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Supporting Information

Synthesis of *N*-Acylbenzimidazoles through [4 + 1] Annulation of *N*-Arylpivalimidamides with Dioxazolones

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I. General experimental information

Commercial reagents were used without further purification. Amidines (**1**),[1] dioxazolones (**2**),[2] and $[RhCp^*Cl_2]_2$[3] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedures for the synthesis of 3a and spectroscopic data of 3a-3mm

To a reaction tube equipped with a stir bar were charged with *N*-phenylpivalimidamide (**1a**, 63.5 mg, 0.36 mmol), ethyl acetate (1.5 mL), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), $Zn(OAc)_2$ (16.5 mg, 0.09 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 48.9 mg, 0.3 mmol). The tube was then sealed, and the resulting mixture was stirred at 110 ℃ under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (69.3 mg, 83%). **3b-3mm** were obtained in a similar manner.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3a)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (69.3 mg, 83%), mp 142-144 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.73-7.69 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.24-7.20 (m, 1H), 7.05-7.01 (m, 1H), 6.56 (d, J = 8.4 Hz, 1H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.8, 163.3, 141.4, 135.4, 134.9, 133.0, 130.9, 129.3, 123.3, 123.1, 119.7, 112.2, 35.4, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O$ 279.1492; Found 279.1509.

(2-(*tert*-Butyl)-6-methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3b)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (67.5 mg, 77%), mp 130-132 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.82 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.72-7.69 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.53-7.51 (m, 2H), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.35 (s, 1H), 2.24 (s, 3H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.9, 162.6, 139.5, 135.7, 134.9, 133.3, 133.0, 130.9, 129.3, 124.5, 119.2, 112.1, 35.4, 29.8, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1649.

(2-(*tert*-Butyl)-6-methoxy-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3c)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (68.5 mg, 74%), mp 99-101 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.82 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.72-7.69 (m, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.54-7.51 (m, 2H), 6.84 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6,03 (d, J = 2.4 Hz, 1H), 3.56 (s, 3H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.8, 162.3, 156.5, 136.0, 134.9, 132.9, 130.9, 129.3, 120.0, 111.3, 97.0, 55.6, 35.4, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2$ 309.1598; Found 309.1599.

(2-(*tert*-Butyl)-6-isopropyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3d)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (84.1 mg, 88%), mp 101-103 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.83 (d, J_1 = 8.4 Hz, J_2 = 1.2, 2H), 7.71-7.68 (m, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 8.4 Hz, 2H), 7.10 (dd, J_1 = 8.4 Hz, J_2 = 1.2, 1H), 6.35 (d, J = 1.2 Hz, 1H), 2.79-2.75 (m, 1H), 1.56 (s, 9H), 1.05 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.9, 162.9, 144.5, 139.8, 135.6, 134.8, 133.2, 130.9, 129.2, 122.1, 119.3, 109.8, 35.4, 34.2, 29.8, 24.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O$ 321.1961; Found 321.1967.

(2-(*tert*-Butyl)-6-fluoro-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3e)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (55.1 mg, 62%), mp 129-131 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.81 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.75-7.72 (m, 1H), 7.69-7.67 (m, 1H), 7.56-7.53 (m, 2H), 6.98-6.95 (m, 1H), 6.25 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 1.56 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.3, 163.8 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 159.5 (d, $^{1}J_{C\text{-}F}$ = 239.8 Hz), 137.8, 135.4 (d, $^{3}J_{C\text{-}F}$ = 13.0 Hz), 135.2, 132.4, 130.9, 129.5, 120.4 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 111.3 (d, $^{2}J_{C\text{-}F}$ = 24.5 Hz), 99.3 (d, $^{2}J_{C\text{-}F}$ = 28.1 Hz), 35.5, 29.7. ^{19}F NMR ($CDCl_3$, 565 MHz): δ -117.60−-117.64 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O$ 297.1398; Found 297.1401.

(2-(*tert*-Butyl)-6-chloro-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3f)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (71.3 mg, 76%), mp 136-138 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.82-7.80 (m, 2H), 7.75-7.72 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.56-7.53 (m, 2H), 7.20 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6,57 (d, *J* = 1.8 Hz, 1H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 164.0, 140.1, 135.9, 135.4, 132.3, 130.9, 129.5, 128.9, 123.8, 120.5, 112.1, 35.5, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1102; Found 313.1104.

(6-Bromo-2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3g)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (75.0 mg, 70%), mp 163-165 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.80 (m, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.34 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.73 (d, *J* = 1.6 Hz, 1H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 163.8, 140.5, 136.4, 135.4, 132.3, 131.0, 129.5, 126.5, 121.0, 116.4, 114.9, 35.5, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrN_2O$ 357.0597; Found 357.0585.

(2-(*tert*-Butyl)-6-iodo-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3h)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (75.2 mg, 62%), mp 179-180 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.80 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.76-7.73 (m, 1H), 7.57-7.52 (m, 4H), 6.92 (s, 1H), 1.54 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 163.6, 141.0, 136.8, 135.4, 132.3, 132.2, 131.0, 129.5, 121.4, 120.8, 86.7, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}IN_2O$ 405.0458; Found 405.0454.

(2-(*tert*-Butyl)-6-nitro-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3i)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (42 mg, 43%), mp 158-160 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.18 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.84-7.82 (m, 3H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.60-7.56 (m, 3H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.6, 168.1, 145.9, 143.8, 136.0, 134.8, 131.8, 131.1, 129.8, 119.8, 119.0, 108.4, 35.9, 29.6. HRMS (ESI)m/z: $[M+H]^+$Calcd for $C_{18}H_{18}N_3O_3$ 324.1343; Found 324.1334.

(2-(*tert*-Butyl)-6-phenyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3j)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (65.9 mg, 62%), mp 213-216 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87-7.85 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 8.4 Hz, 2H), 7.46 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.34-7.30 (m, 4H), 7.27-7.24 (m, 1H), 6.74 (d, *J* = 1.2 Hz, 1H), 1.58 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.7, 163.7, 141.4, 140.9, 137.0, 136.0, 135.1, 132.9, 131.0, 129.4, 128.7, 127.3, 127.0, 123.0, 119.8, 110.7, 35.5, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O$ 355.1805; Found 355.1797.

(2-(*tert*-Butyl)-5-methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3k)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (70.2 mg, 80%), mp 147-149 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.80 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.55 (s, 1H), 7.55-7.49 (m, 2H), 6,84 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.7, 163.3, 141.7, 134.8, 133.5, 133.1, 132.8, 130.9, 129.2, 124.5, 119.6, 111.8, 35.4, 29.7, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1635.

(2-(*tert*-Butyl)-5-chloro-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3l)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (74.1 mg, 79%), mp 167-169 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.80 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.74-7.73 (m, 1H), 7.72-7.71 (m, 1H), 7.54-7.52 (m, 2H), 6.99 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 1.56 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 164.6, 142.4, 135.2, 134.0, 132.6, 130.9, 129.4, 128.7, 123.6, 119.6, 112.8, 35.5, 29.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1102; Found 313.1101.

(2-(*tert*-Butyl)-4-methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3m)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (75.4 mg, 86%), mp 135-136 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.6 Hz,

1H), 6.95 (t, J = 8.0 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 2.72 (s, 3H), 1.62 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 171.0, 162.2, 140.8, 135.2, 134.7, 133.2, 130.9, 129.9, 129.2, 123.4, 123.0, 109.6, 35.5, 29.8, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1648.

(2-(*tert*-Butyl)-4-chloro-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3n)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (81.6 mg, 87%), mp 143-145 ℃. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.80-7.78 (m, 2H), 7.73-7.70 (m, 1H), 7.53-7.51 (m, 2H), 7.23 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 6.95 (t, J = 8.4 Hz, 1H), 6.49 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 1.57 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 170.3, 163.7, 138.9, 136.4, 135.2, 132.5, 131.0, 129.4, 124.7, 123.7, 123.0, 110.6, 35.6, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1102; Found 313.1106.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(*p*-tolyl)methanone (3o)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (64.9 mg, 74%), mp 120-122 ℃. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.76 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H), 7.05-7.02 (m, 1H), 6.62 (d, J = 8.4 Hz, 1H), 2.47 (s, 3H),1.56 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 170.6, 163.1, 146.4, 141.4, 135.5, 131.1, 130.2, 130.0, 123.2, 123.0, 119.7, 112.1, 35.4, 29.8, 21.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1643.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-methoxyphenyl)methanone (3p)[4]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (75.9 mg, 82%), mp 151-153 ℃. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.80-7.78 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.23-7.20 (m, 1H), 7.07-7.04 (m, 1H), 6.98-6.95 (m, 2H), 6.69 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H), 1.55 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 169.9, 165.2, 163.0, 141.3, 135.7, 133.6, 125.0, 123.1, 122.9, 119.6, 114.6, 111.9, 55.7, 35.3, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2$ 309.1598; Found 309.1590.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-(*tert*-butyl)phenyl)methanone (3q)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (56.2 mg, 56%), mp 165-167 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78-7.74 (m, 3H), 7.52-7.50 (m, 2H), 7.23-7.21 (m, 1H), 7.06-7.03 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 1,56 (s, 9H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.6, 163.1, 159.3, 141.4, 135.6, 131.0, 130.0, 126.3, 123.2, 122.9, 119.6, 112.1, 35.5, 35.4, 31.0, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}N_2O$ 335.2118; Found 335.2118.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-fluorophenyl)methanone (3r)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (68.0 mg, 76%), mp 124-126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.84 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.25-7.17 (m, 3H), 7.08-7.03 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 1,56 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.5, 166.8 (d, $^{1}J_{C\text{-}F}$ = 257.1 Hz), 163.1, 141.5, 135.3, 133.8 (d, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 129.2 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 123.4, 123.2, 119.9, 116.7 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 111.9, 35.4, 29.7. ^{19}F NMR ($CDCl_3$, 565 MHz): δ -101.0−-101.1 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O$ 297.1398; Found 297.1398.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-chlorophenyl)methanone (3s)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (69.4 mg, 74%), mp 144-146 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.77-7.75 (m, 3H), 7.51-7.48 (m, 2H), 7.25-7.22 (m, 1H), 7.07-7.04 (m, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 1.56 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.7, 163.2, 141.7, 141.4, 135.2, 132.3, 131.2, 129.8, 123.5, 123.3, 119.9, 112.0, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1102; Found 313.1091.

(4-Bromophenyl)(2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)methanone (3t)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (69.7 mg, 65%), mp 153-154 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 4H), 7.26-7.22 (m, 1H), 7.08-7.04 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 1.56 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.9, 163.2, 141.4, 135.2, 132.8, 132.3, 131.7,

130.5, 123.5, 123.3, 119.9, 112.0, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrN_2O$ 357.0597; Found 357.0592.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-iodophenyl)methanone (3u)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (57.0 mg, 47%), mp 180-182 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 170.2, 163.2, 141.4, 138.8, 135.2, 132.3, 132.0, 123.5, 123.3, 119.9, 112.0, 103.6, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}IN_2O$ 405.0458; Found 405.0451.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (3v)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (70.7 mg, 68%), mp 165-168 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.85-7.81 (m, 3H), 7.31-7.27 (m, 1H), 7.11-7.07 (m, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 1.62 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.6, 163.3, 141.5, 136.08, 136.05 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 135.0, 131.2, 126.4 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 123.6, 123.5, 123.3 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 120.0, 112.1, 35.5, 29.7. ^{19}F NMR ($CDCl_3$, 565 MHz): δ -63,27 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}F_3N_2O$ 347.1366; Found 347.1368.

[1,1'-Biphenyl]-4-yl(2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)methanone (3w)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (59.5 mg, 56%), mp 153-155 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.89 (dt, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.73-7.72 (m, 2H), 7.65-7.64 (m, 2H), 7.49-7.47 (m, 2H), 7.44-7.41 (m, 1H), 7.24-7.22 (m, 1H), 7.07-7.04 (m, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 1.59 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.5, 163.2, 147.8, 141.5, 139.2, 135.5, 131.6, 131.4, 129.2, 128.8, 127.9, 127.4, 123.3, 123.1, 119.7, 112.2, 35.5, 29.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O$ 355.1805; Found 355.1806.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(*m*-tolyl)methanone (3x)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (69.3 mg, 79%), mp 135-136 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.22-7.19 (m, 1H), 7.04-7.00 (m, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.9, 163.3, 141.4, 139.4, 135.8, 135.5, 133.0, 131.2, 129.1, 128.2, 123.2, 123.0, 119.7, 112.2, 35.4, 29.8, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1646.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(3-chlorophenyl)methanone (3y)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (62.9 mg, 67%), mp 156-158 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (t, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.69-7.66 (m, 1H), 7.65-7.62 (m, 1H), 7.45 (t *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 1H), 7.08-7.04 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.5, 163.3, 141.5, 135.7, 135.1, 134.9, 134.7, 130.58, 130.57, 128.9, 123.5, 123.4, 119.9, 112.1, 35.5, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O$ 313.1102; Found 313.1100.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(*o*-tolyl)methanone (3z)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (41.2 mg, 47%), mp 123-126 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.54-7.51 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.21-7.18 (m, 1H), 6.98-6.95 (m, 1H), 6.27 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H), 1.63 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 170.2, 163.5, 141.6, 140.0, 134.8, 133.30, 133.25, 132.2, 130.8, 126.6, 123.5, 123.3, 119.8, 112.3, 35.8, 29.7, 20.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O$ 293.1648; Found 293.1646.

(2-Bromophenyl)(2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)methanone (3aa)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (47.1 mg, 44%), mp 138-139 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.71 (m, 2H), 7.57-7.54 (m, 1H), 7.50-7.45 (m, 2H), 7.24-7.19 (m, 1H), 6.99-6.95 (m, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 1.66 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.6, 163.4, 141.8, 136.0, 134.6, 134.3, 133.7, 131.3, 128.2, 123.9, 123.8, 121.4, 120.1, 112.4, 36.0, 29.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrN_2O$ 357.0597; Found 357.0606.

Benzo[*d*][1,3]dioxol-4-yl(2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)methanone (3bb)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (74.5 mg, 77%), mp 186-188 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.24-7.22 (m, 1H), 7.09-7.07 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.11 (s, 2H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.6, 162.9, 153.7, 148.7, 141.3, 135.6, 128.2, 126.8, 123.2, 123.0, 119.7, 111.9, 110.2, 108.7, 102.5, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O_3$ 323.1390; Found 323.1394.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(naphthalen-1-yl)methanone (3cc)[4]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (53.2 mg, 54%), mp 171-172 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.19-7.15 (m, 1H), 6.89-6.85 (m, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 1.67 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.9, 163.7, 141.5, 135.2, 134.9, 134.2, 131.2, 131.1, 130.3, 128.99, 128.96, 127.2, 125.1, 124.8, 123.4, 123.3, 119.8, 112.6, 35.8, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_2O$ 329.1648; Found 329.1649.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(thiophen-2-yl)methanone (3dd)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (67.4 mg, 79%), mp 147-149 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, J_1 = 3.6 Hz, J_2 = 1.2

Hz, 1H), 7.24 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.15-7.14 (m, 1H), 7.13-7.10 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 1.55 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 164.2, 162.4, 141.4, 137.7, 137.4, 137.1, 135.8, 128.9, 123.3, 123.1, 119.7, 111.6, 35.4, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2OS$ 285.1056; Found 285.1046.

(2-(*tert*-Butyl)-4-methyl-1*H*-benzo[*d*]imidazol-1-yl)(furan-2-yl)methanone (3ee)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (55.9 mg, 66%), mp 68-70 ℃. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.71 (dd, J_1 = 1.8 Hz, J_2 = 0.6 Hz, 1H), 7.21 (dd, J_1 = 3.6 Hz, J_2 = 0.6 Hz, 1H), 7.05-7.00 (m, 2H), 6.66 (d, J = 7.8 Hz, 1H), 6.62 (dd, J_1 = 3.6 Hz, J_2 = 1.8 Hz, 1H), 2.67 (s, 3H), 1.53 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 161.4, 159.6, 149.0, 147.6, 140.8, 135.3, 130.0, 123.5, 123.2, 123.1, 113.3, 108.7, 35.4, 29.7, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}N_2O_2$ 283.1441; Found 283.1441.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-one (3ff)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (30.5 mg, 47%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.02 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.81-7.78 (m, 1H), 7.54-7.51 (m, 1H), 2.91 (s, 3H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 172.7, 167.3, 149.8, 132.9, 129.0, 126.3, 124.7, 122.3, 39.4, 29.6, 21.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}N_2NaO$ 239.1155; Found 239.1159.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)hexan-1-one (3gg)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (25.3 mg, 31%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.06 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.80-7.77 (m, 1H), 7.53-7.50 (m, 1H), 3.24 (t, J = 7.8 Hz, 2H), 1.94-1.89 (m, 2H), 1.51 (s, 9H), 1.46-1.39 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 172.7, 170.4, 150.1, 132.6, 129.1, 126.1, 124.3, 121.8, 39.5, 34.2, 31.7, 29.6, 28.0, 22.6, 14.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}N_2O$ 273.1961; Found 273.1959.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-cyclohexylpropan-1-one (3hh)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (31.9 mg, 34%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.79-7.77 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 3.25 (t, *J* = 7.8 Hz, 2H), 1.85 (d, *J* = 13.2 Hz, 2H), 1.79-1.71 (m, 4H), 1.67-1.65 (m, 1H), 1.49 (s, 9H), 1.38-1.33 (m, 1H), 1.27-1.20 (m, 3H), 1.02-0.96 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 172.7, 170.8, 150.1, 132.6, 129.1, 126.2, 124.3, 121.7, 39.5, 37.5, 36.0, 33.3, 31.9, 29.6, 26.7, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O$ 313.2274; Found 313.2270.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-methylpentan-1-one (3ii)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (29.4 mg, 36%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 3.25 (t, *J* = 7.8 Hz, 2H), 1.78 (q, *J* = 7.8 Hz, 2H),1.73-1.69 (m, 1H), 1.49 (s, 9H), 1.00 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 172.7, 170.7, 150.1, 132.6, 129.1, 126.2, 124.3, 121.7, 39.5, 37.4, 29.7, 29.6, 28.0, 22.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}N_2O$ 273.1961; Found 273.1960.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-phenylpropan-1-one (3jj)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (35.8 mg, 39%), mp 44-46 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.81-7.77 (m, 1H), 7.53-7.49 (m, 1H), 7.31-7.27 (m, 4H), 7.22-7.18 (m, 1H), 3.58 (t, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 8.4 Hz, 2H), 1.50 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 172.7, 169.0, 150.1, 141.7, 132.7, 129.2, 128.5, 128.4, 126.3, 126.1, 124.1, 121.8, 39.6, 35.8, 33.7, 29.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2O$ 307.1805; Found 307.1821.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(*p*-tolyl)propan-1-one (3kk)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (36.6 mg, 38%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 3.54 (t, *J* = 7.8 Hz, 2H), 3.22 (t, *J* = 8.4 Hz, 2H), 2.31 (s, 3H), 1.50 (s,

9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 172.7, 169.2, 150.1, 138.7, 135.5, 132.7, 129.1, 128.4, 126.3, 124.1, 121.8, 39.6, 36.1, 33.3, 29.6, 21.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O$ 321.1961; Found 321.1954.

1-(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(4-chlorophenyl)propan-1-one (3ll)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (40.9 mg, 40%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00-7.97 (m, 2H), 7.80-7.77 (m, 1H), 7.52-7.50 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.54 (t, *J* = 8.4 Hz, 2H), 3.25 (t, *J* = 7.8 Hz, 2H), 1.48 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 172.6, 168.6, 150.1, 140.1, 132.8, 131.8, 129.9, 129.2, 128.5, 126.4, 123.9, 121.7, 39.6, 35.5, 32.8, 29.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}ClN_2O$ 341.1415; Found 341.1410.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(cyclohexyl)methanone (3mm)

Eluent: petroleum ether/ethyl acetate (10:1). Colorless liquid (31.6 mg, 37%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.75 (m, 1H), 7.39-7.36 (m, 1H), 7.32-7.27 (m, 2H), 3.33-3.25 (m, 1H), 2.07 (d, *J* = 13.6 Hz, 2H), 1.91-1.87 (m, 2H), 1.78-1.62 (m, 3H), 1.54 (s, 9H), 1.41-1.30 (m, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 179.1, 162.8, 141.8, 133.7, 123.8, 123.5, 120.3, 111.7, 47.3, 35.8, 29.7, 29.6, 25.55, 25.50. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O$ 285.1961; Found 285.1951.

2. Structural elaborations

2.1. Synthesis of 4[5]

To a reaction tube equipped with a stir bar was charged with **3a** (55.7 mg, 0.2 mmol) and THF (5 mL). The reaction mixture was cooled to 0 ℃ and added with $LiAlH_4$ (15.2 mg, 0.4 mmol). The tube was then sealed, and the resulting mixture was allowed to warm to room temperature and stirred for 2 h. Upon completion, it was quenched with saturated ammonium chloride solution and extracted with ethyl acetate (10 mL × 3). The combined organic phases were washed with saturated brine, dried over Na_2SO_4, filtered and concentrated

under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **4**.

2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazole (4)[6]

Eluent: petroleum ether/ethyl acetate (3:1). White solid (30.7 mg, 88%), mp 222-225 ℃. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 12.1 (s, 1H), 7.52-7.41 (m, 2H), 7.11-7.10 (m, 2H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (DMSO, 150 MHz): δ 162.6, 143.3, 135.1, 121.9, 121.2, 118.8, 111.2, 33.6, 29.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}N_2$ 175.1230; Found 175.1230.

2.2. Synthesis of 5[7]

To a reaction tube equipped with a stir bar were charged with **3aa** (35.7 mg, 0.1 mmol), DMSO (1 mL), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), PPh_3 (5.2 mg, 0.02 mmol), K_3PO_4 (25.5 mg, 0.12 mmol) and ethynylbenzene (16.5 μL, 0.15 mmol). The tube was then sealed, and the resulting mixture was stirred at 80 ℃ for 24 h under argon atmosphere. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to give **5**.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(2-(phenylethynyl)phenyl)methanone (5)

Eluent: petroleum ether/ethyl acetate (20:1). White solid (32.9 mg, 87%), mp 191-193 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69-7.66 (m, 2H), 7.61-7.56 (m, 1H), 7.33-7.30 (m, 3H), 7.26-7.22 (m, 3H), 7.05-7.01 (m, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 1.64 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.0, 163.0, 141.8, 135.6, 134.9, 134.3, 133.0, 131.9, 130.8, 128.92, 128.89, 128.3, 123.7, 123.54, 123.47, 121.9, 119.8, 112.1, 95.2, 85.6, 35.7, 29.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}N_2O$ 379.1805; Found 379.1800.

2.3. Synthesis of 6[8]

To a reaction tube equipped with a stir bar were charged with **3aa** (71.5 mg, 0.2 mmol), piperidine (1 mL), $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol) and CuI (3.8 mg, 0.02 mmol). The tube was then sealed, and the resulting mixture was stirred at room temperature for 15 h. Upon completion, it was quenched with saturated ammonium chloride solution and extracted with ethyl acetate (10 mL × 3). The combined organic phases were washed with saturated brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **6**.

(2-(*tert*-Butyl)-1*H*-benzo[*d*]imidazol-1-yl)(2-(piperidin-1-yl)phenyl)methanone (6)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (23.2 mg, 32%), mp 194-196 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 9.0 Hz, 1H), 2.97 (br s, 2H), 2.79 (br s, 2H), 1.65 (s, 9H), 1.41-1.37 (m, 2H), 1.30-1.26 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 168.6, 163.6, 153.7, 141.7, 135.0, 134.1, 132.3, 126.6, 123.3, 123.2, 121.6, 119.9, 119.7, 113.0, 53.8, 36.3, 29.3, 25.9, 23.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{27}N_3NaO$ 384.2046; Found 384.2068.

2.4. Synthesis of 7[9]

To a reaction tube equipped with a stir bar were charged with **3aa** (35.7 mg, 0.1 mmol), dioxane (1 mL), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), PPh_3 (15.7 mg, 0.06 mmol), K_2CO_3 (55.3 mg, 0.4 mmol) and phenylboronic acid (13.4 mg, 0.11 mmol). The tube was then sealed, and the resulting mixture was stirred at 80 ℃ for 24 h under argon atmosphere. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filetered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1) as the eluent to give **7**.

[1,1'-Biphenyl]-2-yl(2-(*tert*-butyl)-1*H*-benzo[*d*]imidazol-1-yl)methanone (7)

Eluent: petroleum ether/ethyl acetate (40:1). White solid (32.6 mg, 92%), mp 209-211 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.69-7.65 (m, 2H), 7.57 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.50-7.45 (m, 2H), 7.26-7.16 (m, 6H), 7.00-6.98 (m, 1H), 6.30 (d, J = 8.4 Hz, 1H), 1.54 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 169.1, 163.8, 142.9, 141.7, 139.1, 134.5, 134.0, 132.6, 131.7, 130.0, 128.5, 128.3, 128.0, 127.8, 123.6, 123.5, 119.9, 113.3, 36.2, 29.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O$ 355.1805; Found 355.1804.

3. Gram-scale synthesis of 3a

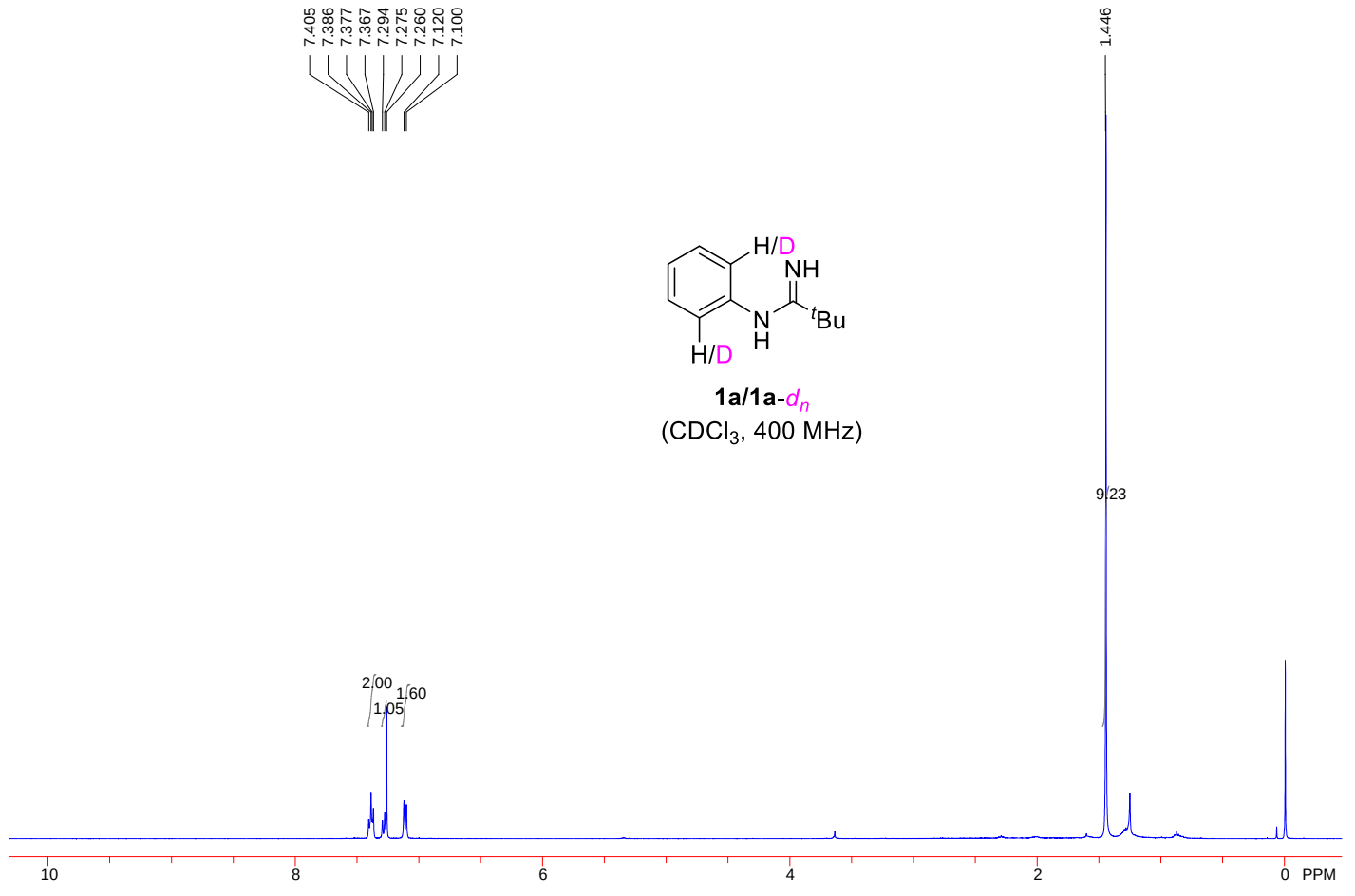
To a reaction tube equipped with a stir bar were charged with *N*-phenylpivalimidamide (**1a**, 1.058 g, 6 mmol), ethyl acetate (25 mL), $[RhCp^*Cl_2]_2$ (77.3 mg, 0.125 mmol), $AgSbF_6$ (171.8 mg, 0.5 mmol), $Zn(OAc)_2$ (275.2 mg, 1.5 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 0.816 g, 5 mmol). The tube was then sealed, and the resulting mixture was stirred at 110 ℃ under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with ethyl acetate (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (0.849 g, 61%).

III. Mechanism studies

1. Mechanism studies (I)

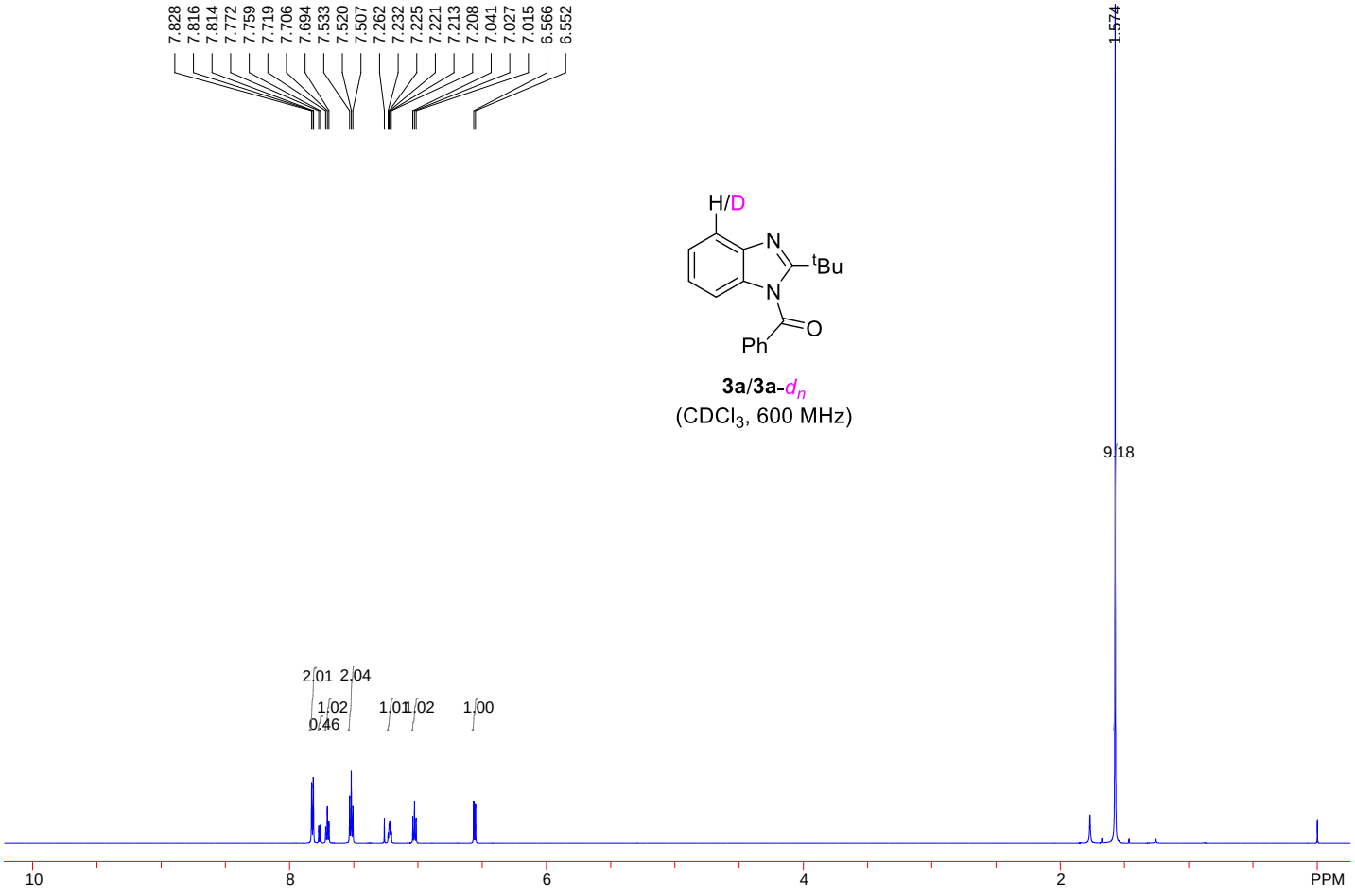
1.1. H/D exchange experiment (I)

To a reaction tube equipped with a stir bar were charged with **1a** (52.9 mg, 0.3 mmol), ethyl acetate (1.5 mL), CD_3OD (0.12 mL, 3 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), and $Zn(OAc)_2$ (16.5 mg, 0.09 mmol). The resulting mixture was stirred at 110 ℃ under air for 30 min. Afterwards, it was cooled to room temperature, quenched with water and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (5:1) as eluent to give a mixture of **1a** and **1a**-d_n. Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration ratio was determined to be 20%.



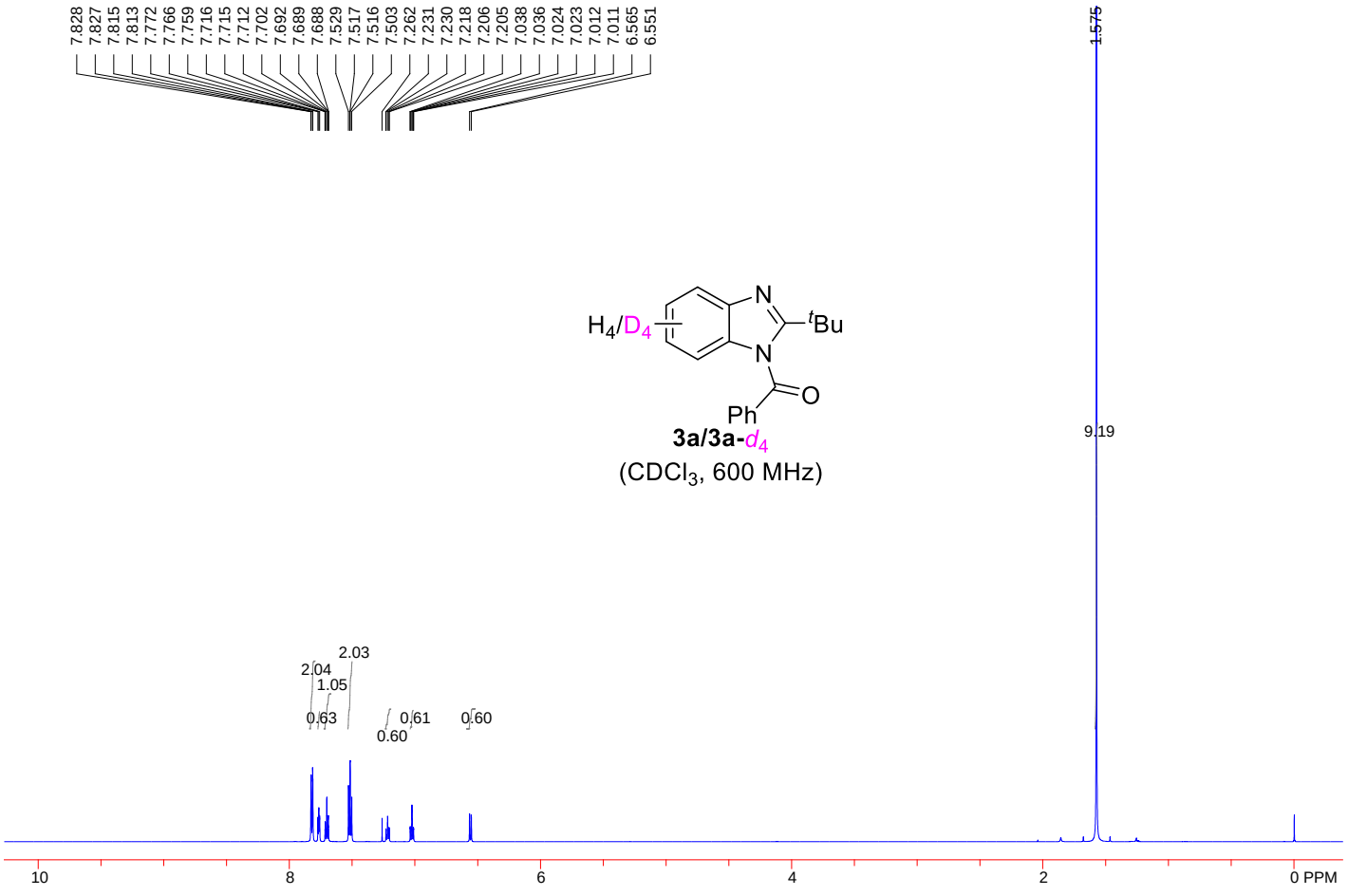
1.2. H/D exchange experiment (II)

To a reaction tube equipped with a stir bar were charged with **1a** (42.3 mg, 0.24 mmol), **2a** (32.6 mg, 0.2 mmol), ethyl acetate (1 mL), CD_3OD (81 μL, 2 mmol), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), and $Zn(OAc)_2$ (11.0 mg, 0.06 mmol). The resulting mixture was stirred at 110 ℃ under air for 3 h. Afterwards, it was cooled to room temperature, quenched with water and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to give a mixture of **3a** and **3a**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture, the deuteration ratio was determined to be 54%.



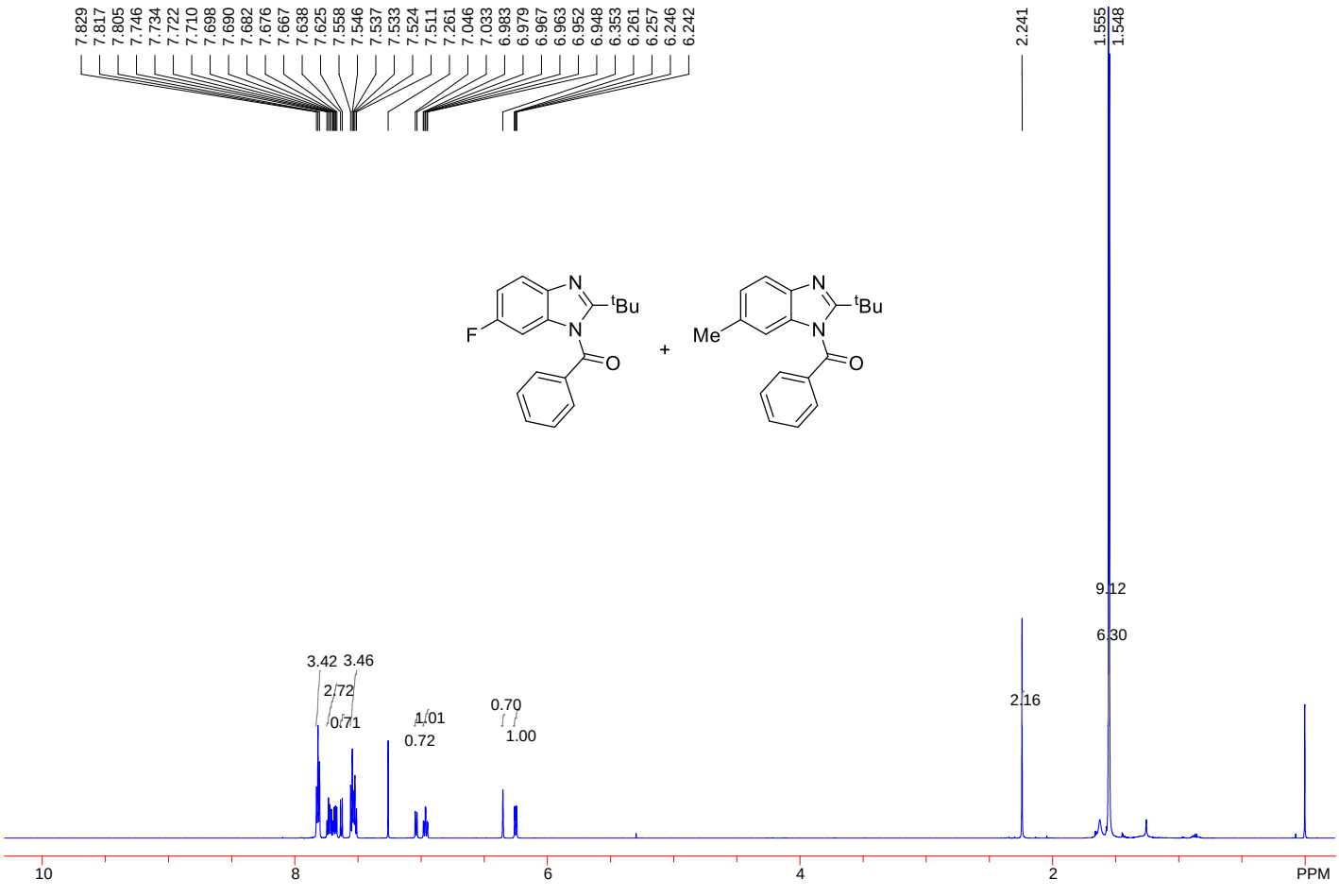
1.3. Kinetic isotope effect study

To a reaction tube equipped with a stir bar were added **1a** (105.6 mg, 0.6 mmol), **1a**-d_5 (108.6 mg, 0.6 mmol), ethyl acetate (2.5 mL), **2a** (97.8 mg, 0.6 mmol), $[RhCp^*Cl_2]_2$ (7.7 mg, 0.0125 mmol), $AgSbF_6$ (17.2 mg, 0.05 mmol) and $Zn(OAc)_2$ (27.5 mg, 0.15 mmol) with stirring. After the tube was sealed, the mixture was stirred at 110 ℃ under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford a mixture of **3a** and **3a**-d_4. Upon analyzing the 1H NMR spectrum of the mixture, the ratio of **3a** to **3a**-d_4 was determined to be 0.6:0.4. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 1.5.



1.4. Competition study of substrates with different electronic characteristics

To a reaction tube equipped with a stir bar were added **1b** (57.1 mg, 0.3 mmol), **1e** (58.3 mg, 0.3 mmol), ethyl acetate (1.5 mL), **2a** (48.9 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol) and $Zn(OAc)_2$ (16.5 mg, 0.09 mmol) with stirring. After the tube was sealed, the mixture was stirred at 110 ℃ under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford a mixture of **3b** and **3e**. Upon analyzing the ^1H NMR spectrum of the mixture, the ratio of **3b** to **3e** was determined to be 0.7:1.



2. Mechanism studies (II)

2.1. To a reaction tube equipped with a stir bar were charged with *N*-phenylpivalimidamide (**1a**, 63.5 mg, 0.36 mmol), ethyl acetate (1.5 mL), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol),

$Zn(OAc)_2$ (16.5 mg, 0.09 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 48.9 mg, 0.3 mmol). The tube was sealed, and the reaction mixture was stirred at room temperature under air for 10 h. Upon completion, it was quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using dichloromethane/methanol (10:1) as eluent to afford **IV** (73.7 mg, 83%).

***N*-(2-Pivalimidamidophenyl)benzamide (IV)**

Eluent: dichloromethane/methanol (10:1). White solid (73.7 mg, 83%), mp 163-164 ℃. ^{1}H NMR (DMSO, 600 MHz): δ 9.20 (br s, 1H), 8.21 (d, *J* = 4.2 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.55 (t *J* = 7.8 Hz, 2H), 7.09-6.94 (m, 3H), 6.22-6.16 (m, 2H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 166.8, 164.9, 137.9, 135.3, 131.6, 131.5, 128.7, 127.0, 124.2, 123.9, 120.5, 120.2, 37.3, 28.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}N_3O$ 296.1757; Found 296.1766.

2.2. To a reaction tube equipped with a stir bar were charged with **IV** (88.6 mg, 0.3 mmol), ethyl acetate (1.5 mL), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol) and $Zn(OAc)_2$ (16.5 mg, 0.09 mmol). The tube was sealed, and the reaction mixture was stirred at 110 ^{o}C under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (78.5 mg, 94%).

2.3. To a reaction tube equipped with a stir bar were charged with **IV** (88.6 mg, 0.3 mmol), ethyl acetate (1.5 mL) and $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol). The tube was sealed, and the reaction mixture was stirred at 110 ^{o}C under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10

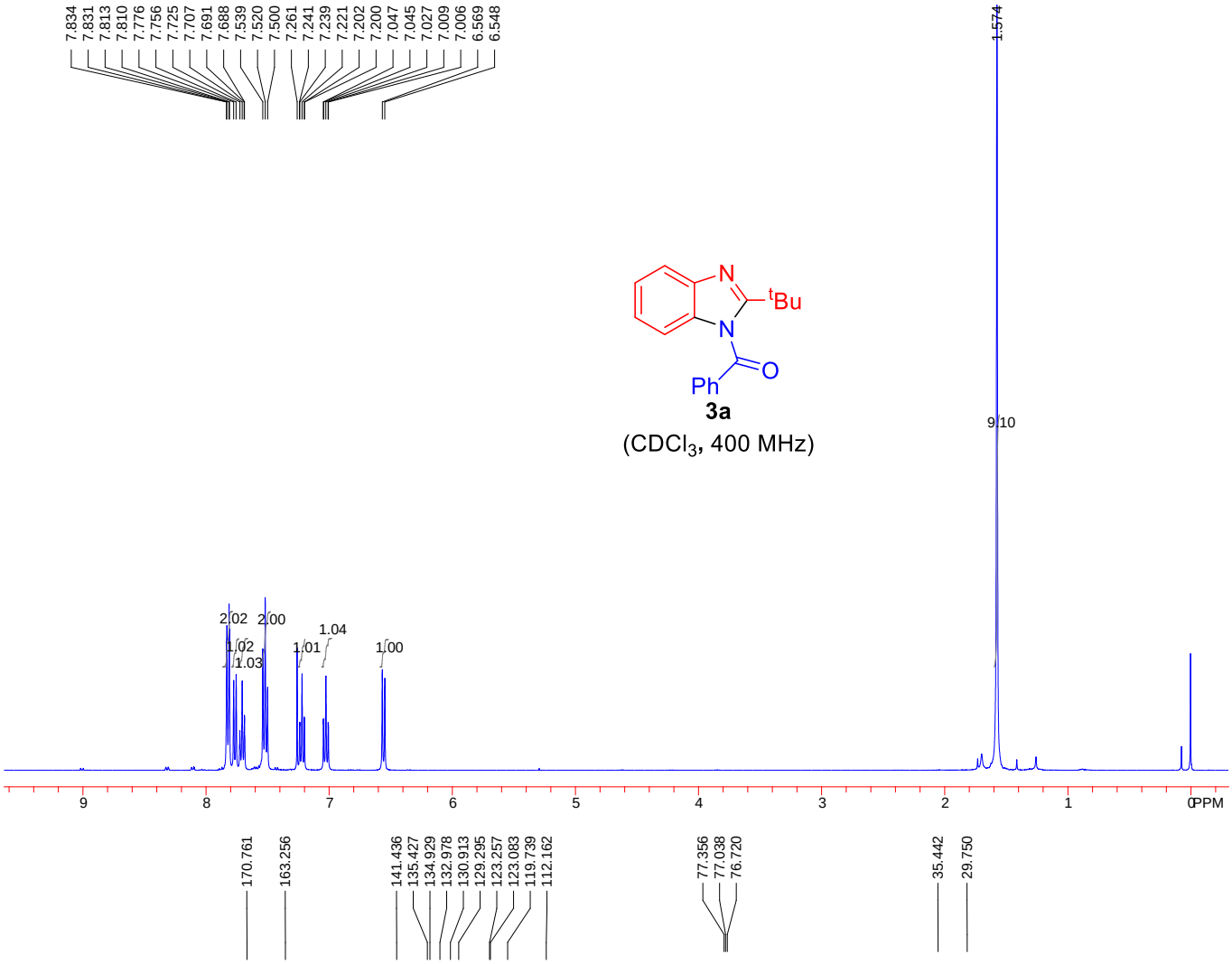
mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (23.4 mg, 28%).

2.4. To a reaction tube equipped with a stir bar were charged with **IV** (88.6 mg, 0.3 mmol), ethyl acetate (1.5 mL) and $AgSbF_6$ (10.3 mg, 0.03 mmol). The tube was sealed, and the reaction mixture was stirred at 110 ^oC under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (73.5 mg, 88%).

2.5. To a reaction tube equipped with a stir bar were charged with **IV** (88.6 mg, 0.3 mmol), ethyl acetate (1.5 mL) and $Zn(OAc)_2$ (16.5 mg, 0.09 mmol). The tube was sealed, and the reaction mixture was stirred at 110 ^oC under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (71.0 mg, 85%).

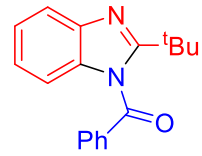
2.6. To a reaction tube equipped with a stir bar were charged with **IV** (88.6 mg, 0.3 mmol) and ethyl acetate (1.5 mL). The tube was sealed, and the reaction mixture was stirred at 110 ^oC under air for 10 h. Upon completion, it was cooled to room temperature, quenched with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (21.7 mg, 26%).

IV. Copies of NMR spectra of products 3a-3mm



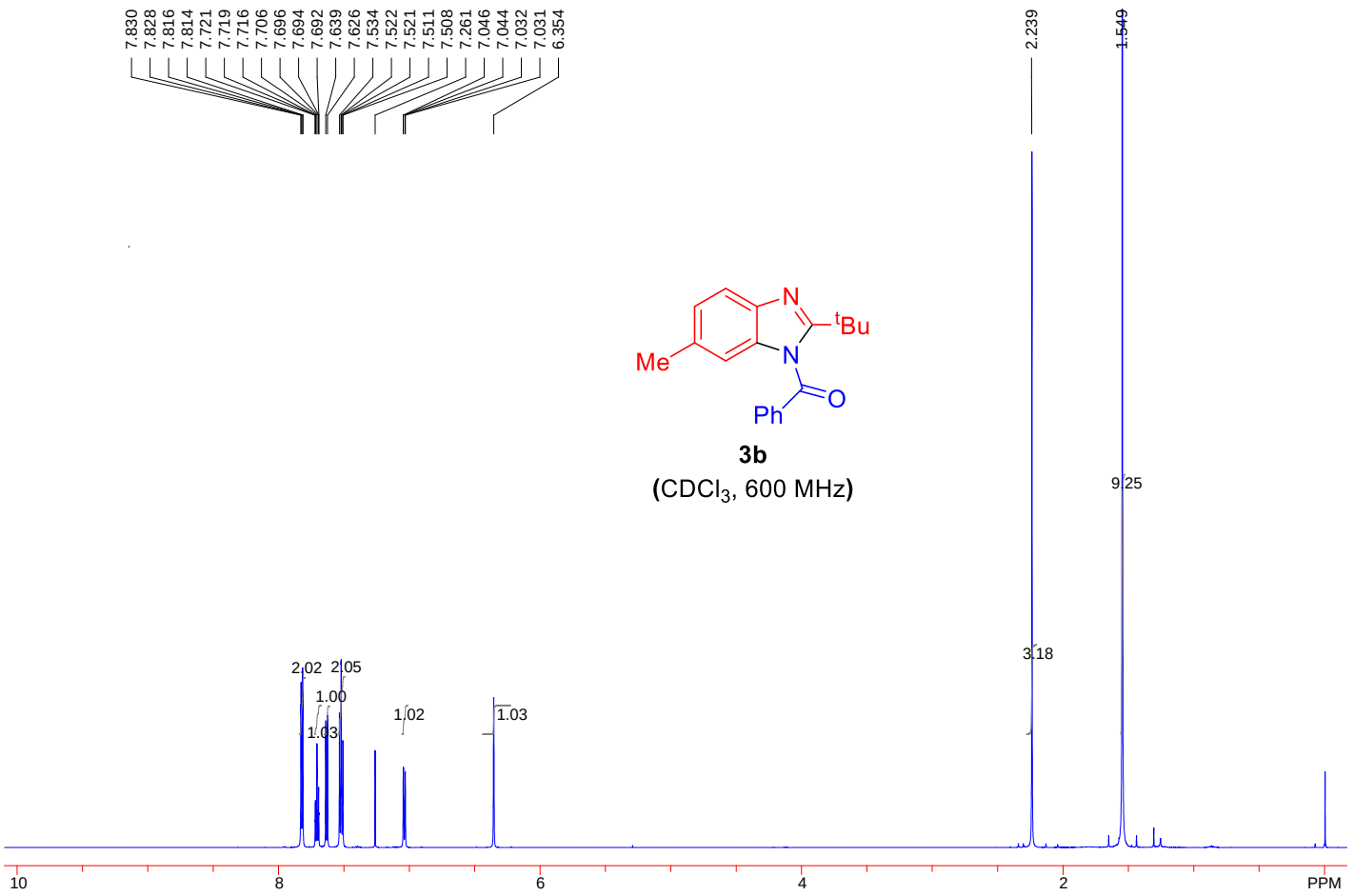
3a

($CDCl_3$, 400 MHz)



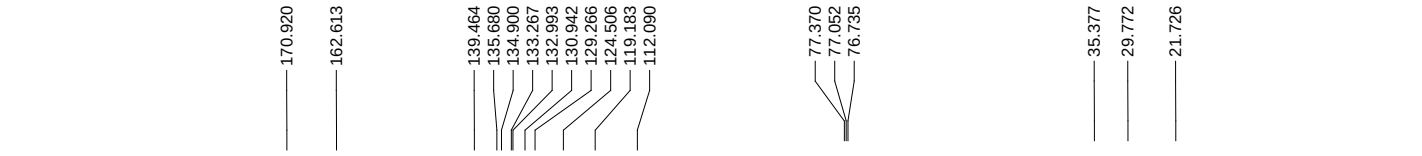
3a

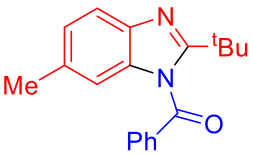
($CDCl_3$, 100 MHz)



3b

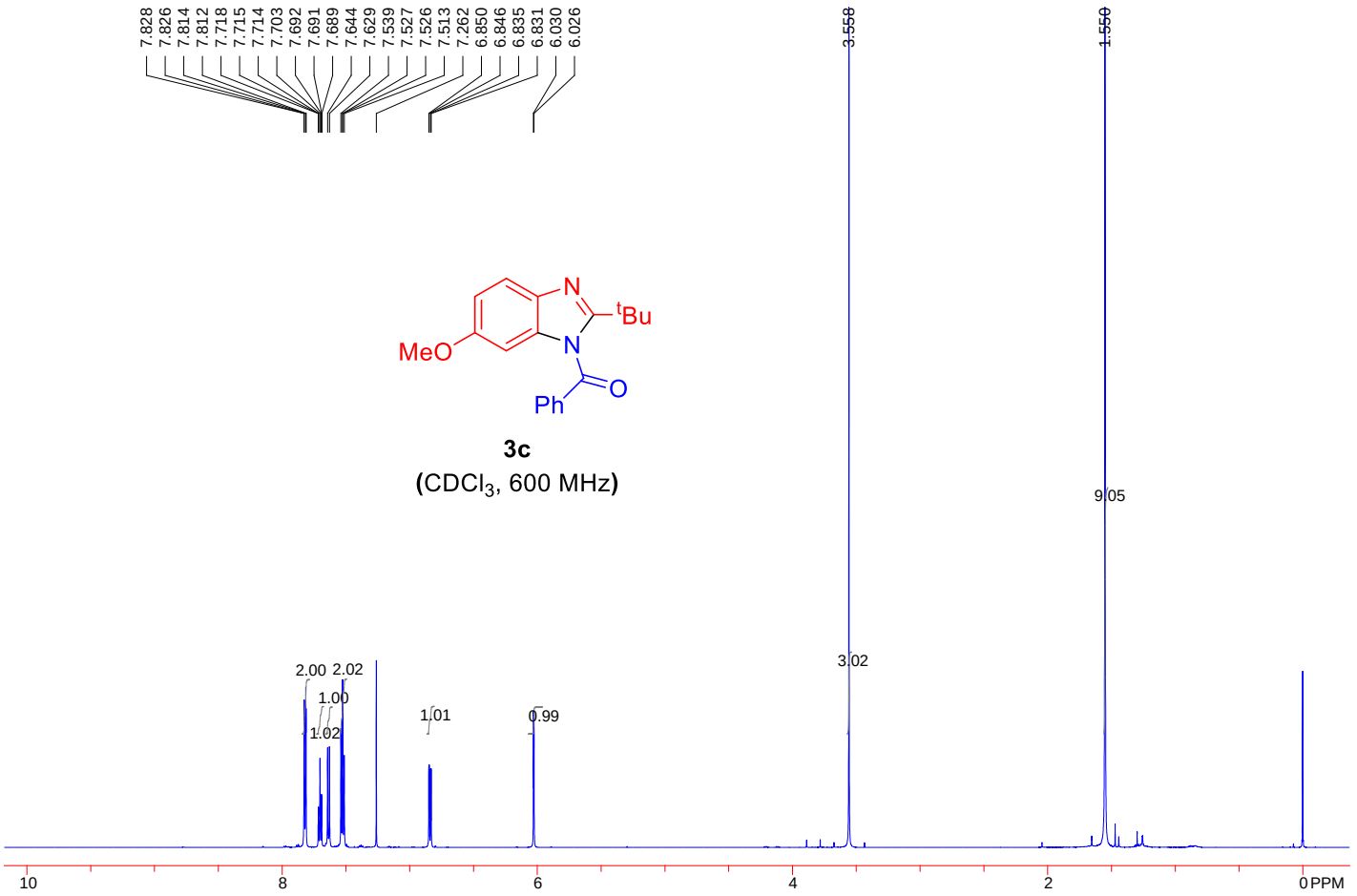
(CDCl$_3$, 600 MHz)





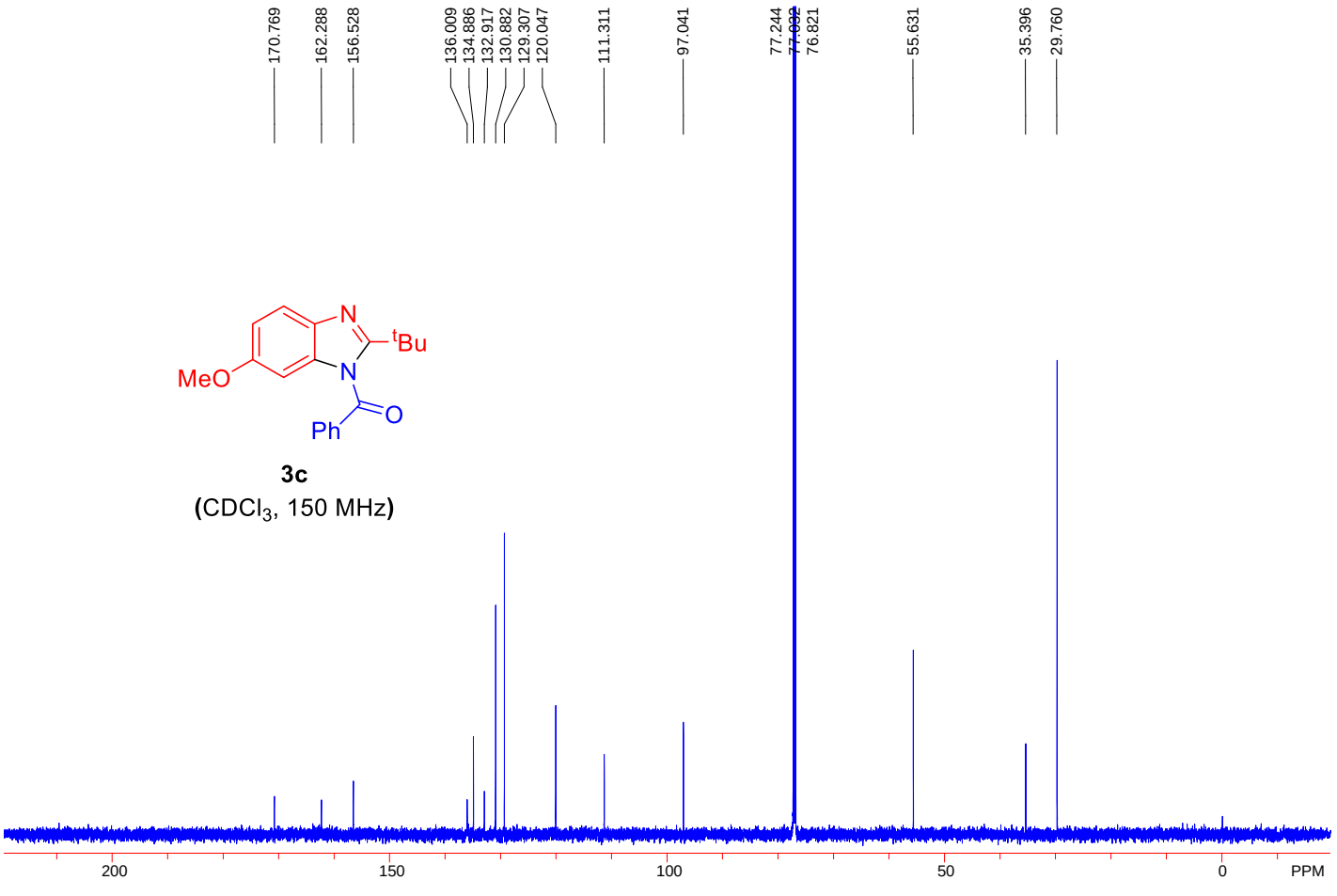
3b

(CDCl$_3$, 100 MHz)



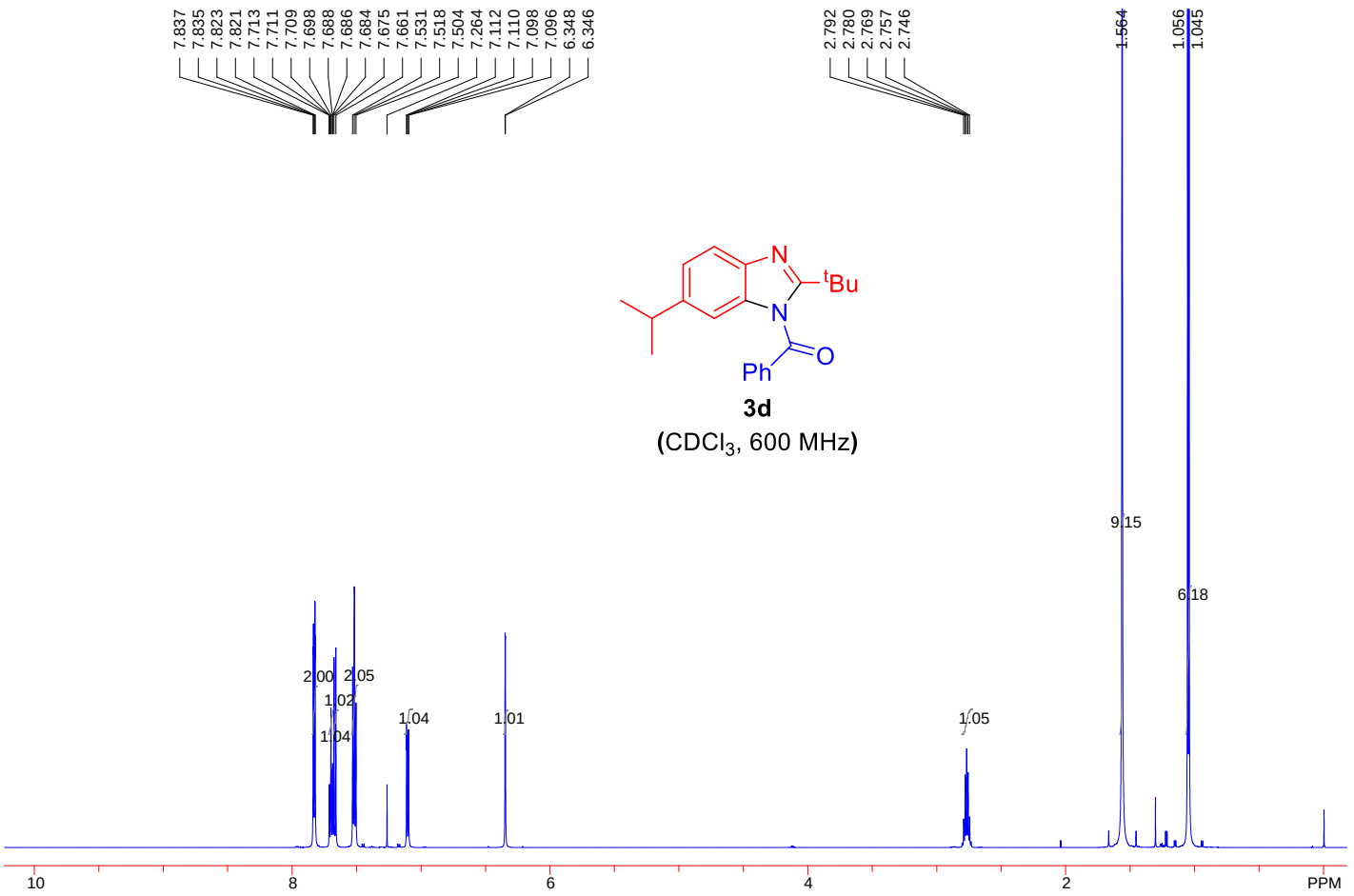
3c

($CDCl_3$, 600 MHz)



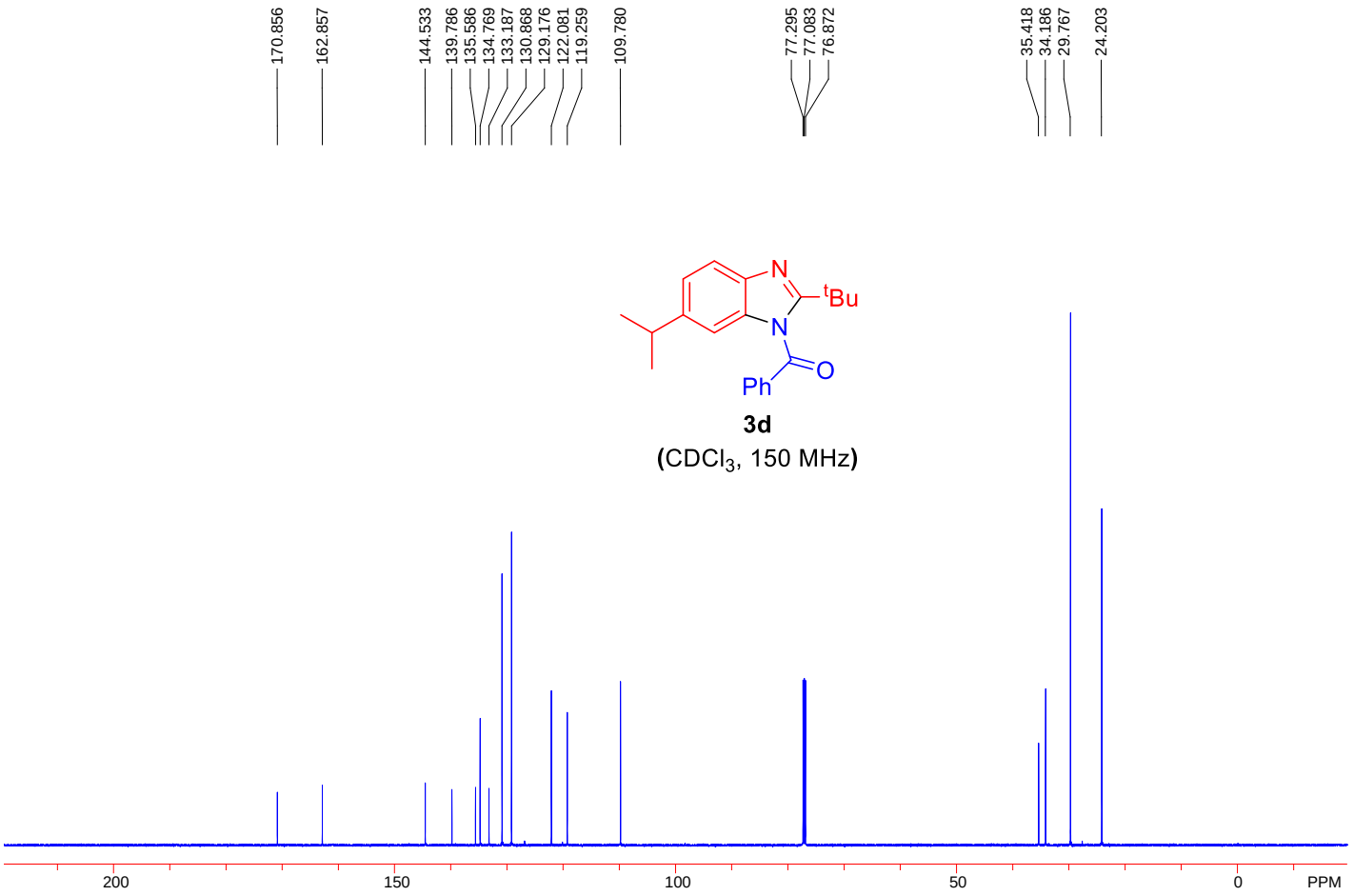
3c

($CDCl_3$, 150 MHz)



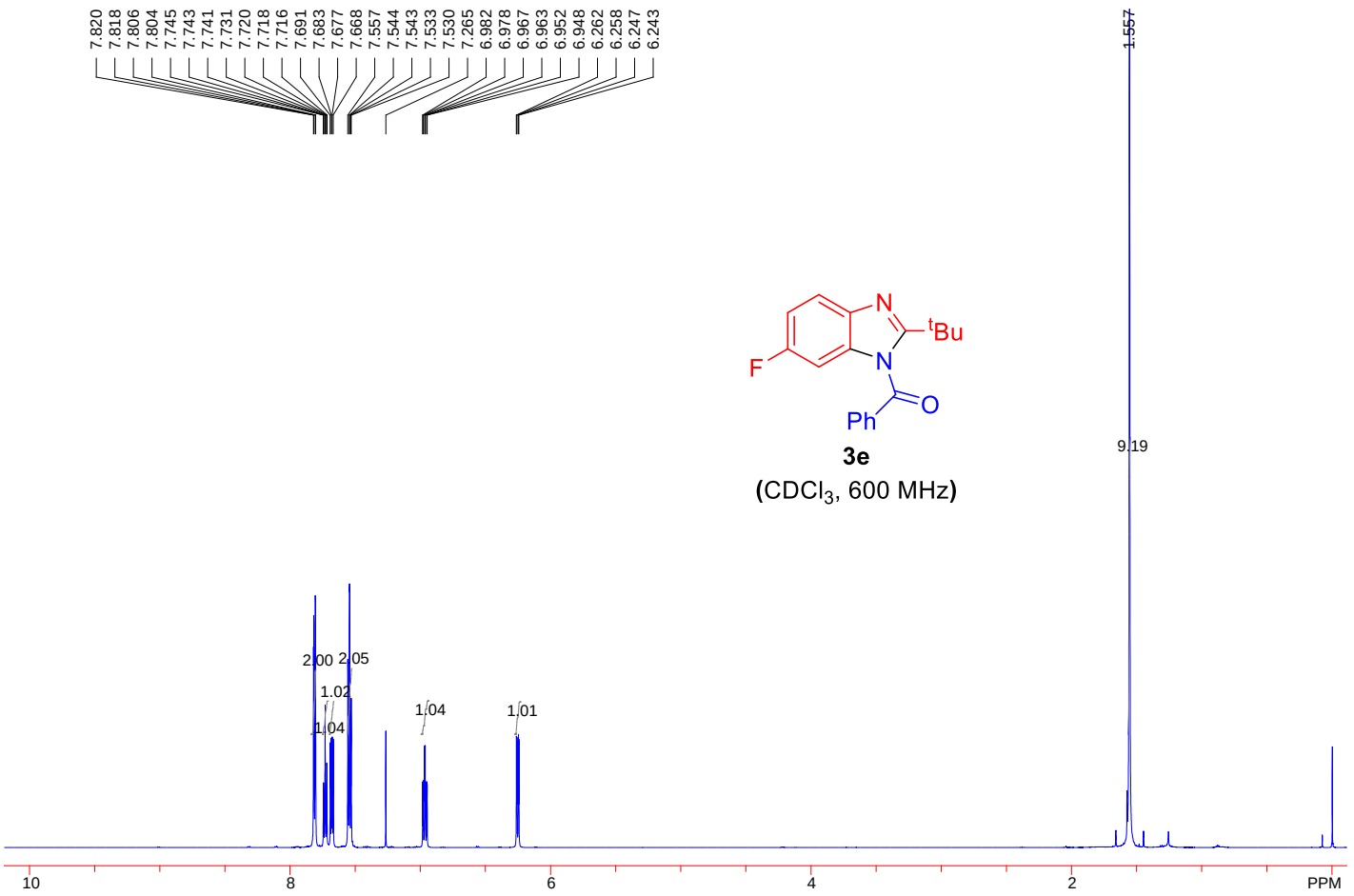
3d

(CDCl$_3$, 600 MHz)



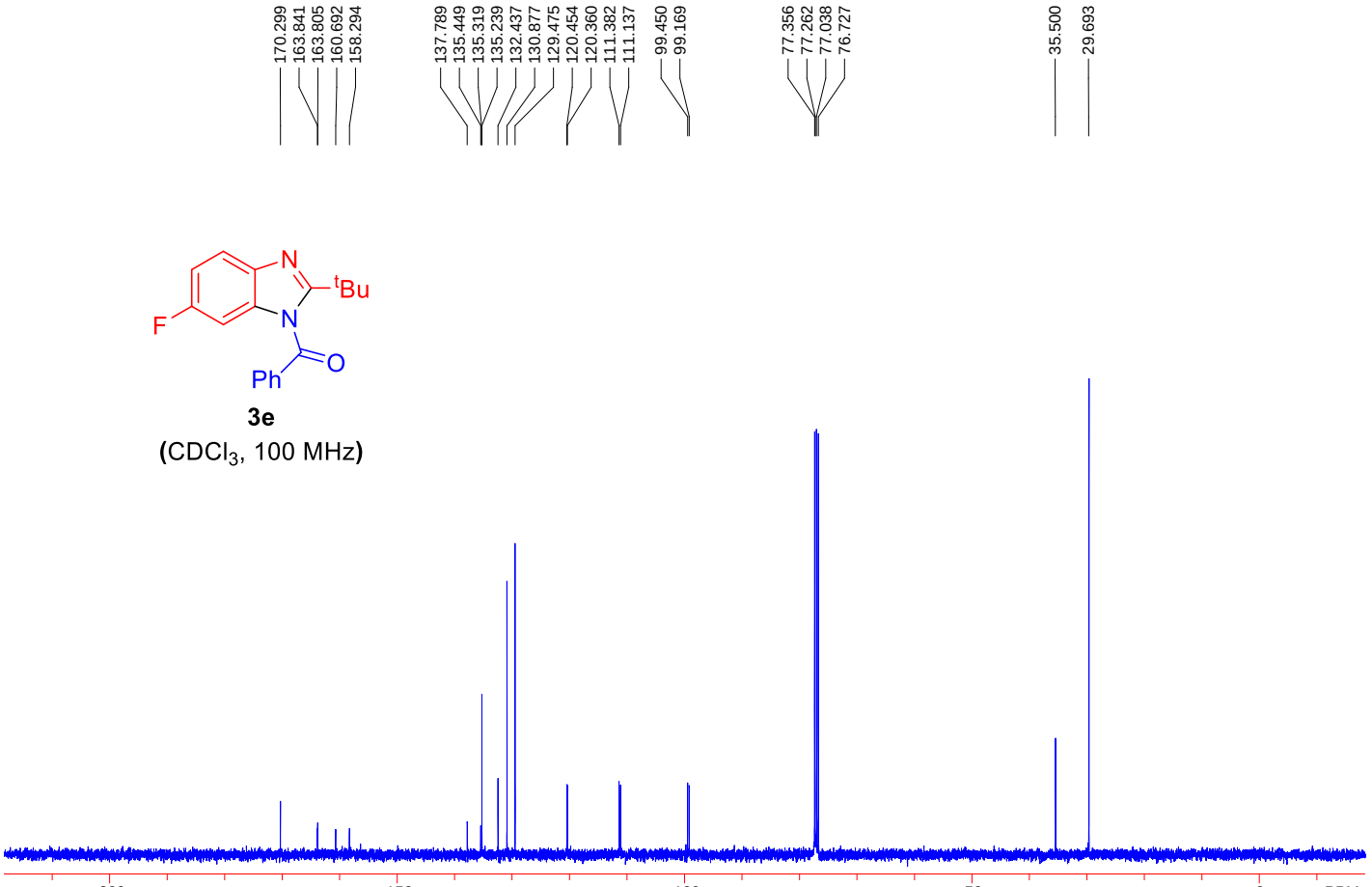
3d

(CDCl$_3$, 150 MHz)



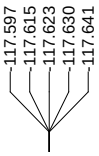
3e

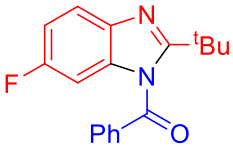
(CDCl$_3$, 600 MHz)



3e

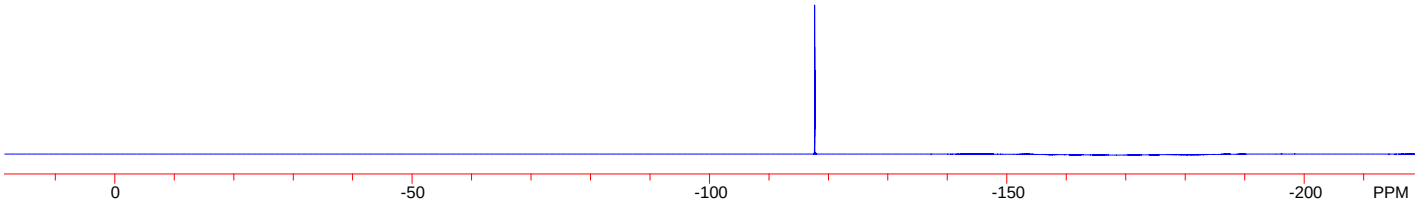
(CDCl$_3$, 100 MHz)

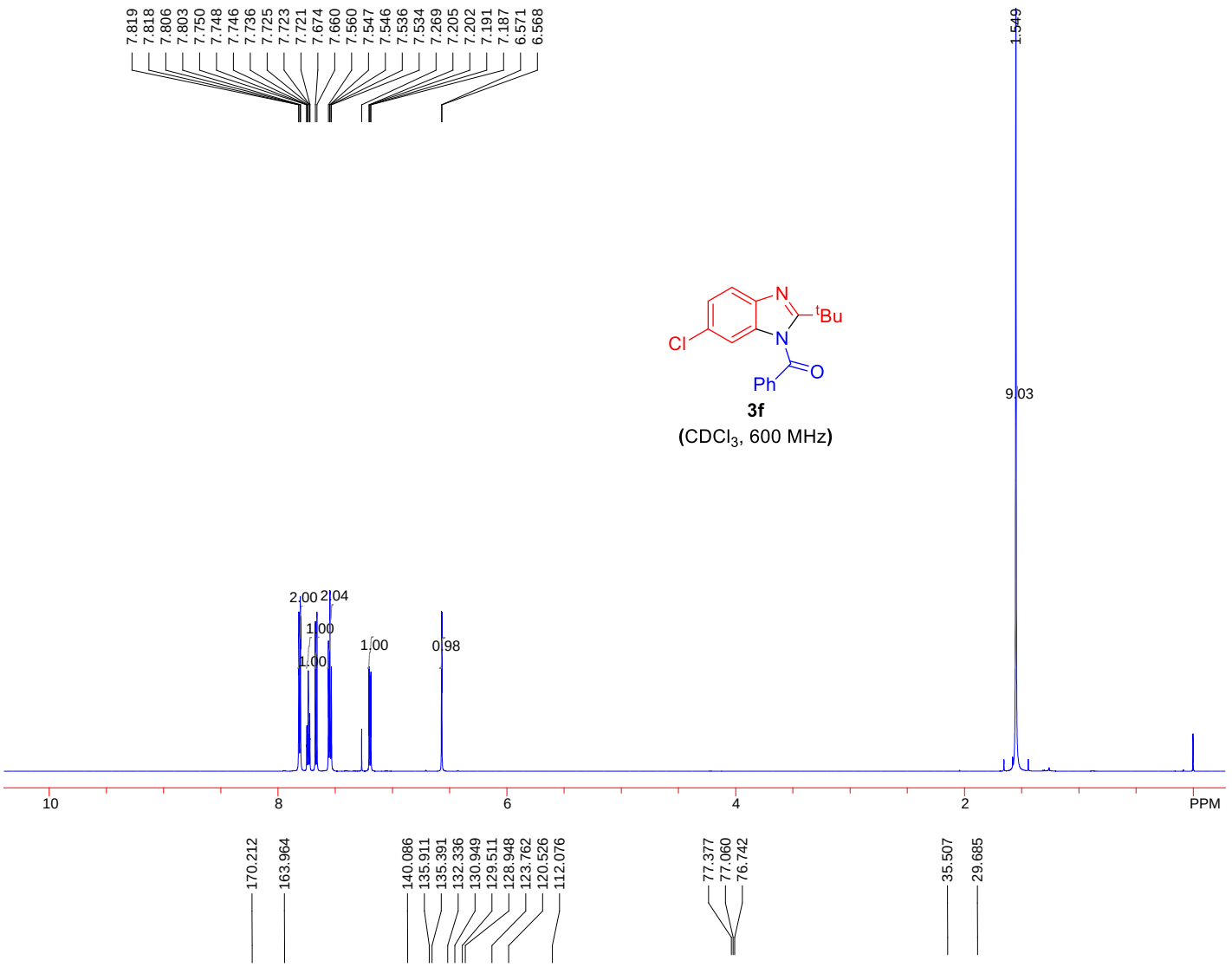




3e

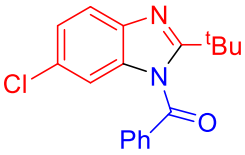
(CDCl$_3$, 565 MHz)





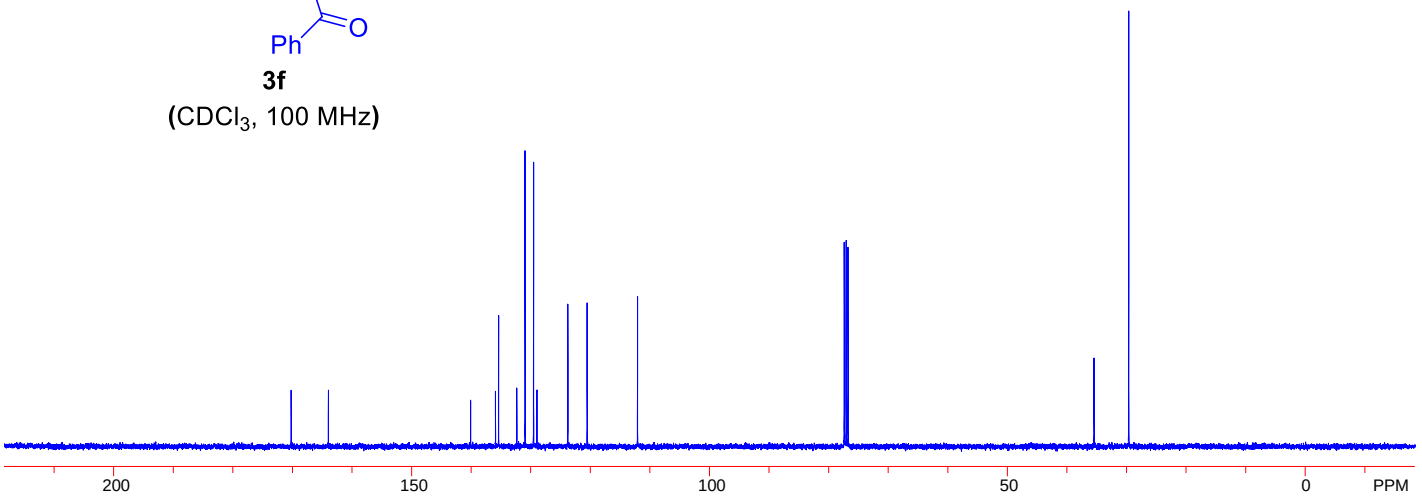
3f

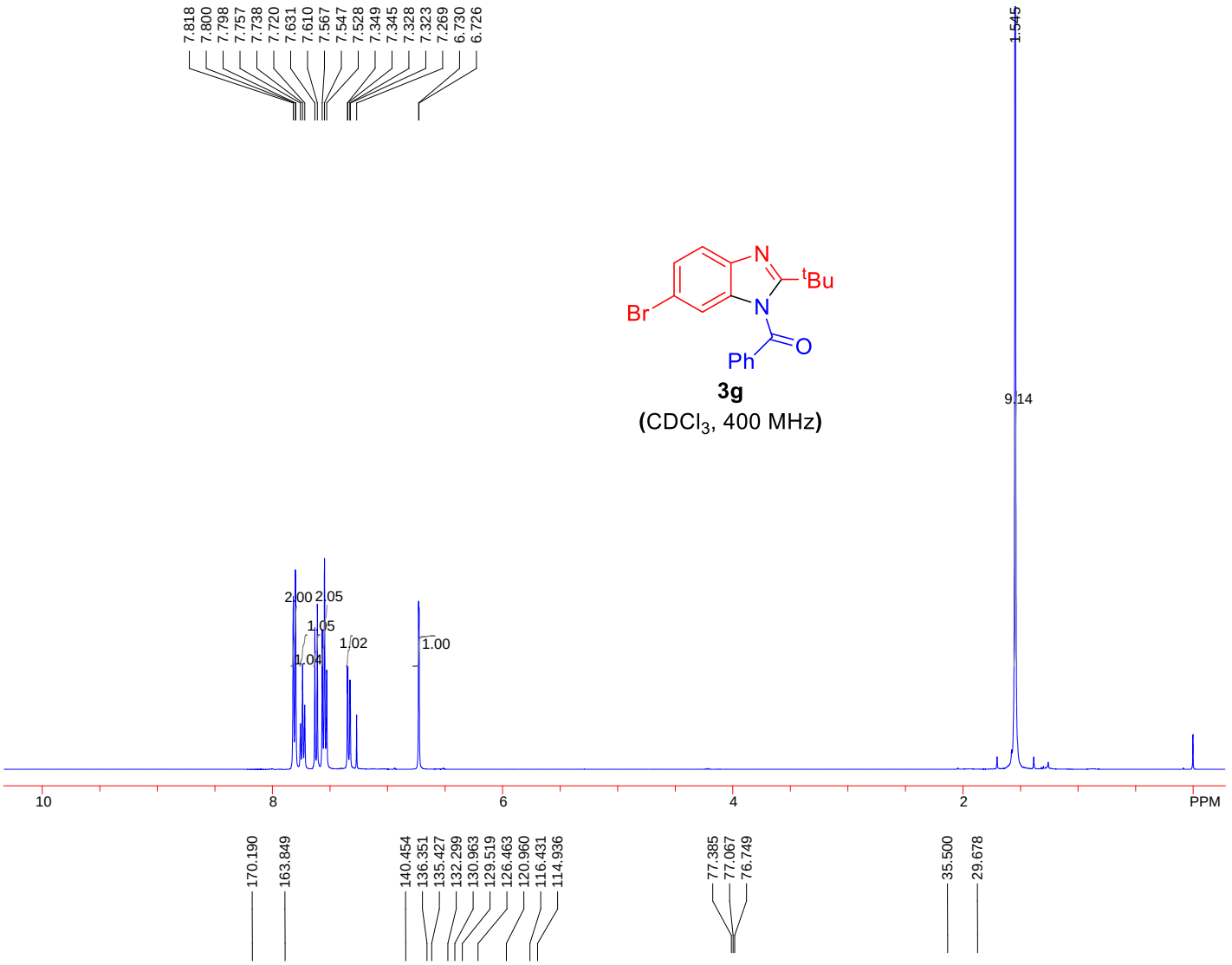
($CDCl_3$, 600 MHz)



3f

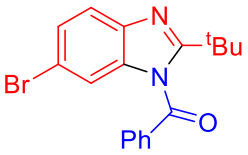
($CDCl_3$, 100 MHz)





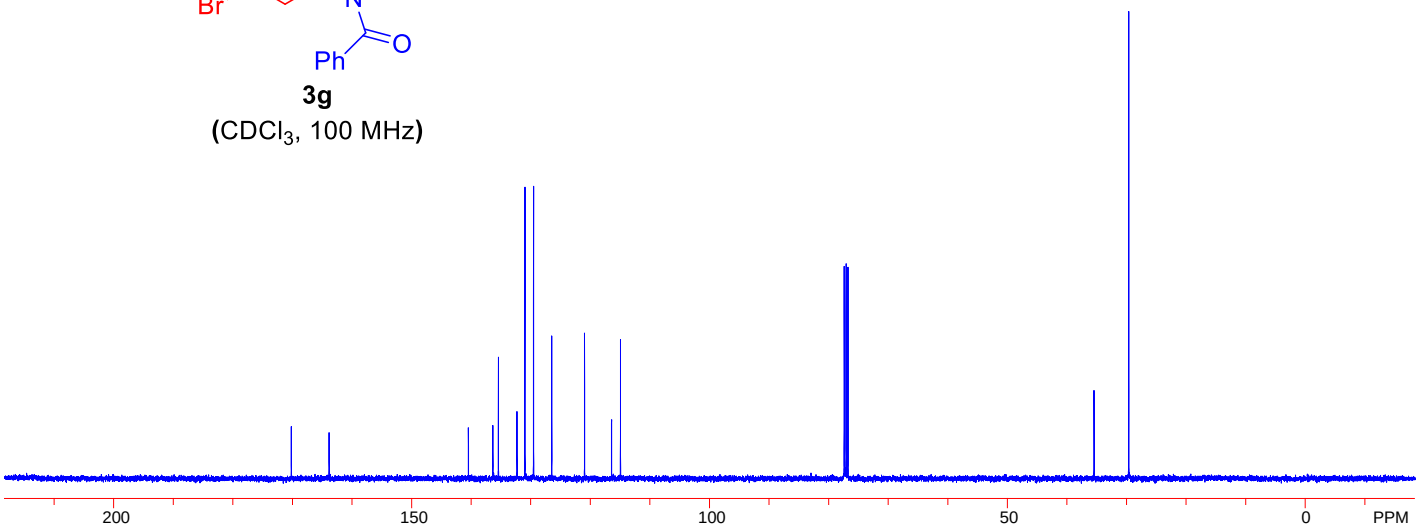
3g

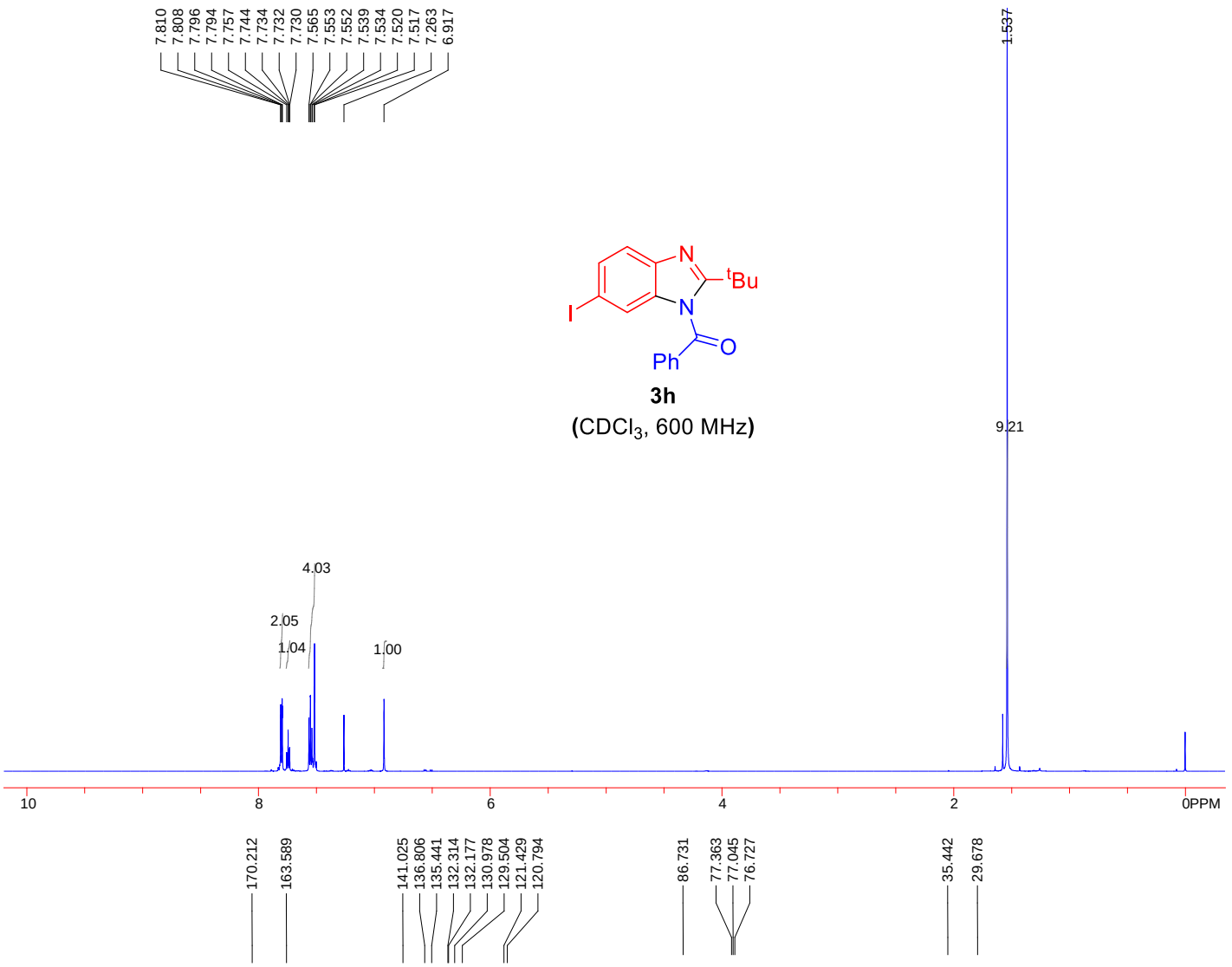
(CDCl$_3$, 400 MHz)



3g

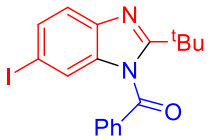
(CDCl$_3$, 100 MHz)





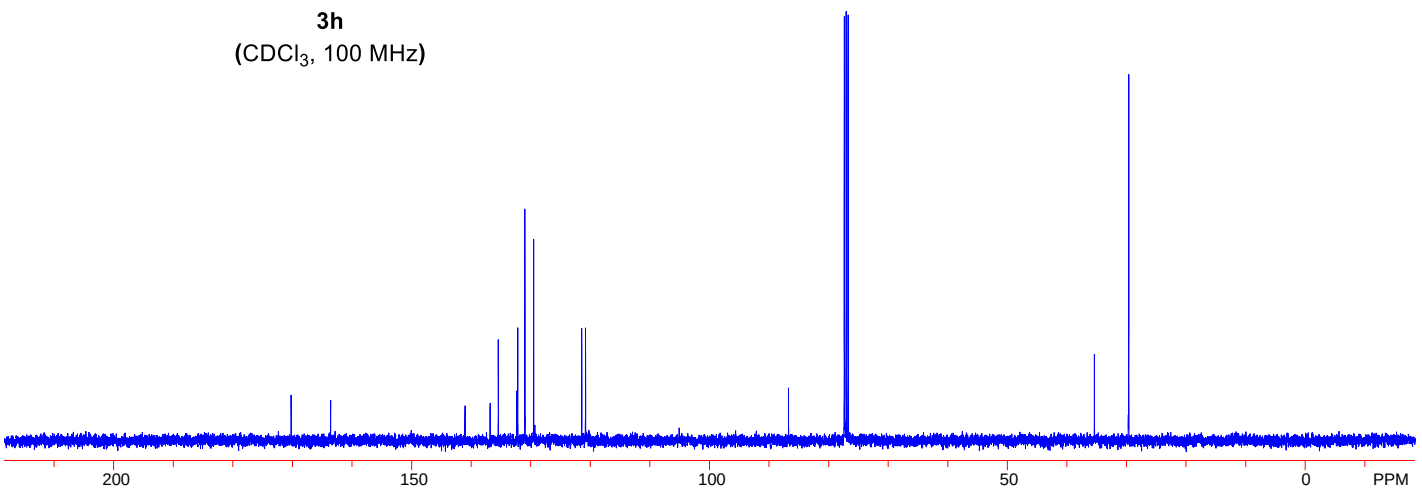
3h

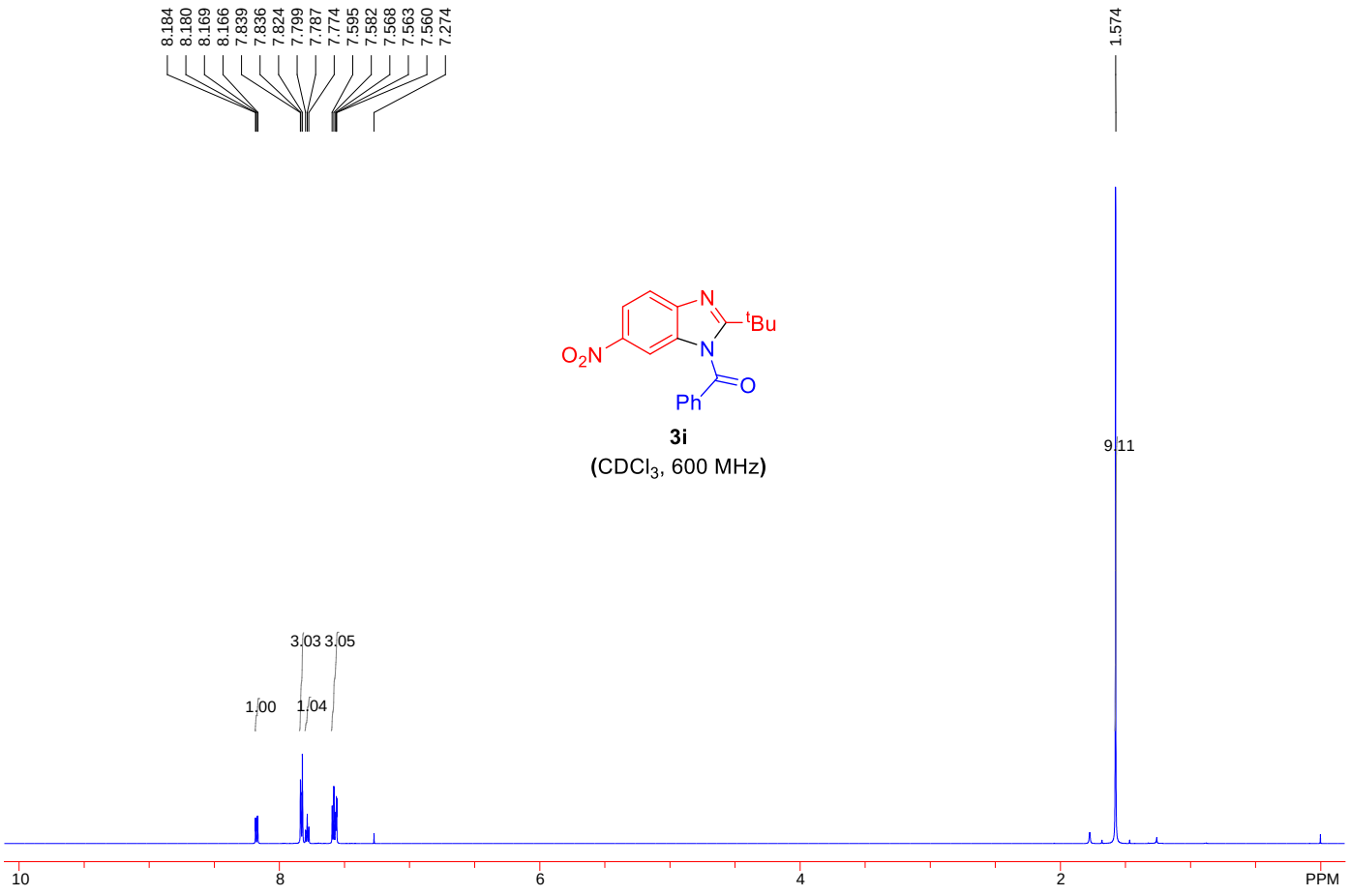
(CDCl$_3$, 600 MHz)



3h

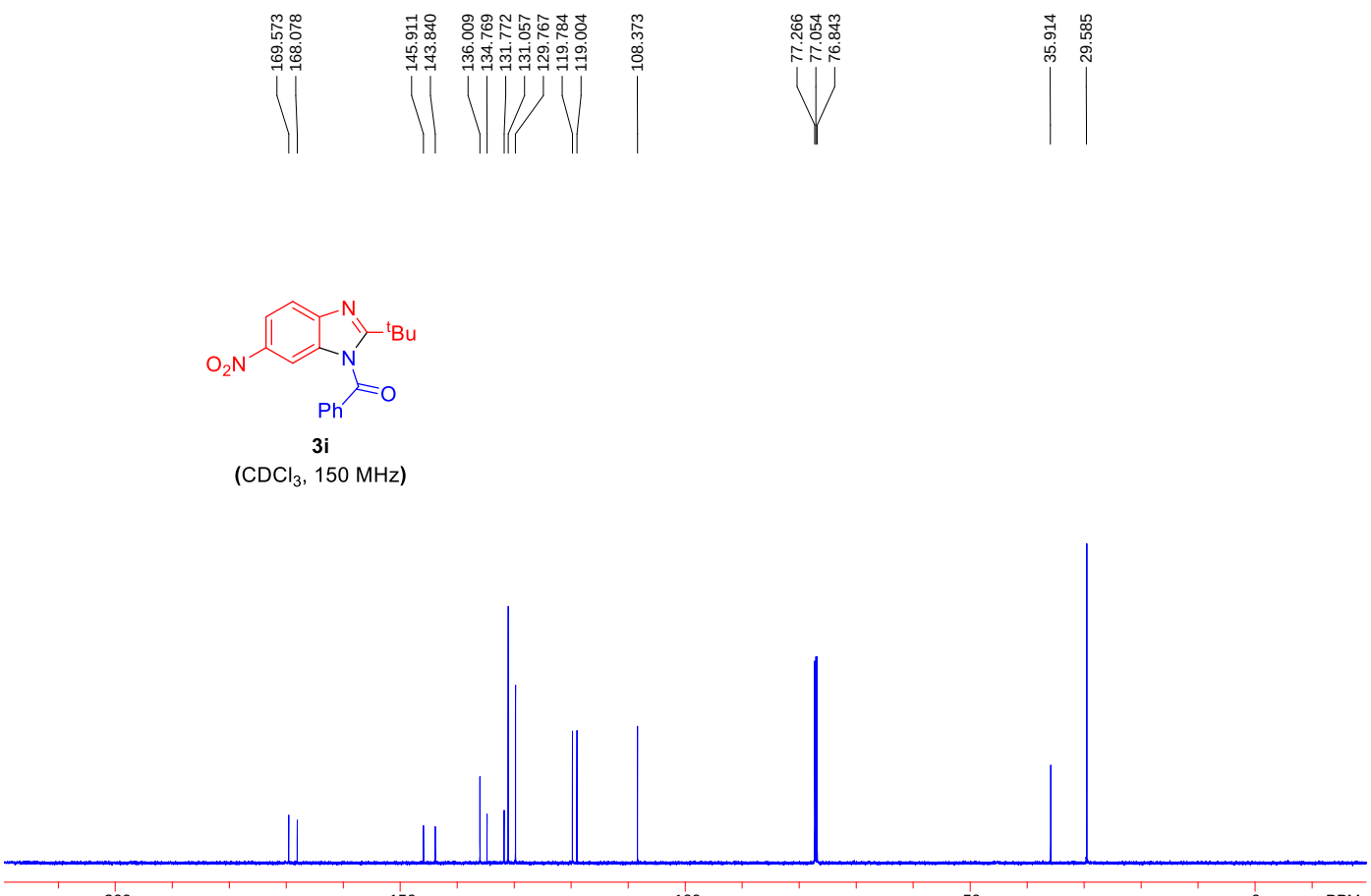
(CDCl$_3$, 100 MHz)





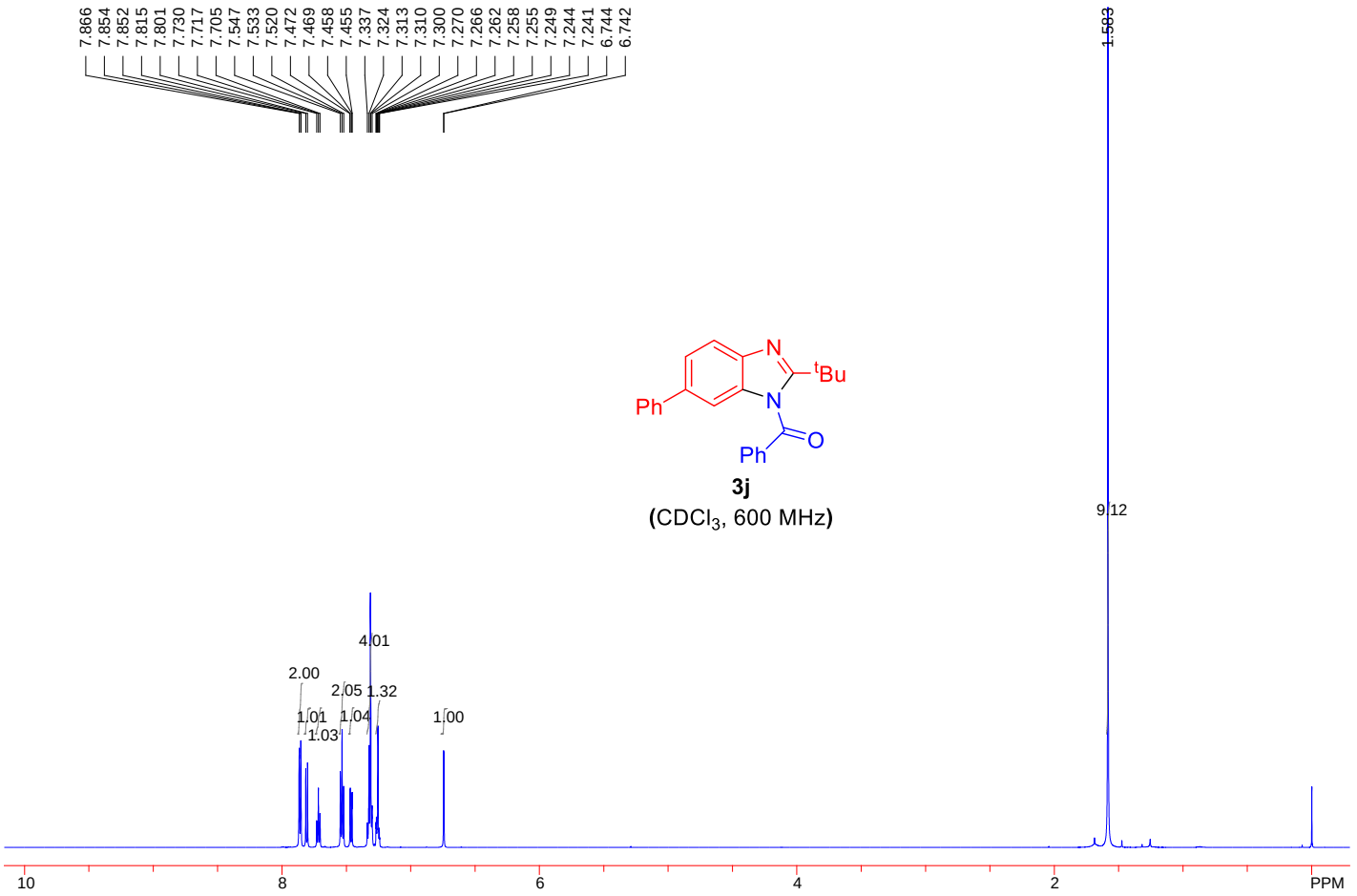
3i

(CDCl$_3$, 600 MHz)



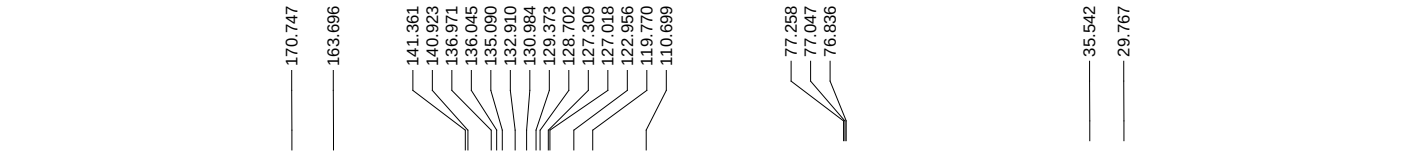
3i

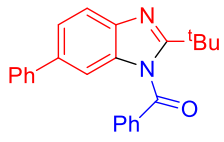
(CDCl$_3$, 150 MHz)



3j

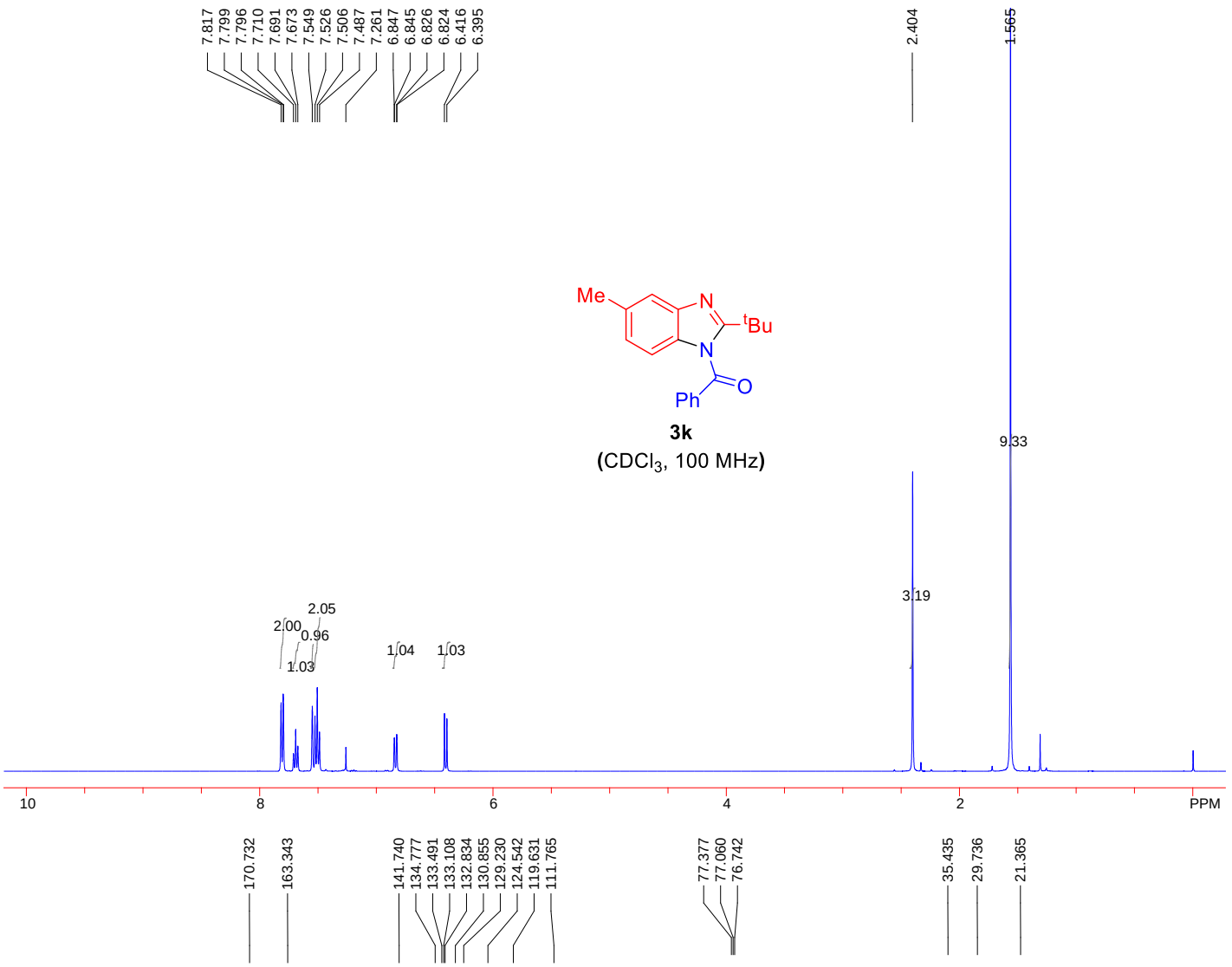
($CDCl_3$, 600 MHz)

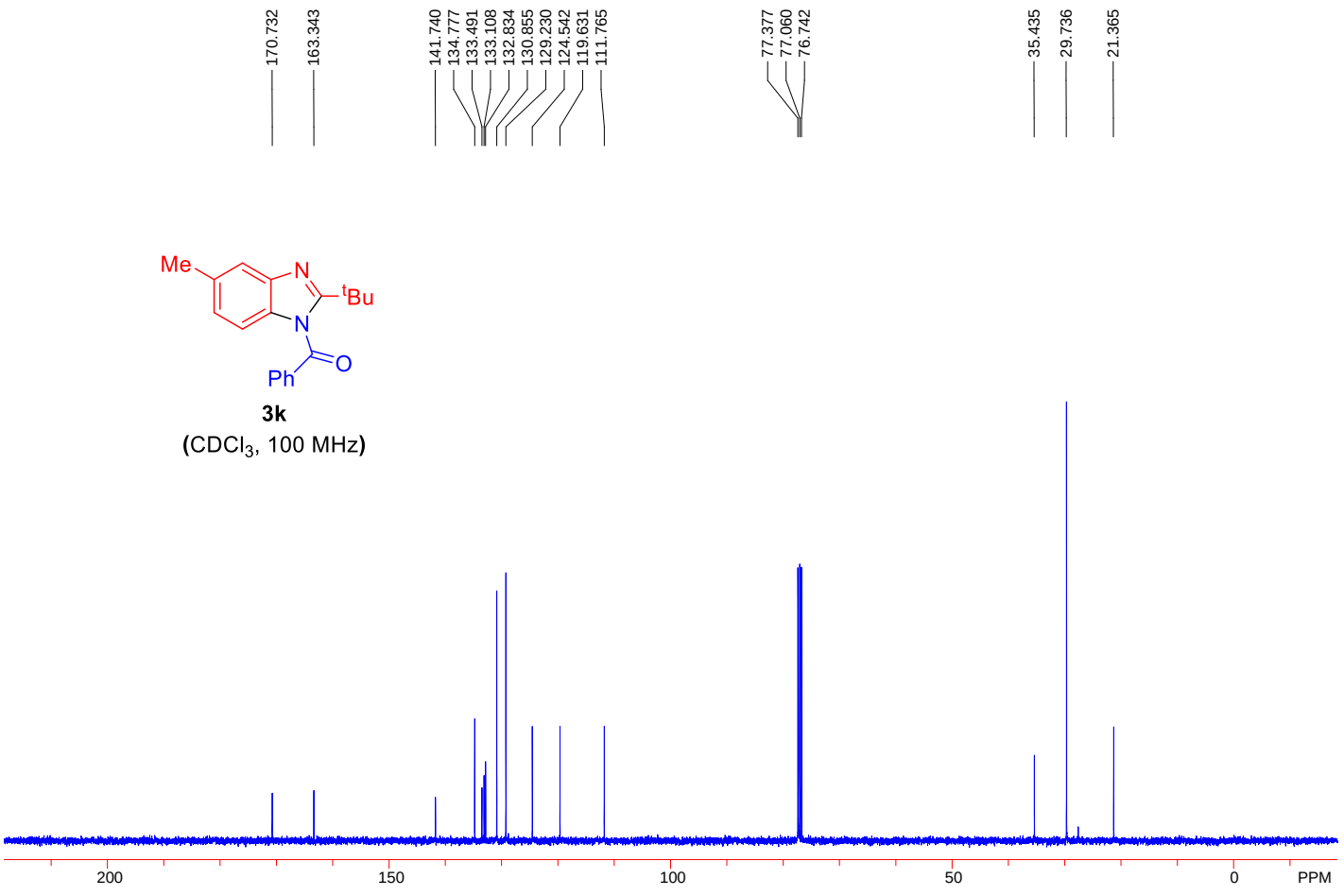


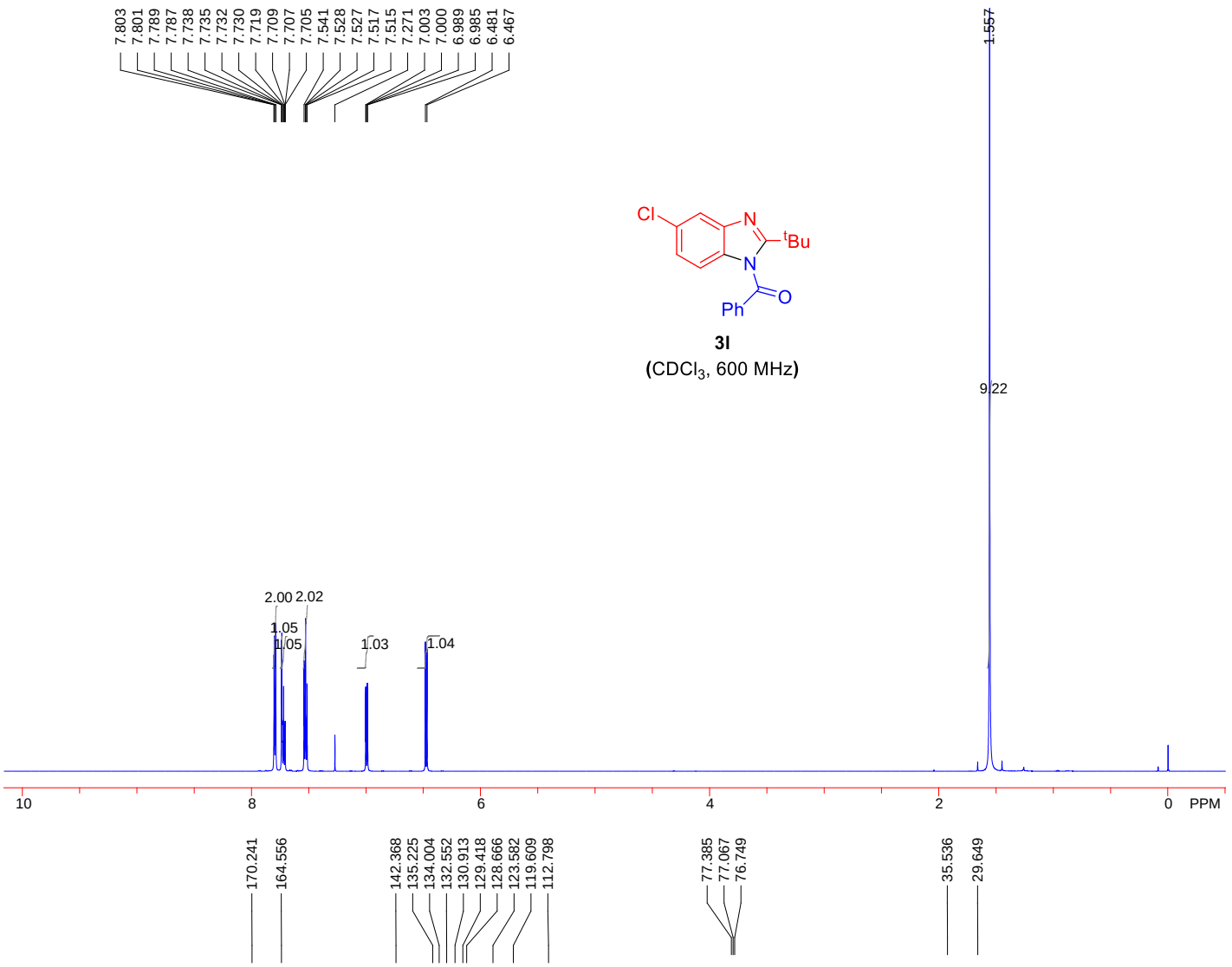


3j

($CDCl_3$, 150 MHz)

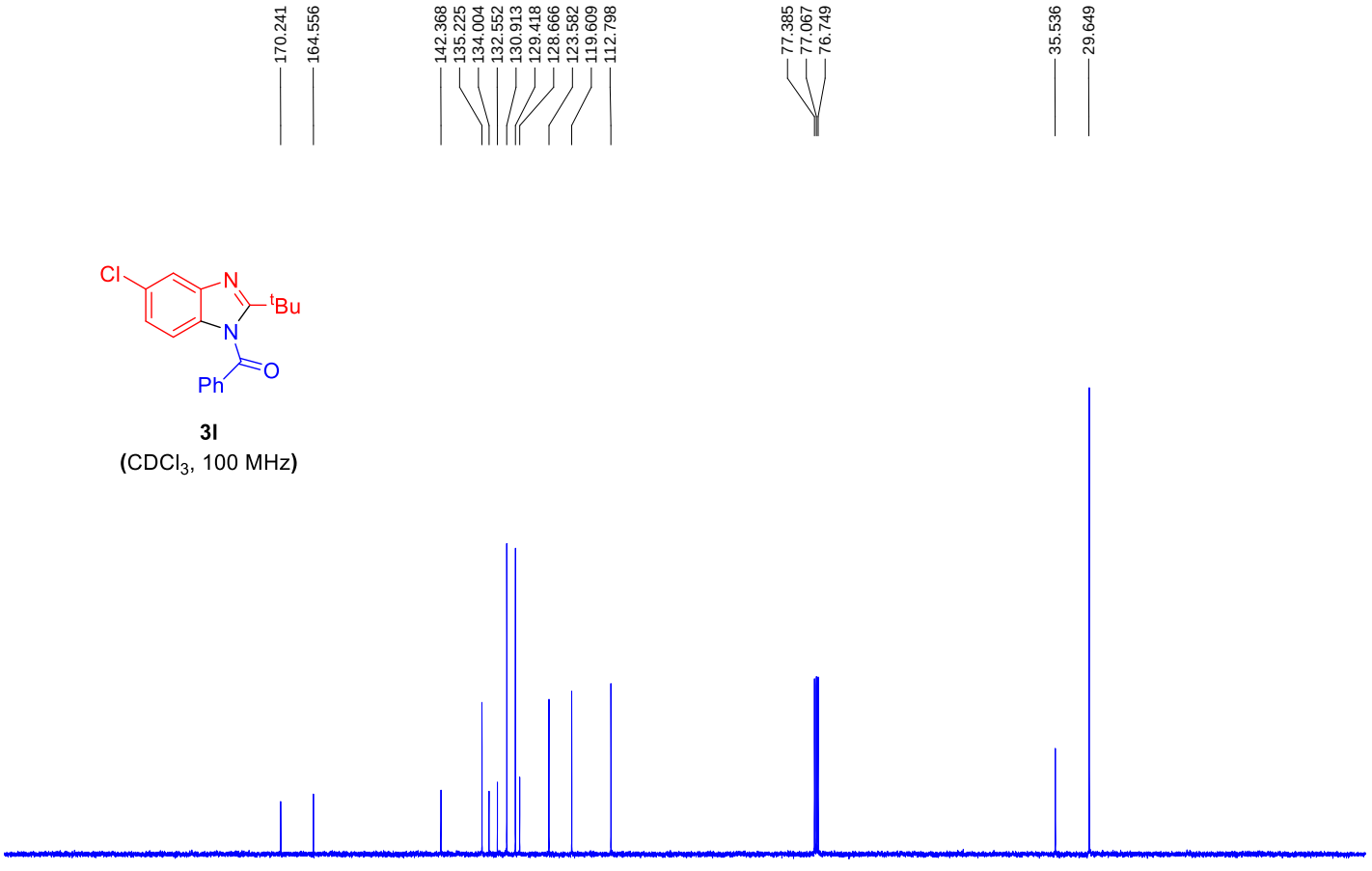

7.817
7.799
7.796
7.710
7.691
7.673
7.549
7.526
7.506
7.487
7.261
6.847
6.845
6.826
6.824
6.416
6.395
2.404
1.565
Me
N
tBu
N
O
Ph
3k
(CDCl3, 100 MHz)
9.33
3.19
2.05
2.00
0.96
1.03
1.04
1.03
10
8
6
4
2
PPM


170.732
163.343
141.740
134.777
133.491
133.108
132.834
130.855
129.230
124.542
119.631
111.765
77.377
77.060
76.742
35.435
29.736
21.365
Me
N
tBu
N
O
Ph
3k
(CDCl3, 100 MHz)
200
150
100
50
0
PPM



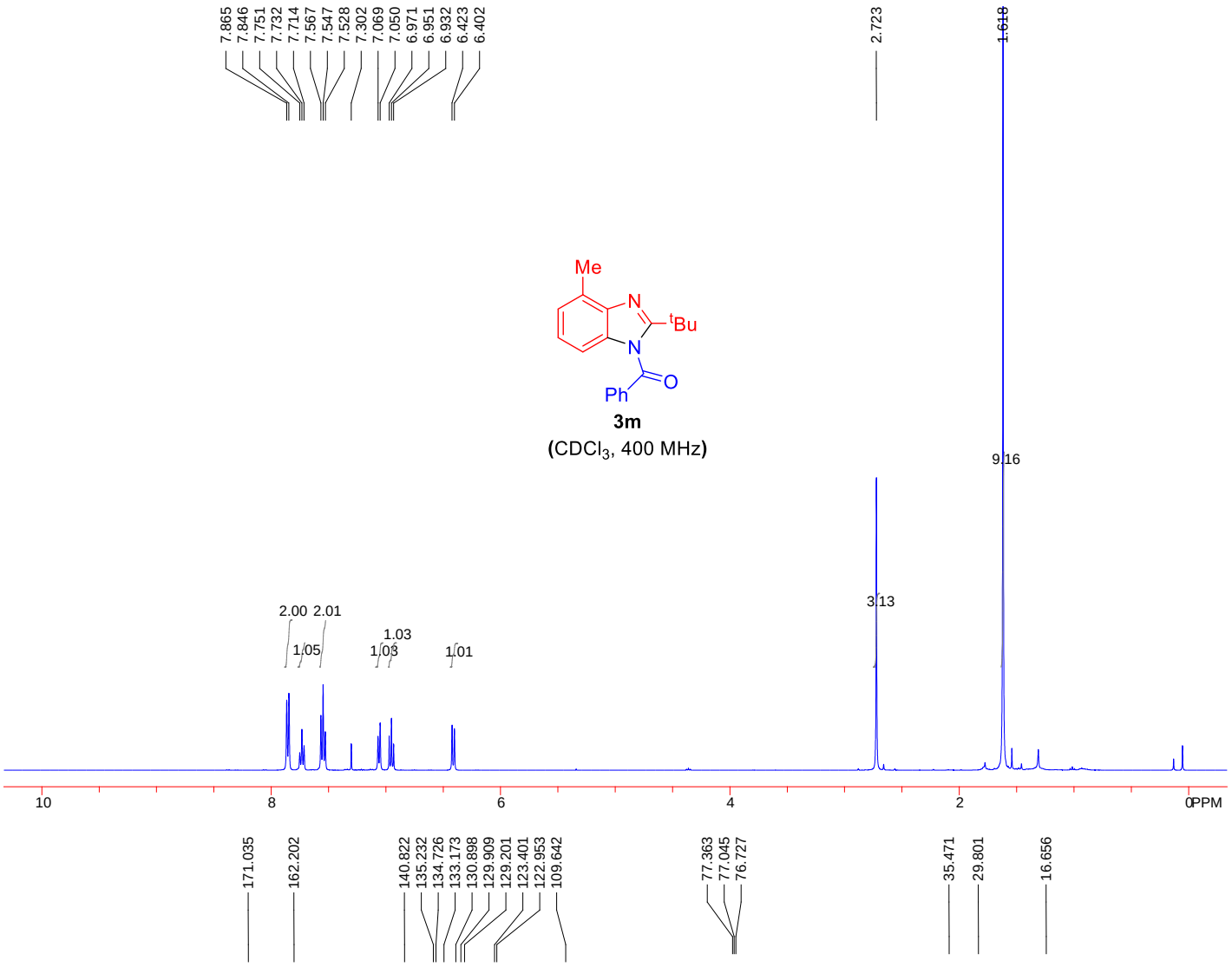
3l

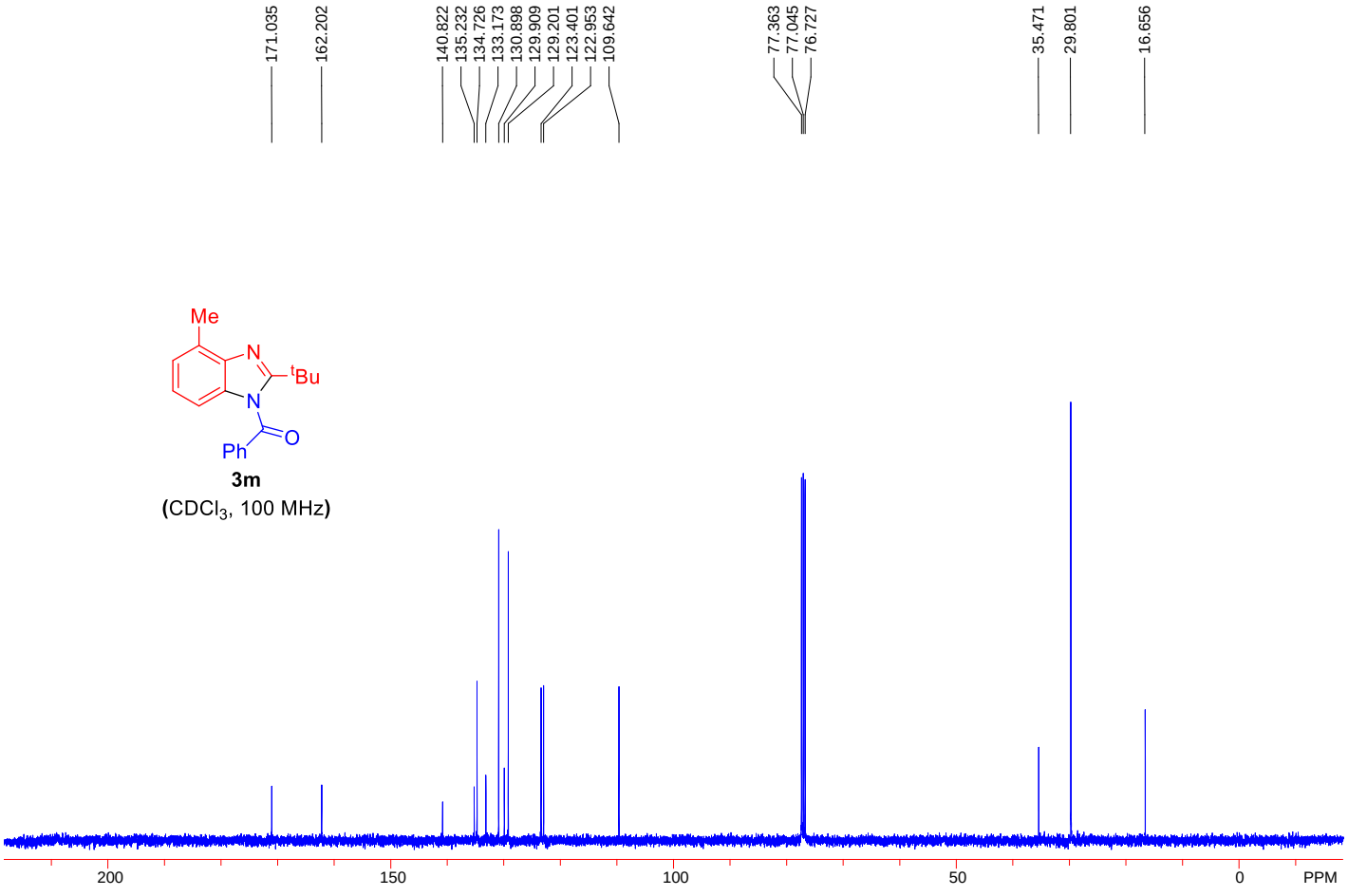
($CDCl_3$, 600 MHz)

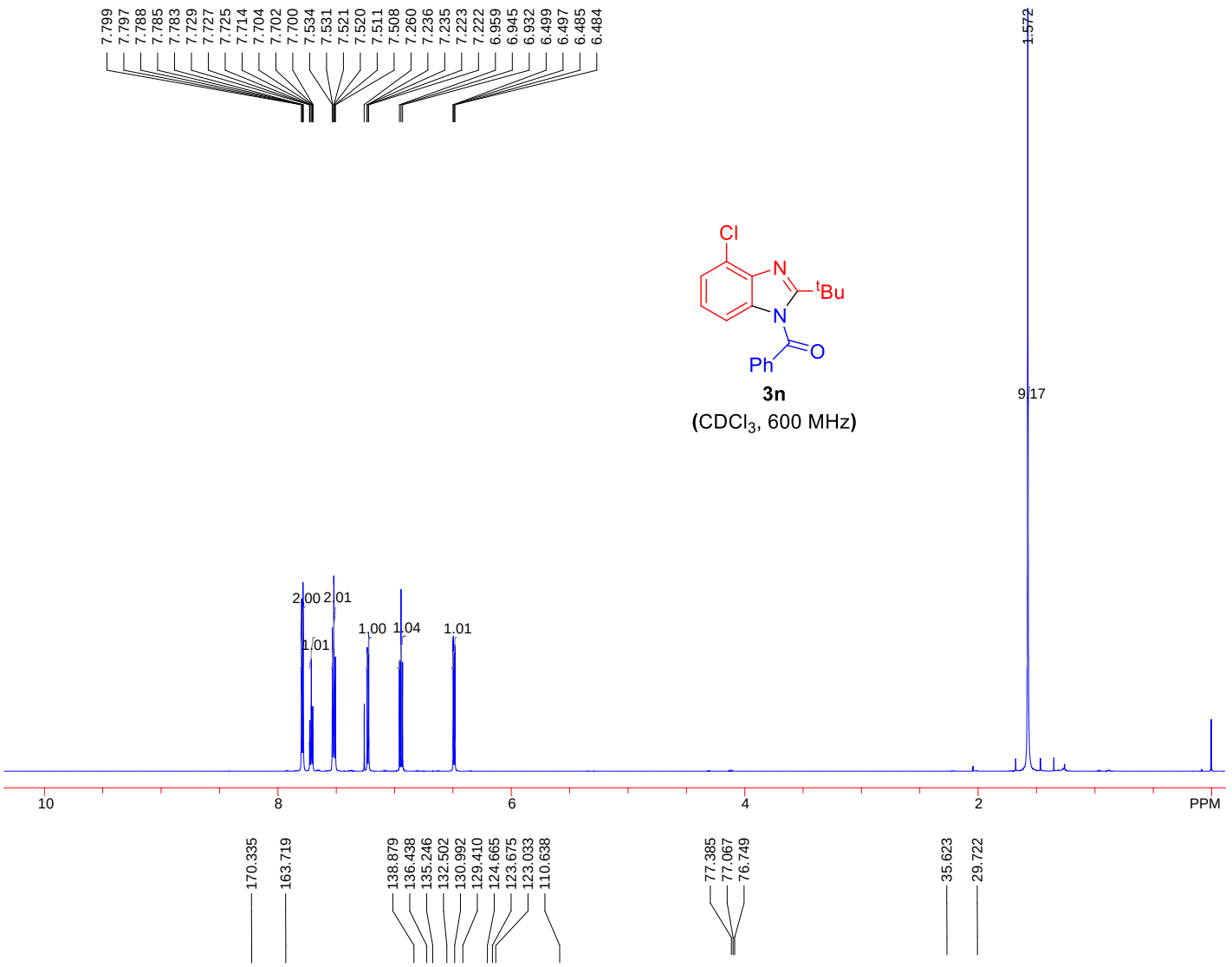


3l

($CDCl_3$, 100 MHz)

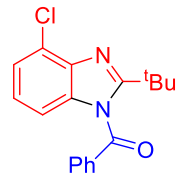

7.865
7.846
7.751
7.732
7.714
7.567
7.547
7.528
7.302
7.069
7.050
6.971
6.951
6.932
6.423
6.402
2.723
1.618
Me
N
tBu
N
O
Ph
3m
(CDCl3, 400 MHz)
9.16
3.13
2.00
2.01
1.05
1.03
1.03
1.01
10
8
6
4
2
0
PPM


171.035
162.202
140.822
135.232
134.726
133.173
130.898
129.909
129.201
123.401
122.953
109.642
77.363
77.045
76.727
35.471
29.801
16.656
Me
N
tBu
N
O
Ph
3m
(CDCl3, 100 MHz)
200
150
100
50
0
PPM



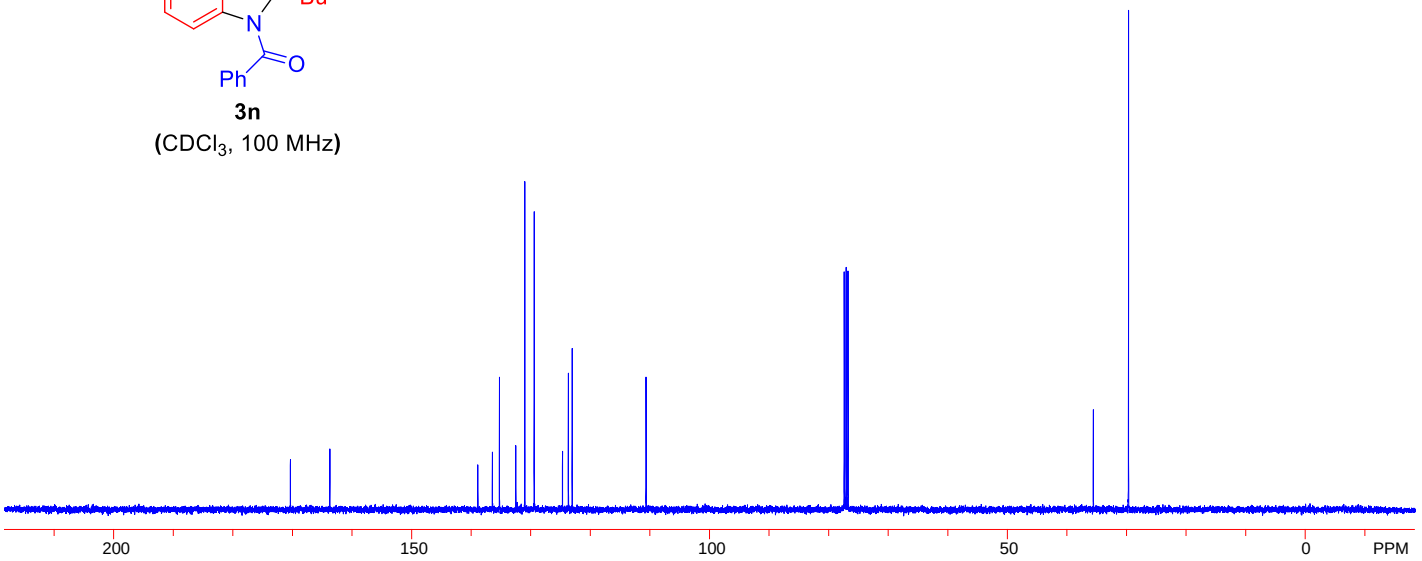
3n

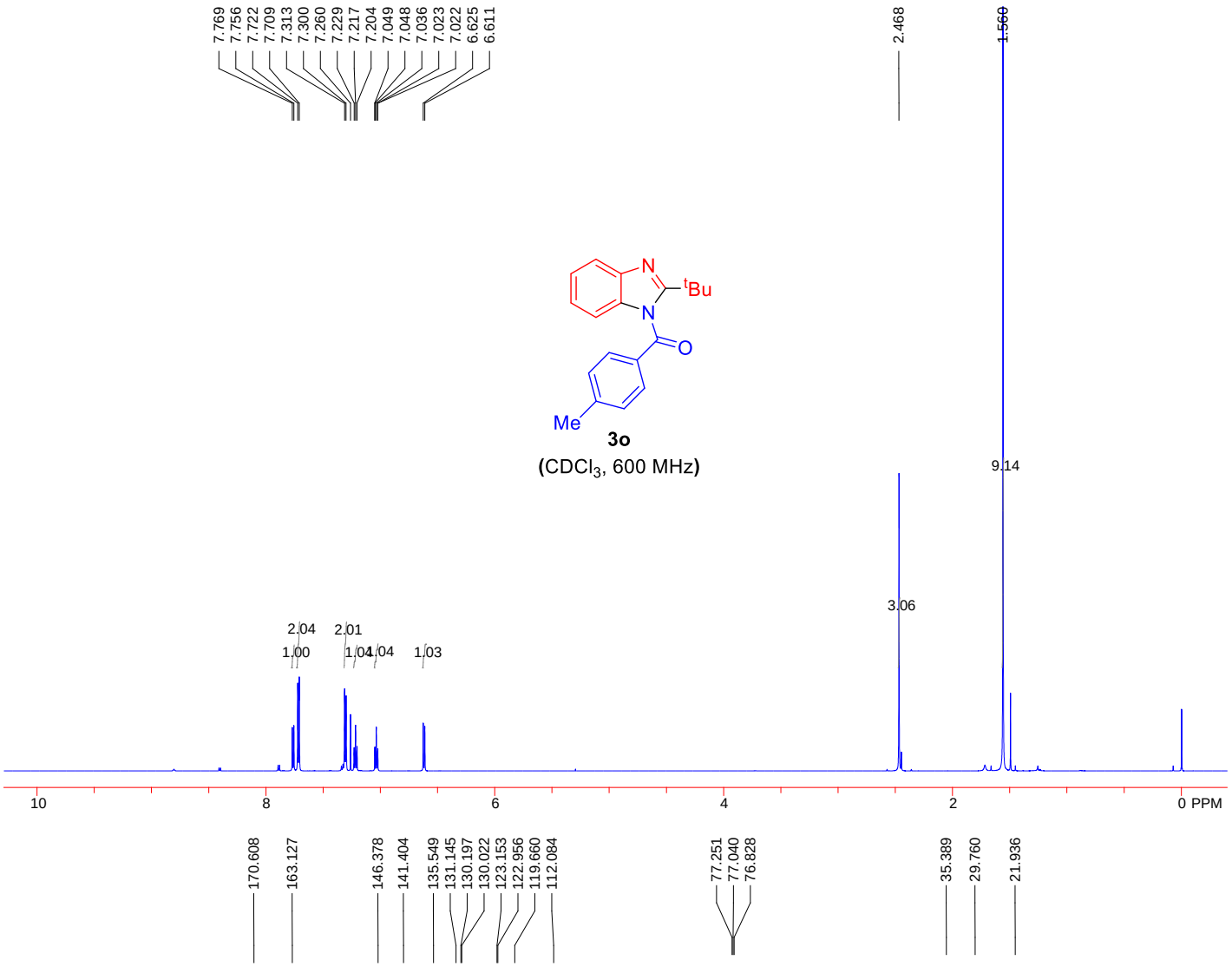
(CDCl$_3$, 600 MHz)

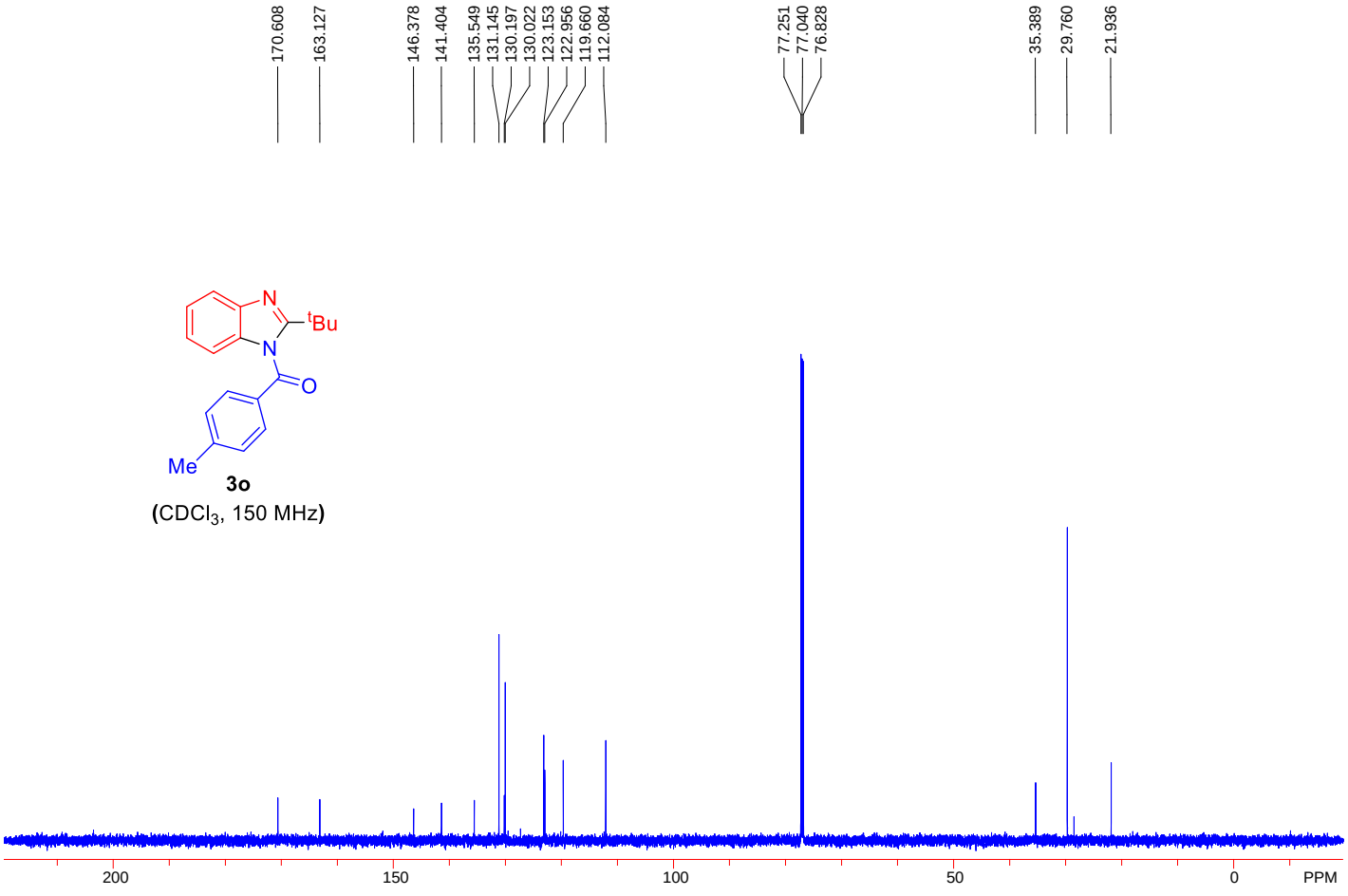


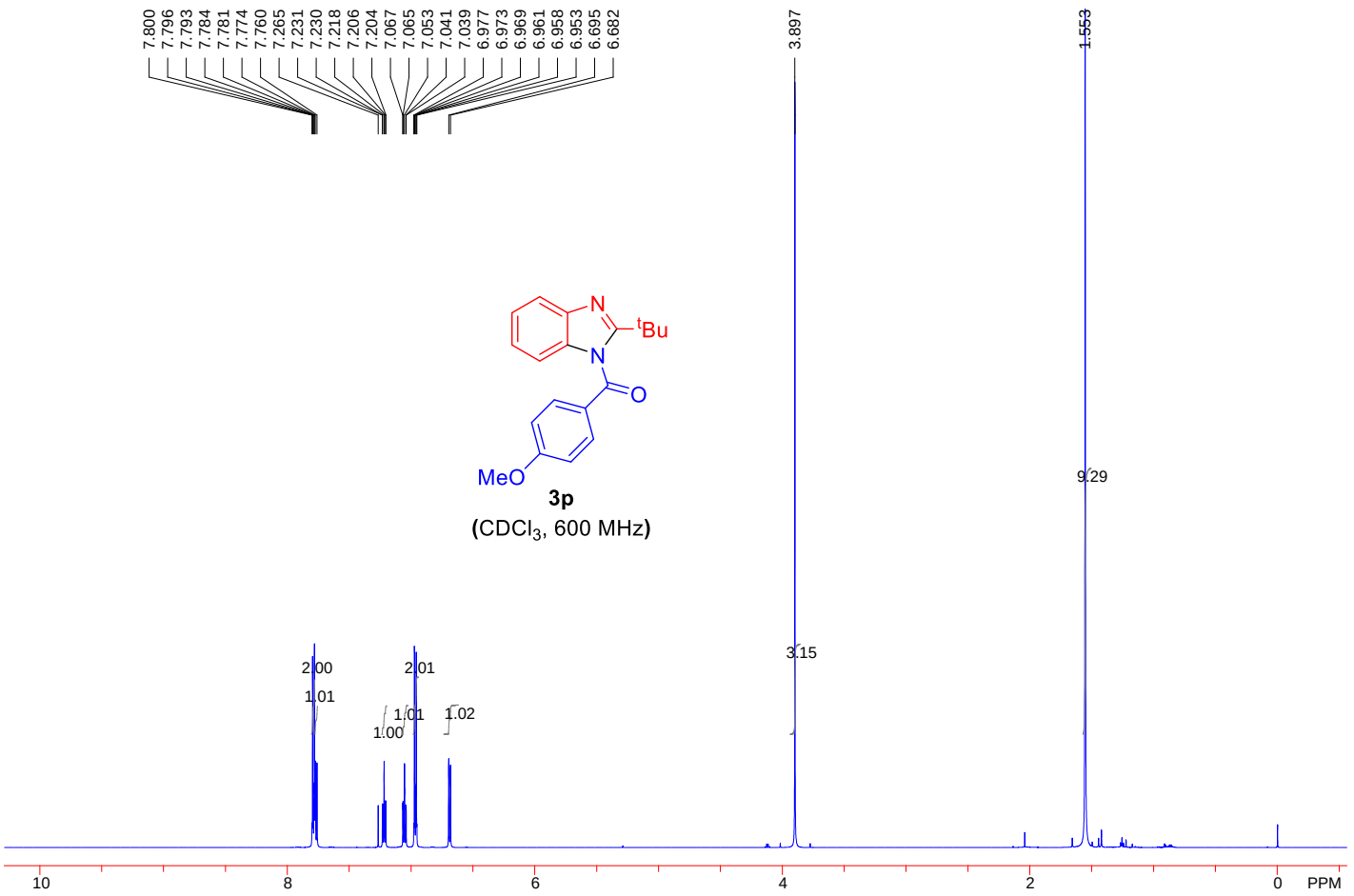
3n

(CDCl$_3$, 100 MHz)



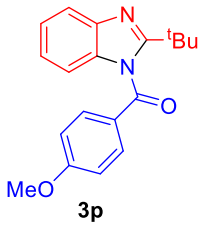

7.769
7.756
7.722
7.709
7.313
7.300
7.260
7.229
7.217
7.204
7.049
7.048
7.036
7.023
7.022
6.625
6.611
2.468
1.560
N
tBu
N
O
Me
3o
(CDCl3, 600 MHz)
9.14
3.06
2.04
2.01
1.00
1.04
1.04
1.03
10
8
6
4
2
0 PPM


170.608
163.127
146.378
141.404
135.549
131.145
130.197
130.022
123.153
122.956
119.660
112.084
77.251
77.040
76.828
35.389
29.760
21.936
N
tBu
N
O
Me
3o
(CDCl3, 150 MHz)
200
150
100
50
0
PPM



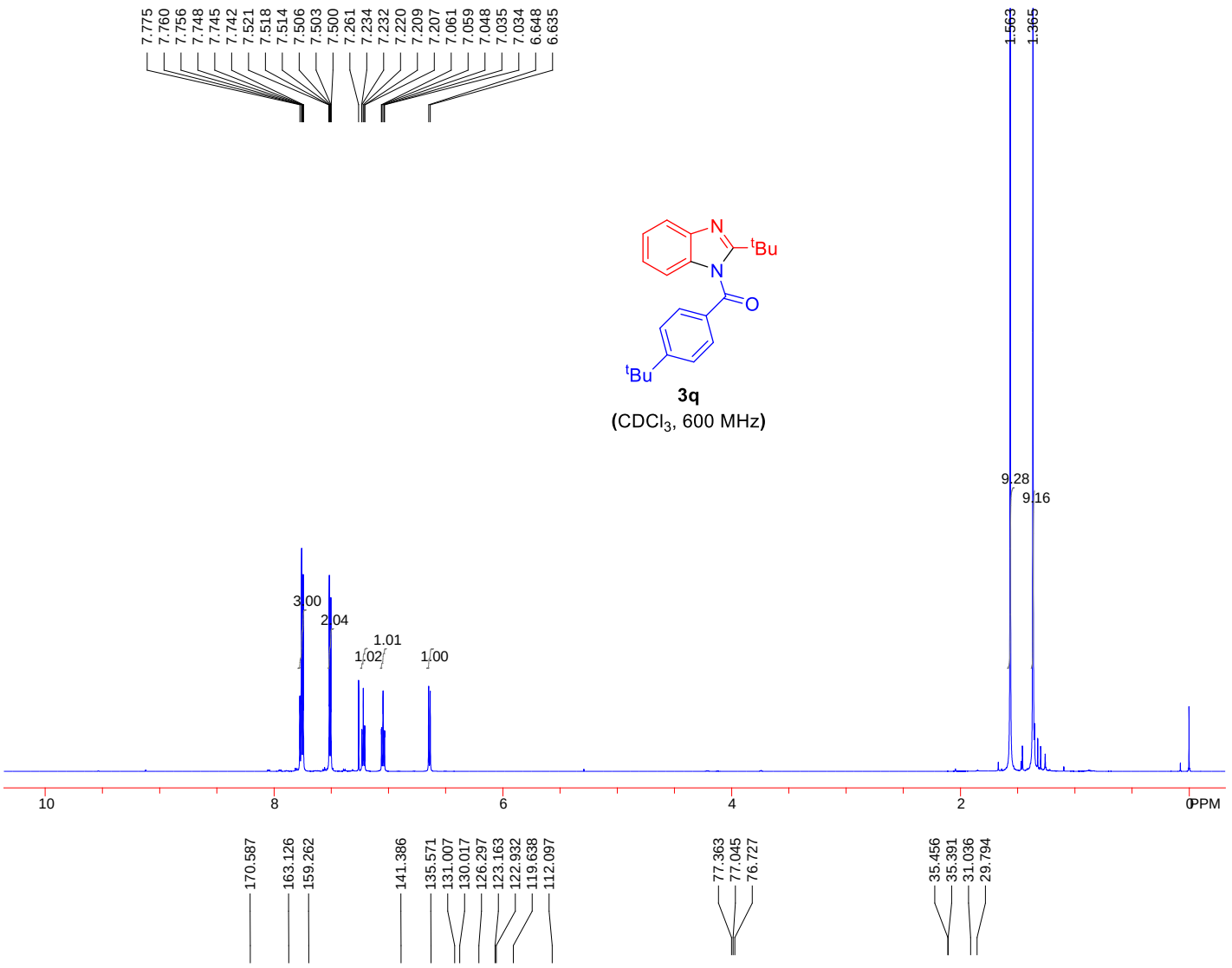
3p

($CDCl_3$, 600 MHz)



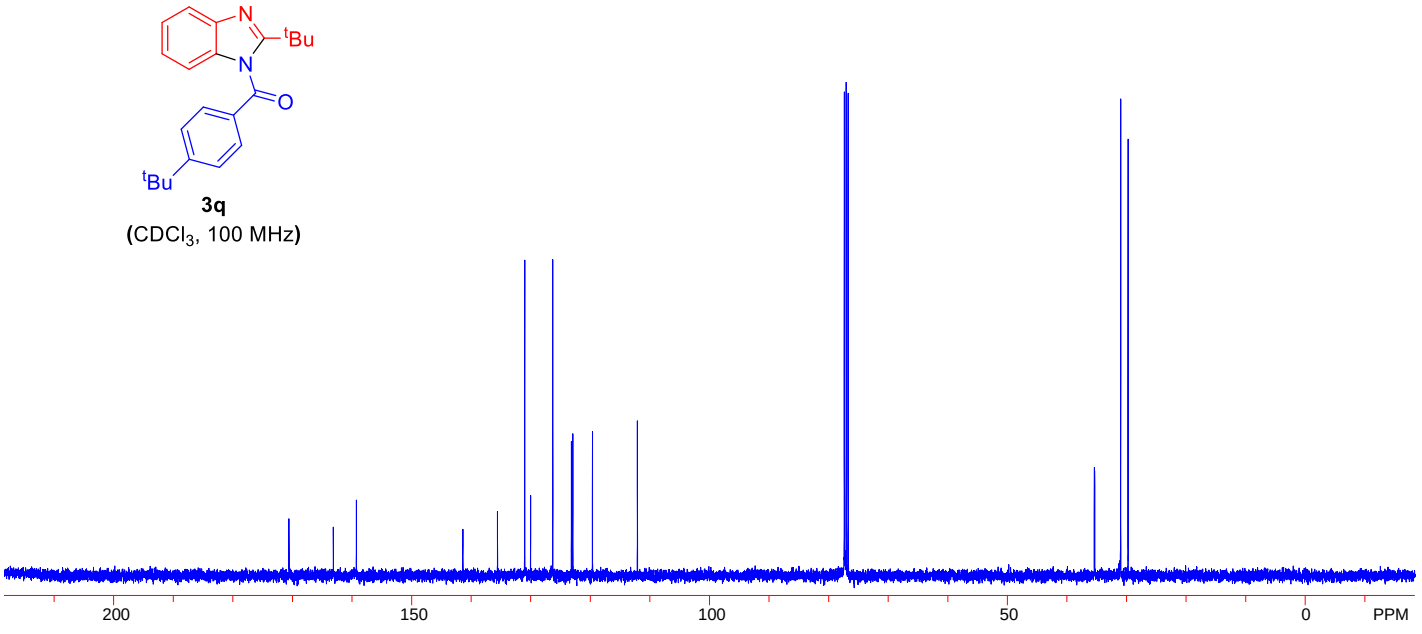
3p

($CDCl_3$, 150 MHz)



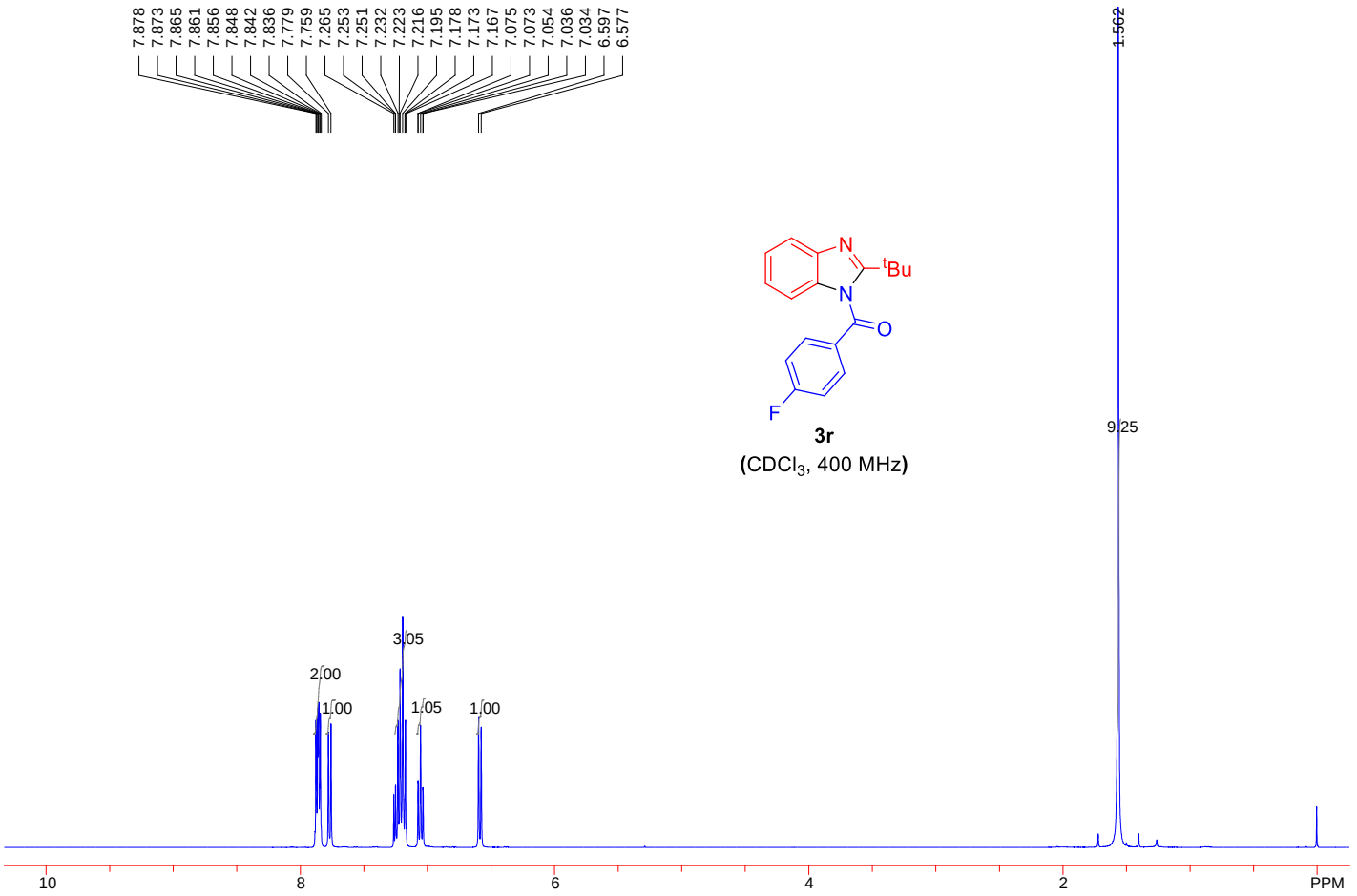
3q

($CDCl_3$, 600 MHz)



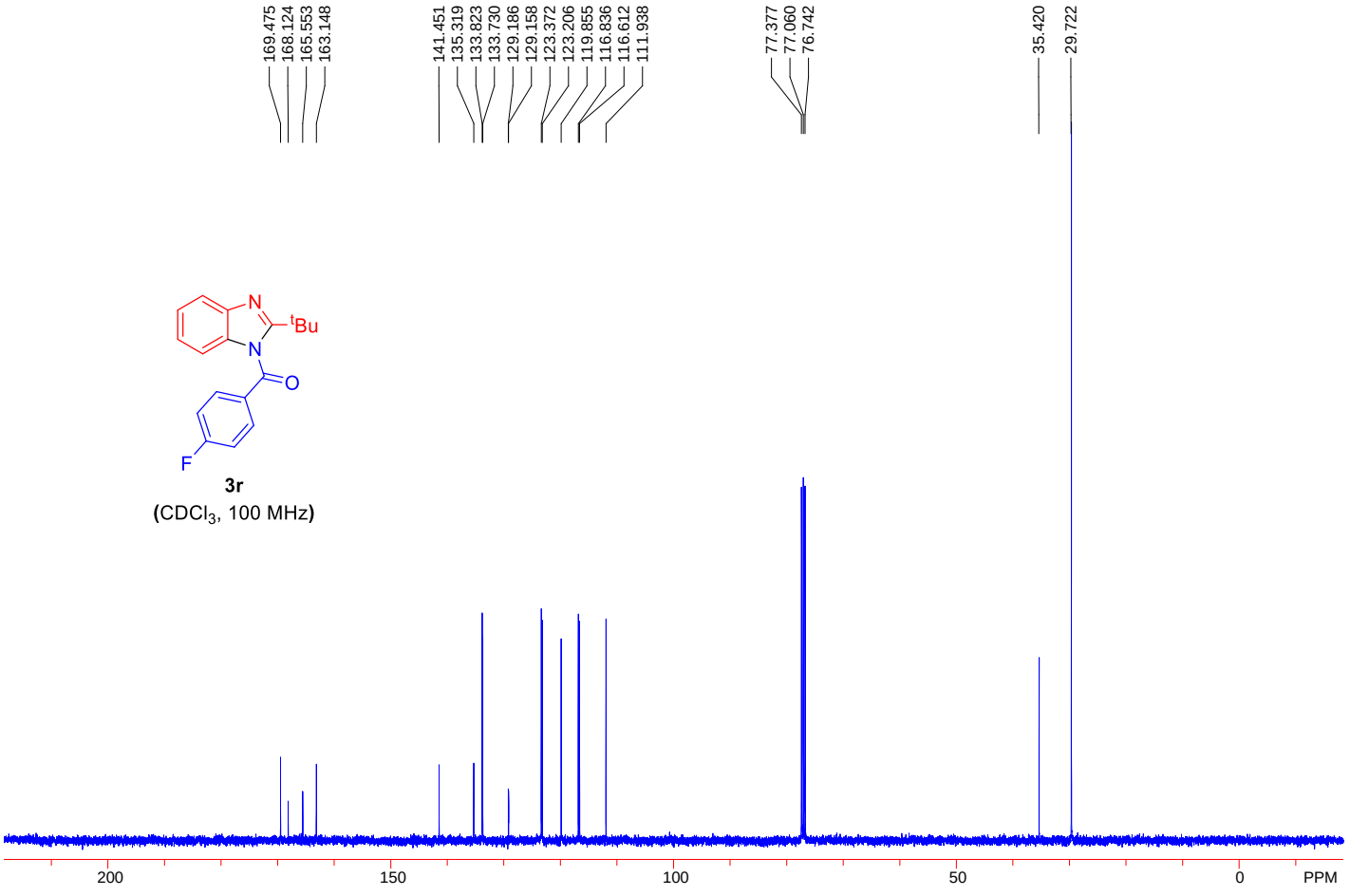
3q

($CDCl_3$, 100 MHz)



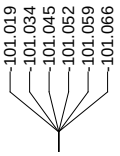
3r

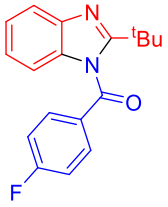
($CDCl_3$, 400 MHz)



3r

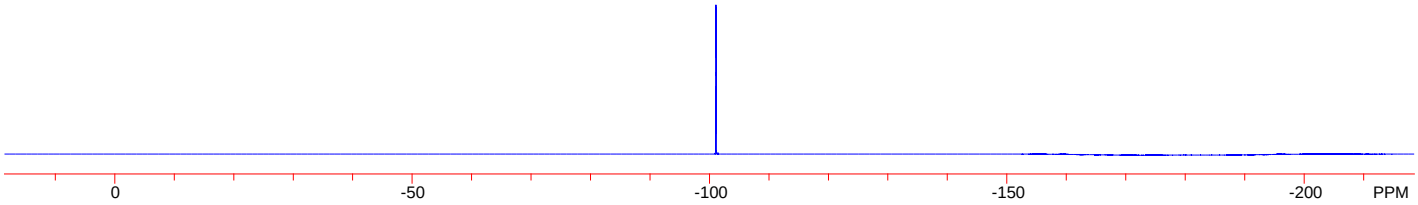
($CDCl_3$, 100 MHz)

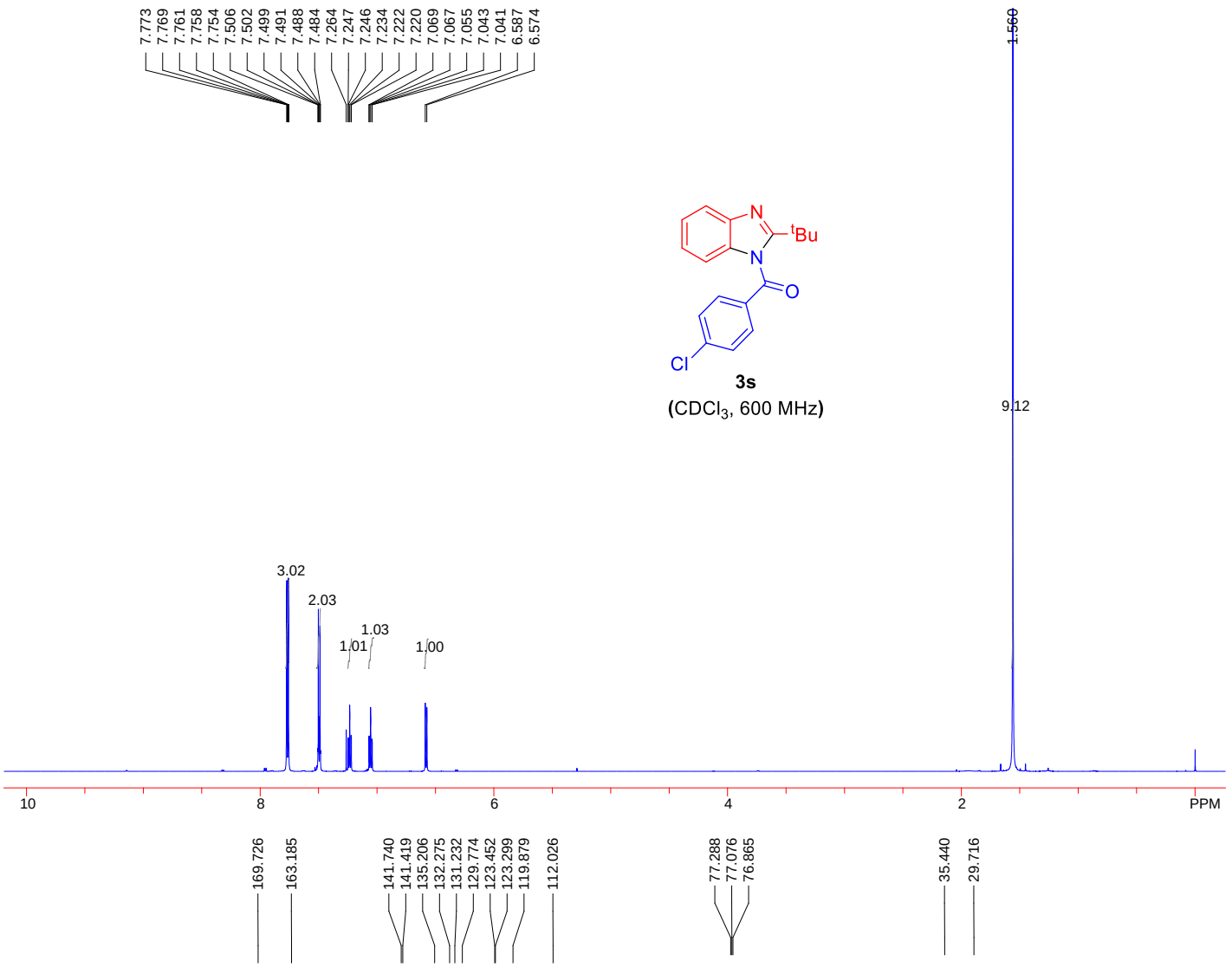




3r

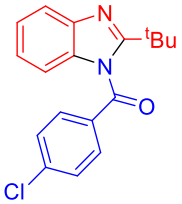
(CDCl$_3$, 565 MHz)





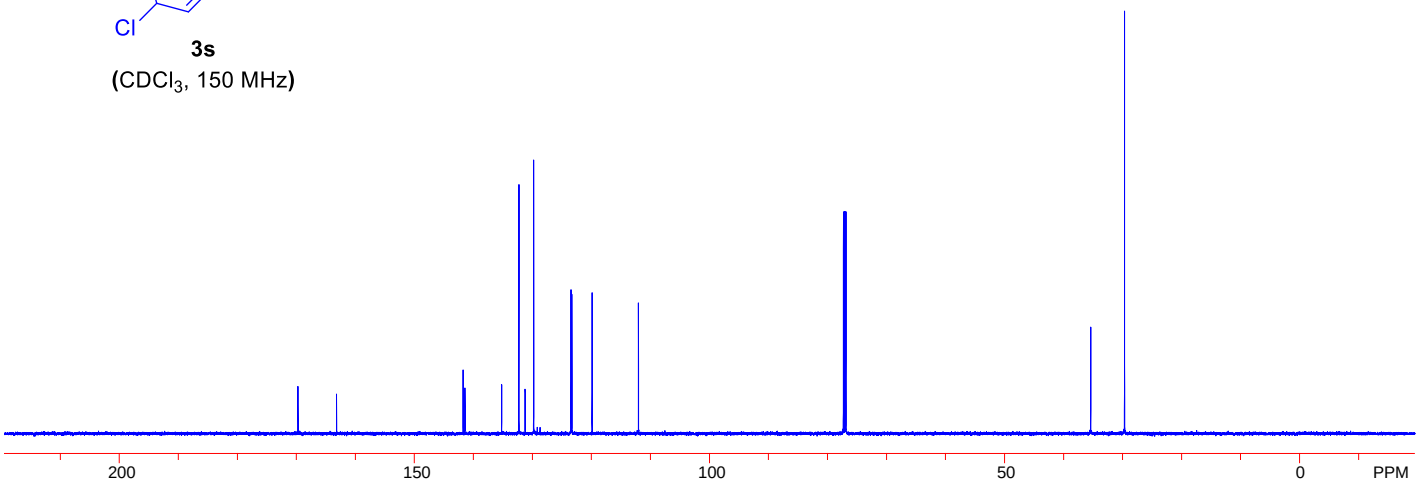
3s

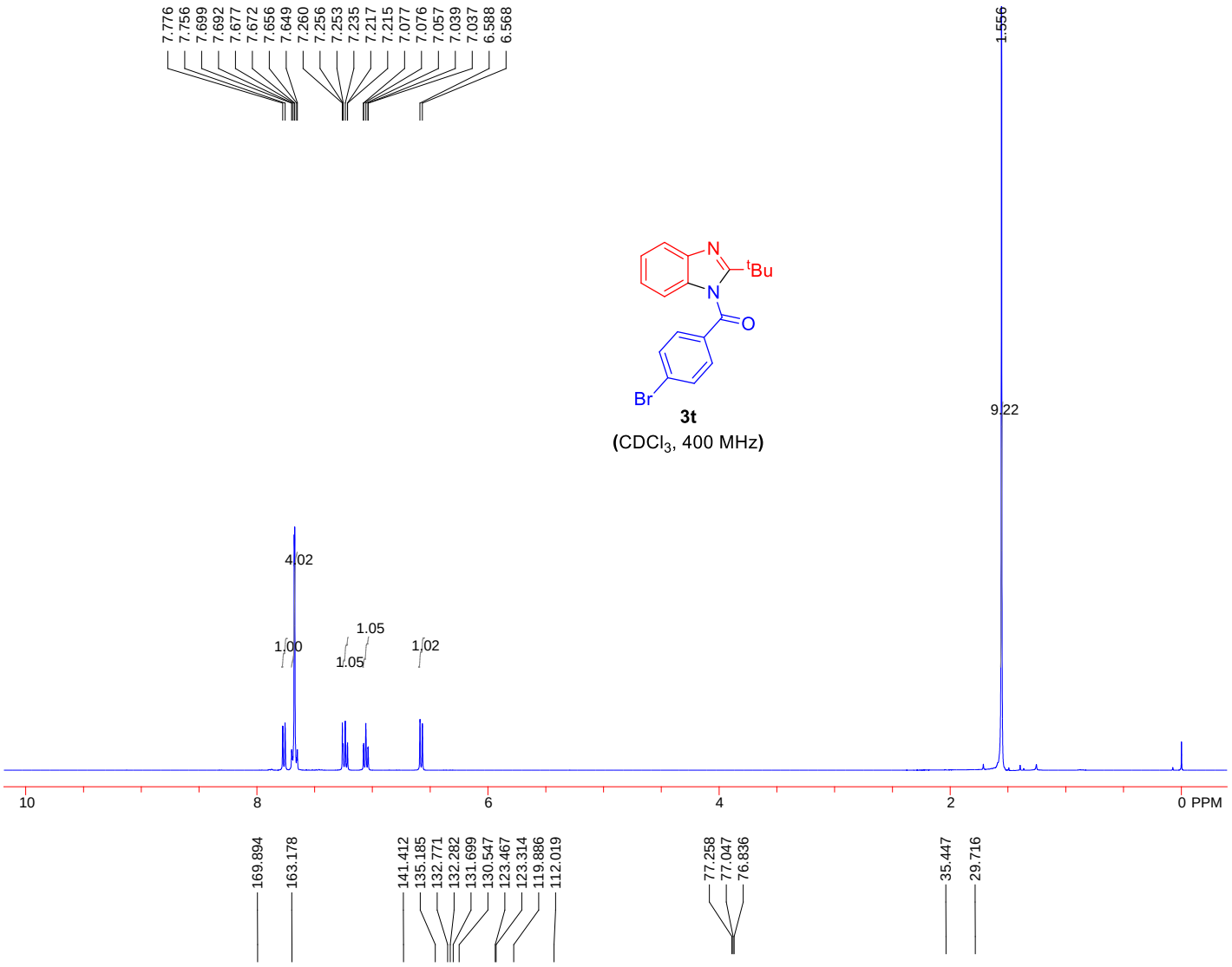
($CDCl_3$, 600 MHz)



3s

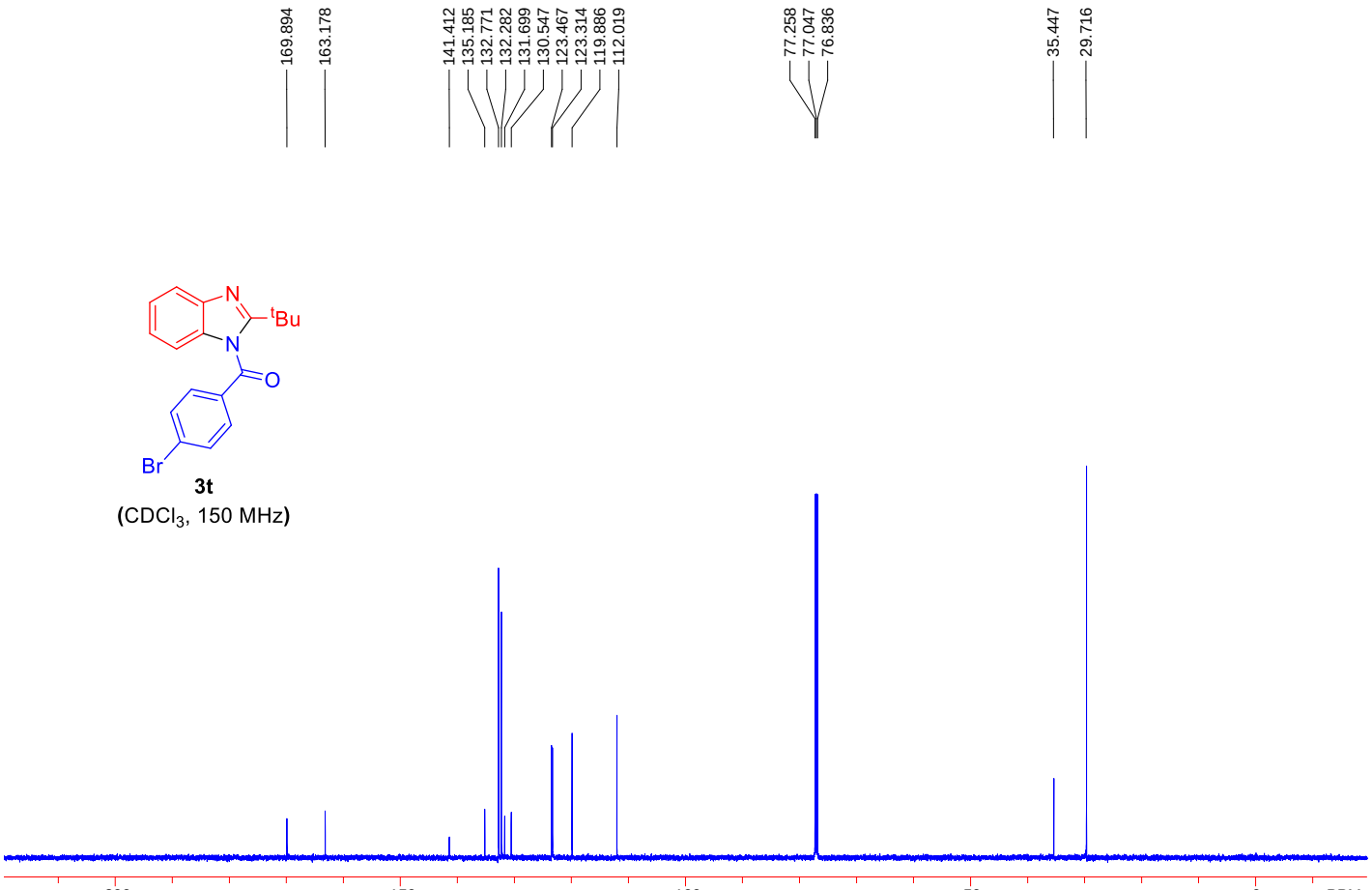
($CDCl_3$, 150 MHz)





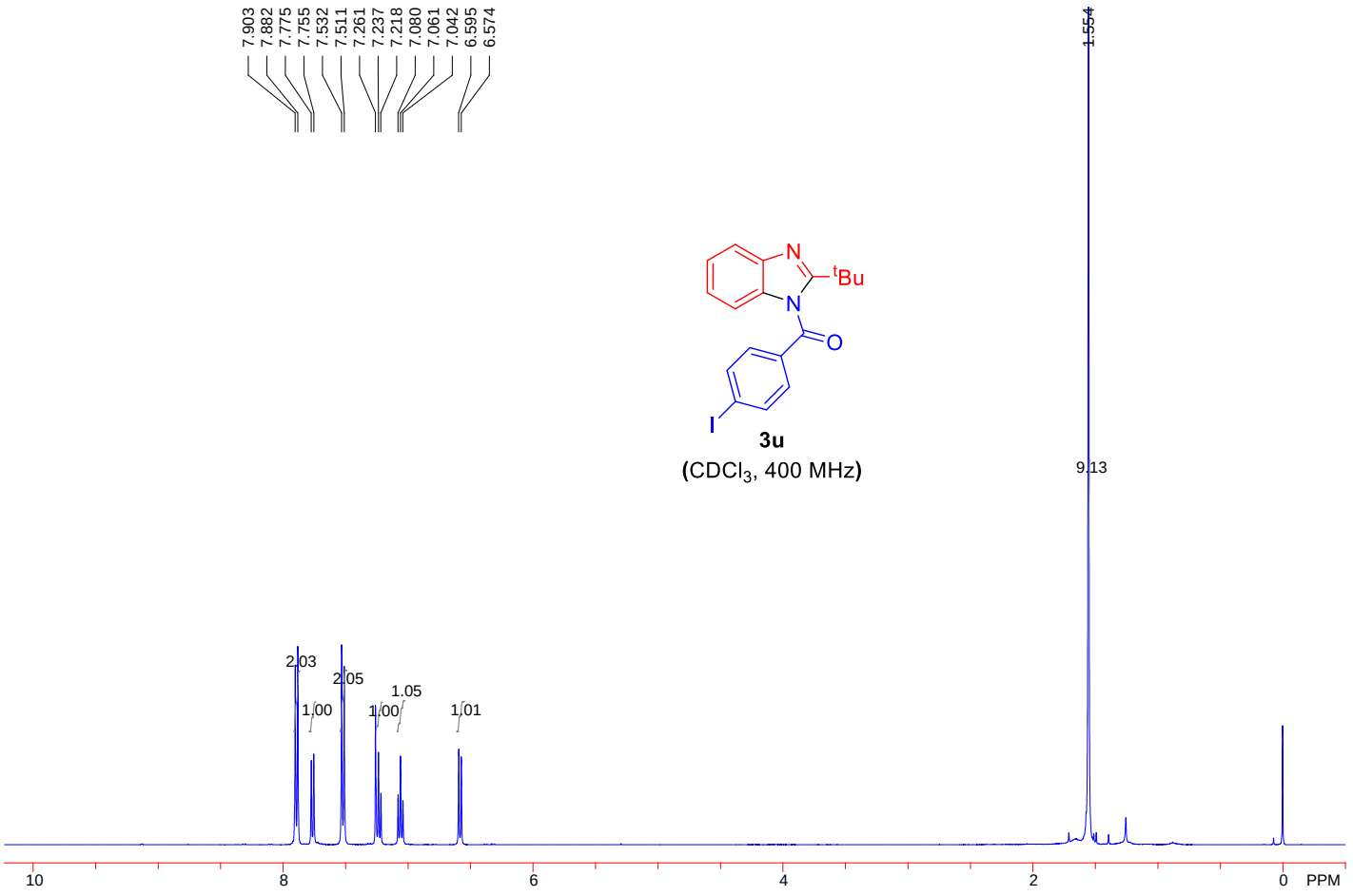
3t

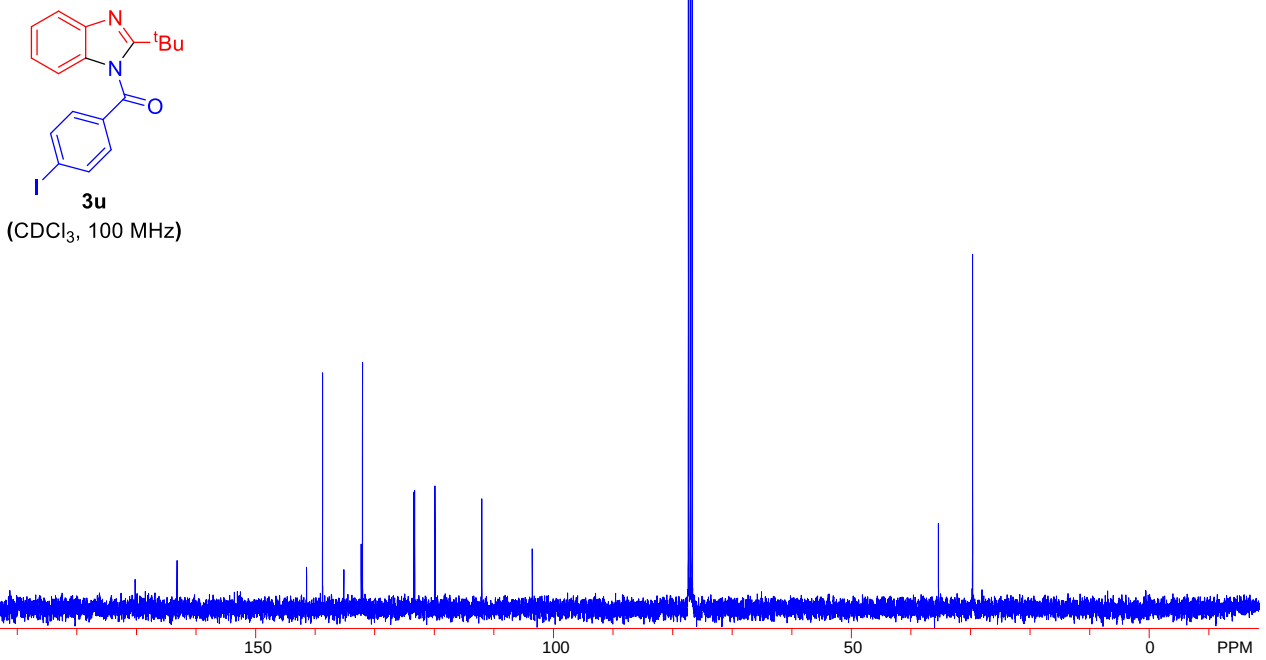
(CDCl$_3$, 400 MHz)



3t

(CDCl$_3$, 150 MHz)



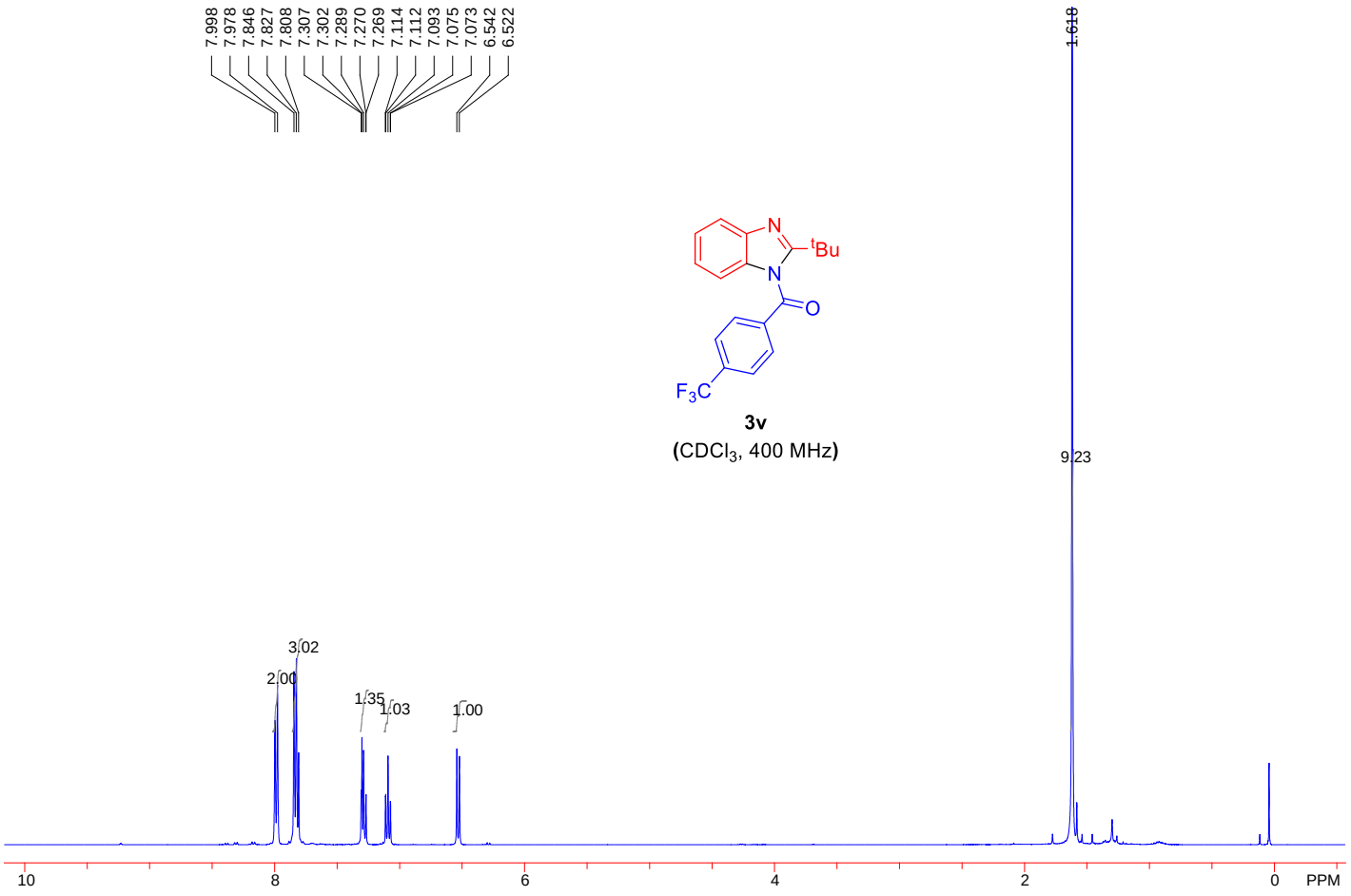


3u

($CDCl_3$, 400 MHz)

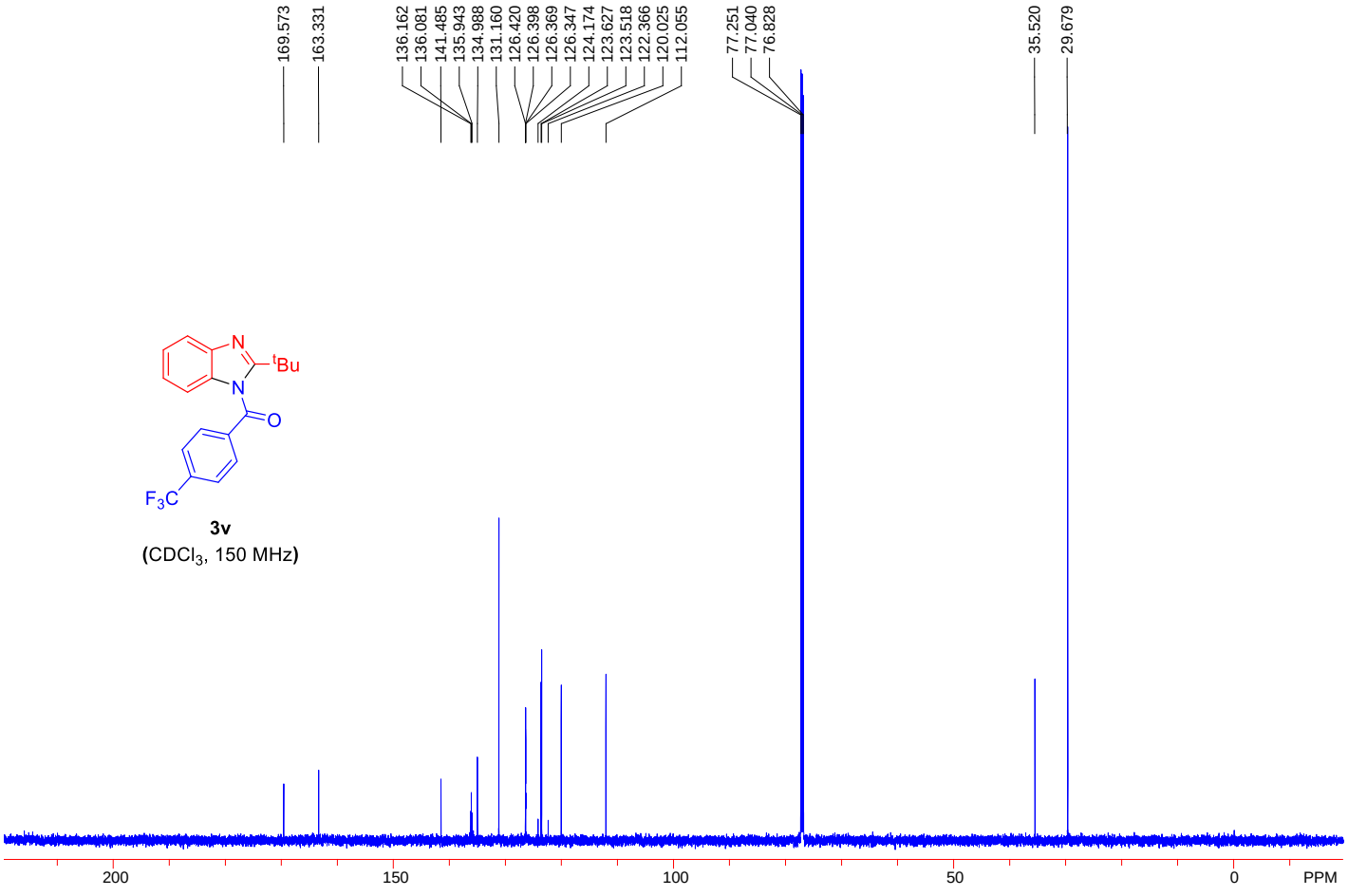
3u

($CDCl_3$, 100 MHz)



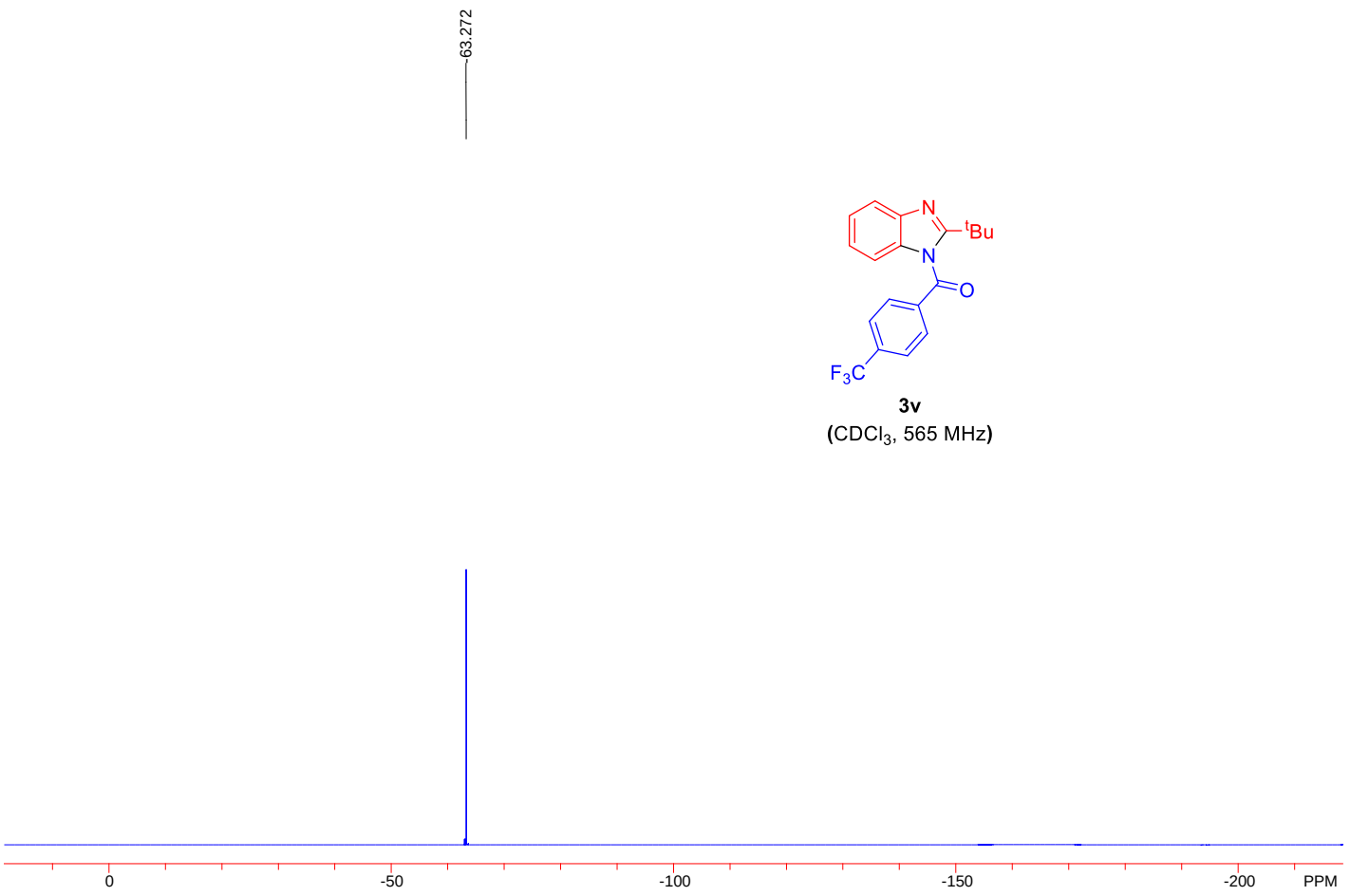
3v

(CDCl$_3$, 400 MHz)



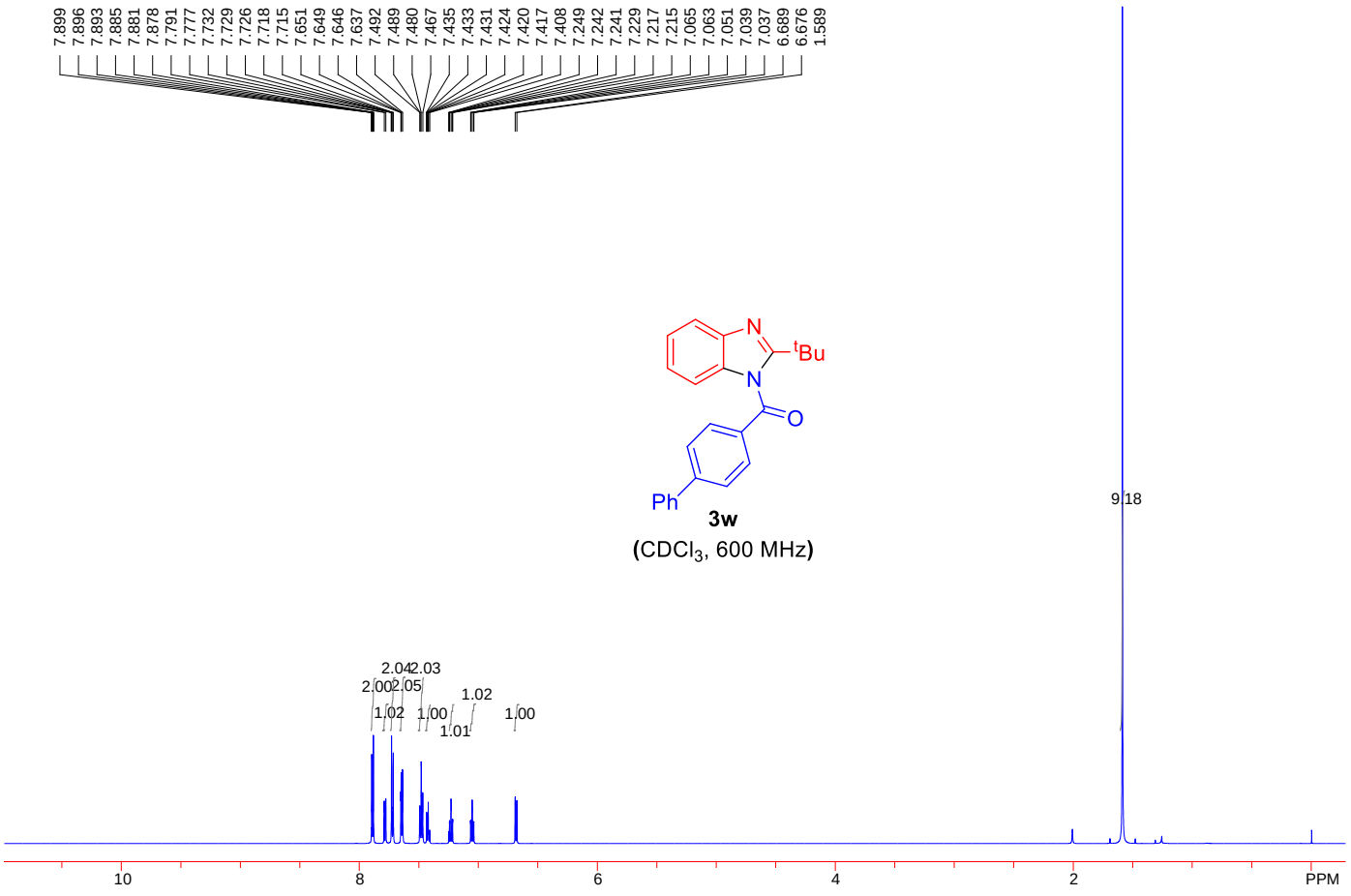
3v

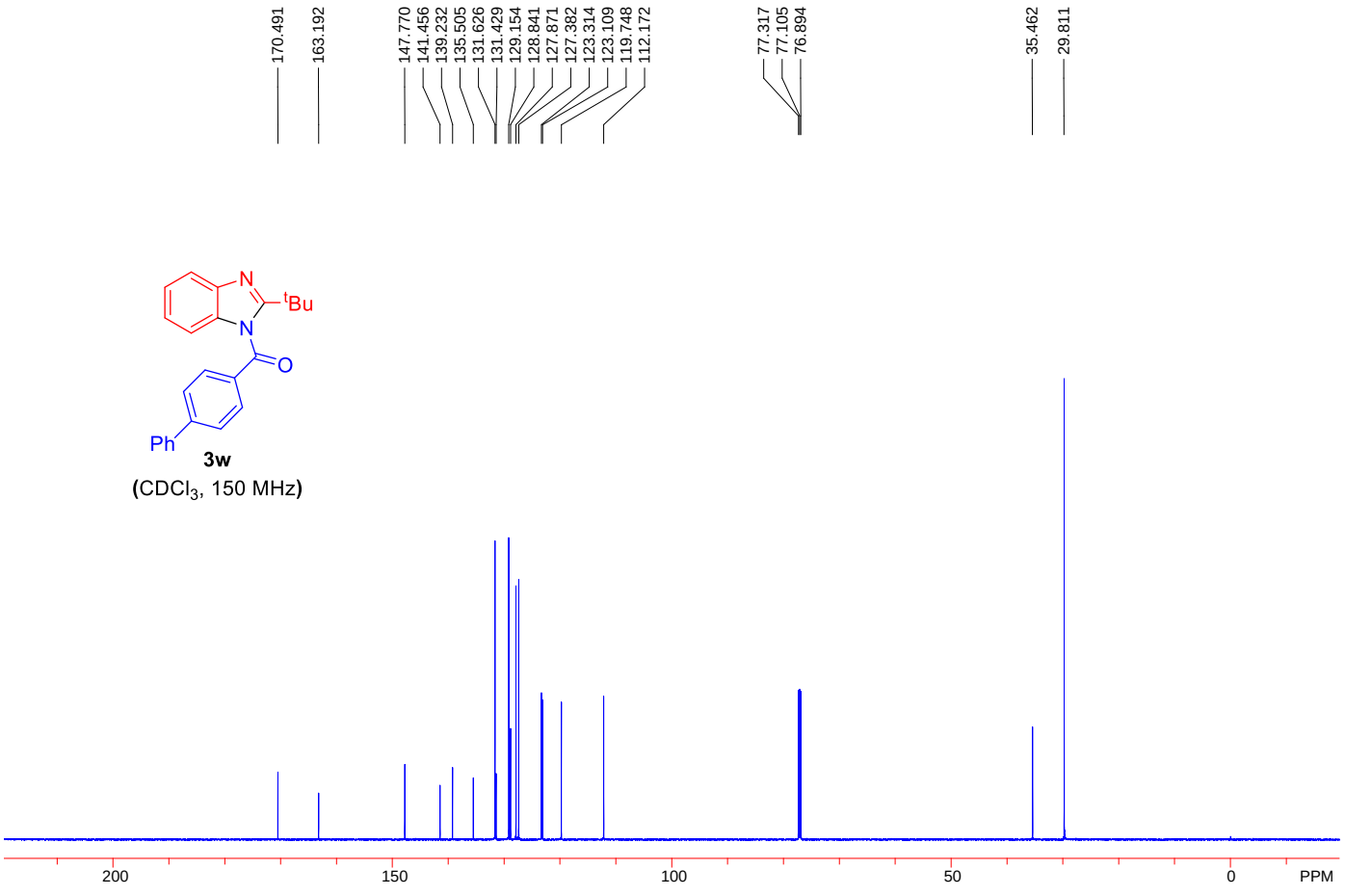
(CDCl$_3$, 150 MHz)

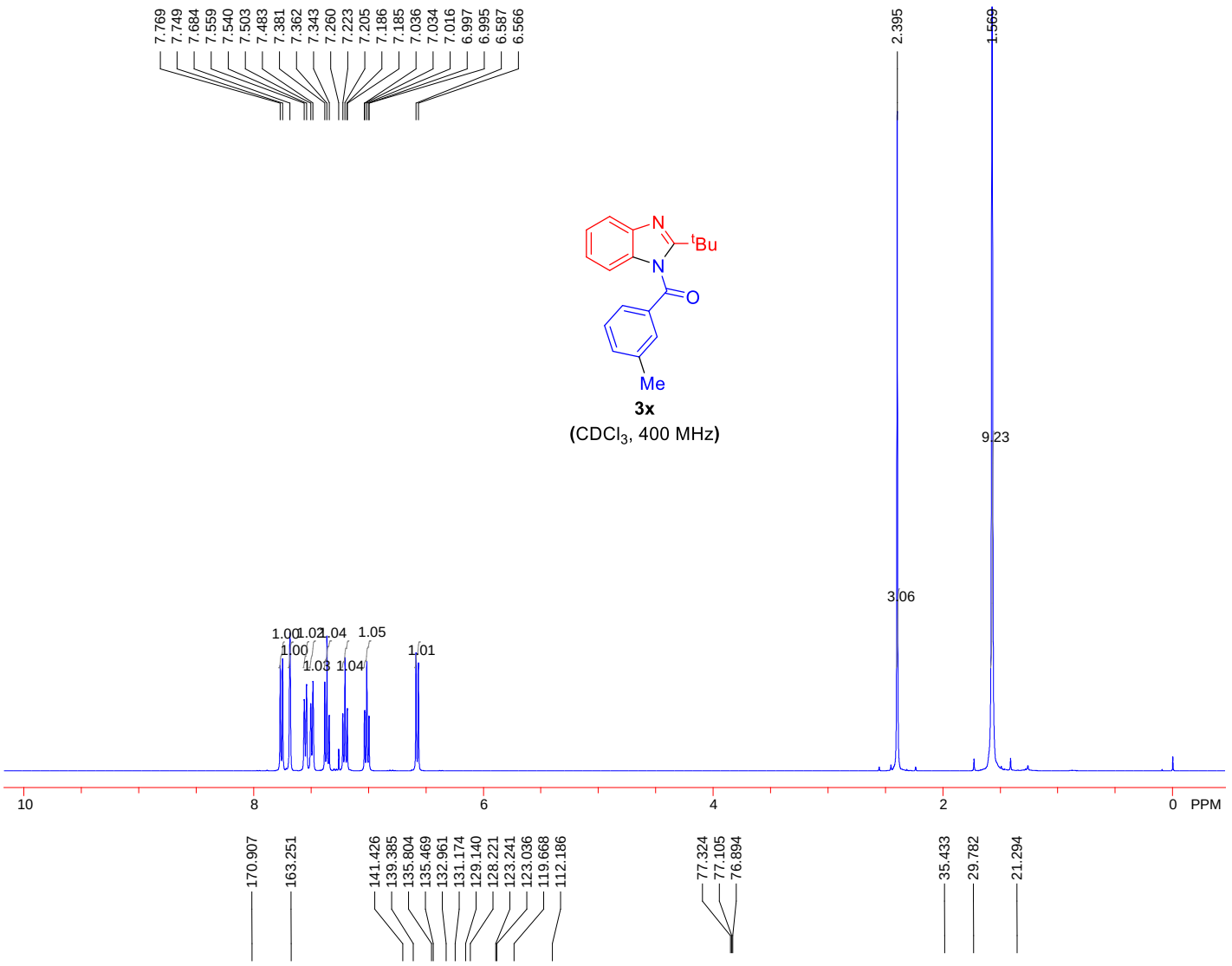


3v

($CDCl_3$, 565 MHz)

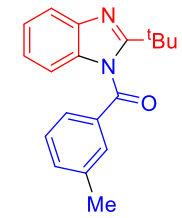

7.899
7.896
7.893
7.885
7.881
7.878
7.791
7.777
7.732
7.729
7.726
7.718
7.715
7.651
7.649
7.646
7.637
7.492
7.489
7.480
7.467
7.435
7.433
7.431
7.424
7.420
7.417
7.408
7.249
7.242
7.241
7.229
7.217
7.215
7.065
7.063
7.051
7.039
7.037
6.689
6.676
1.589
N
tBu
N
O
Ph
3w
(CDCl3, 600 MHz)
9.18
2.04
2.03
2.00
2.05
1.02
1.00
1.02
1.01
1.00
10
8
6
4
2
PPM


170.491
163.192
147.770
141.456
139.232
135.505
131.626
131.429
129.154
128.841
127.871
127.382
123.314
123.109
119.748
112.172
77.317
77.105
76.894
35.462
29.811
N
tBu
N
O
Ph
3w
(CDCl3, 150 MHz)
200
150
100
50
0
PPM



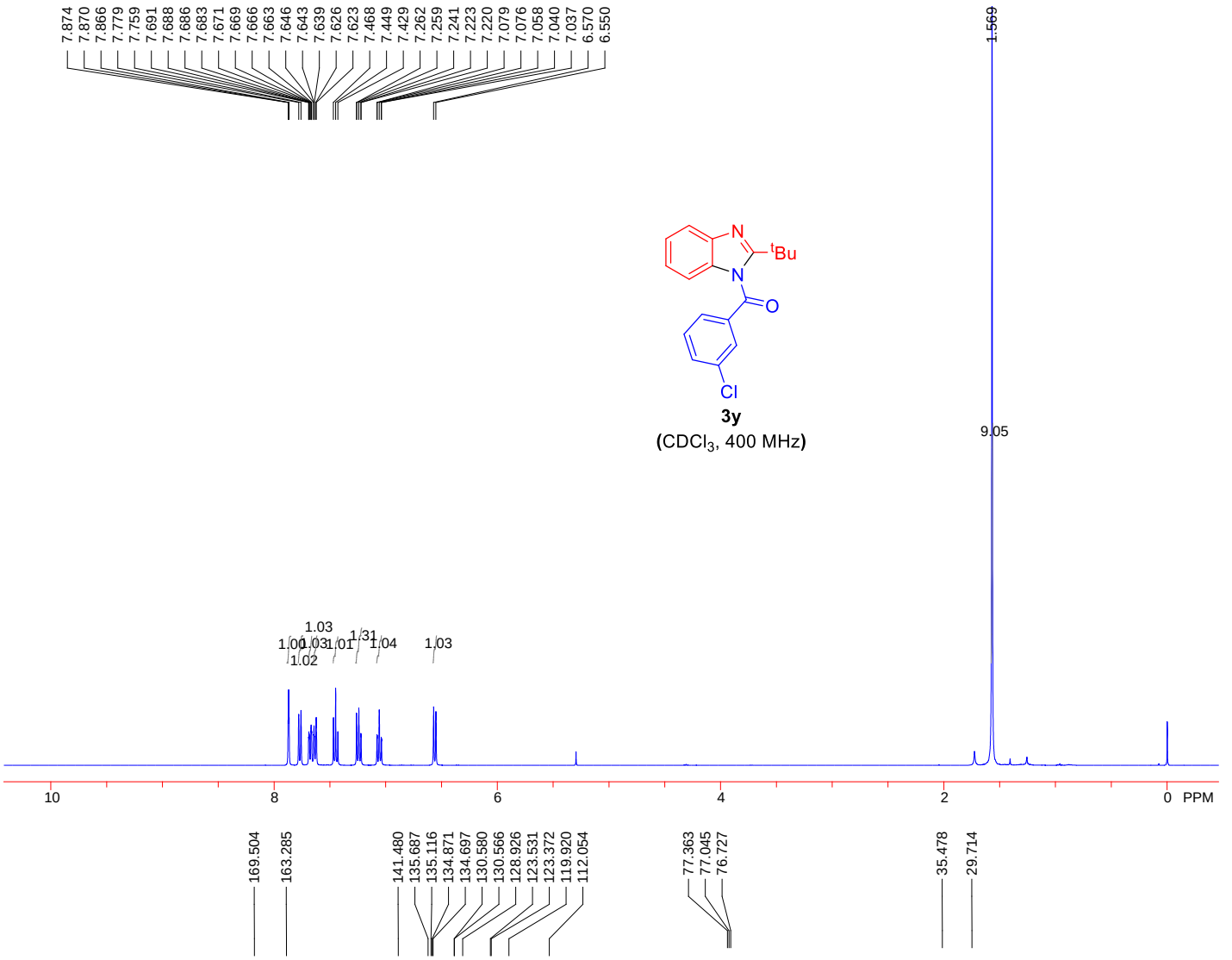
3x

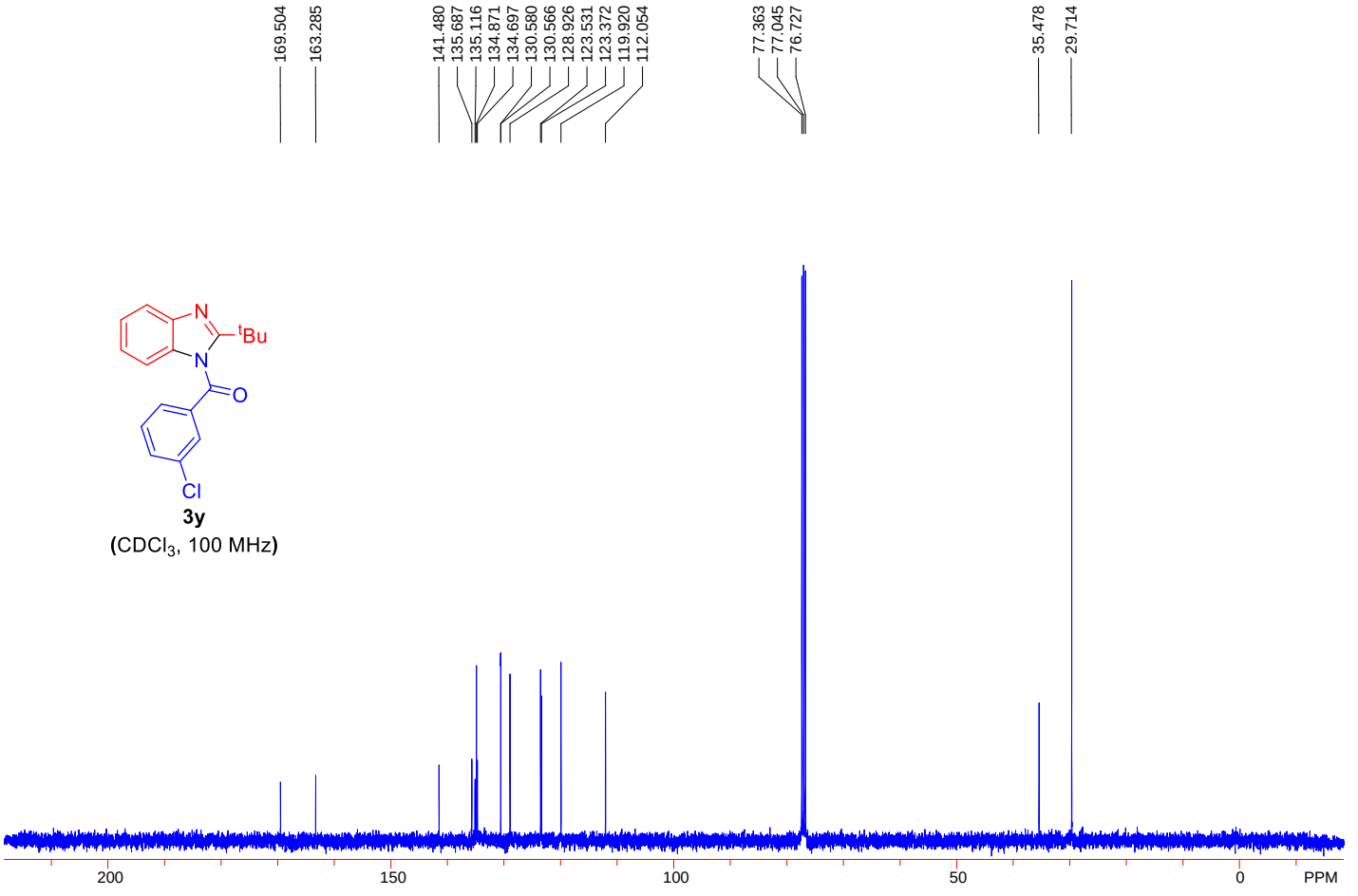
(CDCl$_3$, 400 MHz)

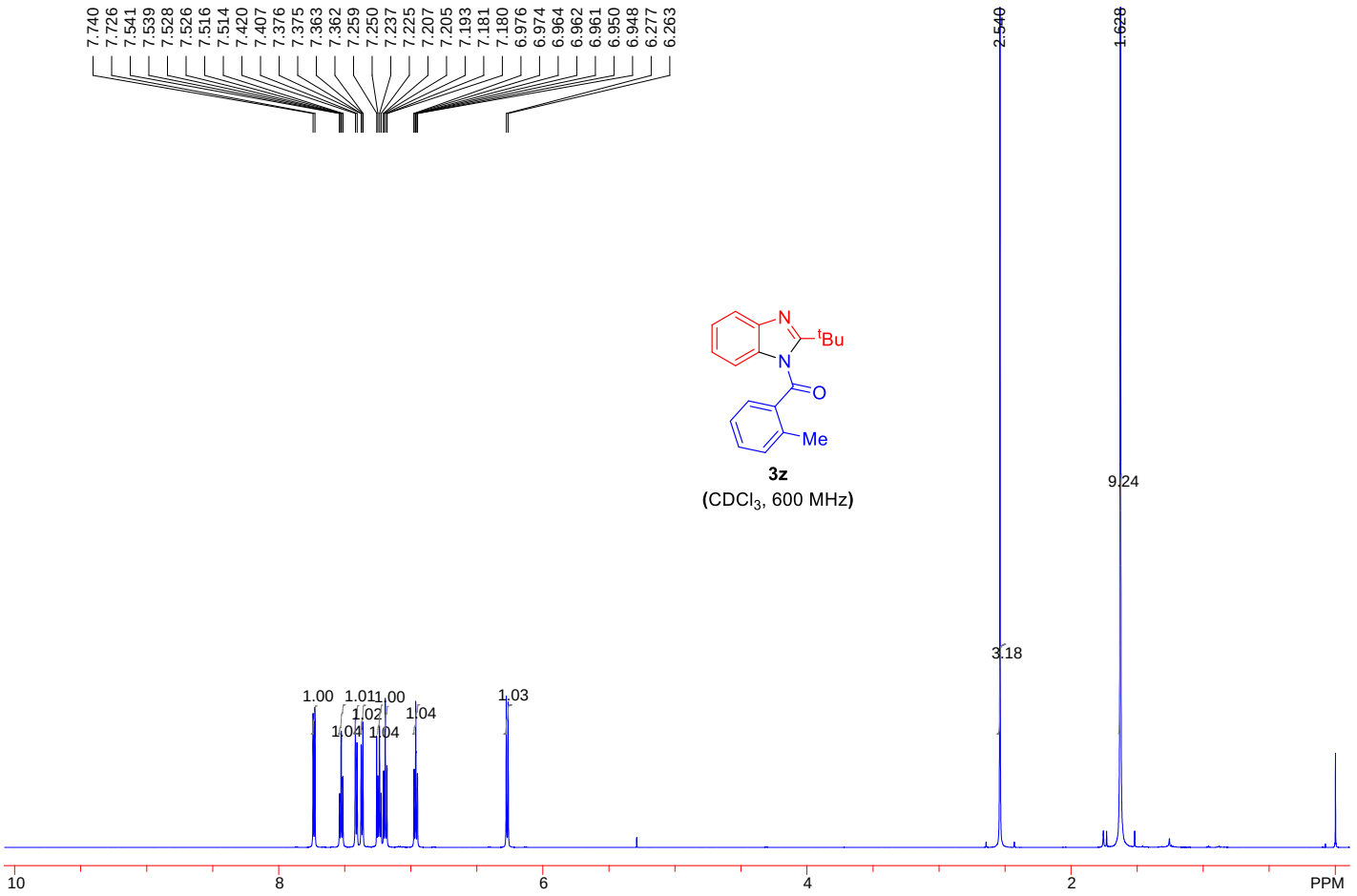


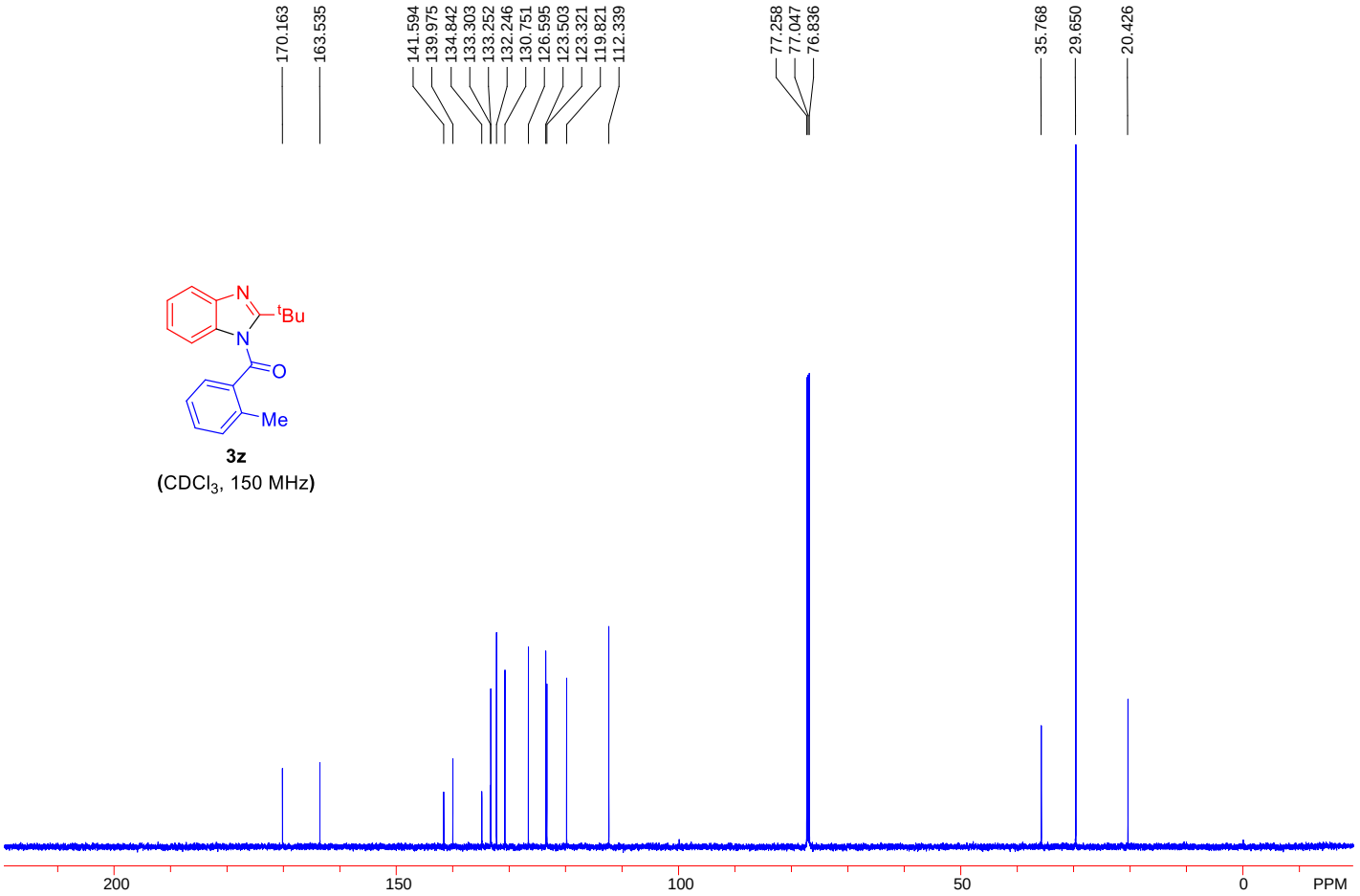
3x

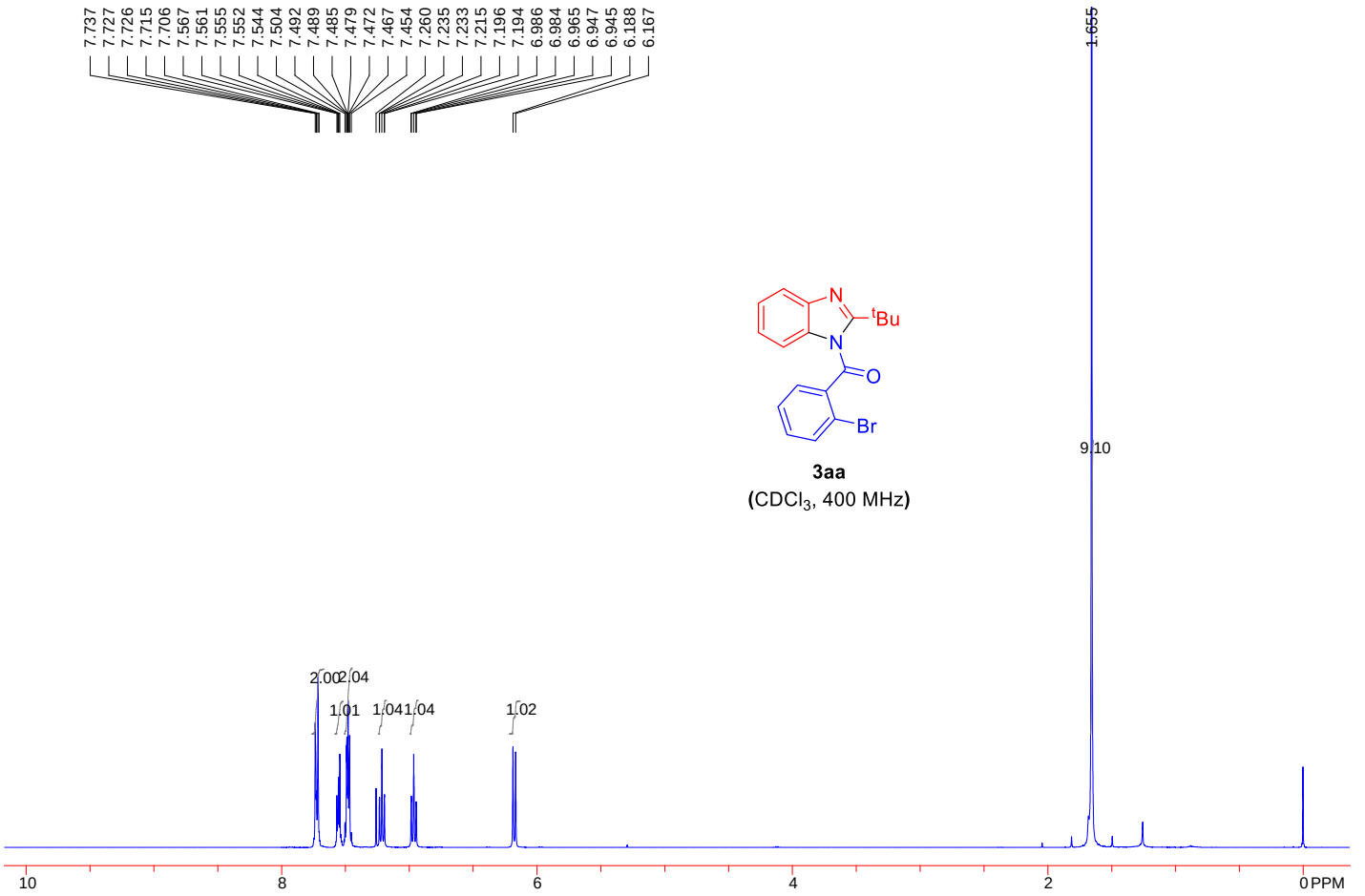
(CDCl$_3$, 150 MHz)


7.874
7.870
7.866
7.779
7.759
7.691
7.688
7.686
7.683
7.671
7.669
7.666
7.663
7.646
7.643
7.639
7.626
7.623
7.468
7.449
7.429
7.262
7.259
7.241
7.223
7.220
7.079
7.076
7.058
7.040
7.037
6.570
6.550
1.569
9.05
1.03
1.00
1.03
1.02
1.01
1.31
1.04
1.03
10
8
6
4
2
0
PPM
N
tBu
N
O
Cl
3y
(CDCl3, 400 MHz)

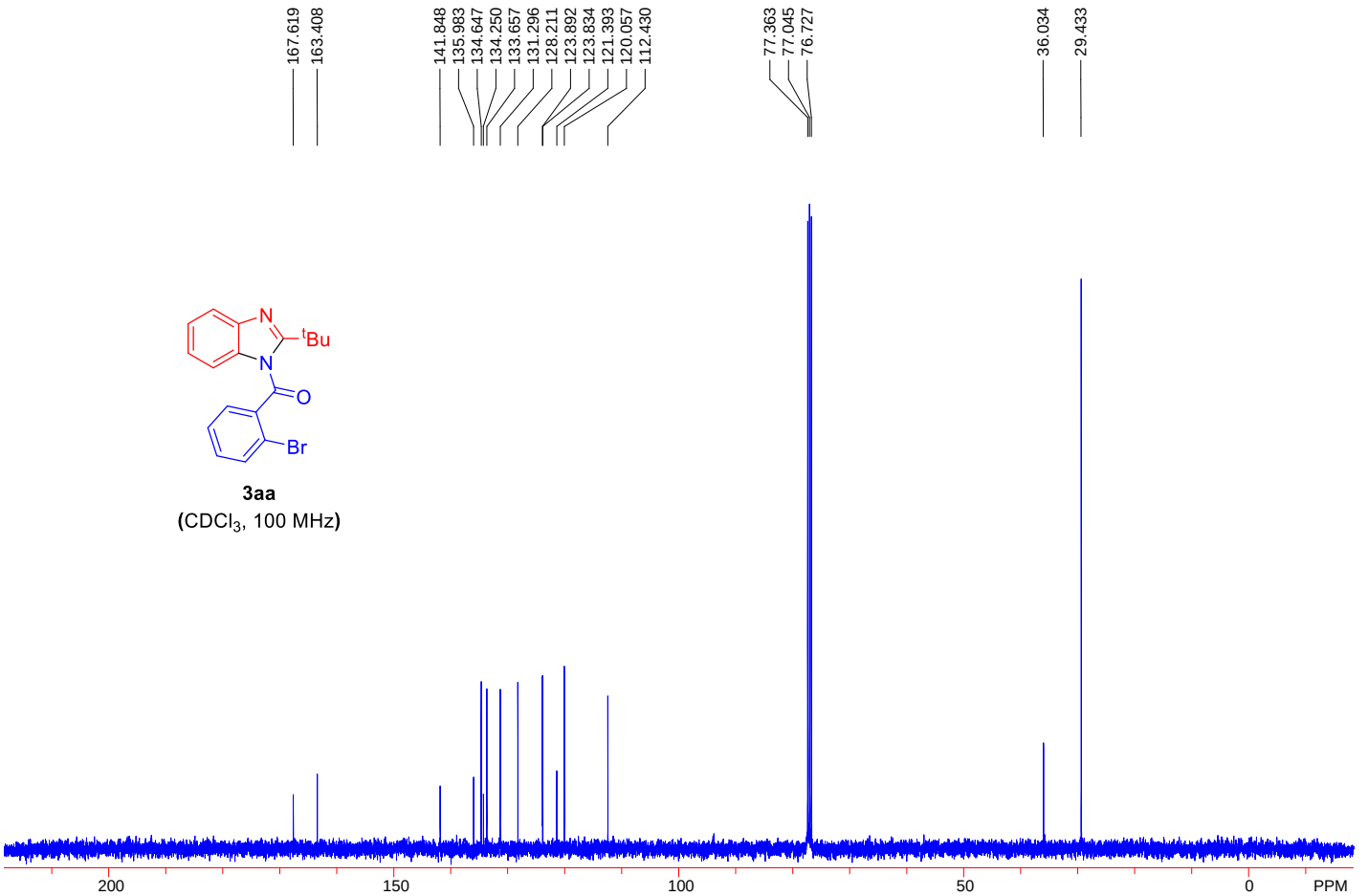

169.504
163.285
141.480
135.687
135.116
134.871
134.697
130.580
130.566
128.926
123.531
123.372
119.920
112.054
77.363
77.045
76.727
35.478
29.714
200
150
100
50
0
PPM
N
tBu
N
O
Cl
3y
(CDCl3, 100 MHz)


7.740
7.726
7.541
7.539
7.528
7.526
7.516
7.514
7.420
7.407
7.376
7.375
7.363
7.362
7.259
7.250
7.237
7.225
7.207
7.205
7.193
7.181
7.180
6.976
6.974
6.964
6.962
6.961
6.950
6.948
6.277
6.263
2.540
1.628
tBu
N
N
O
Me
3z
(CDCl3, 600 MHz)
9.24
3.18
1.00
1.01
1.00
1.02
1.04
1.04
1.04
1.03
10
8
6
4
2
PPM

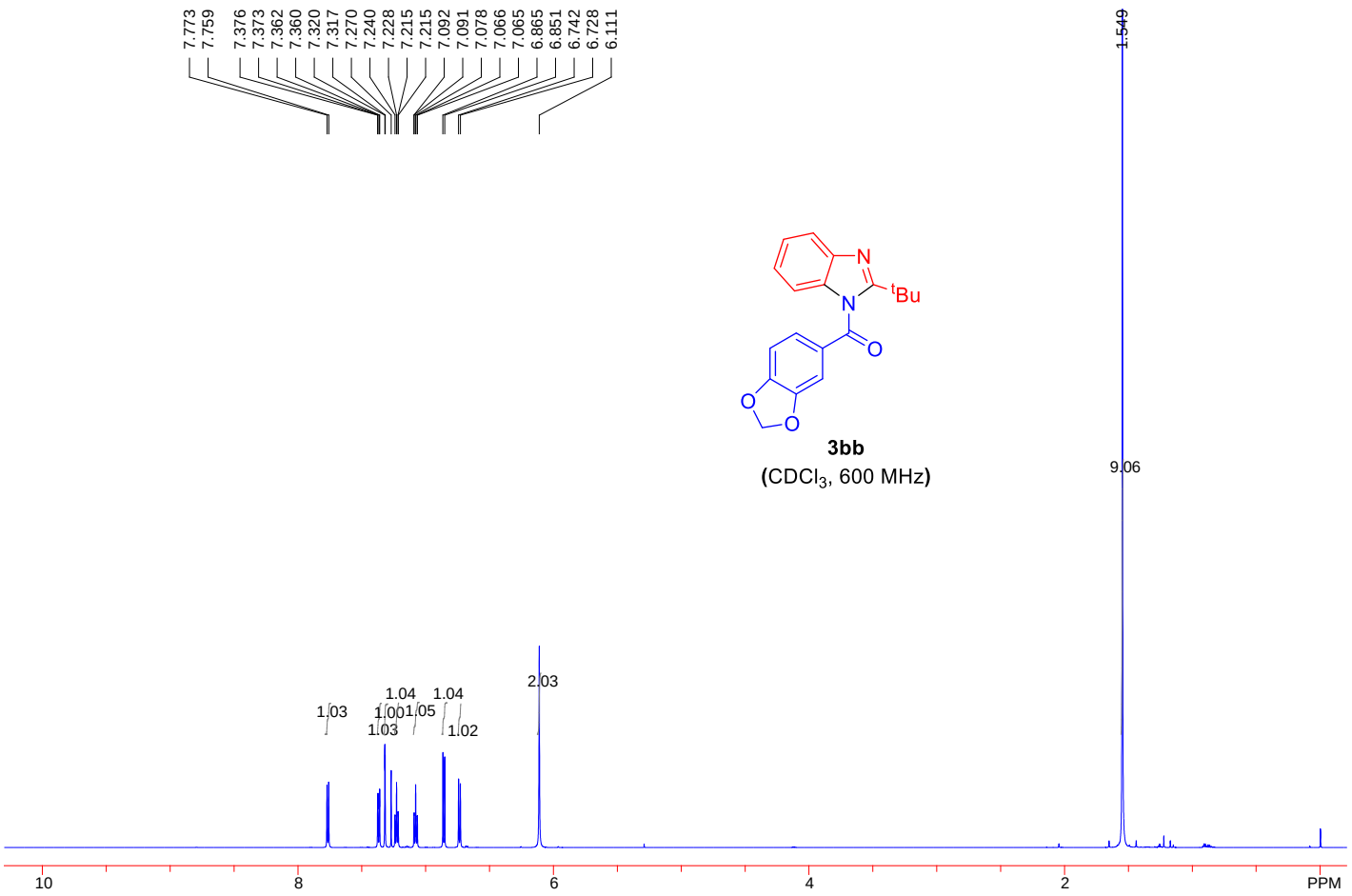

170.163
163.535
141.594
139.975
134.842
133.303
133.252
132.246
130.751
126.595
123.503
123.321
119.821
112.339
77.258
77.047
76.836
35.768
29.650
20.426
tBu
N
N
O
Me
3z
(CDCl3, 150 MHz)
200
150
100
50
0
PPM



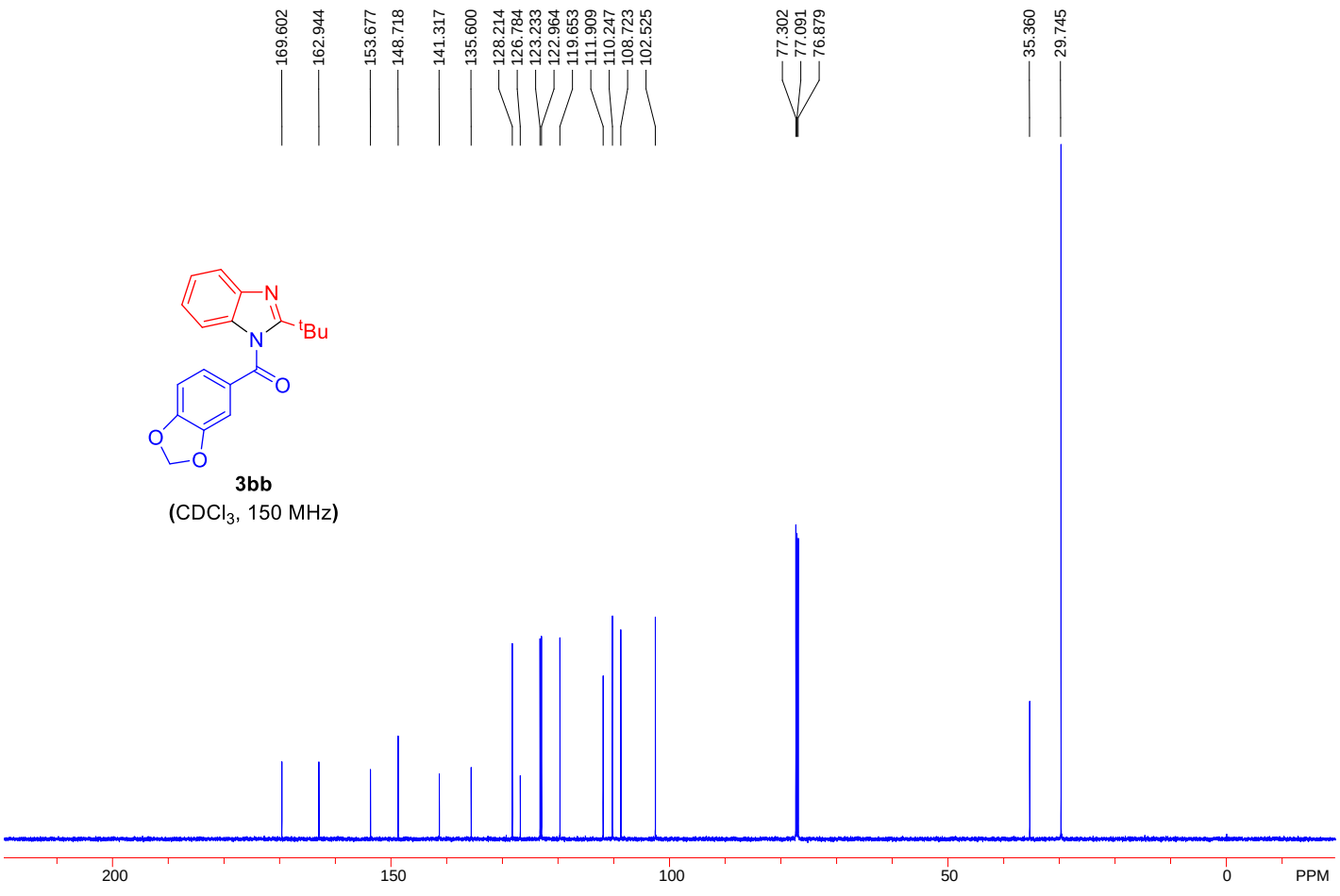
3aa
(CDCl$_3$, 400 MHz)



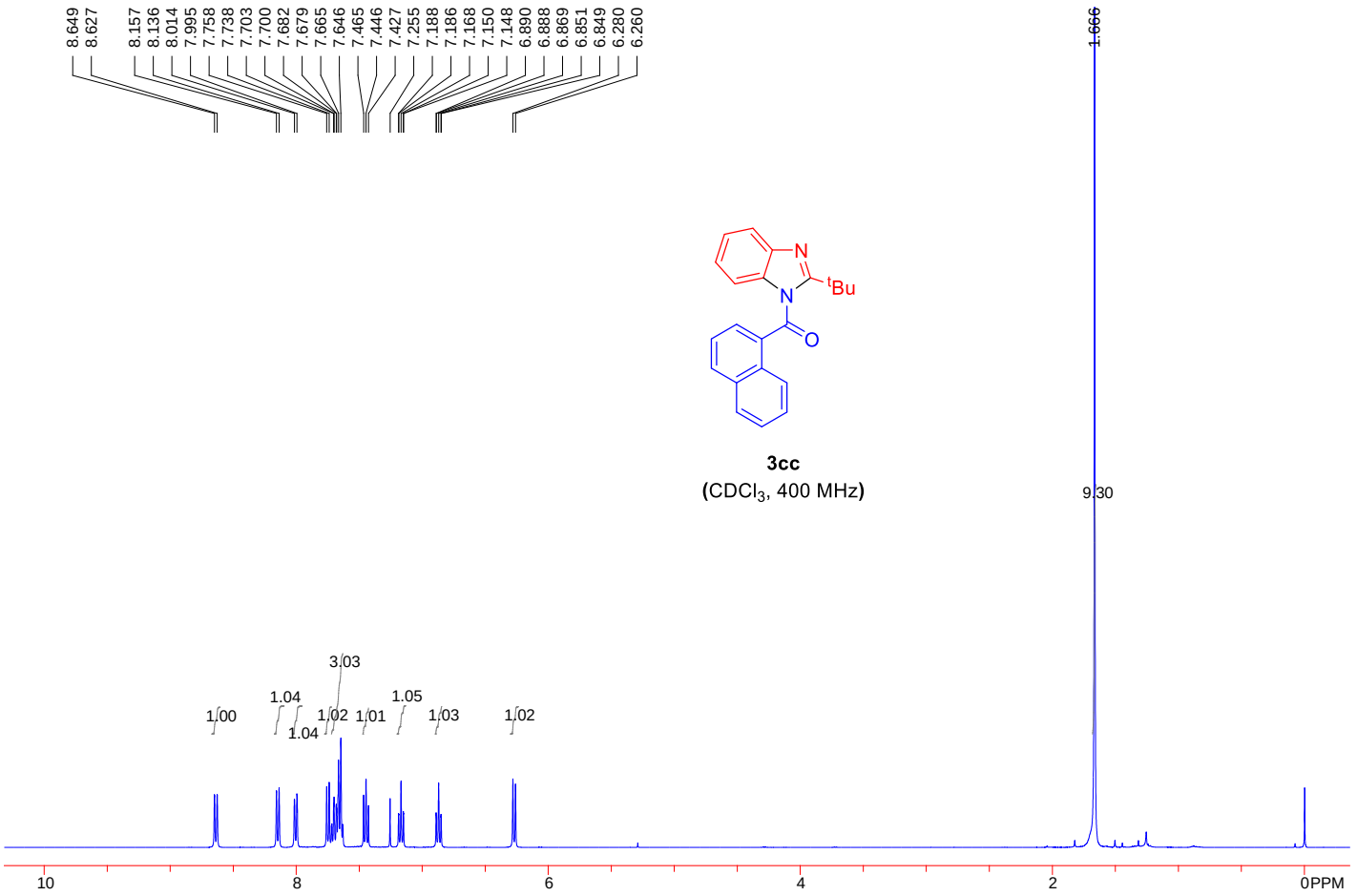
3aa
(CDCl$_3$, 100 MHz)



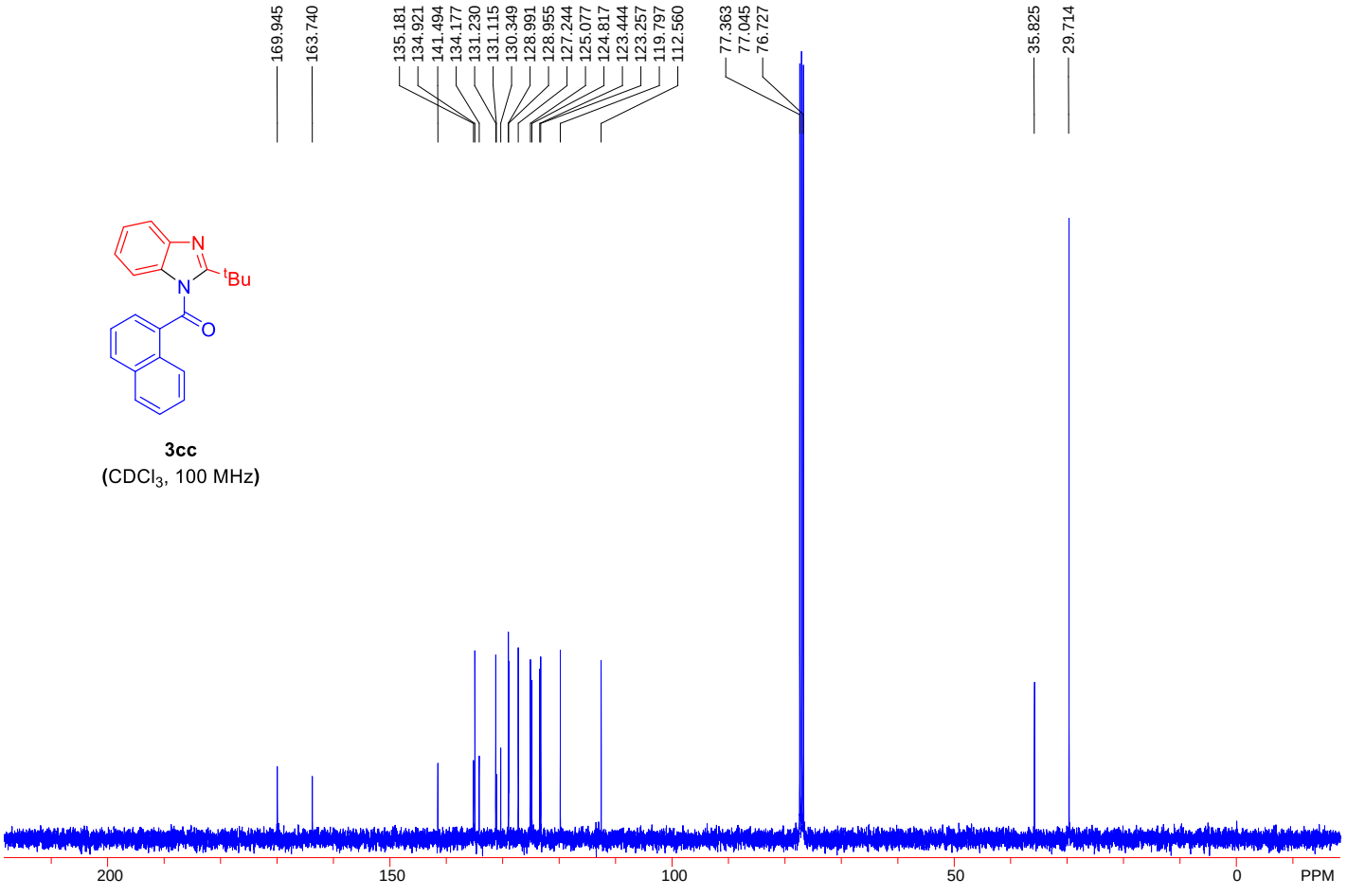
3bb
($CDCl_3$, 600 MHz)



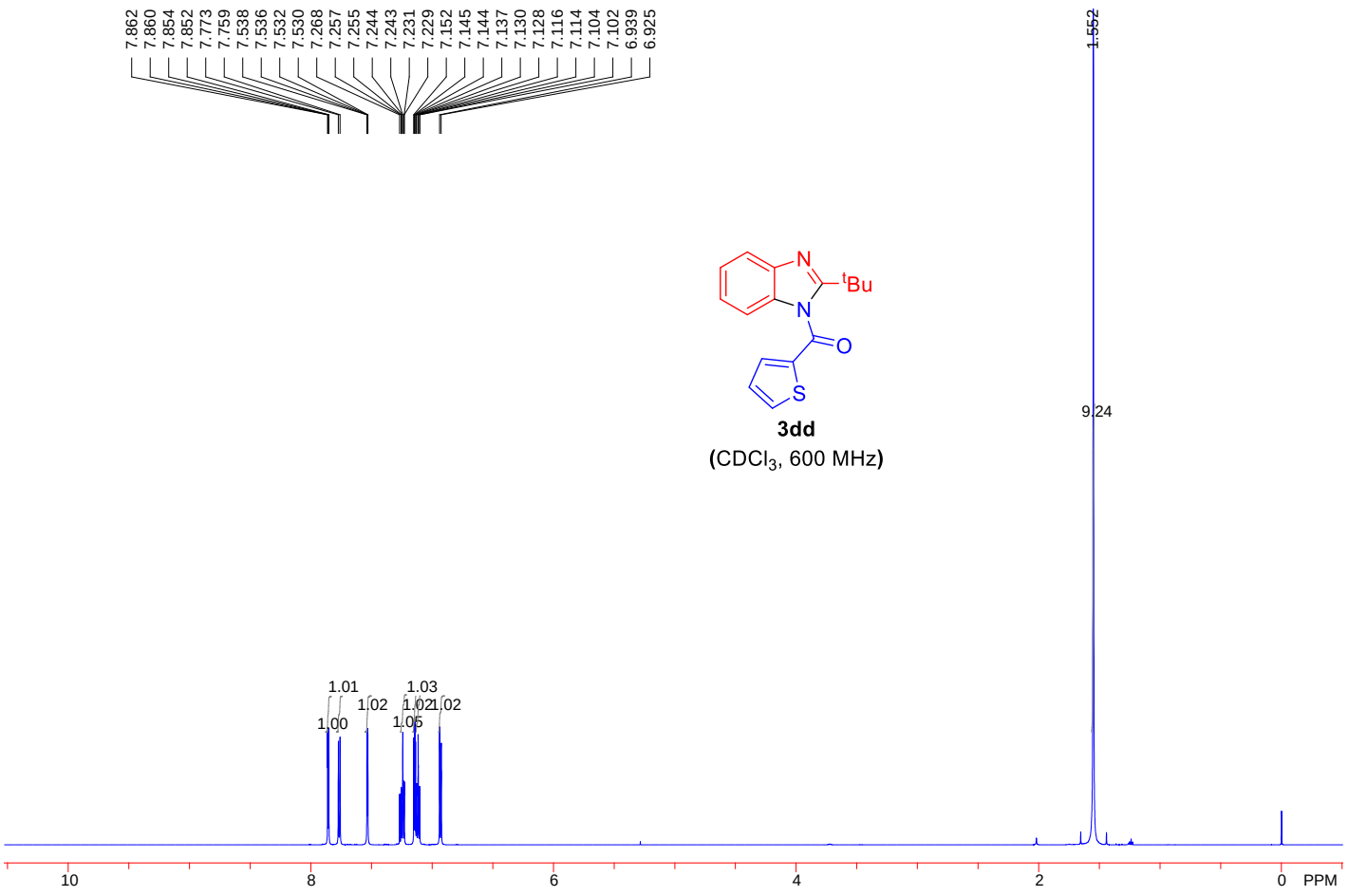
3bb
($CDCl_3$, 150 MHz)



3cc
($CDCl_3$, 400 MHz)

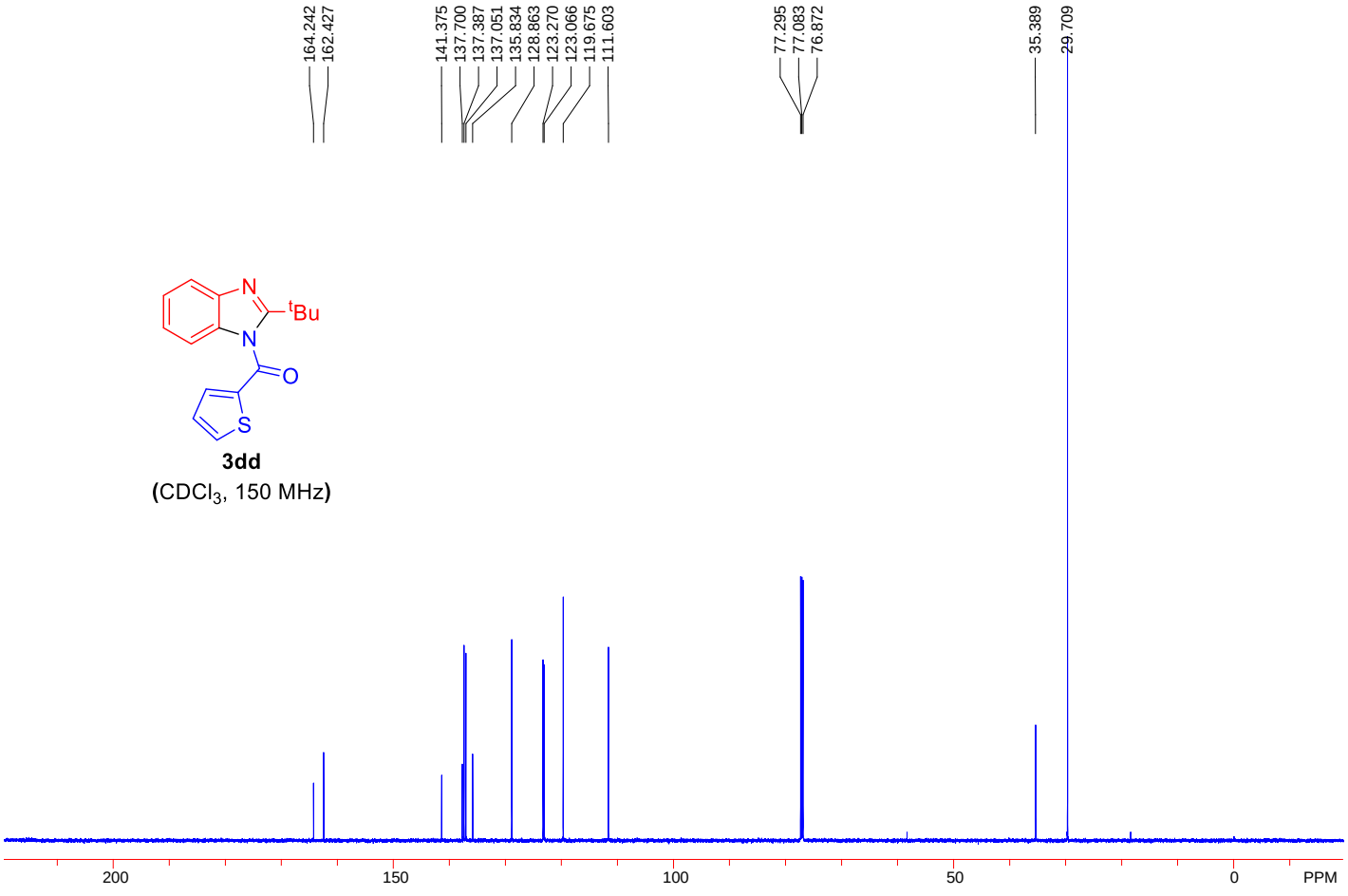


3cc
($CDCl_3$, 100 MHz)



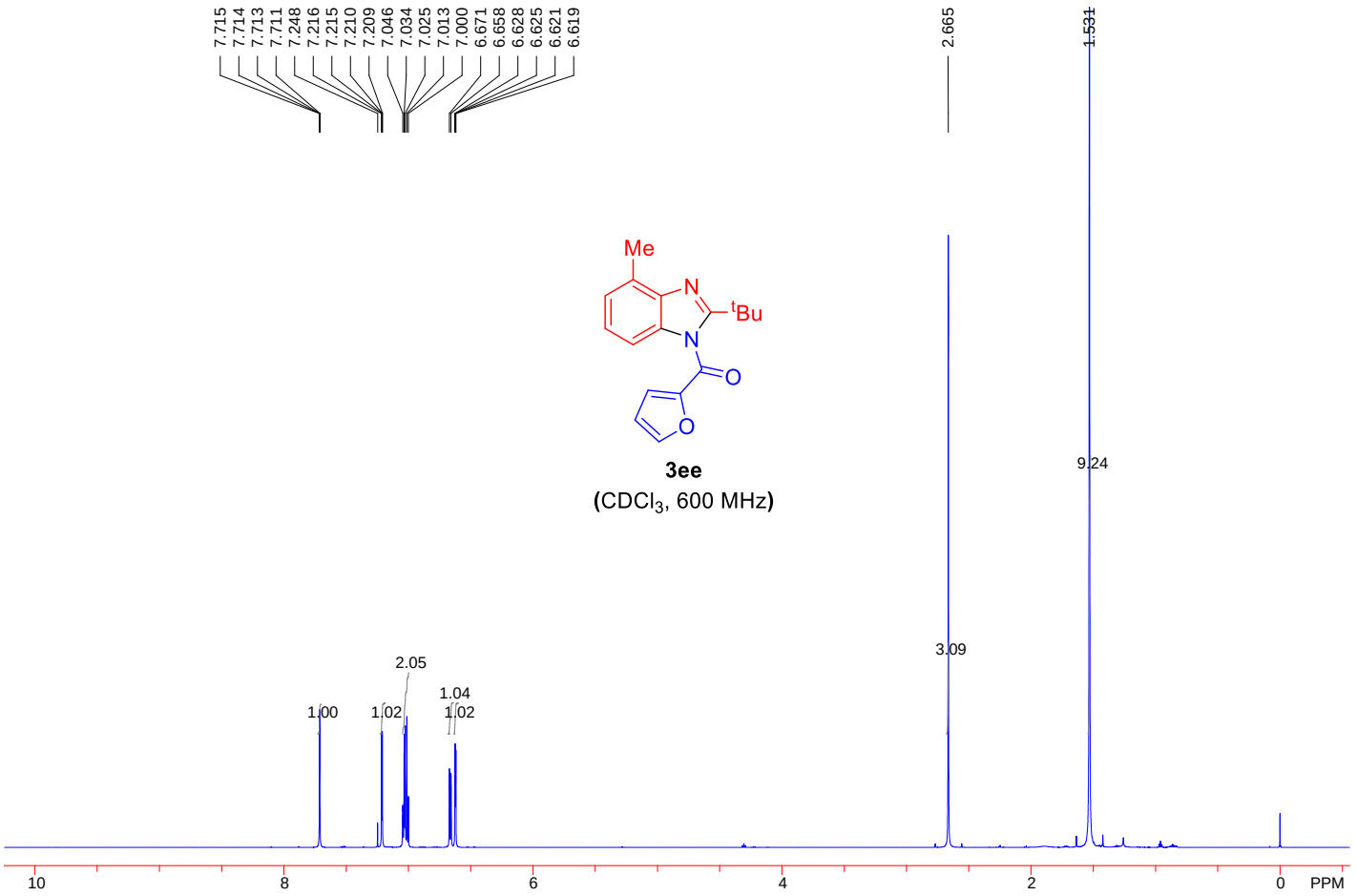
3dd

($CDCl_3$, 600 MHz)



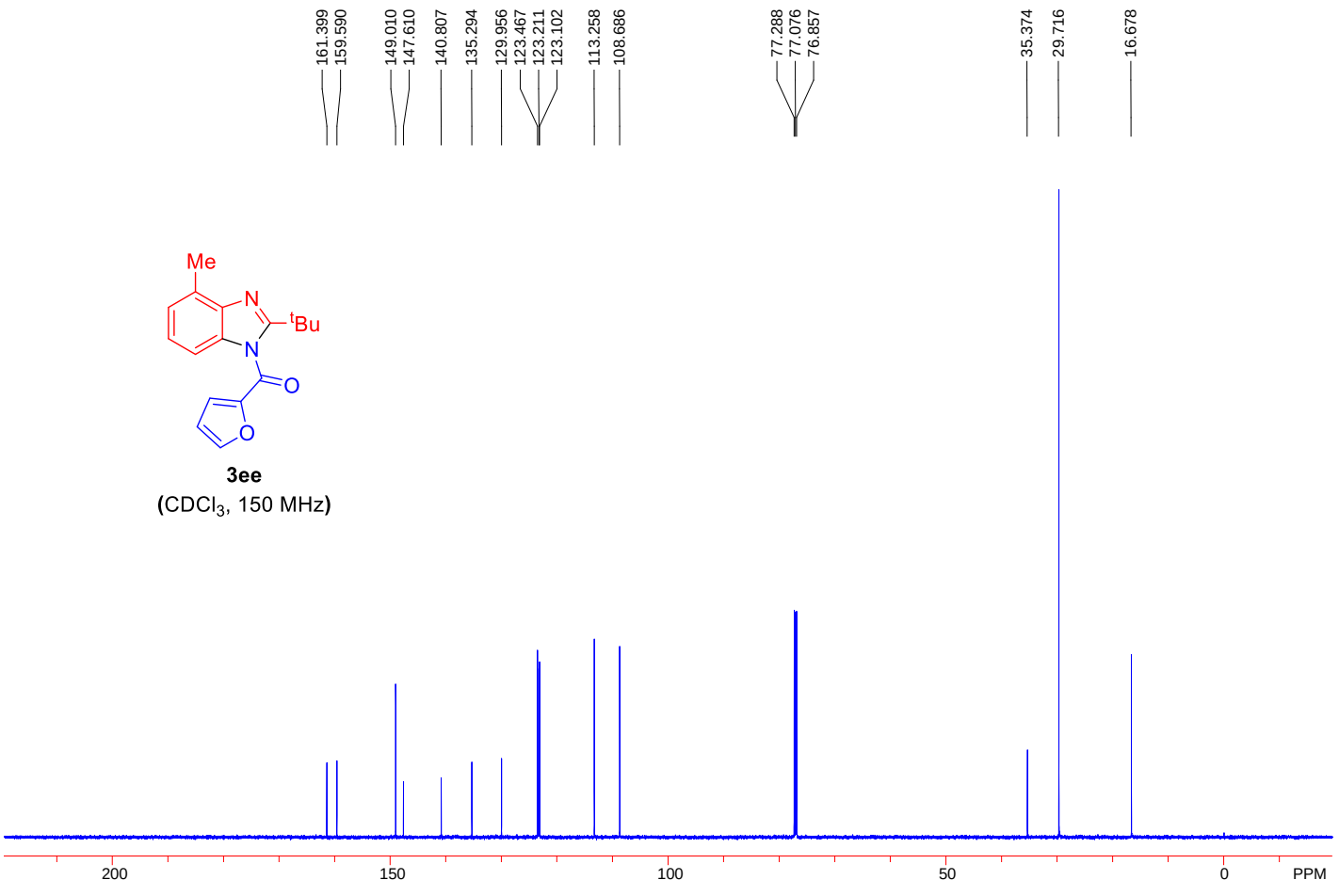
3dd

($CDCl_3$, 150 MHz)



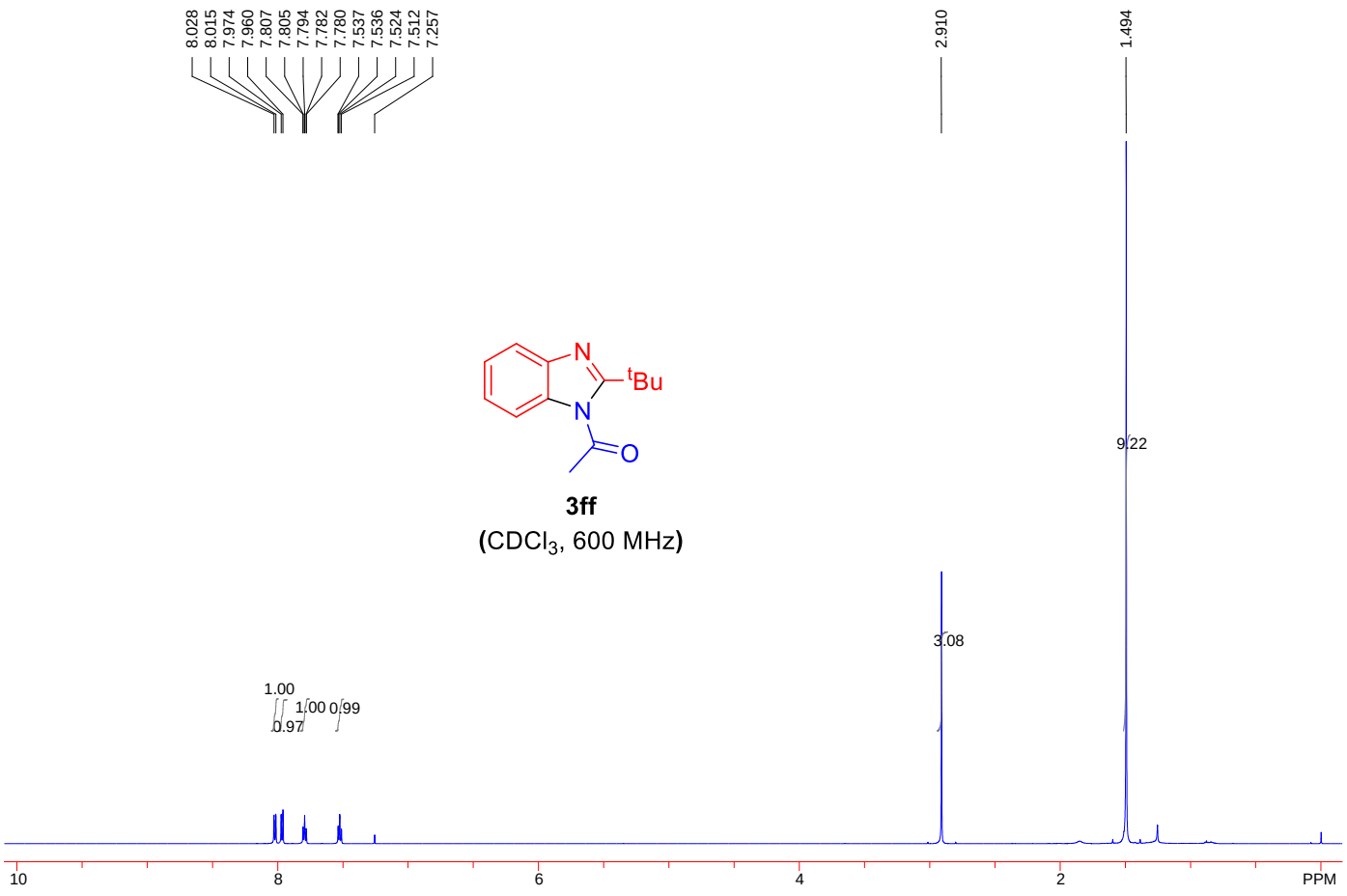
3ee

(CDCl$_3$, 600 MHz)



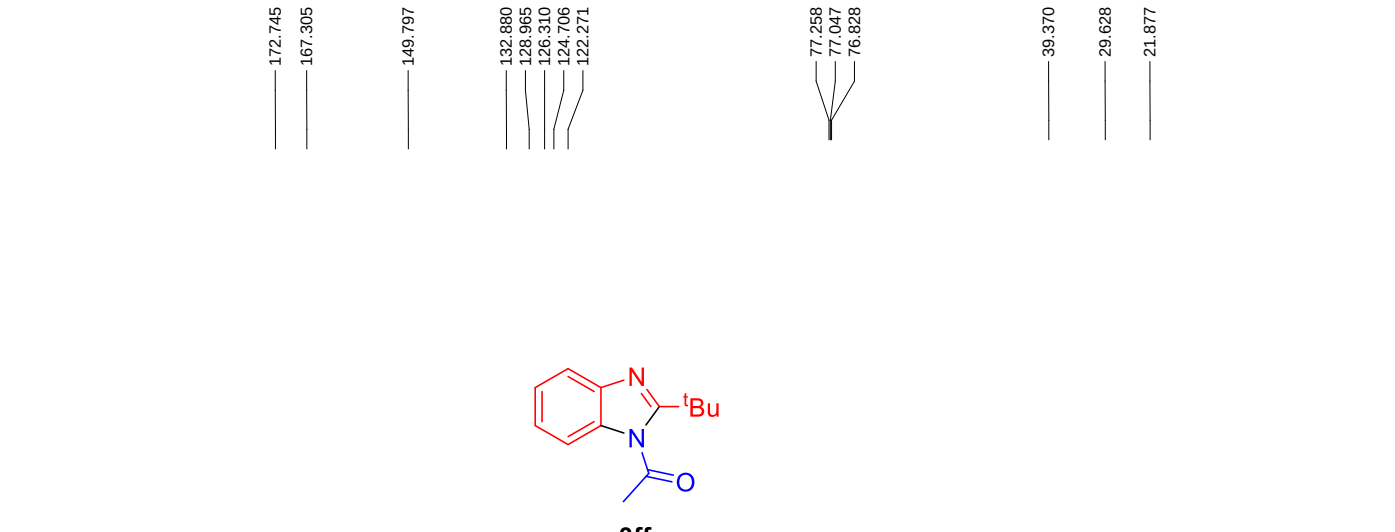
3ee

(CDCl$_3$, 150 MHz)



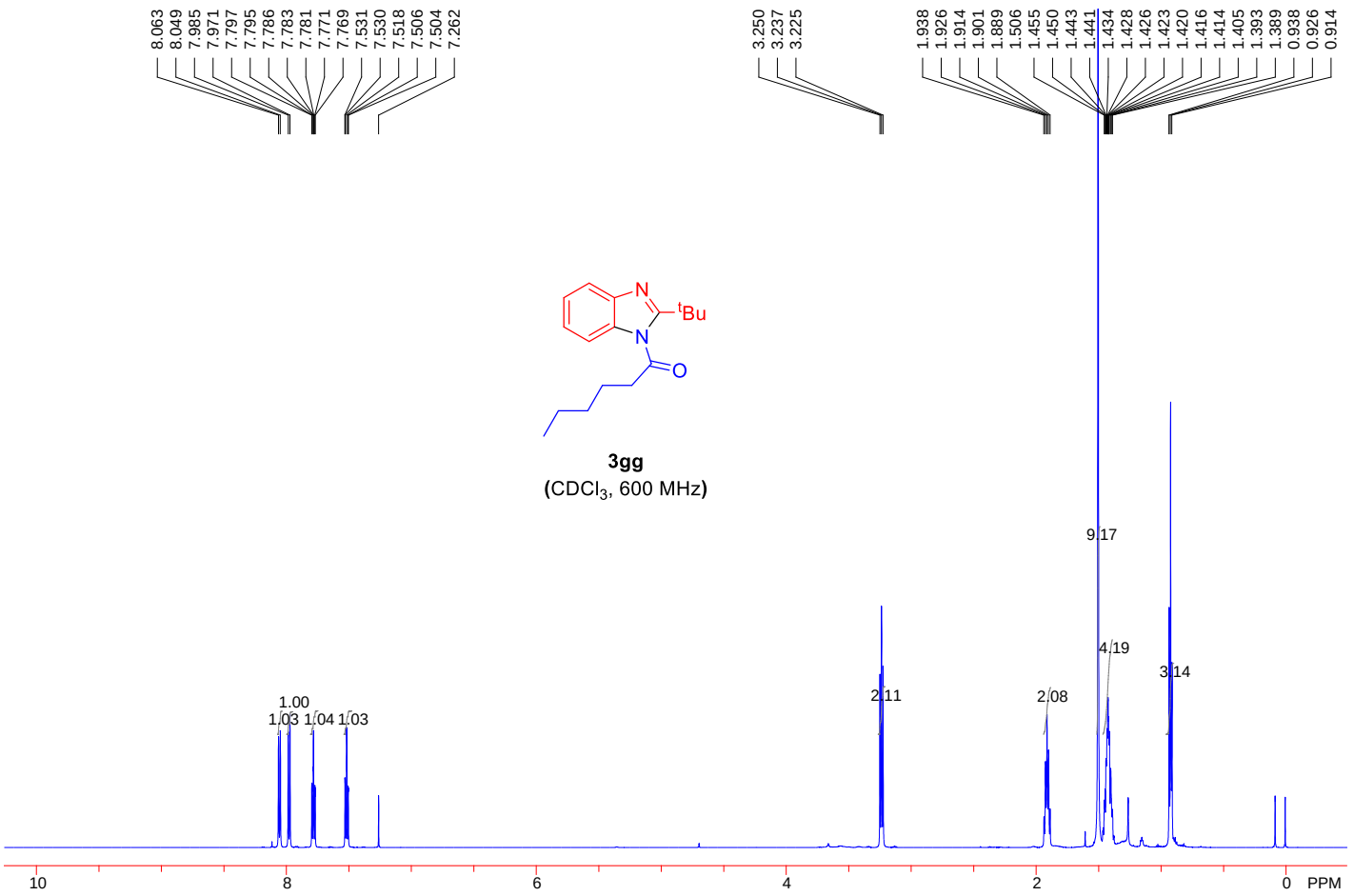
3ff

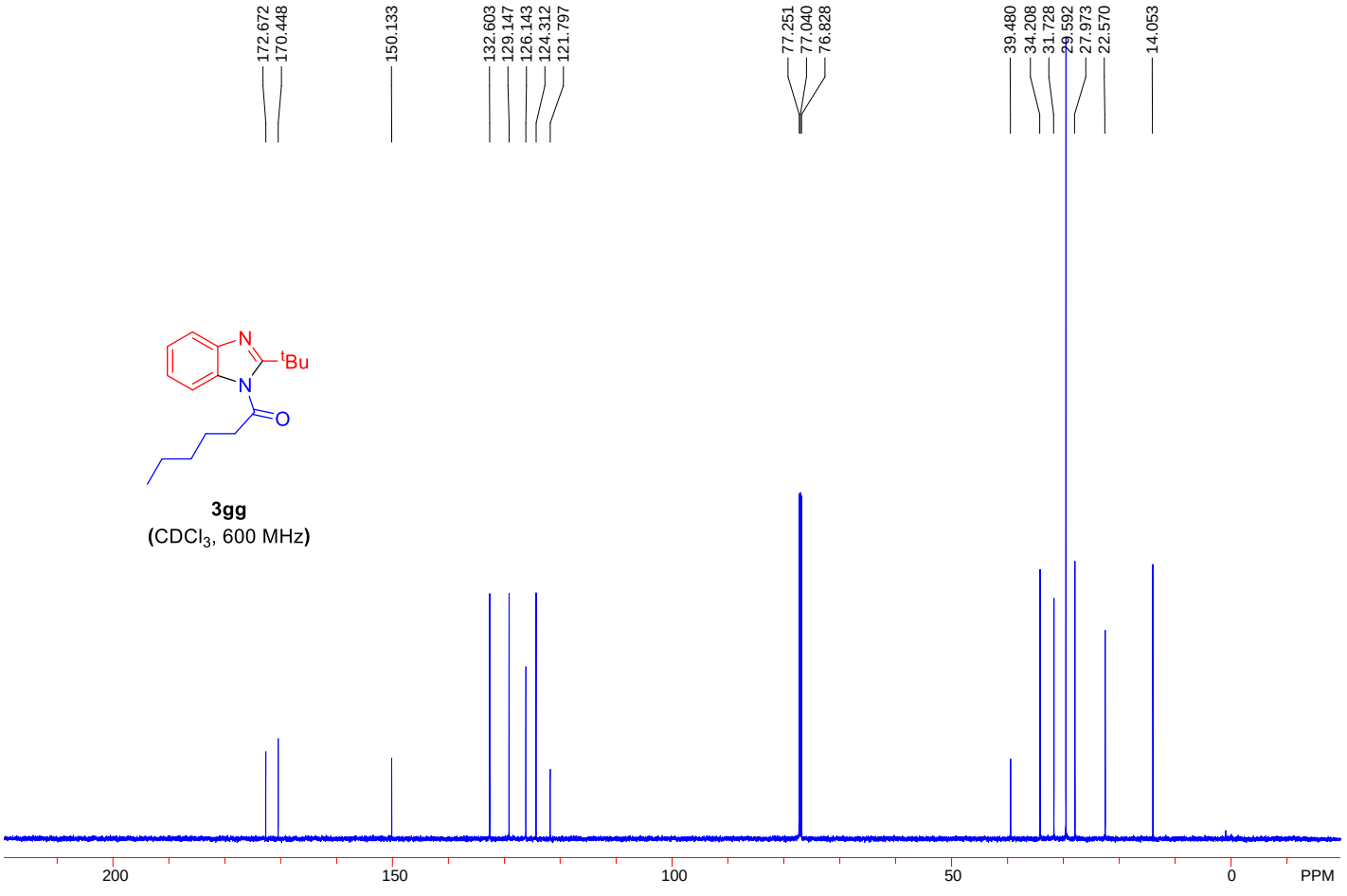
(CDCl$_3$, 600 MHz)

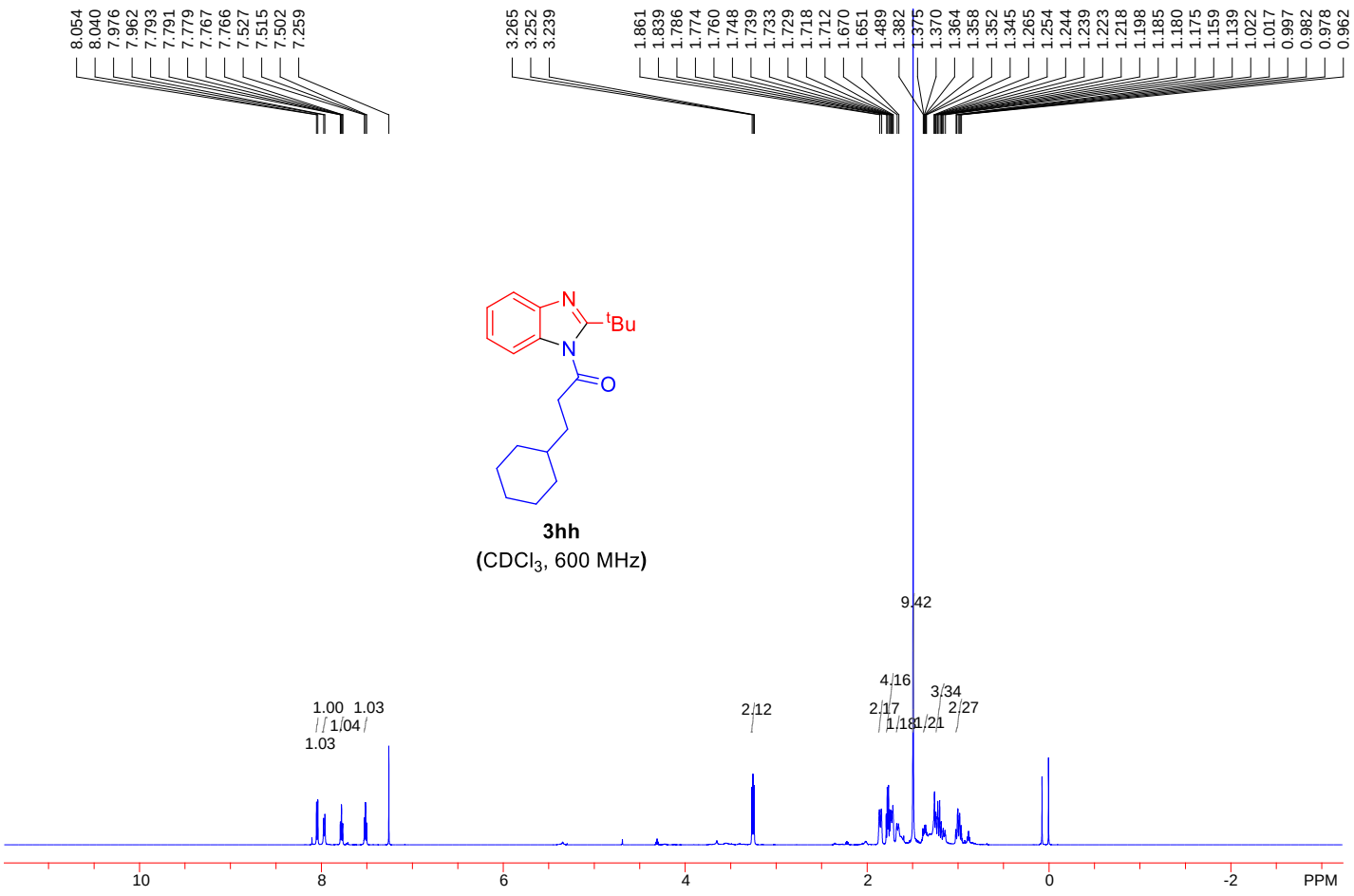


3ff

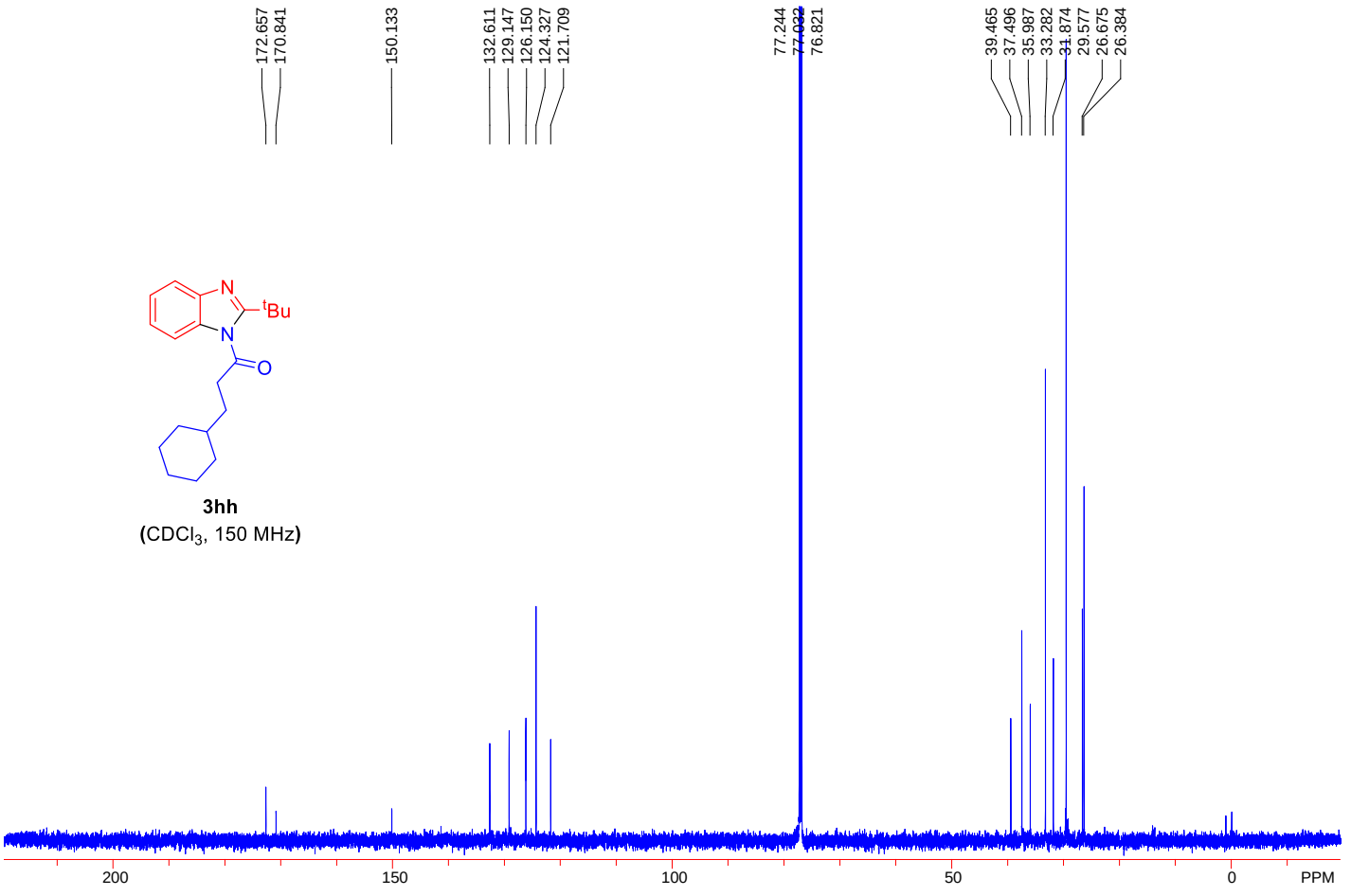
(CDCl$_3$, 150 MHz)


8.063
8.049
7.985
7.971
7.797
7.795
7.786
7.783
7.781
7.771
7.769
7.531
7.530
7.518
7.506
7.504
7.262
3.250
3.237
3.225
1.938
1.926
1.914
1.901
1.889
1.506
1.455
1.450
1.443
1.441
1.434
1.428
1.426
1.423
1.420
1.416
1.414
1.405
1.393
1.389
0.938
0.926
0.914
N
tBu
N
O
3gg
(CDCl3, 600 MHz)
9.17
4.19
3.14
2.11
2.08
1.00
1.03
1.03
1.04
1.03
10
8
6
4
2
0
PPM

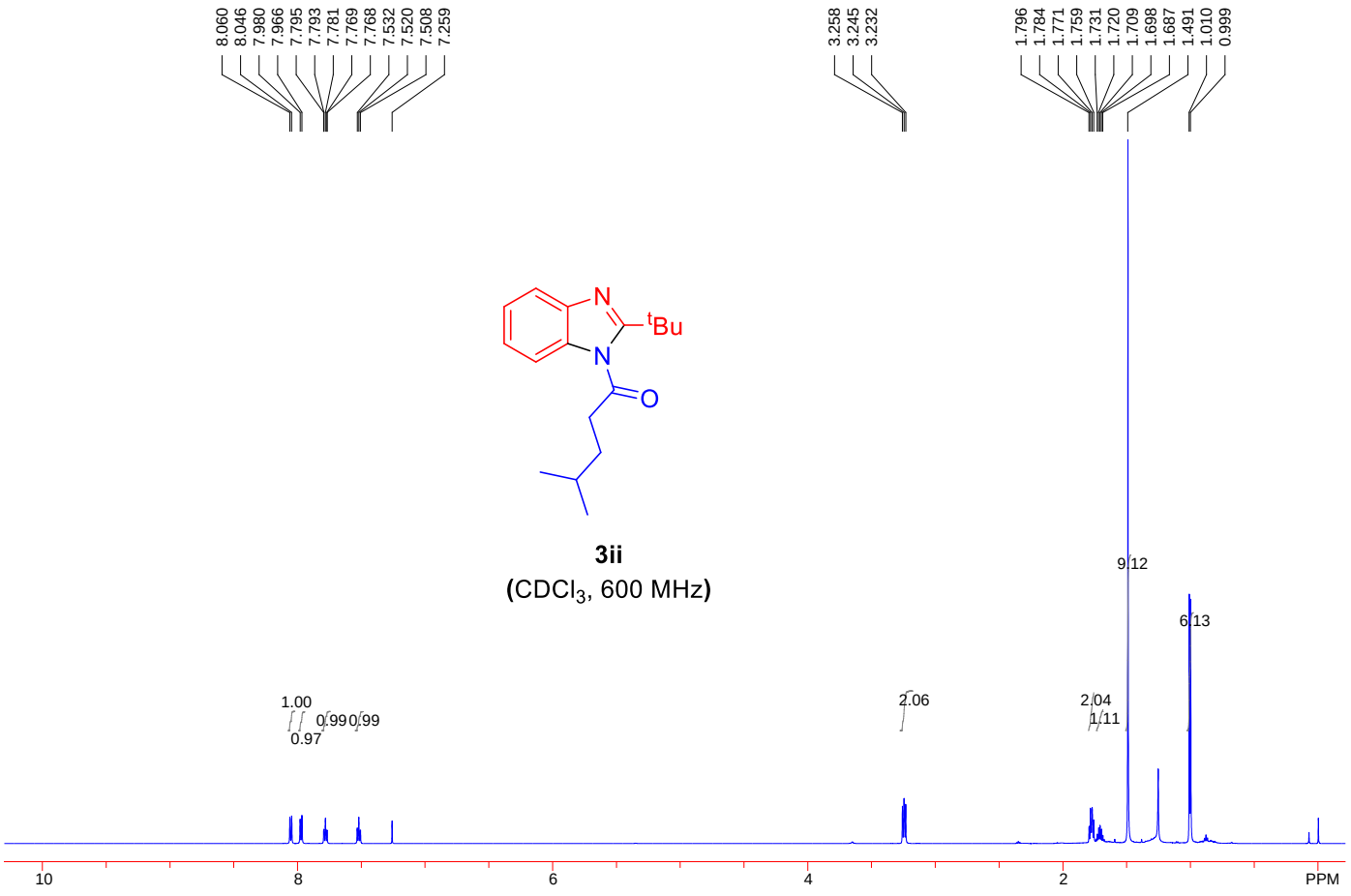

172.672
170.448
150.133
132.603
129.147
126.143
124.312
121.797
77.251
77.040
76.828
39.480
34.208
31.728
29.592
27.973
22.570
14.053
N
tBu
N
O
3gg
(CDCl3, 600 MHz)
200
150
100
50
0
PPM

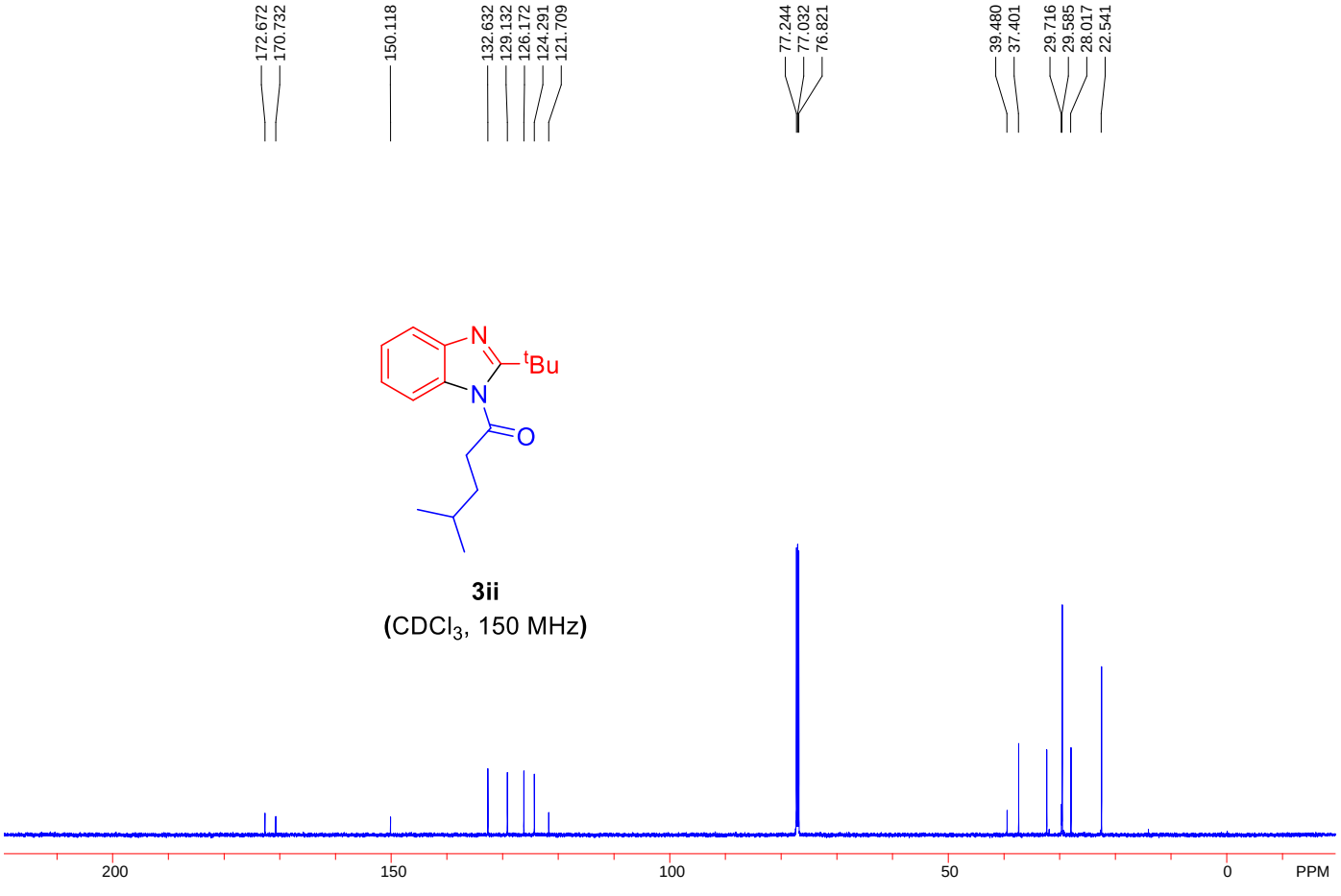


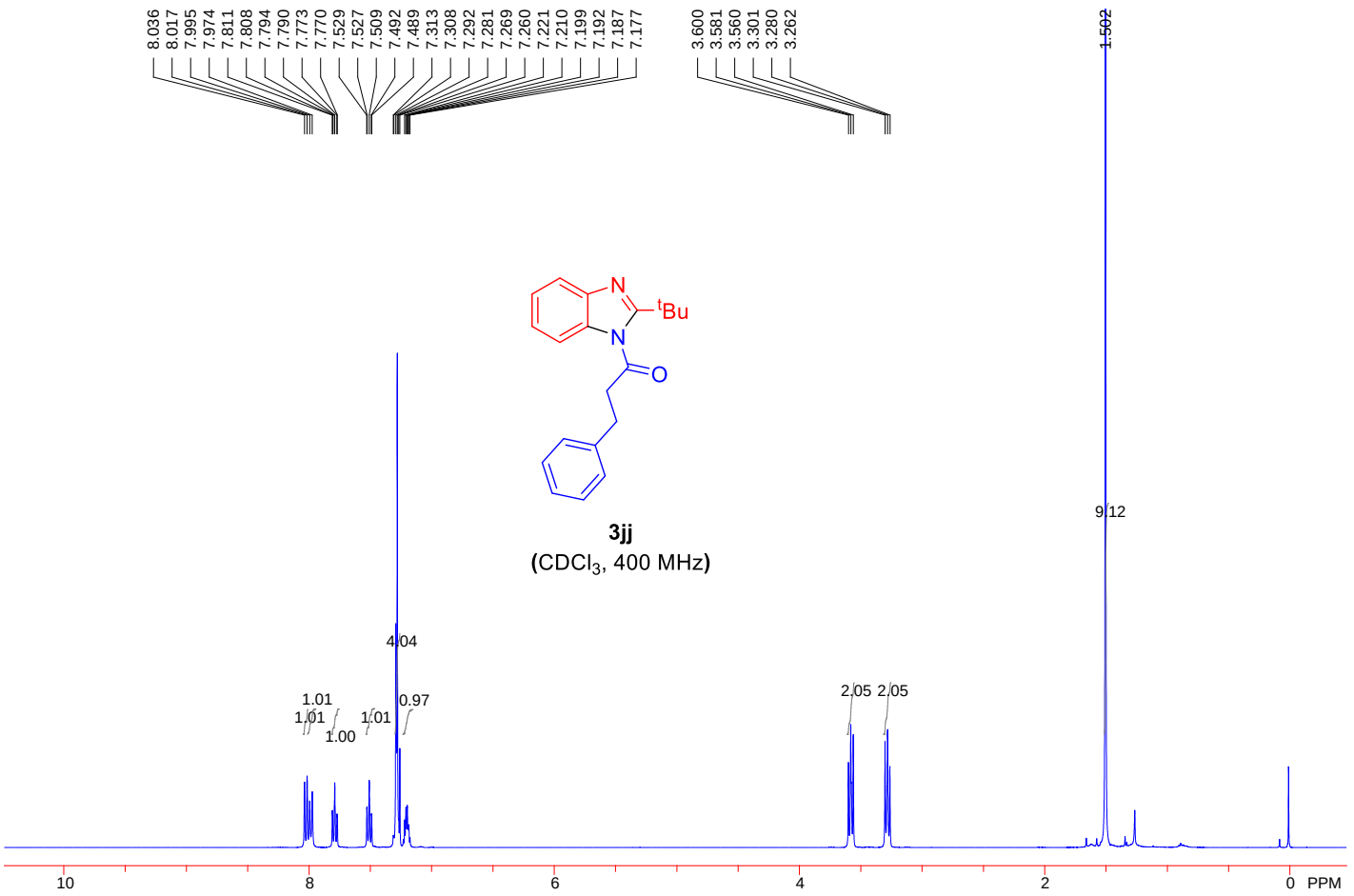
3hh
(CDCl$_3$, 600 MHz)



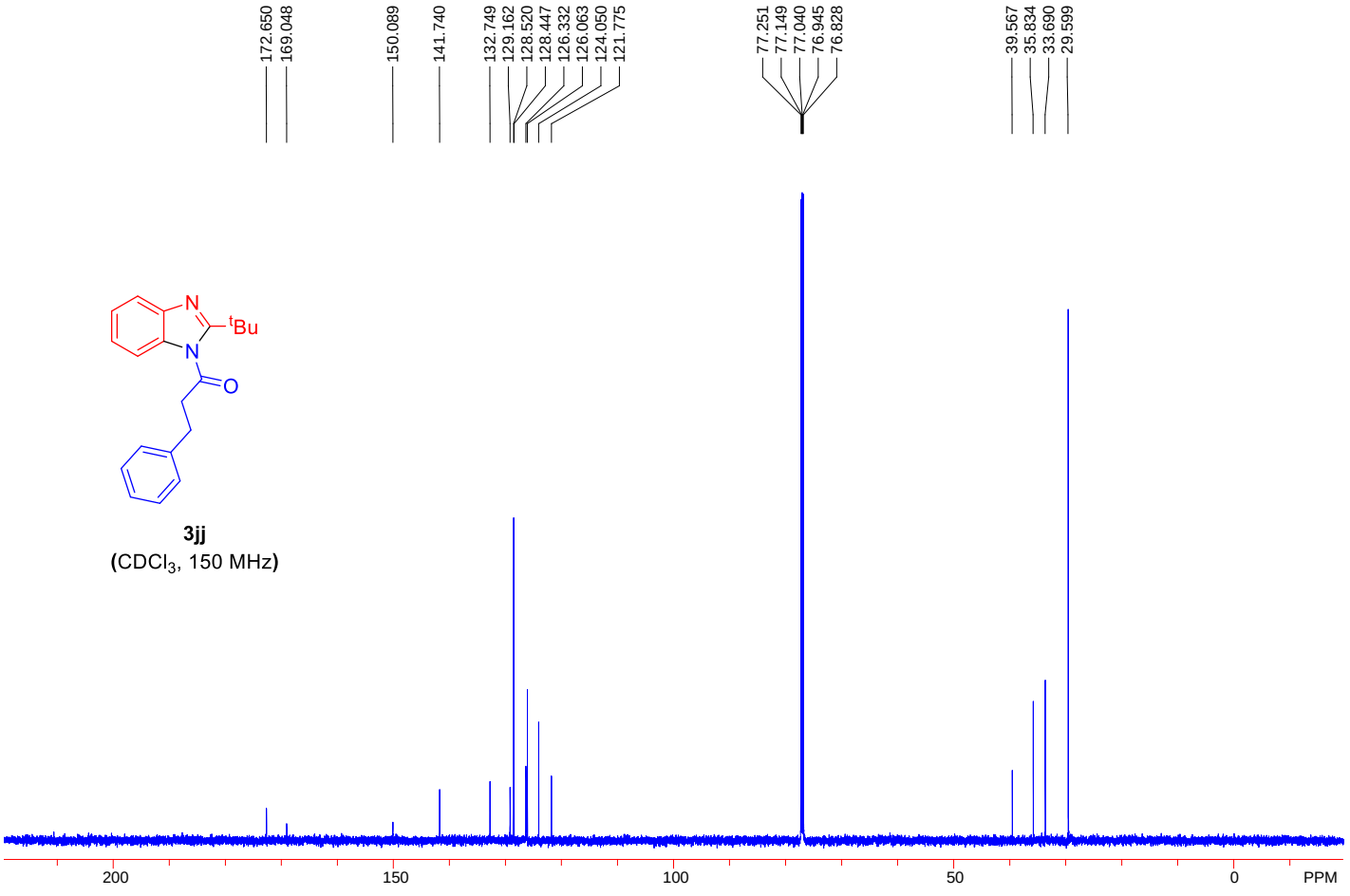
3hh
(CDCl$_3$, 150 MHz)


8.060
8.046
7.980
7.966
7.795
7.793
7.781
7.769
7.768
7.532
7.520
7.508
7.259
3.258
3.245
3.232
1.796
1.784
1.771
1.759
1.731
1.720
1.709
1.698
1.687
1.491
1.010
0.999
N
tBu
N
O
3ii
(CDCl3, 600 MHz)
9.12
6.13
1.00
0.99
0.99
0.97
2.06
2.04
1.11
10
8
6
4
2
PPM

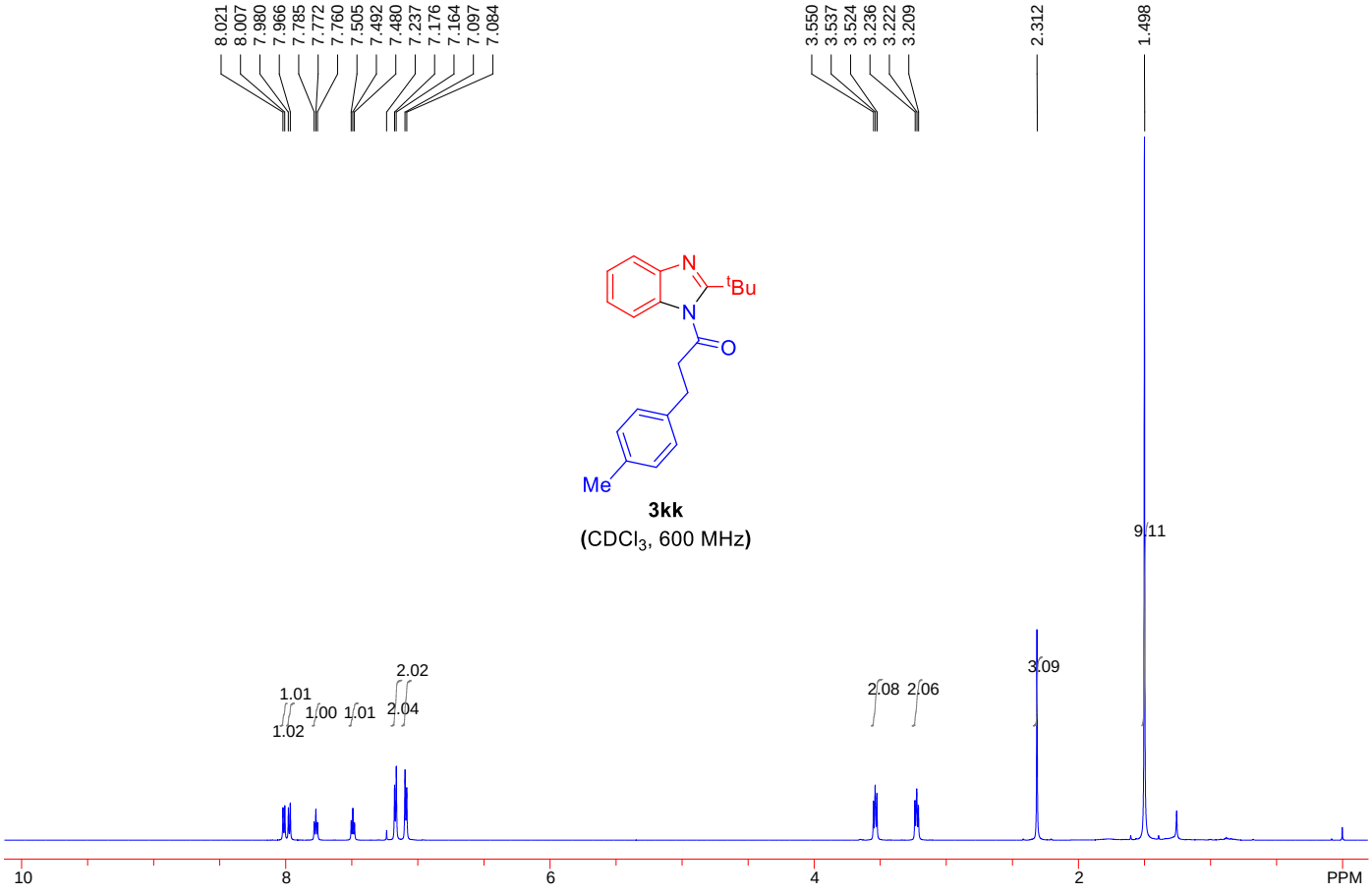

172.672
170.732
150.118
132.632
129.132
126.172
124.291
121.709
77.244
77.032
76.821
39.480
37.401
29.716
29.585
28.017
22.541
N
tBu
N
O
3ii
(CDCl3, 150 MHz)
200
150
100
50
0
PPM



3jj
(CDCl$_3$, 400 MHz)

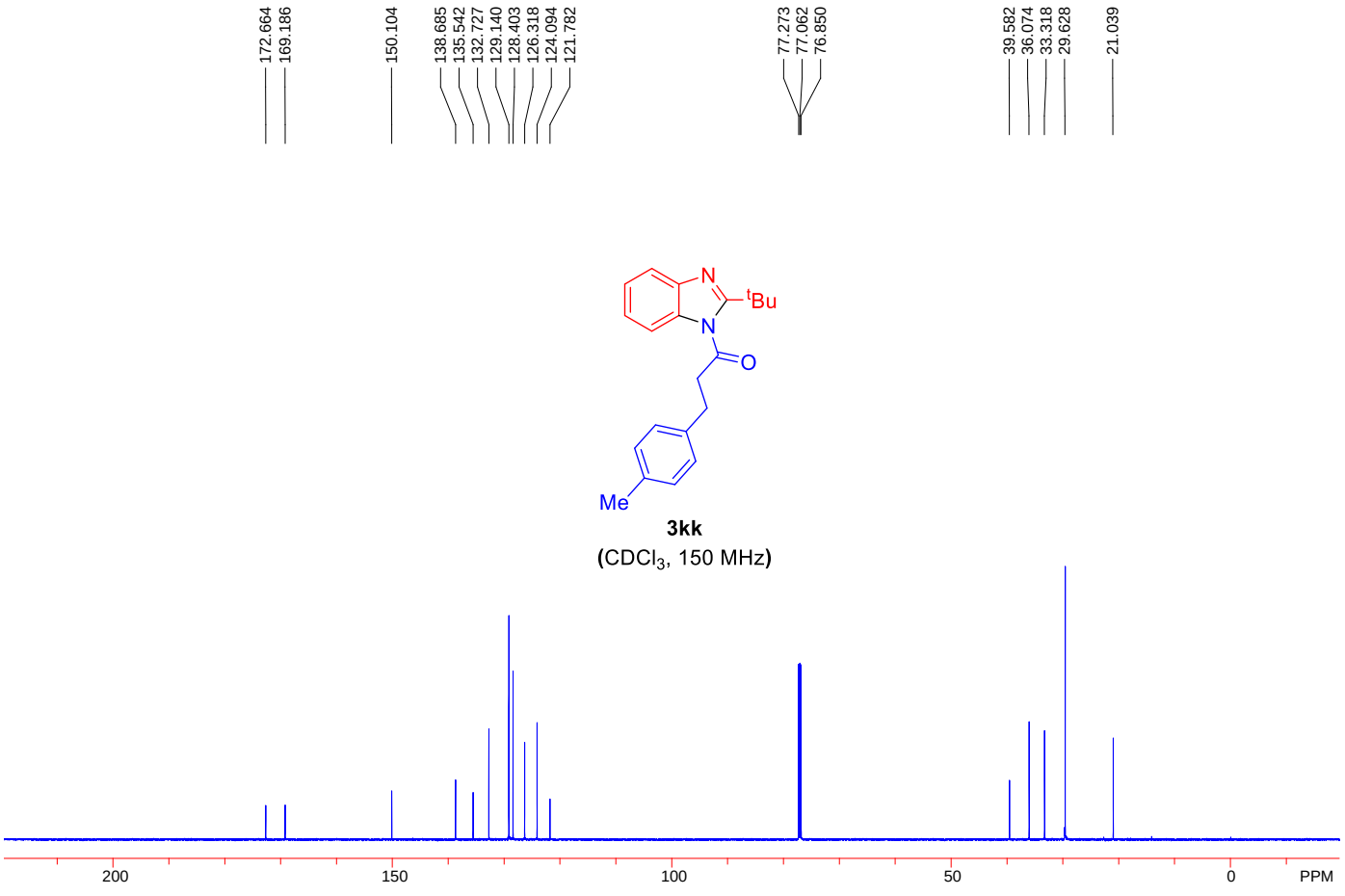


3jj
(CDCl$_3$, 150 MHz)



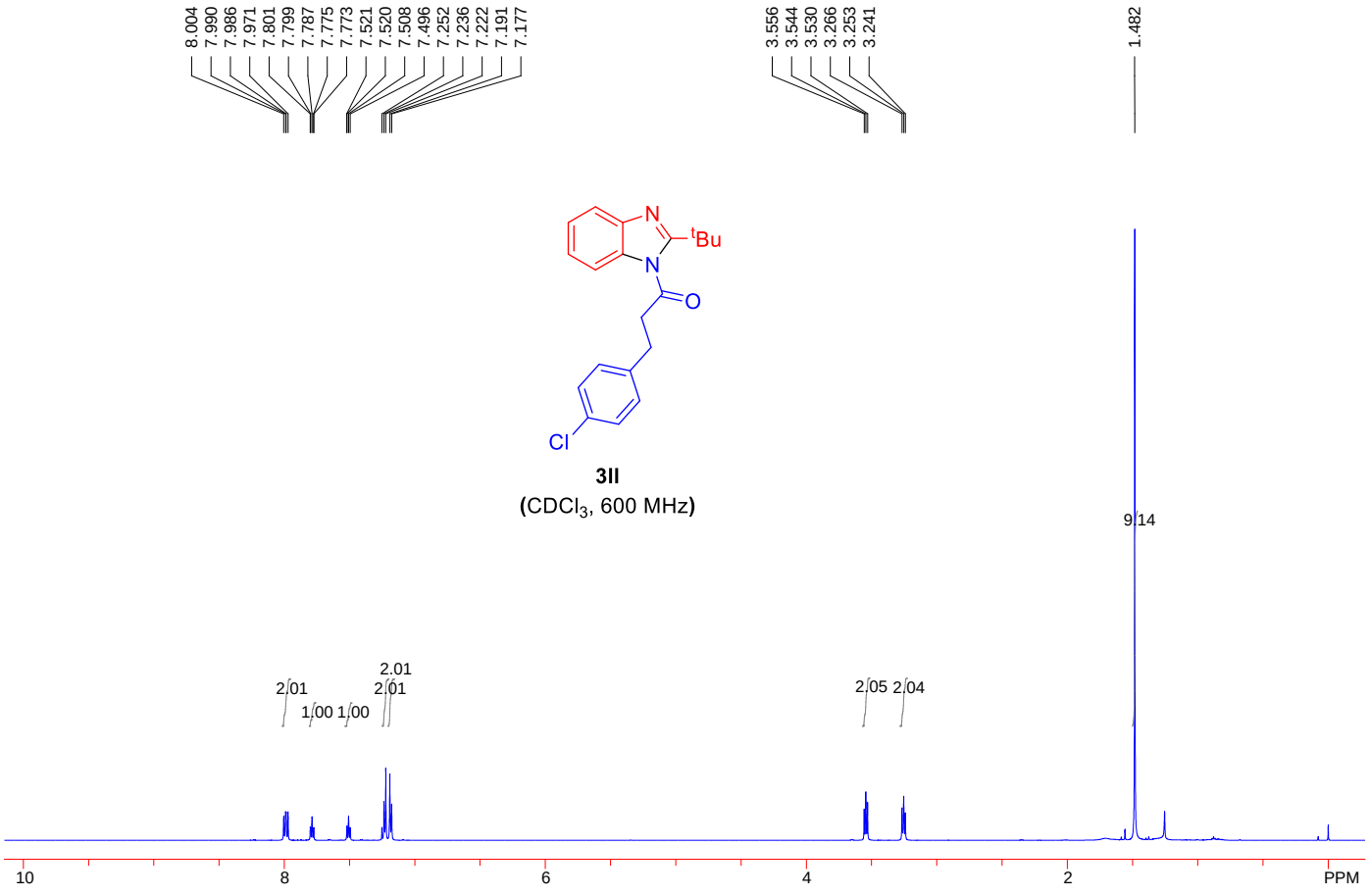
3kk

($CDCl_3$, 600 MHz)



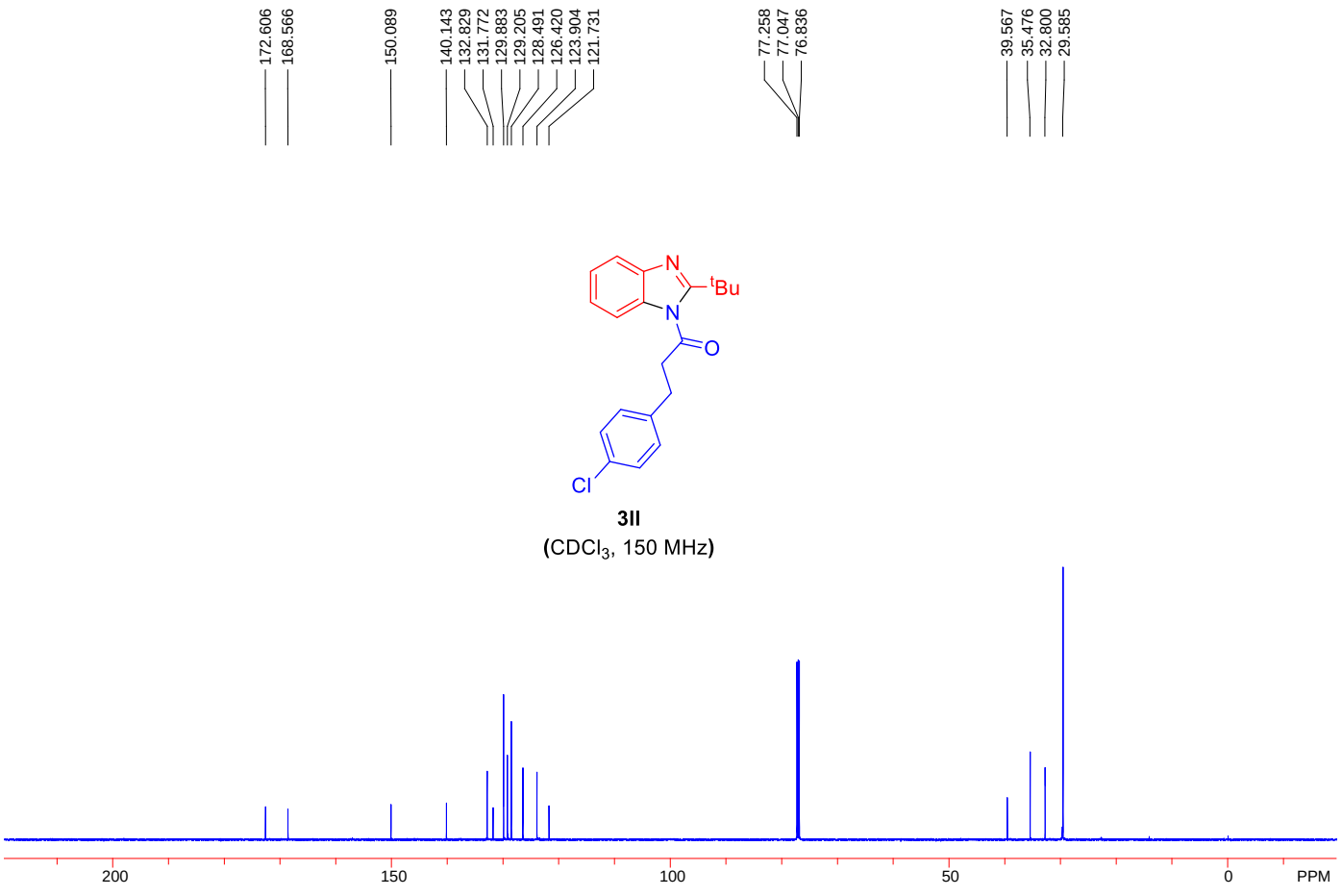
3kk

($CDCl_3$, 150 MHz)



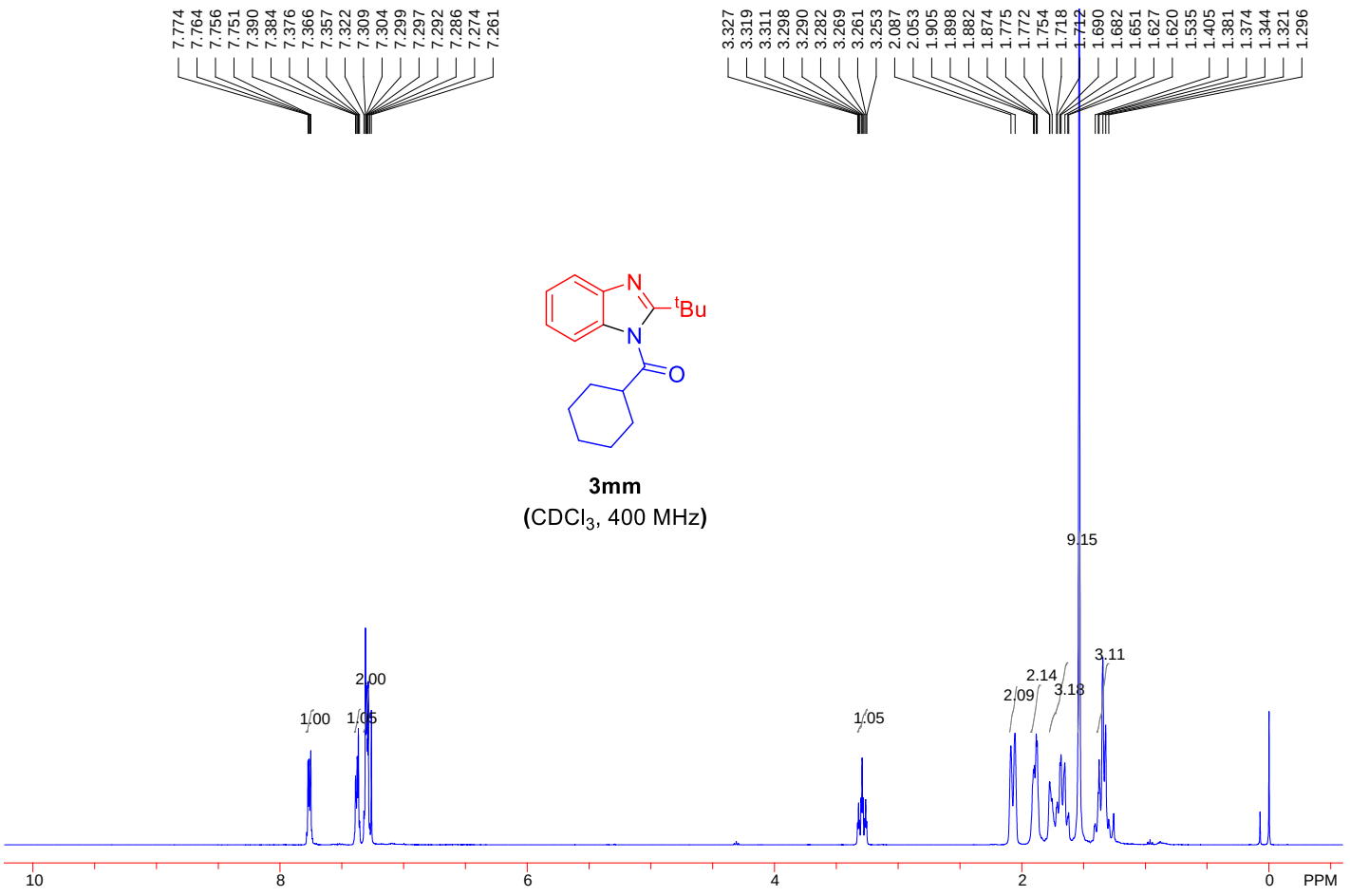
3ll

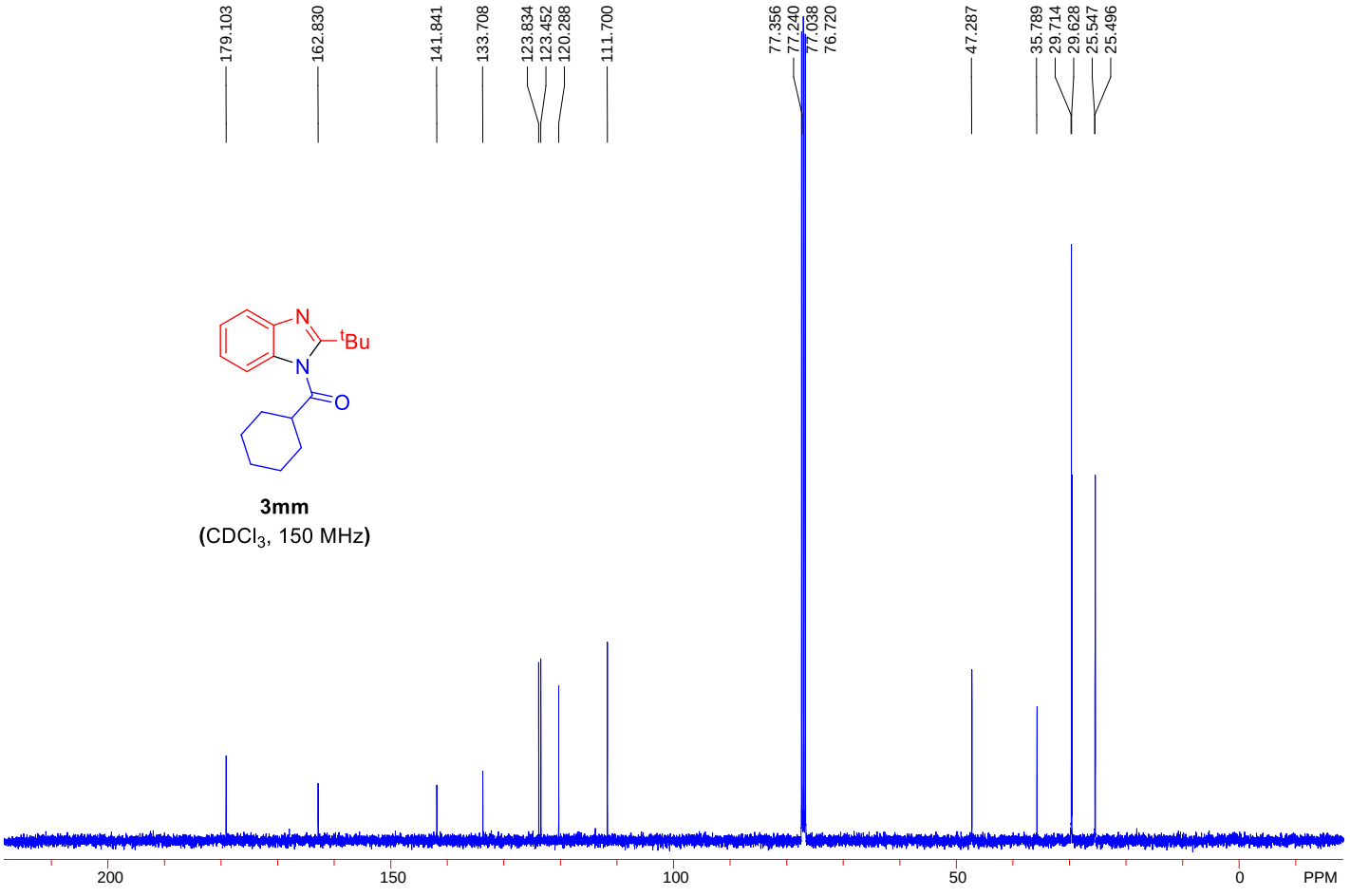
($CDCl_3$, 600 MHz)



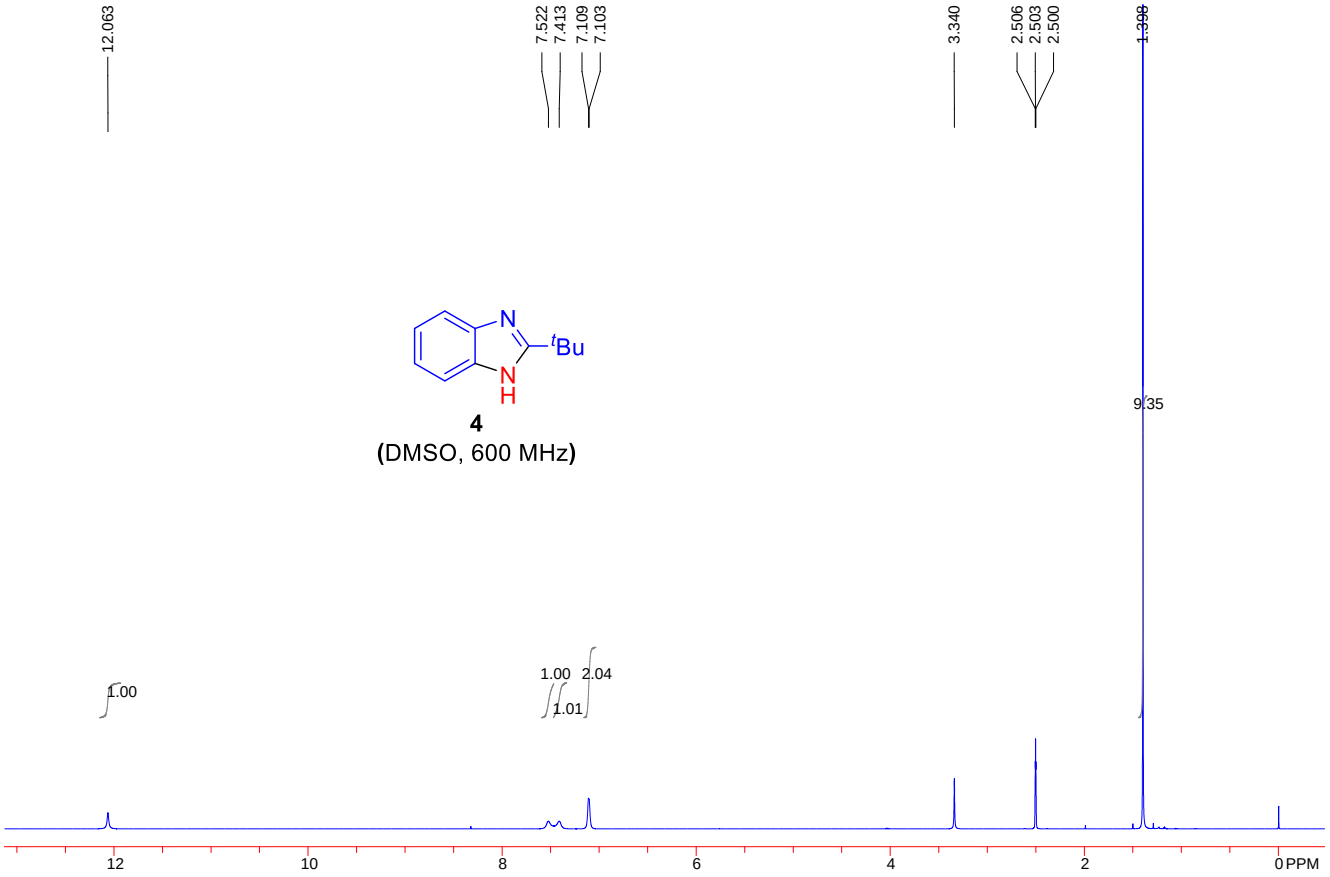
3ll

($CDCl_3$, 150 MHz)


7.774
7.764
7.756
7.751
7.390
7.384
7.376
7.366
7.357
7.322
7.309
7.304
7.299
7.297
7.292
7.286
7.274
7.261
3.327
3.319
3.311
3.298
3.290
3.282
3.269
3.261
3.253
2.087
2.053
1.905
1.898
1.882
1.874
1.775
1.772
1.754
1.718
1.712
1.690
1.682
1.651
1.627
1.620
1.535
1.405
1.381
1.374
1.344
1.321
1.296
N
tBu
N
O
3mm
(CDCl3, 400 MHz)
9.15
3.11
2.14
2.09
3.18
2.00
1.00
1.05
1.05
10
8
6
4
2
0
PPM

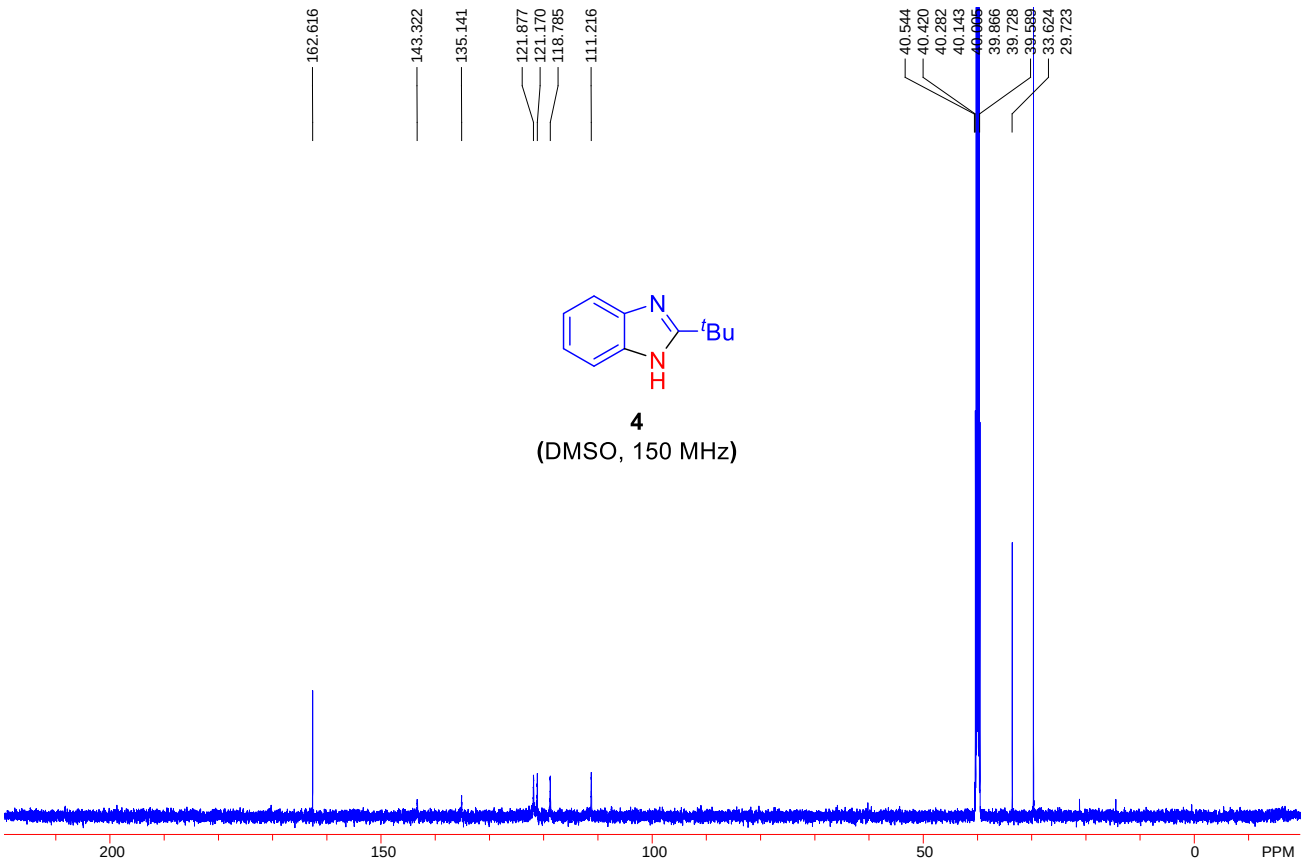

179.103
162.830
141.841
133.708
123.834
123.452
120.288
111.700
77.356
77.240
77.038
76.720
47.287
35.789
29.714
29.628
25.547
25.496
N
tBu
N
O
3mm
(CDCl3, 150 MHz)
200
150
100
50
0
PPM

V Copies of NMR spectra of products 4-7



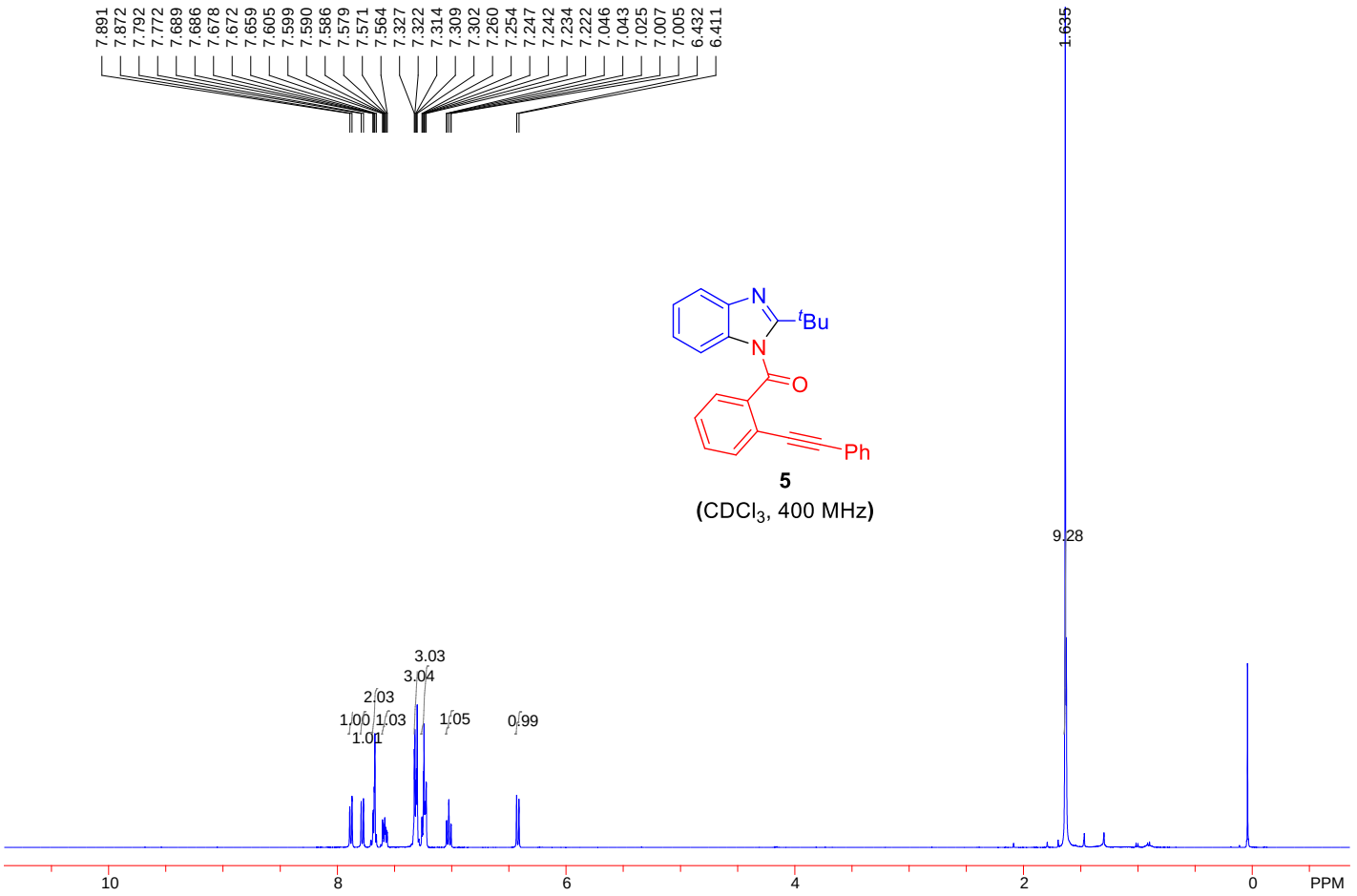
4

(DMSO, 600 MHz)



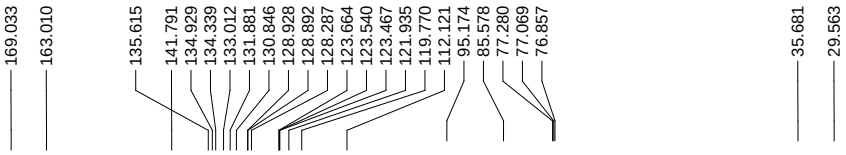
4

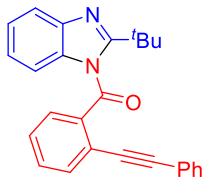
(DMSO, 150 MHz)



5

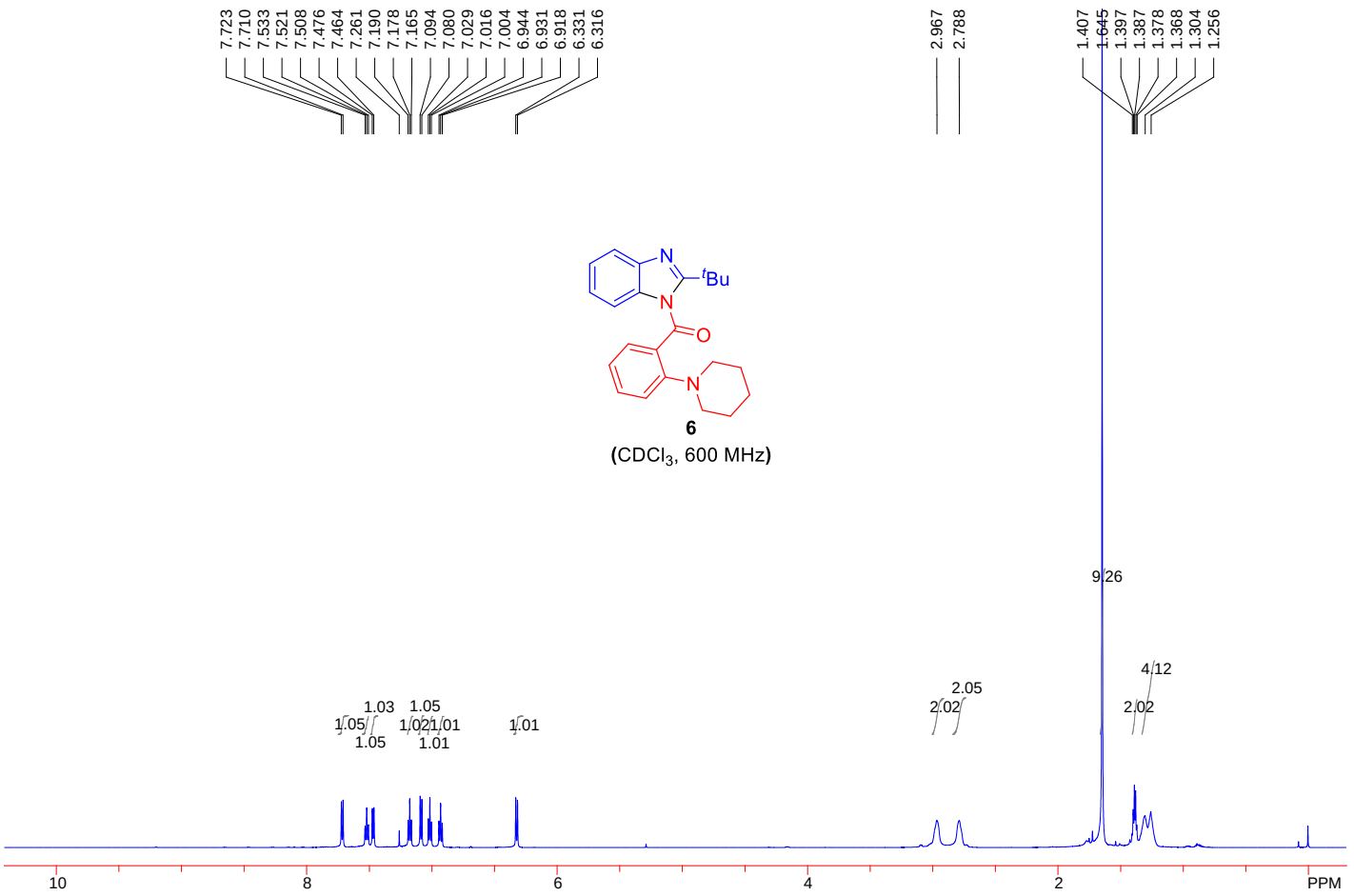
(CDCl$_3$, 400 MHz)





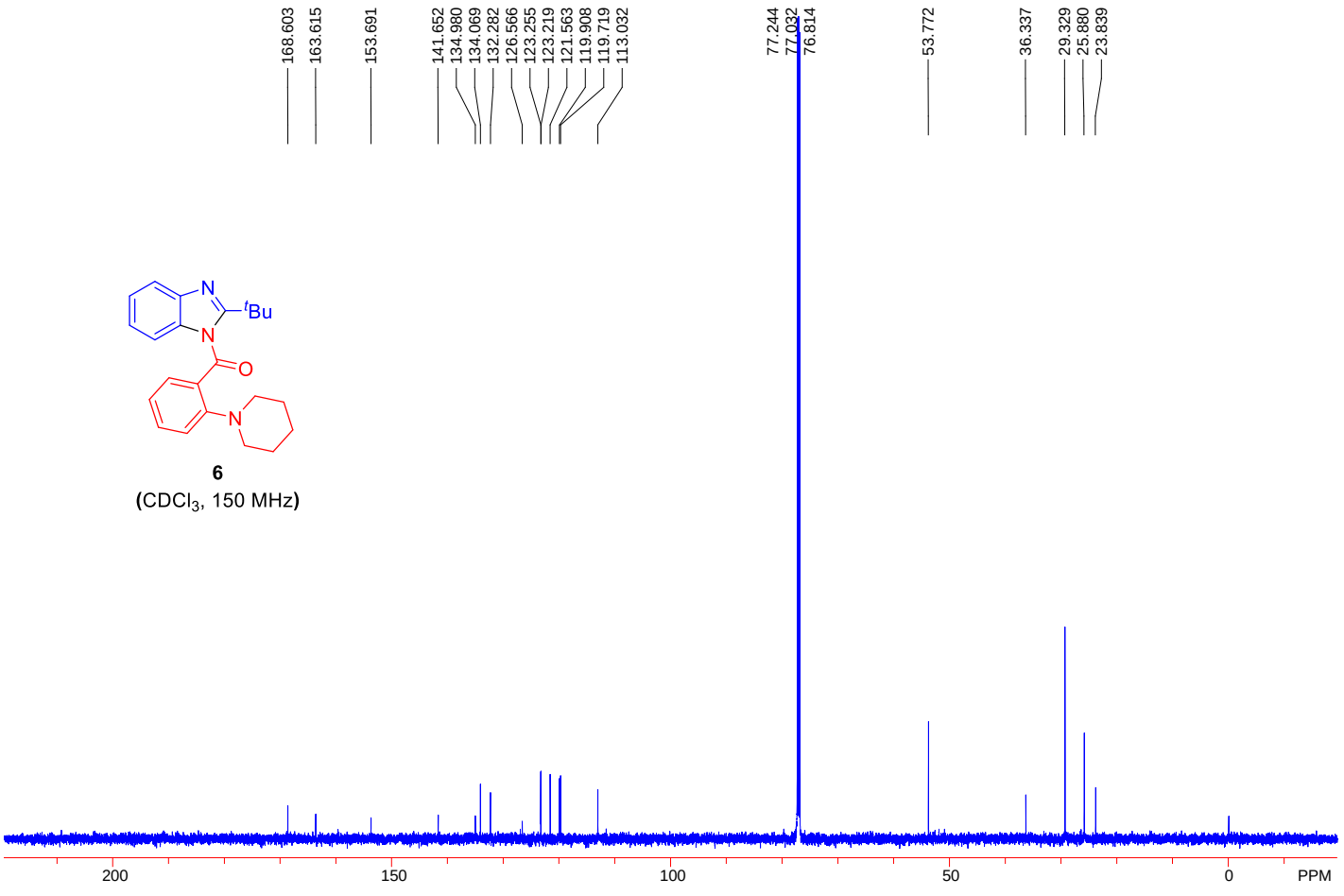
5

(CDCl$_3$, 100 MHz)



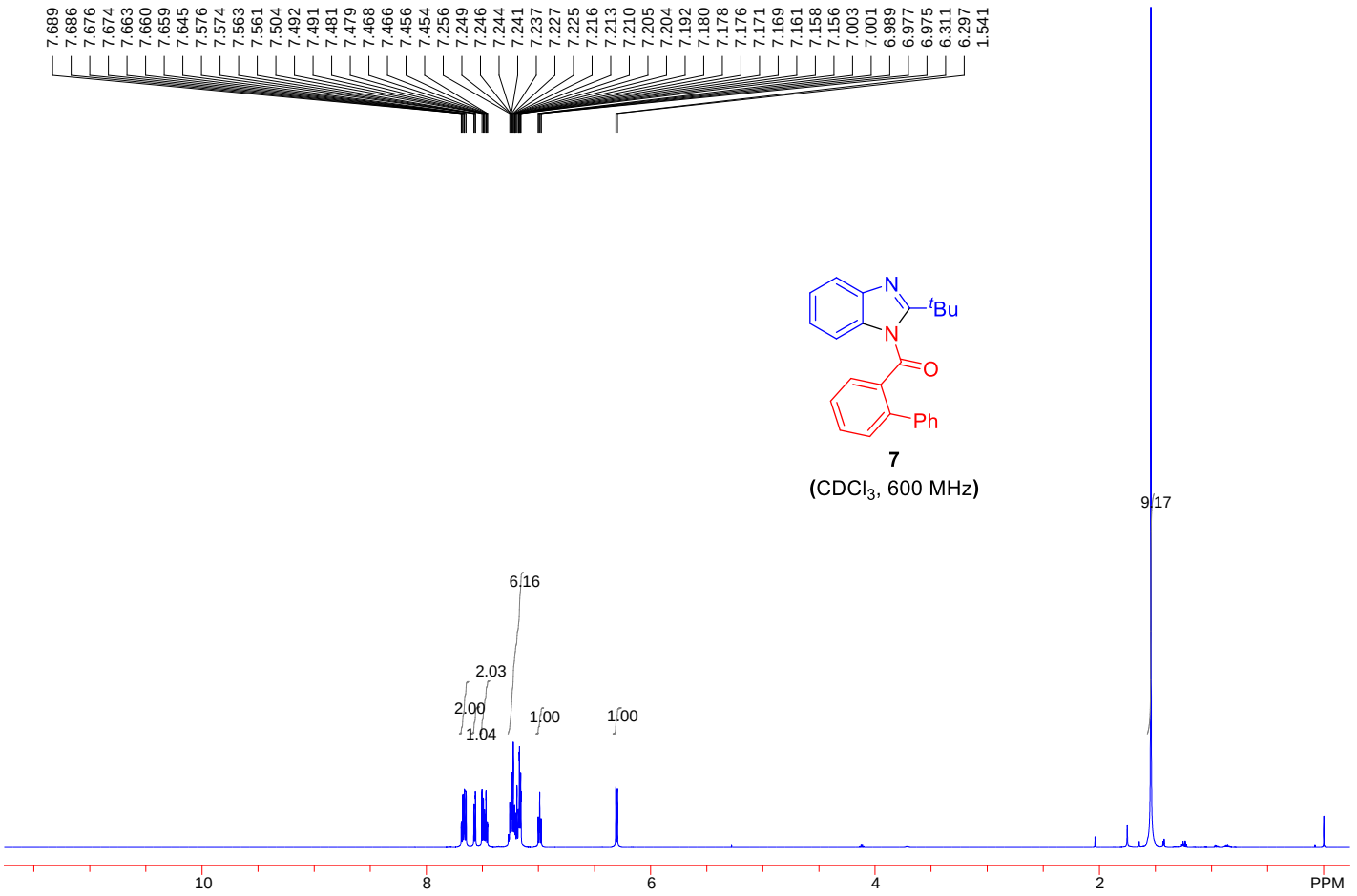
6

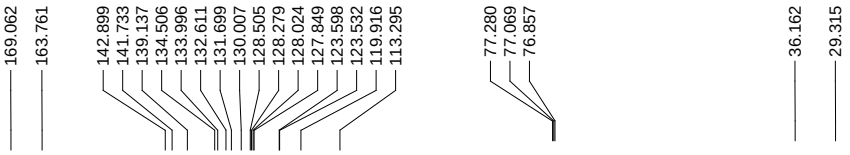
(CDCl$_3$, 600 MHz)

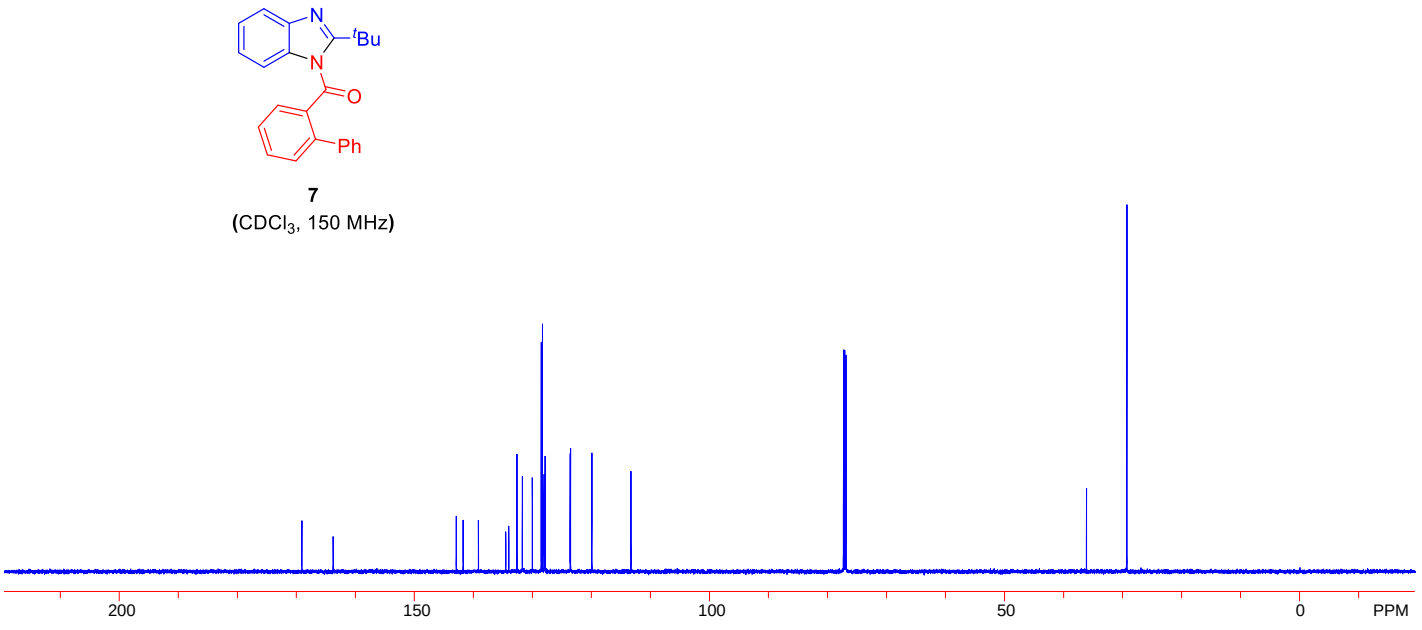


6

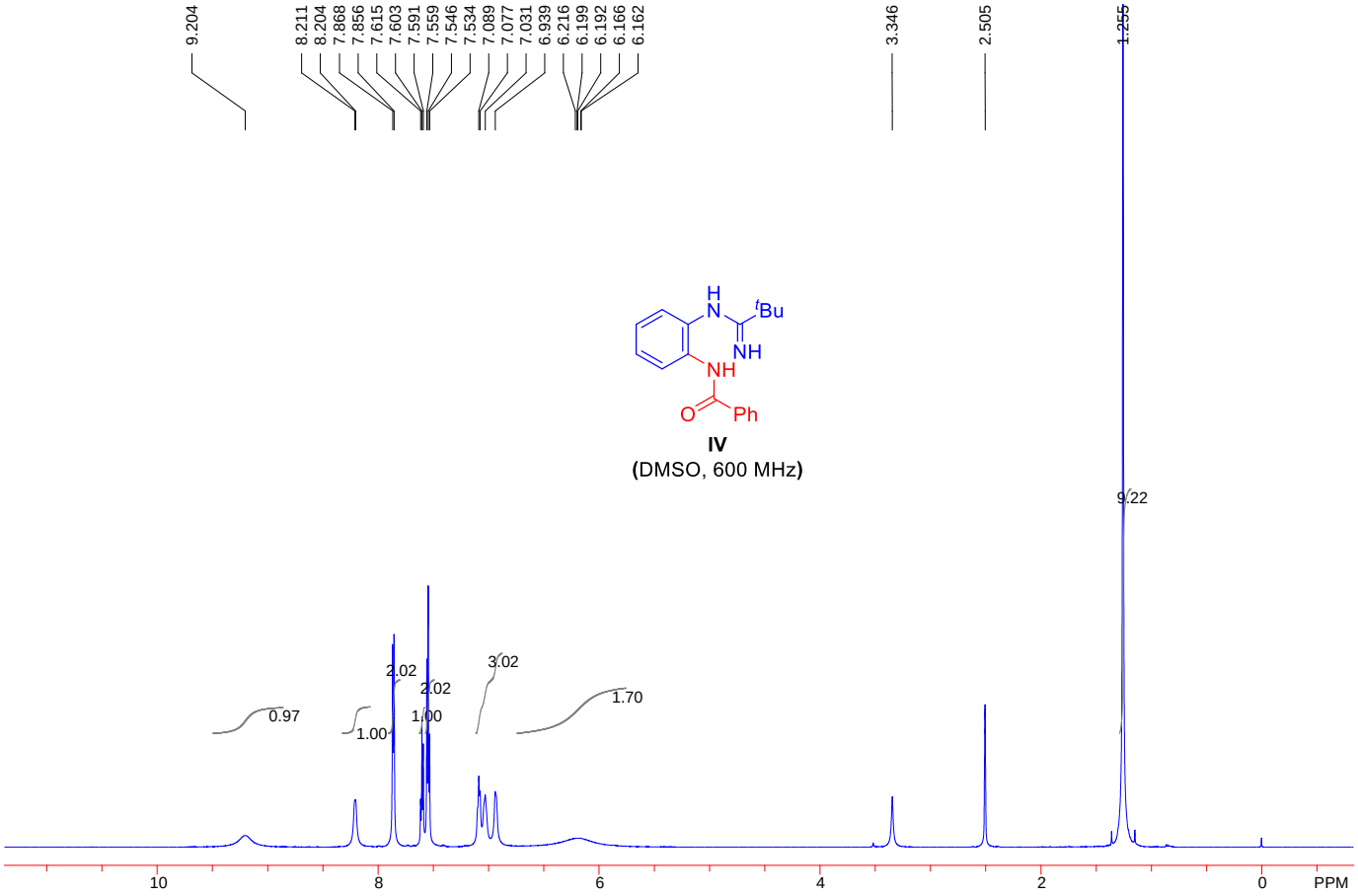
(CDCl$_3$, 150 MHz)

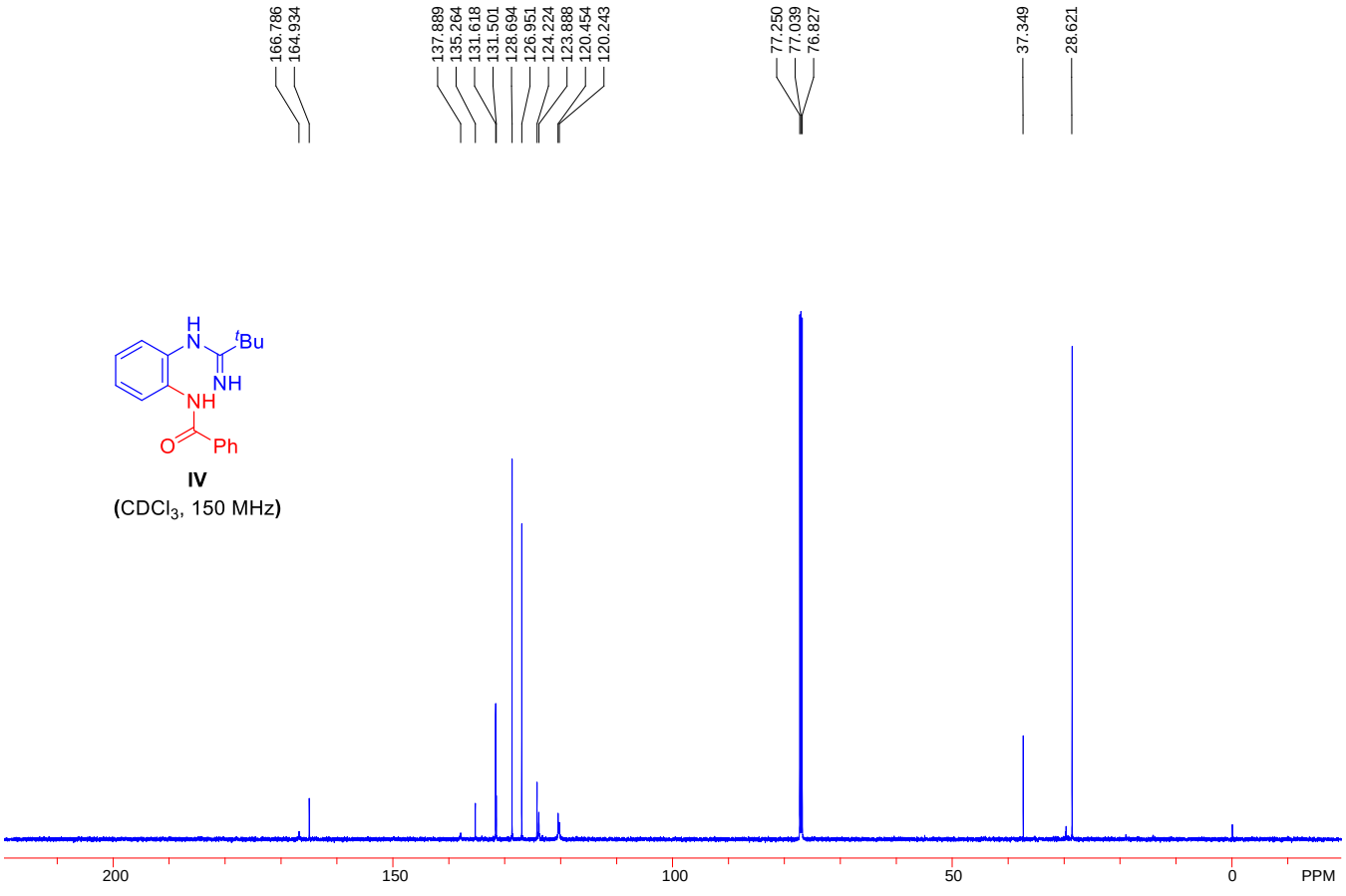

7.689
7.686
7.676
7.674
7.663
7.660
7.659
7.645
7.576
7.574
7.563
7.561
7.504
7.492
7.491
7.481
7.479
7.468
7.466
7.456
7.454
7.256
7.249
7.246
7.244
7.241
7.237
7.227
7.225
7.216
7.213
7.210
7.205
7.204
7.192
7.180
7.178
7.176
7.171
7.169
7.161
7.158
7.156
7.003
7.001
6.989
6.977
6.975
6.311
6.297
1.541
N
tBu
N
O
Ph
7
(CDCl3, 600 MHz)
9.17
6.16
2.03
2.00
1.04
1.00
1.00
10
8
6
4
2
PPM


169.062
163.761
142.899
141.733
139.137
134.506
133.996
132.611
131.699
130.007
128.505
128.279
128.024
127.849
123.598
123.532
119.916
113.295
77.280
77.069
76.857
36.162
29.315


N
tBu
N
O
Ph
7
(CDCl3, 150 MHz)
200
150
100
50
0
PPM

VI. Copies of NMR spectra of intermediate IV





VII. X-ray crystal structure and data of product 3o

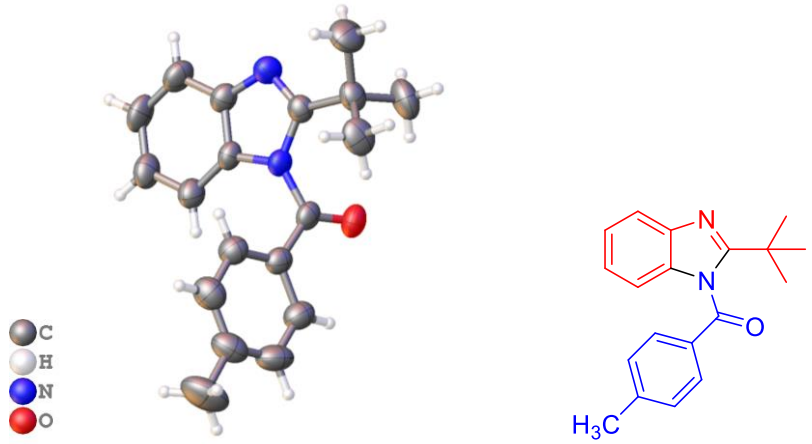


Fig. S1 X-ray crystal structure of **3o** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (8:1) solution of **3o**. Crystal data collection and refinement parameters of **3o** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3o**

Empirical formula	$C_{19}H_{20}N_2O$
Formula weight	292.37
Temp, K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	9.7662(2)
b, Å	9.2325(2)
c, Å	18.7919(4)
α (°)	90

β (°)	101.473(2)
γ (°)	90
Volume, Å^3	1660.54(6)
Z	4
ρ_{calc}, g cm^{-3}	1.169
λ, Å	1.54184
μ, mm^{-1}	0.571
No. of data collected	6499
No. of unique data	3143
R_{int}	0.0189
Goodness-of-fit on F^2	1.070
R_1, wR_2 (I> 2σ(I))	0.0542, 0.1354
R_1, wR_2 (all data)	0.0666, 0.1442

VIII. References

[1] G. Brasche and S. L. Buchwald, C–H Functionalization/C–N Bond Formation: Copper-Catalyzed Synthesis of Benzimidazoles from Amidines, *Angew. Chem. Int. Ed*., 2008, **47**, 1932−1934.

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