.7, 4.6 Hz), 128.7 (d, *J* = 14.3 Hz), 128.7, 125.8 (d, *J* = 2.2 Hz), 125.7 (d, *J* = 5.9 Hz), 120.4 (d, *J* = 9.5 Hz), 108.6 (d, *J* = 19.6 Hz), 60.2, 37.5 (d, *J* = 15.7 Hz), 32.8 (d, *J* = 28.7 Hz), 14.3.^{31}P NMR (162 MHz, $CDCl_3$) -3.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.36. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{27}H_{25}FO_2P$): 431.1571, found: 431.1571.

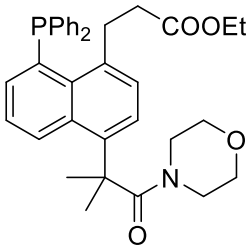


methyl 4-(diphenylphosphaneyl)-5-(3-ethoxy-3-oxopropyl)-1-naphthoate (3ga): The representative procedure **2.1** was followed, using methyl 4-(diphenylphosphaneyl)-1-naphthoate **1g** (74.0 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ga** (56.4 mg, 60 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dt, *J* = 8.8, 1.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.51-7.46 (m, 1H), 7.41-7.38 (m, 1H), 7.37-7.28 (m, 6H), 7.24-7.16 (m, 5H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.98 (s, 3H), 3.83-3.74 (m, 2H), 2.81-2.72 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 168.7, 140.0, 139.7, 138.9 (d, *J* = 2.1 Hz), 137.2 (d, *J* = 12.6 Hz), 135.2 (d, *J* = 18.7 Hz), 134.5, 134.1 (d, *J* = 20.5 Hz), 132.6 (d, *J* = 4.6 Hz), 130.5, 130.3, 129.0, 128.7 (d, *J* = 7.0 Hz), 127.2, 126.8, 125.5, 60.2, 52.4, 37.4 (d, *J* = 14.9 Hz), 33.2 (d, *J* = 29.0 Hz), 29.7, 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -0.54. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{28}O_4P$): 471.1720, found: 471.1720.

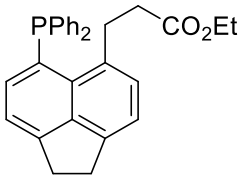


ethyl 2-(5-(diphenylphosphaneyl)-4-(3-ethoxy-3-oxopropyl)naphthalen-1-yl)-2-methylpropanoate (3ha): The representative procedure **2.1** was followed, using ethyl 2-(4-(diphenylphosphaneyl)naphthalen-1-yl)-2-methylpropanoate **1h** (85.2 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/10) yielded **3ha** (56.8 mg, 54 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36-7.27 (m, 7H), 7.26-7.18 (m, 6H), 4.14-4.06 (m, 2H), 3.82-3.73 (m, 2H), 2.88-2.79 (m, 1H), 1.75 (s, 6H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 173.1, 140.6 (d, *J* = 1.8 Hz), 138.1 (d, *J* = 13.3 Hz), 137.9, 136.2 (d, *J* = 20.5 Hz), 135.8, 134.6 (d, *J* = 29.0 Hz), 133.9 (d, *J* = 20.3 Hz), 133.0 (d, *J* = 5.5 Hz), 129.5, 128.6, 128.5 (d, *J* = 10.2 Hz), 126.7, 124.3, 122.8, 60.9, 60.2, 46.5, 37.3 (d, *J* = 15.8 Hz), 33.1 (d, *J* = 30.0 Hz), 27.9, 14.2, 13.9. ^{31}P NMR (162

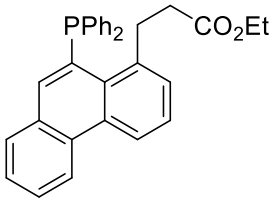
MHz, $CDCl_3$) δ -1.35. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{33}H_{36}O_4P$): 527.2346, found: 527.2347.



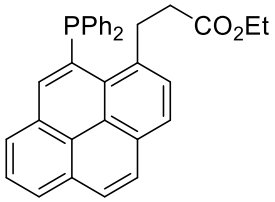
ethyl 3-(8-(diphenylphosphaneyl)-4-(2-methyl-1-morpholino-1-oxopropan-2-yl)naphthalen-1-yl)propanoate (3ia): The representative procedure **2.1** was followed, using 2-(5-(diphenylphosphaneyl)naphthalen-1-yl)-2-methyl-1-morpholinopropan-1-one **1i** (93.4 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/5) yielded **3ia** (59.1 mg, 52 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.46-7.41 (m, 1H), 7.36-7.2 3 (m, 11H), 7.19-7.09 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.02-3.85 (m, 2H), 3.74-3.53 (m, 2H), 3.38-3.20 (m, 2H), 3.01-2.64 (m, 5H), 2.23-2.08 (m, 1H), 1.74 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 172.9, 142.2 (d, *J* = 1.6 Hz), 138.1 (d, *J* = 1.6 Hz), 137.8 (d, *J* = 12.9 Hz), 137.5 (d, *J* = 13.5 Hz), 136.0, 135.9, 135.7, 135.2, 134.9, 134.2, 134.0 (d, *J* = 6.6 Hz), 133.7, 132.7 (d, *J* = 5.0 Hz), 130.1, 128.8, 128.6, 128.6 (d, *J* = 15.5 Hz), 127.2, 124.5, 121.3, 66.8, 65.3, 60.2, 46.7, 43.2, 37.2 (d, *J* = 15.4 Hz), 33.2 (d, *J* = 30.4 Hz), 30.6, 26.8, 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.06. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{35}H_{39}NO_4P$): 568.2617, found: 568.2619.



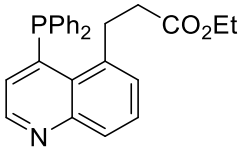
ethyl 3-(6-(diphenylphosphaneyl)-1,2-dihydroacenaphthylen-5-yl)propanoate (3ja): The representative procedure **2.1** was followed, using (1,2-dihydroacenaphthylen-5-yl)diphenylphosphane **1j** (67.6 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ja** (52.6 mg, 60 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 7H), 7.27-7.21 (m, 5H), 7.15-7.11 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.72-3.63 (m, 2H), 3.35 (s, 4H), 2.82-2.73 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 148.9, 145.6 (d, *J* = 2.0 Hz), 140.6 (d, *J* = 6.9 Hz), 138.1 (d, *J* = 12.4 Hz), 137.4, 134.7 (d, *J* = 2.0 Hz), 133.9 (d, *J* = 20.0 Hz), 133.5 (d, *J* = 22.3 Hz), 131.4, 128.8 (d, *J* = 25.4 Hz), 128.5, 128.5, 119.7, 119.3, 60.1, 37.7 (d, *J* = 14.5 Hz), 31.6 (d, *J* = 24.5 Hz), 29.9 (d, *J* = 34.2 Hz), 14.3.^{31}P NMR (162 MHz, $CDCl_3$) δ -6.61. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{28}O_2P$): 439.1821, found: 439.1823.



ethyl 3-(10-(diphenylphosphaneyl)phenanthren-1-yl)propanoate (3ka): The representative procedure **2.1** was followed, using (4b,5-dihydrophenanthren-9-yl)diphenylphosphane **1k** (72.8 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ka** (73.9 mg, 80 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 7.66-7.61 (m, 1H), 7.59-7.54 (m, 1H), 7.53-7.44 (m, 4H), 7.40-7.26 (m, 10H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.89-3.72 (m, 2H), 2.90-2.73 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 139.4 (d, *J* = 2.0 Hz), 138.2, 137.6 (d, *J* = 12.7 Hz), 134.1 (d, *J* = 20.4 Hz), 132.8 (d, *J* = 19.2 Hz), 132.4 (d, *J* = 29.6 Hz), 132.0 (d, *J* = 5.2 Hz), 131.2, 130.8, 130.4, 128.8, 128.6 (d, *J* = 6.9 Hz), 128.5, 127.6, 126.6, 126.1, 122.8, 122.2 (d, *J* = 1.6 Hz), 60.2, 37.7 (d, *J* = 14.9 Hz), 33.1 (d, *J* = 28.7 Hz), 14.2.^{31}P NMR (162 MHz, $CDCl_3$) δ -0.79. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{31}H_{28}O_2P$): 463.1821, found: 463.1822.

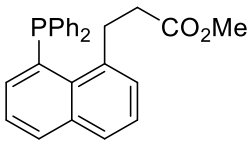


ethyl 3-(10-(diphenylphosphaneyl)pyren-1-yl)propanoate (3la): The representative procedure **2.1** was followed, using (3a1,8-dihydropyren-4-yl)diphenylphosphane **1l** (77.6 mg, 0.2 mmol) and Ethyl acrylate **2a** (80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3la** (68.1 mg, 70 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.04 (m, 3H), 8.05-7.92 (m, 4H), 7.79-7.70 (m, 1H), 7.37-7.27 (m, 6H), 7.29-7.20 (m, 4H), 4.15-4.04 (m, 4H), 3.04-2.85 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.22, 138.28 (d, *J* = 13.1 Hz), 137.69 (d, *J* = 2.0 Hz), 134.69 (d, *J* = 21.2 Hz), 134.48, 133.97 (d, *J* = 20.2 Hz), 132.40, 131.36 (d, *J* = 28.3 Hz), 131.23, 131.02, 130.55, 128.71, 128.66 (d, *J* = 7.1 Hz), 128.09, 127.82, 126.75 (d, *J* = 6.1 Hz), 126.14, 125.26, 125.09, 124.81, 124.03 (d, *J* = 2.0 Hz), 60.28, 36.96 (d, *J* = 16.2 Hz), 33.92 (d, *J* = 31.3 Hz), 14.29. ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.82. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{33}H_{28}O_2P$): 487.1821, found: 487.1821.

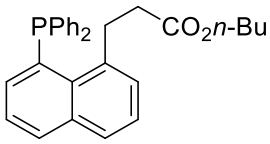


ethyl 3-(4-(diphenylphosphaneyl)quinolin-5-yl)propanoate (3ma): The representative procedure **2.1** was followed, using 5-(diphenylphosphaneyl)quinoline **1m** (62.6 mg, 0.2 mmol) and Ethyl acrylate **2a**

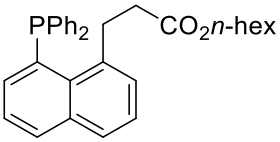
(80.1 mg, 0.8 mmol). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ma** (63.6 mg, 77 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.09-8.00 (m, 1H), 7.64-7.58 (m, 1H), 7.42-7.31 (m, 7H), 7.25-7.18 (m, 4H), 6.96 (t, *J* = 4.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.75-3.67 (m, 2H), 2.78-2.70 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 149.7 (d, *J* = 3.5 Hz), 148.6, 145.8 (d, *J* = 34.6 Hz), 138.8 (d, *J* = 2.3 Hz), 135.8 (d, *J* = 11.2 Hz), 134.2 (d, *J* = 20.7 Hz), 130.2 (d, *J* = 2.0 Hz), 130.0, 129.6 (d, *J* = 16.3 Hz), 129.4, 128.9 (d, *J* = 7.2 Hz), 128.8, 128.3, 60.3, 37.3 (d, *J* = 13.4 Hz), 32.2 (d, *J* = 25.9 Hz), 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.25. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{26}H_{25}NO_2P$): 414.1617, found: 414.1618.



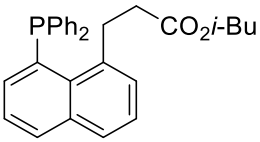
methyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ab): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Methyl acrylate **2b** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ab** (63.7 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77-7.74 (m, 1H), 7.41-7.34 (m, 2H), 7.33-7.26 (m, 7H), 7.24-7.19 (m, 5H), 3.80-3.73 (m, 2H), 3.64 (s, 3H), 2.85-2.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 138.6 (d, *J* = 1.9 Hz), 137.9 (d, *J* = 12.7 Hz), 136.3, 135.6 (d, *J* = 5.6 Hz), 134.9 (d, *J* = 20.5 Hz), 134.0 (d, *J* = 20.2 Hz), 133.8, 133.5, 131.4, 130.2, 129.0 (d, *J* = 1.9 Hz), 128.6, 128.6 (d, *J* = 11.2 Hz), 125.4, 124.8, 51.4, 37.3 (d, *J* = 15.6 Hz), 32.9 (d, *J* = 28.1 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -2.56.. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{26}H_{23}O_2P$): 399.1508, found: 399.1508.



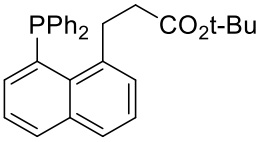
butyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ac): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Butyl Acrylate **2c** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ac** (61.6 mg, 70%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.83 (dd, *J* = 8, 1.6 Hz, 1H), 7.78-7.72 (m, 1H), 7.42-7.34 (m, 2H), 7.34-7.26 (m, 7H), 7.25-7.18 (m, 5H), 4.06 (t, *J* = 6.8 Hz, 2H), 3.83-3.72 (m, 2H), 2.88-2.77 (m, 2H), 1.59-1.51 (m, 2H), 1.37-1.28 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 138.7 (d, *J* = 1.9 Hz), 137.9 (d, *J* = 12.9 Hz), 136.2, 135.6 (d, *J* = 5.5 Hz), 134.9 (d, *J* = 20.2 Hz), 134.0 (d, *J* = 20.3 Hz), 133.7 (d, *J* = 28.7 Hz), 131.4, 130.2, 128.9 (d, *J* = 1.8 Hz), 128.6, 128.6 (d, *J* = 10.6 Hz), 64.4, 37.6 (d, *J* = 15.7 Hz), 32.9 (d, *J* = 28.3 Hz), 31.4, 28.6, 25.6, 22.5, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.43. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{34}H_{30}OP$): 441.1978, found: 441.1979.



hexyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ad): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Hexyl acrylate **2d** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ad** (77.7 mg, 83%) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.71 (m, 1H), 7.42-7.34 (m, 2H), 7.34-7.25 (m, 7H), 7.25-7.19 (m, 5H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.85-3.72 (m, 2H), 2.88-2.76 (m, 2H), 1.60-1.52 (m, 2H), 1.31-1.23 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.22, 138.73 (d, *J* = 2 Hz), 137.98 (d, *J* = 13.1Hz), 136.28, 135.63 (d, *J* = 5.1 Hz), 134.96 (d, *J* = 20.2 Hz), 134.04 (d, *J* = 23.2 Hz), 133.77 (d, *J* = 29.2 Hz), 131.43, 130.28, 128.97 (d, *J* = 2 Hz), 128.64, 128.63 (d, *J* = 11.1 Hz), 64.46, 37.64 (d, *J* = 16.2 Hz), 33.00 (d, *J* = 28.3 Hz), 31.50, 28.67, 25.65, 22.56, 14.06. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.44. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{31}H_{34}O_2P$): 469.2291, found: 469.2291.

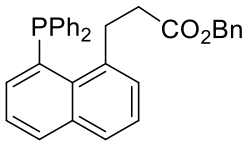


isobutyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ae): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Isobutyl acrylat **2e** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ae** (63.9 mg, 75%) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78-7.73 (m, 1H), 7.40-7.34 (m, 2H), 7.33-7.26 (m, 7H), 7.24-7.19 (m, 5H), 3.84 (d, *J* = 6.4 Hz, 2H), 3.82-3.74 (m, 2H), 2.87-2.78 (m, 2H), 1.93-1.83 (m, 1H), 0.89 (s, 3H), 0.87 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 138.7 (d, *J* = 1.9 Hz), 137.9 (d, *J* = 13.0 Hz), 136.2, 135.6 (d, *J* = 5.4 Hz), 134.9 (d, *J* = 20.3 Hz), 134.0 (d, *J* = 20.3 Hz), 133.7 (d, *J* = 28.8 Hz), 131.4, 130.2, 128.9 (d, *J* = 1.7 Hz), 128.6, 128.6 (d, *J* = 11.1 Hz), 125.4, 124.7, 70.4, 37.6 (d, *J* = 15.6 Hz), 33.0 (d, *J* = 28.3 Hz), 27.7, 19.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.46. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{30}O_2P$): 441.1978, found: 441.1978.

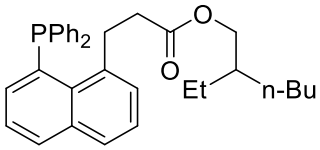


tert-butyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3af): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and tert-Butyl acrylate **2f** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3af** (44 mg, 50%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz,

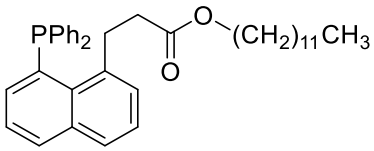
1H), 7.78-7.73 (m, 1H), 7.40-7.35 (m, 2H), 7.34-7.26 (m, 7H), 7.25-7.19 (m, 5H), 3.78-3.70 (m, 2H), 2.77-2.69 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 138.9 (d, *J* = 2.1 Hz), 138.1 (d, *J* = 13.4 Hz), 136.2, 135.5 (d, *J* = 5.5 Hz), 135.0 (d, *J* = 20.2 Hz), 134.0 (d, *J* = 20.4 Hz), 133.8 (d, *J* = 29.0 Hz), 131.3, 130.1, 128.8 (d, *J* = 1.8 Hz), 128.6, 128.5, 125.4, 124.7, 79.9, 38.7 (d, *J* = 15.2 Hz), 33.0 (d, *J* = 28.4 Hz), 28.1.^{31}P NMR (162 MHz, $CDCl_3$) δ -2.43. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{30}O_2P$): 441.1978, found: 441.1978.



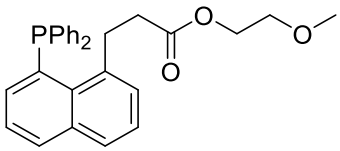
benzyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ag): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Benzylacrylate **2g** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ag** (42.7 mg, 45%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78-7.74 (m, 1H), 7.39-7.34 (m, 2H), 7.33-7.26 (m, 12H), 7.23-7.16 (m, 5H), 5.12 (s, 2H), 3.83-3.76 (m, 2H), 2.92-2.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 138.5 (d, *J* = 1.9 Hz), 137.8 (d, *J* = 12.7 Hz), 136.2, 136.2, 135.6 (d, *J* = 5.5 Hz), 134.8 (d, *J* = 20.2 Hz), 134.0 (d, *J* = 20.2 Hz), 133.7 (d, *J* = 28.6 Hz), 131.4, 130.3, 128.6 (d, *J* = 10.5 Hz), 128.5 (d, *J* = 16.6 Hz), 128.1, 128.0, 125.4, 124.7, 66.0, 37.6 (d, *J* = 16.0 Hz), 32.9 (d, *J* = 28.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.50. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{32}H_{28}O_2P$): 475.1821, found: 475.1821.



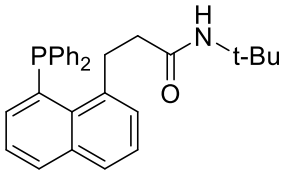
2-ethylhexyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ah): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and 2-Ethylhexyl acrylate **2h** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ag** (38.6 mg, 40%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.74 (m, 1H), 7.42-7.36 (m, 2H), 7.35-7.27 (m, 7H), 7.26-7.19 (m, 5H), 4.02-3.96 (m, 2H), 3.83-3.76 (m, 2H), 2.88-2.81 (m, 2H), 1.57-1.51 (m, 1H), 1.33-1.24 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 138.7 (d, *J* = 2.1 Hz), 137.9 (d, *J* = 13.0 Hz), 136.2, 135.6 (d, *J* = 5.6 Hz), 134.8 (d, *J* = 20.3 Hz), 134.0 (d, *J* = 20.4 Hz), 133.6, 131.4, 130.2, 128.9 (d, *J* = 1.8 Hz), 128.6, 128.6 (d, *J* = 10.9 Hz), 125.4, 124.7, 66.6, 38.7, 37.6 (d, *J* = 15.7 Hz), 33.0 (d, *J* = 28.2 Hz), 30.3, 28.9, 23.7, 22.9, 14.1, 11.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.37. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{33}H_{38}O_2P$): 497.2604, found: 497.2604.



dodecyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3ai): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and Dodecyl acrylate **2i** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3ai** (73.9 mg, 67%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78-7.74 (m, 1H), 7.42-7.34 (m, 2H), 7.34-7.25 (m, 7H), 7.25-7.19 (m, 5H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.83-3.72 (m, 2H), 2.88-2.77 (m, 2H), 1.60-1.54 (m, 2H), 1.24 (s, 16H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 138.7 (d, *J* = 2.1 Hz), 137.9 (d, *J* = 12.9 Hz), 136.2, 135.6 (d, *J* = 5.5 Hz), 134.9 (d, *J* = 20.3 Hz), 134.0 (d, *J* = 20.3 Hz), 133.7 (d, *J* = 28.6 Hz), 131.4, 130.2, 128.9 (d, *J* = 1.8 Hz), 128.6, 128.6 (d, *J* = 10.7 Hz), 125.4, 124.7, 64.4, 37.6 (d, *J* = 15.7 Hz), 32.9 (d, *J* = 28.0 Hz), 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.7, 25.9, 22.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.46. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{37}H_{46}O_2P$): 553.3230, found: 553.3230.

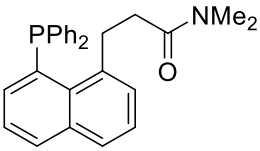


2-methoxyethyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3aj): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and 2-Methoxyethyl acrylate **2j** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3aj** (68.2 mg, 77%) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.74 (m, 1H), 7.41-7.35 (m, 2H), 7.34-7.27 (m, 7H), 7.25-7.18 (m, 5H), 4.25-4.19 (m, 2H), 3.82-3.74 (m, 2H), 3.59-3.53 (m, 2H), 3.35 (s, 3H), 2.91-2.84 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 138.5, 137.9 (d, *J* = 12.7 Hz), 136.2, 135.6, 134.9 (d, *J* = 20.1 Hz), 134.0 (d, *J* = 20.2 Hz), 133.7 (d, *J* = 28.8 Hz), 131.4, 130.3, 129.0, 128.6, 128.6 (d, *J* = 11.2 Hz), 125.4, 124.7, 70.5, 63.3, 59.0, 37.4 (d, *J* = 16.1 Hz), 32.8 (d, *J* = 28.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.49. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{28}O_3P$): 443.1771, found: 443.1770.

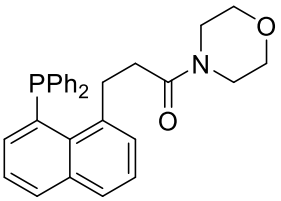


N-(tert-butyl)-3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanamide (3ak): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and N-tert-Butylacrylamide **2k** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/2) yielded **3ak** (29.0 mg, 33%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd,

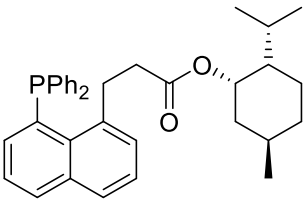
J = 8.0, 1.6 Hz, 1H), 7.81-7.76 (m, 1H), 7.41 (d, *J* = 4.0 Hz, 2H), 7.37-7.27 (m, 7H), 7.23-7.17 (m, 5H), 6.10 (s, 1H), 3.74-3.65 (m, 2H), 2.60-2.52 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 138.7 (d, *J* = 2.2 Hz), 137.3 (d, *J* = 9.7 Hz), 136.0, 135.6 (d, *J* = 5.5 Hz), 134.4 (d, *J* = 19.0 Hz), 133.8 (d, *J* = 20.0 Hz), 132.6 (d, *J* = 25.3 Hz), 131.7, 130.8, 128.9 (d, *J* = 16.5 Hz), 128.7, 125.7, 124.7, 50.9, 41.9 (d, *J* = 12.3 Hz), 35.2 (d, *J* = 25.7 Hz), 28.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.41.HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{31}NOP$): 440.2138, found: 440.2138.



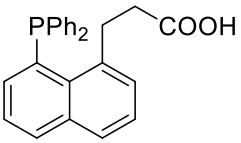
3-(8-(diphenylphosphaneyl)naphthalen-1-yl)-N,N-dimethylpropanamide (3al): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and N,N-Dimethylacrylamide **2k** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/2) yielded **3al** (35.4 mg, 43%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.74 (m, 1H), 7.43-7.38 (m, 2H), 7.34-7.27 (m, 7H), 7.26-7.20 (m, 5H), 3.90-3.82 (m, 2H), 2.91 (s, 3H), 2.74-2.66 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 139.7 (d, *J* = 1.8 Hz), 138.0 (d, *J* = 13.1 Hz), 136.4, 135.6 (d, *J* = 5.6 Hz), 135.0 (d, *J* = 20.3 Hz), 134.0 (d, *J* = 20.2 Hz), 133.7 (d, *J* = 28.6 Hz), 131.5, 130.6, 128.7 (d, *J* = 1.8 Hz), 128.6, 128.5, 125.5, 124.6, 37.0, 36.9 (d, *J* = 13.9 Hz), 35.3, 33.5 (d, *J* = 28.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.27. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{27}H_{27}NOP$): 412.1825, found: 412.1825.



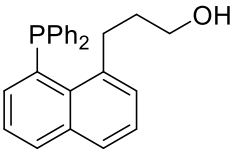
3-(8-(diphenylphosphaneyl)naphthalen-1-yl)-1-morpholinopropan-1-one (3am): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and 4-Acryloylmorpholine **2m** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/2) yielded **3am** (36.3 mg, 40%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81-7.74 (m, 1H), 7.43-7.37 (m, 2H), 7.36-7.27 (m, 7H), 7.25-7.15 (m, 5H), 3.93-3.83 (m, 2H), 3.58 (s, 4H), 3.32 (t, *J* = 4.8 Hz, 2H), 3.13 (t, *J* = 4.8 Hz, 2H), 2.77-2.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 139.2 (d, *J* = 1.9 Hz), 137.8 (d, *J* = 12.6 Hz), 136.4, 135.6 (d, *J* = 5.5 Hz), 134.9 (d, *J* = 20.1 Hz), 133.9 (d, *J* = 20.1 Hz), 133.5 (d, *J* = 28.1 Hz), 131.5, 130.8, 129.0 (d, *J* = 1.9 Hz), 128.7, 128.6 (d, *J* = 10.3 Hz), 125.6, 124.7, 66.6 (d, *J* = 45.0 Hz), 45.7, 41.8, 36.3 (d, *J* = 14.3 Hz), 33.6 (d, *J* = 28.1 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -3.15. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{29}NO_2P$): 454.1930, found: 454.1931.



(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl 3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoate (3n): The representative procedure **2.1** was followed, using 1-naphthalenyldiphenylphosphane **1a** (62.4 mg, 0.2 mmol) and (1S,2S,5S)-2-isopropyl-5-methylcyclohexyl acrylate **2n** (0.8 mmol, 4.0 equiv). Purification by prepared column chromatography (EA/hexane = 1/25) yielded **3an** (58.5 mg, 56%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.73 (m, 1H), 7.41-7.35 (m, 2H), 7.33-7.26 (m, 7H), 7.25-7.18 (m, 5H), 4.74-4.67 (m, 1H), 3.85-3.68 (m, 2H), 2.93-2.74 (m, 2H), 1.99-1.94 (m, 1H), 1.87-1.80 (m, 1H), 1.68-1.61 (m, 2H), 1.51-1.44 (m, 1H), 1.36-1.26 (m, 2H), 1.08-1.00 (m, 1H), 0.93-0.86 (m, 5H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 138.7 (d, *J* = 2.1 Hz), 138.2 (d, *J* = 13.5 Hz), 137.9 (d, *J* = 12.7 Hz), 136.1, 135.6 (d, *J* = 5.4 Hz), 134.9 (d, *J* = 20.0 Hz), 134.1 (d, *J* = 6.9 Hz), 133.9 (d, *J* = 7.0 Hz), 133.6, 131.4, 128.9 (d, *J* = 1.8 Hz), 128.6, 128.6, 128.5, 128.5, 128.5, 125.4, 124.7, 73.8, 47.0, 41.0, 37.8 (d, *J* = 16.5 Hz), 34.3, 33.0 (d, *J* = 28.0 Hz), 31.4, 26.0, 23.3, 22.0, 20.7, 16.2.^{31}P NMR (162 MHz, $CDCl_3$) δ -2.13. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{35}H_{40}O_2P$): 523.2766, found: 523.2769.

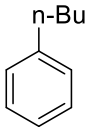


3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propanoic acid (4aa): Purification by prepared column chromatography (EA/hexane = 1/2) yielded **4aa** (167.5 mg, 87%) as a white solid. ^{1} H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80-7.72 (m, 1H), 7.44-7.32 (m, 2H), 7.36-7.24 (m, 8H), 7.27-7.18 (m, 6H), 3.83-3.73 (m, 2H), 2.94-2.83 (m, 2H). ^{13} C NMR (101 MHz, $CDCl_3$) δ 178.37, 138.22 (d, *J* = 1.9 Hz), 137.57 (d, *J* = 11.6 Hz), 136.33, 135.64 (d, *J* = 5.5 Hz), 134.81 (d, *J* = 20.1 Hz), 134.02 (d, *J* = 20.2 Hz), 133.43 (d, *J* = 27.5 Hz), 131.48, 130.31, 129.10 (d, *J* = 1.8 Hz), 128.75, 128.63 (d, *J* = 6.8 Hz), 125.48, 124.79, 37.36 (d, *J* = 15.8 Hz), 32.68 (d, *J* = 27.8 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -2.37.. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{22}O_2P$): 385.1357, found: 385.1359.

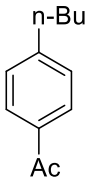


3-(8-(diphenylphosphaneyl)naphthalen-1-yl)propan-1-ol (5aa): Purification by prepared column chromatography (EA/hexane = 1/15) yielded **3aa** (183.6 mg, 99%) as a white solid. ^{1} H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76-7.70 (m, 1H), 7.40-7.27 (m, 8H), 7.26-7.17 (m, 6H), 3.71

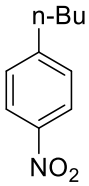
(t, *J* = 6.0 Hz, 2H), 3.57-3.48 (m, 2H), 2.14-2.00 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.03 (d, *J* = 2.2 Hz), 137.64 (d, *J* = 10.8 Hz), 136.17, 135.56 (d, *J* = 5.6 Hz), 134.90 (d, *J* = 19.4 Hz), 133.90 (d, *J* = 19.9 Hz), 133.17 (d, *J* = 26.3 Hz), 131.49, 130.09, 128.71, 128.60 (d, *J* = 6.9 Hz), 128.49 (d, *J* = 1.8 Hz), 125.44, 124.59, 62.66, 36.36 (d, *J* = 9.3 Hz), 34.27 (d, *J* = 26.9 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -1.73. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{24}OP$): 371.1565, found: 371.1567.



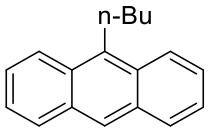
butylbenzene (8a): The representative procedure **2.3** was followed, using bromobenzene **6a** (155.9 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/100) yielded **8a** (128.6mg, 96 %) as a colorless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 2H), 7.19-7.12 (m, 3H), 2.63-2.57 (m, 2H), 1.64-1.55 (m, 2H), 1.40-1.30 (m, 2H), 0.92 (t, *J* = 6.8 Hz 3H).. HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O$): 177.1274, found: 177.1274.



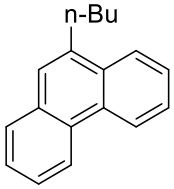
1-(4-butylphenyl)ethan-1-one (8b): The representative procedure **2.3** was followed, using 1-(4-bromophenyl)ethan-1-one **6b** (198.0 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/50) yielded **8b** (174.4 mg, 98 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.55 (s, 3H), 1.64-1.55 (m, 2H), 1.41-1.27 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H). HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O$): 177.1274, found: 177.1274.



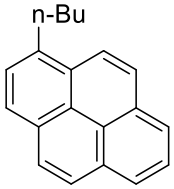
1-butyl-4-nitrobenzene (8c): The representative procedure **2.3** was followed, using 1-bromo-4-nitrobenzene **6c** (201.0 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/50) yielded **8c** (152.2 mg, 85 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 2.75-2.67 (m, 2H), 1.67-1.58 (m, 2H), 1.43-1.30 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{13}NO_2Na$): 202.0838 found: 202.0840.



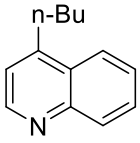
9-butylanthracene (8d): The representative procedure **2.3** was followed, using 9-bromoanthracene **6d** (256.0 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/100) yielded **8d** (231.7.0 mg, 99 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.20 (m, 3H), 7.99-7.91 (m, 2H), 7.53-7.38 (m, 4H), 3.65-3.52 (m, 2H), 1.89-1.76 (m, 2H), 1.64-1.53 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H). HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{19}$): 235.1481, found: 235.1482.



9-butylphenanthrene (8e): The representative procedure **2.3** was followed, using 9-bromophenanthrene **6e** (256.0 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/100) yielded **8e** (231.7.0 mg, 99 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91-8.84 (m, 1H), 8.82-8.77 (m, 1H), 8.33-8.24 (m, 1H), 8.01-7.94 (m, 1H), 7.83-7.77 (m, 2H), 7.77-7.68 (m, 3H), 3.31-3.21 (m, 2H), 2.02-1.93 (m, 2H), 1.73-1.63 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H)..HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{18}H_{19}$): 235.1481, found: 235.1482.



1-butylpyrene (8f): The representative procedure **2.3** was followed, using 1-bromopyrene **6f** (280.0 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/100) yielded **8f** (255.6 mg, 99 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51-8.41 (m, 1H), 8.51-8.41 (m, 1H), 8.37-8.29 (m, 2H), 8.29-8.22 (m, 2H), 8.21-8.12 (m, 3H), 8.05-7.99 (m, 1H), 3.57-3.44 (m, 2H), 2.12-2.00 (m, 2H), 1.80-1.68 (m, 2H), 1.32-1.21 (m, 3H). HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{20}H_{19}$): 259.1481, found: 235.1483.

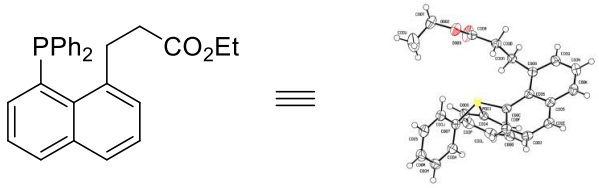


4-butylquinoline (8g): The representative procedure **2.3** was followed, using 4-bromoquinoline **6g** (206.9 mg, 1.0 mmol) and n-Butylboronic acid **7a** (132.5 mg, 1.3 mmol). Purification by prepared column chromatography (EA/hexane = 1/5) yielded **8g** (111.0 mg, 60 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 7.6Hz, 1H), 7.71-7.64 (m, 1H),

7.55-7.47 (m, 1H), 7.25-7.08 (m, 1H), 3.07-2.95 (m, 2H), 1.77-1.65 (m, 2H), 1.51-1.36 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). HRMS (ESI+) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}N$): 186.1277, found: 186.1277.

5. Crystallographic Data

X-ray data for 3aa

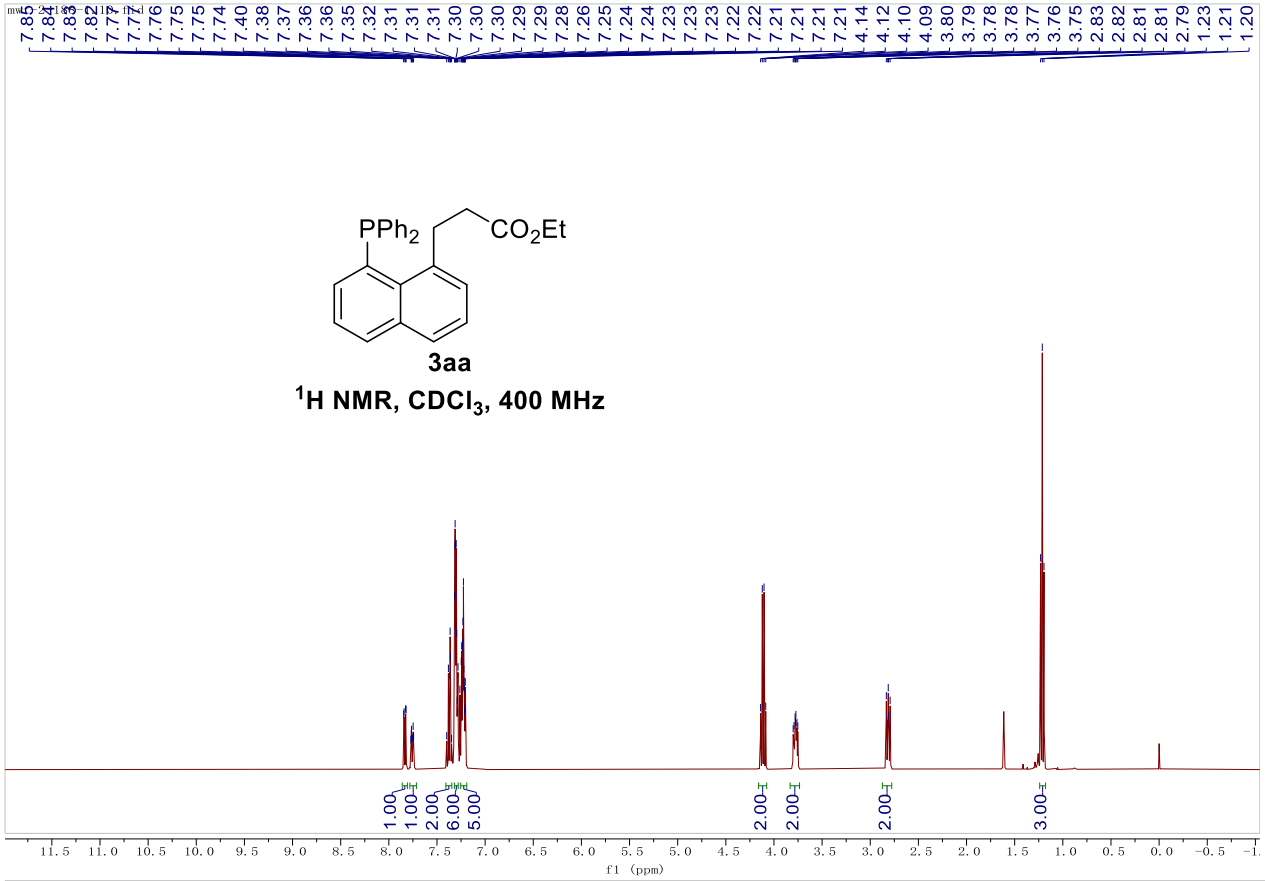


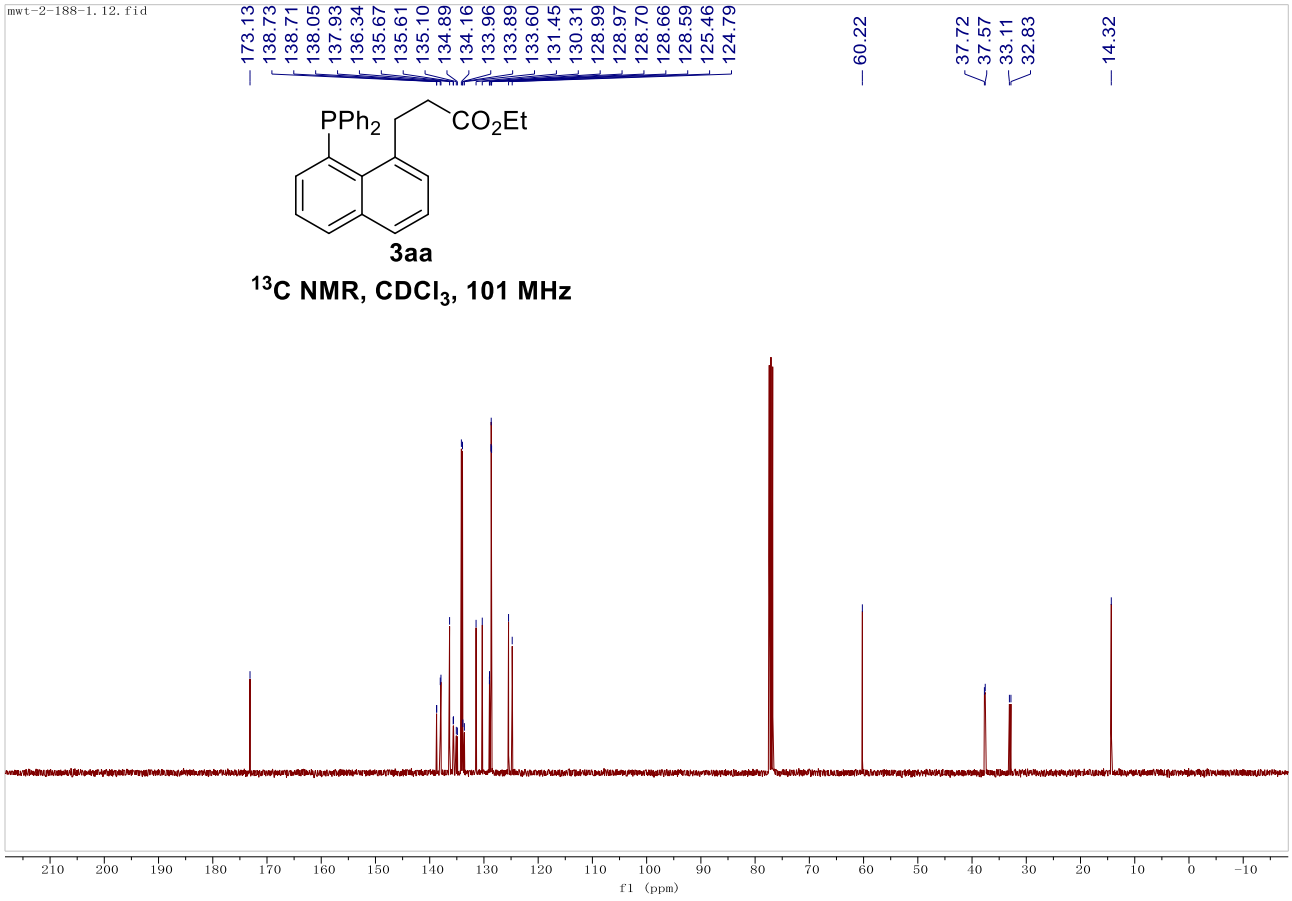
3aa **CCDC** 2156623

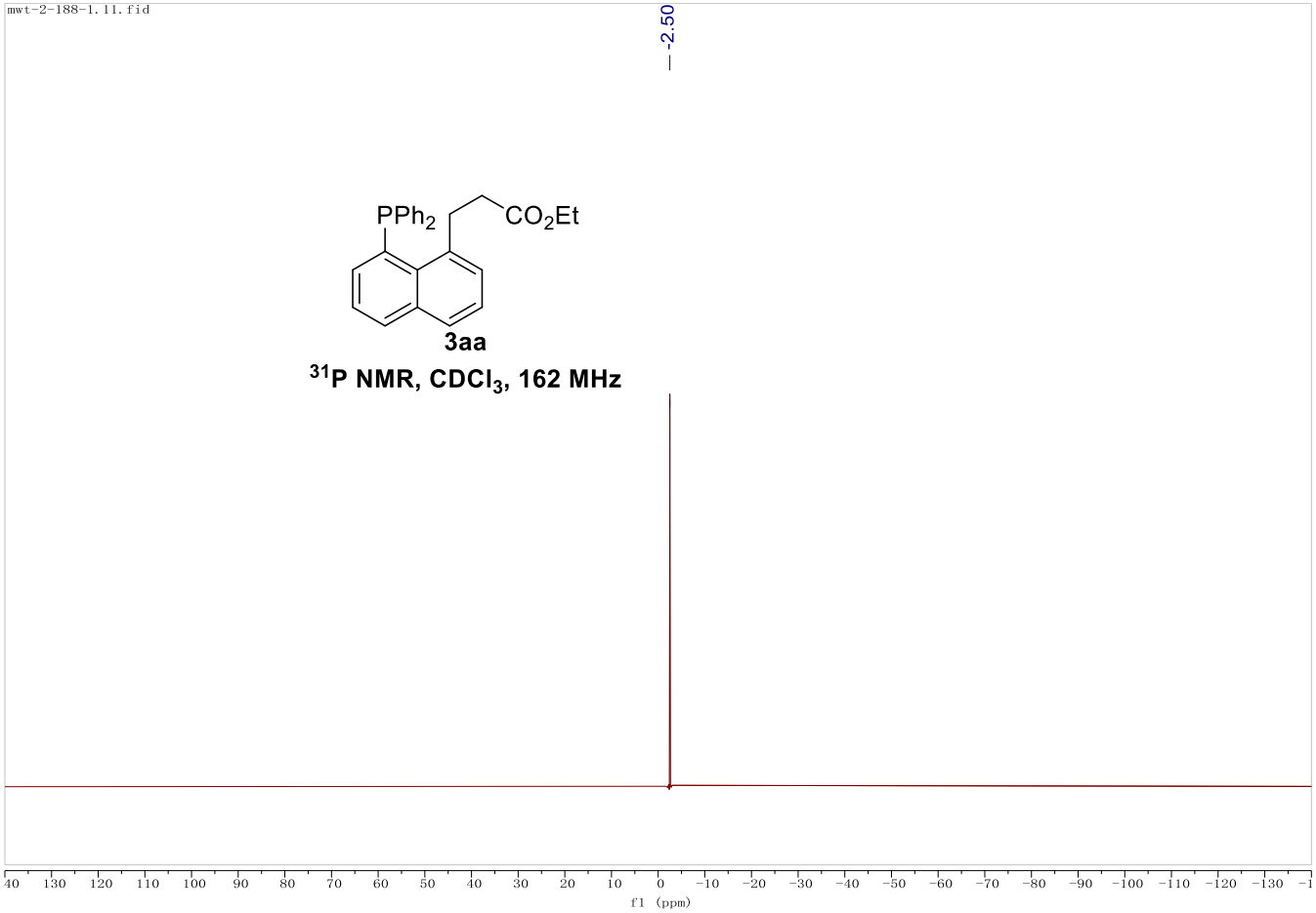
compound	**3aa**
formula	$C_{27}H_{25}O_2P$
formula weight	412.44
T (K)	100.01(10)
crystal system	triclinic
space group	P-1
a (Å)	9.3822(3)
b (Å)	10.1224(4)
c (Å)	13.1212(4)
α (°)	68.499(3)
β (°)	79.973(3)
γ (°)	73.741(3)
V (Å^3)	1109.47(7)
Z	2
D_c.(g cm^{-3})	1.235
μ (mm^{-1})	1.250
reflns coll.	22418
independent reflns	4302
R_{int}	0.0446
$^aR_1$ [I ≥ 2σ(I)]	0.0401
$^bwR_2$(all data)	0.1091
GOF	1.074

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

6. NMR Spectra



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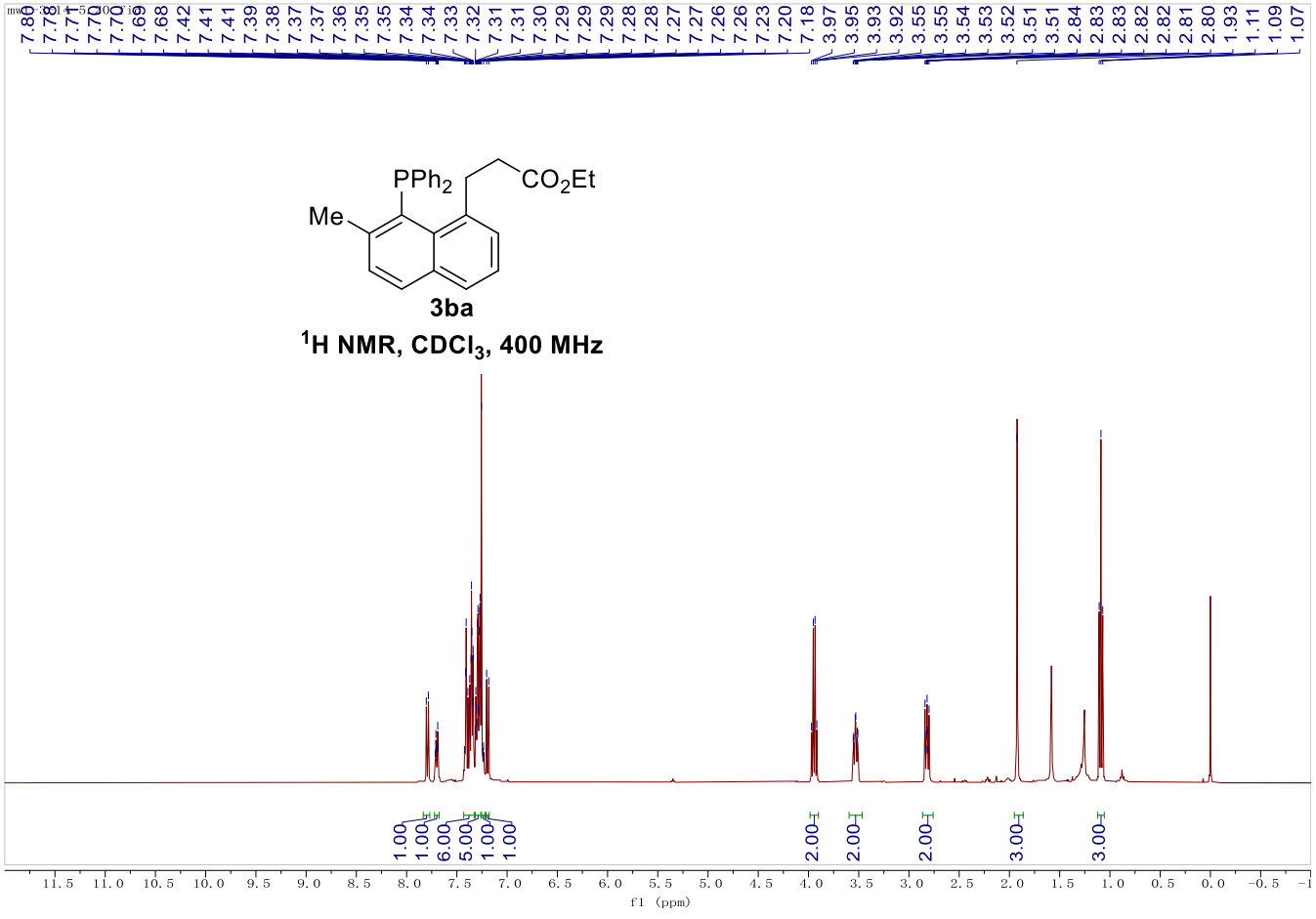
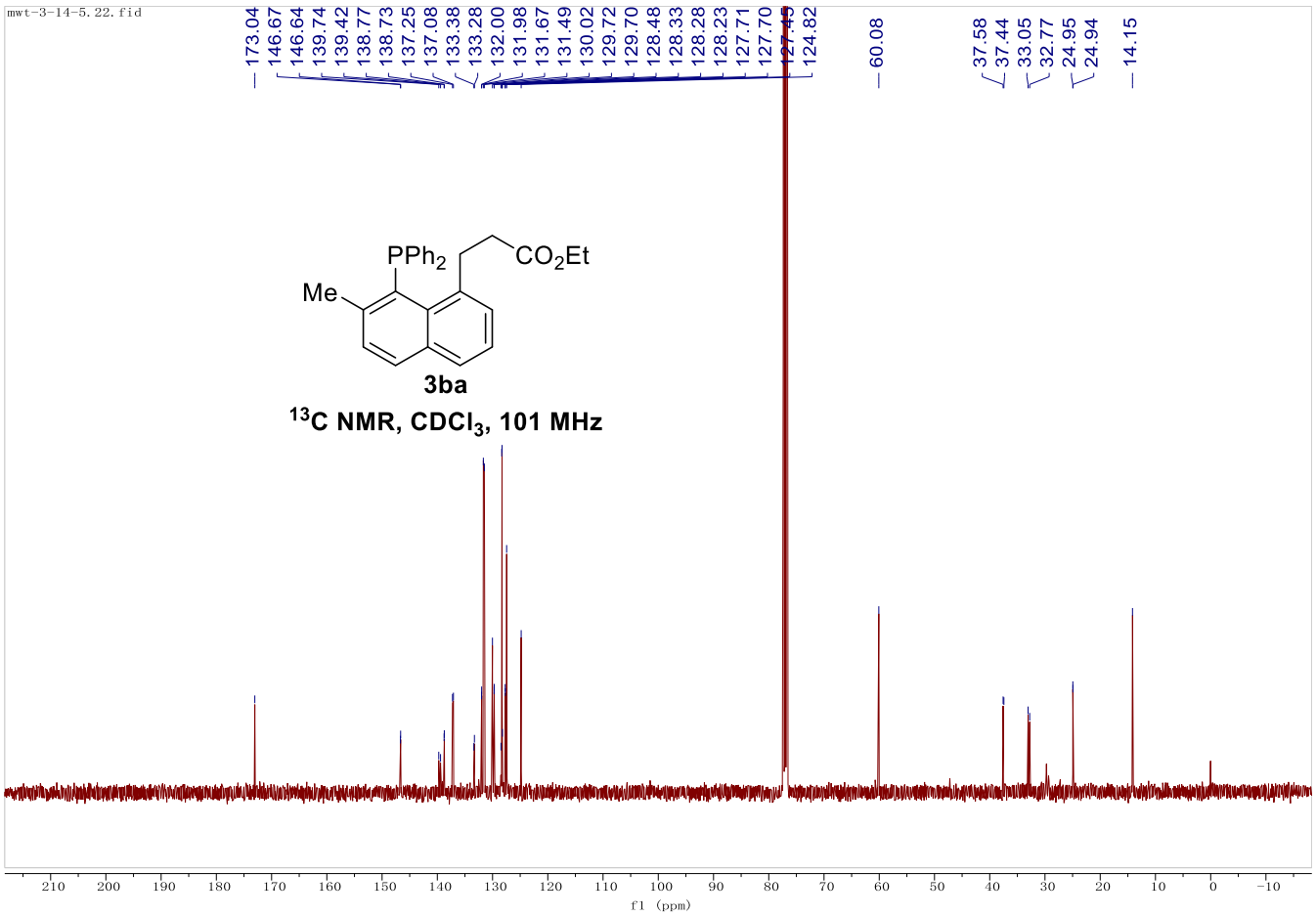
PPh2
CO2Et
3aa
31P NMR, CDCl3, 162 MHz
f1 (ppm)


PPh2
CO2Et
Me
3ba
1H NMR, CDCl3, 400 MHz
f1 (ppm)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173.04
146.67
146.64
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138.73
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133.38
133.28
132.00
131.98
131.67
131.49
130.02
129.72
129.70
128.48
128.33
128.28
128.23
127.71
127.70
127.45
124.82
60.08
37.58
37.44
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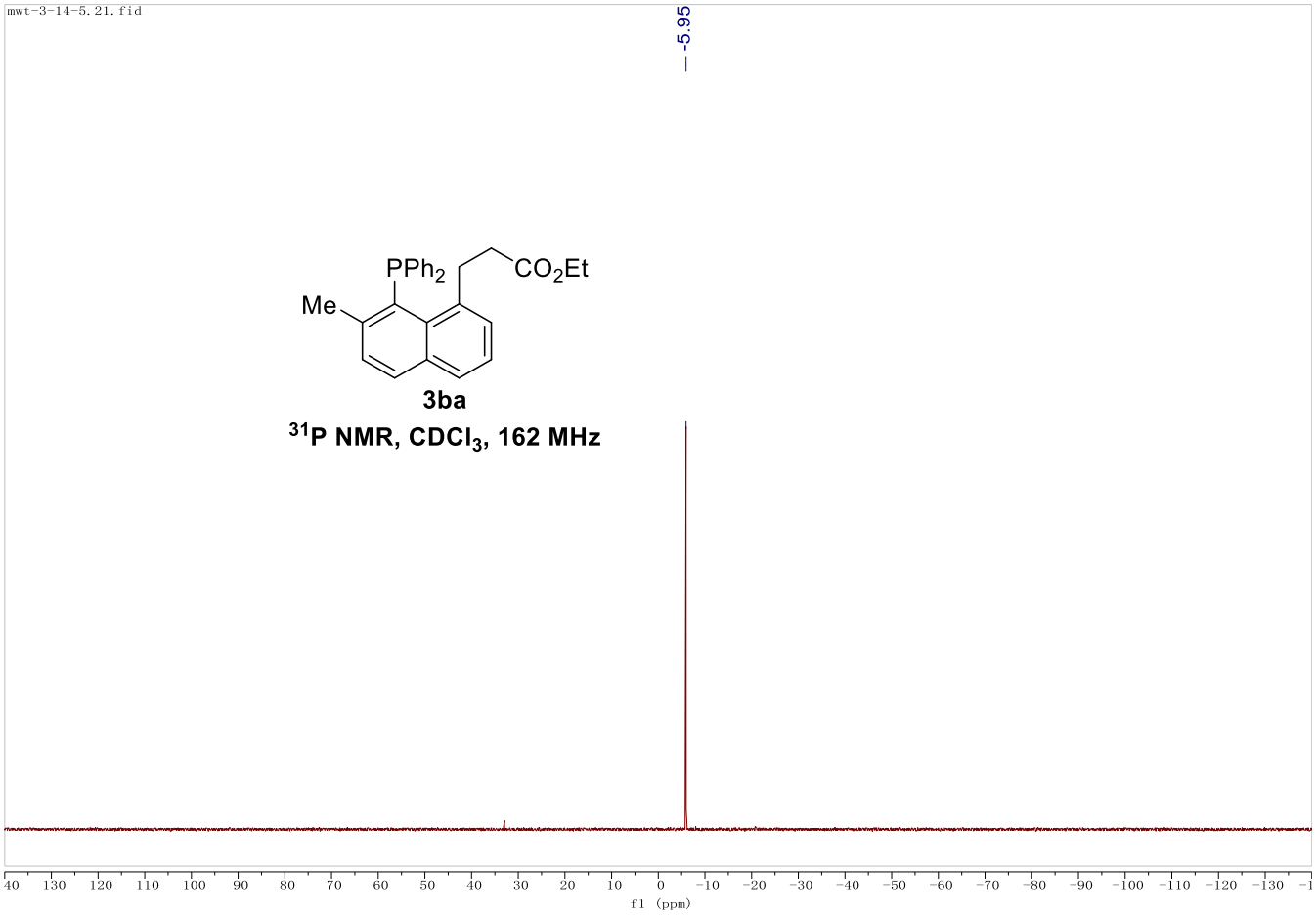
Me
3ba
13C NMR, CDCl3, 101 MHz
f1 (ppm)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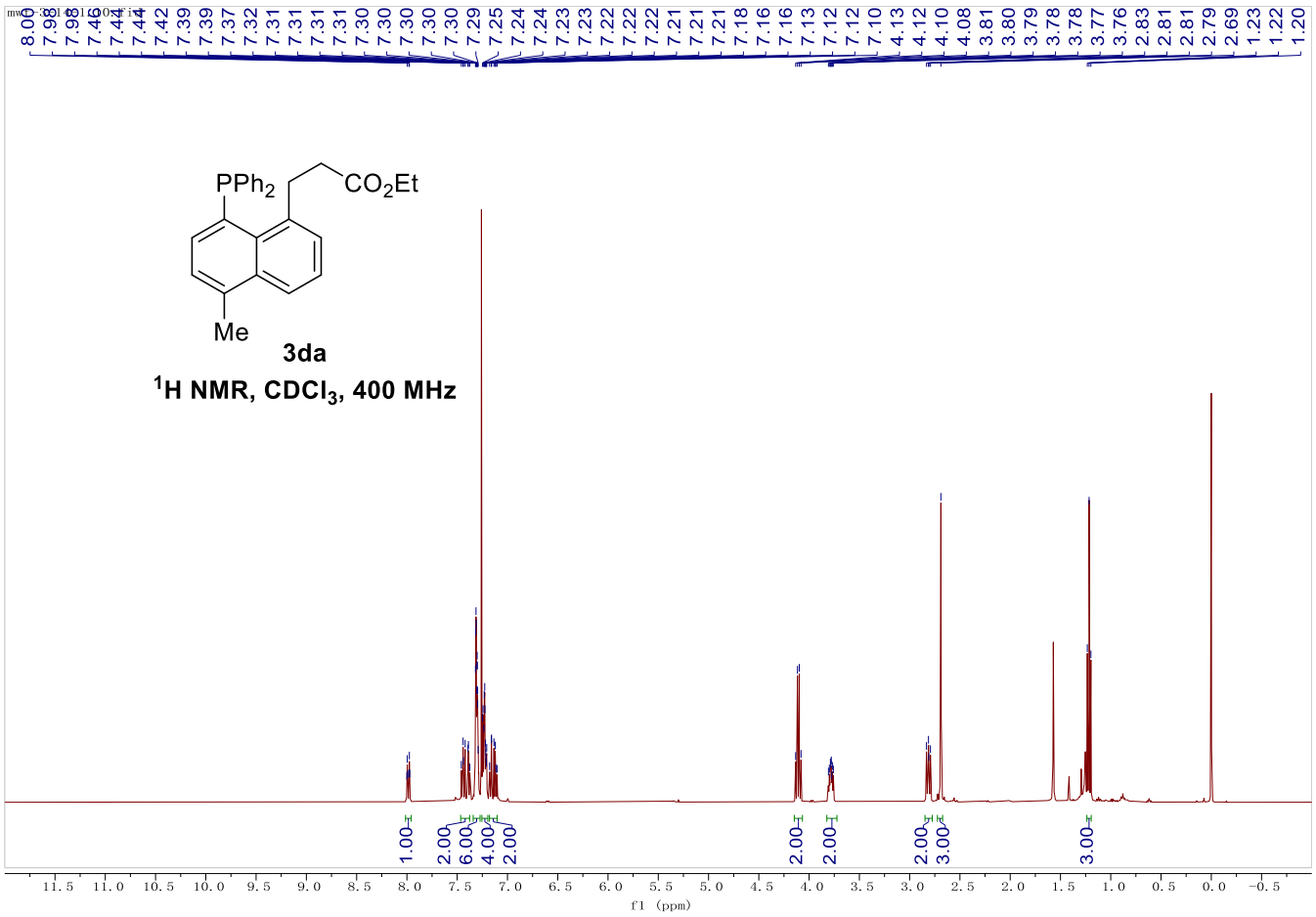
3ba
31P NMR, CDCl3, 162 MHz
f1 (ppm)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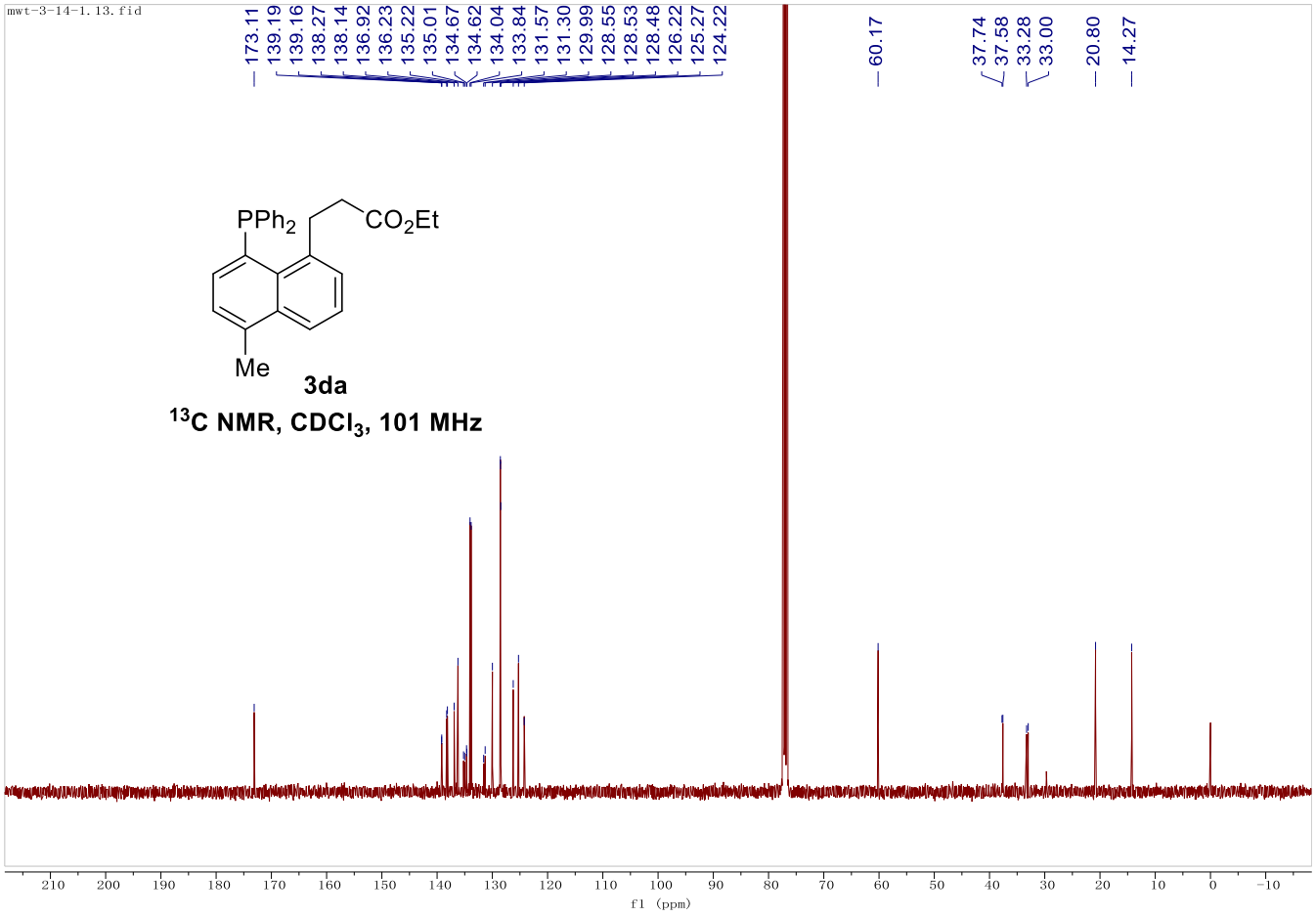
Me
3da
1H NMR, CDCl3, 400 MHz
f1 (ppm)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3da
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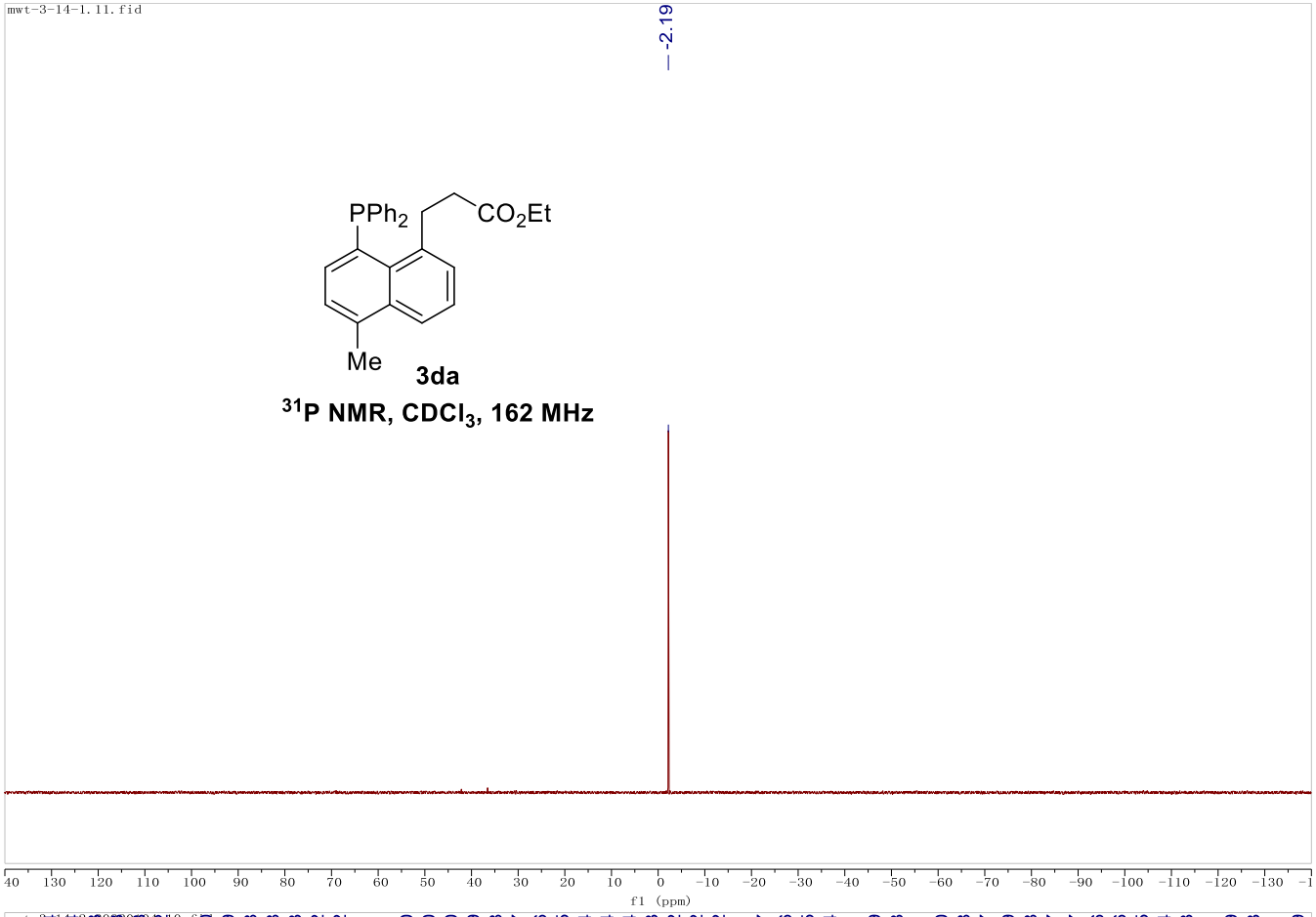
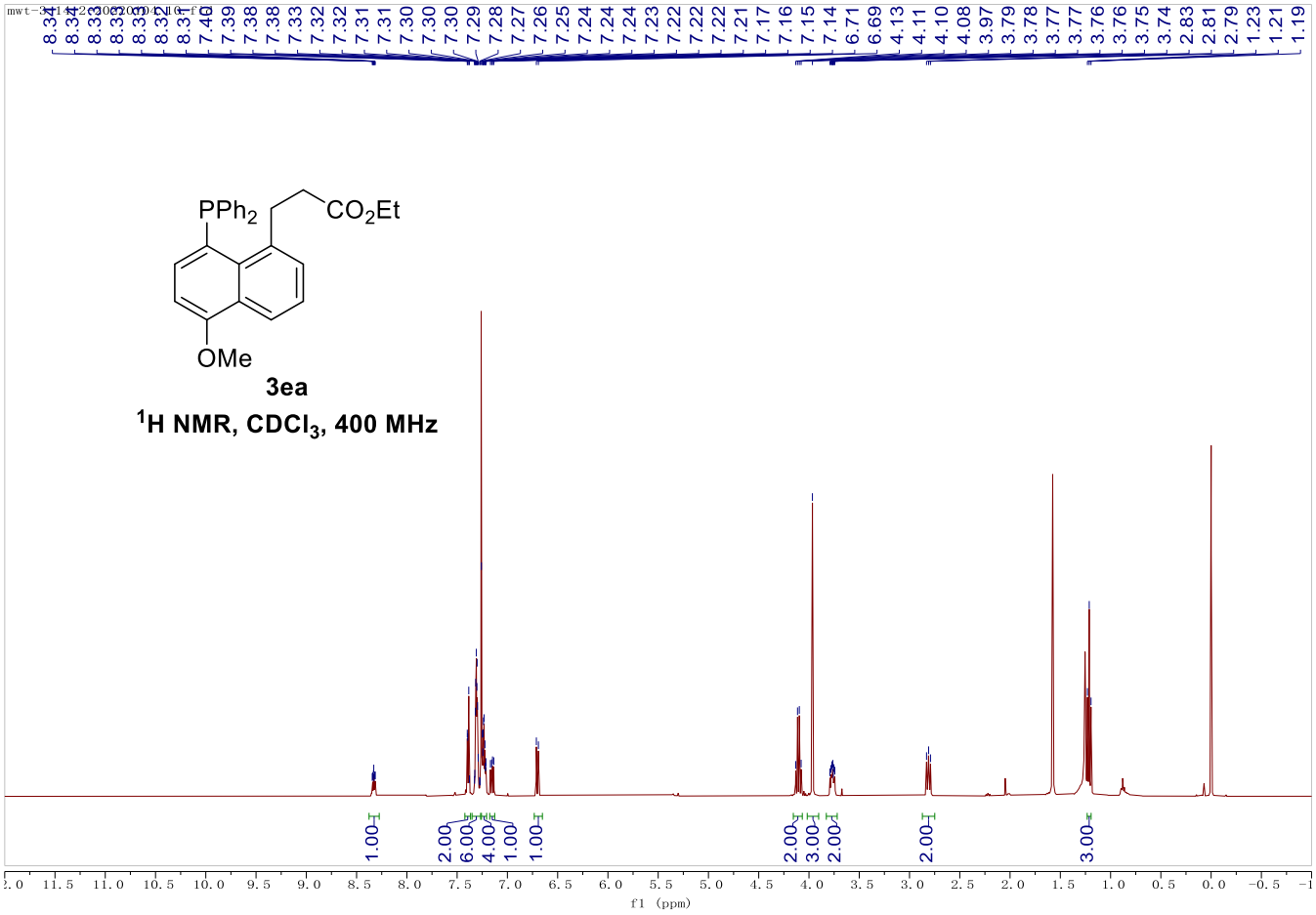
f1 (ppm)



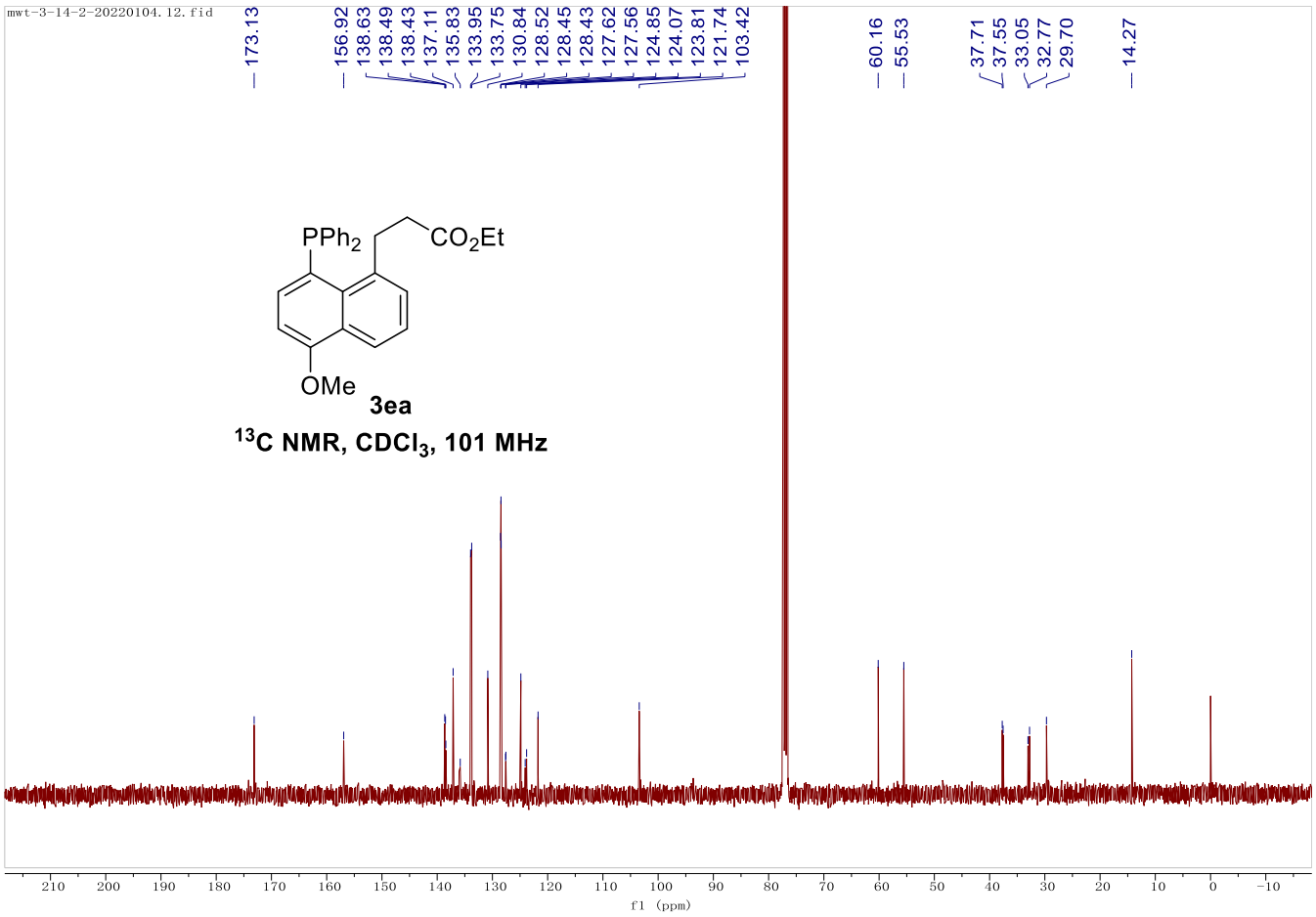
3da

^{31}P NMR, $CDCl_3$, 162 MHz



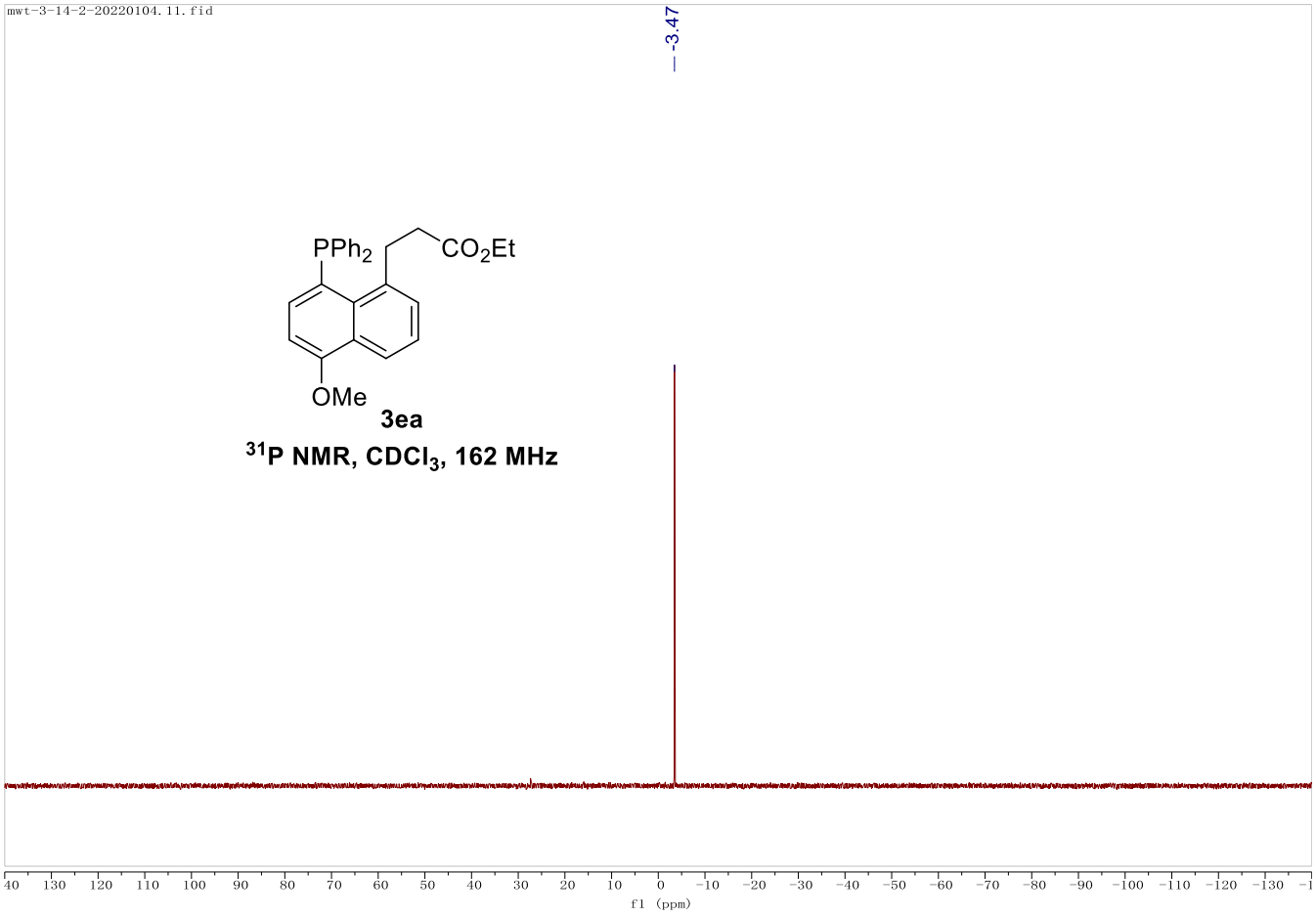
3ea

^{1}H NMR, $CDCl_3$, 400 MHz



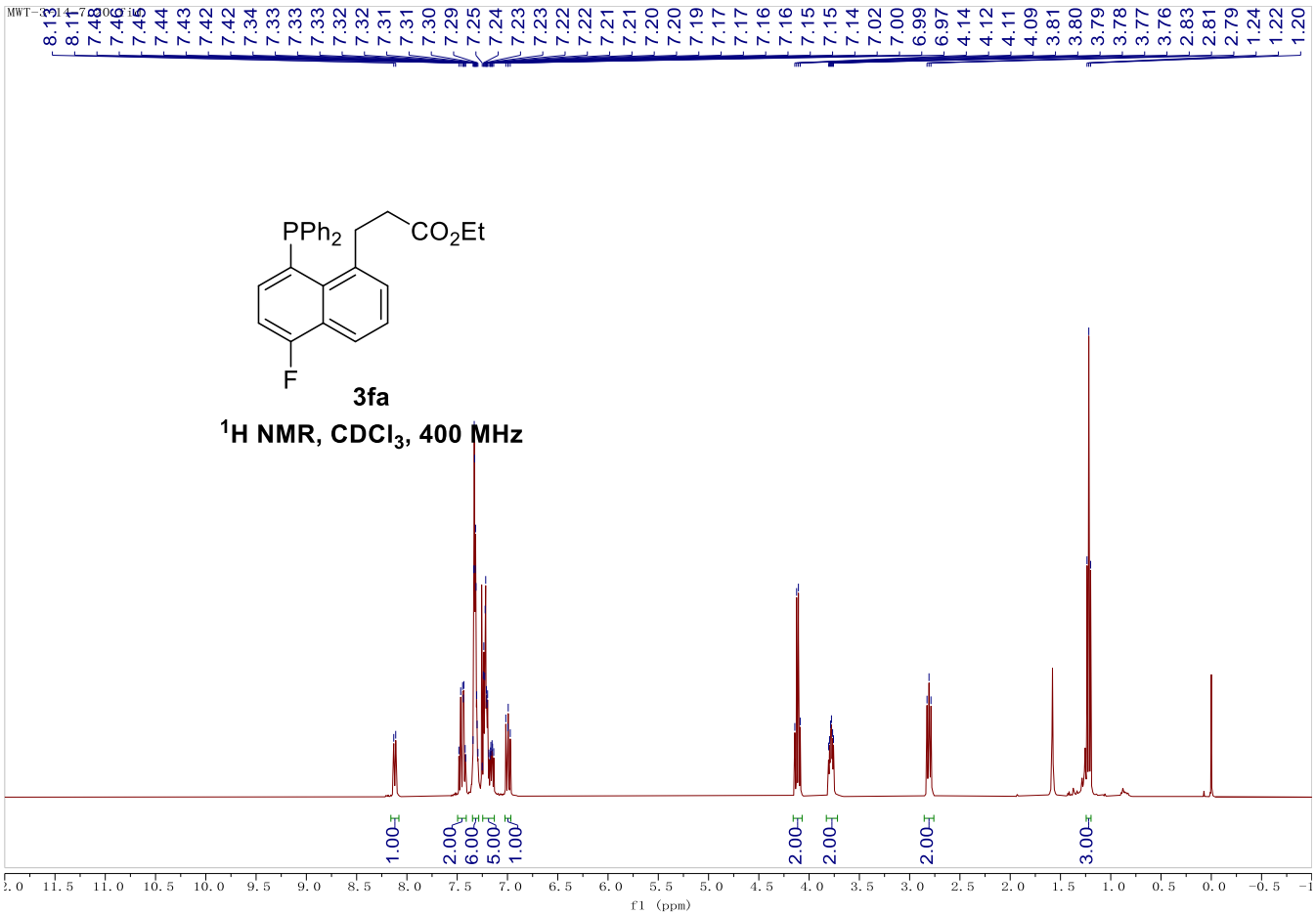
3ea

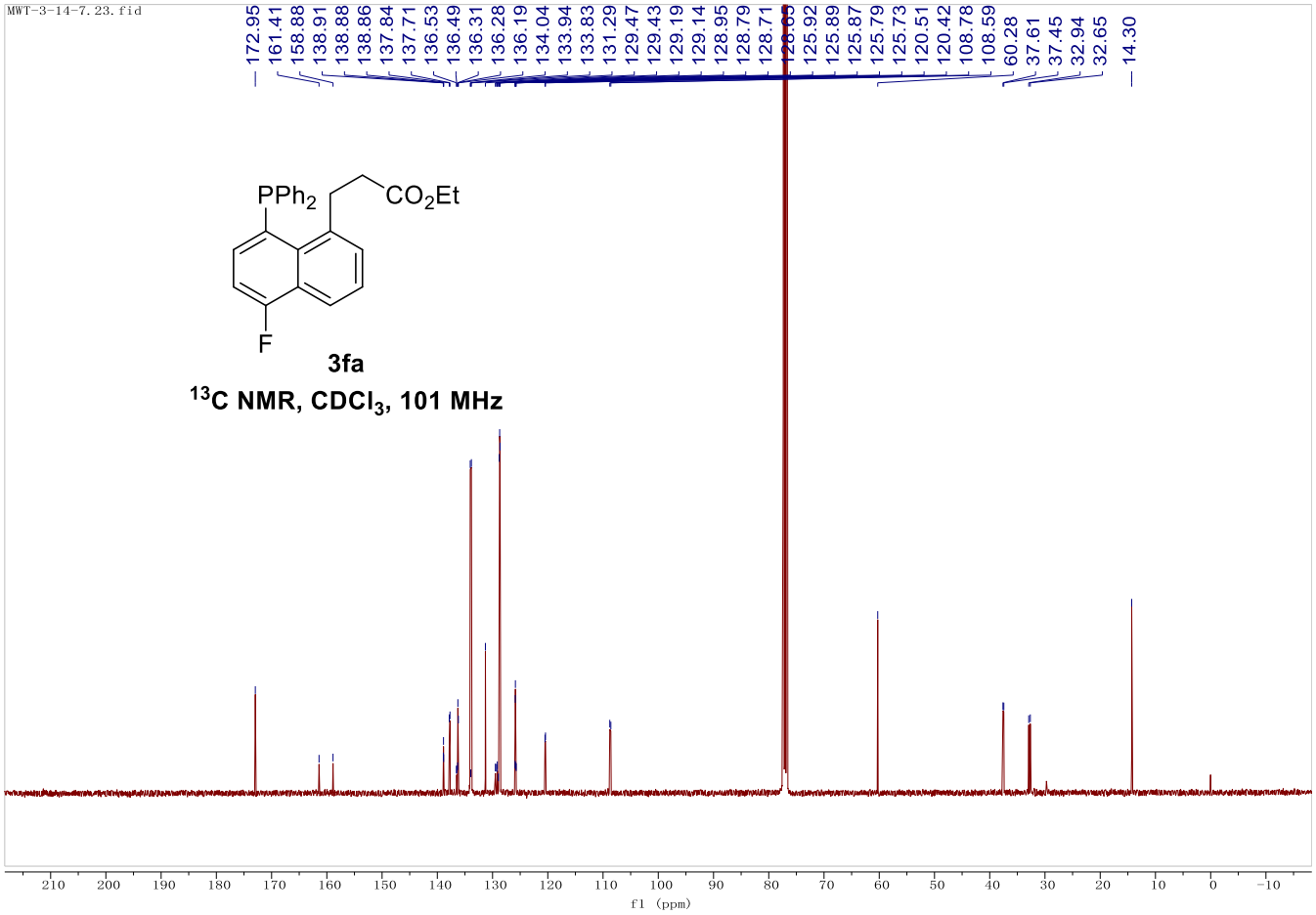
^{13}C NMR, $CDCl_3$, 101 MHz

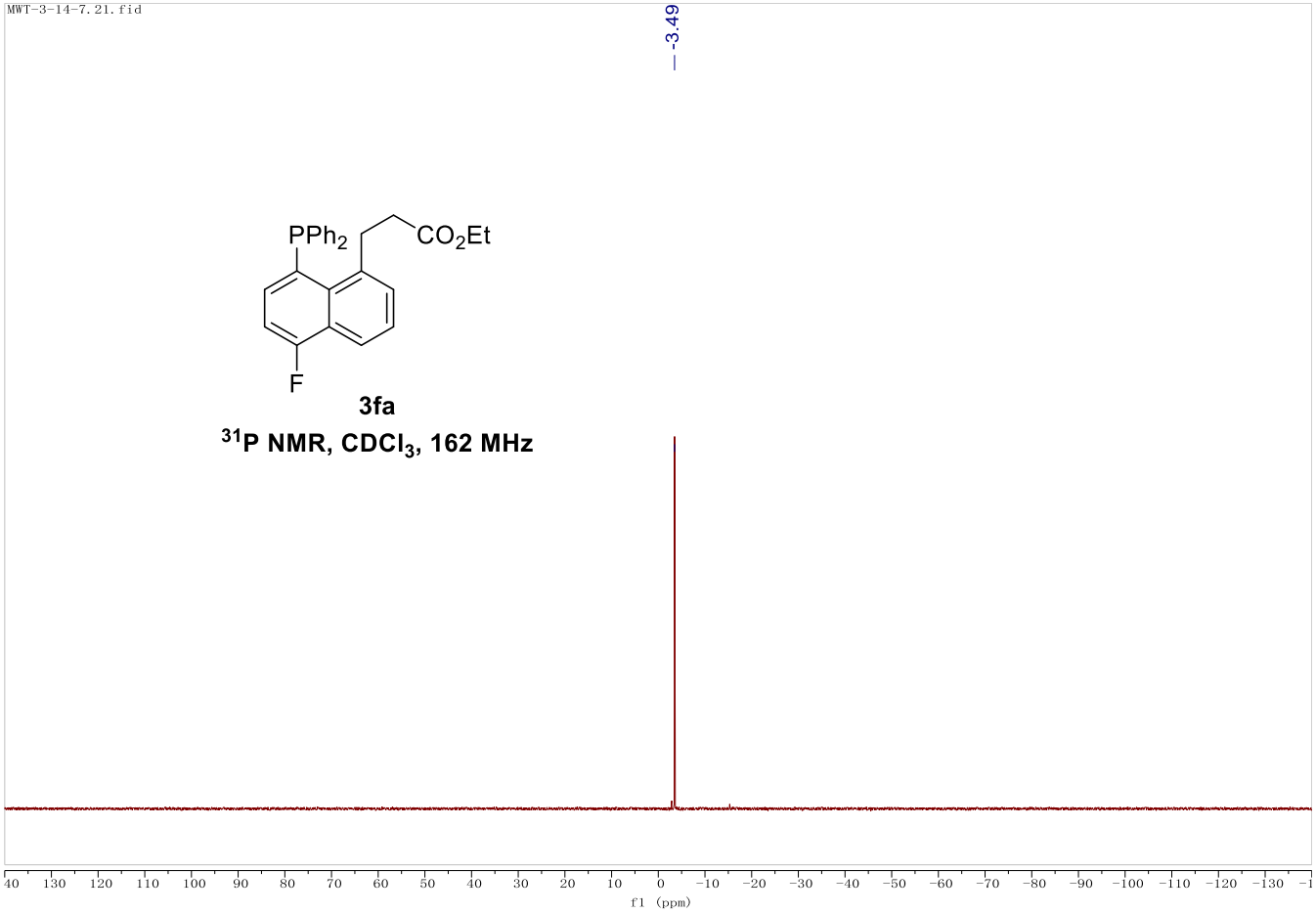


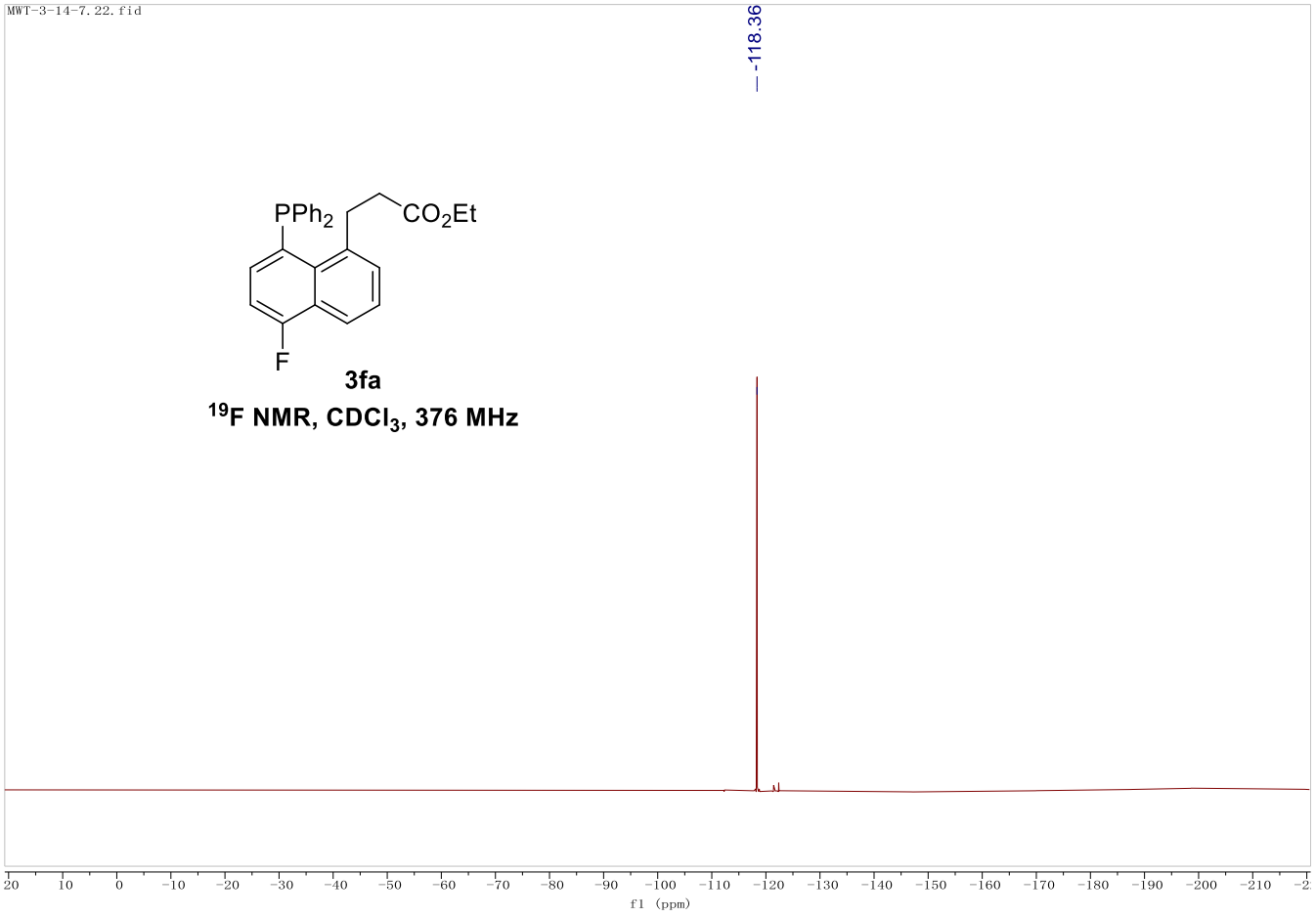
3ea

^{31}P NMR, $CDCl_3$, 162 MHz


PPh2
CO2Et
F
3fa
1H NMR, CDCl3, 400 MHz
f1 (ppm)


PPh2
CO2Et
F
3fa
13C NMR, CDCl3, 101 MHz
f1 (ppm)


MWT-3-14-7.21.fid
-3.49
PPh2
CO2Et
F
3fa
31P NMR, CDCl3, 162 MHz
f1 (ppm)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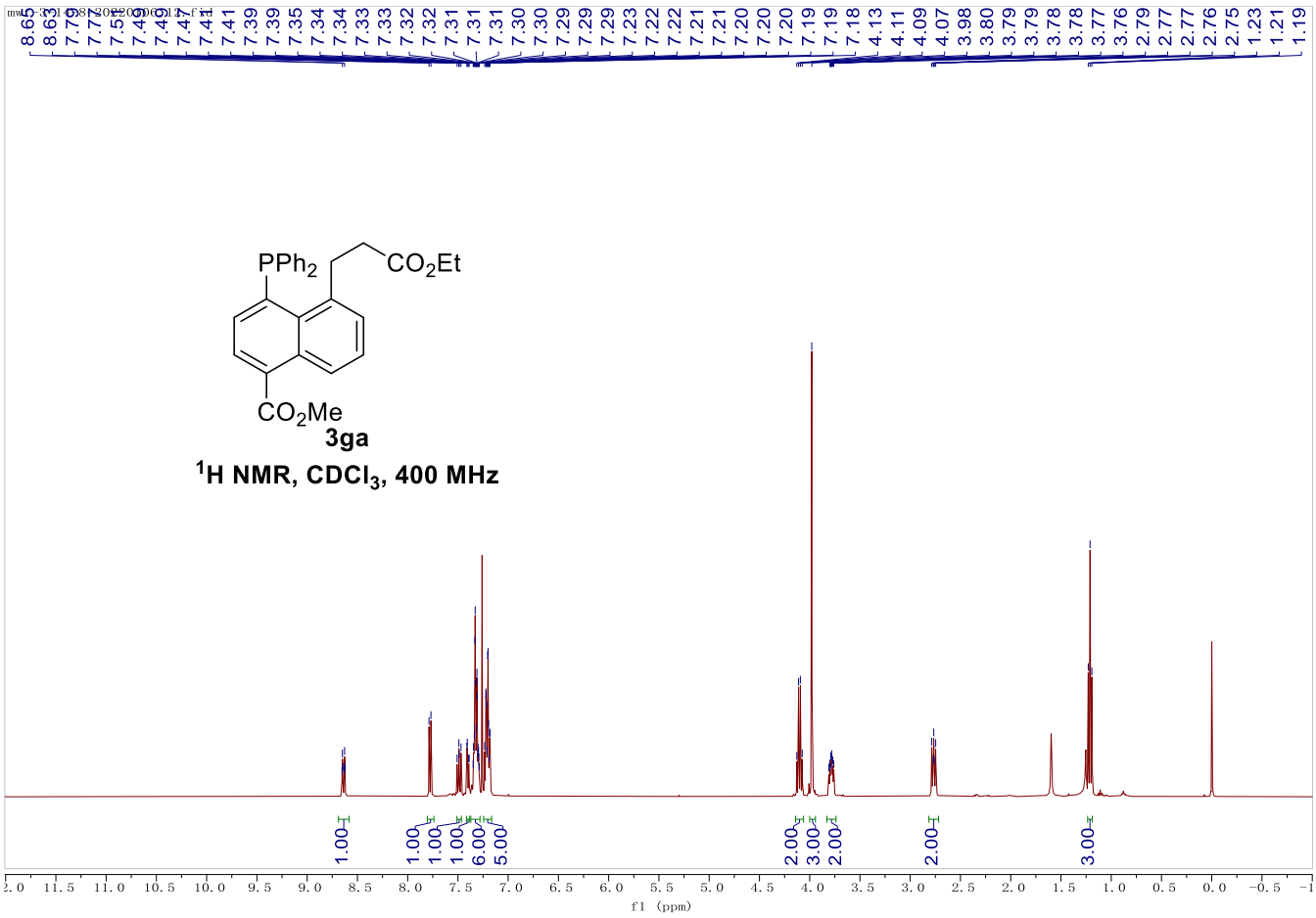
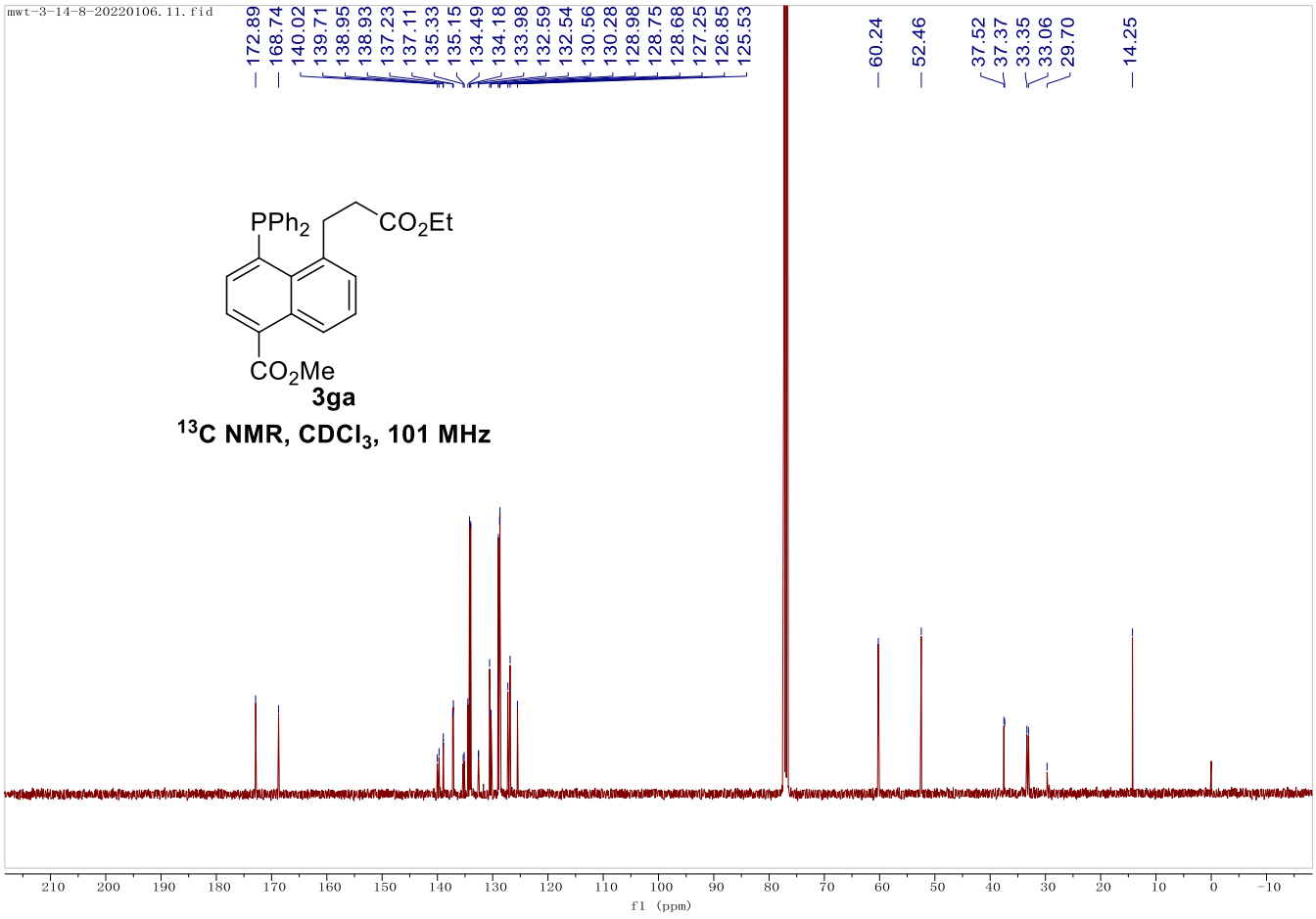
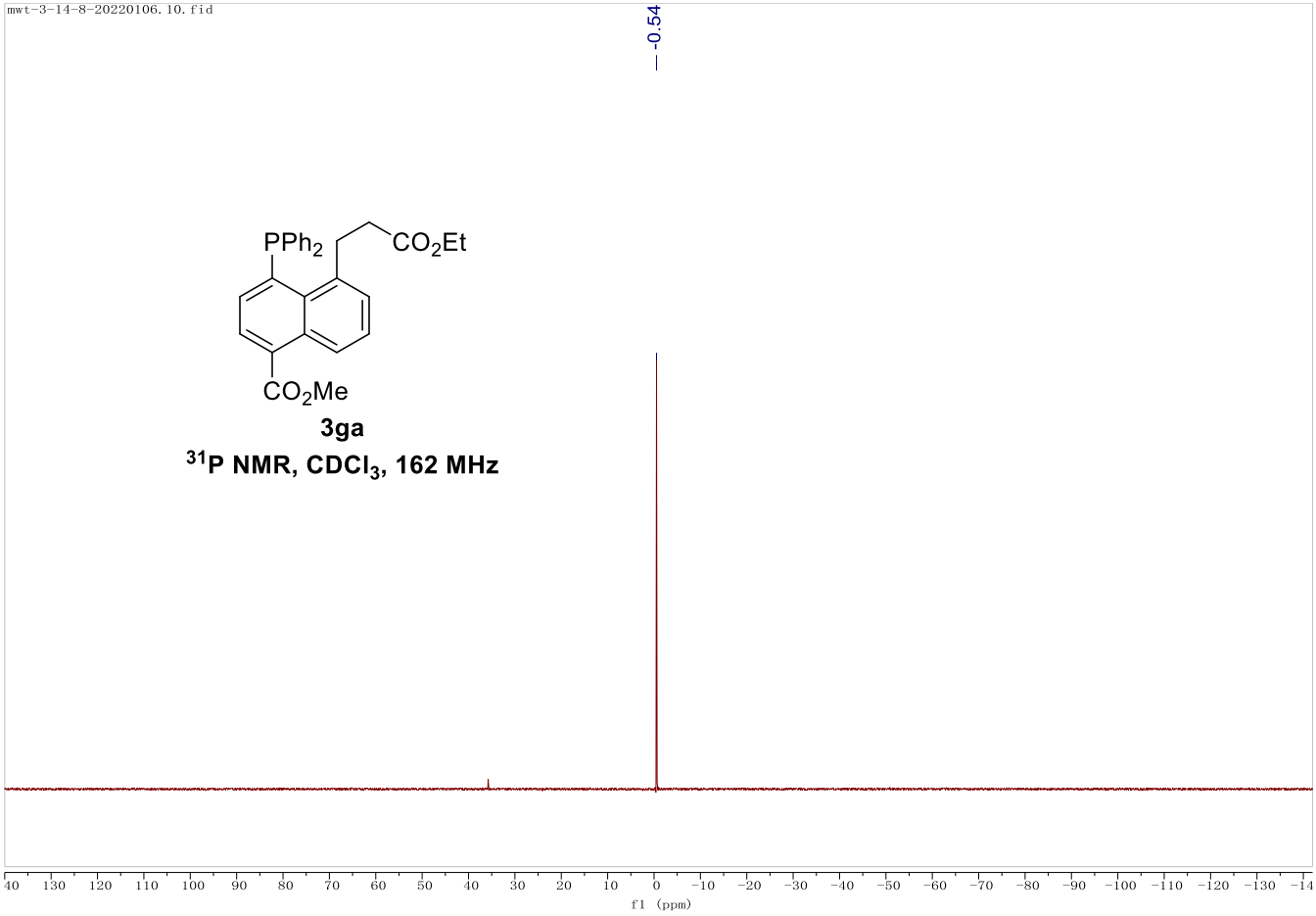
CO2Et
F
3fa
19F NMR, CDCl3, 376 MHz
f1 (ppm)

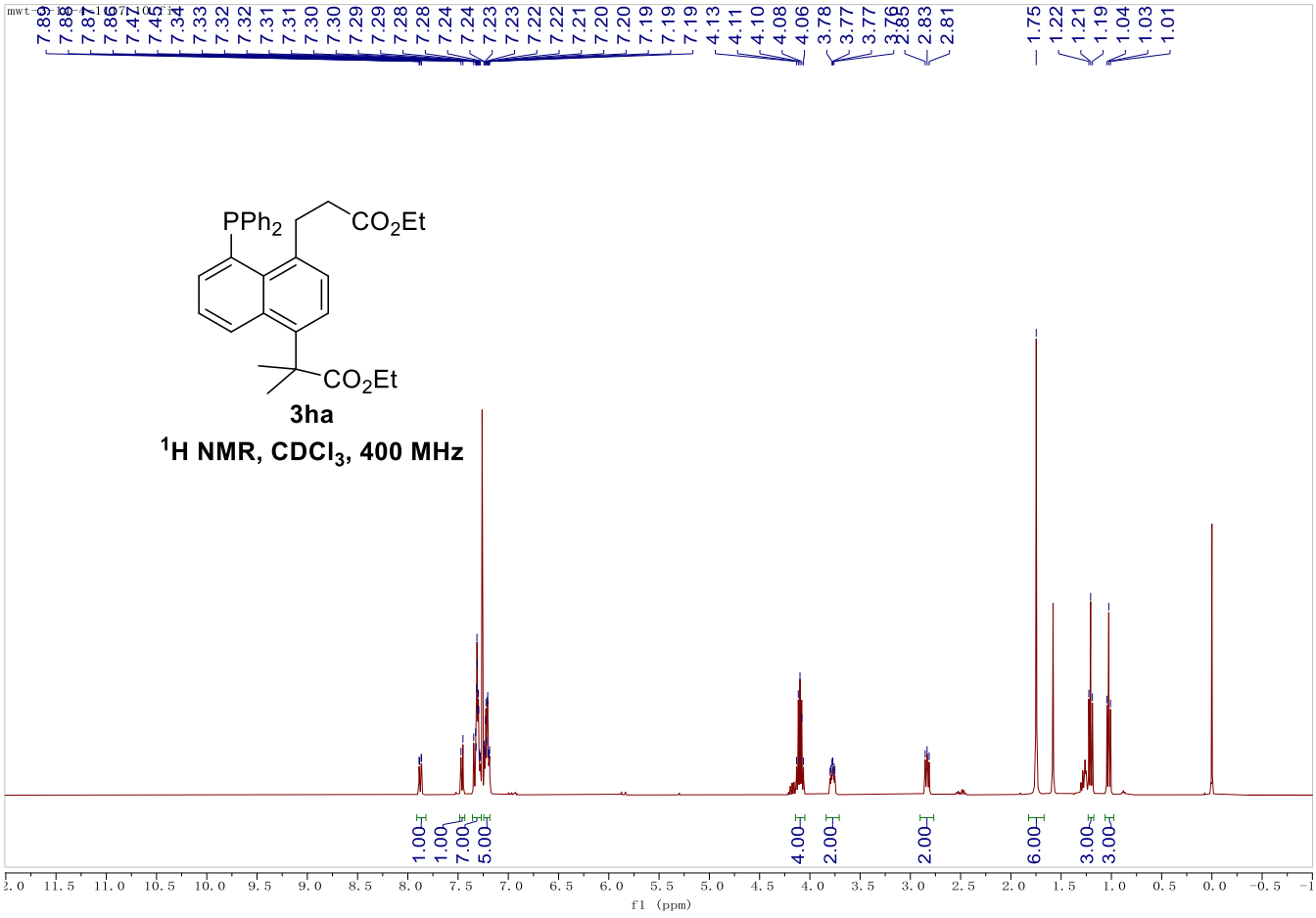

PPh2
CO2Et
CO2Me
3ga
1H NMR, CDCl3, 400 MHz
f1 (ppm)


PPh2
CO2Et
CO2Me
3ga
13C NMR, CDCl3, 101 MHz
f1 (ppm)



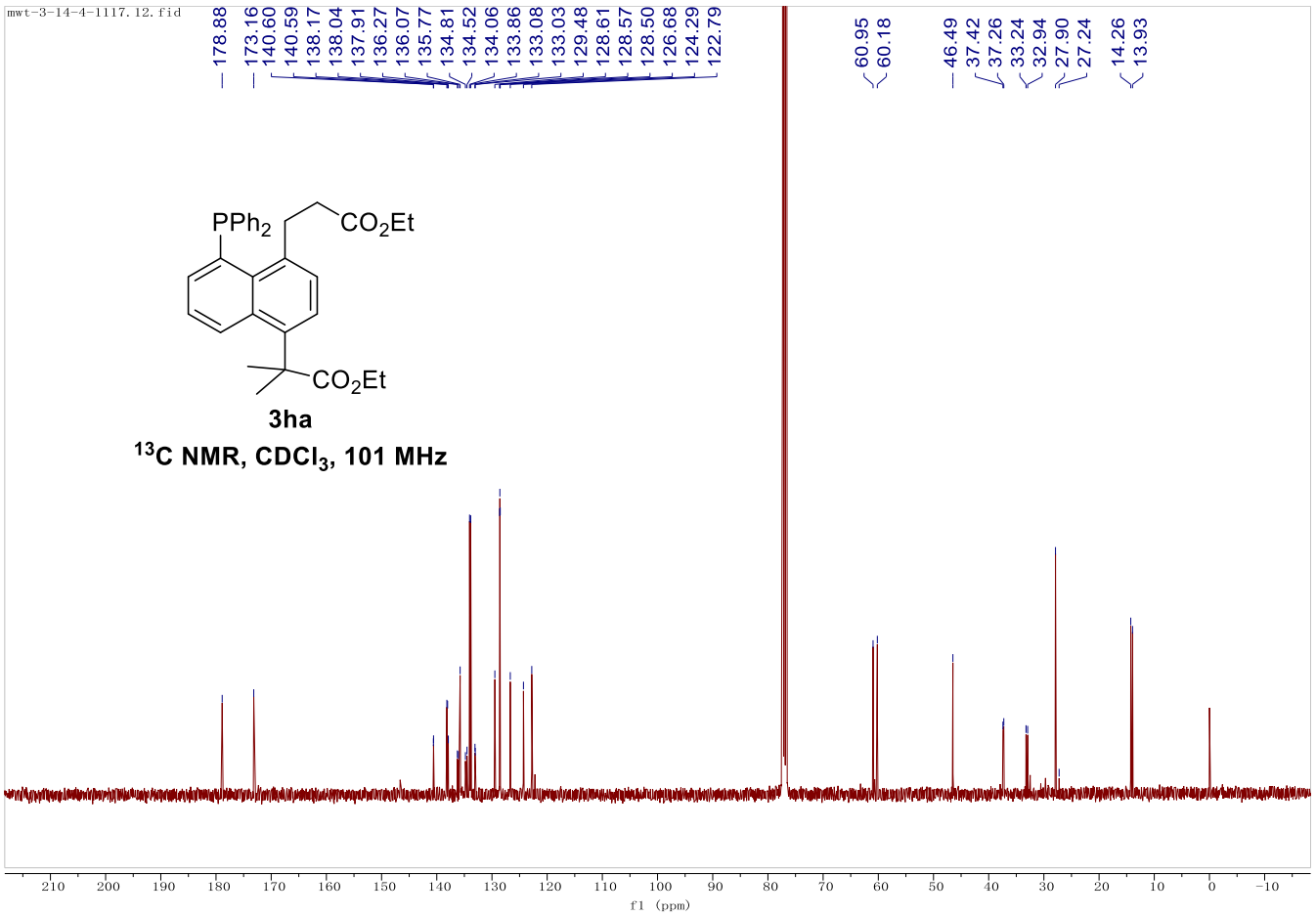
3ga

^{31}P NMR, $CDCl_3$, 162 MHz



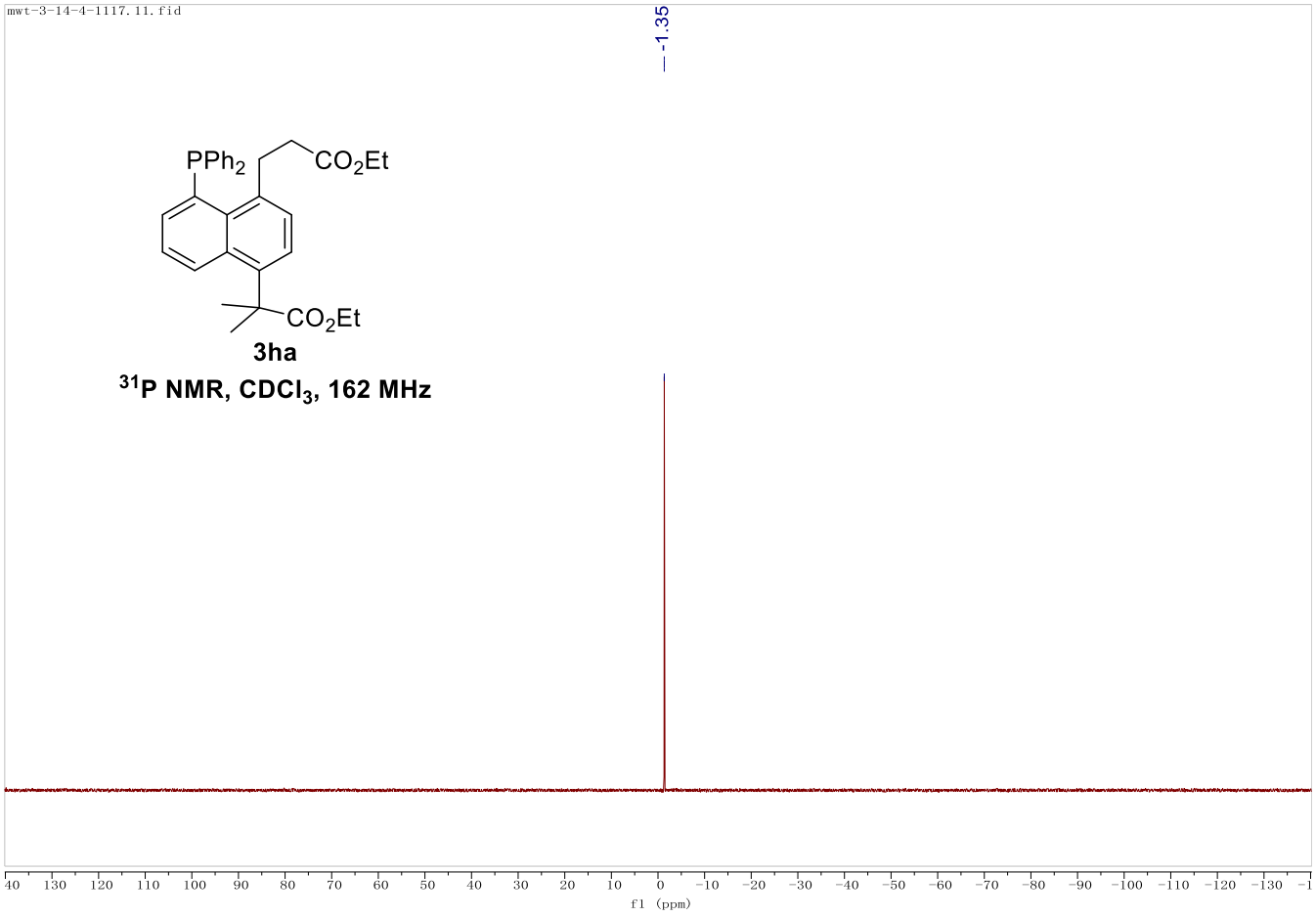
3ha

^{1}H NMR, $CDCl_3$, 400 MHz



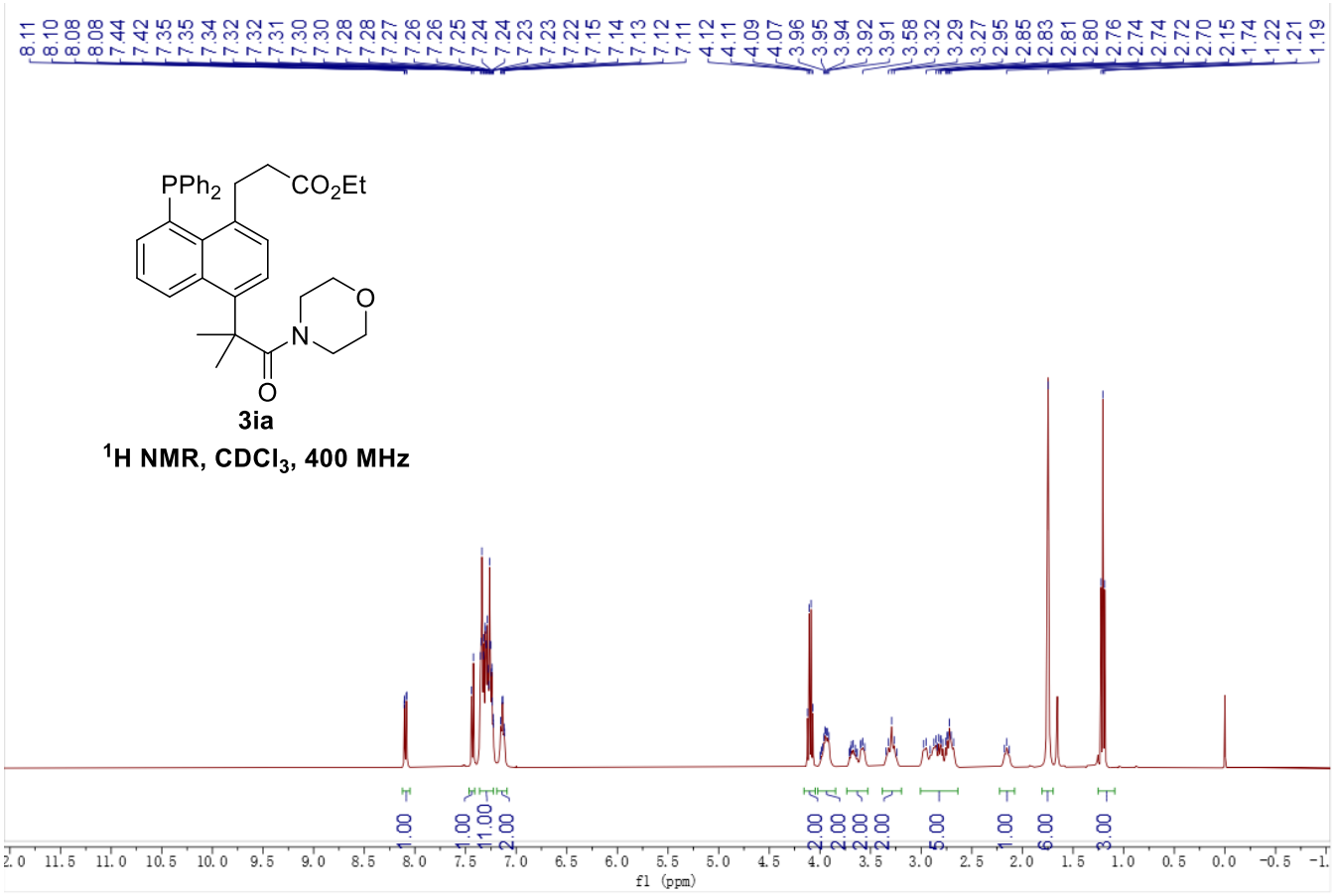
3ha

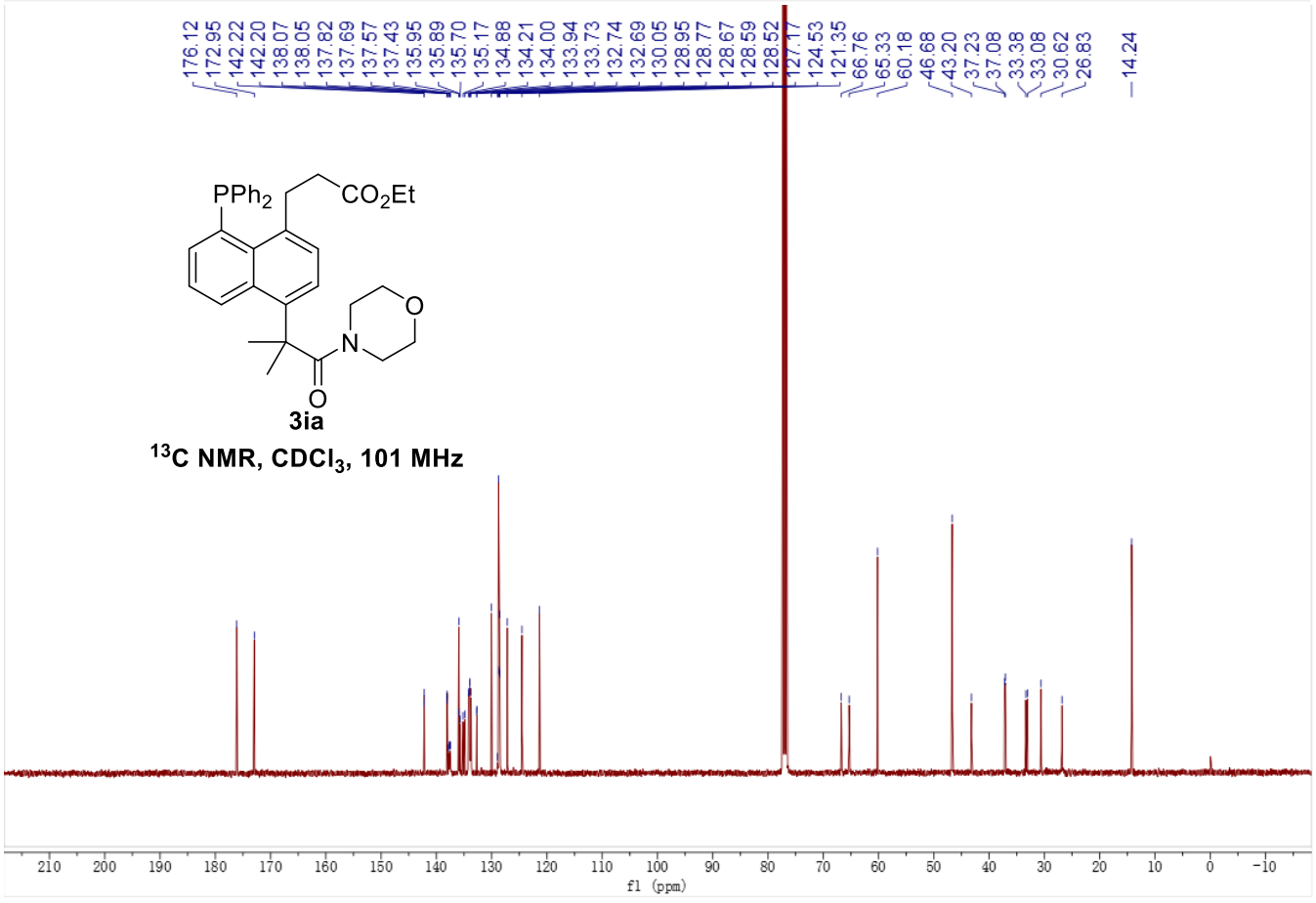
^{13}C NMR, $CDCl_3$, 101 MHz

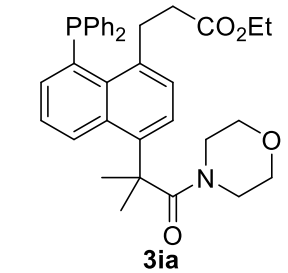


3ha

^{31}P NMR, $CDCl_3$, 162 MHz


PPh2
CO2Et
O
N
O
3ia
1H NMR, CDCl3, 400 MHz
f1 (ppm)


PPh2
CO2Et
O
N
O
3ia
13C NMR, CDCl3, 101 MHz
f1 (ppm)

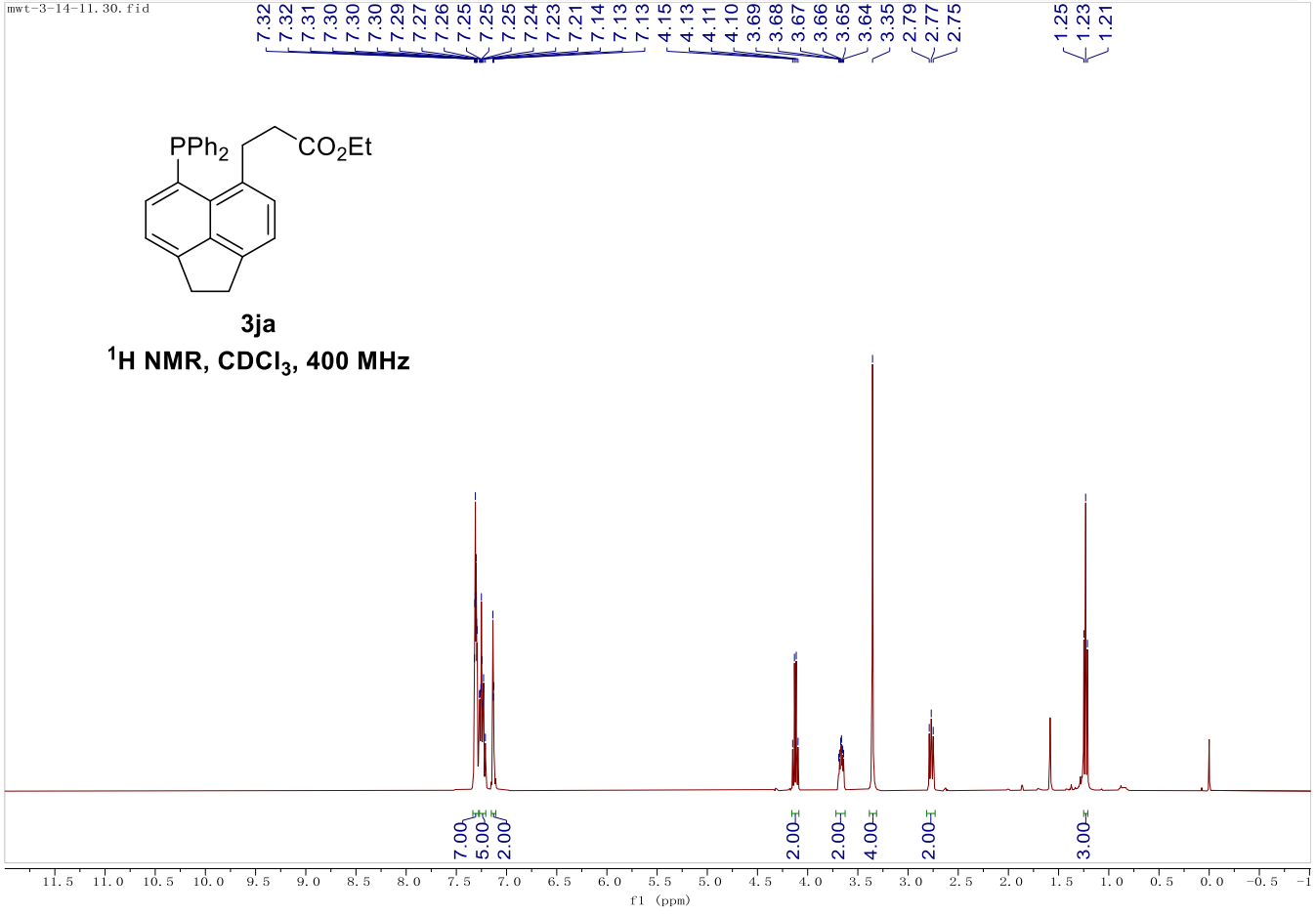


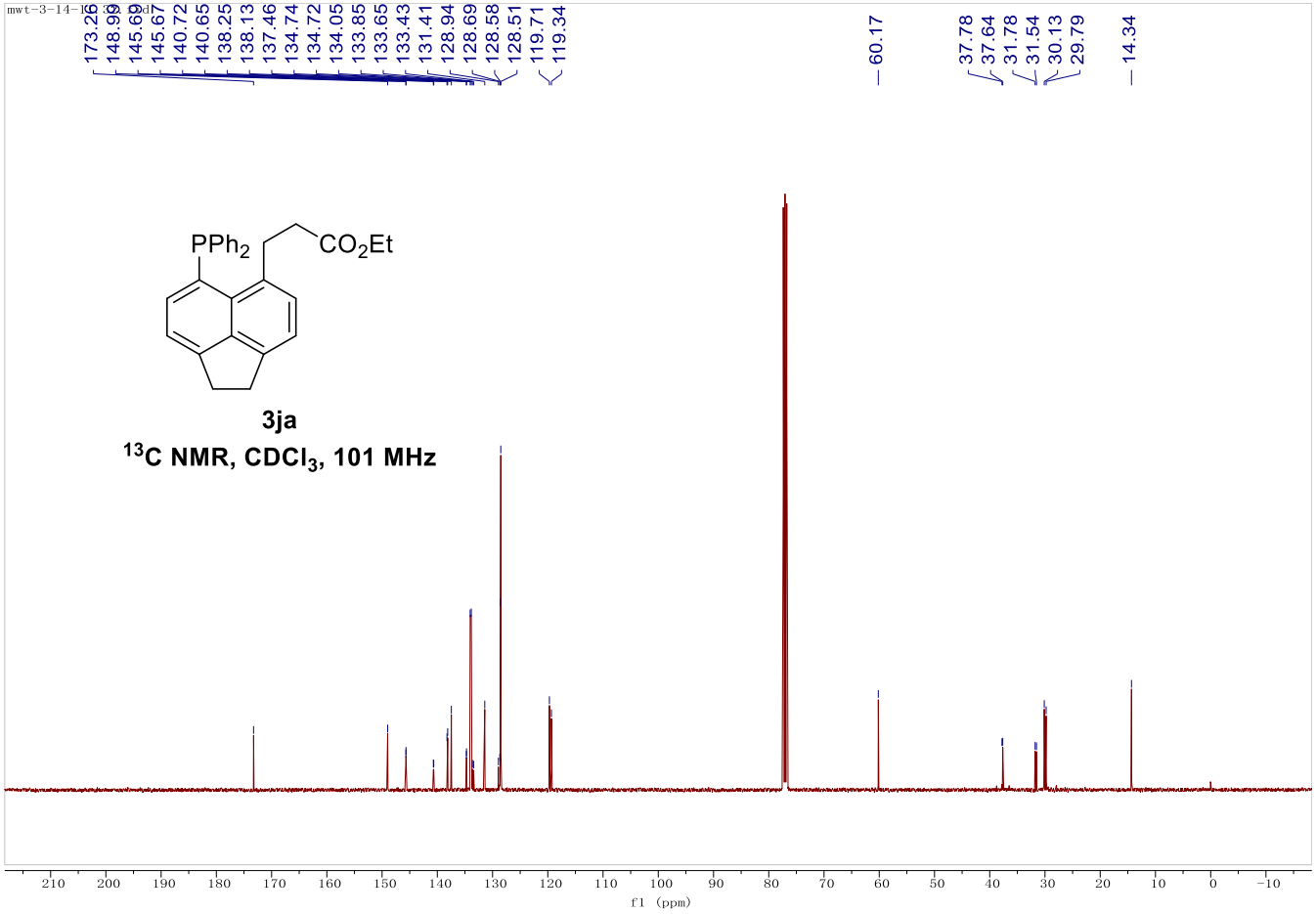
3ia

^{31}P NMR, $CDCl_3$, 162 MHz

3ja

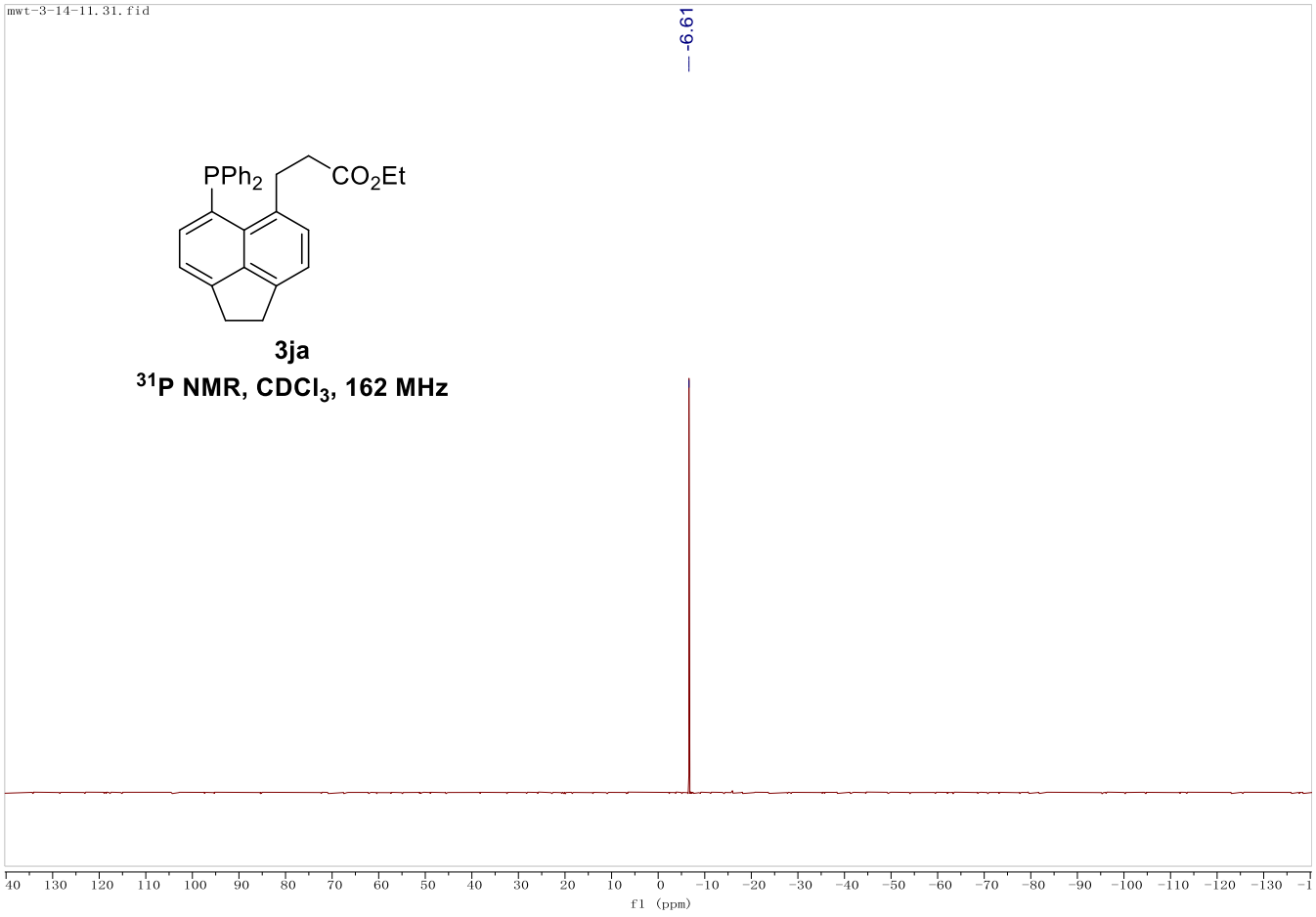
^{1}H NMR, $CDCl_3$, 400 MHz





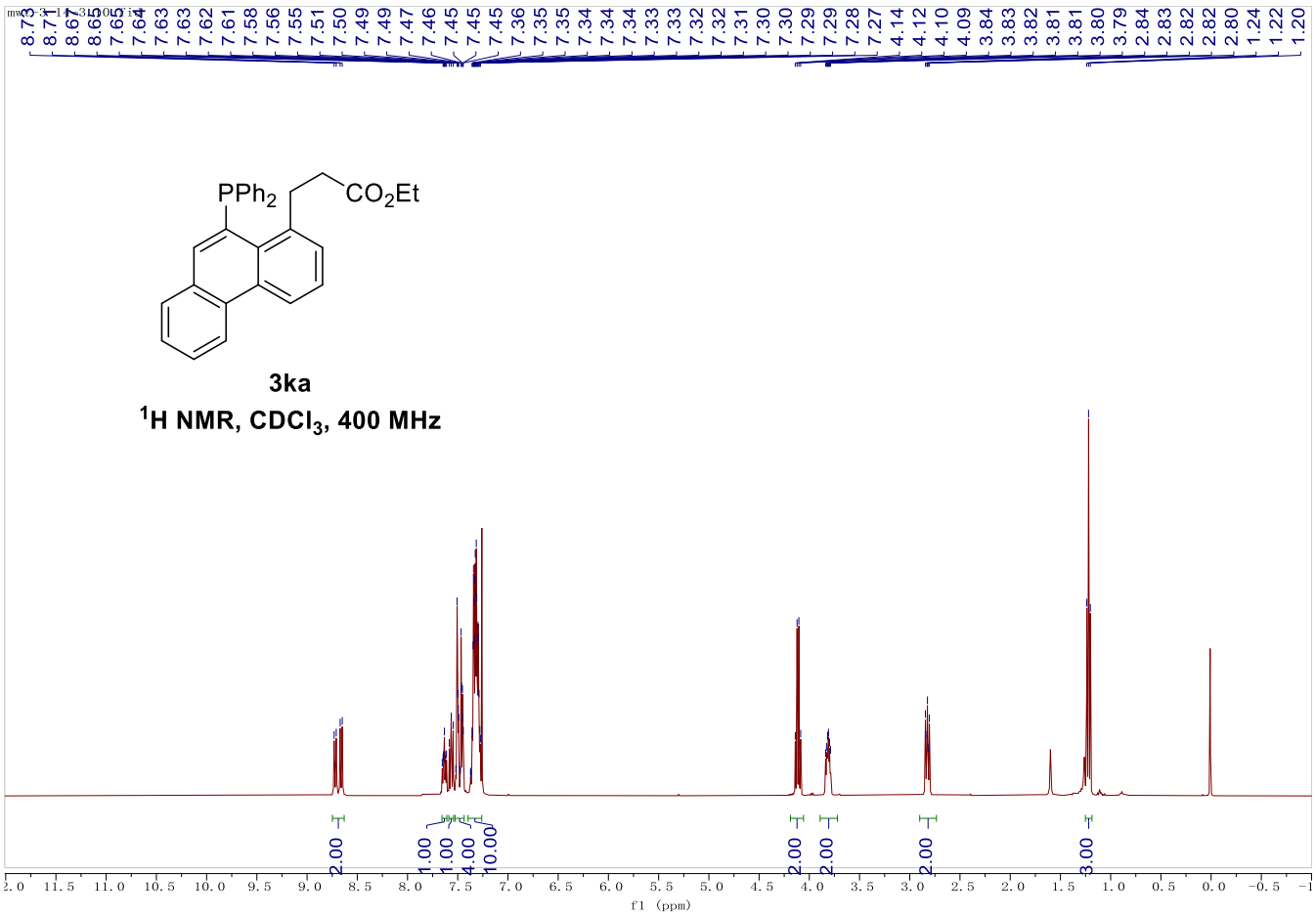
3ja

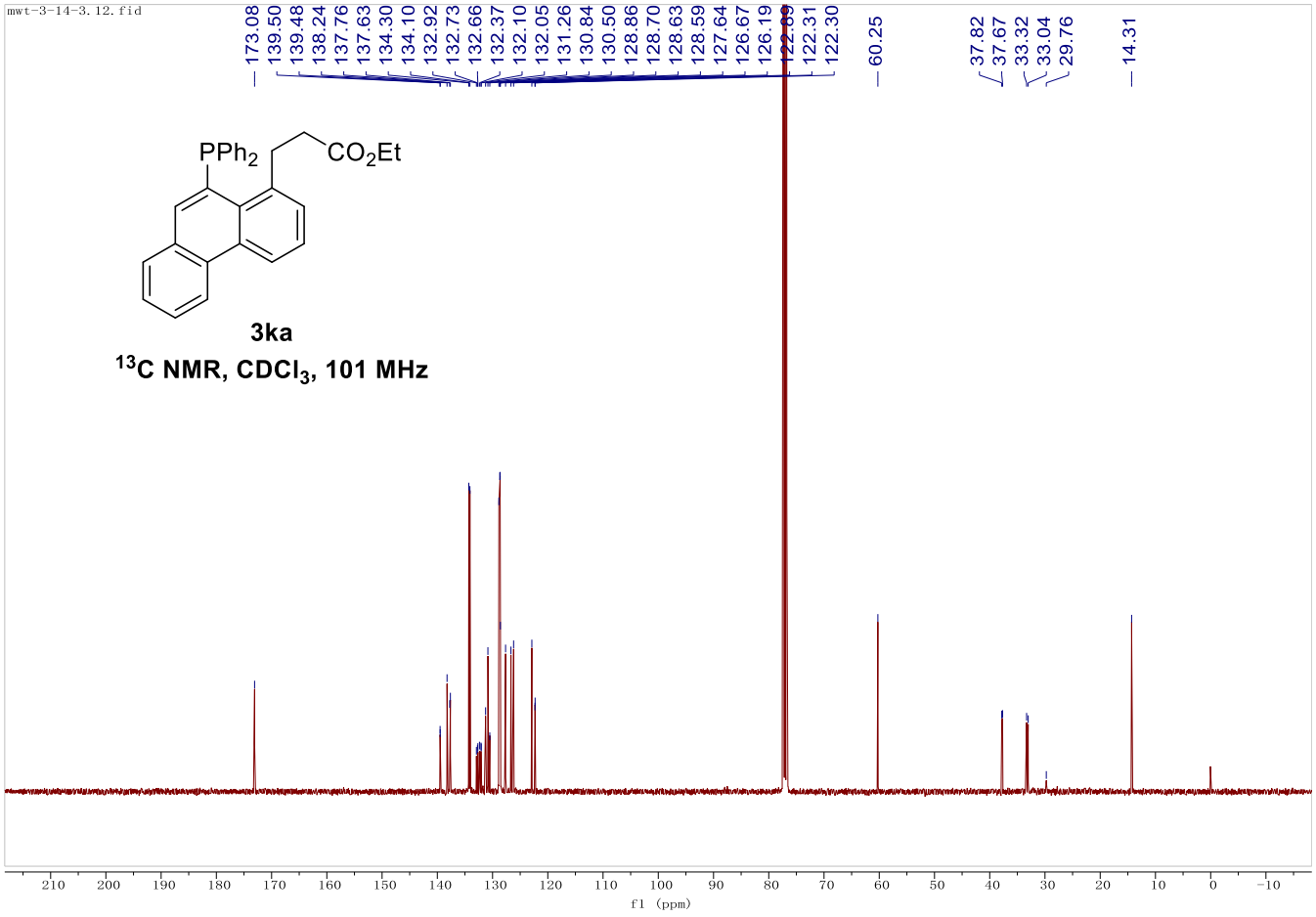
^{13}C NMR, $CDCl_3$, 101 MHz

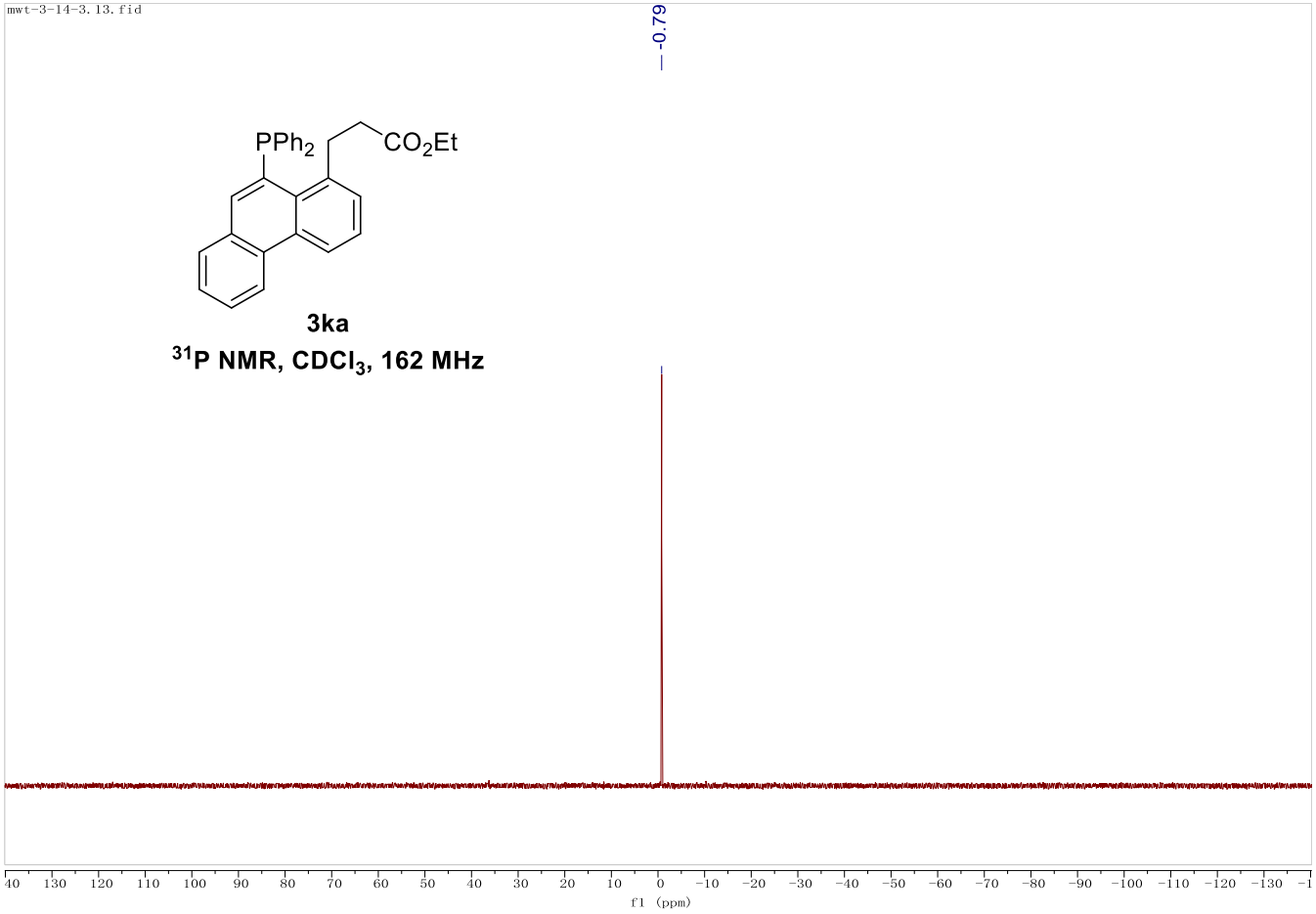


3ja

^{31}P NMR, $CDCl_3$, 162 MHz

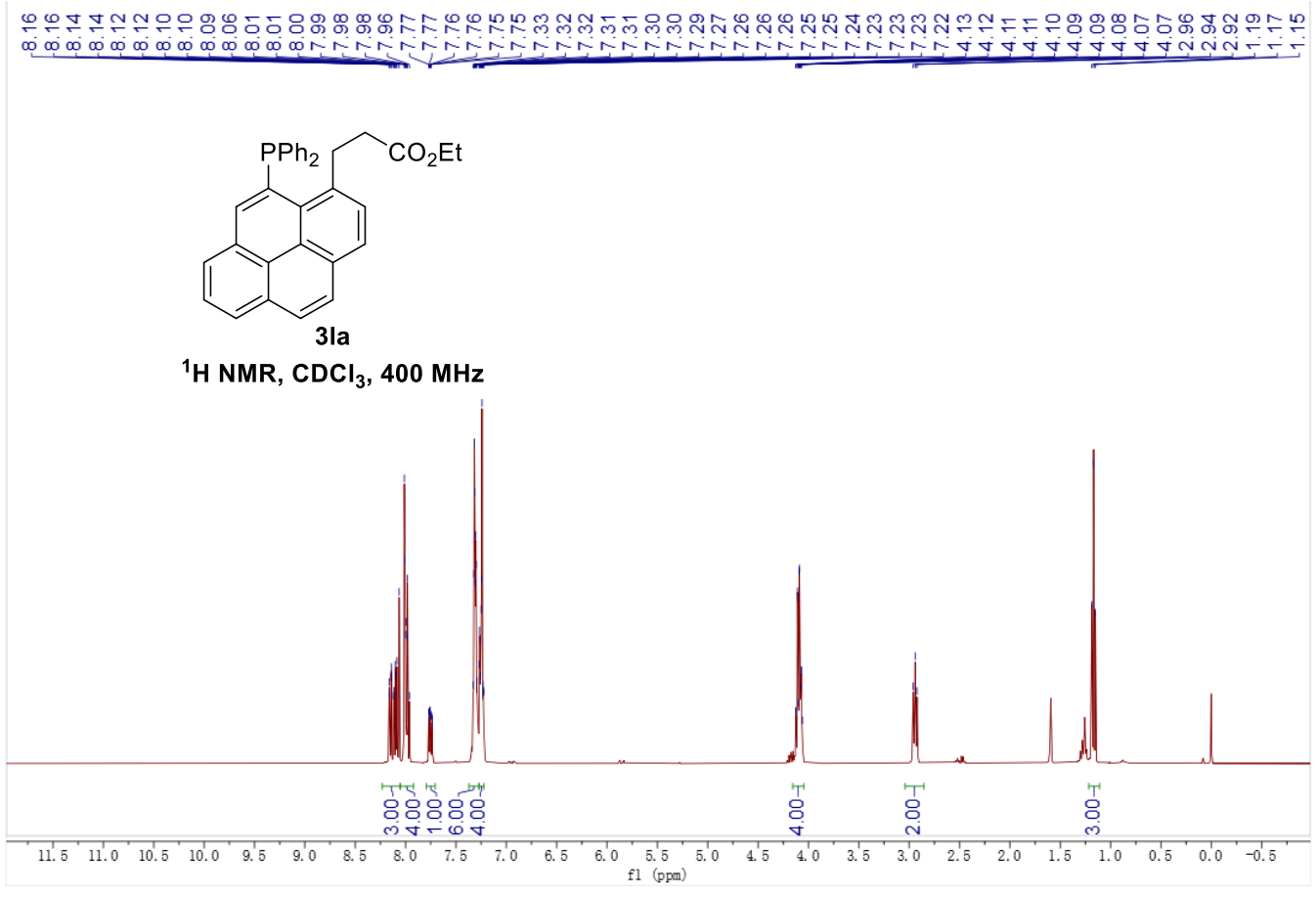

PPh2
CO2Et
3ka
1H NMR, CDCl3, 400 MHz
f1 (ppm)


PPh2
CO2Et
3ka
13C NMR, CDCl3, 101 MHz
f1 (ppm)



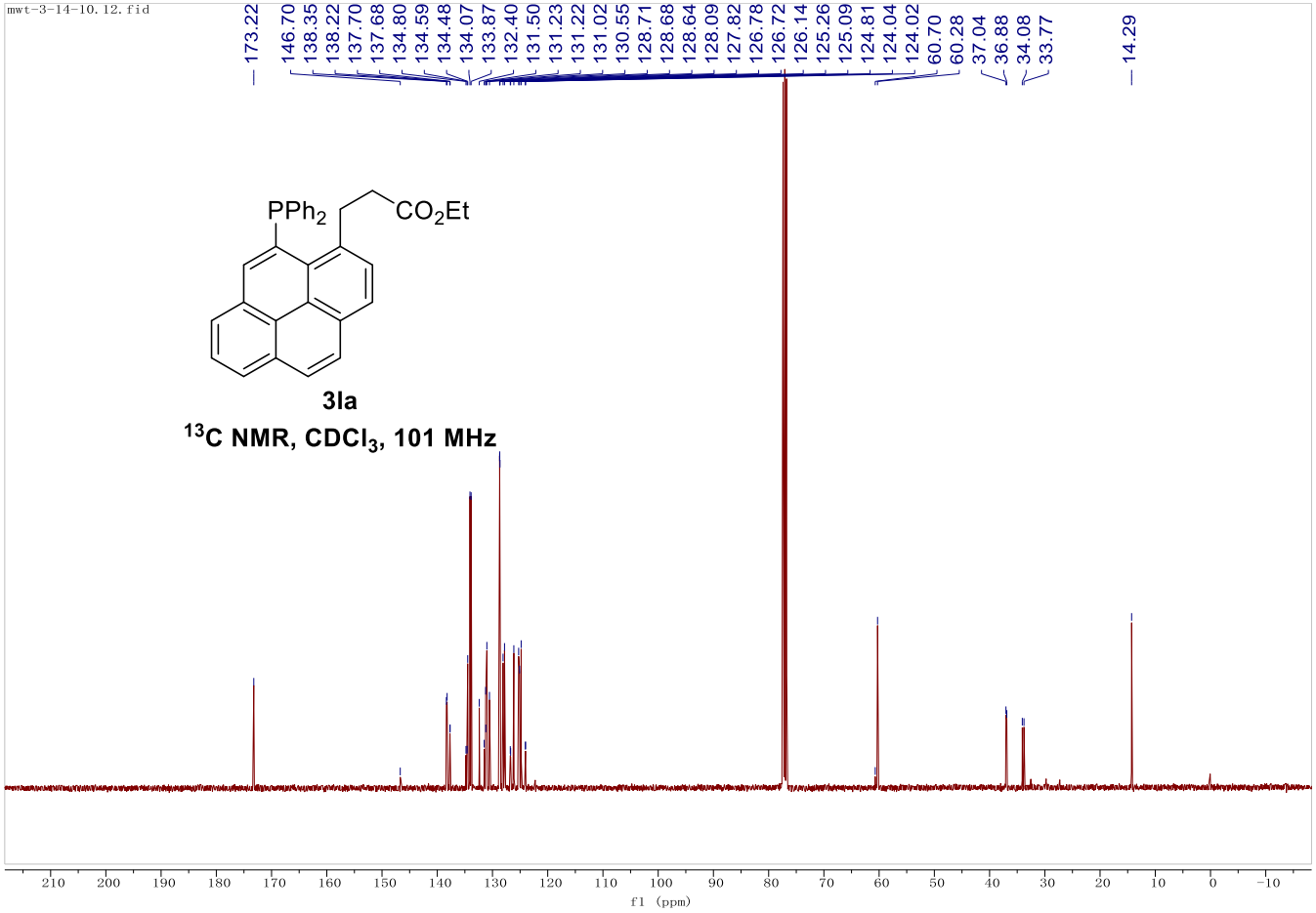
3ka

^{31}P NMR, $CDCl_3$, 162 MHz



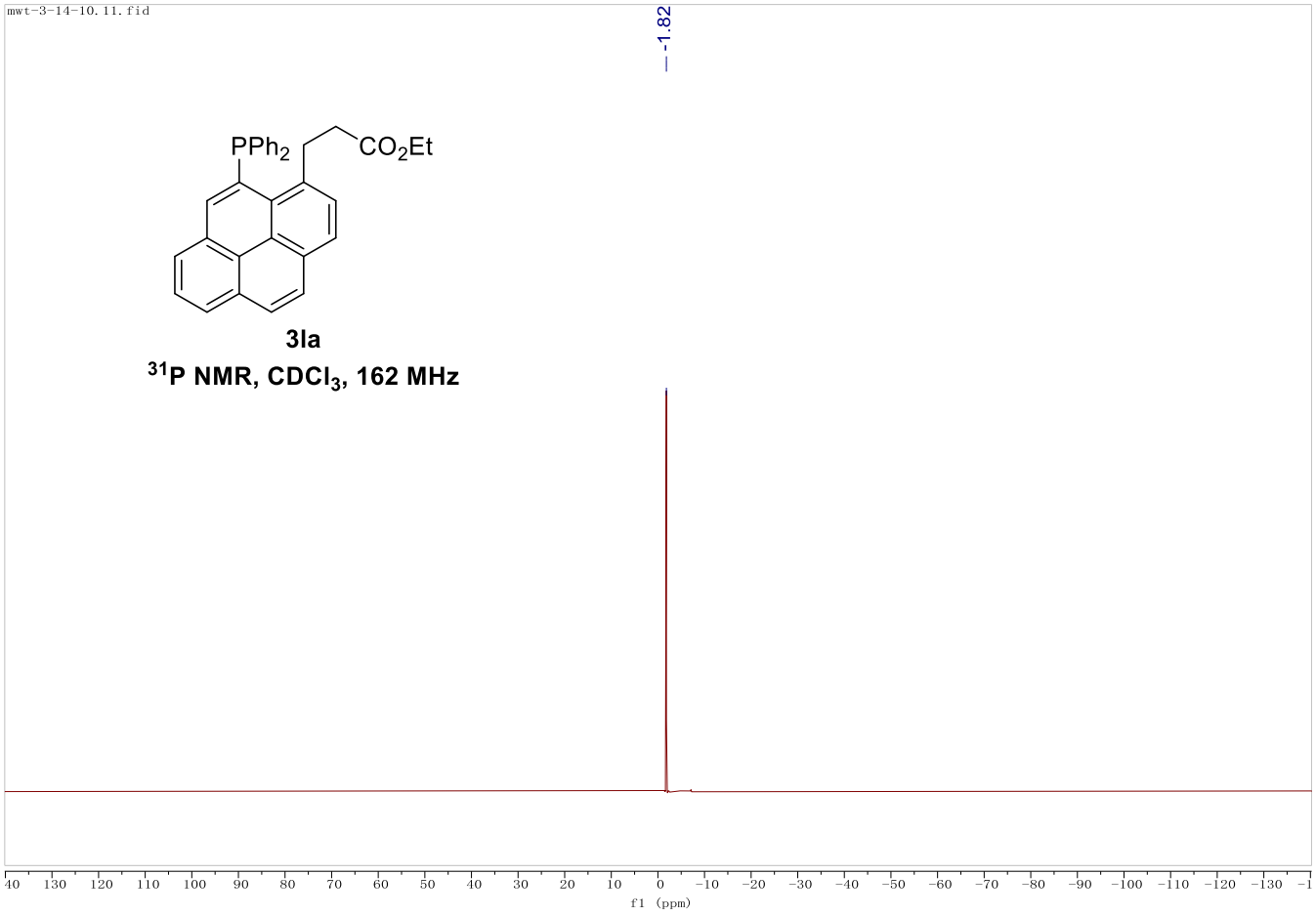
3la

^{1}H NMR, $CDCl_3$, 400 MHz



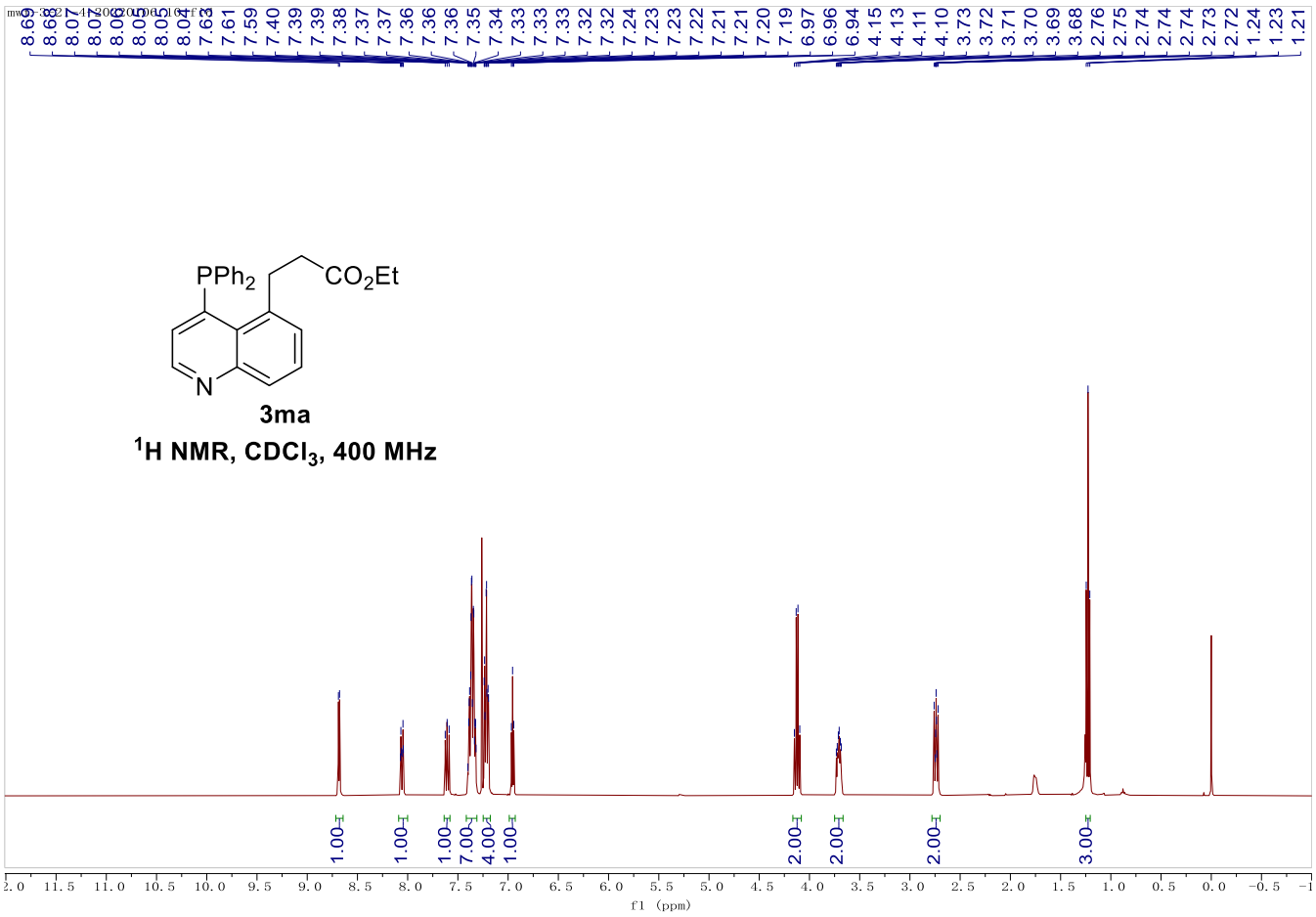
3la

^{13}C NMR, $CDCl_3$, 101 MHz



3la

^{31}P NMR, $CDCl_3$, 162 MHz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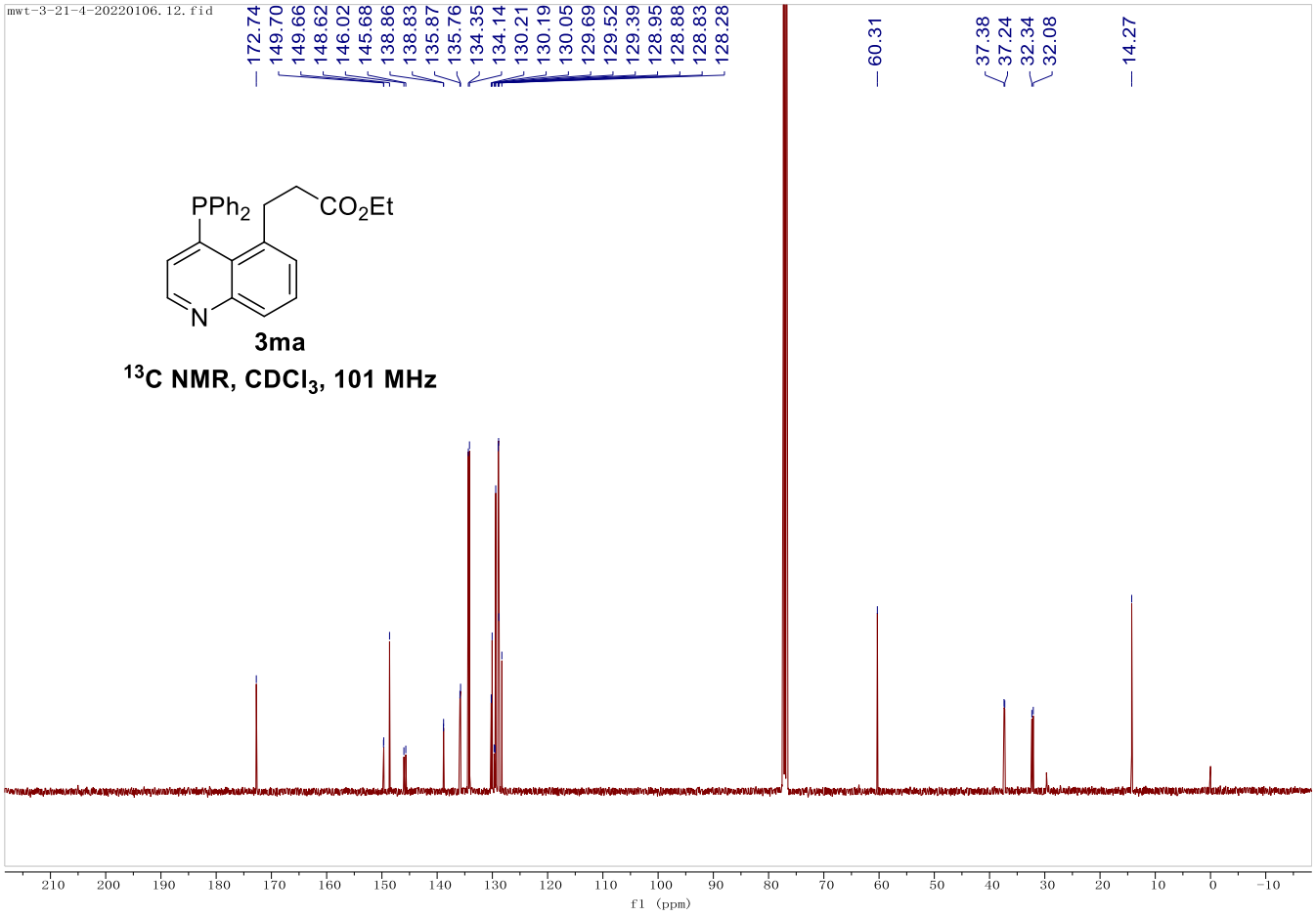
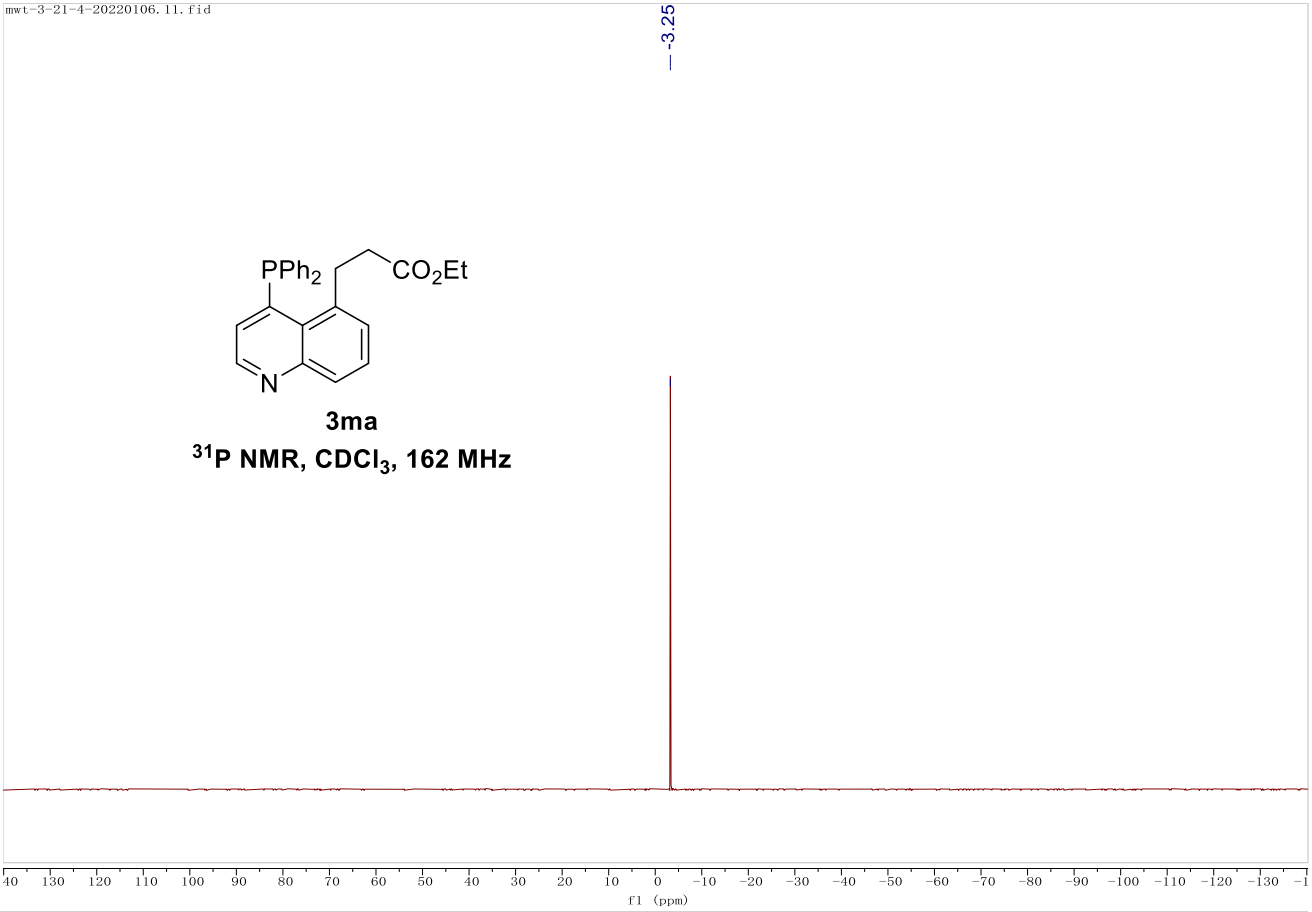
CO2Et
N
3ma
1H NMR, CDCl3, 400 MHz
f1 (ppm)


PPh2
CO2Et
N
3ma
13C NMR, CDCl3, 101 MHz
f1 (ppm)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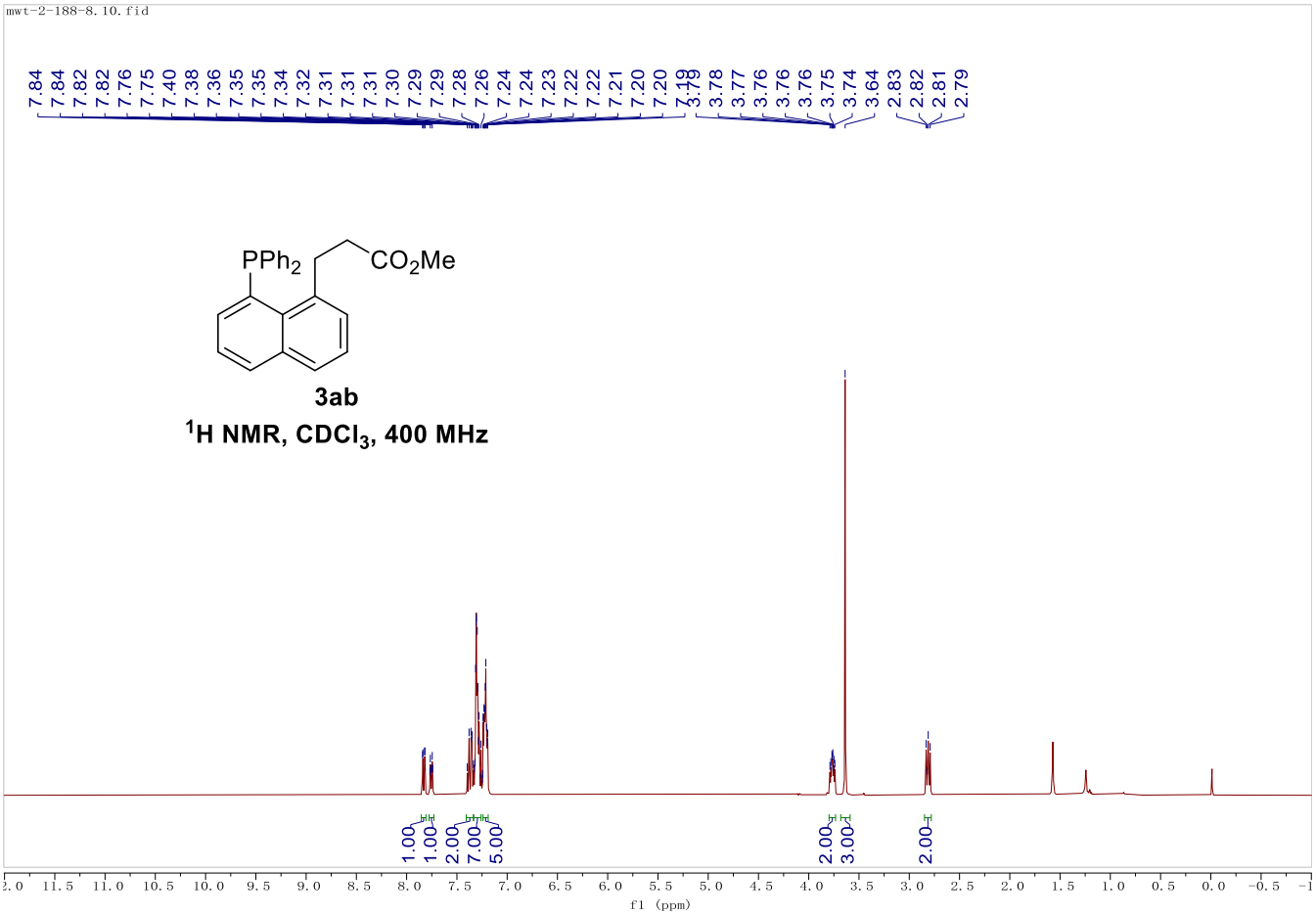
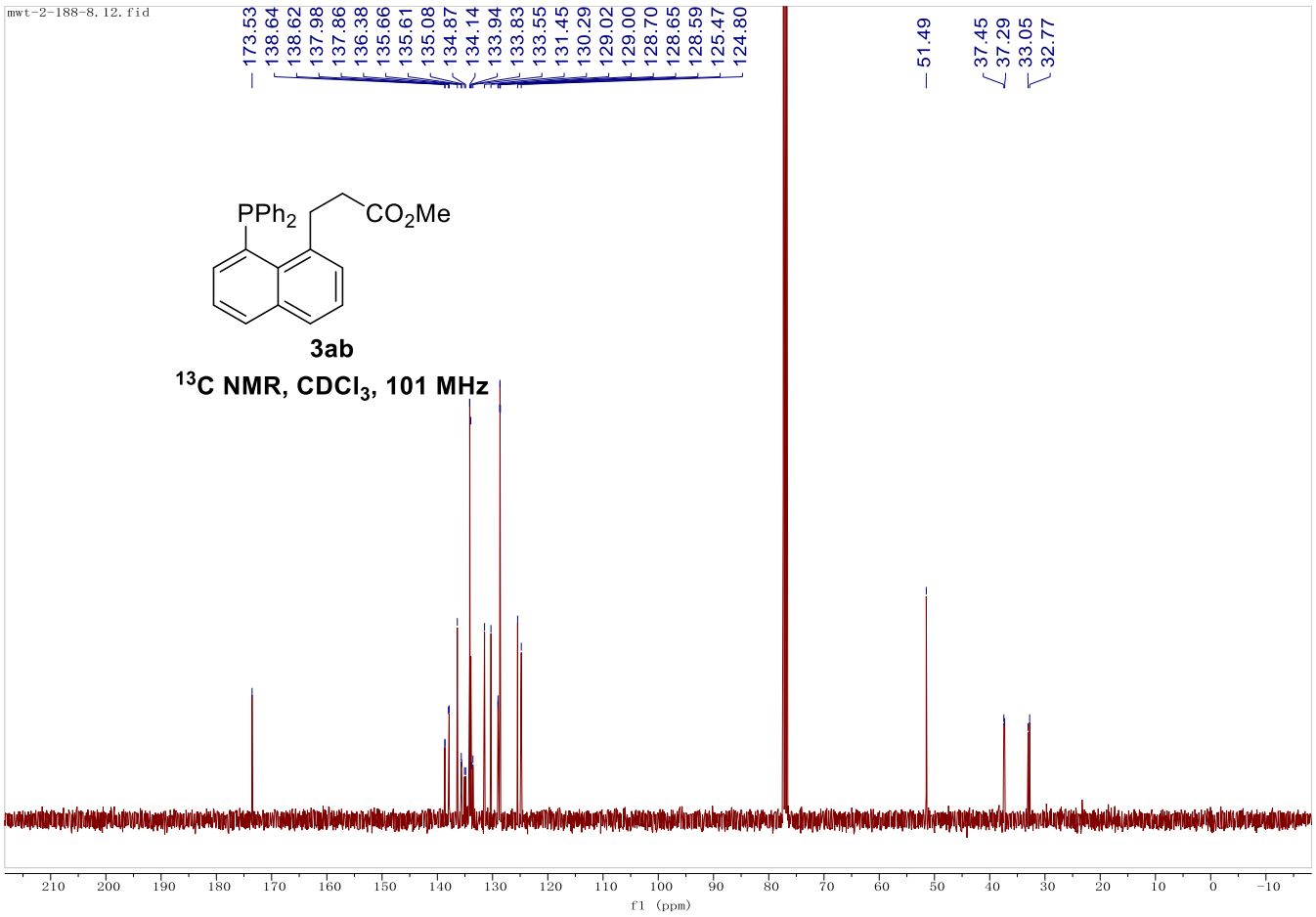
CO2Et
N
3ma
31P NMR, CDCl3, 162 MHz
f1 (ppm)


mwt-2-188-8.10.fid
7.84 7.84 7.82 7.82 7.76 7.75 7.40 7.38 7.36 7.35 7.35 7.34 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.26 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 3.79 3.78 3.77 3.76 3.76 3.75 3.74 3.64 2.83 2.82 2.81 2.79
PPh2
CO2Me
3ab
1H NMR, CDCl3, 400 MHz
1.00 1.00 2.00 7.00 5.00 2.00 3.00 2.00
f1 (ppm)


mwt-2-188-8.12.fid
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138.62
137.98
137.86
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135.61
135.08
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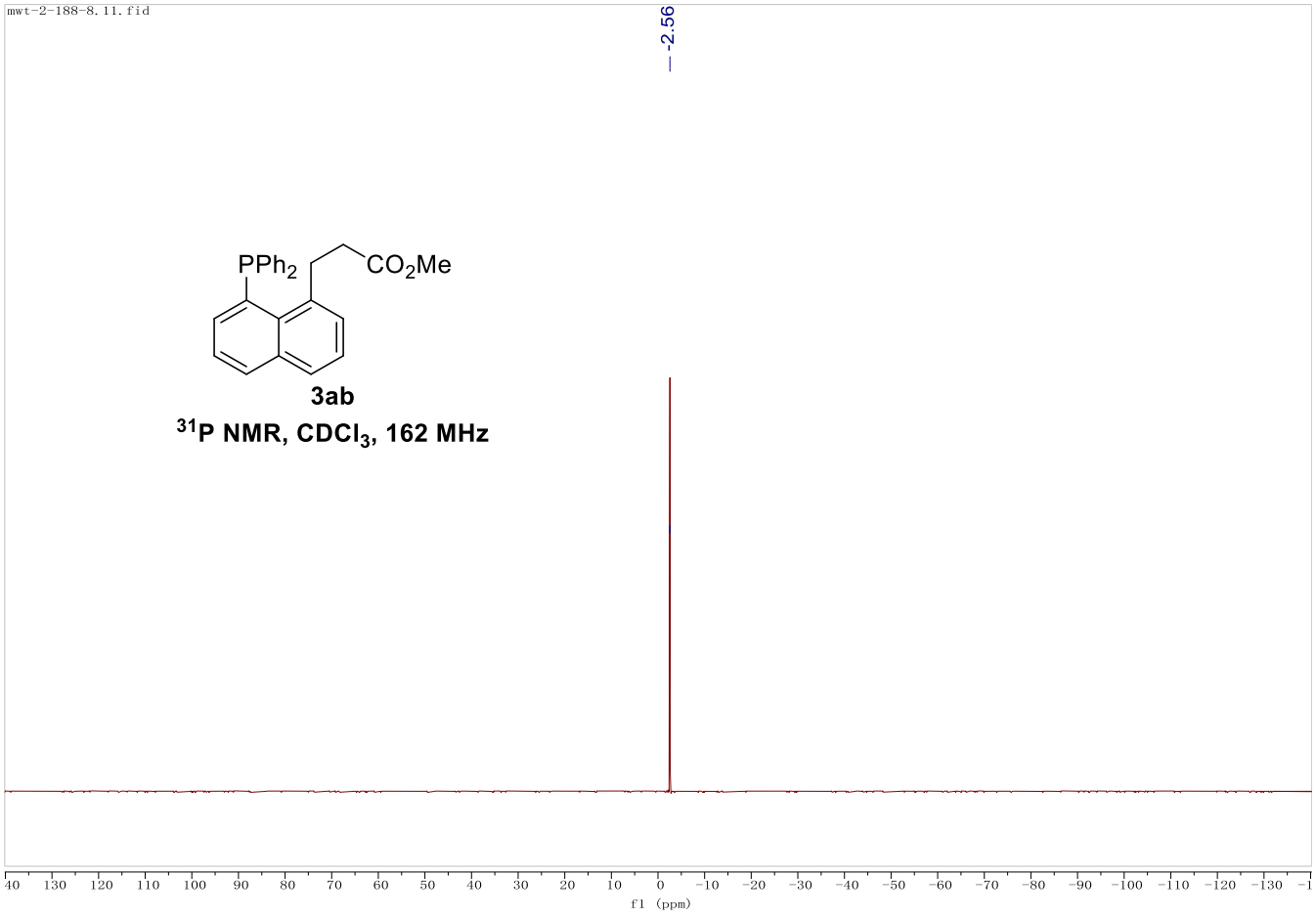
134.14
133.94
133.83
133.55
131.45
130.29
129.02
129.00
128.70
128.65
128.59
125.47
124.80
51.49
37.45
37.29
33.05
32.77
PPh2
CO2Me
3ab
13C NMR, CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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CO2Me
3ab
31P NMR, CDCl3, 162 MHz
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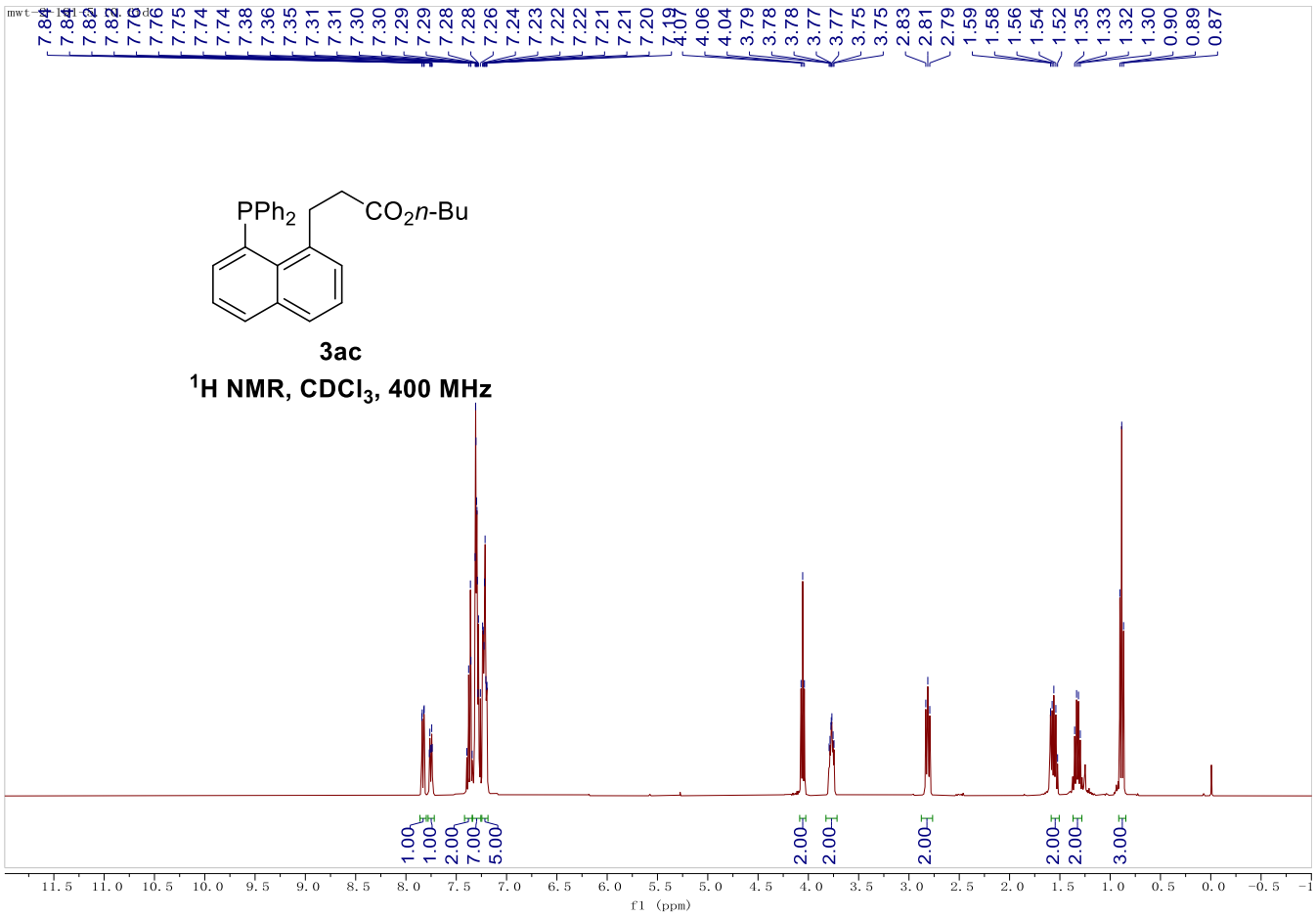
f1 (ppm)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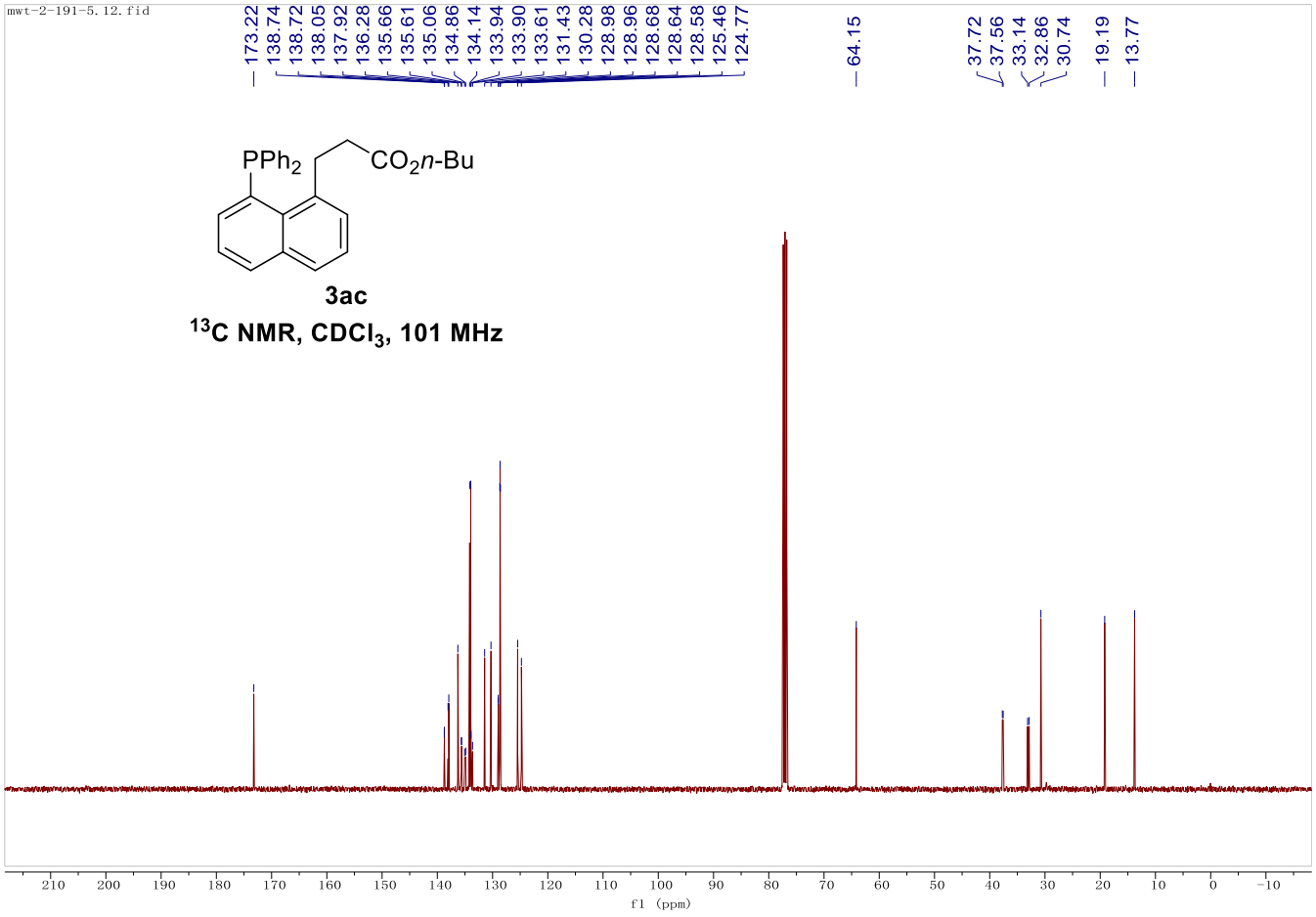
CO2n-Bu
3ac
1H NMR, CDCl3, 400 MHz
f1 (ppm)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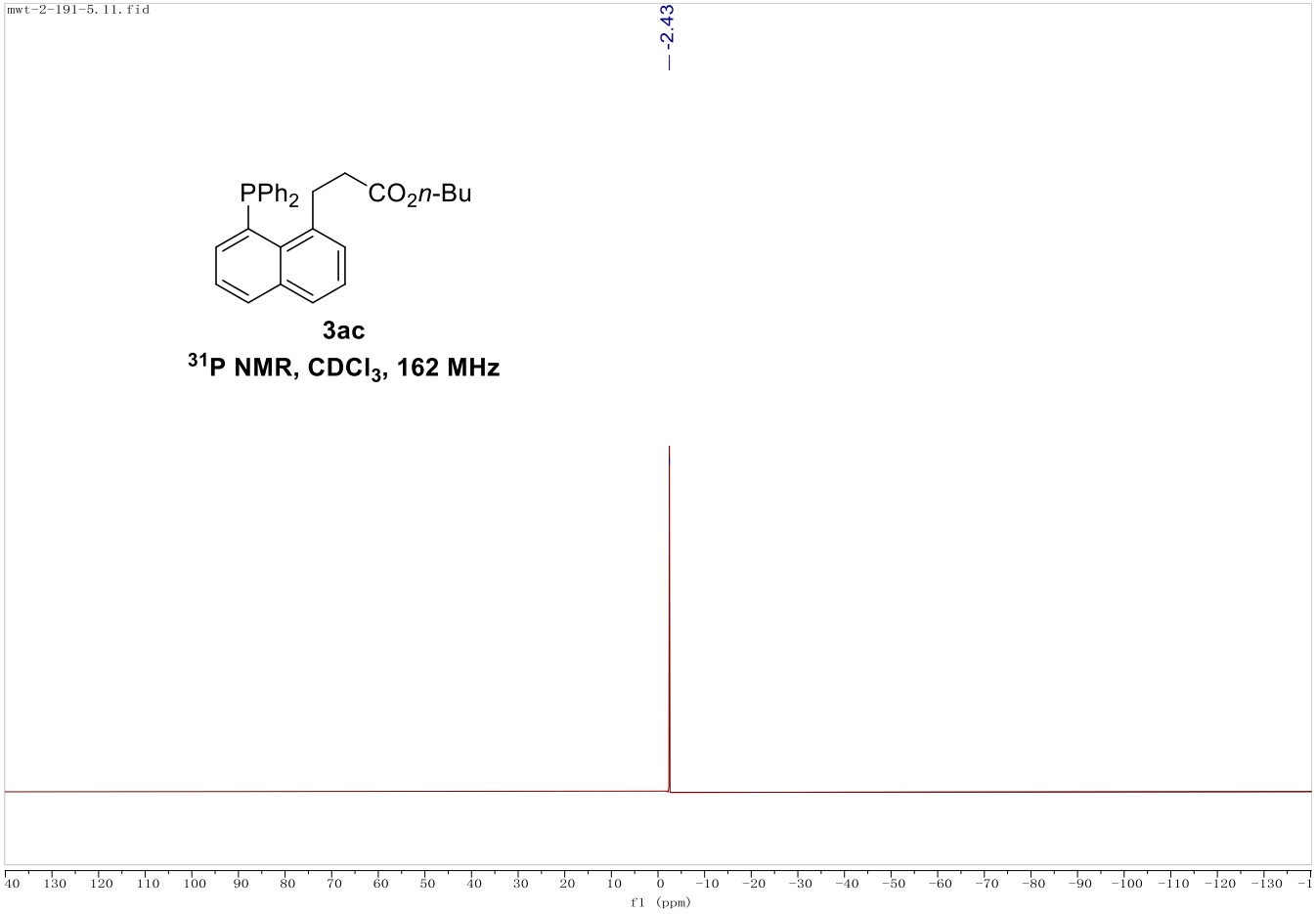
f1 (ppm)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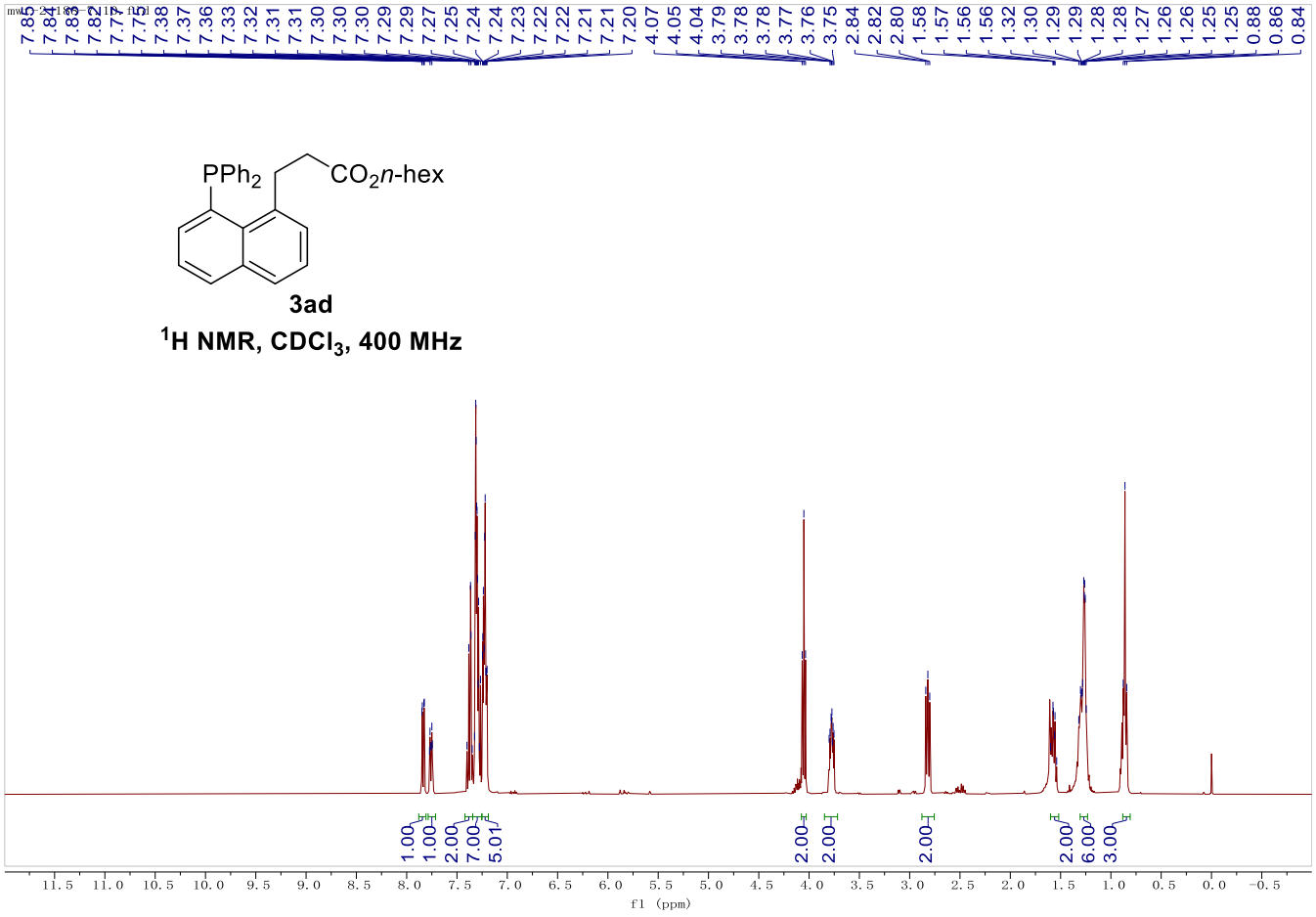
f1 (ppm)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3ad
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1.00
2.00
7.00
5.01
2.00
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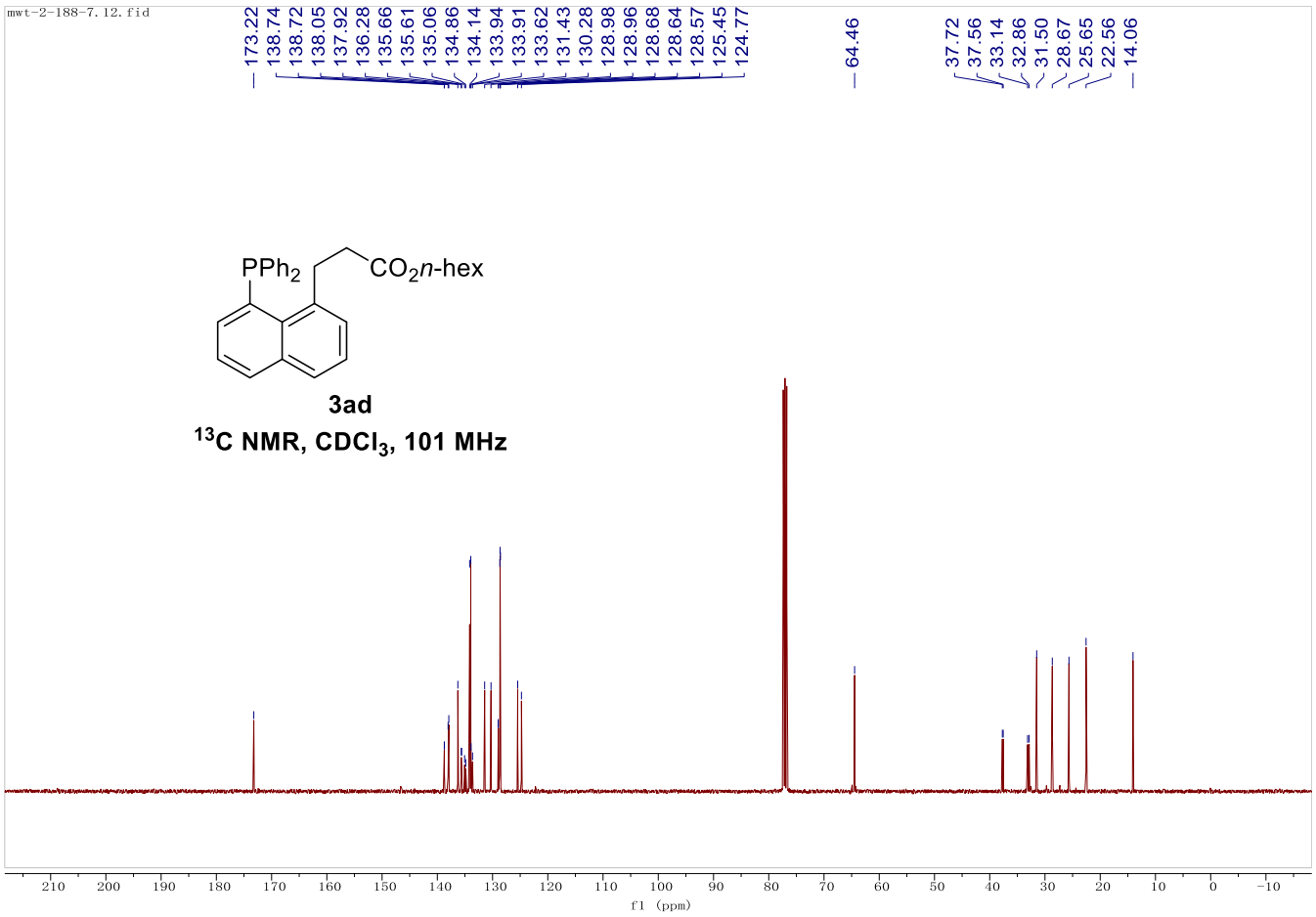
2.00
2.00
6.00
3.00
f1 (ppm)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134.14
133.94
133.91
133.62
131.43
130.28
128.98
128.96
128.68
128.64
128.57
125.45
124.77
64.46
37.72
37.56
33.14
32.86
31.50
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25.65
22.56
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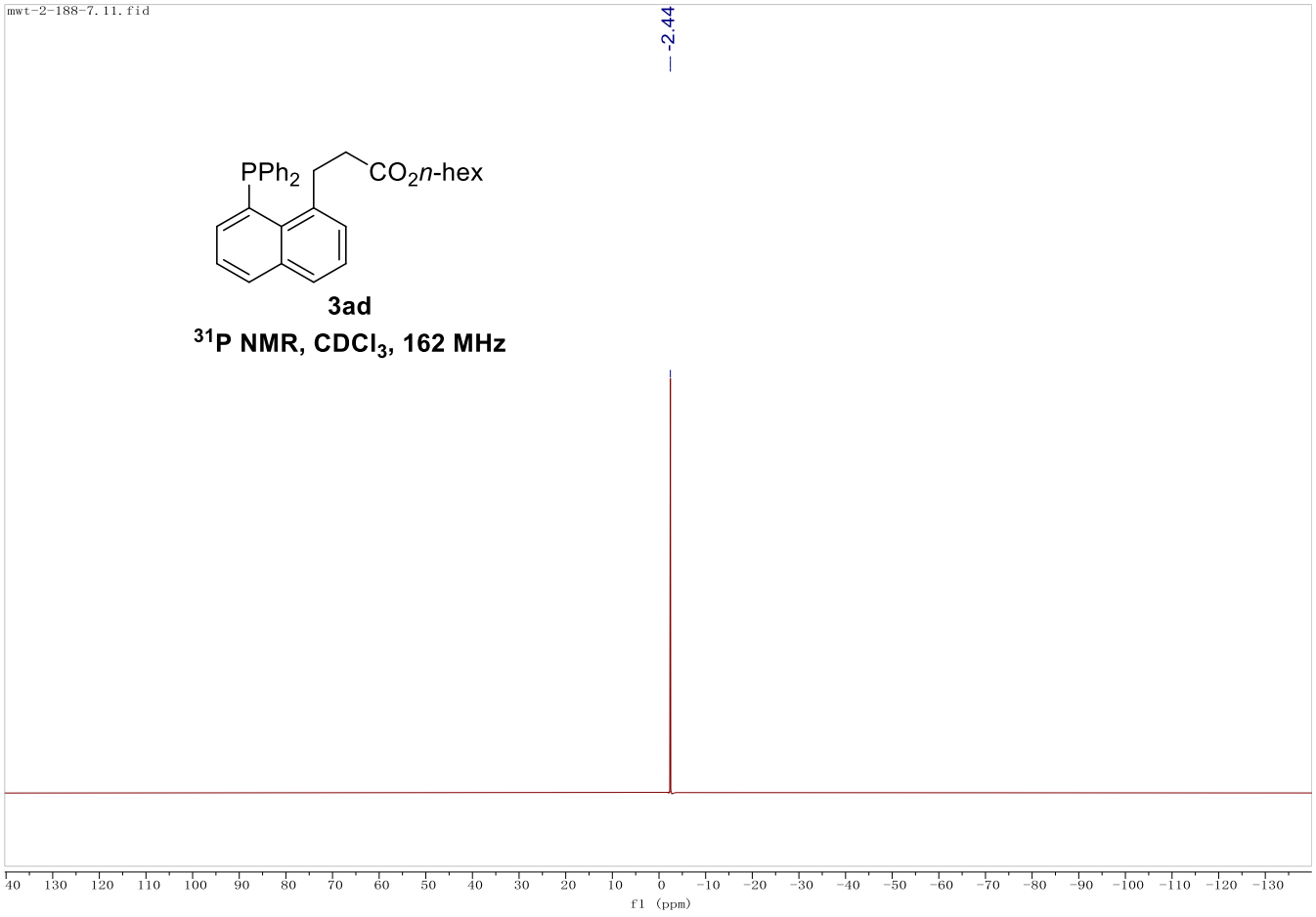
PPh2
CO2n-hex
3ad
13C NMR, CDCl3, 101 MHz
f1 (ppm)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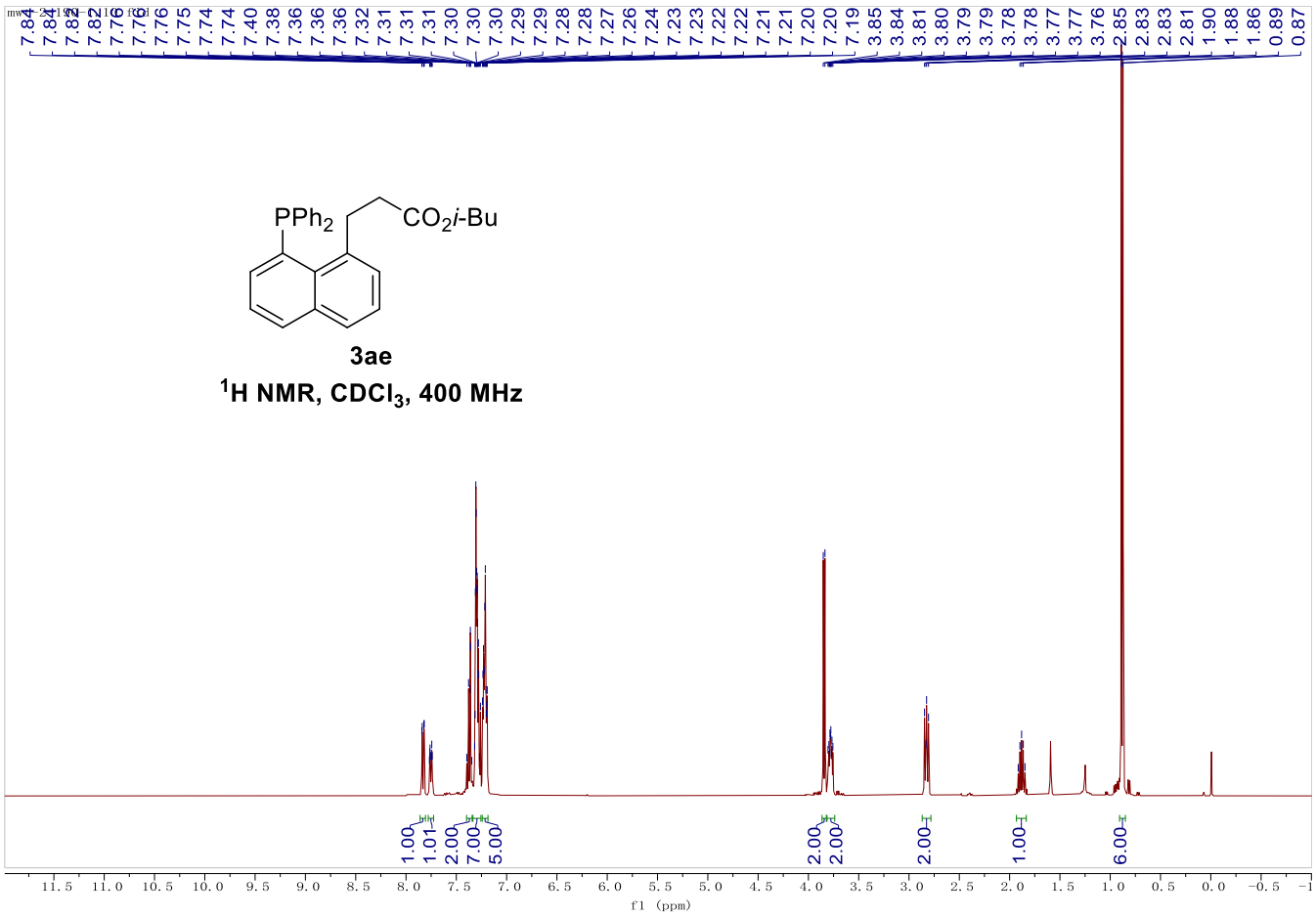
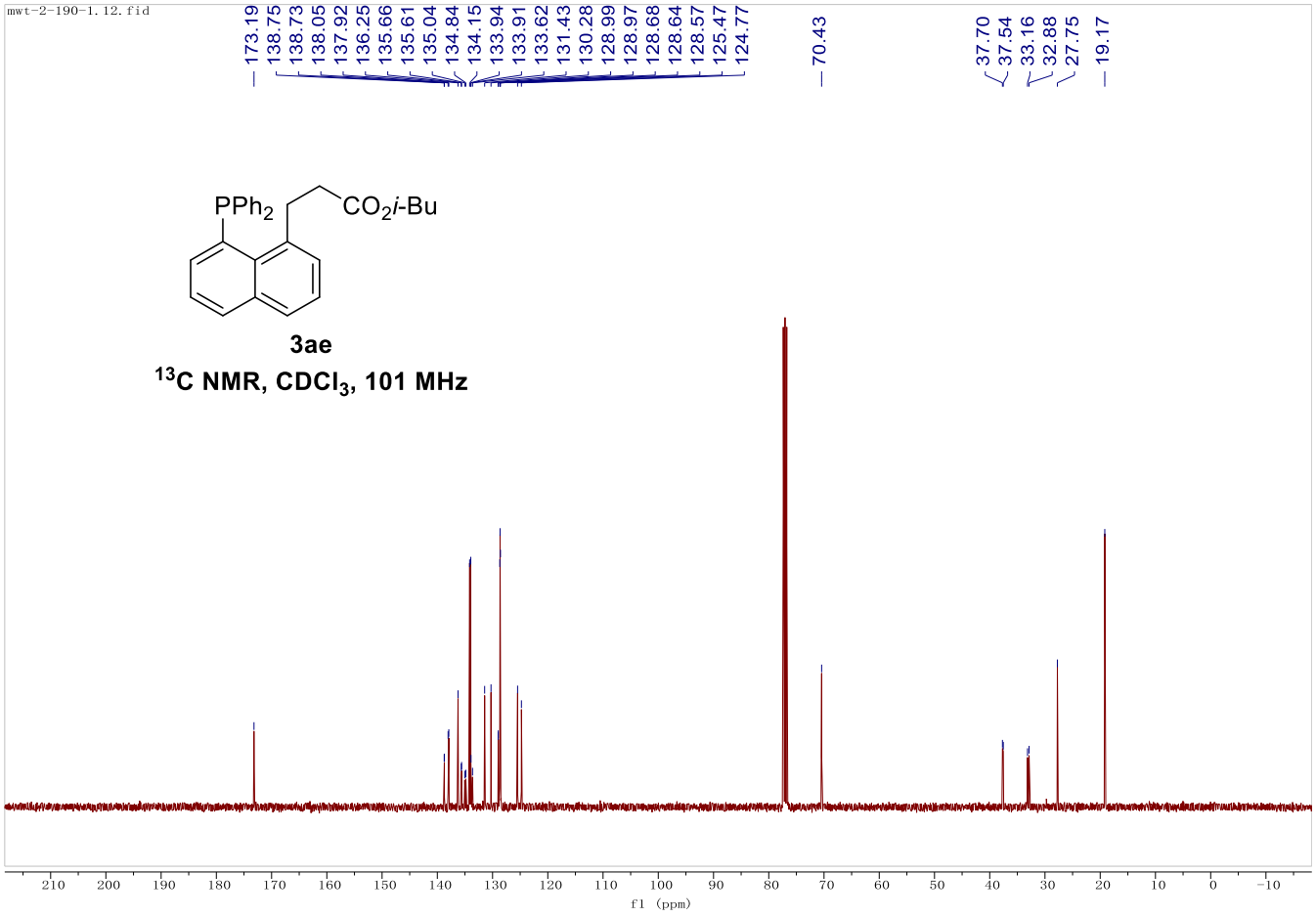
31P NMR, CDCl3, 162 MHz
f1 (ppm)



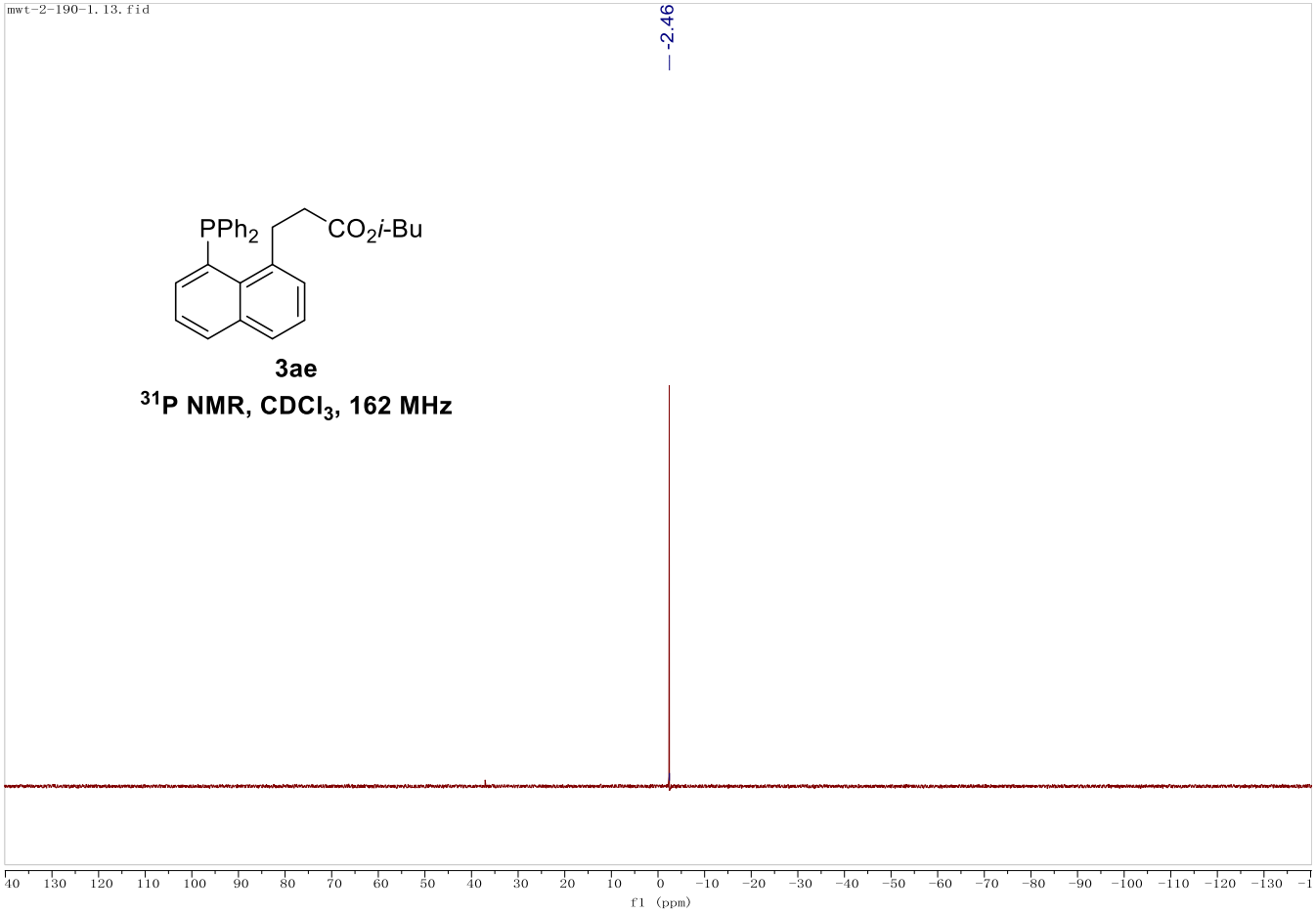
3ae

^{1}H NMR, $CDCl_3$, 400 MHz



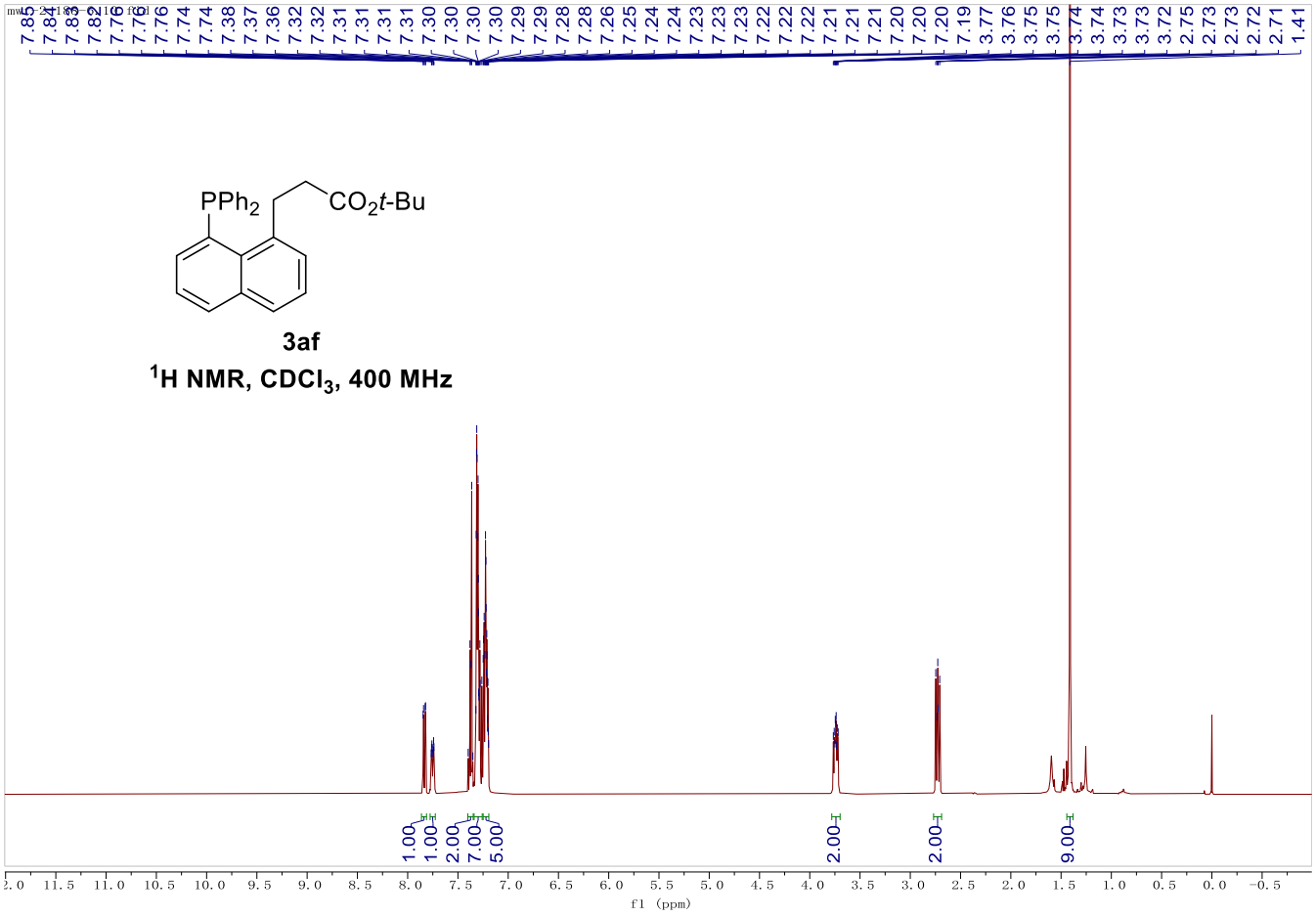
3ae

^{13}C NMR, $CDCl_3$, 101 MHz



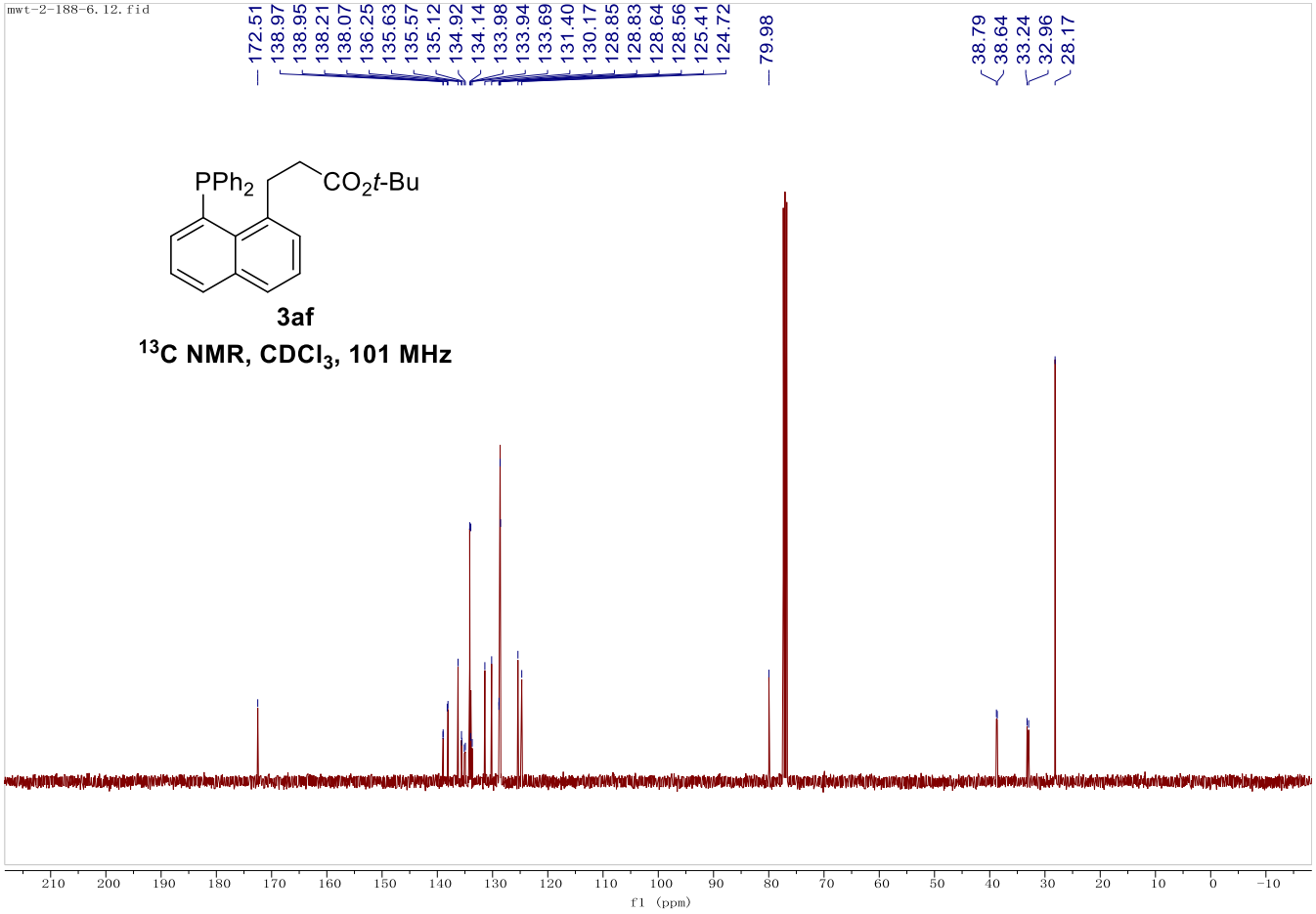
3ae

^{31}P NMR, $CDCl_3$, 162 MHz



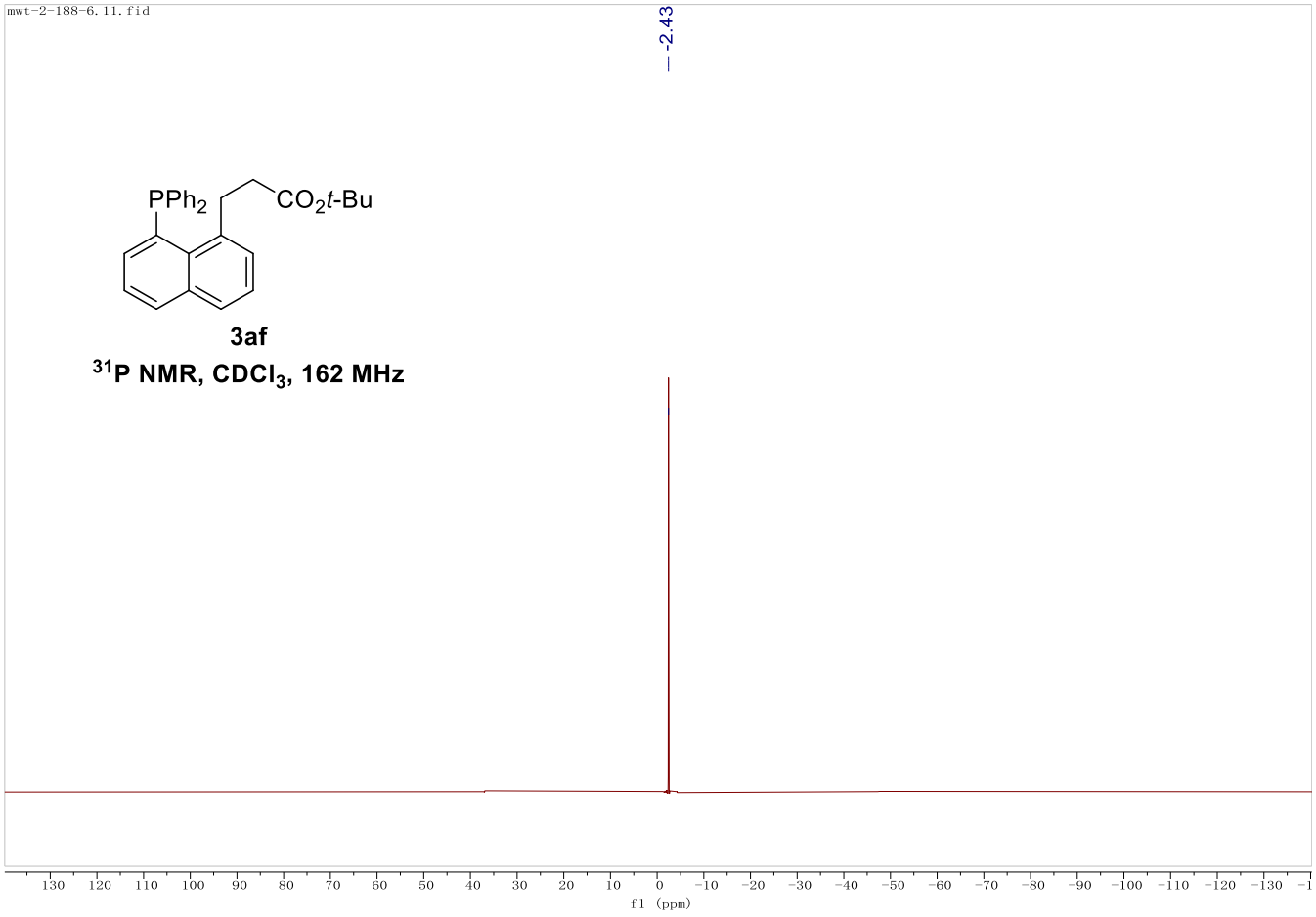
3af

^{1}H NMR, $CDCl_3$, 400 MHz



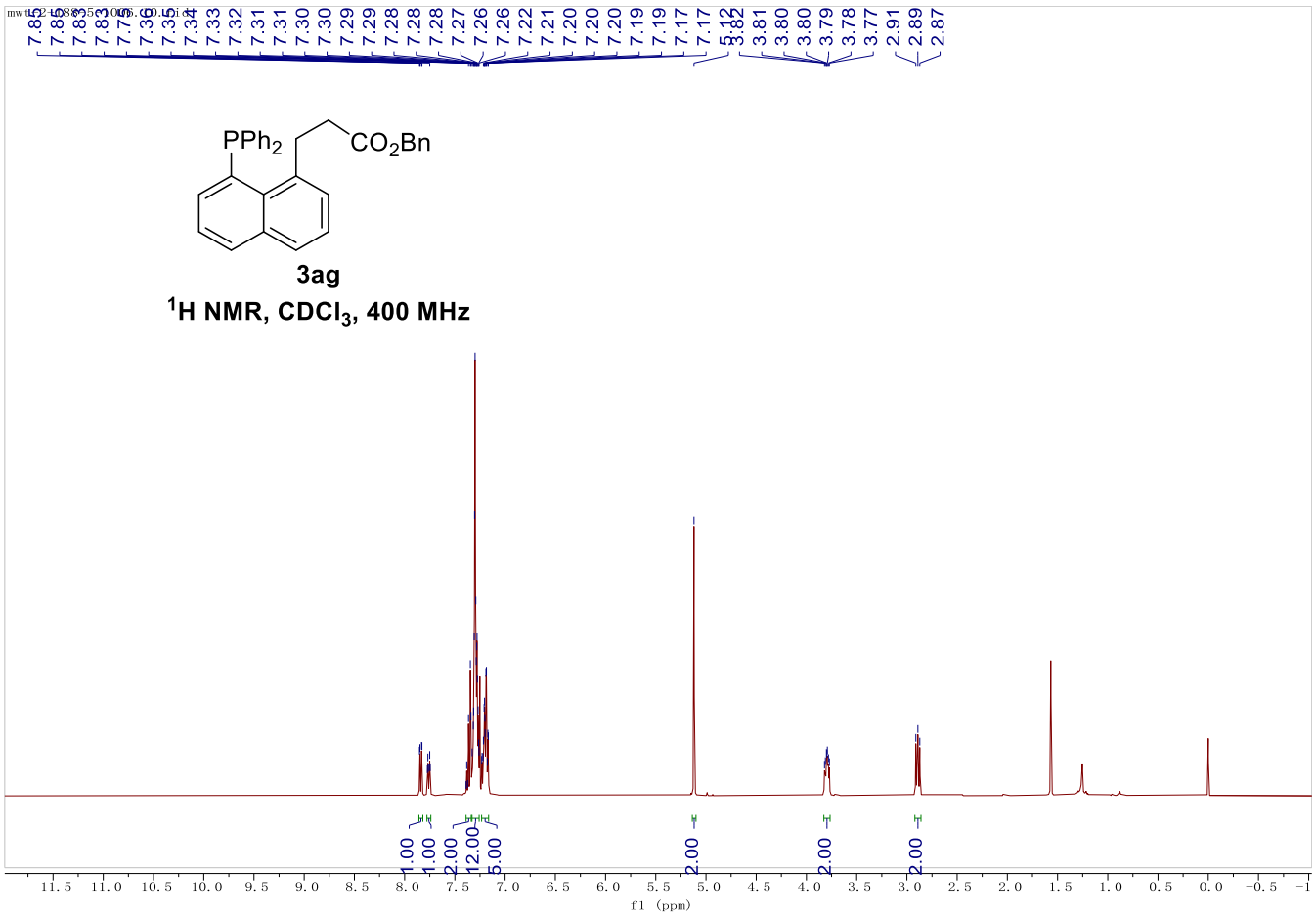
3af

^{13}C NMR, $CDCl_3$, 101 MHz



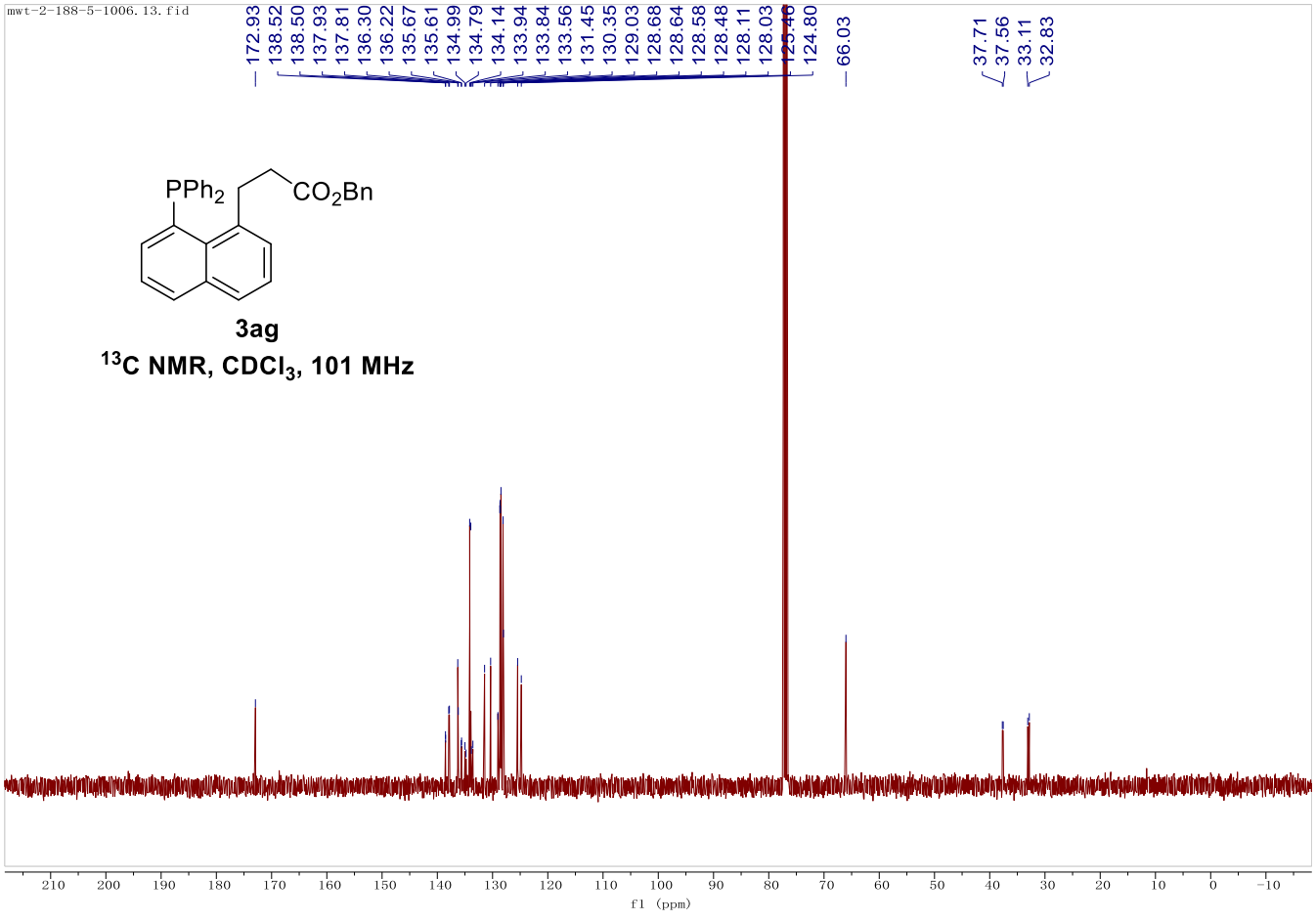
3af

^{31}P NMR, $CDCl_3$, 162 MHz



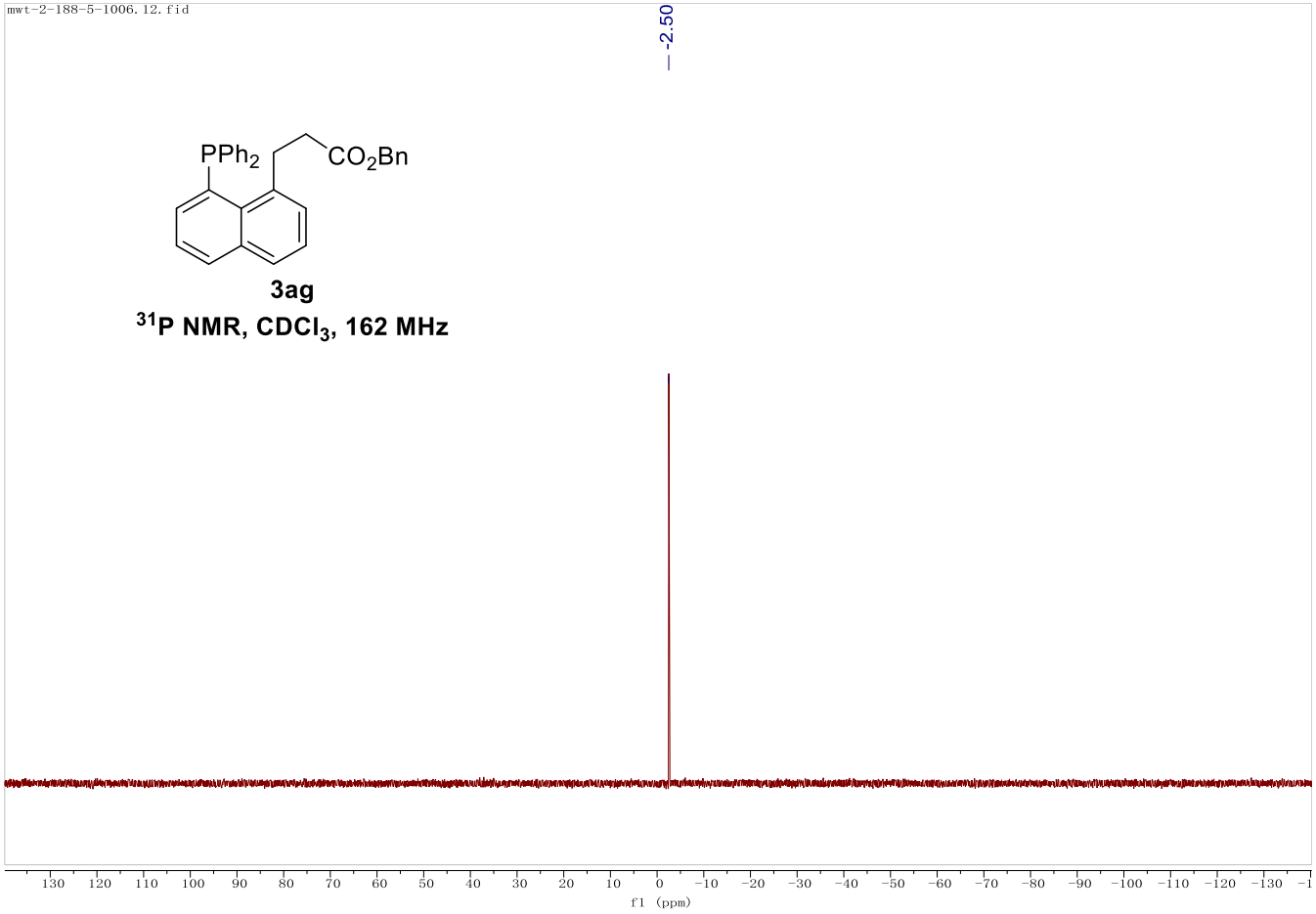
3ag

^{1}H NMR, $CDCl_3$, 400 MHz



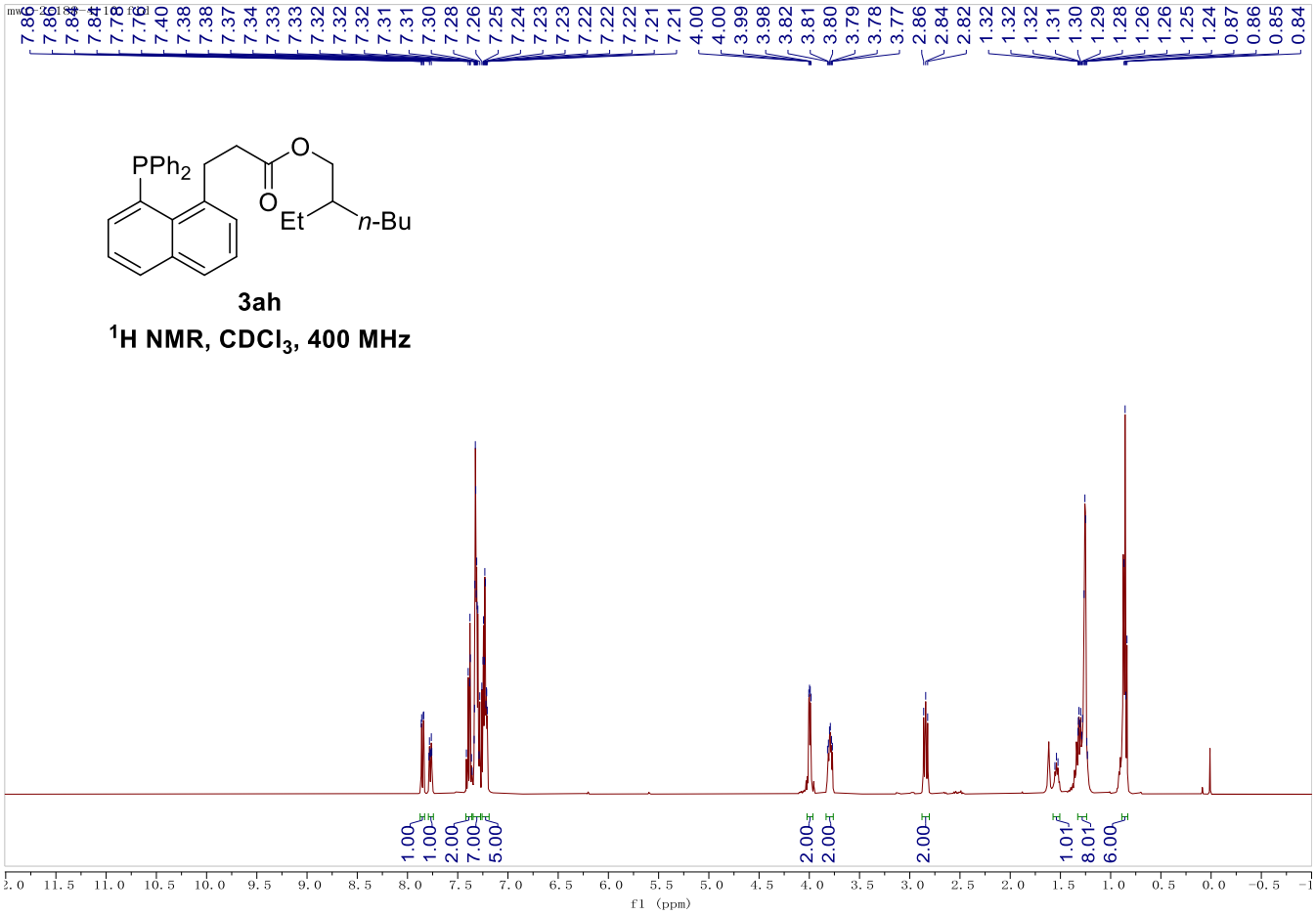
3ag

^{13}C NMR, $CDCl_3$, 101 MHz



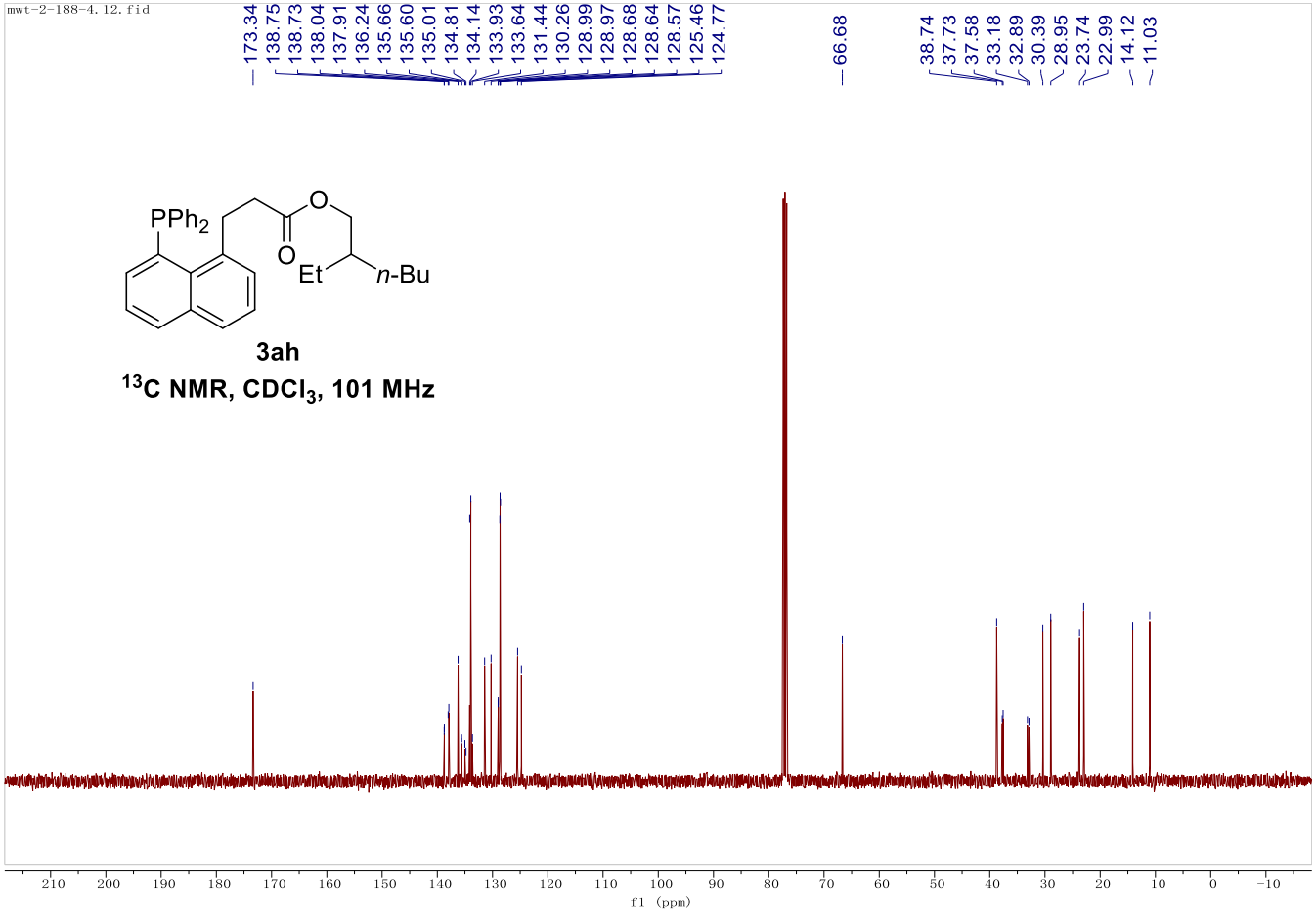
3ag

^{31}P NMR, $CDCl_3$, 162 MHz



3ah

^{1}H NMR, $CDCl_3$, 400 MHz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138.75
138.73
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137.91
136.24
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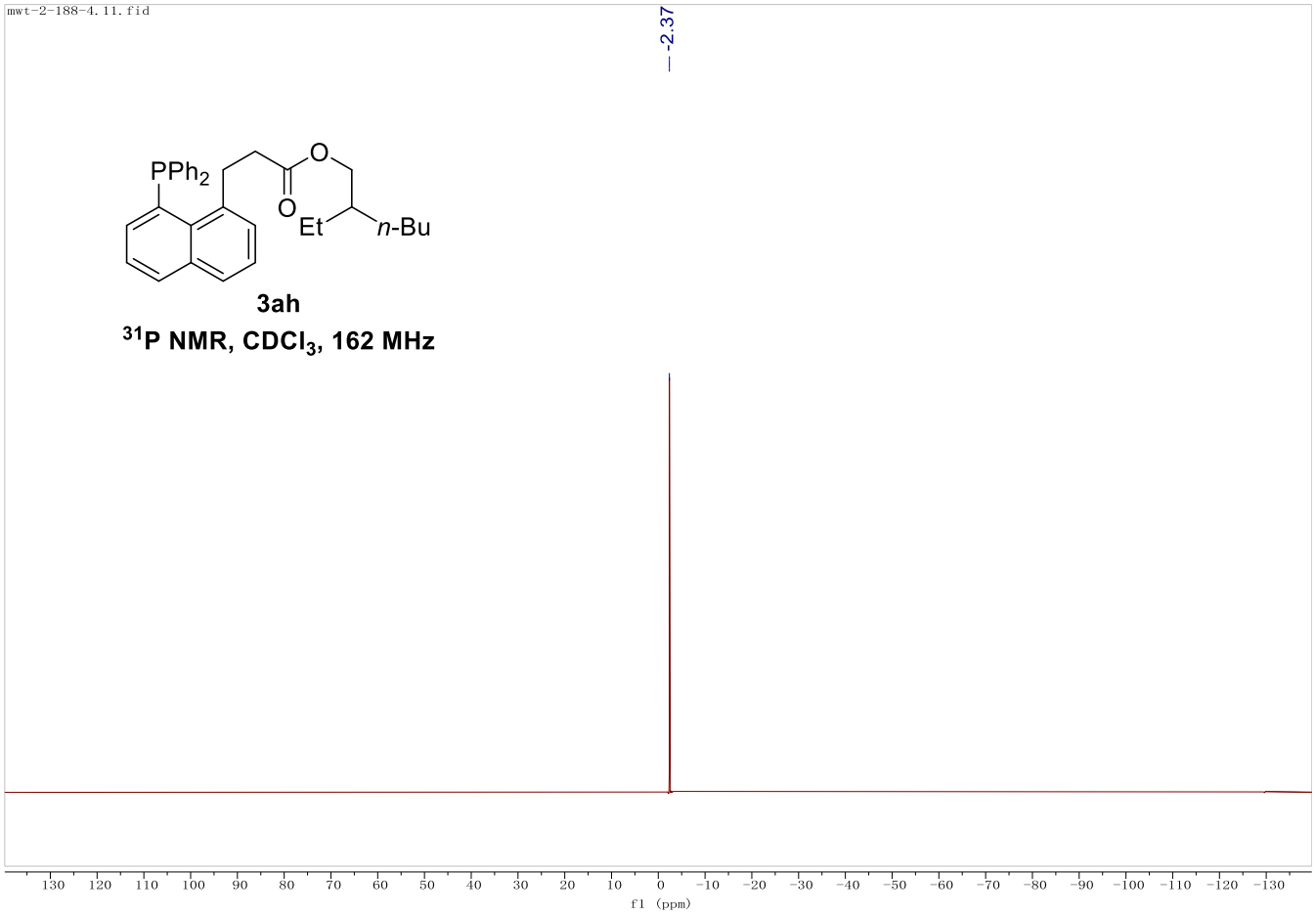
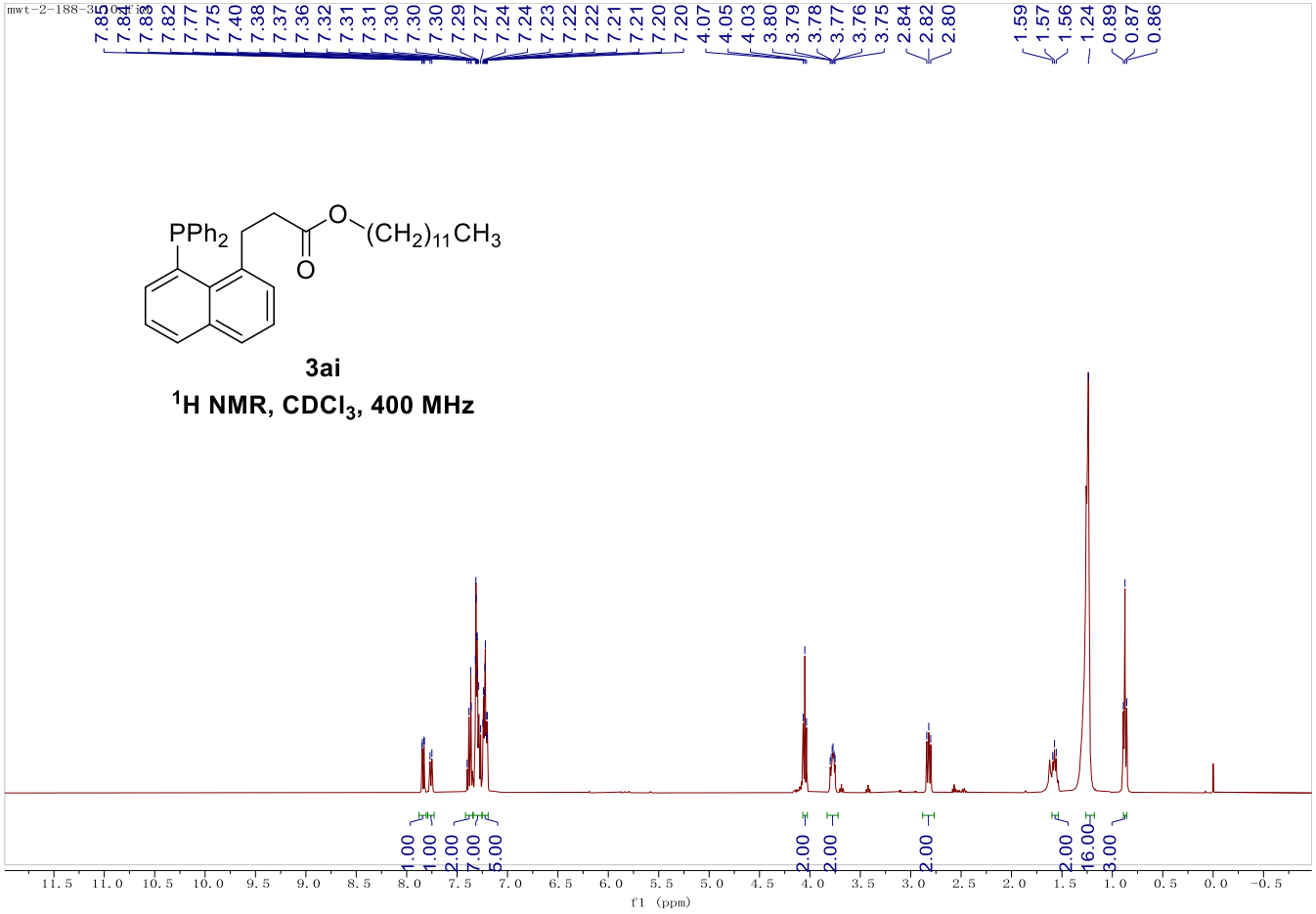
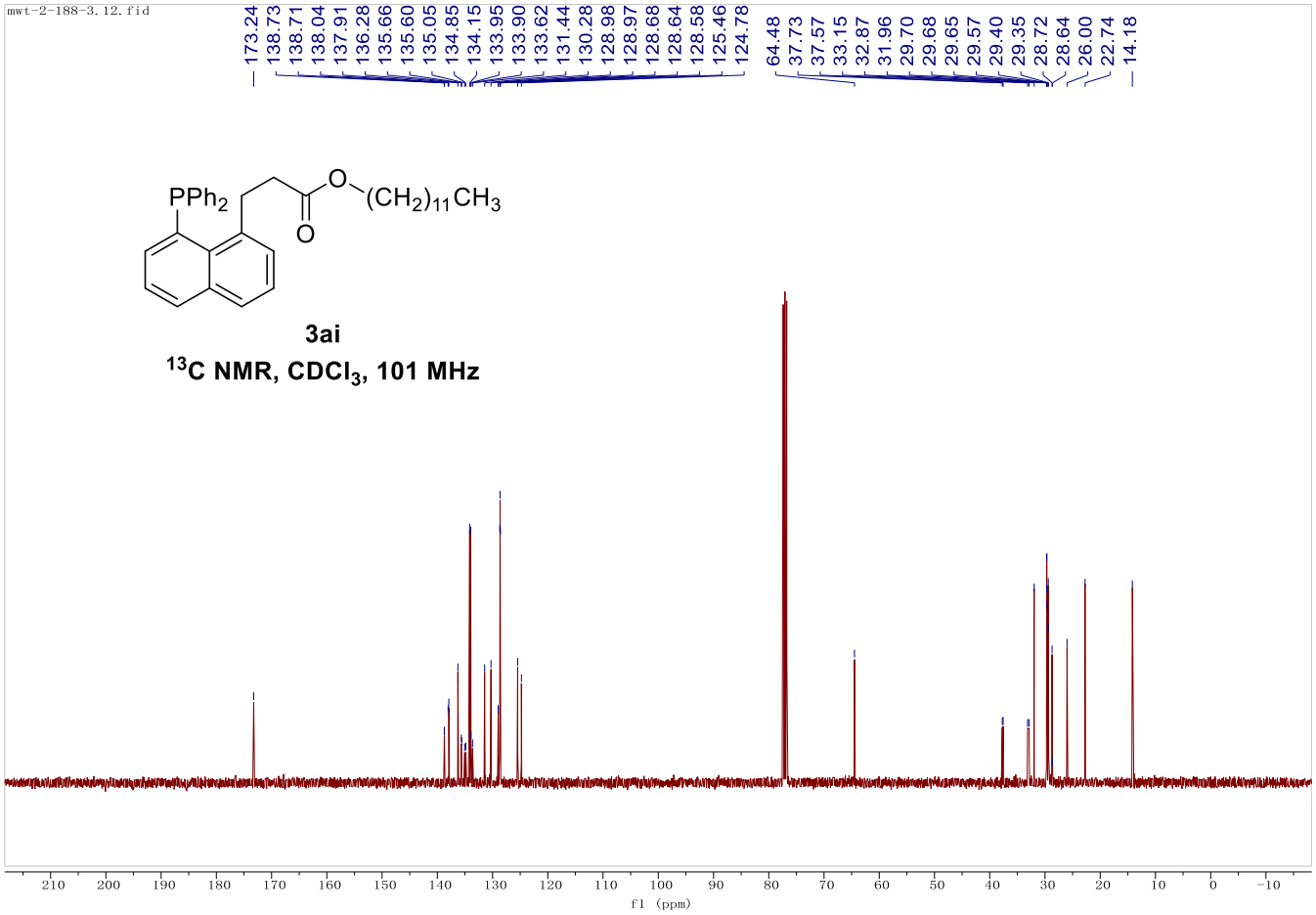
135.01
134.81
134.14
133.93
133.64
131.44
130.26
128.99
128.97
128.68
128.64
128.57
125.46
124.77
66.68
38.74
37.73
37.58
33.18
32.89
30.39
28.95
23.74
22.99
14.12
11.03
PPh2
O
O
Et
n-Bu
3ah
13C NMR, CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


mwt-2-188-4.11.fid
-2.37
PPh2
O
O
Et
n-Bu
3ah
31P NMR, CDCl3, 162 MHz
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)



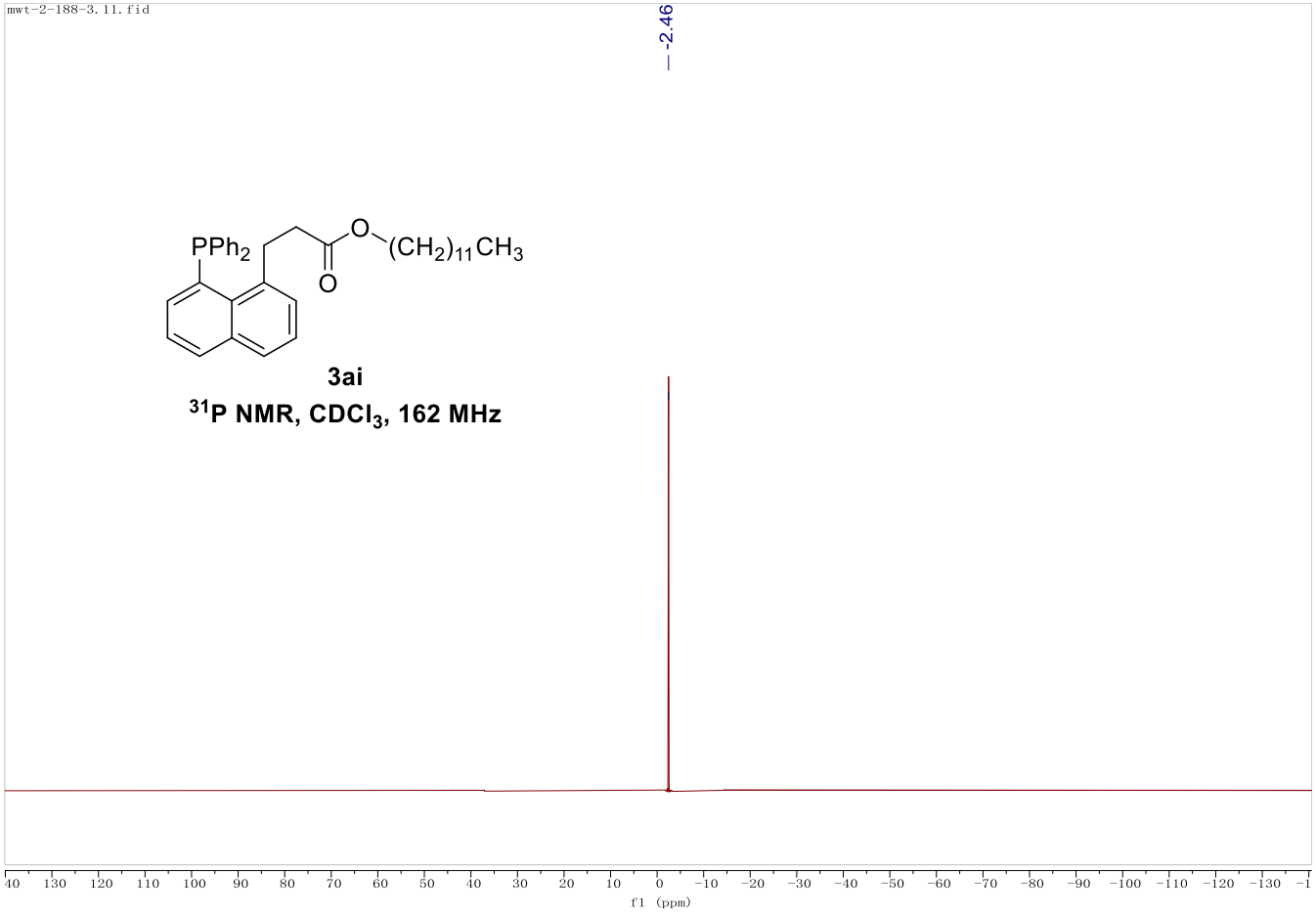
3ai

^{1}H NMR, $CDCl_3$, 400 MHz



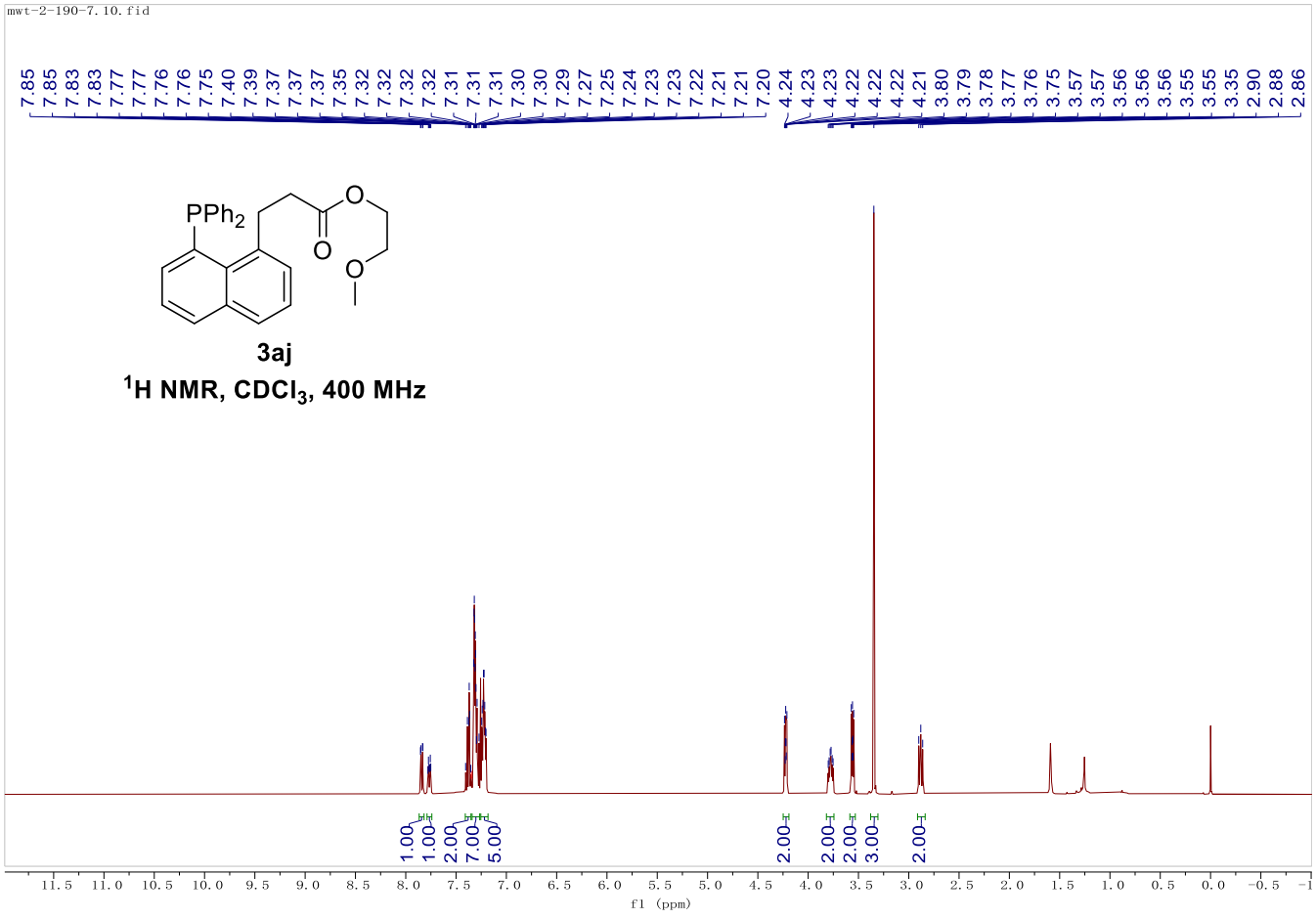
3ai

^{13}C NMR, $CDCl_3$, 101 MHz



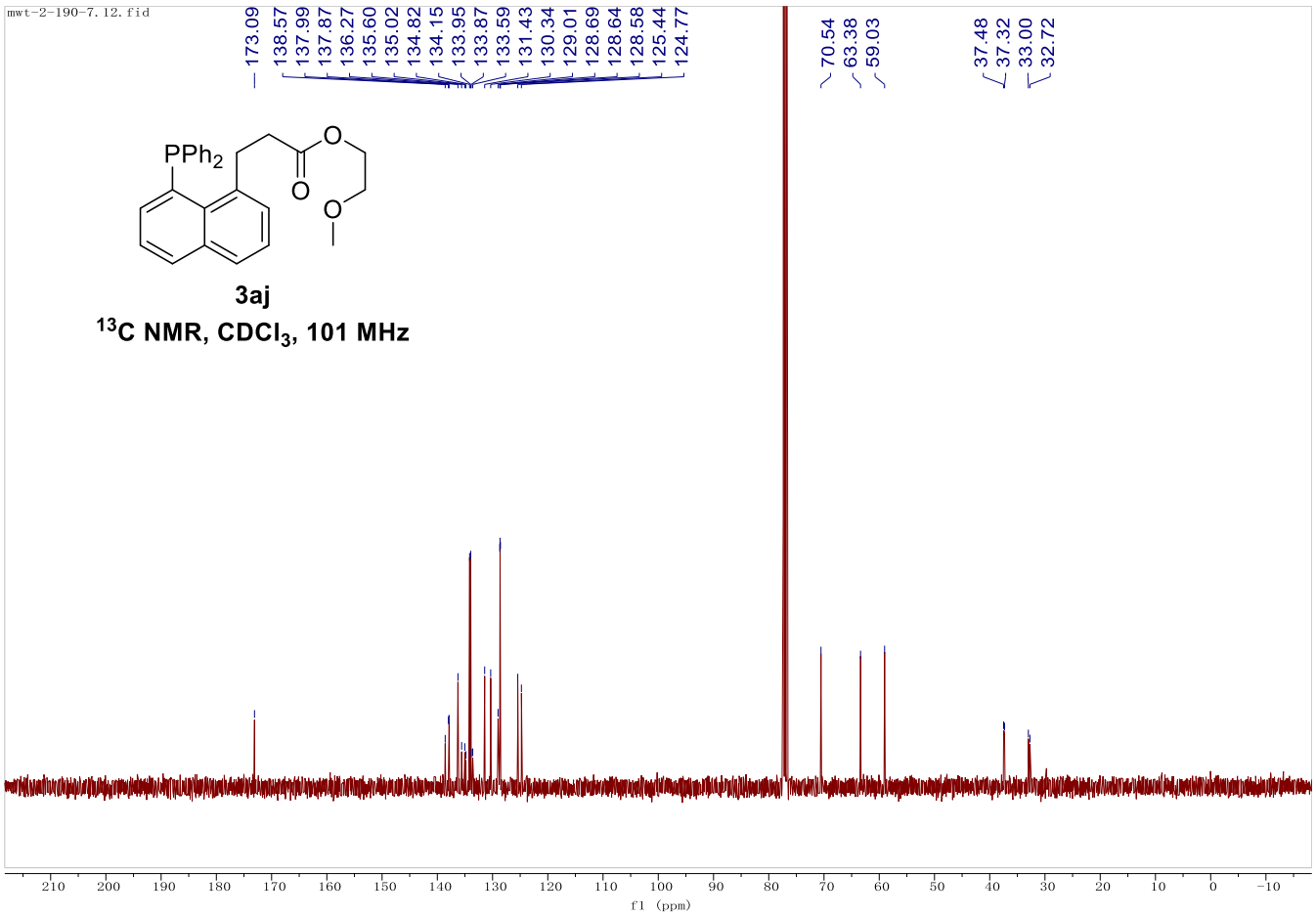
3ai

^{31}P NMR, $CDCl_3$, 162 MHz



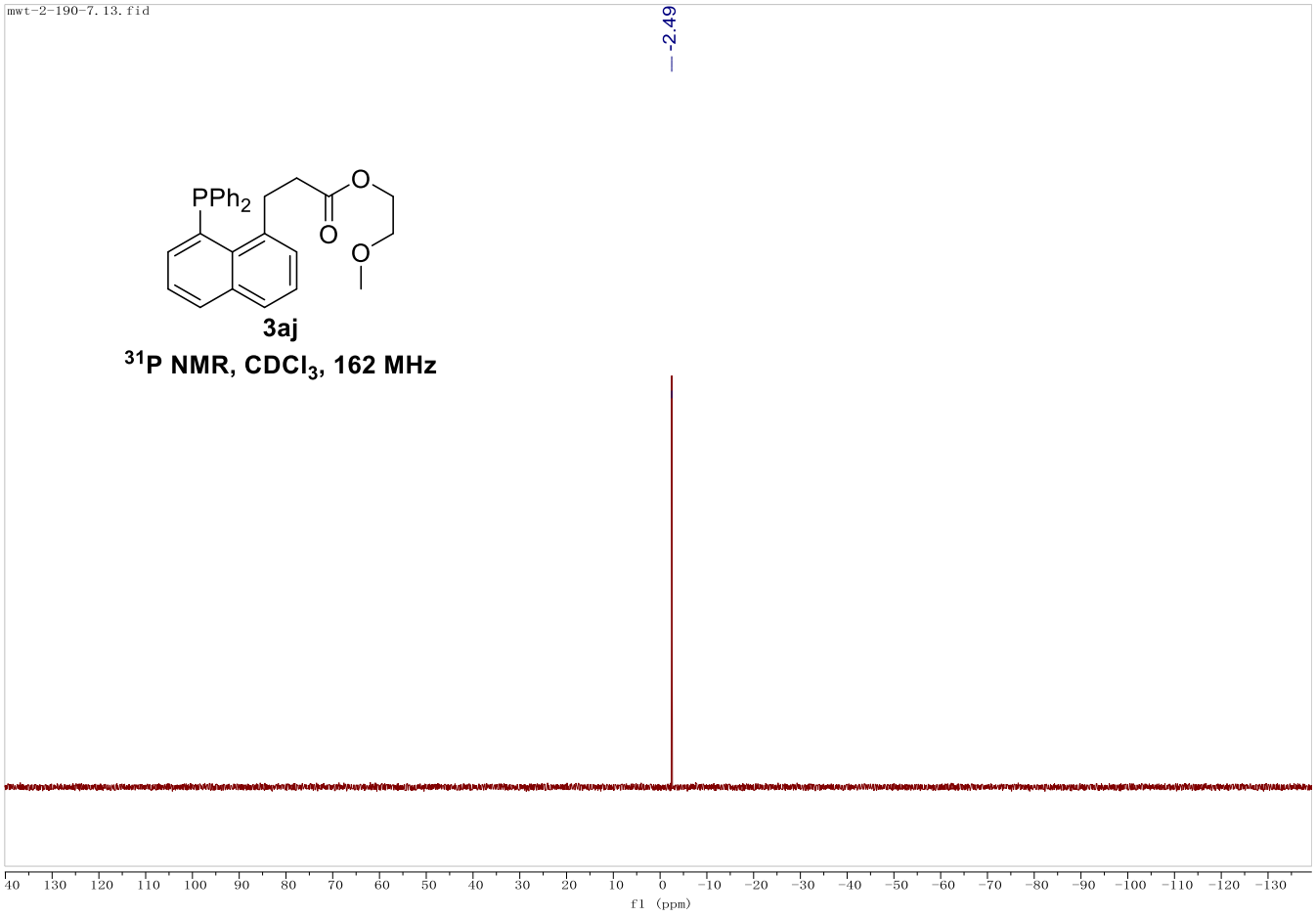
3aj

^{1}H NMR, $CDCl_3$, 400 MHz



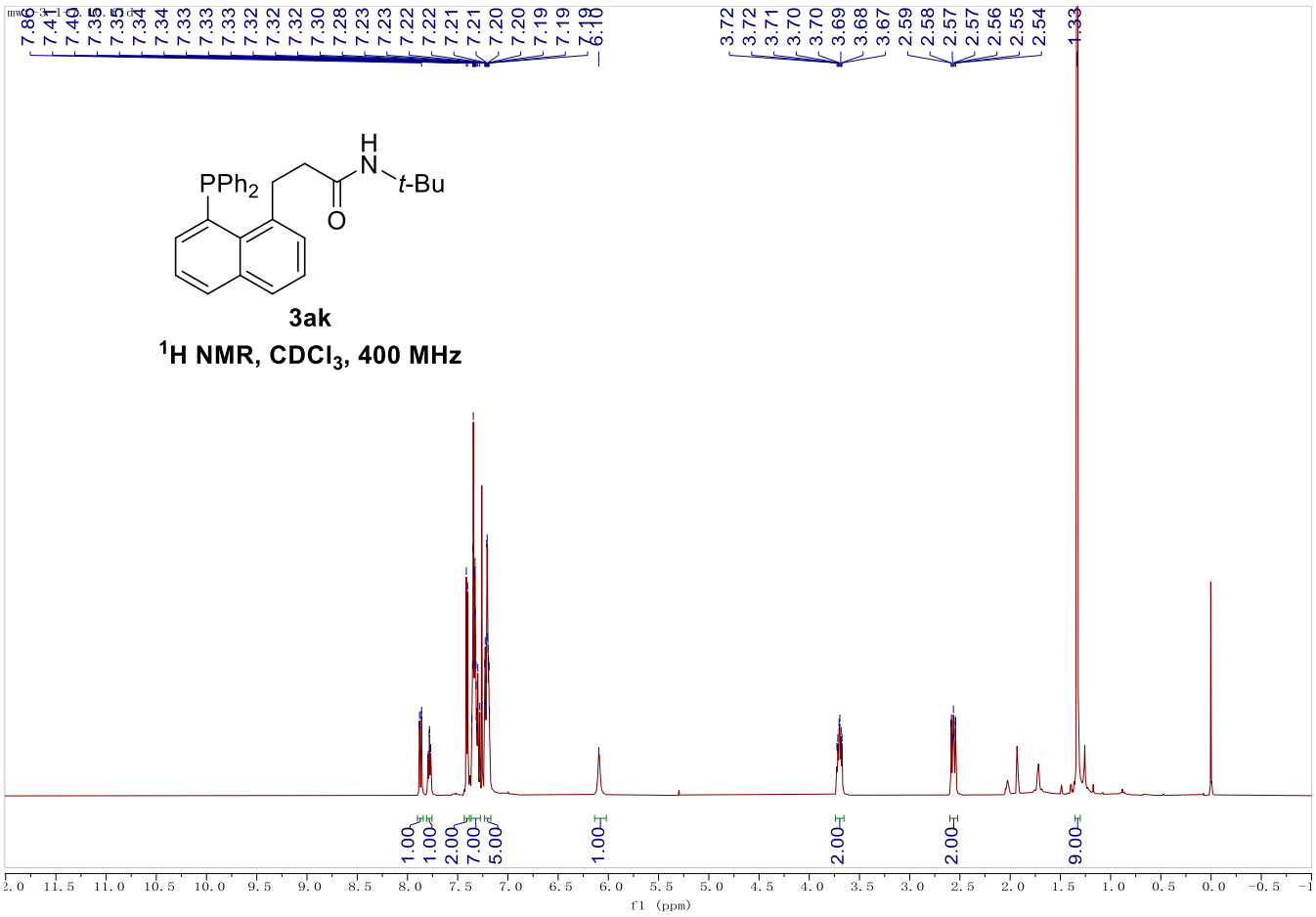
3aj

^{13}C NMR, $CDCl_3$, 101 MHz



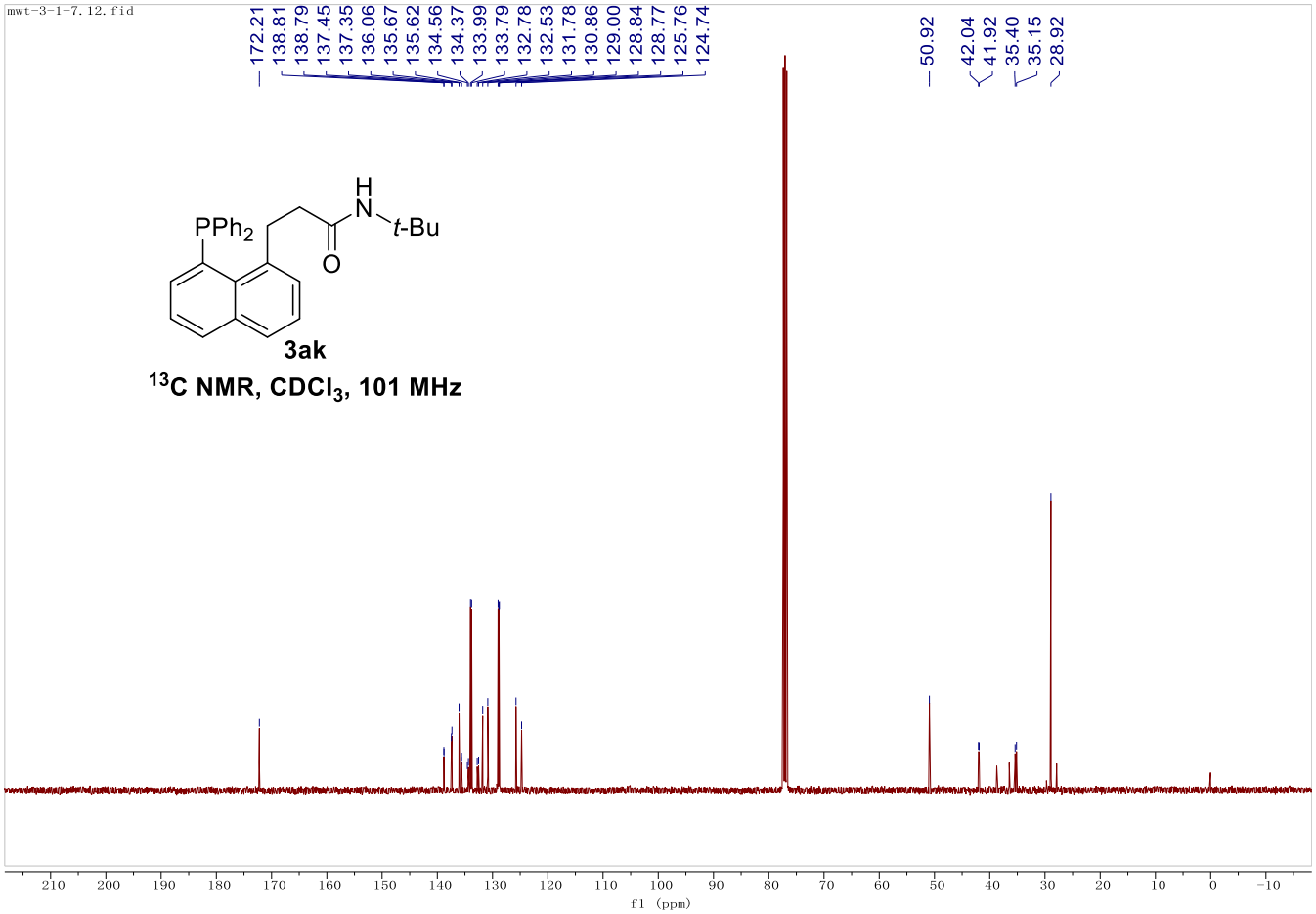
3aj

^{31}P NMR, $CDCl_3$, 162 MHz



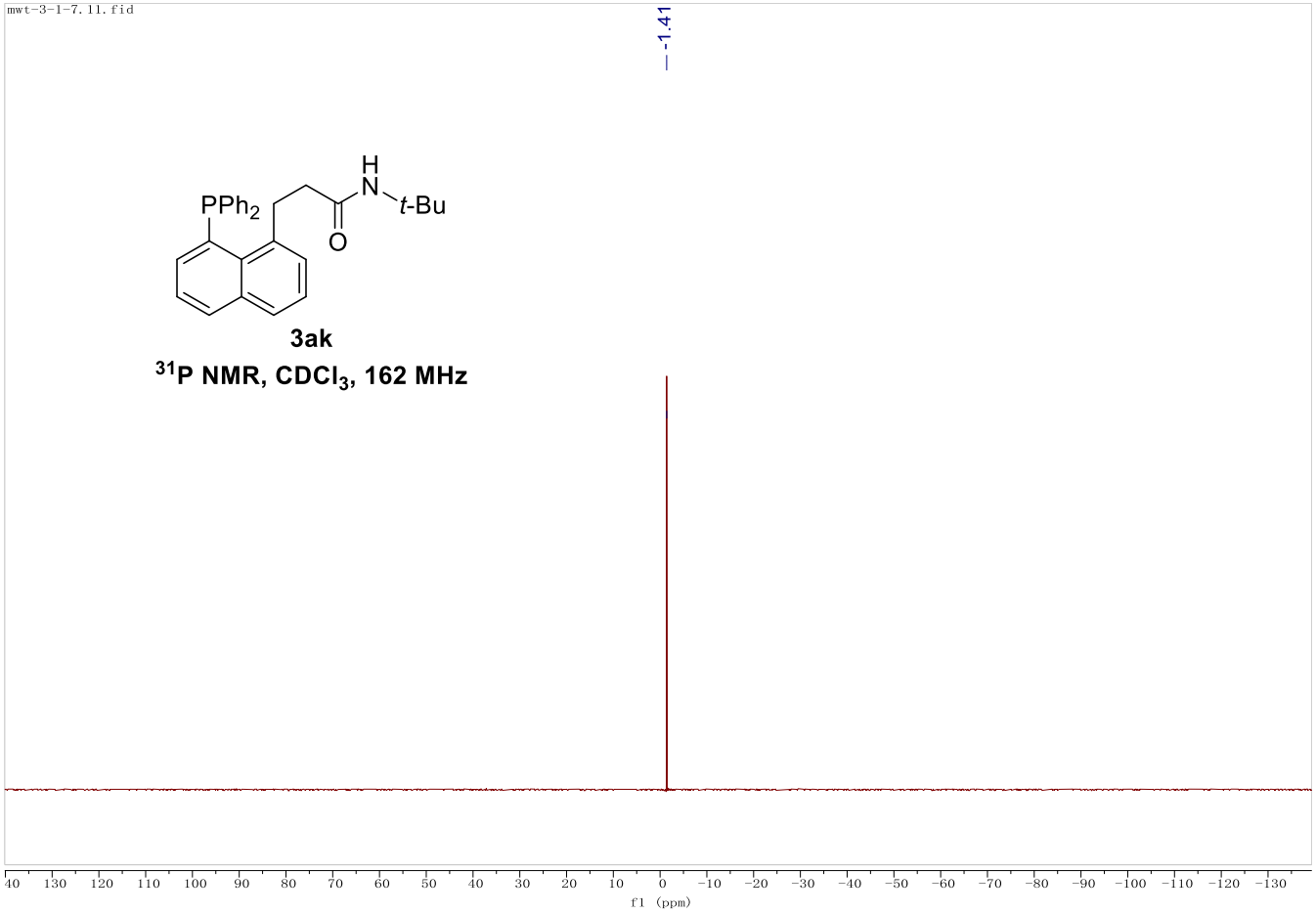
3ak

^{1}H NMR, $CDCl_3$, 400 MHz



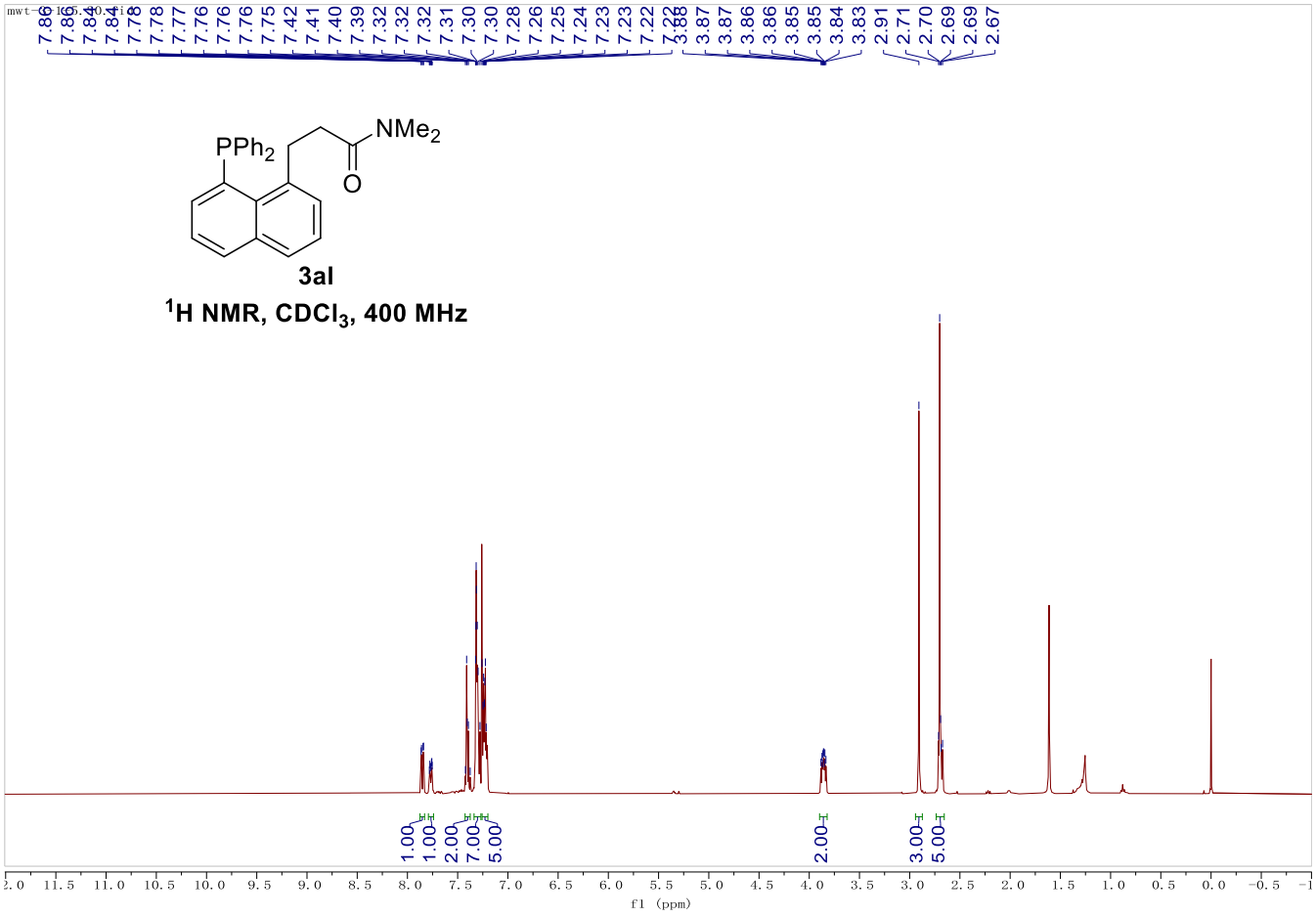
3ak

^{13}C NMR, $CDCl_3$, 101 MHz



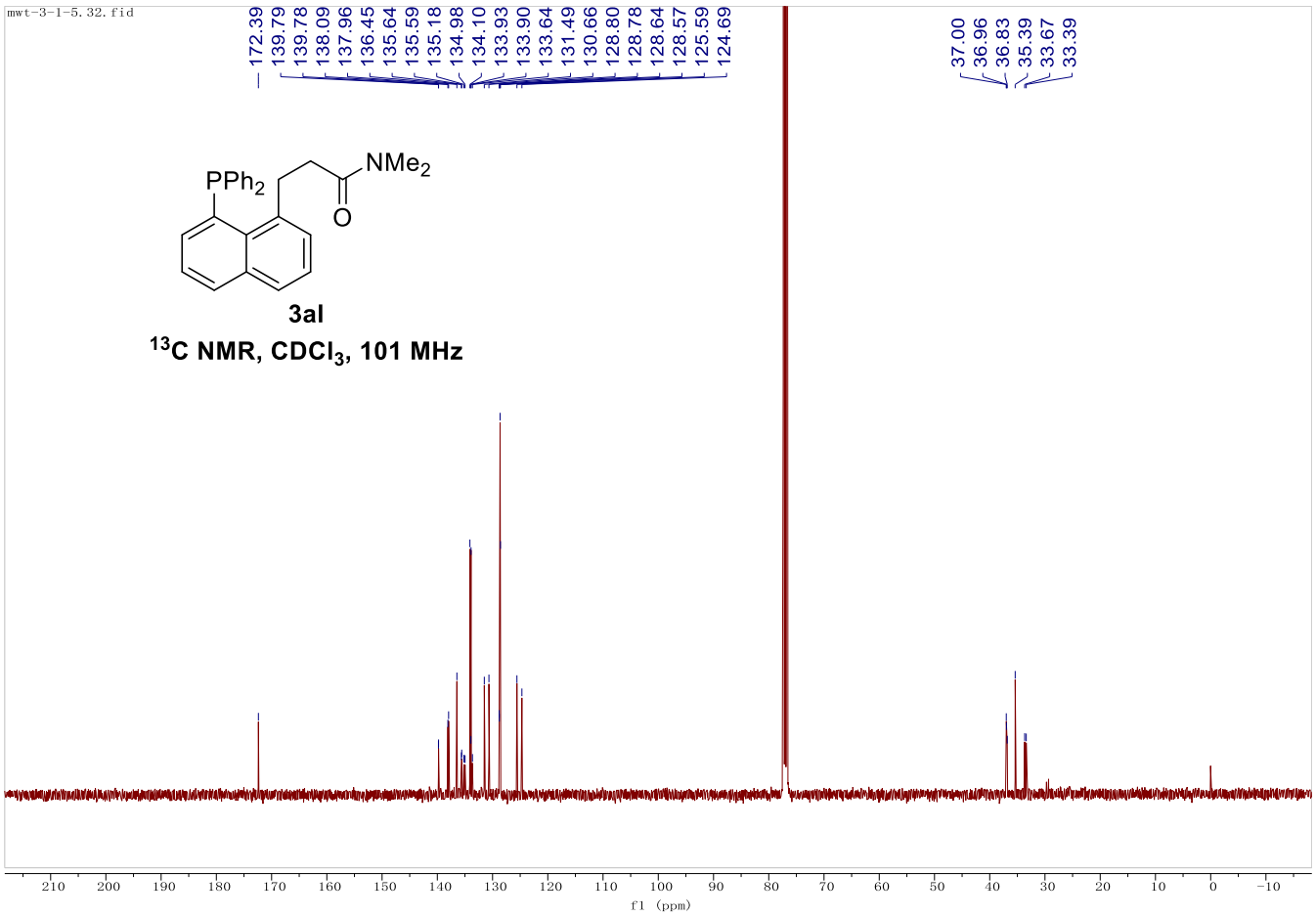
3ak

^{31}P NMR, $CDCl_3$, 162 MHz



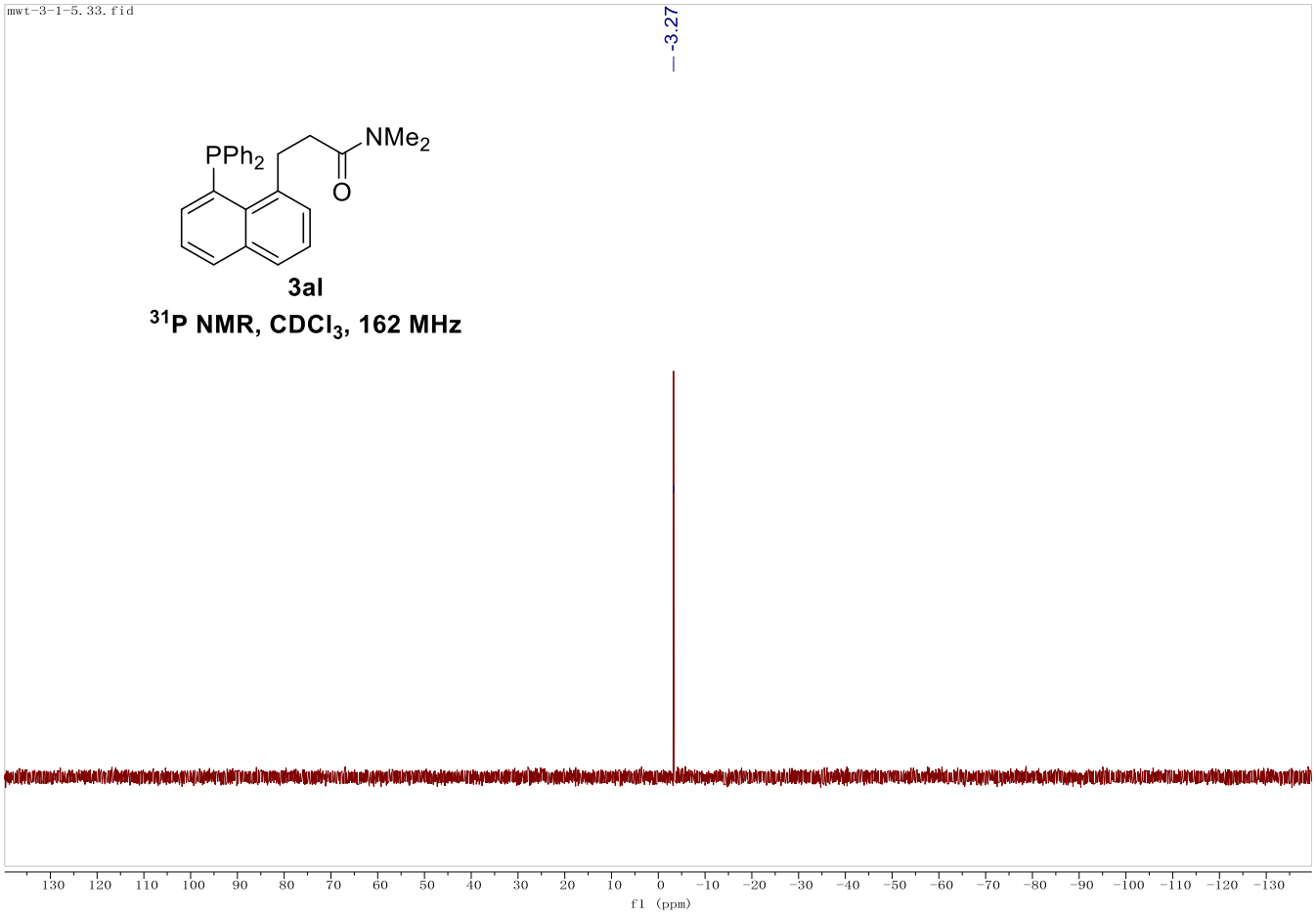
3al

^{1}H NMR, $CDCl_3$, 400 MHz



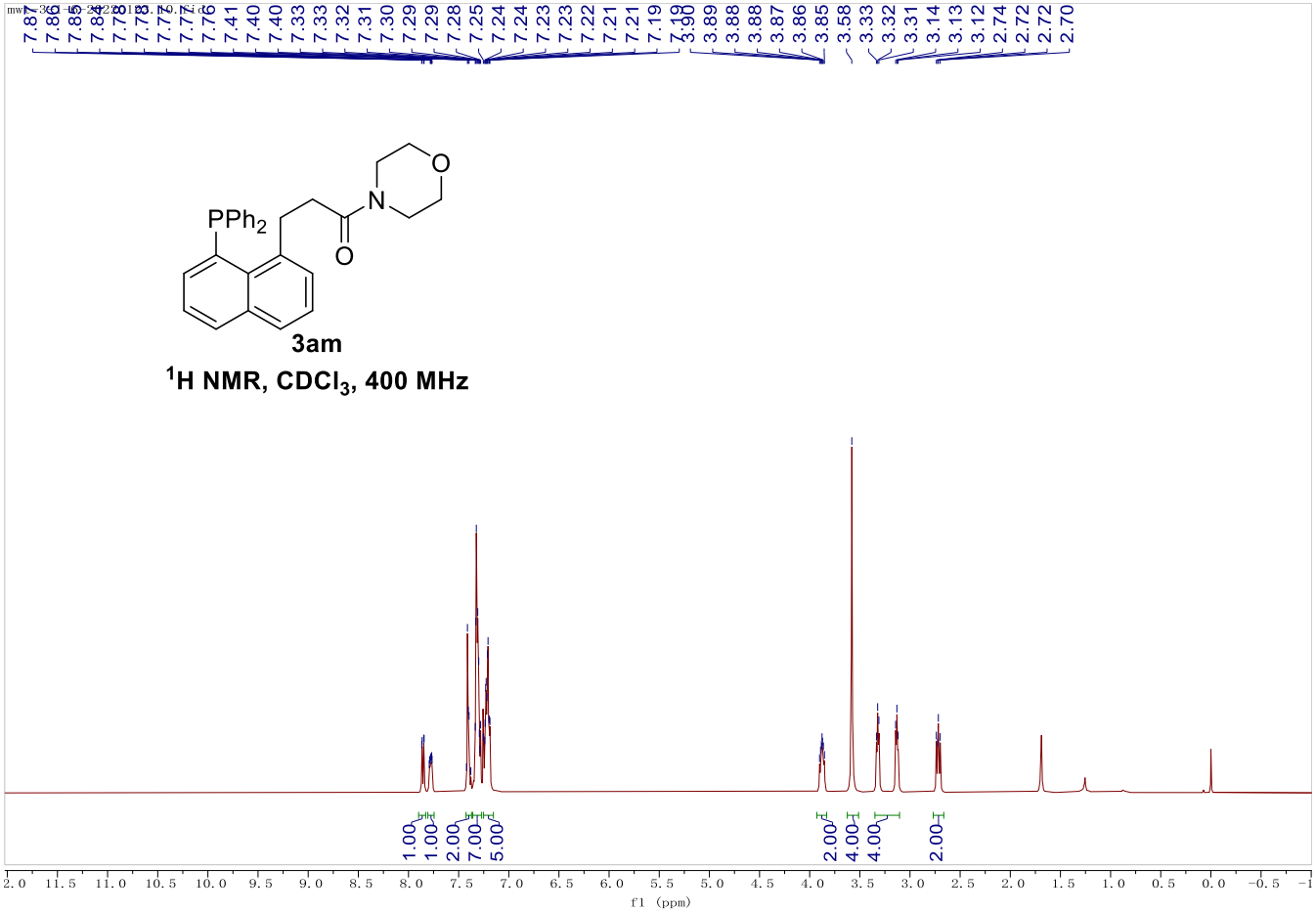
3al

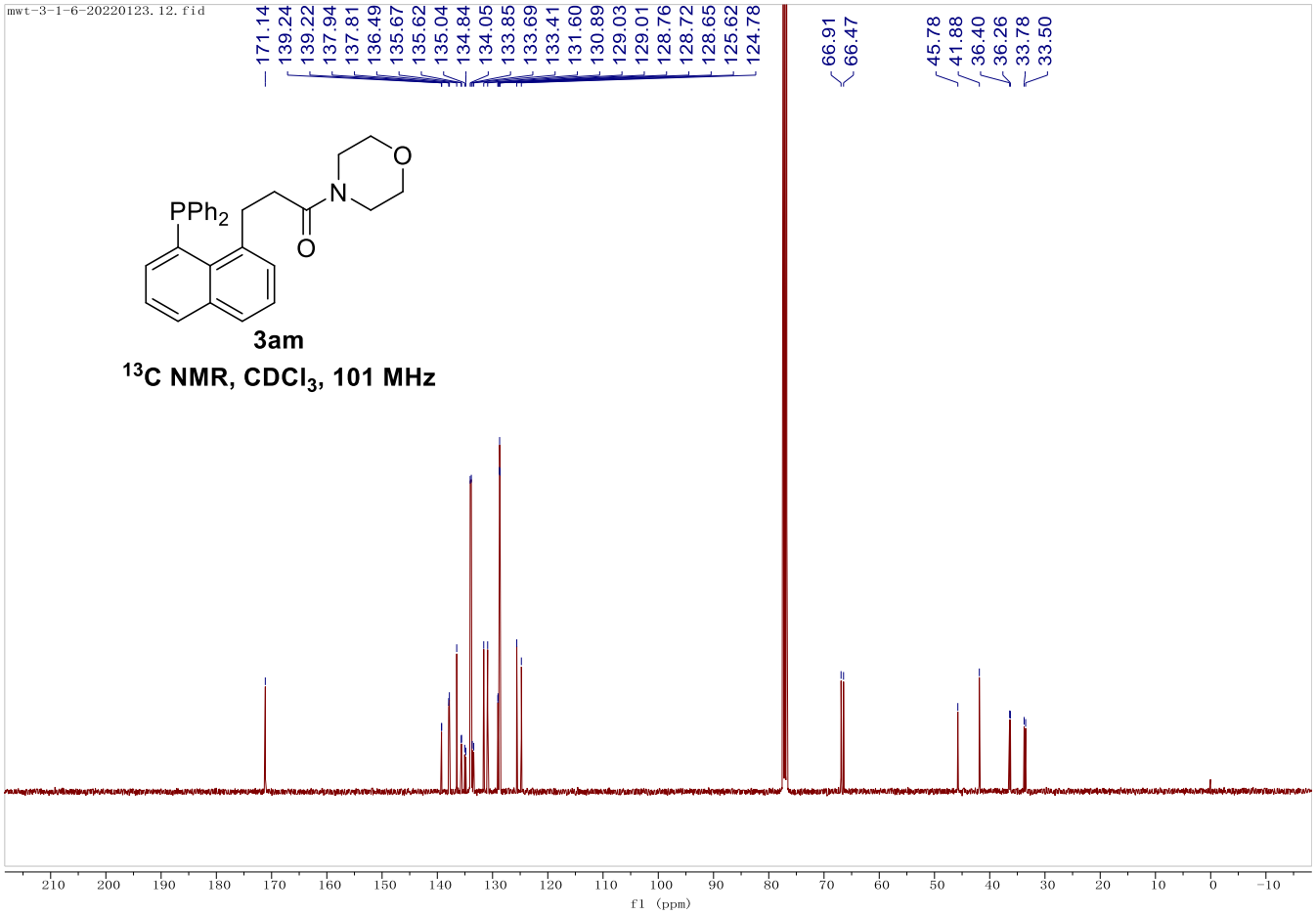
^{13}C NMR, $CDCl_3$, 101 MHz

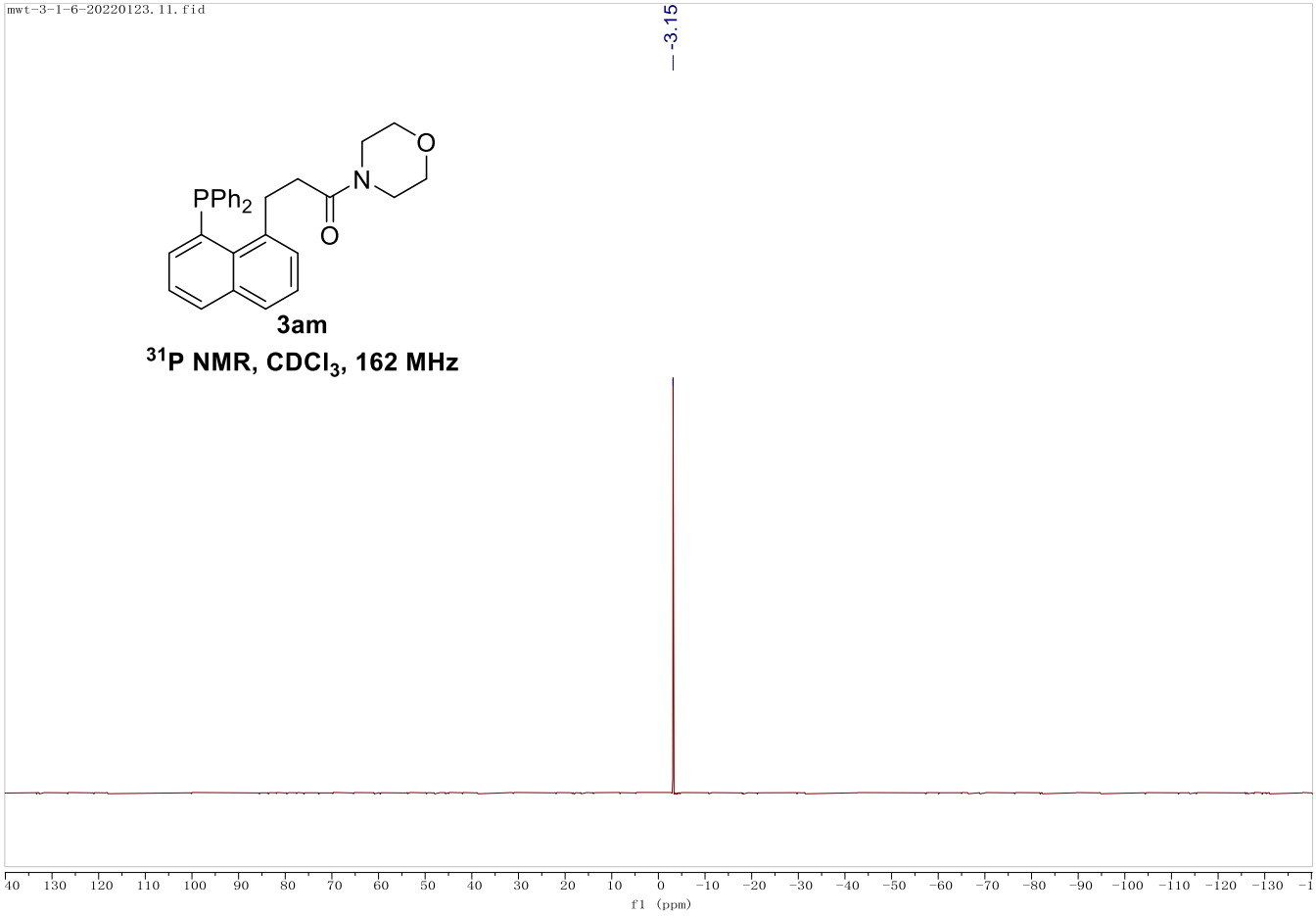


3al

^{31}P NMR, $CDCl_3$, 162 MHz

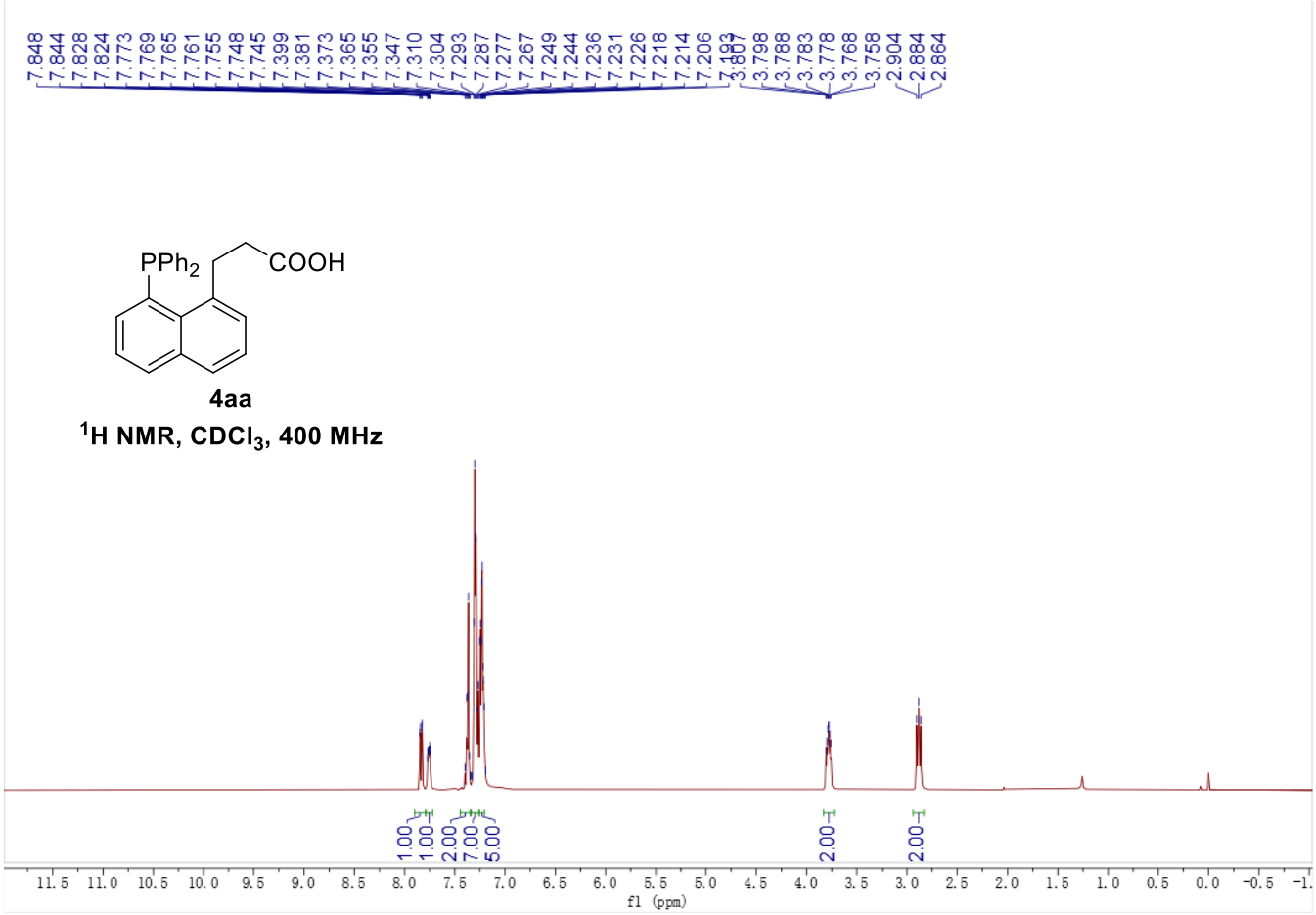

7.87 7.86 7.85 7.84 7.78 7.78 7.77 7.77 7.76 7.41 7.40 7.40 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.19 3.90 3.89 3.88 3.88 3.87 3.86 3.85 3.58 3.33 3.32 3.31 3.14 3.13 3.12 2.74 2.72 2.72 2.70
PPh2
O
N
O
3am
1H NMR, CDCl3, 400 MHz
1.00 1.00 2.00 7.00 5.00 2.00 4.00 4.00 2.00
f1 (ppm)


mwt-3-1-6-20220123.12.fid
171.14 139.24 139.22 137.94 137.81 136.49 135.67 135.62 135.04 134.84 134.05 133.85 133.69 133.41 131.60 130.89 129.03 129.01 128.76 128.72 128.65 125.62 124.78
66.91 66.47
45.78 41.88 36.40 36.26 33.78 33.50
PPh2
O
N
O
3am
13C NMR, CDCl3, 101 MHz
f1 (ppm)



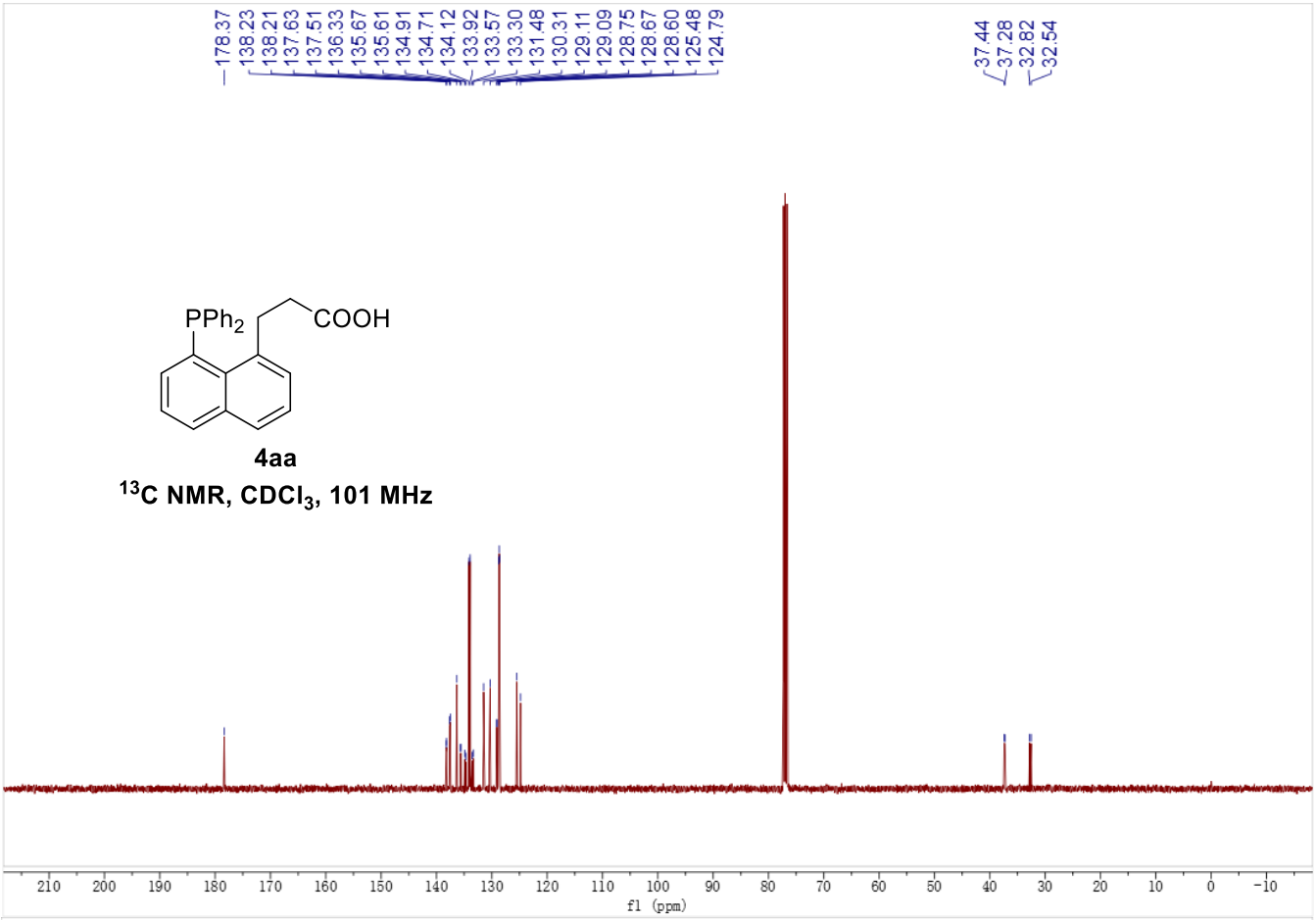
3am

^{31}P NMR, $CDCl_3$, 162 MHz



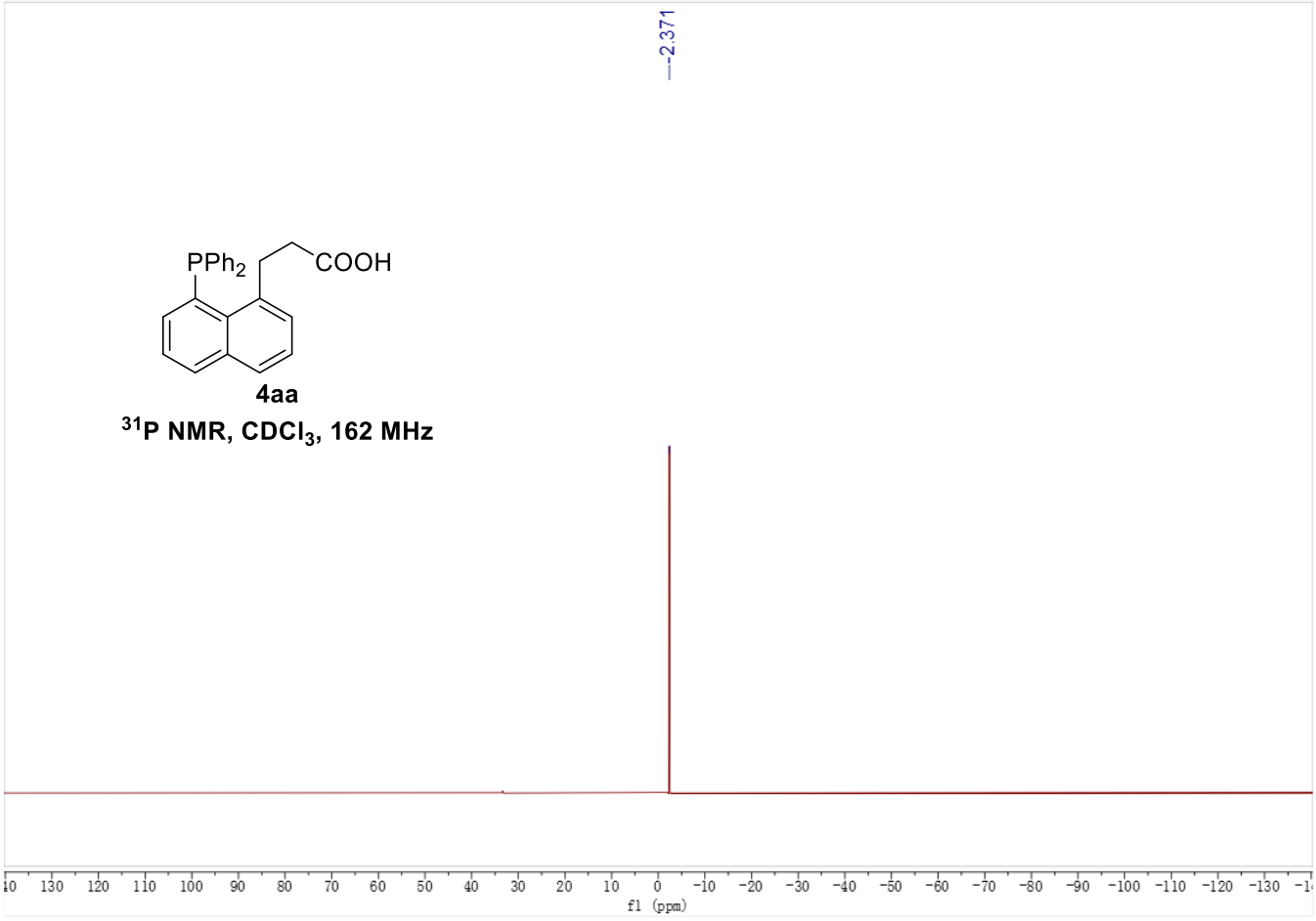
4aa

^{1}H NMR, $CDCl_3$, 400 MHz



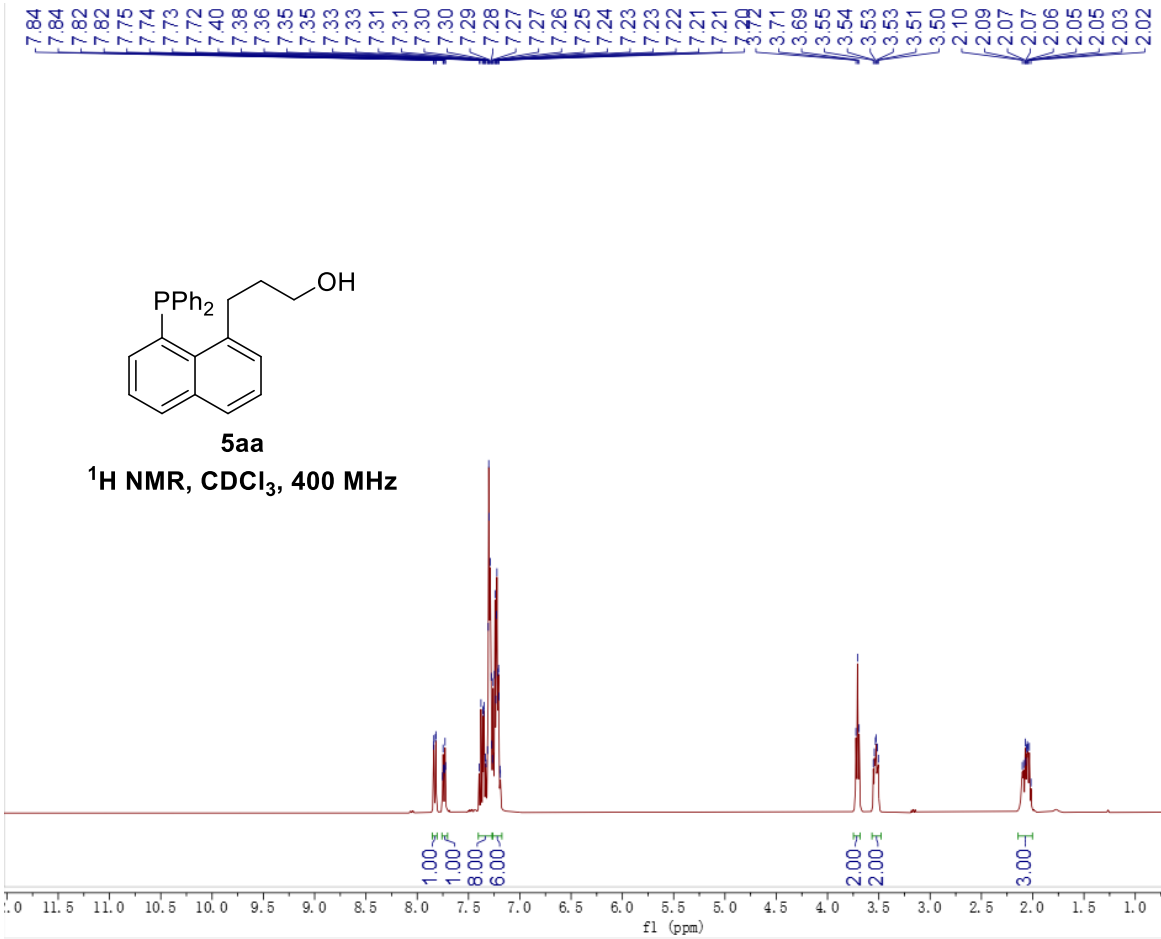
4aa

^{13}C NMR, $CDCl_3$, 101 MHz



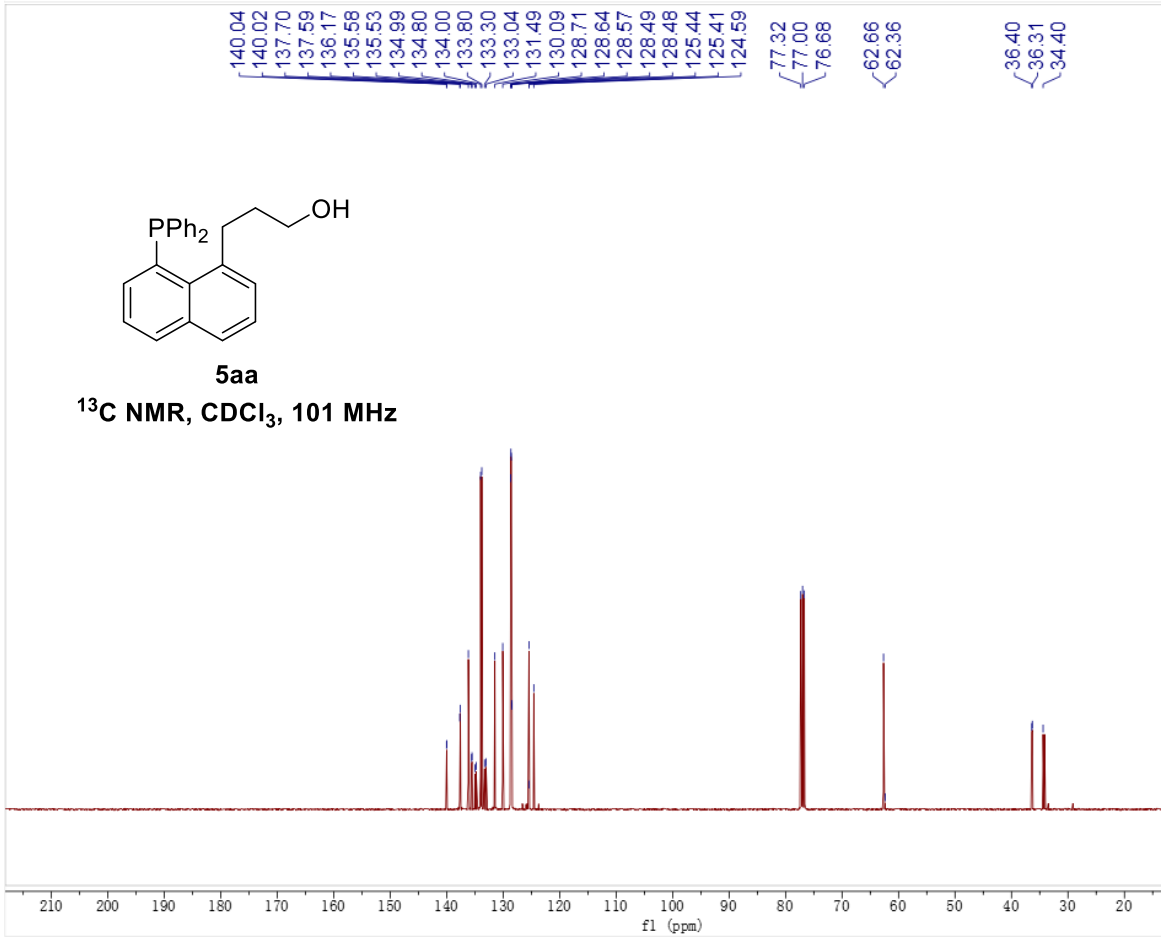
4aa

^{31}P NMR, $CDCl_3$, 162 MHz



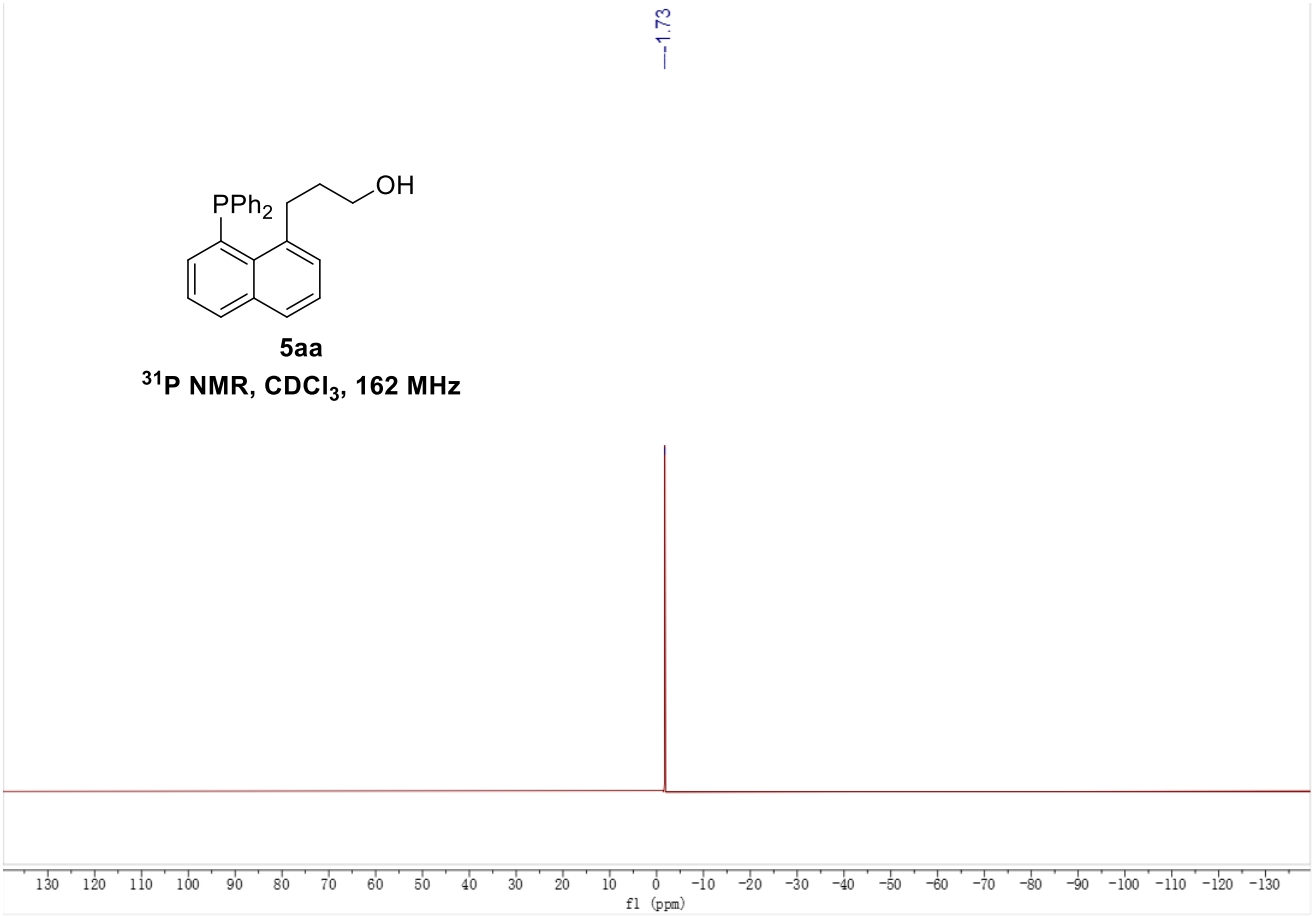
5aa

^{1}H NMR, $CDCl_3$, 400 MHz



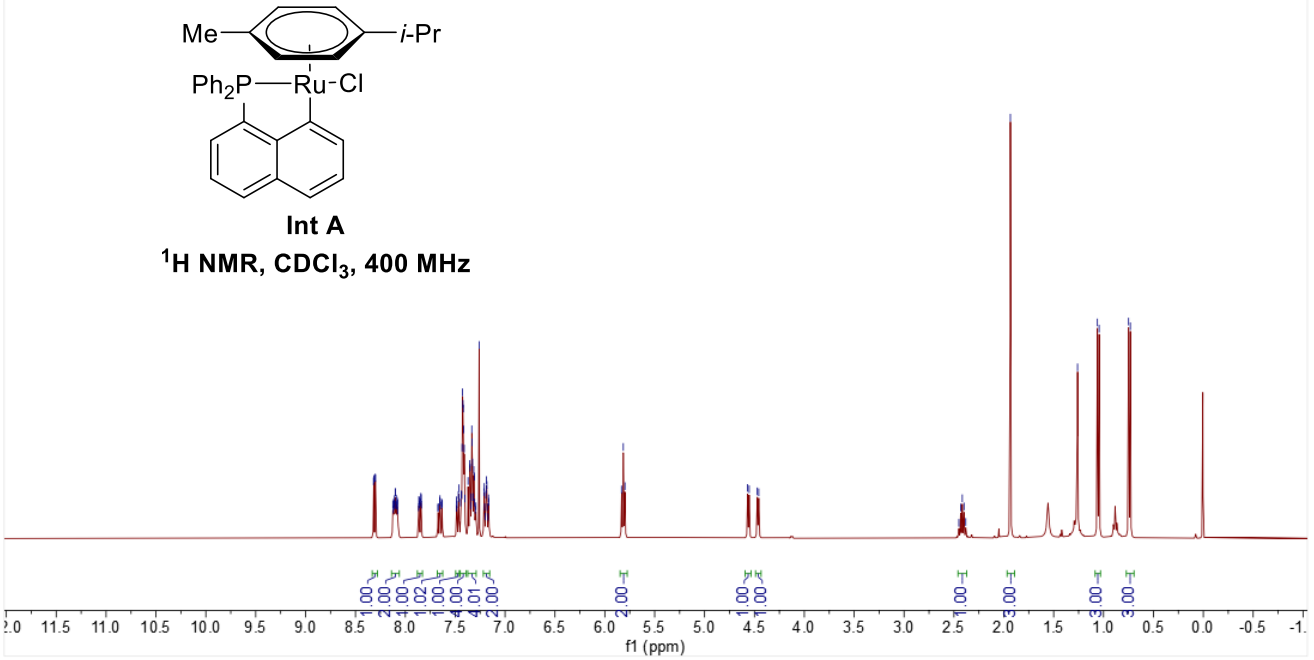
5aa

^{13}C NMR, $CDCl_3$, 101 MHz



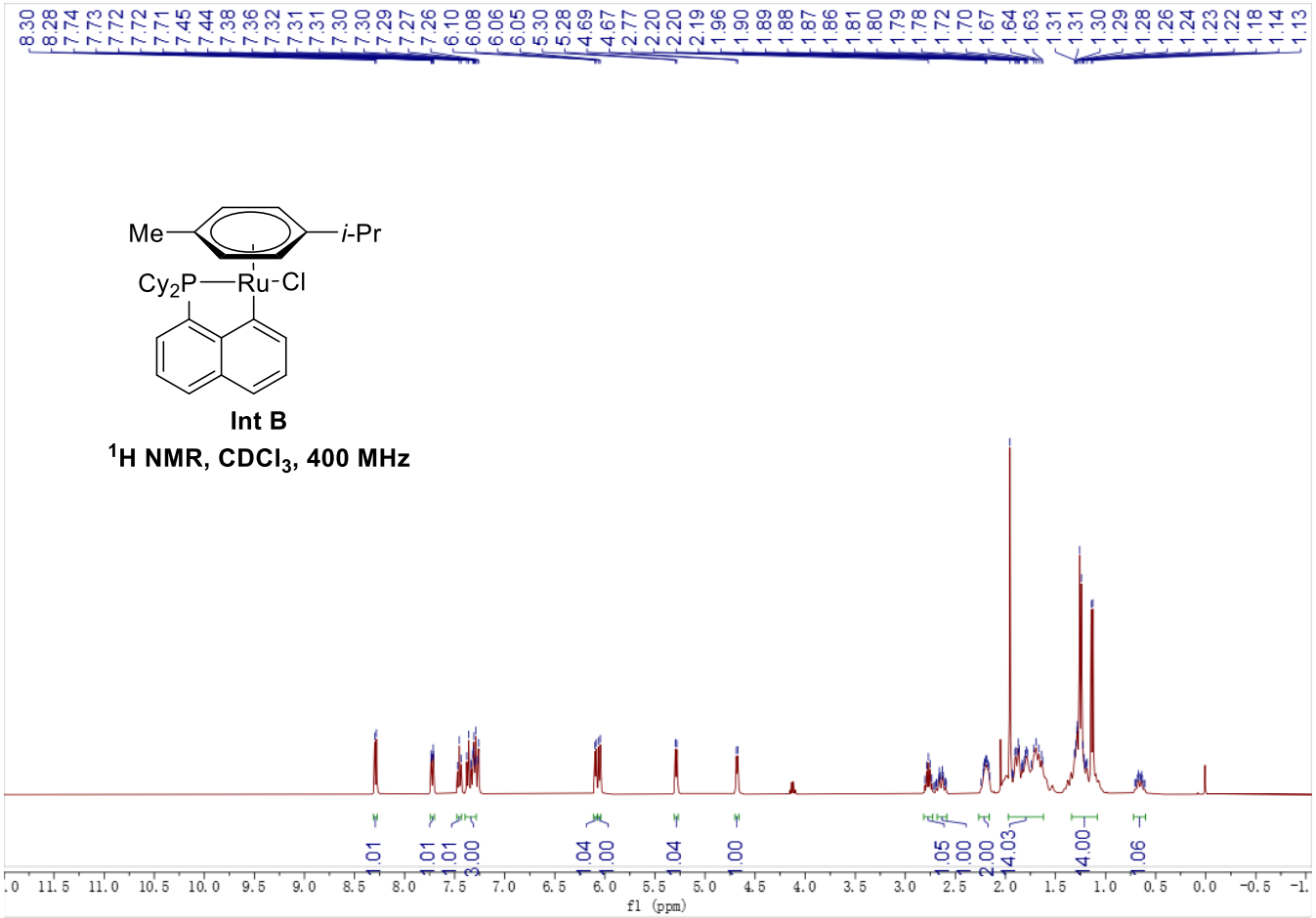
5aa

^{31}P NMR, $CDCl_3$, 162 MHz



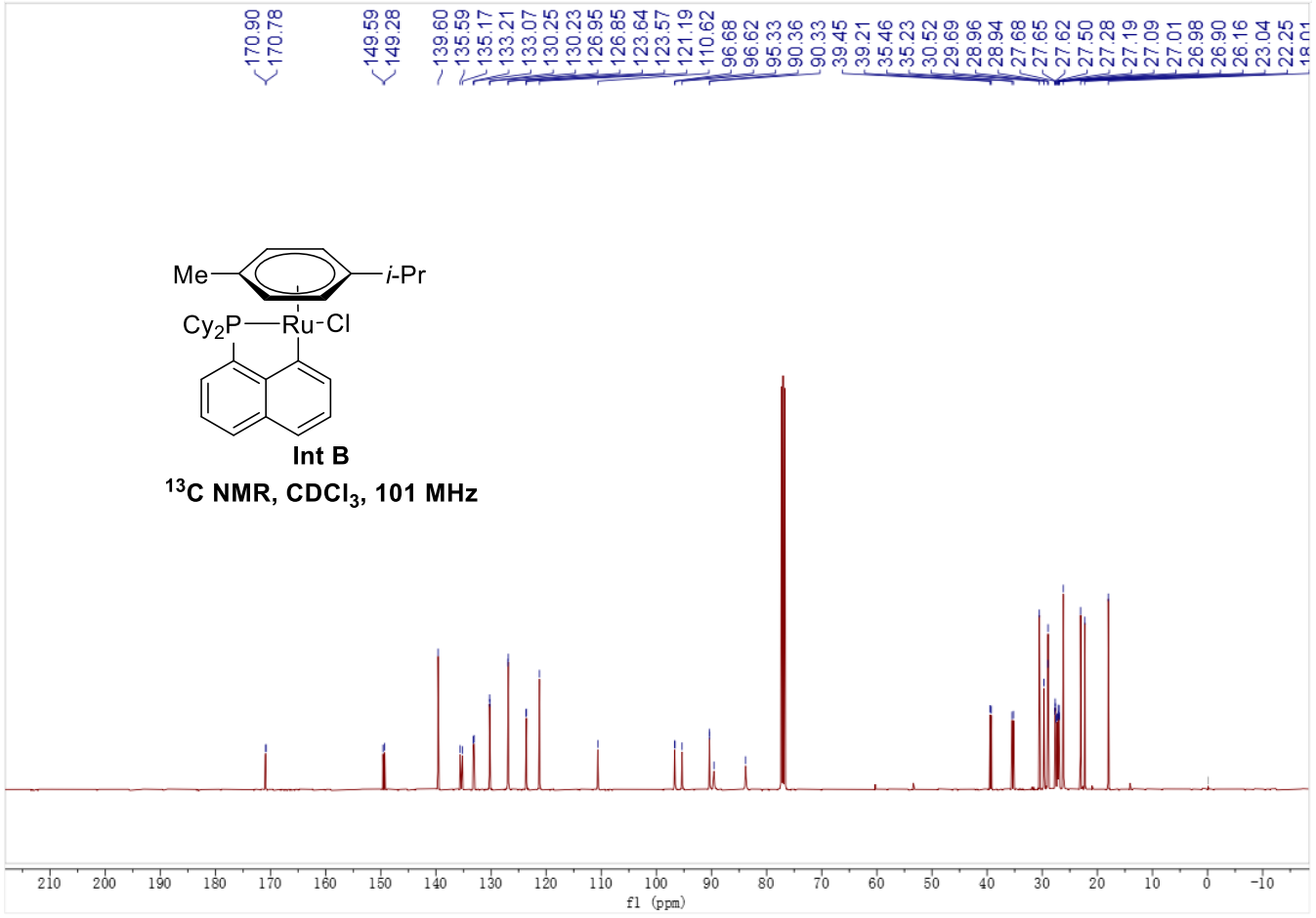
Int A

^{1}H NMR, $CDCl_3$, 400 MHz



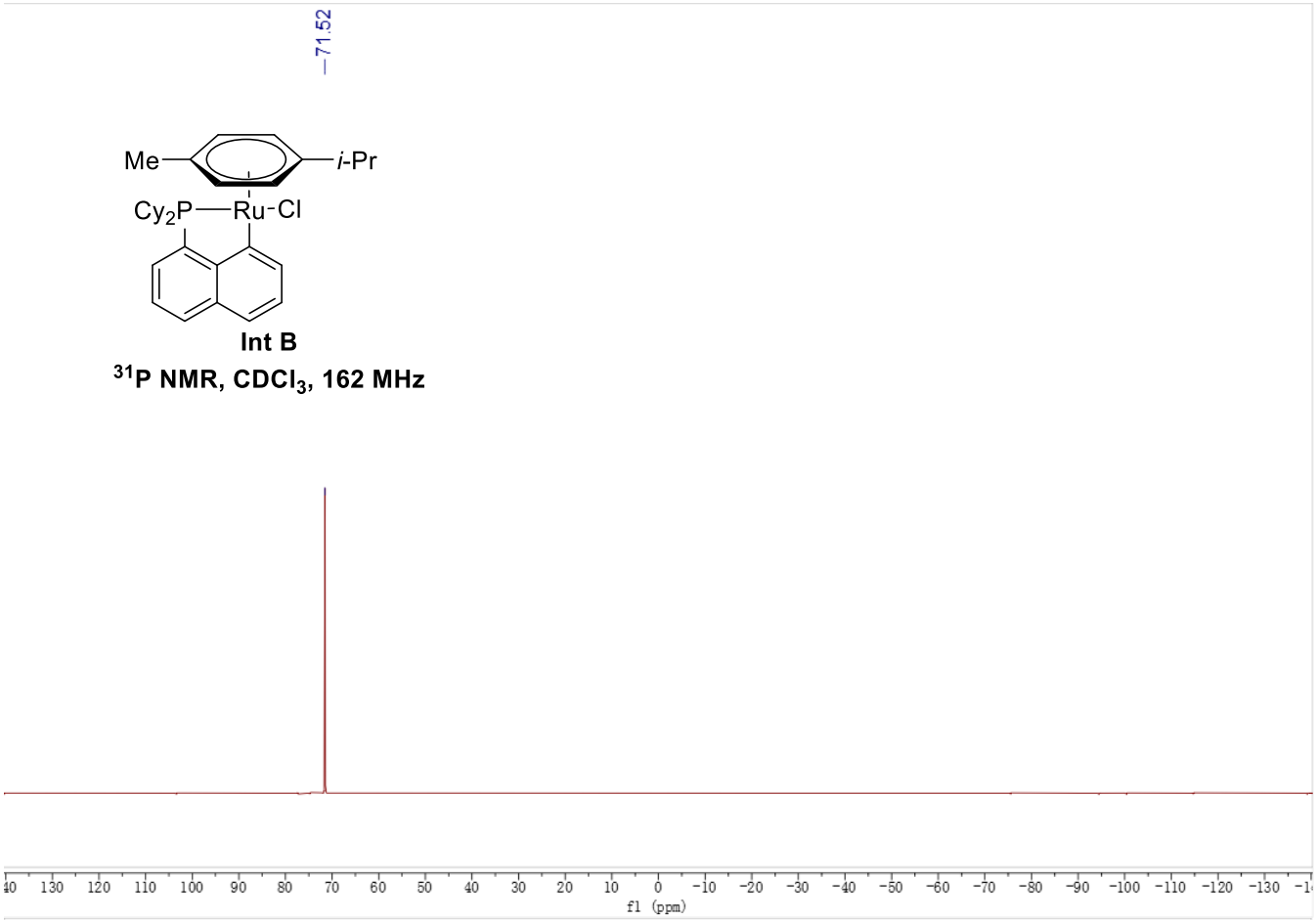
Int B

^{1}H NMR, $CDCl_3$, 400 MHz



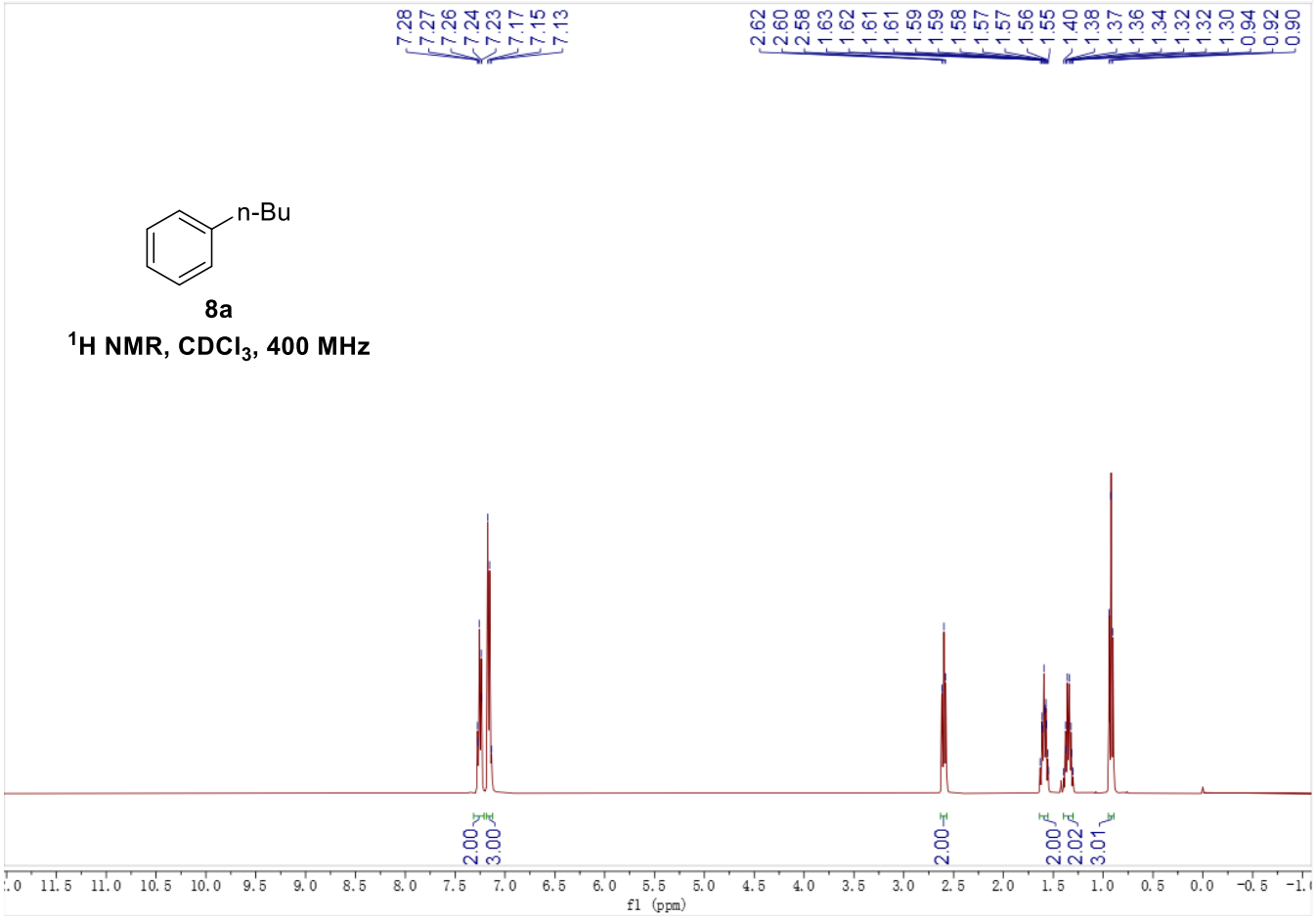
Int B

^{13}C NMR, $CDCl_3$, 101 MHz



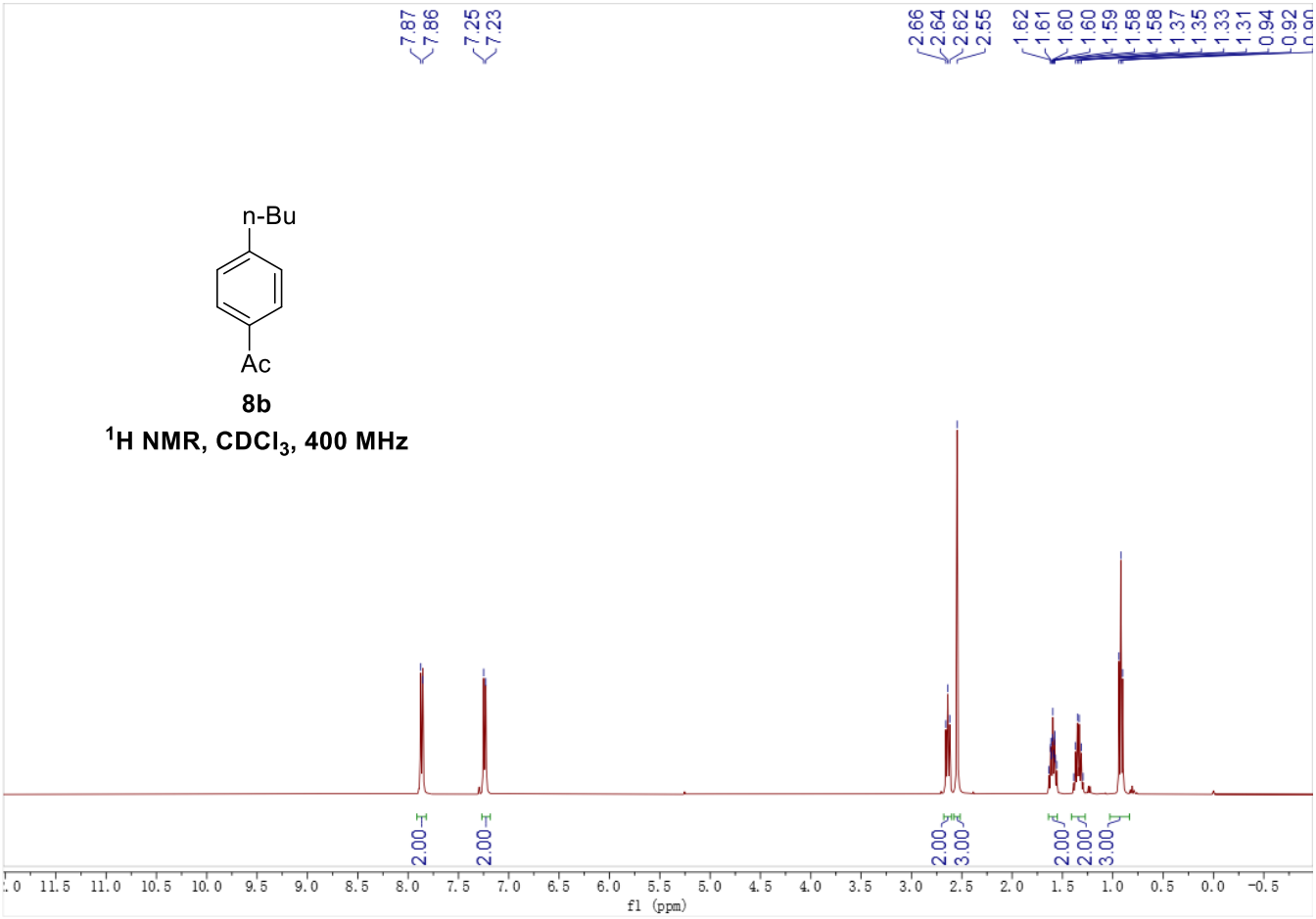
Int B

^{31}P NMR, $CDCl_3$, 162 MHz



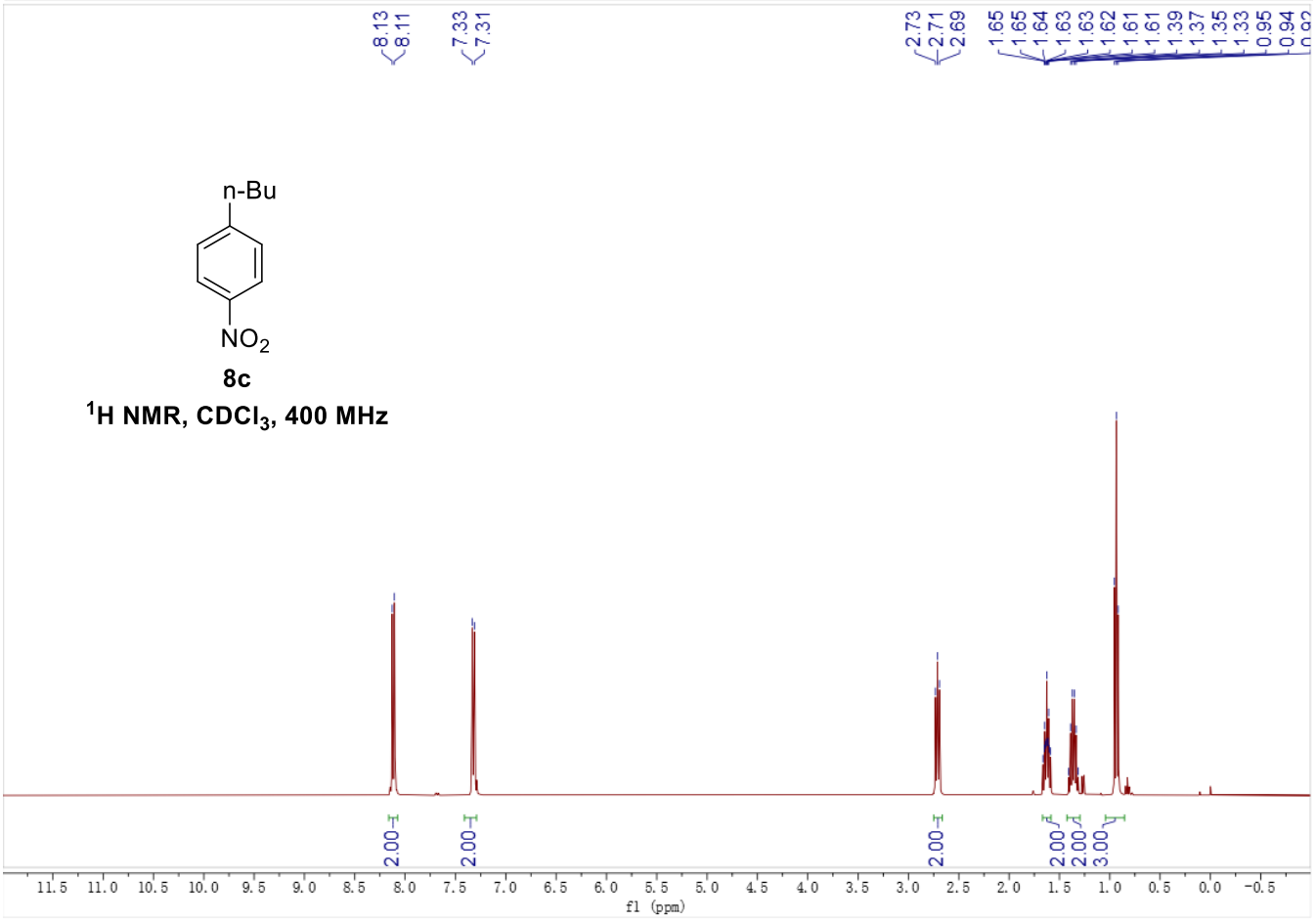
8a

^{1}H NMR, $CDCl_3$, 400 MHz



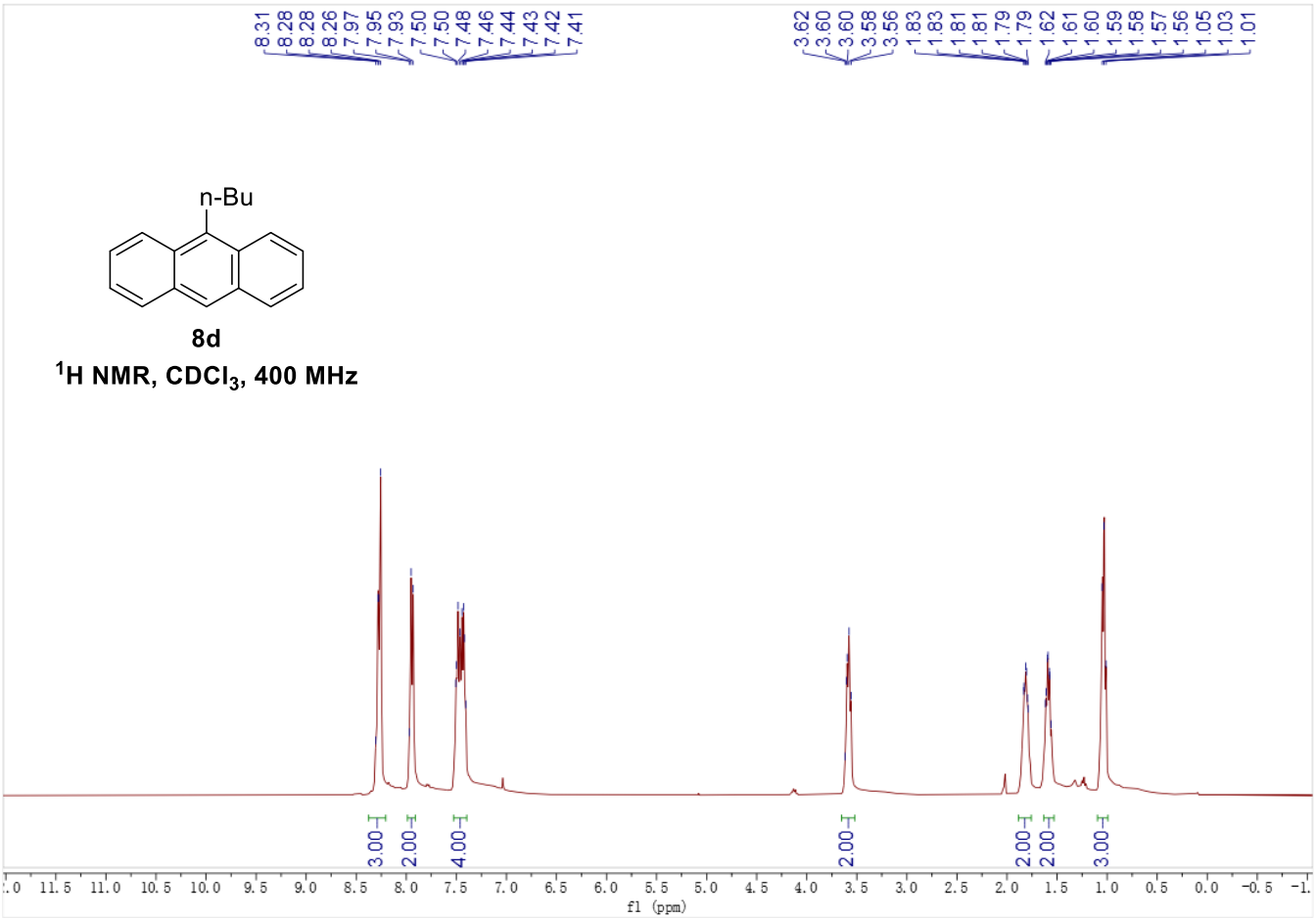
8b

^{1}H NMR, $CDCl_3$, 400 MHz



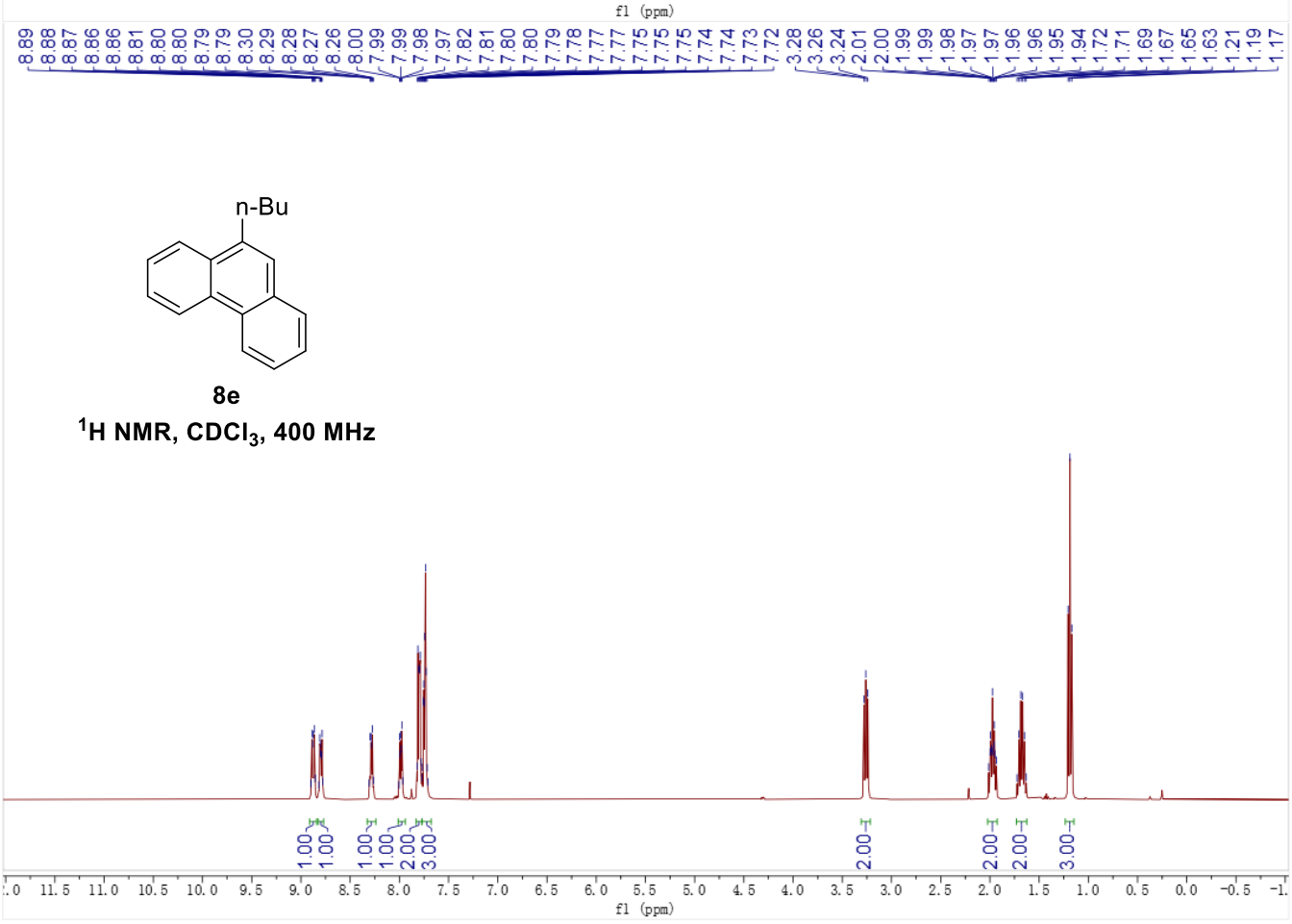
8c

^{1}H NMR, $CDCl_3$, 400 MHz



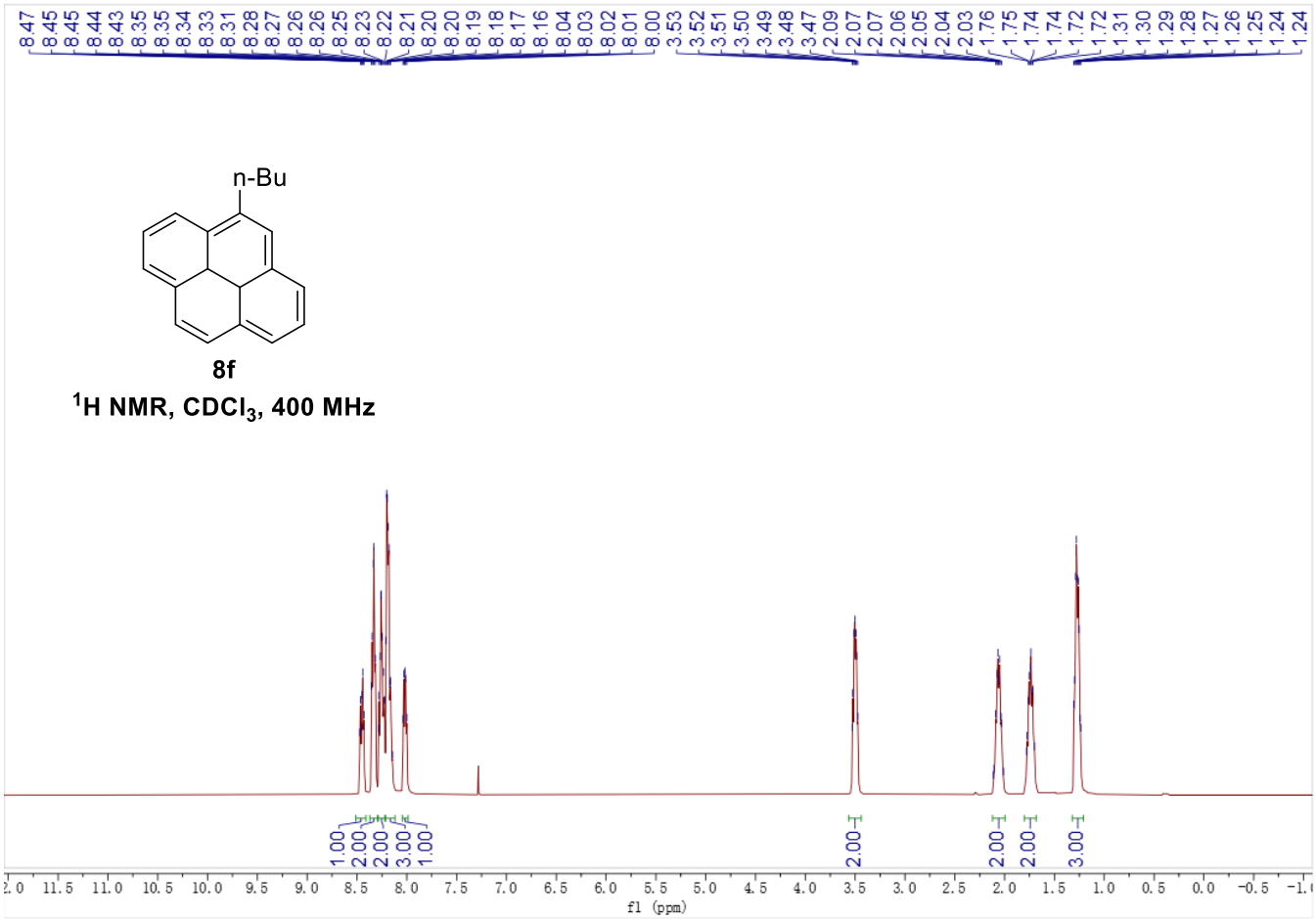
8d

^{1}H NMR, $CDCl_3$, 400 MHz



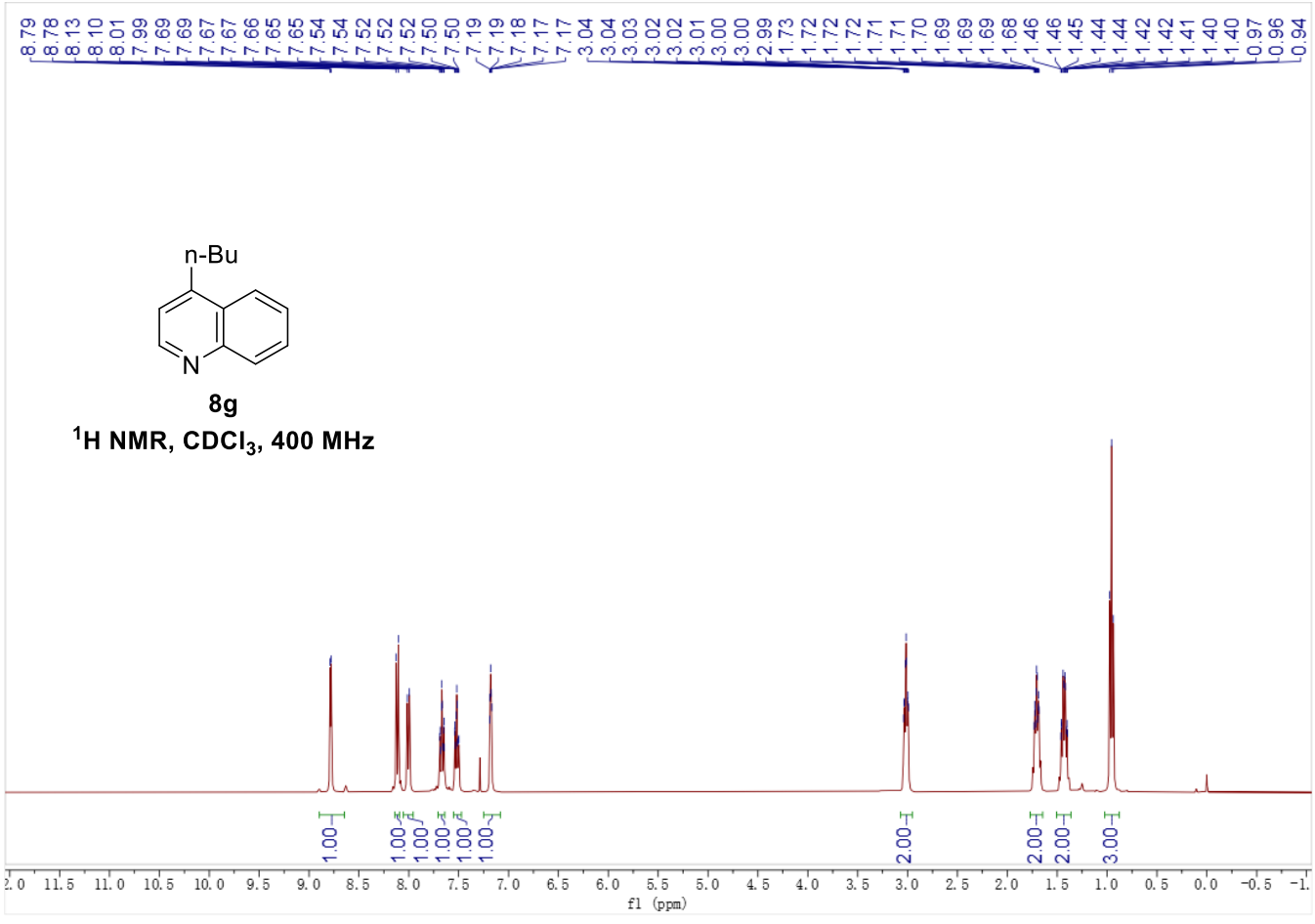
8e

^{1}H NMR, $CDCl_3$, 400 MHz



8f

^{1}H NMR, $CDCl_3$, 400 MHz



8g

^{1}H NMR, $CDCl_3$, 400 MHz