# Brønsted Acid-Catalysed Regiodivergent Phosphorylation of 2-Indolylmethanols to Synthesize Benzylic Site or C3-Phosphorylated Indole Derivatives

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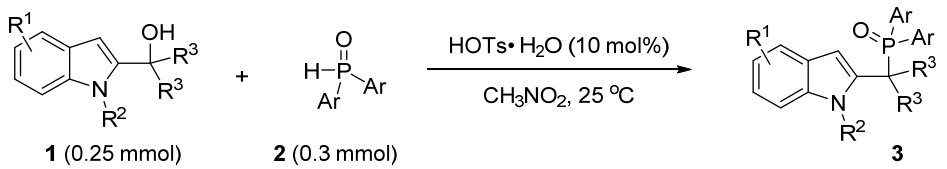
**1. General information:**

Reactions were monitored by thin layer chromatography using UV light to visualize the reaction course. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. $^{1}H$ and $^{13}C$ NMR spectra were obtained using a Bruker DPX-400 or JEOL-600 spectrometer. The $^{31}P$ NMR spectra were recorded at JEOL 243 MHz with 85% $H_3PO_4$ as external standard. The $^{19}F$ NMR spectra were recorded at JEOL 564 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

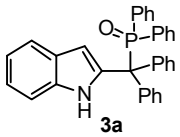
All reactions were run under an atmosphere of air. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous halogenated solvents and $CH_3CN$ were prepared by first distillation over $P_2O_5$ and then from $CaH_2$. Anhydrous ethyl acetate was prepared by first dried in anhydrous $Na_2SO_4$ and then distilled over $P_2O_5$ and stored over MS 4Å. Anhydrous $CH_3NO_2$ was prepared by first dried in anhydrous $Na_2SO_4$ and then distilled under reduced pressure. 2-Indolylmethanols **1**[1] and diarylphosphine oxides **2**[2] were prepared according to the literature report. Commercially available $HOTs{\cdot}H_2O$ (4-methylbenzenesulfonic acid hydrate) and HOTf (trifluoromethanesulfonic acid) were used as received.

[1]. Y.-Y. He, X.-X. Sun, G.-H. Li, G.-J. Mei, F. Shi, *J. Org. Chem*., 2017, **82**, 2462.
[2] S. Molitor, J. Becker, V. H. Gessner, *J. Am. Chem. Soc*., 2014, **136**, 15517.

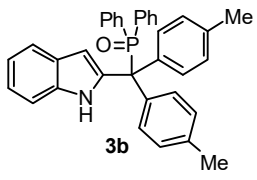
## 2. General procedure for HOTs·$H_2O$-catalyzed regioselective benzylic phosphorylation of 2-indolylmethanols




The reaction was carried out under an air atmosphere. To a 10-mL vial were added 2-indolylmethanols **1** (0.25 mmol, 1.0 equiv), $Ar_2P(O)H$ **2** (0.3 mmol, 1.2 equivs) and 2.5 mL of anhydrous $CH_3NO_2$. After adding HOTs·$H_2O$ (6.8 mg, 10 mol%), the reaction mixture was stirred at room temperature till almost full conversion of **1** by TLC analysis. The reaction mixture was directly subjected to column chromatography using petrol ether/ethyl acetate (generally 10:1 to 5:1, v:v) as the eluent to afford the desired products **3**.

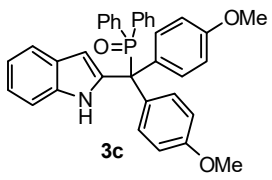



Column chromatography afforded the desired product **3a**[3] in 98% yield (118.3 mg) as white solid; $^1$H NMR (600 MHz, $CDCl_3$): δ = 10.26 (brs, 1H), 7.53-7.50 (m, 1H), 7.47-7.43 (m, 3H), 7.28-7.23 (m, 7H), 7.19-7.08 (m, 9H), 7.03-7.00 (m, 4H), 6.28 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 139.0, 136.2, 132.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.0, 131.4, 130.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.8, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.9, 127.6, 127.0, 122.1, 120.3, 119.6, 111.4, 105.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 60.9 (d, $J_{C\text{-}P}$ = 63.0 Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 37.3.

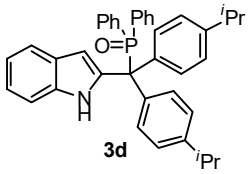



Column chromatography afforded **3b**[3] in 93% yield (118.8 mg) as white solid; $^1$H NMR (600 MHz, $CDCl_3$): δ = 10.31 (brs, 1H), 7.51-7.50 (m, 1H), 7.46-7.44 (m, 3H), 7.28-7.26 (m, 3H), 7.26-7.25 (m, 1H), 7.21-7.17 (m, 5H), 7.11-7.08 (m, 1H), 6.96-6.95 (m, 4H), 6.87-6.86 (m, 4H), 6.24 (s, 1H), 2.31 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 139.3, 137.3, 136.2, 136.1, 133.0 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.9, 131.1, 130.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.6, 128.2 (d, $J_{C\text{-}P}$ = 4.2 Hz), 127.1, 122.0, 120.3, 119.5, 111.5, 105.6, 60.2 (d, $J_{C\text{-}P}$ = 63.0 Hz), 21.0; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 31.8.

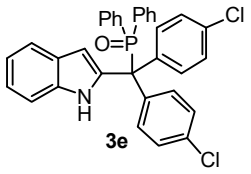
[3] C. Hu, Y. He, C. Zhou, M. C. Kozlowski, L.-M. Wang, *J. Org. Chem*., 2018, **83**, 4739.



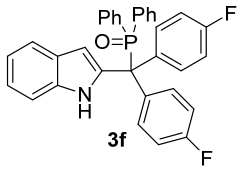

Column chromatography afforded **3c**[3] in 90% yield (122.7 mg) as white solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 10.32 (brs, 1H), 7.51-7.43 (m, 4H), 7.29-7.18 (m, 10H), 7.11-7.07 (m, 1H), 6.91-6.89 (m, 3H), 6.69-6.67 (m, 4H), 6.22 (s, 1H), 3.75 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 158.7 (d, $J_{C\text{-}P}$ = 1.0 Hz), 139.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 136.2, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.0 (m, $J_{C\text{-}P}$ = 5.0 Hz), 131.7 (1.2 Hz), 131.1, 130.8, 128.2 (d, $J_{C\text{-}P}$ = 11.0 Hz), 127.0 (d, $J_{C\text{-}P}$= 2.0 Hz), 122.0, 120.3, 119.5, 113.1, 111.5, 105.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 59.4 (d, $J_{C\text{-}P}$= 63.0 Hz), 55.2 ; $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 31.8.



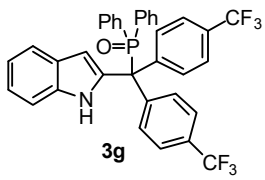

Column chromatography afforded **3d** in 74% yield (104.9 mg) as white solid; Mp: 120-122 ºC; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.18 (brs, 1H), 7.52-7.51 (m, 1H), 7.46-7.43 (m, 3H), 7.26-7.21 (m, 5H), 7.13-7.09 (m, 5H), 7.01-7.00 (m, 4H), 6.90-6.89 (m, 4H), 6.31 (s, 1H), 2.89-2.83 (m, 2H), 1.23-1.21 (m, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 148.2, 139.2, 136.4, 136.2, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.8, 131.7, 131.1, 130.8 (d, $J_{C\text{-}P}$= 6.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 127.1, 125.9, 119.5, 111.4, 105.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 60.3 (d, $J_{C\text{-}P}$= 63.0 Hz), 33.6, 23.9, 23.8; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.3; HRMS (ESI): Exact mass calcd for $C_{39}H_{38}NOP$ $[M+H]^+$: 568.2764, Found: 568.2755.




Column chromatography afforded the desired product **3e**[3] in 54% yield (74.4 mg) as white solid; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.34 (brs, 1H), 7.52-7.46 (m, 4H), 7.33-7.30 (m, 4H), 7.26-7.24 (m, 1H), 7.21-7.18 (m, 4H), 7.15-7.11 (m, 5H), 6.93-6.92 (m, 4H), 6.18 (s, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 137.4, 136.3, 133.9, 133.0 (d, $J_{C\text{-}P}$= 7.5 Hz), 132.4, 132.2, 130.8, 130.1, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.2, 126.9, 122.6, 120.5, 120.0, 111.6, 105.8, 59.9 (d, $J_{C\text{-}P}$= 61.5 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.1.

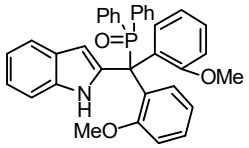



Column chromatography afforded the desired product **3f**[3] in 90% yield (116.8 mg) as white solid; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.31 (brs, 1H), 7.53-7.46 (m, 4H), 7.31-7.29 (m, 4H), 7.25-7.20 (m, 1H), 7.18-7.17 (m, 4H), 7.17-7.12 (m, 1H), 6.97-6.95 (m, 4H), 6.88-6.85 (m, 4H), 6.20 (s, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 162.0 (d, $J_{C\text{-}F}$ = 247.5 Hz), 136.3, 134.8, 132.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.6 (q, $J_{C\text{-}P}$ = 7.5 Hz), 132.3, 130.9, 130.3, 128.5 (d, $J_{C\text{-}P}$= 12.0 Hz), 126.9, 122.5, 120.5, 119.9, 114.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 111.6, 105.6, 59.6 (d, $J_{C\text{-}P}$ = 61.5 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.3; $^{19}$F{$^{1}$H} NMR (565 MHz, $CDCl_3$): $\delta$ = -113.8.



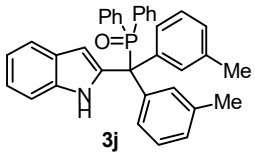
**3g**

Column chromatography afforded the desired product **3g** in 28% yield (43.4 mg) as white solid; Mp: 130-132 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.36 (brs, 1H), 7.54-7.51 (m, 3H), 7.48-7.44 (m, 5H), 7.34-7.31 (m, 4H), 7.28-7.25 (m, 1H), 7.20-7.13 (m, 9H), 6.20 (s, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 142.8, 136.3, 132.9 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.7, 131.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.1 (q, $J_{C\text{-}F}$ = 93.0 Hz), 130.0 (d, $J_{C\text{-}P}$ = 33.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 126.9, 125.0, 123.8 (q, $J_{C\text{-}F}$ = 270.0 Hz), 122.8, 120.6, 120.1, 111.6, 106.0, 60.8 (d, $J_{C\text{-}P}$ = 60.0 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.4; $^{19}$F{$^{1}$H} NMR (565 MHz, $CDCl_3$): $\delta$ = -62.6; HRMS (ESI): Exact mass calcd for $C_{35}H_{24}F_6NOP$ $[M+H]^+$: 620.1572, Found: 620.1564.



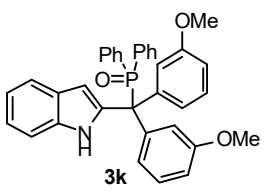
**3i**

Column chromatography afforded the desired product **3i** in 62% yield (84.2 mg) as white solid; Mp: 188-190 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 11.95 (s, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.41 (d, $J$ = 8.0 Hz, 1H), 7.27 (brs, 5H), 7.19-7.12 (m, 7H), 7.06-7.02 (m, 2H), 6.80-6.71 (m, 4H), 6.28 (d, $J$ = 8.0 Hz, 2H), 5.66 (s, 1H), 2.99 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 156.0, 143.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 136.5, 131.4 (d, $J_{C\text{-}P}$ = 8.0 Hz), 128.8, 127.8, 120.8, 119.9, 119.1, 112.1, 110.0, 105.2 (d, $J_{C\text{-}P}$ = 7.0 Hz), 58.9 (d, $J_{C\text{-}P}$ = 60.0 Hz), 53.3; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 51.6; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_3P$ $[M+H]^+$: 544.2036, Found: 544.2029.



**3j**

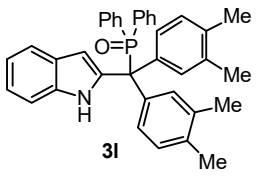
Column chromatography afforded **3j**[3] in 82% yield (104.8 mg) as white solid; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.34 (brs, 1H), 7.53-7.52 (m, 1H), 7.47-7.44 (m, 3H), 7.28-7.25 (m, 4H), 7.23-7.21 (m, 1H), 7.18-7.15 (m, 4H), 7.12-7.10 (m, 1H), 7.09-7.03 (m, 4H), 6.80-6.77 (m, 4H), 6.27 (s, 1H), 2.10 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 138.8, 137.1, 136.2, 133.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.9, 131.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.5, 130.8, 128.3, 128.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.0, 127.8, 127.1, 122.0, 120.4, 119.5, 105.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 60.8 (d, $J_{C\text{-}P}$ = 63.0 Hz), 21.5; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.5.



**3k**

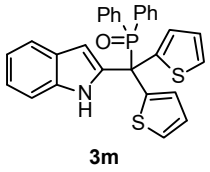
Column chromatography afforded the desired product **3k** in 56% yield (76.0 mg) as white solid; Mp: 198-200 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.37 (brs, 1H), 7.53-7.52 (m, 1H), 7.48-7.45 (m, 3H), 7.30-7.27 (m, 4H), 7.23-7.17 (m, 5H), 7.12-7.11 (m, 1H), 7.08-7.07 (m, 2H), 6.82-6.80 (m, 2H), 6.66 (s, 2H), 6.53-6.51 (m, 2H), 6.31 (s, 1H), 3.42 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz,

$CDCl_3$): δ = 158.8, 140.4, 136.2, 133.0 (d, $J_{C-P}$ = 7.5 Hz), 132.0, 131.7, 131.1, 128.9, 128.3 (d, $J_{C-P}$ = 12.0 Hz), 127.0, 123.5 (d, $J_{C-P}$ = 6.0 Hz), 122.2, 120.4, 119.6, 116.3, 113.9, 111.6, 106.0, 61.0 (d, $J_{C-P}$ = 61.5 Hz), 54.8; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 37.6; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_3P$ $[M+H]^+$: 544.2036, Found: 544.2028.



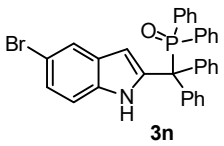
**3l**

Column chromatography afforded the desired product **3l** in 86% yield (115.8 mg) as white solid; Mp: 150-152ºC; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 10.35 (brs, 1H), 7.52-7.50 (m, 1H), 7.46-7.42 (m, 3H), 7.28-7.16 (m, 9H), 7.11-7.07 (m, 1H), 6.92-6.90 (m, 2H), 6.72 (s, 2H), 6.68-6.66 (m, 2H ), 6.23 (s, 1H), 2.21 (s, 6H), 1.99 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.4, 136.2 (d, $J_{C-P}$ = 7.0 Hz), 135.8 (d, $J_{C-P}$ = 2.0 Hz), 135.5, 133.07 (d, $J_{C-P}$ = 9.0 Hz), 132.2 (d, $J_{C-P}$ = 5.0 Hz), 131.9, 131.8 (d, $J_{C-P}$ = 2.0 Hz), 131.0, 129.1, 128.5 (d, $J_{C-P}$ = 6.0 Hz), 128.1 (d, $J_{C-P}$ = 11.0 Hz), 127.1, 121.9, 120.3, 119.4, 111.5, 105.5 (d, $J_{C-P}$ = 6.0 Hz), 60.2 (d, $J_{C-P}$ = 64.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 37.4; HRMS (ESI): Exact mass calcd for $C_{37}H_{34}NOP$ $[M+H]^+$: 540.2451, Found: 540.2444.



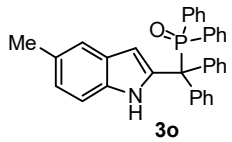
**3m**

Column chromatography afforded the desired product **3m** in 59% yield (73.2 mg) as white solid; Mp: 128-130 ºC; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 7.55-7.49 (m, 4H), 7.36-7.25 (m, 9H), 7.20-7.19 (m, 2H), 7.15-7.11 (m, 1H), 6.86-6.84 (m, 2H), 6.43 (s, 2H), 6.27 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 144.0, 138.6 (d, $J_{C-P}$ = 6.0 Hz), 136.2, 133.3 (d, $J_{C-P}$ = 9.0 Hz), 132.6 (d, $J_{C-P}$ = 3.0 Hz), 130.0, 129.0 (d, $J_{C-P}$ = 5.0 Hz), 128.4 (d, $J_{C-P}$ = 12.0 Hz), 126.8 (d, $J_{C-P}$ = 2.0 Hz), 126.4 (d, $J_{C-P}$ = 2.0 Hz), 126.1 (d, $J_{C-P}$ = 2.0 Hz), 122.6, 120.8, 119.8, 111.7, 105.7 (d, $J_{C-P}$ = 5.0 Hz), 54.3 (d, $J_{C-P}$ = 63.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 37.7; HRMS (ESI): Exact mass calcd for $C_{29}H_{22}NOPS_2$ $[M+H]^+$: 496.0953, Found: 496.0941.



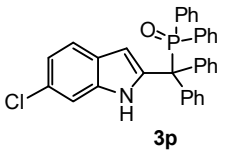
**3n**

Column chromatography afforded **3n** in 85% yield (119.5 mg) as white solid; Mp: 248-250 ºC; $^1H$ NMR (600 MHz, $CDCl_3$): δ = 10.43 (brs, 1H), 7.63 (s, 1H), 7.48-7.45 (m, 2H), 7.32-7.27 (m, 2H), 7.27-7.26 (m, 5H), 7.18-7.13 (m, 9H), 6.99-6.98 (m, 4H), 6.24 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 140.4, 138.7, 134.8, 133.0 (d, $J_{C-P}$ = 9.0 Hz), 132.1, 131.0 (d, $J_{C-P}$ = 93.0 Hz), 130.0 (d, $J_{C-P}$ = 4.5 Hz), 128.7, 128.3 (d, $J_{C-P}$ = 12.0 Hz), 128.0, 127.7, 125.1, 122.8, 113.0, 112.9 (d, $J_{C-P}$ = 15.0 Hz), 105.0 (d, $J_{C-P}$ = 6.0 Hz), 60.8 (d, $J_{C-P}$ = 61.5 Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 37.4; HRMS (ESI): Exact mass calcd for $C_{33}H_{25}BrNOP$ $[M+H]^+$: 562.0930, Found: 562.0927.



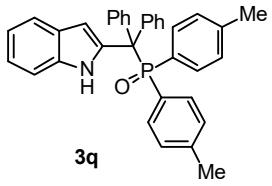
**3o**

Column chromatography afforded the desired product **3o**[3] in 82% yield (101.8 mg) as white solid; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.20 (brs, 1H), 7.46-7.43 (m, 2H), 7.36-7.34 (m, 1H), 7.28-7.24 (m, 6H), 7.17-7.13 (m, 9H), 7.06-7.04 (m, 1H), 7.01-6.99 (m, 4H), 6.19 (s, 1H), 2.45 (s, 3H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 139.1, 134.6, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.0, 131.4, 130.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.8, 128.8, 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 127.9, 127.6, 127.3, 123.8, 120.0, 111.2, 105.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 60.9 (d, $J_{C\text{-}P}$ = 61.5 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.4.



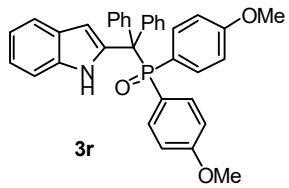
**3p**

Column chromatography afforded the desired product **3p**[3] in 76% yield (98.2 mg) as white solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 10.37 (brs, 1H), 7.48-7.44 (m, 3H), 7.41-7.39 (m, 1H), 7.29-7.27 (m, 6H), 7.17-7.14 (m, 8H), 7.07-7.06 (m, 1H), 6.99-6.98 (m, 4H), 6.28 (s, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 139.9, 138.8, 136.6, 132.9 (d, $J_{C\text{-}P}$ = 8.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.4, 130.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 130.4, 128.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.0, 127.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 125.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 121.2, 120.5, 111.4, 105.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 60.9 (d, $J_{C\text{-}P}$ = 62.0 Hz); $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 37.5.



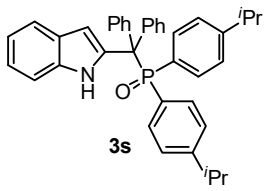
**3q**

Column chromatography afforded the desired product **3q**[3] in 95% yield (121.4 mg) as white solid; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.36 (brs, 1H), 7.52-7.50 (m, 1H), 7.45-7.44 (m, 1H), 7.25-7.23 (m, 2H), 7.22-7.19 (m, 1H), 7.16-7.13 (m, 4H), 7.10-7.08 (m, 1H), 7.06-7.01 (m, 12H), 6.27 (s, 1H), 2.31 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 142.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 139.3, 136.2, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3, 127.8, 127.7, 127.5, 127.1, 122.0, 120.3, 119.5, 111.5, 105.6, 60.8 (d, $J_{C\text{-}P}$ = 61.5 Hz), 21.5; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.8.



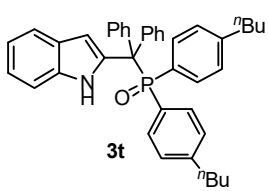
**3r**

Column chromatography afforded the desired product **3r**[3] in 87% yield (118.2 mg) as white solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 10.38 (brs, 1H), 7.52 (d, $J$ = 8.0 Hz, 1H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.26-7.23 (m, 3H), 7.21-7.13 (m, 5H), 7.12-7.01 (m, 8H), 6.77-6.74 (m, 4H), 6.28 (s, 1H), 3.76 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 162.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 139.4, 136.2, 134.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 127.8, 127.4, 127.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 122.8, 122.0, 121.8, 120.3, 119.5, 113.7 (d, $J_{C\text{-}P}$ = 13.0 Hz), 111.5, 105.5, 60.8 (d, $J_{C\text{-}P}$ = 63.0 Hz), 55.2; $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 37.6.



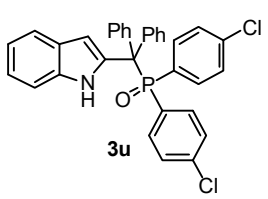
**3s**

Column chromatography afforded the desired product **3s** in 84% yield (119.2 mg) as white solid; Mp: 134-136 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.41 (brs, 1H), 7.53-7.51 (m, 1H), 7.46-7.44 (m, 1H), 7.26-7.19 (m, 3H), 7.16-7.02 (m, 17H), 6.26 (s, 1H), 2.90-2.83 (m, 2H), 1.21-1.19 (m, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 153.0, 139.3, 136.2, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.7, 128.0, 127.8, 127.4, 127.1, 126.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 122.0, 120.3, 119.5, 111.5, 105.5, 60.7 (d, $J_{C\text{-}P}$ = 61.5 Hz), 34.0, 23.6, 23.5; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 37.9; HRMS (ESI): Exact mass calcd for $C_{39}H_{38N}OP$ $[M+H]^+$: 568.2764, Found: 568.2757.



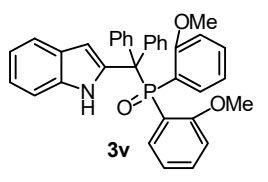
**3t**

Column chromatography afforded the desired product **3t** in 88% yield (130.9 mg) as white solid; Mp: 141-143 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 10.37 (brs, 1H), 7.53-7.51 (m, 1H), 7.46-7.44 (m, 1H), 7.26-7.20 (m, 3H), 7.16-7.10 (m, 5H), 7.08-7.00 (m, 12H), 6.25 (s, 1H), 2.60-2.56 (m, 4H), 1.59-1.51 (m, 4H), 1.35-1.26 (m, 4H), 0.91-0.87 (m, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 147.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 139.3, 136.2, 133.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 128.6, 128.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.8, 127.7, 127.4, 127.1, 122.0, 120.3, 119.5, 111.5, 105.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 60.8 (d, $J_{C\text{-}P}$ = 62.0 Hz), 35.5, 33.0, 22.2, 13.8; $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 38.0; HRMS (ESI): Exact mass calcd for $C_{41}H_{42}NOP$ $[M+H]^+$: 596.3077, Found: 596.3074.



**3u**

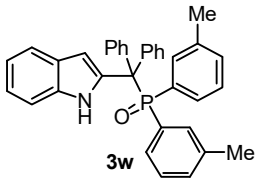
Column chromatography afforded the desired product **3u**[3] in 61% yield (84.2 mg) as white powder; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.01 (brs, 1H), 7.53-7.51 (m, 1H), 7.44-7.42 (m, 1H), 7.31-7.17 (m, 11H), 7.13-7.09 (m, 1H), 7.05-7.00 (m, 8H), 6.32 (s, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 139.0, 138.6, 136.2, 134.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 129.6, 129.0, 128.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.1, 127.9, 126.9, 122.5, 120.5, 119.9, 111.5, 106.0, 60.9 (d, $J_{C\text{-}P}$ = 63.0 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 36.2.



**3v**

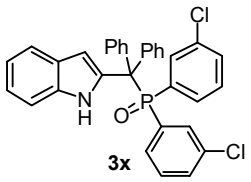
Column chromatography afforded the desired product **3v** in 84% yield (114.0 mg) as white powder; Mp: 140-142 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 11.02 (brs, 1H), 7.53 (s, 2H), 7.45-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.15-7.09 (m, 7H), 7.03-6.99 (m, 5H), 6.87-6.85 (m, 2H), 6.64-6.62 (m, 2H), 5.74 (s, 1H), 3.20 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 160.1, 142.4, 141.1, 136.5, 134.8, 133.6, 131.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.0, 126.6, 126.4, 121.4, 121.3 (d, $J_{C\text{-}P}$ = 94.5 Hz), 120.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 120.2,

119.0, 111.3, 110.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 105.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 64.2 (d, $J_{C\text{-}P}$ = 63.0 Hz), 54.5; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 47.5; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_3P$ $[M+H]^+$: 544.2036, Found: 544.2025.



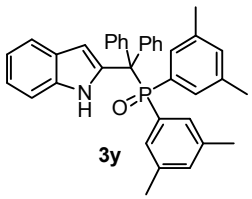
**3w**

Column chromatography afforded the desired product **3w** in 85% yield (108.6 mg) as white powder; Mp: 221-223 °C; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ = 10.22 (brs, 1H), 7.52-7.51 (m, 1H), 7.48-7.47 (m, 1H), 7.28-7.21 (m, 6H), 7.18-7.14 (m, 6H), 7.11-7.09 (m, 1H), 7.02-7.01 (m, 3H), 6.97-6.94 (m, 2H), 6.82-6.80 (m, 2H), 6.30 (s, 1H), 2.07 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 139.2, 138.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 136.2, 133.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.6, 131.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.4, 130.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.0, 127.9, 127.5, 127.0, 122.2, 120.3, 119.6, 111.4, 105.8, 61.0 (d, $J_{C\text{-}P}$ = 61.5 Hz), 21.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 37.8; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NOP$ $[M+H]^+$: 512.2138, Found: 512.2131.



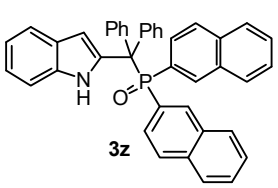
**3x**

Column chromatography afforded the desired product **3x** in 73% yield (100.6 mg) as white powder; Mp: 211-213 °C; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ = 9.91 (brs, 1H), 7.54-7.52 (m, 1H), 7.46-7.44 (m, 3H), 7.33-7.31 (m, 2H), 7.25-7.20 (m, 7H), 7.13-7.11 (m, 1H), 7.06-7.03 (m, 6H), 6.96-6.94 (m, 2H), 6.36 (s, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 138.4, 136.2, 134.7 (d, $J_{C\text{-}P}$ = 15.0 Hz), 133.1, 132.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.5, 132.4, 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.7 (d, $J_{C\text{-}P}$ = 13.5 Hz), 128.2, 128.1, 126.9, 122.6, 120.5, 119.9, 111.5, 106.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 61.1 (d, $J_{C\text{-}P}$ = 63.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 35.2; HRMS (ESI): Exact mass calcd for $C_{33}H_{24}Cl_2NOP$ $[M+H]^+$: 552.1045, Found: 552.1042.



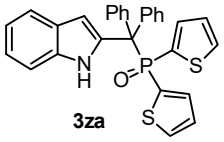
**3y**

Column chromatography afforded the desired product **3y** in 90% yield (121.2 mg) as white powder; Mp: 236-238 °C; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ = 10.13 (brs, 1H), 7.51-7.50 (m, 1H), 7.47-7.46 (m, 1H), 7.29-7.25 (m, 2H), 7.24-7.19 (m, 1H), 7.18-7.14 (m, 4H), 7.10-7.08 (m, 1H), 7.05 (s, 2H), 7.03-7.02 (m, 4H), 6.69-6.62 (m, 4H), 6.31 (s, 1H), 2.07 (s, 12H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 139.3, 137.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 136.2, 133.4, 131.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.9, 130.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 130.3, 127.8, 127.4, 127.1, 122.1, 120.2, 119.6, 111.3, 105.7, 61.2 (d, $J_{C\text{-}P}$ = 60.0 Hz), 21.1; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 38.0; HRMS (ESI): Exact mass calcd for $C_{37}H_{34}NOP$ $[M+H]^+$: 540.2451, Found: 540.2443.



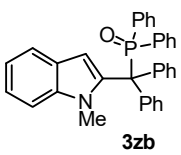
**3z**

Column chromatography afforded the desired product **3z** in 92% yield (134.0 mg) as white powder; Mp: 200-202 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 10.34 (brs, 1H), 7.81-7.79 (m, 2H), 7.73-7.69 (m, 3H), 7.66 (s, 1H), 7.57-7.43 (m, 8H), 7.31-7.26 (m, 3H), 7.19-7.07 (m, 11H), 6.32 (s, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 139.2, 136.3, 135.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 134.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 13.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.1, 128.8, 128.4, 128.0, 127.9 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.8, 127.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.5, 127.1, 126.7, 122.3, 120.4, 119.8, 111.5, 106.1, 61.3 (d, $J_{C\text{-}P}$ = 62.0 Hz); $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 38.1; HRMS (ESI): Exact mass calcd for $C_{41}H_{30}NOP$ $[M+H]^+$: 584.2138, Found: 584.2127.



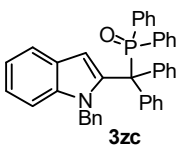
**3za**

Column chromatography afforded the desired product **3za**[3] in 89% yield (110.7 mg) as white powder; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 10.09 (brs, 1H), 7.65 (s, 2H), 7.57-7.56 (m, 1H), 7.46 (brs, 1H), 7.32-7.29 (m, 2H), 7.27-7.25 (m, 1H), 7.23-7.20 (m, 4H), 7.16-7.14 (m, 1H), 7.05 (brs, 6H), 6.85 (s, 2H), 6.30 (s, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 138.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.2, 135.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.8, 128.1, 128.0 (d, $J_{C\text{-}P}$ = 15.0 Hz), 127.9, 127.3, 122.4, 120.5, 119.9, 111.7, 106.4, 61.1 (d, $J_{C\text{-}P}$ = 72.0 Hz); $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 29.9.



**3zb**

Column chromatography afforded **3zb** in 64% yield (79.5 mg) as white powder; Mp: 246-248 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.56 (m, 1H), 7.42-7.34 (m, 8H), 7.28-7.25 (m, 4H), 7.24-7.18 (m, 5H), 7.15-7.11 (m, 2H), 7.08-7.04 (m, 1H), 7.00-6.96 (m, 4H), 2.84 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 138.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 137.5, 136.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 8.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.2, 130.3, 127.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 127.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 126.9, 121.6, 120.9, 119.3, 108.8, 106.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 60.3 (d, $J_{C\text{-}P}$ = 60.0 Hz), 32.2; $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 34.4; HRMS (ESI): Exact mass calcd for $C_{34}H_{28}NOP$ $[M+H]^+$: 498.1981, Found: 498.1975.

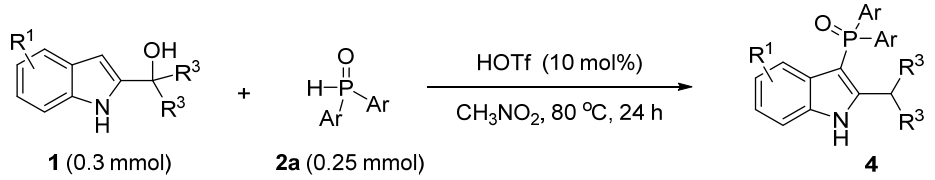


**3zc**

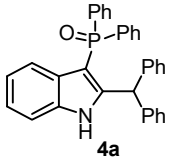
Column chromatography afforded **3zc** in 54% yield (77.4 mg) as white powder; Mp: 170-172 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, $J$ = 8.0 Hz, 1H), 7.45 (s, 1H), 7.40-7.36 (m, 6H), 7.21-7.17 (m, 6H), 7.16-7.10 (m, 4H), 7.06-7.02 (m, 1H), 6.99-6.91 (m, 6H), 6.87-6.83 (m, 2H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.22-6.21 (m, 2H), 4.72 (s, 2H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 138.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 137.3, 136.1, 135.6, 133.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.8, 129.8, 127.8 (d, $J_{C\text{-}P}$ = 13.0

Hz), 127.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 127.5, 126.0, 125.6, 121.8, 120.9, 119.6, 110.5, 106.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 60.2 (d, $J_{C\text{-}P}$ = 60.0 Hz), 49.5; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 34.7; HRMS (ESI): Exact mass calcd for $C_{40}H_{32}NOP$ $[M+H]^+$: 574.2294, Found: 574.2289.

### 3. General procedure for HOTf-catalyzed synthesis of C3-phosphorylated indoles

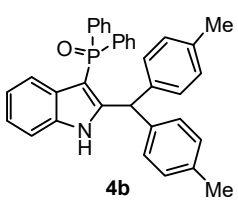



The reaction was carried out under an air atmosphere. To a 10-mL vial were added 2-indolylmethanols **1** (0.30 mmol, 1.2 equivs), $Ar_2P(O)H$ **2** (0.25 mmol, 1.0 equiv) and 2.5 mL of anhydrous $CH_3CN$. After adding HOTf (7.5 mg, 10 mol%) which was prepared as a solution in $CH_3NO_2$, the reaction mixture was stirred at 80 °C for 24 hours. The reaction mixture was directly subjected to column chromatography using dichloromethane /ethyl acetate (generally 10:1 to 6:1, v:v) as the eluent to afford the desired products **4**.



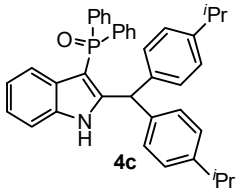
**4a**

Column chromatography afforded the desired product **4a**[3] in 73% yield (77.7 mg) as white powder; $^{1}H$ NMR (600 MHz, DMSO-$d_6$): δ = 11.70 (d, $J$ = 6.0 Hz, 1H), 7.61-7.56 (m, 6H), 7.49-7.45 (m, 4H), 7.41 (d, $J$ = 12.0 Hz, 1H), 7.30-7.26 (m, 4H), 7.23-7.20 (m, 2H), 7.13-7.12 (m, 4H), 7.07-7.03 (m, 1H), 6.82-6.79 (m, 1H), 6.73 (s, 1H), 6.54 (d, $J$ = 12.0 Hz, 1H); $^{31}P\{^{1}H\}$ NMR (243 MHz, DMSO-$d_6$): $\delta$ = 22.1.



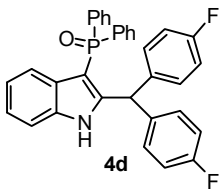
**4b**

Column chromatography afforded the desired product **4b**[3] in 65% yield (83.2 mg) as white powder; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.60-7.57 (m, 4H), 7.47-7.45 (m, 2H), 7.34-7.31 (m, 4H), 7.28 (d, $J$ = 6.0 Hz, 1H), 7.08 (t, $J$ = 6.0 Hz, 1H), 6.98-6.94 (m, 8H), 6.90 (t, $J$ = 6.0 Hz, 1H), 6.82 (d, $J$ = 6.0 Hz, 1H), 6.48 (s, 1H), 2.28 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 149.9 (d, $J_{C\text{-}P}$ = 17.0 Hz), 138.7, 136.1, 135.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.7, 133.6, 131.7 (d, $J_{C\text{-}P}$ = 11.0 Hz), 131.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.4 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 111.2, 100.9 (d, $J_{C\text{-}P}$ = 126.0 Hz), 47.4, 20.9; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 24.2.



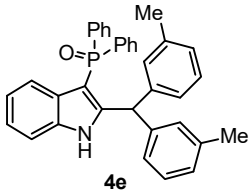
**4c**

Column chromatography afforded the desired product **4c** in 57% yield (80.8 mg) as white powder; Mp: 268-270 ºC; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 7.59-7.56 (m, 4H), 7.46-7.43 (m, 2H), 7.33-7.28 (m, 5H), 7.11-7.08 (m, 1H), 7.04 (AB, $J$ = 6.0 Hz, 4H), 6.98 (AB, $J$ = 12.0 Hz, 4H), 6.92-6.89 (m, 1H), 6.85-6.84 (m, 1H), 6.50 (s, 1H), 2.87-2.80 (m, 2H), 1.22 (d, $J$ = 6.0 Hz, 12H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 150.0 (d, $J_{C\text{-}P}$ = 17.0 Hz), 147.1, 138.9, 135.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.7, 133.6, 131.7 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.9, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.4, 122.1, 120.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 111.1, 100.8 (d, $J_{C\text{-}P}$ = 125.0 Hz), 47.4, 33.6, 24.0, 23.9; $^{31}$P {$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 24.4; HRMS (ESI): Exact mass calcd for $C_{39}H_{38}NOP$ $[M+H]^+$: 568.2764, Found: 568.2758.



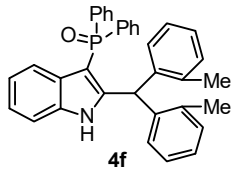
**4d**

Column chromatography afforded the desired product **4d**[3] in 68% yield (88.2 mg) as white powder; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 9.19 (s, 1H), 7.57-7.54 (m, 4H), 7.49-7.47 (m, 2H), 7.35-7.32 (m, 4H), 7.27 (d, $J$ = 6.0 Hz, 1H), 7.06-7.03 (m, 1H), 7.02-7.00 (m, 4H), 6.89-6.86 (m, 1H), 6.80-6.78 (m, 4H), 6.72 (s, 1H), 6.64 (d, $J$ = 6.0 Hz, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 161.6 (d, $J_{C\text{-}F}$ = 244.5 Hz), 149.4 (d, $J_{C\text{-}P}$ = 16.5 Hz), 137.1, 135.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 134.2, 133.5, 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 122.3, 121.1, 120.5, 115.2 (d, $J_{C\text{-}F}$ = 21.0 Hz), 111.4, 101.2 (d, $J_{C\text{-}P}$ = 124.5 Hz), 46.6; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 24.5; $^{19}$F{$^{1}$H} NMR (565 MHz, $CDCl_3$): $\delta$ = -115.7.



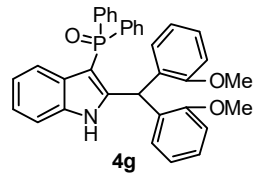
**4e**

Column chromatography afforded the desired product **4e**[3] in 56% yield (71.5 mg) as white powder; $^{1}$H NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 11.55 (d, $J$ 1.8 Hz, 1H), 7.60-7.55 (m, 4H), 7.55-7.52 (m, 2H), 7.44-7.42 (m, 4H), 7.39 (d, $J$ = 8.4 Hz, 1H), 7.12 (t, $J$ = 7.8 Hz, 2H), 7.03-7.00 (m, 1H), 6.98-6.97 (m, 2H), 6.94-6.93 (m, 2H), 6.88 (s, 2H), 6.78-6.75 (m, 1H), 6.61 (s, 1H), 6.52 (d, $J$ = 8.4 Hz, 1H), 2.18 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$+DMSO-$d_6$): δ = 149.8 (d, $J_{C\text{-}P}$ = 17.0 Hz), 141.6, 137.2, 136.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 135.1, 134.0, 131.5, 131.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 129.4, 128.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.0, 127.0, 125.7, 121.5, 120.1, 119.6, 111.9, 99.9 (d, $J_{C\text{-}P}$ = 125.0 Hz), 47.0, 21.1; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$+DMSO-$d_6$): $\delta$ = 23.2.



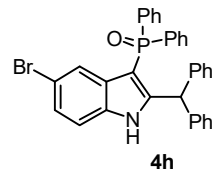
**4f**

Column chromatography afforded the desired product **4f** in 75% yield (76.8 mg) as white powder; Mp: 176-178 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.56-7.52 (m, 4H), 7.44-7.42 (m, 2H), 7.31-7.28 (m, 5H), 7.16-7.11 (m, 5H), 6.98-6.93 (m, 3H), 6.87-6.86 (m, 2H), 6.66-6.65 (m, 2H), 2.20 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 149.1 (d, $J_{C\text{-}P}$ = 16.5 Hz), 139.9, 137.4, 135.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 134.3, 133.6, 131.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.3, 130.6, 129.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.2, 128.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.9, 125.9, 122.1, 120.9 (d, $J_{C\text{-}P}$ = 42.0 Hz), 111.1, 100.6 (d, $J_{C\text{-}P}$ = 124.5 Hz), 43.2, 19.7; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 23.7; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NOP$ $[M+H]^+$: 512.2138, Found: 512.2133.



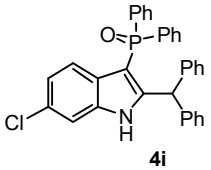
**4g**

Column chromatography afforded the desired product **4g** in 78% yield (105.8 mg) as white powder; Mp: 278-280 °C; $^{1}$H NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 10.75 (d, $J$ = 3.0 Hz, 1H), 7.52-7.49 (m, 4H), 7.46-7.43 (m, 2H), 7.40 (d, $J$ = 8.4 Hz, 1H), 7.32 (td, $J$ = 7.8 Hz, 3.0 Hz, 4H), 7.16 (td, $J$ = 7.8 Hz, 1.8 Hz, 2H), 7.00-6.97 (m, 2H), 6.80 (d, $J$ = 7.8 Hz, 1H), 6.79-6.76 (m, 4H), 6.68-6.67 (m, 2H), 6.63 (s, 1H), 3.44 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$+DMSO-$d_6$): δ = 156.4, 148.5 (d, $J_{C\text{-}P}$ =18.0 Hz), 136.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 135.2, 134.1, 131.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 130.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 130.1, 129.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 128.8, 127.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.5, 121.0, 120.1, 119.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 111.8, 110.3, 98.7 (d, $J_{C\text{-}P}$ = 127.0 Hz), 54.9; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$+DMSO-$d_6$): $\delta$ = 22.0; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_3P$ $[M+H]^+$: 544.2036, Found: 544.2029.



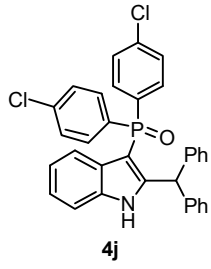
**4h**

Column chromatography afforded the desired product **4h** in 36% yield (50.5 mg) as white powder; Mp: 284-286 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 8.96 (s, 1H), 7.55-7.52 (m, 4H), 7.49-7.47 (m, 2H), 7.34 (td, $J$ = 7.8 Hz, 3.0 Hz, 4H), 7.17-7.11 (m, 8H), 7.01-6.99 (m, 4H), 6.86 (s, 1H), 6.42 (s, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ = 150.2 (d, $J_{C\text{-}P}$ = 17.0 Hz), 141.1, 134.5 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.1, 131.8 (d, $J_{C\text{-}P}$ = 11.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.0, 128.5, 128.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 126.8, 125.2, 123.2, 114.4, 112.7, 101.3 (d, $J_{C\text{-}P}$ = 125.0 Hz), 48.1; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$): $\delta$ = 23.9; HRMS (ESI): Exact mass calcd for $C_{33}H_{25}BrNOP$ $[M+H]^+$: 562.0930, Found: 562.0922.



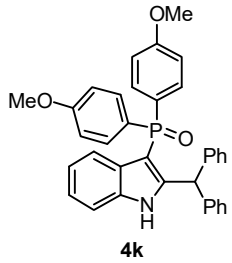
**4i**

Column chromatography afforded the desired product **4i** in 42% yield (54.3 mg) as white powder; Mp: 276-278 °C; $^{1}$H NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 11.82 (d, $J$ = 1.8 Hz, 1H), 7.58-7.55 (m, 6H), 7.48-7.45 (m, 4H), 7.42 (t, $J$ = 1.8 Hz, 1H), 7.29-7.27 (m, 4H), 7.23-7.21 (m, 2H), 7.10-7.09 (m, 4H), 6.87 (dd, $J$ = 9.0 Hz, 1.8 Hz, 1H), 6.63 (s, 1H), 6.54 (d, $J$ = 9.0 Hz, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$): δ = 150.6 (d, $J_{C\text{-}P}$ = 16.0 Hz), 141.4, 137.5 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.8, 133.7, 131.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.8, 128.7, 128.5, 127.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7 (d, $J_{C\text{-}P}$= 2.0 Hz), 121.0, 120.7, 111.7, 100.9 (d, $J_{C\text{-}P}$ = 124.0 Hz), 47.1; $^{31}$P{$^{1}$H} NMR (242 MHz, DMSO-$d_6$): $\delta$ = 22.3; HRMS (ESI): Exact mass calcd for $C_{33}H_{25}ClNOP$ $[M+H]^+$: 518.1435, Found: 518.1430.



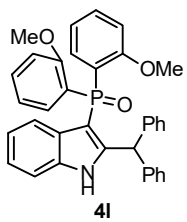
**4j**

Column chromatography afforded the desired product **4j**[3] in 58% yield (80.2 mg) as white powder; $^{1}$H NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 11.76 (s, 1H), 7.59-7.55 (m, 4H), 7.53-7.51 (m, 4H), 7.43 (d, $J$ = 7.8 Hz, 1H), 7.28-7.26 (m, 4H), 7.23-7.20 (m, 2H), 7.13-7.11 (m, 4H), 7.07 (t, $J$ = 7.2 Hz, 1H), 6.85 (t, $J$ = 7.8 Hz, 1H), 6.72 (s, 1H), 6.54 (d, J = 8.4 Hz, 1H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$+DMSO-$d_6$): δ = 150.3 (d, $J_{C\text{-}P}$ = 18.0 Hz), 141.5, 137.1, 133.5, 133.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.8, 128.8 (d, $J_{C\text{-}P}$ = 13.5 Hz), 128.7, 128.4, 127.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.6, 122.0, 120.6, 119.4, 112.3, 99.1 (d, $J_{C\text{-}P}$ = 127.5 Hz), 47.2; $^{31}$P{$^{1}$H} NMR (243 MHz, $CDCl_3$+DMSO-$d_6$): $\delta$ = 22.6.



**4k**

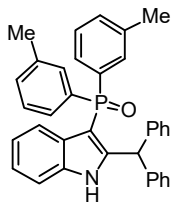
Column chromatography afforded the desired product **4k**[3] in 34% yield (46.2 mg) as white powder; $^{1}$H NMR (600 MHz, DMSO-$d_6$): δ = 11.63 (d, $J$ = 1.8 Hz, 1H), 7.50-7.46 (m, 4H), 7.39 (d, $J$ = 8.4 Hz, 1H), 7.29-7.27 (m, 4H), 7.23-7.20 (m, 2H), 7.15-7.13 (m, 4H), 7.04 (t, $J$ = 7.2 Hz, 1H), 7.01-6.99 (m, 4H), 6.83 (t, $J$ = 7.2 Hz, 1H), 6.79 (s, 1H), 6.62 (d, $J$ = 7.8 Hz, 1H), 3.77 (s, 6H), $^{13}$C{$^{1}$H} NMR (150 MHz, DMSO-$d_6$): δ = 161.8, 149.3 (d, $J_{C\text{-}P}$ = 18.0 Hz), 141.9, 137.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 57.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.8, 126.6, 126.0, 121.8, 120.3, 119.9, 114.1 (d, $J_{C\text{-}P}$ = 13.5 Hz), 112.0, 101.2 (d, $J_{C\text{-}P}$ = 124.5 Hz), 55.4, 47.0; $^{31}$P{$^{1}$H} NMR (243 MHz, DMSO-$d_6$): $\delta$ = 22.1.



**4l**

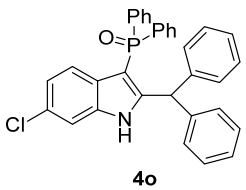
Column chromatography afforded the desired product **4l** in 83% yield (112.6 mg) as white powder; Mp: 230-232 °C; $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 8.79 (s, 1H), 7.41-7.36 (m, 4H), 7.19-7.18 (m, 1H), 7.15-7.13 (m, 10H), 7.00-6.98 (m, 1H), 6.94 (s, 1H), 6.86-6.79 (m, 6H), 3.34 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): δ = 161.8,

148.3 (d, $J_{C\text{-}P}$ = 18.0 Hz), 142.1, 135.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 133.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.1, 129.1, 128.2, 126.3, 122.3, 121.6, 121.5, 120.9, 120.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 120.0, 110.9 (d, $J_{C\text{-}P}$ = 15.0 Hz), 102.3 (d, $J_{C\text{-}P}$ = 132.0 Hz), 55.1, 47.6; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 21.5; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NO_3P$ $[M+H]^+$: 544.2036, Found: 544.2024.



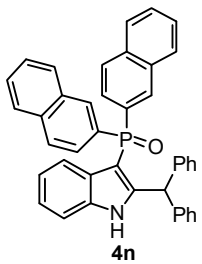
**4n**

Column chromatography afforded product **4n** in 68% yield (86.8 mg) as white powder; Mp: 236-244 °C; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.45-7.43 (m, 2H), 7.36-7.33 (m, 2H), 7.29-7.27 (m, 1H), 7.26-7.25 (m, 2H), 7.23-7.18 (m, 8H), 7.12-7.10 (m, 1H), 7.04-7.03 (m, 4H), 6.98-6.97 (m, 1H), 6.94-6.92 (m, 1H), 6.42 (s, 1H), 2.24 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 148.6 (d, $J_{C\text{-}P}$ = 19.5 Hz), 141.6, 138.1 (d, $J_{C\text{-}P}$ = 12.0 Hz), 135.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 134.3, 133.6, 132.4, 132.3, 129.5 (d, $J_{C\text{-}P}$ 12.0 Hz), 129.1, 128.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.5, 128.1 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.8, 122.3, 121.1 (d, $J_{C\text{-}P}$ = 28.5 Hz), 111.0, 101.8 (d, $J_{C\text{-}P}$ = 124.5 Hz), 48.1, 21.3; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 24.3; HRMS (ESI): Exact mass calcd for $C_{35}H_{30}NOP$ $[M+H]^+$: 512.2128, Found: 512.2132.



**4o**

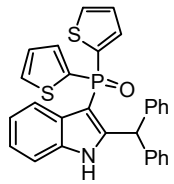
Column chromatography afforded the desired product **4o**[3] in 52% yield (71.6 mg) as white powder; $^{1}H$ NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 11.82 (s, 1H), 7.63-7.62 (m, 2H), 7.54-7.45 (m, 7H), 7.28-7.26 (m, 4H), 7.23-7.21 (m, 2H), 7.12-7.07 (m, 5H), 6.89-6.86 (m, 1H), 6.59-6.58 (m, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$+DMSO-$d_6$): δ = 150.9 (d, $J_{C\text{-}P}$ = 18.0 Hz), 141.8, 137.5 (d, J = 16.5 Hz), 136.7, 134.4 (d, $J_{C\text{-}P}$ = 15.0 Hz), 132.5, 131.4 (d, $J_{C\text{-}P}$ = 13.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 129.2, 128.9, 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.2, 122.6, 121.2, 119.8, 112.9, 99.2 (d, $J_{C\text{-}P}$ = 127.5 Hz), 47.9; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$+DMSO-$d_6$): $\delta$ = 20.9.



**4n**

Column chromatography afforded **4p** in 80% yield (116.6 mg) as white powder; Mp: 280-282 °C; $^{1}H$ NMR 600 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 8.15-8.13 (m, 2H), 7.85-7.84 (m, 2H), 7.80 (dd, $J$ = 5.4 Hz, 3.0 Hz, 2H), 7.74-7.68 (m, 4H), 7,56 (td, $J$ = 6.0 Hz, 1.2 Hz, 2H), 7.49 (td, $J$ = 6.0 Hz, 1.2 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.14-7.07 (m, 7H), 7.02-7.01 (m, 4H), 6.97 (d, $J$ = 8.4 Hz, 1H), 6.88-6.86 (m, 1H), 6.60 (s, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 149.3 (d, $J_{C\text{-}P}$ = 16.5 Hz), 141.3, 135.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 134.6, 133.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 131.6, 130.9, 129.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 129.1, 129.0, 128.4, 128.1 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 19.5 Hz), 126.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.8, 126.5, 122.3, 121.1 (d, $J_{C\text{-}P}$ = 24.0 Hz), 111.2, 101.3 (d, $J_{C\text{-}P}$ = 124.5 Hz), 48.4; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): $\delta$ = 24.0; HRMS (ESI): Exact mass calcd for

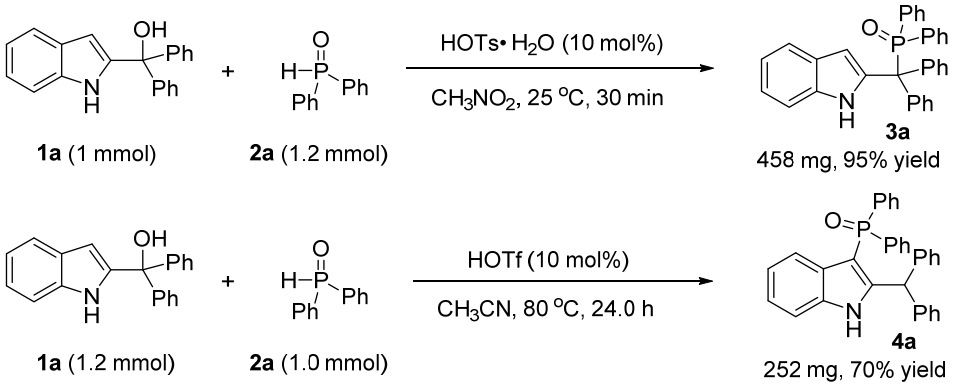
$C_{41}H_{30}NOP$ $[M+H]^+$: 584.2138, Found: 584.2128.



**4q**

Column chromatography afforded the desired product **4q**[3] in 50% yield (62.0 mg) as white powder; $^1$H NMR (600 MHz, $CDCl_3$+DMSO-$d_6$): δ = 11.80 (d, $J$ = 2.4 Hz, 1H), 8.02-8.00 (m, 2H), 7.45-7.42 (m, 3H), 7.34-7.30 (m, 4H), 7.25-7.21 (m, 8H), 7.08 (t, $J$ = 7.8 Hz, 1H), 6.95 (s, 1H), 6.89 (t, $J$ = 7.8 Hz, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$+DMSO-$d_6$): δ = 149.9 (d, $J_{C\text{-}P}$ = 19.0 Hz), 141.8, 137.5, 136.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 136.3, 135.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 128.8, 128.4, 127.6 (d, $J_{C\text{-}P}$ = 13.0 Hz), 126.6, 122.0, 120.4, 119.7, 112.1, 100.8 (d, $J_{C\text{-}P}$ = 138.0 Hz), 46.8; $^{31}$P{$^1$H} NMR (243 MHz, $CDCl_3$+DMSO-$d_6$): $\delta$ = 6.5.

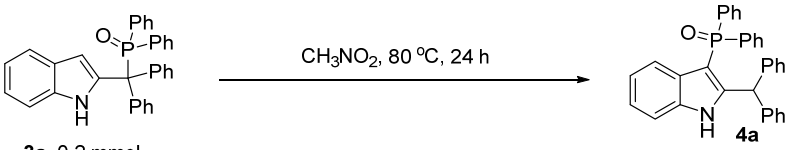
## 4. 1 mmol scale synthesis




The 1 mmol scale synthesis of **3a** utilized the general procedure of HOTs·$H_2O$-catalyzed regioselective benzylic phosphorylation of 2-indolylmethanols and 10.0 mL $CH_3NO_2$ was used in this reaction.

The 1 mmol scale synthesis of **4a** utilized the general procedure for HOTf-catalyzed formation of C3-phosphorylatied indoles and 10.0 mL of $CH_3CN$ was used instead of $CH_3NO_2$ in this reaction.

## 5. Control experiments

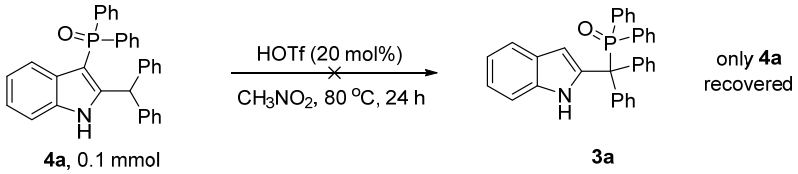



1) with 20 mol% HOTf, 76% yield
2) with HOTs (20 mol%), 41% yield and 40% of **3a** recovered
3) without HOTf, over 90% of **3a** recovered

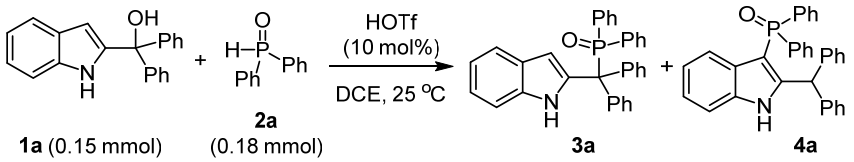
To a 10.0 mL vial was added successively **3a** (96.6 mg, 0.2 mmol), 2.0 mL anhydrous $CH_3NO_2$ and HOTf (6.0 mg, 20 mol%) which was prepared as a solution in $CH_3NO_2$, the reaction mixture was stirred at 80 °C for 24 hours. The reaction mixture was directly subjected to column chromatography using dichloromethane /ethyl acetate (6:1, v:v) as the eluent to afford product **4a** in 76% yield (73.4 mg).

Replacing HOTf with $HOTs{\cdot}H_2O$, only 41% yield of **4a** was isolated along with 40% of **3a** recovered.

The same procedure was followed without HOTf, no desired product **4a** was detected along with over 90% of **3a** recovered.



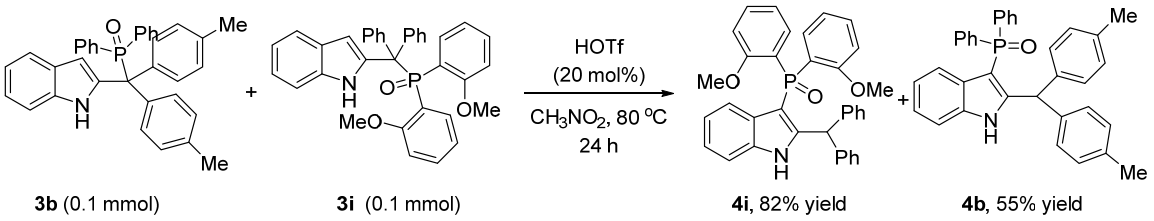

To a 5.0 mL vial was added successively **4a** (48.3 mg, 0.1 mmol), 1.0 mL anhydrous $CH_3NO_2$ and HOTf (3.0 mg, 20 mol%) which was prepared as a solution in $CH_3NO_2$, the reaction mixture was stirred at 80 °C for 24 hours. No product **3a** was observed along with almost **4a** recovered.




1) 30 mins, 79% of **3a** and 15% of **4a**
2) 24 h, 78% of **3a** and 15% of **4a**
3) at 80 °C, 15 mins, 85% of **3a** and <5% of **4a**

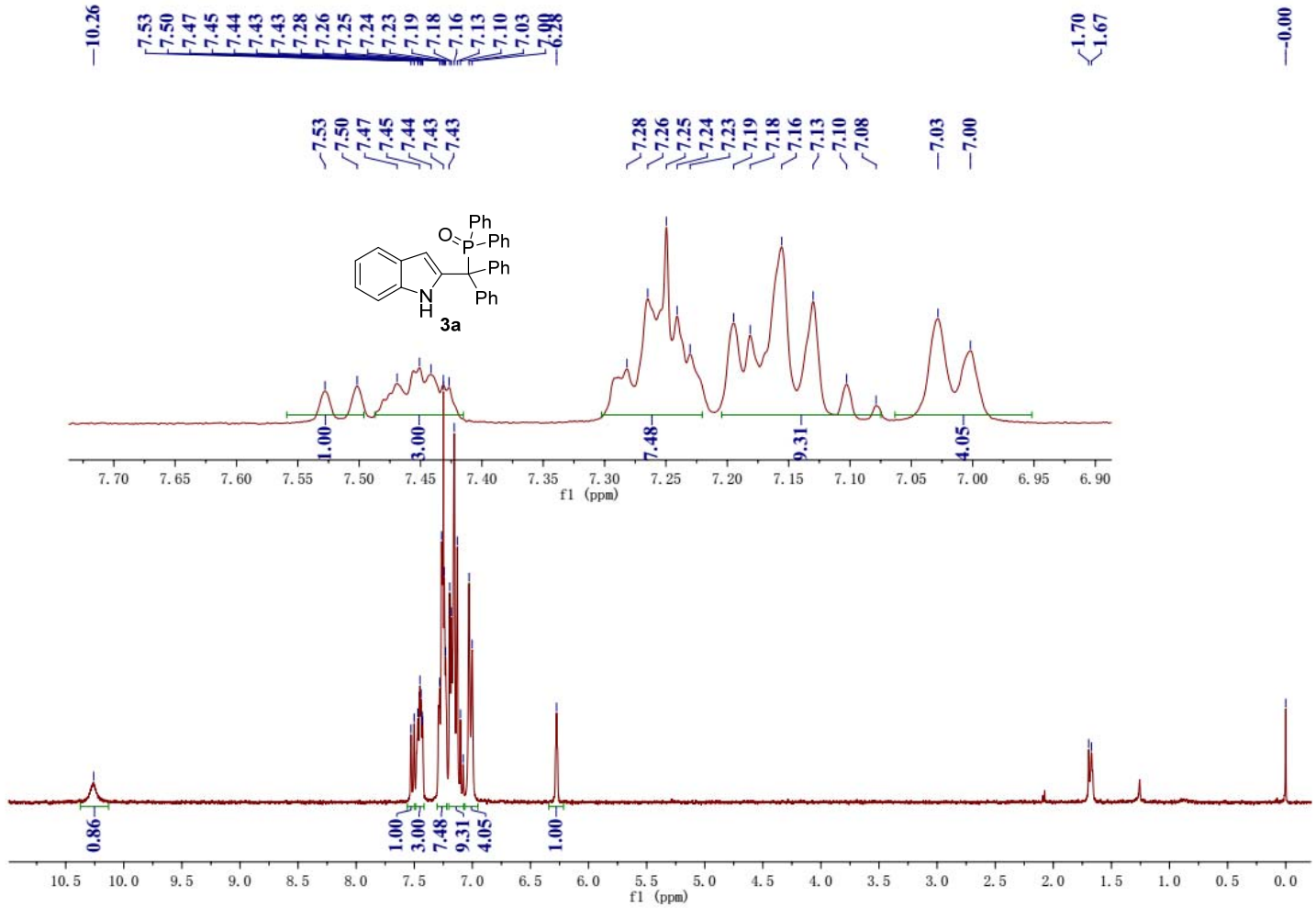
To a 5-mL vial were added 2-indolylmethanol **1a** (0.15 mmol, 1.0 equiv), $Ph_2P(O)H$ **2a** (0.18 mmol, 1.2 equivs) and 1.0 mL of anhydrous $ClCH_2CH_2Cl$. After adding HOTf (2.3 mg, 10 mol%) which was prepared as a solution in $ClCH_2CH_2Cl$, the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was directly subjected to column chromatography using petrol ether/ethyl acetate (generally 10:1 to 3:1, v:v) as the eluent to afford products **3a** and **4a** in 78% and 15% yield.

The same procedure was followed by running the reaction at 80 °C for 15 minutes, **3a** was isolated in 85% yield and **4a** was generated with less than 5% yield.




**3b** (0.1 mmol) **3i** (0.1 mmol) **4i**, 82% yield **4b**, 55% yield

To a 5.0 mL vial was added successively **3b** (51.1 mg, 0.1 mmol), **3i** (54.3 mg, 0.1 mmol), 1.0 mL anhydrous $CH_3NO_2$ and HOTf (3.0 mg, 20 mol%) which was prepared as a solution in $CH_3NO_2$, the reaction mixture was stirred at 80 °C until the disappearance of **3b** and **3i**. The reaction mixture was directly subjected to column chromatography using dichloromethane /ethyl acetate (10: to 6:1, v:v) as the eluent to afford product **4i** in 82% yield (44.6 mg) and **4b** in 55% yield (28.2 mg), respectively.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7.19
7.18
7.16
7.13
7.10
7.03
7.00
6.28
1.70
1.67
0.00
Ph
O
P
Ph
Ph
Ph
N
H
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1.00
3.00
7.48
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f1 (ppm)
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1.00
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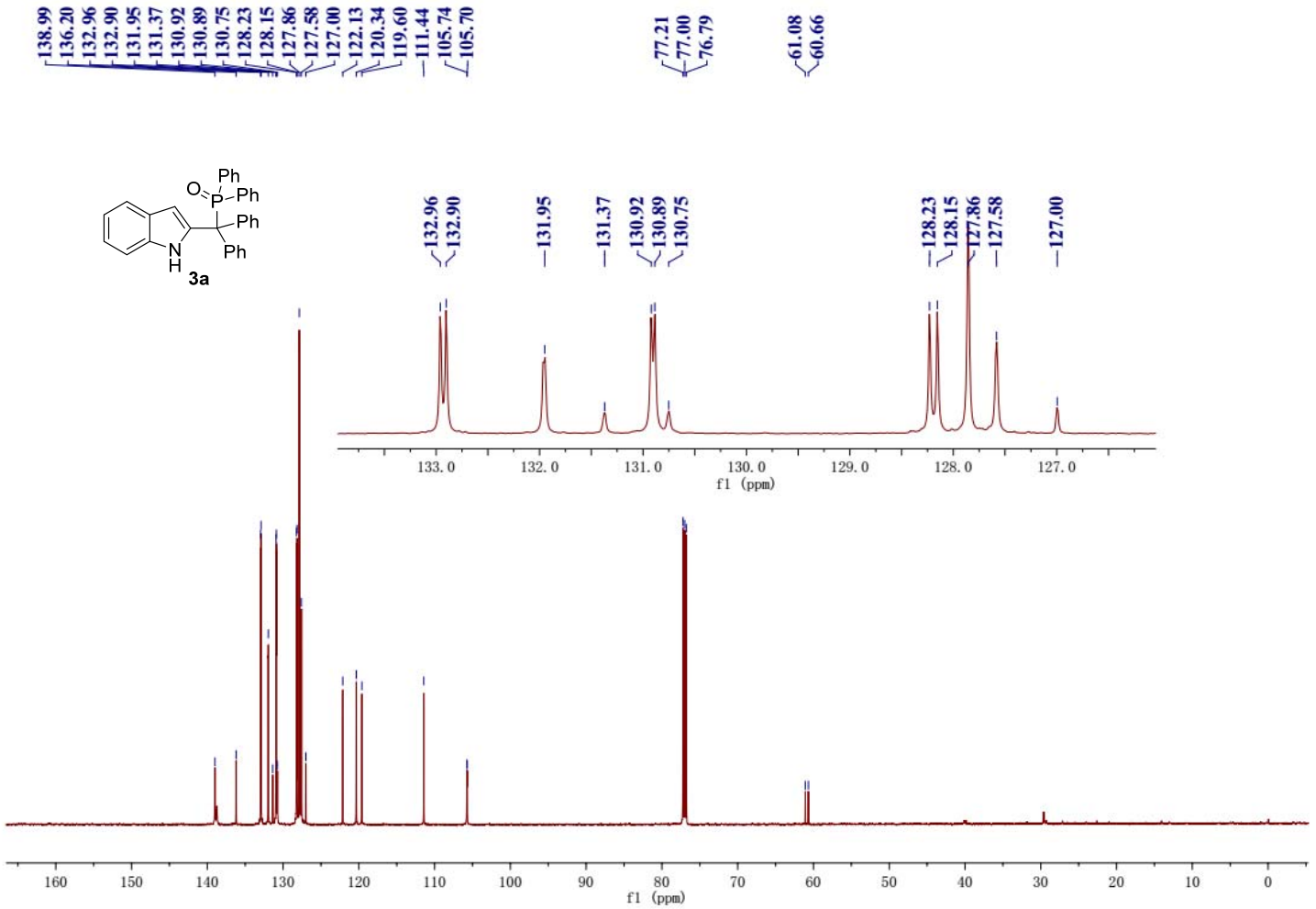
9.31
4.05
1.00
f1 (ppm)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122.13
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119.60
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105.70
77.21
77.00
76.79
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60.66
Ph
O
P
Ph
Ph
Ph
N
H
3a
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131.37
130.92
130.89
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128.15
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127.58
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128.0
127.0
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50
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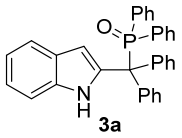
f1 (ppm)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O
P
Ph
Ph
Ph
N
H

**3a**


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300
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200
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100
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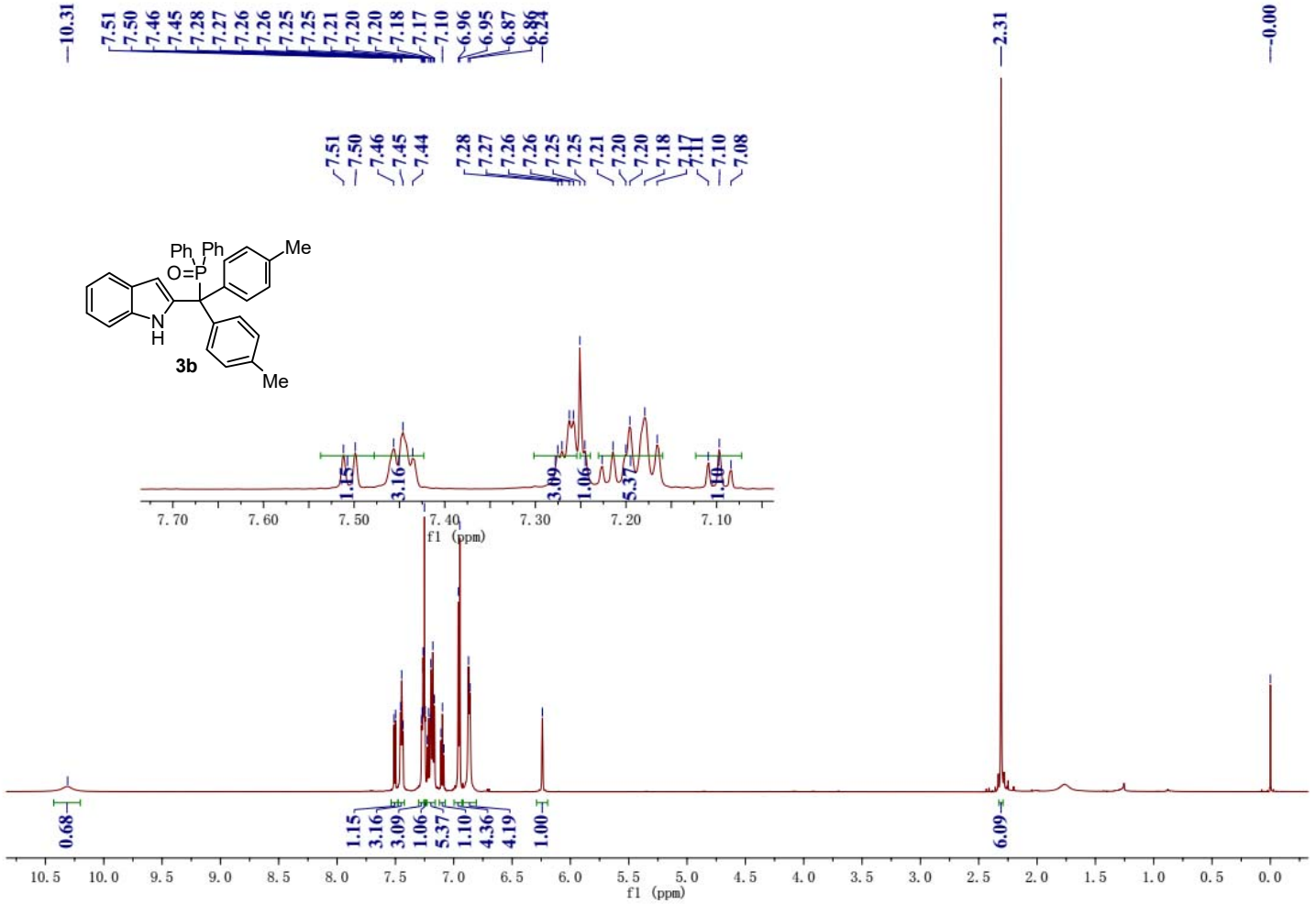
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)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7.17
7.10
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6.95
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6.84
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7.20
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7.17
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7.08
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3.16
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1.10
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7.10
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6.0
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1.0
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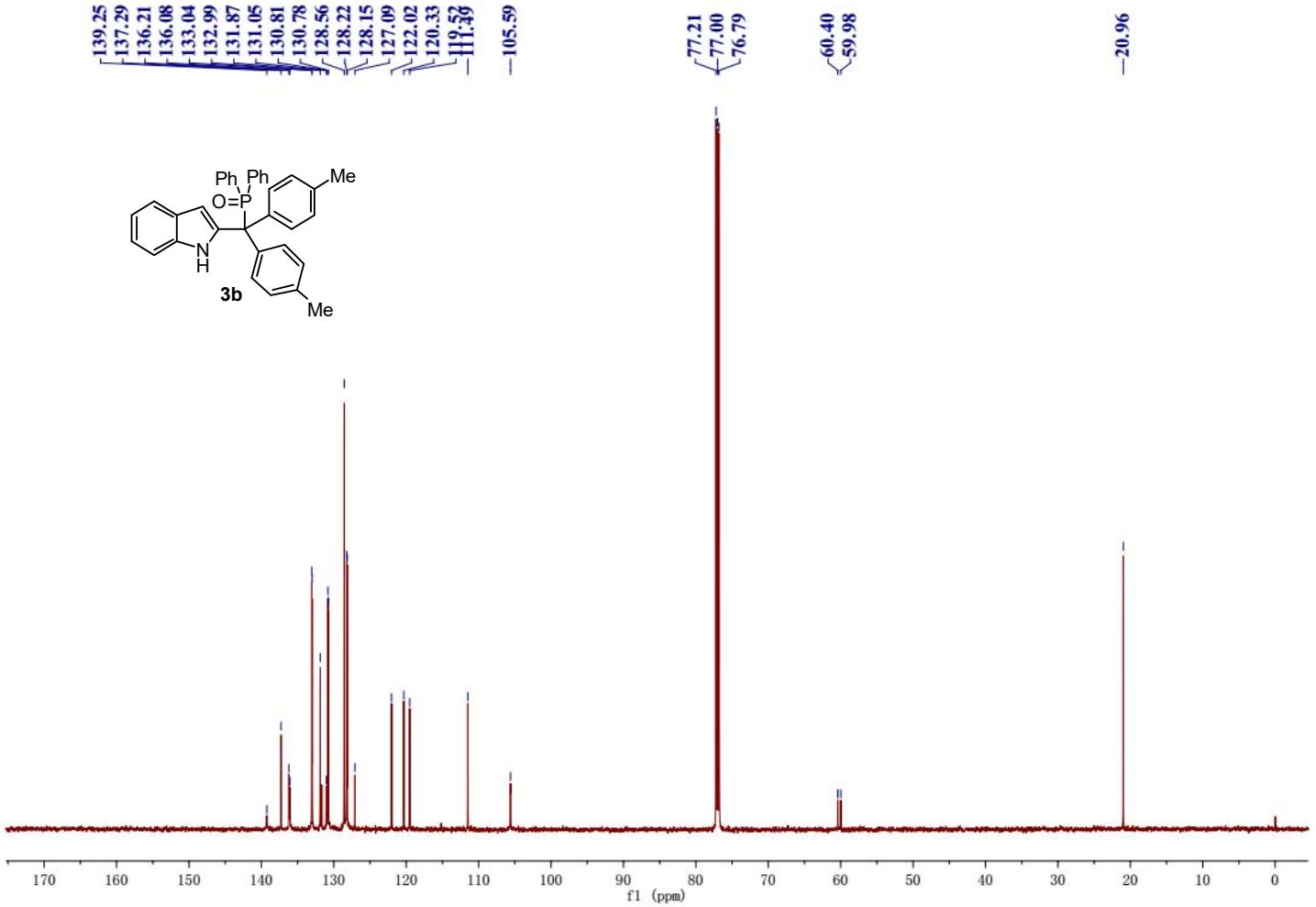
0.0
f1 (ppm)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127.09
122.02
120.33
105.59
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77.00
76.79
60.40
59.98
20.96
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Ph
O=P
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N
H
3b
Me
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120
110
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50
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10
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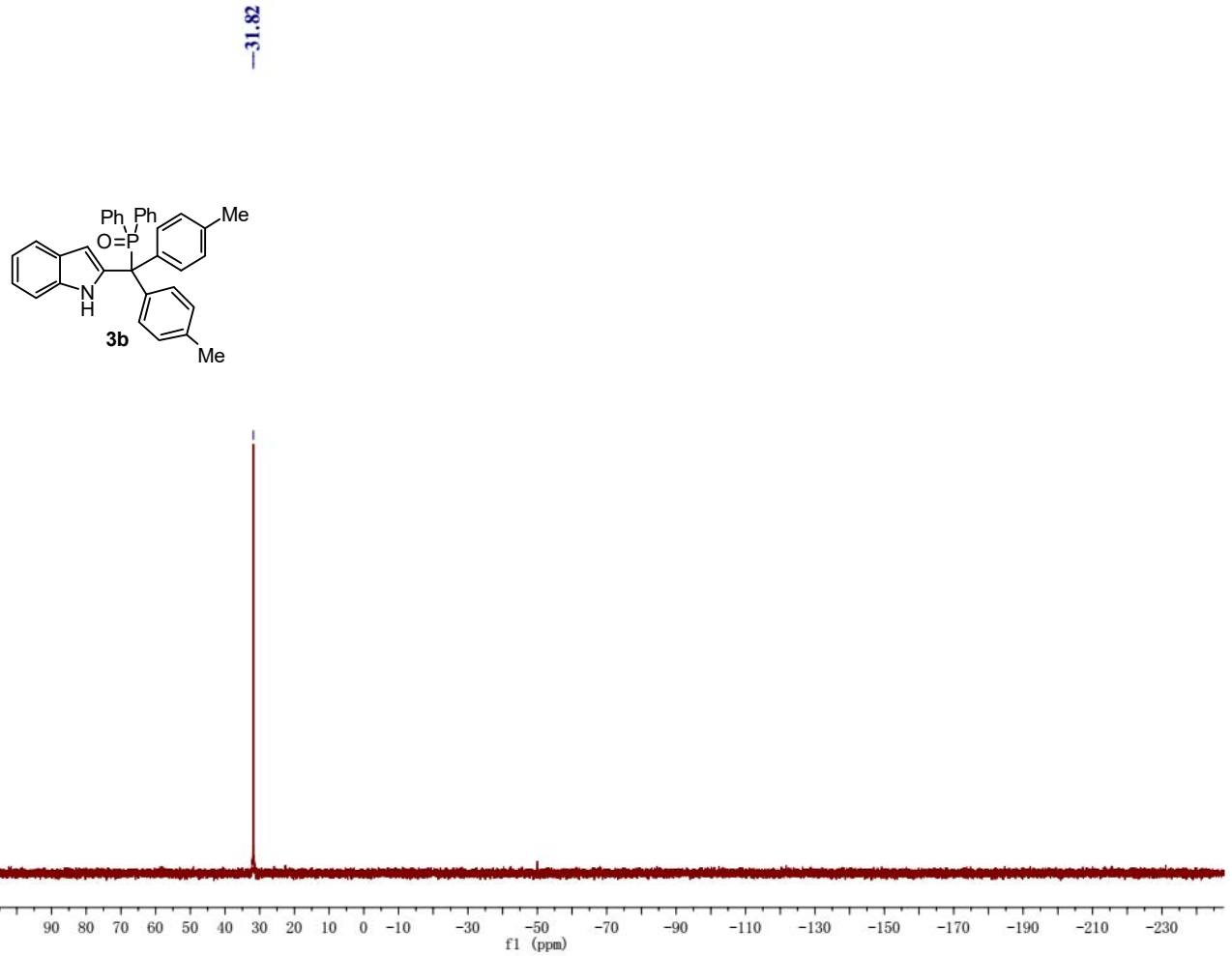
f1 (ppm)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-50
-70
-90
-110
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-150
-170
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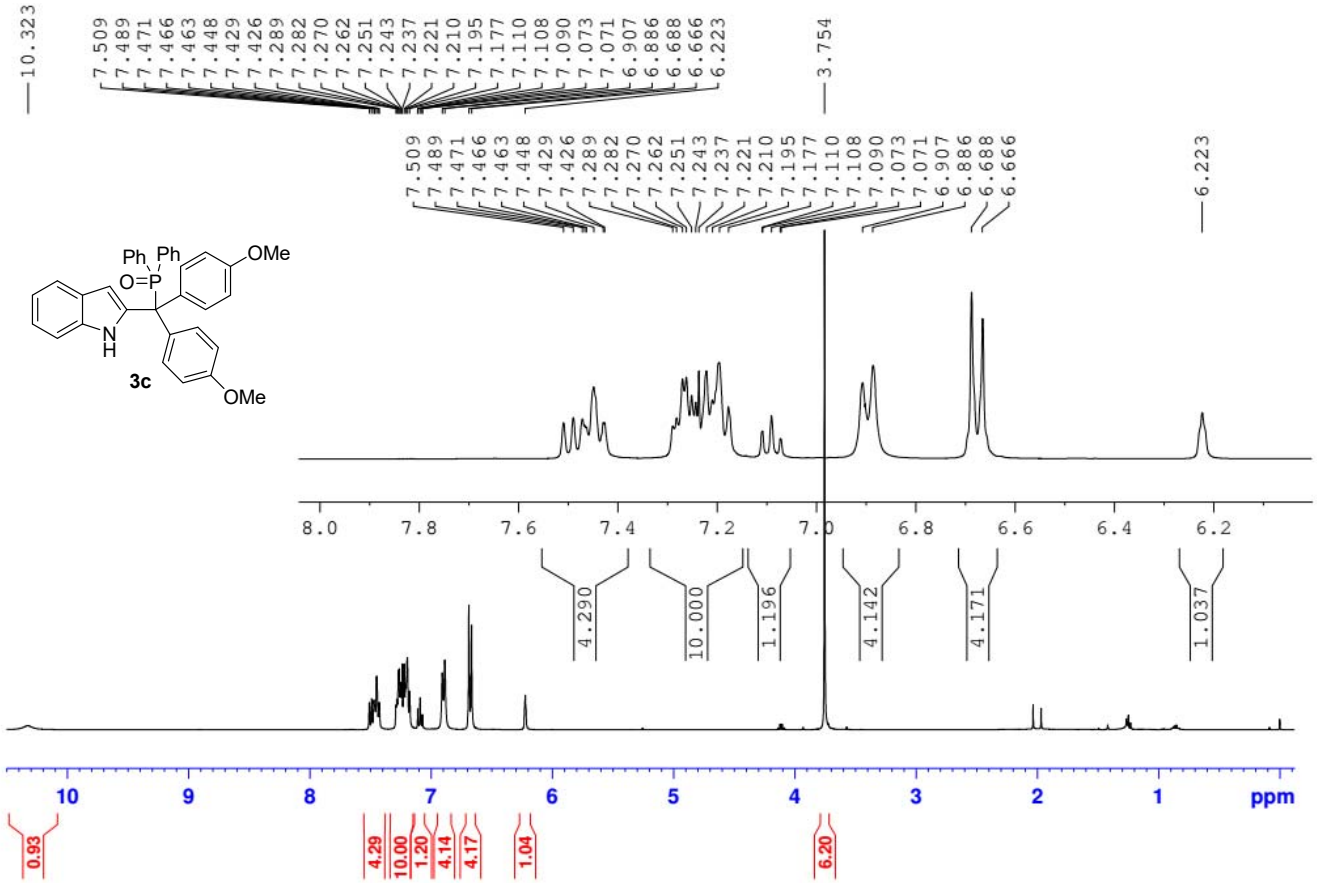
-210
-230
f1 (ppm)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7.251
7.243
7.237
7.221
7.210
7.195
7.177
7.110
7.108
7.090
7.073
7.071
6.907
6.886
6.688
6.666
6.223
3.754
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Ph
O=P
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N
H
3c
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7.6
7.4
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7.0
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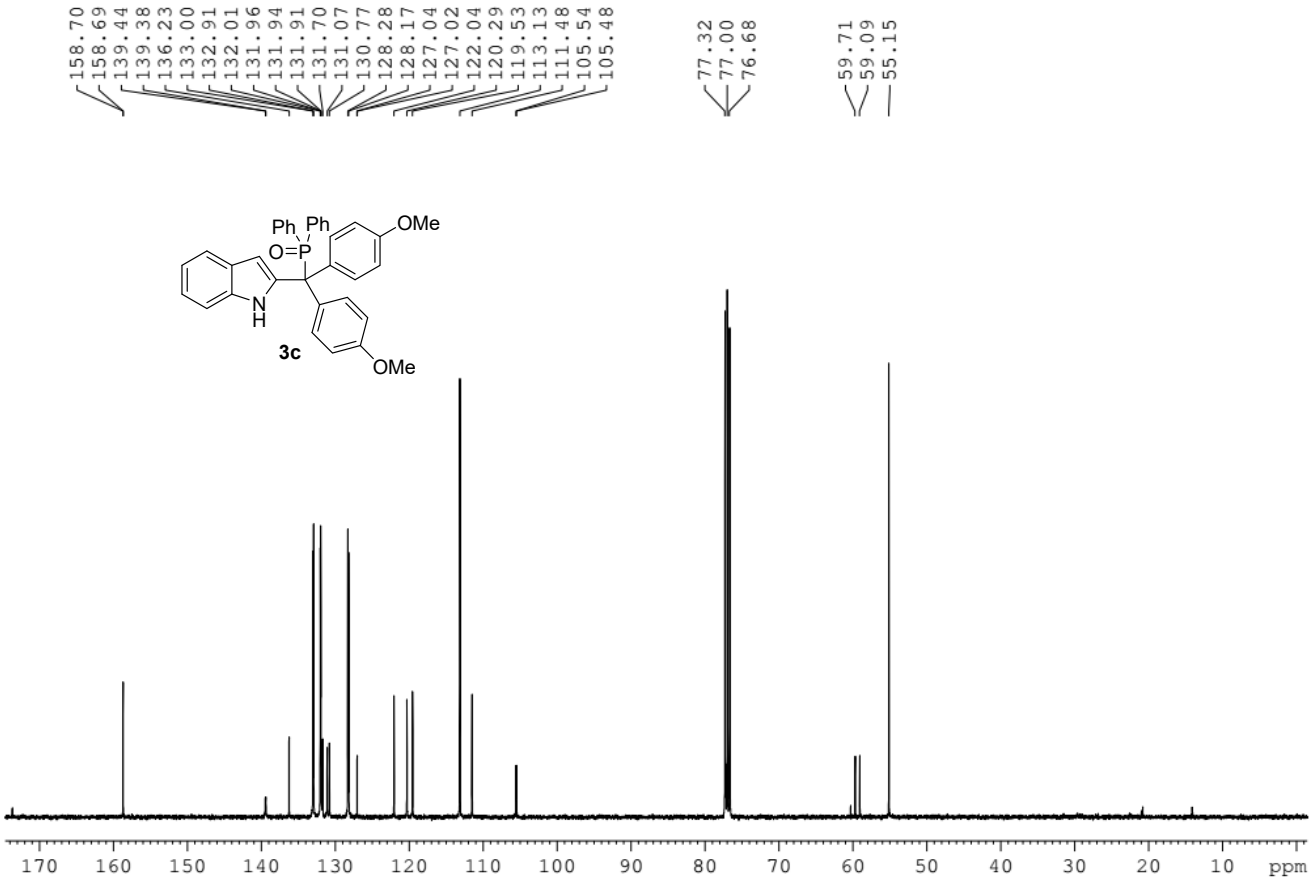
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77.00
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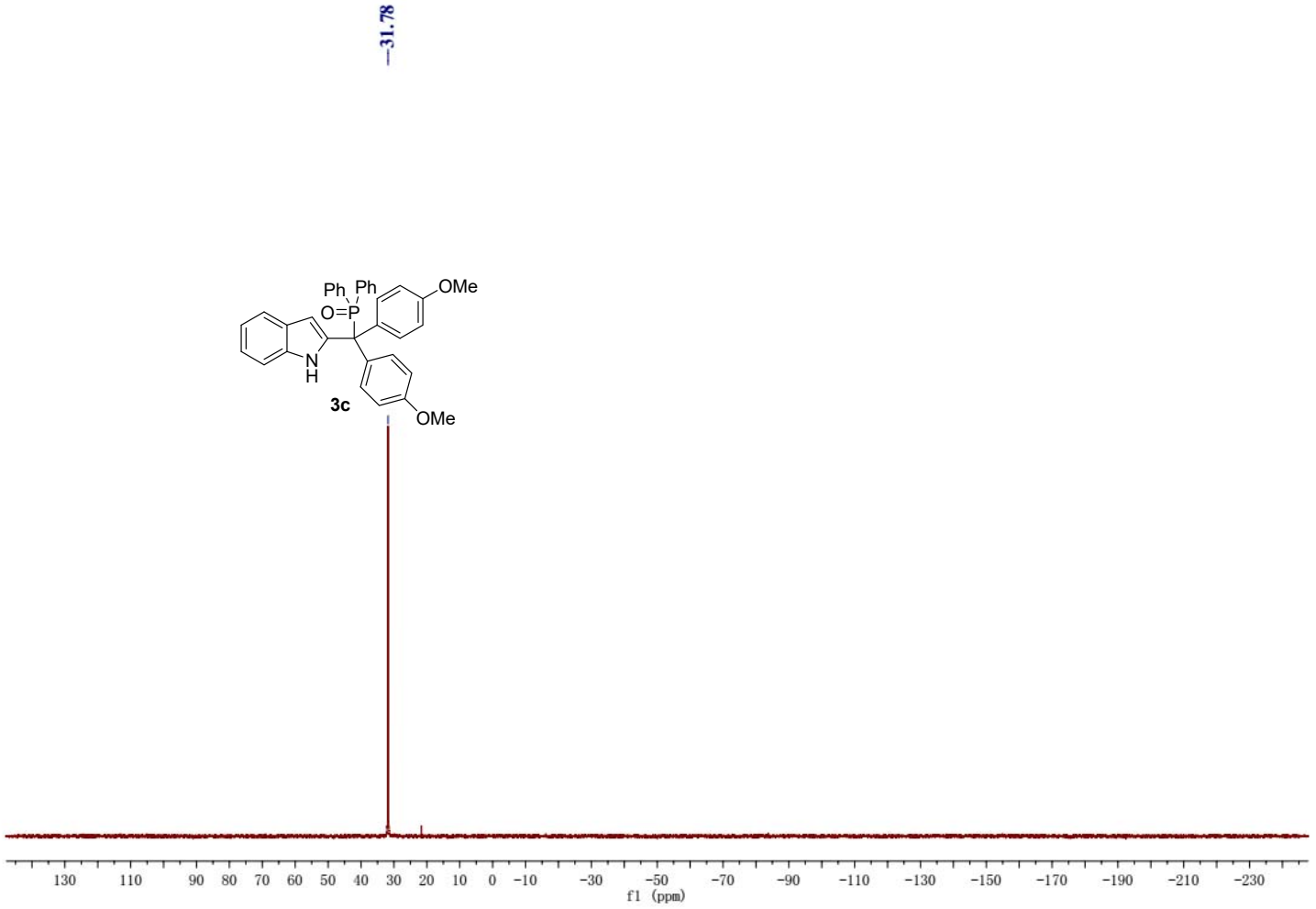
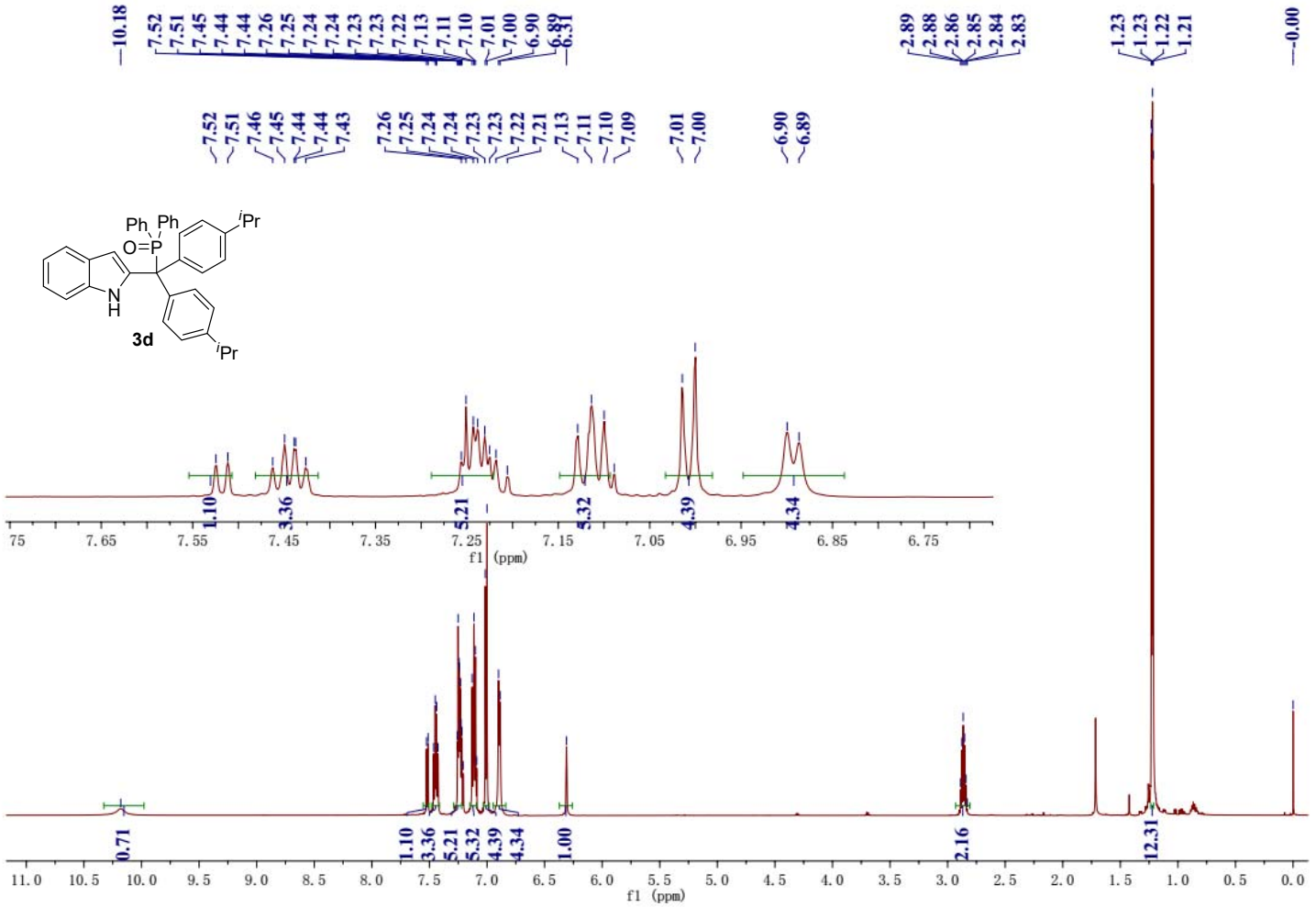
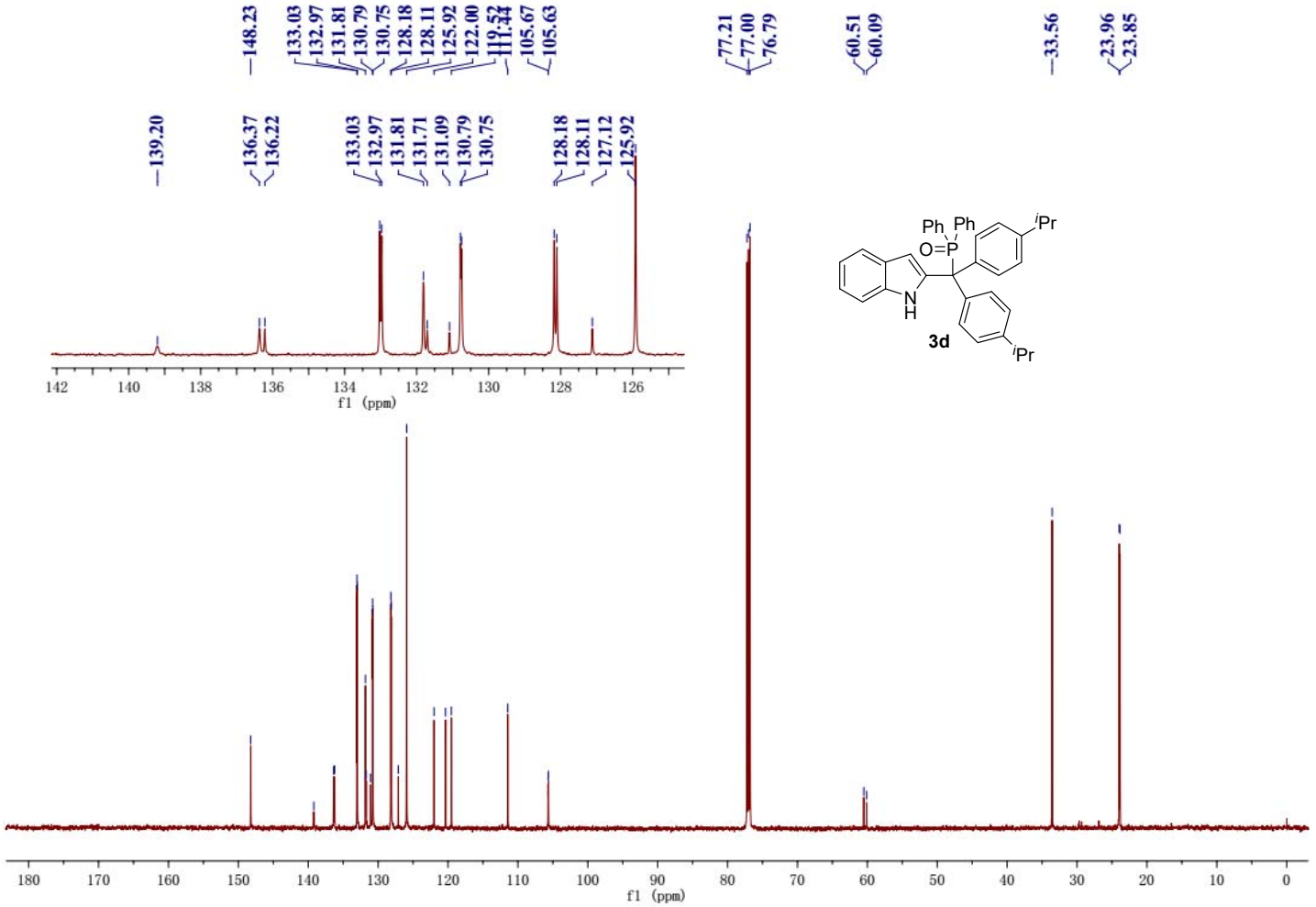
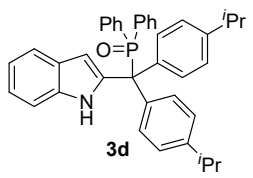
59.71
59.09
55.15
Ph
Ph
O=P
OMe
N
H
3c
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


31.78
Ph
Ph
O=P
OMe
N
H
3c
OMe
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

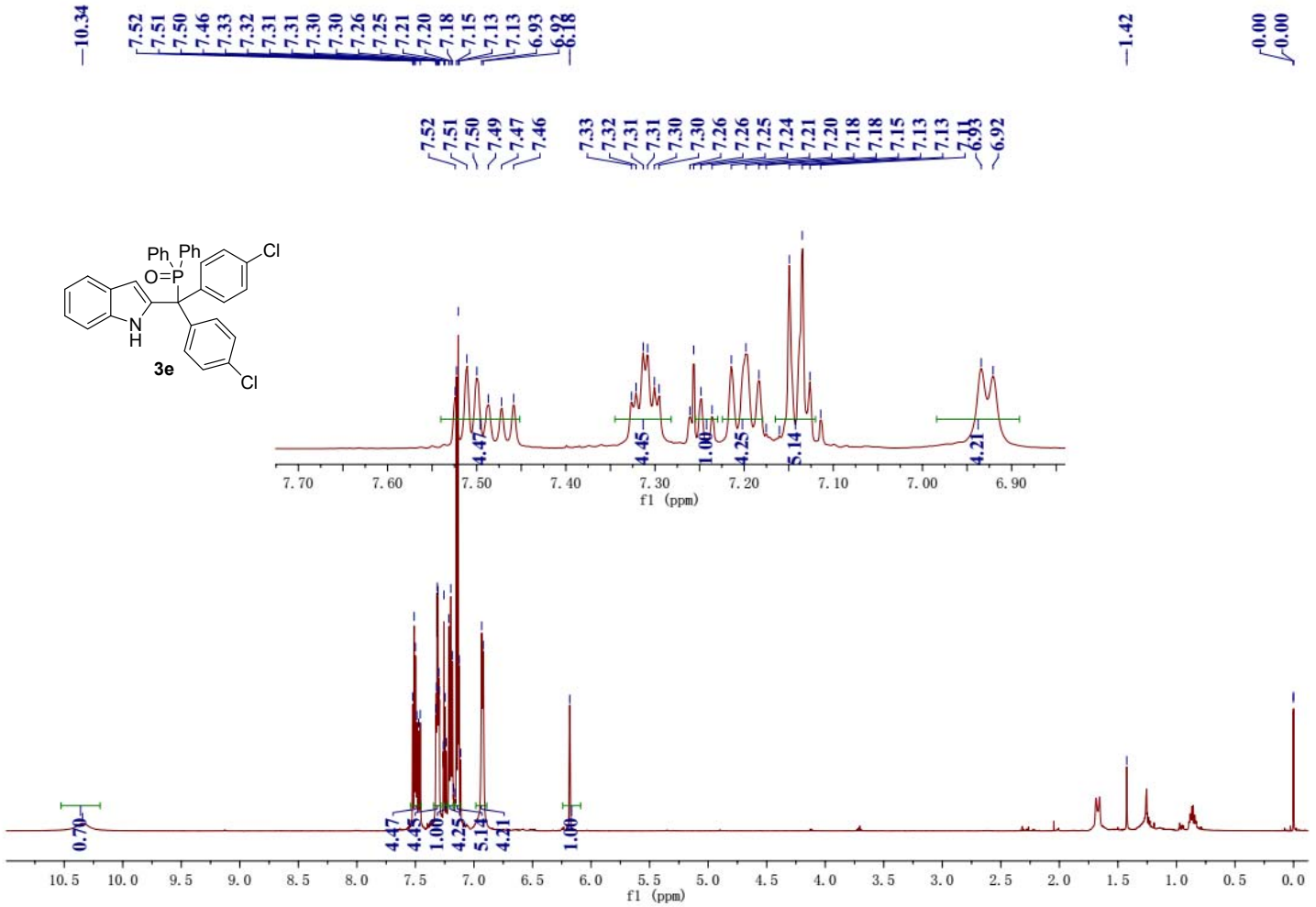

10.18
7.52
7.51
7.45
7.44
7.44
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.13
7.11
7.10
7.01
7.00
6.90
6.89
6.31
2.89
2.88
2.86
2.85
2.84
2.83
1.23
1.23
1.22
1.21
0.00
Ph
Ph
O=P
iPr
N
H
iPr
3d
1.10
3.36
5.21
5.32
4.39
4.34
f1 (ppm)
0.71
1.10
3.36
5.21
5.32
4.39
4.34
1.00
2.16
12.31
f1 (ppm)

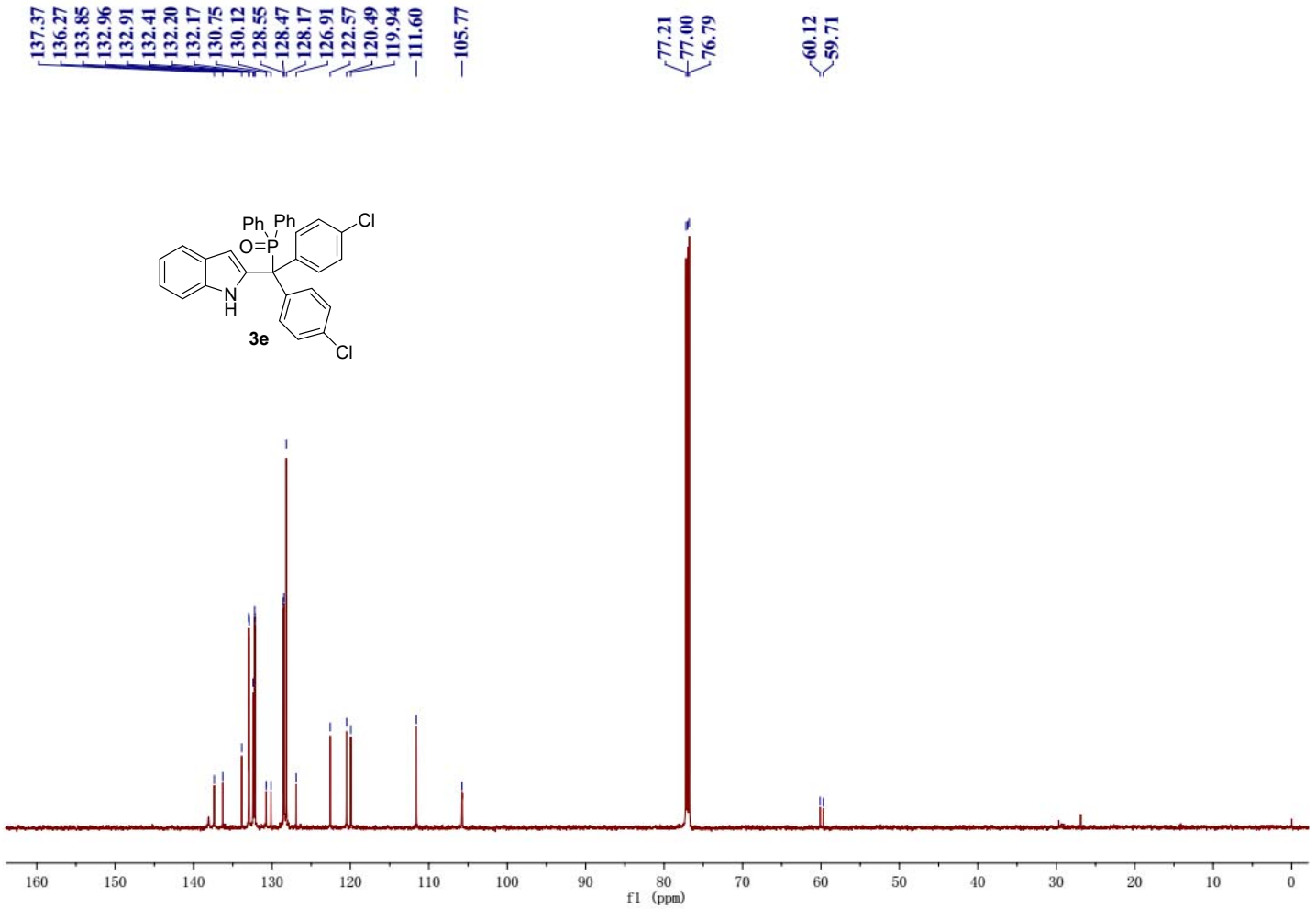

148.23
133.03
132.97
131.81
130.79
130.75
128.18
128.11
125.92
122.00
111.52
111.44
105.67
105.63
77.21
77.00
76.79
60.51
60.09
33.56
23.96
23.85
139.20
136.37
136.22
133.03
132.97
131.81
131.71
131.09
130.79
130.75
128.18
128.11
127.12
125.92
Ph
Ph
O=P
iPr
N
H
3d
iPr
f1 (ppm)
f1 (ppm)

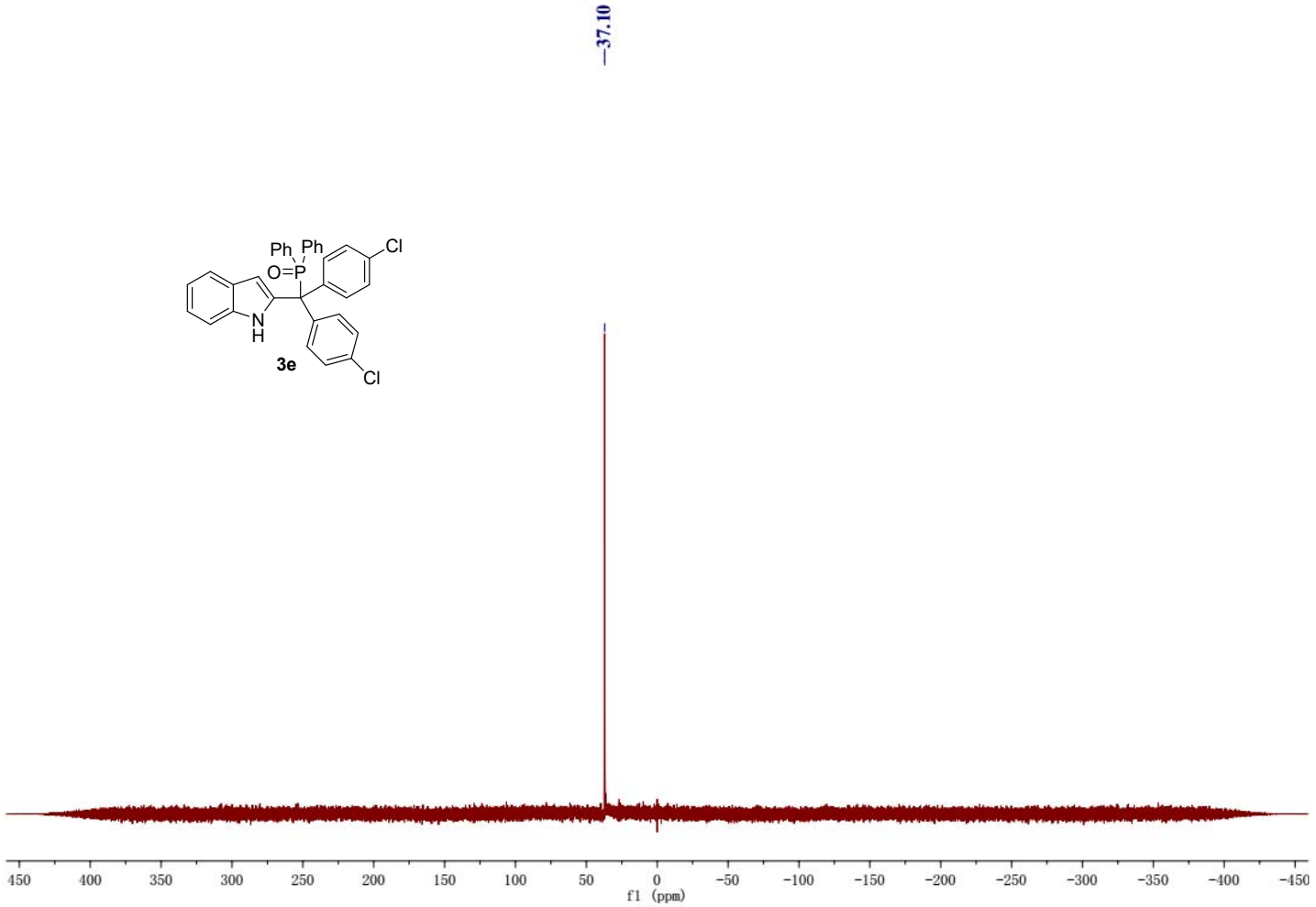

Ph
Ph
O=P
N
H
iPr
iPr

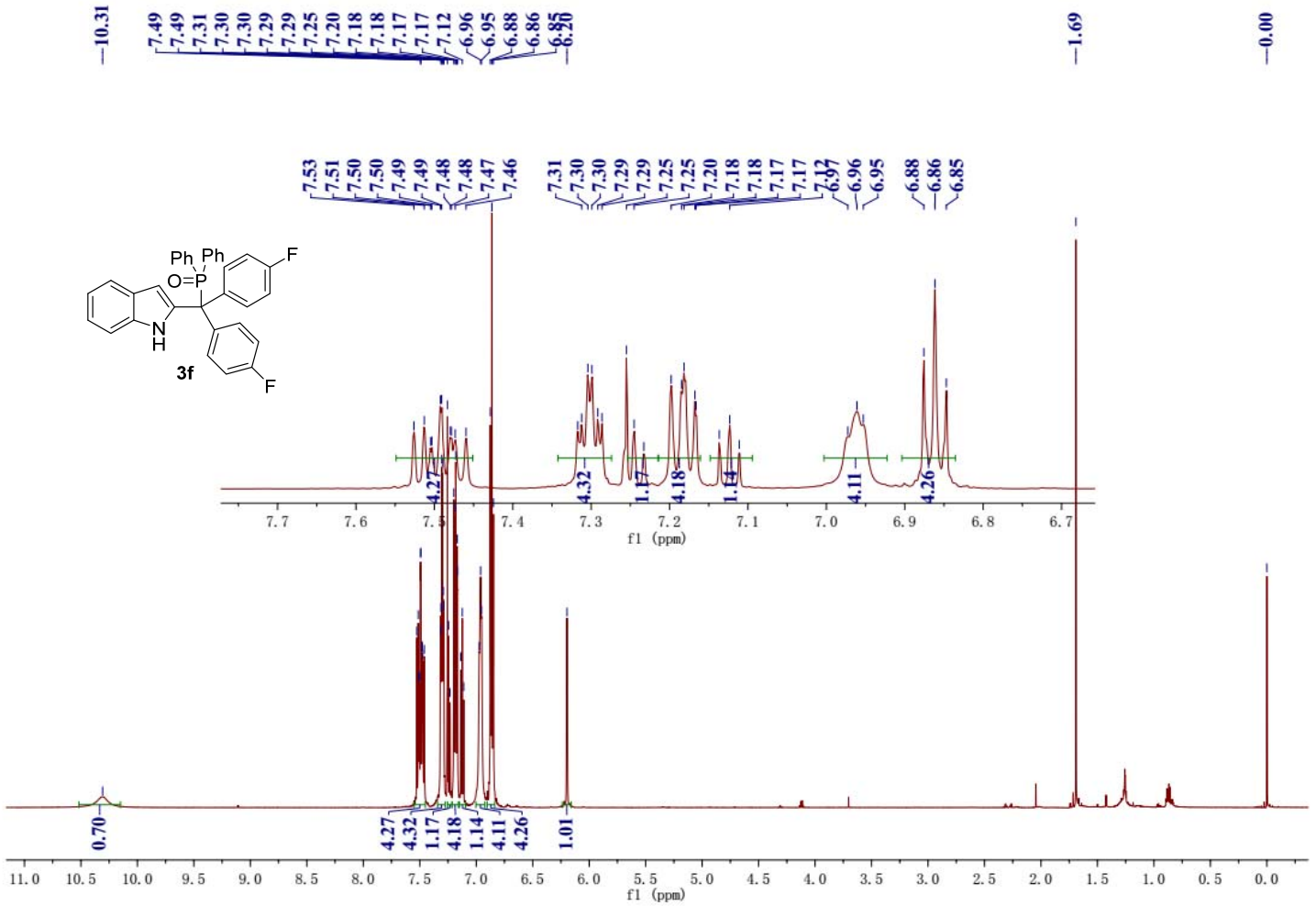
**3d**

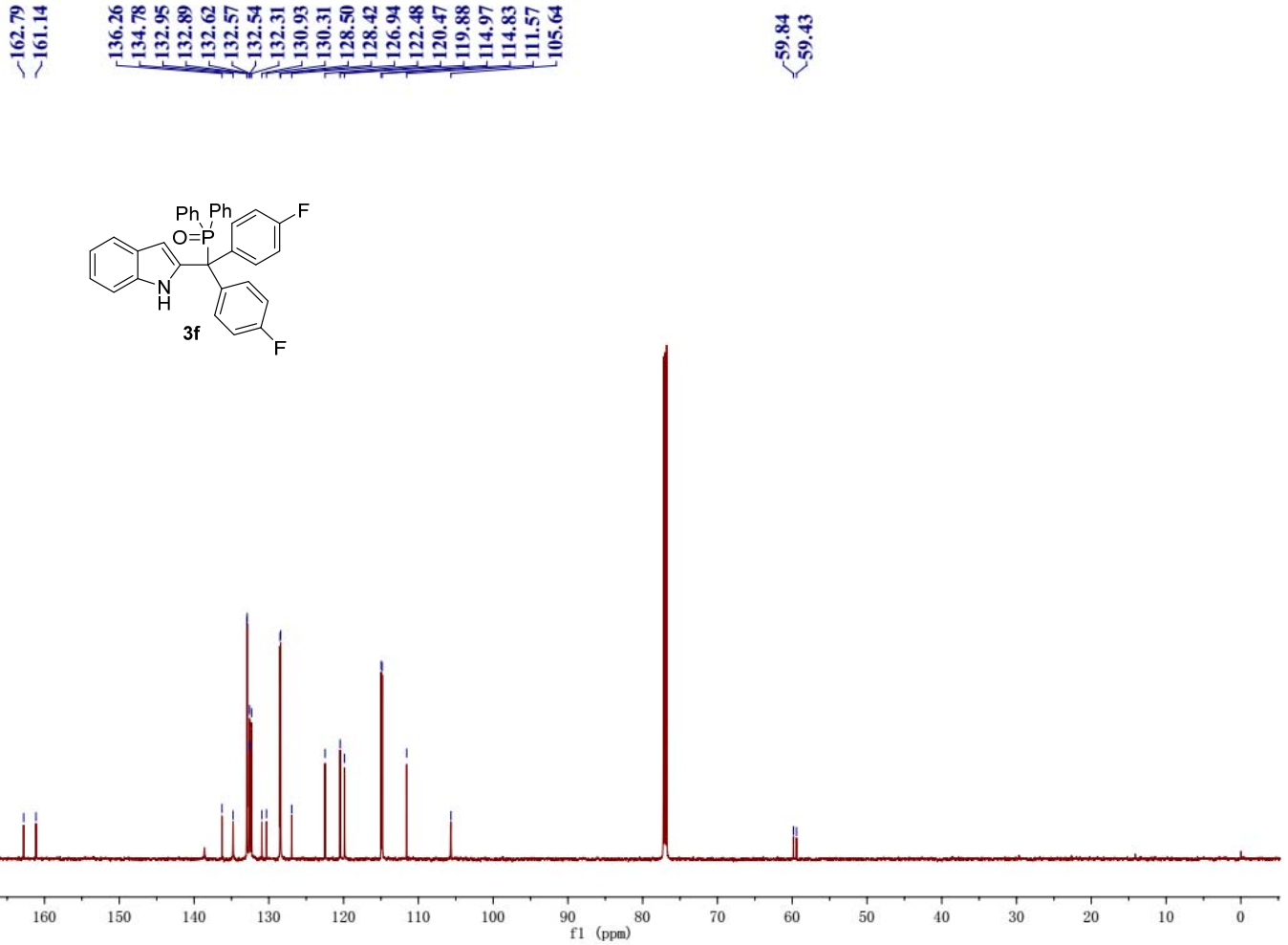

37.29
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

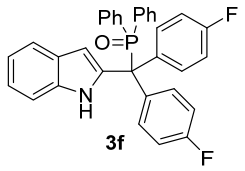

10.34
7.52
7.51
7.50
7.46
7.33
7.32
7.31
7.31
7.30
7.30
7.26
7.25
7.21
7.20
7.18
7.15
7.13
7.13
6.93
6.92
1.42
0.00
0.00
7.52
7.51
7.50
7.49
7.47
7.46
7.33
7.32
7.31
7.31
7.30
7.30
7.26
7.26
7.25
7.24
7.21
7.20
7.18
7.18
7.15
7.13
7.13
7.11
6.93
6.92
Ph
Ph
O=P
Cl
N
H
Cl
3e
4.47
4.45
1.00
4.25
5.14
4.21
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)
0.70
4.47
4.45
1.00
4.25
5.14
4.21
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.37
136.27
133.85
132.96
132.91
132.41
132.20
132.17
130.75
130.12
128.55
128.47
128.17
126.91
122.57
120.49
119.94
111.60
105.77
77.21
77.00
76.79
60.12
59.71
Ph
Ph
O=P
Cl
N
H
Cl
3e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


37.10
Ph
Ph
O=P
Cl
N
H
Cl
3e
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

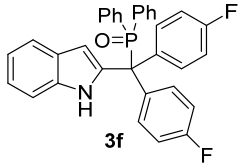

10.31
7.49
7.49
7.31
7.30
7.30
7.29
7.29
7.25
7.20
7.18
7.18
7.17
7.17
7.12
6.96
6.95
6.88
6.86
6.85
6.20
1.69
0.00
7.53
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.31
7.30
7.30
7.29
7.29
7.25
7.25
7.20
7.18
7.18
7.17
7.17
7.12
6.97
6.96
6.95
6.88
6.86
6.85
Ph
Ph
O=P
F
N
H
F
3f
4.27
4.32
1.17
4.18
1.14
4.11
4.26
f1 (ppm)
0.70
4.27
4.32
1.17
4.18
1.14
4.11
4.26
1.01
f1 (ppm)


162.79
161.14
136.26
134.78
132.95
132.89
132.62
132.57
132.54
132.31
130.93
130.31
128.50
128.42
126.94
122.48
120.47
119.88
114.97
114.83
111.57
105.64
59.84
59.43
Ph
Ph
O=P
F
N
H
3f
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

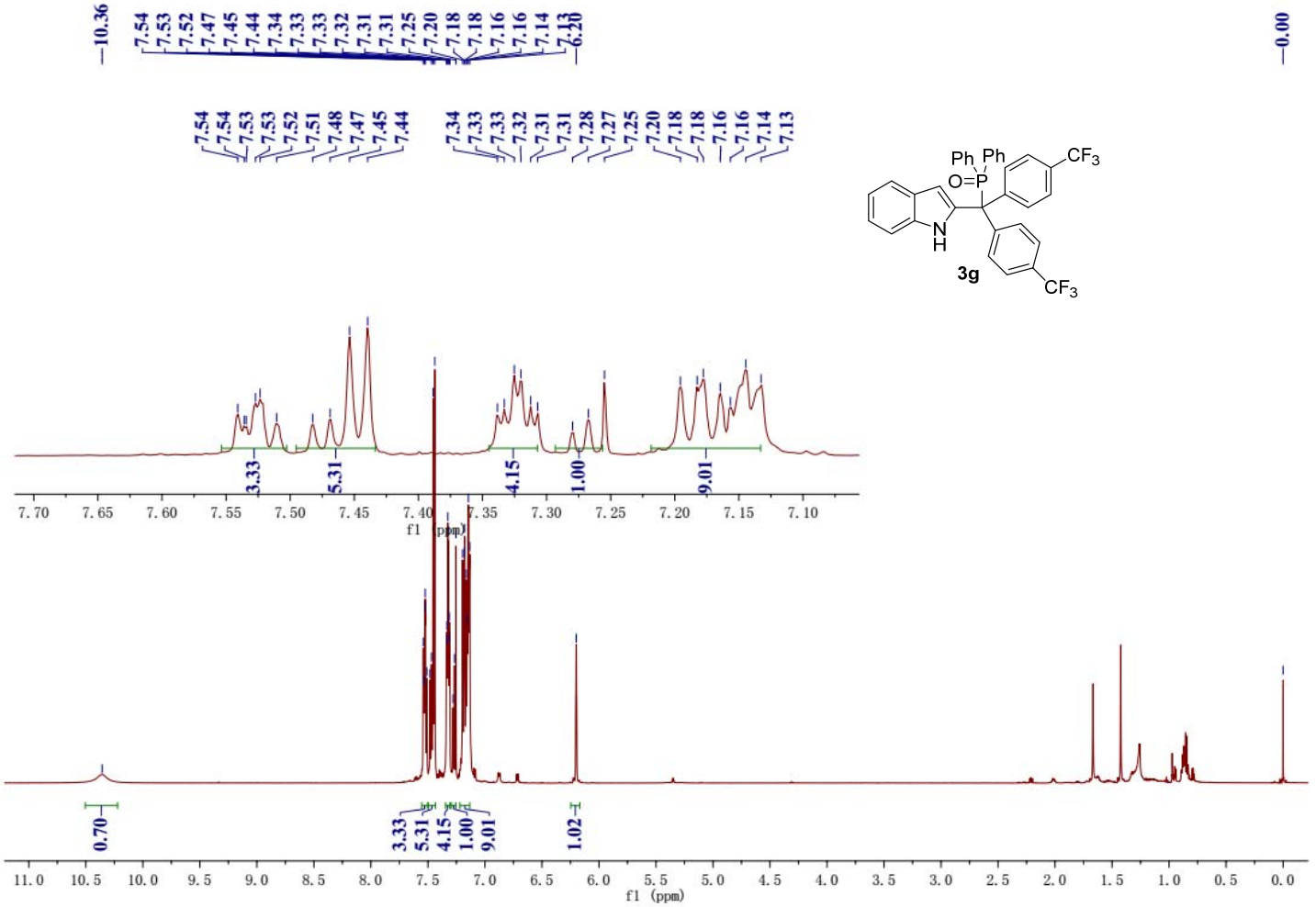

Ph
Ph
O=P
F
N
H
F

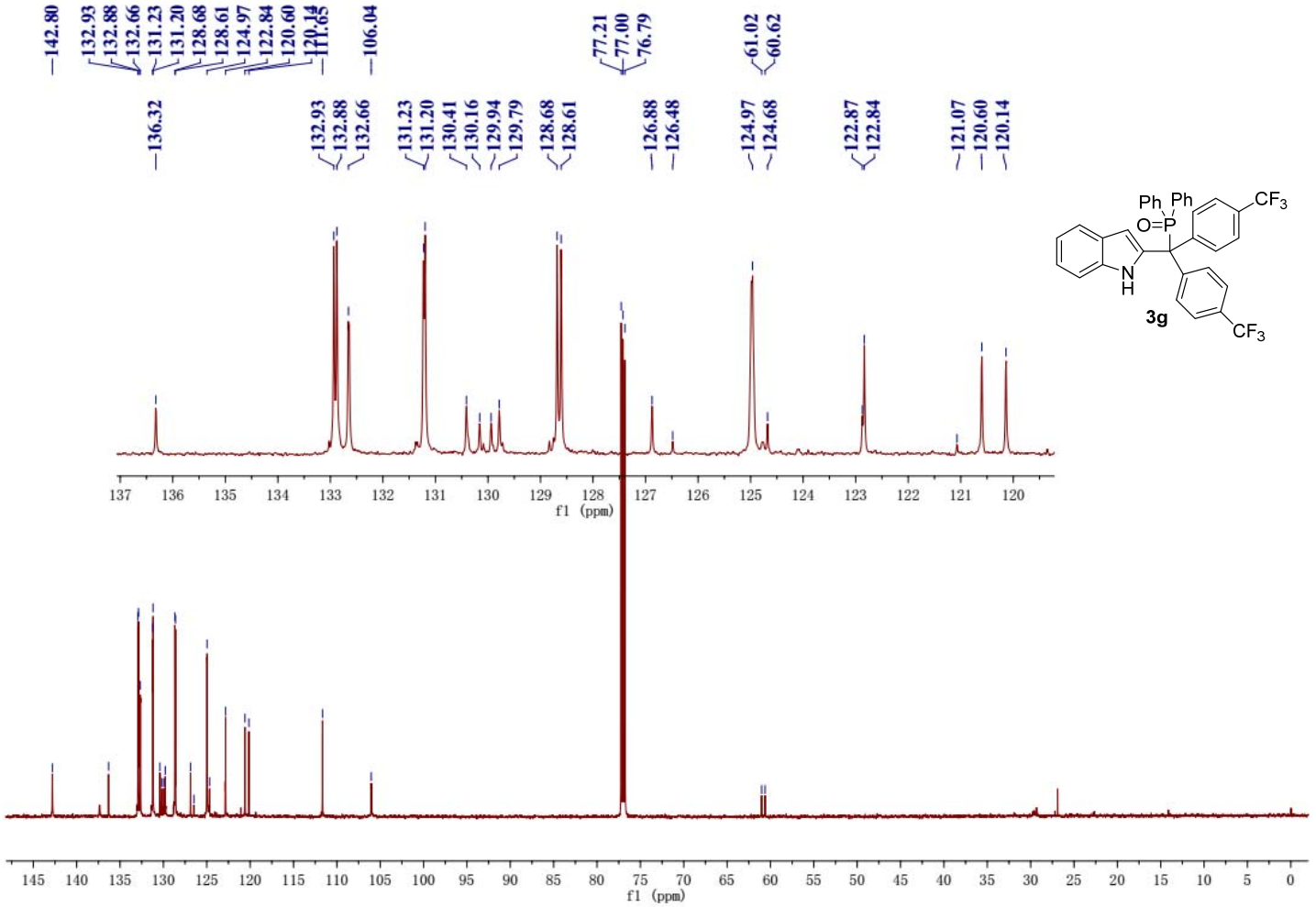
**3f**

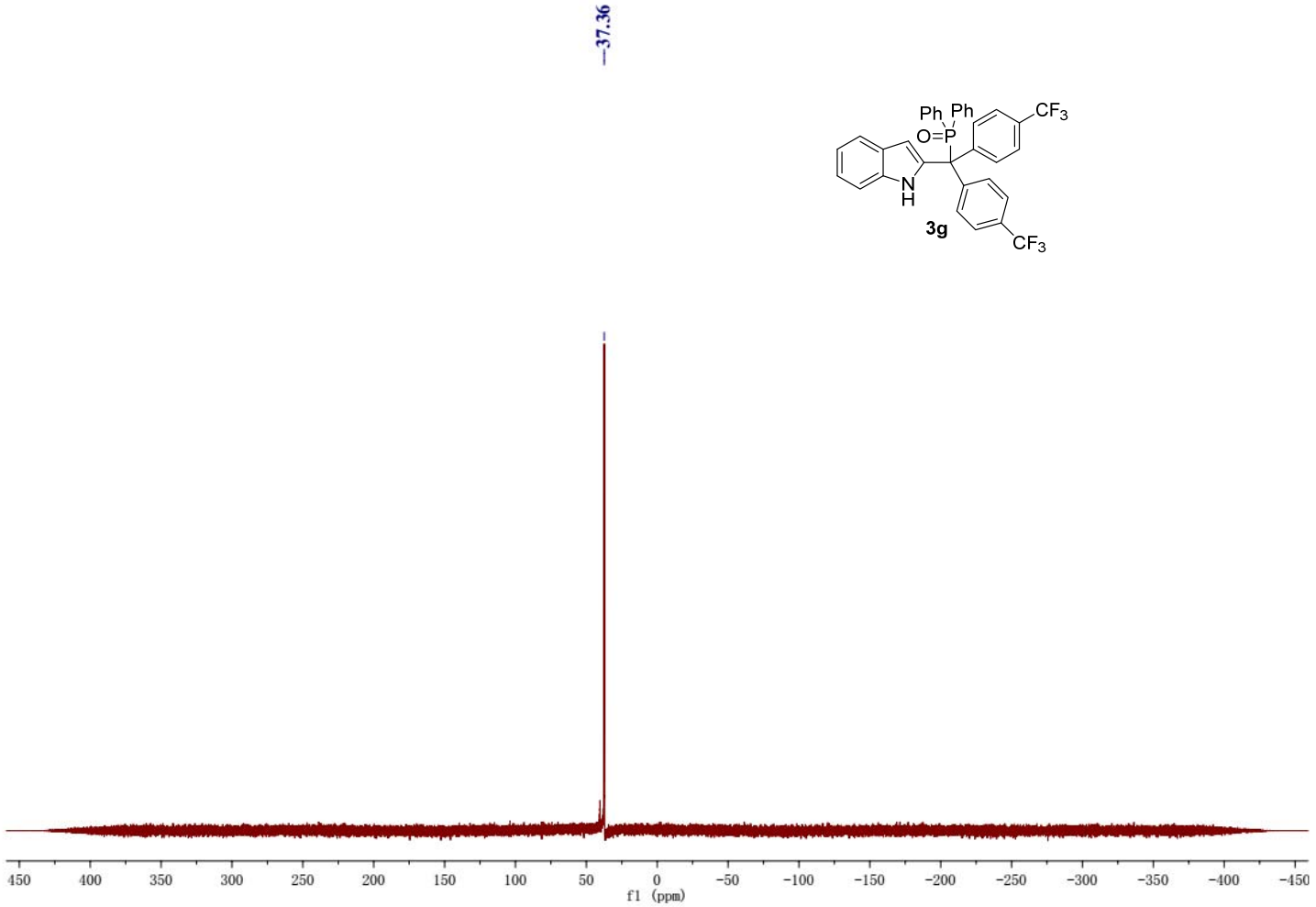

-37.25
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

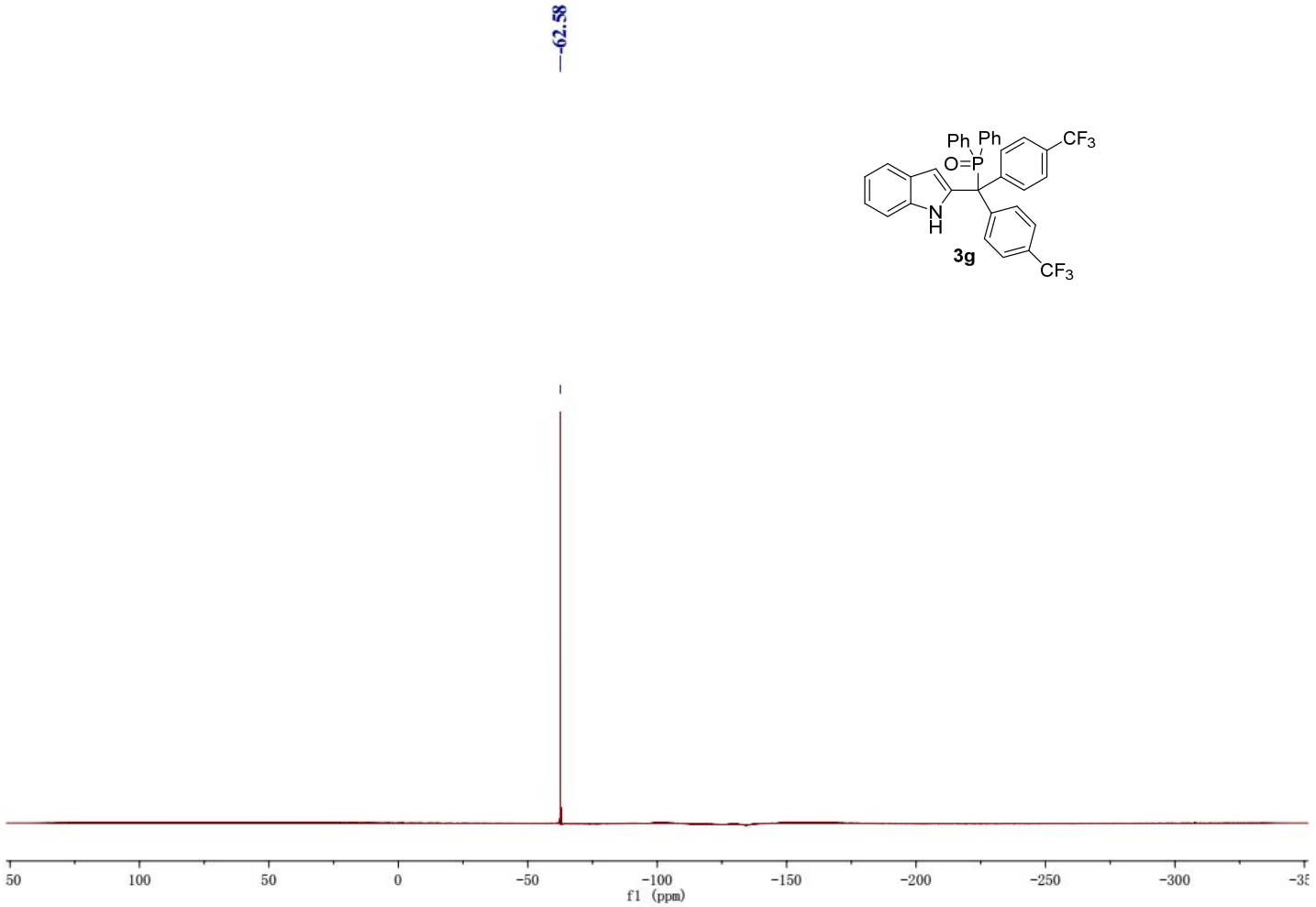


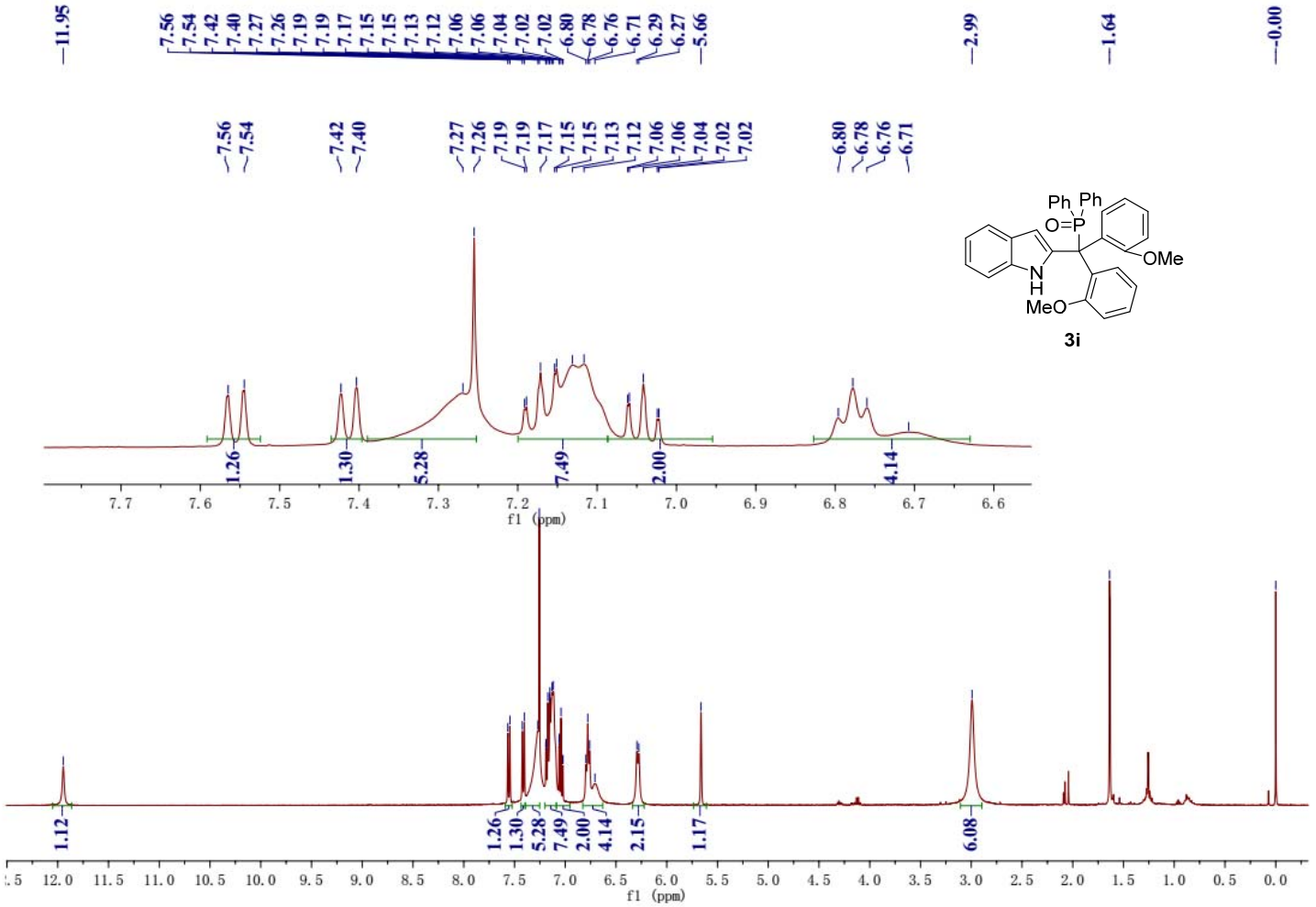

3f

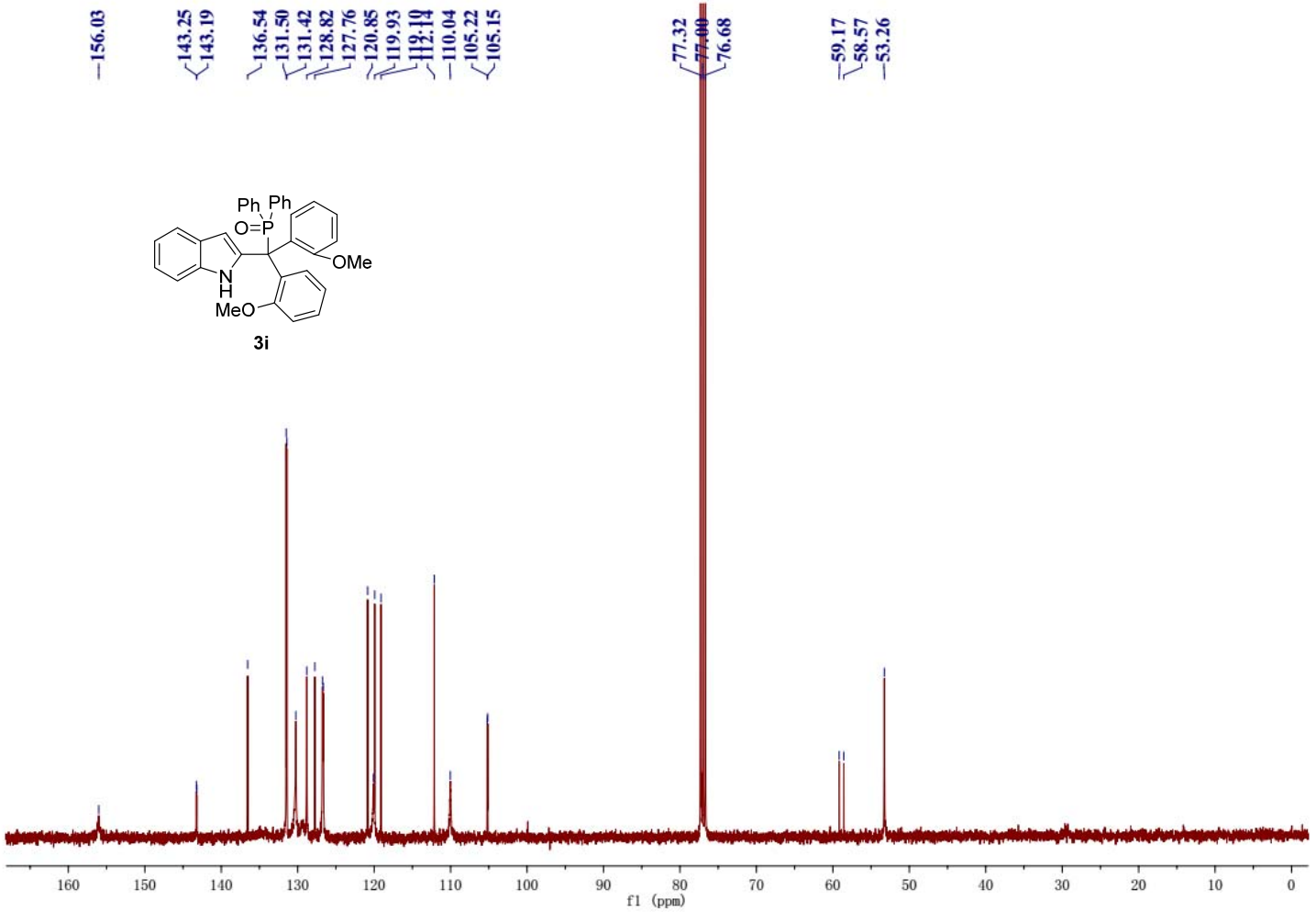

10.36
7.54
7.53
7.52
7.47
7.45
7.44
7.34
7.33
7.33
7.32
7.31
7.31
7.25
7.20
7.18
7.18
7.16
7.16
7.14
7.13
6.20
0.00
Ph
Ph
O=P
CF3
N
H
3g
CF3
3.33
5.31
4.15
1.00
9.01
f1 (ppm)
0.70
3.33
5.31
4.15
1.00
9.01
1.02
f1 (ppm)

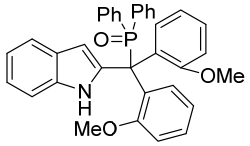

142.80
132.93
132.88
132.66
131.23
131.20
128.68
128.61
124.97
122.84
120.60
120.14
111.65
106.04
77.21
77.00
76.79
61.02
60.62
136.32
132.93
132.88
132.66
131.23
131.20
130.41
130.16
129.94
129.79
128.68
128.61
126.88
126.48
124.97
124.68
122.87
122.84
121.07
120.60
120.14
Ph
Ph
O=P
CF3
N
H
3g
CF3
f1 (ppm)
f1 (ppm)


37.36
Ph
Ph
O=P
CF3
N
H
3g
CF3
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


-62.58
Ph
Ph
O=P
CF3
N
H
3g
CF3
50
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

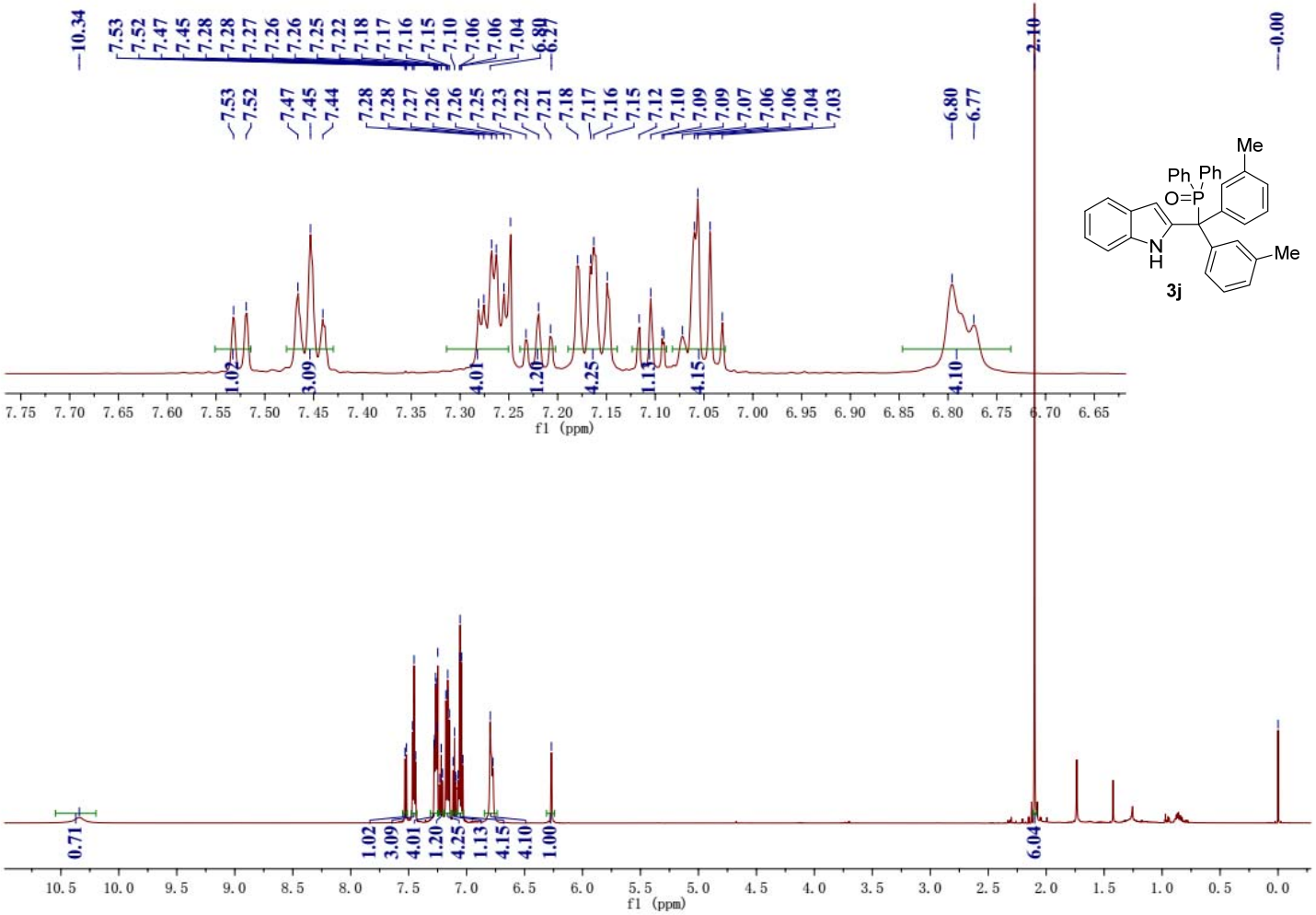

11.95
7.56
7.54
7.42
7.40
7.27
7.26
7.19
7.19
7.17
7.15
7.15
7.13
7.12
7.06
7.06
7.04
7.02
7.02
6.80
6.78
6.76
6.71
6.29
6.27
5.66
2.99
1.64
0.00
Ph
Ph
O=P
OMe
N
H
MeO
3i
1.26
1.30
5.28
7.49
2.00
4.14
f1 (ppm)
1.12
1.26
1.30
5.28
7.49
2.00
4.14
2.15
1.17
6.08
f1 (ppm)

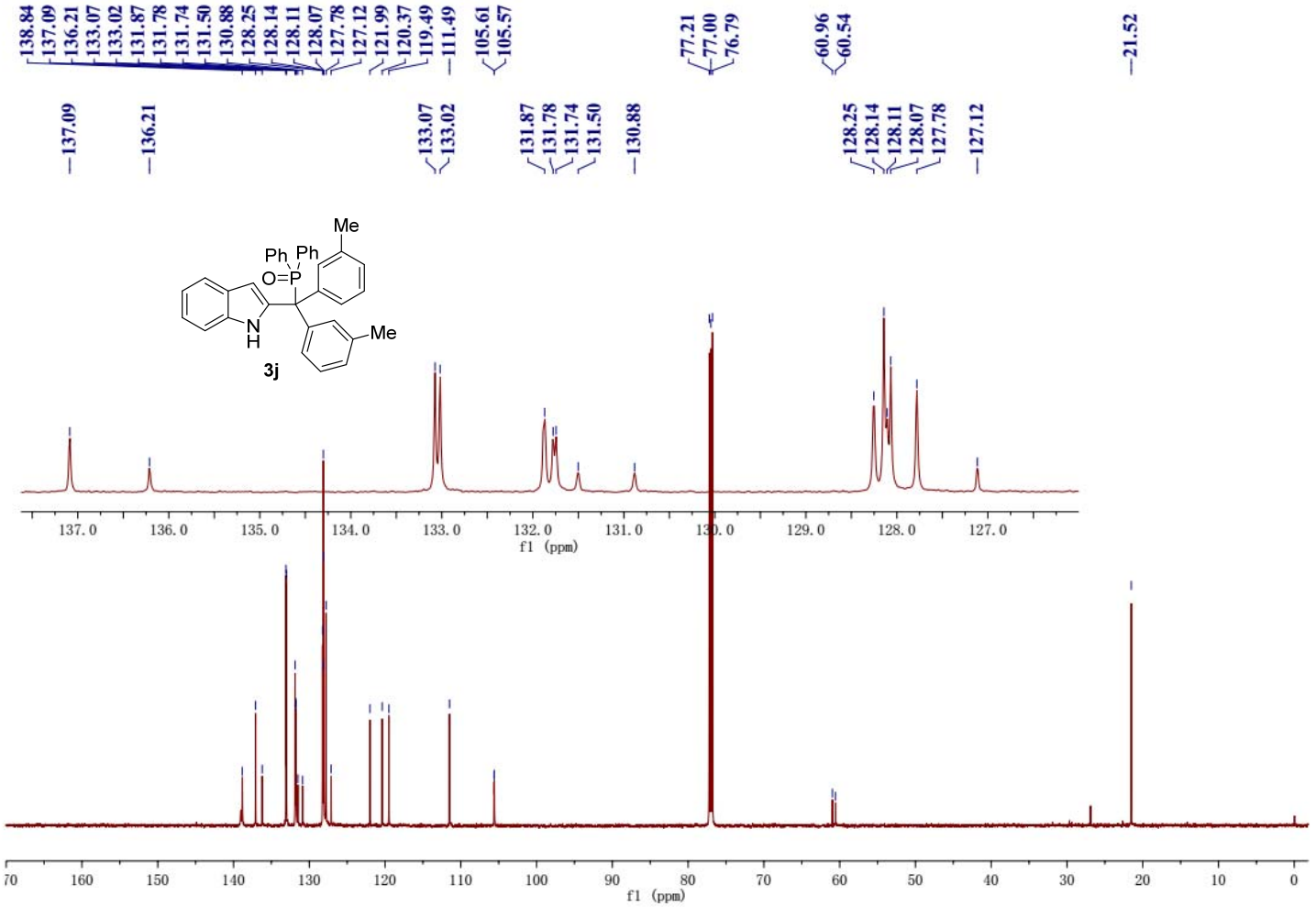

156.03
143.25
143.19
136.54
131.50
131.42
128.82
127.76
120.85
119.93
110.04
105.22
105.15
77.32
77.00
76.68
59.17
58.57
53.26
Ph
Ph
O=P
OMe
N
H
MeO
3i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

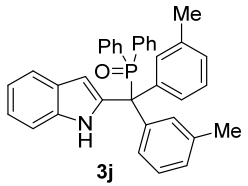

Ph
Ph
O=P
OMe
N
H
MeO

**3i**


51.64
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

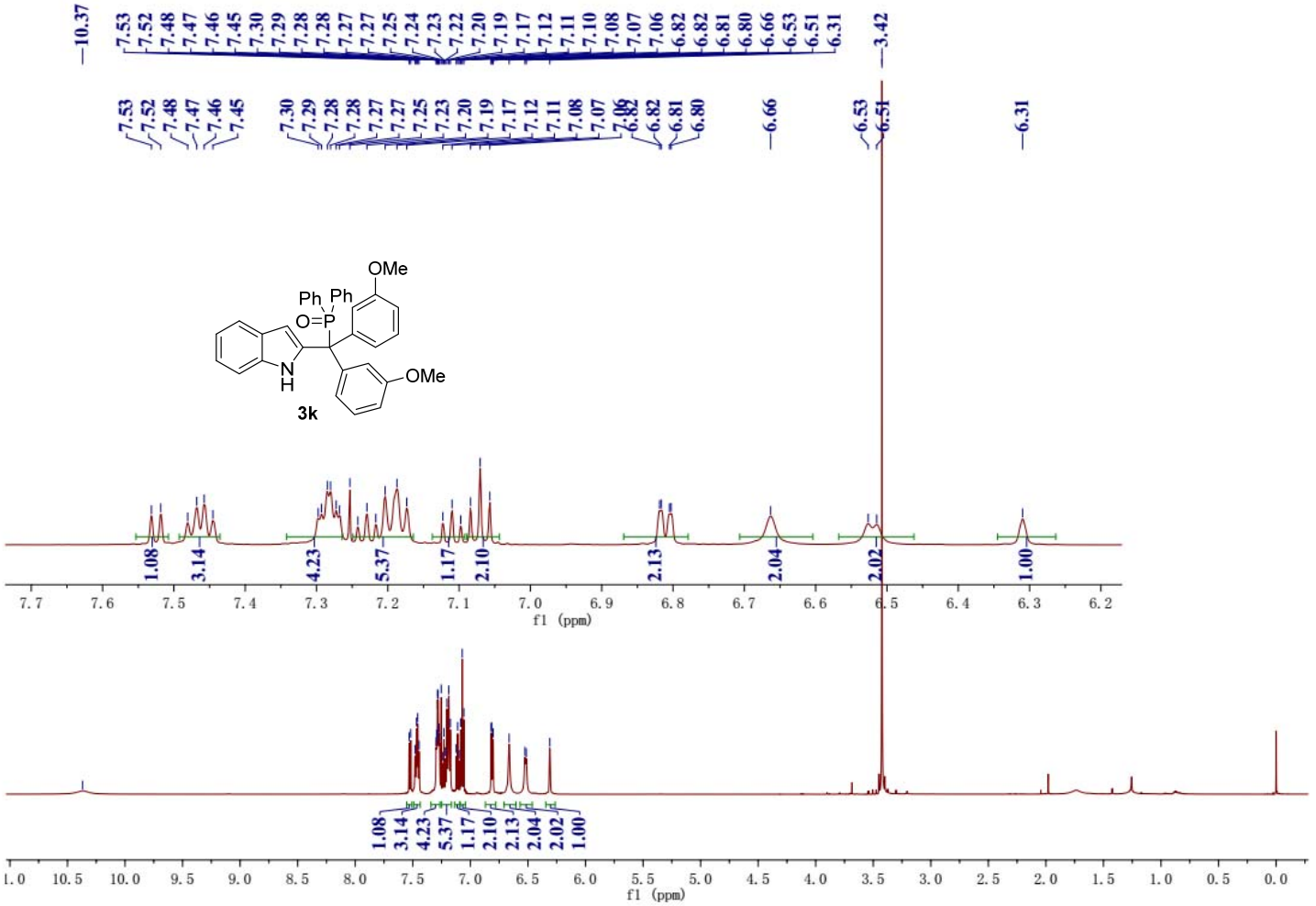

10.34
7.53
7.52
7.47
7.45
7.28
7.28
7.27
7.26
7.26
7.25
7.22
7.18
7.17
7.16
7.15
7.10
7.06
7.06
7.04
6.80
6.77
2.10
0.00
Me
Ph
Ph
O=P
N
H
Me
3j
1.02
3.09
4.01
1.20
4.25
1.13
4.15
4.10
f1 (ppm)
0.71
1.02
3.09
4.01
1.20
4.25
1.13
4.15
4.10
1.00
6.04
f1 (ppm)

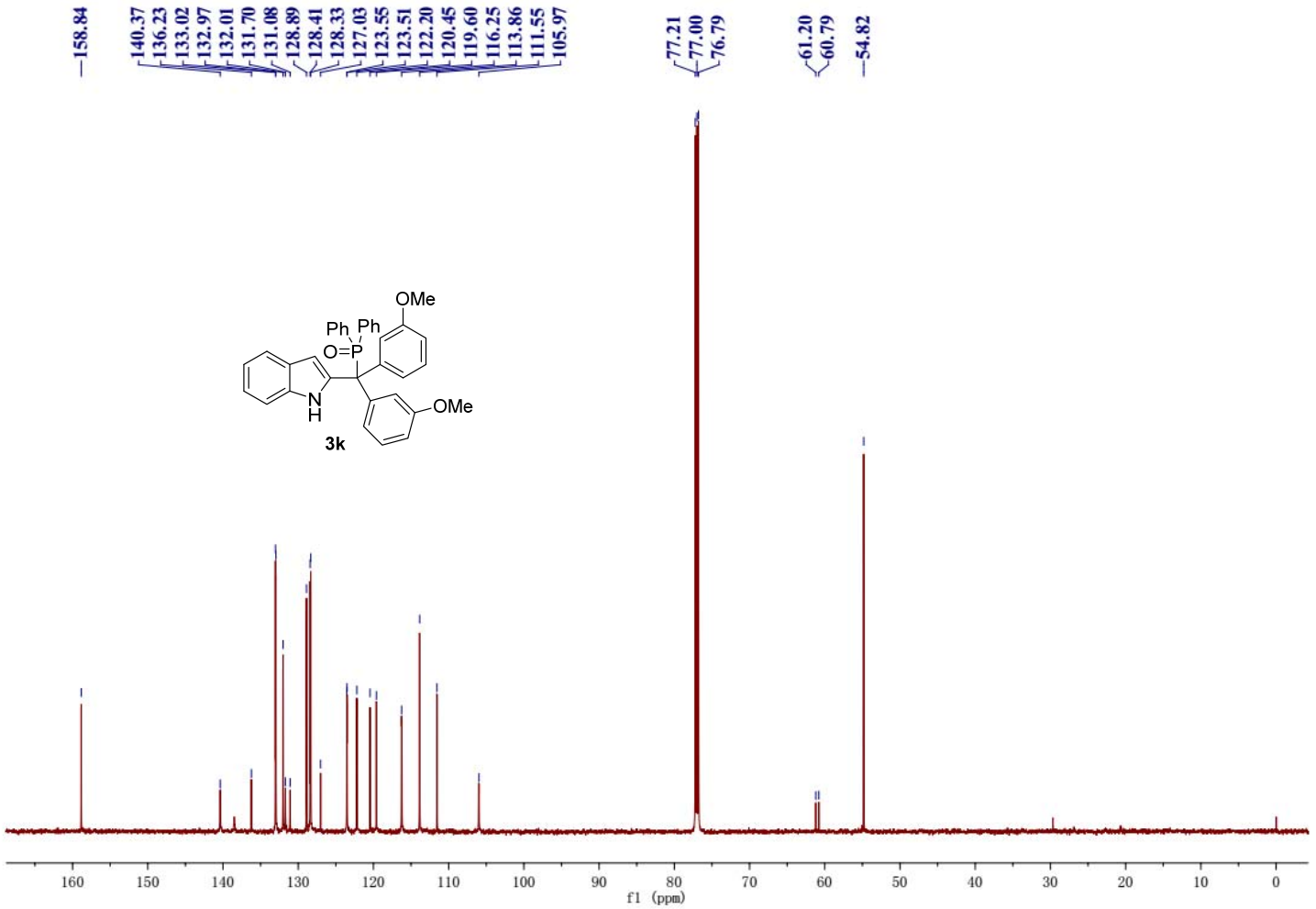

138.84
137.09
136.21
133.07
133.02
131.87
131.78
131.74
131.50
130.88
128.25
128.14
128.11
128.07
127.78
127.12
121.99
120.37
119.49
111.49
105.61
105.57
77.21
77.00
76.79
60.96
60.54
21.52
137.09
136.21
133.07
133.02
131.87
131.78
131.74
131.50
130.88
128.25
128.14
128.11
128.07
127.78
127.12
Me
Ph
Ph
O=P
N
H
Me
3j
f1 (ppm)
f1 (ppm)

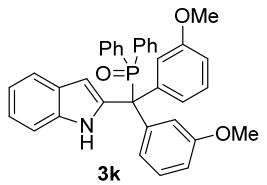

Me
Ph
Ph
O=P
N
H
Me

3j


37.50
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

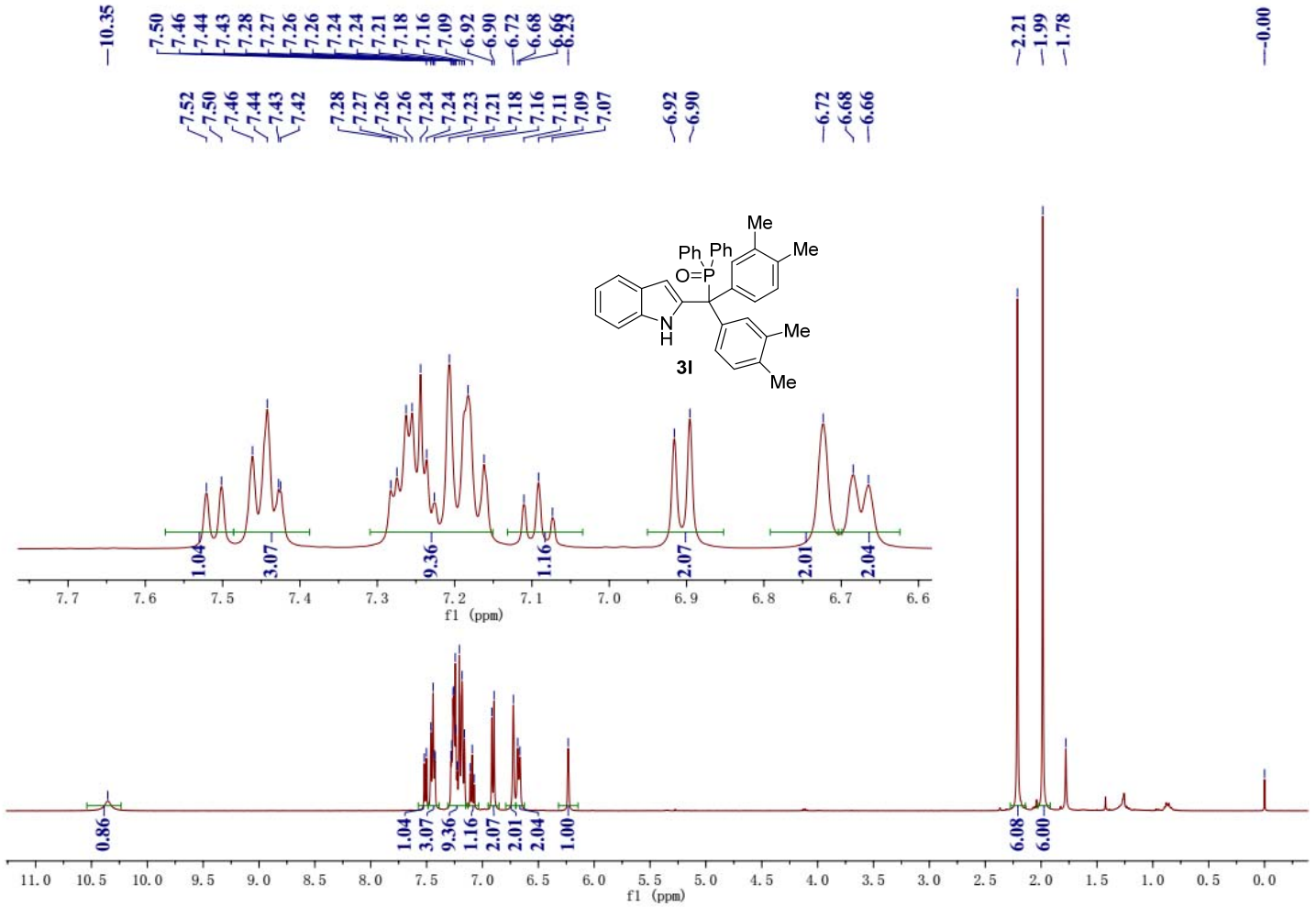

10.37
7.53
7.52
7.48
7.47
7.46
7.45
7.30
7.29
7.28
7.28
7.27
7.27
7.25
7.24
7.23
7.22
7.20
7.19
7.17
7.12
7.11
7.10
7.08
7.07
7.06
6.82
6.82
6.81
6.80
6.66
6.53
6.51
6.31
3.42
OMe
Ph
Ph
O=P
N
H
OMe
3k
1.08
3.14
4.23
5.37
1.17
2.10
2.13
2.04
2.02
1.00
f1 (ppm)

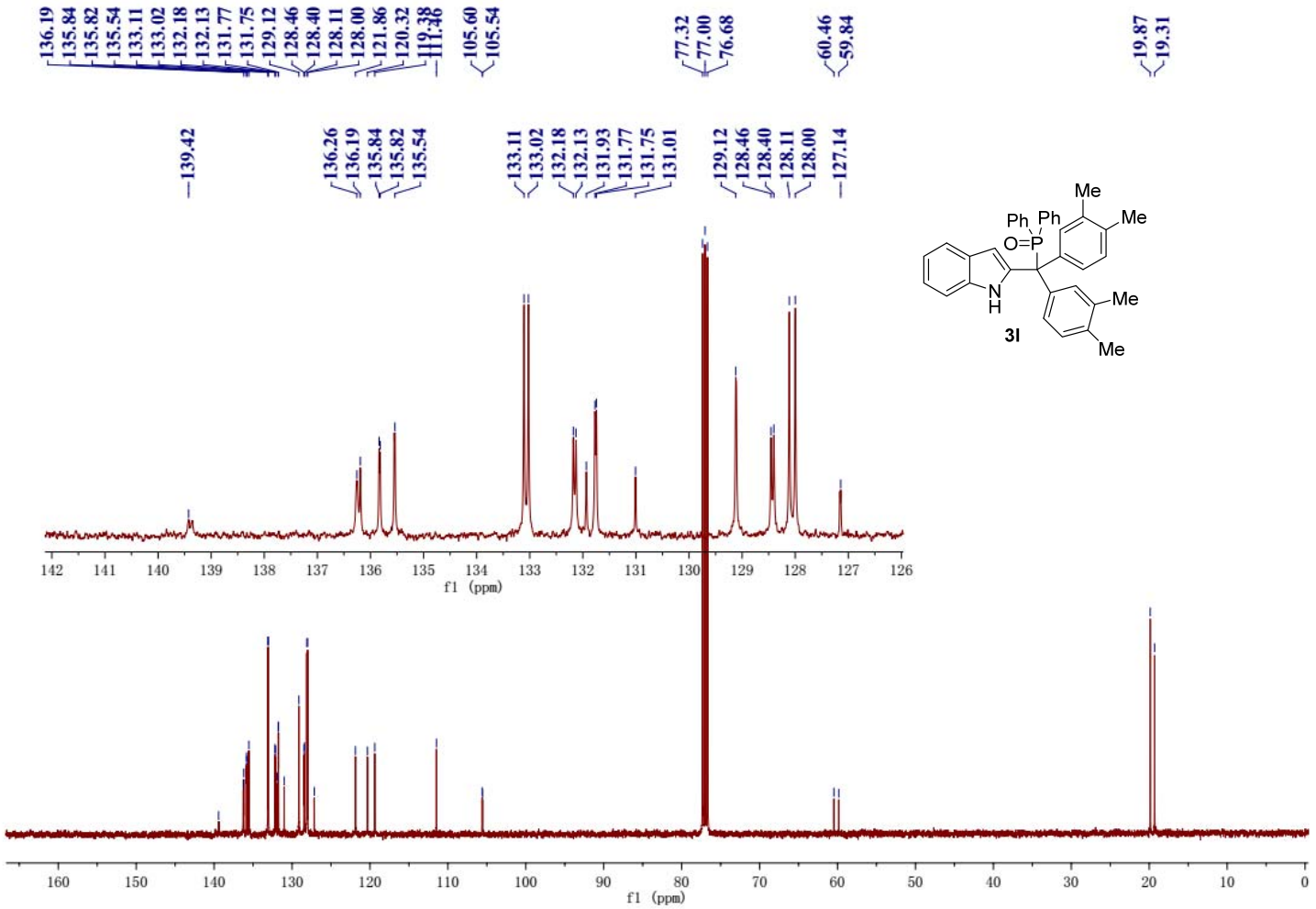

158.84
140.37
136.23
133.02
132.97
132.01
131.70
131.08
128.89
128.41
128.33
127.03
123.55
123.51
122.20
120.45
119.60
116.25
113.86
111.55
105.97
77.21
77.00
76.79
61.20
60.79
54.82
OMe
Ph
Ph
O=P
N
H
OMe
3k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

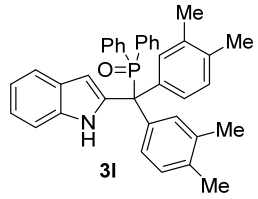

OMe
Ph
Ph
O=P
N
H
OMe

**3k**


37.58
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

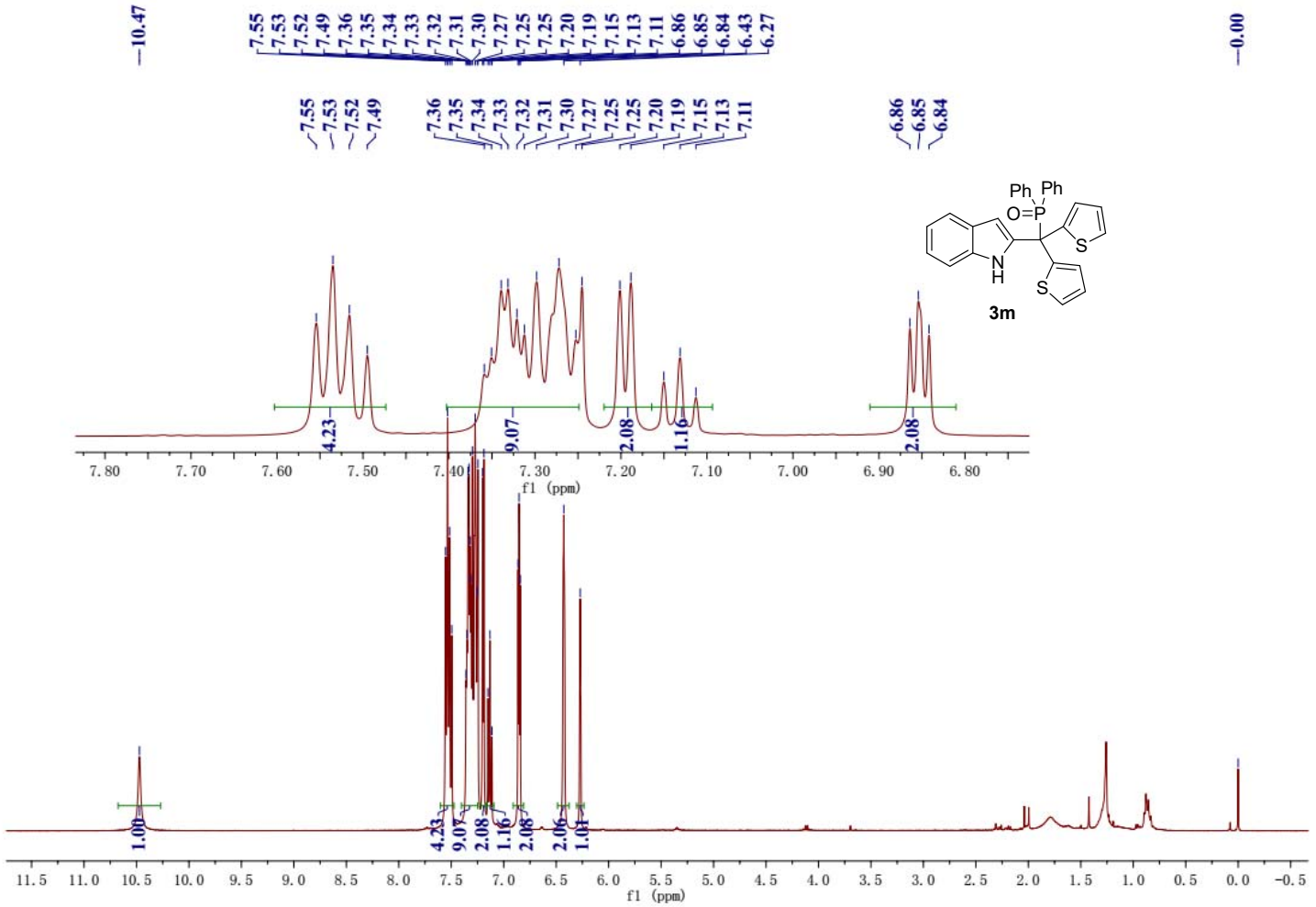

10.35
7.50
7.46
7.44
7.43
7.28
7.27
7.26
7.26
7.24
7.24
7.21
7.18
7.16
7.09
6.92
6.90
6.72
6.68
6.66
6.23
2.21
1.99
1.78
0.00
Me
Ph
Ph
Me
O=P
N
H
Me
Me
3l
1.04
3.07
9.36
1.16
2.07
2.01
2.04
f1 (ppm)
0.86
1.04
3.07
9.36
1.16
2.07
2.01
2.04
1.00
6.08
6.00
f1 (ppm)

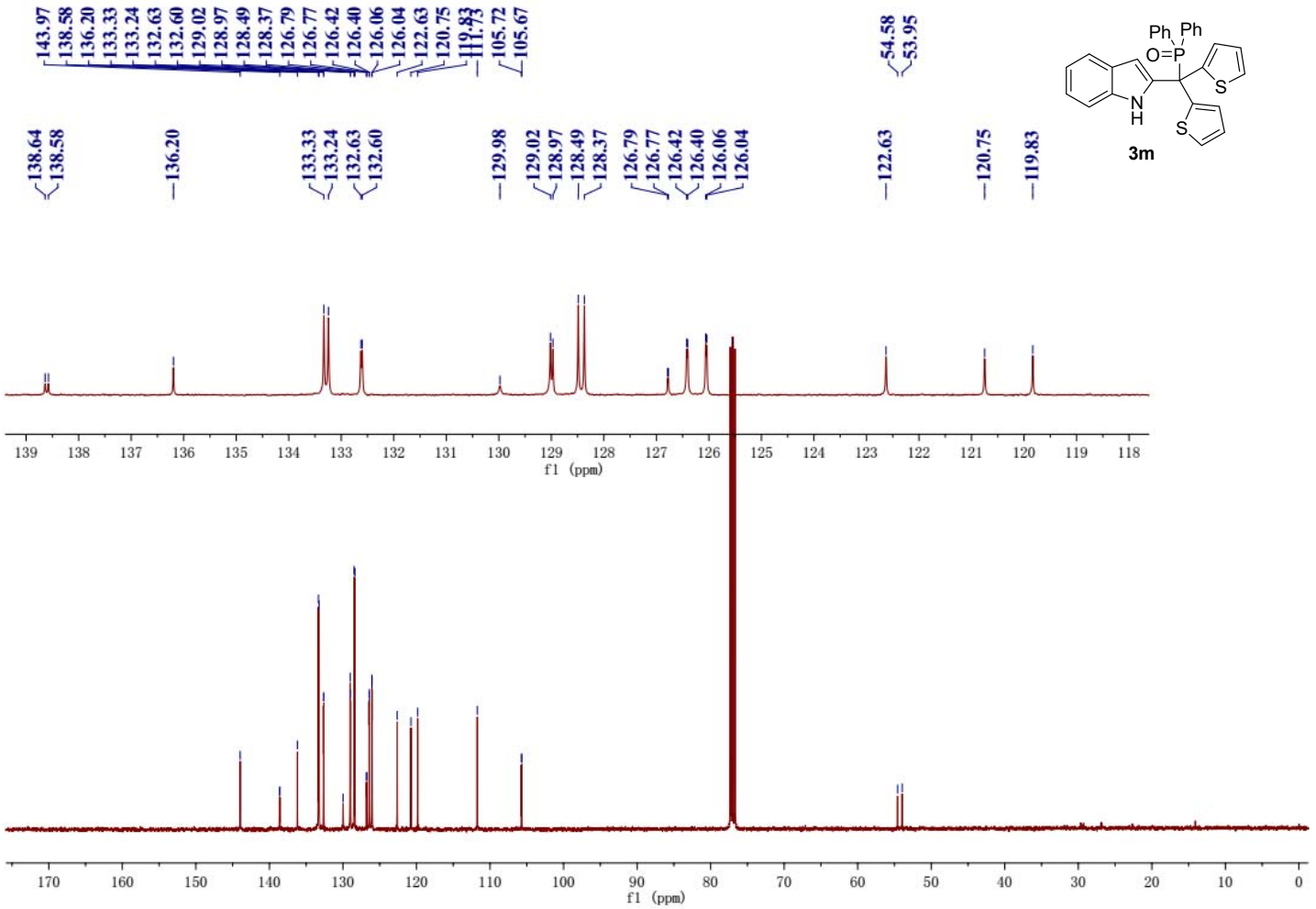

136.19
135.84
135.82
135.54
133.11
133.02
132.18
132.13
131.77
131.75
129.12
128.46
128.40
128.11
128.00
121.86
120.32
105.60
105.54
77.32
77.00
76.68
60.46
59.84
19.87
19.31
139.42
136.26
136.19
135.84
135.82
135.54
133.11
133.02
132.18
132.13
131.93
131.77
131.75
131.01
129.12
128.46
128.40
128.11
128.00
127.14
Me
Ph
Ph
O=P
Me
N
H
Me
Me
3l
f1 (ppm)
f1 (ppm)

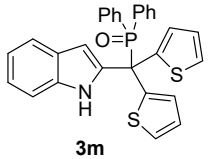

Me
Ph Ph
Me
O=P
N
H
Me
Me

**3l**


-37.42
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

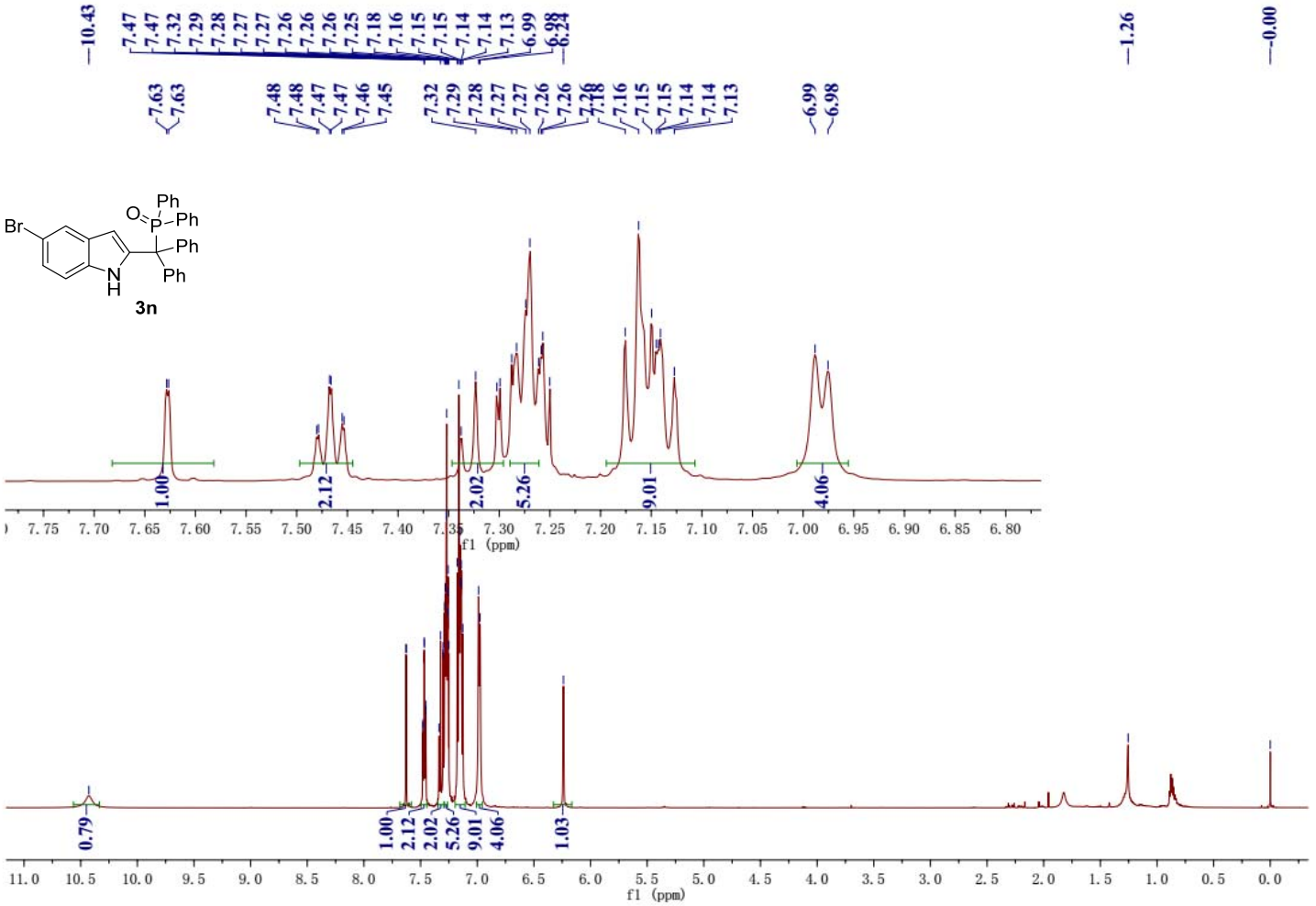

10.47
7.55
7.53
7.52
7.49
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.27
7.25
7.25
7.20
7.19
7.15
7.13
7.11
6.86
6.85
6.84
6.43
6.27
0.00
Ph
Ph
O=P
S
S
N
H
3m
4.23
9.07
2.08
1.16
2.08
f1 (ppm)
1.00
4.23
9.07
2.08
1.16
2.08
2.06
1.01
f1 (ppm)

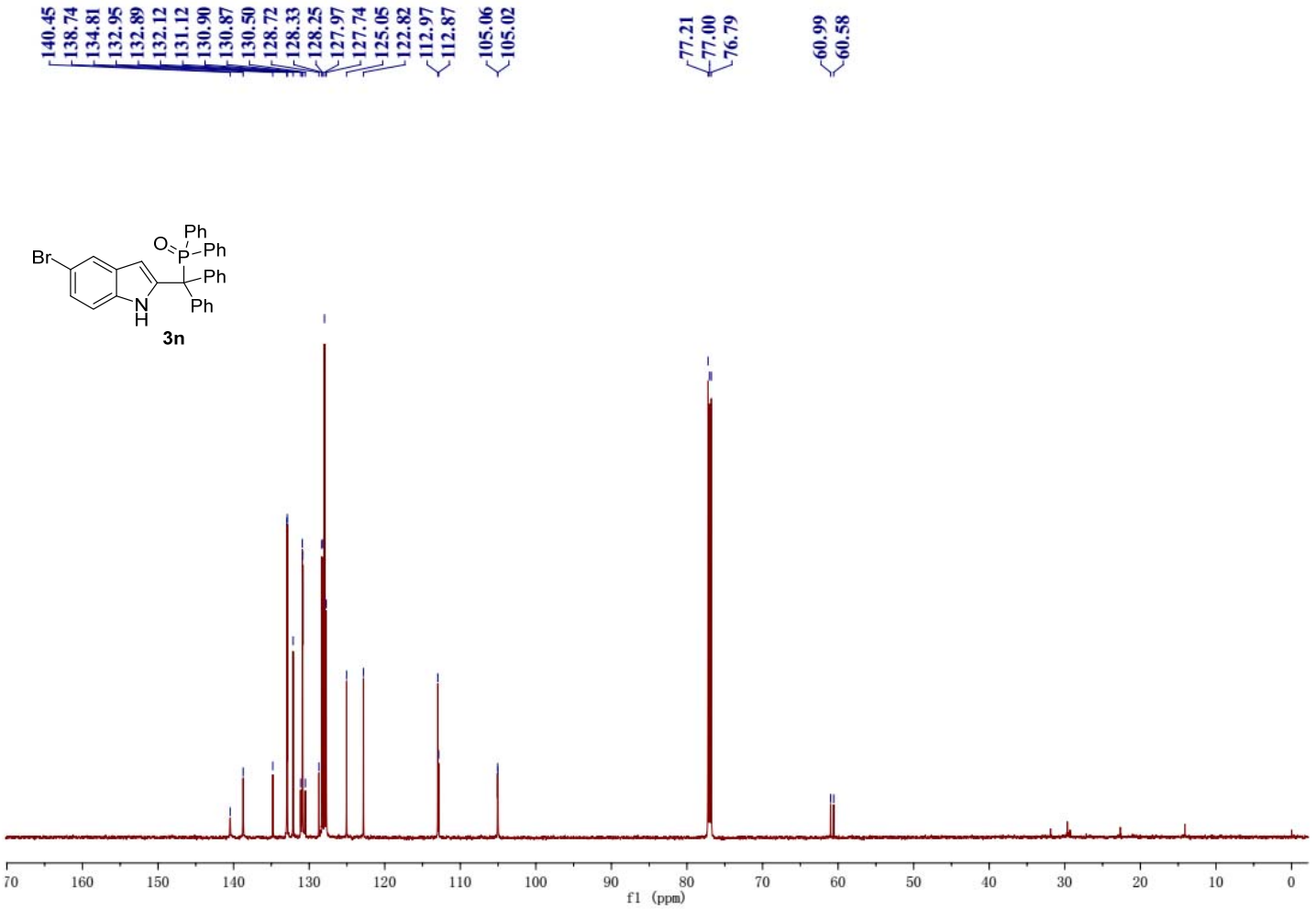

143.97
138.58
136.20
133.33
133.24
132.63
132.60
129.02
128.97
128.49
128.37
126.79
126.77
126.42
126.40
126.06
126.04
122.63
120.75
119.83
111.73
105.72
105.67
54.58
53.95
138.64
138.58
136.20
133.33
133.24
132.63
132.60
129.98
129.02
128.97
128.49
128.37
126.79
126.77
126.42
126.40
126.06
126.04
122.63
120.75
119.83
Ph
Ph
O=P
N
H
S
S
3m
f1 (ppm)
f1 (ppm)

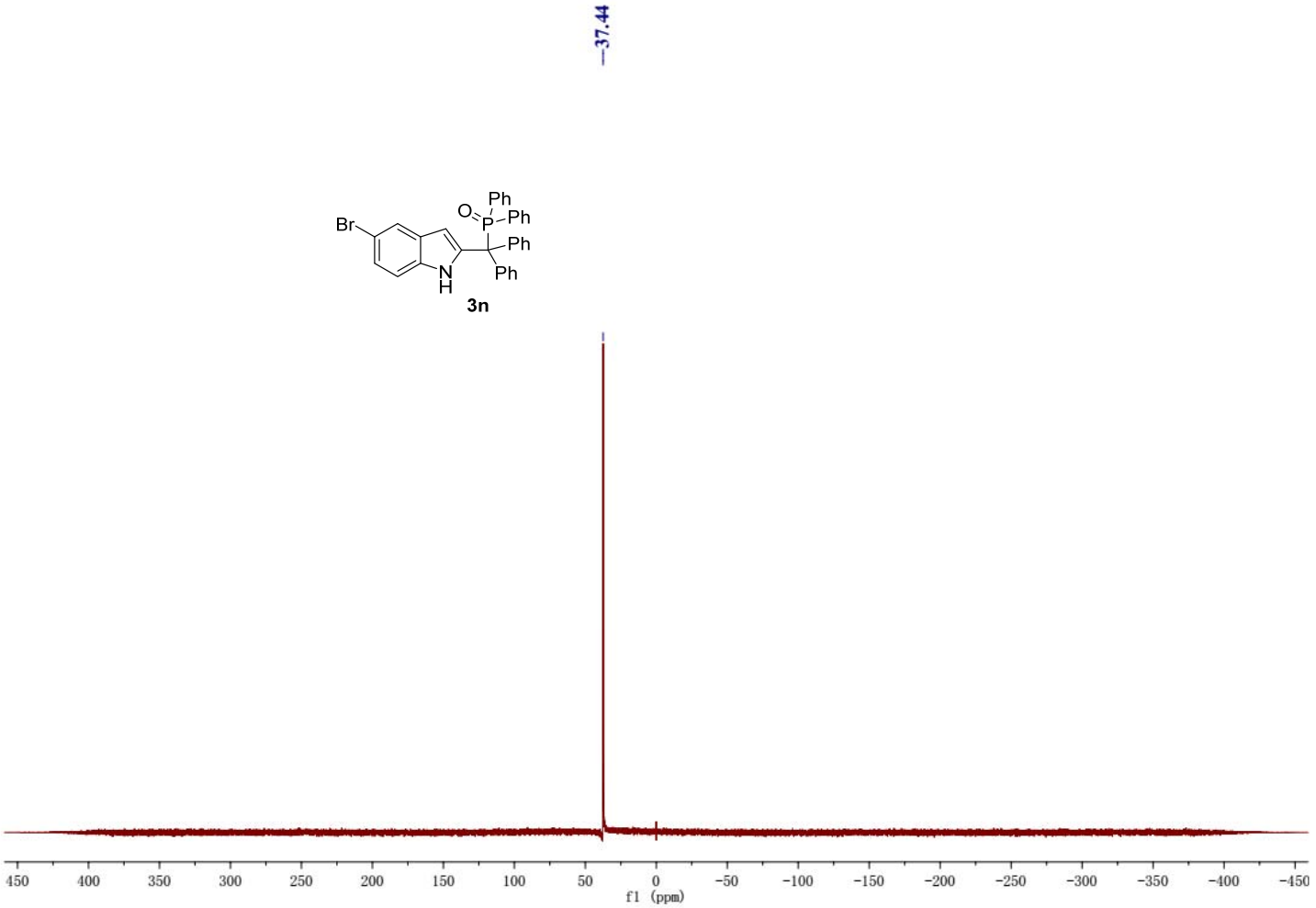

Ph
Ph
O=P
N
H
S
S

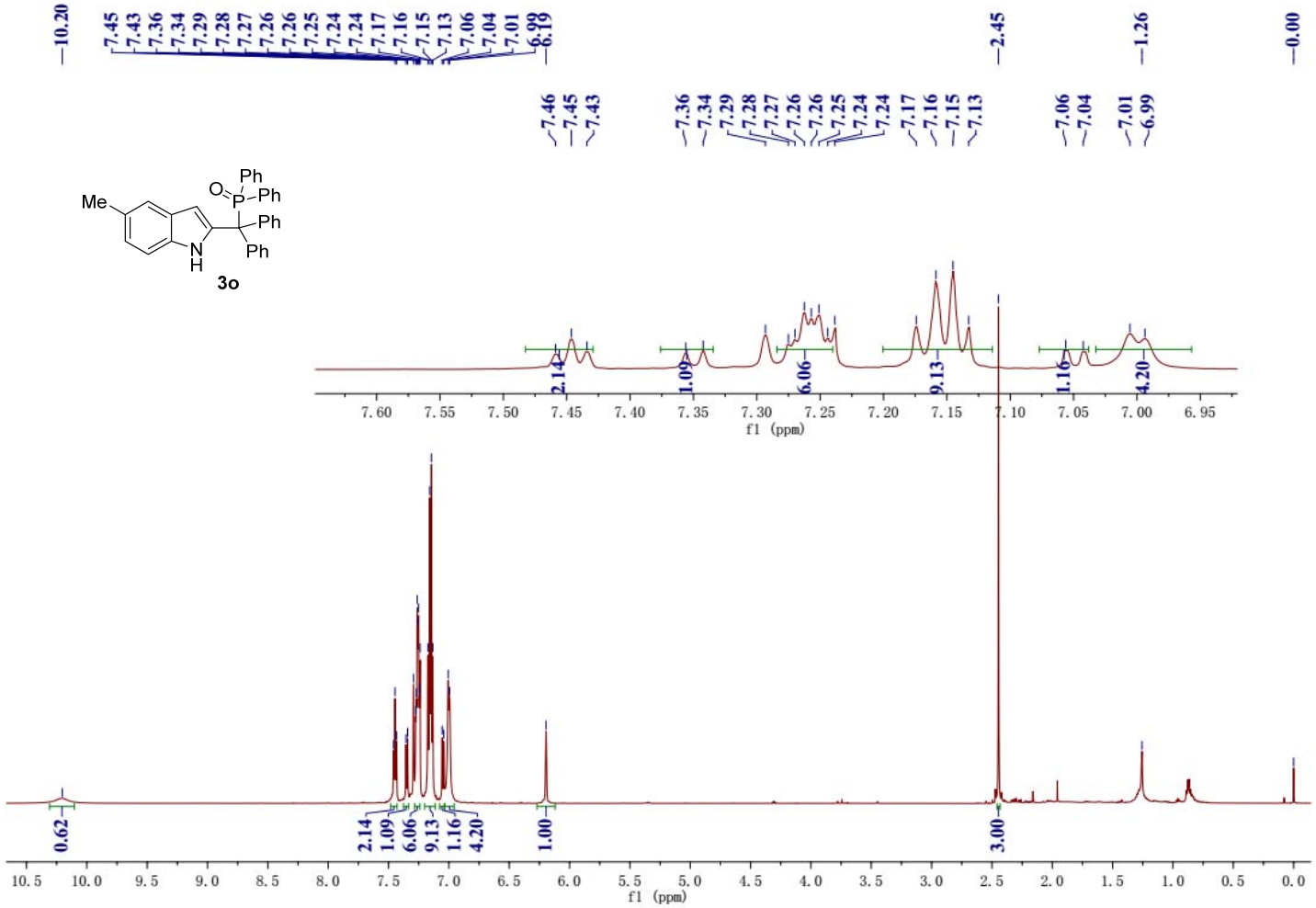
**3m**

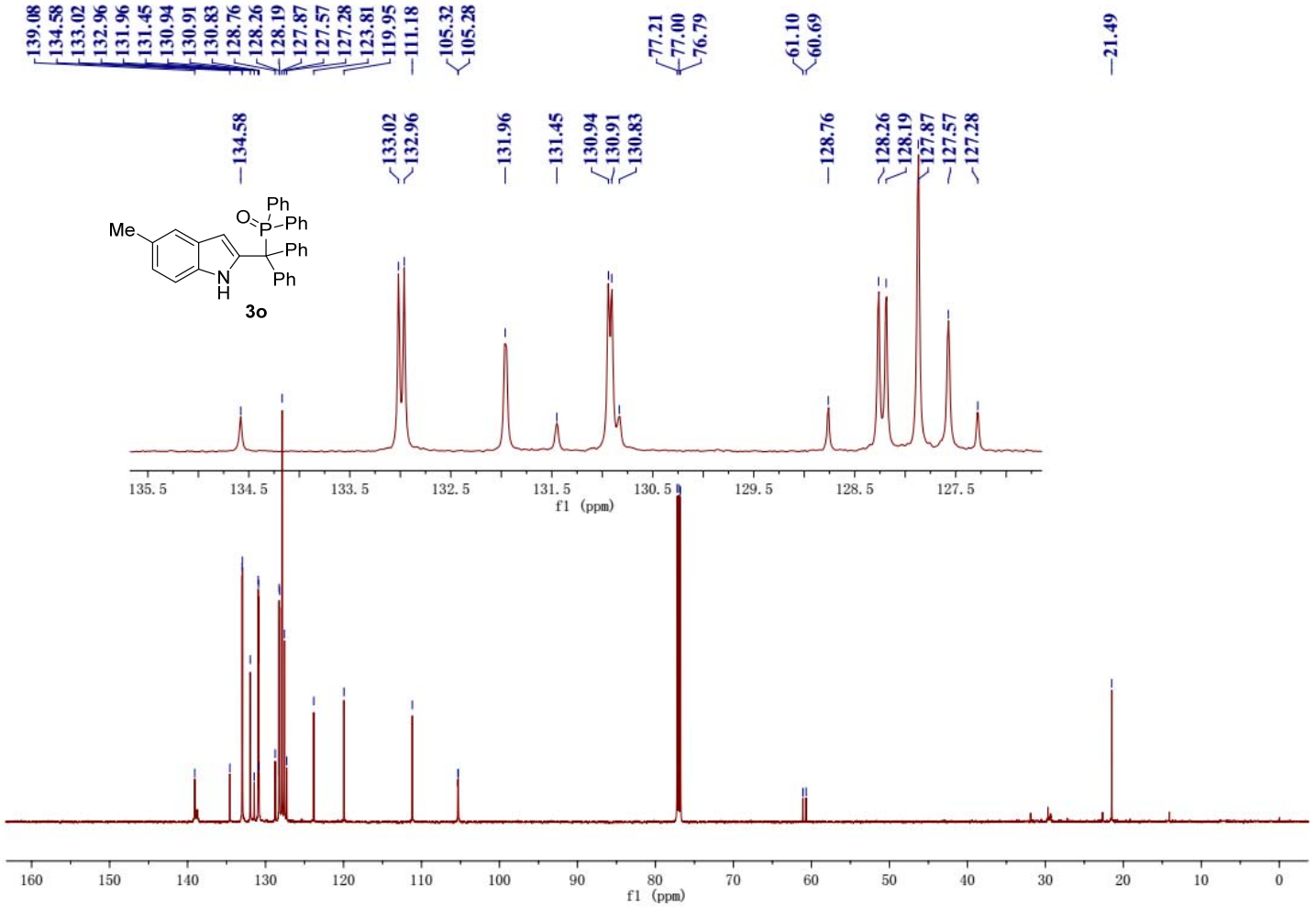

37.67
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

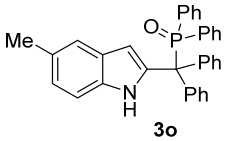

10.43
7.47
7.47
7.32
7.29
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.18
7.16
7.15
7.15
7.14
7.14
7.13
6.99
6.98
1.26
0.00
Br
O
P
Ph
Ph
Ph
Ph
N
H
3n
1.00
2.12
2.02
5.26
9.01
4.06
f1 (ppm)
0.79
1.00
2.12
2.02
5.26
9.01
4.06
1.03
f1 (ppm)


140.45
138.74
134.81
132.95
132.89
132.12
131.12
130.90
130.87
130.50
128.72
128.33
128.25
127.97
127.74
125.05
122.82
112.97
112.87
105.06
105.02
77.21
77.00
76.79
60.99
60.58
Br
O
P
Ph
Ph
Ph
Ph
N
H
3n
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


37.44
Br
O
P
Ph
Ph
Ph
Ph
N
H
3n
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

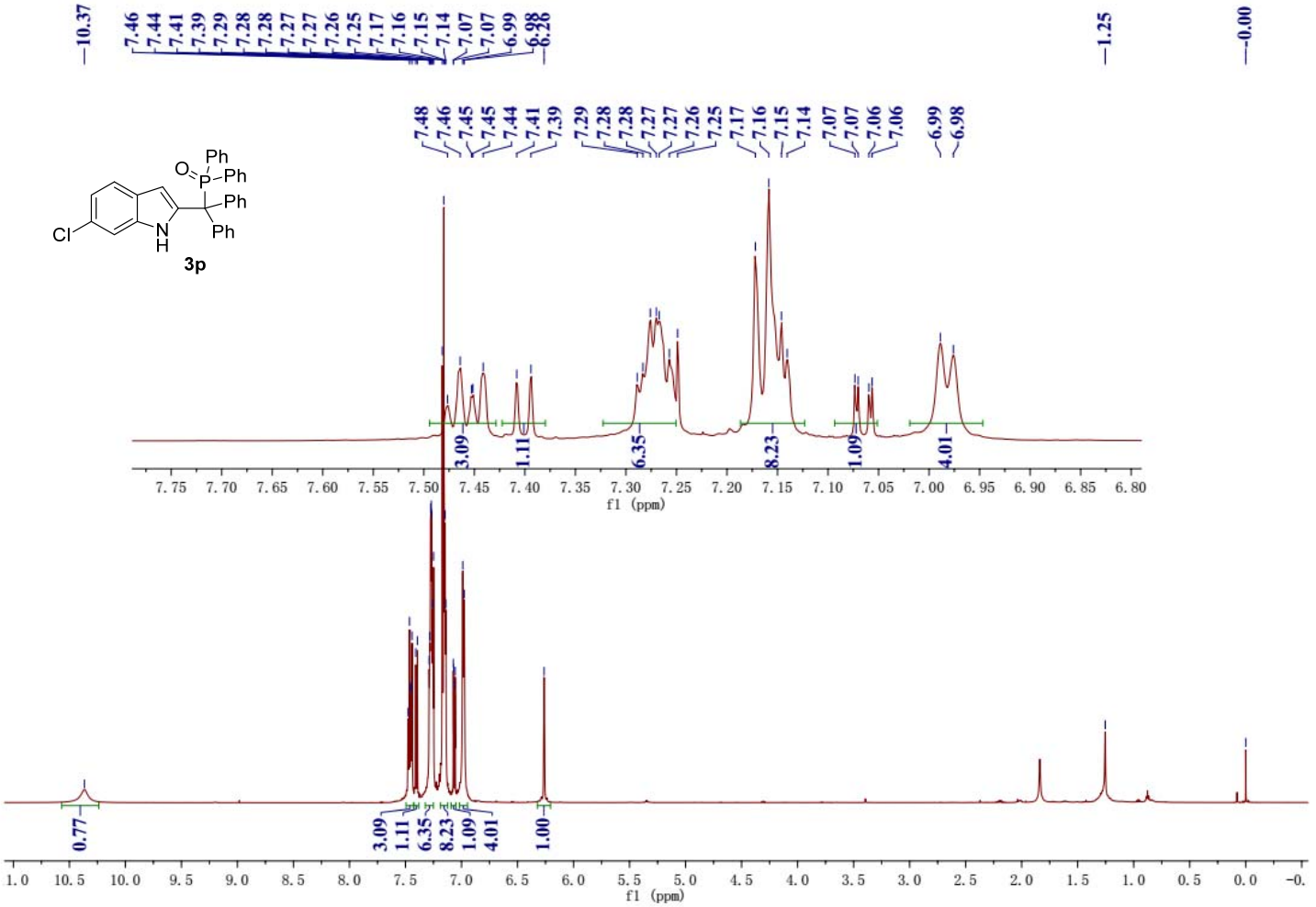

10.20
7.45
7.43
7.36
7.34
7.29
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.17
7.16
7.15
7.13
7.06
7.04
7.01
6.99
6.19
2.45
1.26
0.00
Me
Ph
O
P
Ph
Ph
N
H
Ph
3o
f1 (ppm)
f1 (ppm)

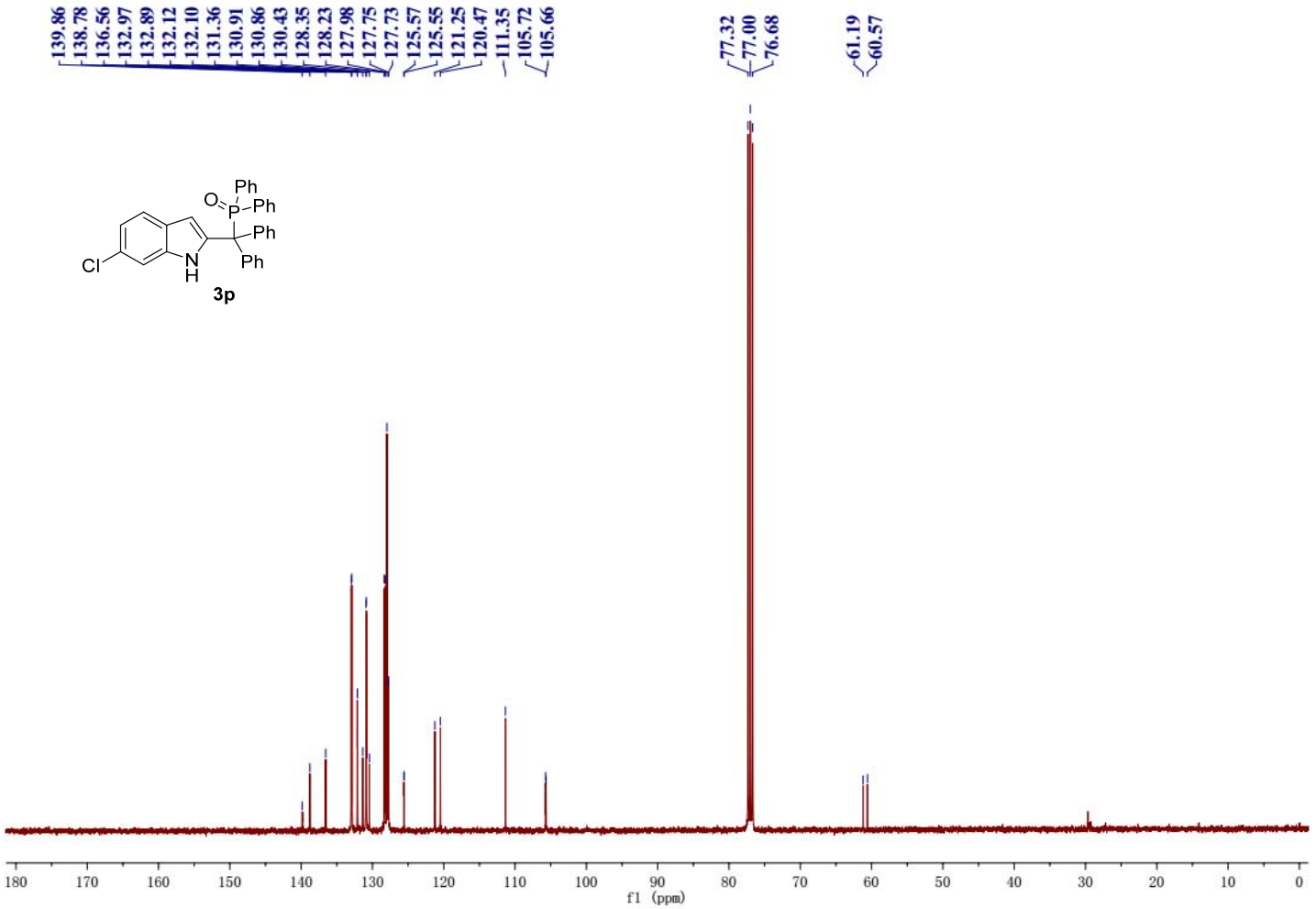

139.08
134.58
133.02
132.96
131.96
131.45
130.94
130.91
130.83
128.76
128.26
128.19
127.87
127.57
127.28
123.81
119.95
111.18
105.32
105.28
77.21
77.00
76.79
61.10
60.69
21.49
Me
Ph
O
P
Ph
Ph
N
H
Ph
3o
f1 (ppm)
f1 (ppm)

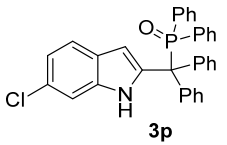

Me
O
P
Ph
Ph
Ph
Ph
N
H

**3o**


-37.35
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

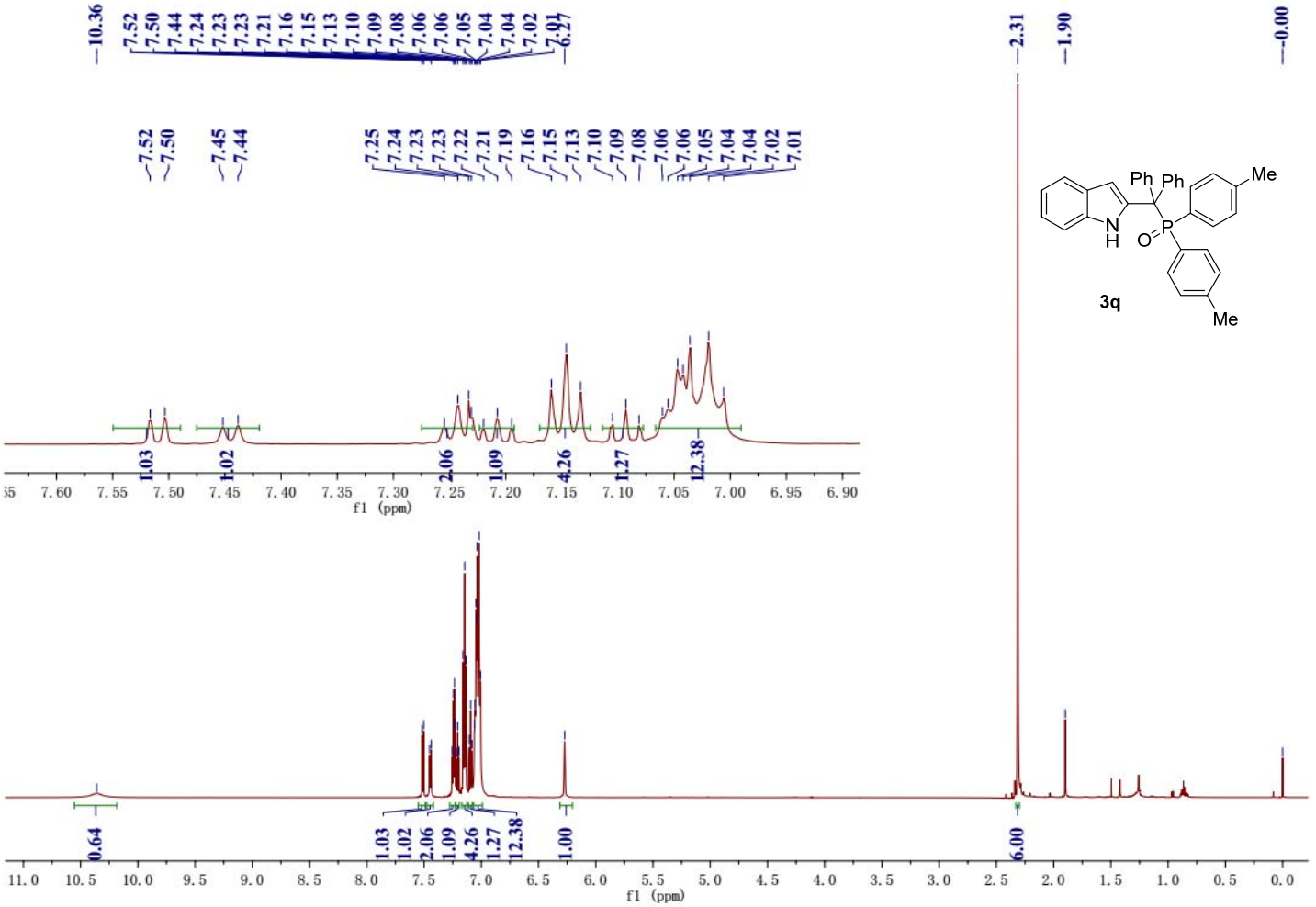

10.37
7.46
7.44
7.41
7.39
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.17
7.16
7.15
7.14
7.07
7.07
6.99
6.98
6.26
1.25
0.00
Ph
O
P
Ph
Ph
Cl
N
H
Ph
3p
7.48
7.46
7.45
7.45
7.44
7.41
7.39
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.17
7.16
7.15
7.14
7.07
7.07
7.06
7.06
6.99
6.98
3.09
1.11
6.35
8.23
1.09
4.01
f1 (ppm)
0.77
3.09
1.11
6.35
8.23
1.09
4.01
1.00
f1 (ppm)

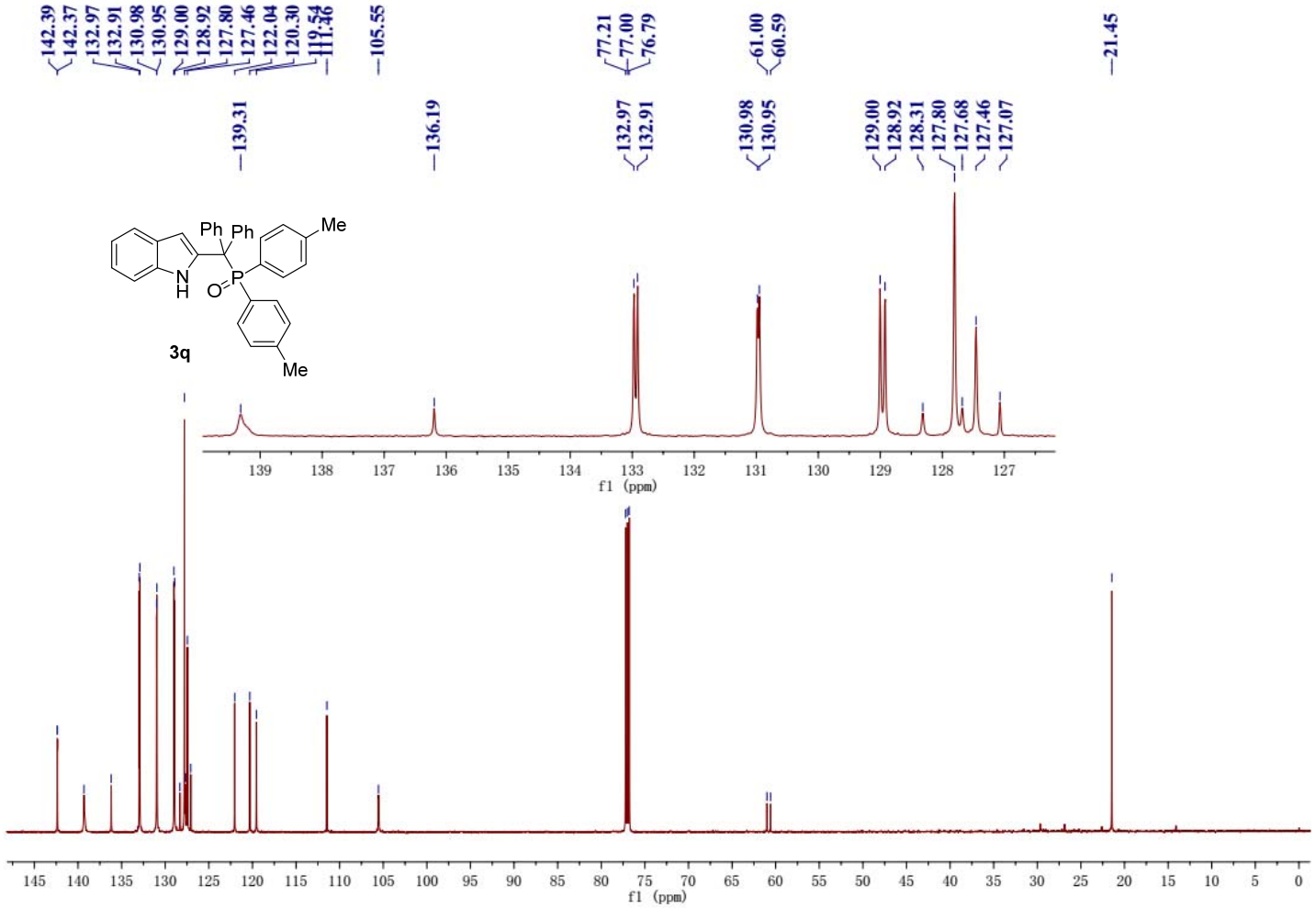

139.86
138.78
136.56
132.97
132.89
132.12
132.10
131.36
130.91
130.86
130.43
128.35
128.23
127.98
127.75
127.73
125.57
125.55
121.25
120.47
111.35
105.72
105.66
77.32
77.00
76.68
61.19
60.57
Ph
O
P
Ph
Ph
Ph
Cl
N
H
3p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

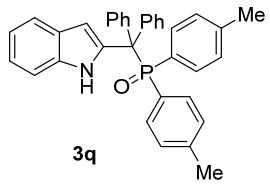

Ph
O
P
Ph
Ph
Ph
Cl
N
H

**3p**


-37.48
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

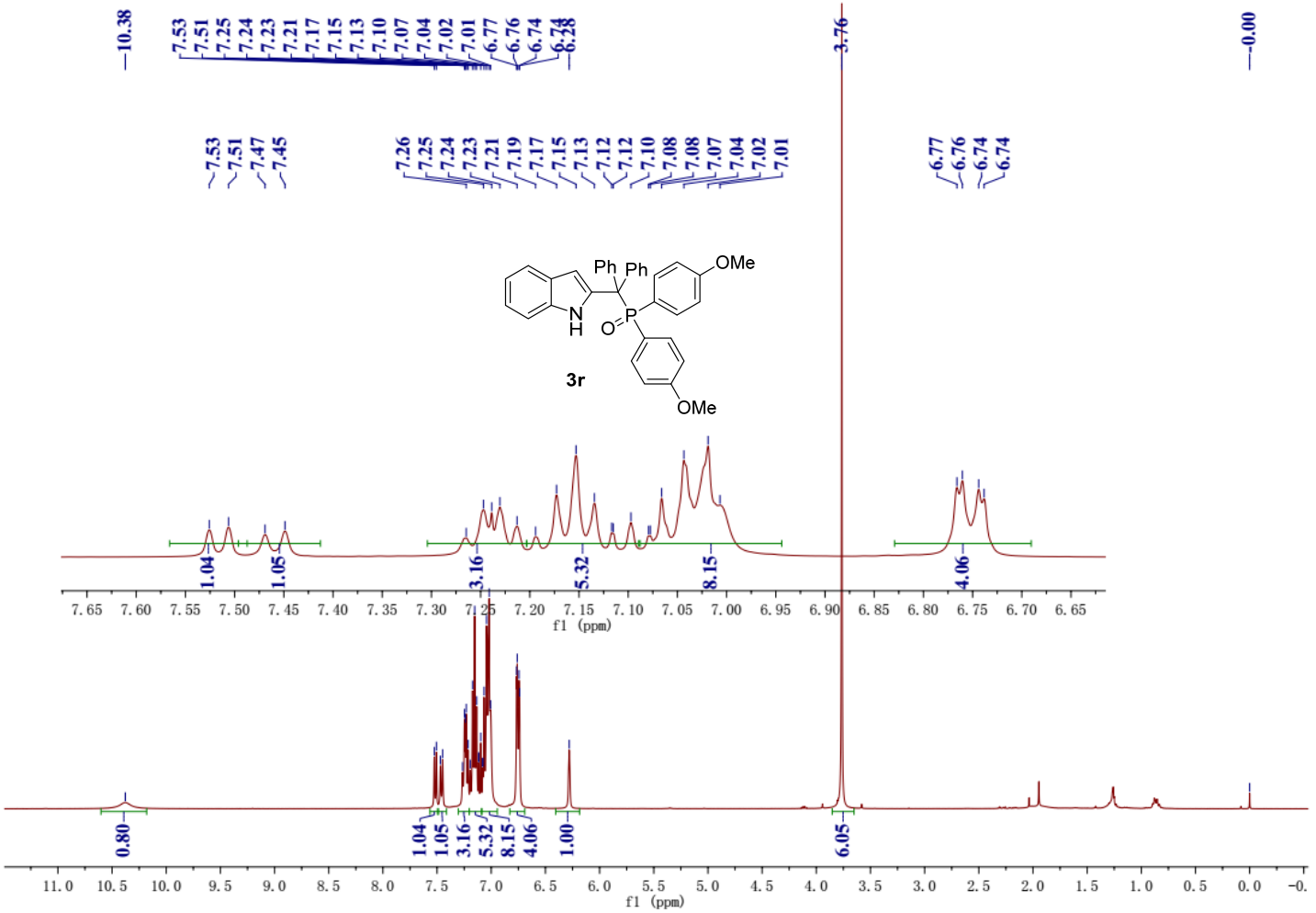

10.36
7.52
7.50
7.44
7.24
7.23
7.23
7.21
7.16
7.15
7.13
7.10
7.09
7.08
7.06
7.06
7.05
7.04
7.04
7.02
7.01
6.27
2.31
1.90
0.00
Ph Ph
Me
N
H
O
P
Me
3q
f1 (ppm)

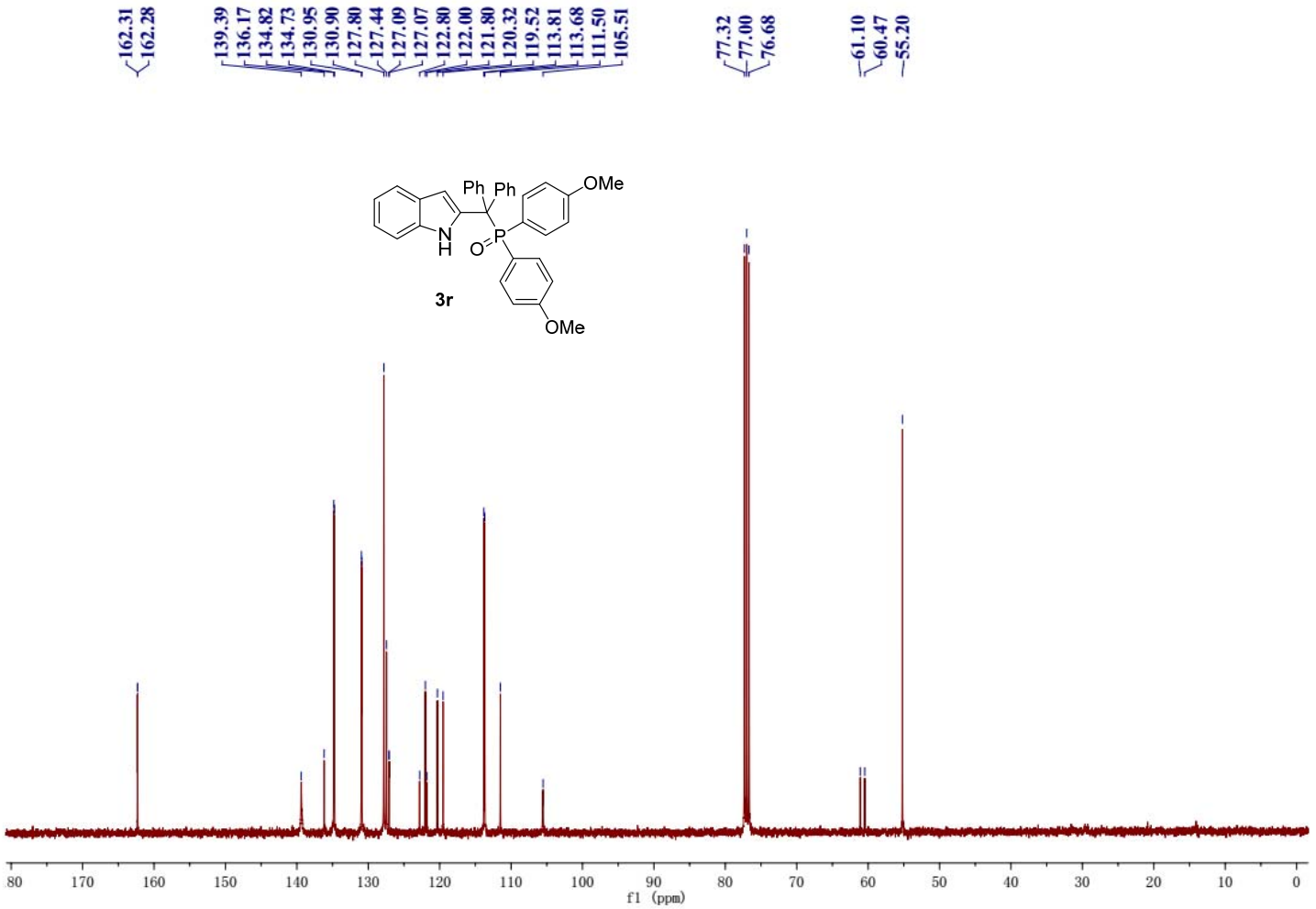

142.39
142.37
132.97
132.91
130.98
130.95
129.00
128.92
127.80
127.46
122.04
120.30
119.54
111.46
105.55
77.21
77.00
76.79
61.00
60.59
21.45
139.31
136.19
132.97
132.91
130.98
130.95
129.00
128.92
128.31
127.80
127.68
127.46
127.07
Ph
Ph
Me
N
H
O
P
Me
3q
f1 (ppm)
f1 (ppm)

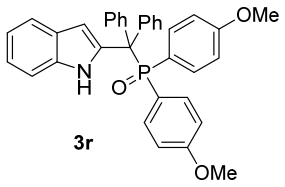

Ph
Ph
Me
N
H
O
P
Me

**3q**


37.80
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

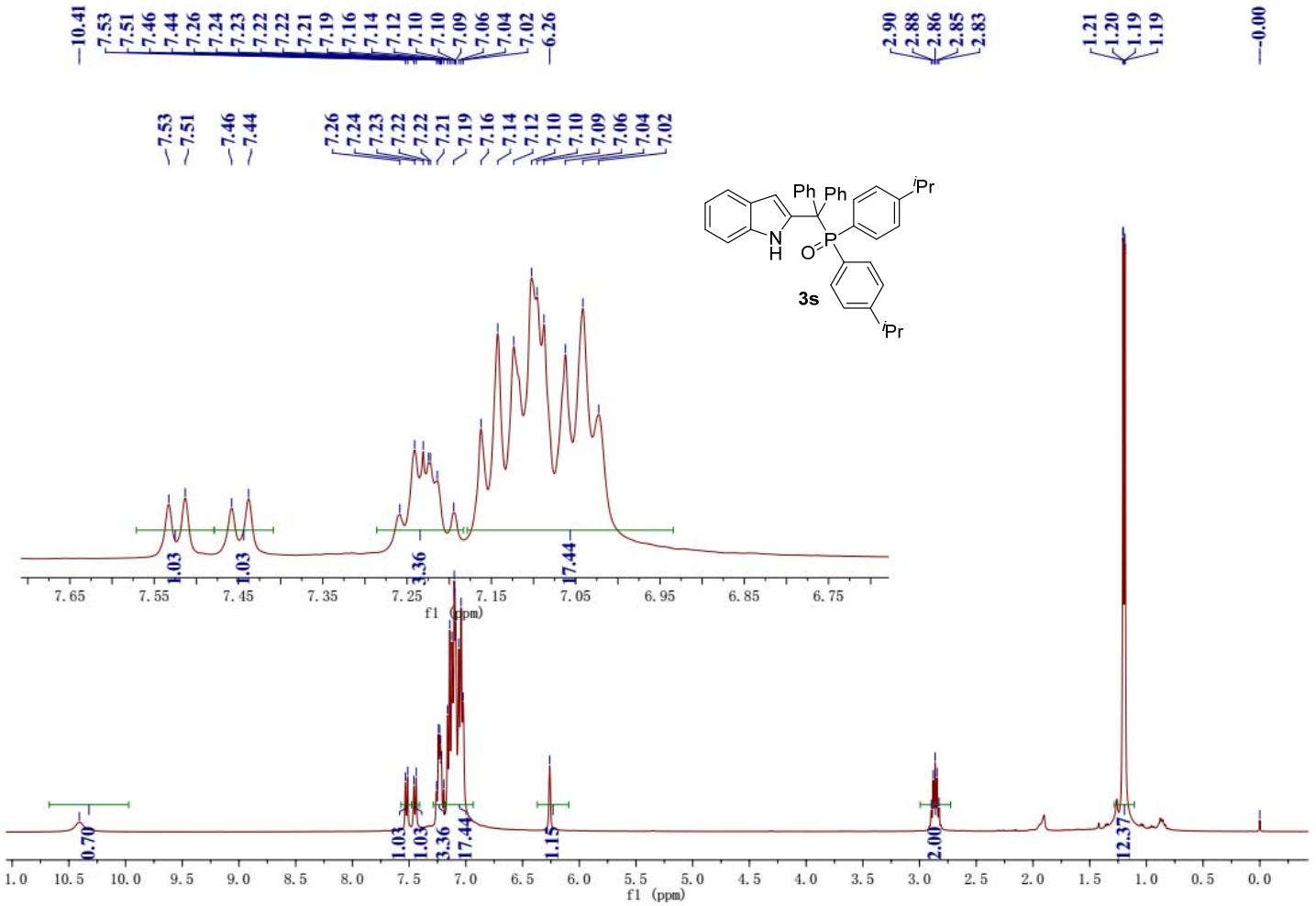

10.38
7.53
7.51
7.25
7.24
7.23
7.21
7.17
7.15
7.13
7.10
7.07
7.04
7.02
7.01
6.77
6.76
6.74
6.74
6.28
3.76
0.00
Ph
Ph
OMe
N
H
O
P
OMe
3r
1.04
1.05
3.16
5.32
8.15
4.06
f1 (ppm)
0.80
1.04
1.05
3.16
5.32
8.15
4.06
1.00
6.05
f1 (ppm)

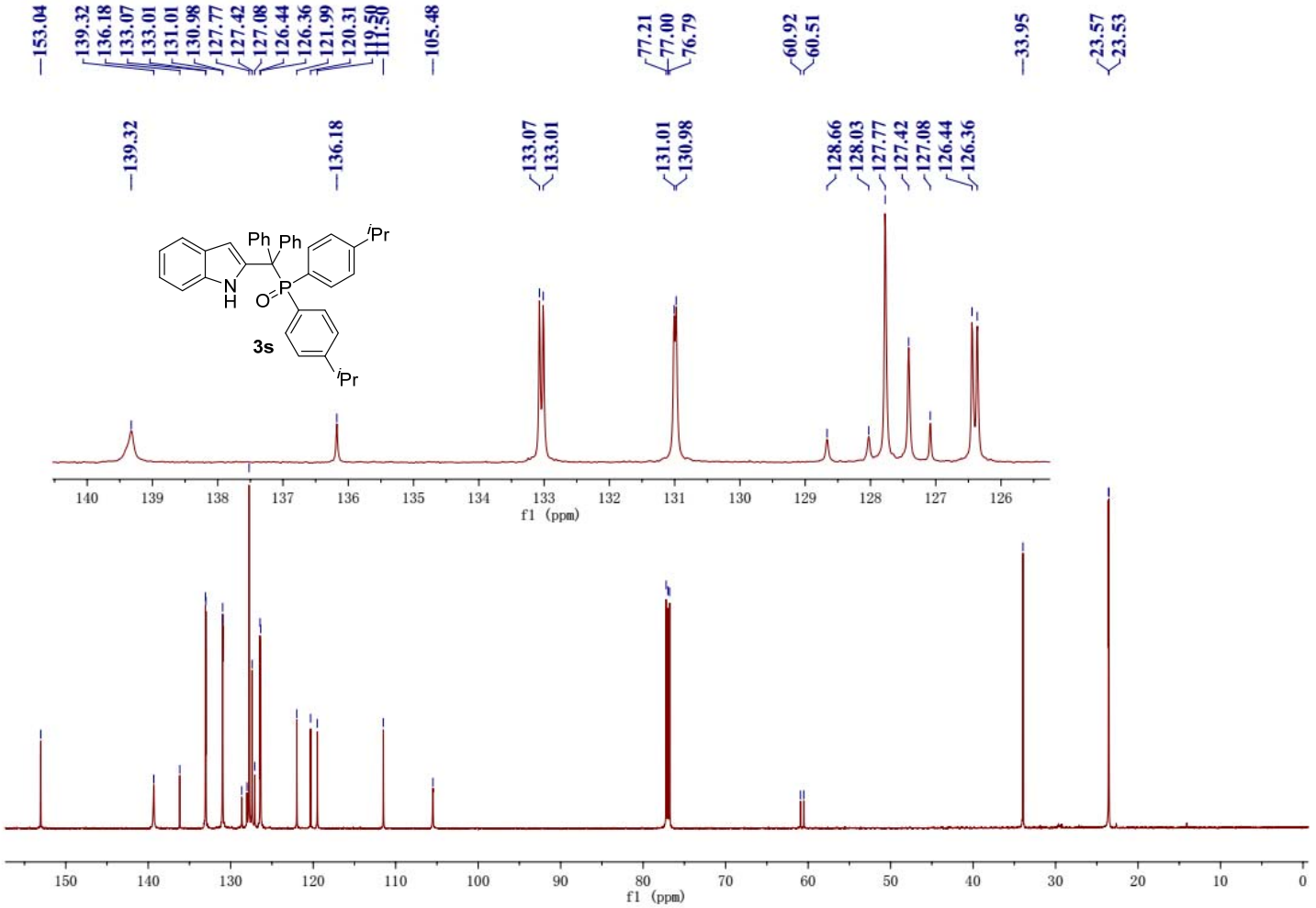

162.31
162.28
139.39
136.17
134.82
134.73
130.95
130.90
127.80
127.44
127.09
127.07
122.80
122.00
121.80
120.32
119.52
113.81
113.68
111.50
105.51
77.32
77.00
76.68
61.10
60.47
55.20
Ph
Ph
OMe
N
H
O
P
OMe
3r
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

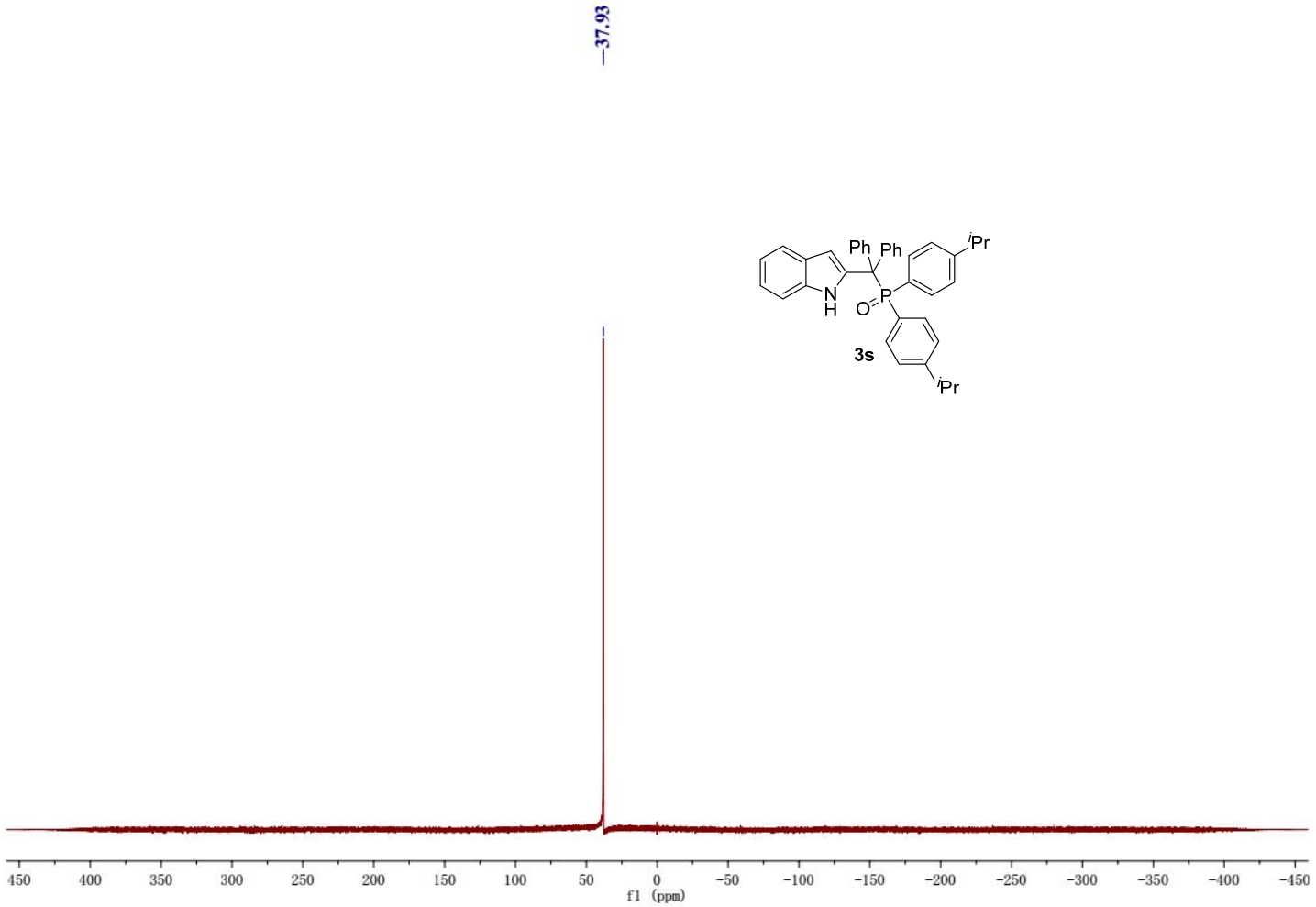

Ph
Ph
OMe
N
H
O
P
OMe

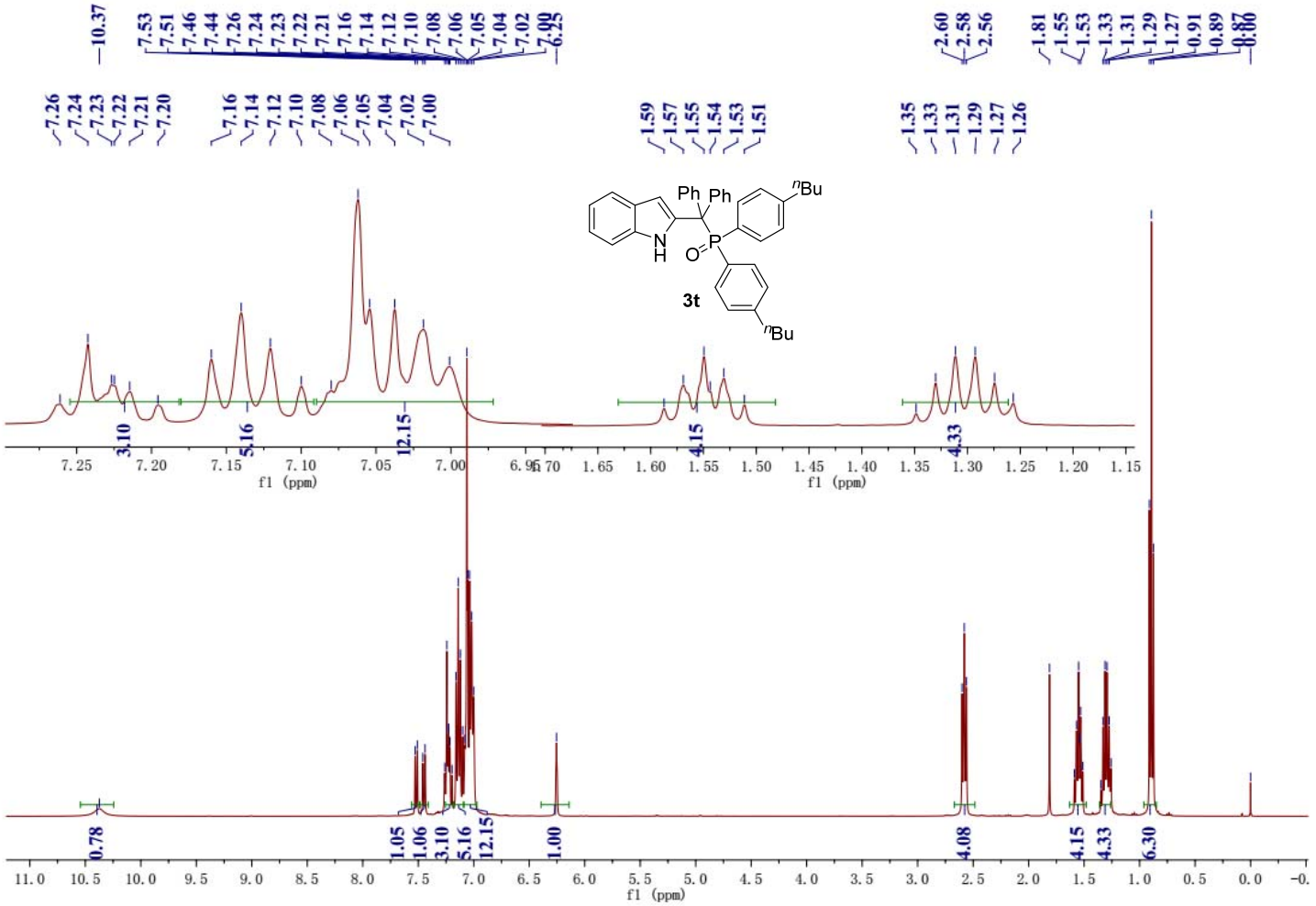
3r

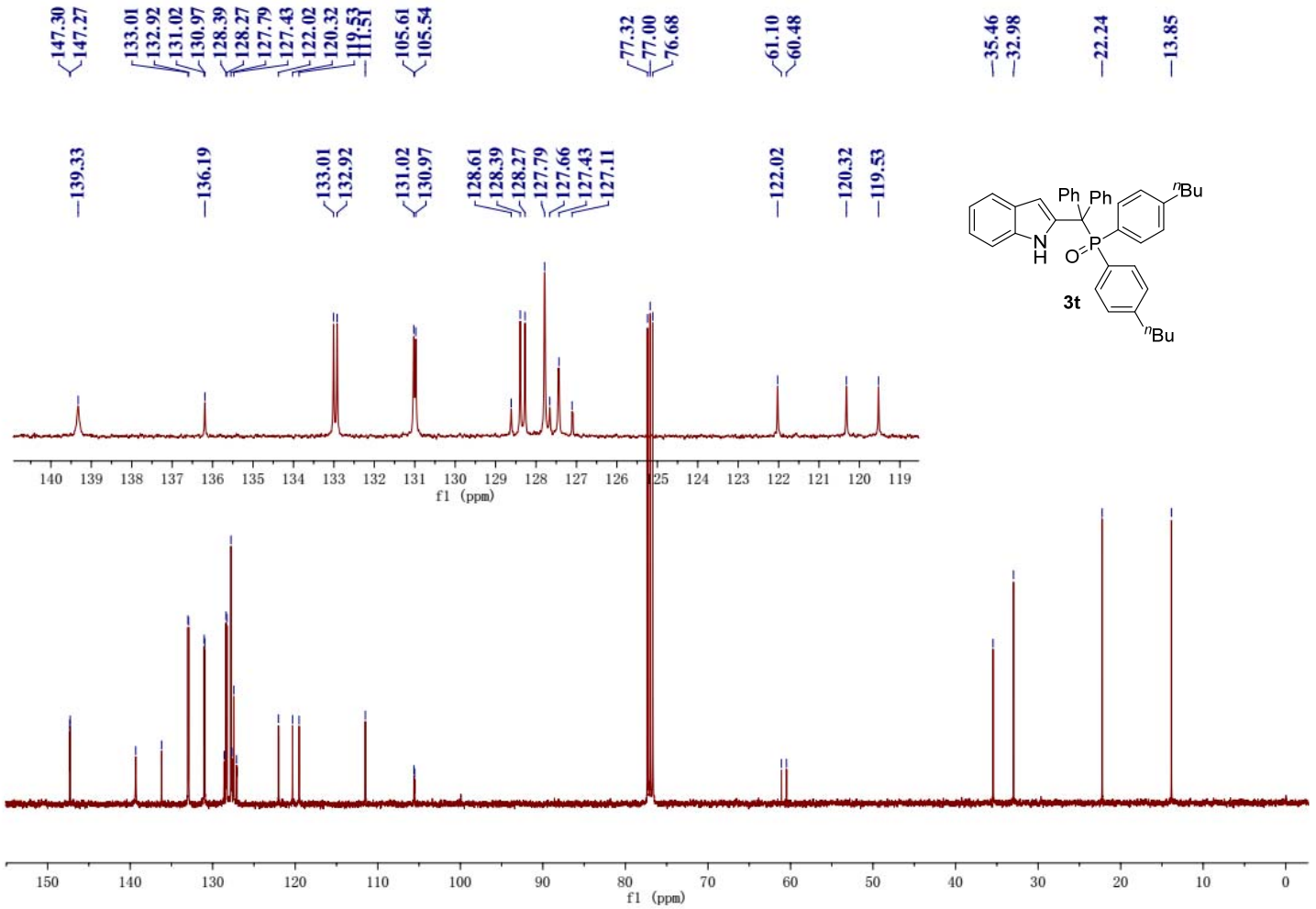

37.65
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

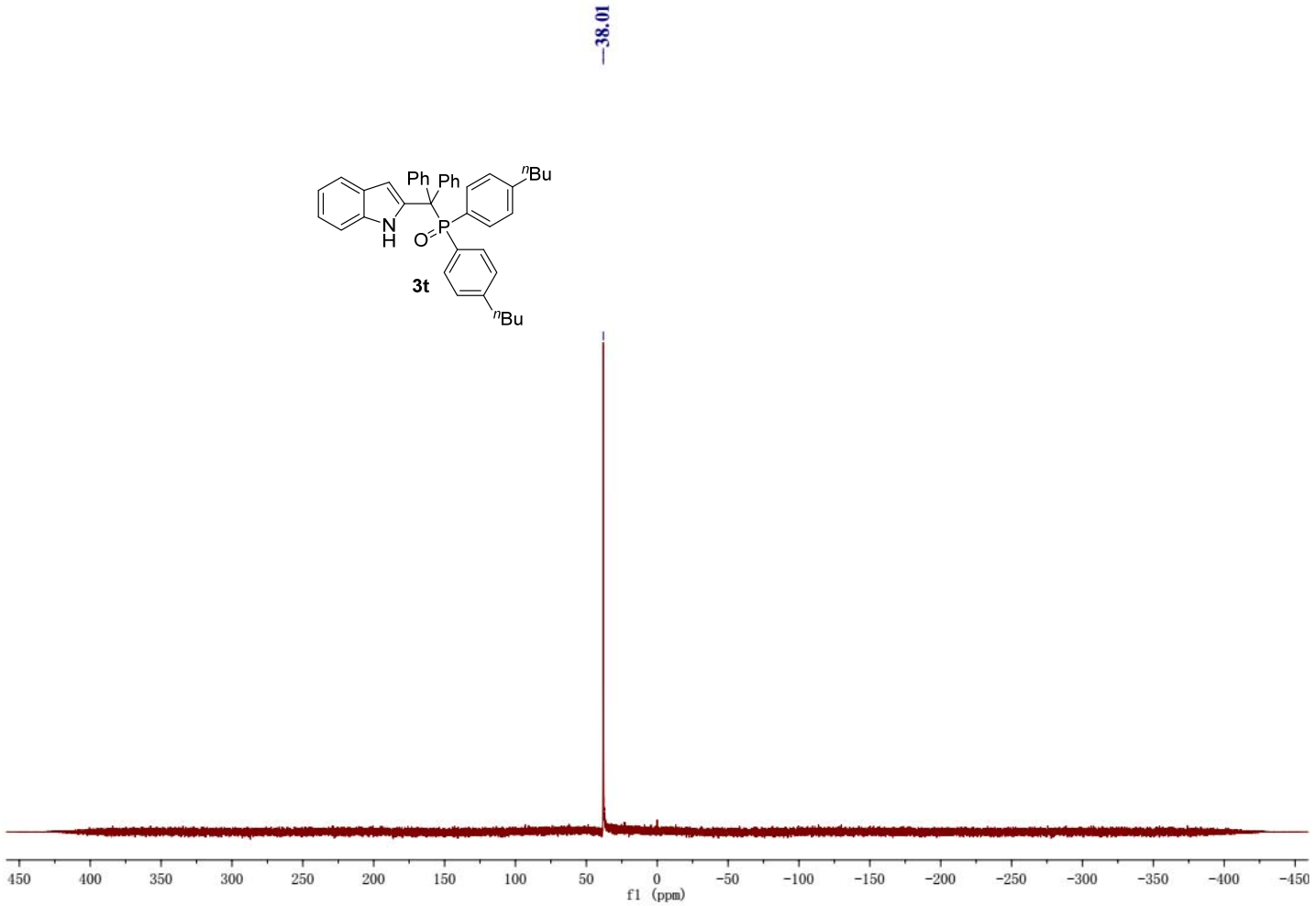

10.41
7.53
7.51
7.46
7.44
7.26
7.24
7.23
7.22
7.22
7.21
7.19
7.16
7.14
7.12
7.10
7.10
7.09
7.06
7.04
7.02
6.26
2.90
2.88
2.86
2.85
2.83
1.21
1.20
1.19
1.19
0.00
Ph
Ph
iPr
N
H
O
P
3s
iPr
1.03
1.03
3.36
17.44
f1 (ppm)
0.70
1.03
1.03
3.36
17.44
1.15
2.00
12.37
f1 (ppm)

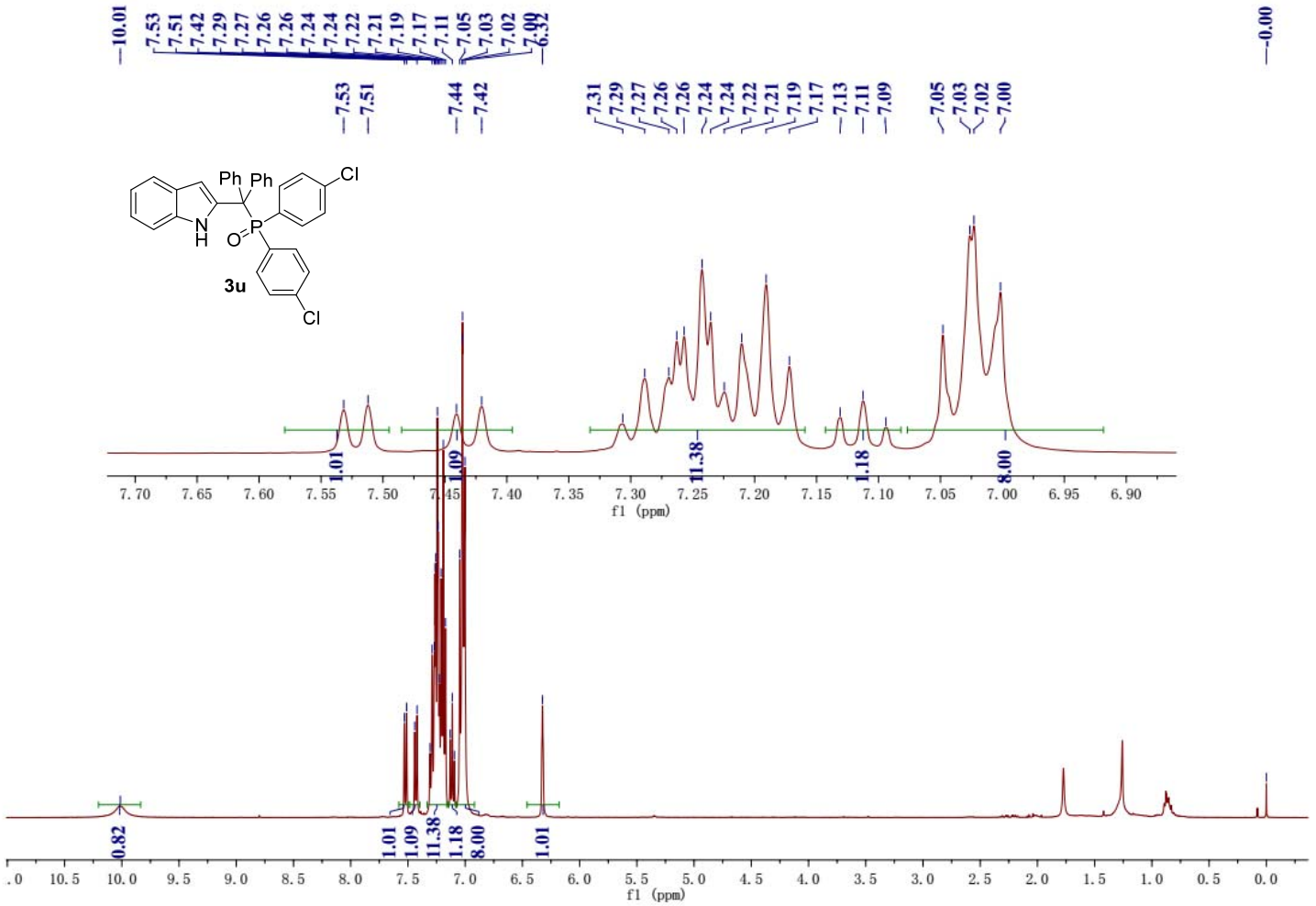

153.04
139.32
136.18
133.07
133.01
131.01
130.98
127.77
127.42
127.08
126.44
126.36
121.99
120.31
119.50
111.50
105.48
77.21
77.00
76.79
60.92
60.51
33.95
23.57
23.53
128.66
128.03
127.77
127.42
127.08
126.44
126.36
Ph
Ph
iPr
iPr
N
H
O
P
3s
f1 (ppm)
f1 (ppm)

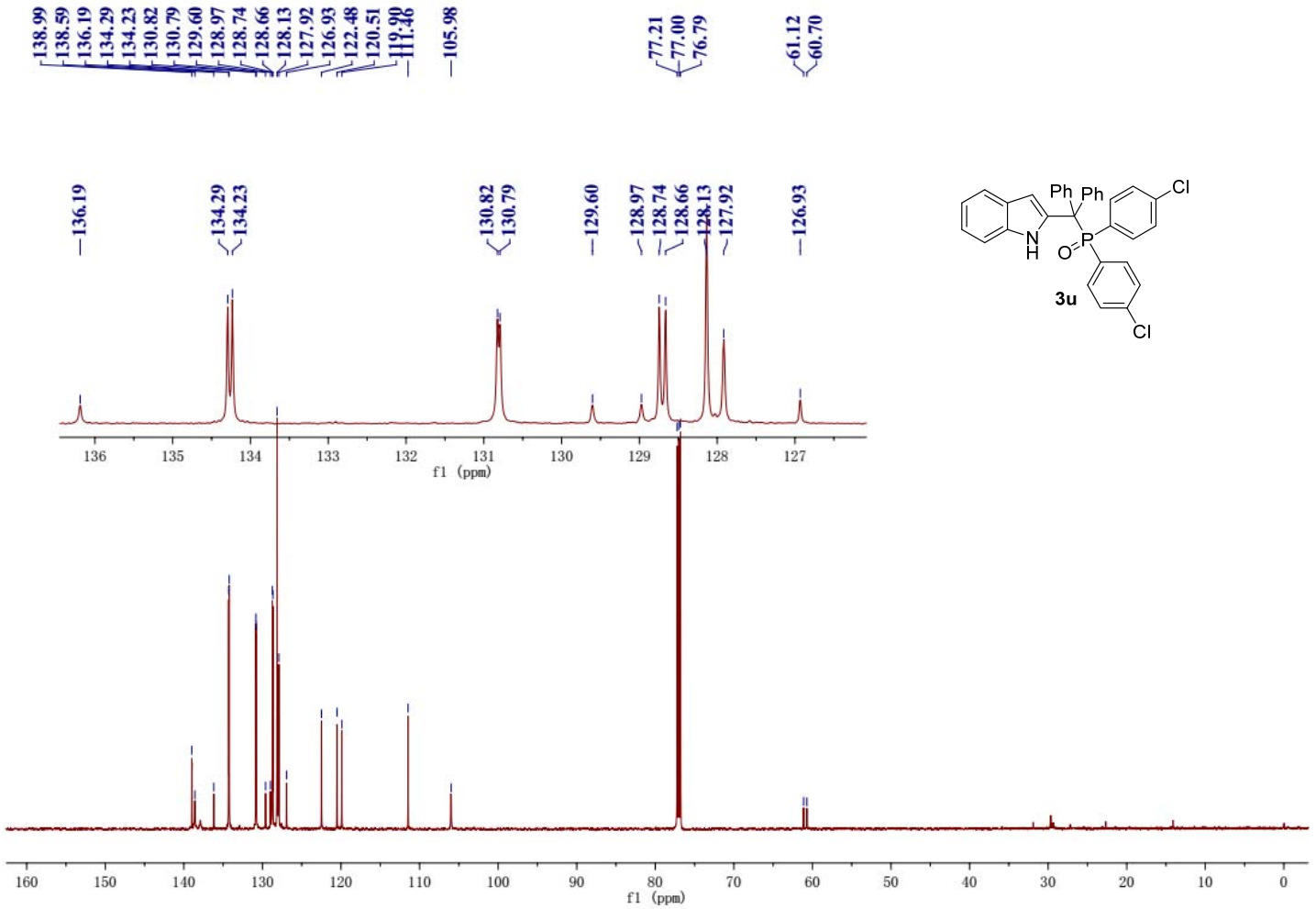

37.93
Ph
Ph
iPr
N
H
O
P
3s
iPr
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

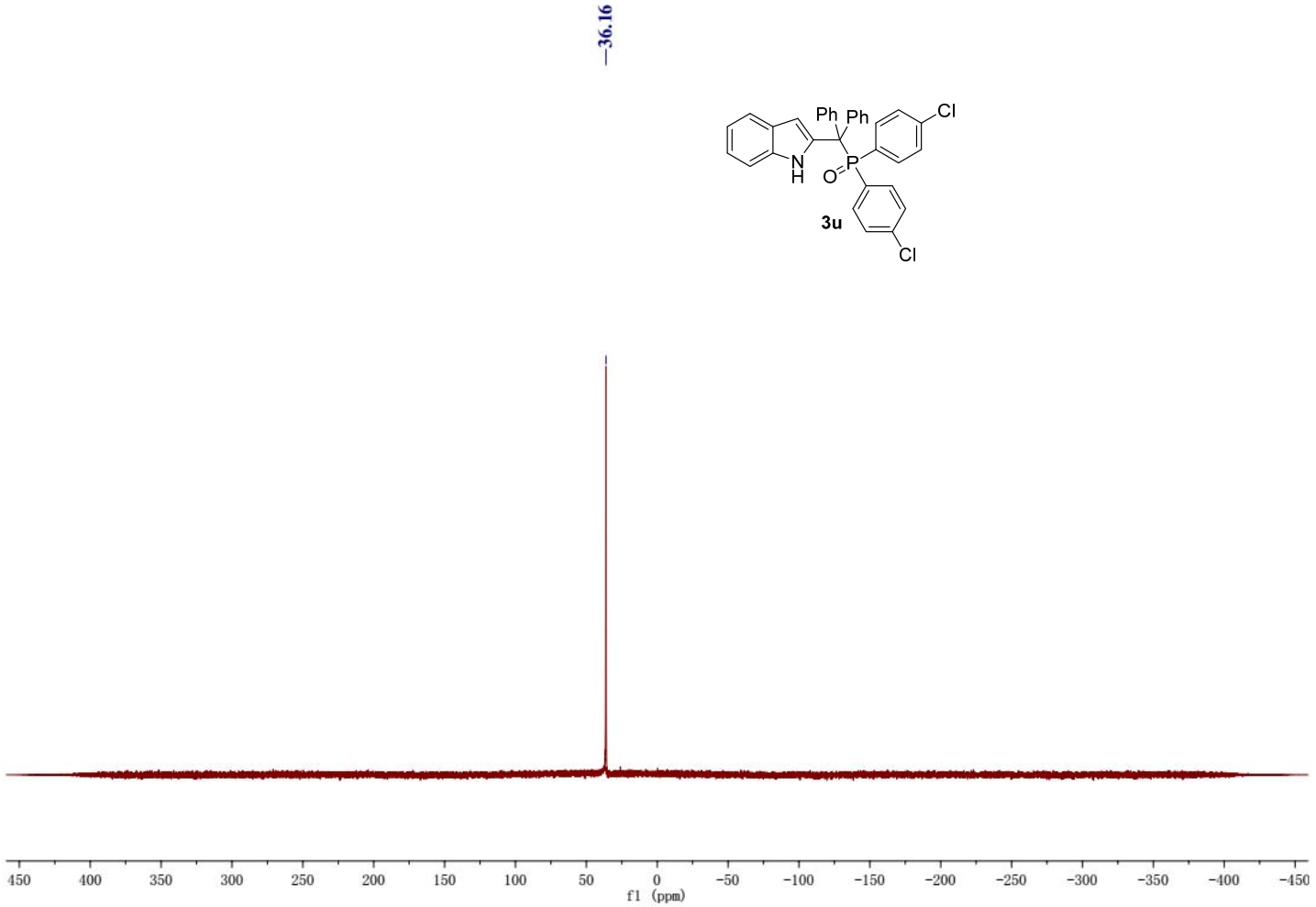

10.37
7.53
7.51
7.46
7.44
7.26
7.24
7.23
7.22
7.21
7.16
7.14
7.12
7.10
7.08
7.06
7.05
7.04
7.02
7.00
6.25
2.60
2.58
2.56
1.81
1.55
1.53
1.33
1.31
1.29
1.27
0.91
0.89
1.59
1.57
1.55
1.54
1.53
1.51
1.35
1.33
1.31
1.29
1.27
1.26
Ph
Ph
nBu
N
H
O
P
nBu
3t
3.10
5.16
12.15
4.15
4.33
f1 (ppm)
0.78
1.05
1.06
3.10
5.16
12.15
1.00
4.08
4.15
4.33
6.30
f1 (ppm)

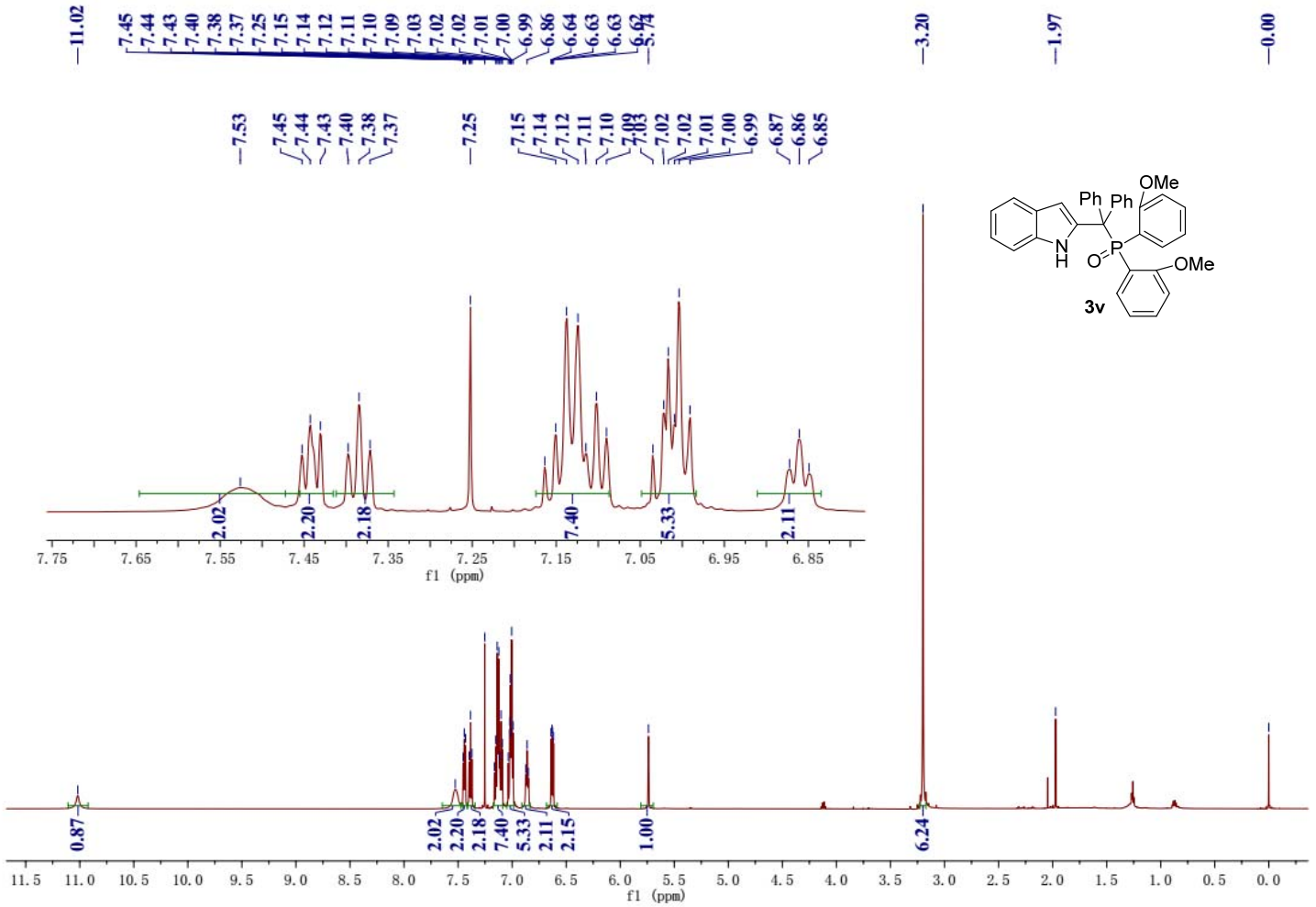

147.30
147.27
133.01
132.92
131.02
130.97
128.39
128.27
127.79
127.43
122.02
120.32
119.53
111.51
105.61
105.54
77.32
77.00
76.68
61.10
60.48
35.46
32.98
22.24
13.85
139.33
136.19
133.01
132.92
131.02
130.97
128.61
128.39
128.27
127.79
127.66
127.43
127.11
122.02
120.32
119.53
Ph
Ph
nBu
N
H
P
O
3t
nBu
140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

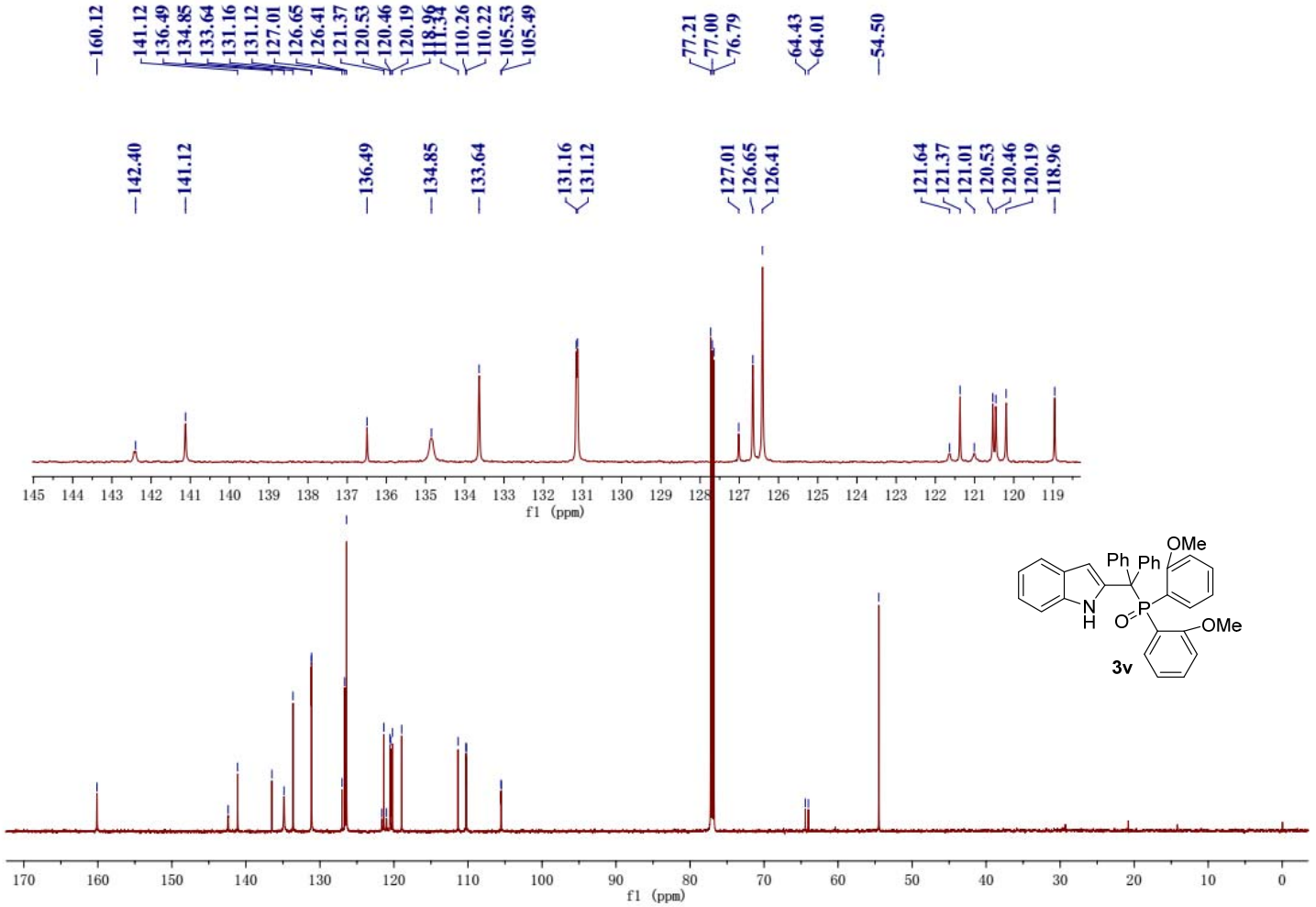

38.01
Ph
Ph
nBu
N
H
O
P
nBu
3t
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

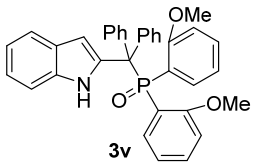

10.01
7.53
7.51
7.42
7.29
7.27
7.26
7.26
7.24
7.24
7.22
7.21
7.19
7.17
7.11
7.05
7.03
7.02
7.00
6.32
0.00
Ph
Ph
Cl
N
H
O
P
Cl
3u
f1 (ppm)
f1 (ppm)


138.99
138.59
136.19
134.29
134.23
130.82
130.79
129.60
128.97
128.74
128.66
128.13
127.92
126.93
122.48
120.51
119.90
111.46
105.98
77.21
77.00
76.79
61.12
60.70
136.19
134.29
134.23
130.82
130.79
129.60
128.97
128.74
128.66
128.13
127.92
126.93
Ph
Ph
Cl
N
H
O
P
Cl
3u
f1 (ppm)
f1 (ppm)


36.16
Ph
Ph
Cl
N
H
P
O
3u
Cl
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

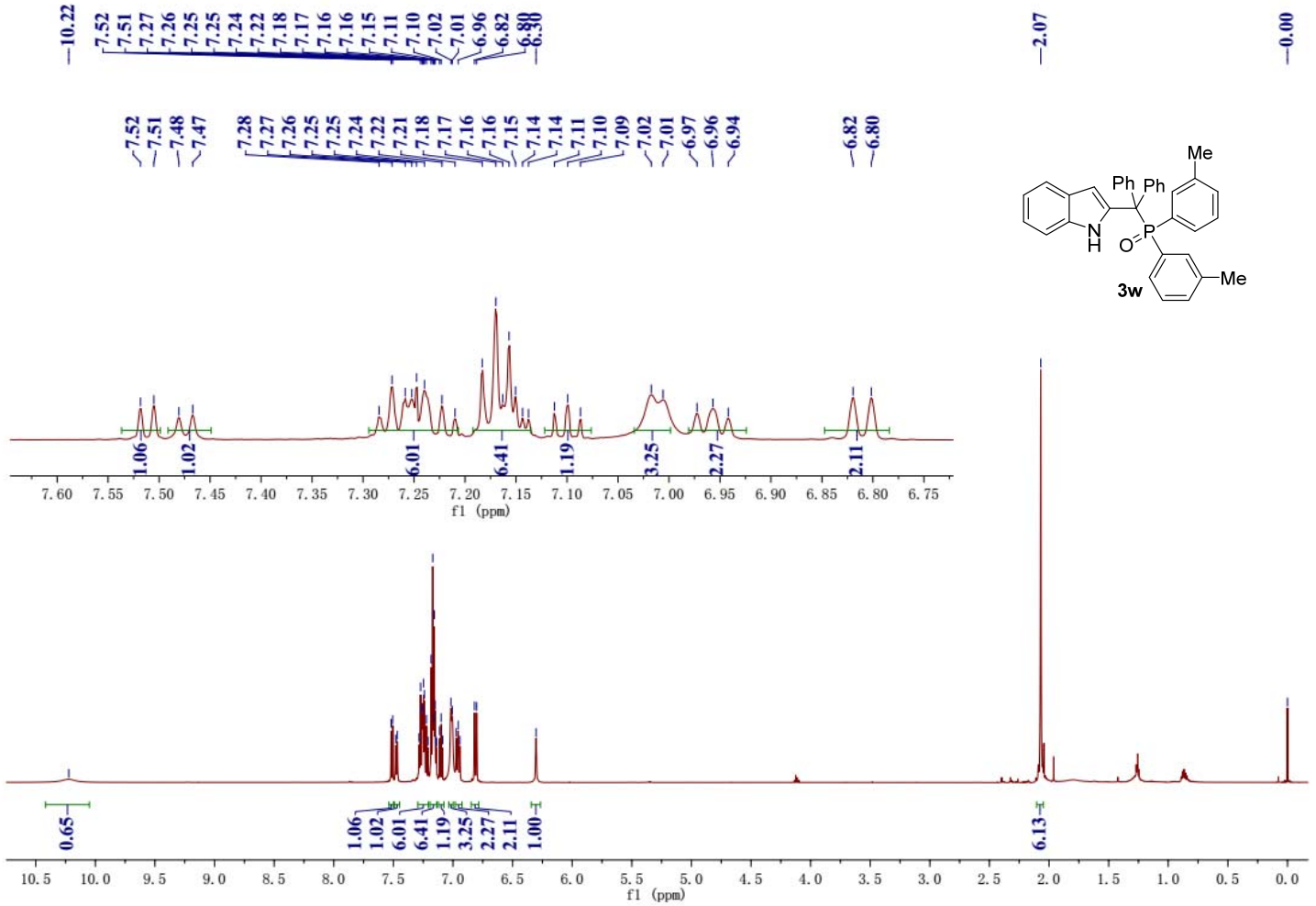

11.02
7.45
7.44
7.43
7.40
7.38
7.37
7.25
7.15
7.14
7.12
7.11
7.10
7.09
7.03
7.02
7.02
7.01
7.00
6.99
6.86
6.64
6.63
6.63
6.62
5.74
3.20
1.97
0.00
7.53
7.45
7.44
7.43
7.40
7.38
7.37
7.25
7.15
7.14
7.12
7.11
7.10
7.02
7.02
7.01
7.00
6.99
6.87
6.86
6.85
OMe
Ph
Ph
N
H
O
P
OMe
3v
2.02
2.20
2.18
7.40
5.33
2.11
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
0.87
2.02
2.20
2.18
7.40
5.33
2.11
2.15
1.00
6.24
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

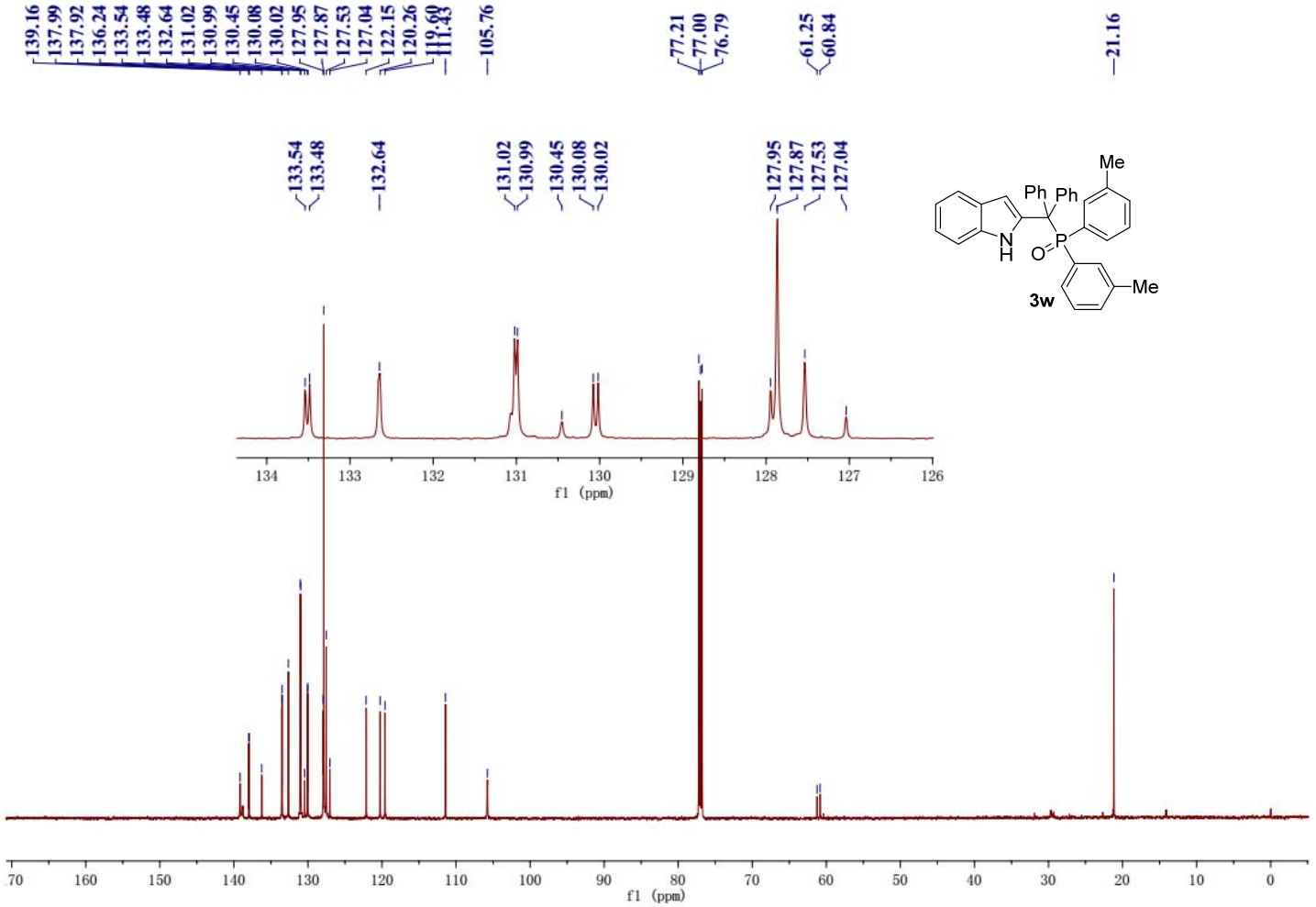

160.12
141.12
136.49
134.85
133.64
131.16
131.12
127.01
126.65
126.41
121.37
120.53
120.46
120.19
118.96
111.34
110.26
110.22
105.53
105.49
77.21
77.00
76.79
64.43
64.01
54.50
142.40
141.12
136.49
134.85
133.64
131.16
131.12
127.01
126.65
126.41
121.64
121.37
121.01
120.53
120.46
120.19
118.96
f1 (ppm)
f1 (ppm)
OMe
Ph
Ph
N
H
O
P
OMe
3v

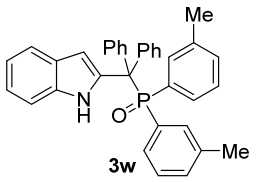

Ph
Ph
OMe
N
H
O
P
OMe

**3v**


47.48
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

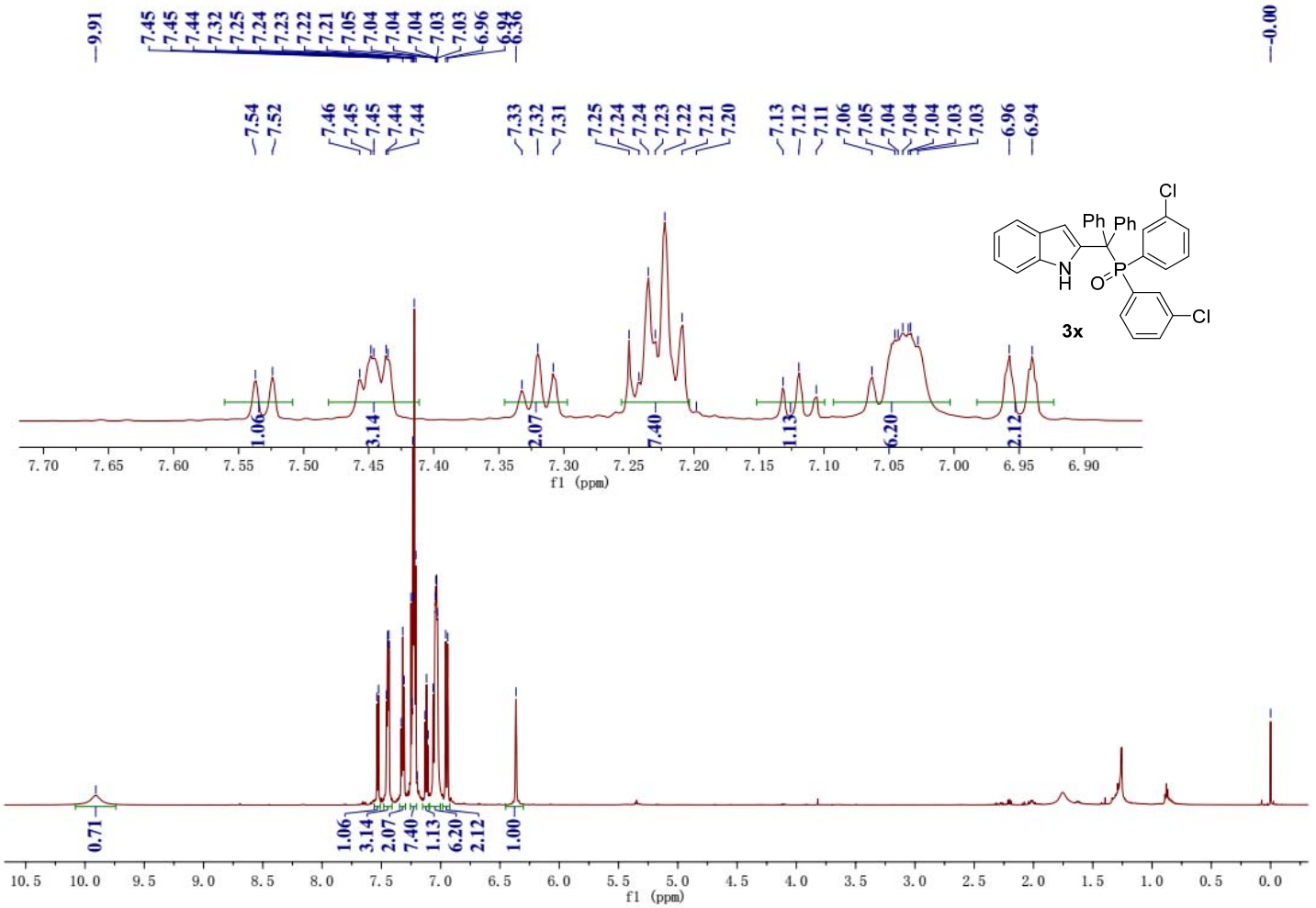

10.22
7.52
7.51
7.27
7.26
7.25
7.25
7.24
7.22
7.18
7.17
7.16
7.16
7.15
7.11
7.10
7.02
7.01
6.96
6.82
6.80
6.80
2.07
0.00
7.52
7.51
7.48
7.47
7.28
7.27
7.26
7.25
7.25
7.24
7.22
7.21
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.11
7.10
7.09
7.02
7.01
6.97
6.96
6.94
6.82
6.80
Me
Ph
Ph
N
H
P
O
Me
3w
1.06
1.02
6.01
6.41
1.19
3.25
2.27
2.11
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)
0.65
1.06
1.02
6.01
6.41
1.19
3.25
2.27
2.11
1.00
6.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

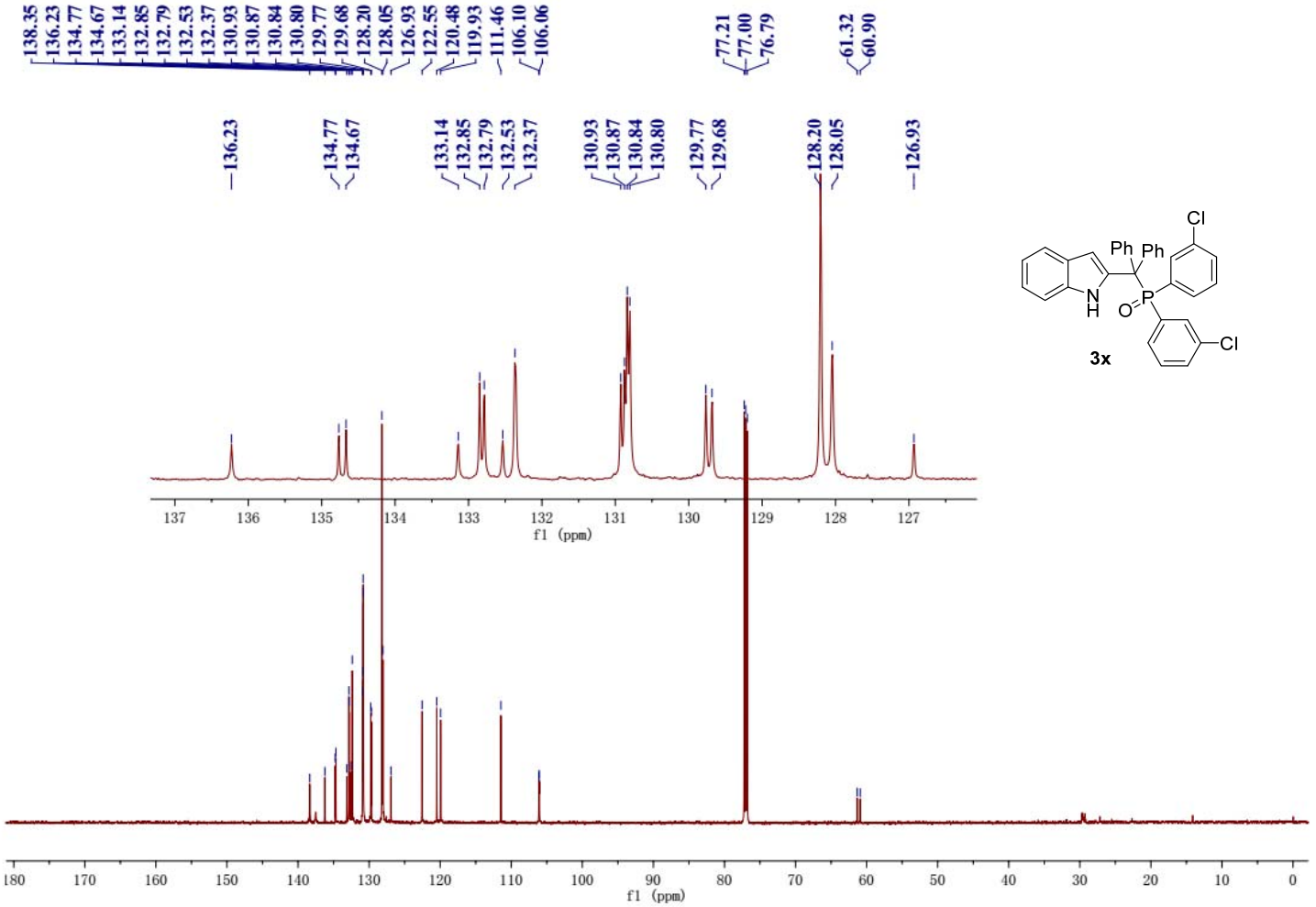

139.16
137.99
137.92
136.24
133.54
133.48
132.64
131.02
130.99
130.45
130.08
130.02
127.95
127.87
127.53
127.04
122.15
120.26
119.60
111.43
105.76
77.21
77.00
76.79
61.25
60.84
21.16
Me
Ph
Ph
N
H
O
P
Me
3w
f1 (ppm)
f1 (ppm)

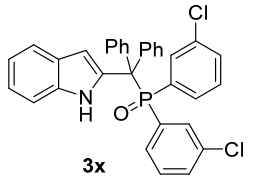

Me
Ph
Ph
N
H
O
P
Me

**3w**


37.81
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

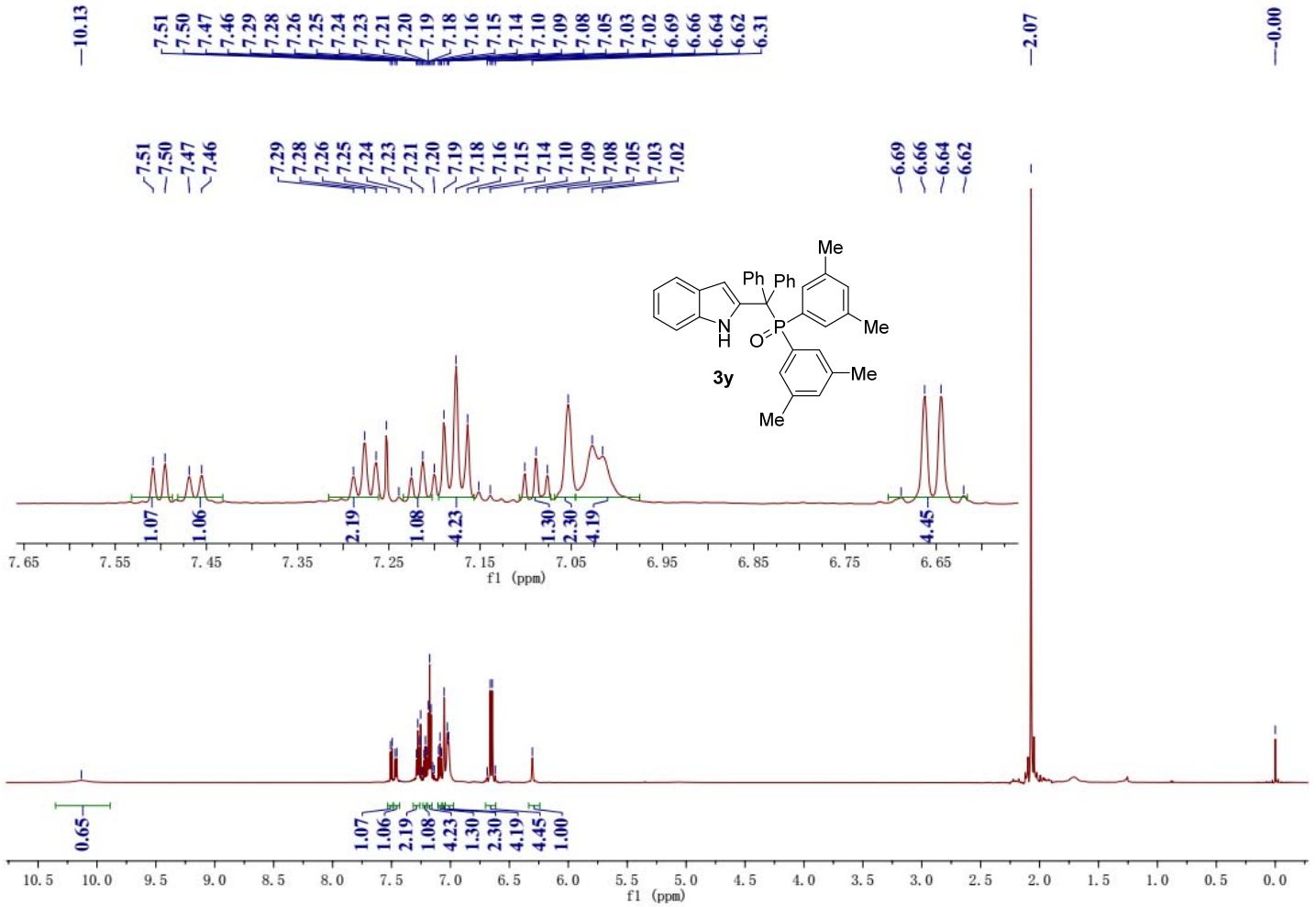

9.91
7.45
7.45
7.44
7.32
7.25
7.24
7.23
7.22
7.21
7.05
7.04
7.04
7.04
7.03
7.03
6.96
6.94
6.36
0.00
7.54
7.52
7.46
7.45
7.45
7.44
7.44
7.33
7.32
7.31
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.13
7.12
7.11
7.06
7.05
7.04
7.04
7.04
7.03
7.03
6.96
6.94
Cl
Ph
Ph
N
H
P
O
Cl
3x
1.06
3.14
2.07
7.40
1.13
6.20
2.12
f1 (ppm)
0.71
1.06
3.14
2.07
7.40
1.13
6.20
2.12
1.00
f1 (ppm)

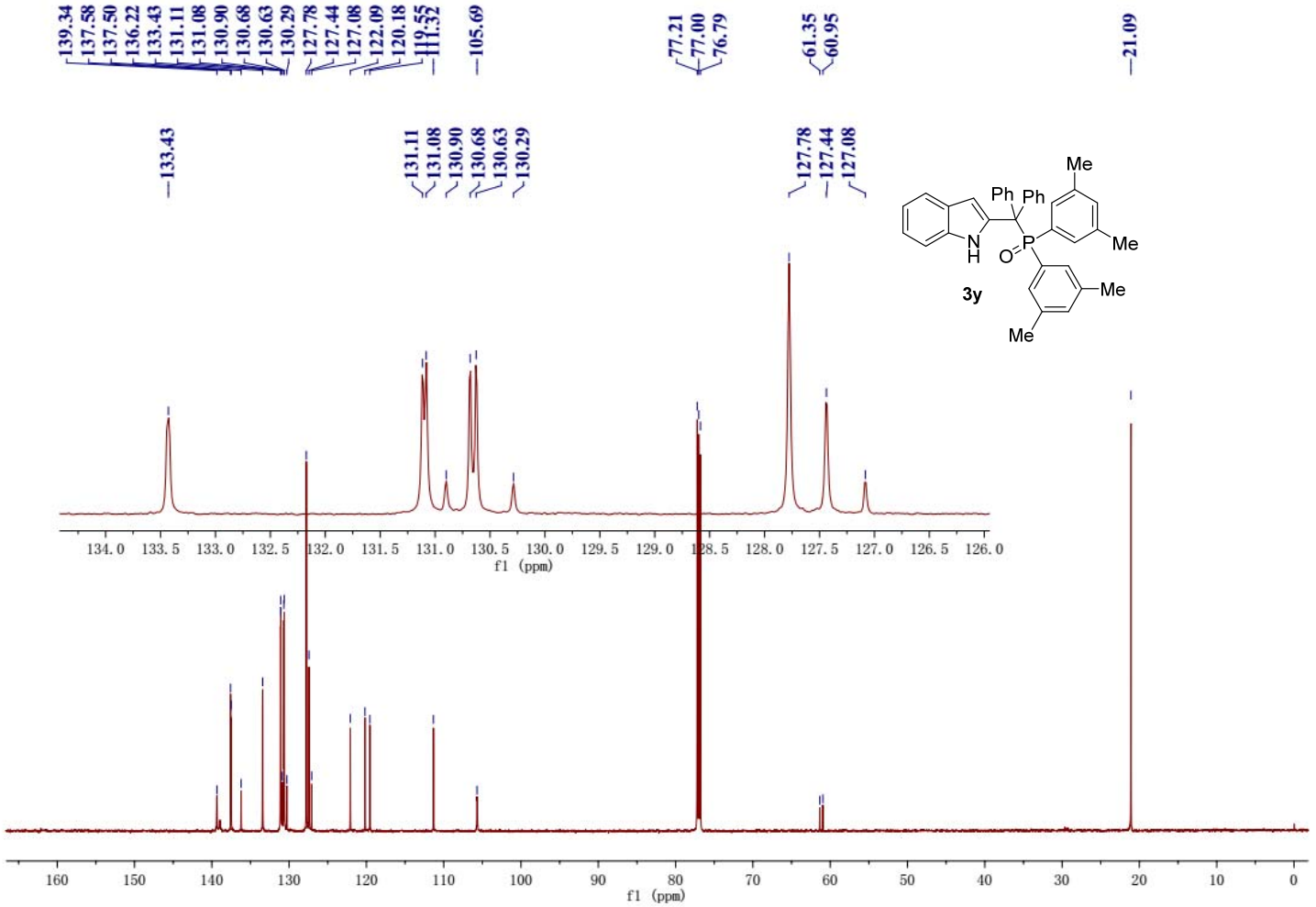

138.35
136.23
134.77
134.67
133.14
132.85
132.79
132.53
132.37
130.93
130.87
130.84
130.80
129.77
129.68
128.20
128.05
126.93
122.55
120.48
119.93
111.46
106.10
106.06
77.21
77.00
76.79
61.32
60.90
f1 (ppm)
Cl
Ph
Ph
N
H
O
P
Cl
3x

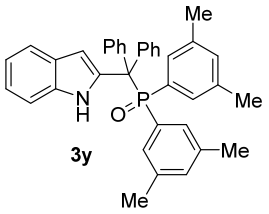

Cl
Ph
Ph
N
H
O
P
Cl

**3x**


-35.16
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

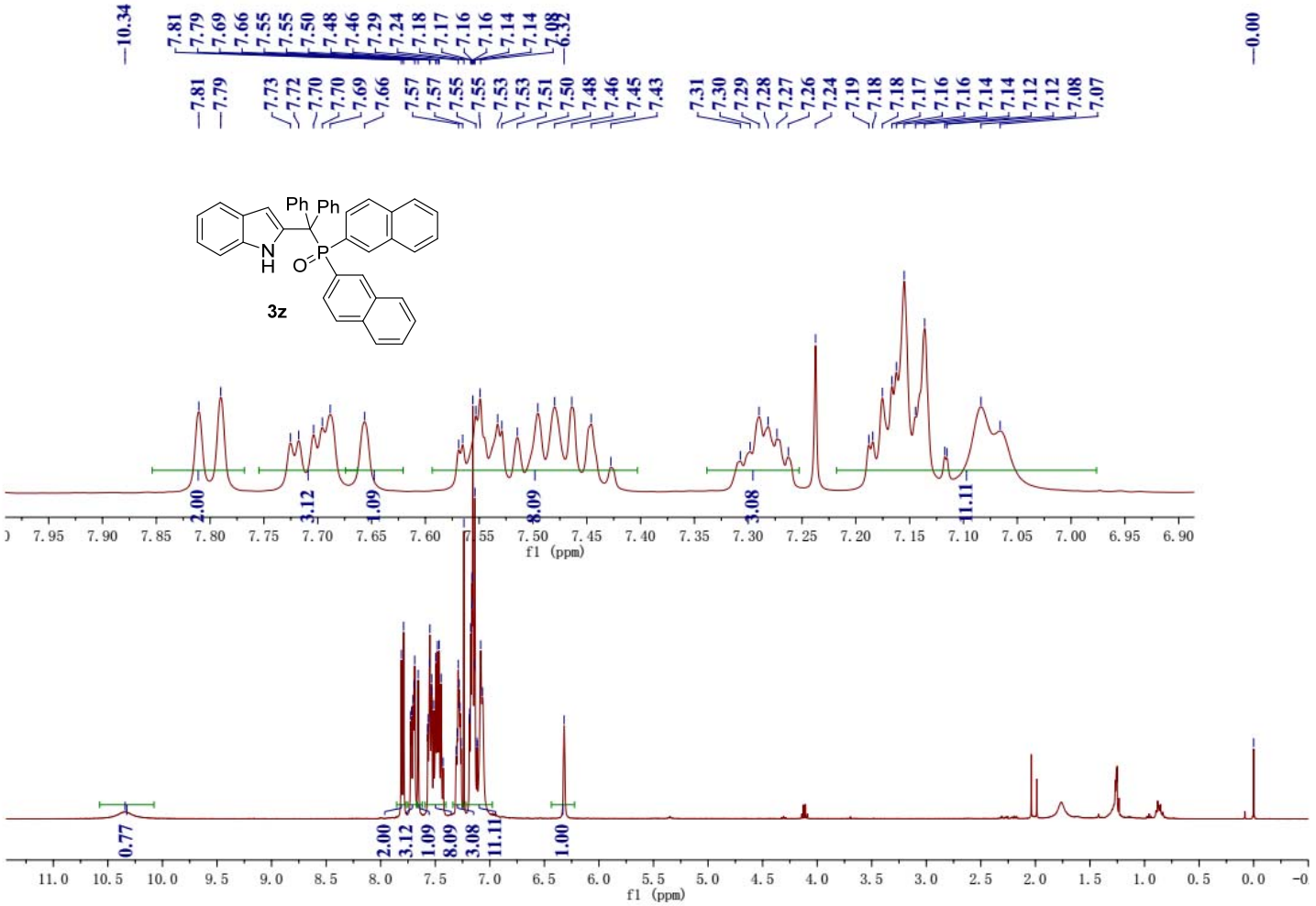

10.13
7.51
7.50
7.47
7.46
7.29
7.28
7.26
7.25
7.24
7.23
7.21
7.20
7.19
7.18
7.16
7.15
7.14
7.10
7.09
7.08
7.05
7.03
7.02
6.69
6.66
6.64
6.62
6.31
2.07
0.00
Me
Ph
Ph
N
H
O
P
Me
Me
Me
3y
1.07
1.06
2.19
1.08
4.23
1.30
2.30
4.19
4.45
f1 (ppm)
0.65
1.00

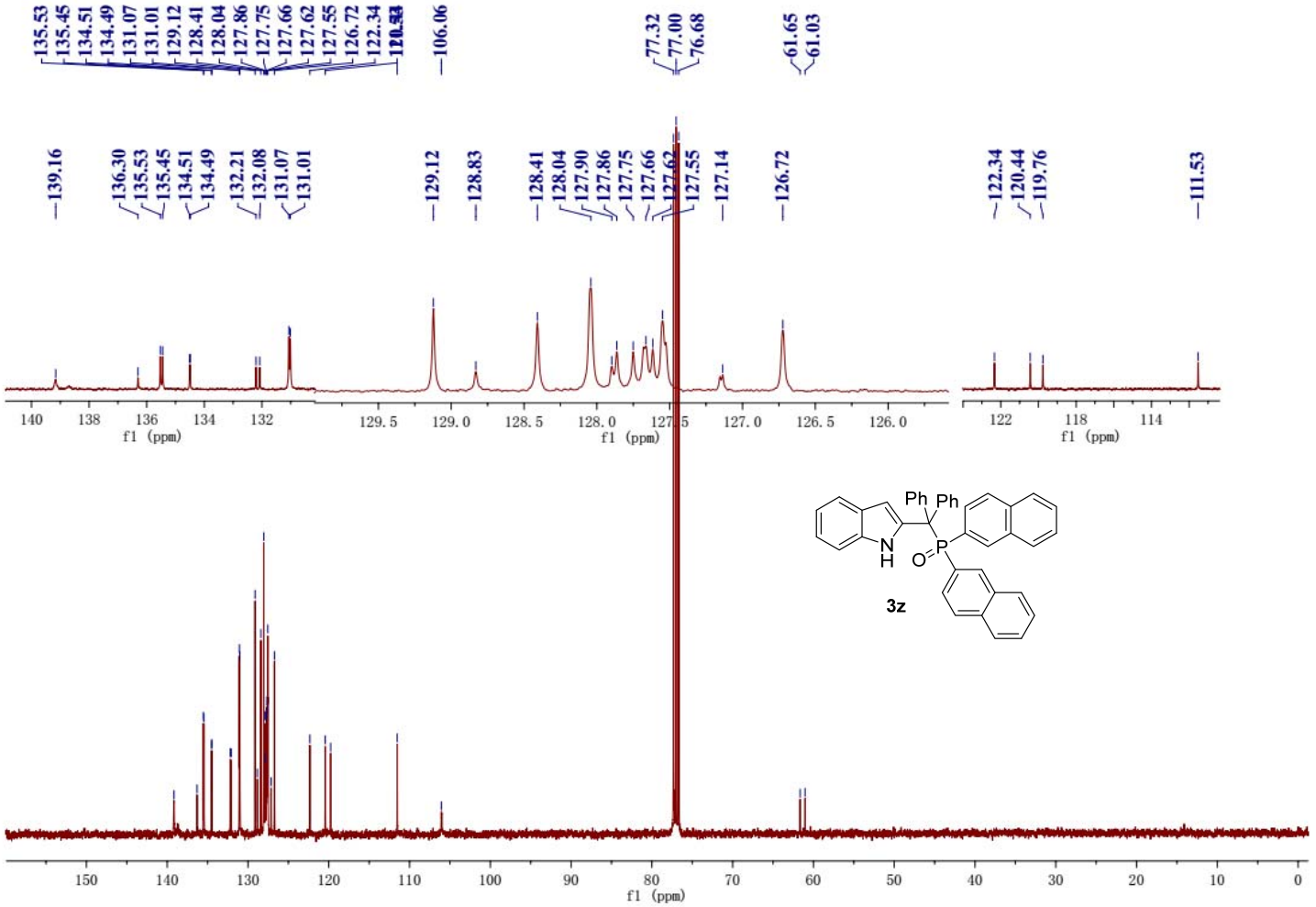

139.34
137.58
137.50
136.22
133.43
131.11
131.08
130.90
130.68
130.63
130.29
127.78
127.44
127.08
122.09
120.18
119.55
111.32
105.69
77.21
77.00
76.79
61.35
60.95
21.09
133.43
131.11
131.08
130.90
130.68
130.63
130.29
127.78
127.44
127.08
Me
Ph
Ph
Me
N
H
O
P
Me
Me
3y
134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

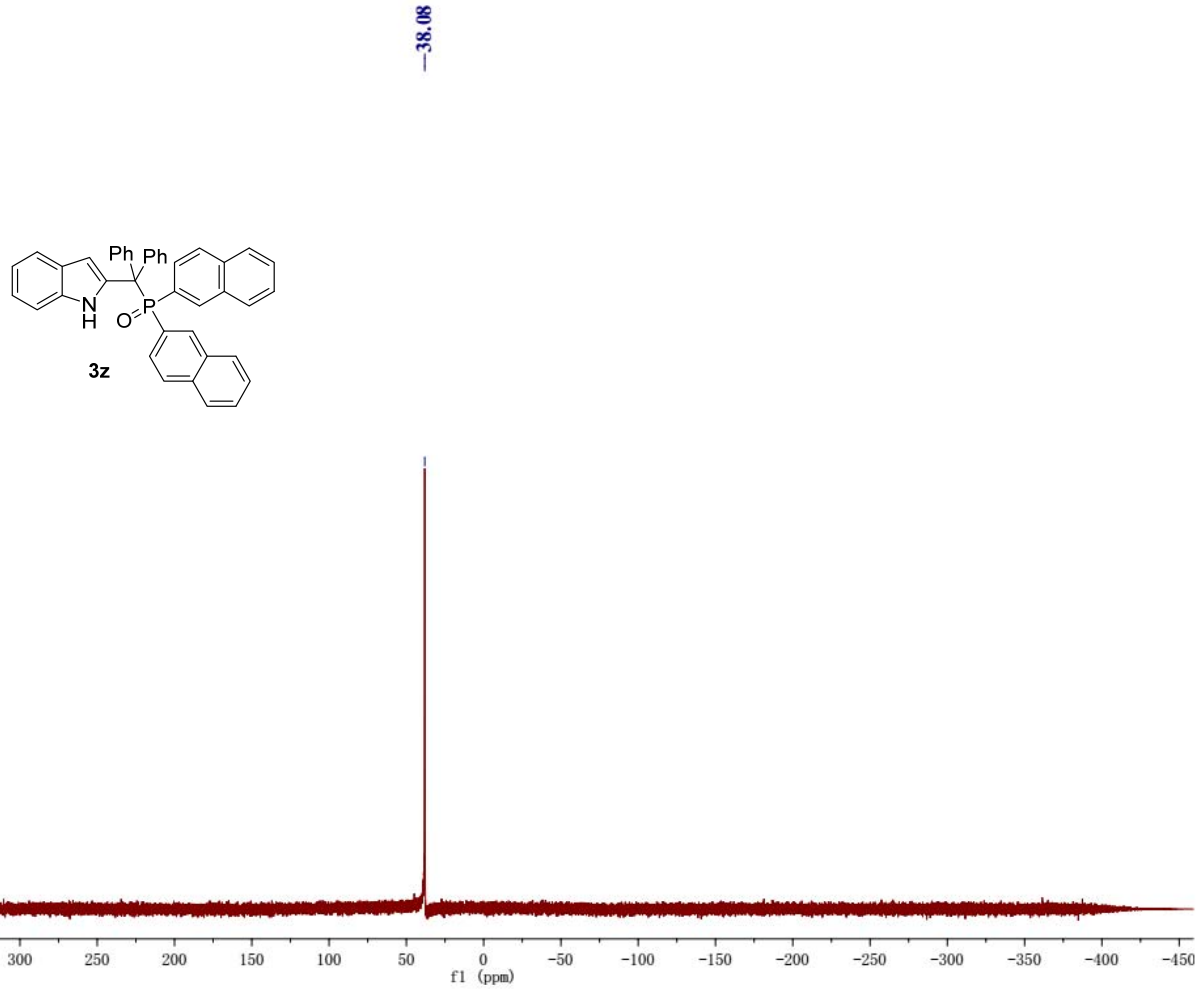

Me
Ph
Ph
N
H
O
P
Me
Me
Me

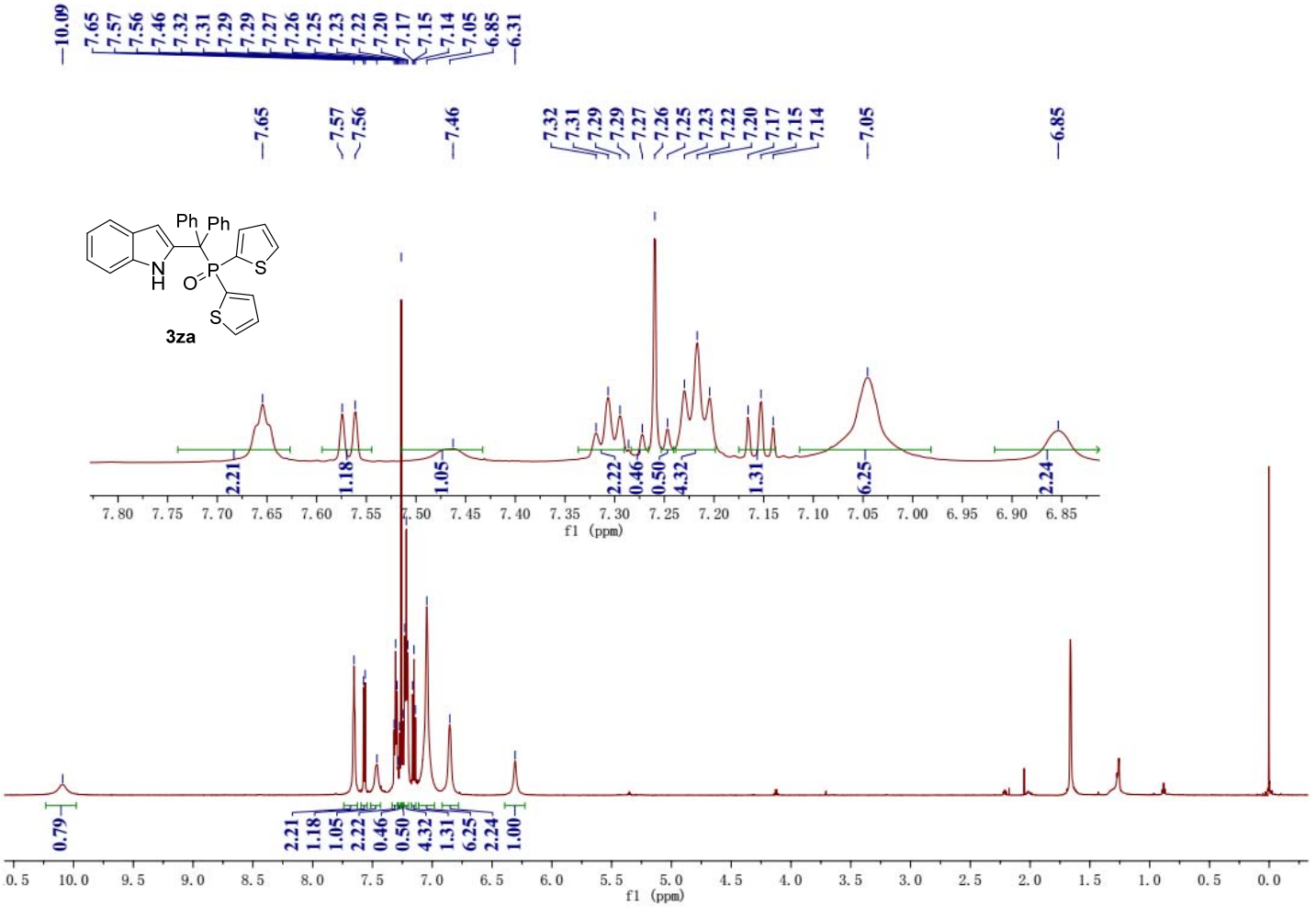
**3y**

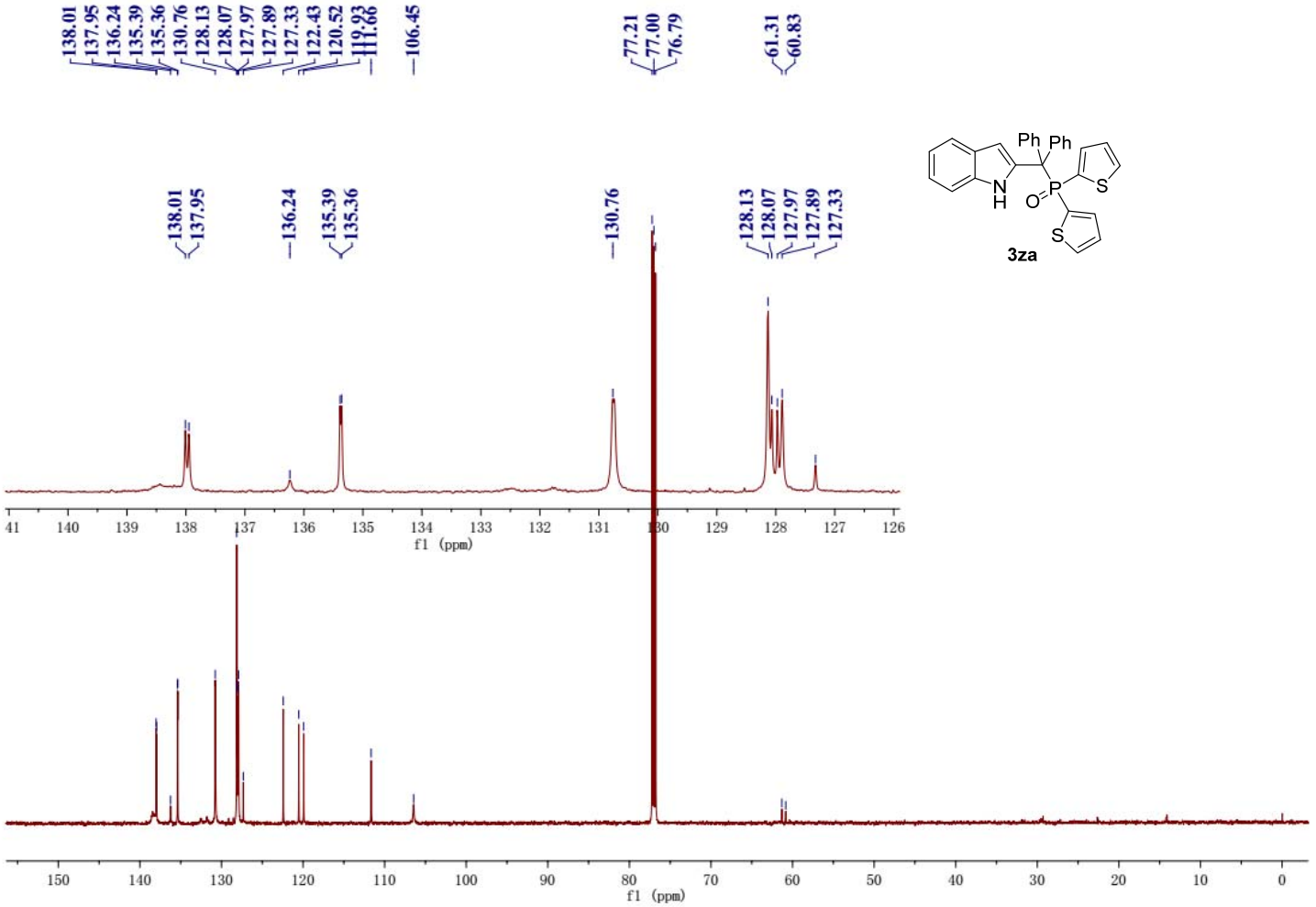

-37.97
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

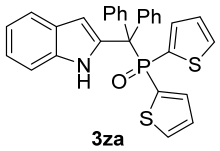

10.34
7.81
7.79
7.69
7.66
7.55
7.55
7.50
7.48
7.46
7.29
7.24
7.18
7.17
7.16
7.16
7.14
7.14
6.32
0.00
7.81
7.79
7.73
7.72
7.70
7.70
7.69
7.66
7.57
7.57
7.55
7.55
7.53
7.53
7.51
7.50
7.48
7.46
7.45
7.43
7.31
7.30
7.29
7.28
7.27
7.26
7.24
7.19
7.18
7.18
7.17
7.16
7.16
7.14
7.14
7.12
7.12
7.08
7.07
Ph
Ph
N
H
P
O
3z
2.00
3.12
1.09
8.09
3.08
11.11
f1 (ppm)
0.77
2.00
3.12
1.09
8.09
3.08
11.11
1.00
f1 (ppm)


135.53
135.45
134.51
134.49
131.07
131.01
129.12
128.41
128.04
127.86
127.75
127.66
127.62
127.55
126.72
122.34
106.06
77.32
77.00
76.68
61.65
61.03
139.16
136.30
135.53
135.45
134.51
134.49
132.21
132.08
131.07
131.01
129.12
128.83
128.41
128.04
127.90
127.86
127.75
127.66
127.62
127.55
127.14
126.72
122.34
120.44
119.76
111.53
f1 (ppm)
Ph
Ph
N
H
O
P
3z


38.08
Ph
Ph
N
H
O
P
3z
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

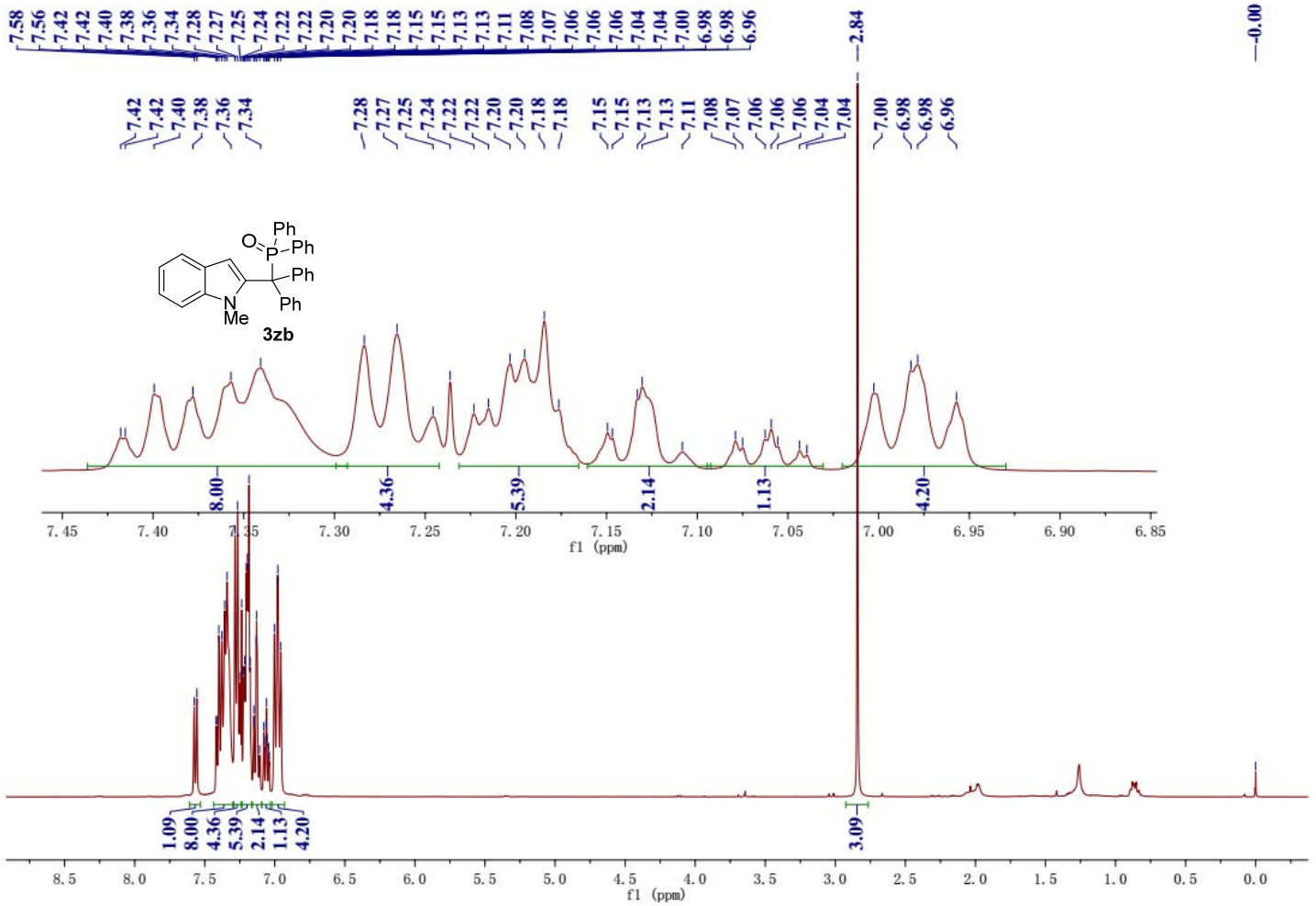

10.09
7.65
7.57
7.56
7.46
7.32
7.31
7.29
7.29
7.27
7.26
7.25
7.23
7.22
7.20
7.17
7.15
7.14
7.05
6.85
6.31
Ph
Ph
N
H
O
P
S
S
3za
2.21
1.18
1.05
2.22
0.46
0.50
4.32
1.31
6.25
2.24
f1 (ppm)
0.79
2.21
1.18
1.05
2.22
0.46
0.50
4.32
1.31
6.25
2.24
1.00
f1 (ppm)

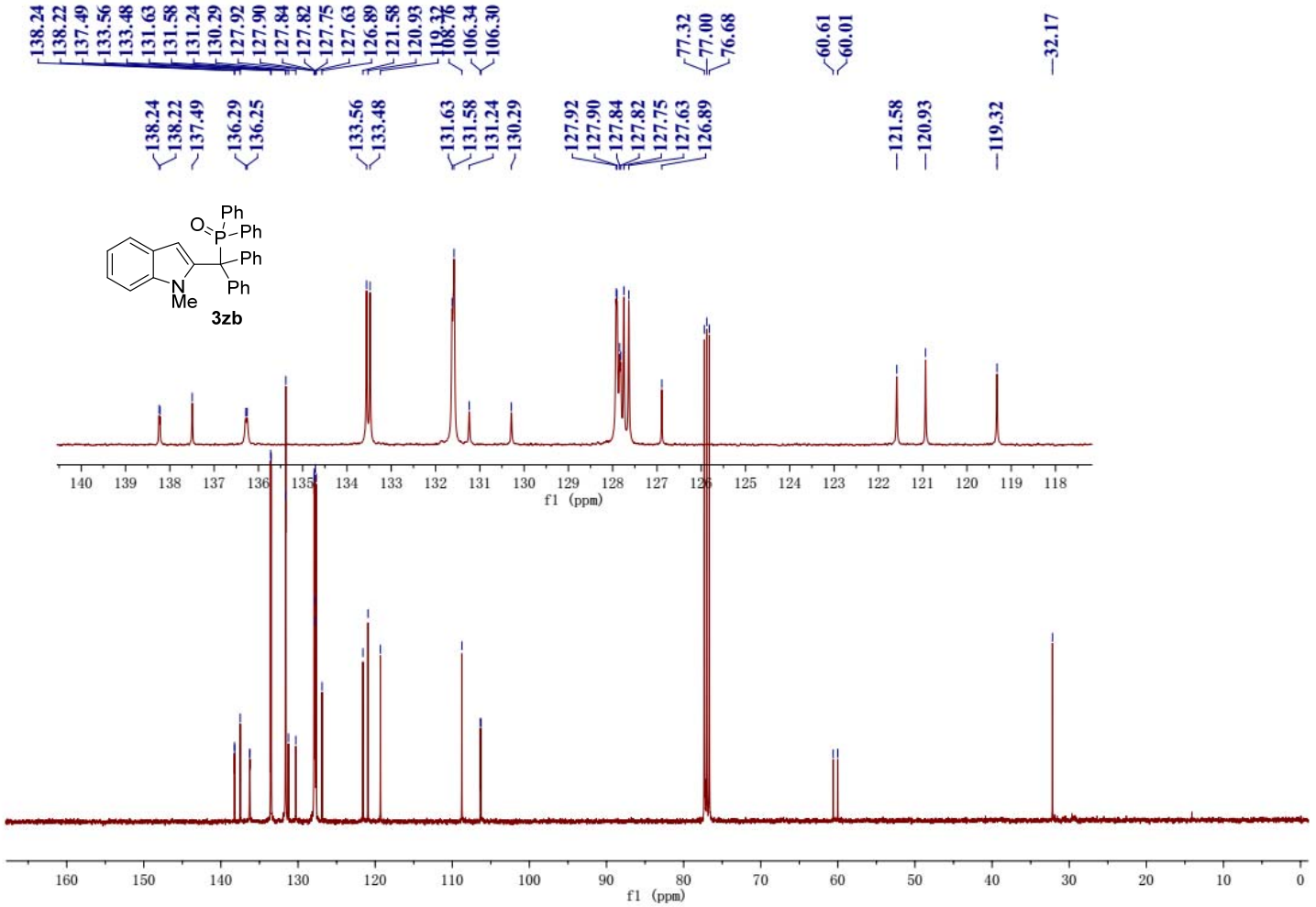

138.01
137.95
136.24
135.39
135.36
130.76
128.13
128.07
127.97
127.89
127.33
122.43
120.52
119.93
111.66
106.45
77.21
77.00
76.79
61.31
60.83
Ph
Ph
N
H
O
P
S
S
3za
f1 (ppm)
f1 (ppm)

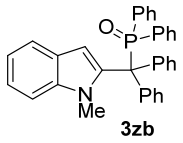

Ph
Ph
N
H
O
P
S
S

**3za**


29.87
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

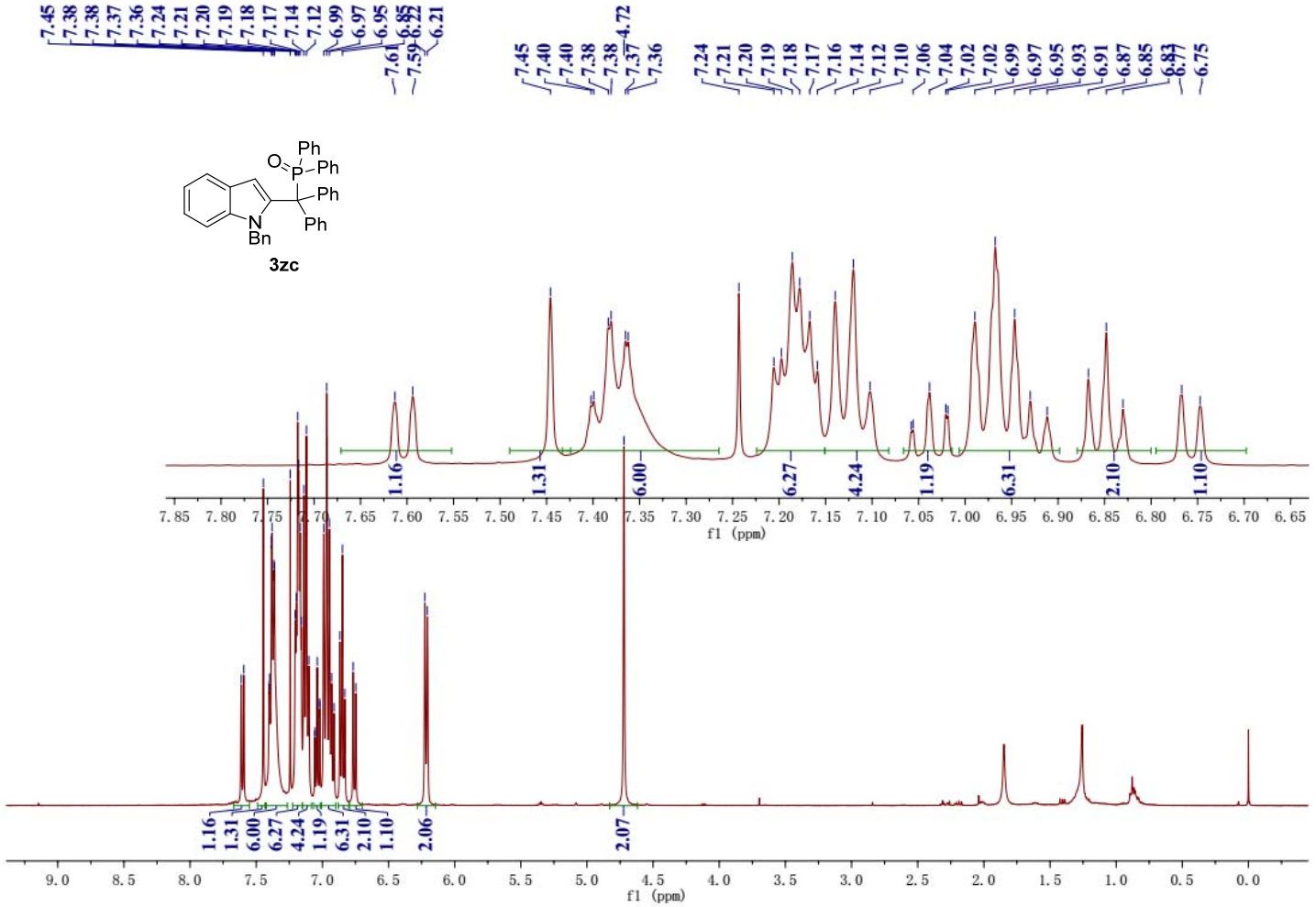

7.58 7.56 7.42 7.42 7.40 7.38 7.36 7.34 7.28 7.27 7.25 7.24 7.22 7.22 7.20 7.20 7.18 7.18 7.15 7.15 7.13 7.13 7.11 7.08 7.07 7.06 7.06 7.06 7.04 7.04 7.00 6.98 6.98 6.96
2.84
0.00
7.42 7.42 7.40 7.38 7.36 7.34 7.28 7.27 7.25 7.24 7.22 7.22 7.20 7.20 7.18 7.18 7.15 7.15 7.13 7.13 7.11 7.08 7.07 7.06 7.06 7.06 7.04 7.04 7.00 6.98 6.98 6.96
Ph
O
P
Ph
Ph
Ph
N
Me
3zb
8.00 4.36 5.39 2.14 1.13 4.20
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)
1.09 8.00 4.36 5.39 2.14 1.13 4.20
3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

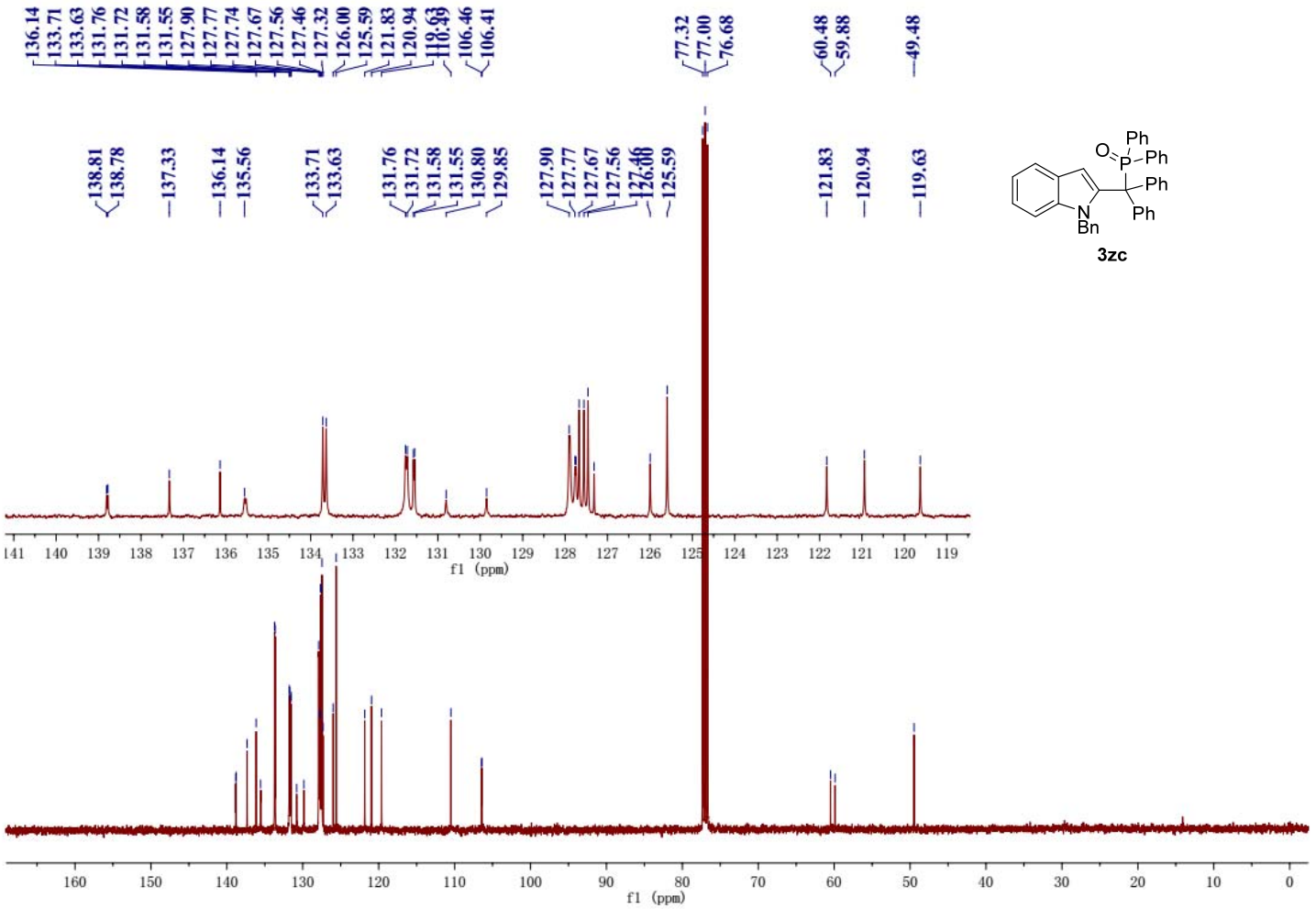

138.24
138.22
137.49
133.56
133.48
131.63
131.58
131.24
130.29
127.92
127.90
127.84
127.82
127.75
127.63
126.89
121.58
120.93
119.32
108.76
106.34
106.30
77.32
77.00
76.68
60.61
60.01
32.17
Ph
O
P
Ph
Ph
Ph
N
Me
3zb
f1 (ppm)
f1 (ppm)

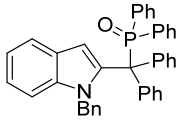

Ph
O
P
Ph
Ph
Ph
N
Me

**3zb**


34.36
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

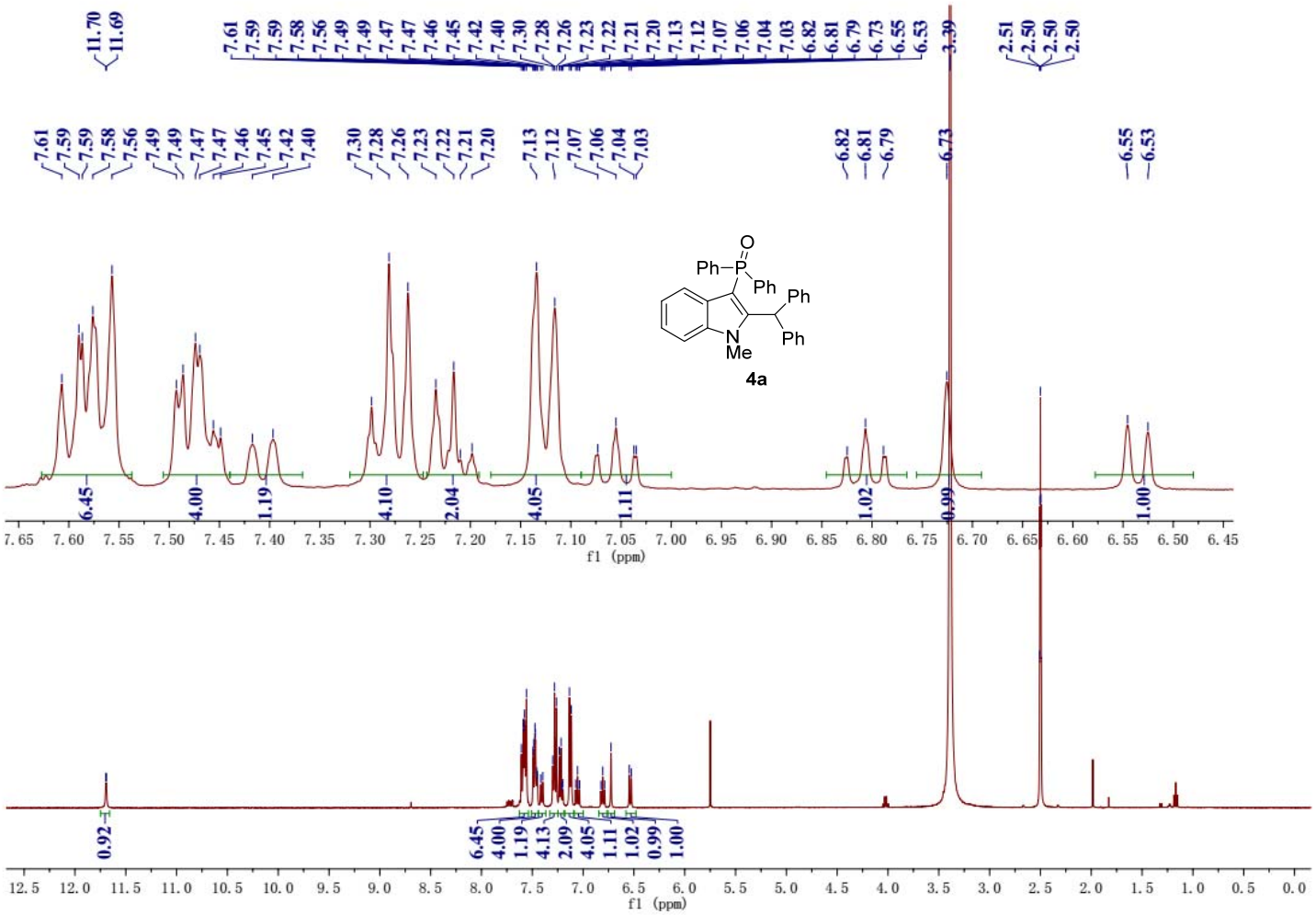

7.45 7.38 7.38 7.37 7.36 7.24 7.21 7.20 7.19 7.18 7.17 7.14 7.12 6.99 6.97 6.95 7.61 7.59 6.22 6.21
7.45 7.40 7.40 7.38 7.38 7.37 4.72 7.36
7.24 7.21 7.20 7.19 7.18 7.17 7.16 7.14 7.12 7.10 7.06 7.04 7.02 7.02 6.99 6.97 6.95 6.93 6.91 6.87 6.85 6.83 6.77 6.75
Ph
O
P
Ph
Ph
Ph
N
Bn
3zc
1.16 1.31 6.00 6.27 4.24 1.19 6.31 2.10 1.10
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65
f1 (ppm)
1.16 1.31 6.00 6.27 4.24 1.19 6.31 2.10 1.10 2.06 2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

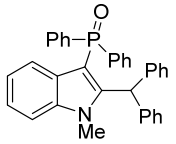

136.14
133.71
133.63
131.76
131.72
131.58
131.55
127.90
127.77
127.74
127.67
127.56
127.46
127.32
126.00
125.59
121.83
120.94
118.63
110.49
106.46
106.41
77.32
77.00
76.68
60.48
59.88
49.48
138.81
138.78
137.33
136.14
135.56
133.71
133.63
131.76
131.72
131.58
131.55
130.80
129.85
127.90
127.77
127.67
127.56
127.46
126.00
125.59
121.83
120.94
119.63
f1 (ppm)
f1 (ppm)
Ph
O
P
Ph
Ph
Ph
N
Bn
3zc


Ph
O
P
Ph
Ph
N
Bn
Ph

**3zc**

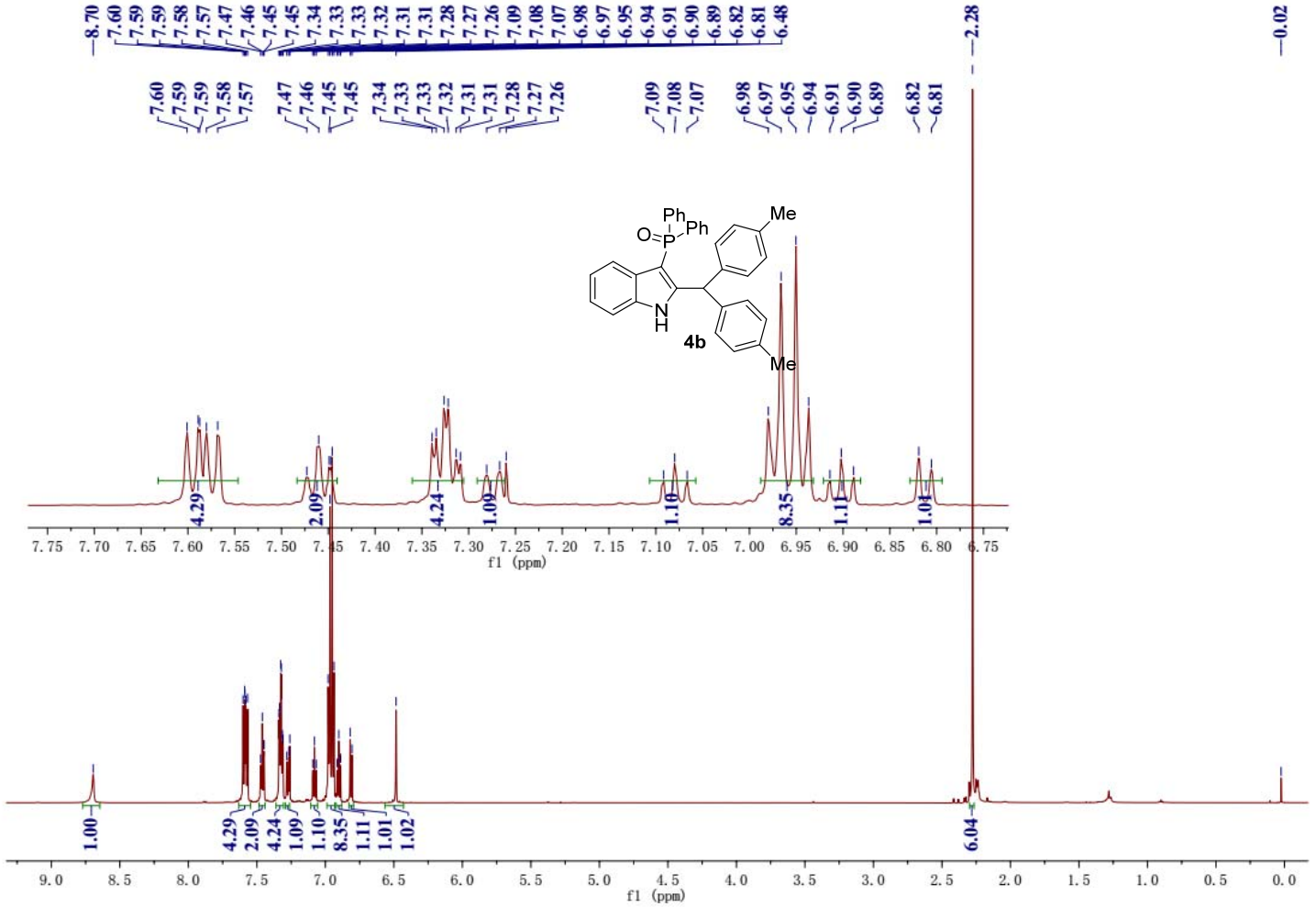

34.70
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

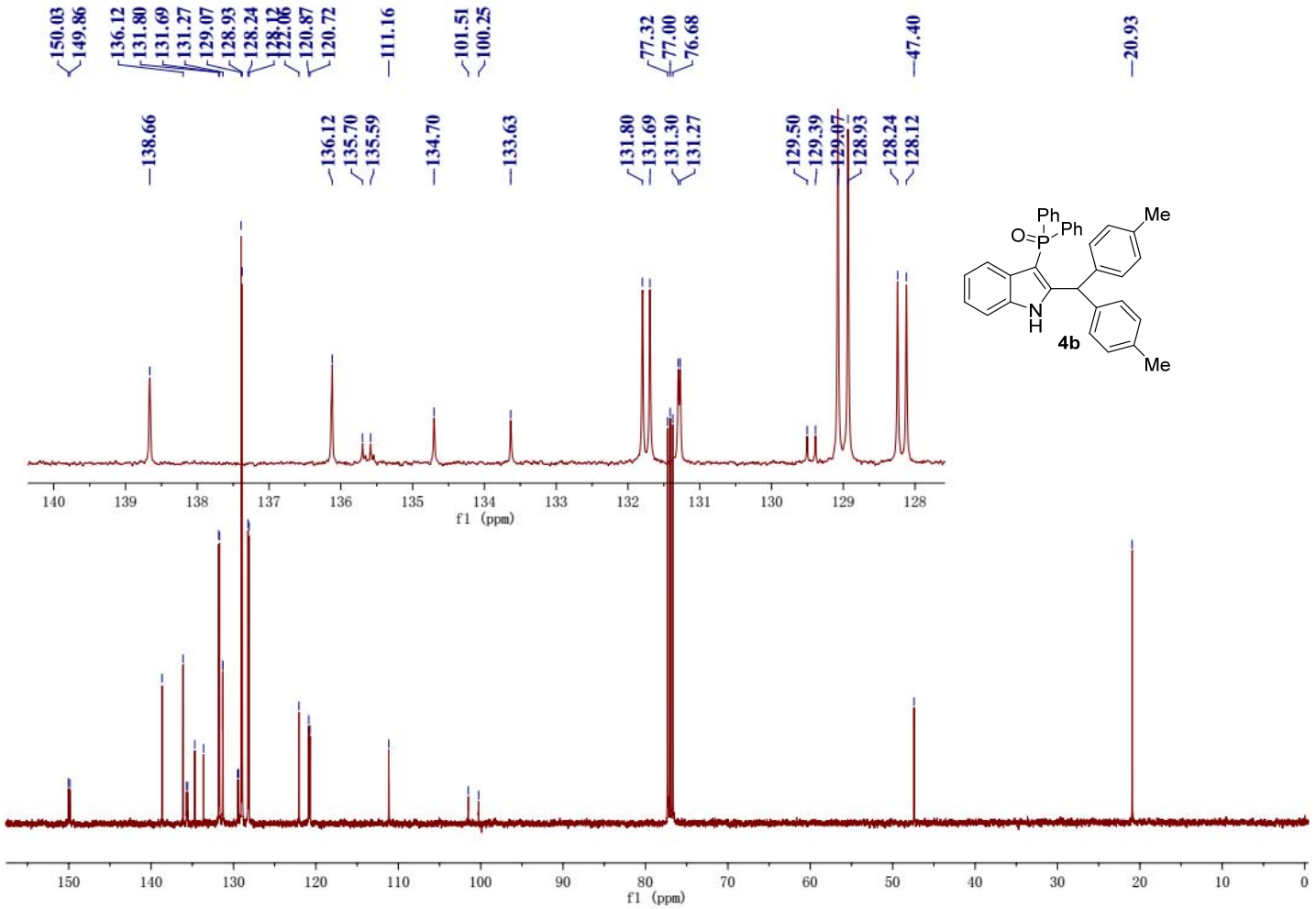

11.70
11.69
7.61
7.59
7.59
7.58
7.56
7.49
7.49
7.47
7.47
7.46
7.45
7.42
7.40
7.30
7.28
7.26
7.23
7.22
7.21
7.20
7.13
7.12
7.07
7.06
7.04
7.03
6.82
6.81
6.79
6.73
6.55
6.53
3.39
2.51
2.50
2.50
2.50
Ph
P
O
Ph
Ph
Ph
N
Me
4a
6.45
4.00
1.19
4.10
2.04
4.05
1.11
1.02
0.99
1.00
f1 (ppm)
0.92
6.45
4.00
1.19
4.13
2.09
4.05
1.11
1.02
0.99
1.00
f1 (ppm)

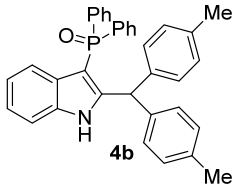

O
Ph
P
Ph
Ph
Ph
N
Me

**4a**


22.12
27.5
27.0
26.5
26.0
25.5
25.0
24.5
24.0
23.5
23.0
22.5
22.0
21.5
21.0
20.5
20.0
19.5
f1 (ppm)

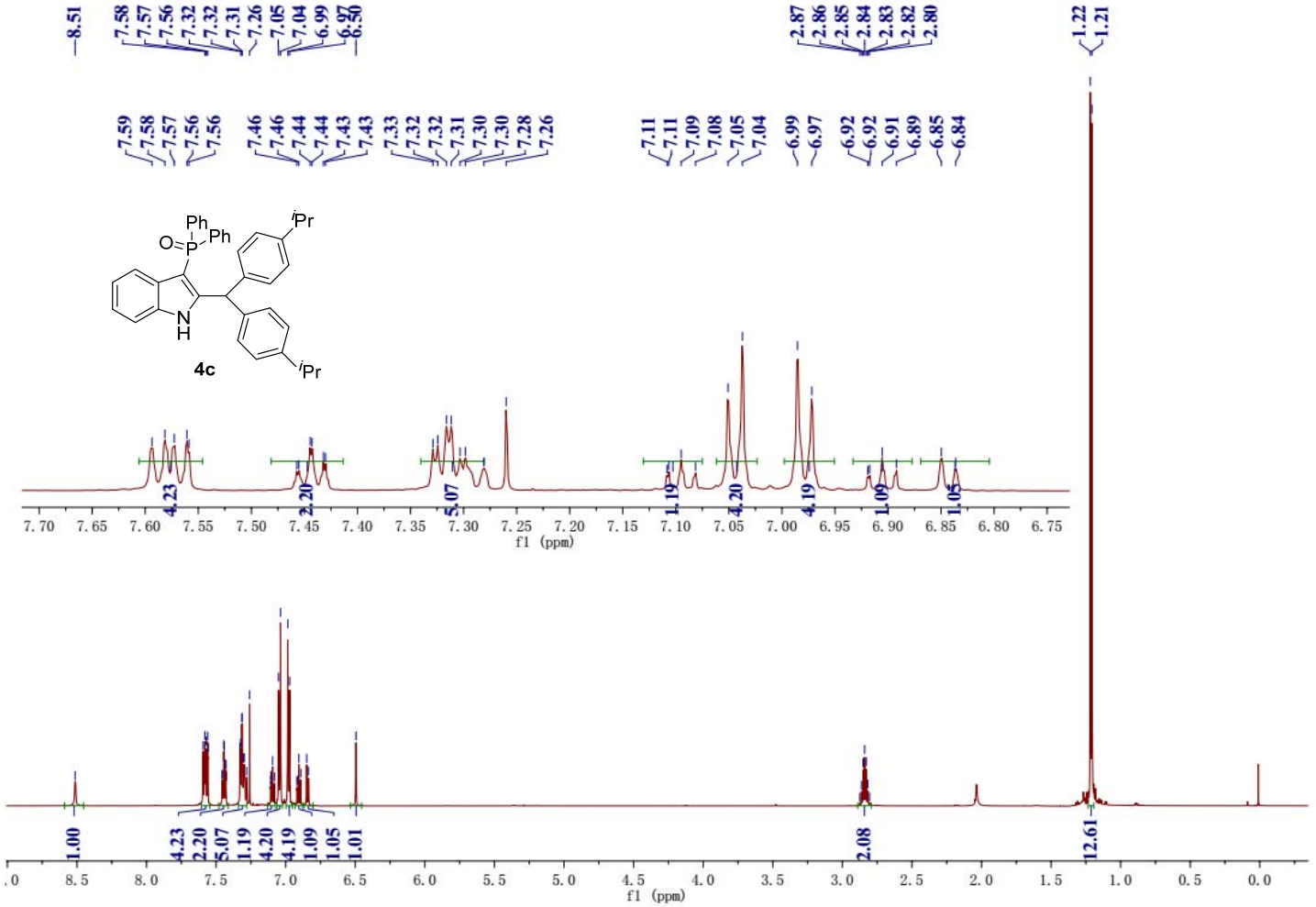

8.70
7.60
7.59
7.59
7.58
7.57
7.47
7.46
7.45
7.45
7.34
7.33
7.33
7.32
7.31
7.31
7.28
7.27
7.26
7.09
7.08
7.07
6.98
6.97
6.95
6.94
6.91
6.90
6.89
6.82
6.81
6.48
2.28
0.02
Ph
Ph
O
P
Me
N
H
Me
4b
4.29
2.09
4.24
1.09
1.10
8.35
1.11
1.01
f1 (ppm)
1.00
4.29
2.09
4.24
1.09
1.10
8.35
1.11
1.01
1.02
6.04
f1 (ppm)

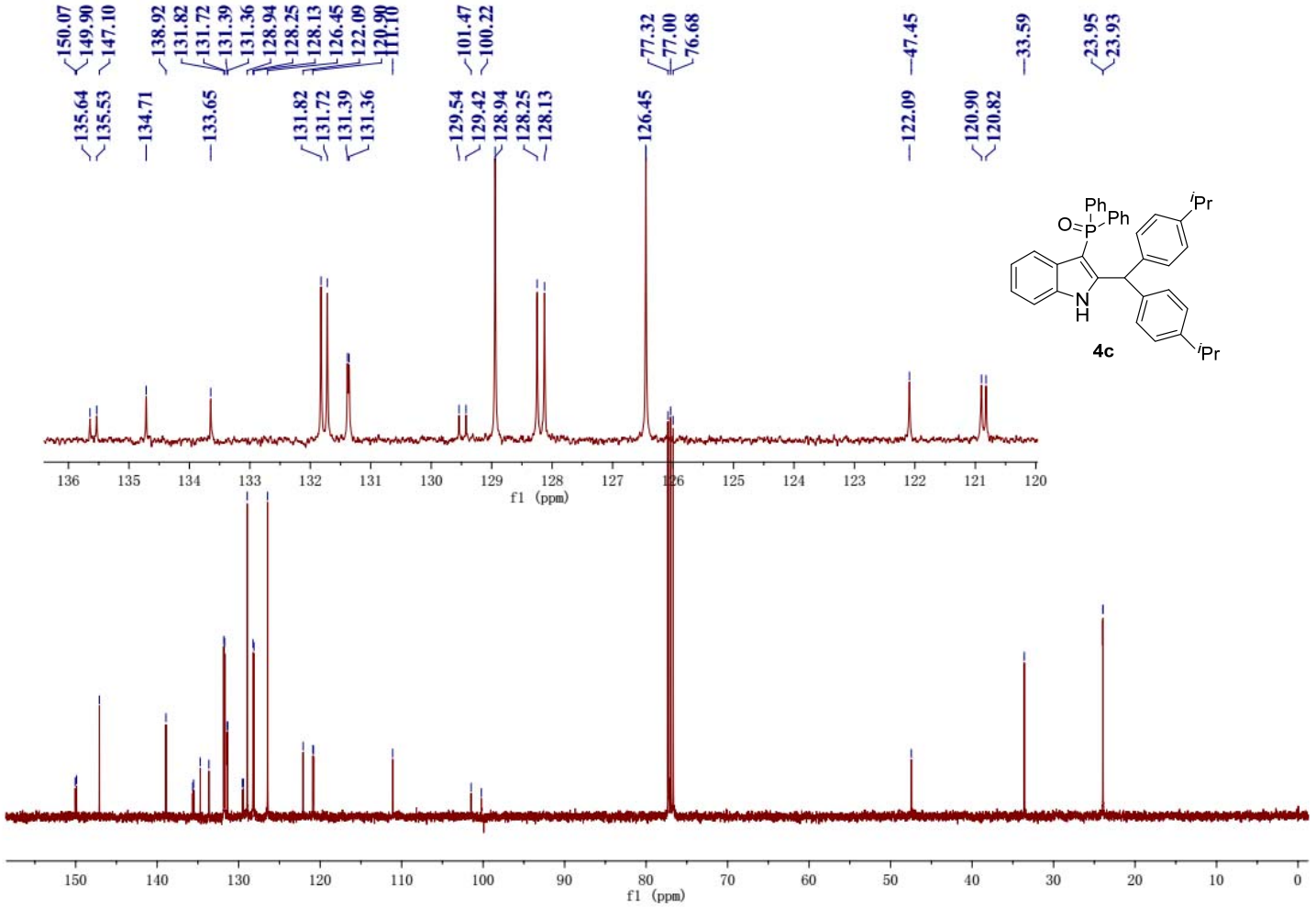

150.03
149.86
136.12
131.80
131.69
131.27
129.07
128.93
128.24
120.87
120.72
111.16
101.51
100.25
77.32
77.00
76.68
47.40
20.93
138.66
136.12
135.70
135.59
134.70
133.63
131.80
131.69
131.30
131.27
129.50
129.39
129.07
128.93
128.24
128.12
Ph
Ph
O
P
Me
N
H
Me
4b
f1 (ppm)
f1 (ppm)

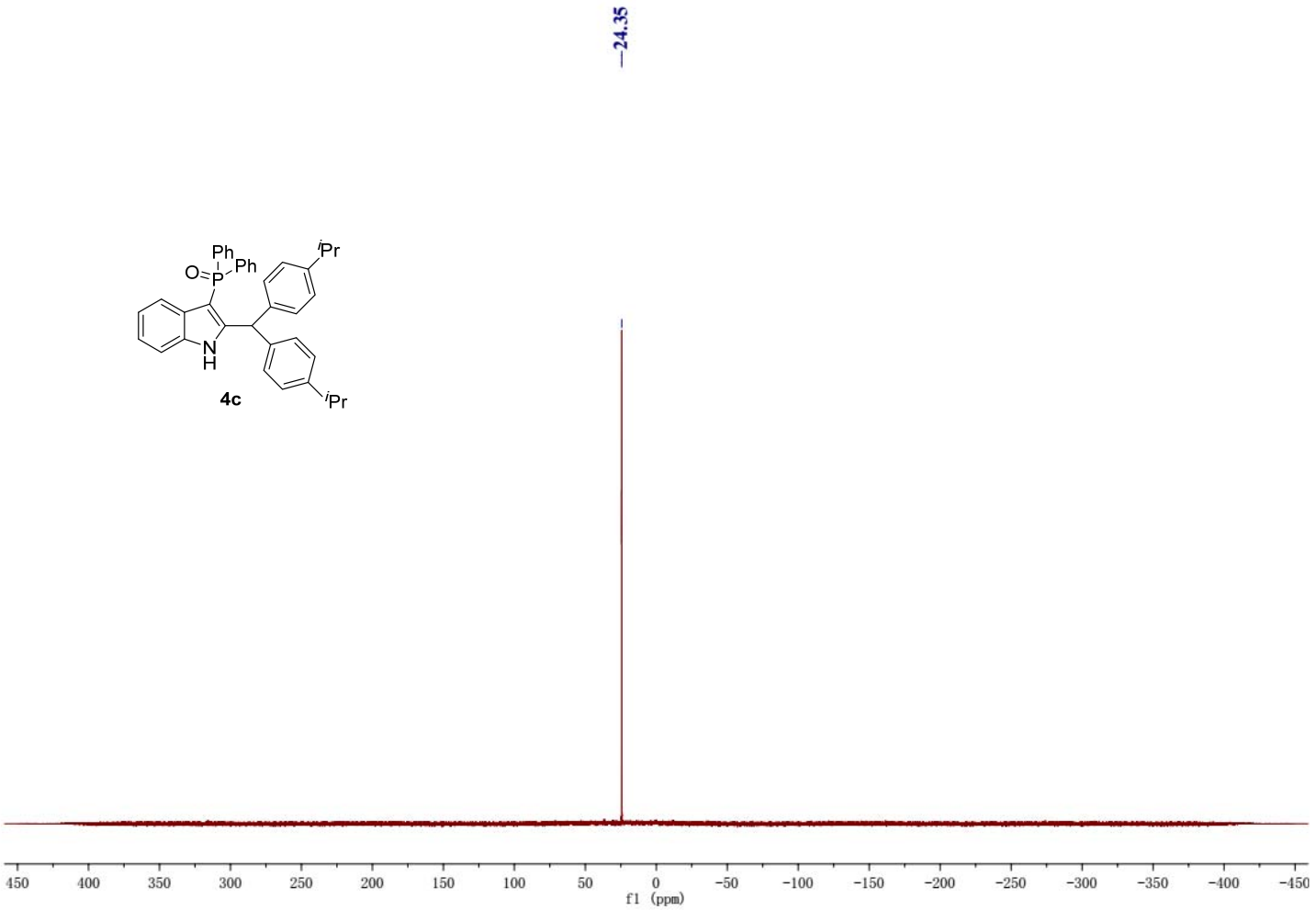

Ph
Ph
O
P
Me
N
H
Me

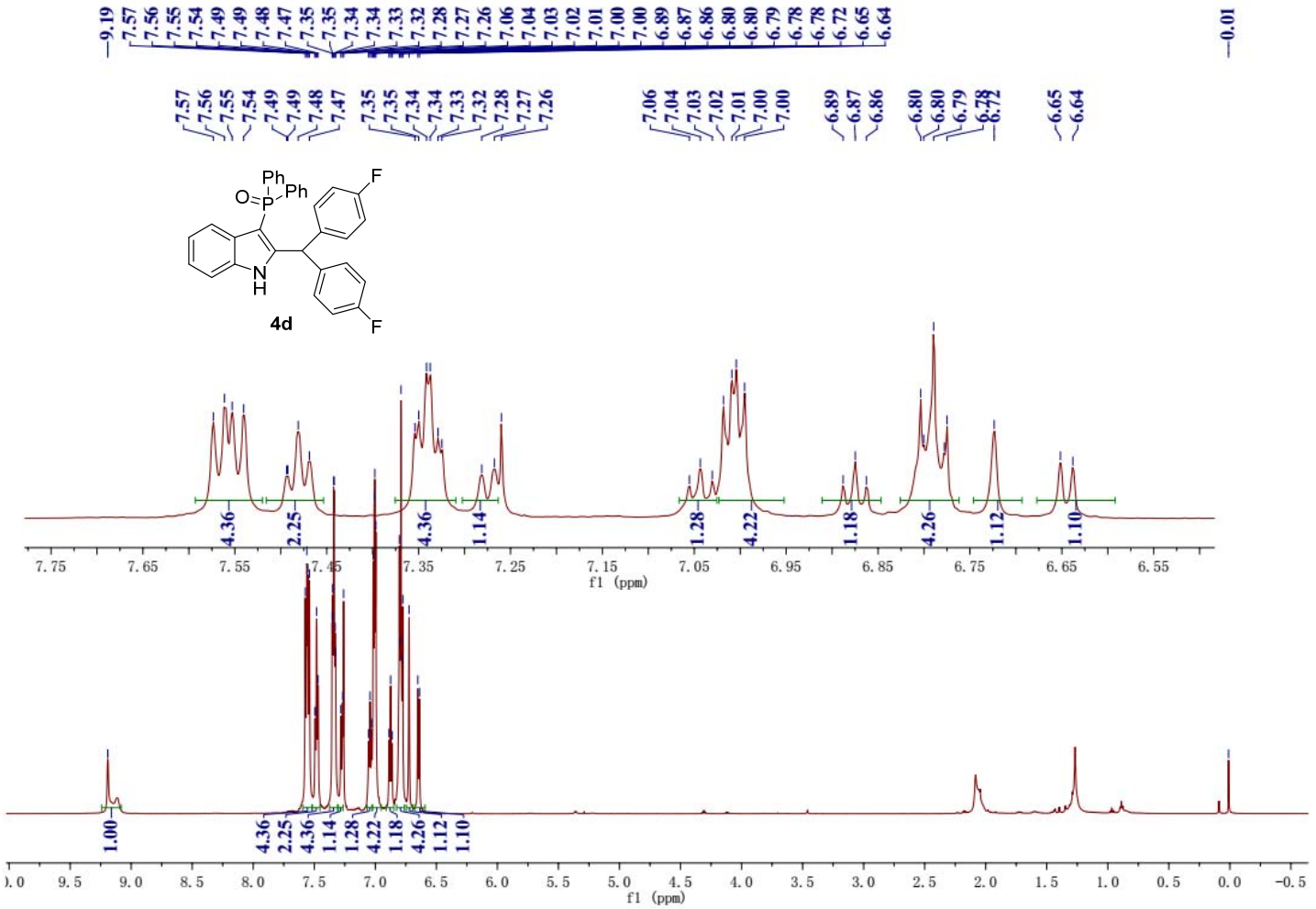
**4b**

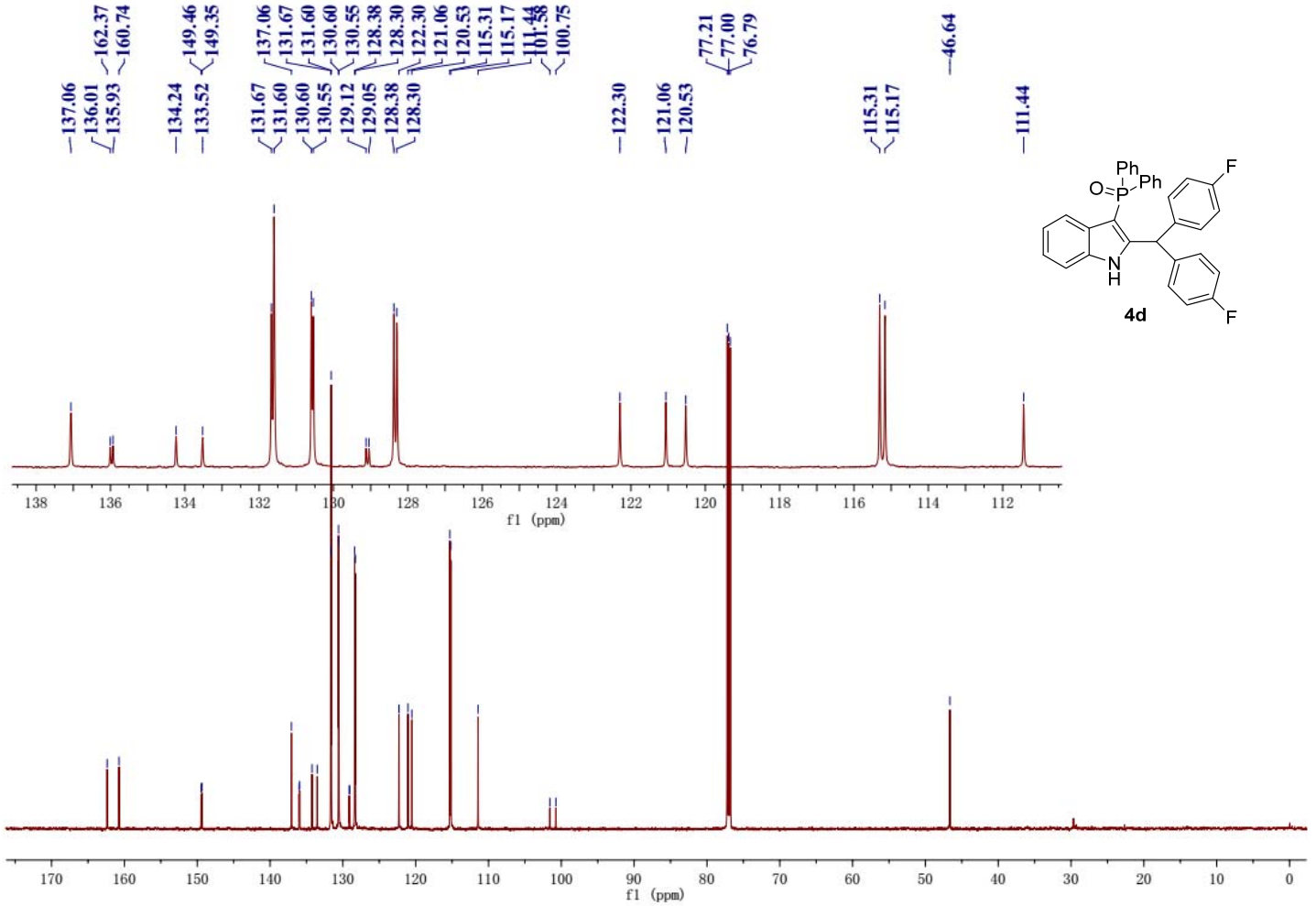

24.19
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

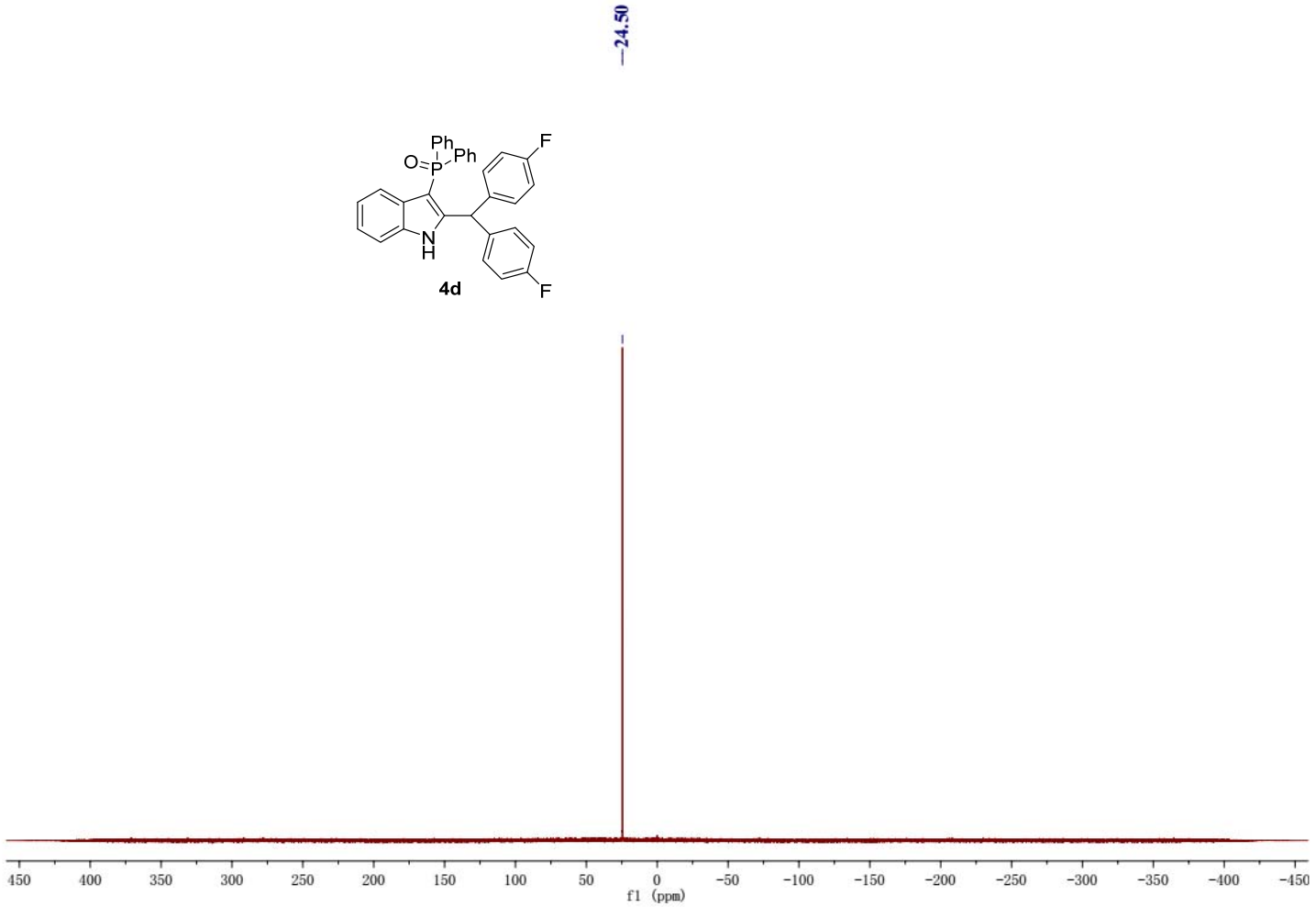

8.51
7.58
7.57
7.56
7.32
7.32
7.31
7.26
7.05
7.04
6.99
6.97
6.50
2.87
2.86
2.85
2.84
2.83
2.82
2.80
1.22
1.21
Ph
Ph
O
P
iPr
N
H
iPr
4c
4.23
2.20
5.07
1.19
4.20
4.19
1.09
1.05
1.01
2.08
12.61
f1 (ppm)

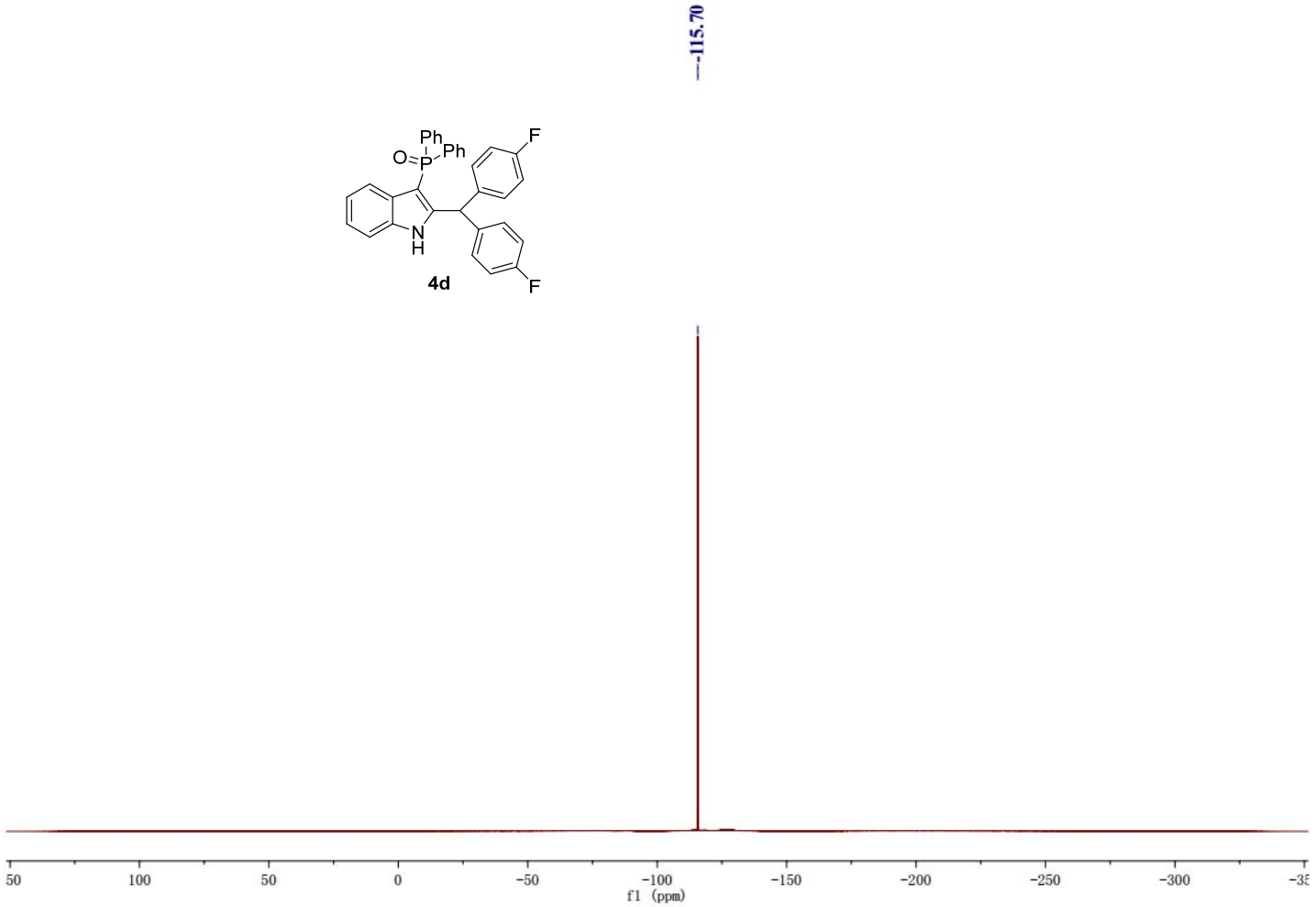

150.07
149.90
147.10
138.92
131.82
131.72
131.39
131.36
128.94
128.25
128.13
126.45
122.09
120.90
111.10
101.47
100.22
77.32
77.00
76.68
47.45
33.59
23.95
23.93
135.64
135.53
134.71
133.65
131.82
131.72
131.39
131.36
129.54
129.42
128.94
128.25
128.13
126.45
122.09
120.90
120.82
Ph
Ph
O
P
N
H
iPr
iPr
4c
f1 (ppm)
f1 (ppm)

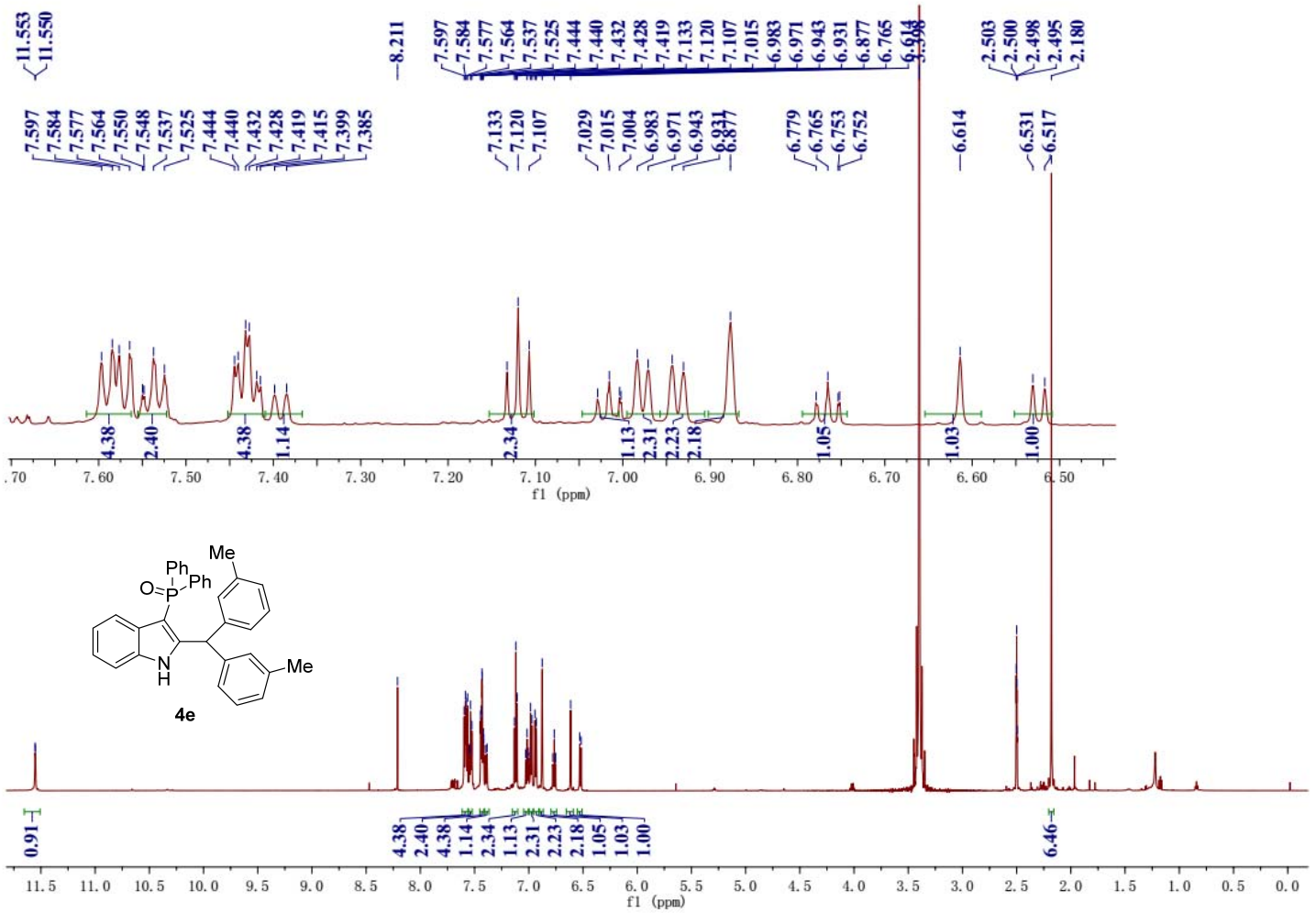

24.35
Ph
Ph
O
P
N
H
iPr
iPr
4c
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

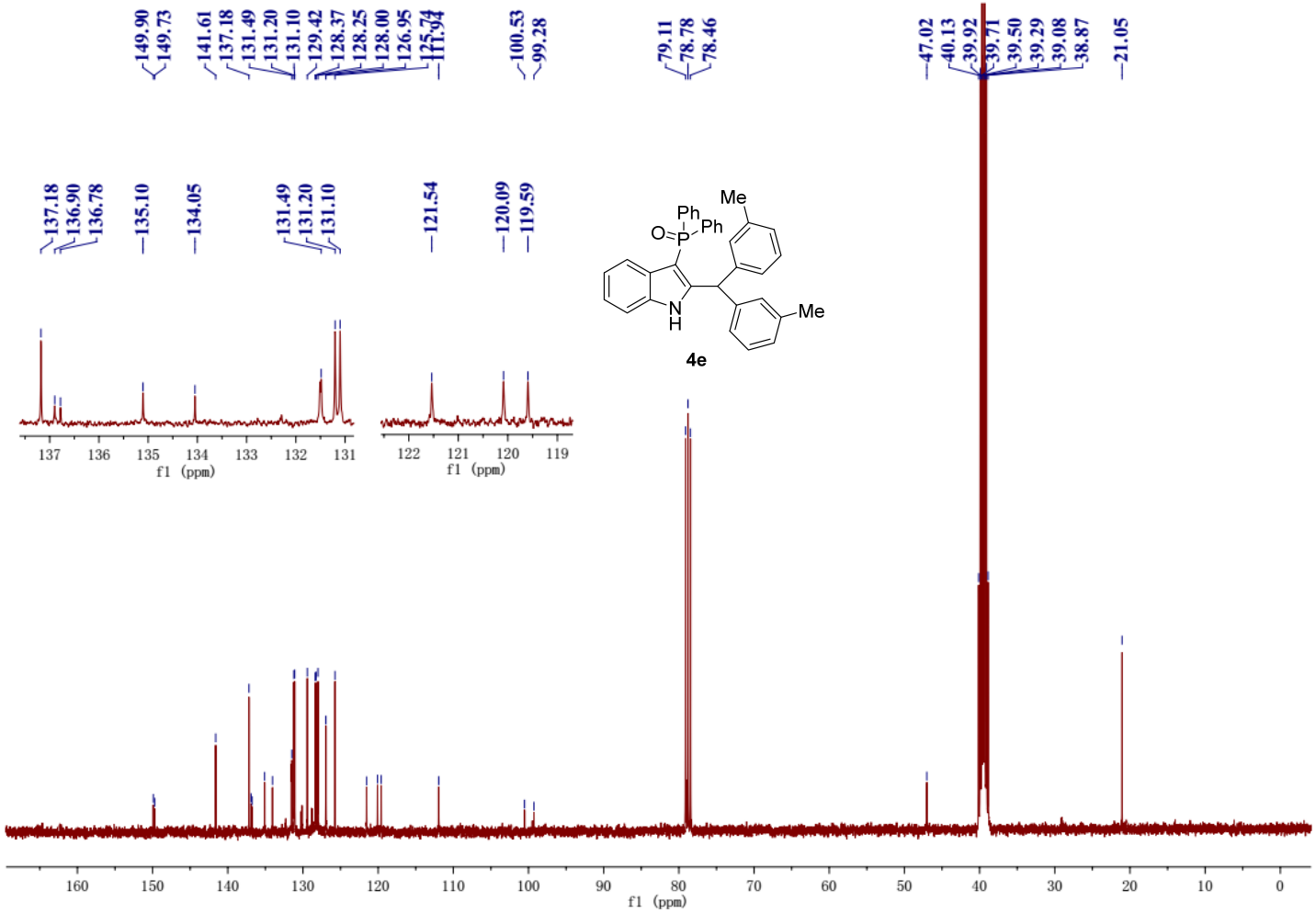

9.19
7.57
7.56
7.55
7.54
7.49
7.49
7.48
7.47
7.35
7.35
7.34
7.34
7.33
7.32
7.28
7.27
7.26
7.06
7.04
7.03
7.02
7.01
7.00
7.00
6.89
6.87
6.86
6.80
6.80
6.79
6.78
6.72
6.65
6.64
0.01
Ph
Ph
O
P
F
N
H
F
4d
4.36
2.25
4.36
1.14
1.28
4.22
1.18
4.26
1.12
1.10
f1 (ppm)
1.00
4.36
2.25
4.36
1.14
1.28
4.22
1.18
4.26
1.12
1.10
f1 (ppm)

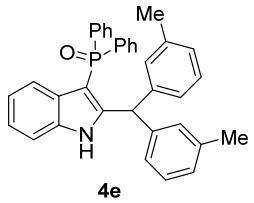

137.06
136.01
135.93
162.37
160.74
134.24
133.52
149.46
149.35
131.67
131.60
130.60
130.55
129.12
129.05
128.38
128.30
137.06
131.67
131.60
131.60
130.60
130.55
128.38
128.30
122.30
122.30
121.06
120.53
120.53
115.31
115.17
115.31
115.17
111.44
101.58
100.75
77.21
77.00
76.79
46.64
111.44
Ph
Ph
O
P
N
H
F
F
4d
f1 (ppm)
f1 (ppm)


24.50
Ph
Ph
O
P
F
N
H
F
4d
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


-115.70
Ph
Ph
O
P
F
N
H
F
4d
50
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

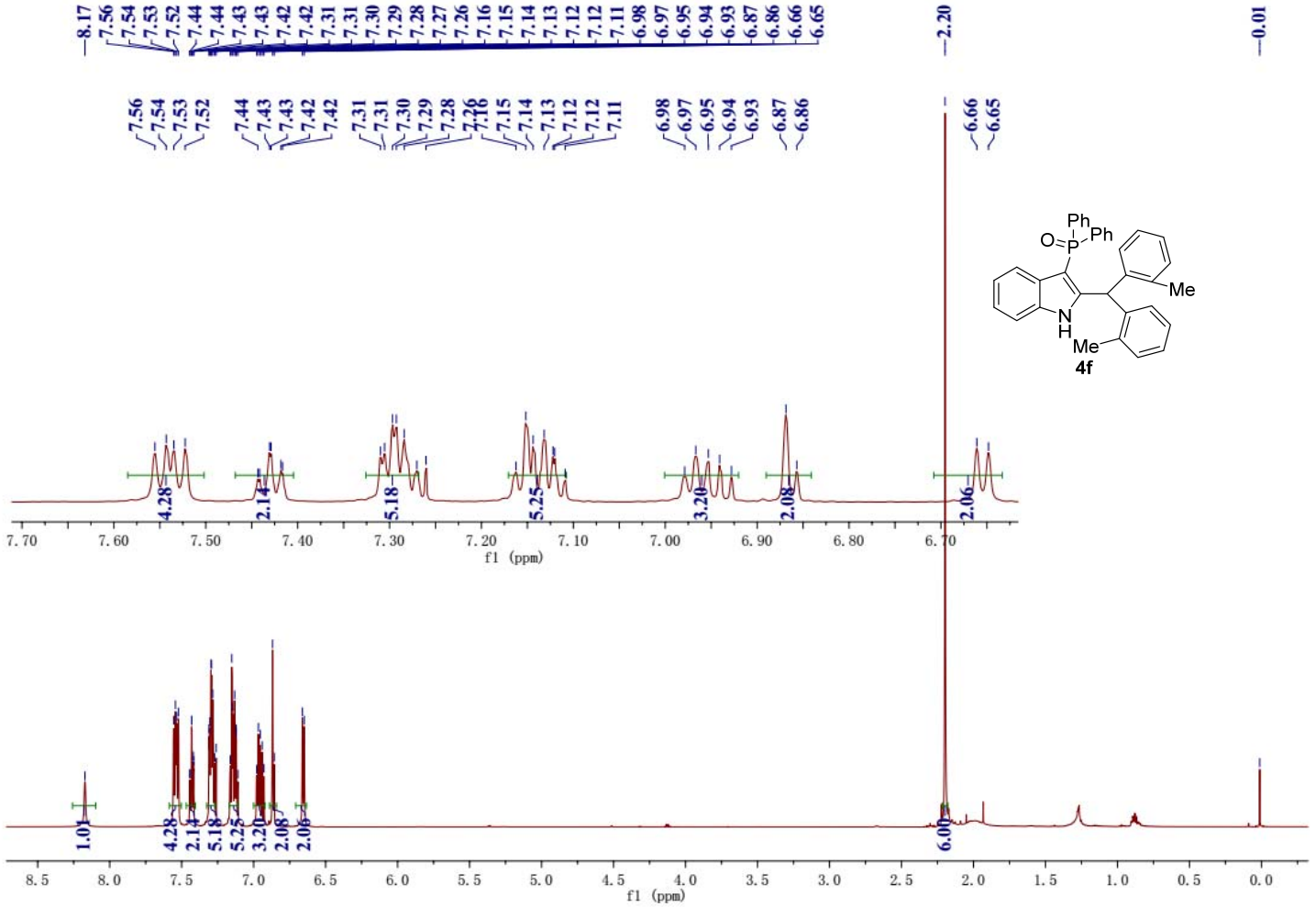

11.553
11.550
8.211
7.597
7.584
7.577
7.564
7.550
7.548
7.537
7.525
7.444
7.440
7.432
7.428
7.419
7.415
7.399
7.385
7.133
7.120
7.107
7.029
7.015
7.004
6.983
6.971
6.943
6.931
6.877
6.779
6.765
6.753
6.752
6.614
6.531
6.517
2.503
2.500
2.498
2.495
2.180
4.38
2.40
4.38
1.14
2.34
1.13
2.31
2.23
2.18
1.05
1.03
1.00
f1 (ppm)
Ph
Ph
O
P
Me
Me
N
H
4e
0.91
6.46
f1 (ppm)

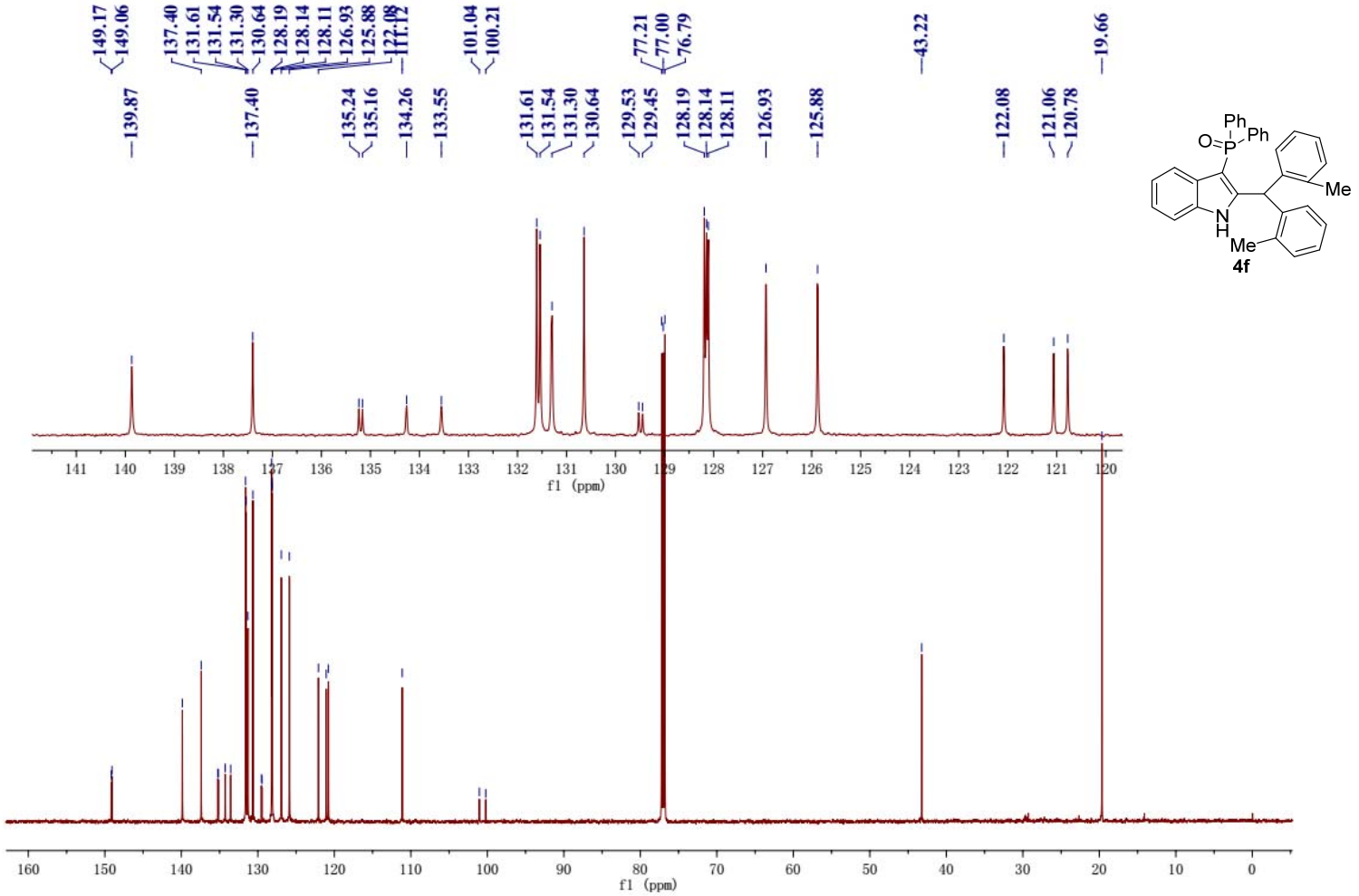

149.90
149.73
141.61
137.18
131.49
131.20
131.10
129.42
128.37
128.25
128.00
126.95
125.74
111.94
100.53
99.28
79.11
78.78
78.46
47.02
40.13
39.92
39.71
39.50
39.29
39.08
38.87
21.05
137.18
136.90
136.78
135.10
134.05
131.49
131.20
131.10
121.54
120.09
119.59
Ph
Ph
O
P
N
H
Me
Me
4e
f1 (ppm)
f1 (ppm)
f1 (ppm)

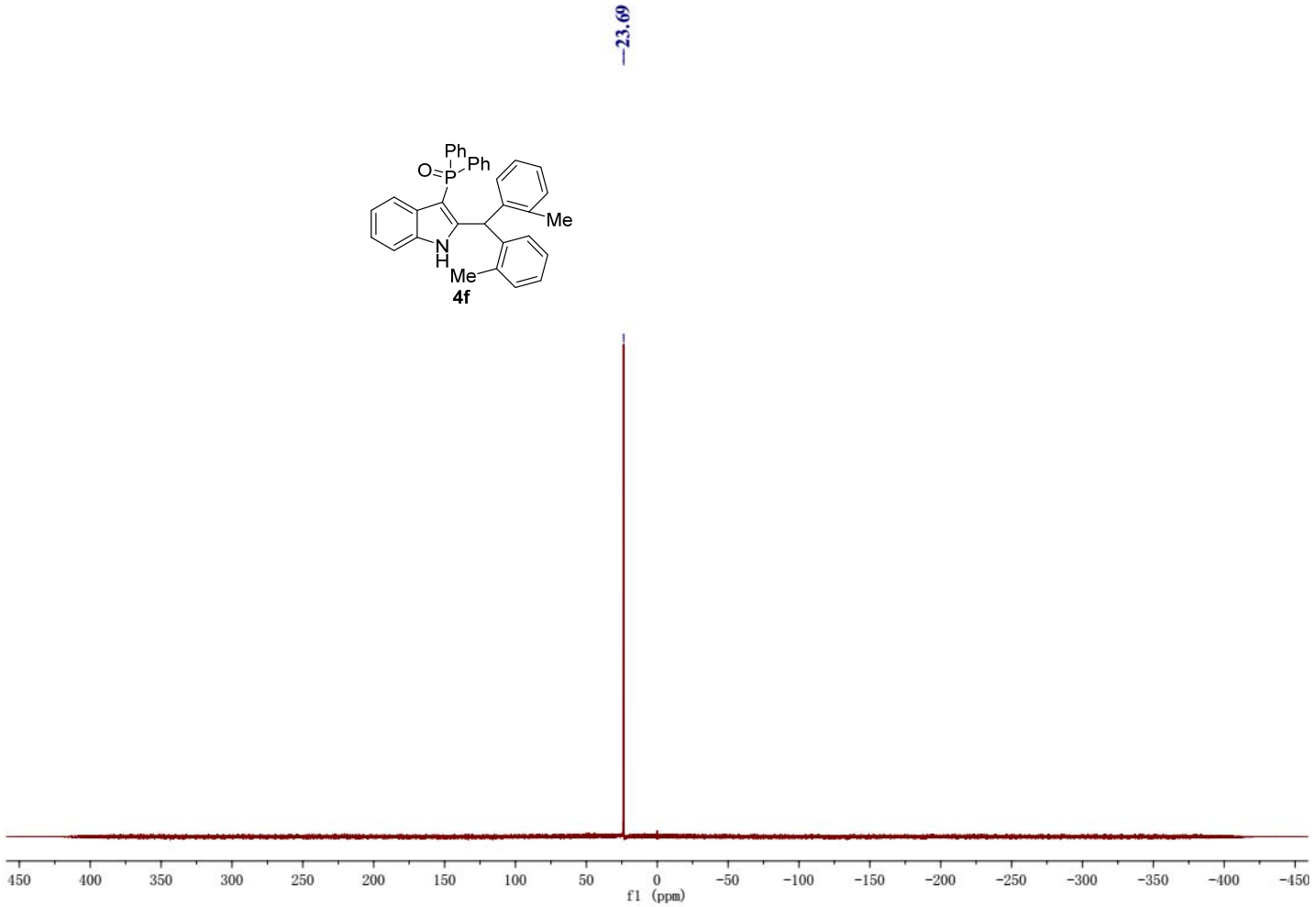

Me
Ph
Ph
O
P
N
H
Me

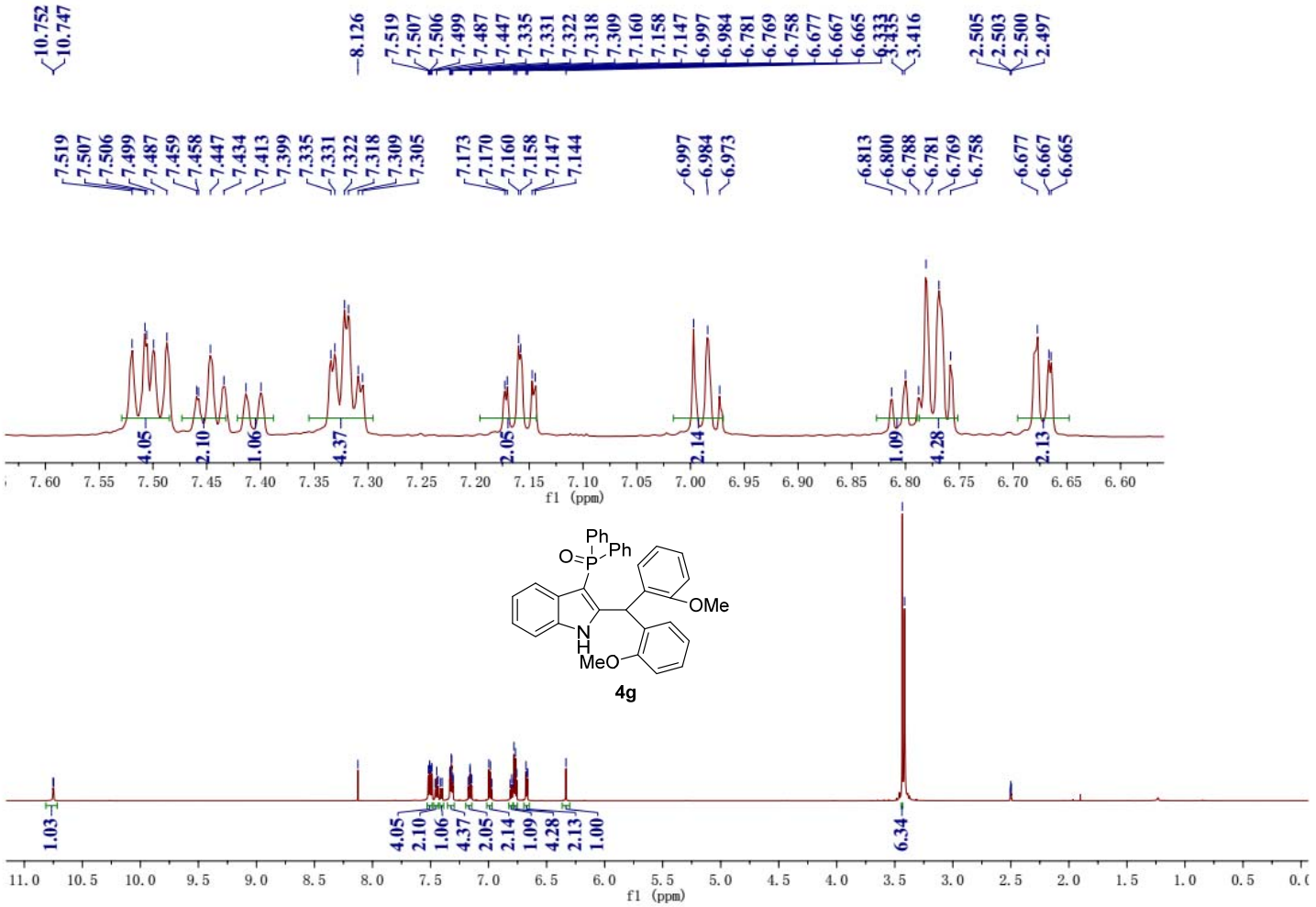
**4e**

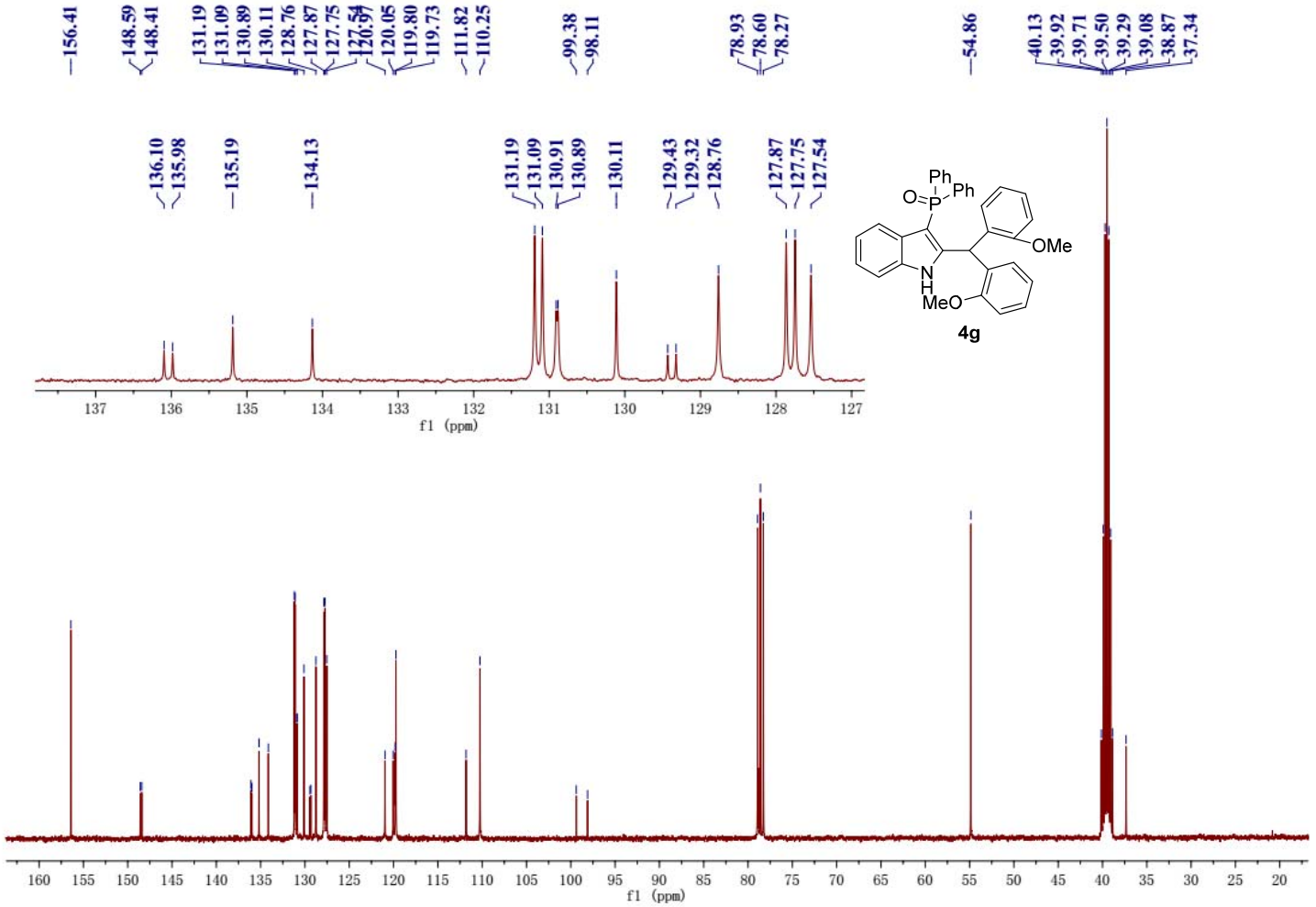

-23.15
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

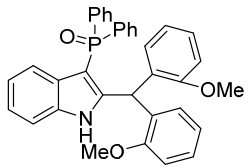

8.17
7.56
7.54
7.53
7.52
7.44
7.44
7.43
7.43
7.42
7.42
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.16
7.15
7.14
7.13
7.12
7.12
7.11
6.98
6.97
6.95
6.94
6.93
6.87
6.86
6.66
6.65
2.20
0.01
Ph
Ph
O
P
Me
N
H
Me
4f
4.28
2.14
5.18
5.25
3.20
2.08
2.06
1.01
6.00
f1 (ppm)


149.17
149.06
137.40
131.61
131.54
131.30
130.64
128.19
128.14
128.11
126.93
125.88
101.04
100.21
77.21
77.00
76.79
43.22
19.66
139.87
137.40
135.24
135.16
134.26
133.55
131.61
131.54
131.30
130.64
129.53
129.45
128.19
128.14
128.11
126.93
125.88
122.08
121.06
120.78
f1 (ppm)
f1 (ppm)
Ph
Ph
O
P
N
H
Me
Me
4f


-23.69
Ph
Ph
O
P
Me
N
H
Me
4f
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

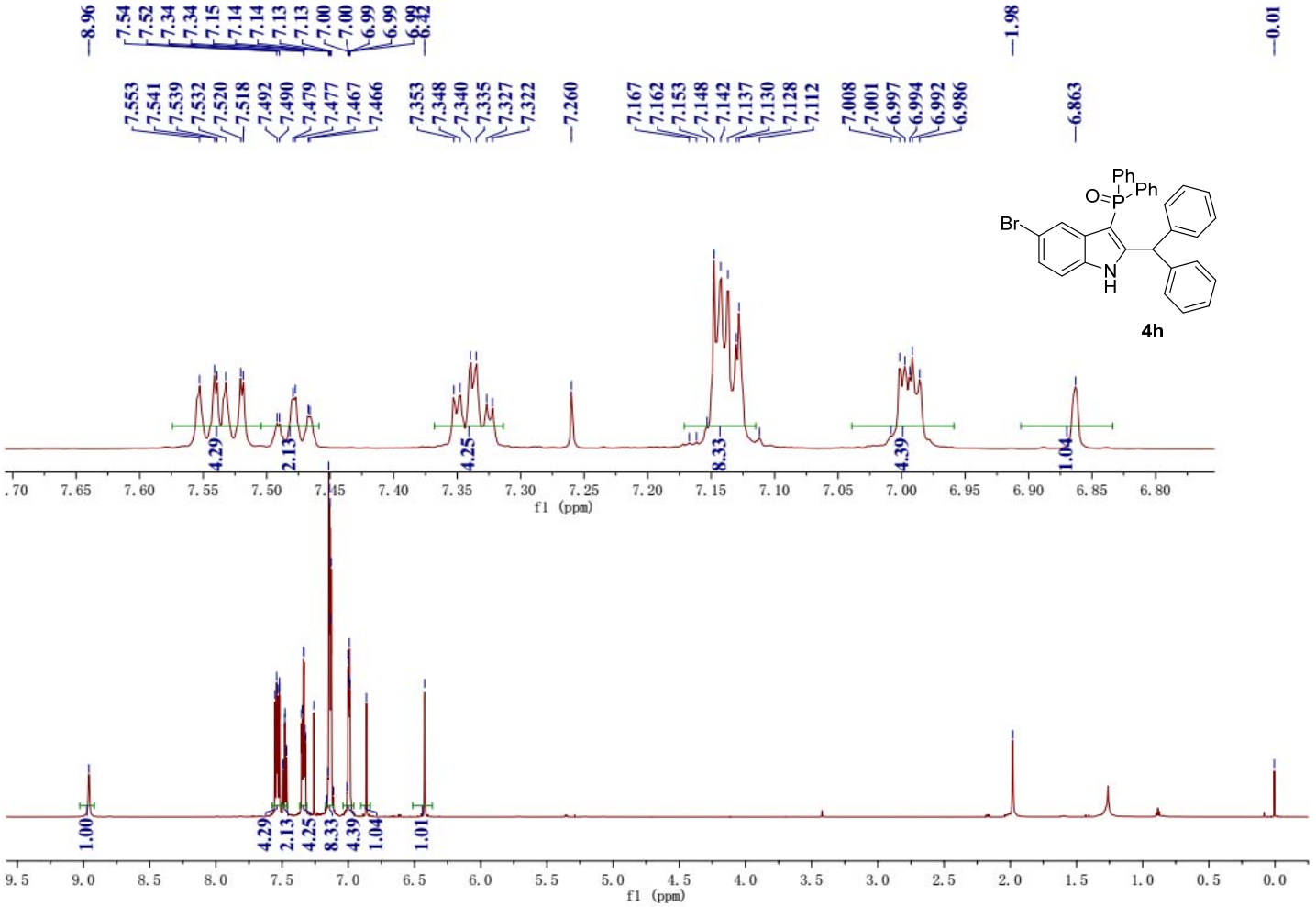

10.752
10.747
8.126
7.519
7.507
7.506
7.499
7.487
7.447
7.335
7.331
7.322
7.318
7.309
7.160
7.158
7.147
6.997
6.984
6.781
6.769
6.758
6.677
6.667
6.665
3.333
3.435
3.416
2.505
2.503
2.500
2.497
7.519
7.507
7.506
7.499
7.487
7.459
7.458
7.447
7.434
7.413
7.399
7.335
7.331
7.322
7.318
7.309
7.305
7.173
7.170
7.160
7.158
7.147
7.144
6.997
6.984
6.973
6.813
6.800
6.788
6.781
6.769
6.758
6.677
6.667
6.665
4.05
2.10
1.06
4.37
2.05
2.14
1.09
4.28
2.13
f1 (ppm)
Ph
Ph
O
P
OMe
N
H
MeO
4g
1.03
4.05
2.10
1.06
4.37
2.05
2.14
1.09
4.28
2.13
1.00
6.34
f1 (ppm)

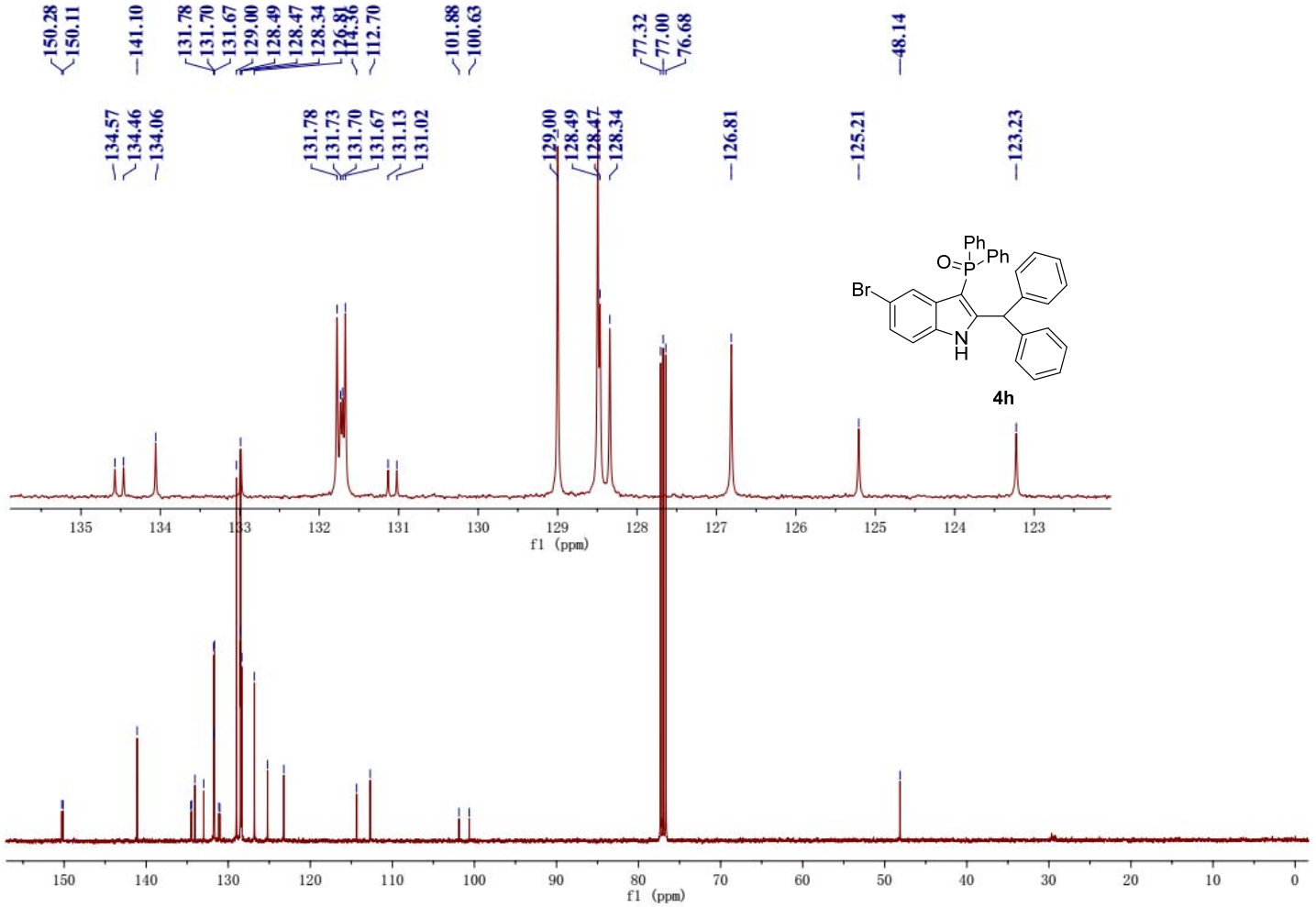

156.41
148.59
148.41
131.19
131.09
130.89
130.11
128.76
127.87
127.75
127.54
120.97
120.05
119.80
119.73
111.82
110.25
99.38
98.11
78.93
78.60
78.27
54.86
40.13
39.92
39.71
39.50
39.29
39.08
38.87
37.34
136.10
135.98
135.19
134.13
131.19
131.09
130.91
130.89
130.11
129.43
129.32
128.76
127.87
127.75
127.54
Ph
O=P
Ph
OMe
N
H
MeO
4g
f1 (ppm)
f1 (ppm)

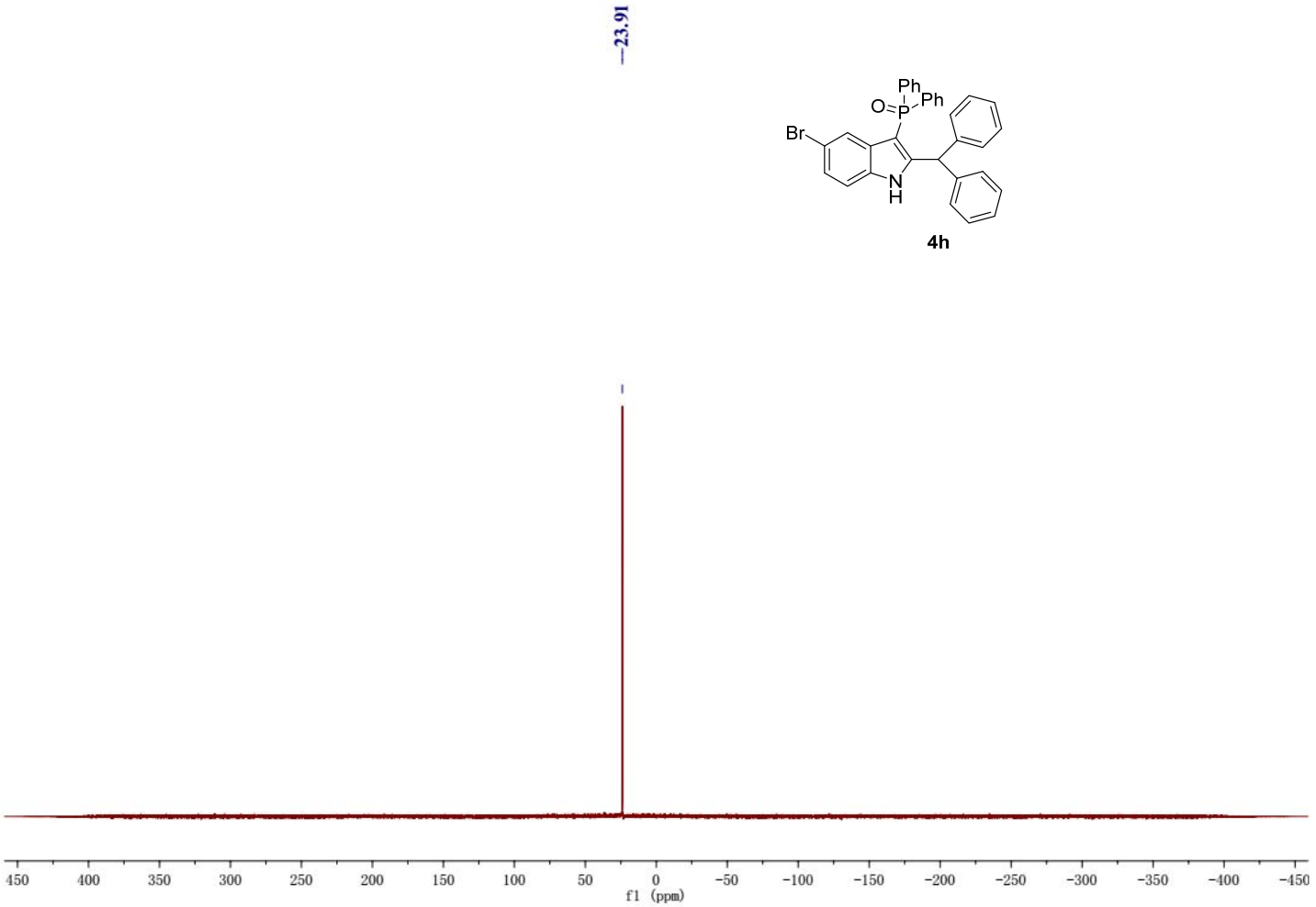

Ph
Ph
O
P
OMe
N
H
MeO

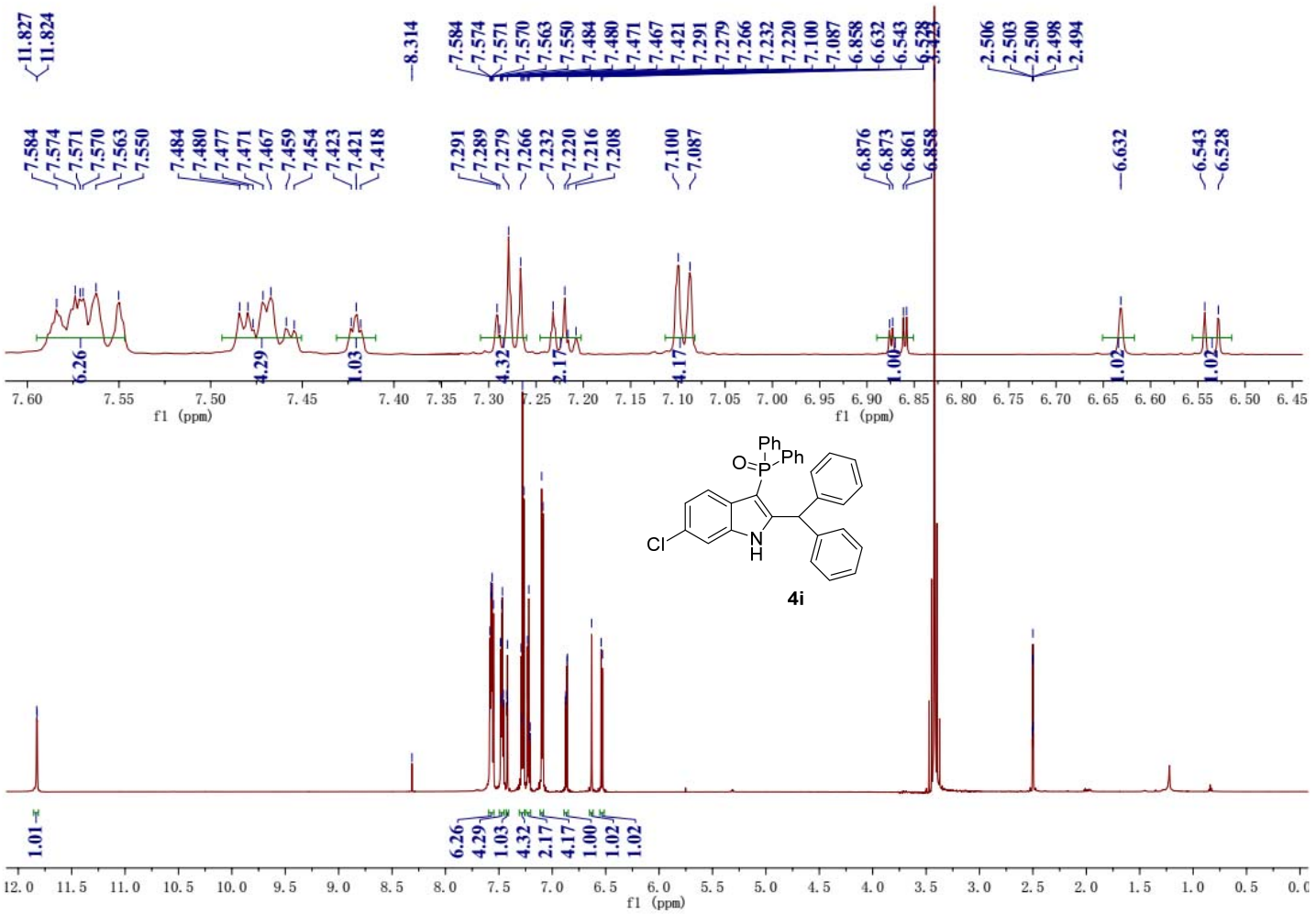
**4g**

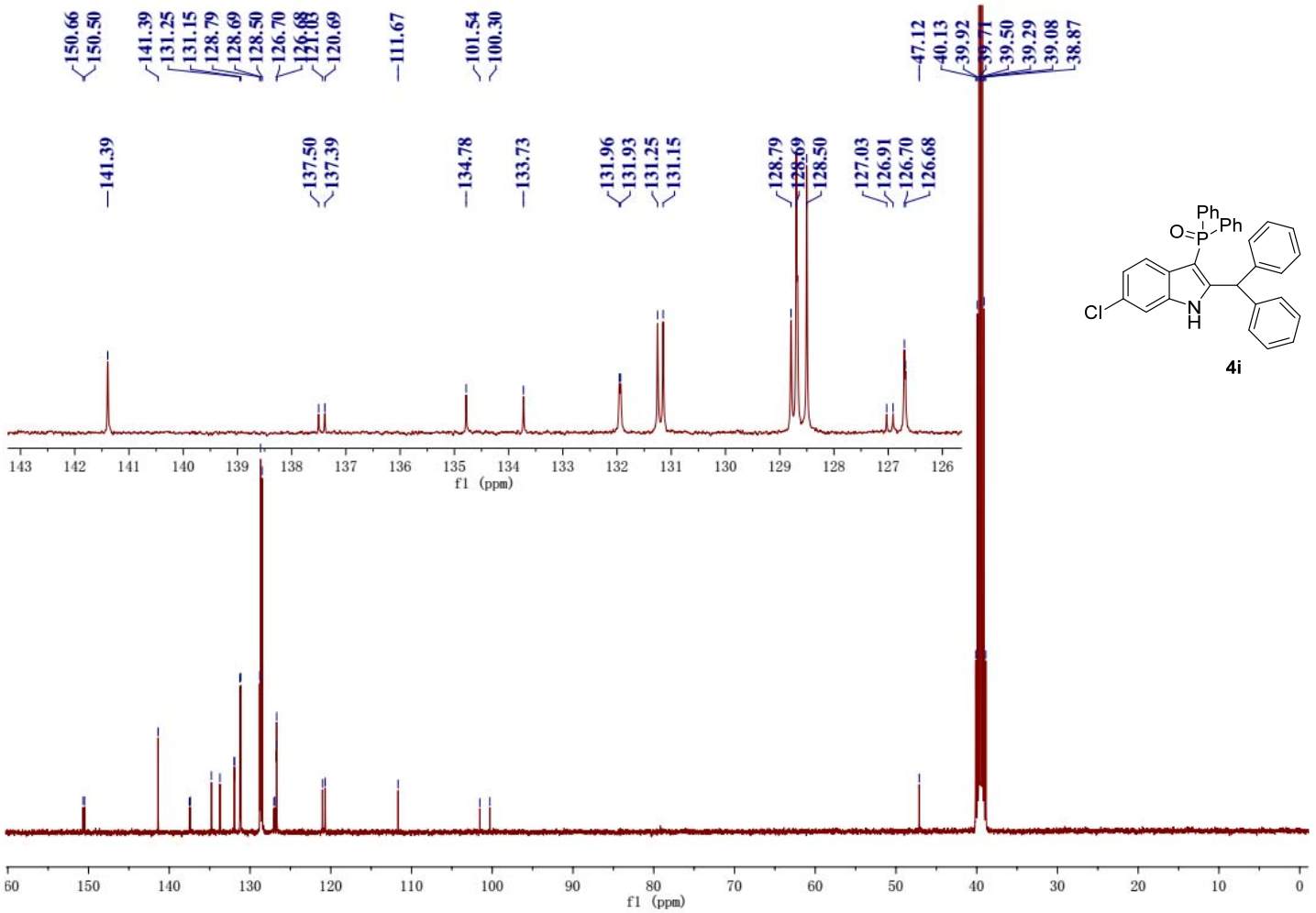

22.01
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

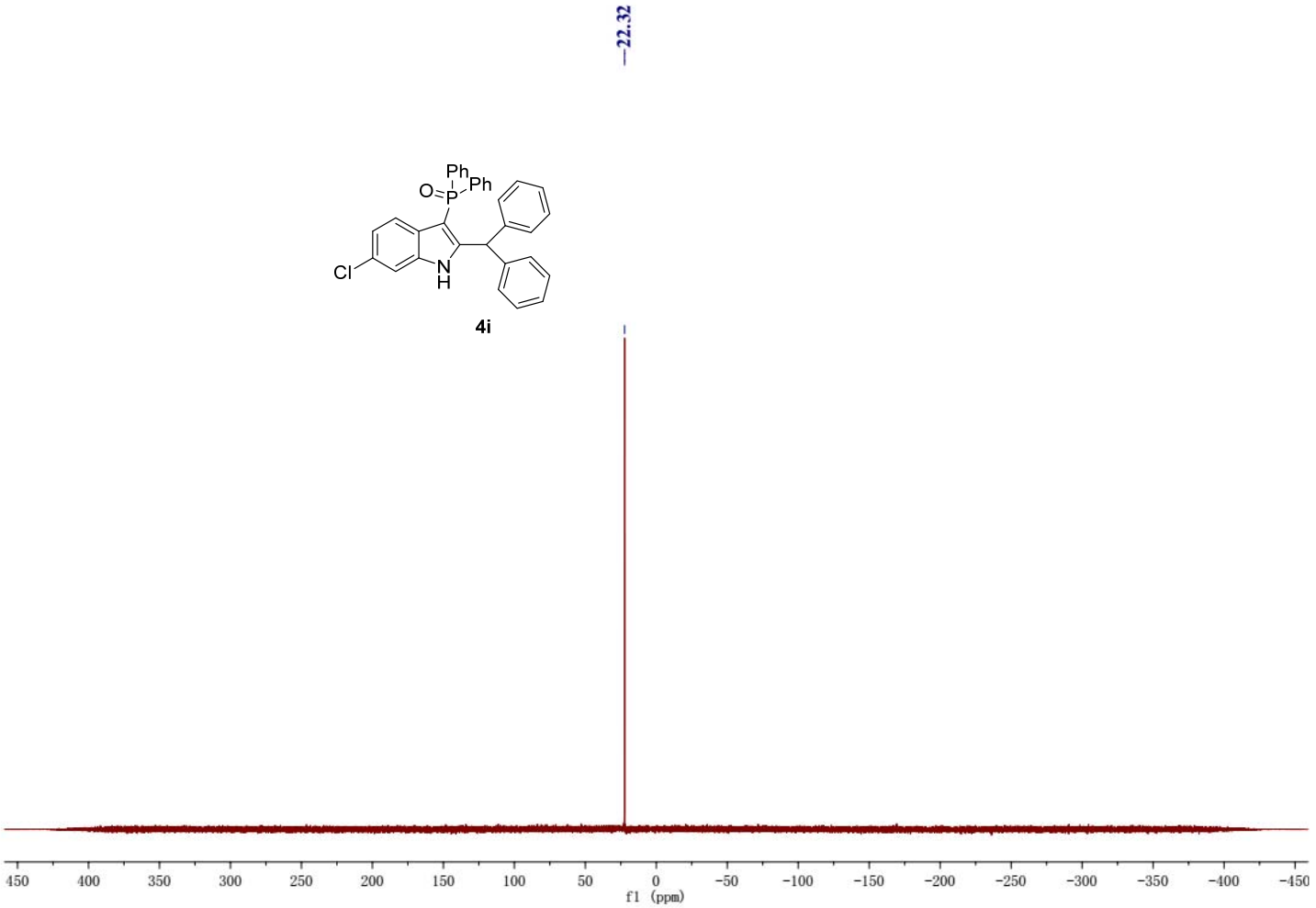

8.96
7.54
7.52
7.34
7.34
7.15
7.14
7.14
7.13
7.13
7.00
7.00
6.99
6.99
6.98
6.97
1.98
0.01
7.553
7.541
7.539
7.532
7.520
7.518
7.492
7.490
7.479
7.477
7.467
7.466
7.353
7.348
7.340
7.335
7.327
7.322
7.260
7.167
7.162
7.153
7.148
7.142
7.137
7.130
7.128
7.112
7.008
7.001
6.997
6.994
6.992
6.986
6.863
Ph
Ph
O
P
Br
N
H
4h
4.29
2.13
4.25
8.33
4.39
1.04
f1 (ppm)
1.00
4.29
2.13
4.25
8.33
4.39
1.04
1.01
f1 (ppm)

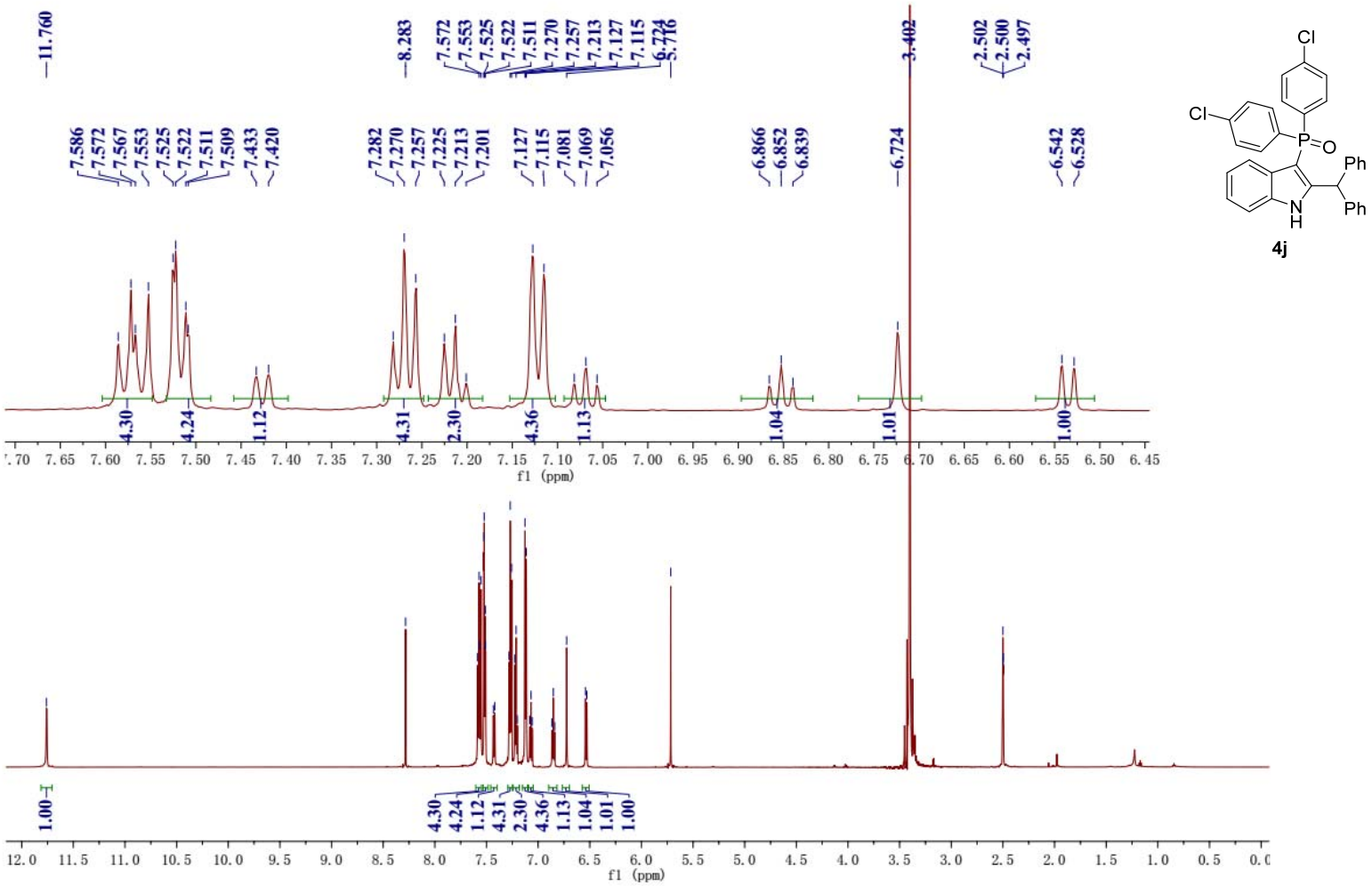

150.28
150.11
141.10
131.78
131.70
131.67
129.00
128.49
128.47
128.34
126.81
114.36
112.70
101.88
100.63
77.32
77.00
76.68
48.14
134.57
134.46
134.06
131.78
131.73
131.70
131.67
131.13
131.02
129.00
128.49
128.47
128.34
126.81
125.21
123.23
Ph
Ph
O
P
Br
N
H
4h
f1 (ppm)
f1 (ppm)


23.91
Ph
Ph
O
P
Br
N
H
4h
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


11.827
11.824
8.314
7.584
7.574
7.571
7.570
7.563
7.550
7.484
7.480
7.477
7.471
7.467
7.459
7.454
7.423
7.421
7.418
7.291
7.289
7.279
7.266
7.232
7.220
7.216
7.208
7.100
7.087
6.876
6.873
6.861
6.858
6.632
6.543
6.528
2.506
2.503
2.500
2.498
2.494
6.26
4.29
1.03
4.32
2.17
4.17
1.00
1.02
1.02
f1 (ppm)
Ph
Ph
O
P
Cl
N
H
4i
1.01
6.26
4.29
1.03
4.32
2.17
4.17
1.00
1.02
1.02
f1 (ppm)

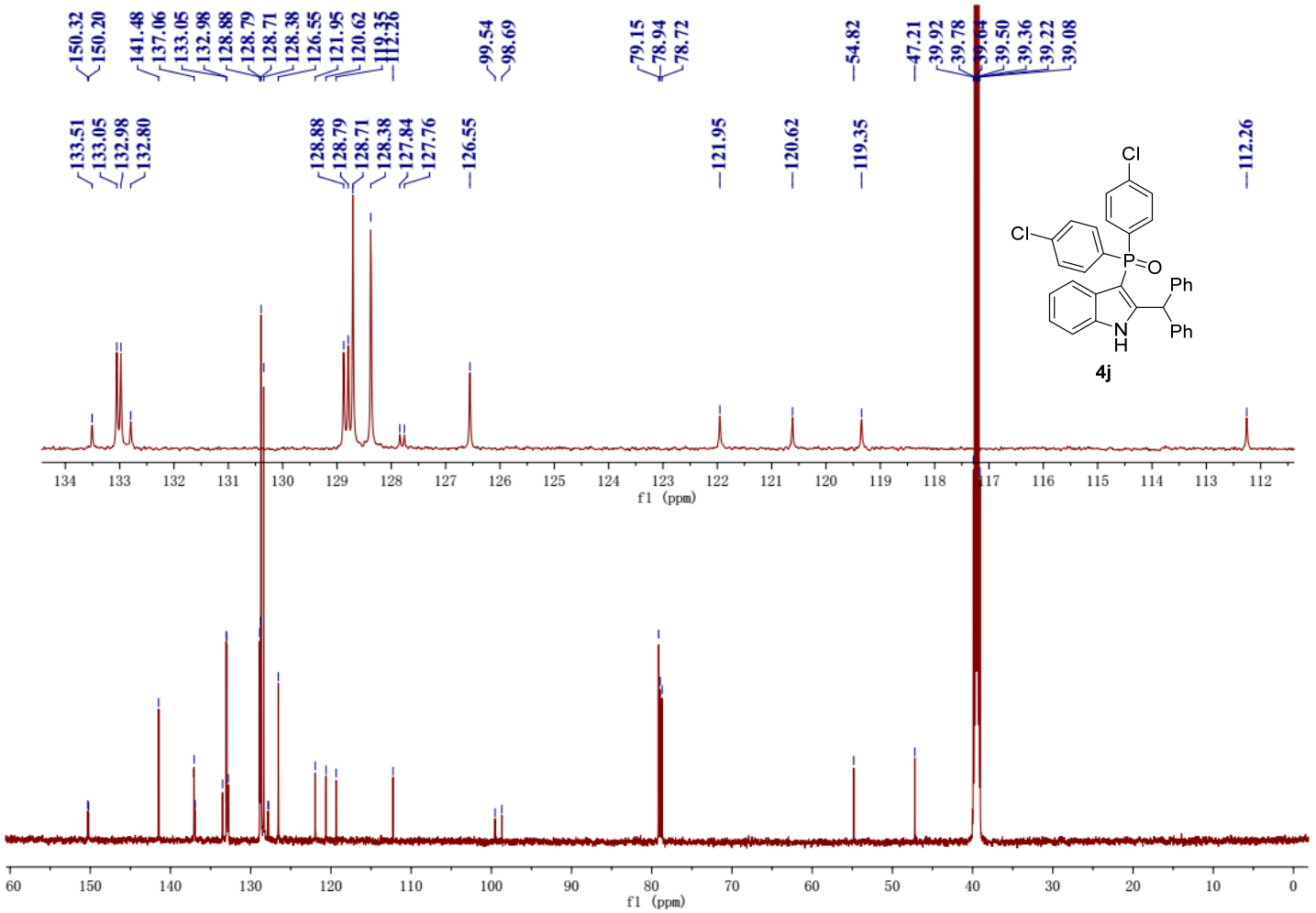

150.66
150.50
141.39
131.25
131.15
128.79
128.69
128.50
126.70
120.69
111.67
101.54
100.30
47.12
40.13
39.92
39.71
39.50
39.29
39.08
38.87
141.39
137.50
137.39
134.78
133.73
131.96
131.93
131.25
131.15
128.79
128.69
128.50
127.03
126.91
126.70
126.68
f1 (ppm)
f1 (ppm)
Ph
Ph
O
P
Cl
N
H
4i

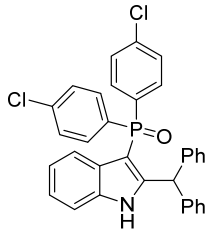

22.32
Ph
Ph
O
P
Cl
N
H
4i
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


11.760
8.283
7.572
7.553
7.525
7.522
7.511
7.270
7.257
7.213
7.127
7.115
6.724
3.402
2.502
2.500
2.497
7.586
7.572
7.567
7.553
7.525
7.522
7.511
7.509
7.433
7.420
7.282
7.270
7.257
7.225
7.213
7.201
7.127
7.115
7.081
7.069
7.056
6.866
6.852
6.839
6.724
6.542
6.528
4.30
4.24
1.12
4.31
2.30
4.36
1.13
1.04
1.01
1.00
f1 (ppm)
1.00
4.30
4.24
1.12
4.31
2.30
4.36
1.13
1.04
1.01
1.00
f1 (ppm)


Cl
Cl
P
O
Ph
Ph
N
H

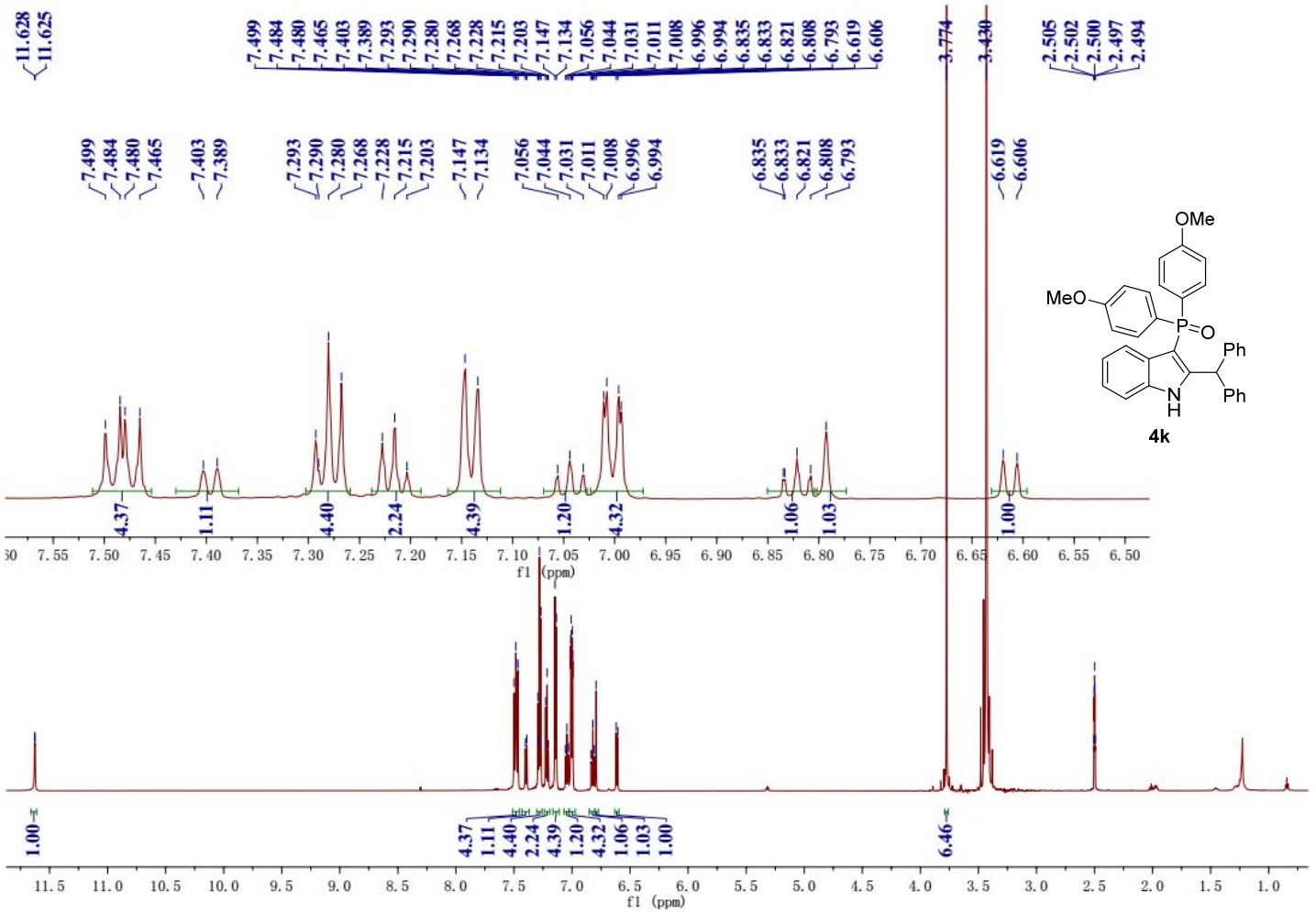
**4j**

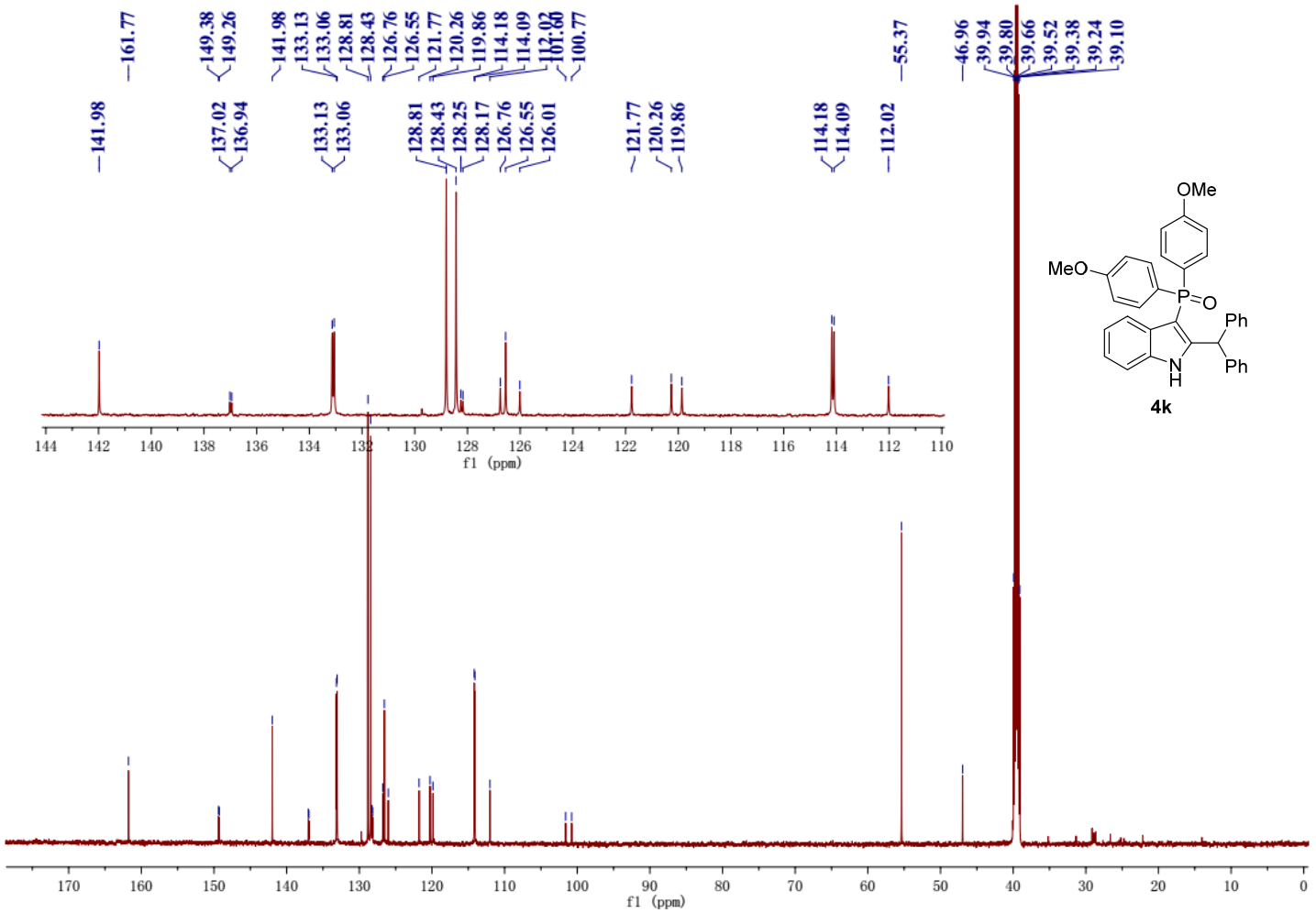

150.32
150.20
141.48
137.06
133.05
132.98
128.88
128.79
128.71
128.38
126.55
121.95
120.62
112.26
99.54
98.69
79.15
78.94
78.72
54.82
47.21
39.92
39.78
39.64
39.50
39.36
39.22
39.08
133.51
133.05
132.98
132.80
128.88
128.79
128.71
128.38
127.84
127.76
126.55
121.95
120.62
119.35
112.26
Cl
Cl
P
O
Ph
Ph
N
H
4j
f1 (ppm)
f1 (ppm)

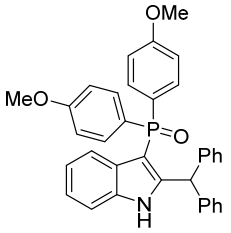

Cl
Cl
P
O
Ph
Ph
N
H

**4j**


22.56
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

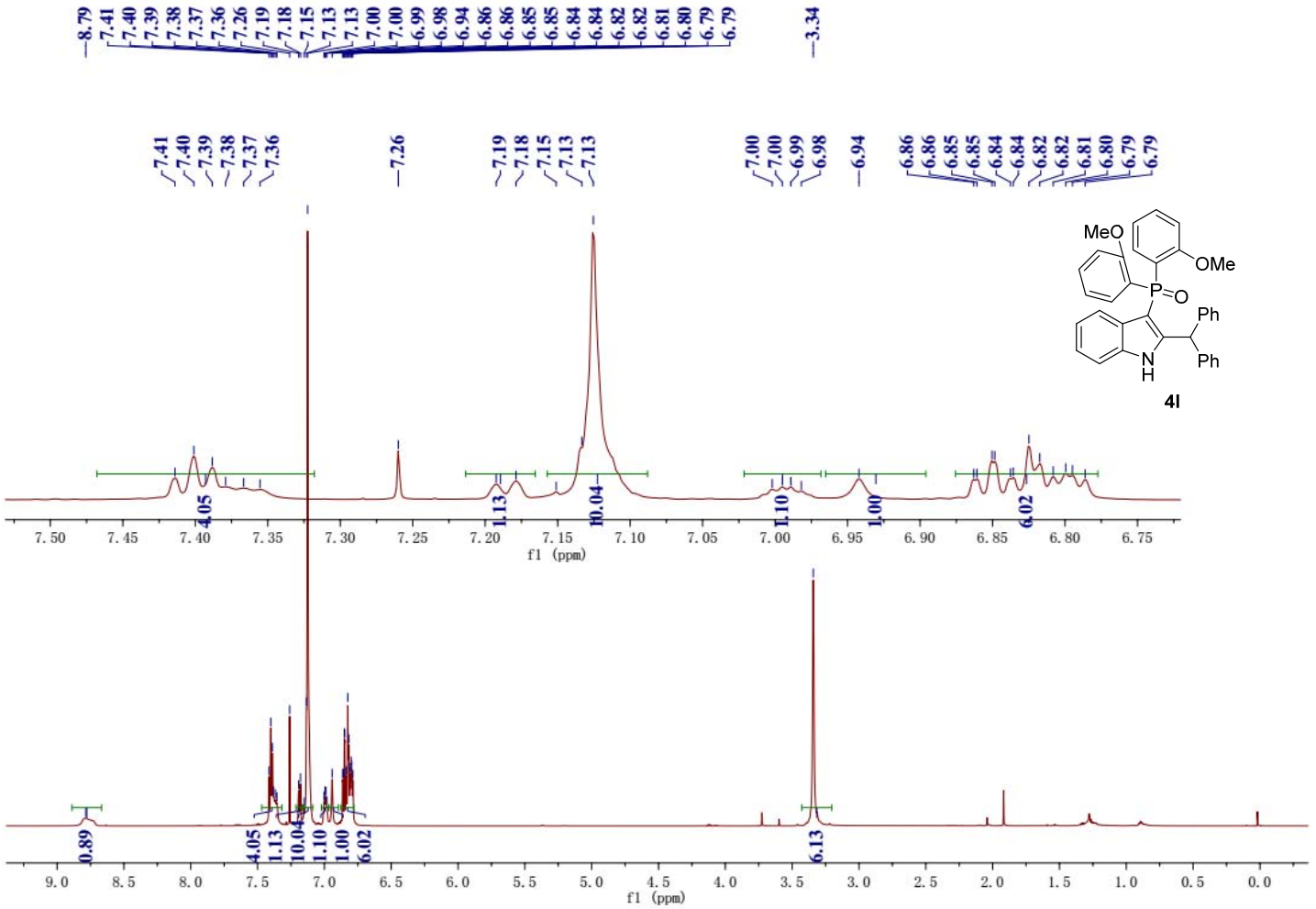

11.628
11.625
7.499
7.484
7.480
7.465
7.403
7.389
7.293
7.290
7.280
7.268
7.228
7.215
7.203
7.147
7.134
7.056
7.044
7.031
7.011
7.008
6.996
6.994
6.835
6.833
6.821
6.808
6.793
6.619
6.606
3.774
3.430
2.505
2.502
2.500
2.497
2.494
4.37
1.11
4.40
2.24
4.39
1.20
4.32
1.06
1.03
1.00
6.46
f1 (ppm)
OMe
MeO
P
O
Ph
Ph
N
H
4k

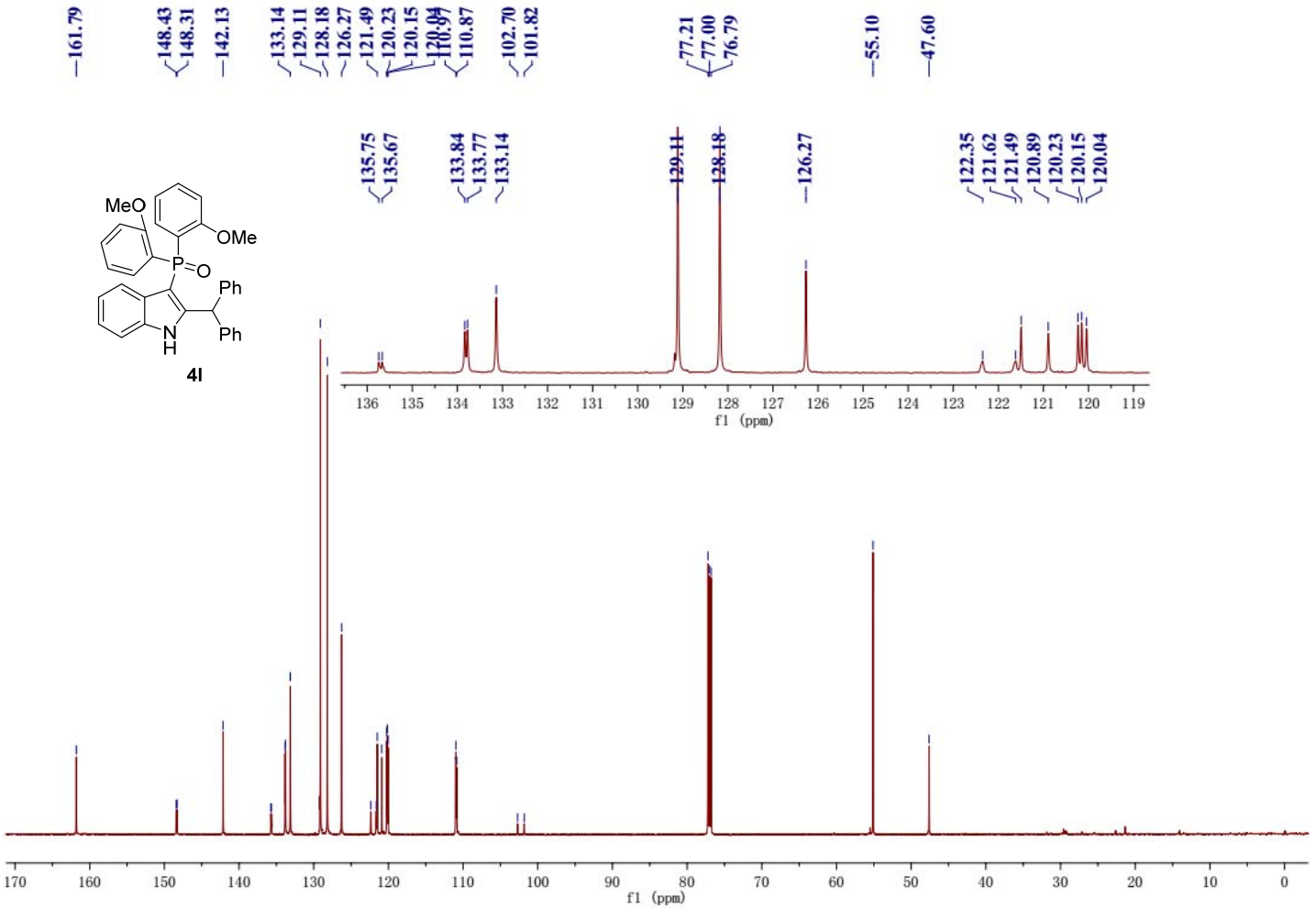

141.98
161.77
149.38
149.26
141.98
133.13
133.06
128.81
128.43
126.76
126.55
121.77
120.26
119.86
114.18
114.09
112.02
101.60
100.77
55.37
46.96
39.94
39.80
39.66
39.52
39.38
39.24
39.10
141.98
137.02
136.94
133.13
133.06
128.81
128.43
128.25
128.17
126.76
126.55
126.01
121.77
120.26
119.86
114.18
114.09
112.02
f1 (ppm)
f1 (ppm)
OMe
MeO
P
O
Ph
Ph
N
H
4k

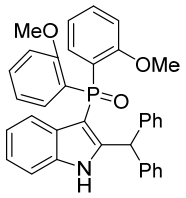

OMe
MeO
P
O
Ph
Ph
N
H

**4k**


22.05
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

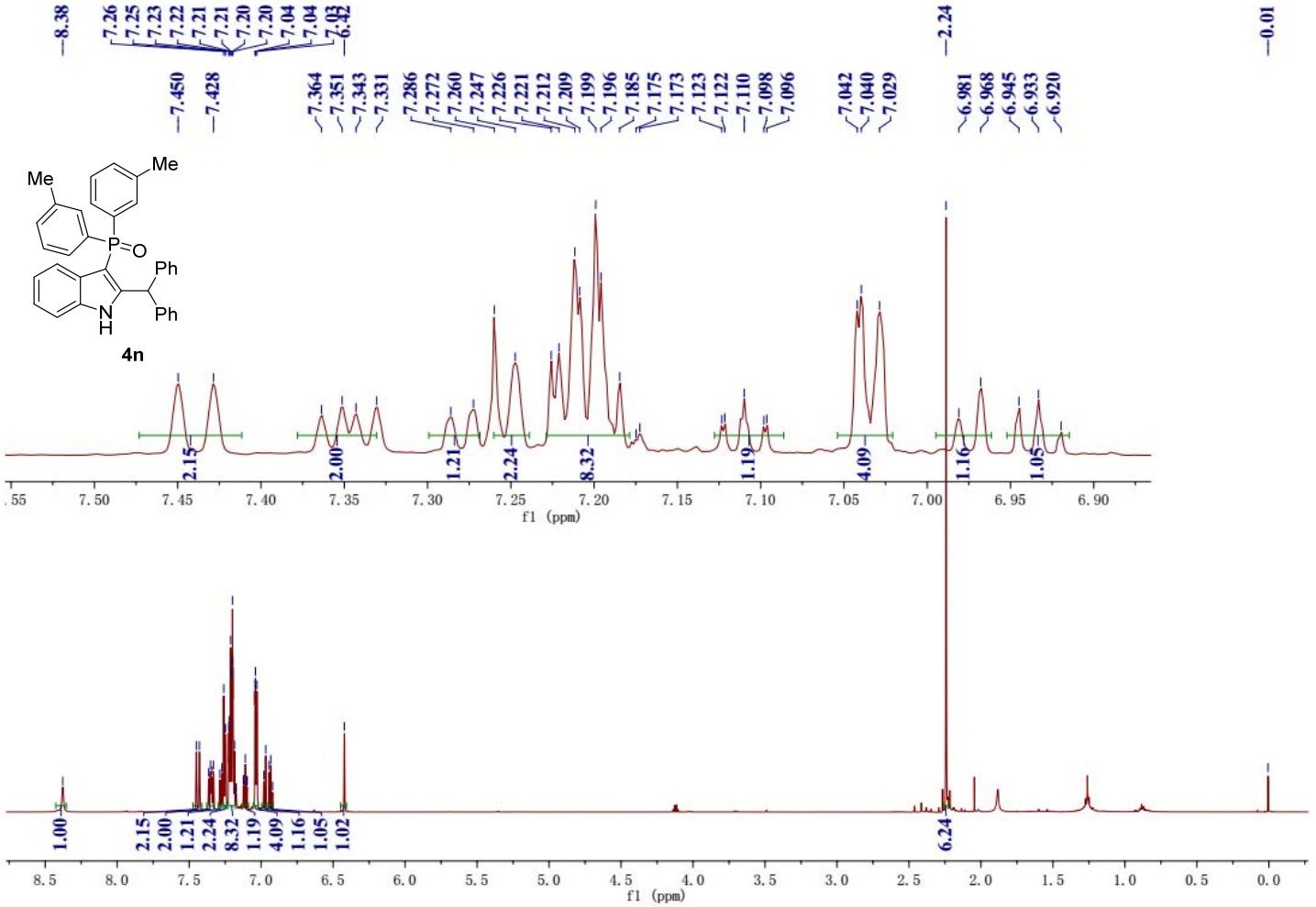

8.79
7.41
7.40
7.39
7.38
7.37
7.36
7.26
7.19
7.18
7.15
7.13
7.13
7.00
7.00
6.99
6.98
6.94
6.86
6.86
6.85
6.85
6.84
6.84
6.82
6.82
6.81
6.80
6.79
6.79
3.34
MeO
OMe
P
O
Ph
Ph
N
H
4l
4.05
1.13
10.04
1.10
1.00
6.02
f1 (ppm)
0.89
4.05
1.13
10.04
1.10
1.00
6.02
6.13
f1 (ppm)

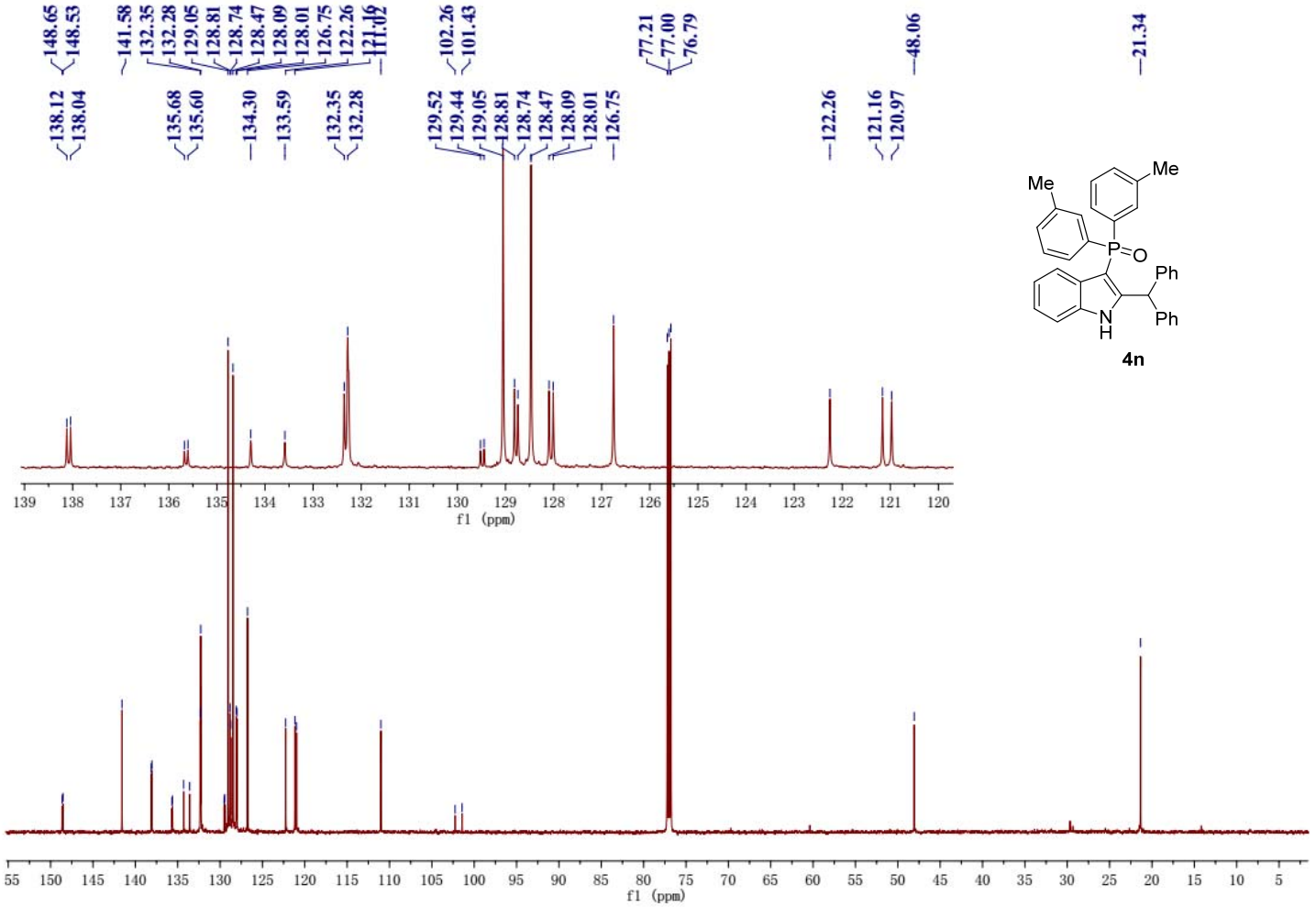

161.79
148.43
148.31
142.13
133.14
129.11
128.18
126.27
121.49
120.23
120.15
120.04
110.97
110.87
102.70
101.82
77.21
77.00
76.79
55.10
47.60
135.75
135.67
133.84
133.77
133.14
129.11
128.18
126.27
122.35
121.62
121.49
120.89
120.23
120.15
120.04
MeO
OMe
P
O
Ph
Ph
N
H
4l
f1 (ppm)
f1 (ppm)

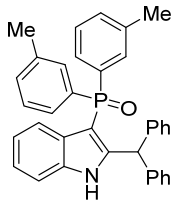

MeO
OMe
P
O
Ph
Ph
N
H

**4l**


21.54
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

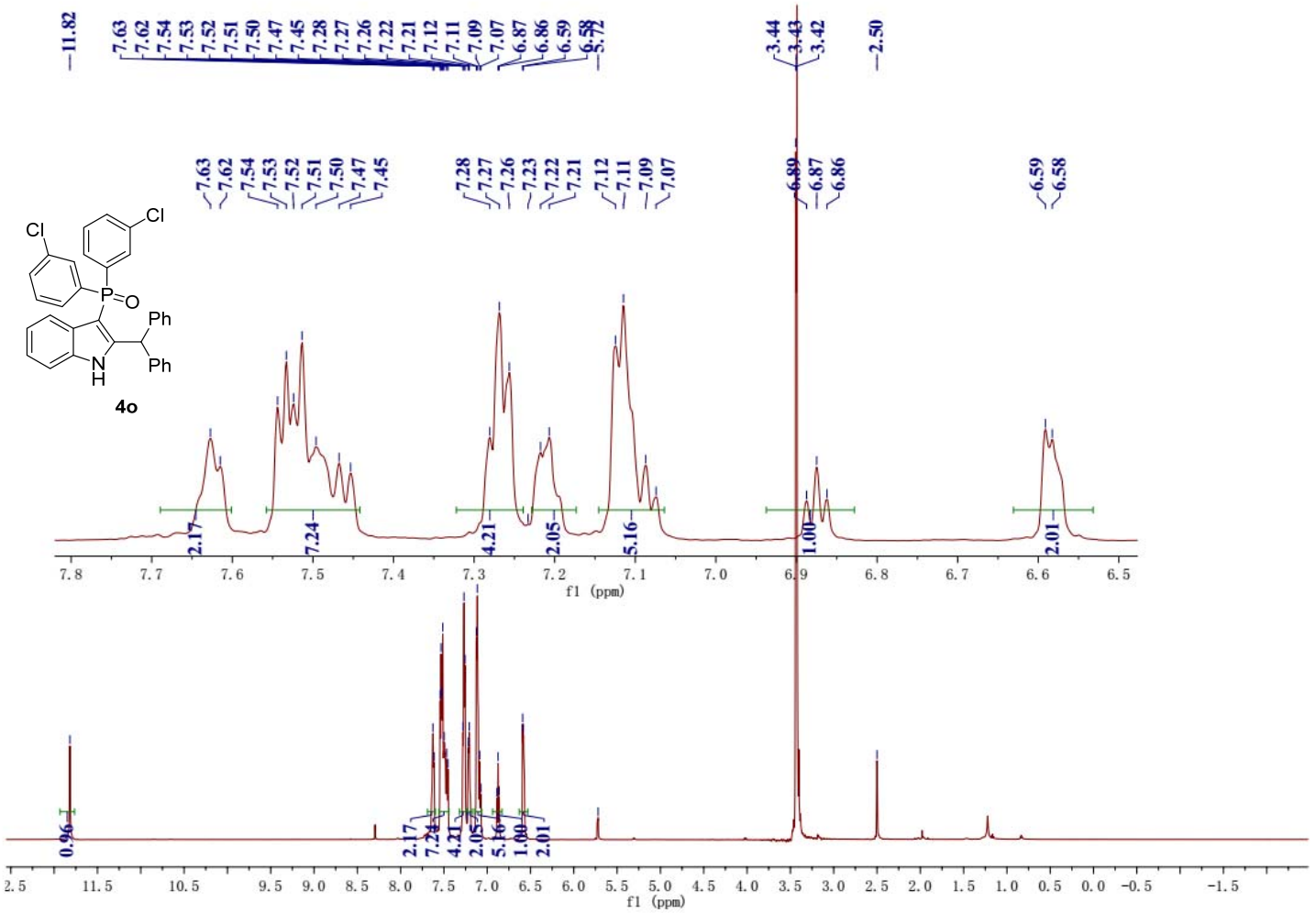

8.38
7.26
7.25
7.23
7.22
7.21
7.21
7.20
7.20
7.04
7.04
7.03
6.42
7.450
7.428
7.364
7.351
7.343
7.331
7.286
7.272
7.260
7.247
7.226
7.221
7.212
7.209
7.199
7.196
7.185
7.175
7.173
7.123
7.122
7.110
7.098
7.096
7.042
7.040
7.029
2.24
6.981
6.968
6.945
6.933
6.920
0.01
Me
Me
P
O
Ph
Ph
N
H
4n
2.15
2.00
1.21
2.24
8.32
1.19
4.09
1.16
1.05
f1 (ppm)
1.00
2.15
2.00
1.21
2.24
8.32
1.19
4.09
1.16
1.05
1.02
6.24
f1 (ppm)

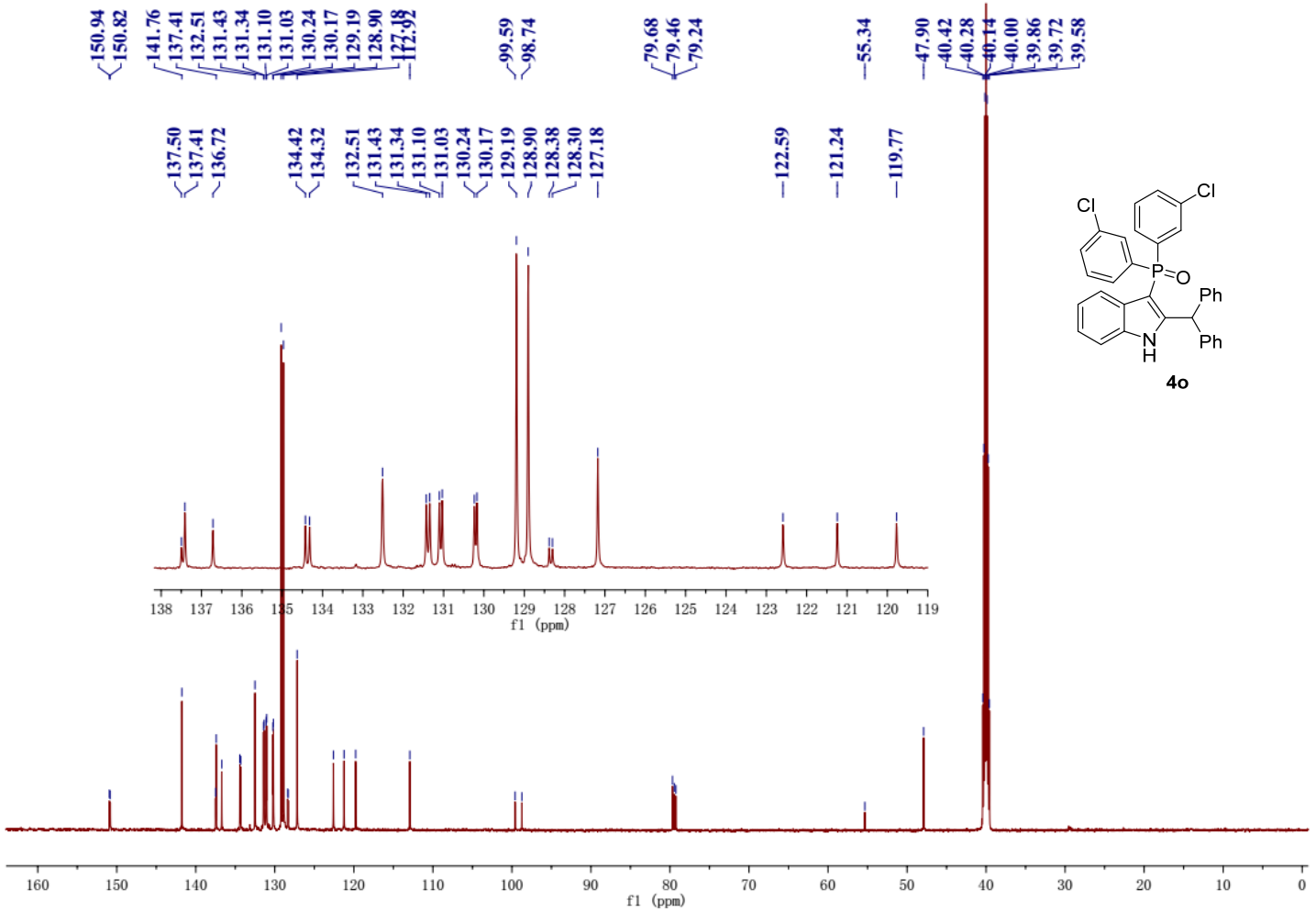

148.65
148.53
141.58
132.35
132.28
129.05
128.81
128.74
128.47
128.09
128.01
126.75
122.26
102.26
101.43
77.21
77.00
76.79
48.06
21.34
138.12
138.04
135.68
135.60
134.30
133.59
132.35
132.28
129.52
129.44
129.05
128.81
128.74
128.47
128.09
128.01
126.75
122.26
121.16
120.97
f1 (ppm)
Me
Me
P
O
Ph
Ph
N
H
4n

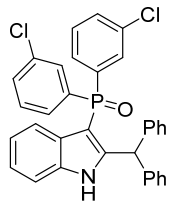

Me
Me
P
O
Ph
Ph
N
H

**4n**


24.31
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

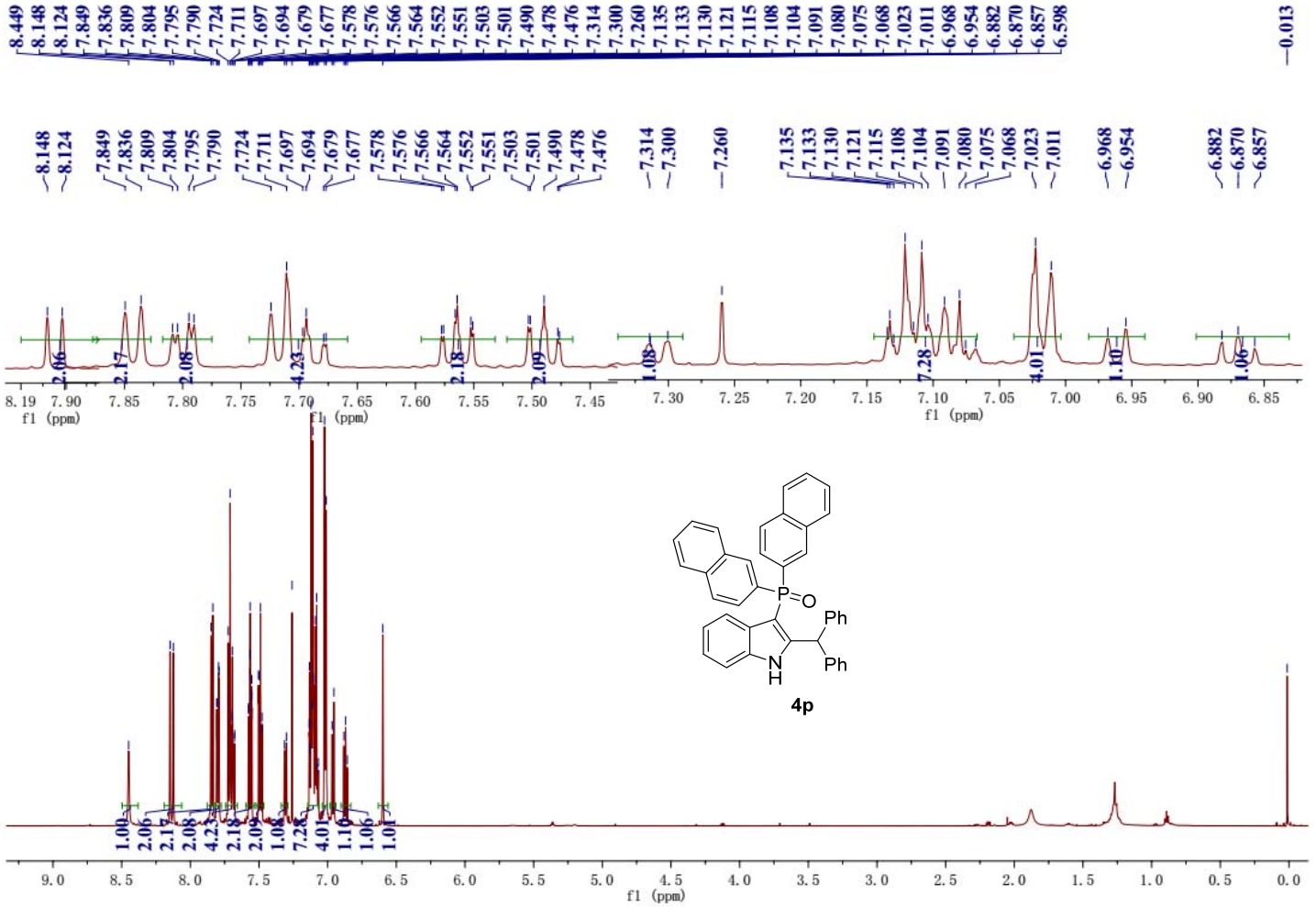

11.82
7.63
7.62
7.54
7.53
7.52
7.51
7.50
7.47
7.45
7.28
7.27
7.26
7.22
7.21
7.12
7.11
7.09
7.07
6.87
6.86
6.59
6.58
5.72
3.44
3.43
3.42
2.50
Cl
Cl
P
O
Ph
Ph
N
H
4o
2.17
7.24
4.21
2.05
5.16
1.00
2.01
f1 (ppm)
0.96

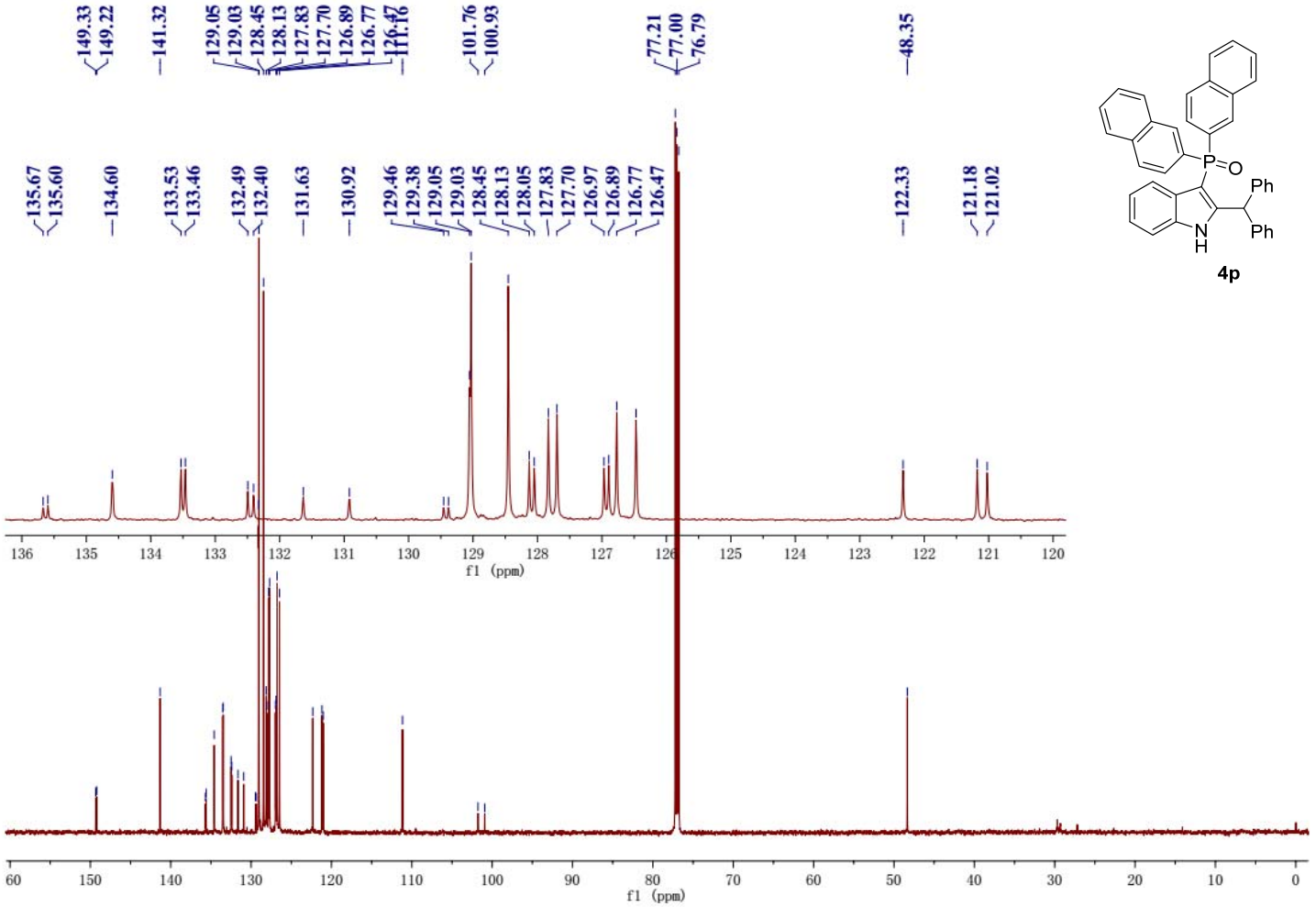

150.94
150.82
141.76
137.41
132.51
131.43
131.34
131.10
131.03
130.24
130.17
129.19
128.90
99.59
98.74
79.68
79.46
79.24
55.34
47.90
40.42
40.28
40.14
40.00
39.86
39.72
39.58
137.50
137.41
136.72
134.42
134.32
132.51
131.43
131.34
131.10
131.03
130.24
130.17
129.19
128.90
128.38
128.30
127.18
122.59
121.24
119.77
f1 (ppm)
f1 (ppm)
Cl
Cl
P
O
Ph
Ph
N
H
4o


Cl
Cl
P
O
Ph
Ph
N
H

**4o**

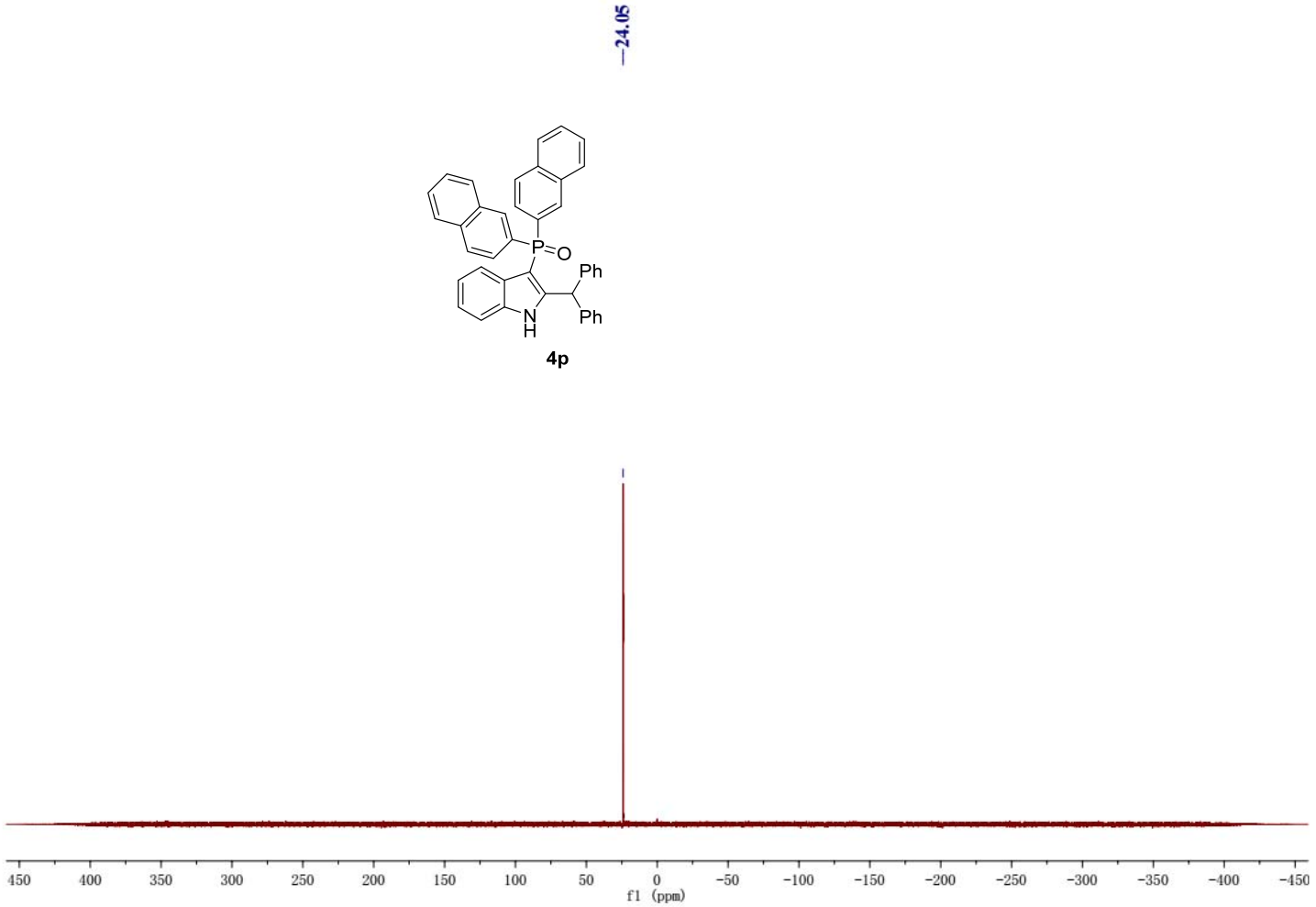

20.89
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

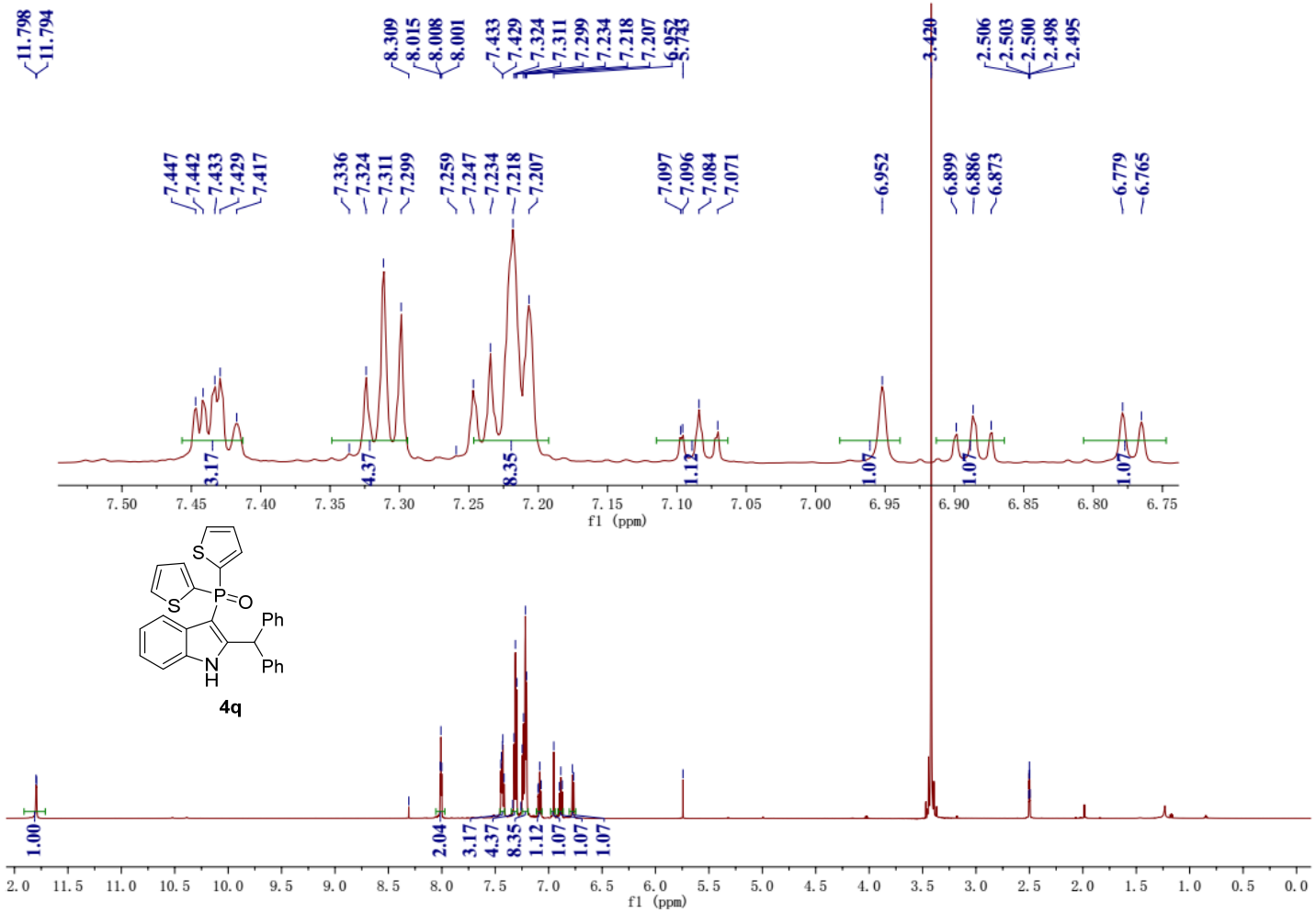

8.449
8.148
8.124
7.849
7.836
7.809
7.804
7.795
7.790
7.724
7.711
7.697
7.694
7.679
7.677
7.578
7.576
7.566
7.564
7.552
7.551
7.503
7.501
7.490
7.478
7.476
7.314
7.300
7.260
7.135
7.133
7.130
7.121
7.115
7.108
7.104
7.091
7.080
7.075
7.068
7.023
7.011
6.968
6.954
6.882
6.870
6.857
6.598
-0.013
f1 (ppm)
P
O
Ph
Ph
N
H
4p

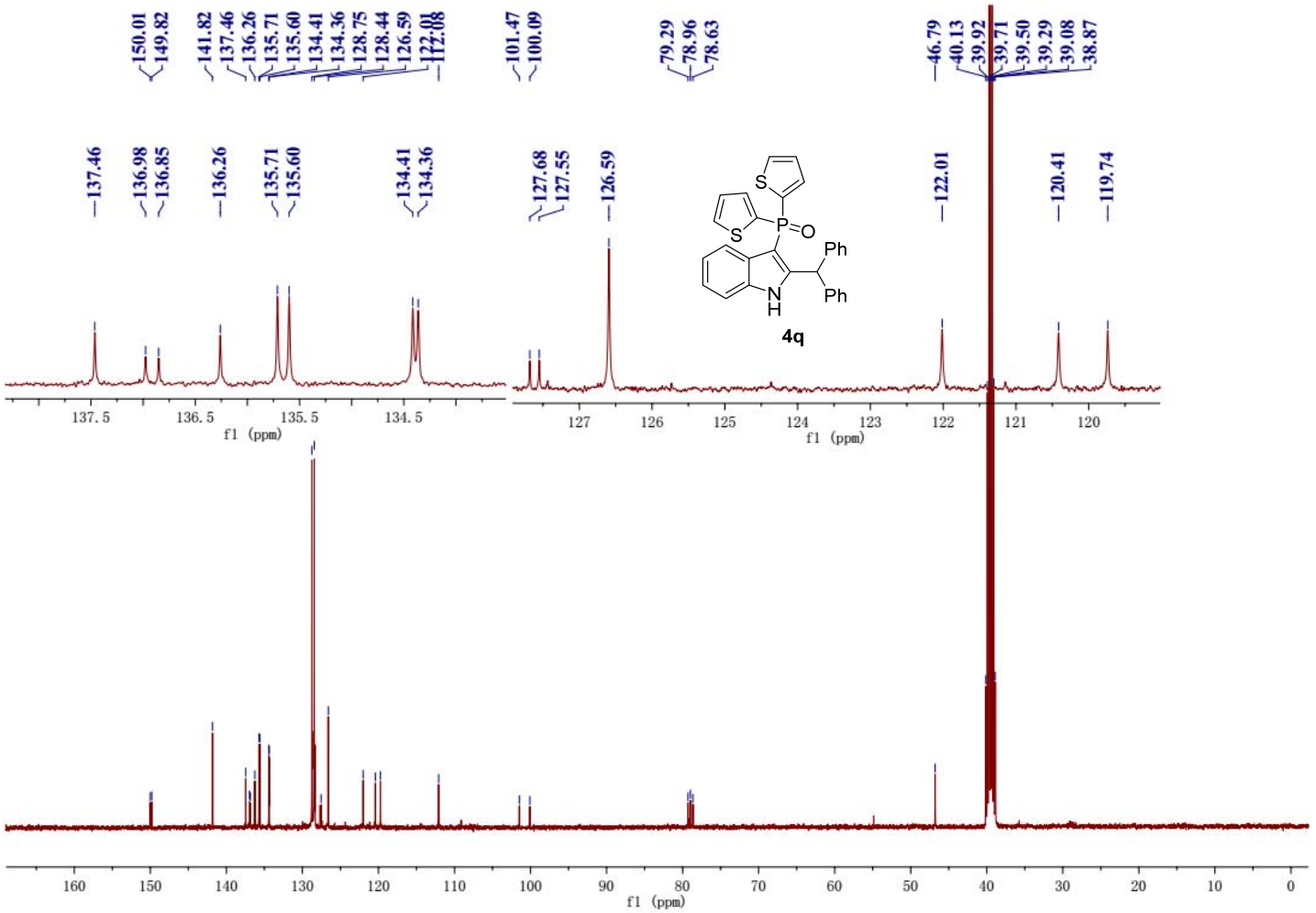

149.33
149.22
141.32
129.05
129.03
128.45
128.13
127.83
127.70
126.89
126.77
126.47
111.16
101.76
100.93
77.21
77.00
76.79
48.35
135.67
135.60
134.60
133.53
133.46
132.49
132.40
131.63
130.92
129.46
129.38
129.05
129.03
128.45
128.13
128.05
127.83
127.70
126.97
126.89
126.77
126.47
122.33
121.18
121.02
f1 (ppm)
f1 (ppm)

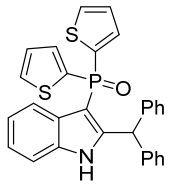

P
O
Ph
Ph
N
H

**4p**


-24.05
P
O
Ph
Ph
N
H
4p
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


11.798
11.794
8.309
8.015
8.008
8.001
7.433
7.429
7.324
7.311
7.299
7.234
7.218
7.207
6.952
3.420
2.506
2.503
2.500
2.498
2.495
7.447
7.442
7.433
7.429
7.417
7.336
7.324
7.311
7.299
7.259
7.247
7.234
7.218
7.207
7.097
7.096
7.084
7.071
6.952
6.899
6.886
6.873
6.779
6.765
3.17
4.37
8.35
1.12
1.07
1.07
1.07
f1 (ppm)
S
P
O
S
Ph
Ph
N
H
4q
1.00
2.04
3.17
4.37
8.35
1.12
1.07
1.07
1.07
f1 (ppm)


150.01
149.82
141.82
137.46
136.26
135.71
135.60
134.41
134.36
128.75
128.44
126.59
122.01
112.08
101.47
100.09
79.29
78.96
78.63
46.79
40.13
39.92
39.71
39.50
39.29
39.08
38.87
137.46
136.98
136.85
136.26
135.71
135.60
134.41
134.36
127.68
127.55
126.59
122.01
120.41
119.74
S
S
P
O
Ph
Ph
N
H
4q
137.5
136.5
135.5
134.5
f1 (ppm)
127
126
125
124
123
122
121
120
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
S
P
O
Ph
Ph
N
H

**4q**


6.49
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)