Supporting Information

Catalytic Synthesis of Functionalized Amidines via Cobalt-Carbene Radical Coupling with Isocyanides and Amines

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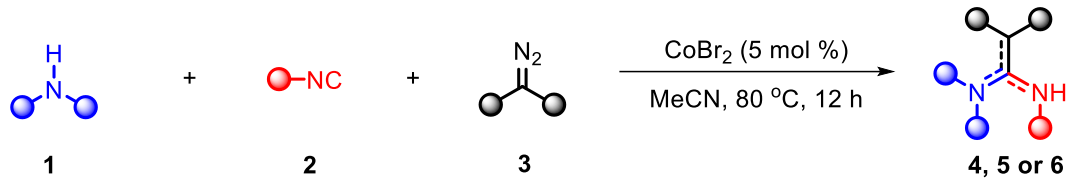
I. General Information

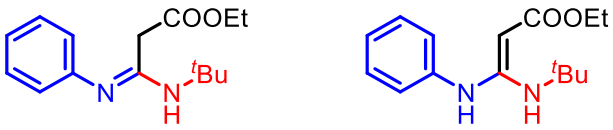
All intermolecular amidation reactions were carried out under atmospheric pressure of carbon monoxide (CO) in oven-dried Schlenk tube. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ^{o}C). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate–Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference DMSO-d_6 and $CDCl_3$ as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of DMSO-d_6 (δ 2.50) and residual proton (δ 7.26) in $CDCl_3$. Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); m (multiplet); br (broad). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of DMSO-d_6 (δ 40.00) and $CDCl_3$ (77.16). Materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, or other commercial suppliers and used as received unless otherwise noted. Sulfonyl azides were purchased if commercially available or prepared from sulfonyl chlorides and sodium azide according to the well-established methods.

II. General Procedure for the Synthesis of Amidines and Characterization Data of Amidines



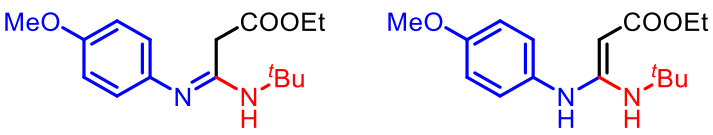
1 **2** **3** **4, 5 or 6**

To an oven-dried Schlenk tube (10 mL) was added the amines **1** (0.5 mmol, 1.0 equiv), isocyanides **2** (0.6 mmol, 1.2 equiv), diazos **3** (0.6 mmol, 1.2 equiv), $CoBr_2$ (5.5 mg, 5.0 mol %), and dry MeCN (3 mL). The tube was backfilled with N_2. After stirring for 12 h at 80 °C, the reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 15:1~10:1) to give the pure desired product **4**, **5** or **6**.



(*E*)-Ethyl-3-(*tert*-butylamino)-3-(phenylimino)propanoate 4a and (*E*)-ethyl-3-(*tert*-butylamino)-3-(phenylamino)acrylate 4a' (4a/4a'= 6/1)

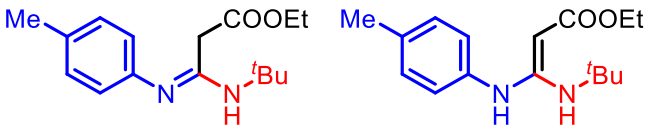
Yield = 82% (107.6 mg). Yellow oil. For **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.97 – 6.93 (m, 1H), 6.74 – 6.72 (m, 2H), 4.89 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 2H), 1.44 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 151.0, 148.0, 128.9, 122.0, 121.8, 61.3, 51.6, 36.7, 28.7, 14.1. For **4a'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (brs, 1H), 7.37 – 7.33 (m, 2H), 7.17-7.13 (m, 3H), 4.38 (brs, 1H), 4.33 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 125.1, 124.6, 66.4, 58.4, 51.2, 29.7, 15.0. HRMS (ESI) calculated for $C_{15}H_{23}N_2O_2$ $(M+H)^+$ 263.1754, found 263.1757.



(*E*)-Ethyl-3-(tert-butylamino)-3-((4-methoxyphenyl)imino)propanoate 4b and

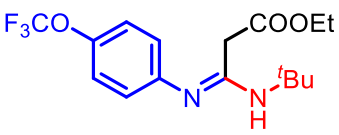
(*E*)-ethyl-3-(tert-butylamino)-3-((4-methoxyphenyl)amino)acrylate 4b' (4b/4b'= 2/1)

Yield = 89% (130.1 mg). Yellow oil. For **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.81 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.09 (s, 2H), 1.43 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 157.9, 154.9, 148.6, 122.7, 114.3, 61.3, 55.6, 36.6, 29.8, 28.8, 14.2. For **4b'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (brs, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.29 (s, 1H), 4.17 (brs, 1H), 3.79 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 157.7, 144.4, 129.9, 127.5, 114.9, 65.5, 58.2, 55.5, 51.1, 30.9, 15.0. HRMS (ESI) calculated for $C_{16}H_{25}N_2O_3$ $(M+H)^+$ 293.1860, found 293.1866.



(*E*)-Ethyl-3-(*tert*-butylamino)-3-(*p*-tolylimino)propanoate 4c and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*p*-tolylamino)acrylate 4c' (4c/4c'= 3/1)

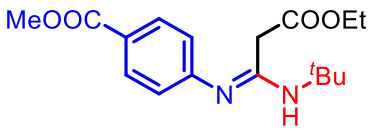
Yield = 86% (118.8 mg). Yellow oil. For **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.85 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 2H), 2.29 (s, 3H), 1.44 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 148.4, 148.1, 130.9, 129.4, 121.8, 61.3, 51.5, 36.6, 28.8, 20.8, 14.2. For **4c'**: 10.32 (brs, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.34 (brs, 1H), 4.31 (s, 1H), 2.33 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 157.3, 135.2, 134.9, 130.4, 125.1, 65.9, 58.3, 51.2, 29.7, 21.0, 15.0. HRMS (ESI) calculated for $C_{16}H_{25}N_2O_2$ $(M+H)^+$ 277.1911, found 277.1908.



(*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-(trifluoromethoxy) phenyl)imino)propanoate

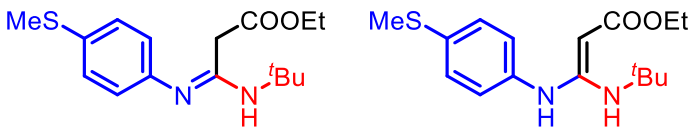
4d (4d/4d' > 20/1)

Yield = 74% (128.2 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.72-6.70 (m, 2H), 4.95 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 2H), 1.43 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 149.8, 148.6, 144.1, 122.9, 121.8, 120.8 (q, J_{CF} = 254 Hz), 61.5, 51.8, 36.7, 28.7, 14.1; HRMS (ESI) calculated for $C_{16}H_{23}F_3N_2O_3$ $(M+H)^+$ 347.1577, found 347.1587.



(*E*)-Methyl-4-((1-(*tert*-butylamino)-3-ethoxy-3-oxopropylidene)amino)benzoate 4e (4e/4e' > 20/1)

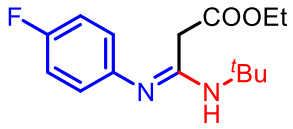
Yield = 56% (89.7 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.08 (brs, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.06 (s, 2H), 1.42 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.4, 155.7, 147.9, 130.8, 123.4, 121.8, 61.5, 51.8, 36.8, 28.6, 14.1; HRMS (ESI) calculated for $C_{17}H_{25}N_2O_4$ $(M+H)^+$ 321.1809, found 321.1820.



(*E*)-Ethyl-3-(tert-butylamino)-3-((4-(methylthio)phenyl)imino)propanoate 4f and (*E*)-ethyl-3-(*tert*-butylamino)-3-((4-(methylthio)phenyl)amino)acrylate 4f' (4f/4f' = 7/1)

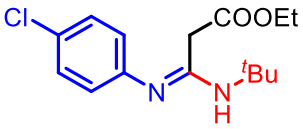
Yield = 65% (100.2 mg). Yellow oil. For **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.90 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 2H), 2.44 (s, 3H), 1.42 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 149.2, 148.3, 130.0, 129.2, 122.6, 61.4, 51.6, 36.6, 28.7, 17.7, 14.1; For **4f'**: 10.33 (brs, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 1H), 4.26 (brs, 1H), 2.47 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9,

128.2, 125.3, 66.5, 58.4, 51.3, 29.7, 16.3, 15.0. HRMS (ESI) calculated for $C_{16}H_{25}N_2O_2S$ $(M+H)^+$ 309.1631, found 309.1646.



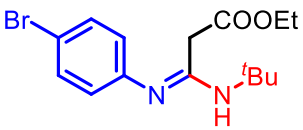
(*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-fluorophenyl)imino) propanoate 4g (4g/4g' > 20/1)

Yield = 71% (99.5 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.89 (m, 2H), 6.65 (dd, *J* = 8.8, 4.8 Hz, 2H), 4.87 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 2H), 1.42 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 158.6 (d, *J* = 237.7 Hz), 148.8, 147.1, 123.0 (d, *J* = 7.7 Hz), 115.4 (d, *J* = 25.0 Hz), 61.4, 51.6, 36.7, 28.7, 14.1; HRMS (ESI) calculated for $C_{15}H_{22}FN_2O_2$ $(M+H)^+$ 281.1660, found 281.1667.



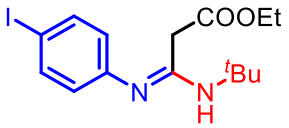
(*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino) propanoate 4h (4h/4h' > 20/1)

Yield = 80% (111.5 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.94 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 2H), 1.42 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 149.6, 148.5, 128.8, 126.8, 123.3, 61.4, 51.7, 36.6, 28.7, 14.1; HRMS(ESI) calcd for $C_{15}H_{22}ClN_2O_2$ $(M+H)^+$ 297.1364, found 297.1360.



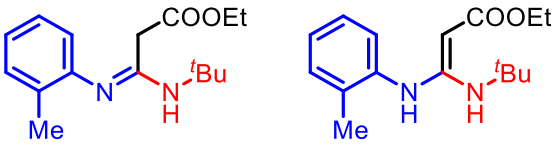
(*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(*tert*-butylamino) propanoate 4i (4i/4i' > 20/1)

Yield = 79% (134.3 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.95 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 2H), 1.42 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 150.1, 148.3, 131.8, 123.8, 114.5, 61.5, 51.7, 36.6, 28.7, 14.1; HRMS(ESI) calcd for $C_{15}H_{22}BrN_2O_2$ $(M+H)^+$ 341.0859, found 341.0867.



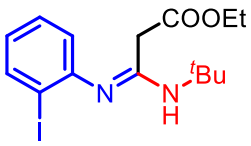
(*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-iodophenyl)imino) propanoate 4j (4j/4j' > 20/1)

Yield = 53% (102.9 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 4.96 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 2H), 1.41 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 150.7, 148.3, 137.8, 124.4, 84.8, 61.5, 51.7, 36.6, 28.7, 14.2; HRMS(ESI) calcd for $C_{15}H_{22}IN_2O_2$ $(M+H)^+$ 389.0720, found 389.0724.



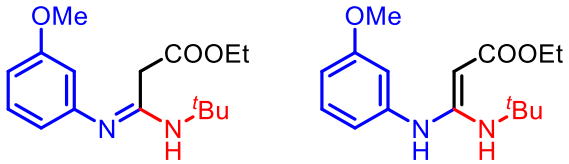
(*E*)-Ethyl-3-(*tert*-butylamino)-3-(*o*-tolylimino)propanoate 4k and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*o*-tolylamino)acrylate 4k' (4k/4k' = 10/1)

Yield = 96% (132.6 mg). Yellow oil. For **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.89 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 4.94 (brs, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.04 (s, 2H), 2.12 (s, 3H), 1.48 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 149.6, 147.5, 130.1, 129.9, 126.3, 121.9, 121.2, 61.2, 51.4, 36.7, 28.8, 18.4, 14.1; For **4k'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (brs, 1H), 4.35 (s, 1H), 2.31 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 131.4, 126.9, 65.6, 58.2, 30.9, 29.7, 18.0, 15.0. HRMS (ESI) calcd for $C_{16}H_{25}N_2O_2$ $(M+H)^+$ 277.1911, found 277.1917.



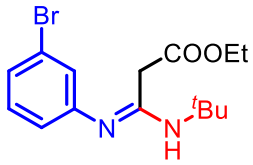
(*E*)-Ethyl-3-(*tert*-butylamino)-3-((2-iodophenyl)imino)propanoate 4l (4l/4l' > 20/1)

Yield = 87% (168.9 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.73 – 6.64 (m, 2H), 5.30 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.01 (s, 2H), 1.50 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 152.4, 148.8, 138.8, 128.9, 123.4, 121.9, 94.2, 61.4, 51.7, 36.8, 29.0, 14.2; HRMS(ESI) calcd for $C_{15}H_{22}IN_2O_2$ $(M+H)^+$ 389.0720, found 389.0724.



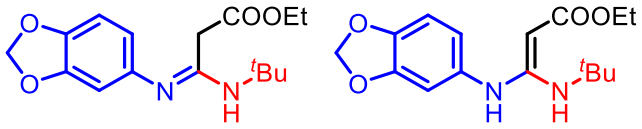
(*E*)-Ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)imino)propanoate 4m and (*E*)-ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)amino)acrylate 4m' (4m/4m' = 8/1)

Yield = 77% (112.6 mg). Yellow oil. For **4m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.10 (m, 1H), 6.53 – 6.50 (m, 1H), 6.33 – 6.29 (m, 2H), 4.89 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 2H), 3.12 (s, 3H), 1.43 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 160.4, 152.4, 148.1, 129.6, 114.6, 107.8, 107.5, 61.4, 55.3, 51.6, 36.7, 28.8, 14.2; For **4m'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (brs, 1H), 4.50 (brs, 1H), 4.32 (s, 1H), 3.78 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 156.8, 130.5, 116.3, 110.9, 109.8, 66.6, 58.4, 55.4, 51.3, 29.8, 15.0. HRMS (ESI) calcd for $C_{16}H_{25}N_2O_3$ $(M+H)^+$ 293.1860, found 293.1860.



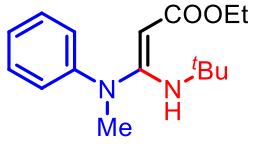
(*E*)-Ethyl-3-((3-bromophenyl)imino)-3-(*tert*-butylamino)propanoate 4n (4n/4n' > 20/1)

Yield = 75% (128.0 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.05 (m, 2H), 6.90 (s, 1H), 6.66-6.64 (m, 1H), 4.99 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 2H), 1.42 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 152.5, 148.5, 130.2, 125.1, 124.6, 122.5, 120.8, 61.5, 51.7, 36.8, 28.6, 14.2; HRMS(ESI) calcd for $C_{15}H_{21}BrN_2NaO_2$ $(M+Na)^+$ 363.0679, found 363.0678.



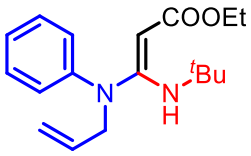
(*E*)-Ethyl-3-(benzo[*d*][1,3]dioxol-5-ylimino)-3-(*tert*-butylamino)propanoate 4o and (*E*)-ethyl-3-(benzo[*d*][1,3]dioxol-5-ylamino)-3-(*tert*-butylamino)acrylate 4o' (4o/4o' = 5/1)

Yield = 78% (119.5 mg). Yellow oil. For **4o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 2.0 Hz, 1H), 6.14 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.88 (s, 2H), 4.83 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.11 (s, 2H), 1.41 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 148.9, 148.0, 145.9, 142.6, 113.8, 108.3, 103.8, 100.8, 61.4, 51.6, 36.7, 28.8, 14.2; For **4o'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (brs, 1H), 5.97 (s, 2H), 4.28 (s, 1H), 4.21 (brs, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 157.7, 148.6, 145.8, 131.3, 119.3, 108.7, 107.4, 101.7, 65.8, 58.3, 51.2, 29.8, 15.0. HRMS (ESI) calcd for $C_{16}H_{23}N_2O_4$ $(M+H)^+$ 307.1652, found 307.1652.



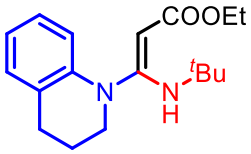
(*E*)-Ethyl-3-(*tert*-butylamino)-3-(methyl(*o*-tolyl)amino) acrylate 4p

Yield = 90% (132.6 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (brs, 1H), 7.18 – 7.14 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.85 – 6.81 m, 1H), 4.38 (s, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 166.7, 148.2, 128.9, 121.0, 118.5, 82.6, 58.9, 54.0, 40.7, 30.9, 14.7; HRMS(ESI) calcd for $C_{16}H_{24}N_2NaO_2$ $(M+Na)^+$ 299.1730, found 299.1731.



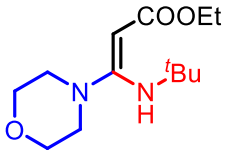
(*E*)-Ethyl-3-(allyl(phenyl)amino)-3-(*tert*-butylamino)acrylate 4q

Yield = 91% (138.0 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (brs, 1H), 7.22 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.90 (dd, *J* = 7.2, 7.6 Hz, 1H), 5.91-5.81 (m, 1H), 5.21-5.15 (m, 2H), 4.60 (s, 1H), 4.24 (d, *J* = 5.6 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 165.5, 146.4, 133.9, 128.9, 121.4, 120.2, 117.9, 83.2, 58.9, 54.7, 54.4, 30.9, 14.7; HRMS(ESI) calcd for $C_{18}H_{27}N_2O_2$ $(M+H)^+$ 303.2067, found 303.2069.



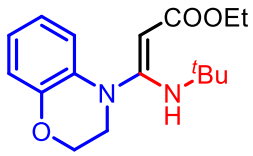
(*E*)-Ethyl-3-(*tert*-butylamino)-3-(3,4-dihydroquinolin-1(2*H*)-yl) acrylate 4r

Yield = 88% (133.3 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 3H), 7.07 – 7.02 (m, 1H), 6.82 (brs, 1H), 4.46 (s, 1H), 4.25 (s, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.45 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.0 Hz, 2H), 1.27 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 169.4, 134.2, 134.0, 129.0, 126.6, 126.3, 126.2, 80.0, 58.7, 54.8, 52.6, 48.0, 30.5, 28.4, 14.7; HRMS(ESI) calcd for $C_{18}H_{27}N_2O_2$ $(M+H)^+$ 303.2067, found 303.2073.



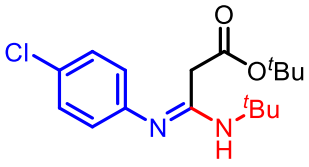
(*E*)-Ethyl-3-(*tert*-butylamino)-3-morpholinoacrylate 4s

Yield = 92% (118.0 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (brs, 1H), 4.39 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 4.8 Hz, 4H), 3.07 (t, *J* = 4.8 Hz, 4H), 1.29 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.5, 80.2, 66.5, 66.4, 58.6, 54.5, 50.8, 30.3, 14.5; HRMS(ESI) calcd for $C_{13}H_{25}N_2O_3$ $(M+H)^+$ 257.1860, found 257.1860.



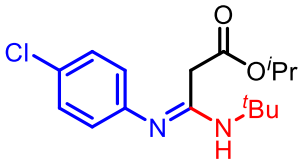
(*E*)-Ethyl-3-(*tert*-butylamino)-3-(2,3-dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)acrylate 4t

Yield = 64% (97.4 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (brs, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.86 – 6.84 (m, 2H), 6.82 – 6.78 (m, 1H), 4.52 (s, 1H), 4.32-4.08 (m, 4H), 3.76-3.22 (m, 2H), 1.38 (s, 9H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 166.4, 146.3, 130.1, 122.8, 122.2, 120.8, 117.3, 85.3, 63.7, 58.9, 54.6, 48.6, 30.9, 14.6; HRMS(ESI) calcd for $C_{17}H_{25}N_2O_3$ $(M+H)^+$ 305.1860, found 305.1870.



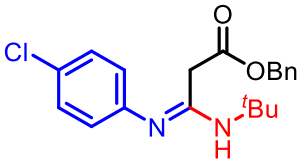
(*E*)-*tert*-Butyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5a

Yield = 90% (146.2 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.84 (brs, 1H), 2.97 (s, 2H), 1.45 (s, 9H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 149.7, 149.0, 128.8, 126.9, 123.5, 82.0, 51.6, 38.2, 28.8, 28.1; HRMS(ESI) calcd for $C_{17}H_{26}ClN_2O_2$ $(M+H)^+$ 325.1677, found 325.1684.



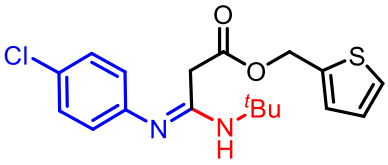
(*E*)-Isopropyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5b

Yield = 91% (141.4 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 5.00 (hept, *J* = 6.0 Hz, 1H), 4.89 (brs, 1H), 3.03 (s, 2H), 1.42 (s, 9H), 1.23 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.7, 148.6, 128.9, 126.9, 123.4, 69.1, 51.7, 37.1, 28.7, 21.8; HRMS(ESI) calcd for $C_{16}H_{24}ClN_2O_2$ $(M+H)^+$ 311.1521, found 311.1532.



(*E*)-Benzyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5c (5c/5c' = 10/1)

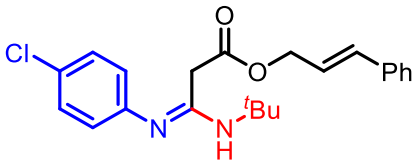
Yield = 80% (143.5 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 5H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 2H), 4.76 (brs, 1H), 3.05 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 149.5, 148.2, 135.3, 128.9, 128.7, 128.7, 128.5, 127.0, 123.3, 67.2, 51.7, 36.8, 28.6; HRMS(ESI) calcd for $C_{20}H_{24}ClN_2O_2$ $(M+H)^+$ 359.1521, found 359.1541.



(*E*)-Thiophen-2-ylmethyl-3-(tert-butylamino)-3-((4-chlorophenyl)imino)propanoate 5d (5d/5d' = 10/1)

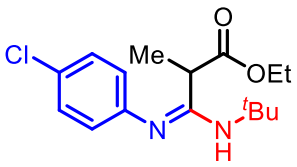
Yield = 81% (147.7 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.0 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 3.2 Hz, 1H), 7.00 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.28 (s, 2H), 4.76 (brs, 1H), 3.10 (s, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.5, 148.0, 137.1, 129.9, 128.9, 128.9, 127.4,

127.0, 127.0, 123.3, 61.2, 51.8, 36.7, 28.6; HRMS(ESI) calcd for $C_{18}H_{22}ClN_2O_2S$ $(M+H)^+$ 365.1085, found 365.1102.



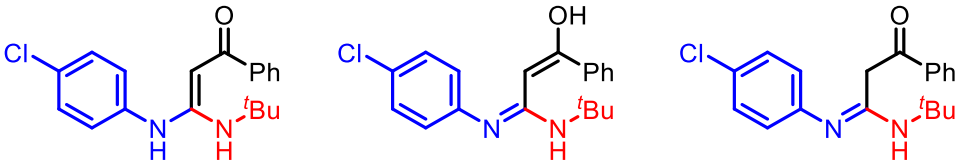
(*E*)-Cinnamyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5e (5e/5e' = 10/1)

Yield = 78% (150.1 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 6H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.65 – 6.60 (m, 3H), 6.24 – 6.16 (m, 1H), 4.90 (brs, 1H), 4.71 (d, *J* = 6.4 Hz, 2H), 3.10 (s, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.6, 148.3, 136.0, 135.1, 128.9, 128.8, 128.4, 127.0, 126.7, 123.3, 122.3, 65.9, 51.8, 36.7, 28.7; HRMS(ESI) calcd for $C_{22}H_{26}ClN_2O_2$ $(M+H)^+$ 385.1677, found 385.1698.



(*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)-2-methylpropanoate 5f

Yield = 84% (130.5 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.68 (brs, 1H), 4.23 – 4.08 (m, 2H), 3.54 (q, *J* = 7.2 Hz, 1H), 1.39 (s, 9H), 1.28 – 1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 153.2, 149.6, 129.0, 126.7, 123.3, 61.4, 51.3, 40.2, 28.6, 16.8, 14.2; HRMS(ESI) calcd for $C_{16}H_{24}ClN_2O_2$ $(M+H)^+$ 311.1521, found 311.1542.

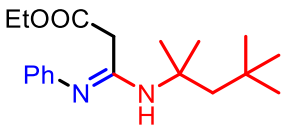


5g/5g'/5g'' = 15/4/1

(*E*)-3-(*tert*-Butylamino)-3-((4-chlorophenyl)amino)-1-phenylprop-2-en-1-one 5g and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-hydroxy-3-phenylacrylimidamide

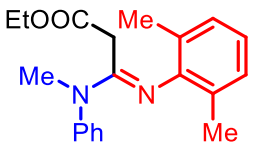
5g' and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-oxo-3-phenylpropanimidamide 5g"

Yield = 88% (130.5 mg). Yellow solid. For **5g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.26 (s, 1H), 7.76 – 7.74 (m, 2H), 7.31 – 7.30 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.48 (s, 1H), 4.57 (brs, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 158.4, 141.6, 135.5, 131.5, 130.1, 130.0, 128.2, 126.6, 126.4, 79.0, 51.8, 30.0; HRMS(ESI) calcd for $C_{19}H_{22}ClN_2O$ $(M+H)^+$ 329.1415, found 329.1421.



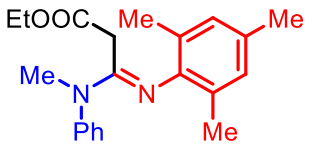
(*E*)-Ethyl-3-(phenylimino)-3-((2,4,4-trimethylpentan-2-yl)amino)propanoate 6a (6a/6a' = 12/1)

Yield = 78% (124.2 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.75 – 6.73 (m, 2H), 4.94 (brs, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.09 (s, 2H), 1.92 (s, 2H), 1.49 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 151.0, 147.4, 128.9, 122.0, 121.7, 61.3, 55.4, 50.3, 36.8, 31.9, 31.6, 29.5, 14.2; HRMS(ESI) calcd for $C_{19}H_{31}N_2O_2$ $(M+H)^+$ 319.2380, found 319.2382.



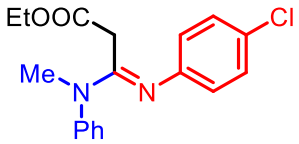
(*E*)-Ethyl-3-((2,6-dimethylphenyl)imino)-3-(methyl(phenyl)amino)propanoate 6b

Yield = 87% (141.1 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.26 – 7.21 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 3.74 (q, *J* = 7.2 Hz, 2H), 3.44 (s, 3H), 3.03 (s, 2H), 2.12 (s, 6H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 152.2, 148.0, 145.6, 129.5, 128.7, 128.2, 128.0, 127.0, 122.2, 60.8, 39.9, 35.4, 18.4, 13.9; HRMS(ESI) calcd for $C_{20}H_{25}N_2O_2$ $(M+H)^+$ 325.1911, found 325.1927.



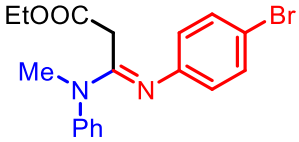
(*E*)-Ethyl-3-(mesitylimino)-3-(methyl(phenyl)amino)propanoate 6c

Yield = 84% (142.1 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.29 – 7.23 (m, 3H), 6.83 (s, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 3.47 (s, 3H), 3.07 (s, 2H), 2.24 (s, 3H), 2.12 (s, 6H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 152.4, 145.7, 145.4, 131.2, 129.5, 128.6, 128.5, 128.2, 126.9, 60.8, 39.8, 35.3, 20.8, 18.3, 13.9; HRMS(ESI) calcd for $C_{21}H_{27}N_2O_2$ $(M+H)^+$ 339.2067, found 339.2085.



(*E*)-Ethyl-3-((4-chlorophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6d (6d/6d' = 16/1)

Yield = 80% (132.3 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.30 – 7.23 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 3H), 3.16 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 152.9, 149.7, 145.2, 129.6, 128.9, 128.2, 127.4, 127.4, 123.4, 61.1, 39.5, 35.2, 14.0; HRMS(ESI) calcd for $C_{18}H_{20}ClN_2O_2$ $(M+H)^+$ 331.1208, found 331.1224.

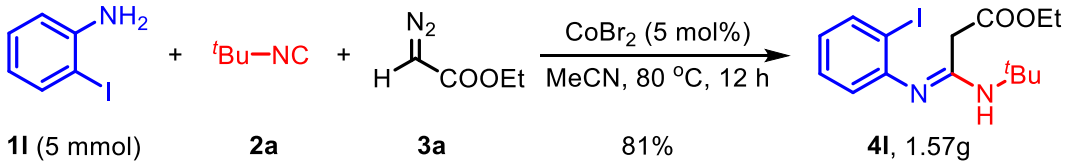


(*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6e (6e/6e' = 16/1)

Yield = 75% (140.7 mg). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 7H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 3H), 3.16 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 152.8, 150.2, 145.1, 131.9, 129.6, 128.2, 127.5, 123.9, 115.1, 61.2, 39.6, 35.2, 14.0; HRMS(ESI) calcd for $C_{18}H_{19}BrN_2O_2$ $(M+H)^+$ 375.0703, found 375.0720.

III. Synthetic Applications and Mechanistic Studies

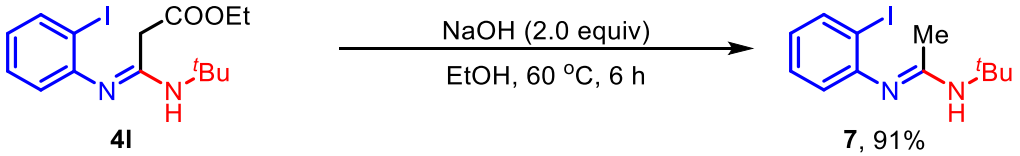
Scale-up reaction



1l (5 mmol) **2a** **3a** 81% **4l**, 1.57g

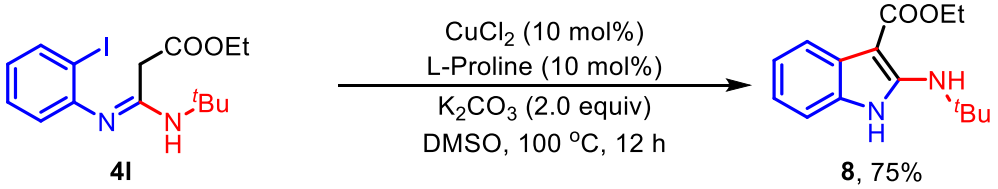
To an oven-dried Schlenk tube (50 mL) was added the amines **1l** (5 mmol, 1.1 g), isocyanides **2a** (6 mmol, 1.2 equiv), diazos **3a** (6 mmol, 1.2 equiv), $CoBr_2$ (55 mg, 5.0 mol %), and anhydrous MeCN (15 mL). The tube was backfilled with N_2. The mixture was concentrated under reduced pressure after stirring at 80 °C for 12 h. The residue was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the desired product **4l** in 81% yield (1.57 g).

Derivatization of Amidine 4l



4l **7**, 91%

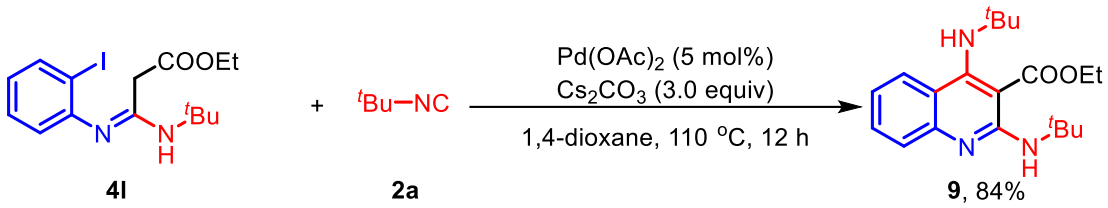
To an oven-dried Schlenk tube (10 mL) was added the amidine **4l** (194.1 mg, 0.5 mmol), NaOH (40.0 mg, 1.0 mmol), and EtOH (3.0 mL). After stirring at 60 °C for 6 h. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the desired product **7** in 91% yield (143.9 mg) as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.21 (m, 1H), 6.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.65 (m, 1H), 4.20 (brs, 1H), 1.65 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 153.9, 138.8, 128.8, 123.0, 121.9, 94.3, 51.6, 29.3, 19.2. HRMS (ESI) m/z calculated for $C_{12}H_{18}IN_2$, $[M+H]^+$ 317.0509; found 317.0527.



4l **8**, 75%

To an oven-dried Schlenk tube (10 mL) was added the amidine **4l** (194.1 mg, 0.5 mmol), $CuCl_2$ (6.7 mg, 10 mol%), L-Proline (5.8 mg, 10 mol%), K_2CO_3 (138.2 mg,

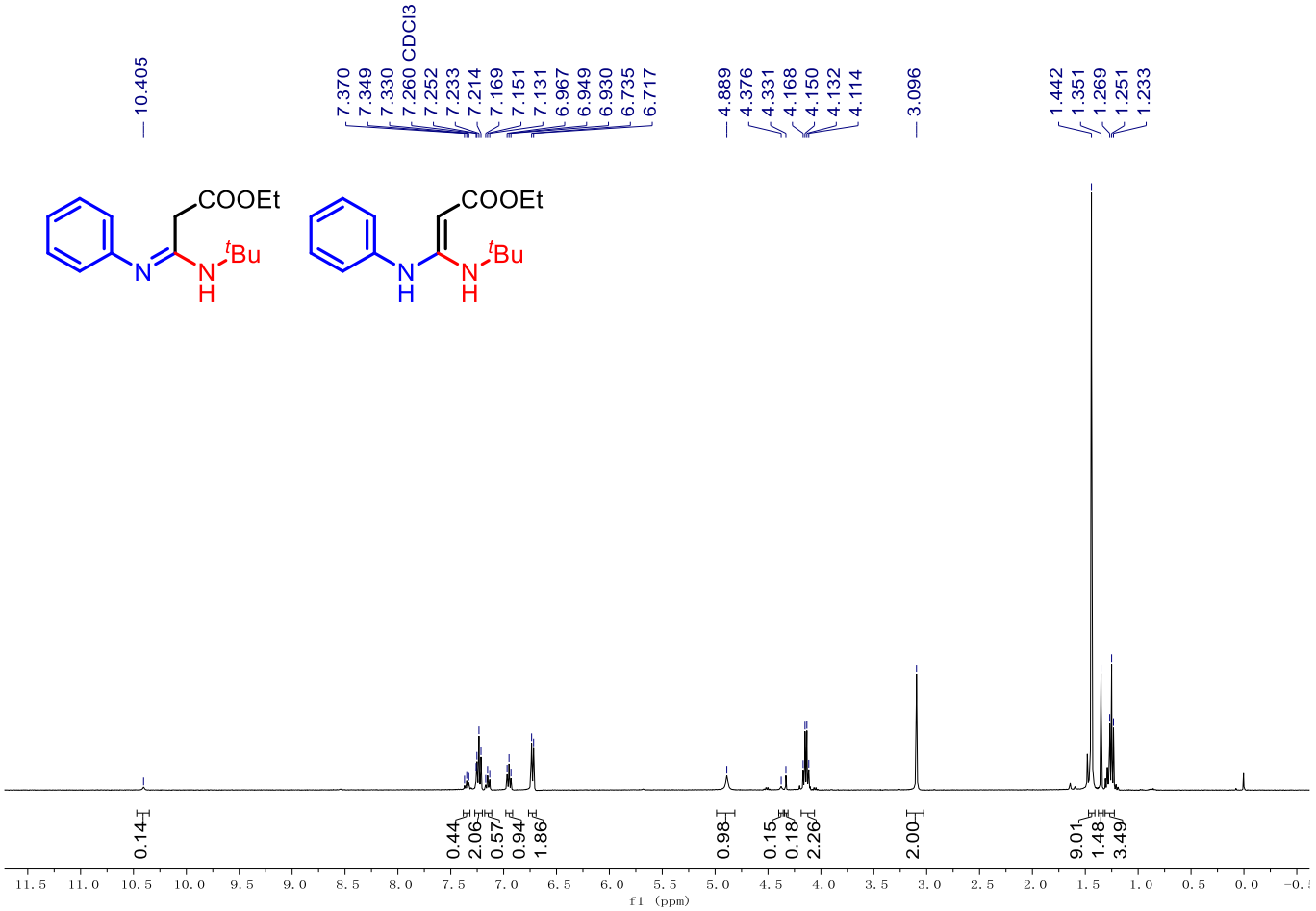
1.0 mmol), and DMSO (3.0 mL). After stirring at 100 °C for 12 h. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the desired product **8** in 75% yield (97.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.51 (brs, 1H), 7.16 – 7.11 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 9H), 1.44 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 152.9, 132.5, 126.5, 121.9, 120.1, 119.2, 109.6, 85.8, 59.1, 51.7, 30.4, 14.9. HRMS (ESI) m/z calculated for $C_{15}H_{21}N_2O_2$, $[M+H]^+$ 261.1598; found 261.1604.



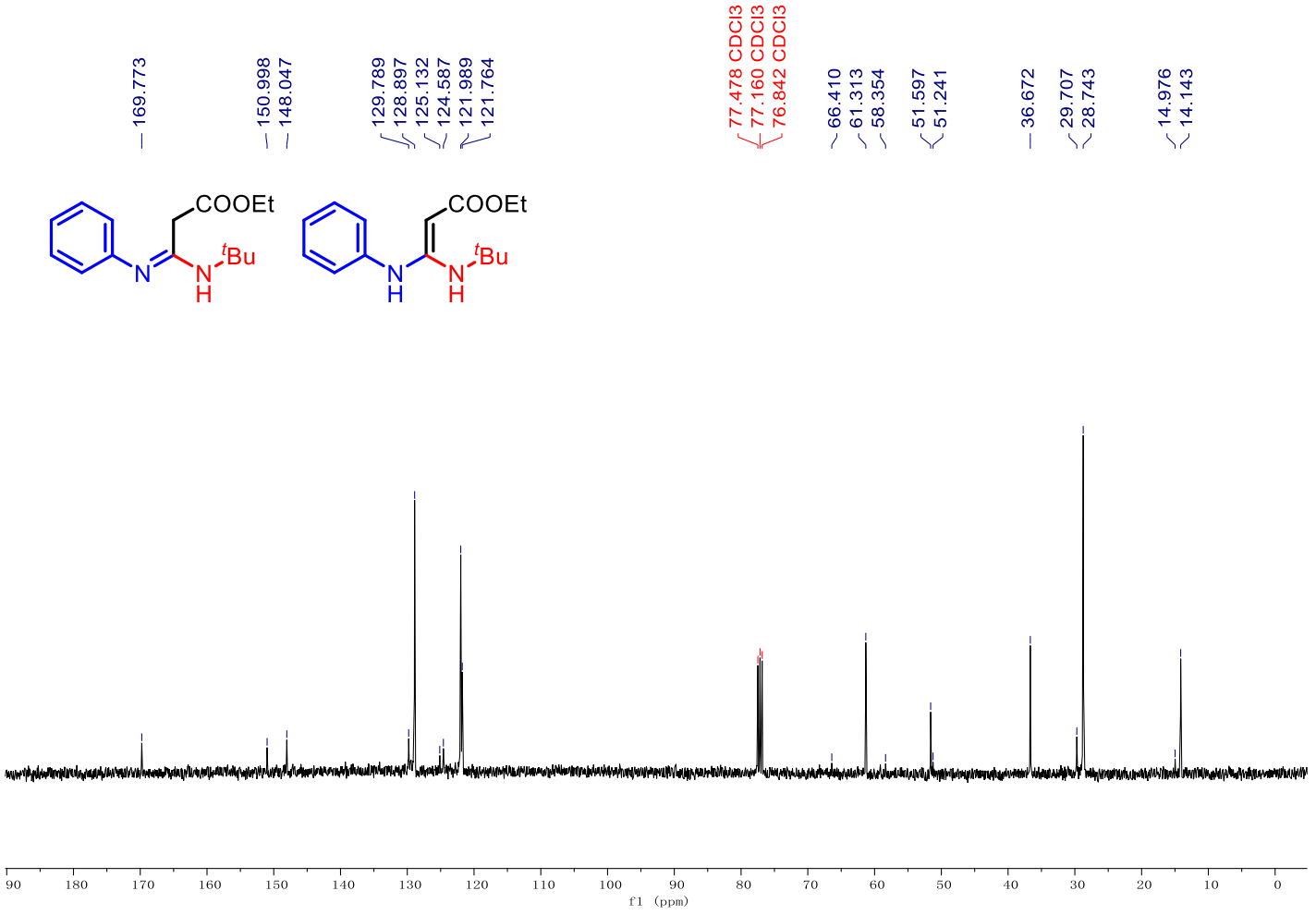
To an oven-dried Schlenk tube (10 mL) was added the amidine **4l** (194.1 mg, 0.5 mmol), isocyanide **2a** (50.0 mg, 0.6 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Cs_2CO_3 (488.7 mg, 1.5 mmol), and 1,4-dioxane (3.0 mL). After stirring at 110 °C for 12 h. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the desired product **9** in 84% yield (144.3 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.49 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.07 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 6.89 (brs, 1H), 5.71 (brs, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.57 (s, 9H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 156.8, 154.3, 149.6, 131.2, 127.7, 126.4, 122.1, 120.2, 107.7, 61.5, 56.7, 51.7, 31.2, 29.5, 14.3. HRMS (ESI) m/z calculated for $C_{20}H_{30}N_3O_2$, $[M+H]^+$ 344.2333; found 344.2354.

V. Copy of NMR Spectra

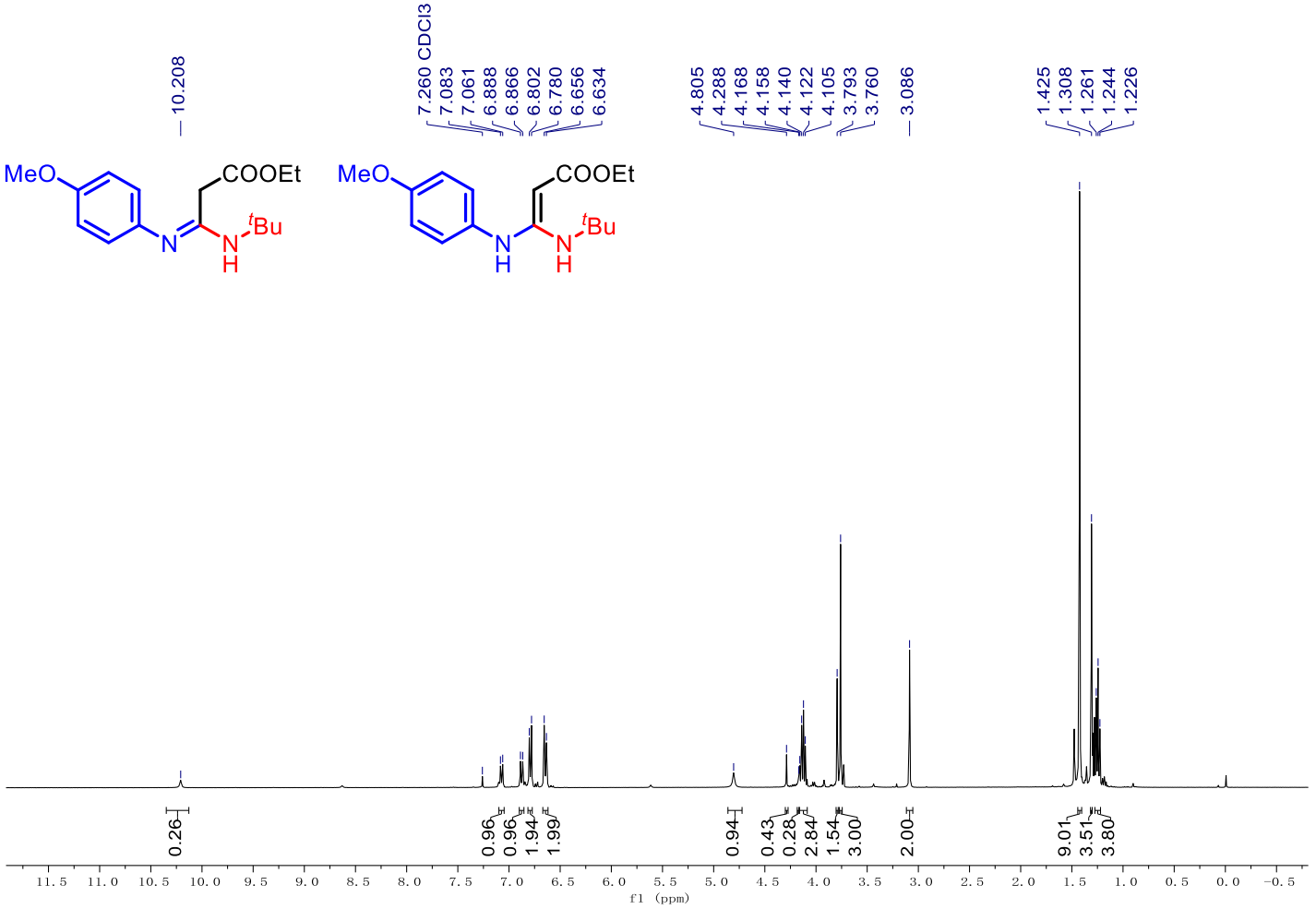
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(phenylimino)propanoate 4a and (*E*)-ethyl-3-(*tert*-butylamino)-3-(phenylamino)acrylate 4a' (4a/4a'= 6/1)



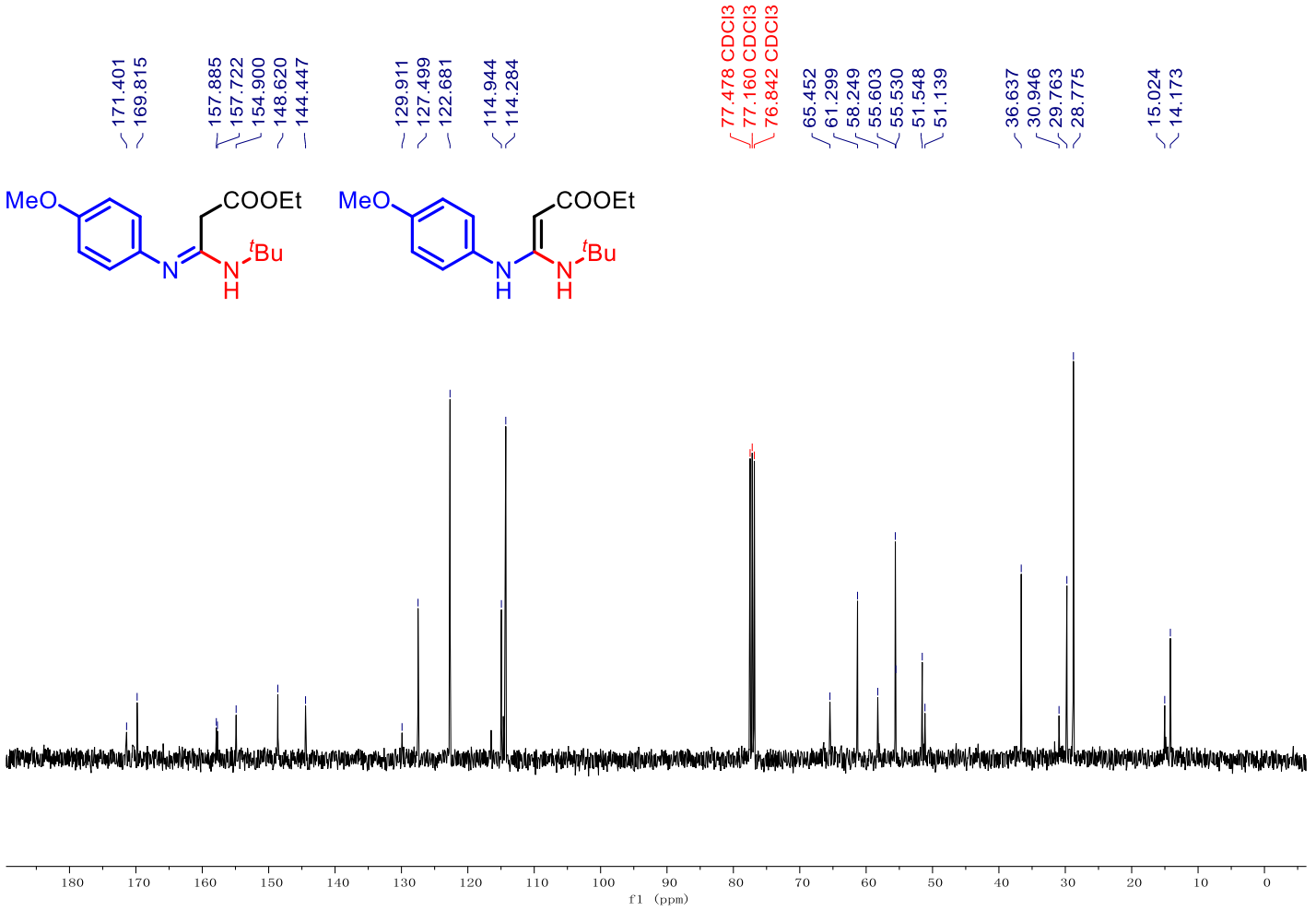
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(phenylimino)propanoate 4a and (*E*)-ethyl-3-(*tert*-butylamino)-3-(phenylamino)acrylate 4a' (4a/4a'= 6.0/1)



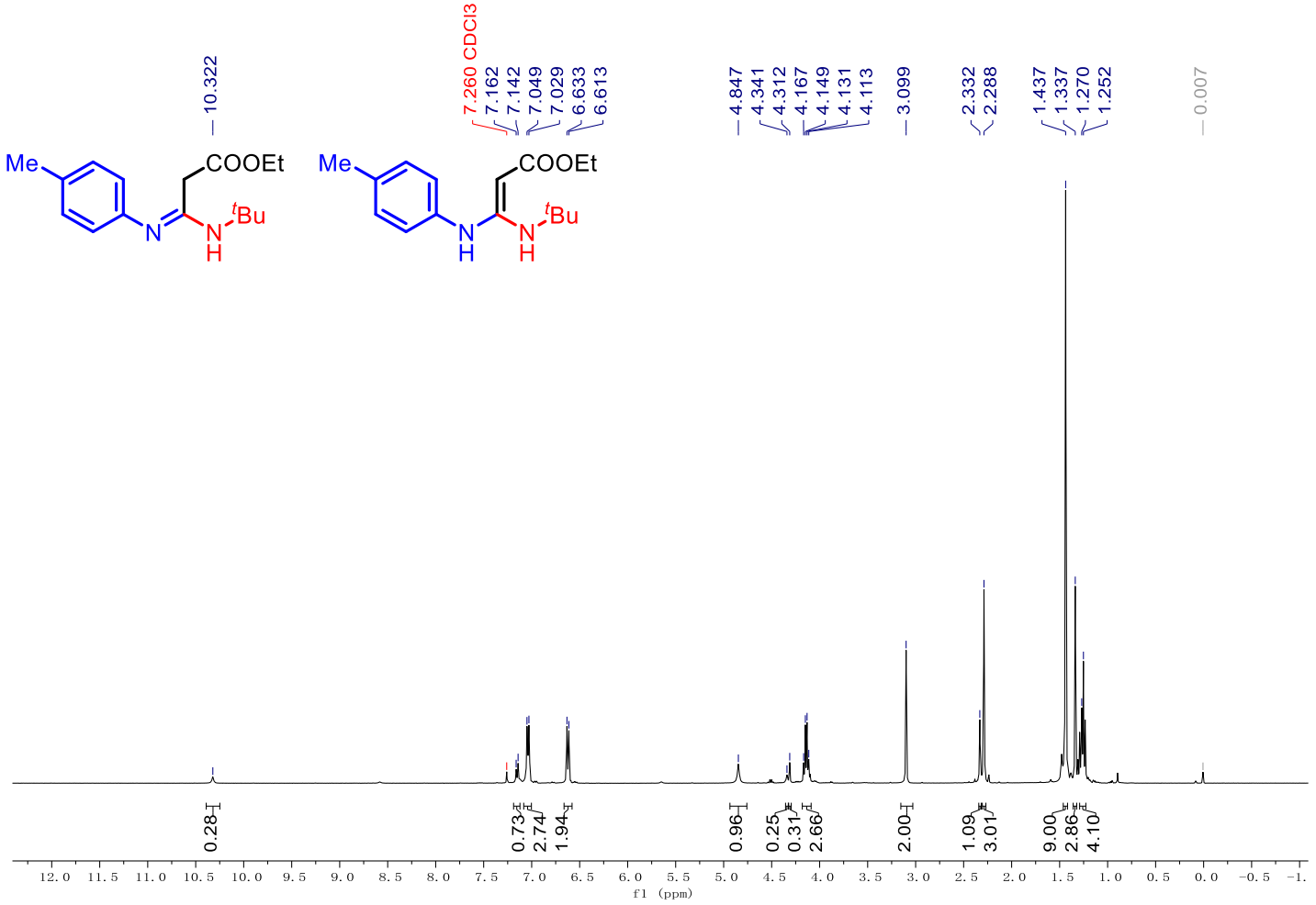
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-methoxyphenyl)imino)propanoate 4b and (*E*)-ethyl-3-(*tert*-butylamino)-3-((4-methoxyphenyl)amino)acrylate 4b' (4b/4b'= 2/1)



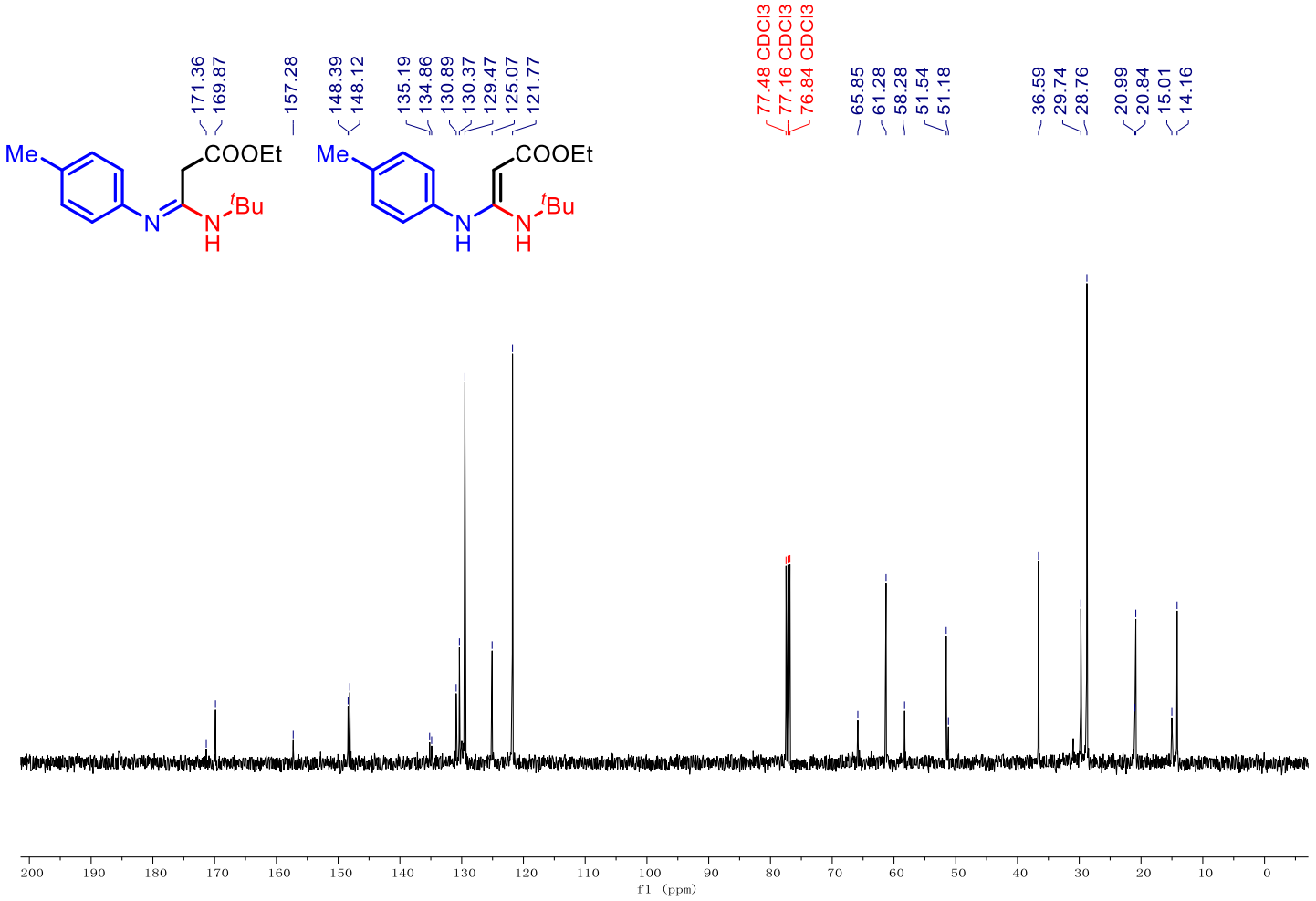
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-methoxyphenyl)imino)propanoate 4b and (*E*)-ethyl-3-(*tert*-butylamino)-3-((4-methoxyphenyl)amino)acrylate 4b' (4b/4b'= 2/1)



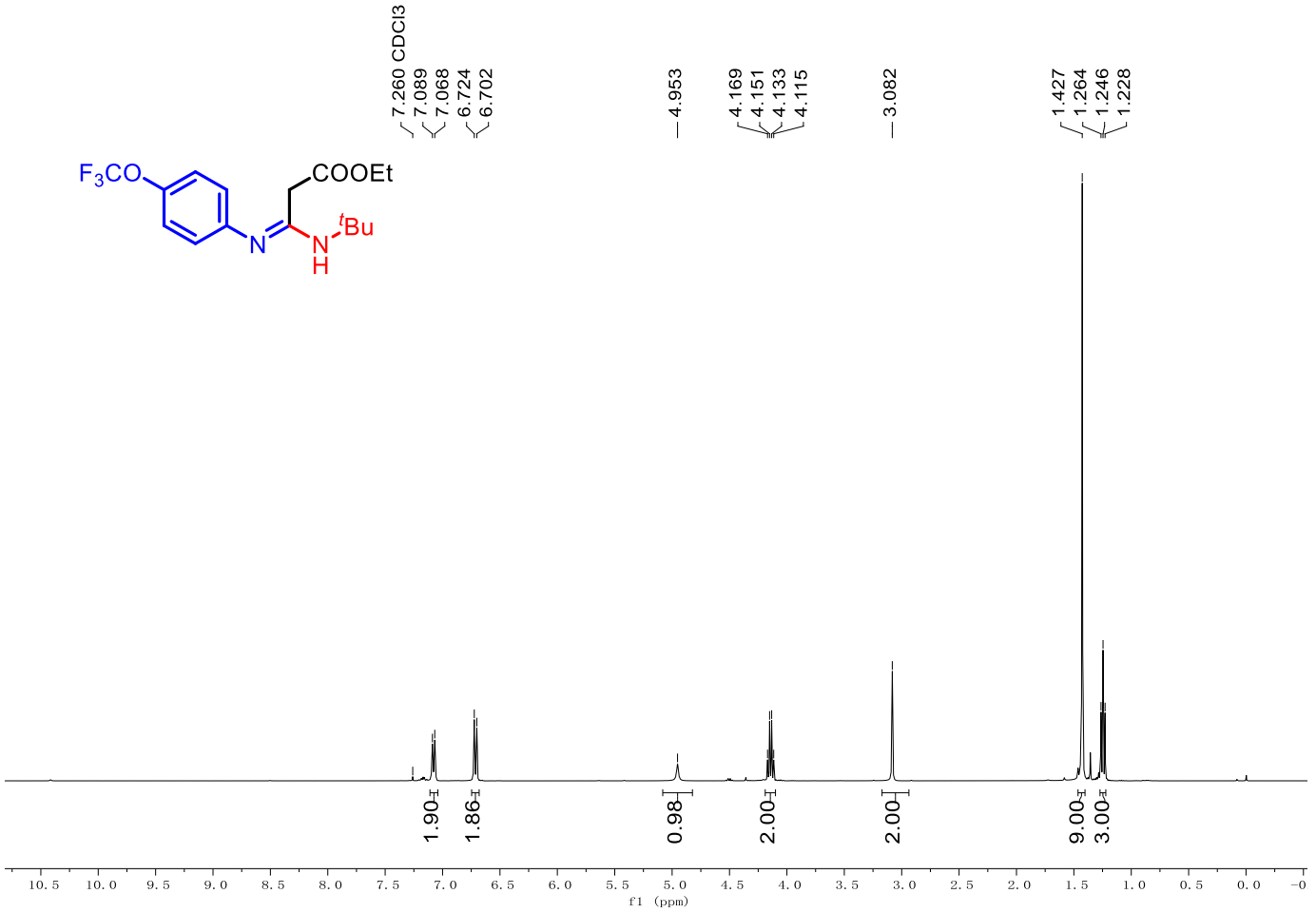
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(*p*-tolylimino)propanoate 4c and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*p*-tolylamino)acrylate 4c' (4c/4c'= 3/1)



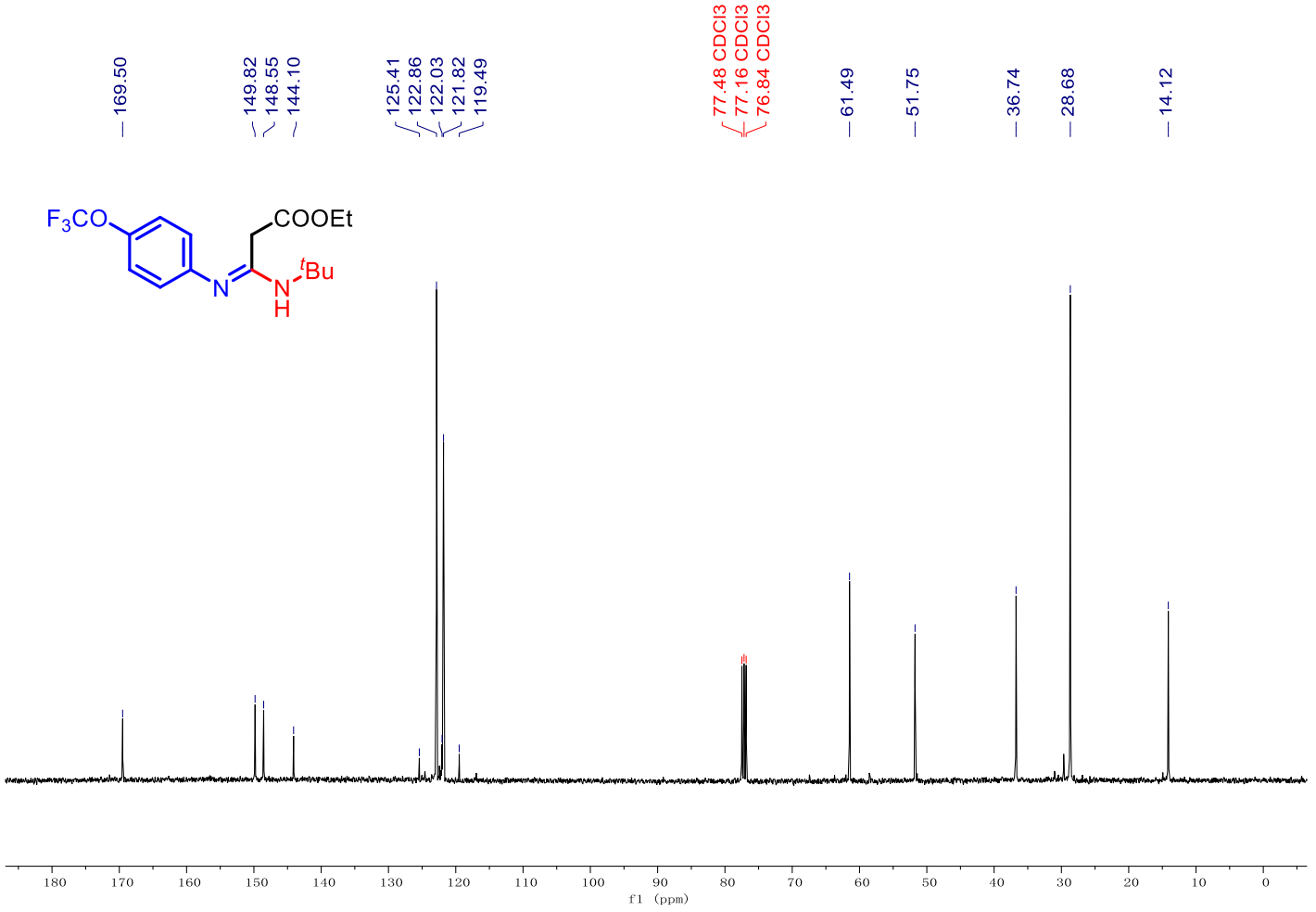
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(*p*-tolylimino)propanoate 4c and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*p*-tolylamino)acrylate 4c' (4c/4c'= 3/1)



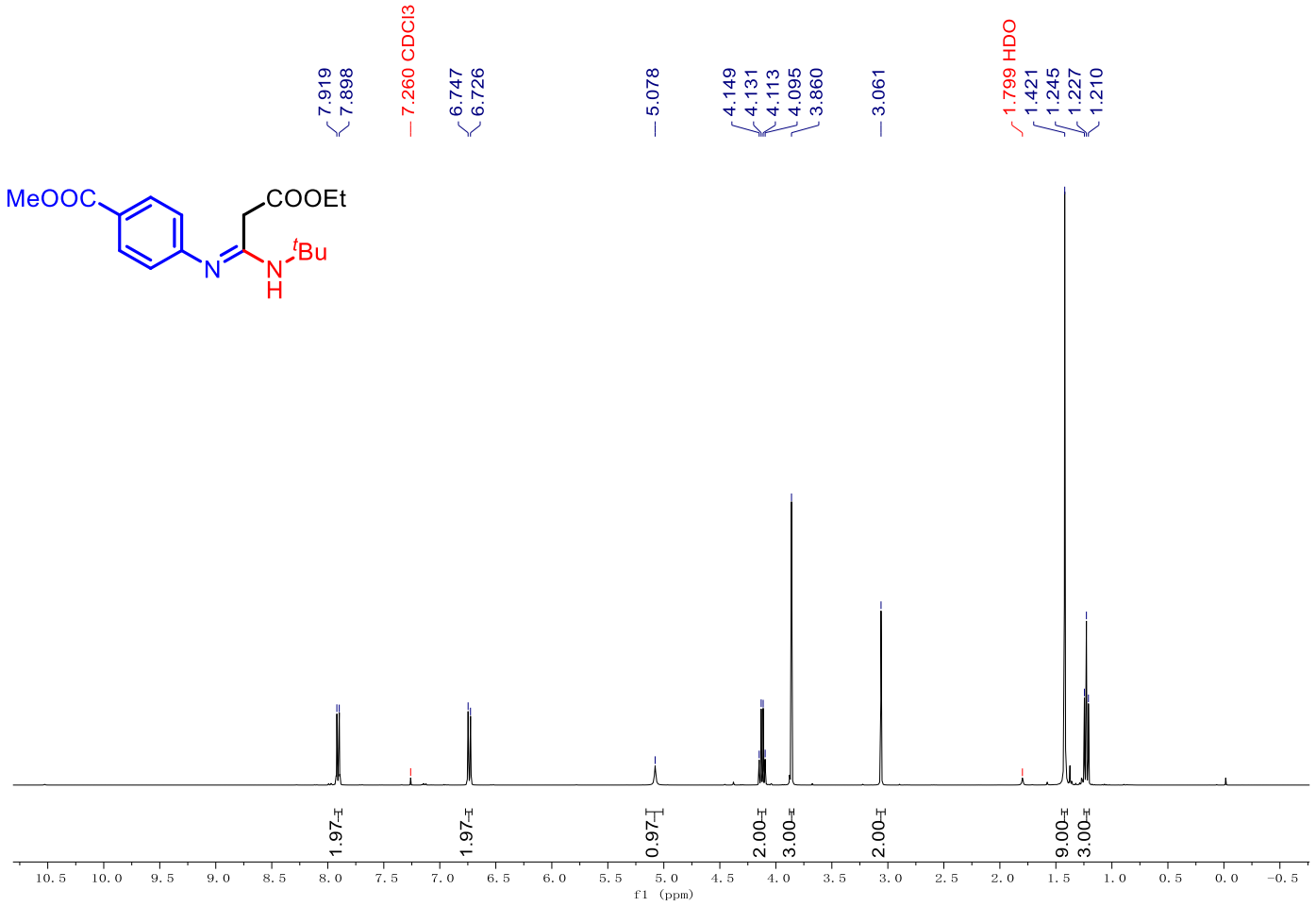
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-(trifluoromethoxy) phenyl)imino)propanoate 4d (4d/4d' > 20/1)



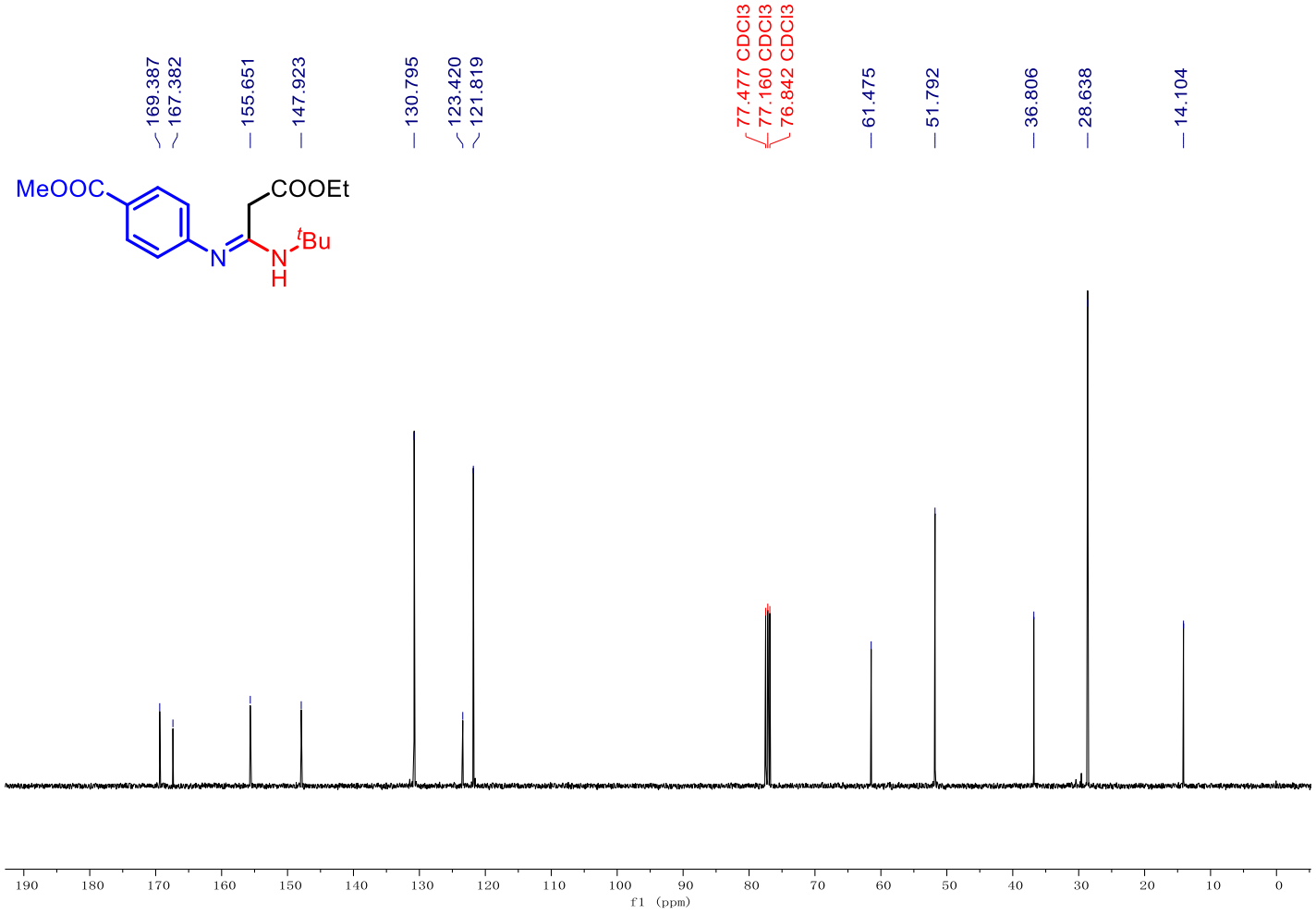
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-(trifluoromethoxy) phenyl)imino)propanoate 4d (4d/4d' > 20/1**)**



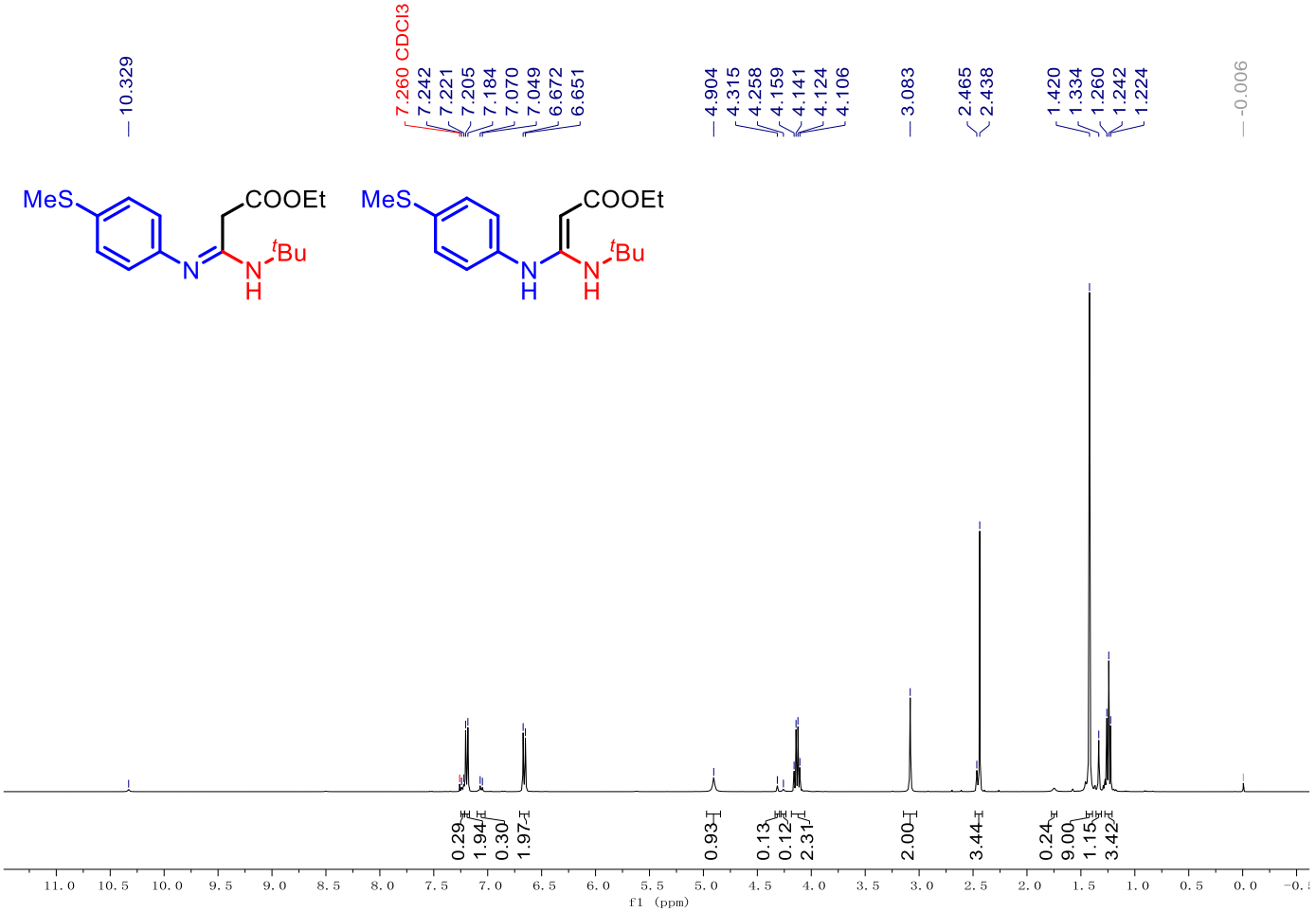
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Methyl-4-((1-(*tert*-butylamino)-3-ethoxy-3-oxopropylidene)amino)benzoate 4e (4e/4e' > 20/1)



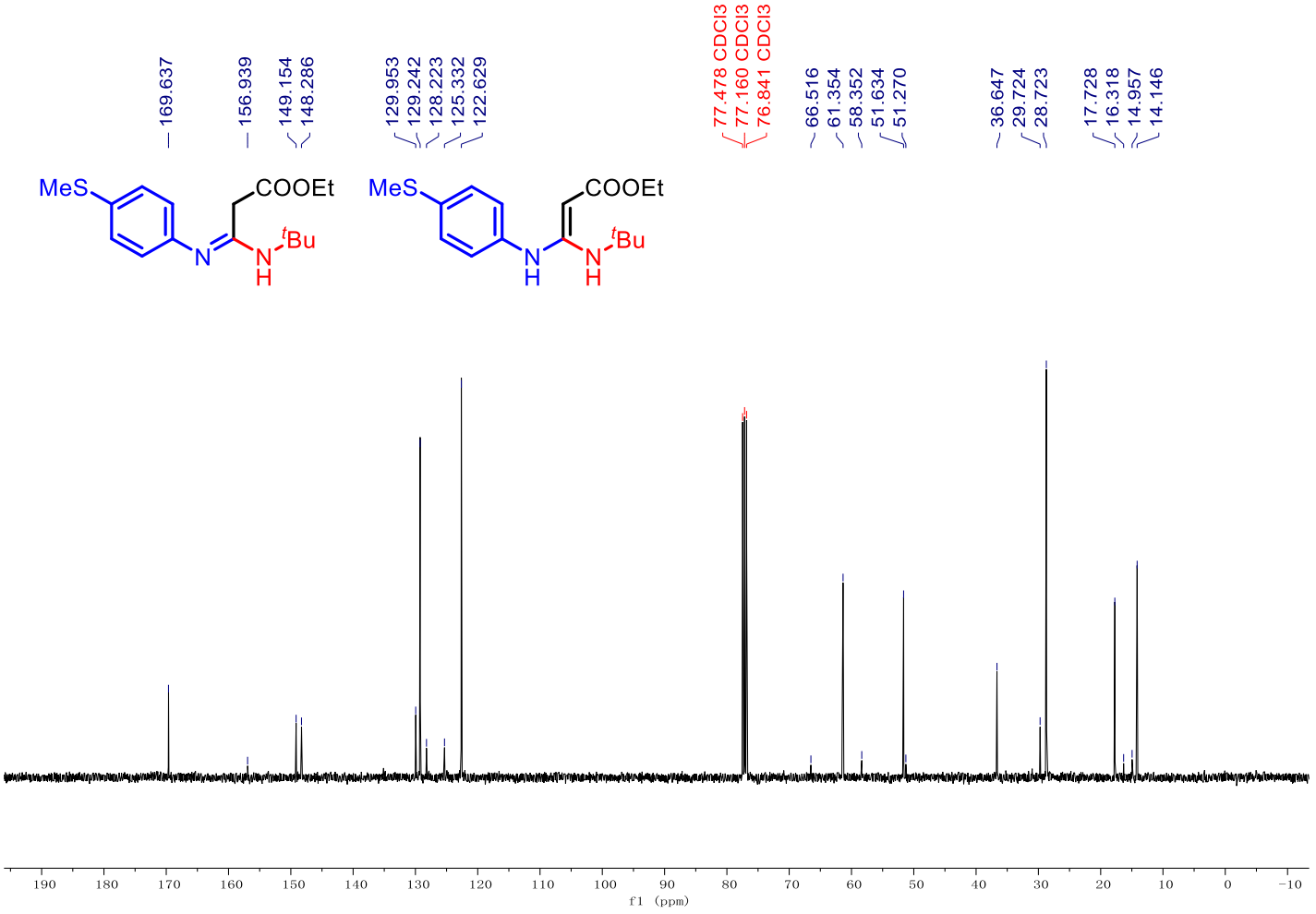
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Methyl-4-((1-(*tert*-butylamino)-3-ethoxy-3-oxopropylidene)amino)benzoate 4e (4e/4e' > 20/1)



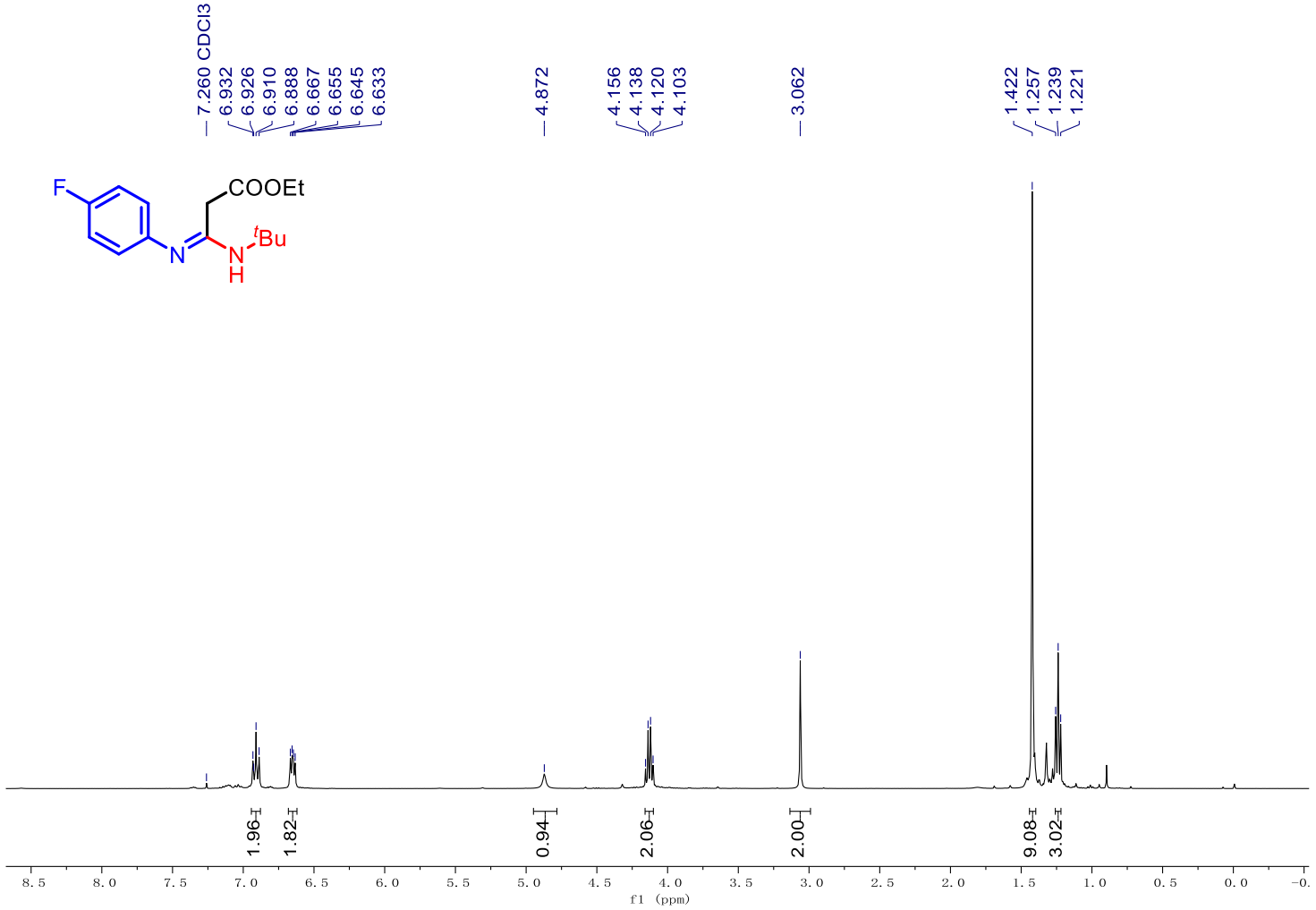
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(tert-butylamino)-3-((4-(methylthio)phenyl)imino)propanoate 4f and (*E*)-ethyl-3-(*tert*-butylamino)-3-((4-(methylthio)phenyl)amino)acrylate 4f' (4f/4f' = 7/1)



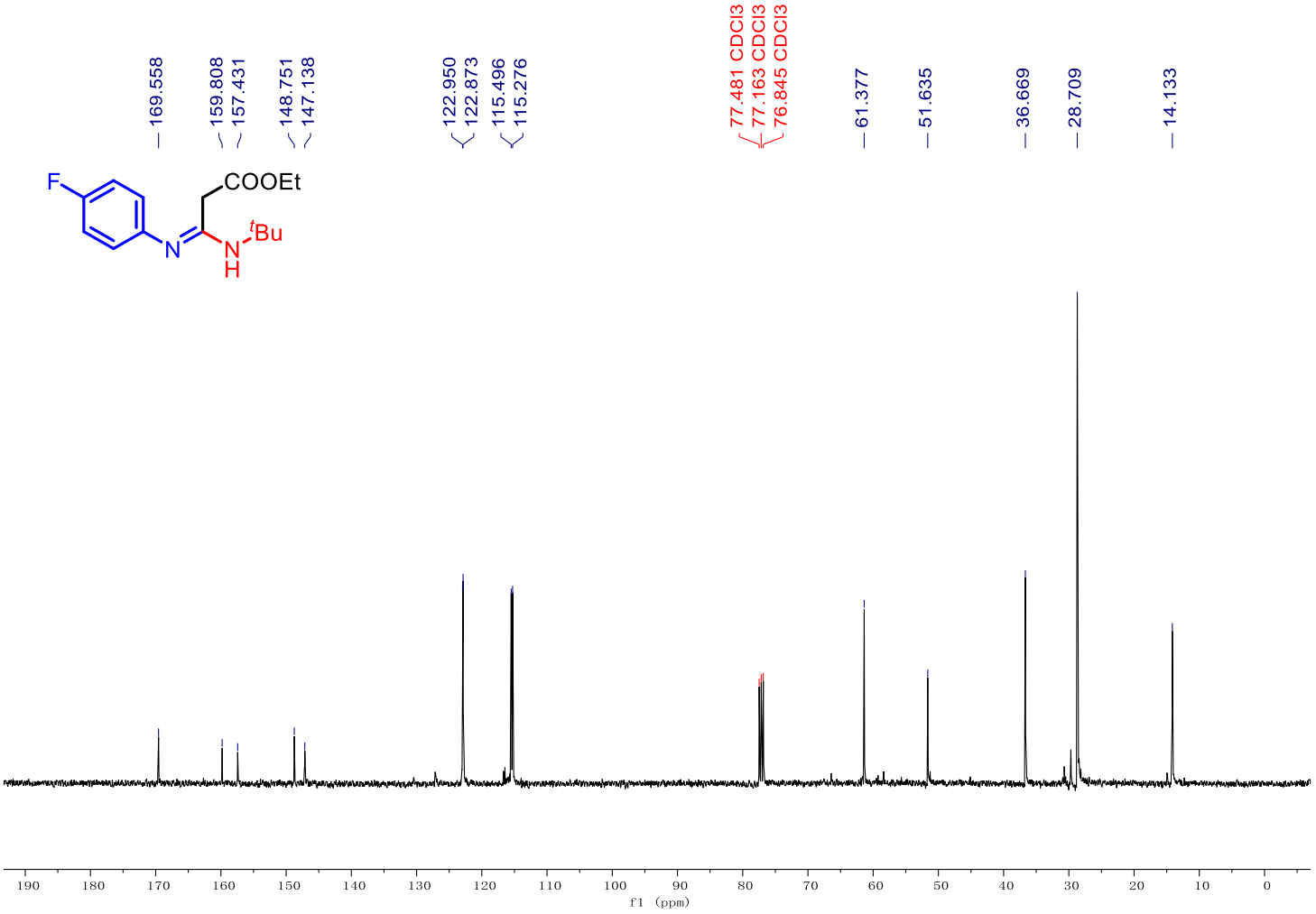
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(tert-butylamino)-3-((4-(methylthio)phenyl)imino)propanoate 4f and (*E*)-ethyl-3-(*tert*-butylamino)-3-((4-(methylthio)phenyl)amino)acrylate 4f' (4f/4f' = 7/1)



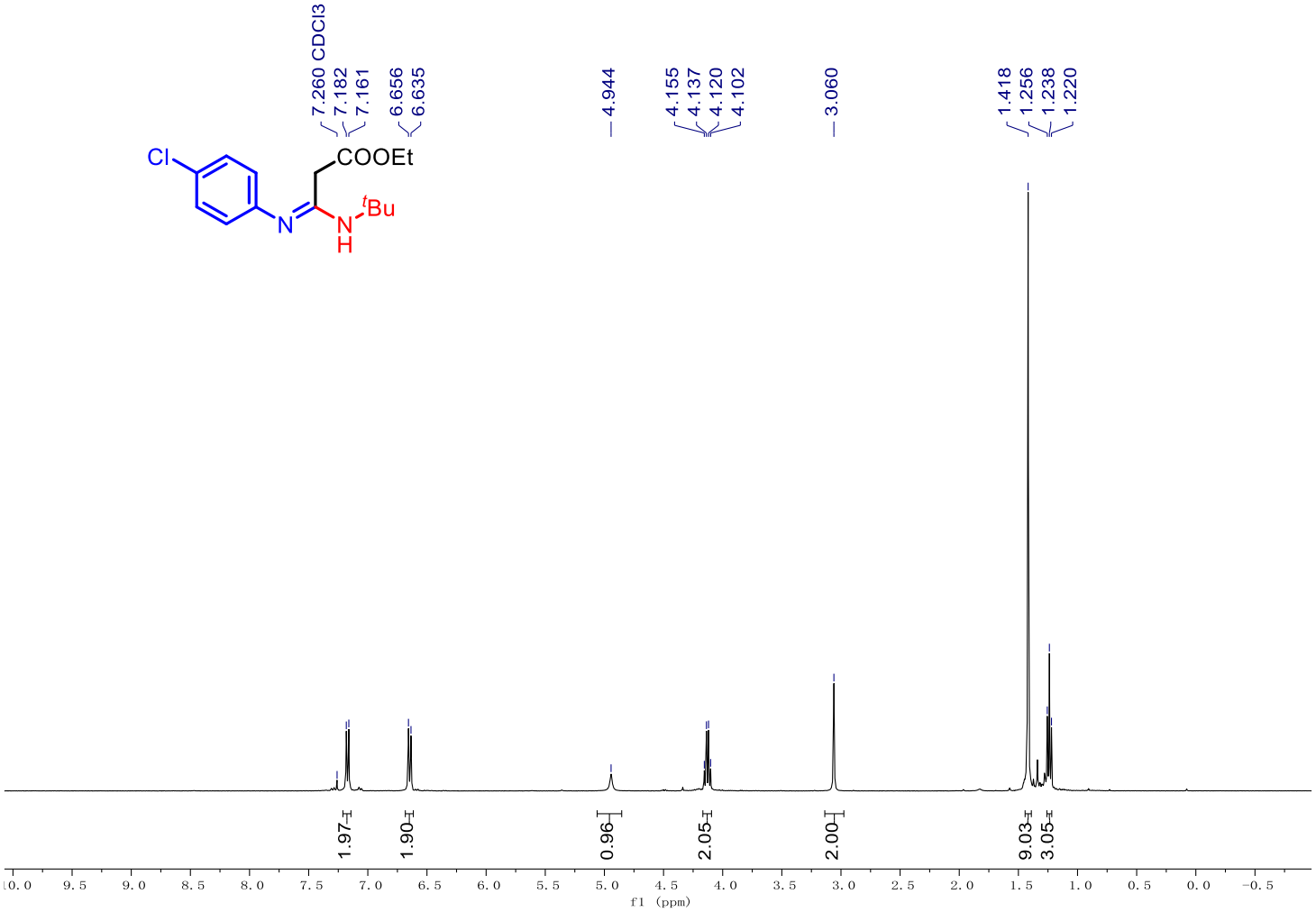
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-fluorophenyl)imino) propanoate 4g (4g/4g' > 20/1)



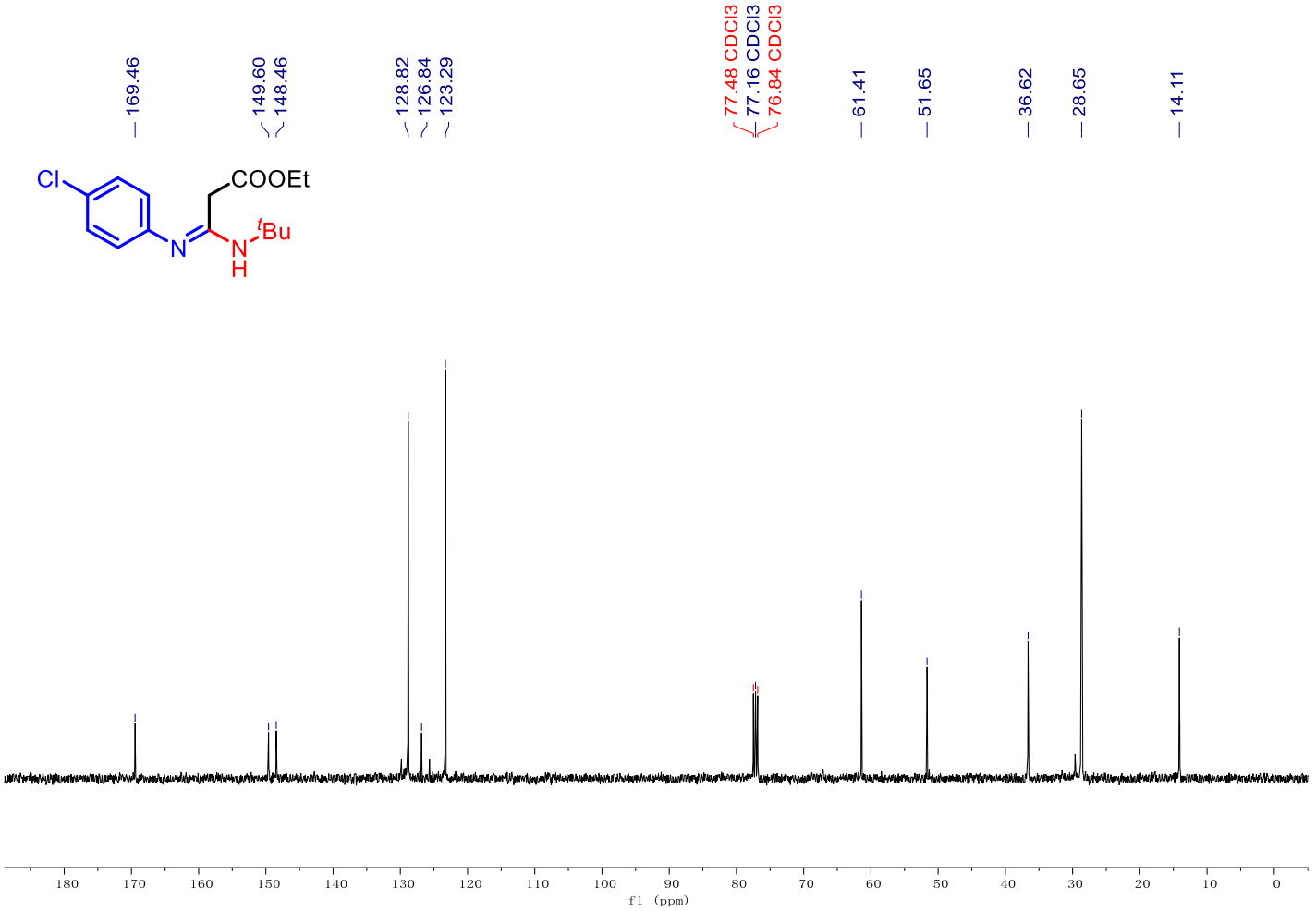
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-fluorophenyl)imino) propanoate 4g (4g/4g' > 20/1)



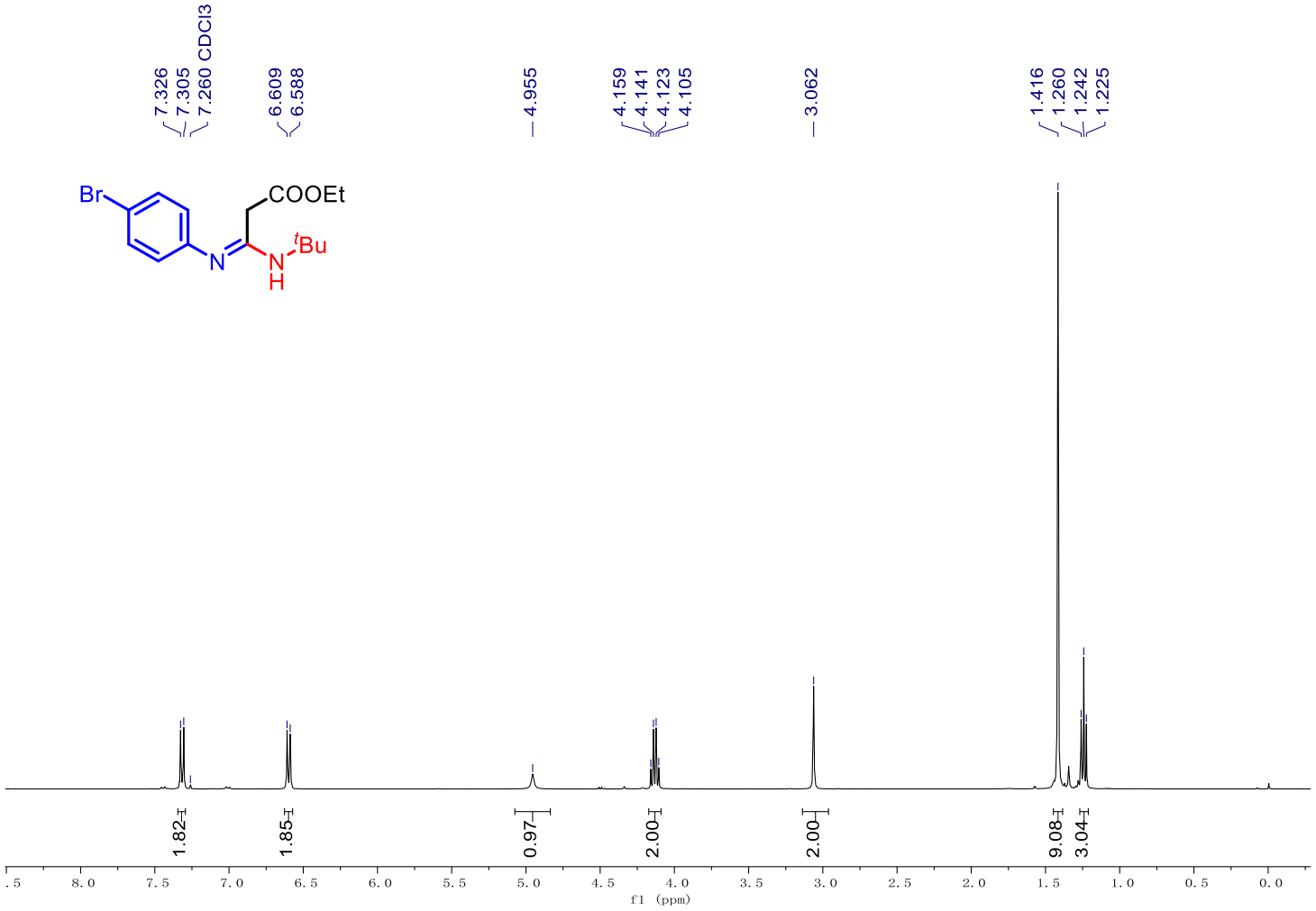
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Ethyl (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino) propanoate 4h (4h/4h' > 20/1)



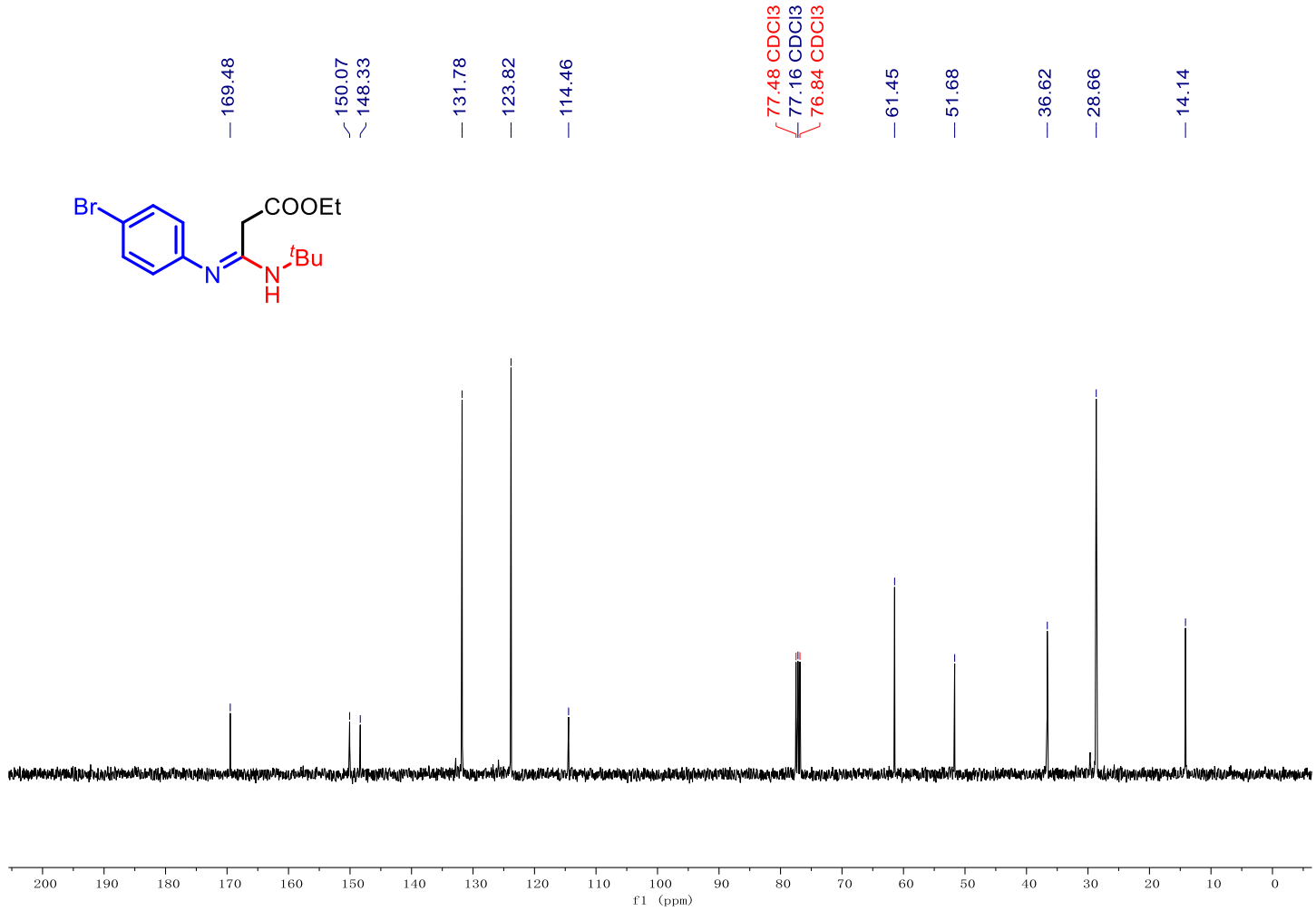
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino) propanoate 4h (4h/4h' > 20/1)



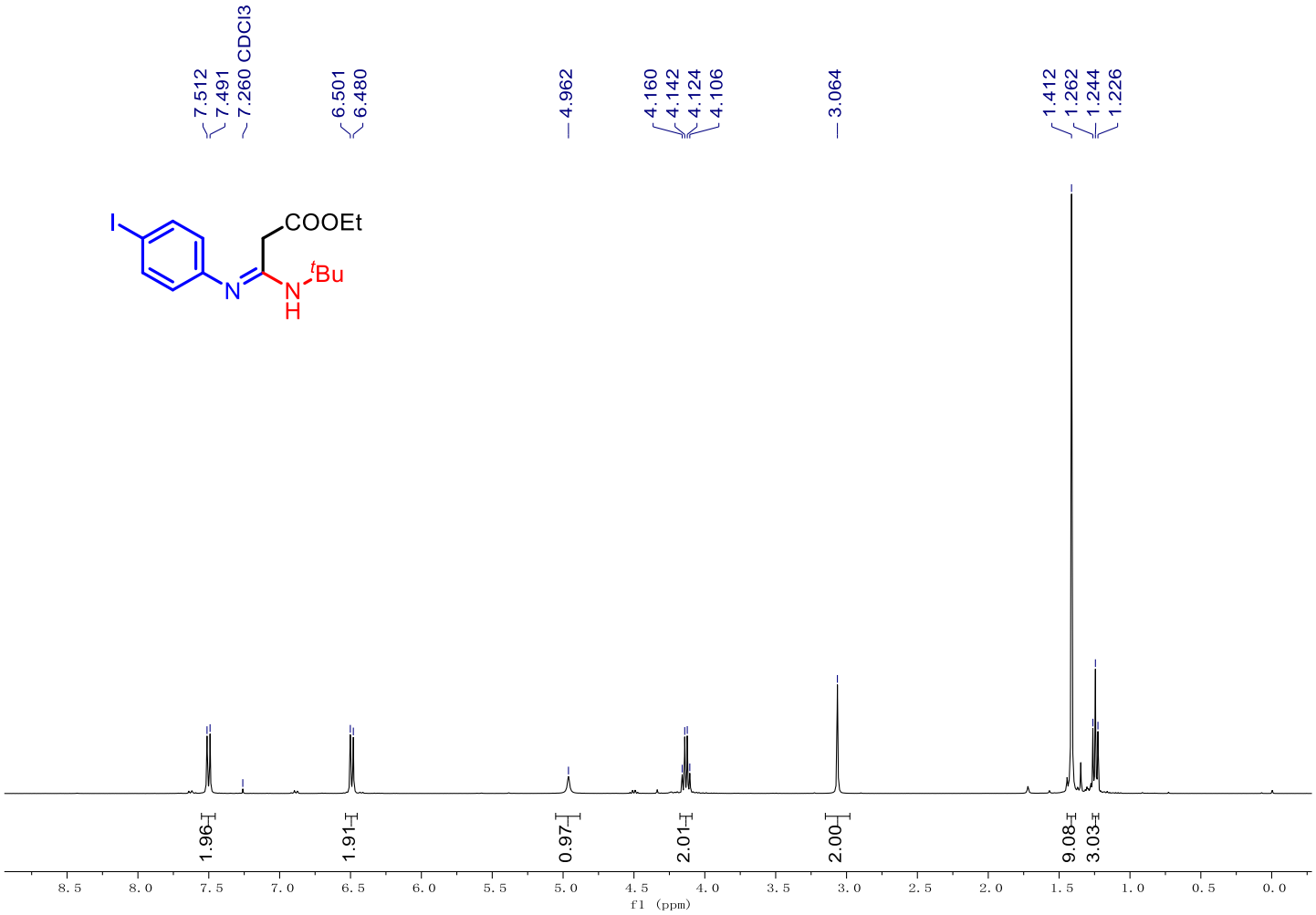
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(*tert*-butylamino) propanoate 4i (4i/4i' > 20/1)



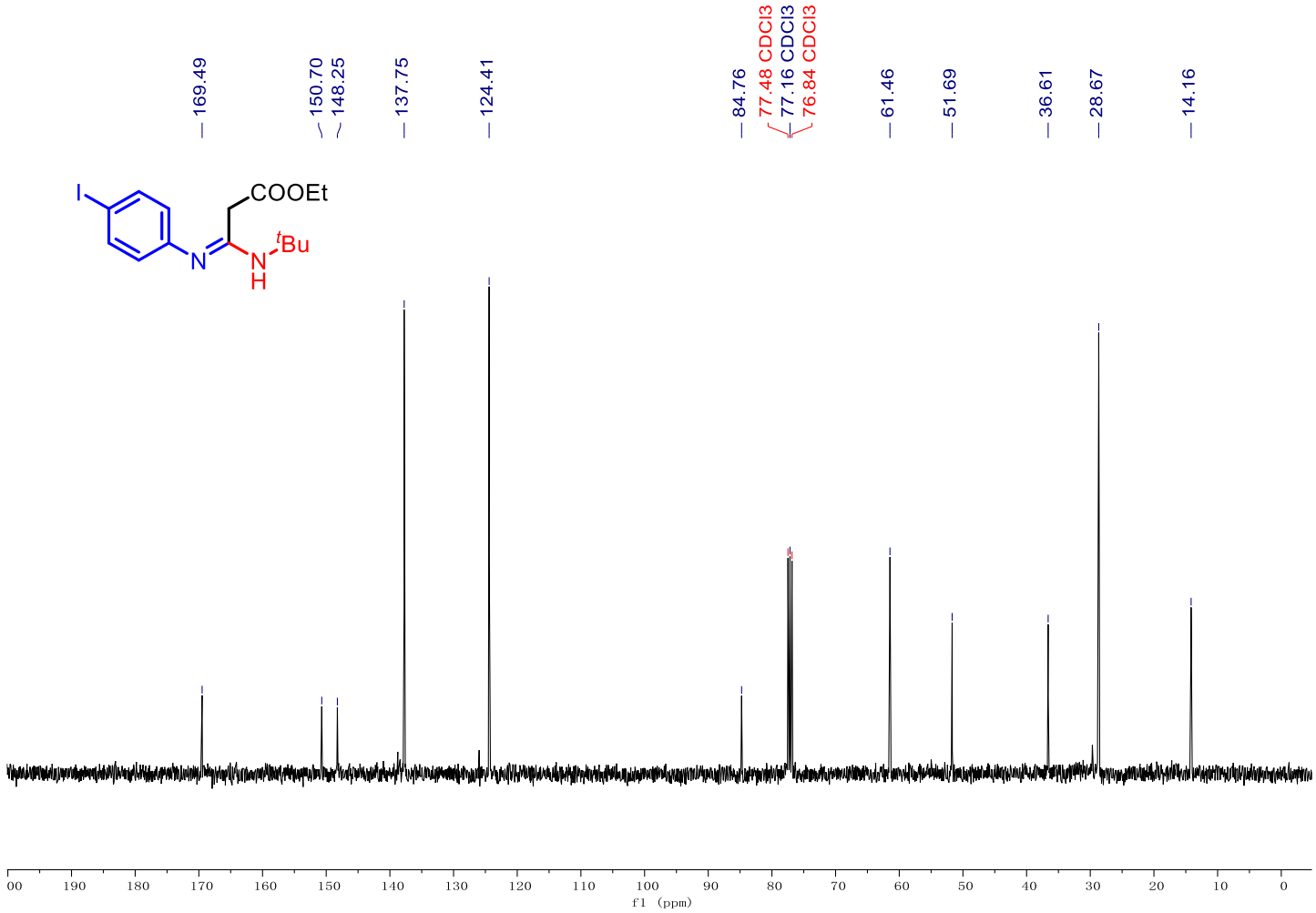
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(*tert*-butylamino) propanoate 4i (4i/4i' > 20/1)



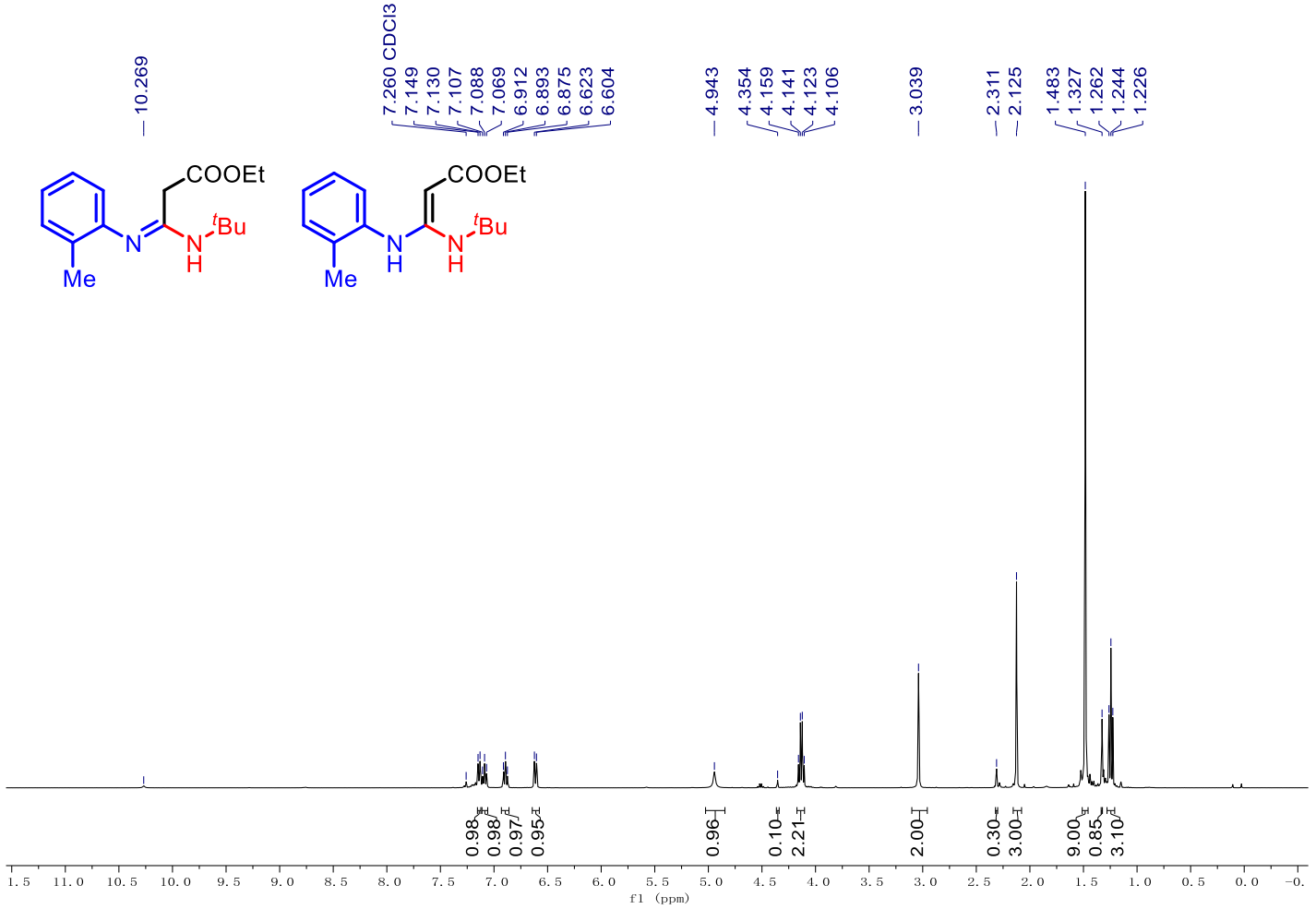
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-iodophenyl)imino) propanoate 4j (4j/4j' > 20/1)



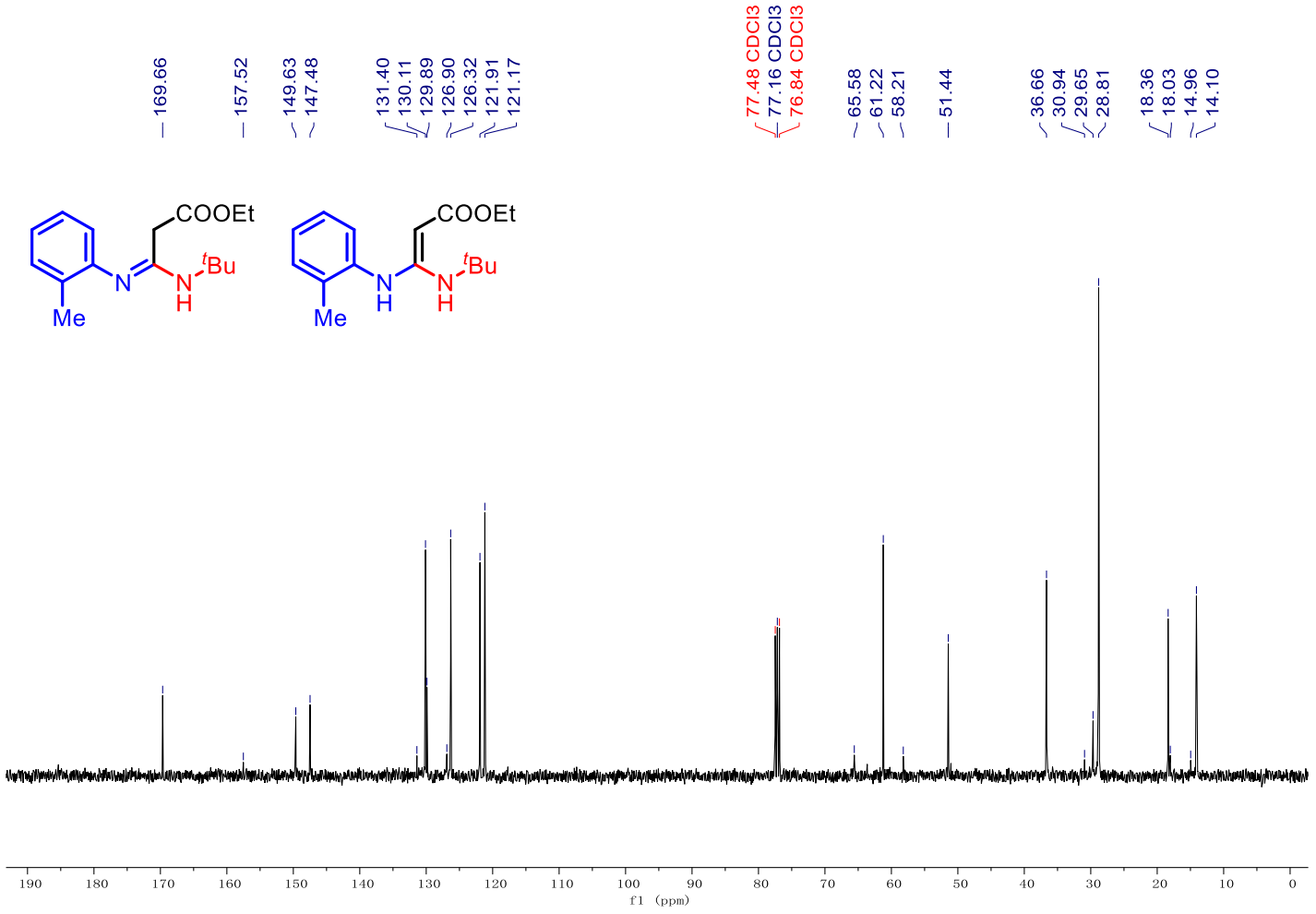
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-iodophenyl)imino) propanoate 4j (4j/4j' > 20/1)



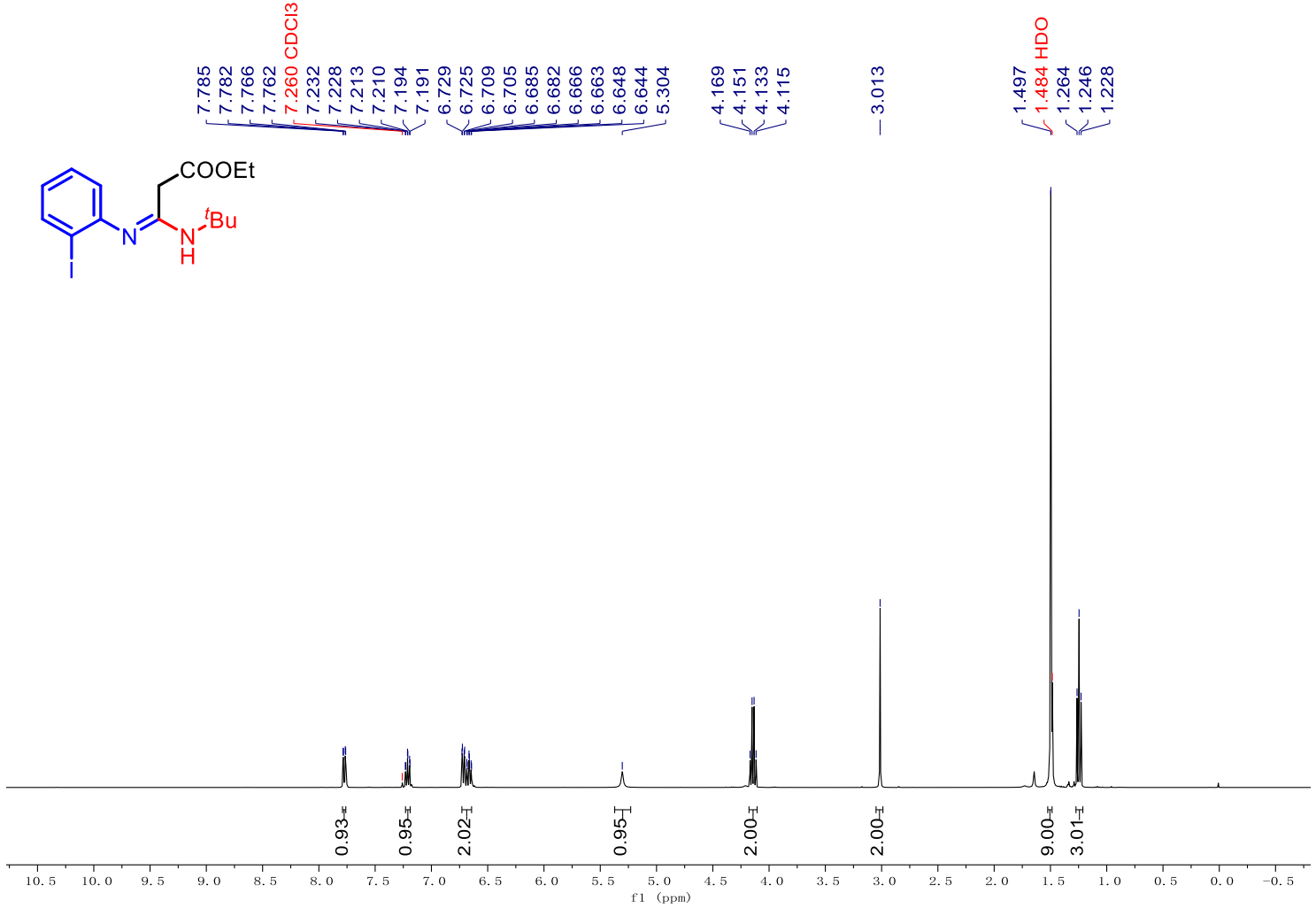
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(*o*-tolylimino)propanoate 4k and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*o*-tolylamino)acrylate 4k' (4k/4k' = 10/1)



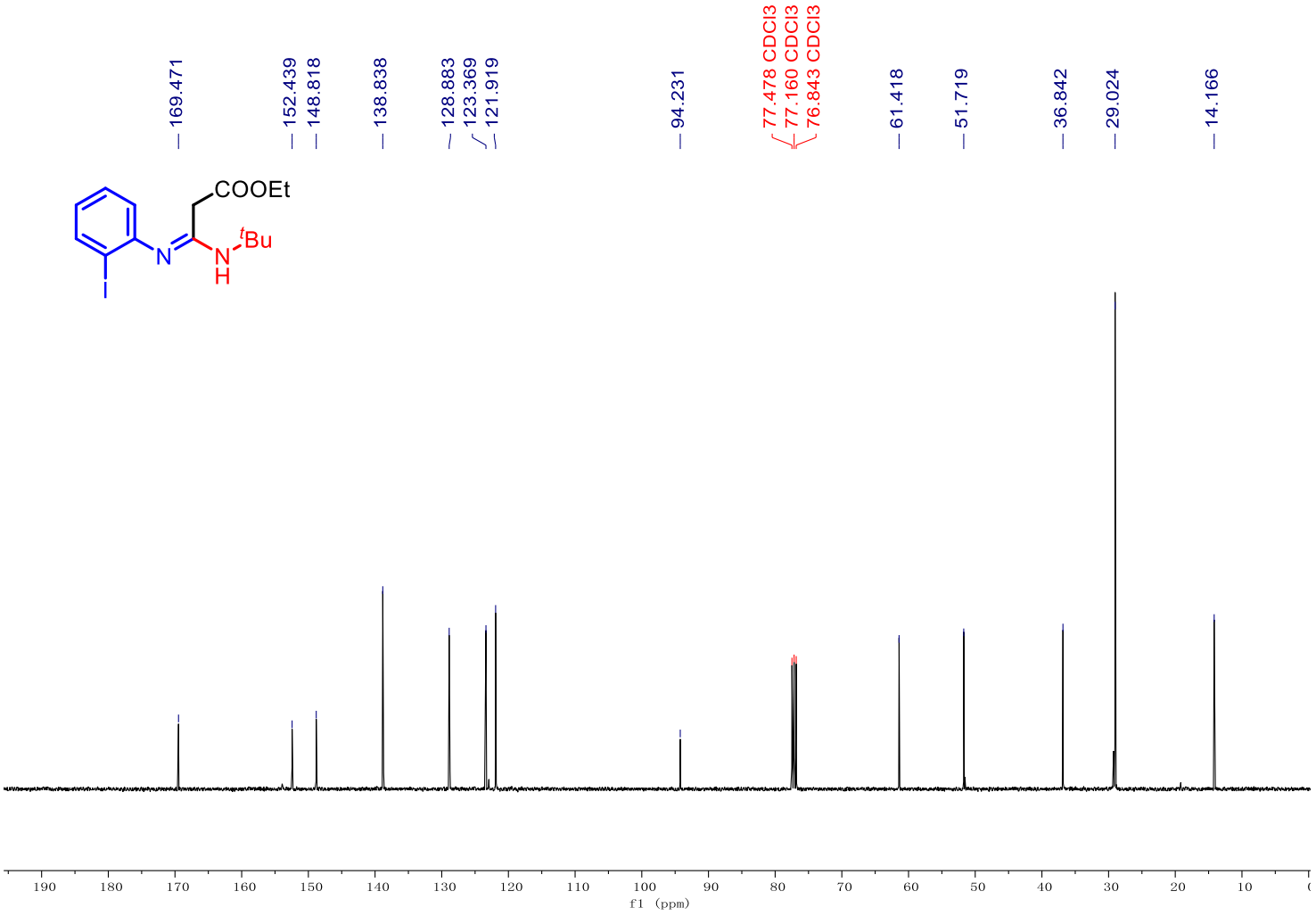
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(*o*-tolylimino)propanoate 4k and (*E*)-ethyl-3-(*tert*-butylamino)-3-(*o*-tolylamino)acrylate 4k' (4k/4k' = 10/1)



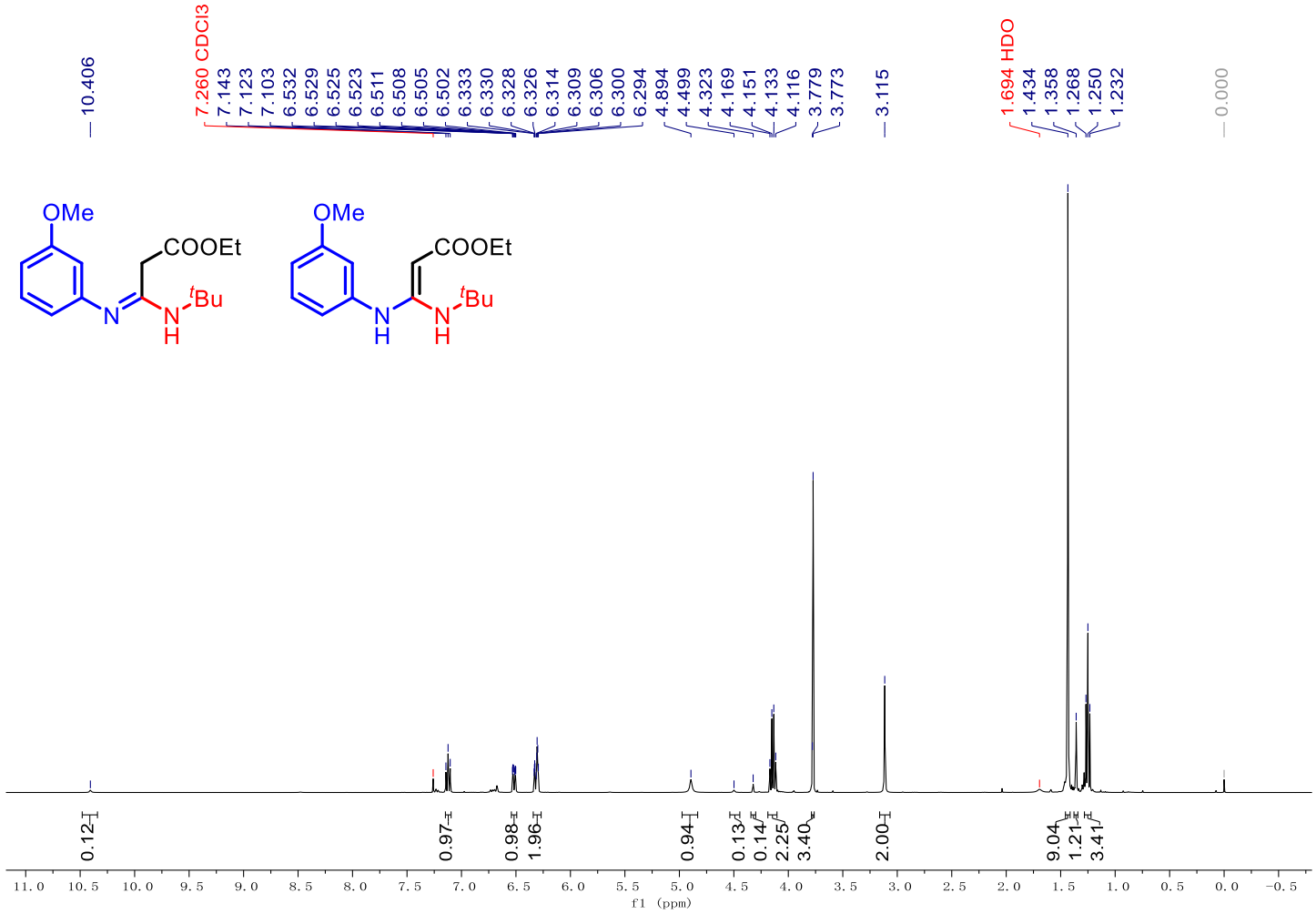
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((2-iodophenyl)imino)propanoate 4l (4l/4l' > 20/1)



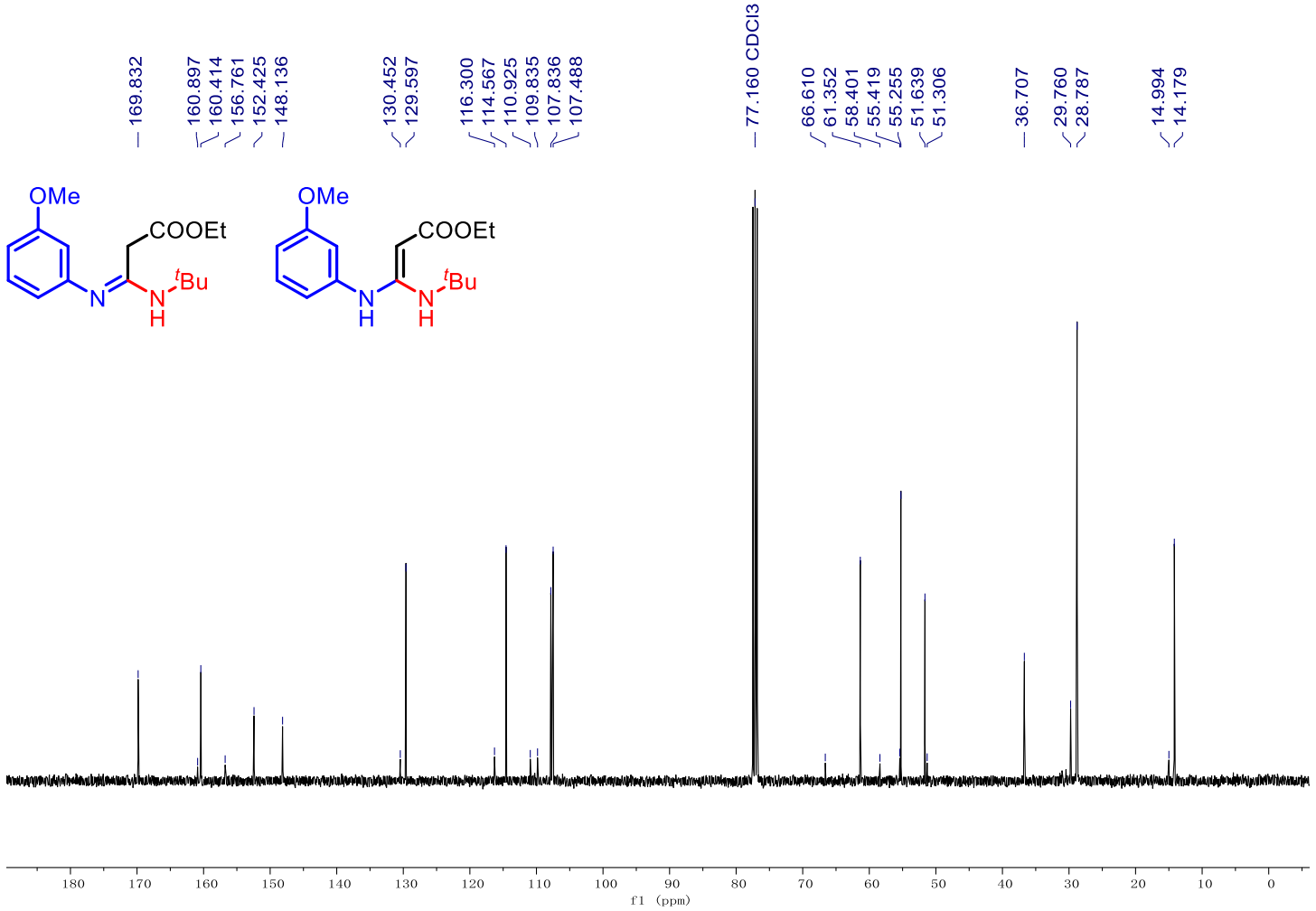
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((2-iodophenyl)imino)propanoate 4l (4l/4l' > 20/1)



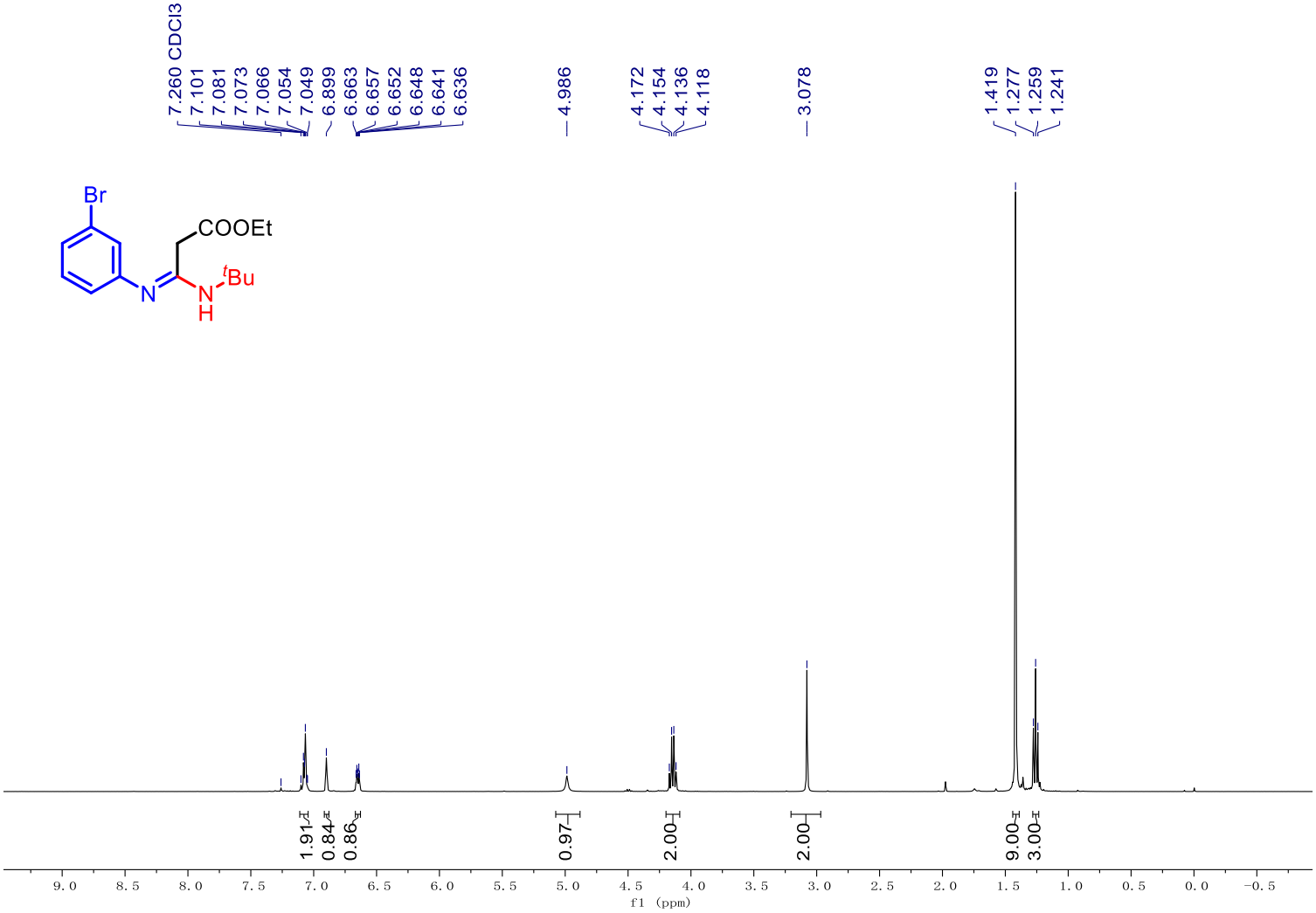
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)imino)propanoate 4m and (*E*)-ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)amino)acrylate 4m' (4m/4m' = 8/1)



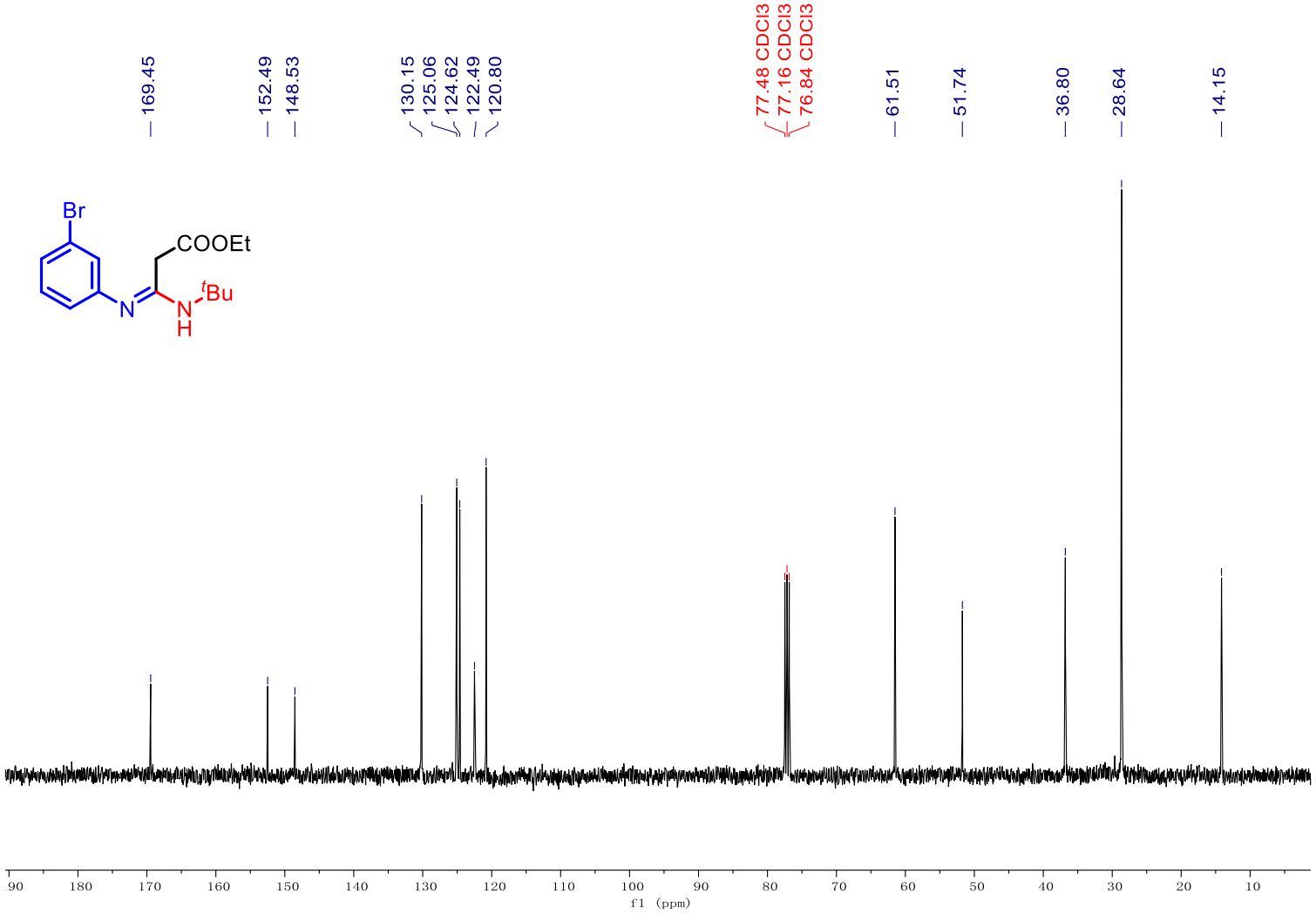
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)imino)propanoate 4m and (*E*)-ethyl-3-(*tert*-butylamino)-3-((3-methoxyphenyl)amino)acrylate 4m' (4m/4m' = 8/1)



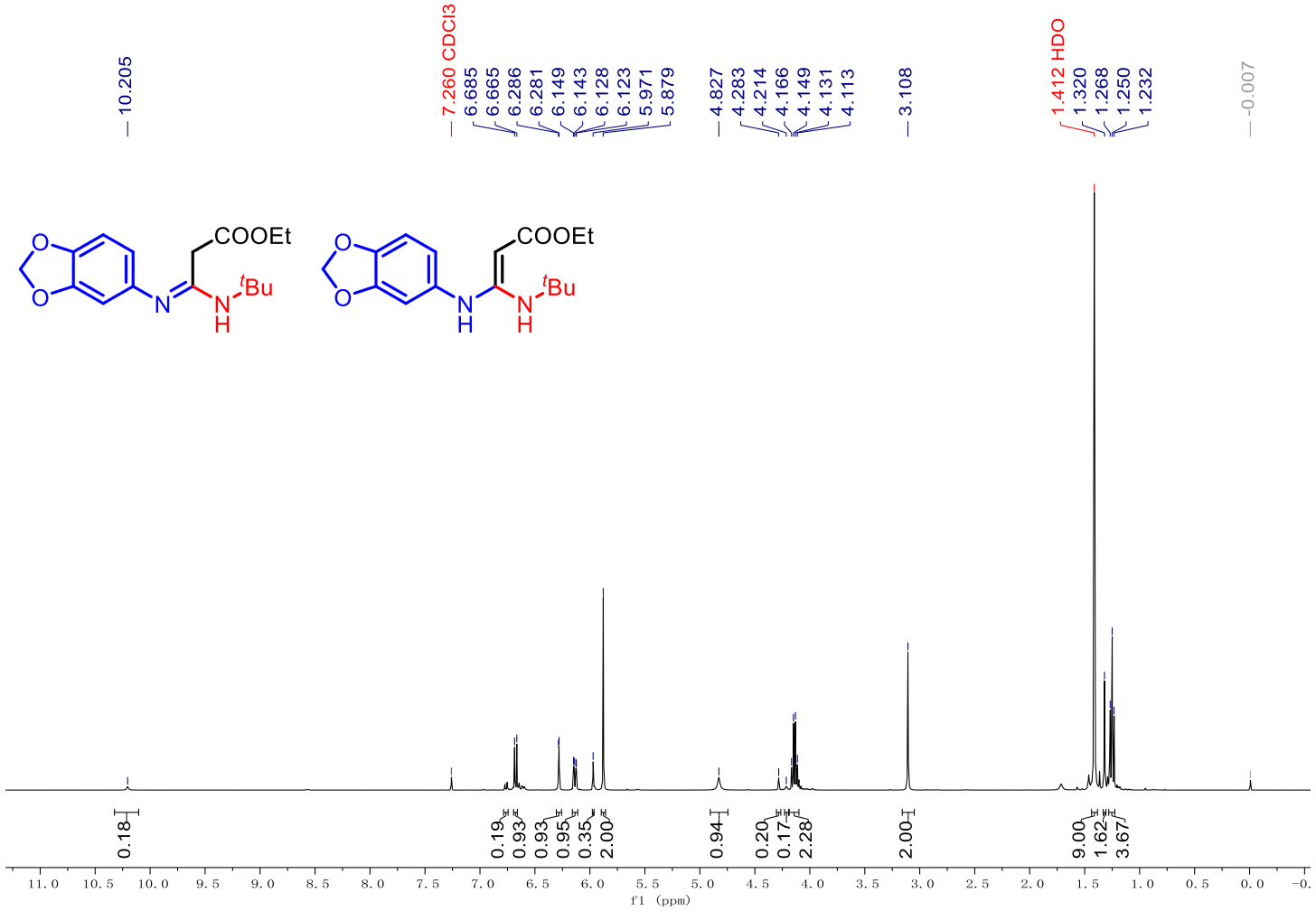
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((3-bromophenyl)imino)-3-(*tert*-butylamino)propanoate 4n (4n/4n' > 20/1)



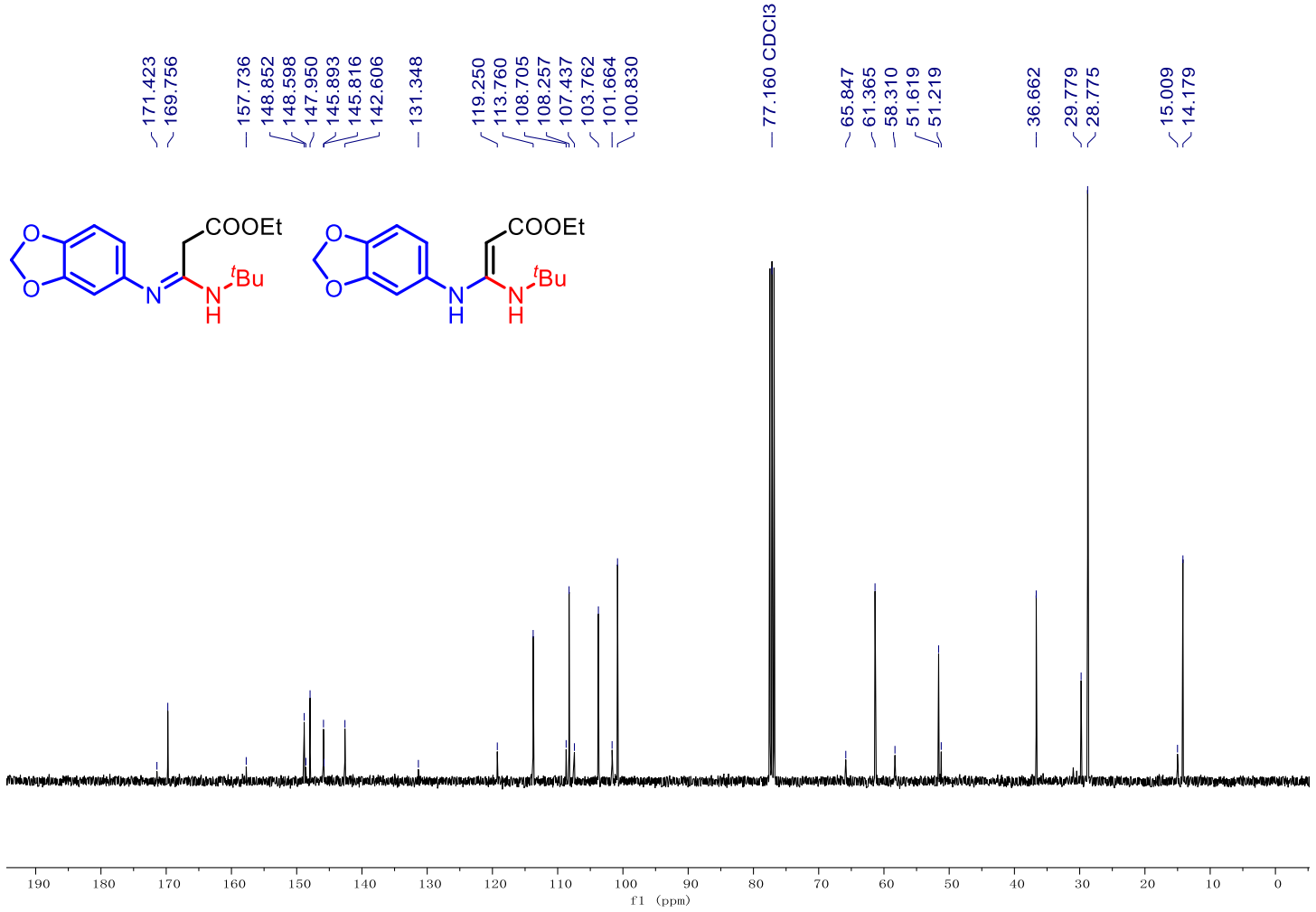
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((3-bromophenyl)imino)-3-(*tert*-butylamino)propanoate 4n (4n/4n' > 20/1)



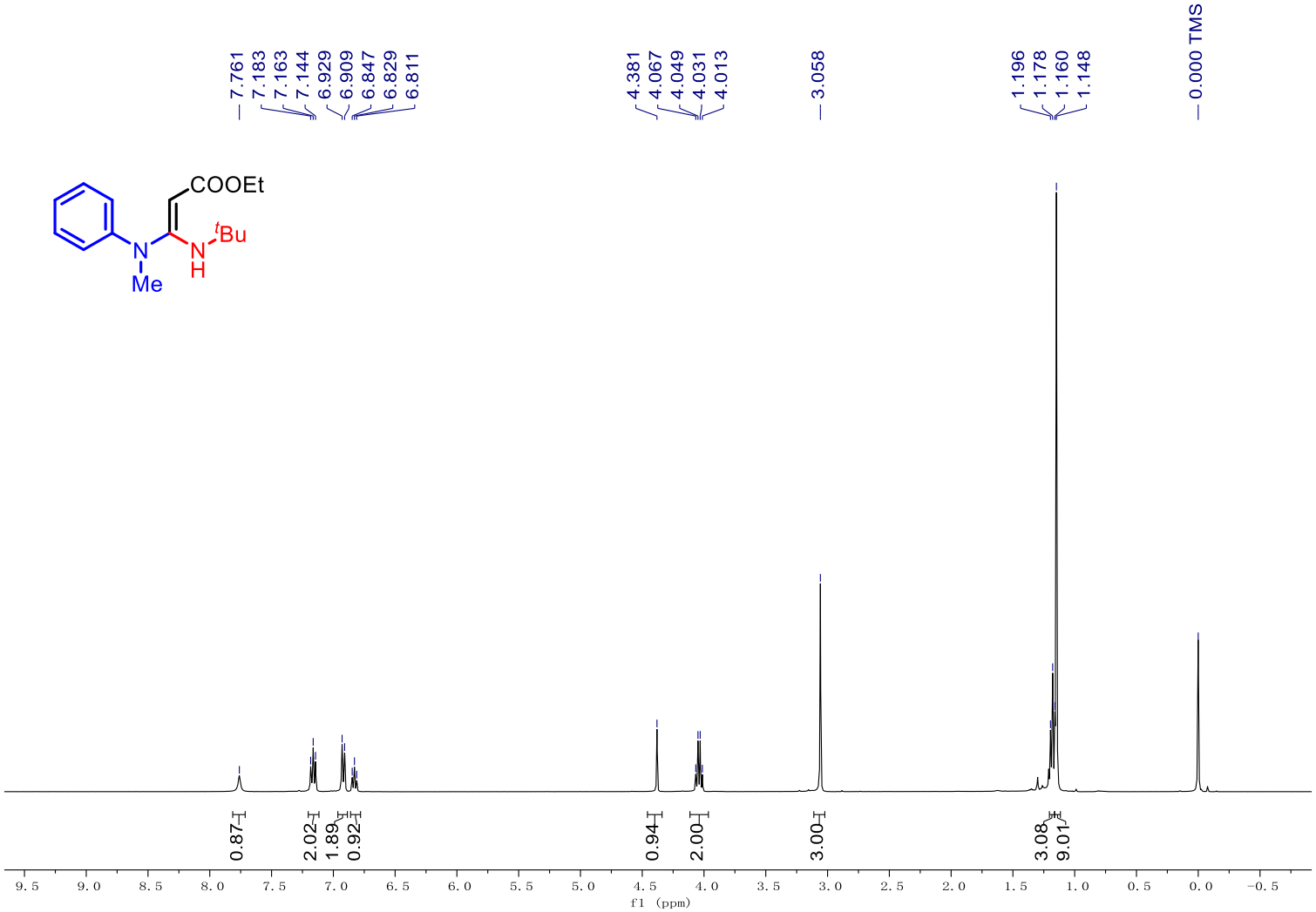
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(benzo[*d*][1,3]dioxol-5-ylimino)-3-(*tert*-butylamino)propanoate 4o and (*E*)-ethyl-3-(benzo[*d*][1,3]dioxol-5-ylamino)-3-(*tert*-butylamino)acrylate 4o' (4o/4o' = 6/1)



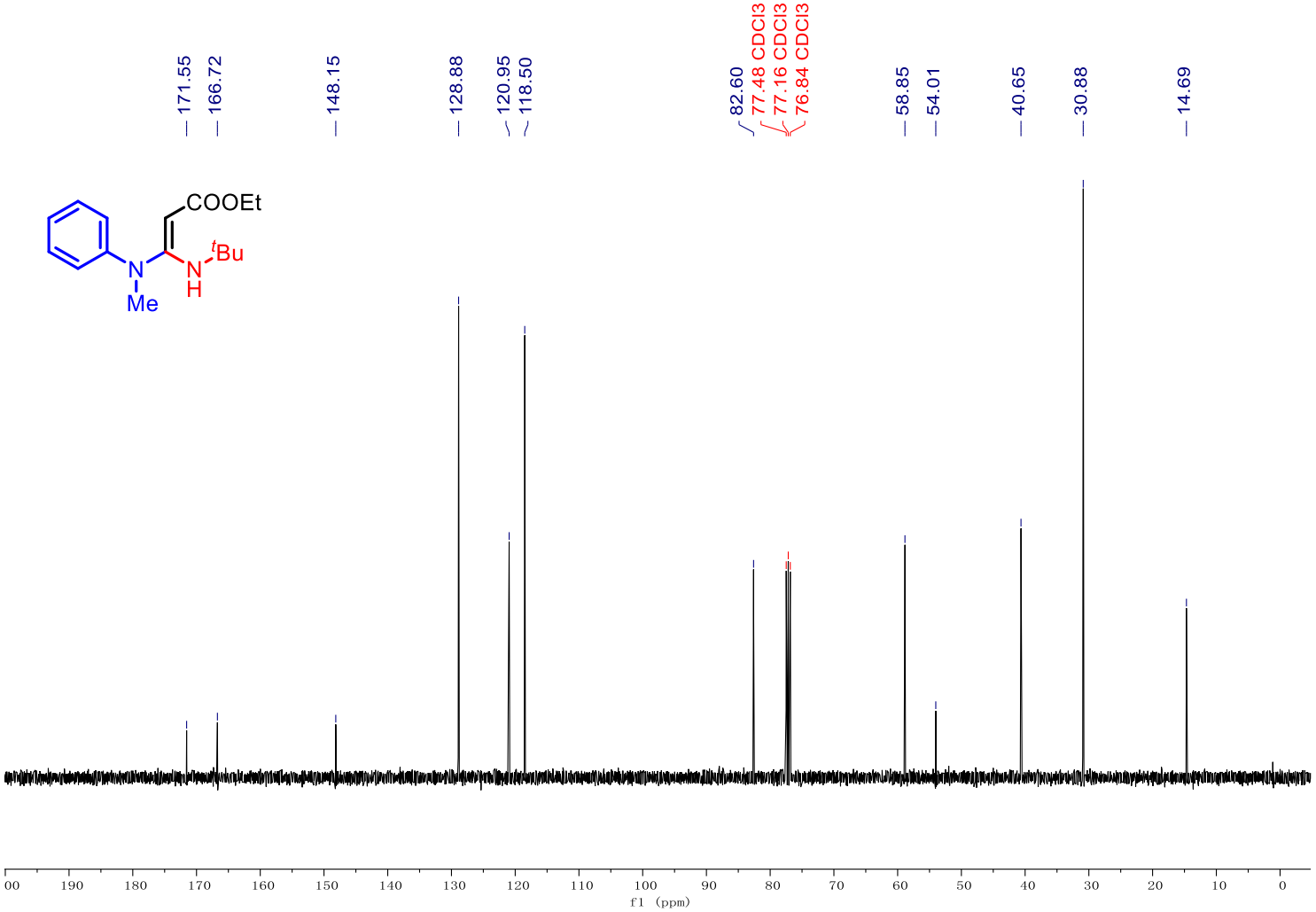
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(benzo[*d*][1,3]dioxol-5-ylimino)-3-(*tert*-butylamino)propanoate 4o and (*E*)-ethyl-3-(benzo[*d*][1,3]dioxol-5-ylamino)-3-(*tert*-butylamino)acrylate 4o' (4o/4o' = 6/1)



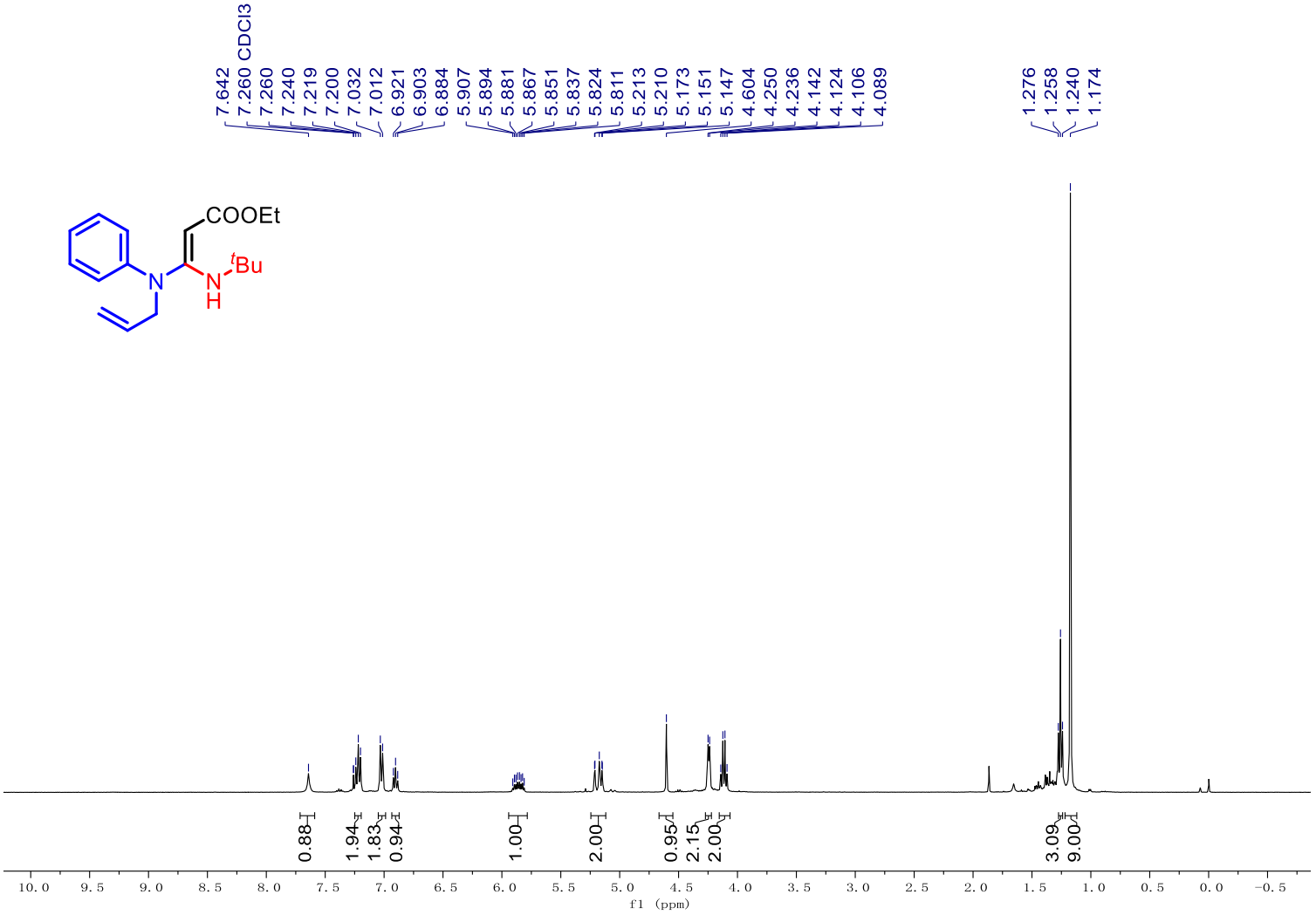
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(methyl(*o*-tolyl)amino) acrylate 4p



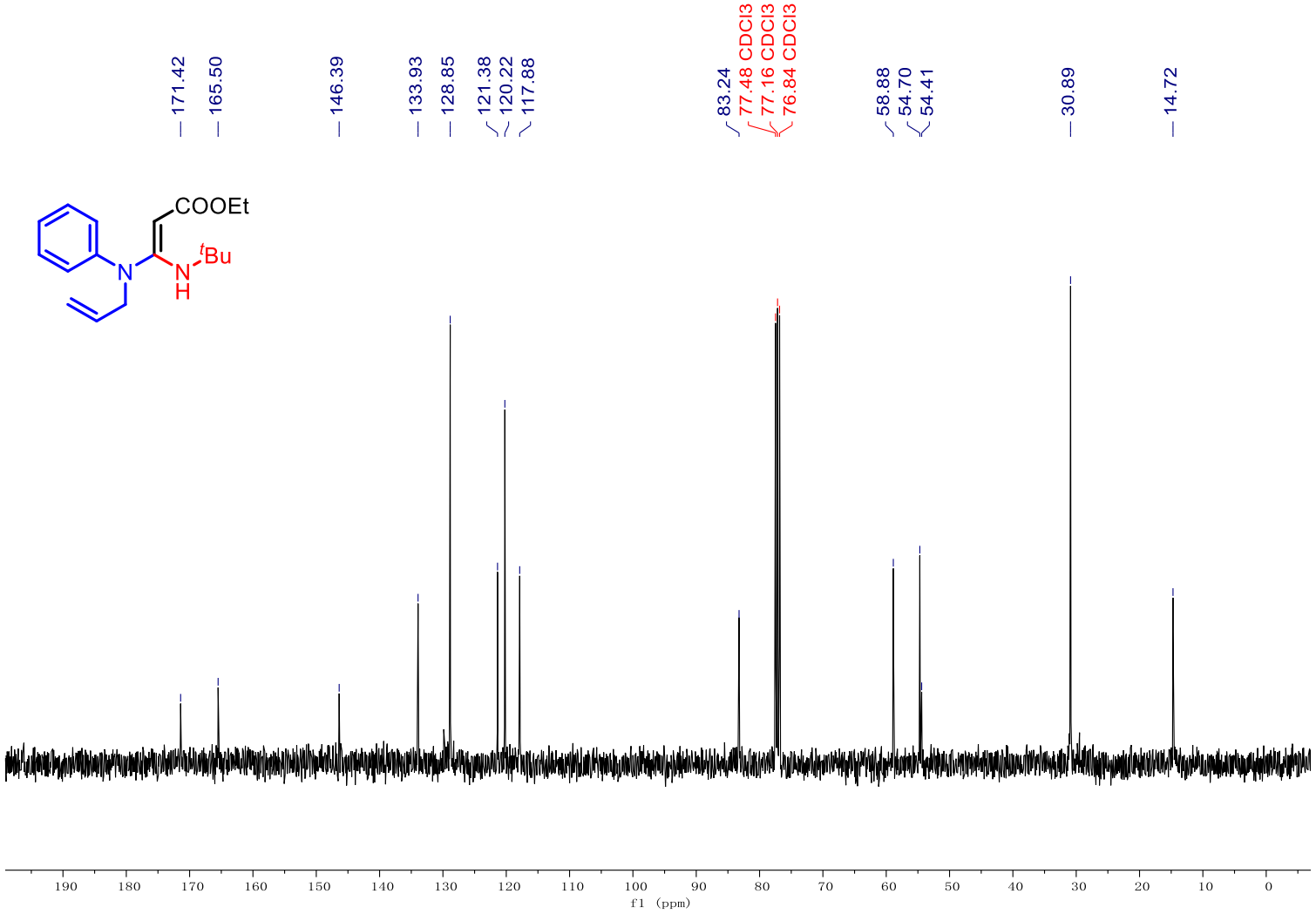
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(methyl(*o*-tolyl)amino) acrylate 4p



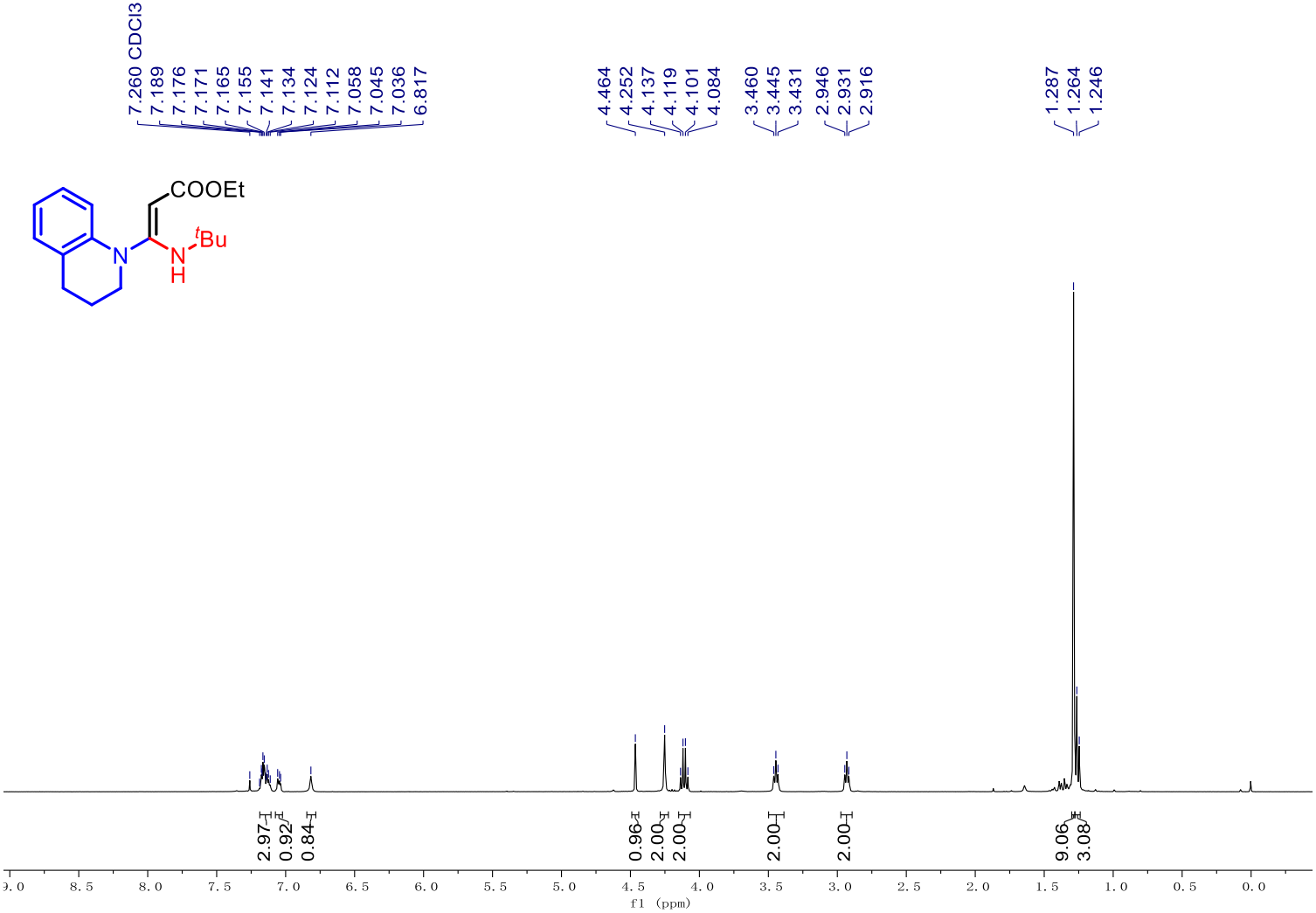
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(allyl(phenyl)amino)-3-(*tert*-butylamino)acrylate 4q



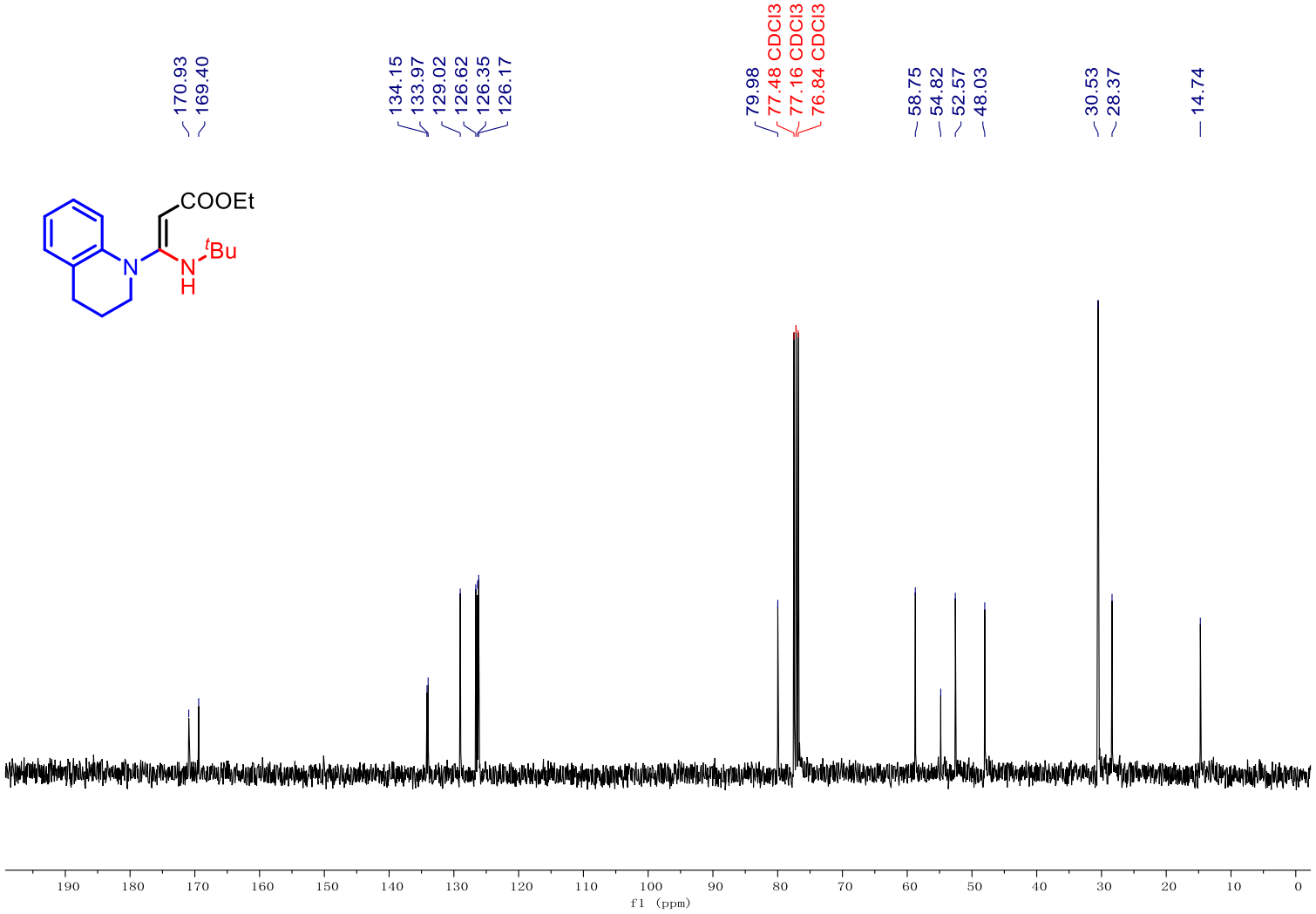
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(allyl(phenyl)amino)-3-(*tert*-butylamino)acrylate 4q



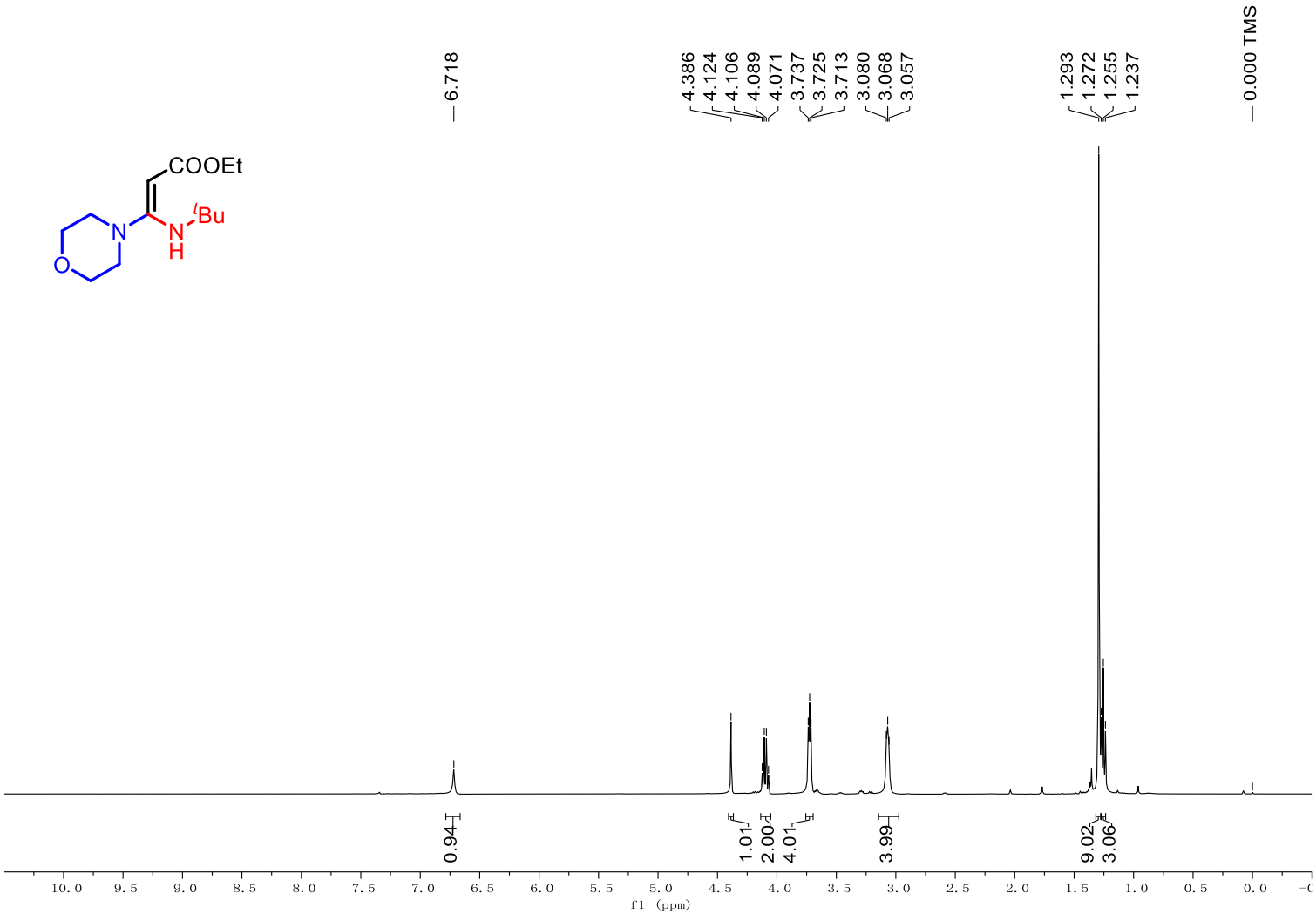
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(3,4-dihydroquinolin-1(2*H*)-yl) acrylate 4r



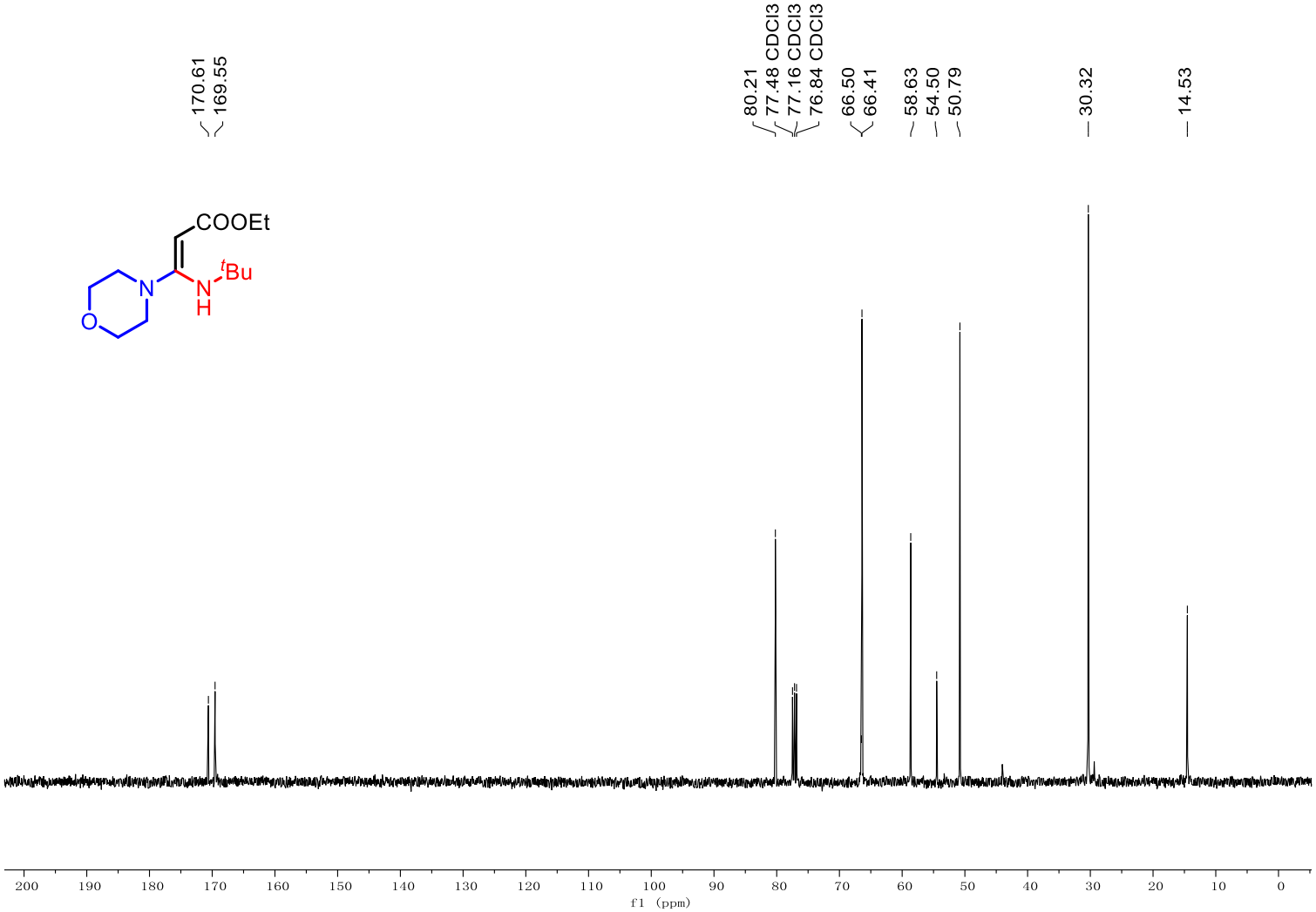
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(3,4-dihydroquinolin-1(2*H*)-yl) acrylate 4r



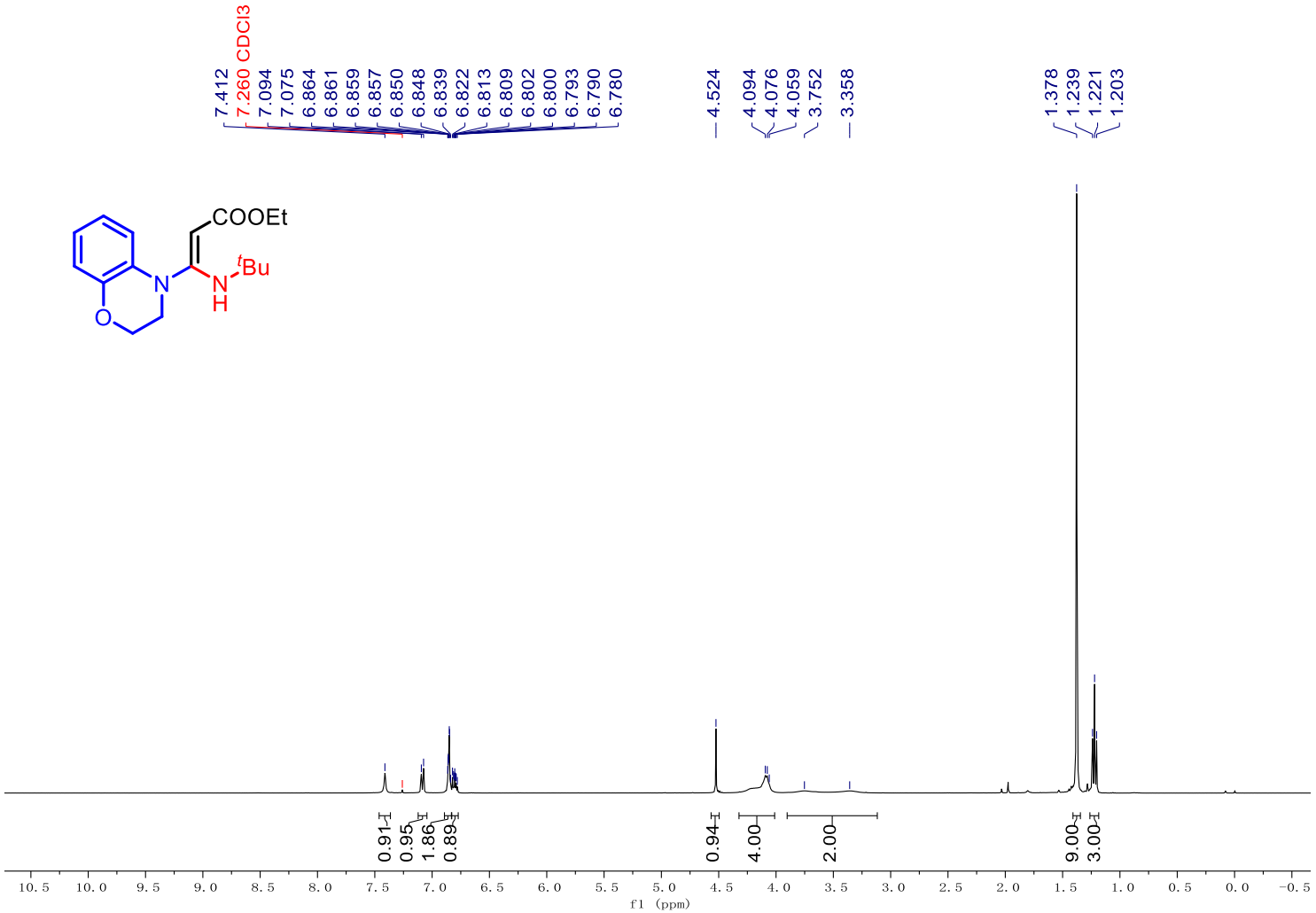
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-morpholinoacrylate 4s



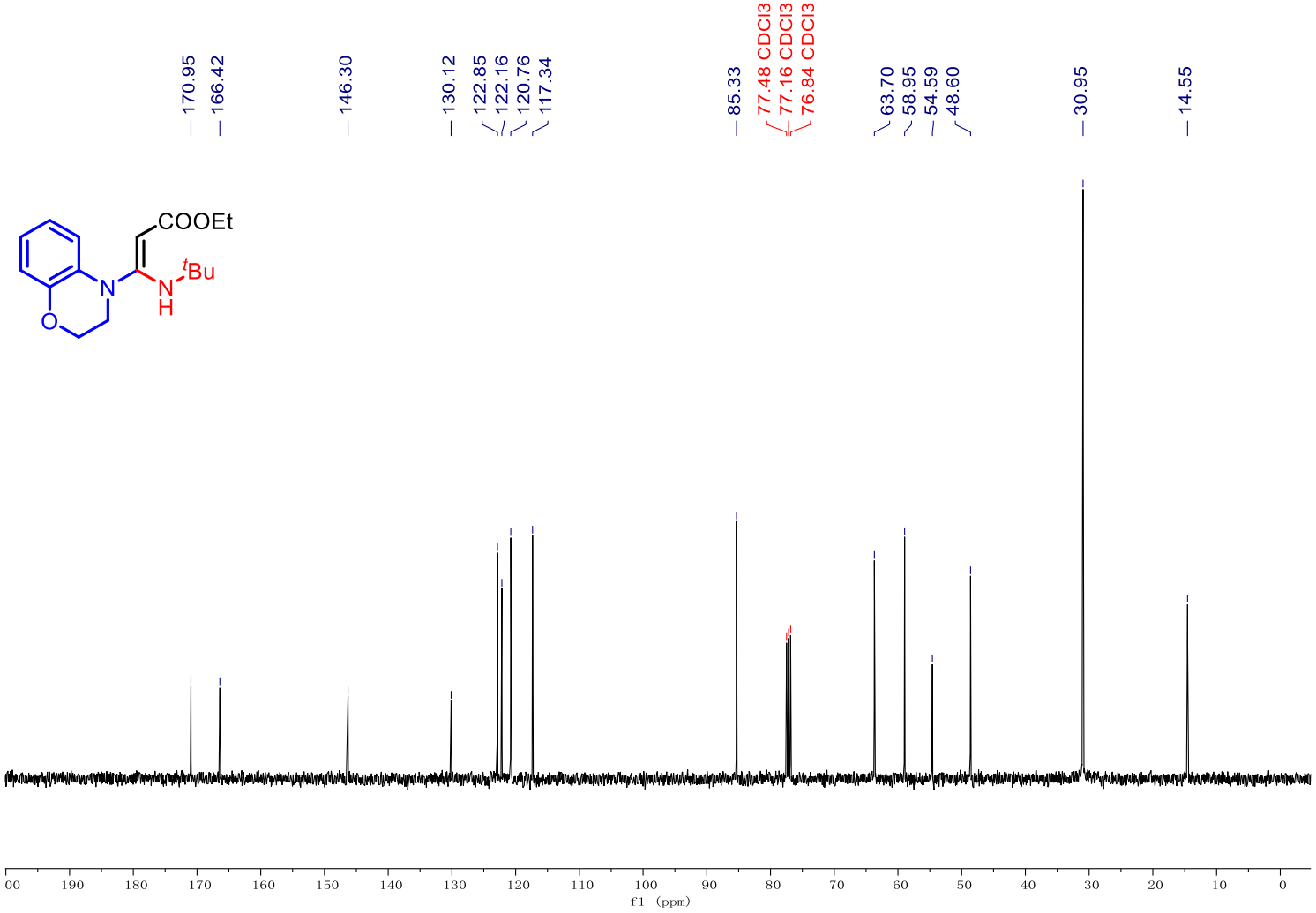
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-morpholinoacrylate 4s



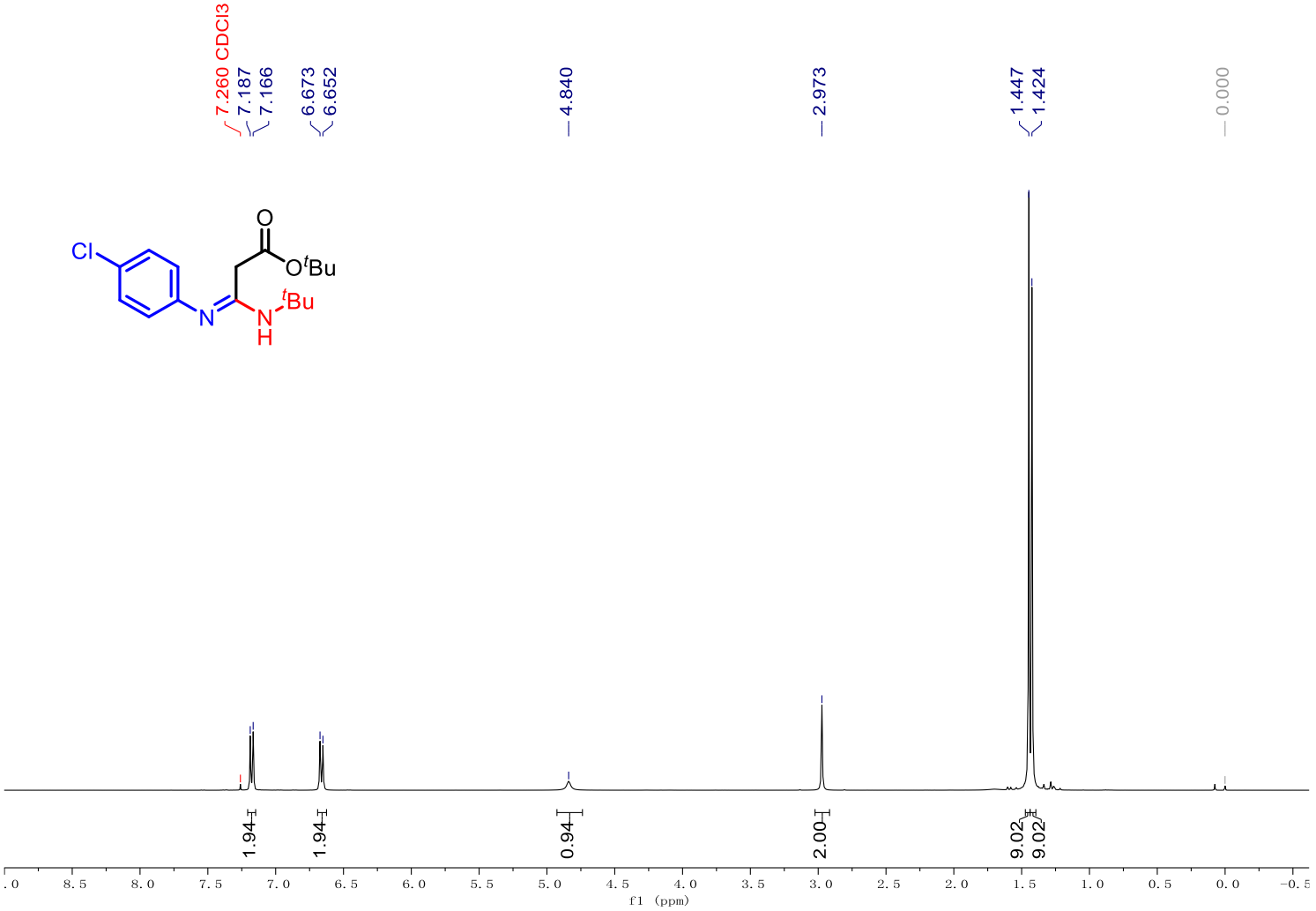
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(2,3-dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)acrylate 4t



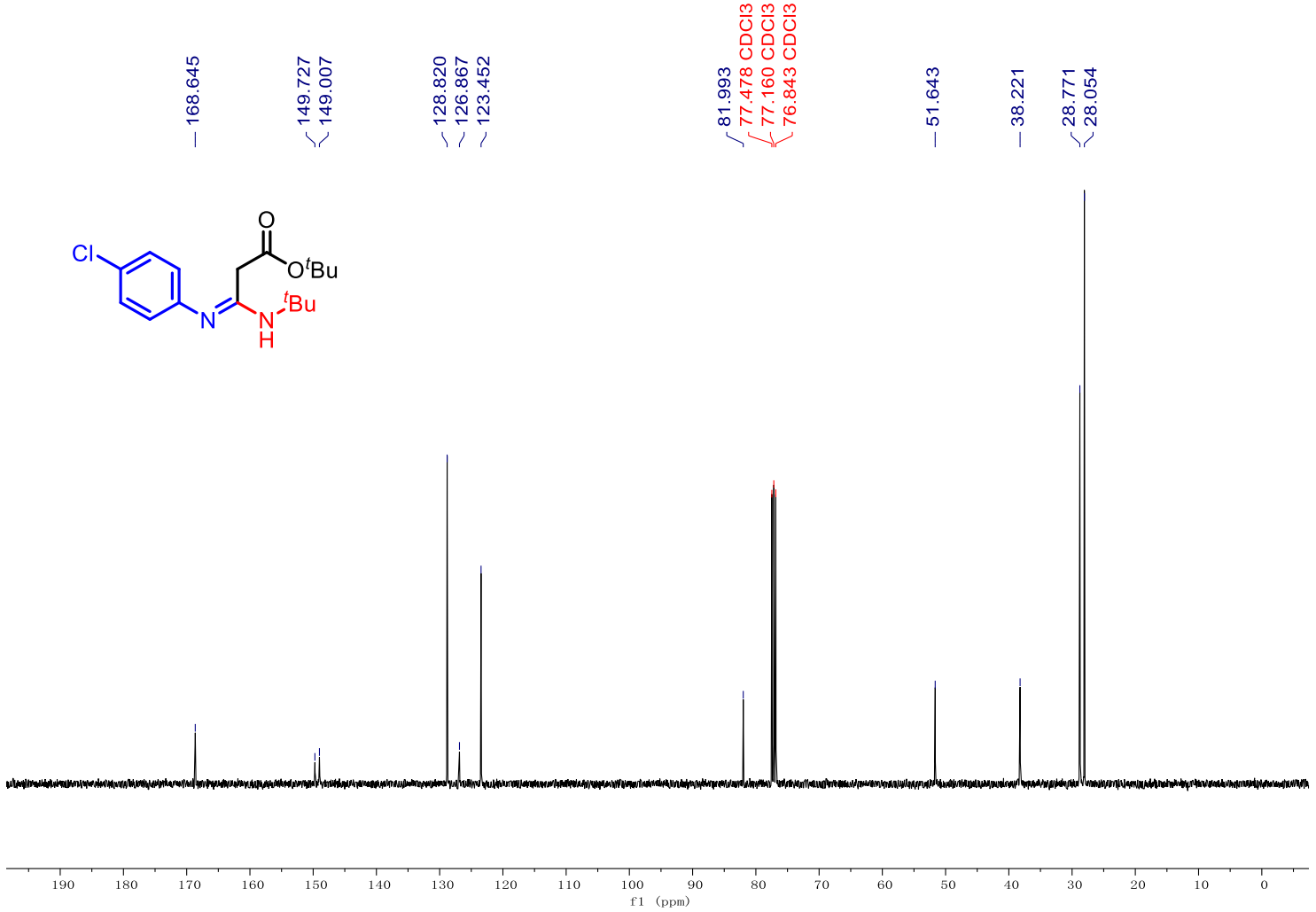
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-(2,3-dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)acrylate 4t



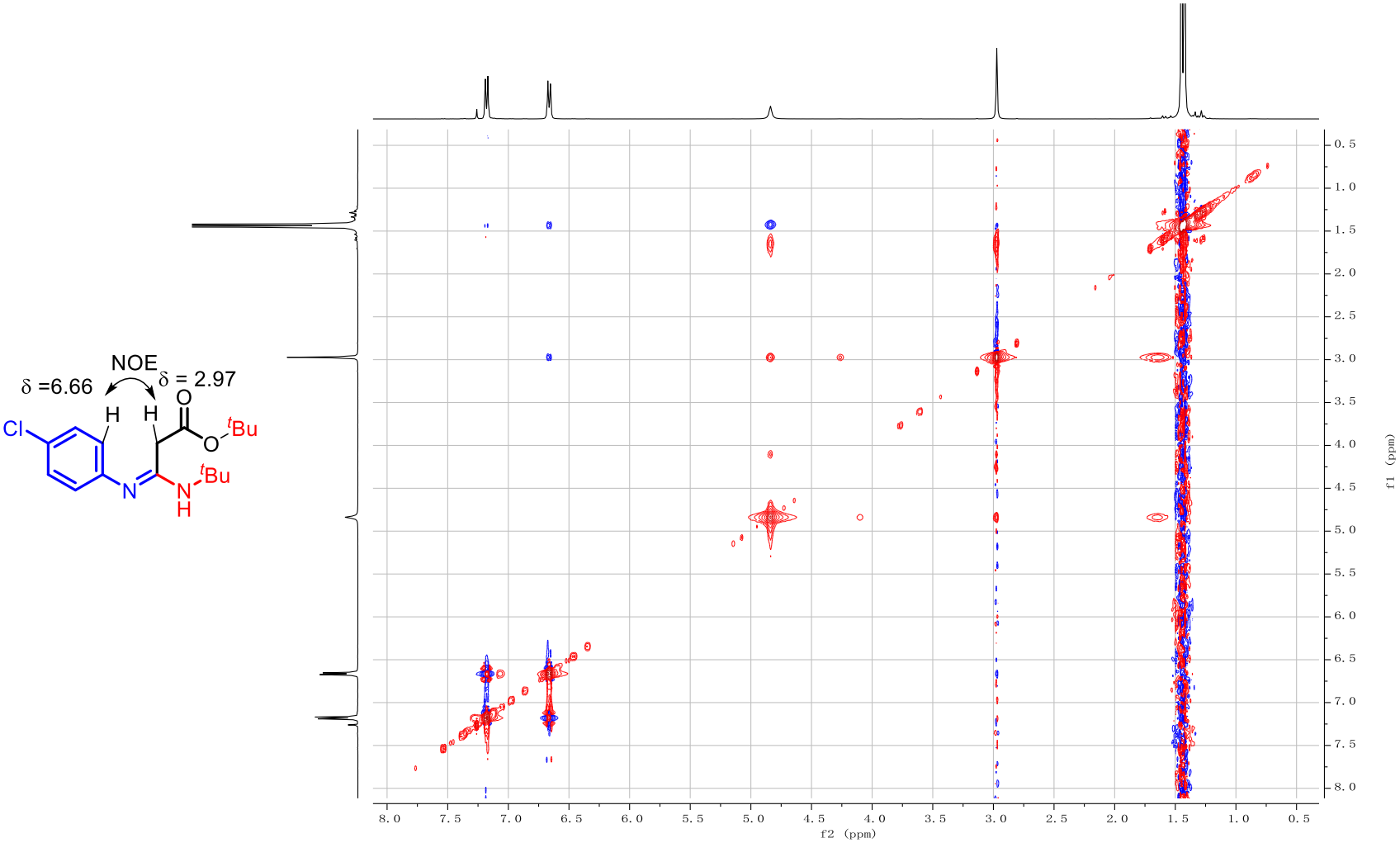
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-*tert*-Butyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5a



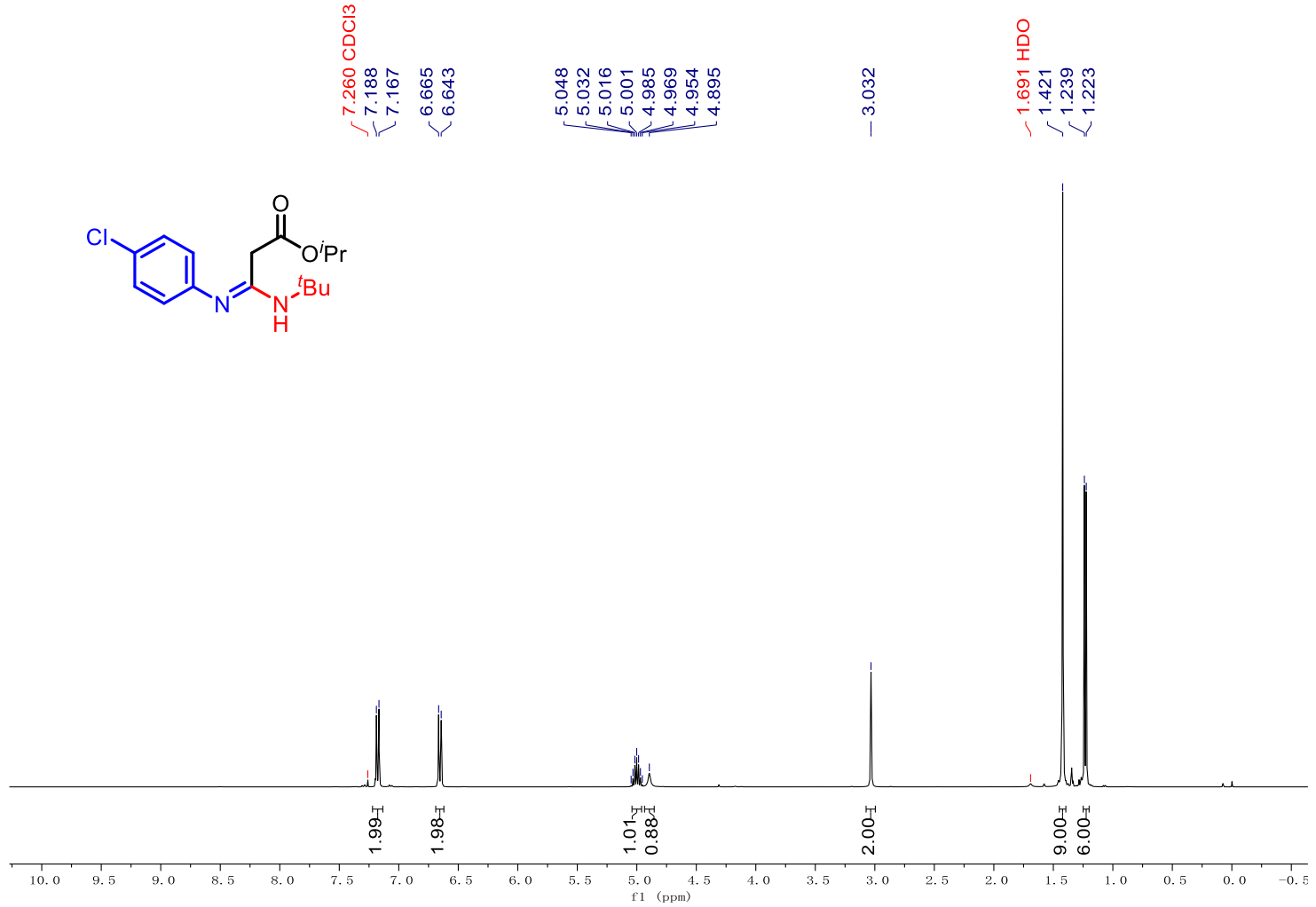
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-*tert*-Butyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5a



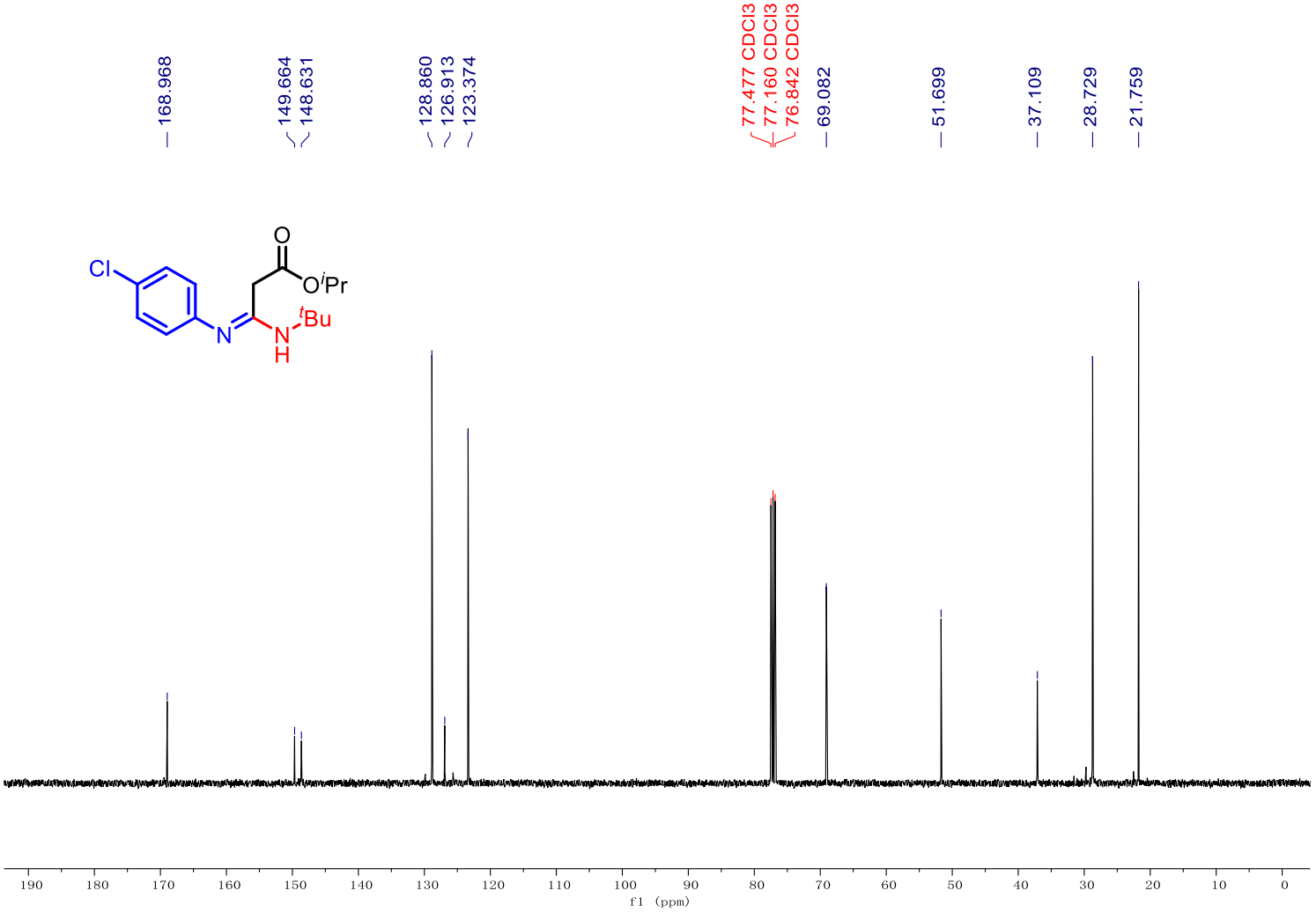
NOE Spectrum of (*E*)-*tert*-Butyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5a



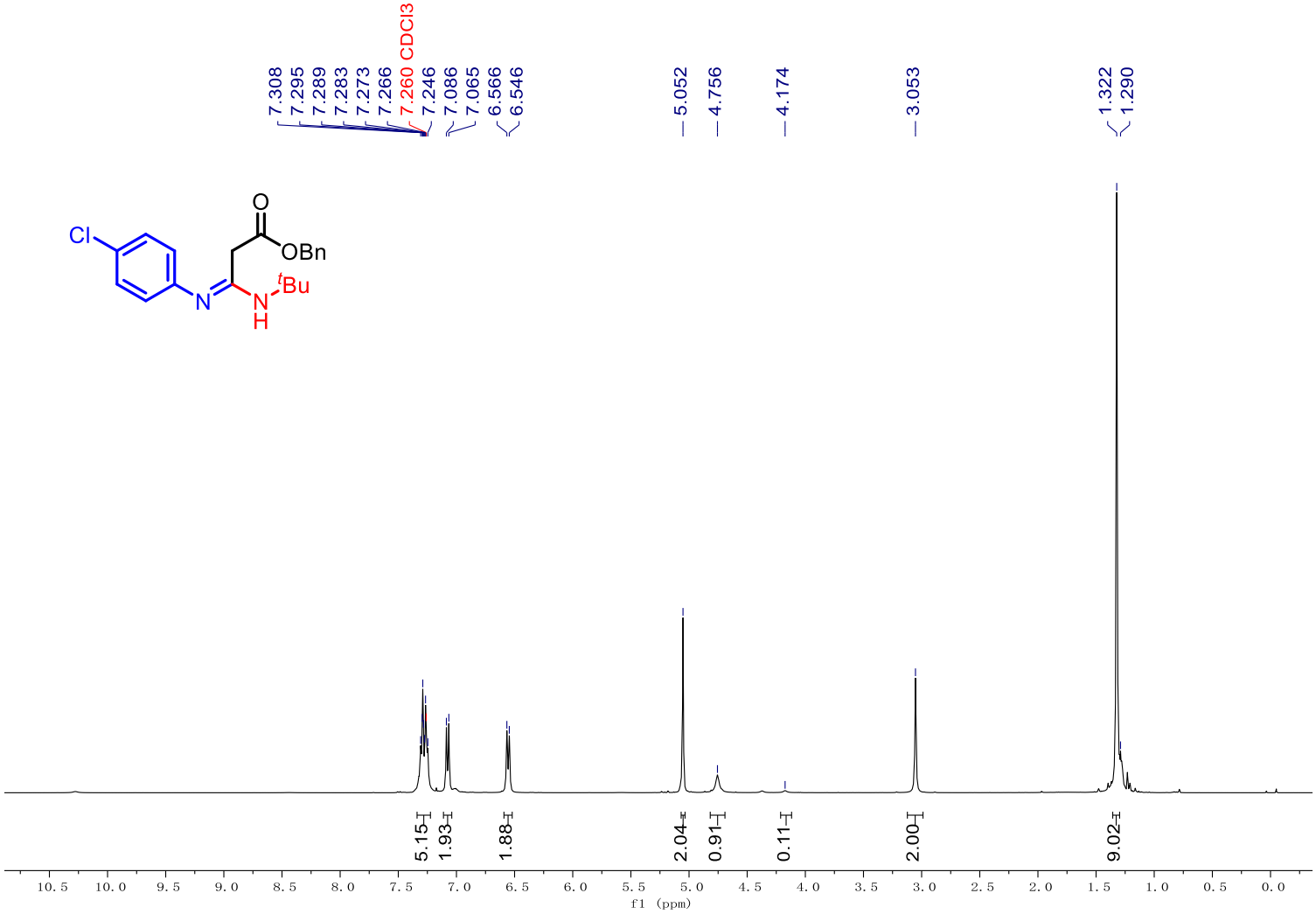
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Isopropyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5b



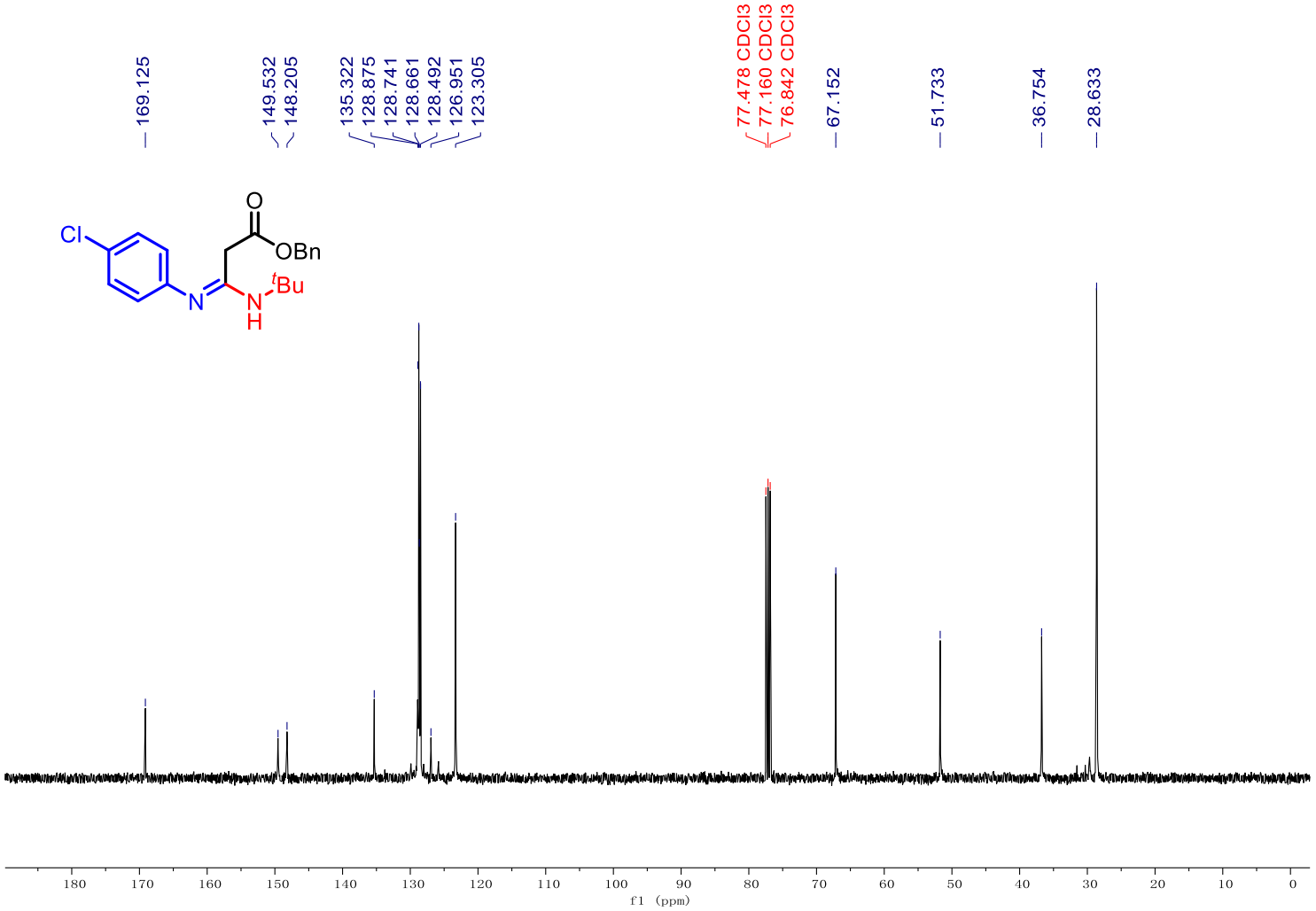
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Isopropyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5b



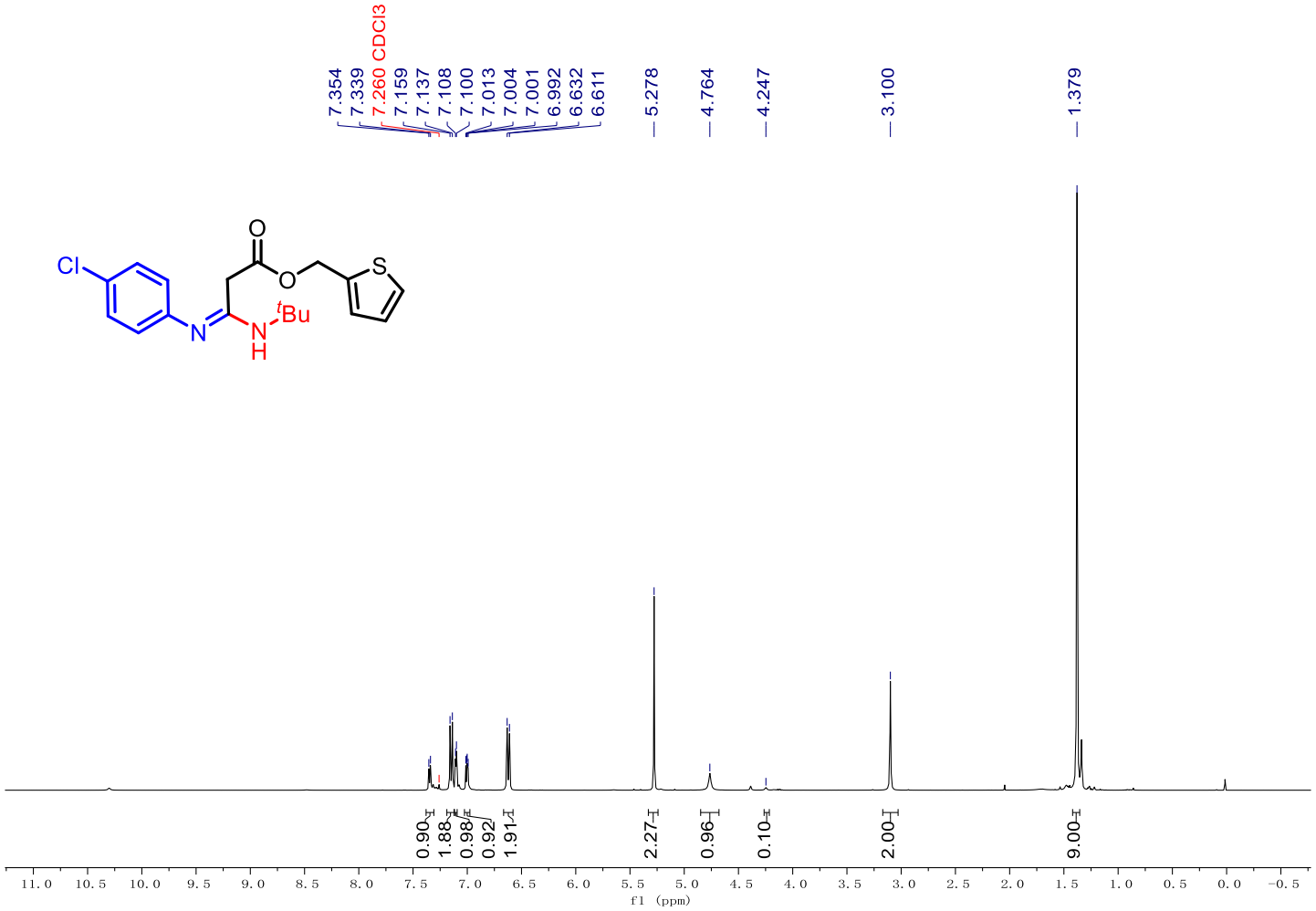
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Benzyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5c (5c/5c' = 10/1)



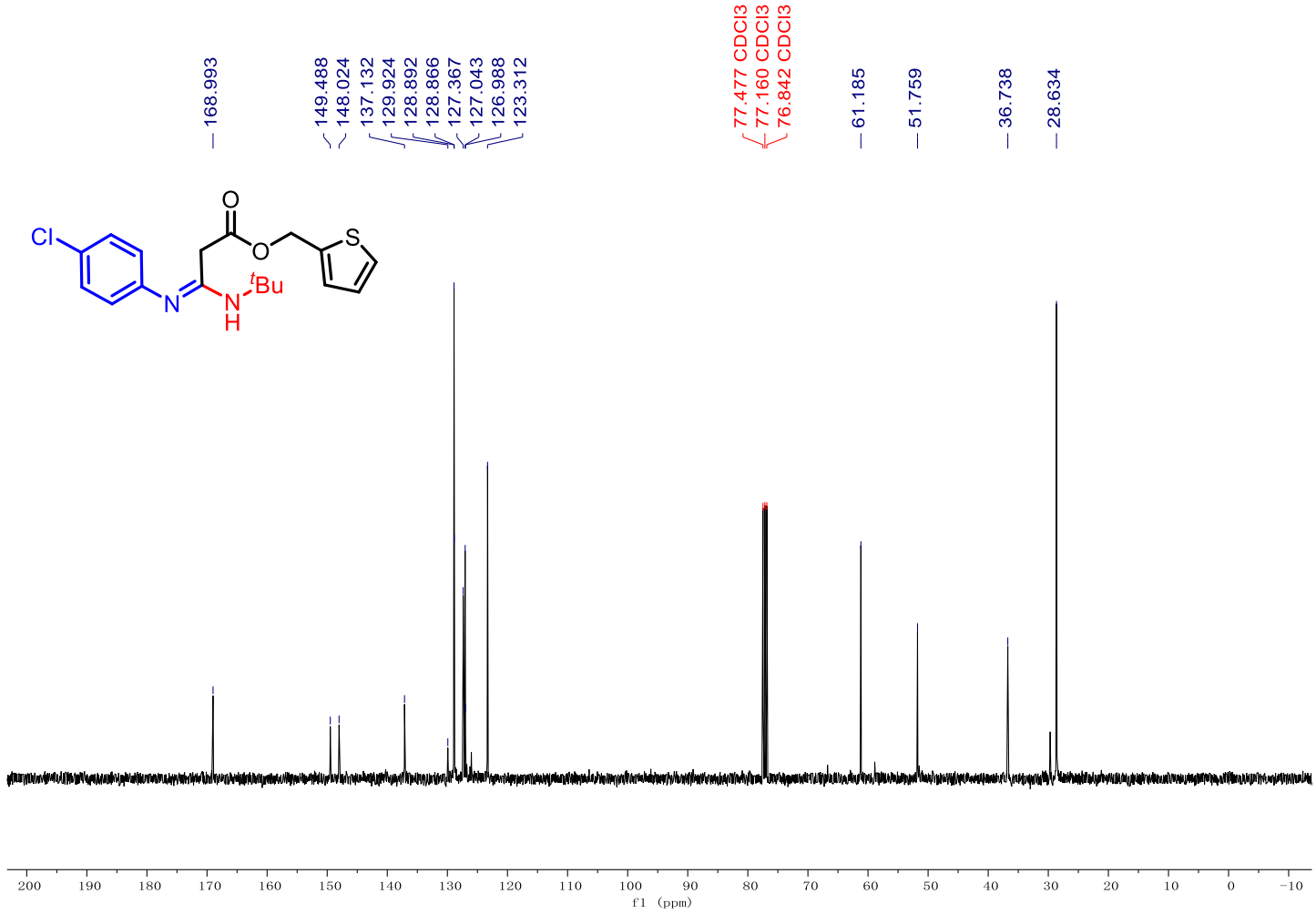
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Benzyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5c (5c/5c' = 10/1)



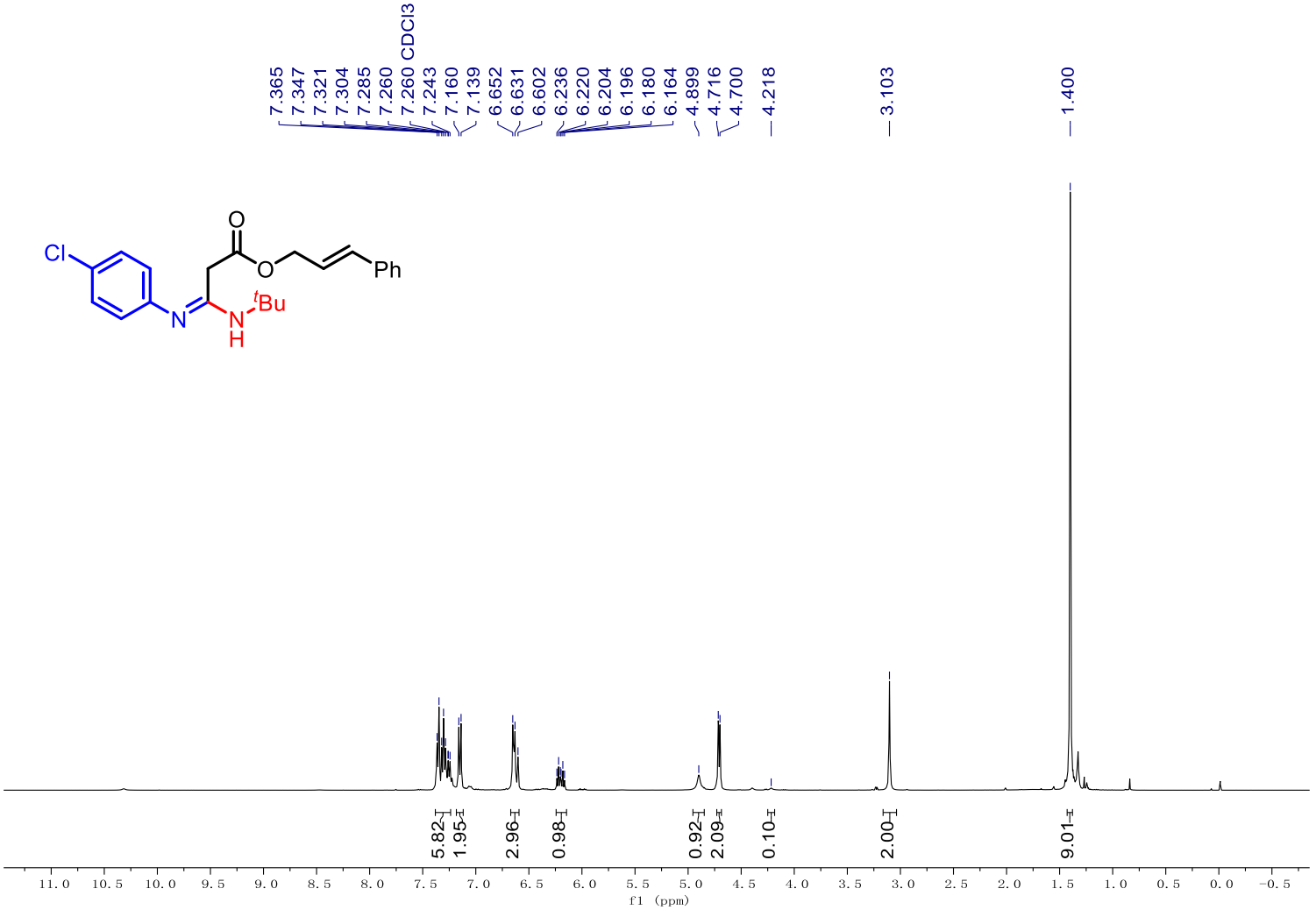
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Thiophen-2-ylmethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5d (5d/5d' = 10/1)



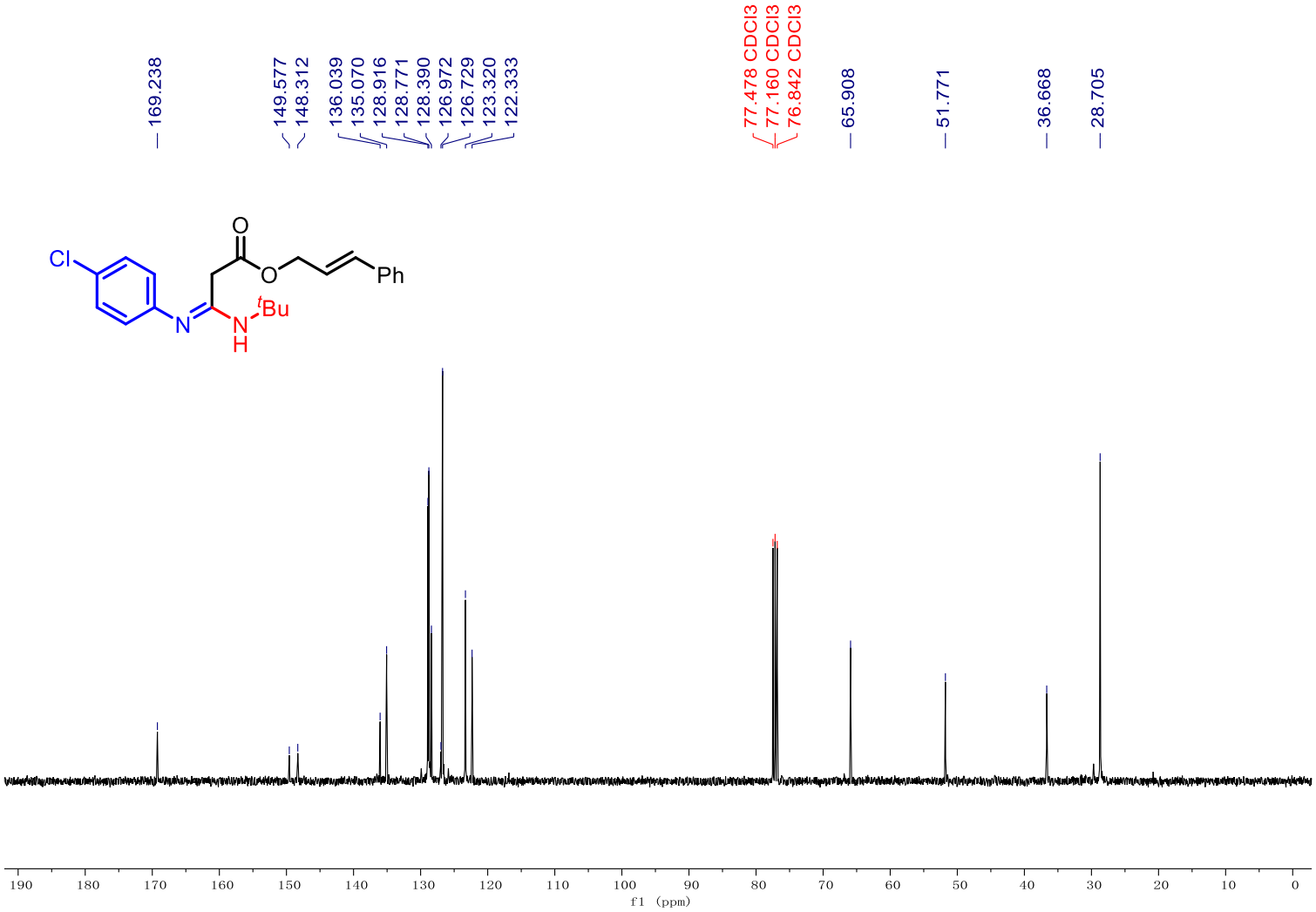
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Thiophen-2-ylmethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5d (5d/5d' = 10/1)



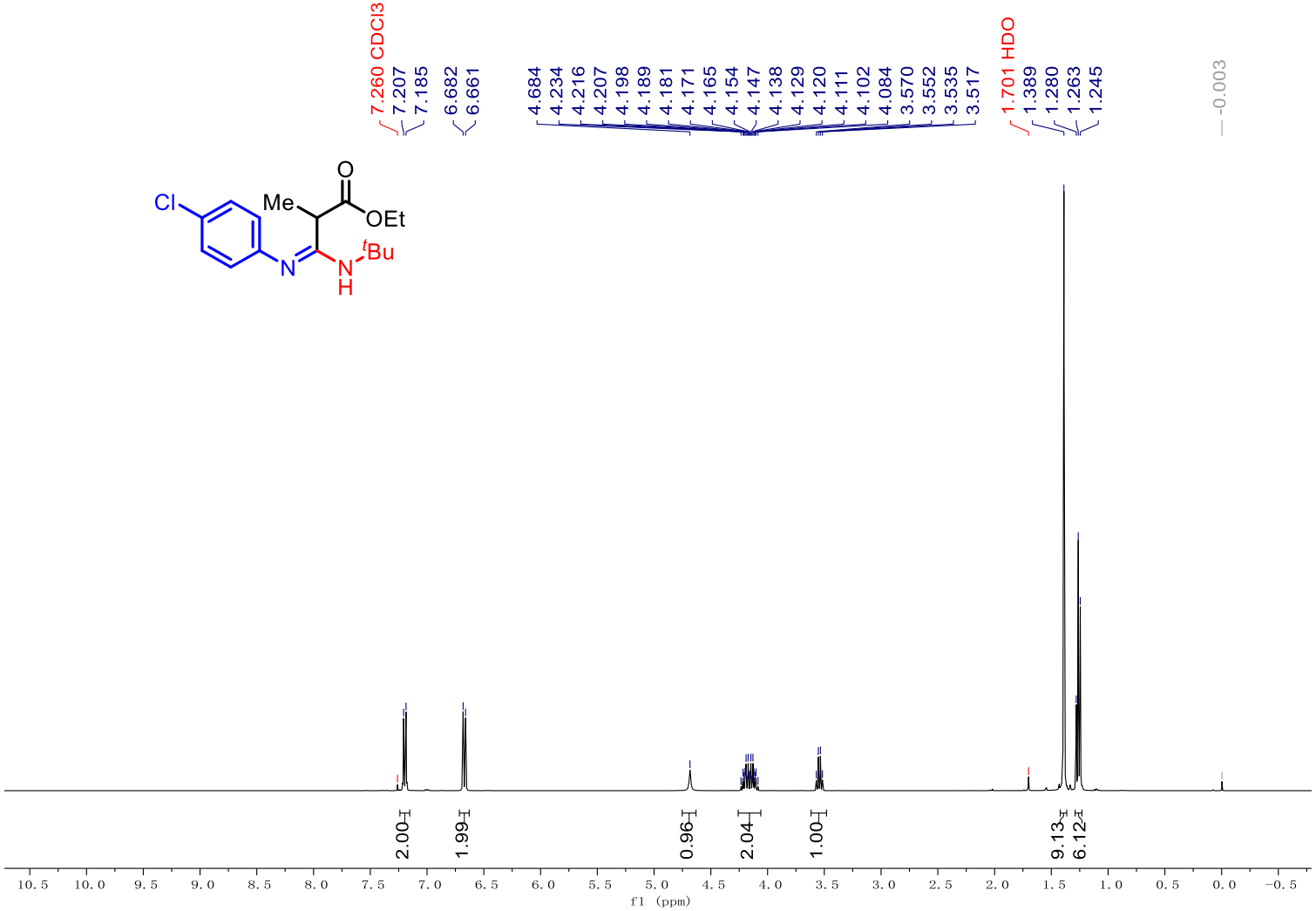
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Cinnamyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5e (5e/5e' = 10/1)



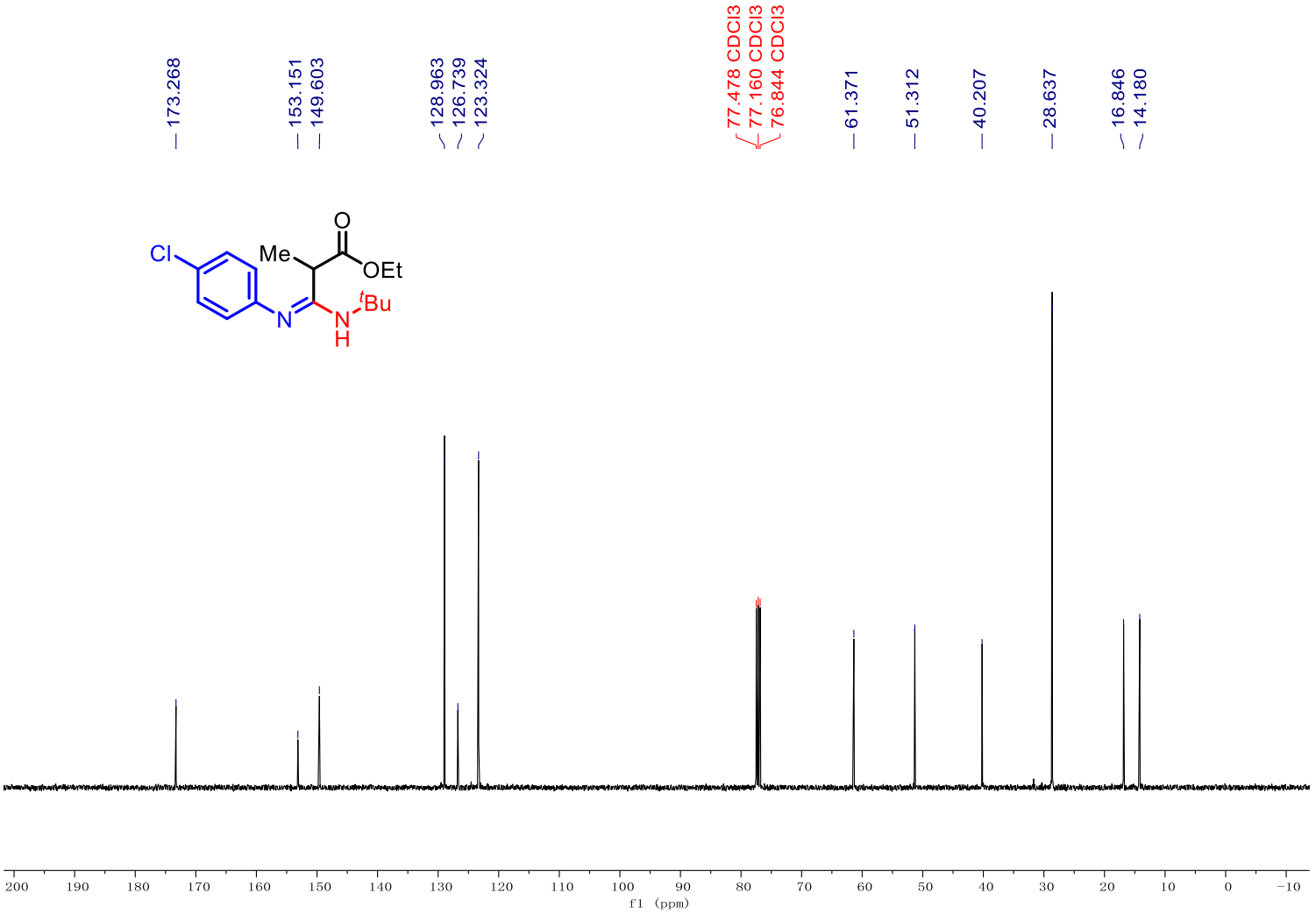
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Cinnamyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)propanoate 5e (5e/5e' = 10/1)



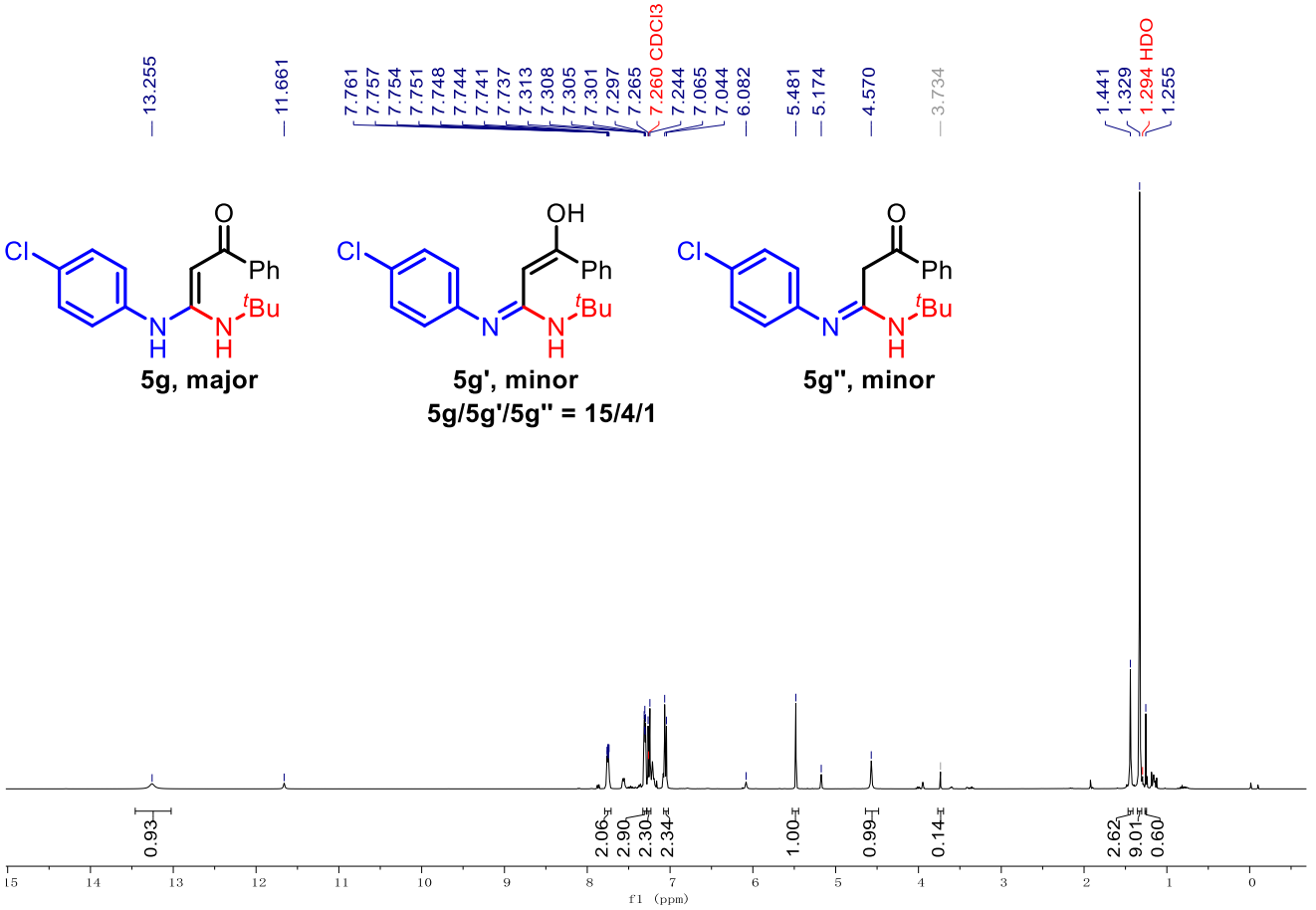
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)-2-methylpropanoate 5f



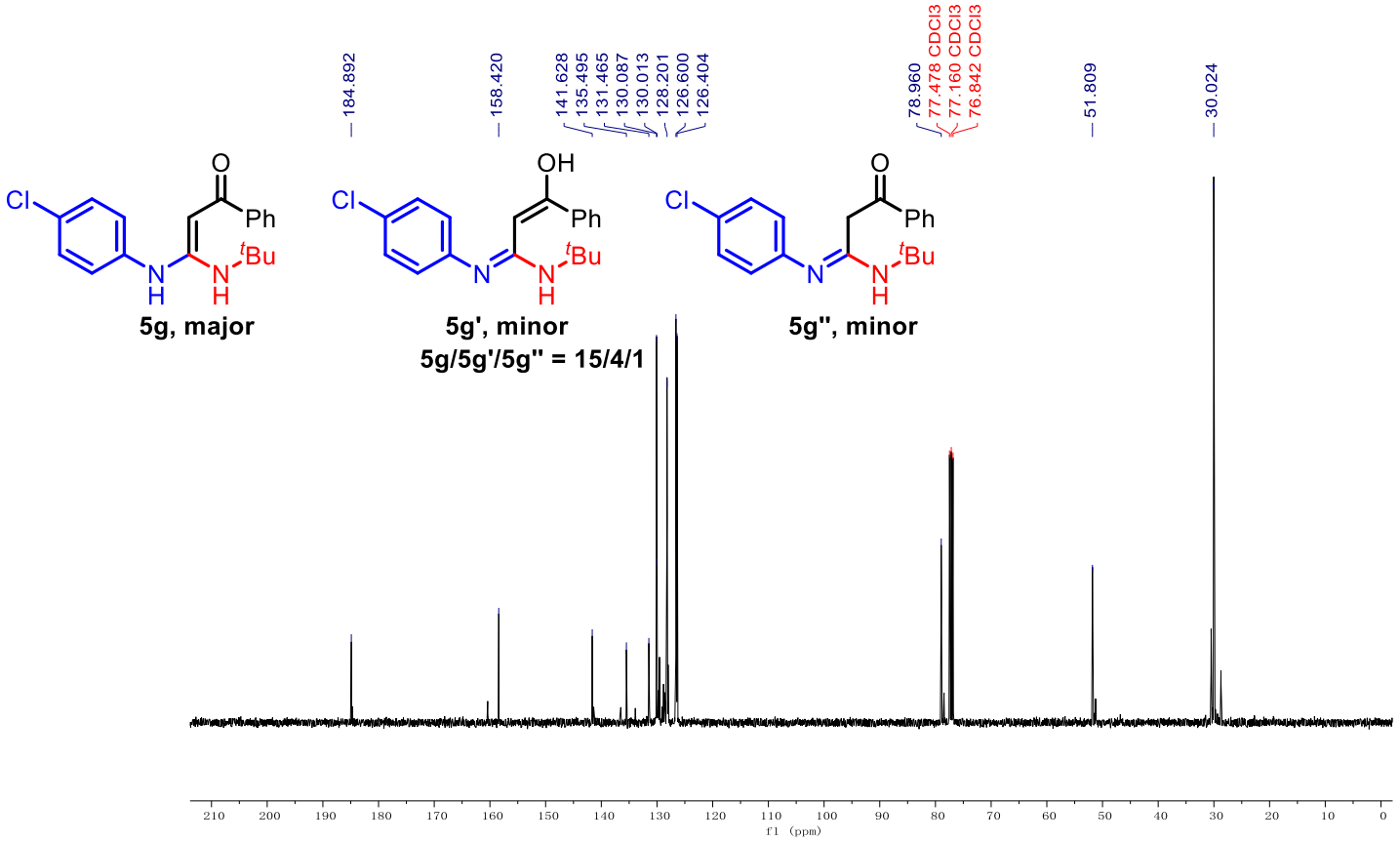
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(*tert*-butylamino)-3-((4-chlorophenyl)imino)-2-methylpropanoate 5f



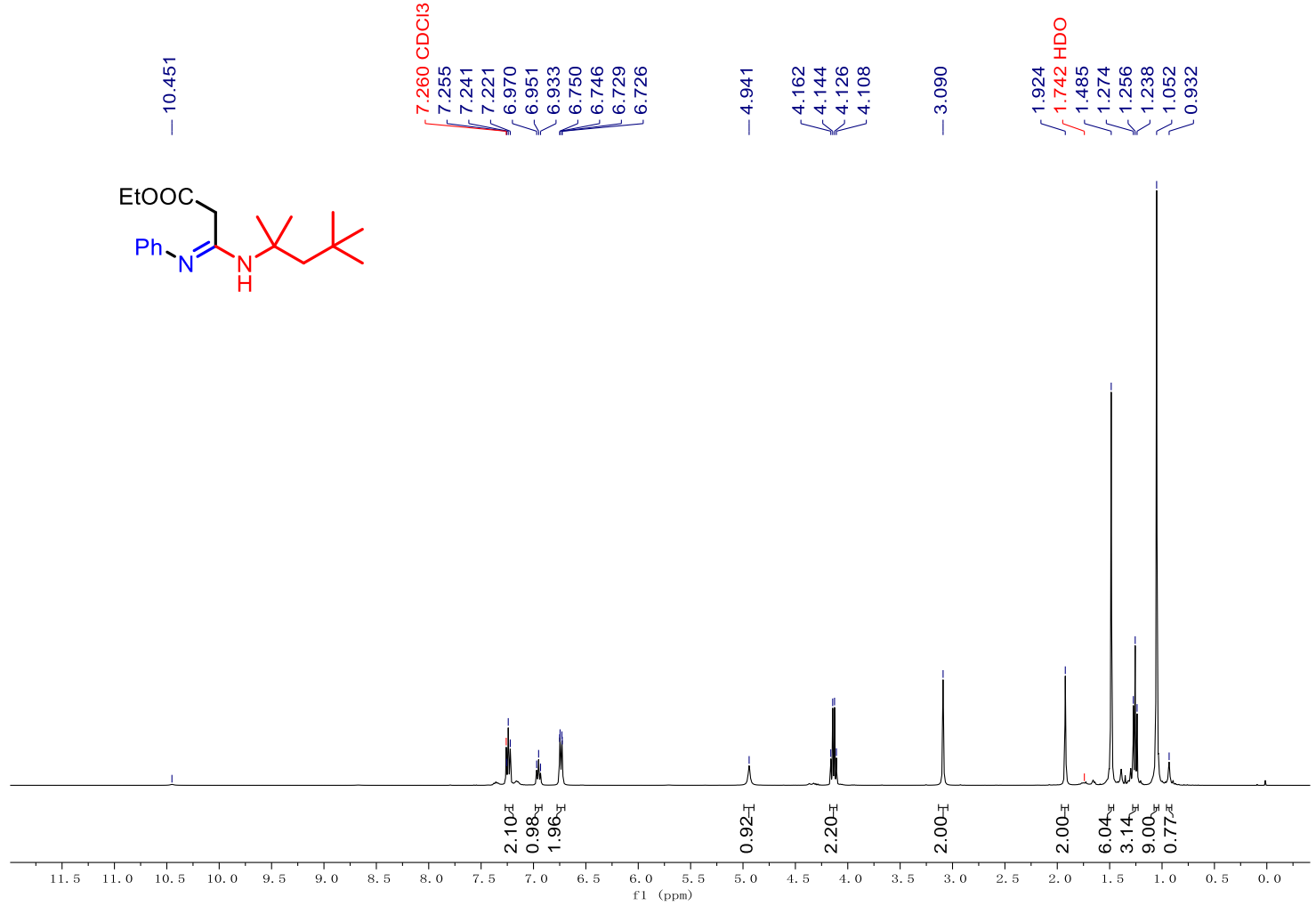
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-3-(*tert*-Butylamino)-3-((4-chlorophenyl)amino)-1-phenylprop-2-en-1-one 5g and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-hydroxy-3-phenylacrylimidamide 5g' and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-oxo-3-phenylpropanimidamide 5g"



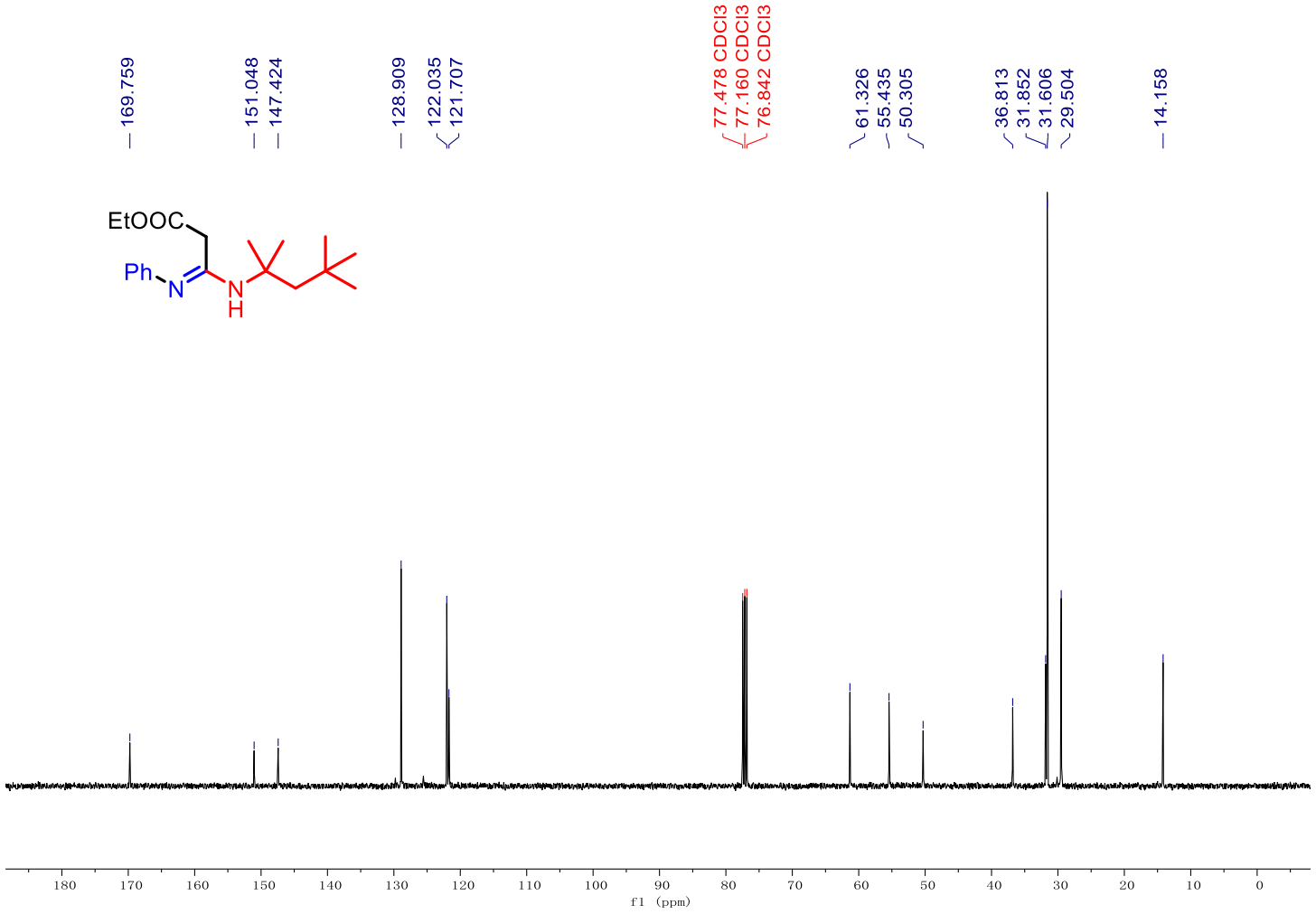
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-3-(*tert*-Butylamino)-3-((4-chlorophenyl)amino)-1-phenylprop-2-en-1-one 5g and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-hydroxy-3-phenylacrylimidamide 5g' and (*E*)-*N*-(*tert*-butyl)-*N'*-(4-chlorophenyl)-3-oxo-3-phenylpropanimidamide 5g"



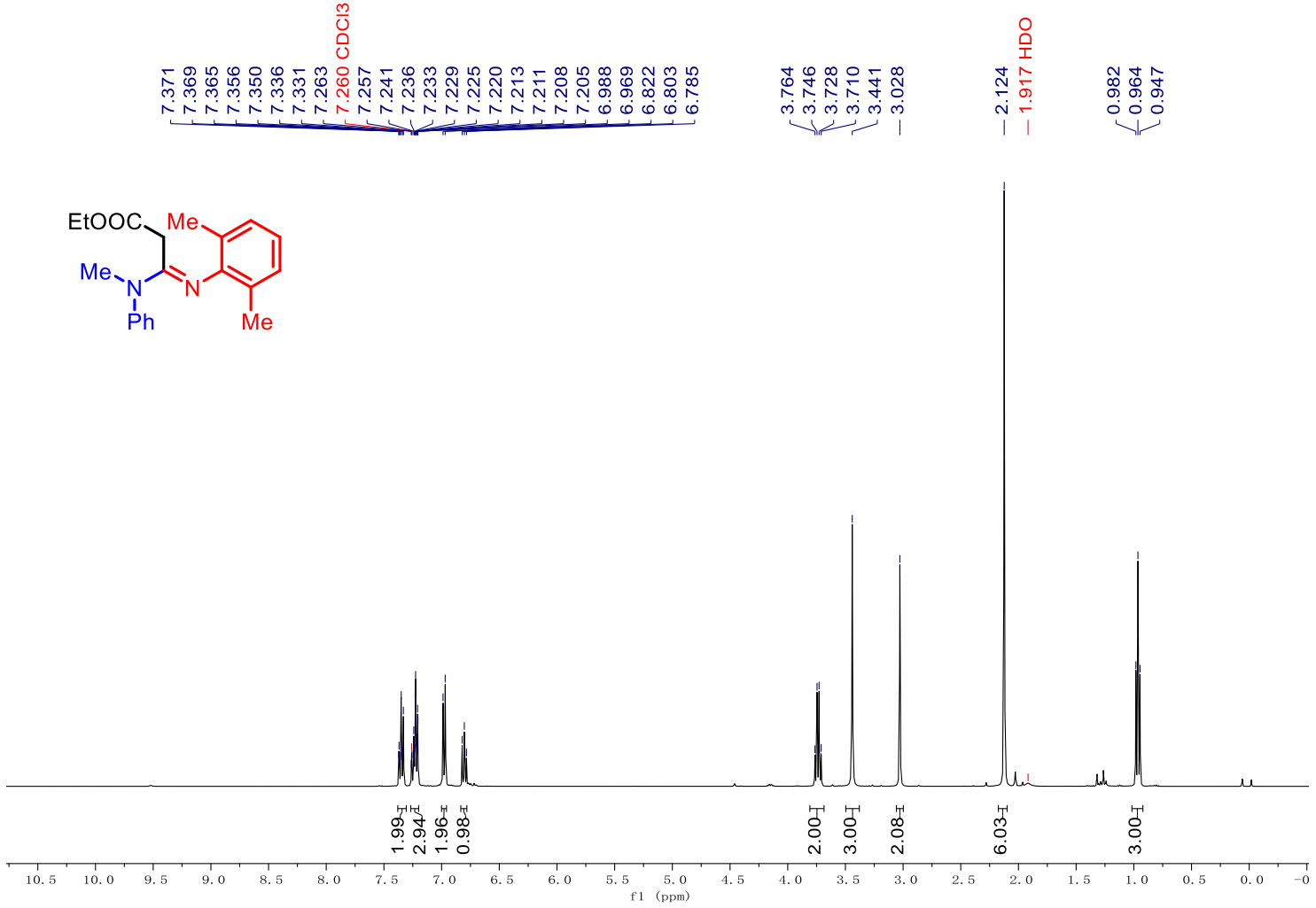
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(phenylimino)-3-((2,4,4-trimethylpentan-2-yl)amino)propanoate 6a (6a/6a' = 12/1)



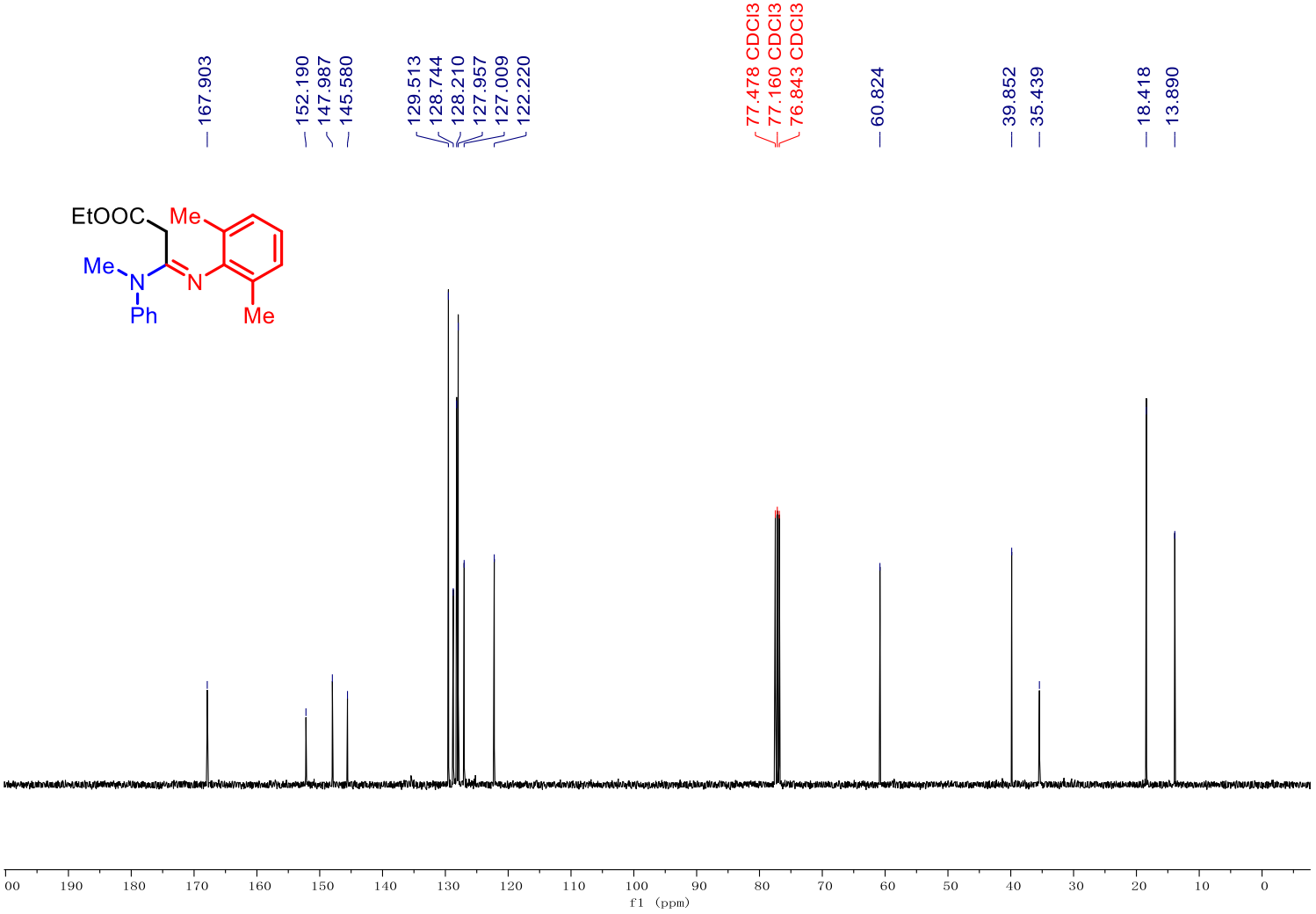
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(phenylimino)-3-((2,4,4-trimethylpentan-2-yl)amino)propanoate 6a (6a/6a' = 12/1)



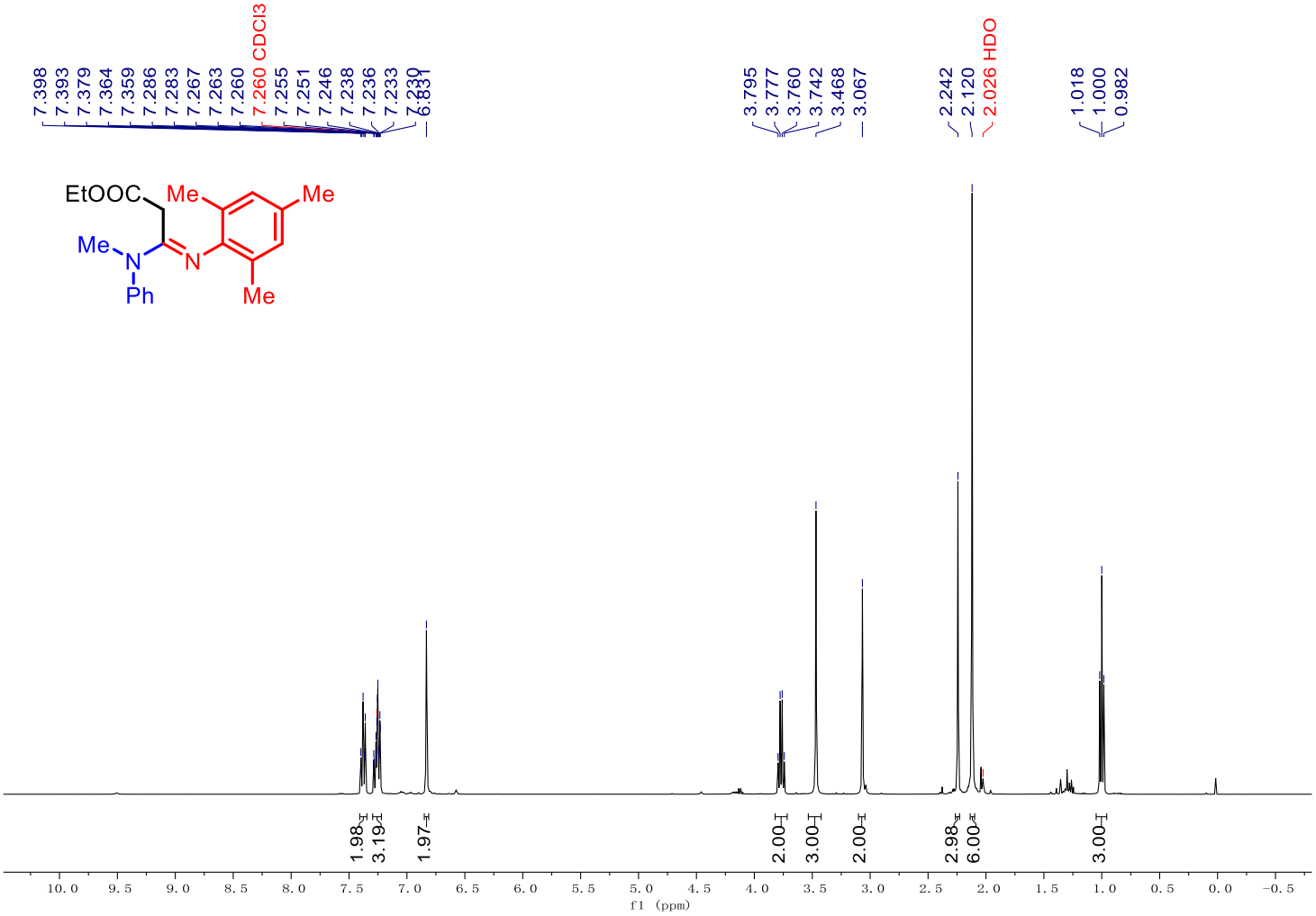
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((2,6-dimethylphenyl)imino)-3-(methyl(phenyl)amino)propanoate 6b



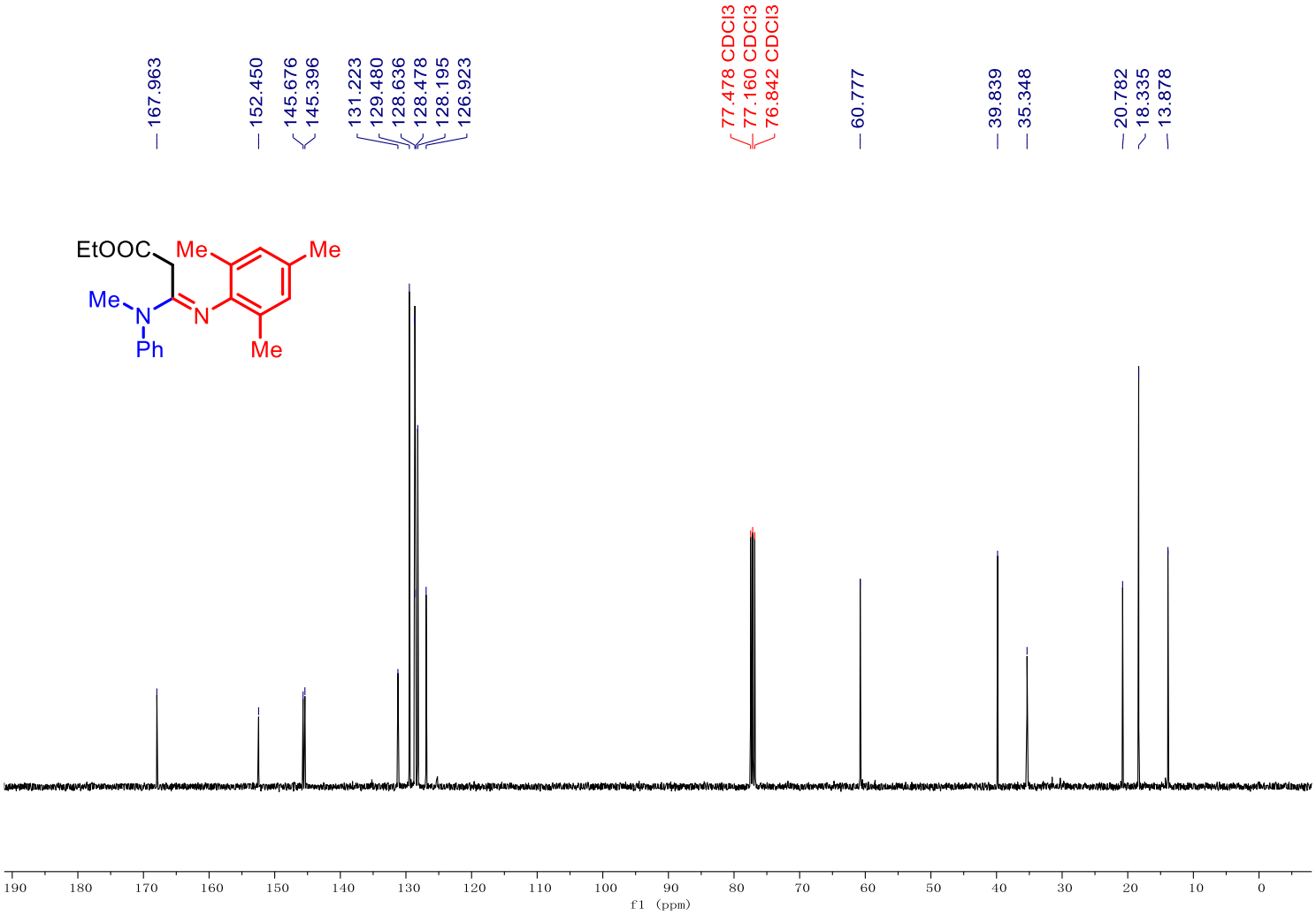
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((2,6-dimethylphenyl)imino)-3-(methyl(phenyl)amino)propanoate 6b



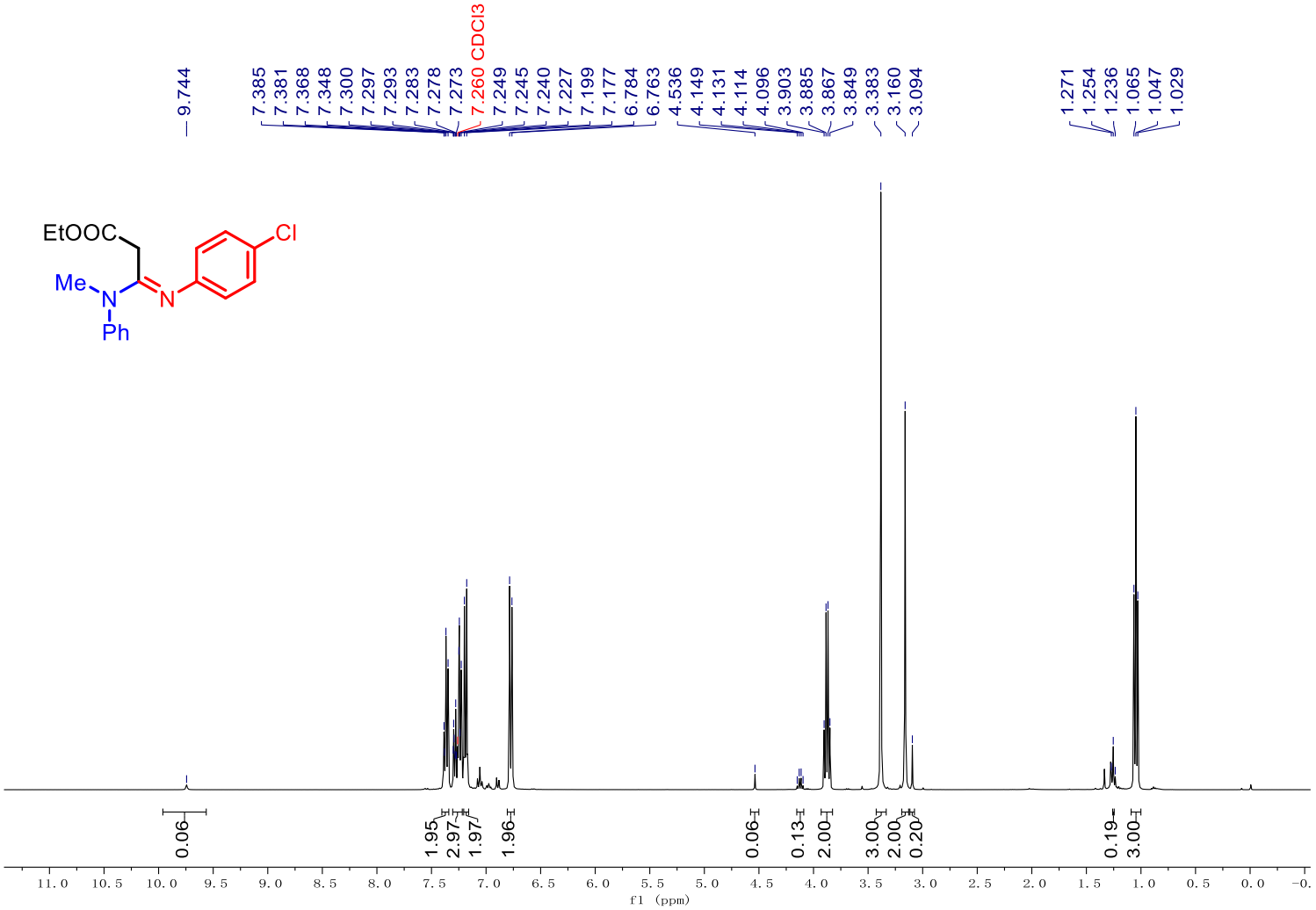
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(mesitylimino)-3-(methyl(phenyl)amino)propanoate 6c



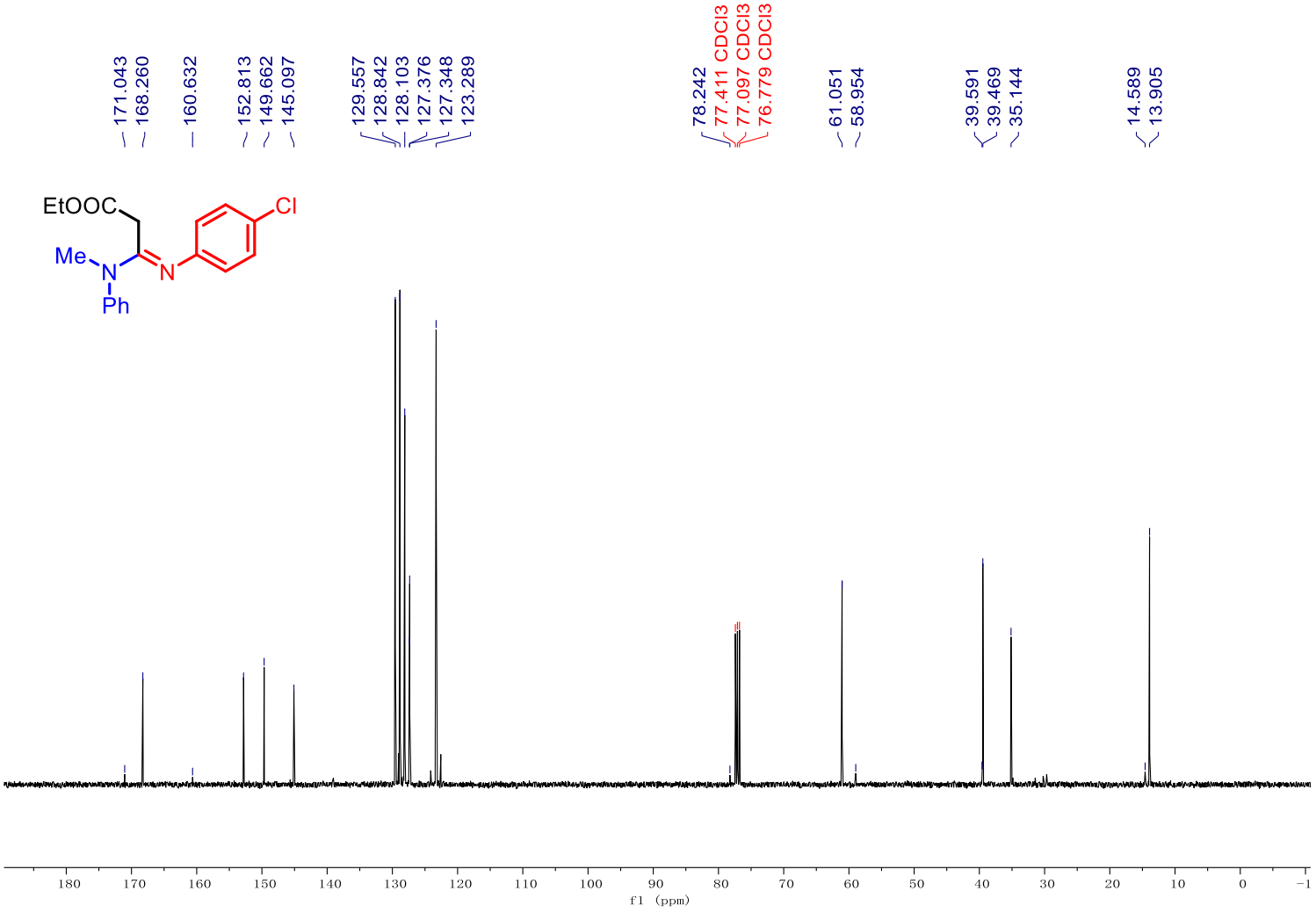
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-(mesitylimino)-3-(methyl(phenyl)amino)propanoate 6c



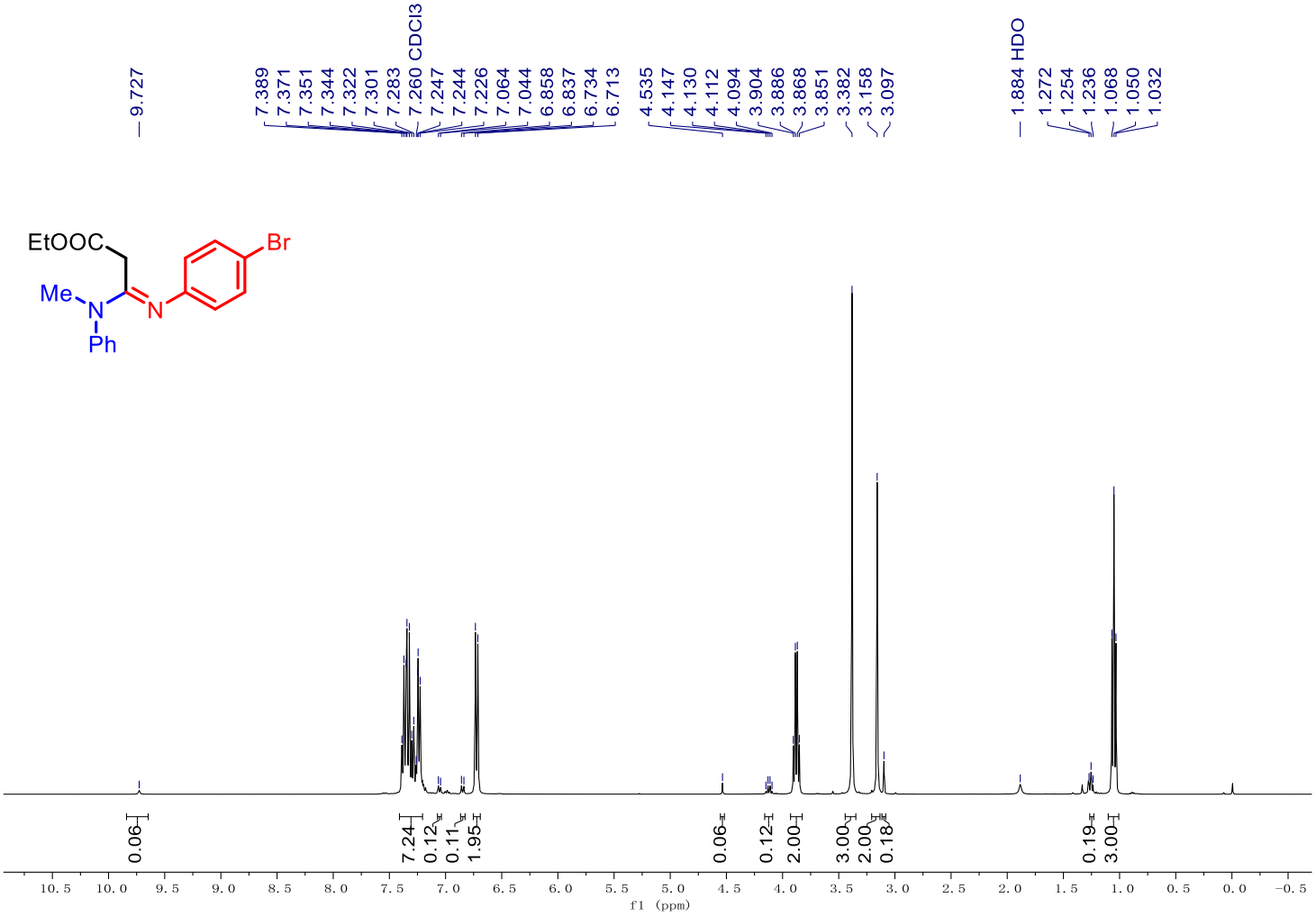
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-chlorophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6d (6d/6d' = 16/1)



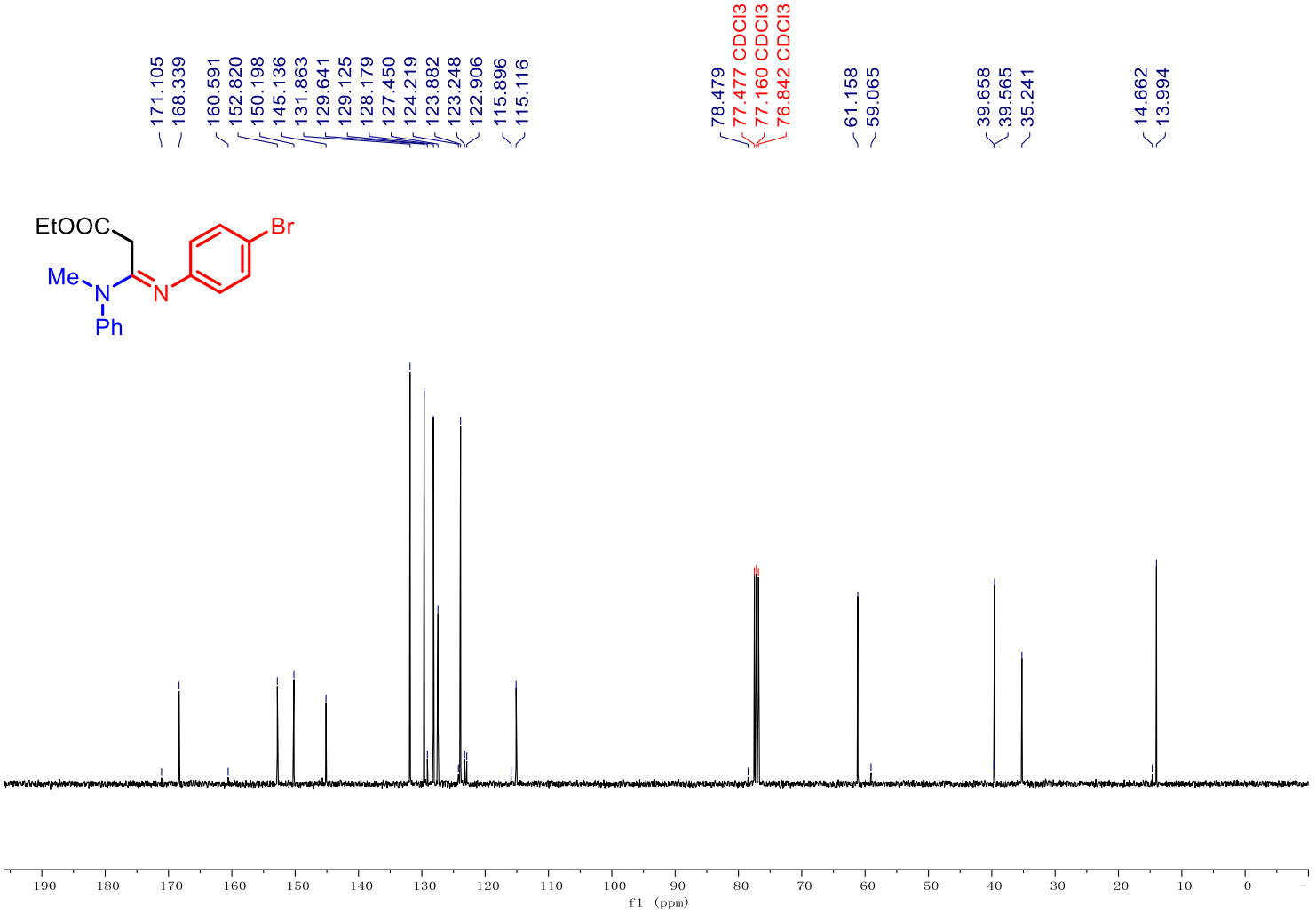
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6e (6e/6e' = 16/1)



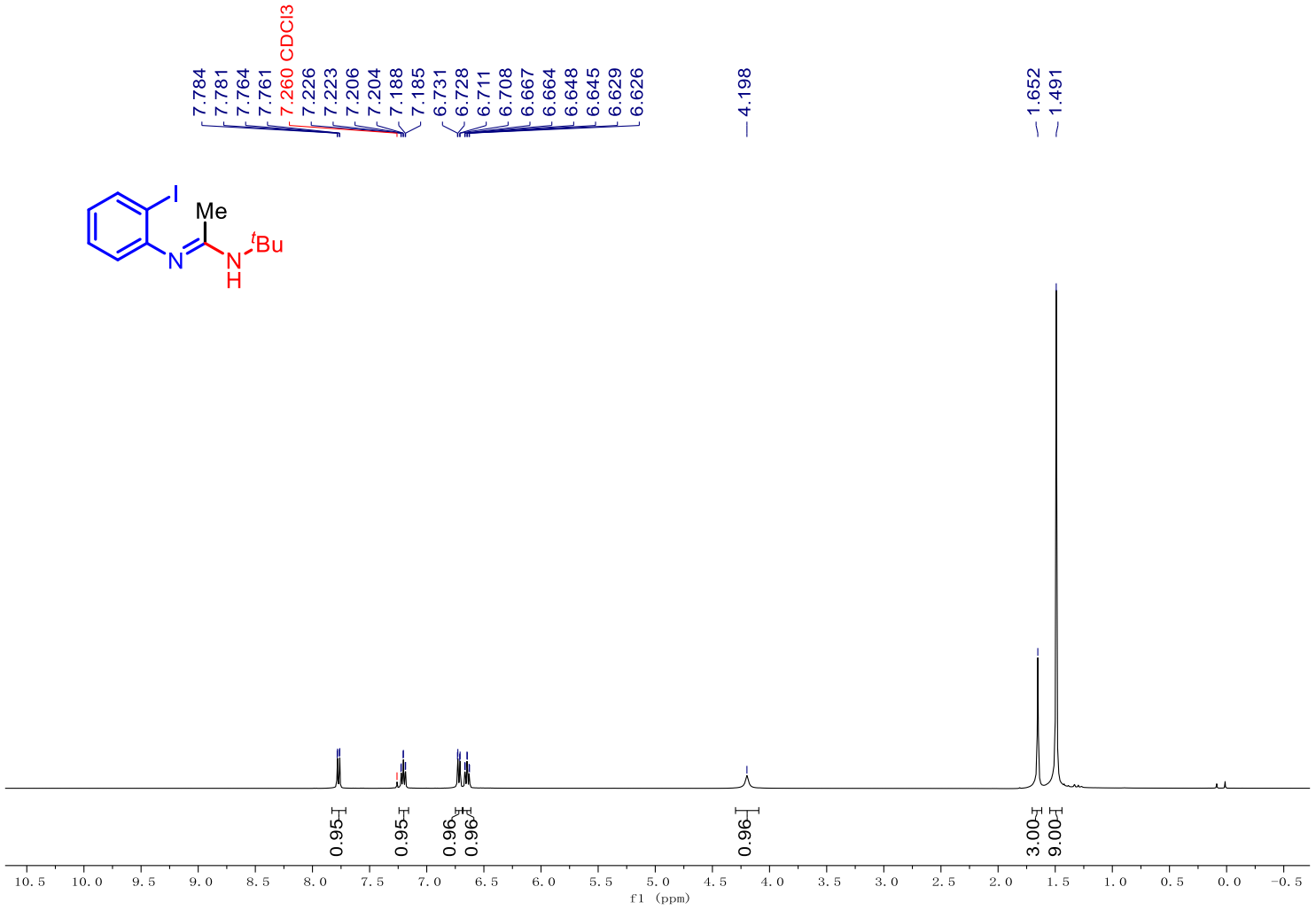
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-bromophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6e (6e/6e' = 16/1)



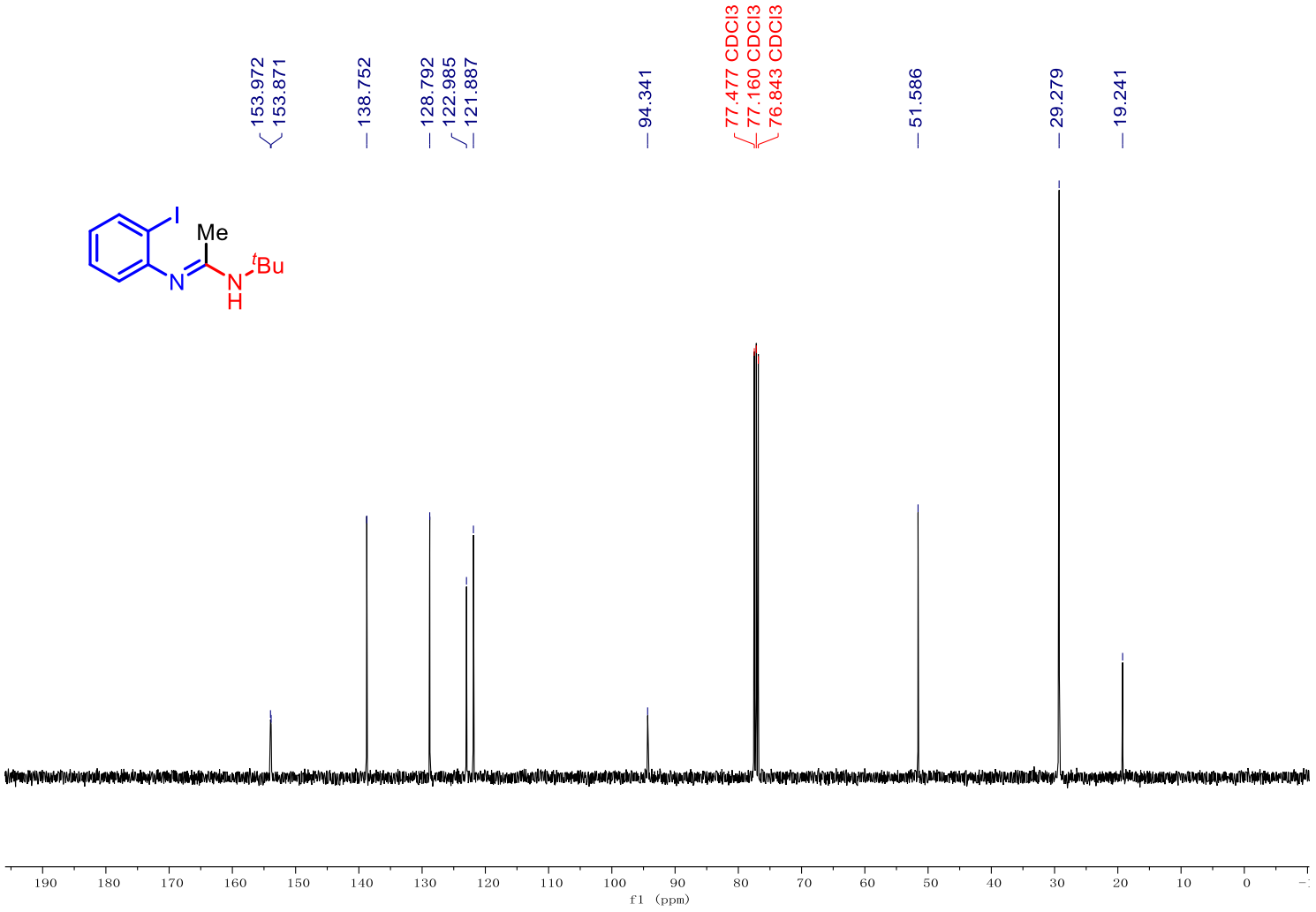
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-Ethyl-3-((4-chlorophenyl)imino)-3-(methyl(phenyl)amino)propanoate 6e (6e/6e' = 16/1)



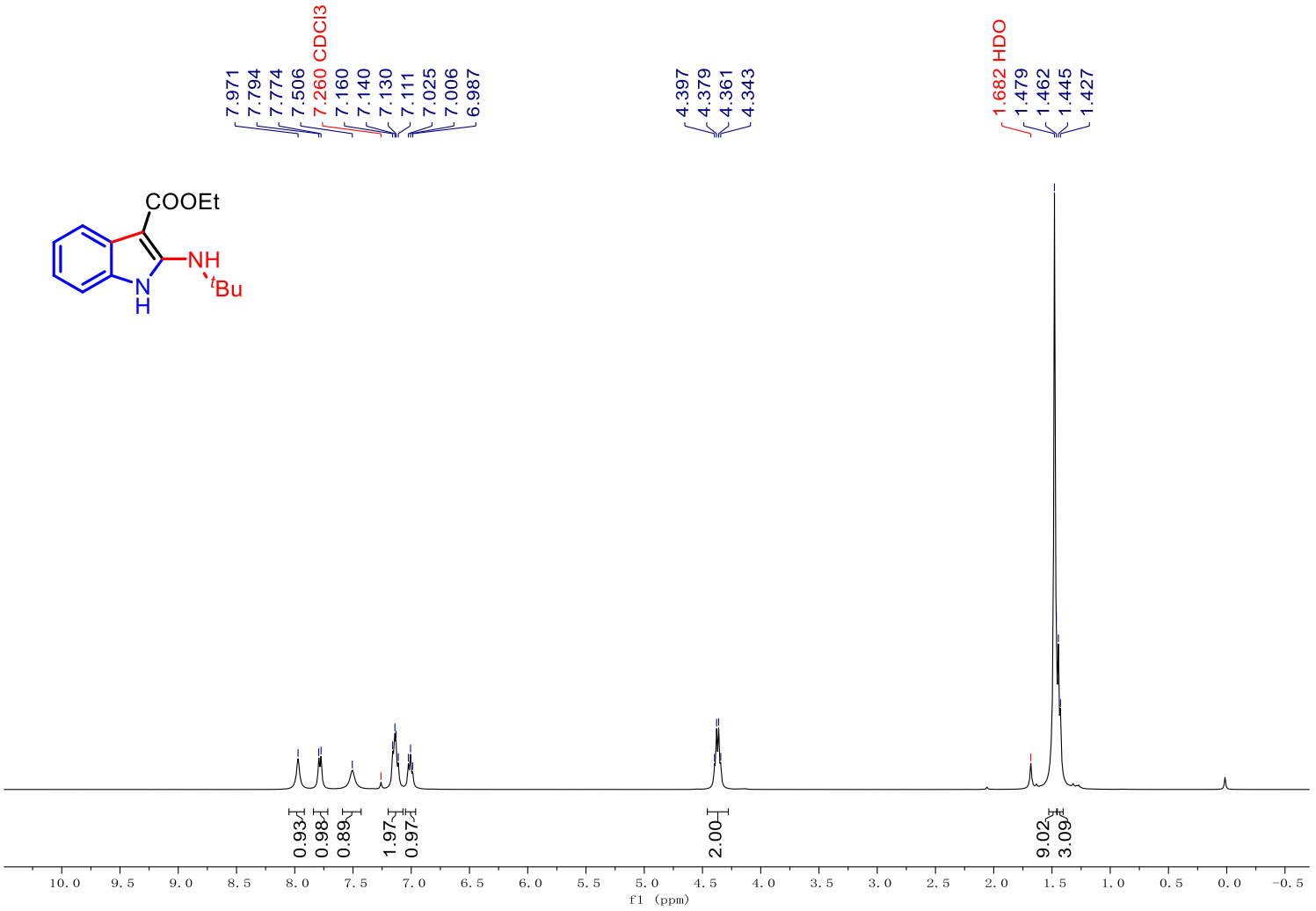
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of (*E*)-*N*-(*tert*-Butyl)-*N'*-(2-iodophenyl)acetimidamide 7



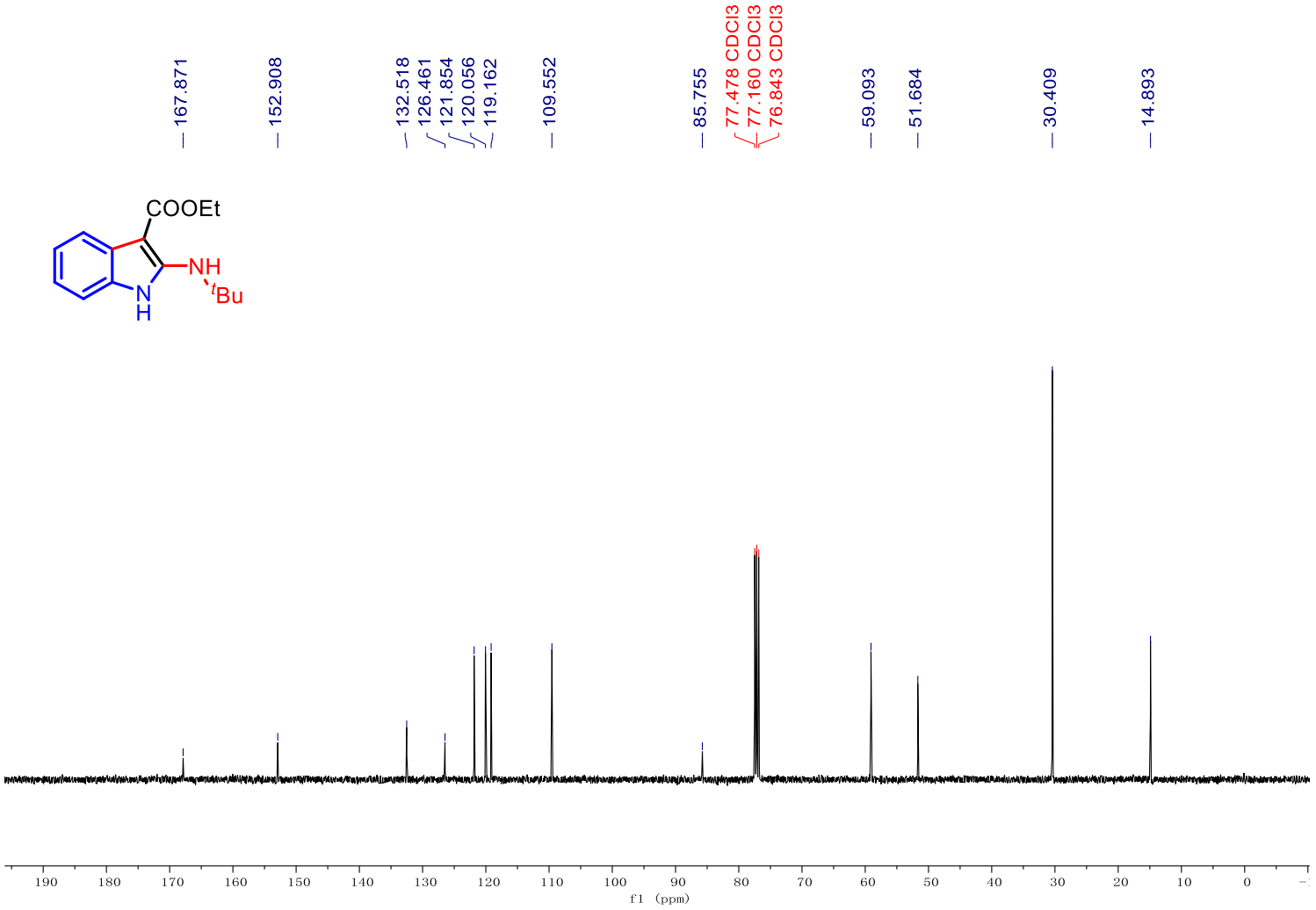
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of (*E*)-*N*-(*tert*-Butyl)-*N'*-(2-iodophenyl)acetimidamide 7



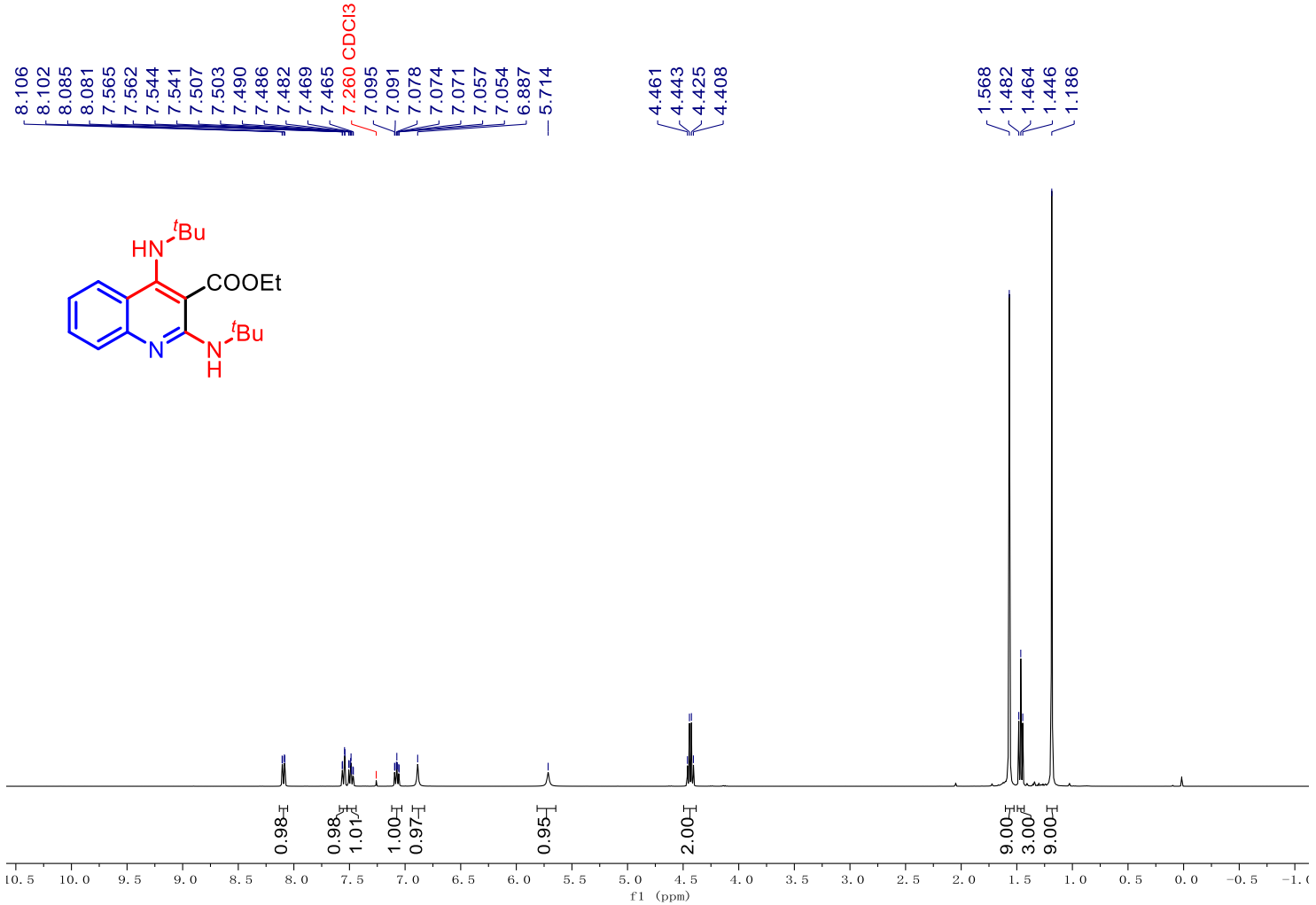
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Ethyl 2-(*tert*-butylamino)-1*H*-indole-3-carboxylate 8



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Ethyl 2-(*tert*-butylamino)-1*H*-indole-3-carboxylate 8



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Ethyl 2,4-bis(*tert*-butylamino)quinoline-3-carboxylate 9



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Ethyl 2,4-bis(*tert*-butylamino)quinoline-3-carboxylate 9