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Catalytic stereospecific allylation of protected hydrazines with enantioenriched primary allylic amines

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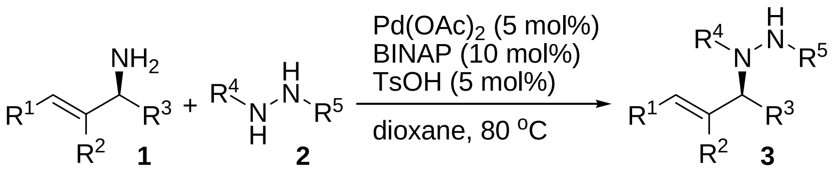
General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump using a Daicel Chiralpak column (AS, AD, 250 x 4.6 mm) with hexane/isopropanol as mobile phase, and the UV detection was monitored at 254 nm or 220 nm. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at $\lambda = 589$ nm and reported as $[\alpha]_D^{T\,^\circ C}$ (c = g/100 mL, solvent). Melting points are uncorrected.

Chiral amines **1a-h** were resolved from the corresponding racemic mixtures with (+)-tartaric acid,[1] and their absolute configuration was assigned by comparison of the optical rotation (or the chiral HPLC trace for the derivative) with that reported in the literature.[1,2] Chiral amines **1i** and **1j** were prepared from amine **1a** according to known procedures.[3] Protected hydrazines **2b-f** were prepared according to literature procedures.[4] The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

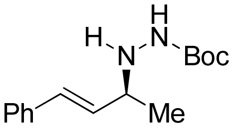
Abbreviations: Ac = acetyl. BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. BINOL = 1,1'-binaphthol. Boc = *N-tert*-butoxycarbonyl. Cbz = benzyloxycarbonyl. Cy = cyclohexyl. dba = dibenzylideneacetone. DME = 1,2-dimethoxyethane. dppb = 1,4-bis(diphenylphosphino)butane. HRMS = high resolution mass spectra. Np = naphthyl. TMEDA = *N,N,N',N'*-tetramethylethylenediamine. Ts = *p*-toluenesulfonyl. Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

General procedure for the stereospecific allylation of protected hydrazines with enantioenriched allylic amines



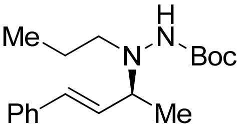
A mixture of amine **1** (0.30 mmol), protected hydrazine **2** (0.36 mmol), $TsOH{\cdot}H_2O$ (2.85 mg, 5 mol%), racemic BINAP (18.7 mg, 10 mol%), and $Pd(OAc)_2$ (3.36 mg, 5 mol%) in dioxane (0.30 mL) was heated under nitrogen at 80 °C for 2 h. The mixture was cooled to room temperature, and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (For **3a-e** and **3m-r**, 1/10; For **3h** and **3i**, 1/5; For **3g**, **3j**, and **3k**, 1/2), to give *N*-allylhydrazine **3**.

Analytical data for the products



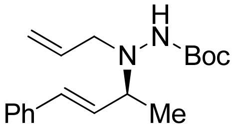
3a

N-Allylhydrazine **3a**, white powder; m.p. 68.6–69.4 °C; $[\alpha]_D^{20}$ = -143 (*c* = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39–7.34 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.19 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.13 (s, br, 1H), 6.06 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.80–3.69 (m, 1H), 1.44 (s, 9H), 1.21 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.8, 136.9, 131.7, 131.5, 128.5, 127.5, 126.4, 80.5, 58.1, 28.3, 19.2; HRMS (ESI) calcd for $C_{15}H_{23}O_2N_2^+$ $(M + H)^+$ 263.1754, found 263.1753. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 13.3 min, t_R (major) = 10.9 min.



3b

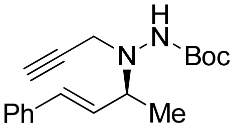
N-Allylhydrazine **3b**, colorless oil; $[\alpha]_D^{20}$ = -167 (*c* = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.35 (m, 2H), 7.34–7.28 (m, 2H), 7.25–7.20 (m, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.29 (s, br, 1H), 3.60–3.45 (m, 1H), 2.76–2.48 (m, 2H), 1.60–1.36 (m, 11H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 155.5, 136.9, 131.8, 130.0, 128.6, 127.6, 126.4, 79.6, 63.4, 57.0, 28.3, 20.5, 18.1, 11.7; HRMS (ESI) calcd for $C_{18}H_{29}O_2N_2^+$ $(M + H)^+$ 305.2224, found 305.2225. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 99:1, flow rate = 0.8 mL/min): t_R (minor) = 9.9 min, t_R (major) = 11.7 min.



3c

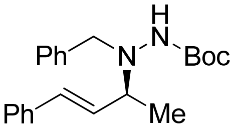
N-Allylhydrazine **3c**, colorless oil; $[\alpha]_D^{20}$ = -61 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.35 (m, 2H), 7.34–7.28 (m, 2H), 7.26–7.20 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.00–5.85 (m, 1H), 5.38 (s, br, 1H), 5.22–5.11 (m, 2H), 3.59–3.46 (m, 1H), 3.47–3.27 (m, 2H), 1.42 (s, 9H), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 155.5, 136.8, 134.2, 132.0, 130.0, 128.6, 127.6, 126.4, 118.5, 79.6, 62.6, 58.3, 28.3, 18.4; HRMS (ESI) calcd for $C_{18}H_{27}O_2N_2^+$

$(M + H)^+$ 303.2067, found 303.2065. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 99:1, flow rate = 1.0 mL/min): t_R (minor) = 19.9 min, t_R (major) = 17.6 min.



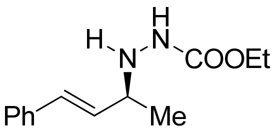
3d

N-Allylhydrazine **3d**, colorless oil; $[\alpha]_D^{20}$ = -50 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.34 (m, 2H), 7.33–7.28 (m, 2H), 7.26–7.20 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.78 (s, br, 1H), 3.78 (d, *J* = 17.6 Hz, 1H), 3.69 (d, *J* = 17.6 Hz, 1H), 3.61–3.44 (m, 1H), 2.32–2.30 (m, 1H), 1.42 (s, 9H), 1.30 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 155.0, 136.7, 131.9, 130.6, 128.6, 127.7, 126.4, 80.1, 74.3, 62.7, 44.7, 28.3, 19.2; HRMS (ESI) calcd for $C_{18}H_{25}O_2N_2^+$ $(M + H)^+$ 301.1911, found 301.1912. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 8.2 min, t_R (major) = 9.8 min.



3e

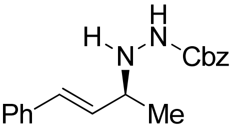
N-Allylhydrazine **3e**, colorless oil; $[\alpha]_D^{20}$ = -39 (*c* = 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.36 (m, 4H), 7.34–7.28 (m, 4H), 7.25–7.21 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.47 (s, br, 1H), 4.07–3.87 (m, 2H), 3.80–3.68 (m, 1H), 1.34 (s, 9H), 1.32 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 155.2, 137.6, 136.9, 132.0, 130.6, 129.3, 128.6, 128.2, 127.6, 127.2, 126.4 , 79.6, 62.0, 58.3, 28.2, 18.7; HRMS (ESI) calcd for $C_{22}H_{29}O_2N_2^+$ $(M + H)^+$ 353.2224, found 353.2224. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 5.2 min, t_R (major) = 7.1 min.



3g

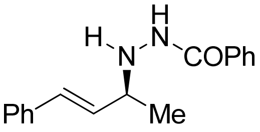
N-Allylhydrazine **3g**, white powder; m.p. 54.5–55.0 °C; $[\alpha]_D^{20}$ = -173 (*c* = 1.13, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.42–7.20 (m, 5H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.17 (s, br, 1H), 6.05 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.15 (m, 2H), 4.03 (s, br, 1H), 3.84–3.68 (m, 1H), 1.30–1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.5, 136.8, 131.9, 131.3, 128.6, 127.6, 126.4, 61.4, 58.2, 19.2, 14.6; HRMS (ESI) calcd for $C_{13}H_{19}O_2N_2^+$

(M + H)$^+$ 235.1441, found 235.1443. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 9.8 min, t_R (major) = 14.5 min.



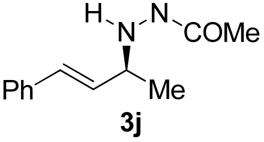
3h

N-Allylhydrazine **3h**, white powder; m.p. 68.6–69.4 °C; $[\alpha]_D^{20}$ = -147 (*c* = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 9H), 7.24–7.20 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.34 (s, br, 1H), 6.04 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.12 (s, 2H), 4.06 (s, br, 1H), 3.80–3.69 (m, 1H), 1.22 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 136.7, 136.1, 132.0, 131.2, 128.6, 128.3, 128.1, 127.6, 126.4, 67.1, 58.2, 19.2; HRMS (ESI) calcd for $C_{18}H_{21}O_2N_2^+$ (M + H)$^+$ 297.1598, found 297.1602. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 22.0 min, t_R (major) = 25.2 min.



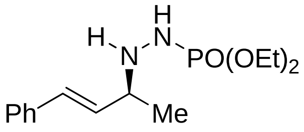
3i

N-Allylhydrazine **3i**, white powder; m.p. 108.7–109.5 °C; $[\alpha]_D^{20}$ = -235 (*c* = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, br, 1H), 7.74–7.69 (m, 2H), 7.51–7.47 (m, 1H), 7.45–7.20 (m, 7H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.22 (s, br, 1H), 3.88–3.77 (m, 1H), 1.31 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 136.7, 132.9, 132.1, 131.9, 131.3, 128.7, 128.6, 127.7, 126.9, 126.4, 58.7, 19.4; HRMS (ESI) calcd for $C_{17}H_{18}ON_2Na^+$ (M + Na)$^+$ 289.1311, found 289.1310. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 92:8, flow rate = 0.8 mL/min): t_R (minor) = 30.6 min, t_R (major) = 26.7 min.



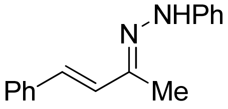
3j

N-Allylhydrazine **3j**,[5] colorless oil; $[\alpha]_D^{20}$ = -201 (*c* = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.33–7.28 (m, 2H), 7.26–7.21 (m, 1H), 7.05 (s, br, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.07 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.06 (s, br, 1H), 3.75–3.64 (m, 1H), 1.94 (s, 3H), 1.24 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 136.7, 131.9, 131.3, 128.6, 127.7, 126.4, 58.5, 21.2, 19.3. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 14.0 min, t_R (major) = 20.5 min.



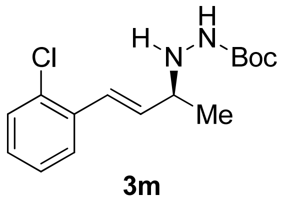
3k

N-Allylhydrazine **3k**, colorless oil; $[\alpha]_D^{20}$ = -64 (*c* = 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 2H), 7.34–7.28 (m, 2H), 7.28–7.21 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.01 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.69 (d, *J* = 28.8 Hz, 1H), 4.20–4.02 (m, 4H), 3.64–3.54 (m, 1H), 1.41–1.21 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.9, 130.2, 128.6, 127.9, 126.4, 63.1 (d, *J* = 5.8 Hz), 63.0 (d, *J* = 5.7 Hz), 59.7 (d, *J* = 4.6 Hz), 18.9, 16.3 (d, *J* = 4.4 Hz), 16.2 (d, *J* = 4.4 Hz); HRMS (ESI) calcd for $C_{14}H_{24}O_3N_2P^+$ $(M + H)^+$ 299.1519, found 299.1519. The ee was determined to be 94% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 22.7 min, t_R (major) = 31.0 min.



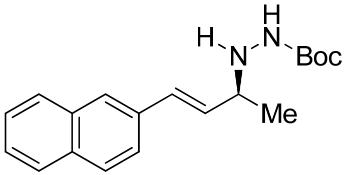
4a

Hydrazone **4a**,[6] white powder; m.p. 156.1–157.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.39–7.32 (m, 3H), 7.31–7.26 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.92–6.84 (m, 1H), 6.74 (d, *J* = 16.4 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.0, 137.2, 130.0, 129.3, 129.2, 128.7, 127.6, 126.5, 120.4, 113.2, 10.1.



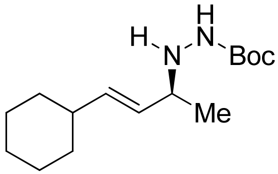
3m

N-Allylhydrazine **3m**, colorless oil; $[\alpha]_D^{20}$ = -156 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 1H), 7.36–7.32 (m, 1H), 7.24–7.13 (m, 2H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.83–3.73 (m, 1H), 1.45 (s, 9H), 1.23 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 135.0, 134.4, 133.0, 129.6, 128.5, 127.8, 126.9, 126.8, 80.5, 58.2, 28.3, 19.1; HRMS (ESI) calcd for $C_{15}H_{22}O_2N_2Cl$ $(M + H)^+$ 297.1364, found 297.1367. The ee was determined to be 96% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 0.7 mL/min): t_R (minor) = 14.7 min, t_R (major) = 13.3 min.



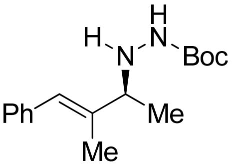
3n

N-Allylhydrazine **3n**, white powder; m.p. 111.5–112.3 °C; $[\alpha]_D^{20}$ = -178 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3H), 7.71 (s, 1H), 7.61–7.57 (m, 1H), 7.48–7.39 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.08 (s, br, 1H), 3.83–3.73 (m, 1H), 1.45 (s, 9H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 134.4, 133.6, 133.0, 132.0, 131.7, 128.2, 127.9, 127.6, 126.3, 126.2, 125.8, 123.6, 80.5, 58.3, 28.3, 19.2; HRMS (ESI) calcd for $C_{19}H_{25}O_2N_2^+$ $(M + H)^+$ 313.1911, found 313.1911. The ee was determined to be 90% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 12.9 min, t_R (major) = 10.7 min.



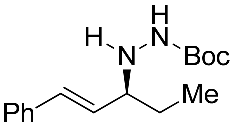
3o

N-Allylhydrazine **3o**, white powder; m.p. 54.3–55.1 °C; $[\alpha]_D^{20}$ = -68 (*c* = 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, br, 1H), 5.55 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.22 (ddd, *J* = 15.6, 8.0, 1.2 Hz, 1H), 3.87 (s, br, 1H), 3.53–3.44 (m, 1H), 1.98–1.85 (m, 1H), 1.78–1.59 (m, 6H), 1.48 (s, 9H), 1.31–1.10 (m, 4H), 1.08 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 139.3, 128.9, 80.3, 57.7, 40.4, 32.9, 28.4, 26.2, 26.0, 19.2; HRMS (ESI) calcd for $C_{15}H_{29}O_2N_2^+$ $(M + H)^+$ 269.2224, found 269.2220. The ee was determined to be 97% by HPLC analysis (Chiralpak AD, λ = 220 nm, hexane/isopropanol = 97:3, flow rate = 0.7 mL/min): t_R (minor) = 35.9 min, t_R (major) = 33.1 min.



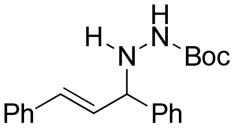
3p

N-Allylhydrazine **3p**, white powder; m.p. 43.6–44.3 °C; $[\alpha]_D^{20}$ = -107 (*c* = 0.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 4H), 7.23–7.18(m, 1H), 6.45 (s, 1H), 5.98 (s, br, 1H), 3.75–3.66 (m, 1H), 1.85 (d, *J* = 1.2 Hz, 3H), 1.46 (s, 9H), 1.20 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 , 139.0, 137.8, 129.0, 128.1, 127.2, 126.3, 80.4, 63.0, 28.4, 17.8, 13.4; HRMS (ESI) calcd for $C_{16}H_{25}O_2N_2^+$ $(M + H)^+$ 277.1911, found 277.1914. The ee was determined to be 96% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 5.2 min, t_R (major) = 6.0 min.



3q

N-Allylhydrazine **3q**, colorless oil; $[\alpha]_D^{20}$ = -159 (*c* = 1.01, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.33–7.28 (m, 2H), 7.25–7.20 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.99 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.55–3.43 (m, 1H), 1.69–1.58 (m, 1H), 1.51–1.37 (m, 10H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 136.9, 133.1, 130.3, 128.5, 127.5, 126.4, 80.4, 64.8, 28.4, 26.2, 10.2; HRMS (ESI) calcd for $C_{16}H_{25}O_2N_2^+$ $(M + H)^+$ 277.1911, found 277.1910. The ee was determined to be 99% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 12.7 min, t_R (major) = 11.1 min.



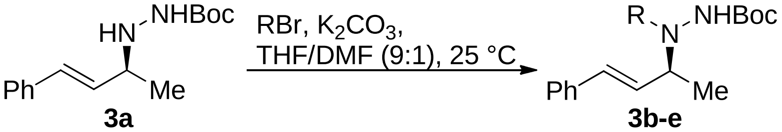
3r

N-Allylhydrazine **3r**, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.38–7.33 (m, 4H), 7.32–7.19 (m, 4H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 15.6, 8.0 Hz, 1H), 6.05 (s, br, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 140.6, 136.7, 132.4 129.6, 128.7, 128.5 127.8, 127.7, 126.5, 80.6, 66.8, 28.3; HRMS (ESI) calcd for $C_{20}H_{24}O_2N_2Na^+$ $(M + Na)^+$ 347.1730, found 347.1726.

Assignment of the absolute configuration

The absolute configuration of compound **3i** was assigned to be *S* by single-crystal X-ray analysis (CCDC 997538) and that of compounds **3a-e**, **3g**, **3h**, **3j**, and **3k** was assigned by correlation with compound **3i** (see below). The absolute configuration of the rest of products was assigned by analogy. Shown below are the methods used for the transformations of compound **3a**.

(a) *N*-Alkylation

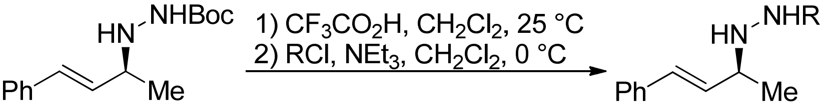


Entry	3	R	Yield (%)
1	**3b**	propyl	45

2	**3c**	allyl	51
3	**3d**	propargyl	90
4	**3e**	benzyl	45

A mixture of compound **3a** (78.7 mg, 0.30 mmol), RBr (0.60 mmol), and K_2CO_3 (41.4 mg, 0.30 mmol) in THF/DMF (1.0 mL) at room temperature was stirred for 24 h. The mixture was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give compound **3b-e**.

(b) Removal of the Boc group followed by protection



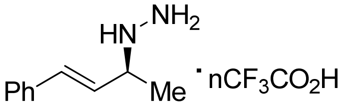
3a **3g-k**

Entry	3	R	Yield (%)
1	**3g**	CO_2Et	35
2	**3h**	Cbz	45
3	**3i**	COPh	77
4	**3j**	COMe	30
5	**3k**	$PO(OEt)_2$	38

Trifluoroacetic acid (342 mg, 0.22 mL, 3.0 mmol) was added slowly to a solution of compound **3a** (78.7 mg, 0.30 mmol) in dichloromethane (3.0 mL) at room temperature. The mixture was stirred for 2 h, and evaporated under reduced pressure to give a hydrazine in its trifluoroacetic acid salt. The salt was taken into dichloromethane (1.0 mL), then triethylamine (91.9 mg, 0.13 mL, 0.90 mmol) and RCl (0.45 mmol) were added in sequence at 0 °C. The mixture was stirred for 30 min and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:2), to give compound **3g-k**.

Transformations of *N*-allylhydrazines

(a) As shown by the above procedure, the removal of the Boc group from compound **3a** with trifluoroacetic acid gave salt **5a**.



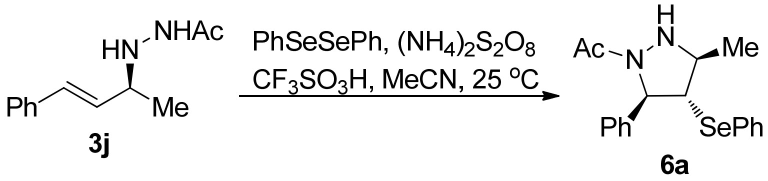
5a

Salt **5a**, colorless oil. $[\alpha]_D^{20}$ = -106 (c = 1.03, H_2O); ^1H NMR (400 MHz, D_2O) δ 7.42 (d, J = 7.2 Hz, 2H), 7.35–7.24 (m, 3H), 6.74 (d, J = 16.0 Hz, 1H), 6.06 (dd, J =

16.0, 8.4 Hz, 1H), 3.94–3.85 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ 137.3, 135.4, 128.9, 126.8, 123.1, 59.9, 15.9; HRMS (ESI) calcd for $C_{10}H_{15}N_2^+$ 163.1230, found 163.1229.

(b) For the proparglation of compound **3a**, see the above procedure.

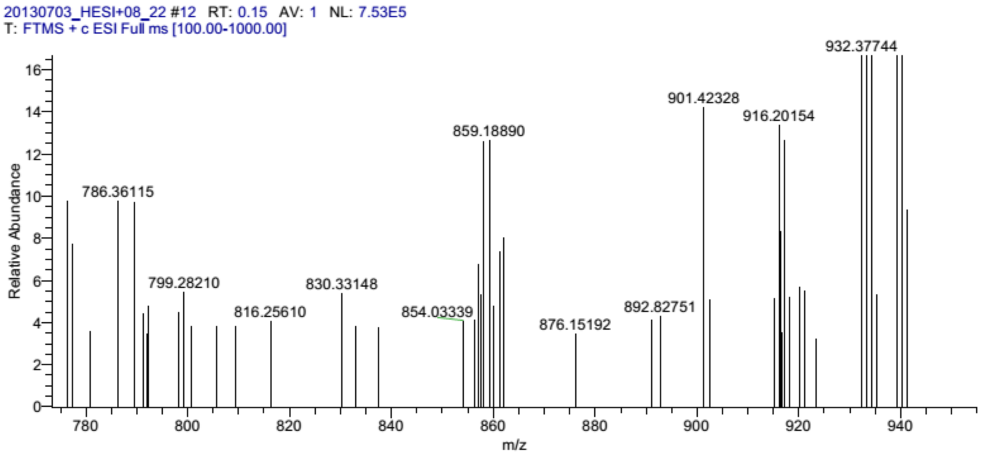
(c) Synthesis of tetrahydropyrazole **6a**

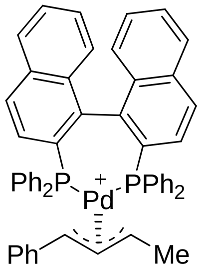


A solution of diphenyl diselenide (93.6 mg, 0.30 mmol), ammonium persulfate (82.2 mg, 0.36 mmol), and trifluoromethanesulfonic acid (49.5 mg, 29 μL, 0.33 mmol) in acetonitrile (0.30 mL) was stirred at room temperature for 15 min. Compound **3j** (61.2 mg, 0.30 mmol) was added, and the mixture was stirred at room temperature for 1 h. The mixture was poured into a 10% aqueous solution of sodium carbonate (10 mL) and extracted with dichloromethane (3 x 10 mL). The organic layer was dried with sodium sulfate, evaporated, and the residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:2), to give tetrahydropyrazole **6a** (81.9 mg, 76%) as a white solid.[5] m.p. 51.2–51.7 °C; $[\alpha]_D^{20}$ = -121 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.36–7.21 (m, 8H), 5.19 (d, *J* = 8.0 Hz, 1H), 4.00 (d, *J* = 12.8 Hz, 1H), 3.18–3.08 (m, 1H), 3.01 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.18 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 140.8, 135.9, 129.3, 128.7, 128.6, 127.5, 126.9, 125.8, 67.3, 62.7, 58.0, 21.5, 15.0. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 220 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 17.3 min, t_R (major) = 21.7 min.

ESI-MS analysis of the reaction mixture

A mixture of amine **1a** (44.2 mg, 0.30 mmol), protected hydrazine **2a** (47.6 mg, 0.36 mmol), $TsOH{\cdot}H_2O$ (2.85 mg, 5 mol%), racemic BINAP (18.7 mg, 10 mol%), and $Pd(OAc)_2$ (3.37 mg, 5 mol%) in dioxane (0.30 mL) was heated under nitrogen at 80 °C for 20 min. The mixture was cooled to room temperature, and subjected to ESI-MS analysis. Copied below is the ESI-MS spectrum we obtained. The following species was tentatively assigned according to the high resolution mass data.





8a

π-Allylpalladium **8a**: HRMS (ESI) calcd for $C_{54}H_{43}P_2Pd^+$ 859.18693, found 859.18890.

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4. For the preparation of compounds **2b** and **2e**, see: (*a*) Z. Zhang, M. Wang, X. Yao, Y. Li, J. Tan, L. Wang, W. Qiao, Y. Geng, Y. Liu and Q. Wang, *Eur. J. Med. Chem.*, 2012, **54**, 33. For the preparation of compound **2c**, see: (*b*) U. Mäeorg and A. Bredihhin, *Org. Lett.*, 2007, **9**, 4975. For the preparation of compound **2d**, see: (*c*) T. M. Bare, D. G. Brown, C. L. Horchler, M. Murphy, R. A. Urbanek, V. Alford, C. Barlaam, M. C. Dyroff, J. B. Empfield, J. M. Forst, K. J. Herzog, R. A. Keith, A. S. Kirschner, C.-M. C. Lee, J. Lewis, F. M. McLaren, K. L. Neilson, G. B. Steelman, S. Trivedi, E. P. Vacek and W. Xiao, *J. Med. Chem.*, 2007, **50**, 3113. For the preparation of compound **2f**, see: (*d*) A. Bredihhin and U. Mäeorg, *Tetrahedron*, 2008, **64**, 6788.
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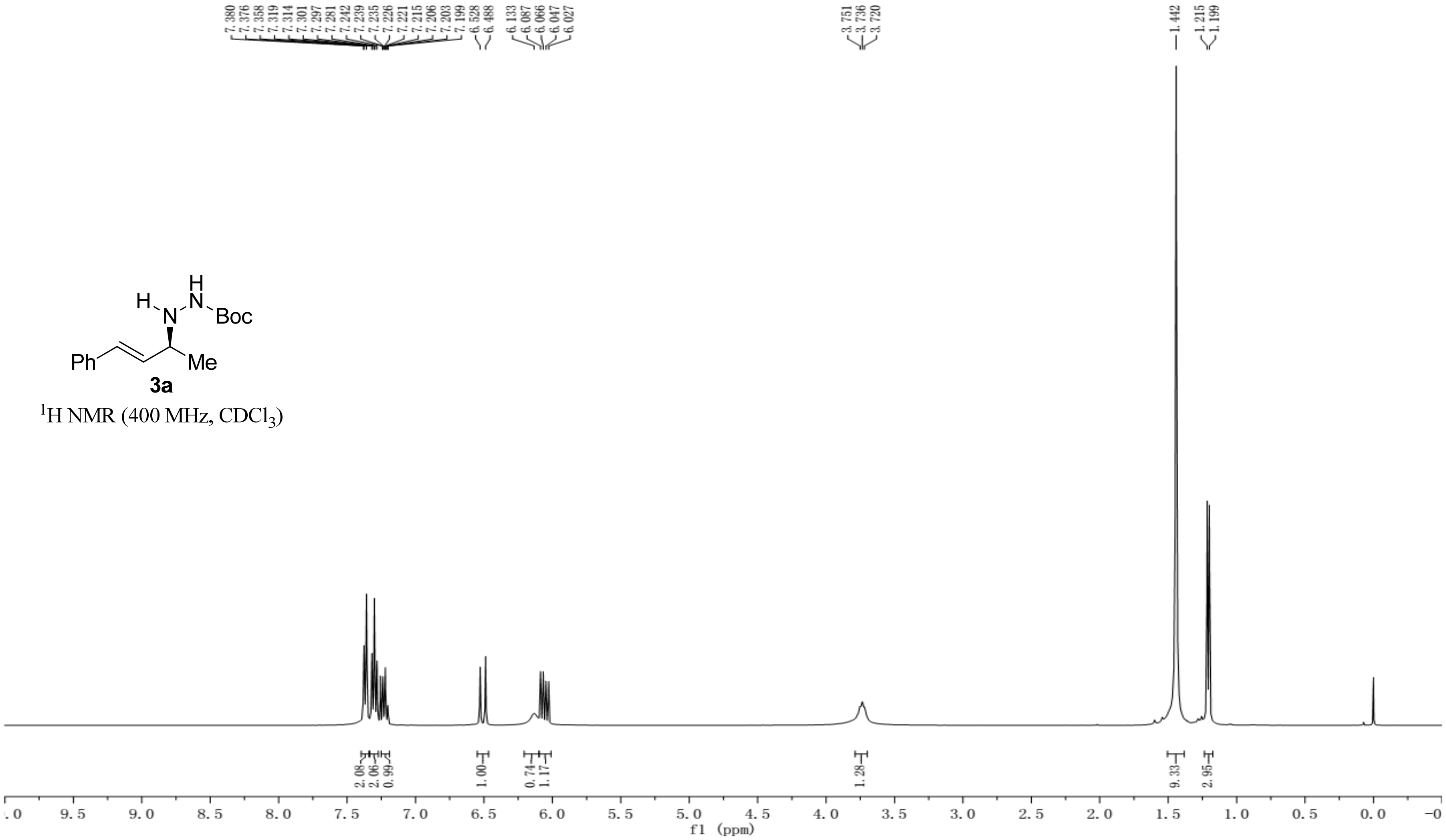
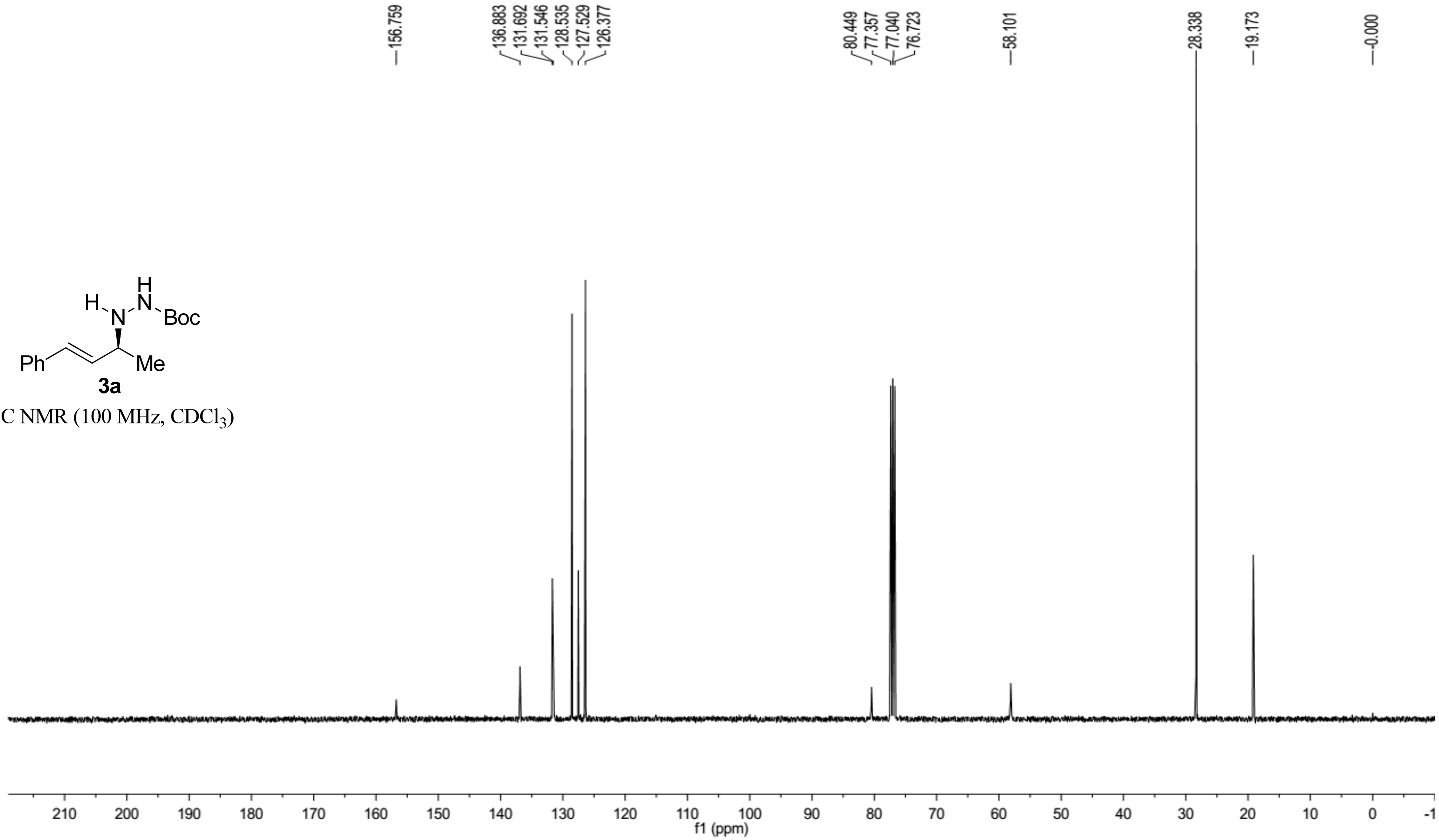


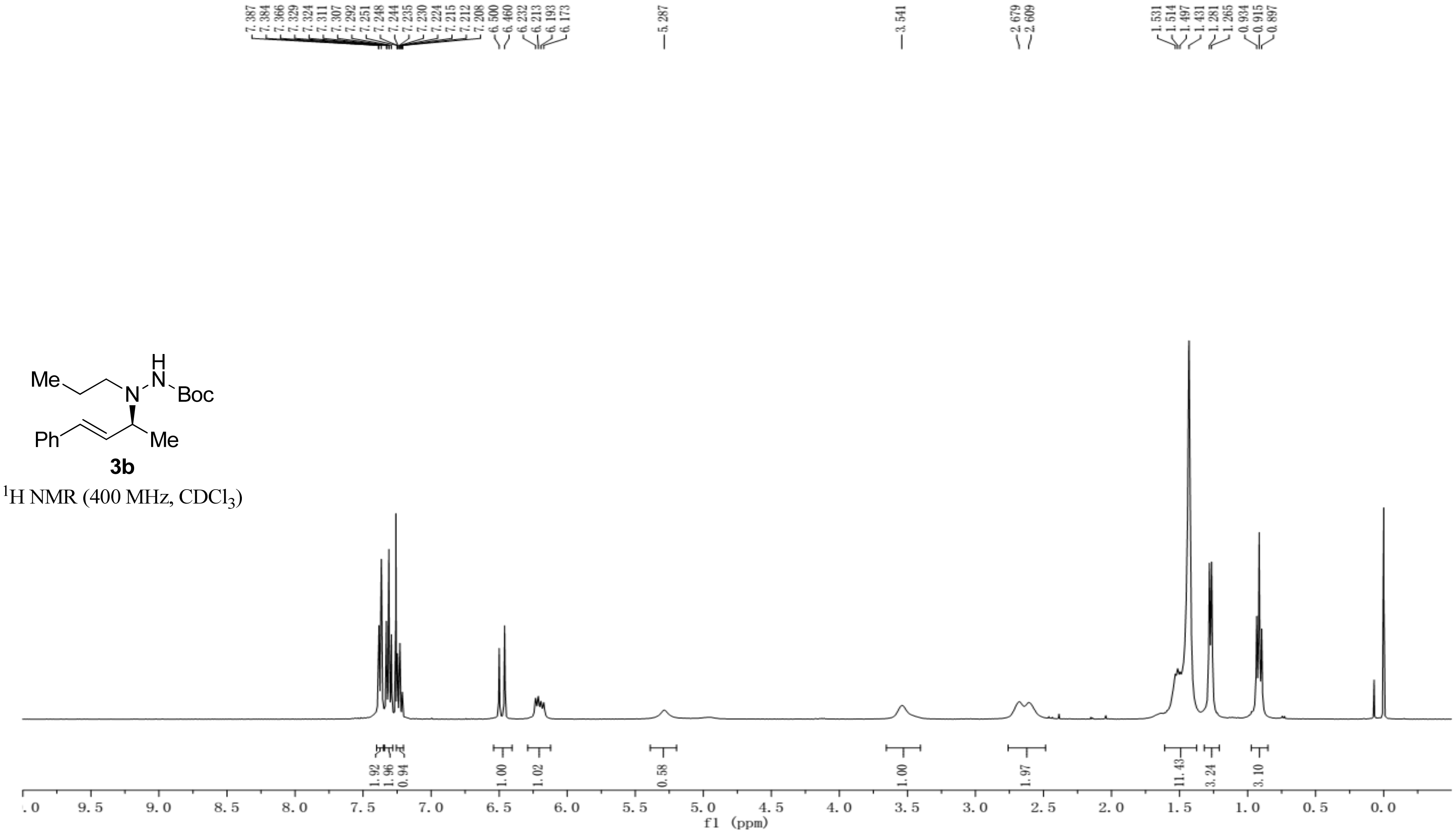
3a

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



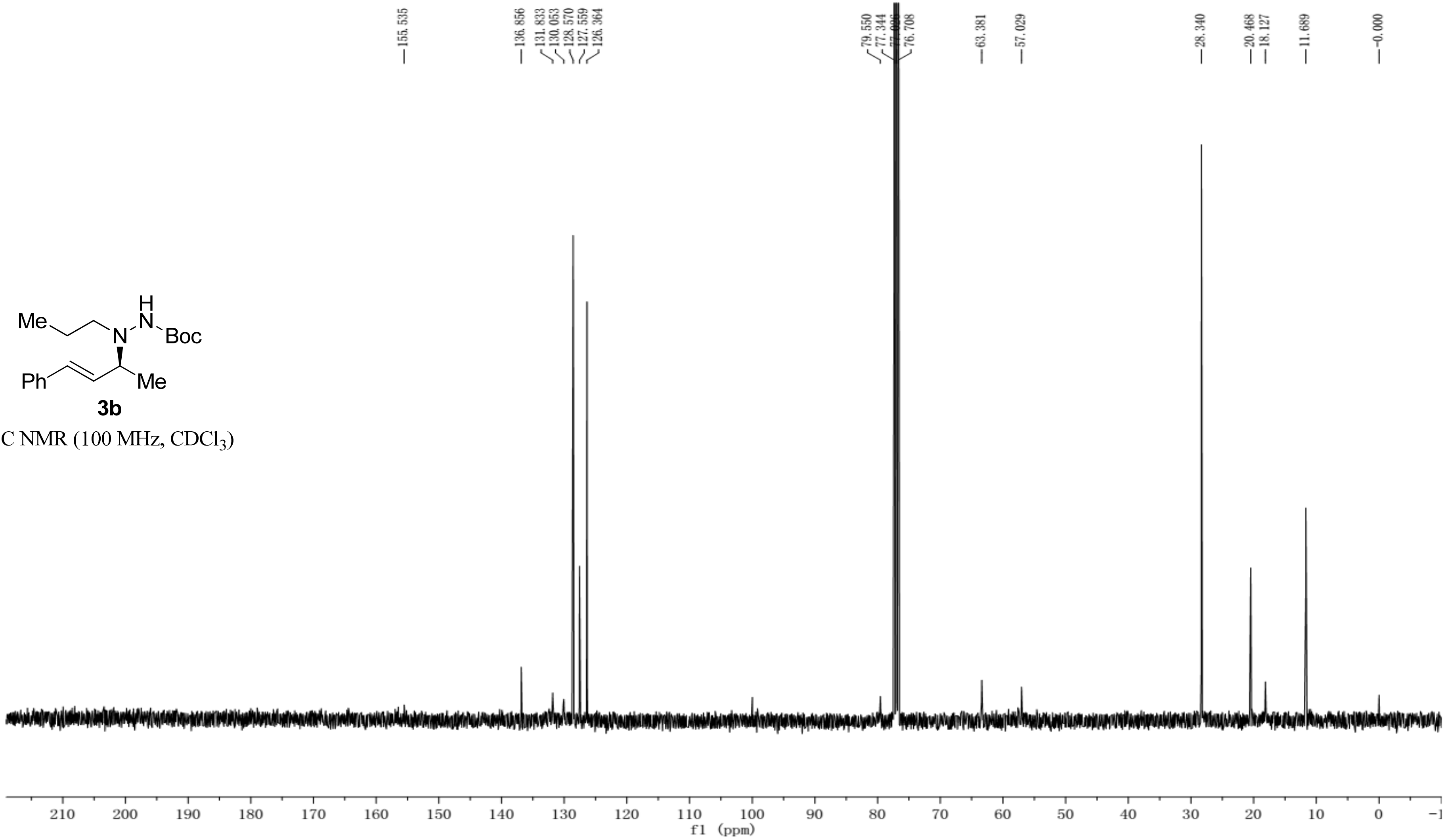
3a

^{13}C NMR (100 MHz, $CDCl_3$)



3b

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



3b

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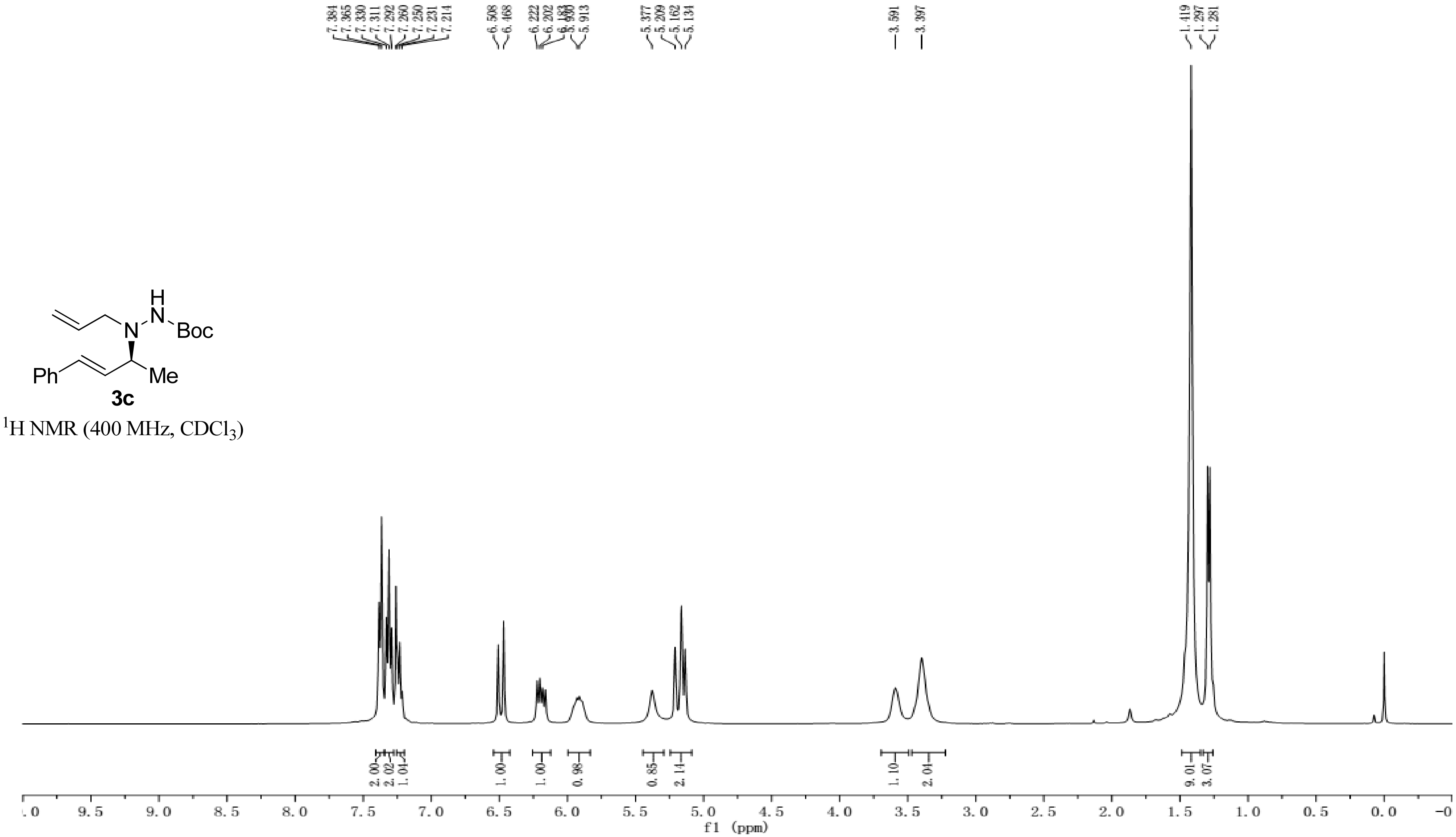

3c

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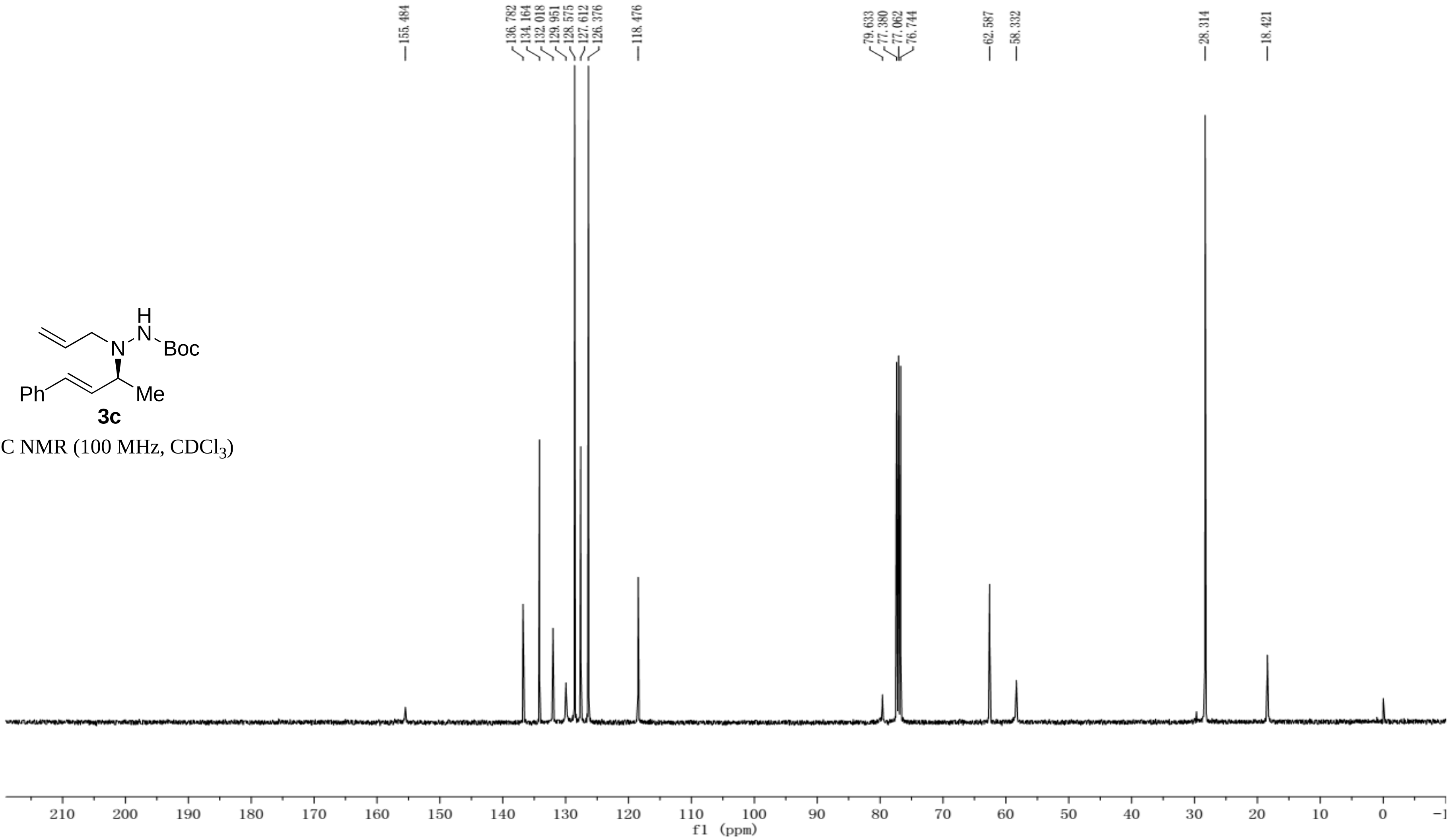

3c

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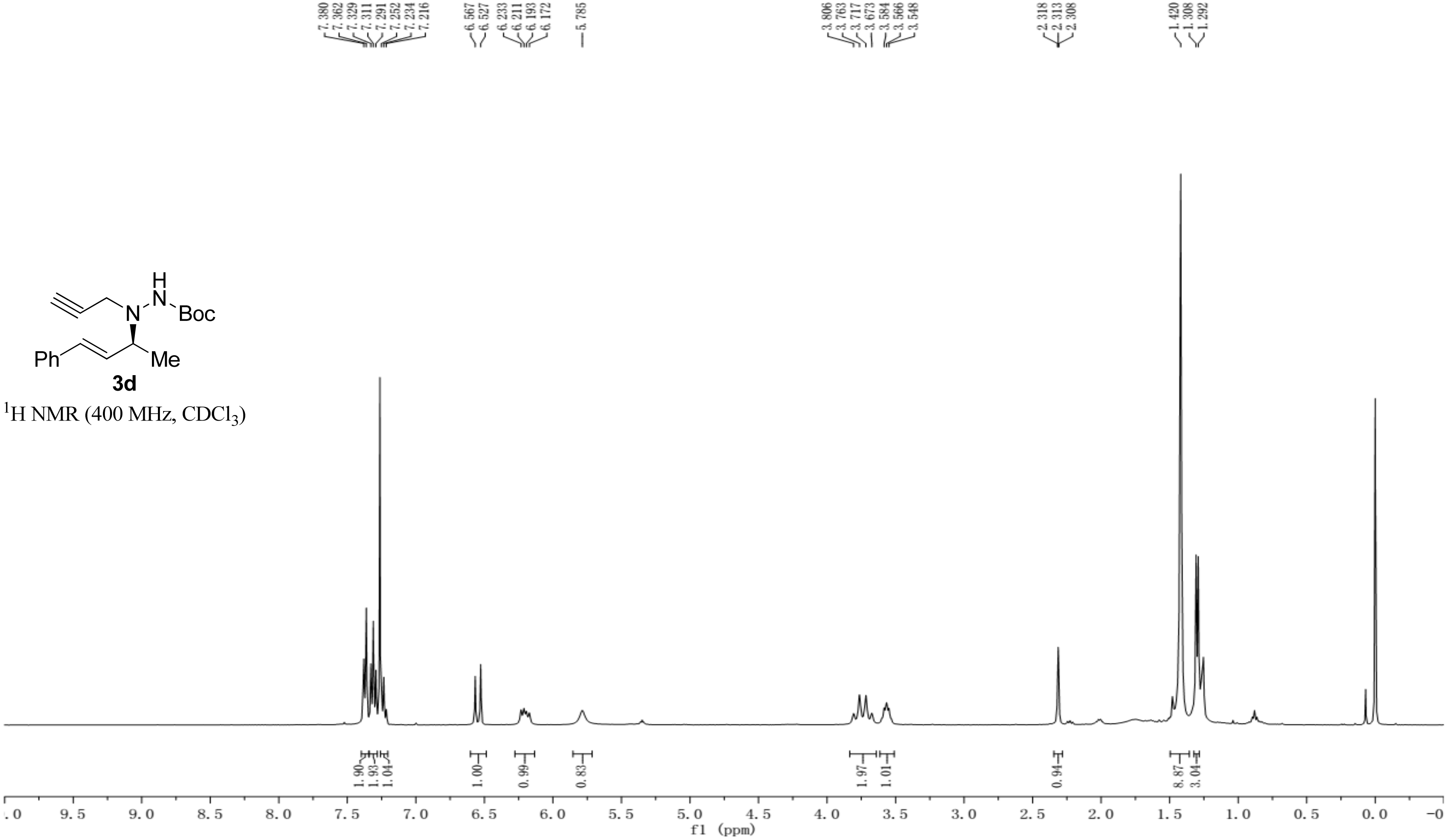

3d

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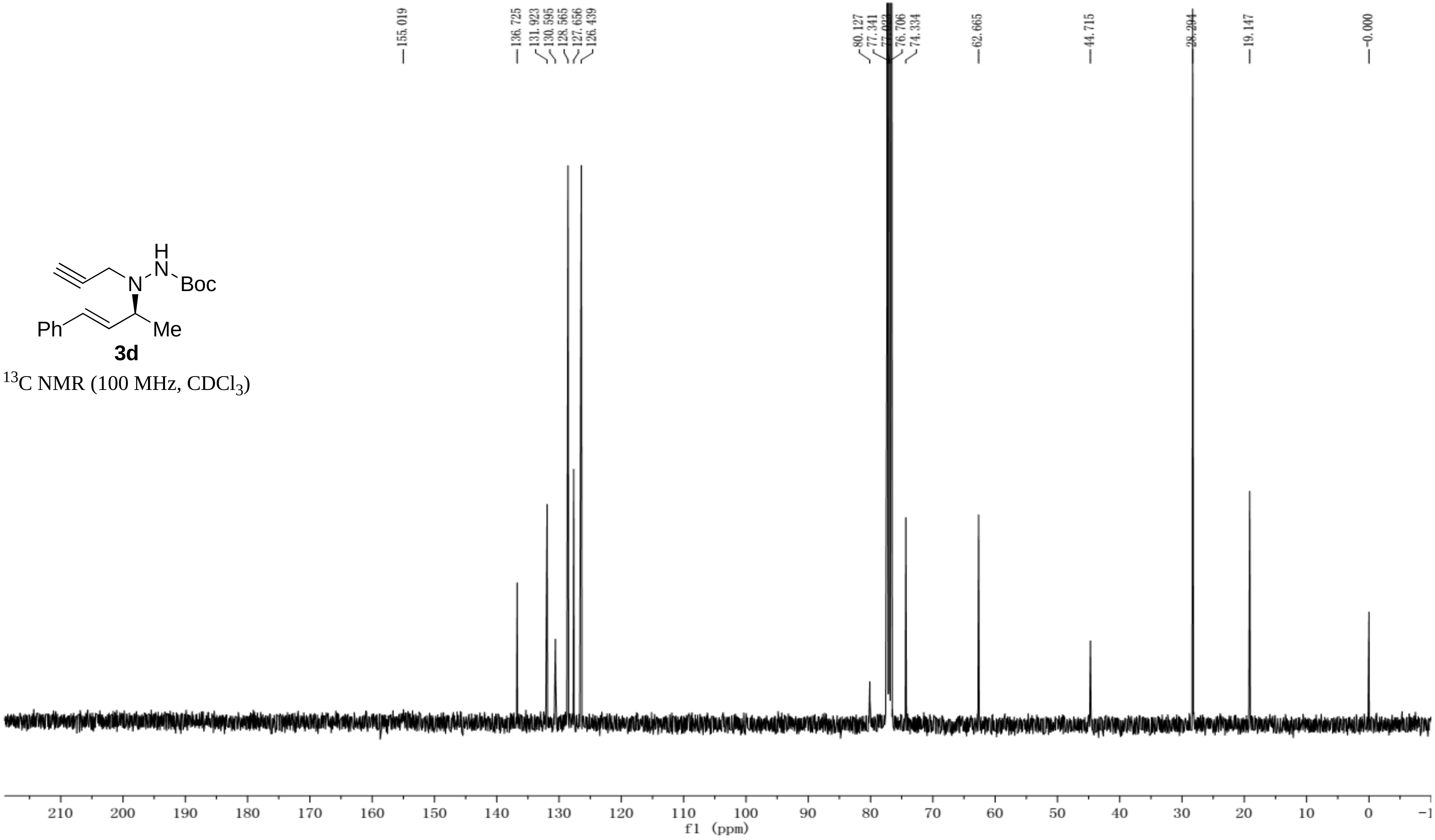

3d

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3e

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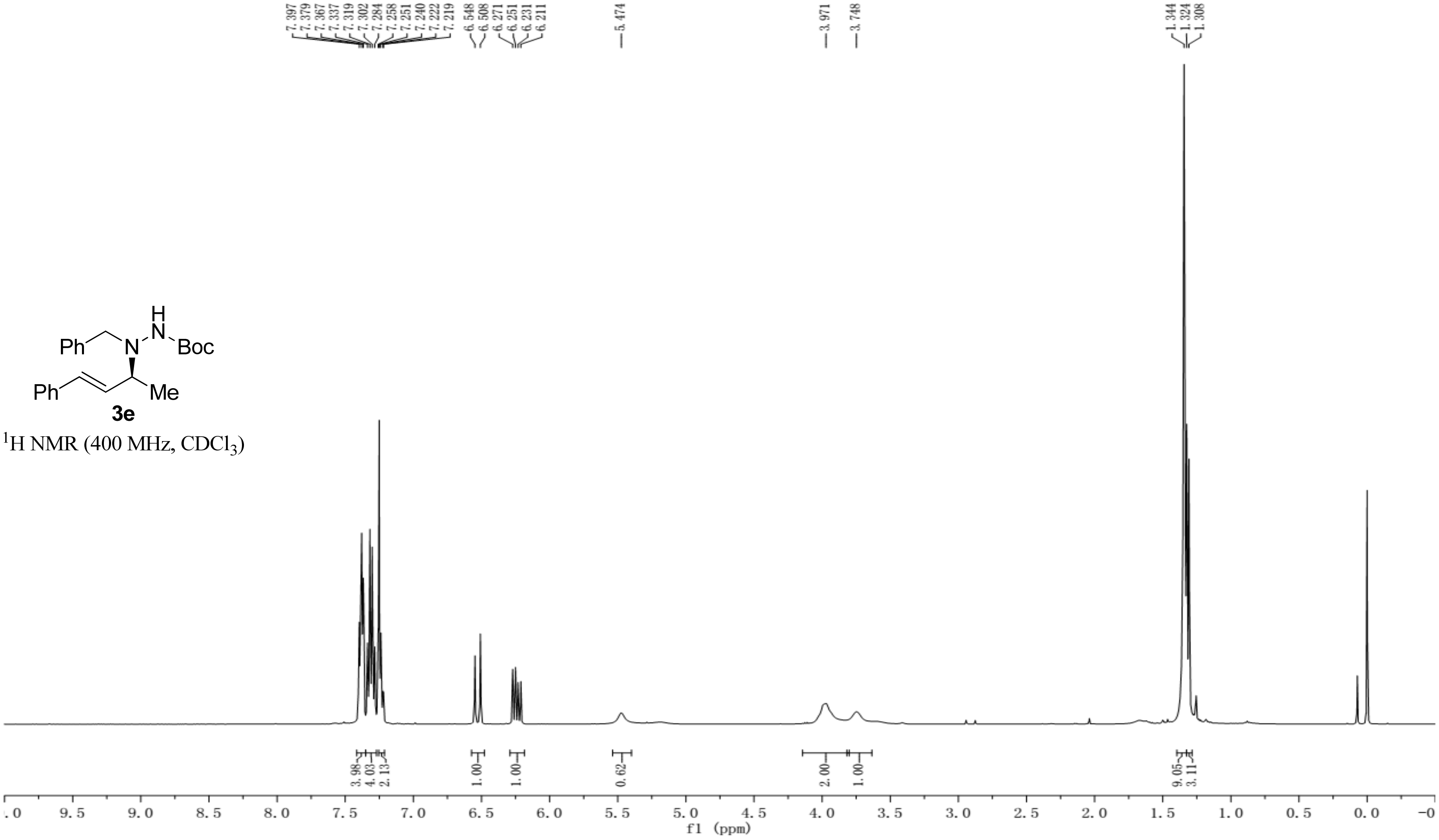

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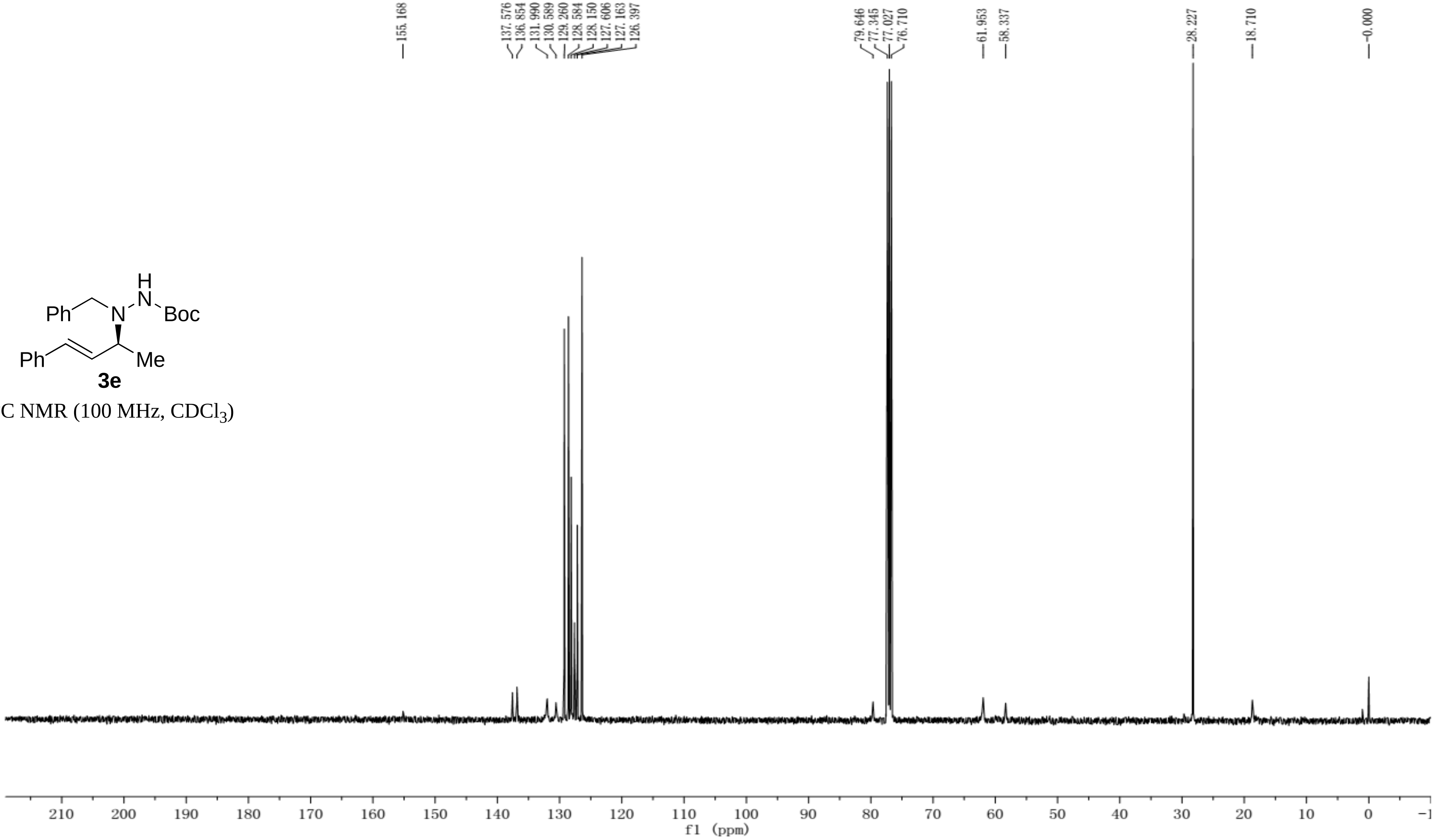

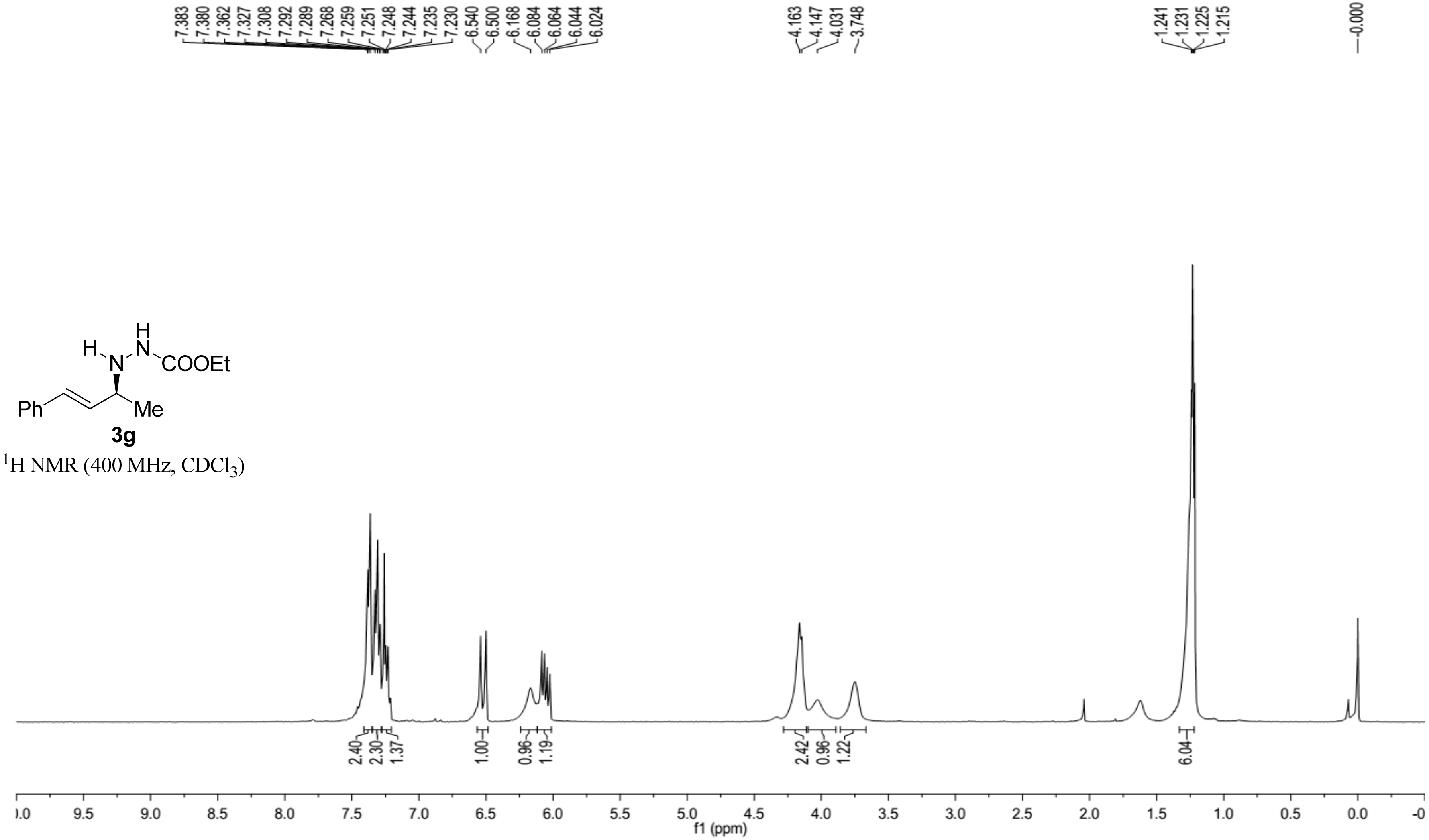

3g

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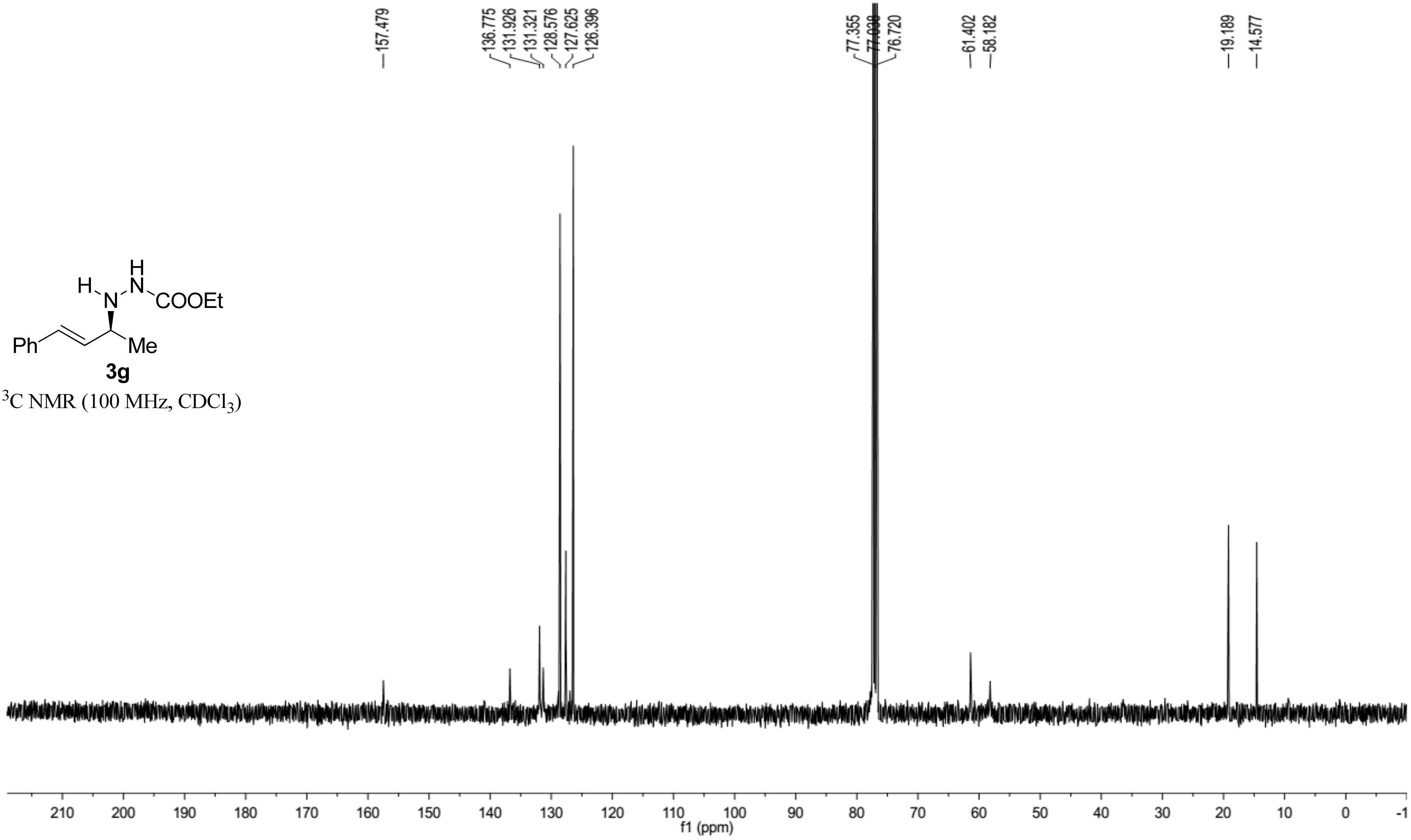

3g

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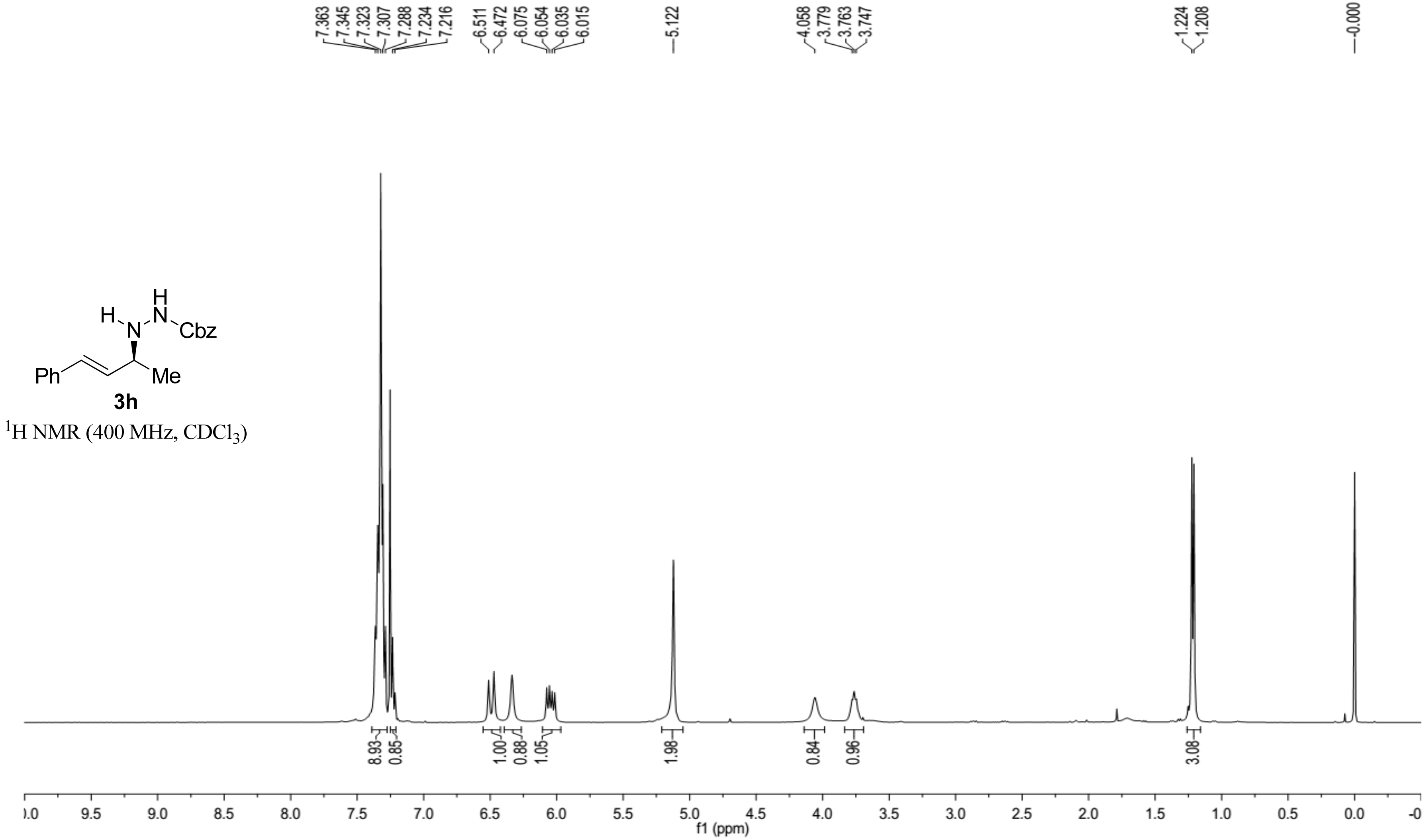
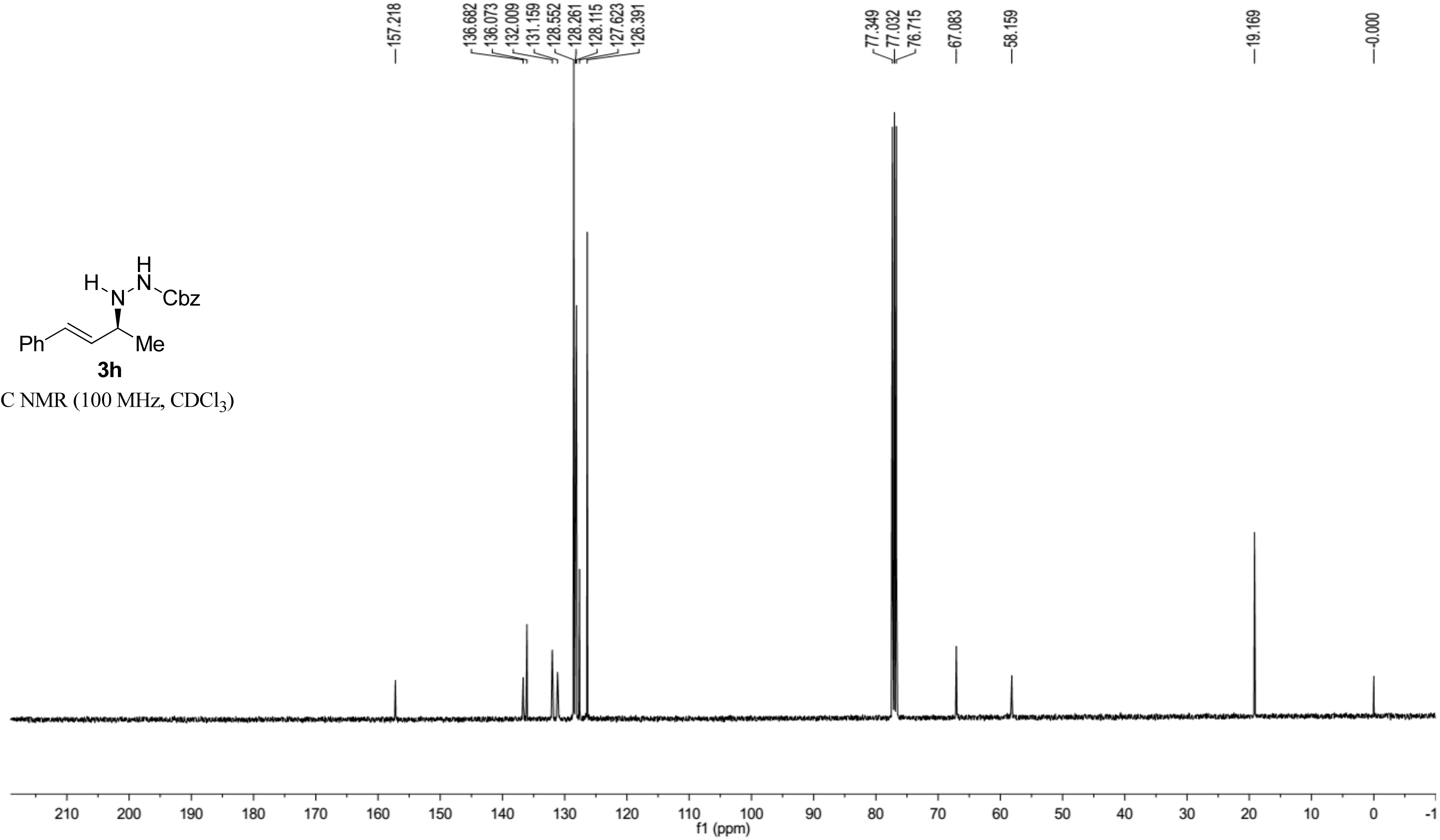


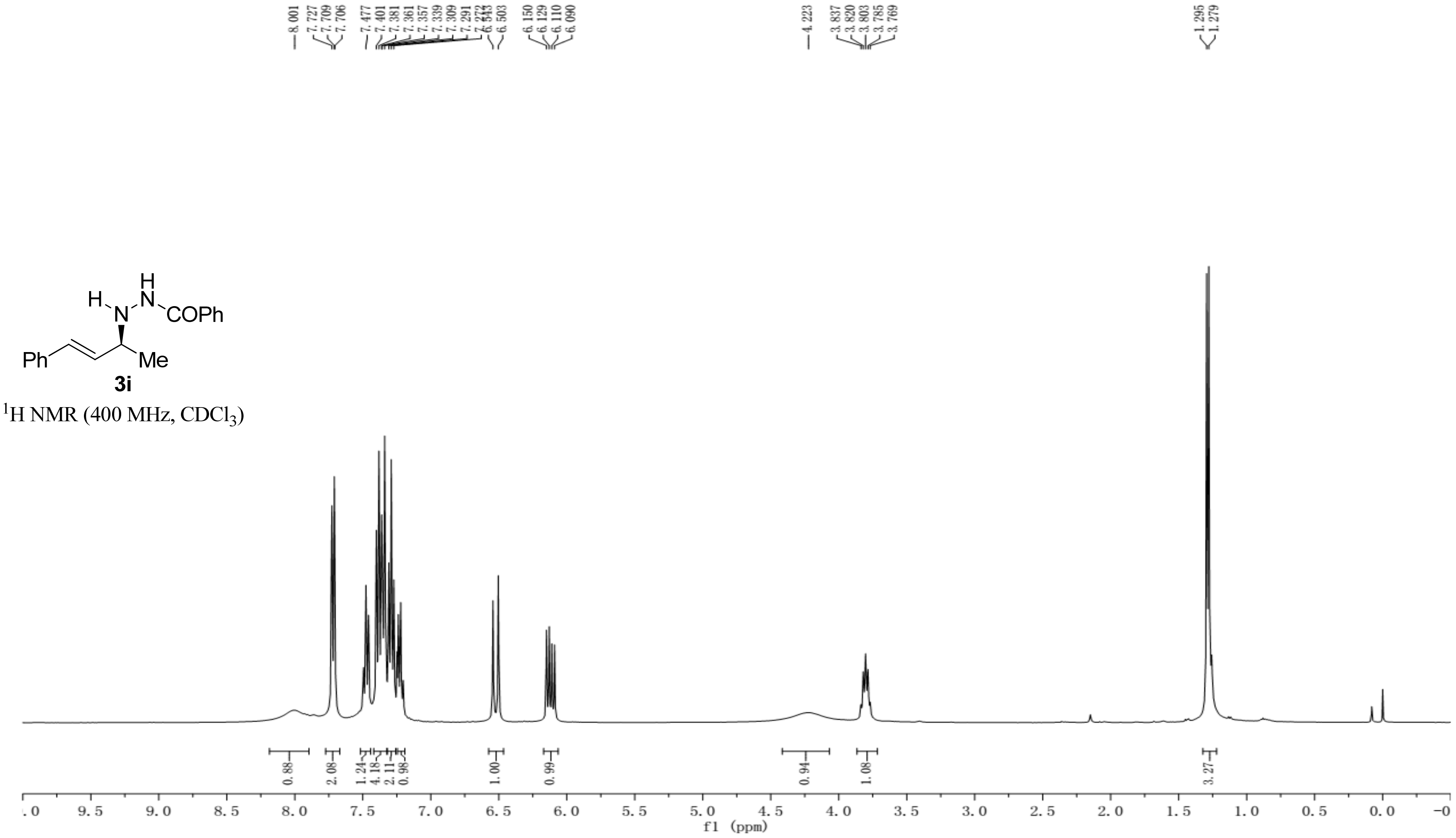
3h

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

3h

^{13}C NMR (100 MHz, CDCl$_3$)





3i

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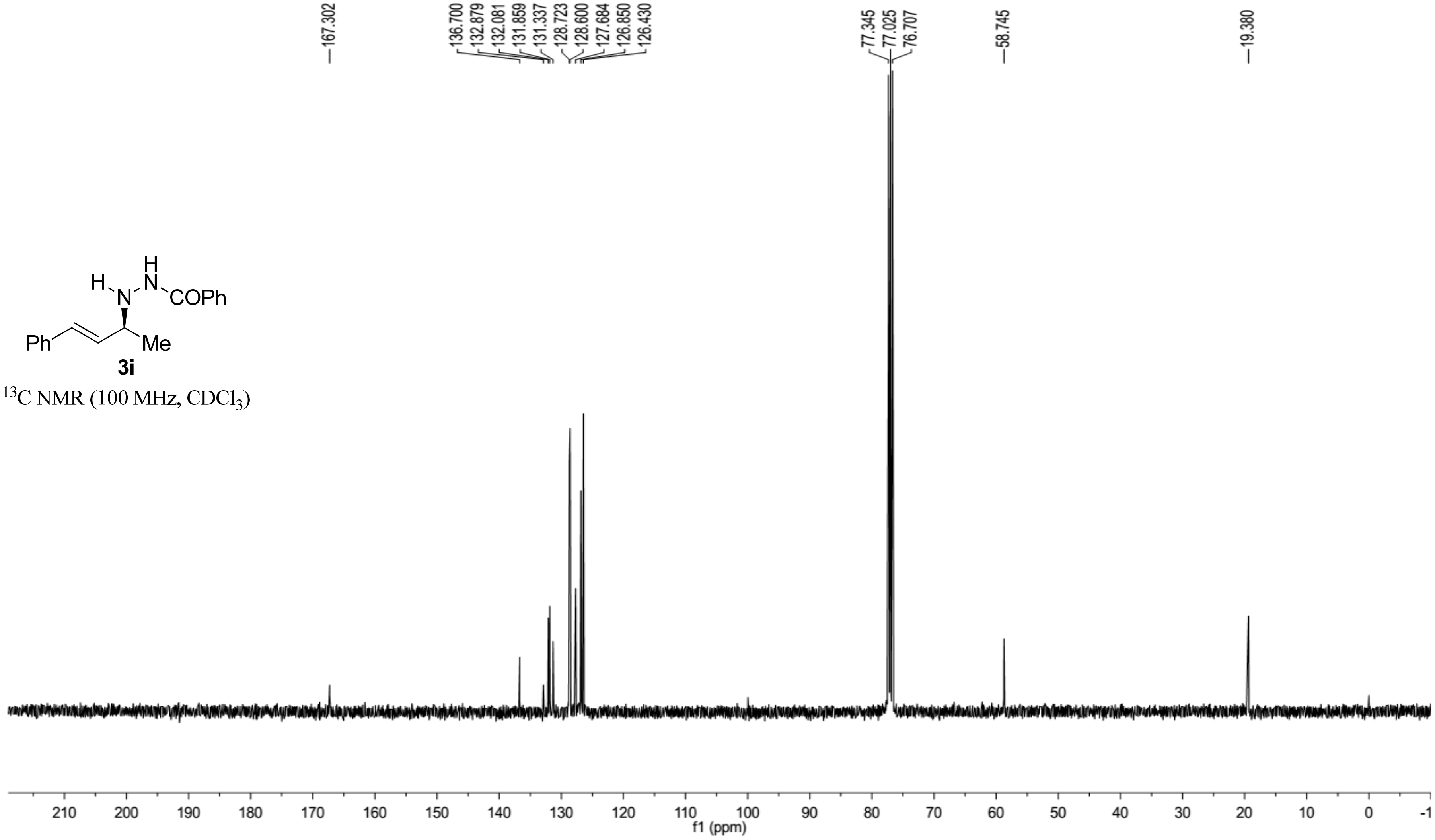

3i

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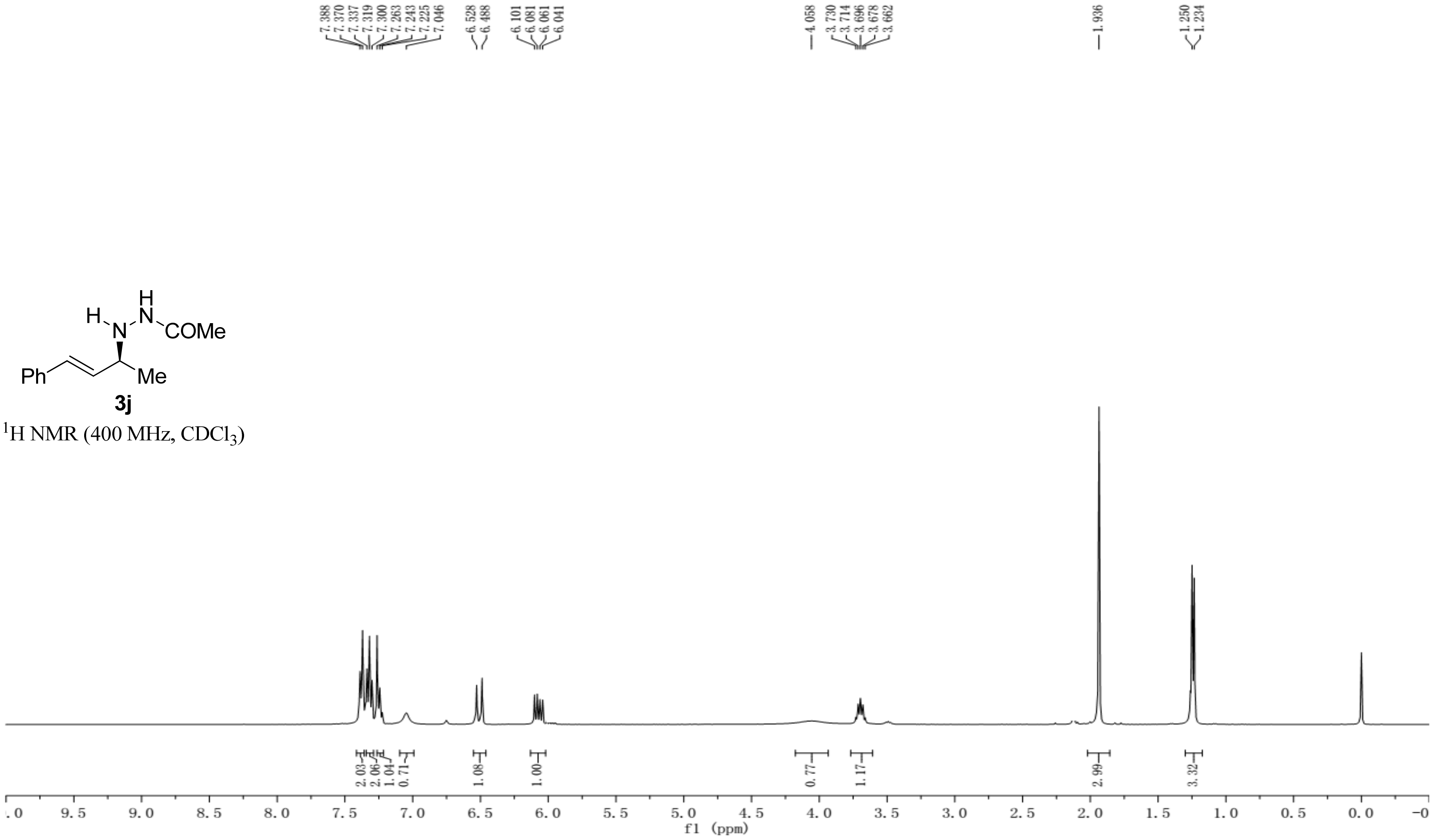

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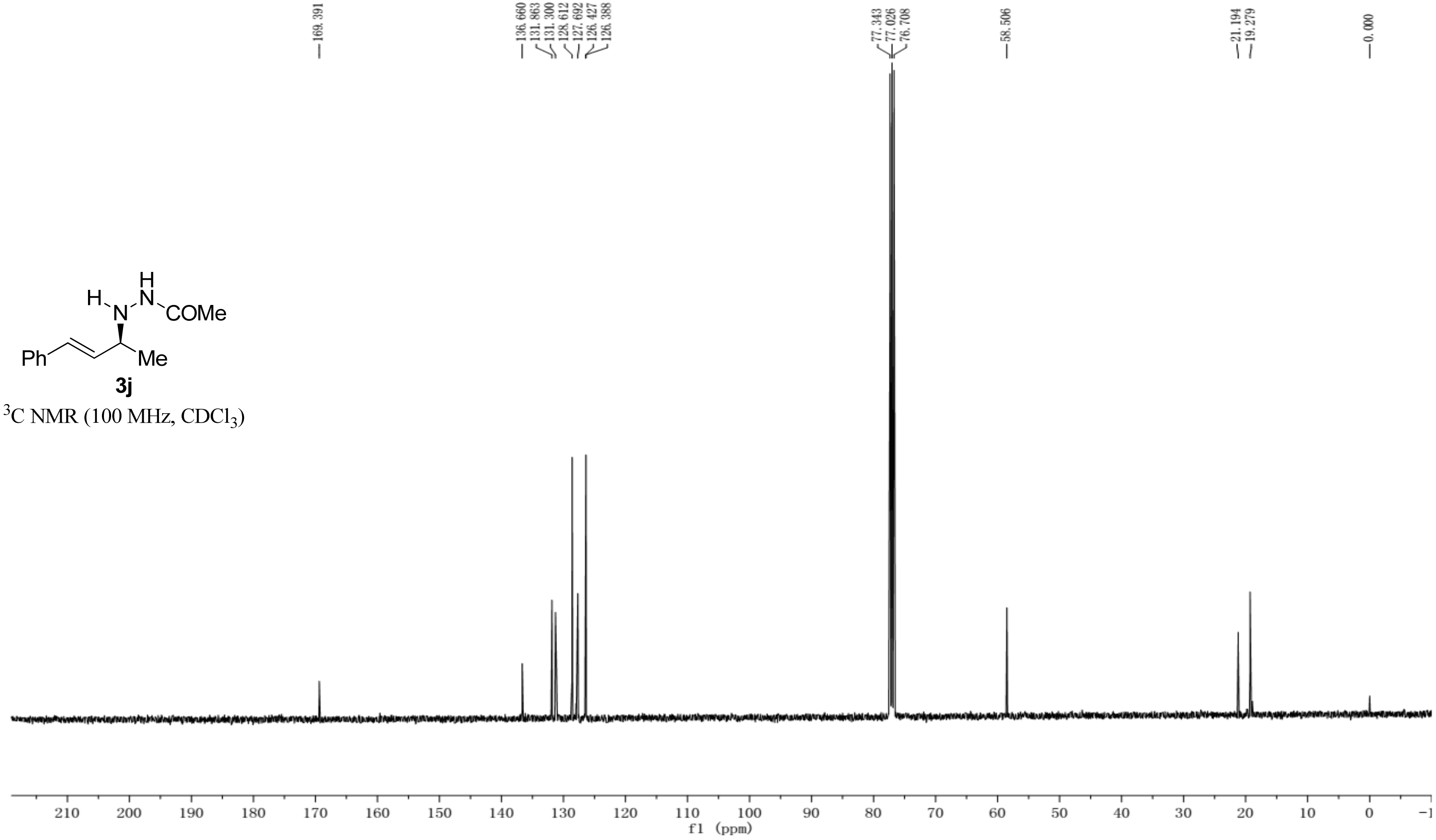

3j

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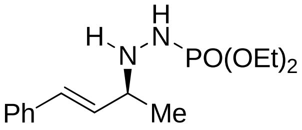

3k

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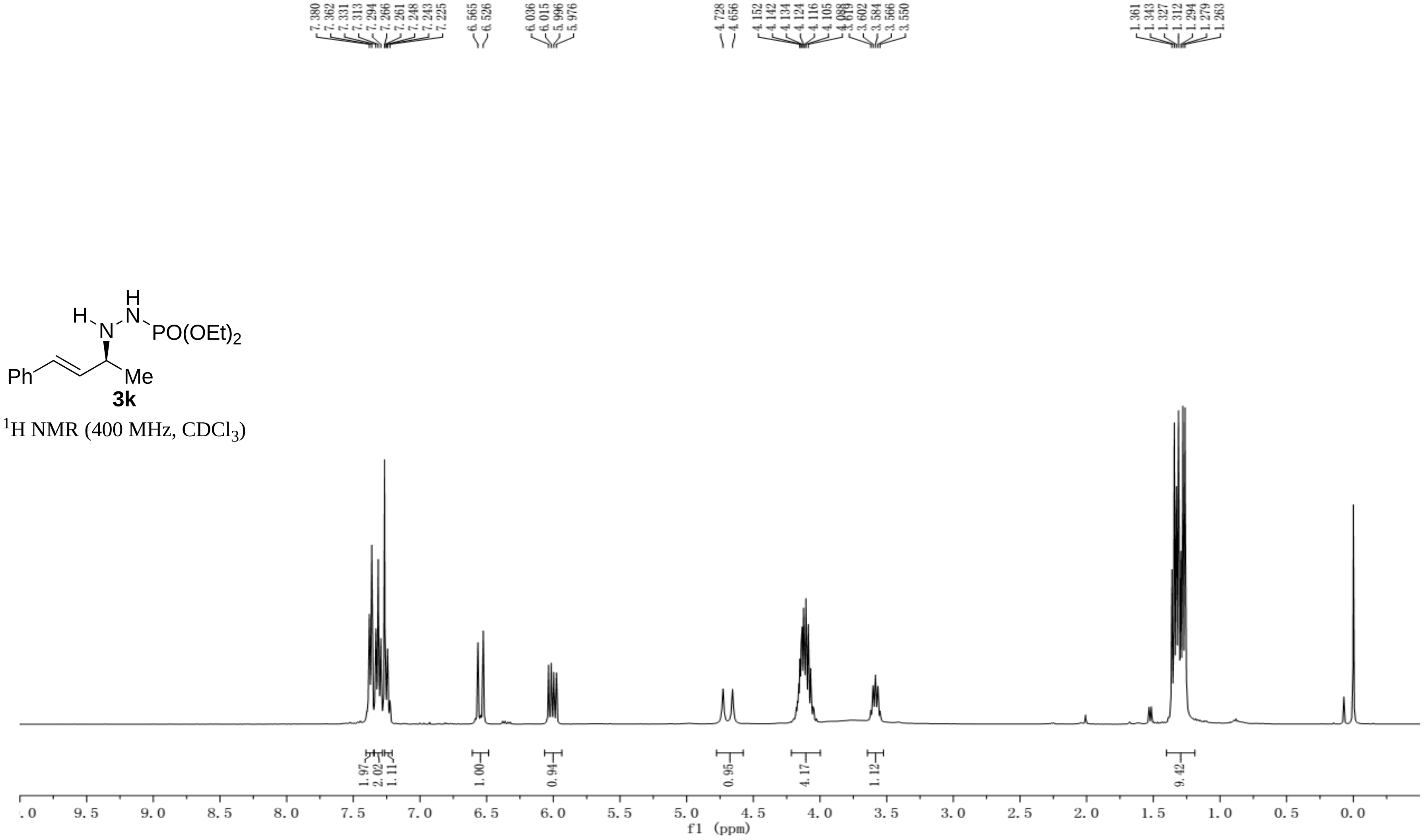

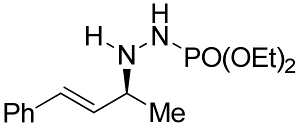

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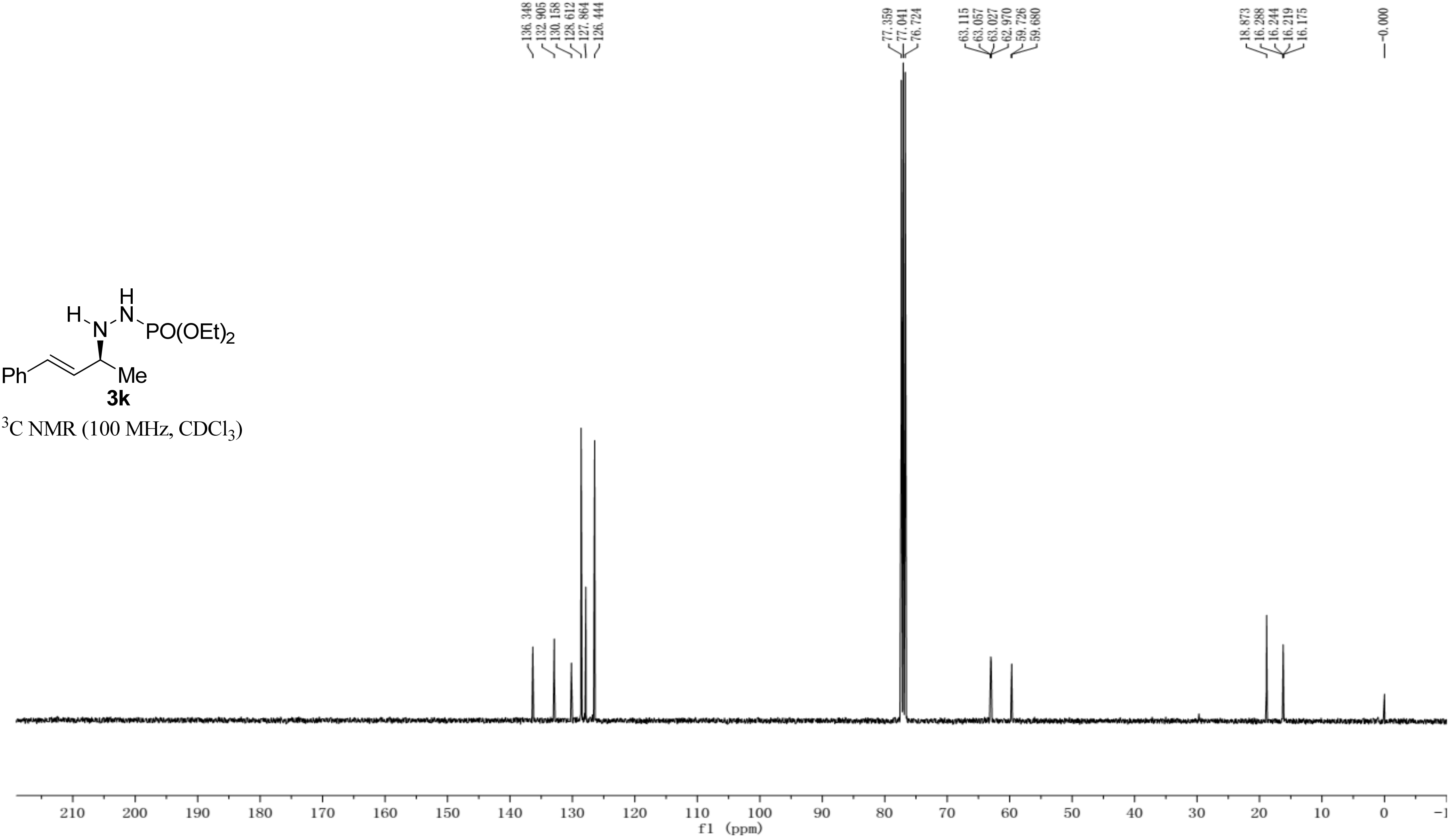
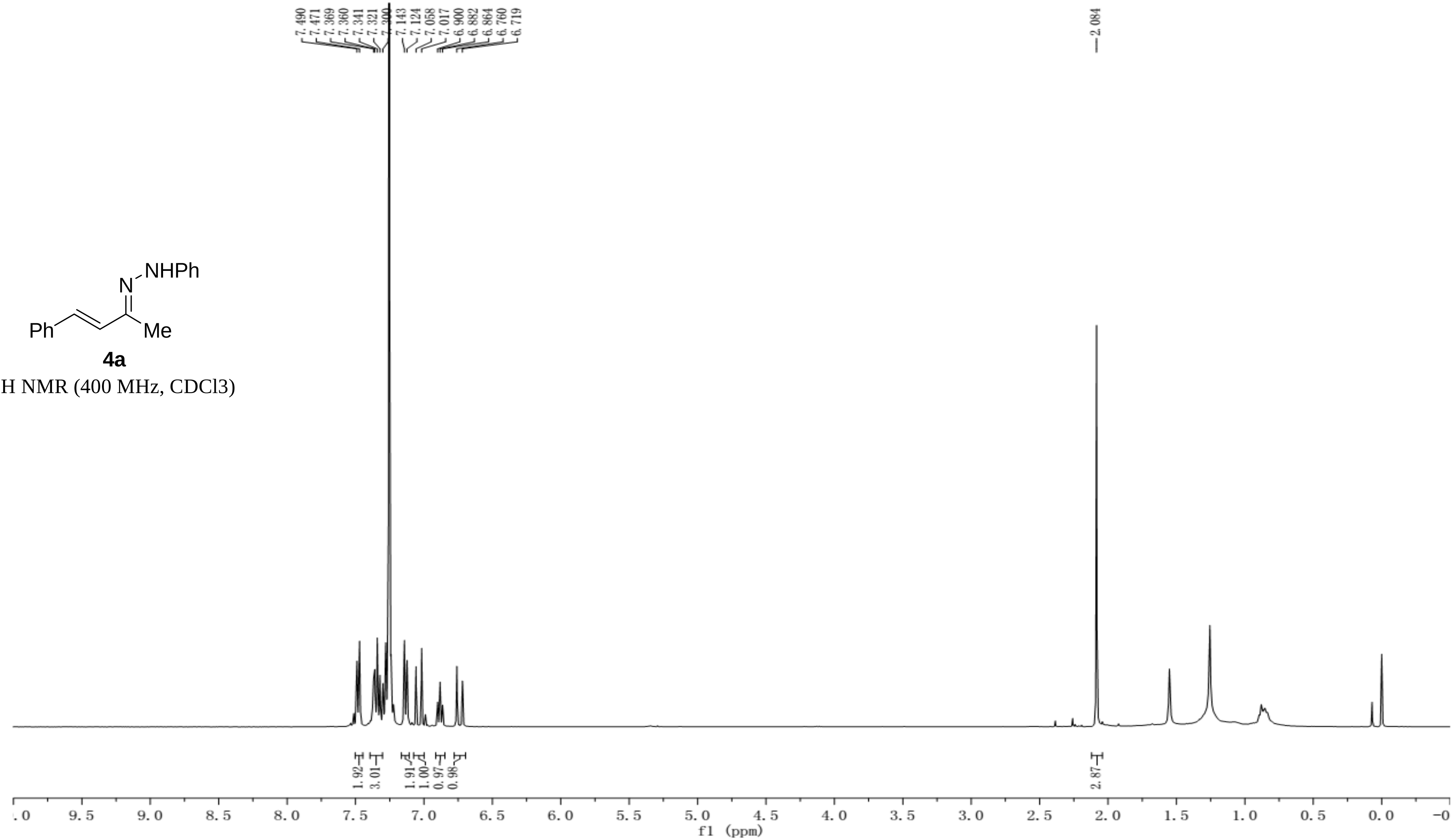
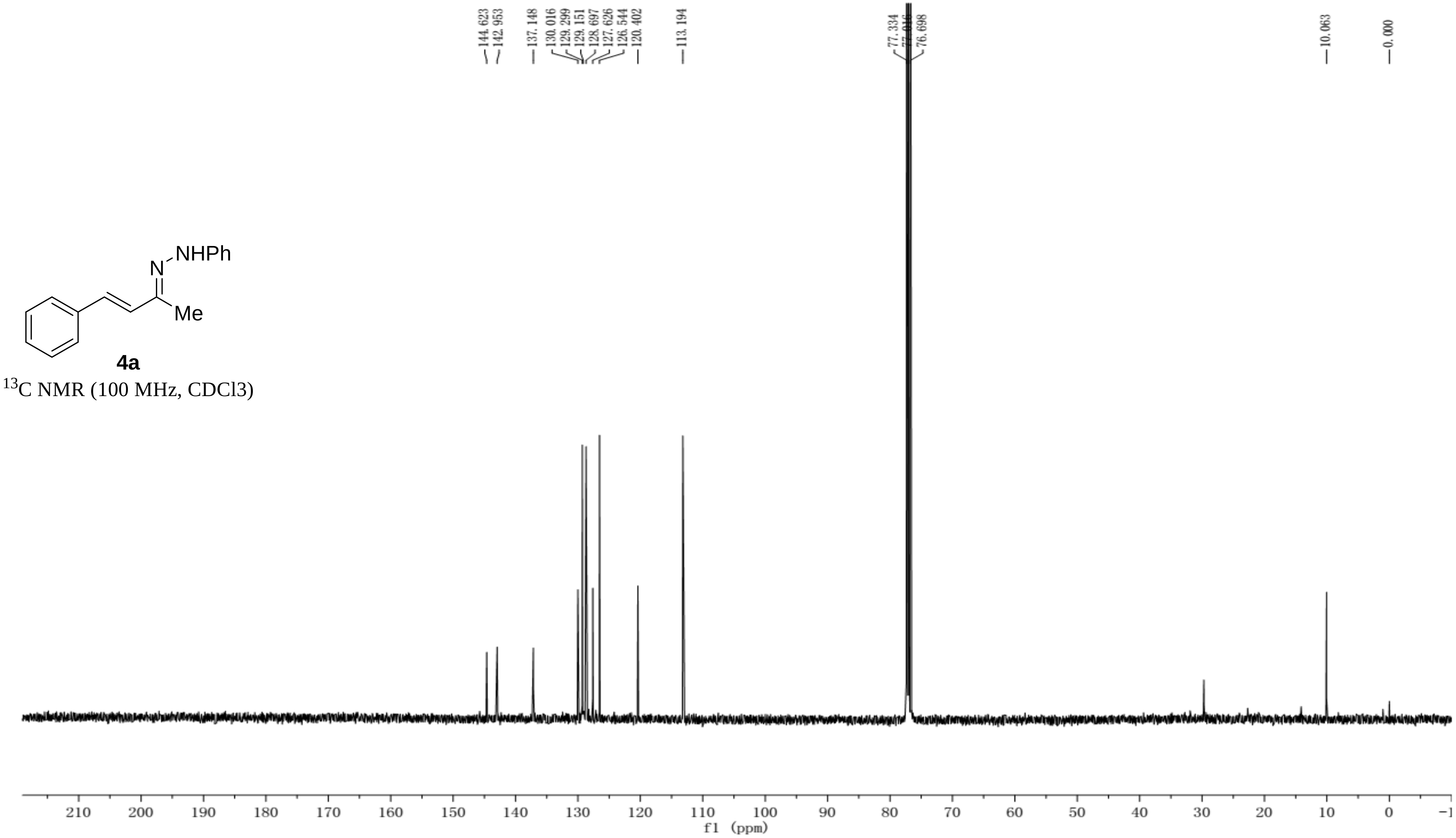




4a

^{1}H NMR (400 MHz, CDCl3)



4a

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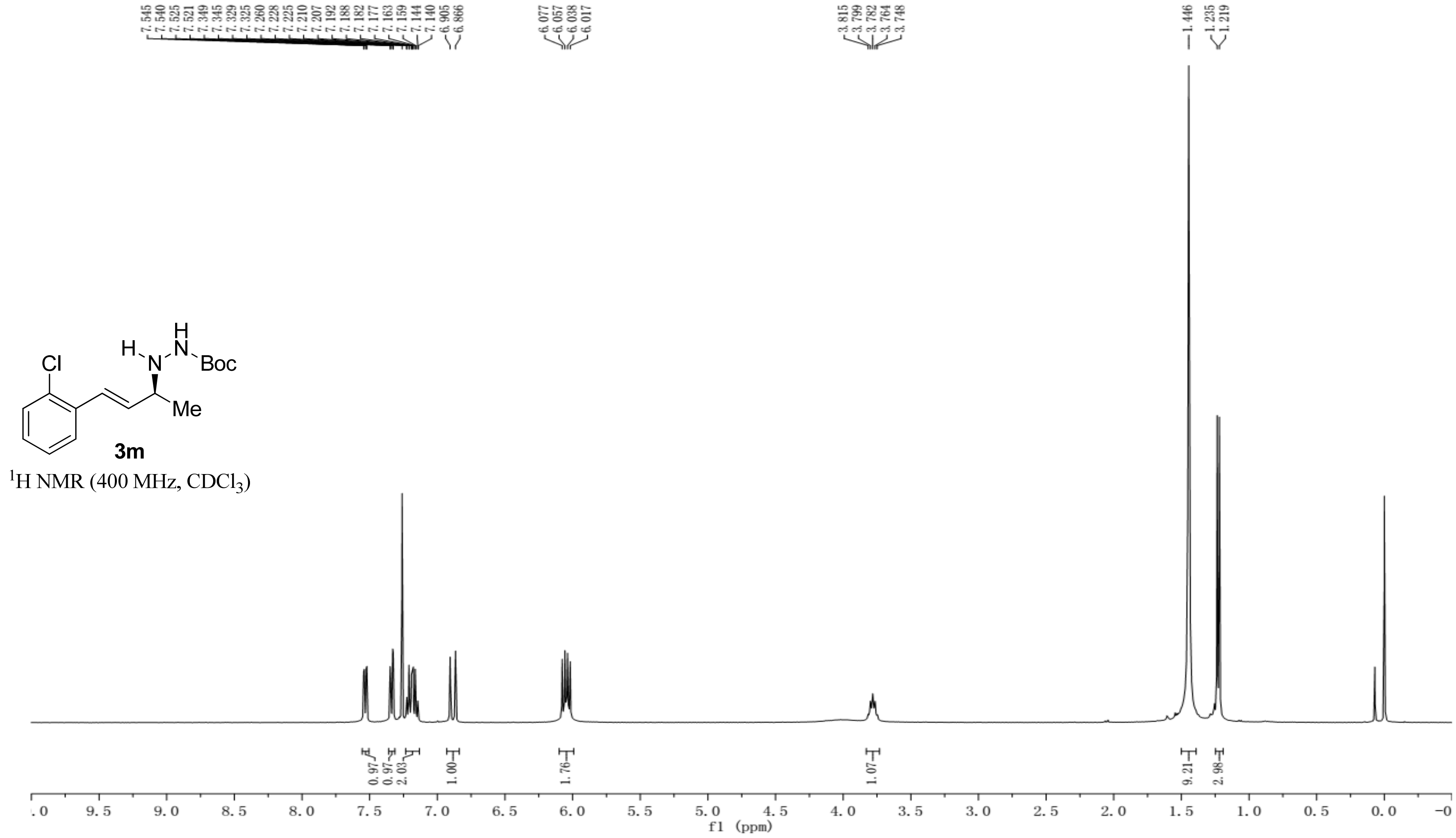

3m

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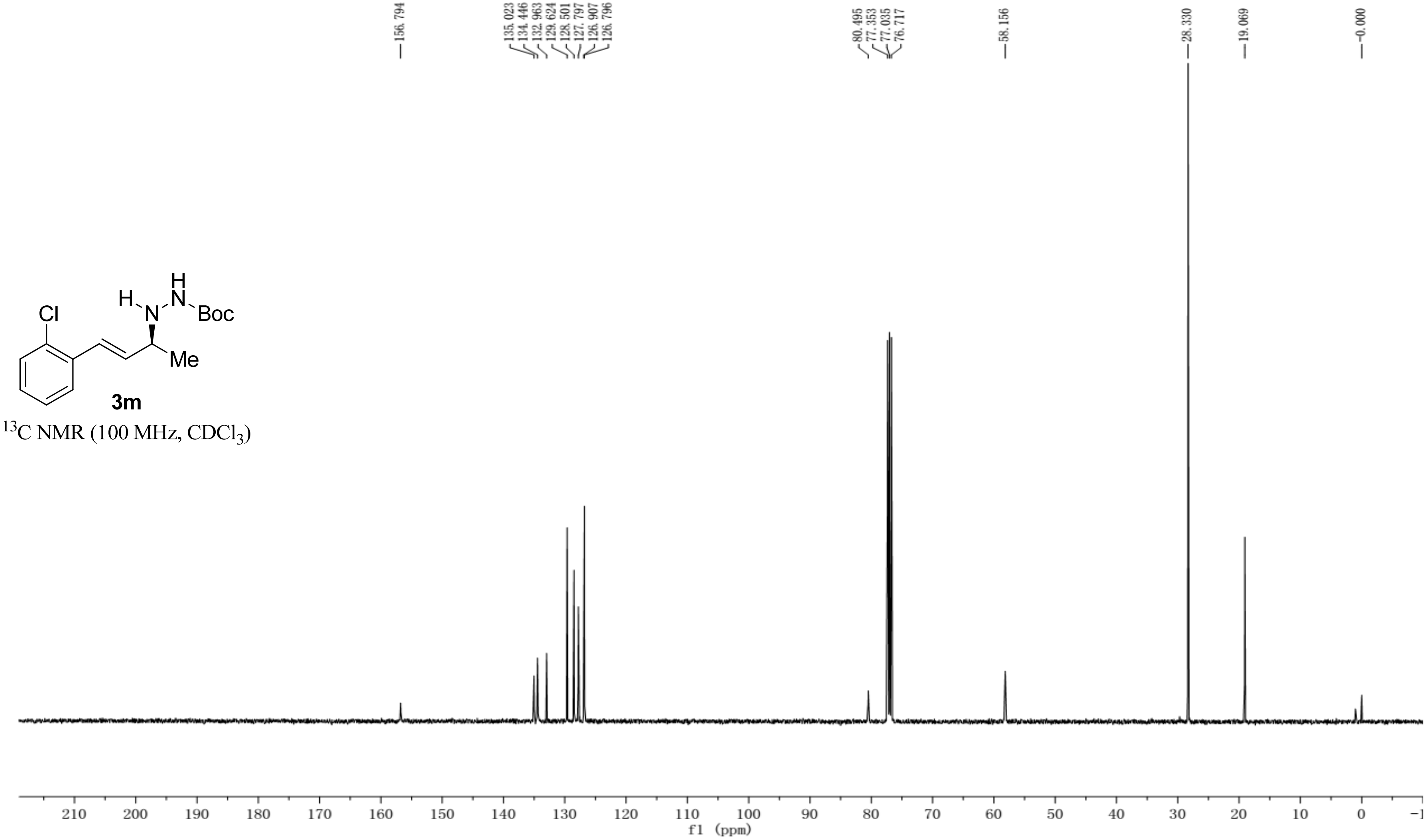

3m

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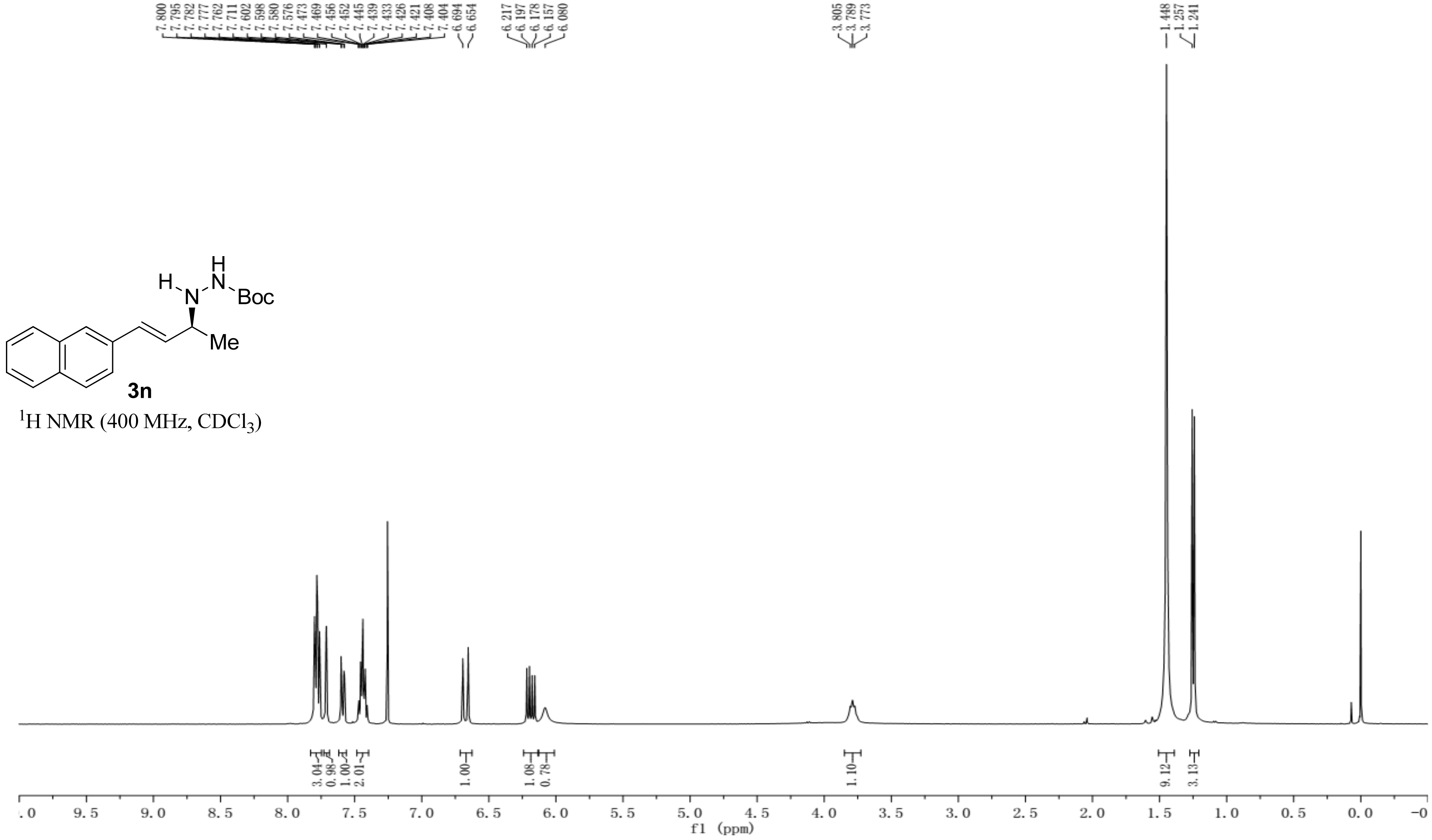

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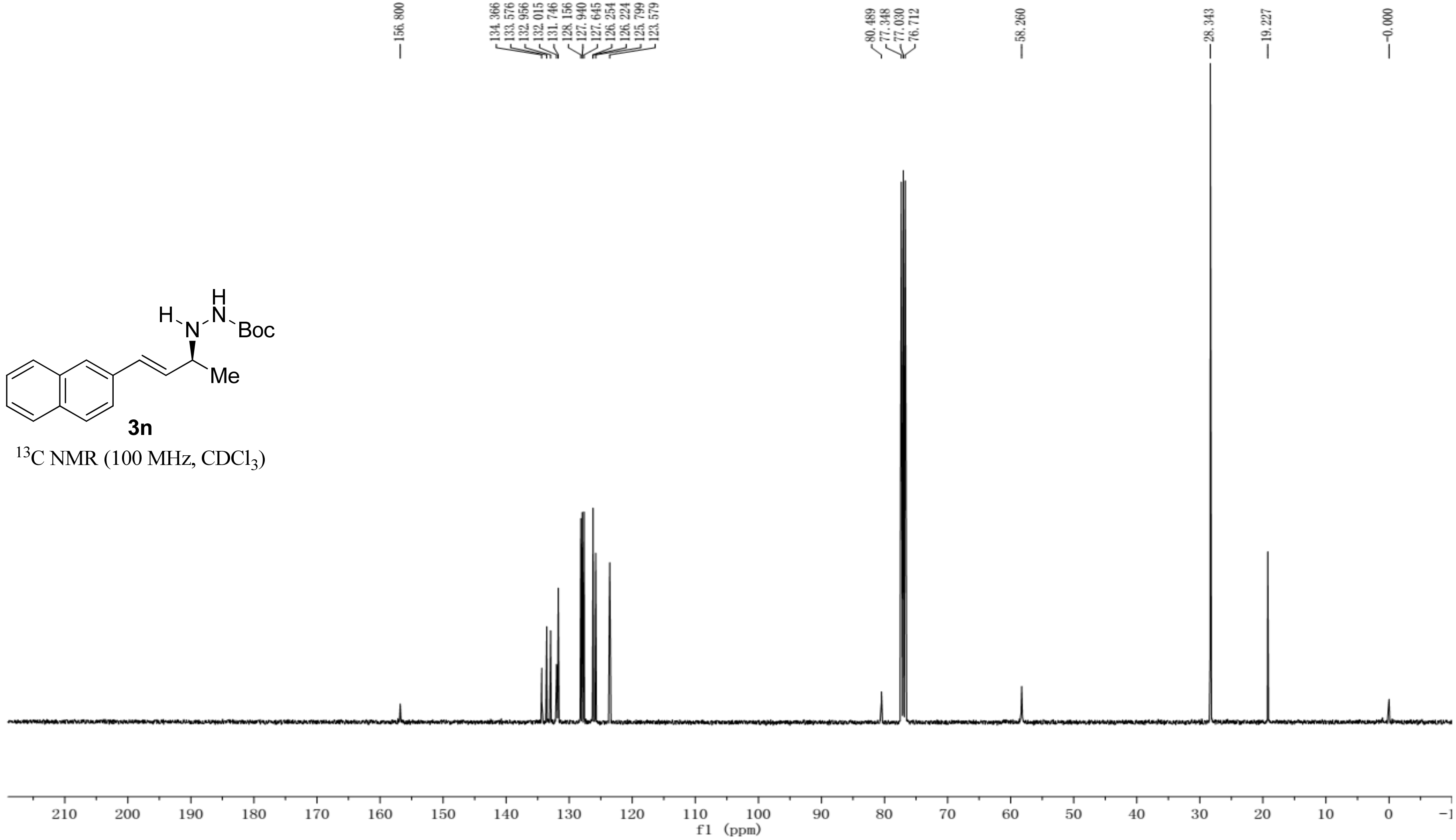
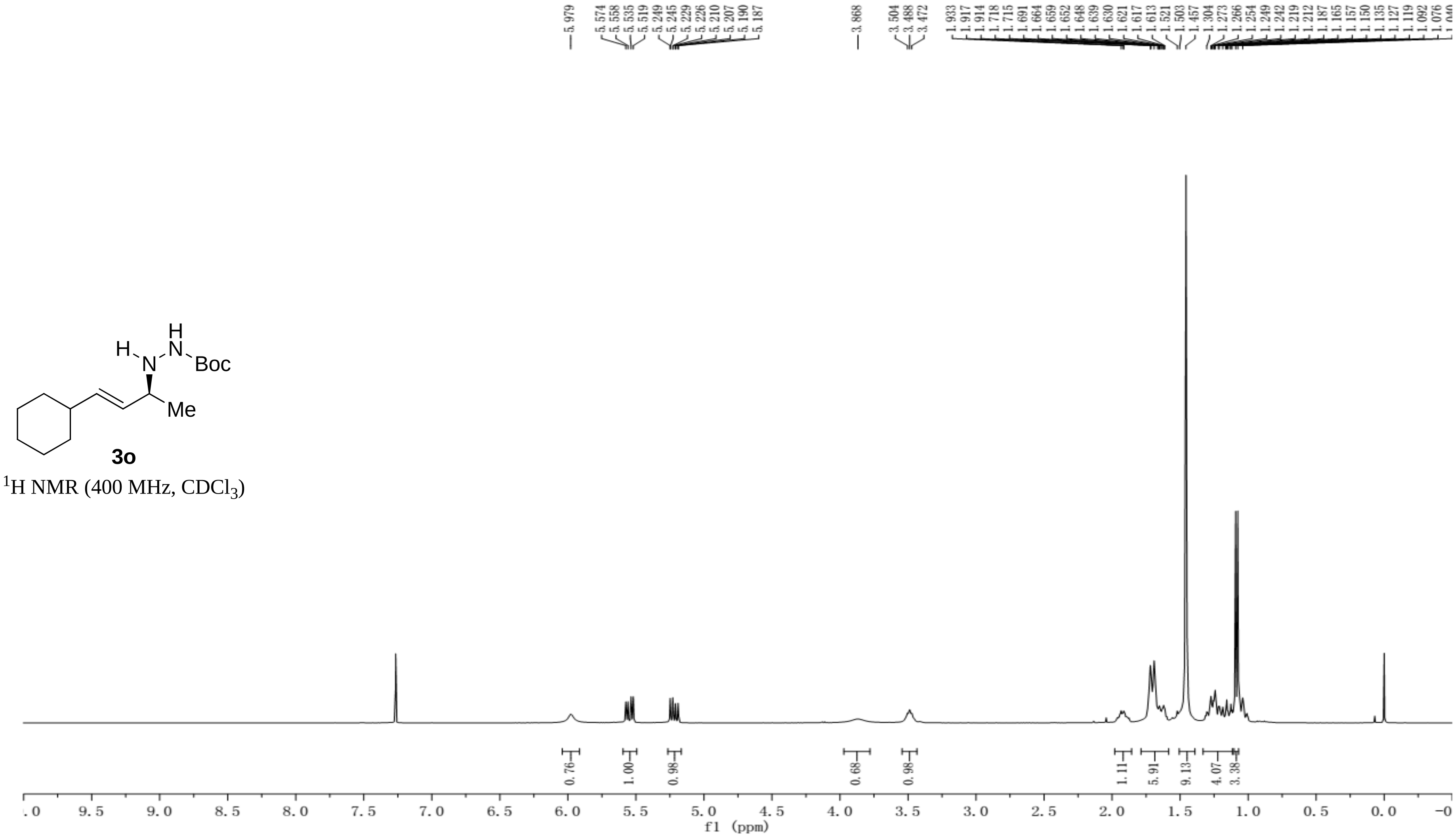


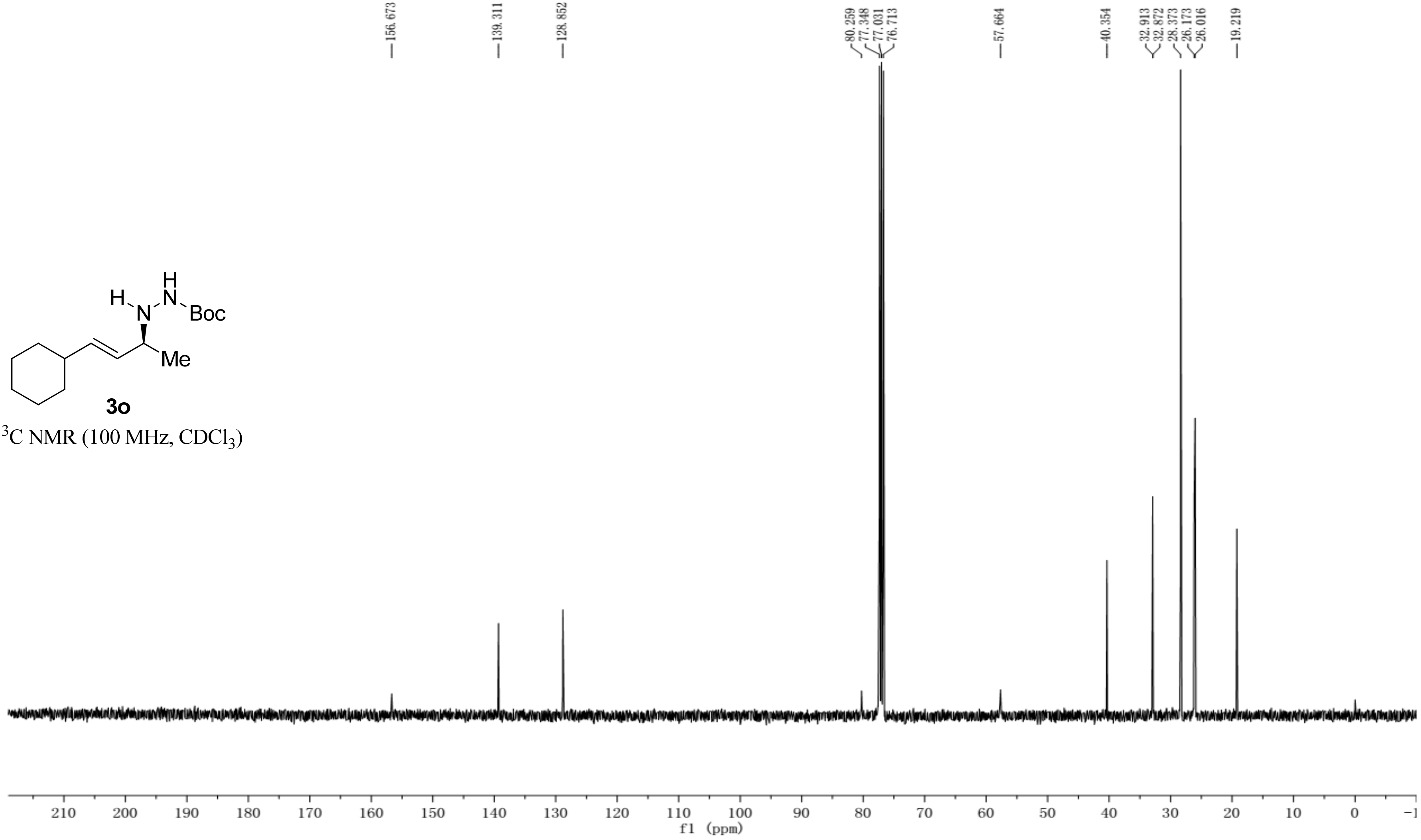
3n

^{13}C NMR (100 MHz, CDCl$_3$)

3o

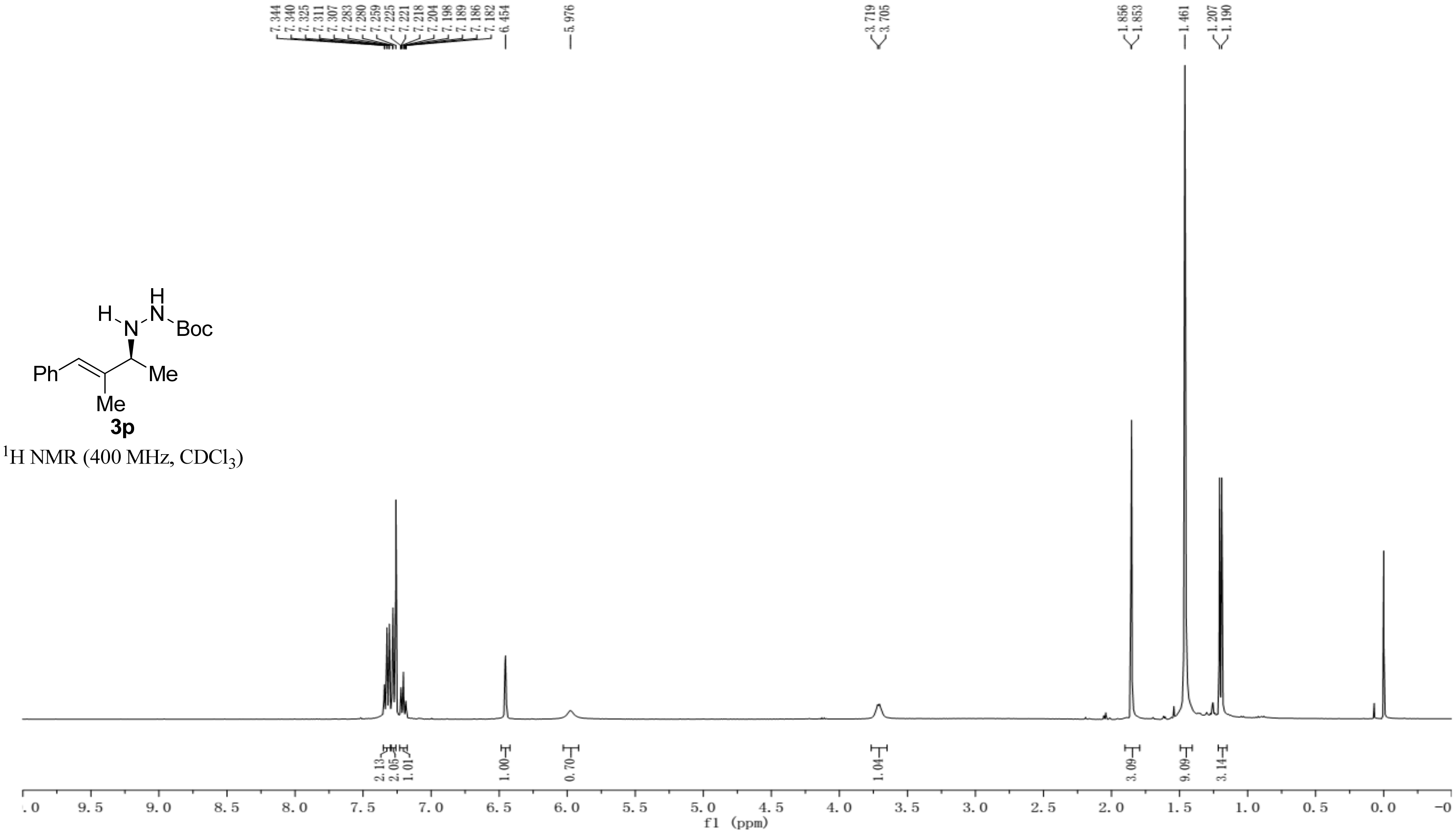
^{1}H NMR (400 MHz, CDCl$_3$)





3o

^{13}C NMR (100 MHz, CDCl$_3$)



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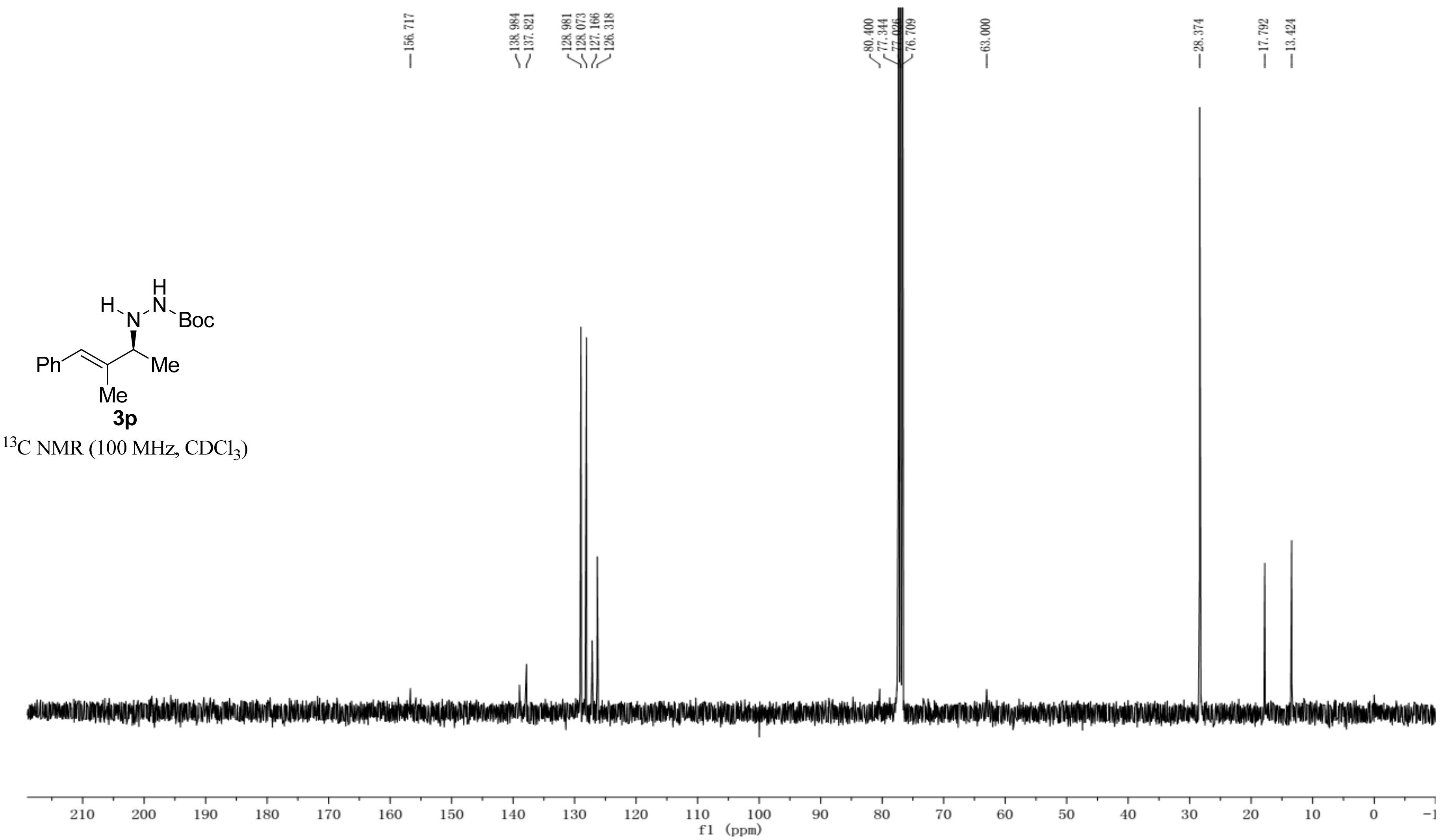
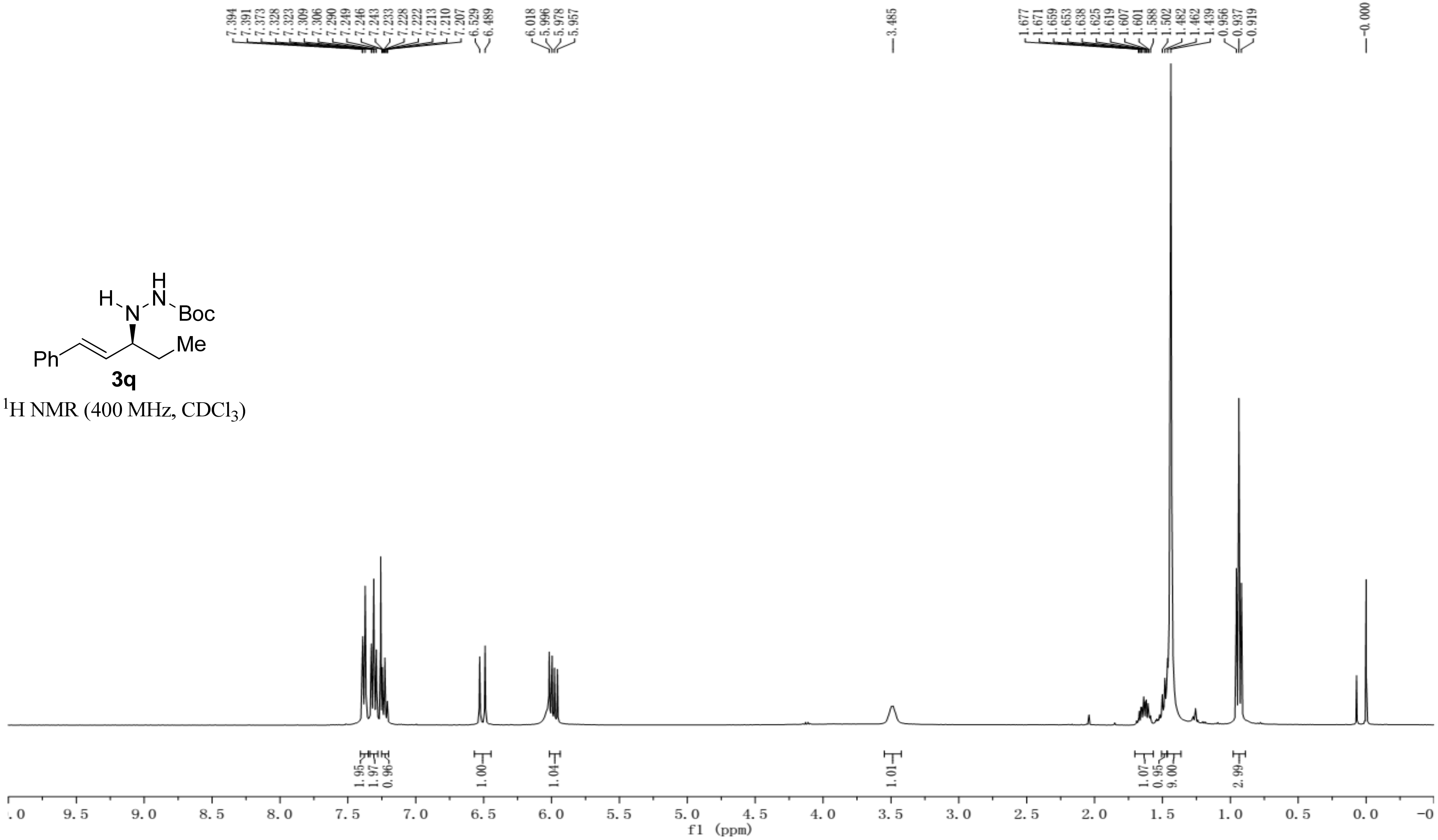


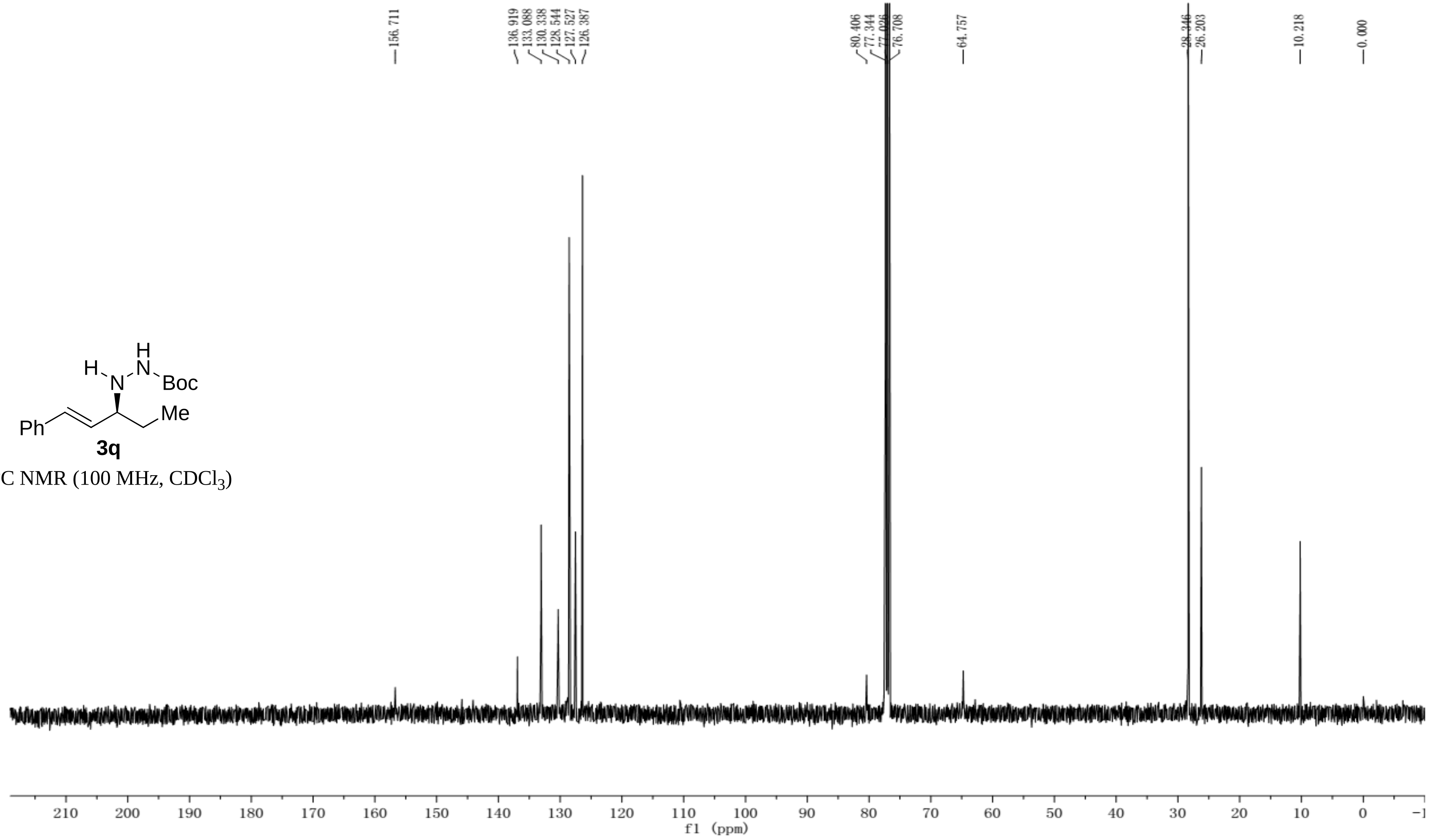
3p

^{13}C NMR (100 MHz, CDCl$_3$)



3q

^{1}H NMR (400 MHz, CDCl$_3$)

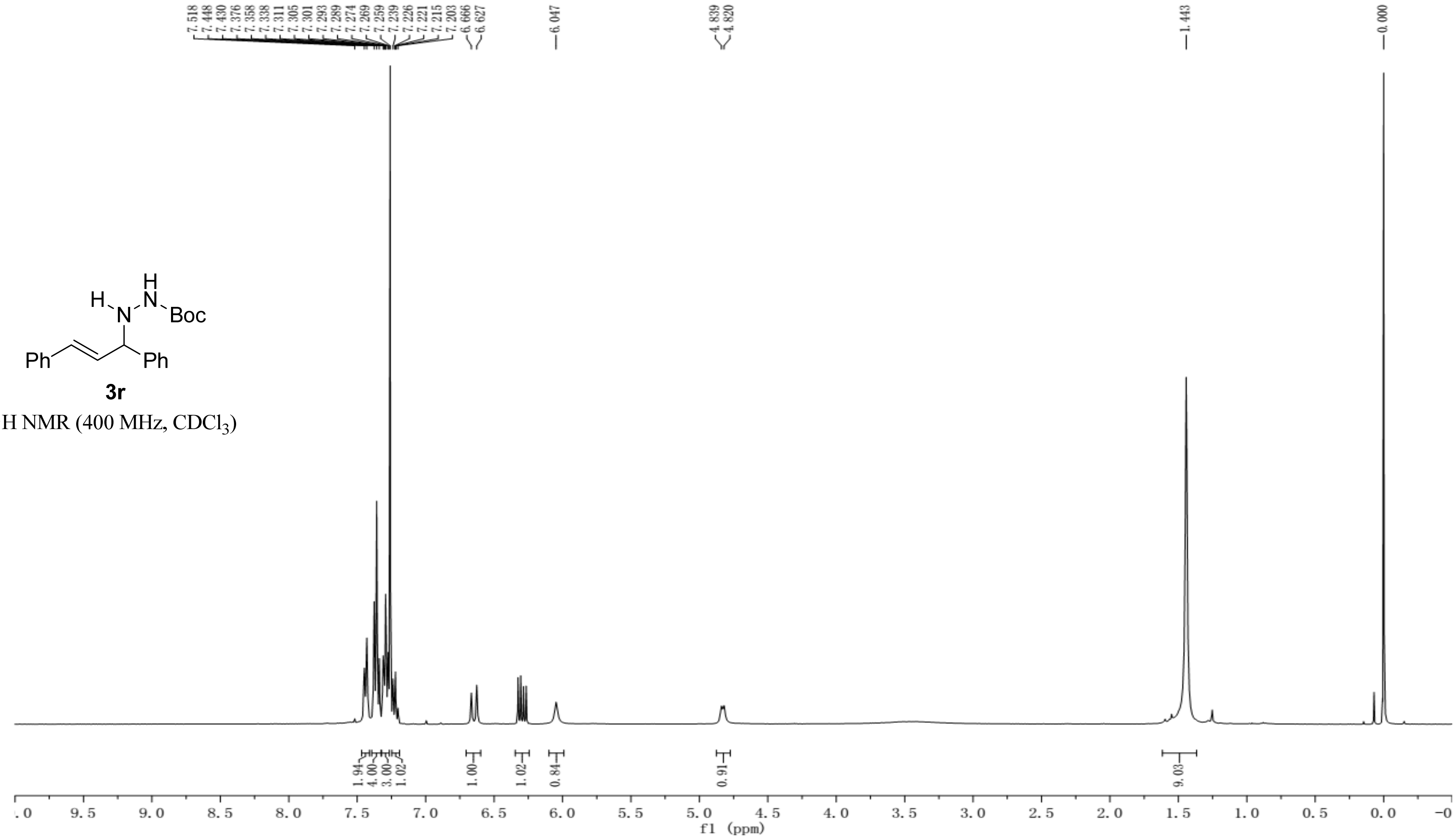


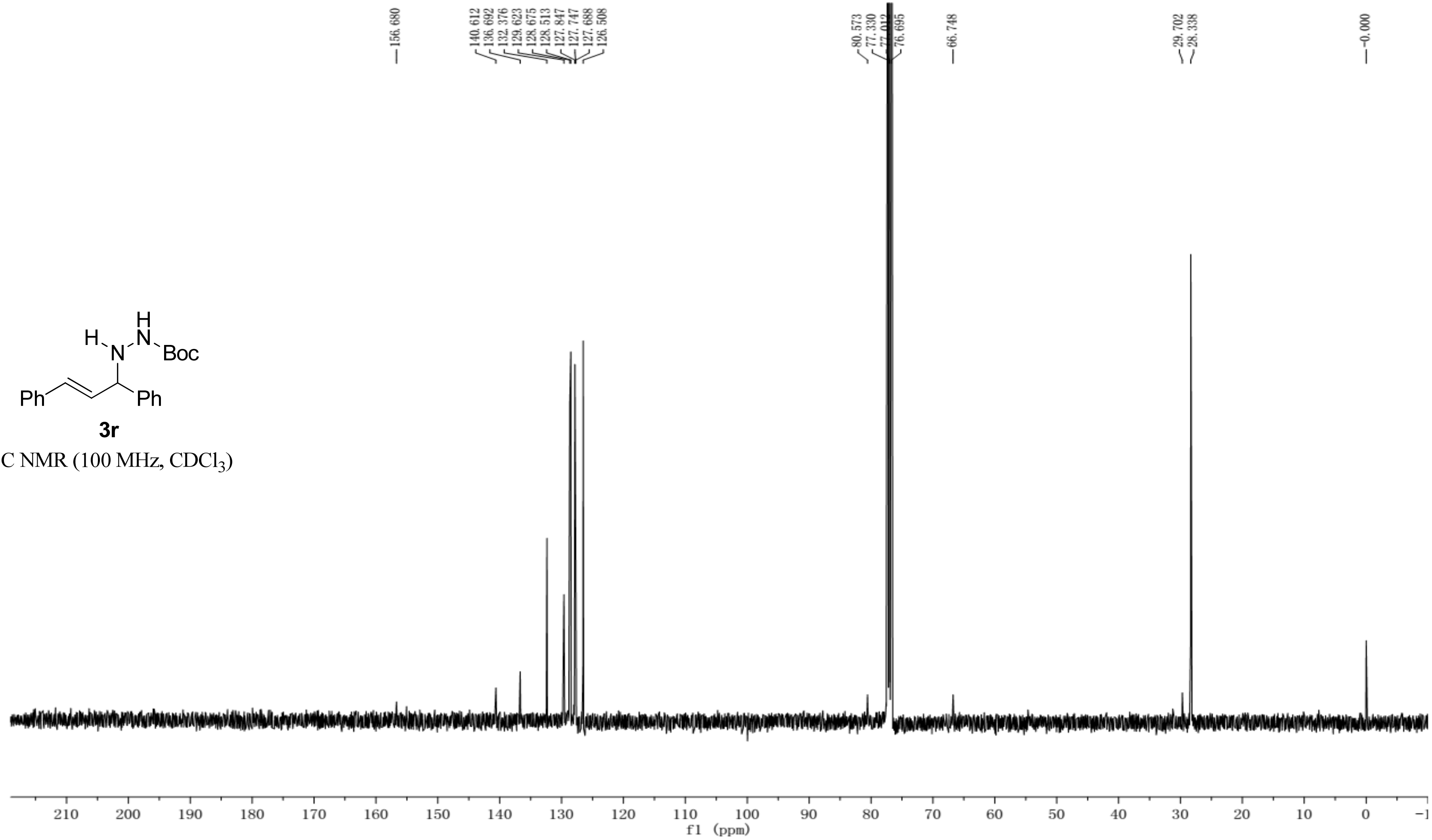
3q

^{13}C NMR (100 MHz, CDCl$_3$)

3r

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



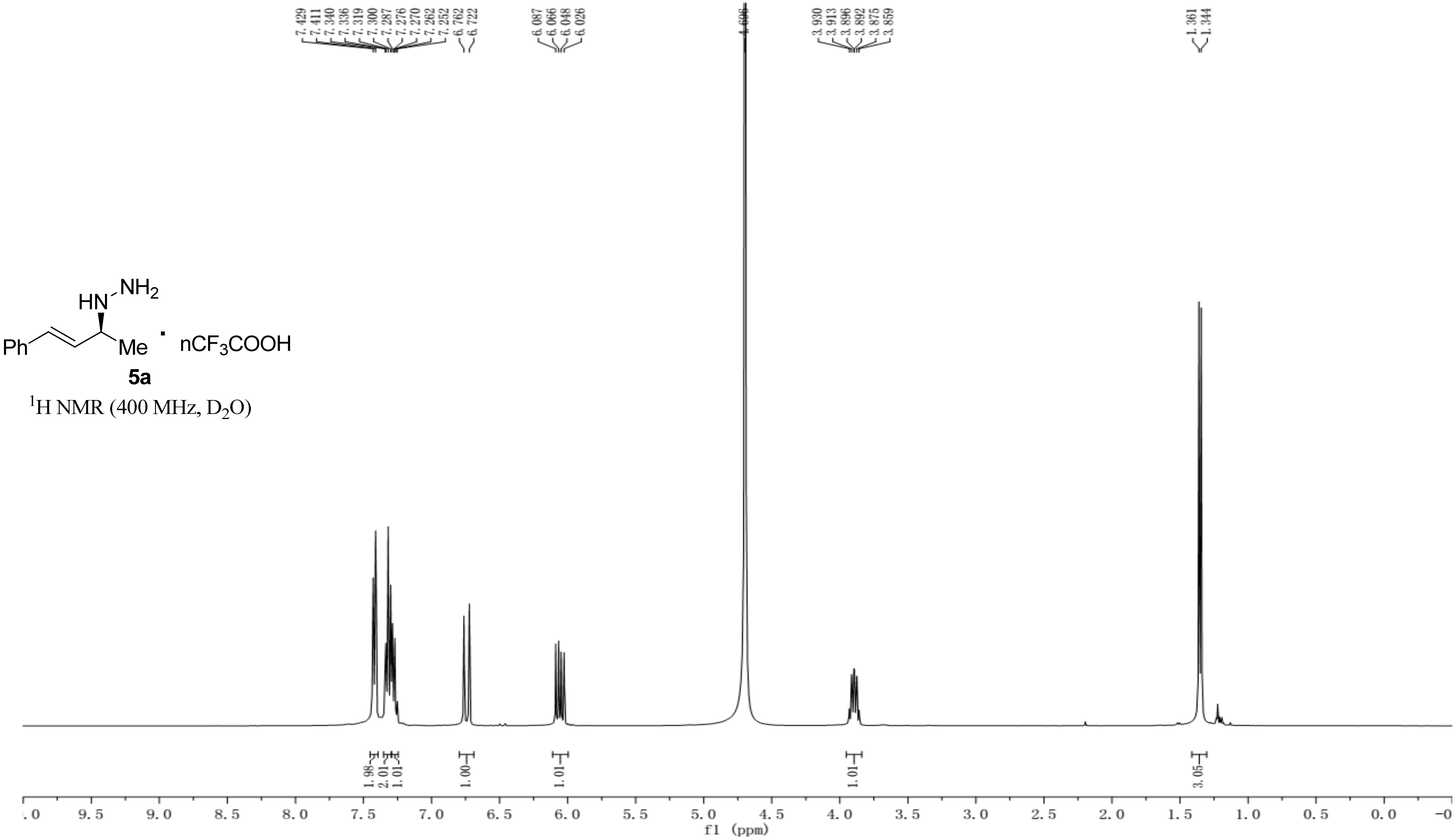


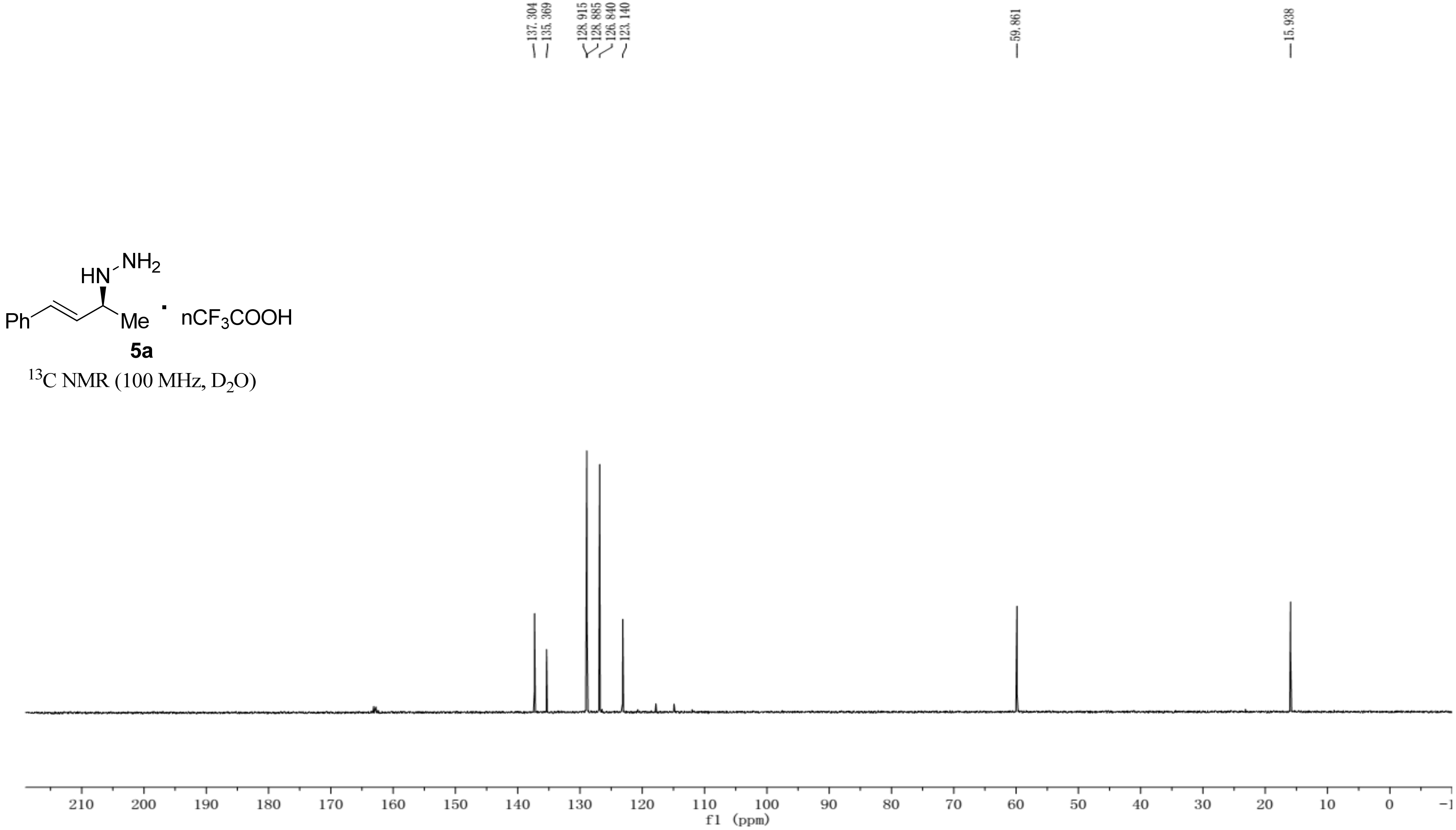
3r

^{13}C NMR (100 MHz, CDCl$_3$)

5a

^{1}H NMR (400 MHz, D_2O)

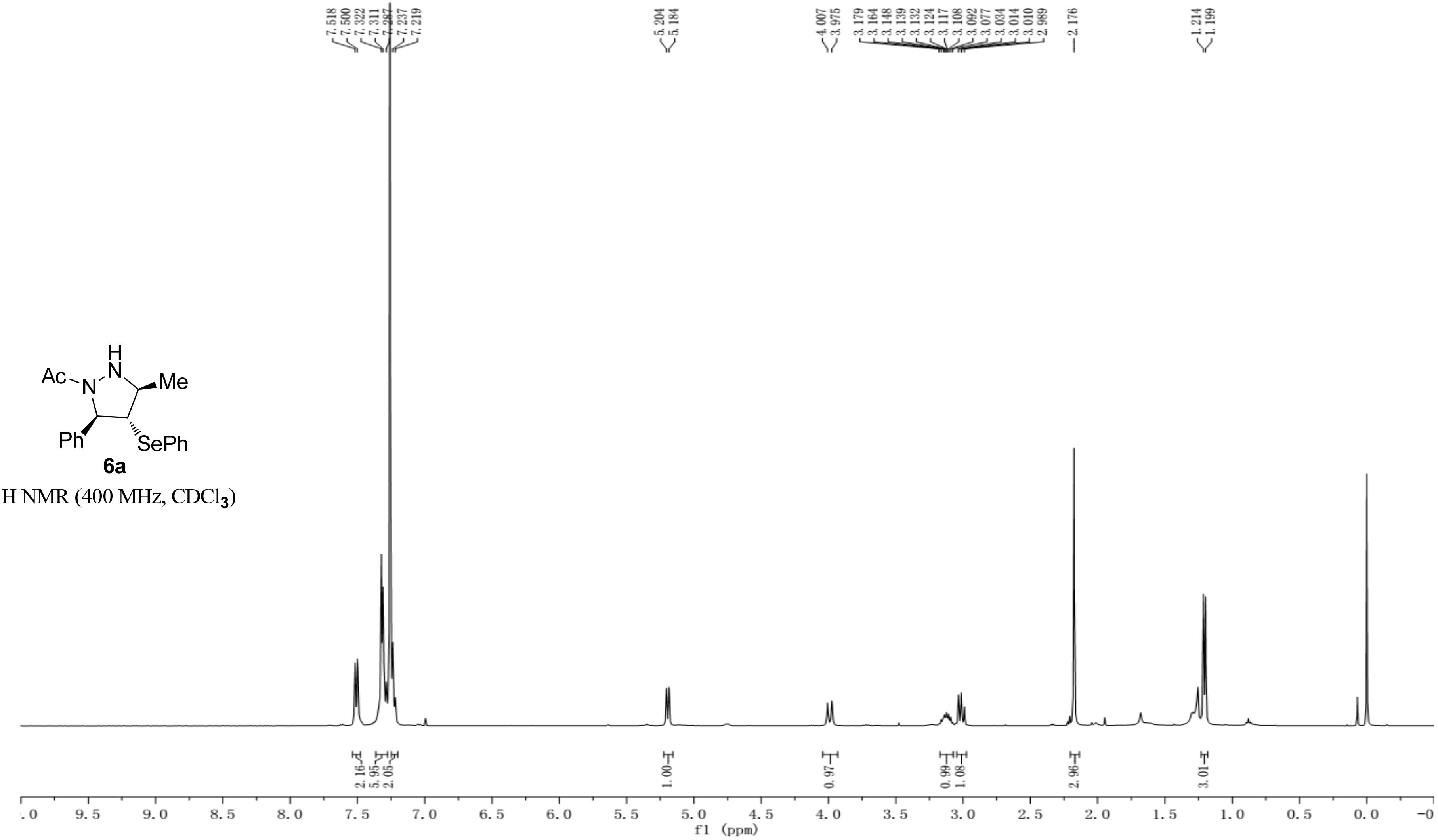




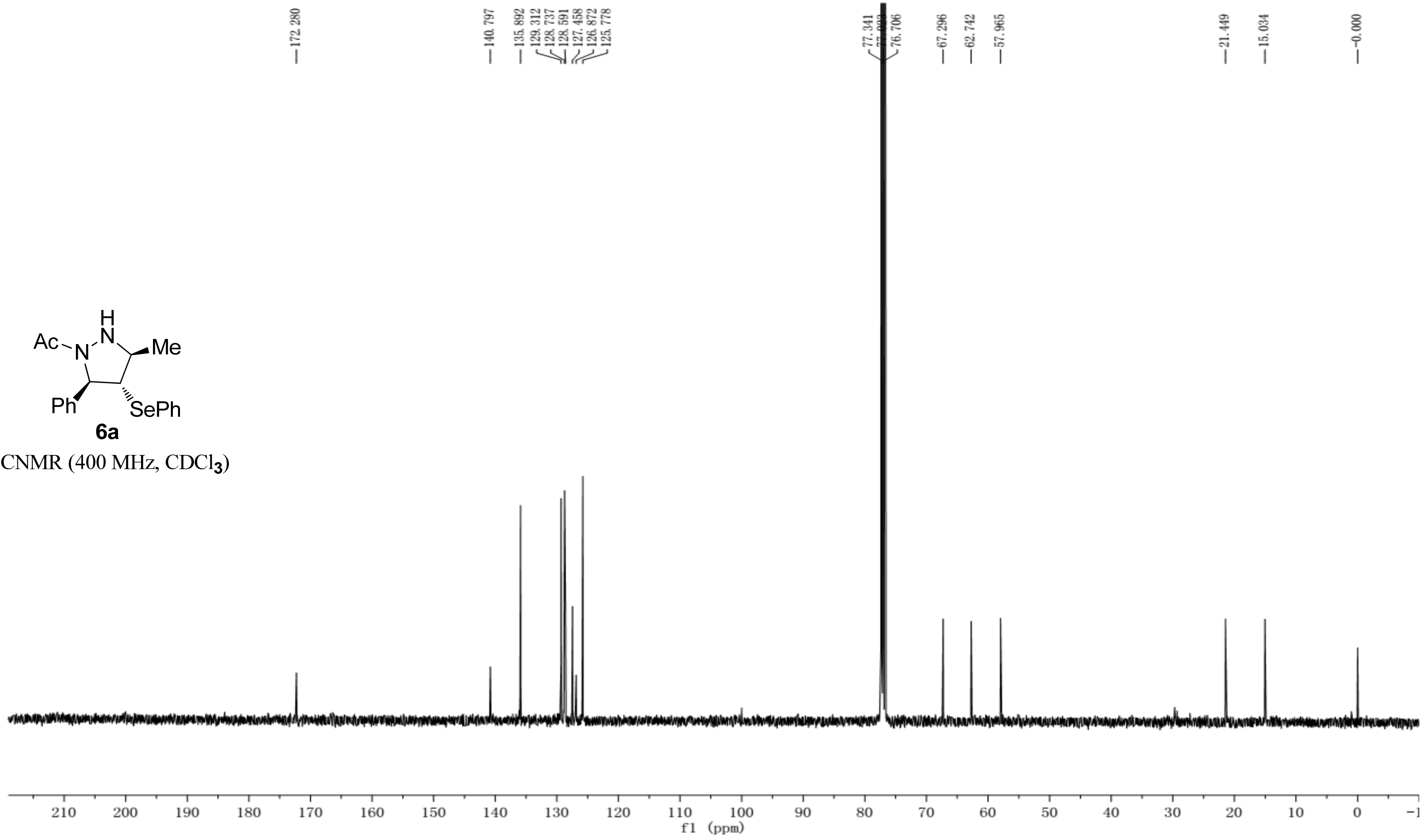
5a

^{13}C NMR (100 MHz, D$_2$O)

6a

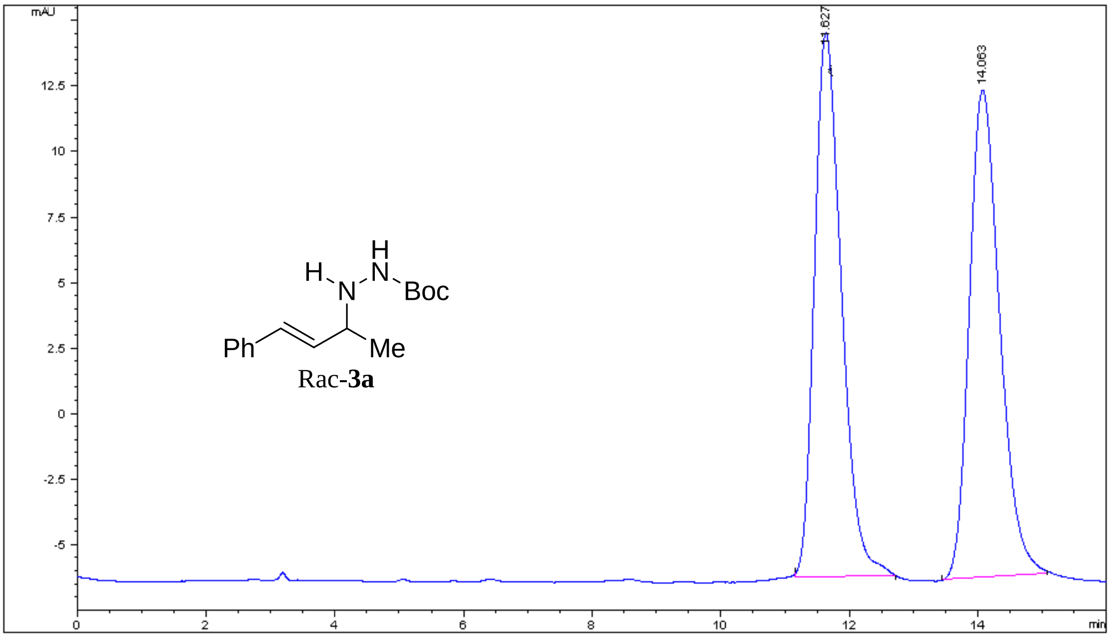


^{1}H NMR (400 MHz, $CDCl_3$)

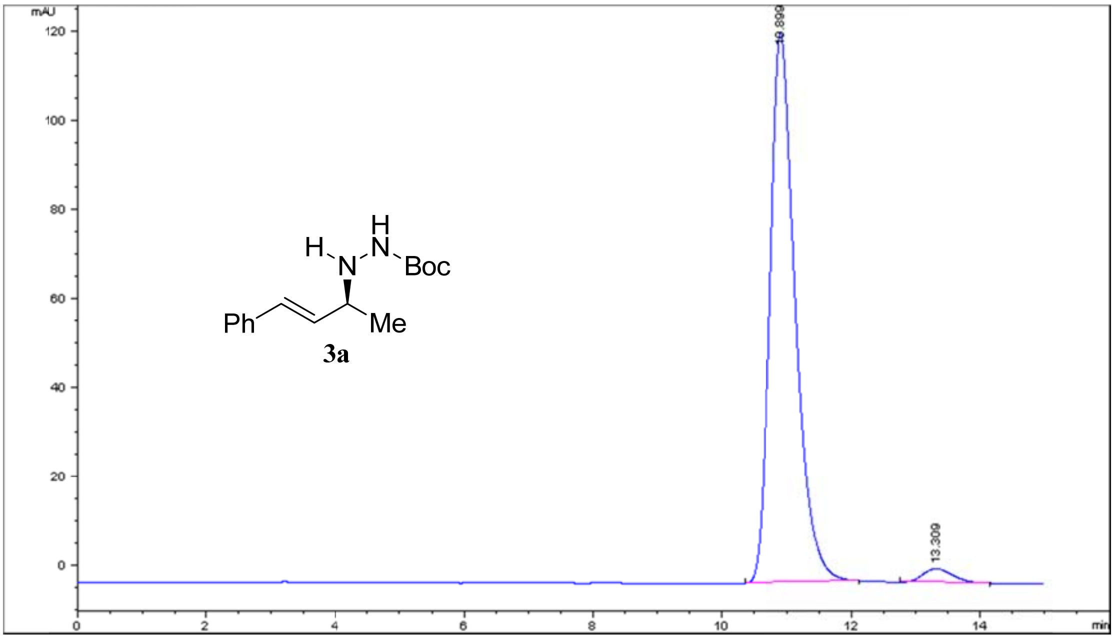


6a

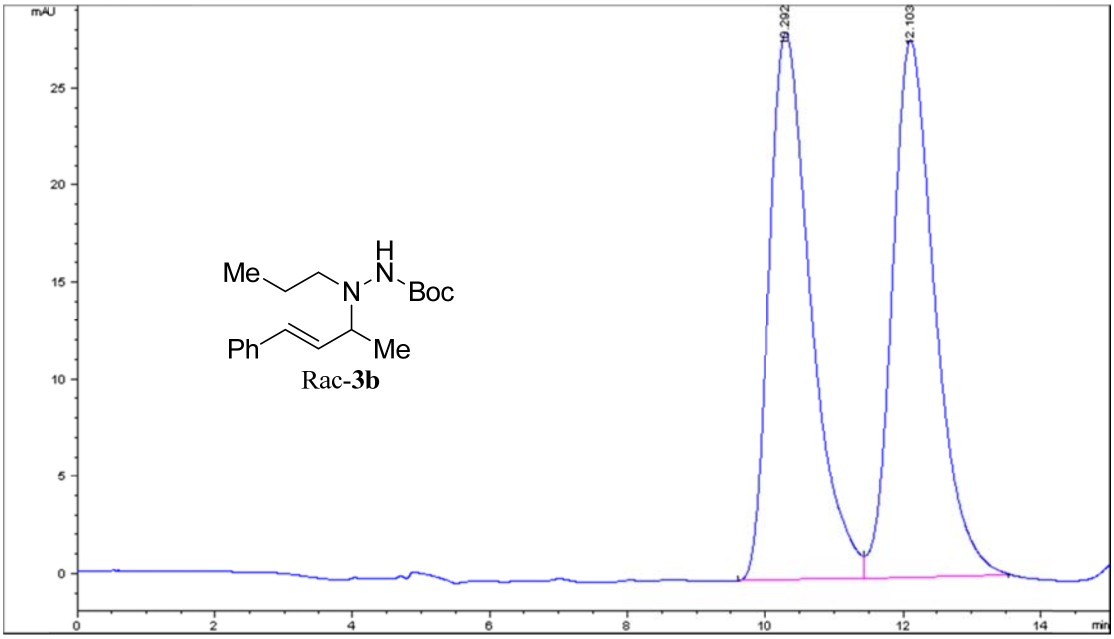
^{13}CNMR (400 MHz, CDCl$_3$)



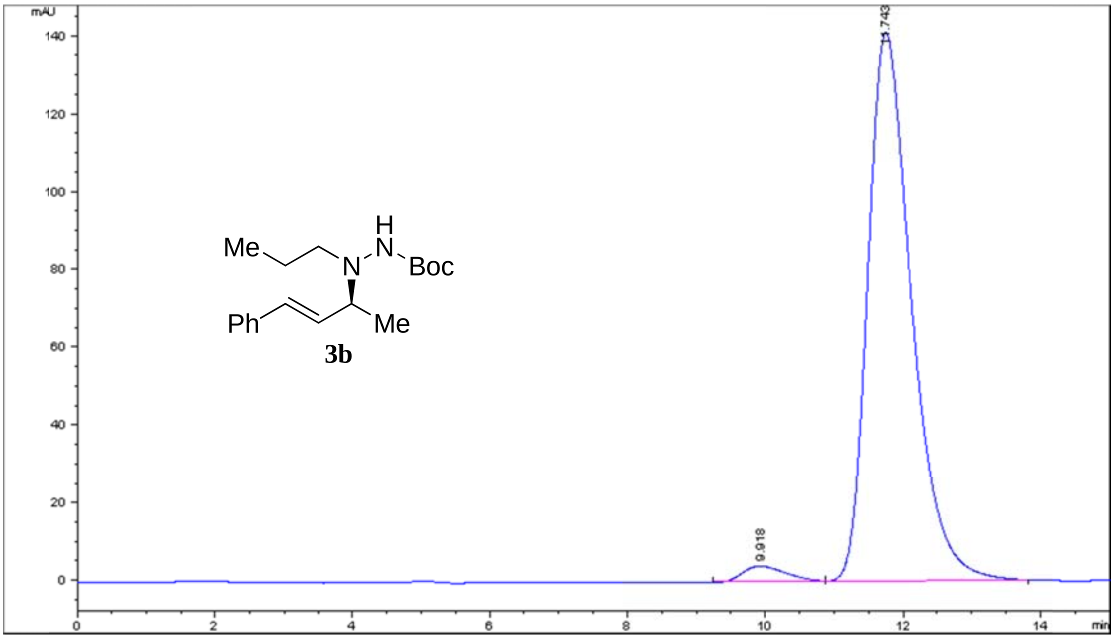
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.627	605.6	20.8	0.4856	0.707	49.739
2	14.063	612	18.6	0.5038	0.734	50.261



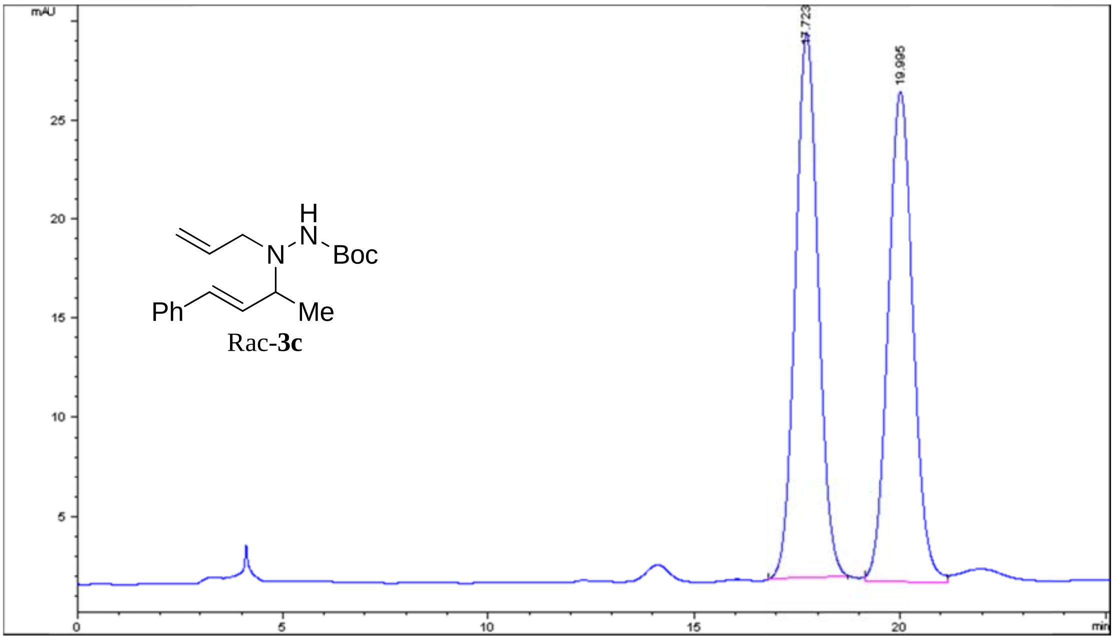
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.899	3355.6	123.6	0.41	0.675	97.086
2	13.309	100.7	3.1	0.4962	0.759	2.941



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.292	1186.3	28.2	0.6413	0.616	49.678
2	12.103	1201.7	27.7	0.6598	0.698	50.322

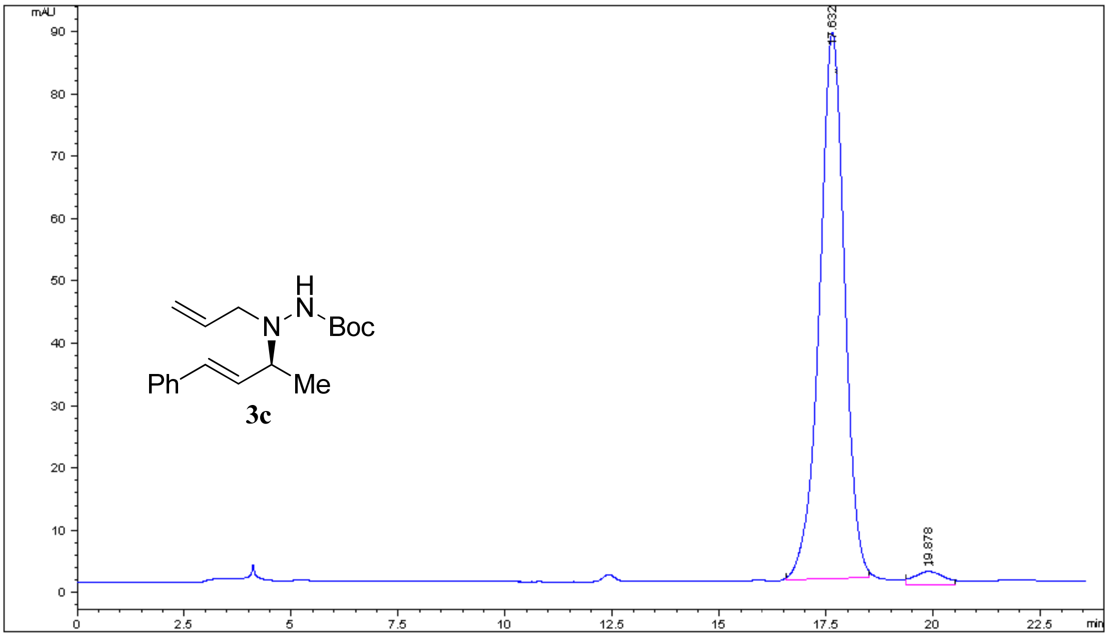


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.918	183.7	4.1	0.6256	0.643	2.854
2	11.743	6252.6	141	0.673	0.646	97.146



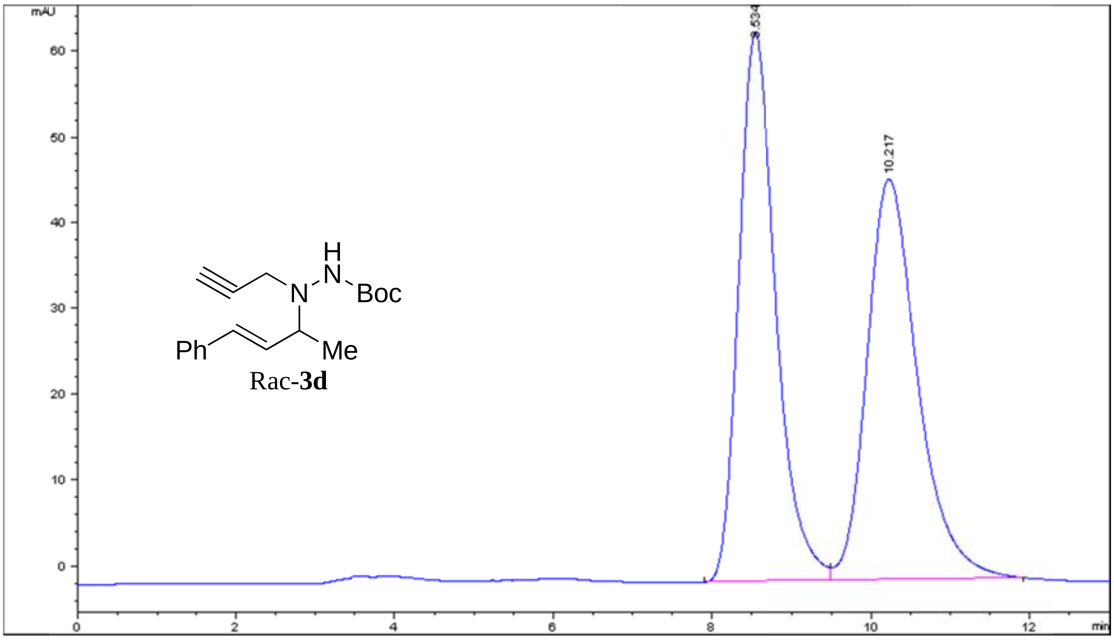
Rac-**3c**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.723	1061.9	27.5	0.5958	0.931	50.117
2	19.995	1056.9	24.8	0.7109	0.913	49.883

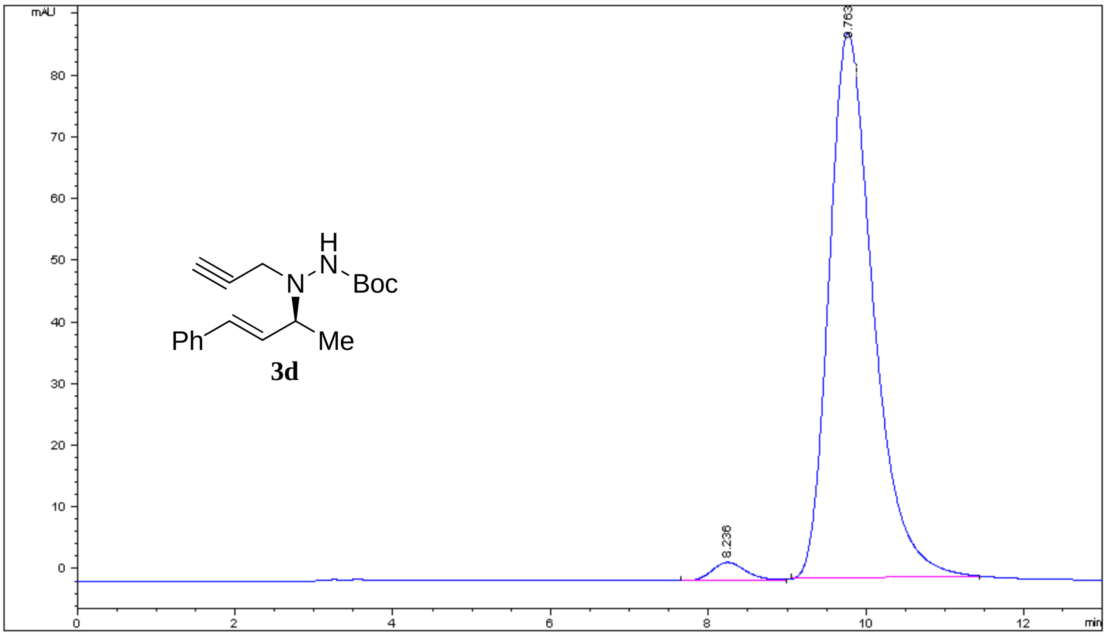


3c

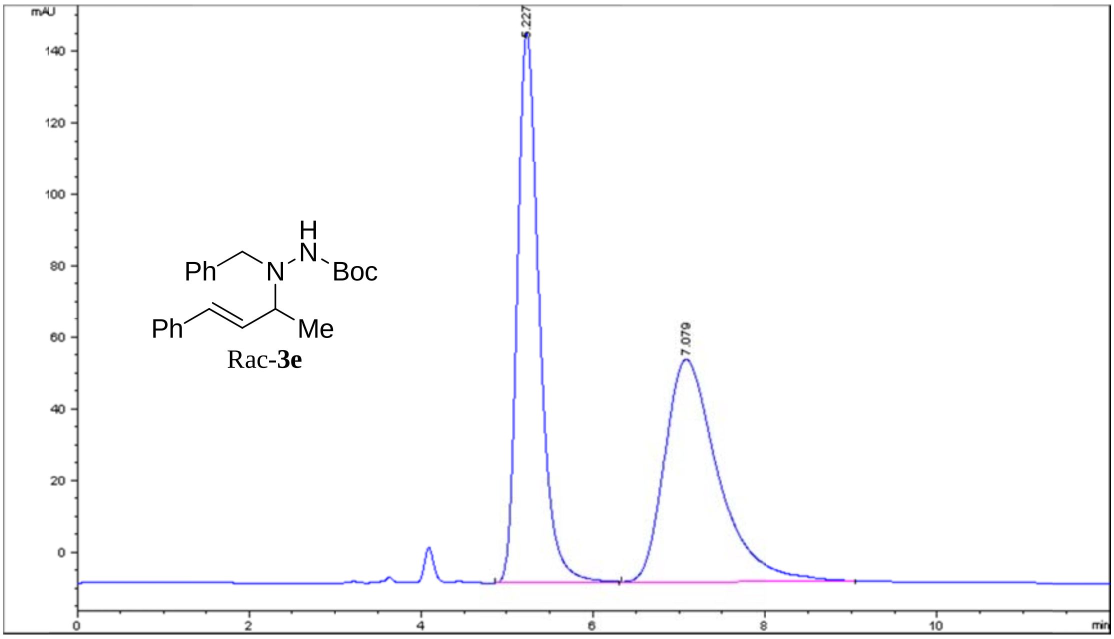
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.632	3569.7	87.6	0.679	1.043	97.110
2	19.878	106.2	2.2	0.8039	0.877	2.890



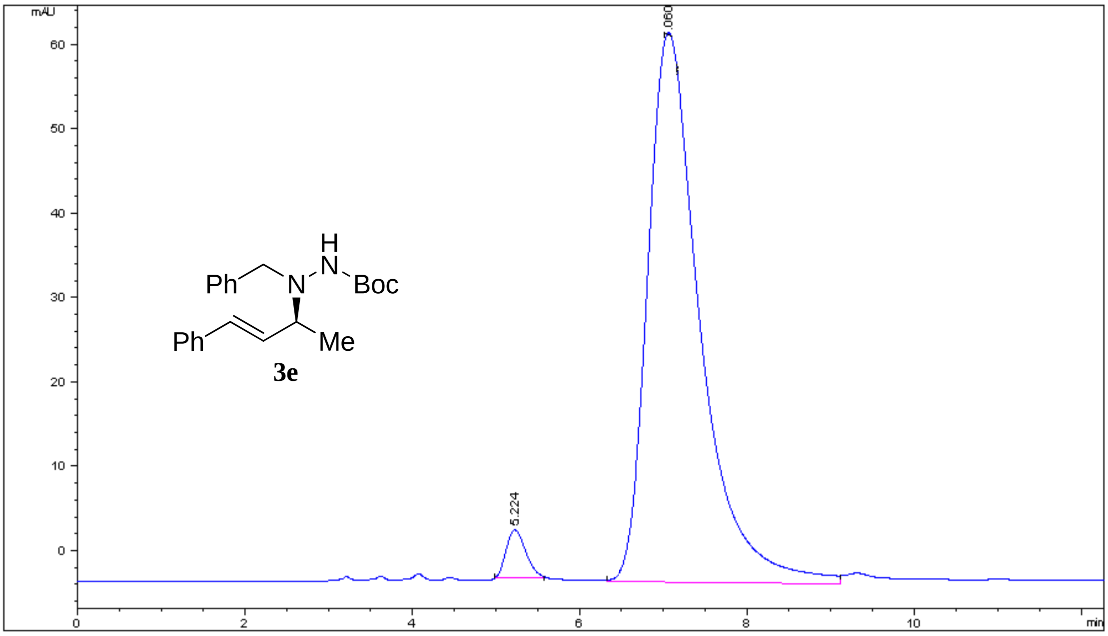
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.534	2083	63.9	0.5009	0.74	50.041
2	10.217	2079.6	46.7	0.6755	0.71	49.959



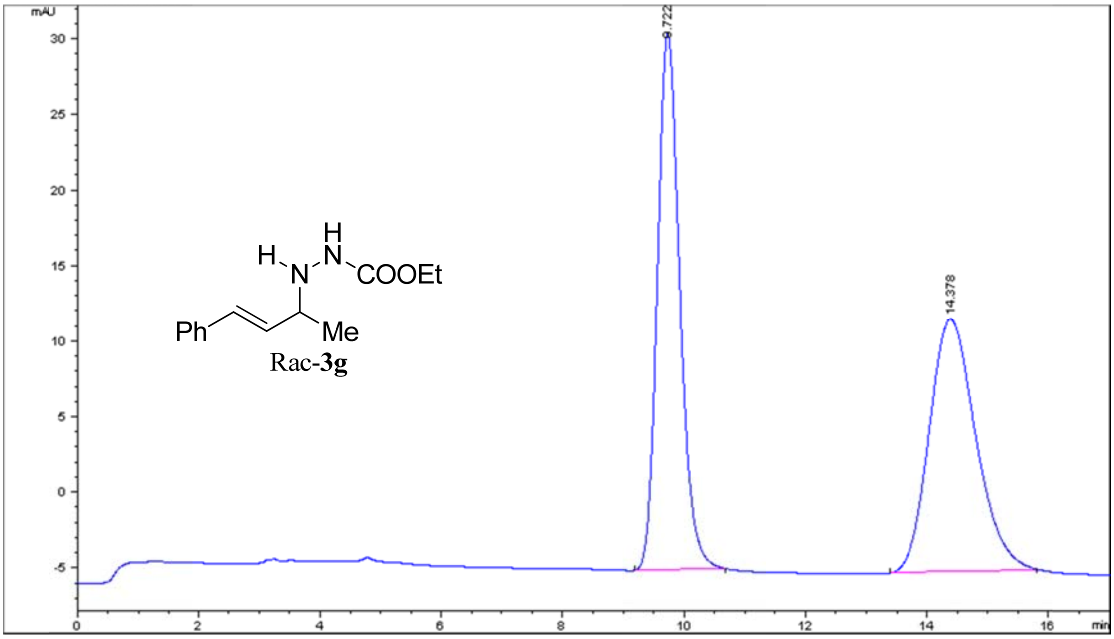
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.236	97.5	3	0.5329	0.809	2.756
2	9.763	3440.1	88.4	0.6489	0.713	97.244


Rac-**3e**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.227	2726.5	153.5	0.2712	0.706	50.533
2	7.079	2669	62	0.6506	0.627	49.467

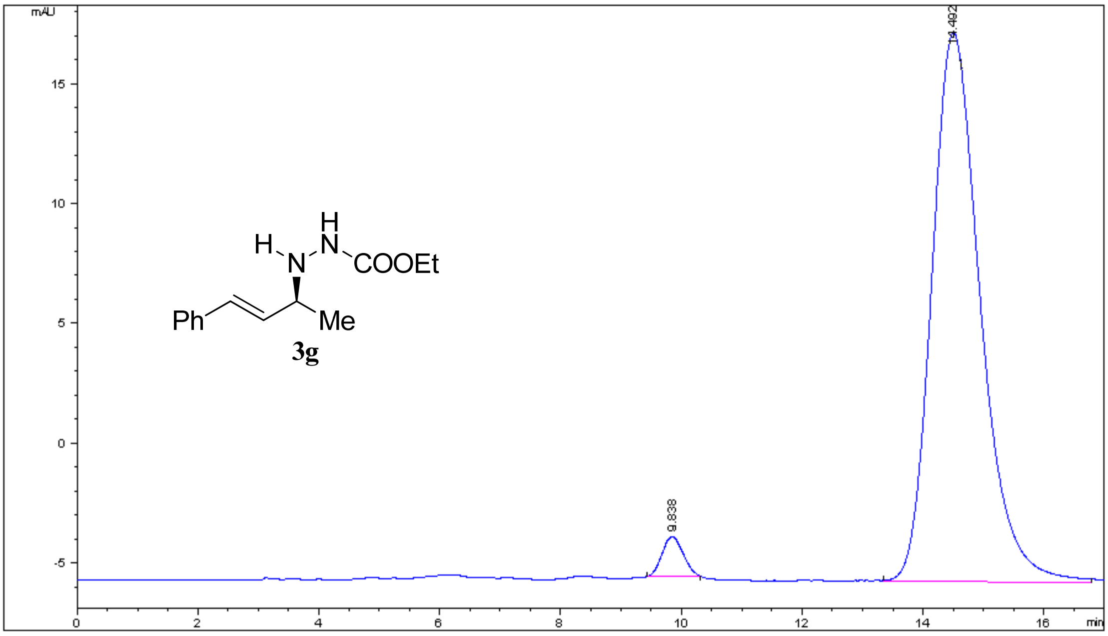

3e

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.224	94.4	5.8	0.2732	0.784	3.226
2	7.06	2831.6	65.2	0.7239	0.625	96.774



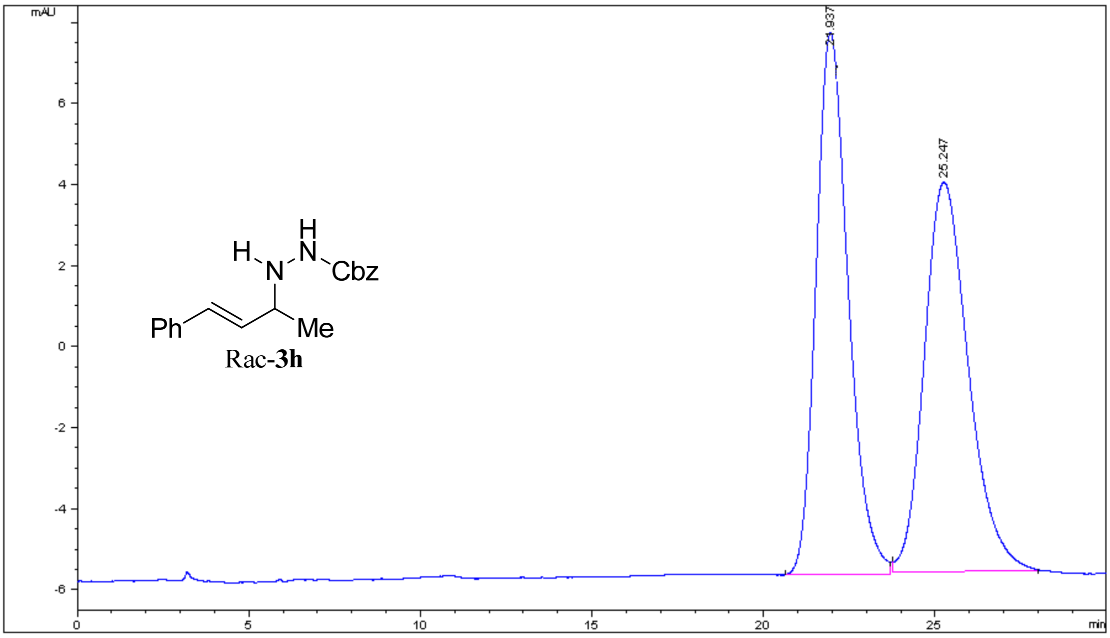
Rac-**3g**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.722	909	35.6	0.3928	0.796	50.376
2	14.378	895.5	16.7	0.8181	0.793	49.624

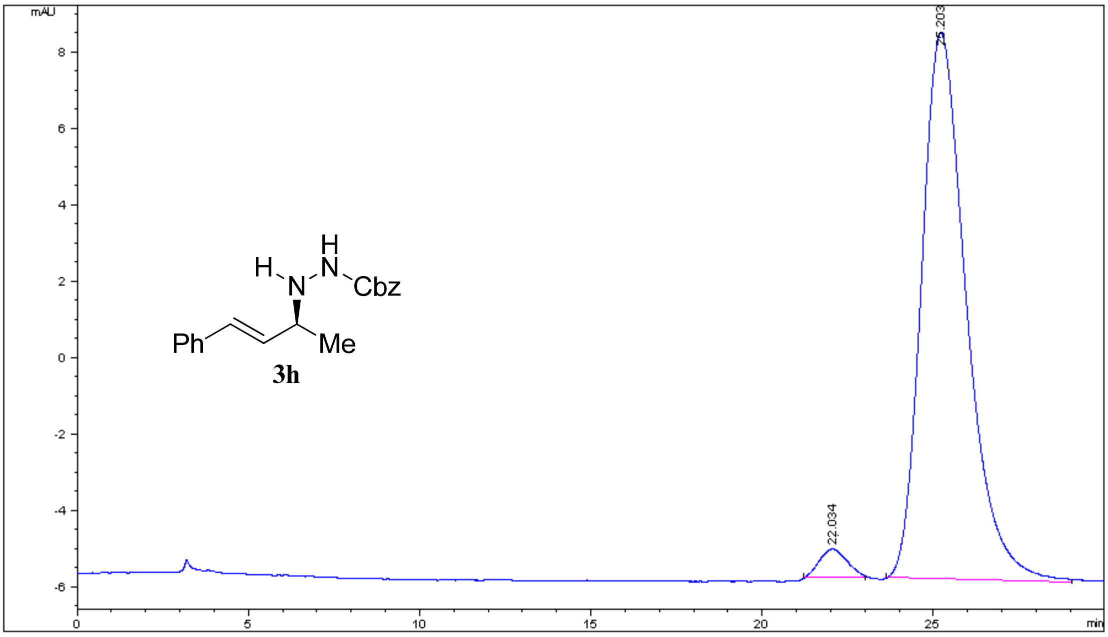


3g

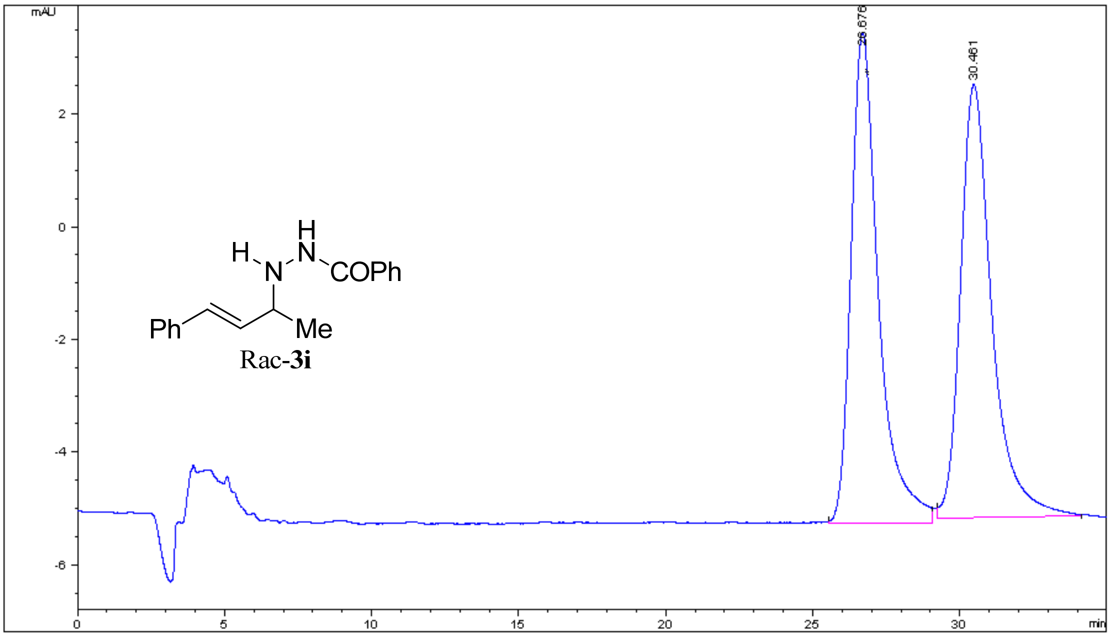
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.838	41.1	1.7	0.4079	0.868	3.125
2	14.492	1275.1	22.9	0.9278	0.765	96.875



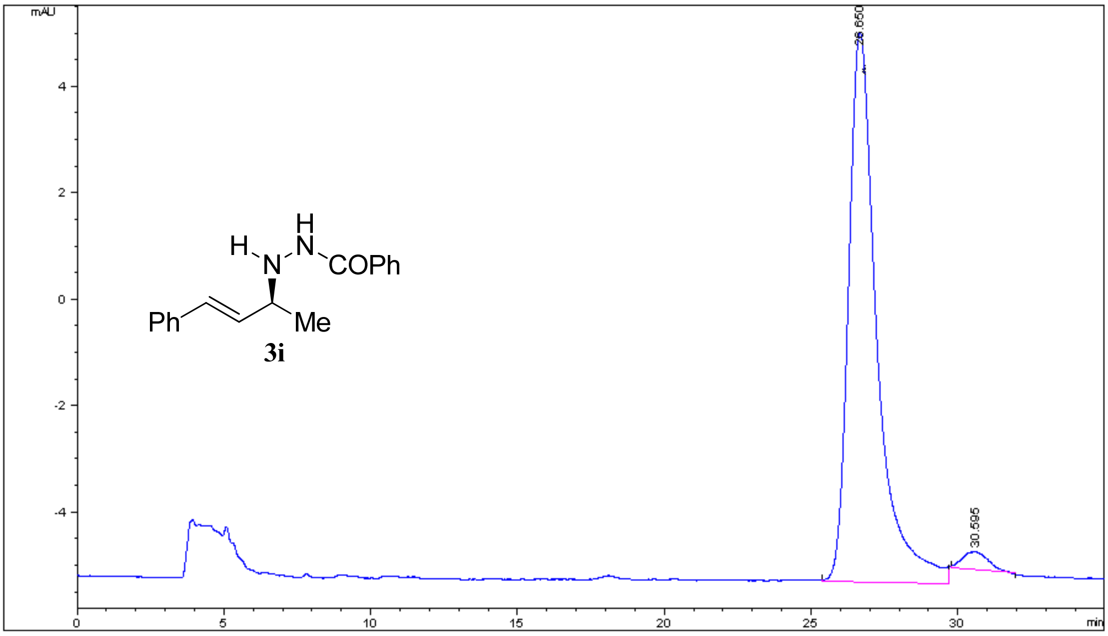
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	21.937	874.2	13.4	1.0905	0.77	50.223
2	25.247	866.4	9.6	1.4992	0.775	49.777



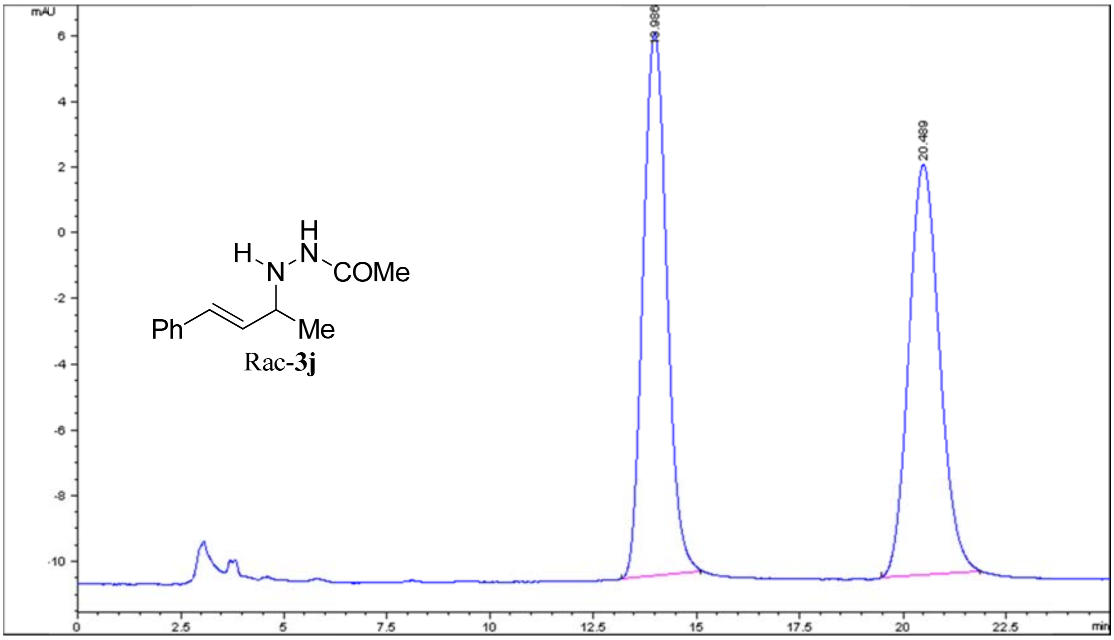
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.034	42.8	7.5E-1	0.9464	0.848	3.184
2	25.203	1301.1	14.3	1.5163	0.72	96.816



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	26.676	568.7	8.7	1.0875	0.67	49.825
2	30.461	572.7	7.7	1.2413	0.694	50.175

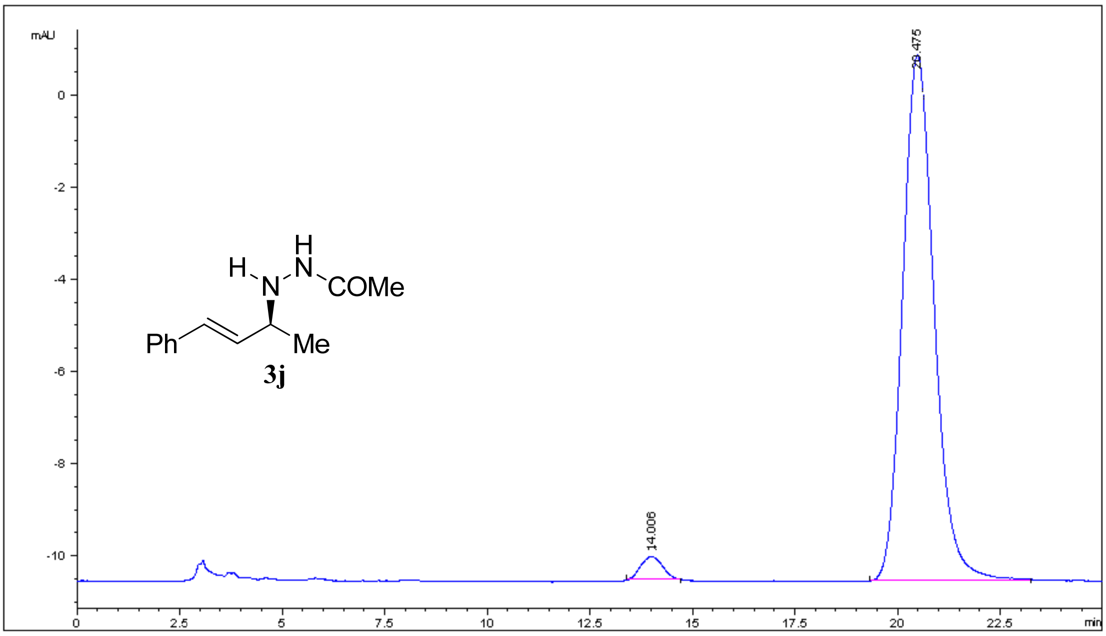


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	26.65	695.5	10.3	1.1226	0.629	97.062
2	30.595	21.1	3.4E-1	1.0317	0.993	2.938



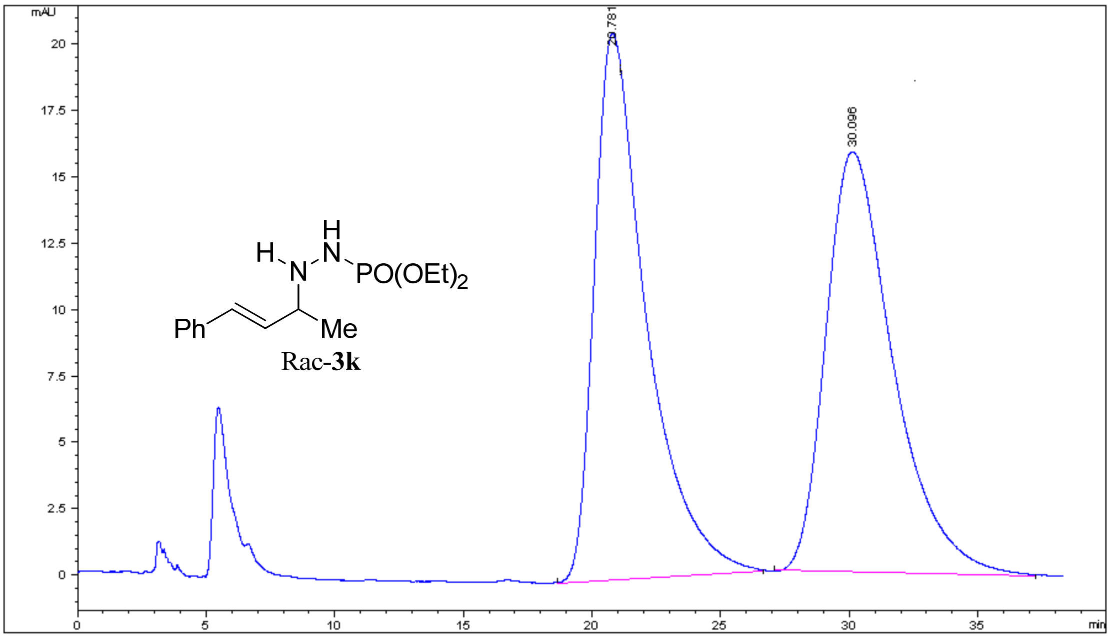
Rac-**3j**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.986	659.1	16.6	0.6306	0.903	50.082
2	20.489	656.9	12.5	0.79	0.877	49.918



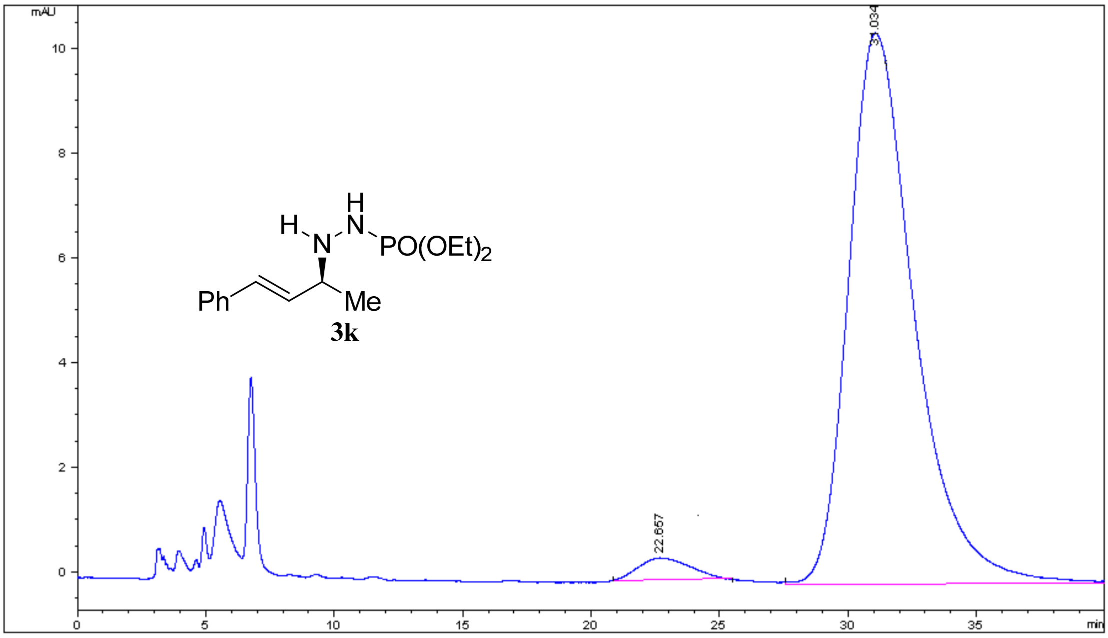
3j

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.006	18.6	5E-1	0.6185	1.014	2.951
2	20.475	613.1	11.4	0.8958	0.839	97.049



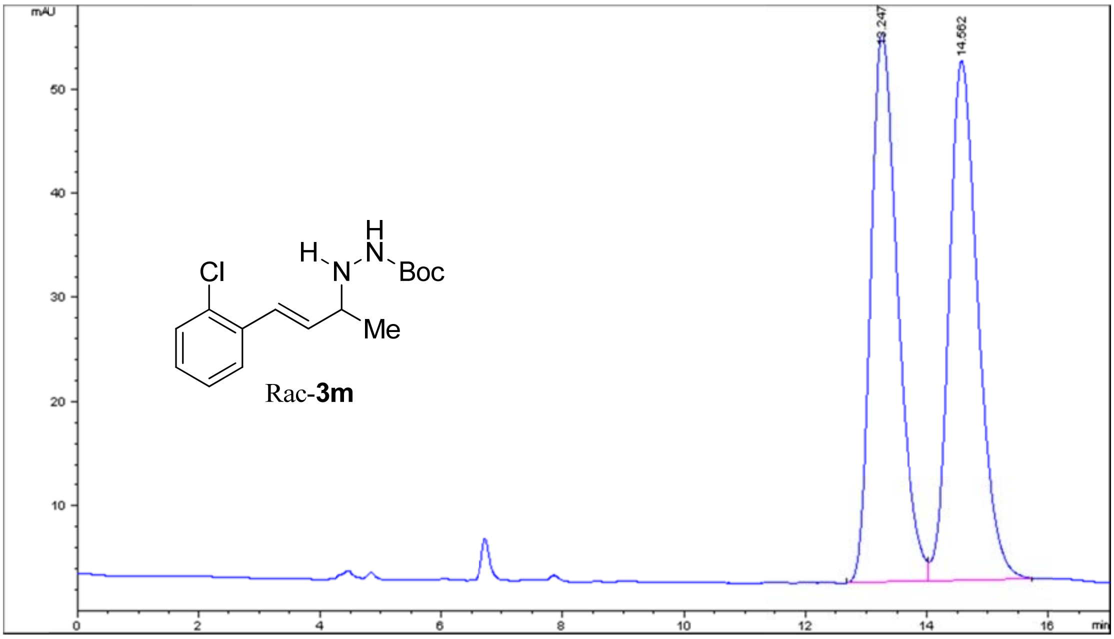
Rac-**3k**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	20.781	2912.5	20.6	2.3537	0.517	50.237
2	30.096	2885	15.8	3.0344	0.621	49.763

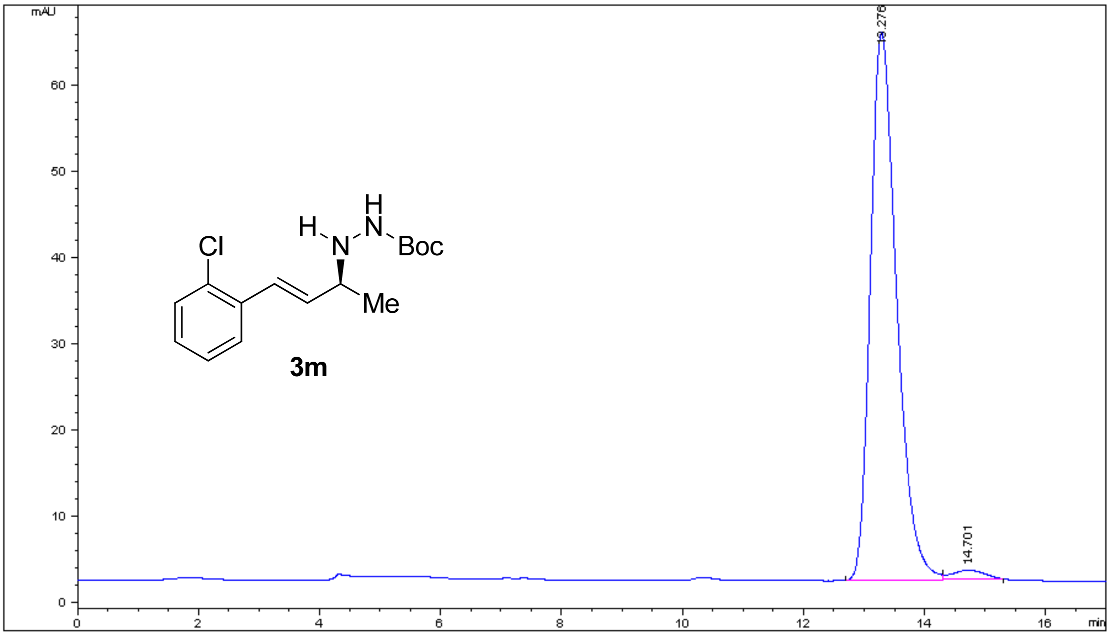


3k

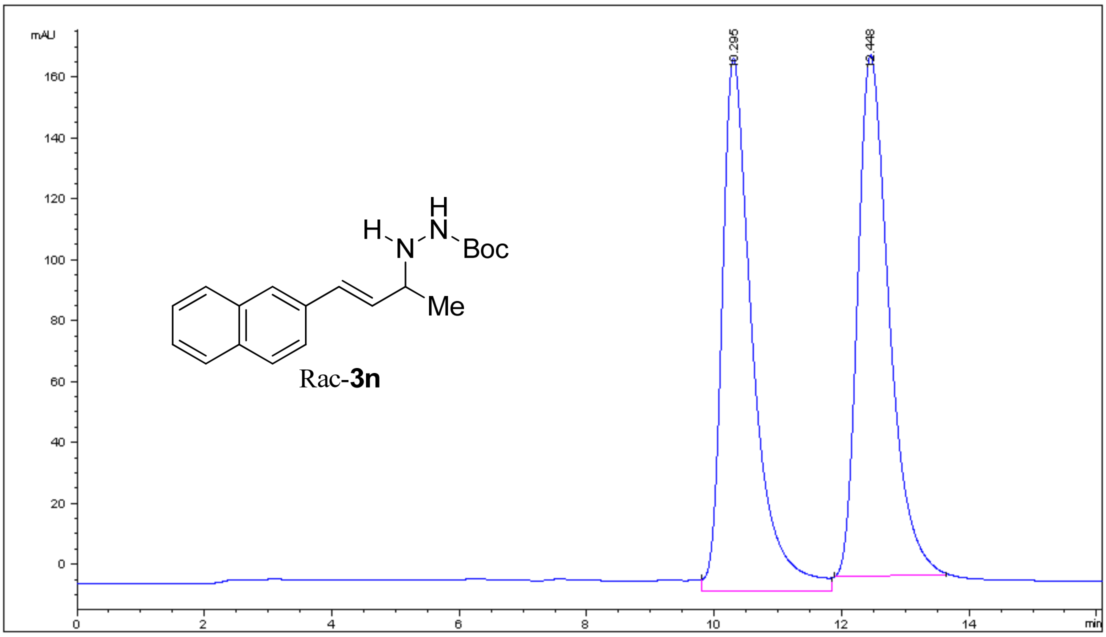
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.657	61.4	4.4E-1	2.3431	0.732	3.174
2	31.034	1874.1	10.5	2.965	0.647	96.826



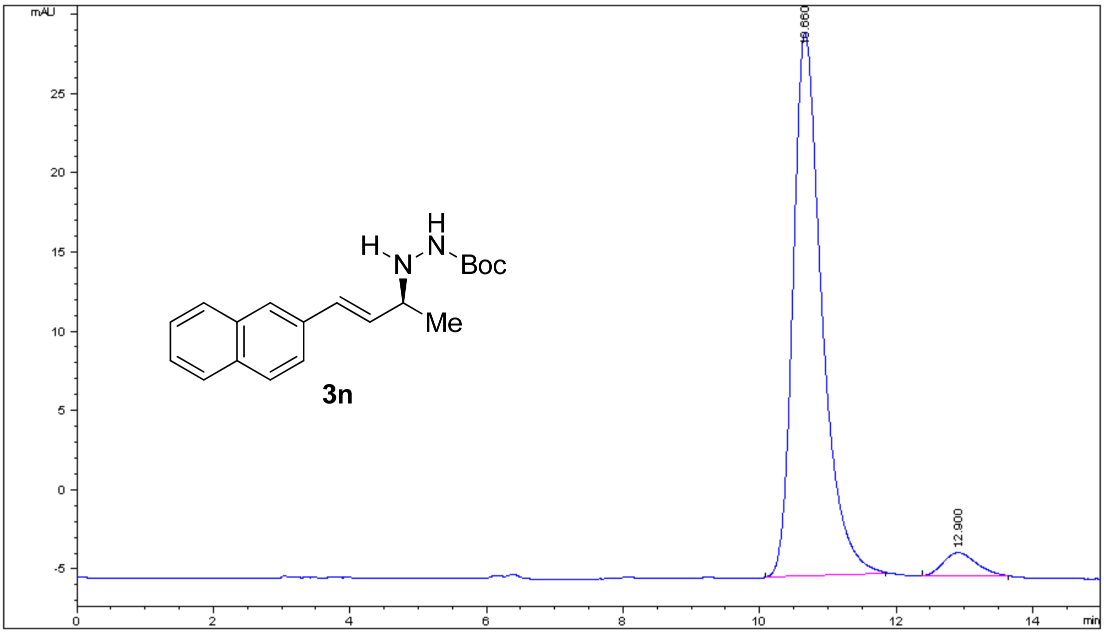
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.247	1625.4	52.6	0.4723	0.68	49.611
2	14.562	1650.9	49.8	0.5063	0.727	50.389



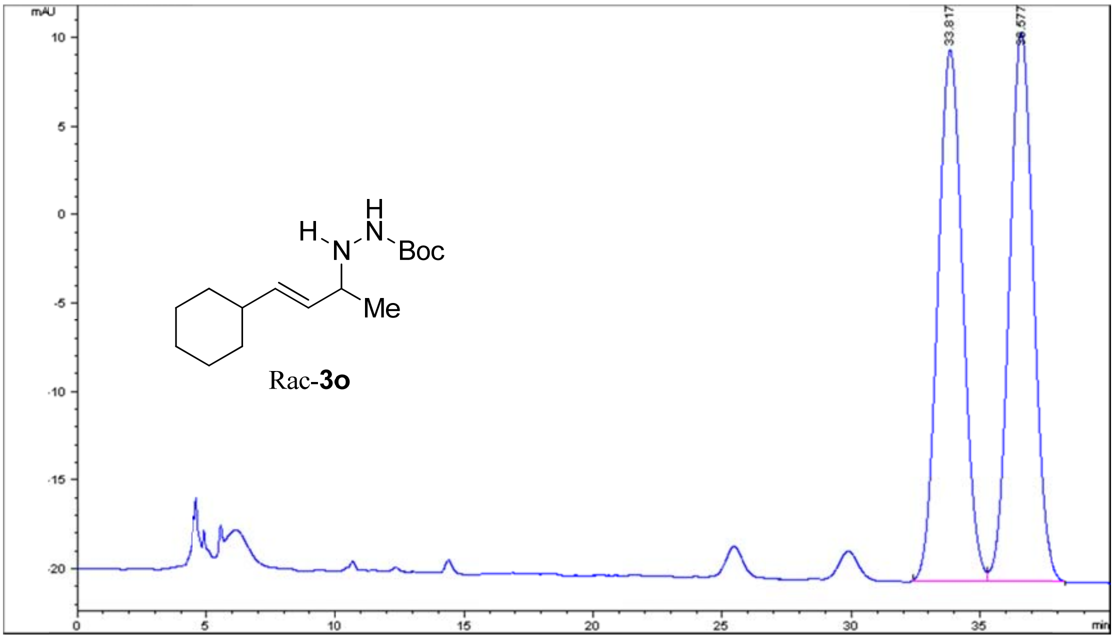
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.276	1926	63.7	0.4605	0.685	97.744
2	14.701	44.5	1.1	0.6444	0.85	2.256



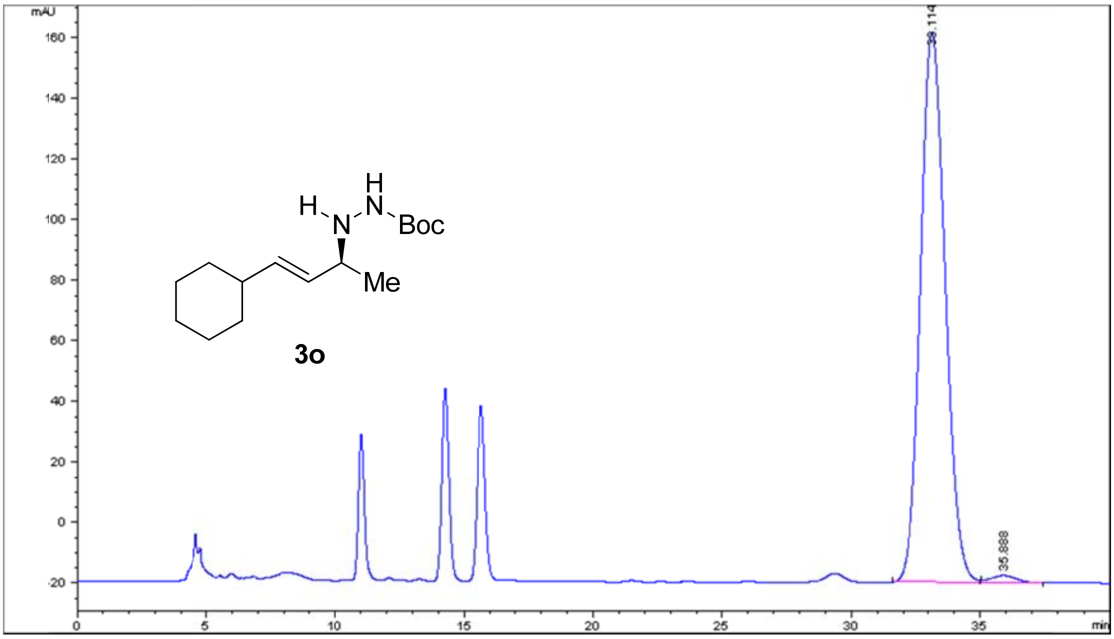
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.295	5868.5	175.3	0.5581	0.566	50.055
2	12.448	5855.6	171.2	0.57	0.673	49.945



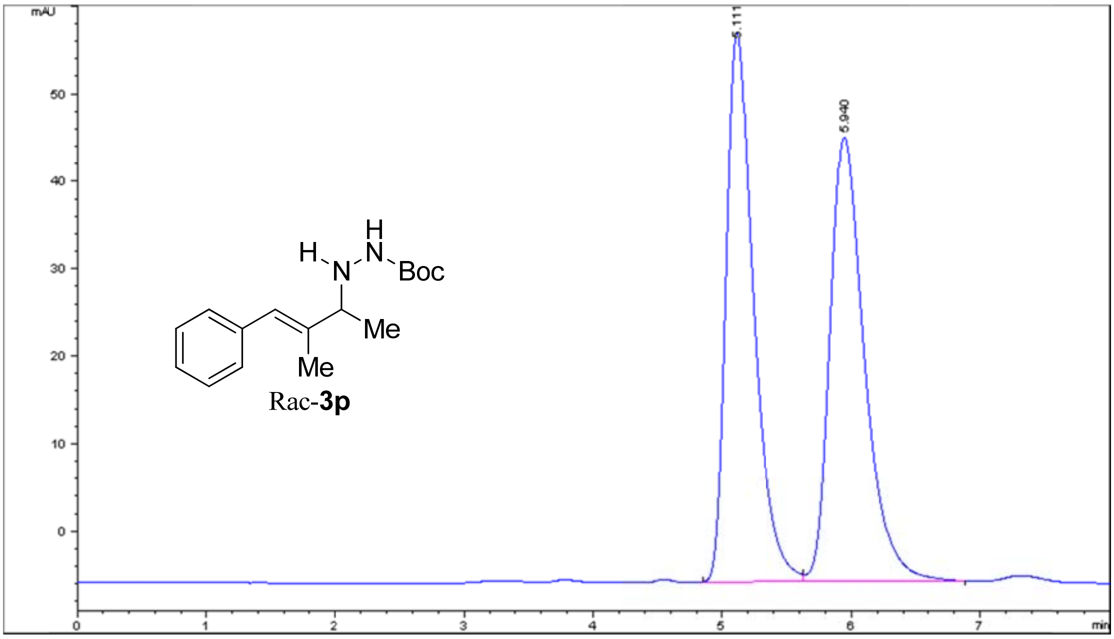
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.66	1004.6	34.3	0.4393	0.658	95.162
2	12.9	51.1	1.5	0.5735	0.775	4.838



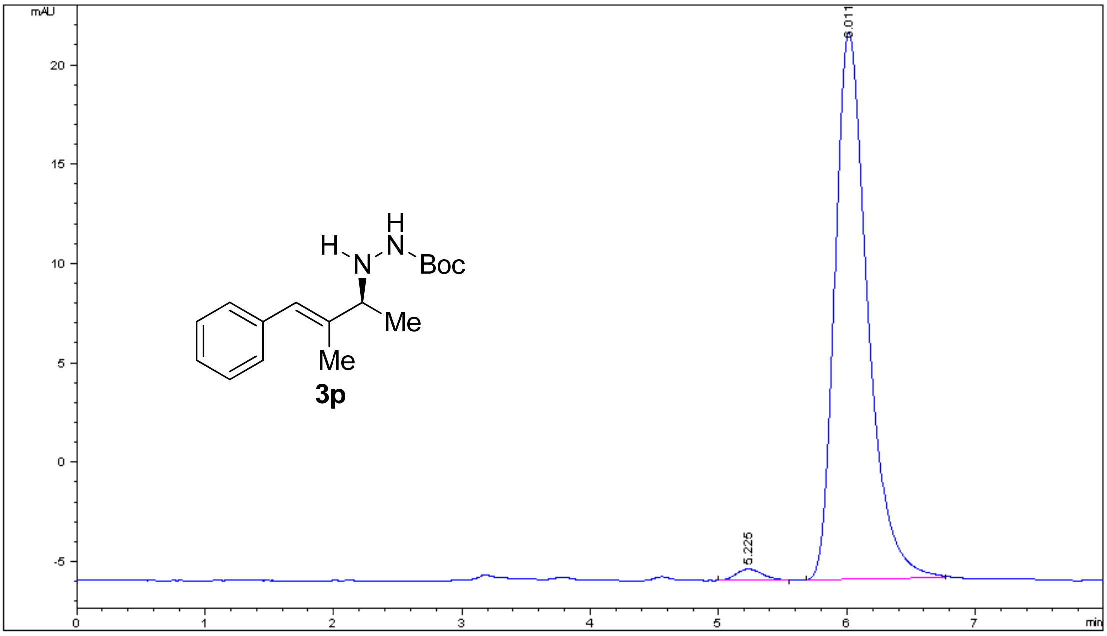
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	33.817	2015.2	30	1.0458	0.933	49.942
2	36.577	2019.9	31	0.9989	0.952	50.058



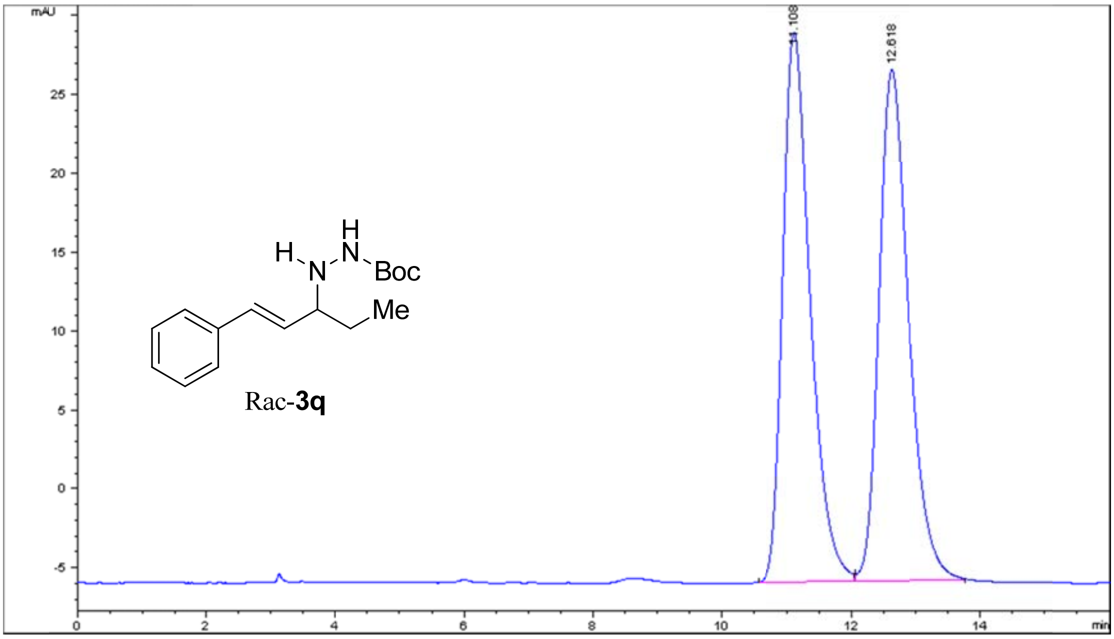
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	33.114	12136.7	181.4	1.0397	0.843	98.671
2	35.888	163.5	2.4	0.8215	1.008	1.329



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.111	934.7	62.8	0.2246	0.611	49.710
2	5.94	945.6	50.9	0.2825	0.643	50.290

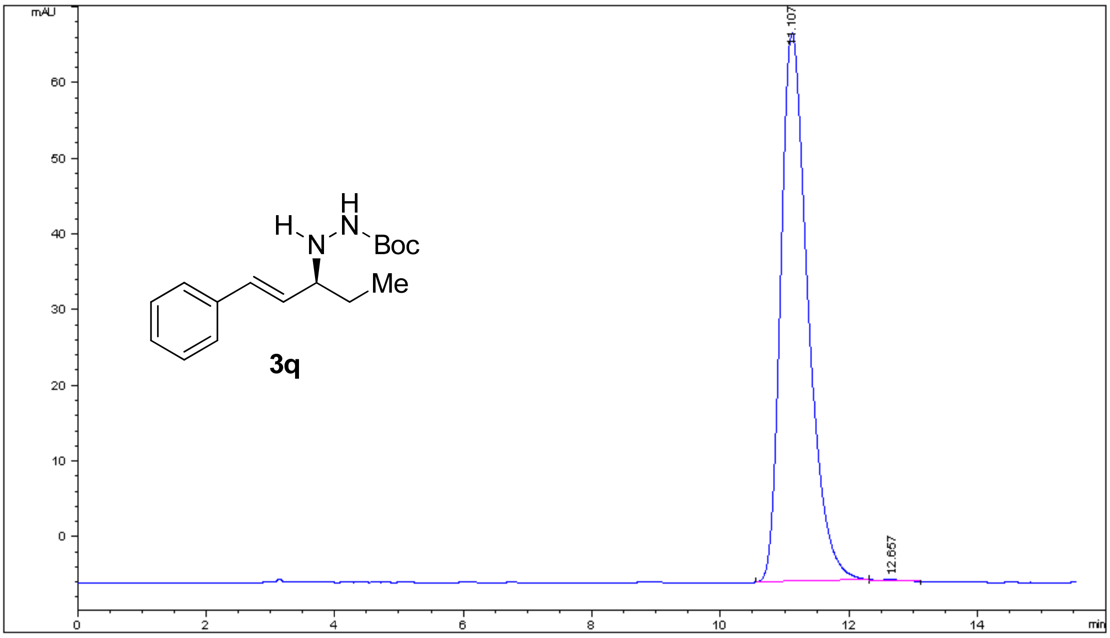


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.225	9.1	5.9E-1	0.2564	0.79	1.837
2	6.011	486.5	27.5	0.2687	0.678	98.163



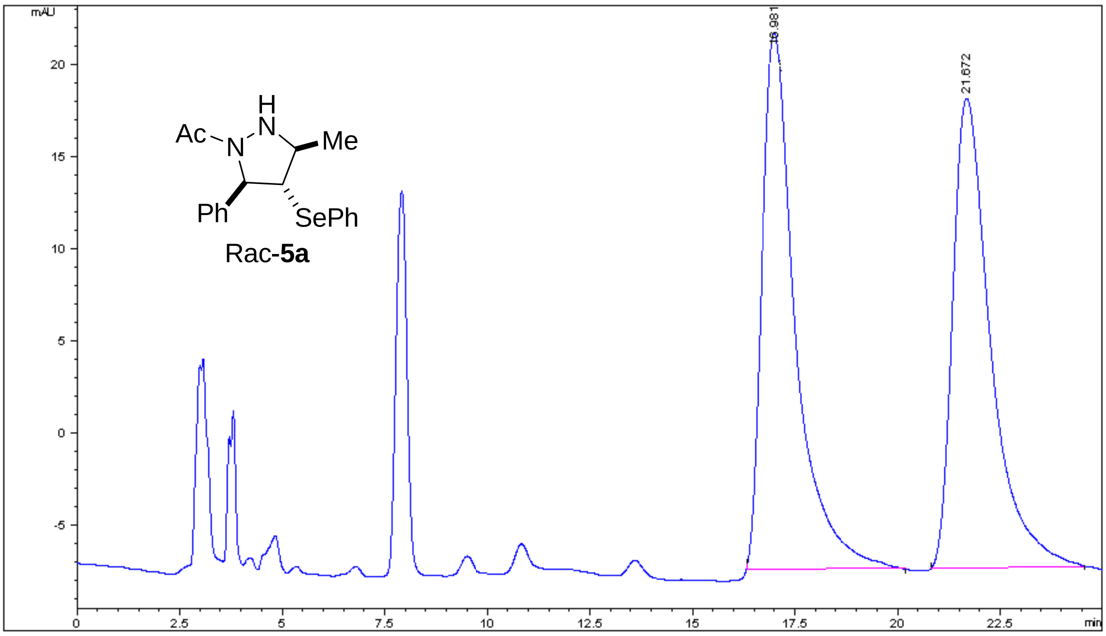
Rac-**3q**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.108	1033.3	34.8	0.4478	0.651	49.871
2	12.618	1038.6	32.4	0.4856	0.7	50.129



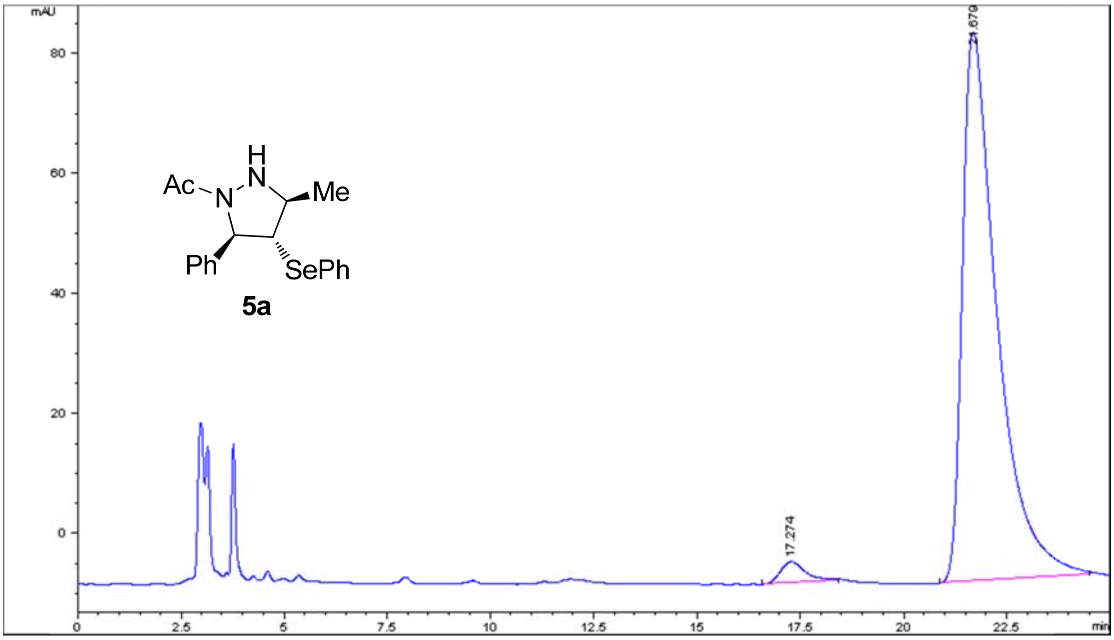
3q

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.107	2129.3	72.5	0.4446	0.655	99.637
2	12.657	7.8	2.4E-1	0.5489	1.189	0.363



Rac-**5a**

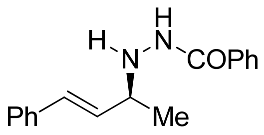
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.981	1660.1	29.1	0.9493	0.538	50.293
2	21.672	1640.7	25.5	1.0718	0.553	49.707



5a

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.274	157.9	3.5	0.6508	0.642	2.865
2	21.679	5353.4	91.4	0.861	0.41	97.135

The optical purity of compound **3i** was improved to >99% ee by recrystallization from ethyl acetate. The crystal of compound **3i** was obtained by leaving alone its solution in ethyl acetate at room temperature open to the air for several days. The absolute configuration of compound **3i** was assigned to be *S* by the single crystal X-ray analysis. The crystal data of compound **3i** have been deposited in CCDC with number 997538.



3i

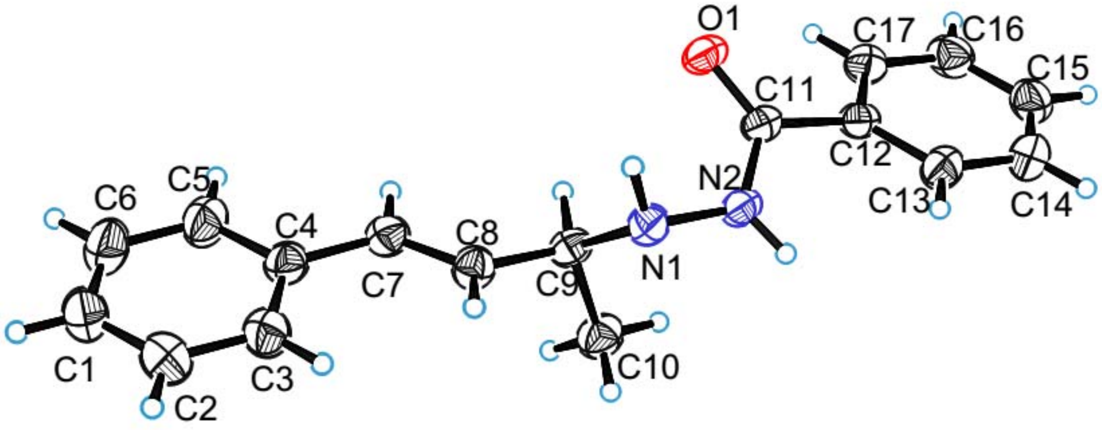


Table 1 Crystal data and structure refinement for 3i

Identification code	wy0703
Empirical formula	$C_{17}H_{18}N_2O$
Formula weight	266.33
Temperature/K	290(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.19550(10)
b/Å	8.58560(10)
c/Å	32.9171(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1468.32(4)
Z	4
ρ_{calc}mg/mm^3	1.205

m/mm^{-1}	0.597
F(000)	568.0
Crystal size/mm^3	0.36 × 0.32 × 0.27
2Θ range for data collection	10.64 to 143.58°
Index ranges	$-5 \le h \le 6$, $-10 \le k \le 10$, $-40 \le l \le 40$
Reflections collected	16033
Independent reflections	2840[R(int) = 0.0237]
Data/restraints/parameters	2840/0/186
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0316, wR_2 = 0.1036
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.1062
Largest diff. peak/hole / e Å^{-3}	0.14/-0.11
Flack parameter	-0.1(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for wy0703. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2094.2(16)	4569.1(11)	5541.0(3)	57.5(2)
N1	6296.4(19)	3651.6(11)	5074.5(3)	46.7(2)
N2	6361.9(18)	4143.2(11)	5485.0(3)	49.3(2)
C11	4256(2)	4595.4(12)	5690.5(3)	45.1(2)
C16	3195(3)	6660.1(18)	6684.1(4)	68.9(4)
C12	4674(2)	5110.8(13)	6121.1(3)	47.0(3)
C10	8270(3)	6113.0(16)	4853.7(4)	64.6(3)
C17	2961(3)	6180.6(15)	6283.9(4)	58.3(3)
C14	6815(3)	4985(2)	6766.9(4)	69.8(4)
C7	4532(3)	4915.0(16)	4076.6(4)	55.7(3)
C3	6512(3)	3542.6(19)	3476.3(4)	67.7(4)
C15	5111(3)	6055.6(18)	6924.6(4)	69.9(4)
C8	6047(3)	4402.8(13)	4366.4(3)	52.3(3)
C9	6034(2)	5001.1(12)	4794.4(3)	47.4(3)
C13	6621(3)	4514.8(16)	6364.2(4)	59.5(3)
C2	6569(3)	3228(2)	3064.3(4)	80.7(5)
C4	4662(2)	4529.6(14)	3641.3(4)	54.9(3)
C5	2887(3)	5194(2)	3377.4(4)	73.1(4)
C1	4798(4)	3908(2)	2806.9(4)	83.4(5)
C6	2976(4)	4883(3)	2963.7(5)	86.4(5)

Table 3 Anisotropic Displacement Parameters ($Å^2\times10^3$) for wy0703. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	36.7(4)	74.2(5)	61.6(5)	-4.9(4)	-5.1(3)	0.9(4)
N1	43.8(5)	47.9(4)	48.5(4)	-3.3(4)	-2.7(4)	0.3(4)
N2	36.4(5)	62.7(5)	48.9(4)	-6.1(4)	-4.3(4)	2.2(4)
C11	37.1(5)	44.8(5)	53.4(5)	1.6(4)	-3.0(4)	-1.7(4)
C16	66.6(9)	76.9(8)	63.2(7)	-10.1(6)	13.1(6)	1.2(8)
C12	39.5(6)	49.6(5)	51.8(5)	1.6(4)	2.2(4)	-3.1(5)
C10	60.1(8)	59.6(6)	74.2(7)	5.3(6)	-8.8(6)	-12.2(6)
C17	50.4(6)	65.7(6)	58.6(6)	-1.8(5)	3.8(5)	3.8(6)
C14	64.2(8)	87.9(9)	57.4(6)	4.9(7)	-11.8(6)	-1.7(8)
C7	47.5(7)	61.3(6)	58.4(6)	3.7(5)	-1.0(5)	2.5(6)
C3	62.9(8)	80.8(8)	59.4(6)	4.9(6)	-1.3(6)	7.0(8)
C15	71.6(9)	88.3(9)	49.8(6)	-6.3(6)	4.5(6)	-13.9(8)
C8	51.9(7)	51.2(5)	53.7(6)	-0.1(4)	-2.1(5)	4.9(5)
C9	40.7(6)	46.0(5)	55.4(5)	-2.1(4)	-2.8(4)	4.4(5)
C13	51.4(7)	68.0(6)	58.9(6)	1.0(5)	-6.0(5)	4.7(6)
C2	75.6(10)	101.8(11)	64.6(8)	-3.9(8)	9.7(8)	1.2(10)
C4	49.7(6)	58.8(6)	56.2(6)	7.9(5)	-3.2(5)	-6.1(6)
C5	68.9(8)	83.8(8)	66.6(7)	6.0(7)	-14.0(7)	9.0(8)
C1	85.3(11)	111.3(12)	53.7(7)	3.3(8)	-2.8(7)	-18.5(11)
C6	84.7(11)	107.3(12)	67.1(8)	13.0(8)	-21.6(8)	-1.3(11)

Table 4 Bond Lengths for wy0703.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C11	1.2264(14)	C14	C13	1.3896(18)
N1	N2	1.4161(12)	C7	C8	1.3128(18)
N1	C9	1.4870(14)	C7	C4	1.4721(17)
N2	C11	1.3436(15)	C3	C2	1.3833(19)
C11	C12	1.5006(15)	C3	C4	1.391(2)
C16	C17	1.3854(17)	C8	C9	1.4997(15)
C16	C15	1.373(2)	C2	C1	1.380(2)
C12	C17	1.3871(17)	C4	C5	1.3898(18)
C12	C13	1.3874(17)	C5	C6	1.389(2)
C10	C9	1.5162(17)	C1	C6	1.365(3)
C14	C15	1.378(2)			

Table 5 Bond Angles for wy0703.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C9	111.20(8)	C16	C15	C14	120.04(12)
C11	N2	N1	123.15(9)	C7	C8	C9	124.41(11)
O1	C11	N2	122.58(10)	N1	C9	C10	109.91(9)
O1	C11	C12	121.14(10)	N1	C9	C8	108.37(9)
N2	C11	C12	116.27(9)	C8	C9	C10	109.44(10)
C15	C16	C17	119.96(13)	C12	C13	C14	119.73(13)
C17	C12	C11	117.86(10)	C1	C2	C3	120.31(16)
C17	C12	C13	119.29(11)	C3	C4	C7	123.27(11)
C13	C12	C11	122.80(10)	C5	C4	C7	119.04(12)
C16	C17	C12	120.52(12)	C5	C4	C3	117.68(12)
C15	C14	C13	120.45(14)	C6	C5	C4	120.78(15)
C8	C7	C4	127.18(12)	C6	C1	C2	119.32(13)
C2	C3	C4	121.10(13)	C1	C6	C5	120.79(15)

Table 6 Hydrogen Bonds for wy0703.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	O1[1]	0.86	2.26	3.0062(13)	145.1

[1]

Table 7 Torsion Angles for wy0703.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C11	C12	C17	-28.94(17)	C3	C2	C1	C6	-0.6(3)
O1	C11	C12	C13	148.29(13)	C3	C4	C5	C6	-0.3(2)
N1	N2	C11	O1	2.40(17)	C15	C16	C17	C12	-1.1(2)
N1	N2	C11	C12	-178.84(9)	C15	C14	C13	C12	-0.9(2)
N2	N1	C9	C10	58.97(12)	C8	C7	C4	C3	-0.7(2)
N2	N1	C9	C8	178.53(9)	C8	C7	C4	C5	-179.74(14)
N2	C11	C12	C17	152.29(11)	C9	N1	N2	C11	76.24(13)
N2	C11	C12	C13	-30.48(16)	C13	C12	C17	C16	0.5(2)
C11	C12	C17	C16	177.79(12)	C13	C14	C15	C16	0.3(2)
C11	C12	C13	C14	-176.66(12)	C2	C3	C4	C7	-179.38(15)
C17	C16	C15	C14	0.7(2)	C2	C3	C4	C5	-0.4(2)
C17	C12	C13	C14	0.5(2)	C2	C1	C6	C5	-0.1(3)
C7	C8	C9	N1	138.73(13)	C4	C7	C8	C9	171.51(12)

C7	C8	C9	C10	-101.41(15)	C4	C3	C2	C1	0.8(3)
C7	C4	C5	C6	178.78(16)	C4	C5	C6	C1	0.5(3)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for wy0703.

Atom	*x*	*y*	*z*	U(eq)
H2	7820	4153	5609	59
H16	2056	7391	6790	83
H10A	9860	5567	4811	97
H10B	8229	6522	5125	97
H10C	8136	6953	4662	97
H17	1644	6579	6123	70
H14	8104	4575	6931	84
H7	3232	5597	4155	67
H3	7729	3087	3646	81
H15	5257	6369	7194	84
H8	7208	3616	4302	63
H9	4410	5544	4848	57
H13	7791	3803	6258	71
H2A	7807	2555	2960	97
H5	1623	5855	3479	88
H1A	4846	3704	2530	100
H6	1780	5344	2791	104
H1	4920(40)	3012(16)	5050(4)	61(4)