An approach to asymmetric synthesis of β-aryl alanines by Pd(0)-catalyzed cross-coupling and cyanate-to-isocyanate rearrangement

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Supporting materials

1. Experimantal procedures

1.1. Synthesis of allyl alcohol 13a. **Step 1:** ***Ethyl (S)-O-(t-butyldimethylsilyl)-lactate*** Ethyl L-lactate (20 g, 19.4 mL, 169 mmol) and imidazole (22 g, 320 mmol) were dissolved in dry CH_2Cl_2 (350 mL). The solution was cooled to –15 °C and a solution of TBSCl (23 g, 155 mmol) in dry CH_2Cl_2 was added. The reaction mixture was stirred for 3 h at room temperature. After that time water (200 mL) was added, the organic phase was separated and dried over anhydr. Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (5% AcOEt in cyclohexane) to afford 31.3 g (80%) of product **4a** as colorless oil. $[\alpha]_D^{22}$ –31.5 (*c* 1.4, CH_2Cl_2) [lit.[1] –31.7 (*c* 0.66, $CHCl_3$)]; *Spectral data:*[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.31 (s, 3H), 4.24–4.10 (m, 2H), 1.39 (d, *J* 6.8 Hz, 3H), 0.90 (s, *J* 6.5 Hz, 9H), 0.10 (s, 3H), 0.07 (s, 3H); 13C NMR (126 MHz, $CDCl_3$) δ: 174.6, 68.4, 51.8, 25.7, 21.4, 18.3, –5.1, –5.3; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{24}O_3SiNa$ [M+Na$^+$] 255.1392. Found 255.1390.

Step 2: ***(S,E)-5-((t-butyldimethylsilyl)oxy)hex-3-en-2-one****:* To a solution of ester (10 g, 43 mmol) in dry CH_2Cl_2 (200 mL) at –78 °C a 1M solution of DIBAL-H in hexanes (43 mL, 43

mmol) was added over 1 h (syringe pump). In a second flask, to a suspension of NaH (2.24 g, 60% disp. in mineral oil, 56 mmol) in dry THF (200 mL) triethyl phosphonoacetate (12.5 g, 11.1 mL, 56 mmol) was slowly added and the mixture was stirred at room temperature for 1 h to produce the HWE reagent solution. When reduction was completed (TLC control, 20% AcOEt in hexanes), the solution of HWE reagent was cannulated into the aldehyde solution at –78 °C. The resulting mixture was allowed to warm up slowly to room temperature and was stirred for 3 h. Sat. aq. Rochelle salt (100 mL) was carefully added to the mixture and stirring was continued for 30 min. The mixture was diluted with Et_2O (300 mL). The organic layer was separated and aqueous solution was extracted with Et_2O (4×50 mL). The combined organic extracts were dried over Na_2SO_4 and solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel (10% AcOEt/hexanes) to give 7.95 g of **5a** (80%) as colorless oil. $[\alpha]_D^{22}$ +8.8 (*c* 2.0, $CHCl_3$); *Spectral data:*[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.73 (dd, *J* 15.8, 3.9 Hz, 1H, C*H*=CHCOMe), 6.22 (d, *J* 15.8 Hz, 1H, CH=C*H*COMe), 4.52–4.41 (m, 1H, C*H*Me), 2.26 (m, 3H, CH_3CO), 1.27 (d, *J* 6.4 Hz, 3H, CH_3CH), 0.91 (s, 9H, *t-Bu*Si), 0.07 (s, 3H, CH_3Si), 0.06 (s, 3H, CH_3Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.9, 150.8, 128.3, 67.9, 27.4, 25.9, 23.8, 18.4, –4.7; IR (film) *v*: 1681 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{24}O_2SiNa$ [M+Na$^+$] 251.1443. Found 251.1438.

Step 3: (*S,E*)-4-((t-butyldimethylsilyl)oxy)pent-2-en-1-ol (13a): To a solution of (***S,E***)**-5-((*t*-butyldimethylsilyl)oxy)hex-3-en-2-one** (4.13 g, 16 mmol) in dry CH_2Cl_2 (150 mL) under nitrogen at –78 °C was added DIBAL-H (35 mL, 1.0 M in hexane, 35 mmol) dropwise over a period of 30 min. After the addition was completed, the reaction mixture was stirred at –78 °C for 1 h and then quenched by addition of MeOH (3 mL). The reaction mixture was stirred for additional 15 min at –78 °C and warmed up to room temperature, and diluted with Et2O. Aqueous sat. Rochelle's salt (80 mL) was added and the resulting mixture was stirred vigorously for 30 min. The organic layer was collected and the aqueous layer was extracted with CH2Cl2 (3 X 50 mL). The combined organic fractions were dried with anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (20% AcOEt in hexanes) to provide allylic alcohol **13a** (3.28 g, 95% yield) as a colorless oil. $[\alpha]_D^{23}$ +4.6 (*c* 1.4, $CHCl_3$); R_f 0.37 (1:4 AcOEt/hexanes); *Spectral data:*[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.79–5.66 (m, 2H, CH=CH), 4.35–4.28 (m, 1H, *CH*CH_3), 4.11 (d, *J* 3.1 Hz, 2H, CH_2OH), 1.20 (d, *J* 6.4 Hz, 3H, CH*CH$_3$*), 0.88 (s, 9H, *(CH$_3$)$_3$*CSi), 0.05 (s, 3H, CH_3Si), 0.04 (s, 3H, CH_3Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.3, 127.3, 68.5, 63.1, 25.9, 24.3, 18.2, –4.7, –4.8; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{24}O_2NaSi$ [M+Na$^+$] 239.1443. Found 239.1437; IR (film) *v*: 3342, 2956, 2929, 2886, 2858, 1471, 1363, 1254, 1150, 1085, 1049, 1005, 970, 834, 810, 776, 664 cm^{-1}.

1.2. Pd(0)-catalyzed cross-coupling of allyl alcohol 13a with arylboronic acids. General procedure: A solution of allyl alcohol **13a** (1 mmol), arylboronic acid (2 mmol), [Pd(PPh$_3$)$_4$] (0.05 mmol) in dry THF (10 mL) was kept at 80 °C for 12 h. The progress of the reaction was followed by TLC. When reaction was completed solvent was removed under diminished pressure and the residue was chromatographed on silica gel. In case of compounds **14e**, **14g**, **14n**, **14s** and **14t** the crude product was not purified but directly carried over to the next step.

(*S*,*E*)-*t*-Butyldimethyl((5-phenylpent-3-en-2-yl)oxy)silane (14a): colorless liquid; column chromatography: silica gel, 100% hexanes; yield 68%; $[\alpha]_D^{23}$ +2.3 (*c* 1.18, $CHCl_3$); R_f 0.83 (1:8 AcOEt:hexanes); Column chromatography (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31–7.25 (m, 2H, Ph), 7.22–7.16 (m, 3H, Ph), 5.71 (dtd, *J* 7.8, 6.8, 1.0 Hz, 1H, CH_2CH=CH), 5.54 (dd, *J* 15.3, 5.8 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 5.9 Hz, 1H, *CH*CH_3), 3.35 (d, *J* 6.7 Hz, 2H, PhCH_2), 1.22 (d, *J* 6.3 Hz, 3H, CHCH_3), 0.89 (s, 9H, $(CH_3)_3$CSi), 0.05 (s, 3H, CH_3Si); 0.04 (s, 3H, CH_3Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.5, 136.4, 128.5, 128.3, 127.5, 125.9, 69.2, 38.5, 25.9, 24.6, 18.3, –4.5, –4.7; IR (film) *v*: 3084, 3062, 3030, 2955,2928, 2994, 2856, 1743, 1600, 1471, 1462, 1369, 1254, 1144, 1079, 1002, 970, 834, 775, 738, 699, 609, 471 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{28}ONaSi$ [M+Na^+] 299.1807. Found 299.1811.

(*S*,*E*)-*t*-Butyl((5-(2-methoxyphenyl)pent-3-en-2-yl)oxy)dimethylsilane (14b): yield 75%; flash column chromatography on silica gel (2% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +5.0 (*c* 5.9, $CHCl_3$); TLC: R_f 0.94 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.21 (m, 1H, Ar), 7.18 (d, *J* 7.4 Hz, 1H, Ar), 6.95 (t, *J* 7.4 Hz, 1H, Ar), 6.89 (d, *J* 8.2 Hz, 1H, Ar), 5.80 (dtd, *J* 7.8, 6.7, 1.1 Hz, 1H, CH_2CH=CH), 5.58 (ddd, *J* 15.3, 5.9, 1.0 Hz, 1H, CH_2CH=*CH*), 4.35 (p, *J* 6.0 Hz, 1H, *CH*CH_3), 3.86 (s, *J* 0.7 Hz, 3H, OCH_3), 3.41 (d, *J* 6.7 Hz, 2H, ArCH_2), 1.27 (dd, *J* 6.4, 1.1 Hz, 3H, CHCH_3), 0.96 (s, 9H, $(CH_3)_3$CSi), 0.11 (s, 3H, CH_3Si), 0.10 (s, 3H, CH_3Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 135.9, 129.7, 129.1, 127.19, 127.15, 120.5, 110.2, 69.4, 55.2, 32.6, 26.0, 24.7, 18.3, –4.5, –4.7; IR (film) *v*: 2955, 2929, 2856, 1601, 1493, 1463, 1244, 1145, 1078, 1036, 1002, 970, 835, 775, 751 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{30}O_2NaSi$ [M+Na^+] 329.1913. Found 329.1915.

(*S*,*E*)-*t*-Butyldimethyl((5-(*p*-tolyl)pent-3-en-2-yl)oxy)silane (14b): Yield 70%; colorless oil; column chromatography: silica gel, 100% hexanes; $[\alpha]_D^{23}$ +9.8 (*c* 2.0, $CHCl_3$); TLC: R_f 0.91 (1:8 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.11–7.08 (m, 2H, Ar), 7.08–7.05 (m, 2H, Ar), 5.73–5.65 (m, 1H, CH_2CH=CH), 5.53 (dd, *J* 15.3, 5.8 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.0 Hz, 1H, *CH*CH_3), 3.31 (d, *J* 6.7 Hz, 2H, ArCH_2), 2.32 (s, 3H, ArCH_3), 1.21 (d, *J* 6.3 Hz, 3H, CHCH_3), 0.89 (s, 9H, $(CH_3)_3$CSi), 0.05 (s, 3H, CH_3Si); 0.04 (s, 3H, CH_3Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.4, 136.1, 135.4, 129.0, 128.4, 127.8, 69.2, 38.0, 25.9, 24.6, 21.0, 18.3, –4.5, –4.7; IR (film) *v*: 2956, 2928, 2893, 2857, 1514, 1471, 1462, 1362, 1254, 1144, 1080, 1002, 969, 834, 804, 775, 664, 438 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{30}ONaSi$ [M+Na^+] 313.1964. Found 313.1959.

(*S*,*E*)-*t*-Butyl((5-(4-methoxyphenyl)pent-3-en-2-yl)oxy)dimethylsilane (14c); yield 75%; colorless oil; column chromatography: silica gel, 1% AcOEt/hexanes; $[\alpha]_D^{23}$ +5.3 (*c* 9.7, $CHCl_3$); TLC: R_f 0.94 (1:8 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* 8.2 Hz, 2H, Ar), 6.85 (d, *J* 8.2 Hz, 2H, Ar), 5.74–5.67 (m, 1H, CH_2CH=CH), 5.56–5.50 (m, 1H, CH_2CH=*CH*), 4.31 (p, *J* 5.8 Hz, 1H, *CH*CH_3), 3.80 (s, 3H, OCH_3), 3.30 (d, *J* 6.6 Hz, 2H, ArCH_2), 1.23 (d, *J* 6.3 Hz, 3H, CHCH_3), 0.91 (s, 9H, $(CH_3)_3$CSi), 0.07 (s, 3H, CH_3Si), 0.06 (s, 3H, CH_3Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.9, 136.0, 132.6, 129.4, 127.9, 113.8, 69.2, 55.2, 37.6, 25.9, 24.6, 18.3, –4.5, –4.7; IR (film) *v*: 3402, 2955, 2929, 2856, 1611, 1512, 1464, 1249, 1175, 1144, 1080, 1039,

1002, 970, 834, 776 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{30}O_2NaSi$ [M+Na^+] 329.1913. Found 329.1911.

(*S*,*E*)-((5-(Benzo[d][1,3]dioxol-5-yl)pent-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (14f); yield 63%; flash column chromatography on silica gel (1% AcOEt/hexanes); colorless oil; $[\alpha]_D^{23}$ +6.1 (*c* 2.4, $CHCl_3$); TLC: R_f 0.94 (1:8 AcOEt\hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.75–6.72 (m, 1H, Ar), 6.68–6.66 (m, 1H, Ar), 6.64–6.61 (m, 1H, Ar), 5.92 (s, 2H, O*CH*$_2$O), 5.67 (ddd, *J* 14.4, 7.2, 6.1 Hz, 1H, CH_2*CH*=CH), 5.53 (dd, *J* 15.3, 5.7 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 6.2 Hz, 1H, *CH*CH_3), 3.27 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.23 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.91 (s, *J* 0.6 Hz, 9H, *(CH*$_3$*)*$_3$CSi), 0.07 (s, 3H, C*H*$_3$Si), 0.06 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.3, 127.6, 121.2, 109.1, 108.1, 100.8, 69.2, 38.2, 25.9, 24.6, 18.3, –4.5, –4.7; IR (film) *v*: 2965, 2928, 2886, 2856, 1489, 1443, 1249, 1041, 834, 776 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{28}O_3NaSi$ [M+Na^+] 343.1705. Found 343.1711.

***t*-Butyl (*S*,*E*)-(4-(4-((*t*-butyldimethylsilyl)oxy)pent-2-en-1-yl)phenyl)carbamate (14g):** yield 70%; colorless liquid; $[\alpha]_D^{23}$ +7.8 (*c* 7.9, $CHCl_3$); TLC: R_f 0.69 (1:8 AcOEt:hexanes); Flash column chromatography (15% AcOEt in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, *J* 8.6 Hz, 2H, Ar), 7.08 (d, *J* 8.4 Hz, 2H, Ar), 6.47 (s, 1H, N*H*), 5.67 (dtd, *J* 7.7, 6.6, 1.0 Hz, 1H, CH_2*CH*=CH), 5.51 (dd, *J* 15.3, 5.8 Hz, 1H, CH_2CH=*CH*), 4.28 (p, *J* 6.2 Hz, 1H, *CH*CH_3), 3.29 (d, *J* 6.6 Hz, 2H, Ar*CH*$_2$), 1.52 (s, 9H, (*CH*$_3$)$_3$CNH), 1.20 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.89 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.05 (s, 3H, C*H*$_3$Si), 0.04 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.9, 136.3, 136.2, 135.2, 129.99, 128.96, 128.9, 128.7, 127.6, 123.0, 118.7, 69.2, 37.8, 28.4, 25.9, 24.6, 18.3, –4.5, –4.7; IR (film) *v*: 3335, 2929, 2895, 2857, 1731, 1704, 1596, 1523, 1412, 1367, 1315, 1250, 1163, 1081, 1054, 1002, 970, 834, 775 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{37}O_3NaNSi$ [M+Na^+] 414.2440. Found 414.2438.

(*S*,*E*)-*t*-Butyl((5-(4-chlorophenyl)pent-3-en-2-yl)oxy)dimethylsilane (14h): yield 60%; flash column chromatography on silica gel (1% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +8.3 (*c* 7.6, $CHCl_3$); TLC: R_f 0.96 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, *J* 8.4 Hz, 2H, Ar), 7.10 (d, *J* 8.4 Hz, 2H, Ar), 5.68 (dtd, *J* 7.6, 6.6, 1.0 Hz, 1H, CH_2*CH*=CH), 5.54 (dd, *J* 15.3, 5.6 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 5.8 Hz, 1H, *CH*CH_3), 3.32 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.22 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.90 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.06 (s, 3H, C*H*$_3$Si), 0.05 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.8, 129.9, 128.4, 126.9, 69.1, 37.8, 25.9, 25.9, 24.6, –4.5, –4.7; IR (film) *v*: 2956, 2928, 2865, 1492, 1254, 1092, 835, 775 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{27}ONaClSi$ [M+Na^+] 333.1417. Found 333.1416.

(*S*,*E*)-*t*-butyl((5-(2-chlorophenyl)pent-3-en-2-yl)oxy)dimethylsilane (14i): yield 78%; flash column chromatography on silica gel (100% hexanes); colorless oil; $[\alpha]_D^{23}$ +0.1 (*c* 4.0, $CHCl_3$); TLC: R_f 0.92 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.32 (m, 1H, Ar), 7.23–7.11 (m, 3H, Ar), 5.71 (dtd, *J* 15.2, 6.6, 1.2 Hz, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.3, 5.7, 1.4 Hz, 1H, CH_2CH=*CH*), 4.33–4.26 (m, 1H, *CH*CH_3), 3.46 (d, *J* 6.6 Hz, 2H, Ar*CH*$_2$), 1.21 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.88 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.04 (s, 3H, C*H*$_3$Si), 0.03 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.2, 136.9, 134.0, 130.3, 129.4, 127.4, 126.7, 125.5, 69.1, 35.9, 25.9, 24.5, 18.3, –

4.6, –4.8; IR (film) *v*: 2956, 2928, 2886, 2856, 1472, 1442, 1254, 1146, 1081, 1002, 969, 835, 775, 750, 680, 453 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{27}ONaClSi$ [M+Na^+] 333.1417. Found 333.1415.

(*S*,*E*)-((5-(2-Bromophenyl)pent-3-en-2-yl)oxy)(*t*-butyl)dimethylsilane (14j); yield 16%; flash column chromatography on silica gel (1% AcOEt in hexanes); $[\alpha]_D^{23}$ +0.9 (*c* 5.9, $CHCl_3$); TLC: R_f 0.88 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.52 (m, 1H, Ar), 7.26–7.20 (m, 2H, Ar), 7.06 (ddd, *J* 8.0, 6.8, 2.3 Hz, 1H, Ar), 5.71 (dtd, *J* 15.2, 6.6, 1.2 Hz, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.3, 5.7, 1.4 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 1.21 (d, *J* 6.3 Hz, 3H, CH*CH_3*), 0.89 (s, 9H, *$(CH_3)_3$*CSi), 0.05 (s, 3H, C*H_3*Si), 0.04 (s, 3H, C*H_3*Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.9, 137.0, 132.7, 130.3, 127.7, 127.4, 125.6, 124.6, 69.1, 38.5, 25.9, 24.5, 18.3, –4.6, –4.8; IR (film) *v*: 2955, 2928, 2856, 1470, 1440, 1362, 1254, 1146, 1080, 1025, 1002, 969, 834, 775, 749, 662, 446 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{27}ONaBrSi$ [M+Na^+] 377.0912. Found 377.0908.

(*S*,*E*)-*t*-Butyldimethyl((5-(naphthalen-1-yl)pent-3-en-2-yl)oxy)silane (14k): yield 75%; column chromatography: silica gel, 100% hexanes; colorless oil; $[\alpha]_D^{23}$ +1.1 (*c* 1.2, $CHCl_3$); TLC: R_f 0.88 (1:8 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 (d, *J* 7.7 Hz, 1H, Ar), 7.87–7.83 (m, 1H, Ar), 7.73 (d, *J* 8.2 Hz, 1H, Ar), 7.51–7.45 (m, 2H, Ar), 7.41 (t, *J* 7.6 Hz, 1H, Ar), 7.33 (d, *J* 6.9 Hz, 1H, Ar), 5.90–5.81 (m, 1H, CH_2*CH*=CH), 5.56 (dd, *J* 15.4, 5.8 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.1 Hz, 1H, *CH*CH_3), 3.81 (d, *J* 6.3 Hz, 2H, Ar*CH_2*), 1.19 (d, *J* 6.3 Hz, 3H, CH*CH_3*), 0.87 (s, 9H, *$(CH_3)_3$*CSi), 0.02 (s, 3H, C*H_3*Si); 0.01 (s, 3H, C*H_3*Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.6, 133.8, 132.0, 128.6, 127.0, 126.8, 126.1, 125.7, 125.6, 125.5, 124.1, 69.2, 35.6, 25.9, 24.6, 18.3, –4.6, –4.8; IR (film) *v*: 3045, 2955, 2927, 2886, 2855, 1924, 1742, 1506, 1470, 1462, 1386, 1368, 1254, 1145, 1079, 1001, 969, 834, 777, 620, 574, 508, 442 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{30}ONaSi$ [M+Na^+] 349.1964. Found 349.1961.

(*S*,*E*)-*t*-Butyldimethyl((5-(naphthalen-2-yl)pent-3-en-2-yl)oxy)silane (14l): yield 67%; flash column chromatography on silica gel (1% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +8.1 (*c* 5.0, $CHCl_3$); TLC: R_f 0.92 (1:8 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (t, *J* 9.6 Hz, 1H, Ar), 7.96–7.91 (m, 1H, Ar), 7.87–7.79 (m, 2H, Ar), 7.66 (s, 1H, Ar), 7.51–7.44 (m, 1H, Ar), 7.37 (dd, *J* 8.4, 1.2 Hz, 1H, Ar), 5.88–5.81 (m, 1H, CH_2*CH*=CH), 5.65 (dd, *J* 15.3, 5.8 Hz, 1H, CH_2CH=*CH*), 4.38 (p, *J* 6.0 Hz, 1H, *CH*CH_3), 3.56 (d, *J* 6.7 Hz, 2H, Ar*CH_2*), 1.29 (d, *J* 6.3 Hz, 3H, CH*CH_3*), 0.96 (s, *J* 6.9 Hz, 9H, *$(CH_3)_3$*CSi), 0.12 (m, 6H, $(CH_3)_2$Si); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.6, 127.8, 127.6, 127.5, 127.4, 127.3, 126.5, 125.9, 125.2, 69.2, 38.6, 25.9, 24.6, 18.3, –4.5, –4.7; IR (film) *v*: 3042, 2957, 2923, 2885, 2861, 1922, 1738, 1511, 1472, 1460, 1383, 1366, 1254, 1146, 1080, 998, 965, 830, 773, 626, 571, 508, 443 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{30}ONaSi$ [M+Na^+] 349.1964. Found 349.1967.

(*S*,*E*)-*t*-Butyldimethyl((5-(4-(trifluoromethyl)phenyl)pent-3-en-2-yl)oxy)silane (14m): yield 58%; flash column chromatography on silica gel (8% AcOEt in hexanes; colorless oil; $[\alpha]_D^{23}$ +2.7 (*c* 3.5, $CHCl_3$); TLC: R_f 0.85 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* 8.0 Hz, 2H, Ar), 7.28 (d, *J* 7.9 Hz, 2H, Ar), 5.70 (dtd, *J* 7.8, 6.7, 1.2 Hz, 1H. CH_2*CH*=CH), 5.56

(ddt, *J* 15.3, 5.6, 1.3 Hz, 1H, CH_2CH=*CH*), 4.30 (pd, *J* 6.3, 0.9 Hz, 1H, *CH*CH_3), 3.40 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.21 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.89 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.05 (s, 3H, C*H*$_3$Si), 0.04 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.6, 144.6, 137.2, 128.8, 126.3, 125.31, 125.27, 125.23, 125.19, 69.0, 38.2, 25.9, 24.5, 18.3, –4.6, –4.8; IR (film) *v*: 2956, 2930, 2888, 2858, 1619, 1472, 1416, 1327, 1255, 1165, 1128, 1068, 1019, 1002, 970, 938, 835, 776, 664, 630, 594 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}F_3ONaSi$ [M+Na$^+$] 367.1681. Found 367.1674.

(*S*,*E*)-4-(4-((*t*-Butyldimethylsilyl)oxy)pent-2-en-1-yl)benzonitrile (14o): yield 39%; flash column chromatography on silica gel (4% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +8.2 (*c* 2.4, $CHCl_3$); TLC: R_f 0.86 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.55 (m, 1H, Ar), 7.54 (d, *J* 1.4 Hz, 1H, Ar), 7.28–7.26 (m, 1H, Ar), 7.26–7.24 (m, 1H, Ar), 5.67 (dtd, *J* 15.2, 6.6, 1.2 Hz, 1H, CH_2CH=CH), 5.55 (ddt, *J* 15.3, 5.4, 1.2 Hz, 1H, CH_2CH=*CH*), 4.32–4.25 (m, 1H, *CH*CH_3), 3.38 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.20 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.87 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.03 (s, 3H, C*H*$_3$Si), 0.01 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.2, 137.7, 132.2, 129.3, 125.6, 119.0, 110.0, 68.8, 38.5, 25.9, 24.5, 18.2, –4.6, –4.7; IR (film) *v*: 2955, 2929, 2887, 2856, 2228, 1607, 1504, 1471, 1362, 1254, 1145, 1080, 1002, 971, 938, 835, 776, 664, 553 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}NOSiNa$ [M+Na$^+$] 324.1760. Found 324.1774.

Methyl (*S*,*E*)-4-(4-((*t*-butyldimethylsilyl)oxy)pent-2-en-1-yl)benzoate (14p): yield 29%; flash column chromatography on silica gel (1% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +7.9 (*c* 10.8, $CHCl_3$); TLC: R_f 0.91 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H, Ar), 7.94 (s, 1H, Ar), 7.24 (s, 1H, Ar), 7.22 (s, 1H, Ar), 5.74–5.65 (m, 1H, CH_2CH=CH), 5.54 (dd, *J* 15.3, 5.6 Hz, 1H, CH_2CH=*CH*), 3.88 (s, 3H, O*CH*$_3$), 3.38 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.20 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$), 0.88 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.04 (s, 3H, C*H*$_3$Si), 0.03 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.0, 146.0, 137.1, 129.7, 128.5, 126.4, 69.0, 51.9, 38.4, 25.9, 25.8, 24.5, 18.2, –4.6, –4.8; IR (film) *v*: 2953, 2928, 2887, 2856, 1725, 1610, 1435, 1279, 1178, 1110, 1002, 970, 835, 775, 711 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{30}O_3NaSi$ [M+Na$^+$] 357.1862. Found 357.1878.

(*S*,*E*)-*t*-Butyldimethyl((5-(4-vinylphenyl)pent-3-en-2-yl)oxy)silane (14r): yield 78%; flash column chromatography on silica gel (1% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ +5.7 (*c* 5.7, $CHCl_3$); TLC: R_f 0.93 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* 7.9 Hz, 2H, Ar), 7.19 (d, *J* 8.0 Hz, 2H, Ar), 6.75 (dd, *J* 17.6, 10.9 Hz, 1H, Ar*CH*=CH_2), 5.79–5.73 (m, 2H, ArCH=*CH*$_2$, CH_2CH=CH), 5.60 (ddd, *J* 15.3, 5.7, 1.3 Hz, 1H, CH_2CH=*CH*), 5.25 (d, *J* 10.9 Hz, 1H, ArCH=*CH*$_2$), 4.36 (p, *J* 6.1 Hz, 1H, CH_3CH), 3.39 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.28 (dd, *J* 6.3, 1.8 Hz, 3H, *CH*$_3$CH), 0.97 (s, 9H, *(CH*$_3$*)*$_3$CSi), 0.12 (s, 3H, C*H*$_3$Si), 0.12 (s, 3H, C*H*$_3$Si); ^{13}C NMR (101 MHz, $CDCl_3$) ciężko opisać; IR (film) *v*: 2956, 2928, 2894, 2856, 1724, 1630, 1510, 1471, 1406, 1361, 1254, 1144, 1079, 990, 970, 904, 832, 775, 741, 664, 472 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{30}ONaSi$ [M+Na$^+$] 325.1964. Found 325.1960.

1.3. Synthesis of allyl alcohols 15. General procedure: To a solution of compound **14a** (450 mg, 1.63 mmol) in dry THF (6 mL) cooled to –25 °C 1M TBAF (2.equiv. 3.26 ml, 3.26 mmol) was added. The reaction was warm spontaneously to rt, and stirred overnight. Solvent was

removed under diminished pressure. The residue was chromatographed on silica gel (1:6 AcOEt/hexanes) to afford 188 mg of alcohol **15a** (94%) as colorless oil. **(*S*,*E*)-5-Phenylpent-3-en-2-ol (15a):** *ee* >99% (HPLC: R_t 8.0 min); $[\alpha]_D^{23}$ –2.4 (*c* 2.3, $CHCl_3$); TLC: R_f 0.27 (1:3 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22–7.18 (m, 2H, Ph), 7.13–7.10 (m, 1H, Ph), 7.09–7.07 (m, 2H, Ph), 5.70 (dtd, *J* 7.8, 6.8, 1.0 Hz, 1H, CH_2*CH*=CH), 5.50 (ddt, *J* 15.3, 6.5, 1.4 Hz, 1H, CH_2CH=*CH*), 4.20 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.27 (d, *J* 6.8 Hz, 2H, Ph*CH*$_2$), 1.18 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.1, 135.5, 129.4, 128.5, 128.4, 126.1, 68.7, 38.5, 23.4; HRMS (EI) *m/z* calcd for $C_{11}H_{14}O$ [M] 162.1045. Found 162.1046; IR (film) *v*: 3353, 3027, 2970, 2925, 1603, 1495, 1453, 1368, 1138, 1060, 971, 747, 699 cm^{-1}. HPLC: Chiralpak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min. Racemic sample retention times: 6.7 min (*R*-enantiomer) and 7.9 min (*S*-enantiomer).

(*S*,*E*)-5-(p-Tolyl)pent-3-en-2-ol (15b): Yield 217 mg (84%) starting from 426 mg (1.47 mmol) of compound **14b**; purification by flash column chromatography on silica gel (1:8 AcOEt/hexanes); colorless oil; $[\alpha]_D^{23}$ –4.6 (*c* 1.4, $CHCl_3$); TLC: R_f 0.45 (1:4 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.01 (d, *J* 7.9 Hz, 2H, Ar), 6.97 (d, *J* 8.0 Hz, 2H, Ar), 5.72–5.64 (m, 1H, CH_2*CH*=CH), 5.49 (dd, *J* 15.3, 6.5 Hz, 1H, CH_2CH=*CH*), 4.19 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.22 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 2.22 (s, 3H, Ar*CH*$_3$), 1.17 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.0, 135.6, 135.3, 129.7, 129.1, 128.4, 68.7, 38.1, 23.3, 20.9; IR (film) *v*: 3352, 2971, 2924, 1514, 1448, 1433, 1368, 1297, 1138, 1061, 970, 909, 806, 570, 479 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{12}H_{16}O$ [M] 176.1201. Found 176.1195.

(*S*,*E*)-5-(4-Methoxyphenyl)pent-3-en-2-ol (15c): Yield 275 mg (85%) starting from 515 mg (1.68 mmol) of compound **14c**; flash column chromatography on silica gel (15% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{25}$ –6.7 (*c* 2.6, $CHCl_3$); TLC: R_f 0.35 (1:4 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09 (d, *J* 8.6 Hz, 2H, Ar), 6.84 (d, *J* 8.5 Hz, 2H, Ar), 5.81–5.73 (m, 1H, CH_2*CH*=CH), 5.58 (dd, *J* 15.3, 6.5 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.79 (s, 3H, O*CH*$_3$), 3.30 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.27 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.0, 135.2, 132.1, 129.8, 129.4, 113.9, 68.7, 55.2, 37.6, 23.4; IR (film) *v*: 3377, 2969, 1611, 1511, 1246, 1176, 1037, 971, 826 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{15}O$ [M^+-OH] 175.1101. Found 175.1155.

(*S*,*E*)-5-(2-Methoxyphenyl)pent-3-en-2-ol (15d): Yield 258 mg (85%); starting from 484 mg (1.58 mmol) of compound **14d**; flash column chromatography on silica gel (20% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{22}$ –4.6 (*c* 11.5, $CHCl_3$); TLC: R_f 0.48 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.18 (m, 1H, Ar), 7.14 (dd, *J* 7.4, 1.7 Hz, 1H, Ar), 6.91 (td, *J* 7.4, 1.1 Hz, 1H, Ar), 6.86 (d, *J* 8.2 Hz, 1H, Ar), 5.81 (dtd, *J* 15.2, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.58 (ddt, *J* 15.4, 6.7, 1.5 Hz, 1H, CH_2CH=*CH*), 4.27 (p, *J* 6.4 Hz, 1H, *CH*CH_3), 3.83 (s, 3H, O*CH*$_3$), 3.37 (d, *J* 6.8 Hz, 2H, Ar*CH*$_2$), 1.26 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 135.2, 129.8, 128.9, 128.7, 127.4, 120.6, 110.4, 68.7, 55.3, 32.7, 23.3; IR (film) *v*: 3361, 2968, 1600, 1587, 1493, 1464, 1439, 1244, 1113, 1052, 1032, 972, 752 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{16}O_2Na$ [M+Na^+] 215.1048. Found 215.1056.

(*S*,*E*)-5-(3,4-Dimethoxyphenyl)pent-3-en-2-ol (15e): Yield 297 mg (58%) (after two steps), starting from crude compound **14e**; flash column chromatography on silica gel (40% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{25}$ –4.4 (*c* 2.4, $CHCl_3$); R_f 0.23 (1:2 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.80 (d, *J* 7.9 Hz, 1H, Ar), 6.72–6.68 (m, 2H, Ar), 5.78 (dtd, *J* 15.2, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.59 (ddt, *J* 15.3, 6.4, 1.4 Hz, 1H, CH_2CH=*CH*), 4.30 (pd, *J* 6.3, 0.8 Hz, 1H, *CH*CH_3), 3.86 (s, 3H, O*CH*$_3$), 3.85 (s, 3H, O*CH*$_3$), 3.31 (d, *J* 0.6 Hz, 1H, Ar*CH*$_2$), 3.29 (d, *J* 0.6 Hz, 1H), 1.27 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.0, 147.5, 135.3, 132.7, 129.6, 120.4, 112.0, 111.4, 68.7, 56.0, 55.8, 38.1, 23.4; IR (film) *v*: 3498, 3398, 2967, 2835, 1515, 1464, 1261, 1234, 1140, 1029, 972, 807, 764 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{18}O_3Na$ [M+Na$^+$] 245.1154. Found 245.1160.

(*S*,*E*)-5-(Benzo[d][1,3]dioxol-5-yl)pent-3-en-2-ol (15f): Yield 243 mg (85%) starting from 445 mg (1.39 mmol) of compound **14f**; flash column chromatography on silica gel (15% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{25}$ –5.5 (*c* 1.7, $CHCl_3$); TLC: R_f 0.28 (1:4 AcOEt/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.73 (d, *J* 7.9 Hz, 1H, Ar), 6.66–6.65 (m, 1H, Ar), 6.63–6.60 (m, 1H, Ar), 5.91 (s, 2H, O*CH*$_2$O), 5.75 (dtd, *J* 15.3, 6.7, 1.0 Hz, 1H, CH_2*CH*=CH), 5.57 (ddt, *J* 15.3, 6.4, 1.4 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.27 (dd, *J* 6.7, 0.6 Hz, 2H, Ar*CH*$_2$), 1.27 (d, *J* 6.4 Hz, 3H CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.7, 145.9, 135.4, 133.9, 129.5, 121.3, 109.0, 108.2, 100.8, 68.6, 38.2, 23.4 HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{14}O_3Na$ [M+Na$^+$] 229.0841. Found 229.0846; IR (film) *v*: 3370, 2968, 2924, 1489, 1442, 1246, 1039, 927, 809 cm^{-1}.

***t*-Butyl (*S*,*E*)-(4-(4-hydroxypent-2-en-1-yl)phenyl)carbamate (15g):** Yield 434 mg (68%) (after two steps), starting from crude compound **14g**; flash column chromatography on silica gel (35% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{25}$ −0.6 (*c* 2.3, $CHCl_3$); TLC: R_f 0.10 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, *J* 8.1 Hz, 2H, Ar), 7.08 (d, *J* 8.4 Hz, 2H, Ar), 6.46 (s, 1H, NH), 5.76 (dtd, *J* 7.5, 6.6, 0.8 Hz, 1H, CH_2*CH*=CH), 5.56 (ddt, *J* 15.4, 6.5, 1.3 Hz, 1H, CH_2CH=*CH*), 4.28 (p, *J* 6.4 Hz, 1H, *CH*CH_3), 3.29 (d, *J* 6.6 Hz, 2H, Ar*CH*$_2$), 1.51 (s, 9H, C(CH_3)$_3$), 1.26 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.9, 136.5, 135.4, 134.8, 129.6, 129.0, 128.7, 118.8, 68.7, 37.8, 28.3, 23.4; IR (film) *v*: 3322, 2979, 1702, 1598, 1525, 1412, 1367, 1316, 1244, 1162, 1055, 971, 910, 833 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_3Na$ [M+Na$^+$] 300.1576. Found 300.1578.

(*S*,*E*)-5-(4-Chlorophenyl)pent-3-en-2-ol (15h): Yield 229 mg (88%) starting from 411 mg (1.32 mmol) of compound **14h**; flash column chromatography on silica gel (25% AcOEt in hexanes). colorless liquid; $[\alpha]_D^{25}$ –2.9 (*c* 1.5, $CHCl_3$); TLC: R_f 0.33 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.23 (m, 2H, Ar), 7.12–7.08 (m, 2H, Ar), 5.76 (dtd, *J* 15.3, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.58 (ddt, *J* 15.3, 6.4, 1.4 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 6.2 Hz, 1H, *CH*CH_3), 3.32 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.27 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.5, 135.9, 131.9, 129.9, 128.8, 128.5, 68.6, 37.8, 23.4; IR (film) *v*: 3345, 2972, 1491, 1407, 1369, 1139, 1091, 1061, 1015, 971, 910, 815, 655, 555, 484 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{13}OClNa$ [M+Na$^+$] 219.0553. Found 219.0542.

(*S*,*E*)-5-(2-Chlorophenyl)pent-3-en-2-ol (15i): Yield 310 mg (95%) starting from 515 mg (1.66 mmol) of compound **ALA-64**; flash column chromatography on silica gel (20% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{22}$ –3.7 (*c* 4.1, $CHCl_3$); TLC R_f 0.34 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (dd, *J* 7.3, 1.3 Hz, 1H, Ar), 7.21–7.12 (m, 3H, Ar), 5.78 (dtd, *J* 15.3, 6.6, 1.1 Hz, 1H, CH_2*CH*=CH), 5.58 (ddt, *J* 15.4, 6.4, 1.4 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.47 (d, *J* 6.6 Hz, 2H, ArCH_2), 1.26 (d, *J* 6.4 Hz, 3H, CHCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.8, 136.2, 134.0, 130.4, 129.5, 127.6, 127.3, 126.9, 68.6, 36.1, 23.3; IR (film) *v*: 3345, 2971, 1473, 1442, 1368, 1142, 1125, 1052, 1038, 970, 751, 680 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{13}NOClNa$ [M+Na^+] 219.0553. Found 219.0537.

(*S*,*E*)-5-(2-Bromophenyl)pent-3-en-2-ol (15j): Yield 97 mg (80%) starting from 178 mg (0.50 mmol) of compound **ALA-60**; flash column chromatography on silica gel (30% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{24}$ –2.6 (*c* 5.7, $CHCl_3$); R_f 0.34 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* 8.4 Hz, 1H, Ar), 7.27–7.19 (m, 2H, Ar), 7.10–7.04 (m, 1H,Ar), 5.82–5.74 (m, 1H, CH_2*CH*=CH), 5.59 (dd, *J* 15.4, 6.4 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.48 (d, *J* 6.5 Hz, 2H, ArCH_2), 1.62 (s, 1H, O*H*), 1.26 (d, *J* 6.4 Hz, 3H, CHCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.5, 136.3, 132.8, 130.4, 127.9, 127.5, 127.3, 124.5, 68.6, 38.6, 23.3; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{13}NOBrCl$ [M+Na^+] 263.0047. Found 263.0043; IR (film) *v*: 3342 2969, 1469, 1439, 1367, 1141, 1060, 1024, 970, 750, 660 cm^{-1}.

(*S*,*E*)-5-(Naphthalen-1-yl)pent-3-en-2-ol (15k): Yield 366 mg (89%) starting from 612 mg (1.87 mmol) of compound **14k**; Purification by flash column chromatography on silica gel (1:8 AcOEt/hexanes); colorless oil; $\alpha_{[D]}^{23}$ –4.8 (*c* 0.8, $CHCl_3$); TLC: R_f 0.42 (1:4 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (d, *J* 8.1 Hz, 1H, Ar), 7.78–7.74 (m, 1H, Ar), 7.64 (d, *J* 8.2 Hz, 1H, Ar), 7.43–7.36 (m, 2H, Ar), 7.33–7.29 (m, 1H, Ar), 7.23 (d, *J* 6.9 Hz, 1H, Ar), 5.83 (dt, *J* 14.4, 6.4 Hz, 1H, CH_2*CH*=CH), 5.52 (dd, *J* 15.4, 6.4 Hz, 1H, CH_2CH=*CH*), 4.18 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.72 (d, *J* 6.4 Hz, 2H, ArCH_2), 1.14 (d, *J* 6.3 Hz, 3H, CHCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.2, 135.8, 133.9, 131.9, 128.8, 128.7, 127.0, 126.2, 125.8, 125.6, 125.5, 123.9, 68.7, 35.7, 23.3; IR (film) *v*: 3353, 3044, 2970, 2925, 1596, 1509, 1396, 1368, 1260, 1139, 1061, 970, 792, 777 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{15}H_{16}O$ [M] 212.1201. Found 212.1204.

(*S*,*E*)-5-(Naphthalen-2-yl)pent-3-en-2-ol (15l): Yield 298 mg (94%) starting from 487 mg (1.49 mmol) of compound **14l**; flash column chromatography on silica gel (15% AcOEt in hexanes). colorless liquid; $[\alpha]_D^{23}$ –6.6 (*c* 2.5, $CHCl_3$); TLC: R_f 0.38 (1:4 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* 8.4 Hz, 1H, Ar), 7.79 (d, *J* 8.3 Hz, 2H, Ar), 7.63 (s, 1H, Ar), 7.50–7.42 (m, 2H, Ar), 7.33 (dd, *J* 8.4, 1.1 Hz, 1H, Ar), 5.88 (dtd, *J* 7.6, 6.7, 0.9 Hz, 1H, CH_2*CH*=CH), 5.69–5.63 (m, 1H, CH_2CH=*CH*), 4.33 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.53 (d, *J* 6.7 Hz, 2H, ArCH_2), 1.30 (d, *J* 6.4 Hz, 3H, CHCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.6, 135.8, 133.6, 132.1, 129.2, 128.0, 127.6, 127.4, 127.3, 126.6, 126.0, 125.3, 68.6, 38.6, 23.4; IR (film) *v*: 3348, 3051, 2970, 1600, 1508, 1366, 1137, 1060, 971, 817, 746, 475 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{15}H_{16}O$ [M] 212.1201. Found 212.1209;

(*S*,*E*)-5-(4-(Trifluoromethyl)phenyl)pent-3-en-2-ol (15m); Yield 249 mg (88%) starting from 423 mg (1.23 mmol) of compound **14m**; flash column chromatography on silica gel (30% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{25}$ –3.5 (*c* 2.8, $CHCl_3$); TLC: R_f 0.12 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* 8.0 Hz, 2H, Ar), 7.28 (d, *J* 8.0 Hz, 2H, Ar), 5.78 (dtd, *J* 15.2, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.61 (ddt, *J* 15.4, 6.3, 1.4 Hz, 1H, CH_2CH=*CH*), 4.30 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.41 (d, *J* 6.7 Hz, 2H, ArCH_2), 1.27 (d, *J* 6.4 Hz, 3H, CHCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.4, 128.8, 128.1, 125.3 (q, $J_{C\text{-}F}$ 3.8 Hz), 68.5, 38.3, 30.8, 23.4; IR (film) *v*: 3348, 2974, 1619, 1417, 1370, 1326, 1164, 1125, 1067, 1019, 971, 912, 831, 630, 594 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}OFNa$ [M+Na$^+$] 253.0816. Found 253.0811.

(*S*,*E*)-1-(4-(4-Hydroxypent-2-en-1-yl)phenyl)ethan-1-one (15n) and **(*S*,*E*)-1-(4-(4-hydroxypent-1-en-1-yl)phenyl)ethan-1-one (15n*):** inseparable mixture in ratio 5.9:1; overall yield 49 mg (54%) (after two steps), starting from crude compound **14a**; flash column chromatography on silica gel (30% AcOEt in hexanes); colorless oil; TLC: R_f 0.37 (1:3 AcOEt:hexanes); Compound **15n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90–7.89 (m, 1H, Ar), 7.88–7.86 (m, 1H, Ar), 7.28–7.26 (m, 1H, Ar), 7.25 (m, 1H, Ar), 5.78 (dtd, *J* 15.3, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.61 (ddt, *J* 15.3, 6.3, 1.4 Hz, 1H, CH_2CH=*CH*), 4.31 (pd, *J* 6.2, 0.5 Hz, 1H *CH*CH_3), 3.41 (d, *J* 6.7 Hz, 2H, ArCH_2), 2.57 (s, 3H, CH_3CO), 1.27 (d, *J* 6.4 Hz, 3H, CHCH_3); Compound **15n***: ^{1}H NMR (400 MHz, 400 MHz, selected signals) δ: 6.51 (d, *J* 15.9 Hz, 1H), 6.38 (dt, *J* 15.8, 7.2 Hz, 1H), 6.16–5.98 (m, 1H), 4.14–4.06 (m, 1H), 3.36-3.32 (m, 1H), 3.27–3.22 (m, 1H), 1.23 (d, *J* 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.8, 145.8, 136.4, 135.4, 128.8, 128.6, 128.1, 126.1, 68.5, 38.4, 26.5, 23.4; IR (film) *v*: 3422, 2970, 1681, 1605, 1413, 1360, 1270, 1182, 1062, 970, 826, 599 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{16}O_2Na$ [M+Na$^+$] 227.1048. Found 227.1044.

(*S*,*E*)-4-(4-hydroxypent-2-en-1-yl)benzonitrile (15o) and (*S*,*E*)-4-(4-Hydroxypent-1-en-1-yl)benzonitrile (15o*): inseparable mixture in ratio 1:1; overall yield 107 mg (63%) starting from 273 mg (0.91 mmol) of compound **14o**; Purification by flash column chromatography on silica gel (47% AcOEt in hexanes); colorless liquid; TLC: R_f 0.36 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, both isomers) δ: 7.52 (m, 4H), 7.41–7.36 (m, 2H, **15o**), 7.25 (m, 2H, **15o***), 6.48–6.33 (m, 2H, **15o***), 5.72 (dtd, *J* 15.2, 6.6, 1.0 Hz, 1H, **15o**), 5.58 (ddt, *J* 15.4, 6.1, 1.3 Hz, 1H, **15o**), 4.32–4.22 (m, 1H, **15o**), 3.93 (m, 1H, **15o***), 3.38 (d, *J* 6.6 Hz, 2H, **15o**), 2.42–2.31 (m, 2H, **15o***), 1.24 (d, *J* 6.6 Hz, 3H, **15o**), 1.21 (d, *J* 6.7 Hz, 3H, **15o***); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 141.9, 137.0, 132.3, 132.2, 131.1, 129.3, 127.1, 126.5, 119.0, 118.9, 110.2, 109.9, 68.2, 67.2, 42.8, 38.5, 23.4, 23.1; IR (film) *v*: 3355, 2970, 2928, 1501, 1369, 1156, 1137, 1064, 1022, 971, 874, 778, 727, 600 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}NONa$ [M+Na$^+$] 210.0895. Found 210.0898.

Methyl (*S*,*E*)-4-(4-hydroxypent-2-en-1-yl)benzoate (15p) and methyl (S,E)-4-(4-hydroxypent-1-en-1-yl)benzoate (15p*): inseparable mixture in ratio 6:1; overall yield 92 mg (64%) starting from 220 mg (0.66 mmol) of compound **14p**; flash column chromatography on

silica gel (22% AcOEt in hexanes); colorless oil; TLC: R_f 0.23 (1:4 AcOEt:hexanes); compound **15p** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (t, *J* 1.9 Hz, 1H, Ar), 7.92 (d, *J* 1.9 Hz, 1H, Ar), 7.22 (s, 1H, Ar), 7.20 (s, 1H, Ar), 5.79–5.71 (m, 1H, CH_2*CH*=CH), 5.58 (ddt, *J* 15.4, 6.3, 1.3 Hz, 1H, CH_2CH=*CH*), 4.28 (p, *J* 6.2 Hz, 1H, *CH*CH_3), 3.87 (s, 3H, COO*CH*$_3$), 3.38 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.89 (s, 1H, *OH*), 1.25 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.1, 145.6, 136.4, 129.8, 128.6, 128.1, 125.9, 68.4, 52.0, 38.5, 23.4; Compound **15p***: ^{1}H NMR (400 MHz, $CDCl_3$, selected signals) δ: 6.48 (d, *J* 15.9 Hz, 1H), 6.35 (dt, *J* 15.9, 7.2 Hz, 1H), 3.93 (m, 1H), 1.20 (d, *J* 6.7 Hz, 3H); IR (film) *v*: 3418, 1720, 1609, 1436, 1281, 1178, 1112, 1061, 1020, 970, 758, 706 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{16}O_3Na$ [M+Na$^+$] 243.0997. Found 243.1005.

(*S*,*E*)-5-(4-Vinylphenyl)pent-3-en-2-ol (15r): Yield 268 mg (89%); starting from 484 mg (1.60 mmol) of compound **ALA-91**; flash column chromatography on silica gel (15% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{22}$ –2.3 (*c* 27.0, $CHCl_3$); TLC: R_f 0.19 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* 8.1 Hz, 2H, Ar), 7.16 (d, *J* 8.1 Hz, 2H, Ar), 6.73 (dd, *J* 17.6, 10.9 Hz, 1H, CH_2=*CH*Ar), 5.82–5.75 (m, 1H, CH_2*CH*=CH), 5.74 (d, *J* 17.8 Hz, 1H, *CH*$_2$=CHAr), 5.61 (dd, *J* 15.3, 6.3 Hz, 1H, *CH*$_2$=CHAr), 5.24 (d, *J* 11.0 Hz, 1H, CH_2CH=*CH*), 4.28 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.36 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 2.46 (s, *J* 2.9 Hz, 1H, O*H*), 1.28 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.9, 136.7, 135.8, 135.6, 129.0, 128.8, 126.4, 113.2, 68.5, 38.3, 23.4; IR (film) *v*: 3352, 2971, 2926, 2898, 1630, 1510, 1406, 1386, 1286, 1138, 1114, 1061, 1017, 989, 971, 907, 828, 717, 648, 567, 474 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{16}ONa$ [M+Na$^+$] 211.1099. Found 211.1104.

(*S*,*E*)-5-(Furan-2-yl)pent-3-en-2-ol (15s); Yield 112 mg (32%)(after two steps); starting from 515 mg (2.3 mmol) of compound **13a**; flash column chromatography on silica gel (25% AcOEt in hexanes). colorless liquid; $[\alpha]_D^{22}$ –1.0 (*c* 7.6, $CHCl_3$); TLC: R_f 0.37 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* 1.1 Hz, 1H, Ar), 6.28 (dd, *J* 2.9, 2.0 Hz, 1H, Ar), 6.00 (d, *J* 2.4 Hz, 1H, Ar), 5.75 (dt, *J* 12.3, 6.5 Hz, 1H, CH_2*CH*=CH), 5.63 (dd, *J* 15.4, 6.2 Hz, 1H, CH_2CH=*CH*), 4.29 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.36 (d, *J* 6.4 Hz, 2H, Ar*CH*$_2$), 1.83 (s, 1H, O*H*), 1.26 (d, *J* 6.4 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.9, 141.2, 136.5, 125.7, 110.2, 105.5, 68.4, 30.9, 23.3; IR (film) *v*: 3362, 2971, 1596, 1506, 1423, 1369, 1146, 1061, 1009, 970, 731, 599 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{12}O_2Na$ [M+Na$^+$] 175.0735. Found 175.0731.

(*S*,*E*)-5-(Furan-3-yl)pent-3-en-2-ol (15t): Yield 138 mg (39%)(after two steps); starting from 500 mg (2.3 mmol) of compound **13a**; flash column chromatography on silica gel (25% AcOEt in hexanes); colorless liquid; $[\alpha]_D^{22}$ –38.5 (*c* 1.24, $CHCl_3$); TLC: R_f 0.34 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (s, 1H, Ar), 7.20 (s, 1H, Ar), 6.25 (s, 1H, Ar), 5.74 (dt, *J* 15.3, 6.4 Hz, 1H, CH_2*CH*=CH), 5.59 (dd, *J* 15.4, 6.3 Hz, 1H, CH_2CH=*CH*), 4.28 (p, *J* 6.3 Hz, 1H, *CH*CH_3), 3.14 (d, *J* 6.4 Hz, 2H, Ar*CH*$_2$), 1.88 (s, 1H, O*H*), 1.25 (d, *J* 6.3 Hz, 3H, CH*CH*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.9, 139.1, 135.5, 128.3, 111.1, 68.5, 53.8, 27.6, 23.4; IR (film) *v* 3401, 2969, 2226, 1650, 1604, 1504, 1413, 1175, 1125, 1063, 971, 844, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{12}O_2Na$ [M+Na$^+$] 175.0735. Found 175.0733.

1.4. Synthesis of carbamates 16. General procedure: To a solution of alcohol **15a** (155 mg, 0.96 mmol) in dry CH_2Cl_2 (5 mL) cooled to –10 °C neat TCA-NCO (235 mg, 148 µL, 1.25 mmol) was added. The progress of the reaction was followed by TLC (1:3 AcOEt/hexanes). After 30 min. solvent was removed under diminished pressure. The residue was dissolved in MeOH (5 mL) and water (1 mL) and K_2CO_3 (531 mg, 3.84 mmol) was added. The progress of the reaction was followed by TLC (1:3 AcOEt/hexanes). After 30 min. water (5 mL) was added and aqueous solution was extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4, and solvent was removed under diminished pressure. The residue was chromatographed on silica gel (1:2 AcOEt/hexanes) to afford 179 mg of carbamate **16a** (91%) as white crystals; m.p. 71-72 °C; $[\alpha]_D^{25}$ –30.4 (*c* 1.7, $CHCl_3$); TLC: R_f 0.15 (1:2 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30–7.26 (m, *J* 7.5 Hz, 2H), 7.21–7.14 (m, 3H), 5.88–5.81 (m, 1H), 5.53 (ddt, *J* 15.4, 6.3, 1.4 Hz, 1H), 5.24 (p, *J* 6.3 Hz, 1H), 4.58 (m, 2H), 3.36 (d, *J* 6.7 Hz, 2H), 1.30 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.2, 139.8, 1312, 131.1, 128.6, 128.4, 126.1, 71.5, 38.5, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{15}NO_2Na$ [M+Na$^+$] 228.1000. Found 228.0996; IR (film) *v*: 3432, 3330, 3265, 3211, 2989, 2978, 1686, 1614, 1400, 1045, 967, 742, 699, 592 cm^{-1}.

(*S*,*E*)-5-(*p*-tolyl)pent-3-en-2-yl carbamate (16b): Yield 240 mg (94%) starting from 205 mg (1.16 mmol) of compound **15b**; flash column chromatography on silica gel (1:4 AcOEt/hexanes); white solid; m.p. 83-84 °C; $[\alpha]_D^{25}$ –32.4 (*c* 1.4, $CHCl_3$); TLC: R_f 0.29 (1:4 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.10 (d, *J* 7.9 Hz, 2H), 7.06 (d, *J* 7.9 Hz, 2H), 5.89–5.80 (m, 1H), 5.54 (dd, *J* 15.4, 6.3 Hz, 1H), 5.25 (p, *J* 6.3 Hz, 1H), 4.61 (s, 2H), 3.38–3.30 (m, 2H), 2.32 (s, *J* 4.2 Hz, 3H), 1.31 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.3, 136.7, 135.6, 131.4, 130.9, 129.1, 128.4, 71.5, 38.1, 21.0, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_2Na$ [M+Na$^+$] 242.1157. Found 242.1159; IR (film) *v*: 3431, 3335, 3270, 3209, 2975, 1686, 1611, 1514, 1402, 1304, 1047, 795, 583 cm^{-1}.

(*S*,*E*)-5-(4-Methoxyphenyl)pent-3-en-2-yl carbamate (16c): Yield 294 mg (92%) starting from 261 mg (1.36 mmol) of compound **15c**; flash column chromatography on silica gel (30% AcOEt in hexanes), white solid; m.p. 78-79 °C; $[\alpha]_D^{25}$ –25.3 (*c* 3.9, $CHCl_3$); TLC: R_f 0.44 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10–7.06 (m, 2H), 6.86–6.81 (m, 2H), 5.83 (dtd, *J* 15.3, 6.7, 1.1 Hz, 1H), 5.52 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H), 5.24 (pd, *J* 6.4, 0.8 Hz, 1H), 4.71 (s, 2H), 3.78 (s, 3H), 3.30 (d, *J* 6.7 Hz, 2H), 1.31 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.0, 156.4, 131.9, 131.6, 130.9, 129.5, 113.9, 71.5, 55.3, 37.6, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_3Na$ [M+Na$^+$] 258.1106. Found 258.1113; IR (film) *v*: 3433, 3331, 3263, 3210, 2974, 1683, 1612, 1509, 1405, 1241, 1041, 979, 813, 587 cm^{-1}.

(*S*,*E*)-5-(2-Methoxyphenyl)pent-3-en-2-yl carbamate (16d): Yield 189 mg (65%) starting from 236 mg (1.23 mmol) of compound **15d**; flash column chromatography on silica gel (20% AcOEt in hexanes); white solid; m.p. 64-65 °C; $[\alpha]_D^{21}$ –16.8 (*c* 16.6, $CHCl_3$); TLC: R_f 0.24 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (td, *J* 8.0, 1.7 Hz, 1H, Ar), 7.12 (dd, *J* 7.4, 1.5 Hz, 1H, Ar), 6.90 (td, *J* 7.4, 0.9 Hz, 1H, Ar), 6.85 (d, *J* 8.2 Hz, 1H, Ar), 5.92–5.84 (m, 1H,

CH_2CH=CH), 5.53 (ddt, *J* 15.4, 6.4, 1.4 Hz, 1H, CH_2CH=*CH*), 5.28–5.21 (m, 1H, CH_3CH), 5.04–4.95 (m, 2H, NH_2), 3.81 (s, 3H, OCH_3), 3.37 (d, *J* 6.7 Hz, 2H, $ArCH_2$), 1.31 (d, *J* 6.5 Hz, 3H, CH_3CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 156.8, 130.8, 130.8, 129.7, 128.4, 127.4, 120.5, 110.4, 71.6, 55.3, 32.7, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_3Na$ [M+Na^+] 258.1106. Found 258.1118; IR (film) *v*: 3426, 3332, 3266, 3210, 1691, 1614, 1493, 1401, 1239, 1106, 1048, 1027, 981, 753, 601, 584 cm^{-1}.

(*S*,*E*)-5-(3,4-Dimethoxyphenyl)pent-3-en-2-yl carbamate (16e): Yield 294 mg (87%) starting from 283 mg (1.27 mmol) of compound **15e**; flash column chromatography on silica gel (40% AcOEt in hexanes); white solid; m.p. 112-113 °C; $[\alpha]_D^{25}$ −21.2 (*c* 3.7, $CHCl_3$); TLC: R_f 0.13 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.79 (d, *J* 7.8 Hz, 1H), 6.69 (d, *J* 8.1 Hz, 2H), 5.88–5.79 (m, 1H), 5.53 (ddd, *J* 15.4, 6.3, 1.3 Hz, 1H), 5.24 (p, *J* 6.3 Hz, 1H), 4.69 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.30 (d, *J* 6.6 Hz, 2H), 1.31 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 148.9, 147.5, 132.4, 131.4, 131.1, 120.4, 112.0, 111.4, 71.5, 55.9, 55.8, 38.0, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{19}NO_4Na$ [M+Na^+] 288.1212. Found 288.1216; IR (film) *v*: 3447, 3350, 2968, 1701, 1517, 1389, 1304, 1263, 1234, 1151, 1136, 1049, 1025, 976, 799, 557 cm^{-1}.

(*R*,*E*)-5-(3,4-Dimethoxyphenyl)pent-3-en-2-yl carbamate (*ent*-16e): yield 81%; $[\alpha]_D^{25}$ +20.2 (*c* 1.7, $CHCl_3$); HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{19}NO_4Na$ [M+Na^+] 288.1212. Found 288.1208.

(*S*,*E*)-5-(Benzo[d][1,3]dioxol-5-yl)pent-3-en-2-yl carbamate (16f); Yield 269 mg (96%) starting from 232 mg (1.12 mmol) of compound **15f**; flash column chromatography on silica gel (30% AcOEt in hexanes); white solid; m.p. 87-88 °C; $[\alpha]_D^{25}$ –24.7 (*c* 2.7, $CHCl_3$); TLC: R_f 0.39 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.72 (d, *J* 7.9 Hz, 1H), 6.65 (d, *J* 1.5 Hz, 1H), 6.61 (dd, *J* 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 5.85–5.76 (m, 1H), 5.52 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H), 5.23 (p, *J* 6.4 Hz, 1H), 4.68 (s, 2H), 3.27 (d, *J* 6.7 Hz, 2H), 1.31 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 147.6, 145.9, 133.6, 131.3, 131.1, 121.3, 109.1, 108.2, 100.8, 71.5, 38.2, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{15}NO_4Na$ [M+Na^+] 279.0899. Found 272.0904; IR (film) *v*: 3427, 3335, 3270, 3212, 2974, 2897, 1961, 1613, 1500, 1487, 1441, 1402, 1245, 1230, 1041, 978, 930, 810, 594 cm^{-1}.

***t*-Butyl (*S*,*E*)-(4-(4-(carbamoyloxy)pent-2-en-1-yl)phenyl)carbamate (16g):** Yield 456 mg (96%) starting from 411 mg (1.48 mmol) of compound **15g**; flash column chromatography on silica gel (40% AcOEt in hexanes); white solid; m.p. 94-95 °C; $[\alpha]_D^{25}$ –16.5 (*c* 7.9, $CHCl_3$); R_f 0.11 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 1H, Ar), 7.26 (s, 1H, Ar), 7.07 (s, 1H, Ar), 7.05 (s, 1H, Ar), 6.67–6.63 (m, 1H, *NH*Boc), 5.81 (dtd, *J* 15.2, 6.7, 1.0 Hz, 1H, CH_2CH=CH), 5.49 (ddt, *J* 15.4, 6.3, 1.4 Hz, 1H, CH_2CH=*CH*), 5.22 (p, *J* 6.0 Hz, 1H, CH_3CH), 4.83–4.78 (m, 2H, NH_2), 3.29 (d, *J* 6.6 Hz, 2H, $ArCH_2$), 1.50 (s, 9H, $C(CH_3)_3$), 1.29 (d, *J* 6.5 Hz, 3H, CH_3CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 153.0, 136.6, 134.4, 131.3, 131.0, 129.0, 128.8, 118.9, 80.4, 71.5, 67.6, 37.8, 28.4, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{24}N_2O_4Na$ [M+Na^+] 343.1634. Found 343.1641; IR (film) *v*: 3477, 3334, 2979, 1704, 1597, 1525, 1412, 1391, 1368, 1316, 1239, 1161, 1052, 971, 834, 778 cm^{-1}.

(*S*,*E*)-5-(4-Chlorophenyl)pent-3-en-2-yl carbamate (16h): Yield 230 mg (91%) starting from 207 mg (1.05 mmol) of compound **15h**; flash column chromatography on silica gel (30% AcOEt in hexanes); white solid; m.p. 98-99 °C; $[\alpha]_D^{25}$ –25.9 (*c* 3.0, $CHCl_3$); TLC: R_f 0.42 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.23 (m, 2H), 7.10–7.07 (m, 2H), 5.86–5.77 (m, 1H), 5.52 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H), 5.23 (pd, *J* 6.4, 0.6 Hz, 1H), 4.69 (s, 2H), 3.33 (d, *J* 6.7 Hz, 2H), 1.30 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 138.2, 131.9, 131.7, 130.5, 129.9, 128.5, 71.4, 37.8, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_2NaCl$ [M+Na$^+$] 262.0611. Found 262.0617; IR (film) *v*: 3429, 3263, 3212, 1682, 1614, 1492, 1410, 1054, 966, 807, 586 cm^{-1}.

(*S*,*E*)-5-(2-Chlorophenyl)pent-3-en-2-yl carbamate (16i): Yield 280 mg (91%) starting from 252 mg (1.28 mmol) of compound **15i**; flash column chromatography on silica gel (32% AcOEt in hexanes); white solid; m.p. 73-74 °C; $[\alpha]_D^{21}$ –28.2(*c* 3.1, $CHCl_3$); TLC: R_f 0.28 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.32 (m, 1H, Ar), 7.20–7.12 (m, 3H, Ar), 5.84 (dtd, *J* 15.4, 6.6, 1.1 Hz, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H, CH_2CH=*CH*), 5.24 (pd, *J* 6.4, 0.8 Hz, 1H, CH_3*CH*), 4.73–4.62 (m, 2H, N*H*$_2$), 3.48 (d, *J* 6.6 Hz, 2H, Ar*CH*$_2$), 1.30 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 137.5, 134.0, 131.9, 130.4, 129.4, 129.1, 127.6, 126.9, 71.4, 36.0, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_2NaCl$ [M+Na$^+$] 262.0611. Found 262.0615; IR (film) *v*: 3428, 3266, 3212, 2977, 1687, 1615, 1403, 1304, 1048, 975, 753 cm^{-1}.

(*S*,*E*)-5-(2-Bromophenyl)pent-3-en-2-yl carbamate (16j): Yield 86 mg (86%) starting from 85 mg (0.35 mmol) of compound **15j**; flash column chromatography on silica gel (22% AcOEt in hexanes); white solid; m.p. 81-82 °C; $[\alpha]_D^{25}$ –22.8 (*c* 6.1, $CHCl_3$); TLC: R_f 0.23 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, *J* 8.0, 1.0 Hz, 1H, Ar), 7.26–7.18 (m, 2H, Ar), 7.09–7.04 (m, 1H, Ar), 5.84 (dtd, *J* 15.3, 6.6, 1.1 Hz, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H, CH_2CH=*CH*), 5.24 (p, *J* 6.4 Hz, 1H, CH_3*CH*), 4.76 (s, 2H, N*H*$_2$), 3.48 (d, *J* 6.6 Hz, 2H, Ar*CH*$_2$), 1.30 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.5, 139.3, 132.8, 132.0, 130.4, 129.2, 127.9, 127.5, 124.6, 71.4, 38.6, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_2NaBr$ [M+Na$^+$] 306.0106. Found 306.0096; IR (film) *v*: 3427, 3331, 3265, 3212, 2975, 1689, 1614, 1403, 1304, 1046, 1023, 750, 596 cm^{-1}.

(*S*,*E*)-5-(Naphthalen-1-yl)pent-3-en-2-yl carbamate (16k): Yield 418 mg (95%) starting from 344 mg (1.72 mmol) of compound **15k**; flash column chromatography on silica gel (1:4 AcOEt/hexanes); white solid; m.p. 123-124 °C; $[\alpha]_D^{25}$ –28.9 (*c* 1.3, $CHCl_3$); TLC: R_f 0.33 (1:4 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (d, *J* 8.1 Hz, 1H), 7.87–7.83 (m, 1H), 7.74 (d, *J* 8.2 Hz, 1H), 7.53–7.45 (m, 2H), 6.01 (dt, *J* 14.4, 6.4 Hz, 1H), 5.56 (dd, *J* 15.5, 6.4 Hz, 1H), 5.25 (p, *J* 6.4 Hz, 1H), 4.56 (s, 2H), 3.83 (d, *J* 6.3 Hz, 2H), 1.29 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 135.9, 133.8, 131.9, 131.5, 130.7, 128.7, 127.0, 126.3, 125.8, 125.6, 125.5, 123.9, 71.6, 35.6, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{17}NO_2Na$ [M+Na$^+$] 278.1157. Found 278.1168; IR (film) *v*: 3431, 3337, 3259, 3211, 2978, 1691, 1610, 1405, 1044, 961, 821, 743, 598, 476 cm^{-1}.

(*S*,*E*)-5-(Naphthalen-2-yl)pent-3-en-2-yl carbamate (16l): Yield 333 mg (93%) starting from 286 mg (1.40 mmol) of compound **15l**; flash column chromatography on silica gel (1:3 AcOEt/hexanes); white solid; m.p. 84-85 °C; $[\alpha]_D^{25}$ –26.2 (*c* 3.3, $CHCl_3$); TLC: R_f 0.42 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6) δ: 7.82–7.74 (m, 3H), 7.60 (s, 1H), 7.47–7.39 (m, 2H), 7.30 (dd, *J* 8.4, 1.8 Hz, 1H), 5.94 (dtd, *J* 15.4, 6.7, 1.2 Hz, 1H), 5.59 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H), 5.27 (pd, *J* 6.4, 0.9 Hz, 1H), 4.71 (s, 2H), 3.52 (d, *J* 6.7 Hz, 2H), 1.32 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$/acetone-d_6) δ: 156.4, 137.3, 133.6, 132.1, 131.5, 131.0, 128.0, 127.6, 127.5, 127.3, 126.7, 126.0, 125.3, 71.5, 38.6, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{17}NO_2Na$ [M+Na$^+$] 278.1157. Found 278.1164; IR (film) *v*: 3432, 3332, 3267, 3212, 2977, 1685, 1610, 1406, 1047, 968, 820, 743, 598, 477 cm^{-1}.

(*S*,*E*)-5-(4-(Trifluoromethyl)phenyl)pent-3-en-2-yl carbamate (16m): Yield 229 mg (86%) starting from 224 mg (0.97 mmol) of compound **15m**; flash column chromatography on silica gel (30% AcOEt in hexanes); white solid; m.p. 84-85 °C; $[\alpha]_D^{25}$ –22.1 (*c* 4.3, $CHCl_3$); TLC: R_f 0.23 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H, Ar), 7.53 (s, 1H, Ar), 7.28 (s, 1H, Ar), 7.26 (s, 1H, Ar), 5.88–5.80 (m, 1H, CH_2*CH*=CH), 5.56 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H, CH_2CH=*CH*), 5.25 (pd, *J* 6.4, 0.7 Hz, 1H, CH_3*CH*), 4.76–4.68 (m, 2H, *NH*$_2$), 3.42 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.31 (d, *J* 6.5 Hz, 3H *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 143.9, 132.2, 129.9, 128.9, 125.4 (q, $J_{C\text{-}F}$ 3.8 Hz), 71.3, 38.2, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NO_2NaF_3$ [M+Na$^+$] 296.0874. Found 296.0879; IR (film) *v*: 3437, 3336, 3276, 3214, 2977, 1692, 1613, 1403, 1328, 1164, 1116, 1068, 981, 893, 850, 818, 594 cm^{-1}.

(*S*,*E*)-5-(4-Acetylphenyl)pent-3-en-2-yl carbamate (16n): purity 80%*; overall yield 256 mg (91%) starting from 232 mg (1.12 mmol) of mixture of **15n/15n***; flash column chromatography on silica gel (45% AcOEt in hexanes); white solid; TLC: R_f 0.13 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90–7.89 (m, 1H, Ar), 7.88–7.87 (m, 1H, Ar), 7.27–7.26 (m, 1H, Ar), 7.25–7.24 (m, 1H, Ar), 5.84 (dtd, *J* 15.3, 6.7, 1.1 Hz, 1H, CH_2*CH*=CH), 5.55 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H, CH_2CH=*CH*), 5.25 (pd, *J* 6.5, 0.8 Hz, 1H, CH_3*CH*), 4.60 (s, 2H, *NH*$_2$), 3.42 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 2.58 (s, 3H, *CH*$_3$CO), 1.31 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.8, 156.2, 145.5, 135.4, 132.1, 123.0, 128.8, 128.6, 126.2, 71.3, 38.4, 26.5, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{17}NO_3Na$ [M+Na$^+$] 270.1106. Found 270.1102; IR (film) *v*: 3455, 3355, 2979, 1716, 1679, 1604, 1378, 1360, 1316, 1270, 1047, 1017, 969, 849, 819, 783, 597 cm^{-1}. *compound **16n** is contaminated with (*S,E*)-5-(4-acetylphenyl)pent-4-en-2-yl carbamate (**16n***, inseparable mixture in ratio 5:1).

(*S*,*E*)-5-(4-Cyanophenyl)pent-3-en-2-yl carbamate (16o) and **(*S*,*E*)-5-(4-Cyanophenyl)pent-4-en-2-yl carbamate (16o*):** inseparable mixture (1:1); purification by flash column chromatography on silica gel (35% AcOEt in hexanes); Overall yield 98 mg (83%) starting from 96 mg (0.51 mmol) of mixture of **15o/15o***; white crystal; TLC: R_f 0.18 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.48 (m, 4H), 7.38 (d, *J* 8.3 Hz, 2H, **16o**), 7.25 (d, *J* 8.2 Hz, 2H, **16o***), 6.43 (d, *J* 15.9 Hz, 1H, **16o***), 6.35–6.22 (m, 1H, **16o***), 5.85–5.71 (m, 1H, **16o**), 5.54 (dd, *J* 15.4, 6.2 Hz, 1H, **16o**), 5.21 (p, *J* 6.3 Hz, 1H, **16o**), 4.91 (m, 5H), 3.39

(d, *J* 6.7 Hz, 2H, **16o**), 2.58–2.38 (m, 2H, **16o***), 1.28 (d, *J* 6.5 Hz, 3H, **16o**), 1.25 (d, *J* 6.3 Hz, 3H, **16o***); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 156.5, 145.5, 141.8, 132.7, 132.3, 132.2, 131.2, 129.9, 129.3, 129.1, 126.6, 119.0, 119.0, 110.4, 110.1, 71.1, 70.6, 53.5, 39.7, 38.4, 20.4, 19.9; IR (film) *v*: 3433, 3343, 3206, 2971, 2227, 1683, 1607, 1505, 1401, 1305, 1177, 1136, 1062, 1047, 976, 852, 813, 787, 580, 548 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}N_2O_2Na$ [M+Na$^+$] 253.0953. Found 253.095.

Methyl (*S*,*E*)-4-(4-(carbamoyloxy)pent-2-en-1-yl)benzoate (16p) and Methyl (*S*,*E*)-4-(4-(carbamoyloxy)pent-1-en-1-yl)benzoate (16p*): inseparable mixture **16p/16p*** (6:1); purification by flash column chromatography on silica gel (35% AcOEt in hexanes). Overall yield 109 mg (97%) starting from 94 mg (0.43 mmol) of mixture of **15p/15p***; TLC: R_f 0.16 (1:4 AcOEt:hexanes); Compound **16p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95–7.93 (m, 2H, Ar), 7.21 (d, *J* 8.4 Hz, 2H, Ar), 5.86–5.78 (m, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.4, 6.3, 1.4 Hz, 1H, CH_2CH=*CH*), 5.22 (p, *J* 6.2 Hz, 1H, CH_3*CH*), 4.88 (s, 2H, *NH*$_2$), 3.88 (s, 3H, CO_2*CH*$_3$), 3.39 (d, *J* 6.7 Hz, 2H, Ar*CH*$_2$), 1.29 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.0, 156.5, 145.3, 132.1, 130.0, 129.9, 129.8, 128.6, 128.2, 126.0, 71.2, 52.0, 38.4, 20.4; Compound **16p*:** ^{1}H NMR (400 MHz, $CDCl_3$, selected signals) δ: 7.37 (d, *J* 8.3 Hz, 2H, Ar), 6.45 (d, *J* 15.9 Hz, 1H, Ar*CH*=CHCH$_2$), 6.28 (dt, *J* 15.8, 7.2 Hz, 1H, ArCH=*CH*CH$_2$), 2.55-2.39 (m, 2H), 1.26 (d, *J* 6.3 Hz, 3H, CH$_3$*CH*); ^{13}C NMR (101 MHz, $CDCl_3$, selected signals) δ: 166.9, 156.7, 141.8, 131.9, 70.8, 39.7, 19.8; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{17}NO_4Na$ [M+Na$^+$] 286.1055. Found 286.1056; IR (film) *v*: 3437, 3319, 3294, 3204, 2985, 1702, 1606, 1436, 1399, 1284, 1180, 1111, 1059, 1018, 966, 857, 766, 719, 575 cm^{-1}.

(*S*,*E*)-5-(4-Vinylphenyl)pent-3-en-2-yl carbamate (16r): yield 302 mg (97%) starting from 254 mg (1.35 mmol) of compound **15r**; flash column chromatography on silica gel (20% AcOEt in hexanes); white crystal; m.p. 70-71 ^{o}C; $\alpha]_D^{21}$ –28.2 (*c* 4.0, $CHCl_3$); TLC: R_f 0.23 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* 8.1 Hz, 2H), 7.13 (d, *J* 8.1 Hz, 2H), 6.69 (dd, *J* 17.6, 10.9 Hz, 1H), 5.85 (dtd, *J* 15.3, 6.7, 1.1 Hz, 1H), 5.71 (dd, *J* 17.6, 0.9 Hz, 1H), 5.54 (ddt, *J* 15.4, 6.3, 1.5 Hz, 1H), 5.25 (ddd, *J* 12.8, 6.4, 0.8 Hz, 1H), 5.20 (dd, *J* 10.9, 0.9 Hz, 1H), 4.71 (s, 2H), 3.36 (d, *J* 6.7 Hz, 2H), 1.31 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 139.5, 136.6, 135.6, 131.3, 131.0, 128.7, 126.3, 113.2, 71.5, 38.2, 20.5; IR (film) *v*: 3434, 3331, 3264, 3212, 2987, 1683, 1614, 1510, 1408, 1318, 1144, 1116, 1057, 991, 965, 897, 849, 827, 787, 586 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{17}NO_2Na$ [M+Na$^+$] 254.1157. Found 254.1158.

(*S*,*E*)-5-(Furan-2-yl)pent-3-en-2-yl carbamate (16s): yield 119 mg (87%) starting from 107 mg (0.70 mmol) of compound **15s**; flash column chromatography on silica gel (28% AcOEt in hexanes); colorless oil; $[\alpha]_D^{21}$ –22.2 (*c* 8.0, $CHCl_3$); TLC: R_f 0.28 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (dd, *J* 1.8, 0.8 Hz, 1H, Ar), 6.27 (dd, *J* 3.1, 1.9 Hz, 1H, Ar), 5.99 (dd, *J* 3.2, 0.9 Hz, 1H, Ar), 5.81 (dtd, *J* 15.4, 6.6, 1.1 Hz, 1H, CH_2*CH*=CH), 5.58 (ddt, *J* 15.4, 6.2, 1.5 Hz, 1H, CH_2CH=*CH*), 5.23 (pd, *J* 6.4, 0.8 Hz, 1H, CH_3*CH*), 4.89 (s, 2H, N*H*$_2$), 3.36 (d, *J* 6.5 Hz, 2H, Ar*CH*$_2$), 1.30 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 153.6, 141.3, 132.2,

127.6, 110.2, 105.6, 71.2, 31.0, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{13}NO_3Na$ [M+Na$^+$] 218.0793. Found 218.0792; IR (film) *v*: 3486, 3348, 2979, 2932, 1711, 1598, 1378, 1314, 1146, 1048, 1010, 970, 734, 600 cm^{-1}.

(*S*,*E*)-5-(Furan-3-yl)pent-3-en-2-yl carbamate (16t): Yield 116 mg (72%) starting from 127 mg (0.83 mmol) of compound **15t**; flash column chromatography on silica gel (25% AcOEt in hexanes); waxy solid; $[\alpha]_D^{21}$ –22.4 (*c* 12.0, $CHCl_3$); TLC: R_f 0.26 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (t, *J* 1.6 Hz, 1H, Ar), 7.19 (s, 1H, Ar), 6.23 (d, *J* 0.9 Hz, 1H, Ar), 5.79 (dtd, *J* 15.4, 6.5, 1.1 Hz, 1H, CH_2*CH*=CH), 5.53 (ddt, *J* 15.4, 6.4, 1.5 Hz, 1H, CH_2CH=*CH*), 5.21 (p, *J* 6.4 Hz, 1H, CH_3*CH*), 4.96 (s, 2H, N*H*$_2$), 3.14 (d, *J* 6.5 Hz, 2H, Ar*CH*$_2$), 1.28 (d, *J* 6.5 Hz, 3H, *CH*$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 142.9, 139.2, 131.1, 130.2, 122.9, 111.1, 71.4, 27.6, 20.4; IR (film) *v*: 3484, 3346, 2982, 2930, 1711, 1594, 1373, 1314, 1146, 1046, 1013, 970, 734, 602 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{13}NO_3Na$ [M+Na$^+$] 218.0793. Found 218.0789.

1.5. Synthesis of allyl amines 18. General procedure. To a cooled to –20 °C solution of carbamate **16a** (150 mg, 0.73 mmol) and Et_3N (443 mg, 608 µL, 4.38 mmol) in dry THF (10 mL), TFAA (307 mg, 203 µL, 1.46 mmol) was added, and the resulting mixture was slowly warmed to room temperature. The progress of the reaction was followed by TLC (1:8 AcOEt/hexanes). In a separate flask 1M soln. of LiHMDS in THF (4.38 mL, 4.38 mmol) was added to anhydr. *t*-BuOH (4 mL) in dry THF (10 mL). When the rearrangement reaction was completed (ca. 1 h) the solution of *t*-BuOLi was cannulated into it, and reaction mixture was stirred overnight at room temperature. Progress of reaction was followed by TLC (1:8 AcOEt/hexanes). After removal of solvents, crude product was absorbed on silica gel and chromatographed (8% AcOEt in hexanes) to give 158 mg of compound **18a** (83%) as white solid.

***t*-Butyl (*R*,*E*)-(1-phenylpent-3-en-2-yl)carbamate (18a);** white solid, m.p. 79-80 °C; $[\alpha]_D^{25}$ –11.5 (*c* 2.0, $CHCl_3$); TLC: R_f 0.56 (1:8 AcOEt/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of rotamers) δ: 7.31–7.25 (m, 2H), 7.23–7.16 (m, 3H), 5.58–5.49 (m, 1H), 5.39 (ddd, *J* 15.3, 6.0, 1.5 Hz, 1H), 4.42 (s, 1H), 4.33 (s, 1H), 2.80 (d, *J* 6.6 Hz, 2H), 1.65 (d, *J* 6.4 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 137.8, 130.9, 129.6, 128.2, 126.3, 126.1, 79.3, 55.3, 42.0, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_2Na$ [M+Na$^+$] 284.1626. Found 284.1631; IR (film) *v*: 3367, 3031, 3005, 2983, 2938, 1684, 1518, 1448, 1390, 1364, 1304, 1290, 1251, 1168, 1021, 1008, 968, 753, 701, 630, 527 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(p-tolyl)pent-3-en-2-yl)carbamate (18b):** yield 232 mg (85%) starting from 217 mg (0.99 mmol) of compound **16b**; flash column chromatography on silica gel (8% AcOEt in hexanes); white solid; m.p. 61-62 °C; $[\alpha]_D^{25}$ –11.8 (*c* 1.4, $CHCl_3$); TLC: R_f 0.72 (1:6 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of rotamers) δ: 7.09 (d, *J* 7.9 Hz, 2H), 7.05 (d, *J* 8.0 Hz, 2H), 5.57–5.48 (m, 1H), 5.38 (dd, *J* 15.9, 5.3 Hz, 1H), 4.41 (s, 1H), 4.30 (s, 1H), 2.79–2.75 (m, 2H), 2.32 (s, 3H), 1.65 (d, *J* 6.4 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 135.8, 134.6, 131.0, 129.5, 128.9, 126.0, 79.1, 41.5, 28.4, 21.0,

17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_2Na$ [M+Na^+] 298.1783. Found 298.1780; IR (film) *v*: 3364, 2979, 2919, 1686, 1519, 1444, 1389, 1365, 1303, 1248, 1173, 1041, 1010, 967, 811, 630 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(4-methoxyphenyl)pent-3-en-2-yl)carbamate (18c):** Purification by flash column chromatography on silica gel (13% AcOEt in hexanes). Yield 300 mg (84%) starting from 288 mg (0.99 mmol) of compound **18c**; white solid; m.p. 74-75 °C; $[\alpha]_D^{25}$ –9.7 (*c* 4.2, $CHCl_3$); TLC: R_f 0.69 (1:6 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.10–7.07 (m, 1H), 7.07–7.05 (m, 1H), 6.84–6.81 (m, 1H), 6.82–6.79 (m, 1H), 5.51 (dqd, *J* 15.3, 6.3, 1.2 Hz, 1H), 5.37 (ddq, *J* 15.3, 6.0, 1.4 Hz, 1H), 3.78 (s, *J* 1.9 Hz, 3H), 2.76–2.72 (m, 2H), 1.65–1.63 (m, 3H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 158.2, 131.0, 130.5, 129.8, 126.1, 113.7, 79.1, 55.2, 39.5, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_3Na$ [M+Na^+] 314.1732. Found 314.1732; IR (film) *v*: 3361, 2978, 2935, 1685, 1513, 1365, 1247, 1175, 1038, 967, 822, 532 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(2-methoxyphenyl)pent-3-en-2-yl)carbamate (18d):** yield 156 mg (84%) starting from 151 mg (0.64 mmol) of compound **16d**; flash column chromatography on silica gel (8% AcOEt in hexanes); waxy solid; $[\alpha]_D^{25}$ –3.9 (*c* 15.0, $CHCl_3$); TLC: R_f 0.54 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.18 (td, *J* 8.1, 1.5 Hz, 1H, Ar), 7.11 (d, *J* 7.4 Hz, 1H, Ar), 6.90–6.82 (m, 2H, Ar), 5.61–5.52 (m, 1H, CH_3CH=*CH*), 5.43 (ddd, *J* 15.3, 5.9, 1.2 Hz, 1H, CH_3*CH*=CH), 4.77 (s, 1H), 4.30 (s, 1H), 3.82 (s, 3H, O*CH_3*), 2.84–2.73 (m, 2H, Ar*CH_2*), 1.65 (d, *J* 6.3 Hz, 3H, *CH_3*CH=CH), 1.35 (s, 9H, C(*CH_3*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 157.6, 132.1, 131.2, 127.6, 126.6, 125.1, 120.5, 110.3, 79.3, 55.2, 38.9, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_3Na$ [M+Na^+] 314.1732. Found 314.1740; IR (film) *v*: 3367, 3009, 2980, 2933, 1683, 1588, 1526, 1496, 1458, 1437, 1308, 1243, 1176, 1035, 1021, 969, 860, 751, 624 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(3,4-dimethoxyphenyl)pent-3-en-2-yl)carbamate (18e):** Purification by flash column chromatography on silica gel (15% AcOEt in hexanes); yield 285 mg (86%) starting from 274 mg (1.03 mmol) of compound **16e**; waxy solid; $[\alpha]_D^{25}$ –11.4 (*c* 3.4, $CHCl_3$); TLC: R_f 0.43 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 6.80–6.76 (m, 1H, Ar), 6.71–6.67 (m, 2H, Ar), 5.52 (dqd, *J* 15.2, 6.3, 1.2 Hz, 1H, CH_3CH=*CH*), 5.37 (ddq, *J* 15.3, 5.9, 1.4 Hz, 1H, CH_3*CH*=CH), 4.47–4.36 (m, 1H, *CH*NH), 4.35–4.24 (m, 1H, *NH*), 3.85 (s, 3H, O*CH_3*), 3.85 (s, 3H, O*CH_3*), 2.79–2.68 (m, 2H, Ar*CH_2*), 1.64 (dt, *J* 6.4, 1.3 Hz, 3H, *CH_3*CH=CH), 1.40 (s, 9H, C(*CH_3*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 148.7, 147.6, 131.0, 130.3, 126.1, 121.6, 112.8, 111.1, 55.9, 55.8, 41.5, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}NO_4Na$ [M+Na^+] 344.1838. Found 344.1842; IR (film) *v*: 3361, 2974, 2933, 1704, 1516, 1365, 1263, 1237, 1171, 1160, 1030, 967, 859, 806, 767 cm^{-1}.

***t*-Butyl (*S*,*E*)-(1-(3,4-dimethoxyphenyl)pent-3-en-2-yl)carbamate (*ent*-18e):** $[\alpha]_D^{25}$ +11.0 (*c* 2.5, $CHCl_3$); HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}NO_4Na$ [M+Na^+] 344.1838. Found 344.1837.

***t*-Butyl (*R*,*E*)-(1-(benzo[d][1,3]dioxol-5-yl)pent-3-en-2-yl)carbamate (18f):** purification by flash column chromatography on silica gel (6% AcOEt in hexanes); yield 262 mg (85%) starting from 252 mg (1.01 mmol) of compound **16f**; yellow solid; m.p. 71-72°C; $[\alpha]_D^{25}$ –8.3 (*c* 2.2, $CHCl_3$); R_f 0.65 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 6.72 (d, *J* 7.9 Hz, 1H), 6.66 (d, *J* 1.6 Hz, 1H), 6.61 (dd, *J* 7.9, 1.6 Hz, 1H), 5.91 (q, *J* 1.6 Hz, 2H), 5.54 (dqd, *J* 12.7, 6.4, 1.2 Hz, 1H), 5.37 (ddd, *J* 15.3, 6.1, 1.6 Hz, 1H), 4.40 (s, 1H), 4.31–4.19 (m, 1H), 2.73–2.70 (m, 2H), 1.66–1.64 (m, 3H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 159.9, 147.5, 131.5, 130.9, 128.4, 126.2, 125.6, 122.5, 109.9, 108.0, 100.8, 79.0, 41.7, 35.8, , 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_4Na$ [M+Na$^+$] 328.1525. Found 328.1529; IR (film) *v*: 3408, 3350, 2975, 2928, 1702, 1503, 1490, 1443, 1365, 1248, 1171, 1041, 967, 932, 810, 700 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(4-((*tert*-butoxycarbonyl)amino)phenyl)pent-3-en-2-yl)carbamate (18g)** Purification by flash column chromatography on silica gel (30% AcOEt in hexanes). Yield 394 mg (77%) starting from 435 mg (1.36 mmol) of compound **16g**; white solid; m.p. 155-156 °C; $[\alpha]_D^{25}$ –8.7 (*c* 7.0, $CHCl_3$); TLC: R_f 0.63 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.27 (s, 1H, Ar), 7.25 (s, 1H, Ar), 7.07 (s, 1H, Ar), 7.05 (s, 1H, Ar), 5.49 (ddd, *J* 15.3, 6.4, 1.2 Hz, 1H, CH_3CH=*CH*), 5.34 (ddd, *J* 15.3, 6.1, 1.5 Hz, 1H, CH_3*CH*=CH), 4.48–4.37 (m, 1H, *CH*NH), 4.34–4.18 (m, 1H, *NH*), 2.80–2.67 (m, 2H, ArCH_2), 1.62 (dt, *J* 6.4, 1.2 Hz, 3H, CH_3CH=CH), 1.50 (s, 9H, C(CH_3)$_3$), 1.40 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 152.9, 136.7, 132.3, 130.9, 130.1, 126.2, 118.5, 80.4, 79.2, 53.2, 41.1, 28.4, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{32}N_2O_4Na$ [M+Na$^+$] 399.2260. Found 399.2262; IR (film) *v*: 3357, 2970, 1696, 1676, 1593, 1517, 1411, 1366, 1313, 1237, 1159, 1050, 1019, 969, 825, 763, 740, 591 cm^{-1}

***t*-Butyl (*R*,*E*)-(1-(4-chlorophenyl)pent-3-en-2-yl)carbamate (18h):** purification by flash column chromatography on silica gel (10% AcOEt in hexanes); yield 216 mg (83%) starting from 252 mg (0.88 mmol) of compound **16h**; white solid; m.p. 109-110 °C; $[\alpha]_D^{25}$ –7.6 (*c* 1.4, $CHCl_3$); TLC: R_f 0.74 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.26–7.22 (m, 2H), 7.09 (d, *J* 8.4 Hz, 2H), 5.52 (dqd, *J* 12.7, 6.4, 1.1 Hz, 1H), 5.35 (ddd, *J* 15.3, 6.1, 1.5 Hz, 1H), 4.39 (s, 1H), 4.28 (s, 1H), 2.83–2.72 (m, 2H), 1.66–1.62 (m, 3H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 136.3, 132.2, 130.9, 130.5, 128.3, 126.7, 79.2, 52.5, 41.3, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_2ClNa$ [M+Na$^+$] 318.1237. Found 318.1241; IR (film) *v*: 3365, 2968, 1684, 1521, 1444, 1366, 1300, 1251, 1170, 1092, 1017, 970, 834, 819, 661, 495 cm^{-1}

***t*-Butyl (*R*,*E*)-(1-(2-chlorophenyl)pent-3-en-2-yl)carbamate (18i):** purification by flash column chromatography on silica gel (9% AcOEt in hexanes); yield 282 mg (84%) starting from 272 mg (1.13 mmol) of compound **16i**; yellow crystals; m.p. 96-97 °C; $[\alpha]_D^{25}$ +11.7 (*c* 4.9, $CHCl_3$); TLC: R_f 0.57 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.33 (dd, *J* 7.4, 1.8 Hz, 1H, Ar), 7.2 –7.11 (m, 3H, Ar), 5.57 (dq, *J* 15.0, 6.3 Hz, 1H, CH_3CH=*CH*), 5.45 (ddd, *J* 15.3, 5.8, 1.4 Hz, 1H, CH_3*CH*=CH), 4.57–4.47 (m, 1H), 4.40 (dt, *J*

14.6, 7.1 Hz, 1H), 2.98 (dd, *J* 13.6, 6.0 Hz, 1H), 2.93–2.86 (m, 1H), 1.65 (d, *J* 6.2 Hz, 3H, *CH*$_3$CH=CH), 1.34 (s, 9H, C(*CH*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 136.0, 134.5, 131.5, 131.0, 129.4, 127.7, 126.6, 126.1, 79.2, 52.6, 39.2, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}N_3O_4NaCl$ [M+Na$^+$] 318.1221. Found 318.1227; IR (film) *v*: 3364, 2981, 2966, 1684, 1525, 1444, 1386, 1307, 1249, 1176, 1019, 970, 753, 682, 639, 446 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(2-bromophenyl)pent-3-en-2-yl)carbamate (18j):** yield 89 mg (91%) starting from 82 mg (0.29 mmol) of compound **16j**; flash column chromatography on silica gel (9% AcOEt in hexanes). white crystals; m.p. 109-110 °C; $[\alpha]_D^{25}$ +12.3 (*c* 6.2, $CHCl_3$); R_f 0.61 (20% AcOEt in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.52 (d, *J* 7.9 Hz, 1H, Ar), 7.23–7.21 (m, *J* 4.4 Hz, 1H, Ar), 7.21–7.20 (m, 1H, Ar), 7.09–7.03 (m, 1H, Ar), 5.62–5.52 (m, 1H, CH$_3$CH=*CH*), 5.46 (dd, *J* 15.9, 5.1 Hz, 1H, CH$_3$*CH*=CH), 4.59–4.49 (m, 1H), 4.46–4.36 (m, 1H), 2.99 (dd, *J* 13.6, 5.8 Hz, 1H), 2.93–2.86 (m, 1H), 1.66 (d, *J* 6.1 Hz, 3H, *CH*$_3$CH=CH), 1.34 (s, 9H, C(*CH*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 137.7, 132.7, 131.5, 131.0, 128.0, 127.2, 126.1, 125.1, 79.2, 52.7, 41.8, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_2NaBr$ [M+Na$^+$] 362.0732. Found 362.0724; IR (film) *v*: 3364, 2980, 2965, 1684, 1524, 1443, 1368, 1249, 1173, 970, 752, 660, 639 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(naphthalen-1-yl)pent-3-en-2-yl)carbamate (18k)** Purification by flash column chromatography on silica gel (8% AcOEt in hexanes). Yield 395 mg (80%) starting from 405 mg (1.59 mmol) of compound **16k**; white solid; m.p. 109-110 °C; $[\alpha]_D^{25}$ –1.4 (*c* 1.7, $CHCl_3$); TLC: R_f 0.65 (1:6 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of rotamers) δ: 8.14 (d, *J* 7.6 Hz, 1H), 7.84 (d, *J* 8.0 Hz, 1H), 7.73 (d, *J* 8.2 Hz, 1H), 7.53 (t, *J* 7.6 Hz, 1H), 7.47 (t, *J* 7.4 Hz, 1H), 7.39 (t, *J* 7.6 Hz, 1H), 7.29 (d, *J* 6.9 Hz, 1H), 5.55–5.47 (m, 1H), 5.44 (dd, *J* 15.3, 3.9 Hz, 1H), 4.50 (s, 2H), 3.36 (s, 1H), 3.24–3.13 (m, 1H), 1.61 (d, *J* 5.8 Hz, 3H), 1.37 (br s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 134.1, 133.9, 132.4, 131.0, 128.7, 127.8, 127.2, 126.3, 125.9, 125.5, 125.2, 124.1, 79.1, 52.9, 39.3, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{25}NO_2Na$ [M+Na$^+$] 334.1783. Found 334.1776; IR (film) *v*: 3411, 3348, 2976, 2932, 1700, 1509, 1499, 1390, 1365, 1245, 1171, 1013, 965, 792, 777 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(naphthalen-2-yl)pent-3-en-2-yl)carbamate (18l):** purification by flash column chromatography on silica gel (11% AcOEt in hexanes); yield 336 mg (91%) starting from 303 mg (1.19 mmol) of compound **16l**; white solid; m.p. 114-115 °C; $[\alpha]_D^{25}$ –12.3 (*c* 3.5, $CHCl_3$); TLC: R_f 0.71 (1:6 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.83–7.75 (m, 3H), 7.62 (s, 1H), 7.48–7.41 (m, 2H), 7.33 (dd, *J* 8.4, 1.7 Hz, 1H), 5.60–5.50 (m, 1H), 5.43 (ddd, *J* 15.3, 5.7, 1.4 Hz, 1H), 4.56–4.36 (m, 2H), 3.04–2.92 (m, 2H), 1.64 (d, *J* 6.2 Hz, 3H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 135.4, 133.5, 132.2, 128.1, 128.0, 127.7, 127.6, 127.5, 126.3, 125.9, 125.4, 79.3, 53.3, 42.1, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{25}NO_2Na$ [M+Na$^+$] 334.1783. Found 334.1789; IR (film) *v*: 3366, 2980, 2965, 1686, 1519, 1365, 1246, 1172, 967, 821, 749, 622, 479 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(4-(trifluoromethyl)phenyl)pent-3-en-2-yl)carbamate (18m)** Purification by flash column chromatography on silica gel (10% AcOEt in hexanes). Yield 218 mg (89%)

starting from 203 mg (0.74 mmol) of compound **16m**; white solid; m.p. 83-84 °C; $[\alpha]_D^{25}$ –1.7(*c* 7.2, $CHCl_3$); R_f 0.77 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.53 (s, 1H, Ar), 7.51 (s, 1H, Ar), 7.29 (s, 1H, Ar), 7.27 (s, 1H, Ar), 5.54 (ddd, *J* 15.3, 6.4, 1.2 Hz, 1H, CH_3CH=*CH*), 5.37 (ddd, *J* 15.4, 6.1, 1.6 Hz, 1H, CH_3*CH*=CH), 4.49–4.40 (m, 1H, *CH*NH), 4.40–4.28 (m, 1H, *NH*), 2.86 (d, *J* 6.7 Hz, 2H, ArCH_2), 1.65 (d, *J* 6.4 Hz, 3H, CH_3CH=CH), 1.38 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.1, 142.1, 130.3, 129.9, 128.4, 128.2, 126.9, 125.1, 125.09, 125.05, 125.01, 79.4, 41.8, 35.8, 31.0, 28.3, 17.6. HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{22}NO_2NaF_3$ [M+Na$^+$] 352.1500. Found 352.1497; IR (film) *v*: 3357, 2985, 2926, 1680, 1524, 1444, 1369, 1326, 1266, 1253, 1158, 1118, 1067, 1020, 968, 843, 829, 642, 599, 498 cm^{-1}

t*-Butyl (*R,E*)-(1-(4-acetylphenyl)pent-3-en-2-yl)carbamate (18n):** Yield 17 mg (22%) starting from **16n/16n; flash column chromatography on silica gel (14% AcOEt in hexanes); waxy solid; $[\alpha]_D^{25}$ –7.2 (*c* 2.0, $CHCl_3$); TLC: R_f 0.42 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.89–7.87 (m, 1H, Ar), 7.87–7.85 (m, 1H, Ar), 7.28–7.26 (s, 1H, Ar), 7.25–7.24 (m, 1H, Ar), 5.57–5.48 (m, 1H, CH_3CH=*CH*), 5.40–5.33 (m, 1H, CH_3*CH*=CH), 4.49 – 4.39 (m, 1H, *CH*NH), 4.39–4.28 (m, 1H, *NH*), 2.93–2.81 (m, 2H, ArCH_2), 2.57 (s, 3H, CH_3CO), 1.64 (d, *J* 6.4 Hz, 3H, CH_3CH=CH), 1.39 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 197.8, 155.0, 143.7, 135.5, 130.4, 129.8, 128.3, 126.8, 79.4, 53.2, 42.0, 28.3, 26.5, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_3Na$ [M+Na$^+$] 326.1732. Found 326.1730; IR (film) *v*: 3349, 2976, 2928, 1683, 1606, 1516, 1363, 1268, 1170, 1017, 964, 820, 595 cm^{-1}.

t*-Butyl (*R,E*)-(1-(4-cyanophenyl)pent-3-en-2-yl)carbamate (18o):** Yield 66 mg (61%) starting from mixture of **16o/16o; flash column chromatography on silica gel (10% AcOEt in hexanes); waxy solid $[\alpha]_D^{25}$ +2.4 (*c* 6.5, $CHCl_3$); TLC: R_f 0.72 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.55 (d, *J* 8.2 Hz, 2H), 7.27 (d, *J* 8.3 Hz, 2H), 5.52 (dqd, *J* 12.7, 6.3, 1.0 Hz, 1H), 5.34 (ddd, *J* 15.3, 6.2, 1.5 Hz, 1H), 4.45 (s, 1H), 4.31 (s, 1H), 2.91–2.80 (m, 2H), 1.63 (d, *J* 6.4 Hz, 3H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.0, 143.8, 132.0, 130.3, 130.1, 127.3, 118.9, 110.2, 79.5, 53.1, 42.1, 28.3, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{22}N_2O_2Na$ [M+Na$^+$] 309.1579; Found 309.1578.

Methyl (*R,E*)-4-(2-((*t*-butoxycarbonyl)amino)pent-3-en-1-yl)benzoate (18p): Yield 79 mg (78%) starting from mixture of **16p/16p***; flash column chromatography on silica gel (8% AcOEt in hexanes); white crystals; m.p. 70-71 °C; $[\alpha]_D^{25}$ –7.9 (*c* 7.9, $CHCl_3$); TLC: R_f 0.63 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.95–7.87 (m, 2H, Ar), 7.26–7.18 (m, 2H, Ar), 5.50 (dq, *J* 12.6, 6.3 Hz, 1H, CH_3CH=*CH*), 5.35 (ddd, *J* 15.3, 6.2, 1.5 Hz, 1H, CH_3*CH*=CH), 4.47 (s, 1H), 4.33 (s, 1H), 2.92–2.78 (m, 2H, ArCH_2), 1.62 (d, *J* 6.4 Hz, 3H, CH_3CH=CH), 1.57 (s, 3H, CO_2CH_3), 1.39 (s, *J* 2.3 Hz, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 167.1, 165.8, 155.1, 143.4, 142.8, 130.4, 129.6, 129.5, 129.4, 129.3, 128.3, 126.8, 126.7, 80.8, 79.4, 68.2, 51.9, 41.9, 28.3, 21.9, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_4Na$ [M+Na$^+$] 342.1681. Found 342.1683; IR (film) *v*: 3365, 2978, 1713, 1611, 1513, 1366, 1280, 1250, 1170, 1111, 1020, 967, 867, 850, 766, 707 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(4-vinylphenyl)pent-3-en-2-yl)carbamate (18r):** Yield 256 mg (85%) starting from 242 mg (1.05 mmol) of compound **16r**; flash column chromatography on silica gel (7% AcOEt in hexanes); waxy solid; TLC: R_f 0.67 (1:4 AcOEt:hexanes); $[\alpha]_D^{25}$ –14.1 (*c* 12.4, $CHCl_3$); TLC: R_f 0.67 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.32 (d, *J* 8.1 Hz, 2H), 7.13 (d, *J* 8.1 Hz, 2H), 6.69 (dd, *J* 17.6, 10.9 Hz, 1H), 5.71 (dd, *J* 17.6, 0.8 Hz, 1H), 5.53 (dqd, *J* 13.7, 6.3, 1.0 Hz, 1H), 5.38 (ddd, *J* 15.3, 6.0, 1.5 Hz, 1H), 5.20 (dd, *J* 10.9, 0.7 Hz, 1H), 4.48 (s, 1H), 4.32 (s, 1H), 2.85–2.74 (m, 2H), 1.64 (d, *J* 6.4 Hz, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 137.5, 136.6, 135.7, 130.9, 129.8, 126.2, 126.1, 113.2, 79.2, 53.3, 41.7, 28.4, 17.6; IR (film) *v*: 3359, 2979, 2967, 1685, 1519, 1446, 1390, 1365, 1304, 1290, 1249, 1170, 1042, 1019, 1006, 990, 971, 904, 844, 828, 750, 634, 521 cm^{-1}. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_2Na$ [M+Na^+] 310.1780. Found 310.1780.

***t*-Butyl (*R*,*E*)-(1-(furan-2-yl)pent-3-en-2-yl)carbamate (18s):** Yield 120 mg (84%) starting from 111 mg (0.57 mmol) of compound **16s**; flash column chromatography on silica gel (9% AcOEt in hexanes); white crystals; m.p. 79-80 °C; $[\alpha]_D^{25}$ –14.2 (*c* 8.4, $CHCl_3$); TLC: R_f 0.67 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.30 (dd, *J* 1.8, 0.8 Hz, 1H, Ar), 6.26 (dd, *J* 3.1, 1.9 Hz, 1H, Ar), 6.04 (dd, *J* 3.2, 0.6 Hz, 1H, Ar), 5.59 (dqd, *J* 12.8, 6.4, 1.3 Hz, 1H, CH_3CH=*CH*), 5.38 (ddd, *J* 15.3, 6.1, 1.6 Hz, 1H, CH_3*CH*=CH), 4.61 (s, 1H), 4.35 (s, 1H), 2.89–2.76 (m, 2H,ArCH_2), 1.66–1.63 (m, 3H, CH_3CH=CH), 1.41 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 152.3, 141.40, 141.39, 130.7, 126.3, 110.16, 110.15, 107.1, 79.3, 51.3, 34.1, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{21}NO_3Na$ [M+Na^+] 274.1419. Found 274.1414; IR (film) *v*: 3364, 2978, 1687, 1522, 1443, 1389, 1365, 1330, 1303, 1275, 1244, 1177, 1147, 1082, 1022, 936, 834, 851, 773, 746, 648, 601 cm^{-1}.

***t*-Butyl (*R*,*E*)-(1-(furan-3-yl)pent-3-en-2-yl)carbamate (18t):** Yield 123 mg (84%) starting from 114 mg (0.58 mmol) of compound **16t**; flash column chromatography on silica gel (8% AcOEt in hexanes); white crystals; m.p. 72-73 °C; $[\alpha]_D^{25}$ –7.8 (*c* 12.1, $CHCl_3$); TLC: R_f 0.53 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.32 (t, *J* 1.5 Hz, 1H, Ar), 7.22 (s, 1H, Ar), 6.25 (s, 1H, Ar), 5.56 (dqd, *J* 12.8, 6.4, 1.1 Hz, 1H, CH_3CH=*CH*), 5.38 (ddd, *J* 15.3, 6.0, 1.5 Hz, 1H, CH_3*CH*=CH), 4.48 (s, 1H), 4.24 (s, 1H), 2.67–2.56 (m, 2H, ArCH_2), 1.65 (d, *J* 6.4 Hz, 3H, CH_3CH=CH), 1.41 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 155.2, 142.7, 140.1, 131.1, 126.2, 120.6, 111.6, 31.0, 28.4, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{21}NO_3Na$ [M+Na^+] 274.1419. Found 274.1432; IR (film) *v*: 3356, 2981, 2937, 2855, 1685, 1525, 1443, 1389, 1366, 1348, 1303, 1274, 1245, 1173, 1042, 1023, 970, 928, 871, 851, 783, 757, 724, 633, 598 cm^{-1}.

1.6. Synthesis of amino acids 19. General procedure. Ozone was passed through a stirred solution of compound **18a** (137 mg, 0.52 mmol) in 10 mL of CH_2Cl_2 and 1.8 mL of 2.5 M methanolic NaOH at –70 °C. The progress of the reaction was followed by TLC (1:4 AcOEt/hexane). After 20 min, yellow precipitation occurred and reaction mixture became blue. At this point, oxygen was bubbled through reaction mixture for 10 min. It was than diluted with water (15 mL) and CH_2Cl_2 (15 mL) and resulting mixture was warmed slowly to

room temperature. Organic layer was separated and aqueous one was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under diminished pressure. The residue was chromatographed on silica gel to (13% AcOEt in hexanes) to afford 99 mg of product **19a** (73%) as white solid.

Methyl (*t*-butoxycarbonyl)-D-phenylalaninate (19a) white solid, m.p. 87-88 °C; $[\alpha]_D^{25}$ –46.0 (*c* 3.1, $CHCl_3$) [Lit.[3] –48.3 (*c* 1, $CHCl_3$)]; TLC: R_f 0.15 (1:8 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31–7.21 (m, 3H), 7.14–7.11 (m, 2H), 4.97 (d, *J* 5.5 Hz, 1H), 4.59 (d, *J* 5.8 Hz, 1H), 3.71 (s, 3H), 3.11 (dd, *J* 13.4, 5.5 Hz, 1H), 3.04 (dd, *J* 13.3, 5.9 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.3, 155.2, 136.0, 129.3, 128.5, 127.0, 79.9, 54.4, 52.1, 38.4, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{21}NO_4Na$ [M+Na$^+$] 302.1368. Found 302.1375; IR (film) *v*: 3366, 2978, 1746, 1716, 1498, 1366, 1169, 1055, 1020, 752, 701 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(*p*-tolyl)propanoate (19b): Yield 206 mg (91%) starting from 213 mg (0.77 mmol) of compound **18b**; flash column chromatography on silica gel (1:8 AcOEt/hexanes); yellow oil; $[\alpha]_D^{25}$ –50.6 (*c* 2.8, $CHCl_3$) [Lit.[4] for ***ent*-19b** +52.1 (*c* 1, CHCl3)]; TLC: R_f 0.24 (1:6 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.08 (d, *J* 7.7 Hz, 2H), 6.99 (d, *J* 7.7 Hz, 2H), 4.95 (s, 1H), 4.54 (d, *J* 6.0 Hz, 1H), 3.70 (s, 3H), 3.10–2.97 (m, 2H), 2.30 (s, 3H), 2.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.4, 155.1, 136.5, 132.8, 129.2, 129.1, 79.8, 54.4, 52.1, 37.8, 30.8, 28.2, 21.0; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_4Na$ [M+Na$^+$] 316.1525. Found 316.1523; IR (film) *v*: 3368, 2978, 1746, 1716, 1515, 1440, 1366, 1251, 1215, 1169, 1059, 1021, 810 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(4-methoxyphenyl)propanoate (19c): yield 290 mg (70%) starting from 289 mg (1.02 mmol) of compound **18c**; flash column chromatography on silica gel (15% AcOEt in hexanes); yellow oil; $[\alpha]_D^{25}$ –57.9 (*c* 4.9, $CHCl_3$) [lit.[5] –59.5 (*c* 1.6, $CHCl_3$); TLC: R_f 0.15 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (d, *J* 8.6 Hz, 2H), 6.83–6.80 (m, 2H), 4.96 (d, *J* 6.7 Hz, 1H), 4.53 (d, *J* 6.7 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.07–2.95 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4, 158.7, 155.1, 130.3, 127.9, 114.0, 79.8, 55.2, 52.1, 37.5, 28.3.; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_5Na$ [M+Na$^+$] 332.1474. Found 332.1479; IR (film) *v*: 3365, 2977, 1746, 1715, 1514, 1366, 1249, 1169, 1035, 824, 548 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(2-methoxyphenyl)propanoate (19d): yield 138 mg (87%) starting from 150 mg (0.52 mmol) of compound **18d**; flash column chromatography on silica gel (14% AcOEt in hexanes); white crystals; m.p. 70-71 °C; $[\alpha]_D^{23}$ −22.6 (*c* 4.9, $CHCl_3$) [lit.[6] for ***ent*-19d** +24 (*c* 1, $CHCl_3$)]; TLC: R_f 0.39 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.21 (td, *J* 8.1, 1.7 Hz, 1H, Ar), 7.07 (dd, *J* 7.4, 1.7 Hz, 1H, Ar), 6.88 (dd, *J* 7.4, 0.9 Hz, 1H, Ar), 6.84 (d, *J* 8.3 Hz, 1H, Ar), 5.20 (d, *J* 6.9 Hz, 1H, N*H*C(CH_3)$_3$), 4.50 (dd, *J* 13.4, 7.1 Hz, 1H, *CH*NHC(CH_3)$_3$), 3.81 (s, 3H, O*CH$_3$*), 3.68 (s, 3H, O*CH$_3$*), 3.05 (t, *J* 6.0 Hz, 2H, ArCH_2), 1.37 (s, 9H, NHC(*CH$_3$*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 172.8, 157.6, 155.2, 131.1, 128.4, 124.7, 120.6, 110.4, 79.5, 55.3, 54.0, 52.0, 32.8, 28.3; IR (film) *v*: 3377, 2977, 2839, 1746, 1716, 1603, 1568, 1406, 1460, 1439, 1366,

1247, 1170, 1116, 1053, 1026, 863, 755 cm^{-1}. HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_5Na$ [M+Na^+] 332.1474. Found 332.1474.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(3,4-dimethoxyphenyl)propanoate (19e): Yield 243 mg (85%) starting from 271 mg (0.84 mmol) of compound **18e**; flash column chromatography on silica gel (28% AcOEt in hexanes); white solid; m.p. 101-102 °C; $[\alpha]_D^{25}$ −65.2 (*c* 2.2, $CHCl_3$) [lit.[7] for ***ent*-19e** +66.1 (*c* 1, $CHCl_3$)]; TLC: R_f 0.12 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 6.76 (d, *J* 8.0 Hz, 1H), 6.66–6.60 (m, 2H), 4.97 (d, *J* 7.0 Hz, 1H), 4.52 (d, *J* 6.2 Hz, 1H), 3.82 (s, 6H), 3.68 (s, 3H), 3.05–2.92 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 172.4, 148.9, 148.1, 128.4, 121.4, 112.4, 111.3, 79.9, 60.3, 55.8, 55.8, 54.5, 52.1, 37.9, 28.3, 21.0, 14.2. HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_6Na$ [M+Na^+] 362.1580. Found 362.1584; IR (film) *v*: 3365, 2976, 2953, 2936, 2836, 1745, 1714, 1592, 1517, 1366, 1264, 1240, 1162, 1028, 859, 764 cm^{-1}.

Methyl (*S*)-2-((*t*-butoxycarbonyl)amino)-3-(3,4-dimethoxyphenyl)propanoate (*ent*-19e): Yield 82%; $[\alpha]_D^{25}$ +66.0 (*c* 2.0, $CHCl_3$) [lit.[7] for ***ent*-19e** +66.1 (*c* 1, $CHCl_3$)]; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_6Na$ [M+Na^+] 362.1580. Found 362.1584.

Methyl (*R*)-3-(benzo[d][1,3]dioxol-5-yl)-2-((*tert*-butoxycarbonyl)amino)propanoate (19f): Yield 187 mg (71%) starting from 249 mg (0.82 mmol) of compound **18f**; flash column chromatography on silica gel (20% AcOEt in hexanes); colorless oil; $[\alpha]_D^{25}$ −38.2 (*c* 9.2, $CHCl_3$); TLC: R_f 0.37 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.70 (d, *J* 7.9 Hz, 1H), 6.59 (s, 1H), 6.55 (dd, *J* 7.9, 1.4 Hz, 1H), 5.90 (dd, *J* 2.4, 1.4 Hz, 2H), 4.99 (d, *J* 6.5 Hz, 1H), 4.50 (d, *J* 6.2 Hz, 1H), 3.70 (s, 3H), 2.98 (qd, *J* 13.9, 5.7 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.2, 155.1, 147.7, 146.6, 129.6, 122.4, 109.6, 108.3, 100.9, 79.9, 54.5, 52.2, 38.0, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}NO_6Na$ [M+Na^+] 346.1267. Found 346.1273; IR (film) *v*: 3386, 2978, 1745, 1714, 1504, 1491, 1444, 1366, 1249, 1168, 1039, 932, 862, 811 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(4-((*t*-butoxycarbonyl)amino)phenyl)-propanoate (19g): Yield 303 mg (75%) starting from 386 mg (1.02 mmol) of compound **18g**; flash column chromatography on silica gel (25% AcOEt in hexanes); white solid; m.p. 125-126 °C; $[\alpha]_D^{25}$ –34.6 (*c* 10.6, $CHCl_3$); TLC: R_f 0.42 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 1H, Ar), 7.26 (s, 1H, Ar), 7.01 (s, 1H, Ar), 6.99 (s, 1H, Ar), 6.65 (s, 1H, Boc*NH*Ar), 4.97 (d, *J* 7.2 Hz, 1H, CH*NH*Boc), 4.51 (d, *J* 6.1 Hz, 1H, *CH*CO_2Me), 3.67 (s, 4H, *CH_2*Ar), 3.06–2.94 (m, 2H), 1.48 (s, 9H, C(*CH_3*)$_3$), 1.39 (s, 9H, C(*CH_3*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.3, 155.1, 152.8, 137.4, 130.4, 129.8, 118.6, 80.4, 79.9, 54.5, 53.4, 52.1, 37.5, 28.3, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{30}N_2O_6Na$ [M+Na^+] 417.2002. Found 417.1993; IR (film) *v*: 3335, 2978, 1703, 1597, 1527, 1367, 1316, 1237, 1163, 1054, 1019, 841, 773, 738, 527 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(4-chlorophenyl)propanoate (19h): Yield 161 mg (75%) starting from 203 mg (0.69 mmol) of compound **18h**; flash column chromatography on silica gel (15% AcOEt in hexanes); white solid; m.p. 69-70 °C; $[\alpha]_D^{25}$ –48.6 (*c* 6.3, $CHCl_3$); [lit.[6] –50.0 (*c* 1, $CHCl_3$)]; TLC: R_f 0.34 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* 8.3

Hz, 2H), 7.04 (d, *J* 8.2 Hz, 2H), 5.01 (d, *J* 6.0 Hz, 1H), 4.54 (d, *J* 5.9 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, *J* 13.7, 5.5 Hz, 1H), 2.98 (dd, *J* 13.4, 5.8 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.0, 155.0, 134.6, 132.9, 130.6, 128.6, 80.0, 54.3, 52.2, 37.7, 28.2; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{20}NO_4ClNa$ [M+Na$^+$] 336.0979. Found 336.0983; IR (film) *v*: 3366, 2979, 1746, 1713, 1494, 1438, 1391, 1366, 1251, 1216, 1168, 1092, 1058, 1016, 860, 839, 813, 780, 521 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(2-chlorophenyl)propanoate (19i): Yield 204 mg (72%) starting from 267 mg (0.90 mmol) of compound **18i**; flash column chromatography on silica gel (25% AcOEt in hexanes); waxy solid; $[\alpha]_D^{23}$ –16.9 (*c* 15.2, $CHCl_3$) [lit.[6] for ***ent*-19i** +18 (*c* 1, $CHCl_3$)]; TLC: R_f 0.38 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.34–7.29 (m, 1H, Ar), 7.18–7.13 (m, 3H, Ar), 5.11 (d, *J* 7.3 Hz, 1H), 4.61 (d, *J* 6.6 Hz, 1H), 3.68 (s, 3H, O*CH*$_3$), 3.26 (dd, *J* 13.8, 5.9 Hz, 1H), 3.07 (dd, *J* 13.2, 7.8 Hz, 1H), 1.35 (s, 9H, NHC(*CH*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 172.3, 155.0, 134.5, 134.3, 131.4, 129.6, 128.4, 126.8, 79.8, 53.5, 52.3, 36.1, 28.2; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{20}NO_4NaCl$ [M+Na$^+$] 336.0979. Found 336.0988; IR (film) *v*: 3365, 2978, 1746, 1716, 1505, 1477, 1440, 1366, 1251, 1217, 1169, 1054, 754 cm^{-1}.

Methyl (*R*)-3-(2-bromophenyl)-2-((*t*-butoxycarbonyl)amino)propanoate (19j): Yield 60 mg (69%) starting from 82 mg (0.24 mmol) of compound **18j**; flash column chromatography on silica gel (12% AcOEt in hexanes); waxy solid; $[\alpha]_D^{23}$ –5.2 (*c* 4.2, $CHCl_3$) [lit.[8] +3.5 (*c* 1, CH_2Cl_2)]; TLC: R_f 0.36 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.54 (d, *J* 7.8 Hz, 1H, Ar), 7.26–7.18 (m, 2H, Ar), 7.10 (t, *J* 7.3 Hz, 1H, Ar), 5.06 (d, *J* 6.6 Hz, 1H), 4.64 (d, *J* 6.5 Hz, 1H), 3.71 (s, 3H, O*CH*$_3$), 3.29 (dd, *J* 13.8, 5.8 Hz, 1H), 3.14–3.06 (m, 1H), 1.37 (s, 9H, NHC(*CH*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 172.4, 155.1, 136.1, 132.9, 132.91, 128.6, 127.4, 125.0, 79.7, 53.5, 52.3, 38.7, 28.2; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{20}NO_4NaBr$ [M+Na$^+$] 380.0473. Found 380.0474; IR (film) *v*: 3366, 2977, 1745, 1716, 1509, 1473, 1439, 1366, 1169, 1050, 1026, 753 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(naphthalen-1-yl)propanoate (19k): Yield 350 mg (89%) starting from 385 mg (1.24 mmol) of compound **18k**; flash column chromatography on silica gel (1:8 AcOEt/hexanes); yellow oil; $[\alpha]_D^{25}$ –19.1 (*c* 2.0, $CHCl_3$) [lit.[6] –20 (*c* 1, $CHCl_3$)]; TLC: R_f 0.22 (1:6 AcOEt:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (d, *J* 8.3 Hz, 1H), 7.86 (d, *J* 7.7 Hz, 1H), 7.76 (d, *J* 8.1 Hz, 1H), 7.54 (t, *J* 7.3 Hz, 1H), 7.49 (t, *J* 7.3 Hz, 1H), 7.39 (t, *J* 7.6 Hz, 1H), 7.30–7.26 (m, 1H), 5.04 (s, 1H), 4.72 (d, *J* 6.4 Hz, 1H), 3.72–3.56 (m, 4H), 3.51–3.44 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.6, 155.0, 133.9, 132.5, 128.8, 127.9, 127.4, 126.3, 125.7, 125.3, 123.5, 79.9, 54.4, 52.1, 35.6, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{23}NO_4Na$ [M+Na$^+$] 352.1525. Found 252.1523; IR (film) *v*: 3366, 2977, 1744, 17134, 1510, 1366, 1165, 1062, 1020, 778 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)propanoate (19l): Yield 290 mg (86%) starting from 319 mg (1.02 mmol) of compound **18l**; flash column chromatography on silica gel (15% AcOEt in hexanes); white solid; m.p. 84-85 °C; $[\alpha]_D^{25}$ –56.1 (*c* 5.2, $CHCl_3$) [lit.[6] –

60 (*c* 1, $CHCl_3$)]; TLC: R_f 0.13 (1:8 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (ddd, *J* 8.7, 6.3, 1.9 Hz, 3H), 7.59 (s, 1H), 7.49–7.42 (m, 2H), 7.26 (dd, *J* 8.1, 1.9 Hz, 1H), 5.02 (d, *J* 6.4 Hz, 1H), 4.67 (d, *J* 6.6 Hz, 1H), 3.71 (s, 3H), 3.29 (dd, *J* 13.7, 5.8 Hz, 1H), 3.21 (dd, *J* 13.7, 6.0 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4, 155.1, 133.6, 133.5, 132.5, 128.2, 128.1, 127.7, 127.6, 127.3, 126.1, 125.7, 79.9, 54.5, 52.2, 38.5, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{23}NO_4Na$ [M+Na$^+$] 352.1525. Found 352.1533; IR (film) *v*: 3365, 2978, 1745, 1714, 1508, 1438, 1366, 1168, 1059, 1019, 819, 747, 476 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(4-(trifluoromethyl)phenyl)propanoate (19m); Yield 153 mg (69%) starting from 211 mg (0.64 mmol) of compound **18m**; flash column chromatography on silica gel (20% AcOEt in hexanes); white solid; m.p. 75-76 °C; $[\alpha]_D^{25}$ –40.4 (*c* 5.1, $CHCl_3$) [Lit.[9] for ***ent*-19m** +28.3 (*c* 1, $CHCl_3$)]; TLC: R_f 0.53 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H, Ar), 7.53 (s, 1H, Ar), 7.26 (s, 1H, Ar), 7.24 (s, 1H, Ar), 5.01 (d, *J* 6.1 Hz, 1H, *NH*), 4.61 (d, *J* 5.7 Hz, 1H, *CH*CO_2Me), 3.71 (s, 3H, *OCH$_3$*), 3.20 (dd, *J* 13.7, 5.4 Hz, 1H, Ar*CH*), 3.07 (dd, *J* 13.2, 5.8 Hz, 1H, Ar*CH*), 1.40 (s, 9H, C(*CH$_3$*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 155.0, 140.3, 129.7, 129.5, 129.2, 125.4 (q, $J_{C\text{-}F}$ 3.8 Hz), 122.8, 80.1, 54.2, 52.3, 38.3, 28.2; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{20}NO_4NaF_3$ [M+Na$^+$] 370.1242. Found 370.1237; IR (film) *v*: 3365, 2979, 1747, 1715, 1619, 1510, 1439, 1367, 1327, 1165, 1125, 1067, 1019, 827, 780, 596 cm^{-1}.

Methyl (*R*)-3-(4-acetylphenyl)-2-((*t*-butoxycarbonyl)amino)propanoate (19n); Yield 10 mg (56%) starting from 16 mg (0.05 mmol) of compound **18n**; flash column chromatography on silica gel (22% AcOEt in hexanes); waxy solid; $[\alpha]_D^{23}$ –70.1 (*c* 0.8, $CHCl_3$); TLC: R_f 0.39 (1:2 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, *J* 8.2 Hz, 1H, Ar), 7.87 (s, 1H, Ar), 7.24 (s, 1H, Ar), 7.22 (s, 1H, Ar), 4.99 (d, *J* 5.7 Hz, 1H, N*H*Boc), 4.61 (d, *J* 6.5 Hz, 1H, *CH*CO_2Me), 3.72 (s, 3H, O*CH$_3$*), 3.14 (ddd, *J* 44.7, 13.6, 5.8 Hz, 2H, Ar*CH$_2$*), 2.58 (s, 3H, *CH$_3$*CO), 1.41 (s, *J* 6.7 Hz, 9H, NHC(*CH$_3$*)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.7, 141.7, 136.0, 129.6, 128.5, 77.2, 52.3, 31.5, 30.3, 28.3, 26.5; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_5Na$ [M+Na$^+$] 344.1474. Found 344.1475; IR (film) *v*: 3357, 2975, 2930, 1746, 1715, 1685, 1608, 1510, 1437, 1364, 1268, 1167, 1057, 1018, 959, 598 cm^{-1}.

Methyl (*R*)-2-((*t*-butoxycarbonyl)amino)-3-(4-cyanophenyl)propanoate (19o): purification by flash column chromatography on silica gel (16% AcOEt in hexanes); yield 37 mg (61%) starting from 57 mg (0.20 mmol) of compound **18o**; waxy solid; $[\alpha]_D^{23}$ −53.6 (*c* 2.3, $CHCl_3$) [Lit.[10] –54 (*c* 0.94, $CHCl_3$)]; TLC: R_f 0.24 (1:3 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* 8.1 Hz, 2H), 7.25 (d, *J* 8.0 Hz, 2H), 5.01 (d, *J* 6.0 Hz, 1H), 4.60 (d, *J* 4.8 Hz, 1H), 3.72 (s, 3H), 3.21 (dd, *J* 13.5, 5.4 Hz, 1H), 3.06 (dd, *J* 13.5, 5.9 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.7, 141.9, 132.2, 130.1, 118.7, 111.0, 54.1, 52.4, 38.7, 31.9, 29.7, 29.3, 28.2, 22.7, 14.1; IR (film) *v*: 3365, 2977, 2955, 2927, 2228, 1745, 1714, 1608, 1506, 1439, 1366, 1252, 1167, 1057, 1021, 825, 558 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{20}N_2O_4Na$ [M+Na$^+$] 327.1321. Found 327.1318.

Methyl (*R*)-4-(2-((*t*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoate (19p): *Method 1:* Yield 43 mg (59%) starting from 69 mg (0.22 mmol) of compound **18p**;. *Method 2:* Yield 94 mg (63%) starting from 127 mg (0.44 mmol) of compound **18r**; flash column chromatography on silica gel (18% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ −49.3 (*c* 2.4, $CHCl_3$); TLC: R_f 0.27 (1:4 AcOEt:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H, Ar), 7.94 (s, 1H, Ar), 7.21 (s, 1H, Ar), 7.18 (s, 1H, Ar), 4.99 (d, *J* 6.5 Hz, 1H), 4.60 (d, *J* 6.4 Hz, 1H), 3.89 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.17 (dd, *J* 13.6, 5.8 Hz, 1H, ArCH_2), 3.08 (dd, *J* 13.3, 6.0 Hz, 1H, ArCH_2), 1.40 (s, 9H, NHC(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.0, 166.9, 155.0, 141.5, 129.8, 129.3, 129.0, 80.1, 54.2, 52.3, 52.0, 38.4, 28.3; IR (film) *v*: 3356, 2978, 2953, 1720, 1612, 1511, 1437, 1366, 1281, 1168, 1107, 1057, 1021, 760, 707 cm^{-1}. HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_6Na$ [M+Na$^+$] 360.1423. Found 360.1429.

1-(*t*-Butyl) 2-methyl (*S*)-indoline-1,2-dicarboxylate (20):[8] Bromide **19j** (0.25 mmol) was dissolved in dry toluene (2 mL under nitrogen) in a 10 mL and Cs_2CO_3 (0.2 g, 1.0 mmol), Pd_2dba_3 (8 mg, 0.008 mmol) and P(*o*-tolyl)$_3$ (10 mg, 0.33 mmol), were added sequentially to the reaction mixture. The mixture was heated to 100 °C and stirring was continued for 20 h. The reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a pad of Celite®. The filtrate was washed with water (2 × 5 mL) and brine (10 mL), dried and evaporated to dryness. Purification by flash column chromatography on silica gel with a suitable hexanes/AcOEt gradient furnished the product **20** as colorless oil. *Spectral data:*[8,11] $[\alpha]_D^{24}$ −69 (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 7.52-7.31 (m, 1H), 7.24-7.15 (m, 1H), 7.12 (d, *J* 6.1 Hz, 1H), 6.97 (t, *J* 7.1 Hz, 1H), 4.96-4.79 (m, 1H), 3.73 (s, 3H), 3.52 (dd, *J* 15.8, 12 Hz, 1H), 3.09 (dd, *J* 15.8, 4.3 Hz, 1H), 1.46 (s, 9H); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.71 (br s, 1H), 7.18-7.15 (m, 2H), 6.93 (t, *J* 7.3 Hz, 1H), 4.87 (dd, *J* 11.6, 4.4 Hz, 1H), 3.67 (s, 3H), 3.51 (dd, *J* 16.7, 11.6 Hz, 1H), 3.03 (br d, *J* 16.3 Hz, 1H), 1.41 (br s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 173.1, 153.0 (x2), 151.4 (x2), 141.8 (x2), 142.4, 128.8, 127.8(x2), 124.7, 124.3 122.5 114.8, 82.0, 81.4, 60.5, 52.1, 31.4, 32.2, 28.0; IR (film) v: 2982, 1743, 1711, 1485, 1392, 1169; HRMS (EI) *m/z* calcd for $C_{15}H_{19}NO_4$ (M) 277.1314. Found 277.1309.

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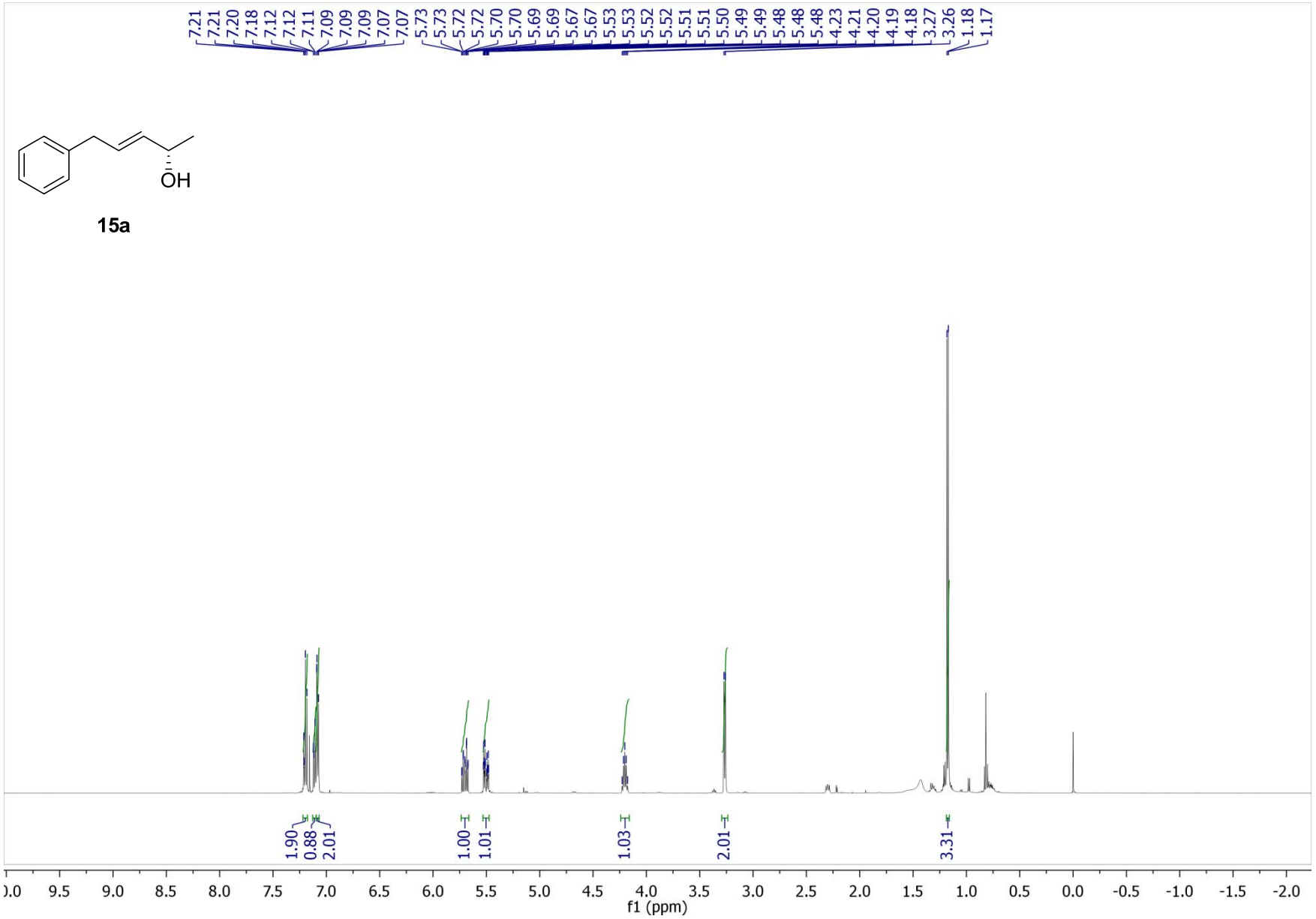
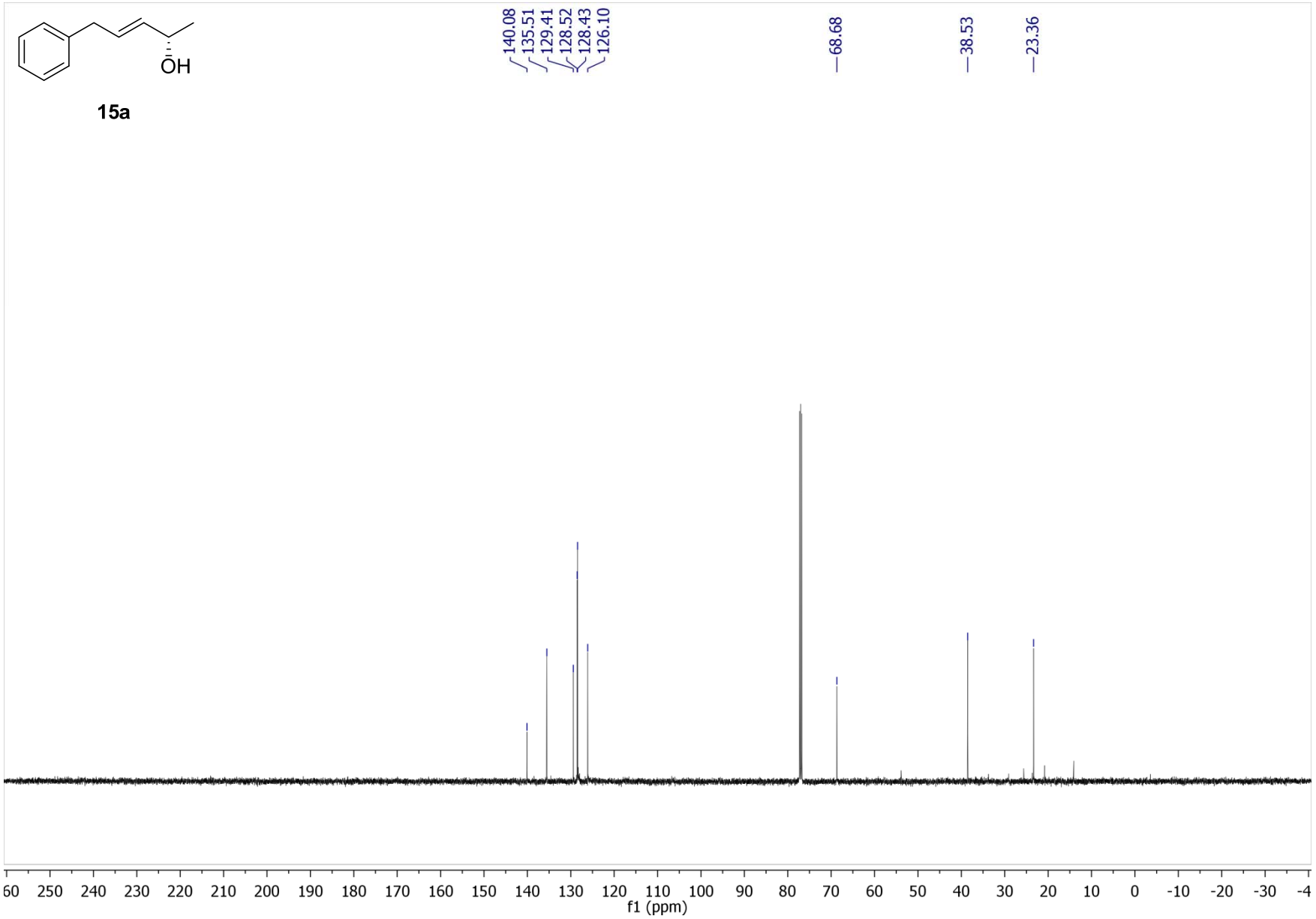
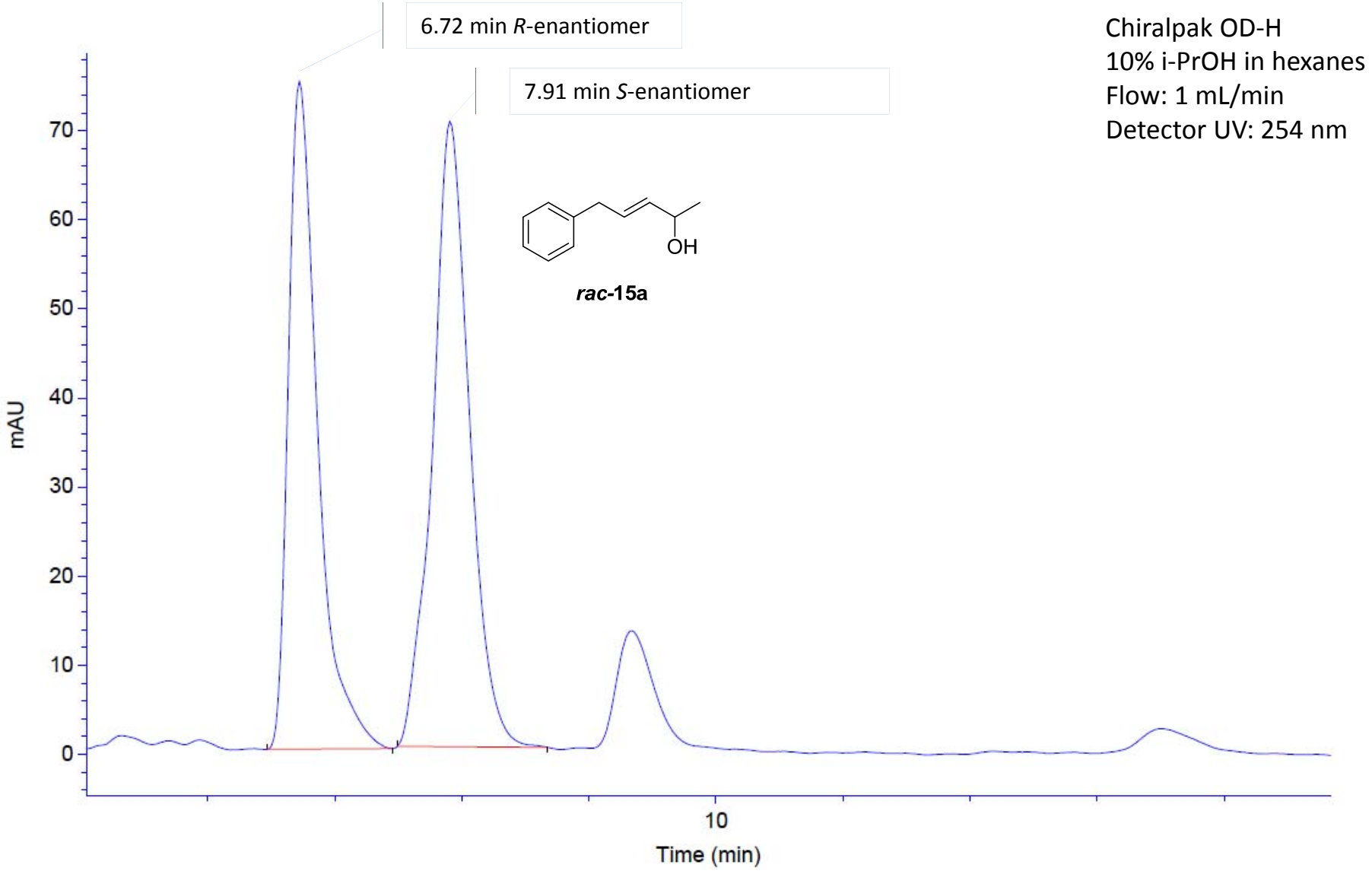

7.21
7.21
7.20
7.18
7.12
7.12
7.11
7.09
7.09
7.09
7.07
7.07
5.73
5.73
5.72
5.72
5.70
5.70
5.69
5.69
5.67
5.67
5.53
5.53
5.52
5.52
5.51
5.51
5.50
5.49
5.49
5.48
5.48
5.48
4.23
4.21
4.20
4.19
4.18
3.27
3.26
1.18
1.17
OH
15a
1.90
0.88
2.01
1.00
1.01
1.03
2.01
3.31
f1 (ppm)


OH
15a
140.08
135.51
129.41
128.52
128.43
126.10
68.68
38.53
23.36
60 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4
f1 (ppm)

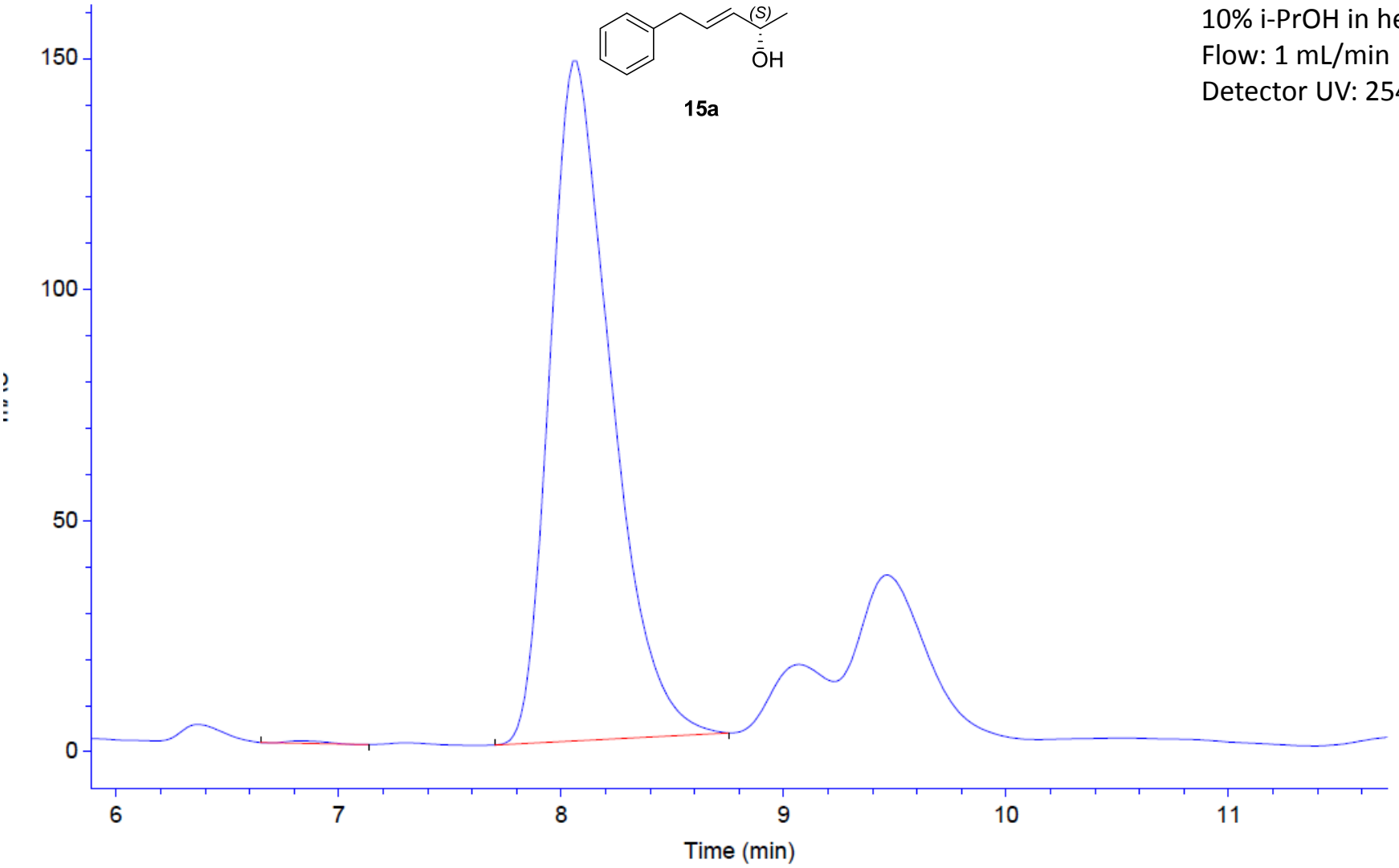
	Ret.time [min]	Start [min]	End [min]	Area [mAU*min]	Height [mAU]	% Area	Width [min]
1	6.721	6.47	7.45	20.0127	75.016	45.8095	0.235
2	7.905	7.49	8.67	23.6741	70.2374	54.1905	0.293

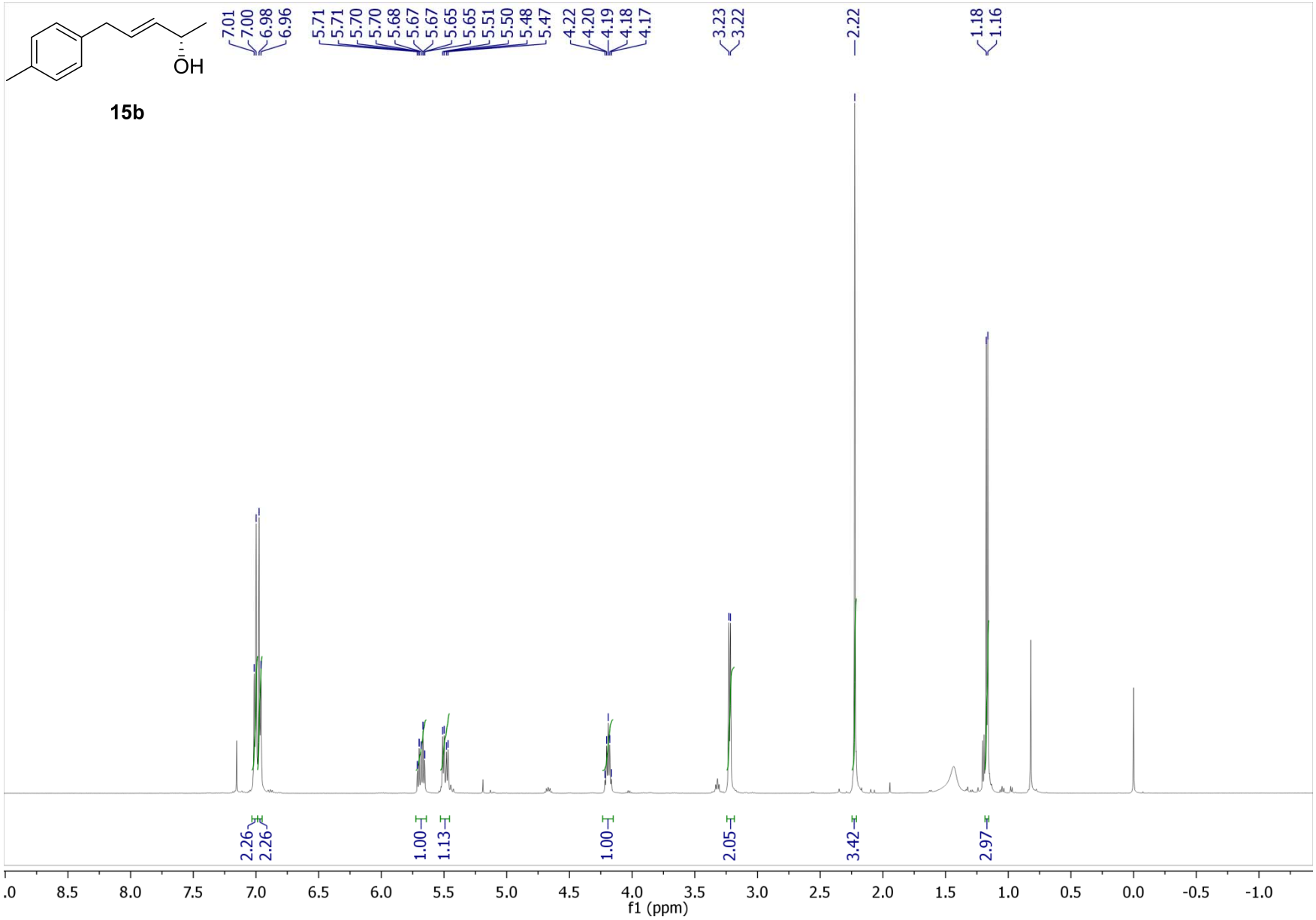


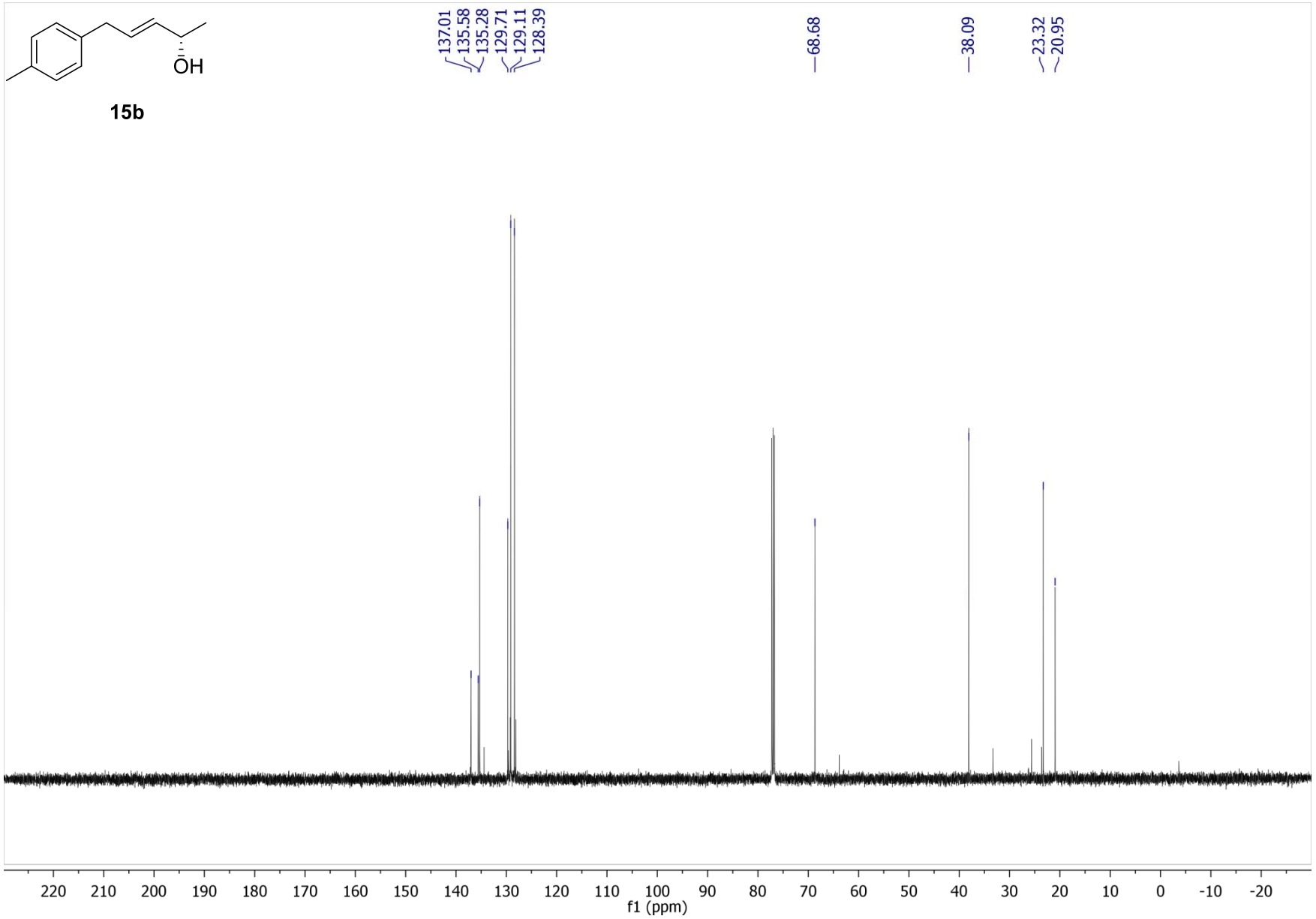
	Ret.time [min]	Start [min]	End [min]	Area [mAU*min]	Height [mAU]	% Area	Width [min]
1	6.836	6.65	7.14	0.10561	0.559111	0.2232	0.201
2	8.070	7.70	8.75	47.2108	147.071	99.7768	0.295

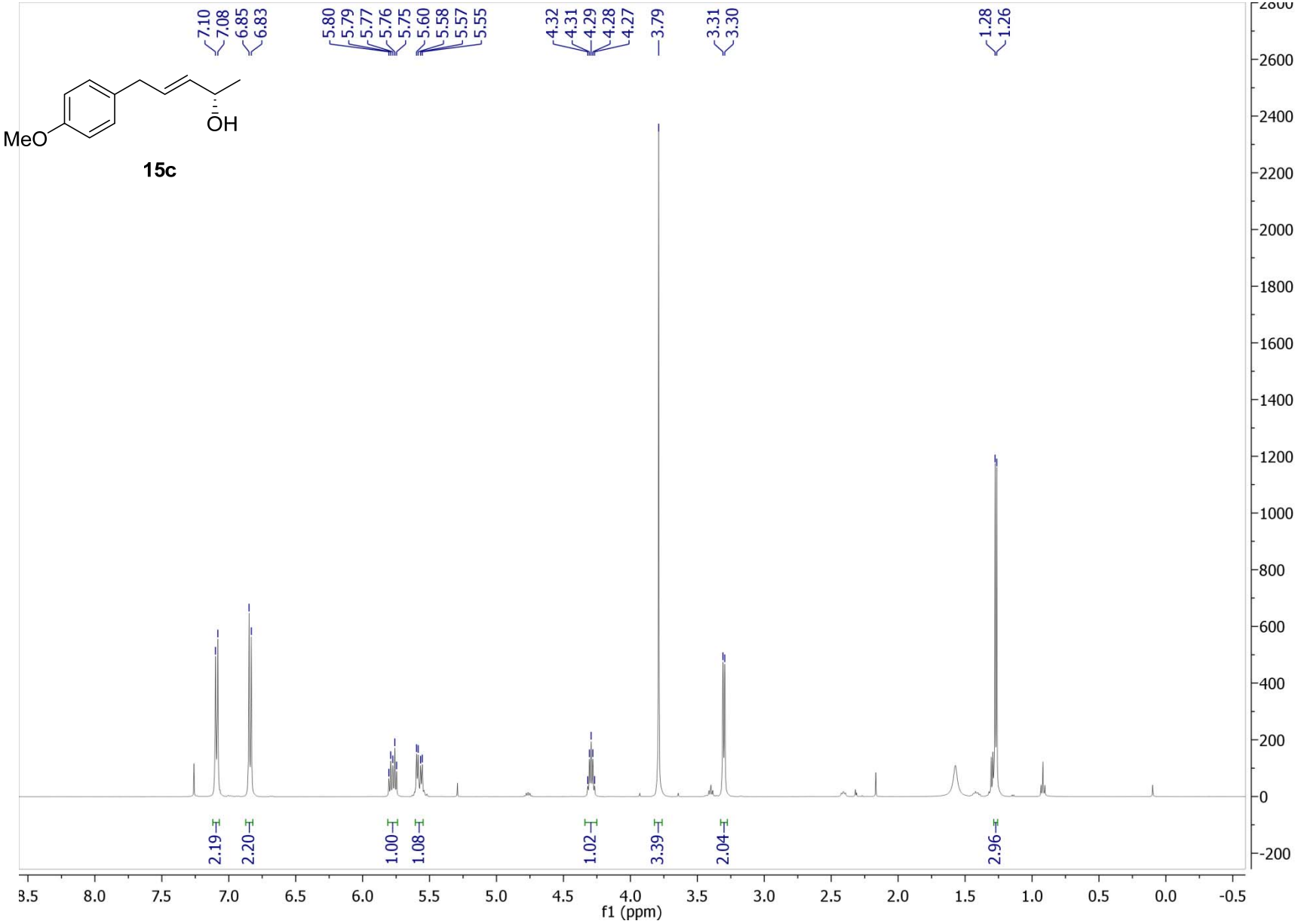
Chiralpak OD-H
10% i-PrOH in hexanes
Flow: 1 mL/min
Detector UV: 254 nm

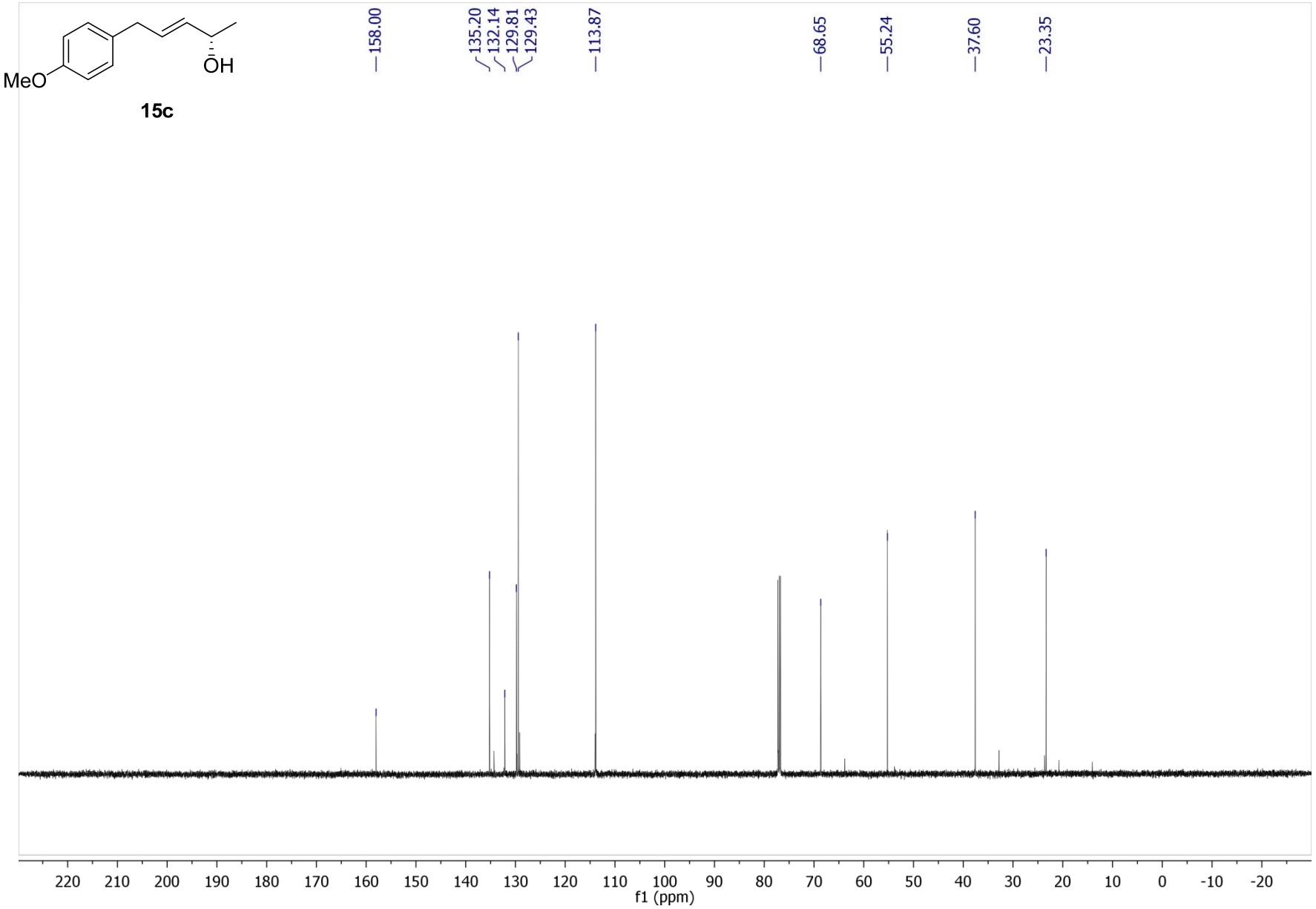
15a

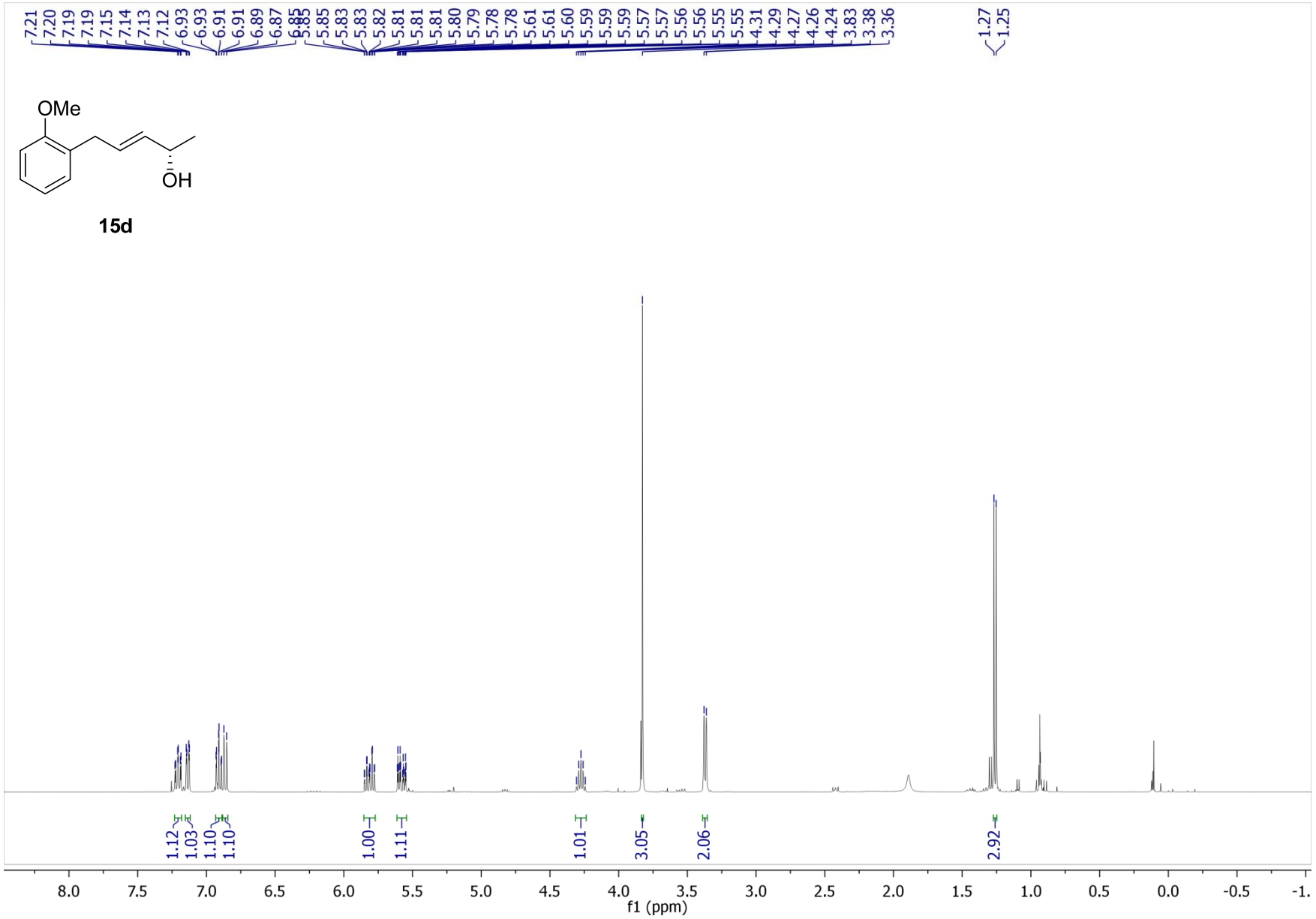


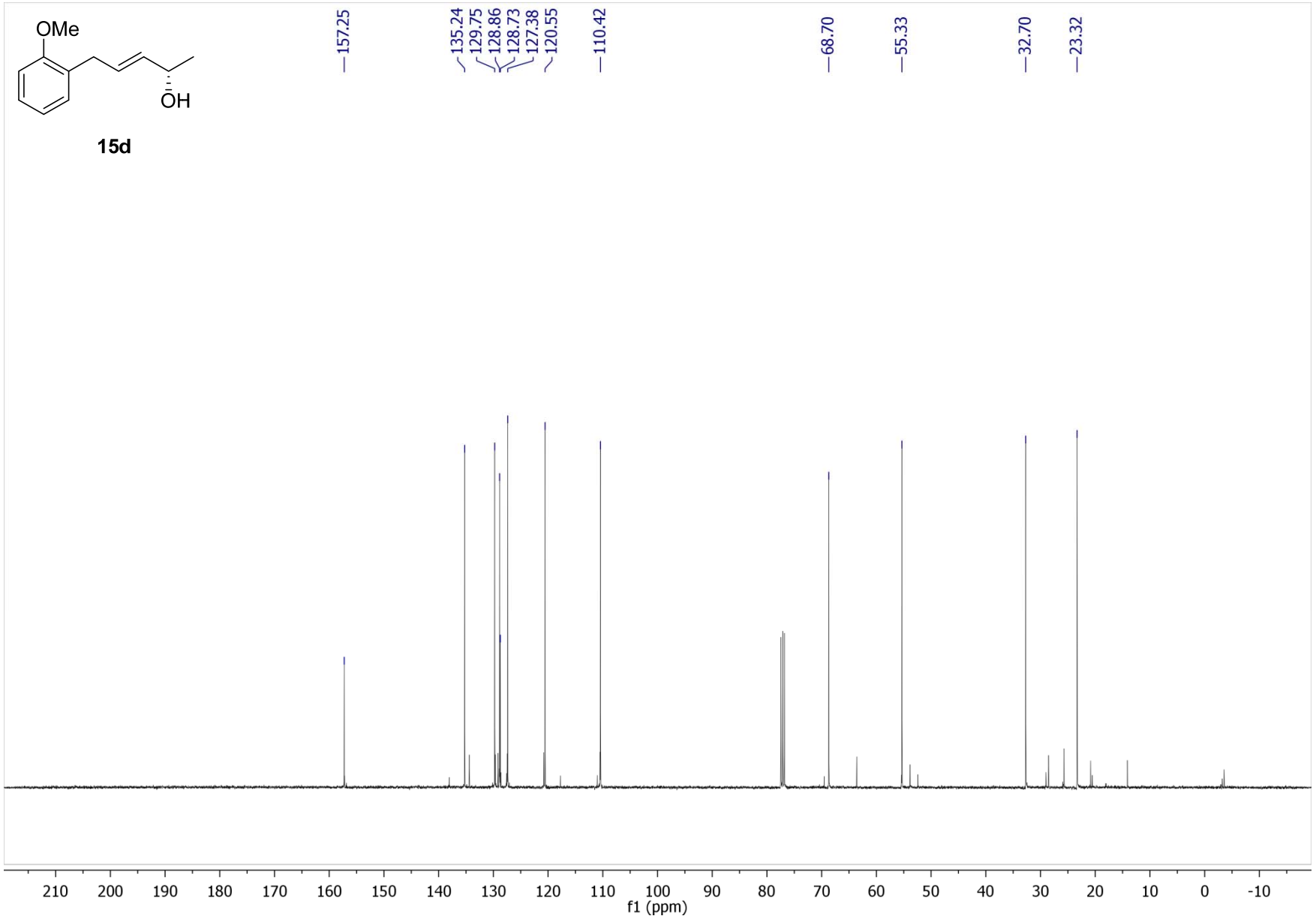

OH
15b
7.01
7.00
6.98
6.96
5.71
5.71
5.70
5.70
5.68
5.67
5.67
5.65
5.65
5.51
5.50
5.48
5.47
4.22
4.20
4.19
4.18
4.17
3.23
3.22
2.22
1.18
1.16
2.26
2.26
1.00
1.13
1.00
2.05
3.42
2.97
f1 (ppm)

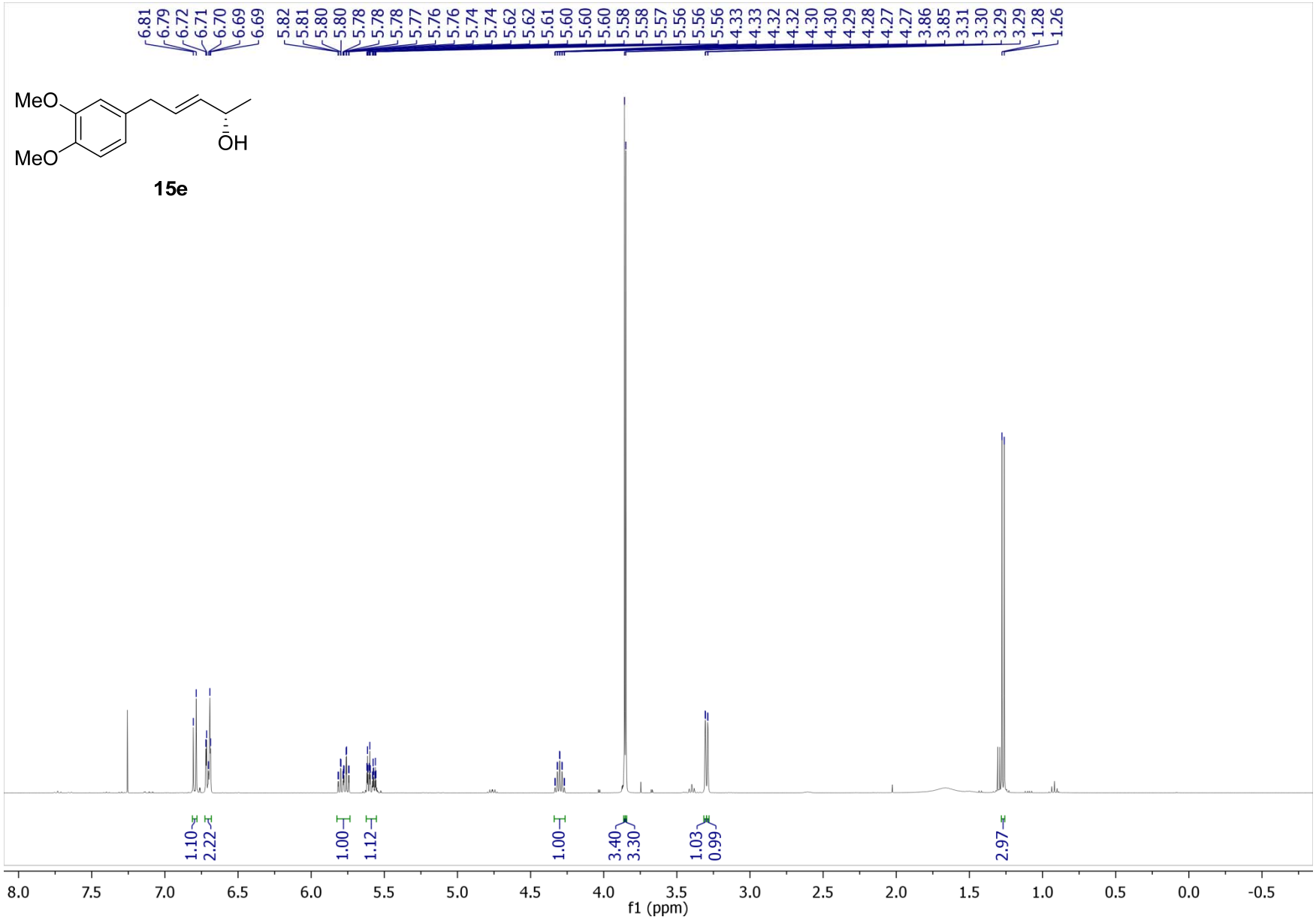

OH
15b
137.01
135.58
135.28
129.71
129.11
128.39
68.68
38.09
23.32
20.95
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

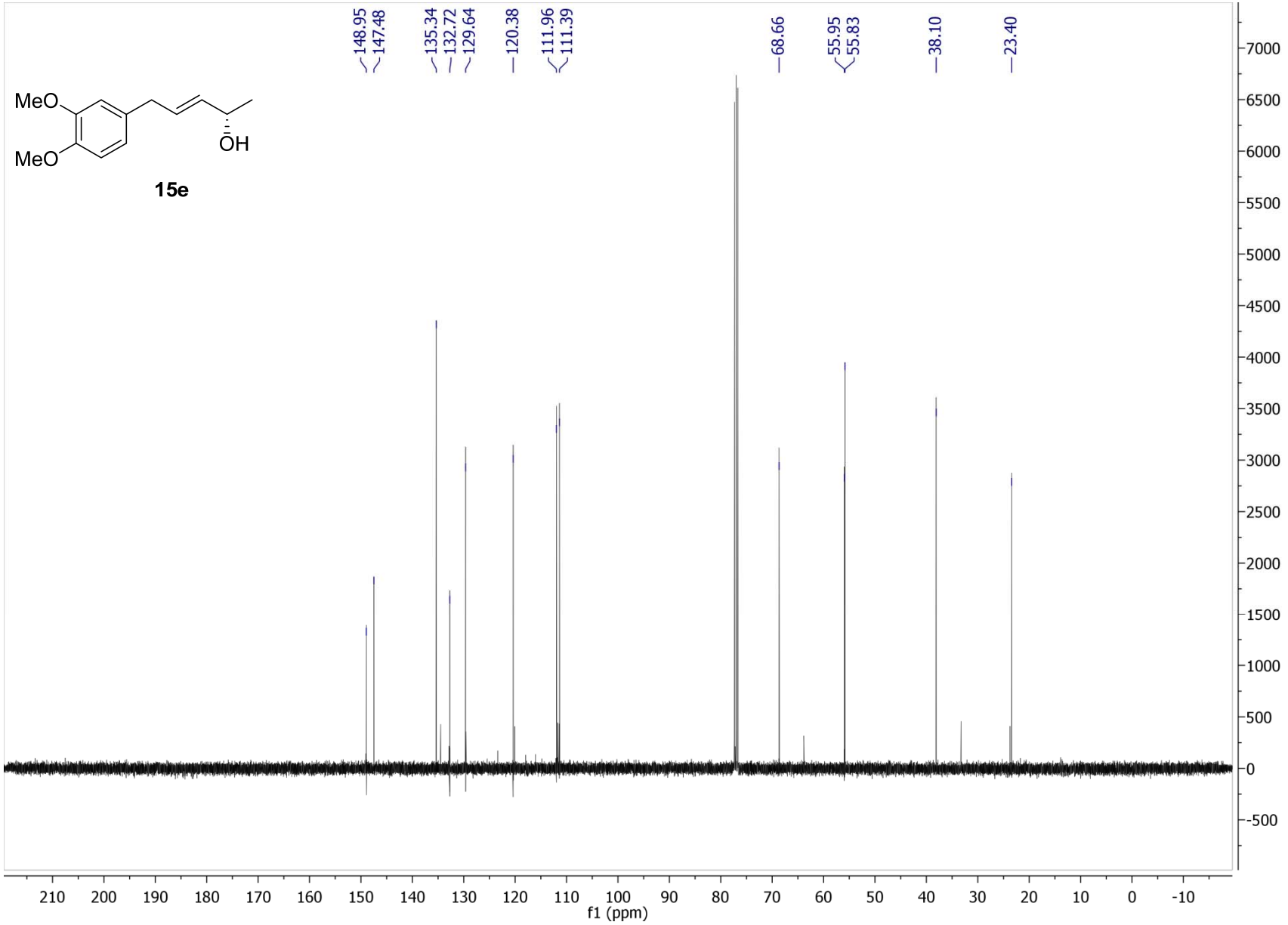

7.10
7.08
6.85
6.83
5.80
5.79
5.77
5.76
5.75
5.60
5.58
5.57
5.55
4.32
4.31
4.29
4.28
4.27
3.79
3.31
3.30
1.28
1.26
MeO
OH
15c
2.19
2.20
1.00
1.08
1.02
3.39
2.04
2.96
f1 (ppm)

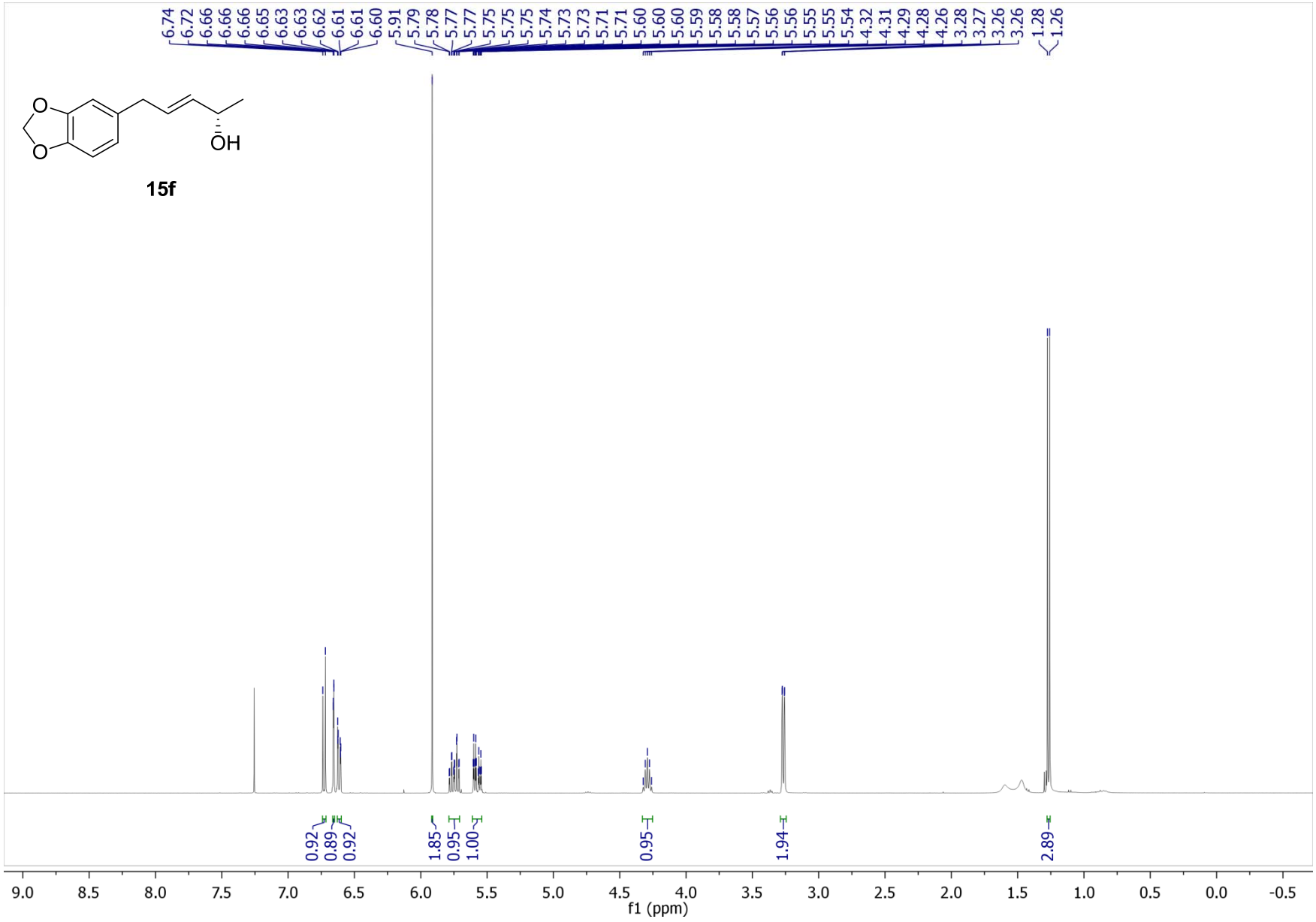

MeO
OH
15c
158.00
135.20
132.14
129.81
129.43
113.87
68.65
55.24
37.60
23.35
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

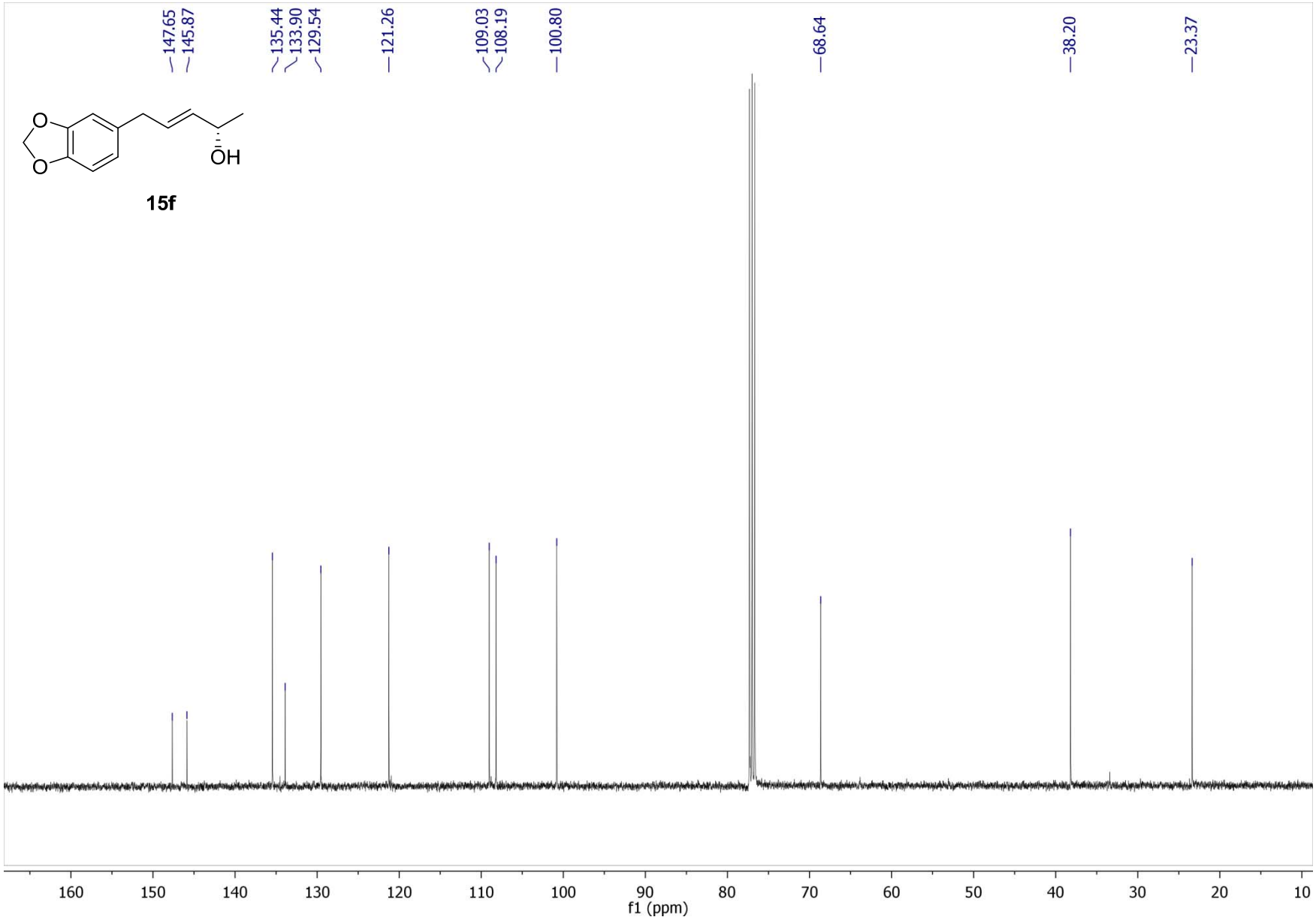

7.21
7.20
7.19
7.19
7.15
7.14
7.13
7.12
6.93
6.93
6.91
6.91
6.89
6.87
5.85
5.85
5.83
5.83
5.82
5.81
5.81
5.81
5.80
5.79
5.78
5.78
5.61
5.61
5.60
5.59
5.59
5.59
5.57
5.57
5.56
5.56
5.55
5.55
4.31
4.29
4.27
4.26
4.24
3.83
3.38
3.36
1.27
1.25
OMe
OH
15d
1.12
1.03
1.10
1.10
1.00
1.11
1.01
3.05
2.06
2.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

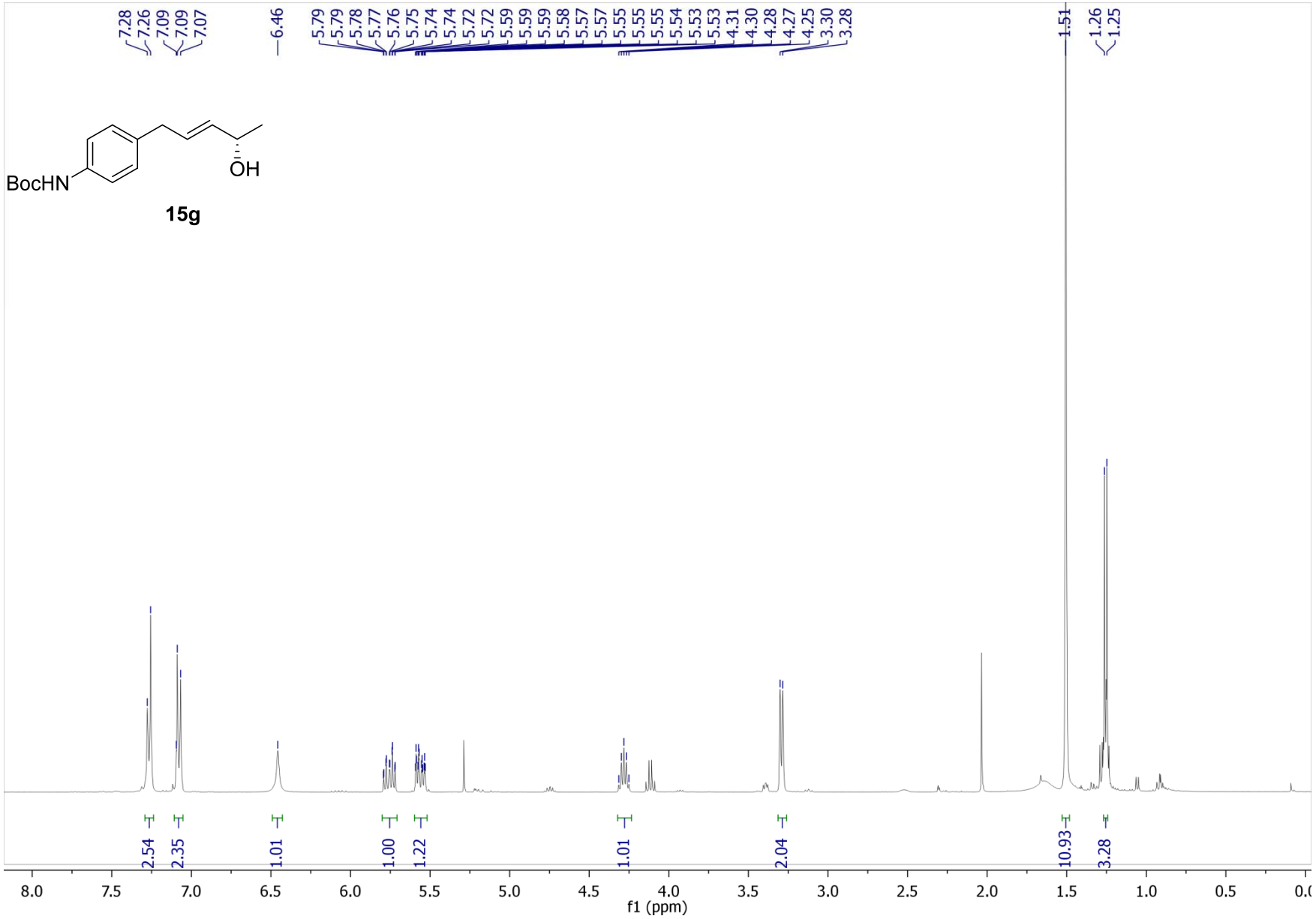

OMe
OH
15d
157.25
135.24
129.75
128.86
128.73
127.38
120.55
110.42
68.70
55.33
32.70
23.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

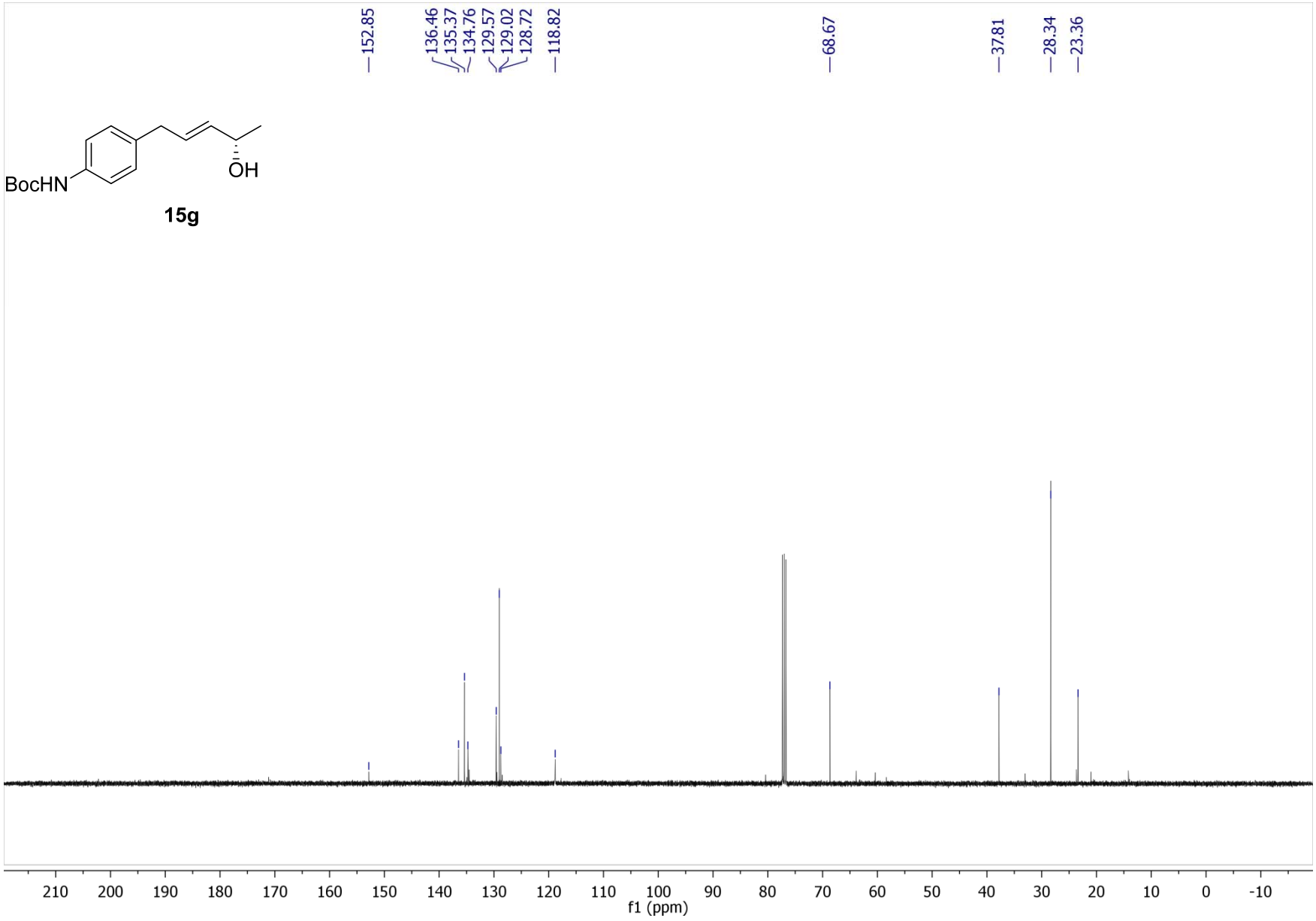

6.81 6.79 6.72 6.71 6.70 6.69 6.69
5.82 5.81 5.80 5.80 5.78 5.78 5.78 5.77 5.76 5.76 5.74 5.74 5.62 5.62 5.61 5.60 5.60 5.60 5.58 5.58 5.57 5.56 5.56 5.56 4.33 4.33 4.32 4.32 4.30 4.30 4.29 4.28 4.27 4.27 3.86 3.85 3.31 3.30 3.29 3.29 1.28 1.26
MeO
MeO
OH
15e
1.10 2.22 1.00 1.12 1.00 3.40 3.30 1.03 0.99 2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

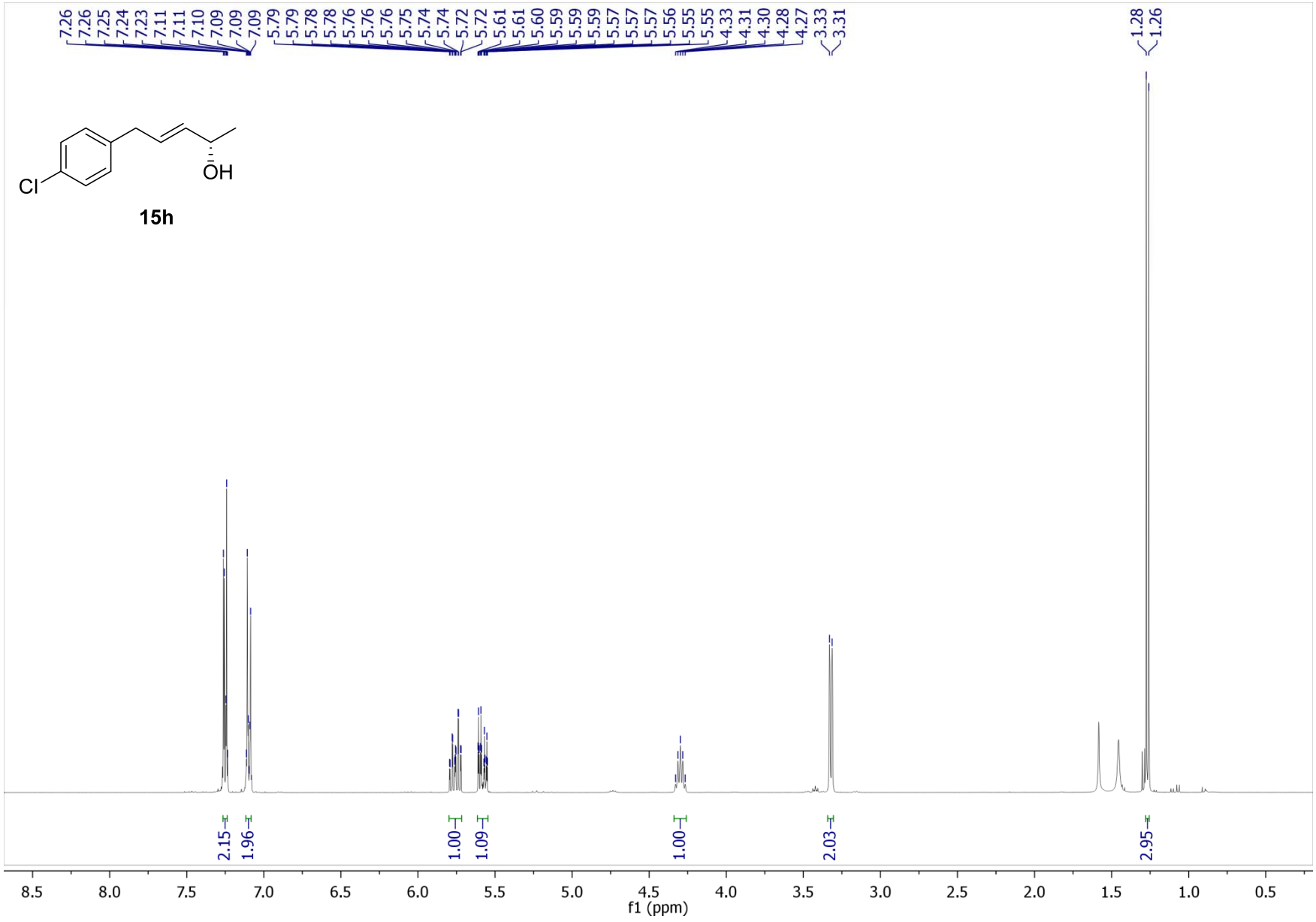

148.95
147.48
135.34
132.72
129.64
120.38
111.96
111.39
68.66
55.95
55.83
38.10
23.40
MeO
MeO
OH
15e
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

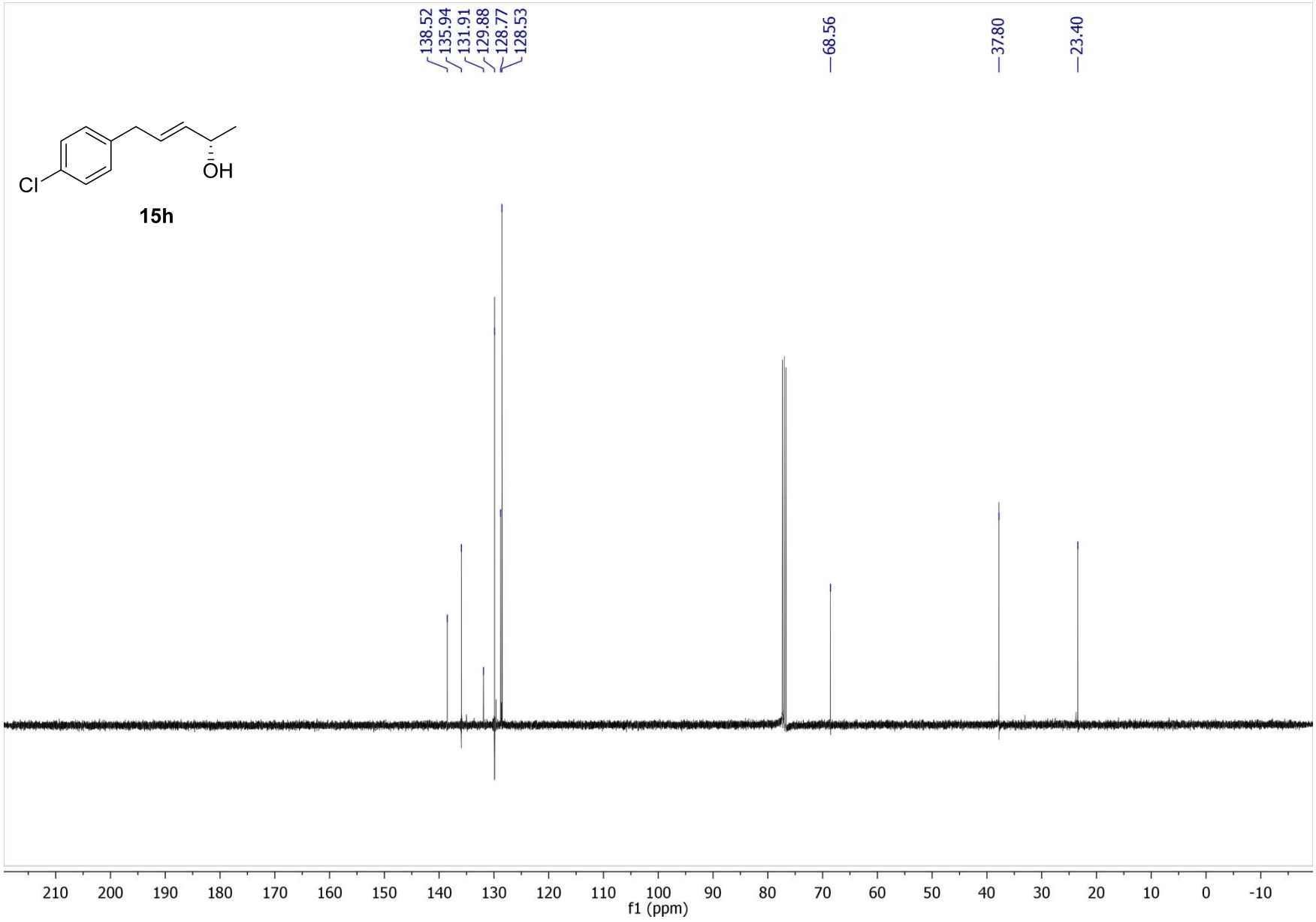

6.74
6.72
6.66
6.66
6.66
6.65
6.63
6.63
6.62
6.61
6.61
6.60
5.91
5.79
5.78
5.77
5.77
5.75
5.75
5.75
5.74
5.73
5.73
5.71
5.71
5.60
5.60
5.60
5.59
5.58
5.58
5.57
5.56
5.56
5.55
5.55
5.54
4.32
4.31
4.29
4.28
4.26
3.28
3.27
3.26
3.26
1.28
1.26
O
O
OH
15f
0.92
0.89
0.92
1.85
0.95
1.00
0.95
1.94
2.89
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


147.65
145.87
135.44
133.90
129.54
121.26
109.03
108.19
100.80
68.64
38.20
23.37
O
O
OH
15f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.28
7.26
7.09
7.09
7.07
6.46
5.79
5.79
5.78
5.77
5.76
5.75
5.74
5.74
5.72
5.72
5.59
5.59
5.59
5.58
5.57
5.57
5.55
5.55
5.55
5.54
5.53
5.53
4.31
4.30
4.28
4.27
4.25
3.30
3.28
1.51
1.26
1.25
BocHN
OH
15g
2.54
2.35
1.01
1.00
1.22
1.01
2.04
10.93
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


152.85
136.46
135.37
134.76
129.57
129.02
128.72
118.82
68.67
37.81
28.34
23.36
BocHN
OH
15g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
7.26
7.25
7.24
7.23
7.11
7.11
7.10
7.09
7.09
7.09
5.79
5.79
5.78
5.78
5.76
5.76
5.76
5.75
5.74
5.74
5.72
5.72
5.61
5.61
5.60
5.59
5.59
5.59
5.57
5.57
5.57
5.56
5.55
5.55
4.33
4.31
4.30
4.28
4.27
3.33
3.31
1.28
1.26
Cl
OH
15h
2.15
1.96
1.00
1.09
1.00
2.03
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


138.52
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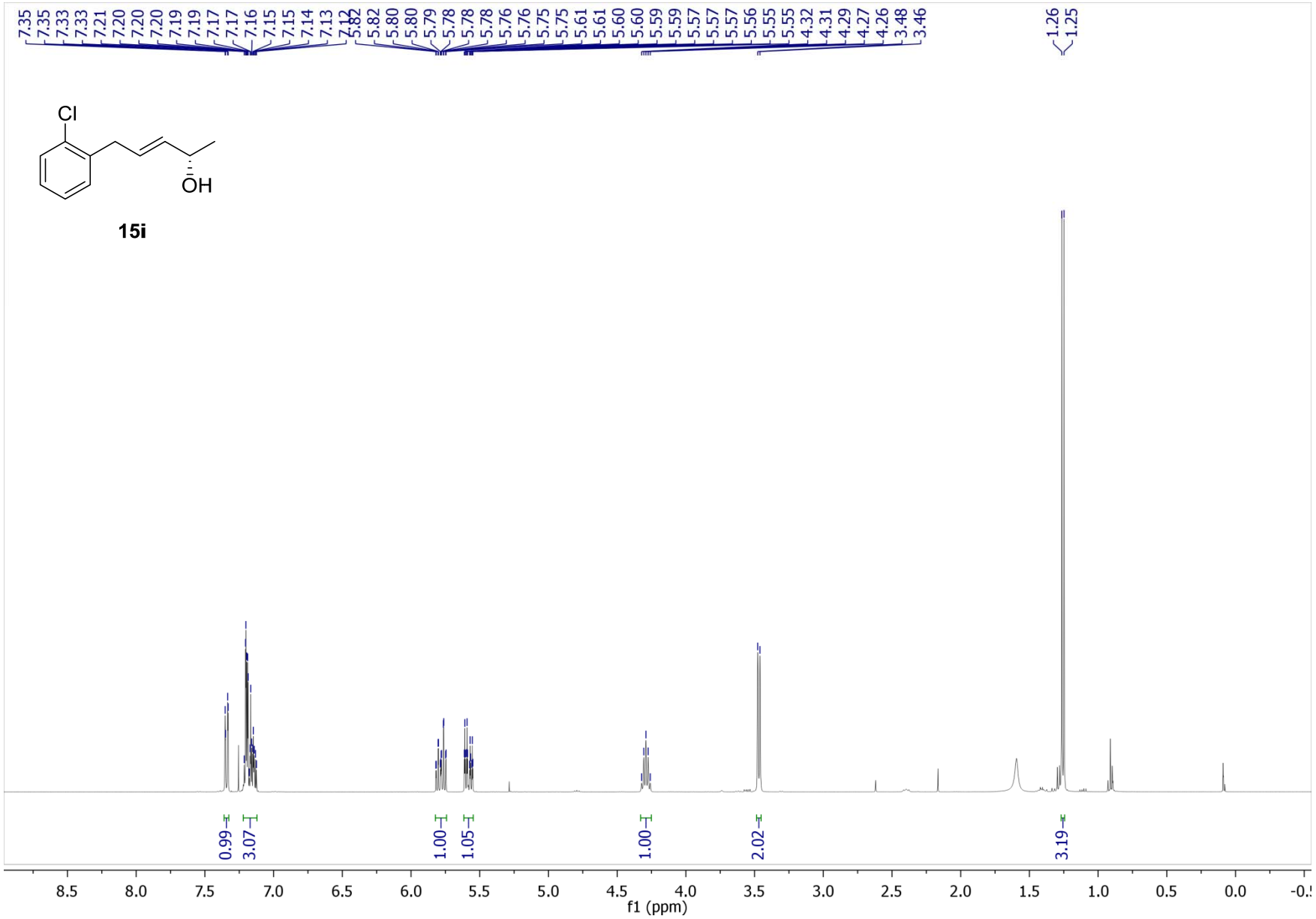
131.91
129.88
128.77
128.53
68.56
37.80
23.40
Cl
OH
15h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.35
7.35
7.33
7.33
7.21
7.20
7.20
7.20
7.19
7.19
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.12
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5.82
5.80
5.80
5.79
5.78
5.78
5.78
5.76
5.76
5.75
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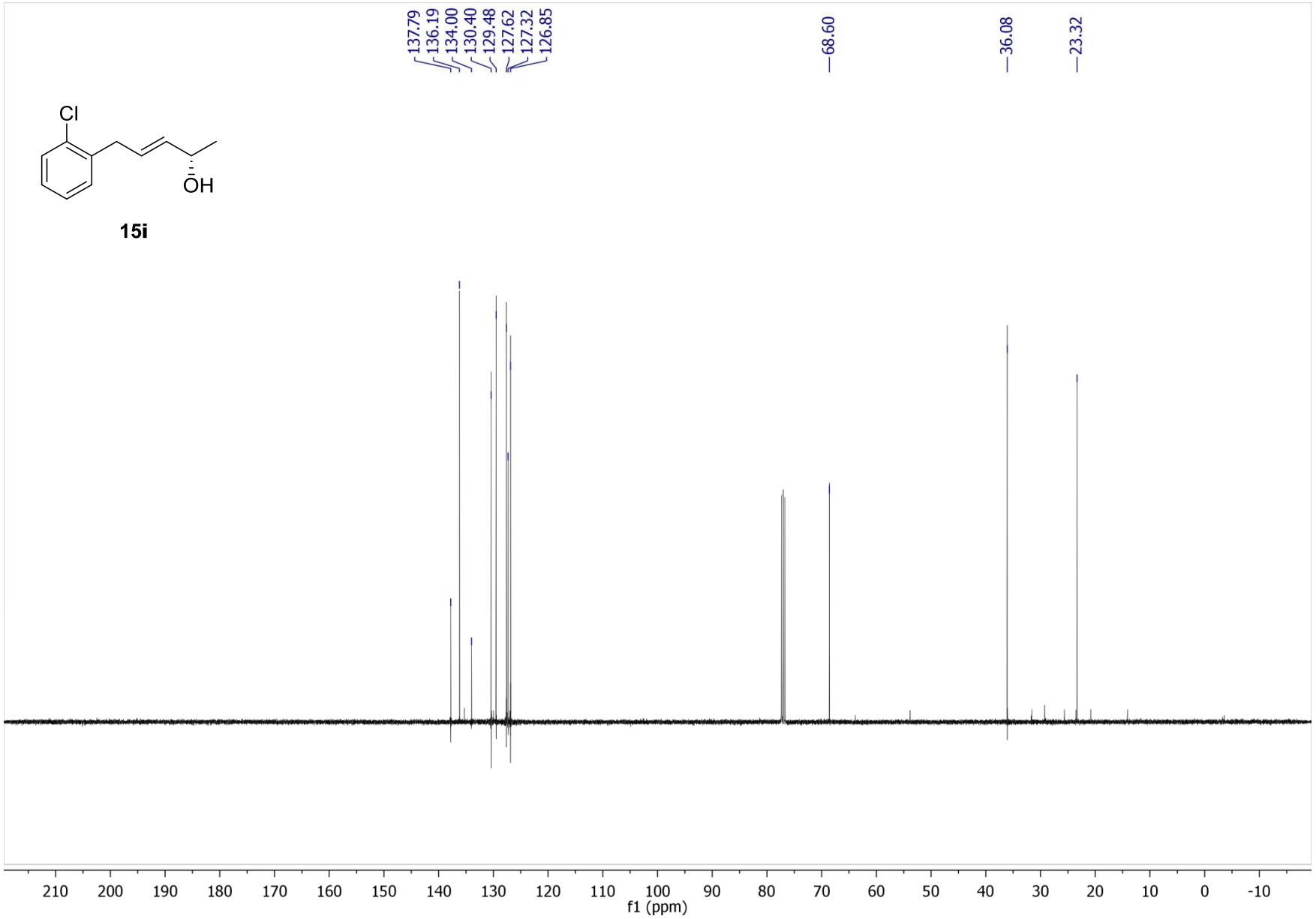
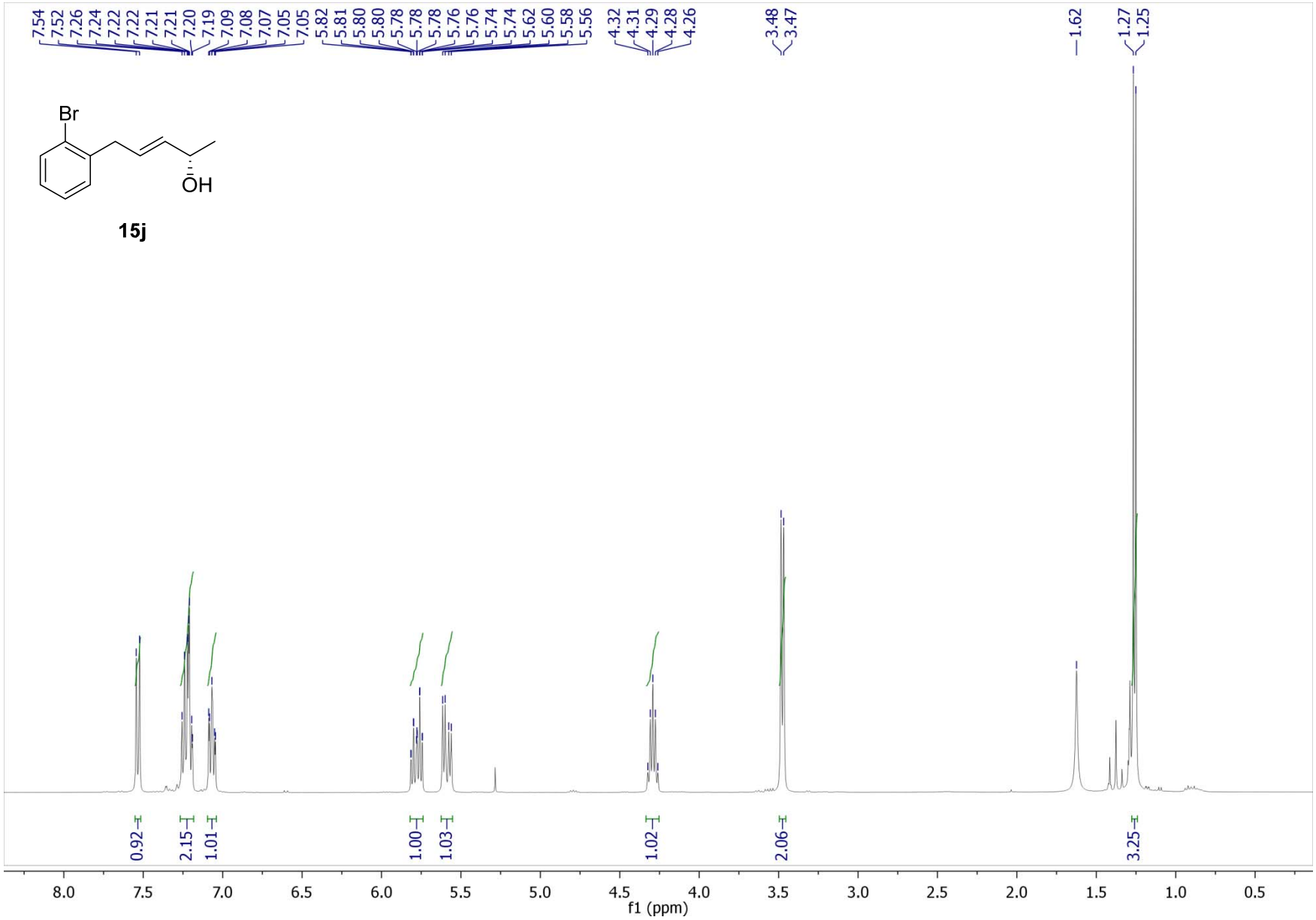
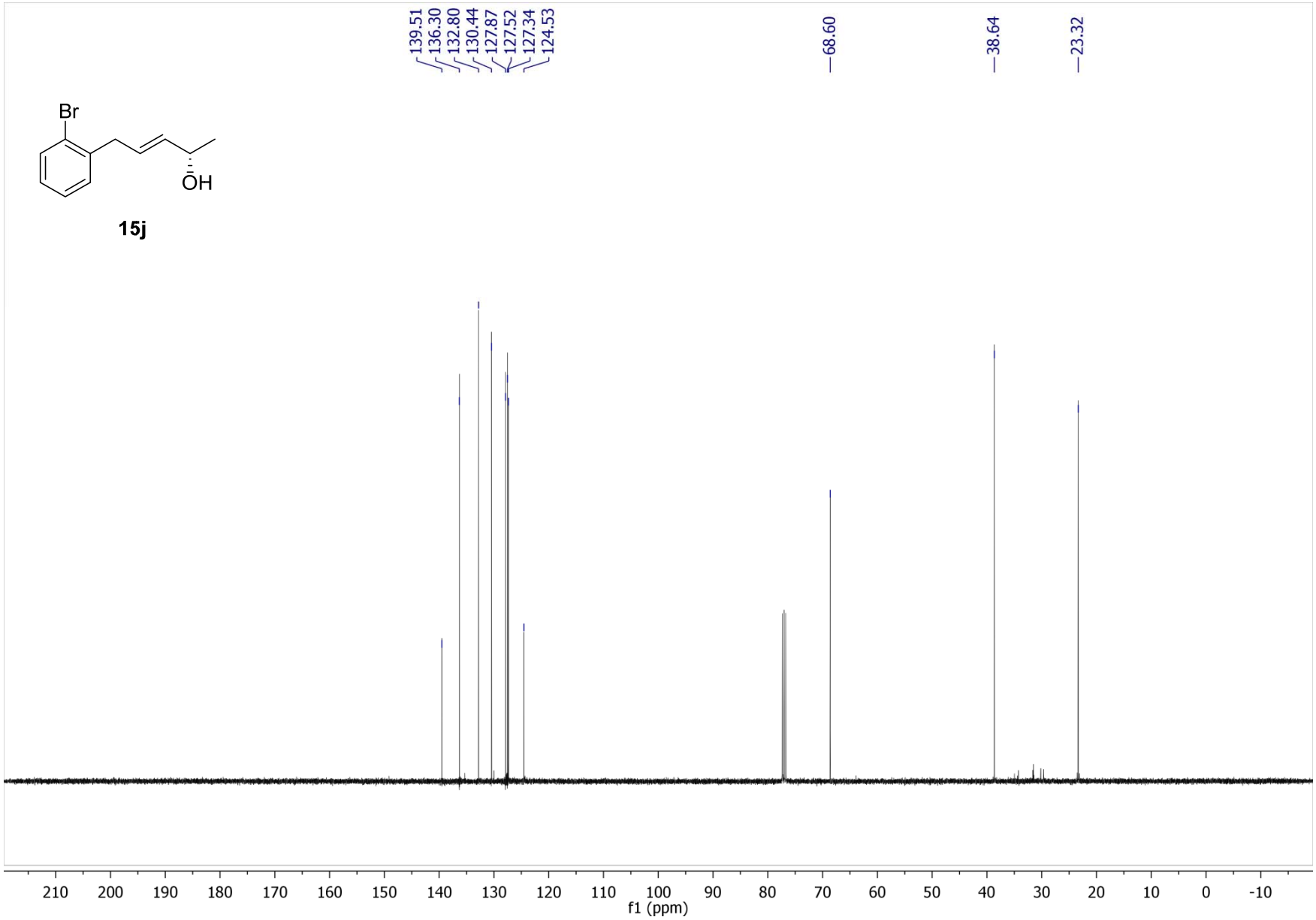
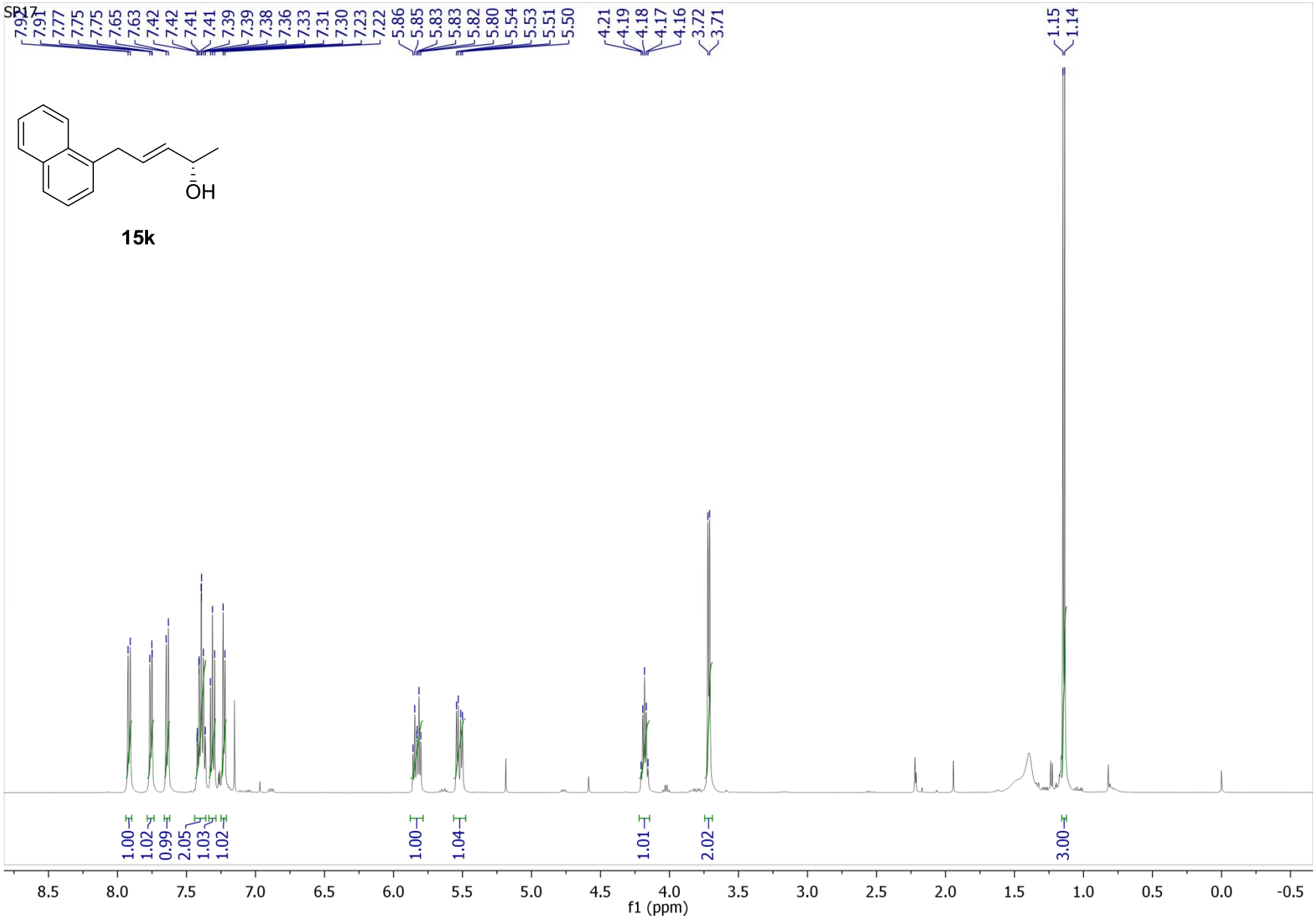
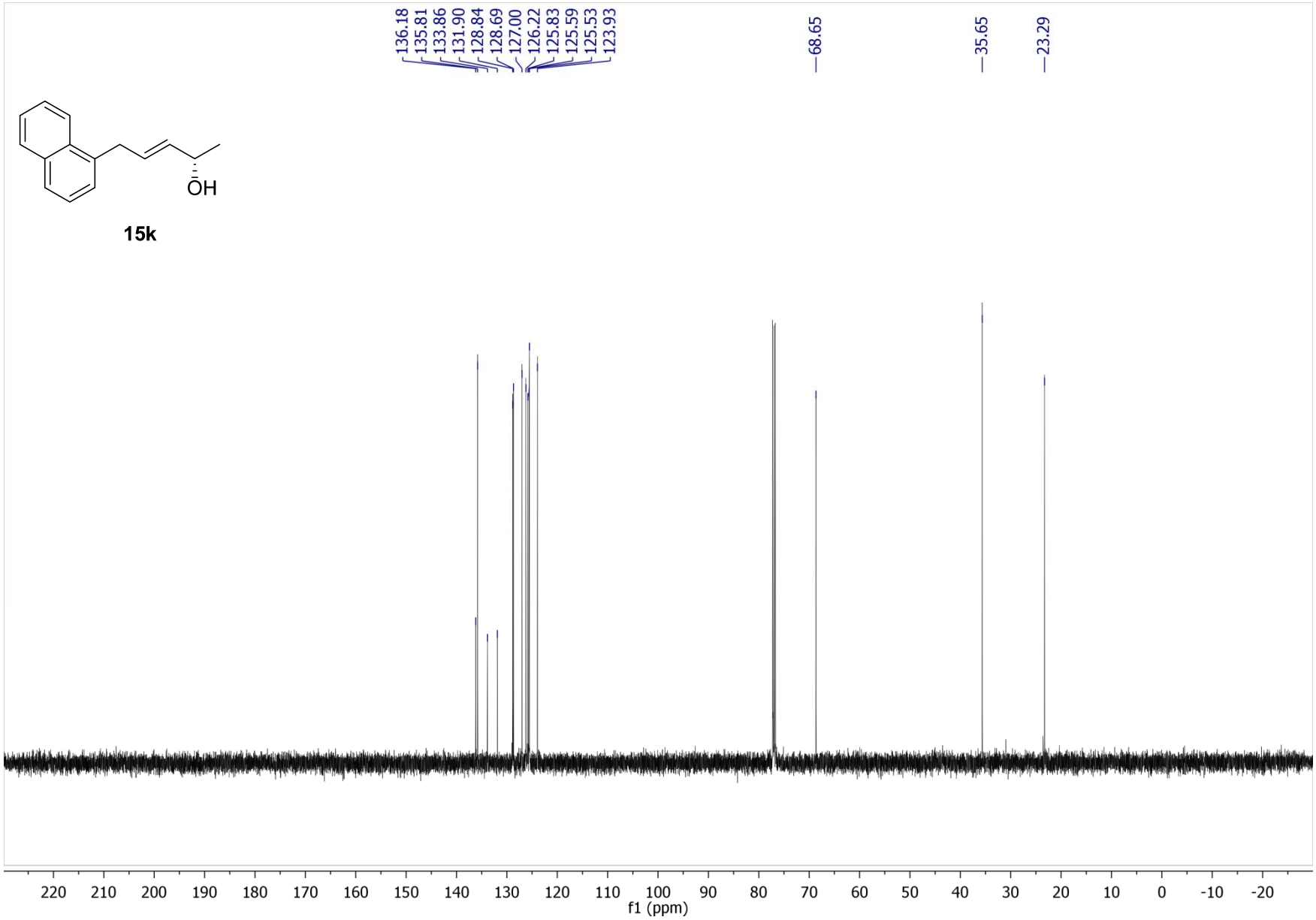
5.60
5.60
5.59
5.59
5.57
5.57
5.57
5.56
5.55
5.55
4.32
4.31
4.29
4.27
4.26
3.48
3.46
1.26
1.25
Cl
OH
15i
0.99
3.07
1.00
1.05
1.00
2.02
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

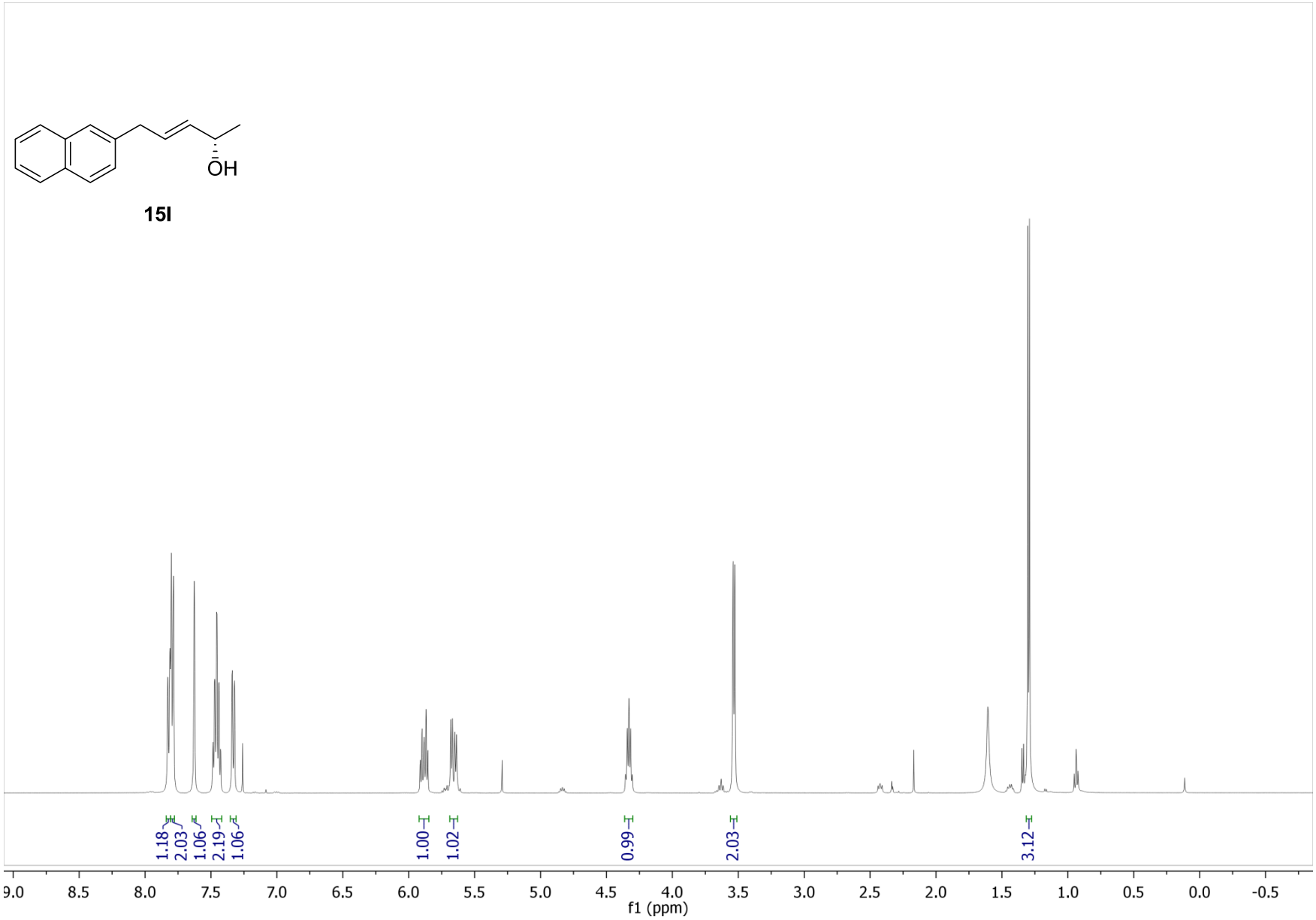

137.79
136.19
134.00
130.40
129.48
127.62
127.32
126.85
68.60
36.08
23.32
Cl
OH
15i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

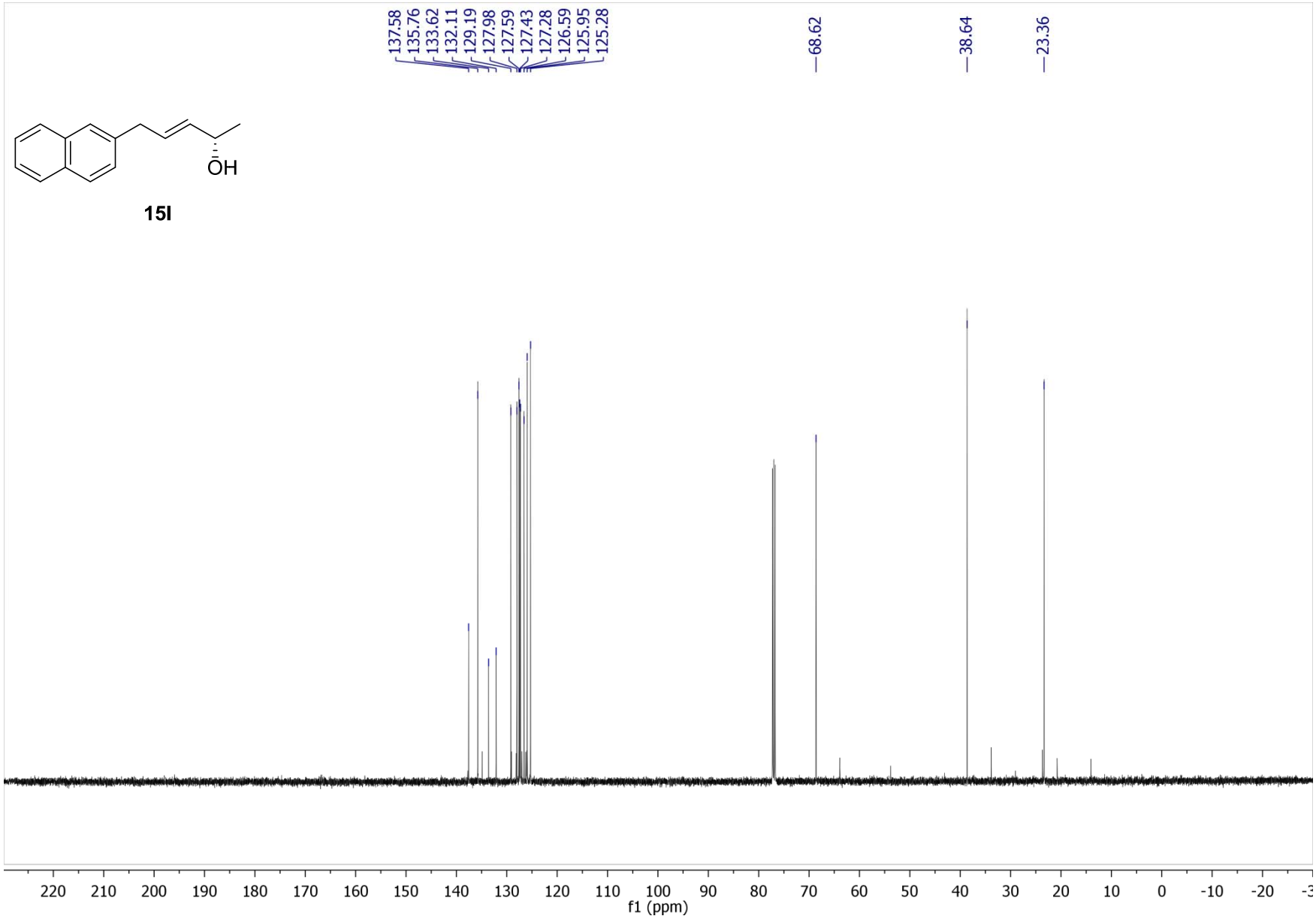

7.54
7.52
7.26
7.24
7.22
7.22
7.21
7.21
7.20
7.19
7.09
7.08
7.07
7.05
7.05
5.82
5.81
5.80
5.80
5.78
5.78
5.78
5.76
5.76
5.74
5.74
5.62
5.60
5.58
5.56
4.32
4.31
4.29
4.28
4.26
3.48
3.47
1.62
1.27
1.25
Br
OH
15j
0.92
2.15
1.01
1.00
1.03
1.02
2.06
3.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

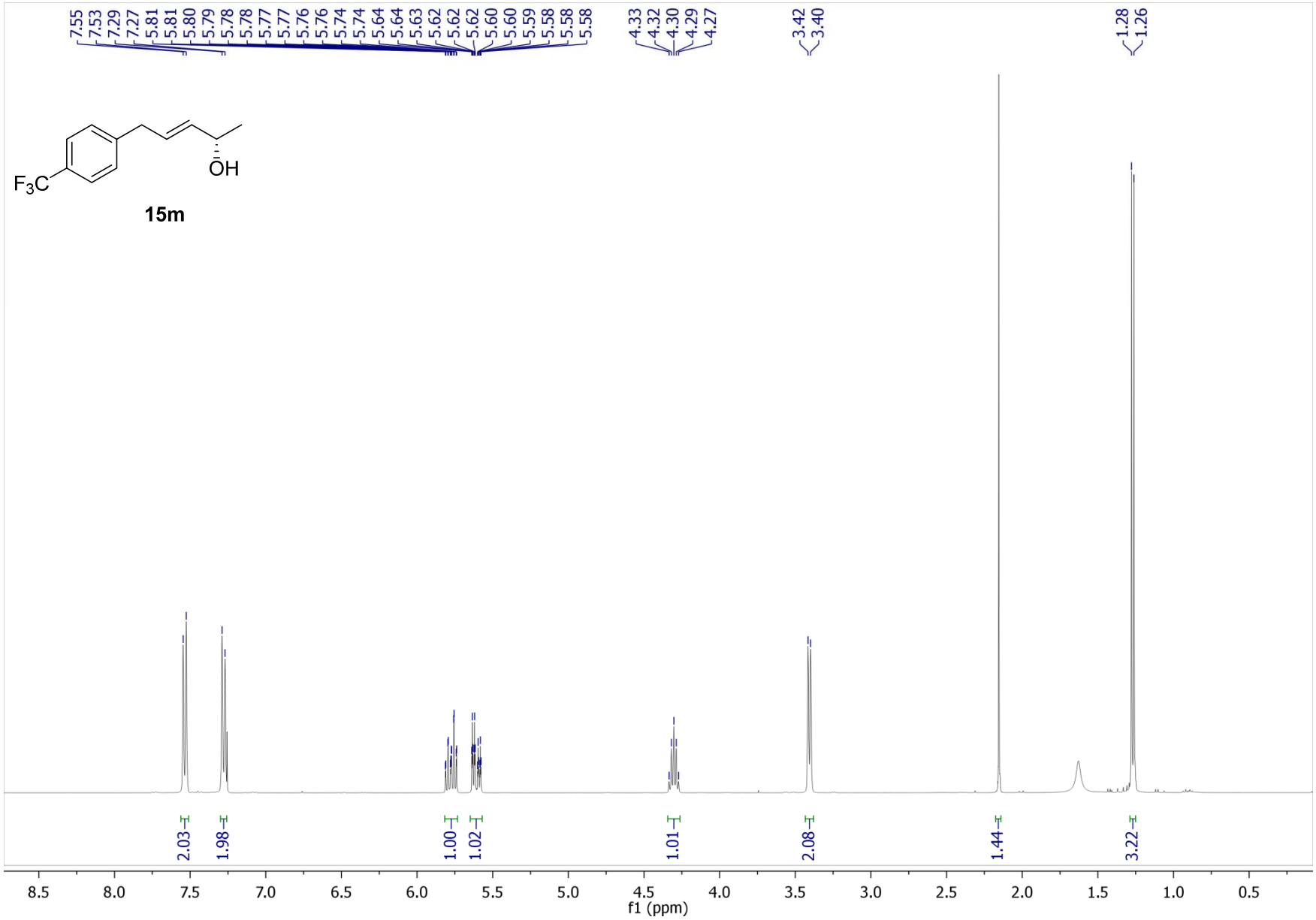

139.51
136.30
132.80
130.44
127.87
127.52
127.34
124.53
68.60
38.64
23.32
Br
OH
15j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

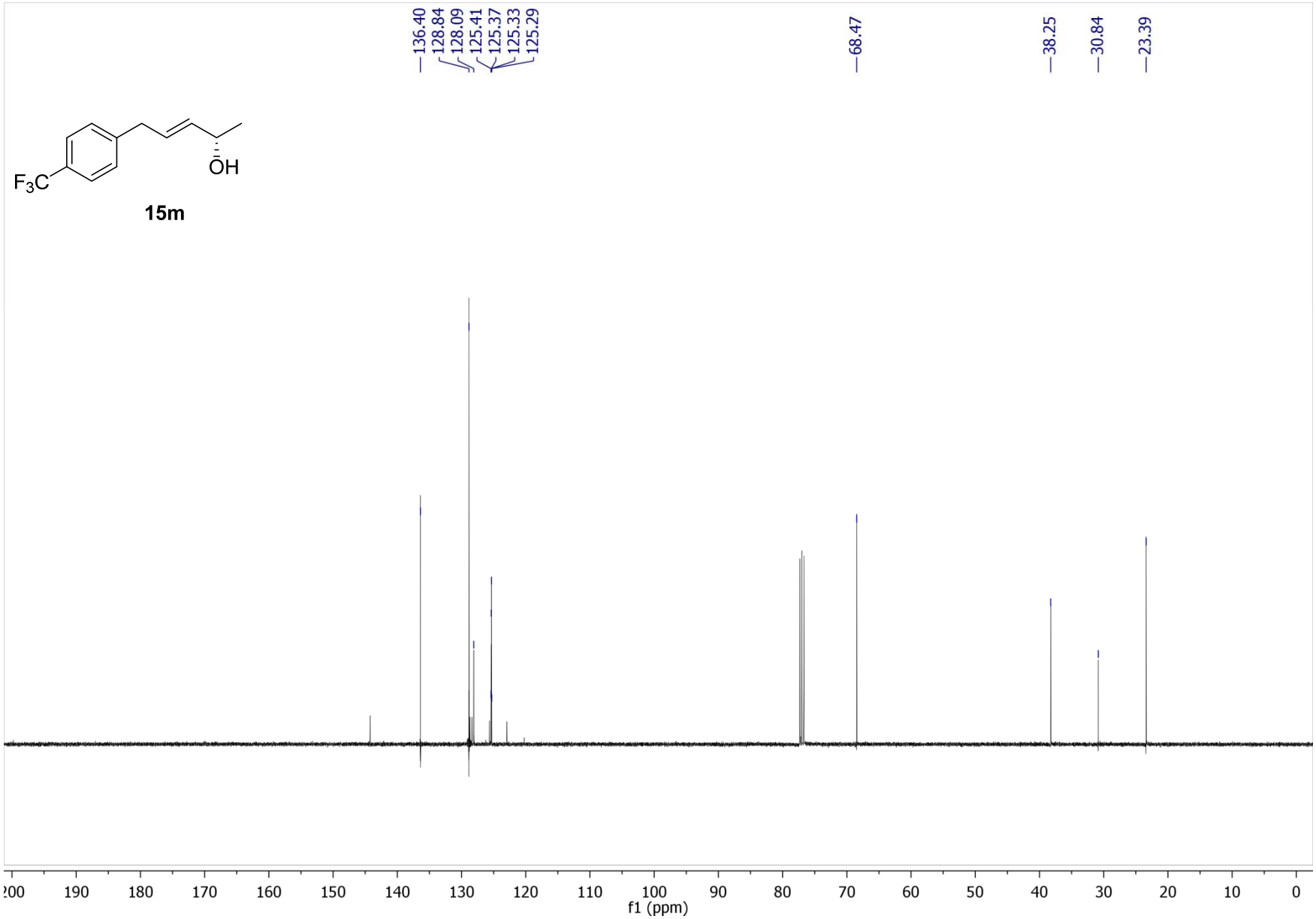

SP17
7.92
7.91
7.77
7.75
7.75
7.65
7.63
7.42
7.42
7.41
7.41
7.39
7.39
7.38
7.36
7.33
7.31
7.30
7.23
7.22
5.86
5.85
5.83
5.83
5.82
5.80
5.54
5.53
5.51
5.50
4.21
4.19
4.18
4.17
4.16
3.72
3.71
1.15
1.14
OH
15k
1.00
1.02
0.99
2.05
1.03
1.02
1.00
1.04
1.01
2.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

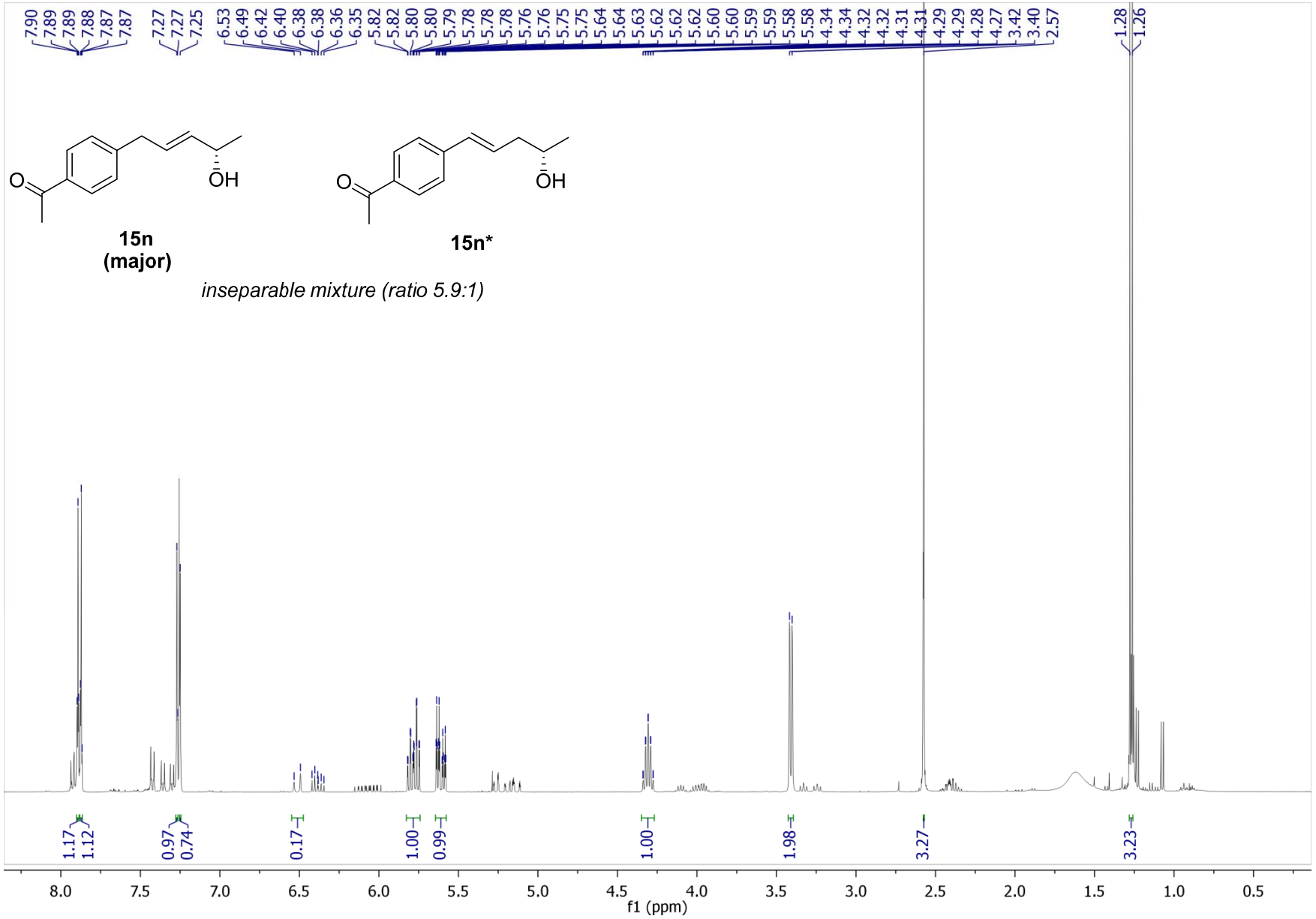

136.18
135.81
133.86
131.90
128.84
128.69
127.00
126.22
125.83
125.59
125.53
123.93
68.65
35.65
23.29
OH
15k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

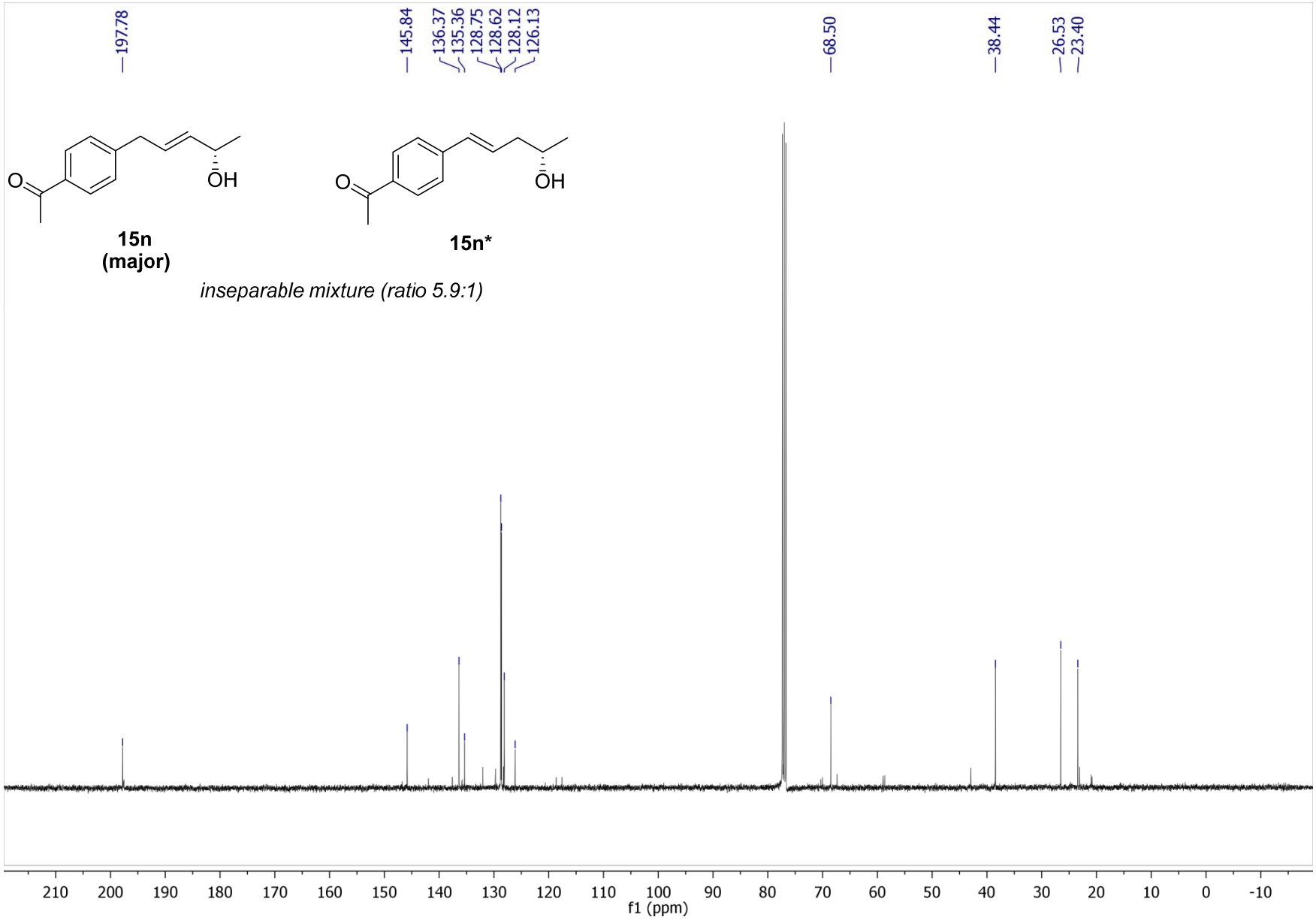

OH
15l
1.18
2.03
1.06
2.19
1.06
1.00
1.02
0.99
2.03
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

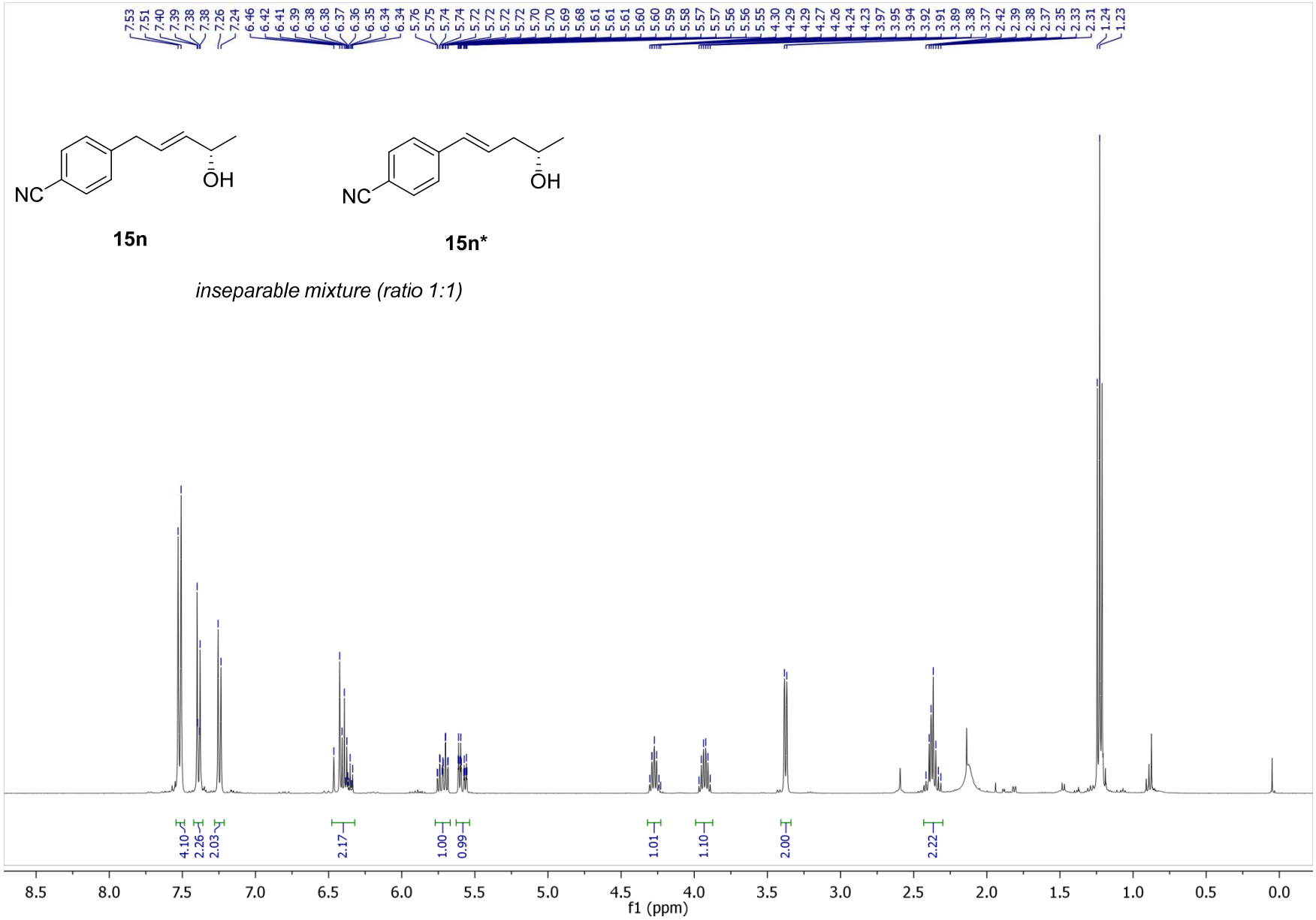

137.58
135.76
133.62
132.11
129.19
127.98
127.59
127.43
127.28
126.59
125.95
125.28
68.62
38.64
23.36
OH
15l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.55
7.53
7.29
7.27
5.81
5.81
5.80
5.79
5.78
5.78
5.77
5.77
5.76
5.76
5.74
5.74
5.64
5.64
5.63
5.62
5.62
5.62
5.60
5.60
5.59
5.58
5.58
5.58
4.33
4.32
4.30
4.29
4.27
3.42
3.40
1.28
1.26
F3C
OH
15m
2.03
1.98
1.00
1.02
1.01
2.08
1.44
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


136.40
128.84
128.09
125.41
125.37
125.33
125.29
68.47
38.25
30.84
23.39
F3C
OH
15m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.90 7.89 7.89 7.88 7.87 7.87
7.27 7.27 7.25
6.53 6.49 6.42 6.40 6.38 6.38 6.36 6.35
5.82 5.82 5.80 5.80 5.79 5.78 5.78 5.78 5.76 5.76 5.75 5.75 5.64 5.64 5.63 5.62 5.62 5.62 5.60 5.60 5.59 5.59 5.58 5.58
4.34 4.34 4.32 4.32 4.31 4.31 4.29 4.29 4.28 4.27
3.42 3.40 2.57
1.28 1.26
O
OH
O
OH
15n
(major)
15n*
inseparable mixture (ratio 5.9:1)
1.17 1.12
0.97 0.74
0.17
1.00
0.99
1.00
1.98
3.27
3.23
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

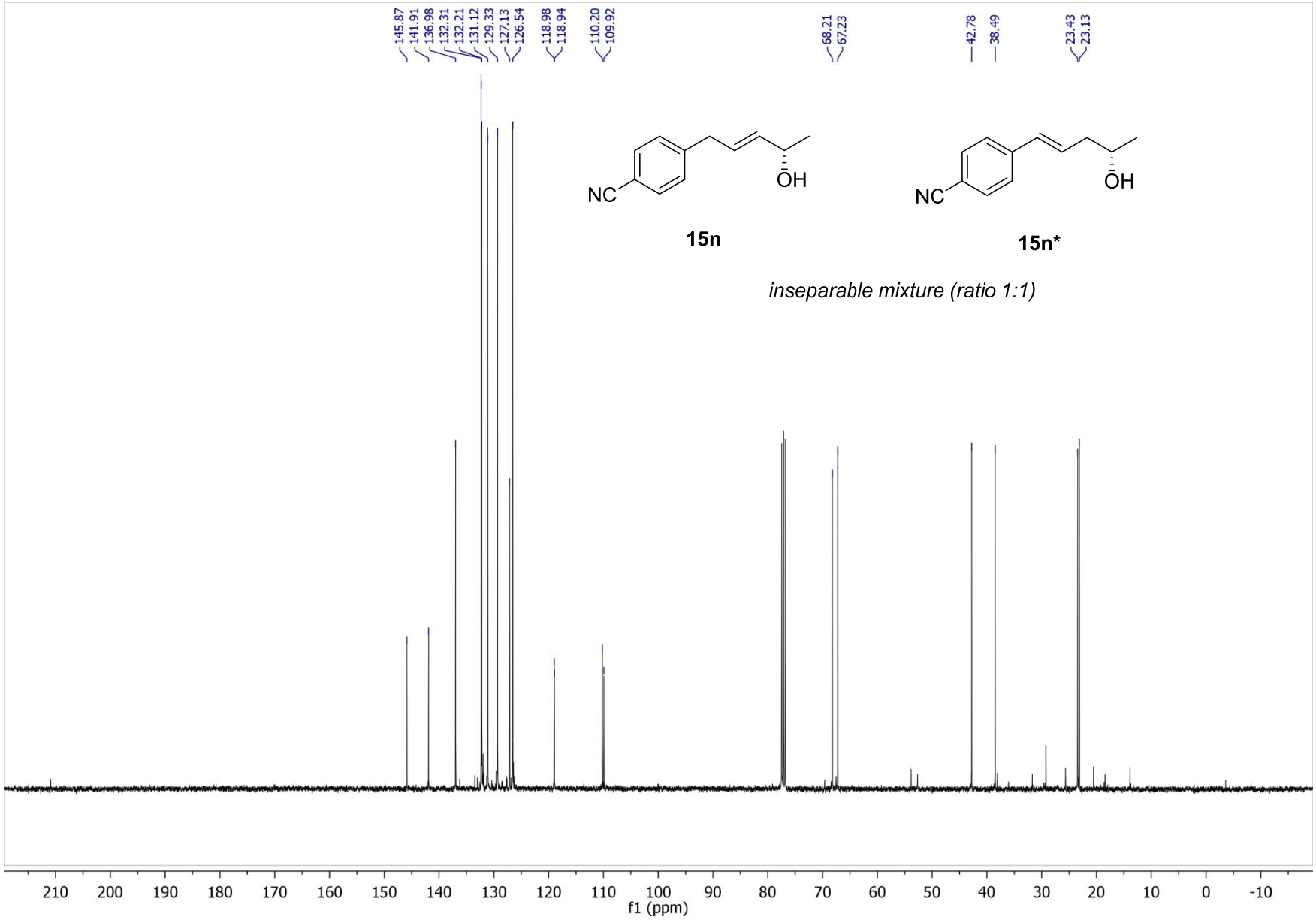

197.78
145.84
136.37
135.36
128.75
128.62
128.12
126.13
68.50
38.44
26.53
23.40
O
OH
O
OH
15n
(major)
15n*
inseparable mixture (ratio 5.9:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

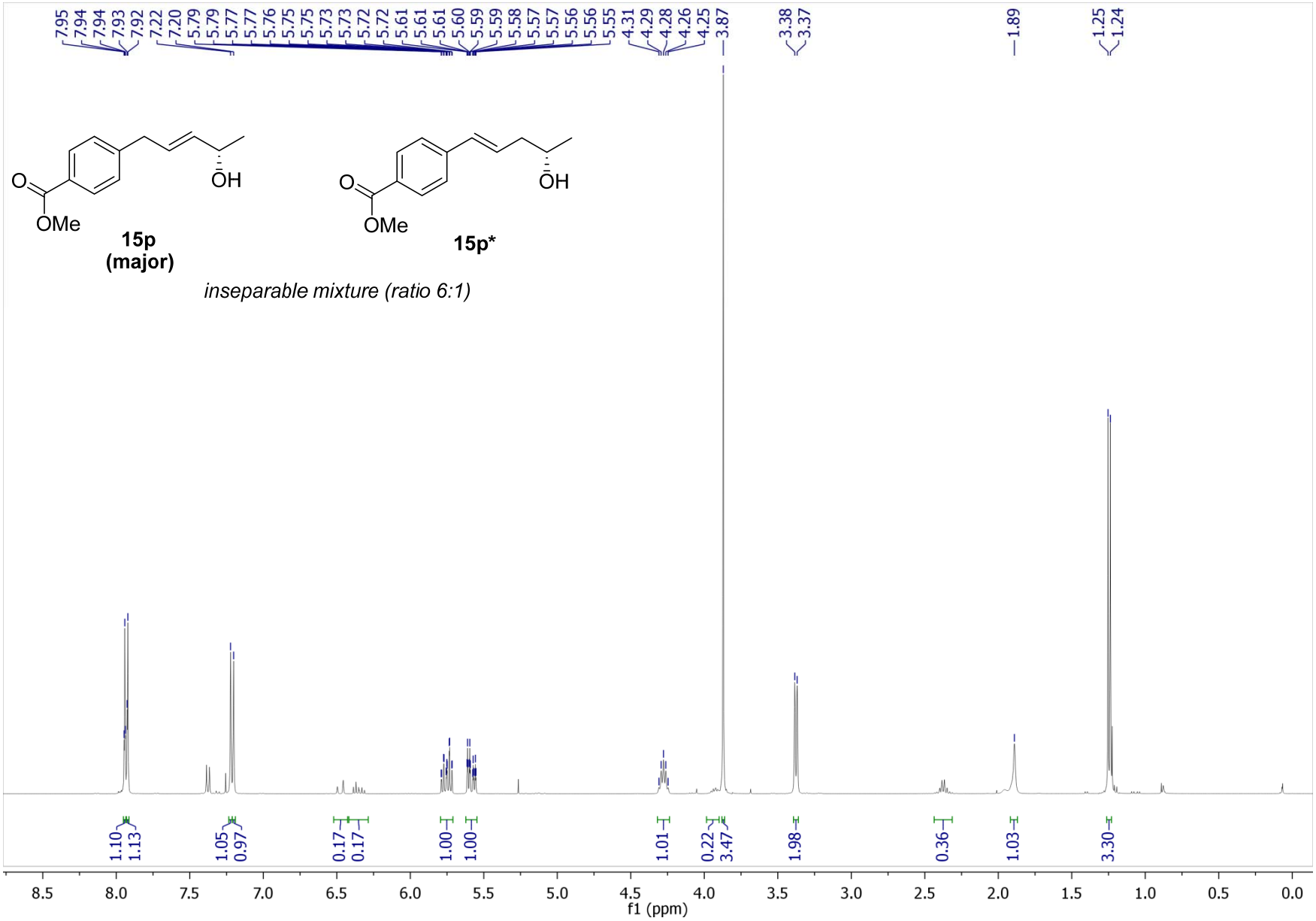


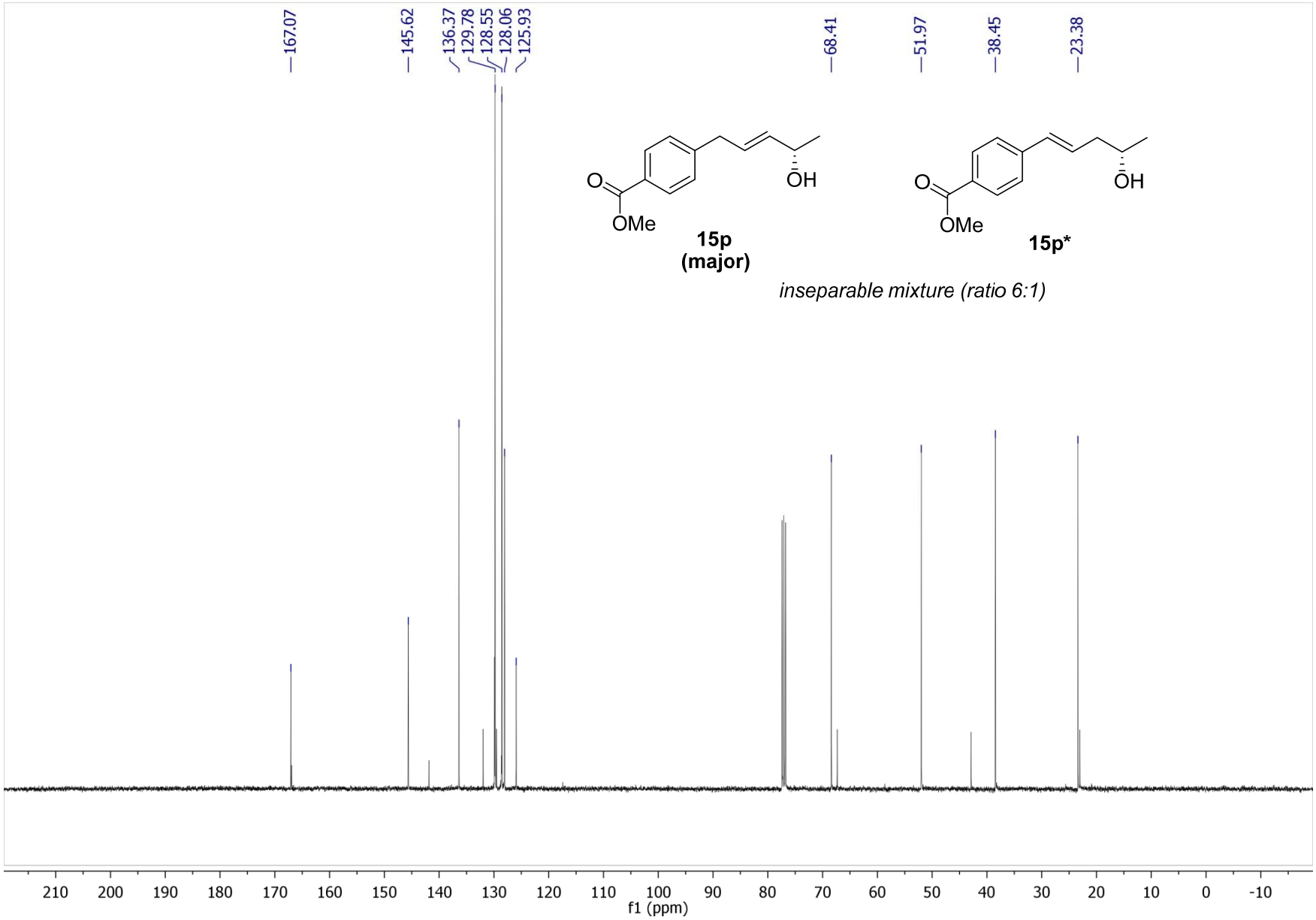
15n

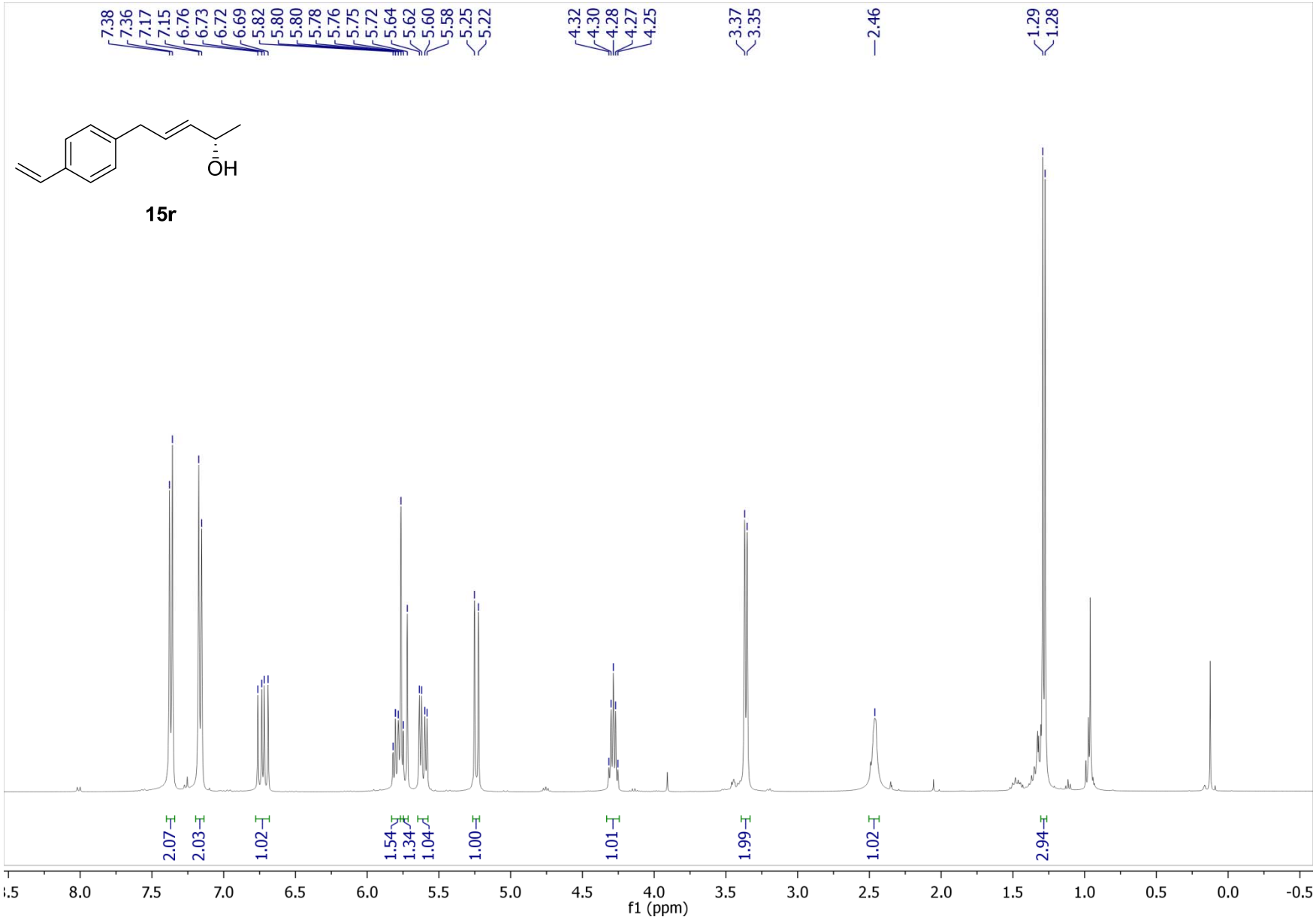
15n*

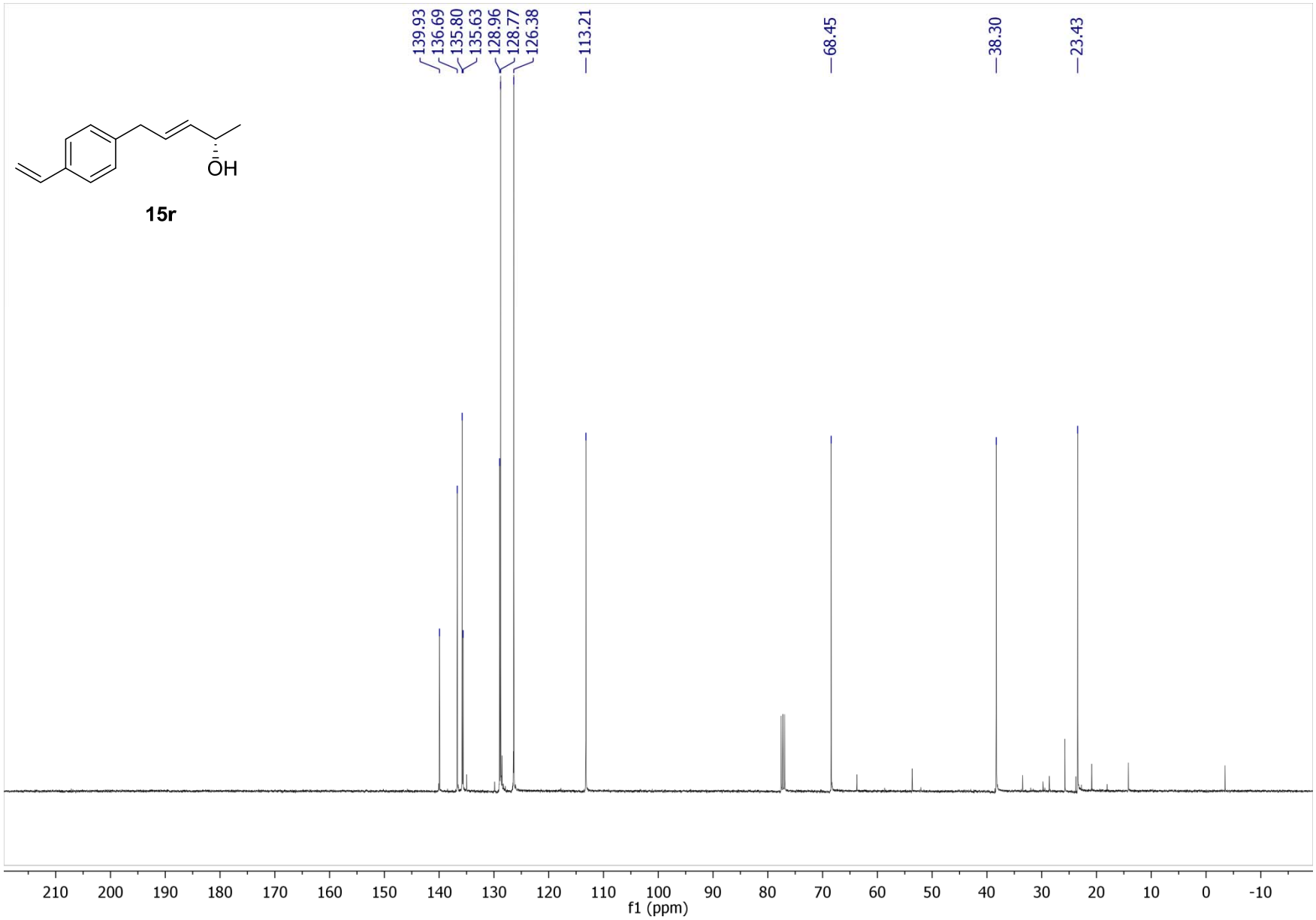
inseparable mixture (ratio 1:1)

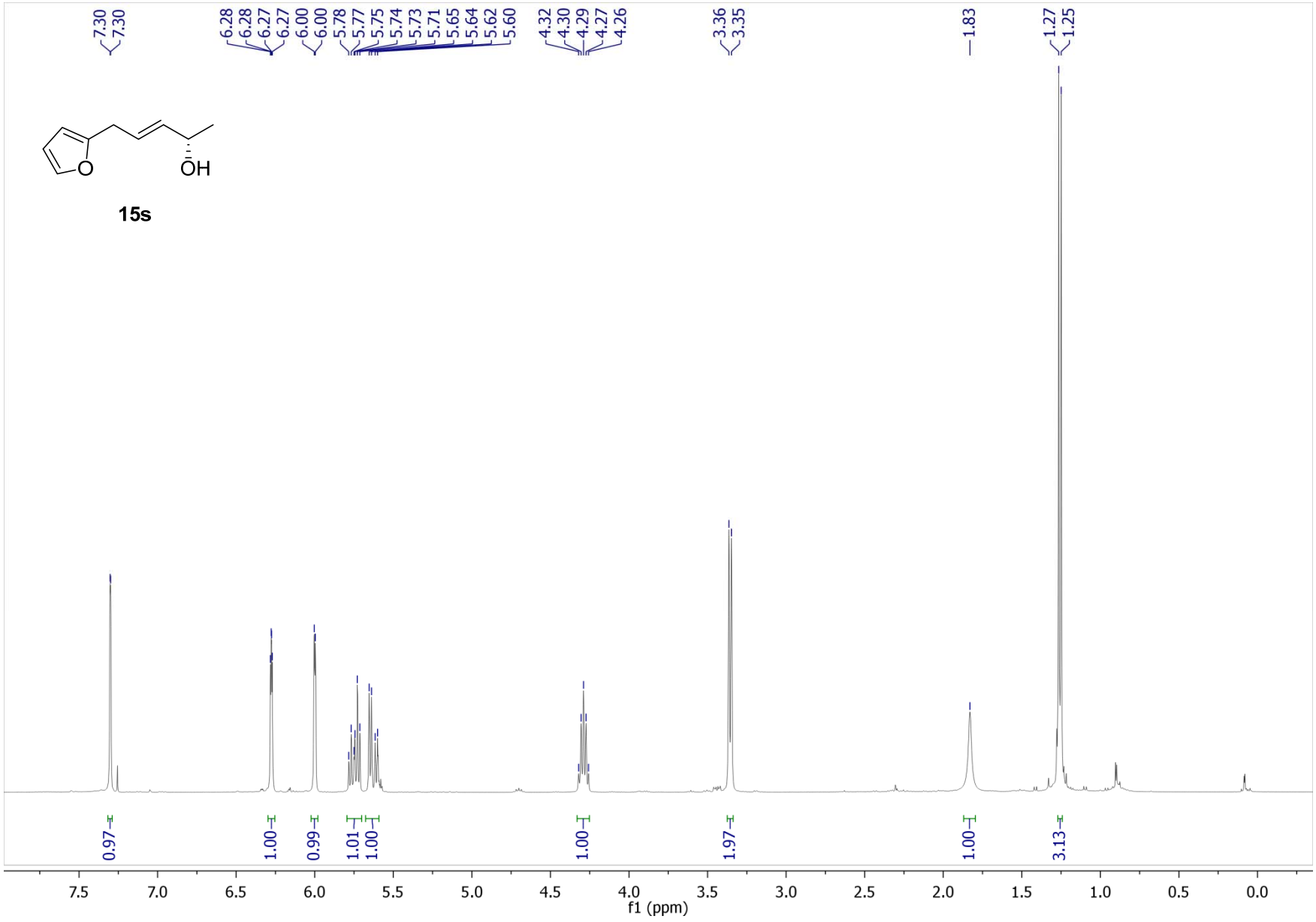

145.87
141.91
136.98
132.31
132.21
131.12
129.33
127.13
126.54
118.98
118.94
110.20
109.92
68.21
67.23
42.78
38.49
23.43
23.13
NC
OH
15n
NC
OH
15n*
inseparable mixture (ratio 1:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

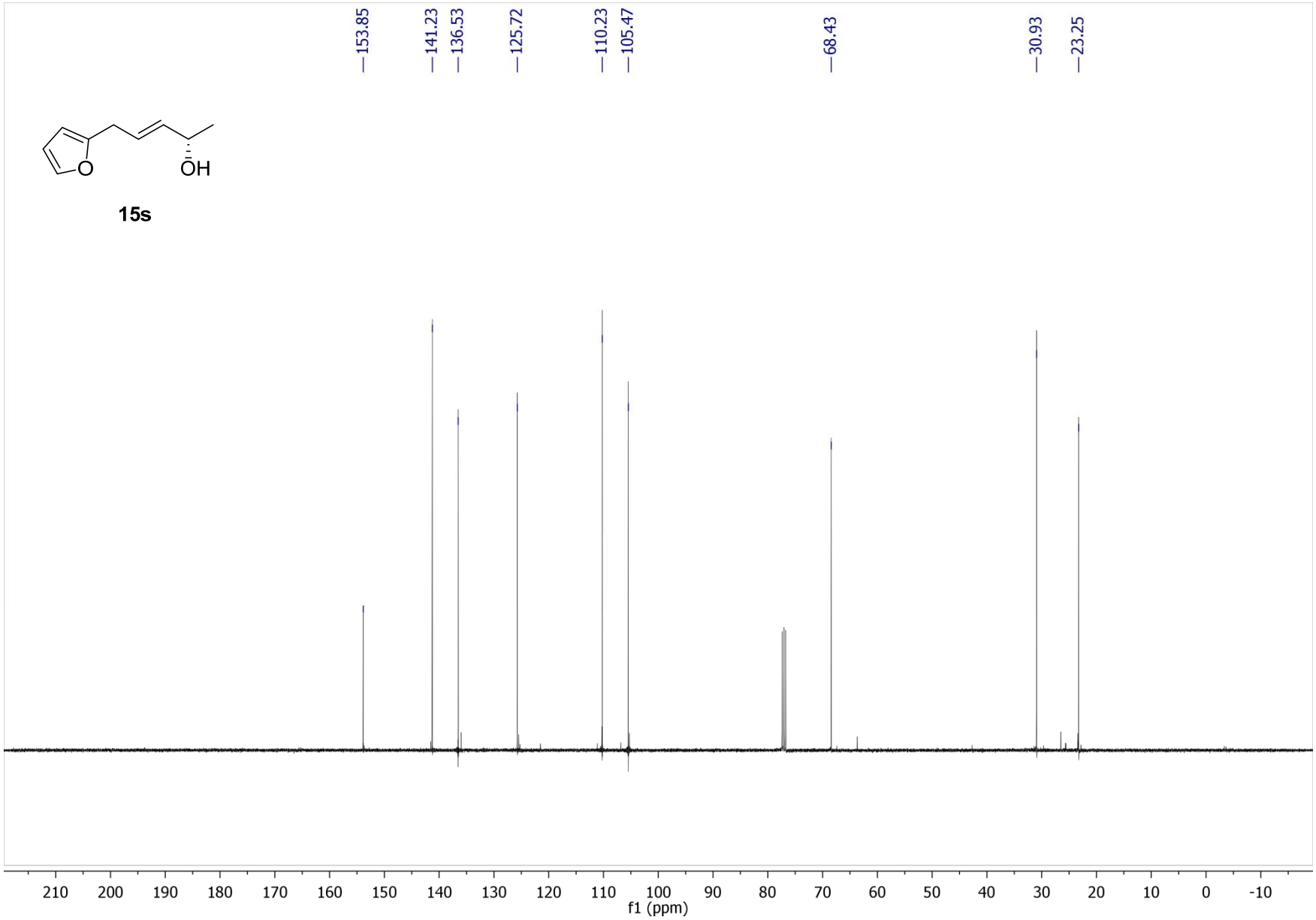

7.95
7.94
7.94
7.93
7.92
7.22
7.20
5.79
5.79
5.77
5.77
5.76
5.75
5.75
5.73
5.73
5.72
5.72
5.61
5.61
5.61
5.60
5.59
5.59
5.58
5.57
5.57
5.56
5.56
5.55
4.31
4.29
4.28
4.26
4.25
3.87
3.38
3.37
1.89
1.25
1.24
O
OH
OMe
15p
(major)
O
OH
OMe
15p*
inseparable mixture (ratio 6:1)
1.10
1.13
1.05
0.97
0.17
0.17
1.00
1.00
1.01
0.22
3.47
1.98
0.36
1.03
3.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

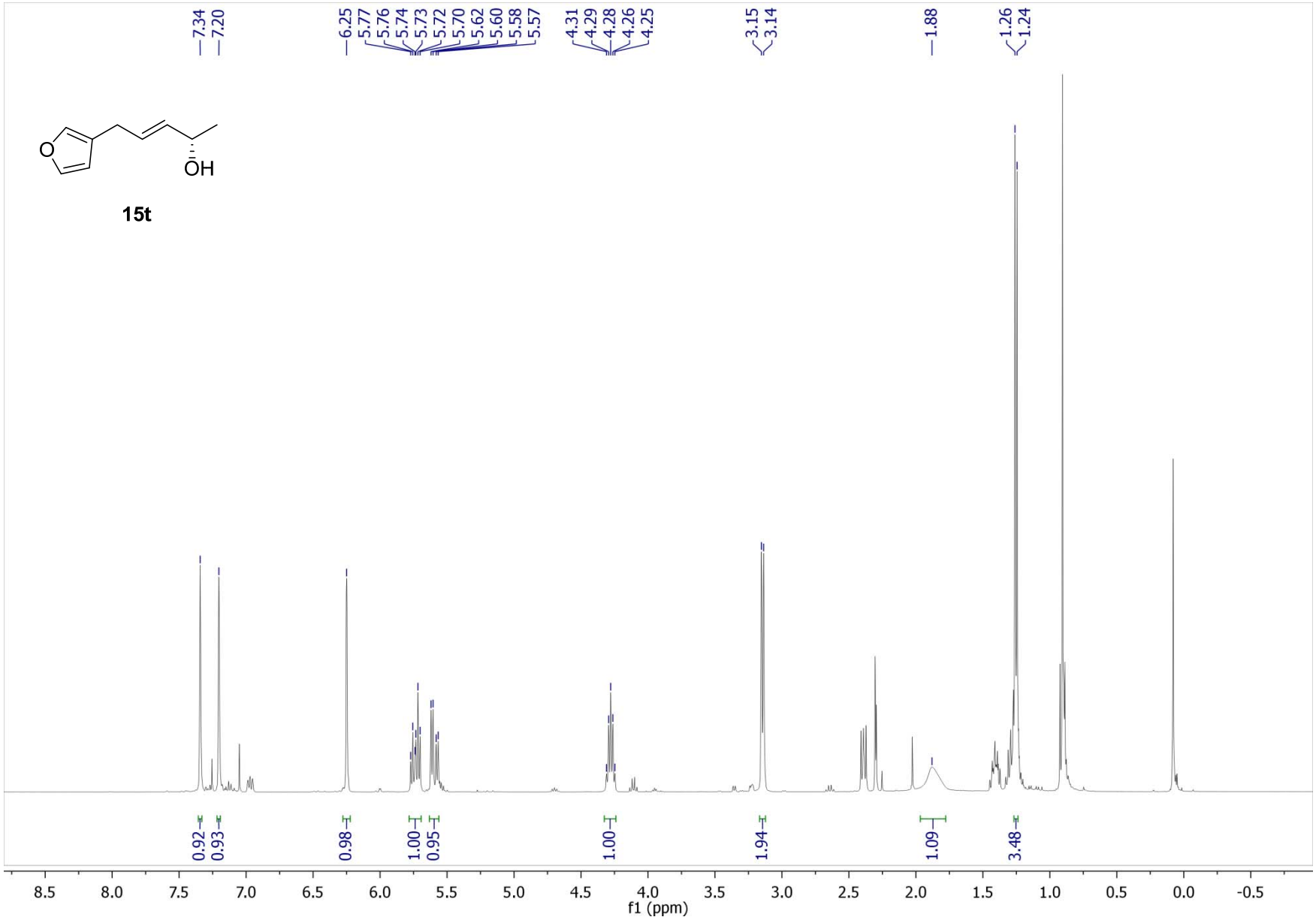

167.07
145.62
136.37
129.78
128.55
128.06
125.93
68.41
51.97
38.45
23.38
O
OMe
OH
15p
(major)
O
OMe
OH
15p*
inseparable mixture (ratio 6:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.38
7.36
7.17
7.15
6.76
6.73
6.72
6.69
5.82
5.80
5.80
5.78
5.76
5.75
5.72
5.64
5.62
5.60
5.58
5.25
5.22
4.32
4.30
4.28
4.27
4.25
3.37
3.35
2.46
1.29
1.28
OH
15r
2.07
2.03
1.02
1.54
1.34
1.04
1.00
1.01
1.99
1.02
2.94
f1 (ppm)

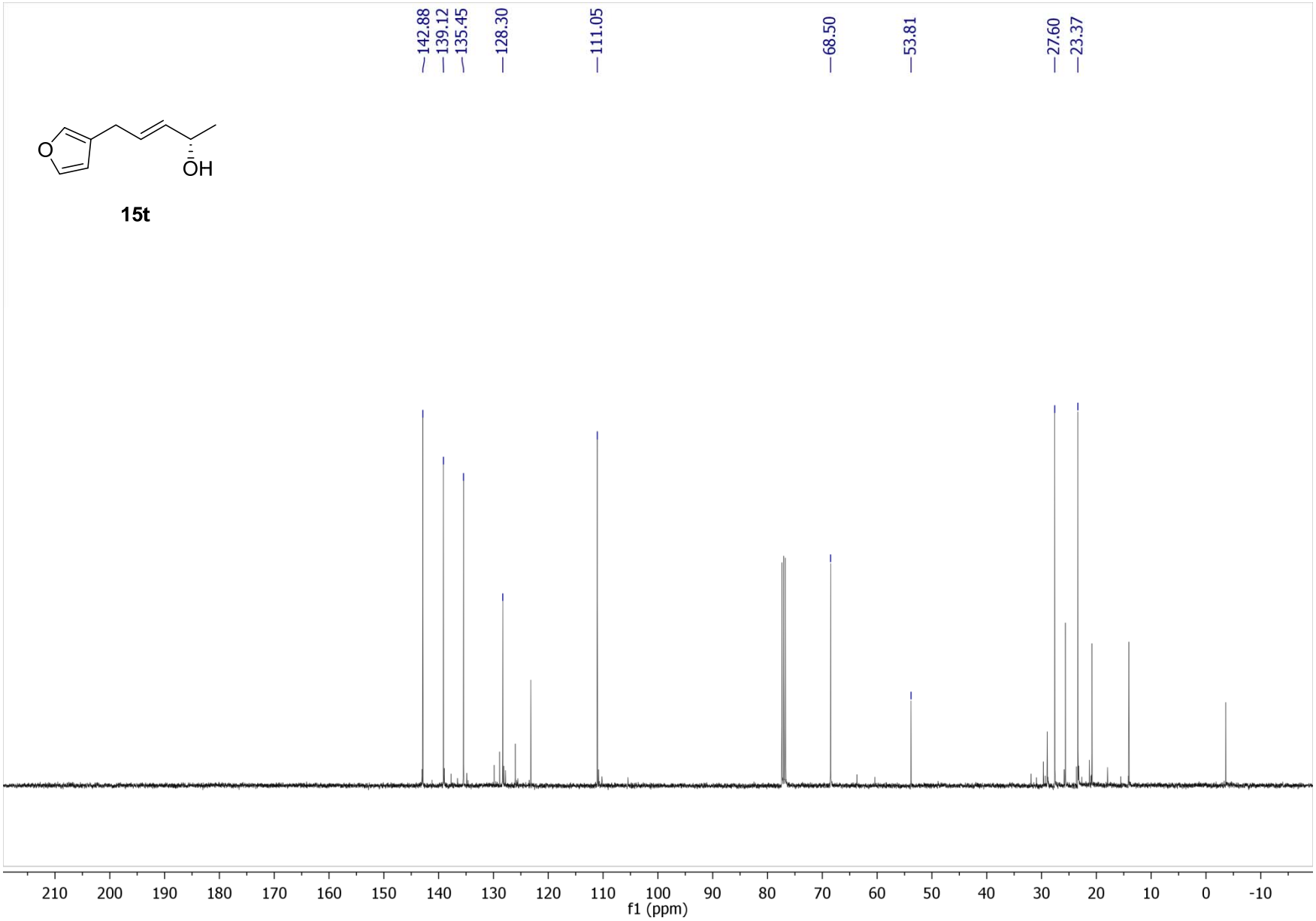

139.93
136.69
135.80
135.63
128.96
128.77
126.38
113.21
68.45
38.30
23.43
OH
15r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

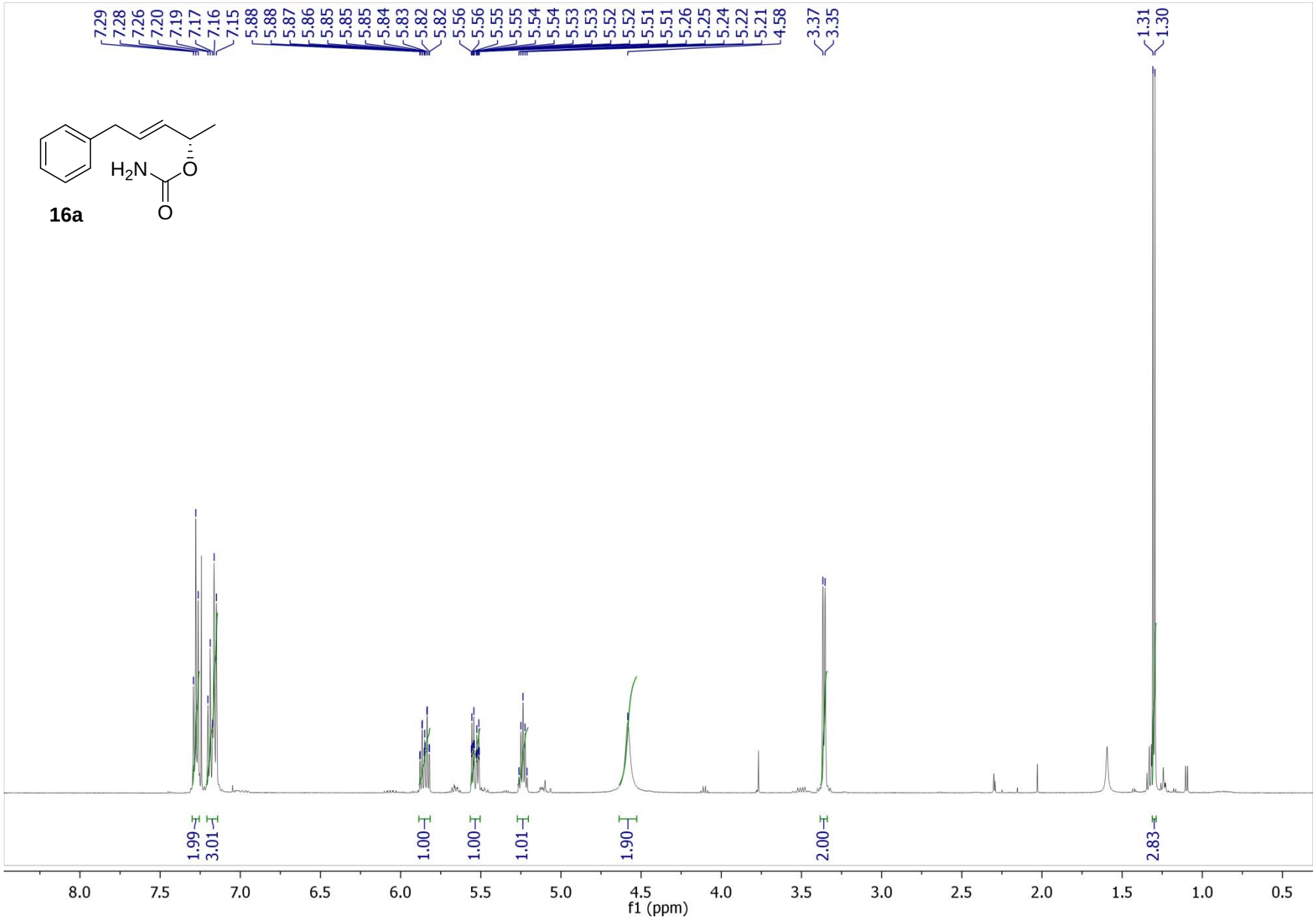

7.30
7.30
6.28
6.28
6.27
6.27
6.00
6.00
5.78
5.77
5.75
5.74
5.73
5.71
5.65
5.64
5.62
5.60
4.32
4.30
4.29
4.27
4.26
3.36
3.35
1.83
1.27
1.25
O
OH
15s
0.97
1.00
0.99
1.01
1.00
1.00
1.97
1.00
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

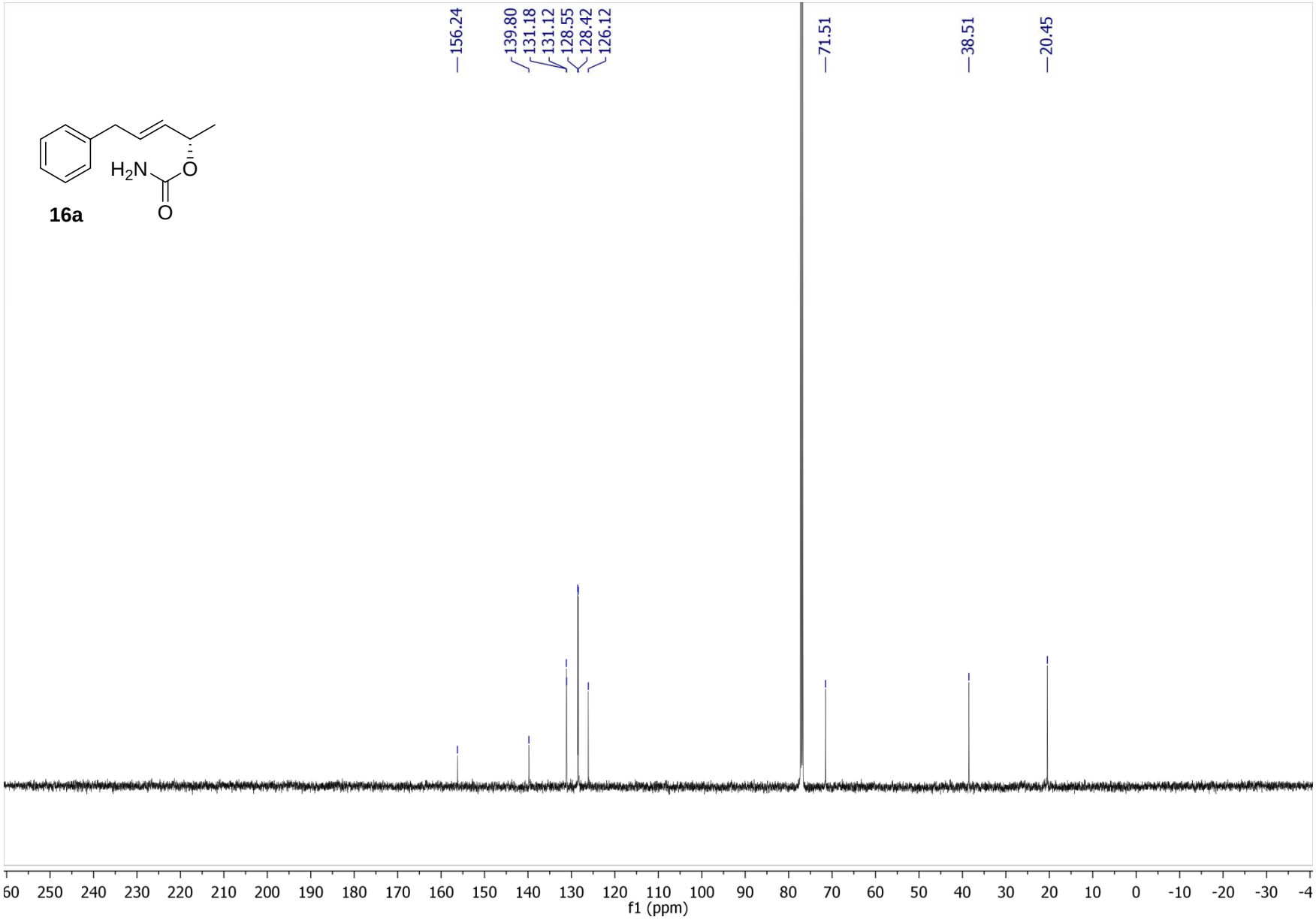

153.85
141.23
136.53
125.72
110.23
105.47
68.43
30.93
23.25
O
OH
15s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

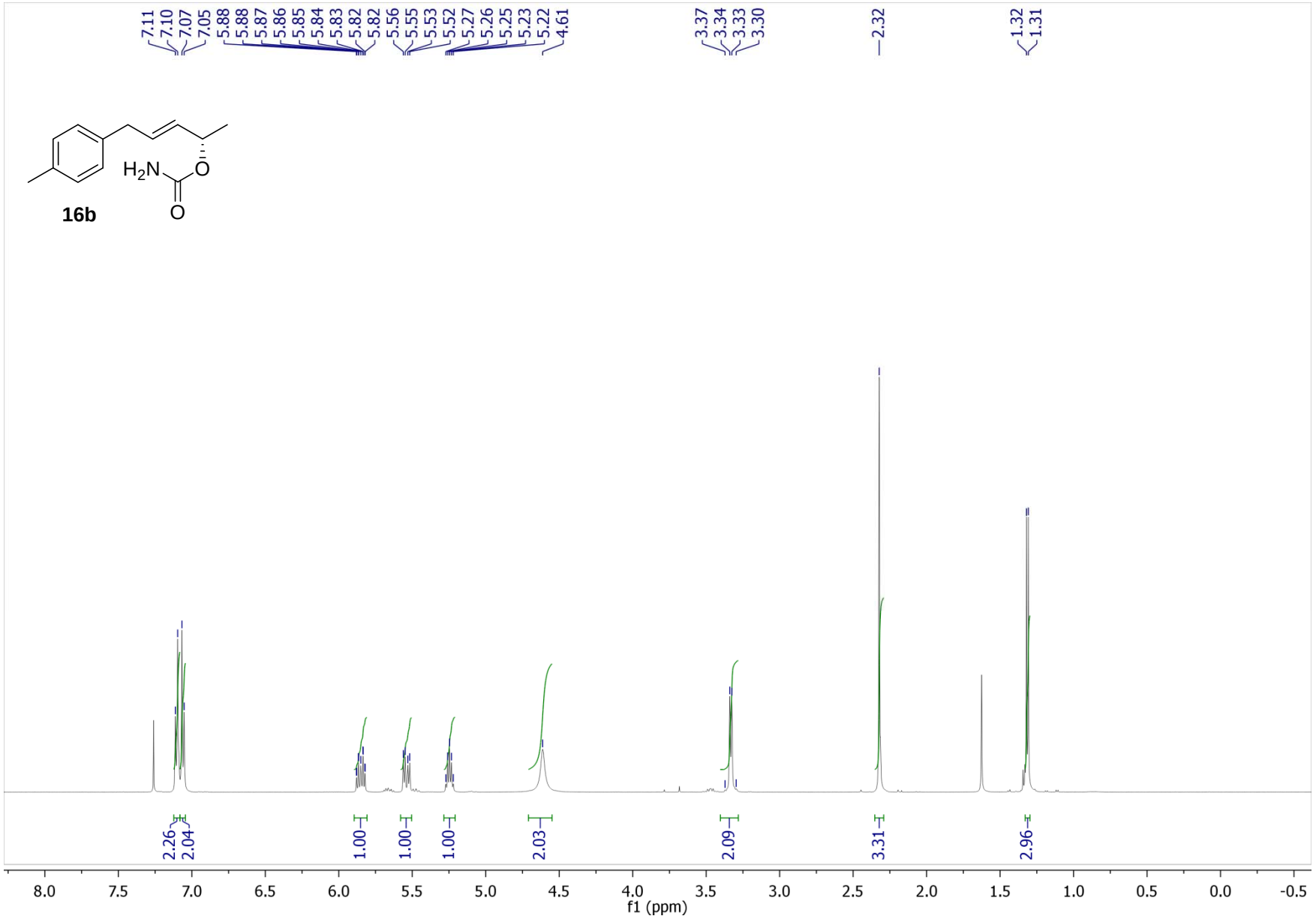

7.34
7.20
6.25
5.77
5.76
5.74
5.73
5.72
5.70
5.62
5.60
5.58
5.57
4.31
4.29
4.28
4.26
4.25
3.15
3.14
1.88
1.26
1.24
O
OH
0.92
0.93
0.98
1.00
0.95
1.00
1.94
1.09
3.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

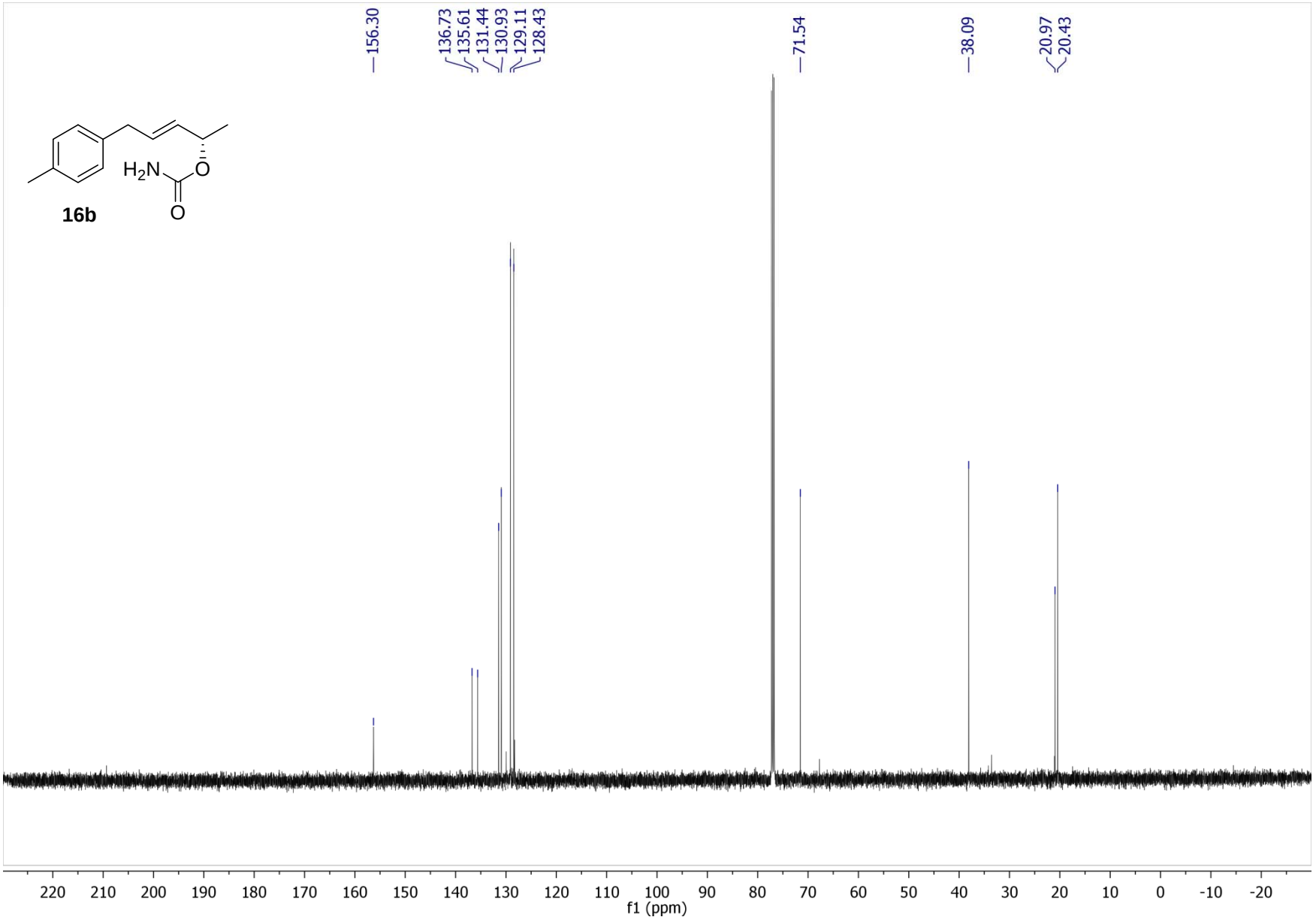
15t

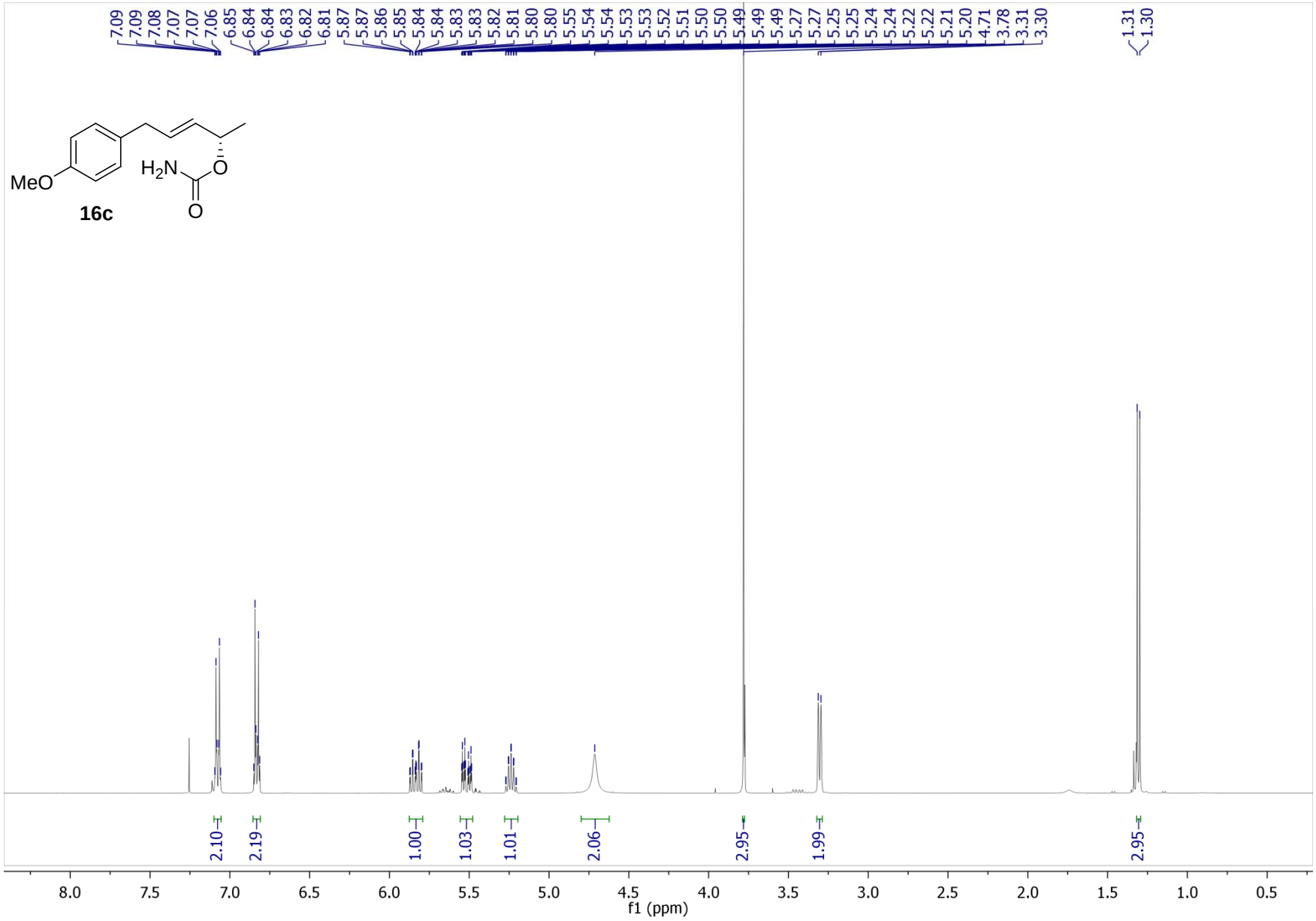

142.88
139.12
135.45
128.30
111.05
68.50
53.81
27.60
23.37
O
OH
15t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.29
7.28
7.26
7.20
7.19
7.17
7.16
7.15
5.88
5.88
5.87
5.86
5.85
5.85
5.85
5.84
5.83
5.82
5.82
5.56
5.56
5.55
5.55
5.54
5.54
5.53
5.53
5.52
5.52
5.51
5.51
5.26
5.25
5.24
5.22
5.21
4.58
3.37
3.35
1.31
1.30
H2N
O
O
16a
1.99
3.01
1.00
1.00
1.01
1.90
2.00
2.83
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


156.24
139.80
131.18
131.12
128.55
128.42
126.12
71.51
38.51
20.45
H2N
O
O
16a
60 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4
f1 (ppm)


7.11
7.10
7.07
7.05
5.88
5.88
5.87
5.86
5.85
5.84
5.83
5.82
5.82
5.56
5.55
5.53
5.52
5.27
5.26
5.25
5.23
5.22
4.61
3.37
3.34
3.33
3.30
2.32
1.32
1.31
H2N
O
O
16b
2.26
2.04
1.00
1.00
1.00
2.03
2.09
3.31
2.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


156.30
136.73
135.61
131.44
130.93
129.11
128.43
71.54
38.09
20.97
20.43
H2N
O
O
16b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.09
7.09
7.08
7.07
7.07
7.06
6.85
6.84
6.84
6.83
6.82
6.81
5.87
5.87
5.86
5.85
5.84
5.84
5.83
5.83
5.82
5.81
5.80
5.80
5.55
5.54
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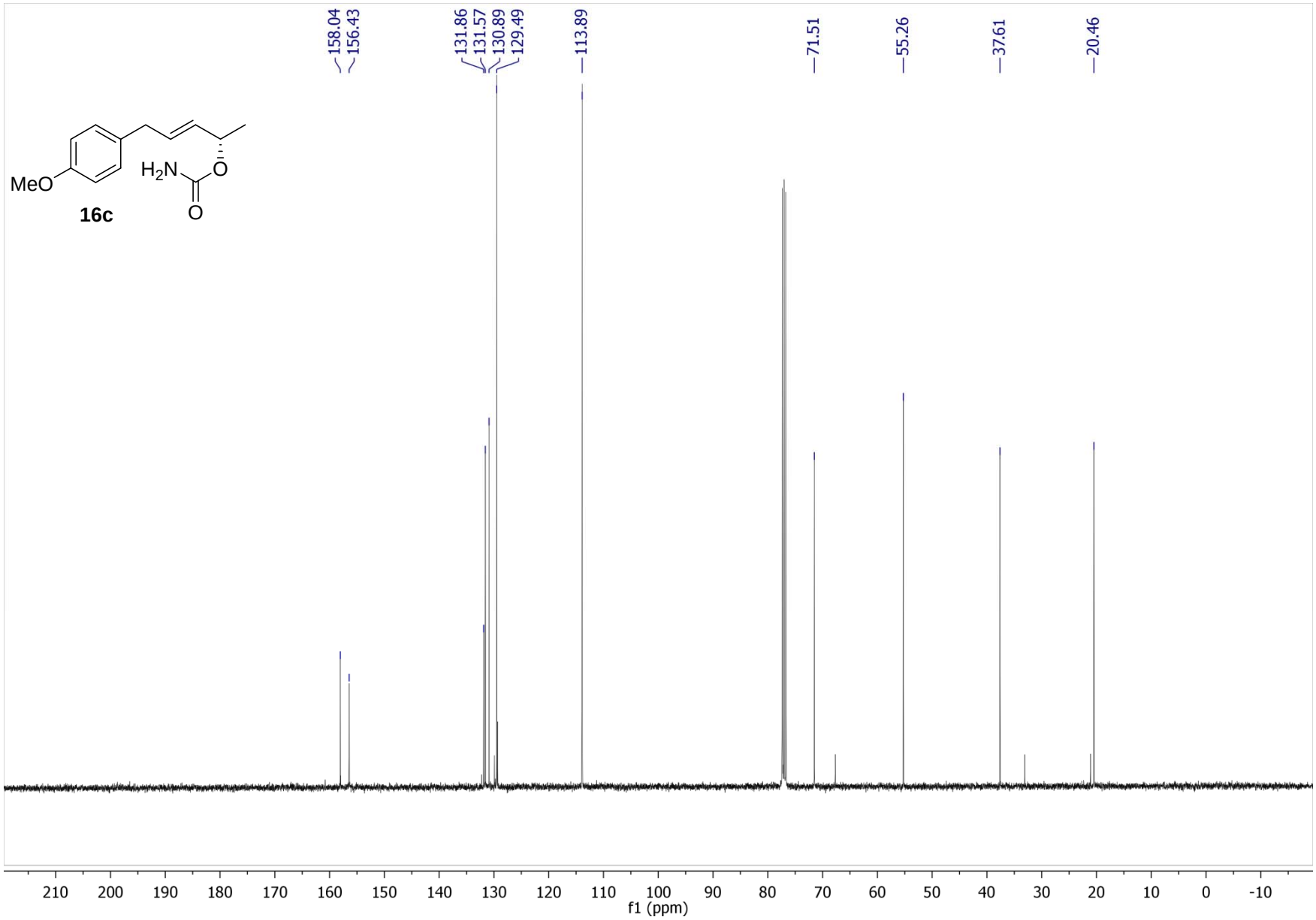
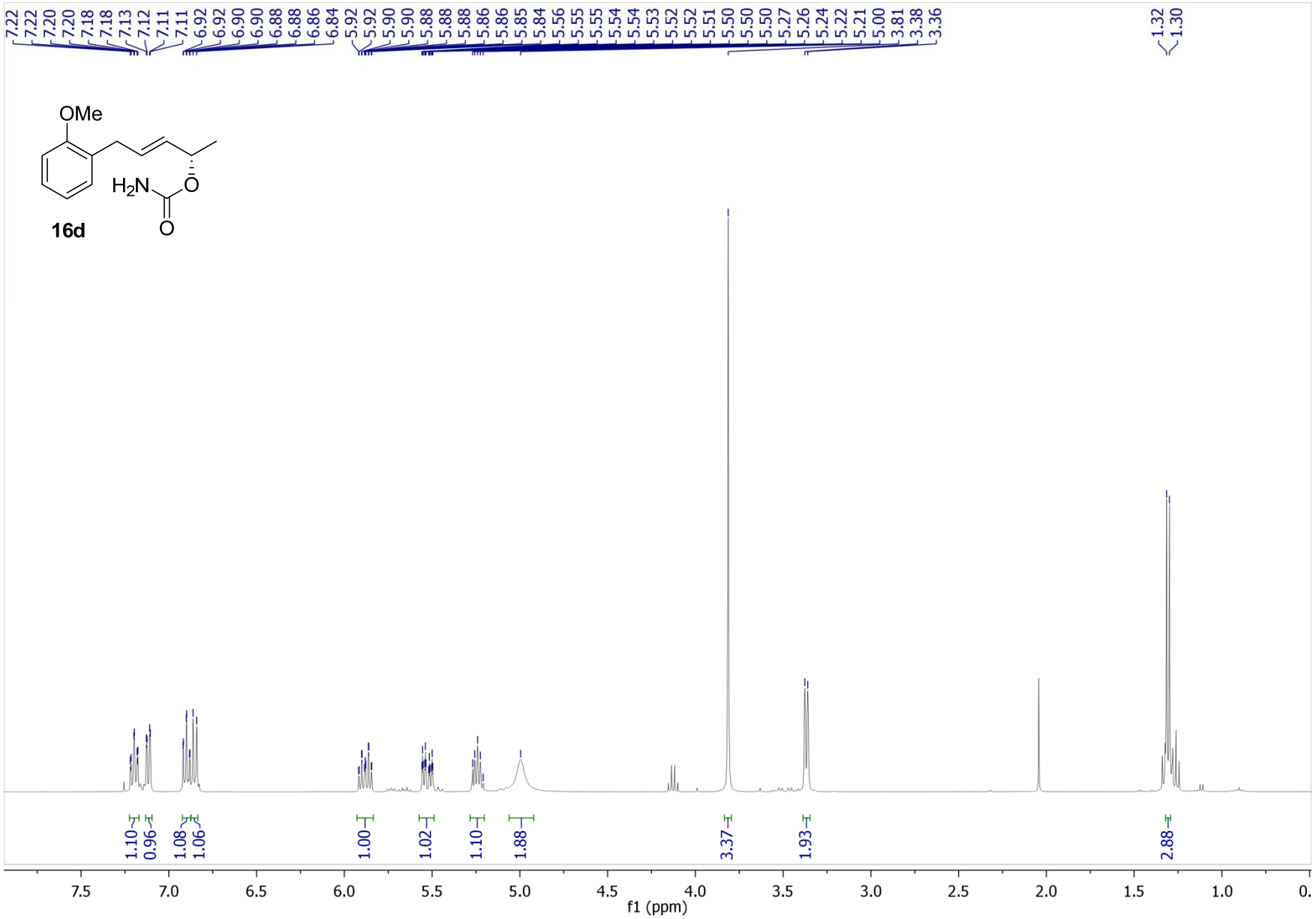
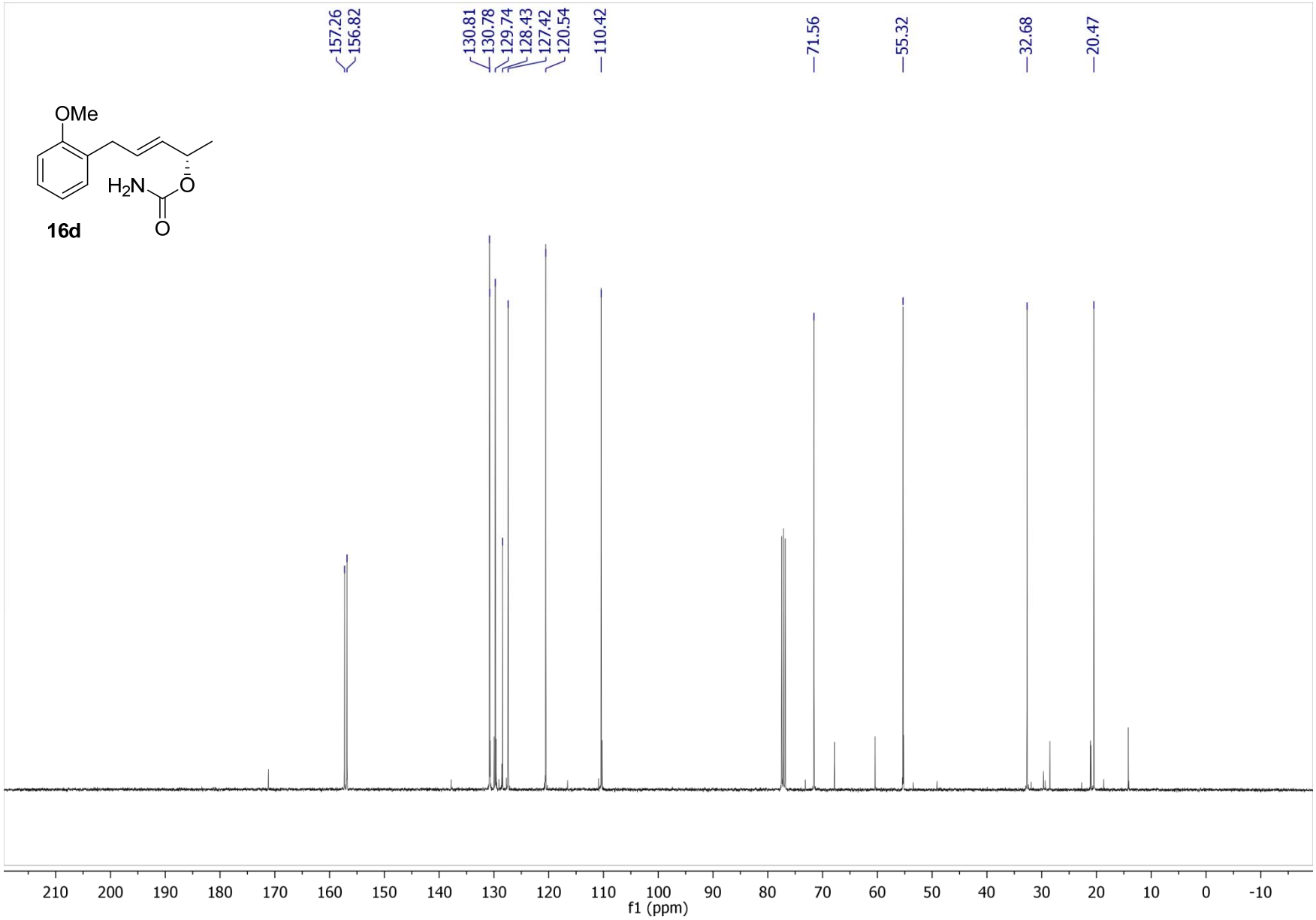
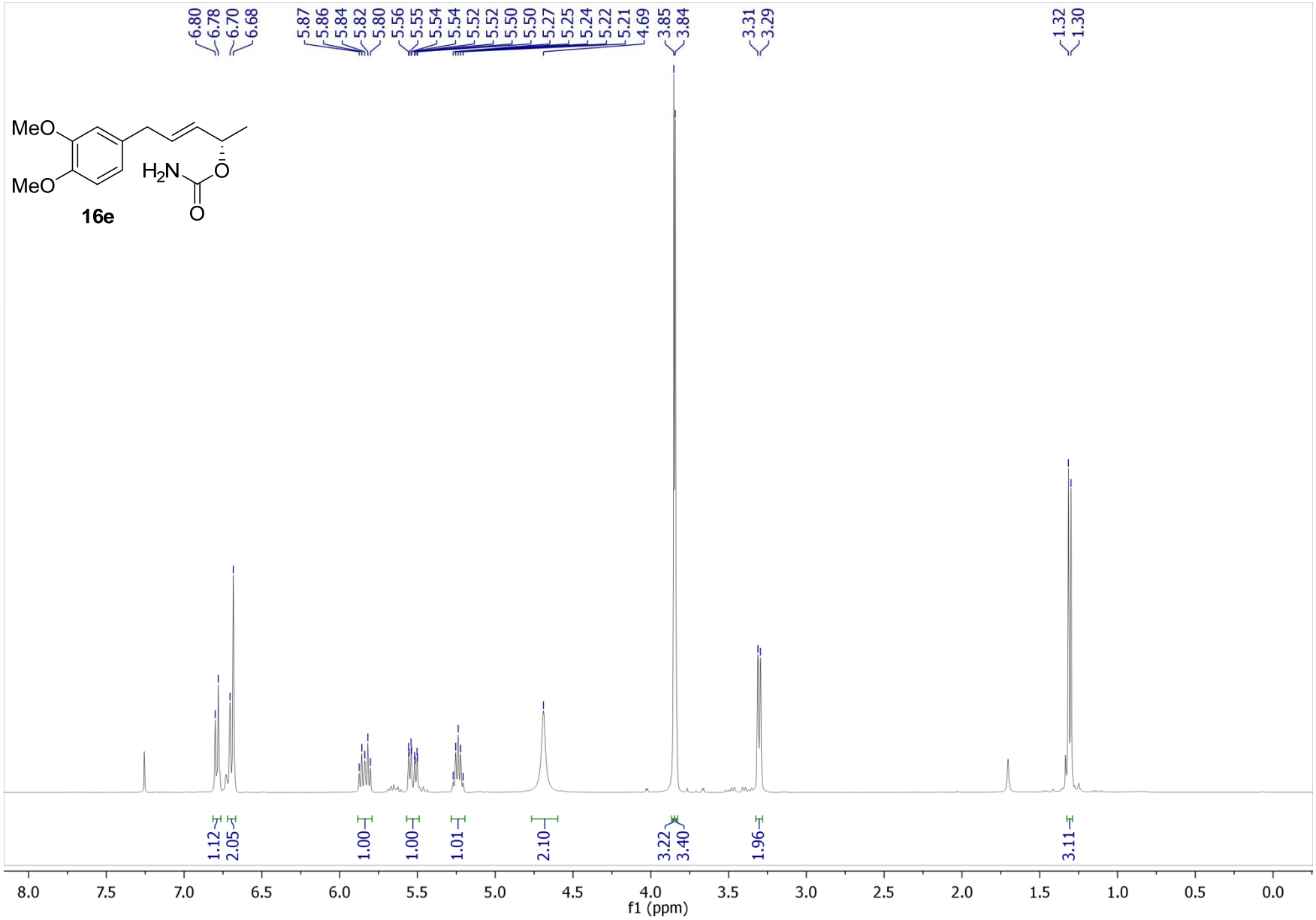
5.53
5.53
5.52
5.51
5.50
5.50
5.49
5.49
5.49
5.27
5.27
5.25
5.25
5.24
5.24
5.22
5.22
5.21
5.20
4.71
3.78
3.31
3.30
1.31
1.30
MeO
H2N
O
O
16c
2.10
2.19
1.00
1.03
1.01
2.06
2.95
1.99
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


158.04
156.43
131.86
131.57
130.89
129.49
113.89
71.51
55.26
37.61
20.46
MeO
H2N
O
O
16c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.22
7.22
7.20
7.20
7.18
7.18
7.13
7.12
7.11
7.11
6.92
6.92
6.90
6.90
6.88
6.88
6.86
6.84
5.92
5.92
5.90
5.90
5.88
5.88
5.88
5.86
5.86
5.85
5.84
5.56
5.55
5.55
5.54
5.54
5.53
5.52
5.52
5.51
5.50
5.50
5.50
5.27
5.26
5.24
5.22
5.21
5.00
3.81
3.38
3.36
1.32
1.30
OMe
H2N
O
O
16d
1.10
0.96
1.08
1.06
1.00
1.02
1.10
1.88
3.37
1.93
2.88
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)


157.26
156.82
130.81
130.78
129.74
128.43
127.42
120.54
110.42
71.56
55.32
32.68
20.47
OMe
H2N
O
O
16d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


6.80
6.78
6.70
6.68
5.87
5.86
5.84
5.82
5.80
5.56
5.55
5.54
5.54
5.52
5.52
5.50
5.50
5.27
5.25
5.24
5.22
5.21
4.69
3.85
3.84
3.31
3.29
1.32
1.30
MeO
MeO
H2N
O
O
16e
1.12
2.05
1.00
1.00
1.01
2.10
3.22
3.40
1.96
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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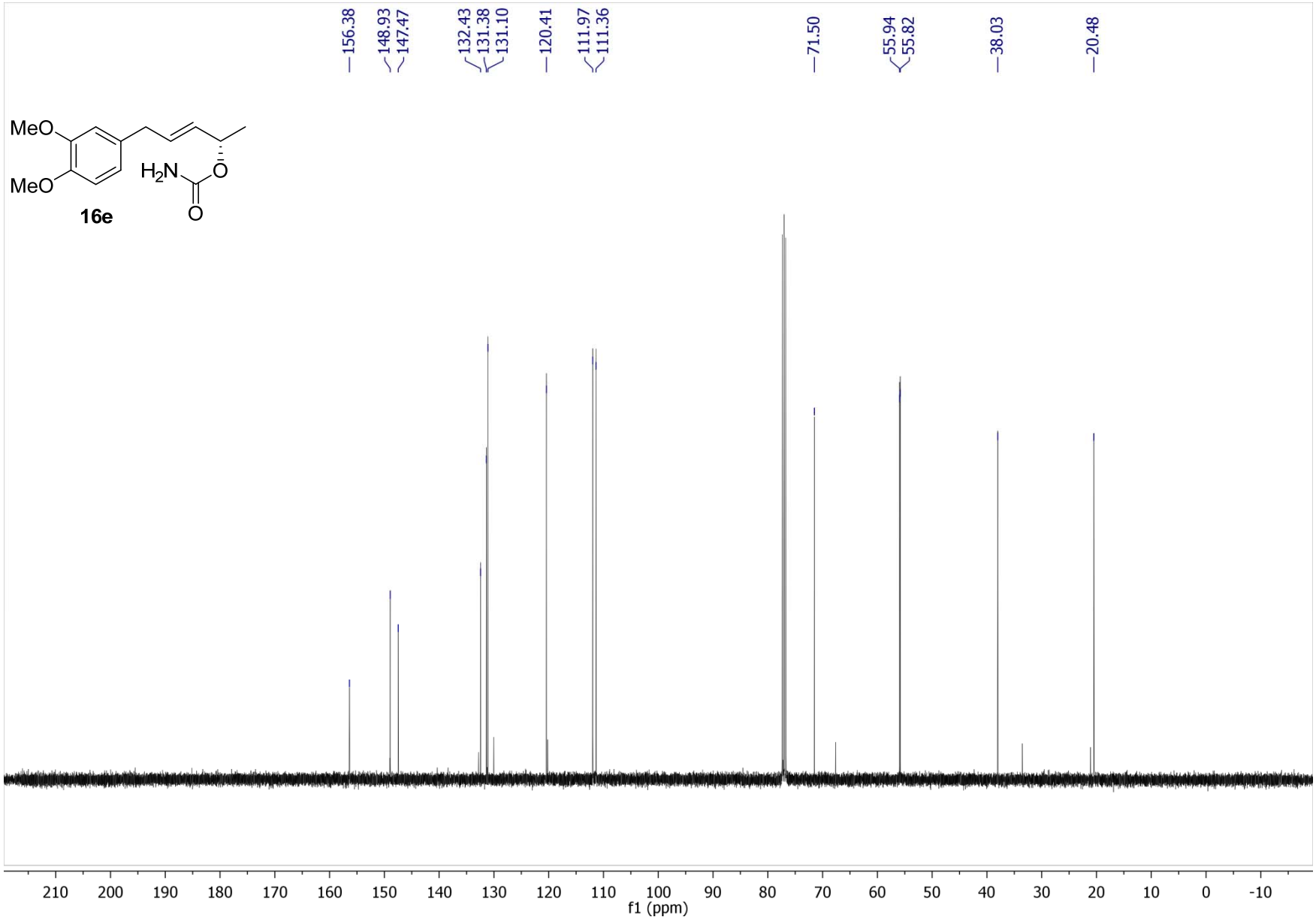
0.0
f1 (ppm)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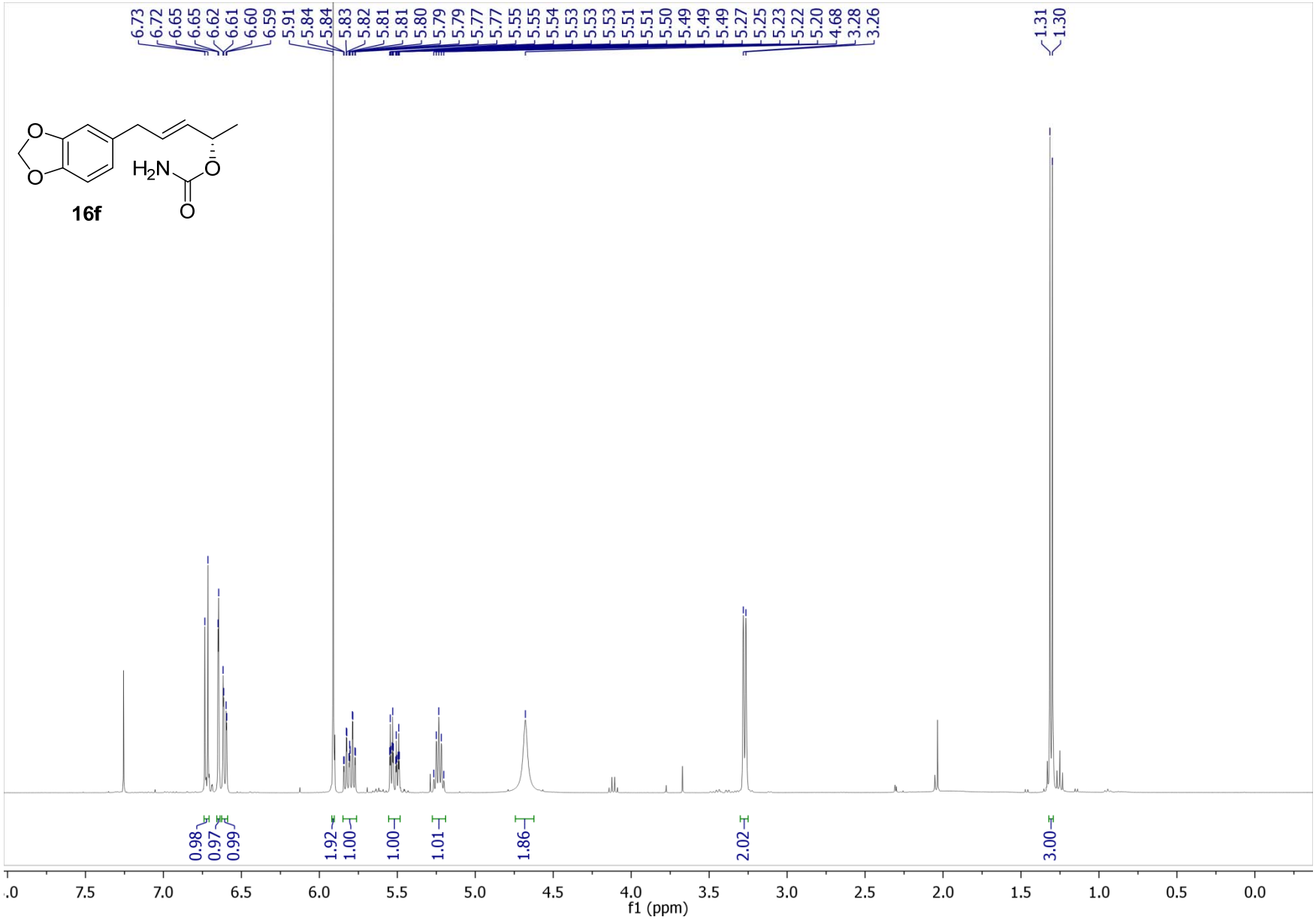
147.47
132.43
131.38
131.10
120.41
111.97
111.36
71.50
55.94
55.82
38.03
20.48
MeO
MeO
H2N
O
O
16e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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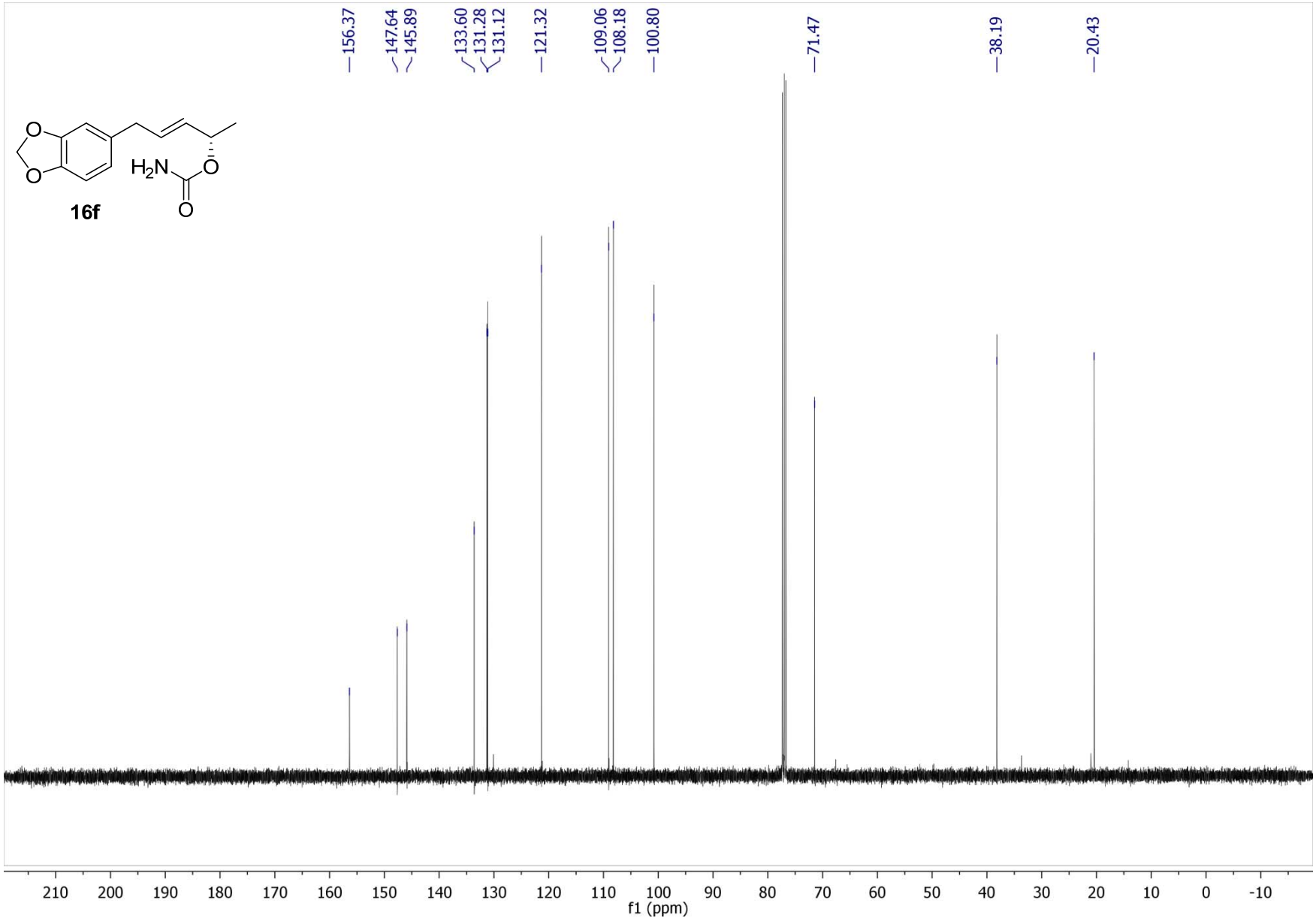
6.59
5.91
5.84
5.84
5.83
5.82
5.81
5.81
5.80
5.79
5.79
5.77
5.77
5.55
5.55
5.54
5.53
5.53
5.53
5.51
5.51
5.50
5.49
5.49
5.49
5.27
5.25
5.23
5.22
5.20
4.68
3.28
3.26
1.31
1.30
O
O
H2N
O
O
16f
0.98
0.97
0.99
1.92
1.00
1.00
1.01
1.86
2.02
3.00
f1 (ppm)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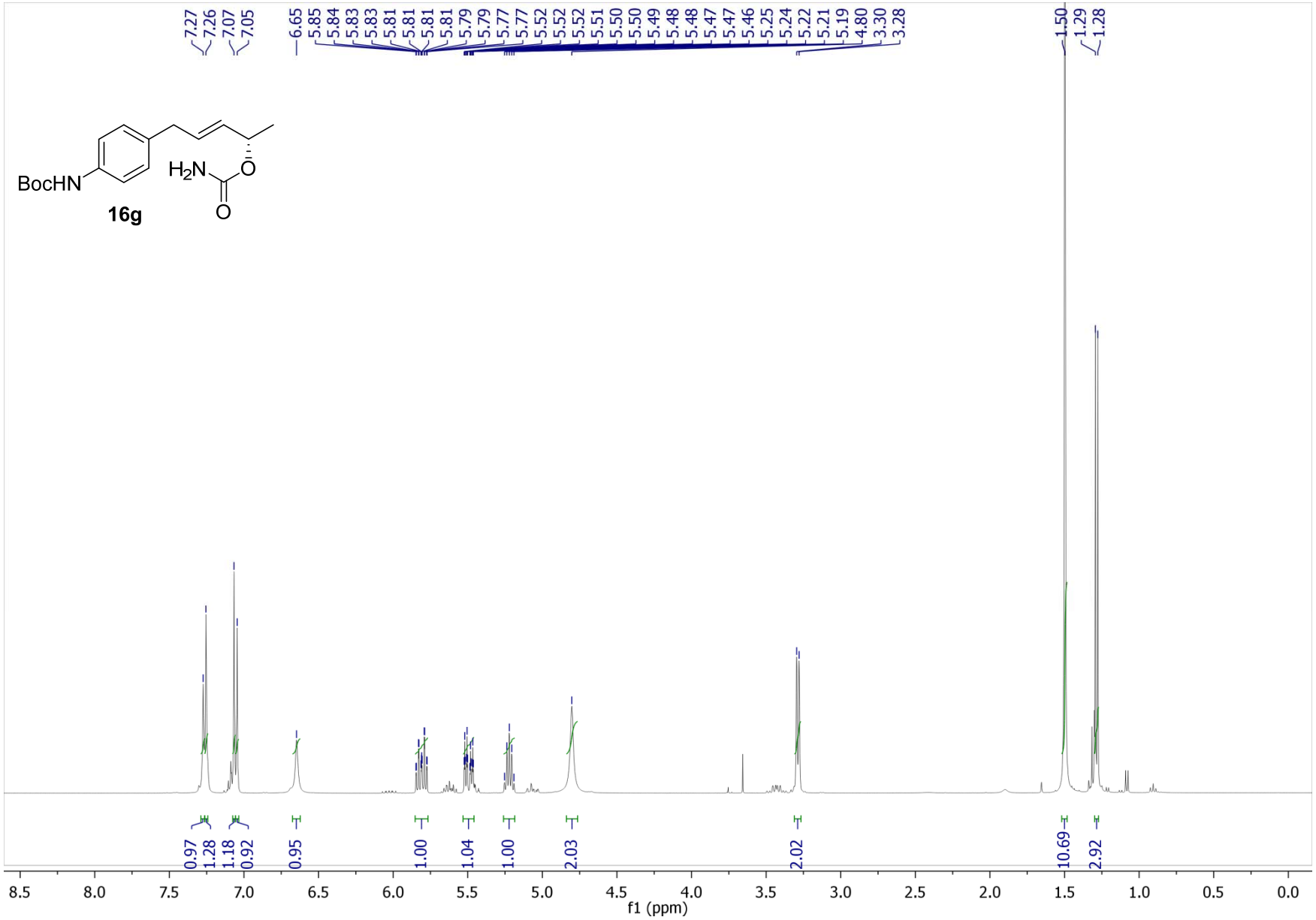
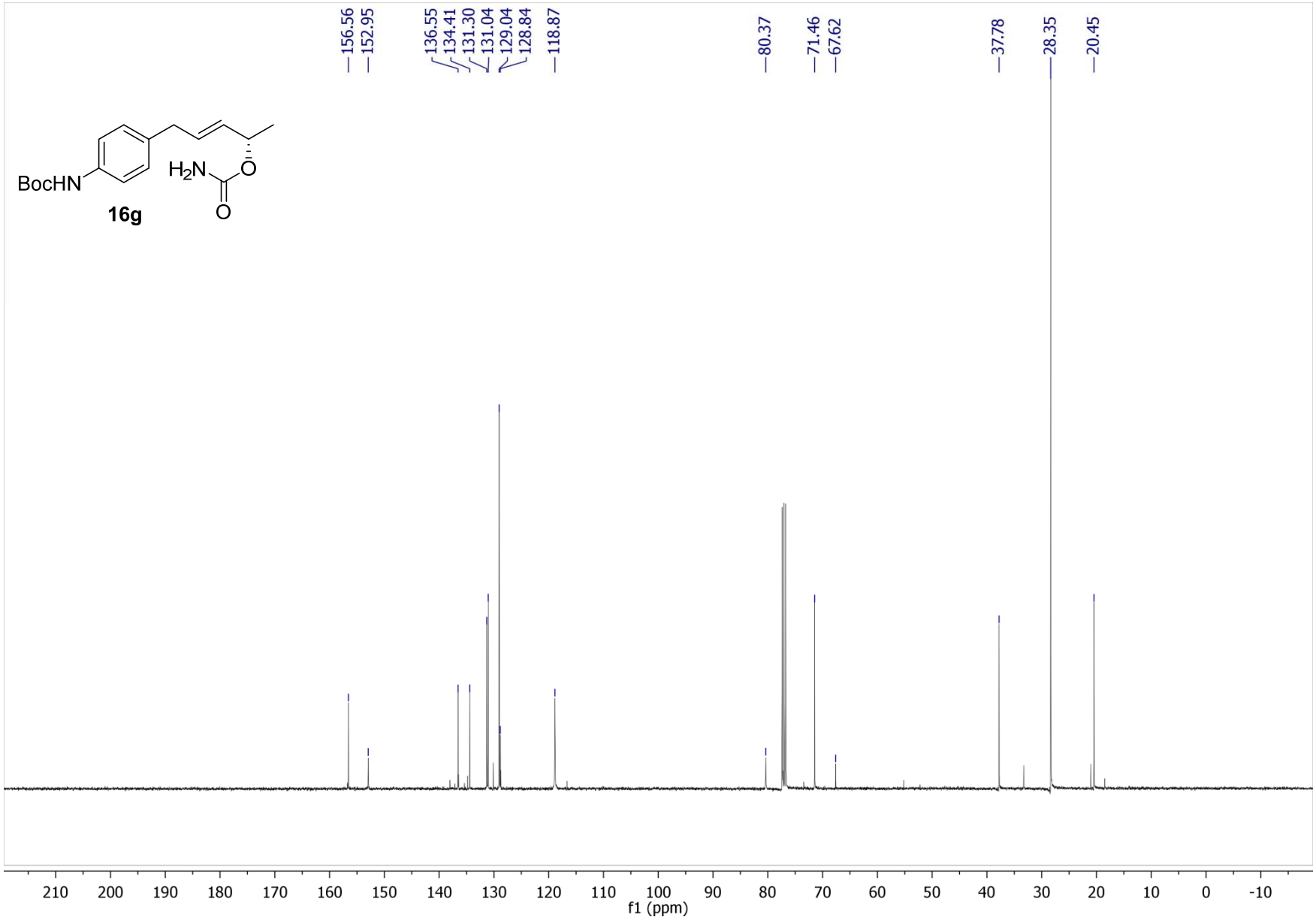
147.64
145.89
133.60
131.28
131.12
121.32
109.06
108.18
100.80
71.47
38.19
20.43
16f
f1 (ppm)


BocHN
H2N
O
O
16g
7.27
7.26
7.07
7.05
6.65
5.85
5.84
5.83
5.83
5.81
5.81
5.81
5.81
5.79
5.79
5.77
5.77
5.52
5.52
5.52
5.51
5.50
5.50
5.49
5.48
5.48
5.47
5.47
5.46
5.25
5.24
5.22
5.21
5.19
4.80
3.30
3.28
1.50
1.29
1.28
0.97
1.28
1.18
0.92
0.95
1.00
1.04
1.00
2.03
2.02
10.69
2.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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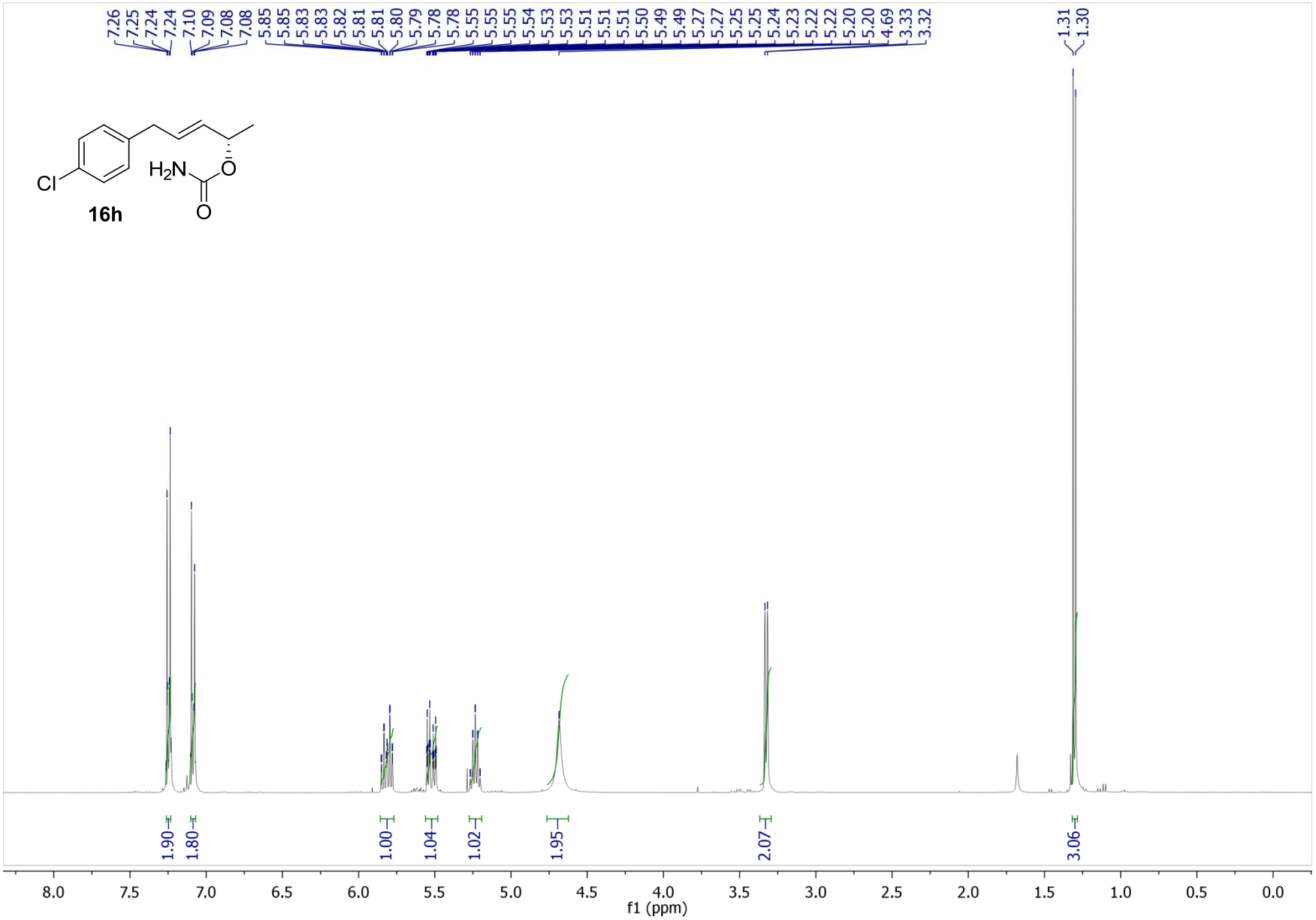
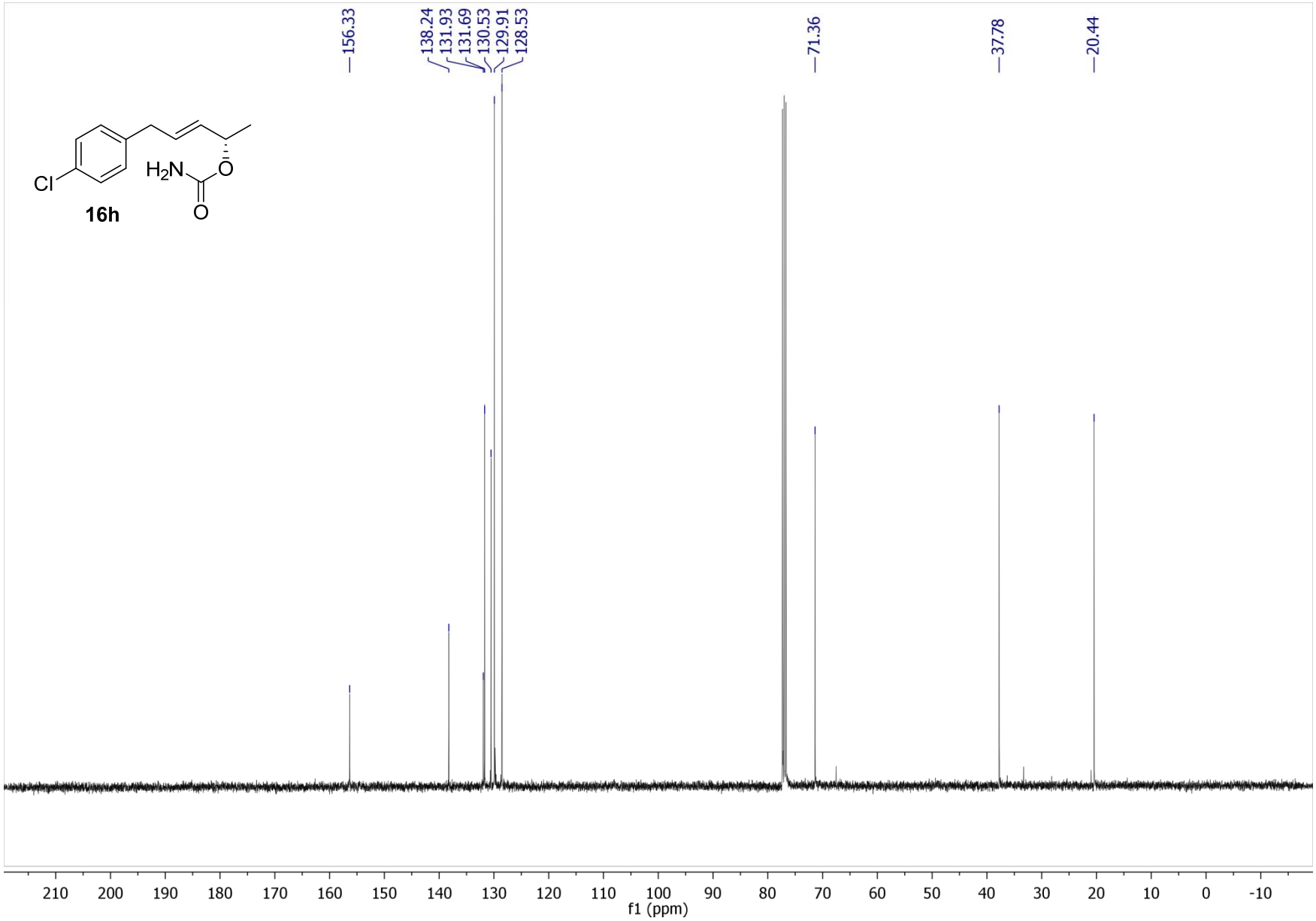
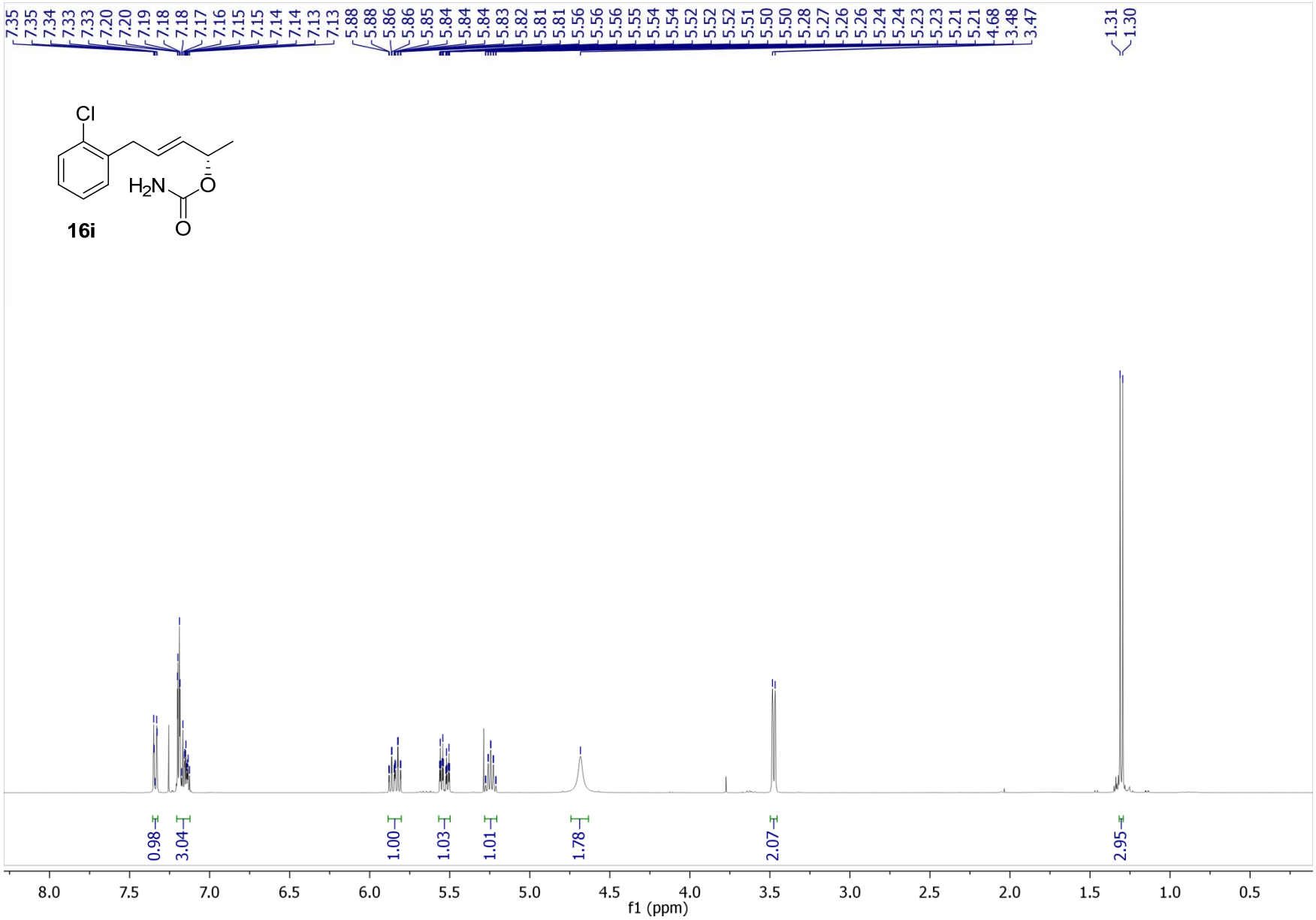
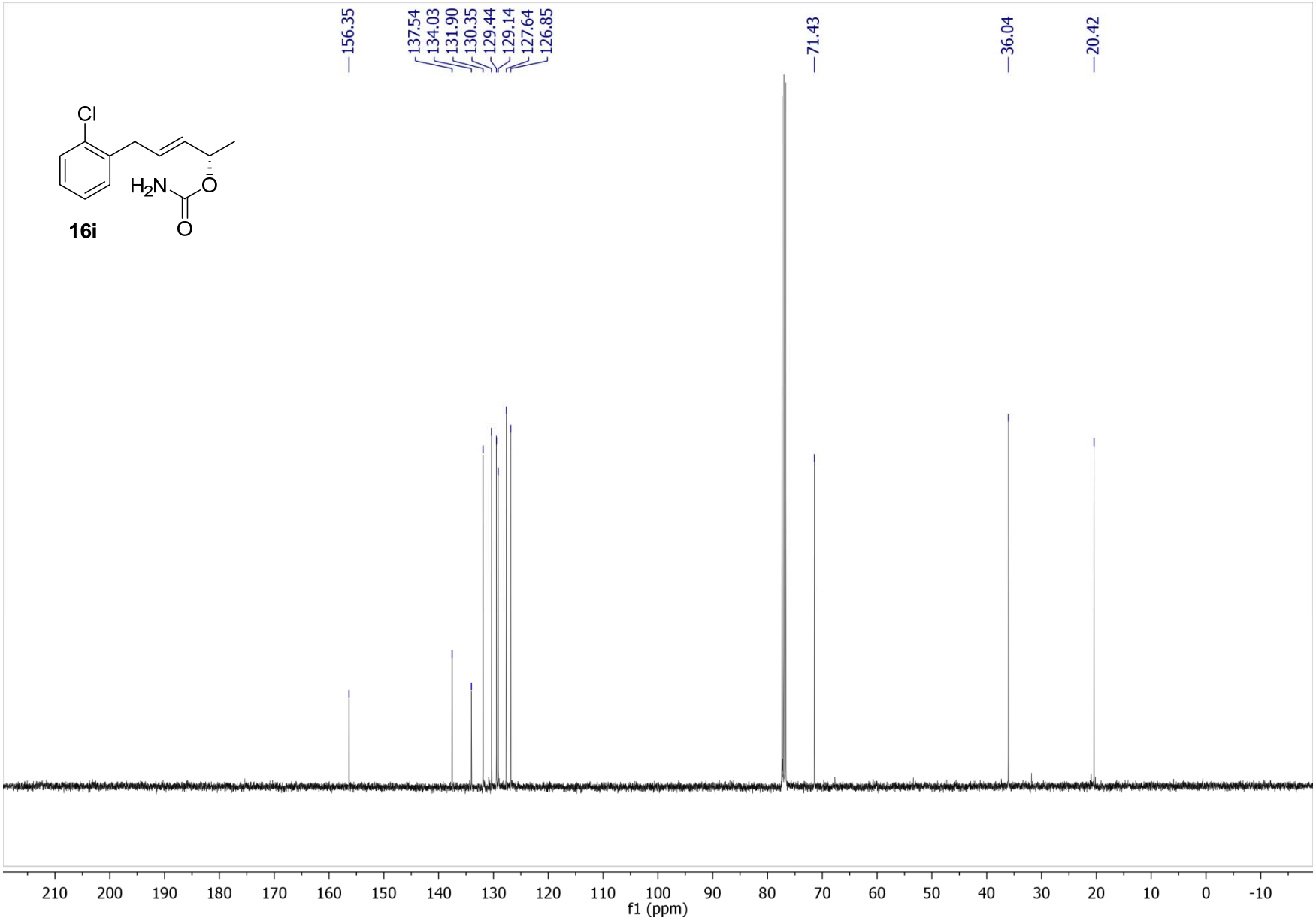
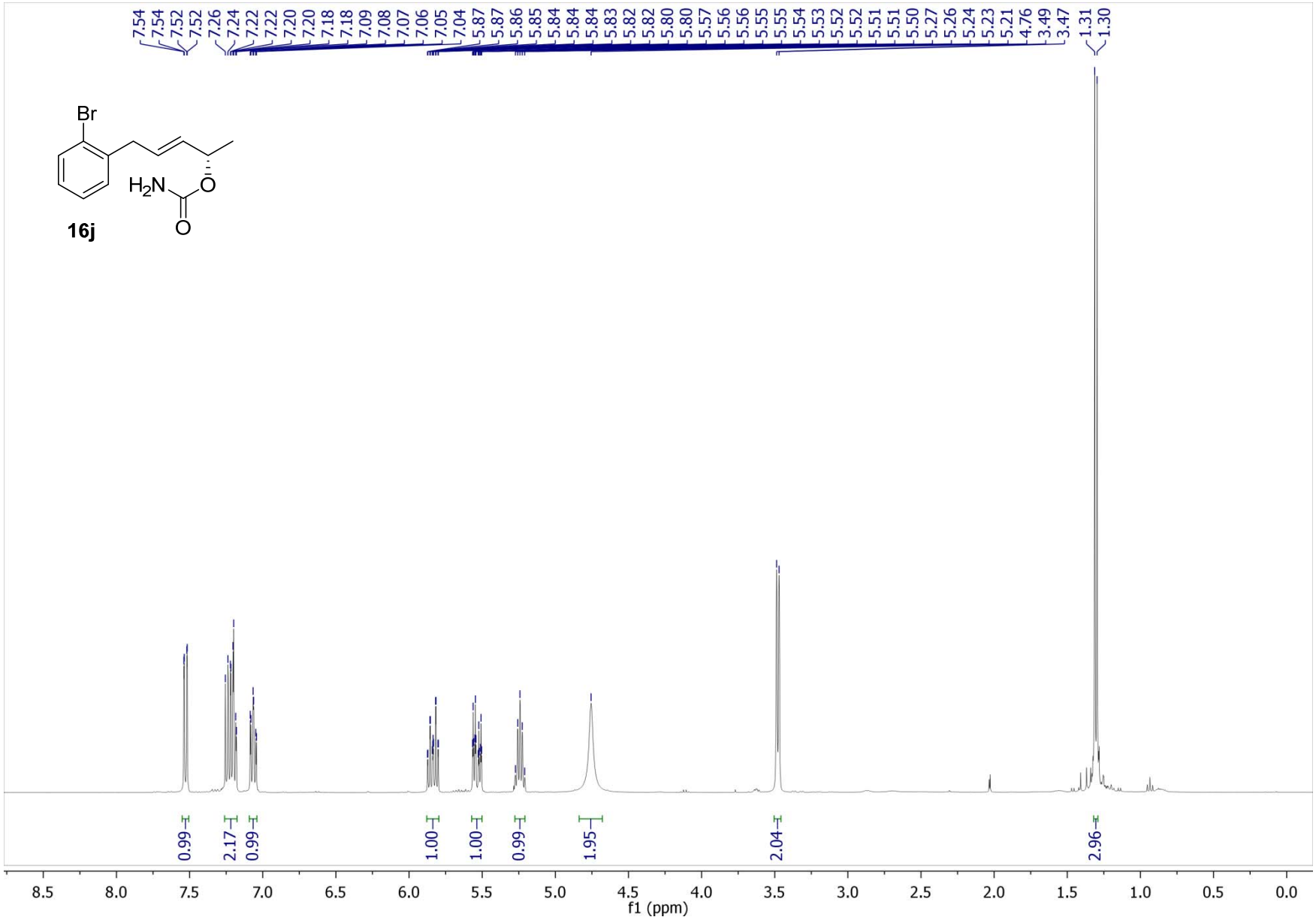
152.95
136.55
134.41
131.30
131.04
129.04
128.84
118.87
80.37
71.46
67.62
37.78
28.35
20.45
BocHN
H2N
O
O
16g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

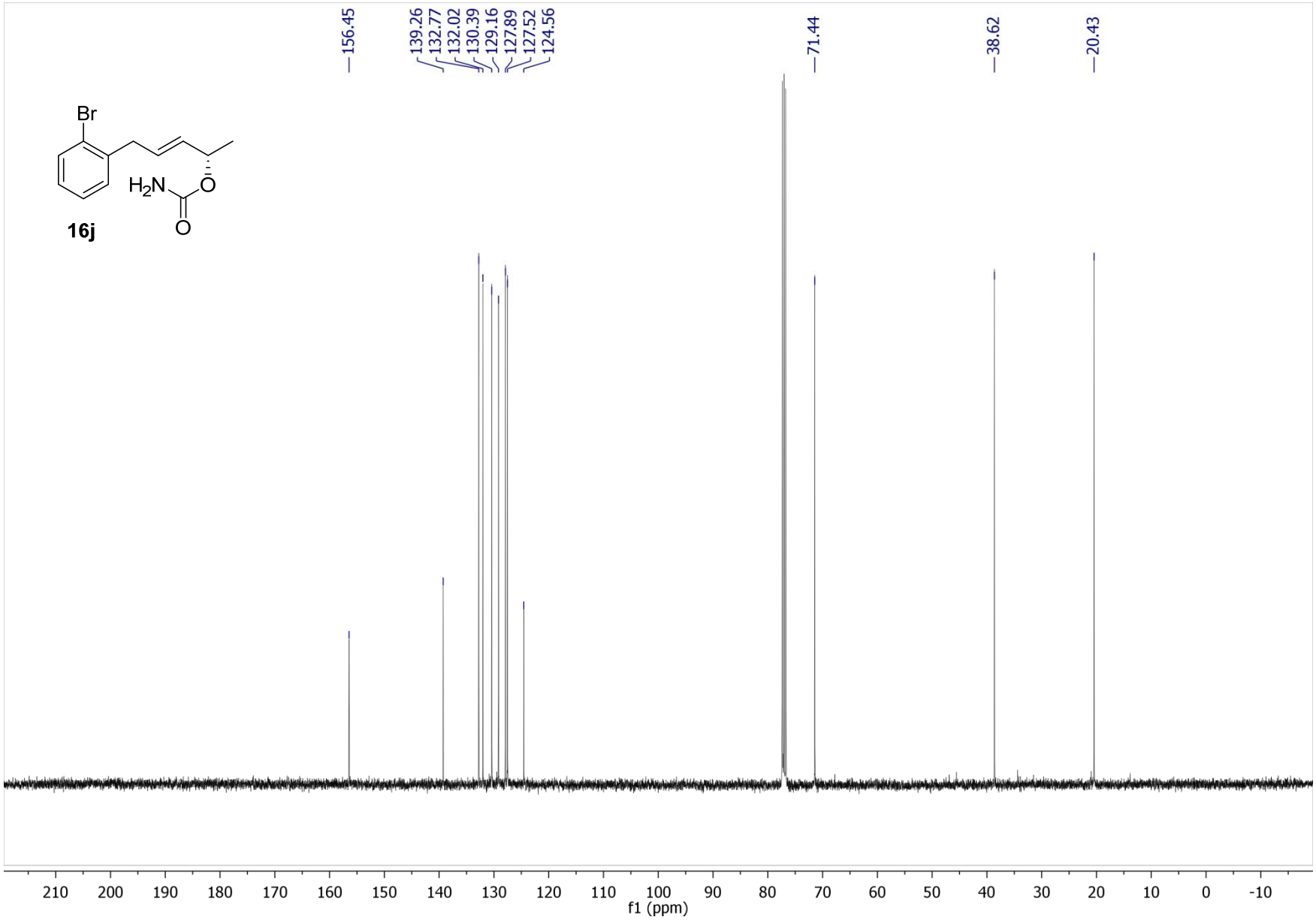

7.26
7.25
7.24
7.24
7.10
7.09
7.08
7.08
5.85
5.85
5.83
5.83
5.82
5.81
5.81
5.80
5.79
5.78
5.78
5.55
5.55
5.55
5.54
5.53
5.53
5.51
5.51
5.51
5.50
5.49
5.49
5.27
5.27
5.25
5.25
5.24
5.23
5.22
5.22
5.20
5.20
4.69
3.33
3.32
1.31
1.30
Cl
H2N
O
O
16h
1.90
1.80
1.00
1.04
1.02
1.95
2.07
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

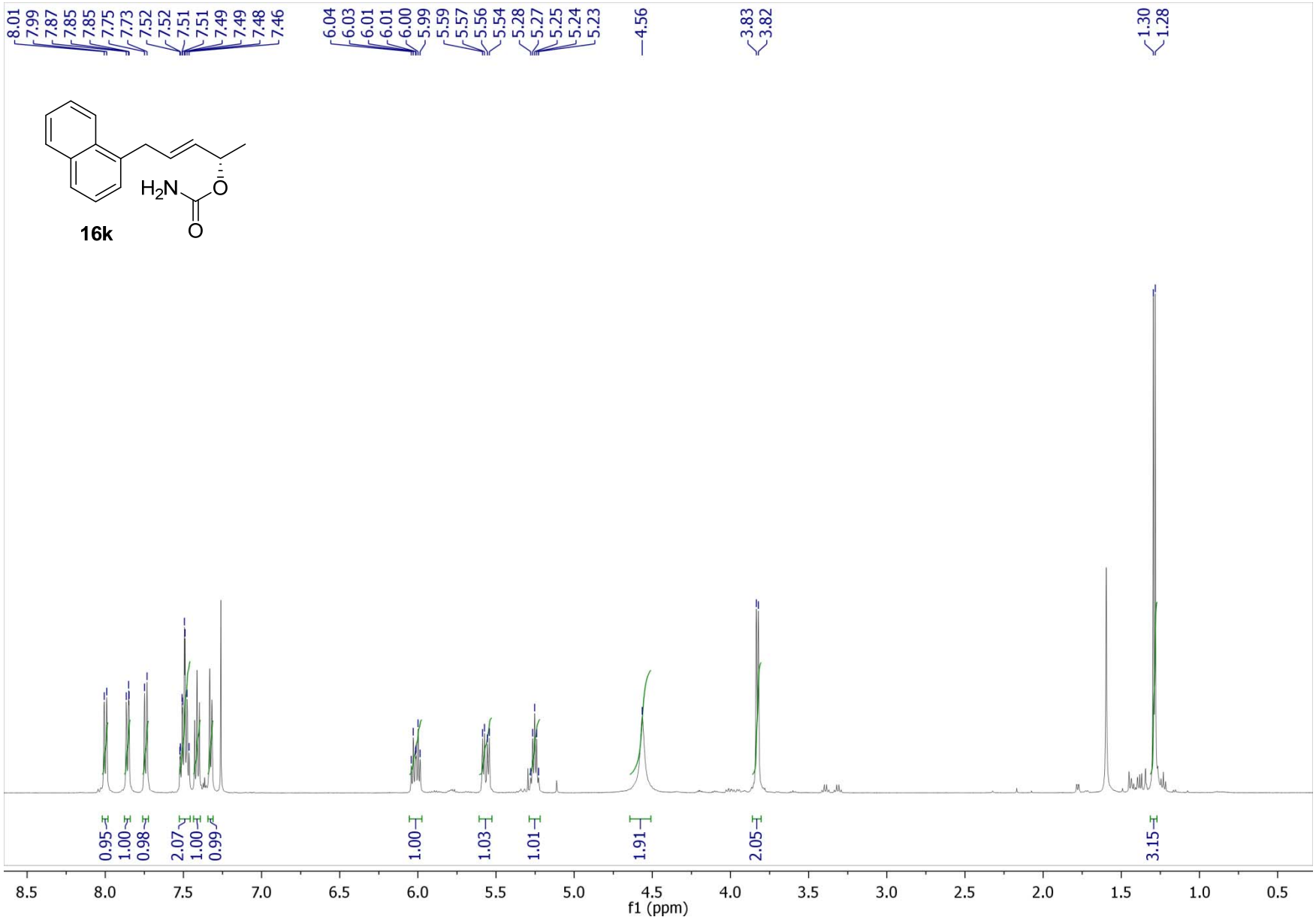

156.33
138.24
131.93
131.69
130.53
129.91
128.53
71.36
37.78
20.44
Cl
H2N
O
O
16h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

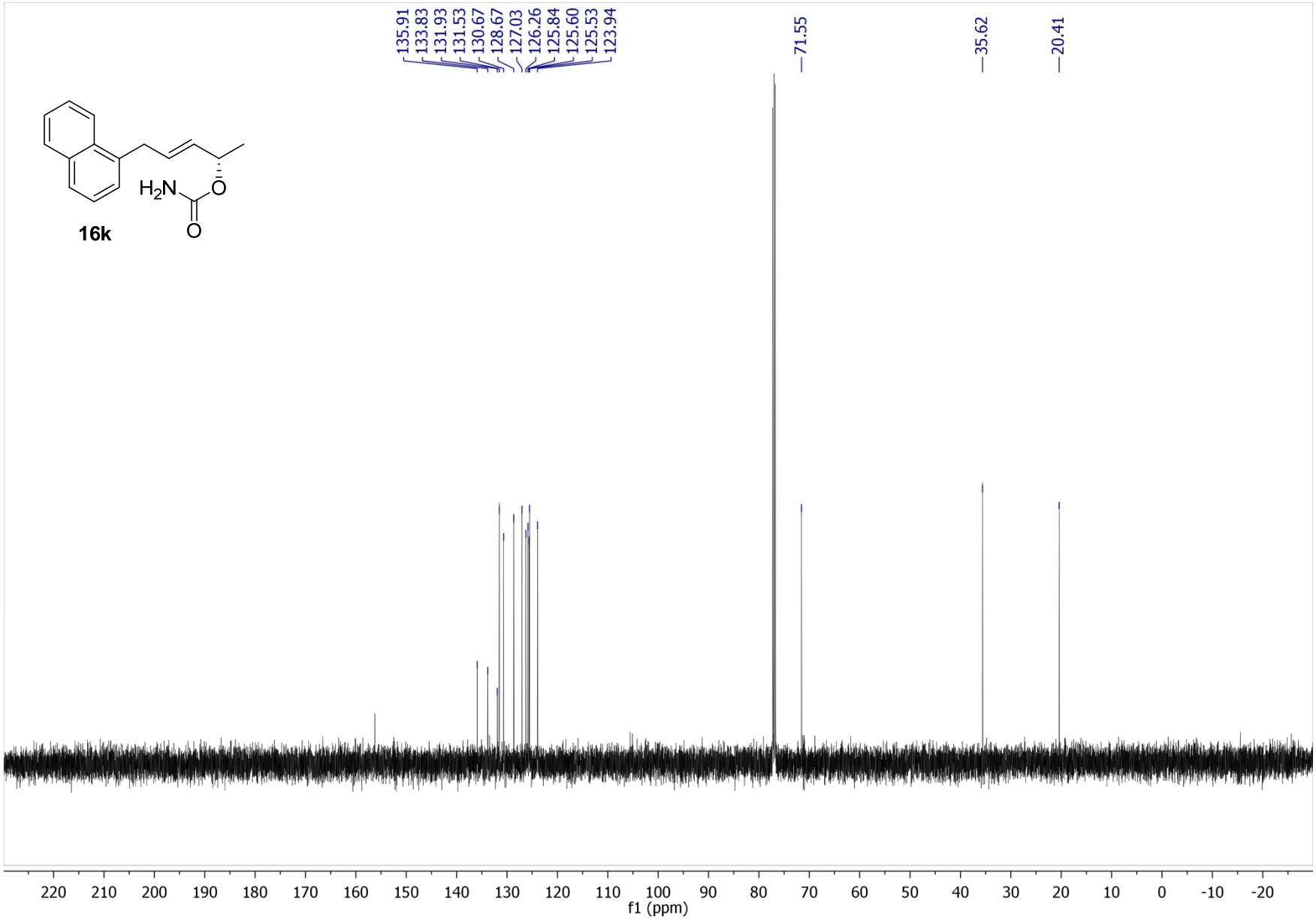

7.35 7.35 7.34 7.33 7.33 7.20 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.13
5.88 5.88 5.86 5.86 5.85 5.84 5.84 5.84 5.83 5.82 5.81 5.81 5.56 5.56 5.56 5.55 5.54 5.54 5.52 5.52 5.52 5.51 5.50 5.50 5.28 5.27 5.26 5.26 5.24 5.24 5.23 5.23 5.21 5.21 4.68 3.48 3.47
1.31 1.30
Cl
H2N
O
O
16i
0.98
3.04
1.00
1.03
1.01
1.78
2.07
2.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

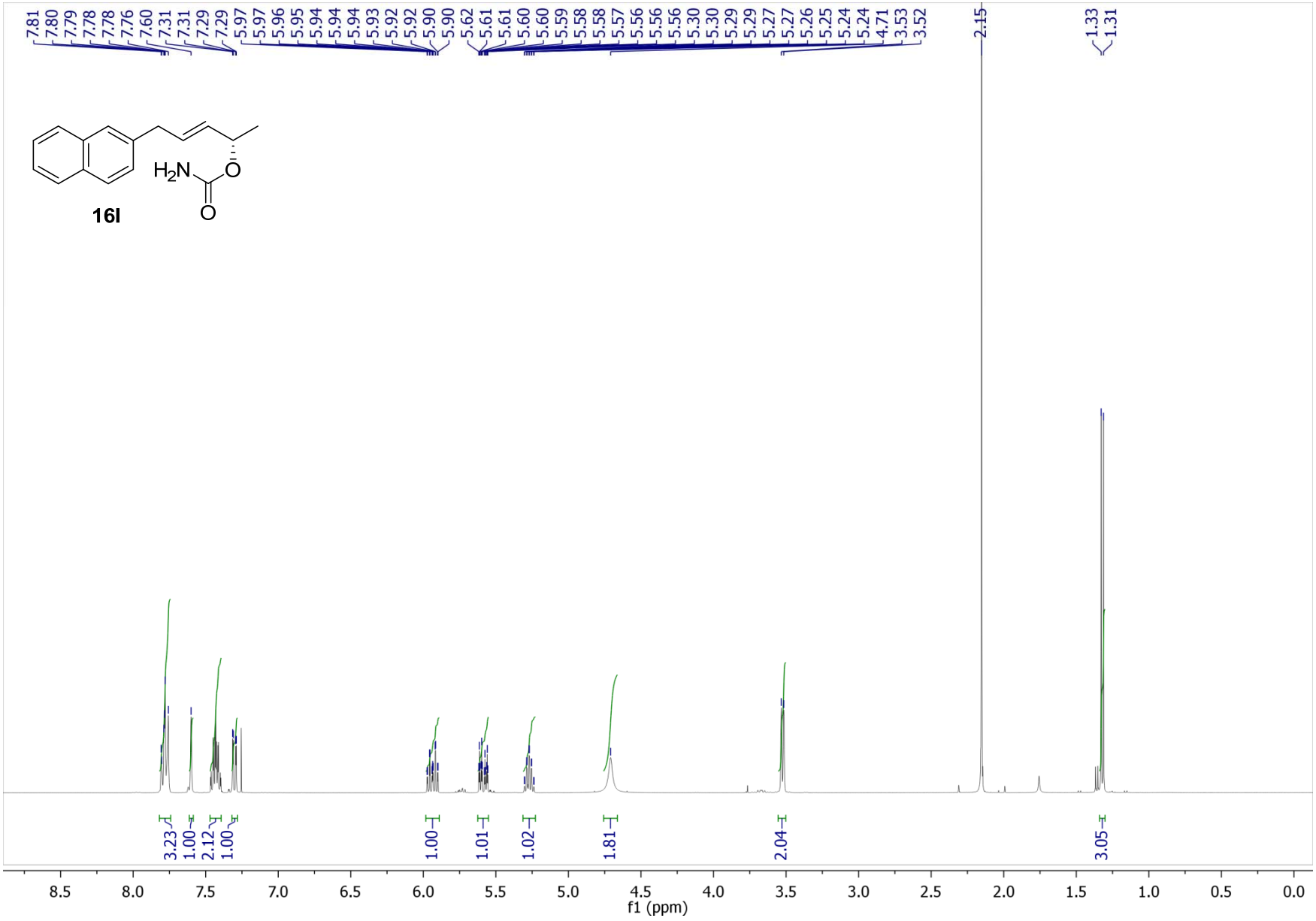

156.35
137.54
134.03
131.90
130.35
129.44
129.14
127.64
126.85
71.43
36.04
20.42
Cl
H2N
O
O
16i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.54
7.54
7.52
7.52
7.26
7.24
7.22
7.22
7.20
7.20
7.18
7.18
7.09
7.08
7.07
7.06
7.05
7.04
5.87
5.87
5.86
5.85
5.84
5.84
5.84
5.83
5.82
5.82
5.80
5.80
5.57
5.56
5.56
5.55
5.55
5.54
5.53
5.52
5.52
5.51
5.51
5.50
5.27
5.26
5.24
5.23
5.21
4.76
3.49
3.47
1.31
1.30
Br
H2N
O
O
16j
0.99
2.17
0.99
1.00
1.00
0.99
1.95
2.04
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.45
139.26
132.77
132.02
130.39
129.16
127.89
127.52
124.56
71.44
38.62
20.43
Br
H2N
O
O
16j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.01
7.99
7.87
7.85
7.85
7.75
7.73
7.52
7.52
7.51
7.51
7.49
7.49
7.48
7.46
6.04
6.03
6.01
6.01
6.00
5.99
5.59
5.57
5.56
5.54
5.28
5.27
5.25
5.24
5.23
4.56
3.83
3.82
1.30
1.28
H2N
O
O
16k
0.95
1.00
0.98
2.07
1.00
0.99
1.00
1.03
1.01
1.91
2.05
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


135.91
133.83
131.93
131.53
130.67
128.67
127.03
126.26
125.84
125.60
125.53
123.94
71.55
35.62
20.41
H2N
O
O
16k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.81
7.80
7.79
7.78
7.78
7.76
7.60
7.31
7.31
7.29
7.29
5.97
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5.96
5.95
5.94
5.94
5.94
5.93
5.92
5.92
5.90
5.90
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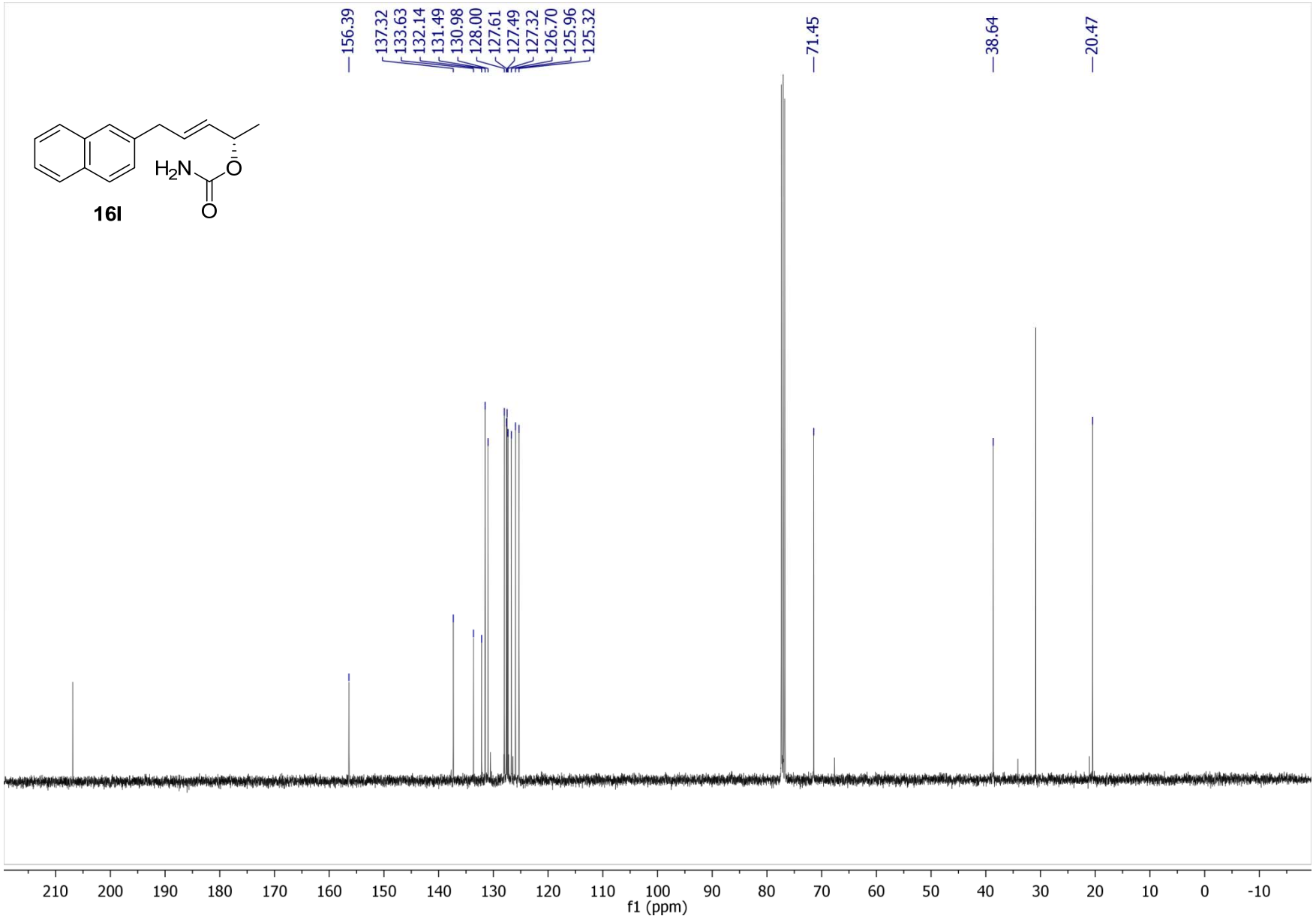
5.61
5.61
5.60
5.60
5.59
5.58
5.58
5.57
5.56
5.56
5.56
5.30
5.30
5.29
5.29
5.27
5.27
5.26
5.25
5.24
5.24
4.71
3.53
3.52
2.15
1.33
1.31
H2N
O
O
16l
3.23
1.00
2.12
1.00
1.00
1.01
1.02
1.81
2.04
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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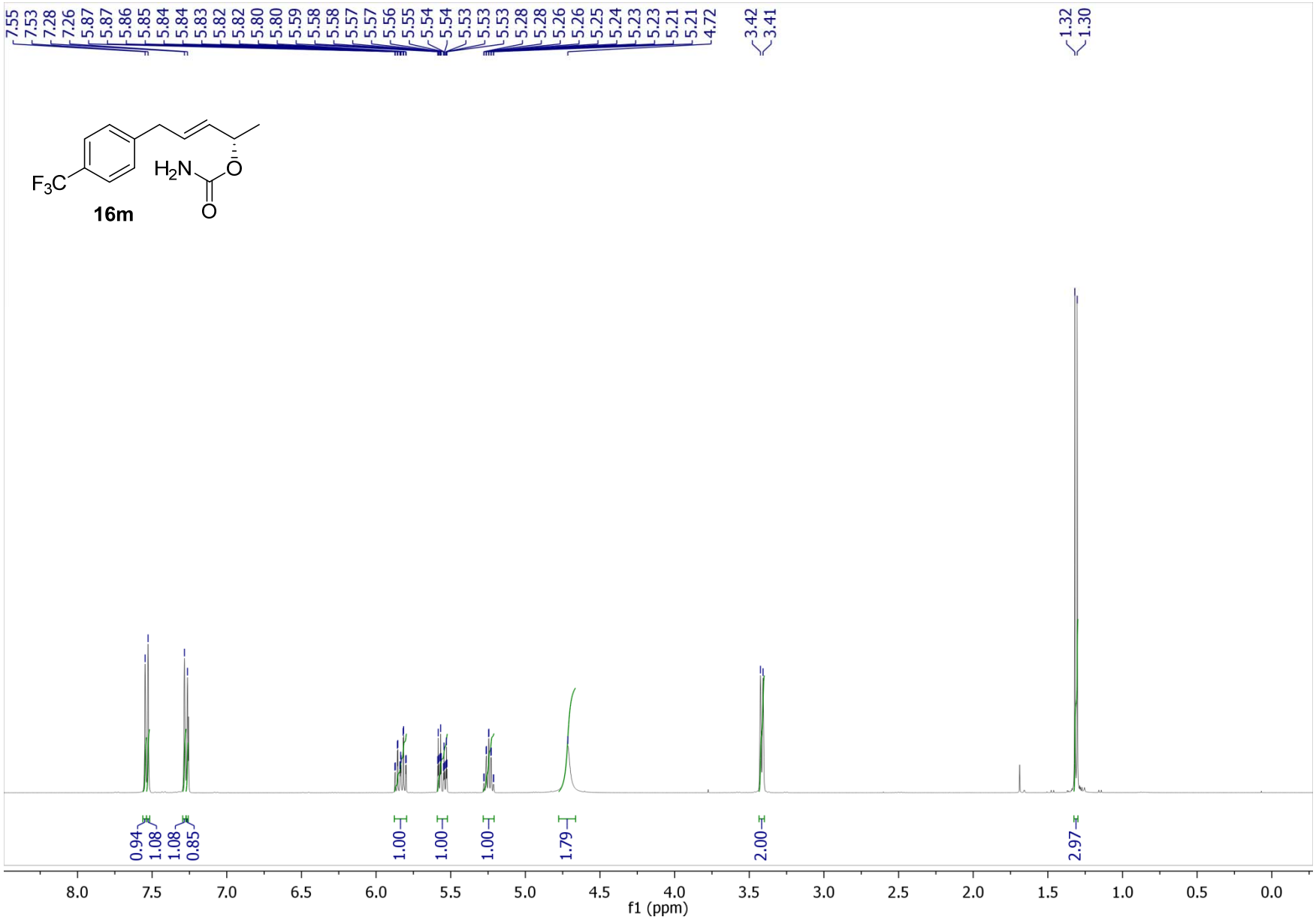
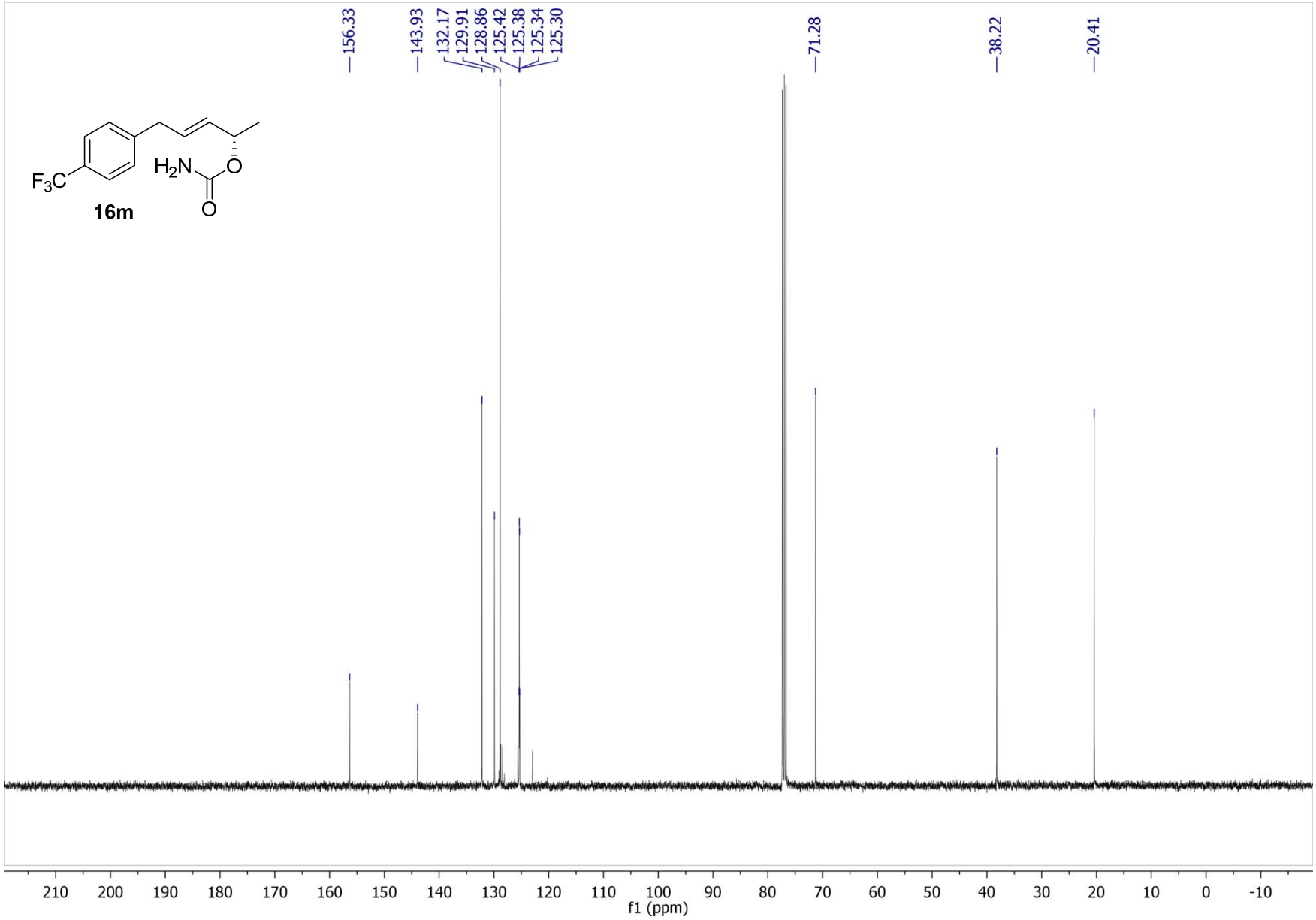
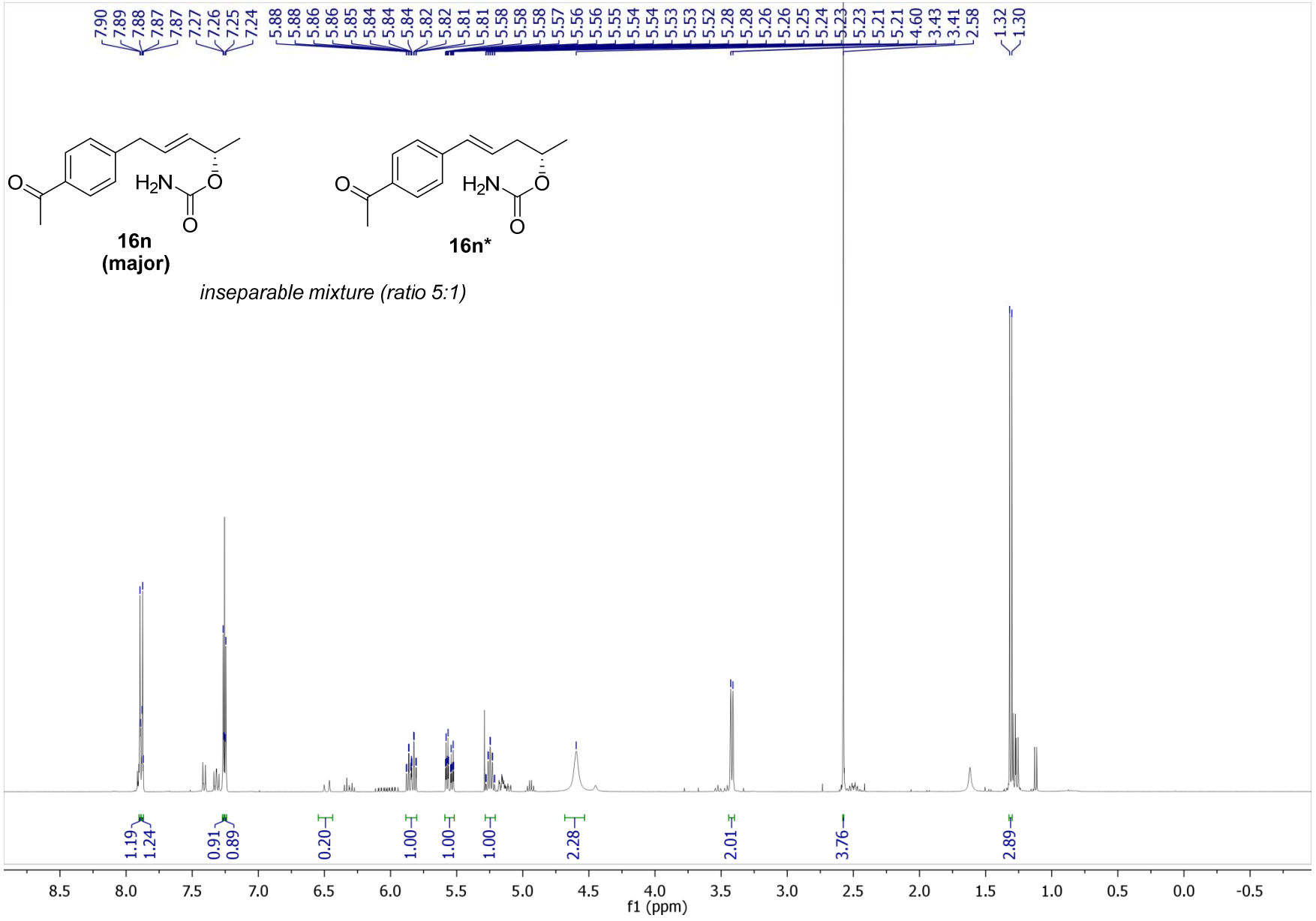
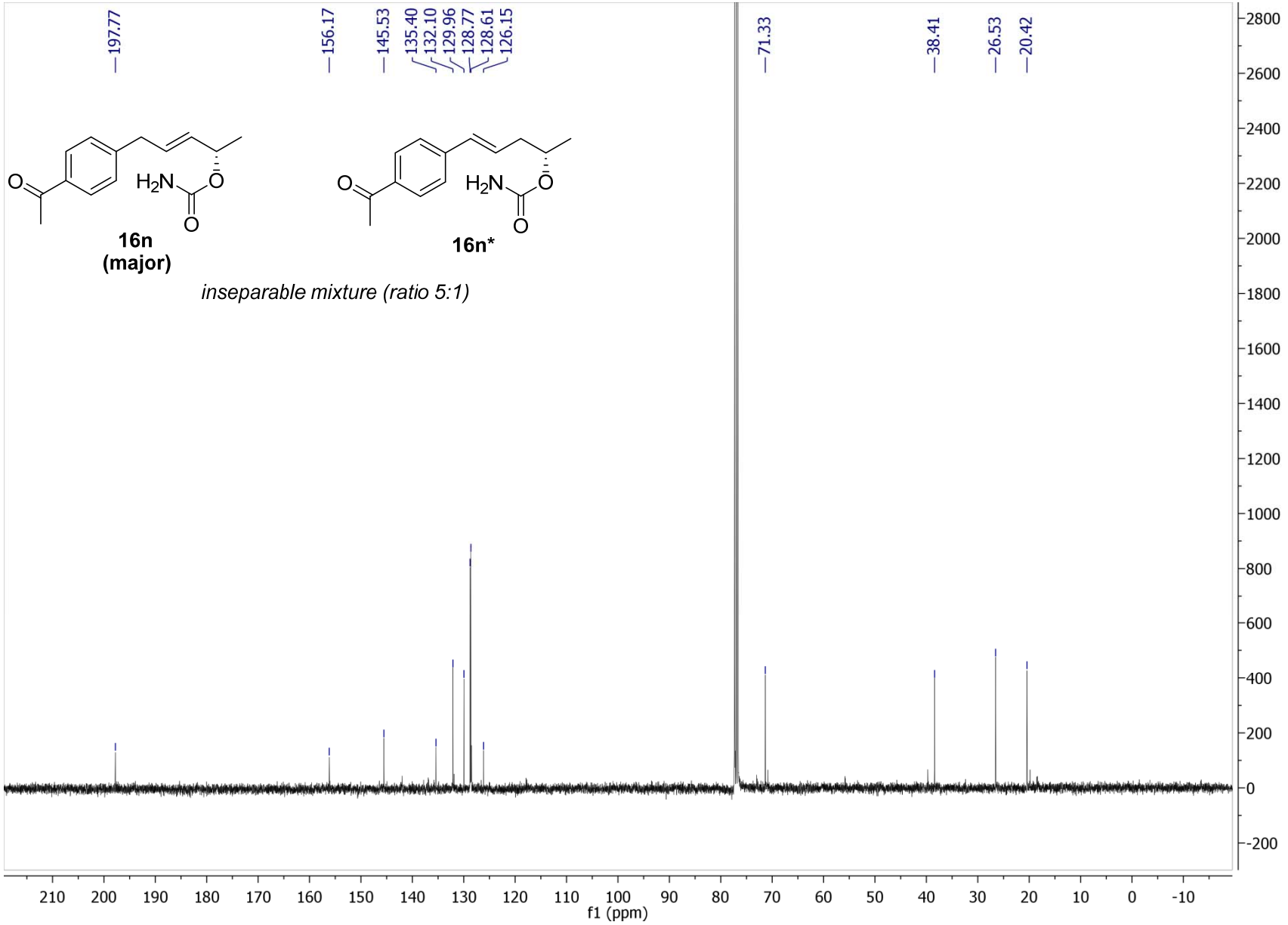
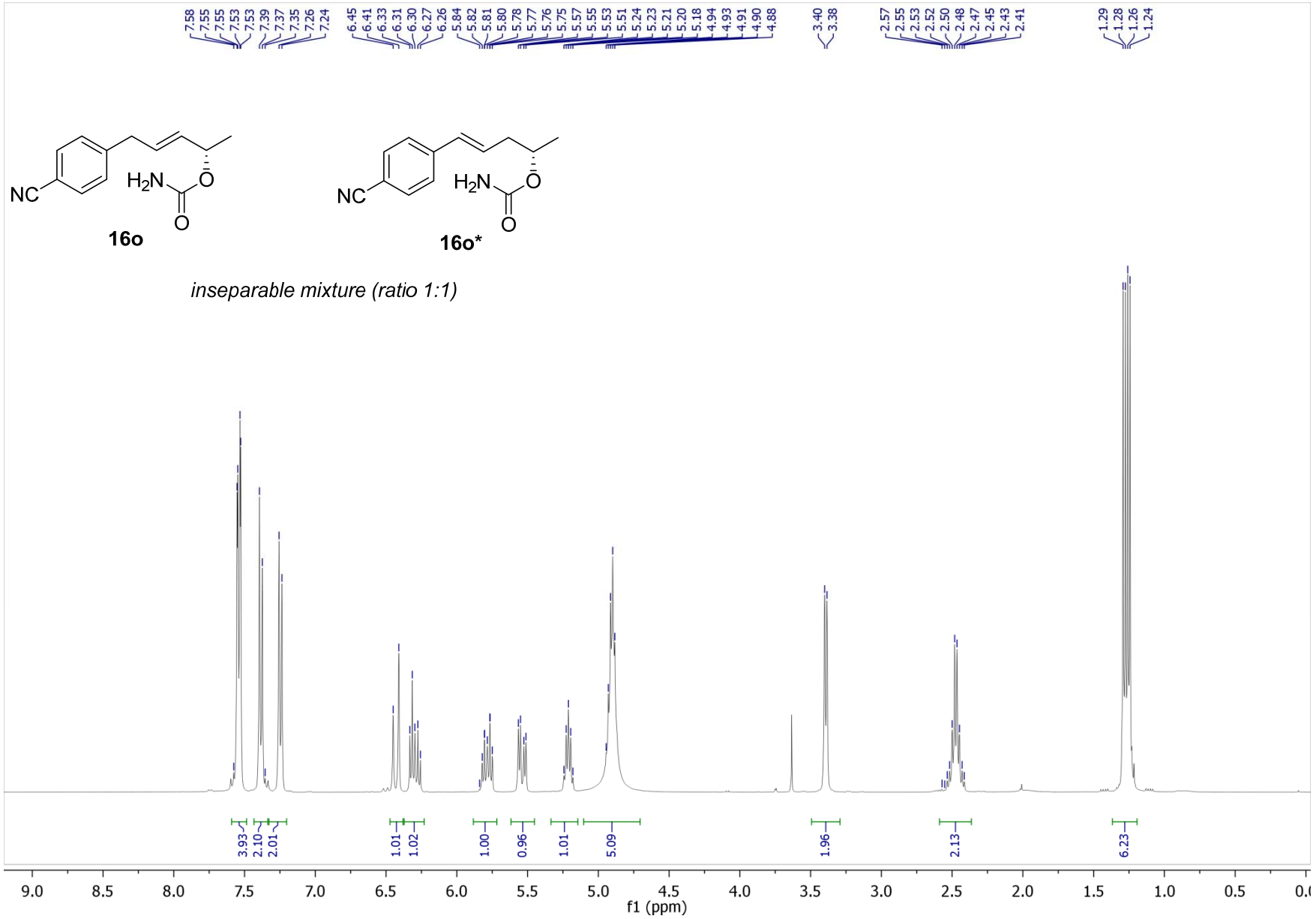
132.14
131.49
130.98
128.00
127.61
127.49
127.32
126.70
125.96
125.32
71.45
38.64
20.47
H2N
O
O
16l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

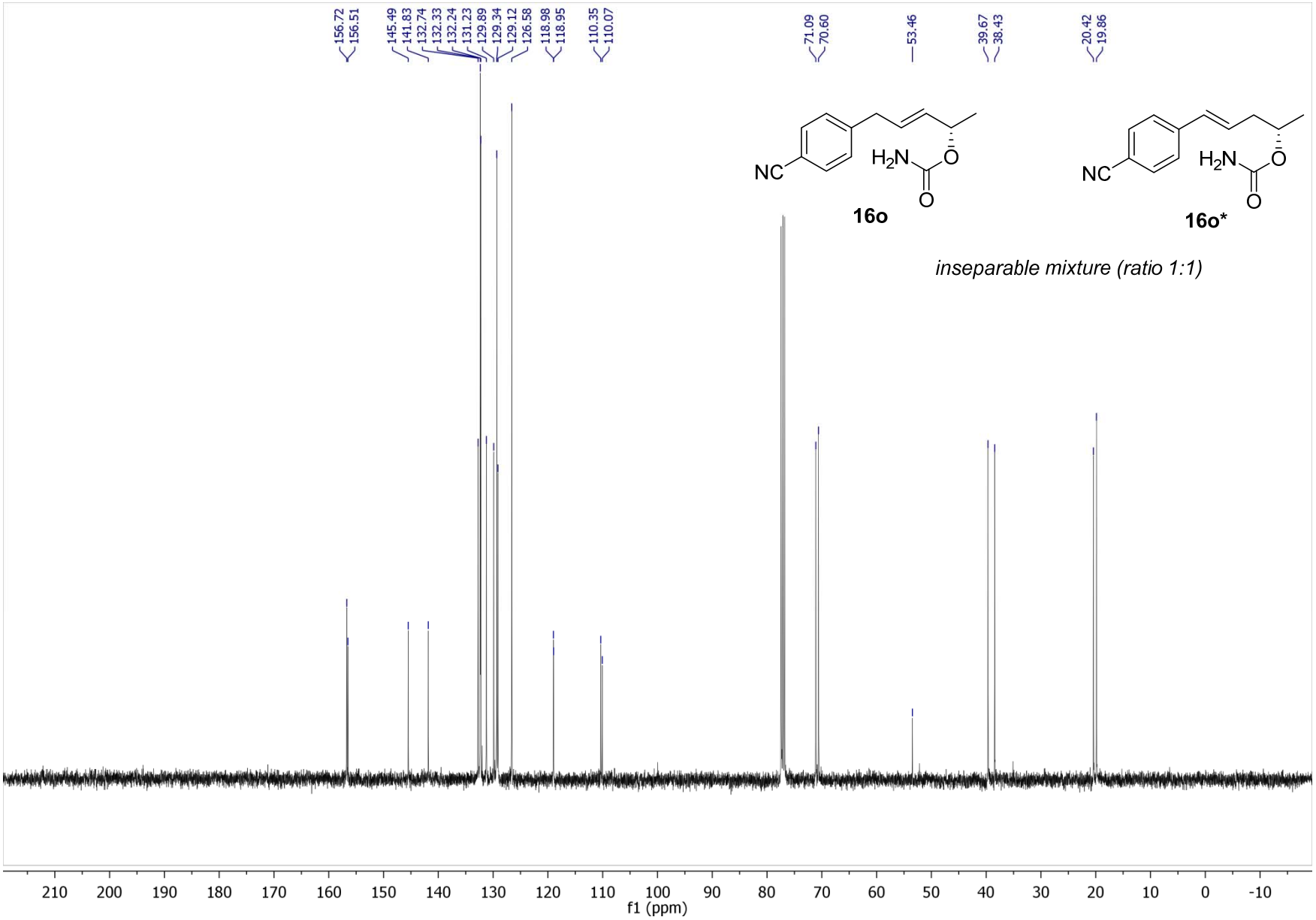

7.55
7.53
7.28
7.26
5.87
5.87
5.86
5.85
5.84
5.84
5.83
5.82
5.82
5.80
5.80
5.59
5.58
5.58
5.57
5.57
5.56
5.55
5.54
5.54
5.53
5.53
5.53
5.28
5.28
5.26
5.26
5.25
5.24
5.23
5.23
5.21
5.21
4.72
3.42
3.41
1.32
1.30
F3C
H2N
O
O
16m
0.94
1.08
1.08
0.85
1.00
1.00
1.00
1.79
2.00
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

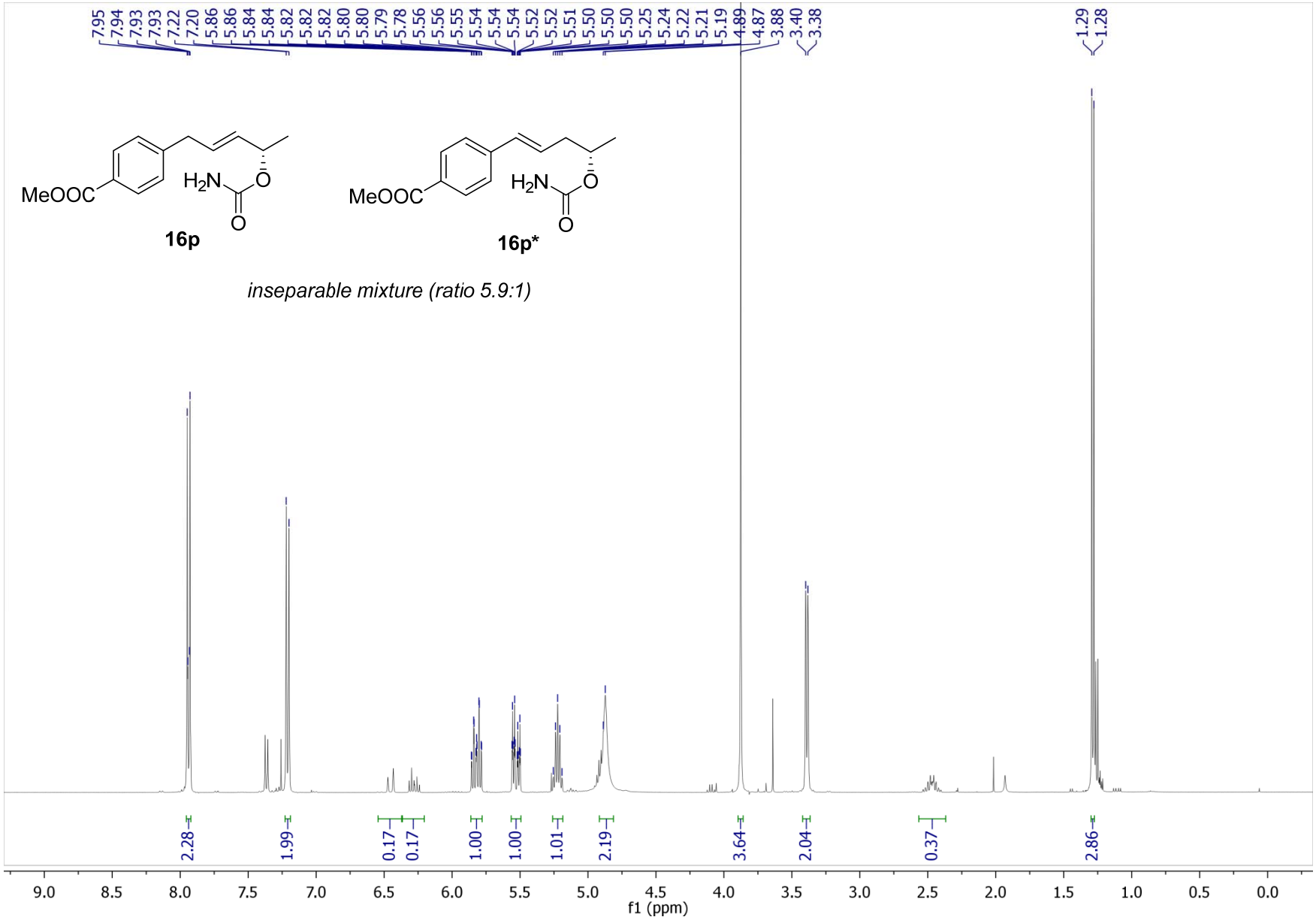

156.33
143.93
132.17
129.91
128.86
125.42
125.38
125.34
125.30
71.28
38.22
20.41
F3C
H2N
O
O
16m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

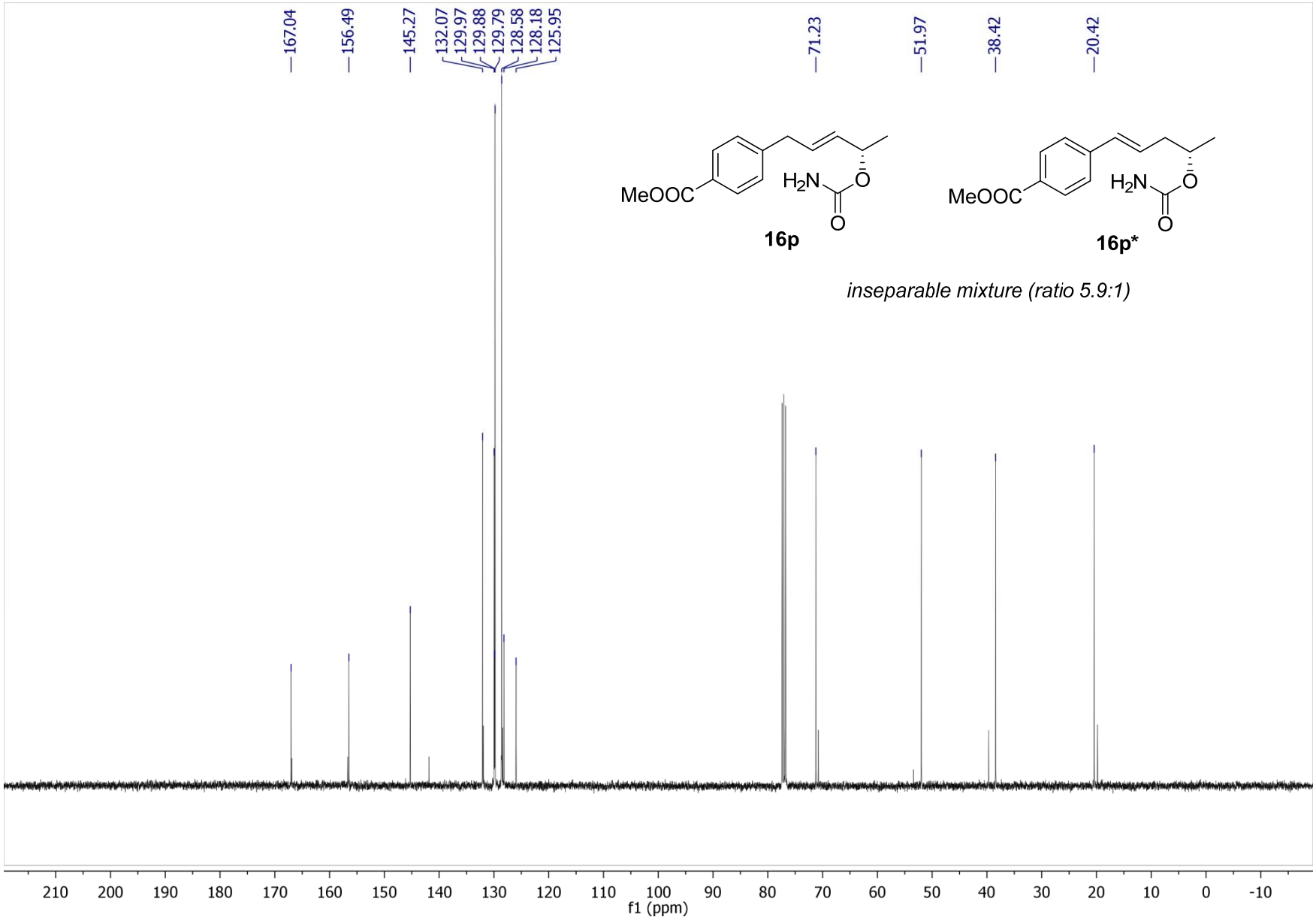

7.90 7.89 7.88 7.87 7.87 7.27 7.26 7.25 7.24 5.88 5.88 5.86 5.86 5.85 5.84 5.84 5.84 5.82 5.82 5.81 5.81 5.58 5.58 5.58 5.57 5.56 5.56 5.55 5.54 5.54 5.53 5.53 5.52 5.28 5.28 5.26 5.26 5.25 5.24 5.23 5.23 5.21 5.21 4.60 3.43 3.41 2.58 1.32 1.30
O
H2N
O
O
16n
(major)
O
H2N
O
O
16n*
inseparable mixture (ratio 5:1)
1.19 1.24 0.91 0.89 0.20 1.00 1.00 1.00 2.28 2.01 3.76 2.89
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

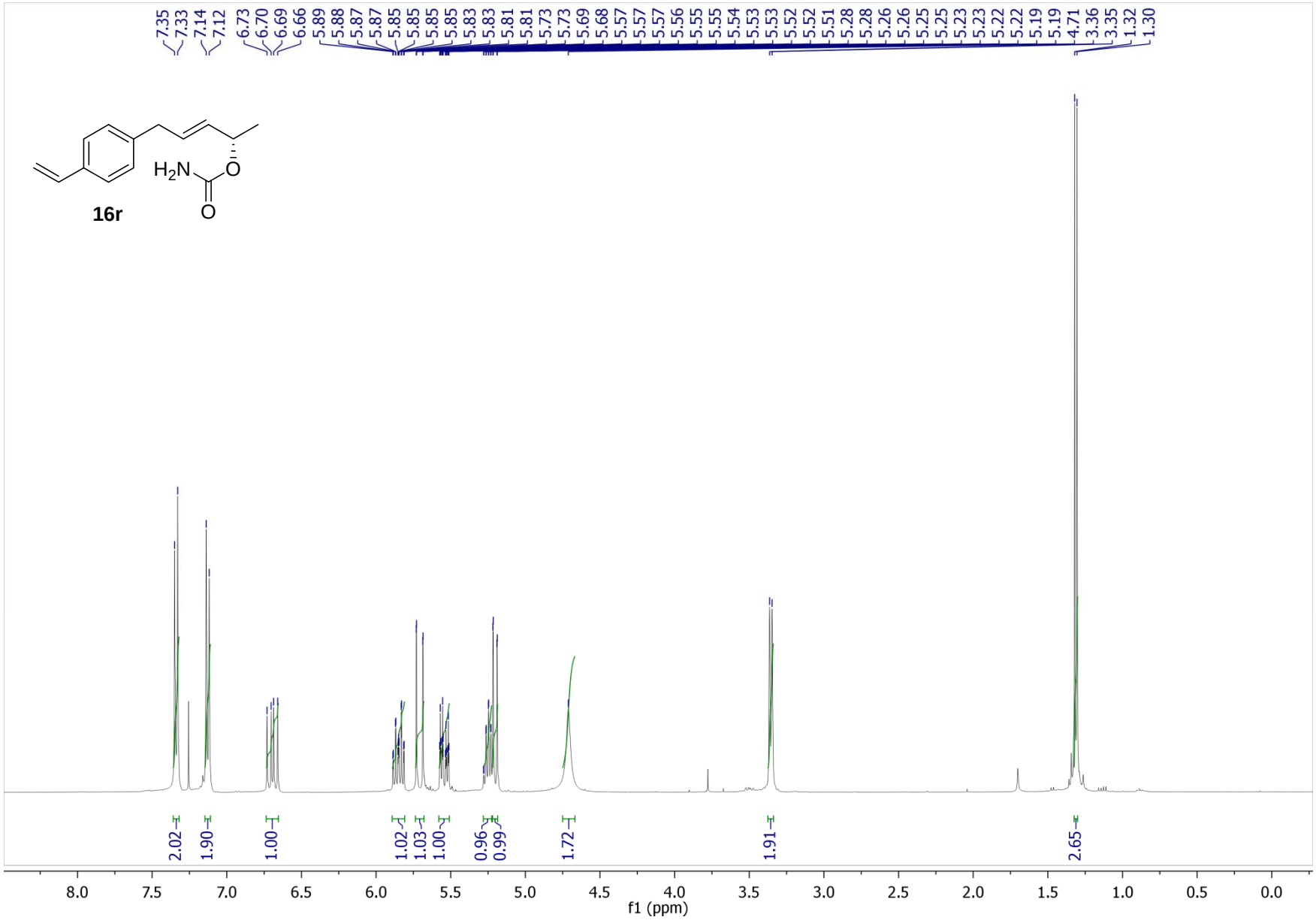

197.77
156.17
145.53
135.40
132.10
129.96
128.77
128.61
126.15
71.33
38.41
26.53
20.42
16n
(major)
16n*
inseparable mixture (ratio 5:1)
f1 (ppm)

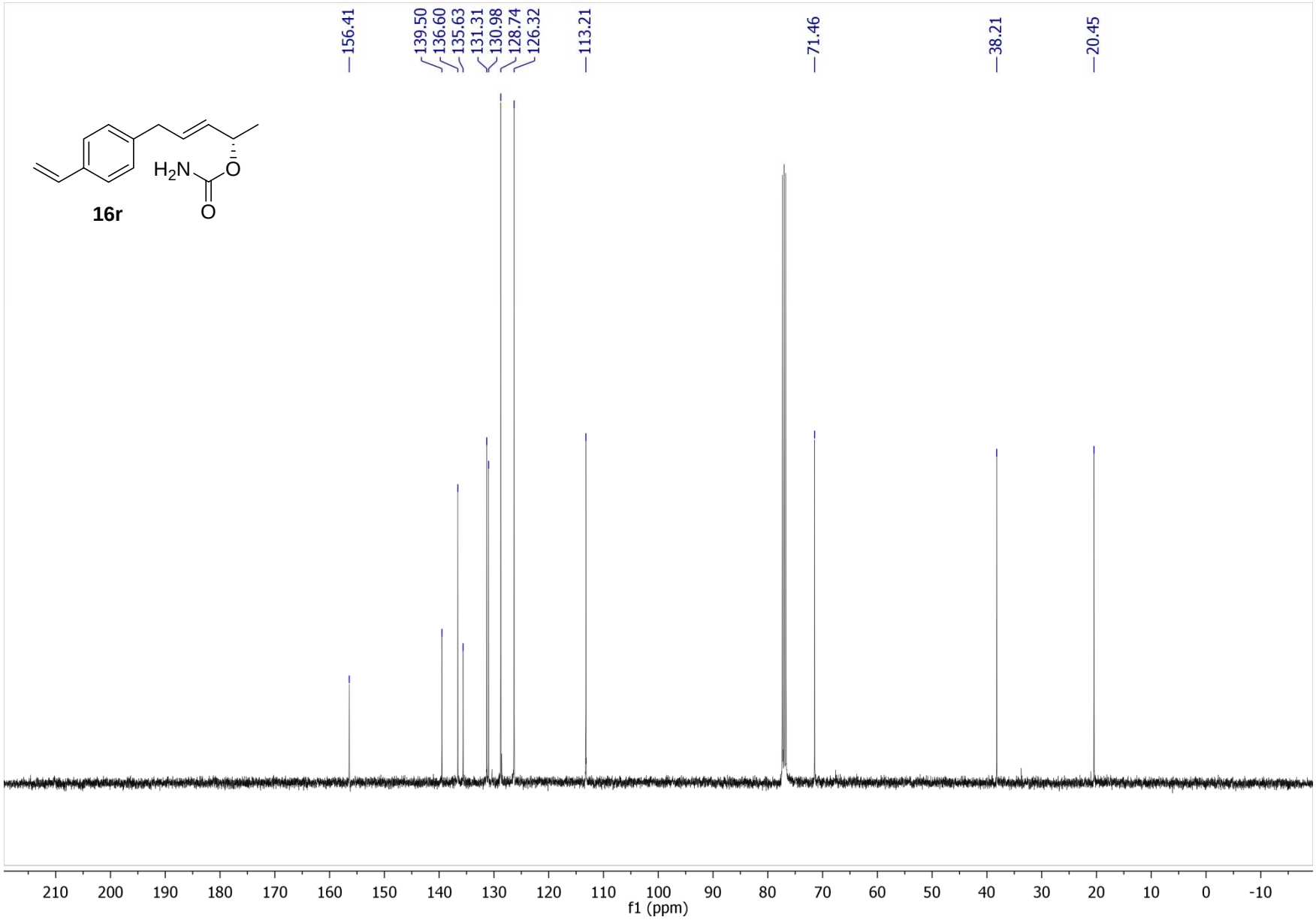

7.58 7.55 7.55 7.53 7.53 7.39 7.37 7.35 7.26 7.24
6.45 6.41 6.33 6.31 6.30 6.27 6.26 5.84 5.82 5.81 5.80 5.78 5.77 5.76 5.75 5.57 5.55 5.53 5.51 5.24 5.23 5.21 5.20 5.18 4.94 4.93 4.91 4.90 4.88
3.40 3.38
2.57 2.55 2.53 2.52 2.50 2.48 2.47 2.45 2.43 2.41
1.29 1.28 1.26 1.24
NC
H2N
O
O
16o
NC
H2N
O
O
16o*
inseparable mixture (ratio 1:1)
3.93 2.10 2.01 1.01 1.02 1.00 0.96 1.01 5.09 1.96 2.13 6.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

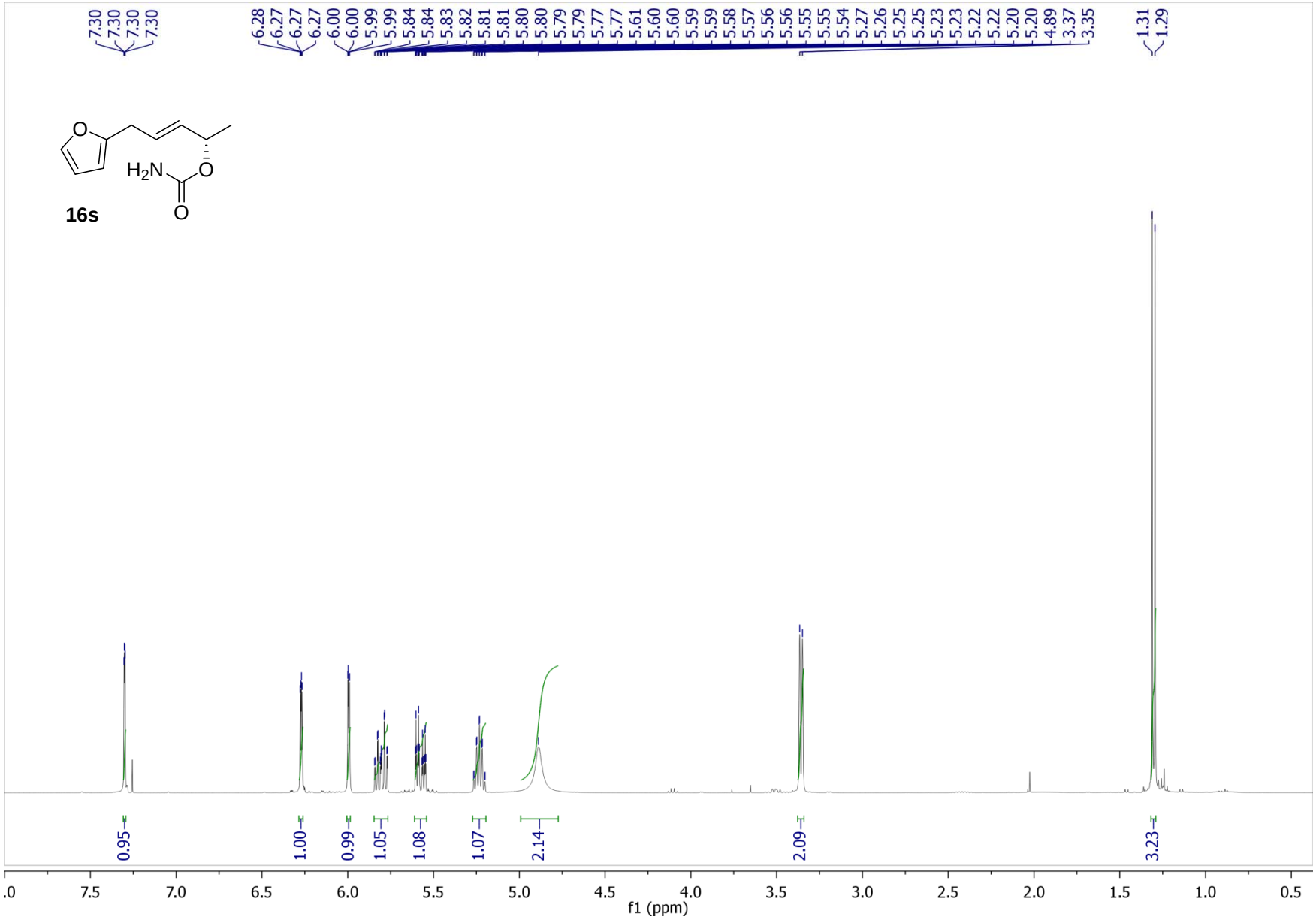

156.72
156.51
145.49
141.83
132.74
132.33
132.24
131.23
129.89
129.34
129.12
126.58
118.98
118.95
110.35
110.07
71.09
70.60
53.46
39.67
38.43
20.42
19.86
NC
H2N
O
O
16o
NC
H2N
O
O
16o*
inseparable mixture (ratio 1:1)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

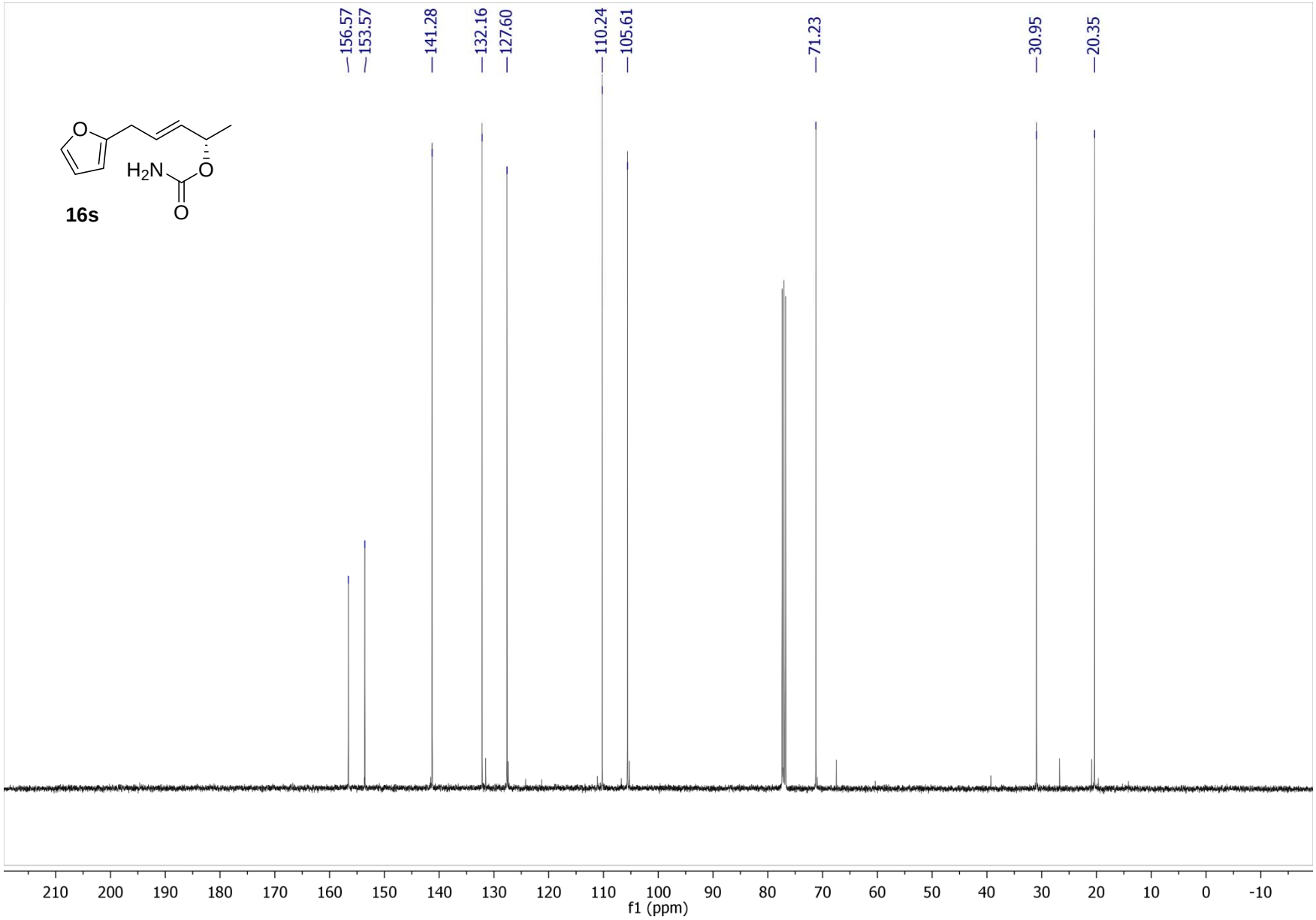

7.95
7.94
7.93
7.93
7.22
7.20
5.86
5.86
5.84
5.84
5.82
5.82
5.82
5.80
5.80
5.79
5.78
5.56
5.56
5.55
5.54
5.54
5.54
5.52
5.52
5.51
5.50
5.50
5.50
5.25
5.24
5.22
5.21
5.19
4.89
4.87
3.88
3.40
3.38
1.29
1.28
MeOOC
H2N
O
O
16p
MeOOC
H2N
O
O
16p*
inseparable mixture (ratio 5.9:1)
2.28
1.99
0.17
0.17
1.00
1.00
1.01
2.19
3.64
2.04
0.37
2.86
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

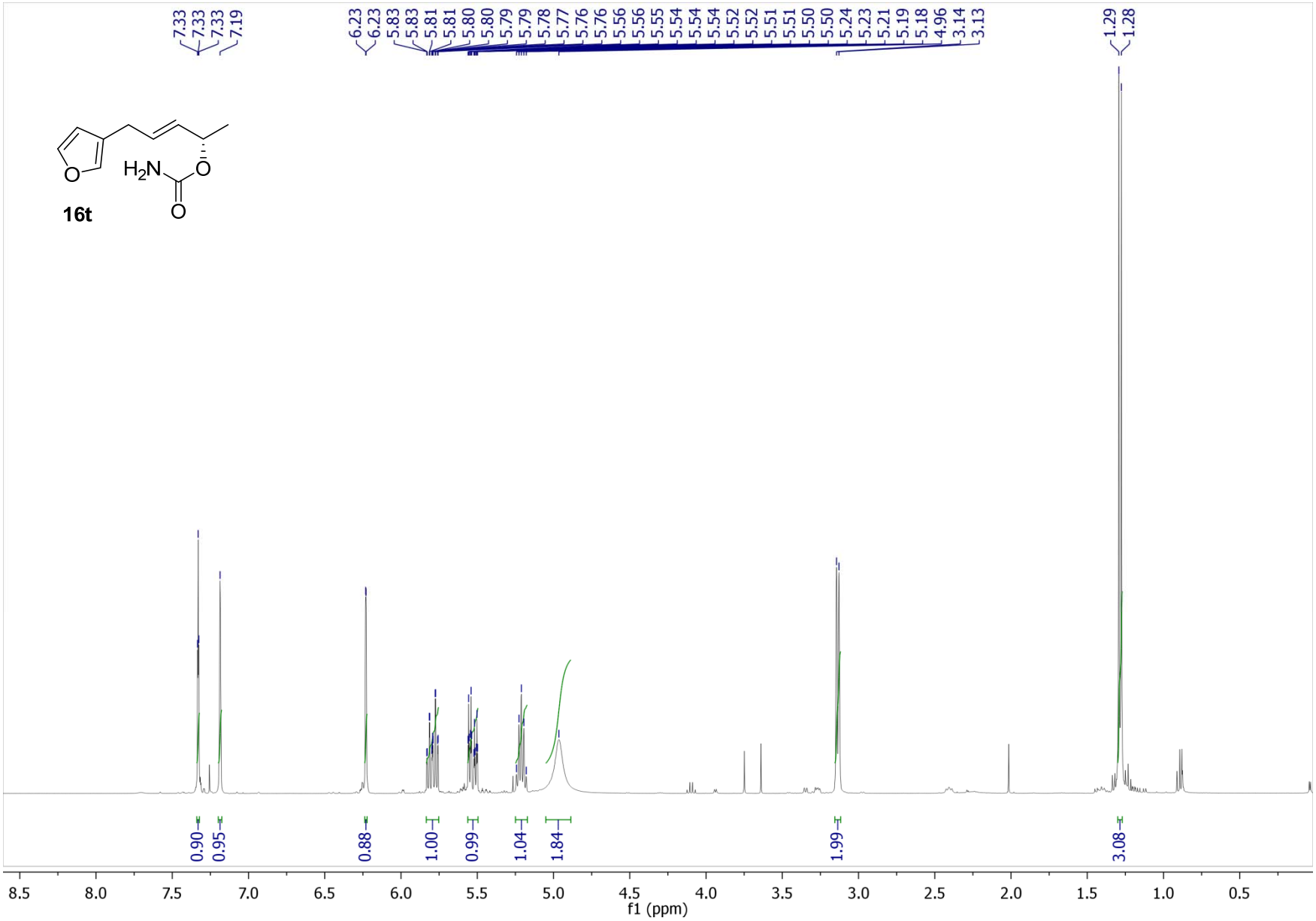

167.04
156.49
145.27
132.07
129.97
129.88
129.79
128.58
128.18
125.95
71.23
51.97
38.42
20.42
MeOOC
H2N
O
O
16p
MeOOC
H2N
O
O
16p*
inseparable mixture (ratio 5.9:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

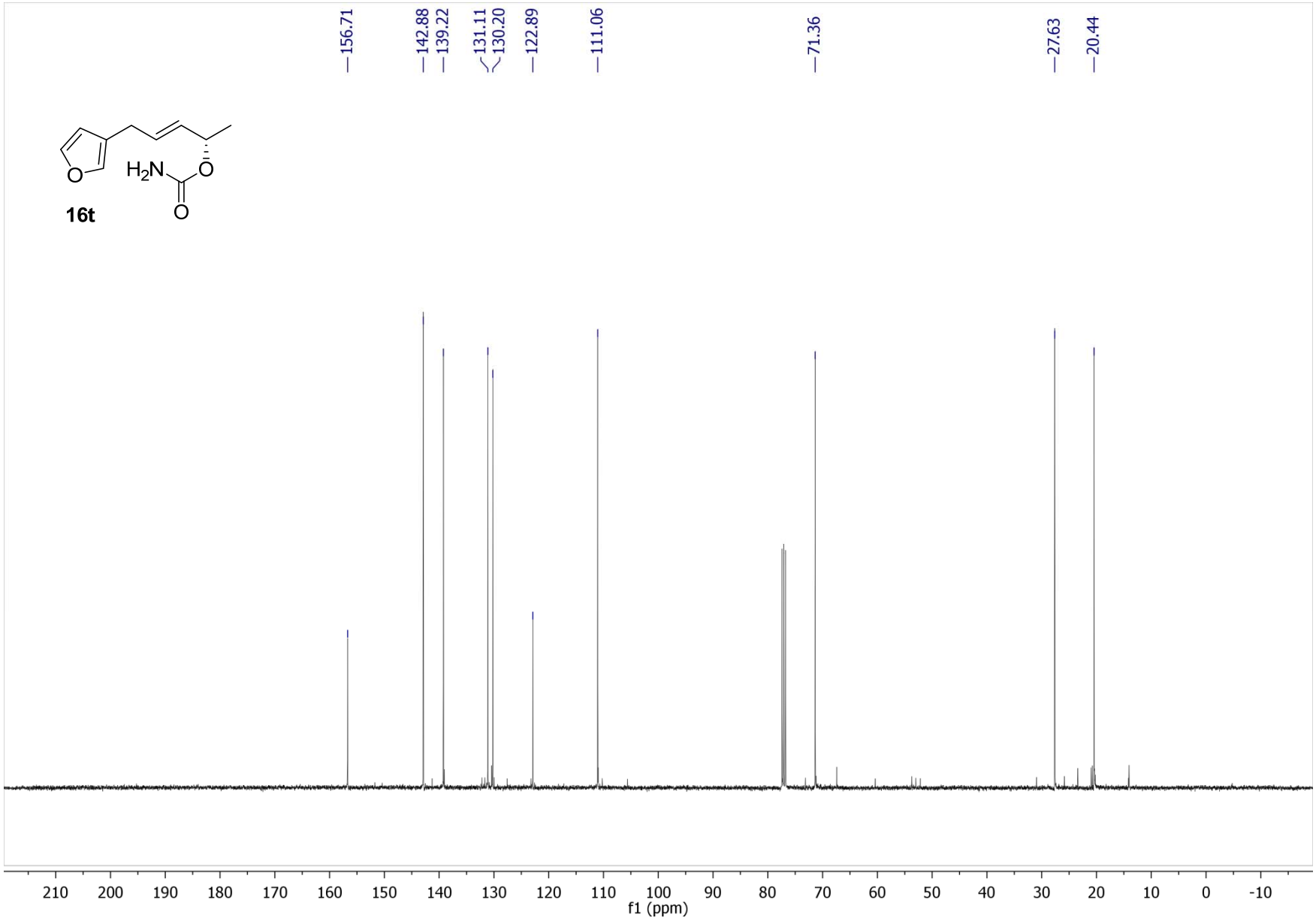

7.35
7.33
7.14
7.12
6.73
6.70
6.69
6.66
5.89
5.88
5.87
5.87
5.85
5.85
5.85
5.85
5.83
5.83
5.81
5.81
5.73
5.73
5.69
5.68
5.57
5.57
5.57
5.56
5.55
5.55
5.54
5.53
5.53
5.52
5.52
5.51
5.28
5.28
5.26
5.26
5.25
5.25
5.23
5.23
5.22
5.22
5.19
5.19
4.71
3.36
3.35
1.32
1.30
H2N
O
O
16r
2.02
1.90
1.00
1.02
1.03
1.00
0.96
0.99
1.72
1.91
2.65
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

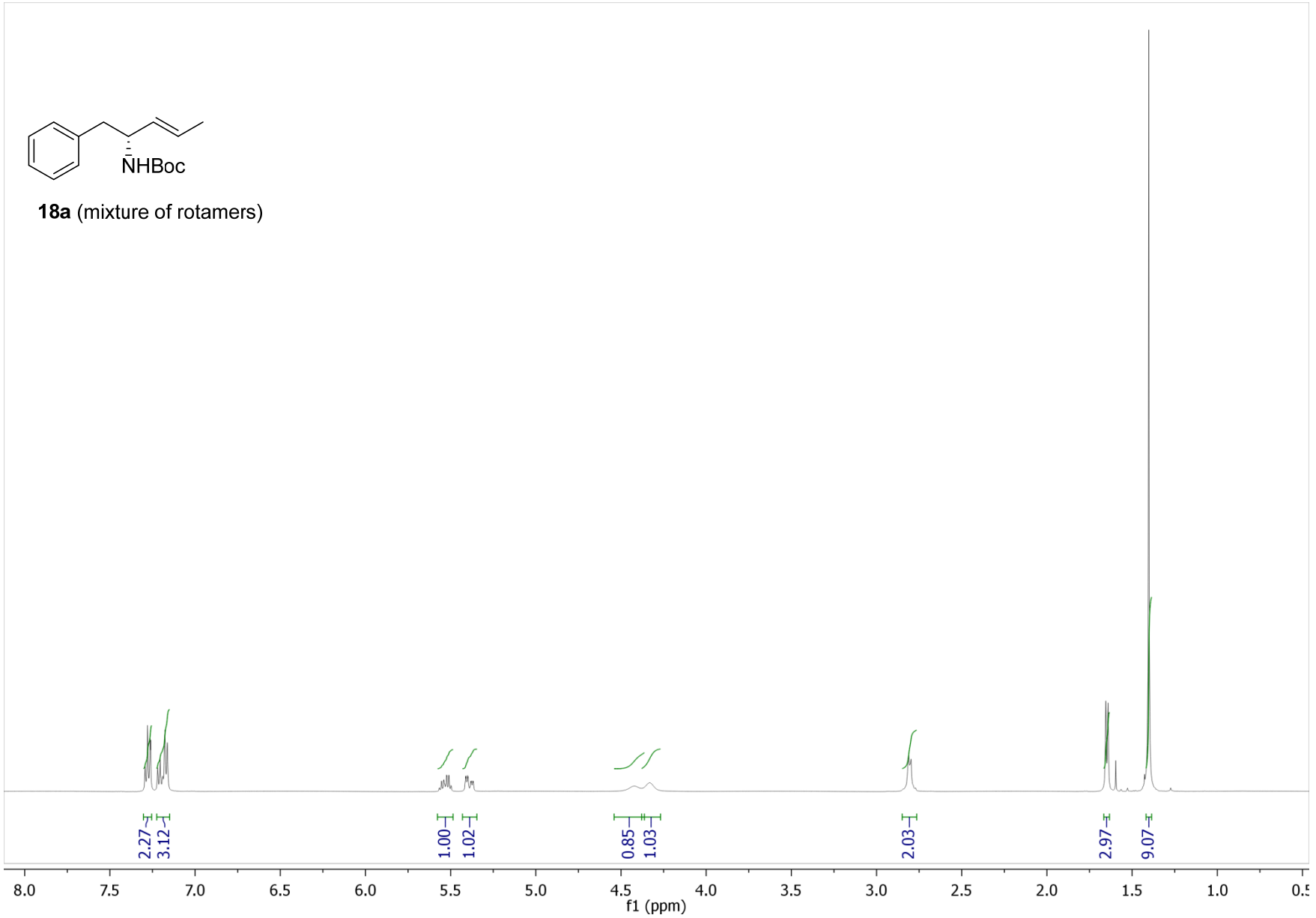

156.41
139.50
136.60
135.63
131.31
130.98
128.74
126.32
113.21
71.46
38.21
20.45
H2N
O
O
16r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

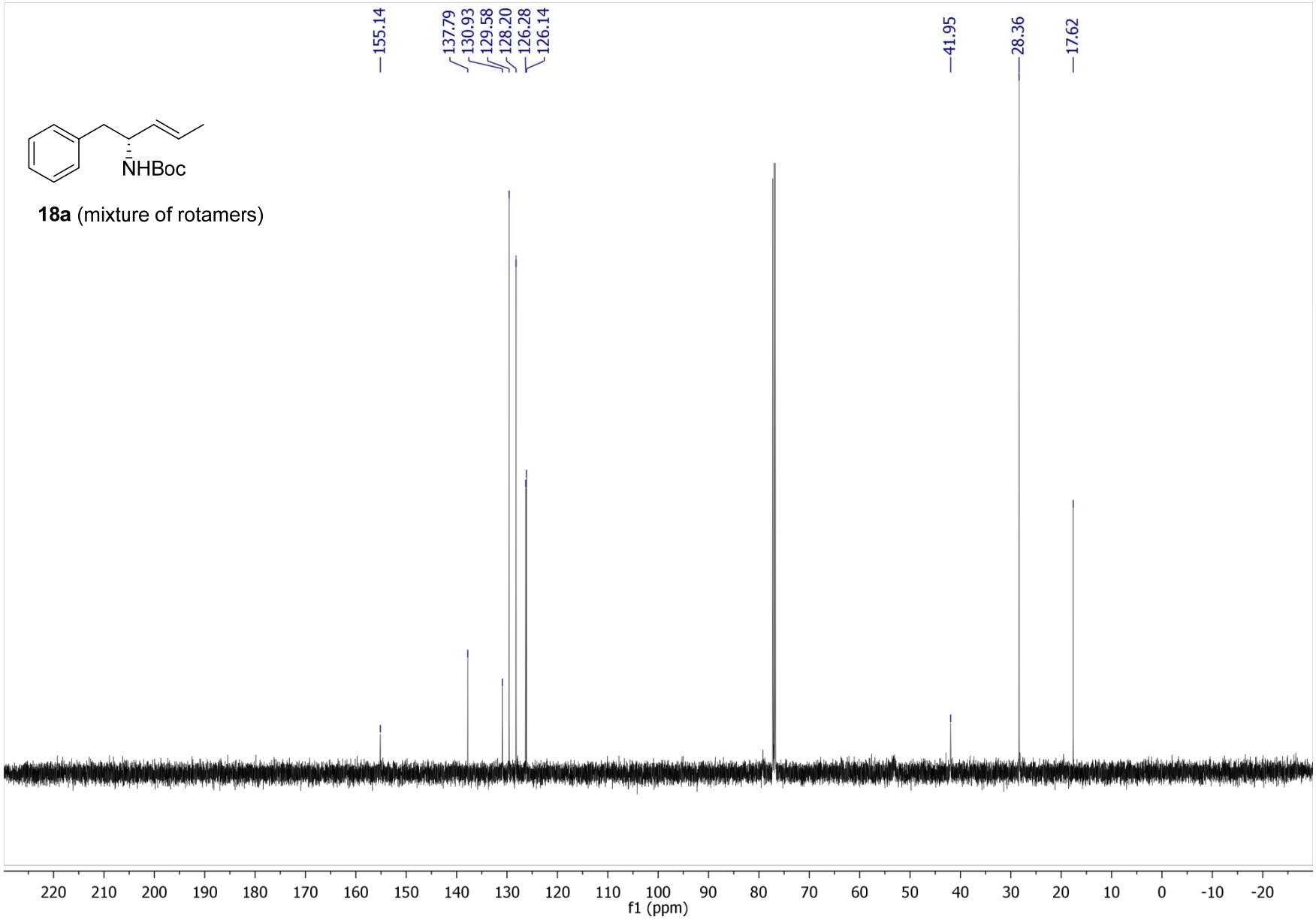

7.30
7.30
7.30
7.30
6.28
6.27
6.27
6.27
6.00
6.00
5.99
5.99
5.84
5.84
5.83
5.82
5.81
5.81
5.80
5.80
5.79
5.79
5.77
5.77
5.61
5.60
5.60
5.59
5.59
5.58
5.57
5.56
5.56
5.55
5.55
5.54
5.27
5.26
5.25
5.25
5.23
5.23
5.22
5.22
5.20
5.20
4.89
3.37
3.35
1.31
1.29
O
H2N
O
O
16s
0.95
1.00
0.99
1.05
1.08
1.07
2.14
2.09
3.23
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

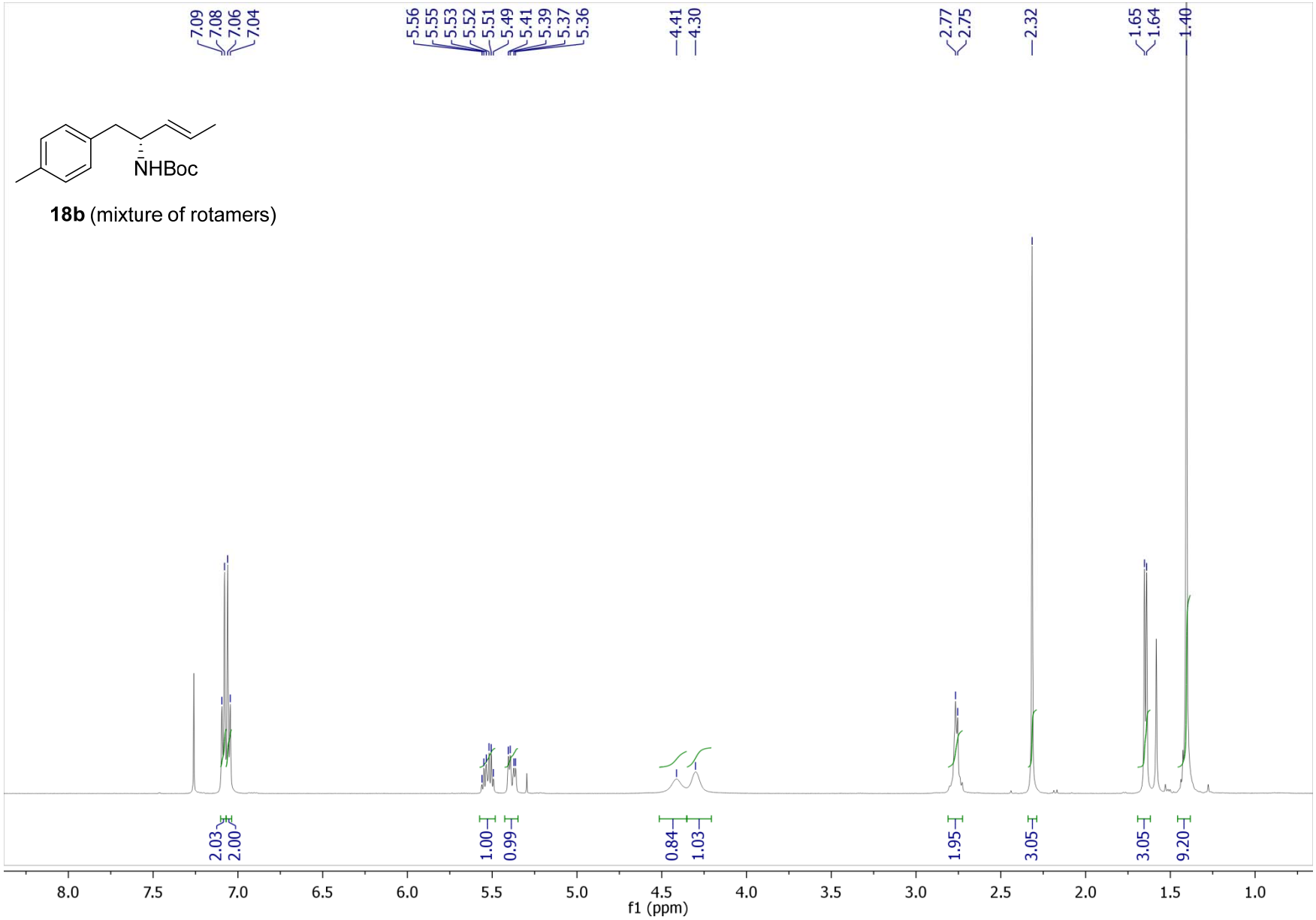

156.57
153.57
141.28
132.16
127.60
110.24
105.61
71.23
30.95
20.35
O
H2N
O
O
16s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.33
7.33
7.33
7.19
6.23
6.23
5.83
5.83
5.81
5.81
5.80
5.80
5.79
5.79
5.78
5.77
5.76
5.76
5.56
5.56
5.55
5.54
5.54
5.54
5.52
5.52
5.51
5.51
5.50
5.50
5.24
5.23
5.21
5.19
5.18
4.96
3.14
3.13
1.29
1.28
O
H2N
O
O
16t
0.90
0.95
0.88
1.00
0.99
1.04
1.84
1.99
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

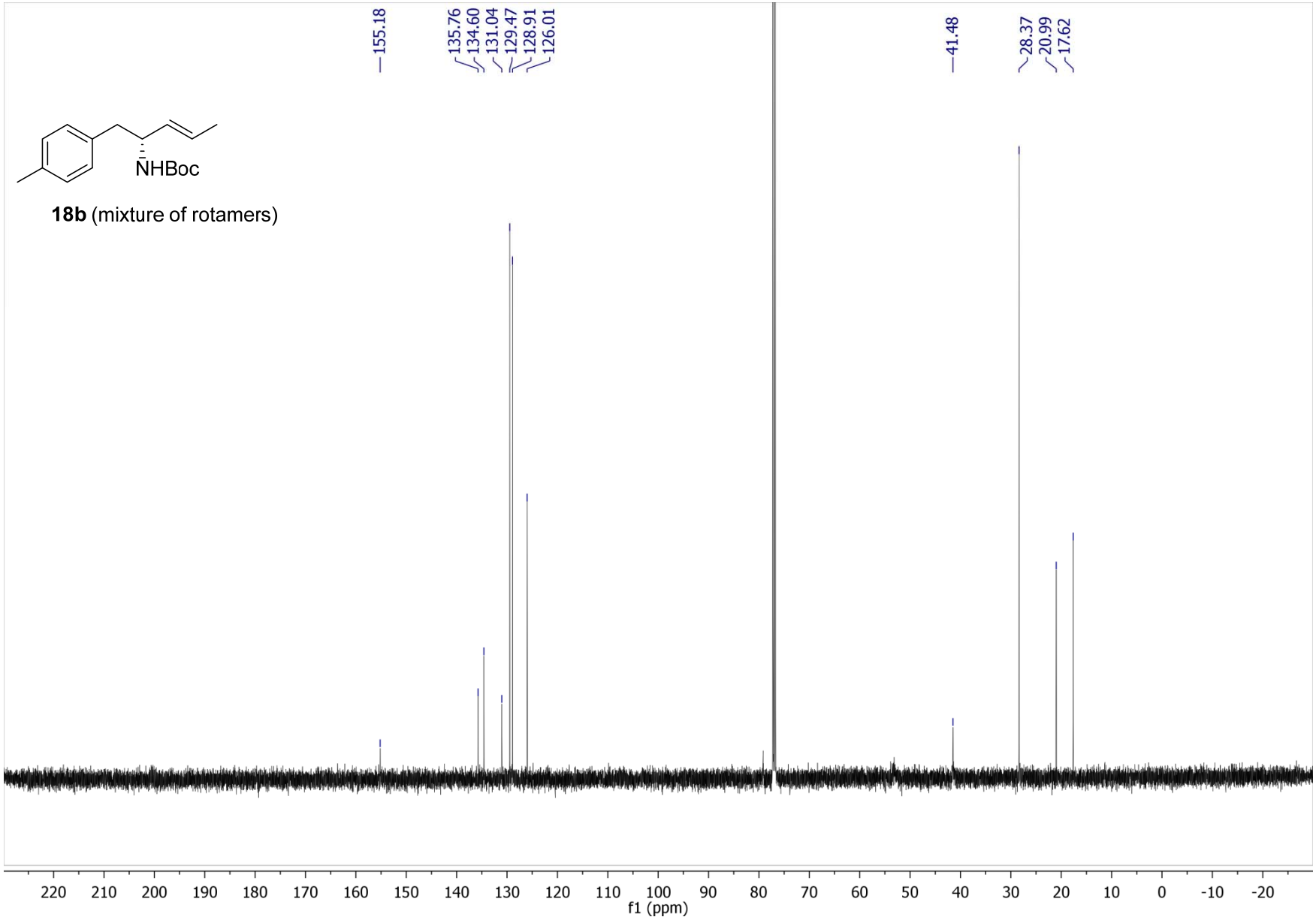

156.71
142.88
139.22
131.11
130.20
122.89
111.06
71.36
27.63
20.44
O
H2N
O
O
16t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

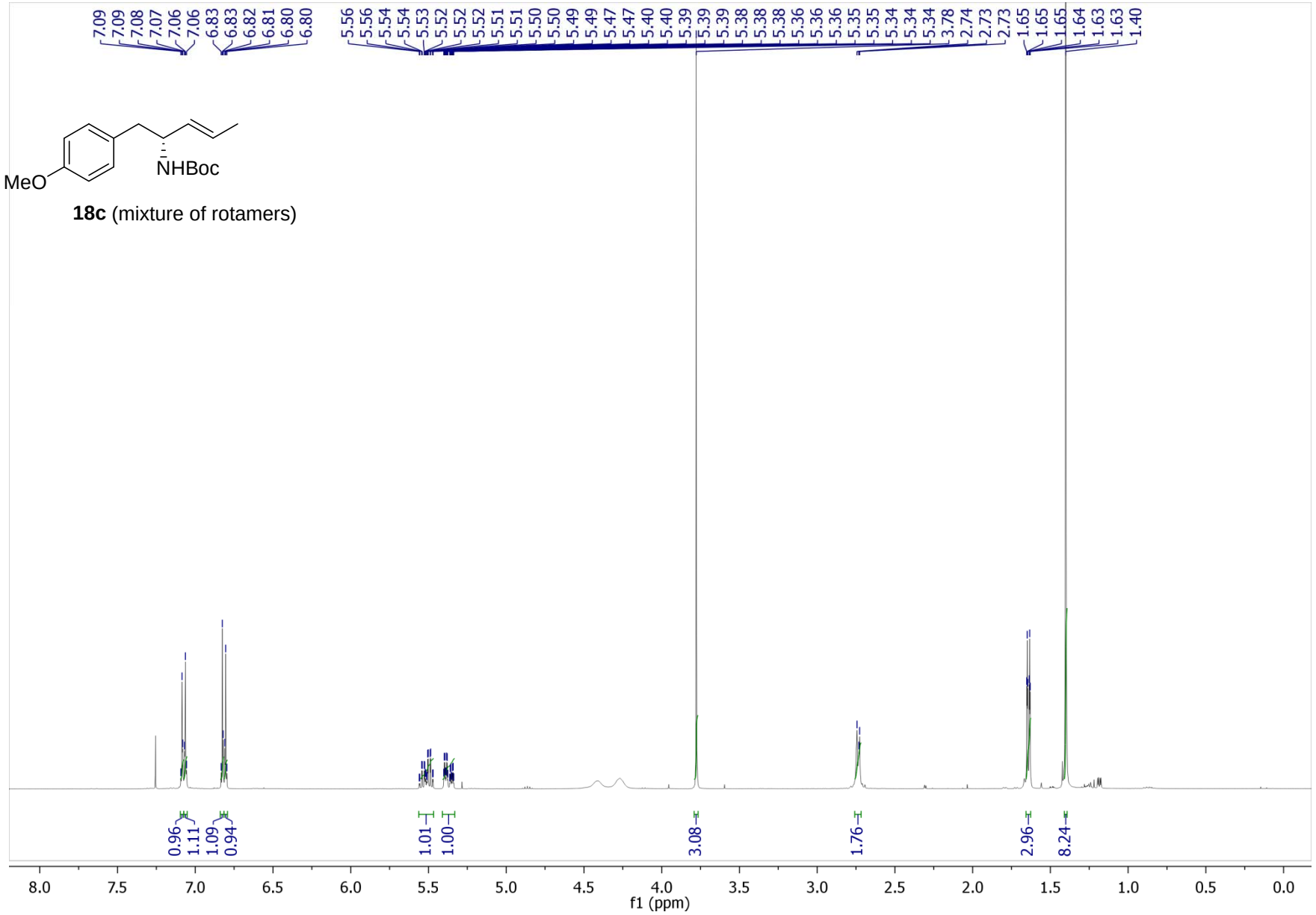

NHBoc
18a (mixture of rotamers)
2.27
3.12
1.00
1.02
0.85
1.03
2.03
2.97
9.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


155.14
137.79
130.93
129.58
128.20
126.28
126.14
41.95
28.36
17.62
NHBoc
18a (mixture of rotamers)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

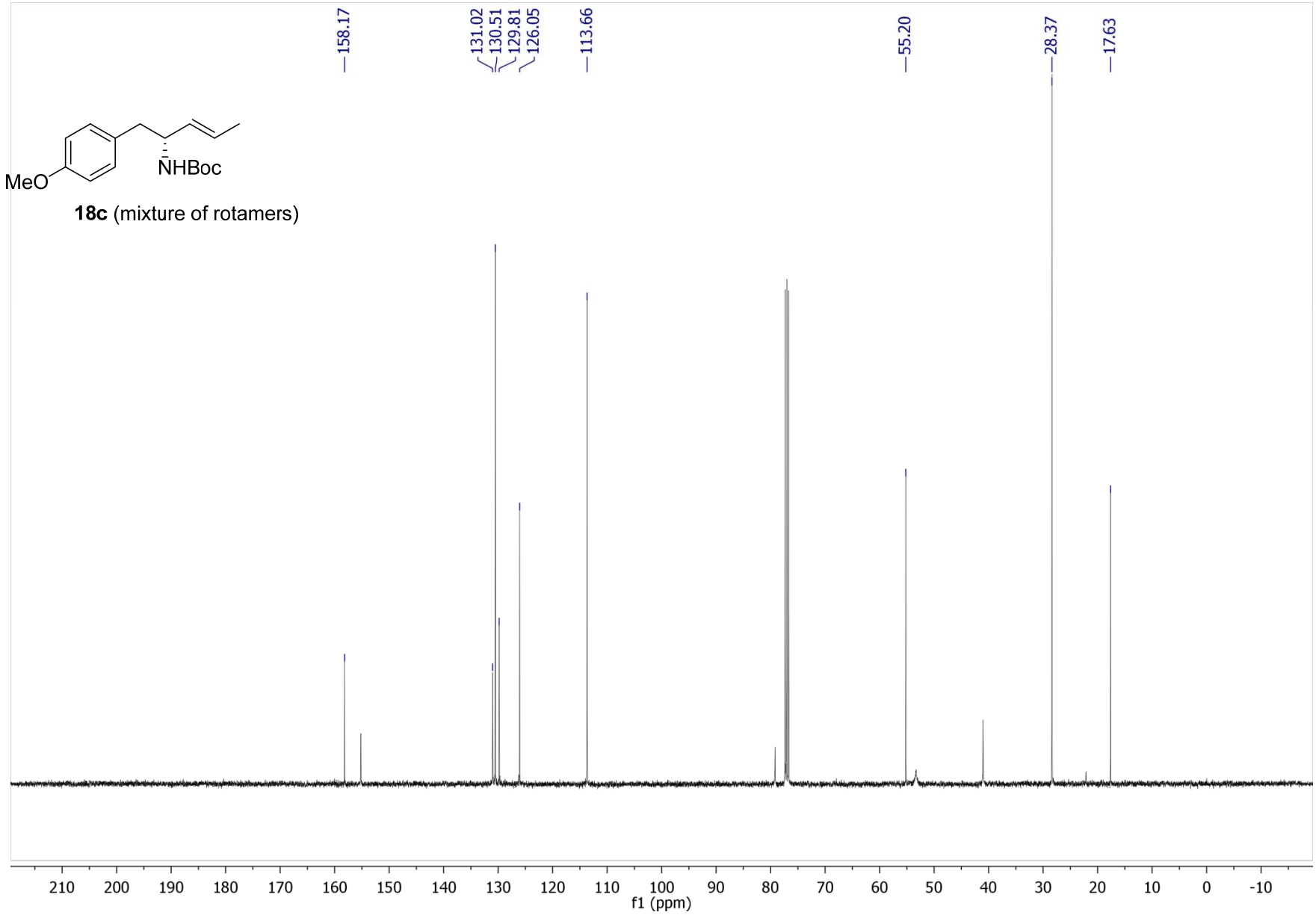


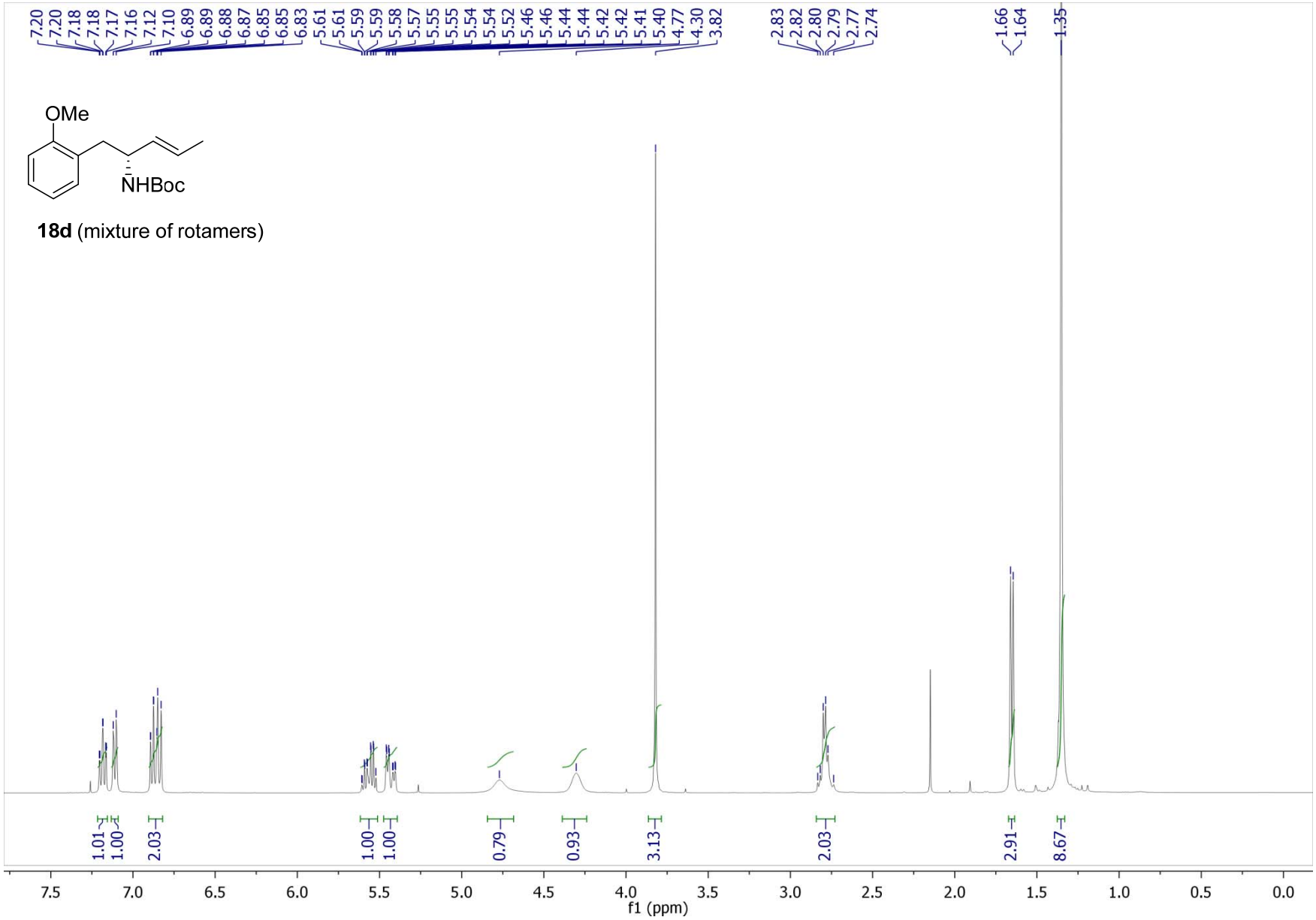
18b (mixture of rotamers)


155.18
135.76
134.60
131.04
129.47
128.91
126.01
41.48
28.37
20.99
17.62
NHBoc
18b (mixture of rotamers)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

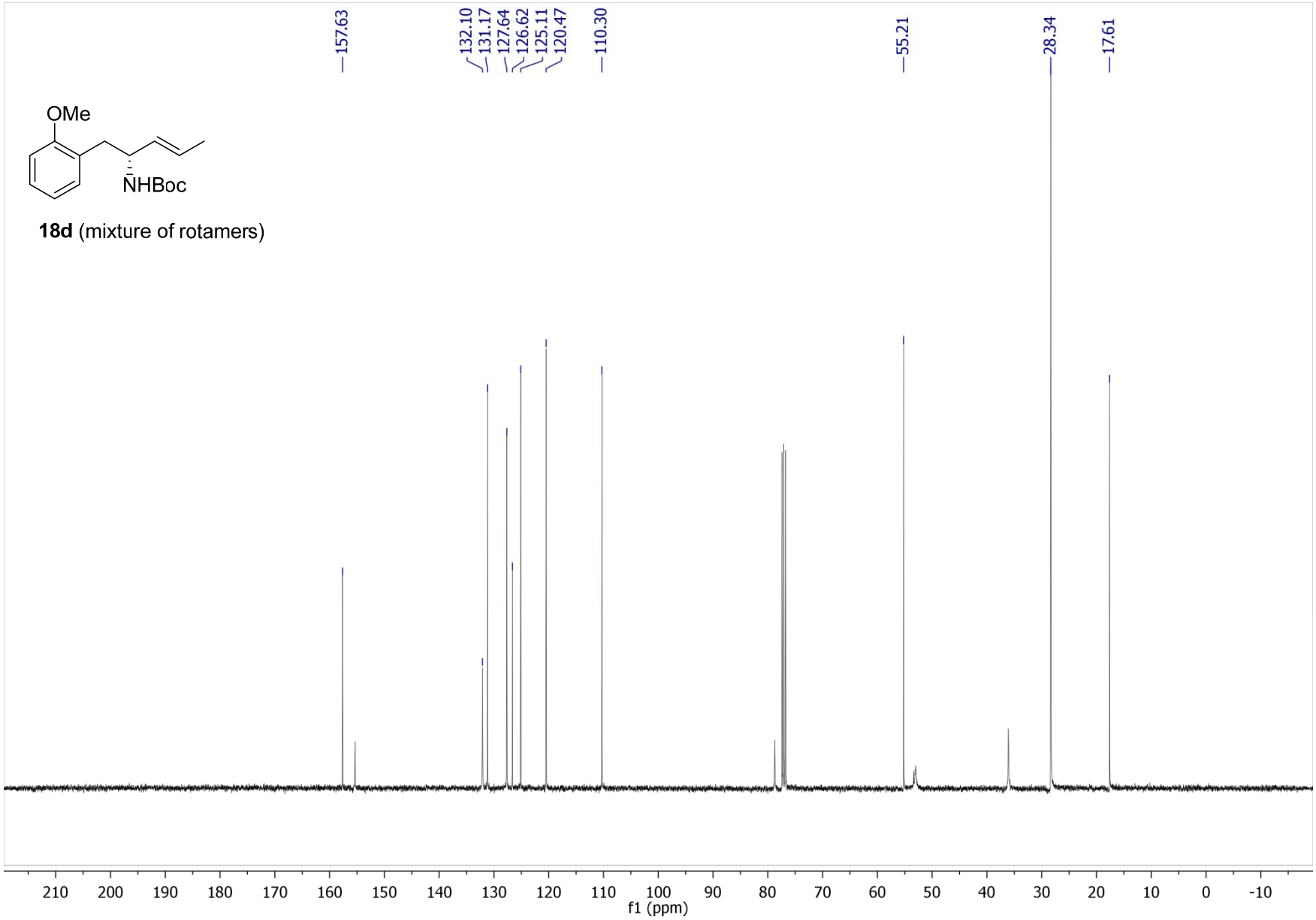


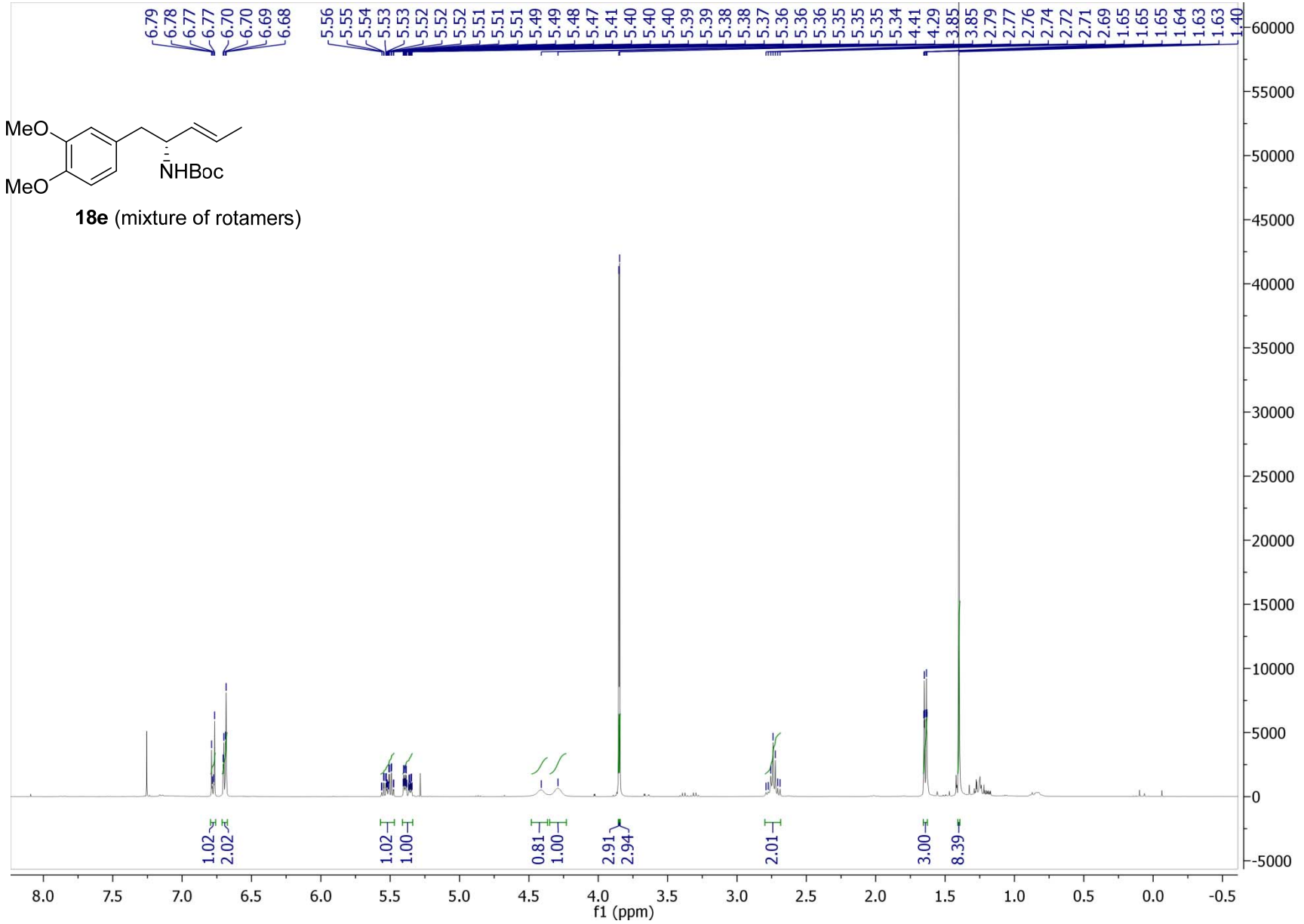
18c (mixture of rotamers)


158.17
131.02
130.51
129.81
126.05
113.66
55.20
28.37
17.63
MeO
NHBoc
18c (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

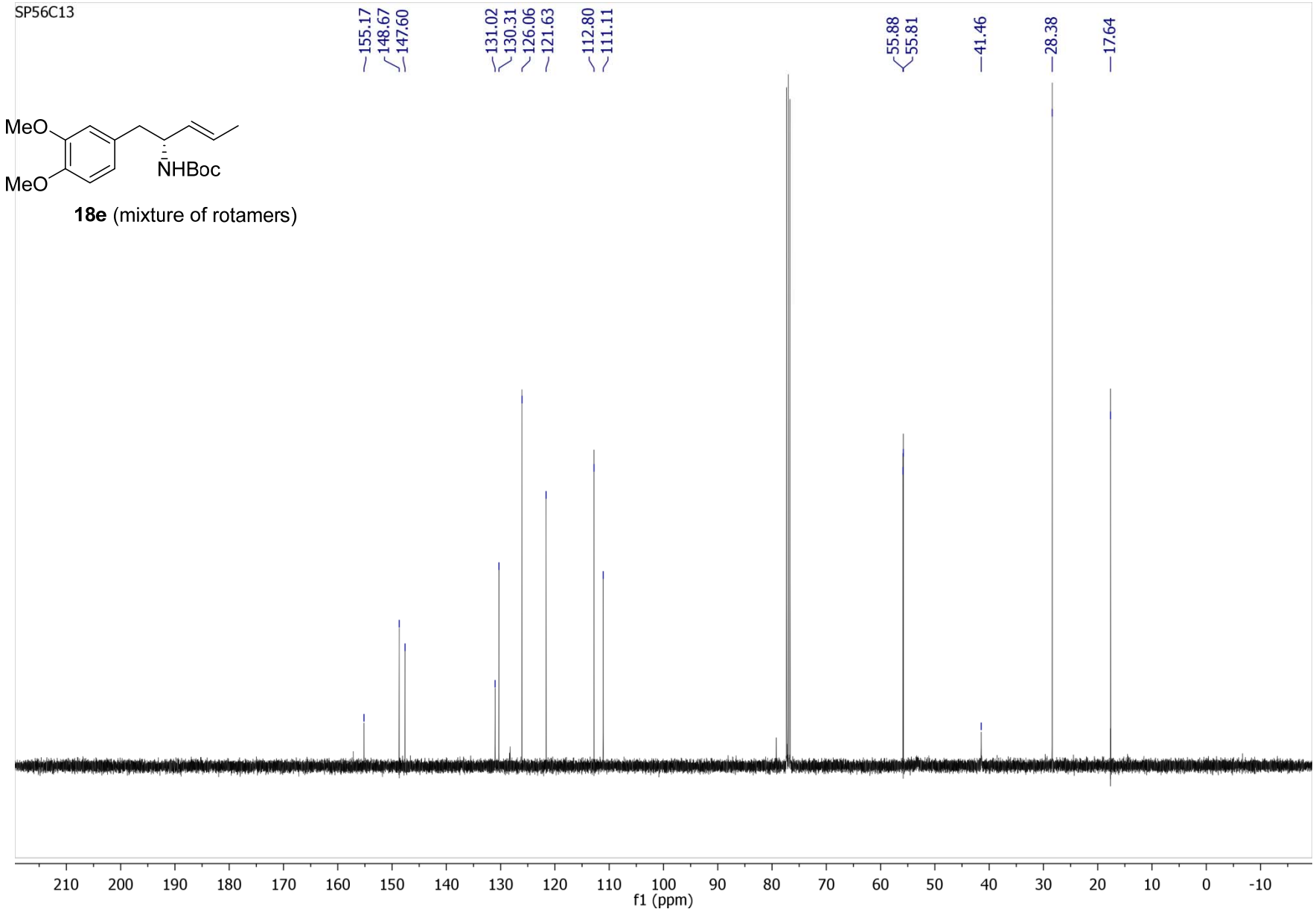


18d (mixture of rotamers)

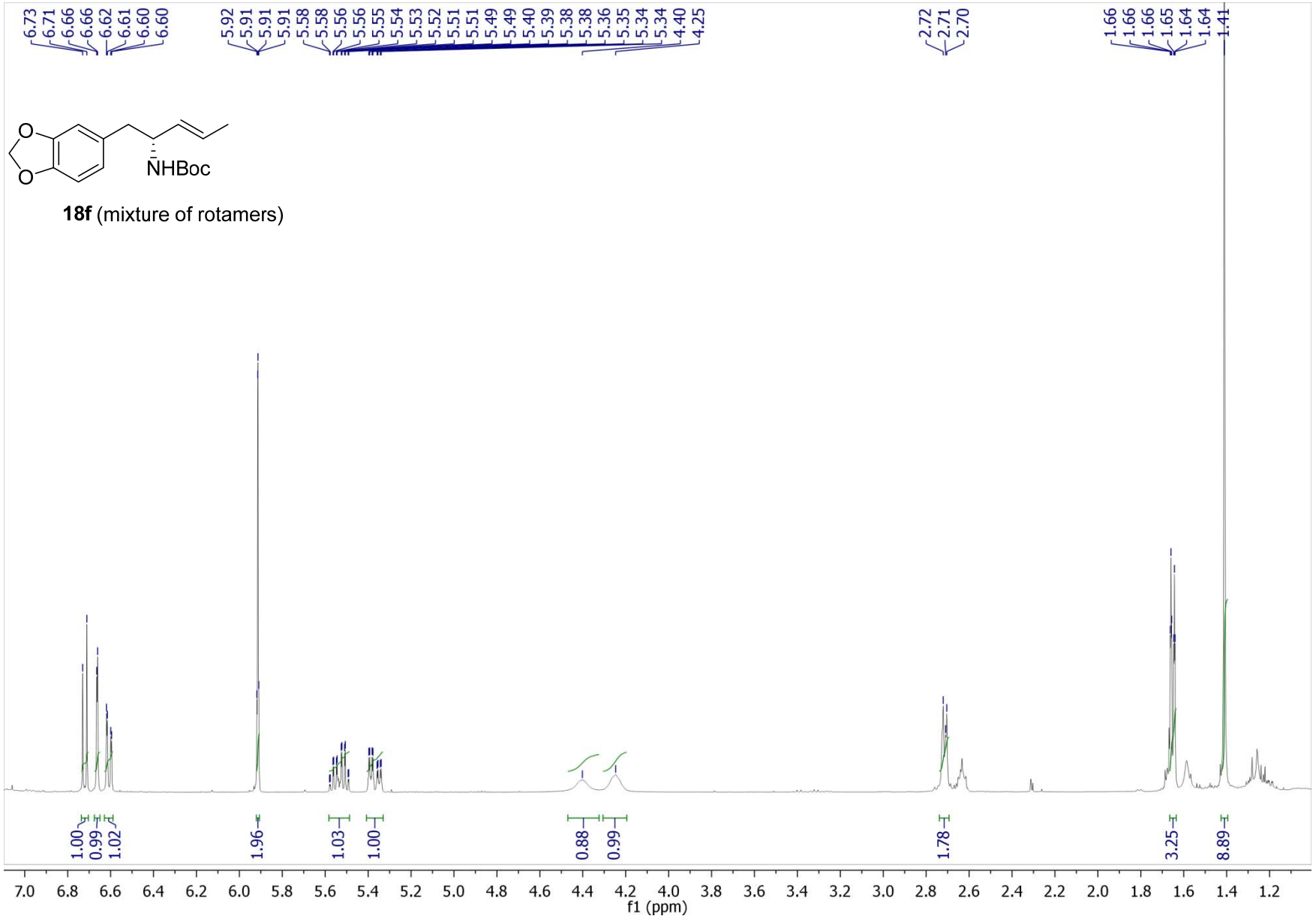

157.63
132.10
131.17
127.64
126.62
125.11
120.47
110.30
55.21
28.34
17.61
OMe
NHBoc
18d (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
MeO
NHBoc
18e (mixture of rotamers)
f1 (ppm)

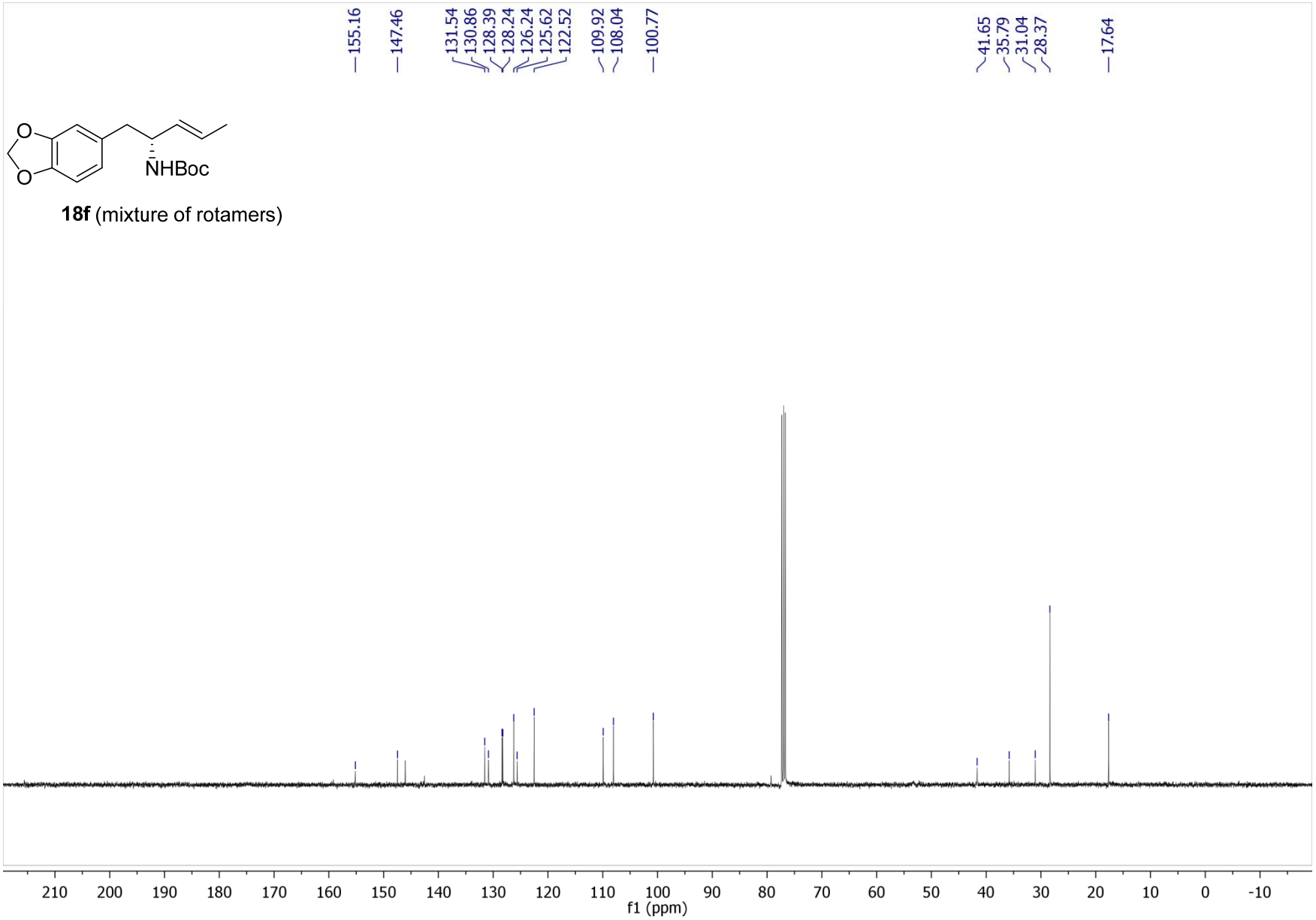
SP56C13



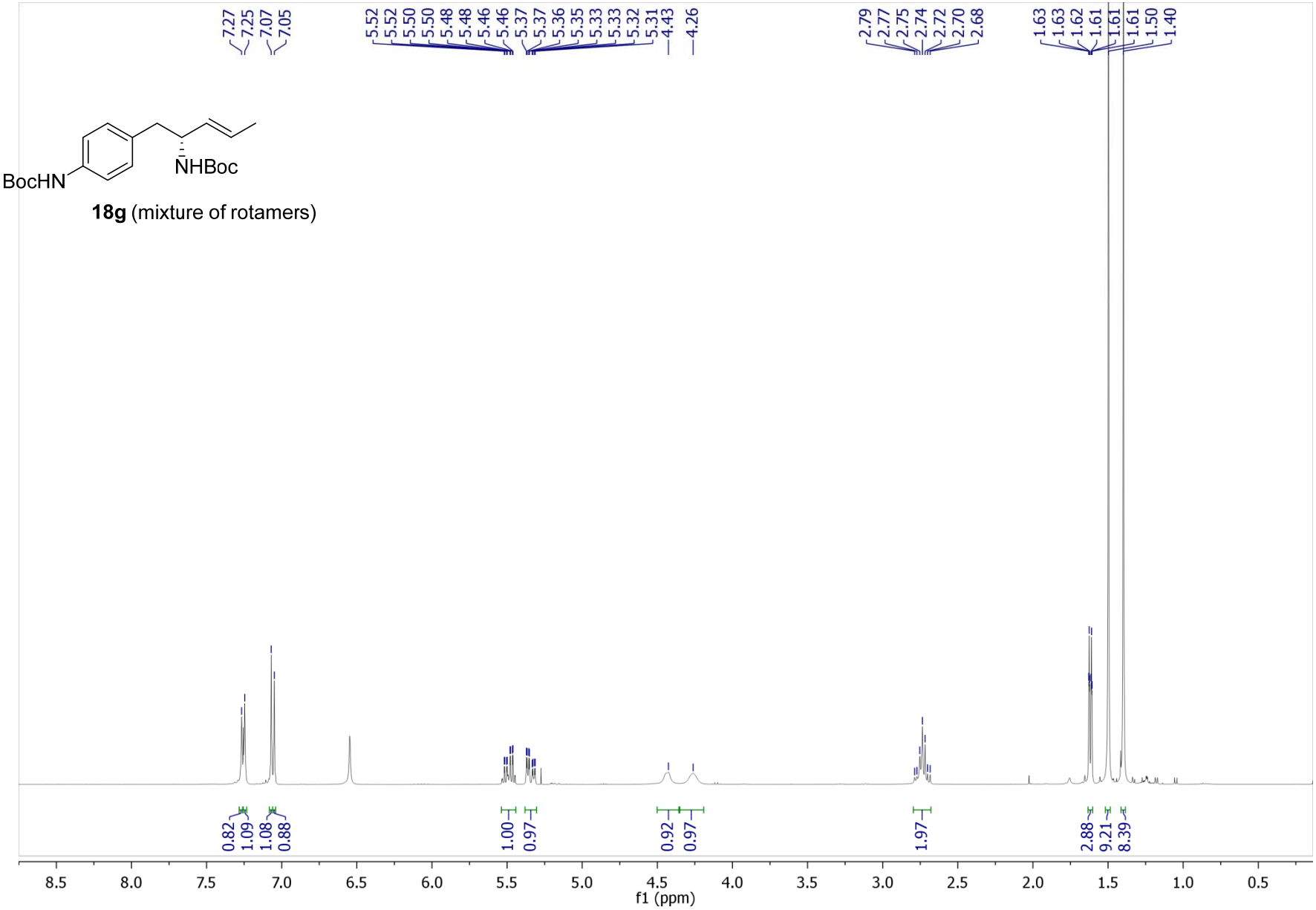
18e (mixture of rotamers)



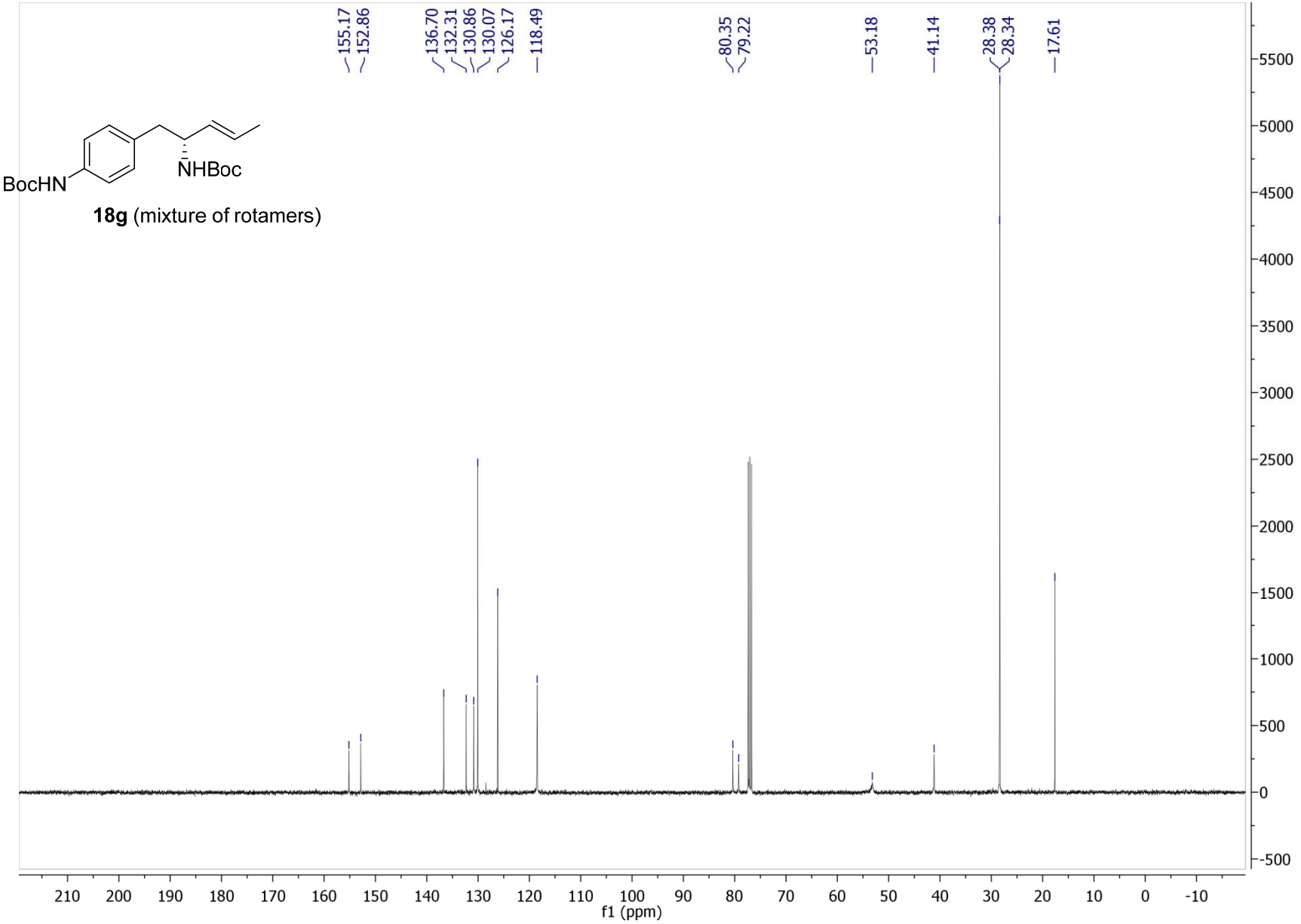
18f (mixture of rotamers)



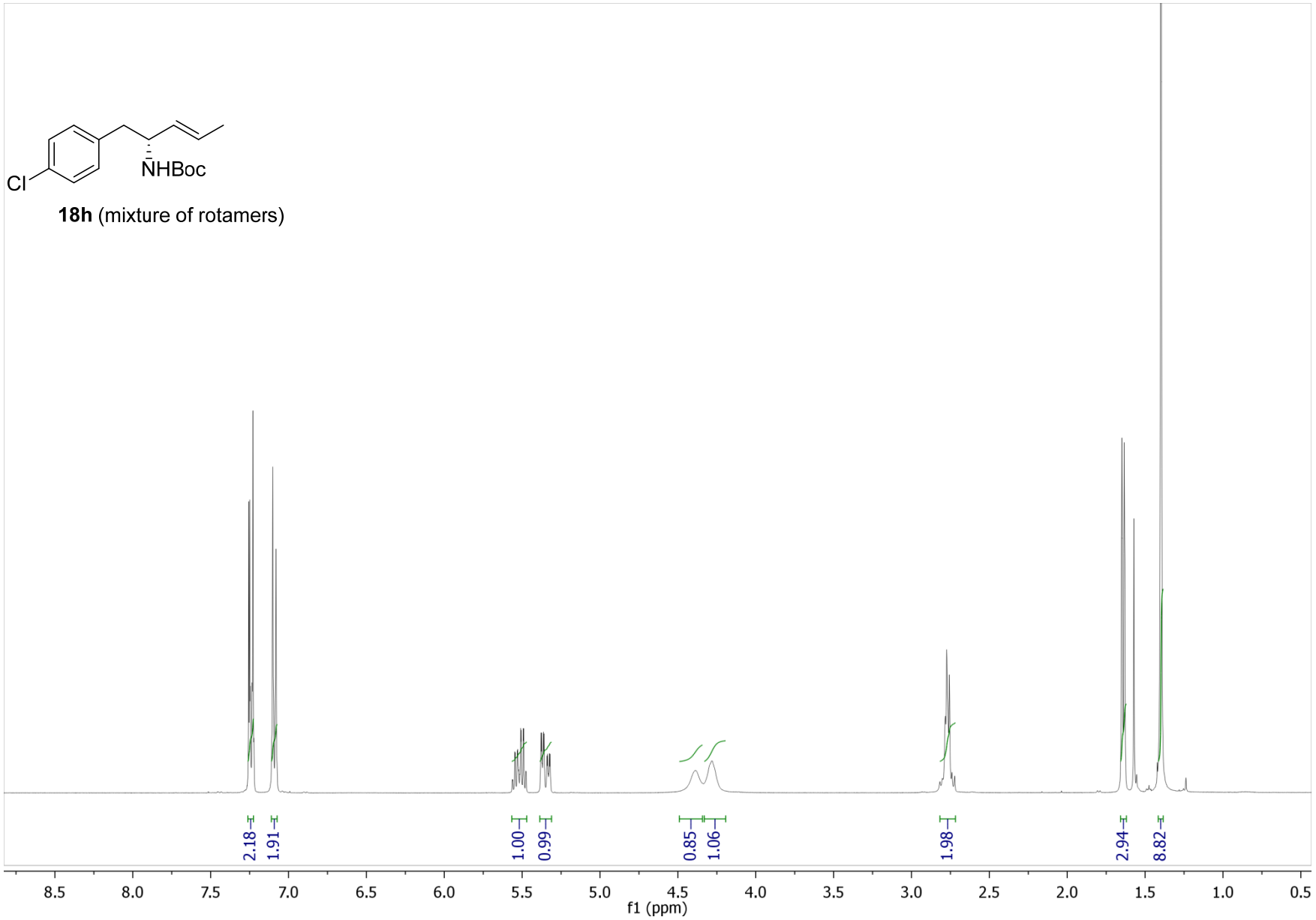
18f (mixture of rotamers)

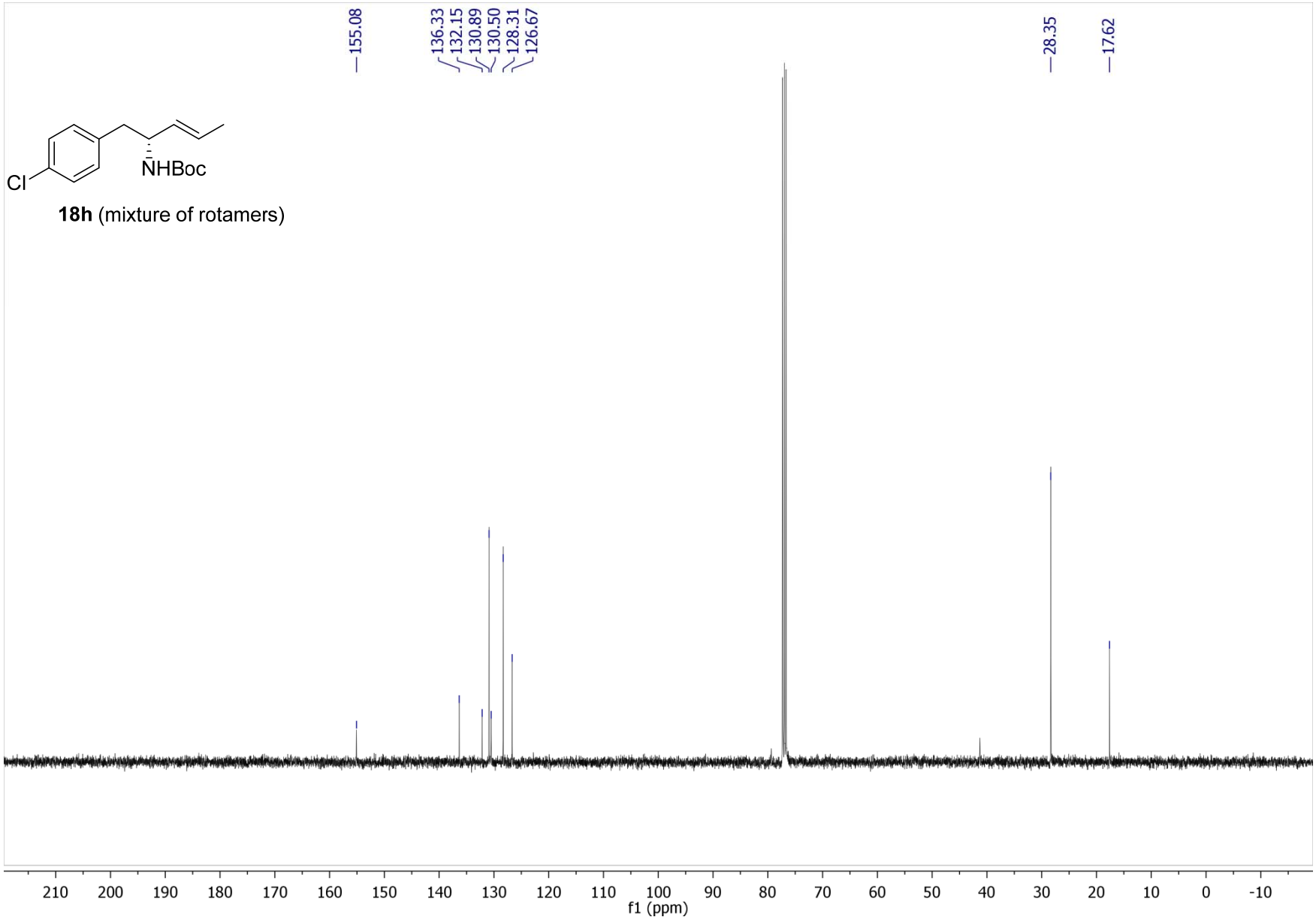


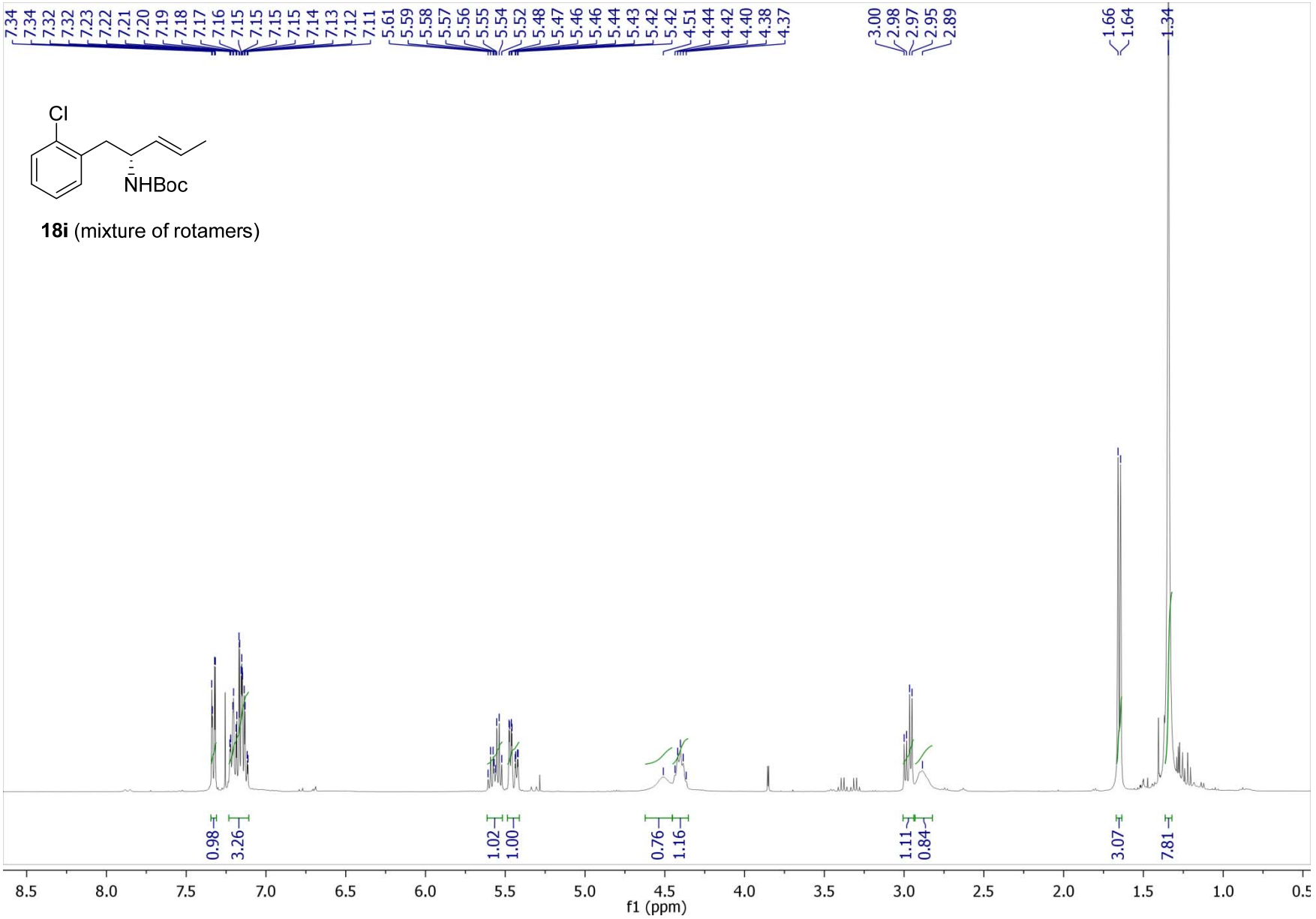
18g (mixture of rotamers)

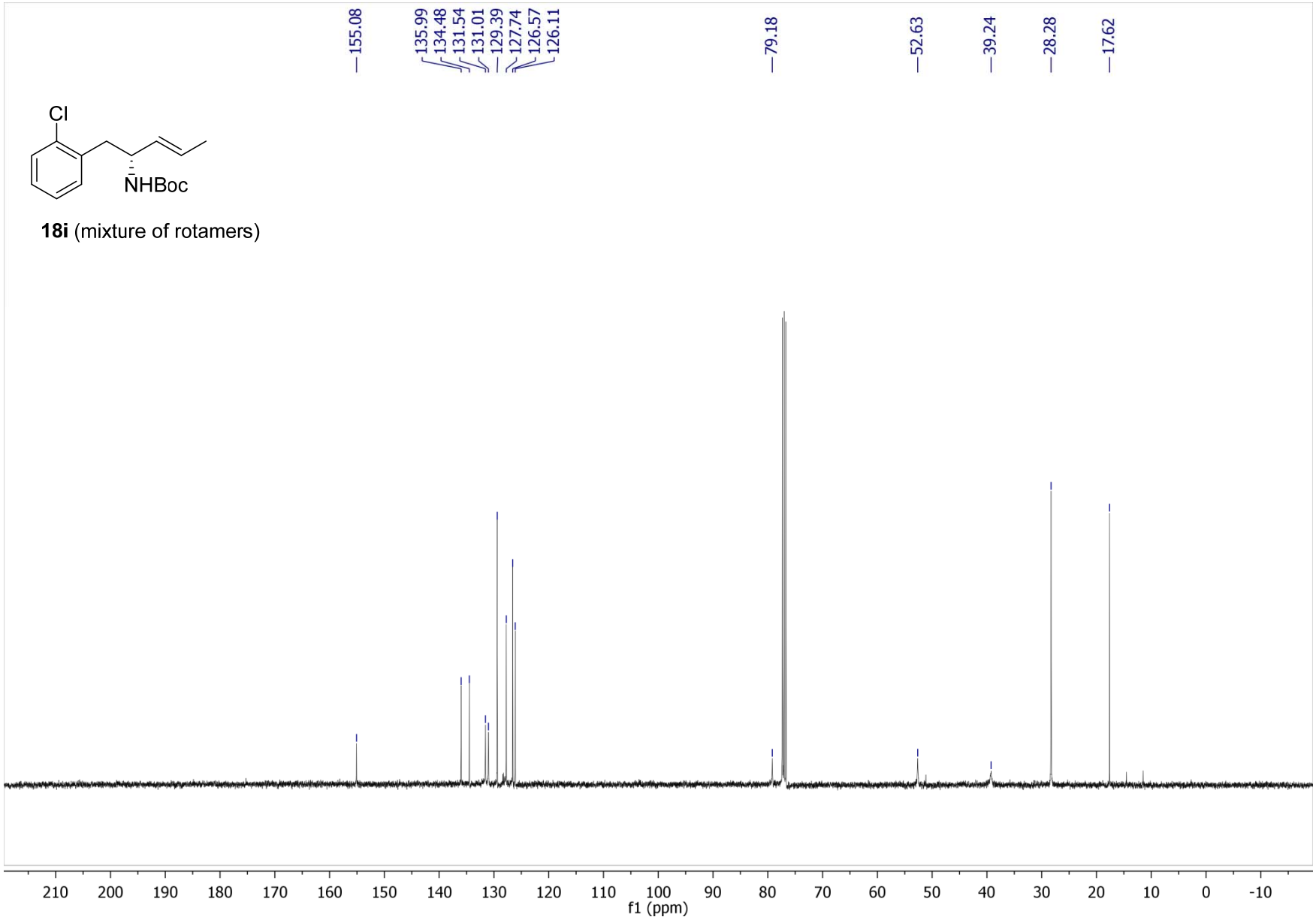


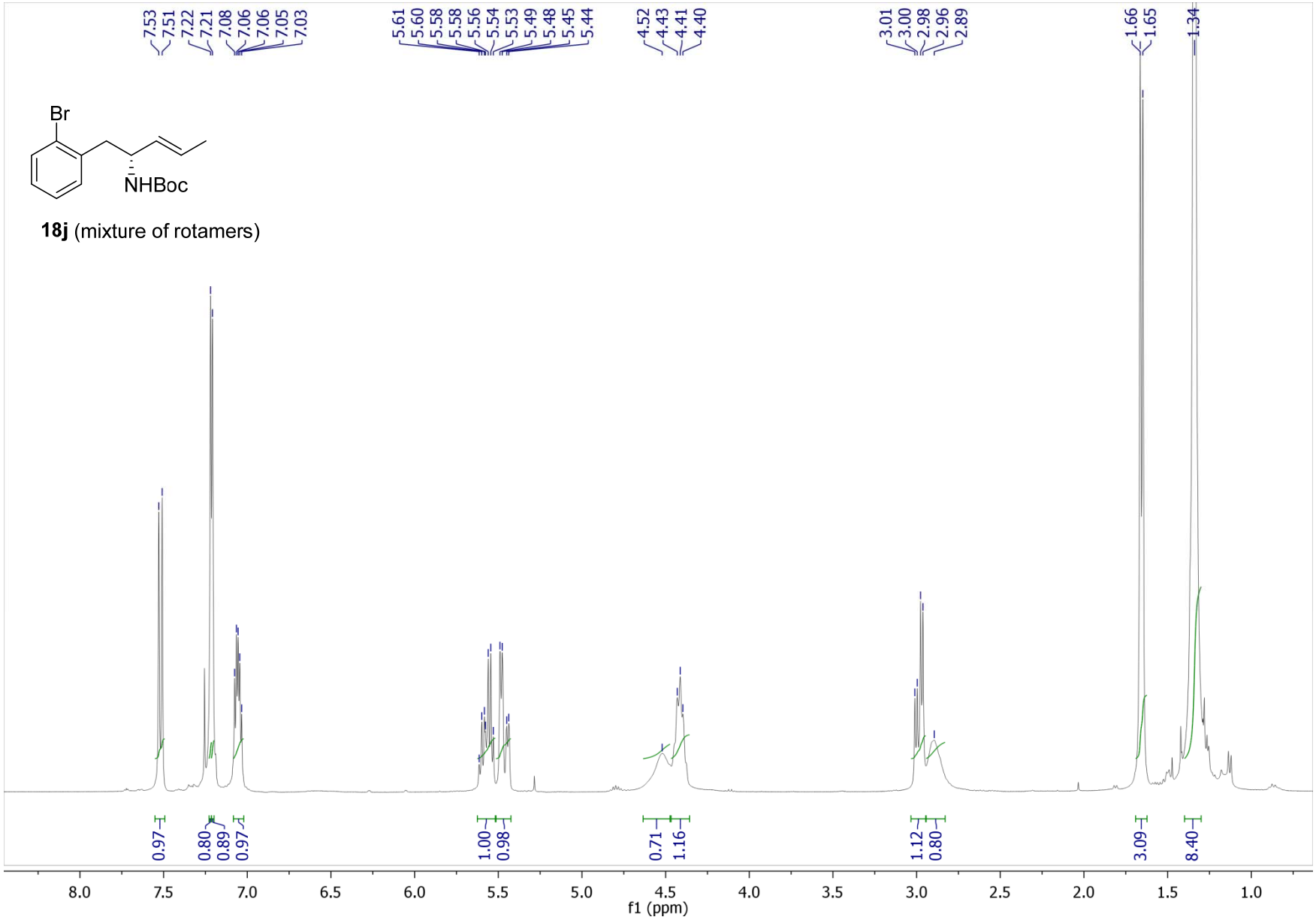
18g (mixture of rotamers)

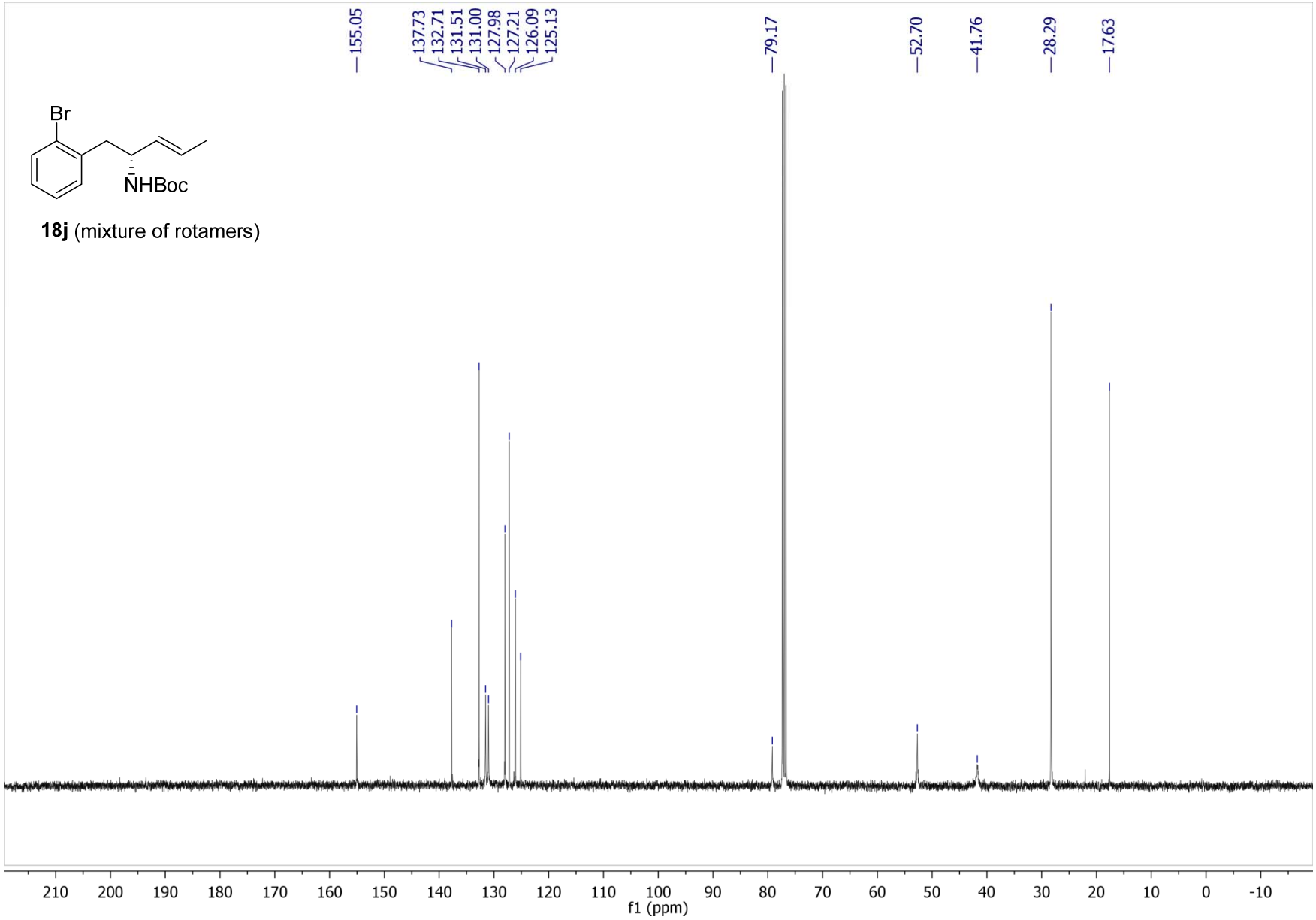

Cl
NHBoc
18h (mixture of rotamers)
2.18
1.91
1.00
0.99
0.85
1.06
1.98
2.94
8.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

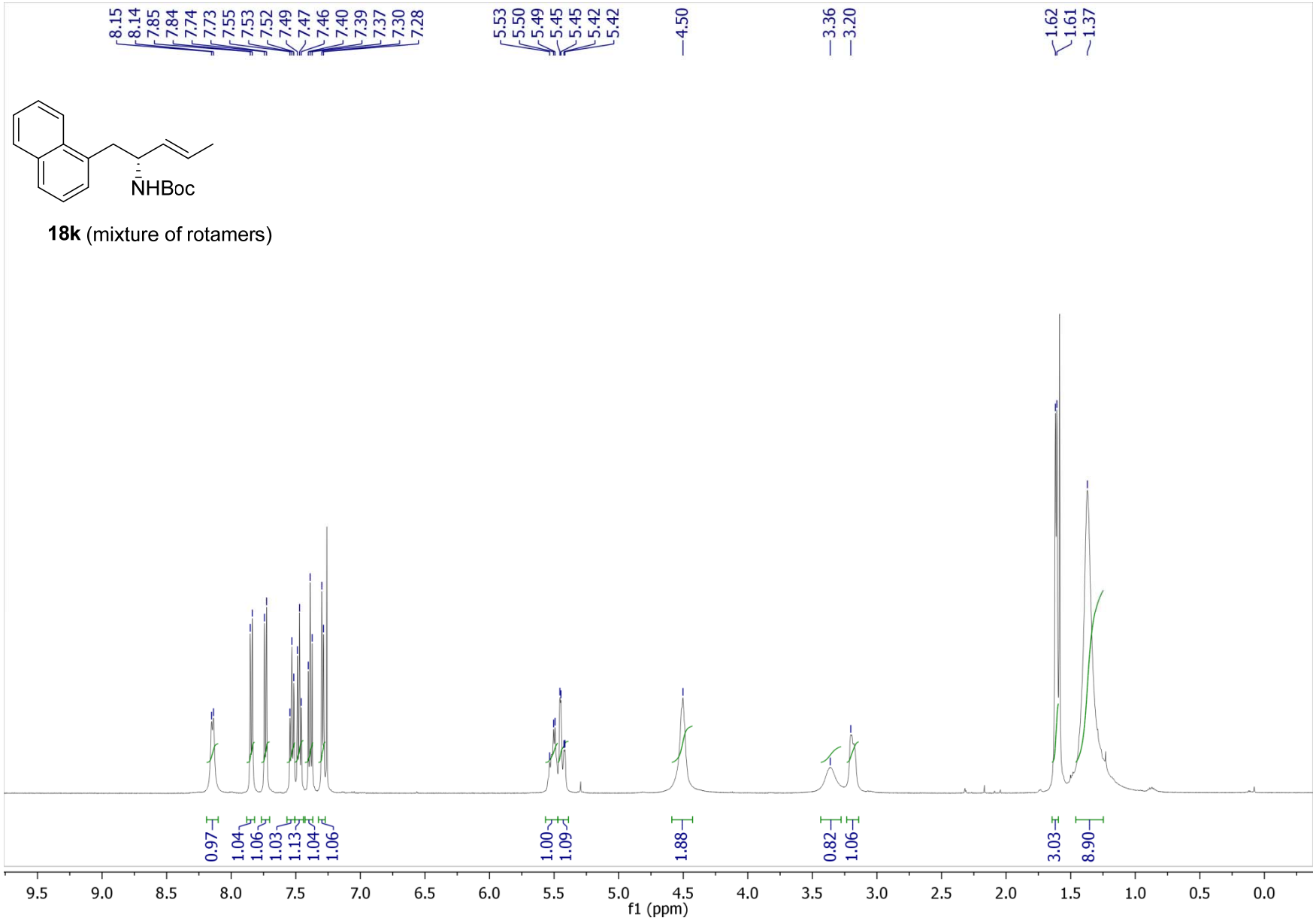

155.08
136.33
132.15
130.89
130.50
128.31
126.67
28.35
17.62
Cl
NHBoc
18h (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.34
7.34
7.32
7.32
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.15
7.15
7.15
7.14
7.13
7.12
7.11
5.61
5.59
5.58
5.57
5.56
5.55
5.54
5.52
5.48
5.47
5.46
5.46
5.44
5.43
5.42
5.42
4.51
4.44
4.42
4.40
4.38
4.37
3.00
2.98
2.97
2.95
2.89
1.66
1.64
1.34
Cl
NHBoc
18i (mixture of rotamers)
0.98
3.26
1.02
1.00
0.76
1.16
1.11
0.84
3.07
7.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

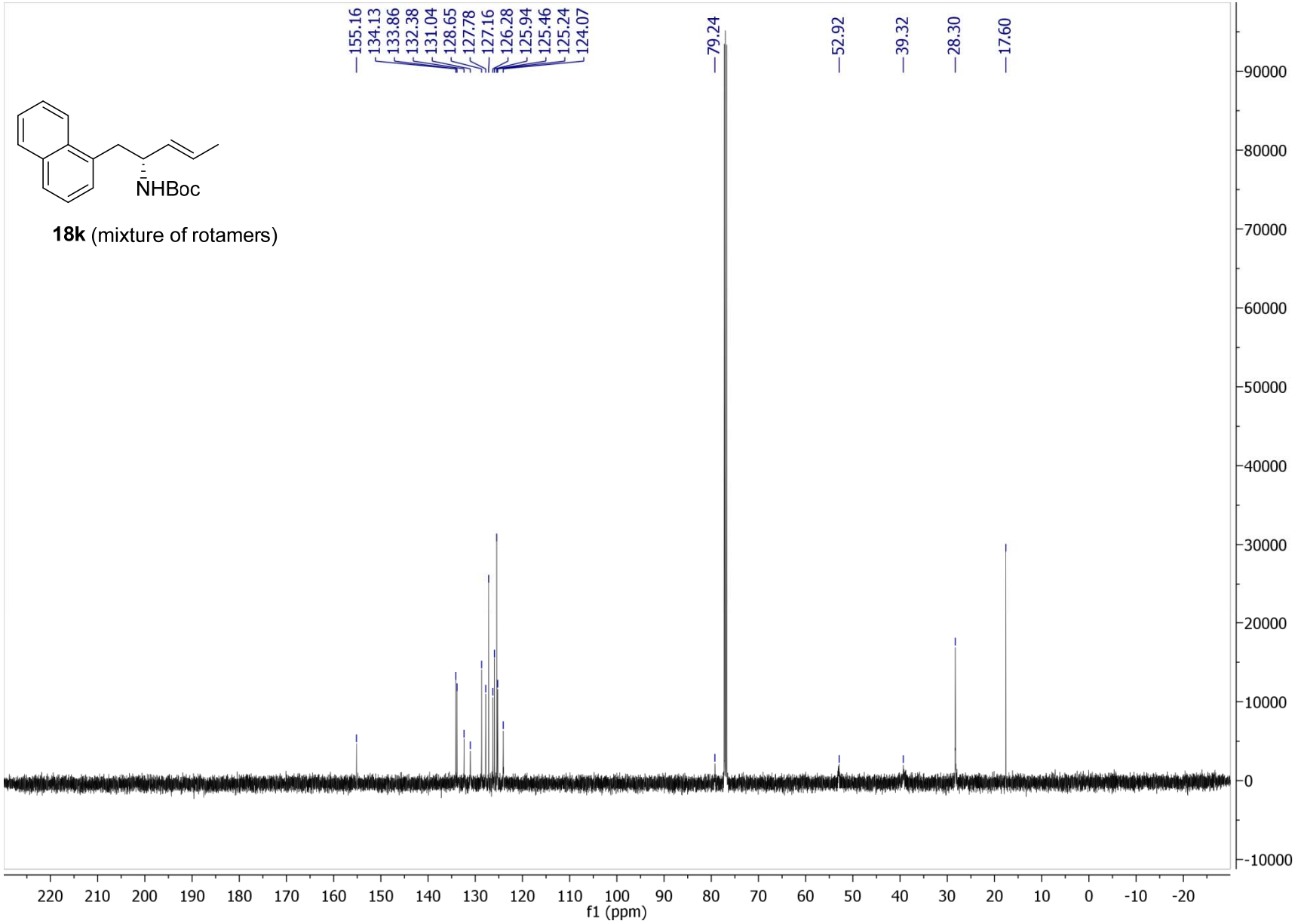

155.08
135.99
134.48
131.54
131.01
129.39
127.74
126.57
126.11
79.18
52.63
39.24
28.28
17.62
Cl
NHBoc
18i (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.53
7.51
7.22
7.21
7.08
7.06
7.06
7.05
7.03
5.61
5.60
5.58
5.58
5.56
5.54
5.53
5.49
5.48
5.45
5.44
4.52
4.43
4.41
4.40
3.01
3.00
2.98
2.96
2.89
1.66
1.65
1.34
Br
NHBoc
18j (mixture of rotamers)
0.97
0.80
0.89
0.97
1.00
0.98
0.71
1.16
1.12
0.80
3.09
8.40
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

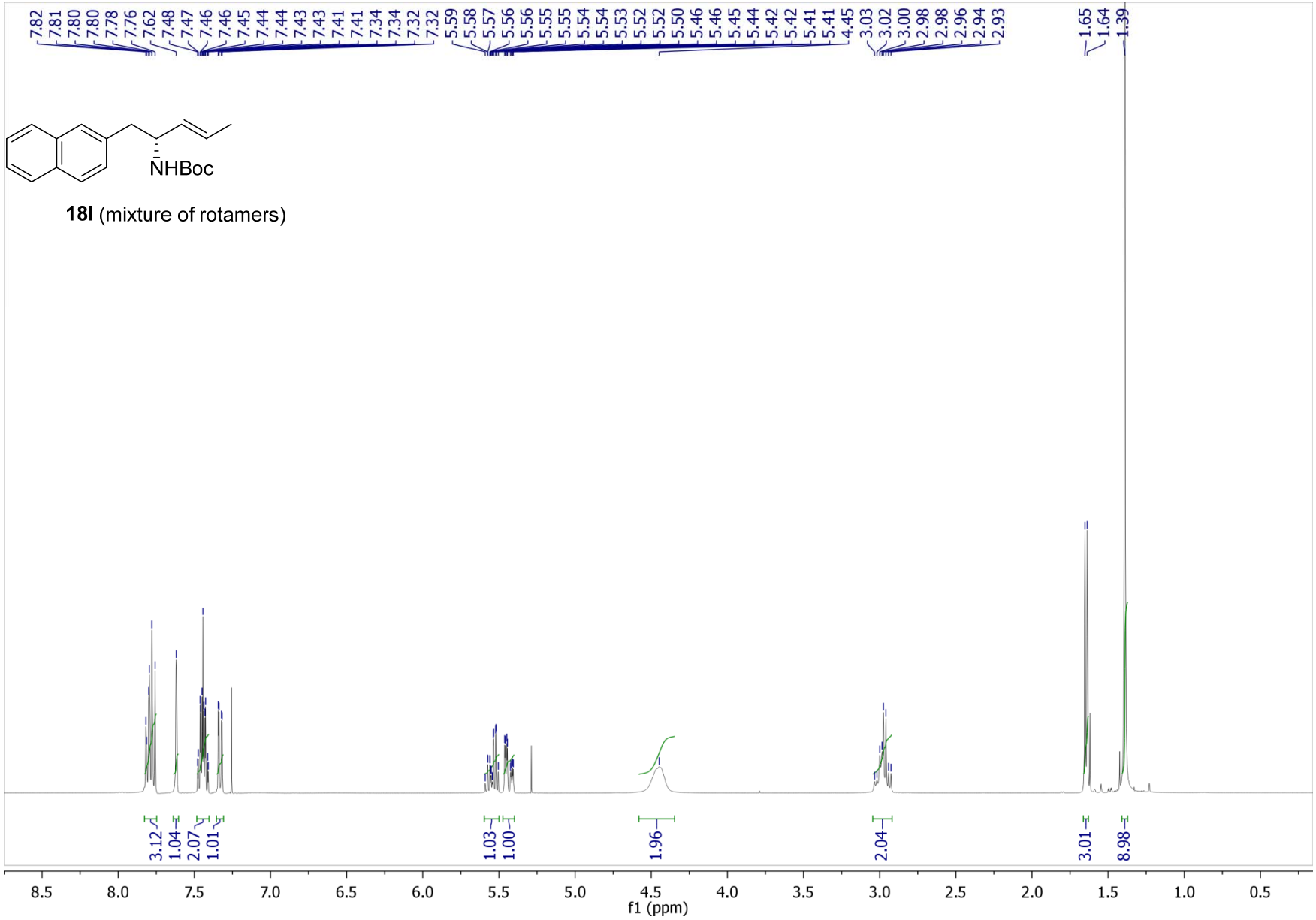

155.05
137.73
132.71
131.51
131.00
127.98
127.21
126.09
125.13
79.17
52.70
41.76
28.29
17.63
Br
NHBoc
18j (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



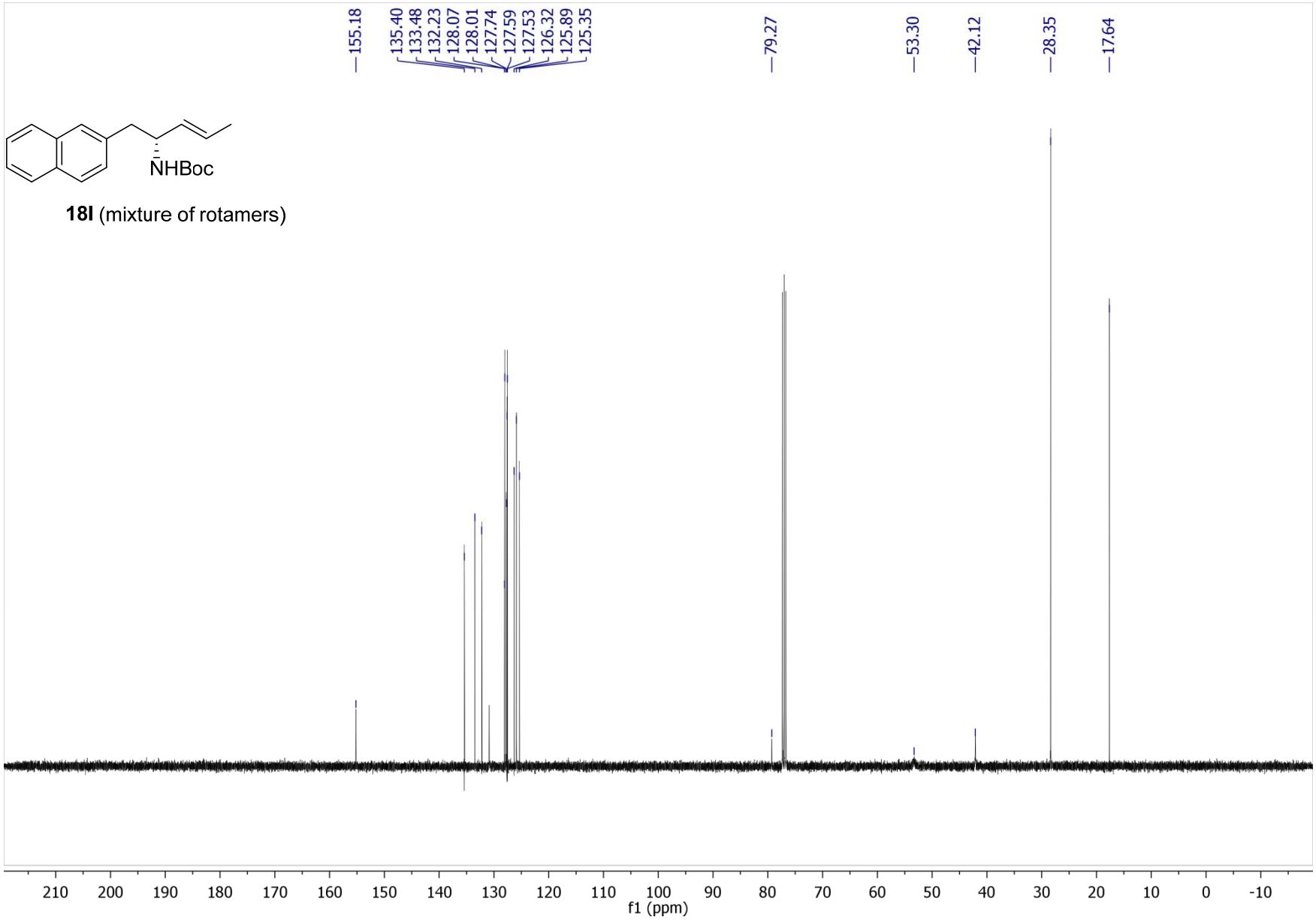
18k (mixture of rotamers)



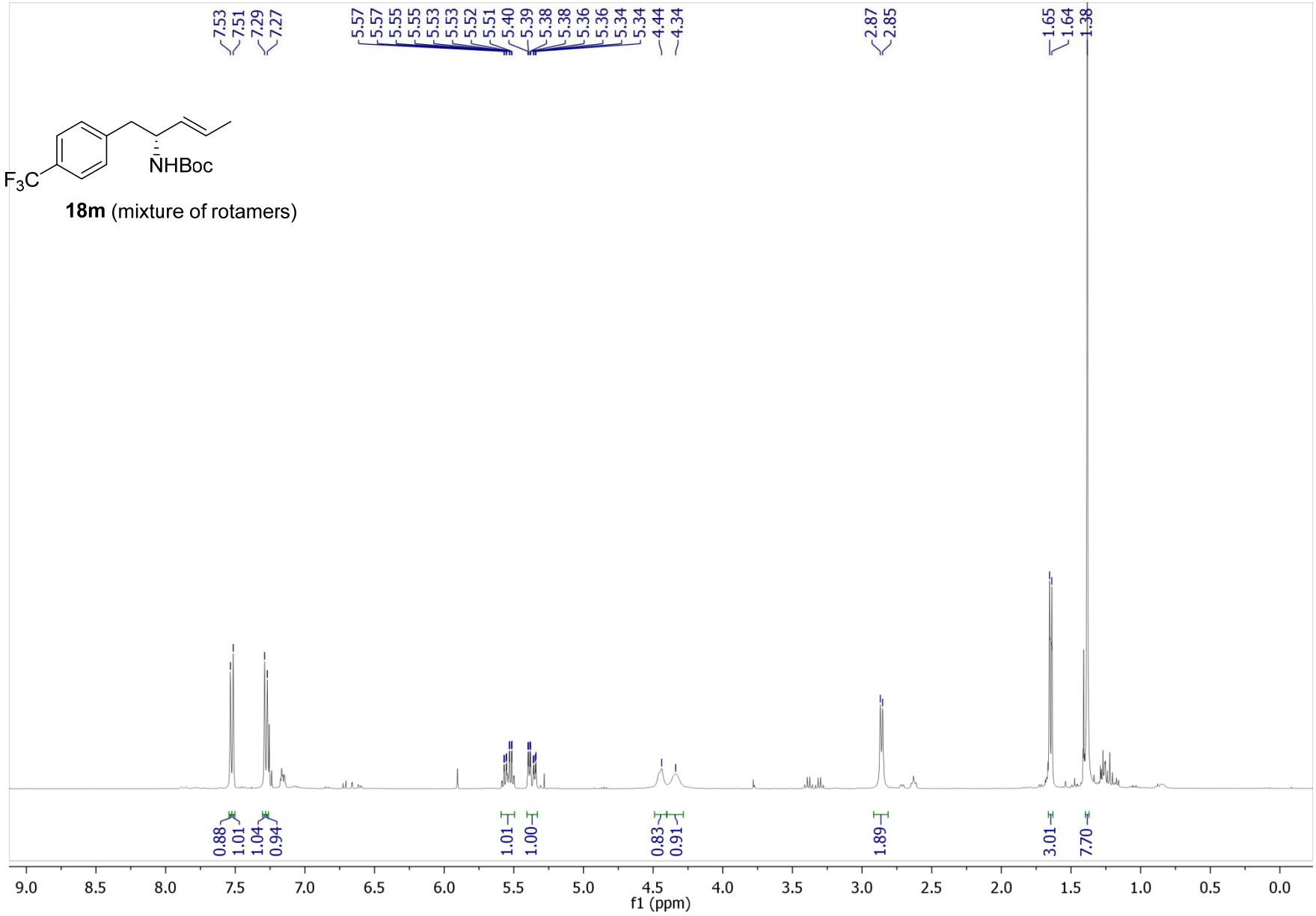
18k (mixture of rotamers)



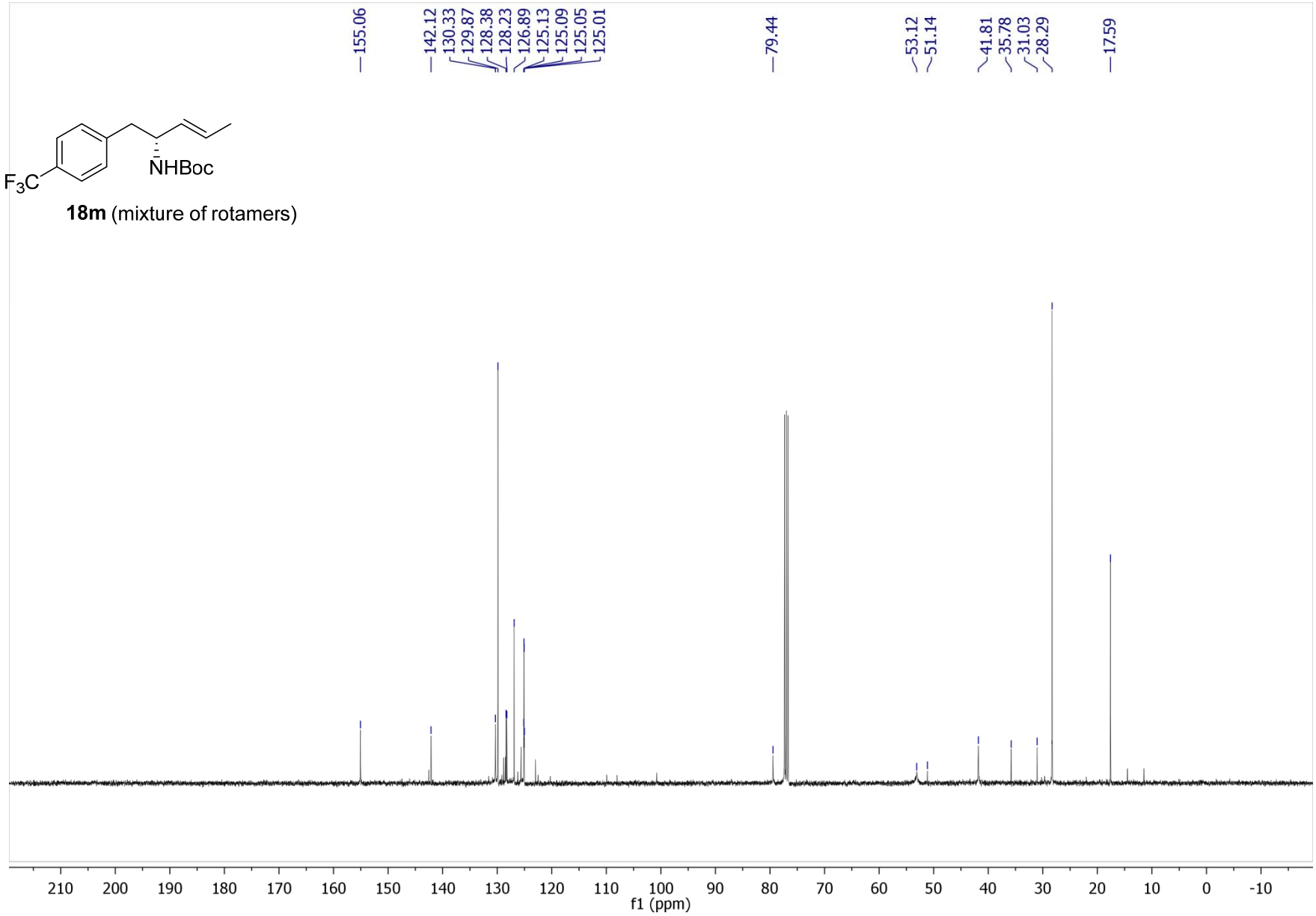
18l (mixture of rotamers)



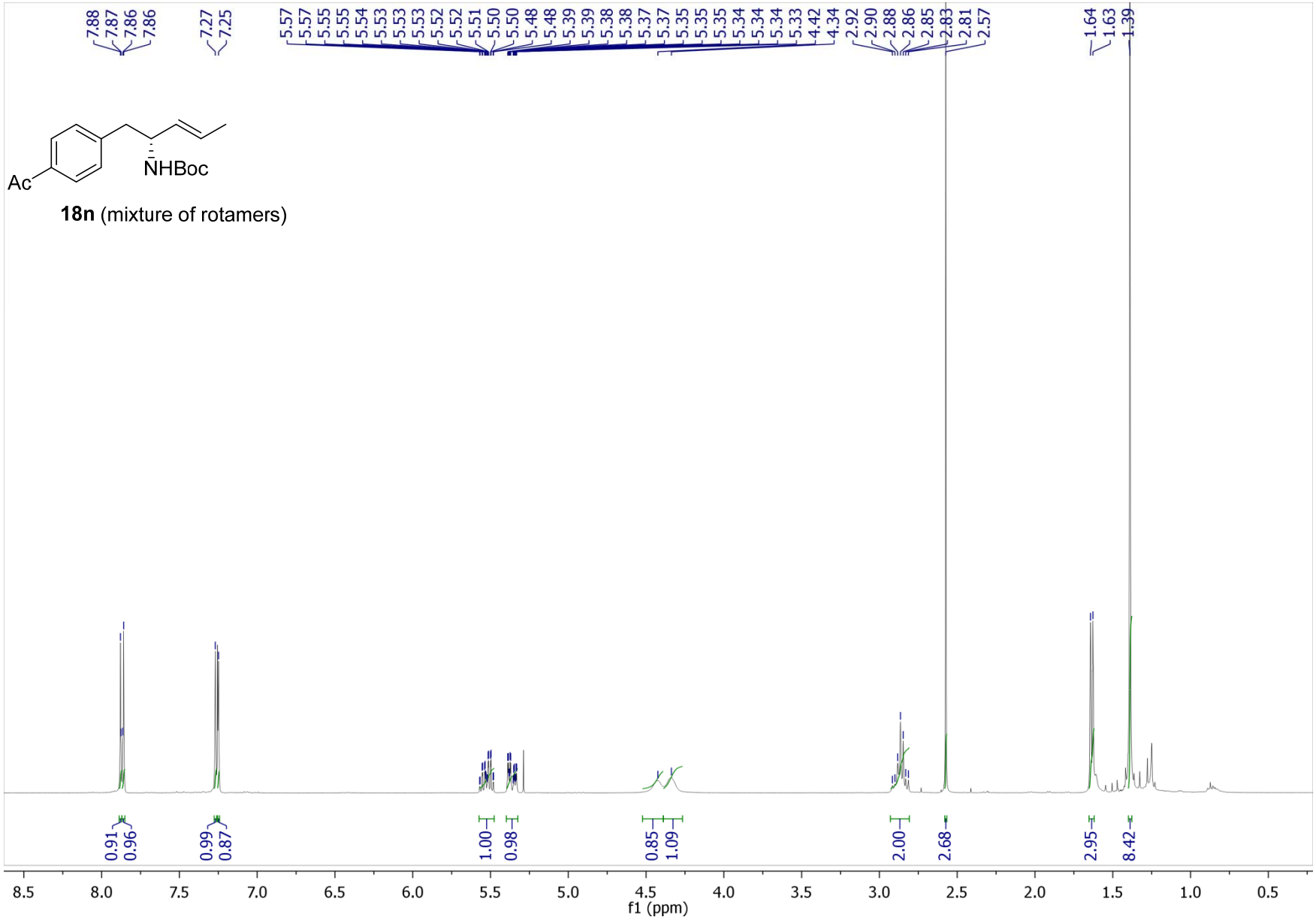
18l (mixture of rotamers)

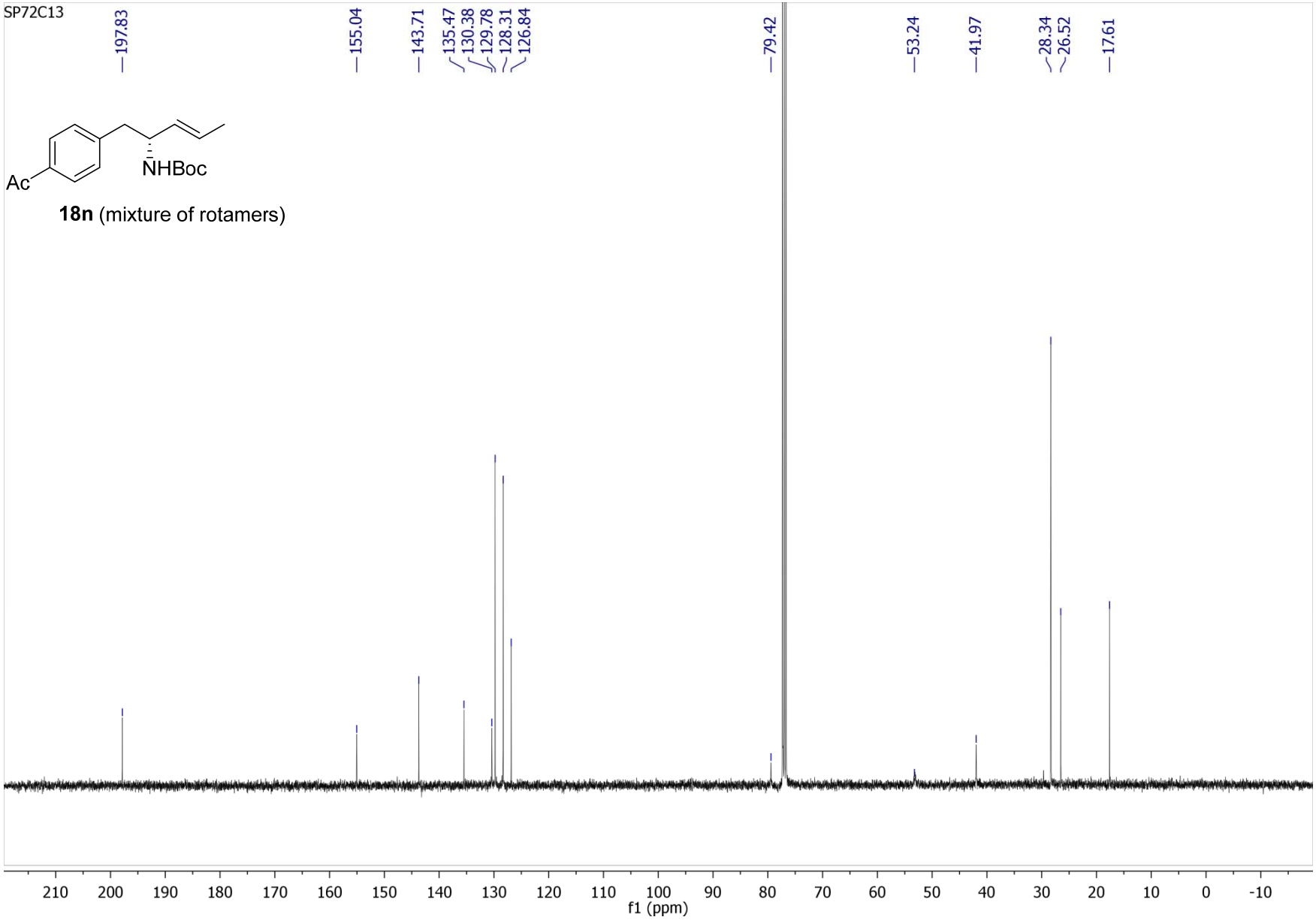


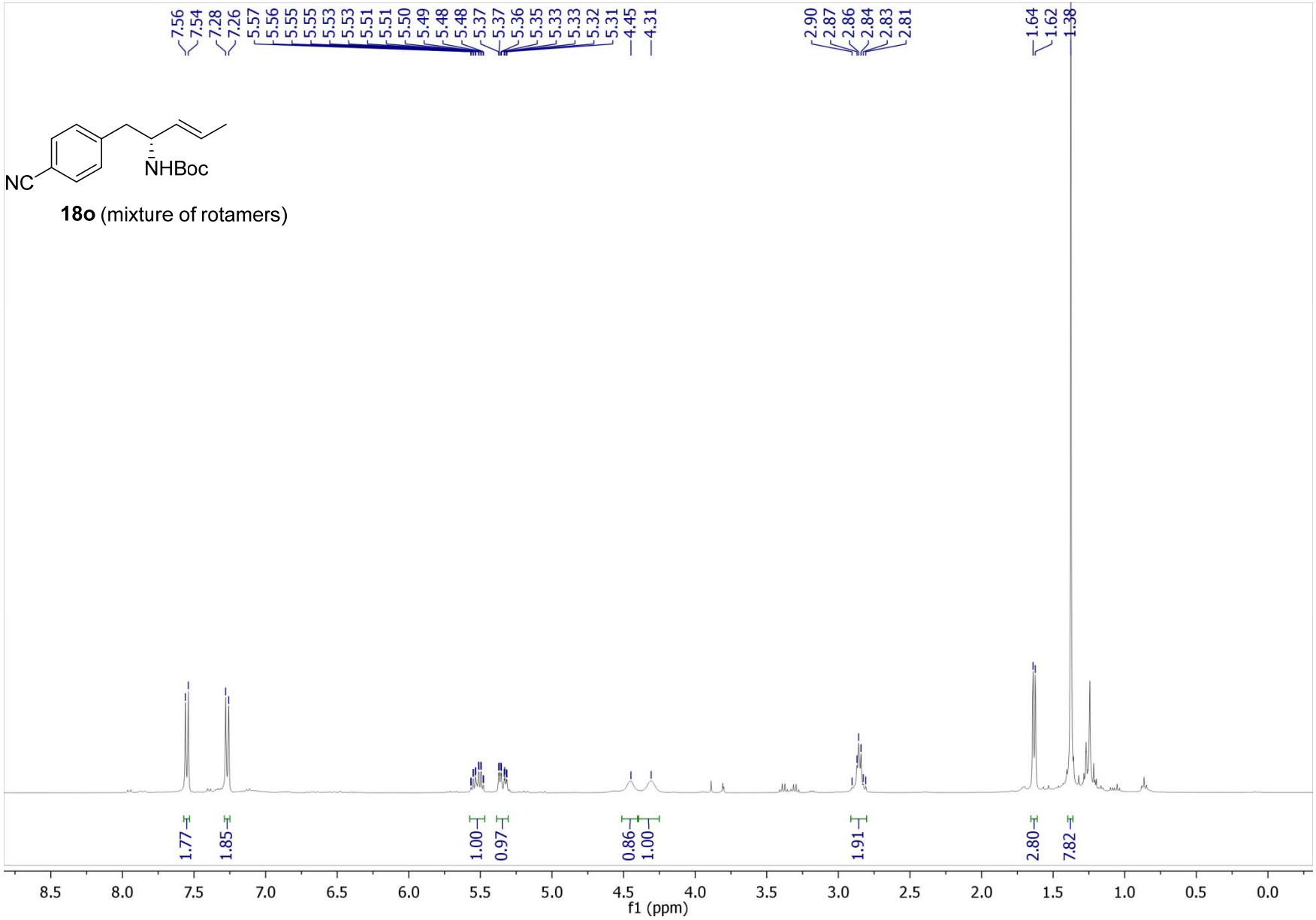
18m (mixture of rotamers)



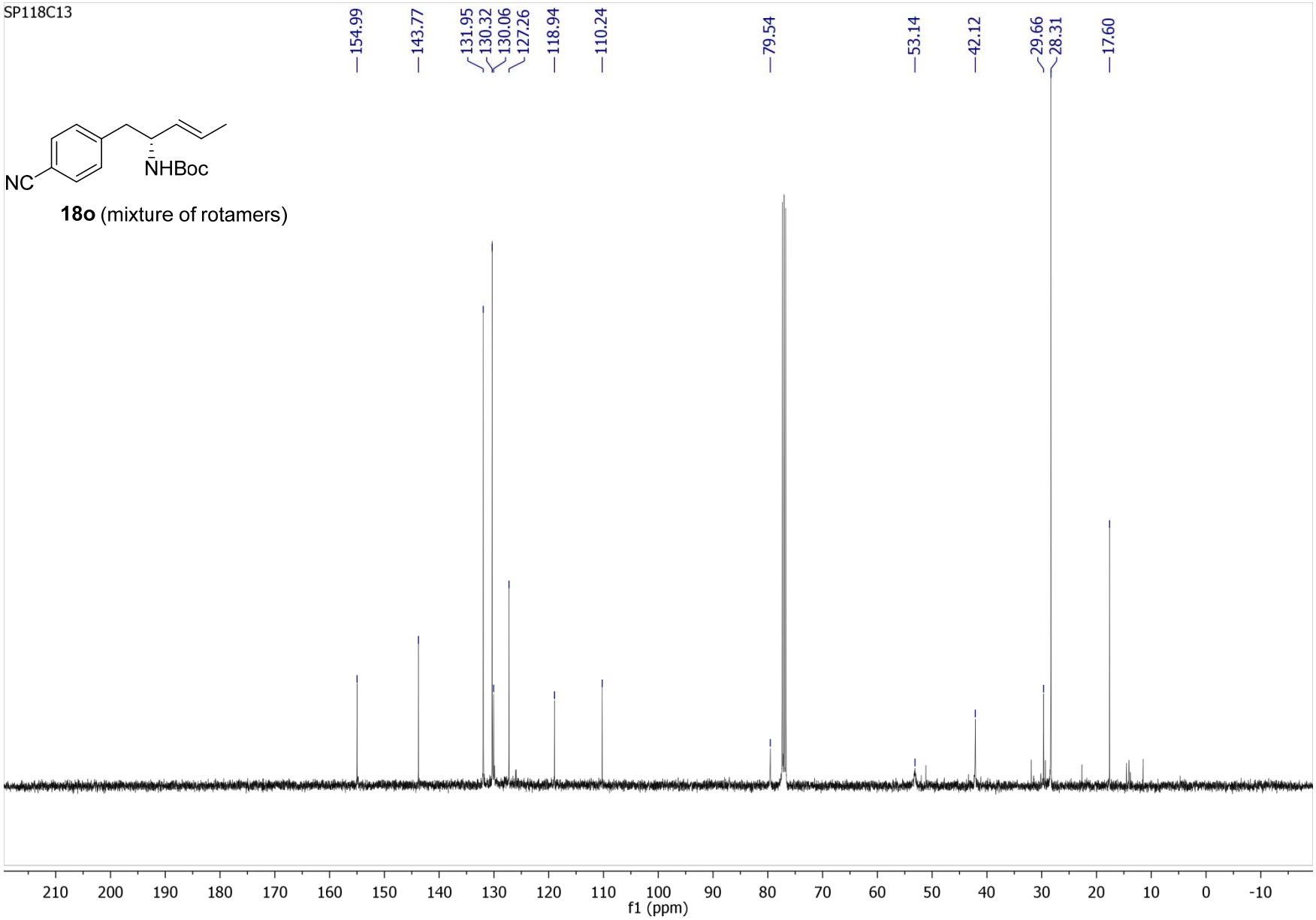
18m (mixture of rotamers)

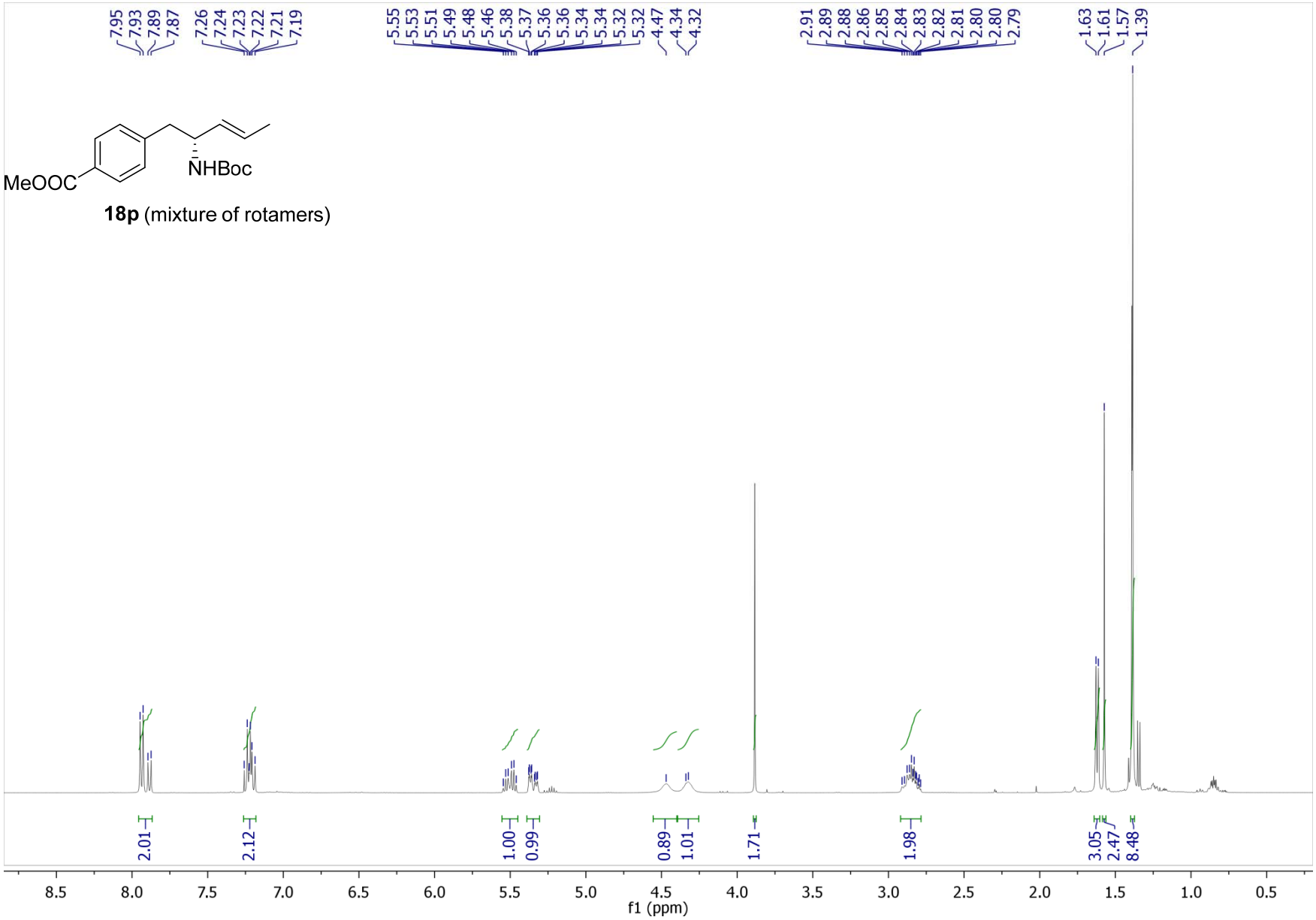

7.88
7.87
7.86
7.86
7.27
7.25
5.57
5.57
5.55
5.55
5.54
5.53
5.53
5.53
5.52
5.52
5.51
5.50
5.50
5.48
5.48
5.39
5.39
5.38
5.38
5.37
5.37
5.35
5.35
5.35
5.34
5.34
5.34
5.33
4.42
4.34
2.92
2.90
2.88
2.86
2.85
2.83
2.81
2.57
1.64
1.63
1.39
Ac
NHBoc
18n (mixture of rotamers)
0.91
0.96
0.99
0.87
1.00
0.98
0.85
1.09
2.00
2.68
2.95
8.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


SP72C13
197.83
155.04
143.71
135.47
130.38
129.78
128.31
126.84
79.42
53.24
41.97
28.34
26.52
17.61
Ac
NHBoc
18n (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

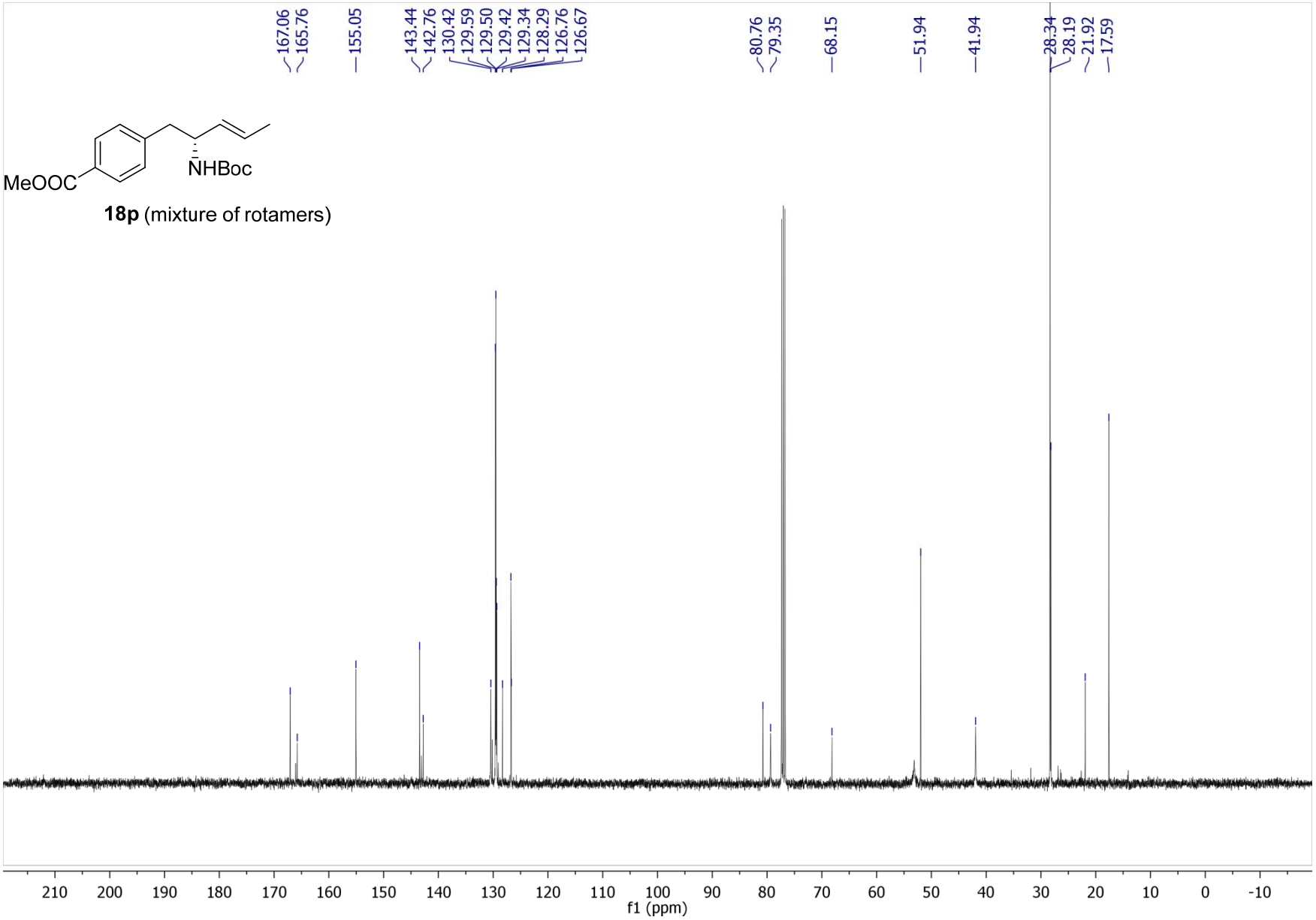


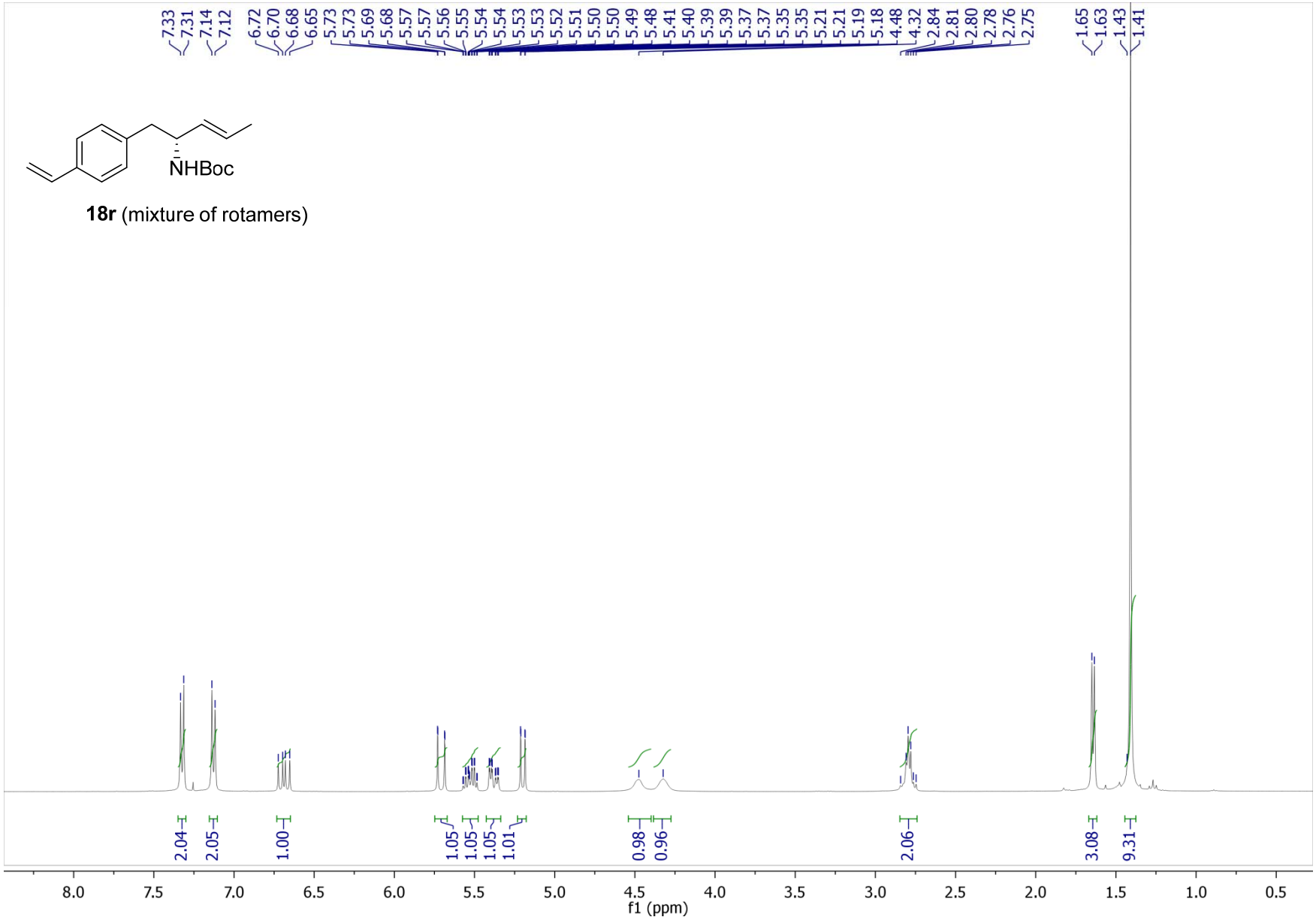
18o (mixture of rotamers)


SP118C13
154.99
143.77
131.95
130.32
130.06
127.26
118.94
110.24
79.54
53.14
42.12
29.66
28.31
17.60
NC
NHBoc
18o (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

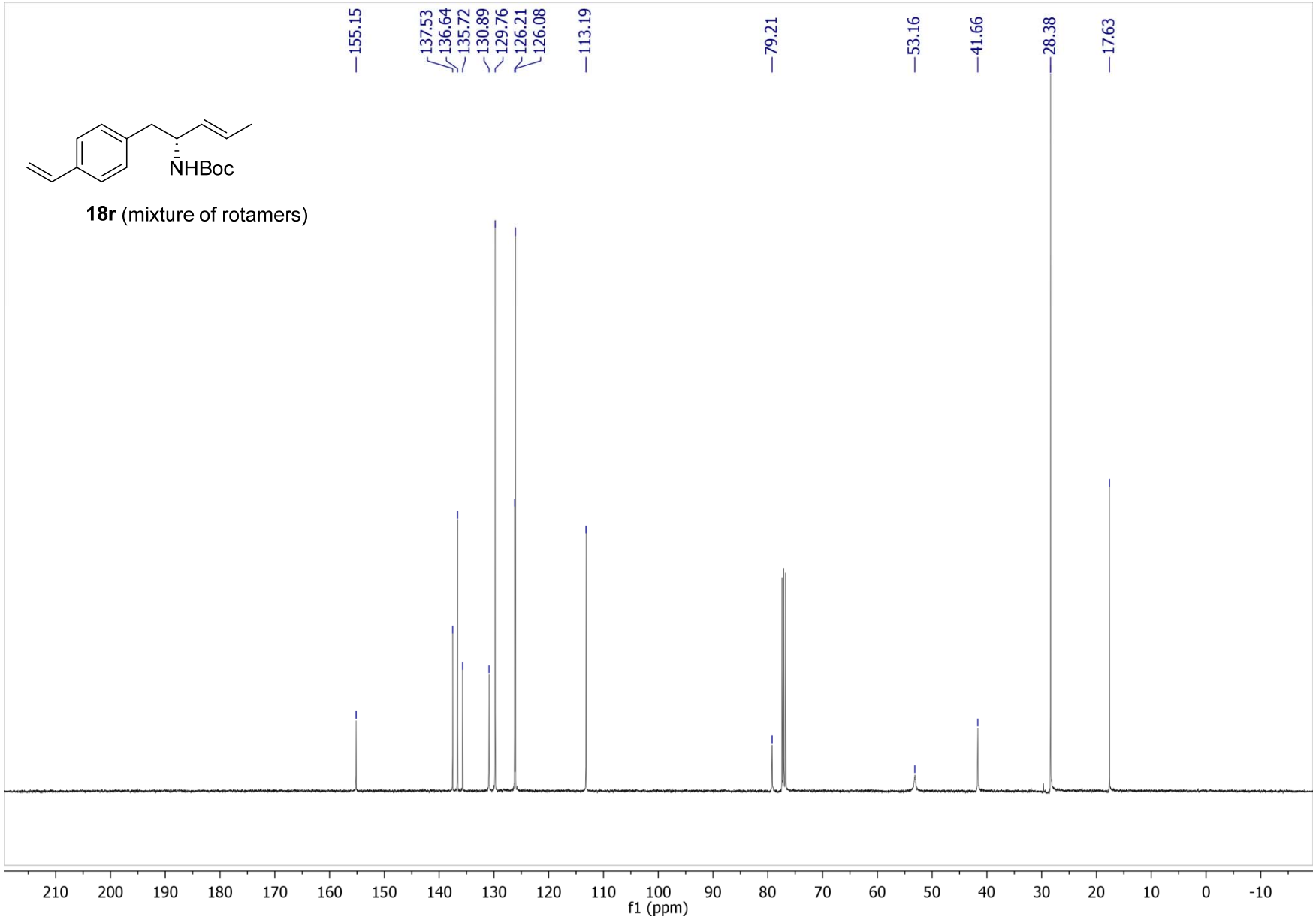


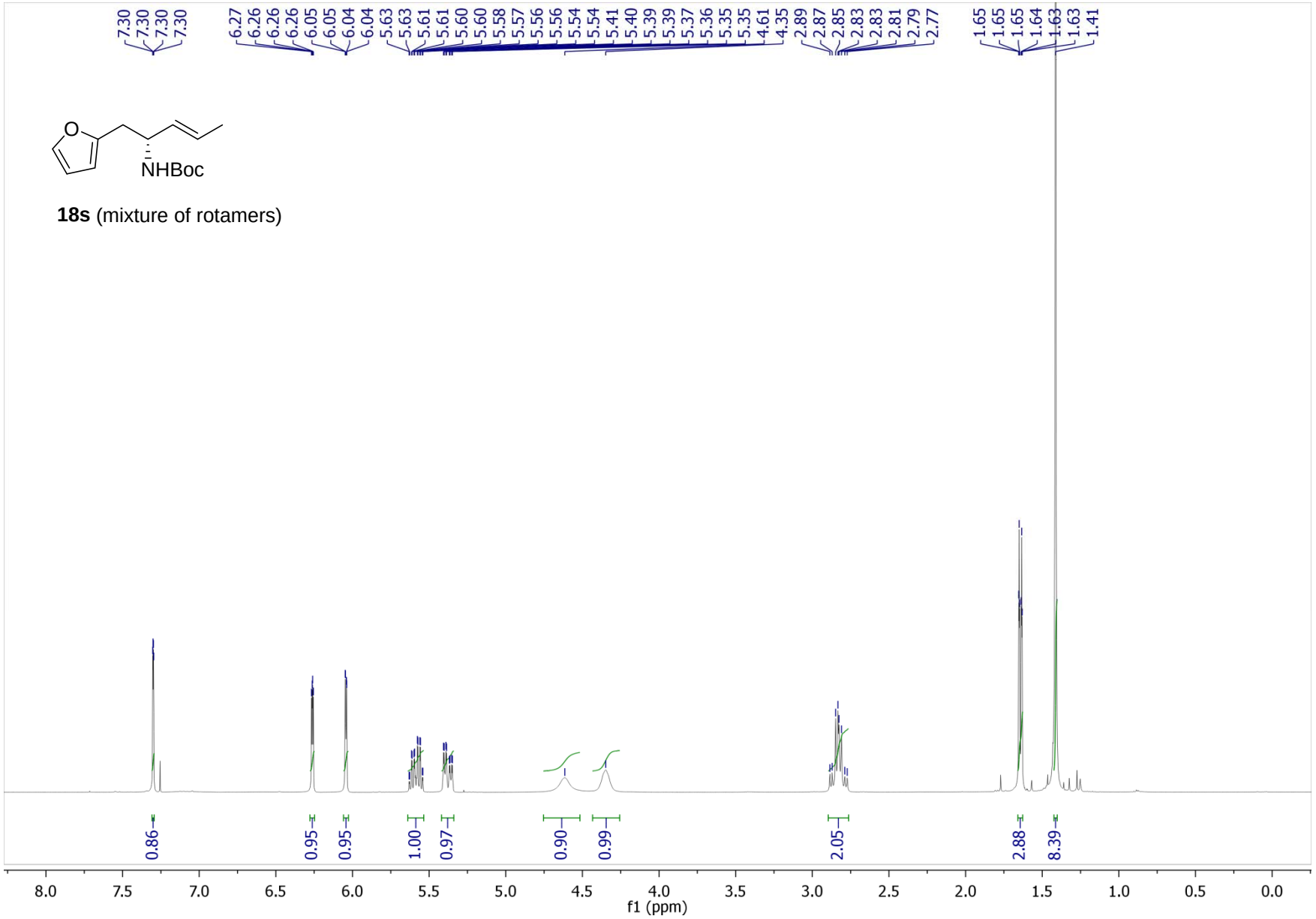
18p (mixture of rotamers)


167.06
165.76
155.05
143.44
142.76
130.42
129.59
129.50
129.42
129.34
128.29
126.76
126.67
80.76
79.35
68.15
51.94
41.94
28.34
28.19
21.92
17.59
MeOOC
NHBoc
18p (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



18r (mixture of rotamers)

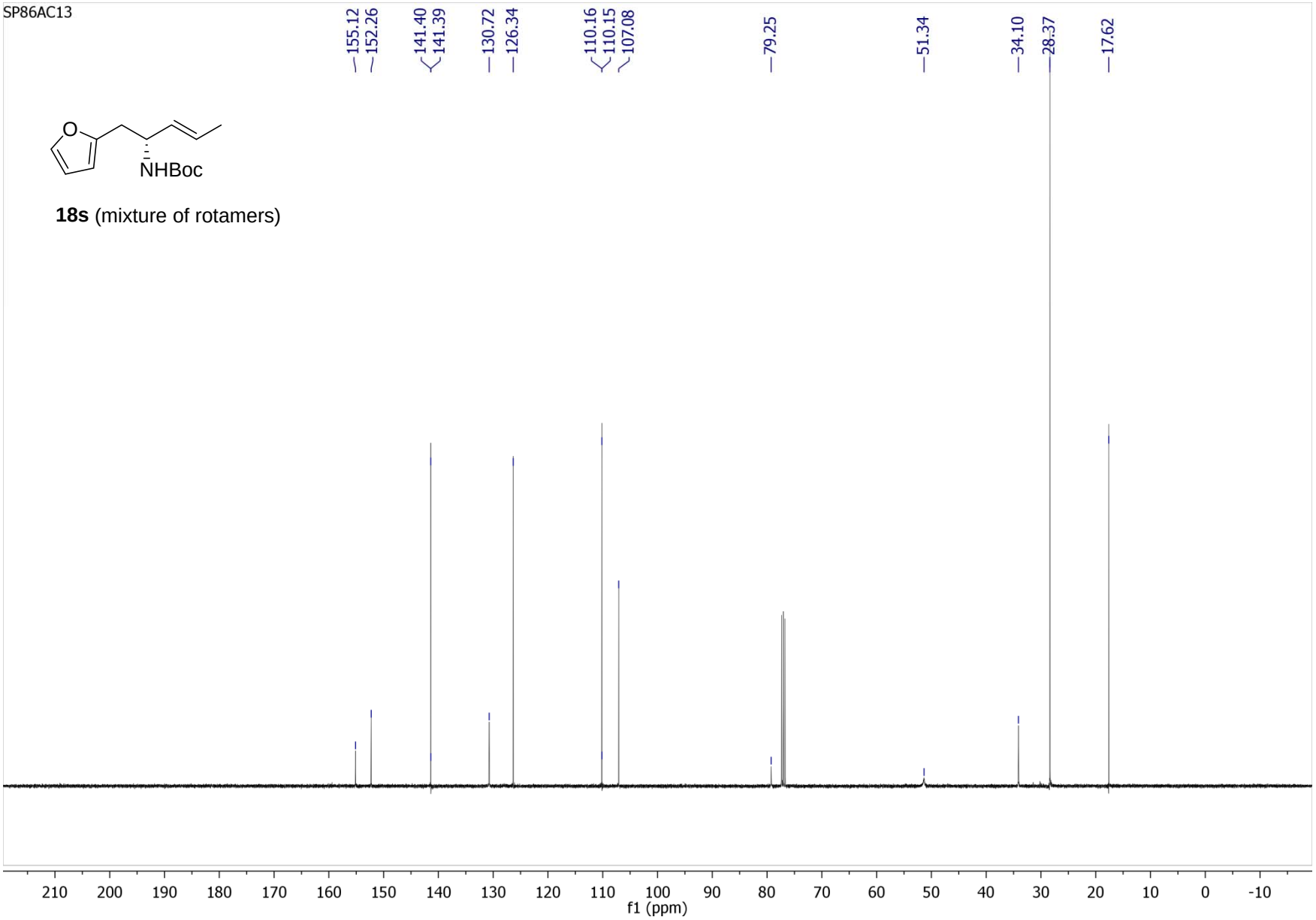

155.15
137.53
136.64
135.72
130.89
129.76
126.21
126.08
113.19
79.21
53.16
41.66
28.38
17.63
NHBoc
18r (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

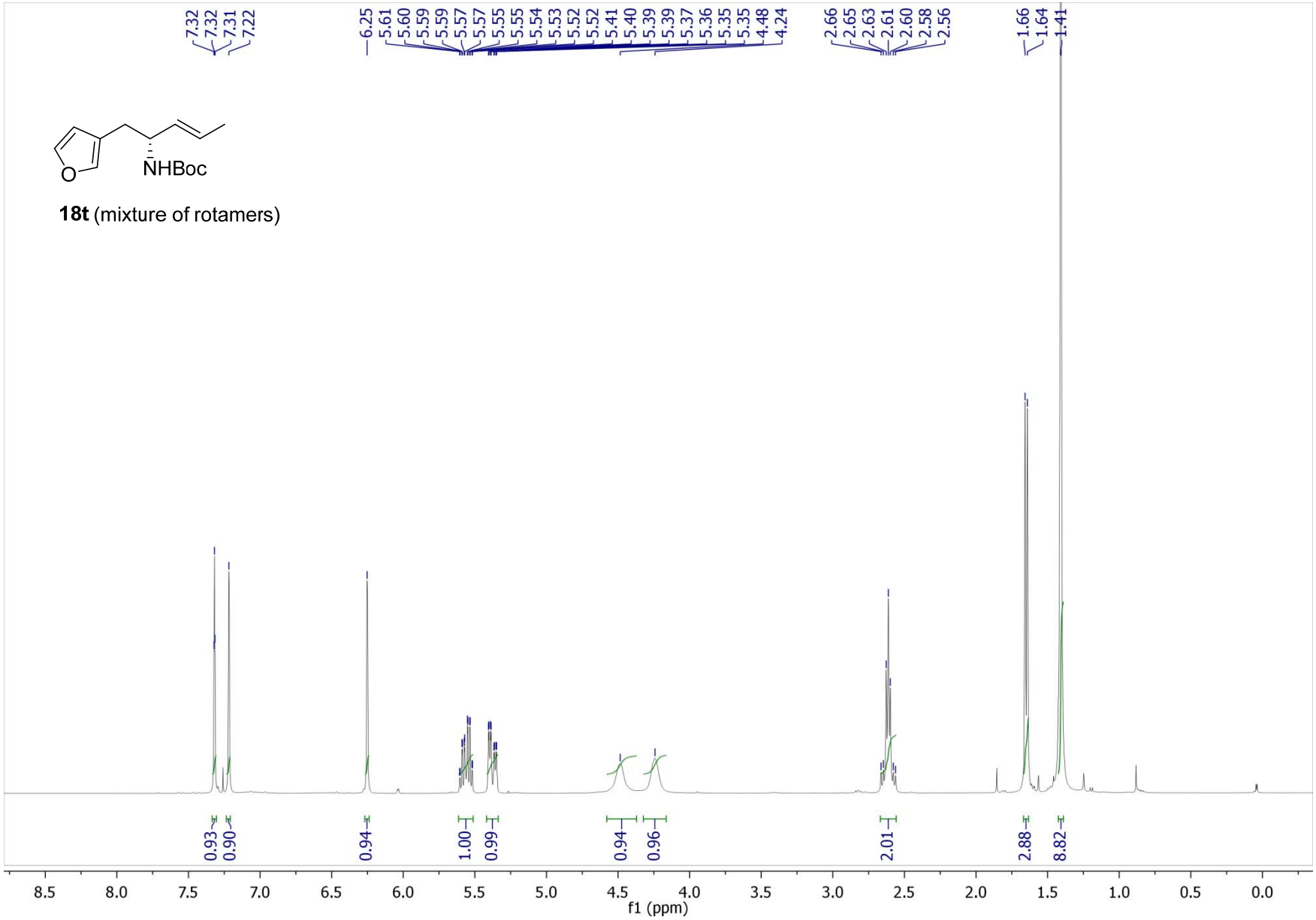


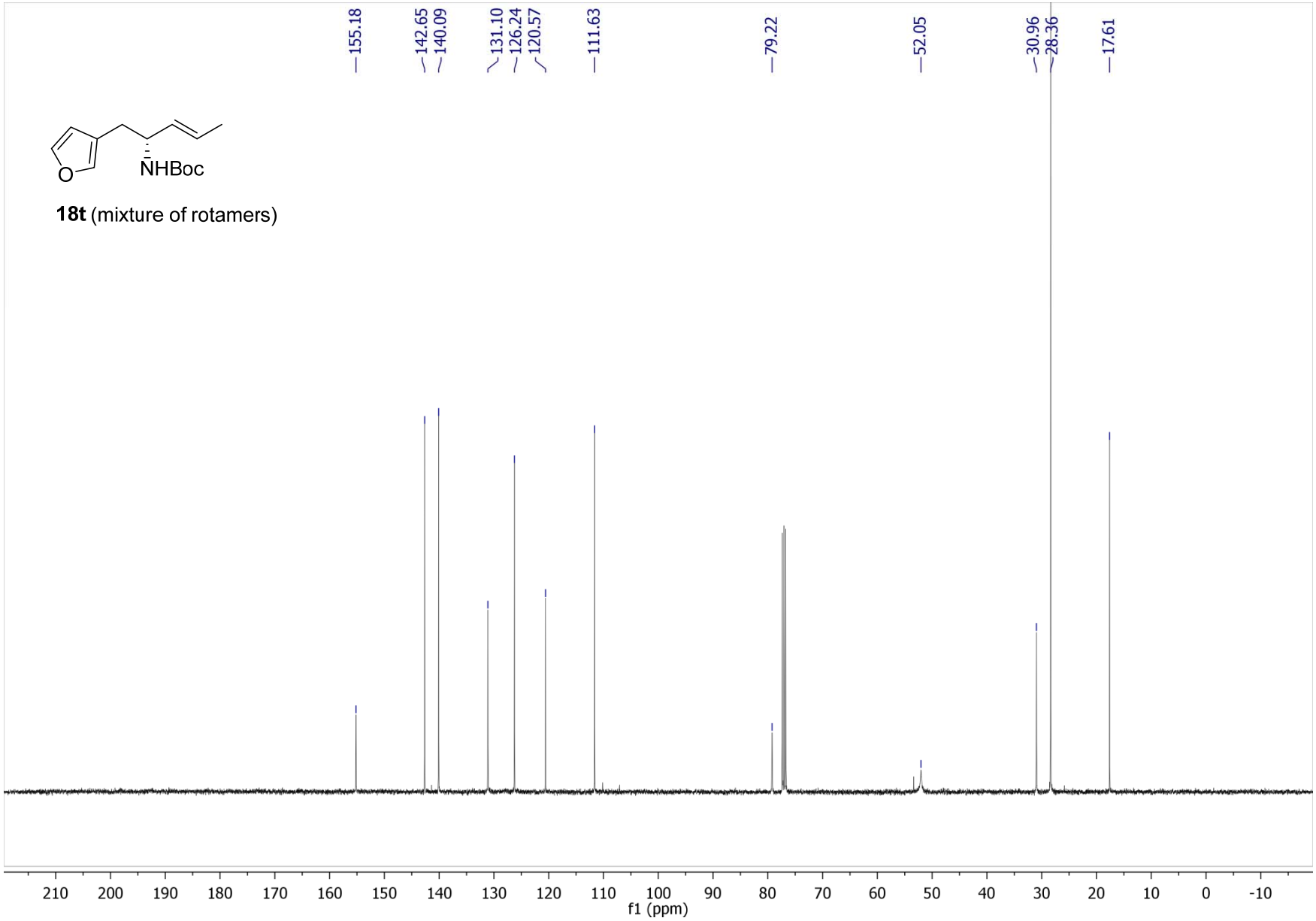
18s (mixture of rotamers)

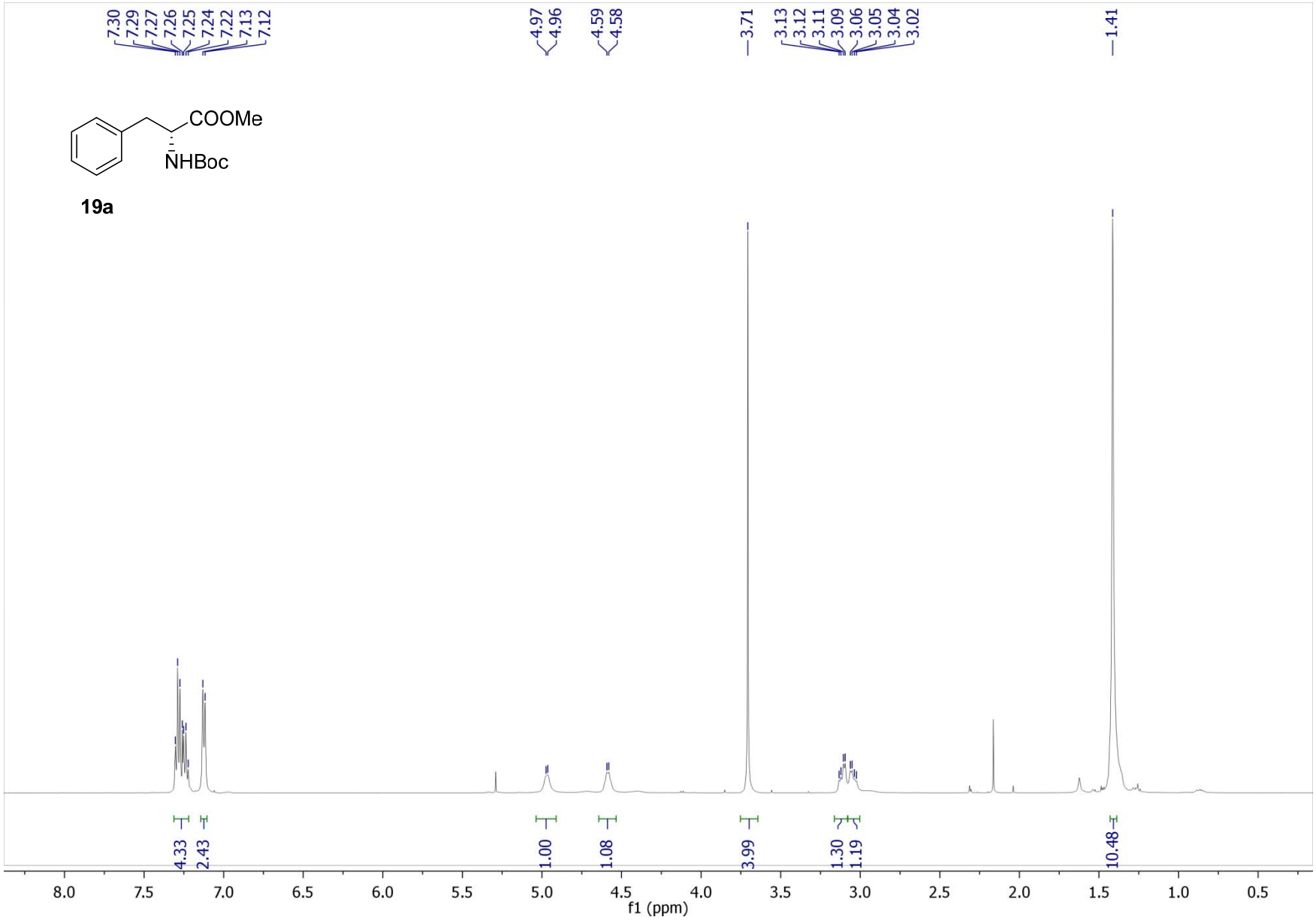
SP86AC13

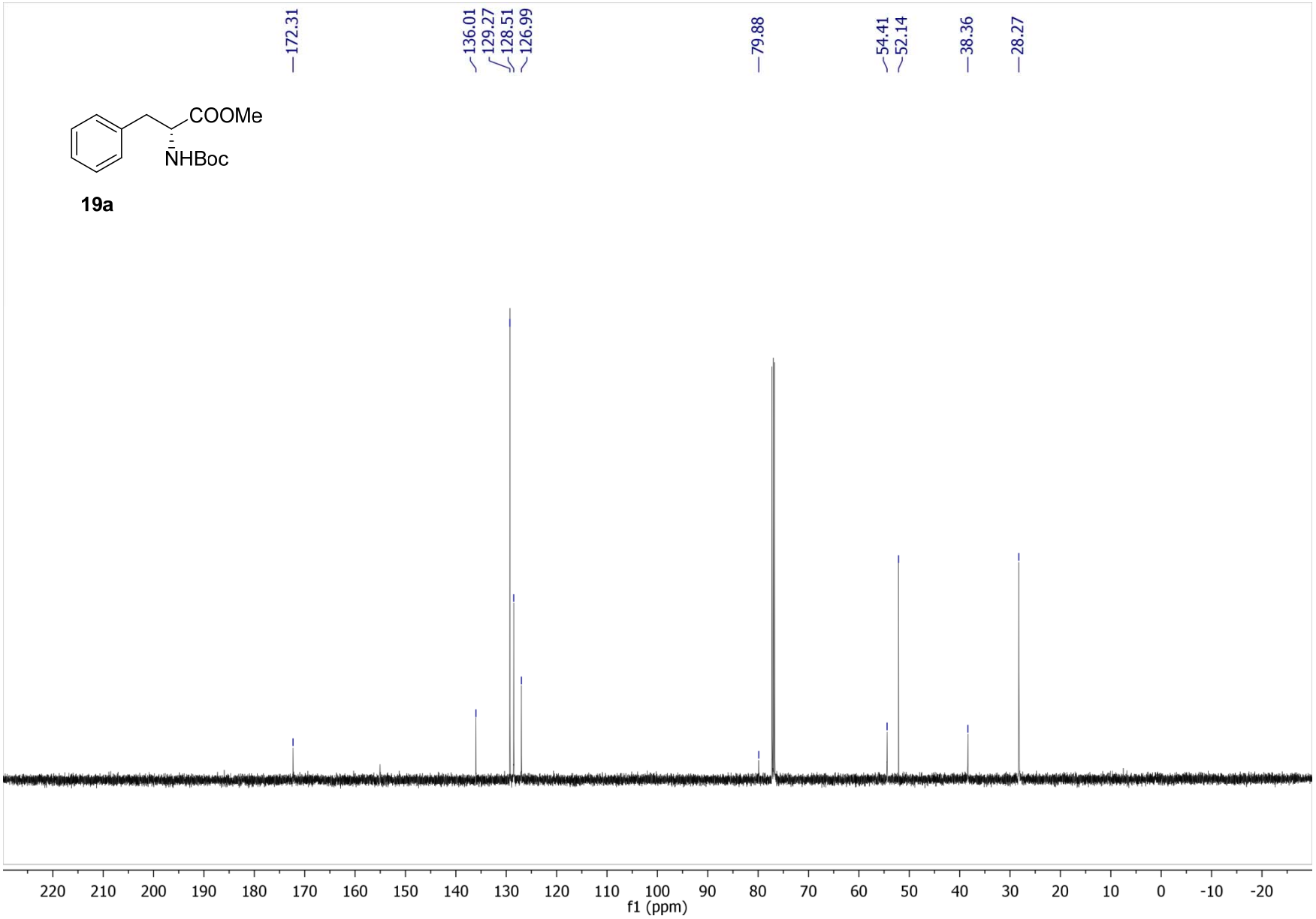
18s (mixture of rotamers)

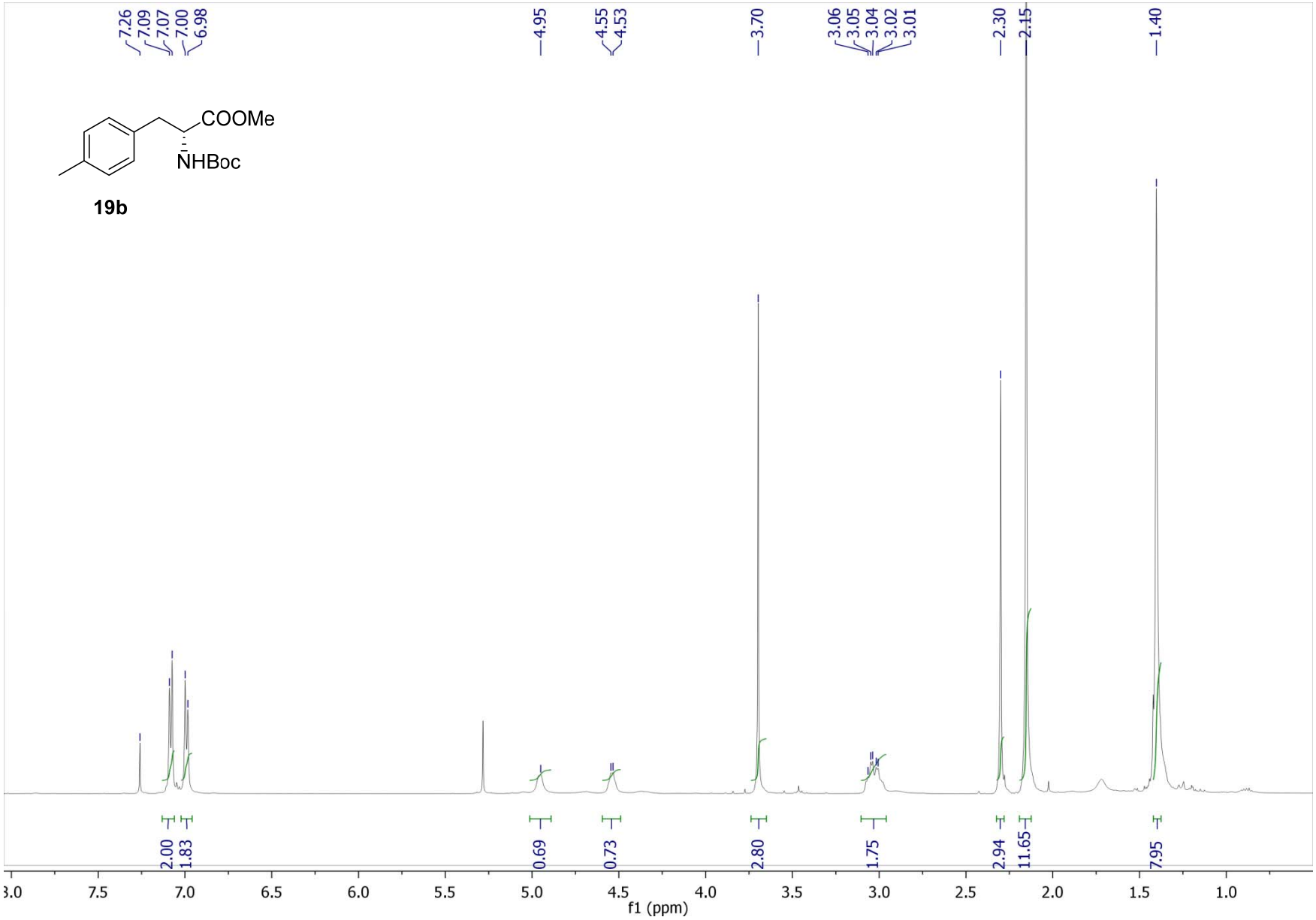


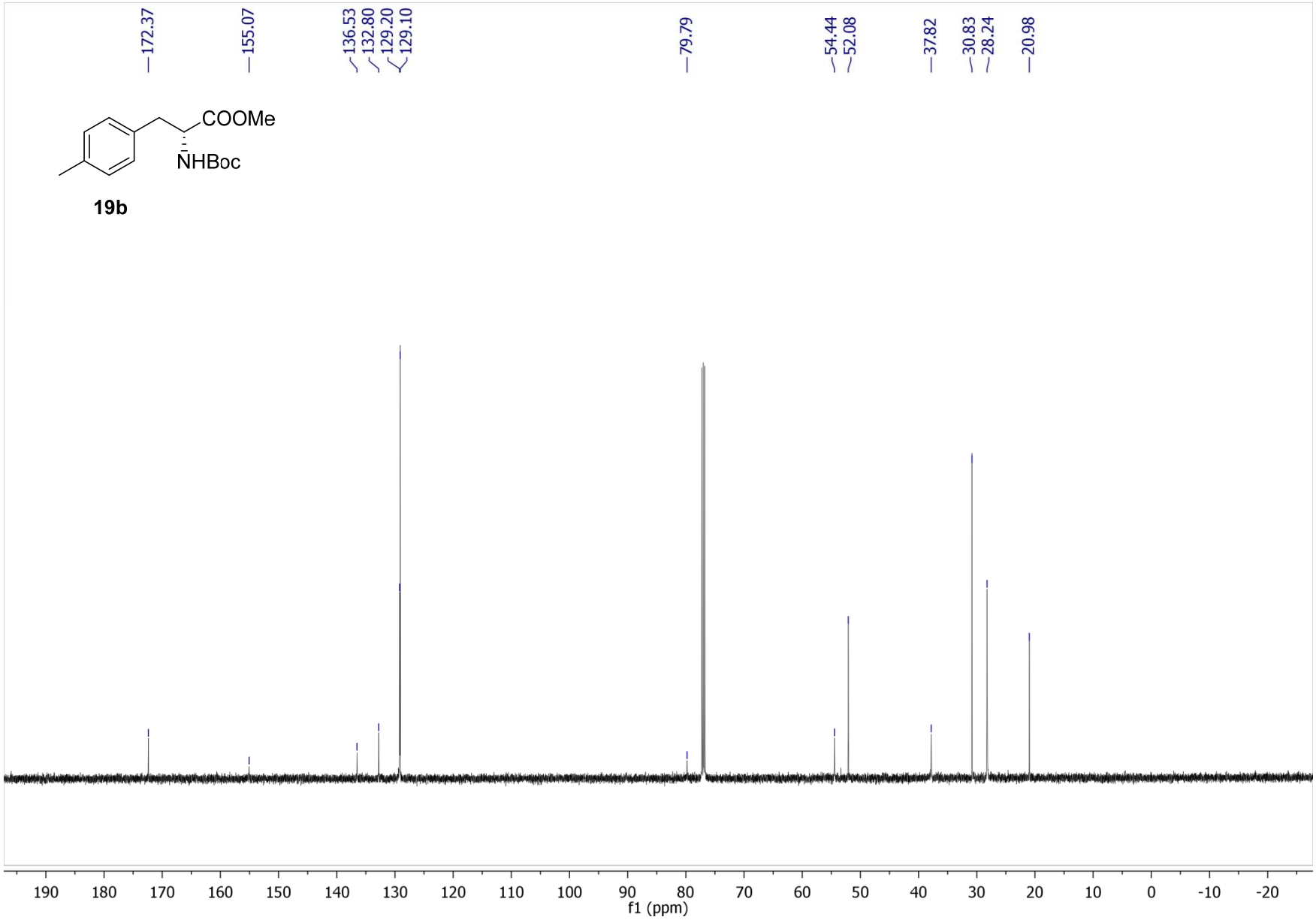

7.32
7.32
7.31
7.22
6.25
5.61
5.60
5.59
5.59
5.57
5.57
5.55
5.55
5.54
5.53
5.52
5.52
5.41
5.40
5.39
5.39
5.37
5.36
5.35
5.35
4.48
4.24
2.66
2.65
2.63
2.61
2.60
2.58
2.56
1.66
1.64
1.41
O
NHBoc
18t (mixture of rotamers)
0.93
0.90
0.94
1.00
0.99
0.94
0.96
2.01
2.88
8.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

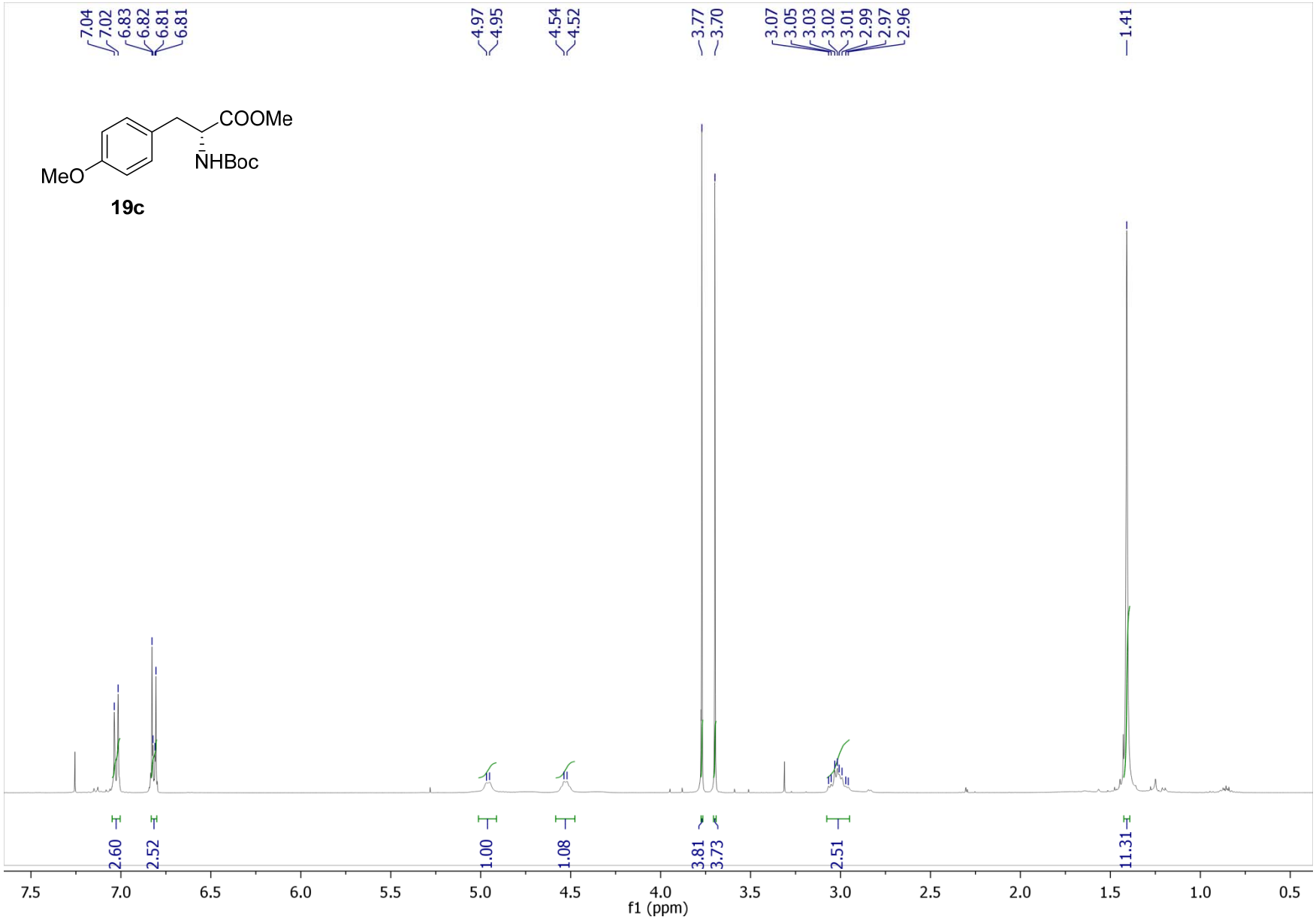

155.18
142.65
140.09
131.10
126.24
120.57
111.63
79.22
52.05
30.96
28.36
17.61
NHBoc
O
18t (mixture of rotamers)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

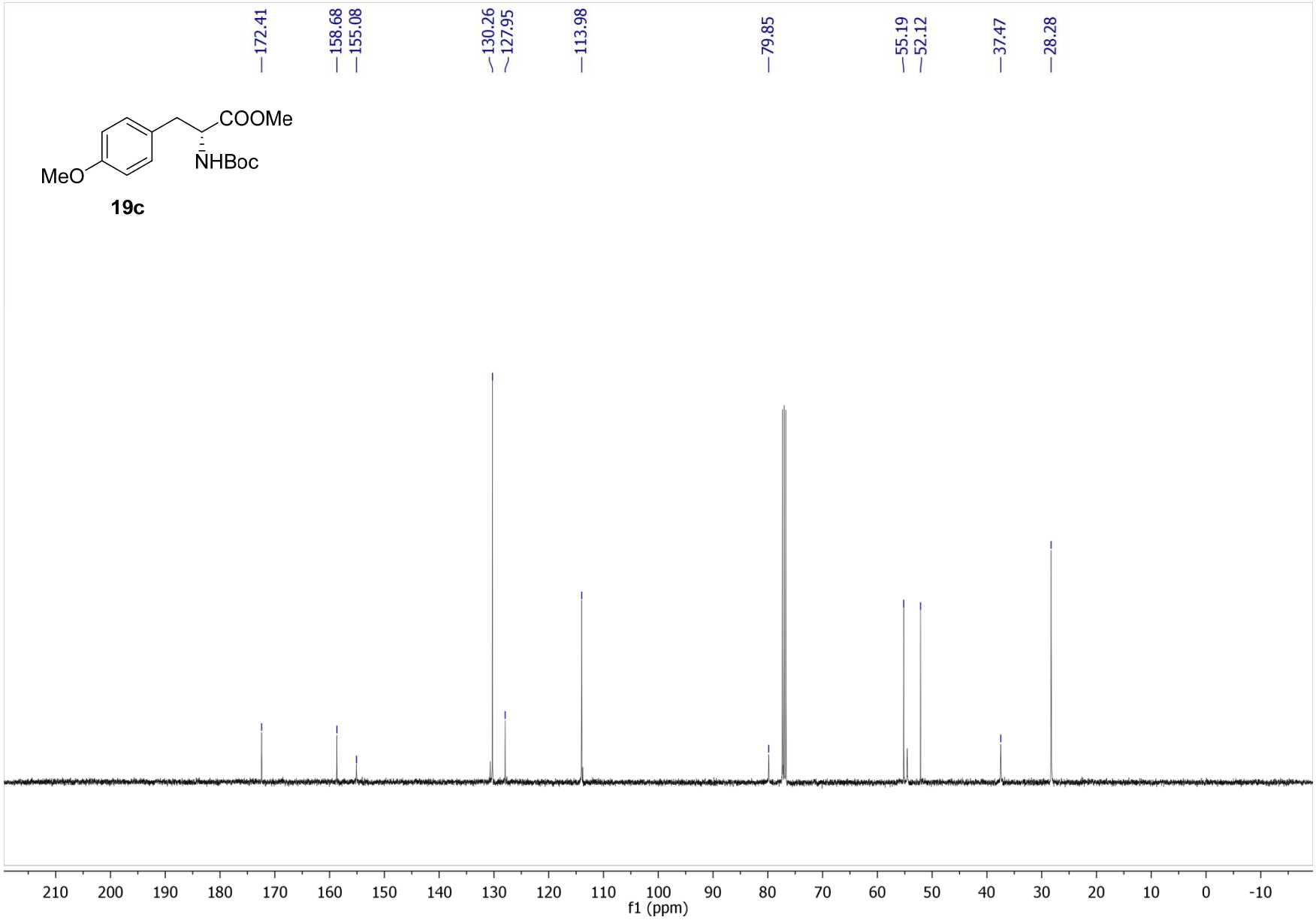

7.30
7.29
7.27
7.26
7.25
7.24
7.22
7.13
7.12
4.97
4.96
4.59
4.58
3.71
3.13
3.12
3.11
3.09
3.06
3.05
3.04
3.02
1.41
COOMe
NHBoc
19a
4.33
2.43
1.00
1.08
3.99
1.30
1.19
10.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

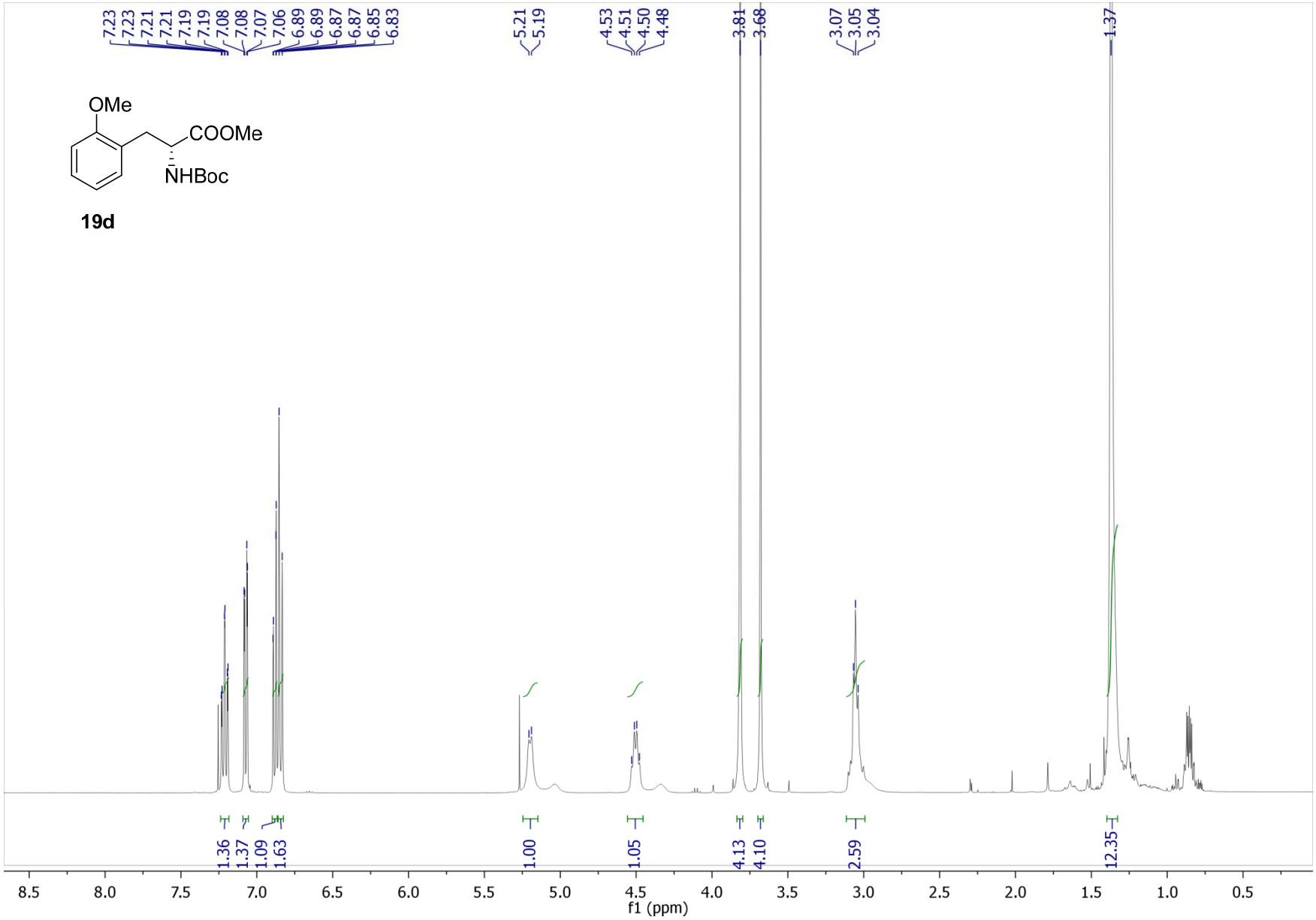

172.31
136.01
129.27
128.51
126.99
79.88
54.41
52.14
38.36
28.27
COOMe
NHBoc
19a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

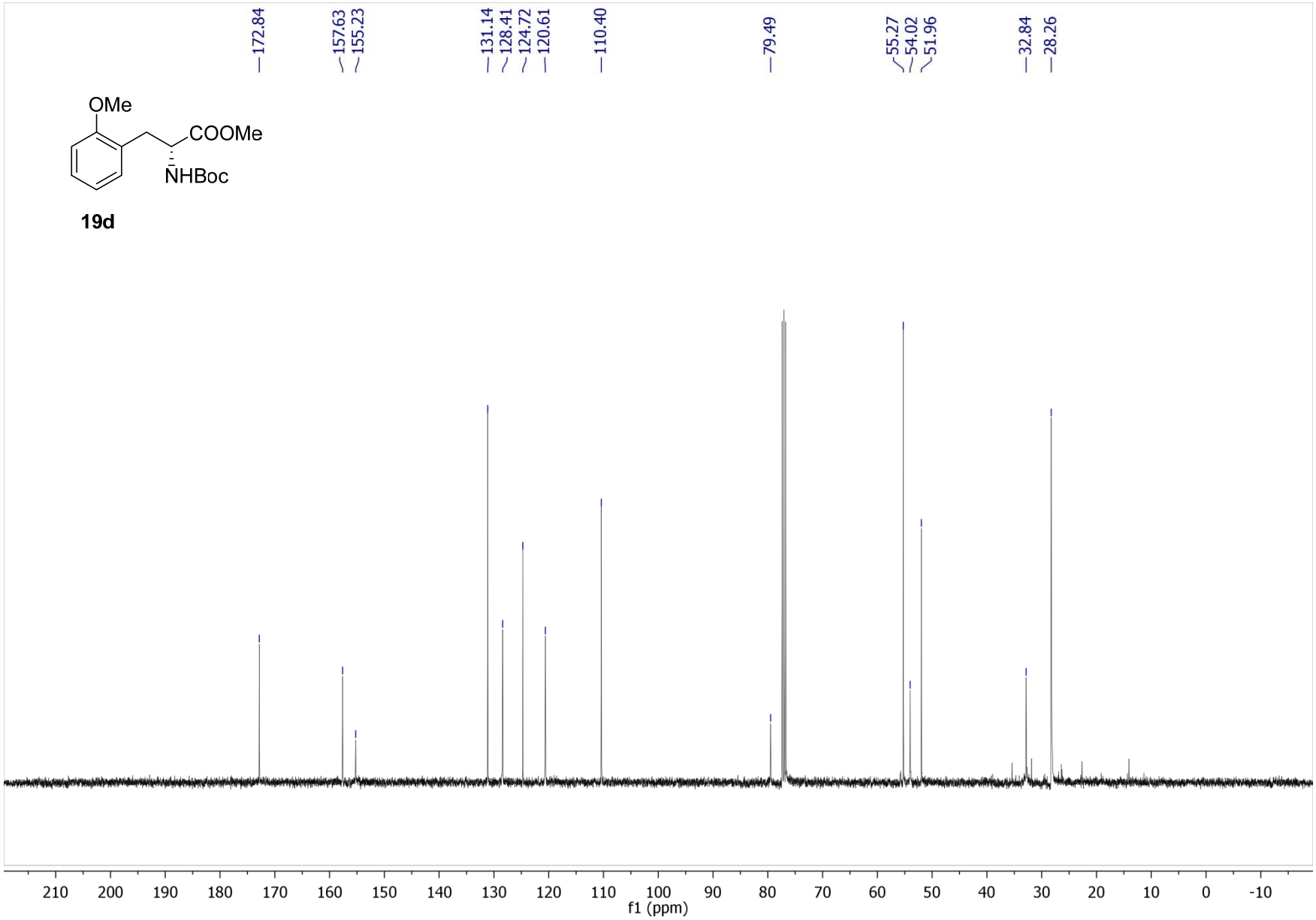

7.26
7.09
7.07
7.00
6.98
4.95
4.55
4.53
3.70
3.06
3.05
3.04
3.02
3.01
2.30
2.15
1.40
COOMe
NHBoc
19b
2.00
1.83
0.69
0.73
2.80
1.75
2.94
11.65
7.95
f1 (ppm)

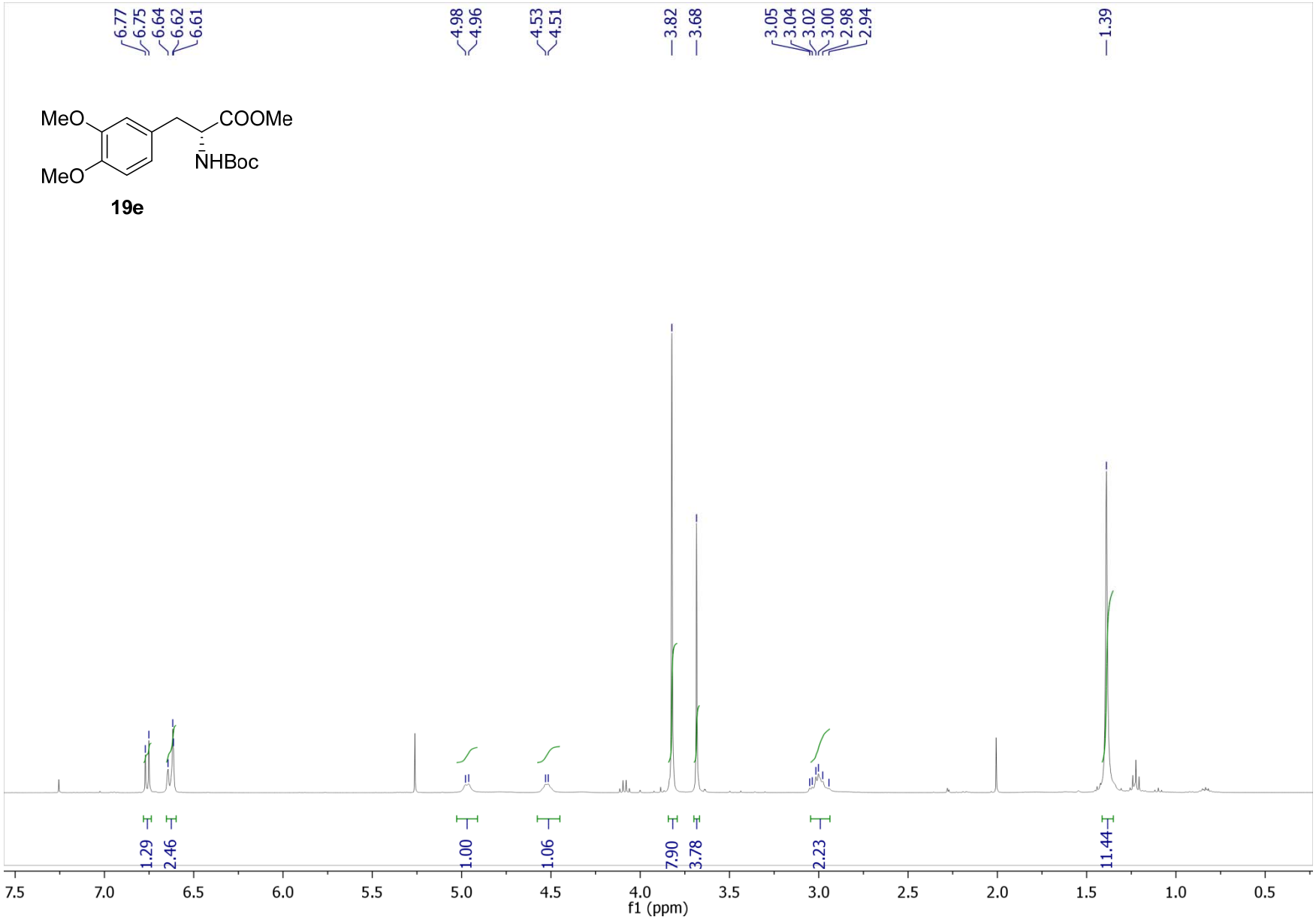

172.37
155.07
136.53
132.80
129.20
129.10
79.79
54.44
52.08
37.82
30.83
28.24
20.98
COOMe
NHBoc
19b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

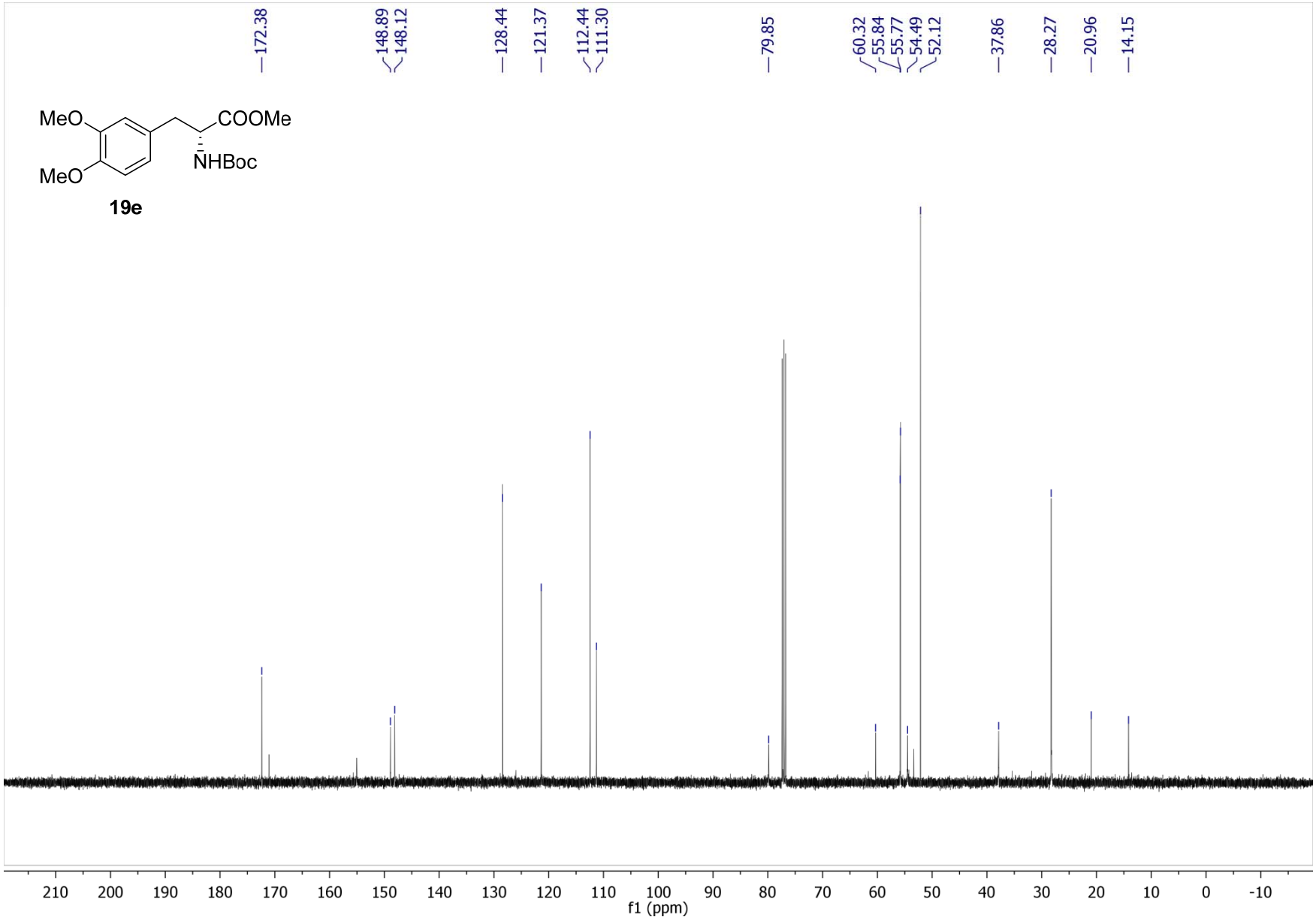

7.04
7.02
6.83
6.82
6.81
6.81
4.97
4.95
4.54
4.52
3.77
3.70
3.07
3.05
3.03
3.02
3.01
2.99
2.97
2.96
1.41
COOMe
NHBoc
MeO
19c
2.60
2.52
1.00
1.08
3.81
3.73
2.51
11.31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

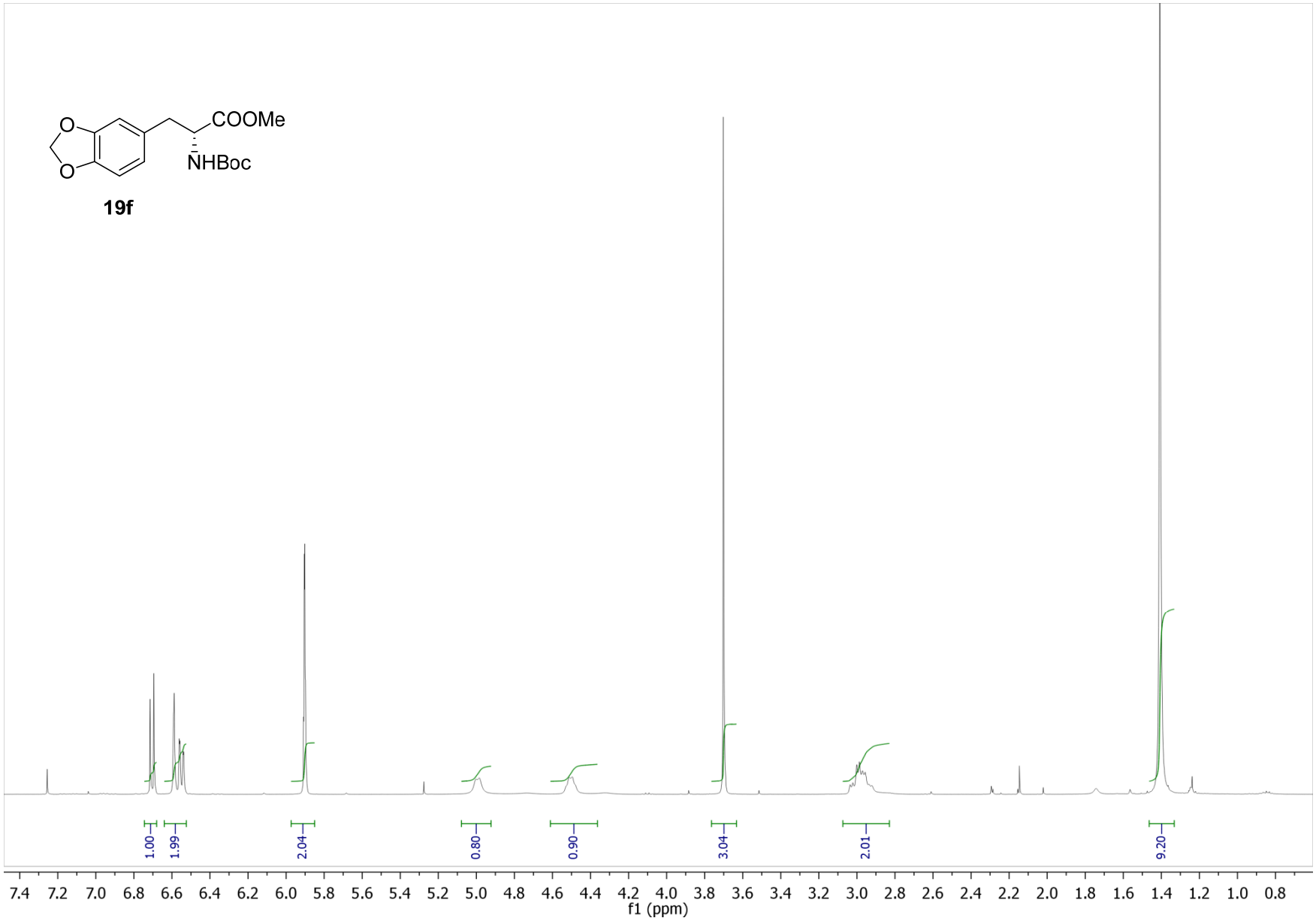

172.41
158.68
155.08
130.26
127.95
113.98
79.85
55.19
52.12
37.47
28.28
COOMe
NHBoc
MeO
19c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

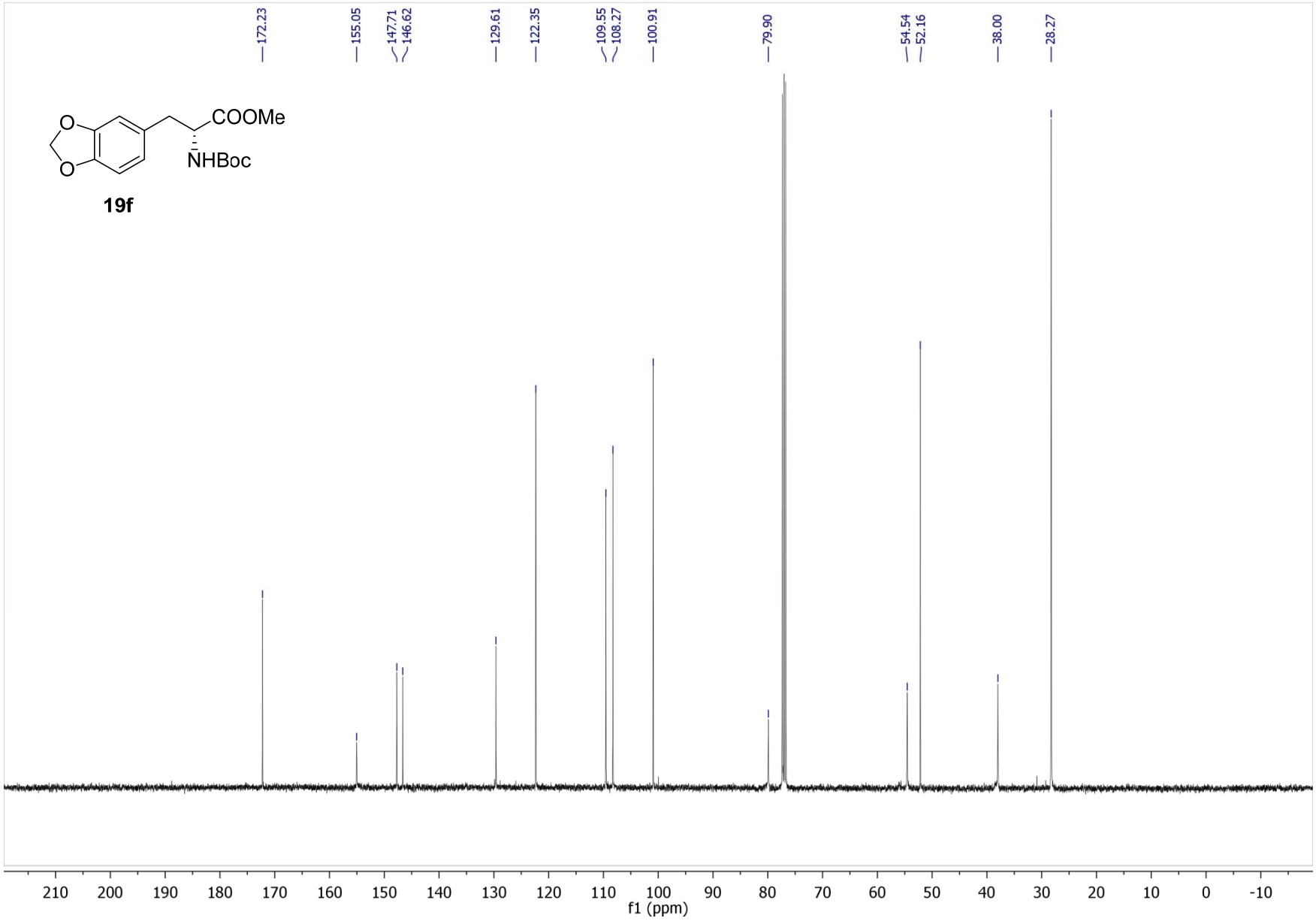

7.23
7.23
7.21
7.21
7.19
7.19
7.08
7.08
7.07
7.06
6.89
6.89
6.87
6.87
6.85
6.83
5.21
5.19
4.53
4.51
4.50
4.48
3.81
3.68
3.07
3.05
3.04
1.37
OMe
COOMe
NHBoc
19d
1.36
1.37
1.09
1.63
1.00
1.05
4.13
4.10
2.59
12.35
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

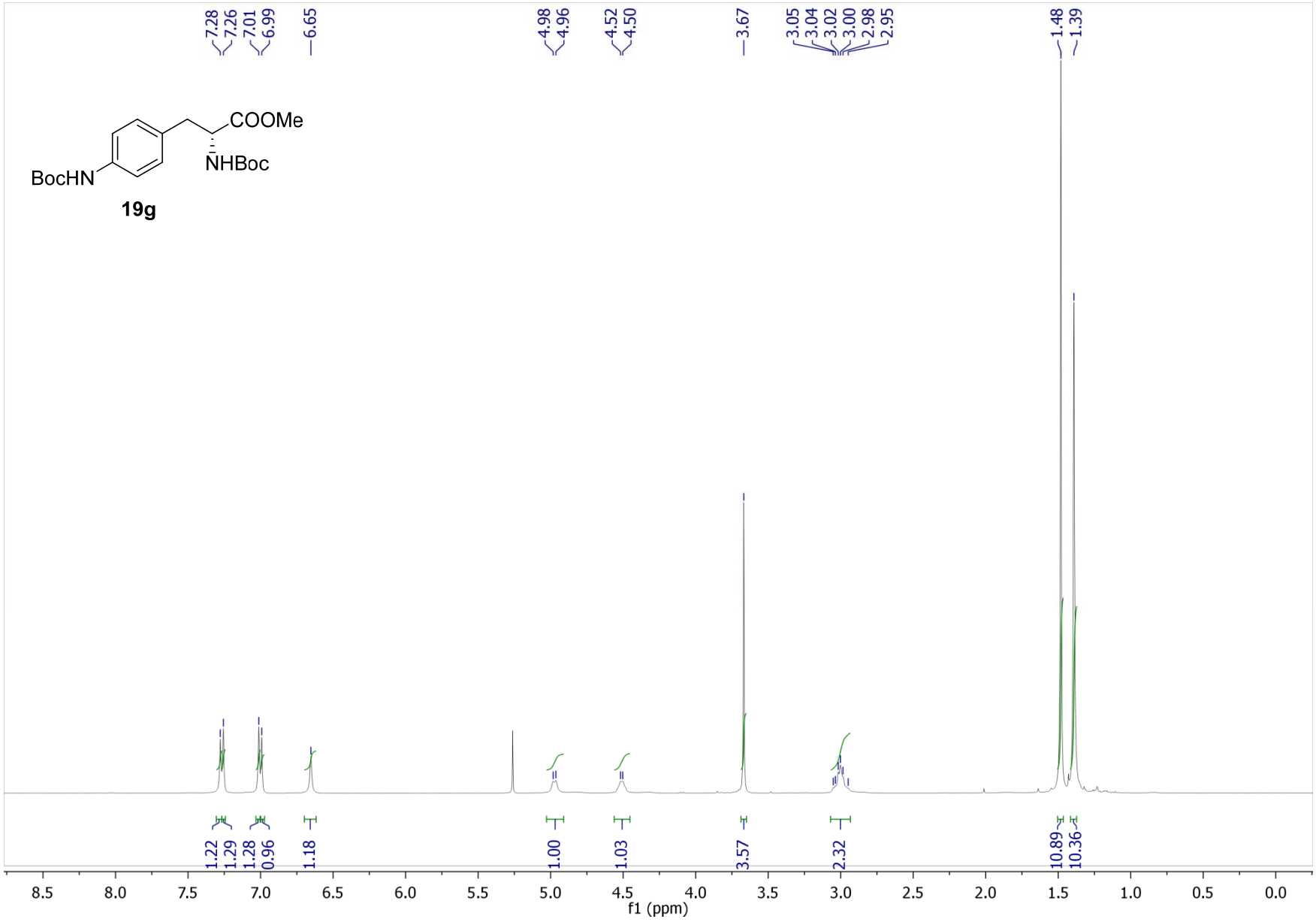

172.84
157.63
155.23
131.14
128.41
124.72
120.61
110.40
79.49
55.27
54.02
51.96
32.84
28.26
OMe
COOMe
NHBoc
19d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

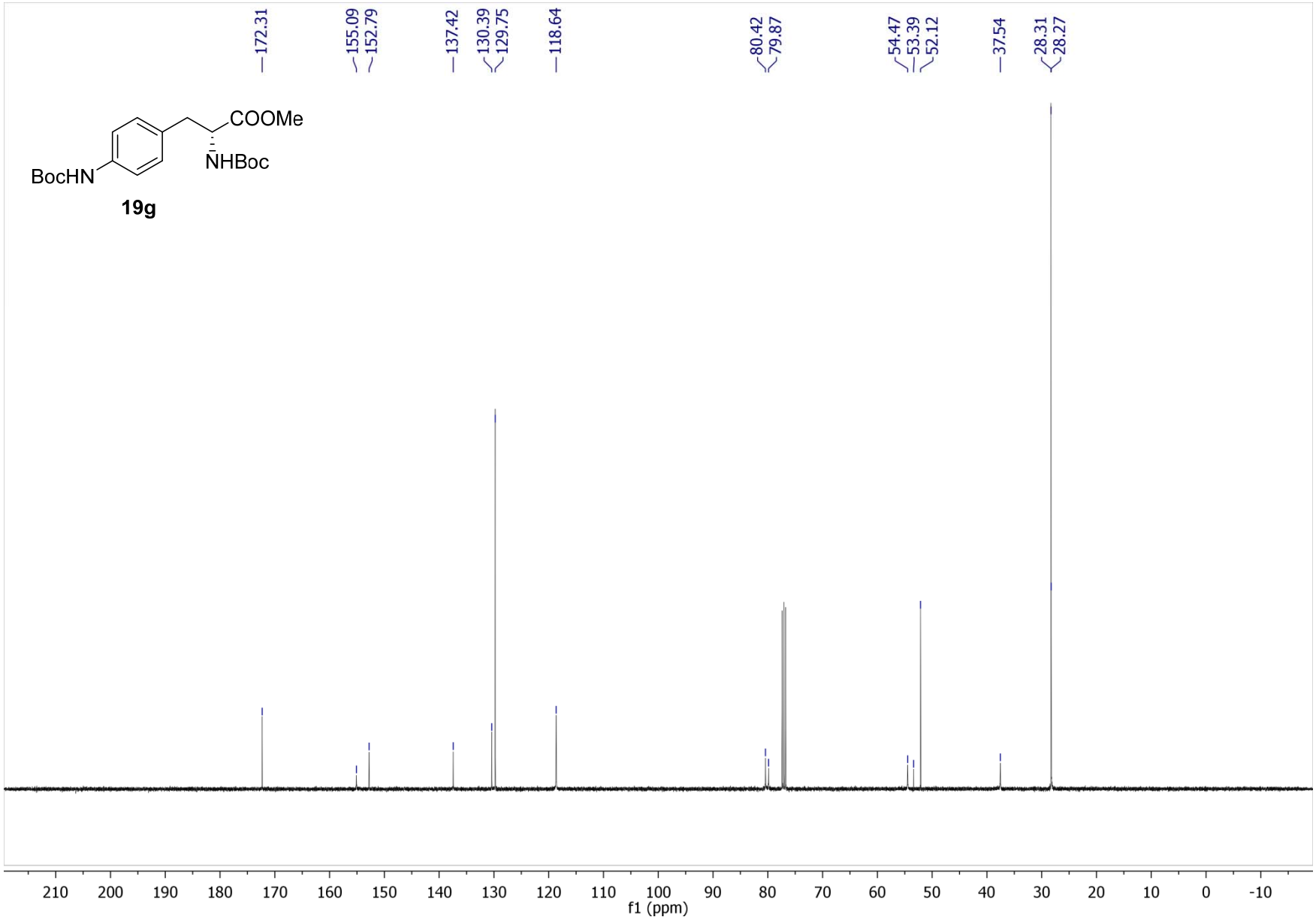

6.77
6.75
6.64
6.62
6.61
4.98
4.96
4.53
4.51
3.82
3.68
3.05
3.04
3.02
3.00
2.98
2.94
1.39
MeO
MeO
COOMe
NHBoc
19e
1.29
2.46
1.00
1.06
7.90
3.78
2.23
11.44
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

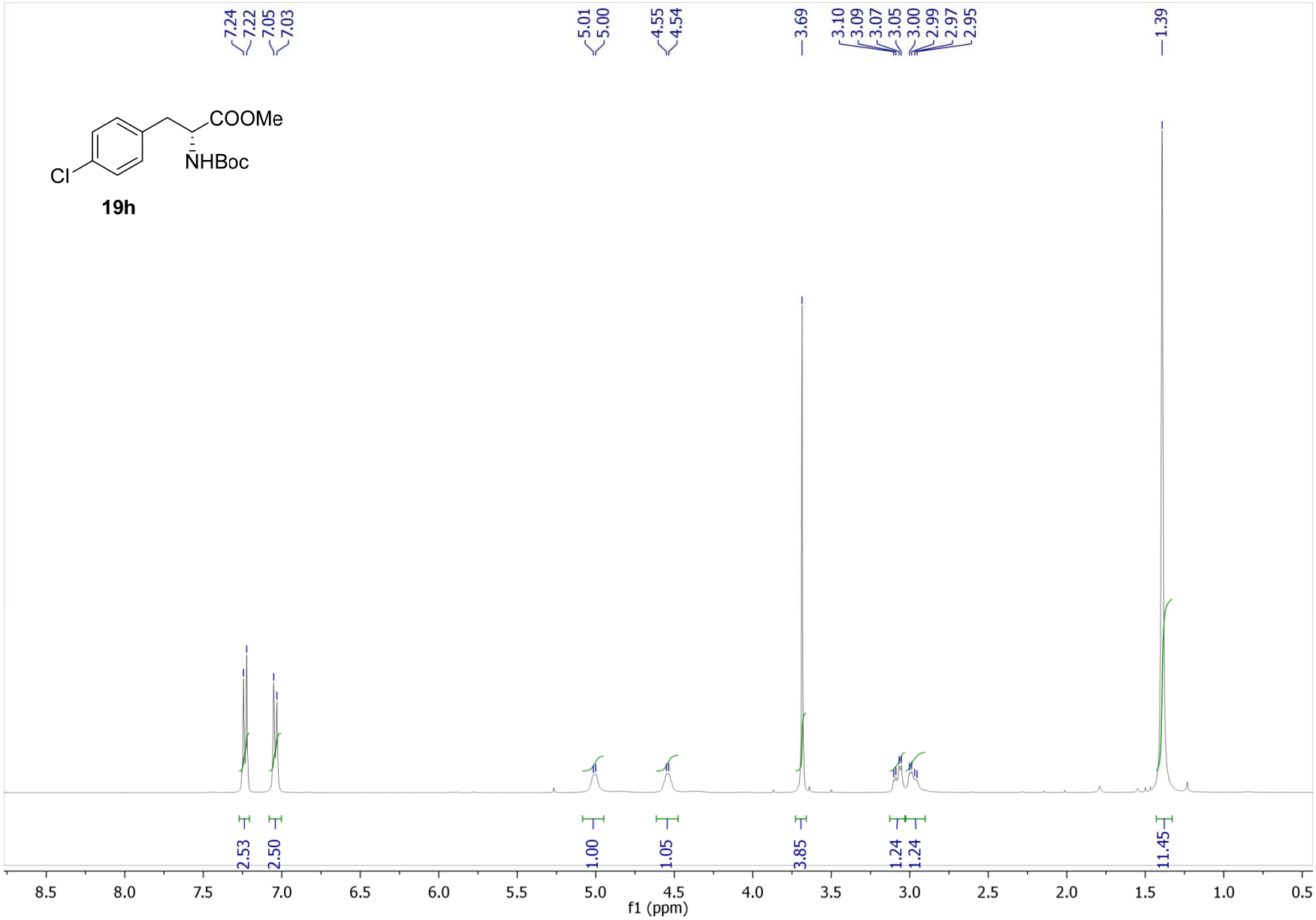

172.38
148.89
148.12
128.44
121.37
112.44
111.30
79.85
60.32
55.84
55.77
54.49
52.12
37.86
28.27
20.96
14.15
MeO
MeO
COOMe
NHBoc
19e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

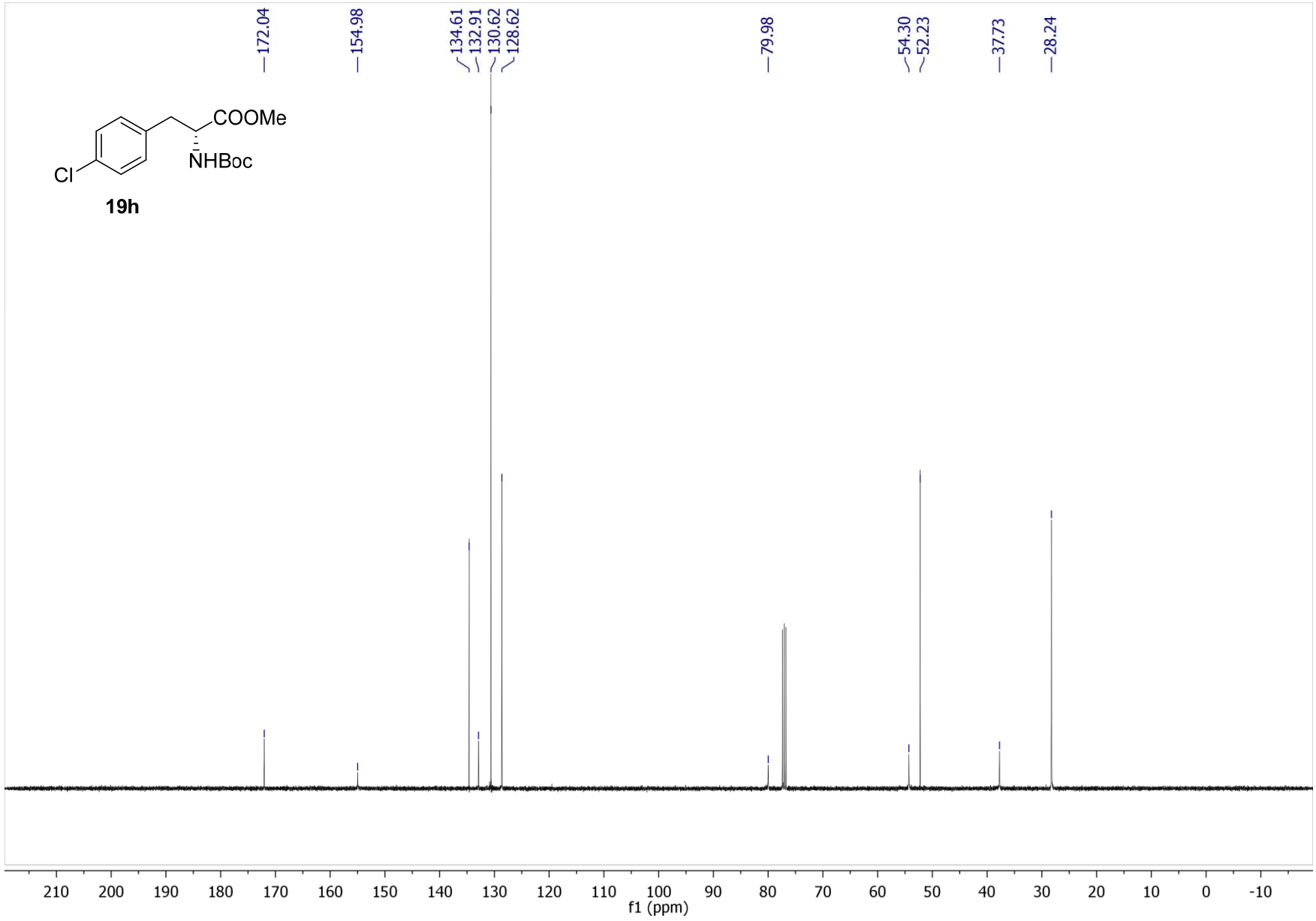

COOMe
NHBoc
O
O
19f
1.00
1.99
2.04
0.80
0.90
3.04
2.01
9.20
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

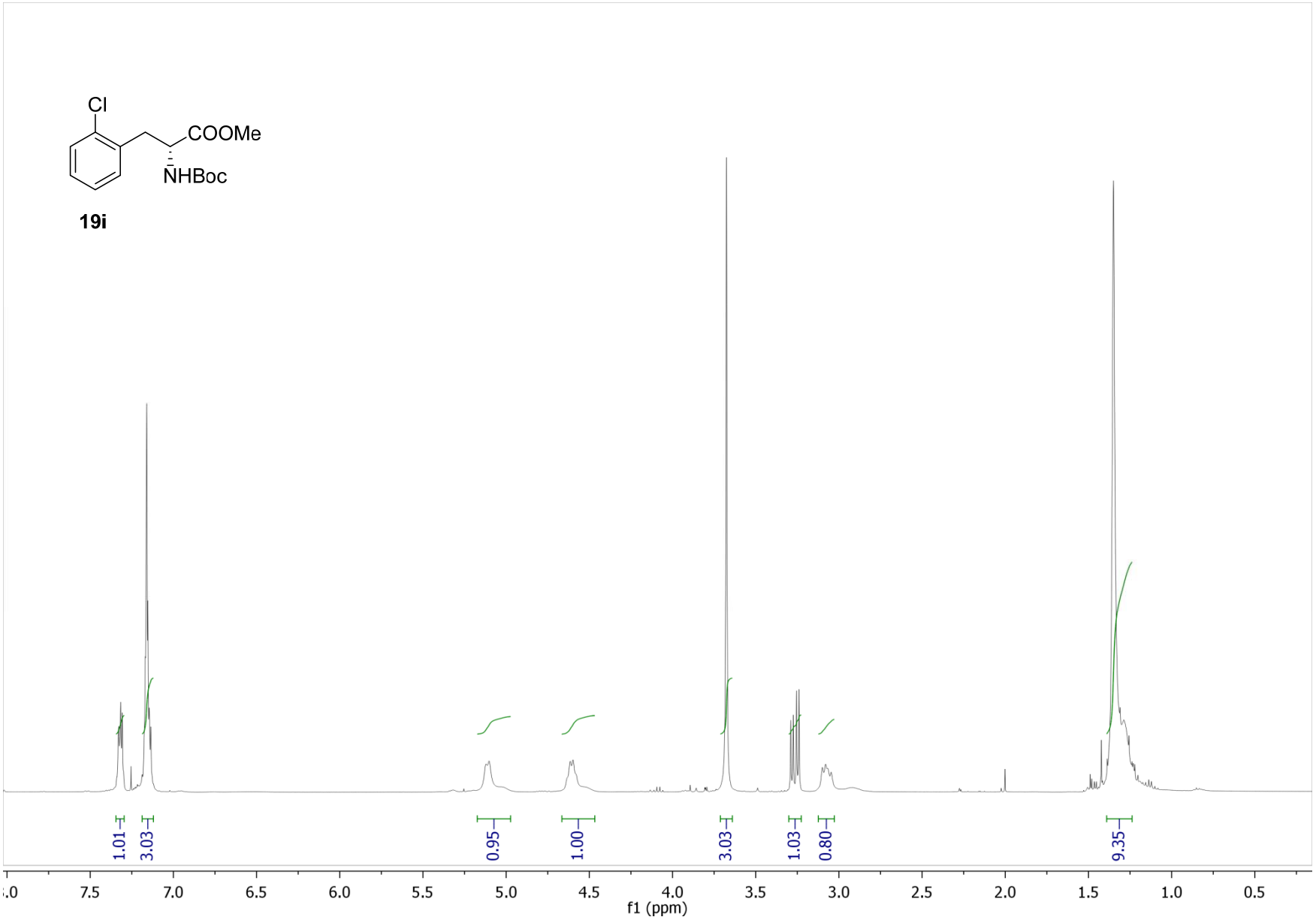

172.23
155.05
147.71
146.62
129.61
122.35
109.55
108.27
100.91
79.90
54.54
52.16
38.00
28.27
COOMe
NHBoc
19f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

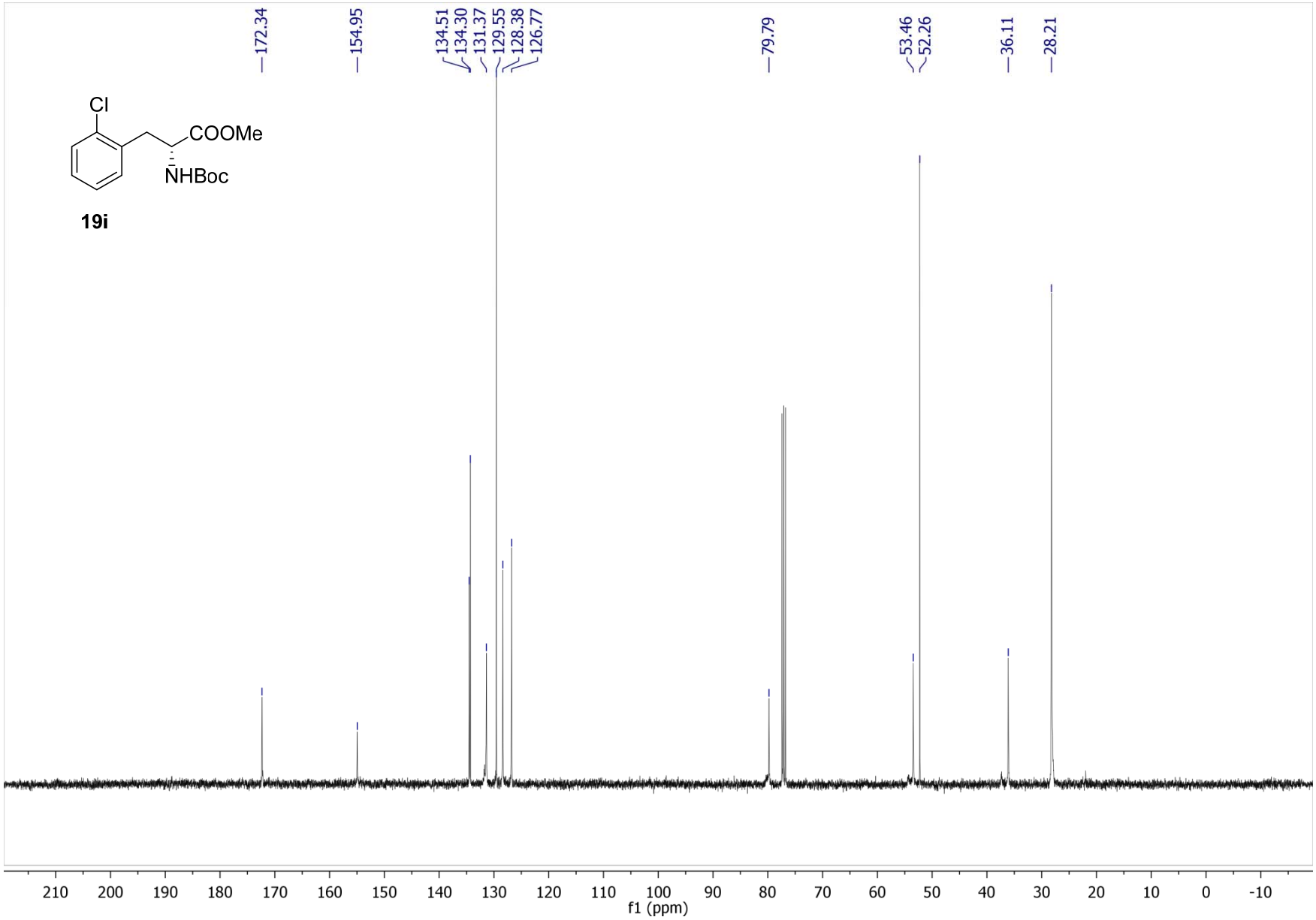

7.28
7.26
7.01
6.99
6.65
4.98
4.96
4.52
4.50
3.67
3.05
3.04
3.02
3.00
2.98
2.95
1.48
1.39
COOMe
NHBoc
BocHN
19g
1.22
1.29
1.28
0.96
1.18
1.00
1.03
3.57
2.32
10.89
10.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.31
155.09
152.79
137.42
130.39
129.75
118.64
80.42
79.87
54.47
53.39
52.12
37.54
28.31
28.27
COOMe
NHBoc
BocHN
19g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.24
7.22
7.05
7.03
5.01
5.00
4.55
4.54
3.69
3.10
3.09
3.07
3.05
3.00
2.99
2.97
2.95
1.39
COOMe
NHBoc
Cl
19h
2.53
2.50
1.00
1.05
3.85
1.24
1.24
11.45
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.04
154.98
134.61
132.91
130.62
128.62
79.98
54.30
52.23
37.73
28.24
COOMe
NHBoc
Cl
19h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
COOMe
NHBoc
19i
1.01
3.03
0.95
1.00
3.03
1.03
0.80
9.35
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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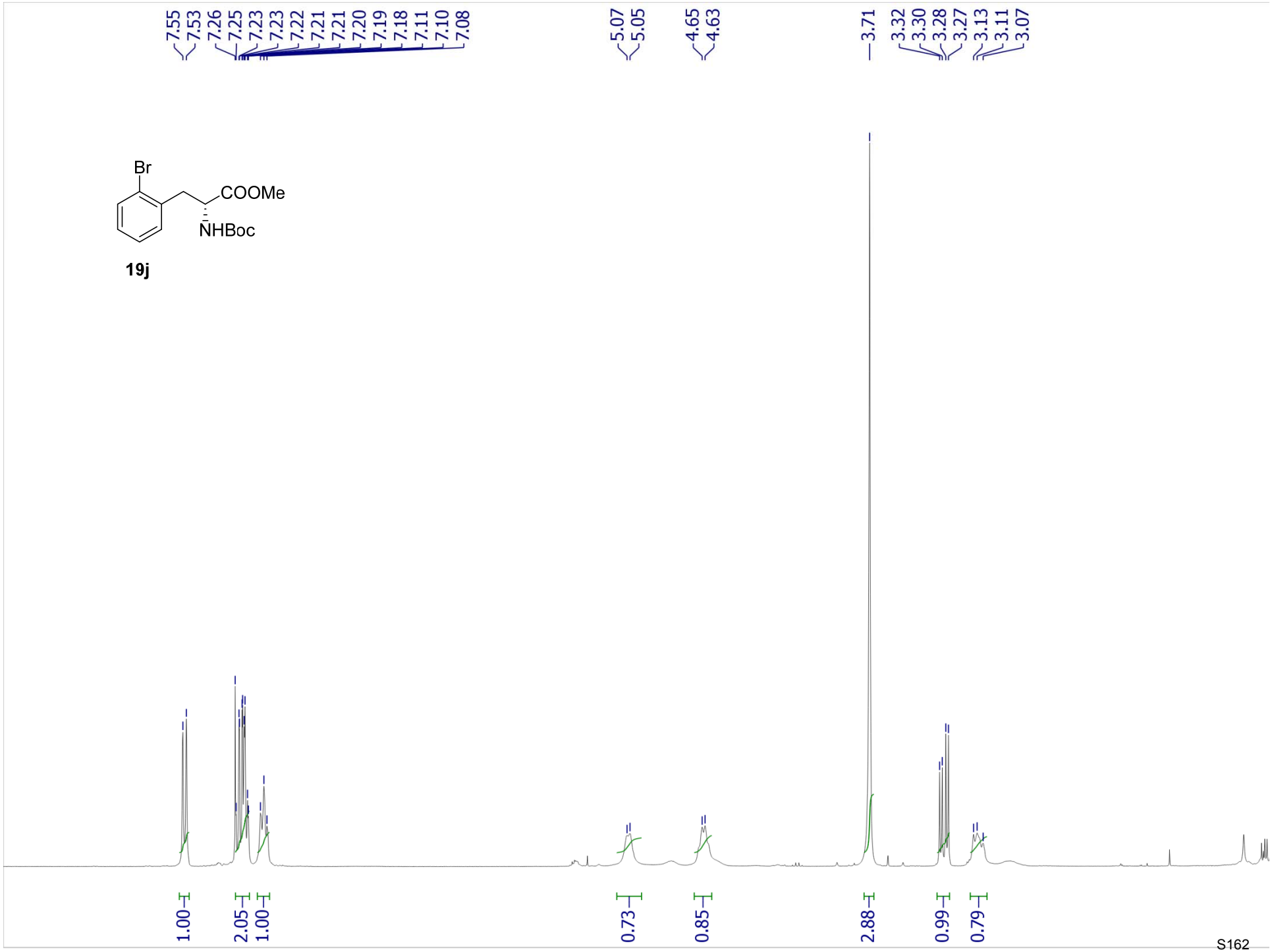
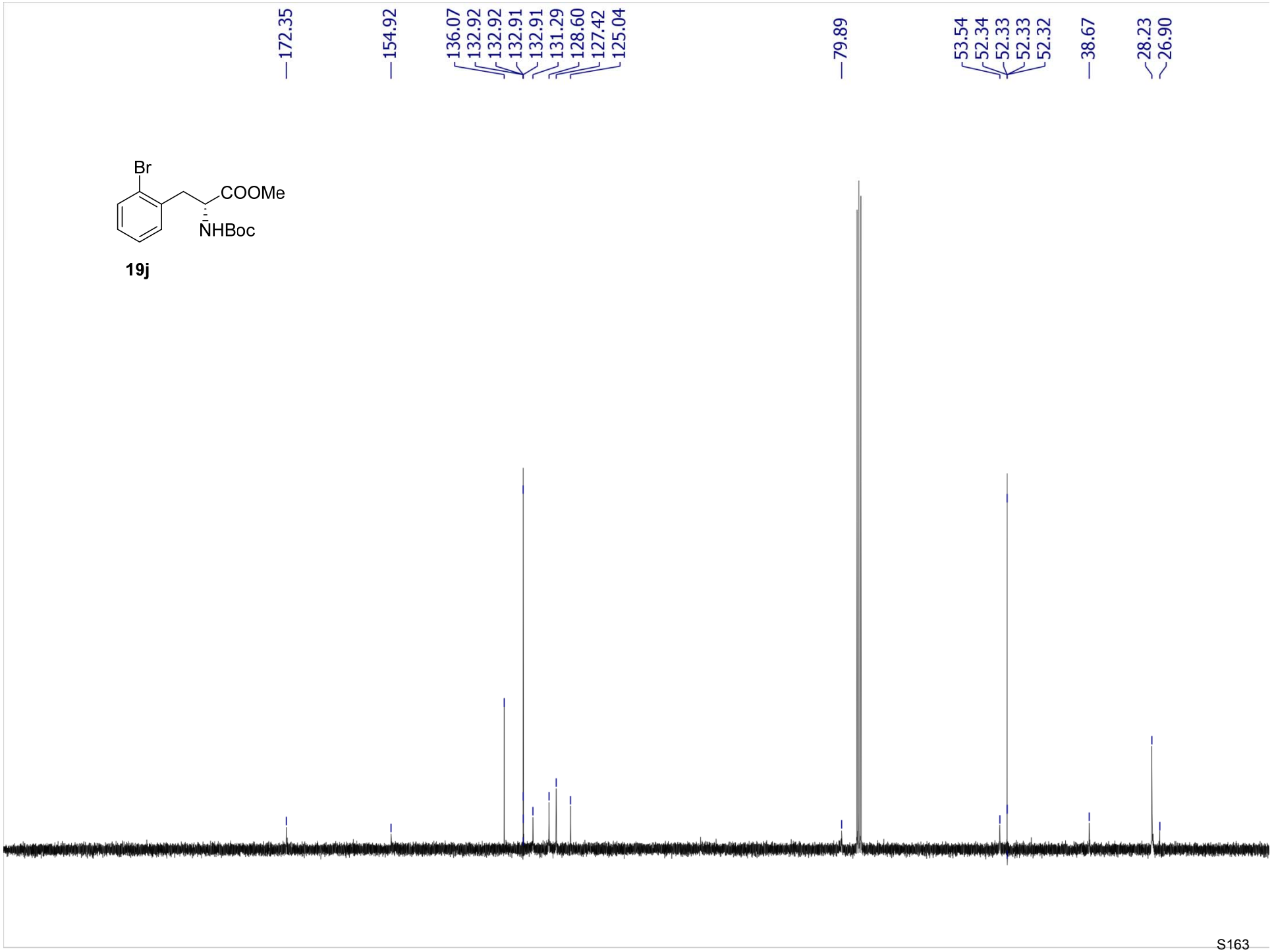
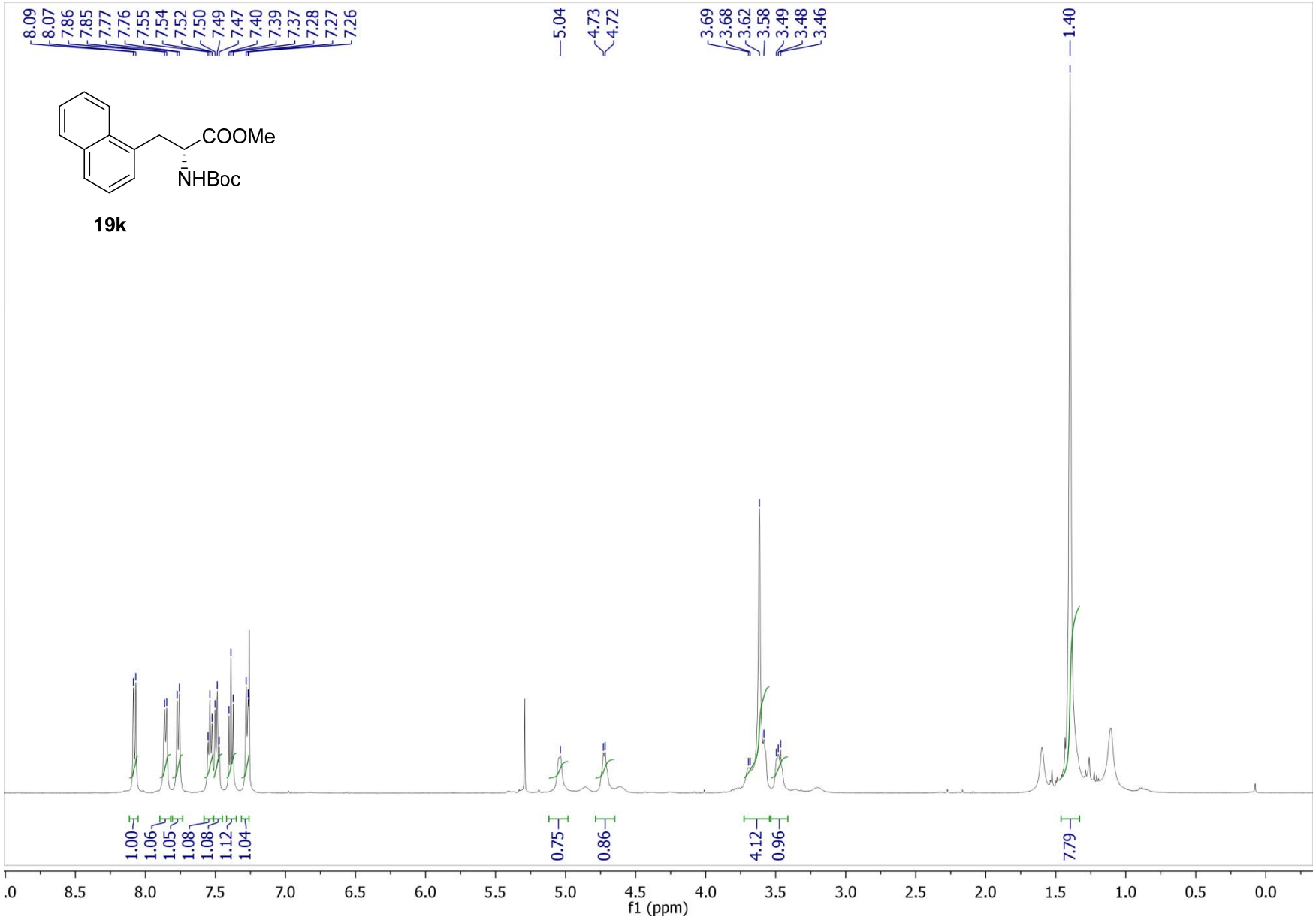
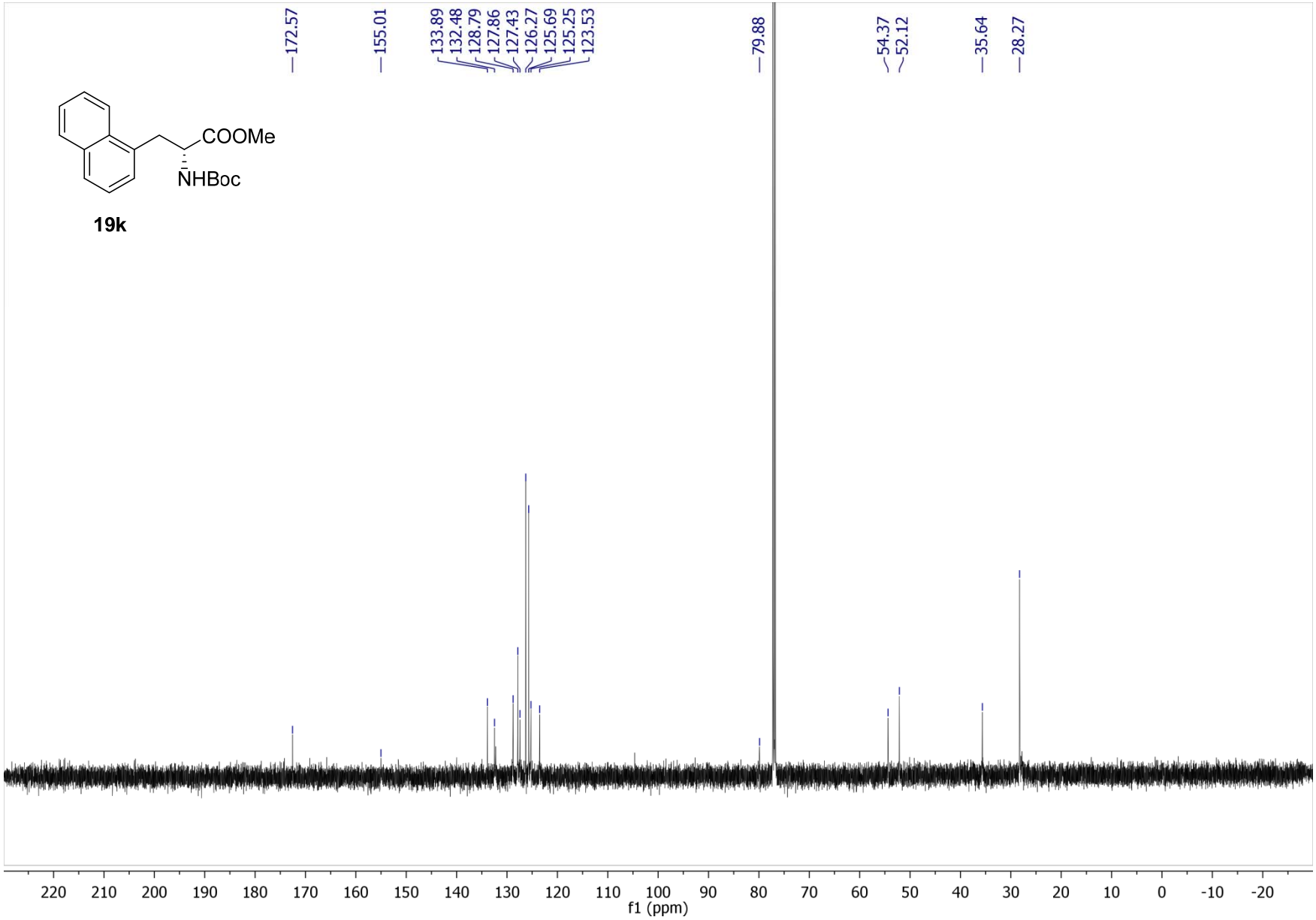
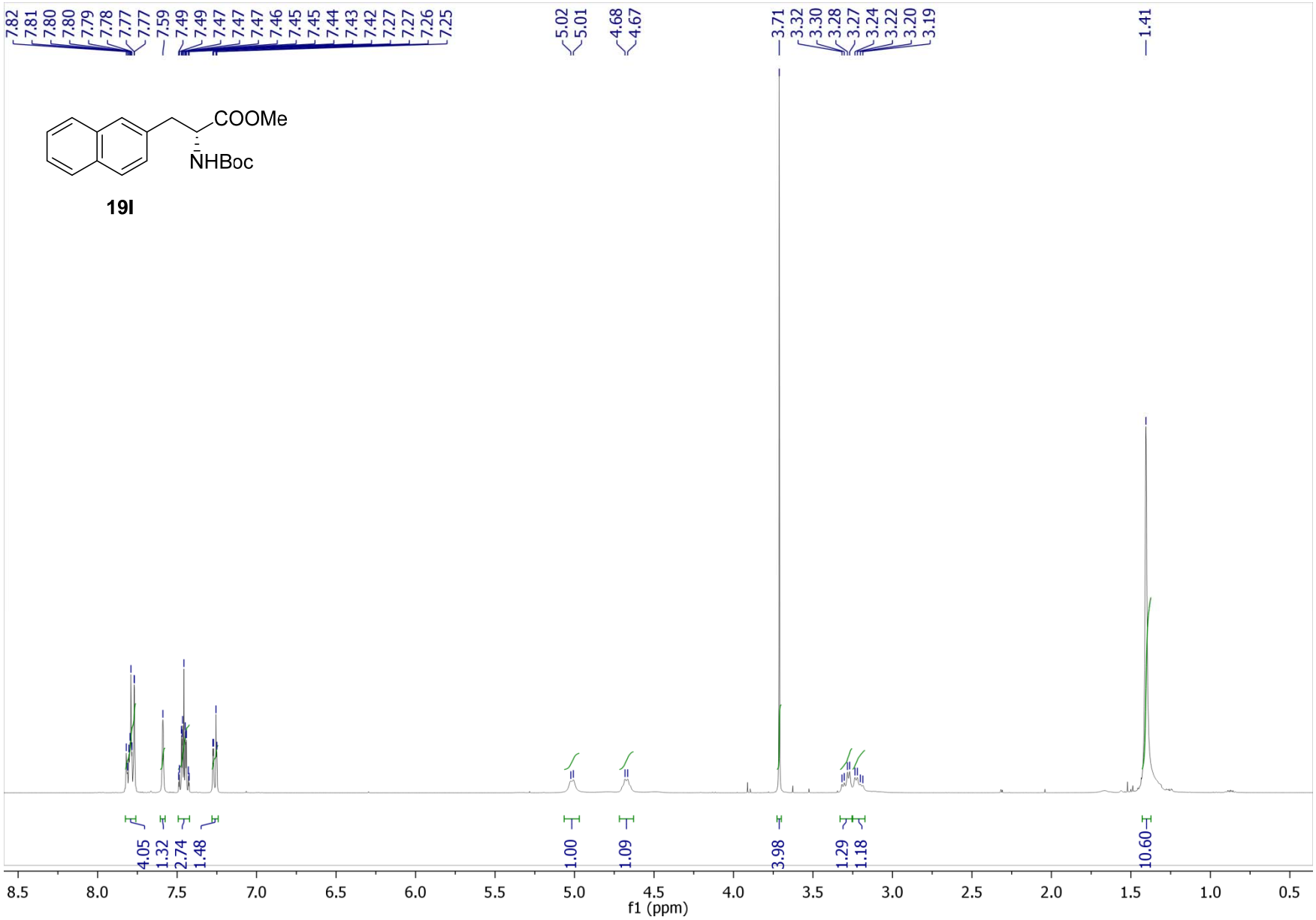
154.95
134.51
134.30
131.37
129.55
128.38
126.77
79.79
53.46
52.26
36.11
28.21
Cl
COOMe
NHBoc
19i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

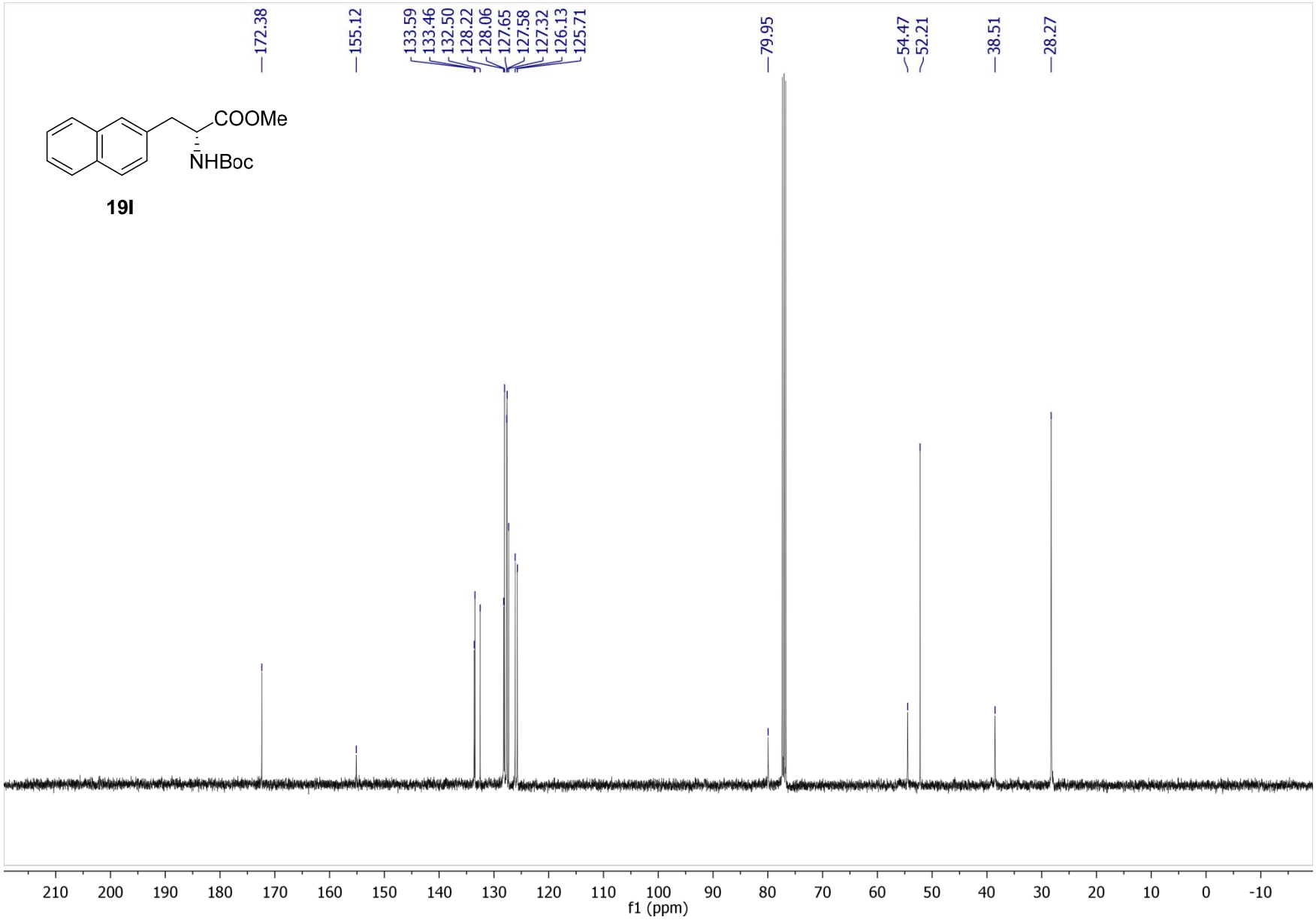

7.55
7.53
7.26
7.25
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.11
7.10
7.08
5.07
5.05
4.65
4.63
3.71
3.32
3.30
3.28
3.27
3.13
3.11
3.07
Br
COOMe
NHBoc
19j
1.00
2.05
1.00
0.73
0.85
2.88
0.99
0.79


172.35
154.92
136.07
132.92
132.92
132.91
132.91
131.29
128.60
127.42
125.04
79.89
53.54
52.34
52.33
52.33
52.32
38.67
28.23
26.90
Br
COOMe
NHBoc
19j


8.09
8.07
7.86
7.85
7.77
7.76
7.55
7.54
7.52
7.50
7.49
7.47
7.40
7.39
7.37
7.28
7.27
7.26
5.04
4.73
4.72
3.69
3.68
3.62
3.58
3.49
3.48
3.46
1.40
COOMe
NHBoc
19k
1.00
1.06
1.05
1.08
1.08
1.12
1.04
0.75
0.86
4.12
0.96
7.79
f1 (ppm)


172.57
155.01
133.89
132.48
128.79
127.86
127.43
126.27
125.69
125.25
123.53
79.88
54.37
52.12
35.64
28.27
COOMe
NHBoc
19k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.82
7.81
7.80
7.80
7.79
7.78
7.77
7.77
7.59
7.49
7.49
7.47
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.27
7.27
7.26
7.25
5.02
5.01
4.68
4.67
3.71
3.32
3.30
3.28
3.27
3.24
3.22
3.20
3.19
1.41
COOMe
NHBoc
19l
4.05
1.32
2.74
1.48
1.00
1.09
3.98
1.29
1.18
10.60
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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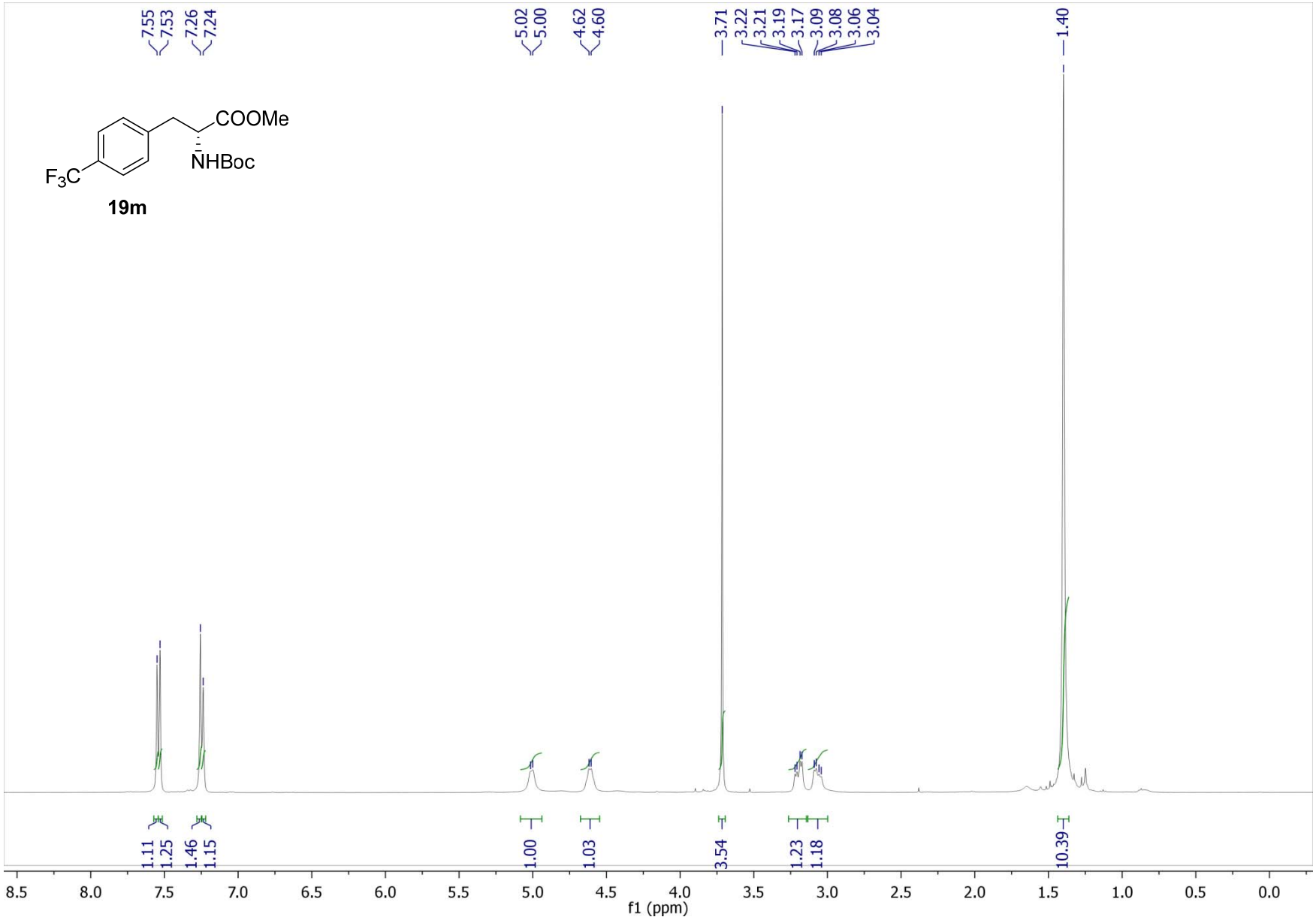
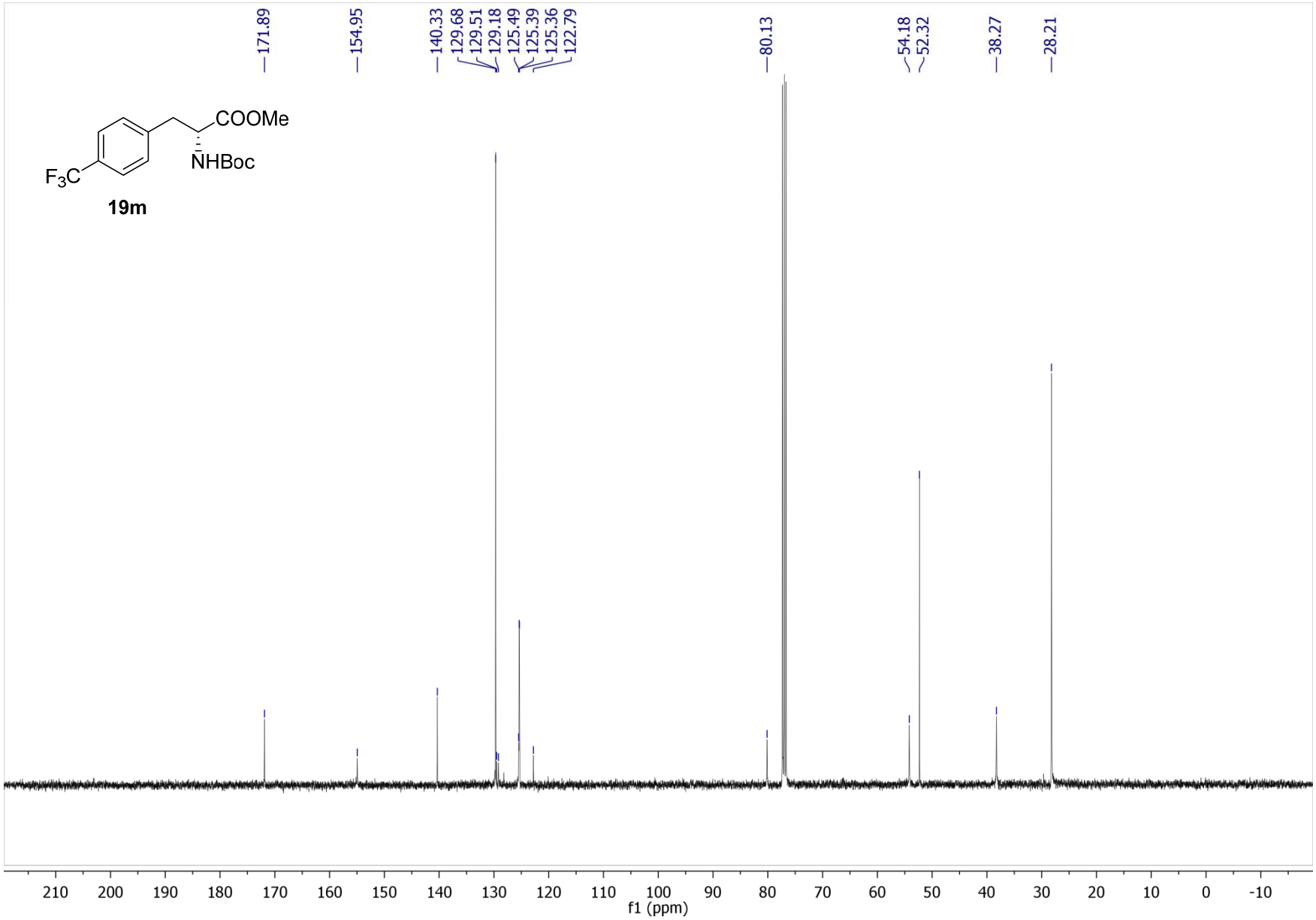
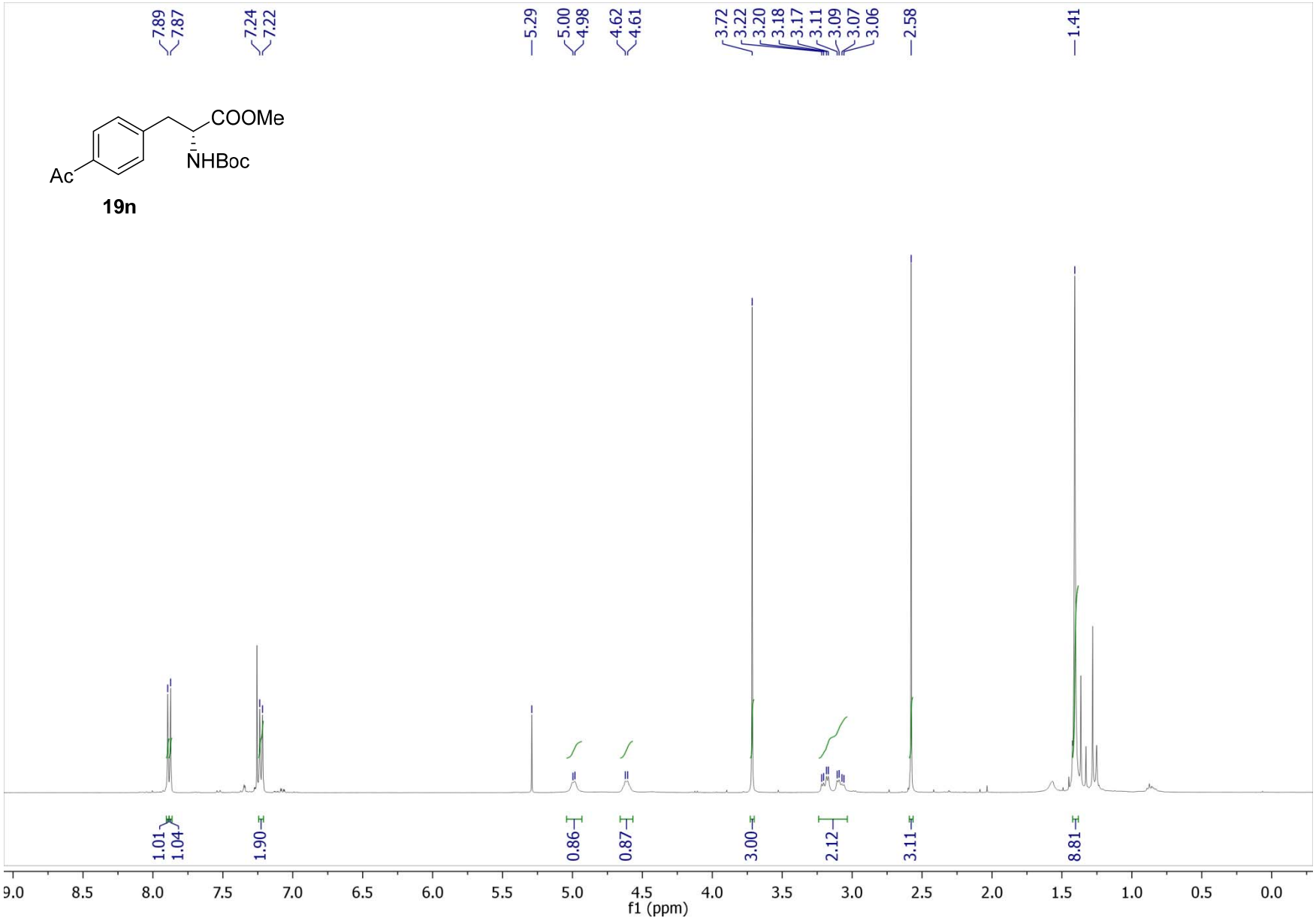
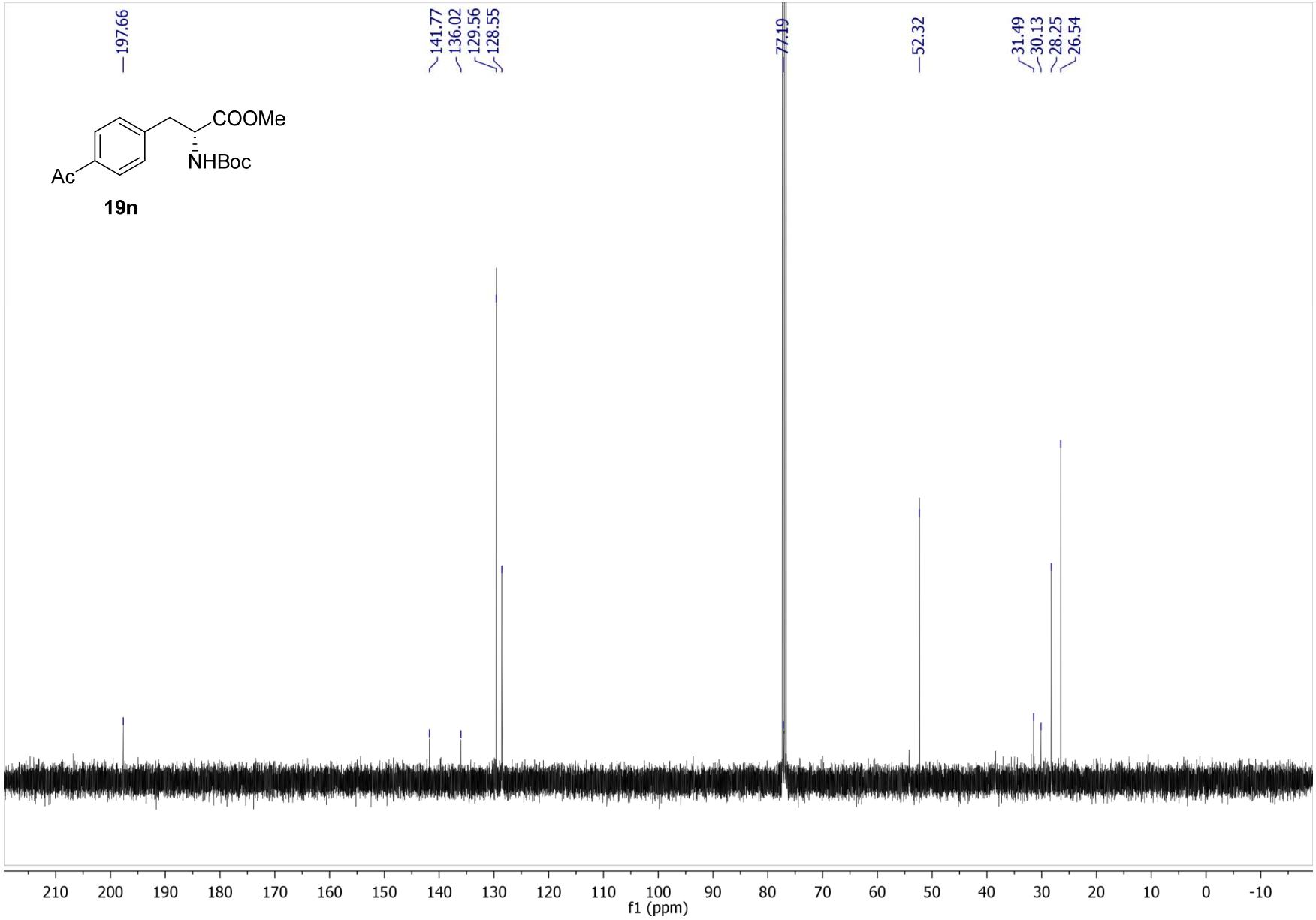
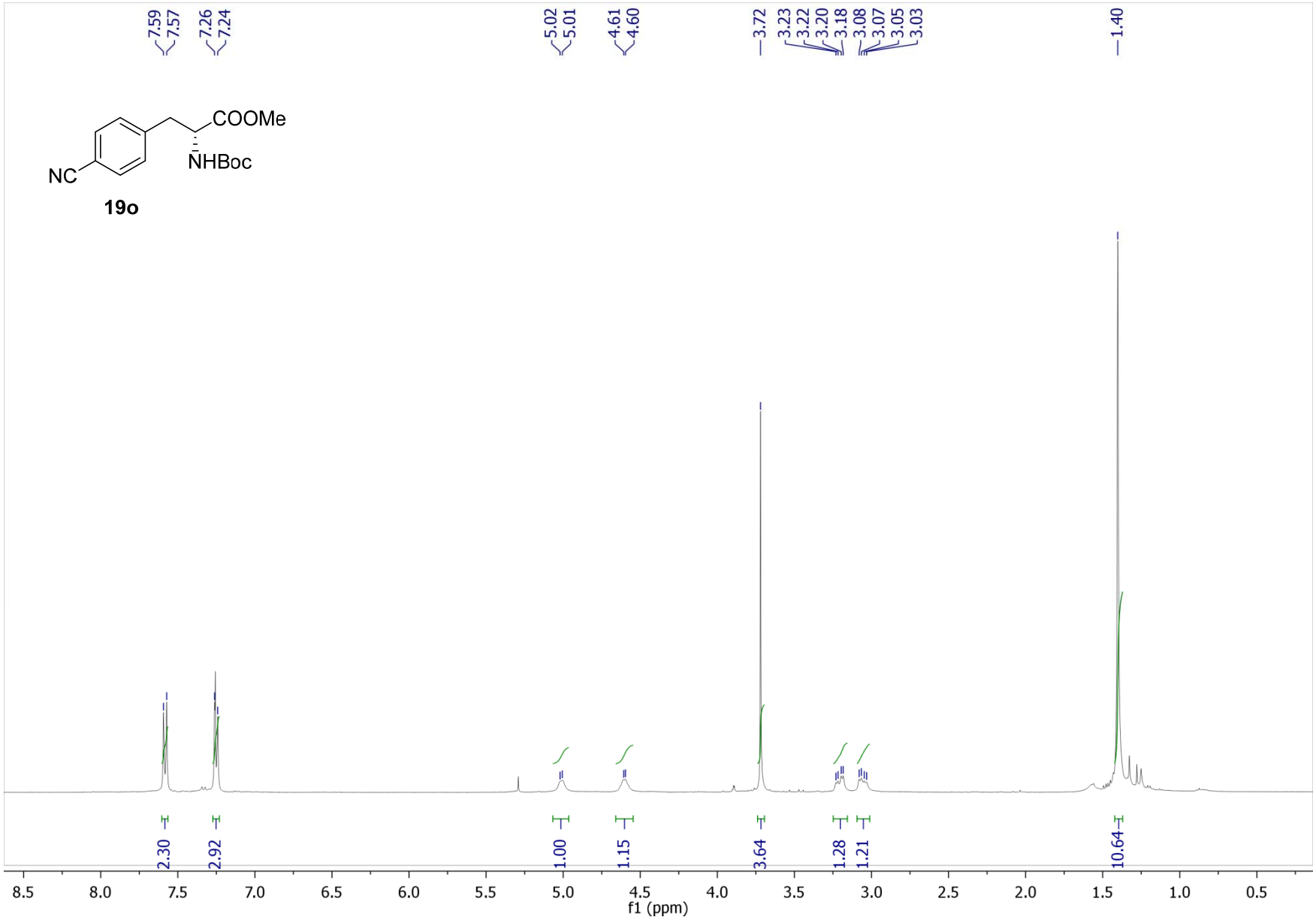
155.12
133.59
133.46
132.50
128.22
128.06
127.65
127.58
127.32
126.13
125.71
79.95
54.47
52.21
38.51
28.27
COOMe
NHBoc
19l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

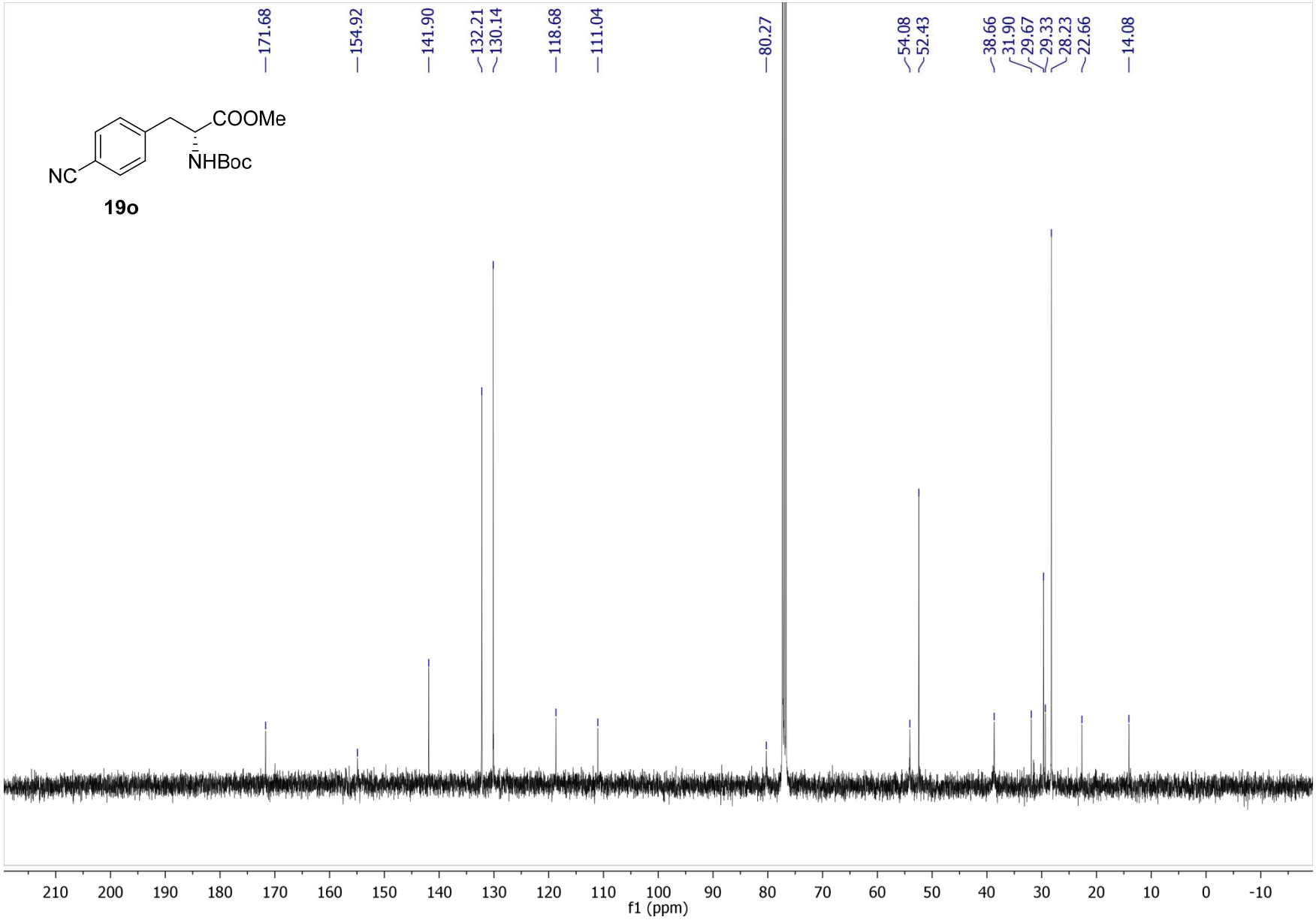

7.55
7.53
7.26
7.24
5.02
5.00
4.62
4.60
3.71
3.22
3.21
3.19
3.17
3.09
3.08
3.06
3.04
1.40
COOMe
NHBoc
F3C
19m
1.11
1.25
1.46
1.15
1.00
1.03
3.54
1.23
1.18
10.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.89
154.95
140.33
129.68
129.51
129.18
125.49
125.39
125.36
122.79
80.13
54.18
52.32
38.27
28.21
COOMe
NHBoc
F3C
19m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.89
7.87
7.24
7.22
5.29
5.00
4.98
4.62
4.61
3.72
3.22
3.20
3.18
3.17
3.11
3.09
3.07
3.06
2.58
1.41
COOMe
NHBoc
Ac
19n
1.01
1.04
1.90
0.86
0.87
3.00
2.12
3.11
8.81
f1 (ppm)


197.66
141.77
136.02
129.56
128.55
77.19
52.32
31.49
30.13
28.25
26.54
COOMe
NHBoc
Ac
19n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.59
7.57
7.26
7.24
5.02
5.01
4.61
4.60
3.72
3.23
3.22
3.20
3.18
3.08
3.07
3.05
3.03
1.40
COOMe
NHBoc
NC
19o
2.30
2.92
1.00
1.15
3.64
1.28
1.21
10.64
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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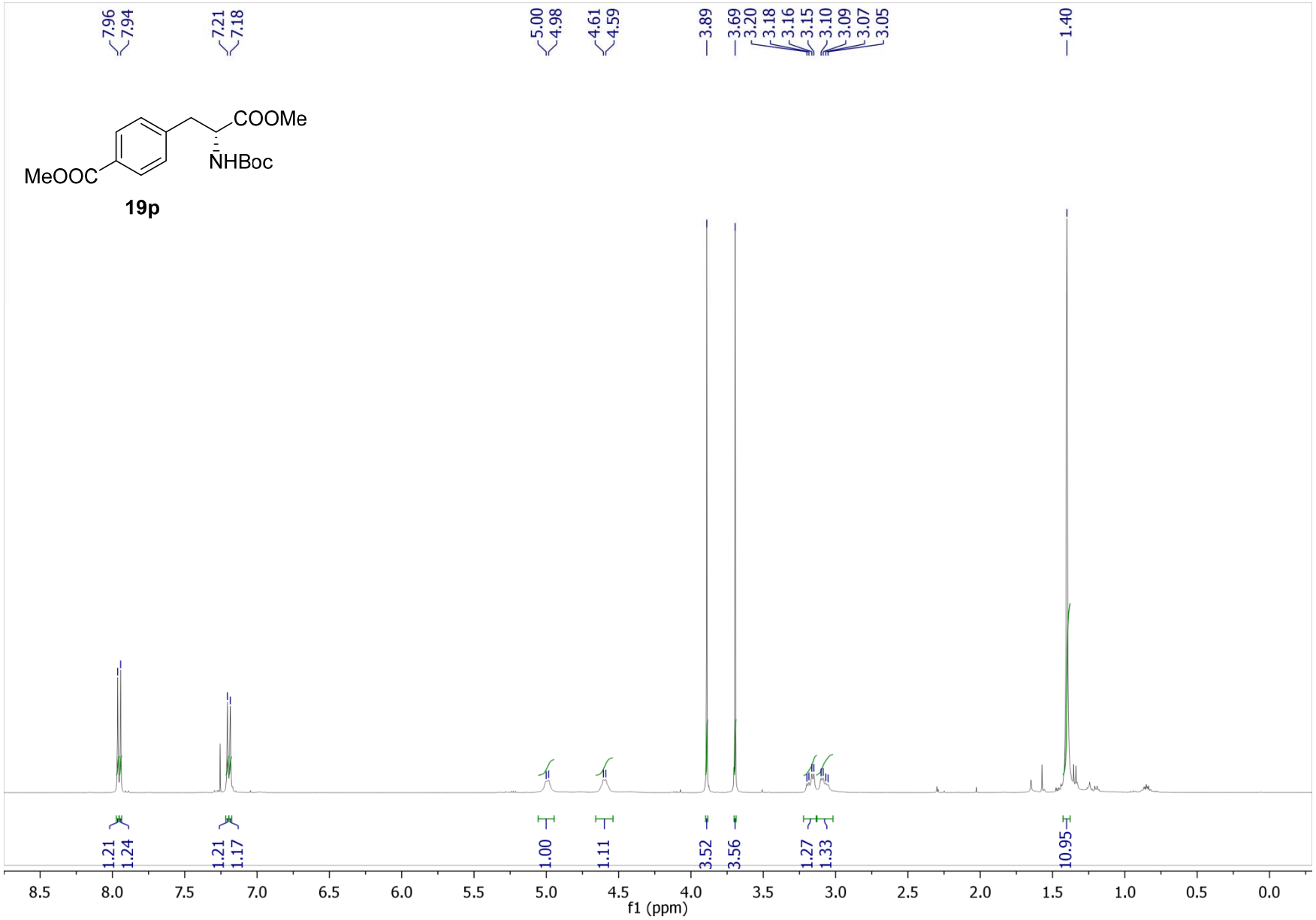
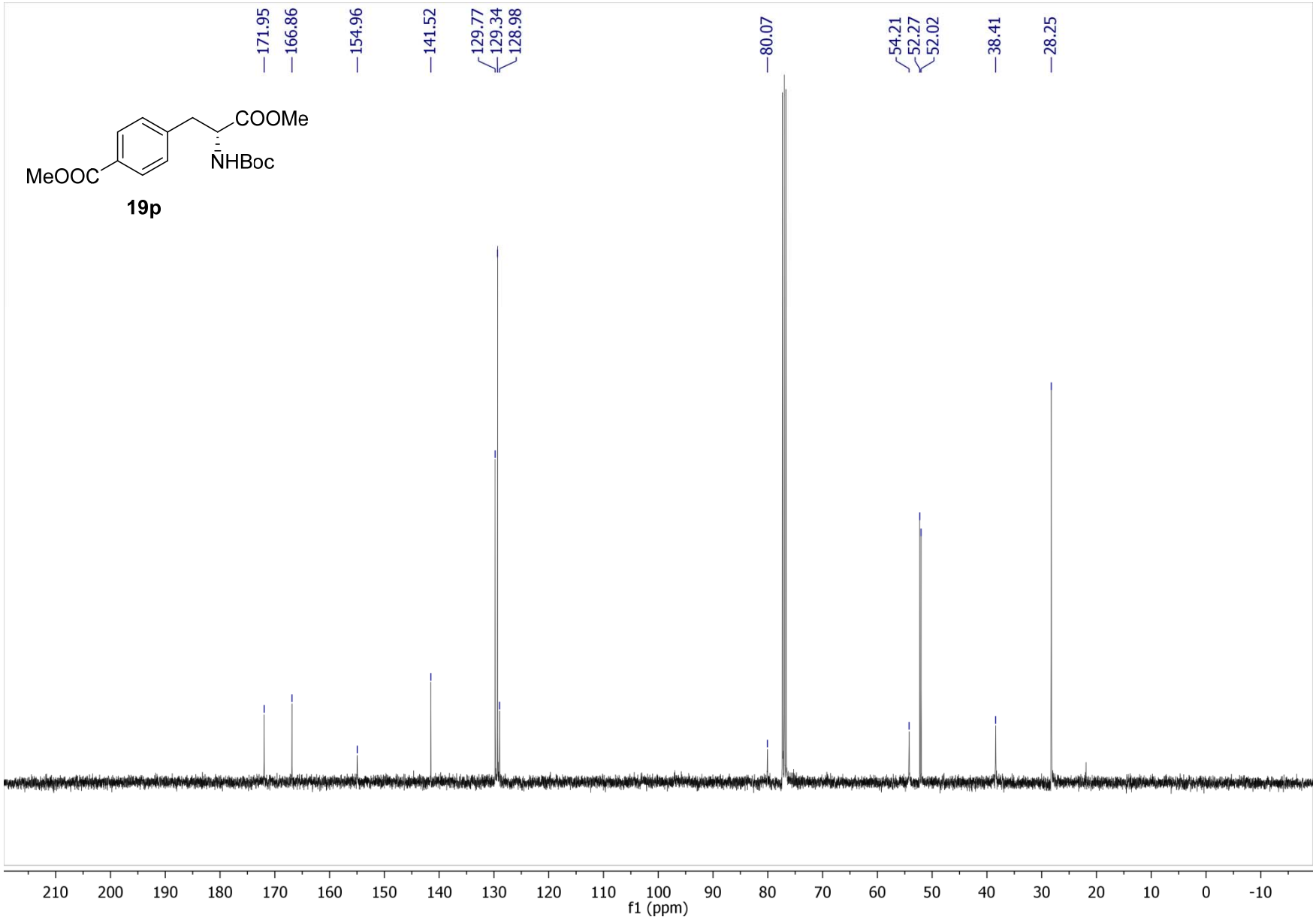
154.92
141.90
132.21
130.14
118.68
111.04
80.27
54.08
52.43
38.66
31.90
29.67
29.33
28.23
22.66
14.08
COOMe
NHBoc
NC
19o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.96
7.94
7.21
7.18
5.00
4.98
4.61
4.59
3.89
3.69
3.20
3.18
3.16
3.15
3.10
3.09
3.07
3.05
1.40
COOMe
NHBoc
MeOOC
19p
1.21
1.24
1.21
1.17
1.00
1.11
3.52
3.56
1.27
1.33
10.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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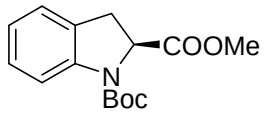
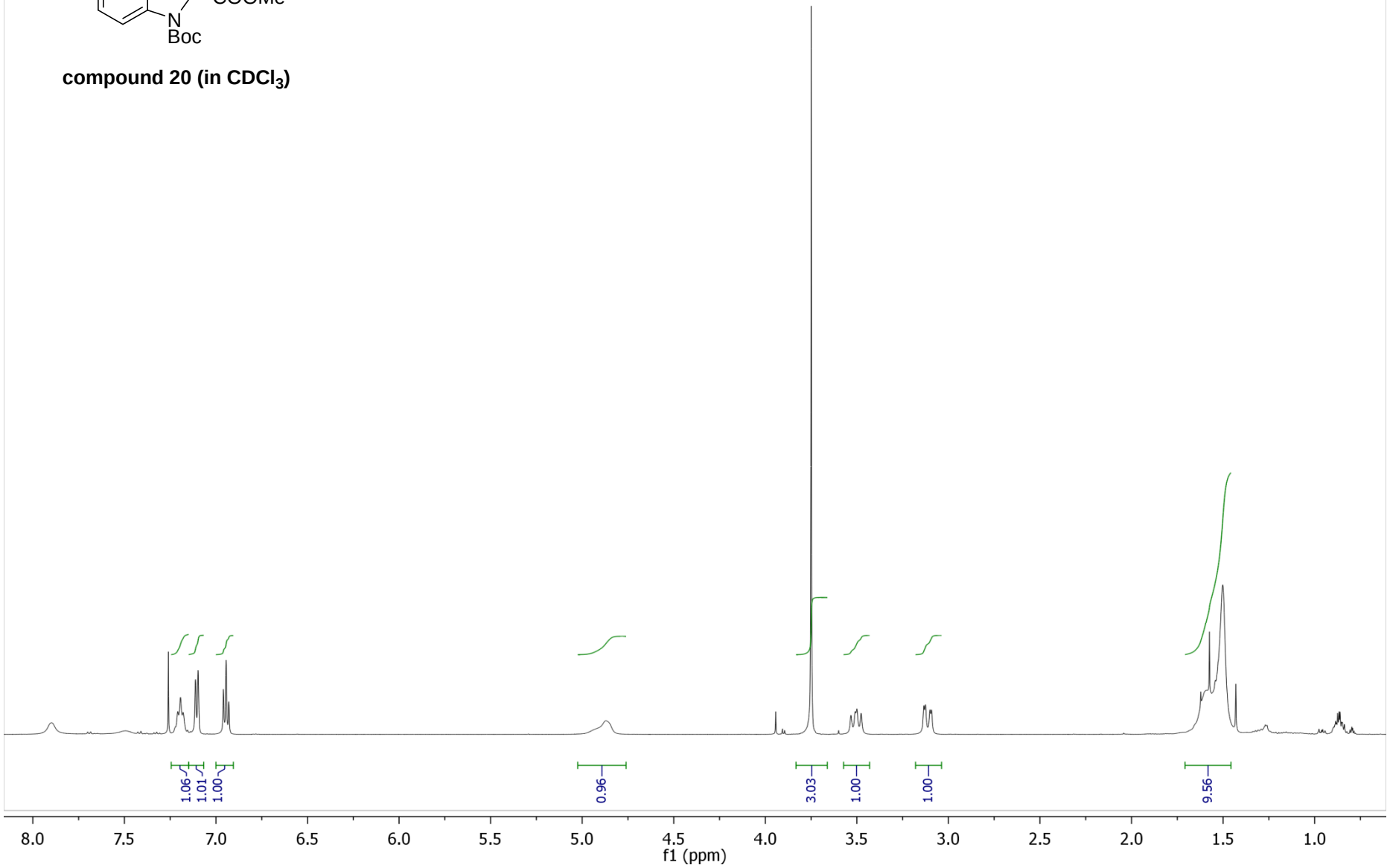
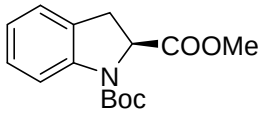
166.86
154.96
141.52
129.77
129.34
128.98
80.07
54.21
52.27
52.02
38.41
28.25
COOMe
NHBoc
MeOOC
19p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

ALA-999.1.fid



compound 20 (in $CDCl_3$)





compound 20 (in DMSO-d_6)