$Y(OTf)_3$-catalyzed Phosphorylation of 2*H*-Chromene Hemiacetals with P(O)-H compounds to 2-Phosphorylated 2*H*-Chromenes

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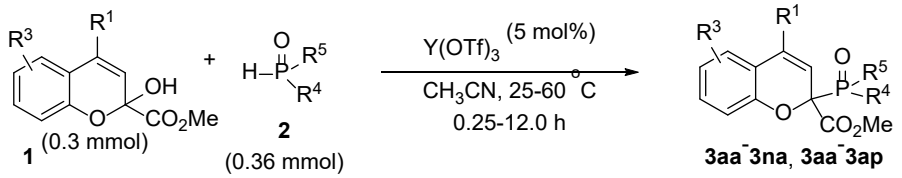
1. General information:

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 H. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-600 or DPX-400 spectrometer. The ^{31}P NMR spectra was recorded at JEOL 243 MHz with 85% H_3PO_4 as external standard. The ^{19}F NMR spectra was recorded at JEOL 565 MHz. HRMS data were collected on a on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). The linear ion trap (LTQ) part of the hybrid MS system was equipped with electrospray ionization (ESI) probe and operated in both positive and negative ion modes. 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.

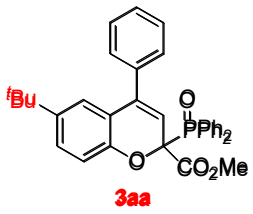
All reactions were run under an atmosphere of air. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone was distilled over anhydrous $CaSO_4$ and stored over MS 4Å. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation 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*H*-chromene hemiacetals **1** were prepared according to the literature report.[1] $Y(OTf)_3$ (99.998%) was purchased from Alfa-Aesar and used as received.

1 Y.-C. Wu, H.-J. Li, L. Liu, N. Demoulin, Z. Liu, D. Wang and Y.-J. Chen, *Adv. Synth. Catal.*, 2011, **353**, 907.

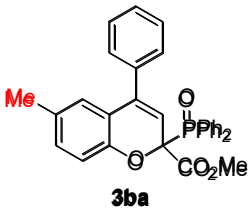
2. General procedure for the dehydrative phosphorylation of 2*H*-chromene hemiacetals with P(O)-H species to 2-phosphorylated 2*H*-chromenes



The reaction was carried out under an air atmosphere. To a 10-mL vial were added 2*H*-chromene hemiacetals **1** (0.3 mmol, 1.0 equiv), $R^4R^5P(O)H$ **2** (0.36 mmol, 1.2 equivs) and 3.0 mL of anhydrous CH_3CN. After adding $Y(OTf)_3$ (8.0 mg, 5 mol%), the reaction mixture was stirred at indicated temperature till almost full conversion of **1** by TLC analysis. The reaction mixture was directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 40:1 to 20:1, v:v) as the eluent to afford the desired products **3**.

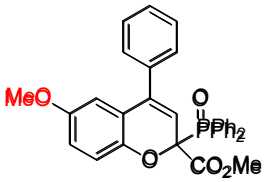


Column chromatography afforded the desired product **3aa** in 91% yield (142.7 mg) as white solid; Mp: 113-115 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20-8.17 (m, 2H), 7.82-7.79 (m, 2H), 7.62-7.60 (m, 1H), 7.57-7.55 (m, 2H), 7.42-7.38 (m, 3H), 7.33-7.30 (m, 3H), 7.24-7.22 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.81-6.77 (m, 2H), 6.28 (d, *J* = 4.8 Hz, 1H), 3.60 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 150.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.3, 138.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.0, 132.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.6, 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 16.5 Hz), 128.3, 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.9, 122.9, 119.4, 116.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.6, 84.6 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.0, 34.1, 31.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.7; HRMS (ESI): Exact mass calcd for $C_{33}H_{31}O_4P$ $[M+Na]^+$: 545.1852, Found: 545.1848.



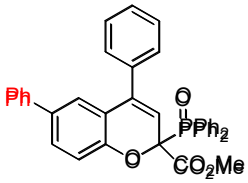
Column chromatography afforded the desired product **3ba** in 96% yield (138.4 mg) as white solid; Mp: 139-141 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05-8.02 (m, 2H), 7.70-7.67 (m, 2H), 7.49-7.47 (m, 1H), 7.44-7.41 (m, 2H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 2H), 7.15-7.13 (m, 5H), 6.73-6.72 (m, 1H), 6.64-6.63 (m, 1H), 6.46 (s, 1H), 6.14 (d, *J* = 5.4 Hz, 1H), 3.46 (s, 3H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 150.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 138.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.0,

132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.55 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.0, 130.4, 129.7 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.45 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.4, 128.2, 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.2, 119.8, 116.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 115.9, 84.4 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.0, 20.5; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.4; HRMS (ESI): Exact mass calcd for $C_{30}H_{25}O_4P$ $[M+Na]^+$: 503.1383, Found: 503.1380.



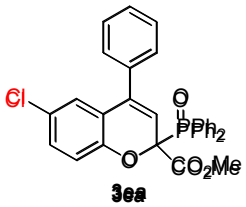
3ca

Column chromatography afforded **3ca** in 91% yield (135.5 mg) as white solid; Mp: 48-50 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06-8.03 (m, 2H), 7.72-7.68 (m, 2H), 7.51-7.48 (m, 1H), 7.46-7.42 (m, 2H), 7.29-7.26 (m, 2H), 7.25-7.24 (m, 1H), 7.18-7.14 (m, 5H), 6.68 (d, J = 8.4 Hz, 1H), 6.49 (dd, J = 8.4 Hz, 3.0 Hz, 1H), 6.25 (d, J = 3.0 Hz, 1H), 6.20 (d, J = 5.4 Hz, 1H), 3.48 (s, 3H), 3.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 154.1, 146.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 138.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.7, 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.45 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.44, 128.42 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.3, 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 120.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 117.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 116.7, 114.8, 111.7, 84.4 (d, $J_{C\text{-}P}$ = 78.0 Hz), 55.6, 53.0; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.4; HRMS (ESI): Exact mass calcd for $C_{30}H_{25}O_5P$ $[M+Na]^+$: 519.1332, Found: 519.1330.



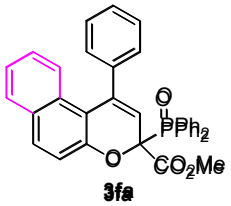
3da

Column chromatography afforded **3da** in 88% yield (143.2 mg) as white solid; Mp: 65-67 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16-8.13 (m, 2H), 7.80-7.76 (m, 2H), 7.59-7.57 (m, 1H), 7.54-7.51 (m, 2H), 7.37-7.32 (m, 3H), 7.30-7.27 (m, 4H), 7.26-7.25 (m, 2H), 7.22-7.18 (m, 5H), 6.95 (d, J = 1.8 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 4.8 Hz, 1H), 3.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 140.4, 138.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 136.7, 134.9, 132.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.66, 132.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.6, 128.54 (d, $J_{C\text{-}P}$ = 45.0 Hz), 128.50 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128. 0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.9, 126.6, 124.5, 120.2, 116.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 116.5, 84.8 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.1; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.3; HRMS (ESI): Exact mass calcd for $C_{35}H_{27}O_4P$ $[M+Na]^+$: 565.1539, Found: 565.1537.



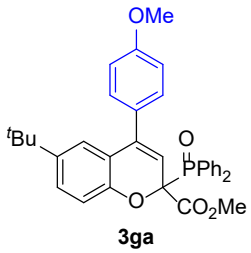
3ea

Column chromatography afforded the desired product **3ea** in 63% yield (94.7 mg) as white solid; Mp: 122-124 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17-8.14 (m, 2H), 7.82-7.79 (m, 2H), 7.64-7.62 (m, 1H), 7.59-7.56 (m, 2H), 7.43-7.38 (m, 4H), 7.30-7.26 (m, 4H), 6.99 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.32 (d, *J* = 4.8 Hz, 1H), 3.60 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 150.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 137.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 136.1, 132.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.6, 129.4 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.1 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7, 125.5, 121.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 117.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 117.4, 84.9 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.3; HRMS (ESI): Exact mass calcd for $C_{29}H_{22}ClO_4P$ $[M+Na]^+$: 523.0836, Found: 523.0837.



3fa

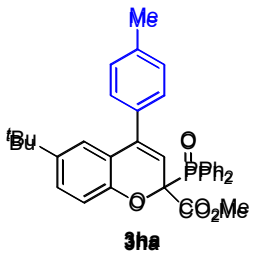
Column chromatography afforded the desired product **3fa** in 61% yield (94.4 mg) as yellow solid; Mp: 164-166 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18-8.15 (m, 2H), 7.81-7.78 (m, 2H), 7.68-7.63 (m, 2H), 7.62-7.59 (m, 1H), 7.57-7.54 (m, 2H), 7.37-7.32 (m, 3H), 7.26-7.25 (m, 1H), 7.24-7.17 (m, 6H), 6.99-6.96 (m, 1H), 6.91-6.90 (m, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 3.55 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 152.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 140.3, 138.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 131.4, 130.7, 130.2, 129.5, 128.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 96.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.9, 127.7, 126.3, 125.3, 123.6, 118.6, 117.6, 115.1, 83.3 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.0; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.7; HRMS (ESI): Exact mass calcd for $C_{33}H_{25}O_4P$ $[M-H]^-$: 515.1418, Found: 515.1421.



3ga

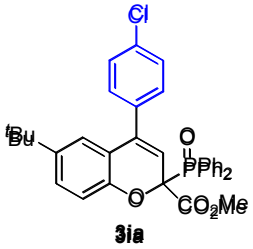
Column chromatography afforded the product **3ga** in 79% yield (131.0 mg) as white solid; Mp: 52-54 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19-8.16 (m, 2H), 7.80-7.77 (m, 2H), 7.62-7.60 (m, 1H), 7.57-7.54 (m, 2H), 7.32-7.26 (m, 3H), 7.23-7.20 (m, 2H), 7.05 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.95-6.93 (m, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 6.24 (d, *J* = 5.4 Hz, 1H), 3.86 (s, 3H), 3.59 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 159.6, 150.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.2, 138.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.2

(d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 99.0 Hz), 129.7, 129.3, 128.5 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7, 122.9, 119.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.4, 113.8, 84.5 (d, $J_{C\text{-}P}$ = 76.5 Hz), 55.3, 53.0, 34.1, 31.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{34}H_{33}O_5P$ $[M+Na]^+$: 575.1958, Found: 575.1958.



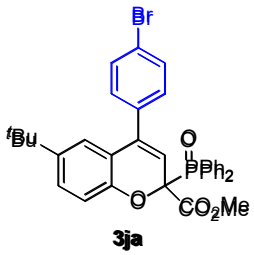
3ha

Column chromatography afforded product **3ha** in 95% yield (152.9 mg) as white solid; Mp: 52-54 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20-8.17 (m, 2H), 7.80-7.77 (m, 2H), 7.62-7.60 (m, 1H), 7.57-7.55 (m, 2H), 7.31-7.29 (m, 1H), 7.24-7.21 (m, 6H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.26 (d, *J* = 5.4 Hz, 1H), 3.59 (s, 3H), 2.40 (s, 3H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 150.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.2, 138.7 (d, $J_{C\text{-}P}$ = 7.5 Hz), 138.1, 134.0, 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.1, 128.5 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.46, 128.4, 127.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7, 122.9, 119.4, 115.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5, 84.5 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.0, 34.1, 31.2, 21.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{34}H_{33}O_4P$ $[M+Na]^+$: 559.2009, Found: 559.2012.



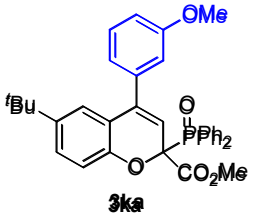
3ia

Column chromatography afforded the desired product **3ia** in 90% yield (150.4 mg) as white solid; Mp: 53-55 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19-8.16 (m, 2H), 7.80-7.77 (m, 2H), 7.64-7.61 (m, 1H), 7.58-7.55 (m, 2H), 7.40-7.38 (m, 2H), 7.34-7.31 (m, 1H), 7.27-7.22 (m, 4H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 5.4 Hz, 1H), 3.60 (s, 3H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 149.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.4, 137.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 135.4, 134.2, 132.61 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.60 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 129.7 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.6, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 94.5 Hz), 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.1, 122.5, 119.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.7, 84.4 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.0, 34.1, 31.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{33}H_{30}ClO_4P$ $[M+Na]^+$: 579.1462, Found: 579.1464.



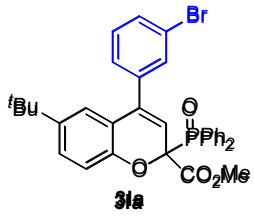
3ja

Column chromatography afforded the desired product **3ja** in 92% yield (166.0 mg) as white solid; Mp: 56-58 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18-8.15 (m, 2H), 7.80-7.76 (m, 2H), 7.63-7.61 (m, 1H), 7.58-7.53 (m, 4H), 7.33-7.30 (m, 1H), 7.24-7.19 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 1H), 6.28 (d, *J* = 5.4 Hz, 1H), 3.59 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.8 (d, J_{C-P} = 4.5 Hz), 149.9 (d, J_{C-P} = 4.5 Hz), 144.5, 137.7 (d, J_{C-P} = 7.5 Hz), 135.9, 132.61, 132.60 (d, J_{C-P} = 7.5 Hz), 132.2 (d, J_{C-P} = 3.0 Hz), 132.1 (d, J_{C-P} = 9.0 Hz), 131.6, 130.1, 129.7 (d, J_{C-P} = 100.5 Hz), 128.5 (d, J_{C-P} = 12.0 Hz), 128.3 (d, J_{C-P} = 94.5 Hz), 127.9 (d, J_{C-P} = 12.0 Hz), 127.1, 122.6, 122.4, 118.9 (d, J_{C-P} = 1.5 Hz), 116.8 (d, J_{C-P} = 3.0 Hz), 115.7, 84.4 (d, J_{C-P} = 76.5 Hz), 53.1, 34.1, 31.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{33}H_{30}BrO_4P$ $[M+Na]^+$: 623.0957, Found: 623.0953.



3ka

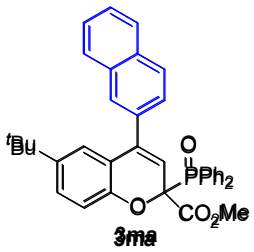
Column chromatography afforded the desired product **3ka** in 73% yield (121.0 mg) as white solid; Mp: 132-134 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19-8.16 (m, 2H), 7.82-7.78 (m, 2H), 7.62-7.60 (m, 1H), 7.57-7.54 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.06 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.94-6.91 (m, 2H), 6.86-6.84 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.29 (d, *J* = 5.4 Hz, 1H), 3.81 (s, 3H), 3.60 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, J_{C-P} = 6.0 Hz), 159.5, 149.9 (d, J_{C-P} = 6.0 Hz), 144.3, 138.6 (d, J_{C-P} = 7.5 Hz), 138.3 (d, J_{C-P} = 1.5 Hz), 132.6 (d, J_{C-P} = 9.0 Hz), 132.5 (d, J_{C-P} = 1.5 Hz), 132.2, 132.1, 129.8 (d, J_{C-P} = 102.0 Hz), 129.4, 128.5 (d, J_{C-P} = 94.5 Hz), 128.4 (d, J_{C-P} = 12.0 Hz), 127.9 (d, J_{C-P} = 12.0 Hz), 126.8, 122.9, 120.9, 119.3 (d, J_{C-P} = 1.5 Hz), 116.3 (d, J_{C-P} = 4.5 Hz), 115.5, 114.3, 113.6, 84.5 (d, J_{C-P} = 76.5 Hz), 55.3, 53.0, 34.1, 31.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{34}H_{33}O_5P$ $[M+Na]^+$: 575.1958, Found: 575.1959.



3la

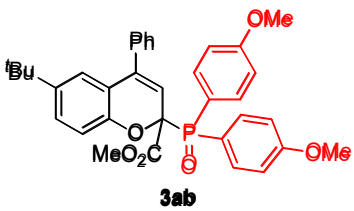
Column chromatography afforded the desired product **3la** in 89% yield (160.6 mg) as white solid; Mp: 146-148 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19-8.16 (m, 2H), 7.81-7.78 (m, 2H), 7.64-7.61 (m, 1H), 7.58-7.55 (m, 2H), 7.53-7.52 (m, 1H), 7.48 (s, 1H), 7.35-7.33 (m, 1H), 7.30-7.28 (m, 1H), 7.27-7.24 (m, 3H), 7.09 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.30 (d, *J* = 5.4 Hz, 1H), 3.60 (s, 3H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.8 (d, J_{C-P} = 4.5 Hz), 149.9 (d, J_{C-P} = 4.5

Hz), 144.5, 139.0, 137.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.61, 132.60 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ =7.5 Hz), 131.5, 131.3, 129.9, 129.7 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 94.5 Hz), 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.1 (d, $J_{C\text{-}P}$ = 13.5 Hz), 122.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 118.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 117.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.7, 84.4 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.1, 34.1, 31.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.2; HRMS (ESI): Exact mass calcd for $C_{33}H_{30}BrO_4P$ $[M+Na]^+$: 623.0957, Found: 623.0948.



3ma

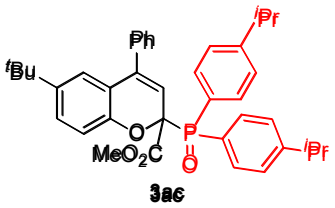
Column chromatography afforded **3ma** in 97% yield (166.6 mg) as white solid; Mp: 62-64 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.22-8.19 (m, 2H), 7.89-7.86 (m, 4H), 7.85-7.81 (m, 2H), 7.64-7.62 (m, 1H), 7.59-7.56 (m, 2H), 7.54-7.52 (m, 2H), 7.40 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.33-7.30 (m, 1H), 7.25-7.22 (m, 2H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 5.4 Hz, 1H), 3.62 (s, 3H), 1.11 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.1, 150.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.5, 138.9 (d, $J_{C\text{-}P}$ = 7.5 Hz), 134.7, 133.4 (d, $J_{C\text{-}P}$ = 39.0 Hz), 132.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.7, 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.0 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.57 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.1 (d, $J_{C\text{-}P}$ = 30.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.0, 126.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.4, 123.2, 116.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.7, 84.8 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.2, 34.2, 31.3; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.8; HRMS (ESI): Exact mass calcd for $C_{37}H_{33}O_4P$ $[M+Na]^+$: 595.2009, Found: 595.2004.



3ab

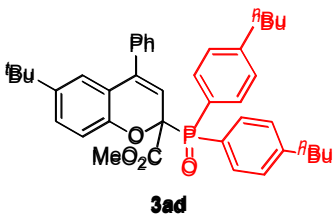
Column chromatography afforded the desired product **3ab** in 63% yield (110.1 mg) as white solid; Mp: 47-49 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11-8.07 (m, 2H), 7.71-7.68 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.33 (m, 2H), 7.06-7.04 (m, 3H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.72-6.71 (m, 2H), 6.28 (d, *J* = 5.4 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 162.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 162.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 150.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.2, 138.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 137.1, 134.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 134.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.5, 128.4, 128.2, 126.6, 122.8, 121.1 (d, $J_{C\text{-}P}$ = 106.5 Hz), 119.6 (d, $J_{C\text{-}P}$ = 100.5 Hz), 119.4, 116.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 115.5, 114.0 (d, $J_{C\text{-}P}$ = 13.5 Hz), 113.4 (d, $J_{C\text{-}P}$ =12.0 Hz), 84.7 (d, $J_{C\text{-}P}$ = 76.5 Hz), 55.3, 55.1, 53.0, 34.1, 31.2; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.3; HRMS (ESI): Exact

mass calcd for $C_{35}H_{35}O_6P$ [M+Na]$^+$: 605.2063, Found: 605.2061.



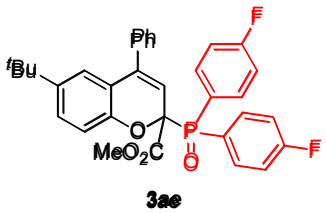
3ac

Column chromatography afforded the desired product **3ac** in 84% yield (152.9 mg) as white solid; Mp: 154-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (ABd, *J* = 10.8 Hz, 8.4 Hz, 2H), 7.74 (ABd, *J* = 10.8 Hz, 8.4 Hz, 2H), 7.40-7.39 (m, 5H), 7.30-7.29 (m, 2H), 7.12-7.10 (m, 2H), 7.6 (dd, *J* = 8.4 Hz, 2.4 H, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 5.4 Hz, 1H), 3.58 (s, 3H), 3.00-2.96 (m, 1H), 2.81-2.76 (m, 1H), 1.29 (d, *J* = 6.6 Hz, 6H), 1.13 (d, *J* = 6.6 Hz, 6H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 153.4 (d, $J_{C\text{-}P}$ = 61.5 Hz), 150.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.2, 138.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.2, 132.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 30.0 Hz), 128.2, 127.2 (d, $J_{C\text{-}P}$ = 102.0 Hz), 126.8 (d, $J_{C\text{-}P}$ = 22.5 Hz), 126.6, 126.1 (d, $J_{C\text{-}P}$ = 13.5 Hz), 125.2 (d, $J_{C\text{-}P}$ = 94.5 Hz), 122.8, 119.3, 116.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5, 84.8 (d, $J_{C\text{-}P}$ = 76.5 Hz), 52.9, 34.2, 34.12, 34.06, 31.3, 23.70, 23.66, 23.6, 23.5; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 29.4; HRMS (ESI): Exact mass calcd for $C_{39}H_{43}O_4P$ [M+Na]$^+$: 629.2791, Found: 629.2785.

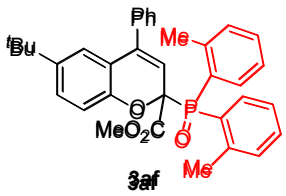


3ad

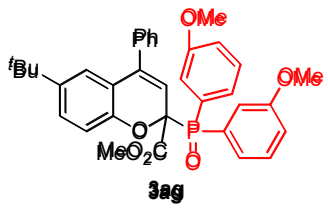
Column chromatography afforded the desired product **3ad** in 65% yield (123.8 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07-8.04 (m, 2H), 7.72-7.68 (m, 2H), 7.42-7.38 (m, 3H), 7.37-7.35 (m, 2H), 7.32-7.31 (m, 2H), 7.06-7.04 (m, 3H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 4.8 Hz, 1H), 3.58 (s, 3H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.48 (t, *J* = 7.8 Hz, 2H), 1.66-1.62 (m, 2H), 1.49-1.44 (m, 2H), 1.40-1.34 (m, 2H), 1.29-1.21 (m, 2H), 1.12 (s, 9H), 0.94 (t, *J* = 1.8 Hz, 3H), 0.85 (t, *J* = 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 150.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 147.7 (d, $J_{C\text{-}P}$ = 72.0 Hz), 144.2, 138.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.1, 132.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 24.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 58.5 Hz), 128.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 126.7, 126.6 (d, $J_{C\text{-}P}$ = 103.5 Hz), 125.2 (d, $J_{C\text{-}P}$ = 97.5 Hz), 122.8, 119.3, 116.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5, 84.7 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.0, 35.8, 35.5, 33.2, 33.0, 31.3, 22.4, 22.2, 13.9, 13.8; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 29.9; HRMS (ESI): Exact mass calcd for $C_{41}H_{47}O_4P$ [M+Na]$^+$: 657.3104, Found: 657.3110.



Column chromatography afforded the desired product **3ae** in 90% yield (150.8 mg) as white solid; Mp: 54-56 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.22-8.18 (m, 2H), 7.78-7.74 (m, 2H), 7.44-7.39 (m, 3H), 7.33-7.32 (m, 2H), 7.28-7.25 (m, 2H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.92-6.89 (m, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 5.4 Hz, 1H), 3.64 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 166.2 (d, $J_{C\text{-}F}$ = 52.5 Hz), 164.5 (d, $J_{C\text{-}F}$ = 52.5 Hz), 149.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.8, 139.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 136.8, 135.22, 135.21 (d, $J_{C\text{-}P}$ = 19.5 Hz), 134.8 (d, $J_{C\text{-}P}$ = 18.0 Hz), 134.77, 128.51, 128.47 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.0, 125.6 (d, $J_{C\text{-}P}$ = 106.5 Hz), 124.2 (d, $J_{C\text{-}P}$ = 97.5 Hz), 123.0, 119.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.1 (d, $J_{C\text{-}F}$ = 34.5 Hz), 116.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 115.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5, 115.4, 115.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 84.6 (d, $J_{C\text{-}P}$ = 79.5 Hz), 53.2, 34.2, 31.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 26.4; ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) : *δ* = -105.0 (1F), -105.8 (1F); HRMS (ESI): Exact mass calcd for $C_{33}H_{29}F_2O_4P$ $[M+Na]^+$: 581.1664, Found: 581.1662.

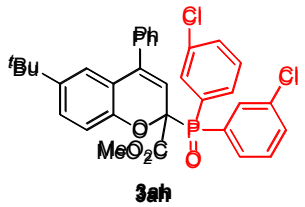


Column chromatography afforded product **3af** in 77% yield (127.2 mg) as white solid; Mp: 49-51 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 7.71 (dd, *J* = 13.2 Hz, 7.8 Hz, 1H), 7.46-7.44 (m, 1H), 7.41-7.36 (m, 4H), 7.29-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.20-7.18 (m, 1H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.02-6.98 (m, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 5.4 Hz, 1H), 3.74 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 169.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 149.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.2, 143.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 138.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 137.1, 134.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.1, 132.0, 131.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 129.5 (d, $J_{C\text{-}P}$ = 93.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.4, 128.2, 126.8, 125.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 122.8, 119.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 117.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.4, 84.6 (d, $J_{C\text{-}P}$ = 79.5 Hz), 53.2, 34.1, 31.2, 21.94, 21.92, 21.5, 21.4; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 33.8; HRMS (ESI): Exact mass calcd for $C_{35}H_{35}O_4P$ $[M+Na]^+$: 573.2165, Found: 573.2162.



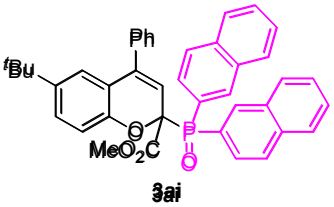
3ag

Column chromatography afforded the desired product **3ag** in 89% yield (155.6 mg) as white solid; Mp: 46-48 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77-7.74 (m, 1H), 7.71-7.68 (m, 1H), 7.48-7.45 (m, 1H), 7.43-7.39 (m, 3H), 7.38-7.35 (m, 1H), 7.36-7.30 (m, 3H), 7.15-7.12 (m, 2H), 7.05 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.84-6.82 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.27 (d, *J* = 12.0 Hz, 1H), 3.88 (s, 3H), 3.62 (s, 3H), 3.61 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 159.5 (d, $J_{C\text{-}P}$ = 15.0 Hz), 158.9 (d, $J_{C\text{-}P}$ = 15.0 Hz), 149.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.3, 138.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 137.0, 131.1 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.7 (d, $J_{C\text{-}P}$ = 93.0 Hz), 129.66 (d, $J_{C\text{-}P}$ = 13.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 15.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.4, 126.9, 125.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 124.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 122.8, 119.3 (d, $J_{C\text{-}P}$ = 1.5 Hz), 119.2, 118.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 117.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 116.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 115.6, 84.7 (d, $J_{C\text{-}P}$ = 78.0 Hz), 55.5, 55.1, 53.1, 34.1, 31.2; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 29.1; HRMS (ESI): Exact mass calcd for $C_{35}H_{35}O_6P$ $[M+Na]^+$: 605.2063, Found: 605.2060.



3ah

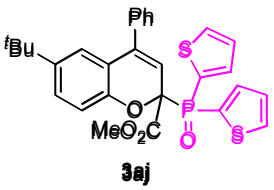
3ah was obtained in 80% yield (142.0 mg) as white solid; Mp: 47-49 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 11.4 Hz, 1H), 8.12-8.09 (m, 1H), 7.75 (d, *J* = 11.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.55-7.52 (m, 1H), 7.44-7.39 (m, 3H), 7.34-7.33 (m, 2H), 7.25 (s, 1H), 7.18-7.15 (m, 1H), 7.09 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.19 (d, *J* = 5.4 Hz, 1H), 3.66 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 149.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 144.6, 139.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.7, 135.2 (d, $J_{C\text{-}P}$ = 15.0 Hz), 134.4 (d, $J_{C\text{-}P}$ = 16.5 Hz), 133.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 97.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.3 (d, $J_{C\text{-}P}$ = 91.5 Hz), 129.96 (d, $J_{C\text{-}P}$ = 16.5 Hz), 129.95, 129.2 (d, $J_{C\text{-}P}$ = 13.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.2, 123.0, 119.0, 115.4, 115.36 (d, $J_{C\text{-}P}$ = 4.5 Hz), 84.8 (d, $J_{C\text{-}P}$ = 78.0 Hz), 53.3, 34.1, 31.1; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 25.0; HRMS (ESI): Exact mass calcd for $C_{33}H_{29}Cl_2O_4P$ $[M+Na]^+$: 613.1073, Found: 613.1070.



3ai

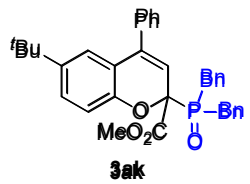
Column chromatography afforded **3ai** in 77% yield (143.8 mg) as white solid; Mp: 176-178 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 13.2 Hz, 1H), 8.42 (d, *J* = 13.8 Hz, 1H), 8.30 (t, *J* = 8.4 Hz, 1H), 8.06-8.02 (m,

2H), 7.94 (d, J = 8.4 Hz, 1H), 7.83 (t, J = 9.0 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.66-7.64 (m, 2H), 7.61-7.58 (m, 1H), 7.49-7.47 (m, 1H), 7.44-7.38 (m, 4H), 7.35-7.33 (m, 2H), 6.92 (dd, J = 9.0 Hz, 2.4 Hz, 1H), 6.77 (d, J = 9.0 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 6.38 (d, J = 4.8 Hz, 1H), 3.58 (s, 3H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, J_{C-P} = 4.5 Hz), 149.8 (d, J_{C-P} = 4.5 Hz), 144.2, 138.9 (d, J_{C-P} = 9.0 Hz), 137.0, 135.1 (d, J_{C-P} = 9.0 Hz), 135.0, 134.8 (d, J_{C-P} = 9.0 Hz), 134.6, 132.5 (d, J_{C-P} = 13.5 Hz), 132.0 (d, J_{C-P} = 13.5 Hz), 129.2, 128.9, 128.5, 128.4, 128.36 (d, J_{C-P} = 27.0 Hz), 128.12, 128.11 (d, J_{C-P} = 12.0 Hz), 127.9, 127.5, 127.4 (d, J_{C-P} = 33.0 Hz), 126.9 (d, J_{C-P} = 82.5 Hz), 126.89, 126.8, 126.7, 126.5, 125.9 (d, J_{C-P} = 100.5 Hz), 122.6, 119.2, 116.4 (d, J_{C-P} = 4.5 Hz), 115.4, 85.1 (d, J_{C-P} = 76.5 Hz), 53.1, 33.9, 31.1; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.4; HRMS (ESI): Exact mass calcd for $C_{41}H_{35}O_4P$ $[M+Na]^+$: 645.2165, Found: 645.2161.



3aj

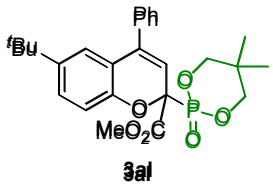
Column chromatography afforded the desired product **3aj** in 89% yield (142.7 mg) as white solid; Mp: 46-48 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.97 (dd, J = 12.6 Hz, 3.6 Hz, 1H), 7.82 (t, J = 4.8 Hz, 1H), 7.67 (dd, J = 7.2 Hz, 3.6 Hz, 1H), 7.62 (t, J = 4.8 Hz, 1H), 7.42-7.37 (m, 3H), 7.32-7.30 (m, 2H), 7.25-7.24 (m, 1H), 7.14 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.02-7.00 (m, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.22 (d, J = 6.6 Hz, 1H), 3.73 (s, 3H), 1.14 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.5 (d, J_{C-P} = 4.5 Hz), 149.9 (d, J_{C-P} = 6.0 Hz), 144.5, 139.4 (d, J_{C-P} = 10.5 Hz), 138.2 (d, J_{C-P} = 10.5 Hz), 137.7 (d, J_{C-P} = 9.0 Hz), 136.9, 135.0 (d, J_{C-P} = 4.5 Hz), 134.9 (d, J_{C-P} = 4.5 Hz), 129.3 (d, J_{C-P} = 117.0 Hz), 128.5 (d, J_{C-P} = 1.5 Hz), 128.4, 128.3, 128.2 (d, J_{C-P} = 109.5 Hz), 128.0 (d, J_{C-P} = 15.0 Hz), 127.7 (d, J_{C-P} = 15.0 Hz), 127.0, 123.0, 119.3 (d, J_{C-P} = 2.0 Hz), 115.7, 115.3 (d, J_{C-P} = 3.0 Hz), 84.0 (d, J_{C-P} = 91.5 Hz), 53.2, 34.1, 31.2; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 19.7; HRMS (ESI): Exact mass calcd for $C_{29}H_{27}O_4PS_2$ $[M+Na]^+$: 557.0981, Found: 557.0984.



3ak

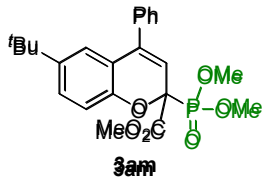
Column chromatography afforded the desired product **3ak** in 30% yield (84.4 mg) as yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 5H), 7.30-7.27 (m, 3H), 7.23-7.19 (m, 3H), 7.15-7.13 (m, 2H), 7.10-7.03 (m, 5H), 5.95 (d, J = 6.0 Hz, 1H), 3.55 (s, 3H), 3.40-3.33 (m, 3H), 3.20 (dd, J = 15.0 Hz, 12.6 Hz, 1H), 1.21 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 168.2 (d, J_{C-P} = 4.5 Hz), 150.0 (d, J_{C-P} = 7.5 Hz), 144.9, 137.6 (d, J_{C-P} = 7.5 Hz), 136.7, 130.7 (d, J_{C-P} = 1.5 Hz), 130.6 (d, J_{C-P} = 3.0 Hz), 130.5 (d, J_{C-P} = 6.0 Hz),

130.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.6, 128.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.3, 128.23, 128.16, 127.2, 126.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 126.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 123.4, 119.9, 116.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 115.9, 81.2 (d, $J_{C\text{-}P}$ = 73.5 Hz), 53.0, 34.3, 33.6, 33.2, 32.9, 32.6, 31.3; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 42.8; HRMS (ESI): Exact mass calcd for $C_{35}H_{35}O_4P$ $[M+Na]^+$: 573.2165, Found: 573.2161.



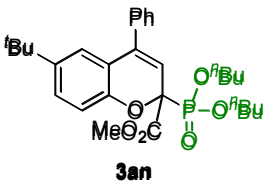
3al

Column chromatography afforded the desired product **3al** in 81% yield (114.3 mg) as white solid; Mp: 167-169 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.38 (m, 5H), 7.26-7.24 (m, 1H), 7.11 (d, J = 1.8 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.15 (d, J = 7.8 Hz, 1H), 4.68 (dd, J = 10.8 Hz, 2.4 Hz, 1H), 4.42 (dd, J = 10.8 Hz, 2.4 Hz, 1H), 4.10-4.05 (m, 1H), 4.00-3.95 (m, 1H), 3.85 (s, 3H), 1.32 (s, 3H), 1.20 (s, 9H), 0.93 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 149.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 145.1, 137.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 136.7, 128.7, 128.3, 127.0, 123.5, 119.9, 116.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 115.4, 83.5 (d, $J_{C\text{-}P}$ = 159.0 Hz), 79.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 79.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 53.5, 34.3, 32.6, 32.5, 31.3, 22.2, 20.6; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 3.4; HRMS (ESI): Exact mass calcd for $C_{26}H_{31}O_6P$ $[M+Na]^+$: 493.1750, Found: 493.1744.



3am

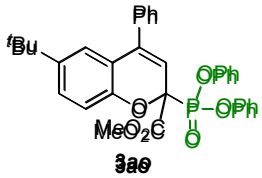
Column chromatography afforded the desired product **3am** in 88% yield (113.6 mg) as white solid; Mp: 57-59 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44-7.37 (m, 5H), 7.24 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 5.98 (d, J = 6.6 Hz, 1H), 3.861 (s, 3H), 3.858 (d, J = 9.0 Hz, 3H), 3.84 (d, J = 9.0 Hz, 3H), 1.18 (s, 9H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 150.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 144.7, 138.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 136.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.2, 123.1, 119.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 115.8, 81.6 (d, $J_{C\text{-}P}$ = 163.5 Hz), 54.92, 54.87, 54.80, 54.75, 53.5, 34.2, 31.3; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 14.8; HRMS (ESI): Exact mass calcd for $C_{23}H_{27}O_6P$ $[M+Na]^+$: 453.1437, Found: 453.1432.



3an

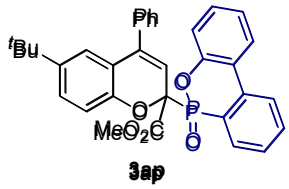
Column chromatography afforded **3an** in 90% yield (138.9 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44-7.37 (m, 5H), 7.22 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.98 (d, J = 6.0 Hz,

1H), 4.22-4.16 (m, 2H), 4.14-4.07 (m, 2H), 3.86 (s, 3H), 1.61-1.52 (m, 4H), 1.36-1.31 (m, 2H), 1.31-1.26 (m, 2H), 1.18 (s, 9H), 0.88 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.9 (d, J_{C-P} = 3.0 Hz), 150.3 (d, J_{C-P} = 7.5 Hz), 144.4, 138.1 (d, J_{C-P} = 10.5 Hz), 137.1 (d, J_{C-P} = 1.5 Hz), 128.5 (d, J_{C-P} = 1.5 Hz), 128.4, 128.2, 127.0, 122.9, 119.6 (d, J_{C-P} = 3.0 Hz), 116.7 (d, J_{C-P} = 6.0 Hz), 115.8, 81.8 (d, J_{C-P} = 160.5 Hz), 68.05, 68.01, 67.93, 67.88, 53.3, 34.2, 32.41, 32.37, 31.3, 18.51, 18.50, 13.5; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 12.3; HRMS (ESI): Exact mass calcd for $C_{29}H_{39}O_6P$ $[M-H]^-$: 513.2411, Found: 513.2417.



3ao

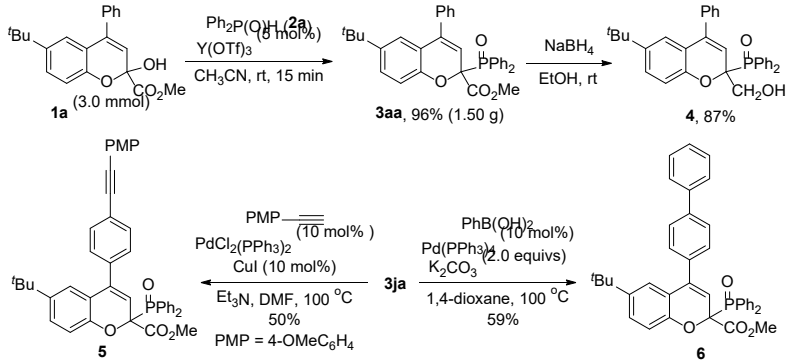
Column chromatography afforded **3ao** in 91% yield (151.4 mg) as yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.39-7.38 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.22 (m, 5H), 7.20-7.16 (m, 3H), 7.12-7.09 (m, 1H), 7.05-7.04 (m, 2H), 6.98 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.89-6.80 (m, 1H), 6.00 (d, J = 6.0 Hz, 1H), 3.83 (s, 3H), 1.19 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 167.0 (d, J_{C-P} = 6.0 Hz), 156.0, 150.7 (d, J_{C-P} =10.5 Hz), 150.4 (d, J_{C-P} = 10.5 Hz), 150.0 (d, J_{C-P} = 4.5 Hz), 144.8, 139.5 (d, J_{C-P} = 10.5 Hz), 136.8, 129.5 (d, J_{C-P} = 19.5 Hz), 129.4, 128.5 (d, J_{C-P} = 1.5 Hz), 128.37, 128.35, 127.4, 125.3 (d, J_{C-P} = 27.0 Hz), 123.2, 120.5 (d, J_{C-P} = 4.5 Hz), 120.2 (d, J_{C-P} = 4.5 Hz), 119.2 (d, J_{C-P} = 3.0 Hz), 115.6 (d, J_{C-P} = 81.0 Hz), 114.9 (d, J_{C-P} = 7.5 Hz), 82.0 (d, J_{C-P} = 165.0 Hz), 53.6, 34.2, 31.3; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 3.8; HRMS (ESI): Exact mass calcd for $C_{33}H_{31}O_6P$ $[M-H]^-$: 553.1785, Found: 553.1792.



3ap

Column chromatography **3ap** in 98% yield (157.7 mg) as white solid; Mp: 58-60 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.02-7.99 (m, 1H), 7.80-7.78 (m, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.36-7.32 (m, 4H), 7.29-7.28 (m, 1H), 7.22-7.19 (m, 1H), 7.15-7.13 (m, 2H), 6.96 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.62 (d, J = 1.8 Hz, 1H), 6.29 (d, J = 8.4 Hz, 1H), 5.92 (d, J = 4.2 Hz, 1H), 3.93 (s, 3H), 1.10 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 166.7, 150.8 (d, J_{C-P} = 9.0 Hz), 149.5 (d, J_{C-P} =1.5 Hz), 144.2, 139.7 (d, J_{C-P} = 10.5 Hz), 136.7 (d, J_{C-P} = 3.0 Hz), 134.2 (d, J_{C-P} = 1.5 Hz), 132.9 (d, J_{C-P} = 9.0 Hz), 130.5, 128.3, 128.2 (d, J_{C-P} = 3.0 Hz), 127.7 (d, J_{C-P} = 13.5 Hz), 126.8, 124.4 (d, J_{C-P} = 75.0 Hz), 122.8 (d, J_{C-P} = 10.5 Hz), 122.6, 121.2 (d, J_{C-P} = 10.5 Hz), 120.7 (d, J_{C-P} = 114.0 Hz), 119.9 (d, J_{C-P} = 6.0 Hz), 119.1 (d, J_{C-P} = 3.0 Hz), 85.0 (d, J_{C-P} = 103.5 Hz), 53.5, 34.0, 31.2; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 24.4; HRMS (ESI): Exact mass calcd for $C_{33}H_{29}O_5P$ $[M+Na]^+$: 559.1645, Found: 559.1649.

3. Gram-scale synthesis and product elaboration



3.1 Gram-scale synthesis

The gram-scale reaction was carried out under an air atmosphere. To a 100 mL three-necked flask were added **1a** (1.01 g, 3.0 mmol, 1.0 equiv), $Ph_2P(O)H$ **2a** (0.73 g, 3.6 mmol, 1.2 equivs) and 30.0 mL of anhydrous CH_3CN. After adding $Y(OTf)_3$ (80 mg, 5 mol%), the reaction mixture was stirred at room temperature till almost full conversion of **1a** by TLC analysis. The reaction mixture was directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 30:1 to 20:1, v:v) as the eluent to afford the desired products **3aa** in 96% yield (1.50 g).

3.2 Product elaboration

1) The synthesis of 4

To a 10-mL vial were added sequentially **3aa** (52.0 mg, 0.1 mmol), $NaBH_4$ (56.7 mg, 1.5 mmol, 15 equivs) and 2.0 mL of ethanol. The reaction mixture was stirred at room temperature till almost full conversion of **3aa** by TLC analysis. After removing the solvent EtOH, 10 mL H_2O was added to the mixture. The organic layer was extract with ethyl acetate (3×10 mL) and then dried with Na_2SO_4. After removing the solvent, the residue was then subjected to column chromatography using dichloromethane/ethyl acetate (generally 6:1, v:v) as the eluent to afford the desired product **4** in 87% yield (43.0 mg) as white solid. Mp: 161-163 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.21-8.18 (m, 2H), 7.71-7.68 (m, 2H), 7.61-7.59 (m, 1H), 7.57-7.54 (m, 2H), 7.38-7.33 (m, 3H), 7.25-7.22 (m, 3H), 7.16-7.13 (m, 2H), 7.09 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.63 (d, J = 1.8 Hz, 1H), 6.09 (d, J = 2.4 Hz, 1H), 4.19 (dd, J = 11.4 Hz, 8.4 Hz, 1H), 4.06-4.02 (m, 1H), 3.34 (brs, 1H), 1.11 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 150.2, 144.2, 139.8, 137.4, 132.4 (d, J_{C-P} = 7.5 Hz), 132.08 (d, J_{C-P} = 61.5 Hz), 132.06 (d, J_{C-P} = 9.0 Hz), 129.86 (d, J_{C-P} = 93.0 Hz), 129.1 (d, J_{C-P} = 90.0 Hz), 128.5 (d, J_{C-P} = 12.0 Hz), 128.4, 128.3, 128.1, 127.6 (d, J_{C-P} = 12.0 Hz), 126.5, 123.0, 120.8, 118.8, 114.8, 82.1 (d, J_{C-P} = 81.0 Hz), 65.9, 65.8, 34.1, 31.2; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.0; HRMS (ESI):

Exact mass calcd for $C_{32}H_{31}O_3P$ $[M+Na]^+$: 517.1903, Found: 517.1905.

2) Sonogashira coupling reaction

Compound **5** was prepared from **3ja** (60.1 mg, 0.1 mmol) and 1-ethynyl-4-methoxybenzene (39.6 mg, 0.3 mmol) according to the literature procedure.[2] Column chromatography afforded the desired product **5** in 50% yield (32.6 mg) as brown solid. Mp: 57-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.15 (m, 2H), 7.82-7.77 (m, 2H), 7.63-7.54 (m, 5H), 7.51-7.46 (m, 2H), 7.34-7.29 (m, 3H), 7.25-7.21 (m, 2H), 7.07 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.91-6.88 (m, 2H), 6.80-6.77 (m, 2H), 6.31 (d, *J* = 5.2 Hz, 1H), 3.83 (s, 3H), 3.60 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 167.9 (d, $J_{C\text{-}P}$ = 4.0 Hz), 159.7, 149.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 144.4, 138.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 136.5, 133.1, 132.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.55, 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.0, 131.4, 130.0 (d, $J_{C\text{-}P}$= 100.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.48 (d, $J_{C\text{-}P}$ = 95.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.0, 123.6, 122.7, 119.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 115.4 (d, $J_{C\text{-}P}$ = 45.0 Hz), 114.0, 90.4, 87.7, 84.5 (d, $J_{C\text{-}P}$ = 77.0 Hz), 55.3, 53.0, 34.1, 31.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{42}H_{37}O_5P$ $[M+Na]^+$: 675.2271, Found: 675.2269.

3) Suzuki coupling reaction

Compound **6** was prepared from **3ja** (60.1 mg, 0.1 mmol) and phenylboronic acid (24.4 mg, 0.2 mmol) according to the literature procedure.[3] Column chromatography afforded **6** in 59% yield (35.3 mg) as white solid. Mp: 50-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22-8.17 (m, 2H), 7.84-7.79 (m, 2H), 7.67-7.65 (m, 4H), 7.62-7.56 (m, 3H), 7.49-7.45 (m, 2H), 7.43-7.37 (m, 3H), 7.33-7.31 (m, 1H), 7.26-7.23 (m, 2H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 5.2 Hz, 1H), 3.61 (s, 3H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 150.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 144.4, 141.1, 140.5, 138.5 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.0, 132.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.0, 128.9, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.4, 128.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 127.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.2 (d, $J_{C\text{-}P}$ = 91.5 Hz), 127.1 (d, $J_{C\text{-}P}$ = 1.5 Hz), 122.9, 119.3, 116.4 (d, $J_{C\text{-}P}$ =3.0 Hz), 115.6, 84.6 (d, $J_{C\text{-}P}$ = 76.5 Hz), 53.0, 34.2, 31.3; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 28.1; HRMS (ESI): Exact mass calcd for $C_{39}H_{35}O_4P$ $[M+Na]^+$: 621.2165, Found: 621.2166.

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[2] Q.-Y. Chen and Z.-Y. Yang, *Tetrahedron Lett*. 1986, **27**, 1171.
[3] N. Eleya, A. Mahal, M. Hein, A. Villiger and P. Langer, *Adv. Synth. Catal.* 2011, **353**, 2761.

4. X-ray Crystallographic Data of 3ca

Data intensity of **3ca** was collected on a 'XtaLAB Synergy R, DW system, HyPix' diffractometer at 299.51(12) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **3ca**: $C_{30}H_{25}O_5P$, T = 299.51(12) K, monoclinic, space group $P2_1/c$ (no. 14), a = 9.32193(5) Å, b = 15.92387(9) Å, c = 17.03098(8) Å, α = 90 deg, β = 91.9636(4) deg, γ = 90 deg, V = 2526.62(2) $Å^3$. Z = 4, d_{calc} = 1.305 g/m^3. 24076 reflections measured (7.602° ≤ 2Θ ≤ 152.992°), 5125 unique [R_{int} = 0.0339, R_{sigma} = 0.0208] which were used in all calculations. The final R_1 was 0.0398 (I > 2σ(I)) and wR_2 was 0.1095 (all data).

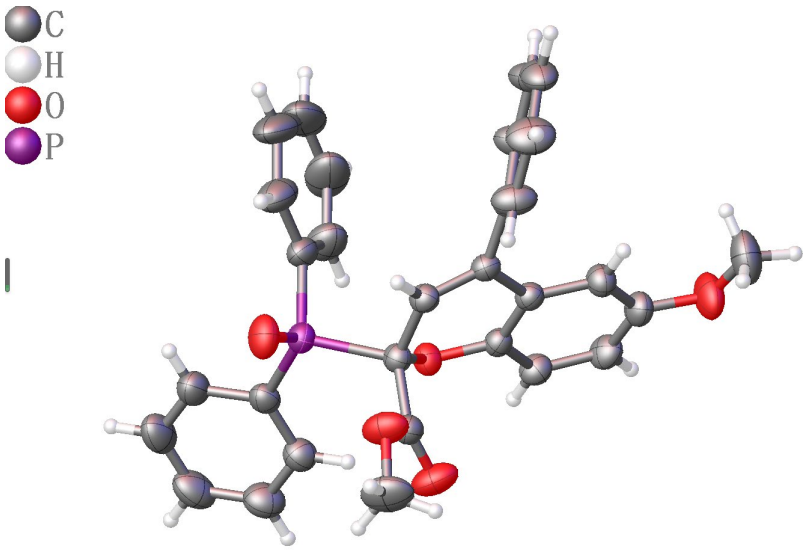
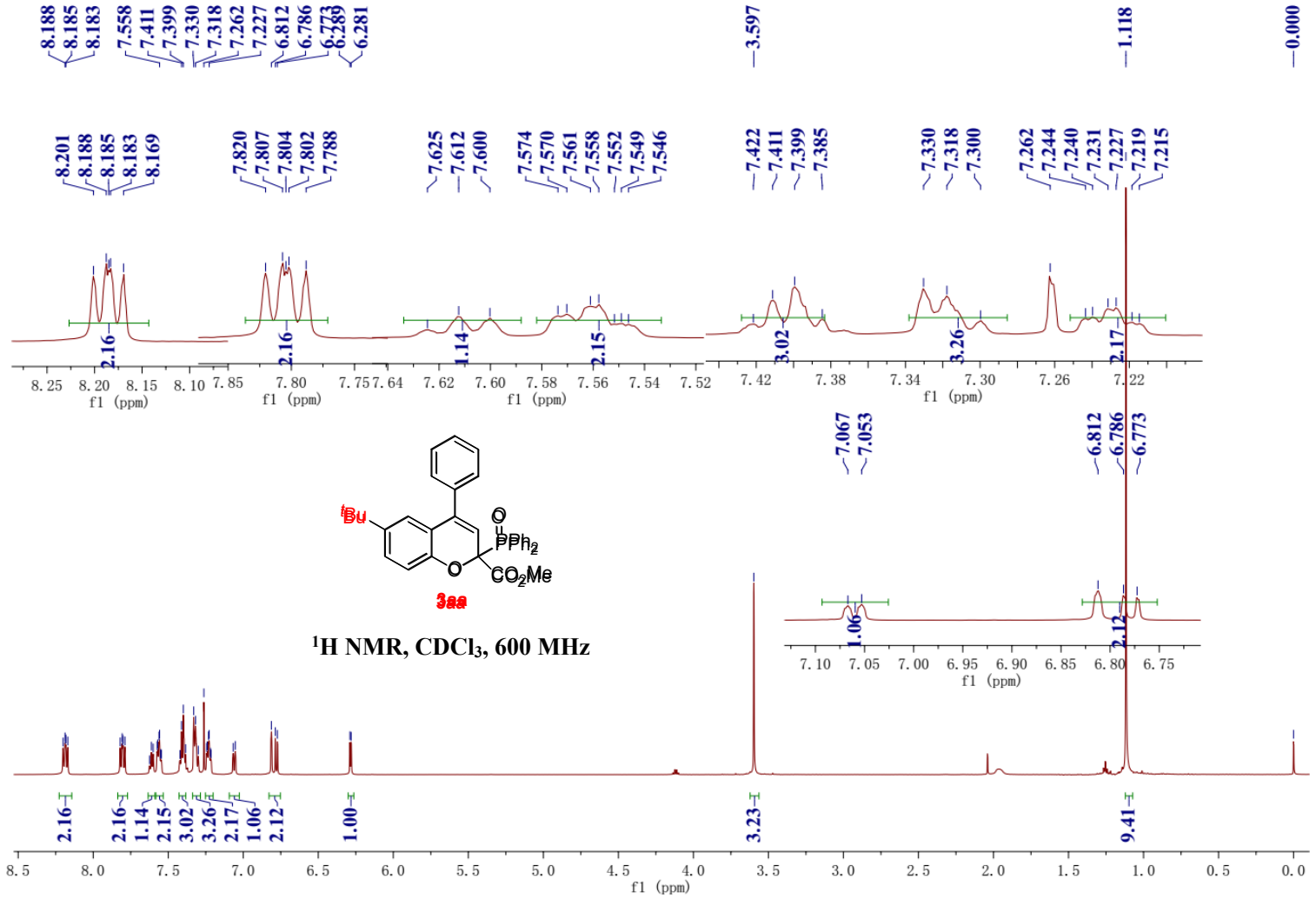


Table S1. Crystal data and structure refinement for exp_1147.

Identification code	exp_1147
Empirical formula	$C_{30}H_{25}O_5P$
Formula weight	496.47
Temperature/K	299.51(12)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.32193(5)
b/Å	15.92387(9)
c/Å	17.03098(8)
α/°	90
β/°	91.9636(4)

γ/°	90
Volume/Å^3	2526.62(2)
Z	4
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	1.284
F(000)	1040.0
Crystal size/mm^3	0.13 × 0.12 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.602 to 152.992
Index ranges	-11 ≤ h ≤ 11, -19 ≤ k ≤ 17, -21 ≤ l ≤ 19
Reflections collected	24076
Independent reflections	5125 [R_{int} = 0.0339, R_{sigma} = 0.0208]
Data/restraints/parameters	5125/0/327
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1079
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.19/-0.35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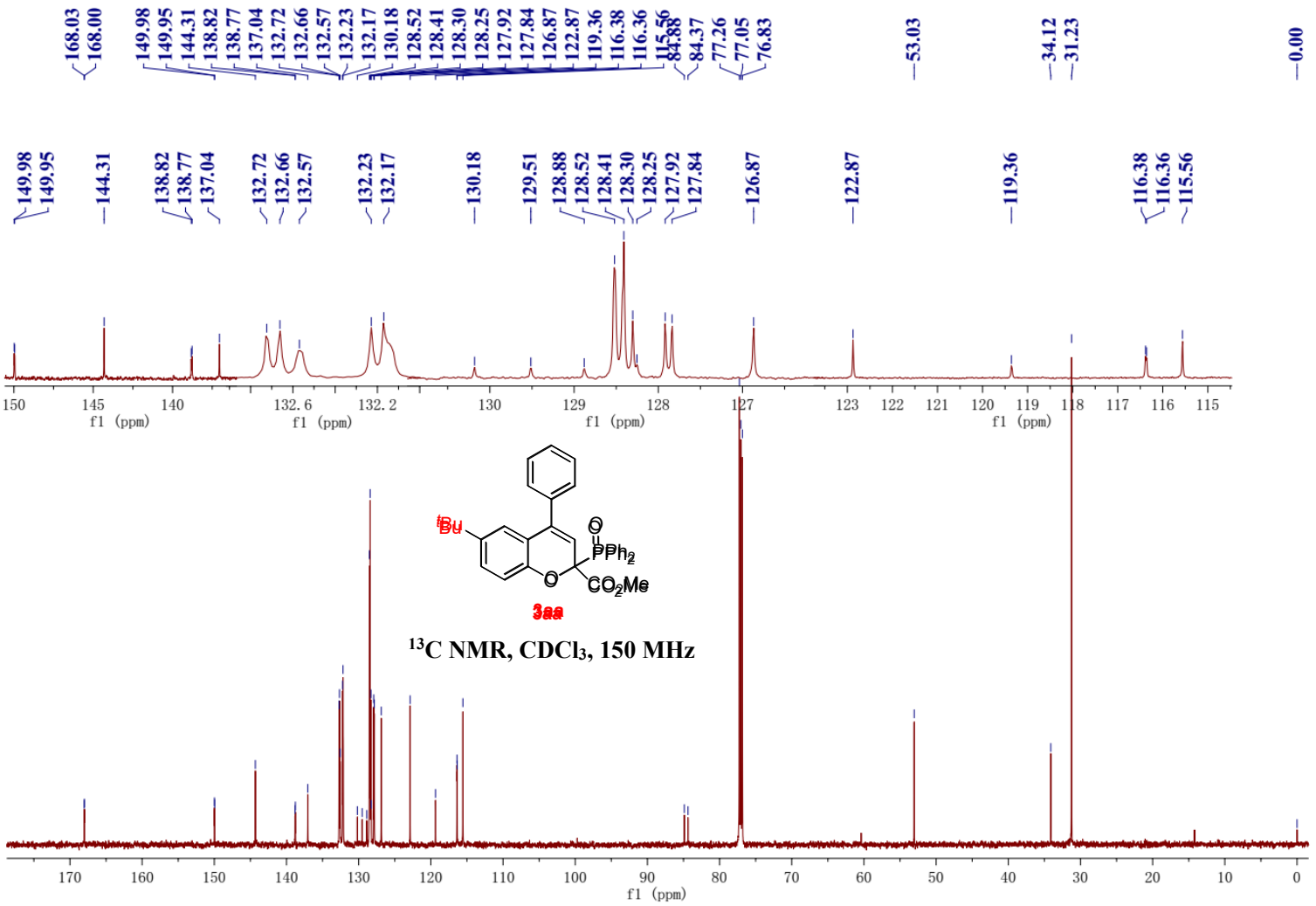
8.185
8.183
7.558
7.411
7.399
7.330
7.318
7.262
7.227
6.812
6.786
6.773
6.289
6.281
3.597
1.118
0.000
8.201
8.188
8.185
8.183
8.169
7.820
7.807
7.804
7.802
7.788
7.625
7.612
7.600
7.574
7.570
7.561
7.558
7.552
7.549
7.546
7.422
7.411
7.399
7.385
7.330
7.318
7.300
7.262
7.244
7.240
7.231
7.227
7.219
7.215
2.16
2.16
1.14
2.15
3.02
3.26
2.17
f1 (ppm)
7.067
7.053
6.812
6.786
6.773
1.06
2.12
tBu
O
PPh2
O
CO2Me
3aa
1H NMR, CDCl3, 600 MHz
2.16
2.16
1.14
2.15
3.02
3.26
2.17
1.06
2.12
1.00
3.23
9.41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132.57
132.23
132.17
130.18
128.52
128.41
128.30
128.25
127.92
127.84
126.87
122.87
119.36
116.38
116.36
115.56
84.88
84.37
77.26
77.05
76.83
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f1 (ppm)
tBu
PPh2
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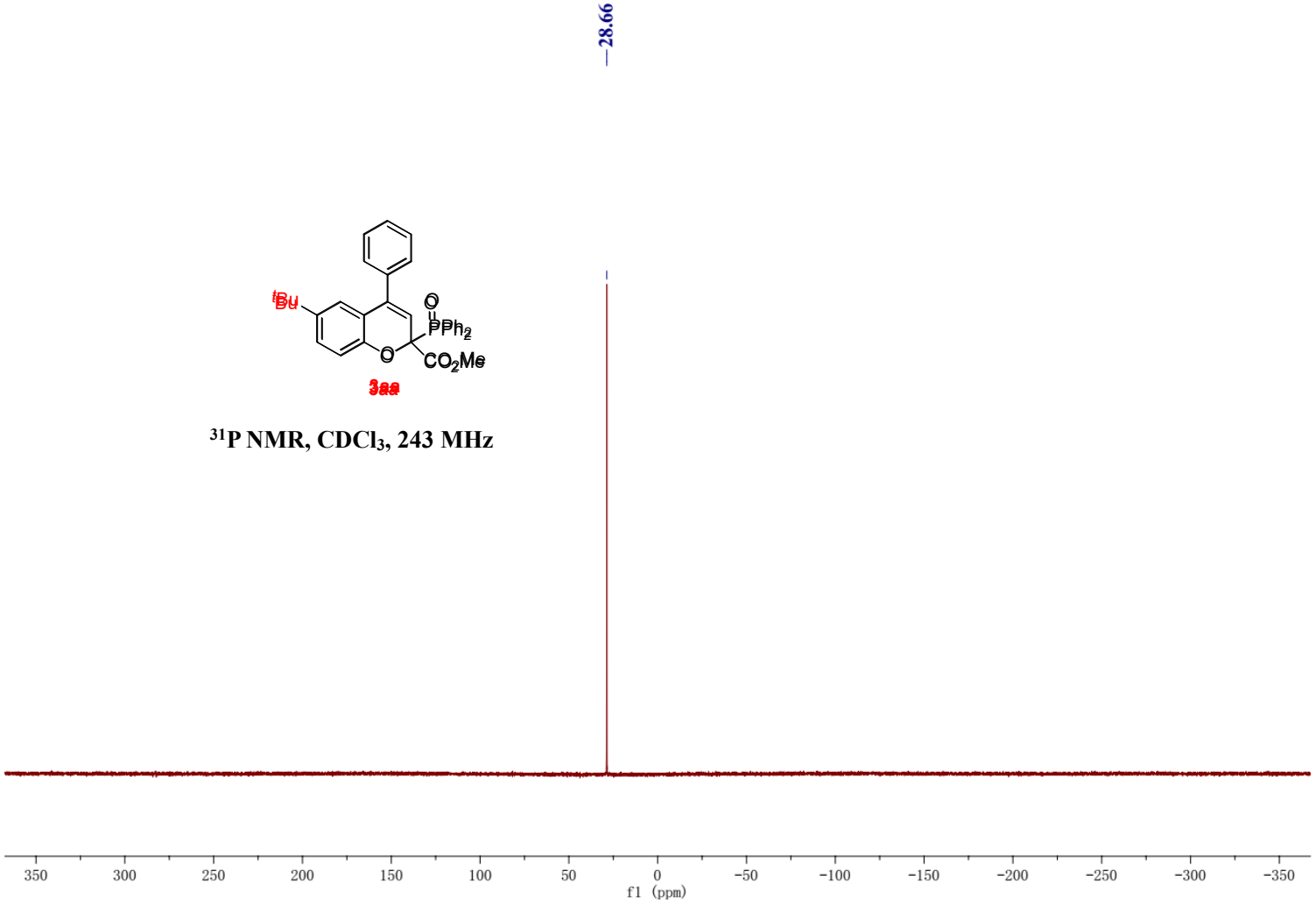
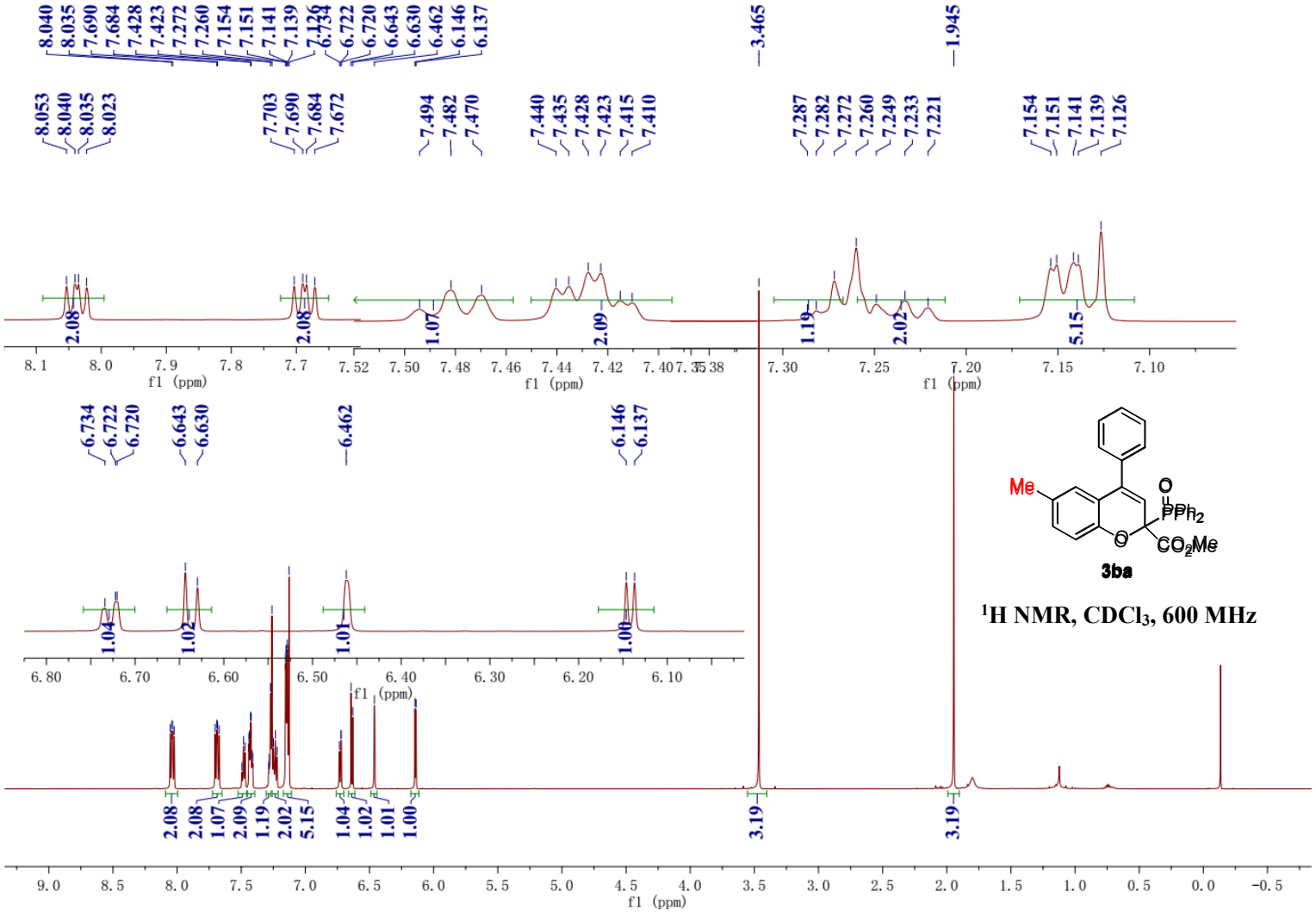
3aa
13C NMR, CDCl3, 150 MHz



^{31}P NMR, $CDCl_3$, 243 MHz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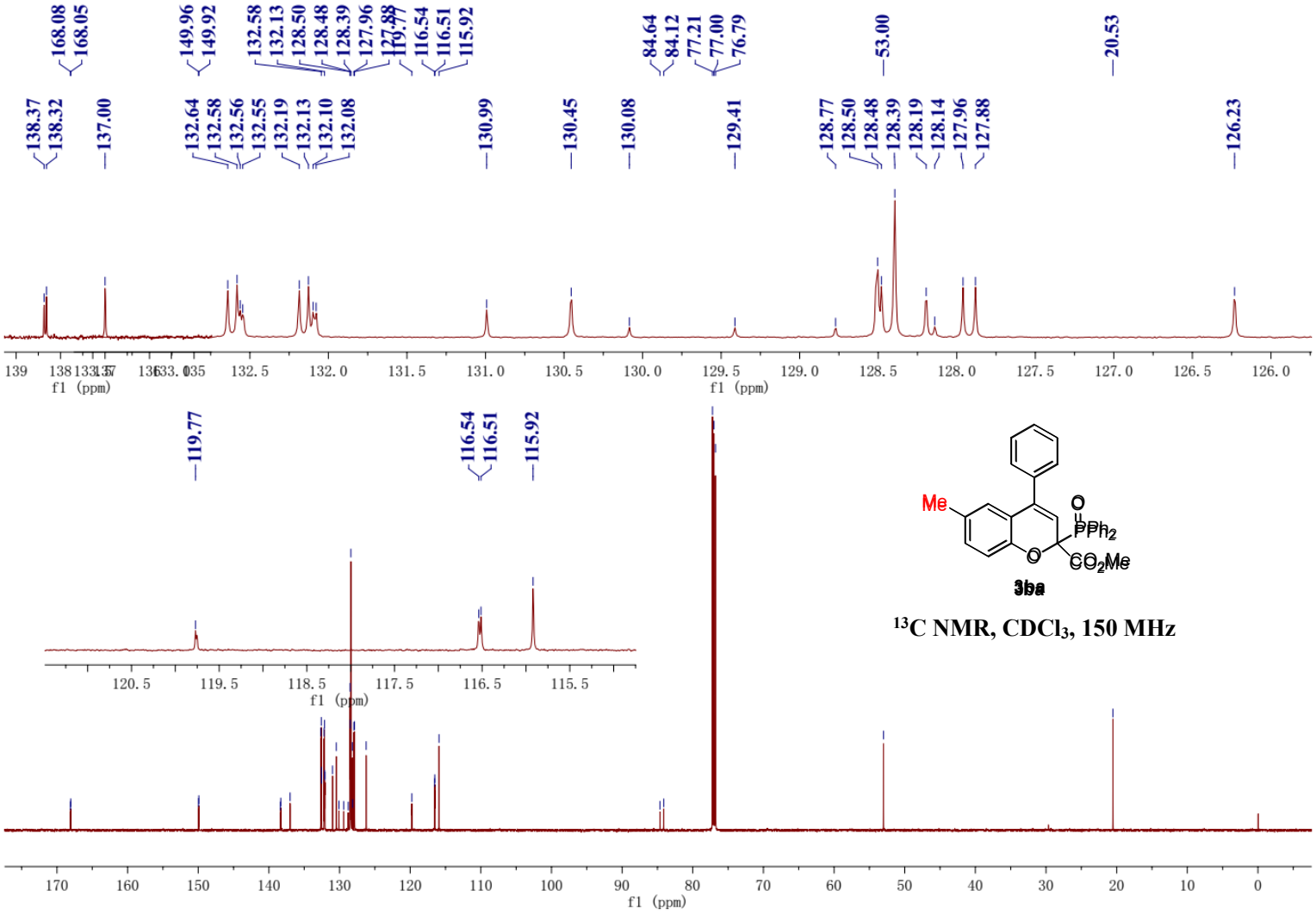
7.428
7.423
7.272
7.260
7.154
7.151
7.141
7.139
7.126
6.734
6.722
6.720
6.643
6.630
6.462
6.146
6.137
3.465
1.945
8.053
8.040
8.035
8.023
7.703
7.690
7.684
7.672
7.494
7.482
7.470
7.440
7.435
7.428
7.423
7.415
7.410
7.287
7.282
7.272
7.260
7.249
7.233
7.221
7.154
7.151
7.141
7.139
7.126
2.08
2.08
1.07
2.09
1.19
2.02
5.15
f1 (ppm)
1.04
1.02
1.01
1.00
Me
O
PPh2
O
CO2Me
3ba
1H NMR, CDCl3, 600 MHz
2.08
2.08
1.07
2.09
1.19
2.02
5.15
1.04
1.02
1.01
1.00
3.19
3.19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116.51
115.92
84.64
84.12
77.21
77.00
76.79
53.00
20.53
138.37
138.32
137.00
132.64
132.58
132.56
132.55
132.19
132.13
132.10
132.08
130.99
130.45
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128.48
128.39
128.19
128.14
127.96
127.88
126.23
f1 (ppm)
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115.92
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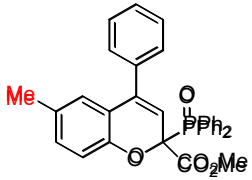
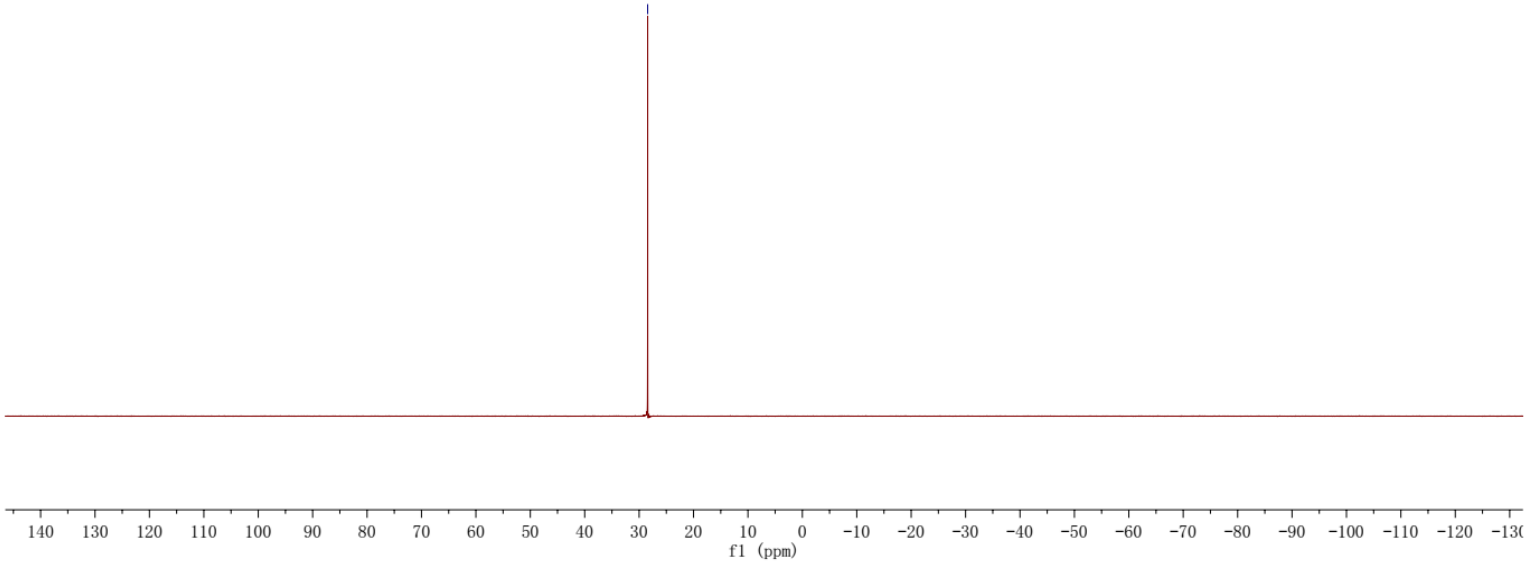
PPh2
O
CO2Me
3ba
13C NMR, CDCl3, 150 MHz

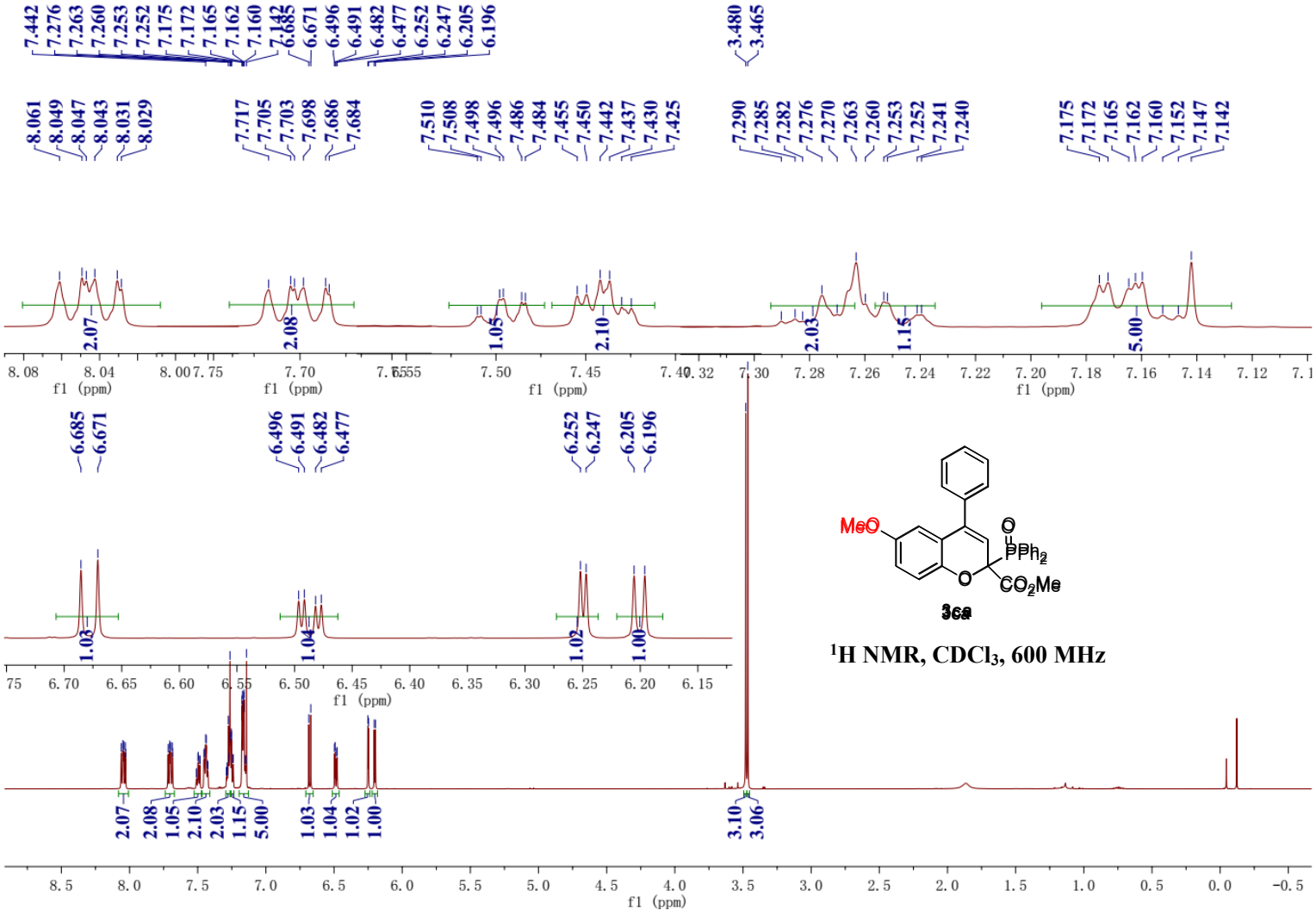
28.43



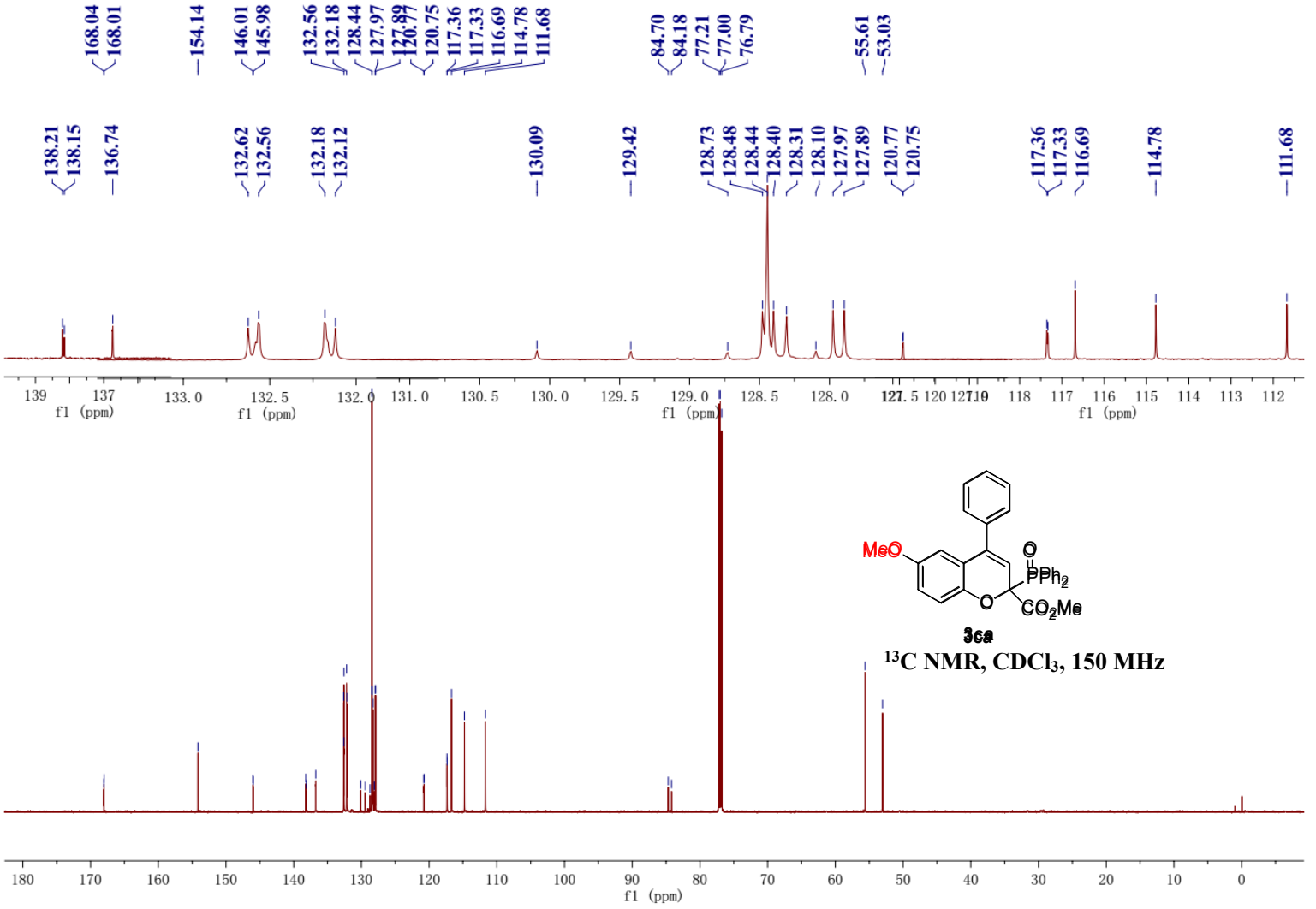
3ba

^{31}P NMR, $CDCl_3$, 243 MHz



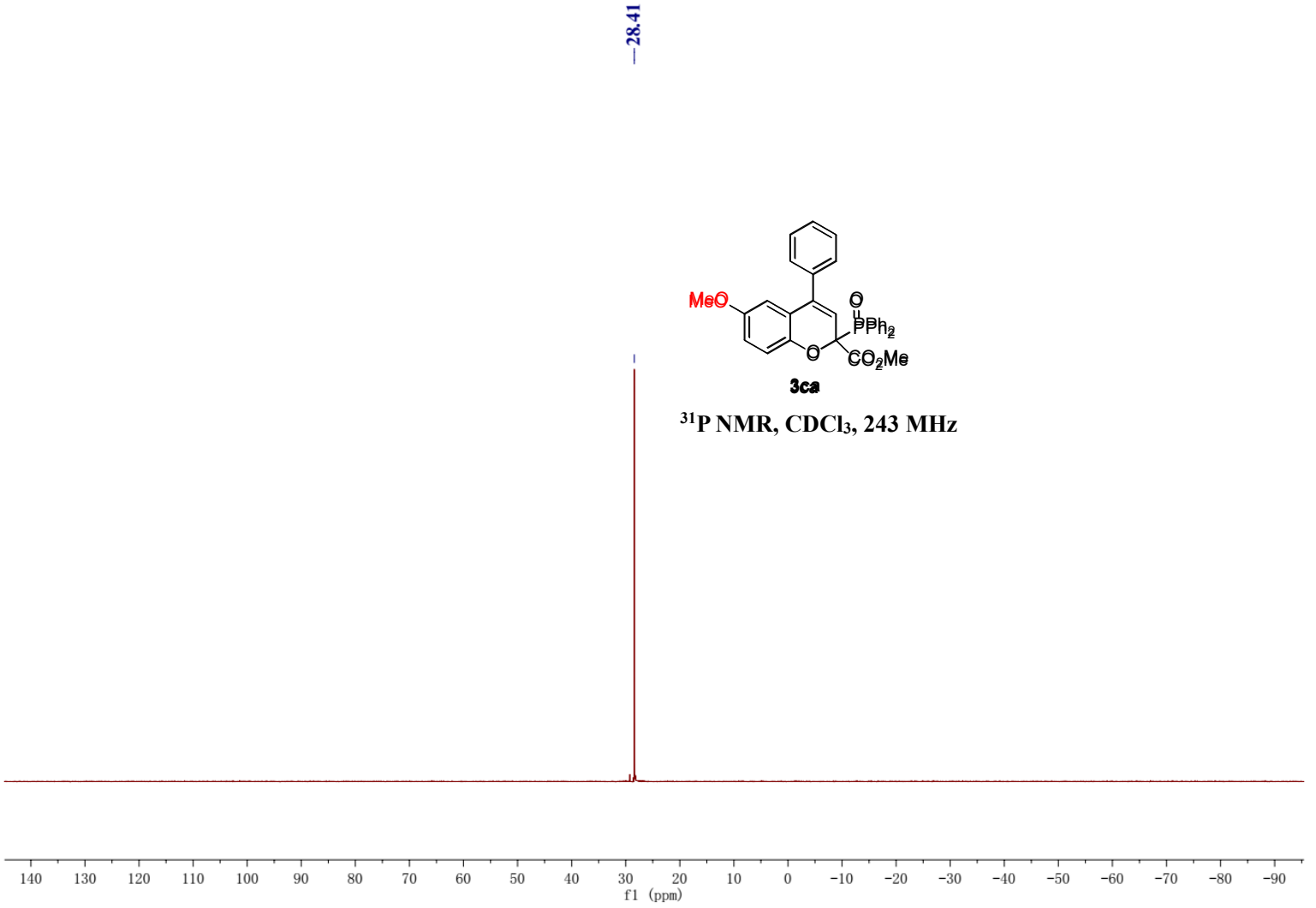


^{1}H NMR, $CDCl_3$, 600 MHz



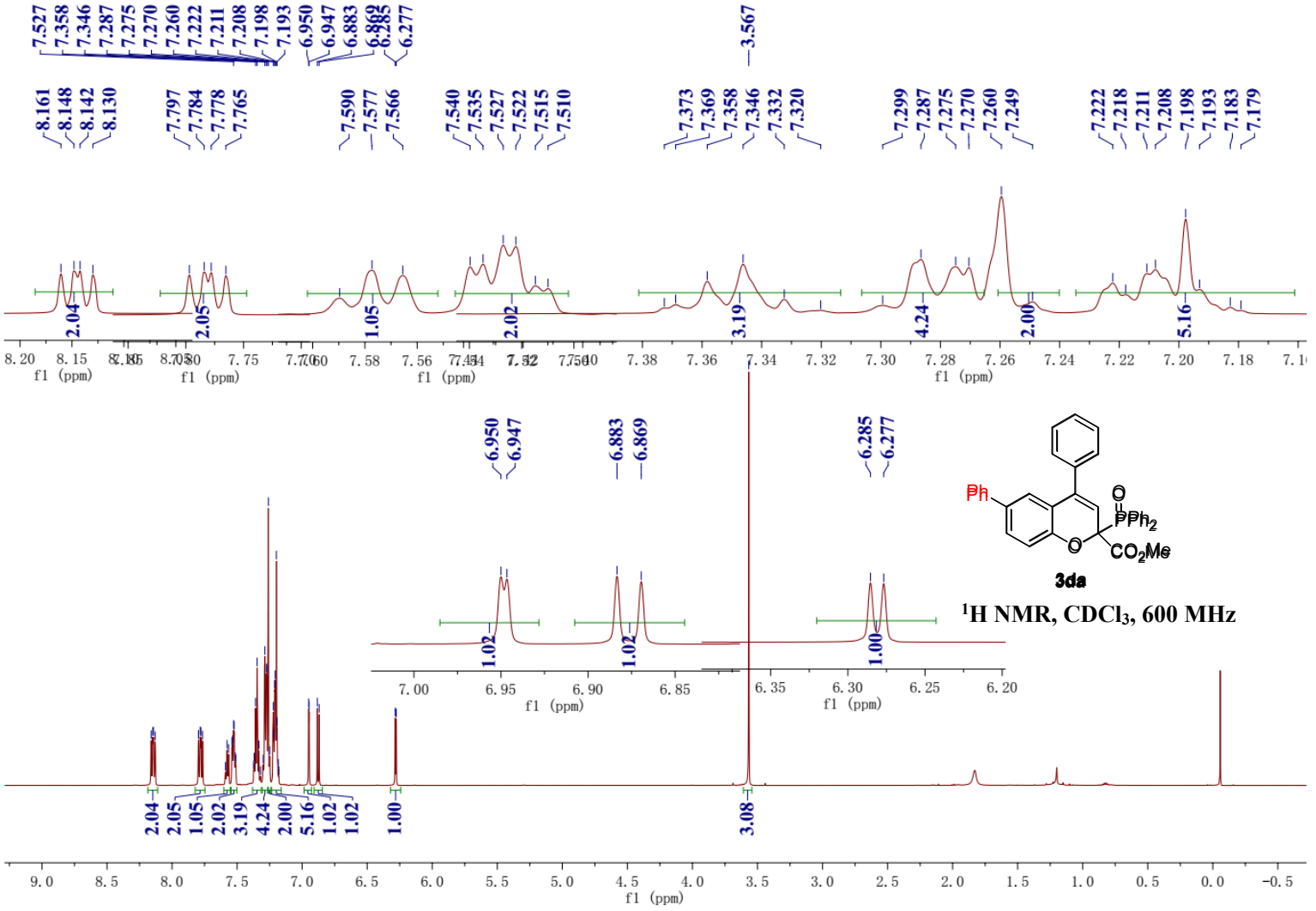
3ca

^{13}C NMR, $CDCl_3$, 150 MHz



3ca

^{31}P NMR, $CDCl_3$, 243 MHz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7.193
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6.947
6.883
6.869
6.285
6.277
3.567
8.161
8.148
8.142
8.130
7.797
7.784
7.778
7.765
7.590
7.577
7.566
7.540
7.535
7.527
7.522
7.515
7.510
7.373
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7.358
7.346
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7.299
7.287
7.275
7.270
7.260
7.249
7.222
7.218
7.211
7.208
7.198
7.193
7.183
7.179
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2.05
1.05
2.02
3.19
4.24
2.00
5.16
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1.00
3.08
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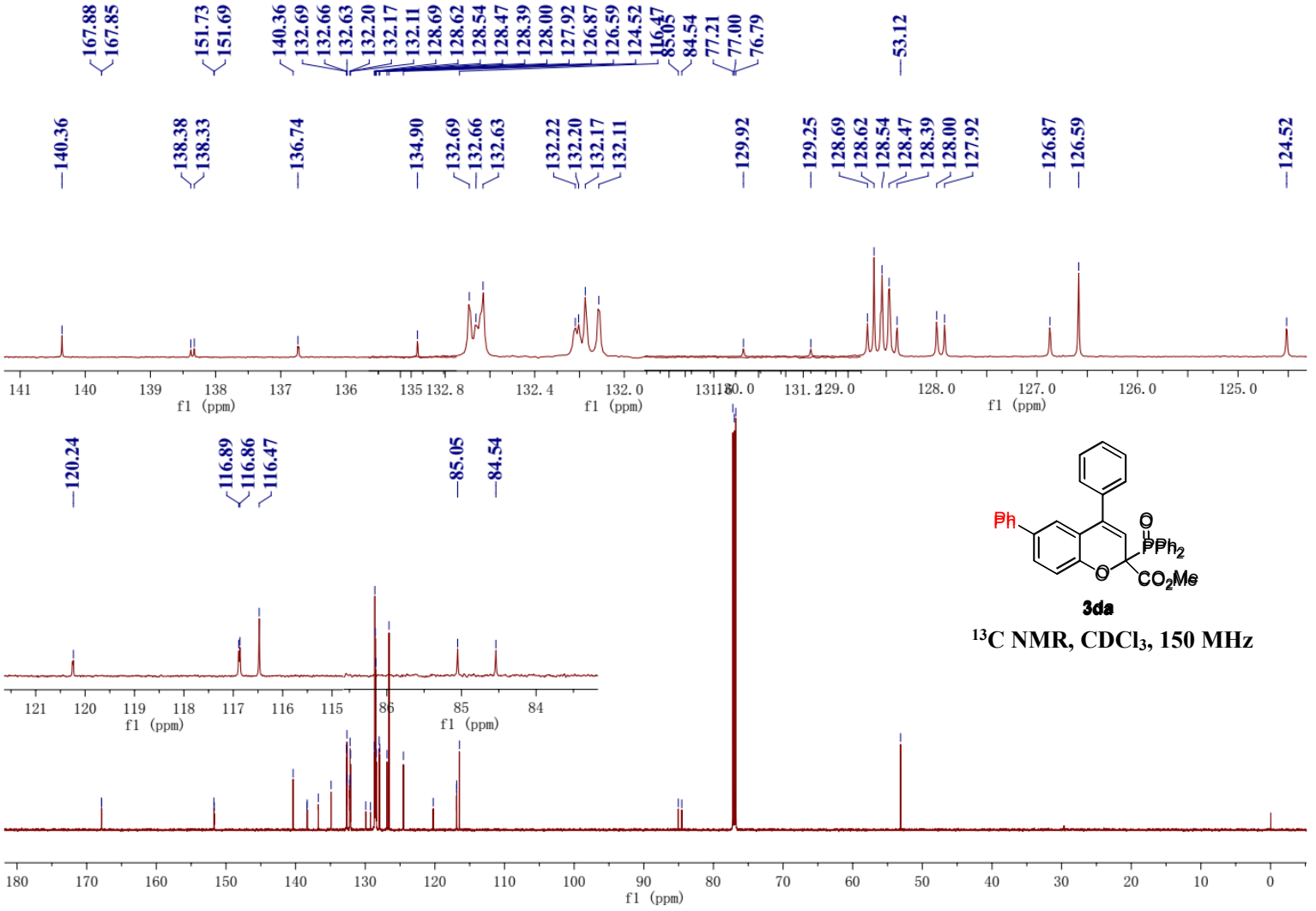
O
CO2Me
3da
1H NMR, CDCl3, 600 MHz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132.63
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132.11
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128.54
128.47
128.39
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127.92
126.87
126.59
124.52
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77.00
76.79
53.12
140.36
138.38
138.33
136.74
134.90
132.69
132.66
132.63
132.22
132.20
132.17
132.11
129.92
129.25
128.69
128.62
128.54
128.47
128.39
128.00
127.92
126.87
126.59
124.52
120.24
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f1 (ppm)
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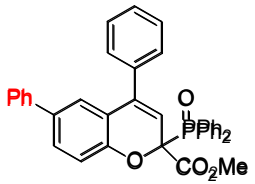
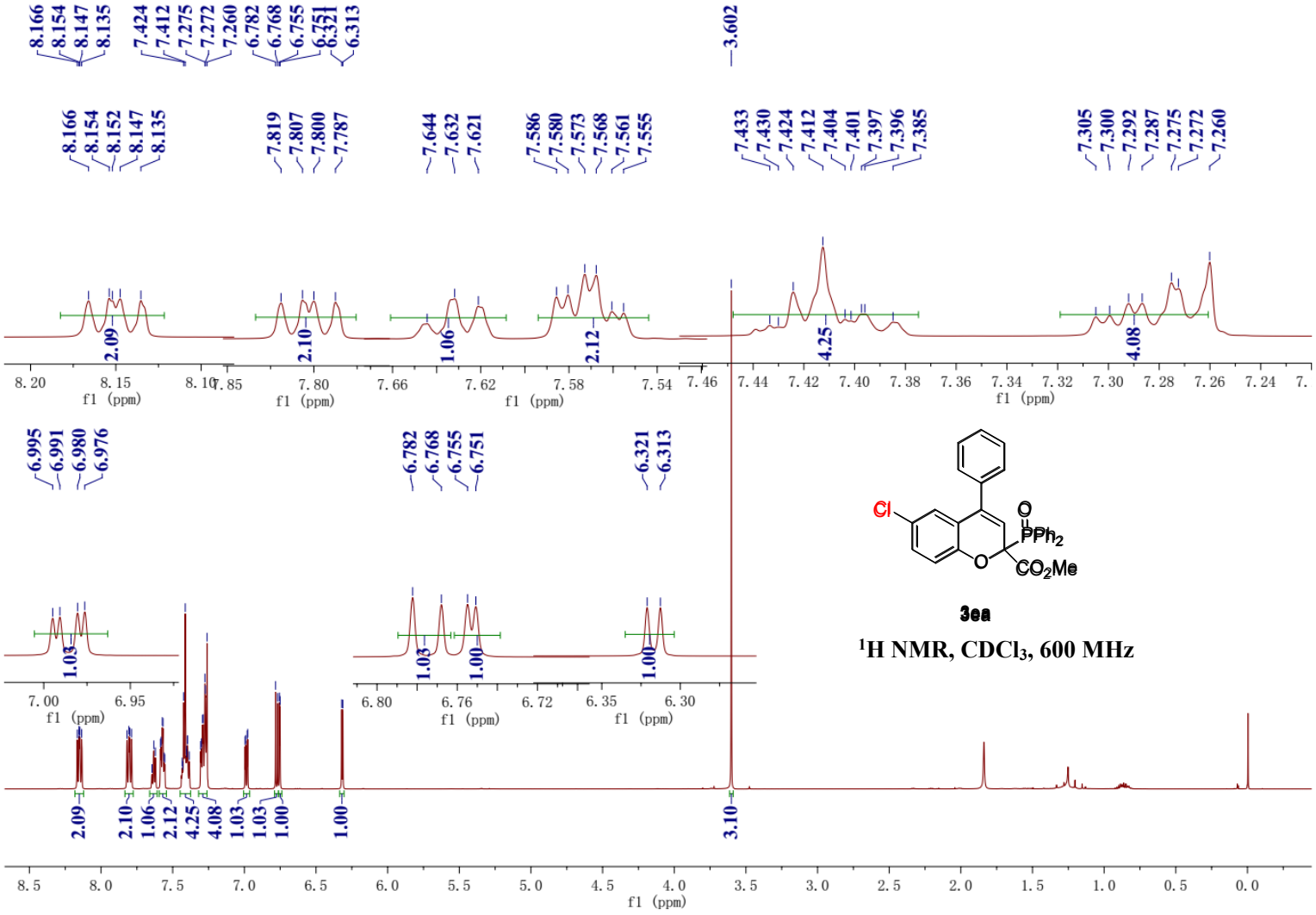
PPh2
CO2Me
3da
13C NMR, CDCl3, 150 MHz



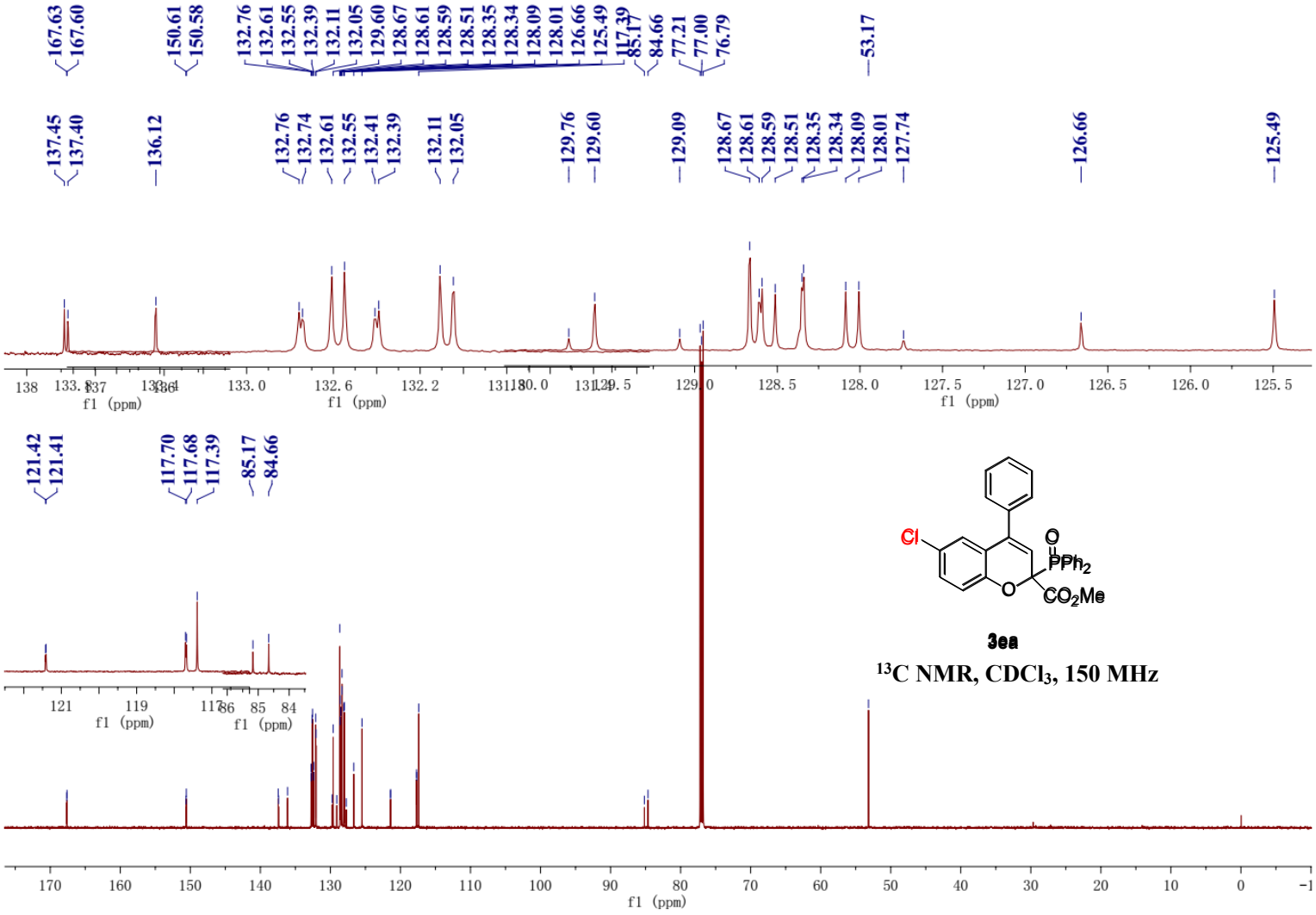
3da

^{31}P NMR, $CDCl_3$, 243 MHz



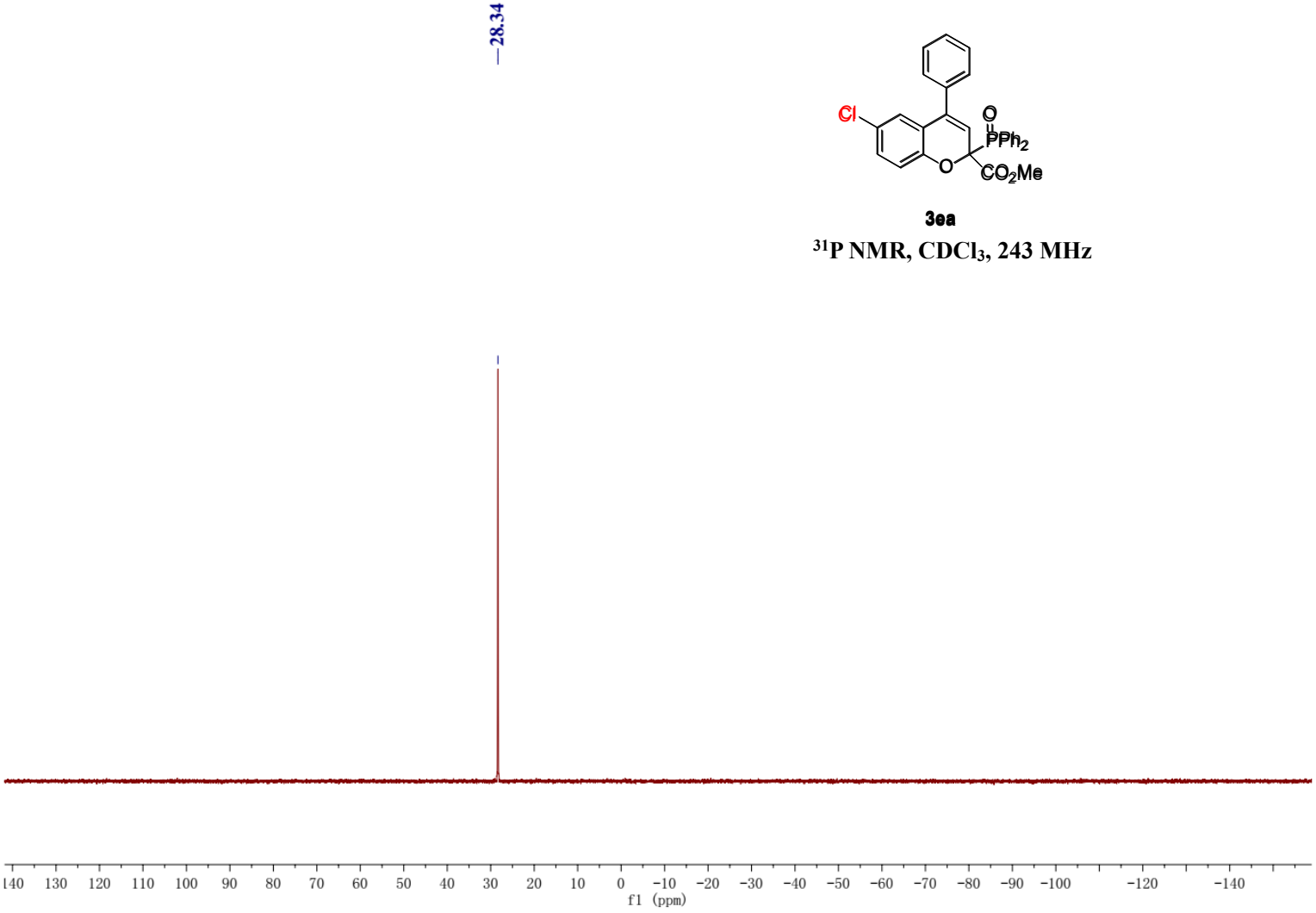
3ea

^{1}H NMR, $CDCl_3$, 600 MHz



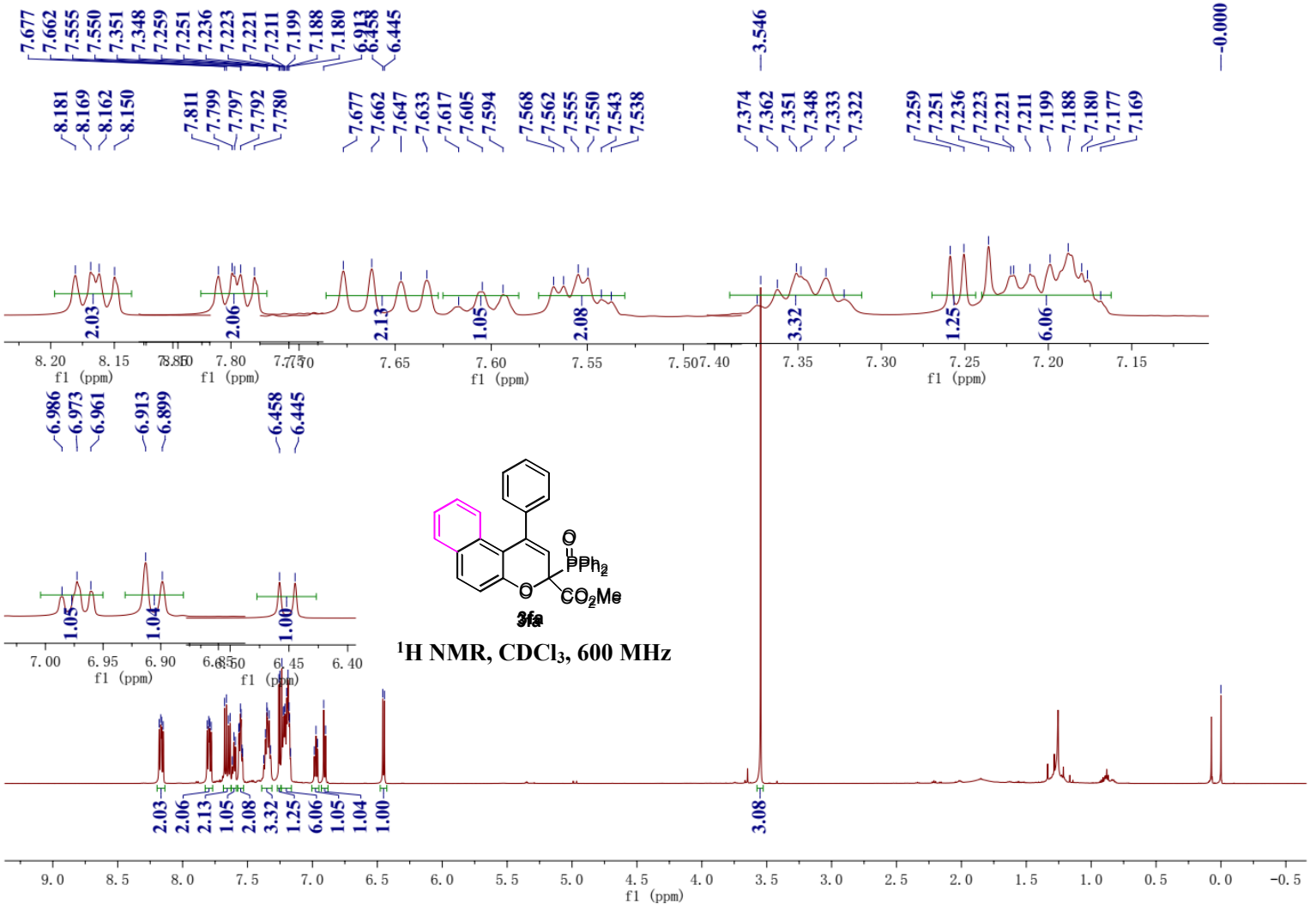
3ea

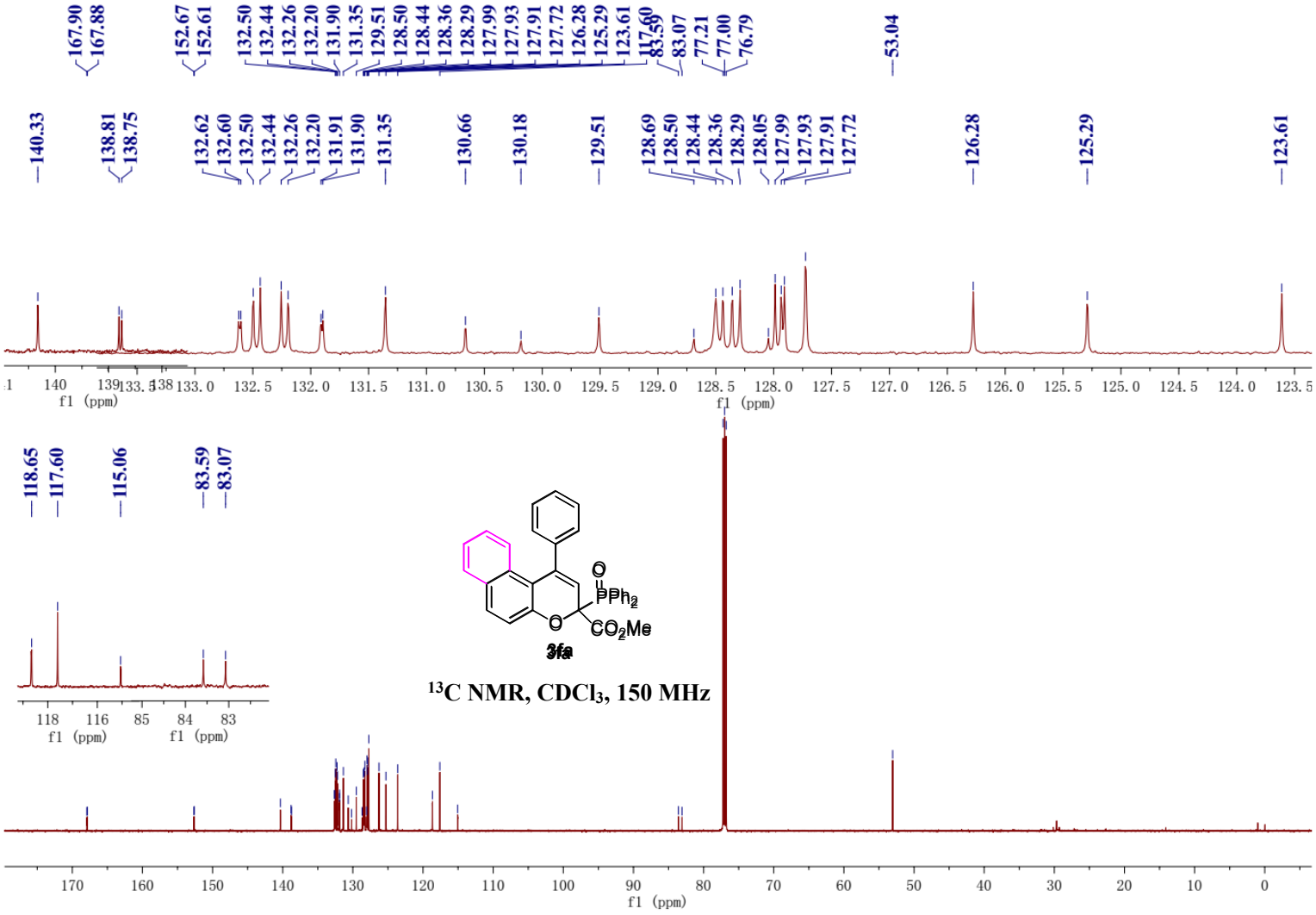
^{13}C NMR, $CDCl_3$, 150 MHz



3ea

^{31}P NMR, $CDCl_3$, 243 MHz


3fa
^{1}H NMR, CDCl$_3$, 600 MHz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132.50
132.44
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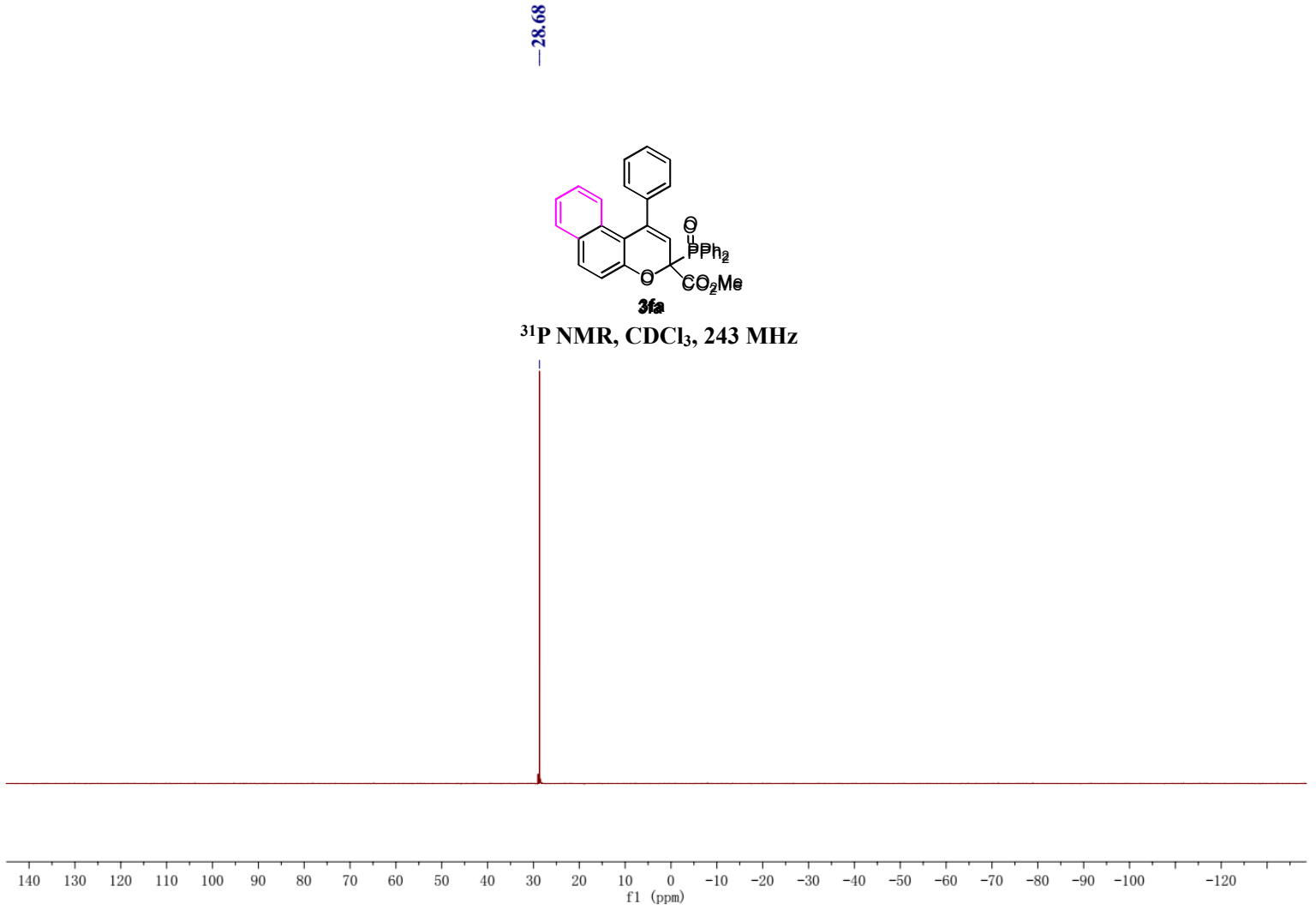
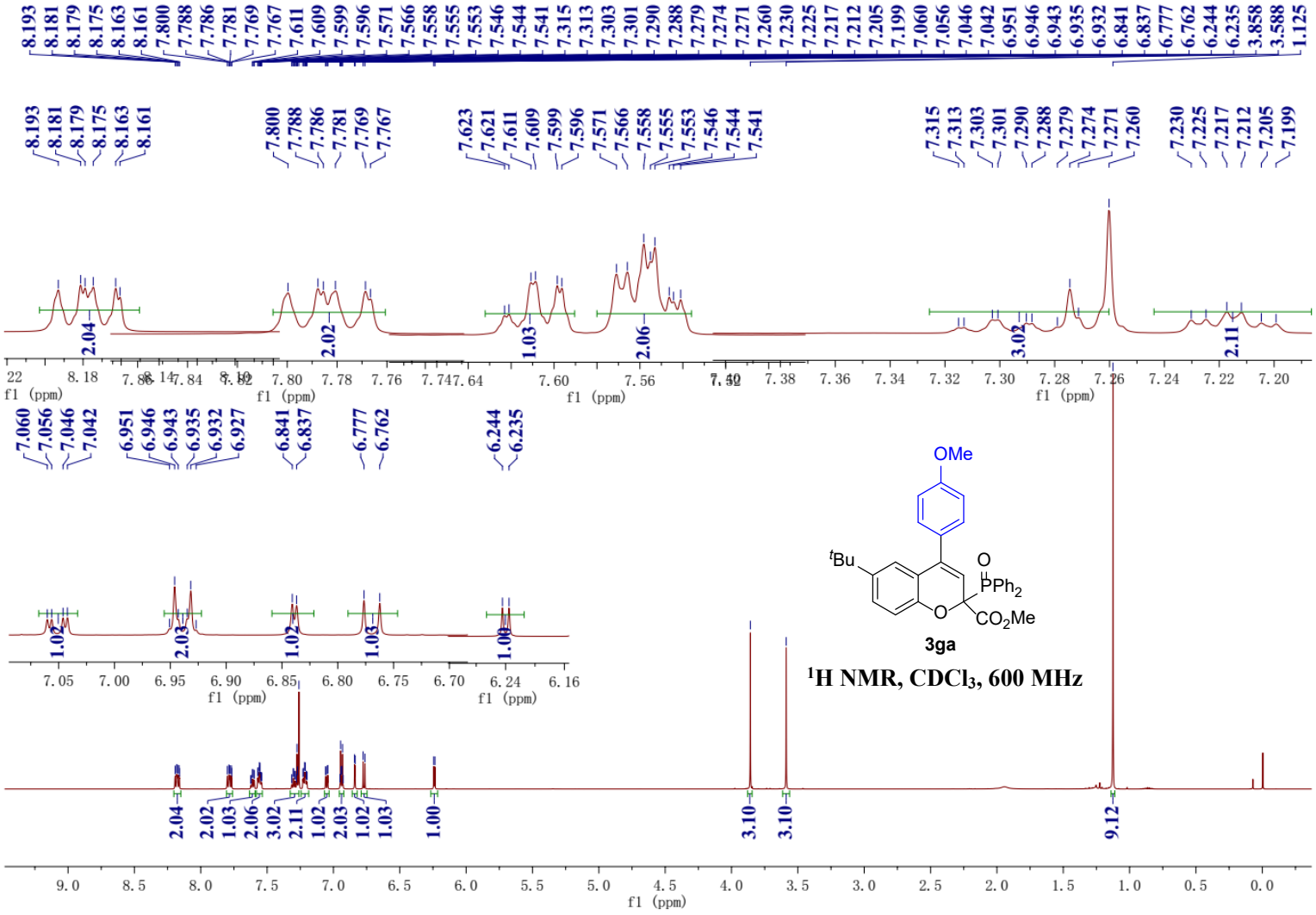
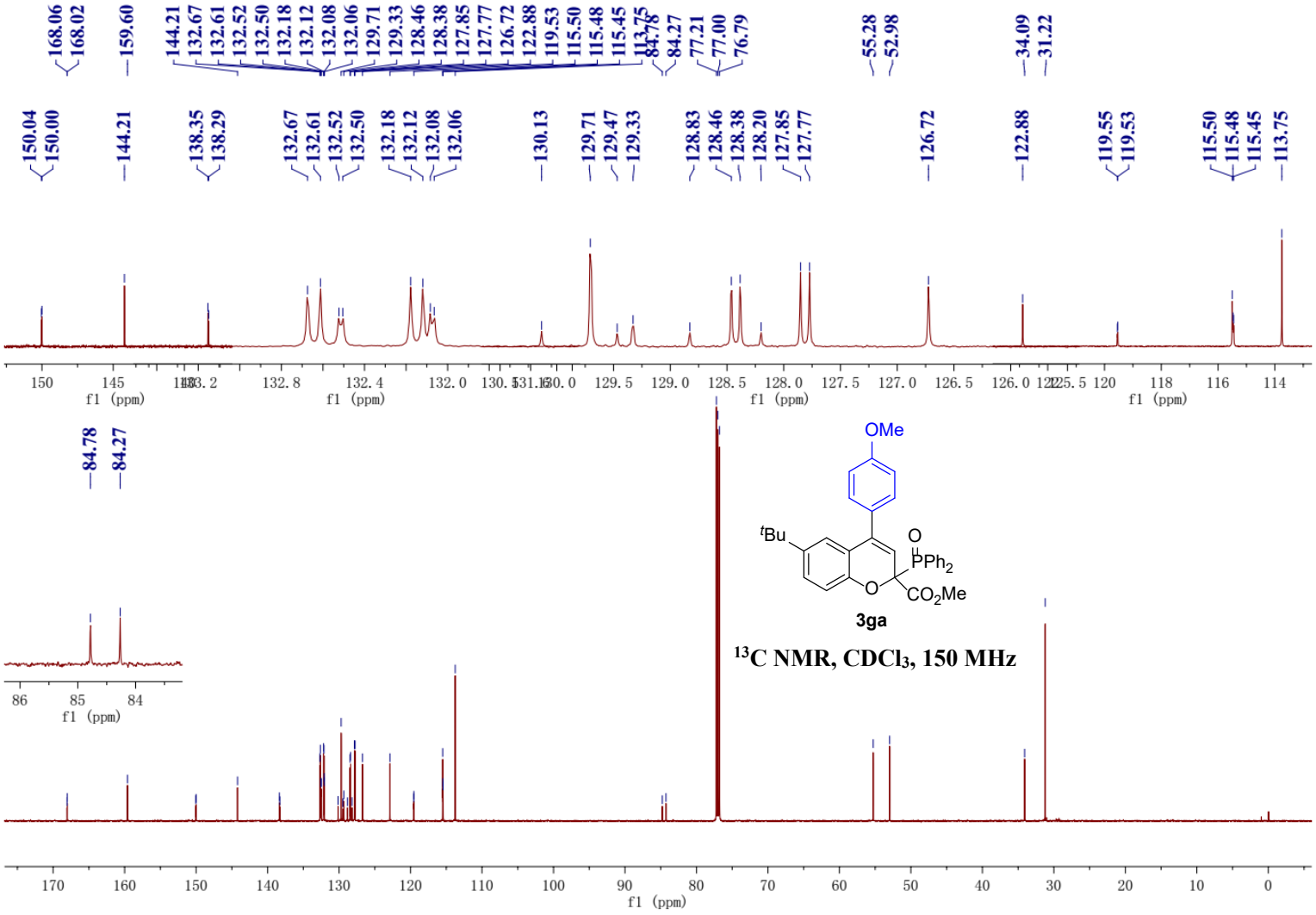
132.20
131.90
131.35
129.51
128.50
128.44
128.36
128.29
127.99
127.93
127.91
127.72
126.28
125.29
123.61
117.60
83.59
83.07
77.21
77.00
76.79
53.04
140.33
138.81
138.75
132.62
132.60
132.50
132.44
132.26
132.20
131.91
131.90
131.35
130.66
130.18
129.51
128.69
128.50
128.44
128.36
128.29
128.05
127.99
127.93
127.91
127.72
126.28
125.29
123.61
f1 (ppm)
118.65
117.60
115.06
83.59
83.07
O
PPh2
O
CO2Me
3fa
13C NMR, CDCl3, 150 MHz

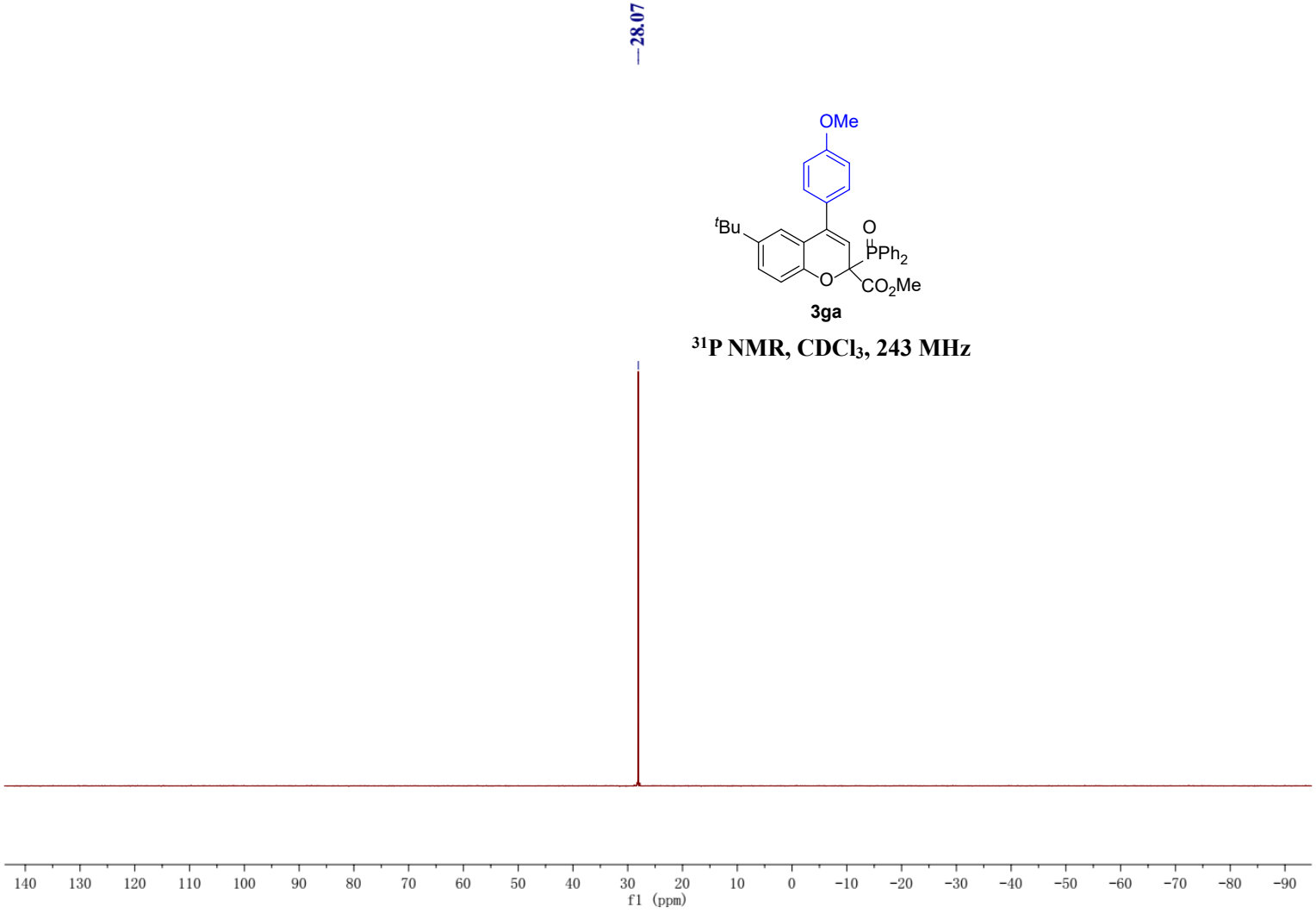

28.68
O
PPh2
O
CO2Me
3fa
31P NMR, CDCl3, 243 MHz
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120
f1 (ppm)

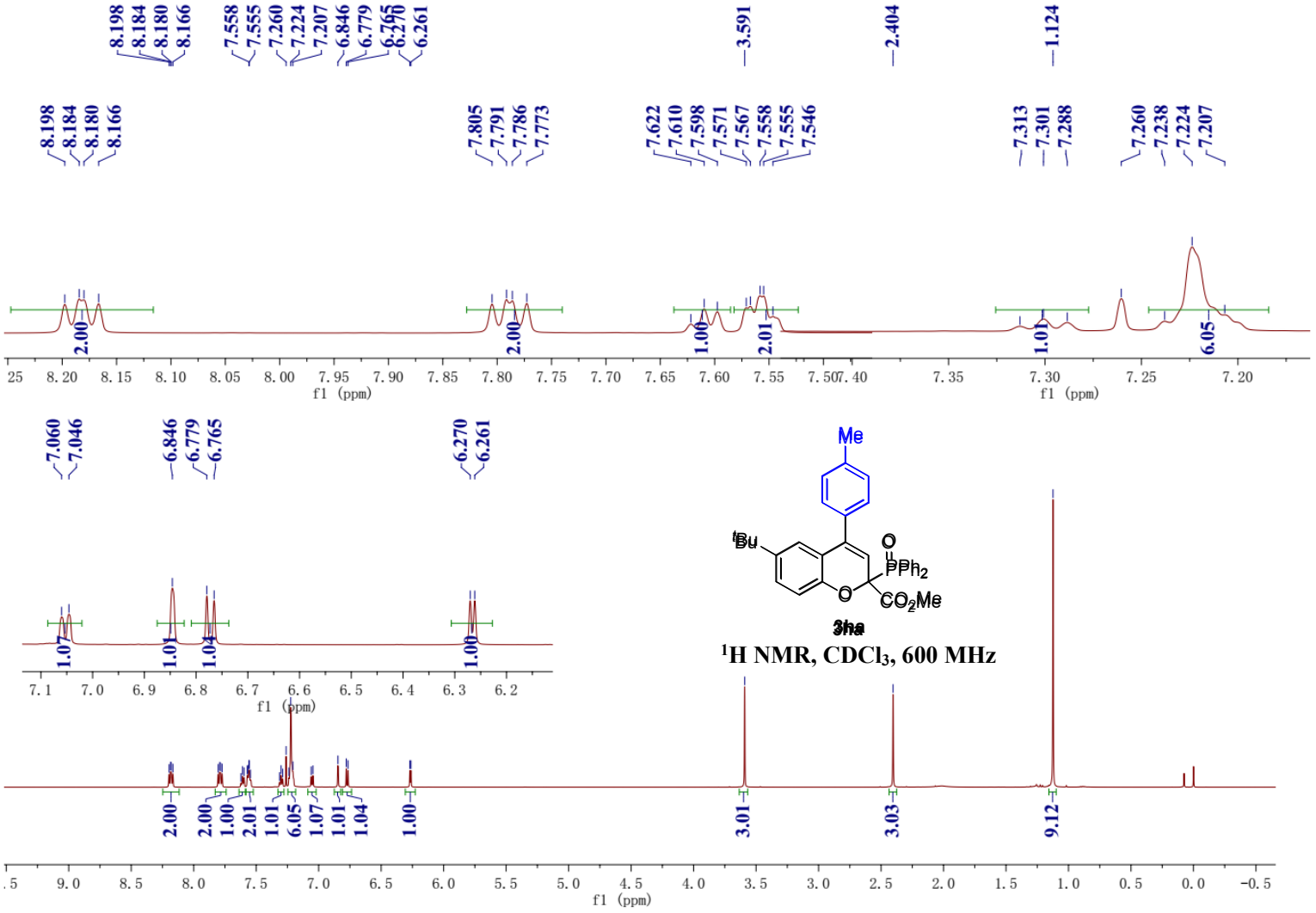


3ga

^{1}H NMR, $CDCl_3$, 600 MHz


168.06
168.02
159.60
144.21
132.67
132.61
132.52
132.50
132.18
132.12
132.08
132.06
129.71
129.33
128.46
128.38
127.85
127.77
126.72
122.88
119.53
115.50
115.48
115.45
113.75
84.78
84.27
77.21
77.00
76.79
55.28
52.98
34.09
31.22
150.04
150.00
144.21
138.35
138.29
132.67
132.61
132.52
132.50
132.18
132.12
132.08
132.06
130.13
129.71
129.47
129.33
128.83
128.46
128.38
128.20
127.85
127.77
126.72
122.88
119.55
119.53
115.50
115.48
115.45
113.75
84.78
84.27
OMe
tBu
O
PPh2
O
CO2Me
3ga
13C NMR, CDCl3, 150 MHz
f1 (ppm)


28.07
OMe
tBu
O
PPh2
O
CO2Me
3ga
31P NMR, CDCl3, 243 MHz
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)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8.184
8.180
8.166
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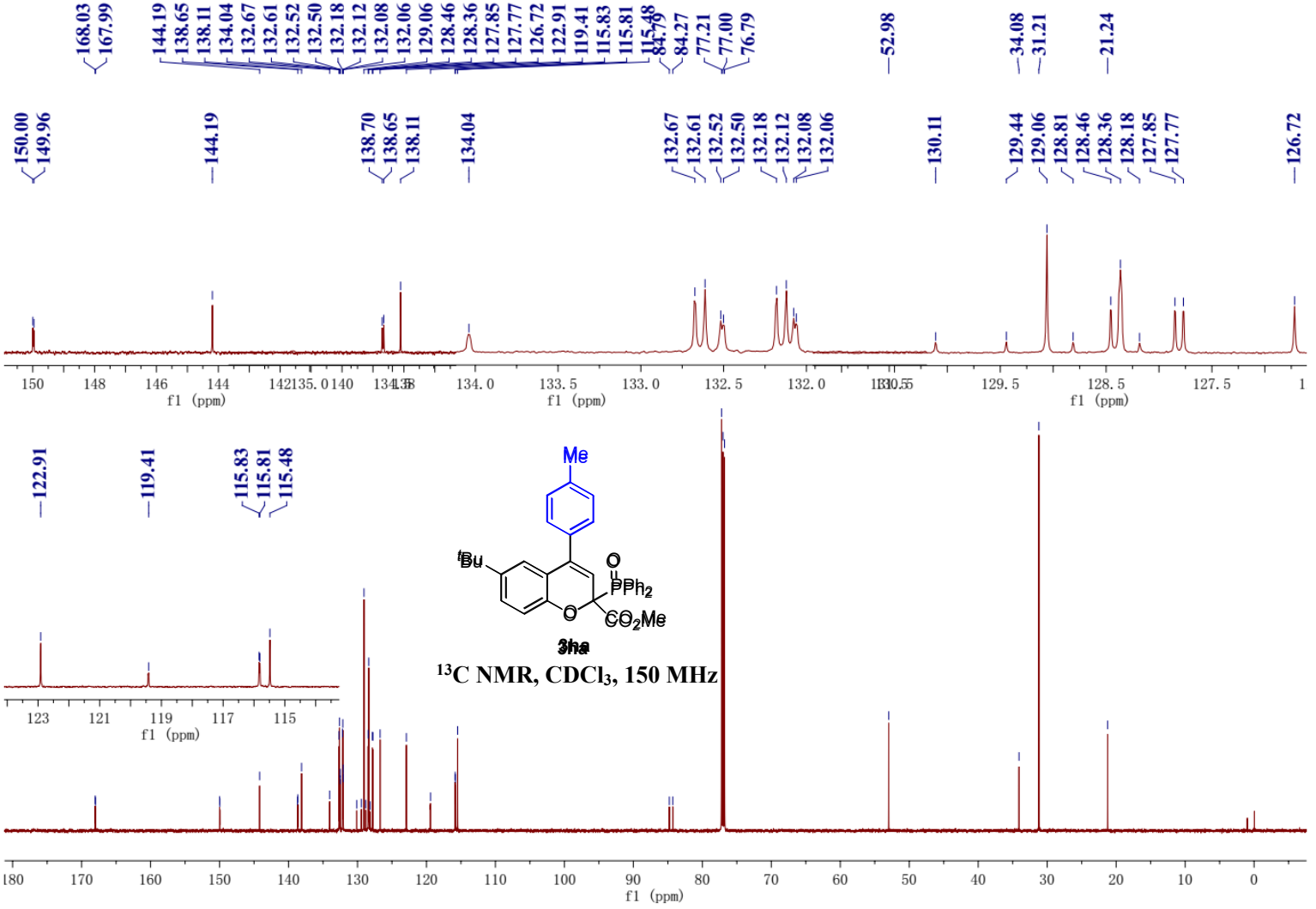
7.555
7.260
7.224
7.207
6.846
6.779
6.765
6.270
6.261
3.591
2.404
1.124
7.805
7.791
7.786
7.773
7.622
7.610
7.598
7.571
7.567
7.558
7.555
7.546
7.313
7.301
7.288
7.260
7.238
7.224
7.207
7.060
7.046
6.846
6.779
6.765
6.270
6.261
Me
tBu
O
PPh2
O
CO2Me
3ha
1H NMR, CDCl3, 600 MHz
f1 (ppm)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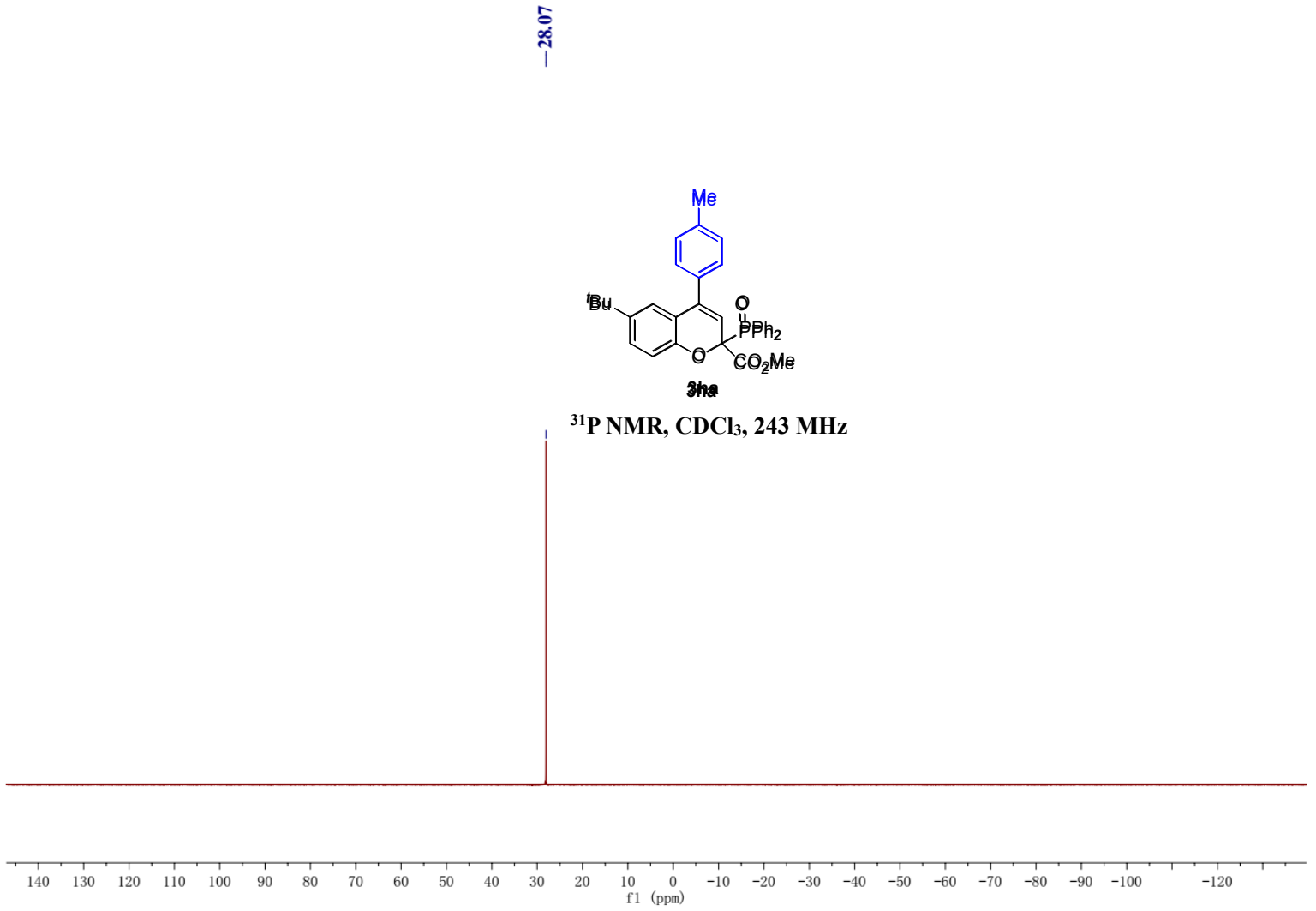
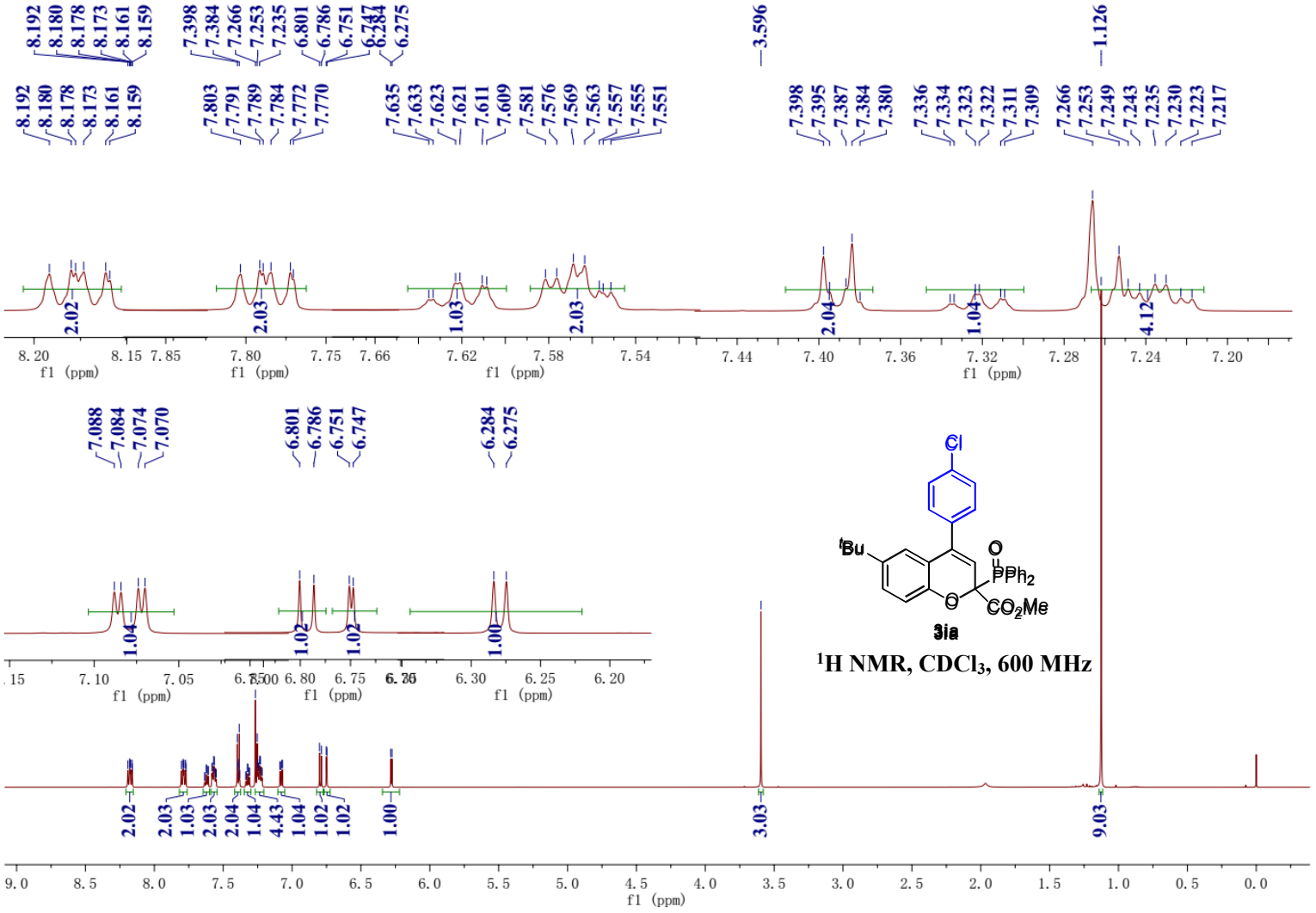
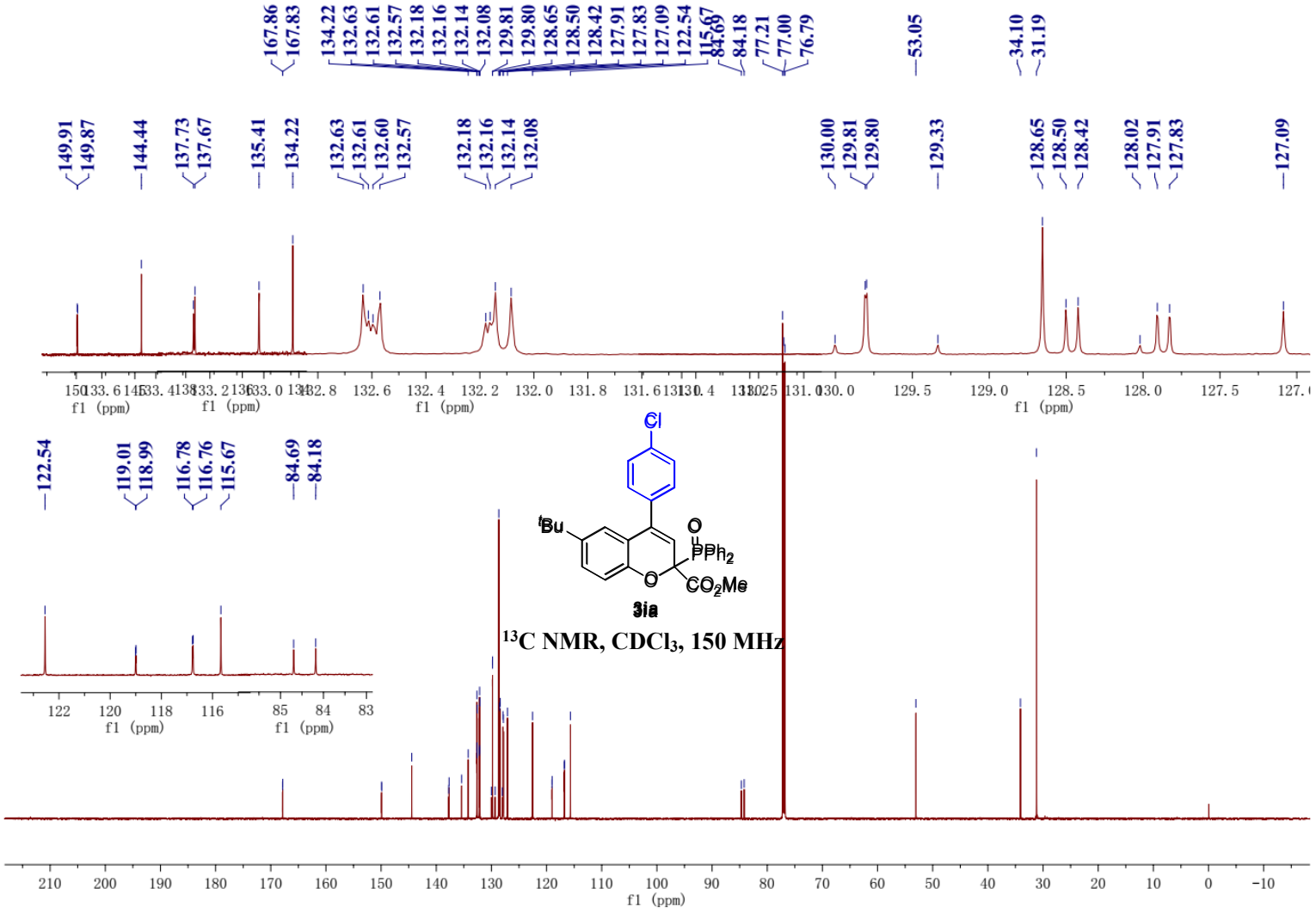
138.11
134.04
132.67
132.61
132.52
132.50
132.18
132.12
132.08
132.06
129.06
128.46
128.36
127.85
127.77
126.72
122.91
119.41
115.83
115.81
115.48
84.79
84.27
77.21
77.00
76.79
52.98
34.08
31.21
21.24
150.00
149.96
144.19
138.70
138.65
138.11
134.04
132.67
132.61
132.52
132.50
132.18
132.12
132.08
132.06
130.11
129.44
129.06
128.81
128.46
128.36
128.18
127.85
127.77
126.72
f1 (ppm)
Me
tBu
O
PPh2
O
CO2Me
3ha
13C NMR, CDCl3, 150 MHz

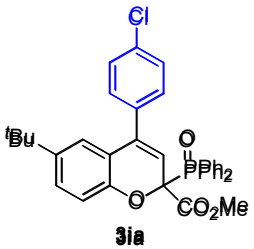


^{31}P NMR, $CDCl_3$, 243 MHz



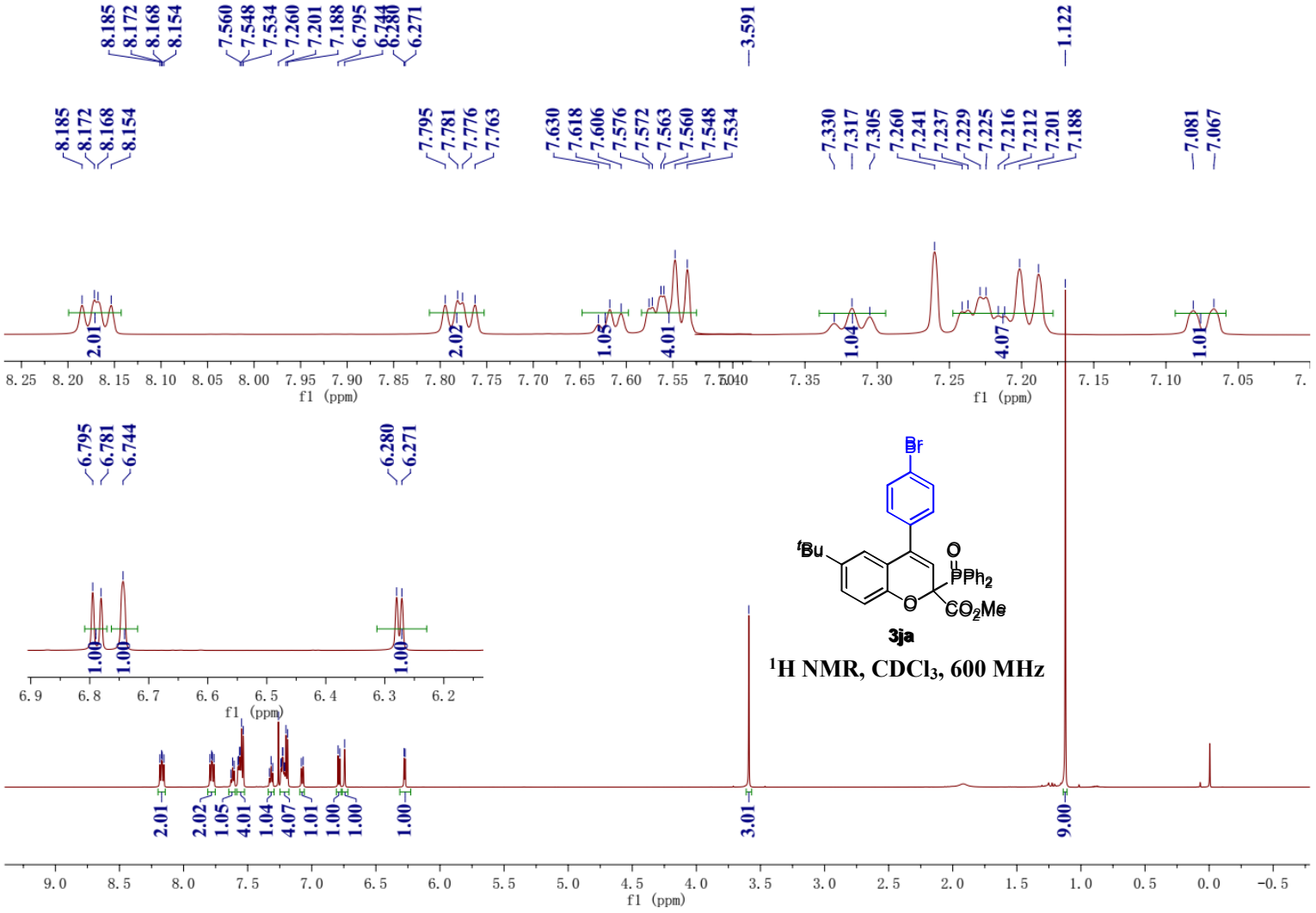
^{1}H NMR, $CDCl_3$, 600 MHz


167.86
167.83
134.22
132.63
132.61
132.57
132.18
132.16
132.14
132.08
129.81
129.80
128.65
128.50
128.42
128.02
127.91
127.83
127.09
122.54
119.01
118.99
116.78
116.76
115.67
84.69
84.18
77.21
77.00
76.79
53.05
34.10
31.19
149.91
149.87
144.44
137.73
137.67
135.41
134.22
132.63
132.61
132.60
132.57
132.18
132.16
132.14
132.08
130.00
129.81
129.80
129.33
f1 (ppm)
Cl
tBu
O
PPh2
O
CO2Me
3ia
13C NMR, CDCl3, 150 MHz



3ia

^{31}P NMR, $CDCl_3$, 243 MHz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8.172
8.168
8.154
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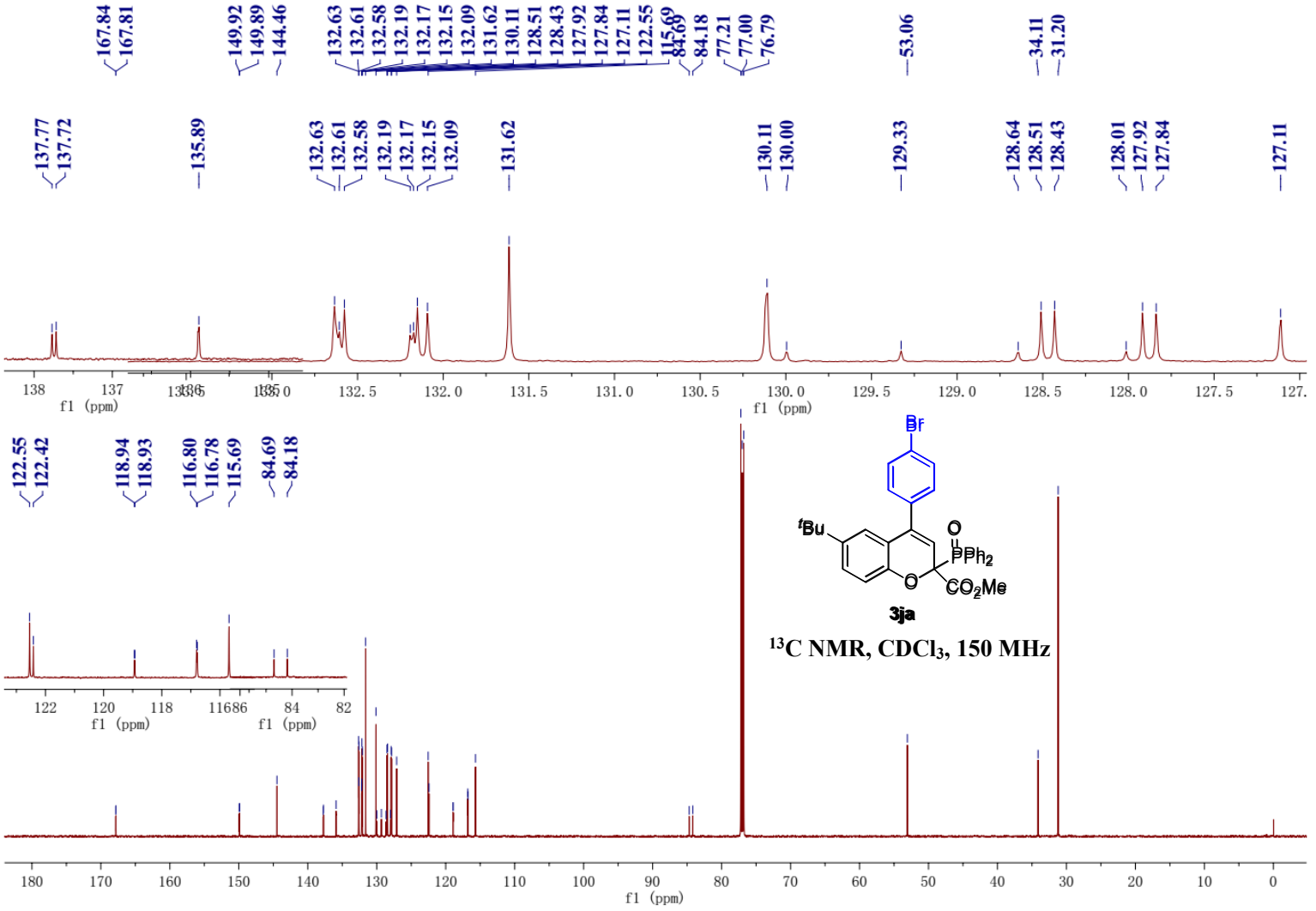
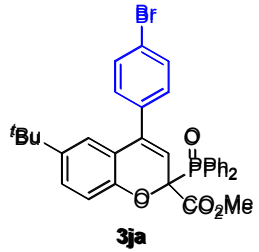
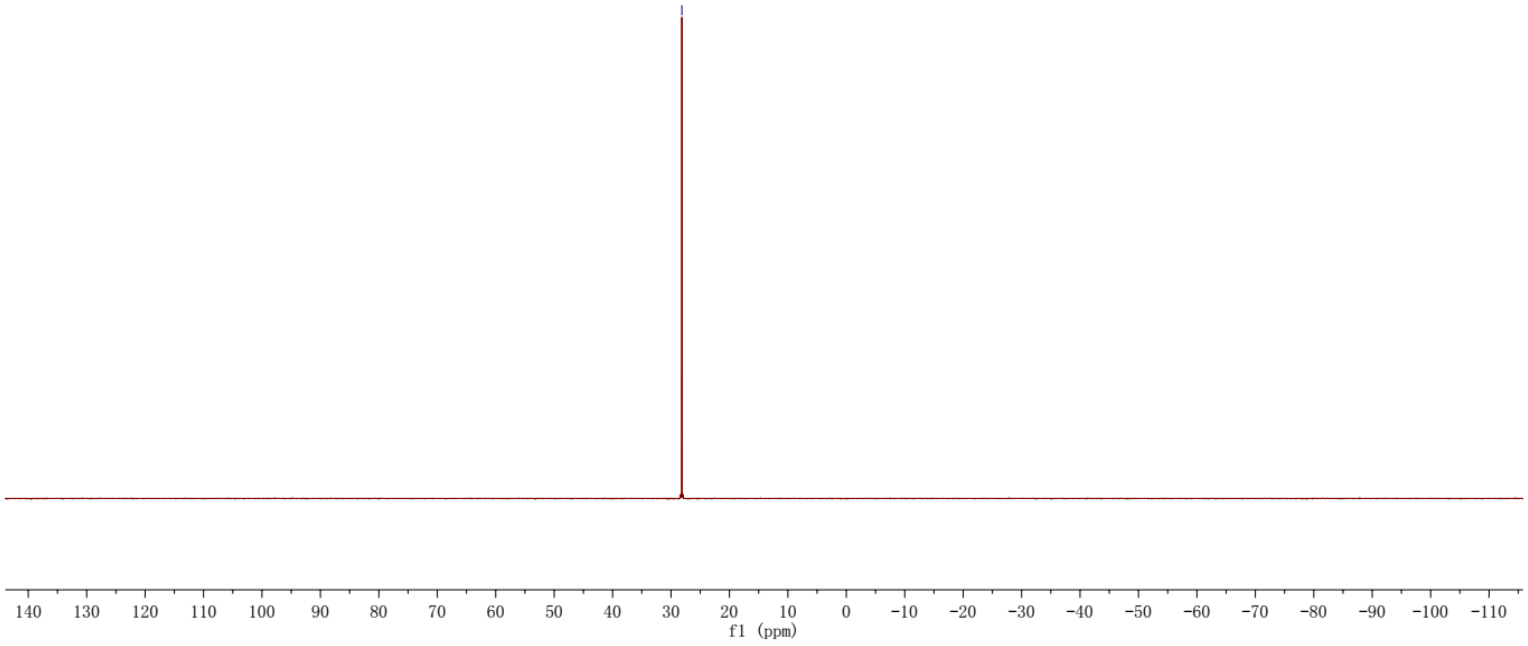
7.548
7.534
7.260
7.201
7.188
6.795
6.744
6.280
6.271
3.591
1.122
7.795
7.781
7.776
7.763
7.630
7.618
7.606
7.576
7.572
7.563
7.560
7.548
7.534
7.330
7.317
7.305
7.260
7.241
7.237
7.229
7.225
7.216
7.212
7.201
7.188
7.081
7.067
2.01
2.02
1.05
4.01
1.04
4.07
1.01
1.00
1.00
1.00
2.01
2.02
1.05
4.01
1.04
4.07
1.01
1.00
1.00
1.00
3.01
9.00
f1 (ppm)
Br
tBu
O
PPh2
O
CO2Me
3ja
1H NMR, CDCl3, 600 MHz

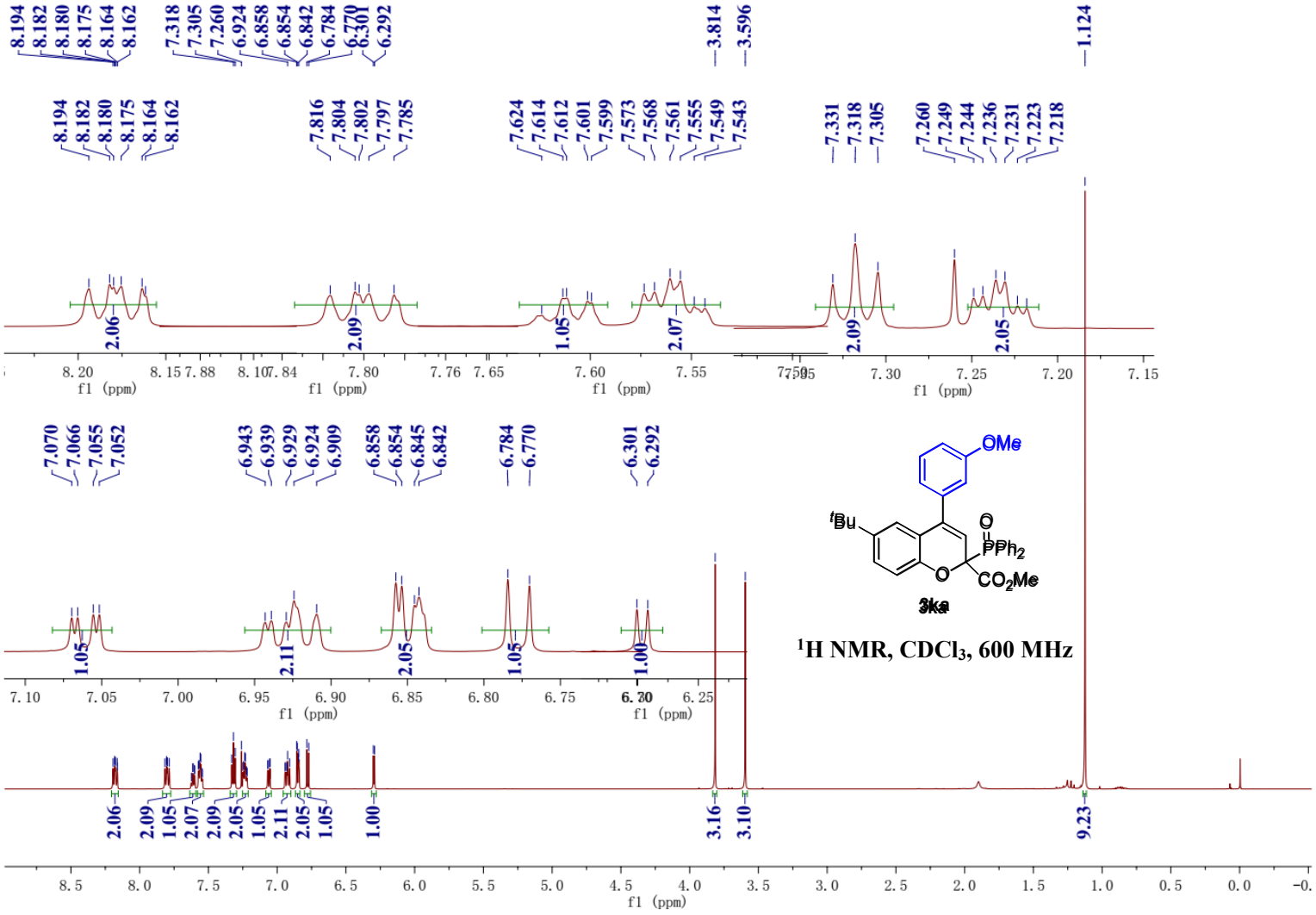

167.84
167.81
149.92
149.89
144.46
132.63
132.61
132.58
132.19
132.17
132.15
132.09
131.62
130.11
128.51
128.43
127.92
127.84
127.11
122.55
115.69
84.69
84.18
77.21
77.00
76.79
53.06
34.11
31.20
137.77
137.72
135.89
132.63
132.61
132.58
132.19
132.17
132.15
132.09
131.62
130.11
130.00
129.33
128.64
128.51
128.43
128.01
127.92
127.84
127.11
f1 (ppm)
122.55
122.42
118.94
118.93
116.80
116.78
115.69
84.69
84.18
Br
tBu
O
PPh2
O
CO2Me
3ja
13C NMR, CDCl3, 150 MHz



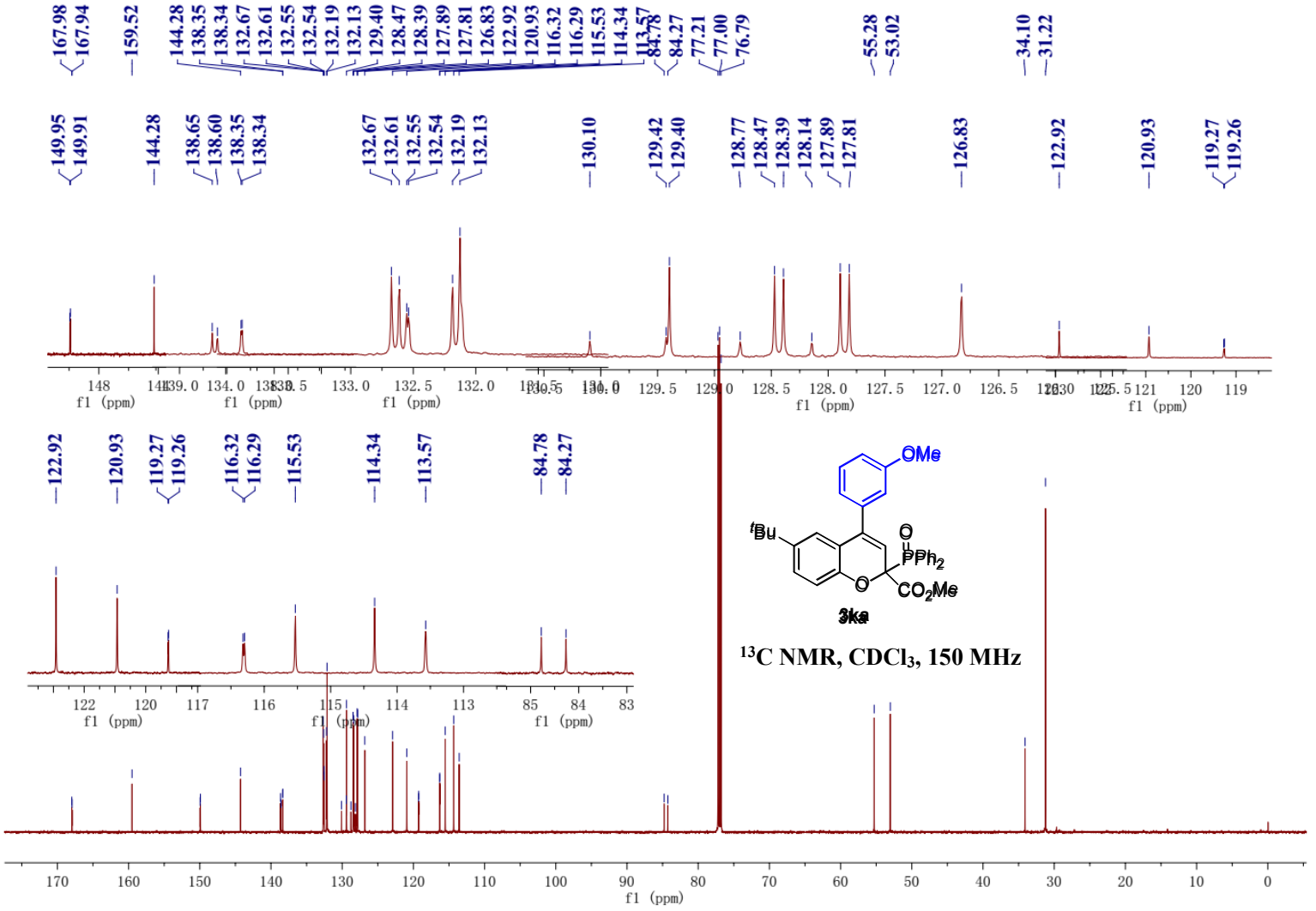
3ja

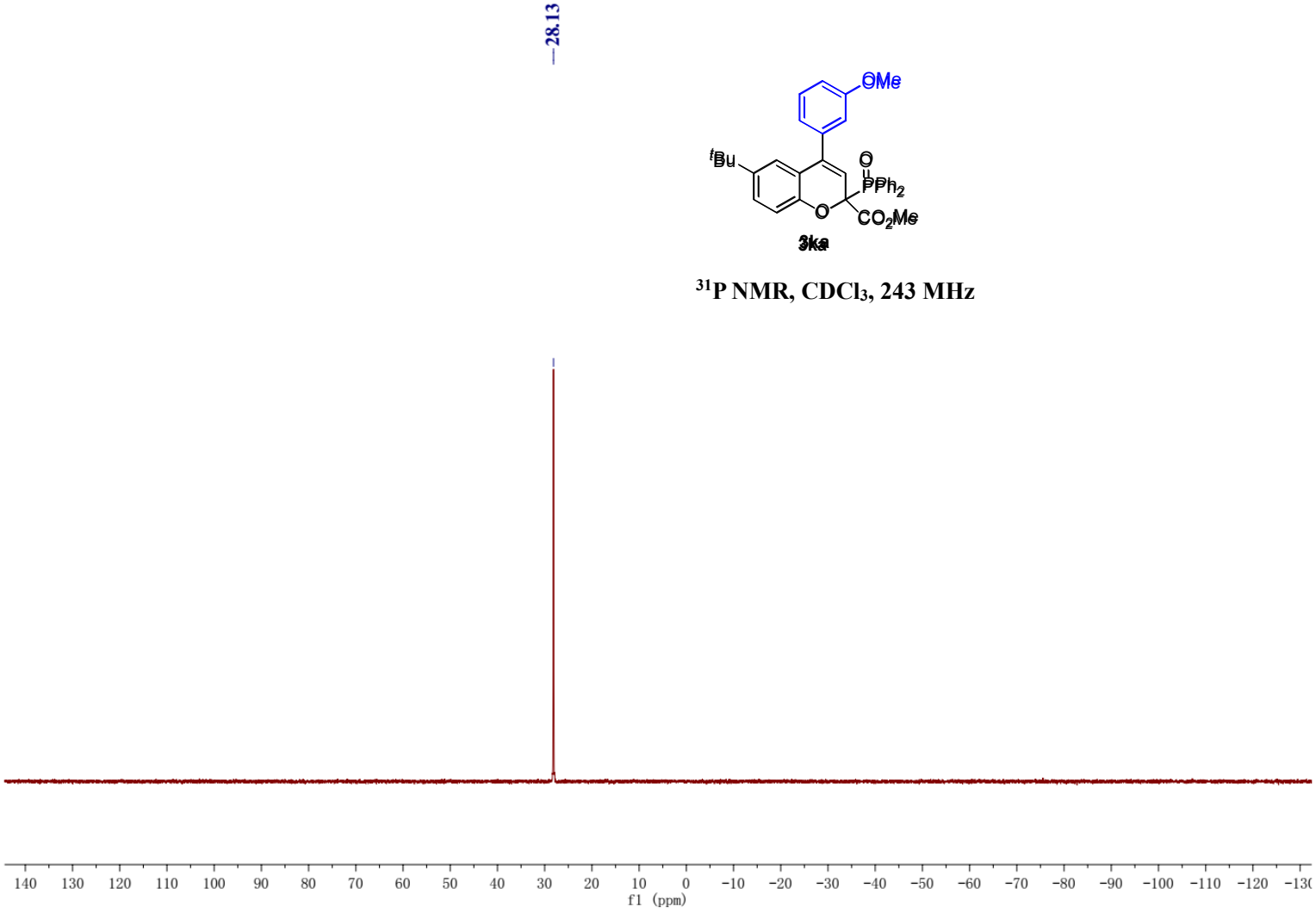
^{31}P NMR, $CDCl_3$, 243 MHz



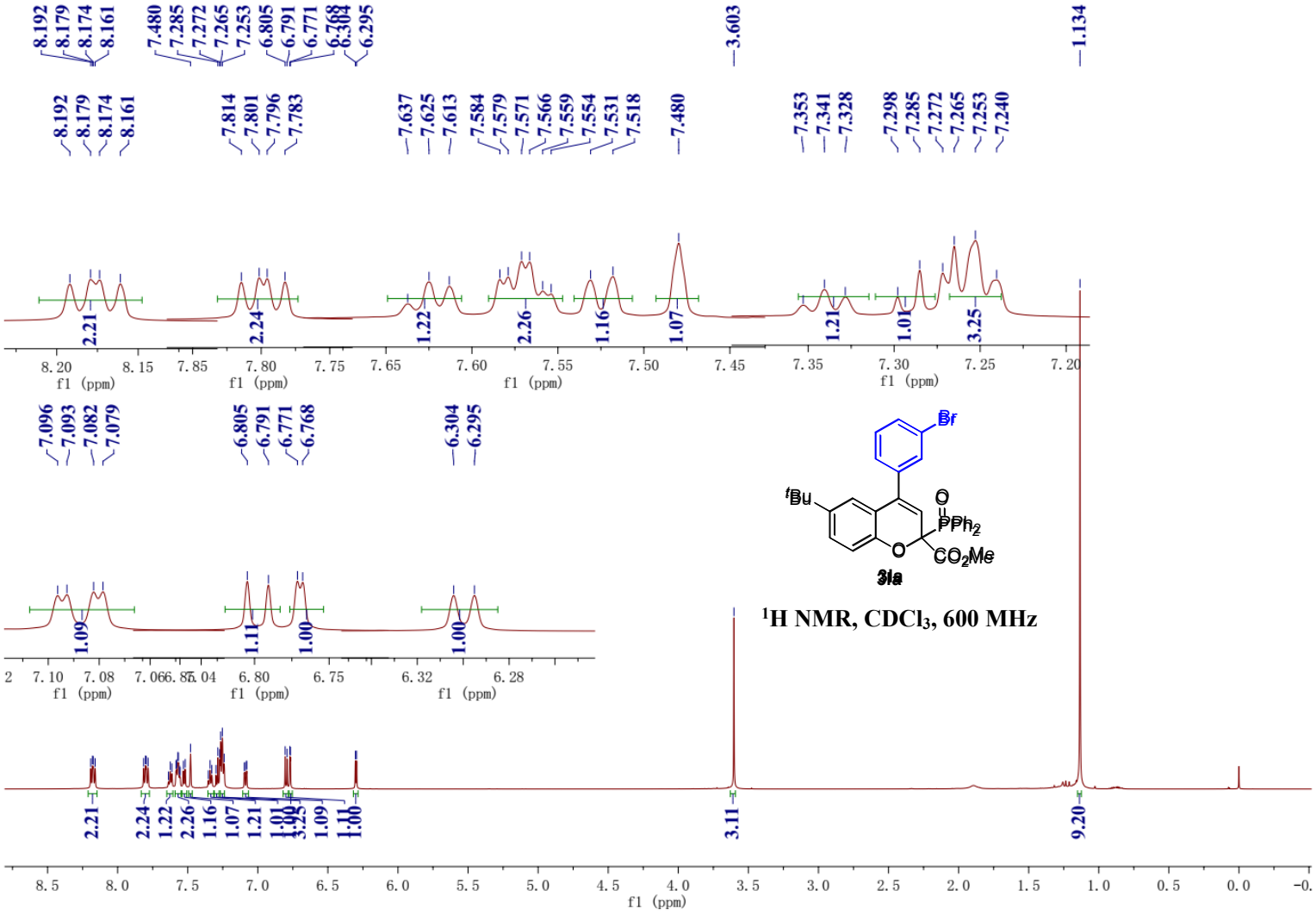


^{1}H NMR, $CDCl_3$, 600 MHz

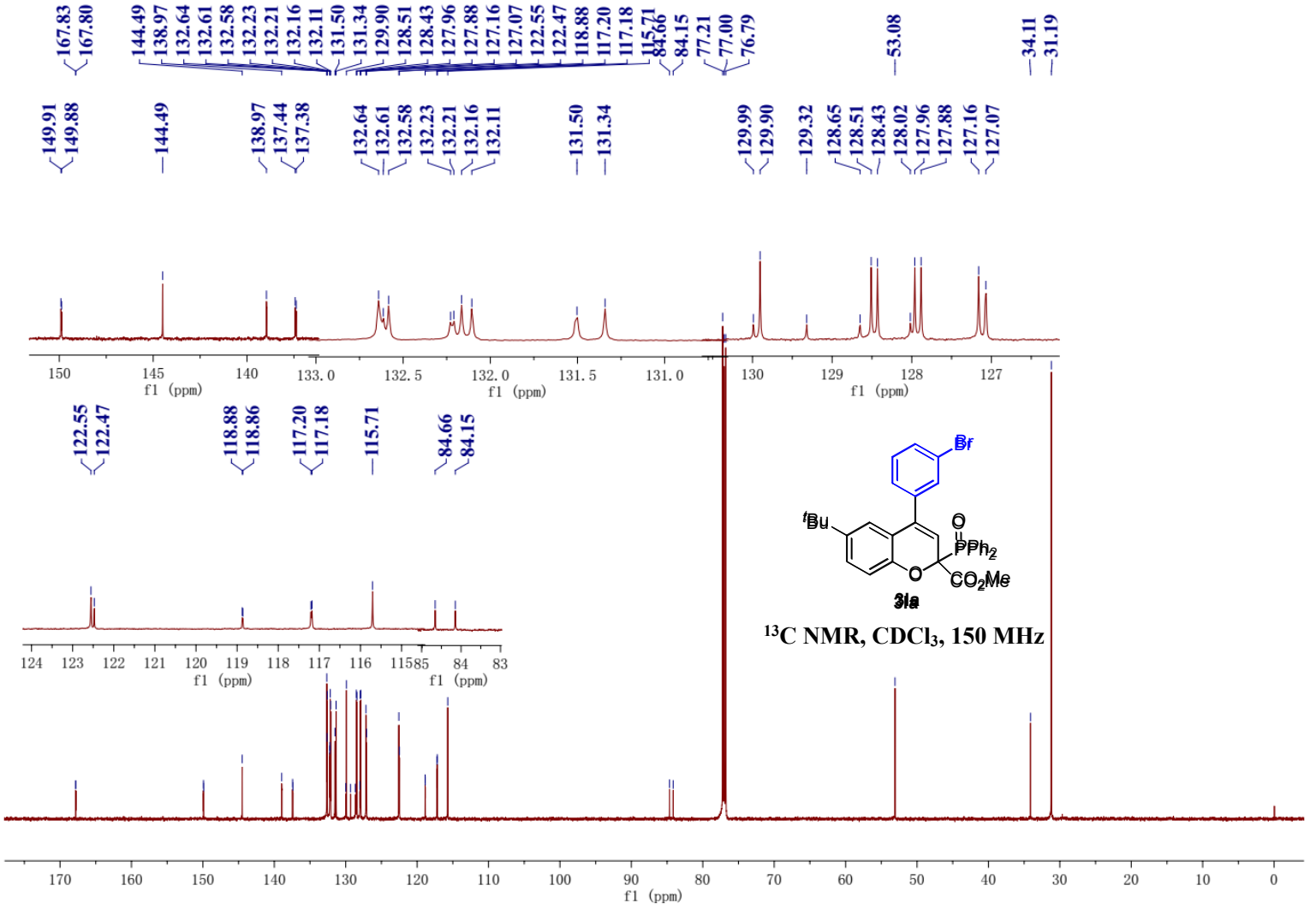

167.98
167.94
159.52
144.28
138.35
138.34
132.67
132.61
132.55
132.54
132.19
132.13
129.40
128.47
128.39
127.89
127.81
126.83
122.92
120.93
116.32
116.29
115.53
114.34
113.57
84.78
84.27
77.21
77.00
76.79
55.28
53.02
34.10
31.22
149.95
149.91
144.28
138.65
138.60
138.35
138.34
132.67
132.61
132.55
132.54
132.19
132.13
130.10
129.42
129.40
128.77
128.47
128.39
128.14
127.89
127.81
126.83
122.92
120.93
119.27
119.26
f1 (ppm)
OMe
tBu
O
PPh2
O
CO2Me
3ka
13C NMR, CDCl3, 150 MHz



^{31}P NMR, $CDCl_3$, 243 MHz



^{1}H NMR, $CDCl_3$, 600 MHz


167.83
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144.49
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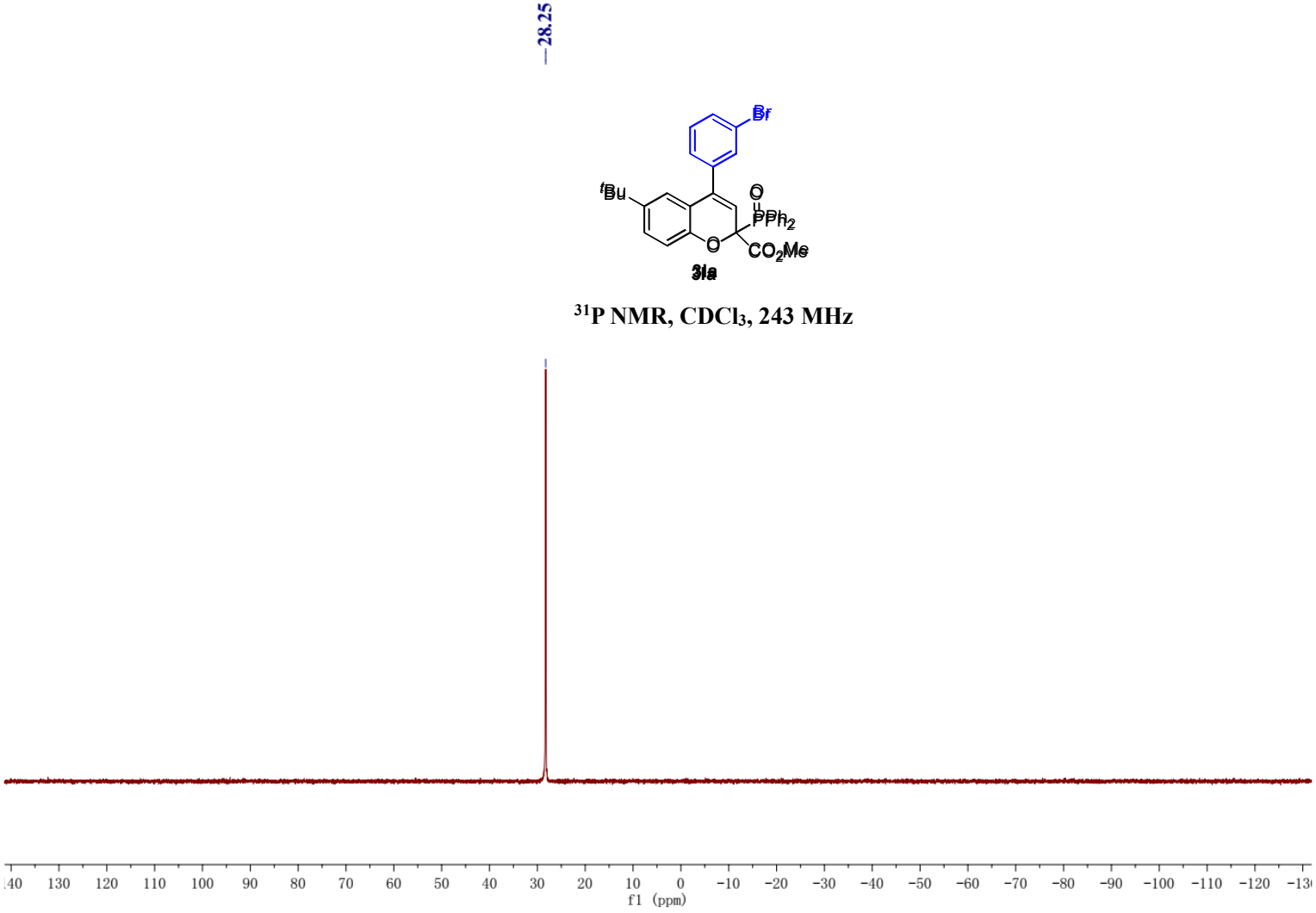
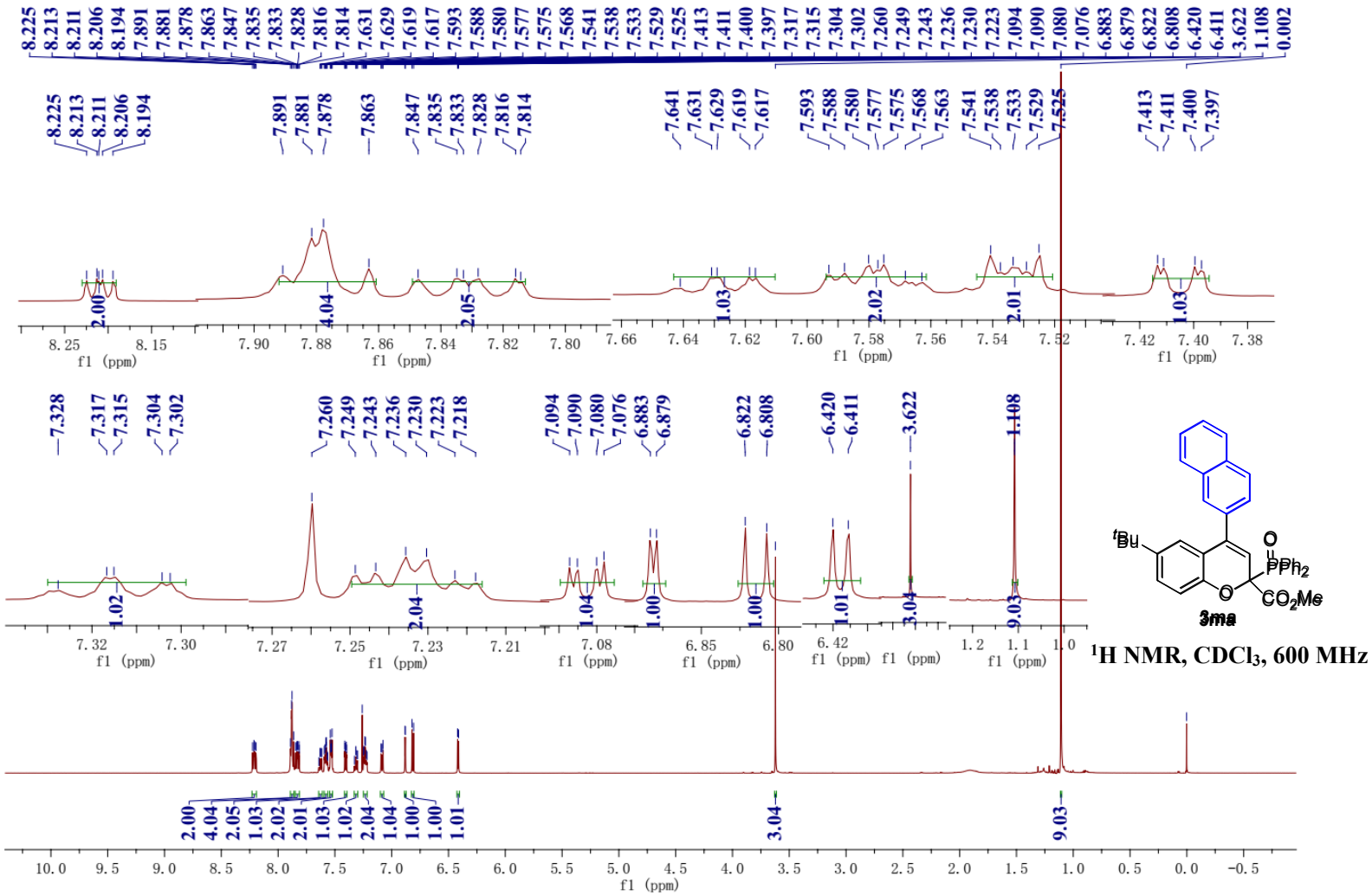
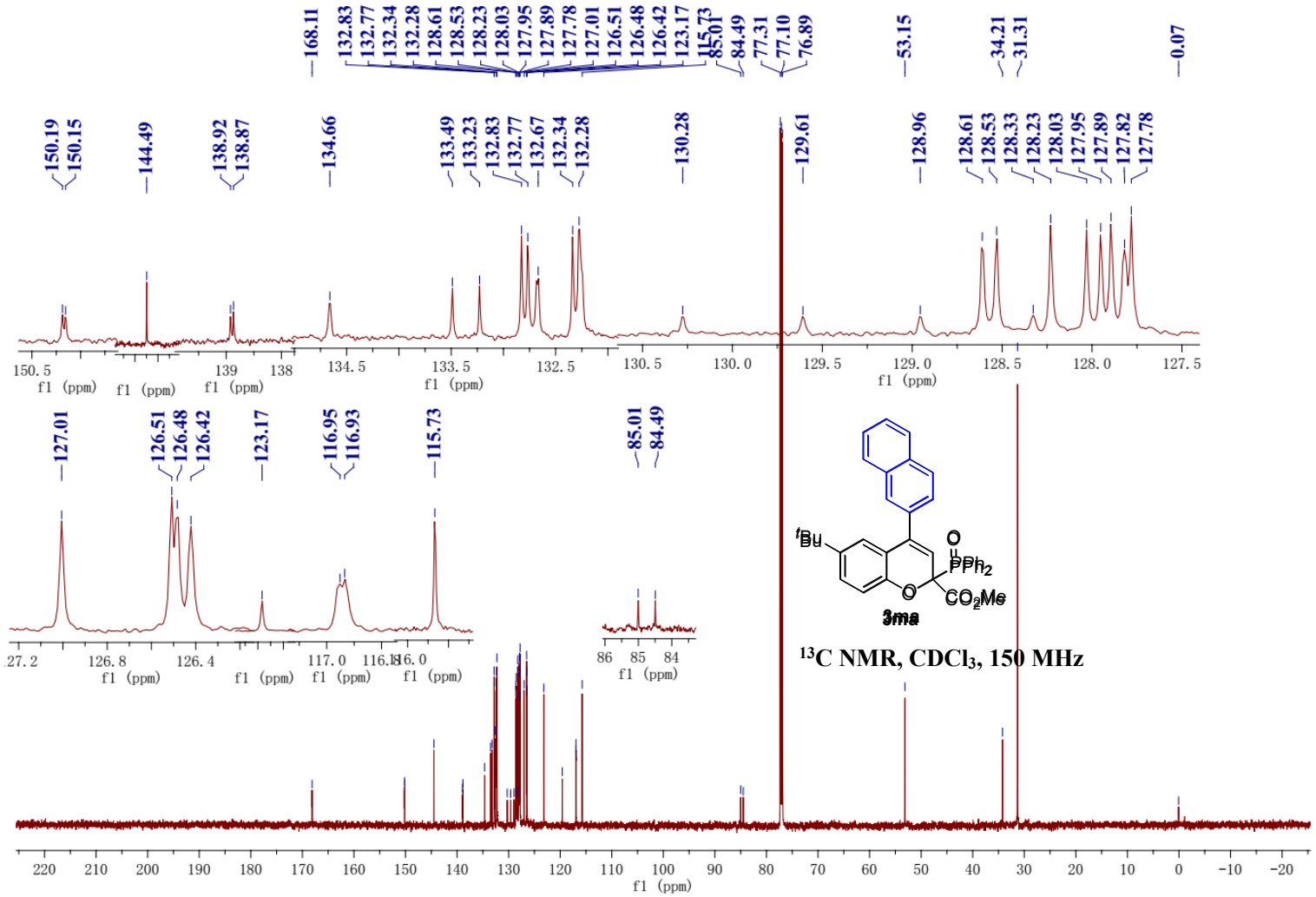
132.61
132.58
132.23
132.21
132.16
132.11
131.50
131.34
129.90
128.51
128.43
127.96
127.88
127.16
127.07
122.55
122.47
118.88
117.20
117.18
115.71
84.66
84.15
77.21
77.00
76.79
53.08
34.11
31.19
149.91
149.88
144.49
138.97
137.44
137.38
132.64
132.61
132.58
132.23
132.21
132.16
132.11
131.50
131.34
129.99
129.90
129.32
128.65
128.51
128.43
128.02
127.96
127.88
127.16
127.07
122.55
122.47
118.88
118.86
117.20
117.18
115.71
84.66
84.15
f1 (ppm)
Br
tBu
O
PPh2
O
CO2Me
3la
13C NMR, CDCl3, 150 MHz



^{31}P NMR, $CDCl_3$, 243 MHz



^{1}H NMR, $CDCl_3$, 600 MHz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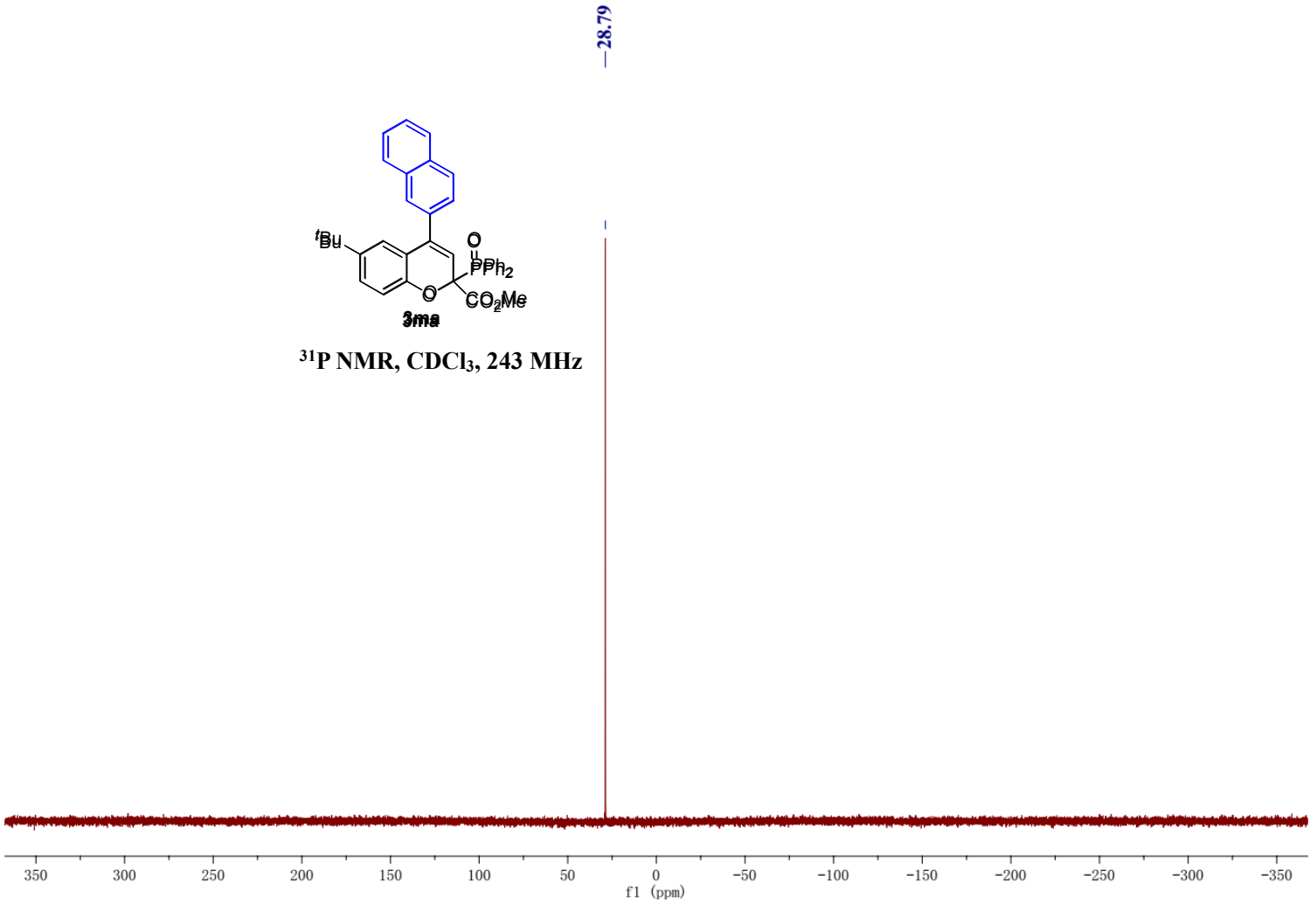
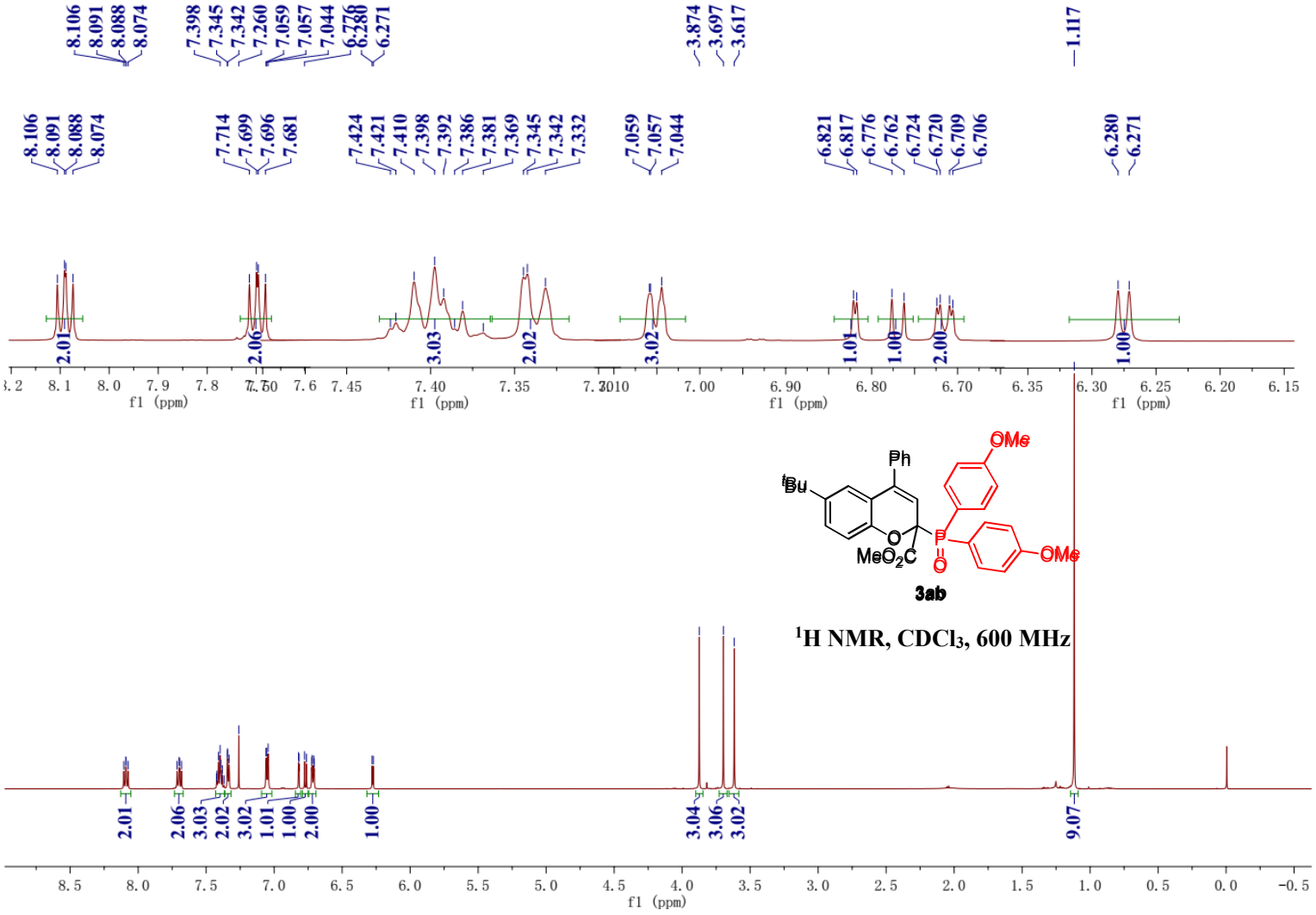
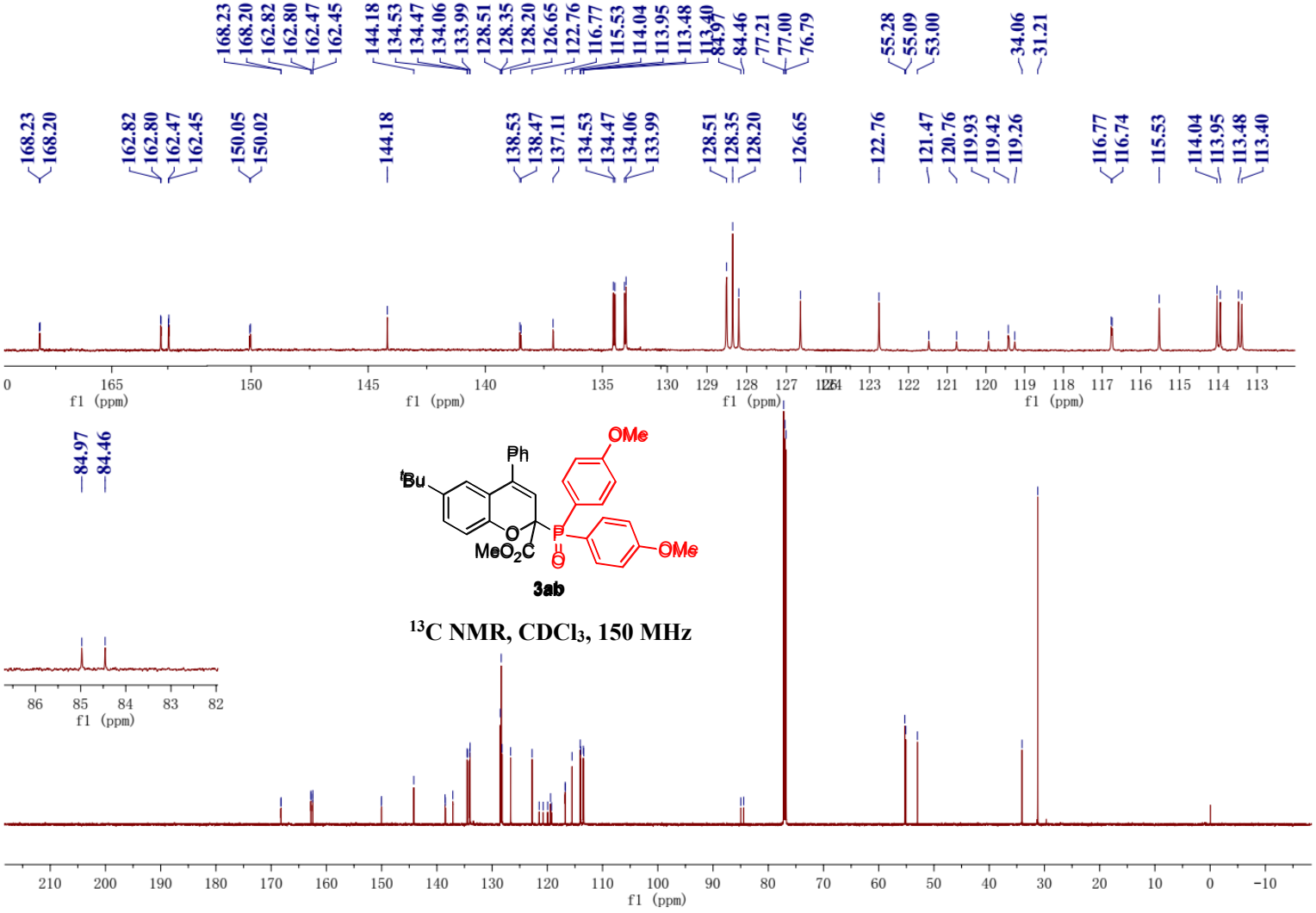
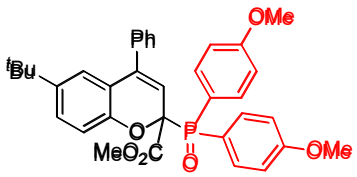
132.83
132.77
132.34
132.28
128.61
128.53
128.23
128.03
127.95
127.89
127.78
127.01
126.51
126.48
126.42
123.17
115.73
85.01
84.49
77.31
77.10
76.89
53.15
34.21
31.31
0.07
150.19
150.15
144.49
138.92
138.87
134.66
133.49
133.23
132.83
132.77
132.67
132.34
132.28
130.28
129.61
128.96
128.61
128.53
128.33
128.23
128.03
127.95
127.89
127.82
127.78
f1 (ppm)
127.01
126.51
126.48
126.42
123.17
116.95
116.93
115.73
85.01
84.49
tBu
O
PPh2
O
CO2Me
3ma
13C NMR, CDCl3, 150 MHz



^{31}P NMR, $CDCl_3$, 243 MHz

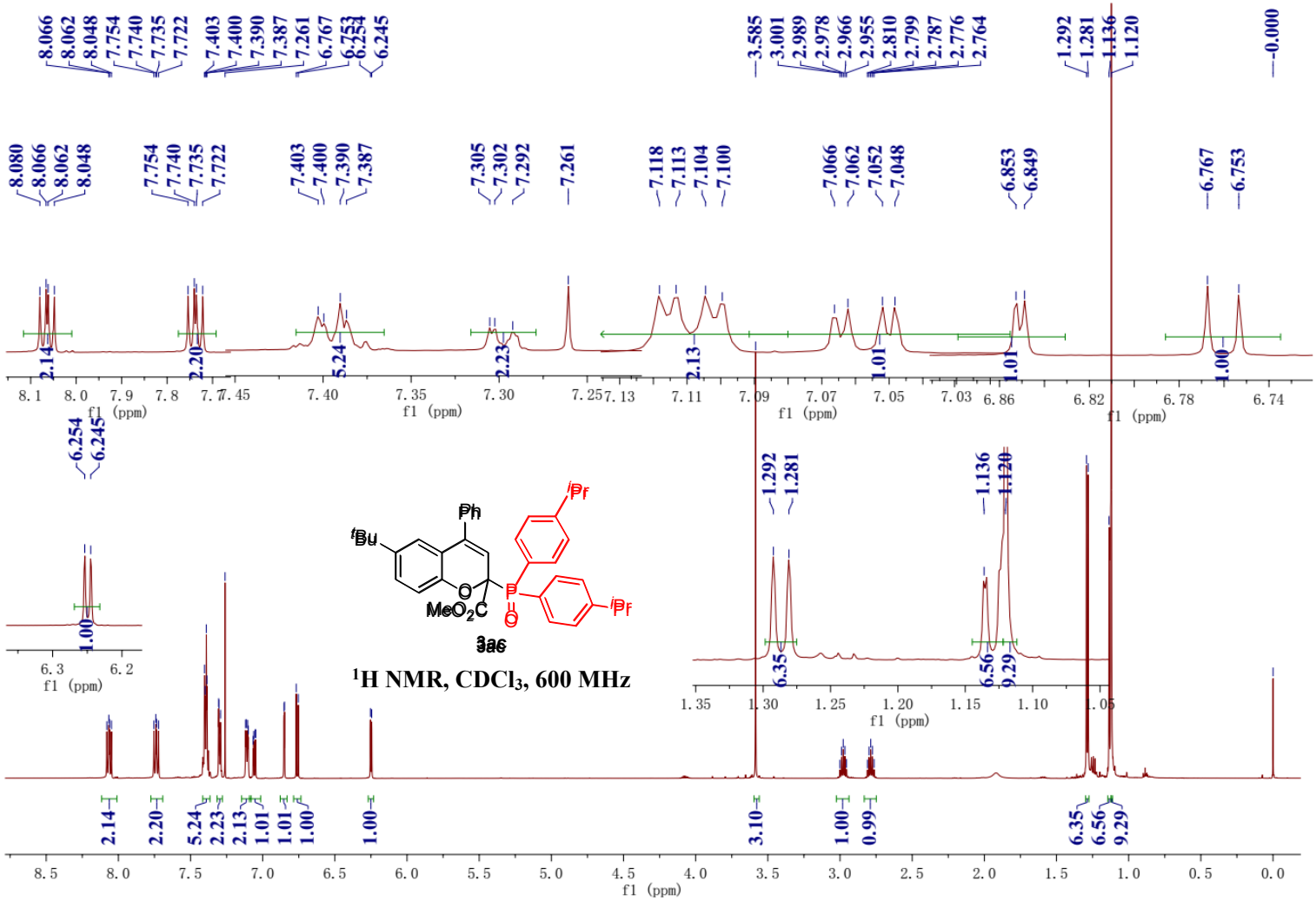

8.106
8.091
8.088
8.074
7.398
7.345
7.342
7.260
7.059
7.057
7.044
6.776
6.280
6.271
3.874
3.697
3.617
1.117
7.714
7.699
7.696
7.681
7.424
7.421
7.410
7.398
7.392
7.386
7.381
7.369
7.345
7.342
7.332
6.821
6.817
6.776
6.762
6.724
6.720
6.709
6.706
2.01
2.06
3.03
2.02
3.02
1.01
1.00
2.00
1.00
f1 (ppm)
Ph
tBu
OMe
OMe
O
MeO2C
P
O
3ab
1H NMR, CDCl3, 600 MHz
2.01
2.06
3.03
2.02
3.02
1.01
1.00
2.00
1.00
3.04
3.06
3.02
9.07

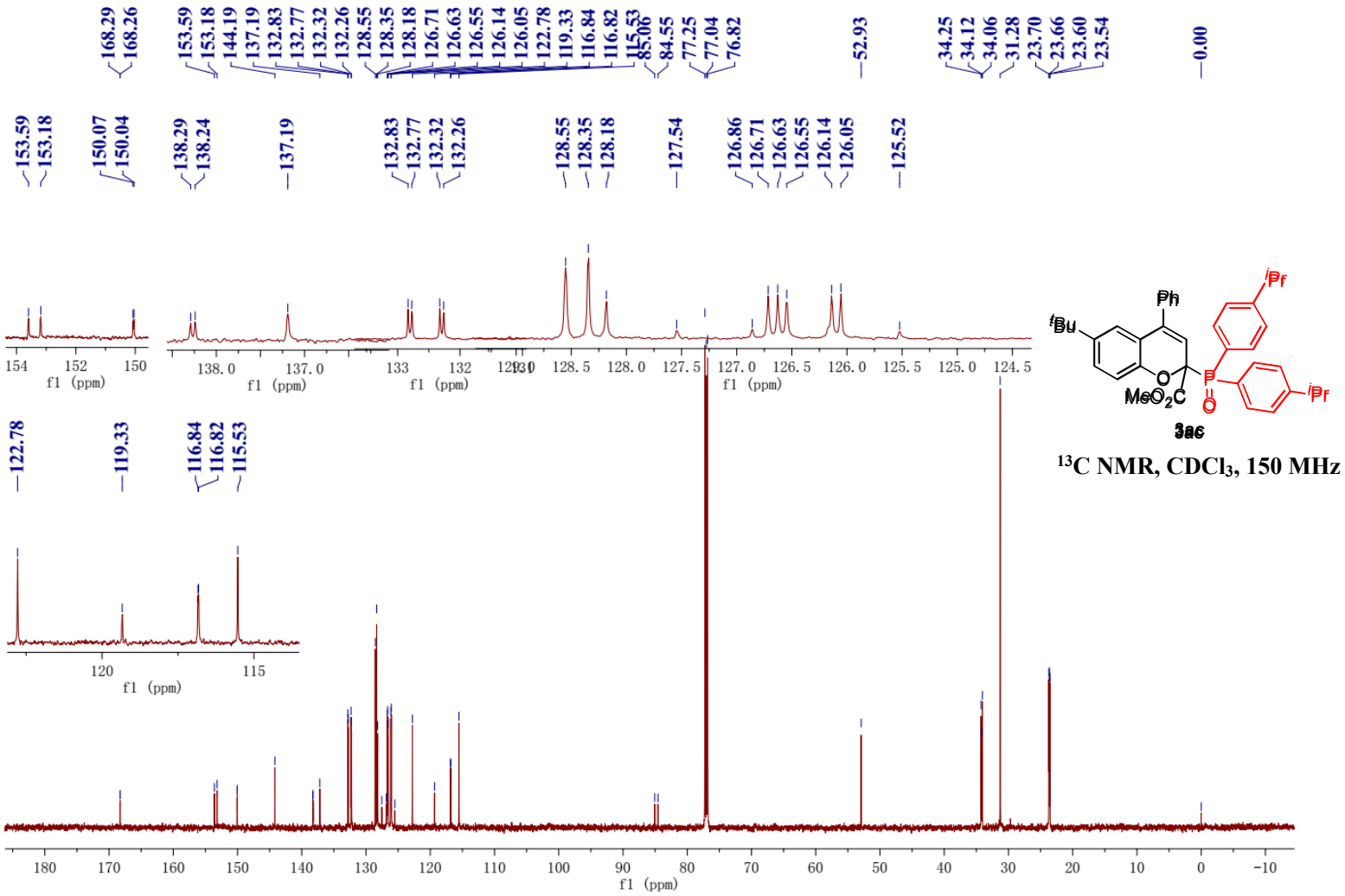

168.23
168.20
162.82
162.80
162.47
162.45
144.18
134.53
134.47
134.06
133.99
128.51
128.35
128.20
126.65
122.76
116.77
115.53
114.04
113.95
113.48
113.40
84.97
84.46
77.21
77.00
76.79
55.28
55.09
53.00
34.06
31.21
150.05
150.02
138.53
138.47
137.11
134.53
134.47
134.06
133.99
128.51
128.35
128.20
126.65
122.76
121.47
120.76
119.93
119.42
119.26
116.77
116.74
115.53
114.04
113.95
113.48
113.40
f1 (ppm)
OMe
OMe
Ph
tBu
MeO2C
P
O
3ab
13C NMR, CDCl3, 150 MHz



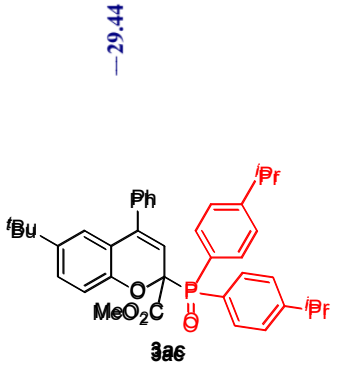
3ab

^{31}P NMR, $CDCl_3$, 243 MHz


8.066
8.062
8.048
7.754
7.740
7.735
7.722
7.403
7.400
7.390
7.387
7.261
6.767
6.753
6.254
6.245
3.585
3.001
2.989
2.978
2.966
2.955
2.810
2.799
2.787
2.776
2.764
1.292
1.281
1.136
1.120
0.000
8.080
8.066
8.062
8.048
7.754
7.740
7.735
7.722
7.403
7.400
7.390
7.387
7.305
7.302
7.292
7.261
7.118
7.113
7.104
7.100
7.066
7.062
7.052
7.048
6.853
6.849
6.767
6.753
2.14
2.20
5.24
2.23
2.13
1.01
1.01
1.00
1.00
3.10
1.00
0.99
6.35
6.56
9.29
f1 (ppm)
Ph
tBu
MeO2C
iPr
iPr
3ac
1H NMR, CDCl3, 600 MHz

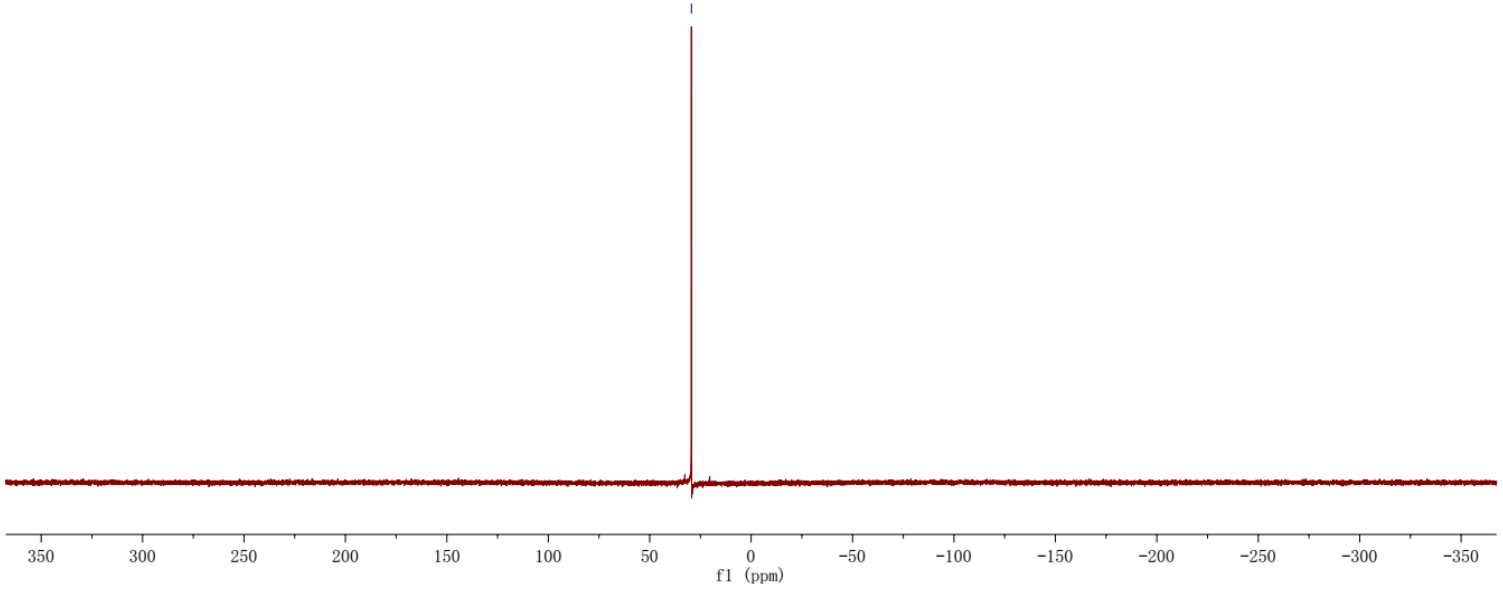


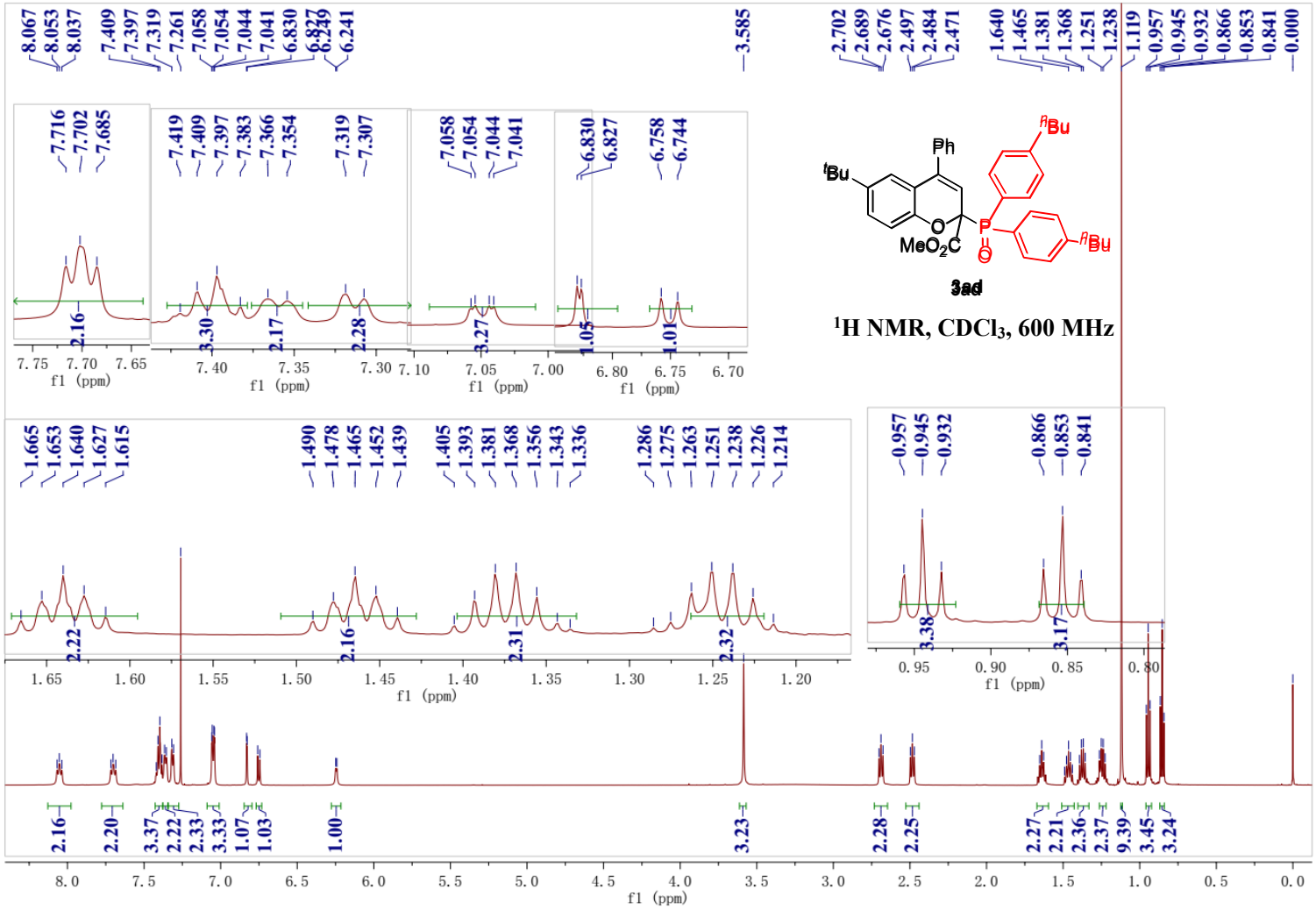
^{13}C NMR, $CDCl_3$, 150 MHz



3ac

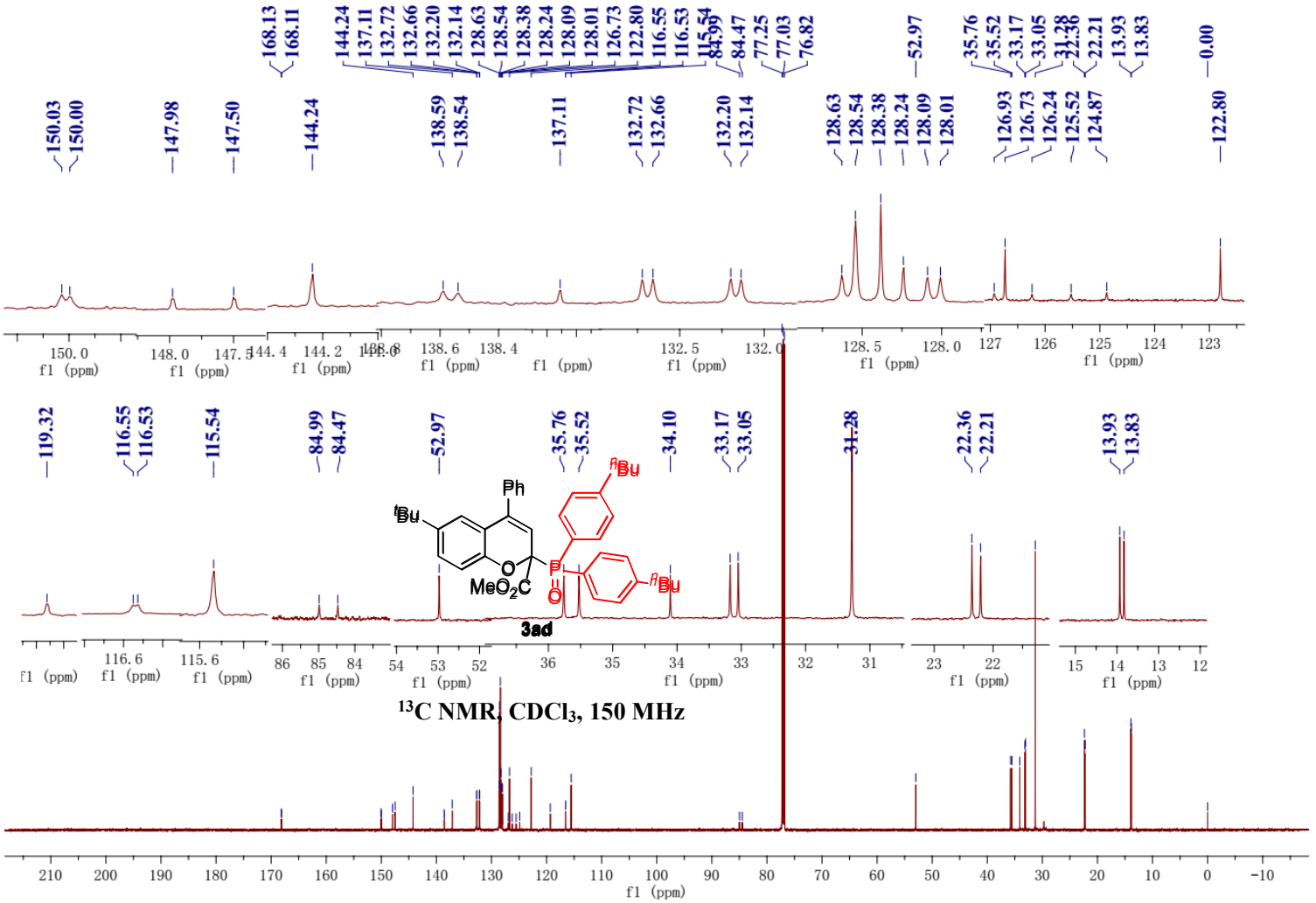
^{31}P NMR, $CDCl_3$, 243 MHz

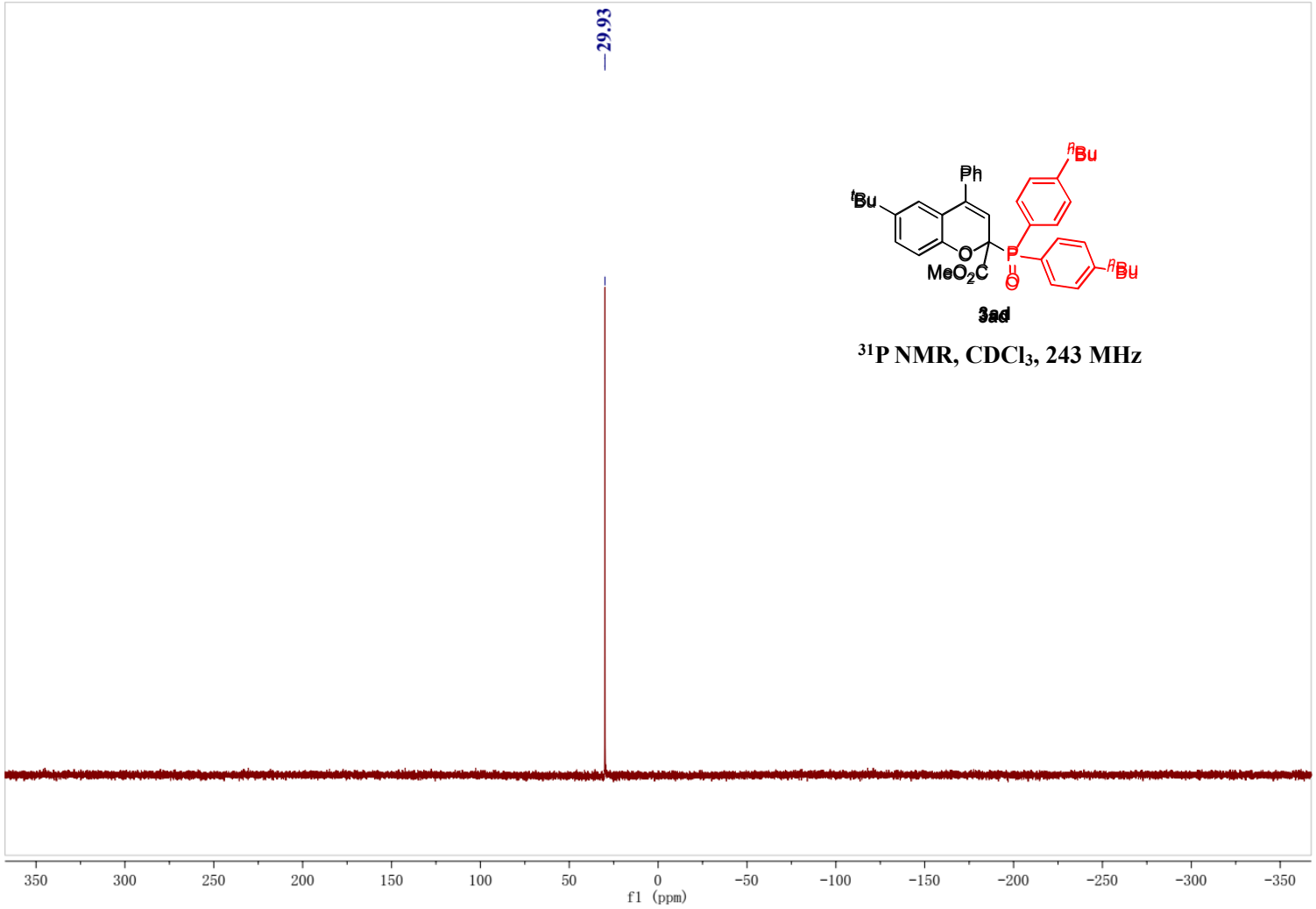




3ad

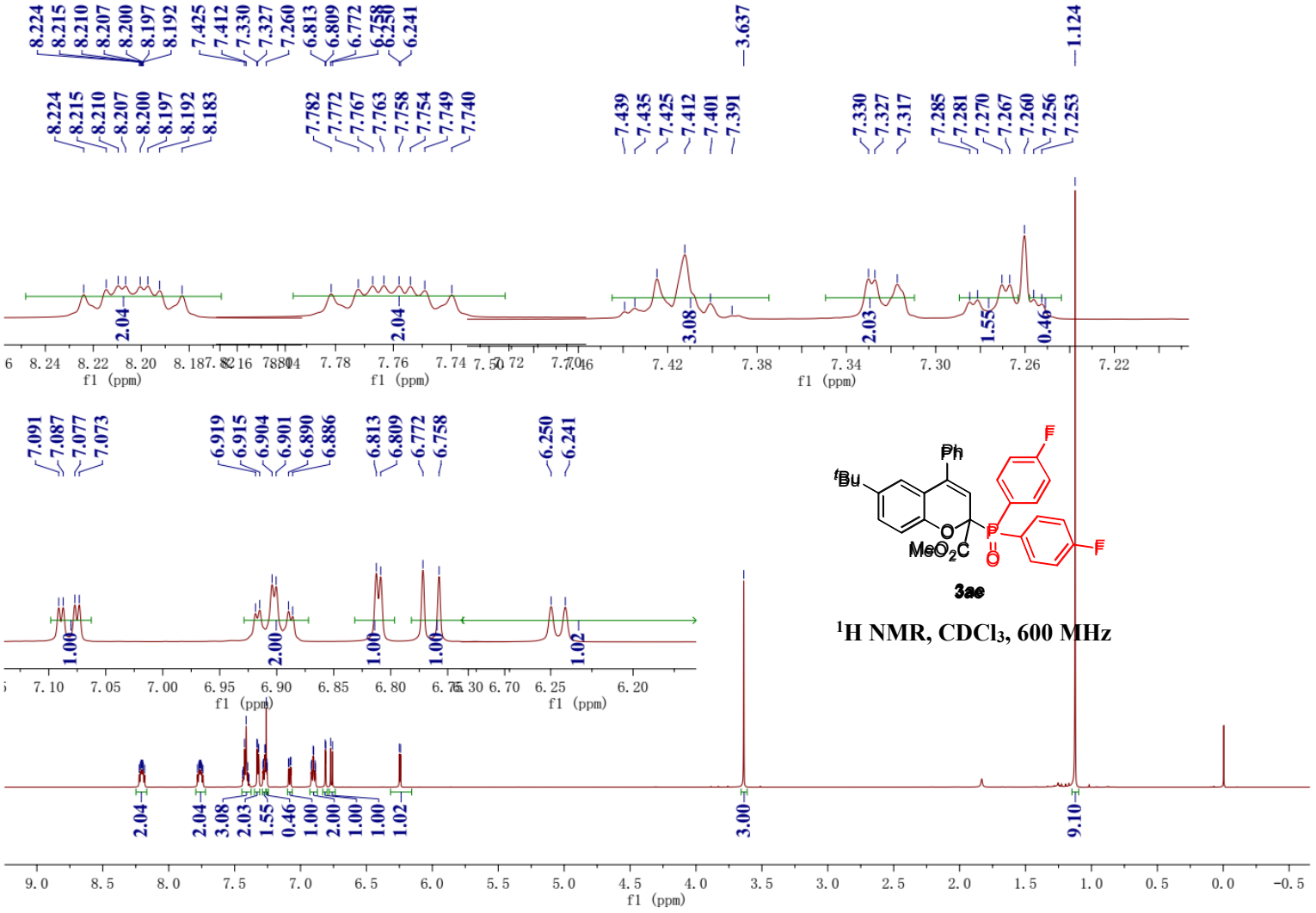
^{1}H NMR, $CDCl_3$, 600 MHz

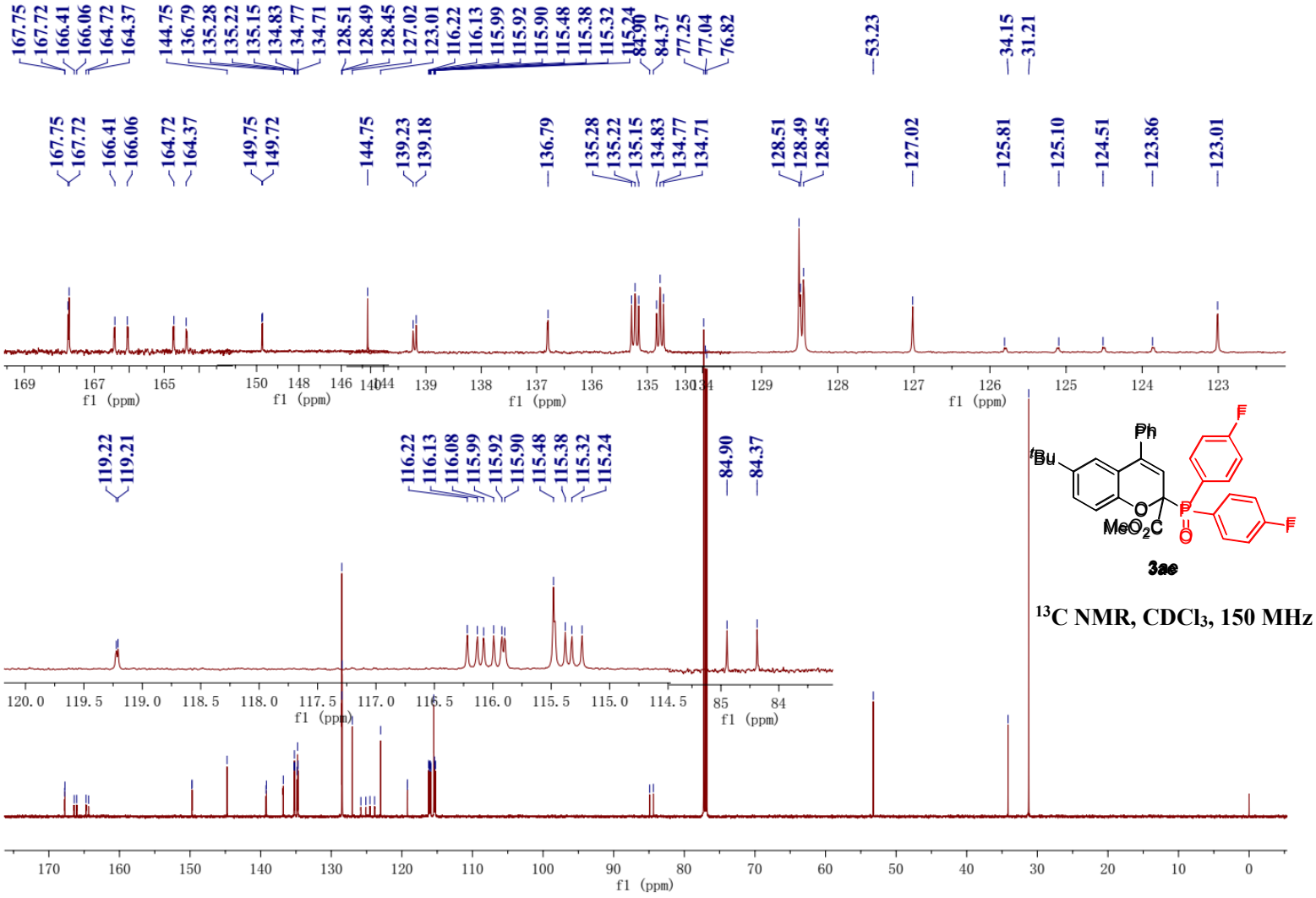

168.13
168.11
144.24
137.11
132.72
132.66
132.20
132.14
128.63
128.54
128.38
128.24
128.09
128.01
126.73
122.80
116.55
116.53
115.54
84.99
84.47
77.25
77.03
76.82
52.97
35.76
35.52
33.17
33.05
31.28
22.36
22.21
13.93
13.83
0.00
150.03
150.00
147.98
147.50
144.24
138.59
138.54
137.11
132.72
132.66
132.20
132.14
128.63
128.54
128.38
128.24
128.09
128.01
126.93
126.73
126.24
125.52
124.87
122.80
119.32
116.55
116.53
115.54
84.99
84.47
52.97
35.76
35.52
34.10
33.17
33.05
31.28
22.36
22.21
13.93
13.83
Ph
tBu
nBu
nBu
O
MeO2C
P
O
3ad
150.0
148.0
147.5
144.4
144.2
138.8
138.6
138.4
132.5
132.0
128.5
128.0
127
126
125
124
123
119.32
116.6
115.6
86
85
84
54
53
52
36
35
34
33
32
31
23
22
15
14
13
12
f1 (ppm)
13C NMR, CDCl3, 150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

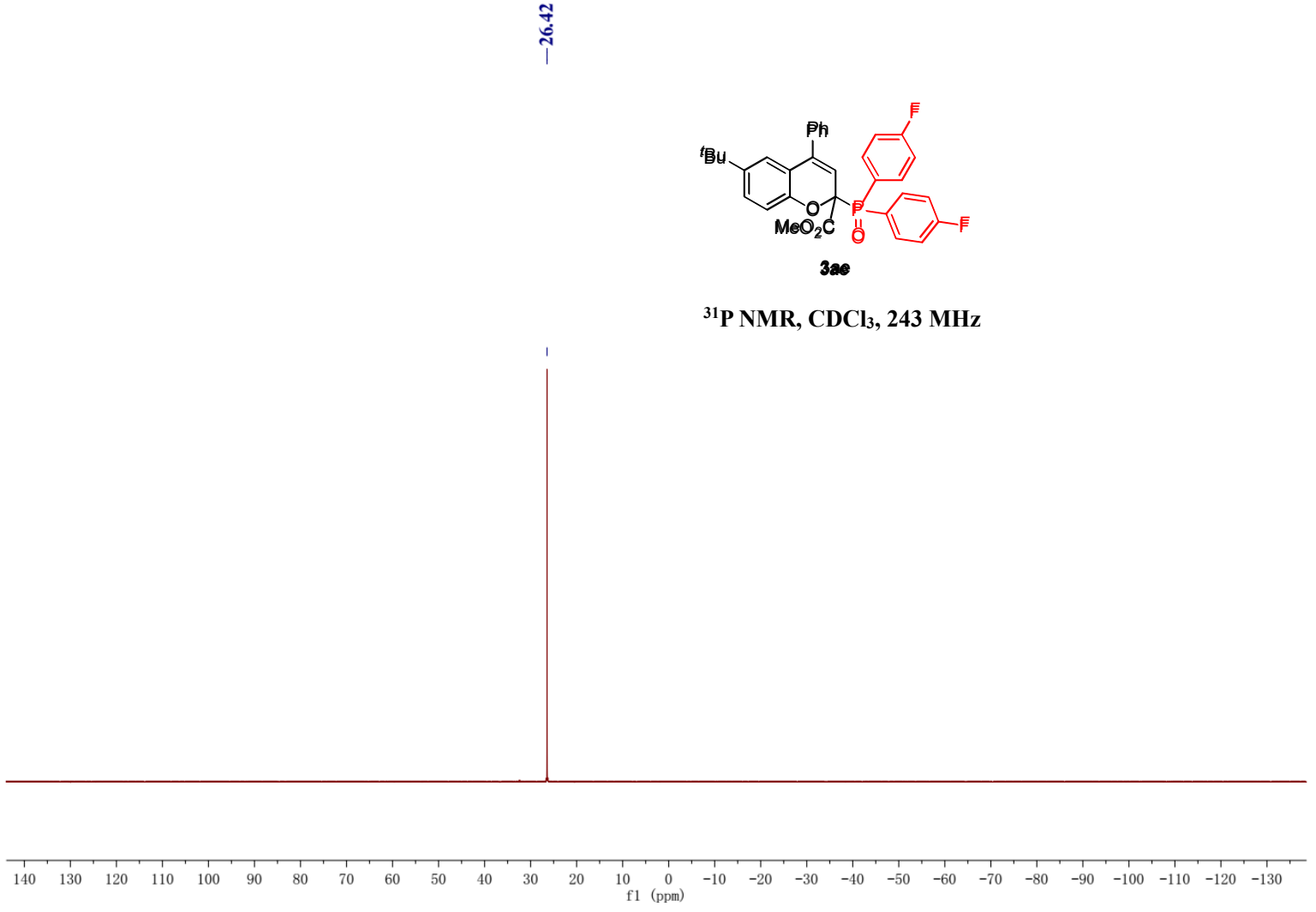


3ad

^{31}P NMR, $CDCl_3$, 243 MHz

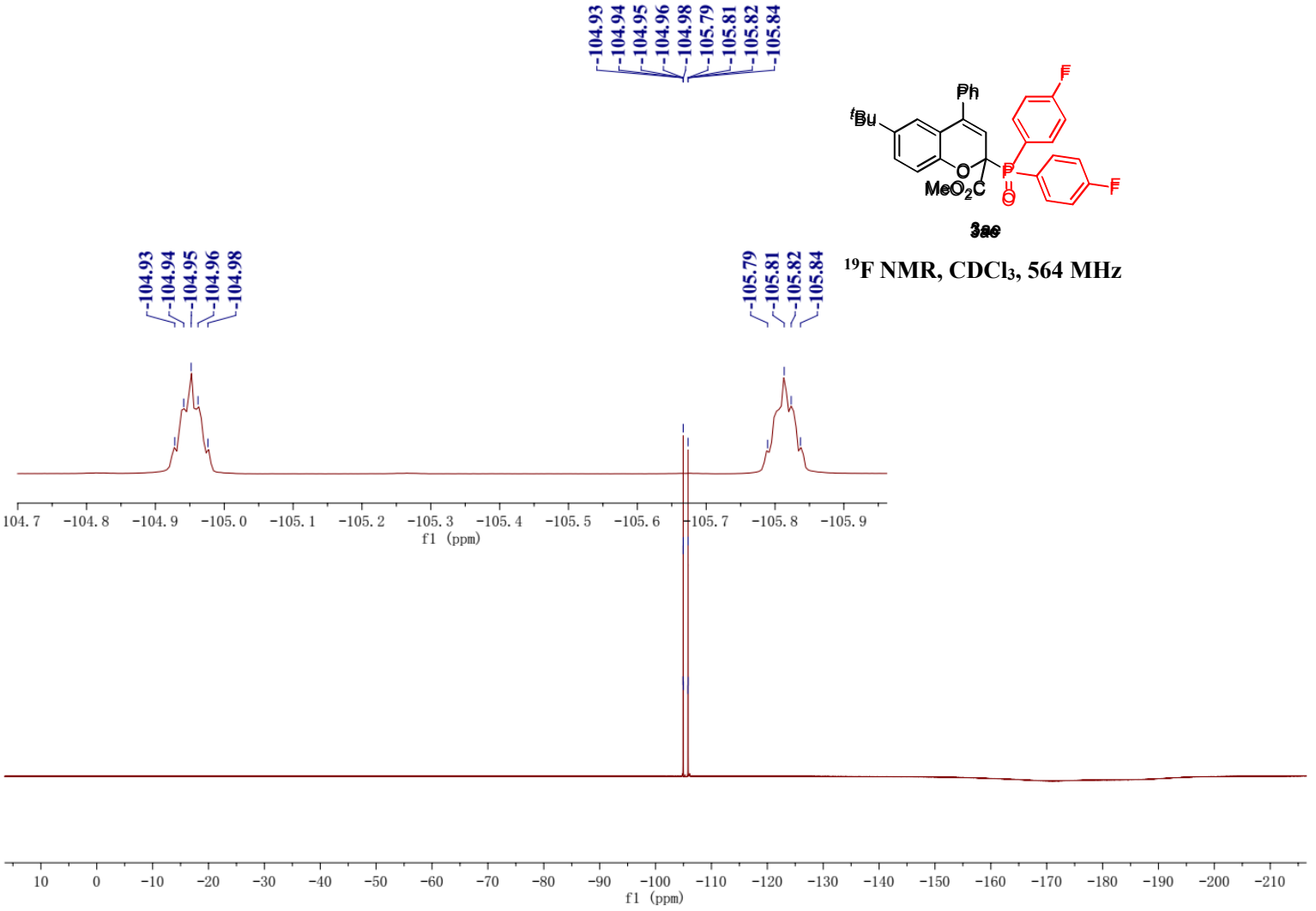

8.224
8.215
8.210
8.207
8.200
8.197
8.192
7.425
7.412
7.330
7.327
7.260
6.813
6.809
6.772
6.758
6.250
6.241
3.637
1.124
7.782
7.772
7.767
7.763
7.758
7.754
7.749
7.740
7.439
7.435
7.425
7.412
7.401
7.391
7.330
7.327
7.317
7.285
7.281
7.270
7.267
7.260
7.256
7.253
7.091
7.087
7.077
7.073
6.919
6.915
6.904
6.901
6.890
6.886
6.813
6.809
6.772
6.758
6.250
6.241
2.04
2.04
3.08
2.03
1.55
0.46
1.00
2.00
1.00
1.00
1.02
2.04
2.04
3.08
2.03
1.55
0.46
1.00
2.00
1.00
1.00
1.02
3.00
9.10
f1 (ppm)
tBu
Ph
F
F
O
MeO2C
P
O
3ae
1H NMR, CDCl3, 600 MHz

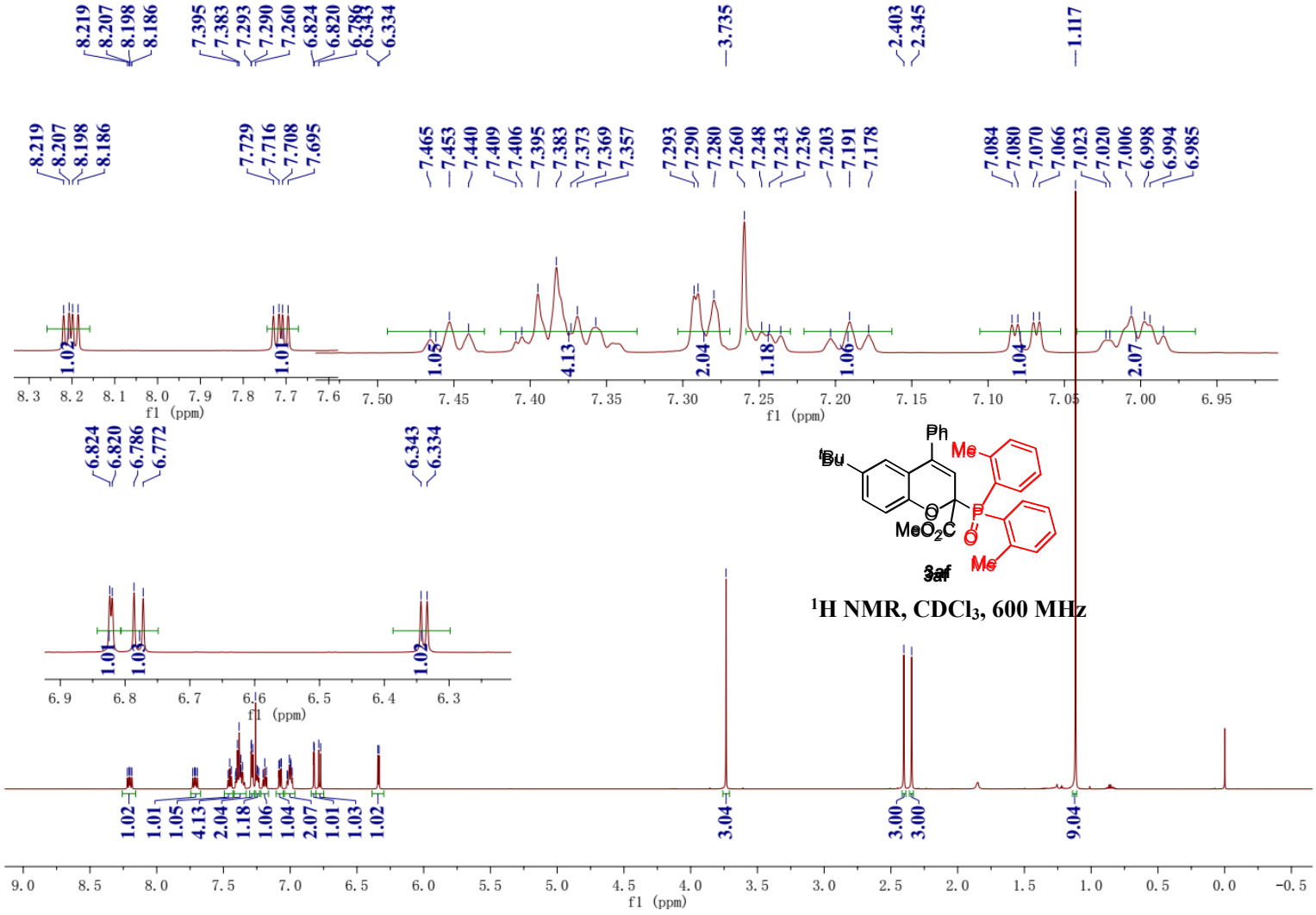

167.75
167.72
166.41
166.06
164.72
164.37
144.75
136.79
135.28
135.22
135.15
134.83
134.77
134.71
128.51
128.49
128.45
127.02
123.01
116.22
116.13
115.99
115.92
115.90
115.48
115.38
115.32
115.24
84.90
84.37
77.25
77.04
76.82
53.23
34.15
31.21
167.75
167.72
166.41
166.06
164.72
164.37
149.75
149.72
144.75
139.23
139.18
136.79
135.28
135.22
135.15
134.83
134.77
134.71
128.51
128.49
128.45
127.02
125.81
125.10
124.51
123.86
123.01
119.22
119.21
116.22
116.13
116.08
115.99
115.92
115.90
115.48
115.38
115.32
115.24
84.90
84.37
f1 (ppm)
Ph
tBu
MeO2C
O
P
O
F
F
3ae
13C NMR, CDCl3, 150 MHz

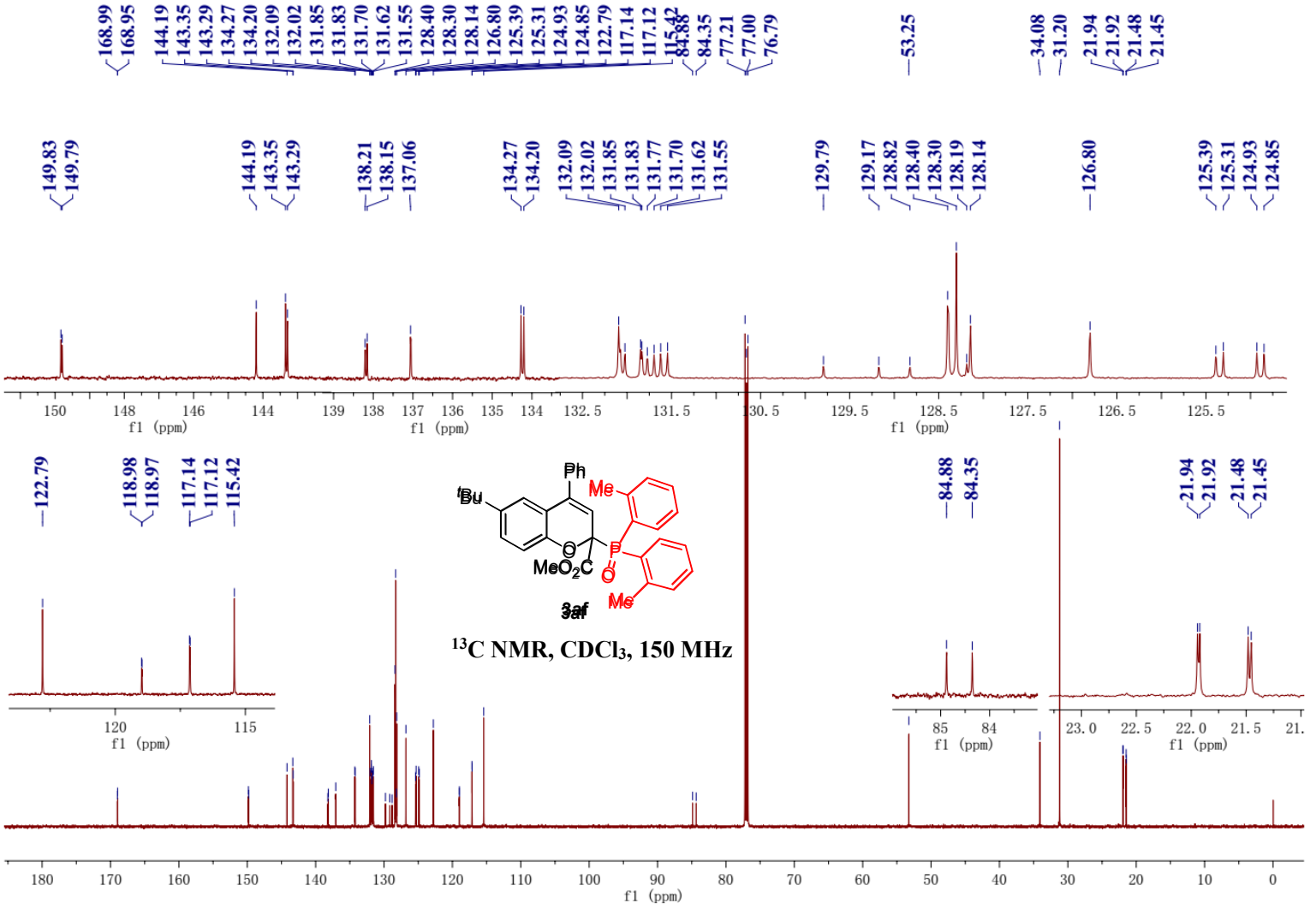


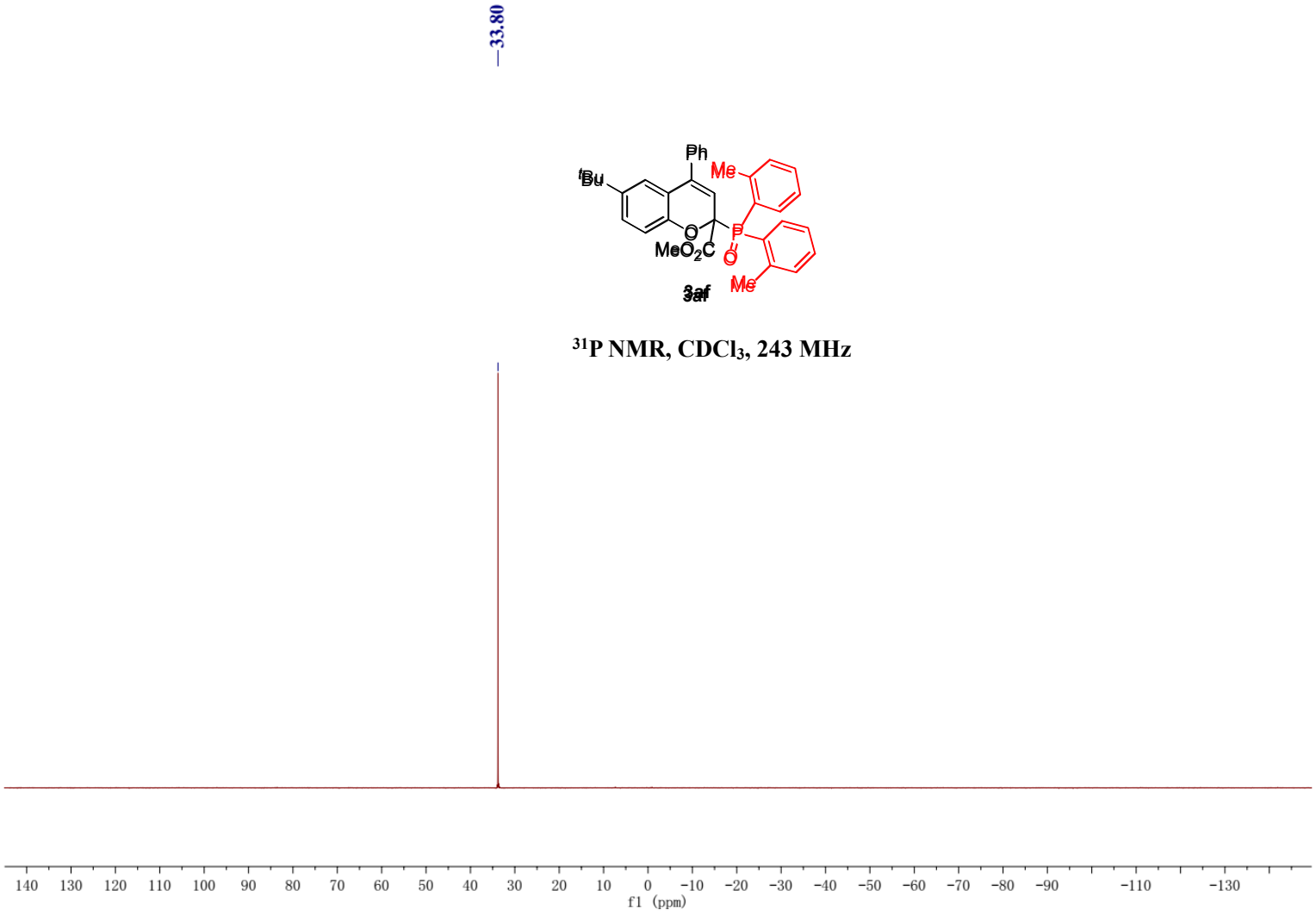
3ae

^{31}P NMR, $CDCl_3$, 243 MHz

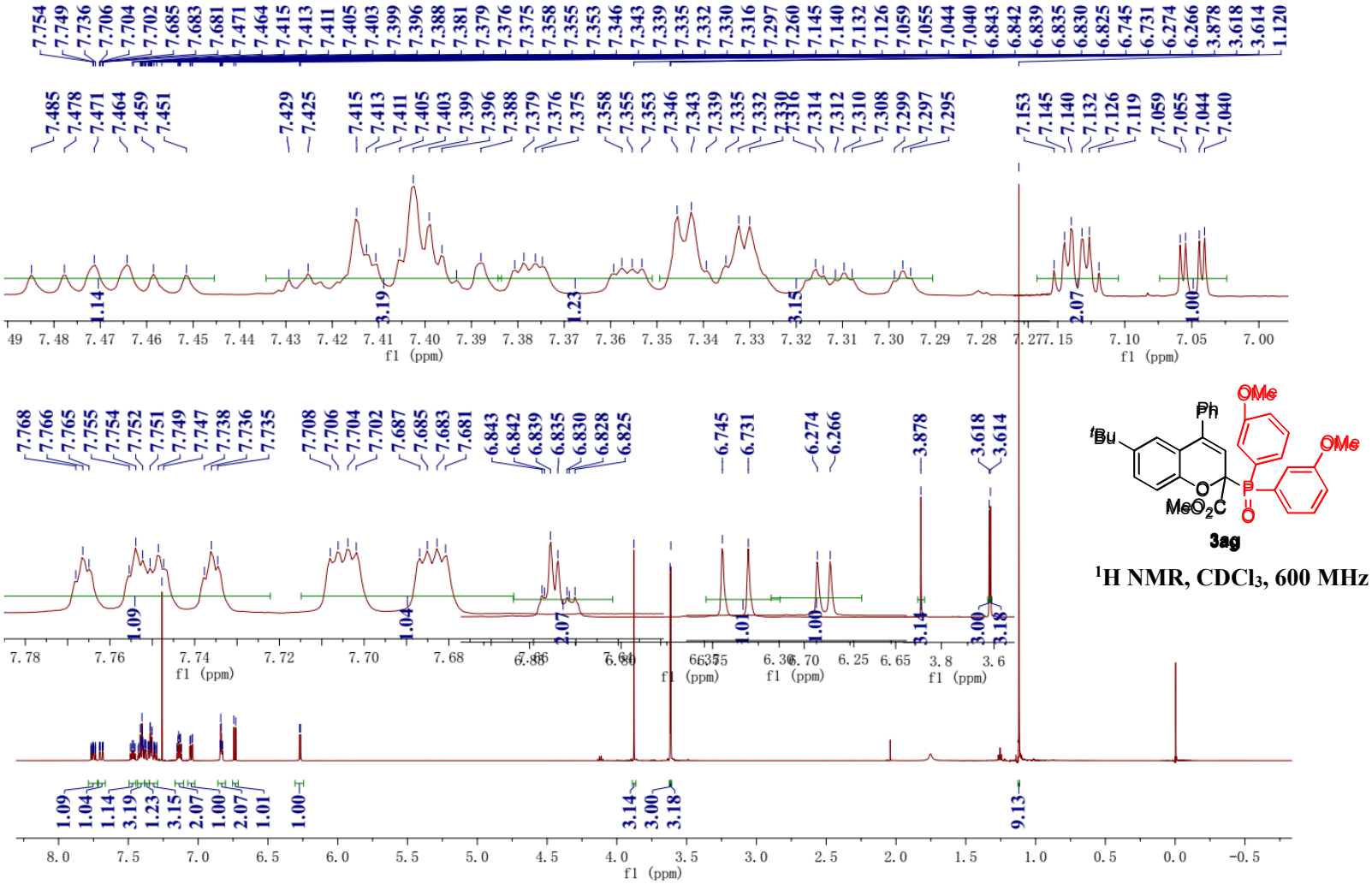

-104.93
-104.94
-104.95
-104.96
-104.98
-105.79
-105.81
-105.82
-105.84
Ph
tBu
O
P
O
MeO2C
F
F
3ae
19F NMR, CDCl3, 564 MHz
f1 (ppm)
f1 (ppm)


8.219
8.207
8.198
8.186
7.395
7.383
7.293
7.290
7.260
6.824
6.820
6.786
6.343
6.334
3.735
2.403
2.345
1.117
7.729
7.716
7.708
7.695
7.465
7.453
7.440
7.409
7.406
7.395
7.383
7.373
7.369
7.357
7.293
7.290
7.280
7.260
7.248
7.243
7.236
7.203
7.191
7.178
7.084
7.080
7.070
7.066
7.023
7.020
7.006
6.998
6.994
6.985
6.772
f1 (ppm)
Ph
Me
tBu
O
P
MeO2C
Me
3af
1H NMR, CDCl3, 600 MHz


168.99
168.95
144.19
143.35
143.29
134.27
134.20
132.09
132.02
131.85
131.83
131.70
131.62
131.55
128.40
128.30
128.14
126.80
125.39
125.31
124.93
124.85
122.79
117.14
117.12
115.42
84.88
84.35
77.21
77.00
76.79
53.25
34.08
31.20
21.94
21.92
21.48
21.45
149.83
149.79
144.19
143.35
143.29
138.21
138.15
137.06
134.27
134.20
132.09
132.02
131.85
131.83
131.77
131.70
131.62
131.55
129.79
129.17
128.82
128.40
128.30
128.19
128.14
126.80
125.39
125.31
124.93
124.85
122.79
118.98
118.97
117.14
117.12
115.42
84.88
84.35
21.94
21.92
21.48
21.45
Ph
tBu
Me
O
P
O
MeO2C
Me
3af
13C NMR, CDCl3, 150 MHz
f1 (ppm)

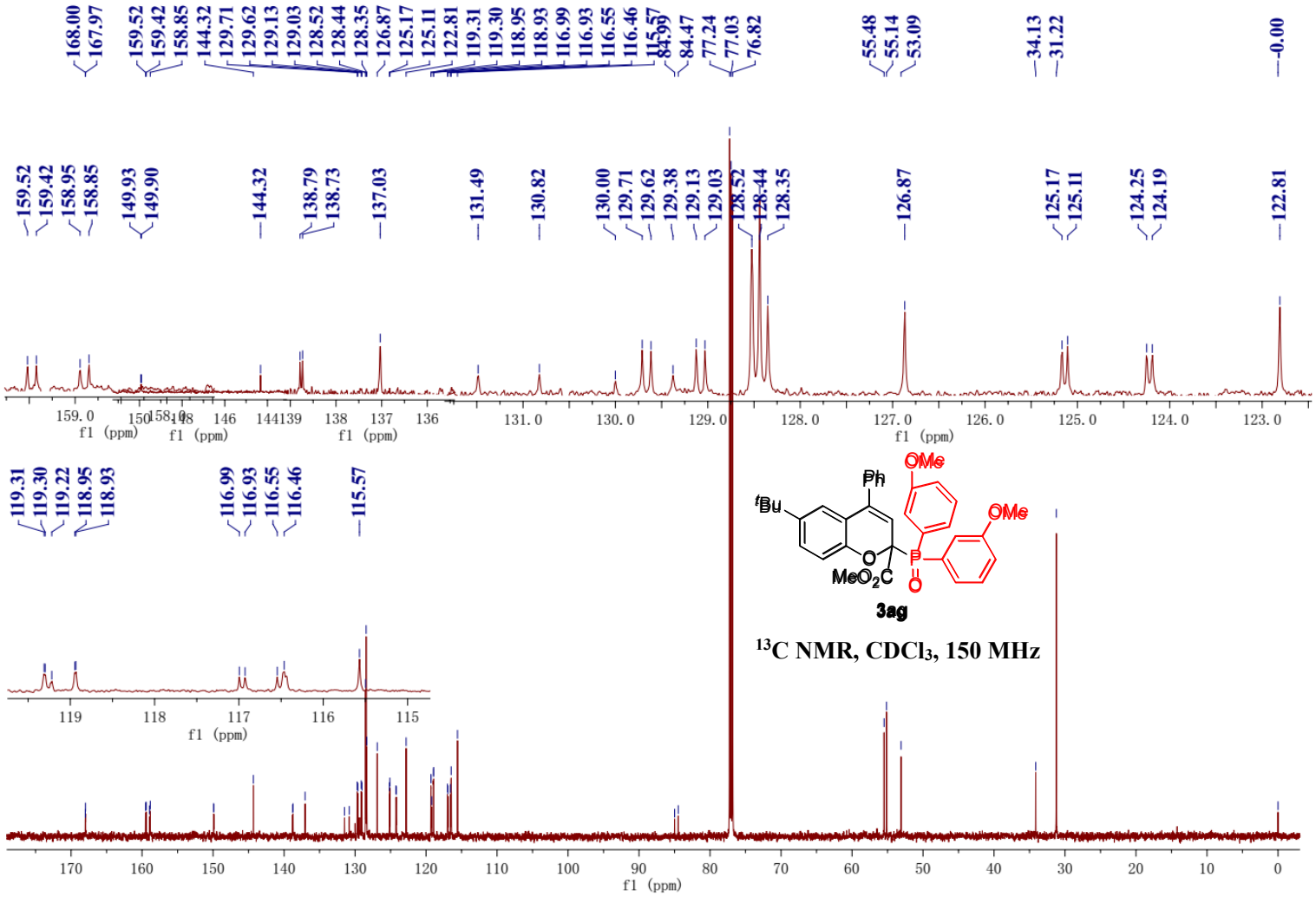


^{31}P NMR, $CDCl_3$, 243 MHz

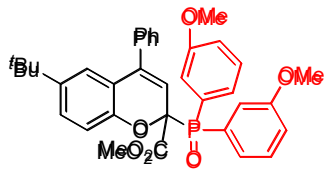


3ag

^{1}H NMR, $CDCl_3$, 600 MHz

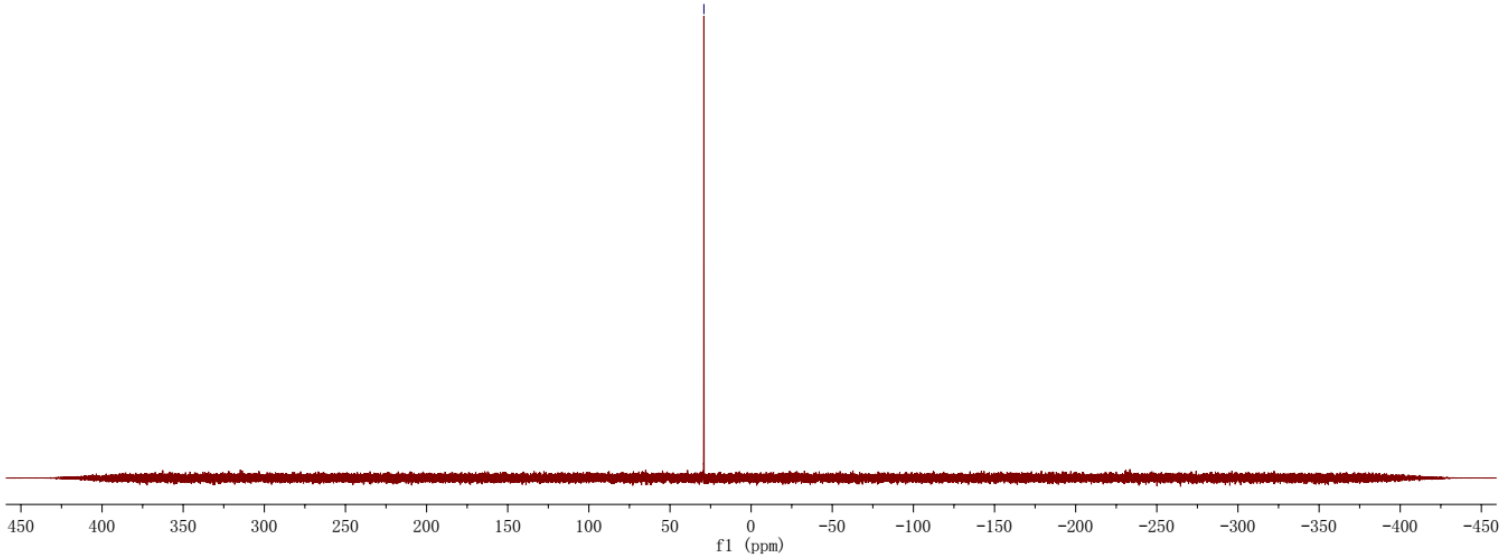

168.00
167.97
159.52
159.42
158.85
144.32
129.71
129.62
129.13
129.03
128.52
128.44
128.35
126.87
125.17
125.11
122.81
119.31
119.30
119.22
118.95
118.93
116.99
116.93
116.55
116.46
115.57
84.99
84.47
77.24
77.03
76.82
55.48
55.14
53.09
34.13
31.22
0.00
159.52
159.42
158.95
158.85
149.93
149.90
144.32
138.79
138.73
137.03
131.49
130.82
130.00
129.71
129.62
129.38
129.13
129.03
128.52
128.44
128.35
126.87
125.17
125.11
124.25
124.19
122.81
f1 (ppm)
OMe
OMe
Ph
tBu
O
P
O
MeO2C
3ag
13C NMR, CDCl3, 150 MHz

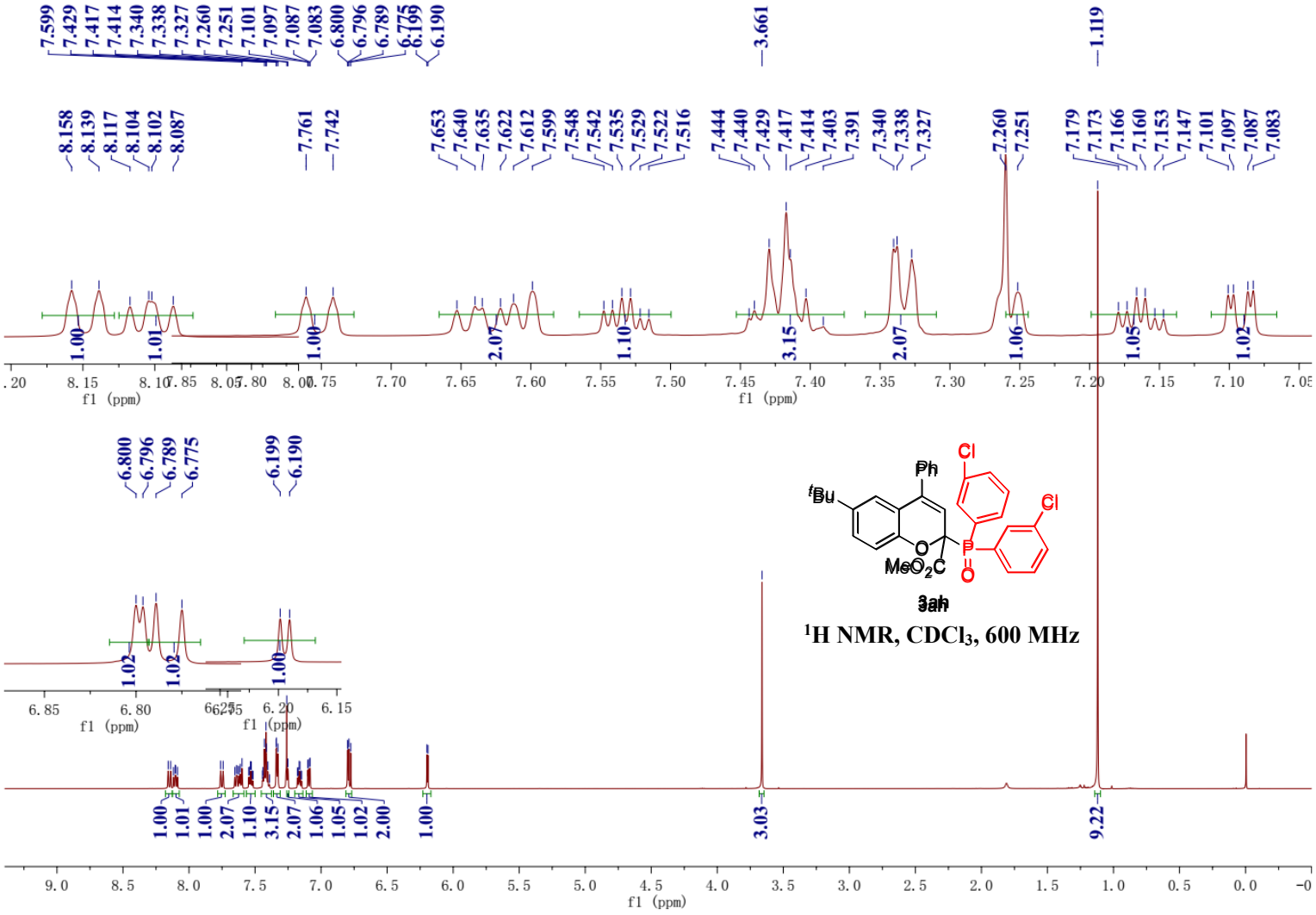
29.11

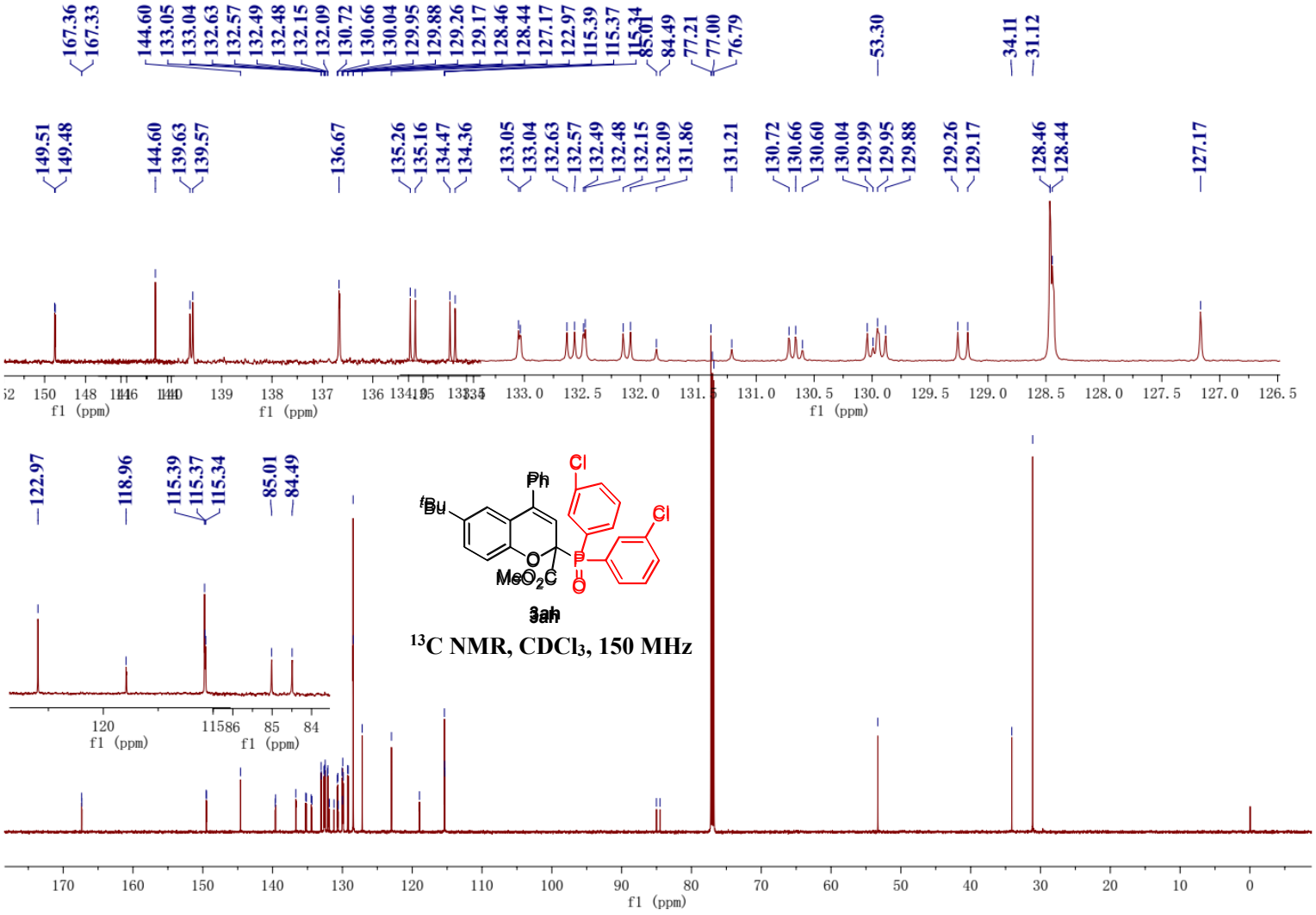


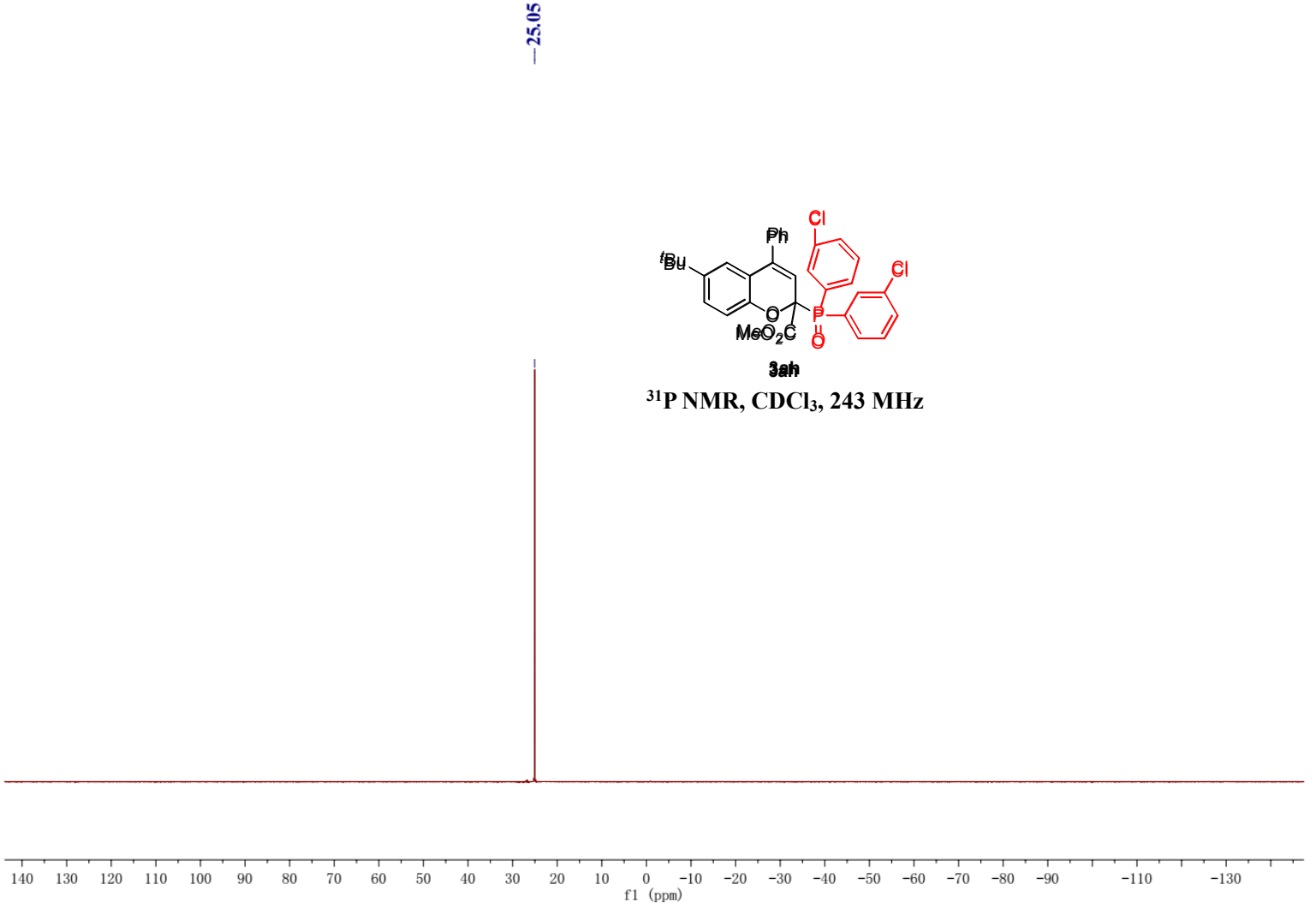
3ag

^{31}P NMR, $CDCl_3$, 243 MHz

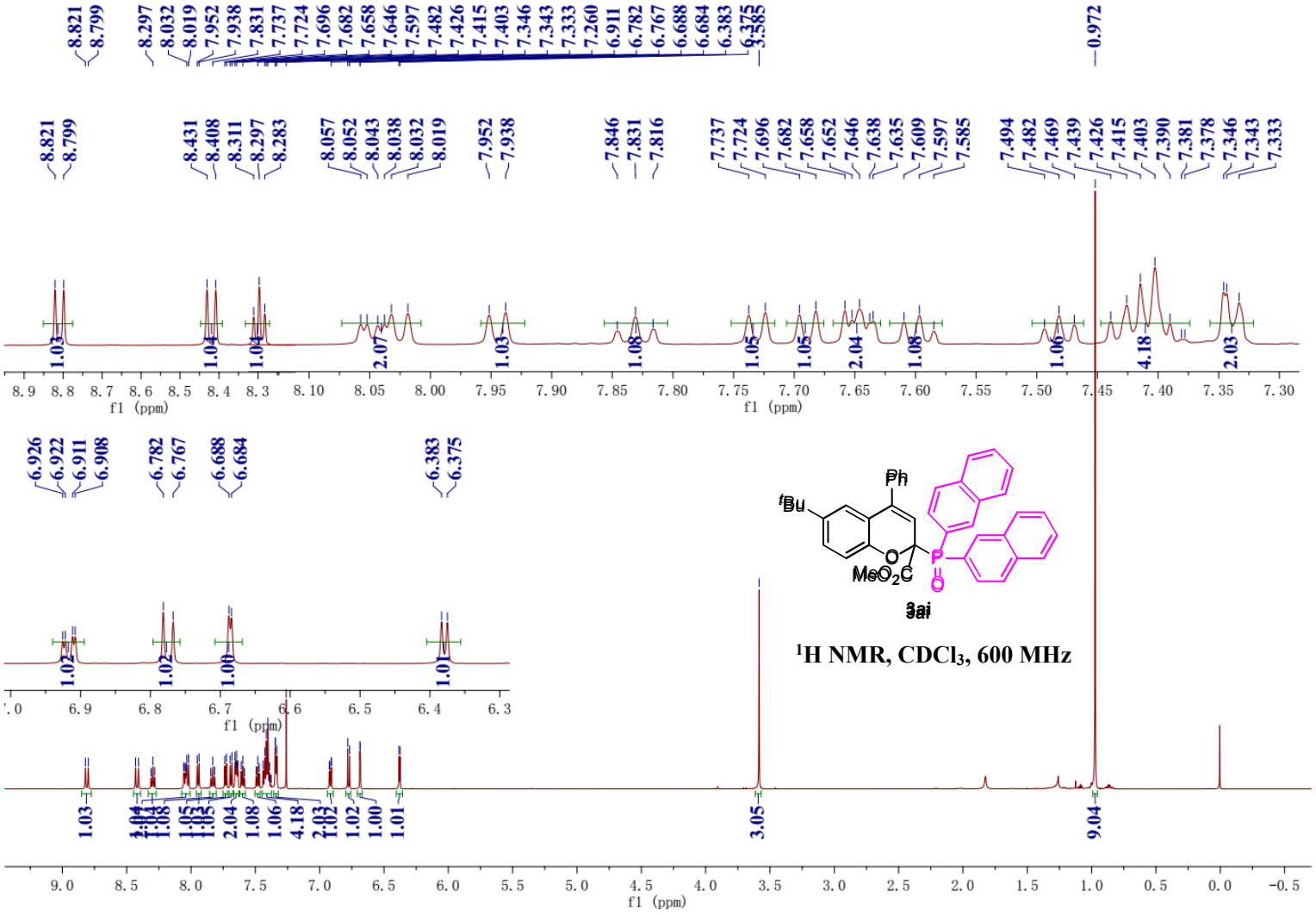


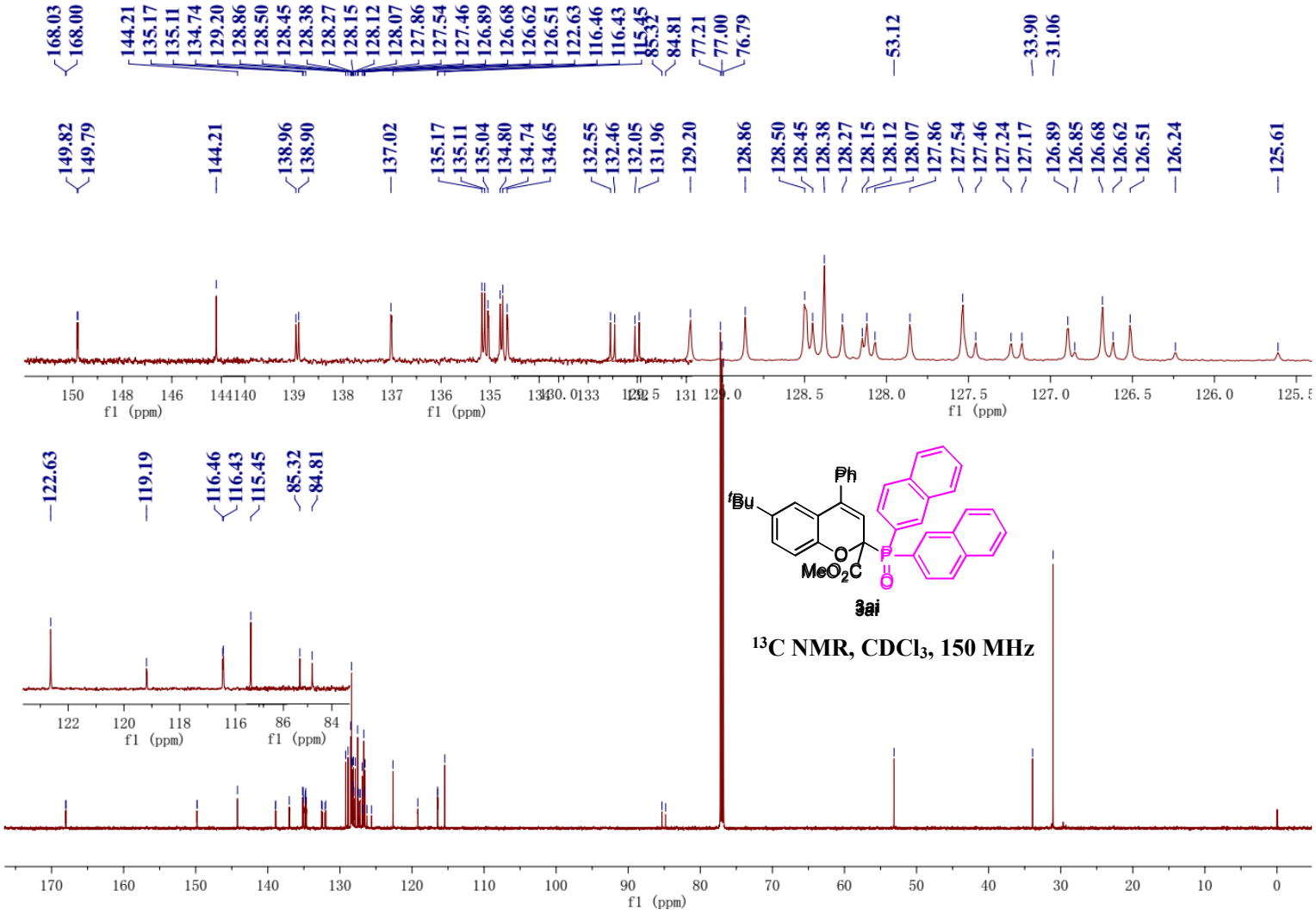

7.599
7.429
7.417
7.414
7.340
7.338
7.327
7.260
7.251
7.101
7.097
7.087
7.083
6.800
6.796
6.789
6.775
6.199
6.190
3.661
1.119
8.158
8.139
8.117
8.104
8.102
8.087
7.761
7.742
7.653
7.640
7.635
7.622
7.612
7.599
7.548
7.542
7.535
7.529
7.522
7.516
7.444
7.440
7.429
7.417
7.414
7.403
7.391
7.340
7.338
7.327
7.260
7.251
7.179
7.173
7.166
7.160
7.153
7.147
7.101
7.097
7.087
7.083
1.00
1.01
1.00
2.07
1.10
3.15
2.07
1.06
1.05
1.02
f1 (ppm)
1.02
1.02
1.00
1.00
1.01
1.00
2.07
1.10
3.15
2.07
1.06
1.05
1.02
2.00
1.00
3.03
9.22
Ph
tBu
Cl
Cl
O
P
O
MeO2C
3ah
1H NMR, CDCl3, 600 MHz

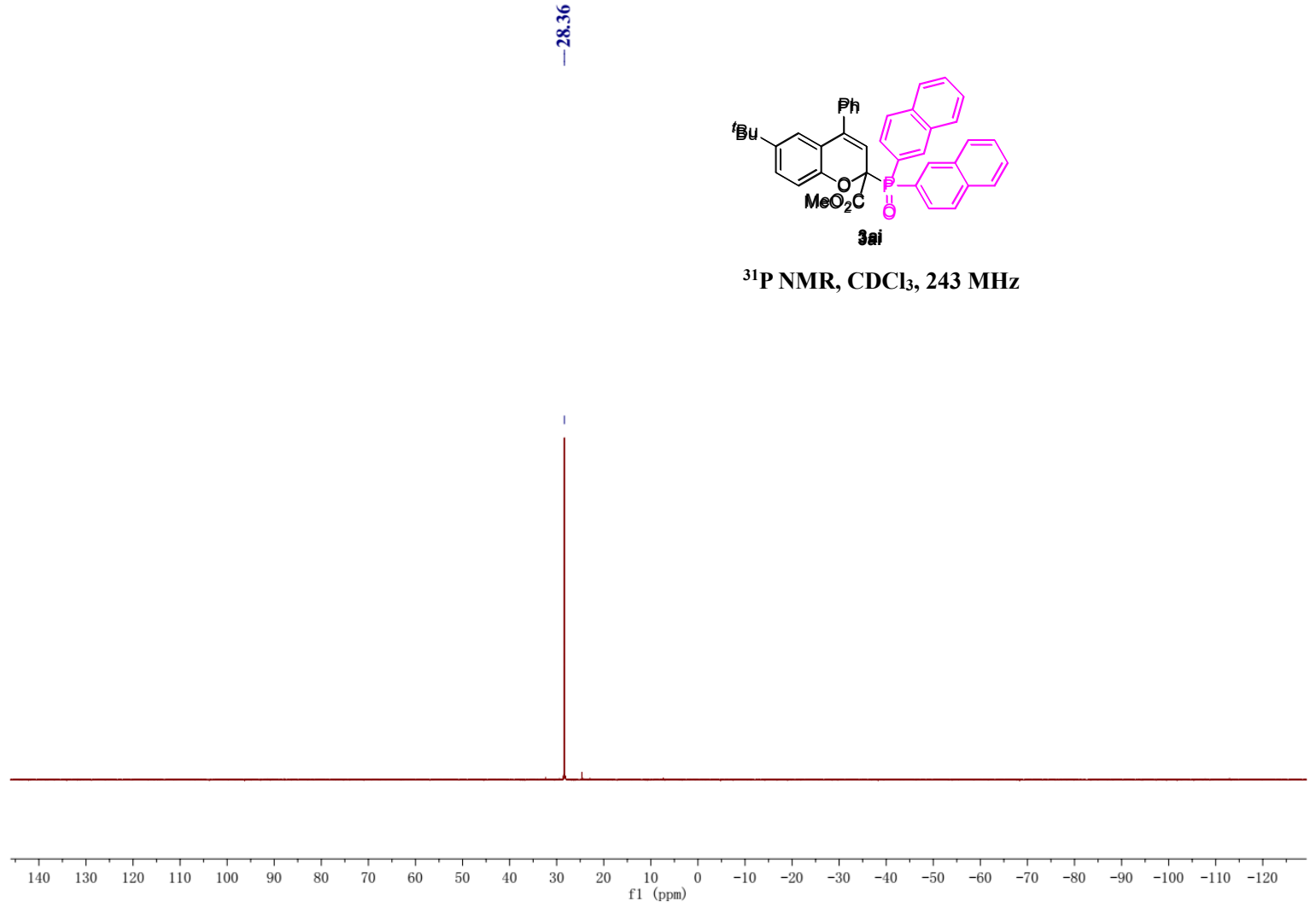

167.36
167.33
144.60
133.05
133.04
132.63
132.57
132.49
132.48
132.15
132.09
130.72
130.66
130.04
129.95
129.88
129.26
129.17
128.46
128.44
127.17
122.97
115.39
115.37
115.34
85.01
84.49
77.21
77.00
76.79
53.30
34.11
31.12
149.51
149.48
144.60
139.63
139.57
136.67
135.26
135.16
134.47
134.36
133.05
133.04
132.63
132.57
132.49
132.48
132.15
132.09
131.86
131.21
130.72
130.66
130.60
130.04
129.99
129.95
129.88
129.26
129.17
128.46
128.44
127.17
f1 (ppm)
Ph
tBu
Cl
Cl
O
P
O
MeO2C
3ah
13C NMR, CDCl3, 150 MHz



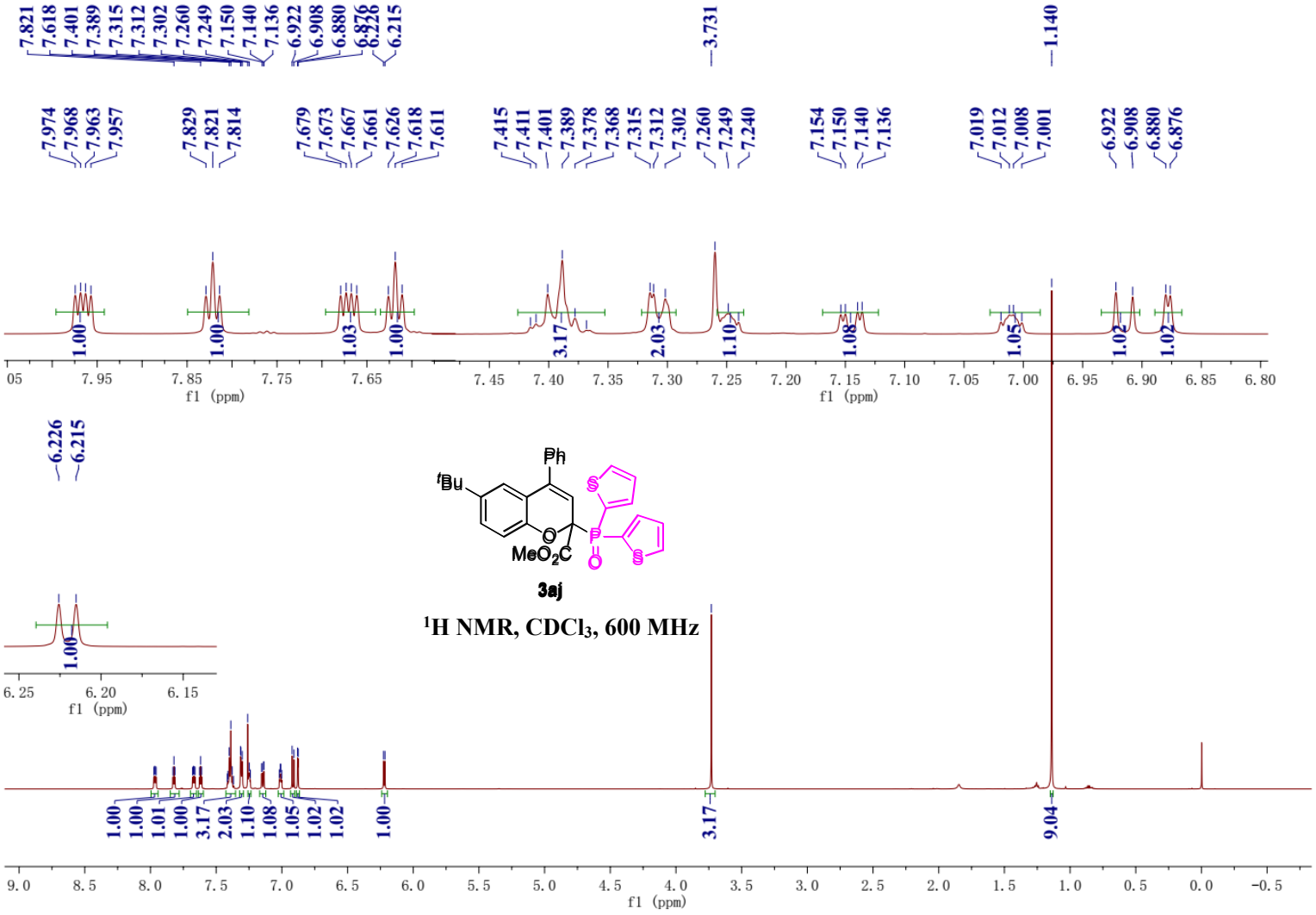
^{31}P NMR, $CDCl_3$, 243 MHz

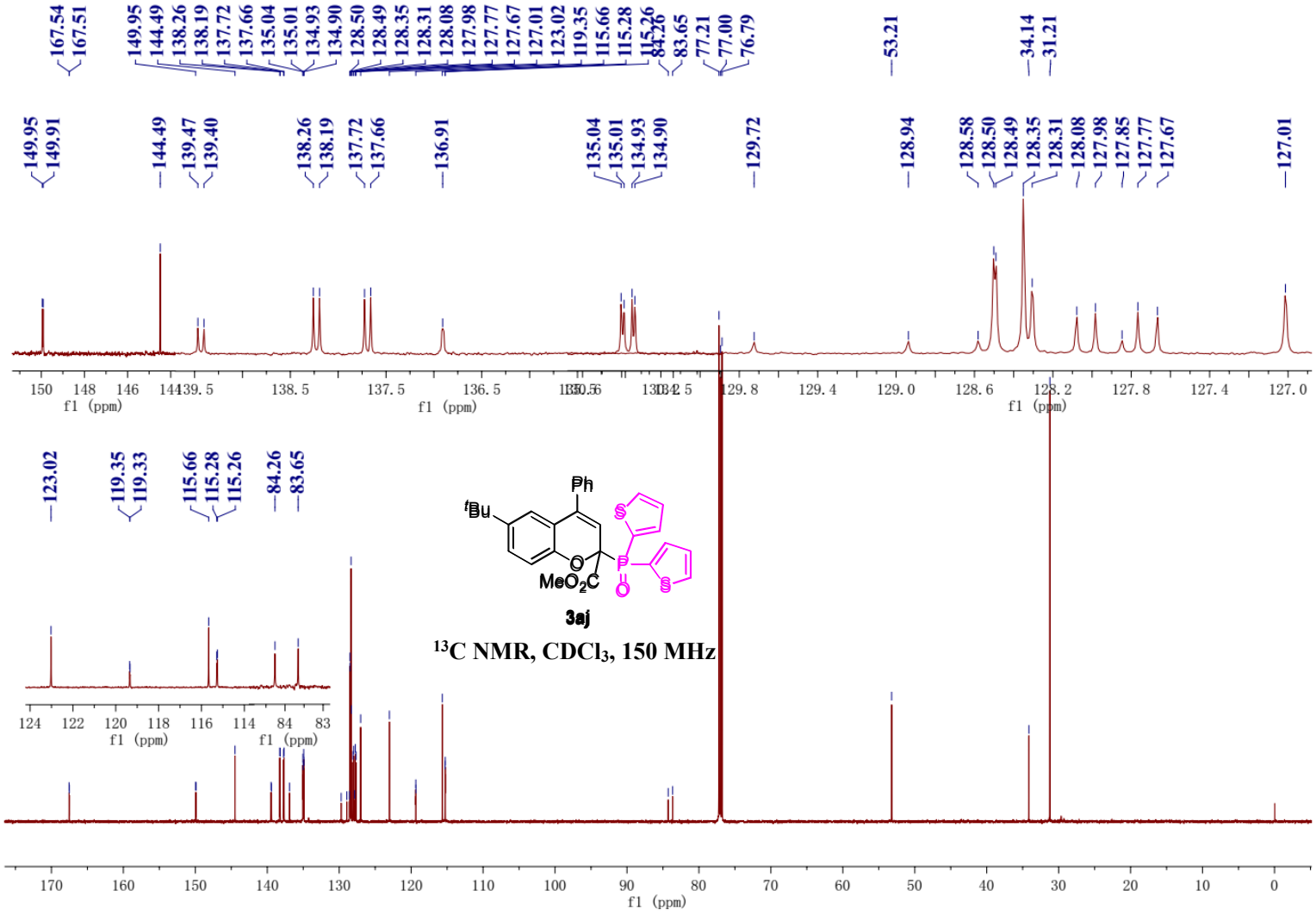

8.821
8.799
8.297
8.032
8.019
7.952
7.938
7.831
7.737
7.724
7.696
7.682
7.658
7.646
7.597
7.482
7.426
7.415
7.403
7.346
7.343
7.333
7.260
6.911
6.782
6.767
6.688
6.684
6.383
6.375
3.585
0.972
8.431
8.408
8.311
8.297
8.283
8.057
8.052
8.043
8.038
8.032
8.019
7.952
7.938
7.846
7.831
7.816
7.737
7.724
7.696
7.682
7.658
7.652
7.646
7.638
7.635
7.609
7.597
7.585
7.494
7.482
7.469
7.439
7.426
7.415
7.403
7.390
7.381
7.378
7.346
7.343
7.333
1.03
1.04
1.04
2.07
1.03
1.08
1.05
1.05
2.04
1.08
1.06
4.18
2.03
f1 (ppm)
6.926
6.922
6.911
6.908
6.782
6.767
6.688
6.684
6.383
6.375
1.02
1.02
1.00
1.01
f1 (ppm)
1.03
3.05
9.04
f1 (ppm)
Ph
tBu
MeO2C
O
P
O
3ai
3ai
1H NMR, CDCl3, 600 MHz

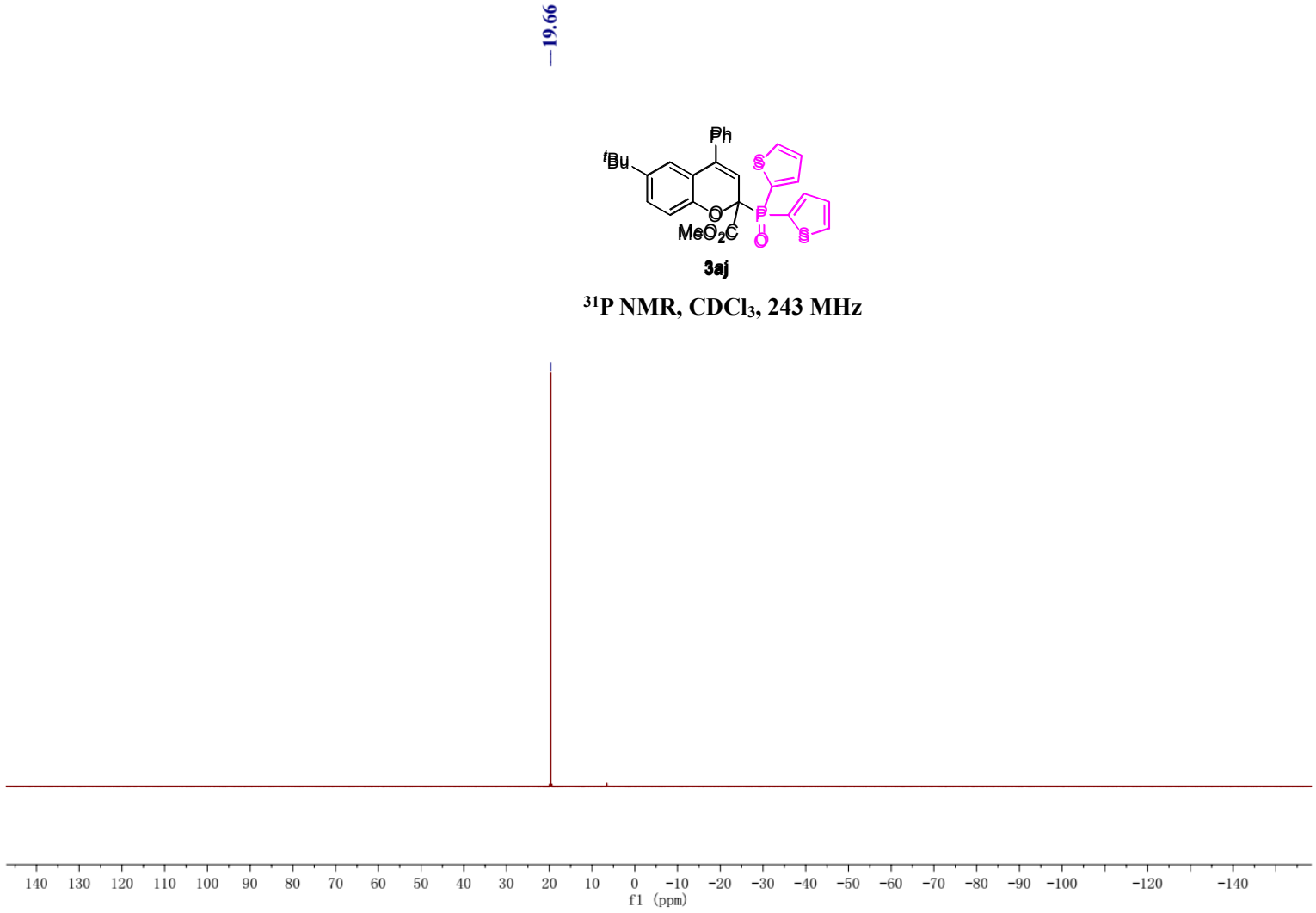

168.03
168.00
144.21
135.17
135.11
134.74
129.20
128.86
128.50
128.45
128.38
128.27
128.15
128.12
128.07
127.86
127.54
127.46
126.89
126.68
126.62
126.51
122.63
116.46
116.43
115.45
85.32
84.81
77.21
77.00
76.79
53.12
33.90
31.06
149.82
149.79
144.21
138.96
138.90
137.02
135.17
135.11
135.04
134.80
134.74
134.65
132.55
132.46
132.05
131.96
129.20
128.86
128.50
128.45
128.38
128.27
128.15
128.12
128.07
127.86
127.54
127.46
127.24
127.17
126.89
126.85
126.68
126.62
126.51
126.24
125.61
f1 (ppm)
122.63
119.19
116.46
116.43
115.45
85.32
84.81
Ph
tBu
O
P
MeO2C
O
3ai
13C NMR, CDCl3, 150 MHz

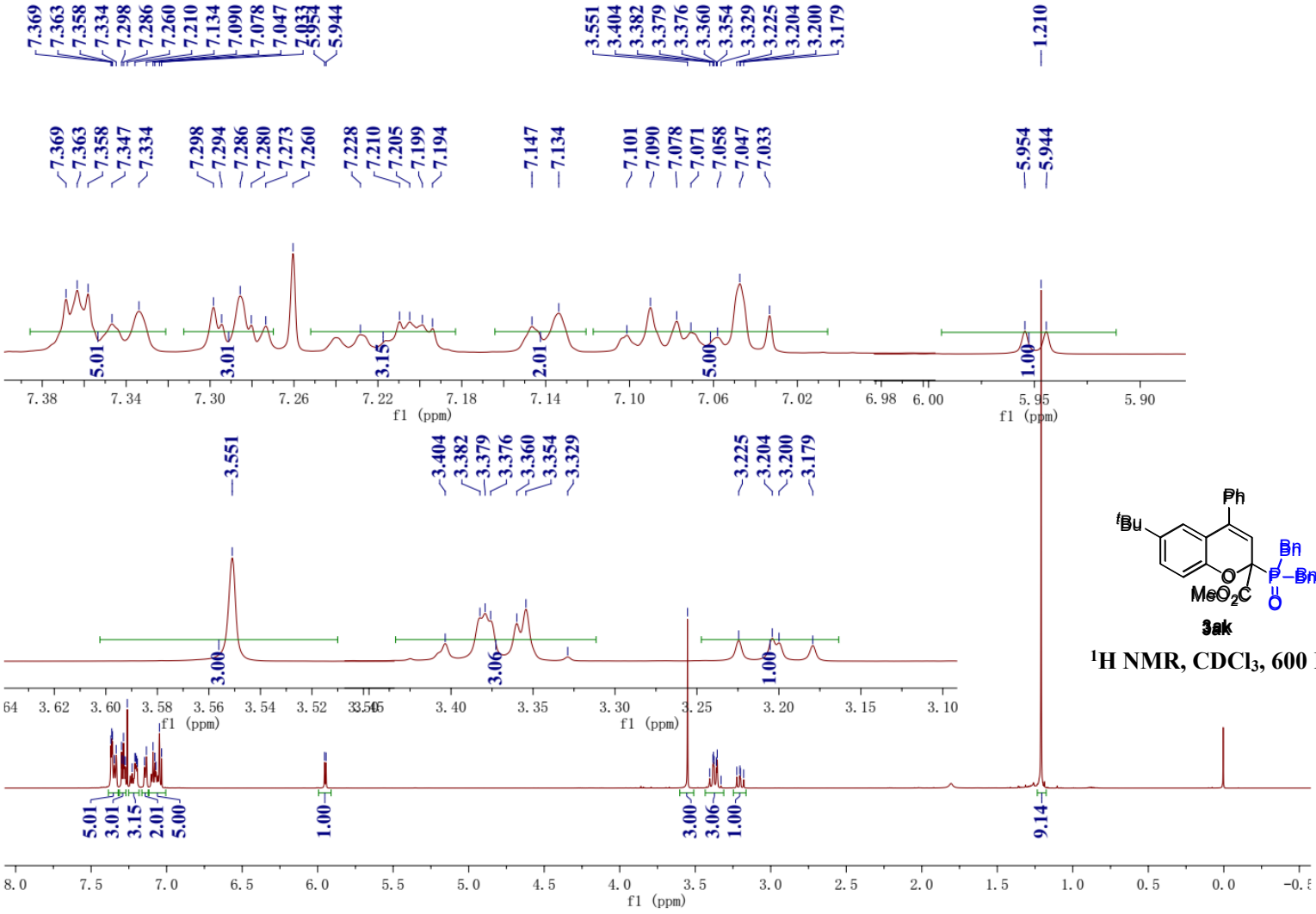


^{31}P NMR, $CDCl_3$, 243 MHz


7.821
7.618
7.401
7.389
7.315
7.312
7.302
7.260
7.249
7.150
7.140
7.136
6.922
6.908
6.880
6.876
6.226
6.215
3.731
1.140
7.974
7.968
7.963
7.957
7.829
7.821
7.814
7.679
7.673
7.667
7.661
7.626
7.618
7.611
7.415
7.411
7.401
7.389
7.378
7.368
7.315
7.312
7.302
7.260
7.249
7.240
7.154
7.150
7.140
7.136
7.019
7.012
7.008
7.001
6.922
6.908
6.880
6.876
1.00
1.00
1.03
1.00
3.17
2.03
1.10
1.08
1.05
1.02
1.02
f1 (ppm)
Ph
tBu
MeO2C
O
P
O
S
S
3aj
1H NMR, CDCl3, 600 MHz
1.00
1.00
1.00
1.01
1.00
3.17
2.03
1.10
1.08
1.05
1.02
1.02
1.00
3.17
9.04

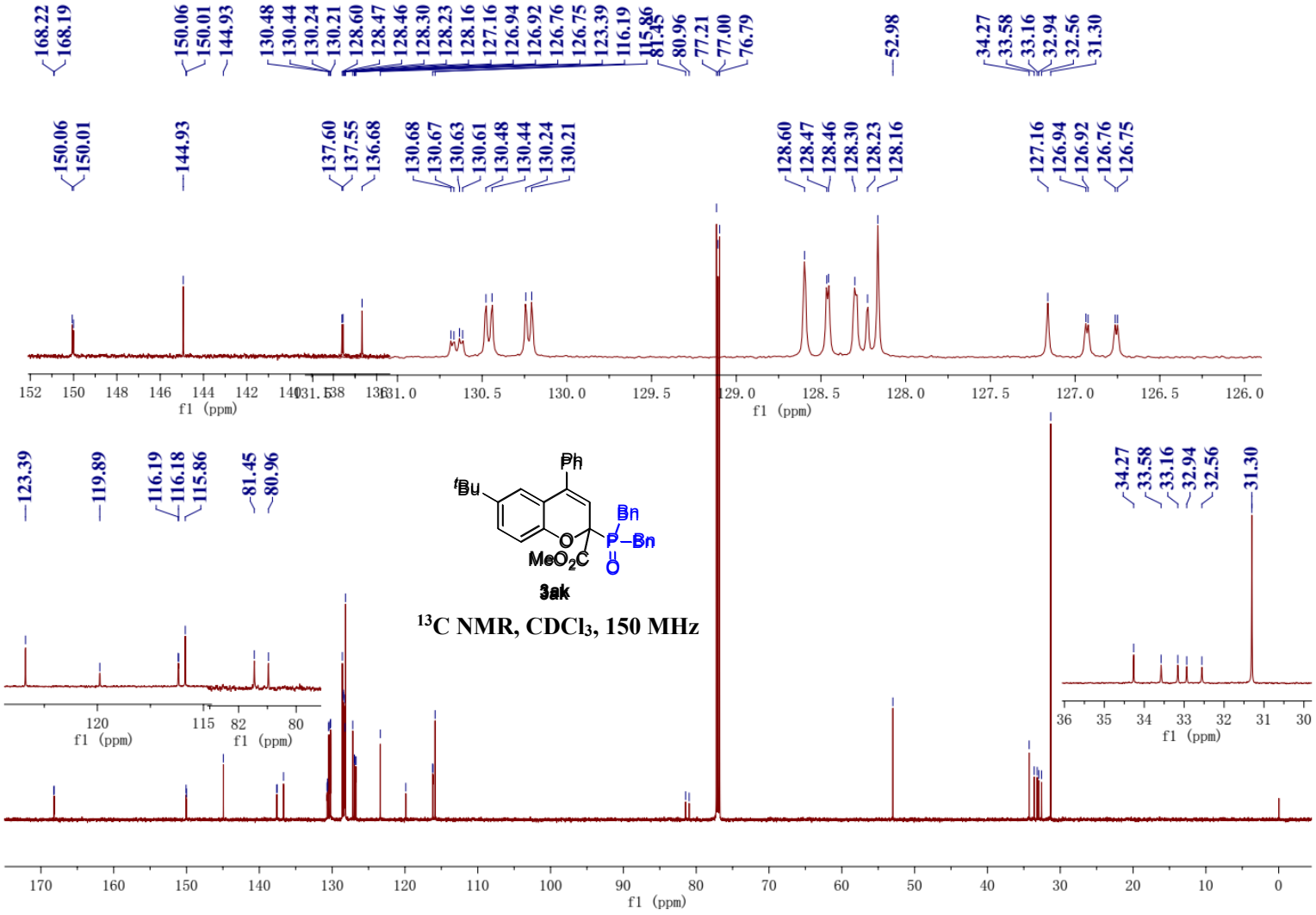

167.54
167.51
149.95
144.49
138.26
138.19
137.72
137.66
135.04
135.01
134.93
134.90
128.50
128.49
128.35
128.31
128.08
127.98
127.77
127.67
127.01
123.02
119.35
115.66
115.28
115.26
84.26
83.65
77.21
77.00
76.79
53.21
34.14
31.21
149.95
149.91
144.49
139.47
139.40
138.26
138.19
137.72
137.66
136.91
135.04
135.01
134.93
134.90
129.72
128.94
128.58
128.50
128.49
128.35
128.31
128.08
127.98
127.85
127.77
127.67
127.01
123.02
119.35
119.33
115.66
115.28
115.26
84.26
83.65
Ph
tBu
MeO2C
O
P
S
3aj
13C NMR, CDCl3, 150 MHz
f1 (ppm)

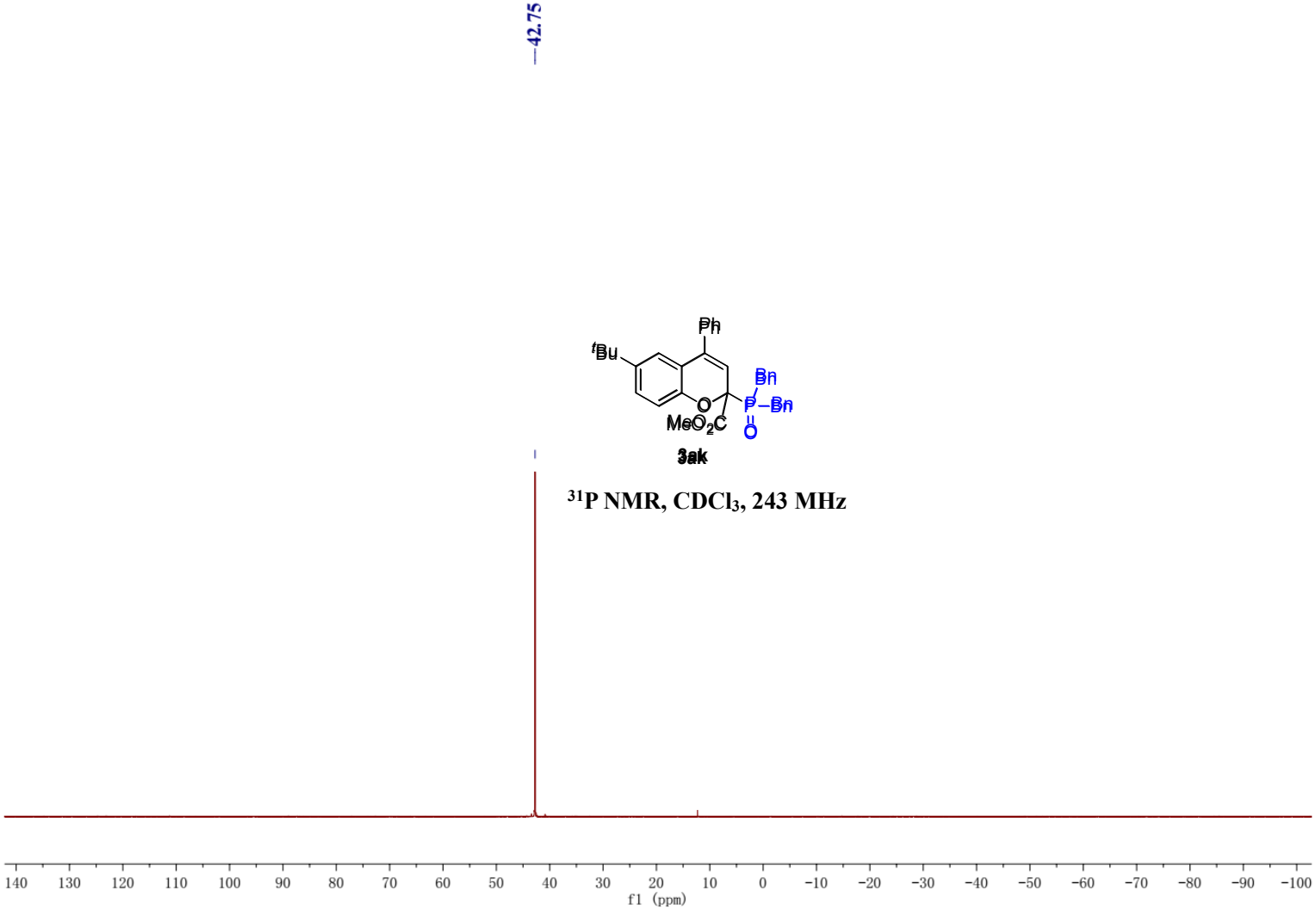

19.66
tBu
Ph
MeO2C
3aj
31P NMR, CDCl3, 243 MHz
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)



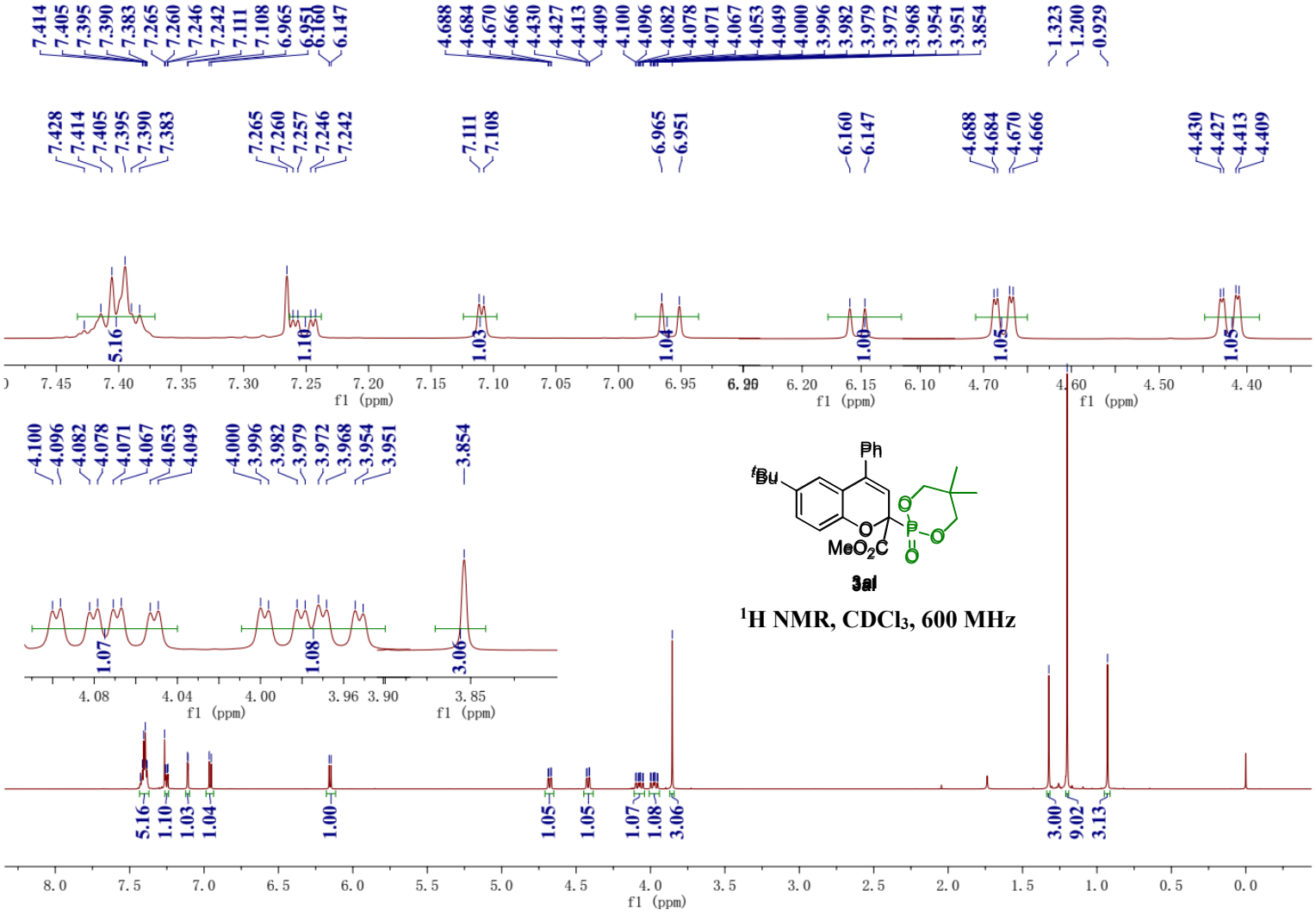
3ak

^{1}H NMR, $CDCl_3$, 600 MHz

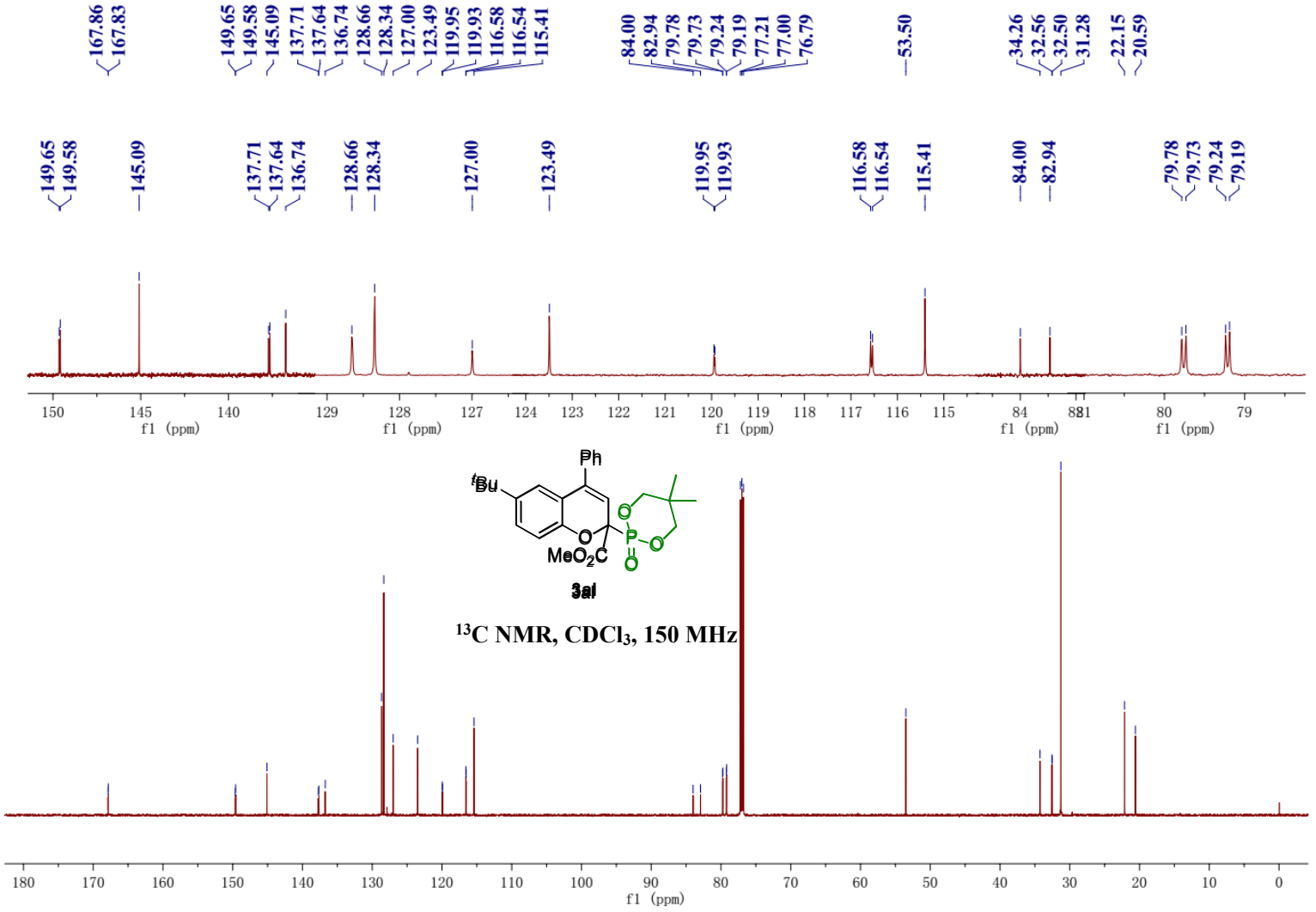

168.22
168.19
150.06
150.01
144.93
130.48
130.44
130.24
130.21
128.60
128.47
128.46
128.30
128.23
128.16
127.16
126.94
126.92
126.76
126.75
123.39
116.19
115.86
81.45
80.96
77.21
77.00
76.79
52.98
34.27
33.58
33.16
32.94
32.56
31.30
f1 (ppm)
Ph
tBu
Bn
Bn
P
O
O
MeO2C
3ak
13C NMR, CDCl3, 150 MHz

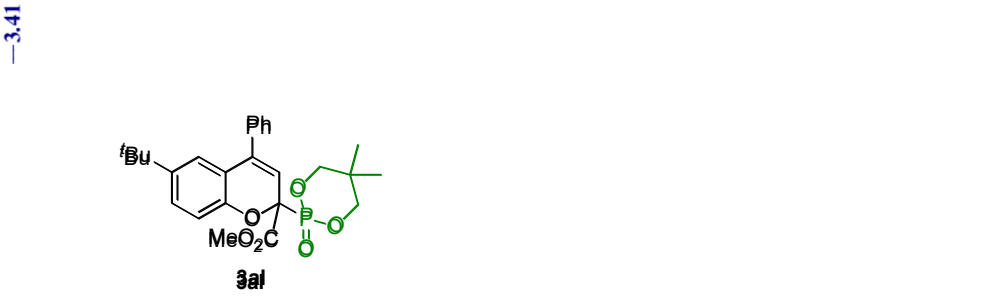


^{31}P NMR, $CDCl_3$, 243 MHz

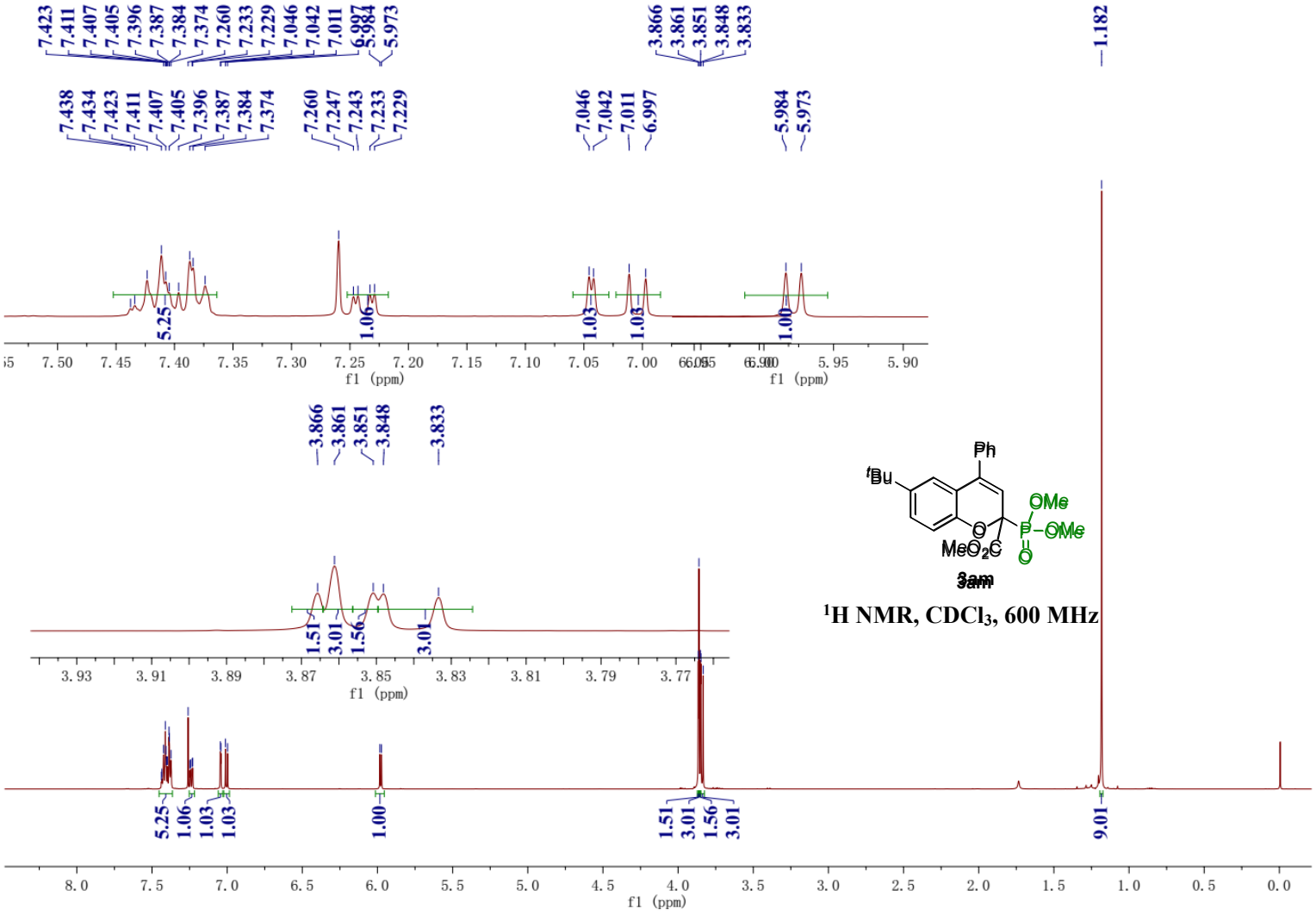


^{1}H NMR, $CDCl_3$, 600 MHz

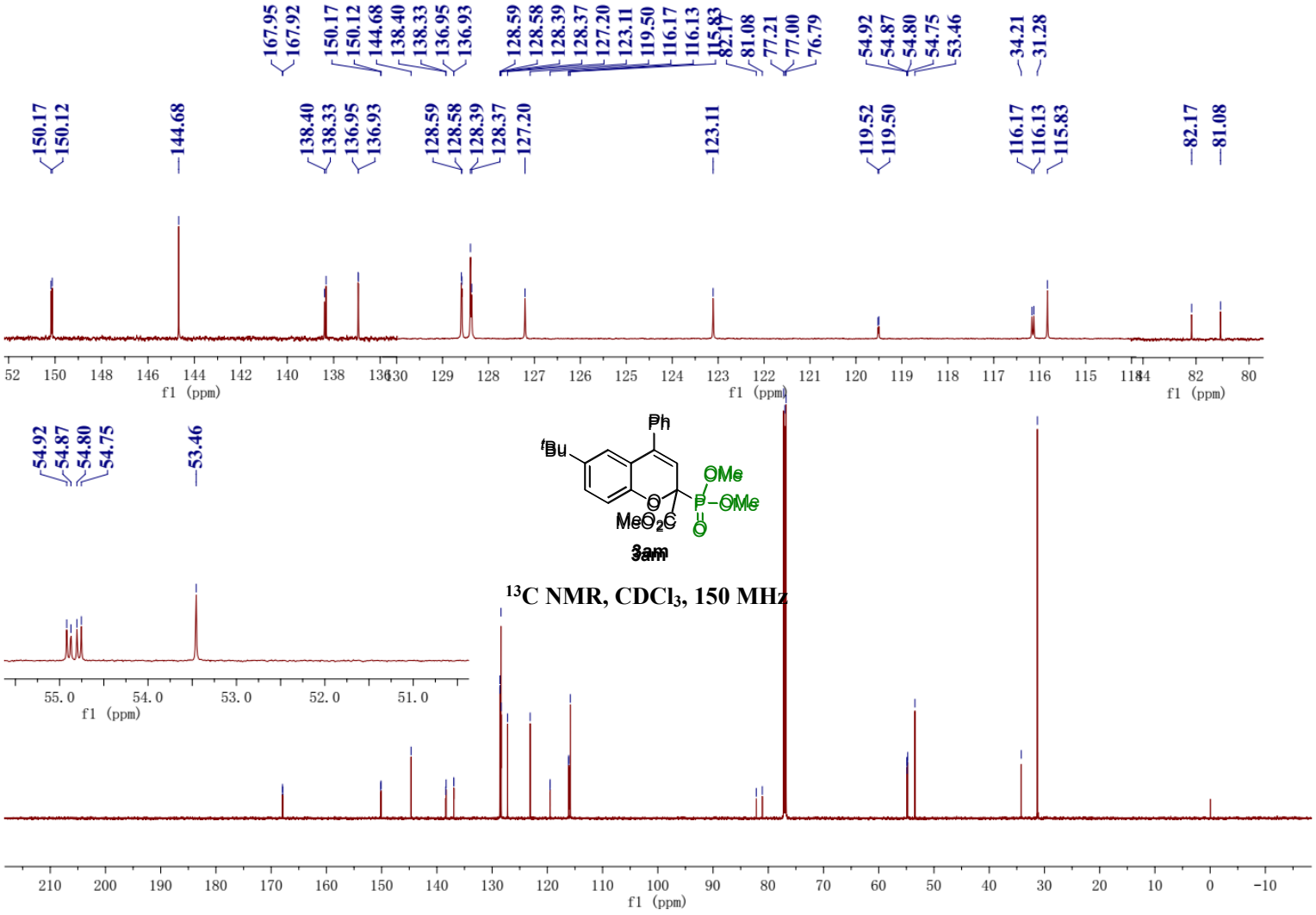

167.86
167.83
149.65
149.58
145.09
137.71
137.64
136.74
128.66
128.34
127.00
123.49
119.95
119.93
116.58
116.54
115.41
84.00
82.94
79.78
79.73
79.24
79.19
77.21
77.00
76.79
53.50
34.26
32.56
32.50
31.28
22.15
20.59
f1 (ppm)
Ph
tBu
MeO2C
3al
13C NMR, CDCl3, 150 MHz

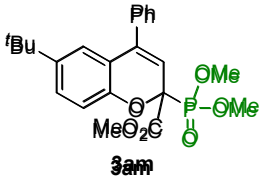


^{31}P NMR, $CDCl_3$, 243 MHz



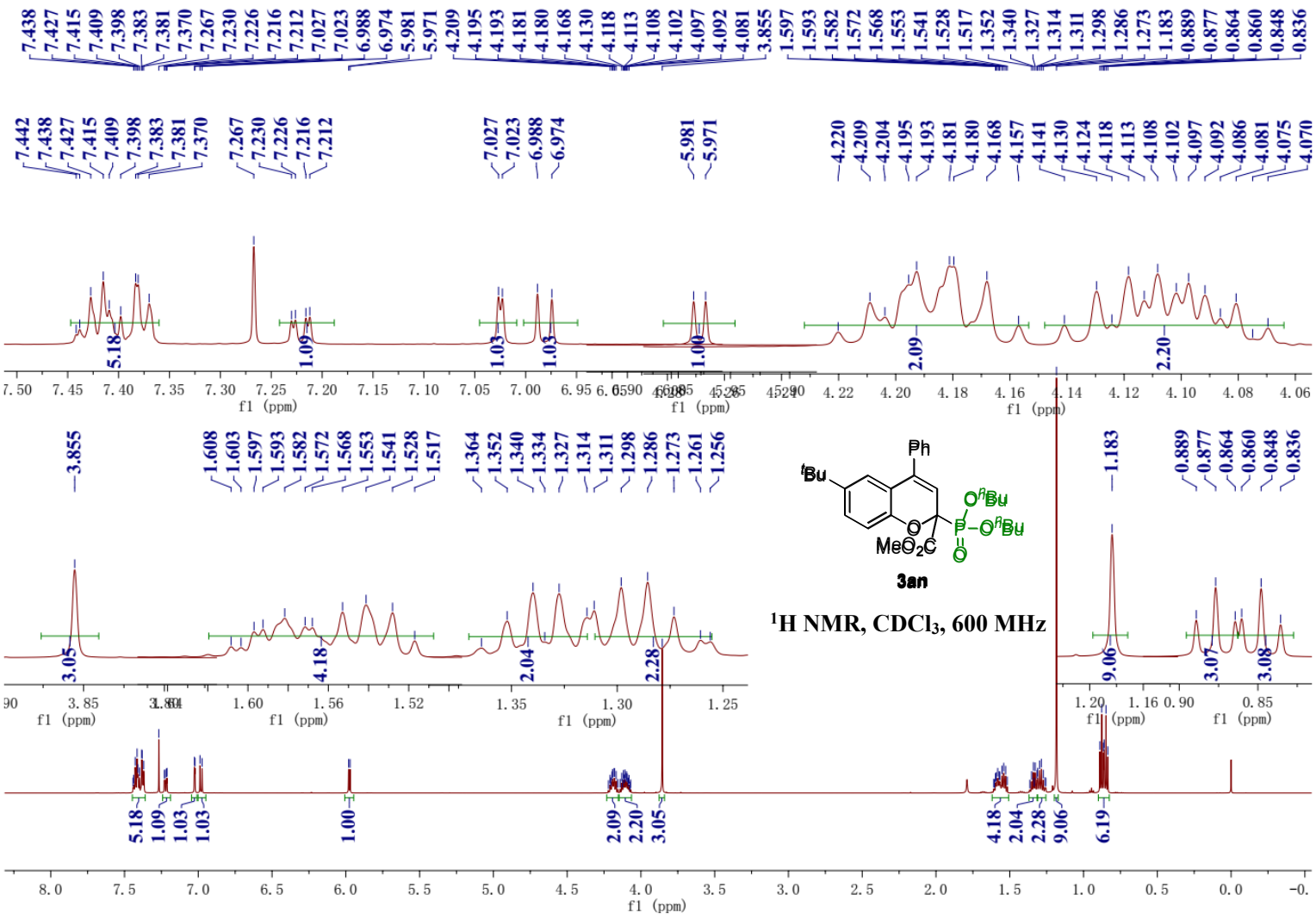
^{1}H NMR, $CDCl_3$, 600 MHz

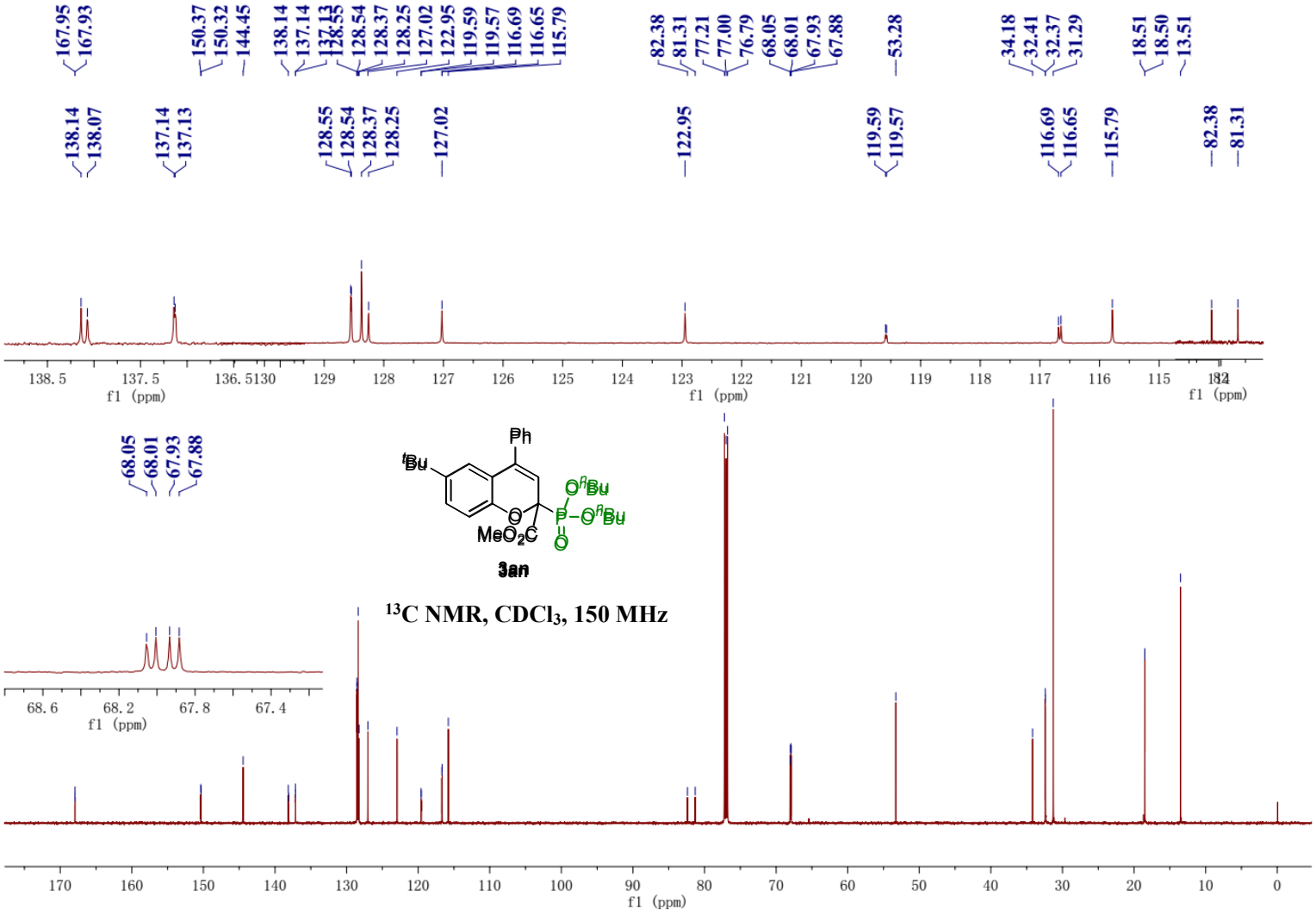

167.95
167.92
150.17
150.12
144.68
138.40
138.33
136.95
136.93
128.59
128.58
128.39
128.37
127.20
123.11
119.50
116.17
116.13
115.83
82.17
81.08
77.21
77.00
76.79
54.92
54.87
54.80
54.75
53.46
34.21
31.28
f1 (ppm)
Ph
tBu
OMe
P
OMe
O
MeO2C
3am
13C NMR, CDCl3, 150 MHz

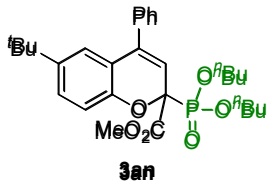


3am

^{31}P NMR, $CDCl_3$, 243 MHz

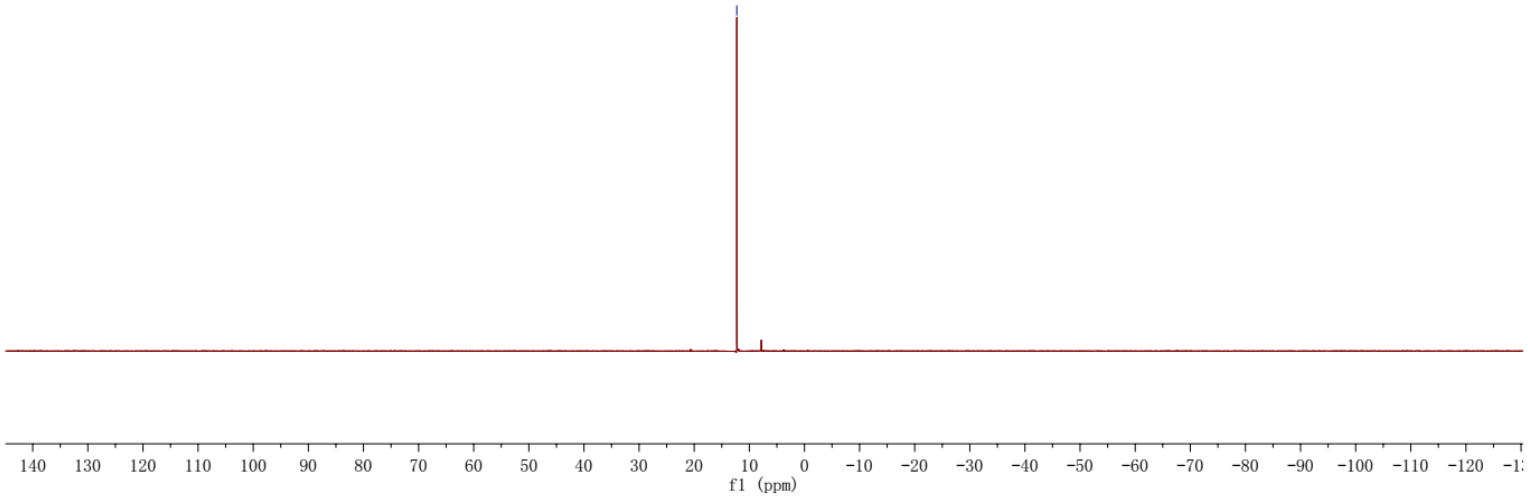

3an
^{1}H NMR, CDCl$_3$, 600 MHz

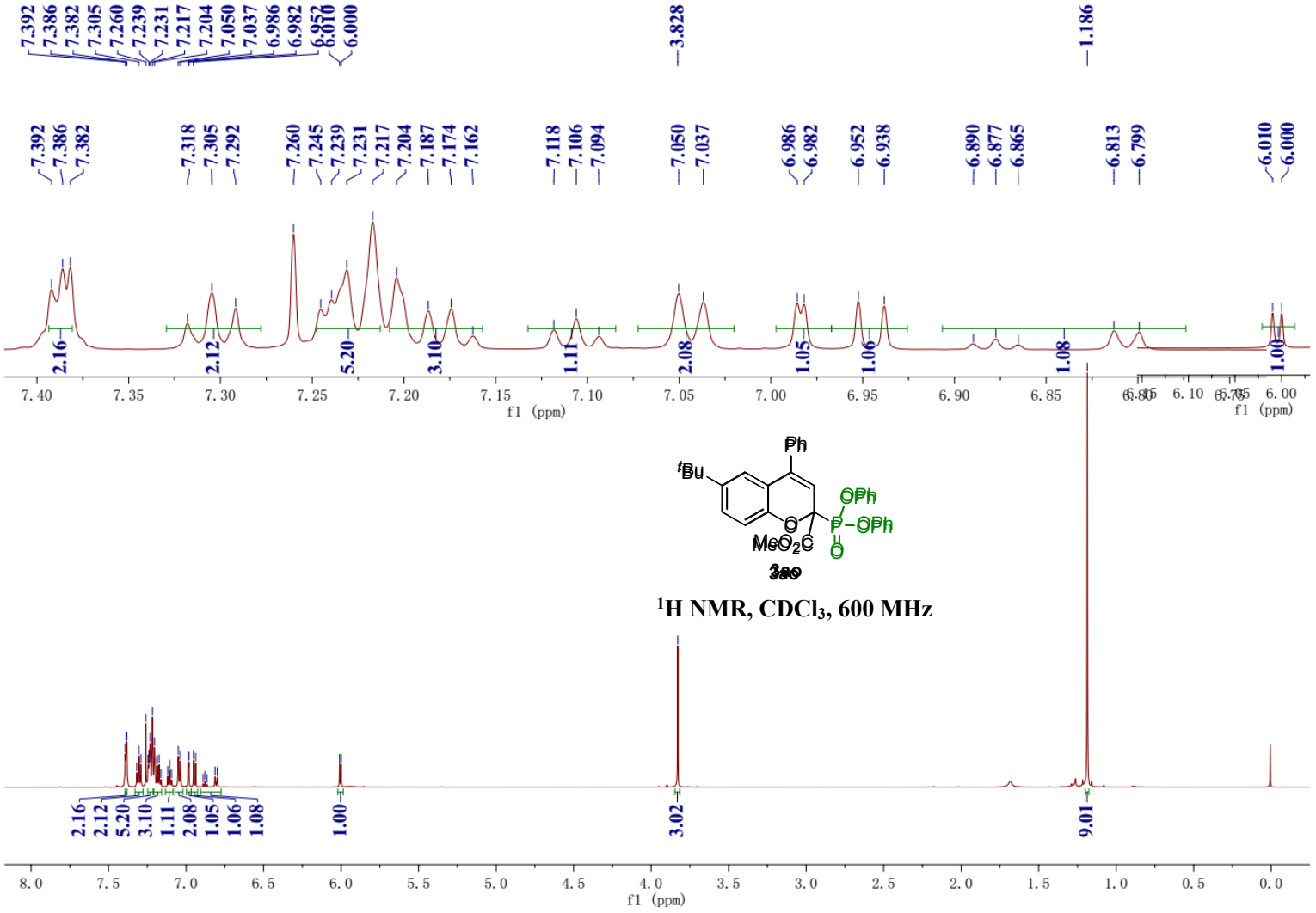

167.95
167.93
150.37
150.32
144.45
138.14
137.14
137.13
128.55
128.54
128.37
128.25
127.02
122.95
119.59
119.57
116.69
116.65
115.79
82.38
81.31
77.21
77.00
76.79
68.05
68.01
67.93
67.88
53.28
34.18
32.41
32.37
31.29
18.51
18.50
13.51
f1 (ppm)
68.05
68.01
67.93
67.88
Ph
tBu
O
nBu
P
MeO2C
3an
13C NMR, CDCl3, 150 MHz

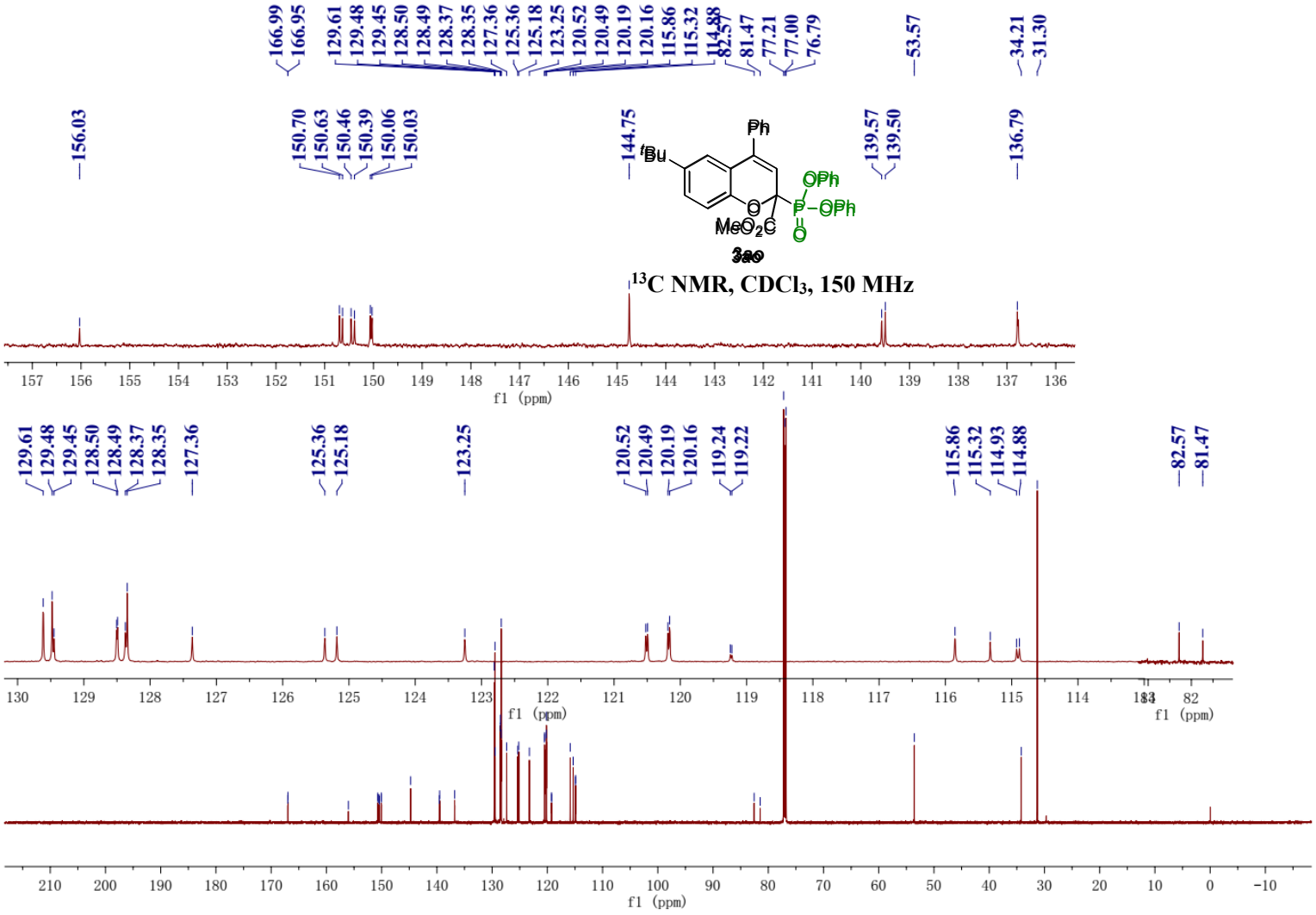


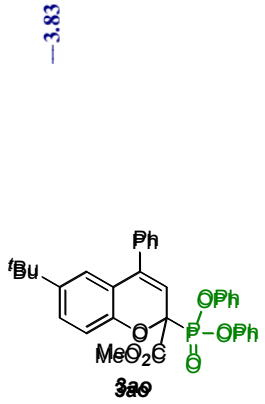
3an

^{31}P NMR, $CDCl_3$, 243 MHz

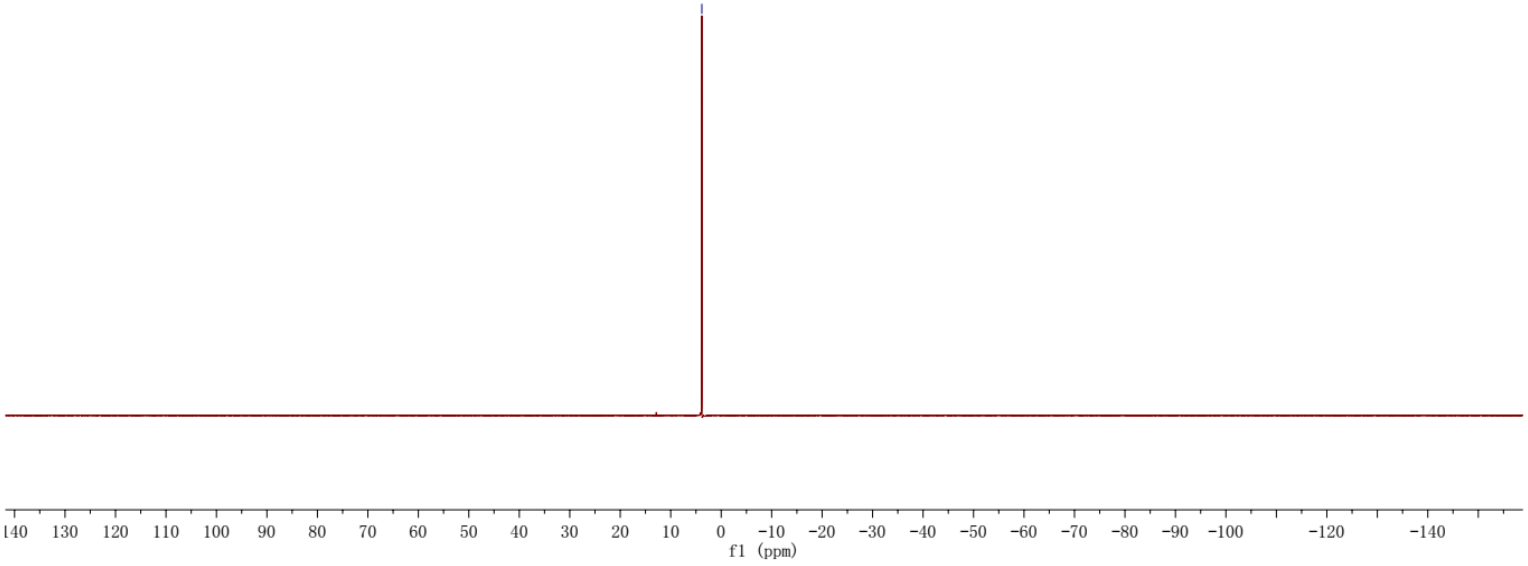


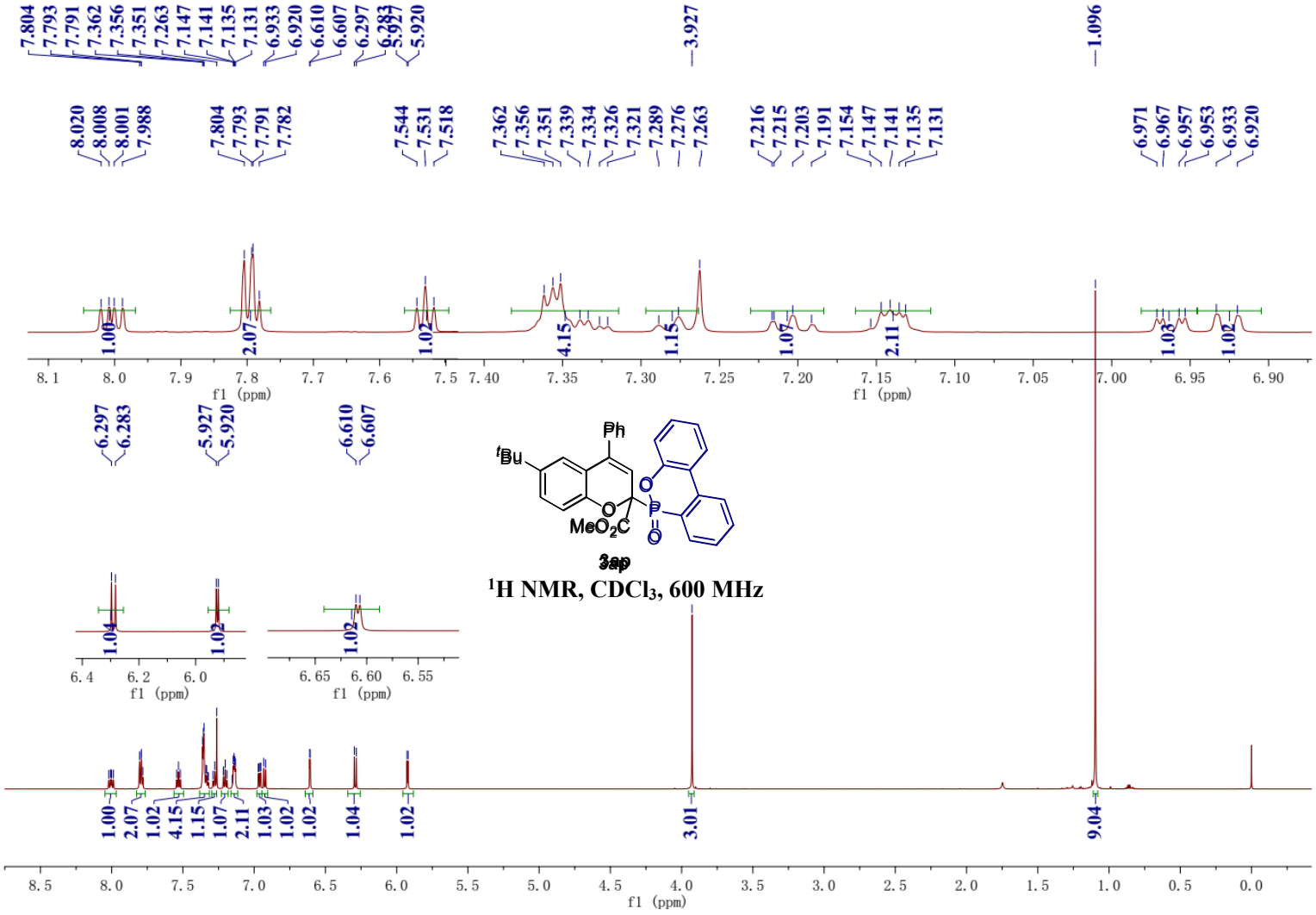

7.392
7.386
7.382
7.305
7.260
7.239
7.231
7.217
7.204
7.050
7.037
6.986
6.982
6.952
6.938
6.010
6.000
3.828
1.186
7.318
7.292
7.245
7.118
7.106
7.094
6.890
6.877
6.865
6.813
6.799
7.187
7.174
7.162
2.16
2.12
5.20
3.10
1.11
2.08
1.05
1.06
1.08
1.00
f1 (ppm)
Ph
tBu
OPh
O
P–OPh
MeO2C
O
3ao
1H NMR, CDCl3, 600 MHz
3.02
9.01

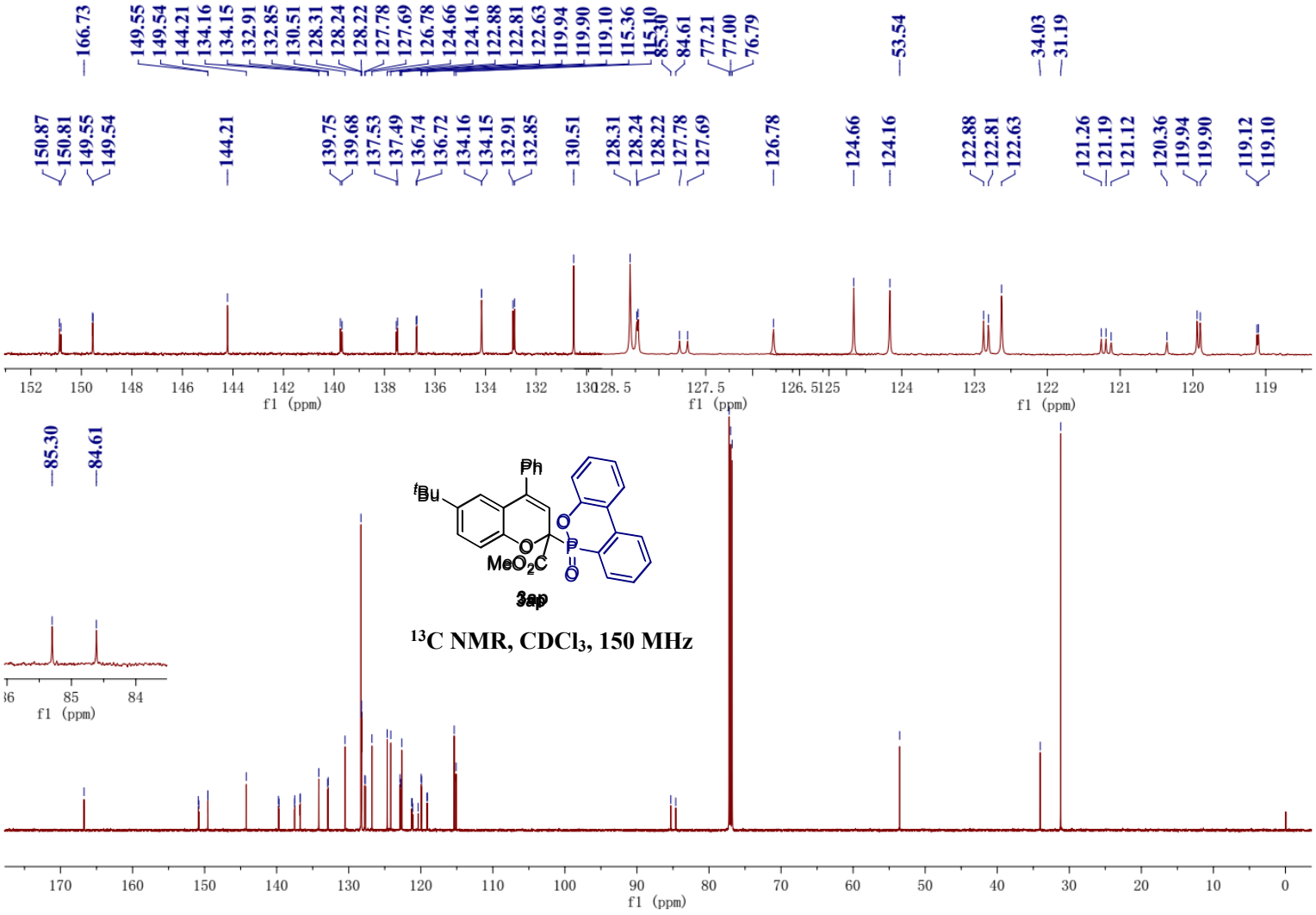

166.99
166.95
129.61
129.48
129.45
128.50
128.49
128.37
128.35
127.36
125.36
125.18
123.25
120.52
120.49
120.19
120.16
115.86
115.32
114.88
82.57
81.47
77.21
77.00
76.79
53.57
34.21
31.30
156.03
150.70
150.63
150.46
150.39
150.06
150.03
144.75
139.57
139.50
136.79
Ph
tBu
OPh
P
OPh
O
O
MeO2C
O
3ao
13C NMR, CDCl3, 150 MHz
f1 (ppm)
f1 (ppm)
f1 (ppm)

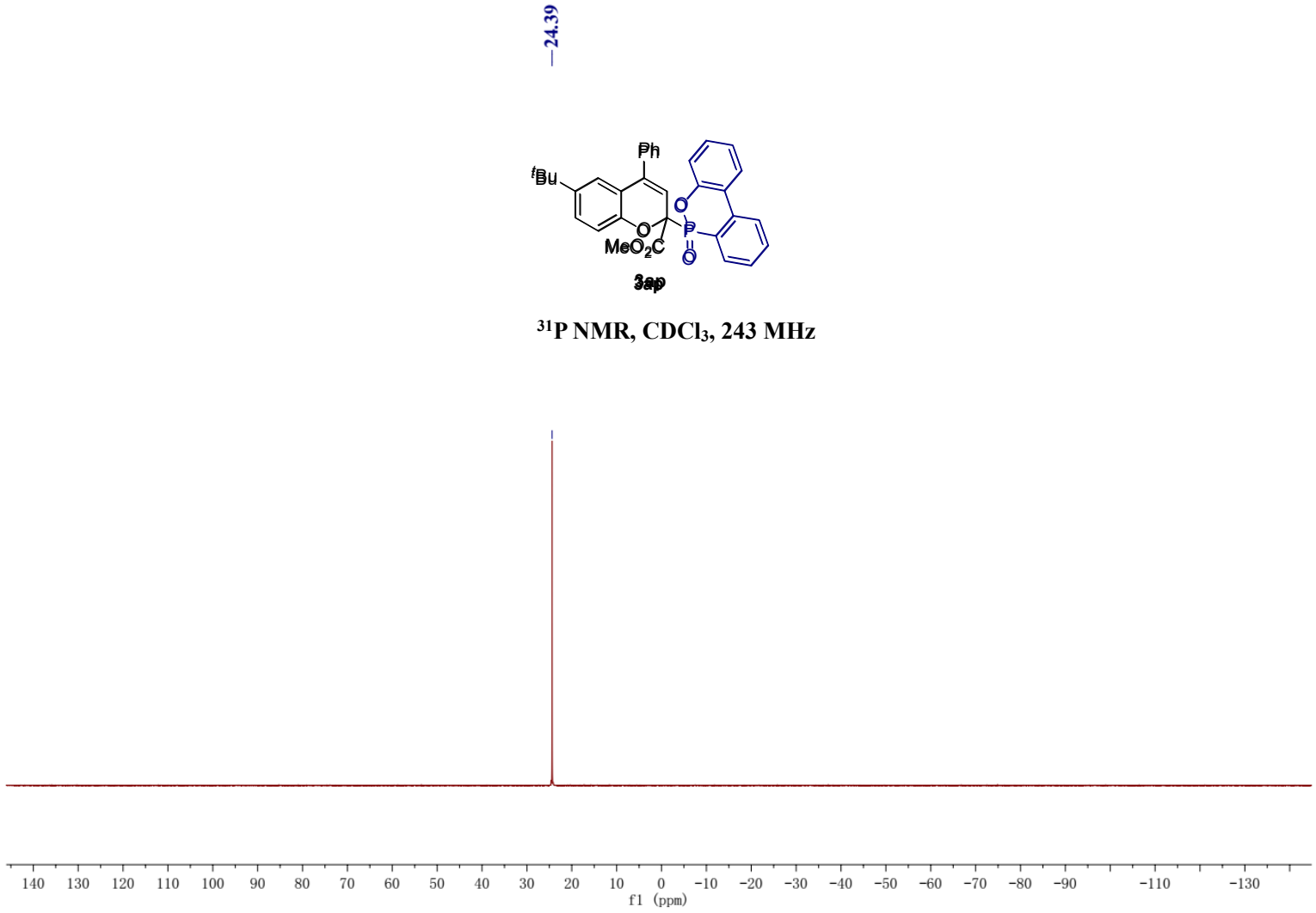


^{31}P NMR, $CDCl_3$, 243 MHz

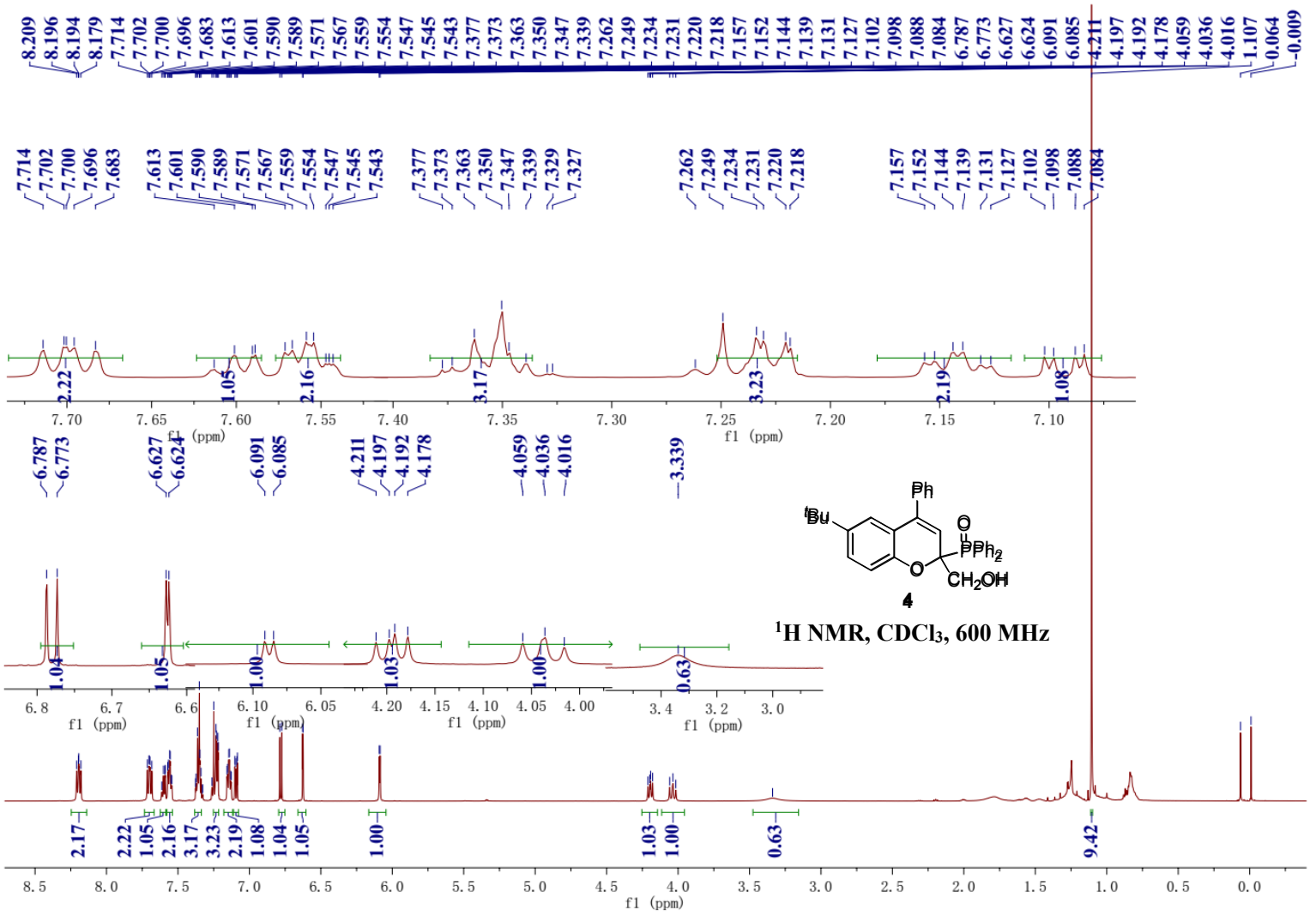


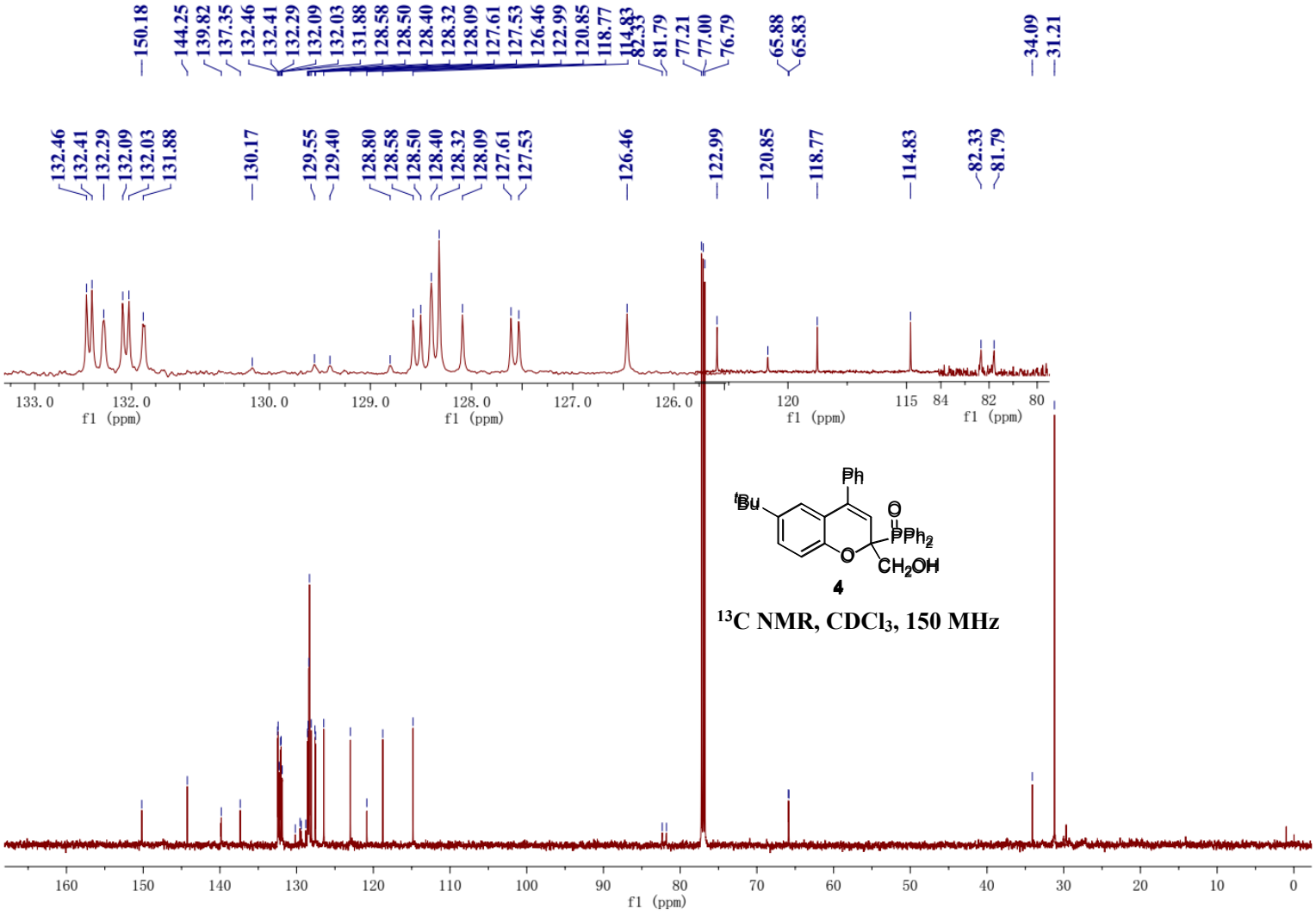

7.804
7.793
7.791
7.362
7.356
7.351
7.263
7.147
7.141
7.135
7.131
6.933
6.920
6.610
6.607
6.297
6.283
5.927
5.920
3.927
1.096
8.020
8.008
8.001
7.988
7.804
7.793
7.791
7.782
7.544
7.531
7.518
7.362
7.356
7.351
7.339
7.334
7.326
7.321
7.289
7.276
7.263
7.216
7.215
7.203
7.191
7.154
7.147
7.141
7.135
7.131
6.971
6.967
6.957
6.953
6.933
6.920
1.00
2.07
1.02
4.15
1.15
1.07
2.11
1.03
1.02
f1 (ppm)
Ph
tBu
O
P
O
MeO2C
3ap
1H NMR, CDCl3, 600 MHz
1.00
2.07
1.02
4.15
1.15
1.07
2.11
1.03
1.02
1.02
1.04
1.02
3.01
9.04


166.73
149.55
149.54
144.21
134.16
134.15
132.91
132.85
130.51
128.31
128.24
128.22
127.78
127.69
126.78
124.66
124.16
122.88
122.81
122.63
119.94
119.90
119.10
115.36
115.10
85.30
84.61
77.21
77.00
76.79
53.54
34.03
31.19
150.87
150.81
149.55
149.54
144.21
139.75
139.68
137.53
137.49
136.74
136.72
134.16
134.15
132.91
132.85
130.51
128.31
128.24
128.22
127.78
127.69
126.78
124.66
124.16
122.88
122.81
122.63
121.26
121.19
121.12
120.36
119.94
119.90
119.12
119.10
f1 (ppm)
Ph
tBu
O
O
P
O
MeO2C
3ap
13C NMR, CDCl3, 150 MHz



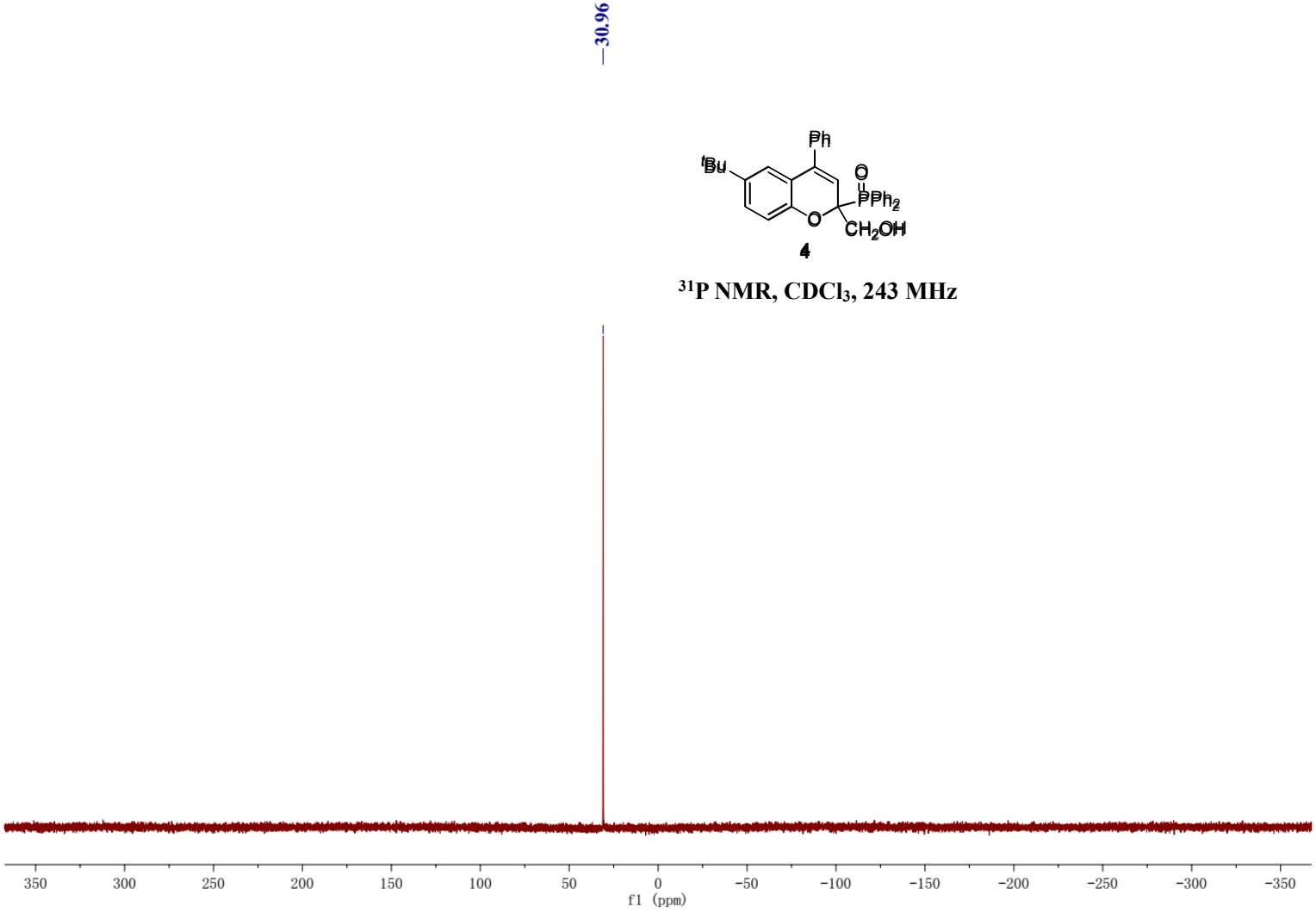
^{31}P NMR, $CDCl_3$, 243 MHz

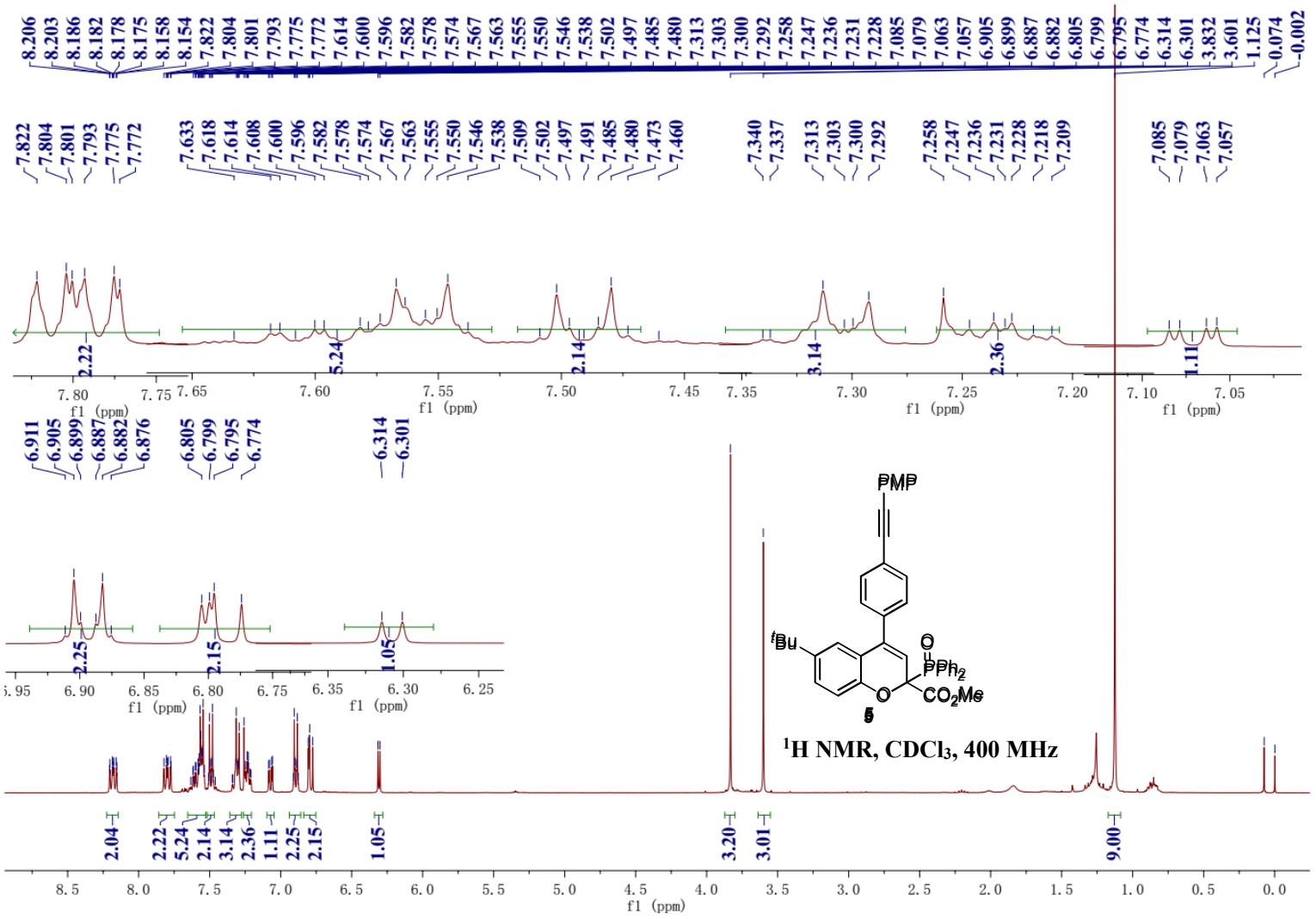

8.209
8.196
8.194
8.179
7.714
7.702
7.700
7.696
7.683
7.613
7.601
7.590
7.589
7.571
7.567
7.559
7.554
7.547
7.545
7.543
7.377
7.373
7.363
7.350
7.347
7.339
7.262
7.249
7.234
7.231
7.220
7.218
7.157
7.152
7.144
7.139
7.131
7.127
7.102
7.098
7.088
7.084
6.787
6.773
6.627
6.624
6.091
6.085
4.211
4.197
4.192
4.178
4.059
4.036
4.016
3.339
2.22
1.05
2.16
3.17
3.23
2.19
1.08
1.04
1.05
1.00
1.03
1.00
0.63
9.42
f1 (ppm)
Ph
tBu
O
PPh2
O
CH2OH
4
1H NMR, CDCl3, 600 MHz

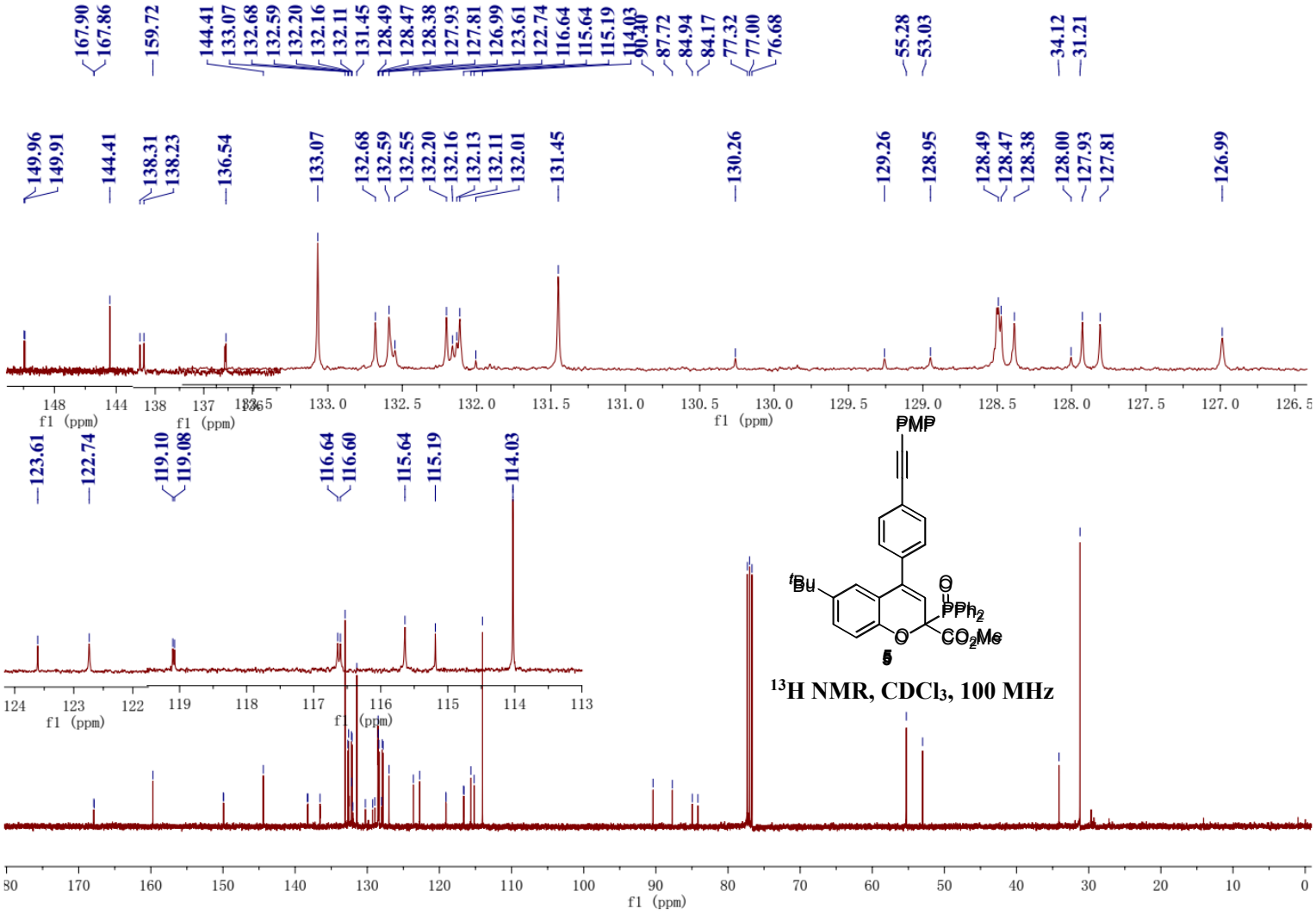


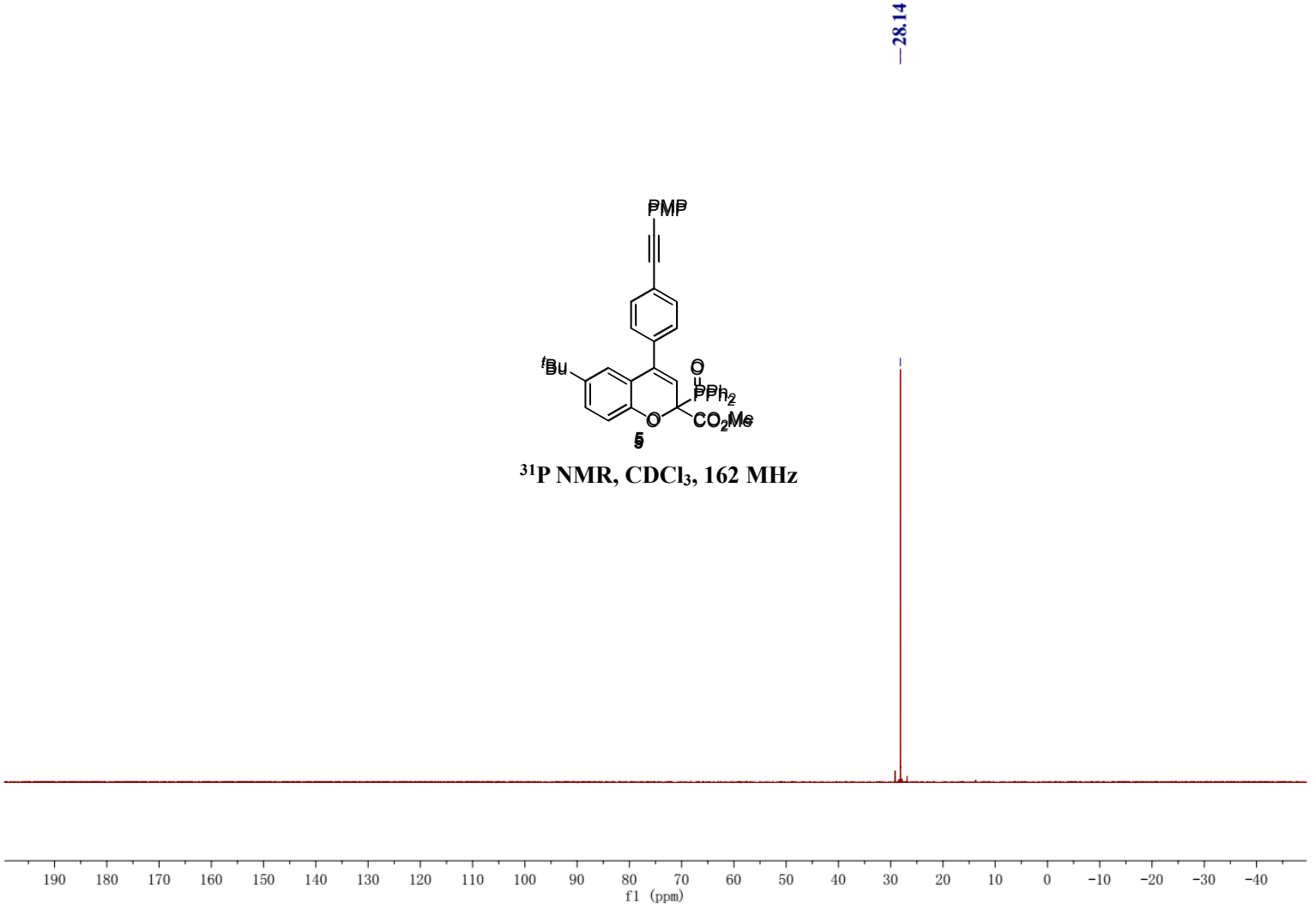
4

^{13}C NMR, $CDCl_3$, 150 MHz

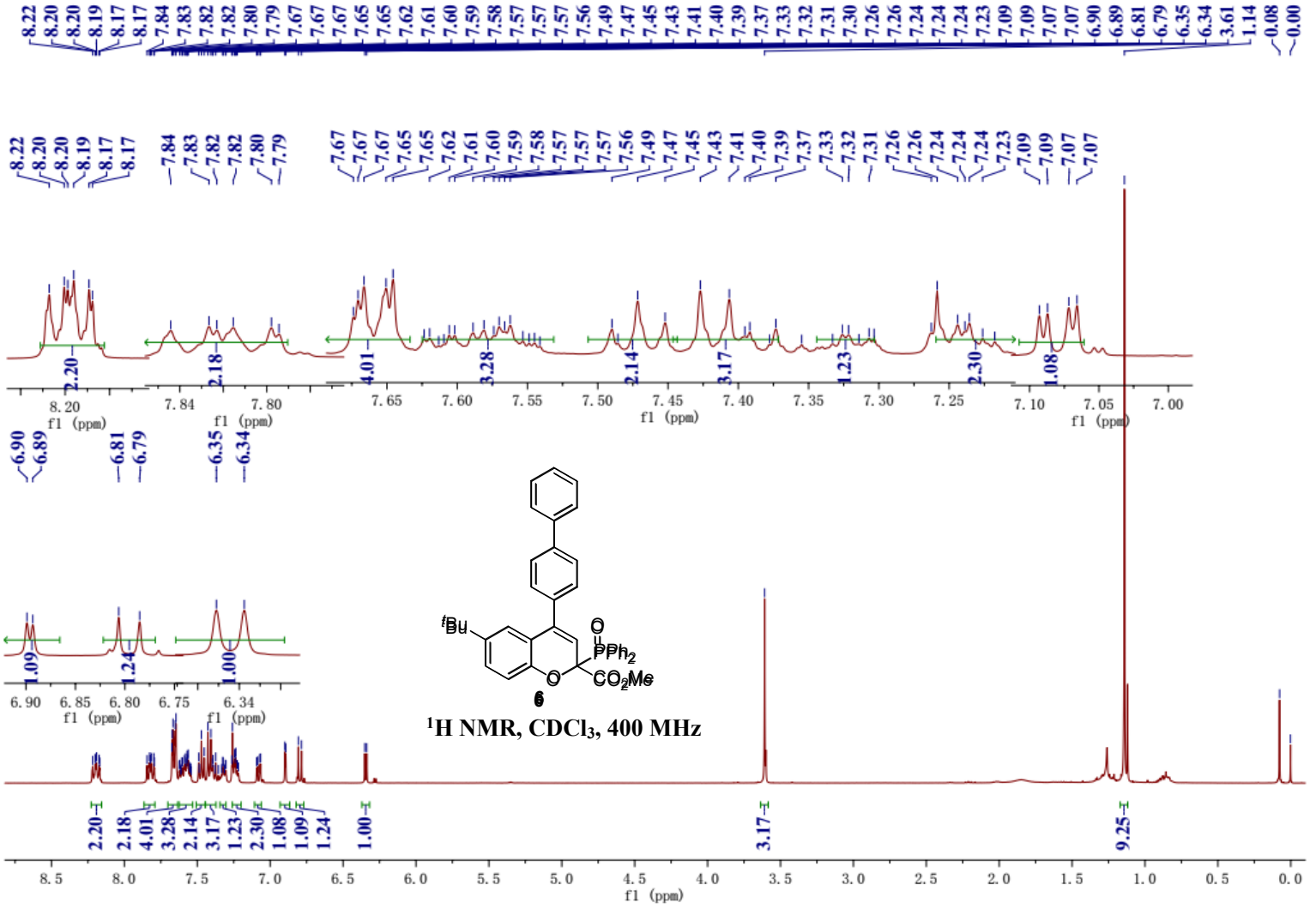

30.96
tBu
Ph
O
PPh2
O
CH2OH
4
31P NMR, CDCl3, 243 MHz
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
f1 (ppm)

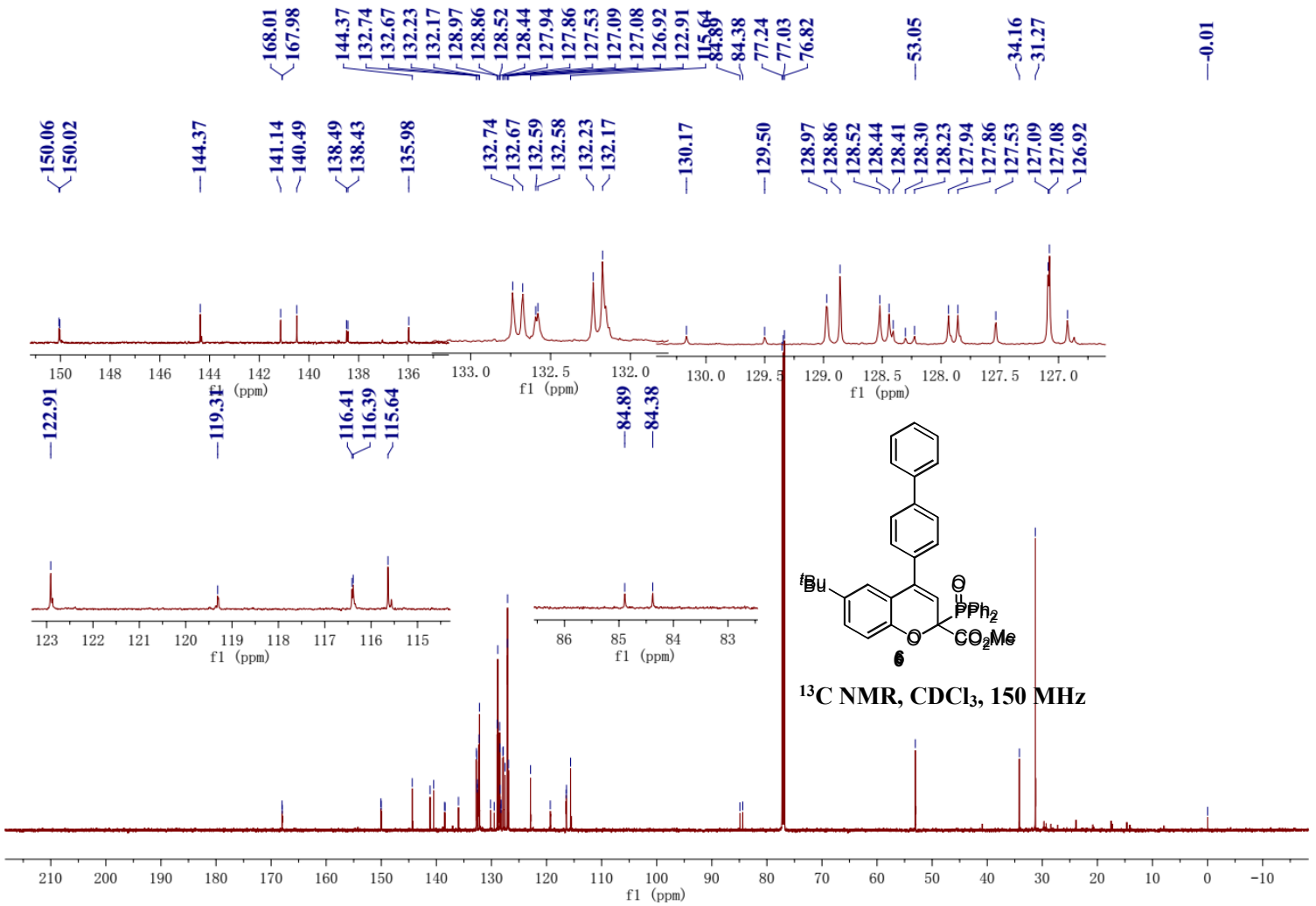

PMP
tBu
O
PPh2
O
CO2Me
5
1H NMR, CDCl3, 400 MHz

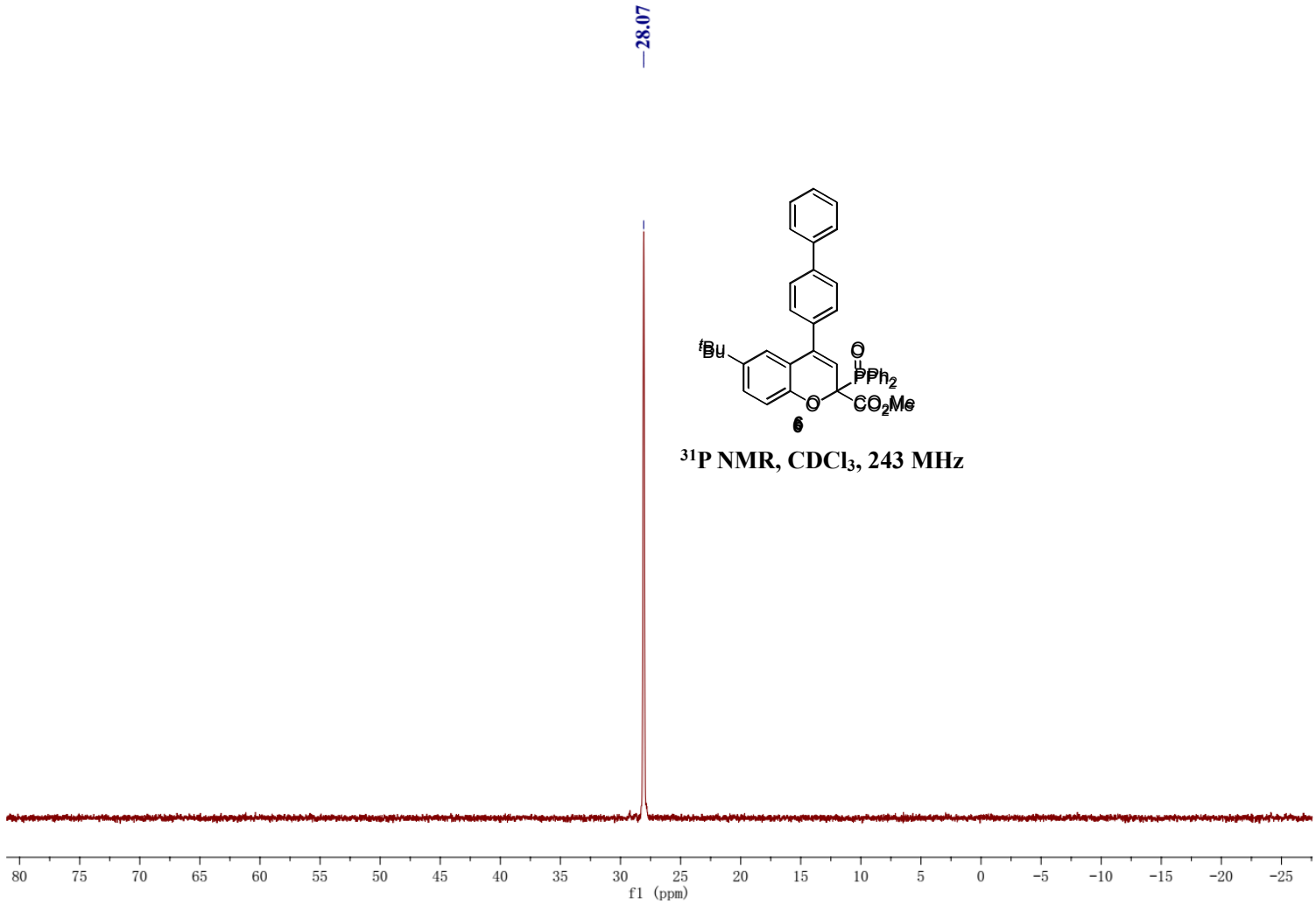

167.90
167.86
159.72
144.41
133.07
132.68
132.59
132.20
132.16
132.11
131.45
128.49
128.47
128.38
127.93
127.81
126.99
123.61
122.74
116.64
115.64
115.19
114.03
90.40
87.72
84.94
84.17
77.32
77.00
76.68
55.28
53.03
34.12
31.21
149.96
149.91
144.41
138.31
138.23
136.54
133.07
132.68
132.59
132.55
132.20
132.16
132.13
132.11
132.01
131.45
130.26
129.26
128.95
128.49
128.47
128.38
128.00
127.93
127.81
126.99
123.61
122.74
119.10
119.08
116.64
116.60
115.64
115.19
114.03
PMP
tBu
O
PPh2
CO2Me
5
13H NMR, CDCl3, 100 MHz
f1 (ppm)



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


8.22 8.20 8.20 8.19 8.17 8.17 7.84 7.83 7.82 7.82 7.80 7.79 7.67 7.67 7.67 7.65 7.65 7.62 7.61 7.60 7.59 7.58 7.57 7.57 7.57 7.56 7.49 7.47 7.45 7.43 7.41 7.40 7.39 7.37 7.33 7.32 7.31 7.30 7.26 7.26 7.24 7.24 7.24 7.23 7.09 7.09 7.07 7.07 6.90 6.89 6.81 6.79 6.35 6.34 3.61 1.14 0.08 0.00
2.20 2.18 4.01 3.28 2.14 3.17 1.23 2.30 1.08
f1 (ppm)
6.90 6.89 6.81 6.79 6.35 6.34
1.09 1.24 1.00
6.90 6.85 6.80 6.75 6.34
f1 (ppm)
tBu
O
PPh2
CO2Me
O
6
1H NMR, CDCl3, 400 MHz
2.20 2.18 4.01 3.28 2.14 3.17 1.23 2.30 1.08 1.09 1.24 1.00 3.17 9.25
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)


168.01
167.98
144.37
132.74
132.67
132.23
132.17
128.97
128.86
128.52
128.44
127.94
127.86
127.53
127.09
127.08
126.92
122.91
115.64
84.89
84.38
77.24
77.03
76.82
53.05
34.16
31.27
0.01
150.06
150.02
144.37
141.14
140.49
138.49
138.43
135.98
132.74
132.67
132.59
132.58
132.23
132.17
130.17
129.50
128.97
128.86
128.52
128.44
128.41
128.30
128.23
127.94
127.86
127.53
127.09
127.08
126.92
122.91
119.31
116.41
116.39
115.64
84.89
84.38
f1 (ppm)
tBu
PPh2
CO2Me
6
13C NMR, CDCl3, 150 MHz



^{31}P NMR, $CDCl_3$, 243 MHz